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Synthesis of aryl benzyl *N*H-sulfoximines

Nicola Barry [a], Nicolas Brondel [a], Simon E. Lawrence [a], Anita R. Maguire [b,*]

[a] Department of Chemistry, Analytical and Biological Chemistry Research Facility, University College Cork, Cork, Ireland
[b] Department of Chemistry and School of Pharmacy, Analytical and Biological Chemistry Research Facility, University College Cork, Cork, Ireland

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ABSTRACT

Efficient synthesis and characterisation of a series of aryl benzyl *N*H-sulfoximines are described. While *N*-protected versions of aryl benzyl sulfoximines have been previously described, reports of their deprotection are very limited, presumably due to lability under the typically harsh deprotection conditions which can be employed with the less reactive aryl alkyl derivatives. Use of *N*-cyanosulfoximines as key intermediates overcomes these difficulties leading to an effective synthetic route to these compounds.

1. Introduction

Sulfoximines were first reported in the early 1950s when Whitehead and Bentley[1] discovered that the sulfoximine of methionine was responsible for the toxicity of wheat flour treated with nitrogen trichloride. These compounds have attracted considerable interest in their use as chiral auxiliaries,[2] backbones in pseudopeptides[3] and applications as chiral ligands in asymmetric synthesis.[4] A number of synthetic methods have been described including imination of the sulfoxide (or sulfide for sulfilimine synthesis) with hydrazoic acid[5] (generated *in situ* from sodium azide and hydrochloric acid) or *O*-mesitylene sulfonyl hydroxylamine (MSH)[6] allowing immediate access to the *N*H-sulfoximines. Metal catalysed[7]and non-metal[8] nitrene transfer to sulfoxides (and sulfides) from iminoiodinates, PhI=NR (preformed or generated *in situ*), has been extensively investigated in recent years with considerable success. The imination of the sulfoxides has also proved successful using electrochemical methods.[9] However, these methods lead to the formation of *N*-tosyl sulfoximines or related *N*-protected derivatives, which can be difficult to convert into the useful *N*H derivatives.

2. Results and discussion

As part of an ongoing research programme focused on crystal engineering employing chiral organosulfur compounds we required access to a series of aryl benzyl *N*H-sulfoximines. Most of the reported syntheses of *N*H-sulfoximines to date are based on aryl alkyl or diaryl systems[7a–d,8a] with just a handful of reports of aryl benzyl *N*H-sulfoximines.[10] There are some reports of *N*-protected aryl benzyl sulfoximines but reports of their deprotection are limited. From a review of the literature it appears that the deprotection of the aryl alkyl sulfoximines is possible, but the harsh conditions required for the cleavage of these *N*-protected derivatives are not compatible with the more labile benzyl derivatives. The synthesis of *N*-tosyl benzyl phenyl sulfoximine has been reported[7e] with no indication of its deprotection. Bach and Korber[11] reported the synthesis of the *N*-Boc benzyl phenyl sulfoximine highlighting the anticipated ease of the removal of the Boc group. However, the paper describes the deprotection of the *N*-Boc benzyl methyl sulfoximine, while deprotection of the *N*-Boc benzyl phenyl compound is not described. The deprotection of the electrochemically produced[9] *N*-phthalimido benzyl phenyl sulfoximine also proved unsuccessful resulting in decomposition of the starting sulfoximine. Following these reports, Bolm and Cho[10b] described the synthesis of aryl benzyl *N*H-sulfoximines via a palladium mediated α-arylation of pre-existing sulfoximines while further eluding to the difficulties in accessing these derivatives via the existing methodologies such as nitrene transfer and deprotection. More recently Bolm's group[7d] has reported increased efficiencies in the nitrene transfer to sulfoxides, including benzyl phenyl sulfoxide, using iron(II) triflate as a catalyst but notably the deprotection of the resulting *N*-nosyl benzyl phenyl sulfoximine is not described in this paper.

The initial approach considered for the synthesis of aryl benzyl sulfoximines involved the reaction of the aryl benzyl sulfoxide, **1**, with hydrazoic acid[5] generated *in situ* from sodium azide and concentrated sulfuric acid, see Scheme 1. This method had been successfully applied within our group to a wide range of aryl methyl derivatives but with the aryl benzyl sulfoxide, **1**, the desired *N*H-sulfoximine, **2**, was isolated in 6% yield and required extensive chromatographic purification from a complex mixture. While aryl methyl sulfoximines survive the harsh conditions associated with the nitrene transfer it has been suggested[4e,12] that use of more labile substituents (e.g., secondary alkyl, benzyl) can lead to the heterolysis of the C–S bond under acidic conditions.

* Corresponding author.
E-mail address: a.maguire@ucc.ie (A.R. Maguire).

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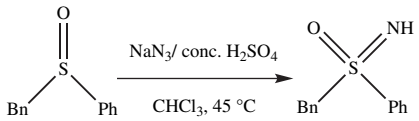
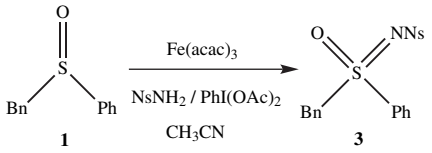


1 2

Scheme 1.

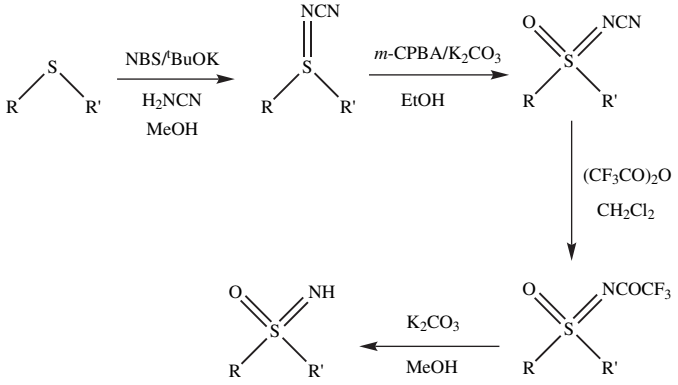
Accordingly, Bolm's procedure[7c] employing Fe(III) catalysed nitrene transfer leading to the *N*-nosyl derivative, **3**, was next explored as summarised in Scheme 2. The efficiency of the transformation proved variable and furthermore attempts to convert the *N*-nosyl sulfoximine to the *N*H-sulfoximine were unproductive. The investigation of the *N*-tosyl derivatives was avoided as harsher conditions are required to cleave the tosyl group (acid hydrolysis with concentrated sulfuric acid at 25 °C[13]) relative to the nosyl group (nucleophilic aromatic substitution with the *in situ* generation of thiophenolate from thiophenol and caesium carbonate[7c]) and this was not envisaged to provide a viable route to the desired aryl benzyl *N*H-sulfoximines.



1 3

Scheme 2.

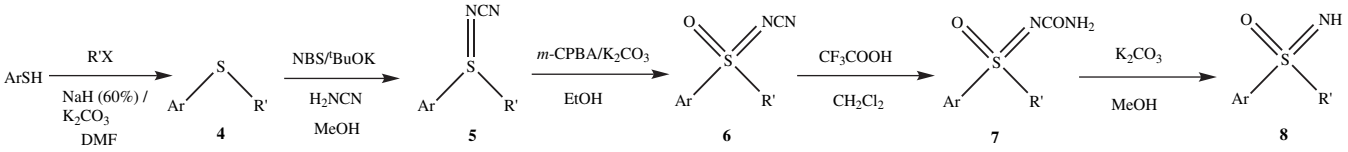
In 2007 the Bolm group reported a multi-step sequence leading to *N*H-sulfoximines via *N*-cyanosulfilimines,[8b] see Scheme 3. While they described the synthesis of benzyl methyl *N*H-sulfoximine following this method, the application of this route to aryl benzyl *N*H-sulfoximines was not described. It was decided to explore the application of this route to aryl benzyl *N*H-sulfoximines and, with some modification (notably use of trifluoroacetic acid in place of trifluoroacetic anhydride for the hydrolysis step), the route has proved successful in leading to the series of compounds **4a**–**8n** as summarised in Table 1.



Scheme 3.

A series of aryl benzyl sulfides were initially prepared via thiolate alkylation in good yields; while most of the sulfides were previously reported, two **4g** and **4j** are novel and were fully characterised during this work. The treatment of the sulfides with NBS, cyanamine and potassium *tert*-butoxide in methanol led efficiently to the series of *N*-cyanosulfilimines in comparable yields to the benzyl methyl derivative reported by Bolm.[8b] Some of these derivatives (**5c**, **5l**, **5m**) were recovered cleanly from the reaction mixtures and were used without further purification, but most of the compounds (**5a**, **5b**, **5d**-**5k**, **5n**) were purified by column chromatography to remove traces of residual sulfide. Interestingly, the efficient transformations were observed with the methoxy substituted compounds **5c**, **5l** and **5m**, presumably related to the

Table 1
Synthesis of aryl benzyl *N*H-sulfoximines



Ar	R′	No.	% Yield	No.	% Yield	No.	% Yield	No.	% Yield	No.	% Yield
C_6H_5	$C_6H_5CH_2$	**4a**	—[a]	**5a**	75[b]	**6a**	80[b]	**7a**	52[b]	**2**[10b]	17[b]
p-FC_6H_4	*p*-$FC_6H_4CH_2$	**4b**[14]	54[c]	**5b**	68[b]	**6b**	77[b]	**7b**	70[b]	**8b**	38[d]
p-$OCH_3C_6H_4$	$C_6H_5CH_2$	**4c**[15]	71[c]	**5c**	83	**6c**	68[b]	**7c**	45[b]	**8c**	67
p-BrC_6H_4	$C_6H_5CH_2$	**4d**[16]	76[c]	**5d**	75[b]	**6d**	83	**7d**	41[b]	**8d**	60[b]
p-$NO_2C_6H_4$	$C_6H_5CH_2$	**4e**[17]	52[c]	**5e**	75[b]	**6e**	41[b]	**7e**	54[b]	**8e**	—[e]
o-BrC_6H_4	$C_6H_5CH_2$	**4f**[18]	37[c]	**5f**	75[b]	**6f**	—[f]	**7f**	—	**8f**	—
o-FC_6H_4	$C_6H_5CH_2$	**4g**	77[c]	**5g**	60[b]	**6g**	—[f]	**7g**	—	**8g**	—
o-ClC_6H_4	$C_6H_5CH_2$	**4h**[19]	78	**5h**	58[b]	**6h**	—[f]	**7h**	—	**8h**	—
p-ClC_6H_4	$C_6H_5CH_2$	**4i**[20]	60[c]	**5i**	78[b]	**6i**	63[b]	**7i**	56[b]	**8i**	86[b]
m-FC_6H_4	$C_6H_5CH_2$	**4j**	82	**5j**	63[b]	**6j**	69[b]	**7j**	56[b]	**8j**	61[b]
m-BrC_6H_4	$C_6H_5CH_2$	**4k**[21]	83	**5k**	88[b]	**6k**	69[b]	**7k**	38[b]	**8k**	50[b]
o-$OCH_3C_6H_4$	$C_6H_5CH_2$	**4l**[22]	69[c]	**5l**	83	**6l**	16[b,g]	**7l**	—	**8l**	—
p-$OCH_3C_6H_4$	*p*-$OCH_3C_6H_4CH_2$	**4m**[15]	78	**5m**	70	**6m**	56[b]	**7m**	—[h]	**8m**	—
p-FC_6H_4	$C_6H_5CH_2$	**4n**[14]	65	**5n**	55[b]	**6n**	67[b]	**7n**	80[b]	**8n**	38[b]

[a] Commercially available.
[b] After column chromatography.
[c] After recrystallisation.
[d] Labile on purification by column chromatography.
[e] Crude ^{1}H NMR shows trace amounts of **8e**.
[f] Crude ^{1}H NMR shows sulfide as predominant product.
[g] On repetition, crude ^{1}H NMR showed molar ratio of **4l**/**5l**/**6l** as 1:2.1:1.
[h] Crude ^{1}H NMR showed decomposition with partial loss of the methoxy groups.

electronic effect of the methoxy substituent. Each of the *N*-cyanosulfilimines is a novel compound, was isolated as a solid and was fully characterised. They are stable compounds, which are easily handled and stored without degradation.

m-CPBA mediated oxidation of the *N*-cyanosulfilimines to the analogous *N*-cyanosulfoximines was undertaken in the presence of potassium carbonate in ethanol. The yields obtained for most of the series of the resulting sulfoximines were reasonable following column chromatography to remove unreacted *N*-cyanosulfilimine. However with the *ortho* substituted derivatives the principal product observed in each case was the analogous sulfide. It is clear that the reaction at sulfur is hindered by the adjacent *ortho* substituent and removal of the NCN group occurs in an unusual reductive transformation at sulfur in the presence of *m*-CPBA. The novel *N*-cyanosulfoximines **6a**–**6n** were stable solids and were fully characterised during this work.

Bolm[8b] described the use of trifluoroacetic anhydride to transform the *N*-cyanosulfoximines to the analogues *N*-trifluoroacetyl compounds followed by hydrolysis using potassium carbonate in methanol. During this research we found that the use of trifluoroacetic acid led to the *N*-carbamoyl sulfoximines (**7a**–**7e**, **7i**-**7k**, **7n**), which are readily deprotected using potassium carbonate in methanol to yield the 'free' *N*H-sulfoximines (**2**, **8b**–**8d**, **8i**–**8k**, **8n**). Acidic hydrolysis of *N*-cyanosulfoximines has precedent.[23] With the activated dimethoxy derivative **7m** formation of a complex reaction mixture was seen during the trifluoroacetic acid hydrolysis indicating that this system was unstable under the reaction conditions. The *N*-carbamoyl nitro derivative **7e** showed only minimal conversion into the desired *N*H-sulfoximine **8e**. Moderate yields were obtained in each of the hydrolysis steps and chromatographic purification was required at each step, except for **8c**, to provide pure compounds for characterisation. Again both the *N*-carbamoyl derivatives (**7a**–**7e**, **7i**–**7k**, **7n**) and the *N*H-sulfoximines (**8b**–**8d**, **8i**–**8k**, **8n**) are novel, other than **2**, and were fully characterised during this work. Each of the compounds was solid and the only issue in handling was with the difluoro derivative **8b**, which proved labile towards chromatography.

