Supporing information for

C—H to C—N Cross-Coupling of Sulfonamides with Olefins

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General Information

The following commercially obtained reagents were used as received: Pd(OAc)$_2$ (Johnson Mattey Chemicals) was stored in a glove box, and weighted out in the air at room temperature prior to use. Trifluoromethanesulfonic anhydride (Oakwood Chemicals) was stored in 5 °C fridge under N$_2$. 1,4-benzoquinone, 2,6-dimethylbenzoquinone and 2,5-dimethylbenzoquinonone was purchased from Sigma-Aldrich and used as received. All allylic amination reactions were run under ambient air with no precautions taken to exclude moisture. All other reactions were run in flame- or oven-dried glassware under an atmosphere of N$_2$ or Ar gas with dry solvents unless otherwise stated. All products were filtered through a glass wool plug prior to obtaining a final weight. Anhydrous solvents were purified by passage through a bed of activated alumina immediately prior to use (Glass Contour, Laguna Beach, California). Chloroform-d was stored over 3Å molecular sieves in a secondary container with drierite. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm) and visualized with UV and Cerium-ammonium-molybdate and potassium permanganate stains. Flash chromatography was performed using American International ZEOprep 60 ECO silica gel (230-400 mesh).

$^1$H-NMR spectra were recorded on a Varian Inova-500 (500 MHz), Varian Unity-500 (500 MHz) or Carver-Bruker 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl$_3$ at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sxt = sextet, hept = septet, m = multiplet, br = broad, app = apparent; coupling constant(s) in Hz; integration. Proton-decoupled $^{13}$C-NMR spectra were recorded on a Varian Unity-500 (125 MHz) or Carver-Bruker 500 (125MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl$_3$ at 77.16 ppm). Chiral gas chromatographic (GC) analysis was performed on an Agilent 6890N Series instrument equipped with FID detectors using a J&W Cyclosil-B column. Chiral high pressure liquid chromatography (HPLC) analysis was performed on an Agilent 1100 Series instrument equipped with a UV detector, using a CHIRALPAK AD-RH or OJ-H column. Optical rotations were measured using a 1 mL cell with a 50 mm path length on a Jasco P-1020 polarimeter. Optical rotations were obtained with a sodium lamp and are reported as follows: [$\alpha$]$_D$° (c = g/100 mL solvent). High-resolution mass spectra were obtained at the University of Illinois Mass Spectrometry Laboratory. Electrospray ionization (ESI) spectra were performed on a Waters Q-Tof uLima spectrometer, and electron ionization (EI) and field desorption (FD) spectra were performed on a Micromass 70-VSE spectrometer.
Synthesis of (±)-SOX ligands

The general procedure for phenyloxazoline synthesis:

General procedure A:

Ligand intermediate S1, S2, S3, S4, S5 and S6 were synthesized according to the method of Helmchen and coworkers using the following general procedure:

To a 100 mL oven-dried round-bottom flask was added the benzoic acid (10 mmol, 1.0 equiv) and CH₂Cl₂ (20 mL, 0.5 M). The solution was cooled to 0 °C, oxalyl chloride (15 mmol, 1.5 equiv) was then added, followed by slowly addition of DMF (1.0 mmol, 0.1 equiv). The reaction was slowly warmed to room temperature and stirred overnight. The reaction was diluted with CH₂Cl₂ (300 mL), the organic layer was washed by 5% NaHCO₃ (200 mL x 2) and dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude 2-bromobenzoyl chloride was carried through to the next step without further purification.

To a 100 mL oven-dried round-bottom flask was added commercial 2-amino-2-methyl-1-propanol (10 mmol, 1.0 equiv, Sigma Aldrich), Et₃N (20 mmol, 2.0 equiv) and 1,4 dioxane (14 mL). The solution was cooled to 0 °C, and the 2-bromobenzoyl chloride from the previous step in 12 mL of 1,4 dioxane was added slowly. The reaction was allowed to warm up to room temperature and stirred for another 1 hour. The reaction mixture was filtered through a silica plug with ethyl acetate and concentrated under reduced pressure. The crude amide was carried through to the next step without further purification.

An oven-dried 300 mL round-bottom flask equipped with condenser was added the crude amide and toluene (70 mL). After cooled to 0 °C, thionyl chloride (2.2 mL, 30 mmol, 3.0 equiv) was
added dropwise and the reaction was heated to reflux for 3 hours. The solution and thionyl chloride was removed by repeated rotary evaporation with ethyl acetate (3 times). The crude product was carried through without further purification.

To the same round-bottom flask was added NaOH (15 mmol, 1.5 equiv) and MeOH (80 mL), and the mixture was heated to reflux open to air for 1 hour. After cooling to room temperature, diethyl ether (200 mL) was added. The resulting solution was washed 3 times with brine. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified via flash column chromatography (0% => 10% acetone in hexanes) to afford the desired phenyloxazoline.

**General procedure B:**

Ligand intermediate S2 was synthesized according to the method of Stoltz and coworkers² using the following general procedure:

To a 100 mL oven-dried round-bottom flask was added the benzoic acid (10 mmol, 1.0 equiv) and CH₂Cl₂ (20 mL, 0.5 M). The solution was cooled to 0 °C, oxalyl chloride (15 mmol, 1.5 equiv) was then added, followed by slow addition of DMF (1.0 mmol, 0.1 equiv). The reaction was slowly warmed to room temperature and stirred overnight. The reaction was diluted with CH₂Cl₂ (300 mL), the organic layer was washed by 5% NaHCO₃ (200 mL x 2) and dried over anhydrous NaSO₄, filtered, and concentrated under reduced pressure. The crude 2-bromobenzoyl chloride was carried through to the next step without further purification.

To a 100 mL oven-dried round-bottom flask was added 2-amino-2,2-diphenylethanol³ (10 mmol, 1.0 equiv), Et₃N (20 mmol, 2.0 equiv) and 1,4 dioxane (14 mL). The solution was cooled to 0 °C, and the crude 2-bromobenzoyl chloride from previous step in 12 ml of 1,4 dioxane was added slowly. The reaction was allowed to warm up to room temperature and stirred for another 1 hour. The reaction mixture was filtered through a silica plug with ethyl acetate and concentrated under reduced pressure. The crude amide was carried through next step without further purification.

To a solution of amide in CH₂Cl₂ (30 mL) was added tosyl chloride (13 mmol, 1.3 equiv) and Et₃N (50 mmol, 5 equiv). The reaction was refluxed at 55 °C for 22 hours. After H₂O (10 mL) was added, the reaction was refluxed at 75 °C for another 2 hours. The reaction was cooled, and the layers were separated. The aqueous layer was extracted with CH₂Cl₂ (30 mL x 2). The combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The crude mixture was purified via flash column chromatography (0% => 10% acetone in hexanes) to afford the desired phenyloxazoline.

**Phenyloxazoline S1** was synthesized following the general procedure A in 73% yield (1.857 g, 7.340 mmol) as a colorless oil.

³¹H NMR (500 MHz, Chloroform-d) δ 7.64 (dd, J = 7.7, 1.8 Hz, 1H), 7.62 (dd, J = 8.0, 1.3 Hz, 1H), 7.33 (ddd, J = 7.5, 7.5, 1.3 Hz), 7.27 (ddd, J = 7.7, 7.5, 1.8 Hz, 1H), 4.14 (s, 2H), 1.41 (s, 6H). These data are in agreement with that previously reported in the literature.⁴
Phenyloxazoline S2 was synthesized following the general procedure B in 53% yield (2.009 g, 5.311 mmol) as a colorless oil.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.81 (dd, $J = 7.7$, 1.8 Hz, 1H), 7.69 (dd, $J = 8.0$, 1.3 Hz, 1H), 7.52-7.49 (m, 4H), 7.41-7.36 (m, 5H), 7.34-7.28 (m, 3H), 5.03 (s, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) 162.5, 145.9, 134.0, 131.9, 131.7, 129.8, 128.6, 127.3, 127.2, 126.8, 122.2, 80.2, 79.9.

HRMS (ESI) m/z calculated for C$_{21}$H$_{17}$NOBr [M+H]$^+$: 378.0494, found 378.0492.

Phenyloxazoline S3 was synthesized following the general procedure A in 51% yield (1.652 g, 5.129 mmol) as a colorless oil.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.91-7.87 (m, 1H), 7.78 (dd, $J = 8.1$, 1.0 Hz, 1H), 7.59 (ddd, $J = 8.1$, 1.7, 0.8 Hz, 1H), 4.16 (s, 2H), 1.42 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 160.7, 133.5 (q, $J = 33.2$ Hz), 131.8, 130.8 (q, $J = 3.8$ Hz), 124.1 (q, $J = 3.6$ Hz), 122.9 (q, $J = 273.1$ Hz), 122.4, 79.8, 68.6, 28.4. $^{19}$F NMR (470 MHz, Chloroform-d) δ -63.09. HRMS (ESI) m/z calculated for C$_{12}$H$_{12}$NOF$_3$Br [M+H]$^+$: 322.0054, found 322.0044.

Phenyloxazoline S4 was synthesized following the general procedure A in 59% yield (1.673 g, 5.887 mmol) as a white solid.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.57 (dd, $J = 8.6$, 0.6 Hz, 1H), 7.10 (d, $J = 2.5$ Hz, 1H), 6.80 (ddd, $J = 8.7$, 2.6, 0.6 Hz, 1H), 4.05 (s, 2H), 3.75 (s, 3H), 1.34 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.47, 161.27, 132.30, 123.48, 122.54, 122.11, 118.90, 113.64, 79.12, 67.84, 55.58, 28.26.

HRMS (ESI) m/z calculated for C$_{12}$H$_{15}$NO$_2$Br [M+H]$^+$: 284.0268, found 284.0293.

Phenyloxazoline S5 was synthesized following the general procedure A in 79% yield (2.251 g, 7.920 mmol) as a white solid.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.48 (d, $J = 8.8$ Hz, 1H), 7.16 (d, $J = 3.1$ Hz, 1H), 6.83 (dd, $J = 8.8$, 3.1 Hz, 1H), 4.14 (s, 2H), 3.81 (s, 3H), 1.41 (s, 6H). These data are in agreement with that previously reported in the literature.

Phenyloxazoline S6 was synthesized following the general procedure A in 79% yield (2.251 g, 7.920 mmol) as a white solid. $^{2}$H NMR (500 MHz, Chloroform-d) δ 7.48 (d, $J = 8.8$ Hz, 1H), 7.16 (d, $J = 3.1$ Hz, 1H), 6.83 (dd, $J = 8.8$, 3.1 Hz, 1H), 4.14 (s, 2H), 3.81 (s, 3H), 1.41 (s, 6H). These data are in agreement with that previously reported in the literature.

Note: The octal values do not correspond to the actual text in the image.
Phenyloxazoline S6 was synthesized following the general procedure A in 62% yield (1.954 g, 6.219 mmol) as a white solid.

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.12 (s, 1H), 6.99 (s, 1H), 4.04 (s, 2H), 3.82 (s, 3H), 3.82 (s, 3H), 1.33 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.5, 150.8, 147.8, 121.8, 116.2, 113.4, 112.7, 79.1, 67.8, 56.1, 56.1, 28.2. HRMS (ESI) m/z calculated for C$_{13}$H$_{17}$NO$_3$Br [M+H]$^+$: 314.0392, found 314.0385.

The general procedure for the synthesis of methyl sulfinites:

Scheme S2: Ligand intermediate S7, S8 and S9.

Ligand intermediates (methyl sulfinites) S7, S8 and S9 was synthesized according to the method of Ruano and coworkers$^6$ using the following general procedure. To a solution of the corresponding disulfide (10 mmol, 1.0 equiv) in MeOH (25 mL, 0.4 M) was slowly added NBS (15 mmol, 1.5 equiv) at room temperature. The reaction mixture was stirred and monitored by TLC. Upon completion, the reaction was diluted with CH$_2$Cl$_2$ (25 mL), washed with sat. aq. NaHSO$_3$ (10 mL) and sat. aq. NaHCO$_3$ (4 x 10 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and the solvent was removed under reduced pressure.

Methyl sulfinate S7 was synthesized according to the general procedure in 95% yield (3.236 g, 19.01 mmol) as a colorless oil.

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.59 (d, $J$ = 8.2 Hz, 2H), 7.34 (d, $J$ = 7.8 Hz, 2H), 3.46 (s, 3H), 2.43 (s, 3H). These data are in agreement with that previously reported in the literature.$^6$

Methyl sulfinate S8 was synthesized according to the general procedure in 91% yield (3.396 g, 18.24 mmol) as a colorless oil.

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.64 (d, $J$ = 8.8, 2H), 7.03 (d, $J$ = 8.8, 2H), 3.87 (s, 3H), 3.46 (s, 3H). These data are in agreement with that previously reported in the literature.$^7$
**Methyl sulfinate S9** was synthesized according to the general procedure in 94% yield (4.215 g, 18.80 mmol) as a colorless oil.

**H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\) 7.90-7.72 (m, 4H), 3.52 (s, 3H). These data are in agreement with that previously reported in the literature.\(^8\)

**The general procedure for (±)-SOX ligand synthesis:**

To an oven-dried round-bottom flask was added a stir bar, phenyloxazoline (5.0 mmol, 1.0 equiv), THF (25 ml, 0.2 M), and tetramethylethylenediamine (TMEDA, 5.5 mmol, 1.1 equiv). The reaction flask was cooled to -78 °C and n-butyllithium (1.6 M in hexane, 5.5 mmol, 1.1 equiv) was added dropwise. The reaction was stirred 20 minutes at -78 °C. Subsequently, the methyl sulfinate (6.0 mmol, 1.2 equiv) was added as a solution in THF (12 ml, 0.5 M) dropwise. The reaction was stirred 1 hour at -78 °C, then 1 hour at 0 °C, then 1 hour at room temperature. The reaction was quenched with water. The mixture was diluted with diethyl ether, and the layers were separated. The aqueous layer was extracted with diethyl ether (20 mL x 3). The combined organic layers were dried over anhydrous MgSO\(_4\), filtered, and concentrated under reduced pressure. The crude residue was purified via flash column chromatography (0% => 15% acetone in hexanes) to afford the (±)-SOX ligand.

(±)-SOX-Ligand 1 (L1) was synthesized following the general procedure. 1.27 g of phenyloxazoline S1 (5.0 mmol, 1.0 equiv) was used, along with 1.02 g of sulfinate S7 (6.0 mmol, 1.2 equiv). The crude residue was purified via flash column chromatography (0% => 20% acetone in hexanes) to afford 1.176 g (3.76 mmol) of pure product as a white solid (75% yield).

**H NMR** (500MHz, CDC13) \(\delta\) 8.37 (dd, \(J = 7.9, 1.1\) Hz, 1H), 7.85 (dd, \(J = 7.7, 1.3\) Hz, 1H), 7.72 (ddd, \(J = 7.7, 7.7, 1.1\) Hz, 1H), 7.65 (d, \(J = 8.4\) Hz, 2H), 7.50 (ddd, \(J = 7.5, 7.5, 0.9\) Hz, 1H), 7.16 (d, \(J = 8.4\) Hz, 2H), 4.25 (dd, \(J = 10.1, 8.8\) Hz, 1H), 4.16 (t, \(J = 8.1\) Hz, 1H), 4.03 (dd, \(J = 10.1, 7.9\) Hz, 1H), 2.32 (s, 3H), 0.97 (s, 9H). These data are in agreement with that previously reported in the literature.\(^9\)
(±)-SOX-Ligand 2 (L2) was synthesized following the general procedure. Phenyloxazoline S2 (1.89 g, 5.0 mmol, 1.0 equiv) and sulfinate S7 (1.02 g, 6.0 mmol, 1.2 equiv) were used. The crude residue was purified via flash column chromatography (0% => 20% acetone in hexanes) to afford 1.597 g (3.64 mmol) of pure product as a white solid (73% yield).

$^1$H NMR (500 MHz, Chloroform-d) δ 8.46 (dd, $J = 8.0$, 1.3 Hz, 1H), 8.01 (dd, $J = 7.7$, 1.4 Hz, 1H), 7.77 (ddd, $J = 7.7$, 7.7, 1.4 Hz, 1H), 7.55 (ddd, $J = 7.5$, 7.5, 1.3 Hz, 1H), 7.51-7.47 (m, 4H), 7.38 (dd, $J = 8.5$, 7.0 Hz, 2H), 7.31-7.27 (m, 1H), 7.23-7.16 (m, 3H), 7.04 (dd, $J = 8.0$, 1.7 Hz, 2H), 7.00 (d, $J = 8.1$, 2H), 4.95 (d, $J = 8.6$, 1H), 4.85 (d, $J = 8.7$, 1H), 2.29 (s, 3H). 13C NMR (125 MHz, CDCl$_3$) δ 159.9, 146.7, 145.6, 145.4, 143.5, 140.7, 132.2, 130.3, 129.9, 129.5, 128.6, 128.28, 127.3, 127.05 126.7, 126.6, 7.7, 7.27 (m, 1H), 7.23 (m, 3H), 7.04 (dd, $J = 8.0$, 1.7 Hz, 2H), 7.00 (d, $J = 8.1$, 2H), 4.95 (d, $J = 8.6$, 1H), 4.85 (d, $J = 8.7$, 1H), 2.29 (s, 3H). HRMS (ESI) m/z calculated for C$_{28}$H$_{24}$NO$_2$S [M+H]$^+$: 438.1528, found 438.1519.

(±)-SOX-Ligand 3 (L3) was synthesized according to the following modified procedure. To an oven-dried flask was added a stir bar, phenyloxazoline S3 (322.1 mg, 1.0 mmol, 1.0 equiv), THF (5 ml, 0.2 M), and TMEDA (168 µL, 1.1 mmol, 1.1 equiv). The reaction flask was cooled to -94 °C and n-butyllithium (688 µL, 1.6 M in hexane, 1.1 mmol, 1.1 equiv) was added dropwise. The reaction was stirred 20 minutes at -94 °C and then the reaction was warmed up to -78 °C, the methyl sulfinate S7 (1.02 g, 1.2 mmol, 1.2 equiv) was added as a solution in THF (5 mL, 0.2M) dropwise. The reaction was stirred 1 hour at -78 °C, then 1 hour at 0 °C, then 1 hour at room temperature. The reaction was then quenched with water. The mixture was diluted with diethyl ether, and the layers were separated. The aqueous layer was extracted with diethyl ether (25 mL x 3). The combined organic layers were dried over anhydrous MgSO$_4$, filtered, and concentrated under reduced pressure. The crude residue was purified via flash column chromatography (0% => 20% acetone in hexanes) to afford 171.6 mg (0.45 mmol) of pure product as a white solid (45% yield).

