

Sulfur-Based Chiral Iodoarenes: An Underexplored Class of Chiral Hypervalent Iodine Reagents

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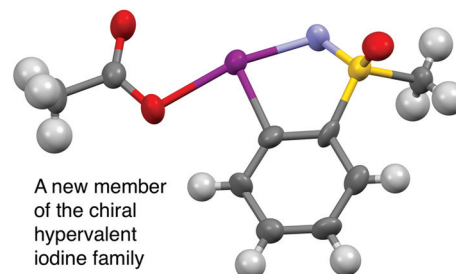
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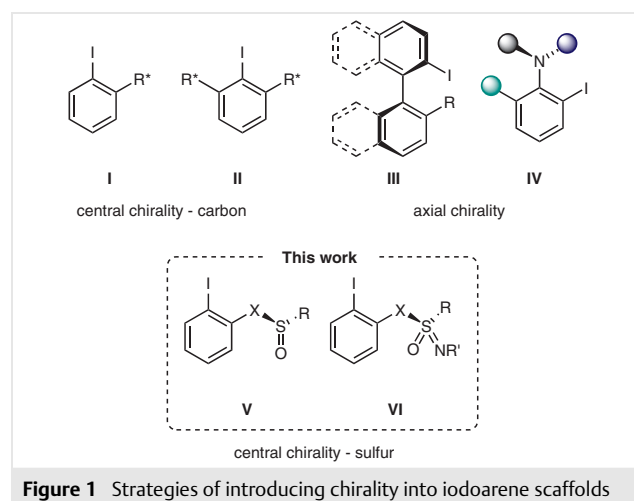
Abstract Chiral hypervalent iodine reagents are active players in modern stereoselective organic synthesis. Structurally diverse chiral hypervalent iodine reagents have been synthesised and extensively studied, but hypervalent iodine reagents containing chiral sulfur stereogenic centre are scarce and their synthesis is challenging. A small library of iodoarenes containing chiral sulfonamide and chiral sulfoximine moieties has been synthesised using commercially available reagents. The oxidation of the chiral iodoarene precursors to iodine(III) reagents was cumbersome due to facile overoxidation of the sulfoxide moiety and hence loss of chirality under various oxidation conditions. Oxidation of chiral sulfonimidoyl derivatives to the corresponding hypervalent iodine reagents was successful and led to novel sulfur-based chiral iodine(III) reagents.

Key words hypervalent iodine, oxidation, stereoselective synthesis, sulfoximines, sulfur derivatives

Chiral hypervalent iodine reagents are widely used as active reagents in stereoselective synthesis.^{1–4} They are extensively studied in a wide range of stereoselective transformations under stoichiometric and catalytic conditions. Stereoselective synthesis of chiral sulfur compounds,^{5,6} oxidative phenol dearomatisation,^{7–11} α -functionalisation of carbonyl compounds,^{12–15} difunctionalisation of alkenes,^{16–20} and oxidative rearrangement reactions^{21–24} are efficiently achieved with high degree of stereochemical control using diverse chiral hypervalent iodine reagents.

The incorporation of chirality into hypervalent iodine reagents is typically achieved through substituents of the iodoarene moiety containing a stereogenic centre (Figure

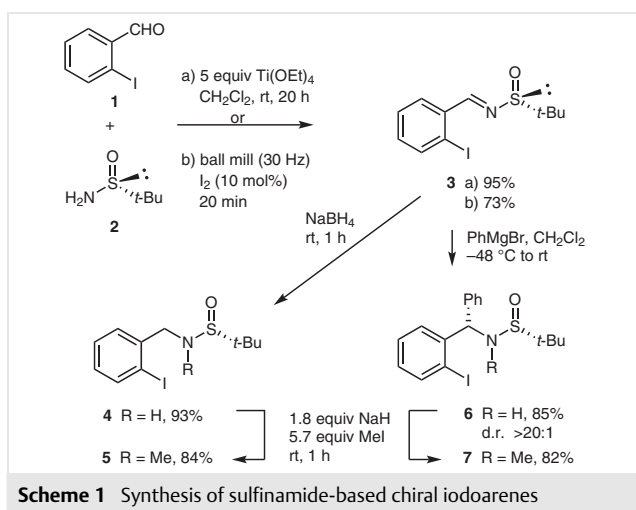
1). Using chiral ligands to the iodine is another strategy, even though limited.^{25–27} The vast majority of chiral hypervalent iodine reagent are synthesised by the oxidation of chiral iodoarenes containing chiral tetrahedral carbon centres **I**, **II** or C–C axis of chirality **III**. C–N axially chiral hypervalent iodine reagents of type **IV** are also gaining interest lately.^{28,29} On the other hand, the synthesis of hypervalent iodine reagents with chiral sulfur moieties is scarcely developed, even though there are a few examples known.^{30,31} To the best of our knowledge only one report on the synthesis and reactions of diaryliodonium salts containing chiral sulfoxide moiety has been published.³² Herein, we report our efforts towards the synthesis of this challenging class of chiral hypervalent iodine reagents from precursors of types **V** and **VI** (Figure 1).



The main challenge of synthesis of hypervalent iodine reagents with chiral sulfoxide moiety is the loss of chirality due to the possible oxidation of sulfoxides to sulfones under

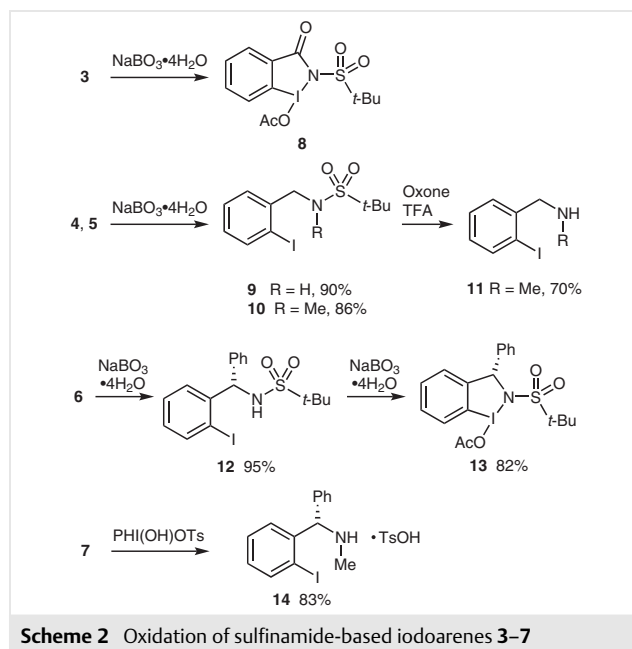
the oxidation conditions to prepare iodine(III) reagents.³² We envisaged that the introduction of a chiral sulfinamide (type **V**) or sulfoximine (type **VI**) and adjusting the substitution pattern around the central sulfur could alleviate this problem.

