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Metal-free synthesis of γ-ketosulfones through Brønsted acid-promoted conjugate addition of sulfinamides†

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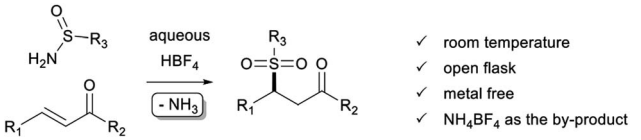
A straightforward and general metal-free method has been developed to add sufinamide-derived sulfone units on Michael acceptors under mild conditions. This reaction enables the preparation of a large variety of original γ-ketosulfones, of which only a few synthetic methods have been reported. The mild reaction conditions used tolerate a wide diversity of functional groups and empower the implementation of a late-stage functionalisation strategy.

Introduction

Sulfur–carbon bond formation belongs to the fundamental transformations in synthetic organic chemistry. Indeed, organosulfur compounds are a relevant class of molecules with applications in various fields of chemistry, including natural products,[1] bioactive compounds,[2] and functional materials science.[3] Among them, sulfones are important molecular frameworks and have drawn much attention for their synthesis.[4] Although effective, most of the synthesis methods suffer from drawbacks such as the use of a toxic additive, a metal catalyst, some hazardous raw materials, and harsh reaction conditions, often generating undesired by-products that can pollute the final product and reduce the environmental attractiveness of these approaches.

Turning more specifically to the relevant subclasses of ketosulfones,[5] while a wide variety of synthetic methods have been developed for the preparation of β-ketosulfones,[6] the synthesis of their γ-ketosulfone isomers remains surprisingly underexplored and challenging. Usually, γ-ketosulfones are obtained in two steps by the conjugate addition of thiol derivatives onto various α,β-unsaturated ketones, followed by the oxidation of the corresponding sulfides into sulfones.[7] The direct introduction of the sulfone moiety has also been investigated mainly using sulfinates[8] or sulfinic acids[9] as a source of sulfonyl derivatives. More specifically, complementary approaches have been devised from alternative sources of sulfone motif such as (i) the photoredox-catalyzed[10a,b] or metal-catalyzed[10e] hydrosulfonylation of enones with *p*-tolyl *N*-sulfonylimine or sulfur dioxide, (ii) a sulfonylation/migration process applied to arylallylic alcohols with arenesulfinic acid in the presence of hypervalent iodine (III) and concentrated sulfuric acid,[10c] (iii) the direct sulfonylation of acrylates or acrylamides with arenesulfonyl hydrazides,[10d] (iv) the asymmetric sulfonation of enones with arene sulfonylimines by cooperative organic multicatalysis,[10f] or (v) the N-heterocyclic carbene-catalyzed Stetter reaction of aldehydes with α,β-unsaturated sulfones.[10g] To our knowledge, no method has explored the use of sulfinamide as a source of sulfone moiety and there is still a strong demand to develop versatile and atom-economical approaches to produce γ-ketosulfones directly under mild conditions.

Our research group has long been interested in developing original environmentally friendly synthetic methods based on conjugate additions.[11] In this context, we have described the preparation of highly substituted sulfonated cyclopentanes *via* an acid-promoted Rauhut–Currier (RC) cascade[12] in the presence of simple and readily available sulfinamides.[13] Mechanistically, the cascade is initiated by the nucleophilic addition of a *S*-nucleophile onto a Michael acceptor playing the role of RC donor. Interestingly, HBF_4 proved the best catalyst among a variety of Lewis and Brønsted acids explored, such as $In(OTf)_3$, $Bi(OTf)_3$, $BF_3{\cdot}OEt_2$, TfOH, *p*-TsOH or Tf_2NH, to efficiently promote the conjugate addition of deactivated nucleophiles.[12c,13] In our continuing effort to develop eco-friendly synthetic methodologies, we have taken advantage of this unique sulfonamide capability to extend this approach to the synthesis γ-ketosulfones (Scheme 1). Indeed, there are several obvious advantages of the present method: (i) cheap and readily



Scheme 1 Acid-promoted synthesis of γ-ketosulfones.

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available aqueous HBF_4 proves to be an efficient promoter instead of a metal catalyst, which is usually expensive and complicated to remove completely from the target product; (ii) the reaction shows broad substrate scopes: cyclic, linear, aromatic, and heteroaromatic compounds are well tolerated at room temperature and in the open air; (iii) for aprotic polar solvent use, acetonitrile is recognised as a sustainable solvent by the Sanofi's Solvent Selection Guide;[14] (iv) the by-product of the reaction is ammonium which is directly captured *in situ* by an acid–base interaction; (v) in general, reactions are clean, allowing the expected products to be easily purified and isolated in moderate to excellent yields.

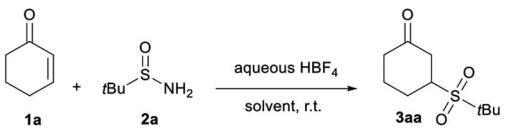
Results and discussion

Based on the optimized conditions of our seminal work,[13] the preliminary study was performed by reacting cyclohex-2-enone **1a** with *tert*-butylsulfinamide **2a** in the presence of one equivalent of aqueous HBF_4 at room temperature (Table 1). Pleasingly, in a CH_2Cl_2/CH_3CN 1 : 4 mixture, the desired γ-sulfone **3aa** was isolated in a 41% yield (entry 1). A subsequent investigation on the solvent effect highlighted that an aprotic polar solvent was essential for the reaction, with CH_3CN giving the best results (entries 2–4). The reaction efficiency was not improved by adjusting the amount of HBF_4: a stoichiometric amount is required to reach full conversion of the starting material (entries 5–6). Conversely, the yield dropped to 73% starting from 2 equivalents of **2a**, whereas the reaction concentration does not influence the reaction efficacy (entries 7–9).

With the optimised reaction conditions established (Table 1, entry 8), the reaction scope was investigated, and Table 2 shows that cyclic enones efficiently participate in the reaction. Good to high yields were obtained for **3aa–3ac** by reacting cyclohex-2-enone **1a** with both alkyl- and aryl-sulfinamides. By starting from the inferior homolog cyclopent-2-enone **1b**, the telescoped reduction of the ketone group was necessary to avoid degradation of the expected adduct. Indeed, during the purification by flash chromatography on silica gel, a retro-Michael reaction was observed restoring the starting material **1b**. Notably, sulfinamides **2a–2c** worked equally well, forming the desired γ-hydroxy sulfones **4ba**, **4bb**, and **4bc** in high yields. Finally, the *cis* diastereoselectivity of the reduction turned out to be very satisfying (>10 : 1).

