Copper-Catalyzed Alkene Diamination: Synthesis of Chiral 2-Aminomethyl Indolines and Pyrrolidines

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Supporting Information I

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General experimental information:
All reagents (including reagent grade solvents MeOH, EtOAc and anhydrous, sureseal 1,2-
dichloroethane) were used out of the bottle as purchased from the supplier without further
purification unless otherwise noted. Anhydrous copper(II) triflate, copper(II) 2-ethylhexanoate,
2,2'-methylenebis[(4R,5S)-4,5-diphenyl-2-oxazoline] and 2,2'-methylenebis[(4R)-4-phenyl-2-
oxazoline] were used as supplied from commercial vendors. Copper(II) triflate was stored and
weighed in a glovebox. Dry MeOH and dry PhCF₃ were distilled over CaH₂. Anhydrous
CH₂Cl₂, benzene, THF, Et₂O and toluene were further purified with a commercial solvent
purification system equipped with alumina-filled columns and under argon. MnO₂ for the
experiments was purchased as activated, ca. 85%, <5 μm. KMnO₄ for the experiments was
purchased as crystal, 99.6%. ¹H NMR spectra were recorded in CDCl₃ (using 7.26 ppm for
reference of residual CHCl₃) at 300, 400 or 500 MHz unless otherwise noted. ¹³C NMR spectra
were recorded in CDCl₃ (using 77.0 ppm as internal reference) at 75.5, 100.6, or 125.7 MHz
unless otherwise noted. IR spectra were taken neat using a Nicolet-Impact 420 FTIR. Wave
numbers in cm⁻¹ are reported for characteristic peaks. High resolution mass spectra were
obtained at SUNY Buffalo’s mass spec. facility on a ThermoFinnigan MAT XL spectrometer.
Optical rotations were obtained using a JASCO P-2000 Polarimeter fitted with a micro cell with
a 100 mm path length. The X-ray crystal structure of 2j (CCDC = 982216) was solved by
William W. Brennessel at the Crystallographic Facility at the Chemistry Department of the
University of Rochester. Melting points are reported as uncorrected.

2-Allylaniline (10)
2-Allylaniline 10 was synthesized from N-allylaniline 9 as previously reported.¹ N-allylaniline
(9.82 g, 74.0 mmol, 1 equiv) was injected into a large pressure tube equipped with a magnetic
stir bar and sealed with a septum under an argon atmosphere, followed by the addition of xylenes
(147 mL) via syringe. The pressure tube was cooled to -78 °C. Boron trifluoride etherate (11.2
mL, 88.0 mmol, 1.2 equiv) was added dropwise via syringe. The pressure tube was sealed with a
cap and warmed to rt, then to 180 °C in an oil bath and stirred for 5.5 h. The reaction was cooled
to 0 °C in an ice bath and quenched with NaOH solution (2 M, 150 mL). The organic layer was
separated, and the aqueous layer was extracted with Et₂O (2x75mL). The organic layers were
combined and dried over MgSO₄ and concentrated in vacuo. The crude 2-allylaniline 10 (7.0 g)
was obtained as a brown oil (71% yield) and was used directly for the next step. ¹H NMR (400
MHz, CDCl₃) δ 7.08-7.05 (m, 2H), 6.76 (t, J=16.0 Hz, 1H), 6.69 (d, J=8.0 Hz, 1H), 6.00-5.93
(m, 1H), 5.15-5.09 (m, 2H), 3.67 (s, 2H), 3.32 (d, J=6.4 Hz, 2H). ¹H NMR matched the
previously reported data.¹
Representative Procedure A for synthesis of sulfonamides

N-(2-Allylphenyl)methanesulfonylamide (1a)
The known sulfonamide 1a was synthesized as previously reported. 2 2-Allylaniline 10 (1.26 g, 9.46 mmol, 1 equiv) was dissolved in dry CH₂Cl₂ (30 mL) in a 250 mL round bottom flask under an argon atmosphere, and was cooled to 0 °C in an ice bath. The solution was stirred with a magnetic stir bar and pyridine (2.32 mL, 28.4 mmol, 3 equiv) was syringed in dropwise. Methanesulfonyl chloride (0.880 mL, 11.4 mmol, 1.2 equiv) was then syringed into the flask and the reaction was stirred at 0 °C and gradually allowed to warm to rt. After 24 h, the reaction was quenched with 30 mL of water and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (2x30 mL), and the organic layers were combined and washed with 1M HCl (90 mL) and with brine (90 mL), then dried over Na₂SO₄, and concentrated in vacuo. Flash chromatography of the resulting crude oil on SiO₂ (20-40% Et₂O in hexanes gradient) afforded sulfonamide 1a as a brown oil in 88% yield (1.76 g, 8.30 mmol). ¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, J=8.4 Hz, 2H), 7.31-7.18 (m, 3H), 6.39 (s, 1H), 5.96-5.95 (m, 1H), 5.20 (dd, J=10.0, 1.2 Hz, 1H), 5.08 (dd, J=17.2, 2 Hz, 1H), 3.44 (d, J = 6.0 Hz, 2H), 3.01 (s, 3H). ¹H NMR matched the previously reported data. 2

N-(2-Allyl-phenyl)-4-methyl-benzenesulfonamide (1b)
The known sulfonamide 1b was obtained from as a white solid using sulfonylation of 2-allylaniline with toluenesulfonyl chloride in 62% yield (1.33 g). ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J=8.0 Hz, 2H), 7.41 (d, J=8.0 Hz, 1H), 7.26-7.18 (m, 3H), 6.39 (s, 1H), 5.96-5.95 (m, 1H), 5.20 (dd, J=10.0, 1.2 Hz, 1H), 5.08 (dd, J=17.2, 2 Hz, 1H), 3.44 (d, J = 6.0 Hz, 2H), 3.01 (s, 3H). The ¹H NMR matched the previously reported data. 2

N-(2-Allylphenyl)(phenyl)methanesulfonamide (1c)
Sulfonamide 1c (495 mg, 46% yield) was obtained as a white solid from 500 mg of 10 using Procedure A, except that the solution was treated with α-toluensulfonyl chloride. Data for compound 1c: mp 55-58 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, J=8.5 Hz, 1H), 7.39-7.32 (m, 3H), 7.29-7.23 (m, 3H), 7.18-7.11 (m, 2H), 6.25 (s, 1H), 5.80-5.72 (m, 1H), 5.04
(dd, $J=10.5$, 1.5 Hz, 1H), 4.90 (dd, $J=17.0$, 1.5 Hz, 1H), 4.39 (s, 2H), 3.11 (d, $J=6.5$ Hz, 2H);
$^{13}$C NMR (75.5 MHz, CDCl$_3$) δ 135.7, 135.2, 130.8, 130.7, 129.2, 128.9, 128.8, 128.6, 128.0,
125.1, 120.2, 117.4, 57.8, 36.4; IR (neat, thin film) ν 3288, 3065, 3034, 3007, 2979, 2928, 2853,
2464, 2309, 1955, 1885, 1813, 1637, 1603, 1585, 1494, 1455, 1402, 1337, 1277, 1232, 1201,
1153, 1131, 1099, 1074, 1048, 1031, 999 cm$^{-1}$; HRMS (ESI) calcd for C$_{16}$H$_{17}$O$_2$N$_1$Na$_1$S$_1$
[M+Na]$^+$ 310.0872, found 310.0864.

$N$-(2-Allylphenyl)cycloproanesulfonamide (1d)
Sulfonamide 1d (79 mg, 88% yield) was obtained as a brown oil from 50 mg of 10 using Procedure A, except that the solution was treated with cyclopropanesulfonyl chloride and the reaction continued for 72 h instead of 24 h.
Data for compound 1d: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.55 (d, $J=8.6$ Hz, 1H), 7.29-7.18 (m,
3H), 6.33 (s, 1H), 6.00-5.93 (m, 1H), 5.19 (dd, $J=10.0$, 1.6 Hz, 1H), 5.08 (dd, $J=17.2$, 1.6 Hz,
1H), 3.48 (d, $J=5.6$ Hz, 2H), 2.50-2.46 (m, 2H), 1.17-1.16 (m, 2H), 0.95 (dd, $J=7.6$, 2.0 Hz, 2H);
$^{13}$C NMR (75.5 MHz, CDCl$_3$) δ 135.7, 135.3, 132.1, 130.7, 127.8, 126.3, 124.3, 117.1, 36.5,
30.2, 5.8; IR (neat, thin film) ν 3280, 3077, 3016, 2978, 2918, 2852, 1638, 1604, 1584, 1493,
1455, 1398, 1331, 1234, 1189, 1151, 1096, 1069, 1043, 998 cm$^{-1}$; HRMS (ESI) calcd for
C$_{12}$H$_{15}$O$_2$N$_1$Na$_1$S$_1$ [M+Na]$^+$ 260.0716, found 260.0721.

Representative Procedure B for synthesis of sulfonamides

$N$-(2-Allylphenyl)-3,5-di-$t$-butyl-4-methoxybenzenesulfonamide (1e)
The known sulfonamide 1e was obtained from sulfonylation of 2-allylaniline with 3,5-bis(1,1-
dimethylethyl)-4-methoxy-benzenesulfonyl chloride, which was synthesized as reported by Toru
and coworkers.$^3$ 2-Allylaniline (0.847 g, 6.40 mmol) was dissolved in 40 mL of dry methylene
chloride and cooled to 0 °C in an ice water bath. The solution was stirred with a magnetic stir bar
and treated with pyridine (2.30 mL, 19.1 mmol, 3 equiv), 3,5-bis(1,1-dimethylethyl)-4-methoxy-
benzenesulfonyl chloride (2.43 g, 7.60 mmol, 1.2 equiv), and 4-dimethylaminopyridine (78 mg,
0.64 mmol, 0.1 equiv). The mixture stirred overnight, warming up to rt. The mixture was diluted
with 40 mL of water and extracted with CH$_2$Cl$_2$ (3×40 mL). The combined organic layers were
washed with brine, dried over MgSO$_4$, and concentrated in vacuo. Flash chromatography of the
resulting crude product on SiO$_2$ (5-20% ether in hexanes gradient) afforded sulfonamide 1e as a
white solid in 67% yield (1.77 g).
Data for compound 1e: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (d, $J$=7.6 Hz, 1H), 7.49 (s, 2H), 7.28-7.23 (m, 1H), 7.13 (t, $J$=16.4 Hz, 1H), 7.04 (d, $J$=8 Hz, 1H), 6.40 (s, 1H), 5.70-5.64 (m, 1H), 5.08 (dd, $J$=8.4, 1.6 Hz, 1H), 4.90 (dd, $J$=15.6, 1.6 Hz, 1H), 3.66 (s, 3H), 2.80 (d, $J$=6 Hz, 2H), 1.31 (s, 18H). $^1$H NMR matched the previously reported data.\(^4\)

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\begin{align*}
\text{N-(2-Allyl-4-methoxyphenyl)-3,5-di-} & \text{tert-butyl-4-methoxybenzenesulfonamide (1f)} \\
\text{Known sulfonamide 1f (397 mg, 48% yield) was obtained as a white solid from 250 mg of 2-allyl-4-methoxyaniline using Procedure B.} \\
\text{Data for compound 1f: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.46 (s, 2H), 7.33 (d, $J$=9.0 Hz, 1H), 6.76 (d, $J$=9.0 Hz, 1H), 6.58 (s, 1H), 6.20 (s, 1H), 5.66-5.60 (m, 1H), 5.05 (dd, $J$=7.0, 1.5 Hz, 1H), 4.89 (dd, $J$=15.5, 1.5 Hz, 1H), 3.76 (s, 3H), 3.67 (s, 3H), 2.72 (d, $J$=6.5 Hz, 2H), 1.32 (s, 18H). $^1$H NMR matched the previously reported data.} \quad \text{\(^4\)}
\end{align*}
\]

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\begin{align*}
\text{N-(2-Allyl-4-bromophenyl)-3,5-di-} & \text{tert-butyl-4-methoxybenzenesulfonamide (1g)} \\
\text{Sulfonamide 1g (280 mg, 47% yield) was obtained as a white solid from 160 mg of 2-allyl-4-bromoaniline using Procedure B.} \\
\text{Data for compound 1g: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 (s, 2H), 7.38-7.37 (m, 2H), 7.19 (s, 1H), 6.34 (s, 1H), 5.67-5.60 (m, 1H), 5.12 (dd, $J$=7.2, 1.6 Hz, 1H), 4.92 (dd, $J$=14.0, 1.6 Hz, 1H), 3.67 (s, 3H), 2.79 (d, $J$=6.0 Hz, 2H), 1.33 (s, 18H). $^1$H NMR matched the previously reported data.} \quad \text{\(^4\)}
\end{align*}
\]

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\begin{align*}
\text{N-(2-Allyl-4-chlorophenyl)-3,5-di-} & \text{tert-butyl-4-methoxybenzenesulfonamide (1h)} \\
\text{Sulfonamide 1h (322 mg, 60% yield) was obtained as a white solid from 160 mg of 2-allyl-4-chloroaniline using Procedure B.}
\end{align*}
\]
Data for compound 1h: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 (s, 2H), 7.44 (d, $J$=8.8 Hz, 1H), 7.22 (d, $J$=8.8 Hz, 1H), 7.04 (s, 1H), 6.36 (s, 1H), 5.65-5.60 (m, 1H), 5.11 (dd, $J$=8.4, 1.2 Hz, 1H), 4.91 (dd, $J$=16.0, 1.2 Hz, 1H), 3.67 (s, 3H), 2.79 (d, $J$=5.6 Hz, 2H), 1.33 (s, 18H). $^1$H NMR matched the previously reported data.$^4$

$N$-(2-Allyl-4-fluorophenyl)-3,5-di-tert-butyl-4-methoxybenzenesulfonamide (1i)

Sulfonamide 1i (360 mg, 55% yield) was obtained as a brown solid from 200 mg of 2-allyl-4-fluoroaniline using Procedure B.