A first set of sulfinamide-based precursors was easily obtained from 2-iodobenzaldehyde (**1**) and (*R*)-*tert*-butanesulfinamide (**2**) (Scheme 1). Condensation of **1** and **2** in the presence of excess Lewis acids such as titanium(IV) alkoxides^{33,34} or under iodine-catalysed solvent-free mechanochemical conditions³⁵ provided imine **3** in high yields (95% and 73%). Reduction of imine **3** with NaBH₄ led to sulfinamide **4** in 93% yield,³⁶ which was then converted into the *N*-methyl derivative **5** upon treatment with NaH and iodomethane. Addition of phenylmagnesium bromide to the chiral imine **3** proceeded smoothly with a high degree of stereochemical control delivering **6** as a single diastereomer (dr >20:1) in 85% yield.³⁷ The absolute configuration of compound **6** was determined by X-ray crystallography.³⁸ Treatment of **6** with NaH/Mel led to the *N*-methyl derivative **7** in 82% yield.



To probe the potential of selective oxidation of the iodine centre without affecting the sensitive sulfoxide moiety, precursors **3–7** were subjected to oxidation using various oxidants and conditions. It is not surprising that the labile sulfoxide group was not tolerated under most of the oxidation protocols. Many oxidants typical for preparing iodine(III) compounds such as Selectfluor, Oxone, perborates, and Koser's reagent [PhI(OH)OTs] were investigated; in addition, anodic oxidation was also attempted.^{39,40} The iodine precursors **3–7** were not reactive under many reaction conditions, only sodium perborate oxidation was productive (Scheme 2). Generally, the selective oxidation of the iodine centre was not possible under the reaction conditions investigated and is either oxidised along with the sulfoxide moiety or the latter is solely oxidised and hence the chirality is lost. Oxidation of the chiral imine **3** with sodium perborate in acetic acid led to the achiral cyclic hypervalent iodine reagent **8** in 85% yield. The chemical constitution of compound **8** was additionally confirmed by X-ray crystallography.³⁸ Oxidation of precursors **4** and **5** with sodium perborate led to the corresponding achiral sulfones **9**³⁸ and **10** with the iodine centre untouched, which could not be further oxidised using perborate or Koser's reagent, while with Oxone in the presence of trifluoroacetic acid the *tert*-butanesulfoxide moiety was cleaved to form **11**. Similarly, the oxidation of precursor **6** with perborate led to sulfone **12** in 95% yield in 2.5 hours. Extended reaction times (12 h) or further oxidation of **12** formed the cyclic iodine(III) compound **13**, which is chiral, but does no longer have a stereogenic sulfur centre. On the other hand, attempted oxidation of **7** via iodine metathesis^{41,42} using Koser's reagent led to the cleavage of the *tert*-butanesulfoxide moiety and formed salt **14**.

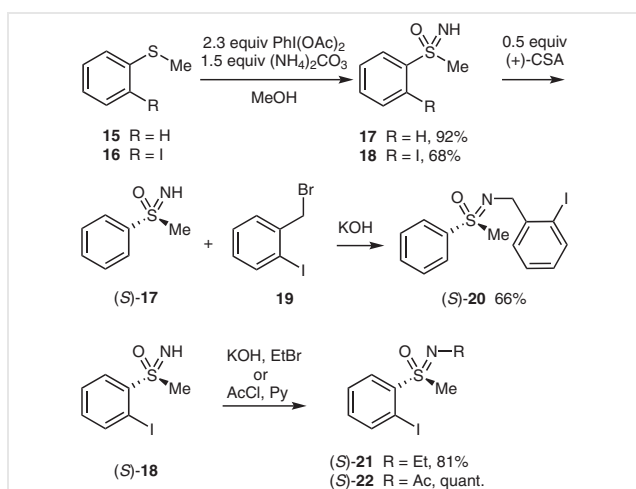
borate in acetic acid led to the achiral cyclic hypervalent iodine reagent **8** in 85% yield. The chemical constitution of compound **8** was additionally confirmed by X-ray crystallography.³⁸ Oxidation of precursors **4** and **5** with sodium perborate led to the corresponding achiral sulfones **9**³⁸ and **10** with the iodine centre untouched, which could not be further oxidised using perborate or Koser's reagent, while with Oxone in the presence of trifluoroacetic acid the *tert*-butanesulfoxide moiety was cleaved to form **11**. Similarly, the oxidation of precursor **6** with perborate led to sulfone **12** in 95% yield in 2.5 hours. Extended reaction times (12 h) or further oxidation of **12** formed the cyclic iodine(III) compound **13**, which is chiral, but does no longer have a stereogenic sulfur centre. On the other hand, attempted oxidation of **7** via iodine metathesis^{41,42} using Koser's reagent led to the cleavage of the *tert*-butanesulfoxide moiety and formed salt **14**.



In view of these results, we envisaged that a replacement of the chiral sulfinamide moiety with a chiral sulfoximine would lead to chiral sulfur-based iodoarene derivatives that could be oxidised to the corresponding hypervalent iodine reagents without loss of chirality. Initially, oxidation of compounds **3**, **4**, and **5** to the corresponding sulfoximines was attempted. However, oxidations using typical procedures such as [Rh₂(OAc)₄] and (diacetoxyiodo)benzene⁴³ or *t*-BuOCl⁴⁴ in the presence of an amine were unsuccessful and led to complex reaction mixtures. The ¹H NMR spectra of the crude reaction mixtures showed the absence of the *t*-Bu moiety suggesting that it cleaved under these conditions. Also, the oxidation of (*R*)-*N*,2-dimethylpropane-2-sulfinamide with *t*BuOCl in the presence of aniline resulted in the formation of *N*-methyl-*N'*-phenyl-sulf-

amide proved that the *t*-Bu group is not tolerated under the reaction conditions used to convert sulfinamides into sulfoximines.