Next, we sought to expand this transformation to the reactivity of diverse acyclic α,β-unsaturated ketones. We were pleased to find that a range of scaffolds were efficiently converted in the presence of *tert*-butylsulfinamide **2a** (Table 3). Either methyl, ethyl, or thien-2-ylmethyl vinyl ketone is compatible with our procedure, leading to **3ca**, **3da** or **3ea**, respectively, in good to excellent yields. When the conjugate cyclohexenyl methyl ketone **1f** was subjected to the procedure, the desired product **3fa** was isolated in 67% yield with a complete *cis* selectivity. Next, we investigated the reactivity of acrolein **1g** with 1 equivalent of the sulfinimine, and the targeted sulfonated scaffold **3ga** was isolated. When the amount of **2a** was increased up to 3 equivalents, we observed the major formation of the corresponding imine **5ga** in a **3ga**/**5ga** 36 : 64 ratio. Adding one more equivalent of acid reverses the reaction

Table 1 Optimisation of the reaction conditions[a]

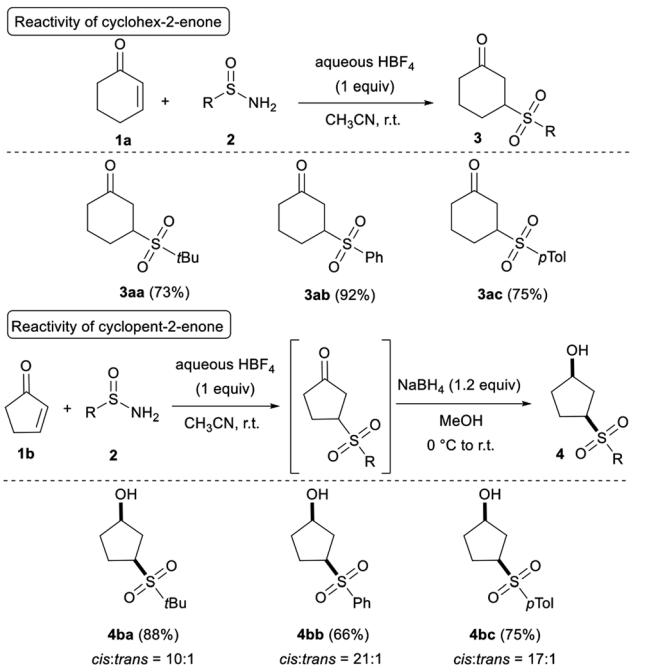


1a 2a 3aa

Entry	Solvent	HBF_4 (equiv.)	$tBuSONH_2$ **2a** (equiv.)	Yield[b] (%)
1	CH_2Cl_2/CH_3CN = 1/4	1	1.6	41
2	CH_2Cl_2	1	1.6	32
3	MeOH	1	1.6	s.m.[c]
4	CH_3CN	1	1.6	46
5	CH_3CN	0.2	1.6	16
6	CH_3CN	0.5	1.6	34
7	CH_3CN	1	1.2	25
8	**CH_3CN**	**1**	**2**	**73**
9[d]	CH_3CN	1	2	71

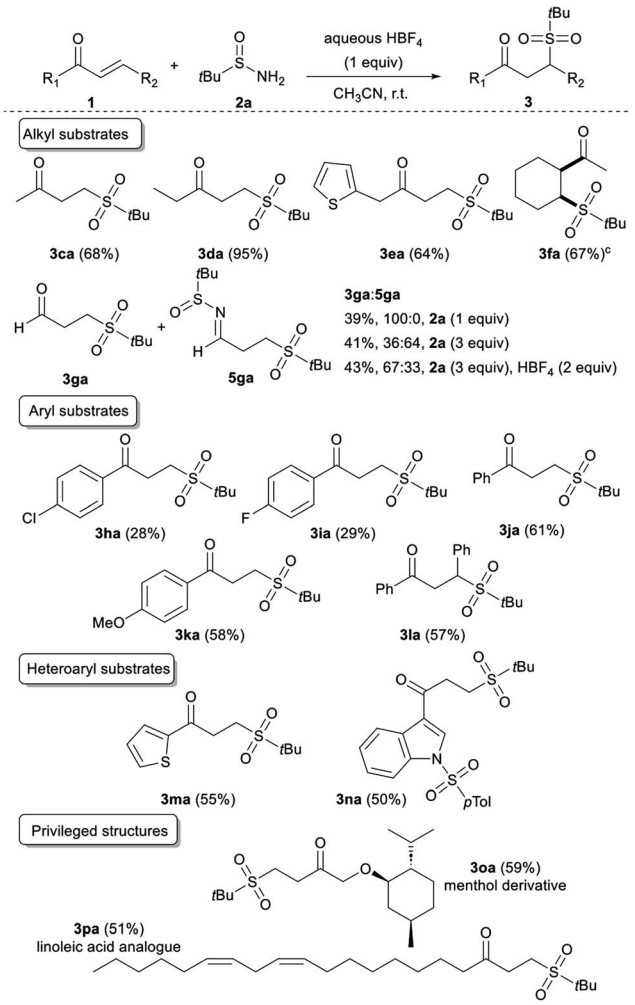
[a] Reaction conditions: cyclohex-2-enone (0.20 mmol, 1 equiv.) under the appropriate reaction conditions (c = 0.4 mol L^{-1}) at room temperature for 24 h. [b] Isolated yield. [c] Starting material. [d] c = 0.8 mol L^{-1}.

Table 2 Reactivity of alicyclic conjugate enones with various sulfinamides[a,b,c]



[a] Unless otherwise noted, reaction conditions: **1a** or **1b** (0.20 mmol, 1 equiv.), **2** (0.40 mmol, 2 equiv.), HBF_4 (0.20 mmol, 1 equiv.) in CH_3CN (c = 0.4 mol L^{-1}) at r.t. for 24 h. For the ketone reduction: $NaBH_4$ (0.24 mmol, 1.2 equiv.) in MeOH (c = 0.1 mol L^{-1}) at 0 °C to r.t. for 2 h. [b] Isolated yield. [c] Diastereomeric ratio and relative configuration were determined by ^1H NMR from the isolated product.

