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

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## Supporting Information I

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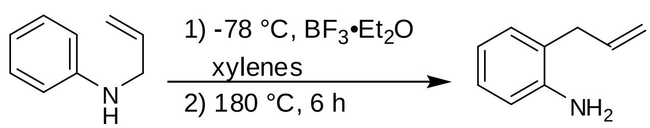
**General experimental information:**

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[(4*R*,5*S*)-4,5-diphenyl-2-oxazoline] and 2,2'-methylenebis[(4*R*)-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 $PhCF_3$ were distilled over $CaH_2$. Anhydrous $CH_2Cl_2$, benzene, THF, $Et_2O$ and toluene were further purified with a commercial solvent purification system equipped with alumina-filled columns and under argon. $MnO_2$ for the experiments was purchased as activated, ca. 85%, <5 µm. $KMnO_4$ for the experiments was purchased as crystal, 99.6%. $^1H$ NMR spectra were recorded in $CDCl_3$ (using 7.26 ppm for reference of residual $CHCl_3$) at 300, 400 or 500 MHz unless otherwise noted. $^{13}C$ NMR spectra were recorded in $CDCl_3$ (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.

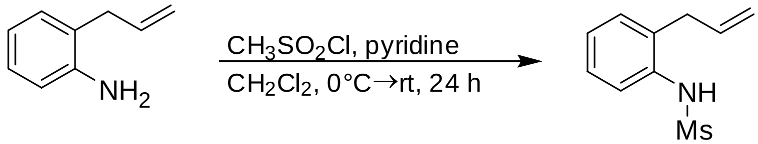



**9** **10**

**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 $Et_2O$ (2x75mL). The organic layers were combined and dried over $MgSO_4$ 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, $CDCl_3$) 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]

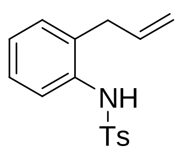
**Representative Procedure A for synthesis of sulfonamides**




**10** **1a**

***N*-(2-Allylphenyl)methanesulfonamide (1a)**

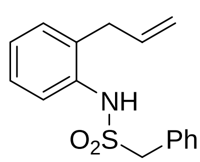
The known sulfonamide **1a** was synthesized as previously reported.[2] 2-Allylaniline **10** (1.26 g, 9.46 mmol, 1 equiv) was dissolved in dry $CH_2Cl_2$ (30 mL) in a 250 mL round bottom flask under an argon atmosphere, and was cooled to 0 °C in an ice bath. The solution was stirred with a magnetic 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 $CH_2Cl_2$ (2x30 mL), and the organic layers were combined and washed with 1M HCl (90 mL) and with brine (90 mL), then dried over $Na_2SO_4$, and concentrated *in vacuo*. Flash chromatography of the resulting crude oil on $SiO_2$ (20-40% $Et_2O$ in hexanes gradient) afforded sulfonamide **1a** as a brown oil in 88% yield (1.76 g, 8.30 mmol). $^1$H NMR (500 MHz, $CDCl_3$) 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). $^1$H NMR matched the previously reported data.[2]




**1b**

***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). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J*=8.0 Hz, 2H), 7.41 (d, *J*=8.0 Hz, 1H), 7.26-7.18 (m, 3H), 7.14-7.06 (m, 2H), 6.53 (s, 1H), 5.83-5.73 (m, 1H), 5.11 (dd, *J*=8.4, 1.6 Hz, 1H), 4.93 (dd, *J*=15.6, 1.6 Hz, 1H), 3.01 (d, *J*=6.0 Hz, 2H), 2.40 (s, 3H). The $^1$H NMR matched the previously reported data.[2]



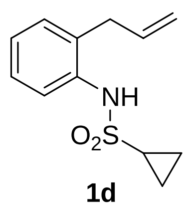

**1c**

***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-toluenesulfonyl chloride.

Data for compound **1c**: mp 55-58 °C; $^1$H NMR (500 MHz, $CDCl_3$) 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) υ 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 $C_{16}H_{17}O_2N_1Na_1S_1$ $[M+Na]^+$ 310.0872, found 310.0864.



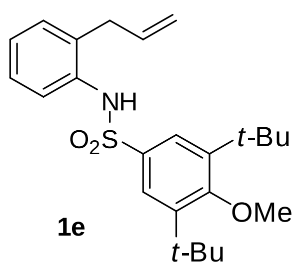
**1d**

***N*-(2-Allylphenyl)cyclopropanesulfonamide (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) υ 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 $C_{12}H_{15}O_2N_1Na_1S_1$ $[M+Na]^+$ 260.0716, found 260.0721.

**Representative Procedure B for synthesis of sulfonamides**

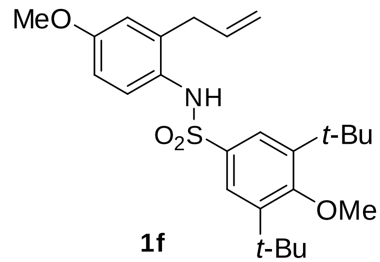


**1e**

***N*-(2-Allylphenyl)-3,5-di-*tert*-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 $CH_2Cl_2$ (3x40 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]

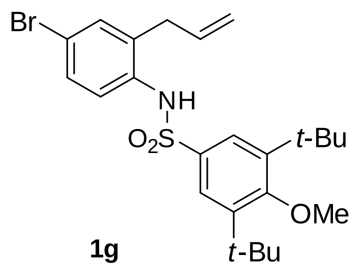



**1f**

***N*-(2-Allyl-4-methoxyphenyl)-3,5-di-*tert*-butyl-4-methoxybenzenesulfonamide (1f)**

Known sulfonamide **1f** (397 mg, 48% yield) was obtained as a white solid from 250 mg of 2-allyl-4-methoxyaniline using Procedure B.

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.[4]

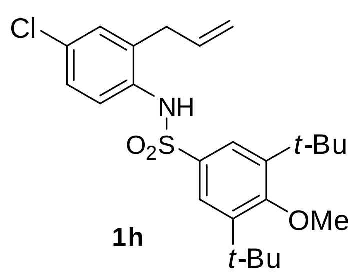



**1g**

***N*-(2-Allyl-4-bromophenyl)-3,5-di-*tert*-butyl-4-methoxybenzenesulfonamide (1g)**

Sulfonamide **1g** (280 mg, 47% yield) was obtained as a white solid from 160 mg of 2-allyl-4-bromoaniline using Procedure B.

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.[4]

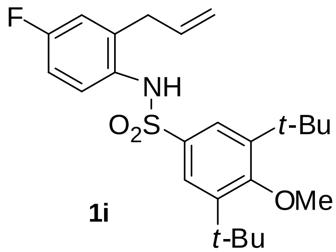



**1h**

***N*-(2-Allyl-4-chlorophenyl)-3,5-di-*tert*-butyl-4-methoxybenzenesulfonamide (1h)**

Sulfonamide **1h** (322 mg, 60% yield) was obtained as a white solid from 160 mg of 2-allyl-4-chloroaniline using Procedure B.

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]

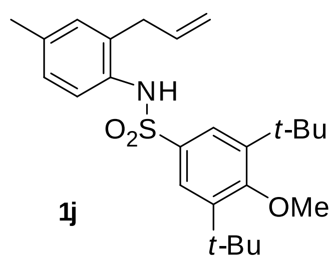



**1i**

***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) υ 3267, 2963, 1493, 1406, 1392, 1335, 1255, 1228, 1165, 1126, 1006, 905 $cm^{-1}$; HRMS (ESI) calcd for $C_{24}H_{33}O_3N_1F_1S_1$ $[M+H]^+$ 434.2160, found 434.2156.

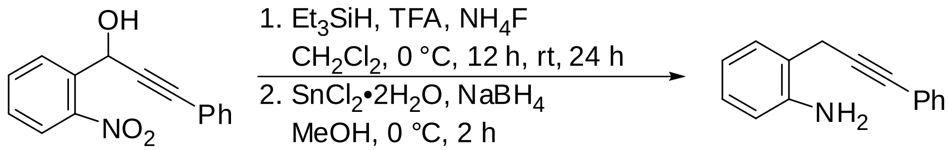



**1j**

***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-methylbenzenamine using Procedure B.

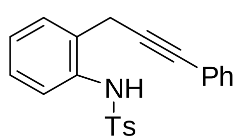
Data for compound **1j:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 2H), 7.36 (d, *J*=8.0 Hz, 1H), 7.05 (d, *J*=8.0 Hz, 1H), 6.84 (s, 1H), 6.29 (s, 1H), 5.70-5.60 (m, 1H), 5.06 (dd, *J*=8.8, 1.6 Hz, 1H), 4.89 (dd, *J*=15.6, 1.6 Hz, 1H), 3.66 (s, 3H), 2.73 (d, *J*=6.0 Hz, 2H), 2.27 (s, 3H), 1.31 (s, 18H). $^{1}$H NMR matched the previously reported data.[4]




**11** **12**

**2-(3-Phenylprop-2-ynyl)benzenamine (12)**

The known 2-(3-phenylprop-2-ynyl)benzenamine **12** was synthesized as previously reported.[5] 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 $Et_2O$ (2x20 mL). The organic layer was then washed with aqueous $NaHCO_3$, dried over $Na_2SO_4$, and concentrated *in vacuo*. Flash chromatography of the resulting crude product on $SiO_2$ (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 $SnCl_2$•$2H_2O$ (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 $NaBH_4$ (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 $H_2O$ and 10 mL of brine. The organic layer was dried over $Na_2SO_4$ 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 ($CDCl_3$, 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.[5]

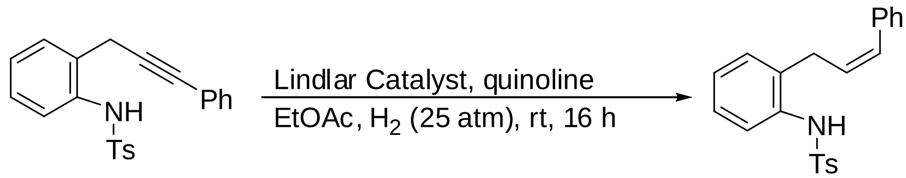



**13**

**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.

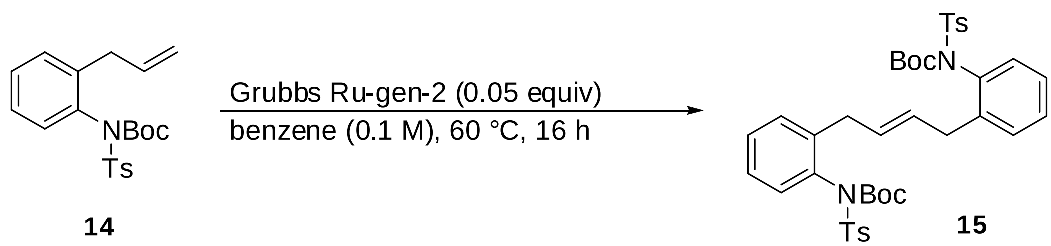
Data for compound **13**: mp 106-109 °C; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J*=8.0 Hz, 2H), 7.44-7.42 (m, 2H), 7.37 (d, *J*=8.4 Hz, 1H), 7.32 (d, *J*=2.0 Hz, 2H), 7.31 (d, *J*=2.0 Hz, 1H), 7.25-7.15 (m, 4H), 7.03 (s, 1H), 3.41 (s, 2H), 2.38 (s, 3H); $^{13}C$ NMR (75.5 MHz, $CDCl_3$) δ 143.8, 136.6, 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) υ 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 $C_{22}H_{19}O_2N_1Na_1S_1$ $[M+Na]^+$ 384.1029, found 384.1033.




**13**

**1k**

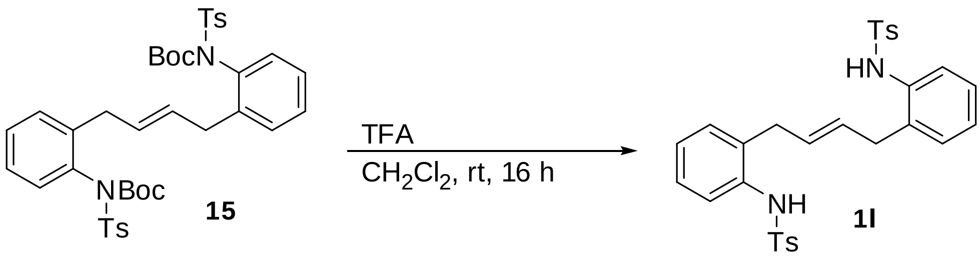
**(*Z*)-4-Methyl-*N*-(2-(3-phenylallyl)phenyl)benzenesulfonamide (1k)**
Sulfonamide **1k** was synthesized as previously reported.[6] 4-Methyl-*N*-(2-(3-phenylprop-2-ynyl)phenyl)benzenesulfonamide (150 mg, 0.415 mmol, 1 equiv) was dissolved in 15 mL of EtOAc. Pd/$CaCO_3$ poisoned with lead (Lindlar catalyst, 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 $SiO_2$ (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; $^1$H NMR (400 MHz, $CDCl_3$) 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); $^{13}$C NMR (75.5 MHz, $CDCl_3$) 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) υ 3284, 3026, 2924, 2856, 1599, 1493, 1453, 1398, 1332 1290, 1231, 1164, 1162, 1092, 1019, 916 $cm^{-1}$; HRMS (ESI) calcd for $C_{22}H_{21}O_2N_1Na_1S_1$ $[M+Na]^+$ 386.1185, found 386.1179.




**14**

**15**

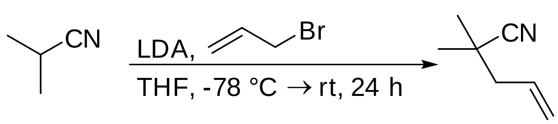
***(E)*-Di-*tert*-butyl (2-di-(4-methylphenylsulfonamido)phenyl)but-2-enyl)carbamate (15)**
The known *tert*-butyl 2-allylphenyl(tosyl)carbamate **14**[7] (146 mg, 0.379 mmol, 1 equiv) was dissolved in 3.8 mL of dry benzene in a 50 mL round bottom flask under an argon atmosphere. The solution was stirred with a magnetic stir bar and Ru(II) Grubbs' catalyst, 2nd generation[8] (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 $SiO_2$ (10-20% 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; $^1$H NMR (400 MHz, $CDCl_3$) 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, 2H), 3.45 (d, *J*=3.6 Hz, 4H), 2.47 (s, 6H), 1.34 (s, 18H); $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 150.8, 144.6, 140.8, 136.8, 135.2, 130.1, 130.0, 129.5, 129.3, 129.11, 128.9, 128.9, 126.8, 84.2, 34.1, 27.9, 21.7; IR (neat, thin film) υ 3028, 2980, 2928, 1732, 1597, 1490, 1452, 1395, 1368, 1290, 1254, 1171, 1150, 1089, 1070, 1042, 972 $cm^{-1}$; HRMS (ESI) calcd for $C_{40}H_{46}O_8N_2Na_1S_2$ $[M+Na]^+$ 769.2588, found 769.2596.




**(*E*)-*N*-(2-(4-(2-(4-Methylphenylsulfonamido)but-2-enyl)phenyl)-4-methylbenzenesulfonamide (1l)**

*(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 in 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 $Na_2SO_4$ and concentrated *in vacuo*. Flash chromatography of the resulting crude product on $SiO_2$ (20-30% EtOAc in hexanes gradient) afforded product **1l** as a white solid in 68% yield (30 mg, 0.055 mmol).

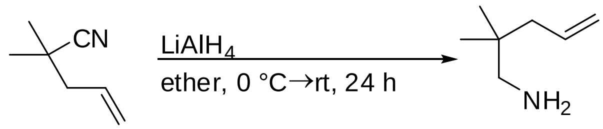
Data for compound **1l**: mp 68-72 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J*=8.1 Hz, 4H), 7.31-7.06 (m, 12H), 6.67 (s, 2H), 5.45 (t, *J*=3.0 Hz, 2H), 3.08 (d, *J*=4.2 Hz, 4H), 2.39 (s, 6H); $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 145.2, 143.8, 136.8, 134.7, 133.8, 130.6, 129.9, 129.7, 128.9, 127.6, 127.1, 126.8, 125.4, 35.2, 21.7, 21.6; IR (neat, thin film) υ 3279, 3029, 2924, 1598, 1492, 1454, 1401, 1332, 1291, 1231, 1161, 1091, 1044, 1019, 910 cm$^{-1}$; HRMS (ESI) calcd for $C_{30}H_{30}O_4N_2Na_1S_2$ $[M+Na]^+$ 569.1539, found 569.1521.




16 17

**2,2-Dimethylpent-4-enenitrile (17)**

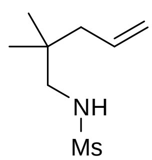
The known allyl nitrile **17** was synthesized as previously reported.[9] Diisopropyl amine (6.75 mL, 48.0 mmol, 1.2 equiv) was dissolved in dry THF (40 mL) under an argon atmosphere. The reaction was cooled to -78 °C in an acetone/dry ice bath with stirring with a magnetic stir bar. The *n*-butyl lithium (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 $CH_2Cl_2$ (40 mL) and quenched with $H_2O$ (80 mL). The layers were separated and the organic layer was washed with $H_2O$ (2x80 mL). The organic layer was dried over $Na_2SO_4$, filtered, and concentrated *in vacuo*. The crude residue **17** (2.5 g) was used directly in the next reaction (58% yield). $^1$H NMR (400 MHz, $CDCl_3$) 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). $^1$H NMR matched with previously reported data.[9]




**17** **18**

**2,2-Dimethylpent-4-en-1-amine (18)**

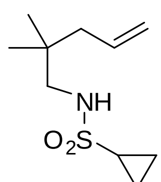
The known allyl amine **18** was synthesized as previously reported.[9] At 0 °C, lithium aluminum hydride (2.14 g, 56.3 mmol, 2.5 equiv) was dissolved in dry $Et_2O$ (145 mL) under an argon atmosphere. Allyl nitrile **17** (2.46 g, 22.5 mmol, 1 equiv) was added and the reaction stirred with a magnetic 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 $Na_2SO_4$, filtered, and concentrated *in vacuo*. The crude amine **18** (quantitative yield) was used directly in the next reaction. $^1$H NMR (400 MHz, $CDCl_3$) 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). $^1$H NMR matched the previously reported data.[9]




**5c**

***N*-(2,2-Dimethylpent-4-enyl)methanesulfonamide (5c)**

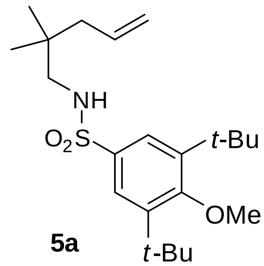
Sulfonamide **5c** (2.19 g, 43% yield) was obtained as a yellow oil from 2.69 g of 2,2-dimethylpent-4-en-1-amine using Procedure B, except methanesulfonyl chloride was used.
Data for compound **5c**: $^1$H NMR (400 MHz, $CDCl_3$) δ 5.86-5.75 (m, 1H), 5.10-5.05 (m, 2H), 4.34 (t, *J*=16.0 Hz, 1H), 2.94 (s, 3H), 2.90 (d, *J*=6.8 Hz, 2H), 2.02 (d, *J*=8.0 Hz, 2H), 0.93 (s, 6H). $^1$H NMR matched the previously reported data.[10]




**5d**

***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 cyclopropanesulfonyl chloride was used.
Data for compound **5d**: $^1$H NMR (400 MHz, $CDCl_3$) 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); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 134.3, 117.8, 52.9, 44.0, 34.2, 29.7, 24.7, 5.1; IR (neat, thin film) υ 3290, 2075, 3005, 2963, 2929, 2872, 1639, 1468, 1423, 1390, 1368, 1329, 1305, 1191, 1151, 1070, 1041, 998 cm$^{-1}$; HRMS (ESI) calcd for $C_{10}H_{19}O_2N_1Na_1S_1$ $[M+Na]^+$ 240.1029, found 240.1029.