3. Conclusion

This multi-step sequence provides ready access to a series of aryl benzyl *N*H-sulfoximines bearing a range of substituents on the aryl rings, failing only when the phenyl ring is *para*-nitro or *ortho* substituted or with highly activated bis(methoxyaryl) compounds.

4. Experimental

4.1. General

All solvents were HPLC grade or were distilled prior to use by the following methods: dichloromethane from phosphorus pentoxide; ethyl acetate from potassium carbonate; hexane was distilled prior to use. Organic phases were dried using anhydrous magnesium sulfate ($MgSO_4$). All commercial reagents, including *m*-chloroperbenzoic acid, were used without further purification.

^{1}H (400 MHz) NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer and ^{1}H (300 MHz) NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer in proton coupled mode. ^{13}C (75.5 MHz) NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer. All spectra were recorded at 20 °C in deuterated chloroform ($CDCl_3$) using trimethylsilane (TMS) as an internal standard. Chemical shifts (δ_H and δ_C) are reported in parts per million (ppm) relative to the TMS signal and coupling constants are expressed in hertz (Hz).

Thin layer chromatography (TLC) was accomplished using precoated silica gel plates (Merck Silica Gel 60 F_{254}). Visualisation was achieved by UV light detection (254 nm). Wet flash column chromatography was carried out using Merck Silica Gel 60, typically with a 30:1 ratio of silica to sample.

Microanalysis was performed by The Microanalysis Laboratory, UCC, Cork, on Perkin–Elmer 240 and Exeter Analytical CE440 elemental analysers. Low resolution mass spectra were recorded on a Waters Quattro Micro triple quadrupole instrument in electrospray ionisation (ESI) mode using 50% acetonitrile/water containing 0.1% formic acid as eluent; samples were made up in acetonitrile. High resolution precise mass spectra (HRMS) were recorded on a Waters LCT Premier TOF LC–MS instrument in electrospray ionisation (ESI) mode using 50% acetonitrile/water containing 0.1% formic acid as eluent; samples were made up in acetonitrile. Infrared spectra were measured as potassium bromide (KBr) discs for solids or thin films on sodium chloride plates for liquids on a Perkin–Elmer Paragon 1000 FT-IR spectrometer. Melting points were measured on an Electrothermal 9100-Melting Point apparatus and a uni-melt Thomas Hoover Capillary melting point apparatus and are uncorrected.

4.2. Benzyl phenyl sulfoxide (1)[24]

Benzyl phenyl sulfide (1.85 g, 9.24 mmol) was stirred in CH_2Cl_2 (50 mL) at 0 °C. A solution of *m*-chloroperbenzoic acid (2.07 g, 77%, 9.24 mmol) in CH_2Cl_2 (40 mL) was added dropwise over 1 h. The reaction mixture was stirred for an additional 30 min at 0 °C. Saturated $NaHCO_3$ (30 mL) was added and the phases separated. The organic layer was further washed with $NaHCO_3$ (2×30 mL), brine (30 mL), dried and concentrated under reduced pressure to give the crude product. Purification was carried out by recrystallisation from hot methanol, which afforded the title compound as a white solid (1.45 g, 71%), mp 121–122 °C (lit.[24] 125–126 °C); ν_{max} (KBr)/cm^{-1} 2960, 1597, 1442, 1415, 1036 (S=O stretch), 745 (C–S stretch); δ_H (300 MHz) ($CDCl_3$) 3.99 (1H, A of AB_{system}, J_{AB} 12.6, one of CH_2), 4.09 (1H, B of AB_{system}, J_{AB} 12.6, one of CH_2), 6.93–7.02 (2H, m, ArH), 7.19–7.32 (3H, m, ArH), 7.33–7.51 (5H, m, ArH).

4.3. *S*-Benzyl-*S*-phenyl-*N*H-sulfoximine (2)[10b]

To a solution of benzyl phenyl sulfoxide (**1**) (1.08 g, 5.0 mmol) in $CHCl_3$ (8 mL) was added sodium azide (1.07 g, 16.5 mmol). Concentrated sulfuric acid (2.88 mL) was then added dropwise to the stirred mixture. *Caution*: might be explosive. The reaction mixture was then heated to exactly 45 °C and stirred at this temperature for 16 h. The reaction mixture was cooled, diluted with water (25 mL) and extracted with CH_2Cl_2 (2×25 mL) (*organic layer* 1). The remaining aqueous layer was made basic by the addition of potassium carbonate (pH>9). This aqueous layer was then further extracted with CH_2Cl_2 (3×20 mL) (*organic layer* 2). Organic layers 1 and 2 were separately washed with brine (20 mL), dried and concentrated under reduced pressure. Organic layer 1 yielded the unreacted sulfoxide. Organic layer 2 yielded a complex mixture of products, which after purification by column chromatography on silica gel using hexane/ethyl acetate (50:50) to ethyl acetate (100) gave **2** as a white solid (6%), mp 104–106 °C (lit.[21] 112–113 °C); δ_H (300 MHz) ($CDCl_3$) 2.76 (1H, br s, NH), 4.37 (1H, A of AB_{system}, J_{AB} 13.5, one of CH_2), 4.45 (1H, B of AB_{system}, J_{AB} 13.5, one of CH_2), 7.10–7.78 (10H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 64.6 (CH_2, *C*H_2), 124.4, 128.6, 128.8, 128.9 (CH, 4×aromatic *C*H), 129.4 (C, aromatic C), 131.1, 133.1 (CH, 2×aromatic *C*H), 140.3 (C, aromatic *C*); *m*/*z* (ESI) 232 [(M+H)$^+$].

4.4. Attempted synthesis of *S*-benzyl-*S*-phenyl-*N*-(*p*-nitrobenzenesulfonyl)sulfoximine (3)[7d]

Benzyl phenyl sulfoxide (**1**) (0.43 g, 2.0 mmol), *p*-nitrobenzenesulfonamide (0.61 g, 3 mmol), diacetoxyiodobenzene

(1.6 equiv) and iron(III) acetylacetonate (0.035 g, 0.1 mmol) were stirred in acetonitrile (20 mL) at room temperature. The reaction progress was monitored by TLC. The reaction mixture was concentrated under reduced pressure. CH_2Cl_2 (25 mL) and water (20 mL) were added and the phases separated. The organic layer was further washed with water (2×20 mL), brine (20 mL), dried and concentrated under reduced pressure to give the crude product as a yellow semi-solid (0.27 g). ^{1}H NMR analysis indicated the presence of a significant amount of benzyl phenyl sulfoxide (**1**) [δ_H (400 MHz) ($CDCl_3$) 4.00 (1H, A of AB_{system}, J_{AB} 12.4, one of CH_2), 4.11 (1H, B of AB_{system}, J_{AB} 12.4, one of CH_2)] and trace amounts of the desired product (**3**) whose signals are tentatively assigned as δ_H (400 MHz) ($CDCl_3$) 4.76 (1H, A of AB_{system}, J_{AB} 13.6, one of CH_2), 4.83 (1H, B of AB_{system}, J_{AB} 14.0, one of CH_2). Molar ratio of **1**/**3** was 1:0.17.

4.5. General procedures

4.5.1. Procedure A. The thiol (1 equiv) was added dropwise to a stirred suspension of NaH (1.05 equiv)/K_2CO_3 (1.05 equiv) in DMF (15 mL) under N_2 at 0 °C. The reaction mixture was stirred for 20 min and the alkyl halide (1 equiv) in DMF (1 mL) was then slowly added over 20 min. The reaction mixture was stirred for a further 16 h at room temperature. Water (50 mL) and CH_2Cl_2 (30 mL) were added and the phases separated. The organic layer was concentrated under reduced pressure. The product was dissolved in CH_2Cl_2 (30 mL), washed with 2 M HCl (3×20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give the crude product. Purification was carried out either by wet flash chromatography, using hexane/ethyl acetate (98:2 to 95:5) as eluent, or recrystallisation from a suitable solvent or by a combination of both methods as indicated for each compound.

4.5.2. Procedure B[8b]. The sulfide (1 equiv), cyanamine (1.3 equiv) and potassium *tert*-butoxide (1.2 equiv) were stirred in methanol (10 mL) at room temperature. *N*-Bromosuccinimide (1.5 equiv) was added to this solution. The reaction progress was monitored by TLC. Once the starting sulfide had been consumed, the reaction mixture was concentrated under reduced pressure. Saturated $Na_2S_2O_3$ solution (10 mL) and CH_2Cl_2 (10 mL) were added to the crude mixture and the phases separated. The aqueous layer was further washed with CH_2Cl_2 (2×10 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give the crude product. Purification was carried out by wet flash chromatography using dichloromethane/acetone (9:1 to 6:1) or hexane/ethyl acetate (60:40) as eluent, where necessary.

4.5.3. Procedure C[8b]. *N*-Cyanosulfilimine (1 equiv) was stirred in ethanol (20 mL) at 0 °C. *m*-Chloroperbenzoic acid (77%, 1.5 equiv) and K_2CO_3 (3 equiv) were added to the solution. The solution was allowed to reach room temperature and stirred until TLC indicated that all of the starting sulfilimine was consumed. The reaction mixture was concentrated under reduced pressure. Water (10 mL) and CH_2Cl_2 (10 mL) were added to the reaction residue and the phases separated. The aqueous layer was further washed with CH_2Cl_2 (2×10 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give the crude product. Purification was carried out by wet flash chromatography using hexane/ethyl acetate (60:40) as eluent, where necessary.

4.5.4. Procedure D. *N*-Cyanosulfoximine (1 equiv) was dissolved in CH_2Cl_2 (20 mL) and the mixture cooled to 0 °C. Trifluoroacetic acid (3 equiv) was slowly added to the above solution and the mixture was allowed to reach room temperature. The reaction progress was monitored by TLC and once the starting sulfoximine had been consumed the mixture was poured onto water (20 mL). The phases were separated and the aqueous layer was further washed with CH_2Cl_2 (2×10 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product. Purification was carried out by wet flash chromatography using hexane/ethyl acetate (60:40 to 50:50) as eluent, where necessary.

4.5.5. Procedure E. The *N*-carbamoylsulfoximine (1 equiv) was dissolved in methanol (10 mL) and K_2CO_3 (5 equiv) was added. The reaction progress was monitored by TLC and once all of the sulfoximine was consumed, the mixture was concentrated under reduced pressure. Water (10 mL) and CH_2Cl_2 (10 mL) were added to the reaction residue and the phases separated. The aqueous layer was further washed with CH_2Cl_2 (2×10 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give the crude product. Purification was carried out by wet flash chromatography using hexane/ethyl acetate (70:30) to ethyl acetate (100) as eluent, where necessary.

*4.5.6. 4-Fluorobenzyl-(4′-fluorophenyl)-sulfide (**4b**)*[14]. Following procedure A, the reaction of NaH (0.27 g, 60% dispersion in oil, 6.83 mmol), 4-fluorobenzene thiol (0.83 g, 0.69 mL, 6.50 mmol) and 4-fluorobenzyl chloride (0.94 g, 0.78 mL, 6.50 mmol) and subsequent recrystallisation from hot methanol afforded **4b** as a white solid (0.83 g, 54%), mp 46–47 °C (lit.[14] 44.5–45.5 °C); ν_{max} (KBr)/cm^{-1} 2923, 1596, 1515, 1494, 1239, 750 (C–S stretch); δ_H (300 MHz) ($CDCl_3$) 3.99 (3H, s, CH_2), 6.88–7.00 (4H, m, ArH), 7.10–7.19 (2H, m, ArH), 7.20–7.30 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 40.2 (CH_2, *C*H$_2$), 115.7 (CH, d, $^2J_{C-F}$ 21.0, aromatic *C*H), 116.4 (CH, d, $^2J_{C-F}$ 21.0, aromatic *C*H), 130.8 (CH, d, $^3J_{C-F}$ 8.3, aromatic *C*H), 133.69, 133.73 (C, 2×aromatic *C*), 134.2 (CH, d, $^3J_{C-F}$ 8.3, aromatic *C*H), 162.3 (C, d, $^1J_{C-F}$ 244.5, *C*–F), 162.6 (C, d, $^1J_{C-F}$ 245.3, *C*–F).

*4.5.7. Benzyl-(4-methoxyphenyl)-sulfide (**4c**)*[15]. Following procedure A, the reaction of NaH (0.27 g, 60% dispersion in oil, 6.83 mmol), 4-methoxybenzene thiol (0.91 g, 0.81 mL, 6.50 mmol) and benzyl bromide (1.11 g, 0.92 mL, 6.50 mmol) and subsequent recrystallisation from hot methanol afforded **4c** as a white solid (1.07 g, 71%), mp 47–48 °C (lit.[15] 48–49 °C); ν_{max} (KBr)/cm^{-1} 2920, 1596, 1571, 1245, 1180, 712 (C–S stretch); δ_H (300 MHz) ($CDCl_3$) 3.78 (3H, s, CH_3), 3.98 (2H, s, CH_2), 6.74–6.83 (2H, m, ArH), 7.14–7.31 (7H, m, ArH).