Data for compound 1i: mp 167-171 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.48 (s, 2H), 7.43 (dd, $J$=8.9, 5.4 Hz, 1H), 6.95 (apparent td, $J$=8.1, 3.0 Hz, 1H), 6.78 (dd, $J$=9.3, 3.0 Hz, 1H), 6.29 (s, 1H), 5.66-5.55 (m, 1H), 5.10 (dd, $J$=9.9, 1.2 Hz, 1H), 4.90 (dd, $J$=17.1, 1.8 Hz, 1H), 3.67 (s, 3H), 2.76 (d, $J$=6.6 Hz, 2H), 1.32 (s, 18H); $^{13}$C NMR (75.5 MHz, CDCl$_3$) δ 163.6, 161.1 (d, $J$ CF=247.6 Hz), 145.3, 136.1 (d, $J$ CF=8.1 Hz), 134.6, 132.8, 130.9 (d, $J$ CF=2.3 Hz), 128.6 (d, $J$ CF=8.1 Hz), 125.6, 117.6, 116.7 (d, $J$ CF=23.0 Hz), 114.3 (d, $J$ CF=21.9 Hz), 64.7, 36.1, 35.7, 31.6; IR (neat, thin film) ν 3267, 2963, 1493, 1406, 1392, 1393, 1355, 1228, 1165, 1126, 1006, 905 cm$^{-1}$; HRMS (ESI) calcd for C$_{24}$H$_{33}$O$_3$N$_1$F$_1$S$_1$ [M+H]$^+$ 434.2160, found 434.2156.

$N$-(2-Allyl-4-methylphenyl)-3,5-di-tert-butyl-4-methoxybenzenesulfonamide (1j)

Sulfonamide 1j (248 mg, 34% yield) was obtained as a white solid from 225 mg of 2-allyl-4-methylbenzamine using Procedure B.

Data for compound 1j: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46 (s, 2H), 7.36 (d, $J$=8.0 Hz, 1H), 7.05 (d, $J$=8.0 Hz, 1H), 6.84 (s, 1H), 6.29 (s, 1H), 5.70-5.60 (m, 1H), 5.06 (dd, $J$=8.8, 1.6 Hz, 1H), 4.89 (dd, $J$=15.6, 1.6 Hz, 1H), 3.66 (s, 3H), 2.73 (d, $J$=6.0 Hz, 2H), 2.27 (s, 3H), 1.31 (s, 18H). $^1$H NMR matched the previously reported data.$^4$
2-(3-Phenylprop-2-ynyl)benzenamine (12)
The known 2-(3-phenylprop-2-ynyl)benzenamine 12 was synthesized as previously reported. The alcohol 11 (1.50 g, 5.92 mmol, 1 equiv) was dissolved in 15.6 mL of dry methylene chloride in a 100 mL round bottom flask under an argon atmosphere and stirred with a magnetic stir bar. Triethylsilane (1.23 mL, 7.70 mmol, 1.3 equiv) and ammonium fluoride (0.285 g, 7.70 mmol, 1.3 equiv) were added to the solution and the flask was cooled to 0 °C. A solution of TFA (2.20 mL, 2.96 mmol, 5 equiv) in 4.2 mL of dry methylene chloride was added via syringe and the reaction was stirred for 12 h at 0 °C and 24 h at room temperature. The reaction was poured over ice water and extracted with Et2O (2x20 mL). The organic layer was then washed with aqueous NaHCO3, dried over Na2SO4, and concentrated in vacuo. Flash chromatography of the resulting crude product on SiO2 (2% ether in hexanes isocratic) afforded the dehydroxylation product in 44% yield (608 mg, 2.60 mmol). The dehydroxylation product was then dissolved in 12.2 mL of methanol, and SnCl2•2H2O (2.90 g, 12.8 mmol, 5 equiv) was added to the solution. The flask was cooled to 0 °C in an ice water bath and NaBH4 (387 mg, 10.2 mmol, 4 equiv) was carefully added to the reaction and stirred for 2 h at 0 °C. The reaction was quenched with 12 mL of saturated aqueous ammonium hydroxide. The solid was filtered off through Celite and the methanol was concentrated in vacuo. The filtrate was dissolved in 10 mL of EtOAc, and washed with 10 mL of DI H2O and 10 mL of brine. The organic layer was dried over Na2SO4 and concentrated in vacuo. The crude 2-(3-phenylprop-2-ynyl)benzenamine 12 (350 mg) was obtained as a brown oil (66% yield) and was used directly for the next step. 1H NMR (CDCl3, 400 MHz) δ 7.44-7.40 (m, 2H), 7.29-7.21 (m, 4H), 7.11 (t, J=7.6 Hz, 1H), 6.80 (t, J=7.2 Hz, 1H), 6.70 (d, J=7.6 Hz, 1H), 3.75 (s, 2H), 3.67 (s, 2H). The 1H NMR spectrum matched the reported values.

4-Methyl-N-(2-(3-phenylprop-2-ynyl)phenyl)benzenesulfonamide (13)
Sulfonamide 13 (304 mg, 50% yield) was obtained as a brown solid from 350 mg of 2-(3-phenylprop-2-ynyl)benzenamine using Procedure B, except toluenesulfonyl chloride was used. Data for compound 13: mp 106-109 °C; 1H NMR (400 MHz, CDCl3) δ 7.63 (d, J=8.0 Hz, 2H), 7.44-7.42 (m, 2H), 7.37 (d, J=8.4 Hz, 1H), 7.32 (d, J=2.0 Hz, 2H), 7.31 (d, J=2.0 Hz, 1H), 7.25-7.15 (m, 4H), 7.03 (s, 1H), 3.41 (s, 2H), 2.38 (s, 3H); 13C NMR (75.5 MHz, CDCl3) δ 143.8, 136.6, 134.6, 131.6, 130.4, 129.7, 129.6, 128.3, 128.0, 127.1, 126.5, 125.0, 122.7, 109.9, 85.4, 83.9, 22.6, 21.5; IR (neat, thin film) ν 3272, 3063, 3032, 2956, 2923, 1919, 1806, 1598, 1492, 1455, 1443, 1402, 1332, 1291, 1231, 1161, 1119, 1091, 1071, 1046, 1030, 1019, 926 cm⁻¹; HRMS (ESI) calcd for C22H19O2N1Na1S1 [M+Na]+ 384.1029, found 384.1033.
(Z)-4-Methyl-N-(2-(3-phenylallyl)phenyl)benzenesulfonamide (1k)

Sulfonamide 1k was synthesized as previously reported. 4-Methyl-N-(2-(3-phenylprop-2-ynyl)phenyl)benzenesulfonamide (150 mg, 0.415 mmol, 1 equiv) was dissolved in 15 mL of EtOAc. Pd/CaCO₃ poisoned with lead (Lindlar catalyst, 5 wt.%, 29 mg) and quinoline (3.70 µL, 0.0311 mmol, 0.08 equiv) were added to the solution. The mixture was shaken under hydrogen (25 atmospheres) in a Parr hydrogenator for 16 h. The suspension was filtered through Celite with EtOAc, and concentrated in vacuo. Flash chromatography of the resulting crude product on SiO₂ (5-25% ether in hexanes gradient) afforded sulfonamide 1k as a white solid in 73% yield (110 mg, 0.415 mmol).

Data for compound 1k: mp 119-122 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.53-7.39 (m, 4H), 7.28 (d, J=6.4 Hz, 1H), 7.22 (t, J=6.0 Hz, 1H), 7.16-7.12 (m, 1H), 7.11-7.08 (m, 4H), 7.00 (d, J=8.0 Hz, 2H), 6.66 (d, J=11.2 Hz, 1H), 6.27 (s, 1H), 5.54-5.46 (m, 1H), 3.18 (dd, J=6.8, 2.0 Hz, 2H), 2.33 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 143.3, 136.4, 136.0, 135.0, 133.0, 131.4, 129.8, 129.3, 129.1, 128.6, 128.3, 127.7, 127.5, 126.9, 126.2, 124.9, 31.4, 21.5 cm⁻¹; IR (neat, thin film) ν 3284, 3026, 2924, 2856, 1599, 1493, 1398, 1332 1290, 1231, 1164, 1162, 1092, 1019, 916 cm⁻¹; HRMS (ESI) calcld for C₂₂H₂₁O₂N₁Na₁S₁ [M+Na]⁺ 386.1185, found 386.1179.

(E)-Di-tert-butyl (2-di-(4-methylphenylsulfonamido)phenyl)but-2-enyl)carbamate (15)

The known tert-butyl 2-allylphenyl(tosyl)carbamate 14 (146 mg, 0.379 mmol, 1 equiv) was dissolved in 3.8 mL of dry benzene in a 50 mL round bottom flask under an argon atmosphere. The solution was stirred with a magnetic stir bar and Ru(II) Grubbs' catalyst, 2nd generation (16.0 mg, 0.0188 mmol, 0.05 equiv) was added in to the solution. The reaction mixture was heated to 60 °C and continued stirring overnight. The reaction was cooled to room temperature and concentrated in vacuo. Flash chromatography of the resulting crude product on SiO₂ (5-20% EtOAc in hexanes gradient) afforded product 15 as a brown solid in 42% yield (60 mg, 0.080 mmol).

Data for compound 15: mp 71-74 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J=6.4 Hz, 4H), 7.39-7.34 (m, 8H), 7.25-7.22 (m, 2H), 7.07 (d, J=8.0 Hz, 2H), 5.74-5.68 (m, 1H), 3.45 (d, J=3.6 Hz, 4H), 2.47 (s, 6H), 1.34 (s, 18H); ¹³C NMR (75.5 MHz, CDCl₃) δ 150.8, 144.6, 140.8, 136.8, 135.2, 130.1, 130.0, 129.5, 129.3, 129.1, 128.9, 128.9, 126.9, 84.2, 34.1, 27.9, 21.7; IR (neat, thin film) ν 3028, 2980, 2928, 1732, 1597, 1490, 1452, 1395, 1368, 1290, 1254, 1171, 1150, 1089, 1070, 1042, 972 cm⁻¹; HRMS (ESI) calcld for C₄₀H₄₆O₇N₂Na₁S₂ [M+Na]⁺ 769.2588, found 769.2596.
(E)-N-(2-(4-(2-(4-Methylphenylsulfonamido)but-2-enyl)phenyl)-4-methylbenzenesulfonamide (11)

(E)-Di-tert-butyl (2-di-(4-methylphenylsulfonamido)phenyl)but-2-enyl 15 (60 mg, 0.080 mmol, 1 equiv) was dissolved in 5 mL of dry methylene chloride in a 50 mL round bottom flask under an argon atmosphere. The solution was stirred with a magnetic stir bar and trifluoroacetic acid (36 μL, 0.48 mmol, 6 equiv) was added to the solution. The reaction mixture continued stirring overnight at room temperature. The reaction was diluted with 10 mL of methylene chloride and then washed with DI water (2x15 mL). The organic layer was dried over Na₂SO₄ and concentrated in vacuo. Flash chromatography of the resulting crude product on SiO₂ (20-30% EtOAc in hexanes gradient) afforded product 11 as a white solid in 68% yield (30 mg, 0.055 mmol).

Data for compound 11: mp 68-72 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, J=8.1 Hz, 4H), 7.31-7.06 (m, 12H), 6.67 (s, 2H), 5.45 (t, J=3.0 Hz, 2H), 3.08 (d, J=4.2 Hz, 4H), 2.39 (s, 6H); ¹³C NMR (75.5 MHz, CDCl₃) δ 145.2, 143.8, 136.8, 134.7, 133.8, 130.6, 129.9, 129.7, 128.9, 127.6, 127.1, 126.8, 125.4, 35.2, 21.7, 21.6; IR (neat, thin film) ν 3279, 3029, 2924, 1598, 1492, 1454, 1401, 1332, 1291, 1231, 1161, 1091, 1044, 1019, 910 cm⁻¹; HRMS (ESI) calcd for C₃₀H₃₀O₄N₂Na₁S₂ [M+Na]⁺ 569.1539, found 569.1521.

2,2-Dimethylpent-4-enenitrile (17)
The known allyl nitrile 17 was synthesized as previously reported. Diisopropyl amine (6.75 mL, 48.0 mmol, 1.2 equiv) was dissolved in dry THF (40 mL) under an argon atmosphere. The reaction was cooled to -78 °C in an acetone/dry ice bath with stirring with a magnetic stir bar. The n-butyl lithium (19.0 mL, 48.0 mmol, 1.2 equiv) was syringed in next and stirred for 30 min. Isobutyronitrile 16 (3.62 mL, 40.0 mmol, 1 equiv) was added to the reaction and the reaction was stirred for 30 min. Allyl bromide (3.48 mL, 40.0 mmol, 1 equiv) was added to the reaction and the reaction gradually warmed to rt for 24 h with stirring. The reaction mixture was diluted with CH₂Cl₂ (40 mL) and quenched with H₂O (80 mL). The layers were separated and the organic layer was washed with H₂O (2x80 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude residue 17 (2.5 g) was used directly in the next reaction (58% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.89-5.84 (m, 1H), 5.23-5.16 (m, 2H), 2.28 (d, J=7.2 Hz, 2H), 1.34 (s, 6H). ¹H NMR matched with previously reported data.
2,2-Dimethylpent-4-en-1-amine (18)
The known allyl amine 18 was synthesized as previously reported. At 0 °C, lithium aluminum hydride (2.14 g, 56.3 mmol, 2.5 equiv) was dissolved in dry Et₂O (145 mL) under an argon atmosphere. Allyl nitrile 17 (2.46 g, 22.5 mmol, 1 equiv) was added and the reaction stirred with a magnetic stir bar overnight, warming from 0 °C to rt. The reaction was cooled to 0 °C and quenched with water (75 mL) and aqueous NaOH (75 mL). The resulting mixture was filtered through Celite with ether and the organic layer was separated, dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude amine 18 (quantitative yield) was used directly in the next reaction. ¹H NMR (400 MHz, CDCl₃) δ 5.83-5.76 (m, 1H), 5.03-4.98 (m, 2H), 2.43 (s, 2H), 1.95 (d, J=7.6 Hz, 2H), 1.18 (s, 6H). ¹H NMR matched the previously reported data.