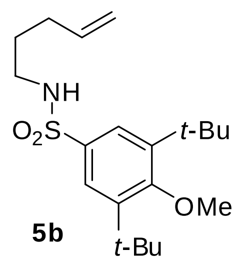


**5a**

**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-methoxy-benzenesulfonyl chloride was used.

Data for compound **5a:** $^1$H NMR (400 MHz, $CDCl_3$) δ $^1$H NMR (500 MHz, $CDCl_3$) δ 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]

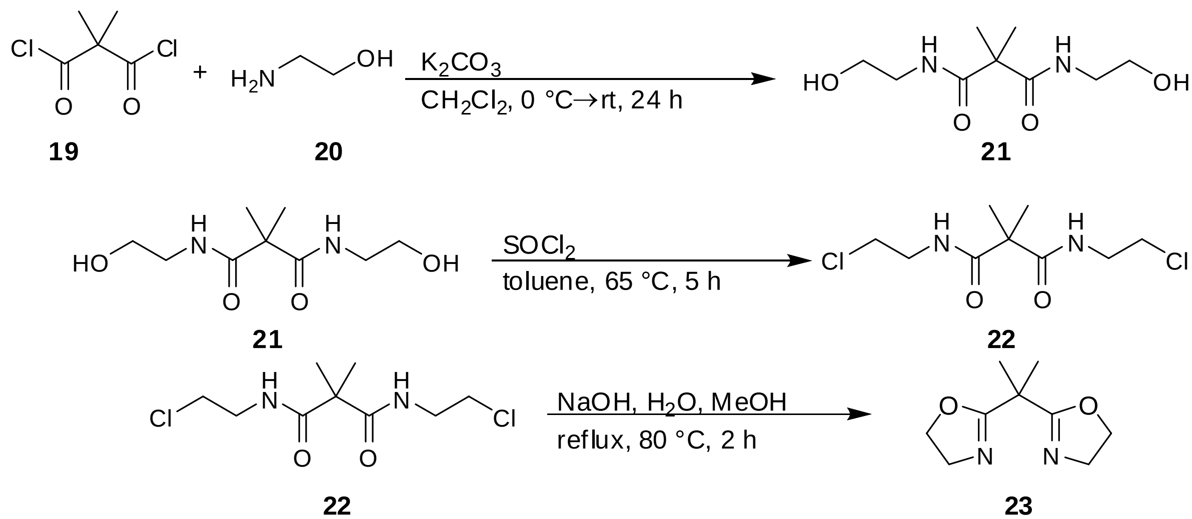


**5b**

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

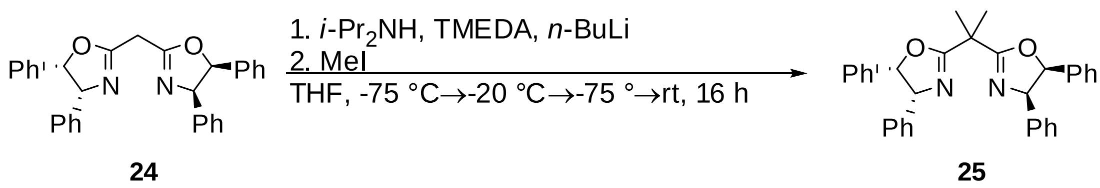
Sulfonamide **5b** was synthesized as previously reported.[12] 4-Penten-1-ol (500 mg, 6 mmol, 1 equiv) was dissolved in dry benzene in a 250 mL round bottom flask under an argon atmosphere. The solution was cooled to 0 ˚C, and was treated with diisopropyl azodicarboxylate (1.76 g, 8.72 mmol, 1.5 equiv) 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 *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, $CDCl_3$) δ 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, $CDCl_3$) δ 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) υ 3277, 2963, 3871, 1447, 1407, 1363, 1324, 1255, 1226, 1162, 1117, 1083, 1005, 889; HRMS (ESI) calcd for $C_{20}H_{33}O_3N_1Na_1S_2$ $[M+Na]^+$ 390.2073, found 390.2062.



**2-(2-(4,5-Dihydrooxazol-2-yl)propan-2-yl)-4,5-dihydrooxazole (23)**

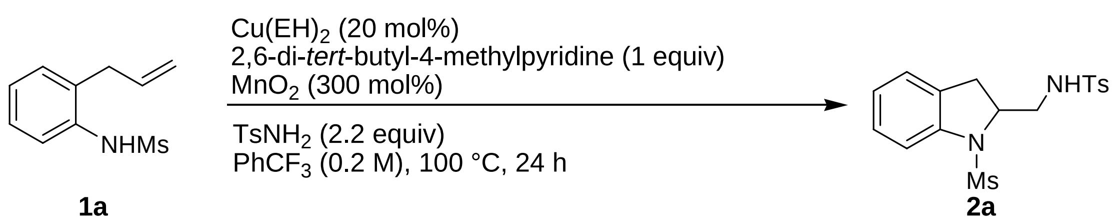
The known ligand **23** was synthesized from dimethylmalonyl dichloride **19** and ethanolamine **20** following a known procedure.[13] The $K_2CO_3$ (5.53 g, 40.0 mmol, 4 equiv) was added into a 250 mL round bottom flask equipped with a magnetic stir bar and sealed with a septum under an argon atmosphere, followed by the addition of dry $CH_2Cl_2$ (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 $CH_2Cl_2$ (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 $NaHCO_3$ solution (20 mL) and extracted with $CH_2Cl_2$ (10x40 mL). The organic layers were dried over $Na_2SO_4$ 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 $H_2O$ 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 $CH_2Cl_2$ (10 mL) and $H_2O$ (10 mL). The organic layer was separated and the aqueous layer was extracted with $CH_2Cl_2$ (4x10 mL). The organic layers were combined and dried over $MgSO_4$ and concenctrated *in vacuo*. The crude ligand **23** (1.06 g) was obtained as a brown solid (58% yield). $^1H$ NMR (400 MHz, $CDCl_3$) 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.[14]




**(4*R*,5*S*)-2-(2-((4*R*,5*S*)-4,5-Diphenyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-diphenyl-4,5-dihydrooxazole (25)**

Alkylation of the bisoxazoline ligand was conducted as previously reported.[10] 2,2'-Methylenebis[(4*R*,5*S*)-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 $NH_4Cl$ and then diluted with 25 mL of DI water. The mixture was extracted with $Et_2O$ (3x50 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated *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, CDCl3) δ 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]

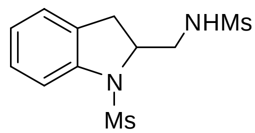
**Representative Procedure C for catalytic diamination (Conditions a, Table 1)**




**4-Methyl-*N*-((1-(methylsulfonyl)indolin-2-yl)methyl)benzenesulfonamide (2a)**

*N*-(2-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-*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 cooled to rt, diluted with EtOAc (10 mL), sonicated, filtered through Celite with EtOAc (140 mL), and concentrated *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, $CDCl_3$) δ 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, $CDCl_3$) δ 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) υ 3299, 2924, 2857, 2257, 1734, 1658, 1597, 1479, 1460, 1337, 1239, 1158, 1096, 981; HRMS (ESI) calcd for $C_{17}H_{20}O_4N_2S_2$ $[M]^+$ 380.0859, found 380.0859.

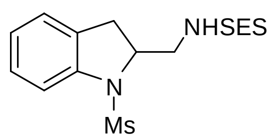



**2b**

***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 $MeSO_2NH_2$ (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 a 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, $CDCl_3$) δ 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, $CD_3CN$) δ 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) υ 3305, 1479, 1457, 1437, 1412, 1331, 1152, 1102, 976, 911; HRMS (ESI) calcd for $C_{11}H_{16}O_4N_2Na_1S_2$ $[M+Na]^+$ 327.0444, found 327.0447.

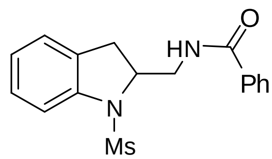



**2c**

***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 $TMS(CH_2)_2SO_2NH_2$ (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, $CDCl_3$) δ 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, $CDCl_3$) δ 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) υ 3294, 2952, 2857, 2252, 1731, 1600, 1479, 1460, 1418, 1345, 1325, 1250, 1158, 1102, 984; HRMS (ESI) calcd for $C_{15}H_{26}O_4N_2Na_1S_2Si_1$ $[M+Na]^+$ 413.0995, found 413.1003.

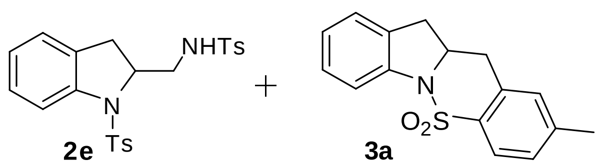



**2d**

**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 $^1$H 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; $^1$H NMR (400 MHz, $CDCl_3$) 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); $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 168.0, 140.5, 134.1, 131.4, 131.2, 128.5, 128.3, 127.0, 125.5, 125.5, 116.9, 61.9, 45.0, 35.7, 33.0; IR (neat, thin film) υ 3397, 3068, 2926, 2853, 2247, 1649, 1603, 1579, 1537, 1479, 1461, 1344, 1241, 1159, 1101, 1025, 985; HRMS (ESI) calcd for $C_{17}H_{18}O_3N_2Na_1S_1$ $[M+Na]^+$ 353.0930, found 353.0931.




**2e** **3a**

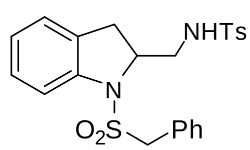
**4-Methyl-N-((1-tosylindolin-2-yl)methyl)benzenesulfonamide (2e)**

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**: $^1$H NMR (300 MHz, $CDCl_3$) 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); $^{13}$C NMR (75.5 MHz, $CDCl_3$) 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) υ 3309, 2927, 2860, 2243, 1733, 1648, 1595, 1477, 1462, 1333, 1241, 1148, 1092, 964; HRMS (ESI) calcd for $C_{23}H_{24}O_4N_2Na_1S_2$ $[M+Na]^+$ 479.1070, found 479.1074.

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

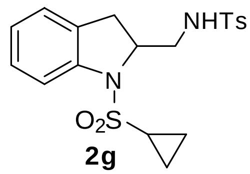
Carboamination adduct **3a** (13.0 mg, 31%) was obtained from the same reaction as **2e** as a colorless solid. $^1$H NMR (500 MHz, $CDCl_3$) 7.74 (d, *J*=8.0 Hz, 1 H), 7.55 (d, *J*=8.0 Hz, 1 H), 7.18-6.96 (m, 5 H), 4.94-4.89 (m, 1 H), 3.49 (dd, *J*=10.5, 5.5 Hz, 1 H), 3.34 (dd, *J*=9.0, 7.0 Hz, 1 H), 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 $^1$H NMR spectrum matched the reported values.[15]




**2f**

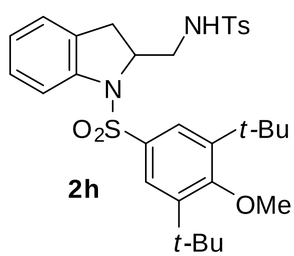
**N-((1-(Benzylsulfonyl)indolin-2-yl)methyl)-4-methylbenzenesulfonamide (2f)**

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 $^{1}$H 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; $^{1}$H NMR (400 MHz, $CDCl_3$) 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); $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 130.8, 130.6, 130.6, 130.3, 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) υ 3280, 3063, 2929, 2255, 1708, 1598, 1495, 1480, 1459, 1338, 1243, 1202, 1158, 1132, 1095, 1042, 982; HRMS (ESI) calcd for $C_{23}H_{24}O_4N_2S_2$ $[M]^+$ 456.1172, found 456.1177.




**2g**

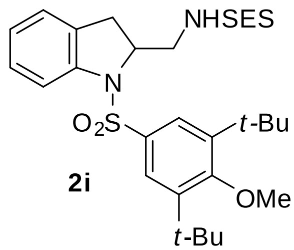
***N*-((1-(Cyclopropylsulfonyl)indolin-2-yl)methyl)-4-methylbenzenesulfonamide (2g)**
Diamination adduct **2g** (64.6 mg, 75% yield) was obtained as a white solid from 50 mg of **1d** Procedure C, except the reaction was run at 110 °C. Based on crude $^{1}$H NMR, the reaction resulted in a >90% conversion to the diamination product, with the remainder of material being trace starting material.
Data for compound **2g**: mp 46-50 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) 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); $^{13}$C NMR (75.5 MHz, $CDCl_3$) 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) υ 3287, 3047, 2928, 2861, 2257, 1598, 1480, 1461, 1342, 1238, 1154, 1095, 1043, 982; HRMS (ESI) calcd for $C_{19}H_{22}O_4N_2Na_1S_2$ $[M+Na]^+$ 429.0913, found 429.0921.




**2h**

***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 $^{1}$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 **2h**: mp 146-148 °C; $^{1}$H NMR (300 MHz, $CDCl_3$) 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

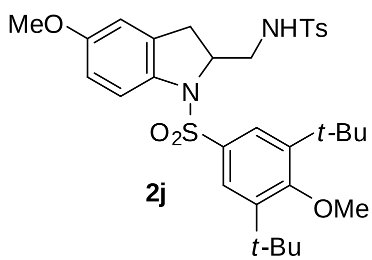
(m, 2H), 5.04 (t, *J*=6.0 Hz, 1H), 4.19-4.10 (m, 1H), 3.02 (s, 3H), 3.21-3.02 (m, 2H), 2.60 (d, *J*=6.0 Hz, 2H), 2.43 (s, 3H), 1.24 (s, 18H); $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 164.0, 145.2, 143.5, 141.1, 136.6, 134.1, 132.0, 130.5, 129.6, 127.9, 127.2, 125.5, 125.0, 118.3, 64.6, 61.1, 47.5, 36.01, 32.11, 31.56, 21.52; IR (neat, thin film) υ 3292, 2963, 1721, 1598, 1478, 1460, 1406, 1341, 1260, 1228, 1163, 1101, 882; HRMS (ESI) calcd for $C_{30}H_{40}O_5N_2Na_1S_2$ $[M+Na]^+$ 607.2271, found 607.2284.




**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 $SESNH_2$ 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.

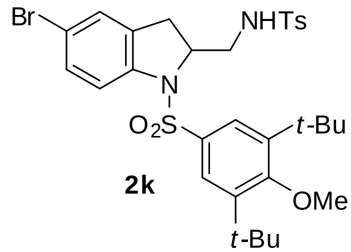
Data for compound **2i**: mp 96-98 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J*=7.6 Hz, 1H), 7.42 (s, 2H), 7.28-7.21 (m, 1H), 7.08-7.02 (m, 2H), 4.82 (t, *J*=5.6 Hz, 1H), 4.23-4.16 (m, 1H), 3.63 (s, 3H), 3.40-3.35 (m, 1H), 3.28-3.23 (m, 1H), 3.01-2.96 (m, 2H), 2.62 (d, *J*=5.6 Hz, 2H), 1.25 (s, 18H), 1.08-1.04 (m, 2H), 0.06 (s, 9H); $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 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) υ 3306, 2959, 2360, 1727, 1478, 1461, 1407, 1355, 1259, 1228, 1169, 1141, 1023, 843; HRMS (ESI) calcd for $C_{29}H_{46}O_5N_2Na_1S_2Si_1$ $[M+Na]^+$ 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, $CDCl_3$) δ 7.75 (d, *J*=7.5 Hz, 2H), 7.48 (d, *J*=8.7 Hz, 1H), 7.33 (s, 2H), 7.30 (d, *J*=7.8 Hz, 2H), 6.75 (d, *J*=9.0 Hz, 1H), 6.54 (s, 1H), 5.06 (t, *J*=6.0 Hz, 1H), 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 Hz, 2H), 2.42 (s, 3H), 1.25 (s, 18H); $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 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) υ 3291, 2963, 2360, 2341, 1719, 1668, 1598, 1487, 1455, 1406, 1342, 1261, 1228, 1164, 1094, 1031, 883; HRMS (ESI) calcd for $C_{32}H_{42}O_6N_2Na_1S_2$ $[M+Na]^+$ 637.2376, found 637.2387.

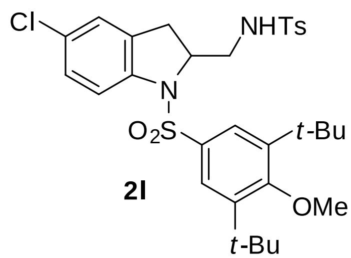


**2k**

***N*-((5-Bromo-1-(3,5-di-*tert*-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, 145.5, 143.6, 140.5, 136.5, 134.4, 130.8, 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) υ 3305, 2962, 2361, 2341, 1734, 1470, 1406, 1406, 1357, 1261, 1164, 1112, 800; HRMS (ESI) calcd for $C_{31}H_{39}O_5N_2Br_1Na_1S_2$ $[M+Na]^+$ 685.1376, found 685.1390.

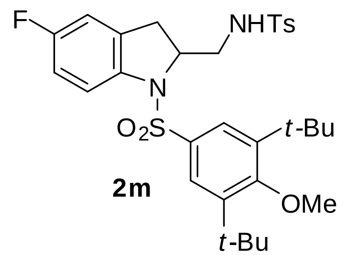


**2l**

***N*-((5-Chloro-1-(3,5-di-*tert*-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) υ 3294, 2961, 1724, 1598, 1471, 1406, 1355, 1256, 1228, 1165, 1114, 1005, 883; HRMS (ESI) calcd for $C_{31}H_{40}O_5N_2Cl_1S_2$ $[M+H]^+$ 619.2062, found 619.2064.

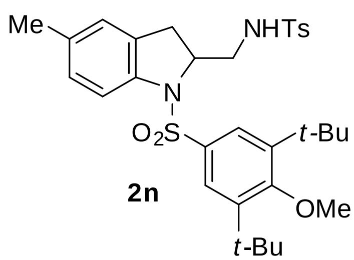



**2m**

***N*-((1-(3,5-Di-*tert*-butyl-4-methoxyphenylsulfonyl)-5-fluoroindolin-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 $^{1}$H 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; $^{1}$H NMR (300 MHz, $CDCl_3$) 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); $^{13}$C NMR (75.5 MHz, $CDCl_3$) 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) υ 3293, 2962, 2871, 1724, 1600, 1481, 1445, 1407, 1353, 1259, 1229, 1165, 1126, 1094, 1006, 938; HRMS (ESI) calcd for $C_{31}H_{40}O_5N_2F_1S_2$ $[M+H]^+$ 603.2357, found 603.2358.

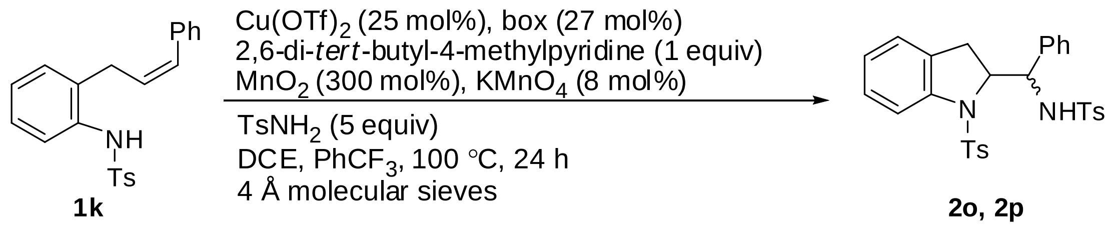



**2n**

***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 $^{1}$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 **2n**: mp 193-194 °C; $^{1}$H NMR (300 MHz, $CDCl_3$) 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); $^{13}$C NMR (75.5 MHz, $CDCl_3$) 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) υ 3305, 2924, 2361, 1724, 1599, 1486, 1457, 1406, 1351, 1259, 1228, 1165, 1094, 885; HRMS (ESI) calcd for $C_{32}H_{43}O_5N_2S_2$ $[M+H]^+$ 599.2608, found 599.2607.



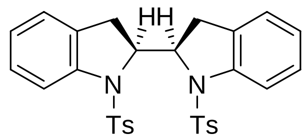
**2-(Phenyl(tosyl)methyl)-1-tosylindoline (2o, 2p)**

$Cu(OTf)_2$ (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 $PhCF_3$ (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 $TsNH_2$ (94.2 mg, 0.55 mmol, 5 equiv). A heterogeneous mixture of $MnO_2$ (28.7 mg, 0.33 mmol, 3 equiv) and $KMnO_4$ (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 $SiO_2$ (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, $CDCl_3$) 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), 6.72 (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); $^{13}C$ NMR (75.5 MHz, $CDCl_3$) 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, 127.6, 127.1, 127.0, 125.2, 124.4, 117.8, 65.3, 61.3, 31.4, 21.5, 21.5; IR (neat, thin film) υ 3272, 3031, 2924, 2360, 2340, 1598, 1479, 1458, 1334, 1259, 1162, 1090, 1028, 910; HRMS (ESI) calcd for $C_{29}H_{28}O_4N_2Na_1S_2$ $[M+Na]^+$ 555.1383, found 555.1376.

Data for compound minor **2p**: mp 70-73 °C; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J*=10.8 Hz, 2H), 7.39 (d, *J*=11.2 Hz, 2H), 7.24-7.10 (m, 11H), 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); $^{13}C$ NMR (75.5 MHz, $CDCl_3$) 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**.



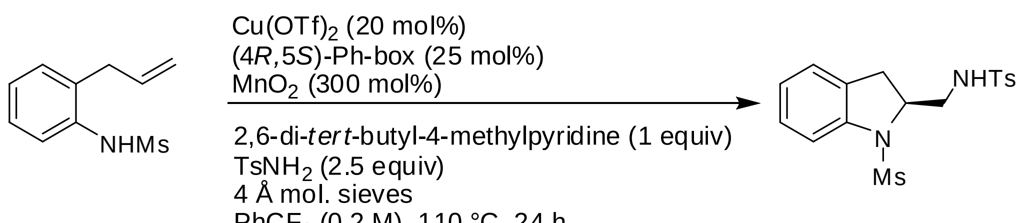

**2q**

**(*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 **1l** 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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) υ 3030, 2924, 2853, 1739, 1598, 1480, 1451, 1354, 1292, 1250, 1224, 1168, 1091, 1025, 971; HRMS (ESI) calcd for $C_{30}H_{28}O_4N_2Na_1S_2$ $[M+Na]^+$ 567.1383, found 567.1390.