To avoid the difficulties encountered during the oxidation of the above compounds, the synthesis of different sulfoximine containing chiral iodoarenes was attempted (Scheme 3). Relying on the oxidation of thioanisole (**15**) and 2-iodothioanisole (**16**) to sulfoximines **17** and **18** followed by chiral resolution with (+)-camphorsulfonic acid (CSA), the chiral sulfoximine derivatives (*S*)-**17** and (*S*)-**18** were obtained and converted into the *N*-substituted derivatives **20**–**22** in high yields.

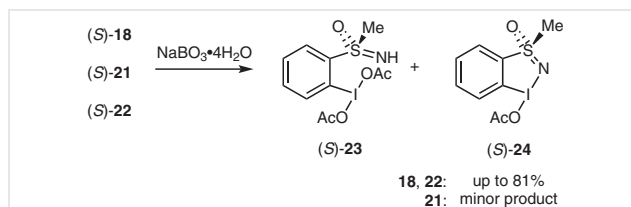


Scheme 3 Synthesis of iodoarene scaffolds with chiral sulfoximine moieties

The oxidation of (*S*)-**20** to the corresponding chiral hypervalent iodine reagent using Selectfluor in the presence of acetic acid was unsuccessful, leaving the starting material unreacted. Sodium perborate as oxidant or aerobic oxidation in the presence of a CoCl_2 catalyst⁴⁵ led to complex reaction mixtures with 2-iodobenzoic acid identified as one of the products. Similar outcomes were obtained upon oxidation of compounds (*S*)-**18**, (*S*)-**21**, and (*S*)-**22** using Selectfluor or the CoCl_2 -catalysed aerobic oxidation protocol.

With sodium perborate the formation of a cyclic chiral hypervalent iodine reagent (*S*)-**24** was observed as a major product in the case of precursors (*S*)-**18** and (*S*)-**22** and as a minor product in the case of precursor (*S*)-**21** (Scheme 4). The ^1H NMR analysis of the crude reaction mixture showed the formation of the hypervalent iodine reagent (*S*)-**23** along with the cyclic product (*S*)-**24** that is formed most likely through cyclization of (*S*)-**23**.

The ratio of **23**:**24** varies with the reaction time and the equivalents of sodium perborate, but **24** was the major product in all cases. The non-cyclic product **23** was only detected in the crude reaction mixture, but could not be isolated, while the cyclic product **24** was isolated and crystallised. The structure of (*S*)-**24** was proven by single crystal X-



Scheme 4 Oxidation of chiral sulfoximine-based iodoarenes **18**, **21**, and **22**

ray crystallography (Figure 2). Analysis of the X-ray data of compound **24** showed a strong interaction (2.100 Å) between the sulfoximine nitrogen [(N(1))] and the iodine centre [I(1)], which is shorter than the iodine–oxygen bond [I(1)–O(2), 2.249 Å]. The observed angle [N(1)–I(1)–O(2)] of compound **24** (167.15°) is in the range of the distorted T-shaped geometry characteristic to λ^3 -iodanes.^{30,46}

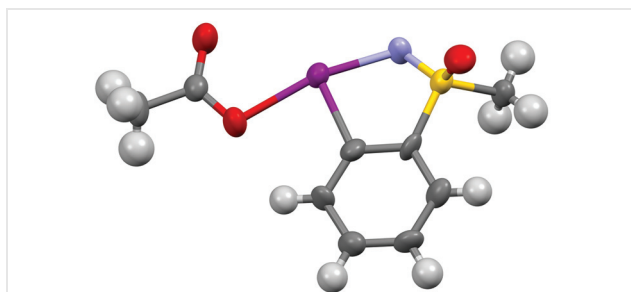


Figure 2 3D structure and absolute configuration the cyclic chiral sulfoximine-based hypervalent iodine reagent (*S*)-**24**

In conclusion, various sulfur-based chiral iodoarenes were synthesised starting with readily available chemicals. Chiral iodoarenes containing sulfinamide units and compounds containing sulfoximine unit have been prepared. Oxidation of both categories to the corresponding chiral hypervalent iodine reagents was cumbersome. All sulfinamide derivatives underwent overoxidation and, hence, the chirality is lost. Chiral sulfoximine units are more robust and cannot undergo further oxidation. However, the oxidation of the sulfoximines to the corresponding chiral hypervalent iodine reagents was not easy due to the degradation of some precursors. Only the oxidation of chiral 1-iodo-2-(*S*-methylsulfonylimidoyl)benzene derivatives was successful and led to a cyclic chiral-at-sulfur iodine(III) reagent. Applications of sulfur-based chiral hypervalent iodine reagents in stereoselective oxidative transformations are ongoing in our laboratory.

All starting materials were purchased from commercial suppliers and used without further purification and all solvents used were dried and purified by standard techniques. Reactions requiring the exclusion of moisture were carried out under an atmosphere of argon or N_2

in oven-dried glassware. Flash chromatography was carried out using Merck silica gel (35–70 μm) or on a Biotage Isolera Four platform using SNAP Ultra (25 μm) cartridges. Melting points were recorded on a Gallenkamp MPD350 apparatus. IR measurements were taken using a PerkinElmer 1600 FTIR spectrometer. NMR spectra were recorded on Bruker DPX 300, Bruker DPX 400, or Bruker DPX 500. ^1H NMR spectra were measured at 300, 400, and 500 MHz. ^{13}C $\{^1\text{H}\}$ NMR spectra were recorded at 75, 100, and 125 MHz using CDCl_3 as the solvent and internal reference. Coupling constants J are given in hertz (Hz). Standard abbreviations were used for denoting multiplicity. High-resolution mass spectrometry (HRMS) was carried out using a Waters LCT Premier XE mass spectrometer using electrospray ionisation (ESI). Optical rotations were measured with a UniPol L polarimeter at 20 $^\circ\text{C}$. High-performance liquid chromatography (HPLC) analysis was conducted using Shimadzu LC-10 AD coupled diode array-detector SPD-MA-10A-VP.