Table 3 Reactivity of various open-chain α,β-unsaturated ketones with *tert*-butylsulfinamide **2a** [a,b]



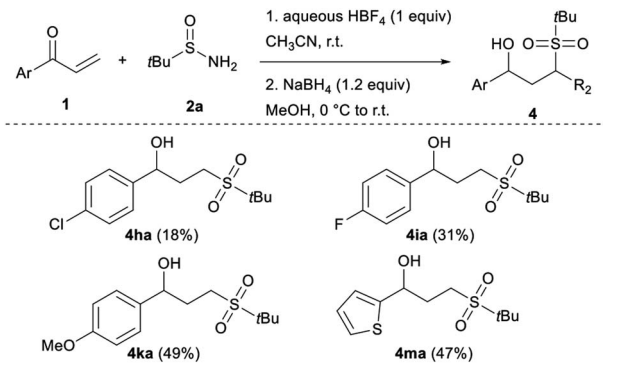
[a] Unless otherwise noted, reaction conditions: **1** (0.20 mmol, 1 equiv.), **2a** (0.40 mmol, 2 equiv.), HBF_4 (0.20 mmol, 1 equiv.) in CH_3CN (c = 0.4 mol L^{-1}) at r.t. for 4–48 h. [b] Isolated yield. [c] Relative configuration determined by NMR from the isolated product.

chemoselectivity, highlighting the key role of the acid in both the selectivity and the mechanism of the reaction.

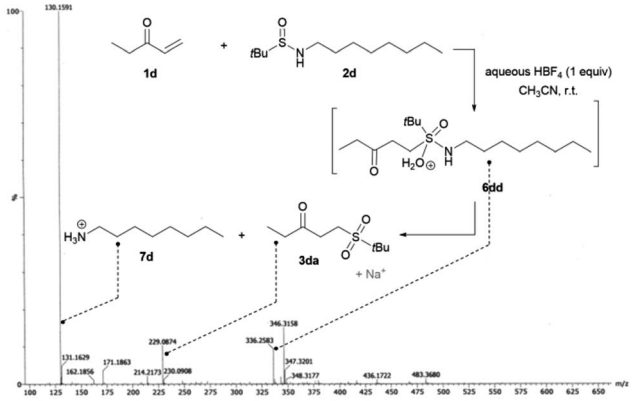
Useful 4-chloro- and 4-fluoro-phenyl vinyl ketones were also accommodated, albeit in lower yields (**3ha** and **3ia**). The reaction is more efficient by using electron-rich or -neutral arenes such as **1j** and **1k**, respectively giving **3ja** and **3ka** in good yields. Furthermore, as chalcones have historically received intensive attention from chemists because of their prominent drug activity,[15] chalcone **1l** was submitted to the reaction conditions affording the sulfone **3la** in a 57% yield. Similarly, knowing the widespread presence of heteroarenes in many biologically active natural and synthetic products,[16] heteroaryl vinyl ketones, such as **1m** and **1n** were also evaluated as substrates in our system. They provided access to the corresponding original heterocyclic γ-ketosulfones **3ma** and **3na** in satisfying yields. Given that this strategy promises to rapidly access sulfonyl compounds to explore structure–activity relationships,[17] we speculated that our mild reaction conditions might be compatible with highly functionalised bioactive molecules. Therefore, we applied our approach to more complex structures derived from menthol and linoleic acid. The corresponding sulfonated **3oa** and **3pa**, respectively, were cleanly isolated, demonstrating the generality of this sulfonyl unit transfer method. Even if most of the synthesised γ-ketosulfones were isolated in good to high yields, **3ha**, **3ia**, **3ka**, and **3ma** were obtained in moderate yields. To evaluate the part of instability of the considered γ-ketosulfones in these unsatisfactory results, we studied the effect of telescoping a reduction step to the sulfonylation reaction (Table 4). Unfortunately, the newly formed γ-hydroxy sulfones **4ha**, **4ia**, **4ka**, and **4ma** were isolated in similar yields ruling out the involvement of a retro-Michael reaction to explain the yield erosion and questioning the stability of the starting vinyl ketones under acidic reaction conditions.

From a mechanistic point of view, in our early work, we showed that prior acid hydrolysis of sulfinamide to sulfinic acid could not be excluded and that the sulfone formation could result from the addition of both proton-activated sulfinamide or sulfinic acid (Scheme 3).[13] To further decipher the reaction mechanism, we tried identifying some reaction intermediates by exploring the reactivity of *N*-octyl *tert*-butyl sulfinamide **2d** with ethyl vinyl ketone **1d** (Scheme 2). The sulfinamide **2d** was chosen because the possibly expected *N*-alkylated sulfoximine intermediate should be less sensitive to hydrolytic conditions and thus, easier to characterise. After 5 h of reaction according to our procedure, an aliquot of the crude mixture was directly analysed by electrospray ionisation mass spectrometry analysis (ESI-MS). In positive ion mode, three major cationic intermediates were trapped: the hydrated sulfinyl adduct **6dd** (m/z [M + H+ H_2O]$^+$), the sulfonated sodium adduct **3da** (m/z [M + Na]$^+$) and the octylamine **7d** (m/z [M + H]$^+$) (Scheme 2).[18] No sulfinic acid was detected in either positive or negative mode. Even if

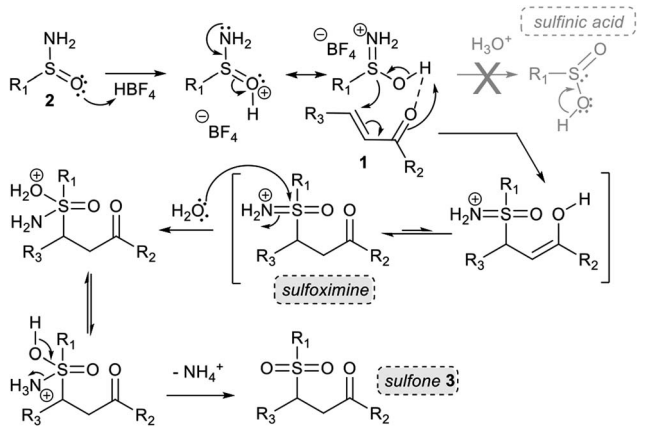
Table 4 Reactivity of various aryl vinyl ketones with *tert*-butylsulfinamide **2a**.[a,b]



[a] Unless otherwise noted, reaction conditions: **1** (0.20 mmol, 1 equiv.), **2a** (0.40 mmol, 2 equiv.), HBF_4 (0.20 mmol, 1 equiv.) in the presence of CH_3CN (c = 0.4 mol L^{-1}) at r.t. for 4 h. Then, $NaBH_4$ (0.24 mmol, 1.2 equiv.) in MeOH (c = 0.1 mol L^{-1}) at 0 °C to r.t. for 2 h. [b] Isolated yield.