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

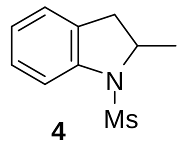



**1a** **2a**

**(*S*)-4-Methyl-*N*-((1-(methylsulfonyl)indolin-2-yl)methyl)benzenesulfonamide (2a)**

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 (4*R*,5*S*)-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%

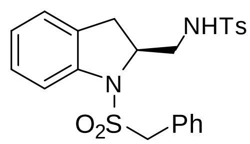
EtOAc/hexanes gradient) to give the diamination product **2a** in 68% yield (63.1 mg, 0.162 mmol) as a white solid. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [CHIRALPAK AD-RH, 60% $CH_3CN/H_2O$, 0.75 mL/min, λ=254 nm, t(major) = 6.39 min, t(minor) = 5.57 min] revealing 81% enantiomeric excess. $[\alpha]_D^{22}$ = +49.0 (*c* 0.3, $CHCl_3$).




**4**

**2-Methyl-1-(methylsulfonyl)indolines (4)**

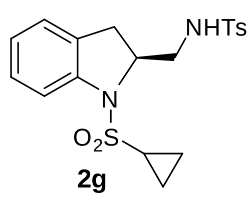
Hydroamination adduct **4** (7.5 mg, 15% yield) was obtained as a white solid from 50 mg of **1a** using Procedure D as a side product to the diamination. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J*=8.8 Hz, 1H), 7.22-7.18 (m, 2H), 7.05 (t, *J*=16.0 Hz, 1H), 4.47-4.42 (m, 1H), 3.49-3.42 (m, 1H), 2.84 (s, 3H), 2.70 (dd, *J*=12.4, 4.0 Hz, 1H), 1.45 (d, *J*=6.8 Hz, 3H). This $^1$H NMR matched the reported values.[16]




**2f**

**(*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 $^1$H NMR. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [CHIRALPAK AD-RH, 45% $CH_3CN/H_2O$, 0.75 mL/min, λ=254 nm, t(major) = 40.35 min, t(minor) = 35.10 min] revealing 79% enantiomeric excess. $[\alpha]_D^{23}$ = +93.8 (*c* 0.40, $CHCl_3$).

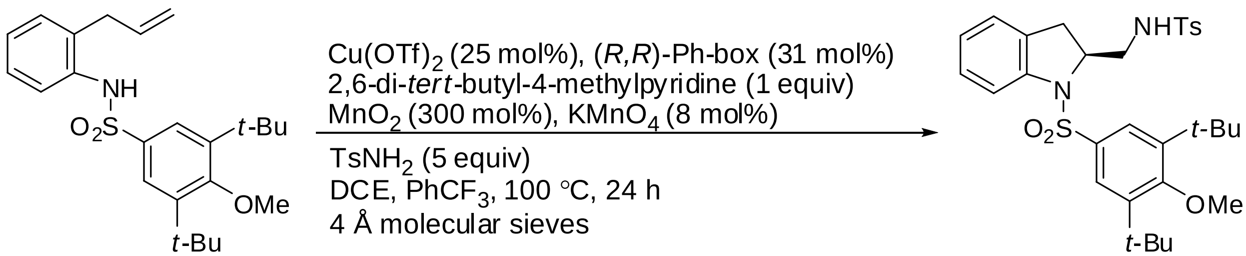



**2g**

**(*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 $^1$H NMR. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [CHIRALPAK AD-RH, 45% $CH_3CN/H_2O$, 0.75 mL/min, λ=254 nm, t(major) = 22.50 min, t(minor) = 19.07 min] revealing 76.5% enantiomeric excess. $[\alpha]_D^{23}$ = +48.1 (*c* 1.0, $CHCl_3$).

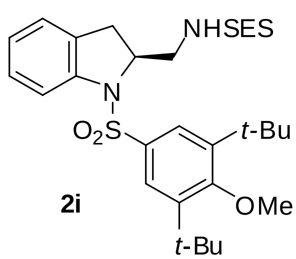
**Representative Procedure E for catalytic enantioselective diamination (Table 3, entry 9)**




**1e** **2h**

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

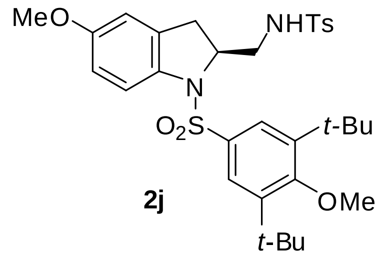
Cu(OTf)$_2$ (8.7 mg, 0.024 mmol, 25 mol %) was placed in a glass reaction tube, under an argon atmosphere in a dry box, with a magnetic stir bar. (*R,R*)-Ph-box (9.9 mg, 0.030 mmol, 31 mol %) in PhCF$_3$ (0.48 mL) was added via syringe through a septum. The tube was capped and the reaction mixture was 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 mol. 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, λ=254 nm, t(major) = 44.62 min, t(minor) = 36.43 min] revealing 90% enantiomeric excess. $[\alpha]_D^{21}$ = +71.9 (*c* 0.40, CHCl$_3$).




**2i**

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

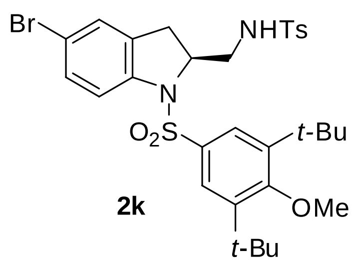
Diamination adduct **2i** (33.8 mg, 59% yield) was obtained as a white solid from 40 mg of **1e** using Procedure E, except SESNH$_2$ was used as the nucleophile. The diamination to carboamination ratio was determined to be 66:34 based on the relative integrations of the hydrogen peak at 4.20 ppm at 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, λ=254 nm, t(major) = 32.71 min, t(minor) = 27.60 min] revealing 91% enantiomeric excess. $[\alpha]_D^{23}$ = +42.9 (*c* 0.15, $CHCl_3$).



**2j**

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

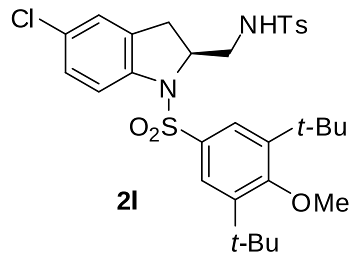
Diamination adduct **2j** (33.6 mg, 61% yield) was obtained as a white solid from 40 mg of **1f** using Procedure E. The diamination to carboamination ratio was determined to be 66:34 based on the relative integrations of the hydrogen peak at 4.10 ppm at the 2-position on the diamination product to the 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, λ=254 nm, t(major) = 38.86 min, t(minor) = 31.32 min] revealing 85% enantiomeric excess. $[\alpha]_D^{19}$ = +80.4 (*c* 0.30, $CHCl_3$).



**2k**

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

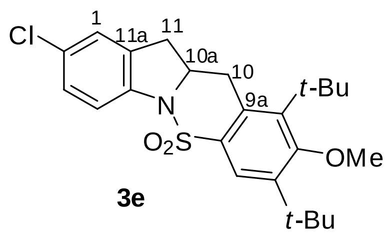
Diamination adduct **2k** (31.7 mg, 59% yield) was obtained as a white solid from 40 mg of **1g** using Procedure E. The diamination to carboamination ratio was determined to be 63:37 based on the relative integrations of the hydrogen peak at 4.26 ppm at the 2-position on the diamination product to the 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, λ=254 nm, t(major) = 31.27 min, t(minor) = 24.99 min] revealing 84% enantiomeric excess. $[\alpha]_D^{23}$ = +66.9 (*c* 0.16, $CHCl_3$).




**2l**

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

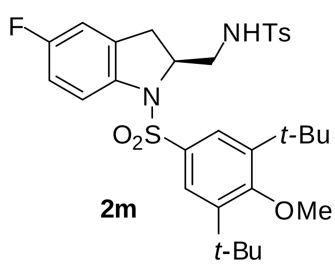
Diamination adduct **2l** (33.0 mg, 60% yield) was obtained as a white solid from 40 mg of **1h** using Procedure E. The diamination to carboamination ratio was determined to be 63:37 based on the relative integrations of the hydrogen peak at 4.16 ppm at the 2-position on the diamination product to the hydrogen peak at 3.88 ppm at the 10-position of the carboamination product in the crude $^1$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, λ=254 nm, t(major) = 19.29 min, t(minor) = 16.31 min] revealing 83% enantiomeric excess. $[\alpha]_D^{22}$ = +103.9 (*c* 0.15, $CHCl_3$).




**3e**

**7,9-Di-*tert*-butyl-2-chloro-8-methoxy-10a,11-dihydro-10H-5-thia-4b-aza-benzo[b]fluorene 5,5-dioxide (3e)**

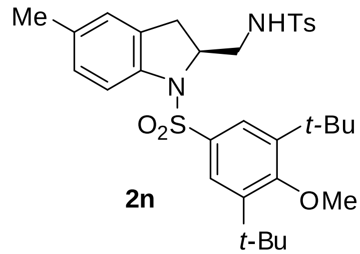
Carboamination adduct **3e** (10.1 mg, 20%) was obtained as a colorless oil from the same reaction as **2l**. Data for **3e**: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.39 (d, *J*=8.0 Hz, 1H), 7.14 (d, *J*=8.5 Hz, 1H), 7.04 (s, 1H), 4.96-4.82 (m, 1H), 3.96-3.82 (m, 1H), 3.67 (d, *J*=12.8 Hz, 1H), 3.56 (s, 3H), 3.11-2.99 (m, 1H), 2.92-2.79 (m, 1H), 1.55 (s, 9H), 1.35 (s, 9H). $^1$H NMR matched the previously reported data.[4]




**2m**

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

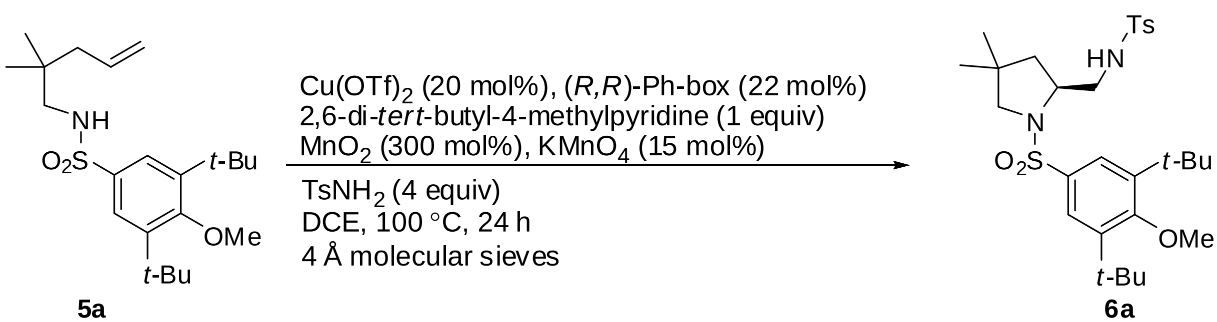
Diamination adduct **2m** (33 mg, 60% yield) was obtained as a white solid from 40 mg of **1i** using Procedure E. The diamination to carboamination ratio was determined to be 64:36 based on the relative integrations of the hydrogen peak at 4.16 ppm at the 2-position on the diamination product to the hydrogen peak at 3.87 ppm at the 10-position of the carboamination product in the crude $^1$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, λ=254 nm, t(major) = 19.68 min, t(minor) = 16.29 min] revealing 85% enantiomeric excess. $[\alpha]_D^{21}$ = +54.5 (*c* 0.27, $CHCl_3$).




**(*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, λ=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)**



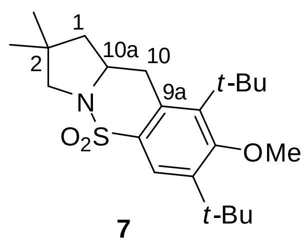

**(*S*)-*N*-((1-(3,5-Di-*tert*-butyl-4-methoxyphenylsulfonyl)-4,4-dimethylpyrrolidin-2-yl)methyl)-4-methylbenzenesulfonamide (6a)**

$Cu(OTf)_2$ (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 $^{1}$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); $^{1}$H NMR (500 MHz, $CDCl_3$) δ 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); $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 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) υ 3291, 2959, 2360, 2341, 1732, 1598, 1455, 1406, 1334, 1255, 1226, 1162, 1123, 1093, 1034, 1006, 974; HRMS (ESI) calcd for $C_{29}H_{44}O_5N_2Na_1S_2$ $[M+Na]^+$ 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, λ=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**.

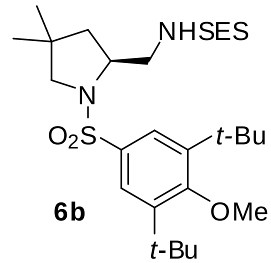



**7**

**7,9-Di-*tert*-butyl-8-methoxy-2,2-dimethyl-2,3,10,10a-5,5-dioxide-tetrahydro-1H-benzo[e]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**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 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); $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 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) υ 3016, 2961, 2871, 1579, 1538, 1468, 1450, 1413, 1400, 1370, 1332, 1290, 1268, 1232, 1194, 1162, 1124, 1093, 1050, 1020, 965; HRMS (ESI) calcd for $C_{22}H_{36}O_3N_1S_1$ $[M+H]^+$ 394.2410, found 394.2408.



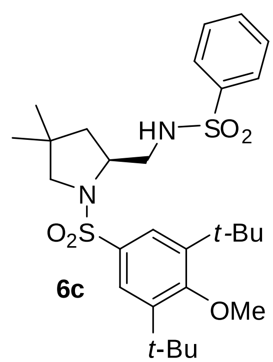

**6b**

**(*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 (4*R*,5*S*)-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) υ 3305, 2924, 2361, 1406, 1331, 1253, 1226, 1164, 842; HRMS (ESI) calcd for $C_{27}H_{51}O_5N_2S_2Si_1$ $[M+H]^+$ 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.



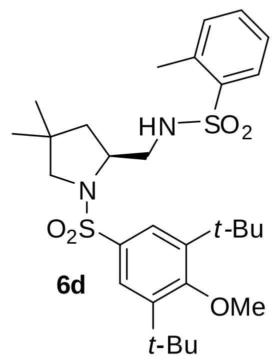

**6c**

**(*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 $PhSO_2NH_2$ was used as the nucleophile and (4*R*,5*S*)-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),

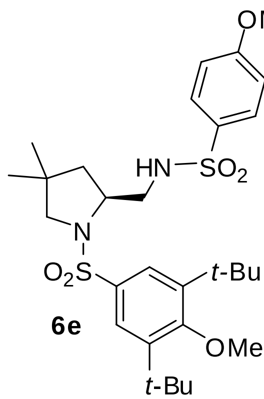
3.67 (s, 3H), 3.58-3.54 (m, 1H), 3.34-3.28 (m, 1H), 3.20-3.14 (m, 2H), 3.06 (d, $J$=11.2 Hz, 1H), 1.79-1.74 (m, 1H), 1.68-1.63 (m, 1H), 1.43 (s, 18H), 0.99 (s, 3H), 0.27 (s, 3H); $^{13}$C NMR (75.5 MHz, $CDCl_3$) δ 163.8, 145.4, 139.9, 132.6, 130.3, 129.2, 126.9, 125.9, 64.7, 62.1, 59.7, 47.1, 44.0, 37.0, 36.1, 31.8, 26.0, 25.3; IR (neat, thin film) υ 3285, 2960, 2872, 1724, 1577, 1448, 1406, 1333, 1254, 1226, 1163, 1123, 1093, 1033, 1006, 974; HRMS (ESI) calcd for $C_{28}H_{43}O_5N_2S_2$ $[M+H]^+$ 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.



**6d**

**(*S*)-*N*-((1-(3,5-Di-*tert*-butyl-4-methoxyphenylsulfonyl)-4,4-dimethylpyrrolidin-2-yl)methyl)-2-methylbenzenesulfonamide (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 $2\text{-}MeC_6H_4SO_2NH_2$ was used as the nucleophile and (4*R*,5*S*)-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; $[\alpha]_D^{23}$ = -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) υ 3305, 2962, 1575, 1532, 1463, 1406, 1332, 1259, 1226, 1162, 1033, 885; HRMS (ESI) calcd for $C_{29}H_{45}O_5N_2S_2$ $[M+H]^+$ 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.



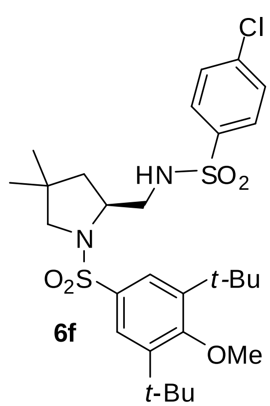

**6e**

**(*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-$MeOC_6H_4SO_2NH_2$ was used as the nucleophile and (4*R*,5*S*)-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 $^1$H NMR.

Data for compound **6e**: mp 60-62 °C; $[\alpha]_D^{22}$ = -65.4 (*c* 0.18, $CHCl_3$, >95% ee); $^1$H NMR (300 MHz, $CDCl_3$) 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); $^{13}$C NMR (75.5 MHz, $CDCl_3$) 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) υ 3287, 2961, 2872, 1724, 1598, 1580, 1499, 1463, 1406, 1334, 1260, 1226, 1159, 1094, 1030, 975; HRMS (ESI) calcd for $C_{29}H_{44}O_6N_2Na_1S_2$ $[M+H]^+$ 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.



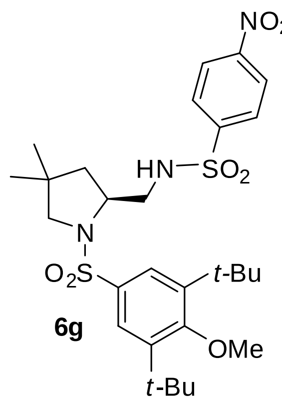

**6f**

**(*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-$ClC_6H_4SO_2NH_2$ was used as the nucleophile and (4*R*,5*S*)-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, $CDCl_3$) 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, $CDCl_3$) δ 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, 26.0, 25.3; IR (neat, thin film) υ 3291, 2925, 1733, 1576, 1457, 1396, 1337, 1259, 1226, 1163, 1094, 1033, 885; HRMS (ESI) calcd for $C_{28}H_{42}O_5N_2Cl_1S_2$ $[M+H]^+$ 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, λ=254 nm, t(major) = 57.48 min, t(minor) = 55.87 min] revealing >95% enantiomeric excess.

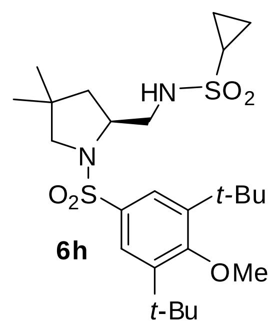



**6g**

**(*S*)-*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-$NO_2C_6H_4SO_2NH_2$ was used as the nucleophile and (4*R*,5*S*)-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, $CDCl_3$) δ 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, $CDCl_3$) δ 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) υ 3283, 2961, 1607, 1532, 1465, 1405, 1348, 1254, 1226, 1164, 1122, 1092, 1033, 1007, 975; HRMS (ESI) calcd for $C_{28}H_{42}O_7N_3S_2$ $[M+H]^+$ 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 $K_2CO_3$ (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 $CH_2Cl_2$ (2x1 mL), and the organic layers were combined and washed with 1M HCl (90 mL) and with brine (90 mL), then dried over $Na_2SO_4$, and concentrated *in vacuo*. Flash chromatography of the resulting crude oil on $SiO_2$ (10-25% $Et_2O$ 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.



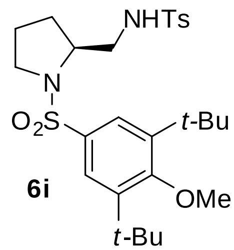

**6h**

**(*S*)-*N*-((1-(3,5-Di-*tert*-butyl-4-methoxyphenylsulfonyl)-4,4-dimethylpyrrolidin-2-yl)methyl)cyclopropanesulfonamide (6h)**

Diamination adduct **6h** (31.7 mg, 61% yield) was obtained as a white waxy solid from 40 mg of **5a** using Procedure F, except $C_3H_5SO_2NH_2$ was used as the nucleophile and (4*R*,5*S*)-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 $^1$H NMR.

Data for compound **6h**: mp 112-115 °C; $[\alpha]_D^{20}$ = -80.6 (*c* 0.19, $CHCl_3$, >95% ee); $^1$H NMR (300 MHz, $CDCl_3$) 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); $^{13}$C NMR (75.5 MHz, $CDCl_3$) 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) υ 3292, 3015, 2962, 1725, 1576, 1464, 1406, 1332, 1260, 1226, 1162, 1097, 1033, 891; HRMS (ESI) calcd for $C_{25}H_{43}O_5N_2S_2$ $[M+H]^+$ 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.



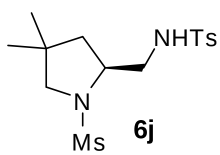
6i

**(*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 (4*R*,5*S*)-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 $^{1}$H NMR.

Data for compound **6i**: mp 43-46 °C; $[\alpha]_D^{24}$ = -63.9 (*c* 0.13, $CHCl_3$, 89% ee); $^{1}$H NMR (400 MHz, $CDCl_3$) 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); $^{13}$C NMR (75.5 MHz, $CDCl_3$) 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) υ 3286, 2963, 2872, 2361, 2341, 1943, 1725, 1599, 1576, 1449, 1406, 1333, 1260, 1228, 1201, 1160, 1092, 1021, 866; HRMS (ESI) calcd for $C_{27}H_{41}O_5N_2S_2$ $[M+H]^+$ 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.