$^1$H NMR (500 MHz, Chloroform-d) δ 8.68 (d, $J = 1.8$, 1H), 7.99 (d, $J = 8.0$, 1H), 7.74 (dd, $J = 8.1$, 1.8 Hz, 1H), 7.56 (d, $J = 8.3$, 2H), 7.16 (d, $J = 8.0$, 2H), 4.03 (d, $J = 8.1$, 1H) 4.00 (d, $J = 8.1$, 1H), 2.31 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H). 13C NMR (126 MHz, Chloroform-d) δ 158.2, 148.4, 142.9, 141.6, 133.6 (q, $J = 33.4$, Hz), 130.4, 129.6, 128.7, 127.1, 127.0 (q, $J = 3.7$, Hz), 123.5 (q, $J = 273.2$, 1H), 122.3 (q, $J = 3.8$, Hz), 79.1, 69.0, 28.6, 28.1, 21.4. 19F NMR (470 MHz, Chloroform-d) δ -63.20. HRMS (ESI) m/z calculated for C$_{19}$H$_{19}$NO$_2$SF$_3$ [M+H]$^+$: 382.1089, found 382.1092.

(±)-SOX-Ligand 4 (L4) was synthesized following the general procedure. Phenyloxazoline S4 (1.42 g, 5.0 mmol, 1.0 equiv) and sulfinate S7 (1.02 g, 6.0 mmol, 1.2 equiv) were used. The crude residue was purified via flash column chromatography (0% => 30% acetone in hexanes) to afford 1.371 g (3.99 mol) of pure product as a white solid (80% yield).
\[^1\text{H}\ \text{NMR}\ (500\ \text{MHz},\ \text{CDCl}_3)\ \delta\ 7.89\ (d,\ J = 2.6\ \text{Hz},\ 1\text{H}),\ 7.78\ (d,\ J = 8.6\ \text{Hz},\ 1\text{H}),\ 7.54\ (d,\ J = 8.2 \text{Hz},\ 2\text{H}),\ 7.12\ (d,\ J = 8.0\ \text{Hz},\ 2\text{H}),\ 6.94\ (ddd,\ J = 8.6,\ 2.7,\ 0.7\ \text{Hz},\ 1\text{H}),\ 3.91\ (s,\ 2\text{H}),\ 3.90\ (s,\ 3\text{H}),\ 2.27\ (s,\ 3\text{H}),\ 1.25\ (s,\ 3\text{H}),\ 1.18\ (s,\ 3\text{H}).\]

\[^{13}\text{C}\ \text{NMR}\ (125\ \text{MHz},\ \text{CDCl}_3)\ \delta\ 162.5,\ 159.0,\ 148.3,\ 143.5,\ 141.0,\ 131.5,\ 129.4,\ 127.0,\ 117.7,\ 116.3,\ 109.3,\ 78.6,\ 77.4,\ 77.2,\ 76.9,\ 68.29,\ 55.8,\ 28.6,\ 28.1,\ 21.3\].

\[\text{HRMS (ESI)}\ m/z\ \text{calculated for } C_{19}H_{22}NO_3S\ [M+H]^+:\ 344.1320,\ \text{found}\ 344.1322.\]

\((\pm)\text{-MeO-SOX-Ligand 5 (L5)}\) was synthesized following the general procedure. Phenyloxazoline S5 (1.42 g, 5.0 mmol, 1.0 equiv) and methyl sulfinate S7 (1.02 g, 6.0 mmol, 1.2 equiv). The crude residue was purified via flash column chromatography (0% => 30% acetone in hexanes) to afford 1.371 g (3.99 mmol) of pure product as a white solid (80% yield).

\[^1\text{H}\ \text{NMR}\ (500\ \text{MHz},\ \text{Chloroform-d})\ \delta\ 8.18\ (d,\ J = 8.8\ \text{Hz},\ 1\text{H}),\ 7.54\ (d,\ J = 8.2\ \text{Hz},\ 2\text{H}),\ 7.34\ (d,\ J = 2.8\ \text{Hz},\ 1\text{H}),\ 7.15\ (d,\ J = 8.9,\ 2.7\ \text{Hz},\ 1\text{H}),\ 7.12\ (d,\ J = 8.3\ \text{Hz},\ 2\text{H}),\ 3.96\ (d,\ J = 1.5\ \text{Hz},\ 2\text{H}),\ 3.81\ (s,\ 3\text{H}),\ 2.27\ (s,\ 3\text{H}),\ 1.27\ (s,\ 3\text{H}),\ 1.22\ (s,\ 3\text{H}).\]

\[^{13}\text{C}\ \text{NMR}\ (126\ \text{MHz},\ \text{CDCl}_3)\ \delta\ 161.0,\ 159.1,\ 144.0,\ 140.7,\ 137.3,\ 129.3,\ 127.0,\ 126.9,\ 126.5,\ 117.4,\ 114.6,\ 78.9,\ 68.5,\ 55.7,\ 28.5,\ 28.1,\ 21.3.\]

\[\text{HRMS (ESI)}\ m/z\ \text{calculated for } C_{19}H_{22}NO_3S\ [M+H]^+:\ 344.1320,\ \text{found}\ 344.1318.\]

\((\pm)\text{-SOX-Ligand 6 (L6)}\) was synthesized following the general procedure. Phenyloxazoline S1 (1.27 g, 5.0 mmol, 1.0 equiv) and methyl sulfinate S8 (1.12 g, 6.0 mmol, 1.2 equiv). The crude residue was purified via flash column chromatography (0% => 20% acetone in hexanes) to afford 1.381 g (4.19 mmol) of pure product as a white solid (84% yield).

\[^1\text{H}\ \text{NMR}\ (500\ \text{MHz},\ \text{Chloroform-d})\ \delta\ 8.37\ (dd,\ J = 8.0,\ 1.3\ \text{Hz},\ 1\text{H}),\ 7.86\ (dd,\ J = 7.7,\ 1.4\ \text{Hz},\ 1\text{H}),\ 7.70\ (ddd,\ J = 8.0,\ 7.4,\ 1.4\ \text{Hz},\ 1\text{H}),\ 7.61-7.57\ (m,\ 2\text{H}),\ 7.49\ (td,\ J = 7.5,\ 1.3\ \text{Hz},\ 1\text{H}),\ 6.86-6.82\ (m,\ 2\text{H}),\ 3.98\ (d,\ J = 1.9\ \text{Hz},\ 2\text{H}),\ 3.75\ (s,\ 3\text{H}),\ 1.29\ (s,\ 3\text{H}),\ 1.24\ (s,\ 3\text{H}).\]

\[^{13}\text{C}\ \text{NMR}\ (125\ \text{MHz},\ \text{CDCl}_3)\ \delta\ 161.5,\ 159.3,\ 146.5,\ 138.1,\ 131.7,\ 130.2,\ 129.8,\ 129.0,\ 125.5,\ 124.9,\ 114.2,\ 78.9,\ 68.6,\ 55.5,\ 28.7,\ 28.2.\]

\[\text{HRMS (ESI)}\ m/z\ \text{calculated for } C_{19}H_{20}NO_3S\ [M+H]^+:\ 330.1164,\ \text{found}\ 330.1160.\]

\((\pm)\text{-SOX-Ligand 7 (L7)}\) was synthesized following the general procedure. Phenyloxazoline S6 (1.57 g, 5.0 mmol, 1.0 equiv) and methyl sulfinate S7 (1.02 g, 6.0 mmol, 1.2 equiv) were used. The crude residue was purified via flash column chromatography (0% => 30% acetone in hexanes) to afford 1.438 g (3.85 mmol) of pure product as a white solid (77% yield).

\[^1\text{H}\ \text{NMR}\ (500\ \text{MHz},\ \text{Chloroform-d})\ \delta\ 7.80\ (s,\ 1\text{H}),\ 7.51\ (d,\ J = 8.2\ \text{Hz},\ 2\text{H}),\ 7.34\ (s,\ 1\text{H}),\ 7.12\ (d,\ J = 8.0\ \text{Hz},\ 2\text{H}),\ 3.98\ (s,\ 3\text{H}),\ 3.95-3.91\ (m,\ 2\text{H}),\ 3.89\ (s,\ 3\text{H}),\ 2.27\ (s,\ 3\text{H}),\ 1.24\ (s,\ 3\text{H}),\ 1.19\ (s,\]
$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 159.0, 151.7, 149.9, 143.9, 140.8, 138.6, 129.4, 126.6, 118.1, 112.0, 107.1, 78.8, 68.3, 56.4, 56.3, 28.5, 28.1, 21.3. HRMS (ESI) $m/z$ calculated for C$_{20}$H$_{24}$NOS \([\text{M+H}]^+\): 374.1426, found 374.1426.

(±)-SOX-Ligand 8 (L8) was synthesized following the general procedure. Phenyloxazoline S5 (1.42 g, 5.0 mmol, 1.0 equiv) and methyl sulfinate S8 (1.12 g, 6.0 mmol, 1.2 equiv). The crude residue was purified via flash column chromatography (0% $\rightarrow$ 30% acetone in hexanes) to afford 1.350 g (3.75 mmol) of pure product as a white solid (75% yield).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.21 (d, $J = 8.8$ Hz, 1H), 7.60-7.54 (m, 2H), 7.35 (d, $J = 2.7$ Hz, 1H), 7.18 (dd, $J = 8.8, 2.7$ Hz, 1H), 6.84-6.81 (m, 2H), 3.96 (s, 2H), 3.83 (s, 3H), 3.74 (s, 3H), 1.28 (s, 3H), 1.22 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.3, 161.0, 159.1, 138.5, 137.3, 128.6, 126.9, 126.9, 117.4, 114.8, 114.1, 78.9, 68.6, 55.7, 55.4, 28.6, 28.2. HRMS (ESI) $m/z$ calculated for C$_{19}$H$_{22}$NO$_4$S \([\text{M+H}]^+\): 360.1270, found 360.1268.
Preparation of N-Triflyl protected amine nucleophiles

General procedure for N-triflyl protected amine nucleophiles:

Procedure A (From amines)
An oven dried round-bottom flask equipped with a stir bar was charged with amine (5.0 mmol, 1.0 equiv), CH$_2$Cl$_2$ (10ml, 0.5M) and Et$_3$N (767 µL, 5.5 mmol, 1.1 equiv). The flask was cooled to -78 °C, and trifluoromethanesulfonic anhydride (840 µL, 1.41 g, 5.0 mmol, 1.0 equiv) was added dropwise. The reaction was stirred vigorously at -78 °C for 30 min and allowed to gradually warm up to room temperature. The reaction was then quenched with 20 mL H$_2$O. The reaction mixture was partitioned between H$_2$O and CH$_2$Cl$_2$ and layers were separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (20ml x 3). The organic layers were combined, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The reaction mixture was applied directly to a flash silica column for purification (acetone/hexanes).

Procedure B (From amine hydrochlorides)
An oven dried round-bottom flask equipped with a stir bar was charged with amine hydrochloride (5.0 mmol, 1.0 equiv), CH$_2$Cl$_2$ (10ml, 0.5M) and Et$_3$N (1.53 mL, 11 mmol, 2.2 equiv). The flask was cooled to -78 °C, and Trifluoromethanesulfonic anhydride (840 µL, 1.41 g, 5.0 mmol, 1.0 equiv) was added dropwise. The reaction was stirred vigorously at -78 °C for 30 min and allowed to gradually warm up to r.t. The reaction was then quenched with 20 mL H$_2$O. The reaction mixture was partitioned between H$_2$O and CH$_2$Cl$_2$ and layers were separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (20ml x 3). The organic layers were combined, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The reaction mixture was applied directly to a flash silica column for purification (Acetone/Hexanes).

NOTE: Most N-triflyl protected amines are bench stable for at least one year. (Some of them exhibited color change and suboptimal reactivity (10-15% drop in yield) after storing on bench for over 12 months, repurification by flash column usually restored reactivity in these cases.

N-(2-Phenylethyl)trifluoromethanesulfonamide (S10). The reaction was performed according general procedure A with distilled 2-phenylethylamine (630 µL, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 2.5% acetone/hexanes => 10% acetone/hexanes) to give 1.192 g (4.71 mmol) pure N-triflyl protected amine (S10) as a white solid in 94% yield.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.36 (m, 2H), 7.29 (m, 1H), 7.20 (dd, $J$ = 7.9 Hz, 1.1 Hz, 1H), 4.67 (br s, 1H), 3.58 (q, $J$ = 6.3 Hz, 2H), 2.92 (t, $J$ = 6.8 Hz, 2H). These data are in agreement with that previously reported in the literature.
1,1,1-trifluoro-N-phenylmethanesulfonamide (S11). The reaction was performed according to general procedure A with aniline (460 µL, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 2.5% acetone/hexanes => 10% acetone/hexanes) to give 1.079 g (4.79 mmol) pure N-triflyl protected amine (S11) as a white solid in 96% yield.

$^{1}H$ NMR (500 MHz, CDCl$_3$) $\delta$ 7.40 (dd, $J$ = 8.4Hz, 6.9 Hz, 2H), 7.33 (m, 1H), 7.27 (m, 2H), 6.68 (br s, 1H). These data are in agreement with that previously reported in the literature.  

$N$-benzyl-1,1,1-trifluoromethanesulfonamide (S12). The reaction was performed according to general procedure A with distilled benzylamine (516 µL, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100mL silica gel, 2.5% acetone/hexanes => 10% acetone/hexanes) to give 1.103 g (4.61 mmol) pure N-triflyl protected amine (S12) as a white solid in 92% yield.

$^{1}H$ NMR (500 MHz, CDCl$_3$) $\delta$ 7.44-7.30 (m, 5H), 4.94 (br s, 1H), 4.46 (d, $J$ = 5.8 Hz, 2H). These data are in agreement with that previously reported in the literature.

1,1,1-trifluoro-N-(naphthalen-1-ylmethyl)methanesulfonamide (S13). The reaction was performed according to general procedure A with 1-naphthylmethylamine (733 µL, 786 mg, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100ml silica gel, 5% acetone/hexanes => 10% acetone/hexanes) to give 1.298 g (4.49 mmol) pure N-triflyl protected amine (S13) as a white solid in 90% yield.

$^{1}H$ NMR (500 MHz, Chloroform-d) $\delta$ 8.01 (dd, $J$ = 8.4, 1.0 Hz, 1H), 7.94-7.90 (m, 1H), 7.89 (dt, $J$ = 7.9, 1.1 Hz, 1H), 7.62 (ddd, $J$ = 8.4, 6.8, 1.4 Hz, 1H), 7.56 (ddd, $J$ = 8.1, 6.9, 1.2 Hz, 1H), 7.51-7.45 (m, 2H), 4.98 (t, $J$ = 5.3 Hz, 1H), 4.90 (d, $J$ = 5.1 Hz, 2H). $^{13}C$ NMR (125 MHz, CDCl$_3$) $\delta$ 134.1, 131.0, 130.3, 130.1, 129.3, 127.4, 127.4, 126.6, 125.5, 122.6, 119.9(q, $J$ = 321.4 Hz), 46.5. $^{19}F$ NMR (470 MHz, Chloroform-d) $\delta$ -76.84. HRMS (ESI) m/z calculated for C$_{12}$H$_{10}$NO$_{2}$SF$_{3}$Na [M+Na]$^+$: 312.0282, found 312.0293. 

1,1,1-trifluoro-N-methylmethanesulfonamide (S14). The reaction was performed according to general procedure B with methylamine hydrochloride (378 mg, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 5% acetone/hexanes) => give 698 mg (4.28 mmol) pure N-triflyl protected amine (S14) as a colorless oil in 86% yield.

$^{1}H$ NMR (500 MHz, Chloroform-d) $\delta$ 4.99 (s, 1H), 2.98 (q, $J$ = 1.2 Hz, 3H). $^{13}C$ NMR (125 MHz, Chloroform-d) $\delta$ 119.9 (q, $J$ = 321.2 Hz), 30.2. $^{19}F$ NMR (470 MHz, Chloroform-d) $\delta$ -76.90. HRMS (EI) m/z calculated for C$_2$H$_4$NO$_2$SF$_3$ [M]$^+$: 162.9915, found 162.9915.
**N-butyl-1,1,1-trifluoromethanesulfonamide (S15).** The reaction was performed according to general procedure A with butylamine (494 μL, 366 mg, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel using 2.5% acetone/hexanes => 5% acetone/hexanes as eluent) to give 864 mg (4.21 mmol) pure N-triflyl protected amine (S15) as a white solid in 84% yield.

**1H NMR** (500 MHz, Chloroform-d) δ 5.11 (br s, 1H), 3.35-3.16 (m, 2H), 1.57 (tt, J = 7.8, 6.5 Hz, 2H), 1.45-1.28 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). These data are in agreement with that previously reported in the literature.

**tert-Butyl (2-((trifluoromethyl)sulfonamido)ethyl)carbamate (S16).** The reaction was performed according to general procedure A with N-boc-ethylenediamine (792 μL, 801 mg, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 5% acetone/hexanes => 10% acetone/hexanes) to give 1.388 g (4.75 mmol) pure N-triflyl protected amine (S16) as a white solid in 95% yield.

**1H NMR** (500 MHz, Chloroform-d) δ 6.80 (br s, 1H), 5.05 (br s, 1H), 3.36 (t, J = 5.6 Hz, 2H), 3.31 (q, J = 5.8 Hz, 2H), 1.44 (s, 9H). **13C NMR** (125 MHz, CDCl3) δ 157.5, 120.0 (q, J = 321.3), 80.9, 45.3, 40.6, 28.4. **19F NMR** (470 MHz, Chloroform-d) δ -77.85. **HRMS** (EI) m/z calculated for C_{8}H_{16}N_{2}O_{4}SF_{3} [M+H]^+: 293.0783, found 293.0786.

**1,1,1-trifluoro-N-(2-methoxyethyl)methanesulfonamide (S17).** The reaction was performed according to general procedure A with 2-methoxyethylamine (435 μL, 376 mg, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 5% acetone/hexanes => 10% acetone/hexanes) to give 999 mg (4.82 mmol) pure N-triflyl protected amine (S17) as a white solid in 96% yield.

**1H NMR** (500 MHz, Chloroform-d) δ 5.35 (br s, 1H), 3.53 (m, 2H), 3.48-3.43 (m, 2H), 3.39 (s, 3H). **13C NMR** (125 MHz, Chloroform-d) δ 119.8 (q, J = 321.0 Hz), 71.0, 59.1, 44.1. **19F NMR** (470 MHz, Chloroform-d) δ -77.87. **HRMS** (EI) m/z calculated for C_{4}H_{8}NO_{3}SF_{3} [M+H]^+: 208.02553, found 208.02523.
**N-(2-bromoethyl)-1,1,1-trifluoromethanesulfonamide (S18).** An oven dried 100 mL round-bottom flask equipped with a stir was charged with 2-bromoethylamine hydrobromide (2.05 g, 10.0 mmol, 1.0 equiv), CH₂Cl₂ (20 mL, 0.5 M). The flask was cooled to -78 °C, and anhydrous K₂CO₃ (1.38 g, 10.0 mmol, 2.0 equiv) was added in one batch followed by slowly addition of trifluoromethanesulfonic anhydride (1.68 mL, 2.82 g, 10.0 mmol, 1.0 equiv). The reaction was stirred vigorously at -78 °C for 30 min. After warmed up to 0 °C, the reaction was quenched with 20 mL cold H₂O. The reaction mixture was partitioned between H₂O and CH₂Cl₂ and the layers were separated. The aqueous layer was then extracted with CH₂Cl₂ (20mL x 3). The organic layers were combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure.). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 2.5% acetone/hexanes => 5% acetone/hexanes) to give 1.213 g (4.74 mmol) pure N-triflyl protected amine (S18) as a colorless oil in 47% yield.

