Rh-Catalyzed Diastereoselective Addition of Arylboronic Acids to α-Keto N-tert-Butanesulfinyl Aldimines: Synthesis of α-Amino Ketones

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1. General information

All experiments were conducted with a Schlenk tube under an argon atmosphere. Flash column chromatography was performed over silica gel (200-300 mesh). $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded at ambient temperature using Bruker Ascend TM 400 (400 MHz) spectrometer, Bruker AVANCE III 500M spectrometers or JNM-ECZ500R/S1 (500 MHz) spectrometer. $^1$H NMR chemical shifts (in ppm) were referenced to CDCl$_3$ (δ = 7.26 ppm), CD$_3$OD (δ = 3.31 ppm) as internal standards. $^{13}$C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$ (δ = 77.0 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd, = double doublet, dt = double triplet, td = triple doublet, m = multiplet. HRMS data were obtained on Thermo Scientific Orbitrap Elite Mass Spectrometer with an ESI source (Ion Trap). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was accomplished by UV light (254 nm). Enantioselectivities were recorded on Waters or Agilent HPLC. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

![Proposed catalytic cycle](image-url)

Figure S1. Proposed catalytic cycle.
2. General procedure 1 of synthesis of N-Sulfinyl imines 1

![Chemical structure](image)

**Compound A**

**Compound B**

**1**

**Step 1:** SeO₂ (9 mmol), 1,4-dioxane (9 mL) and water (1 mL) were added to a 100 mL three-necked bottle and fitted it with an condenser. The mixture was heated to 50-55 °C and stirred until the solid dissolved. Then followed by addition of Compound A (5 mmol) and the reaction was maintained at reflux temperature. After the reaction was complete, as monitored by TLC, the mixture was filtered through a pad of Celite. The filtrate was evaporated to afford a crude product B.¹

**Step 2:** To a solution of Compound B and (R)-tert-butanesulfinamide (1.1 equiv) in dry dichloromethane (15 mL) under argon was added anhydrous CuSO₄ (2 equiv) and the reaction mixture was stirred at room temperature for 24 h. The solid was filtered off, washed with ethyl acetate (3 × 10 mL) and the organic layer was evaporated. The resulting residue was purified by column chromatography silica gel, to yield pure compounds 1. Yields, physical and spectroscopic data for these compounds follow.²

**(R)-2-methyl-N-(2-oxo-2-phenylethylidene) propane-2-sulfinamide (1a)**

![Chemical structure](image)

Following the general procedure 1 on 5 mmol scale, yellow oil liquid, yield: 65% (750 mg), Rₜ = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v). Known compound.²

¹H NMR (500 MHz, Chloroform-d) δ 8.47 (s, 1H), 8.12 (dd, J = 8.5, 1.4 Hz, 2H), 7.69 – 7.58 (m, 1H), 7.50 (dd, J = 8.3, 7.4 Hz, 2H), 1.27 (s, 9H).

**(R)-2-methyl-N-(2-oxo-2-(p-tolyl)ethylidene)propane-2-sulfinamide (1b)**

![Chemical structure](image)

Following the general procedure 1 on 5 mmol scale, yellow oil liquid, yield: 60% (750 mg), Rₜ = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).
\(^1\)H NMR (500 MHz, Chloroform-d) δ 8.37 (s, 1H), 7.95 (d, \(J = 8.3\) Hz, 2H), 7.21 (d, \(J = 8.1\) Hz, 2H), 2.33 (s, 3H), 1.19 (s, 9H).

\(^{13}\)C NMR (126 MHz, Chloroform-d) δ 187.2, 160.8, 145.1, 131.6, 129.8, 129.1, 58.1, 22.2, 21.4.

HRMS (ESI) \(m/z\): \([M+H]^+\) Calcd. for C\(_{13}\)H\(_{18}\)NO\(_2\)S\(^+\) 252.1053; Found: 252.1050.

\([\alpha]\)\(^{25}\)D: -54.5 (c 0.5, Chloroform).

(R)-2-methyl-N-(2-oxo-2-(m-toly)ethylidene)propane-2-sulfinamide (1c)

\(\begin{align*}
\text{Me} & \quad \text{N} \quad \text{S} \quad \text{tBu} \\
\end{align*}\)

1c

Following the general procedure 1 on 5 mmol scale, yellow oil liquid, yield: 58% (739 mg), \(R_f = 0.7\) (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

\(^1\)H NMR (500 MHz, Chloroform-d) δ 8.50 (s, 1H), 7.94 – 7.90 (m, 2H), 7.48 – 7.43 (m, 1H), 7.39 (t, \(J = 7.9\) Hz, 1H), 2.42 (s, 3H), 1.28 (s, 9H).

\(^{13}\)C NMR (126 MHz, Chloroform-d) δ 188.2, 161.0, 138.6, 135.1, 134.5, 130.4, 128.6, 127.4, 58.6, 22.7, 21.3.

HRMS (ESI) \(m/z\): \([M+H]^+\) Calcd. for C\(_{13}\)H\(_{18}\)NO\(_2\)S\(^+\) 252.1053; Found: 252.1051.

\([\alpha]\)\(^{25}\)D: -234.5 (c 0.5, Chloroform).

(R)-N-(2-(4-ethylphenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide(1d)

\(\begin{align*}
\text{El} & \quad \text{N} \quad \text{S} \quad \text{tBu} \\
\end{align*}\)

1d

Following the general procedure 1 on 5 mmol scale, yellow oil liquid, yield: 60% (750 mg), \(R_f = 0.7\) (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

\(^1\)H NMR (500 MHz, Chloroform-d) δ 8.48 (s, 1H), 8.06 (d, \(J = 8.3\) Hz, 2H), 7.34 – 7.31 (d, \(J = 10\) Hz, 2H), 2.72 (q, \(J = 7.6\) Hz, 2H), 1.27 (s, 9H), 1.25 (d, \(J = 7.7\) Hz, 3H).

\(^{13}\)C NMR (126 MHz, Chloroform-d) δ 187.6, 161.1, 151.6, 132.2, 130.3, 128.3, 58.5, 29.0, 22.7, 15.0.

HRMS (ESI) \(m/z\): \([M+H]^+\) Calcd. for C\(_{14}\)H\(_{20}\)NO\(_2\)S\(^+\) 266.1209; Found: 266.1206.

\([\alpha]\)\(^{25}\)D: -21.2 (c 0.5, Chloroform).
(R)-N-(2-(3-methoxyphenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1e)

Following the general procedure 1 on 5 mmol scale, yellow oil liquid, yield: 60% (761 mg), R_f = 0.65 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 15: 1, v/v).

1H NMR (500 MHz, Chloroform-d) δ 8.29 (s, 1H), 7.58 – 7.53 (m, 1H), 7.47 (d, J = 2.1 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.05 – 6.99 (m, 1H), 3.68 (s, 3H), 1.13 (s, 9H).

13C NMR (126 MHz, Chloroform-d) δ 187.2, 160.6, 159.3, 135.1, 129.2, 122.4, 120.4, 113.4, 58.0, 54.9, 22.1.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{13}H_{18}NO_{3}S^+ 268.1002; Found: 268.1003.

[α]_{25}^{D} : -54.8 (c 0.5, Chloroform).

(R)-N-(2-(3,4-dimethoxyphenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1f)

Following the general procedure 1 on 5 mmol scale, yellow oil liquid, yield: 50% (742 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 10: 1, v/v).

1H NMR (500 MHz, Chloroform-d) δ 8.43 (s, 1H), 7.80 (dd, J = 8.4, 2.0 Hz, 1H), 7.61 (d, J = 2.0 Hz, 1H), 6.88 (d, J = 8.5 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 1.23 (s, 9H).

13C NMR (126 MHz, Chloroform-d) δ 186.1, 161.1, 154.4, 149.2, 127.5, 125.8, 111.0, 110.0, 58.3, 56.0, 55.8, 22.5.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{14}H_{20}NO_{4}S^+ 298.1108; Found: 298.1109.

[α]_{25}^{D} : -16.3 (c 0.5, Chloroform).

(R)-2-methyl-N-(2-(4-(methylthio)phenyl)-2-oxoethylidene)propane-2-sulfinamide (1g)

Following the general procedure 1 on 5 mmol scale, yellow oil liquid, yield: 48% (693 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 15: 1, v/v).
$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.43 (s, 1H), 8.05 (d, $J = 8.6$ Hz, 2H), 7.27 (d, $J = 8.7$ Hz, 2H), 2.51 (s, 3H), 1.26 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 186.8, 161.0, 148.2, 130.7, 130.4, 124.8, 58.5, 22.6, 14.5.

HRMS (ESI) $m/z$: [M+H]$^+$ Calcd. for C$_{13}$H$_{18}$NO$_2$S$_2$+ 284.0773; Found: 284.0771.

$[\alpha]_{25}^D$: 31.0 (c 0.5, Chloroform).

$(R)$-$N$-(2-(4-iodophenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1h)

Following the general procedure $I$ on 5 mmol scale, yellow oil liquid, yield: 70% (1272 mg), $R_f = 0.7$ (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.39 (s, 1H), 7.85 (d, $J = 5.0$ Hz, 4H), 1.26 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 187.2, 160.6, 138.0, 133.6, 131.3, 102.9, 58.7, 22.7.

HRMS (ESI) $m/z$: [M+H]$^+$ Calcd. for C$_{12}$H$_{15}$INO$_2$S$^+$ 363.9863; Found: 363.9861.

$[\alpha]_{25}^D$: -4.3 (c 0.5, Chloroform).

$(R)$-$N$-(2-(3-iodophenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1i)

Following the general procedure $I$ on 5 mmol scale, yellow oil liquid, yield: 63% (1143 mg), $R_f = 0.7$ (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.48 (t, $J = 1.8$ Hz, 1H), 8.38 (s, 1H), 8.12 – 8.05 (m, 1H), 7.97 – 7.90 (m, 1H), 7.24 (t, $J = 7.8$ Hz, 1H), 1.29 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 186.4, 160.4, 142.8, 138.9, 136.1, 130.3, 129.2, 94.2, 58.9, 22.7.

HRMS (ESI) $m/z$: [M+H]$^+$ Calcd. for C$_{12}$H$_{15}$INO$_2$S$^+$ 363.9863; Found: 363.9865.

$[\alpha]_{25}^D$: -31.8 (c 0.5, Chloroform).
(R)-N-(2-(3-bromophenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1j)

Following the general procedure I on 5 mmol scale, yellow oil liquid, yield: 60% (946 mg), R_f = 0.7 (silica gel, PE: EA = 3:1, v/v), column chromatography (silica gel, PE: EA = 20:1, v/v).

H NMR (500 MHz, Chloroform-d) δ 8.38 (s, 1H), 8.28 (t, J = 1.8 Hz, 1H), 8.06 (m, 1H), 7.74 (m, 1H), 7.38 (t, J = 7.9 Hz, 1H), 1.28 (s, 9H).

