Supplementary Information

Accessing chiral sulfones bearing quaternary carbon stereocenters via photoinduced radical sulfur dioxide insertion and Truce-Smiles rearrangement

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1 Supplementary Notes

Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm). 

$^1$H and $^{13}$C NMR spectra were recorded on Bruker 400 MHz spectrometer in CDCl$_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for $^1$H NMR are recorded as follows: chemical shift ($\delta$, ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; p = pentet; m = multiplet; brs = broad singlet), coupling constant (Hz), integration. Data for $^{13}$C NMR are reported in terms of chemical shift ($\delta$, ppm). The enantiomeric excess values were determined by chiral HPLC with an Shimadzu instrument and a Daicel CHIRALCEL and CHIRALPAK column. High resolution mass spectroscopy (HRMS) analyses were performed at a Q-Exactive (Thermo Scientific) Inc mass instrument (HESI).
2 Supplementary Methods

2.1 General procedures for the preparation of products

Set-up of the photoredox reaction: All photoredox reactions were carried out in the apparatus shown below.

Light source: 35 W LED strip, Greethink (Manufacturer), GT-5050-Blue (Model)
Wavelength of peak intensity: 460-470 nm
Material of the irradiation vessel: borosilicate glass
Distance of the irradiation vessel from the light source: approximately 3 cm.

Supplementary Figure 1. Set-up of the photoredox reaction: a reaction device, b light source, c reaction tube.

Method A: arylidiazonium tetrafluoroborates system

In a glove box, a dry quartz vial equipped with a magnetic stir bar is charged sequentially with 1 (0.2 mmol), 2 (0.4 mmol), Na$_2$S$_2$O$_4$ (0.4 mmol), NaHSO$_3$ (0.3 mmol), Mes-AcrClO$_4$ (2 mol%), and dry MeCN (3.0 mL). The reaction mixture is stirred for 18 h at 900 rpm in a thermostatic water bath at 20 degrees under a 35 W blue LED light. When the reaction is completed (monitored by TLC), the mixture is purified by flash chromatography on silica gel eluted with PE/EA (5/1) to afford the corresponding products.
Method B: thianthrenium salts system

In a glove box, a dry quartz vial equipped with a magnetic stir bar is charged sequentially with 1 (0.2 mmol), 3 (0.4 mmol), Rongalite (0.24 mmol), DABSO (0.4 mmol), NaOH (0.24 mmol), fac-Ir(ppy)$_3$ (2 mol%) and dry MeCN (3.0 mL). The reaction mixture is stirred for 18 h at 900 rpm in a thermostatic water bath at 20 degrees under a 35 W blue LED light. When the reaction is completed (monitored by TLC), the mixture is purified by flash chromatography on silica gel eluted with PE/EA (5/1) to afford the corresponding products.

2.2 Optimization of the reaction conditions

Supplementary Table 1. Optimization of the reaction conditions in terms of thianthrenium salts (Method B).[a]

| Entry | PC     | “SO$_2$” (x equiv) | Additive (y equiv) | Yield$^{[b]}$ (%) | Ee$^{[c]}$ (%) |
|-------|--------|--------------------|--------------------|-------------------|--------------|
| 1     | Mes-AcrClO$_4$ | Na$_2$SO$_4$ (2.0) | NaHSO$_3$ (1.5)    | trace             | /            |
| 2     | fac-Ir(ppy)$_3$ | Na$_2$SO$_4$ (2.0) | NaHSO$_3$ (1.5)    | 43                | 93           |
| 3     | fac-Ir(ppy)$_3$ | DABSO (2.0)        | /                  | 38                | 94           |
| 4     | fac-Ir(ppy)$_3$ | K$_2$SO$_4$ (2.0)  | /                  | 29                | 94           |
| 5     | fac-Ir(ppy)$_3$ | NaHSO$_3$ (2.0)    | /                  | trace             | /            |
| 6     | fac-Ir(ppy)$_3$ | Rongalite (2.0)    | NaOH (2.0)         | 47                | 94           |
| 7     | fac-Ir(ppy)$_3$ | Rongalite (2.0)    | NaOH (2.0) + NaHSO$_3$ (1.5) | 61                | 94           |
| 8     | fac-Ir(ppy)$_3$ | Rongalite (2.0)    | NaOH (2.0) + Na$_2$SO$_3$ (1.5) | 43                | 94           |
| 9     | fac-Ir(ppy)$_3$ | Rongalite (2.0)    | NaOH (2.0) + DABSO (1.5) | 66                | 96           |
| 10    | fac-Ir(ppy)$_3$ | Rongalite (3.0)    | NaOH (3.0) + DABSO (1.5) | 69                | 96           |
| 11    | fac-Ir(ppy)$_3$ | Rongalite (1.5)    | NaOH (1.5) + DABSO (1.5) | 68                | 97           |
| 12    | fac-Ir(ppy)$_3$ | Rongalite (1.2)    | NaOH (1.2) + DABSO (1.5) | 69                | 97           |
| 13    | fac-Ir(ppy)$_3$ | Rongalite (1.2)    | NaOH (1.2) + DABSO (1.0) | 67                | 97           |
| 14    | fac-Ir(ppy)$_3$ | Rongalite (1.2)    | NaOH (1.2) + DABSO (2.0) | 75                | 97           |
| 15    | fac-Ir(ppy)$_3$ | Rongalite (1.2)    | NaOH (1.2) + DABSO (3.0) | 70                | 97           |
| 16    | /      | Rongalite (1.2)    | NaOH (1.2) + DABSO (2.0) | 0                 | /            |
| 17$^{[d]}$ | fac-Ir(ppy)$_3$ | Rongalite (1.2)    | NaOH (1.2) + DABSO (3.0) | 0                 | /            |

[a] Reaction conditions: 1a (0.1 mmol), 3a (0.2 mmol), “SO$_2$” source (x mmol), photocatalyst (2 mol%), additive (y equiv), solvent (1.5 mL), 35 W blue LED, under N$_2$ at 20 °C for 18 h. [b] Determined by $^1$H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] Determined by HPLC analysis. [d] In the dark.
2.3. Mechanistic studies

2.3.1 Radical trapping experiments

Supplementary Table 2. Radical trapping experiments

| Entry | Additive           | (rac)-4a | Targets |
|-------|--------------------|----------|---------|
| 1     | TEMPO              | 0        | 0       |
| 2     | BHT                | 35%      | 0       |
| 3     | 1,1-Diphenylethylene | 0       | 5, 39%  |

The synthesis of 4a is carried out under standard conditions with the addition of a radical scavenger (3.0 equiv). When the reaction is completed (monitored by TLC), the mixture is purified by flash chromatography on silica gel to afford the product 4a and trapped targets. The compound structure is determined by $^1$H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

(2-Tosylethene-1,1-diyl)dibenzene (5)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, $J = 8.2$ Hz, 2H), 7.39 – 7.34 (m, 2H), 7.32 – 7.28 (m, 4H), 7.21 – 7.19 (m, 2H), 7.14 (d, $J = 8.4$ Hz, 2H), 7.10 – 7.08 (m, 2H), 6.99 (s, 1H), 2.37 (s, 3H).

Supplementary Figure 2. $^1$H NMR-spectrum of 5, recorded at 400 MHz and 25 °C in CDCl$_3$. 
2.3.2 Measurement of quantum yield

The experimental procedures were referred to the published paper.\(^1\) Determination of photon flux of LED blue light by standard potassium ferric oxalate photometric method. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (328 mg) in 5 mL of H\(_2\)SO\(_4\) (0.20 M) solution. A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (54.1 mg) and sodium acetate (1.23 g) in 20 mL of H\(_2\)SO\(_4\) (0.20 M) solution. To determine the photon flux of the LEDs, the ferrioxalate solution (2.0 mL) was placed in a cuvette and irradiated for 90 s at \(\lambda_{\text{max}} = 420\) nm. After irradiation, the phenanthroline solution (0.35 mL) was added to the cuvette, and the mixture was allowed to stir in the dark for 1 h to allow the ferrous ions to completely coordinate with phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. The calculation method of the amount of ferrous ions generated is as follows:

\[
\frac{n}{Fe^{2+}} = \frac{V \times \Delta A}{l \times \epsilon} 
\]

where \(V\) is the total volume (0.00235 L) of the measurement sample, \(\Delta A\) is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions \([\Delta A = 2.503, l\) is the optical path of the sample in the spectrophotometer (1 cm), and \(\epsilon\) is the extinction coefficient of the complex Fe\(^{II}\)(phen)\(^3\)\(^2+\) at 510 nm (11100 L mol\(^{-1}\) cm\(^{-1}\)).

\[
\text{photon flux} = \frac{n}{Fe^{2+}} \times 4 \times 10^{-9}
\]

where \(\Phi\) is the quantum yield for the ferrioxalate actinometer (1.12 at \(\lambda_{\text{ex}} = 420\) nm), \(t\) is the irradiation time (90 s), and \(f\) is the fraction of light absorbed at \(\lambda_{\text{ex}} = 420\) nm by the ferrioxalate actinometer.

\[
f = 1 - 10^{-A(420nm)} = 1 - 10^{-4.952} = 0.999 
\]

\[
n/Fe^{2+} = \frac{V \times \Delta A}{l \times \epsilon} = \frac{0.00235 \times 2.503}{1 \times 11100 \times 10^{-3} \times 11100} = 5.299 \times 10^{-7} \text{ mol}
\]

\[
\text{photon flux} = \frac{n/Fe^{2+}}{\Phi \times f} = \frac{5.299 \times 10^{-7}}{1.12 \times 90 \times 0.999} = 5.26 \times 10^{-9} \text{ einstein s}^{-1}
\]

**Method A:** aryldiazenium tetrafluoroborates system

Under nitrogen, a dry quartz vial equipped with a magnetic stir bar was charged with \(1a\) (0.1 mmol), \(2a\) (0.2 mmol), Na\(_2\)S\(_2\)O\(_4\) (0.2 mmol), NaHSO\(_3\) (0.15 mmol) and Mes-AcrClO\(_4\) (2 mol%), then add into dry MeCN (1.5 mL). Then cap the vial Close the lid, remove from the glove box, and keep the temperature at 20-22 °C. The reaction mixture was placed in a water bath Stir for 1 hour at 900 rpm under 35 W blue LED light. After the reaction, the solvent was removed under reduced pressure, and 1,3,5-trimethoxybenzene was used as the internal standard, and the product yield was 62.0% (1.00×10\(^{-5}\) mol) by \(^1\)H NMR.

\[
\Phi (4a) = \frac{\text{Mol product}}{\text{Flux} \times t \times f} = \frac{6.20 \times 10^{-5}}{5.26 \times 10^{-9} \times 3600 \times 0.999} = 3.28
\]
Method B: thianthrenium salts system

Under nitrogen, a dry quartz vial equipped with a magnetic stir bar was charged with 1a (0.1 mmol), 3a (0.2 mmol), Rongalite (0.12 mmol), DABCO·(SO₂)₂ (0.2 mmol), NaOH (0.12 mmol) and fac-Ir(ppy)₃ (2 mol%), then add into dry MeCN (1.5 mL). Then cap the vial, close the lid, remove from the glove box, and keep the temperature at 20-22 °C. The reaction mixture was placed in a water bath and stirred for 1 hour at 900 rpm under 35 W blue LED light. After the reaction, the solvent was removed under reduced pressure, and 1,3,5-trimethoxybenzene was used as the internal standard, and the product yield was 46.0% (2.60×10⁻⁵ mol) by ¹H NMR.

Φ (4a) = \frac{\text{Mol product}}{\text{flux} \times t \times f} = \frac{4.60 \times 10^{-5}}{5.26 \times 10^{-9} \times 3600 \times 0.99} = 2.43

Conclusion: The quantum yields of the reaction was determined to be 2.43, showing that the extended radical-chain reactions were possible.

2.3.3 Stern-Volmer fluorescence quenching experiments.

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 0.1 mM Ir(ppy)₃ in degassed dry CH₃CN added with the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. The solutions were irradiated at 395 nm and fluorescence was measured from 460 nm to 640 nm.

![Supplementary Figure 3. Fluorescence quenching experiments of Ir(ppy)₃ and 1c](image-url)
Supplementary Figure 4. Fluorescence quenching experiments of Ir(ppy)$_3$ and 3a

Supplementary Figure 5. Stern-Volmer plots of Ir(ppy)$_3$ with different quenchers

**Conclusion:** the Stern-Volmer quenching experiments showed that substrate 3a could effectively quench the excited *Ir(ppy)$_3$, whereas 1c could not.
2.3.4 Plausible mechanism of thianthrenium salts system

On basis of experimental results and previous reports, a plausible mechanism for this transformation is proposed. Irradiation of Ir(ppy)$_3$ with visible light produces a long-lived ($t = 1.9 \mu$s) photoexcited state, *Ir(ppy)$_3$ ($E_{1/2}[\text{Ir(ppy)$_3$}^{\text{3+}}/\text{Ir(ppy)$_3$}^\text{3+}] = -1.73$ V vs. SCE), which can be readily oxidized by an appropriate quencher. Initially, photoexcited Ir(III)* would reduce thianthrenium salt 3 via a single electron transfer (SET) to generate radical species B, which could readily capture the SO$_2$ from DABCO·(SO$_2$)$_2$ to give to sulfonyl radical species C.