N-(2,2-Dimethylpent-4-enyl)methanesulfonamide (5c)
Sulfonamide 5c (2.19 g, 43% yield) was obtained as a yellow oil from 2.69 g of 2,2-dimethylpent-4-en-1-amine using Procedure B, except methanesulfonyl chloride was used. Data for compound 5c: ¹H NMR (400 MHz, CDCl₃) δ 5.86-5.75 (m, 1H), 5.10-5.05 (m, 2H), 4.34 (t, J=16.0 Hz, 1H), 2.94 (s, 3H), 2.90 (d, J=6.8 Hz, 2H), 2.02 (d, J=8.0 Hz, 2H), 0.93 (s, 6H). ¹H NMR matched the previously reported data.

N-(2,2-Dimethylpent-4-enyl)cyclopropanesulfonamide (5d)
Sulfonamide 5d (270 mg, 58% yield) was obtained as a yellow oil from 232 mg of 2,2-dimethylpent-4-en-1-amine using Procedure B, except cycloproanesulfonyl chloride was used. Data for compound 5d: ¹H NMR (400 MHz, CDCl₃) δ 5.87-5.76 (m, 1H), 5.10 (d, J=1.6 Hz, 1H), 5.06 (d, J=8.4 Hz, 1H), 4.19 (s, 1H), 2.94 (d, J=6.4 Hz, 2H), 2.43-2.37 (m, 1H), 2.02 (d, J=8.0 Hz, 2H), 1.17 (dd, J=4.8, 2.0 Hz, 2H), 0.99 (dd, J=8.0, 2.4 Hz, 2H), 0.94 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 134.3, 117.8, 52.9, 44.0, 34.2, 29.7, 24.7, 5.1; IR (neat, thin film) ν 3290, 2075, 3005, 2963, 2929, 2872, 1639, 1468, 1423, 1390, 1368, 1329, 1305, 1191, 1151, 1070, 1041, 998 cm⁻¹; HRMS (ESI) calcd for C₁₀H₁₉O₂N₁Na₁S₁ [M+Na]⁺ 240.1029, found 240.1029.
3,5-Di-tert-butyl-N-(2,2-dimethylpent-4-enyl)-4-methoxybenzenesulfonamide (5a)

Sulfonamide 5a (1.33 mg, 62% yield) was obtained as a yellow oil from 614 mg of 2,2-dimethylpent-4-en-1-amine using Procedure B, except 3,5-bis(1,1-dimethylethyl)-4-methoxybenzenesulfonyl chloride was used.

Data for compound 5a: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) \(7.70 (s, 2H), 5.68 (m, 1H), 5.00-4.95 (m, 2H), 4.36 (s, 1H), 3.70 (s, 3H), 2.73 (d, \(J=6.5\) Hz, 2H), 1.91 (d, \(J=7.0\) Hz, 2H), 1.43 (s, 18H), 0.85 (s, 6H). The \(^1\)H NMR spectrum matched the reported values.\(^{11}\)

3,5-Di-tert-butyl-4-methoxy-N-(pent-4-enyl)benzenesulfonamide (5b)

Sulfonamide 5b was synthesized as previously reported.\(^{12}\) 4-Penten-1-ol (500 mg, 6 mmol, 1 equiv) was dissolved in dry benzene in a 250 mL round bottom flask under an argon atmosphere. The solution was cooled to 0 °C, and was treated with diisopropyl azodicarboxylate (1.76 g, 8.72 mmol, 1.5 equiv) and triphenylphosphine (2.29 g, 8.72 mmol, 1.5 equiv) and stirred for 30 min with a magnetic stir bar. 3,5-Di-tert-butyl-4-methoxybenzenesulfonamide (2.61 g, 8.72 mmol, 1.5 equiv) was then added to the reaction, and the reaction was allowed to warm to room temperature and continued stirring overnight. The reaction was filtered through Celite with 100 mL of a EtOAc, and then washed with 150 mL of DI water. The organic layer was dried over MgSO\(_4\) and concentrated \textit{in vacuo}. Flash chromatography of the resulting crude solid on SiO\(_2\) (5-20% EtO\(_2\) in hexanes isocratic) afforded the sulfonamide in 43% yield (918 mg, 2.50 mmol).

Data for compound 5b: mp 64-66 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.73 (s, 2H), 5.76-5.62 (m, 1H), 4.98-4.91 (m, 2H), 4.45 (bs, 1H), 3.71 (s, 3H), 3.00 (t, \(J=6.9\) Hz, 2H), 2.07-2.00 (m, 2H), 1.64-1.51 (m, 2H), 1.43 (s, 18H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)) \(\delta\) 163.3, 145.2, 137.2, 133.5, 125.6, 115.5, 64.6, 42.6, 36.1, 31.8, 30.6, 28.6; IR (neat, thin film) \(\nu\) 3277, 2963, 3871, 1447, 1407, 1363, 1324, 1255, 1226, 1162, 1117, 1083, 1005, 889; HRMS (ESI) calcd for C\(_{20}\)H\(_{33}\)O\(_3\)N\(_1\)Na\(_1\)S\(_2\) [M+Na]\(^+\) 390.2073, found 390.2062.
The known ligand 23 was synthesized from dimethylmalonyl dichloride 19 and ethanolamine 20 following a known procedure. The K₂CO₃ (5.53 g, 40.0 mmol, 4 equiv) was added into a 250 mL round bottom flask equipped with a magnetic stir bar and sealed with a septum under an argon atmosphere, followed by the addition of dry CH₂Cl₂ (100 mL) via syringe. Ethanolamine (1.28 mL, 21.0 mmol, 2.1 equiv) was added dropwise to the reaction and the flask was cooled to 0 °C in an ice water bath. A solution of dimethylmalonyl dichloride (1.32 mL, 10.0 mmol, 1 equiv) dissolved in dry CH₂Cl₂ (20 mL) was prepared in a separate 100 mL round bottom flask and added dropwise to the reaction. The reaction stirred for 24 h, during which time, the reaction warmed from 0 °C to rt. After 24 h, MeOH (100 mL) was added to the reaction, and after 30 min, the reaction was filtered through celite and concentrated in vacuo. The resulting solid 21 was put under vacuum and flushed with argon. Dry toluene (60 mL) was syringed into the flask and the flask was heated to 65 °C with stirring from a magnetic stir bar. The sulfonyl chloride (4.76 g, 40.0 mmol, 4 equiv) was added quickly to the reaction and the reaction ran for 5 h at 70 °C. The reaction was cooled to 0 °C and quenched with saturated NaHCO₃ solution (20 mL) and extracted with CH₂Cl₂ (10x40 mL). The organic layers were dried over Na₂SO₄ and concentrated in vacuo. The result 22 was transferred to a 100 mL round bottom flask and was treated with 5% methanolic NaOH solution (1.66 g NaOH in 1.70 mL of H₂O diluted with 32.3 mL MeOH). The mixture was put under reflux at 80 °C for 2 h. The reaction was concentrated in vacuo and partitioned between CH₂Cl₂ (10 mL) and H₂O (10 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (4x10 mL). The organic layers were combined and dried over MgSO₄ and concentrated in vacuo. The crude ligand 23 (1.06 g) was obtained as a brown solid (58% yield). ¹H NMR (400 MHz, CDCl₃) δ 4.30 (t, J=18.8 Hz, 4H), 3.89 (t, J=18.8 Hz, 4H), 1.534 (s, 6H). ¹H NMR matched previously reported data.
Alkylation of the bisoxazoline ligand was conducted as previously reported.\(^{10}\) 2,2'-Methylenebis[(4R,5S)-4,5-diphenyl-2-oxazoline] \(24\) (501 mg, 10.9 mmol, 1 equiv) was dissolved in 33 mL of dry THF in a 250 mL round bottom flask under an argon atmosphere. To this solution, diisopropylamine (0.15 mL, 1.1 mmol, 1.01 equiv) and \(N, N, N, N\)-tetramethylethylenediamine (0.33 mL, 2.2 mmol, 2.01 equiv) were added via syringe. The solution was then cooled to -70 °C in a dry ice in isopropanol bath, and \(n\)-butyl lithium (1.37 mL, 2.20 mmol, 1.6 M solution in hexanes) was added dropwise. The reaction mixture was then warmed to -20 °C and allowed to stir for 30 min. The mixture was cooled to -70 °C and iodomethane (0.14 mL, 2.3 mmol, 2.06 equiv) was added via syringe. The reaction was allowed to warm to room temperature and proceed for an additional 16 h. The reaction mixture was quenched with 35 mL of saturated aqueous NH\(_4\)Cl and then diluted with 25 mL of DI water. The mixture was extracted with Et\(_2\)O (3x50 mL) and the combined organic layers were dried over MgSO\(_4\) and concentrated \textit{in vacuo}. Flash chromatography of the resulting crude solid on SiO\(_2\) (50% EtOAc in hexanes isocratic) afforded the (4\(R\),5\(S\))-di-Ph-box ligand \(25\) in 84% yield (445 mg, 0.916 mmol). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta 7.01\) (s, 10H), \(6.96\) (s, 10H), \(5.97\) (d, \(J=10.0\) Hz, 2H), \(5.58\) (d, \(J=10.4\) Hz, 2H), \(1.92\) (s, 6H). \(^{1}H\) NMR matched previously reported data.\(^{10}\)

**Representative Procedure C for catalytic diamination (Conditions a, Table 1)**

\[
\text{Cu(EH)}_2 (20 \text{ mol\%}) \quad \text{2,6-di-\textit{tert}-butyl-4-methylpyridine (1 equiv)} \quad \text{MnO}_2 (300 \text{ mol\%}) \quad \text{TsNH}_2 (2.2 \text{ equiv}) \quad \text{PhCF}_3 (0.2 \text{ M}) \quad 100 \text{ °C, 24 h}
\]

\(4\text{-Methyl-N-}[(1\text{-methylsulfonyl})\text{indolin-2-yl}]\text{methyl}benzenesulfonamide (2a)\)

\(N\)-\(2\text{-allylphenyl}\)methanesulfonamide \(1a\) (50.0 mg, 0.237 mmol, 1 equiv) was dissolved in PhCF\(_3\) (1.19 mL) and was added via syringe to a glass tube, under an argon atmosphere, equipped with a magnetic stir bar and was treated with 2,6-di-\textit{tert}-butyl-4-methylpyridine (48.7 mg, 0.240 mmol, 1 equiv), MnO\(_2\) (61.8 mg, 0.720 mmol, 3 equiv), TsNH\(_2\) (89.4 mg, 0.520 mmol, 2.2 equiv), and Cu(2-ethyl hexanoate)\(_2\) (16.6 mg, 0.0480 mmol, 20 mol %). The tube was capped and the reaction mixture was stirred at rt for 20 min before being placed in a 100 °C oil bath and stirred. After 24 h, the reaction mixture was stirred at rt, diluted with EtOAc (10 mL), sonicated, filtered through Celite with EtOAc (140 mL), and concentrated \textit{in vacuo}. Based on crude \(^{1}H\) NMR, the reaction resulted in a >95% conversion to the diamination product, with the remainder of material being trace starting material. The resulting solid was purified by flash chromatography on SiO\(_2\) (30-45% EtOAc/hexanes gradient) to give the diamination product \(2a\) in 83% yield (75.0 mg, 0.197 mmol) as a white solid.

Data for compound \(2a\): mp 155-157 °C; \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.71\) (d, \(J=8.5\) Hz, 2H), 7.38 (d, \(J=8.0\) Hz, 1H), 7.30-7.28 (m, 2H), 7.20 (apparent t, \(J=7.5\) Hz, 2H), 7.11-7.09 (m, 1H),
4.97 (t, J=11.5 Hz, 1H), 4.39-4.37 (m, 1H), 3.40 (dd, J=16.5, 10.0 Hz, 1H), 3.22-3.19 (m, 2H), 3.06, (dd, J=16.5, 4.0 Hz, 1H), 2.78 (s, 3H), 2.42 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 143.6, 140.7, 136.5, 130.5, 129.8, 128.2, 127.1, 125.6, 125.2, 115.9, 61.4, 47.9, 35.4, 32.4, 21.5; IR (neat, thin film) \(\nu\) 3299, 2924, 2857, 2257, 1734, 1658, 1597, 1479, 1460, 1337, 1239, 1158, 1096, 981; HRMS (ESI) calcd for C\(_{17}\)H\(_{20}\)O\(_4\)N\(_2\)S\(_2\) [M\(^+\)] 380.0859, found 380.0859.

2b

\(N\)-(1-(Methylsulfonyl)indolin-2-yl)methyl)methanesulfonamide (2b)

Diamination adduct 2b (50 mg, 69% yield) was obtained as a white solid from 50 mg of 1a using Procedure C, except MeSO\(_2\)NH\(_2\) (49.7 mg, 0.520 mmol) was used as the amine nucleophile and the reaction was run at 110 °C. Based on crude \(^1\)H NMR, the reaction resulted in an 87% conversion to the diamination product, with the remainder of material being starting material.

Data for 2b: mp 167-169 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47 (d, J=8.0 Hz, 1H), 7.23-7.20 (m, 2H), 7.15-7.11 (m, 1H), 4.80 (t, J=12 Hz, 1H), 4.45-4.44 (m, 1H), 3.51-3.43 (m, 2H), 3.39-3.34 (m, 1H), 3.02 (d, J=3.6 Hz, 1H), 2.98 (s, 3H), 2.82 (s, 3H); \(^{13}\)C NMR (500 MHz, CD\(_3\)CN) \(\delta\) 142.0, 132.3, 128.3, 126.1, 125.3, 116.2, 62.1, 48.0, 39.7, 35.7, 32.2; IR (neat, thin film) \(\nu\) 3305, 1479, 1457, 1437, 1412, 1331, 1152, 1102, 976, 911; HRMS (ESI) calcd for C\(_{11}\)H\(_{16}\)O\(_4\)N\(_2\)Na\(_1\)S\(_2\) [M+Na\(^+\)] 327.0444, found 327.0447.