C NMR (126 MHz, Chloroform-d) δ 186.5, 160.4, 137.0, 136.1, 133.0, 130.2, 128.6 122.8, 58.9, 22.7.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{12}H_{15}BrNO2S^+ 316.0001; Found: 315.9995.

[a]^{25}D: -69.2 (c 0.5, Chloroform).

(R)-N-(2-(4-chlorophenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1k)

Following the general procedure I on 5 mmol scale, yellow oil liquid, yield: 60% (813 mg), R_f = 0.7 (silica gel, PE: EA = 3:1, v/v), column chromatography (silica gel, PE: EA = 20:1, v/v).

H NMR (400 MHz, Chloroform-d) δ 8.41 (s, 1H), 8.10 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 1.27 (s, 9H).

C NMR (126 MHz, Chloroform-d) δ 186.7, 160.6, 141.0, 132.7, 131.5, 129.1, 58.8, 22.7.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{12}H_{15}ClNO2S^+ 272.0507; Found: 272.0500.

[a]^{25}D: -18.2 (c 0.5, Chloroform).

(R)-N-(2-(4-fluorophenyl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1l)

Following the general procedure I on 5 mmol scale, yellow oil liquid, yield: 61% (770mg), R_f = 0.7 (silica gel, PE: EA = 3:1, v/v), column chromatography (silica gel, PE: EA = 20:1, v/v).

H NMR (500 MHz, Chloroform-d) δ 8.41 (s, 1H), 8.20 (dd, J = 9.0, 5.4 Hz, 2H), 7.17 (dd, J = 9.0, 8.3 Hz, 2H), 1.27 (s, 9H).
\(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 186.4, 166.4 (d, \(J = 257.6\) Hz), 160.8, 133.0 (d, \(J = 9.4\) Hz), 130.9 (d, \(J = 3.1\) Hz), 116.0 (d, \(J = 21.9\) Hz), 58.7, 22.7.

\(^{19}\)F NMR (471 MHz, Chloroform-\(d\)) \(\delta\) -102.17.

HRMS (ESI) \(m/z\): [M+H]\(^+\) Calcd. for \(C_{12}H_{15}FNO_2S\) 256.0802; Found: 256.0800.

\([\alpha]\)^{25}_D: -7.2 (c 0.5, Chloroform).

\((R)-2\)-methyl-\(N\)-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyldiene)propane-2-sulfinamide (1m)

\[
\begin{array}{c}
\text{CF}_3 \\
\text{O} \\
\text{N} \\
\text{S} \\
\text{tBu}
\end{array}
\]

1m

Following the general procedure 1 on 5 mmol scale, yellow oil liquid, yield: 63% (961 mg), \(R_t = 0.7\) (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 8.38 (s, 1H), 8.23 (dd, \(J = 8.9, 0.8\) Hz, 2H), 7.73 (d, \(J = 8.0\) Hz, 2H), 1.25 (s, 9H).

\(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 187.4, 165.8, 160.4, 137.5, 134.5, 129.9, 129.6, 58.7, 52.4, 22.6.

\(^{19}\)F NMR (471 MHz, Chloroform-\(d\)) \(\delta\) -63.25.

HRMS (ESI) \(m/z\): [M+H]\(^+\) Calcd. for \(C_{13}H_{18}NO_4S\) 296.0951; Found: 296.0946.

\([\alpha]\)^{25}_D: -5.4 (c 0.5, Chloroform).

methyl \((R)-4\)-(2-((tert-butyldisulfanyl)imino)acetyl)benzoate (1n)

\[
\begin{array}{c}
\text{MeO}_2\text{C} \\
\text{O} \\
\text{N} \\
\text{S} \\
\text{tBu}
\end{array}
\]

1n

Following the general procedure 1 on 5 mmol scale, yellow oil liquid, yield: 63% (923 mg), \(R_t = 0.5\) (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 10: 1, v/v).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 8.38 (s, 1H), 8.13 (d, \(J = 15.2\) Hz, 4H), 3.90 (s, 3H), 1.23 (s, 9H).

\(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 187.4, 165.8, 160.4, 137.5, 134.5, 129.9, 129.6, 58.7, 52.4, 22.6.

HRMS (ESI) \(m/z\): [M+H]\(^+\) Calcd. for \(C_{14}H_{18}NO_4S\) 296.0951; Found: 296.0946.

\([\alpha]\)^{25}_D: -29.1 (c 0.5, Chloroform).

\((R)-2\)-methyl-\(N\)-(2-(naphthalen-2-yl)-2-oxoethylidene)propane-2-sulfinamide (1o)
Following the general procedure 1 on 5 mmol scale, yellow oil liquid, yield: 50% (729 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

^1^H NMR (500 MHz, Chloroform-d) δ 8.73 (s, 1H), 8.62 (d, J = 2.4 Hz, 1H), 8.14 (dd, J = 8.8, 2.4 Hz, 1H), 7.98 – 7.91 (m, 2H), 7.89 (d, J = 8.2 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.58 (d, J = 7.2 Hz, 1H), 1.32 (s, 9H).

^1^3^C NMR (126 MHz, Chloroform-d) δ 187.8, 161.1, 136.1, 133.1, 132.3, 131.9, 129.9, 129.4, 128.8, 127.9, 127.0, 124.5, 58.7, 22.8.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{16}H_{18}NO_2S^+ 288.1053; Found: 288.1049.

[α]^2^5^D: -4.3 (c 0.5, Chloroform).

(R)-N-(2-(furan-2-yl)-2-oxoethylidene)-2-methylpropane-2-sulfinamide (1p)

Following the general procedure 1 on 5 mmol scale, yellow oil liquid, yield: 65% (750 mg), R_f = 0.6 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 15: 1, v/v).

^1^H NMR (500 MHz, Chloroform-d) δ 8.33 (s, 1H), 7.76 (dd, J = 1.7, 0.7 Hz, 1H), 7.67 (dd, J = 3.6, 0.8 Hz, 1H), 6.62 (dd, J = 3.7, 1.7 Hz, 1H), 1.29 (s, 9H).

^1^3^C NMR (126 MHz, Chloroform-d) δ 174.0, 159.6, 150.4, 148.9, 123.0, 112.9, 59.0, 22.8.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{10}H_{14}NO_3S^+ 228.0689; Found: 228.0684

[α]^2^5^D: -73.8 (c 0.5, Chloroform).

(R)-2-methyl-N-(2-(1-methyl-1H-pyrrol-2-yl)-2-oxoethylidene)propane-2-sulfinamide (1q)

Following the general procedure 1 on 5 mmol scale, yellow oil liquid, yield: 53% (636 mg), R_f = 0.7 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 20: 1, v/v).

^1^H NMR (500 MHz, Chloroform-d) δ 8.46 (s, 1H), 7.35 (dd, J = 4.3, 1.7 Hz, 1H), 6.98 (t, J = 2.1 Hz, 1H), 6.23 (dd, J = 4.3, 2.4 Hz, 1H), 4.02 (s, 3H), 1.28 (s, 9H).

^1^3^C NMR (126 MHz, Chloroform-d) δ 175.5, 161.0, 133.8, 129.7, 123.4, 109.6, 58.5, 37.9, 22.7.
3. General procedure 2 of synthesis of α-amino ketones 3

To a Schlenk tube added [RhCl(COD)]₂ (4.5 mg, 0.0125 mmol, 5 mol %), (R)-N-tert-butanesulfinyl imines (1) (0.2 mmol), arylboronic acids (2) (0.4 mmol) and KOAc (0.4 mmol) under nitrogen atmosphere. Then toluene (0.75 mL) and water (0.25 mL) were added and the mixture was stirred at 30 °C for 3 h. The reaction mixture was diluted with EtOAc. The organic layer was washed with saturated ammonium chloride aqueous solution and brine. The aqueous layer was extracted with EtOAc (3×15 mL). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography to isolate the product.

(R)-N-((R)-1-(4-methoxyphenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3a)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 75% (56 mg), Rₗ = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

¹H NMR (500 MHz, Chloroform-d) δ 7.88 (dd, J = 8.4, 1.3 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.36 (dd, J = 8.4, 7.3 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 5.91 (d, J = 3.8 Hz, 1H), 5.08 (d, J = 3.8 Hz, 1H), 3.74 (s, 3H), 1.20 (s, 9H).

¹³C NMR (151 MHz, Chloroform-d) δ 196.3, 159.5, 134.5, 133.4, 129.9, 129.7, 129.0, 128.6, 114.5, 62.6, 55.9, 55.1, 22.6.

HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₁₉H₂₅NO₃S⁺ 346.1471; Found: 346.1474.

[α]²⁵D: -94.4 (c 0.5, Chloroform).
(R)-N-((R)-1-(4-methoxyphenyl)-2-oxo-2-(p-tolyl)ethyl)-2-methylpropane-2-sulfinamide (3b)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 81% (59 mg), R<sub>f</sub> = 0.3 (silica gel, PE: EA = 3:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v). dr: >98: 2

$^1$H NMR (500 MHz, Chloroform-d) δ 7.80 – 7.77 (m, 2H), 7.24 – 7.19 (m, 2H), 7.16 – 7.12 (m, 2H), 6.80 (d, $J$ = 8.8 Hz, 2H), 5.89 (d, $J$ = 3.7 Hz, 1H), 5.10 (d, $J$ = 3.7 Hz, 1H), 3.73 (s, 3H), 2.32 (s, 3H), 1.19 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 195.7, 159.4, 144.4, 131.8, 130.2, 129.6, 129.2, 129.1, 114.4, 62.4, 55.8, 55.1, 22.5, 21.6.

HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd. for C<sub>20</sub>H<sub>26</sub>NO<sub>3</sub>S<sup>+</sup> 360.1628; Found: 360.1621.

$[\alpha]^{25}$D: -180.2 (c 0.5, Chloroform).

(R)-N-((R)-1-(4-methoxyphenyl)-2-oxo-2-(m-tolyl)ethyl)-2-methylpropane-2-sulfinamide (3c)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 77% (56 mg), R<sub>f</sub> = 0.3 (silica gel, PE: EA = 3:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v). dr: >98: 2

$^1$H NMR (500 MHz, Chloroform-d) δ 7.71 (s, 1H), 7.66 (d, $J$ = 7.6 Hz, 1H), 7.28 (d, $J$ = 7.3 Hz, 1H), 7.23 (dd, $J$ = 8.3, 6.6 Hz, 3H), 6.81 (d, $J$ = 8.7 Hz, 2H), 5.91 (d, $J$ = 3.8 Hz, 1H), 5.08 (d, $J$ = 3.9 Hz, 1H), 3.73 (s, 3H), 2.32 (s, 3H), 1.19 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 196.5, 159.4, 138.4, 134.4, 134.2, 130.0, 129.6, 129.5, 128.3, 126.2, 114.4, 62.5, 55.8, 55.1, 22.5, 21.2.

HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd. for C<sub>20</sub>H<sub>26</sub>NO<sub>3</sub>S<sup>+</sup> 360.1628; Found: 360.1626.

$[\alpha]^{25}$D: -87.3 (c 0.5, Chloroform).
(R)-N-((R)-2-(4-ethylphenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3d)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 72% (54 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

^1^H NMR (500 MHz, Chloroform-d) δ 7.82 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 5.89 (d, J = 3.8 Hz, 1H), 5.09 (d, J = 3.8 Hz, 1H), 3.74 (s, 3H), 2.62 (q, J = 7.6 Hz, 2H), 1.21 – 1.17 (m, 12H).

^13^C NMR (126 MHz, Chloroform-d) δ 195.8, 159.4, 150.5, 132.0, 130.2, 129.6, 129.3, 128.1, 114.4, 62.4, 55.8, 55.1, 28.8, 22.5, 14.9.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{21}H_{28}NO_{3}S^+ 374.1784; Found: 374.1778.

[α]^{25}D: -161.3 (c 0.5, Chloroform).

(R)-N-((R)-2-(3-methoxyphenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3e)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 76% (58 mg), R_f = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

^1^H NMR (500 MHz, Chloroform-d) δ 7.46 (m, 1H), 7.41 (dd, J = 2.6, 1.6 Hz, 1H), 7.25 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 8.7 Hz, 2H), 7.01 (m, 1H), 6.82 (d, J = 8.8 Hz, 2H), 5.89 (d, J = 3.9 Hz, 1H), 5.06 (d, J = 3.9 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 1.20 (s, 9H).

^13^C NMR (126 MHz, Chloroform-d) δ 196.1, 159.6, 159.5, 135.7, 129.9, 129.6, 129.5, 121.6, 120.0, 114.4, 113.25, 62.7, 55.9, 55.3, 55.1, 22.5.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{20}H_{26}NO_{3}S^+ 376.1577; Found: 376.1579.

[α]^{25}D: -150.0 (c 0.5, Chloroform).
(R)-N-((R)-2-(3,4-dimethoxyphenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3f)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 75% (62 mg), Rf = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98:2

1H NMR (500 MHz, Chloroform-d) δ 7.52 (dd, J = 8.5, 2.1 Hz, 1H), 7.44 (d, J = 2.0 Hz, 1H), 7.22 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 8.5 Hz, 1H), 5.86 (d, J = 4.0 Hz, 1H), 5.09 (d, J = 3.9 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.72 (s, 3H), 1.18 (s, 9H).

13C NMR (126 MHz, Chloroform-d) δ 194.6, 159.4, 153.5, 148.8, 130.6, 129.4, 127.2, 123.9, 114.4, 111.1, 110.0, 62.1, 55.9, 55.8, 55.8, 55.1, 22.5.

HRMS (ESI) m/z: [M+H]+ Calcd. for C21H28NO5S+ 406.1683; Found: 460.1685.

[a]25D: -118.2 (c 0.5, Chloroform).

(R)-N-((R)-1-(4-methoxyphenyl)-2-(4-(methylthio)phenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3g)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 70% (55 mg), Rf = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98:2

1H NMR (500 MHz, Chloroform-d) δ 7.80 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 5.86 (d, J = 3.7 Hz, 1H), 5.09 (d, J = 3.7 Hz, 1H), 3.75 (s, 3H), 2.46 (s, 3H), 1.20 (s, 9H).

13C NMR (126 MHz, Chloroform-d) δ 195.1, 159.5, 146.8, 130.5, 130.3, 129.6, 129.4, 124.8, 114.5, 62.4, 55.9, 55.2, 22.6, 14.5.

HRMS (ESI) m/z: [M+H]+ Calcd. for C20H26NO3S2+ 392.1349; Found: 392.1349.

[a]25D: -59.7 (c 0.5, Chloroform).
(R)-N-((R)-2-(4-iodophenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3h)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 82% (78 mg), Rf = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

$^1$H NMR (500 MHz, Chloroform-d) δ 7.72 (d, $J = 8.6$ Hz, 2H), 7.58 (d, $J = 8.6$ Hz, 2H), 7.19 (d, $J = 8.7$ Hz, 2H), 6.82 (d, $J = 8.7$ Hz, 2H), 5.83 (d, $J = 3.8$ Hz, 1H), 5.03 (d, $J = 3.7$ Hz, 1H), 3.75 (s, 3H), 1.19 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 195.6, 159.6, 137.9, 133.6, 130.2, 129.6, 129.4, 114.6, 101.7, 62.5, 55.9, 55.1, 22.5.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for C$_{19}$H$_{23}$INO$_3$S$^+$ 472.0438; Found: 472.0434.

[$\alpha$]$^{25}$D: -117.0 (c 0.5, Chloroform).

(R)-N-((R)-2-(3-iodophenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3i)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 74% (71 mg), Rf = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: 81: 19

$^1$H NMR (500 MHz, Chloroform-d) δ 8.22 (t, $J = 1.7$ Hz, 1H), 7.82 – 7.74 (m, 2H), 7.20 (d, $J = 8.7$ Hz, 2H), 7.09 (t, $J = 7.8$ Hz, 1H), 6.83 (d, $J = 8.7$ Hz, 2H), 5.84 (d, $J = 3.2$ Hz, 1H), 5.00 (d, $J = 3.8$ Hz, 1H), 3.75 (s, 3H), 1.20 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 195.0, 159.6, 142.2, 137.8, 136.1, 130.2, 129.7, 129.2, 128.0, 114.6, 94.3, 62.6, 55.9, 55.2, 22.5.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for C$_{19}$H$_{23}$INO$_3$S$^+$ 472.0438; Found: 472.0432.

[$\alpha$]$^{25}$D: -107.0 (c 0.5, Chloroform).
(R)-N-((R)-2-(3-bromophenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3j)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 62% (53 mg), Rf = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

\[^1\text{H} \text{ NMR}\] (500 MHz, Chloroform-d) δ 8.02 (t, J = 1.8 Hz, 1H), 7.78 (m, 1H), 7.60 (m, 1H), 7.25 (d, J = 7.9 Hz, 1H), 7.21 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.85 (d, J = 3.9 Hz, 1H), 5.00 (d, J = 3.9 Hz, 1H), 3.76 (s, 3H), 1.20 (s, 9H).

\[^{13}\text{C} \text{ NMR}\] (126 MHz, Chloroform-d) δ 195.1, 159.7, 136.3, 136.2, 131.9, 130.1, 129.7, 129.2, 127.5, 122.9, 114.6, 62.7, 55.9, 55.2, 22.5.

HRMS (ESI) m/z: [M+H]\(^+\) Calcd. for C\(_{19}\)H\(_{23}\)BrNO\(_3\)S\(^+\) 424.0577; Found: 424.0573.

\([\alpha]^{25}\text{D}\): -85.5 (c 0.5, Chloroform).

(R)-N-((R)-2-(4-chlorophenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3k)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 78% (60 mg), Rf = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: 93: 7

\[^1\text{H} \text{ NMR}\] (500 MHz, Chloroform-d) δ 7.82 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 5.86 (d, J = 3.8 Hz, 1H), 5.04 (d, J = 3.8 Hz, 1H), 3.74 (s, 3H), 1.19 (s, 9H).

\[^{13}\text{C} \text{ NMR}\] (126 MHz, Chloroform-d) δ 195.1, 159.6, 139.6, 139.9, 132.7, 130.4, 129.6, 129.5, 128.9, 114.6, 62.6, 55.9, 55.1, 22.5.

HRMS (ESI) m/z: [M+H]\(^+\) Calcd. for C\(_{19}\)H\(_{23}\)ClNO\(_3\)S\(^+\) 379.1082; Found: 380.1074.

\([\alpha]^{25}\text{D}\): -132.8 (c 0.5, Chloroform).
(R)-N-((R)-2-(4-fluorophenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3l)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 83% (61 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

^1H NMR (500 MHz, Chloroform-d) δ 7.92 (dd, J = 8.9, 5.3 Hz, 2H), 7.21 (d, J = 8.7 Hz, 2H), 7.04 (t, J = 8.6 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.86 (d, J = 4.0 Hz, 1H), 5.05 (d, J = 3.9 Hz, 1H), 3.75 (s, 3H), 1.20 (s, 9H).

^13C NMR (126 MHz, Chloroform-d) δ 194.7, 159.6, 131.7 (d, J = 9.4 Hz), 130.8 (d, J = 2.4 Hz), 129.8, 129.6 115.8 (d, J = 19.4 Hz), 114.6, 62.6, 55.9, 55.2, 22.5.

^19F NMR (471 MHz, Chloroform-d) δ -103.6.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{19}H_{23}FNO_{3}S^+ 364.1377; Found: 364.1376.

[a]^{25}D: -116.0 (c 0.5, Chloroform).

(R)-N-((R)-1-(4-methoxyphenyl)-2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-2-methylpropane-2-sulfinamide (3m)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 65% (54 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

^1H NMR (500 MHz, Chloroform-d) δ 7.97 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.90 (d, J = 3.8 Hz, 1H), 5.03 (d, J = 3.8 Hz, 1H), 3.75 (s, 3H), 1.21 (s, 9H).

^13C NMR (126 MHz, Chloroform-d) δ 195.5, 159.7, 137.2, 135.7, 134.5 (q, J = 33.1 Hz), 129.5 (d, J = 57.2 Hz), 128.9, 125.6 (d, J = 4.2 Hz), 123.3 (d, J = 272.8 Hz), 114.7, 63.0, 56.0, 55.2, 22.5.

^19F NMR (471 MHz, Chloroform-d) δ -63.20.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{20}H_{23}F_{3}NO_{3}S^+ 414.1345; Found: 414.1347.

[a]^{25}D: -87.1 (c 0.5, Chloroform).
methyl 4-((R)-2-(((R)-tert-butylsulfinyl)amino)-2-(4-methoxyphenyl)acetyl)benzoate (3n)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 70% (54 mg), $R_f = 0.2$ (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2
$^1$H NMR (500 MHz, Chloroform-d) δ 8.02 (d, $J = 8.6$ Hz, 2H), 7.91 (d, $J = 8.7$ Hz, 2H), 7.21 (d, $J = 8.7$ Hz, 2H), 6.82 (d, $J = 8.8$ Hz, 2H), 5.91 (d, $J = 3.7$ Hz, 1H), 5.04 (d, $J = 3.7$ Hz, 1H), 3.90 (s, 3H), 3.74 (s, 3H), 1.21 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 196.0, 166.0, 160.0, 137.8, 134.1, 129.7, 129.7, 129.2, 128.9, 114.6, 63.0, 55.9, 55.2, 52.5, 22.5.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for C$_{22}$H$_{26}$NO$_5$S$^+$ 384.1805; Found: 384.1796.