2-Iodobenzaldehyde (1)

Pyridinium chlorochromate (3.11 g, 14.45 mmol, 1.16 equiv) and Celite (13.12 g, 21.84 mmol, 1.74 equiv) were dried under vacuum in a 3-necked round-bottomed flask and then flushed with N_2 , and suspended in anhyd CH_2Cl_2 (145 mL). A solution of 2-iodobenzyl alcohol (2.92 g, 12.5 mmol) in anhyd CH_2Cl_2 (40 mL) was added dropwise at rt. The reaction mixture turned from red to brown to black and is stirred at rt overnight. After filtration through Celite, the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (9:1 hexane:EtOAc); yield: 2.15 g (9.26 mmol, 74%); white solid; mp 37.3–37.4 $^\circ\text{C}$ (Lit.²¹ mp 37 $^\circ\text{C}$).

^1H NMR (400 MHz, CDCl_3): δ = 10.07 (s, 1 H), 7.96 (d, J = 7.9 Hz, 1 H), 7.89 (d, J = 7.7 Hz, 1 H), 7.47 (t, J = 7.5 Hz, 1 H), 7.29 (t, J = 7.6 Hz, 1 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 196.0, 140.8, 135.6, 135.3, 130.4, 128.9, 100.9.

The spectral data are in agreement with literature.⁴⁴

(R,E)-N-(2-Iodobenzylidene)-2-methylpropane-2-sulfinamide (3)

A solution of 2-iodobenzaldehyde (**1**; 1.12 g, 4.82 mmol) and $\text{Ti}(\text{OEt})_4$ (5.05 mL) in anhyd CH_2Cl_2 (48 mL) was stirred for 5 min under N_2 . Then, (R)-(+)-2-methyl-2-propanesulfinamide (**2**; 0.58 g, 4.82 mmol) was added portionwise. The reaction mixture was stirred at rt for 20 h. Sat. aq NaHCO_3 (30 mL) was added until white titanium salt stopped precipitating. The suspension was filtered off a short pad of Celite washing with small portions of EtOAc. The aqueous filtrate was extracted with EtOAc and the combined organic layers were washed with brine, dried (anhyd MgSO_4), and concentrated in vacuo. The crude product (yellow oil) was purified by flash chromatography (silica gel, 9:1 hexane:EtOAc) to give the pure sulfinamide **3** as a yellow solid; yield: 1.53 g (4.58 mmol, 95%); mp 77.5–77.7 $^\circ\text{C}$; $[\alpha]_{\text{D}} -179.18$ (c 1.23, CHCl_3).

IR (neat): 2956, 2360, 1577, 1554, 1460, 1074, 1012, 771, 740, 441 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 8.79 (s, 1 H), 7.99 (d, J = 7.8 Hz, 1 H), 7.94 (d, J = 7.9 Hz, 1 H), 7.43 (t, J = 7.5 Hz, 1 H), 7.18 (t, J = 7.6 Hz, 1 H), 1.28 (s, 9 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 166.7, 140.5, 135.6, 133.5, 129.9, 128.6, 101.4, 58.2, 22.9.

The spectral data are in agreement with literature.³⁴

(R)-N-(2-Iodobenzyl)-2-methylpropane-2-sulfinamide (4)

Sulfinamide **3** (1.71 g, 5.1 mmol) was dissolved in 98:2 THF:H₂O (15 mL) and cooled down to 0 $^\circ\text{C}$. NaBH_4 (0.579 g, 15.32 mmol, 3 equiv) was added and the resulting solution was warmed to rt and monitored by TLC (7:3 hexane:EtOAc). After 1 h, the TLC showed the consumption of the starting material. Then, H₂O (20 mL) was added, and the mixture was stirred at rt for 5 min. THF was evaporated off before extracting with CH_2Cl_2 (3 \times 10 mL). The combined CH_2Cl_2 layers were dried (anhyd MgSO_4) and evaporated off to give the crude product, which was purified by flash chromatography (silica gel, 9:1 hexane:EtOAc) to give the pure reduced imine **4** as a white solid; yield: 1.61 g (4.77 mmol, 93%); mp 134.6 $^\circ\text{C}$; $[\alpha]_{\text{D}} -15.45$ (c 1.03, CHCl_3).

IR (neat): 3194, 3059, 2976, 2360, 1583, 1564, 1436, 1363, 1074, 1040, 744, 428 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.85 (dd, J = 7.9, 1.2 Hz, 1 H), 7.39 (dd, J = 7.6, 1.8 Hz, 1 H), 7.34 (td, J = 7.4, 1.2 Hz, 1 H), 7.00 (td, J = 7.6, 1.8 Hz, 1 H), 4.42 (dd, J = 14.2, 5.4 Hz, 1 H), 4.29 (dd, J = 14.2, 7.7 Hz, 1 H), 3.58 (t, J = 5.6 Hz, 1 H), 1.24 (s, 9 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 141.0, 139.9, 129.9, 129.6, 128.7, 99.5, 56.3, 54.1, 22.8.

The spectral data are in agreement with literature.⁴⁵

(R)-N-(2-Iodobenzyl)-N,2-dimethylpropane-2-sulfinamide (5)

To a solution of the sulfinamide **4** (317 mg, 0.94 mmol) in anhyd THF (5.5 mL) were added 60% NaH in mineral oil (68 mg, 1.69 mmol, 1.8 equiv) and MeI (760 mg, 0.33 mL, 5.36 mmol, 5.7 equiv). The reaction mixture was stirred at rt under N_2 for 1 h, and the solvent was removed under reduced pressure. The residue was dissolved in Et₂O (5 mL) and washed with H₂O (5 mL). The aqueous phase was extracted with Et₂O (3 \times 5 mL). The combined Et₂O extracts were washed with 10% aq $\text{Na}_2\text{S}_2\text{O}_3$ (5 mL) and H₂O (5 mL), dried (MgSO_4), filtered. The filtrate was evaporated under vacuum to give methylated product **5** as a pale-yellow oil; yield: 277 mg (0.79 mmol, 84%); $[\alpha]_{\text{D}} +20.54$ (c 0.73, CHCl_3).

IR (neat): 2953, 2864, 2360, 2331, 1562, 1508, 1458, 1435, 1359, 1068, 1012, 748, 432 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.81 (dd, J = 7.9, 1.1 Hz, 1 H), 7.39 (dd, J = 7.7, 1.7 Hz, 1 H), 7.33 (td, J = 7.5, 1.2 Hz, 1 H), 6.95 (td, J = 7.8, 1.8 Hz, 1 H), 4.27 (d, J = 15.8 Hz, 1 H), 4.18 (d, J = 15.9 Hz, 1 H), 2.66 (s, 3 H), 1.18 (s, 9 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 139.8, 139.4, 129.2, 129.2, 128.5, 99.5, 77.4, 61.7, 58.8, 23.6.