As an intensification strategy for this process, another alternative pathway to provide radical species B and SO$_2$ was introduced in this system as follows. With the assistance of strong base NaOH, rongalite could release formaldehyde to generate sulfur dioxide anion G (SO$_2^2-$), which would undergo single-electron transfer (SET) with Ir(IV) to produce sulfur dioxide radical anions A. Further single-electron transfer (SET) between dioxide radical anions A and thianthrenium salt 3 would occur to release radical species B, with simultaneous extrusion of SO$_2$. Subsequently, sulfonyl radical species C would add to the double bond to form new radical intermediate D. The radical Truce-Smiles rearrangement proceeds spontaneously to generate the SO-centred radical F, traversing through a spirocyclic transition state E in an exothermic process. The SO-centred radical F undergoes SET oxidation with Ir (IV) and further reacts with NaOH to convert into final product 4 and NaHSO$_3$. Furthermore, the SO-centred radical F will reduce thianthrenium salt 3 to generate radical species B and re-enter the cycle, thereby rationally explaining the quantum yields of 2.43 for the reaction.
2.4 Synthesis procedures and characterization data of substrates 1

The synthesis of compounds 1 was referred to the published paper.\textsuperscript{2}

Supplementary Figure 7. Synthetic route of compound (rac)-1

**Step 1**
Formation of racemic N-arylsulfinamides
In a 50 mL two-necked round bottomed flask under nitrogen flow, the corresponding aniline (15 mmol, 2.5 equiv) was dissolved in THF (12 mL) and cooled to -78 °C. Then n-BuLi solution (1.6 M in n-hexane, 5.0 mL, 12.0 mmol, 2 equiv) was added dropwise. After 20 min, a solution of methylsulfinate (6.0 mmol, 1 equiv) in THF (8 mL) was added slowly. After 1 hour, the mixture was quenched at -78 °C with an aqueous saturated NaHCO\textsubscript{3} solution (3 x 30 mL). The mixture was extracted with EtOAc (3 x 20 mL). The organic phases were combined, dried over MgSO\textsubscript{4}, filtered and concentrated in vacuo. N-hexane (10 mL) was added to the residue and the precipitate was filtered through a Buchner funnel, washed with additional n-hexane (20 mL) and dried in vacuo to afford the pure N-arylsulfinamides.

**Step 2**
Formation of racemic N-aryl-N-sulfinylacrylamides
To an oven-dried two-necked round bottomed flask were sequentially added the corresponding sulfinamide (2.0 mmol, 1 equiv), Et\textsubscript{3}N (1.7 mL, 12.0 mmol, 6.0 equiv) and DMAP (12.0 mg, 0.1 mmol, 0.05 equiv) in THF (50 mL, 0.04 M) under nitrogen flow. The mixture was cooled to 0 °C (ice bath) and methacryloyl chloride (0.3 mL, 3.0 mmol, 1.5 equiv) was added dropwise. After 1 hour, the reaction mixture was diluted with EtOAc (15 mL), filtered and transferred into a separatory funnel. The mixture was washed with an aqueous saturated NaHCO\textsubscript{3} solution (3 x 30 mL). The combined organic phases were dried over MgSO\textsubscript{4}, filtered and concentrated in vacuo. N-hexane (10 mL) was added to the residue and the precipitate was filtered through a Buchner funnel, washed with additional n-hexane (20 mL) and dried in vacuo to afford the sulfinylacrylamides, which were further purified by precipitation or crystallization.

Formation of racemic N-alkyl-N-sulfinylacrylamides
In a 50 mL two-necked round bottomed flask under nitrogen flow, the corresponding
N-alkylphenylsulfinamide (1 mmol, 1 equiv) was dissolved in THF (25 mL) and cooled to -78 °C.
Then n-BuLi solution (1.6 M in n-hexane, 0.75 mL, 1.2 mmol, 1.2 equiv) was added dropwise.
After 20 min, methacryloyl chloride (1.1 mmol, 1.1 equiv) was added slowly. After 2 minutes,
the mixture was washed with an aqueous saturated NaHCO₃ solution (10 mL). The mixture was
extracted with EtOAc (3 x 20 mL). The organic phases were combined, dried over MgSO₄,
filtered and concentrated in vacuo to afford the sulfinylacrylamides, which were further purified
by precipitation or crystallization.

**Supplementary Figure 8.** Synthetic route of compound (S)-1

**Step 1**
**Formation of enantiopure N-aryl and N-alkylsulfinamides**
The same procedures described for the synthesis of racemic N-aryl and N-alkylsulfinamides were
followed using (1R, 2S, 5R)-(−)-Menthyl (S)-p-toluenesulfinate(Leyan.com).

**Step 2**
**Formation of enantiopure N-aryl and N-alkyl-N-sulfinylacrylamides**
The same procedures described for the synthesis of racemic N-aryl and N-sulfinylacrylamides
were followed.
(S)-N-(p-Tolyl)-N-(p-tolylsulfanyl)methacrylamide (1a)

60% yield, > 99.0 %ee

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (d, $J$ = 8.2 Hz, 2H), 7.16 (d, $J$ = 8.0 Hz, 2H), 6.99 (d, $J$ = 8.2 Hz, 2H), 6.62 (d, $J$ = 7.8 Hz, 2H), 5.36 (s, 1H), 5.29 (s, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 1.87 (s, 3H).

HPLC analysis: OJ-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 233$ nm, $t_R = 9.2$ min (minor), 16.4 min (major).

Supplementary Figure 9. HPLC Spectra of compound 1a
(S)-N-(4-Methoxyphenyl)-N-(p-tolylsulfinyl)methacrylamide (1b)

62% yield, > 99.0 %ee

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 (d, $J = 8.2$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 6.71 – 6.64 (m, 4H), 5.37 (s, 1H), 5.30 (s, 1H), 3.76 (s, 3H), 2.36 (s, 3H), 1.87 (s, 3H).

**HPLC analysis**: AS-H column, $n$-hexane/i-PrOH = 80/20, flow rate = 1.0 mL·min$^{-1}$, $\lambda$ = 254 nm, $t_R$ = 11.2 min (minor), 17.5 min (major).

Supplementary Figure 10. HPLC Spectra of compound 1b
(S)-N-(4-Fluorophenyl)-N-(p-tolylsulfinyl)methacrylamide (1c)

62% yield, > 99.0 %ee

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 – 7.24 (m, 2H), 7.17 (d, $J = 7.9$ Hz, 2H), 6.90 – 6.86 (m, 2H), 6.73 (dd, $J = 8.0$, 5.0 Hz, 2H), 5.42 (s, 1H), 5.37 (s, 1H), 2.36 (s, 3H), 1.93 (s, 3H).

HPLC analysis: OJ-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R = 9.5$ min (minor), 13.9 min (major).

Supplementary Figure 11. HPLC Spectra of compound 1c
(S)-N-Benzyl-N-(p-tolylsulfinyl)methacrylamide (1d)

58% yield, > 99.0 %ee

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J = 8.2$ Hz, 2H), 7.28 – 7.26 (m, 2H), 7.19 – 7.14 (m, 3H), 7.09 (dd, $J = 7.2$, 1.9 Hz, 2H), 5.52 (d, $J = 8.2$ Hz, 2H), 4.39 (d, $J = 15.0$ Hz, 1H), 4.30 (d, $J = 15.1$ Hz, 1H), 2.40 (s, 3H), 2.09 (s, 3H).

**HPLC analysis:** 1A column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R$ = 19.1 min (major), 26.2 min (minor).

Supplementary Figure 12. HPLC Spectra of compound 1d
(S)-N-((4-bromophenyl)sulfinyl)-N-phenylmethacrylamide (1e)

58% yield, > 99.0 %ee

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J$ = 8.5 Hz, 2H), 7.34 – 7.26 (m, 3H), 7.24 – 7.20 (m, 2H), 6.75 (d, $J$ = 7.4 Hz, 2H), 5.39 (s, 1H), 5.33 (s, 1H), 1.86 (s, 3H).

HPLC analysis: OD-H column, $n$-hexane/i-PrOH = 80/20, flow rate = 1.0 mL·min$^{-1}$, $\lambda$ = 254 nm, $t_R$ = 14.4 min (major), 22.2 min (minor).

Supplementary Figure 13. HPLC Spectra of compound 1e
(S)-N-benzyl-N-(p-tolylsulfinyl)acrylamide (1f)

58% yield, 99.0 %ee

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 8.3$ Hz, 2H), 7.21 – 6.97 (m, 6H), $\delta$ 6.56 (d, $J = 16.6$ Hz, 1H), 5.90 (d, $J = 10.4$ Hz, 1H), 4.57 – 4.33 (m, 2H), 2.39 (s, 3H).

HPLC analysis: 1A column, $n$-hexane/i-PrOH = 80/20, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R = 27.7$ min (major), 32.5 min (minor).

Supplementary Figure 14. HPLC Spectra of compound 1f
(S)-N,2-dibenzyl-N-(p-tolylsulfinyl)acrylamide (1g)

58% yield, 99.0 % ee

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 – 7.24 (m, 5H), 7.19 – 7.07 (m, 7H), 6.77 (d, $J$ = 8.1 Hz, 2H), 5.63 (d, $J$ = 13.9 Hz, 2H), 4.14 (s, 2H), 3.88 (d, $J$ = 14.4 Hz, 1H), 3.64 (d, $J$ = 14.5 Hz, 1H), 2.33 (s, 3H).

**HPLC analysis:** IA column, $n$-hexane/i-PrOH = 80/20, flow rate = 1.0 mL·min$^{-1}$, $\lambda$ = 254 nm, $t_R$ = 27.6 min (major), 37.2 min (minor).

**Supplementary Figure 15.** HPLC Spectra of compound 1g
2.5 Characterization data of products 4

\((R)-2\text{-Methyl-}N\text{-phenyl-2-}(\rho\text{-tolyl})\text{-3tosylpropanamide (4a)}\)

**Method A:** 78% yield, 96% ee; **Method B:** 75% yield, 97% ee.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 (d, \(J = 8.2\) Hz, 2H), 7.32 – 7.23 (m, 4H), 7.19 – 7.14 (m, 4H), 7.09 – 7.03 (m, 3H), 6.93 (s, 1H), 4.12 (d, \(J = 14.8\) Hz, 1H), 3.82 (d, \(J = 14.8\) Hz, 1H), 2.38 (s, 3H), 2.31 (s, 3H), 2.09 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 172.9, 144.0, 138.2, 138.0, 137.4, 136.3, 129.6, 129.5, 128.9, 127.6, 127.0, 124.6, 120.1, 64.1, 50.0, 22.7, 21.6, 21.0. HRMS (ESI) m/z Calcd for \([\text{C}_{24}\text{H}_{25}\text{NNaO}_3\text{S}, \text{M}^+\text{Na}^+]\): 430.1447, found: 430.1452. \([\alpha]_D^{20} = -45\) (c= 1.0, EtOAc).

**HPLC analysis:** AD-H column, \(n\)-hexane/i-PrOH = 50/50, flow rate = 1.0 mL·min\(^{-1}\), \(\lambda = 254\) nm, \(t_R = 12.0\) min (minor), 17.1 min (major).

**Supplementary Figure 16. HPLC Spectra of compound 4a (Method A)**
Supplementary Figure 17. HPLC Spectra of compound 4a (Method B)
(R)-3-((4-Methoxyphenyl)sulfonyl)-2-methyl-N-phenyl-2-(p-tolyl)propanamide (4b)

Method A: 75% yield, 97% ee; Method B: 62% yield, 98% ee.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 – 7.53 (m, 2H), 7.31 (d, $J$ = 7.6 Hz, 2H), 7.26 (d, $J$ = 7.9 Hz, 2H), 7.19 (d, $J$ = 8.2 Hz, 2H), 7.09 – 7.05 (m, 3H), 6.93 (s, 1H), 6.83 – 6.79 (m, 2H), 4.13 (d, $J$ = 14.8 Hz, 1H), 3.82(d, $J$ = 14.8 Hz, 1H), 3.82 (s, 3H), 2.31 (s, 3H), 2.09 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.9, 163.3, 137.9, 137.4, 136.4, 132.7, 129.7, 129.6, 128.9, 127.0, 124.6, 120.1, 114.1, 64.2, 55.6, 50.0, 22.7, 21.0. HRMS (ESI) m/z Calcd for [C$_{24}$H$_{25}$NNaO$_4$S, M+Na]$^+$: 446.1397, found: 446.1402. [$\alpha$]$_D^{20}$ = -30 (c= 0.6, EtOAc).

HPLC analysis: AD-H column, n-hexane/i-PrOH = 50/50, flow rate = 1.0 mL·min$^{-1}$, $\lambda$ = 254 nm, $t_R$ = 13.4 min (minor), 17.8 min (major).