Scheme 2 ESI-MS analysis for the crude reaction mixture of **1d** with **2d**.



Scheme 3 Plausible mechanism for the synthesis of γ-ketosulfone.

attempts to isolate the sulfinyl adduct **6dd** were unsuccessful, these results support the fact that a highly hydrolysable sulfoximine might be a transient intermediate of the reaction. These observations enabled us to revisit our firstly proposed mechanism.[13] Indeed, as we demonstrated in our previous work, the nucleophilic strength of the deactivated amine and the acidity of the proton source act as a Lewis pair and are key parameters to control the selectivity of the Michael reaction.[11c] Thus, in acetonitrile, the protonation of the oxygen atom of the sulfinamide by aqueous HBF_4 is preferred due to its stronger basicity,[22] which increases the nucleophilicity of the sulfur atom (Scheme 3). The corresponding protonated sulfinamide, acting as a proton shuttle, would favour the addition of the *S*-nucleophile by promoting enolization of the Michael acceptor. The resulting sulfoximine intermediate would then be rapidly hydrolyzed to sulfone **3** under the reaction conditions (Scheme 3).

Conclusions

We have developed a metal-free, operationally simple, and environmentally friendly method for the synthesis of γ-ketosulfones at ambient temperature by using various readily available sulfinamides as the sulfur source. This easy-to-implement protocol represents not only new routes to the synthesis of original γ-ketosulfones but more importantly is tolerant to a wide range of substrates, including complex molecules. This chemistry should provide access to other sulfone-containing bioactive compound libraries which are difficult to synthesise *via* other methods.

Experimental section

General procedure for the synthesis of ketosulfones 3

To a solution of alkenone **1** (0.20 mmol) in CH_3CN (c = 0.4 mol L^{-1}) were successively added sulfinamide **2** (0.40 mmol) and aqueous HBF_4 48% wt. (0.20 mmol). The resulting mixture was stirred at room temperature until the disappearance of the starting material (4 to 48 hours) before quenching with the addition of water (2 mL). The solution was then extracted with CH_2Cl_2 (3 × 10 mL). The organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography with cyclohexane/ethyl acetate to yield the desired γ-ketosulfone **3**.

3-(*tert*-Butylsulfonyl)cyclohexanone (3aa)

3aa was prepared following the general procedure by reacting **1a** (19.4 μL, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 24 hours. Flash chromatography (cyclohexane/ethyl acetate: 4/6) afforded the title compound **3aa** as a white solid (32 mg, 73%). M.p.: 108–109 °C; IR (neat) ν_{max}/cm^{-1} 2968, 1705, 1270, 1110, 664; ^1H NMR (300 MHz, $CDCl_3$) δ 3.57–3.47 (m, 1H), 2.75 (d, J = 9.1 Hz, 2H), 2.40–2.21 (m, 4H), 2.08–1.97 (m, 1H), 1.75–1.63 (m, 1H), 1.42 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.4, 61.4, 55.8, 42.4, 40.5, 25.3, 24.2 (3C), 23.8; HRMS (TOF-ESI) m/z: calcd for $C_{10}H_{18}O_3NaS$ $[M + Na]^+$ 241.0869, found 241.0875.

3-(Benzenesulfonyl)cyclohexanone (3ab)

3ab was prepared following the general procedure by reacting **1a** (19.4 μL, 0.20 mmol), benzenesulfinamide **2b** (56 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 24 hours. Flash chromatography (cyclohexane/ethyl acetate: 7 : 3 to 6 : 4) afforded the title compound **3ab** as a white solid (44 mg, 92%). M.p.: 87–88 °C; IR (neat) ν_{max}/cm^{-1} 2965, 1706, 1260, 1137, 1084, 1019, 798; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (br d, J = 7.2 Hz, 2H), 7.68 (br t, J = 7.7 Hz, 1H), 7.57 (br t, J = 7.2 Hz, 2H), 3.33–3.23 (m, 1H), 2.57 (m, 2H), 2.41–2.17 (m, 4H), 1.91 (qd, J = 12.7, 3.1 Hz, 1H), 1.71–1.57 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.6, 136.8, 134.4, 129.6 (2C), 129.1 (2C), 62.4, 40.6, 40.5, 23.8, 23.6; HRMS (TOF-ESI) m/z: calcd for $C_{12}H_{14}O_3NaS$ $[M + Na]^+$ 261.0556, found 261.0562. The data presented above agrees with that detailed in the literature.[19]

3-Tosyl cyclohexanone (3ac)

3ac was prepared following the general procedure by reacting **1a** (19.4 μL, 0.20 mmol), *p*-toluenesulfinamide **2c** (62 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 24 hours. Flash

chromatography (cyclohexane/ethyl acetate: 7 : 3 to 6 : 4) afforded the title compound **3ac** as a yellow solid (38 mg, 75%). M.p.: 82–83 °C; IR (neat) ν_{max}/cm^{-1} 2952, 1713, 1283, 1086, 1018, 664; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 3.30–3.20 (m, 1H), 2.53 (m, 2H), 2.44 (s, 3H), 2.41–2.18 (m, 4H), 1.95–1.73 (m, 1H), 1.67–1.58 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.7, 145.4, 133.6, 130.1 (2C), 129.0 (2C), 62.4, 40.6 (2C), 23.8, 23.6, 21.7; HRMS (TOF-ESI) m/z: calcd for $C_{13}H_{16}O_3NaS$ [M + Na]$^+$ 275.0712, found 275.0721. The data presented above agree with that detailed in the literature.[19]

4-(*tert*-Butylsulfonyl)butan-2-one (3ca)