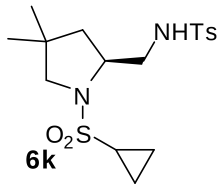
6j

**(*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 $^{1}$H NMR, the reaction resulted in a 70% conversion to the diamination product, with the remainder of material being starting material.

Data for compound **6j**: $[\alpha]_D^{24}$ = -14.4 (*c* 0.30, $CHCl_3$); $^{1}$H NMR (400 MHz, $CDCl_3$) 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); $^{13}$C NMR (75.5 MHz, $CDCl_3$) 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) υ 3284, 3024, 2962, 2874, 2256, 1598, 1495, 1455, 1372, 1326, 1253, 1220, 1185, 1158, 1093, 1040, 963; HRMS (ESI) calcd for $C_{15}H_{24}O_4N_2Na_1S_2$ $[M+Na]^+$ 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.



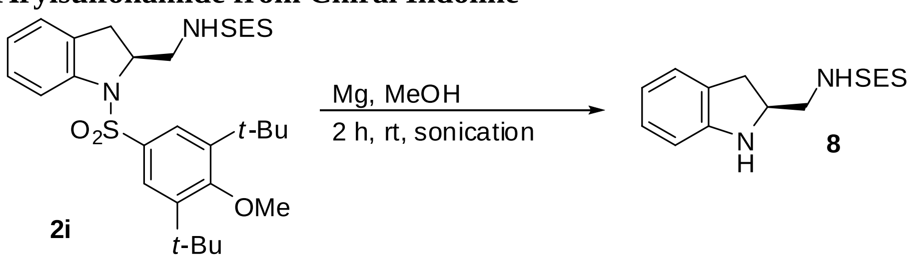

6k

**(*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 a 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*=10.8 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, $CDCl_3$) δ 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) υ 3276, 3023, 2961, 2874, 2444, 2361, 2341, 1921, 1724, 1598, 1495, 1454, 1422, 1372, 1330, 1259, 1218, 1188, 1160, 1144, 1093, 1047, 973; HRMS (ESI) calcd for $C_{17}H_{27}O_4N_2S_2$ $[M+H]^+$ 387.1407, found 387.1407. The product was further purified by HPLC and subsequently analyzed via chiral HPLC column [CHIRALPAK AD-RH, 40% $CH_3CN/H_2O$, 0.20 mL/min, λ=254 nm, t(major) = 100.37 min, t(minor) = 117.18 min] revealing 72% enantiomeric excess.

**Removal of Arylsulfonamide from Chiral Indoline**



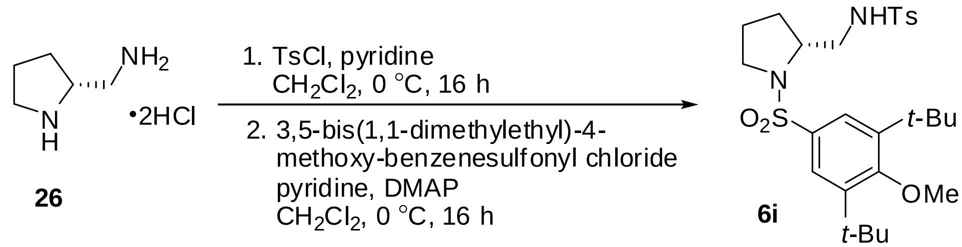

***N*-(Indolin-2-ylmethyl)-2-(trimethylsilyl)ethanesulfonamide (8)**

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.*[17] 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 $NH_4Cl$, and the aqueous layer was separated and extracted with $Et_2O$ (2x1 mL). The combined organic layers were dried of $Na_2SO_4$ 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, $CDCl_3$) δ 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

(75.5 MHz, $CDCl_3$) δ 152.7, 131.0, 128.2, 125.4, 115.2, 108.0, 60.0, 49.2, 46.1, 33.0, 10.5, -2.0; IR (neat, thin film) υ 3272, 2952, 2361, 2341, 1635, 1481, 1399, 1322, 1251, 1169, 1140, 1108, 841; HRMS (ESI) calcd for $C_{14}H_{25}O_2N_2S_1Si_1$ $[M+H]^+$ 313.1401, found 313.1406.

**Assignment of Absolute Configuration of 6i**

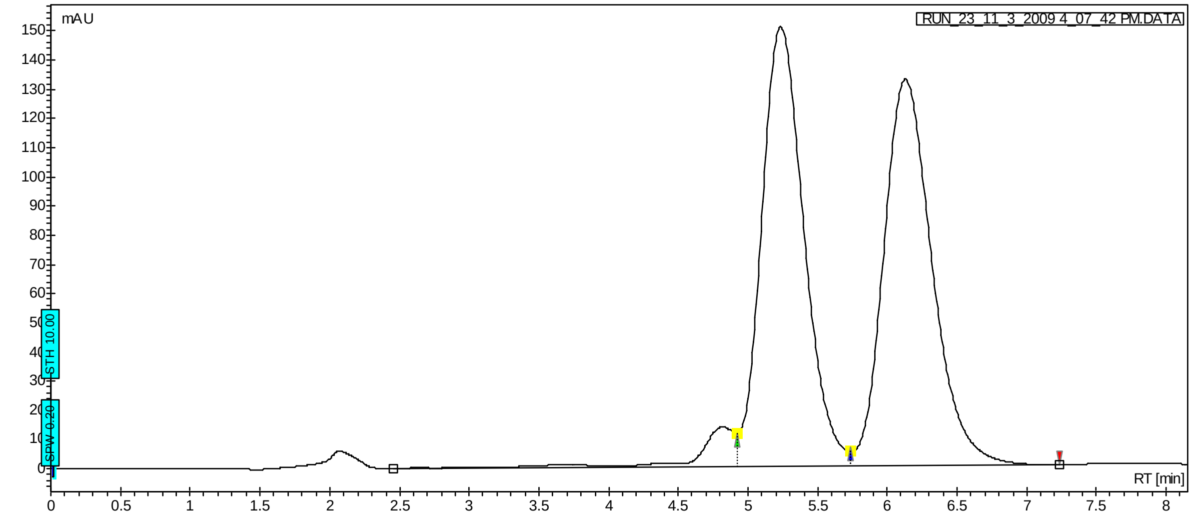



**(*R*)-*N*-((1-(3,5-Di-*tert*-butyl-4-methoxyphenylsulfonyl)pyrrolidin-2-yl)methyl)-4-methylbenzenesulfonamide (6i)**

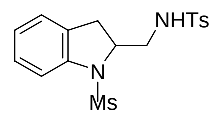
(*R*)-2-(Aminomethyl)pyrrolidine dihydrochloride **26** (0.200 g, 1.16 mmol, 1 equiv) was dissolved in dry $CH_2Cl_2$ (10 mL) in a 100 mL round bottom flask under an argon atmosphere, and was cooled to 0 °C in an ice bath. The solution was stirred with a magnetic stir bar and pyridine (0.38 mL, 0.46 mmol, 4 equiv) was syringed in dropwise. Toluenesulfonyl chloride (141 mg, 0.74 mmol, 0.64 equiv) was then syringed into the flask and the reaction was stirred at 0 °C and gradually allowed to warm to rt. After 16 h, the reaction was quenched with 10 mL of water and the organic layer was separated. The aqueous layer was extracted with $CH_2Cl_2$ (2x10 mL), and the organic layers were combined and washed with 1M NaOH (30 mL) and with brine (30 mL), then dried over $Na_2SO_4$, and concentrated *in vacuo*. The crude oil was dissolved in 5 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 (57 μL, 0.73 mmol, 3 equiv), 3,5-bis(1,1-dimethylethyl)-4-methoxy-benzenesulfonyl chloride (93.3 mg, 0.293 mmol, 1.2 equiv), and 4-dimethylaminopyridine (3.0 mg, 0.024 mmol, 0.1 equiv). The mixture stirred overnight, warming up to rt. The mixture was diluted with 50 mL of water and extracted with $CH_2Cl_2$ (3x5 mL). The combined organic layers were washed with brine, dried over $Na_2SO_4$, and concentrated *in vacuo*. Flash chromatography of the resulting crude product on $SiO_2$ (10-25% EtOAc in hexanes gradient) afforded sulfonamide **6i** as a white solid in 35% yield over two steps. $[\alpha]_D^{19}$ = +69.4 (*c* = 0.13, $CHCl_3$).

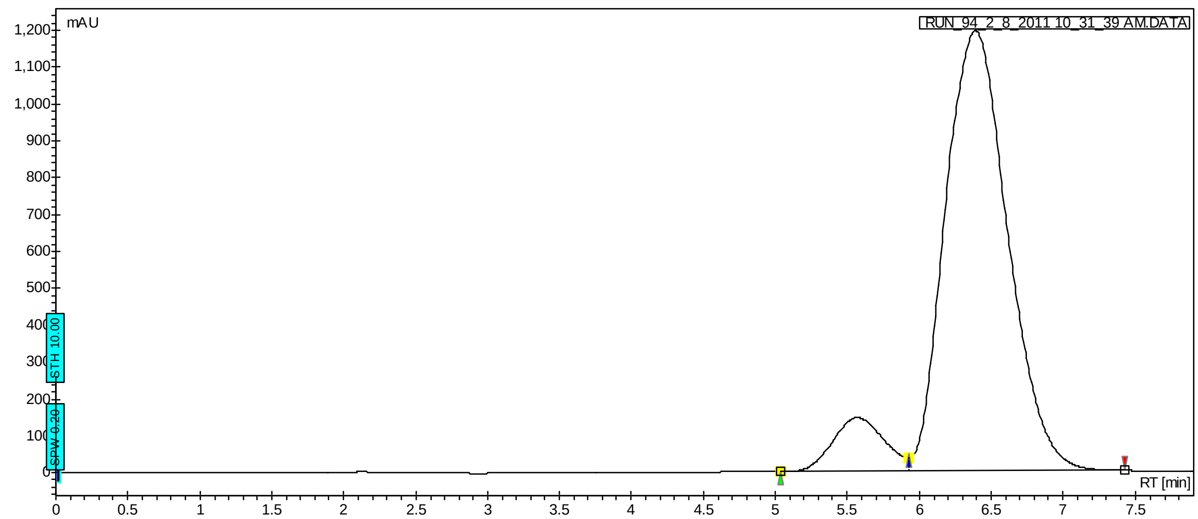
Optical rotation comparison to **6i** obtained via the enantioselective diamination above revealed it to be opposite in sign and similar in magnitude, indicating the **6i** synthesized by the catalytic diamination procedure has (*S*) configuration, opposite to the one synthesized from the known (*R*)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

## HPLC Traces

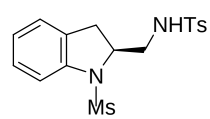


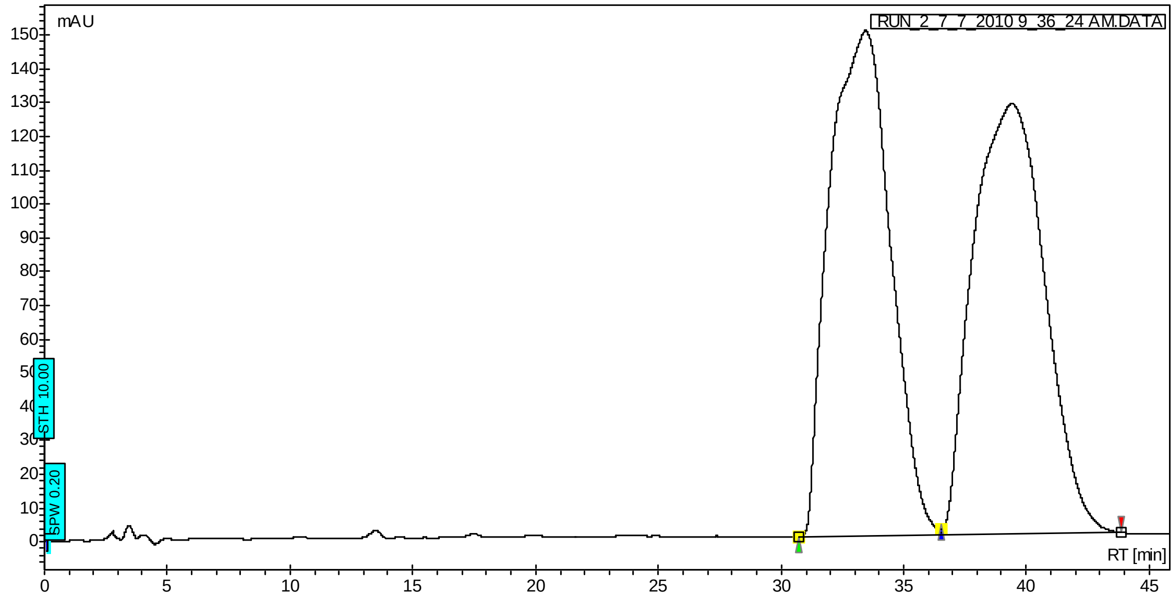

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 5.23 | 49.84 |
| 2 | 6.13 | 50.16 |




| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 5.57 | 9.16 |
| 2 | 6.39 | 90.84 |






| # | Time[min] | Area[%] |
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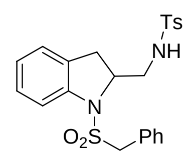
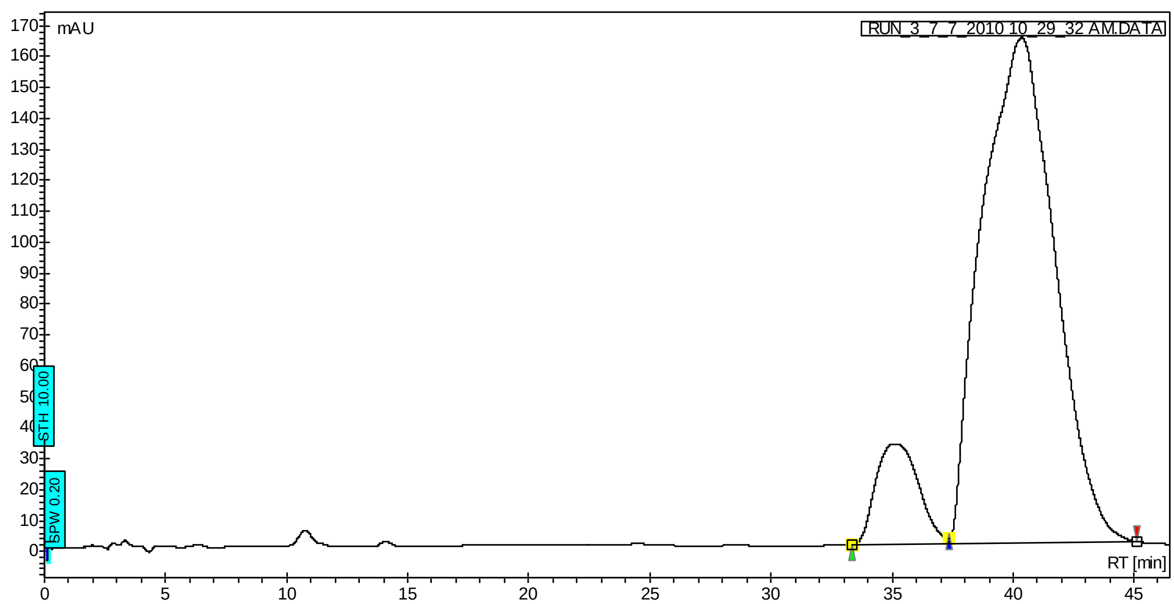
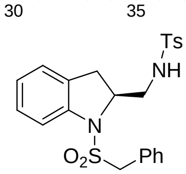
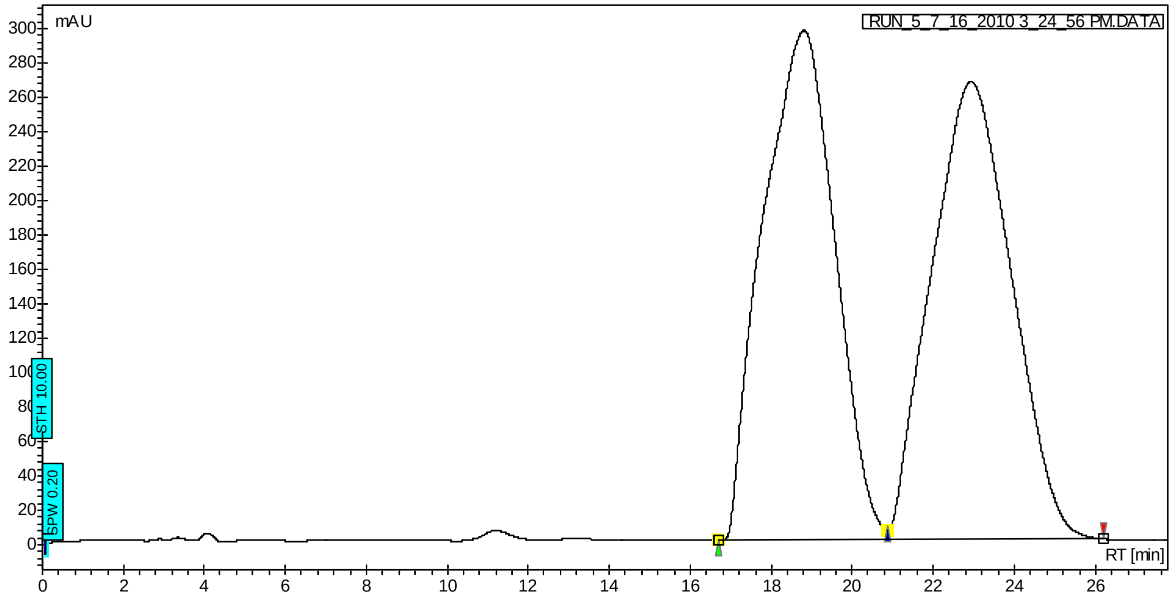
| 2 | 39.40 | 50.05 |




| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 35.10 | 10.45 |
| 2 | 40.35 | 89.55 |






| # | Time[min] | Area[%] |
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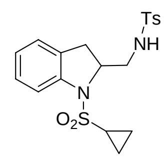
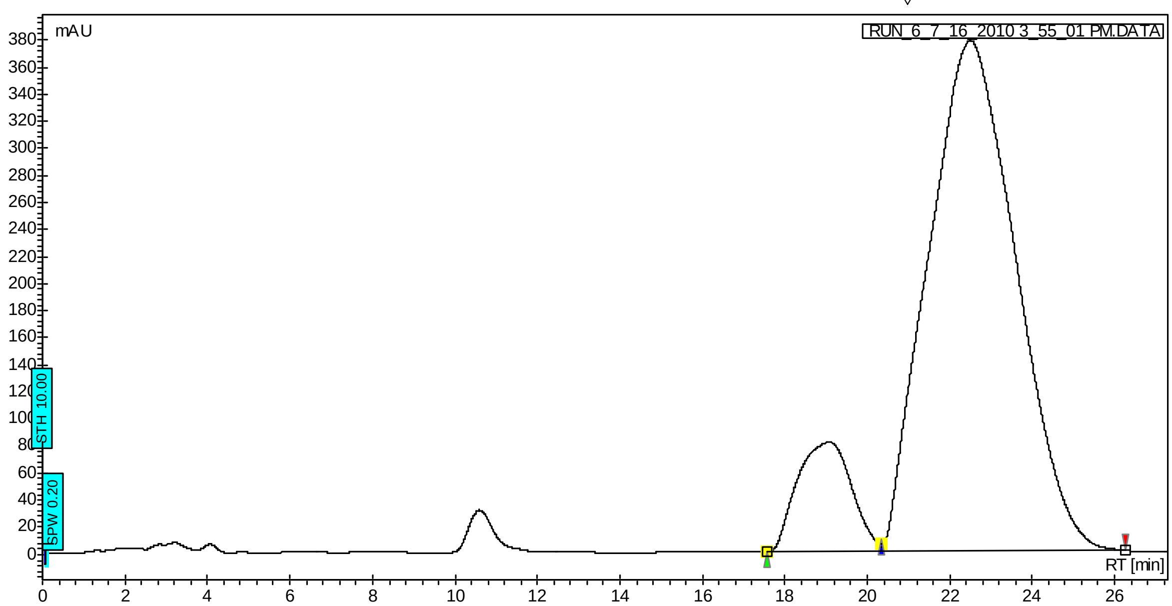
| 2 | 22.95 | 50.02 |

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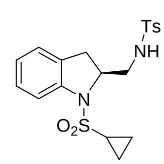