**1H NMR** (500 MHz, Chloroform-d) δ 5.52 (br s, 1H), 3.70 (q, J = 5.9 Hz, 2H), 3.51 (t, J = 5.8 Hz, 2H). **13C NMR** (125 MHz, Chloroform-d) δ 119.6 (q, J = 320.5 Hz), 45.7, 31.4. **19F NMR** (470 MHz, Chloroform-d) δ -77.90. **HRMS** (EI) m/z calculated for C₅H₆NO₂BrSF₃ [M+H]⁺:255.92546, found 255.92546.

![TfHN-CF₃](image)

**1,1,1-Trifluoro-N-(2,2,2-trifluoroethyl)methanesulfonamide (S19).** An oven dried round-bottom flask equipped with a stir bar was charged with 2,2,2-trifluoroethylamine hydrochloride (677.6 mg, 5.0 mmol, 1.0 equiv), CH₂Cl₂ (10 mL, 0.5M) and Et₃N (1.53 mL, 11mmol, 2.2 equiv). The flask was cooled to -78 °C, and Trifluoromethanesulfonic anhydride (840 µL, 1.41 g, 5.0 mmol, 1.0 equiv) was added dropwise. The reaction was stirred vigorously at -78 °C for 30 min and allowed to gradually warm up to r.t. The reaction mixture was concentrated under reduced pressure, the remaining mixture was dissolve in 20 mL 3 M NaOH, extracted with CH₂Cl₂ (20 mL x 3), the aqueous layer was neutralized with 3 M HCl, and extracted with 3 x 20 mL CH₂Cl₂. The combined organic layers were concentrated to afford 982 mg (4.25 mmol) pure N-triflyl protected amine (S19) as a colorless oil in 85% yield.

**1H NMR** (500 MHz, Chloroform-d) δ 5.27 (br s, 1H), 3.91-3.84 (m, 2H). **13C NMR** (125 MHz, Chloroform-d) δ 122.8 (q, J = 278.1 Hz), 122.0 (q, J = 320.1 Hz), 45.4 (q, J = 36.7 Hz). **19F NMR** (470 MHz, Chloroform-d) δ -73.50, -77.64. **HRMS** (ESI) m/z calculated for C₅H₆NO₂SF₆ [M-H]⁻: 229.9710, found 229.9705.

![TfHN-OMe](image)

**Methyl ((trifluoromethyl)sulfonyl)-L-alaninate (S20).** The reaction was performed according to general procedure B with L-alanine methyl ester hydrochloride (698 mg, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 5% acetone/hexanes => 10% acetone/hexanes) to give 1.069 g (4.55 mmol) pure N-triflyl protected amine (S20) as a white solid in 91% yield.

**1H NMR** (500 MHz, Chloroform-d) δ 5.53 (s, 1H), 4.32 (q, J = 7.2 Hz, 1H), 3.83 (s, 3H), 1.54 (d, J = 7.2 Hz, 3H). These data are in agreement with that previously reported in the literature.¹⁴
(+)-Methyl ((trifluoromethyl)sulfonyl)-L-phenylalaninate (S21). The reaction was performed according to general procedure B with L-phenylalanine methyl ester hydrochloride (1.08 g, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 5% acetone/hexanes => 10% acetone/hexanes) to give 1.442 g (4.63 mmol) pure N-triflyl protected amine (S21) as a white solid in 93% yield.

1H NMR (500 MHz, Chloroform-d) δ 7.39-7.28 (m, 3H), 7.16-7.10 (m, 2H), 5.33 (br s, 1H), 4.53 (dt, J = 9.3, 5.5 Hz, 1H), 3.79 (s, 3H), 3.24-3.10 (m, 2H).

13C NMR (125 MHz, Chloroform-d) δ 170.8, 134.3, 129.5, 128.8, 127.7, 119.5 (q, J = 320.7 Hz), 58.2, 53.0, 39.5. These data are in agreement with that previously reported in the literature.10 [α]23D = 28.4º (c = 1.01, CHCl3).

(-)-Methyl ((trifluoromethyl)sulfonyl)-D-phenylalaninate (S22). The reaction was performed under general procedure B with D-phenylalanine methyl ester hydrochloride (1.08 g, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 5% acetone/hexanes => 10% acetone/hexanes) to give 1.424 g (4.57 mmol) pure N-triflyl protected amine (S22) as a white solid in 91% yield.

1H NMR (500 MHz, Chloroform-d) δ 7.37-7.27 (m, 3H), 7.17-7.15 (m, 2H), 5.91 (br s, 1H), 4.51 (t, J = 6.0 Hz, 1H), 3.76 (s, 3H), 3.14 (d, J = 6.0 Hz, 2H).

13C NMR (126 MHz, CDCl3) δ 170.7, 134.2, 129.5, 128.9, 127.8, 119.5 (q, J = 320.8 Hz), 58.1, 53.1, 39.6. 19F NMR (470 MHz, Chloroform-d) δ -77.72. HRMS (ESI) m/z calculated for C11H13NO4FsS [M+H]+: 312.0517, found 312.0506. [α]23D = -28.3º (c = 1.00, CHCl3).

Methyl ((trifluoromethyl)sulfonyl)-L-isoleucinate (S23). The reaction was performed according to general procedure B with L-isoleucine methyl ester hydrochloride (909 mg, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 5% acetone/hexanes => 10% acetone/hexanes) to give 1.221 g (4.40 mmol) pure N-triflyl protected amine (S23) as a colorless oil in 88% yield.

1H NMR (500 MHz, Chloroform-d) δ 5.51 (br s, 1H), 4.13 (d, J = 4.7 Hz, 1H), 3.81 (s, 3H), 1.94 (dq, J = 9.3, 4.6, 2.4 Hz, 1H), 1.49-1.33 (m, 1H), 1.19 (dt, J = 13.7, 7.3, 2.0 Hz, 1H), 0.99 (d, J = 6.8 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H). These data are in agreement with that previously reported in the literature.14

1,1,1-Trifluoro-N-(4-fluorobenzyl)methanesulfonamide (S24). The reaction was performed under general procedure B with 4-fluorobenzylamine (568 µL, 626 mg, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 5%
acetone/hexanes —> 10% acetone/hexanes) to give 1.203 g (4.68 mmol) pure N-triflyl protected amine (S24) as a colorless oil in 93% yield.

1H NMR (500 MHz, Chloroform-d) δ 7.31 (dd, J = 8.7, 5.2 Hz, 2H), 7.11-7.04 (m, 2H), 5.11 (s, 1H), 4.42 (s, 2H). 13C NMR (125 MHz, Chloroform-d) δ 163.0 (d, J = 248.0 Hz), 131.1 (d, J = 3.3 Hz), 129.9 (d, J = 8.4 Hz), 119.8 (q, J = 321.0 Hz), 116.2 (d, J = 21.8 Hz), 47.7. 19F NMR (470 MHz, Chloroform-d) δ -77.61, -113.30. HRMS (ESI) m/z calculated for C₈H₇NO₂NaSF₄ [M+Na]+: 280.0031, found 280.0026.

N-(3,4-dimethoxybenzyl)-1,1,1-trifluoromethanesulfonamide (S25). The reaction was performed according to general procedure A with 3,4-Dimethoxyphenyl)methanamine (745 µL, 836 mg, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 5% acetone/hexanes -> 20% acetone/hexanes) to give 1.373 g (4.59 mmol) pure N-triflyl protected amine (S25) as a white solid in 92% yield.

1H NMR (500 MHz, Chloroform-d) δ 6.80 (dd, J = 8.2, 2.0 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 6.72 (d, J = 2.0 Hz, 1H), 5.71 (br d, J = 5.2 Hz, 1H), 4.32 (d, J = 4.3 Hz, 2H), 3.80 (s, 3H), 3.77 (s, 3H). 13C NMR (125 MHz, CDCl₃) δ 149.1, 149.0, 128.0, 120.6, 119.9 (q, J = 321.2 Hz) 111.5, 111.1, 56.0, 55.8, 48.1. 19F NMR (470 MHz, CDCl₃) δ -77.22. HRMS (ESI) m/z calculated for C₁₀H₁₂NO₄F₃SNa [M+Na]+: 322.0337, found 322.0349.

N-(4-(dimethylamino)benzyl)-1,1,1-trifluoromethanesulfonamide (S26). The reaction was performed according to general procedure A with 4-(aminomethyl)-N,N-dimethylaniline (745 µL, 836 mg, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 5% acetone/hexanes -> 20% acetone/hexanes) to give 1.158 g (4.10 mmol) pure N-triflyl protected amine (S26) as a white solid in 82% yield.

1H NMR (500 MHz, Chloroform-d) δ 7.15 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 8.8 Hz, 2H), 5.13 (br s, 1H), 4.32 (s, 2H), 2.95 (s, 6H). 13C NMR (125 MHz, CDCl₃) δ 150.8, 129.3, 122.7, 119.9 (q, J = 321.3 Hz), 113.0, 48.3, 40.7. 19F NMR (470 MHz, CDCl₃) δ -77.15. HRMS (ESI) m/z calculated for C₁₀H₁₄N₂O₂F₃S [M+H]+: 283.0728, found 283.0739.

(-)-(S)-1,1,1-trifluoro-N-(1-(4-nitrophenyl)ethyl)methanesulfonamide (-)-S27. The reaction was performed according to general procedure A with (S)-α-methyl-4-nitrobenzylamine hydrochloride (1.01 g, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 5% acetone/hexanes -> 20% acetone/hexanes) to give 1.425 g (4.78 mmol) pure N-triflyl protected amine (-)-S27 as a light yellow solid in 95% yield.

1H NMR (500 MHz, Chloroform-d) δ 8.24 (d, J = 8.7 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 5.55 (d, J = 8.5 Hz, 1H), 4.90 (app p, J = 7.2 Hz, 1H), 1.66 (d, J = 7.0 Hz, 3H). 13C NMR (125 MHz,
Chloroform-d) δ 148.7, 147.6, 127.0, 124.4, 119.5 (q, J = 320.8 Hz), 54.7, 23.4. **19F NMR** (470 MHz, Chloroform-d) δ -78.0. **HRMS (ESI)** m/z calculated for C₉H₈N₂O₄F₃S [M-H]+: 297.0157, found 297.0151. [α]²²D = -54.7° (c = 1.00, CHCl₃).

(+)-N-triflyl protected dihydroabietylamine (+)-S28. (-)-(N-nitroisooindolyl)dihydroabietylamine¹⁵ (1.15g, 2.5 mmol) was dissolved in hot ethanol (20 mL 0.125 M), treated with hydrazine monohydrate (0.72 mL, 15 mmol) and heated at reflux for 3 hours. Then, without cooling a white solid was filtered off and washed with fresh ethanol to give the crude dihydroabietylamine. Triflyl protection was performed directly on the crude dihydroabietylamine under general procedure A. The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 5% acetone/hexanes => 10% acetone/hexanes) to give 868 mg (2.08 mmol) pure N-triflyl protected amine (+)-S28 as a white solid in 83% yield over two steps.

**1H NMR** (500 MHz, Chloroform-d) δ 7.27 (d, J = 8.6 Hz, 1H), 7.10 (dd, J = 8.2, 2.0 Hz, 1H), 7.00 (d, J = 2.0 Hz, 1H), 5.32 (br s, 1H), 3.25 (d, J = 13.2 Hz, 1H), 3.17 (d, J = 13.2 Hz, 1H), 3.04-2.95 (m, 2H), 2.93 (hept, J = 6.9 Hz, 1H), 2.44-2.38 (m, 1H), 1.89-1.75 (m, 4H), 1.61-1.43 (m, 3H), 1.37 (dd, J = 13.2, 4.6 Hz, 1H), 1.33 (d, J = 7.0 Hz, 6H), 1.33 (s, 3H), 1.06 (s, 3H). **13C NMR** (125 MHz, CDCl3) δ 146.8, 145.9, 134.5, 127.0, 124.2, 124.0, 119.9 (q, J = 321.7 Hz), 55.1, 45.2, 38.2, 37.5, 37.1, 35.7, 33.6, 29.9, 25.3, 24.1, 24.0, 18.9, 18.4, 18.1. **19F NMR** (470 MHz, Chloroform-d) δ -77.17. **HRMS (ESI)** m/z calculated for C₂₁H₃₀NO₂F₃SNa [M+Na]+: 440.1847, found 440.1846. [α]²³D = +25.3° (c = 0.50, CHCl₃).

Methyl-(S)-2-(((trifluoromethyl)sulfonamido)-3-(4-(((trifluoromethyl)sulfonyl) oxy) phenyl) propanoate (S29). The reaction was performed according to reported procedure¹⁶ with L-tyrosine methyl ester hydrochloride (1.16 g, 5 mmol) affording 1.035 g (2.25 mmol) pure N-triflyl protected amine (S29) as a white solid in 45% yield.

**1H NMR** (500 MHz, Chloroform-d) δ 7.33-7.18 (m, 4H), 5.39 (br s, 1H), 4.51 (t, J = 5.9 Hz, 1H), 3.79 (d, J = 1.0 Hz, 3H), 3.25-3.12 (m, 2H). These data are in agreement with that previously reported in the literature.¹⁶
1,1,1-trifluoro-N-((1-methyl-1H-indol-3-yl) methyl) methanesulfonamide (S30). The reaction was performed according to general procedure A with 3-(aminomethyl)-1-methylindole (730 mL, 801 mg, 5.0 mmol). The reaction mixture was purified by flash column chromatography on silica (100 mL silica gel, 20% CH₂Cl₂/hexanes => 50% CH₂Cl₂/hexanes) to give 1.180 g (4.04 mmol) pure N-triflyl protected amine (S30) as a white solid in 81% yield.

¹H NMR (500 MHz, Chloroform-d) δ 7.67 (d, J = 7.9 Hz, 1H), 7.39-7.29 (m, 2H), 7.22 (ddd, J = 8.0, 6.7, 1.2 Hz, 1H), 7.07 (s, 1H), 5.03 (br s, 1H), 4.60 (s, 2H), 3.77 (s, 3H).

¹³C NMR (125 MHz, Chloroform-d) δ 137.2, 128.7, 126.5, 122.5, 120.0, 119.9 (q, J = 321.3 Hz), 118.5, 109.8, 108.3, 40.0, 32.8. ¹⁹F NMR (470 MHz, Chloroform-d) δ -77.50. HRMS (ESI) m/z calculated for C₁₁H₁₂N₂O₂F₃S [M+H]⁺: 293.0572, found 293.0563.
Preparation of Olefins

*N, N-diethylbut-3-enamide* (S31). An oven-dried round-bottom flask was charged with a stir bar and vinyl acetic acid (426 µL, 5 mmol, 1.0 equiv). Oxalyl chloride (465 µL, 5.5 mmol, 1.1 equiv) was added dropwise to the reaction mixture at 0 °C and the reaction was warmed up to room temperature and stirred for 3 hours. The acid chloride was carried through to the next step without purification. To a solution of Et₃N (730 µL, 5.25 mmol, 1.05 equiv) and Et₂NH (517 µL, 5 mmol) in CH₂Cl₂ (25 mL, 0.2 M) at 0 °C was slowly added the acid chloride (1.0 equiv) and the reaction was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of sat. aq. NH₄Cl, extracted with CH₂Cl₂, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (100 mL silica gel, 10% ethyl acetate/hexanes => 20% ethyl acetate/hexanes) to give 593 mg (4.20 mmol) product in 84% yield as a colorless oil.

1H NMR (500 MHz, Chloroform-d) δ 5.98 (ddt, J = 16.9, 10.2, 6.5, 1H), 5.22-5.01 (m, 2H), 3.37 (q, J = 7.1, 2H), 3.30 (q, J = 7.2, 2H), 3.11 (m, 2H), 1.17 (td, J = 7.2, 1.1 Hz, 3H), 1.11 (td, J = 7.2, 1.2 Hz, 3H).

13C NMR (125 MHz, CDCl₃) δ 170.1, 132.3, 117.4, 42.2, 40.2, 38.7, 14.5, 13.2.

HRMS (ESI) m/z calculated for C₈H₁₆NO [M+H]⁺: 142.1232, found 142.1230.

Dec-9-en-5-one (S32). An oven-dried round-bottom flask was charged with a stir bar, N-methoxy-N-methylhex-5-enamide (786 mg, 5 mmol) and THF (20 mL, 0.25 M). The reaction mixture was cooled to -78 °C and n-BuLi (1.6 M in hexanes, 3.75 mL, 6.0 mmol, 1.2 equiv) was added dropwise. The reaction was stirred for 30 min and quenched with sat. aq. NH₄Cl. Layers were separated, aqueous layer was extracted with Et₂O, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (100 mL silica gel, 5% ethyl acetate/hexanes => 10% ethyl acetate/hexanes) to give 625 mg (4.05 mmol) product in 81% yield as a colorless oil.

1H NMR (500 MHz, Chloroform-d) δ 5.76 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.05-4.94 (m, 2H), 2.39 (q, J = 7.5 Hz, 4H), 2.10-2.02 (m, 2H), 1.67 (p, J = 7.3 Hz, 2H), 1.60-1.49 (m, 2H), 1.36-1.22 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H).

13C NMR (125 MHz, CDCl₃) δ 211.4, 138.2, 115.3, 42.4, 42.0, 33.3, 26.1, 23.0, 22.5, 14.0.

HRMS (EI) m/z calculated for C₁₀H₁₇O [M-H]⁻: 153.1276, found 153.12766.

Dec-9-en-5-one (S32)
(±)-(E)-tert-butylidimethyl(nona-1,7-dien-4-yloxy)silane (S35).

An oven-dried round-bottom flask was charged with a stir bar, Weinreb amide ((4E)-N-methoxy-N-methyl-4-hexenamide)\textsuperscript{18} (786 mg, 5 mmol, 1.0 equiv) and THF (20 mL, 0.25 M). The reaction mixture was cooled to -10 °C and allylmagnesium bromide (1.0 M in Et₂O, 6.5 mL, 6.5 mmol, 1.3 equiv) was added dropwise. The reaction was stirred for 30 min at -10 °C and poured onto a mixture of crushed ice (40 mL), sat. aq. NH₄Cl (70 mL) and 1M HCl (15 mL). Layers were separated, aqueous layer was extracted with Et₂O, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (5% ethyl acetate/hexanes => 10% ethyl acetate/hexanes) to give 622 mg (4.05 mmol) product (S33) in 90% yield as a colorless oil.