2c

\(N\)-(1-(Methylsulfonyl)indolin-2-yl)methyl)-2-(trimethylsilyl)ethanesulfonamide (2c)

Diamination adduct 2c (63 mg, 80%) was obtained as a white solid using Procedure C, except TMS(CH\(_2\))\(_2\)SO\(_2\)NH\(_2\) (80.0 mg, 0.440 mmol) was used as the amine nucleophile and the reaction was run at 110 °C. Based on crude \(^1\)H NMR, the reaction resulted in a >90% conversion to the diamination product, with the remainder of material being trace starting material.

Data for 2c: mp 134-135 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.46 (d, J=8.0 Hz, 1H), 7.25-7.21 (m, 2H), 7.14-7.10 (m, 1H), 4.72 (t, J=12 Hz, 1H), 4.43-4.40 (m, 1H), 3.48-3.42 (m, 2H), 3.38-3.33 (m, 1H), 3.05 (dd, J=16.8, 4.0 Hz, 1H), 2.95 (dd, J=12.4, 4.0 Hz, 2H), 2.82 (s, 3H), 1.00 (dd, J=11.6, 6.4 Hz, 2H), 0.04 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 140.8, 130.6, 128.4, 125.7, 125.3, 116.0, 61.9, 49.0, 48.0, 35.4, 32.3, 10.5, -2.0; IR (neat, thin film) \(\nu\) 3294, 2952, 2857, 2252, 1731, 1600, 1479, 1460, 1418, 1345, 1325, 1250, 1158, 1102, 984; HRMS (ESI) calcd for C\(_{15}\)H\(_{26}\)O\(_4\)N\(_2\)Na\(_1\)S\(_2\)Si \([M+Na\(^+\)]\) 413.0995, found 413.1003.
2d  

N-((1-(Methylsulfonyl)indolin-2-yl)methyl)benzamide (2d)

Diamination adduct 2d (46.7 mg, 50% yield) was obtained as a white solid from 50 mg of 1a using Procedure C, except benzamide was used as the nucleophile. Based on crude ¹H NMR, the reaction resulted in a 71% conversion to the diamination product, with the remainder of material being starting material.

Data for compound 2d: mp 141-143 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.74-7.71 (m, 2H), 7.52-7.44 (m, 2H), 7.41-7.37 (m, 2H), 7.26-7.22 (m, 2H), 7.14-7.10 (m, 1H), 6.99 (t, J=16.0, 1H), 4.60-4.54 (m, 1H), 3.81-3.75 (m, 1H), 3.63-3.57 (m, 1H), 3.56-3.48 (m, 1H), 2.92 (dd, J=16.0, 2.4 Hz, 1H), 2.83 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 168.0, 140.5, 134.1, 131.4, 128.5, 128.3, 127.0, 125.5, 125.5, 116.9, 61.9, 45.0, 35.7, 33.0; IR (neat, thin film) ν 3397, 3068, 2926, 2853, 2247, 1649, 1603, 1579, 1537, 1461, 1344, 1241, 1159, 1101, 1025, 985; HRMS (ESI) calcd for C₁₇H₁₈O₃N₂Na₁S₁ [M+Na]+ 353.0930, found 353.0931.

2e  

4-Methyl-N-((1-tosylindolin-2-yl)methyl)benzenesulfonamide (2e)

Diamination adduct 2e (50 mg, 64% yield) was obtained as a yellow oil from 50 mg of 1b using Procedure C.

Data for compound 2e: ¹H NMR (300 MHz, CDCl₃) δ 7.75 (d, J=8.1 Hz, 2H), 7.58 (d, J=8.1 Hz, 1H), 7.44 (d, J=8.1 Hz, 2H), 7.31 (d, J=8.1 Hz, 2H), 7.23-7.14 (m, 3H), 7.07-7.02 (m, 2H), 5.05 (t, J=13.5, 6.6 Hz, 1H), 4.24-4.16 (m, 1H), 3.24-3.11 (m, 2H), 2.78 (dd, J=15.9, 9.0 Hz, 1H), 2.66 (dd, J=16.5, 3.6 Hz, 1H), 2.44 (s, 3H), 2.35 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 144.4, 143.5, 140.8, 136.7, 134.0, 131.4, 123.0, 129.7, 127.9, 127.2, 127.1, 125.3, 125.2, 117.61, 61.0, 47.6, 32.2, 21.5; IR (neat, thin film) ν 3309, 2927, 2860, 2243, 1733, 1648, 1595, 1477, 1462, 1333, 1241, 1148, 1092, 964; HRMS (ESI) calcd for C₂₃H₂₄O₄N₂Na₁S₂ [M+Na]+ 479.1070, found 479.1074.

3a  

8-Methyl-10a,11-dihydro-10H-5-thia-4b-aza-benzo[b]fluorene 5,5-dioxide (3a)

Carboamination adduct 3a (13.0 mg, 31%) was obtained from the same reaction as 2e as a colorless solid. ¹H NMR (500 MHz, CDCl₃) 7.74 (d, J=8.0 Hz, 1 H), 7.55 (d, J=8.0 Hz, 1 H), 7.18-6.96 (m, 5 H), 4.94-4.89 (m, 1 H), 3.49 (dd, J=10.5, 5.5 Hz, 1 H), 3.34 (dd, J=9.0, 7.0 Hz, 1 H), 3.07 (dd, J=9.5, 6.6 Hz, 1 H), 2.93 (dd, J=8.0, 7.5 Hz, 1 H), 2.37 (s, 3 H). The ¹H NMR spectrum matched the reported values.

N-((1-(Benzylsulfonyl)indolin-2-yl)methyl)-4-methylbenzenesulfonamide (2f)
Diamination adduct 2f (51.5 mg, 65% yield) was obtained as a white solid from 50 mg of 1c using Procedure C, except the reaction was run at 110 °C. Based on crude ¹H NMR, the reaction resulted in a 80% conversion to the diamination product, with the remainder of material being starting material.

Data for compound 2f: mp 151-153 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, J=8.4 Hz, 2H), 7.41-7.33 (m, 2H), 7.29-7.20 (m, 1H), 7.16-7.07 (m, 2H), 7.03 (d, J=7.2 Hz, 2H), 4.72 (t, J=12.4 Hz, 1H), 4.31 (d, J=5.2 Hz, 2H), 3.68-3.65 (m, 1H), 3.01-2.95 (m, 2H), 2.75 (d, J=7.6 Hz, 2H), 2.40 (s, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ 130.8, 130.6, 130.6, 130.3, 130.3, 130.3, 129.7, 129.1, 128.8, 128.8, 128.1, 127.6, 127.0, 127.0, 125.6, 124.7, 62.4, 55.7, 48.2, 31.9, 21.5; IR (neat, thin film) ν 3280, 3063, 2929, 2255, 1708, 1598, 1495, 1480, 1459, 1338, 1243, 1202, 1158, 1132, 1095, 1042, 982; HRMS (ESI) calcd for C₂₃H₂₄O₄N₂S₂ [M]⁺ 456.1172, found 456.1177.

N-((1-(Cyclopropylsulfonyl)indolin-2-yl)methyl)-4-methylbenzenesulfonamide (2g)

Diamination adduct 2g (64.6 mg, 75% yield) was obtained as a white solid from 50 mg of 1d Procedure C, except the reaction was run at 110 °C. Based on crude ¹H NMR, the reaction resulted in a >90% conversion to the diaminat on product, with the remainder of material being trace starting material.

Data for compound 2g: mp 46-50 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J=8.4 Hz, 2H), 7.39 (d, J=8.0 Hz, 1H), 7.28 (d, J=8.0 Hz, 2H), 7.20-7.16 (m, 2H), 7.07 (t, J=14.0 Hz, 1H), 4.94 (t, J=12.8 Hz, 1H), 4.48-4.42 (m, 1H), 3.47-3.40 (m, 1H), 3.21-3.09 (m, 2H), 2.96 (dd, J=16.8, 2.8 Hz, 1H), 2.41 (s, 3H), 2.31-2.25 (m, 1H), 1.22-1.08 (m, 2H), 0.93-0.81 (m, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 143.5, 140.9, 136.5, 131.0, 130.4, 129.8, 128.0, 127.1, 125.4, 125.0, 116.6, 61.4, 47.7, 32.7, 27.1, 21.5, 4.8, 4.4; IR (neat, thin film) ν 3287, 3047, 2928, 2861, 2257, 1598, 1480, 1461, 1342, 1238, 1154, 1095, 1043, 982; HRMS (ESI) calcd for C₁₉H₂₂O₄N₂Na₁S₂ [M+Na]⁺ 429.0913, found 429.0921.

N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)indolin-2-yl)methyl)-4-methylbenzenesulfonamide (2h)

Diamination adduct 2h (59.1 mg, 84% yield) was obtained as a white solid from 50 mg of 1e using the Procedure C, except the reaction was run at 110 °C. Based on crude ¹H NMR, the reaction resulted in a >95% conversion to the diaminat ion product, with the remainder of material being trace starting material.

Data for compound 2h: mp 146-148 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.75 (d, J=8.1 Hz, 2H), 7.60 (d, J=8.4 Hz, 1H), 7.37 (s, 2H), 7.31 (d, J=8.4 Hz, 2H), 7.22 (t, J= 5.7 Hz, 1H), 7.07-7.00
N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)indolin-2-yl)methyl)-2-(trimethylsilyl)ethanesulfonamide (2i)

Diamination adduct 2i (44 mg, 77% yield) was obtained as a white solid from 40 mg of 1e via Procedure C, except SESNH₂ was used as the nucleophile and the reaction was run at 110 °C. Based on crude \(^1\)H NMR, the reaction resulted in a >95% conversion to the diamination product, with the remainder of material being trace starting material.

Data for compound 2i: mp 96-98 °C; \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.71 (d, \(J=7.6 \text{ Hz}, 1\text{H}\)), 7.42 (s, 2H), 7.28-7.21 (m, 1H), 7.08-7.02 (m, 2H), 4.82 (t, \(J=5.6 \text{ Hz}, 1\text{H}\)), 4.23-4.16 (m, 1H), 3.63 (s, 3H), 3.40-3.35 (m, 1H), 3.28-3.23 (m, 1H), 3.01-2.96 (m, 2H), 2.62 (d, \(J=5.6 \text{ Hz}, 2\text{H}\)), 1.25 (s, 18H), 1.08-1.04 (m, 2H), 0.06 (s, 9H); \(^13\)C NMR (75.5 MHz, CDCl₃) \(\delta\) 164.0, 145.3, 141.2, 132.1, 130.5, 128.1, 125.7, 125.6, 125.2, 118.4, 64.7, 61.5, 49.1, 47.6, 36.0, 32.1, 31.6, 10.4, -2.0; IR (neat, thin film) \(\nu\) 3306, 2959, 2360, 1727, 1478, 1461, 1407, 1355, 1259, 1228, 1169, 1141, 1023, 843; HRMS (ESI) calcd for C\(_{29}\)H\(_{46}\)O\(_5\)N\(_2\)Na\(_1\)S\(_2\) [M+Na\(^+\)] 617.2510, found 617.2504.

N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)-5-methoxyindolin-2-yl)methyl)-4-methylbenzenesulfonamide (2j)

Diamination adduct 2j (41.3 mg, 75% yield) was obtained as a white solid from 40 mg of 1f using Procedure C, except the reaction was run at 110 °C. Based on crude \(^1\)H NMR, the reaction resulted in a >90% conversion to the diamination product, with the remainder of material being trace starting material.

Data for compound 2j: mp 184-186 °C; \(^1\)H NMR (300 MHz, CDCl₃) \(\delta\) 7.75 (d, \(J=7.5 \text{ Hz}, 2\text{H}\)), 7.48 (d, \(J=8.7 \text{ Hz}, 1\text{H}\)), 7.33 (s, 2H), 7.30 (d, \(J=7.8 \text{ Hz}, 2\text{H}\)), 6.75 (d, \(J=9.0 \text{ Hz}, 1\text{H}\)), 6.54 (s, 1H), 5.06 (t, \(J=6.0 \text{ Hz}, 1\text{H}\)), 4.15-4.05 (m, 1H), 3.72 (s, 3H), 3.62 (s, 3H), 3.18-3.10 (m, 1H), 3.07-2.98 (m, 1H), 2.44 (d, \(J=13.5 \text{ Hz}, 2\text{H}\)), 2.42 (s, 3H), 1.25 (s, 18H); \(^13\)C NMR (75.5 MHz, CDCl₃) \(\delta\) 163.8, 158.2, 145.1, 143.4, 136.6, 134.2, 134.0, 130.2, 129.7, 127.2, 125.6, 119.5,
113.4, 110.5, 64.7, 61.4, 55.7, 47.3, 36.0, 32.3, 31.6, 21.5; IR (neat, thin film) ν 3291, 2963, 2360, 2341, 1719, 1487, 1455, 1406, 1342, 1261, 1164, 1094, 1031, 883; HRMS (ESI) calcd for C_{32}H_{42}O_6N_2Na_1S_2 [M+Na]^+ 637.2376, found 637.2387.

\[ \text{N-}((5\text{-Bromo-1-(3,5-di-} \text{t} \text{-butyl-4-methoxyphenylsulfonyl)indolin-2-yl)methyl)-4-methylbenzenesulfonamide (2k)} \]

Diamination adduct 2k (36.4 mg, 68% yield) was obtained as a white solid from 40 mg of 1g using Procedure C, except the reaction was run at 110 °C. Based on crude \(^1\)H NMR, the reaction resulted in a 79% conversion to the diamination product, with the remainder of material being starting material.