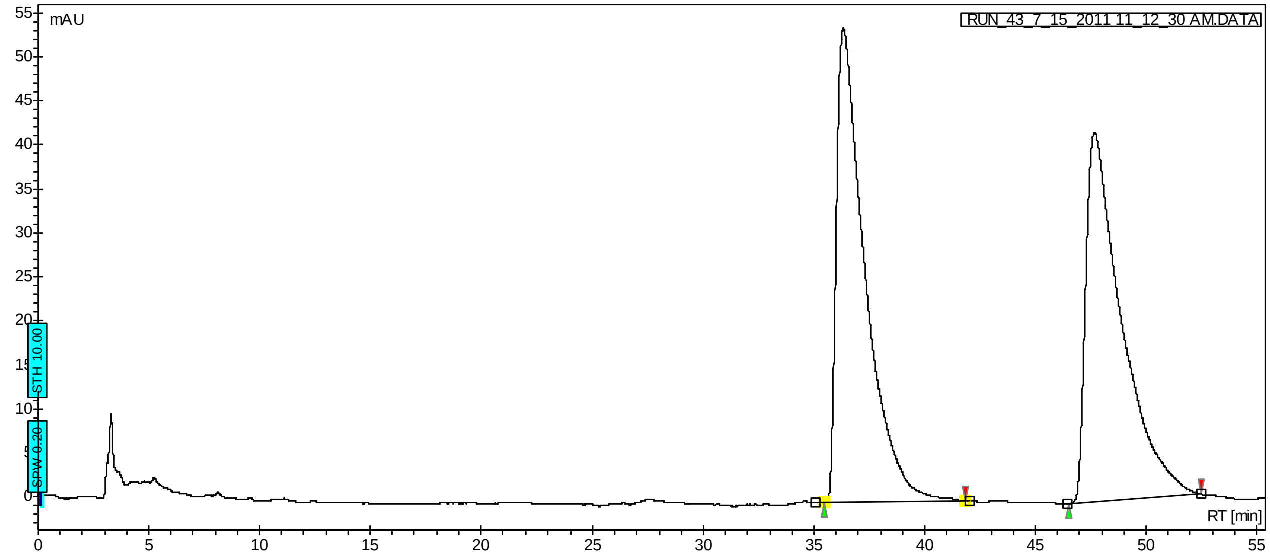


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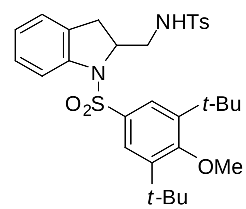
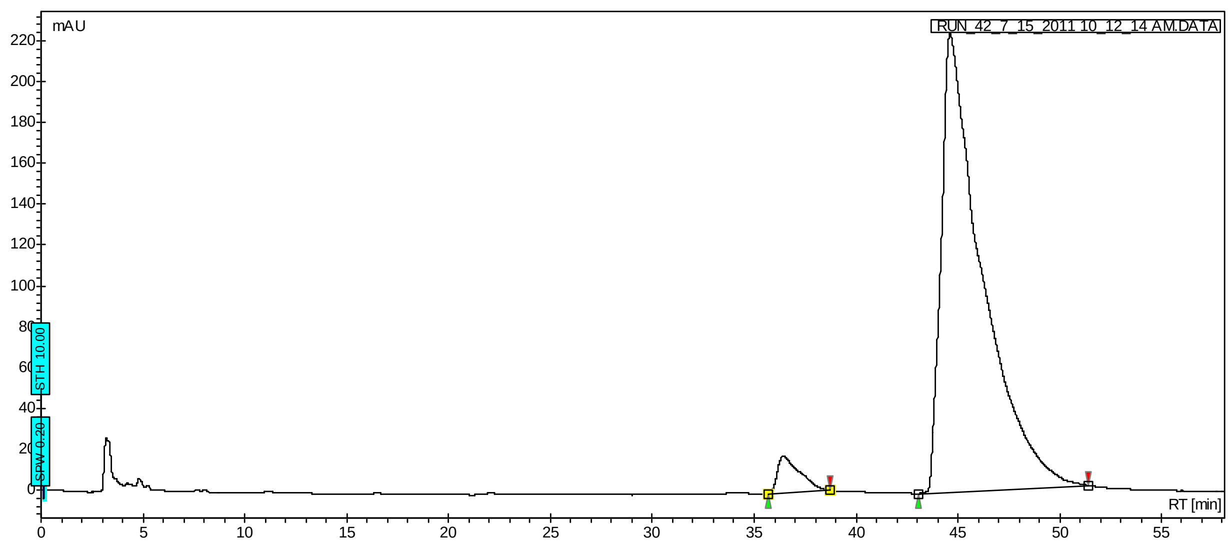
| 1 | 36.33 | 50.74 |
| 2 | 47.67 | 49.26 |

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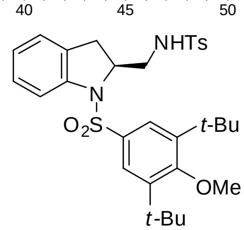
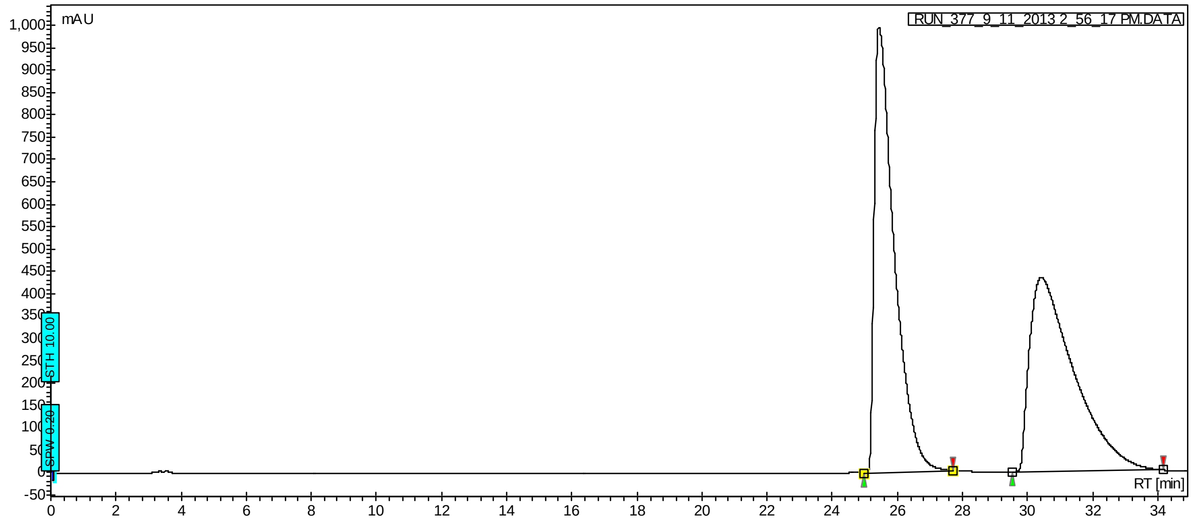
| 2 | 44.62 | 95.79 |



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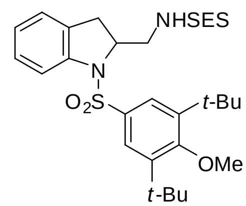
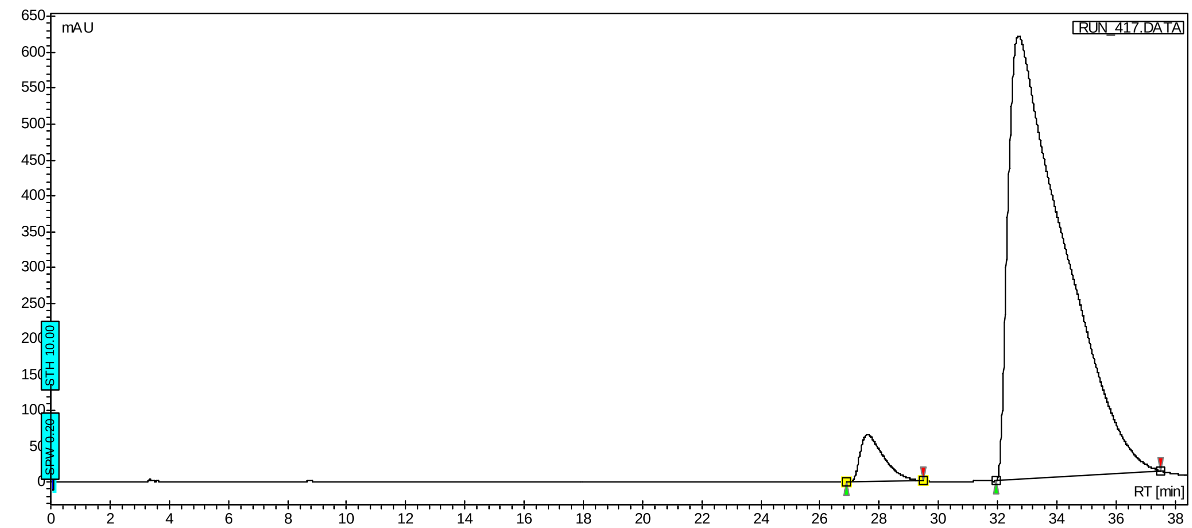
| 2 | 30.42 | 49.26 |

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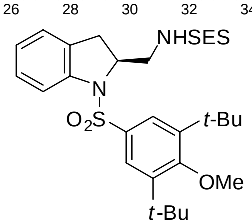
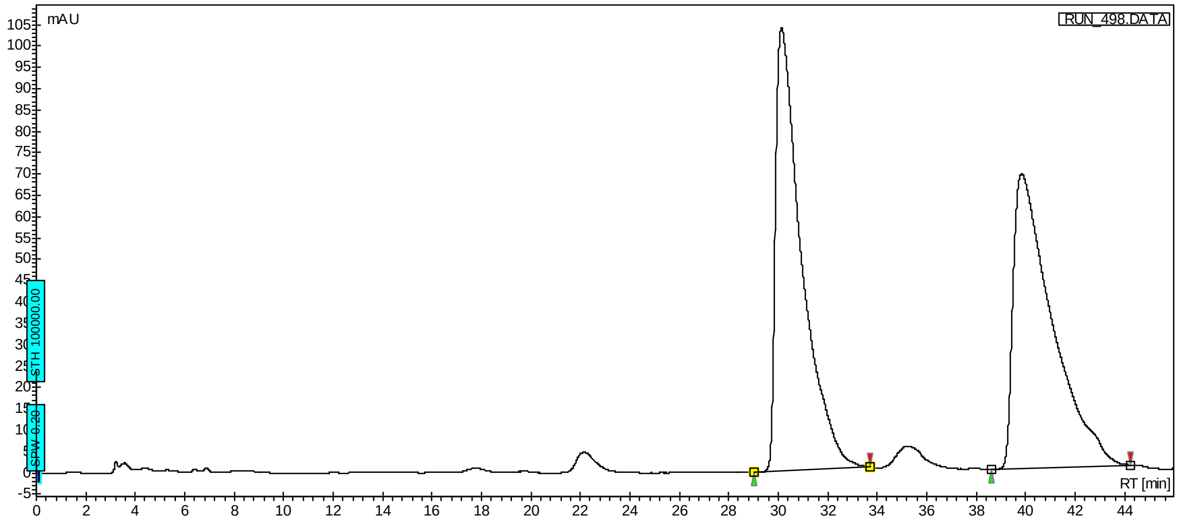
| 2 | 32.71 | 95.66 |





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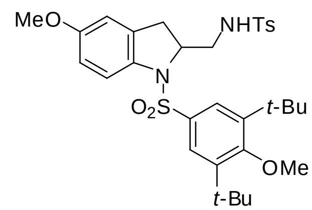
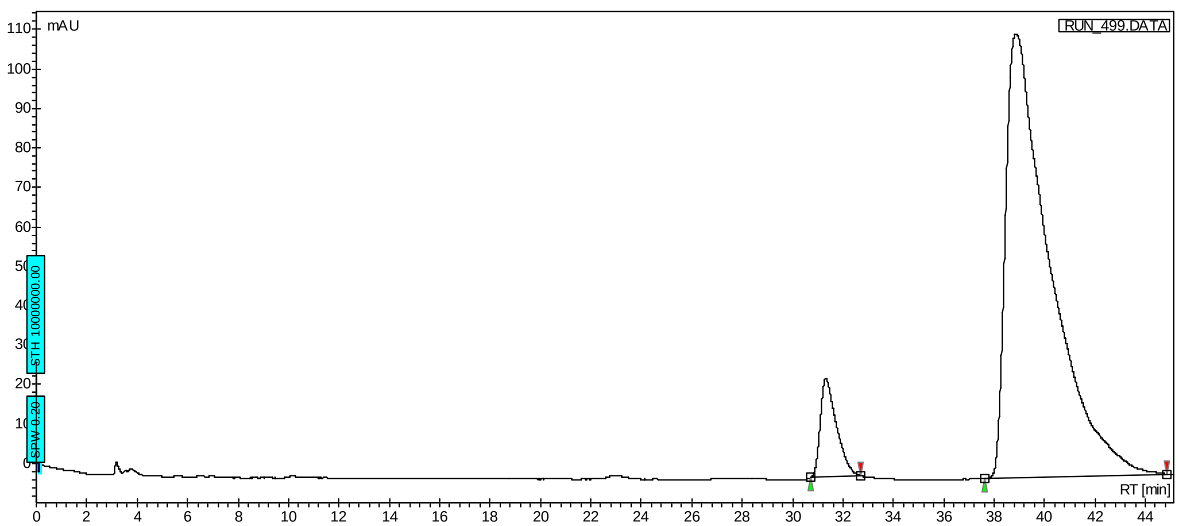
| 2 | 39.85 | 49.79 |





| # | Time[min] | Area[%] |
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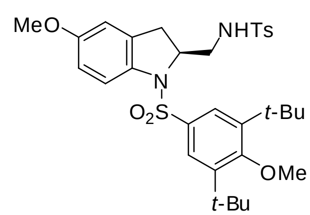
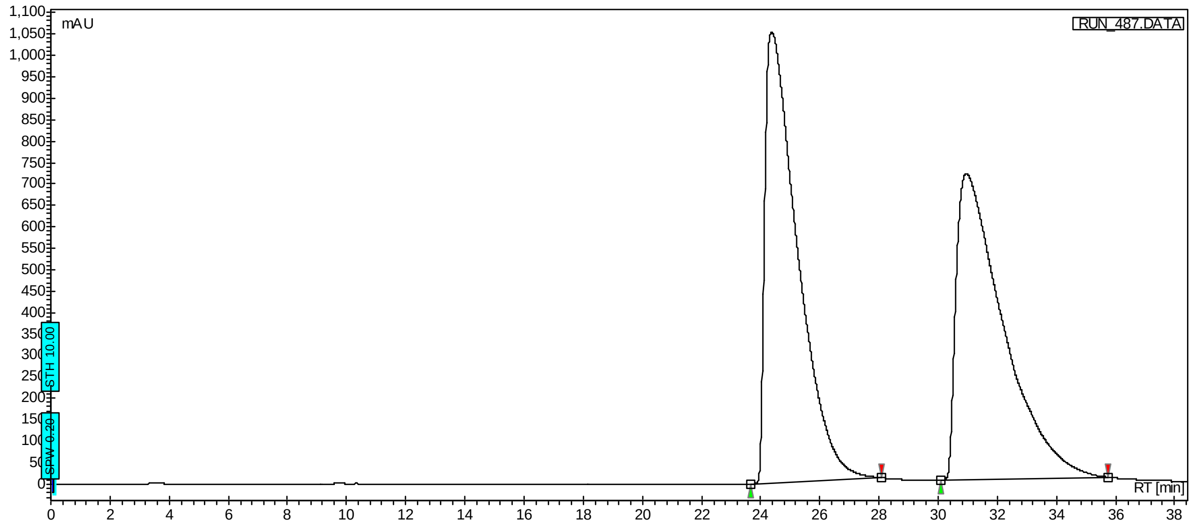
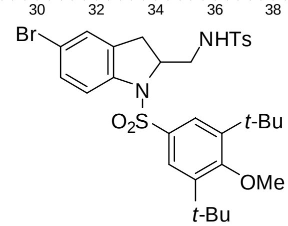
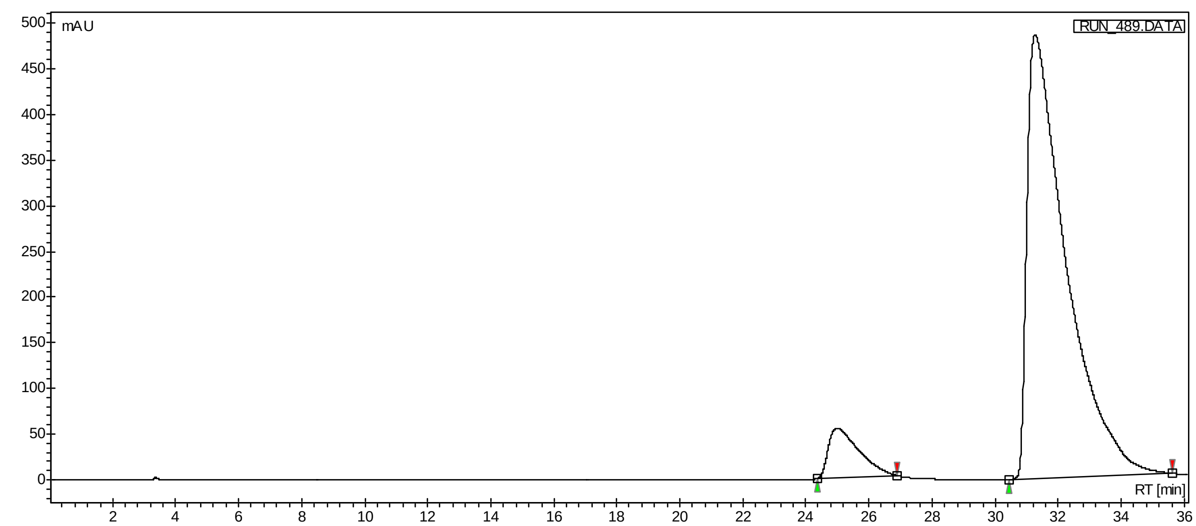
| 2 | 38.86 | 92.47 |






| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 24.37 | 50.52 |
| 2 | 30.95 | 49.48 |




| # | Time[min] | Area[%] |
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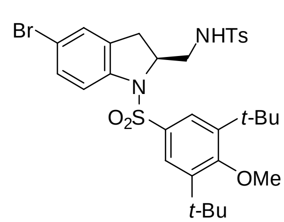
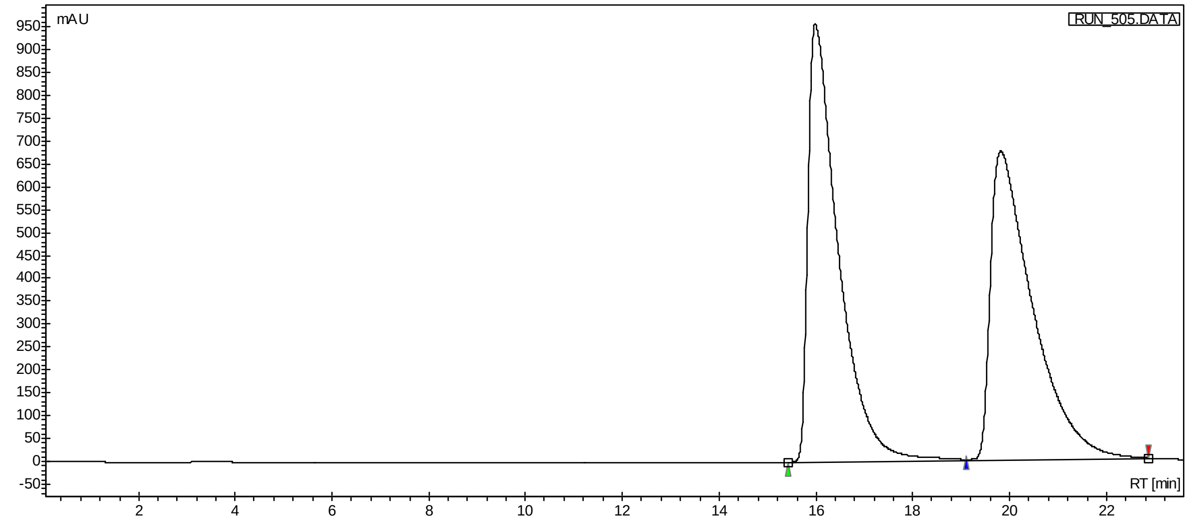
| 1 | 24.99 | 8.02 |
| 2 | 31.27 | 91.98 |





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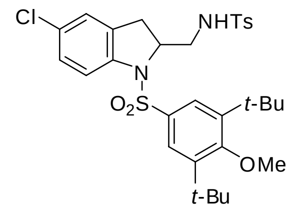