*4.5.8. Benzyl-(4-bromophenyl)-sulfide (**4d**)*[16]. Following procedure D, the reaction of NaH (0.27 g, 60% dispersion in oil, 6.83 mmol), 4-bromobenzene thiol (1.23 g, 6.50 mmol) and benzyl bromide (1.11 g, 0.92 mL, 6.50 mmol) and subsequent recrystallisation from hot methanol afforded **4d** as a white solid (1.38 g, 76%), mp 61–63 °C (lit.[16] 63–64 °C); ν_{max} (KBr)/cm^{-1} 2923, 1470, 1453, 1111, 711 (C–S stretch); δ_H (300 MHz) ($CDCl_3$) 4.08 (2H, s, CH_2), 7.11–7.18 (2H, m, ArH), 7.20–7.32 (5H, m, ArH), 7.33–7.39 (2H, m, ArH).

*4.5.9. Benzyl-(4-nitrophenyl)-sulfide (**4e**)*[17]. Following procedure A, the reaction of K_2CO_3 (0.58 g, 4.2 mmol), 4-nitrobenzene thiol (0.62 g, 4.0 mmol) and benzyl bromide (0.68 g, 0.48 mL, 4.0 mmol) and subsequent recrystallisation from hot methanol afforded **4e** as a yellow solid (0.51 g, 52%), mp 117–120 °C (lit.[17] 122 °C); ν_{max} (KBr)/cm^{-1} 1593, 1574, 1508 (asymmetric NO_2 stretch), 1333 (symmetric NO_2 stretch), 719 (C–S stretch); δ_H (300 MHz) ($CDCl_3$) 4.25 (2H, s, CH_2), 7.23–7.42 (7H, m, ArH), 8.06–8.14 (2H, m, ArH).

*4.5.10. Benzyl-(2-bromophenyl)-sulfide (**4f**)*[18]. Following procedure A, the reaction of K_2CO_3 (0.44 g, 3.15 mmol), 2-bromobenzene thiol (0.57 g, 0.35 mL, 3.00 mmol) and benzyl bromide (0.51 g, 0.36 mL,

3.00 mmol) and subsequent recrystallisation from hot methanol afforded **4f** as a white solid (0.31 g, 37%), mp 49–50 °C (lit.[18] 44–45 °C); ν_{max} (KBr)/cm^{-1} 2912, 1627, 1452, 1435, 718 (C–S stretch); δ_H (300 MHz) ($CDCl_3$) 4.15 (2H, s, CH_2), 6.99–7.06 (1H, m, ArH), 7.17–7.39 (7H, m, ArH), 7.52–7.58 (1H, m, ArH).

*4.5.11. Benzyl-(2-fluorophenyl)-sulfide (**4g**).* Following procedure A, the reaction of K_2CO_3 (0.44 g, 3.15 mmol), 2-fluorobenzene thiol (0.38 g, 0.32 mL, 3.00 mmol) and benzyl bromide (0.51 g, 0.36 mL, 3.00 mmol) and subsequent recrystallisation from hot methanol afforded **4g** as a white solid (0.50 g, 77%), mp 43–47 °C. (Found: C, 71.53; H, 4.86; S 15.05; F 9.01. $C_{13}H_{11}FS$ requires C, 71.53; H, 5.08; S 14.69; F 8.70%.) ν_{max} (KBr)/cm^{-1} 2918, 1567, 1468, 1446, 741 (C–S stretch); δ_H (300 MHz) ($CDCl_3$) 4.10 (2H, s, CH_2), 6.98–7.09 (2H, m, ArH), 7.17–7.30 (7H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 38.4 (CH_2, d, $^4J_{C-F}$ 2.3, *C*H_2), 115.6 (CH, d, $^2J_{C-F}$ 21.5, aromatic *C*H), 122.8 (C, d, $^2J_{C-F}$ 18.0, aromatic *C*), 124.3 (CH, d, J_{C-F} 3.8, aromatic *C*H), 127.3, 128.5 (CH, 2×aromatic *C*H), 128.8 (CH, d, J_{C-F} 7.5, aromatic *C*H), 128.9 (CH, aromatic *C*H), 133.1 (CH, br d, J_{C-F} 1.5, aromatic *C*H), 137.2 (C, aromatic *C*), 161.7 (C, d, $^1J_{C-F}$ 243.8, *C*–F).

*4.5.12. Benzyl-(2-chlorophenyl)-sulfide (**4h**)[19].* Following procedure A, the reaction of K_2CO_3 (0.73 g, 5.25 mmol), 2-chlorobenzene thiol (0.72 g, 0.57 mL, 5.00 mmol) and benzyl bromide (0.86 g, 0.59 mL, 5.00 mmol) afforded, without further purification, **4h** as a yellow oil (0.91 g, 78%); ν_{max} (KBr)/cm^{-1} 3022, 1576, 1495, 1453, 745 (C–S stretch); δ_H (400 MHz) ($CDCl_3$) 4.14 (2H, s, CH_2), 7.07–7.40 (9H, m, ArH).

*4.5.13. Benzyl-(4-chlorophenyl)-sulfide (**4i**)[20].* Following procedure A, the reaction of K_2CO_3 (0.44 g, 3.15 mmol), 4-chlorobenzene thiol (0.43 g, 3.00 mmol) and benzyl bromide (0.51 g, 0.36 mL, 3.00 mmol) and subsequent recrystallisation from hot methanol afforded **4i** as a white solid (0.42 g, 60%), mp 52–55 °C (lit.[20] 49–50 °C); ν_{max} (KBr)/cm^{-1} 2919, 1495, 1453, 712 (C–S stretch); δ_H (400 MHz) ($CDCl_3$) 4.08 (2H, s, CH_2), 7.19–7.32 (9H, m, ArH).

*4.5.14. Benzyl-(3-fluorophenyl)-sulfide (**4j**).* Following procedure A, the reaction of K_2CO_3 (0.44 g, 3.15 mmol), 2-fluorobenzene thiol (0.38 g, 0.32 mL, 3.00 mmol) and benzyl bromide (0.51 g, 0.36 mL, 3.00 mmol) afforded, without further purification, **4j** as a white solid (0.53 g, 82%), mp 39–41 °C. (Found: C, 71.24; H, 4.78; S 15.13; F 8.99. $C_{13}H_{11}FS$ requires C, 71.53; H, 5.08; S 14.69; F 8.70%.) ν_{max} (KBr)/cm^{-1} 3029, 1600, 1576, 1495, 1264, 716 (C–S stretch); δ_H (400 MHz) ($CDCl_3$) 4.13 (2H, s, CH_2), 6.82–6.89 (1H, m, ArH), 6.96–7.08 (2H, m, ArH), 7.17–7.34 (6H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 38.5 (CH_2, *C*H_2), 113.1 (CH, d, $^2J_{C-F}$ 21.2, aromatic *C*H), 115.9 (CH, d, $^2J_{C-F}$ 22.8, aromatic *C*H), 124.7 (CH, d, $^4J_{C-F}$ 2.9, aromatic *C*H), 127.4, 128.6, 128.8 (CH, 3×aromatic *C*H), 130.1 (CH, d, $^3J_{C-F}$ 8.6, aromatic *C*H), 136.8 (C, aromatic *C*), 139.0 (C, d, $^3J_{C-F}$ 8.0, aromatic *C*), 162.8 (C, d, $^1J_{C-F}$ 246.8, *C*–F).

*4.5.15. Benzyl-(3-bromophenyl)-sulfide (**4k**)[21].* Following procedure A, the reaction of K_2CO_3 (0.73 g, 5.25 mmol), 3-bromobenzene thiol (0.95 g, 0.59 mL, 5.00 mmol) and benzyl bromide (0.86 g, 0.59 mL, 5.00 mmol) afforded, without further purification, **4k** as a white solid (1.16 g, 83%), mp 43–46 °C (lit.[21] 40–41 °C); ν_{max} (KBr)/cm^{-1} 1574, 1560, 1456, 719 (C–S stretch); δ_H (300 MHz) ($CDCl_3$) 4.12 (2H, s, CH_2), 7.07–7.14 (1H, m, ArH), 7.17–7.32 (7H, m, ArH), 7.44 (1H, t, *J* 2.0, ArH).

*4.5.16. Benzyl-(2-methoxyphenyl)-sulfide (**4l**)[22].* Following procedure A, the reaction of NaH (0.27 g, 60% dispersion in oil, 6.83 mmol), 2-methoxybenzene thiol (0.91 g, 0.79 mL, 6.50 mmol) and benzyl bromide (1.11 g, 0.92 mL, 6.50 mmol) and subsequent recrystallisation from hot methanol afforded **4l** as a white solid (1.04 g, 69%), mp 67–68 °C; ν_{max} (KBr)/cm^{-1} 2925, 1575, 1477, 1235, 741 (C–S stretch); δ_H (300 MHz) ($CDCl_3$) 3.89 (3H, s, CH_3), 4.09 (2H, s, CH_2), 6.82–6.89 (2H, m, ArH), 7.15–7.33 (7H, m, ArH).

*4.5.17. 4-Methoxybenzyl-(4′-methoxyphenyl)-sulfide (**4m**)[15].* Following procedure A, the reaction of NaH (0.27 g, 60% dispersion in oil, 6.83 mmol), 4-methoxybenzene thiol (0.91 g, 0.81 mL, 6.50 mmol) and 4-methoxybenzyl chloride (1.02 g, 0.88 mL, 6.50 mmol) afforded, without further purification, **4m** as a white solid (1.32 g, 78%), mp 86–89 °C (lit.[15] 89–90 °C); ν_{max} (KBr)/cm^{-1} 2923, 1612, 1596, 1515, 1494, 1182, 741 (C–S stretch); δ_H (300 MHz) ($CDCl_3$) 3.78 (6H, s, 2×CH_3), 3.95 (2H, s, CH_2), 6.74–6.83 (4H, m, ArH), 7.05–7.15 (2H, m, ArH), 7.20–7.29 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 41.0 (CH_2, *C*H_2), 55.6, 55.7 (CH_3, 2×*C*H_3), 114.1, 114.8 (CH, 2×aromatic *C*H), 126.6 (C, aromatic *C*), 130.4 (CH, aromatic *C*H), 130.5 (C, aromatic *C*), 134.4 (CH, aromatic *C*H), 159.0, 159.5 (C, 2×aromatic *C*–O).

*4.5.18. Benzyl-(4-fluorophenyl)-sulfide (**4n**)[14].* Following procedure A, the reaction of NaH (0.27 g, 60% dispersion in oil, 6.83 mmol), 4-fluorobenzene thiol (0.83 g, 0.69 mL, 6.50 mmol) and benzyl bromide (1.11 g, 0.92 mL, 6.50 mmol) afforded, without further purification, **4n** as a white solid (0.93 g, 65%), mp 33–34 °C (lit.[14] 32.5–33 °C); ν_{max} (KBr)/cm^{-1} 2923, 1590, 1490, 1230, 708 (C–S stretch); δ_H (300 MHz) ($CDCl_3$) 4.03 (2H, s, CH_2), 6.89–6.99 (2H, m, ArH), 7.17–7.32 (7H, m, ArH).

*4.5.19. N-Cyano-S-benzyl-S-phenylsulfilimine (**5a**).* Following procedure B, the reaction of benzyl phenyl sulfide (1.50 g, 7.5 mmol), cyanamine (0.41 g, 9.7 mmol), potassium *tert*-butoxide (1.09 g, 9.0 mmol) and *N*-bromosuccinimide (2.00 g, 11.0 mmol) in methanol (30 mL) and subsequent purification by column chromatography on silica gel using CH_2Cl_2/acetone (9:1) afforded **5a** as a white solid (1.35 g, 75%); mp 72–73 °C. (Found: C, 69.41; H, 5.02; N, 11.49. $C_{14}H_{12}N_2S$ requires C, 69.97; H, 5.03; N, 11.66%.) ν_{max} (KBr)/cm^{-1} 2918, 2144 (C≡N stretch), 1492, 1451, 1165, 1026; δ_H (300 MHz) ($CDCl_3$) 4.28 (1H, A of AB_{system}, J_{AB} 12.6, one of CH_2,), 4.57 (1H, B of AB_{system}, J_{AB} 12.6, one of CH_2), 7.11–7.19 (2H, m, ArH), 7.24–7.43 (3H, m, ArH), 7.48–7.68 (5H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 58.7 (CH_2, *C*H_2), 120.7 (C, *C*≡N), 126.8 (CH, aromatic *C*H), 127.4 (C, aromatic *C*), 129.2, 129.7, 130.0, 130.7, 133.2 (CH, 5×aromatic *C*H), 134.2 (C, aromatic *C*); *m/z* (ESI) 241 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{13}N_2S$ [M+H]$^+$ 241.0799, found 241.0803.

*4.5.20. N-Cyano-S-(4-fluorobenzyl)-S-(4′-fluorophenyl)sulfilimine (**5b**).* Following procedure B, the reaction of 4-fluorobenzyl-(4′-fluorophenyl)-sulfide (**4b**) (0.48 g, 2.0 mmol), cyanamine (0.12 g, 2.6 mmol), potassium *tert*-butoxide (0.27 g, 2.4 mmol) and *N*-bromosuccinimide (0.53 g, 3.0 mmol) and subsequent purification by column chromatography on silica gel using dichloromethane/acetone (6:1) afforded **5b** as a white solid (0.38 g, 68%), mp 112–115 °C. (Found: C, 60.80; H, 3.62; N, 10.44; S, 11.64; F 13.32. $C_{14}H_{10}F_2N_2S$ requires C, 60.86; H, 3.65; N, 10.14; S, 11.60; F 13.75%.) ν_{max} (KBr)/cm^{-1} 2144 (C≡N stretch), 1597, 1509, 1493, 1233, 1176, 1160, 1014, 835; δ_H (300 MHz) ($CDCl_3$) 4.26 (1H, A of AB_{system}, J_{AB} 13.1, one of CH_2,), 4.50 (1H, B of AB_{system}, J_{AB} 12.8, one of CH_2), 6.98–7.09 (2H, m, ArH), 7.09–7.18 (2H, m, ArH), 7.19–7.31 (2H, m, ArH), 7.60–7.71 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 57.9 (CH_2, *C*H_2), 116.3 (CH, d, $^2J_{C-F}$ 21.8, aromatic *C*H), 117.6 (CH, d, $^2J_{C-F}$ 23.2, aromatic *C*H), 120.5 (C, *C*≡N), 122.8 (C, d, $^4J_{C-F}$ 3.8, aromatic *C*), 129.3 (C, aromatic *C*) overlapping with 129.3 (CH, d, $^3J_{C-F}$ 9.0, aromatic *C*H), 132.7 (CH, d, $^3J_{C-F}$ 9.0, aromatic *C*H), 163.5 (C, d, $^1J_{-F}$ 249.0, *C*–F), 165.5 (C, d, $^1J_{C-F}$ 255.0, *C*–F); *m/z* (ESI) 277 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{11}F_2N_2S$ [M+H]$^+$ 277.0611, found 277.0615.