Data for compound 2k: mp 198-201 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.74 (d, J=8.7 Hz, 2H), 7.47 (d, J=8.7 Hz, 1H), 7.38 (s, 2H), 7.35 (d, J=4.5 Hz, 1H), 7.31 (d, J=8.1 Hz, 2H), 4.99 (t, J=6.0 Hz, 1H), 4.30-4.22 (m, 1H), 3.63 (s, 3H), 3.23-3.05 (m, 2H), 2.70-2.53 (m, 2H), 2.43 (s, 3H), 1.27 (s, 18H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)) δ 164.1, 145.4, 143.6, 140.9, 136.5, 134.0, 130.9, 130.2, 129.8, 128.2, 127.2, 125.5, 119.5, 118.5, 64.7, 61.4, 47.4, 36.0, 31.8, 31.6, 21.5; IR (neat, thin film) ν 3305, 2962, 2361, 2341, 1734, 1598, 1471, 1406, 1357, 1261, 1164, 1112, 800; HRMS (ESI) calcd for C_{32}H_{42}O_6N_2Na_1S_2 [M+Na]^+ 685.1376, found 685.1390.

\[ \text{N-}((5\text{-Chloro-1-(3,5-di-} \text{t} \text{-butyl-4-methoxyphenylsulfonyl)indolin-2-yl)methyl)-4-methylbenzenesulfonamide (2l)} \]

Diamination adduct 2l (38.4 mg, 70% yield) was obtained as a white solid from 40 mg of 1h using Procedure C, except the reaction was run at 110 °C. Based on crude \(^1\)H NMR, the reaction resulted in a >90% conversion to the diamination product, with the remainder of material being trace starting material.

Data for compound 2l: mp 202-205 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.74 (d, J=8.1 Hz, 2H), 7.52 (d, J=8.7 Hz, 1H), 7.38 (s, 2H), 7.31 (d, J=7.8 Hz, 2H), 7.19 (dd, J=9.0, 2.4 Hz, 1H), 6.99 (d, J=1.8 Hz, 1H), 5.01 (t, J=6.3 Hz, 1H), 4.19-4.11 (m, 1H), 3.63 (s, 3H), 3.21-3.05 (m, 2H), 2.67-2.53 (m, 2H), 2.43 (s, 3H), 1.27 (s, 18H); \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)) δ 164.1, 145.4, 143.6, 139.9, 136.5, 134.0, 130.9, 130.2, 129.8, 127.9, 127.2, 125.5, 125.2, 119.1, 64.7, 61.5, 47.4, 36.0, 31.9, 31.6, 21.5; IR (neat, thin film) ν 3294, 2961, 1724, 1598, 1471, 1406, 1355, 1256, 1228, 1165, 1114, 1005, 883; HRMS (ESI) calcd for C_{31}H_{40}O_5N_2Br_1Na_1S_2 [M+Na]^+ 619.2062, found 619.2064.
**N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)-5-fluorindolin-2-yl)methyl)-4-methylbenzenesulfonamide (2m)**

Diamination adduct 2m (38.9 mg, 70% yield) was obtained as a white solid from 40 mg of 1i using Procedure C, except the reaction was run at 110 °C. Based on crude ¹H NMR, the reaction resulted in a 85% conversion to the diamination product, with the remainder of material being starting material.

Data for compound 2m: mp 184-186 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.74 (d, J=6.3 Hz, 2H), 7.54 (dd, J=6.9, 4.8 Hz, 1H), 7.37 (s, 2H), 7.31 (d, J=8.4 Hz, 2H), 6.92 (apparent td, J=8.7, 3.0 Hz, 1H), 6.72 (dd, J=7.8, 2.4 Hz, 1H), 4.98 (t, J=6.0 Hz, 1H), 4.18-4.13 (m, 1H), 3.63 (s, 3H), 3.20-3.03 (m, 2H), 2.65-2.50 (m, 2H), 2.43 (s, 3H), 1.26 (s, 18H); ¹³C NMR (75.5 MHz, CDCl₃) δ 164.0, 145.4, 143.5, 137.2, 135.4 (d, J_CF=235.0 Hz), 132.8, 130.2, 129.8 (d, J_CF=8.4 Hz), 128.0, 127.2, 125.6, 119.4 (d, J_CF=8.4 Hz), 114.6 (d, J_CF=23.8 Hz), 112.2 (d, J_CF=23.8 Hz), 64.7, 61.6, 47.4, 36.0, 32.1, 31.6, 29.7, 21.5, 14.2, 14.1; IR (neat, thin film) ν 3293, 2962, 2871, 1724, 1600, 1481, 1445, 1407, 1353, 1259, 1229, 1165, 1126, 1094, 1006, 938; HRMS (ESI) calcd for C₃₁H₄₀O₅N₂F₁S₂ [M+H]⁺ 603.2357, found 603.2358.

**N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)-5-methylindolin-2-yl)methyl)-4-methylbenzenesulfonamide (2n)**

Diamination adduct 2n (44.5 mg, 80% yield) was obtained as a white solid from 40 mg of 1j using the general catalytic procedure, except the reaction was run at 110 °C. Based on crude ¹H NMR, the reaction resulted in a >90% conversion to the diamination product, with the remainder of material being trace starting material.

Data for compound 2n: mp 193-194 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.75 (d, J=8.1 Hz, 2H), 7.46 (d, J=8.4 Hz, 1H), 7.34 (s, 2H), 7.30 (d, J=8.4 Hz, 2H), 7.02 (d, J=8.1 Hz, 1H), 6.81 (s, 1H), 5.06 (t, J=6.0 Hz, 1H), 4.13-4.08 (m, 1H), 3.61 (s, 3H), 3.19-3.11 (m, 1H), 3.08-3.00 (m, 1H), 2.48 (d, J=7.8 Hz, 2H), 2.42 (s, 3H), 2.25 (s, 3H), 1.24 (s, 18H); ¹³C NMR (75.5 MHz, CDCl₃) δ 163.8, 145.1, 143.4, 138.7, 136.6, 135.9, 132.3, 130.4, 129.7, 128.5, 127.2, 125.6, 125.5, 118.3, 64.6, 61.2, 47.4, 36.0, 32.0, 31.5, 21.5, 20.9; IR (neat, thin film) ν 3305, 2924, 2361, 1724, 1599, 1486, 1457, 1406, 1351, 1259, 1228, 1165, 1094, 885; HRMS (ESI) calcd for C₃₂H₄₃O₅N₂S₂ [M+H]⁺ 599.2608, found 599.2607.
2-(Phenyl(tosyl)methyl)-1-tosylindoline (2o, 2p)

Cu(OTf)2 (10.0 mg, 0.028 mmol, 25 mol %) was placed in a glass tube, under an argon atmosphere in a dry box, with a magnetic stir bar. Achiral bis(oxazoline) ligand 23 (5.4 mg, 0.030 mmol, 27 mol %) in PhCF3 (0.55 mL) was added via syringe through a septum. The tube was capped and the reaction mixture was placed in a 60 °C oil bath and stirred. After 2 h, the catalyst solution was cooled to rt. (Z)-4-Methyl-N-(2-(3-phenylallyl)phenyl)benzenesulfonamide (1k) (40 mg, 0.11 mmol, 1 equiv) was dissolved in DCE (0.55 mL) and was added via syringe to the glass tube, under an argon atmosphere, and the resulting solution was treated with 2,6-di-tert-butyl-4-methylpyridine (22.6 mg, 0.11 mmol, 1 equiv) and TsNH2 (94.2 mg, 0.55 mmol, 5 equiv). A heterogeneous mixture of MnO2 (28.7 mg, 0.33 mmol, 3 equiv) and KMnO4 (1.4 mg, 0.0088 mmol, 0.08 equiv) was prepared using a mortar and pestle and added to the pressure tube. 4 Å mol. sieves (22.0 mg) were flame dried for 5 min and added to the reaction mixture. The tube was capped and the reaction mixture was stirred at rt for 20 min before being placed in a 100 °C oil bath and stirred. After 24 h, the reaction mixture was cooled to rt, diluted with EtOAc (10 mL), sonicated, filtered through Celite with EtOAc (140 mL), and concentrated in vacuo.

The resulting solid was purified by flash chromatography on SiO2 (15-30% EtOAc in hexanes gradient) to give the diamination products 2o and 2p in 76% yield (44.5 mg, 0.084 mmol) in a 58:42 diastereomeric ratio as a white solid. The diastereomers were separated using HPLC.

Data for compound major 2o: mp 70-73 °C; 1H NMR (400 MHz, CDCl3) δ 7.64 (d, J=6.4 Hz, 1H), 7.52 (d, J=8.0 Hz, 2H), 7.38 (d, J=8.8 Hz, 2H), 7.25-7.14 (m, 2H), 7.13-7.10 (m, 5H), 7.01-6.96 (m, 3H), 6.83 (t, J=7.6 Hz, 1H), 6.62 (d, J=7.6 Hz, 1H), 5.98 (d, J=7.2 Hz, 1H), 4.58-4.56 (m, 1H), 4.40-4.36 (m, 1H), 2.60 (d, J=6.0 Hz, 2H), 2.37 (s, 3H), 2.33 (s, 3H); 13C NMR (75.5 MHz, CDCl3) δ 144.4, 142.9, 141.7, 137.5, 135.5, 134.0, 131.4, 129.7, 129.2, 127.9, 127.7, 127.6, 127.1, 127.0, 125.2, 124.4, 117.8, 65.3, 61.3, 31.4, 21.5, 21.5; IR (neat, thin film) ν 3272, 3031, 2924, 2360, 2340, 1598, 1479, 1458, 1358, 1344, 1259, 1162, 1090, 1028, 910; HRMS (ESI) calcd for C29H28O4N2Na1S2 [M+Na]+ 555.1383, found 555.1376.

Data for compound minor 2p: mp 70-73 °C; 1H NMR (400 MHz, CDCl3) δ 7.63 (d, J=10.8 Hz, 2H), 7.39 (d, J=11.2 Hz, 2H), 7.24-7.10 (m, 1H), 7.02 (t, J=9.2 Hz, 1H), 6.91 (d, J=9.2 Hz, 1H), 6.23 (d, J=3.6 Hz, 1H), 4.17 (t, J=10.0 Hz, 1H), 3.97 (dd, J=10.0, 3.6 Hz, 1H), 2.40 (s, 3H), 2.36-2.21 (m, 2H), 2.31 (s, 3H); 13C NMR (75.5 MHz, CDCl3) δ 144.5, 142.7, 140.2, 138.3, 136.8, 134.3, 131.8, 129.8, 129.4, 128.6, 128.3, 128.1, 127.6, 127.4, 126.9, 125.8, 124.8, 119.0, 64.3, 60.0, 31.2, 21.5.

Note: Reaction of 1k with [Cu(R,R)-Ph-box](OTf)2 gave racemic 2o.
(R)-1-Tosyl-2-((S)-1-tosylindolin-2-yl)indoline (2q)

Diamination adduct 2q (10.9 mg, 73% yield, dr >20:1) was obtained as a tan solid from 15 mg of 11 using the Cu(OTf)$_2$ catalytic procedure used for 2-(phenyl(tosyl)methyl)-1-tosylindoline 2o and 2p, except no TsNH$_2$ was used and (R,R)-Ph-box was used as the ligand. The lack of optical rotation indicates this compound is the meso diastereomer.

Data for compound 2q: mp 176-179 °C; $[\alpha]_D^{17} = 0$ (c 0.2, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta $ 7.73 (d, $J=8.5$ Hz, 4H), 7.71 (d, $J=8.0$ Hz, 2H), 7.24 (d, $J=8.0$ Hz, 4H), 7.18 (t, $J=7.0$ Hz, 2H), 6.98-6.92 (m, 4H), 4.93-4.90 (m, 2H), 2.96 (dd, $J=14.5$, 10.5 Hz, 2H), 2.66 (dd, $J=17.0$, 4.5 Hz, 2H), 2.37 (s, 6H); $^{13}$C NMR (75.5 MHz, CDCl$_3$) $\delta $ 144.3, 142.5, 133.3, 131.3, 129.8, 127.8, 127.64, 125.0, 124.5, 116.1, 63.7, 28.9, 21.6; IR (neat, thin film) $\nu $ 3030, 2924, 2853, 1739, 1598, 1598, 1480, 1451, 1354, 1292, 1250, 1224, 1168, 1091, 1025, 971; HRMS (ESI) calcd for C$_{30}$H$_{28}$O$_4$N$_2$Na$_1$S$_2$ [M+Na]$^+$ 567.1383, found 567.1390.

Procedure D for catalytic enantioselective diamination (Table 2, entry 5)

Cu(OTf)$_2$ (20 mol%) (4R,5S)-Ph-box (25 mol%)
MnO$_2$ (300 mol%)

Cu(OTf)$_2$ (17.1 mg, 0.048 mmol, 20 mol %) was placed in a glass tube, under an argon atmosphere in a dry box, with a magnetic stir bar. A solution of (4R,5S)-di-Ph-box (28.8 mg, 0.059 mmol, 25 mol %) in PhCF$_3$ (0.30 mL) was added via syringe through a septum. An additional 0.60 mL of PhCF$_3$ was added to the reaction mixture. The tube was capped and the reaction mixture was placed in a 60 °C oil bath and stirred. After 2 h, the catalyst solution was cooled to rt. $N$-(2-allylphenyl)methanesulfonamide (1a) (50 mg, 0.24 mmol, 1 equiv) was dissolved in PhCF$_3$ (0.29 mL) and was added via syringe to the glass tube, under an argon atmosphere, and the resulting solution was treated with 2,6-di-tert-butyl-4-methylpyridine (48.7 mg, 0.24 mmol, 1 equiv), MnO$_2$ (61.8 mg, 0.72 mmol, 3 equiv), and TsNH$_2$ (69.1 mg, 0.41 mmol, 2.5 equiv). Flame-dried 4 Å mol. sieves (23.8 mg) were added to the reaction mixture. The tube was capped and the reaction mixture was stirred at rt for 20 min before being placed in a 110 °C oil bath and stirred. After 24 h, the reaction mixture was cooled to rt, diluted with EtOAc (10 mL), sonicated, filtered through Celite with EtOAc (140 mL), and concentrated in vacuo. The diamination to hydroamination ratio was determined to be 84:16 based on the relative integrations of the hydrogen peak at 4.38 ppm at the 2-position on the diamination product to the hydrogen peak at 4.45 ppm at the 2-position of the hydroamination product in the crude $^1$H NMR. The resulting solid was purified by flash chromatography on SiO$_2$ (30-45%...
EtOAc/hexanes gradient) to give the diamination product 2a in 68% yield (63.1 mg, 0.162 mmol) as a white solid. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [CHIRALPAK AD-RH, 60% CH₃CN/H₂O, 0.75 mL/min, λ=254 nm, t(major) = 6.39 min, t(minor) = 5.57 min] revealing 81% enantiomeric excess. [α]D₂₂ = +49.0 (c 0.3, CHCl₃).