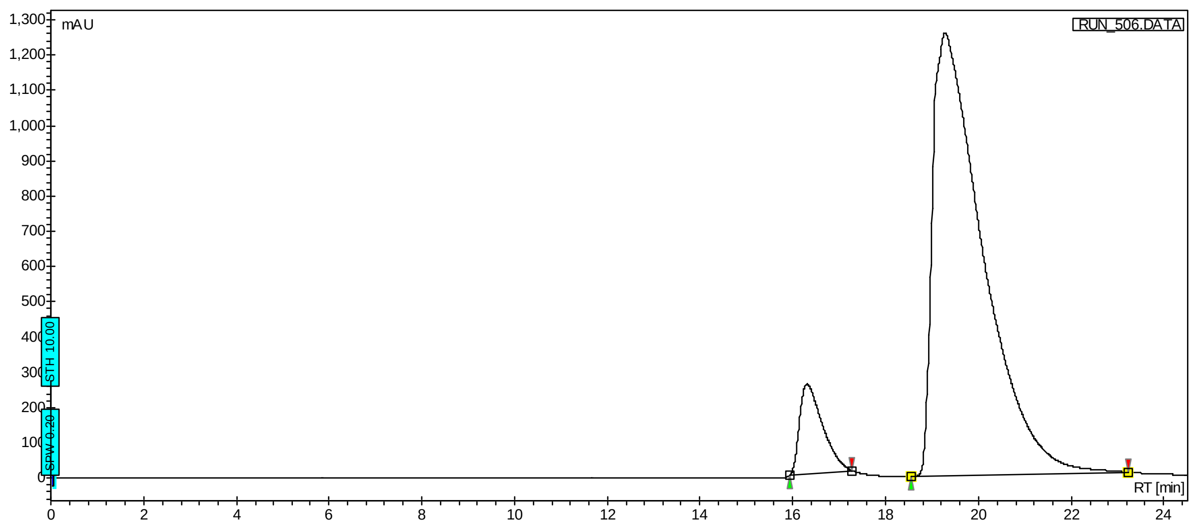

| # | Time[min] | Area[%] |
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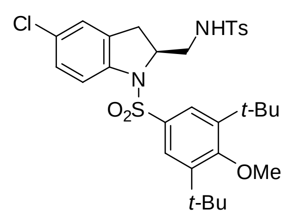
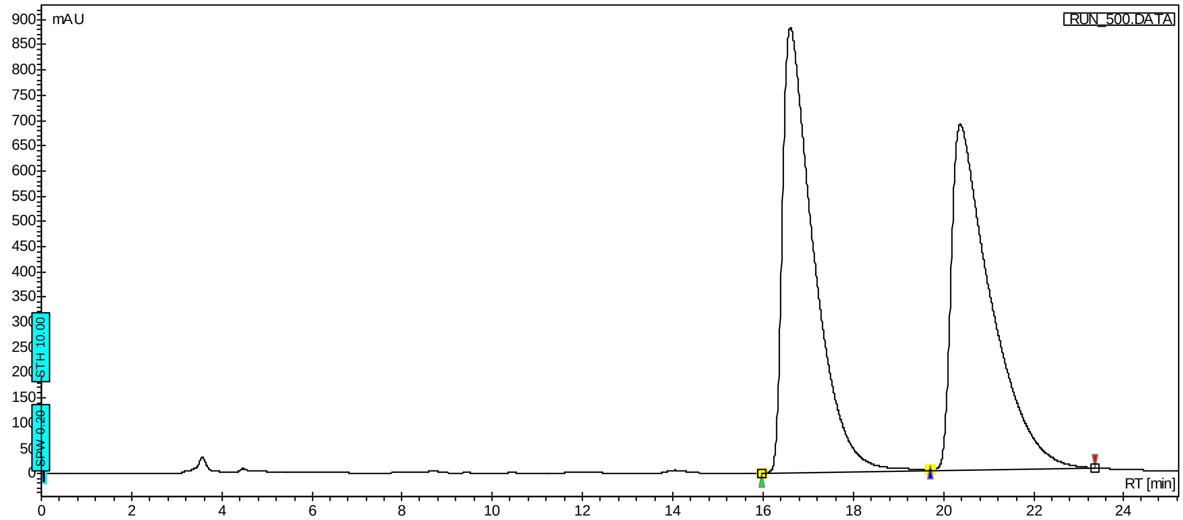
| 2 | 19.29 | 91.51 |





| # | Time[min] | Area[%] |
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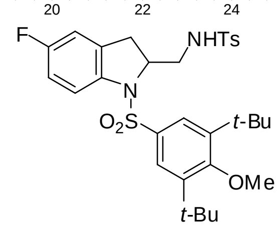
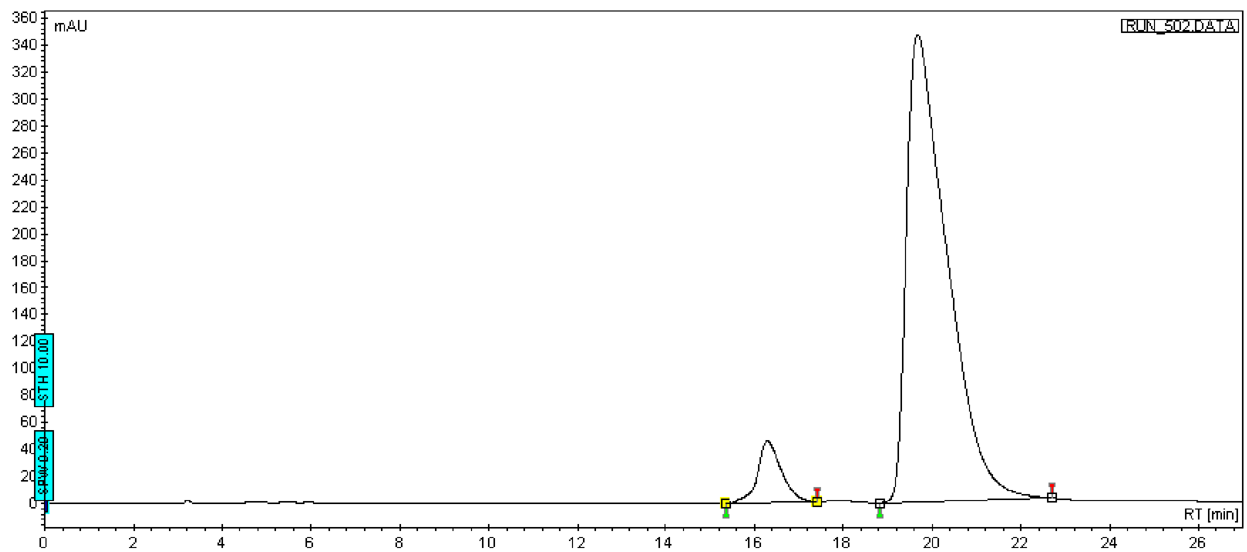
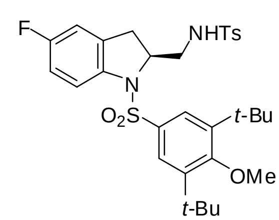
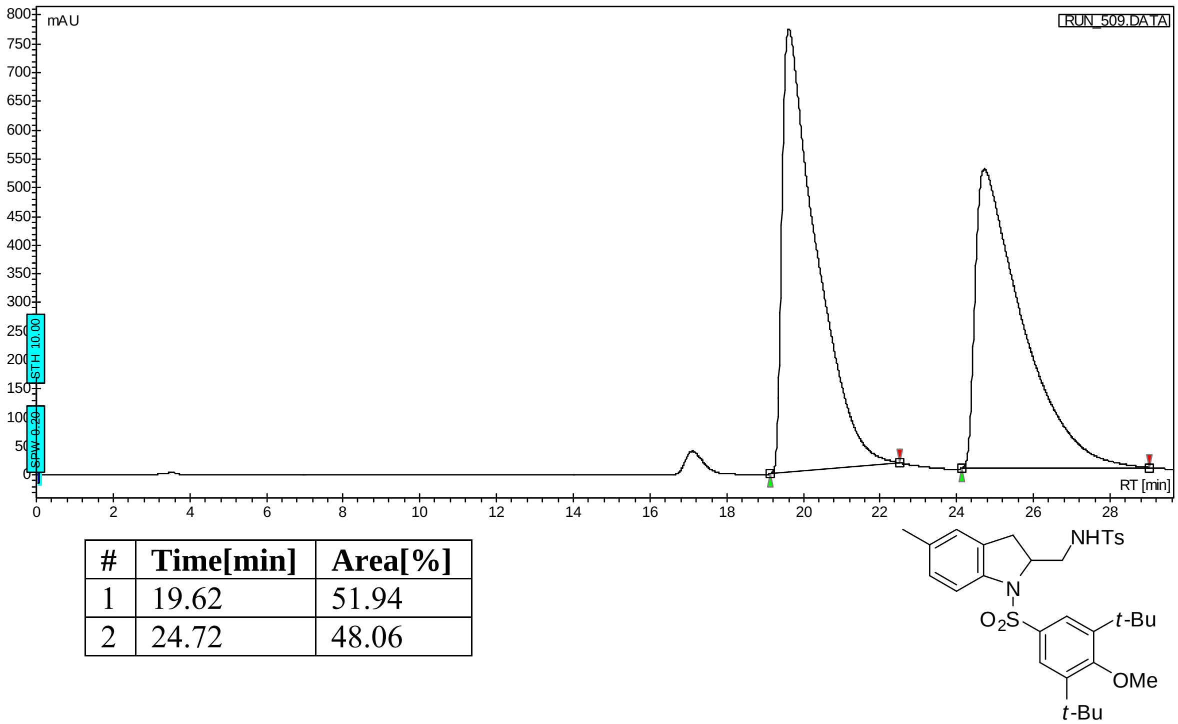
| 2 | 20.37 | 49.47 |



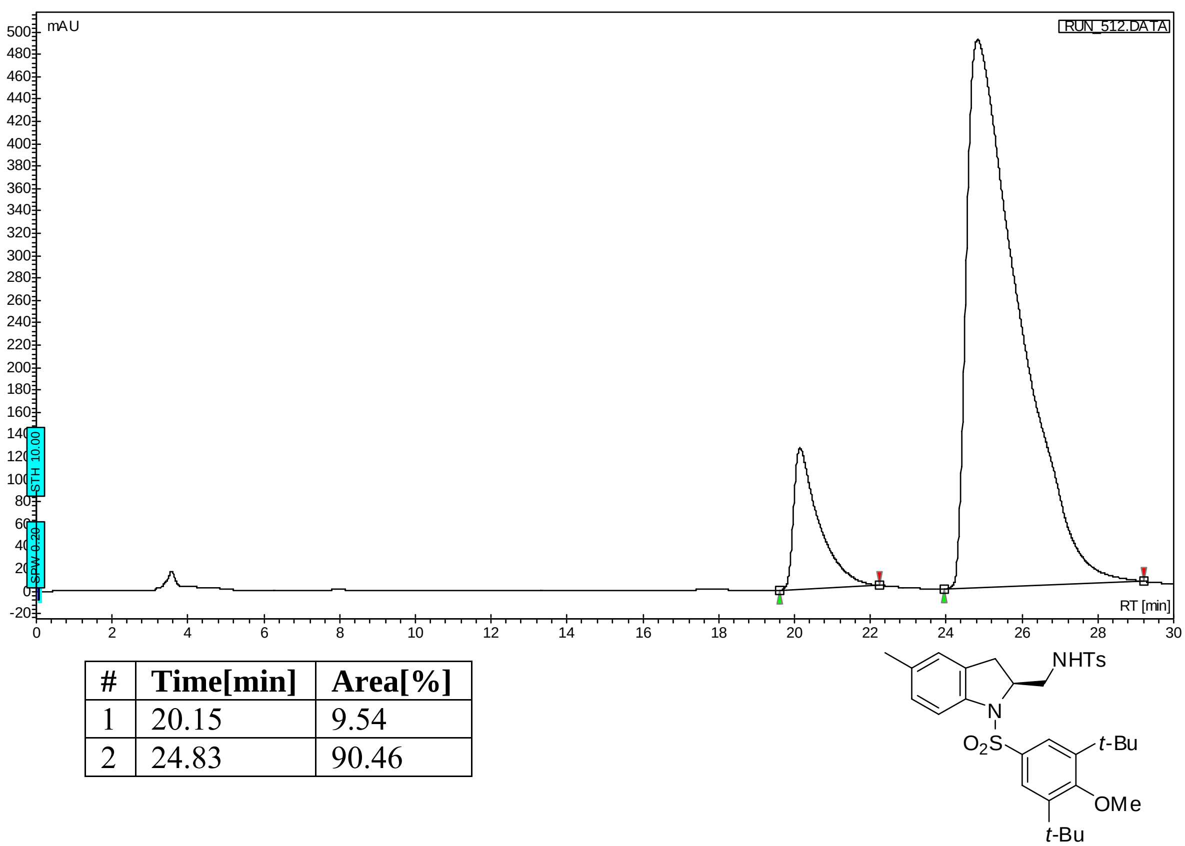


| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 16.29 | 7.20 |
| 2 | 19.68 | 92.8 |

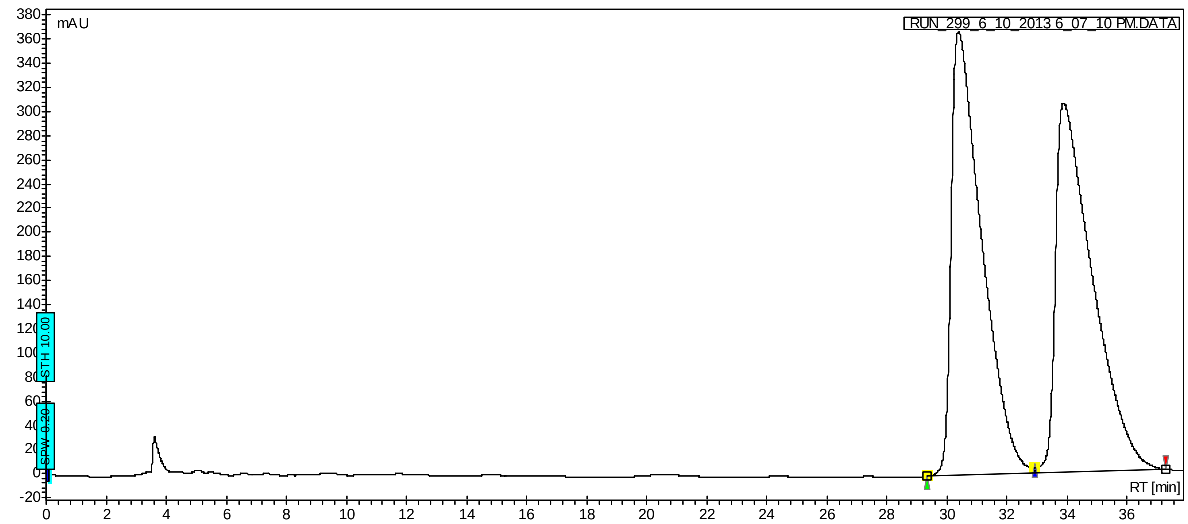




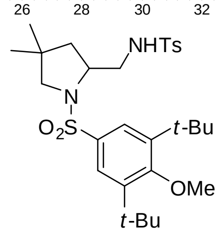
| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 19.62 | 51.94 |
| 2 | 24.72 | 48.06 |

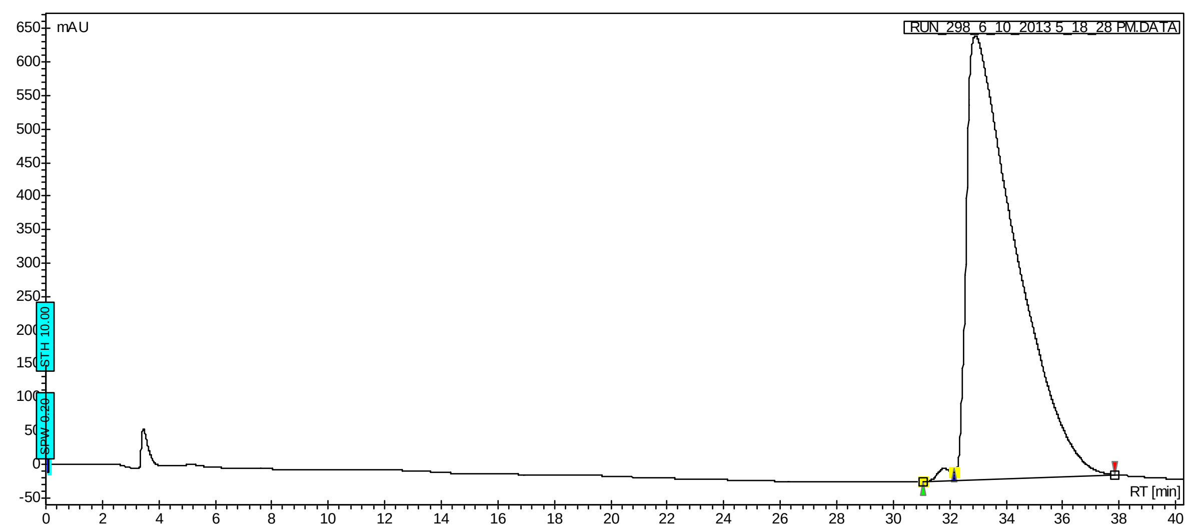


| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 20.15 | 9.54 |
| 2 | 24.83 | 90.46 |

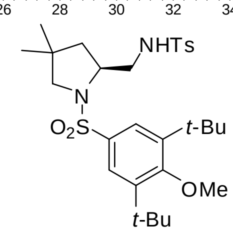


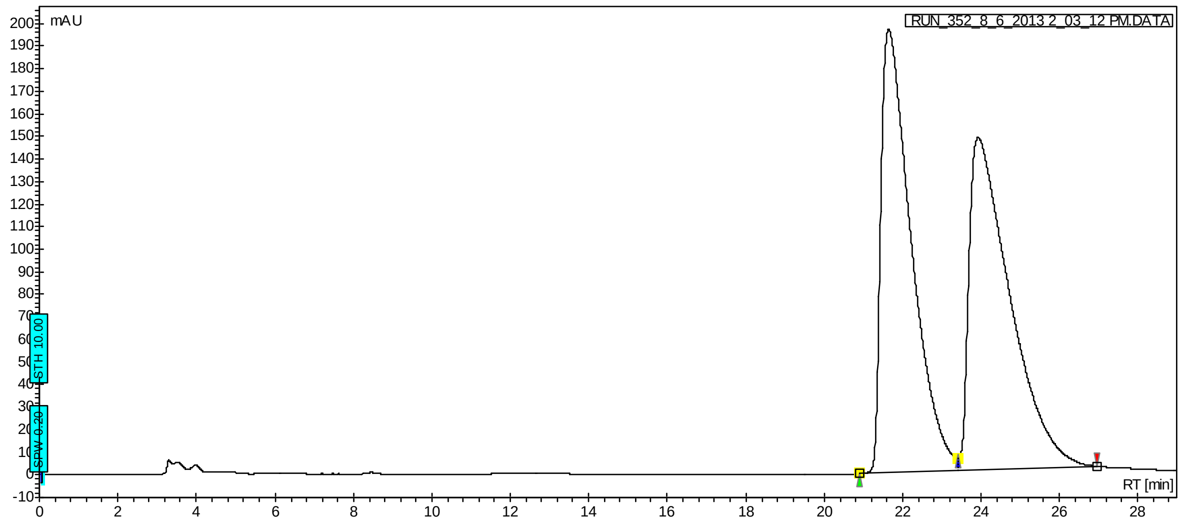

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 30.38 | 49.77 |
| 2 | 33.88 | 50.23 |



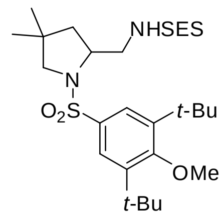



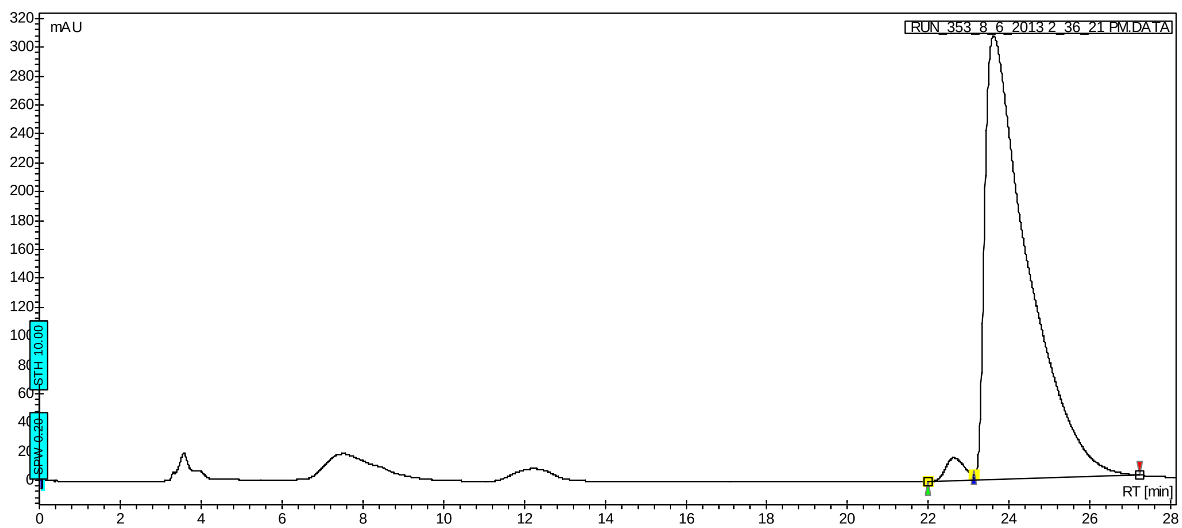

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 31.79 | 0.80 |
| 2 | 32.91 | 99.20 |