An oven-dried round-bottom flask was charged with a stir bar, ketone (S33) (622 mg, 4.05 mmol, 1.0 equiv) and MeOH (8.0 mL, 0.5 M). The reaction was cooled to 0 °C and NaBH₄ (613 mg, 16.2 mmol, 4.0 equiv) was added in one portion. The reaction was allowed to warm up to room temperature and stirred overnight. The reaction was quenched with water. The resulting layers were separated and the aqueous layer was extracted by ethyl acetate (20 mL x 3). The crude mixture was purified by flash column chromatography (10% ethyl acetate/hexanes => 20% ethyl acetate/hexanes) to give 495 mg (3.52 mmol) product (S34) in 87% yield as a colorless oil.

To an oven-dried round-bottom flask with a stir bar was added alcohol (S34) (495 mg, 3.52 mmol, 1.0 equiv), CH₂Cl₂ (18 mL, 0.2 M), TBSCI (583 mg, 5.87 mmol, 1.1 equiv) and imidazole (359 mg, 5.28 mmol, 1.5 equiv). The reaction mixture was cooled to 0 °C and DMAP (43 mg, 0.1 equiv) was added in one portion. The reaction was allowed to warm up to room temperature and stirred overnight. The reaction was quenched with water. The resulting layers were separated and the aqueous layer was extracted by CH₂Cl₂ (20 mL x 3). Organic layers were combined, dried with anhydrous MgSO₄ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (5% ethyl acetate/hexanes => 10% ethyl acetate/hexanes) to give 769 mg (3.02 mmol) product (S35) in 86% yield as a colorless oil.

\textsuperscript{1}H NMR (500 MHz, Chloroform-d) \(\delta\) 5.81 (ddt, \(J = 16.8, 10.4, 7.2\) Hz, 1H), 5.42 (m, 2H), 5.08-4.97 (m, 2H), 3.70 (p, \(J = 5.8\) Hz, 1H), 2.21 (dddt, \(J = 6.8, 5.3, 4.0, 1.3\) Hz, 2H), 2.11-1.92 (m, 2H), 1.64 (dd, \(J = 3.5, 1.3\) Hz, 3H), 1.54-1.42 (m, 2H), 0.89 (s, 9H), 0.05 (d, \(J = 0.9\) Hz, 6H). \textsuperscript{13}C NMR (125 MHz, CDCl₃) \(\delta\) 135.5, 131.4, 124.9, 116.8, 71.7, 42.1, 36.9, 28.7, 26.1, 18.3, 18.1, -4.2, -4.4. HRMS (EI) \(m/z\) calculated for C₁₅H₂₉OSi [M-H]\(^+\): 253.1988, found 253.1982.

\[\text{5-(pent-4-en-1-yl)-5H-dibenz[b,f]azepine (S36).} \]

To an oven-dried round-bottom flask with a stir bar was added 5H-dibenz[b,f]azepine (193 mg, 1.0 mmol), 1,2-dichloroethane (5 mL, 0.2M), acetic acid (172 µL, 3.0 mmol, 3.0 equiv) and 4-pentenal (197 µL, 2.0 mmol, 2.0 equiv). The reaction was stirred under room temperature for 30 min. Then NaBH(OAc)₃ (423 mg, 2.0 mmol, 2.0 equiv) was added, the reaction was stirred for 2 hours. Upon completion, the reaction mixture was poured into a separatory funnel with sat. aq. NaHCO₃. Layers were separated, and aqueous layers was extracted with ethyl acetate (10 mL x 3). The crude mixture was purified by flash column chromatography (pure pentane) to give 238 mg (0.91 mmol) product (S36) in 91% yield as a bright yellow oil.
**1H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\) 7.25 (ddd, \(J = 8.1, 7.2, 1.7\) Hz, 2H), 7.06 (dd, \(J = 7.6, 1.7\) Hz, 2H), 7.01 (dd, \(J = 7.4, 1.2\) Hz, 2H), 6.73 (s, 2H), 6.76 (ddt, \(J = 17.0, 10.2, 6.7\) Hz, 1H), 5.03-4.83 (m, 2H), 3.72 (t, \(J = 6.9\) Hz, 2H), 2.19-2.09 (m, 2H), 1.72-1.57 (m, 2H).

**13C NMR** (125 MHz, Chloroform-\(d\)) \(\delta\) 151.2, 138.5, 134.1, 132.3, 129.3, 128.9, 123.3, 120.6, 115.0, 49.9, 31.1, 26.9.

**HRMS (ESI)** \(m/z\) calculated for C\(_{19}\)H\(_{20}\)N [M+H]\(^{+}\): 262.1596, found 262.1594.

2-(4-allylphenyl)-1,3,4-oxadiazole (S37).

To an oven-dried round-bottom-flask equipped with a condenser was added a stir bar, LiCl (1.06 g, 25 mmol, 5.0 equiv), THF (50 mL, 0.1 M), allyltributylstannane (1.7 mL, 5.5 mmol, 1.1 equiv), 2-(4-bromo phenyl)-1,3,4-oxadiazole (1.13 g, 5.0 mmol, 1.0 equiv) and Pd\((\text{PPh}_3)_4\) (578 mg, 0.50 mmol, 0.1 equiv). The reaction was heated to reflux and stirred overnight. Upon completion, the reaction was cooled to room temperature, transferred into a separatory funnel with ice cold 10% NH\(_4\)OH solution (50 mL, diluted from 30% NH\(_4\)OH solution) and shaken vigorously. Layers were separated, aqueous layer was extracted with ethyl acetate (30 mL x 3). Organic layers were combined and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (acetone/hexanes) to give 884 mg (4.75 mmol) product (S37) in 95% yield as a white solid.

**1H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\) 8.45 (s, 1H), 8.11 (d, \(J = 8.0\) Hz, 2H), 7.34 (d, \(J = 8.0\) Hz, 2H), 6.05-5.85 (m, 1H), 5.17-5.05 (m, 2H), 3.46 (dd, \(J = 6.7, 1.6\) Hz, 2H).

**13C NMR** (125 MHz, CDCl\(_3\)) \(\delta\) 164.6, 152.5, 144.4, 136.2, 129.3, 127.1, 121.3, 116.7, 40.0. **HRMS (ESI)** \(m/z\) calculated for C\(_{11}\)H\(_{11}\)N\(_2\)O [M+H]\(^{+}\): 187.0871, found 187.0871.

**General Procedure to form olefin substrates from phenolic compounds**

To an oven-dried round-bottom flask with a stir bar was added phenol starting material (5.0 mmol, 1.0 equiv), CH\(_2\)Cl\(_2\) (25 mL, 0.2 M), Et\(_3\)N (1.39 mL, 10 mmol, 2.0 equiv). The reaction was cooled to 0 °C. Trifluoromethanesulfonic anhydride (Tf\(_2\)O, 1.0 mL, 6.0 mmol, 1.2 equiv) was added dropwise and the reaction was stirred at 0 °C for 30 min. After warming up to room temperature, the reaction was quenched with addition of cold water. The layers were separated, and the aqueous layer was extracted with ethyl acetate (30 mL x 3). The organic layers were combined and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (acetone/hexanes) to give 884 mg (4.75 mmol) product (S37) in 95% yield as a white solid.

To an oven-dried round bottom flask equipped with condenser was added a stir bar, LiCl (4.0 equiv), DMF (0.25 M), allyltributylstannane (1.1 equiv), phenol triflate (1.0 equiv) and Pd\((\text{PPh}_3)_4\) (0.03 equiv). The reaction was heated to 100 °C and stirred for 12 hours. Upon completion, the reaction was cooled to room temperature, transferred into a separatory funnel with iced 10% NH\(_4\)OH solution (1:1 to DMF) and shake vigorously. Layers were separated, aqueous layer was
extracted with ethyl acetate (30 mL x 3). The organic layers were combined and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to give allylated olefin product.

**6-allyl-2H-chromen-2-one (S38)** was synthesized according to the general procedure from 6-hydroxycoumarin (811 mg, 5.0 mmol) in 60% yield (550.2 mg, 3.0 mmol) over two steps as a white solid.

**1H NMR** (500 MHz, Chloroform-d) δ 7.67 (d, J = 9.6 Hz, 1H), 7.35 (dd, J = 8.4, 2.1 Hz, 1H), 7.28 (d, J = 2.1 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 9.5 Hz, 1H), 5.95 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H), 5.20-4.98 (m, 2H), 3.43 (dt, J = 6.6, 1.5 Hz, 2H).

**13C NMR** (126 MHz, CDCl3) δ 161.1, 152.7, 143.5, 136.7, 136.5, 132.5, 127.5, 118.9, 117.0, 116.8, 39.4. HRMS (ESI) m/z calculated for C12H11O2 [M+H]+: 187.0759, found 187.0764.

**(+)-Allylated-δ-Tocopherol derivative (S39)** was synthesized according to the general procedure from (+)-δ-Tocopherol (2.01 g, 5.0 mmol) in 75% yield (1.602 g, 3.7 mmol) over two steps as a colorless oil.

**1H NMR** (500 MHz, Chloroform-d) δ 6.80 (d, J = 2.2 Hz, 1H), 6.73 (d, J = 2.1 Hz, 1H), 5.97 (ddt, J = 16.8, 10.0, 6.8 Hz, 1H), 5.13-4.95 (m, 2H), 3.28 (d, J = 6.8 Hz, 2H), 2.80-2.61 (m, 2H), 2.16 (s, 3H), 1.86-1.71 (m, 2H), 1.64-1.03 (m, 24H), 0.91-0.84 (m, 12H). **13C NMR** (125 MHz, CDCl3) δ 150.5, 138.5, 130.2, 128.6, 126.8, 126.3, 120.4, 115.2, 75.96, 40.3, 39.7, 39.5, 37.6, 37.4, 33.0, 32.9, 31.4, 28.1, 25.0, 24.6, 24.4, 22.9, 22.8, 22.5, 21.1, 19.9, 19.8, 16.2. HRMS (ESI) m/z calculated for C30H50O [M]+: 426.3862, found 426.3851. [α]22D = +5.6 o (c = 1.05, CHCl3)

**(-)-Allylated ethinyl estradiol derivative (S41).**

**Allylated estrone (S40)** was synthesized according to general procedure to form olefin substrates from phenolic compounds from estrone (1.35 g, 5.0 mmol, 1.0 equiv) in 73% yield (1.07 g, 3.64 mmol) over 2 steps as a light yellow solid.
Following the procedure of Dierra and coworkers, \textsuperscript{19} t-BuLi (8.8 mL, 1.7 M in pentane, 5.0 equiv) was carefully added dropwise to a solution of ethynyltrimethylsilane (2.22 mL, 15.0 mmol, 5.0 equiv) in THF (60 mL) at -78 °C. After stirring at this temperature for 30 min the reaction was warmed up to 0 °C and then a solution of allylated estrone (883 mg, 3.0 mmol, 1.0 equiv) was added. The reaction was allowed to reach room temperature and stirred for 2 hours. Upon completion (monitored by TLC). The reaction mixture was cooled to 0 °C and quenched by sat. aq. NH\textsubscript{4}Cl. The layers were separated, and the aqueous layer was extracted with ethyl acetate (30 mL x 3). The combined organic layers were washed with brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (0 => 5% ethyl acetate/hexanes, 100 mL silica gel) to give allylated ethinyl estradiol derivative (S41) in 93% yield (1.104 g, 2.81 mmol) as a colorless gel.

\textsuperscript{1}H NMR (500 MHz, Chloroform-d) \(\delta\) 7.26 (d, \(J = 8.1\) Hz, 1H), 6.99 (d, \(J = 8.1\) Hz, 1H), 6.92 (s, 1H), 5.96 (ddt, \(J = 16.8, 10.1, 6.8\) Hz, 1H), 5.15-5.00 (m, 2H), 3.34 (d, \(J = 6.8\) Hz, 2H), 2.86 (dd, \(J = 7.7, 3.1\) Hz, 2H), 2.40 (dq, \(J = 13.1, 4.0\) Hz, 1H), 2.31 (ddd, \(J = 13.5, 9.6, 5.6\) Hz, 1H), 2.27-2.19 (m, 1H), 2.00 (ddd, \(J = 13.6, 11.9, 3.9\) Hz, 1H), 1.94-1.75 (m, 4H), 1.74-1.66 (m, 2H), 1.55-1.34 (m, 4H), 0.87 (s, 3H), 0.18 (s, 9H).

\textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 138.0, 137.7, 137.3, 136.8, 129.2, 126.0, 125.6, 115.7, 109.7, 90.1, 80.2, 49.8, 47.3, 44.2, 39.9, 39.4, 39.0, 33.0, 27.4, 26.4, 23.0, 12.9, 0.2. HRMS (EI) \(m/z\) calculated for C\textsubscript{26}H\textsubscript{36}OSi [M\textsuperscript{+}]: 392.2536, found 392.2533.

\(\alpha\)\textsubscript{D} = -9.0 ° (c = 0.51, CHCl\textsubscript{3})

(+)-Allylated dextromethorphan derivative (S42) was synthesized from 3-(OTf) dextromethorphan\textsuperscript{20} (1.95g, 5.0 mmol, 1.0 equiv) under the allylation condition from general procedure. The crude mixture was purified by flash column chromatography (5% => 20%, 100 mL Act II basic Al\textsubscript{2}O\textsubscript{3}) to give allylated olefin product (S42) in 88% yield (1.239 g, 4.40 mmol) as a colorless gel.

\textsuperscript{1}H NMR (500 MHz, Chloroform-d) \(\delta\) 7.05 (s, 1H), 7.03 (d, \(J = 7.8\) Hz, 1H), 6.93 (dd, \(J = 7.7, 1.8\) Hz, 1H), 5.97 (ddt, \(J = 16.8, 10.1, 6.7\) Hz, 1H), 5.12-5.00 (m, 2H), 3.35 (d, \(J = 6.7\) Hz, 2H), 3.00 (d, \(J = 18.4\) Hz, 1H), 2.81 (dd, \(J = 5.8, 3.1\) Hz, 1H), 2.61 (dd, \(J = 18.4, 5.8\) Hz, 1H), 2.46-2.37 (m, 2H), 2.40 (s, 3H) 2.07 (td, \(J = 12.3, 3.3\) Hz, 1H), 1.83 (dt, \(J = 12.8, 3.2\) Hz, 1H), 1.74 (td, \(J = 12.6, 4.8\) Hz, 1H), 1.67-1.61 (m, 1H), 1.54-1.48 (m, 1H), 1.44-1.22 (m, 5H), 1.18-1.08 (m, 1H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 140.5, 138.0, 137.8, 135.5, 127.8, 125.7, 125.6, 115.6, 58.1, 47.4, 45.7, 42.9, 42.3, 40.3, 37.2, 36.7, 26.9, 26.8, 24.0, 22.3. HRMS (EI) \(m/z\) calculated for C\textsubscript{20}H\textsubscript{28}N [M+H\textsuperscript{+}]: 282.2222, found 282.2213. \(\alpha\)\textsubscript{D} = +59.5 ° (c = 0.51, CHCl\textsubscript{3})
**Reaction development of Pd-Sulfoxide catalyzed allylic C—H Amination**

**Table S1. Reaction development**

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<th>% Yield</th>
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**Bis-sulfoxide:**

**SOX ligands:**

| L-1: R₁ = H, R₂ = H, R₃ = Me, R₄ = Me | L-2: R₁ = H, R₂ = H, R₃ = Ph, R₄ = Me |
| L-3: R₁ = H, R₂ = CF₃, R₃ = Me, R₄ = Me | L-4: R₁ = H, R₂ = OMe, R₃ = Me, R₄ = Me |
| L-5: R₁ = OMe, R₂ = H, R₃ = Me, R₄ = OMe | L-6: R₁ = H, R₂ = OMe, R₃ = Me, R₄ = OMe |
| L-7: R₁ = OMe, R₂ = OMe, R₃ = Me, R₄ = Me | L-8: R₁ = OMe, R₂ = H, R₃ = Me, R₄ = OMe |

Isolated yields are average of two runs. * Conditions: 0.2 mmol (1.0 equiv.) olefin, 0.2 mmol amine nucleophile, 10 mol% Pd(OAc)₂/bis-sulfoxide, 2.0 equiv. BQ, 6% Cr(salen)Cl or 6% DIPEA, 0.66M TBME, 45°C, 72h. † 96% recovered amine nucleophile. ‡ 55°C.

**Entry 1**

Reaction proceeded according to reported procedure using Pd(OAc)₂/bissulfoxide (10 mg, 0.02 mmol, 0.1 equiv), Cr(salen)Cl (7.6 mg, 0.012 mmol, 0.06 equiv), 1,4 benzoquinone (43.2 mg, 0.4 mmol, 2.0 equiv), allylcyclohexane (30.9 mg, 0.2 mmol, 1.0 equiv), N-(2-Phenylethyl)trifluoromethanesulfonamide (50.6 mg, 0.2 mmol, 1.0 equiv) and 0.3 mL TBME (0.66 M). The mixture was concentrated under reduced pressure, the remaining mixture was diluted with 2 mL CDCl₃ and crude ¹H NMR was taken with internal standard (trifluorotoluene 14.6 mg, 0.1 mmol, 0.5 equiv). Trace amount of product was observed by crude ¹H NMR. The mixture was concentrated under reduced pressure and subjected to flash column chromatography (0% => 10% acetone in hexanes). No product was isolated by flash column chromatography.

Reaction proceeded according to reported procedure using Pd(OAc)₂/bissulfoxide (10 mg, 0.02 mmol, 0.1 equiv), DIPEA (2.1 µL, 0.012 mmol, 0.06 equiv), BQ, (1,4 benzoquinone) (43.2 mg,
0.4 mmol, 2.0 equiv), allylcyclohexane (30.9 mg, 0.2 mmol, 1.0 equiv), N-(2-
Phenylethyl)trifluoromethanesulfonamide (50.6 mg, 0.2 mmol, 1.0 equiv) and 0.3 mL TBME
(0.66 M). Trace amount of product was observed by crude $^1$H NMR. No product was isolated by
flash column chromatography.

Entry 2
To a ½ dram vial was added a stir bar, Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), ligand 1 (6.3 mg,
0.02 mmol, 0.1 equiv), 2,6 DMBQ (2,6-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv),
allylcyclohexane (30.9 mg, 0.2 mmol, 1.0 equiv) and N-(2-
Phenylethyl)trifluoromethanesulfonamide (50.6 mg, 0.2 mmol, 1.0 equiv). Toluene (0.2 mL, 1.0
M) was added and the vial was capped and heated to 45 °C for 72 hours. The vial was allowed to
cool to room temperature and diluted with 1 mL acetone. The reaction mixture was filtered through
a pipette silica plug into a 20mL vial with acetone. The mixture was concentrated under reduced
pressure, diluted with 2 mL CDCl$_3$ and analyzed by crude $^1$H NMR with internal standard
(trifluorotoluene 14.6 mg, 0.1 mmol, 0.5 equiv). The mixture was then concentrated under reduced
pressure and subjected to flash column chromatography (0% => 10% acetone in hexanes) to
provide allylic amine product 1 as a clear oil. Run 1 (22.1 mg, 29.4% yield); Run 2 (22.9 mg, 30.5%
yield); Average: 30% yield.