HRMS (ESI+): m/z $[M + H^+]$ calcd for $\text{C}_{12}\text{H}_{19}\text{INOS}$: 352.0227; found: 352.0230.

(R)-N-[(S)-(2-Iodophenyl)(phenyl)methyl]-2-methylpropane-2-sulfinamide (6)

To a solution of the imine **3** (322 mg, 0.96 mmol) in CH_2Cl_2 (5.8 mL) was added phenylmagnesium bromide (348 mg, 0.69 mL, 1.92 mmol, 2 equiv) at -48 $^\circ\text{C}$. The reaction mixture was stirred at -48 $^\circ\text{C}$ for 6 h and then allowed to warm to rt and stirred overnight. The mixture was quenched with sat. aq NH_4Cl (2 mL) and the aqueous layer was extracted with EtOAc (3 \times 3 mL). The combined organic layers were dried (Na_2SO_4) and concentrated to provide the crude product, which was purified by crystallization from hexane: CH_2Cl_2 (10:1) to give the pure product **6** as colourless crystals; yield: 337 mg (0.82 mmol, 85%); mp 145–146 $^\circ\text{C}$; $[\alpha]_{\text{D}} -68.14$ (c 0.66, CHCl_3).

IR (neat): 3213, 2981, 2962, 1560, 1494, 1465, 1448, 1357, 1033, 391 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.85 (dd, J = 7.9, 1.2 Hz, 1 H), 7.56 (dd, J = 7.8, 1.7 Hz, 1 H), 7.41–7.36 (m, 3 H), 7.33 (ddd, J = 7.4, 4.6, 1.4 Hz, 2 H), 7.30–7.26 (m, 1 H), 6.99 (td, J = 7.6, 1.7 Hz, 1 H), 5.97 (d, J = 2.8 Hz, 1 H), 3.73 (d, J = 2.4 Hz, 1 H), 1.25 (s, 9 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 143.4, 141.2, 140.2, 129.5 (2 C), 129.0, 128.4, 128.2, 128.1, 100.1, 65.8, 56.2, 22.8.

HRMS (ESI+): m/z [$M + H^+$] calcd for $\text{C}_{17}\text{H}_{21}\text{INOS}$: 414.0383; found: 414.0382.

(*R*)-*N*-[(*S*)-(2-Iodophenyl)(phenyl)methyl]-*N*,2-dimethylpropane-2-sulfonamide (**7**)

To a solution of the sulfinamide **6** (413 mg, 1 mmol) in anhyd THF (6 mL) were added 60% NaH in mineral oil (72 mg, 1.8 mmol, 1.8 equiv) and MeI (795 mg, 0.34 mL, 5.6 mmol, 5.6 equiv). The reaction mixture was stirred at rt under N_2 for 1 h, and the solvent was removed under reduced pressure. The residue was dissolved in Et_2O (5 mL) and washed with H_2O (5 mL). The aqueous phase was extracted with Et_2O (3×5 mL). The combined ether extracts were washed with 10% aq $\text{Na}_2\text{S}_2\text{O}_3$ (5 mL) and H_2O (5 mL), dried (MgSO_4), filtered, and the filtrate was evaporated under vacuum to give methylated product **7** as a white solid; yield: 350 mg (0.82 mmol, 82%); mp 98–99 °C; $[\alpha]_D^{25} +88.11$ (c 1.29, CHCl_3).

IR (neat): 2954, 2920, 1452, 1072, 565 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.87 (dd, J = 7.9, 1.2 Hz, 1 H), 7.56 (dd, J = 7.8, 1.6 Hz, 1 H), 7.40 (td, J = 7.6, 1.2 Hz, 1 H), 7.31–7.25 (m, 3 H), 7.22–7.18 (m, 2 H), 6.99 (td, J = 7.6, 1.6 Hz, 1 H), 5.95 (s, 1 H), 2.60 (s, 3 H), 1.12 (s, 9 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 142.4, 140.3, 138.7, 129.7, 129.6, 129.4, 128.5, 128.5, 127.8, 101.2, 77.1, 59.1, 29.8, 24.2.

HRMS (ESI+): m/z [$M + H^+$] calcd for $\text{C}_{18}\text{H}_{23}\text{INOS}$: 428.0540; found: 428.0535.

2-(*tert*-Butylsulfonyl)-3-oxo-2,3-dihydro-1*H*-1 λ^3 -benzo[d][1,2]-iodazol-1-yl Acetate (**8**)

To a solution of sulfinamide **3** (67 mg, 0.2 mmol) in glacial AcOH (4 mL) was added $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ (312 mg, 2.0 mmol, 10 equiv). The reaction mixture was stirred at 40–45 °C for 4 h. The solvent was removed under reduced pressure and the white solid left was partitioned between H_2O (5 mL) and CH_2Cl_2 (5 mL). The two layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were washed with brine (5 mL) and dried (anhyd MgSO_4), filtered, and concentrated under pressure to give the crude product **8** as a white solid, which was purified by recrystallisation from hexane:AcOH (8:2) to obtain **8** as a white solid; yield: 73 mg (0.17 mmol, 85%).

^1H NMR (400 MHz, acetone- d_6): δ = 8.17 (dd, J = 7.6, 1.1 Hz, 1 H), 8.13 (d, J = 8.4 Hz, 1 H), 8.03 (t, J = 7.2 Hz, 1 H), 7.84 (t, J = 7.5 Hz, 1 H), 2.19 (s, 3 H), 1.54 (s, 9 H).

^{13}C NMR (101 MHz, acetone- d_6): δ = 176.4, 163.2, 137.2, 134.5, 132.9, 132.0, 130.6, 117.8, 64.0, 25.1, 20.5.

N-(2-Iodobenzyl)-2-methylpropane-2-sulfonamide (**9**)

To a solution of sulfinamide **4** (135 mg, 0.4 mmol) in glacial AcOH (6 mL) was added $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ (615 mg, 4 mmol, 10 equiv) and the reaction mixture was stirred at 40–45 °C. After 1 h, the TLC (hexane:EtOAc 7:3) showed the consumption of the starting material. The solvent was removed under reduced pressure and the white solid left was treated with H_2O (5 mL) and CH_2Cl_2 (5 mL). The two layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×5 mL).