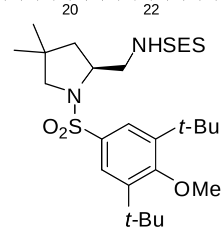


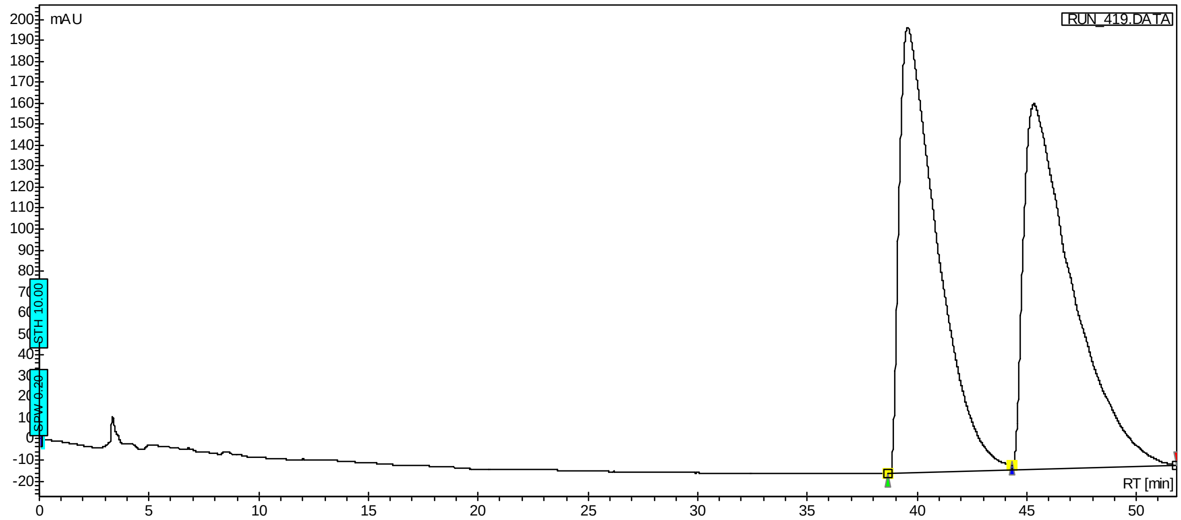

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 21.64 | 49.71 |
| 2 | 23.92 | 50.29 |



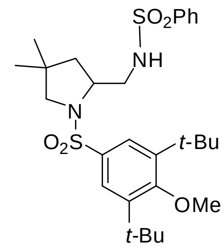



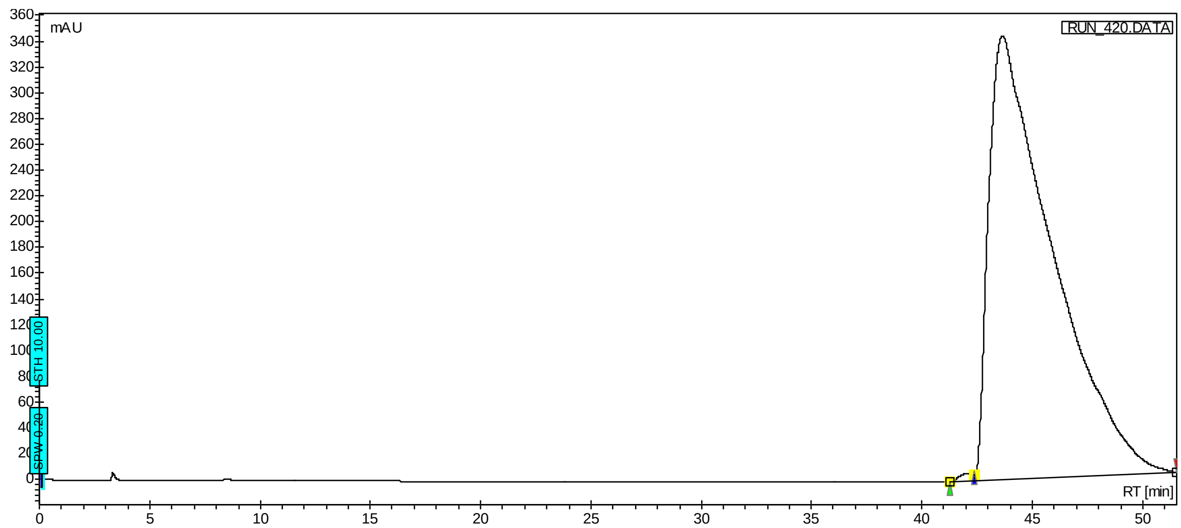

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 22.62 | 97.74 |
| 2 | 23.61 | 2.26 |



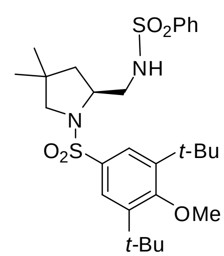


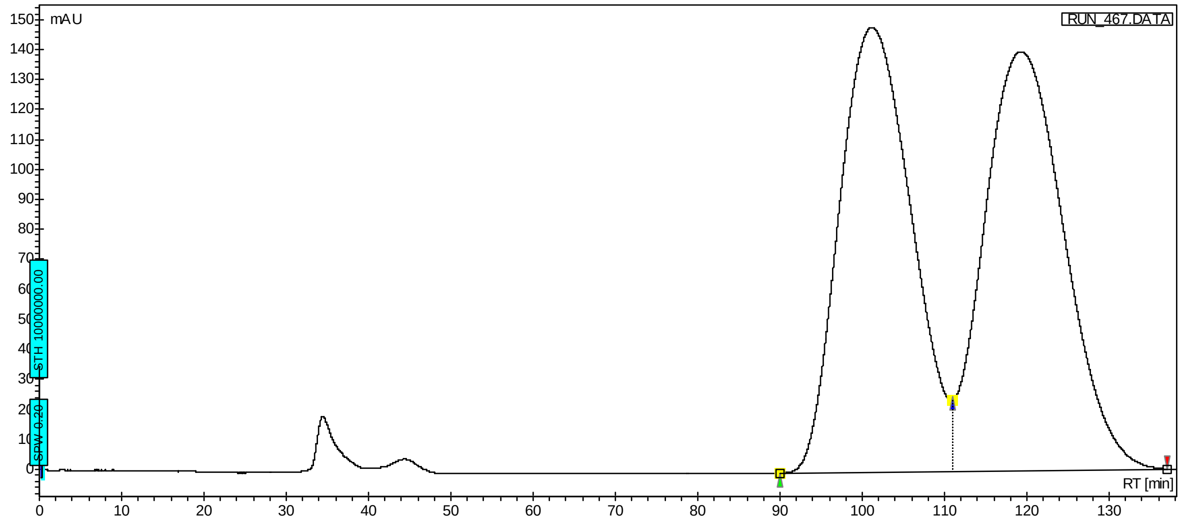

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 39.57 | 48.71 |
| 2 | 45.32 | 51.29 |



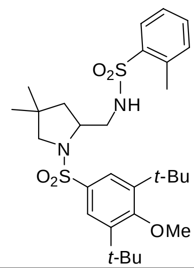



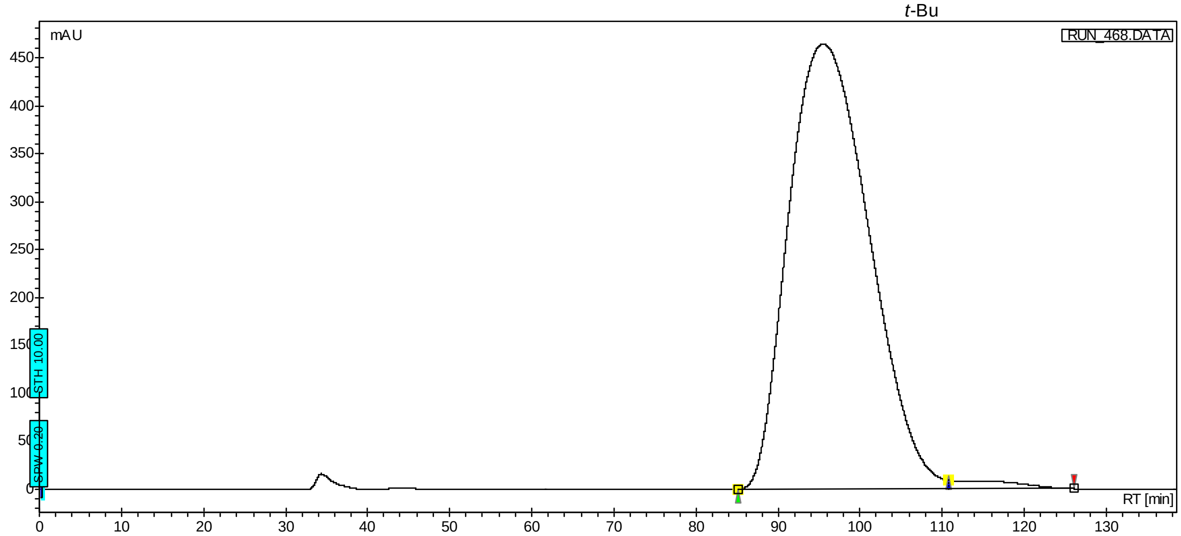

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 41.99 | 99.64 |
| 2 | 43.65 | 0.36 |



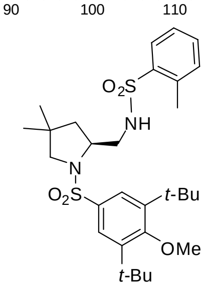


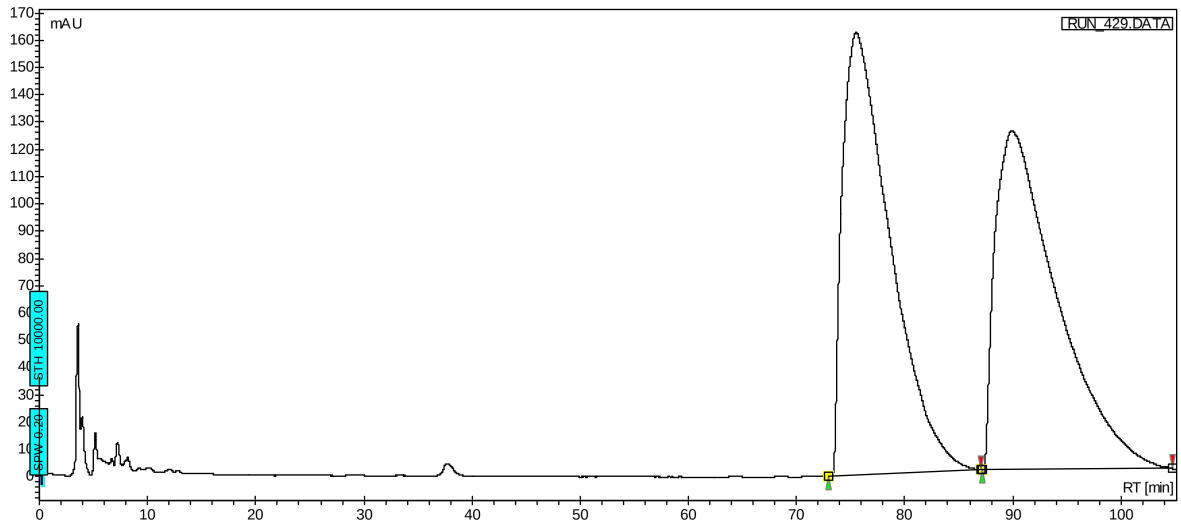

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 101.23 | 48.84 |
| 2 | 119.27 | 51.16 |



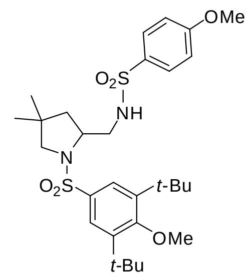



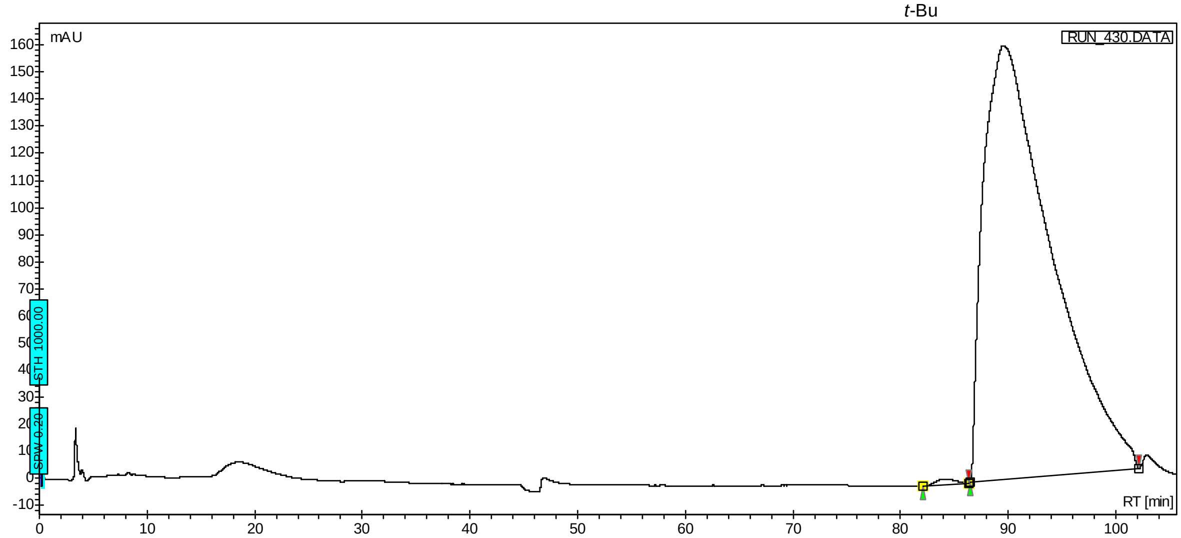

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 95.51 | 98.51 |
| 2 | 110.80 | 1.49 |



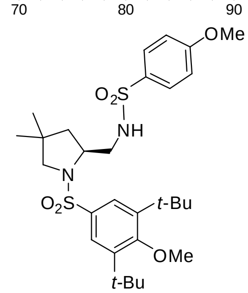


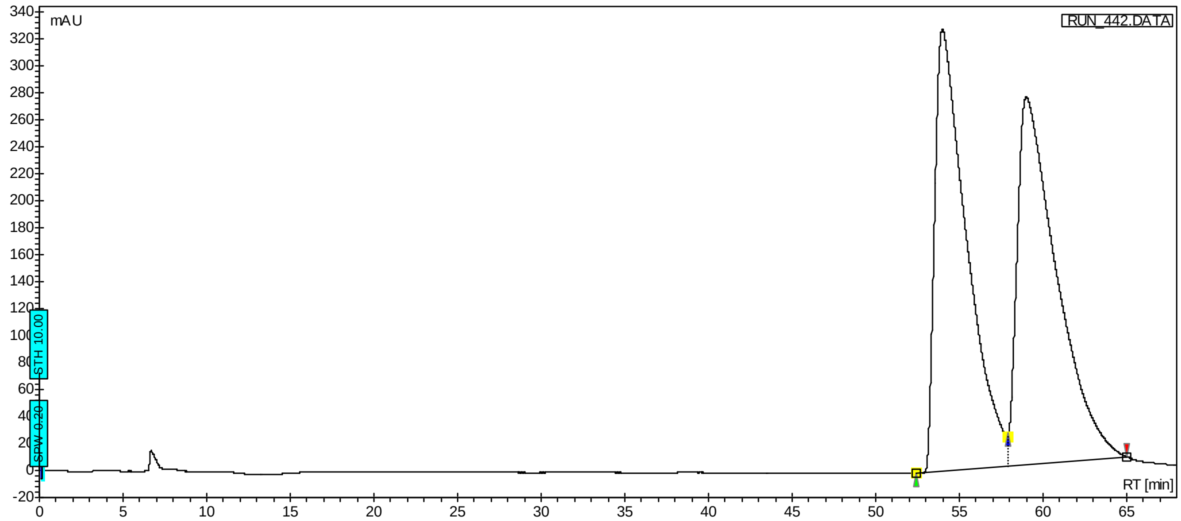

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 75.51 | 50.27 |
| 2 | 89.93 | 49.73 |



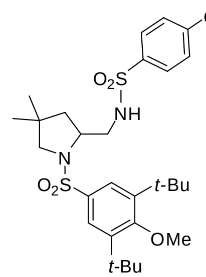



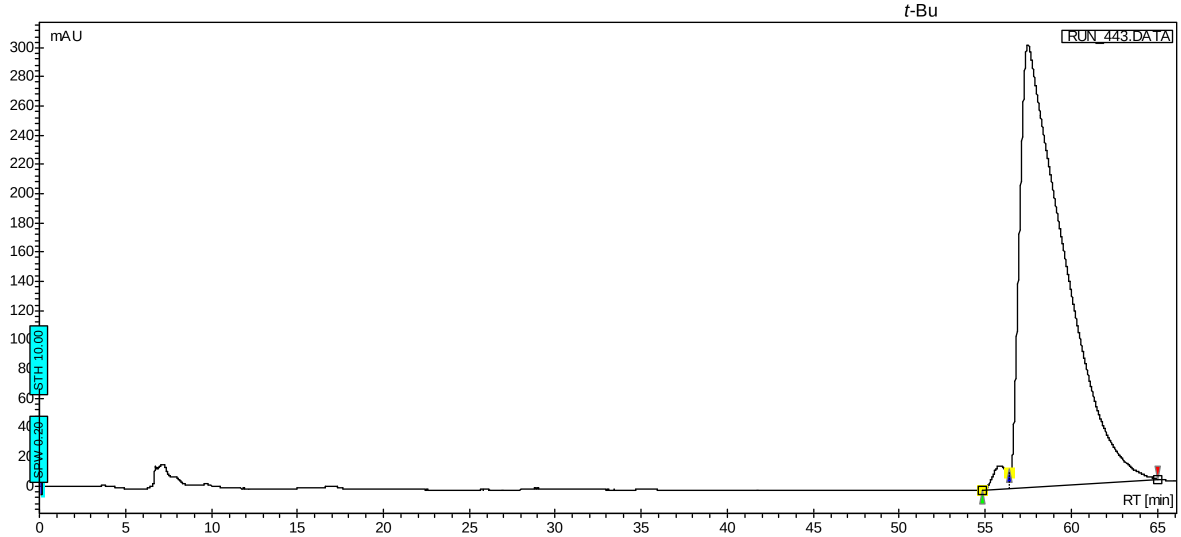

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 84.21 | 0.33 |
| 2 | 89.56 | 99.67 |



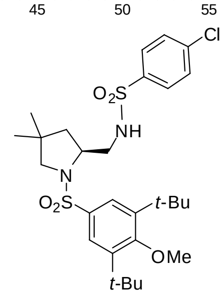


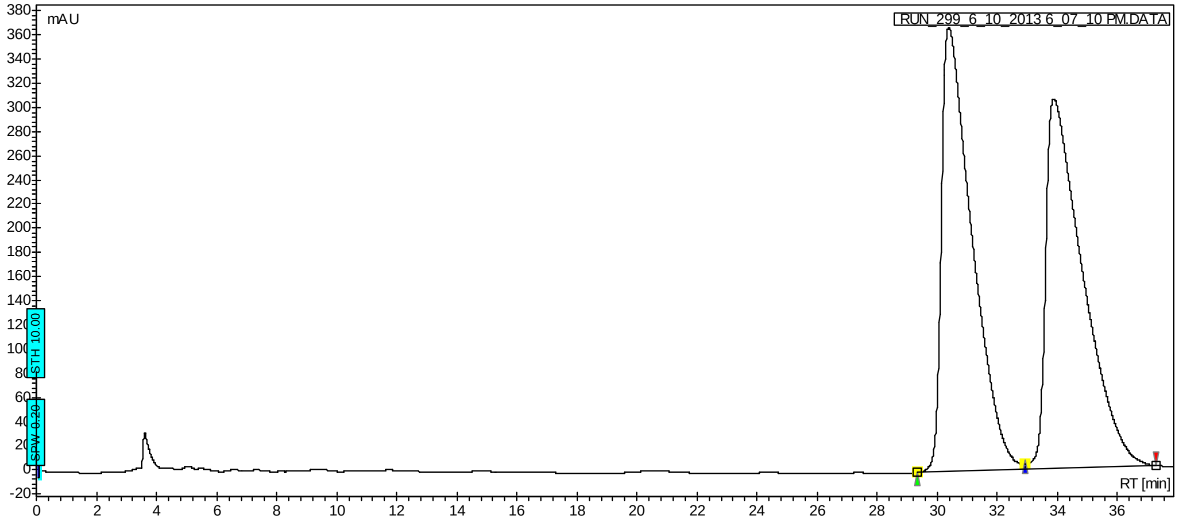

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 53.99 | 49.36 |
| 2 | 59.01 | 50.64 |