3ca was prepared following the general procedure by reacting **1c** (16.7 μL, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 7 hours. Flash chromatography (cyclohexane/ethyl acetate 3 : 7 ratio) afforded the title compound **3ca** as a white solid (26 mg, 68%). M.p.: 56–57 °C; IR (neat) ν_{max}/cm^{-1} 2978, 1714, 1475, 1300, 1160, 1108 (CH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.20 (t, J = 6.9 Hz, 2H), 3.02 (t, J = 7.7 Hz, 2H), 2.24 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.7, 59.2, 40.2, 34.1, 30.1, 23.4 (3C); HRMS (TOF-ESI) m/z: calcd for $C_8H_{16}O_3NaS$ [M + Na]$^+$ 215.0712, found 215.0719. The data presented above agree with that detailed in the literature.[20]

1-(*tert*-Butylsulfonyl)pentan-3-one (3da)

3da was prepared following the general procedure by reacting **1d** (19.9 μL, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 7 hours. Flash chromatography (cyclohexane/ethyl acetate: 5/5 to 4/6) afforded the title compound **3da** as a white solid (39 mg, 95%). M.p.: 55–56 °C; IR (neat) ν_{max}/cm^{-1} 2978, 1714, 1414, 1265, 1114, 976; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.21 (t, J = 6.9 Hz, 2H), 2.98 (t, J = 7.6 Hz, 2H), 2.51 (q, J = 7.3 Hz, 2H), 1.40 (s, 9H), 1.07 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.6, 59.1, 40.1, 36.2, 32.7, 23.4 (3C), 7.9; HRMS (TOF-ESI) m/z: calcd for $C_9H_{18}O_3NaS$ [M + Na]$^+$ 229.0869, found 229.0865.

4-(*tert*-Butylsulfonyl)-1-(thien-2-yl)butan-2-one (3ea)

3ea was prepared following the general procedure by reacting **1e** (30 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 10 hours. Flash chromatography (cyclohexane/ethyl acetate: 75/25) afforded the title compound **3ea** as a white solid (35 mg, 64%). M.p.: 84–85 °C; IR (neat) ν_{max}/cm^{-1} 2962, 1717, 1473, 1265, 1108, 1007, 669; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (dd, J = 5.1, 1.1 Hz, 1H), 6.98 (dd, J = 5.0, 3.6 Hz, 1H), 6.91 (m, 1H), 3.99 (s, 2H), 3.21 (t, J = 6.6 Hz, 2H), 3.08 (t, J = 6.8 Hz, 2H), 1.71 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.5, 134.4, 127.5, 127.4, 125.7, 59.3, 43.9, 40.4, 32.5, 23.6 (3C); HRMS (TOF-ESI) m/z: calcd for $C_{12}H_{18}O_3NaS_2$ [M + Na]$^+$ 297.0590, found 297.0592.

1-Acetyl-2-*tert*-butylsulfonyl cyclohexane (3fa)

3fa was prepared following the general procedure by reacting **1f** (25.7 μL, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 48 hours. Flash chromatography (cyclohexane/ethyl acetate: 5/5) afforded the title compound **3fa** as a brown foam (33 mg, 67%). IR (neat) ν_{max}/cm^{-1} 2944, 1711, 1271, 1110, 681; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.59 (m, 1H), 2.90 (m, 1H), 2.62–2.51 (m, 1H), 2.23 (s, 3H), 2.02 (m, 2H), 1.81–1.74 (m, 2H), 1.47–1.41 (m, 3H), 1.36 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.9, 61.1, 57.1, 48.3, 29.1, 27.6, 26.2, 24.6, 23.5 (3C), 21.9; HRMS (TOF-ESI) m/z: calcd for $C_{12}H_{22}O_3SNa$ [M + Na]$^+$ 269.1182, found 269.1180.

3-(*tert*-Butylsulfonyl)propanal (3ga)

3ga was prepared following the general procedure by reacting **1g** (13.4 μL, 0.20 mmol), *tert*-butylsulfinamide **2a** (24 mg, 0.20 mmol), HBF_4 (26 μL, 0.20 mmol) for 4 hours. Flash chromatography (cyclohexane/ethyl acetate: 3/7) afforded the title compound **3ga** as a colourless oil (14 mg, 39%). IR (neat) ν_{max}/cm^{-1} 2988, 1723, 1297, 1110; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.87 (s, 1H), 3.25 (t, J = 7.4 Hz, 2H), 3.10 (t, J = 7.0 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8, 59.4, 38.7, 34.8, 23.5 (3C); HRMS (TOF-ESI) m/z: calcd for $C_7H_{14}O_3NaS$ [M + Na]$^+$ 201.0556, found 201.0564.

(*E*)-*N*-[3-(*tert*-Butylsulfonyl)propyliden-1-yl]-*tert*-butylsulfinamide (5ga)

5ga was prepared following the general procedure by reacting **1g** (13.4 μL, 0.20 mmol), *tert*-butylsulfinamide **2a** (73 mg, 0.60 mmol), HBF_4 (26 μL, 0.20 mmol) for 24 hours. Flash chromatography (cyclohexane/ethyl acetate: 3/7) afforded the title compound **5ga** as a white solid (14.5 mg, 26%). M.p.: 101–102 °C; IR (neat) ν_{max}/cm^{-1} 2985, 1651, 1300, 1263, 1117, 1078; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (t, J = 3.1 Hz, 1H), 3.34–3.28 (m, 2H), 3.15–3.09 (m, 2H), 1.45 (s, 9H), 1.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 59.4, 57.2, 41.2, 27.5, 23.6 (3C), 22.5 (3C); HRMS (TOF-ESI) m/z: calcd for $C_{11}H_{24}NO_3S_2$ [M + H]$^+$ 282.1192, found 282.1205.

3-(*tert*-Butylsulfonyl)-1-(4-chlorophenyl)propan-1-one (3ha)

3ha was prepared following the general procedure by reacting **1h** (33 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 5 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3) afforded the title compound **3ha** as a white solid (16 mg, 28%). M.p.: 146–147 °C; IR (neat) ν_{max}/cm^{-1} 2982, 1674, 1588, 1301, 1265, 1116; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 3.55 (dd, J = 8.5, 6.4 Hz, 2H), 3.38 (dd, J = 8.5, 6.5 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3, 140.5, 134.4, 129.7 (2C), 129.3 (2C), 59.3, 40.5, 29.8, 23.5 (3C); HRMS (TOF-ESI) m/z: calcd for $C_{13}H_{17}O_3NaSCl$ [M + Na]$^+$ 311.0479, found 311.0476.