*4.5.21. N-Cyano-S-benzyl-S-(4-methoxyphenyl)sulfilimine (**5c**).* Following procedure B, the reaction of benzyl-(4-methoxyphenyl)-sulfide (**4c**) (0.46 g, 2.0 mmol), cyanamide (0.11 g, 2.6 mmol),

potassium *tert*-butoxide (0.27 g, 2.4 mmol) and *N*-bromosuccinimide (0.53 g, 3.0 mmol) afforded, without further purification, a white solid identified as **5c** (0.45 g, 83%), mp 72–75 °C; ν_{max} (KBr)/cm^{-1} 2360, 2145 (C≡N stretch), 1496, 1455, 1260, 1177, 1023, 832; δ_H (300 MHz) ($CDCl_3$) 3.86 (3H, s, OCH_3), 4.28 (1H, A of AB_{system}, J_{AB} 12.3, one of CH_2), 4.46 (1H, B of AB_{system}, J_{AB} 12.7, one of CH_2), 6.94–7.05 (2H, m, ArH), 7.12–7.19 (2H, m, ArH), 7.26–7.40 (3H, m, ArH), 7.54–7.63 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 55.8 (CH_3, *C*H_3 of OCH_3), 58.3 (CH_2, *C*H_2), 115.4 (CH, aromatic *C*H), 124.6, 127.6 (C, 2×aromatic *C*), 129.08, 129.13, 129.5, 130.7 (CH, 4×aromatic *C*H), 163.6 (C, aromatic *C*–O), 1×*C*≡N signal absent; *m*/*z* (ESI) 271 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{15}H_{15}N_2OS$ [M+H]$^+$ 271.0905, found 271.0904.

*4.5.22. N-Cyano-S-benzyl-S-(4-bromophenyl)sulfilimine (**5d**).* Following procedure B, the reaction of benzyl-(4-bromophenyl)-sulfide (**4d**) (0.56 g, 2.0 mmol), cyanamide (0.11 g, 2.6 mmol), potassium *tert*-butoxide (0.27 g, 2.4 mmol) and *N*-bromosuccinimide (0.53 g, 3.0 mmol) and subsequent purification by column chromatography on silica gel using dichloromethane/acetone (9:1) afforded **5d** as a white solid (0.48 g, 75%), mp 121–125 °C. (Found: C, 52.49; H, 3.49; N, 8.68; S 10.23. $C_{14}H_{11}BrN_2S$ requires C, 52.68; H, 3.47; N, 8.78; S 10.04%.) ν_{max} (KBr)/cm^{-1} 2153 (C≡N stretch), 1475, 1454, 1388, 1186, 1066, 1007, 833; δ_H (300 MHz) ($CDCl_3$) 4.28 (1H, A of AB_{system}, J_{AB} 13.0, one of CH_2), 4.54 (1H, B of AB_{system}, J_{AB} 13.0, one of CH_2), 7.11–7.20 (2H, m, ArH), 7.26–7.43 (3H, m, ArH), 7.44–7.54 (2H, m, ArH), 7.60–7.70 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 58.8 (CH_2, *C*H_2), 120.5 (C, *C*≡N), 127.0 (C, aromatic *C*), 128.1, 129.2, 129.8, 130.8, 133.2 (CH, 5×aromatic *C*H), 133.1 (C, aromatic *C*), 1×aromatic *C* signal absent; *m*/*z* (ESI) 319, 321 (1:1) [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}{}^{79}BrN_2S$ [M+H]$^+$ 318.9905, found 318.9904.

*4.5.23. N-Cyano-S-benzyl-S-(4-nitrophenyl)sulfilimine (**5e**).* Following procedure B, the reaction of benzyl-(4-nitrophenyl)-sulfide (**4e**) (0.49 g, 2.0 mmol), cyanamide (0.11 g, 2.6 mmol), potassium *tert*-butoxide (0.27 g, 2.4 mmol) and *N*-bromosuccinimide (0.53 g, 3.0 mmol) and subsequent purification by column chromatography on silica gel using dichloromethane/acetone (9:1) afforded a yellow solid identified as **5e** (0.43 g, 75%), mp 135–139 °C. (Found: C, 58.71; H, 4.08; N, 14.63; S, 11.38. $C_{14}H_{11}N_3O_2S$ requires C, 58.93; H, 3.89; N, 14.73; S, 11.24%.) ν_{max} (KBr)/cm^{-1} 2925, 2146 (C≡N stretch), 1606, 1579, 1539 (asymmetric NO_2 stretch), 1351 (symmetric NO_2 stretch), 1183, 1012; δ_H (300 MHz) ($CDCl_3$) 4.33 (1H, A of AB_{system}, J_{AB} 12.6, one of CH_2), 4.62 (1H, B of AB_{system}, J_{AB} 12.6, one of CH_2), 7.10–7.18 (2H, m, ArH), 7.31–7.46 (3H, m, ArH), 7.74–7.81 (2H, m, ArH), 8.31–8.39 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 59.4 (CH_2, *C*H_2), 124.8 (CH, aromatic *C*H), 126.2 (C, aromatic *C*), 127.8, 129.5, 130.3, 130.8 (CH, 4×aromatic *C*H), 140.8 (C, aromatic *C*), 1×*C*≡N signal absent, 1×aromatic *C* signal absent; *m*/*z* (ESI) 286 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}N_3O_2S$ [M+H]$^+$ 286.0650, found 286.0655.

*4.5.24. N-Cyano-S-benzyl-S-(2-bromophenyl)sulfilimine (**5f**).* Following procedure B, the reaction of benzyl-(2-bromophenyl)-sulfide (**4f**) (0.28 g, 1.0 mmol), cyanamide (0.06 g, 1.3 mmol), potassium *tert*-butoxide (0.14 g, 1.2 mmol) and *N*-bromosuccinimide (0.27 g, 1.5 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **5f** as a white solid (0.24 g, 75%), mp 132–133 °C. (Found: C, 52.54; H, 3.41; N, 8.74; S 10.36. $C_{14}H_{11}BrN_2S$ requires C, 52.68; H, 3.47; N, 8.78; S 10.04%.) ν_{max} (KBr)/cm^{-1} 2973, 2157 (C≡N stretch), 1565, 1495, 1455, 1180, 1019; δ_H (300 MHz) ($CDCl_3$) 4.32 (1H, A of AB_{system}, J_{AB} 12.9, one of CH_2), 4.44 (1H, B of AB_{system}, J_{AB} 12.9, one of CH_2), 7.23–7.60 (7H, m, ArH), 7.64–7.72 (1H, m, ArH), 7.87–7.95 (1H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 57.9 (CH_2, *C*H_2), 120.7, 120.8, 127.4 (C, 1×*C*≡N, 2×aromatic *C*), 128.3, 129.0, 129.2, 129.9, 130.9, 133.6, 134.0 (CH, 7×aromatic *C*H), 134.8 (C, aromatic *C*); *m*/*z* (ESI) 319, 321 (1:1) [(M+H)$^+$].

*4.5.25. N-Cyano-S-benzyl-S-(2-fluorophenyl)sulfilimine (**5g**).* Following procedure B, the reaction of benzyl-(2-fluorophenyl)-sulfide (**4g**) (0.44 g, 2.0 mmol), cyanamine (0.12 g, 2.6 mmol), potassium *tert*-butoxide (0.27 g, 2.4 mmol) and *N*-bromosuccinimide (0.53 g, 3.0 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **5g** as a white solid (0.31 g, 60%), mp 116–120 °C; ν_{max} (KBr)/cm^{-1} 2982, 2928, 2143 (C≡N stretch), 1597, 1584, 1473, 1455, 1153, 1027; δ_H (300 MHz) ($CDCl_3$) 4.41 (1H, A of AB_{system}, J_{AB} 12.9, one of CH_2,), 4.49 (1H, B of AB_{system}, J_{AB} 12.6, one of CH_2), 7.14–7.46 (7H, m, ArH), 7.55–7.66 (1H, m, ArH), 7.87–7.97 (1H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 57.7 (CH_2, d, $^4J_{C-F}$ 1.7, *C*H_2), 116.5 (CH, d, $^2J_{C-F}$ 20.0, aromatic *C*H), 120.4 (C, *C*≡N), 121.9 (C, d, $^2J_{C-F}$ 15.5, aromatic *C*), 126.1 (CH, d, J_{C-F} 3.4, aromatic *C*H), 127.1 (C, aromatic *C*), 127.6, 129.1, 129.9, 130.8 (CH, 4×aromatic *C*H), 134.9 (CH, d, J_{C-F} 8.0, aromatic *C*H), 158.5 (C, d, $^1J_{C-F}$ 248.3, *C*–F); *m*/*z* (ESI) 259 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}FN_2S$ [M+H]$^+$ 259.0705, found 259.0700.

*4.5.26. N-Cyano-S-benzyl-S-(2-chlorophenyl)sulfilimine (**5h**).* Following procedure B, the reaction of benzyl-(2-chlorophenyl)-sulfide (**4h**) (0.47 g, 2.0 mmol), cyanamide (0.11 g, 2.6 mmol), potassium *tert*-butoxide (0.27 g, 2.4 mmol) and *N*-bromosuccinimide (0.53 g, 3.0 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **5h** as a white solid (0.32 g, 58%), mp 140–142 °C. (Found: C, 61.14; H, 3.96; N, 10.10; S 11.89; Cl 13.18. $C_{14}H_{11}ClN_2S$ requires C, 61.20; H, 4.04; N, 10.20; S 10.67; Cl 12.90%.) ν_{max} (KBr)/cm^{-1} 2973, 2918, 2153 (C≡N stretch), 1569, 1494, 1439, 1176, 1029; δ_H (300 MHz) ($CDCl_3$) 4.34 (1H, A of AB_{system}, J_{AB} 12.9, one of CH_2), 4.43 (1H, B of AB_{system}, J_{AB} 12.9, one of CH_2), 7.21–7.29 (2H, m, ArH), 7.30–7.44 (3H, m, ArH), 7.45–7.60 (3H, m, ArH), 7.88–7.97 (1H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 57.6 (CH_2, *C*H_2), 120.7 (C, *C*≡N), 127.3 (C, aromatic *C*–Cl), 127.9, 128.6, 129.0, 129.8, 130.4, 130.9 (CH, 6×aromatic *C*H), 131.7, 132.9 (C, 2×aromatic *C*), 133.8 (CH, aromatic *C*H); *m*/*z* (ESI) 275, 277 (3:1) [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}{}^{35}ClN_2S$ [M+H]$^+$ 275.0410, found 275.0400.

*4.5.27. N-Cyano-S-benzyl-S-(4-chlorophenyl)sulfilimine (**5i**).* Following procedure B, the reaction of benzyl-(4-chlorophenyl)-sulfide (**4i**) (0.35 g, 1.50 mmol), cyanamide (0.08 g, 1.90 mmol), potassium *tert*-butoxide (0.20 g, 1.80 mmol) and *N*-bromosuccinimide (0.40 g, 2.25 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **5i** as a white solid (0.32 g, 78%), mp 122–125 °C. (Found: C, 61.09; H, 3.85; N, 10.04; S 11.72; Cl 13.21. $C_{14}H_{11}ClN_2S$ requires C, 61.20; H, 4.04; N, 10.20; S 10.67; Cl 12.90%.) ν_{max} (KBr)/cm^{-1} 3081, 2157 (C≡N stretch), 1570, 1475, 1452, 1187, 1010; δ_H (300 MHz) ($CDCl_3$) 4.27 (1H, A of AB_{system}, J_{AB} 12.9, one of CH_2), 4.56 (1H, B of AB_{system}, J_{AB} 12.6, one of CH_2), 7.10–7.19 (2H, m, ArH), 7.29–7.44 (3H, m, ArH), 7.45–7.61 (4H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 58.9 (CH_2, *C*H_2), 120.4 (C, *C*≡N), 127.0 (C, aromatic *C*–Cl), 128.1, 129.3, 129.8, 130.3, 130.7 (CH, 5×aromatic *C*H), 132.5, 139.9 (C, 2×aromatic *C*); *m*/*z* (ESI) 275, 277 (3:1) [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}{}^{35}ClN_2S$ [M+H]$^+$ 275.0410, found 275.0402.