Supplementary Figure 18. HPLC Spectra of compound 4b (Method A)
Supplementary Figure 19. HPLC Spectra of compound 4b (Method B)
(R)-2-Methyl-3-((4-(methylthio)phenyl)sulfonyl)-N-phenyl-2-(p-tolyl)propanamide (4c)

**Method A**: 81% yield, 94% ee.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J = 8.6$ Hz, 2H), 7.30 – 7.22 (m, 4H), 7.14 (d, $J = 8.2$ Hz, 2H), 7.10 – 7.04 (m, 3H), 7.02 (d, $J = 7.1$ Hz, 2H), 6.96 (s, 1H), 6.96 (s, 1H), 4.11 (d, $J = 14.9$ Hz, 1H), 3.84 (d, $J = 14.9$ Hz, 1H), 2.47 (s, 3H), 2.30 (s, 3H), 2.07 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.9, 146.4, 138.1, 137.4, 136.5, 136.1, 129.6, 128.9, 127.8, 127.0, 125.0, 124.7, 120.2, 64.1, 49.9, 22.6, 21.0, 14.8. HRMS (ESI) m/z Calcd for [C$_{24}$H$_{25}$NNaO$_3$S$_2$, M+Na]$^+$: 462.1168, found: 462.1170. $[\alpha]_{D}^{20} = -35$ (c=0.12, EtOAc).

**HPLC analysis**: AD-H column, $n$-hexane/i-PrOH = 80/20, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R = 26.7$ min (minor), 31.9 min (major).

**Supplementary Figure 20. HPLC Spectra of compound 4c (Method A)**
(R)-3-((4-(Tert-butyl)phenyl)sulfonyl)-2-methyl-N-phenyl-2-(p-tolyl)propanamide (4d)

**Method A:** 59% yield, 97%ee; **Method B:** 60% yield, 96% ee.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.27 – 7.23 (m, 2H), 7.17 (d, $J = 8.1$ Hz, 2H), 7.08 – 7.01 (m, 3H), 6.90 (s, 1H), 4.12 (d, $J = 14.9$ Hz, 1H), 3.87 (d, $J = 14.9$ Hz, 1H), 2.30 (s, 3H), 2.10 (s, 3H), 1.31 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.0, 156.9, 138.0, 137.8, 137.4, 136.2, 129.6, 128.9, 127.3, 127.0, 125.9, 124.6, 120.1, 64.0, 50.0, 35.1, 31.1, 22.8, 21.1. HRMS (ESI) m/z Calcd for $[\text{C}_{27}\text{H}_{31}\text{N}_2\text{O}_3\text{S}]^{+}$: 472.1917, found: 472.1921. $[\alpha]_D^{20} = -19$ (c= 0.14, EtOAc).

**HPLC analysis:** IA column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R = 9.8$ min (minor), 12.7 min (major).

**Supplementary Figure 21.** HPLC Spectra of compound 4d (Method A)
Supplementary Figure 22. HPLC Spectra of compound 4d (Method B)
(R)-2-Methyl-N-phenyl-2-(p-tolyl)-3-((4-(trifluoromethyl)phenyl)sulfonyl)propanamide (4e)

**Method A:** 65% yield, 95% ee.

**H NMR** (400 MHz, CDCl₃) δ 7.61 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.28 – 7.23 (m, 4H), 7.09 – 7.06 (m, 3H), 6.93 (d, J = 8.0 Hz, 2H), 6.82 (s, 1H), 4.11 (d, J = 15.3 Hz, 1H), 4.00 (d, J = 15.3 Hz, 1H), 2.26 (s, 3H), 2.10 (s, 3H). **C NMR** (100 MHz, CDCl₃) δ 172.9, 143.9, 138.4, 137.2, 135.2, 134.3 (q, J = 33.0 Hz), 129.6, 129.0, 128.1, 127.2, 125.8 (q, J = 4.0 Hz), 124.8, 123.2 (q, J = 272.8 Hz), 120.1, 64.0, 49.8, 22.5, 20.8. **HRMS** (ESI) m/z Calcd for [C₂₄H₂₂F₃NNaO₃S, M+Na⁺]: 484.1165, found: 484.1166. [α]D²⁰ = −45 (c= 0.1, EtOAc).

**HPLC analysis:** IA column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min⁻¹, λ = 254 nm, tᵣ = 12.3 min (minor), 16.9 min (major).

**Supplementary Figure 23.** HPLC Spectra of compound 4e (Method A)
(R)-3-((4-Cyanophenyl)sulfonyl)-2-methyl-N-phenyl-2-(p-tolyl)propanamide (4f)

**Method A:** 65% yield, 96% ee.

**1H NMR** (400 MHz, CDCl₃) δ 7.65 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.30 – 7.24 (m, 4H), 7.12 – 7.07 (m, 3H), 7.00 (d, J = 7.9 Hz, 2H), 6.89 (s, 1H), 4.12 (d, J = 15.1 Hz, 1H), 3.94 (d, J = 15.1 Hz, 1H), 2.31 (s, 3H), 2.10 (s, 3H). 13C NMR (100 MHz, CDCl₃) δ 172.6, 144.7, 138.6, 137.2, 135.5, 132.5, 129.7, 129.0, 128.3, 127.1, 124.9, 120.2, 117.2, 116.4, 64.2, 49.9, 22.5, 21.0.

**HRMS** (ESI) m/z Calcd for [C₂₄H₂₂N₂O₃S, M+Na]⁺: 441.1243, found: 441.1253. [α]D²⁰ = -45 (c= 0.1, EtOAc).

**HPLC analysis:** IA column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min⁻¹, λ = 254 nm, t_R = 25.6 min (minor), 38.2 min (major).

Supplementary Figure 24. HPLC Spectra of compound 4f (Method A)
(R)-2-Methyl-3-((4-nitrophenyl)sulfonyl)-N-phenyl-2-(p-tolyl)propanamide (4g)

**Method A:** 54% yield, 95% ee.

**1H NMR** (400 MHz, CDCl₃) δ 8.12 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 7.29 – 7.24 (m, 4H), 7.11 – 7.07 (m, 3H), 6.97 (d, J = 8.0 Hz, 2H), 6.83 (s, 1H), 4.14 (d, J = 15.3 Hz, 1H), 3.99 (d, J = 15.3 Hz, 1H), 2.28 (s, 3H), 2.11 (s, 3H). **13C NMR** (100 MHz, CDCl₃) δ 172.6, 150.0, 146.0, 138.7, 137.1, 135.4, 129.7, 129.0, 127.2, 124.9, 124.4, 123.9, 120.1, 64.3, 49.9, 22.5, 20.9. **HRMS** (ESI) m/z Calcd for [C₂₃H₂₃N₂NaO₅S, M+Na⁺]: 461.1142, found: 461.1148. [α]D²⁰ = -40 (c = 0.1, EtOAc).

**HPLC analysis:** IA column, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL·min⁻¹, λ = 254 nm, tᵣ = 27.0 min (minor), 40.3 min (major).

**Supplementary Figure 25. HPLC Spectra of compound 4g (Method A)**
(R)-3-((4-Fluorophenyl)sulfonyl)-2-methyl-N-phenyl-2-(p-tolyl)propanamide (4h)

Method A: 65% yield, 95% ee.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (dd, $J = 8.7, 5.1$ Hz, 2H), 7.31 – 7.23 (m, 4H), 7.15 (d, $J = 8.2$ Hz, 2H), 7.09 – 6.98 (m, 5H), 6.92 (s, 1H), 4.12 (d, $J = 15.0$ Hz, 1H), 3.87 (d, $J = 15.0$ Hz, 1H), 2.31 (s, 3H), 2.10 (s, 3H). $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.9, 165.4 (d, $J = 255.6$ Hz), 138.2, 137.3, 137.0 (d, $J = 3.1$ Hz), 135.9, 130.4 (d, $J = 9.6$ Hz), 129.7, 129.0, 127.0, 124.8, 120.2, 116.1 (d, $J = 22.7$ Hz), 64.3, 50.0, 22.6, 21.0. HRMS (ESI) m/z Calcd for [C$_{23}$H$_{22}$FNNaO$_3$S, M+Na]$^+$: 434.1197, found: 434.1201. $[\alpha]_D^{20} = -38$ (c= 0.12, EtOAc).

HPLC analysis: IA column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R$ = 15.4 min (minor), 24.6 min (major).

Supplementary Figure 26. HPLC Spectra of compound 4h (Method A)
(R)-3-((4-Chlorophenyl)sulfonyl)-2-methyl-N-phenyl-2-(p-tolyl)propanamide (4i)

Method A: 63% yield, 95% ee; Method B: 60% yield, 96% ee.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 8.6$ Hz, 2H), 7.33 – 7.24 (m, 6H), 7.13 (d, $J = 8.2$ Hz, 2H), 7.10 – 7.06 (m, 1H), 7.03 (d, $J = 8.0$ Hz, 2H), 6.83 (s, 1H), 4.12 (d, $J = 15.1$ Hz, 1H), 3.89 (d, $J = 15.1$ Hz, 1H), 2.32 (s, 3H), 2.10 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.8, 139.6, 139.2, 138.4, 137.2, 135.6, 129.7, 129.1, 129.0, 127.1, 124.8, 120.1, 64.1, 49.9, 22.6, 21.0. HRMS (ESI) m/z Calcd for [C$_{23}$H$_{22}$ClNNaO$_3$S, M+Na]$^+$: 450.0901 (452.0872), found: 450.0901 (452.0882), $[\alpha]_{D}^{20} = -30$ (c= 0.12, EtOAc).

HPLC analysis: AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R = 19.5$ min (major), 25.0 min (minor).

Supplementary Figure 27. HPLC Spectra of compound 4i (Method A)
Supplementary Figure 28. HPLC Spectra of compound 4i (Method B)
(R)-3-((3-Bromophenyl)sulfonyl)-2-methyl-N-phenyl-2-(p-tolyl)propanamide (4j)

**Method A**: 61% yield, 94% ee.

**¹H NMR** (400 MHz, CDCl₃) δ 7.58 – 7.50 (m, 3H), 7.30 – 7.18 (m, 5H), 7.12 – 7.06 (m, 3H), 7.00 (d, J = 8.0 Hz, 2H), 6.82 (s, 1H), 4.09 (d, J = 15.2 Hz, 1H), 3.97 (d, J = 15.2 Hz, 1H), 2.82 (s, 3H), 2.09 (s, 3H).

**¹³C NMR** (100 MHz, CDCl₃) δ 173.0, 142.4, 138.4, 137.3, 135.8, 135.1, 130.6, 130.4, 129.7, 129.0, 127.2, 126.0, 124.8, 122.8, 120.1, 64.0, 49.9, 22.6, 21.2. **HRMS** (ESI) m/z Calcd for [C₂₃H₂₂BrNNaO₃S, M+Na]⁺: 494.0396 (496.0376), found: 494.0400 (496.0382). [α]D²⁰ = -73 (c= 0.11, EtOAc).

**HPLC analysis**: IA column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min⁻¹, λ = 254 nm, tᵣ = 11.1 min (minor), 16.4 min (major).

![HPLC Spectra of compound 4j (Method A)](image-url)
(R)-3-((3-(Benzyloxy)phenyl)sulfonyl)-2-methyl-N-phenyl-2-(p-tolyl)propanamide (4k)

Method A: 35% yield, 96% ee.

\[ \text{Method A: 35\% yield, 96\% ee.} \]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.37 (m, 4H), 7.33 – 7.30 (m, 3H), 7.26 – 7.20 (m, 4H), 7.12 – 7.06 (m, 5H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.93 (s, 1H), 4.98 (s, 2H), 4.11 (d, $J = 15.0$ Hz, 1H), 3.89 (d, $J = 15.0$ Hz, 1H), 2.26 (s, 3H), 2.07 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.0, 158.7, 142.0, 138.0, 137.4, 136.0, 135.9, 130.1, 129.6, 129.0, 128.8, 128.4, 127.6, 127.1, 124.7, 120.4, 120.2, 120.0, 112.8, 70.2, 64.0, 50.0, 22.7, 21.0. HRMS (ESI) m/z Calcd for [C$_{30}$H$_{29}$NNaO$_4$S, M+Na]$^+$: 522.1710, found: 522.1714. \([\alpha]_D^{20} = -40\) (c= 0.6, EtOAc).

HPLC analysis: IA column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R = 13.3$ min (minor), 21.9 min (major).

Supplementary Figure 30. HPLC Spectra of compound 4k (Method A)
(R)-3-((2,3-Dihydrobenzofuran-5-yl)sulfonyl)-2-methyl-N-phenyl-2-(p-tolyl)propanamide (4I)

Method A: 74% yield, 96% ee; Method B: 61% yield, 95% ee.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (dd, $J = 8.4$, 1.8 Hz, 1H), 7.39 (s, 1H), 7.32 – 7.30 (m, 2H), 7.28 – 7.24 (m, 2H), 7.19 (d, $J = 8.2$ Hz, 2H), 7.09 – 7.06 (m, 3H), 6.95 (s, 1H), 6.70 (d, $J = 8.4$ Hz, 1H), 4.62 (t, $J = 8.8$ Hz, 2H), 4.14 (d, $J = 14.8$ Hz, 1H), 3.80 (d, $J = 14.8$ Hz, 1H), 3.12 (t, $J = 8.7$ Hz, 2H), 2.32 (s, 3H), 2.09 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.9, 164.2, 137.8, 137.4, 136.5, 132.6, 129.6, 129.3, 128.9, 128.1, 127.0, 124.9, 124.6, 120.1, 109.4, 72.4, 64.2, 50.0, 28.8, 22.7, 21.0.

HRMS (ESI) m/z Calcd for [C$_{25}$H$_{25}$NNaO$_4$S, M+Na$^+$]: 458.1397, found: 458.1397.