The combined organic layers were washed with brine (5 mL), dried (anhyd MgSO_4), filtered, and concentrated under pressure to give the sulfinamide **9** as a pale-yellow solid; yield: 128 mg (0.36 mmol, 90%); mp 77–78 °C.

IR (neat): 3277, 2976, 2879, 2360, 1683, 1456, 1436, 1398, 1300, 1112, 1010, 742, 511 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.83 (dd, J = 7.9, 1.2 Hz, 1 H), 7.47 (dd, J = 7.7, 1.7 Hz, 1 H), 7.36 (td, J = 7.5, 1.2 Hz, 1 H), 7.01 (td, J = 7.6, 1.7 Hz, 1 H), 4.40 (d, J = 6.2 Hz, 2 H), 4.36–4.30 (m, 1 H), 1.41 (s, 9 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 140.3, 139.7, 130.1, 130.0, 129.0, 99.0, 60.3, 53.0, 24.5.

HRMS (ESI+): m/z [$M + H^+$] calcd for $\text{C}_{11}\text{H}_{17}\text{INO}_2\text{S}$: 354.0019; found: 354.0018.

N-(2-Iodobenzyl)-*N*,2-dimethylpropane-2-sulfonamide (**10**)

To a solution of sulfinamide **5** (140 mg, 0.4 mmol, 1 equiv) in glacial AcOH (6 mL) was added $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ (615 mg, 4 mmol, 10 equiv). The reaction mixture was stirred at 40–45 °C. After 1 h, the TLC (hexane:EtOAc 7:3) showed the consumption of the starting material. The solvent was removed under reduced pressure and the white solid left was partitioned between H_2O (5 mL) and CH_2Cl_2 (5 mL). The two layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were washed with brine (5 mL) and dried (anhyd MgSO_4), filtered, and concentrated under pressure to give the sulfinamide **10** as a pale-yellow solid; yield: 126 mg (0.34 mmol, 86%); mp 82–83 °C.

IR (neat): 2360, 1695, 1581, 1436, 1317, 1261, 1120, 1016, 790, 511, 418 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.82 (dd, J = 7.9, 1.2 Hz, 1 H), 7.55 (dd, J = 7.8, 1.6 Hz, 1 H), 7.40 (td, J = 7.7, 1.2 Hz, 1 H), 6.99 (td, J = 7.8, 1.7 Hz, 1 H), 4.52 (s, 2 H), 2.90 (s, 3 H), 1.47 (s, 9 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 139.5, 138.3, 129.5, 129.1, 128.9, 98.8, 62.4, 59.8, 36.4, 25.2.

HRMS (ESI+): m/z [$M + H^+$] calcd for $\text{C}_{12}\text{H}_{19}\text{INO}_2\text{S}$: 368.0176; found: 368.0179.

1-(2-Iodophenyl)-*N*-methylmethanamine (**11**)

To a solution of **10** (43 mg, 0.12 mmol) in a mixture of trifluoroacetic acid (1.2 mL) and CHCl_3 (0.4 mL) was added Oxone (111 mg, 0.18 mmol, 1.5 equiv). The reaction mixture was stirred at rt and monitored by TLC. After completion of reaction, the solvent was evaporated under vacuum and the residue was treated with CHCl_3 (2 mL). The insoluble residue of inorganic salts was collected by filtration, washed with CHCl_3 (2 mL), and discarded. Evaporation of combined CHCl_3 layers under reduced pressure afforded amino compound **11** as a pale-yellow oil; yield: 21 mg (0.0841 mmol, 70%).

IR (neat): 3014, 2818, 2742, 2358, 2331, 1778, 1670, 1176, 1138, 1014, 798, 756, 403 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.82 (dd, J = 8.0, 1.2 Hz, 1 H), 7.48 (dd, J = 7.7, 1.6 Hz, 1 H), 7.33 (td, J = 7.6, 1.2 Hz, 1 H), 7.02 (td, J = 7.8, 1.6 Hz, 1 H), 3.79 (s, 2 H), 2.47 (s, 3 H).

The spectral data are in agreement with literature.⁴⁷

(*S*)-*N*-[(2-Iodophenyl)(phenyl)methyl]-2-methylpropane-2-sulfonamide (**12**)

To a solution of sulfinamide **6** (52 mg, 0.125 mmol) in glacial AcOH (2.5 mL) was added $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ (289 mg, 1.88 mmol, 15 equiv). The reaction mixture was stirred at 40–45 °C. After 2.5 h, the TLC (hex-

ane:EtOAc 3:1) showed the consumption of the starting material. The solvent was removed under reduced pressure and the white solid left was treated with H₂O (5 mL) and CH₂Cl₂ (5 mL). The two layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were washed with brine (5 mL) and dried (anhyd MgSO₄), filtered, and concentrated under pressure to give the sulfonamide **12** as a white solid; yield: 51 mg (0.12 mmol, 95%).

¹H NMR (300 MHz, CDCl₃): δ = 7.87 (dd, *J* = 7.9, 0.7 Hz, 1 H), 7.53–7.40 (m, 2 H), 7.36–7.19 (m, 5 H), 7.04 (ddd, *J* = 7.9, 6.7, 2.4 Hz, 1 H), 6.03 (d, *J* = 9.0 Hz, 1 H), 4.81 (d, *J* = 8.9 Hz, 1 H), 1.32 (s, 9 H).

(S)-2-(tert-Butylsulfonyl)-3-phenyl-2,3-dihydro-1H-1λ³-benzo[d][1,2]iodazol-1-yl Acetate (13)

Compound **13** was prepared following the above procedure (for compound **12**) starting with **6** or **12** but using 12 h as reaction time leading to **13** as a white solid; yield: 40 mg (0.082 mmol, 82%); mp 144–146 °C; [α]_D +29.67 (c 0.4, CHCl₃).

¹H NMR (300 MHz, CDCl₃): δ = 7.90 (d, *J* = 9.4 Hz, 1 H), 7.50–7.46 (m, 1 H), 7.46–7.43 (m, 1 H), 7.42–7.38 (m, 1 H), 7.37–7.29 (m, 5 H), 6.23 (s, 1 H), 2.13 (s, 3 H), 1.26 (s, 9 H).