$[\alpha]^{25}$D: -88.6 (c 0.5, Chloroform).

(R)-N-((R)-1-(4-methoxyphenyl)-2-(naphthalen-2-yl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3o)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 66% (66 mg), $R_f = 0.3$ (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2
$^1$H NMR (500 MHz, Chloroform-d) δ 8.44 (s, 1H), 7.93 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.87 (dd, $J = 8.1, 1.2$ Hz, 1H), 7.79 (d, $J = 8.7$ Hz, 2H), 7.55 (m, 1H), 7.49 (m, 1H), 7.30 (d, $J = 8.8$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 2H), 6.10 (d, $J = 3.7$ Hz, 1H), 5.16 (d, $J = 3.8$ Hz, 1H), 3.71 (s, 3H), 1.23 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 196.4, 159.6, 135.7, 132.3, 131.9, 131.2, 130.2, 129.8, 128.9, 128.6, 127.8, 127.0, 124.5, 114.6, 62.7, 56.0, 55.2, 22.7.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for C$_{23}$H$_{28}$NO$_3$S$^+$ 396.1628; Found: 396.1631.

$[\alpha]^{25}$D: -48.8 (c 0.5, Chloroform).
(R)-N-((R)-2-(furan-2-yl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3p)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 90% (66 mg), \( R_f = 0.1 \) (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

\(^1\)H NMR (500 MHz, Chloroform-d) \( \delta \) 7.52 (dd, \( J = 1.7, 0.7 \) Hz, 1H), 7.30 (d, \( J = 8.7 \) Hz, 2H), 7.14 (dd, \( J = 3.6, 0.8 \) Hz, 1H), 6.84 (d, \( J = 8.8 \) Hz, 2H), 6.45 (dd, \( J = 3.6, 1.7 \) Hz, 1H), 5.72 (d, \( J = 4.0 \) Hz, 1H), 4.96 (d, \( J = 4.0 \) Hz, 1H), 3.76 (s, 3H), 1.20 (s, 9H).

\(^{13}\)C NMR (126 MHz, Chloroform-d) \( \delta \) 184.9, 159.6, 150.4, 147.0, 129.7, 129.4, 119.4, 114.2, 112.5, 62.4, 55.9, 55.2, 22.5.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C\(_{17}\)H\(_{22}\)NO\(_4\)S^+ 336.1264; Found: 336.1255.

[\( \alpha \)]\text{D}^25: -153.0 (c 0.5, Chloroform).

\((R)-N-((R)-1-(4-methoxyphenyl)-2-(1-methyl-1H-pyrrol-2-yl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3q)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 83% (53 mg), \( R_f = 0.1 \) (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 2: 1, v/v). dr: >98: 2

\(^1\)H NMR (500 MHz, Chloroform-d) \( \delta \) 7.27 (d, \( J = 8.8 \) Hz, 2H), 6.94 (dd, \( J = 4.2, 1.6 \) Hz, 1H), 6.83 (d, \( J = 8.8 \) Hz, 2H), 6.78 (t, \( J = 2.0 \) Hz, 1H), 6.06 (dd, \( J = 4.2, 2.4 \) Hz, 1H), 5.64 (d, \( J = 4.7 \) Hz, 1H), 5.01 (d, \( J = 4.7 \) Hz, 1H), 3.90 (s, 3H), 3.76 (s, 3H), 1.20 (s, 9H).

\(^{13}\)C NMR (126 MHz, Chloroform-d) \( \delta \) 186.3, 159.2, 132.0, 131.6, 129.1, 128.2, 120.8, 114.2, 108.7, 62.5, 55.8, 55.1, 37.7, 22.6.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C\(_{18}\)H\(_{25}\)N\(_2\)O\(_3\)S^+ 349.1580; Found: 349.1573.

[\( \alpha \)]\text{D}^25: -139.2 (c 0.5, Chloroform).
(R)-2-methyl-N-((R)-2-oxo-1,2-diphenylethyl)propane-2-sulfinamide (3r)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 61% (39 mg), Rf = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

1H NMR (500 MHz, Chloroform-d) δ 7.90 (d, J = 7.0 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.27 – 7.22 (m, 1H), 5.96 (d, J = 4.0 Hz, 1H), 5.15 (d, J = 4.0 Hz, 1H), 1.20 (s, 9H).

13C NMR (126 MHz, Chloroform-d) δ 196.2, 138.0, 134.3, 133.6, 129.1, 129.0, 128.6, 128.4, 128.3, 63.3, 55.9, 22.5.

HRMS (ESI) m/z: [M+H]+ Calcd. for C18H22NO2S+ 316.1366; Found: 316.1364.

[α]25D: -314.0 (c 0.5, Chloroform).

(R)-2-methyl-N-((R)-2-oxo-2-phenyl-1-(p-tolyl)ethyl)propane-2-sulfinamide (3s)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 81% (52 mg), Rf = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

1H NMR (500 MHz, Chloroform-d) δ 7.90 (d, J = 7.0 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.20 (dd, J = 8.1, 2.2 Hz, 2H), 7.10 (d, J = 7.7 Hz, 2H), 5.92 (d, J = 3.3 Hz, 1H), 5.11 (d, J = 3.9 Hz, 1H), 2.28 (s, 3H), 1.20 (s, 9H).

13C NMR (126 MHz, Chloroform-d) δ 196.3, 138.2, 134.9, 134.4, 133.5, 129.8, 129.0, 128.6, 128.3, 63.0, 55.9, 22.6, 21.1.

HRMS (ESI) m/z: [M+H]+ Calcd. for C19H24NO2S+ 330.1522; Found: 330.1523.

[α]25D: -133.6 (c 0.5, Chloroform).
(R)-N-((R)-1-(4-isopropylphenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3t)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 61% (44 mg), R<sub>f</sub> = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

<sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 7.91 (d, J = 7.1 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.37 (dd, J = 8.5, 7.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 5.94 (d, J = 4.4 Hz, 1H), 5.14 (d, J = 4.4 Hz, 1H), 2.83 (p, J = 6.9 Hz, 1H), 1.21 (s, 9H), 1.18 (d, J = 6.9 Hz, 6H).

<sup>13</sup>C NMR (126 MHz, Chloroform-d) δ 196.4, 149.0, 135.1, 134.4, 133.5, 129.1, 128.5, 128.2, 127.1, 62.9, 55.9, 33.6, 23.7, 22.6.

HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd. for C<sub>21</sub>H<sub>28</sub>NO<sub>2</sub>S<sup>+</sup> 358.1835; Found: 358.1837.

[α]<sup>25</sup>D: -150.8 (c 0.5, Chloroform).

(R)-N-((R)-1-(4-(tert-butyl)phenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3u)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 53% (40 mg), R<sub>f</sub> = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

<sup>1</sup>H NMR (600 MHz, Chloroform-d) δ 7.93 (dd, J = 8.4, 1.3 Hz, 2H), 7.50 (m, 1H), 7.38 (dd, J = 8.4, 7.4 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 5.94 (d, J = 4.6 Hz, 1H), 5.11 (d, J = 4.6 Hz, 1H), 1.25 (s, 9H), 1.21 (s, 9H).

<sup>13</sup>C NMR (126 MHz, Chloroform-d) δ 196.5, 151.3, 134.8, 134.5, 133.5, 129.1, 128.6, 127.9, 126.0, 62.8, 55.9, 34.5, 31.2, 22.6.

HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd. for C<sub>22</sub>H<sub>30</sub>NO<sub>2</sub>S<sup>+</sup> 372.1992; Found: 372.1998.

[α]<sup>25</sup>D: -82.2 (c 0.5, Chloroform).
Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 53% (37 mg), R<sub>f</sub> = 0.2 (silica gel, PE: EA = 3:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v). dr: >98:2

1<sup>H</sup> NMR (600 MHz, Chloroform-<d>) δ 7.91 (d, J = 7.1 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 10.0 Hz 2H), 7.21 (t, J = 7.9 Hz, 1H), 5.92 (d, J = 4.1 Hz, 1H), 5.13 (d, J = 4.1 Hz, 1H), 3.74 (s, 3H), 1.21 (s, 9H).

13<sup>C</sup> NMR (126 MHz, Chloroform-<d>) δ 196.1, 160.0, 139.4, 134.4, 133.6, 130.1, 129.0, 128.6, 120.8, 113.9, 113.8, 63.2, 56.0, 55.2, 22.6.

HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd. for C<sub>19</sub>H<sub>24</sub>NO<sub>3</sub>S<sup>+</sup> 346.1471; Found: 346.1479.

[α]<sup>25</sup>D: -100.2 (c 0.5, Chloroform).

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 70% (51 mg), R<sub>f</sub> = 0.3 (silica gel, PE: EA = 3:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v). dr: >98:2

1<sup>H</sup> NMR (500 MHz, Chloroform-<d>) δ 7.90 (d, J = 7.7 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.4 Hz, 2H), 7.11 (d, J = 8.0 Hz, 1H), 7.06 (s, 1H), 6.72 (d, J = 8.4 Hz, 1H), 5.87 (d, J = 3.3 Hz, 1H), 5.06 (t, J = 3.1 Hz, 1H), 3.75 (s, 3H), 2.14 (s, 3H), 1.20 (s, 9H).

13<sup>C</sup> NMR (126 MHz, Chloroform-<d>) δ 196.4, 157.6, 134.5, 133.4, 130.5, 129.3, 129.0, 128.5, 127.4, 127.1, 110.1, 62.6, 55.8, 55.2, 22.6, 16.2.

HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd. for C<sub>20</sub>H<sub>26</sub>NO<sub>3</sub>S<sup>+</sup> 360.1628; Found: 360.1629.

[α]<sup>25</sup>D: -74.5 (c 0.5, Chloroform).
Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 43% (33 mg), Rf = 0.2 (silica gel, PE: EA = 3:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v). dl: >96: 4

**1H NMR** (500 MHz, Chloroform-d) δ 7.89 (dd, J = 8.4, 1.3 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.36 (dd, J = 8.2, 7.4 Hz, 2H), 6.91 (dd, J = 8.2, 2.1 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 6.75 (d, J = 2.1 Hz, 1H), 5.90 (d, J = 3.6 Hz, 1H), 5.05 (d, J = 3.6 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 1.21 (s, 9H).

**13C NMR** (126 MHz, Chloroform-d) δ 196.2, 149.4, 149.0, 134.5, 133.5, 130.2, 128.9, 128.5, 121.3, 111.2, 110.8, 62.8, 55.9, 55.8, 22.5.