[$\alpha$]$_D^{20}$ = -24 (c= 0.6, EtOAc).

HPLC analysis: AD-H column, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL·min$^{-1}$, λ = 254 nm, t$_R$ = 14.0 min (minor), 22.2 min (major).

Supplementary Figure 3i. HPLC Spectra of compound 4I (Method A)
Supplementary Figure 32. HPLC Spectra of compound 4l (Method B)
(R)-2-Methyl-3-((4-methyl-2-oxo-2H-chromen-7-yl)sulfonyl)-N-phenyl-2-(p-tolyl) Propanamide (4m)

**Method A**: 51% yield, 98% ee.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 – 7.55 (m, 2H), 7.29 – 7.22 (m, 5H), 7.12 (d, $J$ = 8.2 Hz, 2H), 7.09 – 7.05 (m, 1H), 6.96 (d, $J$ = 8.0 Hz, 2H), 6.88 (s, 1H), 6.38 (d, $J$ = 1.0 Hz, 1H), 4.14 (d, $J$ = 15.2 Hz, 1H), 3.99 (d, $J$ = 15.2 Hz, 1H), 2.45 (d, $J$ = 0.8 Hz, 3H), 2.21 (s, 3H), 2.11 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.7, 159.4, 152.7, 151.1, 143.3, 138.4, 137.2, 135.5, 129.6, 128.9, 127.1, 125.4, 124.8, 123.2, 122.7, 120.1, 117.6, 116.8, 64.2, 49.9, 22.6, 20.9, 18.8. HRMS (ESI) m/z Calcd for [C$_{27}$H$_{25}$NNaO$_5$S, M+Na]$^+$: 498.1346, found: 498.1346. $[^{\alpha}]D^{20}$ = -118 (c= 0.1, EtOAc).

**HPLC analysis**: AD-H column, $n$-hexane/i-PrOH = 60/40, flow rate = 1.0 mL·min$^{-1}$, $\lambda$ = 254 nm, $t_R$ = 28.4 min (major), 42.5 min (minor).

**Supplementary Figure 33.** HPLC Spectra of compound 4m (Method A)
(R)-2-Methyl-3-(naphthalen-1-ylsulfonyl)-N-phenyl-2-(p-tolyl)propanamide (4n)

**Method A:** 59% yield, 86% ee.

**¹H NMR** (400 MHz, CDCl₃) δ 8.60 (d, J = 7.7 Hz, 1H), 7.95 – 7.78 (m, 3H), 7.66 – 7.57 (m, 2H), 7.28 – 7.24 (m, 5H), 7.04 – 6.97 (m, 3H), 6.81 – 6.80 (m, 3H), 4.28 (d, J = 14.8 Hz, 1H), 4.17 (d, J = 14.9 Hz, 1H), 2.22 (s, 3H), 2.13 (s, 3H).

**¹³C NMR** (100 MHz, CDCl₃) δ 173.2, 137.9, 137.3, 135.5, 135.4, 134.4, 133.9, 130.0, 129.3, 129.1, 128.9, 128.7, 128.3, 126.9, 126.8, 124.6, 124.2, 124.1, 120.0, 63.2, 50.1, 22.8, 21.0.

**HRMS** (ESI) m/z Calcd for [C₂₇H₂₅NNaO₃S, M+Na]⁺: 466.1447, found: 466.1450. [α]D₂₀ = -40 (c= 0.1, EtOAc).

**HPLC analysis:** IA column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min⁻¹, λ = 254 nm, tᵣ = 11.3 min (minor), 16.5 min (major).

Supplementary Figure 34. HPLC Spectra of compound 4n (Method A)
(R)-2-Methyl-3-((4-(methylthio)phenyl)sulfonyl)-N,2-di-p-tolylpropanamide (4o)

**Method A:** 70% yield, 93% ee.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 – 7.43 (m, 2H), 7.18 – 7.08 (m, 10H), 6.86 (s, 1H), 4.11 (d, $J = 14.9$ Hz, 1H), 3.85 (d, $J = 15.0$ Hz, 1H), 2.48 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H), 2.07 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.8, 146.4, 138.0, 136.5, 136.1, 134.8, 134.4, 129.6, 129.4, 127.8, 127.0, 125.0, 120.2, 64.1, 49.9, 22.6, 21.1, 20.9, 14.8. HRMS (ESI) m/z Caled for [C$_{25}$H$_{27}$NNaO$_3$S$_2$, M+Na]$^+$: 476.1325, found: 476.1329. $\alpha_D^{20} = -30$ (c= 0.12, EtOAc).

HPLC analysis: AD-H column, $n$-hexane/i-PrOH = 60/40, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R$ = 30.9 min (minor), 61.0 min (major).

Supplementary Figure 35. HPLC Spectra of compound 4o (Method A)
(R)-3-((2-Chlorophenyl)sulfonyl)-2-methyl-N,2-di-p-tolylpropanamide (4p)

**Method A**: 63% yield, 94% ee.

**1H NMR** (400 MHz, CDCl₃) δ 7.42 (dd, J = 7.9, 1.4 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.09 – 7.04 (m, 5H), 6.97 (d, J = 8.3 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H), 6.67 (s, 1H), 4.41 (d, J = 15.5 Hz, 1H), 4.07 (d, J = 15.5 Hz, 1H), 2.19 (s, 3H), 2.14 (s, 3H), 2.00 (s, 3H).  

**13C NMR** (100 MHz, CDCl₃) δ 173.2, 138.2, 137.9, 135.3, 134.7, 134.4, 133.6, 132.2, 131.4, 131.0, 129.5, 129.4, 127.2, 127.0, 120.1, 61.9, 49.9, 23.1, 21.0, 20.9.  

**HRMS (ESI) m/z** Calcd for [C₂₄H₂₅ClNO₃S, M+H]⁺: 442.1238 (444.1209), found: 442.1249 (444.1238).  
\[^{[\alpha]}_D^{20}\] = -33 (c = 0.1, EtOAc).  

**HPLC analysis**: IA column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min⁻¹, λ = 254 nm, tᵣ = 17.3 min (minor), 25.7 min (major).

Supplementary Figure 36. HPLC Spectra of compound 4p (Method A)
(R)-2-Methyl-N,2-di-p-tolyl-3-(m-tolylsulfonyl)propanamide (4q)

Method A: 57% yield, 92% ee.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, $J = 7.5$ Hz, 1H), 7.26 (s, 1H), 7.22 – 7.15 (m, 2H), 7.12 – 7.08 (m, 4H), 6.99 – 6.93 (m, 4H), 6.77 (s, 1H), 4.03 (d, $J = 14.9$ Hz, 1H), 3.80 (d, $J = 14.9$ Hz, 1H), 2.22 (s, 6H), 2.19 (s, 3H), 2.02 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.0, 140.8, 139.0, 137.9, 136.0, 134.8, 134.4, 133.7, 129.5, 129.4, 128.8, 128.0, 127.1, 124.6, 120.2, 63.9, 49.9, 22.7, 21.2, 21.1, 20.9. HRMS (ESI) m/z Calcd for [C$_{25}$H$_{27}$NNaO$_3$S, M+Na]$^+$: 444.1604, found: 444.1612. [α]$_D^{25}$ = -52 (c= 0.16, EtOAc).

HPLC analysis: AD-H column, n-hexane/i-PrOH = 50/50, flow rate = 1.0 mL·min$^{-1}$, $\lambda$ = 254 nm, t$_R$ = 7.5 min (minor), 13.4 min (major).

Supplementary Figure 37. HPLC Spectra of compound 4q (Method A)
(R)-N-(4-Methoxyphenyl)-2-methyl-2-(p-tolyl)-3-tosylpropanamide (4r)

Method A: 59% yield, 98% ee; Method B: 57% yield, 91% ee.

^1^H NMR (400 MHz, CDCl3) δ 7.48 (d, J = 8.1 Hz, 2H), 7.23 – 7.10 (m, 6H), 7.01 (d, J = 8.1 Hz, 2H), 6.95 (s, 1H), 6.77 (d, J = 8.9 Hz, 2H), 4.11 (d, J = 14.8 Hz, 1H), 3.81 (d, J = 14.8 Hz, 1H), 3.74 (s, 3H), 2.37 (s, 3H), 2.29 (s, 3H), 2.07 (s, 3H). ^1^C NMR (100 MHz, CDCl3) δ 172.8, 156.7, 143.9, 138.1, 137.8, 136.5, 130.4, 129.5, 129.5, 127.6, 126.9, 122.3, 114.0, 64.1, 55.5, 49.8, 22.6, 21.6, 21.0. HRMS (ESI) m/z Calcd for [C25H27NNaO4S, M+Na]^+: 460.1553, found: 460.1555. [α]_D^{20} = -34 (c = 1.0, EtOAc).

HPLC analysis: OD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min⁻¹, λ = 254 nm, t_R = 32.6 min (major), 40.3 min (minor).

Supplementary Figure 38. HPLC Spectra of compound 4r (Method A)
Supplementary Figure 39. HPLC Spectra of compound 4r (Method B)
(R)-N-(4-Fluorophenyl)-2-methyl-2-(p-tolyl)-3-tosylpropanamide (4s)

**Method A:** 50% yield, 95% ee; **Method B:** 51% yield, 97% ee.

**H NMR (400 MHz, CDCl3)** δ 7.52 (d, J = 8.3 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.19 – 7.16 (m, 4H), 7.05 (d, J = 8.1 Hz, 2H), 6.99 (s, 1H), 6.98 – 6.91 (m, 2H), 4.12 (d, J = 14.8 Hz, 1H), 3.78 (d, J = 14.8 Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H), 2.09 (s, 3H).

**13C NMR (100 MHz, CDCl3)** δ 172.9, 159.6 (d, J = 243.9 Hz), 144.1, 138.1, 138.0, 136.3, 133.33 (d, J = 2.8 Hz), 129.6, 129.6, 127.6, 126.8, 122.23 (d, J = 8.0 Hz), 115.6 (d, J = 22.5 Hz), 64.1, 49.9, 22.6, 21.6, 21.0. **HRMS (ESI) m/z** Calcd for [C24H24FNNaO3S, M+Na]+: 448.1353, found: 448.1358. [α]D20 = -4 (c= 0.11, EtOAc).

**HPLC analysis:** AS-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL·min⁻¹, λ = 254 nm, tR = 29.2 min (minor), 42.8 min (major).

**Supplementary Figure 40. HPLC Spectra of compound 4s (Method A)**
Supplementary Figure 41. HPLC Spectra of compound 4s (Method B)
(R)-N-Benzyl-2-methyl-2-(p-tolyl)-3-tosylpropanamide (4t)

**Method A:** 45% yield, 92% ee.

**H NMR** (400 MHz, CDCl₃) δ 7.39 (d, J = 8.5 Hz, 2H), 7.21 – 7.15 (m, 3H), 7.06 – 7.00 (m, 6H), 6.91 (d, J = 8.0 Hz, 2H), 5.53 (t, J = 5.9 Hz, 1H), 4.33 (dd, J = 15.0, 5.9 Hz, 1H), 4.22 (dd, J = 15.0, 5.9 Hz, 1H), 4.05 (d, J = 14.8 Hz, 1H), 3.71 (d, J = 14.8 Hz, 1H), 2.41 (s, 3H), 2.21 (s, 3H), 1.93 (s, 3H).

**C NMR** (100 MHz, CDCl₃) δ 174.7, 146.3, 138.0, 137.7, 136.8, 136.6, 129.4, 128.6, 127.8, 127.4, 126.8, 125.0, 64.4, 49.1, 43.8, 22.5, 21.0, 14.8.

**HRMS (ESI) m/z** Calcd for [C₂₅H₂₇NNaO₃S₂, M+Na]⁺: 476.1325, found: 476.1321. [α]D²⁰ = 6 (c=0.1, EtOAc).

**HPLC analysis:** AD-H column, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL·min⁻¹, λ = 254 nm, tR = 16.1 min (minor), 22.6 min (major).

Supplementary Figure 42. HPLC Spectra of compound 4t (Method A)
(R)-N-benzyl-2-(p-tolyl)-3-tosylpropanamide (4u)

Method B: 46% yield, 97% ee.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, $J = 8.5$ Hz, 2H), 7.35 – 7.25 (m, 6H), 7.15 – 7.08 (m, 5H), 6.87 (s, 1H), 4.07 (d, $J = 15.0$ Hz, 1H), 3.87 (d, $J = 15.0$ Hz, 1H), 2.52 (s, 3H), 2.10 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.0, 146.9, 138.1, 137.1, 136.1, 132.0, 129.0, 128.9, 127.7, 125.0, 125.0, 122.5, 120.2, 64.0, 49.9, 22.59, 14.8. HRMS (ESI) m/z Calcd for [C$_2$H$_2$NNaO$_3$S$_2$, M+Na]$^+$: 526.0122 (528.0102), found: 526.0158 (528.0135). [$\alpha$]$_D^{20}$ = -56 (c= 0.1, EtOAc).

HPLC analysis: IA column, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL·min$^{-1}$, $\lambda$ = 254 nm, $t_R$ = 22.0 min (minor), 34.5 min (major).