¹³C NMR (101 MHz, CDCl₃): δ = 143.7, 140.7, 140.4, 129.6, 129.0, 128.9, 128.8, 128.00, 127.97, 99.1, 65.3, 60.3, 24.3.

(S)-1-(2-Iodophenyl)-N-methyl-1-phenylmethanamine 4-Methylbenzenesulfonate (14)

Koser's reagent (42 mg, 0.11 mmol) was added to a stirred solution of **12** (50 mg, 0.12 mmol, 1.1 equiv) in anhyd CH₂Cl₂ (1 mL) at rt. The reaction was stirred and monitored by TLC. After the completion of the reaction, the solvent was removed under reduced pressure and the solid residue was filtered and washed with Et₂O several times, then dried in vacuum to give **14** as a white solid; yield: 48 mg (0.114 mmol, 83%).

¹H NMR (300 MHz, CD₃OD): δ = 8.02 (d, *J* = 7.80 Hz, 1 H), 7.70 (d, *J* = 8.02 Hz, 2 H), 7.66–7.57 (m, 1 H), 7.53–7.39 (m, 5 H), 7.23 (d, *J* = 7.78 Hz, 2 H), 7.20–7.13 (m, 1 H), 5.71 (s, 1 H), 2.72 (s, 3 H), 2.37 (s, 3 H), 1.15 (s, 1 H).

rac-S-Methyl-S-phenylsulfoximine (17)

To a solution of thioanisole **15** (1.24 g, 10.0 mmol) in MeOH (100 mL) was added (NH₄)₂CO₃ (1.50 g, 15.6 mmol, 1.5 equiv). After the dissolution of (NH₄)₂CO₃, (diacetoxyiodo)benzene (7.43 g, 23.1 mmol, 2.3 equiv) was added. The reaction mixture was stirred at rt overnight, then evaporated to dryness and purified by column chromatography (hexane:EtOAc 1:1) affording pure **17** as a yellow oil that solidified after few days; yield: 1.43 g (9.20 mmol, 92%); mp 33–34 °C (Lit.⁴⁸ mp 34–35 °C).

¹H NMR (400 MHz, CDCl₃): δ = 8.05–8.00 (m, 2 H), 7.66–7.60 (m, 1 H), 7.59–7.53 (m, 2 H), 3.13 (s, 3 H).

The spectral data are in agreement with literature.⁴⁹

rac-S-Methyl-S-2-iodophenylsulfoximine (18)

Prepared following the above procedure (for **17**), starting with 2-iodothioanisole (**16**; 1.0 g, 4.0 mmol). Compound **18** was obtained as a yellow oil that solidified after a few days; yield: 0.765 g (2.72 mmol, 68%); mp 64–66 °C.

IR (neat): 3287, 1564, 1422, 1314, 1204, 1080, 986, 932, 754, 700, 509 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.30 (d, *J* = 7.9 Hz, 1 H), 8.12 (d, *J* = 7.8 Hz, 1 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.21 (t, *J* = 7.6 Hz, 1 H), 3.28 (s, 3 H), 2.75 (s, 1 H).

¹³C NMR (101 MHz, CDCl₃): δ = 145.6, 143.1, 133.9, 130.6, 129.0, 93.3, 42.6.

HRMS: *m/z* [M + H]⁺ calcd for [C₇H₉INOS]: 281.9444; found: 281.9452.

(+)-(S)-S-Methyl-S-phenylsulfoximine [(S)-17]

To a solution of racemic *S*-methyl-*S*-phenylsulfoximine (*rac*-**17**; 1.43 g, 9.2 mmol) in acetone (6 mL) was added a solution of (+)-camphorsulfonic acid (1.2 g, 5.1 mmol 0.55 equiv) in acetone (14 mL). The reaction mixture was stirred at rt overnight. The formed precipitate was collected by filtration and washed thoroughly with acetone. The obtained solid was then suspended in CH₂Cl₂ (30 mL). Sat. aq K₂CO₃ (30 mL) was added with stirring. Stirring was continued at rt for 1 h. The organic phase was separated, and the aqueous phase was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were dried (anhyd MgSO₄) and evaporated to dryness affording pure (*S*)-**17** as a colourless oil that solidified after a few days; yield: 0.46 g (2.95 mmol, 32%).

¹H NMR (400 MHz, CDCl₃): δ = 8.04–7.99 (m, 1 H), 7.65–7.60 (m, 1 H), 7.58–7.53 (m, 1 H), 3.11 (s, 3 H).

(+)-(S)-S-Methyl-S-2-iodophenylsulfoximine [(S)-18]

Obtained following the above procedure [for (*S*)-**17**], starting with racemic *S*-methyl-*S*-2-iodophenylsulfoximine (*rac*-**18**; 0.764 g, 2.72 mmol) and (+)-camphorsulfonic acid (0.32 g, 1.36 mmol 0.5 equiv). Compound (*S*)-**18** was obtained as a colourless oil that solidified after a few days; yield: 0.36 mg (1.28 mmol, 47%); mp 63–65 °C; [α]_D +30 (c 2.6, CHCl₃).

¹H NMR (400 MHz, CDCl₃): δ = 8.30 (d, *J* = 7.9 Hz, 1 H), 8.12 (d, *J* = 7.8 Hz, 1 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.21 (t, *J* = 7.6 Hz, 1 H), 3.28 (s, 3 H), 2.75 (s, 1 H).

¹³C NMR (101 MHz, CDCl₃): δ = 145.6, 143.1, 133.9, 130.6, 129.0, 93.3, 42.6.

(S)-N-2-Iodobenzyl-S-methyl-S-phenylsulfoximine [(S)-20]

To a solution of (*S*)-*S*-methyl-*S*-phenylsulfoximine [(*S*)-**17**; 0.459 g, 2.95 mmol] in DMSO (1.5 mL) was added KOH (0.33 g, 5.9 mmol, 2.0 equiv). The reaction was stirred at rt under argon for 5 min. 2-Iodobenzyl bromide (**19**; 1.31 g, 4.42 mmol, 1.5 equiv) was added and stirring was continued at rt overnight. The reaction was quenched by the addition of H₂O (5 mL) and the aqueous phase was extracted with CH₂Cl₂ (3 × 5 mL). The organic layers were combined, dried (anhyd MgSO₄) and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane:EtOAc 9:1) affording pure (*S*)-**20** as a dark yellow oil; yield: 0.73 g (1.95 mmol, 66%); [α]_D +1.23 (c 0.6, CHCl₃).