2-Methyl-1-(methylsulfonyl)indolines (4)
Hydroamination adduct 4 (7.5 mg, 15% yield) was obtained as a white solid from 50 mg of 1a using Procedure D as a side product to the diamination. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J=8.8 Hz, 1H), 7.22-7.18 (m, 2H), 7.05 (t, J=16.0 Hz, 1H), 4.47-4.42 (m, 1H), 3.49-3.42 (m, 1H), 2.84 (s, 3H), 2.70 (dd, J=12.4, 4.0 Hz, 1H), 1.45 (d, J=6.8 Hz, 3H). This ¹H NMR matched the reported values.¹⁶

(S)-N-((1-(Benzylsulfonyl)indolin-2-yl)methyl)-4-methylbenzenesulfonamide (2f)
Diamination adduct 2f (38 mg, 49% yield) was obtained using Procedure D. The diamination to hydroamination ratio was determined to be 60:40 based on the relative integrations of the hydrogen peak at 3.68 ppm at the 2-position on the diamination product to the hydrogen peak at 1.34 ppm for the hydrogens of the methyl group that is at the 2-position on the hydroamination product in the crude ¹H NMR. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [CHIRALPAK AD-RH, 45% CH₃CN/H₂O, 0.75 mL/min, λ=254 nm, t(major) = 40.35 min, t(minor) = 35.10 min] revealing 79% enantiomeric excess. [α]D₂₃ = +93.8 (c 0.40, CHCl₃).

(S)-N-((1-(cyclopropylsulfonyl)indolin-2-yl)methyl)-4-methylbenzenesulfonamide (2g)
Diamination adduct 2g (49.6 mg, 58% yield) was obtained using Procedure D. The diamination to hydroamination ratio was determined to be 70:30 based on the relative integrations of the hydrogen peak at 4.45 ppm at the 2-position on the diamination product to the hydrogen peak at 4.52 ppm at the 2-position of the hydroamination product in the crude ¹H NMR. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [CHIRALPAK AD-RH, 45% CH₃CN/H₂O, 0.75 mL/min, λ=254 nm, t(major) = 22.50 min, t(minor) = 19.07 min] revealing 76.5% enantiomeric excess. [α]D₂₃ = +48.1 (c 1.0, CHCl₃).
Representative Procedure E for catalytic enantioselective diamination (Table 3, entry 9)

**(S)-N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)indolin-2-yl)methyl)-4-methylbenzenesulfonamide (2h)**

Cu(OTf)$_2$ (8.7 mg, 0.024 mmol, 25 mol %) was placed in a glass reaction tube, under an argon atmosphere in a dry box, with a magnetic stir bar. (R,R)-Ph-box (9.9 mg, 0.030 mmol, 31 mol %) in PhCF$_3$ (0.48 mL) was added via syringe through a septum. The tube was capped and the reaction mixture was placed in a 60 °C oil bath and stirred. After 2 h, the catalyst solution was cooled to rt. N-(2-Allylphenyl)-3,5-di-tert-butyl-4-methoxybenzenesulfonamide **1e** (40 mg, 0.096 mmol, 1 equiv) was dissolved in DCE (0.48 mL) and was added via syringe to the glass tube, under an argon atmosphere, and the resulting solution was treated with 2,6-di-tert-butyl-4-methylpyridine (19.7 mg, 0.096 mmol, 1 equiv) and TsNH$_2$ (82.2 mg, 0.48 mmol, 5 equiv). A heterogeneous mixture of MnO$_2$ (25.0 mg, 0.29 mmol, 3 equiv) and KMnO$_4$ (1.2 mg, 0.0077 mmol, 0.08 equiv) was prepared using a mortar and pestle and added to the tube. 4 Å molecular sieves (19.2 mg) were flame dried for 5 min and added to the reaction mixture. The tube was capped and the reaction mixture was stirred at rt for 20 min before being placed in a 100 °C oil bath and stirred. After 24 h, the reaction mixture was cooled to rt, diluted with EtOAc (10 mL), sonicated, filtered through Celite with EtOAc (140 mL), and concentrated *in vacuo*. The diamination to carboamination ratio was determined to be 69:31 based on the relative integrations of the hydrogen peak at 4.15 ppm at the 2-position on the diamination product to the hydrogen peak at 3.92 ppm at the 10-position of the carboamination product in the crude $^1$H NMR. The resulting solid was purified by flash chromatography on SiO$_2$ (15-30% EtOAc in hexanes gradient) to give the diamination product in a 64% yield (35.9 mg, 0.061 mmol) as a white solid. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [Regis (S,S)-Whelk, 8% IPA/hexanes, 1 mL/min, $\lambda$=254 nm, t(major) = 44.62 min, t(minor) = 36.43 min] revealing 90% enantiomeric excess. \([\alpha]_D^{21} = +71.9 \ (c \ 0.40, \text{CHCl}_3)\).

**(S)-N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)indolin-2-yl)methyl)-2-(trimethylsilyl)ethanesulfonamide (2i)**

Diamination adduct **2i** (33.8 mg, 59% yield) was obtained as a white solid from 40 mg of **1e** using Procedure E, except SESNH$_2$ was used as the nucleophile. The diamination to
carboamination ratio was determined to be 66:34 based on the relative integrations of the hydrogen peak at 4.20 ppm at the 2-position on the diamination product to the hydrogen peak at 3.95 ppm at the 10-position of the carboamination product in the crude $^1$H NMR. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [Regis (S,S)-Whelk, 5% IPA/hexanes, 1 mL/min, $\lambda$=254 nm, t(major) = 32.71 min, t(minor) = 27.60 min] revealing 91% enantiomeric excess. $[\alpha]_D^{23} = +42.9$ (c 0.15, CHCl$_3$).

![Diagram of 2j](attachment:2j-diagram.png)

**(S)-N-(((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)-5-methoxyindolin-2-yl)methyl)-4-methylbenzenesulfonamide (2j))**

Diamination adduct 2j (33.6 mg, 61% yield) was obtained as a white solid from 40 mg of 1f using Procedure E. The diamination to carboamination ratio was determined to be 66:34 based on the relative integrations of the hydrogen peak at 4.10 ppm at the 2-position on the diamination product to the hydrogen peak at 3.93 ppm at the 10-position of the carboamination product in the crude $^1$H NMR. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [Regis (S,S)-Whelk, 8% IPA/hexanes, 1 mL/min, $\lambda$=254 nm, t(major) = 38.86 min, t(minor) = 31.32 min] revealing 85% enantiomeric excess. $[\alpha]_D^{19} = +80.4$ (c 0.30, CHCl$_3$).

![Diagram of 2k](attachment:2k-diagram.png)

**(S)-N-((5-Bromo-1-(3,5-di-tert-butyl-4-methoxyphenylsulfonyl)indolin-2-yl)methyl)-4-methylbenzenesulfonamide (2k)**

Diamination adduct 2k (31.7 mg, 59% yield) was obtained as a white solid from 40 mg of 1g using Procedure E. The diamination to carboamination ratio was determined to be 63:37 based on the relative integrations of the hydrogen peak at 4.26 ppm at the 2-position on the diamination product to the hydrogen peak at 3.96 ppm at the 10-position of the carboamination product in the crude $^1$H NMR. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [Regis (S,S)-Whelk, 5% IPA/hexanes, 1 mL/min, $\lambda$=254 nm, t(major) = 31.27 min, t(minor) = 24.99 min] revealing 84% enantiomeric excess. $[\alpha]_D^{23} = +66.9$ (c 0.16, CHCl$_3$).
(S)-N-((5-Chloro-1-(3,5-di-tert-butyl-4-methoxyphenylsulfonyl)indolin-2-yl)methyl)-4-methylbenzenesulfonamide (2l)
Diamination adduct 2l (33.0 mg, 60% yield) was obtained as a white solid from 40 mg of 1h using Procedure E. The diamination to carboamination ratio was determined to be 63:37 based on the relative integrations of the hydrogen peak at 4.16 ppm at the 2-position on the diamination product to the hydrogen peak at 3.88 ppm at the 10-position of the carboamination product in the crude 1H NMR. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [Regis (S,S)-Whelk, 12% IPA/hexanes, 1 mL/min, λ=254 nm, t(major) = 19.29 min, t(minor) = 16.31 min] revealing 83% enantiomeric excess. [α]D22 = +103.9 (c 0.15, CHCl3).

7,9-Di-tert-butyl-2-chloro-8-methoxy-10a,11-dihydro-10H-5-thia-4b-aza-benzo[b]fluorene 5,5-dioxide (3e)
Carboamination adduct 3e (10.1 mg, 20%) was obtained as a colorless oil from the same reaction as 2l. Data for 3e: 1H NMR (400 MHz, CDCl3) δ 7.67 (s, 1H), 7.39 (d, J=8.0 Hz, 1H), 7.14 (d, J=8.5 Hz, 1H), 7.04 (s, 1H), 4.96-4.82 (m, 1H), 3.96-3.82 (m, 1H), 3.67 (d, J=12.8 Hz, 1H), 3.56 (s, 3H), 3.11-2.99 (m, 1H), 2.92-2.79 (m, 1H), 1.55 (s, 9H), 1.35 (s, 9H). 1H NMR matched the previously reported data.4

(S)-N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)-5-fluoroindolin-2-yl)methyl)-4-methylbenzenesulfonamide (2m)
Diamination adduct 2m (33 mg, 60% yield) was obtained as a white solid from 40 mg of 1i using Procedure E. The diamination to carboamination ratio was determined to be 64:36 based on the relative integrations of the hydrogen peak at 4.16 ppm at the 2-position on the diamination product to the hydrogen peak at 3.87 ppm at the 10-position of the carboamination product in the crude 1H NMR. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [Regis (S,S)-Whelk, 12% IPA/hexanes, 1 mL/min, λ=254 nm, t(major) = 19.68 min, t(minor) = 16.29 min] revealing 85% enantiomeric excess. [α]D21 = +54.5 (c 0.27, CHCl3).
(S)-N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)-5-methylindolin-2-yl)methyl)-4-methylbenzenesulfonamide (2n)

Diamination adduct 2n (35.1 mg, 63% yield) was obtained as a white solid from 40 mg of 1j using Procedure E. The diamination to carboamination ratio was determined to be 67:23 based on the relative integrations of the hydrogen peak at 4.11 ppm at the 2-position on the diamination product to the hydrogen peak at 3.87 ppm at the 10-position of the carboamination product in the crude $^1$H NMR. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [Regis (S,S)-Whelk, 12% IPA/hexanes, 1 mL/min, $\lambda=254$ nm, t(major) = 24.83 min, t(minor) = 20.15 min] revealing 81% enantiomeric excess. $[\alpha]_D^{21} = +36.19$ (c 0.34, CHCl$_3$).

**Representative Procedure F for catalytic enantioselective diamination (Table 5, entry 1)**

(S)-N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)-4,4-dimethylpyrrolidin-2-yl)methyl)-4-methylbenzenesulfonamide (6a)

Cu(OTf)$_2$ (7.3 mg, 0.020 mmol, 20 mol %) was placed in a glass pressure tube, under an argon atmosphere in a dry box, with a magnetic stir bar. (R,R)-Ph-box (7.4 mg, 0.022 mmol, 22 mol %) in PhCF$_3$ (0.50 mL) was added via syringe through a septum. The tube was capped and the reaction mixture was placed in a 60 °C oil bath and stirred. After 2 h, the catalyst solution was cooled to rt. 3,5-Di-tert-butyl-N-(2,2-dimethylpent-4-enyl)-4-methoxybenzenesulfonamide (5a) (40 mg, 0.101 mmol, 1 equiv) was dissolved in DCE (0.50 mL) and was added via syringe to the glass pressure tube, under an argon atmosphere, and the resulting solution was treated with 2,6-di-tert-butyl-4-methylpyridine (20.7 mg, 0.101 mmol, 1 equiv) and TsNH$_2$ (69.2 mg, 0.404 mmol, 4 equiv). A heterogeneous mixture of MnO$_2$ (26.4 mg, 0.303 mmol, 3 equiv) and KMnO$_4$ (2.4 mg, 0.015 mmol, 0.15 equiv) was prepared using a mortar and pestle and added to the pressure tube. 4 Å mol. sieves (20.2 mg) were flame dried for 5 min and added to the reaction mixture. The tube was capped and the reaction mixture was stirred at rt for 20 min before being placed in a 100 °C oil bath and stirred. After 24 h, the reaction mixture was cooled to rt, diluted with EtOAc (10 mL), sonicated, filtered through Celite with EtOAc (140 mL), and concentrated in vacuo. The diamination to carboamination ratio was determined to be 67:33 based on the relative integrations of the hydrogen peak at 3.55 ppm at the 2-position on the diamination.
product to the hydrogen peak at 4.27 ppm at the 10a-position of the carboamination product in the crude \( ^1 \text{H} \) NMR. The resulting solid was purified by flash chromatography on SiO\(_2\) (10-25\% EtOAc in hexanes gradient) to give the diamination product in a 64\% yield (36.5 mg, 0.064 mmol) as a white waxy solid.

Data for compound \( 6a \): mp 64-68 °C; \([\alpha]_D^{22} = -72.2 \) (c 0.20, CHCl\(_3\), >95\% ee); \( ^1 \text{H} \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.75 (d, \( J=7.0 \) Hz, 2H), 7.67 (s, 2H), 7.32 (d, \( J=7.5 \) Hz, 2H), 5.31 (t, \( J=7.0 \) Hz, 1H), 3.67 (s, 3H), 3.58-3.52 (m, 1H), 3.30-3.26 (m, 1H), 3.18-3.12 (m, 2H), 3.06 (d, \( J=11.0 \) Hz, 1H), 2.43 (s, 3H), 1.80-1.77 (m, 1H), 1.68-1.64 (m, 1H), 1.43 (s, 18H), 1.00 (s, 3H), 0.27 (s, 3H); \( ^{13} \text{C} \) NMR (75.5 MHz, CDCl\(_3\)) \( \delta \) 163.8, 145.4, 143.4, 136.9, 130.4, 129.8, 127.0, 126.0, 64.7, 62.1, 59.7, 47.1, 44.0, 37.0, 36.1, 31.8, 26.0, 25.4, 25.3, 21.5; IR (neat, thin film) \( \nu \) 3291, 2959, 2360, 2341, 1732, 1598, 1455, 1406, 1334, 1255, 1226, 1162, 1123, 1093, 1034, 1006, 974; HRMS (ESI) calced for C\(_{29}\)H\(_{44}\)O\(_5\)N\(_2\)Na\(_2\) [M+Na\(^+\)] 587.2584, found 587.2576.