Supplementary Figure 43. HPLC Spectra of compound 4u (Method B)
(R)-3-((2,4-Dimethylphenyl)sulfonyl)-2-methyl-N-phenyl-2-(p-tolyl)propanamide (4aa)

**Method B:** 81% yield, 91% ee.

**1H NMR** (400 MHz, CDCl₃) δ 7.49 (d, J = 8.1 Hz, 1H), 7.31 – 7.23 (m, 4H), 7.19 (d, J = 8.0 Hz, 2H), 7.09 – 7.03 (m, 3H), 6.99 (s, 1H), 6.93 (d, J = 6.7 Hz, 2H), 4.12 (d, J = 14.8 Hz, 1H), 3.83 (d, J = 14.8 Hz, 1H), 2.59 (s, 3H), 2.31 (d, J = 8.1 Hz, 6H), 2.09 (s, 3H).

**13C NMR** (100 MHz, CDCl₃) δ 173.0, 144.0, 138.0, 137.4, 137.3, 136.3, 136.1, 133.1, 129.8, 129.6, 128.9, 126.9, 126.8, 124.6, 120.1, 62.9, 50.0, 22.8, 21.3, 21.1, 20.3. **HRMS (ESI) m/z** Caled for [C₂₅H₂₇NNaO₃S, M+Na]⁺: 444.1604, found: 444.1607. [α]D₂₀ = -35 (c= 0.1, EtOAc).

**HPLC analysis:** AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL·min⁻¹, λ = 254 nm, tᵣ = 22.3 min (minor), 27.5 min (major).

**Supplementary Figure 44.** HPLC Spectra of compound 4aa (Method B)
(R)-3-((3-Cyano-4-isobutoxyphenyl)sulfonyl)-2-methyl-N-phenyl-2-(p-tolyl)propanamide (4ab)

Method B: 58% yield, 93% ee.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.74 (dd, $J$ = 8.9, 2.2 Hz, 1H), 7.44 (d, $J$ = 2.2 Hz, 1H), 7.29 – 7.25 (m, 4H), 7.10 – 7.08 (m, 3H), 7.03 (d, $J$ = 8.1 Hz, 2H), 6.86 (d, $J$ = 8.9 Hz, 1H), 6.83 (s, 1H), 4.10 (s, 1H), 3.94 (d, $J$ = 15.3 Hz, 1H), 3.85 (d, $J$ = 6.4 Hz, 2H), 2.34 (s, 3H), 2.19 (d, $J$ = 13.2, 6.6 Hz, 1H), 2.09 (s, 3H), 1.12 – 1.07 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.9, 163.7, 138.6, 137.2, 135.2, 133.8, 133.9, 132.8, 129.8, 129.0, 127.2, 124.8, 120.1, 114.4, 112.0, 102.5, 76.0, 64.2, 49.8, 28.1, 22.5, 21.1, 19.0. HRMS (ESI) m/z Calcd for [C$_{28}$H$_{30}$N$_2$O$_4$S, M+Na]+$^+$: 513.1818, found: 513.1824. [α]$_D^{20} = -46$ (c= 0.1, EtOAc).

HPLC analysis: AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL·min$^{-1}$, λ = 254 nm, t$_R$ = 17.3 min (minor), 20.0 min (major).

[Graphs of HPLC analysis]

Supplementary Figure 45. HPLC Spectra of compound 4ab (Method B)
(R)-2-Methyl-3-((4-phenoxyphenyl)sulfonyl)-N-phenyl-2-(p-tolyl)propanamide (4ac)

**Method B:** 58% yield, 96% ee.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J = 8.8$ Hz, 2H), 7.43 – 7.39 (m, 2H), 7.32 (d, $J = 7.6$ Hz, 2H), 7.29 – 7.18 (m, 6H), 7.11 – 7.00 (m, 5H), 6.90 (s, 1H), 6.87 (d, $J = 8.8$ Hz, 2H), 4.14 (d, $J = 14.9$ Hz, 1H), 3.85 (d, $J = 14.9$ Hz, 1H), 2.32 (s, 3H), 2.11 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.9, 162.0, 155.0, 138.0, 137.4, 136.2, 134.6, 130.2, 129.8, 129.6, 128.9, 127.0, 125.0, 124.7, 120.3, 120.1, 117.3, 64.3, 50.0, 22.7, 21.1.

HRMS (ESI) m/z Calcd for [C$_{29}$H$_{27}$NNaO$_4$S, M+Na]$^+$: 508.1553, found: 508.1562. $[\alpha]_D^{20} = -12$ (c= 0.1, EtOAc).

**HPLC analysis:** IA column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R = 19.7$ min (minor), 25.0 min (major).

![HPLC Spectra of compound 4ac (Method B)](image-url)
**Method B**: 45% yield, 95% ee.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.26 (d, $J = 9.2$ Hz, 2H), 7.70 (d, $J = 8.8$ Hz, 2H), 7.33 (d, $J = 7.6$ Hz, 2H), 7.30 – 7.20 (m, 4H), 7.12 - 7.07 (m, 5H), 7.03 (d, $J = 8.7$ Hz, 2H), 6.93 (s, 1H), 4.17 (d, $J = 14.8$ Hz, 1H), 3.86 (d, $J = 14.8$ Hz, 1H), 2.33 (s, 3H), 2.14 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.7, 161.2, 159.2, 143.8, 138.2, 137.3, 137.2, 136.3, 130.3, 129.7, 129.0, 127.0, 126.2, 124.8, 120.1, 119.5, 118.7, 64.4, 50.1, 22.7, 21.1. **HRMS** (ESI) m/z Calcd for [C$_{29}$H$_{26}$N$_2$O$_6$S, M+Na]$^+$: 553.1404, found: 553.1414. $\left[\alpha\right]_{D}^{20} = -3$ (c= 0.1, EtOAc).

**HPLC analysis**: AD-H column, $n$-hexane/i-PrOH = 70/30, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R = 37.7$ min (minor), 56.2 min (major).

**Supplementary Figure 47.** HPLC data of 4ad (Method B)
(R)-3-((4-Acetamidophenyl)sulfonyl)-2-methyl-N-phenyl-2-(p-tolyl)propanamide (4ae)

**Method B:** 61% yield, 96% ee.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.15 (s, 1H), 7.45-7.40 (m, 4H), 7.23 (d, $J$ = 7.6 Hz, 2H), 7.19-7.15 (m, 2H), 7.09 (d, $J$ = 8.2 Hz, 2H), 7.02 – 6.98 (m, 3H), 6.96 (s, 1H), 4.05 (d, $J$ = 14.7 Hz, 1H), 3.73 (d, $J$ = 14.8 Hz, 1H), 2.21 (s, 3H), 2.00 (d, $J$ = 6.7 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.0, 168.1, 141.8, 137.2, 136.1, 135.2, 134.0, 128.7, 127.9, 127.6, 125.7, 123.9, 119.4, 118.0, 63.1, 48.9, 23.5, 21.7, 19.9. HRMS (ESI) m/z Calcd for [C$_{25}$H$_{26}$N$_2$NaO$_4$S, M+Na]$^+$: 473.1505, found: 473.1518. [α]$_{D}^{20}$ = 36 (c= 0.1, EtOAc).

**HPLC analysis:** AD-H column, $n$-hexane/i-PrOH = 70/30, flow rate = 1.0 mL·min$^{-1}$, $\lambda$ = 254 nm, $t_R = 7.8$ min (minor), 18.5 min (major).

![HPLC Spectra of compound 4ae (Method B)](image)

**Supplementary Figure 48.** HPLC Spectra of compound 4ae (Method B)
(R)-2-Methyl-3-((4-(2-oxopyrrolidin-1-yl)phenyl)sulfonyl)-N-phenyl-2-(p-tolyl)propanamide (4af)

**Method B:** 66% yield, 97% ee.

**1H NMR** (400 MHz, CDCl₃) δ 7.61 – 7.48 (m, 4H), 7.24 (d, J = 7.6 Hz, 2H), 7.21 – 7.14 (m, 2H), 7.11 (d, J = 8.2 Hz, 2H), 7.01 - 6.97 (m, 3H), 6.89 (s, 1H), 4.06 (d, J = 14.9 Hz, 1H), 3.85 – 3.68 (m, 3H), 2.55 (t, J = 8.1 Hz, 2H), 2.23 (s, 3H), 2.16 - 2.07 (m, 2H), 2.01 (s, 3H).

**13C NMR** (100 MHz, CDCl₃) δ 173.7, 171.8, 142.4, 137.0, 136.3, 135.2, 134.5, 128.6, 127.8, 127.5, 125.9, 123.6, 119.0, 117.7, 63.2, 49.0, 47.4, 31.8, 21.6, 20.0, 16.7. **HRMS (ESI)** m/z Calcd for [C₂₇H₂₈N₂NaO₄S, M+Na⁺]: 499.1662, found: 499.1670. [α]D²⁰ = -26 (c= 0.1, EtOAc).

**HPLC analysis:** AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL·min⁻¹, λ = 254 nm, tᵣ = 50.1 min (minor), 108.1 min (major).

![Supplementary Figure 49. HPLC Spectra of compound 4af (Method B)](image-url)
(R)-3-(Dibeno[b,d]furan-2-ylsulfonyl)-2-methyl-N-phenyl-2-(p-tolyl)propanamide (4ag)

**Method B:** 60% yield, 96% ee.

$^1$H NMR (400 MHz, CDCl₃) δ 7.97 (d, $J = 1.6$ Hz, 1H), 7.88 (d, $J = 7.7$ Hz, 1H), 7.75 (dd, $J = 8.7$, 1.7 Hz, 1H), 7.63-7.57 (m, 1H), 7.51 (d, $J = 8.7$ Hz, 2H), 7.42 (t, $J = 7.4$ Hz, 1H), 7.28 - 7.21 (m, 5H), 7.08 (d, $J = 8.2$ Hz, 2H), 6.83 (d, $J = 8.1$ Hz, 2H), 6.77 (s, 1H), 4.20 (d, $J = 15.2$ Hz, 1H), 4.04 (d, $J = 15.2$ Hz, 1H), 2.13 (s, 3H), 1.80 (s, 3H). $^{13}$C NMR (100 MHz, CDCl₃) δ 173.1, 158.2, 156.9, 138.2, 137.3, 135.4, 135.1, 129.3, 128.9, 128.5, 127.1, 123.7, 121.5, 121.2, 120.0, 64.2, 49.9, 22.7, 20.4. HRMS (ESI) m/z Calcd for [C₂₉H₂₅NNaO₄S, M+Na]$^+$: 506.1397, found: 506.1406. [$\alpha$]$_{D}^{20}$ = -71 (c= 0.1, EtOAc).

**HPLC analysis:** AD-H column, n-hexane/i-ProOH = 70/30, flow rate = 1.0 mL·min$^{-1}$, λ = 254 nm, t$_R$ = 13.7 min (minor), 19.8 min (major).

**Supplementary Figure 50. HPLC Spectra of compound 4ag (Method B)**
(R)-2-Methyl-N,2-di-p-tolyl-3-tosylpropanamide (4ah)

Method B: 79% yield, 91% ee.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J$ = 8.2 Hz, 2H), 7.19 - 7.13 (m, 6H), 7.06 - 7.02 (m, 4H), 6.89 (s, 1H), 4.11 (d, $J$ = 14.9 Hz, 1H), 3.82 (d, $J$ = 14.9 Hz, 1H), 2.37 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H), 2.08 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.8, 143.9, 138.1, 137.9, 136.3, 134.8, 134.3, 129.6, 129.5, 129.4, 127.6, 127.0, 120.2, 64.1, 49.9, 22.7, 21.6, 21.0, 20.9. HRMS (ESI) m/z Calcd for [C$_{25}$H$_{27}$NNaO$_3$S, M+Na$^+$]: 444.1604, found: 444.1606. [α]$_{D}^{20}$ = 11 (c= 0.1, EtOAc).

HPLC analysis: IA column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min$^{-1}$, $\lambda$ = 254 nm, $t_R$ = 17.2 min (minor), 22.1 min (major).

Supplementary Figure 51. HPLC Spectra of compound 4ah (Method B)
(R)-N-Benzyl-2-methyl-2-(p-tolyl)-3-tosylpropanamide (4ai)

Method B: 64% yield, 91% ee.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J = 8.3$ Hz, 2H), 7.29 – 7.21 (m, 3H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.14 – 7.05 (m, 4H), 6.99 (d, $J = 8.1$ Hz, 2H), 5.67 (t, $J = 5.6$ Hz, 1H), 4.41 (dd, $J = 15.0, 5.6$ Hz, 1H), 4.29 (dd, $J = 15.0, 5.6$ Hz, 1H), 4.12 (d, $J = 14.7$ Hz, 1H), 3.75 (d, $J = 14.7$ Hz, 1H), 2.38 (s, 3H), 2.28 (s, 3H), 2.01 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.6, 143.9, 138.3, 138.0, 137.6, 136.8, 129.5, 129.4, 128.6, 127.4, 126.8, 64.3, 49.1, 43.8, 22.5, 21.6, 21.0. HRMS (ESI) m/z Calcd for $[C_{25}H_{27}NNaO_3S, M+Na]^+$: 444.1604, found: 444.1602. $[\alpha]_D^{20} = -39$ (c = 0.1, EtOAc).