**HRMS (ESI) m/z:** [M+H]+ Calcd. for C20H26NO4S+ 376.1577; Found: 376.1580.

**[α]25D:** -122.8 (c 0.5, Chloroform).

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Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 57% (43 mg), Rf = 0.2 (silica gel, PE: EA = 3:1, v/v), column chromatography (silica gel, PE: EA = 3:1, v/v). dl: >98: 2

**1H NMR** (600 MHz, Chloroform-d) δ 7.91 (dd, J = 8.4, 1.3 Hz, 2H), 7.55 – 7.43 (m, 1H), 7.38 (dd, J = 8.3, 7.4 Hz, 2H), 6.45 (d, J = 2.2 Hz, 2H), 6.32 (t, J = 2.3 Hz, 1H), 5.85 (d, J = 4.1 Hz, 1H), 5.11 (d, J = 4.1 Hz, 1H), 3.72 (s, 6H), 1.22 (s, 9H).

**13C NMR** (126 MHz, ) δ 196.0, 161.2, 140.1, 134.4, 133.6, 129.0, 128.6, 106.4, 100.1, 63.3, 56.0, 55.3, 22.6.

**HRMS (ESI) m/z:** [M+H]+ Calcd. for C20H26NO4S+ 376.1577; Found: 376.1574.

**[α]25D:** -162.8 (c 0.5, Chloroform).
(R)-N-((R)-1-(4-(benzyloxy)phenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3z)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 45% (38 mg), Rf = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

\[^1^H \text{NMR}\] (500 MHz, Chloroform-\(d\)) \(\delta\) 7.90 (d, \(J = 7.1\) Hz, 2H), 7.49 (t, \(J = 7.4\) Hz, 1H), 7.39 – 7.34 (m, 6H), 7.32 (dd, \(J = 7.3, 1.6\) Hz, 1H), 7.24 (d, \(J = 8.7\) Hz, 2H), 6.90 (d, \(J = 8.7\) Hz, 2H), 5.93 (d, \(J = 3.9\) Hz, 1H), 5.09 (d, \(J = 3.9\) Hz, 1H), 4.98 (s, 2H), 1.21 (s, 9H).

\[^{13}^C \text{NMR}\] (126 MHz, Chloroform-\(d\)) \(\delta\) 196.3, 158.7, 136.6, 134.4, 133.5, 130.2, 129.7, 129.0, 128.6, 128.0, 127.5, 116.8, 115.3, 70.0, 62.6, 65.9, 22.5.

HRMS (ESI) m/z: \([M+H]^+\) Calcd. for C\(_{25}\)H\(_{28}\)NO\(_3\)S\(_2^+\) 422.1784; Found: 422.1781.

\([\alpha]^{25D}\): -108.2 (c 0.5, Chloroform).

(R)-2-methyl-N-((1R)-2-oxo-2-phenyl-1-(4-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)ethyl)propane-2-sulfinamide (3aa)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 65% (54 mg), Rf = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: 1: 1

\[^1^H \text{NMR}\] (500 MHz, \(\delta\)) 7.95 – 7.80 (m, 2H), 7.51 – 7.43 (m, 1H), 7.36 (m, 2H), 7.21 (d, \(J = 8.7\) Hz, 2H), 6.96 (dd, \(J = 8.7, 0.7\) Hz, 2H), 5.91 (dd, \(J = 4.0, 1.8\) Hz, 1H), 5.33 (q, \(J = 3.6\) Hz, 1H), 5.08 (t, \(J = 3.8\) Hz, 1H), 3.85 (m, 1H), 3.64 – 3.38 (m, 1H), 1.94 (m, 1H), 1.82 – 1.72 (m, 2H), 1.68 – 1.53 (m, 3H), 1.20 (s, 9H).

\[^{13}^C \text{NMR}\] (126 MHz, Chloroform-\(d\)) \(\delta\) 196.3, 157.1, 134.4, 133.5, 130.8, 129.6, 129.5, 129.1, 128.6, 128.5, 116.8, 116.8, 96.4, 96.3, 62.6, 62.6, 62.6, 62.2, 55.9, 30.3, 25.1, 22.6, 18.8, 18.8.

HRMS (ESI) m/z: \([M+H]^+\) Calcd. for C\(_{23}\)H\(_{36}\)NO\(_4\)S\(_2^+\) 416.1890; Found: 416.1887.

\([\alpha]^{25D}\): -115.6 (c 0.5, Chloroform).
(R)-N-((R)-1-(2,3-dihydrobenzofuran-5-yl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3ab)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 68% (49 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: 93: 7

^1H NMR (500 MHz, Chloroform-d) δ 7.90 (d, J = 7.2 Hz, 2H), 7.48 (m, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.11 (s, 1H), 7.07 (d, J = 8.1 Hz, 1H), 6.69 (d, J = 8.2 Hz, 1H), 5.89 (d, J = 3.9 Hz, 1H), 5.05 (d, J = 3.9 Hz, 1H), 4.52 (m, 2H), 3.13 (t, J = 8.7 Hz, 2H), 1.21 (s, 9H).

^13C NMR (126 MHz, Chloroform-d) δ 196.4, 160.2, 134.4, 133.5, 129.7, 129.0, 128.7, 128.6, 128.0, 124.9, 109.7, 71.4, 62.8, 55.8, 29.5, 22.6.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{20}H_{24}NO_{3}S^+ 358.1471; Found: 358.1474.

[α]_{25}^{25}D: -81.8 (c 0.5, Chloroform).

(R)-2-methyl-N-((R)-1-(4-(methylthio)phenyl)-2-oxo-2-phenylethyl)propane-2-sulfinamide (3ac)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 51% (37 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

^1H NMR (600 MHz, Chloroform-d) δ 7.88 (d, J = 7.1 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 5.92 (d, J = 3.8 Hz, 1H), 5.11 (d, J = 3.8 Hz, 1H), 2.42 (s, 3H), 1.20 (s, 9H).

^13C NMR (126 MHz, Chloroform-d) δ 196.0, 139.1, 134.4, 134.3, 133.6, 129.0, 128.8, 128.6, 126.5, 62.7, 55.9, 22.5, 15.2.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{19}H_{23}NO_{2}S_{2}^+ 362.1243; Found: 362.1245.

[α]_{25}^{25}D: -163.0 (c 0.5, Chloroform).
(R)-N-((R)-1-(4-(diphenylamino)phenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3ad)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 55% (41 mg), R_f = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 2: 1, v/v). dr: >98: 2

^1H NMR (500 MHz, Chloroform-d) δ 7.96 – 7.92 (m, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.23 (dd, J = 8.8, 7.1 Hz, 4H), 7.14 (d, J = 8.6 Hz, 2H), 7.06 – 6.99 (m, 6H), 6.95 (d, J = 8.6 Hz, 2H), 5.91 (d, J = 4.4 Hz, 1H), 5.08 (d, J = 4.4 Hz, 1H), 1.23 (s, 9H).

^13C NMR (126 MHz, Chloroform-d) δ 196.3, 147.8, 147.2, 134.5, 133.6, 130.9, 129.3, 129.1, 128.6, 124.8, 123.4, 122.8, 62.6, 55.9, 22.6.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{30}H_{31}N_{2}O_{2}S+ 483.2101; Found: 483.2108.

[^){\alpha}]^{25}D: -54.3 (c 0.5, Chloroform).

(R)-N-((R)-1-(4-(dimethylamino)phenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3ae)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 35% (25 mg), R_f = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

^1H NMR (500 MHz, Chloroform-d) δ 7.96 – 7.85 (m, 2H), 7.49 – 7.42 (m, 1H), 7.35 (dd, J = 8.4, 7.1 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 6.60 (d, J = 8.9 Hz, 2H), 5.87 (d, J = 3.9 Hz, 1H), 5.02 (d, J = 4.0 Hz, 1H), 2.89 (s, 6H), 1.20 (s, 9H).

^13C NMR (126 MHz, Chloroform-d) δ 196.5, 150.2, 134.7, 133.3, 129.4, 129.0, 128.5, 124.8, 112.5, 62.7, 55.8, 40.2, 22.6.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{20}H_{27}N_{2}O_{2}S+ 359.1788; Found: 359.1785.

[^){\alpha}]^{25}D: -152.8 (c 0.5, Chloroform).
(R)-N-((R)-1-(4-fluorophenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3af)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 79% (53 mg), Rf = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

1H NMR (500 MHz, Chloroform-d) δ 7.87 (dd, J = 8.5, 1.3 Hz, 2H), 7.55 – 7.47 (m, 1H), 7.38 (dd, J = 8.3, 7.4 Hz, 2H), 7.30 (dd, J = 8.7, 5.2 Hz, 2H), 6.99 (t, J = 8.6 Hz, 2H), 5.96 (d, J = 3.7 Hz, 1H), 5.12 (d, J = 3.7 Hz, 1H), 1.20 (s, 9H).

13C NMR (126 MHz, Chloroform-d) δ 196.0, 162.5 (d, J = 248.0 Hz), 134.2, 133.9, 133.9, 133.7, 130.2 (d, J = 8.3 Hz), 128.8 (d, J = 41.5 Hz), 116.1 (d, J = 21.7 Hz), 62.3, 56.0, 22.5.

19F NMR (471 MHz, Chloroform-d) δ -112.9.

HRMS (ESI) m/z: [M+H]+ Calcd. for C18H21F2NO2S+ 334.1272; Found: 334.1269.

[α]25D: -67.6 (c 0.5, Chloroform).

(R)-N-((R)-1-(4-fluoro-2-methylphenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3ag)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 55% (38 mg), Rf = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

1H NMR (500 MHz, Chloroform-d) δ 7.76 (dd, J = 8.4, 1.3 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.35 (dd, J = 8.3, 7.4 Hz, 2H), 7.10 (dd, J = 8.6, 5.7 Hz, 1H), 6.93 – 6.84 (m, 1H), 6.83 – 6.77 (m, 1H), 5.95 (d, J = 4.0 Hz, 1H), 5.11 (d, J = 3.9 Hz, 1H), 2.47 (s, 3H), 1.20 (s, 9H).

13C NMR (126 MHz, Chloroform-d) δ 196.8, 162.33 (d, J = 247.6 Hz), 139.1 (d, J = 8.0 Hz), 134.5, 133.6, 132.1, 132.0, 130.9 (d, J = 8.6 Hz), 128.6 (d, J = 4.8 Hz), 118.2 (d, J = 21.4 Hz), 113.6 (d, J = 21.2 Hz), 60.8, 55.9, 22.5, 19.6.

19F NMR (471 MHz, Chloroform-d) δ -113.5.

HRMS (ESI) m/z: [M+H]+ Calcd. for C19H23FNO2S+ 348.1428; Found: 348.1420.
[α]_{25}^D: -54.4 (c 0.5, Chloroform).

(R)-N-((R)-1-(4-chlorophenyl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3ah)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 53% (37 mg), R_{f} = 0.35 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v).