The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [Regis (S,S)-Whelk, 5\% IPA/hexanes, 1 mL/min, \( \lambda=254 \) nm, t(major) = 32.91 min, t(minor) = 31.79 min] revealing >95\% enantiomeric excess.

Note: Racemic samples of pyrrolidine diamines \( 6 \) necessary for HPLC analysis were obtained by running the catalytic reaction with the achiral bis(oxazoline) ligand \( 23 \).

\[
7,9-\text{Di-}^\text{tert}-\text{butyl-8-methoxy-2,2-dimethyl-2,3,10a-5,5-dioxide-tetrahydro-1H-benzo[}e\text{]pyrrolo[1,2-b][1,2]thiazine (7)\]
\]

Carboamination adduct \( 7 \) (10.0 mg, 25\% yield) was obtained as a brown oil from 40 mg of \( 5a \) using Procedure E as a side product to \( 6a \) in the diamination reaction.

Data for compound \( 7 \): \( ^1 \text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.72 (s, 1H), 4.32-4.22 (m, 1H), 3.56 (s, 3H), 3.38 (bs, 1H), 3.12 (d, \( J=8.2 \) Hz, 1H), 2.47 (bs, 1H), 1.68 (d, \( J=8.4 \) Hz, 1H), 1.51 (s, 9H), 1.39 (s, 9H), 1.25 (d, \( J=2.8 \) Hz, 2H), 1.14 (s, 6H); \( ^{13} \text{C} \) NMR (75.5 MHz, CDCl\(_3\)) \( \delta \) 163.9, 142.8, 134.6, 132.1, 122.5, 110.0, 64.7, 59.2, 44.9, 37.2, 36.9, 35.8, 32.7, 31.1, 29.7, 29.3, 26.0, 25.6; IR (neat, thin film) \( \nu \) 3016, 2961, 2871, 1579, 1538, 1468, 1450, 1413, 1400, 1370, 1332, 1290, 1268, 1232, 1194, 1162, 1124, 1093, 1050, 1020, 965; HRMS (ESI) calced for C\(_{22}\)H\(_{36}\)O\(_3\)N\(_1\)S\(_1\) [M+H\(^+\)] 394.2410, found 394.2408.
(S)-N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)-4,4-dimethylpyrrolidin-2-yl)methyl)-2-(trimethylsilyl)ethanesulfonamide (6b)

Diamination adduct 6b (33.7 mg, 58% yield) was obtained as a white waxy solid from 40 mg of 5a using Procedure F, except SESNH$_2$ was used as the nucleophile and (4R,5S)-di-Ph-box was used as the ligand. The diamination to carboamination ratio was determined to be 63:37 based on the relative integrations of the hydrogen peak at 3.56 ppm at the 2-position on the diamination product to the hydrogen peak at 4.27 ppm at the 10a-position of the carboamination product in the crude $^1$H NMR.

Data for compound 6b: mp 58-60 °C; $[\alpha]_D^{22} = -31.6$ (c 0.16, CHCl$_3$, >95% ee); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.71 (s, 2H), 5.10 (t, $J$=5.2 Hz, 1H), 3.68 (s, 3H), 3.58-3.53 (m, 2H), 3.34-3.26 (m, 2H), 3.21 (d, $J$=10.8 Hz, 1H), 3.09 (d, $J$=10.8 Hz, 1H), 3.00-2.96 (m, 2H), 1.85-1.79 (m, 1H), 1.69-1.64 (m, 1H), 1.44 (s, 18H), 1.09-1.05 (m, 2H), 1.02 (s, 3H), 0.28 (s, 3H), 0.07 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.9, 145.4, 130.3, 126.0, 64.8, 62.2, 60.1, 46.9, 43.7, 36.9, 36.1, 34.9, 31.8, 26.0, 25.3, 10.6, -2.0; IR (neat, thin film) ν 3305, 2924, 2361, 1406, 1331, 1253, 1226, 1164, 842; HRMS (ESI) calcd for C$_{27}$H$_{51}$O$_5$N$_2$S$_2$Si$_1$ [M+H]$^+$ 575.3003, found 575.3005.

The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [Regis (S,S)-Whelk, 5% IPA/hexanes, 1 mL/min, λ=254 nm, t(major) = 23.61 min, t(minor) = 22.62 min] revealing >95% enantiomeric excess.

(S)-N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)-4,4-dimethylpyrrolidin-2-yl)methyl)benzenesulfonamide (6c)

Diamination adduct 6c (35.0 mg, 63% yield) was obtained as a white waxy solid from 40 mg of 5a using Procedure F, except PhSO$_2$NH$_2$ was used as the nucleophile and (4R,5S)-di-Ph-box was used as the ligand. The diamination to carboamination ratio was determined to be 69:31 based on the relative integrations of the hydrogen peak at 3.56 ppm at the 2-position on the diamination product to the hydrogen peak at 4.28 ppm at the 10a-position of the carboamination product in the crude $^1$H NMR.

Data for compound 6c: mp 111-114 °C; $[\alpha]_D^{23} = -75.0$ (c 0.25, CHCl$_3$, >95% ee); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, $J$=7.6 Hz, 2H), 7.67 (s, 2H), 7.59-7.52 (m, 3H), 5.41 (t, $J$=6.4 Hz, 1H),
3.67 (s, 3H), 3.58-3.54 (m, 1H), 3.34-3.28 (m, 1H), 3.20-3.14 (m, 2H), 3.06 (d, J=11.2 Hz, 1H), 1.79-1.74 (m, 1H), 1.68-1.63 (m, 1H), 1.43 (s, 18H), 0.99 (s, 3H), 0.27 (s, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$) δ 163.8, 145.4, 139.9, 132.6, 130.3, 129.2, 126.9, 125.9, 64.7, 62.1, 59.7, 47.1, 44.0, 37.0, 36.1, 31.8, 26.0, 25.3; IR (neat, thin film) ν 3285, 2960, 2872, 1724, 1577, 1448, 1406, 1333, 1254, 1226, 1163, 1123, 1093, 1033, 1006, 974; HRMS (ESI) calcd for C$_{28}$H$_{43}$O$_5$N$_2$S$_2$ [M+H]$^+$ 551.2608, found 551.2616.

The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [Regis (S,S)-Whelk, 5% IPA/hexanes, 1 mL/min, λ=254 nm, t(major) = 43.65 min, t(minor) = 41.99 min] revealing >95% enantiomeric excess.

(S)-N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)-4,4-dimethylpyrrolidin-2-yl)methyl)-2-methylbenzenesulfonylamide (6d)

Diamination adduct 6d (25.4 mg, 62% yield) was obtained as a white waxy solid from 40 mg of 5a using Procedure F, except 2-MeC$_6$H$_4$SO$_2$NH$_2$ was used as the nucleophile and (4R,5S)-di-Ph-box was used as the ligand. The diamination to carboamination ratio was determined to be 68:32 based on the relative integrations of the hydrogen peak at 3.54 ppm at the 2-position on the diamination product to the hydrogen peak at 4.27 ppm at the 10a-position of the carboamination product in the crude $^1$H NMR.

Data for compound 6d: mp 54-56 °C; [α]$_D^{23}$ = -61.9 (c 0.37, CHCl$_3$, >95% ee); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, J=8.0 Hz, 1H), 7.68 (s, 2H), 7.46 (t, J=7.2 Hz, 1H), 7.35-7.30 (m, 2H), 5.58 (t, J=6.8 Hz, 1H), 3.67 (s, 3H), 3.56-3.52 (m, 1H), 3.33-3.29 (m, 1H), 3.18 (d, J=10.8 Hz, 1H), 3.10-3.04 (m, 2H), 2.71 (s, 3H), 1.76-1.59 (m, 2H), 1.43 (s, 18H), 0.98 (s, 3H), 0.27 (s, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$) δ 163.9, 145.4, 137.9, 137.1, 132.7, 132.7, 130.3, 129.2, 126.1, 126.0, 64.7, 62.2, 59.8, 46.8, 44.2, 36.9, 36.1, 31.8, 29.7, 26.0, 25.3, 20.3; IR (neat, thin film) ν 3305, 2962, 1575, 1532, 1463, 1406, 1332, 1259, 1226, 1162, 1033, 885; HRMS (ESI) calcd for C$_{29}$H$_{45}$O$_5$N$_2$S$_2$ [M+H]$^+$ 565.2764, found 565.2767.

The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [CHIRALPAK OD-H, 4% IPA/hexanes, 1 mL/min, λ=254 nm, t(major) = 95.51 min, t(minor) = 110.80 min] revealing >95% enantiomeric excess.
(S)-N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)-4,4-dimethylpyrrolidin-2-yl)methyl)-
4-methoxybenzenesulfonamide (6e)
Diamination adduct 6e (36.5 mg, 60% yield) was obtained as a white waxy solid from 40 mg of
5a using Procedure F, except 4-MeOC₆H₄SO₂NH₂ was used as the nucleophile and (4R,5S)-di-Ph-box was used as the ligand. The diamination to carboamination ratio was determined to be 66:34 based on the relative integrations of the hydrogen peak at 3.57 ppm at the 2-position on the
diamination product to the hydrogen peak at 4.27 ppm at the 10a-position of the carboamination
product in the crude ¹H NMR.
Data for compound 6e: mp 60-62 °C; [α]D²² = -65.4 (c 0.18, CHCl₃, >95% ee); ¹H NMR (300
MHz, CDCl₃) δ 7.81 (d, J=9.0 Hz, 2H), 7.67 (s, 2H), 6.99 (d, J=8.7 Hz, 2H), 5.29 (t, J=6.6 Hz,
1H), 3.88 (s, 3H), 3.67 (s, 3H), 3.60-3.53 (m, 1H), 3.30-3.24 (m, 1H), 3.19-3.08 (m, 2H), 3.06 (d,
J=11.1 Hz, 1H), 1.81-1.63 (m, 2H), 1.43 (s, 18H), 1.00 (s, 3H), 0.27 (s, 3H); ¹³C NMR (75.5
MHz, CDCl₃) δ 163.8, 162.9, 145.4, 131.5, 130.4, 129.1, 126.0, 114.3, 64.7, 62.1, 59.7, 55.6,
47.1, 44.0, 37.0, 36.1, 31.8, 30.0, 29.7, 26.0, 25.3; IR (neat, thin film) v 3287, 2961, 2872, 1724,
1598, 1580, 1499, 1463, 1406, 1334, 1260, 1226, 1159, 1094, 1030, 975; HRMS (ESI) calcd for
C₂₉H₄₄O₆N₂Na₂S₂ [M+H]+ 603.2533, found 603.2535.
The product was further purified by HPLC and subsequently analyzed via chiral HPLC column
[Regis (S,S)-Whelk, 5% IPA/hexanes, 1.0 mL/min, λ=254 nm, t(major) = 89.56 min, t(minor) =
84.21 min] revealing >95% enantiomeric excess.

(S)-4-Chloro-N-((1-(3,5-di-tert-butyl-4-methoxyphenylsulfonyl)-4,4-dimethylpyrrolidin-2-
yl)methyl)benzenesulfonamide (6f)
Diamination adduct 6f (35.4 mg, 60% yield) was obtained as a white waxy solid from 40 mg of
5a using Procedure F, except 4-ClC₆H₄SO₂NH₂ was used as the nucleophile and (4R,5S)-di-Ph-
box was used as the ligand. The diamination to carboamination ratio was determined to be 64:36 based on the relative integrations of the hydrogen peak at 3.55 ppm at the 2-position on the diamination product to the hydrogen peak at 4.28 ppm at the 10a-position of the carboamination product in the crude $^1$H NMR.

Data for compound 6f: mp 63-66 °C; [$\alpha$]$_D^{23}$ = -70.0 (c 0.22, CHCl$_3$, >95% ee); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J$=8.0 Hz, 2H), 7.67 (s, 2H), 7.51 (d, $J$=8.4 Hz, 2H), 5.49 (t, $J$=6.4 Hz, 1H), 3.67 (s, 3H), 3.57-3.53 (m, 1H), 3.33-3.28 (m, 1H), 3.19-3.12 (m, 2H), 3.07 (d, $J$=11.2 Hz, 1H), 1.77-1.64 (m, 2H), 1.43 (s, 18H), 1.00 (s, 3H), 0.28 (s, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$) $\delta$ 163.9, 145.5, 139.1, 138.4, 130.2, 129.5, 128.5, 126.0, 64.7, 62.2, 59.6, 47.1, 44.1, 37.0, 36.1, 31.8, 27.0, 25.3; IR (neat, thin film) $\nu$ 3291, 2925, 1733, 1576, 1457, 1396, 1337, 1259, 1226, 1163, 1094, 1033, 885; HRMS (ESI) calcd for C$_{28}$H$_{42}$O$_5$N$_2$Cl$_1$S$_2$ [M+H]$^+$ 585.2218, found 585.2221.

The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [Regis (S,S)-Whelk, 5% IPA/hexanes, 0.5 mL/min, $\lambda$=254 nm, t(major) = 57.48 min, t(minor) = 55.87 min] revealing >95% enantiomeric excess.

![Chemical structure](image)

(5)-N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)-4,4-dimethylpyrrolidin-2-yl)methyl)-4-nitrobenzenesulfonamide (6g)

Diamination adduct 6g (34.9 mg, 58% yield) was obtained as a white waxy solid from 40 mg of 5a Procedure F, except 5 equivalents of 4-NO$_2$C$_6$H$_4$SO$_2$NH$_2$ was used as the nucleophile and (4R,5S)-di-Ph-box was used as the ligand. The diamination to carboamination ratio was determined to be 64:36 based on the relative integrations of the hydrogen peak at 3.56 ppm at the 2-position on the diamination product to the hydrogen peak at 4.28 ppm at the 10a-position of the carboamination product in the crude $^1$H NMR.