HPLC analysis: AS-H column, n-hexane/i-ProOH = 80/20, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R = 22.4$ min (minor), 28.9 min (major).

Supplementary Figure 52. HPLC Spectra of compound 4ai (Method B)
(R)-2-Methyl-3-(phenethylsulfonyl)-N-phenyl-2-(p-tolyl)propanamide (4aj)

**Method B:** 60% yield, 79% ee.

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.38 - 7.35 (m, 4H), 7.33 – 7.19 (m, 7H), 7.10 (t, $J = 7.3$ Hz, 1H), 7.03 (d, $J = 7.1$ Hz, 2H), 7.01 (s, 1H), 3.87 (d, $J = 15.0$ Hz, 1H), 3.62 (d, $J = 15.0$ Hz, 1H), 3.04 – 2.88 (m, 2H), 2.79 – 2.61 (m, 2H), 2.34 (s, 3H), 2.08 (s, 3H).

**13C NMR** (100 MHz, CDCl$_3$) $\delta$ 172.9, 138.6, 137.6, 137.3, 136.8, 130.0, 129.0, 128.8, 128.3, 127.1, 126.9, 124.8, 120.2, 61.5, 56.3, 50.0, 27.8, 22.8, 21.0.

**HRMS** (ESI) m/z Calcd for [C$_{25}$H$_{27}$NNaO$_3$S, M+Na]$^+$: 444.1604, found: 444.1601. $\alpha$$_{D}^{20}$ = 4 (c= 0.7, EtOAc).

**HPLC analysis:** IA column, $n$-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min$^{-1}$, $\lambda$ = 254 nm, $t_R$ = 14.4 min (minor), 17.8 min (major).

**Supplementary Figure 53.** HPLC Spectra of compound 4aj (Method B)
Method B: 75% yield, 81% ee.

\( ^1H \text{ NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.37 – 7.34 (m, 4H), 7.31 – 7.23 (m, 4H), 7.21 - 7.16 (m, 3H), 7.11 - 7.08 (m, 3H), 7.04 (s, 1H), 3.84 (d, \( J = 14.9 \text{ Hz} \), 1H), 3.59 (d, \( J = 14.9 \text{ Hz} \), 1H), 2.55 – 2.39 (m, 4H), 2.35 (s, 3H), 2.05 (s, 3H), 1.75 – 1.62 (m, 2H), 1.56 - 1.50 (m, 2H).

\( ^{13}C \text{ NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 173.0, 141.4, 138.5, 137.4, 136.8, 130.0, 129.0, 128.5, 128.4, 127.0, 126.1, 124.8, 120.3, 61.0, 55.0, 50.0, 35.3, 30.2, 22.7, 21.5, 21.1.  

HRMS (ESI) m/z Calcd for \([C_{27}H_{31}NNaO_3S, M+Na]^{+}\): 472.1917, found: 472.1925. \([\alpha]_D^{20} = -36 \text{ (c= 0.2, EtOAc)}\).

**HPLC analysis:** 1A column, \( n\)-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min\(^{-1}\), \( \lambda = 254 \text{ nm, } t_R = 16.7 \text{ min (major), 23.1 min (minor).} \)

Supplementary Figure 54. HPLC Spectra of compound 4ak (Method B)
(R)-2-Methyl-N-phenyl-3-[(2-(thiophen-2-yl)ethyl)sulfonyl]-2-(p-tolyl)propanamide (4al)

**Method B:** 47% yield, 74% ee.

**1H NMR** (400 MHz, CDCl$_3$) δ 7.37 - 7.35 (m, 4H), 7.31 – 7.21 (m, 4H), 7.16 – 7.07 (m, 2H), 7.00 (s, 1H), 6.89 (dd, $J = 5.0$, 3.5 Hz, 1H), 6.71 - 6.70 (m, 1H), 3.86 (d, $J = 15.0$ Hz, 1H), 3.63 (d, $J = 15.0$ Hz, 1H), 3.23 – 3.10 (m, 2H), 2.81 – 2.65 (m, 2H), 2.35 (s, 3H), 2.08 (s, 3H).

**13C NMR** (100 MHz, CDCl$_3$) δ 172.9, 139.7, 138.7, 137.3, 136.6, 130.1, 129.0, 127.0, 127.0, 125.5, 124.8, 124.3, 120.2, 61.6, 56.2, 50.0, 22.6, 22.4, 21.1. **HRMS** (ESI) m/z Calcd for [C$_{23}$H$_{25}$NNaO$_3$S$_2$, M+Na]$^+$: 450.1168, found: 450.1168. [$\alpha$]$_D^{20} = -20$ (c = 0.7, EtOAc).

**HPLC analysis:** IA column, $n$-hexane/$i$-PrOH = 90/10, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R$ = 14.7 min (minor), 18.5 min (major).

**Supplementary Figure 55.** HPLC Spectra of compound 4al (Method B)
**(R)-3-((3-Bromopropyl)sulfonyl)-2-methyl-N-phenyl-2-(p-tolyl)propanamide (4am)**

**Method B:** 62% yield, 79% ee.

**1H NMR** (400 MHz, CDCl₃) δ 7.37 – 7.35 (m, 4H), 7.32 – 7.20 (m, 4H), 7.11 (t, J = 7.3 Hz, 1H), 7.01 (s, 1H), 3.92 (d, J = 15.0 Hz, 1H), 3.63 (d, J = 15.0 Hz, 1H), 3.36 (t, J = 6.3 Hz, 2H), 2.77 – 2.56 (m, 2H), 2.37 (s, 3H), 2.30 – 2.15 (m, 2H), 2.07 (s, 3H). **13C NMR** (100 MHz, CDCl₃) δ 172.8, 138.7, 137.2, 136.6, 130.1, 129.0, 126.9, 124.9, 120.3, 61.9, 53.6, 50.0, 31.1, 24.8, 22.6, 21.1. **HRMS** (ESI) m/z Calcd for [C₂₀H₂₄BrNNaO₃S, M+Na]+: 460.0552 (462.0532), found: 460.0559 (462.0543). [α]D⁰ = -10 (c= 0.1, EtOAc).

**HPLC analysis:** IA column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min⁻¹, λ = 254 nm, tR = 18.8 min (major), 22.5 min (minor).

**Supplementary Figure 56. HPLC Spectra of compound 4am (Method B)**
Method B: 58% yield, 96% ee.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.47 (d, J = 8.2 \text{ Hz}, 2\text{H}), 7.34 – 7.25 (m, 6\text{H}), 7.19 – 7.08 (m, 5\text{H}), 6.89 (s, 1\text{H}), 4.07 (d, J = 15.0 \text{ Hz}, 1\text{H}), 3.84 (d, J = 15.0 \text{ Hz}, 1\text{H}), 2.41 (s, 3\text{H}), 2.10 (s, 3\text{H}). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 172.1, 144.4, 138.2, 137.7, 137.1, 132.0, 129.7, 129.0, 128.8, 127.5, 124.9, 122.6, 120.2, 63.8, 49.9, 22.5, 21.6.\) HRMS (ESI) m/z Calcd for [C\(_{23}\)H\(_{22}\)BrNNaO\(_3\)S, M+Na\(^+\): 494.0401 (496.0381), found: 494.0398 (494.0378). \([\alpha]_D^{20} = -32 \text{ (c= 0.1, EtOAc).}\)

HPLC analysis: 1A column, \(n\)-hexane/i-PrOH = 80/20, flow rate = 1.0 mL·min\(^{-1}\), \(\lambda = 254 \text{ nm, } t_R = 18.7 \text{ min (minor), 23.8 min (major).}\)

Supplementary Figure 57. HPLC Spectra of compound 4an (Method B)
(R)-N-benzyl-2-(p-tolyl)-3-tosylpropanamide (4ao)

Method B: 45% yield, 94% ee.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 (d, $J = 8.0$ Hz, 2H), 7.30 – 7.16 (m, 6H), 7.12 – 7.04 (m, 6H), 6.07 (t, $J = 4.8$ Hz, 1H), 4.35 – 4.22 (m, 3H), 4.09 – 4.06 (m, 1H), 3.37 (dd, $J = 14.1$, 5.1 Hz, 1H), 2.41 (s, 3H), 2.29 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.4, 144.6, 137.8, 137.7, 136.5, 134.4, 129.8, 129.7, 128.6, 128.0, 127.7, 127.5, 127.4, 58.9, 46.5, 43.9, 21.7, 21.1.

HRMS (ESI) m/z Caled for [C$_{24}$H$_{25}$NNaO$_3$S, M+Na$^+$]: 430.1453, found: 430.1448. [$\alpha$]$_D^{20}$ = -21 (c= 0.1, EtOAc).

HPLC analysis: OD-H column, $n$-hexane/i-PrOH = 90/10, flow rate = 1.0 mL·min$^{-1}$, $\lambda$ = 232 nm, $t_R =$ 20.6 min (major), 36.7 min (minor).

Supplementary Figure 58. HPLC data of 4ao (Method B)
(2R)-2-Methyl-3-((4-((5-methyl-2, 4-dioxo-5-(4-phenoxyphenyl)oxazolidin-3-yl)amino)phenyl) sulfonyl)-N-phenyl-2-(p-tolyl)propanamide (4ap)

Method B: 66% yield, 98% de.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 8.7$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.39-7.35 (m, 2H), 7.29 (d, $J = 7.8$ Hz, 2H), 7.27 - 7.20 (m, 2H), 7.19 - 7.13 (m, 3H), 7.08 - 7.00 (m, 7H), 6.99 (s, 1H), 6.91 (s, 1H), 6.49 (d, $J = 8.2$ Hz, 2H), 4.07 (d, $J = 14.8$ Hz, 1H), 3.77 (d, $J = 14.8$ Hz, 1H), 2.29 (s, 1.5H), 2.27 (s, 1.5H), 2.05 (s, 3H), 1.94 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.1, 171.6, 158.7, 156.1, 152.3, 148.5, 138.2, 137.2, 136.2, 136.1, 133.9, 130.0, 129.9, 129.7, 129.5, 129.0, 126.9, 126.1, 124.8, 124.2, 120.3, 119.7, 118.6, 112.6, 85.3, 64.1, 50.0, 25.5, 22.8, 21.0, 21.0. HRMS (ESI) m/z Calcd for [C$_{39}$H$_{35}$N$_3$O$_7$S, M+Na]$^+$: 712.2088, found: 712.2106 (462.0543). $[\alpha]D^{20} = 18$ (c= 0.1, EtOAc).

HPLC analysis: AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL·min$^{-1}$, $\lambda = 254$ nm, $t_R = 33.8$ min (minor), 56.7 min (major), 68.9 min (minor), 113.1 min (major).

Supplementary Figure 59. HPLC Spectra of compound 4ap (Method B)
(R)-3-(8R,9S,13S,14S)-3-Methoxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)sulfonyl)-2-methyl-N-phenyl-2-(p-toly)propanamide (4aq)

**Method B:** 70% yield, 94% de.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.45 (s, 1H), 7.30 (d, $J$ = 7.8 Hz, 2H), 7.31 – 7.29 (m, 2H), 7.19 (d, $J$ = 8.1 Hz, 2H), 7.09 – 7.02 (m, 2H), 6.99 (d, $J$ = 8.0 Hz, 2H), 6.53 (s, 1H), 4.26 (d, $J$ = 15.1 Hz, 1H), 4.19 (d, $J$ = 15.1 Hz, 1H), 3.87 (s, 3H), 2.93 – 2.80 (m, 2H), 2.54 – 2.47 (m, 1H), 2.27 (s, 4H), 2.20 – 1.95 (m, 9H), 1.63 (d, $J$ = 11.3 Hz, 1H), 1.54 – 1.46 (m, 2H), 1.43 (d, $J$ = 9.7 Hz, 2H), 0.94 (s, 3H). **$^{13}$C NMR** (100 MHz, CDCl$_3$) $\delta$ 173.2, 154.5, 144.6, 137.5, 137.5, 136.6, 131.8, 129.3, 128.9, 127.0, 126.9, 125.6, 124.5, 119.9, 112.2, 61.6, 56.1, 50.2, 50.0, 47.9, 43.6, 38.1, 35.8, 31.4, 29.9, 26.1, 25.5, 23.2, 21.6, 21.2, 13.9. **HRMS (ESI)** m/z Calcd for [C$_{36}$H$_{41}$NNaO$_5$S, M+Na]$^+$/m/z: 622.2598, found: 622.2614. [α]$_D^{20}$ = 64 (c= 0.1, EtOAc).

**HPLC analysis:** IA column, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL·min$^{-1}$, $\lambda$ = 254 nm, $t_R$ = 18.4 min (minor), 23.0 min (major).