$^1$H NMR (500 MHz, Chloroform-d) δ 7.87 (dd, J = 8.4, 1.3 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.39 (dd, J = 8.3, 7.4 Hz, 2H), 7.27 (d, J = 2.8 Hz, 4H), 5.94 (d, J = 3.7 Hz, 1H), 5.13 (d, J = 3.7 Hz, 1H), 1.21 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 195.8, 136.5, 134.4, 134.1, 133.8, 129.7, 129.4, 129.0, 128.7, 62.4, 56.0, 22.5.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{18}H_{21}ClNO_{2}S^+ 350.0976; Found: 350.0968.

[α]_{25}^D: -54.6 (c 0.5, Chloroform).

(R)-2-methyl-N-((R)-1-(naphthalen-1-yl)-2-oxo-2-phenylethyl)propane-2-sulfinamide (3ai)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 51% (22 mg), R_{f} = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

$^1$H NMR (600 MHz, Chloroform-d) δ 8.26 (d, J = 8.5 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.60 (m, 1H), 7.52 (m, 1H), 7.43 – 7.34 (m, 3H), 7.27 – 7.23 (m, 2H), 6.50 (d, J = 4.6 Hz, 1H), 5.27 (d, J = 4.6 Hz, 1H), 1.14 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 197.2, 134.5, 134.4, 133.7, 133.5, 130.9, 129.5, 129.1, 128.8, 128.5, 127.8, 127.0, 126.1, 125.4, 123.4, 61.5, 56.0, 22.5.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C_{22}H_{24}NO_{2}S^+ 366.1522; Found: 366.1523.

[α]_{25}^D: -108.3 (c 0.5, Chloroform).
(R)-N-([R]-1-(naphthalen-2-yI)-2-oxo-2-phenylethyl)propane-2-sulfinamide (3aj)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 51% (34 mg), \( R_f = 0.3 \) (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

\(^1\)H NMR (500 MHz, Chloroform-d) \( \delta \) 7.95 (dd, \( J = 8.5, 1.3 \) Hz, 2H), 7.84 (s, 1H), 7.81 (dd, \( J = 7.4, 1.9 \) Hz, 1H), 7.38 (dd, \( J = 8.6, 1.9 \) Hz, 1H), 7.34 (dd, \( J = 8.4, 7.2 \) Hz, 2H), 6.14 (d, \( J = 3.7 \) Hz, 1H), 5.23 (d, \( J = 3.8 \) Hz, 1H), 1.20 (s, 9H).

\(^{13}\)C NMR (126 MHz, Chloroform-d) \( \delta \) 196.1, 135.3, 134.3, 133.6, 133.3, 133.0, 129.2, 129.1, 128.6, 128.1, 128.0, 127.7, 126.6, 126.5, 125.4, 63.4, 56.0, 22.6.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C\textsubscript{22}H\textsubscript{24}NO\textsubscript{2}S^+ 366.1522; Found: 366.1525.

\([\alpha]\)\textsuperscript{25}D: -54.9 (c 0.5, Chloroform).

(R)-N-([R]-1-(4-methoxynaphthalen-1-yl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3ak)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 63% (50 mg), \( R_f = 0.3 \) (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

\(^1\)H NMR (500 MHz, Chloroform-d) \( \delta \) 8.35 – 8.26 (m, 1H), 8.17 (d, \( J = 8.5 \) Hz, 1H), 7.81 (dd, \( J = 8.5 \) Hz, 2H), 7.59 (m, 1H), 7.50 (m, 1H), 7.45 – 7.36 (m, 1H), 7.29 (d, \( J = 8.0 \) Hz, 1H), 7.27 – 7.22 (m, 2H), 6.69 (d, \( J = 8.0 \) Hz, 1H), 6.40 (d, \( J = 4.7 \) Hz, 1H), 5.18 (d, \( J = 4.7 \) Hz, 1H), 3.94 (s, 3H), 1.14 (s, 9H).

\(^{13}\)C NMR (126 MHz, Chloroform-d) \( \delta \) 197.5, 156.0, 134.7, 133.3, 131.9, 128.7, 128.4, 127.4, 126.4, 125.4, 125.4, 123.2, 122.8, 103.2, 61.5, 55.9, 55.4, 22.6.

HRMS (ESI) m/z: [M+H]^+ Calcd. for C\textsubscript{23}H\textsubscript{26}NO\textsubscript{3}S^+ 396.1628; Found: 396.1619.

\([\alpha]\)\textsuperscript{25}D: -241.8 (c 0.5, Chloroform).
(R)-N-((R)-1-(6,9-diphenyl-9H-carbazol-3-yl)-2-oxo-2-phenylethyl)-2-methylpropane-2-sulfinamide (3al)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 65% (73 mg), R<sub>f</sub> = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

<sup>1</sup>H NMR (600 MHz, Chloroform-<d>) δ 8.36 (d, <i>J</i> = 1.8 Hz, 1H), 8.18 (d, <i>J</i> = 1.5 Hz, 1H), 8.00 (dd, <i>J</i> = 8.4, 1.3 Hz, 2H), 7.72 (dd, <i>J</i> = 8.3, 1.3 Hz, 2H), 7.66 (dd, <i>J</i> = 8.5, 1.8 Hz, 1H), 7.59 (dd, <i>J</i> = 8.3, 7.3 Hz, 2H), 7.52 (dd, <i>J</i> = 8.4, 1.3 Hz, 2H), 7.51 – 7.46 (m, 3H), 7.46 – 7.41 (m, 2H), 7.40 – 7.33 (m, 5H), 6.21 (d, <i>J</i> = 3.6 Hz, 1H), 5.26 (d, <i>J</i> = 3.7 Hz, 1H), 1.23 (s, 9H).

<sup>13</sup>C NMR (126 MHz, Chloroform-<d>) δ 196.3, 141.6, 141.0, 140.6, 137.2, 134.5, 133.8, 133.4, 129.9, 129.5, 129.1, 128.8, 128.5, 127.6, 127.2, 126.8, 126.7, 126.4, 125.8, 124.0, 123.4, 120.6, 118.9, 110.6, 110.2, 63.5, 55.8, 22.6.

HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd. for C<sub>36</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub>S: 557.2257; Found: 557.2250.

[α]<sup>25</sup>D: -114.0 (c 0.5, Chloroform).

(R)-N-((R)-1-(6,9-diphenyl-9H-carbazol-3-yl)-2-(4-iodophenyl)-2-oxoethyl)-2-methylpropane-2-sulfinamide (3am)

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 58% (79 mg), R<sub>f</sub> = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v). dr: >98: 2

<sup>1</sup>H NMR (500 MHz, Chloroform-<d>) δ 8.34 (dd, <i>J</i> = 1.8, 0.6 Hz, 1H), 8.12 (dd, <i>J</i> = 1.8, 0.7 Hz, 1H), 7.73 – 7.70 (m, 3H), 7.69 (d, <i>J</i> = 7.2 Hz, 3H), 7.67 – 7.65 (m, 1H), 7.60 (dd, <i>J</i> = 8.2, 7.2 Hz, 2H), 7.55 – 7.52 (m, 2H), 7.49 (dd, <i>J</i> = 8.3, 7.0 Hz, 3H), 7.43 (dd, <i>J</i> = 8.6, 0.7 Hz, 1H), 7.39 – 7.30 (m, 3H), 6.12 (d, <i>J</i> = 3.5 Hz, 1H), 5.20 (d, <i>J</i> = 3.5 Hz, 1H), 1.22 (s, 9H).
$^{13}$C NMR (126 MHz, Chloroform-$d$) δ 195.7, 141.6, 141.1, 140.7, 137.9, 137.2, 133.9, 133.7, 130.4, 129.9, 129.1, 128.8, 127.8, 127.3, 126.9, 126.7, 126.0, 124.1, 123.0, 118.9, 110.8, 110.2, 101.6, 63.5, 55.9, 22.6.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for C$_{36}$H$_{32}$IN$_2$O$_2$S$^+$ 683.1224; Found: 683.1221.

$[^{25}]D$: -94.4 (c 0.5, Chloroform).

4. Scale-up synthesis and synthetic applications

Scale-up synthesis

To a Schlenk tube added $[\text{RhCl(COD)}]_2$ (35 mg, 0.0125 mmol, 2.5 mol %) , N-Sulfinyl imine (1h) (3 mmol), arylboronic acid (2a) (6 mmol) and KOAc (6 mmol) under nitrogen atmosphere. Then toluene (3 mL) and water (1 mL) were added and the mixture was stirred at 30 °C for 3 h. The reaction mixture was diluted with EtOAc. The organic layer was washed with saturated ammonium chloride aqueous solution and brine. The aqueous layer was extracted with EtOAc. The combined organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography (eluent: petroleum ether/EtOAc 3: 1) to isolate the product 3h (1074 mg, >98: 2 dr) as yellow oil.

Synthetic applications

The synthesis of $(R)$-$N$-(2-(4-iodophenyl)-1-(4-methoxyphenyl)-2-oxoethyl)-2-methylpropane-2-sulfonamide (4)

In a Schlenk tube, $m$-CPBA (0.4 mmol, 2 equiv) was added to the solution of 3h (0.2 mmol) in DCM (1.5 mL) at 0 ºC. The mixture was stirred for 1 h at rt and subsequently quenched with a aqueous solution containing both sodium bicarbonate and sodium metabisulfite. The reaction mixture was poured into a separatory funnel containing a mixture of water and diethyl ether. The organic layer was separated, washed with brine, dried over Na$_2$SO$_4$, and filtered. Solvent was removed under reduced pressure and dried in
vacuo to provide the crude product. The crude reaction product was purified by flash column chromatography (PE/EA, 4: 1) to get product 4. 3

\[(R)-N-(2-\text{4-iodophenyl})-1-(\text{4-methoxyphenyl})-2\text{-oxoethyl)-2-methylpropane-2-sulfonamide (4)}\]

![Image of compound 4]

White solid (mp: 150-153 °C), yield: 90% (87 mg), \(R_f = 0.5\) (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v).

\(^1\)H NMR (500 MHz, Chloroform-d) \(\delta\) 7.73 (d, \(J = 8.6\) Hz, 2H), 7.61 (d, \(J = 8.6\) Hz, 2H), 7.21 (d, \(J = 8.8\) Hz, 2H), 6.81 (d, \(J = 8.7\) Hz, 2H), 6.03 (d, \(J = 7.3\) Hz, 1H), 5.68 (dd, \(J = 7.3, 1.3\) Hz, 1H), 3.73 (s, 3H), 1.26 (s, 9H).

\(^{13}\)C NMR (126 MHz, Chloroform-d) \(\delta\) 195.1, 159.7, 138.0, 133.2, 130.3, 129.3, 128.9, 114.7, 102.1, 61.7, 59.8, 55.2, 24.0.

HRMS (ESI) m/z: [M+H]\(^+\) Calcd. for C\(_{19}\)H\(_{23}\)INO\(_4\)S\(^+\) 488.0387; Found: 488.0383.