Entry 3
The same conditions used in Entry 3 were used except using BQ (benzoquinone) (23.8 mg, 0.22
mmol, 1.1 equiv). Run 1 (17.9 mg, 23.8% yield); Run 2 (18.2 mg, 24.2% yield); Average: 24%
yield.

Entry 4
**General procedure:** The following procedure was used with no effort to exclude air or moisture.
To a ½ dram vial was added a stir bar, Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-SOX-Ligand
1(L1) (6.3 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol,
1.1 equiv), allylcyclohexane (30.9 mg, 0.2 mmol, 1.0 equiv) and N-(2-
Phenylethyl)trifluoromethanesulfonamide (50.6 mg, 0.2 mmol, 1.0 equiv). Toluene (0.2 mL, 1.0
M) was added and the vial was capped and heated to 45 °C for 72 hours. The vial was allowed to
cool to room temperature and diluted with 1 mL acetone. The reaction mixture was filtered through
a pipette silica plug into a 20mL vial with acetone. The mixture was concentrated under reduced
pressure, diluted with 2 mL CDCl$_3$ and analyzed by crude $^1$H NMR with internal standard
(trifluorotoluene 14.6 mg, 0.1 mmol, 0.5 equiv). The mixture was then concentrated under reduced
pressure and subjected to flash column chromatography (0% => 20% CH$_2$Cl$_2$ in hexanes) to
provide allylic amine 1 as a clear oil. Run 1 (38.8 mg, 51.7% yield); Run 2 (39.4 mg, 52.5% yield);
Average: 52% yield.

Entry 5
The general procedure was followed using (±)-SOX-Ligand 2 (L2) (8.7 mg, 0.02 mmol, 0.1 equiv).
Run 1 (15.7 mg, 20.9% yield); Run 2 (16.0 mg, 21.3% yield); Average: 21% yield.

Entry 6
The general procedure was followed using (±)-SOX-Ligand 3 (L3) (7.6 mg, 0.02 mmol, 0.1 equiv).
Run 1 (23.8 mg, 31.7% yield); Run 2 (23.7 mg, 31.6% yield); Average: 32% yield.
Entry 7
The general procedure was followed using (±)-SOX-Ligand 4 (L4) (6.9 mg, 0.02 mmol, 0.1 equiv). Run 1 (41.3 mg, 54.9% yield); Run 2 (41.8 mg, 55.7% yield); Average: **55% yield**.

Entry 8
The general procedure was followed using (±)-MeO-SOX Ligand (L5) (6.9 mg, 0.02 mmol, 0.1 equiv). Run 1 (56.9 mg, 75.8% yield); Run 2 (56.1 mg, 74.7% yield); Run 3 (56.6 mg, 75.3% yield); Average: **75% yield**.

Entry 9
The general procedure was followed using (±)-SOX-Ligand 6 (L6) (6.6 mg, 0.02 mmol, 0.1 equiv). Run 1 (46.6 mg, 62.1% yield); Run 2 (47.2 mg, 62.9% yield); Average: **63% yield**.

 Entry 10
The general procedure was followed using (±)-SOX-Ligand 7 (L7) (7.4 mg, 0.02 mmol, 0.1 equiv). Run 1 (41.7 mg, 55.5% yield); Run 2 (41.2 mg, 54.8% yield); Average: **55% yield**.

Entry 11
The general procedure was followed using (±)-SOX-Ligand 8 (L8) (7.2 mg, 0.02 mmol, 0.1 equiv). Run 1 (55.2 mg, 73.5% yield); Run 2 (55.4 mg, 73.7% yield); Average: **74% yield**.

Entry 12
The reaction proceeded under general procedure using Pd(OAc)$_2$ (2.2 mg, 0.01 mmol, 0.05 equiv) (±)-MeO-SOX Ligand (L5) (3.4 mg, 0.01 mmol, 0.05 equiv). Run 1(39.9 mg, 53.1% yield); Run 2 (40.1 mg, 53.4% yield); Average: **53% yield**.

Entry 13
The general procedure was followed without any ligand. No product was detected by crude $^1$H NMR. No product or allylcyclohexene (volatile under reduced pressure) could be isolated by flash column chromatography, but 96% N-triflyl protected phenylethylamine was recovered.

Entry 14
The general procedure was followed and the reaction was stopped at 48 h. Run 1 (54.6 mg, 72.7% yield); Run 2 (55.1 mg, 73.4% yield); Average: **73% yield**.

Entry 15
The general procedure was followed and the reaction was stopped at 24 h. Run 1 (40.7 mg, 54.2% yield); Run 2 (40.1 mg, 53.4% yield); Average: **54% yield**.

Entry 16
The general procedure was followed. The reaction was run at 55 and was stopped at 24 h. Run 1 (49.4 mg, 65.8% yield); Run 2 (48.8 mg, 65.0% yield); Average: **65% yield**.
(E)-N-(3-cyclohexylallyl)-1,1,1-trifluoro-N-phenethylmethanesulfonamide (I).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.35 (dd, \(J = 8.1, 6.7\) Hz, 2H), 7.30-7.25 (m, 1H), 7.22-7.18 (m, 2H), 5.69 (dd, \(J = 15.4, 6.8\) Hz, 1H), 5.37 (dt, \(J = 15.4, 7.0\) Hz, 1H), 3.92 (d, \(J = 7.0\) Hz, 2H), 3.55 (br s, 2H), 2.94 (t, \(J = 8.0\) Hz, 2H), 2.09-2.00 (m, 1H), 1.77 (m, 4H), 1.72-1.67 (m, 1H), 1.37-1.26 (m, 2H), 1.24-1.07 (m, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 144.0, 137.6, 128.9, 127.0, 120.6 120.2 (q, \(J = 323.3\) Hz), 51.2, 48.8, 40.5, 35.5, 32.7, 26.1, 26.0. (one carbon missing probably due to overlapping) \(^{19}\)F NMR (470 MHz, Chloroform-\(d\)) \(\delta\) -76.42. HRMS (ESI) \(m/z\) calculated for C\(_{18}\)H\(_{24}\)NO\(_2\)F\(_3\)SNa [M+Na\(^+\)]: 398.1378, found 398.1377.
Reaction scope

General procedure:

The following procedure was used with no effort to exclude air or moisture. To a ½ dram vial was added a stir bar, Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), olefin (0.2 mmol, 1.0 equiv) and $N$-trityl protected amine (0.2 mmol, 1.0 equiv). Toluene (0.2 mL, 1.0 M) was added and the vial was capped and heated to 45 °C for 24-72 hours (monitored by TLC). The vial was allowed to cool to room temperature and diluted with 1 mL acetone. The reaction mixture was filtered through a pipette silica plug into a 20 mL vial with acetone. The mixture was concentrated under reduced pressure, diluted with 2 mL CDCl$_3$ and analyzed by crude $^1$H NMR with internal standard (trifluorotoluene 14.6 mg, 0.1 mmol, 0.5 equiv). The mixture was then concentrated under reduced pressure and subjected to flash column chromatography.

$^{(E)}$-$N$-(3-cyclohexylallyl)-1,1,1-trifluoro-$N$-phenylmethanesulfonamide (2). Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allyl cyclohexane (24.8 mg, 0.2 mmol, 1.0 equiv) and $N$-benzyl-1,1,1-trifluoromethanesulfonamide (S11) (45.0 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 30% CH$_2$Cl$_2$ in hexanes) provided pure product 2 as a colorless oil. Run 1: (48.1 mg, 69.2% yield); Run 2: (49.1 mg, 70.6% yield); Run 3: (49.2 mg, 70.8% yield). Average: 70% yield ± 0.9%.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.42-7.34 (m, 3H), 7.29-7.23 (m, 2H), 5.43-5.33 (m, 2H), 4.27 (d, J = 5.2 Hz, 2H), 1.92-1.82 (m, 1H), 1.69-1.51 (m, 5H), 1.28-1.15 (m, 2H), 1.14-1.05 (m, 1H), 0.98-0.87 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 144.2, 136.9, 129.8, 129.4, 129.2, 120.5 (q, J = 323.7), 120.4, 56.1, 40.3, 32.5, 26.1, 25.9.

$^{19}$F NMR (470 MHz, CDCl$_3$) δ -76.67.

HRMS (ESI) m/z calculated for C$_{16}$H$_{20}$NO$_2$F$_3$SNa [M+Na]$^+$: 370.1065, found 370.1074.

$^{(E)}$-$N$-benzyl-$N$-(3-cyclohexylallyl)-1,1,1-trifluoromethanesulfonamide (3). Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allyl cyclohexane (24.8 mg, 0.2 mmol, 1.0 equiv) and $N$-benzyl-1,1,1-trifluoromethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 30% CH$_2$Cl$_2$ in hexanes) provided pure product 3 as a colorless oil. Run 1: (58.9 mg, 81.5% yield); Run 2: (59.4 mg, 82.2% yield); Run 3: (59.6 mg, 82.4% yield). Average: 82% yield ± 0.5%.

S 28
**HRMS (EI) m/z calculated for C_{17}H_{22}NO_{2}F_{3}S [M]^+: 361.1323, found 361.1322.**

(E)-N-(3-cyclohexallyl)-1,1,1-trifluoro-N-(naphthalen-1-ylmethyl)methanesulfonamide (4). Pd(OAc)_2 (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allyl cyclohexane (24.8 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-(naphthalen-1-ylmethyl)methanesulfonamide (S13) (57.9 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 30% CH₂Cl₂ in hexanes) provided pure product 4 as a colorless oil. Run 1: (57.9 mg, 70.4% yield); Run 2: (57.0 mg, 69.3% yield); Run 3: (58.5 mg, 71.1% yield). **Average: 70% yield ± 0.9%.**

**1H NMR** (500 MHz, Chloroform-d) δ 8.12 (dd, J = 8.4, 1.1 Hz, 1H), 7.91-7.88 (m, 1H), 7.86 (d, J = 7.4 Hz, 1H), 7.60-7.45 (m, 4H), 5.36-5.19 (m, 2H), 5.01 (br s, 2H), 3.83 (br s, 2H), 1.90-1.76 (m, 1H), 1.70-1.59 (m, 3H), 1.57-1.50 (m, 2H), 1.29-1.15 (m, 2H), 1.14-1.03 (m, 1H), 0.94-0.82 (m, 2H). **13C NMR** (126 MHz, CDCl₃) δ 144.0, 134.0, 131.6, 129.5, 129.4, 129.0, 127.3, 126.9, 126.2, 125.3, 122.9, 120.4 (q, J = 323.8 Hz), 119.9, 50.2, 48.8, 40.4, 32.5, 26.1, 25.9. **19F NMR** (470 MHz, Chloroform-d) δ -75.47. **HRMS (ESI) m/z calculated for C_{21}H_{24}NO_{2}F_{3}SNa [M+Na]^+: 434.1378, found 434.1388.

(E)-N-(3-cyclohexallyl)-1,1,1-trifluoro-N-methylmethanesulfonamide (5). Pd(OAc)_2 (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allyl cyclohexane (24.8 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-methylmethanesulfonamide (S14) (32.6 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 30% CH₂Cl₂ in hexanes) provided pure product 5 as a colorless oil. Run 1: (41.7 mg, 73.1% yield); Run 2: (41.4 mg, 72.6% yield); Run 3: (41.9 mg, 73.6% yield). **Average: 73% yield ± 0.5%.**

**1H NMR** (500 MHz, Chloroform-d) δ 5.68 (dd, J = 15.4, 6.7 Hz, 1H), 5.34 (dt, J = 15.3, 6.9 Hz, 1H), 3.87 (br s, 2H), 2.94 (s, 3H), 2.07-1.90 (m, 1H), 1.76-1.61 (m, 5H), 1.33-1.22 (m, 2H), 1.20-1.12 (m, 1H), 1.12-1.02 (m, 2H). **13C NMR** (126 MHz, Chloroform-d) δ 144.0, 120.3 (q, J = 323.6 Hz), 120.2, 53.2, 40.5, 34.3, 32.8, 26.2, 26.0. **19F NMR** (470 MHz, Chloroform-d) δ -75.77. **HRMS (EI) m/z calculated for C_{11}H_{18}NO_{2}F_{3}S [M]^+: 285.1010, found 285.1012.
(E)-N-butyl-N-(3-cyclohexylallyl)-1,1,1-trifluoromethanesulfonamide (6). Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allyl cyclohexane (24.8 mg, 0.2 mmol, 1.0 equiv) and N-butyl-1,1-trifluoromethanesulfonamide (S15) (41.0 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 30% CH$_2$Cl$_2$ in hexanes) provided pure product 6 as a colorless oil. Run 1: (33.1 mg, 50.5% yield); Run 2: (33.6 mg, 51.3% yield); Run 3: (33.4 mg, 51.0% yield). **Average: 51% yield ± 0.4%**.

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 5.66 (dd, $J = 15.4, 6.7$ Hz, 1H), 5.34 (dt, $J = 15.4, 7.0$, 1H), 3.91 (d, $J = 7.0$ Hz, 2H), 3.30 (br s, 2H), 2.06-1.95 (m, 1H), 1.77-1.67 (m, 5H), 1.57 (p, $J = 7.7$ Hz, 2H), 1.36-1.21 (m, 4H), 1.21-1.13 (m, 1H), 1.12-1.02 (m, 2H), 0.92 (t, $J = 7.4$ Hz, 3H). $^1$C NMR (125 MHz, CDCl$_3$) $\delta$ 143.6, 120.7, 120.18 (q, $J = 323.4$ Hz), 50.5, 47.2, 40.5, 32.7, 30.1, 26.2, 26.0, 19.7, 13.8. **HRMS (ESI) $m/z$ calculated for C$_{14}$H$_{23}$NO$_3$F$_3$S [M-H]$^+$: 342.1351, found: 342.1345. **

**tert-Butyl (E)-(2-((N-(3-cyclohexylallyl)-1,1,1-trifluoromethyl)sulfonamido)ethyl)carbamate (7).** Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allyl cyclohexane (24.8 mg, 0.2 mmol, 1.0 equiv) and tert-butyl (2-((trifluoromethyl)sulfonamido)ethyl)carbamate (S16) (58.4 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 5% acetone in hexanes) and preparative TLC (10% ethyl acetate in hexanes) provided pure product 7 as a colorless oil. Run 1: (52.3 mg, 63.1% yield); Run 2: (51.9 mg, 62.6% yield); Run 3: (52.9 mg, 63.9% yield). **Average: 63% yield ± 0.7%**.

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 5.73 (dd, $J = 15.5, 6.7$ Hz, 1H), 5.38-5.28 (m, 1H), 4.74 (d, $J = 6.4$ Hz, 1H), 3.97 (d, $J = 7.1$ Hz, 2H), 3.41 (br s, 2H), 3.30 (br q, $J = 6.2$ Hz, 2H), 2.05-1.93 (m, 1H), 1.77-1.61 (m, 5H), 1.44 (s, 9H), 1.31-1.21 (m, 2H), 1.19-1.12 (m, 1H), 1.12-1.02 (m, 2H). $^1$C NMR (125 MHz, CDCl$_3$) $\delta$ 156.0, 144.7, 120.11 (q, $J = 120.1$), 120.1, 79.9, 51.0, 46.6, 40.5, 38.4, 32.6, 28.4, 26.1, 26.0. **$^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -76.28.** **HRMS (ESI) $m/z$ calculated for C$_{17}$H$_{30}$N$_2$O$_3$F$_3$S [M+H]$^+$: 415.1878, found: 415.1866. **

(E)-N-(3-cyclohexylallyl)-1,1,1-trifluoro-N-(2-methoxyethyl) methanesulfonamide (8). Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allyl cyclohexane (24.8 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-(2-methoxyethyl) methanesulfonamide (S17) (41.4 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 20% acetone in hexanes) provided pure product 8 as a colorless oil. Run 1: (40.9 mg, 62.1% yield); Run 2: (41.6 mg, 63.1% yield); Run 3: (42.2 mg, 64.1% yield). **Average: 63% yield ± 1.0%.**
$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 5.68 (dd, $J$ = 15.5, 6.6 Hz, 1H), 5.34 (dt, $J$ = 15.3, 7.0, 1H), 4.00 (d, $J$ = 6.9 Hz, 2H), 3.54 (t, $J$ = 5.7 Hz, 2H), 3.48 (br s, 2H), 3.34 (s, 3H), 2.04-1.95 (m, 1H), 1.75-1.68 (m, 4H), 1.68-1.63 (m, 1H), 1.31-1.05 (m, 5H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.0, 121.4, 121.4 (q, $J$ = 321.3 Hz), 71.3, 59.0, 52.0, 46.4, 40.5, 32.7, 26.2, 26.0. $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -76.43. HRMS (ESI) $m/z$ calculated for C$_{13}$H$_{22}$NO$_3$F$_3$SNa [M+Na]$^+$: 352.1170, found 352.1169.

(E)-N-(2-bromoethyl)-N-(3-cyclohexylallyl)-1,1,1-trifluoromethanesulfonamide (9). Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allyl cyclohexane (24.8 mg, 0.2 mmol, 1.0 equiv) and N-(2-bromoethyl)-1,1,1-trifluoromethanesulfonamide (S18) (51.2 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 30% CH$_2$Cl$_2$ in hexanes) provided pure product 9 as a colorless oil. Run 1: (44.9 mg, 59.4% yield); Run 2: (45.7 mg, 60.5% yield); Run 3: (45.6 mg, 60.3% yield). Average: 60% yield ± 0.6%.

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 5.82-5.60 (m, 1H), 5.36 (ddt, $J$ = 15.4, 7.1, 1.3 Hz, 1H), 4.09-3.90 (br s, 2H), 3.66 (br s, 2H), 3.44 (t, $J$ = 7.5 Hz, 2H), 2.11-1.95 (m, 1H), 1.85-1.58 (m, 4H), 1.33-1.22 (m, 2H), 1.21-1.14 (m, 1H), 1.13-1.03 (m, 2H). $^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 144.8, 120.3, 120.0 (q, $J$ = 323.0 Hz), 52.2, 48.7, 40.5, 32.6, 27.9, 26.1, 26.0. $^{19}$F NMR (470 MHz, Chloroform-d) $\delta$ -76.20. HRMS (ESI) $m/z$ calculated for C$_{12}$H$_{19}$NO$_3$F$_3$SNa [M+Na]$^+$: 400.0170, found 400.0179.