**Supplementary Figure 60.** HPLC Spectra of compound 4aq (Method B)
2.6 Crystal data and structure refinement for 4p

The crystal structure of compound 4p has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2208406). The data is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

Supplementary Figure 61. Crystal data and structure refinement for 4p (CCDC 2208406)

Supplementary Table 3. Crystal data and structure refinement for 4p.

| Identification code | 4p                  |
|---------------------|---------------------|
| Empirical formula   | C₂₆H₂₄ClNO₃S        |
| Formula weight      | 441.95              |
| Temperature/K       | 273.15              |
| Crystal system      | orthorhombic        |
| Space group         | C222₁               |
| a/Å                 | 13.418(2)           |
| b/Å                 | 17.769(2)           |
| c/Å                 | 19.232(3)           |
| α/°                 | 90                  |
| β/°                 | 90                  |
| γ/°                 | 90                  |
| Volume/Å³           | 4585.4(11)          |
| Z                   | 8                   |
| ρ calc g/cm³        | 1.280               |
μ/mm⁻¹ 0.282
F(000) 1856.0
Crystal size/mm³ 0.26 × 0.25 × 0.24
Radiation MoKα (λ = 0.71073)
2Θ range for data collection° 5.694 to 54.798
Index ranges -15 ≤ h ≤ 16, -22 ≤ k ≤ 11, -24 ≤ l ≤ 24
Reflections collected 13754
Independent reflections 5103 [Rint = 0.0282, Rsigma = 0.0357]
Data/restraints/parameters 5103/520/372
Goodness-of-fit on F² 0.906
Final R indexes [I>=2σ (I)] R1 = 0.0366, wR2 = 0.0994
Final R indexes [all data] R1 = 0.0555, wR2 = 0.1181
Largest diff. peak/hole / e Å⁻³ 0.20/-0.19
Flack parameter 0.01(2)

**Supplementary Table 4.** Fractional atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å²×10³) for 4p. Ueq is defined as 1/3 of of the trace of the orthogonalised Uij tensor.

| Atom | x      | y      | z      | U(eq) |
|------|--------|--------|--------|-------|
| C7   | 5218(4)| 7052(4)| 5027(3)| 45.8(13) |
| S1   | 4948.8(16)| 7302.8(15)| 4146.6(11)| 43.6(5) |
| O1   | 5334(4)| 8041(2)| 3996(2)| 55.8(10) |
| O2   | 3887(2)| 7190(3)| 4071(2)| 62.9(12) |
| C1   | 6203(5)| 6962(3)| 3089(4)| 50.7(13) |
| C2   | 6666(5)| 6501(4)| 2606(3)| 64.6(15) |
| C3   | 6517(5)| 5741(4)| 2623(3)| 72.5(16) |
| C4   | 5877(6)| 5425(3)| 3103(3)| 70.4(15) |
| C5   | 5381(4)| 5881(3)| 3584(3)| 57.2(13) |
| Cl1  | 4569(4)| 5448.0(15)| 4154.9(12)| 96.8(10) |
| C6   | 5559(7)| 6655(3)| 3584(4)| 43.7(9) |
| C7'  | 5260(30)| 6890(30)| 5032(19)| 45.8(13) |
| S1'  | 4768(14)| 7093(12)| 4184(9)| 60(3) |
| O1'  | 4950(20)| 7908(15)| 4048(16)| 60(5) |
| O2'  | 3798(16)| 6830(20)| 4166(14)| 62(5) |
| C1'  | 6040(40)| 7070(20)| 3120(30)| 53(3) |
| C2'  | 6580(30)| 6760(20)| 2590(20)| 59(3) |
| C3'  | 6720(30)| 6020(20)| 2540(20)| 64(4) |
| C4'  | 6320(30)| 5514(18)| 3019(18)| 62(3) |
| C5'  | 5690(30)| 5815(15)| 3539(19)| 58(3) |
| Cl1' | 5080(20)| 5287(12)| 4163(10)| 106(4) |
| C6'  | 5520(50)| 6600(16)| 3570(30)| 52(3) |
Supplementary Table 5. Anisotropic displacement parameters (Å$^2\times10^3$) for 4p. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*^2U_{11}+2hka^*b^*U_{12}+\ldots].$

| Atom | $U_{11}$  | $U_{22}$  | $U_{33}$  | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|------|-----------|-----------|-----------|---------|---------|---------|
| C7   | 33.8(16)  | 65(3)     | 38.7(15)  | 0.3(17) | -1.4(12) | 7.2(18) |
| S1   | 34.9(7)   | 56.1(10)  | 40.0(6)   | 1.4(6)  | -5.1(5)  | 9.9(6)  |
| O1   | 62(3)     | 49.5(17)  | 55.5(19)  | 1.8(14) | -4.3(19) | 10.8(15)|
| O2   | 34.2(16)  | 97(3)     | 58(2)     | 8(2)    | -9.8(13) | 14.3(17)|
| C1   | 50(3)     | 63(3)     | 39(2)     | -3(2)   | -4(2)    | 7(2)    |
| C2   | 59(3)     | 90(4)     | 45(2)     | -17(3)  | -4.8(19) | 16(3)   |
| C3   | 71(3)     | 87(4)     | 60(3)     | -33(3)  | -15(2)   | 21(3)   |
| C4   | 76(4)     | 62(3)     | 73(3)     | -24(2)  | -29(3)   | 10(2)   |
| C5   | 60(3)     | 56(2)     | 56(2)     | -3.0(18)| -23(2)   | -1.3(19)|
| Cl1  | 127(2)    | 77.8(12)  | 85.9(10)  | 5.6(8)  | -10.0(14)| -47.6(14)|
| C6   | 42.6(19)  | 51.8(19)  | 36.7(17)  | -2.1(16)| -14.4(16) | 7.0(17) |
| C7'  | 33.8(16)  | 65(3)     | 38.7(15)  | 0.3(17) | -1.4(12) | 7.2(18) |
| S1'  | 54(5)     | 75(5)     | 50(4)     | 4(4)    | -5(3)    | 18(4)   |
| O1'  | 65(11)    | 64(8)     | 51(9)     | 9(6)    | -5(9)    | 18(7)   |
| O2'  | 51(7)     | 93(12)    | 42(9)     | 8(9)    | -7(6)    | 10(7)   |
| C1'  | 54(6)     | 63(6)     | 42(6)     | -8(5)   | -10(5)   | 11(5)   |
| C2'  | 59(6)     | 69(6)     | 49(6)     | -14(5)  | -9(5)    | 9(6)    |
| C3'  | 66(6) | 68(6) | 56(6) | -17(6) | -14(6) | 9(6) |
| C4'  | 64(7) | 62(6) | 60(6) | -13(5) | -20(6) | 8(6) |
| C5'  | 59(6) | 60(5) | 56(6) | -7(5)  | -21(5) | 5(5) |
| C11' | 104(9)| 108(8)| 106(7)| 19(6)  | -26(7) | -37(8) |
| C6'  | 50(5) | 61(5) | 45(5) | -4(4)  | -11(5) | 8(4) |
| O3   | 40.2(13) | 128(2) | 50.6(14) | 22.9(15) | -5.2(11) | -22.4(14) |
| N1   | 34.5(14) | 71.8(19) | 36.3(13) | 7.0(12) | 1.6(11) | -9.6(13) |
| C8   | 32.0(14) | 54.0(18) | 38.3(15) | -0.4(13) | -0.9(11) | 5.0(13) |
| C9   | 57(2)  | 53.1(19) | 55(2)  | -3.2(16) | 4.6(16) | 10.2(16) |
| C10  | 29.6(13) | 48.2(16) | 32.1(13) | 0.7(12)  | 4.6(16) | 10.2(16) |
| C11  | 46.7(18) | 49.6(19) | 51.2(18) | 4.9(14)  | 4.9(15) | -0.4(15) |
| C12  | 57(2)  | 52(2)  | 64(2)  | -8.7(17) | 5.5(18) | 4.6(17) |
| C13  | 39.2(17) | 68(2)  | 45.6(17) | -11.7(15) | -0.7(13) | 0.3(16) |
| C14  | 68(3)  | 102(3) | 79(3)  | -31(3)  | 18(2)  | 2(2) |
| C15  | 42.5(17) | 72(2)  | 39.3(17) | 4.4(14)  | 4.1(13) | -6.8(15) |
| C16  | 42.8(16) | 51.9(18) | 40.8(15) | 2.9(14)  | 0.0(13) | -2.6(14) |
| C17  | 37.2(15) | 57.7(19) | 34.2(15) | -0.9(13) | 1.3(11) | -3.7(14) |
| C18  | 39.4(16) | 48.0(18) | 32.5(14) | -3.1(12) | -2.8(12) | -7.2(12) |
| C19  | 37.6(15) | 55.1(18) | 40.2(16) | -4.5(14) | 1.8(13) | -1.1(13) |
| C20  | 54(2)  | 56(2)  | 36.5(15) | -2.1(13) | 4.6(14) | -6.8(15) |
| C21  | 60(2)  | 45.6(17) | 40.4(16) | -1.9(13) | -7.0(15) | -7.5(15) |
| C22  | 90(3)  | 72(3)  | 52(2)  | 11.9(18) | -15(2) | -4(2) |
| C23  | 43.6(19) | 62(2)  | 55(2)  | 0.4(16)  | -7.2(15) | 2.6(16) |
| C24  | 39.1(17) | 64(2)  | 42.6(17) | -2.5(15) | 2.5(13) | -2.4(15) |

**Supplementary Table 6. Bond lengths for 4p.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| C7   | S1   | 1.788(4) | C5'  | C11' | 1.72(2)  |
| C7   | C8   | 1.546(5) | C5'  | C6'  | 1.42(2)  |
| S1   | O1   | 1.439(4) | O3   | C17  | 1.221(4) |
| S1   | O2   | 1.446(3) | N1   | C17  | 1.349(4) |
| S1   | C6   | 1.779(4) | N1   | C18  | 1.424(4) |
| C1   | C2   | 1.386(7) | C8   | C9   | 1.544(5) |
| C1   | C6   | 1.397(6) | C8   | C10  | 1.534(4) |
| C2   | C3   | 1.364(8) | C8   | C17  | 1.550(4) |
| C3   | C4   | 1.381(9) | C10  | C11  | 1.398(5) |
| C4   | C5   | 1.398(7) | C10  | C16  | 1.382(4) |
| C5   | C11  | 1.727(5) | C11  | C12  | 1.373(5) |
| C5   | C6   | 1.396(6) | C12  | C13  | 1.382(5) |
| C7   | S1'  | 1.80(2)  | C13  | C14  | 1.515(5) |

S67
| Atom | Atom | Atom | Angle/° | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|---------|
| C8   | C7   | S1   | 119.4(4) | C17  | N1   | C18     | 126.5(3) |
| O1   | S1   | C7   | 110.2(2) | C7   | C8   | C9      | 109.8(3) |
| O1   | S1   | O2   | 117.4(2) | C7   | C8   | C17     | 105.0(3) |
| O1   | S1   | C6   | 107.6(2) | C9   | C8   | C7'     | 120(2)   |
| O2   | S1   | C7   | 105.1(2) | C9   | C8   | C17     | 106.1(3) |
| O2   | S1   | C6   | 107.6(3) | C10  | C8   | C7      | 111.2(3) |
| C6   | S1   | C7   | 108.8(3) | C10  | C8   | C7'     | 105(2)   |
| C2   | C1   | C6   | 120.2(5) | C10  | C8   | C9      | 113.4(3) |
| C3   | C2   | C1   | 120.2(5) | C10  | C8   | C17     | 110.8(2) |
| C2   | C3   | C4   | 120.7(5) | C17  | C8   | C7'     | 99.9(12) |
| C3   | C4   | C5   | 120.1(5) | C11  | C10  | C8      | 119.8(3) |
| C4   | C5   | C11  | 117.5(4) | C16  | C10  | C8      | 122.8(3) |
| C4   | C5   | C6   | 119.3(5) | C16  | C10  | C11     | 117.3(3) |
| C6   | C5   | C11  | 123.1(4) | C12  | C11  | C10     | 121.0(3) |
| C1   | C6   | S1   | 116.5(4) | C11  | C12  | C13     | 122.2(4) |
| C1   | C6   | C5   | 119.4(4) | C12  | C13  | C14     | 121.7(4) |
| C5   | C6   | S1   | 124.0(4) | C15  | C13  | C12     | 117.1(3) |
| C8   | C7'  | S1'  | 125(2)   | C15  | C13  | C14     | 121.2(4) |
| O1'  | S1'  | C7'  | 106.9(19)| C13  | C15  | C16     | 121.4(3) |
| O1'  | S1'  | C6'  | 105.5(16)| C10  | C16  | C15     | 121.0(3) |
| O2'  | S1'  | C7'  | 107.6(16)| O3   | C17  | N1      | 122.9(3) |
| O2'  | S1'  | O1'  | 118.9(17)| O3   | C17  | C8      | 121.3(3) |
| O2'  | S1'  | C6'  | 110(2)   | N1   | C17  | C8      | 115.7(3) |
| C6'  | S1'  | C7'  | 107(2)   | C19  | C18  | N1      | 122.2(3) |
| C2'  | C1'  | C6'  | 120(3)   | C19  | C18  | C24     | 119.2(3) |
| C3'  | C2'  | C1'  | 121(3)   | C24  | C18  | N1      | 118.5(3) |
| C2'  | C3'  | C4'  | 123(3)   | C20  | C19  | C18     | 119.4(3) |
| C3'  | C4'  | C5'  | 117(2)   | C21  | C20  | C19     | 122.1(3) |
Supplementary Table 8. Torsion angles for 4p.