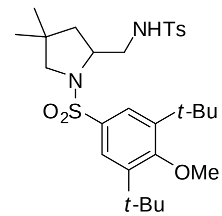



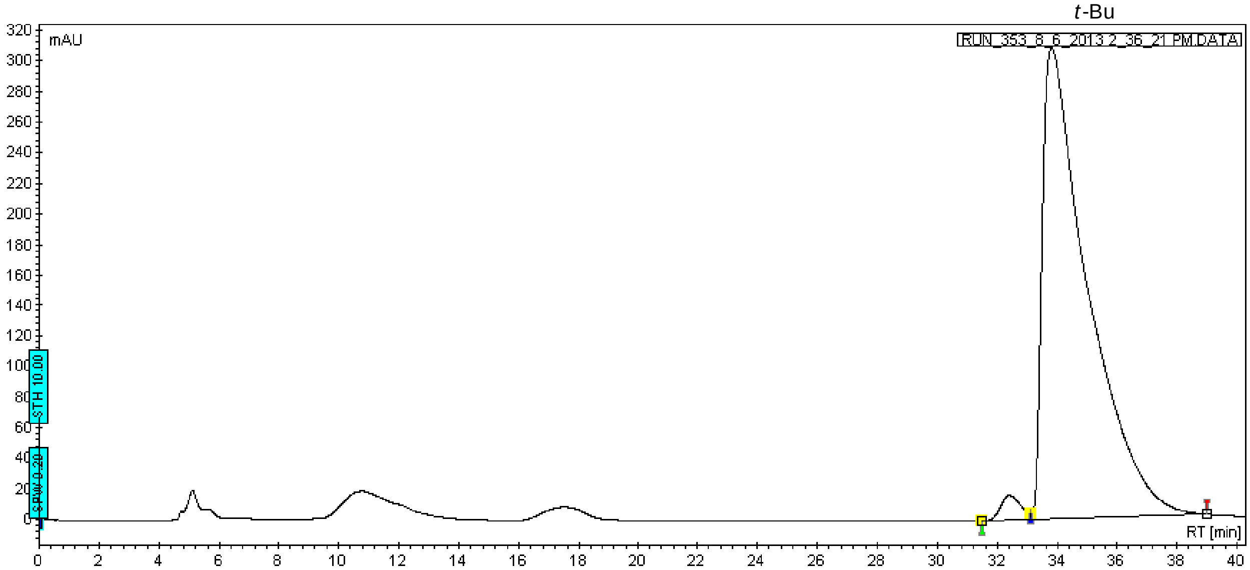

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 55.87 | 1.65 |
| 2 | 57.48 | 98.35 |



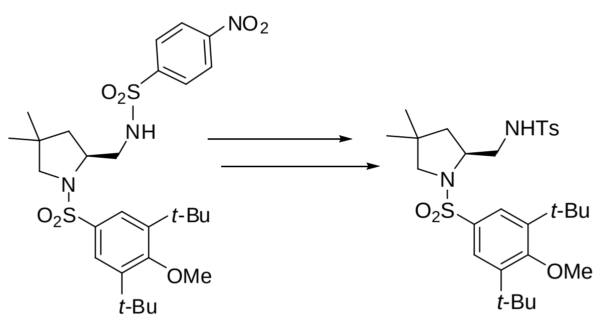



| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 30.38 | 49.77 |
| 2 | 33.88 | 50.23 |

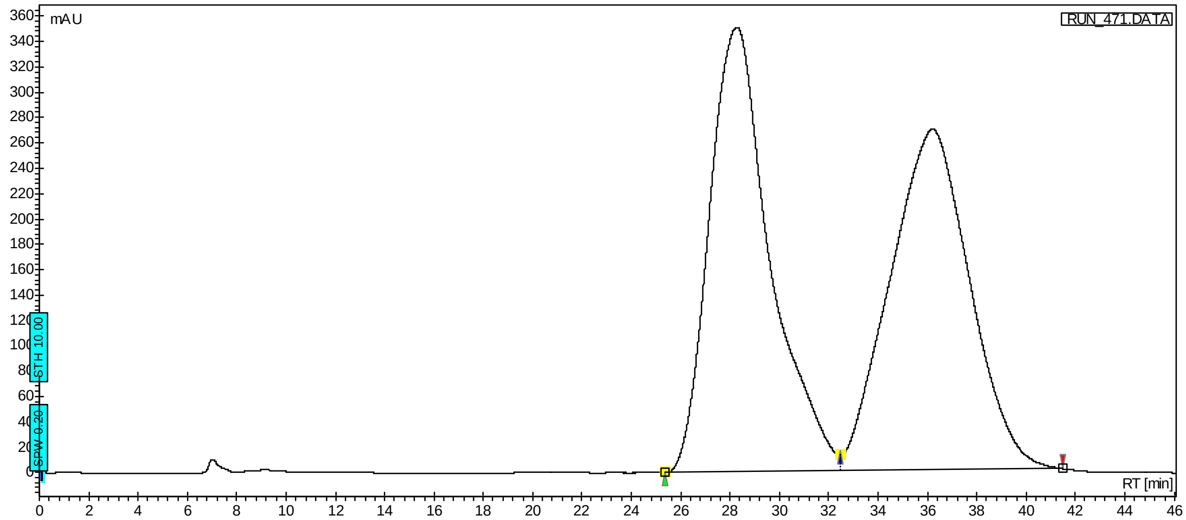


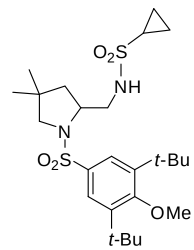

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 32.42 | 1.50 |
| 2 | 34.21 | 98.50 |

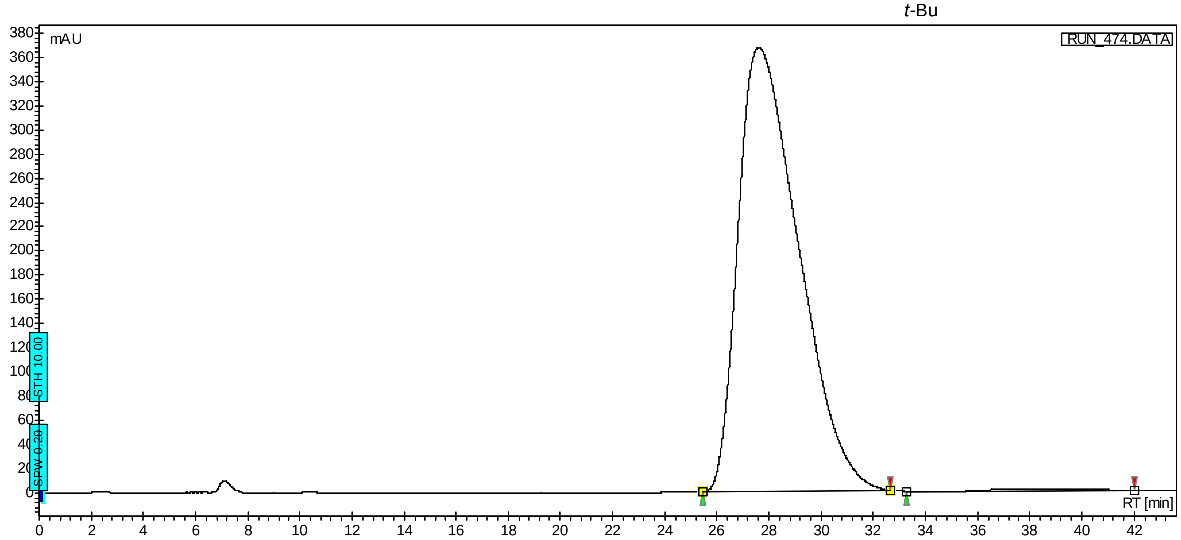



*Note: The ee was recorded by deprotecting the Nosyl group from **9g** using thiophenol, and then protecting that position with TsCl to be compared against a known racemic trace.

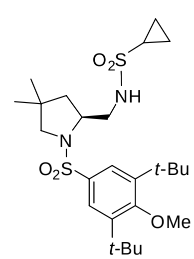


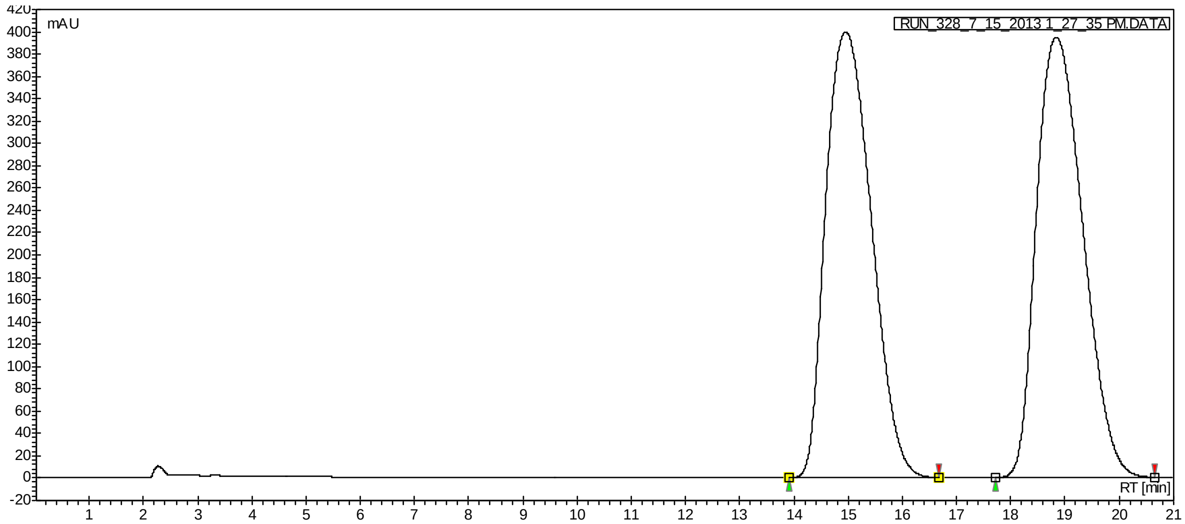

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 28.27 | 50.01 |
| 2 | 36.21 | 49.99 |



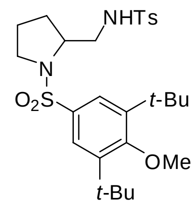



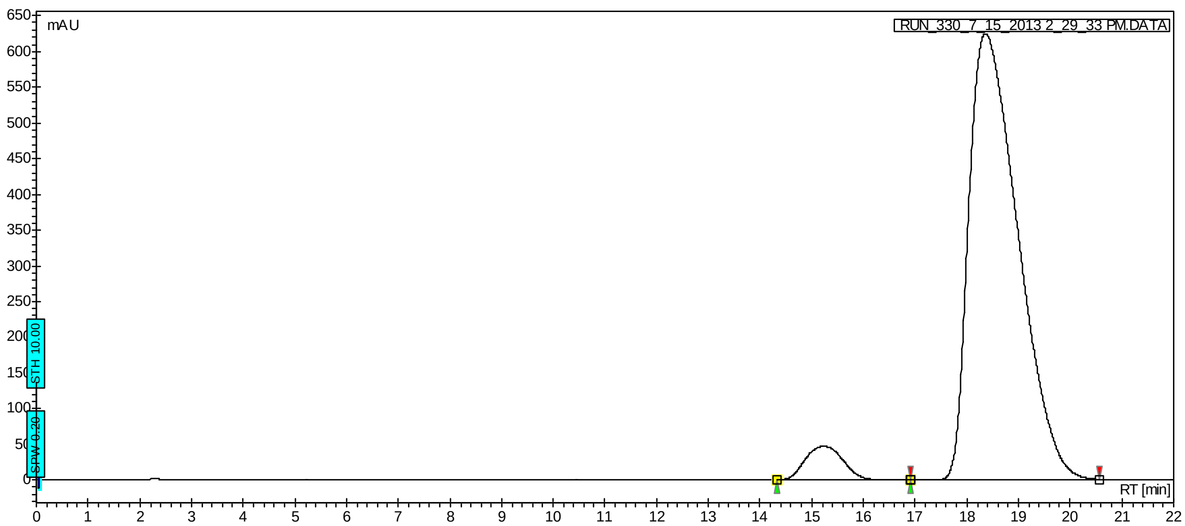

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 27.60 | 99.28 |
| 2 | 38.85 | 0.72 |



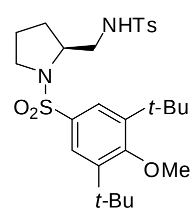


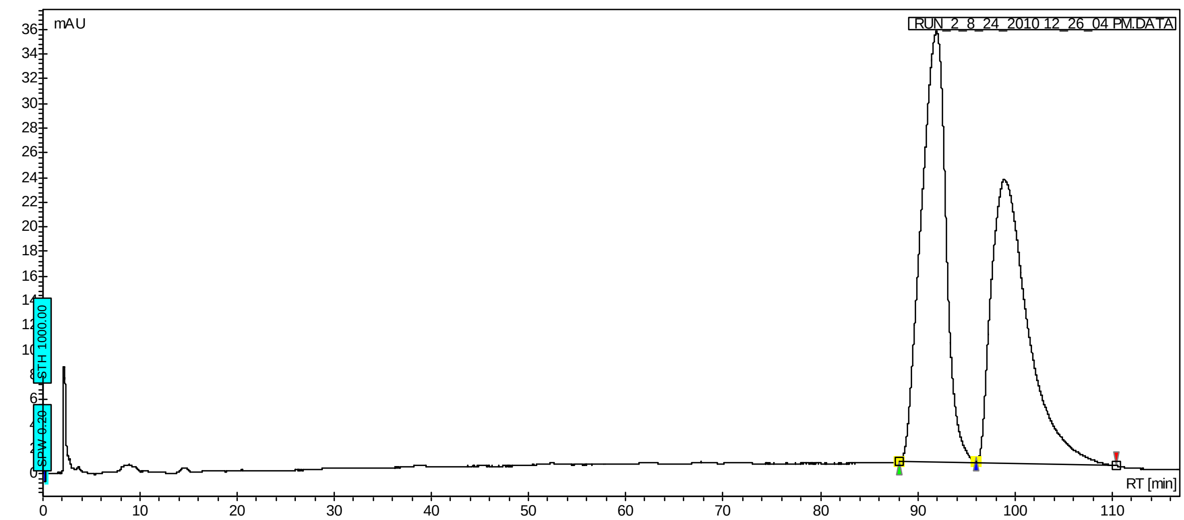

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 14.95 | 49.88 |
| 2 | 18.84 | 50.12 |



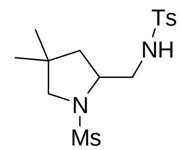



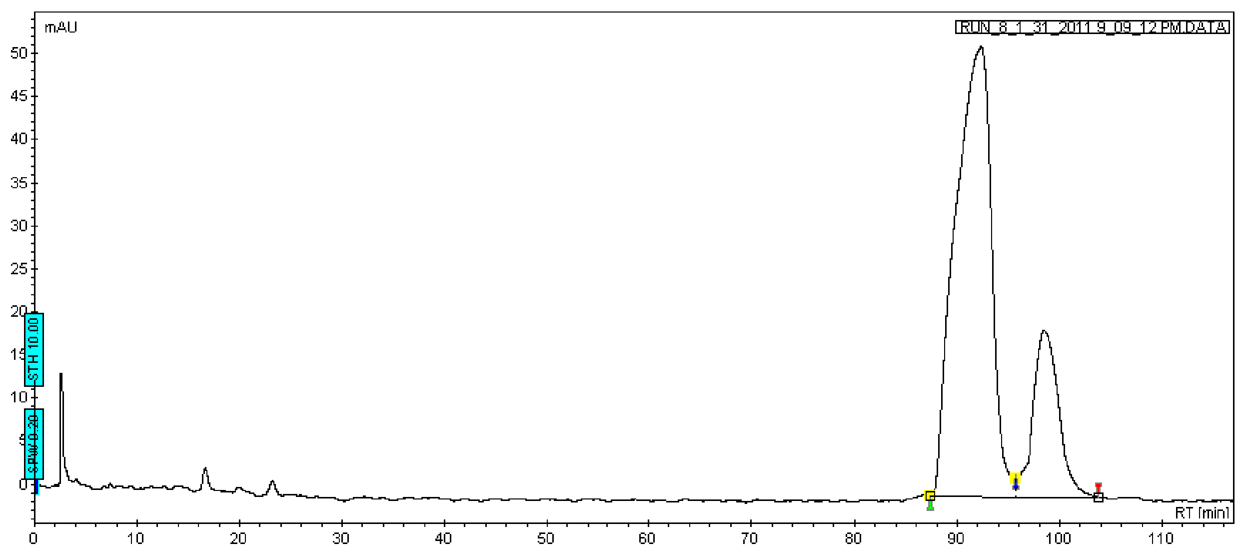

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 15.23 | 5.58 |
| 2 | 18.36 | 94.42 |



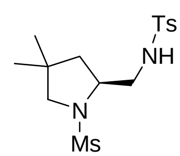


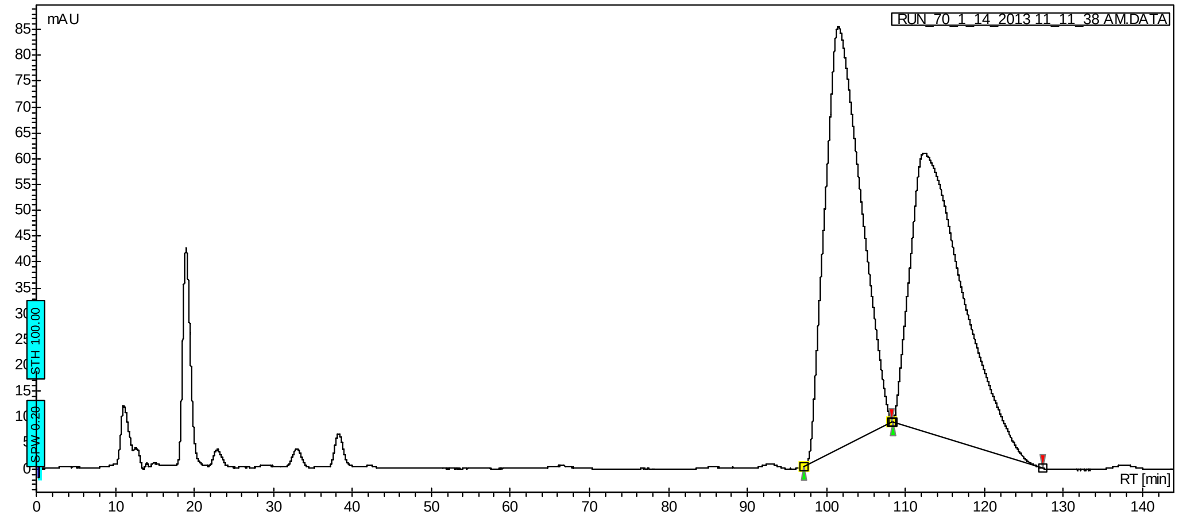

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 91.96 | 50.46 |
| 2 | 98.93 | 49.54 |



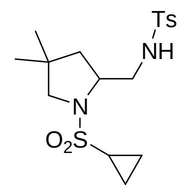



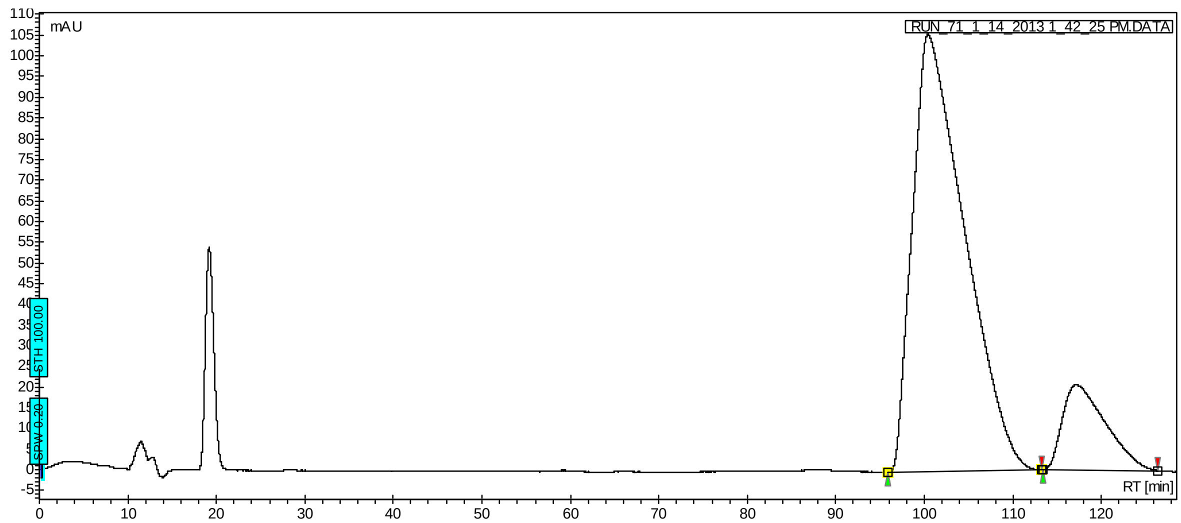

| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 92.06 | 81.94 |
| 2 | 98.12 | 18.06 |



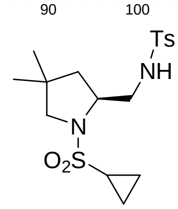



| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 101.47 | 50.51 |
| 2 | 112.42 | 49.49 |




| # | Time[min] | Area[%] |
|---|---|---|
| 1 | 100.37 | 86.05 |
| 5 | 117.18 | 13.95 |



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