(E)-N-(3-cyclohexylallyl)-1,1,1-trifluoro-N-(2,2,2-trifluoroethyl)methanesulfonamide (10). Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allyl cyclohexane (24.8 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-(2,2,2-trifluoroethyl)methanesulfonamide (S19) (46.2 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 30% CH$_2$Cl$_2$ in hexanes) provided pure product 10 as a colorless oil. Run 1: (63.2 mg, 89.5% yield); Run 2: (64.1 mg, 90.7% yield); Run 3: (63.5 mg, 89.8% yield). Average: 90% yield ± 0.6%.

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 5.77 (dd, $J$ = 15.5, 6.8 Hz, 1H), 5.38-5.23 (m, 1H), 4.06 (d, $J$ = 7.3 Hz, 2H), 3.89 (q, $J$ = 8.4 Hz, 2H), 2.04 (dtt, $J$ = 10.8, 6.9, 3.5 Hz, 1H), 1.79-1.63 (m, 5H), 1.34-1.22 (m, 2H), 1.22-1.14 (m, 1H), 1.14-1.05 (m, 2H). $^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 146.9, 123.58 (q, $J$ = 280.3 Hz), 119.83 (q, $J$ = 322.2 Hz), 118.5, 52.0, 46.22 (q, $J$ = 35.8 Hz), 40.6, 32.6, 26.0, 25.9. $^{19}$F NMR (470 MHz, Chloroform-d) $\delta$ -69.96, -76.32. HRMS (EI) $m/z$ calculated for C$_{12}$H$_{17}$NO$_2$F$_6$S$_2$ [M]$: 353.0884, found 353.0871.
(-)-Methyl (E)-N-(3-cyclohexylallyl)-N-((trifluoromethyl)sulfonyl)-L-alaninate (11).  
Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (-)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allyl cyclohexane (24.8 mg, 0.2 mmol, 1.0 equiv) and methyl ((trifluoromethyl)sulfonyl)-L-alaninate (S20) (47.0 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 30% CH$_2$Cl$_2$ in hexanes) provided pure product (-)-11 as a colorless oil. Run 1: (57.3 mg, 80.2% yield); Run 2: (57.0 mg, 79.7% yield); Run 3: (57.8 mg, 80.9% yield). **Average: 80% yield ± 0.6%**.  
$^1$H NMR (500 MHz, Chloroform-d) δ 5.61 (dd, $J$ = 15.5, 6.6, 1H), 5.41 (dt, $J$ = 14.8, 6.8 Hz, 1H), 4.56 (q, $J$ = 7.3 Hz, 1H), 4.01 (d, $J$ = 6.6 Hz, 2H), 3.76 (s, 3H), 1.99-1.90 (m, 1H), 1.77-1.61 (m, 5H), 1.53 (d, $J$ = 7.4 Hz, 3H), 1.31-1.21 (m, 2H), 1.20-1.12 (m, 1H), 1.10-0.99 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 170.8, 142.6, 122.3, 119.9 (q, $J$ = 323.0), 56.5, 52.7, 50.0, 41.4, 32.5, 26.2, 26.0, 16.6. $^{19}$F NMR (470 MHz, CDCl$_3$) δ -76.61. **HRMS (ESI) m/z calculated for C$_{14}$H$_{22}$NO$_4$F$_3$SNa [M+Na]$^+$: 380.1119, found 380.1120.** [α]$^{23}_{D}$ = -1.84° (c = 0.51, CHCl$_3$) 

(+)-methyl (E)-N-(3-cyclohexylallyl)-N-((trifluoromethyl)sulfonyl)-L-alaninate (12).  
Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allyl cyclohexane (24.8 mg, 0.2 mmol, 1.0 equiv) and methyl ((trifluoromethyl)sulfonyl)-L-alaninate (S21) (62.2 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 30% CH$_2$Cl$_2$ in hexanes) provided pure product (+)-12 as a colorless oil. Run 1: (60.0 mg, 69.2% yield); Run 2: (60.9 mg, 70.2% yield); Run 3: (61.4 mg, 70.8% yield). **Average: 70% yield ± 0.8%**.  
$^1$H NMR (500 MHz, Chloroform-d) δ 7.34-7.30 (m, 2H), 7.28-7.22 (m, 3H), 5.68 (dd, $J$ = 15.5, 6.5, 1H), 5.42 (dt, $J$ = 15.4, 6.9, 1H), 4.71 (t, $J$ = 7.4 Hz, 1H), 4.06 (dd, $J$ = 7.0, 3.7 Hz, 2H), 3.71 (s, 3H), 3.44 (dd, $J$ = 14.1, 8.0 Hz, 1H), 3.04 (dd, $J$ = 14.1, 6.8 Hz, 1H), 2.06-1.89 (m, 1H), 1.84-1.58 (m, 5H), 1.34-1.22 (m, 2H), 1.22-1.14 (m, 1H), 1.14-1.02 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 169.9, 143.0, 136.3, 129.4, 128.9, 127.4, 122.2, 119.9 (q, $J$ = 323.5 Hz) 62.3, 52.7, 50.3, 40.5, 37.3, 32.6, 26.3, 26.1. $^{19}$F NMR (470 MHz, Chloroform-d) δ -75.98. **HRMS (ESI) m/z calculated for C$_{20}$H$_{26}$NO$_4$F$_3$SNa [M+Na]$^+$: 454.1432, found 454.1422.** [α]$^{23}_{D}$ = -36.8° (c = 0.50, CHCl$_3$) 

Complete stereoretention was proven by chiral HPLC analysis. The enantiomeric excess was determined to be > 99% ee by chiral HPLC analysis (against mixture of (-)-12 (52%) and (+)-12 (48%)) (CHIRALPAK AD-RH column, 0.25 mL/min, 80% EtOH in H$_2$O, $\lambda$ = 220 nm (4nm). **tR(major) = 20.177 min.** 

(-)-methyl N-(E)-3-cyclohexylallyl)-N-((trifluoromethyl)sulfonyl)-L-alloisoleucinate (13).  
Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (-)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1
equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allyl cyclohexane (24.8 mg, 0.2 mmol, 1.0 equiv) and Methyl ((trifluoromethyl)sulfonyl)-L-isoleucinate (S23) (55.5 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 30% CH₂Cl₂ in hexanes) provided pure product (−)-13 as a colorless oil. Run 1: (60.0 mg, 75.1% yield); Run 2: (60.4 mg, 75.6% yield); Run 3: (59.7 mg, 74.7% yield). Average: 75% yield ± 0.5%.

**1H NMR** (500 MHz, Chloroform-d) δ 5.64 (dd, J = 15.5, 6.5 Hz, 1H), 5.52-5.43 (m, 1H), 4.24 (dd, J = 16.0, 8.4 Hz, 1H), 4.16-4.05 (m, 2H), 3.74 (s, 3H), 2.05-1.90 (m, 2H), 1.75-1.62 (m, 6H), 1.31-0.98 (m, 6H), 0.93-0.86 (m, 6H). **13C NMR** (125 MHz, CDCl₃) δ 170.7, 141.8, 123.0, 119.9 (q, J = 323.2 Hz), 65.7, 52.1, 49.3, 40.4, 34.4, 32.5, 26.2, 26.0, 25.2, 15.4, 10.7. **19F NMR** (470 MHz, CDCl₃) δ -75.45. **HRMS (ESI)** m/z calculated for C₁₇H₂₅NO₄F₃SNa [M+Na]+: 422.1589, found 422.1587. [α]23D = -52.0 (c = 0.53, CHCl₃)

![Methyl-(E)-7-((1,1,1-trifluoro-N-phenethylmethyl)sulfonylamido)hept-5-enoate](image)

Methyl-(E)-7-((1,1,1-trifluoro-N-phenethylmethyl)sulfonylamido)hept-5-enoate (14). Pd(OAc)₂ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), 6-Heptenoic acid methyl ester (28.4 mg, 0.2 mmol, 1.0 equiv) and N-(2-Phenylethyl)trifluoromethanesulfonamide (S10) (50.6 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 10% acetone in hexanes) and preparative TLC provided pure product 14 as a colorless oil. Run 1: (46.6 mg, 59.2% yield); Run 2: (47.4 mg, 60.3% yield); Run 3: (47.8 mg, 60.8% yield). Average: 60% yield ± 0.8%.

**1H NMR** (500 MHz, Chloroform-d) δ 7.33-7.29 (m, 2H), 7.27-7.23 (m, 1H), 7.21-7.14 (m, 2H), 5.72-5.62 (m, 1H), 5.41 (dt, J = 15.3, 6.9, 1H), 3.88 (d, J = 6.9 Hz, 2H), 3.67 (s, 3H), 3.52 (br s, 2H), 2.91 (t, J = 7.9 Hz, 2H), 2.32 (t, J = 7.4 Hz, 2H), 2.18-2.08 (m, 2H), 1.74 (p, J = 7.5 Hz, 2H). **13C NMR** (126 MHz, Chloroform-d) δ 173.8, 137.5, 136.8, 128.9, 128.9, 127.0, 124.2, 120.1 (q, J = 323.2 Hz), 51.7, 50.8, 48.9, 35.5, 33.4, 31.6, 24.2. **19F NMR** (470 MHz, Chloroform-d) δ -76.45. **HRMS (ESI)** m/z calculated for C₁₇H₂₅NO₄F₃SNa [M+Na]+: 416.1119, found 416.1116.

![Heptenoic acid methyl ester](image)

(E)-4-((N-(2-bromoethyl)-1,1,1-trifluoromethyl)sulfonylamido)-N,N-diethylbut-2-ename (15). Pd(OAc)₂ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), N, N-diethylbut-3-ename (S31) (28.2 mg, 0.2 mmol, 1.0 equiv) and N-(2-bromoethyl)-1,1,1-trifluoromethanesulfonamide (S18) (51.2 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 0% => 10% acetone in hexanes) and preparative TLC provided pure product 15 as colorless oil. Run 1: (67.4 mg, 85.3% yield); Run 2: (66.7 mg, 84.4% yield); Run 3: (68.0 mg, 86.0% yield). Average: 85% yield ± 0.8%.

**1H NMR** (500 MHz, Chloroform-d) δ 6.74 (dt, J = 15.1, 6.3 Hz, 1H), 6.45 (d, J = 15.1, 1H), 4.22 (d, J = 6.3 Hz, 2H), 3.72 (br s, 2H), 3.46 (t, J = 7.1 Hz, 2H), 3.42 (q, J = 7.2 Hz, 2H), 3.36 (q, J = 7.2 Hz, 2H), 1.19 (t, J = 7.2 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H). **13C NMR** (126 MHz, Chloroform-
(E)-N-benzyl-1,1,1-trifluoro-N-(6-oxodec-2-en-1-yl) methanesulfonamide (16). Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2.5-dimethylbenzooquinone) (30 mg, 0.22 mmol, 1.1 equiv), Dec-9-en-5-one (S32) (30.9 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% ⇔ 5% acetone in hexanes) and preparative TLC (40% CH$_2$Cl$_2$ in hexanes) provided pure product 16 as a colorless oil. Run 1: (42.5 mg, 54.3% yield); Run 2: (43.1 mg, 55.0% yield); Run 3: (43.4 mg, 55.5% yield). **Average: 55% yield ± 0.6%**.

**1H NMR** (500 MHz, Methylene Chloride-d$_2$) $\delta$ 7.39-7.30 (m, 3H), 7.30-7.26 (m, 2H), 5.59-5.45 (m, 1H), 5.37-5.27 (m, 1H), 4.45 (br s, 2H), 3.78 (br s, 2H), 2.41 (t, $J$ = 7.2 Hz, 2H), 2.35 (t, $J$ = 7.5 Hz, 2H), 2.27-2.19 (m, 2H), 1.49 (p, $J$ = 7.5 Hz, 2H), 1.32-1.21 (m, 2H), 0.87 (t, $J$ = 7.4 Hz, 3H). **13C NMR** (126 MHz, Chloroform-d) $\delta$ 120.3, 137.7, 135.2, 129.6, 129.3, 129.1, 123.8, 122.2 (q, $J$ = 323.8 Hz), 51.4, 50.2, 43.2, 42.1, 26.9, 26.7, 23.1, 14.4. **19F NMR** (470 MHz, Methylene Chloride-d$_2$) $\delta$ -76.87. **HRMS (ESI) m/z** calculated for C$_{18}$H$_{25}$NO$_3$F$_3$S [M+H]+: 392.1507, found 392.1524.

(+)-**tert**-butyl-(S,E)-2-((1,1,1-trifluoro-N-(3-(4-(oxiran-2-ylmethoxy) phenyl) allyl) methyl) sulfonamido) ethyl) carbamate (17). Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2.5-dimethylbenzooquinone) (30 mg, 0.22 mmol, 1.1 equiv), (S)-2-((4-allylphenoxy)methyl) oxirane$^{22}$ (30.9 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S16) (47.8 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 0% ⇔ 15% acetone in hexanes) provided pure product 17 as a white solid. Run 1: (86.9 mg, 90.4% yield); Run 2: (85.6 mg, 89.1% yield); Run 3: (87.7 mg, 91.3% yield). **Average: 90% yield ± 1.1%**.

**1H NMR** (500 MHz, Chloroform-d) $\delta$ 7.33 (d, $J$ = 8.7 Hz, 2H), 6.88 (d, $J$ = 8.7 Hz, 2H), 6.61 (d, $J$ = 15.7 Hz, 1H), 5.97 (dt, $J$ = 15.7, 7.2 Hz, 1H), 4.81-4.75 (m, 1H), 4.24 (dd, $J$ = 11.0, 3.1 Hz, 1H), 4.18 (d, $J$ = 7.2 Hz, 2H), 3.95 (dd, $J$ = 11.1, 5.8 Hz, 1H), 3.47 (br s, 2H), 3.39-3.30 (m, 3H), 2.91 (t, $J$ = 4.5 Hz, 1H), 2.76 (dd, $J$ = 4.9, 2.6 Hz, 1H), 1.44 (s, 9H). **13C NMR** (126 MHz, Chloroform-d) $\delta$ 158.9, 156.1, 136.8, 129.2, 128.11 (q, $J$ = 323.0 Hz), 119.8, 114.9, 80.0, 68.9, 51.1, 50.2, 46.9, 44.8, 38.4, 28.5. **19F NMR** (470 MHz, Chloroform-d) $\delta$ -76.29. **HRMS (ESI) m/z** calculated for C$_{20}$H$_{27}$N$_2$O$_6$F$_3$SNa [M+Na]+: 503.1434, found 503.1441. [α]$_{D}$ = +2.5° (c = 0.58, CHCl$_3$)
(±)-N-benzyl-N-((2E,7E)-4-((tert-butyldimethylsilyl)oxy)nona-2,7-dien-1-yl)-1,1,1-trifluoromethanesulfonamide (18). Pd(OAc)₂ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (25-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (±)-(E)-tert-butyldimethyl(nona-1,7-dien-4-yloxy)silane (S35) (50.9 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-phenylethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 0% => 5% acetone in hexanes) provided pure product (±)-18 as a colorless oil. Run 1: (58.7 mg, 59.7% yield); Run 2: (59.7 mg, 60.7% yield); Run 3: (59.4 mg, 60.4% yield). Average: 60% yield ± 0.5%.

1H NMR (500 MHz, Chloroform-d) δ 7.42-7.33 (m, 3H), 7.32-7.29 (m, 2H), 5.64-5.50 (m, 2H), 5.48-5.36 (m, 2H), 4.48 (br s, 2H), 4.14 (q, J = 5.7 Hz, 1H), 3.85 (br s, 2H), 2.07-1.97 (m, 2H), 1.66 (d, J = 4.9, 3H), 1.61-1.42 (m, 2H), 0.92 (s, 9H), 0.07 (s, 3H), 0.04 (s, 3H). 13C NMR (126 MHz, Chloroform-d) δ 141.1, 134.1, 130.8, 129.1, 128.7, 128.6, 126.4, 121.5, 120.19 (q, J = 322.7 Hz), 71.7, 50.5, 48.7, 38.0, 28.3, 25.9, 18.3, 18.1, -4.3, -4.7. 19F NMR (470 MHz, Chloroform-d) δ -76.53. HRMS (ESI) m/z calculated for C₂₃H₃₆NO₃F₃SiNa [M+Na]⁺: 514.2035, found 514.2032.

(-)-(R,E)-N-(4,8-dimethylnona-2,7-dien-1-yl)-1,1,1-trifluoro-N-phenylethlaminesulfonamide (19). Pd(OAc)₂ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (25-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (R)-4,8-dimethylnona-1,7-diene²³ (30.5 mg, 0.2 mmol, 1.0 equiv) and N-(2-Phenylethyl)trifluoromethanesulfonamide (S10) (50.6 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 30% CH₂Cl² in hexanes) provided pure product 14 as colorless oil. Run 1: (54.4 mg, 67.4% yield); Run 2: (55.1 mg, 68.3% yield); Run 3: (55.7 mg, 69.0% yield). Average: 68% yield ± 0.8%.

1H NMR (500 MHz, Chloroform-d) δ 7.35-7.29 (m, 2H), 7.29-7.22 (m, 1H), 7.20-7.16 (m, 2H), 5.59 (dd, J = 15.3, 7.8, 1H), 5.36 (dt, J = 14.6, 7.0, 1H), 5.12-5.05 (m, 1H), 3.96-3.85 (m, 2H), 3.55 (br s, 2H), 2.92 (t, J = 8.0 Hz, 2H), 2.21 (hept, J = 7.0 Hz, 1H), 1.96 (q, J = 7.6 Hz, 2H), 1.69 (s, 3H), 1.58 (s, 3H), 1.35 (q, J = 7.3 Hz, 2H), 1.02 (d, J = 6.7, 3H). 13C NMR (126 MHz, Chloroform-d) δ 144.0, 137.6, 131.9, 128.9, 128.9, 127.1, 124.2, 121.5, 120.1 (q, J = 323.3 Hz), 51.0, 48.8, 36.8, 36.2, 35.4, 25.9, 25.9, 20.4, 17.8. 19F NMR (470 MHz, Chloroform-d) δ -76.47. HRMS (ESI) m/z calculated for C₂₀H₂₈NO₂F₃SiNa [M+Na]⁺: 426.1691, found 426.1700. [α]²³_D = -16.9° (c = 0.50, CHCl₃)

Complete stereoretention was determined by chiral HPLC analysis. The enantiomeric excess was determined to be >99% ee (from pure chiral olefin starting material) by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.25 mL/min, 80% EtOH in H₂O, λ = 214 nm (4nm). tR(major) = 14.804 min).
(E)-N-(5-(5H-dibenz[b,f]azepin-5-yl)pent-2-en-1-yl)-1,1,1-trifluoro-N-methylmethanesulfonamide (20). Pd(OAc)2 (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinine) (30 mg, 0.22 mmol, 1.1 equiv), 5-(pent-4-en-1-yl)-5H-dibenz[b,f]azepine (S36) (52.3 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-methylmethanesulfonamide (S14) (32.6 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 30% CH2Cl2 in hexanes) provided pure product 20 as a yellow oil. Run 1: (50.3 mg, 59.5% yield); Run 2: (51.1 mg, 60.5% yield); Run 3: (51.3 mg, 60.7% yield). Average: 60% yield ± 0.6%.