3-(*tert*-Butylsulfonyl)-1-(4-fluorophenyl)propan-1-one (3ia)

3ia was prepared following the general procedure by reacting **1i** (30 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 5 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3 to 6/4) afforded the title compound **3ia** as a white solid (16 mg, 29%). M.p.: 103–104 °C;

IR (neat) ν_{max}/cm^{-1} 2925, 1684, 1596, 1267, 1108, 979, 736; ^1H NMR (300 MHz, $CDCl_3$) δ 8.03 (m, 2H), 7.16 (br t, $J = 8.7$ Hz, 2H), 3.56 (dd, $J = 8.4$, 6.3 Hz, 1H), 3.38 (dd, $J = 8.5$, 6.4 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9, 166.3 (d, $J = 254.4$ Hz), 131.0 (d, $J = 9.3$ Hz, 2C), 116.1 (d, $J = 21.9$ Hz, 2C), 59.4, 40.7, 29.8, 23.6 (3C); HRMS (TOF-ESI) *m*/*z*: calcd for $C_{13}H_{17}O_3NaSF$ $[M + Na]^+$ 295.0775, found 295.0779.

3-(*tert*-Butylsulfonyl)-1-phenylpropan-1-one (3ja)

3ja was prepared following the general procedure by reacting 1 h (26.4 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 5 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3 to 6/4) afforded the title compound **3ja** as a white solid (31 mg, 61%). M.p.: 120–121 °C; IR (neat) ν_{max}/cm^{-1} 2935, 2920, 1687, 1262, 1108, 1002, 740, 688; ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (br d, $J = 7.3$ Hz, 2H), 7.60 (br t, $J = 7.6$ Hz, 1H), 7.49 (br t, $J = 7.7$ Hz, 2H), 3.60 (dd, $J = 8.5$, 6.6 Hz, 1H), 3.39 (dd, $J = 8.6$, 6.7 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 136.1, 133.9, 128.9, 128.3, 59.3, 40.6, 29.8, 23.6 (3C); HRMS (TOF-ESI) *m*/*z*: calcd for $C_{13}H_{18}O_3NaS$ $[M + Na]^+$ 277.0869, found 277.0887.

3-(*tert*-Butylsulfonyl)-1-(4-methoxyphenyl)propan-1-one (3ka)

3ka was prepared following the general procedure by reacting **1k** (32 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 4 hours. Flash chromatography (cyclohexane/ethyl acetate: 5/5) afforded the title compound **3ka** as a white solid (33 mg, 58%). M.p.: 75–76 °C; IR (neat) ν_{max}/cm^{-1} 2926, 1674, 1601, 1573, 1251, 1112, 977; ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, $J = 8.9$ Hz, 2H), 6.95 (d, $J = 8.9$ Hz, 2H), 3.87 (s, 3H), 3.54 (dd, $J = 8.5$, 6.8 Hz, 2H), 3.37 (dd, $J = 8.5$, 6.6 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9, 164.1, 130.6 (2C), 129.2, 114.1 (2C), 59.3, 55.7, 40.7, 29.3, 23.5 (3C); HRMS (TOF-ESI) *m*/*z*: calcd for $C_{14}H_{20}O_4NaS$ $[M + Na]^+$ 307.0975, found 307.0982.

3-(*tert*-Butylsulfonyl)-1,3-diphenyl propan-1-one (3la)

3la was prepared following the general procedure by reacting **1l** (42 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 48 hours. Flash chromatography (cyclohexane/ethyl acetate: 9/1 to 8/2) afforded the title compound **3la** as a white solid (38 mg, 57%) M.p.: 136–137 °C; IR (neat) ν_{max}/cm^{-1} 2926, 1687, 1281, 1177, 1108; ^1H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, $J = 7.3$ Hz, 2H), 7.62 (d, $J = 7.9$ Hz, 2H), 7.55 (t, $J = 7.1$ Hz, 1H), 7.43 (m, 2H), 7.40–7.29 (m, 3H), 5.19 (dd, $J = 9.2$ Hz, $J = 3.5$ Hz, 1H), 4.15 (dd, $J = 17.9$ Hz, $J = 3.5$ Hz, 1H), 3.72 (dd, $J = 17.9$ Hz, $J = 9.2$ Hz, 1H), 1.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4, 136.4, 135.0, 133.7, 129.9 (2C), 129.0 (3C), 128.8 (2C), 128.3 (2C), 62.4, 60.1, 39.6, 24.4 (3C); HRMS (TOF-ESI) *m*/*z*: calcd for $C_{19}H_{22}O_3NaS$ $[M + Na]^+$ 353.1182, found 353.1189.

3-(*tert*-Butylsulfonyl)-1-(thien-3-yl)propan-1-one (3ma)

3ma was prepared following the general procedure by reacting **1m** (28 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 6 hours. Flash chromatography (cyclohexane/ethyl acetate: 6/4) afforded the title compound **3ma** as a white solid (29 mg, 55%). M.p.: 133–134 °C; IR (neat) ν_{max}/cm^{-1} 2952, 1669, 1416, 1264, 1106, 771; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, $J = 3.4$ Hz, 1H), 7.67 (d, $J = 4.9$ Hz, 1H), 7.15 (t, $J = 4.6$ Hz, 1H), 3.52 (dd, $J = 8.3$, 6.2 Hz, 1H), 3.37 (dd, $J = 8.5$, 6.6 Hz, 1H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.1, 143.0, 134.6, 132.8, 128.5, 59.3, 40.5, 30.2, 23.5 (3C); HRMS (TOF-ESI) *m*/*z*: calcd for $C_{11}H_{16}O_3S_2Na$ $[M + Na]^+$ 283.0433, found 283.0435.