*4.5.28. N-Cyano-S-benzyl-S-(3-fluorophenyl)sulfilimine (**5j**).* Following procedure B, the reaction of benzyl-(3-fluorophenyl)-sulfide (**4j**) (1.10 g, 5.0 mmol), cyanamine (0.28 g, 6.6 mmol), potassium *tert*-butoxide (0.69 g, 6.1 mmol) and *N*-bromosuccinimide (1.37 g, 7.7 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **5j** as

a white solid (0.81 g, 63%), mp 114–117 °C. (Found: C, 65.23; H, 4.29; N 10.80; S 12.80; F 7.80. $C_{14}H_{11}FN_2S$ requires C, 65.10; H, 4.29; N 10.84; S 12.41; F 7.35%.) ν_{max} (KBr)/cm^{-1} 3027, 2156 (C≡N stretch), 1585, 1473, 1418, 1223, 1187, 1079; δ_H (300 MHz) ($CDCl_3$) 4.28 (1H, A of AB_{system}, J_{AB} 12.6, one of CH_2), 4.55 (1H, B of AB_{system}, J_{AB} 12.6, one of CH_2), 7.11–7.21 (2H, m, ArH), 7.23–7.45 (6H, m, ArH), 7.46–7.57 (1H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 59.1 (CH_2, *C*H_2), 113.9 (CH, d, $^2J_{C-F}$ 24.0, aromatic *C*H), 120.3 (C, *C*≡N), 120.4 (CH, d, $^2J_{C-F}$ 21.0, aromatic *C*H), 122.5 (CH, d, $^4J_{C-F}$ 3.8, aromatic *C*H), 126.9 (C, aromatic *C*), 129.2, 129.9, 130.7 (CH, 3×aromatic *C*H), 131.6 (CH, d, $^3J_{C-F}$ 7.5, aromatic *C*H), 136.3 (C, d, $^3J_{C-F}$ 6.0, aromatic *C*), 162.9 (C, d, $^1J_{C-F}$ 252.8, *C*–F); *m*/*z* (ESI) 259 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}FN_2S$ [M+H]$^+$ 259.0705, found 259.0706.

*4.5.29. N-Cyano-S-benzyl-S-(3-bromophenyl)sulfilimine (**5k**).* Following procedure B, the reaction of benzyl-(3-bromophenyl)-sulfide (**4k**) (0.56 g, 2.0 mmol), cyanamide (0.11 g, 2.6 mmol), potassium *tert*-butoxide (0.27 g, 2.4 mmol) and *N*-bromosuccinimide (0.53 g, 3.0 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **5k** as a white solid (0.56 g, 88%), mp 140–143 °C. (Found: C, 52.52; H, 3.21; N, 8.40; S 10.38. $C_{14}H_{11}BrN_2S$ requires C, 52.68; H, 3.47; N, 8.78; S 10.04%.) ν_{max} (KBr)/cm^{-1} 2924, 2143 (C≡N stretch), 1567, 1457, 1151, 1102, 883; δ_H (300 MHz) ($CDCl_3$) 4.26 (1H, A of AB_{system}, J_{AB} 12.9, one of CH_2), 4.55 (1H, B of AB_{system}, J_{AB} 12.6, one of CH_2), 7.12–7.20 (2H, m, ArH), 7.30–7.46 (4H, m, ArH), 7.51–7.59 (1H, m, ArH), 7.66–7.77 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 59.3 (CH_2, *C*H_2), 120.3 (C, *C*≡N), 123.9 (C, aromatic *C*–Br), 125.1 (CH, aromatic *C*H), 126.8 (C, aromatic *C*), 129.2, 129.3, 130.0, 130.8, 131.3 (CH, 5×aromatic *C*H), 136.1 (C, aromatic *C*), 136.2 (CH, aromatic *C*H); *m*/*z* (ESI) 319, 321 (1:1) [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}{}^{79}BrN_2S$ [M+H]$^+$ 318.9905, found 318.9897.

*4.5.30. N-Cyano-S-benzyl-S-(2-methoxyphenyl)sulfilimine (**5l**).* Following procedure B, the reaction of benzyl-(2-methoxyphenyl)-sulfide (**4l**) (0.46 g, 2.0 mmol), cyanamide (0.11 g, 2.6 mmol), potassium *tert*-butoxide (0.27 g, 2.4 mmol) and *N*-bromosuccinimide (0.53 g, 3.0 mmol) afforded, without further purification, a white solid identified as **5l** (0.45 g, 83%), mp 72–75 °C. (Found: C, 66.83; H, 5.22; N, 9.96; S 11.56. $C_{15}H_{14}N_2OS$ requires C, 66.64; H, 5.22; N, 10.36; S 11.86%.) ν_{max} (KBr)/cm^{-1} 2924, 2153 (C≡N stretch), 1585, 1479, 1453, 1251, 1163, 1130, 1013, 748; δ_H (300 MHz) ($CDCl_3$) 3.93 (3H, s, OCH_3), 4.30 (1H, A of AB_{system}, J_{AB} 12.9, one of CH_2), 4.40 (1H, B of AB_{system}, J_{AB} 12.6, one of CH_2), 6.94–7.03 (1H, m, ArH), 7.12–7.42 (6H, m, ArH), 7.49–7.60 (1H, m, ArH), 7.78–7.87 (1H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 56.4 (CH_3, *C*H_3 of OCH_3), 56.8 (CH_2, *C*H_2), 111.4 (CH, aromatic *C*H), 121.5, 121.9 (C, 1×*C*≡N, 1×aromatic *C*), 122.3, 127.2 (CH, 2×aromatic *C*H), 128.2 (C, aromatic *C*), 128.8, 129.4, 130.8, 134.0 (CH, 4×aromatic *C*H), 155.8 (C, aromatic *C*–O); *m*/*z* (ESI) 271 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{15}H_{15}N_2OS$ [M+H]$^+$ 271.0905, found 271.0898.

*4.5.31. N-Cyano-S-(4-methoxybenzyl)-S-(4′-methoxyphenyl)sulfilimine (**5m**).* Following procedure B, the reaction of 4-methoxybenzyl-(4′-methoxyphenyl)-sulfide (**4m**) (0.26 g, 1.0 mmol), cyanamide (0.06 g, 1.3 mmol), potassium *tert*-butoxide (0.14 g, 1.2 mmol) and *N*-bromosuccinimide (0.27 g, 1.5 mmol) afforded, without further purification, a yellow solid identified as **5m** (0.21 g, 70%), mp 114–117 °C. (Found: C, 64.07; H, 5.56; N, 8.92; S 11.07. $C_{16}H_{16}N_2O_2S$ requires C, 63.98; H, 5.37; N, 9.33; S 10.67%.) ν_{max} (KBr)/cm^{-1} 2924, 2141 (C≡N stretch), 1615, 1509, 1496, 1256, 1153, 1106, 1021; δ_H (300 MHz) ($CDCl_3$) 3.79 (3H, s, OCH_3), 3.87 (3H, s, OCH_3), 4.23 (1H, A of AB_{system}, J_{AB} 12.6, one of CH_2), 4.50 (1H, B of AB_{system}, J_{AB} 12.6, one of CH_2), 6.78–6.86 (2H, m, ArH), 6.95–7.11 (4H, m, ArH), 7.53–7.62 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 55.3, 55.7 (CH_3, 2×*C*H_3 of OCH_3), 58.1 (CH_2, *C*H_2), 114.5, 115.4 (CH, 2×aromatic *C*H), 119.3, 121.0, 124.7 (C, 1×*C*≡N, 2×aromatic *C*), 129.1, 132.0 (CH, 2×aromatic *C*H), 160.5, 163.5 (C, 2×aromatic *C*–O); *m*/*z* (ESI) 301 [(M+H)$^+$].

*4.5.32. N-Cyano-S-benzyl-S-(4-fluorophenyl)sulfilimine (**5n**).* Following procedure B, the reaction of benzyl-(4-fluorophenyl)-sulfide (**4n**) (0.65 g, 3.0 mmol), cyanamine (0.16 g, 3.9 mmol), potassium *tert*-butoxide (0.40 g, 3.6 mmol) and *N*-bromosuccinimide (0.80 g, 4.5 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **5n** as a white solid (0.42 g, 55%), mp 121–125 °C; ν_{max} (KBr)/cm^{-1} 2918, 2148 (C≡N stretch), 1583, 1491, 1451, 1226, 1180, 1158, 1007; δ_H (300 MHz) ($CDCl_3$) 4.27 (1H, A of AB_{system}, J_{AB} 12.6, one of CH_2,), 4.57 (1H, B of AB_{system}, J_{AB} 12.6, one of CH_2), 7.05–7.43 (7H, m, ArH), 7.58–7.69 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 58.9 (CH_2, *C*H_2), 117.4 (CH, d, $^2J_{C-F}$ 22.5, aromatic *C*H), 120.5 (C, *C*≡N), 127.0 (C, aromatic *C*), 129.2 (CH, aromatic *C*H), 129.4 (CH, d, $^3J_{C-F}$ 9.8, aromatic *C*H), 129.6 (C, d, $^4J_{C-F}$ 3.0, aromatic *C*), 129.8, 130.7 (CH, 2×aromatic *C*H), 165.5 (C, d, $^1J_{C-F}$ 255.0, *C*–F); *m*/*z* (ESI) 259 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}FN_2S$ [M+H]$^+$ 259.0705, found 259.0704.

*4.5.33. N-Cyano-S-benzyl-S-phenyl sulfoximine (**6a**).* Following procedure C, the reaction of *N*-cyano-benzyl-phenyl sulfilimine (**5a**) (1.30 g, 5.4 mmol), *m*-chloroperbenzoic acid (1.82 g, 77%, 8.1 mmol) and K_2CO_3 (2.24 g, 16.0 mmol) and subsequent purification by column chromatography using hexane/ethyl acetate (60:40) afforded **6a** as a white solid (1.12 g, 80%), mp 169–173 °C; ν_{max} (KBr)/cm^{-1} 2978, 2919, 2197 (C≡N stretch), 1448, 1244 (asymmetric SON stretch), 1185, 1081 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.62 (2H, s, CH_2), 7.01–7.09 (2H, m, ArH), 7.23–7.33 (2H, m, ArH), 7.34–7.43 (1H, m, ArH), 7.49–7.59 (2H, m, ArH), 7.60–7.77 (3H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 63.4 (CH_2, *C*H_2), 112.1 (C, *C*≡N), 125.5 (C, aromatic *C*), 128.9, 129.2, 129.7, 130.0, 131.3 (CH, 5×aromatic *C*H), 133.1 (C, aromatic *C*), 135.4 (CH, aromatic *C*H); *m*/*z* (ESI) 257 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{13}N_2OS$ [M+H]$^+$ 257.0749, found 257.0738.

*4.5.34. N-Cyano-S-(4-fluorobenzyl)-S-(4′-fluorophenyl)sulfoximine (**6b**).* Following procedure C, the reaction of *N*-cyano-*S*-(4-fluorobenzyl)-*S*-(4′-fluorophenyl)sulfilimine (**5b**) (0.30 g, 1.1 mmol), *m*-chloroperbenzoic acid (0.36 g, 77%, 1.6 mmol) and K_2CO_3 (0.45 g, 3.3 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **6b** as a white solid (0.25 g, 77%), mp 109–114 °C; ν_{max} (KBr)/cm^{-1} 2194 (C≡N stretch), 1587, 1509, 1492, 1240 (asymmetric SON stretch), 1191, 1158, 1087 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.60 (2H, s, CH_2), 6.96–7.12 (4H, m, ArH), 7.20–7.31 (2H, m, ArH), 7.61–7.71 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 62.6 (CH_2, *C*H_2), 111.2 (C, *C*≡N), 116.3 (CH, d, $^2J_{C-F}$ 21.8, aromatic *C*H), 117.4 (CH, d, $^2J_{C-F}$ 22.5, aromatic *C*H), 121.3 (C, d, $^4J_{C-F}$ 3.8, aromatic *C*), 128.6 (C, d, $^4J_{C-F}$ 3.0, aromatic *C*), 132.2 (CH, d, $^3J_{C-F}$ 9.8, aromatic *C*H), 133.2 (CH, d, $^3J_{C-F}$ 9.0, aromatic *C*H), 163.7 (C, d, $^1J_{C-F}$ 249.8, *C*–F), 166.9 (C, d, $^1J_{C-F}$ 258.8, *C*–F); *m*/*z* (ESI) 293 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{11}F_2N_2OS$ [M+H]$^+$ 293.0560, found 293.0570.

*4.5.35. N-Cyano-S-benzyl-S-(4-methoxyphenyl)sulfoximine (**6c**).* Following procedure C, the reaction of *N*-cyano-*S*-benzyl-*S*-(4-methoxyphenyl)sulfilimine (**5c**) (0.40 g, 1.5 mmol), *m*-chloroperbenzoic acid (0.50 g, 77%, 4.5 mmol) and K_2CO_3 (0.62 g, 4.5 mmol) and subsequent purification by column chromatography using hexane/ethyl acetate (60:40) afforded **6c** as a white solid (0.29 g, 68%), mp 129–133 °C. (Found: C, 62.65; H, 4.93; N, 9.65; S 10.81. $C_{15}H_{14}N_2O_2S$ requires C, 62.92; H, 4.93; N, 9.78; S 11.20%.) ν_{max} (KBr)/cm^{-1} 2965, 2185 (C≡N stretch), 1590, 1495, 1247 (asymmetric SON stretch), 1172, 1090 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 3.89 (3H, s, CH_3), 4.59 (2H, s, CH_2), 6.96 (2H, d, *J*

9.3, ArH), 7.08 (2H, d, *J* 8.2, ArH), 7.23–7.44 (3H, m, ArH), 7.54 (2H, d, *J* 9.3, ArH); δ_C (75.5 MHz) ($CDCl_3$) 55.9 (CH_3, *C*H_3), 63.5 (CH_2, *C*H_2), 112.5 (C, *C*≡N), 115.0 (CH, aromatic *C*H), 123.5, 125.9 (C, 2×aromatic *C*), 128.9, 129.8, 131.3, 131.5 (CH, 4×aromatic *C*H), 165.1 (C, aromatic *C*–O); *m*/*z* (ESI) 287 [$(M+H)^+$]; HRMS (ESI): exact mass calculated for $C_{15}H_{15}N_2O_2S$ $[M+H]^+$ 287.0854, found 287.0850.