1H NMR (500 MHz, Methanol-d4) δ 7.23 (ddd, J = 8.2, 7.2, 1.7 Hz, 2H), 7.02 (m, 4H), 6.95 (ddd, J = 7.4, 1.1 Hz, 2H), 5.74 (dt, J = 15.1, 6.9, 1H), 5.23 (dt, J = 15.1, 6.8, 1H), 3.88-3.68 (m, 4H), 2.84 (s, 3H), 2.24 (q, J = 6.6, 2H). 13C NMR (126 MHz, Methanol-d4) δ 152.0, 136.1, 135.4, 133.1, 130.2, 130.0, 125.4, 124.4, 121.6, 121.6 (q, J = 323.0 Hz), 53.6, 51.0, 34.9, 31.2. 19F NMR (470 MHz, Methanol-d4) δ -77.66. HRMS (ESI) m/z calculated for C29H32NO11F3SNa [M+Na]+: 682.1534, found 682.1552. [α]D22 = +65.3° (c = 0.56, CHCl3)

(+)-(2R,3R,4R,5S,6R)-2-(acetoxyethyl)-6-((E)-3-((1,1,1-trifluoro-N-(naphthalen-1-ylmethyl)methyl)sulfonyl)prop-1-en-1-yl)tetrahydro-2H-pyran-3,4,5-triy l triacetate (21). Pd(OAc)2 (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinine) (30 mg, 0.22 mmol, 1.1 equiv), 1-allyl -2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside24 (74.5 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-(naphthalen-1-ylmethyl)methanesulfonamide (S13) (57.9 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (50 mL silica gel, 0% => 20% Acetone in hexanes) and preparative TLC (66% Et2O in hexanes) provided pure product (+)-21 as a white solid. Run 1: (91.4 mg, 69.3% yield); Run 2: (93.5 mg, 70.9% yield); Run 3: (92.7 mg, 70.3% yield). Average: 70% yield ± 0.8%.

1H NMR (500 MHz, Chloroform-d) δ 8.17-8.14 (m, 1H), 7.90 (td, J = 7.7, 7.2, 1.8 Hz, 2H), 7.61 (ddd, J = 8.5, 1.4 Hz, 1H), 7.55 (ddd, J = 8.1, 1.1 Hz, 1H), 7.52-7.48 (m, 2H), 5.68 (dt, J = 14.3, 6.4 Hz, 1H), 5.48 (dd, J = 15.8, 5.1 Hz, 1H), 5.40-4.60 (br s, 2H), 5.11 (dd, J = 10.1, 9.1 Hz, 1H), 5.01-4.92 (m, 2H), 4.50 (s, 1H), 4.11 (dd, J = 12.3, 5.1 Hz, 1H), 4.03-3.98 (m, 1H), 3.94-3.83 (m, 2H), 3.59 (s, 1H), 2.07 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 170.8, 170.2, 169.5, 169.5, 133.9, 131.6, 130.2, 130.0, 129.2, 128.8, 128.0, 127.9, 127.3, 126.6, 125.2, 122.8, 120.3 (q, J = 323.6 Hz), 72.0, 70.5, 70.1, 69.6, 68.8, 62.3, 50.1, 49.3, 20.8, 20.8, 20.7, 20.7. 19F NMR (470 MHz, Chloroform-d) δ -75.25. HSQC and DEPT 135 please see supporting information. HRMS (ESI) m/z calculated for C29H32NO11F3SNa [M+Na]+: 682.1546, found 682.1552. [α]D22 = +65.3° (c = 0.56, CHCl3)
Methyl (E)-4-(3-(phenethylamino)prop-1-en-1-yl)benzoate (22).

Pd(OAc)$_2$ (6.7 mg, 0.03 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (10.2 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2.5-dimethylbenzoquinone) (45 mg, 0.33 mmol, 1.1 equiv), methyl 4-allylbenzoate (51.3 mg, 0.3 mmol, 1.0 equiv) and 4-nitro-N-phenethylbenzenesulfonamide (91.8 mg, 0.3 mmol, 1.0 equiv) were reacted according to the general procedure in dioxane (0.3 mL, 1.0 M) for 72 hours. Purification by flash column chromatography (100 mL silica gel, 0% => 15% acetone in hexanes provided a mixture of product 22 with 4-nitro-N-phenethylbenzenesulfonamide.

To a 20 mL vial was added a stir bar, mixture from last step, Cs$_2$CO$_3$ (325.8 mg, 1.0 mmol), DMF (1 mL) and PhSH (307.3 µL, 3.0 mmol). The reaction was heated to 45 °C for 2 hours. The vial was allowed to cool to room temperature. 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.2 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.2 mmol, 1.1 equiv), methyl 4-allylbenzoate (51.3 mg, 0.3 mmol, 1.0 equiv) and 4-nitro-N-phenethylbenzenesulfonamide (91.8 mg, 0.3 mmol, 1.0 equiv) were reacted according to the general procedure in dioxane (0.3 mL, 1.0 M) for 72 hours. Purification by flash column chromatography (100 mL silica gel, 0% => 15% acetone in hexanes provided a mixture of product 22 with 4-nitro-N-phenethylbenzenesulfonamide.

Run 1: (48.9 mg, 55.2% yield); Run 2: (47.2 mg, 53.0% yield); Run 3: (48.5 mg, 54.7% yield). **Average: 54% yield ± 1.2%** over two steps.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.97 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.24 – 7.19 (m, 3H), 6.57 – 6.50 (m, 1H), 6.39 (dt, J = 15.9, 6.1 Hz, 1H), 3.90 (s, 3H), 3.46 (dd, J = 6.2, 1.6 Hz, 2H), 2.96 (t, J = 7.3 Hz, 2H), 2.86 (t, J = 7.1 Hz, 2H), 1.91 (br s, 1H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 167.0, 141.7, 139.9, 131.1, 130.6, 130.0, 129.0, 128.9, 128.7, 126.4, 126.3, 52.2, 51.7, 50.7, 36.4. **HRMS (ESI) m/z** calculated for C$_{19}$H$_{22}$NO$_2$ [M+H]$^+$. 296.1651, found 296.1647.

(+)-(S,E)-N-methoxy-N,2-dimethyl-5-((1,1,1-trifluoro-N-phenethylmethyl)sulfonamido)pent-3-enamide (23). Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2.5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (S)-N-methoxy-N,2-dimethylpent-4-enamide (31.44 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-phenethylmethylene sulfonamide (S10) (50.6 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (column1: 50 mL silica gel, 0% => 20% Acetone in hexanes; column 2: 50 mL silica gel, 100% CH$_2$Cl$_2$ => 0.5% MeOH in CH$_2$Cl$_2$) provided pure product (+)-23 as a colorless oil. Run 1: (49.9 mg, 61.1% yield); Run 2: (50.8 mg, 62.2% yield); Run 3: (51.8 mg, 63.4% yield). **Average: 62% yield ± 1.2%**.

When stopped at 24 h. Run 1: (41.0 mg, 50.2% yield); Run 2: (42.0 mg, 51.4% yield); Run 3: (42.5 mg, 52.0% yield). **Average: 51% yield ± 0.9%**.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.33-7.29 (m, 2H), 7.26-7.22 (m, 1H), 7.17 (dd, J = 8.1, 1.3 Hz, 2H), 5.85 (dd, J = 15.5, 8.0, 1H), 5.50 (dt, J = 15.3, 7.0, 1H), 3.91 (d, J = 7.0 Hz, 2H), 3.69 (s,
Purification by flash column chromatography (column 1: 50 mL silica gel, (±)enamide dimethylbenzoquinone (30 mg, 0.22 mmol, 1.1 equiv), (±)((trifluoromethyl)sulfonyl)Cl) 19F NMR (470 MHz, CDCl3) δ -76.40. HRMS (ESI) m/z calculated for C17H24N2O4F3S [M+H]+: 409.1409, found 409.1399. [α]23D = +5.4 ° (c = 0.57, CHCl3)

Complete stereoretention was proven by chiral GC and HPLC analysis. Olefin starting material was determined by chiral GC analysis to be 94% ee. The allylic amine product 22 was determined by chiral HPLC analysis to be 94% ee. (CHIRALPAK AD-RH column, 0.3 mL/min, 50% EtOH in H2O, λ = 210nm (4nm). tR(major) = 61.526 min, tR(major) = 67.559 min.) See HPLC trace for product 22 and GC trace for the chiral olefin starting material.

(-)-methyl N-((S,E)-5-(methoxy(methyl)amino)-4-methyl-5-oxopent-2-en-1-yl)-N-((trifluoromethyl)sulfonyl)-L-phenylalaninate (24). Pd(OAc)2 (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5 dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (S)-N-methoxy-N,2-dimethylpent-4-enamide21 (31.44 mg, 0.2 mmol, 1.0 equiv) and (+)-methyl ((trifluoromethyl)sulfonyl)-L-phenylalaninate (S21) (62.3 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 0% => 20% Acetone in hexanes; column 2: 50 mL silica gel, 100% CH2Cl2 => 1% MeOH in CH2Cl2) provided pure product (-)-24 as a colorless oil. Run 1: (58.0 mg, 62.1% yield); Run 2: (57.6mg, 61.7% yield); Run 3: (58.7 mg, 62.9% yield). Average: 62% yield ± 0.6%.

1H NMR (500 MHz, Chloroform-d) δ 7.33-7.28 (m, 2H), 7.26-7.21 (m, 3H), 5.86 (dd, J = 15.6, 7.7 Hz, 1H), 5.59 (dt, J = 16.0, 6.8 Hz, 1H), 4.71 (t, J = 7.5 Hz, 1H), 4.08 (qd, J = 16.0, 6.8 Hz, 2H), 3.69 (s, 3H), 3.69 (s, 3H), 3.63-3.57 (m, 1H), 3.42 (dd, J = 14.2, 8.0 Hz, 1H), 3.17 (s, 3H), 3.03 (dd, J = 14.2, 7.0 Hz, 1H), 1.24 (d, J = 6.9 Hz, 3H). 13C NMR (125 MHz, CDCl3) δ 174.8, 169.7, 156.1, 136.0, 129.3, 128.8, 127.4, 125.9, 119.8 (q, J = 323.4 Hz), 62.4, 61.7, 52.7, 49.7, 38.6, 37.3, 32.5, 17.3. 19F NMR (470 MHz, CDCl3) δ -75.93. HRMS (ESI) m/z calculated for C17H24N2O4F3S [M+H]+: 467.1481, found 467.1480. [α]23D = -26.4 ° (c = 0.50, CHCl3)

(+)-methyl N-((S,E)-5-(methoxy(methyl)amino)-4-methyl-5-oxopent-2-en-1-yl)-N-((trifluoromethyl)sulfonyl)-D-phenylalaninate (25). Pd(OAc)2 (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5 dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (S)-N-methoxy-N,2-dimethylpent-4-enamide21 (31.44 mg, 0.2 mmol) and (-)-methyl ((trifluoromethyl)sulfonyl)-D-phenylalaninate (S22) (62.3 mg, 0.2 mmol) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 0% => 20% Acetone in
hexanes; column 2: 50 mL silica gel, 100% CH₂Cl₂ => 1% MeOH in CH₂Cl₂) provided pure product (+)-25 as a colorless oil. Run 1: (55.3 mg, 59.3% yield); Run 2: (56.4 mg, 60.4% yield); Run 3: (57.2 mg, 61.3% yield). **Average: 60% yield ± 1.0%**.

**1H NMR** (500 MHz, Chloroform-d) δ 7.33-7.28 (m, 2H), 7.26-7.20 (m, 3H), 5.85 (dd, J = 15.5, 7.8, 1H), 5.58 (dt, J = 15.3, 6.9, 1H), 4.72 (t, J = 7.5 Hz, 1H), 4.09 (t, J = 6.3 Hz, 2H), 3.71 (s, 3H), 3.69 (s, 3H), 3.58 (q, J = 6.3, 5.4 Hz, 1H), 3.41 (dd, J = 14.2, 7.8 Hz, 1H), 3.17 (s, 3H), 3.03 (dd, J = 14.2, 7.2 Hz, 1H), 1.24 (d, J = 6.9 Hz, 3H). **13C NMR** (125 MHz, CDCl₃) δ 174.8, 169.8, 136.1, 136.0, 129.3, 128.8, 127.4, 126.1, 119.8 (q, J = 323.7 Hz), 62.4, 61.7, 52.7, 49.7, 38.8, 37.1, 32.5, 17.5. **19F NMR** (470 MHz, Chloroform-d) δ -75.92. **HRMS (ESI) m/z** calculated for C₁₉H₂₈N₂O₈F₃S [M+H]⁺: 467.1464, found 464.1460. [α]²³_D = +25.9° (c = 0.59, CHCl₃)

(−)-**methyl N-((R,E)-4-(( tert-butyldimethylsilyl)oxy)-5-((4-methoxybenzyl)oxy)pent-2-en-1-yl)-N-(( trifluoromethyl)sulfonyl)-L-phenylalaninate** (26). Pd(OAc)₂ (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (R)-tert-butyl((4-methoxybenzyl)oxy)pent-4-en-2-yl)oxy(dimethylsilane)²¹ (67.3 mg, 0.2 mmol, 1.0 equiv) and (−)-methyl ((trifluoromethyl)sulfonyl)-L-phenylalaninate (S21) (62.3 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 0% => 20% Acetone in hexanes; column 2: 50 mL silica gel, 100% CH₂Cl₂ => 2% MeOH in CH₂Cl₂) provided pure product (+)-26 as a colorless oil. Run 1: (96.7 mg, 74.9% yield); Run 2: (97.9 mg, 75.8% yield); Run 3: (95.6 mg, 74.0% yield). **Average: 75% yield ± 0.9%**.

**When stopped at 24 hour:** Run 1: (86.3 mg, 66.8% yield); Run 2: (87.7 mg, 67.9% yield); Run 3: (85.8 mg, 66.4% yield). **Average: 67% yield ± 0.8%**.

**1H NMR** (500 MHz, Chloroform-d) δ 7.33 (dd, J = 8.1, 6.5 Hz, 2H), 7.30-7.20 (m, 5H), 6.88 (d, J = 8.6 Hz, 2H), 5.90-5.77 (m, 2H), 4.72 (t, J = 7.5 Hz, 1H), 4.50 (br s, 2H), 4.38-4.32 (m, 1H), 4.14 (d, J = 5.2 Hz, 2H), 3.82 (s, 3H), 3.70 (s, 3H), 3.47-3.34 (m, 3H), 3.04 (dd, J = 14.0, 6.7 Hz, 1H), 0.93 (s, 9H), 0.09 (s, 3H), 0.07(s, 3H). **13C NMR** (126 MHz, CDCl₃) δ 169.7, 159.3, 136.8, 136.0, 130.4, 129.4, 129.3, 128.8, 127.3, 124.8, 119.7 (q, J = 323.8 Hz), 113.8, 74.3, 73.2, 71.2, 62.1, 55.4, 52.7, 49.3, 37.4, 25.9, 18.3, -4.6, -4.7. **19F NMR** (470 MHz, Chloroform-d) δ -75.93. **HRMS (ESI) m/z** calculated for C₃₀H₄₂NO₇F₃SiNa [M+Na]⁺: 668.2301, found 668.2304. [α]²³_D = -8.4° (c = 1.02, CHCl₃)

(+)-**methyl N-((R,E)-4-(( tert-butyldimethylsilyl)oxy)-5-((4-methoxybenzyl)oxy)pent-2-en-1-yl)-N-(( trifluoromethyl)sulfonyl)-D-phenylalaninate** (27). Pd(OAc)₂ (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (R)-tert-butyl((1-(4-...
methoxybenzyl)oxy)pent-4-en-2-yl)oxy)dimethylsilane\(^{21}\) (67.3 mg, 0.2 mmol, 1.0 equiv) and (-)-methyl ((trifluoromethyl)sulfonyl)-D-phenylalaninate (S\(^{22}\)) (62.3 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 0\% \rightarrow 20\% Acetone in hexanes; column 2: 50 mL silica gel, 100\% CH\(_2\)Cl\(_2\) \rightarrow 2\% MeOH in CH\(_2\)Cl\(_2\)) provided pure product (+)-27 as a colorless oil.

Run 1: (101.3 mg, 78.4\% yield); Run 2: (100.0 mg, 77.4\% yield); Run 3: (101.5 mg, 78.6 \% yield).

**Average: 78\% yield ± 0.6\%**.

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.35 (dd, \(J = 8.0, 6.4\) Hz, 2H), 7.32-7.24 (m, 5H), 6.88 (d, \(J = 8.6\) Hz, 2H), 5.85 (s, 2H), 4.74 (t, \(J = 7.6\) Hz, 1H), 4.55-4.46 (m, 2H), 4.41-4.35 (m, 1H), 4.27-4.19 (m, 1H), 4.13 (s, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 3.48-3.37 (m, 3H), 3.09 (dd, \(J = 13.9, 6.6\) Hz, 1H), 0.95 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 169.7, 159.3, 136.4, 135.9, 130.4, 129.3, 128.8, 127.3, 125.3, 119.7 (q, \(J = 324.0\) Hz), 113.8, 74.4, 73.2, 71.4, 62.6, 55.4, 52.7, 49.4, 37.7, 25.9, 18.4, -4.6, -4.7. \(^{19}\)F NMR (470 MHz, Chloroform-\(d\)) \(\delta\) -75.90. **HRMS (ESI) m/z** calculated for C\(_{30}\)H\(_{42}\)NO\(_7\)F\(_3\)SiNa \([\text{M+Na}]^+\): 668.2301, found 668.2284. \([\alpha]^{23}\)\(_D\) = +31.3 \(^o\) (\(c = 1.06\), CHCl\(_3\)).
Natural product derivatizations

General procedure:
No effort to exclude air or moisture is required. To a ½ dram vial was added a stir bar, Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), ligand (0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), olefin (0.2 mmol, 1.0 equiv) and N-triflyl protected amine (0.2 mmol, 1.0 equiv). Toluene (0.2 mL, 1.0M) was added and the vial was capped and heated to 45 °C for 24-72 hours (monitored by TLC). The vial was allowed to cool to room temperature and diluted with acetone. The reaction mixture was filtered through a ½ inch pipette silica plug into a 20mL vial with acetone. The mixture was concentrated under reduced pressure, diluted with 2 mL CDCl$_3$ and an internal standard (trifluorotoluene 14.6 mg, 0.1 mmol, 0.5 equiv) for crude $^1$HNMR analysis, the mixture was concentrated under reduced pressure and subjected to flash column chromatography for purification.