Data for compound 6g: mp 83-86 °C; [$\alpha$]$_D^{23}$ = -75.9 (c 0.2, CHCl$_3$, >95% ee); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.38 (d, $J$=9.2 Hz, 2H), 8.08 (d, $J$=9.2 Hz, 2H), 7.66 (s, 2H), 5.80 (t, $J$=6.0 Hz, 1H), 3.67 (s, 3H), 3.58-3.54 (m, 1H), 3.39-3.33 (m, 1H), 3.21-3.16 (m, 2H), 3.06 (d, $J$=10.8 Hz, 1H), 1.76-1.66 (m, 2H), 1.43 (s, 18H), 1.00 (s, 3H), 0.26 (s, 3H); $^{13}$C NMR (75.5 MHz, CDCl$_3$) $\delta$ 164.0, 150.1, 145.7, 145.5, 129.9, 128.3, 126.0, 124.5, 110.0, 64.8, 62.2, 59.6, 47.2, 44.1, 36.9, 36.1, 31.8, 26.0, 25.2; IR (neat, thin film) $\nu$ 3283, 2961, 1607, 1532, 1465, 1405, 1348, 1254, 1226, 1164, 1122, 1092, 1033, 1007, 975; HRMS (ESI) calcd for C$_{28}$H$_{42}$O$_5$N$_2$Cl$_1$S$_2$ [M+H]$^+$ 596.2459, found 596.2469.

The product was further purified by HPLC, but the product was not able to be separated via chiral HPLC. The nosyl protecting group was then removed by dissolving the nosyl substrate 9g (26.3 mg, 0.0441 mmol, 1 equiv) in 3 mL of DMF. The solution was treated with K$_2$CO$_3$ (18.3
mg, 0.132 mmol, 3 equiv) and thiophenol (5.40 μL, 0.0530 mmol, 1.2 equiv) was added via syringe. The reaction stirred at rt overnight. The reaction was concentrated in vacuo and used directly for the next reaction. The crude product was dissolved in 1 mL of DCM cooled to 0 °C, and pyridine (11.0 μL, 0.131 mmol, 3 equiv) was syringed in dropwise, followed by the addition of TsCl (10.0 mg, 0.0526 mmol, 1.2 equiv). After 24 h, the reaction was quenched with 1 mL of water and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (2x1 mL), and the organic layers were combined and washed with 1M HCl (90 mL) and with brine (90 mL), then dried over Na₂SO₄, and concentrated in vacuo. Flash chromatography of the resulting crude oil on SiO₂ (10-25% Et₂O in hexanes gradient) afforded (S)-N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)-4,4-dimethylpyrrolidin-2-yl)methyl)-4-methylbenzenesulfonamide 6a in a 43% yield (10.3 mg, 0.188 mmol) and was subsequently analyzed via chiral HPLC column [Regis (S,S)-Whelk, 5% IPA/hexanes, 1.0 mL/min, λ=254 nm, t(major) = 32.42 min, t(minor) = 34.21 min] revealing >95% enantiomeric excess.

Diamination adduct 6h (31.7 mg, 61% yield) was obtained as a white waxy solid from 40 mg of 5a using Procedure F, except C₃H₅SO₂NH₂ was used as the nucleophile and (4R,5S)-di-Ph-box was used as the ligand. The diamination to carboamination ratio was determined to be 67:33 based on the relative integrations of the hydrogen peak at 3.60 ppm at the 2-position on the diamination product to the hydrogen peak at 4.27 ppm at the 10a-position of the carboamination product in the crude 1H NMR.

Data for compound 6h: mp 112-115 °C; [α]D²⁰ = -80.6 (c 0.19, CHCl₃, >95% ee); ¹H NMR (300 MHz, CDCl₃) 7.71 (s, 2H), 5.09 (t, J=5.1 Hz, 1H), 3.68 (s, 3H), 3.65-3.56 (m, 1H), 3.38-3.33 (m, 1H), 3.20 (d, J=11.1 Hz, 1H), 3.09 (d, J=11.1 Hz, 1H), 2.48-2.43 (m, 1H), 1.84-1.77 (m, 1H), 1.69-1.63 (m, 1H), 1.44 (s, 18H), 1.25-1.21 (m, 2H), 1.08-1.01 (m, 2H), 1.04 (s, 3H), 0.28 (s, 3H); ¹³C NMR (75.5 MHz, CDCl₃) δ 163.9, 145.4, 130.4, 126.0, 65.0, 62.2, 59.9, 47.0, 43.8, 37.0, 36.1, 31.8, 29.8, 29.7, 26.0, 25.3, 5.6, 5.1; IR (neat, thin film) ν 3292, 3015, 2962, 1725, 1576, 1464, 1406, 1332, 1260, 1226, 1162, 1097, 1033, 891; HRMS (ESI) calcd for C₂₅H₄₃O₅N₂S₂ [M+H]+ 515.2608, found 515.2618.

The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [CHIRALPAK OD-H, 4% IPA/hexanes, 0.5 mL/min, λ=254 nm, t(major) = 27.60 min, t(minor) = 38.85 min] revealing >95% enantiomeric excess.
(S)-N-((1-(3,5-Di-tert-butyl-4-methoxyphenylsulfonyl)pyrrolidin-2-yl)methyl)-4-methylbenzenesulfonamide (6i)

Diamination adduct 6i (35.6 mg, 61% yield) was obtained as a white waxy solid from 40 mg of 5b using Procedure F, except (4R,5S)-di-Ph-box was used as the ligand. The diamination to carboamination ratio was determined to be 66:34 based on the relative integrations of the hydrogen peak at 3.61 ppm at the 2-position on the diamination product to the hydrogen peak at 4.08 ppm at the 10a-position of the carboamination product in the crude 1H NMR.

Data for compound 6i: mp 43-46 °C; [α]D 24 = -63.9 (c 0.13, CHCl3, 89% ee); 1H NMR (400 MHz, CDCl3) δ 7.76 (d, J=8.8 Hz, 2H), 7.64 (s, 2H), 7.32 (d, J=8.4 Hz, 2H), 5.25 (t, J=6.0 Hz, 1H), 3.70 (s, 3H), 3.63-3.60 (m, 1H), 3.37-3.31 (m, 1H), 3.18-3.12 (m, 2H), 3.09-3.02 (m, 1H), 2.43 (s, 3H), 1.83-1.76 (m, 2H), 1.70-1.63 (m, 1H), 1.42 (s, 18H), 1.25 (t, J=7.2 Hz, 1H); 13C NMR (75.5 MHz, CDCl3) δ 165.72, 145.42, 143.41, 137.39, 130.53, 129.76, 127.09, 126.04, 64.65, 59.36, 49.77, 47.50, 36.08, 31.78, 29.64, 24.12, 21.51; IR (neat, thin film) ν 3286, 2963, 2872, 2361, 2341, 1943, 1725, 1599, 1576, 1449, 1406, 1333, 1260, 1197, 1160, 1092, 866; HRMS (ESI) calcd for C27H41O5N2S2 [M+H]+ 537.2451, found 537.2453.

The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [CHIRALPAK AD-RH, 5% IPA/hexanes, 1 mL/min, λ=254 nm, t(major) = 18.36 min, t(minor) = 15.23 min] revealing 89% enantiomeric excess.

(S)-N-((4,4-Dimethyl-1-(methylsulfonyl)pyrrolidin-2-yl)methyl)-4-methylbenzenesulfonamide (6j)

Diamination adduct 6j (50.4 mg, 54% yield) was obtained as a yellow oil from 50 mg of N-(2,2-dimethylpent-4-enyl)methanesulfonamide 5c using the Procedure D. Based on crude 1H NMR, the reaction resulted in a 70% conversion to the diamination product, with the remainder of material being starting material.

Data for compound 6j: [α]D 24 = -14.4 (c 0.30, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.74-7.71 (m, 2H), 7.30 (d, J=8.0 Hz, 2H), 5.24 (t, J=13.2 Hz, 1H), 3.85-3.79 (m, 1H), 3.22-3.08 (m, 4H), 2.85 (s, 3H), 2.42 (s, 3H), 1.87 (dd, J=12.8, 7.2 Hz, 1H), 1.77 (dd, J=12.4, 8.8 Hz, 1H), 1.10 (s, 3H), 1.04 (s, 3H); 13C NMR (75.5 MHz, CDCl3) δ 143.5, 136.8, 130.5, 130.3, 129.7, 126.9, 61.9, 59.3, 47.1, 44.0, 37.5, 36.6, 26.4, 26.0, 21.5; IR (neat, thin film) ν 3284, 3024, 2962, 2874, 2256, 1598, 1495, 1455, 1372, 1326, 1253, 1220, 1185, 1158, 1093, 1040, 963; HRMS (ESI) calcd for C15H24O4N2Na1S2 [M+Na]+ 383.1070, found 383.1071.

The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [CHIRALPAK AD-RH, 5% IPA/hexanes, 1 mL/min, λ=254 nm, t(major) = 92.06 min, t(minor) = 98.12 min] revealing 64% enantiomeric excess.
(S)-N-((1-(Cyclopropylsulfonyl)-4,4-dimethylpyrrolidin-2-yl)methyl)-4-methylbenzenesulfonamide (6k)

Diamination adduct 6k (55.1 mg, 63% yield) was obtained as a yellow oil from 50 mg of N-(2,2-dimethylpent-4-enyl)cyclopropanesulfonamide 5d using Procedure D. Based on crude $^1$H NMR, the reaction resulted in an 80% conversion to the diamination product, with the remainder of material being starting material.

Data for compound 6k: $[\alpha]_{D}^{24} = -12.0$ (c 0.88, CHCl$_3$, 72% ee); $^1$H NMR (400 MHz, CDCl$_3$) 7.72 (d, $J=8.8$ Hz, 2H), 7.30 (d, $J=8.8$ Hz, 2H), 5.20 (t, $J=8.0$ Hz, 1H), 3.99-3.93 (m, 1H), 3.27 (d, $J=8.0$ Hz, 1H), 3.23-3.17 (m, 1H), 3.13 (d, $J=10.4$ Hz, 1H), 3.11-3.07 (m, 1H), 2.42 (s, 3H), 2.35-2.30 (m, 1H), 1.90-1.85 (m, 1H), 1.79-1.74 (m, 1H), 1.20-1.14 (m, 2H), 1.11 (s, 3H), 1.10 (s, 3H), 1.00-0.94 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.4, 136.9, 129.7, 127.0, 62.1, 59.2, 47.1, 44.1, 37.5, 27.4, 26.3, 25.9, 21.5, 5.0, 4.7; IR (neat, thin film) $\nu$ 3276, 3023, 2961, 2874, 2443, 2431, 2341, 1921, 1724, 1598, 1495, 1454, 1422, 1372, 1188, 1160, 1144, 1093, 1047, 973; HRMS (ESI) calcd for C$_{17}$H$_{27}$O$_4$N$_2$S$_2$ [M+H]$^+$ 387.1407, found 387.1407. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [CHIRALPAK AD-RH, 40% CH$_3$CN/H$_2$O, 0.20 mL/min, $\lambda$=254 nm, t(major) = 100.37 min, t(minor) = 117.18 min] revealing 72% enantiomeric excess.

Removal of Arylsulfonamide from Chiral Indoline

$N$-(Indolin-2-ylmethyl)-2-(trimethylsilyl)ethanesulfonamide (8)

The deprotection of the aryl sulfonyl functional group from $N$-((1-(3,5-di-tert-butyl-4-methoxyphenylsulfonyl)indolin-2-yl)methyl)-2-(trimethylsilyl)ethanesulfonamide using a procedure reported by Matthews et al. Magnesium powder (4.4 mg, 0.179 mmol, 10 equiv) was treated with 0.12 mL dry methanol (distilled over CaH$_2$) in a 10 mL round bottom flask under an argon atmosphere. A solution of the indoline 2i (11 mg, 0.0179 mmol, 1 equiv) in 0.15 mL dry methanol was syringed into the flask, and the reaction was sonicated at room temperature. The reaction was monitored by TLC until there was no starting material visible after 2 h. The reaction was quenched with saturated aqueous NH$_4$Cl, and the aqueous layer was separated and extracted with Et$_2$O (2x1 mL). The combined organic layers were dried of Na$_2$SO$_4$ and concentrated in vacuo. Flash chromatography of the resulting crude oil on SiO$_2$ (25-40% EtOAc in hexanes gradient) afforded the deprotected indoline in 82% yield (4.6 mg, 0.015 mmol) as a brown oil.

Data for compound 8: $[\alpha]_{D}^{23} = +8.6$ (c 0.20, CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.14-7.07 (m, 2H), 6.88-6.80 (m, 2H), 5.04 (t, $J=6.6$ Hz, 1H), 4.26-4.16 (m, 1H), 3.40-3.34 (m, 1H), 3.30-3.19 (m, 2H), 3.01-2.95 (m, 2H), 2.92-2.85 (m, 2H), 1.05-0.99 (m, 2H), 0.06 (s, 9H); $^{13}$C NMR
 Assignment of Absolute Configuration of 6i

\[ \text{Assignment of Absolute Configuration of 6i} \]

\[
\begin{align*}
\text{(R)-N-}\{(1-(3,5-\text{Di-\text{tert}-butyl-4-methoxyphenylsulfonyl})\text{pyrrolidin-2-yl})\text{methyl}\}-{4-\text{methylbenzenesulfonamide (6i)}}
\end{align*}
\]

Optical rotation comparison to 6i obtained via the enantioselective diamination above revealed it to be opposite in sign and similar in magnitude, indicating the 6i synthesized by the catalytic diamination procedure has (S) configuration, opposite to the one synthesized from the known (R) diamine.
HPLC Traces

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The diagram shows the chromatographic analysis of two compounds, each with different retention times and areas.
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References