*4.5.36. N-Cyano-S-benzyl-S-(4-bromophenyl)sulfoximine (**6d**).* Following procedure C, the reaction of *N*-cyano-*S*-benzyl-*S*-(4-bromophenyl)sulfilimine (**5d**) (0.40 g, 1.25 mmol), *m*-chloroperbenzoic acid (0.42 g, 77%, 1.88 mmol) and K_2CO_3 (0.52 g, 3.75 mmol) afforded, without further purification, a white solid identified as **6d** (0.35 g, 83%), mp 141–143 °C. (Found: C, 50.13; H, 3.14; N, 8.26; S 9.83. $C_{14}H_{11}BrN_2OS$ requires C, 50.16; H, 3.31; N, 8.36; S 9.57.) ν_{max} (KBr)/cm^{-1} 2918, 2184 (C≡N stretch), 1570, 1494, 1246 (asymmetric SON stretch), 1204, 1190, 1070 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.63 (2H, s, CH_2), 7.04–7.12 (2H, m, ArH), 7.24–7.50 (5H, m, ArH), 7.63–7.71 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 63.3 (CH_2, *C*H_2), 111.7 (C, *C*≡N), 125.3 (C, aromatic *C*–Br), 129.1, 130.1, 130.6, 131.3 (CH, 4×aromatic *C*H), 132.1 (C, aromatic *C*), 133.1 (CH, aromatic *C*H); *m*/*z* (ESI) 335, 337 (1:1) [$(M+H)^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}{}^{79}BrN_2OS$ $[M+H]^+$ 334.9854, found 334.9859.

*4.5.37. N-Cyano-S-benzyl-S-(4-nitrophenyl)sulfoximine (**6e**).* Following procedure C, the reaction of *N*-cyano-*S*-benzyl-*S*-(4-nitrophenyl)sulfilimine (**5e**) (0.38 g, 1.30 mmol), *m*-chloroperbenzoic acid (0.44 g, 77%, 1.95 mmol) and K_2CO_3 (0.54 g, 3.90 mmol) and subsequent purification by column chromatography using hexane/ethyl acetate (60:40) afforded **6e** as a yellow solid (0.16 g, 41%), mp 145–148 °C; ν_{max} (KBr)/cm^{-1} 2931, 2197 (C≡N stretch), 1607, 1533 (asymmetric NO_2 stretch), 1494, 1455, 1346 (symmetric NO_2 stretch), 1254 (asymmetric SON stretch), 1203, 1174, 1085 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.70 (2H, br s, CH_2), 7.05–7.12 (2H, m, ArH), 7.18–7.47 (3H, m, ArH), 7.79–7.86 (2H, m, ArH), 8.32–8.38 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 63.4 (CH_2, *C*H_2), 124.6 (CH, aromatic *C*H), 124.7 (C, aromatic *C*), 129.3, 130.5, 130.8, 131.3 (CH, 4×aromatic *C*H), 139.0, 151.7 (C, 2×aromatic *C*), 1×*C*≡N signal absent; *m*/*z* (ESI) 302 [$(M+H)^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}N_3O_3S$ $[M+H]^+$ 302.0599,. found 302.0599.

*4.5.38. N-Cyano-S-benzyl-S-(4-chlorophenyl)sulfoximine (**6i**).* Following procedure C, the reaction of *N*-cyano-*S*-benzyl-*S*-(4-chlorophenyl)sulfilimine (**5i**) (0.15 g, 0.55 mmol), *m*-chloroperbenzoic acid (0.18 g, 77%, 0.83 mmol) and K_2CO_3 (0.23 g, 1.65 mmol) and subsequent purification by column chromatography using hexane/ethyl acetate (60:40) afforded **6i** as a white solid (0.10 g, 63%), mp 123–126 °C; ν_{max} (KBr)/cm^{-1} 2920, 2193 (C≡N stretch), 1571, 1475, 1247 (asymmetric SON stretch), 1182, 1084 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.63 (2H, br s, CH_2), 7.03–7.12 (2H, m, ArH), 7.25–7.45 (3H, m, ArH), 7.46–7.59 (4H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 63.4 (CH_2, *C*H_2), 111.8 (C, *C*≡N), 125.3 (C, aromatic *C*), 129.1, 130.0, 130.1, 130.6, 131.3 (CH, 5×aromatic *C*H), 131.5, 142.6 (C, 2×aromatic *C*); *m*/*z* (ESI) 291, 293 (3:1) [$(M+H)^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}{}^{35}ClN_2OS$ $[M+H]^+$ 291.0359, found 291.0351.

*4.5.39. N-Cyano-S-benzyl-S-(3-fluorophenyl)sulfoximine (**6j**).* Following procedure C, the reaction of *N*-cyano-*S*-benzyl-*S*-(3-fluorophenyl)sulfilimine (**5j**) (0.15 g, 0.58 mmol), *m*-chloroperbenzoic acid (0.19 g, 77%, 0.87 mmol) and K_2CO_3 (0.24 g, 1.74 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **6j** as a white solid (0.11 g, 69%), mp 130–131 °C; ν_{max} (KBr)/cm^{-1} 2967, 2194 (C≡N stretch), 1593, 1476, 1242 (asymmetric SON stretch), 1179, 1078 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.64 (2H, br s, CH_2), 7.04–7.12 (2H, m, ArH), 7.24–7.49 (6H, m, ArH), 7.49–7.60 (1H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 63.3 (CH_2, *C*H_2), 111.6 (C, *C*≡N), 116.6 (CH, d, $^2J_{C-F}$ 24.8, aromatic *C*H), 122.8 (CH, d, $^2J_{C-F}$ 21.8, aromatic *C*H), 125.0 (CH, d, $^4J_{C-F}$ 3.5, aromatic *C*H), 125.1 (C, aromatic C), 129.1, 130.2, 131.3 (CH, 3×aromatic *C*H), 131.6 (CH, d, $^3J_{C-F}$ 7.5, aromatic *C*H), 135.2 (C, d, $^3J_{C-F}$ 6.8, aromatic *C*), 162.5 (C, d, $^1J_{C-F}$ 252.8, *C*–F); *m*/*z* (ESI) 275 [$(M+H)^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}FN_2OS$ $[M+H]^+$ 275.0654, found 275.0649.

*4.5.40. N-Cyano-S-benzyl-S-(3-bromophenyl)sulfoximine (**6k**).* Following procedure C, the reaction of *N*-cyano-*S*-benzyl-*S*-(3-bromophenyl)sulfilimine (**5k**) (0.15 g, 0.47 mmol), *m*-chloroperbenzoic acid (0.16 g, 77%, 0.71 mmol) and K_2CO_3 (0.19 g, 1.41 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **6k** as a white solid (0.11 g, 69%), mp 120–122 °C; ν_{max} (KBr)/cm^{-1} 2922, 2195 (C≡N stretch), 1568, 1455, 1246 (asymmetric SON stretch), 1181, 1077 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.63 (2H, br s, CH_2), 7.03–7.12 (2H, m, ArH), 7.28–7.47 (4H, m, ArH), 7.52–7.58 (1H, m, ArH), 7.73 (1H, t, *J* 1.8, ArH), 7.81–7.87 (1H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 63.5 (CH_2, *C*H_2), 123.8, 125.1 (C, 2×aromatic *C*), 127.7, 129.1, 130.3, 131.0, 131.3, 131.9 (CH, 6×aromatic *C*H), 135.0 (C, aromatic *C*), 138.4 (CH, aromatic *C*H), 1×*C*≡N signal absent; *m*/*z* (ESI) 335, 337 (1:1) [$(M+H)^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}{}^{79}BrN_2OS$ $[M+H]^+$ 334.9854, found 334.9846.

*4.5.41. N-Cyano-S-benzyl-S-(2-methoxyphenyl)sulfoximine (**6l**).* Following procedure C, the reaction of *N*-cyano-*S*-benzyl-*S*-(2-methoxyphenyl)sulfilimine (**5l**) (0.30 g, 1.10 mmol), *m*-chloroperbenzoic acid (0.37 g, 77%, 1.65 mmol) and K_2CO_3 (0.46 g, 3.33 mmol) and subsequent purification by column chromatography using hexane/ethyl acetate (1:4) afforded **6l** as a white solid (0.05 g, 16%),[†] mp 145–148 °C; ν_{max} (KBr)/cm^{-1} 2929, 2186 (C≡N stretch), 1593, 1576, 1481, 1236 (asymmetric SON stretch), 1176, 1059 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.13 (3H, s, CH_3), 4.80 (1H, A of AB_{system}, J_{AB} 13.8, one of CH_2), 4.94 (1H, B of AB_{system}, J_{AB} 13.8, one of CH_2), 7.01–7.09 (1H, m, ArH), 7.11–7.21 (3H, m, ArH), 7.22–7.38 (3H, m, ArH), 7.61–7.72 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 57.0 (CH_3, *C*H_3), 60.5 (CH_2, *C*H_2), 112.3 (C, *C*≡N), 112.9 (CH, aromatic *C*H), 120.9 (C, aromatic *C*), 121.6 (CH, aromatic *C*H), 125.7 (C, aromatic *C*), 128.9, 129.8, 131.1, 131.9, 137.5 (CH, 5×aromatic *C*H), 157.2 (C, aromatic *C*–O); *m*/*z* (ESI) 287 [$(M+H)^+$]; HRMS (ESI): exact mass calculated for $C_{15}H_{15}N_2O_2S$ $[M+H]^+$ 287.0854, found 287.0843.

*4.5.42. N-Cyano-S-(4-methoxybenzyl)-S-(4′-methoxyphenyl)sulfoximine (**6m**).* Following procedure C, the reaction of *N*-cyano-*S*-(4-methoxybenzyl)-*S*-(4′-methoxyphenyl)sulfilimine (**5m**) (0.15 g, 0.50 mmol), *m*-chloroperbenzoic acid (0.17 g, 77%, 0.75 mmol) and K_2CO_3 (0.21 g, 1.50 mmol) and subsequent purification by column chromatography using hexane/ethyl acetate (70:30) afforded **6m** as a white solid (0.09 g, 56%), mp 160–164 °C; ν_{max} (KBr)/cm^{-1} 2964, 2184 (C≡N stretch), 1611, 1586, 1571, 1247 (asymmetric SON stretch), 1172, 1090 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 3.80 (3H, s, CH_3), 3.89 (3H, s, CH_3), 4.51 (1H, A of AB_{system}, J_{AB} 14.4, one of CH_2), 4.56 (1H, B of AB_{system}, J_{AB} 14.1, one of CH_2), 6.76–6.84 (2H, m, ArH), 6.92–7.02 (4H, m, ArH), 7.49–7.58 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 55.3, 55.9 (CH_3, 2×*C*H_3), 63.1 (CH_2, *C*H_2), 114.3, 115.0 (CH, 2×aromatic *C*H), 117.6, 123.7 (C, 2×aromatic *C*), 131.6, 132.7 (CH, 2×aromatic *C*H), 160.8, 165.1 (C, 2×aromatic *C*–O),

[†] This reaction was repeated. Crude ^1H NMR analysis showed molar ratio of **4l**/**5l**/**6l** was 1:2.1:1.

1×C≡N signal absent; *m/z* (ESI) 317 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{16}H_{17}N_2O_3S$ [M+H]$^+$ 317.0960, found 317.0951.

*4.5.43. N-Cyano-S-benzyl-S-(4-fluorophenyl)sulfoximine (**6n**).* Following procedure C, the reaction of *N*-cyano-*S*-benzyl-*S*-(4-fluorophenyl)sulfilimine (**5n**) (0.28 g, 1.08 mmol), *m*-chloroperbenzoic acid (0.36 g, 77%, 1.62 mmol) and K_2CO_3 (0.45 g, 3.25 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **6n** as a white solid (0.20 g, 67%), mp 137–139 °C; ν_{max} (KBr)/cm^{-1} 2973, 2193 (C≡N stretch), 1592, 1493, 1255 (asymmetric SON stretch), 1157, 1089 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.63 (2H, br s, CH_2), 7.02–7.10 (2H, m, ArH), 7.15–7.44 (5H, m, ArH), 7.58–7.69 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 63.5 (CH_2, *C*H$_2$), 111.9 (C, *C*≡N), 117.2 (CH, d, $^2J_{C-F}$ 23.3, aromatic *C*H), 125.5 (C, aromatic *C*), 128.8 (C, d, $^4J_{C-F}$ 3.0, aromatic *C*), 129.1, 130.1, 131.3 (CH, 3×aromatic *C*H), 132.3 (CH, d, $^3J_{C-F}$ 9.8, aromatic *C*H), 166.9 (C, d, $^1J_{C-F}$ 258.0, *C*–F); *m/z* (ESI) 275 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{12}FN_2OS$ [M+H]$^+$ 275.0654, found 275.0651.

*4.5.44. N-Carbamoyl-S-benzyl-S-phenyl sulfoximine (**7a**).* Following procedure D, the reaction of *N*-cyano-*S*-benzyl-*S*-phenyl sulfoximine (**6a**) (0.09 g, 0.35 mmol) and trifluoroacetic acid (0.12 g, 0.08 mL, 1.05 mmol) and subsequent purification by column chromatography using hexane/ethyl acetate (60:40) afforded **7a** as a white solid (0.05 g, 52%), mp 175–178 °C; ν_{max} (KBr)/cm^{-1} 3430 (asymmetric NH_2 stretch), 3193 (symmetric NH_2 stretch), 1647 (C=O stretch), 1607, 1454, 1203 (asymmetric SON stretch), 1181, 1084 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.76 (1H, A of AB_{system}, J_{AB} 13.8, one of CH_2), 4.93 (3H, B of AB_{system} overlapping with br s, J_{AB} 13.5, one of CH_2 and NH_2), 6.93–7.02 (2H, m, ArH), 7.15–7.34 (3H, m, ArH), 7.39–7.50 (2H, m, ArH), 7.55–7.70 (3H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 62.1 (CH_2, *C*H$_2$), 127.9 (C, aromatic *C*), 128.5, 128.7, 128.9, 129.0, 131.2, 133.7 (CH, 6×aromatic *C*H), 135.6 (C, aromatic *C*), 161.7 (C, *C*=O); *m/z* (ESI) 275 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{15}N_2O_2S$ [M+H]$^+$ 275.0854, found 275.0841.