HPLC analysis: DAICEL CHIRALCEL OD-H, hexane/isopropanol = 90/10, 1 mL/min, \(\lambda = 254\) nm, \(t_R\) (minor) = 3.993 min, \(t_R\) (major) = 18.541 min, 95% ee.

\(\{\alpha\}\)^{25D}: -12.00 (c 0.5, Chloroform).
The synthesis of \((R)-N-((1R,2S)-2-hydroxy-2-(4-iodophenyl)-1-(4-methoxyphenyl)ethyl)-2-methylpropane-2-sulfinamide\) (5)

To a Schlenk tube added 3h (94.2 mg, 0.2 mmol, 1.0 equiv) and MeOH (0.5 mL, 0.4 M). The resulting solution was cooled to 0 °C and NaBH₄ was added in one portion (9 mg, 0.24 mmol, 1.2 equiv). The reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was diluted with EtOAc (3 mL) and was washed with distilled water. The aqueous layer was extracted with EtOAc (3 x 10 ml), and the combined organic extracts were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography (eluent: petroleum ether/EtOAc 2: 1) to isolate the product 5 (74 mg, >98: 2 dr) as white solid.⁴
(R)-N-((1R,2S)-2-hydroxy-2-(4-iodophenyl)-1-(4-methoxyphenyl)ethyl)-2-methylpropane-2-sulfanamide (5)

White solid (mp: 210-214 °C), yield: 78% (73 mg), Rf = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 2: 1, v/v).

\(^1\)H NMR (500 MHz, Chloroform-d) δ 7.51 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.4 Hz, 2H), 4.97 (d, J = 4.1 Hz, 1H), 4.68 (dd, J = 6.3, 4.0 Hz, 1H), 4.06 (d, J = 6.5 Hz, 1H), 3.77 (s, 3H), 1.19 (s, 9H).

\(^13\)C NMR (126 MHz, Chloroform-d) δ 159.0, 138.6, 136.7, 129.5, 129.1, 128.9, 113.5, 93.3, 76.8, 64.4, 56.0, 55.1, 22.7.

HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₁₉H₂₃INO₄S⁺ 474.0594; Found: 474.0597.

\([\alpha]^{25}_D\): -58.00 (c 0.5, Chloroform).

The synthesis of N-((1R, 2S)-2-hydroxy-2-(4-iodophenyl)-1-(4-methoxyphenyl)ethyl)-2-methylpropane-2-sulfonamide (6)

To a Schlenk tube add m-CPBA (2 equiv) was added to the solution of 5 in anhydrous DCM (1.5 mL) at 0 °C. The mixture was stirred for 1 h at rt and subsequently quenched with a aqueous solution containing both sodium bicarbonate and sodium metabisulfite. The reaction mixture was poured into a separatory funnel containing a mixture of water and diethyl ether. The organic layer was separated, washed with brine, dried over Na₂SO₄, and filtered. Solvent was removed under reduced pressure and dried in vacuo to provide the crude product. The crude reaction product was purified by flash column chromatography (PE/EA, 4: 1) to get product 6.³
N-((1R, 2S)-2-hydroxy-2-(4-iodophenyl)-1-(4-methoxyphenyl)ethyl)-2-methylpropane-2-sulfonamide (6)

![Chemical Structure](image)

White solid (mp: 179-181 °C), yield: 83% (60 mg), Rf = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 2: 1, v/v).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.52 (d, $J = 8.4$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 6.75 (d, $J = 8.7$ Hz, 2H), 6.73 (d, $J = 8.3$ Hz, 2H), 5.19 (d, $J = 10.0$ Hz, 1H), 5.08 (t, $J = 4.1$ Hz, 1H), 4.65 (dd, $J = 10.0$, 3.5 Hz, 1H), 3.77 (s, 3H), 3.17 (d, $J = 4.8$ Hz, 1H), 1.24 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 159.0, 139.2, 137.0, 129.0, 128.5, 128.4, 113.5, 93.4, 77.4, 63.1, 60.0, 55.1, 24.0.

HRMS (ESI) m/z: [M+H]$^+$ Calcd. for C$_{19}$H$_{23}$INO$_4$S$^+$ 490.0543; Found: 490.0539.

$[\alpha]_{25}^D$: 29.20 (c 0.5, Chloroform).

3r (63 mg, 0.2 mmol, 1.0 equiv) was taken up in MeOH (1.3 mL, 0.15 M) and was treated with 4.0 M HCl in dioxane (0.25 mL, 5.0 equiv. HCl) at room temperature for 3 h. The reaction mixture was concentrated in vacuo, and the amine hydrochloride was precipitated with dry diethyl ether. The precipitate was collected by filtration and washed with diethyl ether to yield the amine hydrochloride (40 mg, 80%) as white solid.$^4$

(R)-2-amino-1,2-diphenylethan-1-one hydrochloride (7)

![Chemical Structure](image)

White solid (mp: >230 °C), yield: 70% (34 mg), Known compound.$^5$

$^1$H NMR (500 MHz, Methanol-d$_4$) $\delta$ 8.02 – 7.97 (d, $J = 7.5$ Hz, 2H), 7.60 (t, $J = 7.5$ Hz, 1H), 7.54 – 7.50 (m, 2H), 7.49 – 7.42 (m, 5H), 6.22 (s, 1H).

$^{13}$C NMR (151 MHz, Methanol-d4) $\delta$ 194.0, 135.4, 134.3, 133.4, 131.1, 130.7, 130.1, 129.8, 129.8, 60.5.
HRMS (ESI) m/z: [M+Na]^+ Calcd. for C_{14}H_{14}ClNNaO^+ 270.0656; Found: 270.0660.

[α]^{25}D: -102.6 (c 0.5, CH₃OH).

**Benzyl (R)-(2-oxo-1,2-diphenylethyl)carbamate (8)**

In a Schlenk tube, 2-Oxo-1,2- diphenylethan-1-aminium chloride 7 (50 mg, 0.2 mmol, 1.0 equiv) was suspended in tetrahydrofuran (THF, 1 mL) and cooled to 0 °C in an ice–salt bath. Triethylamine (131 mg, 180 μl, 1.3 mmol, 6.5 equiv) was added dropwise to the reaction mixture and stirred at the same temperature for 30 min. During the addition of triethylamine, the initially cloudy reaction mixture became clear. To the reaction mixture, benzyl chloroformate (34 mg, 0.4 mmol, 2.0 equiv) in THF (1 mL) was added dropwise and the resulting reaction mixture was stirred at 0 °C for 30 min followed by overnight stirring at rt. Once the reaction was complete (assessed by TLC), water (15 mL) and DCM (5 mL) were added and the organic layer was separated. The aqueous layer was extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO₄, and concentrated under reduced pressure to give the crude product. The crude material was purified by column chromatography (PE/EA, 5: 1) to afford product 8 as a white solid (0.410 g, 1.31 mmol, 94%).

**benzyl (R)-(2-oxo-1,2-diphenylethyl)carbamate (8)**

White solid (mp: 92-94 °C), yield: 94% (64 mg), Rₕ = 0.4 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 5: 1, v/v). Known compound.

**1H NMR** (600 MHz, Chloroform-d) δ 8.03 – 7.90 (m, 2H), 7.57 – 7.46 (m, 1H), 7.44 – 7.37 (m, 4H), 7.35 (d, J = 4.4 Hz, 4H), 7.33 – 7.30 (m, 4H), 7.27 (d, J = 7.4 Hz, 1H), 6.41 (d, J = 7.4 Hz, 1H), 6.34 (d, J = 7.4 Hz, 1H), 5.39 – 4.68 (m, 2H).

**HPLC analysis:** DAICEL CHIRALCEL OD-H, hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, tₘ (major) = 18.23 min, tₘ (minor) = 20.82 min, 98% ee.

[α]^{25}D: -162.2 (c 0.5, Chloroform).
To a Schlenk tube added 3r (126 mg, 0.4 mmol, 1.0 equiv) in MeOH (0.5 mL, 0.4 M). The resulting solution was cooled to 0 °C and NaBH₄ was added in one portion (18 mg, 0.48 mmol, 1.2 equiv). The
reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was diluted with EtOAc (3 mL) and was washed with distilled water. The aqueous layer was extracted with EtOAc (3 x 10 ml), and the combined organic extracts were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography (eluent: petroleum ether/EtOAc 2:1) to isolate the product 9.⁴

(R)-N-((1R,2S)-2-hydroxy-1,2-diphenylethyl)-2-methylpropane-2-sulfinamide (9)

![structure](image)

White solid (mp: >320 °C), yield: 80% (101 mg), Rf = 0.2 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 2: 1, v/v).

¹H NMR (600 MHz, Chloroform-d) δ 7.30 – 7.27 (m, 3H), 7.24 – 7.21 (m, 3H), 7.09 (dd, J = 7.5, 2.1 Hz, 2H), 6.99 – 6.95 (m, 2H), 5.07 (d, J = 4.3 Hz, 1H), 4.78 (dd, J = 7.2, 4.3 Hz, 1H), 3.88 (d, J = 7.3 Hz, 1H), 1.21 (s, 9H).

¹³C NMR (151 MHz, Chloroform-d) δ 138.45, 138.40, 128.22, 127.96, 127.88, 127.69, 127.61, 127.24, 77.62, 65.53, 56.02, 22.71.

HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₁₈H₂₄N₂O₂S⁺ 318.1522; Found: 318.1516. 

[α]⁺⁺ D: -87.9 (c 0.5, Chloroform).

To the solution of t-butanesulfinamide 9 (0.32 mmol) in MeOH (0.42 ml) was added HCl in 1,4-dioxane 4.0 M (0.64 mmol, 0.16 ml). The solution was stirred for 1 h, then Et₂O was added. The precipitate was filtered off and washed with diethyl ether to afford the amine hydrochloride. The amine hydrochloride was basified with 1 M NaOH (30 ml) and extracted with EtOAc (15 ml x 2). The EtOAc layers were combined, washed with water and brine, dried over Na₂SO₄, and concentrated in vacuo. 10 was obtained as a white solid.

(1S,2R)-2-amino-1,2-diphenylethan-1-ol (10)

![structure](image)

white solid (mp: 142 – 145 °C), yield: 80% (54 mg), Rf = 0.3 (silica gel, EA), column chromatography (silica gel, PE: DCM = 1: 1, v/v). Known compound.⁷

¹H NMR (500 MHz, Chloroform-d) δ 7.32 – 7.26 (m, 6H), 7.26 – 7.20 (m, 4H), 4.73 (d, J = 6.3 Hz, 1H), 4.15 (d, J = 6.3 Hz, 1H).
**HPLC analysis:** DAICEL CHIRALCEL OJ-H, hexane/isopropanol = 95/5, 1mL/min, $\lambda = 254$ nm, Absolute configurations were determined by HPLC compared with commercial (1S,2R)-2-amino-1,2-diphenylethan-1-ol

HPLC diagram of commercial (1S, 2R) - 2-amino-1,2-diphenylethane-1-alcohol
(R)-2-methyl-N-((R)-2-(1-methyl-1H-pyrrol-2-yl)-2-oxo-1-phenylethyl)propane-2-sulfinamide

Following the general procedure 2 on 0.2 mmol scale, yellow oil liquid, yield: 70% (43 mg), R<sub>f</sub> = 0.3 (silica gel, PE: EA = 3: 1, v/v), column chromatography (silica gel, PE: EA = 3: 1, v/v).