3-(*tert*-Butylsulfonyl)-1-(1-tosyl-1*H*-indol-3-yl)propan-1-one (3na)

3na was prepared following the general procedure by reacting **1n** (65 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 24 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3 to 6/4) afforded the title compound **3na** as a brown solid (45 mg, 50%). M.p.: 143–144 °C; IR (neat) ν_{max}/cm^{-1} 2971, 1666, 1539, 1266, 1116, 978; ^1H NMR (300 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.25 (dd, $J = 7.3$, 2.2 Hz, 1H), 7.96 (dd, $J = 6.9$, 1.3 Hz, 1H), 7.85 (d, $J = 8.4$ Hz, 2H), 7.40–7.26 (m, 4H), 3.54–3.50 (m, 2H), 3.44–3.38 (m, 2H), 2.36 (s, 3H, CH_3-Ar), 1.47 (s, 9H, *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 146.2, 135.0, 134.5, 133.2, 132.5, 130.4 (2C), 127.4 (2C), 126.0, 125.1, 122.9, 120.4, 113.3, 59.4, 40.3, 30.7, 23.5 (3C), 21.8; HRMS (TOF-ESI) *m*/*z*: calcd for $C_{22}H_{25}NO_5NaS_2$ $[M + Na]^+$ 470.1066, found 470.1073.

4-(*tert*-Butylsulfonyl)-1-{[(1*R*,2*S*,5*R*)-2-isopropyl-5-methyl cyclohex-1-yl]oxy} but-3-en-2-one (3oa)

3oa was prepared following the general procedure by reacting **1o** (44 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) in a mixture of CH_2Cl_2/CH_3CN (8/2, 1 mL) for 17 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3) afforded the title compound **3oa** as a yellow oil (41 mg, 59%). IR (neat) ν_{max}/cm^{-1} 2955, 2920, 1722, 1301, 1116; ^1H NMR (300 MHz, $CDCl_3$) δ 4.20 (d, $J = 16.8$ Hz, 1H), 4.00 (d, $J = 16.8$ Hz, 1H), 3.26–6.09 (m, 4H), 2.22 (m, 1H), 2.03 (br d, $J = 11.3$ Hz, 1H), 1.64 (m, 2H), 1.43 (s, 9H), 1.35–1.18 (m, 4H), 0.91 (m, 8H), 0.78 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.6, 80.6, 73.9, 59.3, 48.2, 40.0, 39.9, 34.5, 31.6, 30.5, 25.8, 23.5 (3C), 23.4, 22.4, 21.1, 16.4; HRMS (TOF-ESI) *m*/*z*: calcd for $C_{18}H_{34}O_4NaS$ $[M + Na]^+$ 369.2070, found 369.2080.

(11*Z*,14*Z*)-1-(*tert*-butylsulfonyl)icosa-11,14-dien-3-one (3pa)

3pa was prepared following the general procedure by reacting **1p** (58 mg, 0.20 mmol), *tert*-butylsulfinamide (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 6 hours. Flash chromatography (cyclohexane/ethyl acetate: 7/3) afforded the title compound **3pa** as a yellow foam (42 mg, 51%). IR (neat) ν_{max}/cm^{-1} 2982, 1712, 1268, 1102; ^1H NMR (300 MHz, $CDCl_3$) δ 5.35–5.27 (m, 4H), 3.21 (t, $J = 7.8$ Hz, 2H), 2.99 (t, $J = 7.2$ Hz, 2H), 2.76 (t, $J = 5.8$ Hz, 2H), 2.49 (t, $J = 7.4$ Hz, 2H), 2.03 (m, 4H), 1.60 (m, 2H), 1.42 (s, 9H), 1.30 (m, 14H), 0.88 (t, $J = 7.0$ Hz, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.3, 130.3, 130.2, 128.2, 128.0, 59.2, 43.1, 40.2, 33.1, 31.7, 29.7, 29.5, 29.4, 29.2, 28.2, 27.3, 25.8, 24.9,

23.9, 23.5 (3C), 22.7, 14.2; HRMS (TOF-ESI) *m*/*z*: calcd for $C_{24}H_{44}O_3NaS$ $[M + Na]^+$ 435.2903, found 435.2915.

General procedure for the synthesis of hydroxysulfones (4)

The ketosulfone **3** (0.20 mmol) was dissolved in MeOH (c = 0.1 mol L^{-1}) at 0 °C and $NaBH_4$ (0.24 mmol) was then added. After stirring at room temperature for 2 hours, the reaction mixture was quenched by the addition of acetone (2 mL) before evaporation of the solvent. Water (2 mL) was then added, the aqueous layer was extracted with AcOEt (3 × 10 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography with cyclohexane/ethyl acetate to yield the desired hydroxysulfone **4**.

3-(*tert*-Butylsulfonyl)cyclopentanol (4ba)

4ba was prepared following the general procedure by reacting **1b** (32.8 μL, 0.40 mmol), *tert*-butylsulfinamide **2a** (96 mg, 0.80 mmol), HBF_4 (52 μL, 0.40 mmol) for 24 hours. $NaBH_4$ (18 mg, 0.48 mmol) was next added. Flash chromatography (cyclohexane/ethyl acetate: 1/9) afforded the title compound **4ba** as a white solid (73 mg, 88%, *cis*/*trans* = 10/1). M.p.: 79–80 °C; IR (neat) ν_{max}/cm^{-1} 3499, 2993, 1282, 1143, 688; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.31 (br s, 1H), 3.72–3.62 (m, 1H), 2.47–2.20 (m, 4H), 2.13–2.06 (m, 1H), 2.02–1.91 (m, 1H), 1.79–1.72 (m, 1H), 1.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 72.4, 60.3, 55.7, 37.4, 35.6, 25.8, 24.3 (3C); HRMS (TOF-ESI) *m*/*z*: calcd for $C_9H_{18}O_3NaS$ $[M + Na]^+$ 229.0869, found 229.0868.

3-(Benzenesulfonyl)cyclopentanol (4bb)

4bb was prepared following the general procedure by reacting **1b** (16.8 μL, 0.20 mmol), benzenesulfinamide **2b** (56 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 24 hours. $NaBH_4$ (9.1 mg, 0.24 mmol) was next added. Flash chromatography (cyclohexane/ethyl acetate: 3/7 to 2/8) afforded the title compound **4bb** as a colourless oil (30 mg, 66%, *cis*/*trans* = 21/1). IR (neat) ν_{max}/cm^{-1} 3480, 1446, 1284, 1142, 1085; 690; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (br d, J = 7.4 Hz, 2H), 7.67 (br t, J = 7.8 Hz, 1H), 7.57 (br t, J = 6.9 Hz, 2H), 4.32 (br s, 1H), 3.61 (qt, J = 8.5 Hz, 1H), 2.35–2.10 (m, 4H), 1.96–1.85 (m, 2H), 1.83–1.73 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 134.0, 129.5 (2C), 128.7 (2C), 72.7, 63.2, 36.3, 35.6, 24.8; HRMS (TOF-ESI) *m*/*z*: calcd for $C_{11}H_{14}O_3NaS$ $[M + Na]^+$ 249.0556, found 249.0560.