IR (neat): 1445, 1221, 1140, 1011, 741, 689, 513 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.95 (d, *J* = 7.6 Hz, 2 H), 7.75 (d, *J* = 7.8 Hz, 1 H), 7.67 (d, *J* = 7.6 Hz, 1 H), 7.62 (t, *J* = 7.2 Hz, 1 H), 7.56 (t, *J* = 7.5 Hz, 2 H), 7.33 (t, *J* = 7.4 Hz, 1 H), 6.91 (d, *J* = 7.5 Hz, 1 H), 4.15 (d, *J* = 15.5 Hz, 1 H), 4.05 (d, *J* = 15.5 Hz, 1 H), 3.20 (s, 3 H).

¹³C NMR (101 MHz, CDCl₃): δ = 143.0, 139.3, 139.1, 133.3, 129.7, 129.3, 128.8, 128.5, 128.4, 98.8, 52.4, 45.4.

HRMS: *m/z* calcd [M + H]⁺ for [C₁₄H₁₅INOS]: 371.9914; found: 371.9916.

(S)-N-Ethyl-S-methyl-S-2-iodophenylsulfoximine [(S)-21]

To a solution of (S)-S-methyl-S-2-iodophenylsulfoximine [(S)-18; 0.168 g, 0.6 mmol] in DMSO (1.5 mL) was added KOH (90 mg, 1.6 mmol, 2.2 equiv). The reaction was stirred at rt under argon for 5 min. EtBr (0.10 mL, 1.34 mmol, 2.1 equiv) was added and stirring was continued at rt overnight. The reaction was quenched by the addition of H₂O (5 mL) and the aqueous phase was extracted with CH₂Cl₂ (3 × 5 mL). The organic layers were combined, dried (anhyd MgSO₄) and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane:EtOAc 9:1) affording pure (S)-21 as a white solid; yield: 0.151 g (0.49 mmol, 81%); mp 53–55 °C; [α]_D²⁰ +160 (c 5.9, CHCl₃).

IR (neat): 2967, 2843, 2359, 1740, 1558, 1217, 1144, 1080, 1013, 750, 517 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.29 (dd, *J* = 7.9, 1.7 Hz, 1 H), 8.12 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.56 (ddd, *J* = 7.9, 7.4, 1.2 Hz, 1 H), 7.24–7.20 (m, 1 H), 3.26 (s, 3 H), 2.94 (dq, *J* = 12.2, 7.2 Hz, 1 H), 2.78 (dq, *J* = 12.2, 7.2 Hz, 1 H), 1.21 (t, *J* = 7.2 Hz, 3 H).

¹³C NMR (101 MHz, CDCl₃): δ = 143.1, 141.5, 133.8, 133.0, 129.2, 93.8, 42.1, 38.9, 18.0.

HRMS: *m/z* [M + H]⁺ calcd for [C₉H₁₃INOS]: 309.9757; found: 309.9751.

(S)-N-Acetyl-S-methyl-S-2-iodophenylsulfoximine [(S)-22]

To a solution of (S)-S-methyl-S-2-iodophenylsulfoximine [(S)-18; 309 mg, 1.09 mmol] in CH₂Cl₂ (8 mL) at 0 °C was added pyridine (0.12 mL, 0.14 mmol, 1.3 equiv) followed by AcCl (77 μ L, 1.09 mmol). The reaction mixture was stirred at 0 °C for 1 h, then allowed to warm to rt and stirring was continued overnight. The reaction was quenched with ice cold water (10 mL). The organic phase was separated, and the aqueous phase was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were dried (anhyd MgSO₄) and evaporated. The crude product was purified by column chromatography (hexane:EtOAc 1:1) affording pure (S)-22 as white crystals; yield: 348 mg (1.08 mmol, 99%); mp 137–139 °C; [α]_D²⁰ +11.5 (c 0.59 in CHCl₃).

IR (neat): 2359, 1740, 1636, 1361, 1315, 1213, 1026, 972, 827, 756, 613, 501, 444 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.32 (dd, *J* = 8.0, 1.4 Hz, 1 H), 8.12 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.63–7.59 (m, 1 H), 7.30–7.26 (m, 1 H), 3.45 (s, 3 H), 2.16 (s, 3 H).

¹³C NMR (101 MHz, CDCl₃): δ = 179.8, 143.3, 140.9, 134.5, 131.5, 129.4, 91.6, 41.2, 26.5.

HRMS: *m/z* [M + H]⁺ calcd for [C₉H₁₁INO₂S]: 323.9550; found: 323.9557.

The spectral data are in agreement with literature.⁵⁰

(S)-3-Methyl-3-oxido-1H-1 λ ,3 λ -benzo[d][1,3,2]iodathiazol-1-yl Acetate [(S)-24]

To a stirred solution of iodoarene (S)-18, (S)-21, or (S)-22 (1.0 mmol) in AcOH (30 mL) at 45 °C was added NaBO₃·4H₂O (30 mmol, 30 equiv) portionwise over 15 min. The mixture was stirred at 45 °C overnight. The AcOH was evaporated under reduced pressure, and to the residue were added H₂O (10 mL) and CH₂Cl₂ (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (2 × 10 mL). The combined organic layers were dried (anhyd MgSO₄), filtered, and concentrated under reduced pressure. The residue was washed with *n*-hexane to afford the pure product as a white solid; yield: 275 mg (81%) from (S)-18 and 170 mg (50%) from (S)-22; mp 176–178 °C; [α]_D²⁰ +2.6 (c 1.54, CHCl₃).

IR (neat): 3001, 2365, 1717, 1603, 1312, 1208, 991, 754 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.35 (d, *J* = 7.6 Hz, 1 H), 7.90 (dd, *J* = 7.0, 1.9 Hz, 1 H), 7.86–7.80 (m, 2 H), 3.40 (s, 3 H), 2.11 (s, 3 H).

¹³C NMR (101 MHz, CDCl₃): δ = 178.1, 134.4, 133.9, 132.3, 131.3, 128.2, 117.5, 47.7, 22.2.

Conflict of Interest

The authors declare no conflict of interest

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