*4.5.45. N-Carbamoyl-S-(4-fluorobenzyl)-S-(4′-fluorophenyl)sulfoximine (**7b**).* Following procedure D, the reaction of *N*-cyano-*S*-(4-fluorobenzyl)-*S*-(4′-fluorophenyl)sulfoximine (**6b**) (0.10 g, 0.34 mmol) and trifluoroacetic acid (0.12 g, 0.08 mL, 1.05 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) to ethyl acetate (100) afforded **7b** as a white solid (0.06 g, 70%), mp 189–192 °C. (Found: C, 53.48; H, 3.80; N, 9.09. $C_{14}H_{12}F_2N_2O_2S$ requires C, 54.19; H, 3.90; N, 9.03%.) ν_{max} (KBr)/cm^{-1} 3492 (asymmetric NH_2 stretch), 3169 (symmetric NH_2 stretch), 1661 (C=O stretch), 1588, 1511, 1490, 1361, 1216 (asymmetric SON stretch), 1151, 1081 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.73 (1H, A of AB_{system}, J_{AB} 13.8, one of CH_2), 4.93 (3H, B of AB_{system} overlapping with br s, J_{AB} 13.8, one of CH_2 and NH_2), 6.88–7.02 (4H, m, ArH), 7.08–7.20 (2H, m, ArH), 7.60–7.70 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 61.3 (CH_2, *C*H$_2$), 115.7 (CH, d, $^2J_{C-F}$ 21.8, aromatic *C*H), 116.4 (CH, d, $^2J_{C-F}$ 22.5, aromatic *C*H), 123.7 (C, d, $^4J_{C-F}$ 3.8, aromatic *C*), 131.2 (C, d, $^4J_{C-F}$ 3.0, aromatic *C*), 131.6 (CH, d, $^3J_{C-F}$ 9.0, aromatic *C*H), 132.9 (CH, d, $^3J_{C-F}$ 8.3, aromatic *C*H), 161.4 (C, *C*=O), 163.2 (C, d, $^1J_{C-F}$ 248.3, *C*–F), 166.0 (C, d, $^1J_{C-F}$ 263.3, *C*–F); δ_F (376.5 MHz) 50.15–50.20 (1F, m, aromatic C–*F*), 58.56–58.62 (1F, m, aromatic C–*F*); *m/z* (ESI) 311 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{13}F_2N_2O_2S$ [M+H]$^+$ 311.0666,. found 311.0667.

*4.5.46. N-Carbamoyl-S-benzyl-S-(4-methoxyphenyl)sulfoximine (**7c**).* Following procedure D, the reaction of *N*-cyano-*S*-benzyl-*S*-(4-methoxyphenyl)sulfoximine (**6c**) (0.18 g, 0.6 mmol) and trifluoroacetic acid (0.21 g, 0.14 mL, 1.8 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **7c** as a white solid (0.08 g, 45%), mp 142–144 °C; ν_{max} (KBr)/cm^{-1} 3403 (asymmetric NH_2 stretch), 3192 (symmetric NH_2 stretch), 1654 (C=O stretch), 1593, 1499, 1362, 1269 (asymmetric SON stretch), 1183, 1077 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 3.86 (3H, s, OCH_3), 4.74 (1H, A of AB_{system}, J_{AB} 13.5, one of CH_2), 4.96 (3H, B of AB_{system} overlapping with br s, J_{AB} 13.8, one of CH_2 and NH_2), 6.85–6.92 (2H, m, ArH), 6.96–7.03 (2H, m, ArH), 7.18–7.34 (3H, m, ArH), 7.50–7.57 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 55.7 (CH_3, OCH_3), 62.2 (CH_2, *C*H$_2$), 114.2 (CH, aromatic *C*H), 128.3 (C, aromatic *C*), 128.4, 128.8, 130.9, 131.2 (CH, 4×aromatic *C*H), 161.7, 163.8 (C, 1×aromatic *C*–O, 1×*C*=O); *m/z* (ESI) 305 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{15}H_{17}N_2O_3S$ [M+H]$^+$ 305.0960, found 305.0953.

*4.5.47. N-Carbamoyl-S-benzyl-S-(4-bromophenyl)sulfoximine (**7d**).* Following procedure D, the reaction of *N*-cyano-*S*-benzyl-*S*-(4-bromophenyl)sulfoximine (**6d**) (0.30 g, 0.89 mmol) and trifluoroacetic acid (0.30 g, 0.21 mL, 2.67 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) to ethyl acetate (100) afforded **7d** as a white solid (0.13 g, 41%), mp 205–209 °C; ν_{max} (KBr)/cm^{-1} 3488 (asymmetric NH_2 stretch), 3164 (symmetric NH_2 stretch), 1660 (C=O stretch), 1593, 1570, 1456, 1367, 1218 (asymmetric SON stretch), 1065 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.73 (1H, A of AB_{system}, J_{AB} 14.3, one of CH_2), 4.87 (2H, br s, NH_2) overlapping with 4.91 (1H, B of AB_{system}, J_{AB} 13.8, one of CH_2), 6.95–7.05 (2H, m, ArH), 7.18–7.36 (3H, m, ArH), 7.41–7.51 (2H, m, ArH), 7.52–7.61 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 62.1 (CH_2, *C*H$_2$), 127.6 (C, aromatic *C*), 128.6, 129.2, 130.3, 131.2, 132.2 (CH, 5×aromatic *C*H), 134.9 (C, aromatic *C*), 161.3 (C, *C*=O), 1×aromatic C signal absent; *m/z* (ESI) 353, 355 (1:1) [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{14}{}^{79}BrN_2O_2S$ [M+H]$^+$, 352.9959, found 352.9953.

*4.5.48. N-Carbamoyl-S-benzyl-S-(4-nitrophenyl)sulfoximine (**7e**).* Following procedure D, the reaction of *N*-cyano-*S*-benzyl-*S*-(4-nitrophenyl)sulfoximine (**6e**) (0.12 g, 0.4 mmol) and trifluoroacetic acid (0.14 g, 0.09 mL, 1.2 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (50:50) to ethyl acetate (100) afforded **7e** as a yellow solid (0.07 g, 54%), mp 199–201 °C; ν_{max} (KBr)/cm^{-1} 3429 (asymmetric NH_2 stretch), 3105 (symmetric NH_2 stretch), 2924, 1652 (C=O stretch), 1589, 1531 (asymmetric NO_2 stretch), 1386 (symmetric NO_2 stretch), 1346, 1220 (asymmetric SON stretch), 1134, 1080 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.76 (1H, A of AB_{system}, J_{AB} 13.8, one of CH_2), 4.91 (3H, B of AB_{system} overlapping with br s, J_{AB} 13.8, one of CH_2 and NH_2), 6.98–7.05 (2H, m, ArH), 7.20–7.38 (3H, m, ArH), 7.77–7.84 (2H, m, ArH), 8.21–8.29 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 62.1 (CH_2, *C*H$_2$), 123.9 (CH, aromatic *C*H), 126.9 (C, aromatic C), 128.8, 129.5, 130.2, 131.2 (CH, 4×aromatic *C*H), 142.1, 150.7 (C, 2×aromatic *C*), 160.9 (C, *C*=O); *m/z* (ESI) 320 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{14}N_3O_4S$ [M+H]$^+$ 320.0705, found 320.0720.

*4.5.49. N-Carbamoyl-S-benzyl-S-(4-chlorophenyl)sulfoximine (**7i**).* Following procedure D, the reaction of *N*-cyano-*S*-benzyl-*S*-(4-chlorophenyl)sulfoximine (**6i**) (0.08 g, 0.28 mmol) and trifluoroacetic acid (0.09 g, 0.06 mL, 0.83 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) to ethyl acetate (100) afforded **7i** as a white solid (0.05 g, 56%), mp 213–216 °C; ν_{max} (KBr)/cm^{-1} 3488 (asymmetric NH_2 stretch), 3166 (symmetric NH_2 stretch), 1661 (C=O stretch), 1592, 1367, 1218 (asymmetric SON stretch), 1085 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.74 (1H, A of AB_{system}, J_{AB} 13.8, one of CH_2), 4.88 (2H, br s, NH_2) overlapping with 4.92 (1H, B of AB_{system}, J_{AB} 13.8, one of CH_2), 7.00 (2H, d, *J* 7.2, ArH), 7.18–7.35 (3H, m, ArH), 7.36–7.45 (2H, m, ArH), 7.50–7.61 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 62.1 (CH_2, *C*H$_2$), 127.6 (C, aromatic *C*), 128.6, 129.2, 129.2, 130.2, 131.2 (CH, 5×aromatic *C*H), 134.2, 140.6 (C, 2×aromatic *C*), 161.4 (C, *C*=O); *m/z*

(ESI) 309, 311 (3:1) [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{14}{}^{35}ClN_2O_2S$ [M+H]$^+$ 309.0465, found 309.0468.

*4.5.50. N-Carbamoyl-S-benzyl-S-(3-fluorophenyl)sulfoximine (**7j**).* Following procedure D, the reaction of *N*-cyano-*S*-benzyl-*S*-(3-fluorophenyl)sulfoximine (**6j**) (0.09 g, 0.31 mmol) and trifluoroacetic acid (0.11 g, 0.07 mL, 0.93 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) to ethyl acetate (100) afforded **7j** as a white solid (0.05 g, 56%), mp 134–136 °C; ν_{max} (KBr)/cm^{-1} 3374 (asymmetric NH_2 stretch), 3192 (symmetric NH_2 stretch), 1648 (C=O stretch), 1593, 1476, 1362, 1222 (asymmetric SON stretch), 1139, 1107 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.75 (1H, A of AB_{system}, J_{AB} 13.8, one of CH_2), 4.91 (1H, B of AB_{system}, J_{AB} 13.8, one of CH_2) overlapping with 4.97 (2H, br s, NH_2), 6.96–7.05 (2H, m, ArH), 7.18–7.51 (7H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 62.1 (CH_2, *C*H_2), 116.2 (CH, d, $^2J_{C-F}$ 25.5, aromatic *C*H), 120.9 (CH, d, $^2J_{C-F}$ 21.0, aromatic *C*H), 124.5 (CH, d, $^4J_{C-F}$ 3.8, aromatic *C*H), 127.5 (C, aromatic C), 128.6, 129.2 (CH, 2×aromatic CH), 130.7 (CH, d, $^3J_{C-F}$ 7.7, aromatic *C*H), 131.2 (CH, aromatic *C*H), 137.9 (C, d, $^3J_{C-F}$ 6.9, aromatic *C*), 161.4 (C, *C*=O), 162.3 (C, d, $^1J_{C-F}$ 251.25, *C*–F); *m*/*z* (ESI) 293 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{14}FN_2O_2S$ [M+H]$^+$ 293.0760, found 293.0761.

*4.5.51. N-Carbamoyl-S-benzyl-S-(3-bromophenyl)sulfoximine (**7k**).* Following procedure D, the reaction of *N*-cyano-*S*-benzyl-*S*-(3-bromophenyl)sulfoximine (**6k**) (0.45 g, 1.35 mmol) and trifluoroacetic acid (0.46 g, 0.31 mL, 4.00 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) to ethyl acetate (100) afforded **7k** as a white solid (0.56 g, 38%), mp 138–140 °C; ν_{max} (KBr)/cm^{-1} 3473 (asymmetric NH_2 stretch), 3187 (symmetric NH_2 stretch), 1650 (C=O stretch), 1586, 1570, 1456, 1359, 1222 (asymmetric SON stretch), 1141, 1114 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.73 (1H, A of AB_{system}, J_{AB} 13.8, one of CH_2), 4.91 (1H, B of AB_{system}, J_{AB} 13.8, one of CH_2) overlapping with 4.97 (2H, br s, NH_2), 6.95–7.05 (2H, m, ArH), 7.19–7.39 (4H, m, ArH), 7.50–7.61 (1H, m, ArH), 7.67–7.78 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 62.2 (CH_2, *C*H_2), 122.9 (C, aromatic *C*–Br), 127.3 (CH, aromatic *C*H), 127.5 (C, aromatic *C*), 128.6, 129.3, 130.3, 131.2, 131.6, 136.7 (CH, 6×aromatic *C*H), 137.6 (C, aromatic *C*), 161.4 (C, *C*=O); *m*/*z* (ESI) 353, 355 (1:1) [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{14}{}^{79}BrN_2O_2S$ [M+H]$^+$ 352.9955, found 352.9959.

*4.5.52. N-Carbamoyl-S-benzyl-S-(4-fluorophenyl)sulfoximine (**7n**).* Following procedure D, the reaction of *N*-cyano-*S*-benzyl-*S*-(4-fluorophenyl)sulfoximine (**6n**) (0.14 g, 0.51 mmol) and trifluoroacetic acid (0.17 g, 0.12 mL, 1.53 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) to ethyl acetate (100) afforded **7n** as a white solid (0.12 g, 80%), mp 155–158 °C; ν_{max} (KBr)/cm^{-1} 3430 (asymmetric NH_2 stretch), 3193 (symmetric NH_2 stretch), 1648 (C=O stretch), 1592, 1494, 1365, 1244 (asymmetric SON stretch), 1137, 1081 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 4.74 (1H, A of AB_{system}, J_{AB} 13.5, one of CH_2), 4.88 (2H, br s, NH_2) overlapping with 4.94 (1H, B of AB_{system}, J_{AB} 13.8, one of CH_2), 6.95–7.03 (2H, m, ArH), 7.05–7.15 (2H, m, ArH), 7.18–7.36 (3H, m, ArH), 7.57–7.67 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 62.2 (CH_2, *C*H_2), 116.2 (CH, d, $^2J_{C-F}$ 22.5, aromatic *C*H), 127.8 (C, aromatic *C*), 128.6, 129.1, 131.2 (CH, 3×aromatic *C*H), 131.6 (CH, d, $^3J_{C-F}$ 9.0, aromatic *C*H), 161.4 (C, *C*=O), 165.9 (C, d, $^1J_{C-F}$ 255.0, *C*–F), 1×aromatic C signal absent; *m*/*z* (ESI) 293 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{14}FN_2O_2S$ [M+H]$^+$ 293.0750, found 293.0760.