<sup>1</sup>H NMR (500 MHz, Chloroform-<d>) δ 7.38 – 7.34 (m, 2H), 7.33 – 7.29 (m, 2H), 7.27 – 7.23 (m, 1H), 6.97 (dd, J = 4.2, 1.6 Hz, 1H), 6.79 (t, J = 2.0 Hz, 1H), 6.07 (dd, J = 4.3, 2.4 Hz, 1H), 5.68 (d, J = 5.0 Hz, 1H), 5.08 (d, J = 5.0 Hz, 1H), 3.91 (s, 3H), 1.20 (s, 9H).

<sup>1</sup>C NMR (126 MHz, Chloroform-<d>) δ 186.1, 139.6, 132.2, 128.8, 128.2, 128.0, 127.9, 121.0, 108.7, 63.2, 55.9, 37.7, 22.6.

HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd. for C<sub>17</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> 319.1475; Found: 319.1468.

[α]<sup>25</sup>D: -188.6 (c 0.5, Chloroform).
(R)-2-amino-1-(1-methyl-1H-pyrrol-2-yl)-2-phenylethanol-1-one hydrochloride (14)

![Chemical Structure](image)

13 (50.0 mg, 0.2 mmol, 1.0 equiv) was taken up in MeOH (1.3 mL, 0.15 M) and was treated with 4.0 M HCl in dioxane (0.25 mL, 5.0 equiv. HCl) at room temperature for 3 h. The reaction mixture was concentrated in vacuo, and the amine hydrochloride was precipitated with dry diethyl ether. The precipitate was collected by filtration and washed with diethyl ether to yield the amine hydrochloride (40 mg, 80%) as gray solid.\(^4\)

**HPLC analysis:** DAICEL CHIRALCEL OZ-3, hexane/isopropanol = 85/15, 1 mL/min, \(\lambda = 254\) nm, \(t_R\) (major) = 20.9 min, \(t_R\) (minor) = 26.1 min, >99% ee. (The ee value was determined after an amidation with benzyl chloroformate) \(^5\)

**\(^1\)H NMR** (500 MHz, Methanol-\(d_4\)) \(\delta 7.58 – 7.50\) (m, 2H), \(7.48 – 7.36\) (m, 3H), \(7.10\) (dd, \(J = 4.3, 1.7\) Hz, 1H), \(7.07\) (t, \(J = 2.0\) Hz, 1H), \(6.12\) (dt, \(J = 4.3, 2.1\) Hz, 1H), \(5.83\) (d, \(J = 1.8\) Hz, 1H), \(3.96\) (d, \(J = 1.7\) Hz, 3H).

In a Schlenk tube, hydrochloride 14 (50 mg, 0.2 mmol, 1.0 equiv) was suspended in DCM (10 ml) and cooled to 0 °C in an ice−salt bath. Triethylamine (131 mg, 180 \(\mu\)l, 1.3 mmol, 6.5 equiv) was added dropwise to the reaction mixture and stirred at the same temperature for 30 min. During the addition of triethylamine, the initially cloudy reaction mixture became clear. To the reaction mixture, Benzyl chloroformate (34 mg, 0.4 mmol, 2.0 equiv) in DCM (1 mL) was added dropwise and the resulting reaction mixture was stirred at 0 °C for 30 min followed by overnight stirring at rt. Once the reaction was complete (assessed by TLC), water (15 mL) and DCM (15 mL) were added and the organic layer was separated. The aqueous layer was extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over \(\text{Na}_2\text{SO}_4\), and concentrated under reduced pressure to give the crude product. The crude material was purified by column chromatography (PE/EA, 5: 1) to afford product as colorless liquid.\(^5\)
**H NMR** (500 MHz, Chloroform-\(d\)) δ 7.45 – 7.41 (m, 2H), 7.34 (d, \(J = 4.4\) Hz, 4H), 7.31 (d, \(J = 7.6\) Hz, 3H), 7.28 – 7.23 (m, 1H), 7.07 (dd, \(J = 4.3, 1.7\) Hz, 1H), 6.80 (t, \(J = 2.0\) Hz, 1H), 6.33 (d, \(J = 7.6\) Hz, 1H), 6.10 (dd, \(J = 4.3, 2.4\) Hz, 1H), 6.04 (d, \(J = 7.5\) Hz, 1H), 5.24 – 4.95 (dd, \(J = 45.1\) Hz, \(J = 12.3\) Hz, 2H), 3.91 (s, 3H).

**13C NMR** (101 MHz, Chloroform-\(d\)) δ 185.3, 155.4, 138.8, 136.4, 132.2, 128.9, 128.5, 128.5, 128.3, 128.0, 127.58, 126.9, 121.1, 108.8, 66.8, 59.9, 37.6.

**HRMS (ESI) m/z:** [M+H]+ Calcd. for C_{21}H_{21}N_{2}O_{3}+ 349.1547; Found: 349.1540. 

\([\alpha]^{25}_{D}\): -176.0 (c 0.5, Chloroform).

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6. Copies of $^1$H, $^{13}$C and $^{19}$F Spectra

$^1$H NMR spectrum of 1a

$^1$H NMR spectrum of 1b
$^{13}$C NMR spectrum of 1b

1b

$^1$H NMR spectrum of 1c

1c
$^{13}$C NMR spectrum of 1c

$^1$H NMR spectrum of 1d
$^{13}$C NMR spectrum of 1d

1d

$^1$H NMR spectrum of 1e

1e
$^{13}$C NMR spectrum of 1e

$^1$H NMR spectrum of 1f
$^{13}$C NMR spectrum of 1f

$^1$H NMR spectrum of 1g
$^{13}$C NMR spectrum of 1g

$^1$H NMR spectrum of 1h
$^{13}$C NMR spectrum of 1h

1h

$^1$H NMR spectrum of 1i

1i
$^{13}$C NMR spectrum of 1i

$^1$H NMR spectrum of 1j
$^{13}$C NMR spectrum of 1j

1j

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$^{13}$C NMR spectrum of 1k

$^1$H NMR spectrum of 1l
$^{13}$C NMR spectrum of 1l

$^{19}$F NMR spectrum of 1l
$^1$H NMR spectrum of 1m

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$^{19}$F NMR spectrum of 1m

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$^{13}$C NMR spectrum of 1n

$^1$H NMR spectrum of 1o
$^{13}$C NMR spectrum of 1o

1o

$^1$H NMR spectrum of 1p

1p
$^{13}$C NMR spectrum of 1p

$^1$H NMR spectrum of 1q
$^{13}$C NMR spectrum of 1q

![13C NMR spectrum of 1q](image)

$^1$H NMR spectrum of 3a

![$^1$H NMR spectrum of 3a](image)
$^{13}$C NMR spectrum of 3a

$^1$H NMR spectrum of 3b
$^{13}$C NMR spectrum of 3b

$^1$H NMR spectrum of 3c
$^{13}$C NMR spectrum of 3c

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$^1\text{H}$ NMR spectrum of 3f
$^{13}$C NMR spectrum of 3f

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$^1$H NMR spectrum of 3i
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$^1$H NMR spectrum of 3o
$^{13}$C NMR spectrum of 3o

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$^{13}$C NMR spectrum of 3t

$^1$H NMR spectrum of 3u
$^{13}$C NMR spectrum of 3u

$^1$H NMR spectrum of 3v
$^{13}$C NMR spectrum of 3v

\[
\text{Ph} \quad \text{N} \quad \text{SO}\]
\[
\text{O} \quad \text{Me}
\]

3v

$^1$H NMR spectrum of 3w

\[
\text{Ph} \quad \text{N} \quad \text{SO}\]
\[
\text{O} \quad \text{Me}
\]

3w
$^1$H NMR spectrum of 3x

$^{13}$C NMR spectrum of 3w
$^{13}$C NMR spectrum of 3x

![$^{13}$C NMR spectrum of 3x](image)

$^1$H NMR spectrum of 3y

![$^1$H NMR spectrum of 3y](image)
$^{13}$C NMR spectrum of 3y

$^1$H NMR spectrum of 3z
$^{13}$C NMR spectrum of $3z$

$^1$H NMR spectrum of $3aa$
$^{13}$C NMR spectrum of 3aa

$^1$H NMR spectrum of 3ab
$^{13}$C NMR spectrum of 3ab

$^1$H NMR spectrum of 3ac
$^{13}$C NMR spectrum of 3ac

$^1$H NMR spectrum of 3ad
$^{13}$C NMR spectrum of 3ad

$^1$H NMR spectrum of 3ae
$^{13}$C NMR spectrum of 3ae

$^1$H NMR spectrum of 3af
$^{13}$C NMR spectrum of 3af

19F NMR spectrum of 3af
$^1$H NMR spectrum of 3ag

$^{13}$C NMR spectrum of 3ag
**$^1$H NMR spectrum of 3ah**

![H NMR spectrum of 3ah](image)

**$^1$F NMR spectrum of 3ag**

![F NMR spectrum of 3ag](image)
$^{13}$C NMR spectrum of 3ah

$^1$H NMR spectrum of 3ai
$^{13}$C NMR spectrum of 3ai

[Diagram of 3ai]

$^1$H NMR spectrum of 3aj

[Diagram of 3aj]
$^{13}$C NMR spectrum of 3aj

$^1$H NMR spectrum of 3ak
$^{13}$C NMR spectrum of 3ak

![13C NMR spectrum of 3ak](image)

$^1$H NMR spectrum of 3al

![$^1$H NMR spectrum of 3al](image)
$^{13}$C NMR spectrum of 3a1

$^1$H NMR spectrum of 3am
$^{13}$C NMR spectrum of 3am

$^1$H NMR spectrum of 4
$^{13}$C NMR spectrum of 4

$^1$H NMR spectrum of 5
$^{13}$C NMR spectrum of 5

$^1$H NMR spectrum of 6
$^{13}$C NMR spectrum of 6

![6, $^{13}$C NMR spectrum]

$^1$H NMR spectrum of 7

![7, $^1$H NMR spectrum]
$^{13}$C NMR spectrum of 7

$^{1}$H NMR spectrum of 8
$^1$H NMR spectrum of 10

$^1$H NMR spectrum of 13
$^{13}$C NMR spectrum of 13

$^1$H NMR spectrum of 14
$^{1}$H NMR spectrum

$^{13}$C NMR spectrum