| A    | B    | C    | D    | Angle/° | A    | B    | C    | D    | Angle/° |
|------|------|------|------|---------|------|------|------|------|---------|
| C7   | S1   | C6   | C1   | -124.0(8) | C4'  | C5'  | C6'  | S1'  | -179(5) |
| C7   | S1   | C6   | C5   | 60.1(9)  | C4'  | C5'  | C6'  | C1'  | -5(10)  |
| C7   | C8   | C10  | C11  | -69.9(4) | C11' C5' | C6'  | S1'  | 1(9)   |
| C7   | C8   | C10  | C16  | 105.8(4) | C11' C5' | C6'  | C1'  | 175(6) |
| C7   | C8   | C17  | O3   | -9.5(5)  | C6'  | C1'  | C2'  | C3'  | -8(9)   |
| C7   | C8   | C17  | N1   | 172.6(4) | N1   | C18  | C19  | C20  | 179.2(3)|
| S1   | C7   | C8   | C9   | 73.3(5)  | N1   | C18  | C24  | C23  | -179.7(3)|
| S1   | C7   | C8   | C10  | -53.1(5) | C8   | C7   | S1   | O1   | -43.2(5)|
| S1   | C7   | C8   | C17  | -173.0(4)| C8   | C7   | S1   | O2   | -170.6(4)|
| O1   | S1   | C6   | C1   | -4.7(9)  | C8   | C7   | S1   | C6   | 74.5(6) |
| O1   | S1   | C6   | C5   | 179.4(7) | C8   | C7'  | S1'  | O1'  | -40(5)  |
| O2   | S1   | C6   | C1   | 122.7(8)| C8   | C7'  | S1'  | O2'  | -168(4)|
| O2   | S1   | C6   | C5   | -53.2(9) | C8   | C7'  | S1'  | C6'  | 73(5)   |
| C1   | C2   | C3   | C4   | 2.4(9)   | C8   | C10  | C11  | C12  | 174.9(3)|
| C2   | C1   | C6   | S1   | -176.5(6)| C8   | C10  | C16  | C15  | -174.2(3)|
| C2   | C1   | C6   | C5   | -0.4(13) | C9   | C8   | C10  | C11  | 165.8(3)|
| C2   | C3   | C4   | C5   | -0.7(8)  | C9   | C8   | C10  | C16  | -18.5(4)|
| C3   | C4   | C5   | C11  | 178.4(4)| C9   | C8   | C17  | O3   | 106.7(4)|
| C3   | C4   | C5   | C6   | -1.6(9)  | C9   | C8   | C17  | N1   | -71.2(4)|
| C4   | C5   | C6   | S1   | 177.8(6)| C10  | C8   | C17  | O3   | -129.7(3)|
| C4   | C5   | C6   | C1   | 2.1(12)  | C10  | C8   | C17  | N1   | 52.4(4) |
| C11  | C5   | C6   | S1   | -2.2(11)| C10  | C11  | C12  | C13  | -0.6(5) |
| C11  | C5   | C6   | C1   | -177.9(7)| C11  | C10  | C16  | C15  | 1.6(4)  |
| C6   | C1   | C2   | C3   | -1.9(11)| C11  | C12  | C13  | C14  | -177.1(4)|
| C7'  | S1'   | C6'  | C1'  | -115(6)  | C11  | C12  | C13  | C15  | 1.6(5)  |
| C7'  | S1'   | C6'  | C5'  | 58(7)    | C12  | C13  | C15  | C16  | -0.9(5) |
| C7'  | C8   | C10  | C11  | -60.6(15)| C13  | C15  | C16  | C10  | -0.7(5) |
| C7'  | C8   | C10  | C16  | 115.1(14)| C14  | C13  | C15  | C16  | 177.8(3)|
| C7'  | C8   | C17  | O3   | -19(2)   | C16  | C10  | C11  | C12  | -1.0(5) |
| C7'  | C8   | C17  | N1   | 163(2)   | C17  | N1   | C18  | C19  | -33.3(5)|
| S1'  | C7'  | C8   | C9   | 65(5)    | C17  | N1   | C18  | C24  | 148.0(3)|
Supplementary Table 9. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for 4p.

| Atom | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| H7A  | 4733  | 7303  | 5320  | 55    |
| H7B  | 5103  | 6515  | 5074  | 55    |
| H1   | 6322  | 7478  | 3084  | 61    |
| H2   | 7079  | 6710  | 2269  | 78    |
| H3   | 6850  | 5434  | 2308  | 87    |
| H4   | 5776  | 4907  | 3107  | 84    |
| H7'A | 4749  | 7031  | 5361  | 55    |
| H7'B | 5327  | 6349  | 5058  | 55    |
| H1'  | 6017  | 7587  | 3179  | 64    |
| H2'  | 6864  | 7079  | 2253  | 71    |
| H3'  | 7101  | 5827  | 2176  | 76    |
| H4'  | 6461  | 5002  | 2999  | 75    |
| H1A  | 7610(30) | 6970(20) | 6190(20) | 57 |
| H9A  | 7037  | 8180  | 5616  | 82    |
| H9B  | 5904  | 8228  | 5810  | 82    |
| H9C  | 6243  | 8343  | 5037  | 82    |
| H11  | 6840  | 5802  | 5108  | 59    |
| H12  | 7973  | 5287  | 4363  | 70    |
| H14A | 9588  | 5522  | 3646  | 124   |
| H14B | 9611  | 6279  | 3228  | 124   |
| H14C | 8816  | 5663  | 3049  | 124   |
| H15  | 8743  | 7324  | 3698  | 61    |
| H16  | 7621  | 7858  | 4464  | 54    |
| H19  | 6028  | 6653  | 7507  | 53    |
| Atom | Occupancy | Atom | Occupancy | Atom | Occupancy |
|------|-----------|------|-----------|------|-----------|
| C7   | 0.866(11) | H7A  | 0.866(11) | H7B  | 0.866(11) |
| S1   | 0.866(11) | O1   | 0.866(11) | O2   | 0.866(11) |
| C1   | 0.866(11) | H1   | 0.866(11) | C2   | 0.866(11) |
| H2   | 0.866(11) | C3   | 0.866(11) | H3   | 0.866(11) |
| C4   | 0.866(11) | H4   | 0.866(11) | C5   | 0.866(11) |
| Cl1  | 0.866(11) | C6   | 0.866(11) | C7'  | 0.134(11) |
| H7'A | 0.134(11) | H7'B | 0.134(11) | S1'  | 0.134(11) |
| O1'  | 0.134(11) | O2'  | 0.134(11) | C1'  | 0.134(11) |
| H1'  | 0.134(11) | C2'  | 0.134(11) | H2'  | 0.134(11) |
| C3'  | 0.134(11) | H3'  | 0.134(11) | C4'  | 0.134(11) |
| H4'  | 0.134(11) | C5'  | 0.134(11) | Cl1' | 0.134(11) |
| C6'  | 0.134(11) |      |           |      |           |
3 Supplementary Figures

3.1 NMR Spectra of substrates 1

Supplementary Figure 6. $^1$H NMR-spectrum of 1a, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 6. $^1$H NMR-spectrum of 1b, recorded at 400 MHz and 25 °C in CDCl$_3$.
Supplementary Figure 64. $^1$H NMR-spectrum of 1c, recorded at 400 MHz and 25 °C in CDCl₃

Supplementary Figure 65. $^1$H NMR-spectrum of 1d, recorded at 400 MHz and 25 °C in CDCl₃
Supplementary Figure 66. $^1$H NMR-spectrum of 1e, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 67. $^1$H NMR-spectrum of 1f, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 68. $^1$H NMR-spectrum of 1g, recorded at 400 MHz and 25 °C in CDCl$_3$
3.2 NMR Spectra of products 4

Supplementary Figure 69. $^1$H NMR-spectrum of 4a, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 70. $^{13}$C NMR-spectrum of 4a, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 71. $^1$H NMR-spectrum of 4b, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 72. $^{13}$C NMR-spectrum of 4b, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 73. $^1$H NMR-spectrum of 4c, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 74. $^{13}$C NMR-spectrum of 4c, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 75. $^1$H NMR-spectrum of 4d, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 76. $^{13}$C NMR-spectrum of 4d, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 77. $^1$H NMR-spectrum of 4e, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 78. $^{13}$C NMR-spectrum of 4e, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 79. $^1$H NMR-spectrum of 4f, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 80. $^{13}$C NMR-spectrum of 4f, recorded at 400 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 81. $^1$H NMR-spectrum of 4g, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 82. $^{13}$C NMR-spectrum of 4g, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 8. $^1$H NMR-spectrum of 4h, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 84. $^{13}$C NMR-spectrum of 4h, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 85. $^1$H NMR-spectrum of 4i, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 86. $^{13}$C NMR-spectrum of 4i, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 87. $^1$H NMR-spectrum of 4j, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 88. $^{13}$C NMR-spectrum of 4j, recorded at 400 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 89. $^1$H NMR-spectrum of 4k, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 90. $^{13}$C NMR-spectrum of 4k, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 91. $^1$H NMR-spectrum of 4l, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 92. $^{13}$C NMR-spectrum of 4l, recorded at 400 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 93. $^1$H NMR-spectrum of 4m, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 94. $^{13}$C NMR-spectrum of 4m, recorded at 400 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 95. $^1$H NMR-spectrum of 4n, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 96. $^{13}$C NMR-spectrum of 4n, recorded at 400 MHz and 25 °C in CDCl$_3$.
Supplementary Figure 97. $^1$H NMR-spectrum of 4o, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 98. $^{13}$C NMR-spectrum of 4o, recorded at 400 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 99. $^1$H NMR-spectrum of 4p, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 100. $^{13}$C NMR-spectrum of 4p, recorded at 400 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 10. $^1$H NMR-spectrum of 4q, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 10. $^{13}$C NMR-spectrum of 4q, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 103. $^1$H NMR-spectrum of 4r, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 104. $^{13}$C NMR-spectrum of 4r, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 105. $^1$H NMR-spectrum of 4s, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 106. $^{13}$C NMR-spectrum of 4s, recorded at 400 MHz and 25 °C in CDCl$_3$. 

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Supplementary Figure 107. $^1$H NMR-spectrum of 4t, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 108. $^{13}$C NMR-spectrum of 4t, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 109. $^1$H NMR-spectrum of 4u, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 110. $^{13}$C NMR-spectrum of 4u, recorded at 400 MHz and 25 °C in CDCl$_3$.
Supplementary Figure 111. $^1$H NMR-spectrum of 4aa, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 112. $^{13}$C NMR-spectrum of 4aa, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 113. $^1$H NMR-spectrum of 4ab, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 114. $^{13}$C NMR-spectrum of 4ab, recorded at 400 MHz and 25 °C in CDCl$_3$.
Supplementary Figure 115. $^1$H NMR-spectrum of 4ac, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 116. $^{13}$C NMR-spectrum of 4ac, recorded at 400 MHz and 25 °C in CDCl$_3$.
Supplementary Figure 117. $^1$H NMR-spectrum of 4ad, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 118. $^{13}$C NMR-spectrum of 4ad, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 119. $^1$H NMR-spectrum of 4ae, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 120. $^{13}$C NMR-spectrum of 4ae, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 121. $^1$H NMR-spectrum of 4af, recorded at 400 MHz and 25 °C in CDCl₃

Supplementary Figure 122. $^{13}$C NMR-spectrum of 4af, recorded at 400 MHz and 25 °C in CDCl₃
Supplementary Figure 123. $^1$H NMR-spectrum of 4ag, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 124. $^{13}$C NMR-spectrum of 4ag, recorded at 400 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 125. $^1$H NMR-spectrum of 4ah, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 126. $^{13}$C NMR-spectrum of 4ah, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 127. $^1$H NMR-spectrum of 4ai, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 128. $^{13}$C NMR-spectrum of 4ai, recorded at 400 MHz and 25 °C in CDCl$_3$. 

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Supplementary Figure 129. $^1$H NMR-spectrum of 4aj, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 130. $^{13}$C NMR-spectrum of 4aj, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 13. $^1$H NMR-spectrum of 4ak, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 13. $^{13}$C NMR-spectrum of 4ak, recorded at 400 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 133. $^1$H NMR-spectrum of 4al, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 134. $^{13}$C NMR-spectrum of 4al, recorded at 400 MHz and 25 °C in CDCl$_3$. 

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Supplementary Figure 135. $^1$H NMR-spectrum of 4am, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 136. $^{13}$C NMR-spectrum of 4am, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 137. $^1$H NMR-spectrum of 4an, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 138. $^{13}$C NMR-spectrum of 4an, recorded at 400 MHz and 25 °C in CDCl$_3$
**Supplementary Figure 139.** $^1$H NMR-spectrum of 4ao, recorded at 400 MHz and 25 °C in CDCl$_3$.

**Supplementary Figure 140.** $^{13}$C NMR-spectrum of 4ao, recorded at 400 MHz and 25 °C in CDCl$_3$. 
Supplementary Figure 14. $^1$H NMR-spectrum of 4ap, recorded at 400 MHz and 25 °C in CDCl$_3$

Supplementary Figure 142. $^{13}$C NMR-spectrum of 4ap, recorded at 400 MHz and 25 °C in CDCl$_3$
Supplementary Figure 143. $^1$H NMR-spectrum of 4aq, recorded at 400 MHz and 25 °C in CDCl$_3$.

Supplementary Figure 144. $^{13}$C NMR-spectrum of 4aq, recorded at 400 MHz and 25 °C in CDCl$_3$. 
4 Supplementary References

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