*4.5.53. S-Benzyl-S-phenyl-NH-sulfoximine (**2**)*[21]. Following procedure E, the reaction of *N*-carbamoyl-*S*-benzyl-*S*-phenyl sulfoximine (**7a**) (0.21 g, 0.76 mmol) and K_2CO_3 (0.53 g, 3.83 mmol) and subsequent purification by column chromatography using ethyl acetate/acetone (2:1) afforded **2** as a white solid (0.03 g, 17%), mp 106–110 °C (lit.[21] 112–113 °C); ν_{max} (KBr)/cm^{-1} 3319 (NH stretch), 2925, 1493, 1445, 1216 (asymmetric SON stretch), 1110, 1084 (symmetric SON stretch), 974; δ_H (300 MHz) ($CDCl_3$) 2.80 (1H, br s, NH), 4.31 (1H, A of AB_{system}, J_{AB} 13.2, one of CH_2), 4.40 (1H, B of AB_{system}, J_{AB} 13.2, one of CH_2), 7.07–7.16 (2H, m, ArH), 7.23–7.38 (3H, m, ArH), 7.42–7.51 (2H, m, ArH), 7.54–7.63 (1H, m, ArH), 7.73–7.81 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 64.6 (CH_2, *C*H_2), 128.5, 128.8, 128.9, 131.1, 133.1 (CH, 5×aromatic *C*H), 140.3 (C, aromatic *C*), 1×aromatic *C*H signal absent, 1×aromatic *C* signal absent.

*4.5.54. S-(4-Fluorobenzyl)-S-(4′-fluorophenyl)-NH-sulfoximine (**8b**).* Following procedure E, the reaction of *N*-carbamoyl-*S*-(4-fluorobenzyl)-*S*-(4′-fluorophenyl)sulfoximine (**7b**) (0.18 g, 0.58 mmol) and K_2CO_3 (0.40 g, 2.90 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **8b** as a white solid (0.06 g, 38%), mp 122–124 °C; ν_{max} (KBr)/cm^{-1} 3269 (NH stretch), 2918, 1602, 1594, 1506, 1496, 1230 (asymmetric SON stretch), 1086 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 2.78 (1H, br s, NH), 4.27 (1H, A of AB_{system}, J_{AB} 13.8, one of CH_2), 4.35 (1H, B of AB_{system}, J_{AB} 13.8, one of CH_2), 6.91–7.03 (2H, m, ArH), 7.04–7.19 (4H, m, ArH), 7.68–7.80 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 63.9 (CH_2, *C*H_2), 115.7 (CH, d, $^2J_{C-F}$ 21.5, aromatic *C*H), 116.2 (CH, d, $^2J_{C-F}$ 22.4, aromatic *C*H), 124.5 (C, d, $^4J_{C-F}$ 3.3, aromatic *C*), 131.7 (CH, d, $^3J_{C-F}$ 9.5, aromatic *C*H), 132.8 (CH, d, $^3J_{C-F}$ 8.5, aromatic *C*H), 163.2 (C, d, $^1J_{C-F}$ 247.3, *C*–F), 165.7 (C, d, $^1J_{C-F}$ 254.2, *C*–F), 1×aromatic *C* signal absent; *m*/*z* (ESI) 268 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{13}H_{12}F_2NOS$ [M+H]$^+$ 268.0608, found 268.0595.

*4.5.55. S-Benzyl-S-(4-methoxyphenyl)-NH-sulfoximine (**8c**).* Following procedure E, the reaction of *N*-carbamoyl-*S*-benzyl-*S*-(4-methoxyphenyl)sulfoximine (**7c**) (0.07 g, 0.23 mmol) and K_2CO_3 (0.21 g, 1.50 mmol) afforded, without further purification, a white solid identified as **8c** (0.04 g, 67%), mp 96–99 °C. (Found: C, 63.97; H, 5.78; N, 5.46; S 11.95. $C_{14}H_{15}NO_2S$ requires C, 64.34; H, 5.79; N, 5.36; S 12.27%.) ν_{max} (KBr)/cm^{-1} 3313 (NH stretch), 2909, 1595, 1575, 1496, 1455, 1214 (asymmetric SON stretch), 1106, 1078 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 2.72 (1H, br s, NH), 3.86 (3H, s, OCH_3), 4.28 (1H, A of AB_{system}, J_{AB} 13.1, one of CH_2), 4.37 (1H, B of AB_{system}, J_{AB} 13.3, one of CH_2), 6.86–6.94 (2H, m, ArH), 7.07–7.15 (2H, m, ArH), 7.22–7.37 (3H, m, ArH), 7.61–7.70 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 55.6 (CH_3, *C*H_3 of OCH_3), 64.9 (CH_2, *C*H_2), 114.0, 128.4, 128.7 (CH, 3×aromatic *C*H), 129.0 (C, aromatic *C*), 131.01, 131.04 (CH, 2×aromatic *C*H), 131.9 (C, aromatic *C*), 163.4 (C, aromatic *C*–O); *m*/*z* (ESI) 262 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{14}H_{16}NO_2S$ [M+H]$^+$ 262.0902, found 262.0902.

*4.5.56. S-Benzyl-S-(4-bromophenyl)-NH-sulfoximine (**8d**).* Following procedure E, the reaction of *N*-carbamoyl-*S*-benzyl-*S*-(4-bromophenyl)sulfoximine (**7d**) (0.08 g, 0.23 mmol) and K_2CO_3 (0.16 g, 1.10 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (70:30) to ethyl acetate (100) afforded **8d** as a white solid (0.04 g, 60%), mp 114–115 °C. (Found: C, 50.07; H, 3.79; N, 4.37; S 10.32. $C_{13}H_{12}BrNOS$ requires C, 50.33; H, 3.90; N, 4.52; S 10.34%.) ν_{max} (KBr)/cm^{-1} 3240 (NH stretch), 1571, 1495, 1466, 1456, 1386, 1228 (asymmetric SON stretch), 1163, 1065 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 2.80 (1H, br s, NH), 4.30 (1H, A of AB_{system}, J_{AB} 13.7, one of CH_2), 4.38 (1H, B of AB_{system}, J_{AB} 13.3, one of CH_2), 7.08–7.15 (2H, m, ArH), 7.24–7.39 (3H, m, ArH), 7.54–7.63 (4H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 64.7 (CH_2, *C*H_2), 128.4, 128.5 (C, 2×aromatic *C*), 128.6, 129.0 130.5, 131.1, 132.1 (CH, 5×aromatic *C*H), 139.6 (C, aromatic *C*); *m*/*z* (ESI) 310, 312 (1:1) [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{13}H_{13}{}^{79}BrNOS$ [M+H]$^+$ 309.9901, found 309.9909.

*4.5.57. S-Benzyl-S-(4-chlorophenyl)-NH-sulfoximine (**8i**).* Following procedure E, the reaction of *N*-carbamoyl-*S*-benzyl-*S*-(4-chlorophenyl)sulfoximine (**7i**) (0.04 g, 0.13 mmol) and K_2CO_3 (0.09 g,

0.65 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (60:40) afforded **8i** as a white solid (0.03 g, 86%), mp 98–100 °C; ν_{max} (KBr)/cm^{-1} 3254 (NH stretch), 2912, 1572, 1470, 1454, 1385, 1230 (asymmetric SON stretch), 1086 (symmetric SON stretch), 1008; δ_H (300 MHz) ($CDCl_3$) 2.80 (1H, br s, NH), 4.30 (1H, A of AB_{system}, J_{AB} 13.5, one of CH_2), 4.39 (1H, B of AB_{system}, J_{AB} 13.5, one of CH_2), 7.08–7.15 (2H, m, ArH), 7.24–7.45 (5H, m, ArH), 7.63–7.71 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 64.7 (CH_2, *C*H_2), 128.4 (C, aromatic *C*), 128.6, 129.0 129.1, 130.4, 131.1 (CH, 5×aromatic *C*H), 139.9 (C, aromatic *C*), 1×aromatic *C* signal absent; *m*/*z* (ESI) 266, 268 (3:1) [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{13}H_{13}{}^{35}ClNOS$ [M+H]$^+$ 266.0406, found 266.0403.

*4.5.58. S-Benzyl-S-(3-fluorophenyl)-NH-sulfoximine (**8j**).* Following procedure E, the reaction of *N*-carbamoyl-*S*-benzyl-*S*-(3-fluorophenyl)sulfoximine (**7j**) (0.21 g, 0.72 mmol) and K_2CO_3 (0.50 g, 3.59 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (70:30) afforded **8j** as a white solid (0.11 g, 61%), mp 90–92 °C; ν_{max} (KBr)/cm^{-1} 3318 (NH stretch), 2924, 1588, 1472, 1456, 1268, 1219 (asymmetric SON stretch), 1107 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 2.82 (1H, br s, NH), 4.36 (1H, A of AB_{system}, J_{AB} 13.5, one of CH_2), 4.40 (1H, B of AB_{system}, J_{AB} 13.2, one of CH_2), 7.09–7.17 (2H, m, ArH), 7.23–7.39 (4H, m, ArH), 7.40–7.50 (2H, m, ArH), 7.53–7.58 (1H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 64.6 (CH_2, *C*H_2), 116.3 (CH, d, $^2J_{C-F}$ 24.0, aromatic *C*H), 120.3 (CH, d, $^2J_{C-F}$ 21.0, aromatic *C*H), 124.7 (CH, d, $^4J_{C-F}$ 3.8, aromatic *C*H), 128.2 (C, aromatic C), 128.6, 129.0 (CH, 2×aromatic CH), 130.5 (CH, d, $^3J_{C-F}$ 7.5, aromatic *C*H), 131.0 (CH, aromatic *C*H), 142.8 (C, d, $^3J_{C-F}$ 6.0, aromatic *C*), 162.3 (C, d, $^1J_{C-F}$ 249.8, *C*–F); *m*/*z* (ESI) 250 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{13}H_{13}FNOS$ [M+H]$^+$ 250.0702, found 250.0712.

*4.5.59. S-Benzyl-S-(3-bromophenyl)-NH-sulfoximine (**8k**).* Following procedure E, the reaction of *N*-carbamoyl-*S*-benzyl-*S*-(3-bromophenyl)sulfoximine (**7k**) (0.21 g, 0.59 mmol) and K_2CO_3 (0.41 g, 2.97 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (70:30) afforded **8k** as a white solid (0.09 g, 50%), mp 110–111 °C; ν_{max} (KBr)/cm^{-1} 3260 (NH stretch), 2915, 1566, 1493, 1454, 1409, 1234 (asymmetric SON stretch), 1141 (symmetric SON stretch), 1025; δ_H (300 MHz) ($CDCl_3$) 2.82 (1H, br s, NH), 4.30 (1H, A of AB_{system}, J_{AB} 13.5, one of CH_2), 4.39 (1H, B of AB_{system}, J_{AB} 13.2, one of CH_2), 7.09–7.17 (2H, m, ArH), 7.24–7.41 (4H, m, ArH), 7.63–7.74 (2H, m, ArH), 7.90 (1H, t, *J* 2.1, ArH); δ_C (75.5 MHz) ($CDCl_3$) 64.7 (CH_2, *C*H_2), 122.9 (C, aromatic *C*–Br), 127.4 (CH, aromatic CH), 128.2 (C, aromatic C), 128.6, 129.0, 130.3, 131.1, 131.8, 136.1 (CH, 6×aromatic *C*H), 142.5 (C, aromatic *C*); *m*/*z* (ESI) 310, 312 (1:1) [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{13}H_{13}{}^{79}BrNOS$ [M+H]$^+$ 309.9901, found 309.9901.

*4.5.60. S-Benzyl-S-(4-fluorophenyl)-NH-sulfoximine (**8n**).* Following procedure E, the reaction of *N*-carbamoyl-*S*-benzyl-*S*-(4-fluorophenyl)sulfoximine (**7n**) (0.10 g, 0.32 mmol) and K_2CO_3 (0.22 g, 1.62 mmol) and subsequent purification by column chromatography on silica gel using hexane/ethyl acetate (70:30) to ethyl acetate (100) afforded **8n** as a white solid (0.03 g, 38%), mp 107–109 °C; ν_{max} (KBr)/cm^{-1} 3269 (NH stretch), 2918, 1591, 1497, 1455, 1234 (asymmetric SON stretch), 1110 (symmetric SON stretch); δ_H (300 MHz) ($CDCl_3$) 2.78 (1H, br s, NH), 4.30 (1H, A of AB_{system}, J_{AB} 13.5, one of CH_2), 4.39 (1H, B of AB_{system}, J_{AB} 13.5, one of CH_2), 7.05–7.17 (4H, m, ArH), 7.24–7.39 (3H, m, ArH), 7.69–7.80 (2H, m, ArH); δ_C (75.5 MHz) ($CDCl_3$) 64.9 (CH_2, *C*H_2), 116.0 (CH, d, $^2J_{C-F}$ 22.5, aromatic *C*H), 128.6, 128.9, 131.0 (CH, 3×aromatic *C*H), 131.7 (CH, d, $^3J_{C-F}$ 9.0, aromatic *C*H), 165.6 (C, d, $^1J_{C-F}$ 253.5, *C*–F), 2×aromatic C signal absent; *m*/*z* (ESI) 250 [(M+H)$^+$]; HRMS (ESI): exact mass calculated for $C_{13}H_{13}FNOS$ [M+H]$^+$ 250.0702, found 250.0711.

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