3-(*p*-Toluensulfonyl)-cyclopentan1-ol (4bc)

4bc was prepared following the general procedure by reacting **1b** (16.8 μL, 0.20 mmol), *p*-toluenesulfinamide **2c** (62 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 24 hours. $NaBH_4$ (9.1 mg, 0.24 mmol) was next added. Flash chromatography (cyclohexane/ethyl acetate: 4/6) afforded the title compound **4bc** as a colourless oil (36 mg, 75%, *cis*/*trans* = 17/1). IR (neat) ν_{max}/cm^{-1} 3492, 1478, 1284, 1185; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 4.31 (br s, 1H), 3.58 (qt, J = 6.7 Hz, 1H), 2.45 (s, 3H), 2.28–2.13 (m, 4H), 1.95–1.84 (m, 2H), 1.79–1.74 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 135.0, 130.0 (2C), 128.6 (2C), 72.6, 63.2, 36.2, 35.5, 24.6, 21.6; HRMS (TOF-ESI) *m*/*z*: calcd for $C_{12}H_{16}O_3NaS$ $[M + Na]^+$ 263.0712, found 263.0710. The data presented above are in agreement with that detailed in the literature.[21]

3-(*tert*-Butylsulfonyl)-1-(4-chlorophenyl)propan-1-ol (4ha)

4ha was prepared following the general procedure by reacting **1h** (33 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 5 hours. $NaBH_4$ (9.1 mg, 0.24 mmol) was next added. Flash chromatography (cyclohexane/ethyl acetate: 4/6) afforded the title compound **4ha** as a colourless oil (11 mg, 18%). IR (neat) ν_{max}/cm^{-1} 3469, 2924, 1282, 1110, 748; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (m, 4H), 4.95 (dd, J = 8.5, 4.5 Hz, 1H), 3.07 (t, J = 7.3 Hz, 2H), 2.33–2.21 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 133.8, 129.0 (2C), 127.2 (2C), 71.8, 59.3, 42.1, 30.2, 23.6 (3C); HRMS (TOF-ESI) *m*/*z*: calcd for $C_{13}H_{19}O_3NaSCl$ $[M + Na]^+$ 313.0636, found 313.0638.

3-(*tert*-Butylsulfonyl)-1-(4-fluorophenyl)propan-1-ol (4ia)

4ia was prepared following the general procedure by reacting **1i** (30 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 5 hours. $NaBH_4$ (9.1 mg, 0.24 mmol) was next added. Flash chromatography (cyclohexane/ethyl acetate: 4/6 to 3/7) afforded the title compound **4ia** as a white solid (17 mg, 31%). M.p.: 61–62 °C; IR (neat) ν_{max}/cm^{-1} 3479, 2990, 1509, 1260, 1109; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.7 Hz, J = 5.4 Hz, 2H), 7.04 (t, J = 8.6 Hz, 2H), 4.91 (dd, J = 8.0, 4.6 Hz, 1H), 3.07 (t, J = 7.5 Hz, 2H), 2.52 (br s, 1H), 2.31–2.22 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5 (d, J = 245 Hz), 139.3, 127.5 (d, J = 8.0 Hz, 2C), 115.6 (d, J = 21.3 Hz, 2C), 71.9, 59.3, 42.2, 30.2, 23.6 (3C); HRMS (TOF-ESI) *m*/*z*: calcd for $C_{13}H_{19}O_3FNaS$ $[M + Na]^+$ 297.0931, found 297.0937.

3-(*tert*-Butylsulfonyl)-1-(4-methoxyphenyl)propan-1-ol (4ka)

4ka was prepared following the general procedure by reacting **1k** (32 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 4 hours. $NaBH_4$ (9.1 mg, 0.24 mmol) was next added. Flash chromatography (cyclohexane/ethyl acetate: 4/6) afforded the title compound **4ka** as a yellow oil (28 mg, 49%). IR (neat) ν_{max}/cm^{-1} 3490, 2938, 1672, 1512, 1244, 1109, 1030; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 4.84 (t, J = 6.5 Hz, 2H), 3.80 (s, 3H), 3.11–2.98 (m, 2H), 2.27 (q, J = 7.5 Hz, 2H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 135.6, 127.1 (2C), 114.2 (2C), 72.3, 59.2, 55.4, 42.5, 30.0, 23.6 (3C); HRMS (TOF-ESI) *m*/*z*: calcd for $C_{14}H_{22}O_4NaS$ $[M + Na]^+$ 309.1131, found 309.1143.

3-(*tert*-Butylsulfonyl)-1-(thien-3-yl)propan-1-ol (4ma)

4ma was prepared following the general procedure by reacting **1m** (28 mg, 0.20 mmol), *tert*-butylsulfinamide **2a** (48 mg, 0.40 mmol), HBF_4 (26 μL, 0.20 mmol) for 6 hours. $NaBH_4$ (9.1 mg, 0.24 mmol) was next added. Flash chromatography

(cyclohexane/ethyl acetate: 4/6) afforded the title compound **4ma** as a white solid (24 mg, 47%). M.p.: 82–83 °C; IR (neat) ν_{max}/cm^{-1} 3473, 2977, 1255, 1086, 777; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, $J = 4.7$ Hz, 1H), 7.00–6.96 (m, 2H), 5.17 (dd, $J =$ 7.3, 5.3 Hz, 1H), 3.11 (t, $J = 7.4$ Hz, 2H), 2.71 (br s, 1H), 2.45–2.35 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2, 127.0, 125.0, 124.1, 68.6, 59.3, 42.2, 30.3, 25.6 (3C); HRMS (TOF-ESI) *m*/*z*: calcd for $C_{11}H_{18}O_2NaS_2$ $[M + Na]^+$ 285.0590, found 285.0601.

Conflicts of interest

There are no conflicts to declare.

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