δ-Tocopherol derivative (+)-28. The reaction was performed according to the general procedure using Pd(OAc)$_2$ (2.2 mg, 0.01 mmol, 0.05 equiv), (±)-MeO-SOX ligand (L-5) (3.4 mg, 0.01 mmol, 0.05 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (+)-allylated-δ-Tocopherol derivative (S39) (85.3 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv) for 24 hours. The reaction mixture was purified by flash column chromatography (50 mL silica gel, 0% => 20% acetone in hexanes) to provide pure desired product (+)-28 as a colorless oil. Run 1: (116.8 mg, 88.0% yield); Run 2: (118.4 mg, 89.2% yield); Run 3: (117.0 mg, 88.1% yield). Average: 88% yield ± 0.7%.

$^{1}$H NMR (500 MHz, Chloroform-d) δ 7.46-7.33 (m, 5H), 7.00 (d, $J$ = 2.2 Hz, 1H), 6.92 (d, $J$ = 2.2 Hz, 1H), 6.32 (d, $J$ = 15.6 Hz, 1H), 5.87 (dt, $J$ = 15.7, 7.2 Hz, 1H), 4.56 (br s, 2H), 4.01 (br s, 2H), 2.81-2.74 (m, 2H), 2.20 (s, 3H), 1.86 (dt, $J$ = 13.8, 6.7 Hz, 1H), 1.79 (dt, $J$ = 13.3, 6.5 Hz, 1H), 1.65-1.04 (m, 24H), 0.93-0.82 (m, 12H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 152.95, 136.86, 134.37, 129.06, 128.73, 128.56, 126.81, 126.75, 126.53, 125.70, 120.73, 120.25 (q, 322.7 Hz), 118.04, 76.67, 50.52, 49.86, 40.29, 39.52, 37.59, 37.57, 37.43, 32.95, 32.83, 31.28, 28.13, 24.96, 24.60, 24.41, 22.87, 22.78, 22.42, 21.12, 19.91, 19.81, 16.23. $^{19}$F NMR (470 MHz, CDCl$_3$) δ -76.37. HRMS (ESI) m/z calculated for C$_{38}$H$_{57}$NO$_3$F$_3$S [M+H]$^+$: 664.4011, found 664.3995. [$\alpha$]$^2$D = +17.2 ° ($c$ = 0.52, CHCl$_3$)

Dextramethorphan derivative (+)-29. To a ½ dram vial equipped with a stir bar, (+)-allylated dextramethorphan derivative (S42) (56.3 mg, 0.2 mmol, 1.0 equiv) and toluene (0.2 mL, 1.0 M) were added, followed by dichloroacetic acid (16.5 µL, 0.2 mmol, 1.0 equiv). The mixture was
stirred at 45 °C for 20 min. Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5-dimethylbenzoquinone (2,5 DMBQ) (30 mg, 0.22 mmol, 1.1 equiv) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv) was added and the vial was capped and heated to 45 °C for 24 hours (monitored by TLC). The vial was allowed to cool to room temperature and diluted with ethyl acetate (1 mL). The reaction mixture was washed with sat. aq. K$_2$CO$_3$, layers are separated and the aqueous layer was extracted with ethyl acetate (20 mL x 3). The mixture was concentrated under reduced pressure, diluted with 2 mL CDCl$_3$ and an internal standard (trifluorotoluene 14.6 mg, 0.1 mmol, 0.5 equiv) was added for crude $^1$H NMR analysis. The mixture was then concentrated under reduced pressure and subjected to flash column chromatography (50ml silica gel, 0% => 10% MeOH in CH$_2$Cl$_2$) to provide desired product (+)-29 as a colorless oil. Run 1: (95.7 mg, 92.3% yield); Run 2: (94.9 mg, 91.5% yield); Run 3: (94.8 mg, 91.4% yield). **Average: 92% yield ± 0.5%**. Without dichloroacetic acid following general procedure, 31.4 mg, 30% yield.

**$^1$H NMR** (500 MHz, Chloroform-d) δ 7.42-7.32 (m, 5H), 7.17-7.13 (m, 2H), 7.10 (d, $J = 7.8$ Hz, 1H), 6.38 (d, $J = 15.7$ Hz, 1H), 5.94 (dt, $J = 15.7$, 7.1 Hz, 1H), 4.55 (br s, 2H), 4.02 (br s, 2H), 3.05 (d, $J = 18.9$, 1H), 3.00 (s, 1H), 2.79 (dd, $J = 18.9$, 5.8 Hz, 1H), 2.68-2.60 (m, 1H), 2.51 (s, 3H), 2.41 (d, $J = 13.9$ Hz, 1H), 2.18 (t, $J = 12.7$ Hz, 1H), 2.02 (d, $J = 10.5$ Hz, 1H), 1.91 (t, $J = 13.0$, 4.7 Hz, 1H), 1.66 (d, $J = 12.5$ Hz, 1H), 1.57 (d, $J = 13.4$ Hz, 1H), 1.48-1.35 (m, 4H), 1.29-1.20 (m, 1H), 1.15-1.03 (m, 1H). **$^{13}$C NMR** (125 MHz, CDCl$_3$) δ 140.22, 137.19, 136.46, 136.28, 134.28, 134.25, 129.03, 128.68, 128.62, 128.36, 124.26, 123.73, 120.89, 120.17 (q, 322.8 Hz.), 58.46, 51.10, 49.90, 47.34, 44.24, 42.37, 41.15, 36.84, 36.11, 26.57, 26.34, 24.50, 22.07. **$^{19}$F NMR** (470 MHz, CDCl$_3$) δ -76.25. **HRMS (ESI) m/z** calculated for C$_{28}$H$_{34}$N$_2$O$_2$F$_3$S [M+H]+: 519.2293, found 519.2301. [$\alpha$]$^D_{23}$ = +19.6 ° (c = 0.50, CHCl$_3$)

**Ethynyl estradiol derivative (-)-30.** The reaction was performed according to the general procedure, 31.4 mg, 30% yield. Without dichloroacetic acid following general procedure, 31.4 mg, 30% yield. **Average: 90% yield ± 0.5%**. Without dichloroacetic acid following general procedure, 31.4 mg, 30% yield. Without dichloroacetic acid following general procedure, 31.4 mg, 30% yield. Without dichloroacetic acid following general procedure, 31.4 mg, 30% yield. Without dichloroacetic acid following general procedure, 31.4 mg, 30% yield. Without dichloroacetic acid following general procedure, 31.4 mg, 30% yield. Without dichloroacetic acid following general procedure, 31.4 mg, 30% yield.
Estrone derivative (+)-31. The reaction was performed according to the general procedure using Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allylated estrone (S40) (58.9 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv) for 24 hours. The reaction mixture was purified by flash column chromatography (50 mL silica gel, 0% => 10% acetone in hexanes) to provide pure desired product (+)-31 as a white solid. Run 1: (79.9 mg, 75.2% yield); Run 2: (80.5 mg, 75.7% yield); Run 3: (79.1 mg, 74.3% yield). Average: 75% yield ± 0.7%.

1H NMR (500 MHz, Chloroform-d) $\delta 7.44$-7.36 (m, 3H), 7.34 (d, $J = 6.7$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 1H), 7.15 (d, $J = 8.1$ Hz, 1H), 7.08 (s, 1H), 6.38 (d, $J = 15.7$ Hz, 1H), 6.00 (dt, $J = 15.9$, 7.0 Hz, 1H), 4.54 (br s, 2H), 4.01 (br s, 2H), 2.94 (dd, $J = 9.3$, 4.2 Hz, 2H), 2.52 (dd, $J = 18.9$, 8.7 Hz, 1H), 2.47-2.41 (m, 1H), 2.37-2.28 (m, 1H), 2.16 (dt, $J = 18.2$, 8.8 Hz, 1H), 2.11-2.03 (m, 2H), 2.01-1.97 (m, 1H), 1.71-1.41 (m, 6H), 0.93 (s, 3H). 13C NMR (125 MHz, CDCl$_3$) $\delta 220.81$, 140.51, 137.01, 136.30, 134.17, 133.31, 129.07, 128.69, 128.63, 127.35, 125.88, 124.16, 120.19, 50.81, 50.58, 49.68, 48.06, 44.57, 38.20, 35.95, 31.68, 29.46, 26.52, 25.81, 21.70, 13.94. HRMS (ESI) $m/z$ calculated for C$_{29}$H$_{33}$NO$_3$F$_3$S [M+H]$^+$: 532.2133, found 532.2129. $[\alpha]^{22}_D = +46.7^\circ$ (c = 0.50, CHCl$_3$)

Estrone derivative (+)-31a.

To an oven-dried 25 mL round-bottom flask equipped with a stir bar, (+)-44 (531.6 mg, 1.0 mmol, 1.0 equiv) and THF (10 mL, 0.1 M) were added. The reaction flask was cooled to -78 °C and allylmagnesium chloride (0.6 mL, 2.0 M, 1.2 equiv) was added dropwise. The reaction was allowed to stir at -78 °C for 1 h and then quenched with sat. aq. NH$_4$Cl. Layers were separated and the aqueous layer was extracted with diethyl ether (20 ml x 3). The organic layers were combined and dried over MgSO$_4$, filtered, concentrated under vacuum and subjected to a flash column chromatography (100 mL silica gel, 0% => 10% Acetone in hexanes) to provide pure product as a colorless oil. Run 1: (485.4 mg, 84.6% yield); Run 2: (492.2 mg, 85.8% yield). Average: 85% yield.

An oven-dried 25 ml round-bottom flask was charged with a stir bar, product from last step (286.9 mg, 0.5 mmol, 1.0 equiv) and toluene (10 ml, 0.05 M). The reaction was cooled to 0 °C and Red-Al (3.5 M in toluene) (sodium bis(2-methoxyethoxy)aluminumhydride) (5.0 mmol, 1.42 mL)
was added dropwise and the reaction was allowed to warm up to room temperature and stirred at room temperature for 16 hours. Upon completion, the reaction was cooled to 0 °C and 5% NH₄Cl was added. Layers were separated and the aqueous layer was further extracted with CH₂Cl₂ (30 ml x 3). The organic layers were combined and dried over Na₂SO₄, filtered, concentrated under vacuum and subjected to a flash column chromatography (100 mL silica gel, 0% => 5% MeOH in CH₂Cl₂) to provide pure product as a colorless gel. Run 1: (201.9 mg, 91.4% yield); Run 2: (199.6 mg, 90.4 % yield) Average: 91% yield.

1H NMR (500 MHz, Chloroform-d) δ 7.36 – 7.31 (m, 4H), 7.28 – 7.23 (m, 2H), 7.17 (d, J = 8.1, 1H), 7.10 (s, 1H), 6.49 (d, J = 16.1 Hz, 1H), 6.27 (dt, J = 15.9, 6.4 Hz, 1H), 6.02 (ddt, J = 17.2, 10.2, 7.1 Hz, 1H), 5.25 – 5.11 (m, 2H), 3.84 (s, 2H), 3.43 (d, J = 6.4, 2H), 2.87 – 2.80 (m, 2H), 2.41 – 2.32 (m, 2H), 2.24-2.18 (m, 2H), 2.05 – 1.96 (m, 1H), 1.95-1.88 (m, 1H), 1.79 – 1.32 (m, 11H), 0.93 (s, 3H).

13C NMR (126 MHz, CDCl3) δ 140.2, 139.8, 136.9, 135.0, 134.5, 131.5, 128.5, 128.3, 127.5, 127.1, 127.0, 125.6, 123.6, 119.2, 82.5, 53.2, 49.7, 46.5, 44.3, 41.9, 39.4, 34.9, 31.9, 29.6, 27.5, 26.2, 23.5, 14.4. HRMS (ESI) m/z calculated for C₃₁H₄₀NO [M+H⁺]: 442.3110, found 442.3113.

[α]²²D = +85.3º (c = 0.53, CHCl₃)

Estrone derivative (+)-31b.

To a flame-dried 250 mL round bottom flask equipped with a stir bar was added (+)-44 (1.595 g, 3.0 mmol, 1.0 equiv) and THF (20 mL). The reaction mixture was cooled down to -78 °C, with stirring. LHMDS (551 mg, 3.3 mmol, 1.1 equiv) was dissolved in THF (20 mL), and was slowly added into the reaction mixture. The reaction was stirred for 1 h. PhN(SO₂CF₃)₂ (1.18 g, 3.3 mmol, 1.1 equiv) was then dissolved in THF (3 mL) and was added dropwise into the reaction mixture via syringe. The reaction was stirred for an additional 20 min and then allowed to warm up to room temperature and stirred for an additional hour. Water (5 mL) was then added to quench the reaction and THF was removed in vacuo. Diethyl ether (20 mL) was added to extract the product, and the organic layer was washed with sat. aq. NH₄Cl (10 mL) and brine (10 mL). The organic layer was then separated, dried over MgSO₄ and concentrated in vacuo. Purification by flash chromatography on silica eluting with 2 => 5% EtOAc/hexanes yielded the product as a white solid. Run 1: (1.585 g, 79.6% yield); Run 2: (1.609 mg, 80.8% yield). Average: 80% yield, with minor PhN(SO₂CF₃)₂ as impurity, which was removed in the subsequent step.

The product (2.655 g, 2.0 mmol, 1.0 equiv) was dissolved in DMSO (60 mL) at 60 °C and cannulated into a flame-dried 500 mL Schlenk flask charged with LiCl (1.02 g, 24 mmol, 60 equiv), Pd(PPh₃)₄ (462.2 mg, 0.4 mmol, 0.10 equiv), CuCl (1.98 g, 20 mmol, 5.0 equiv), DMSO (100 mL) and a magnetic stir bar. 3-(tributylstanny)pyridine (2.6 mL, 4 mmol, 2.0 equiv) was then added via syringe. The mixture was degassed through freeze-pump-thaw (-78 °C→0 °C) three
times, and was stirred for 1 h at room temperature. The reaction flask was then placed into 60 °C oil bath and stirred vigorously for 20 h. The reaction was then quenched with the mixed solution of concentrated NH₄OH (5 mL) and brine (100 mL), extracted with diethyl ether (4 x 50 mL). The organic layers were then combined, dried over MgSO₄ and concentrated in vacuo. Purification by flash chromatography on silica eluting with 2 => 10% Methanol in hexanes yielded product as a colorless gel. Run 1: (1.036 g, 87.4% yield); Run 2: (1.020 g, 86.1% yield). **Average: 87% yield.**

An oven-dried 25 ml round-bottom flask was charged with a stir bar, product from last step (296.1 mg, 0.5 mmol, 1.0 equiv) and toluene (10 ml, 0.05 M). The reaction was cooled to 0 °C and Red-Al (3.5 M in toluene) (sodium bis(2-methoxyethoxy)aluminumhydride) (5.0 mmol, 1.42 mL) was added dropwise and the reaction was allowed to warm up to room temperature and stirred at room temperature for 16 hours. Upon completion, the reaction was cooled to 0 °C and 5% NH₄Cl was added. Layers were separated and the aqueous layer was further extracted with CH₂Cl₂ (30 ml x 3). The organic layers were combined and dried over Na₂SO₄, filtered, concentrated under vacuum and subjected to a flash column chromatography (100 mL silica gel, 0% => 10% MeOH in CH₂Cl₂) to provide pure product as a colorless gel. Run 1: (147.7 mg, 64.1% yield); Run 2: (142.8 mg, 62.0% yield). **Average: 63% yield.**

**1H NMR** (500 MHz, Chloroform-d) δ 8.65 (dd, J = 2.3, 0.9 Hz, 1H), 8.48 (dd, J = 4.8, 1.6 Hz, 1H), 7.68 (dt, J = 7.9, 1.9 Hz, 1H), 7.35 – 7.32 (m, 4H), 7.29 – 7.22 (m, 3H), 7.18 (dd, J = 8.1, 1.9 Hz, 1H), 7.12 (d, J = 1.8 Hz, 1H), 6.53 – 6.47 (m, 1H), 6.28 (dt, J = 15.8, 6.3 Hz, 1H), 6.03 (dd, J = 3.3, 1.8 Hz, 1H), 3.84 (s, 2H), 3.44 (d, J = 6.32Hz), 3.00 – 2.83 (m, 2H), 2.45 – 2.31 (m, 3H), 2.22 – 2.11 (m, 2H), 1.99 (m , 1H), 1.83 (m, 2H), 1.74 – 1.63 (m, 3H), 1.57 – 1.44 (m, 1H), 1.05 (s, 3H). **13C NMR** (126 MHz, CDCl₃) δ 152.0, 148.1, 140.4, 139.9, 136.9, 134.7, 133.8, 133.1, 131.5, 129.2, 128.6, 128.4, 127.8, 127.1, 127.1, 125.4, 123.7, 123.2, 57.0, 53.4, 51.4, 47.9, 44.7, 37.3, 35.5, 31.7, 29.6, 27.8, 26.5, 16.8. **HRMS** (ESI) m/z calculated for C₃₅H₇₃N₂ [M+H]+: 461.2957, found 461.2948. \([\alpha]^{22}_{D} = +23.8^\circ (c = 0.82, \text{CHCl}_3)\)

**Estrone derivative (+)-32.**

Pd(OAc)₂ (6.7 mg, 0.03 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (10.2 mg, 0.03 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (45 mg, 0.33 mmol, 1.1 equiv), allylated estrone (S40) (88.4 mg, 0.3 mmol, 1.0 equiv) and 4-nitro-N-phenethylbenzenesulfonamide (91.8 mg, 0.3 mmol, 1.0 equiv) were reacted according to the general procedure in dioxane (0.3 mL, 1.0 M) for 72 hours. The mixture was concentrated under reduced pressure, diluted with 2 mL CDCl₃ and analyzed by crude ¹H NMR with internal standard (trifluorotoluene 44.1 mg, 0.1 0.302 mmol, 1.01 equiv): about 66% NMR yield (see spectrum). Purification by flash column chromatography (100 mL silica gel, 0% => 15% Acetone in hexanes provided a mixture of product 32 with 4-nitro-N-phenethylbenzenesulfonamide.

To a 20 mL vial was added a stir bar, mixture from last step, Cs₂CO₃ (325.8 mg, 1.0 mmol), DMF (1 mL) and PhSH (307.3µL, 3.0 mmol). The reaction was heated to 45 °C for 2 hours. The vial was allowed to cool to room temperature, diluted with 10 mL Et₂O and added 5% aq. NaHCO₃. Layers were separated, aqueous layer was extracted with Et₂O. Organic layers were combined, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The crude mixture was
purified by flash silica plug (50 mL silica gel, 100 mL 2% MeOH/CH$_2$Cl$_2$ then switch to 4% MeOH/CH$_3$Cl to give pure product as a colorless oil.
Run 1: (60.5 mg, 50.5% yield); Run 2: (63.7 mg, 53.1% yield); Run 3: (64.0 mg, 53.4% yield).  
Average: 52% yield ± 1.9% over two steps.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.40 – 7.31 (m, 4H), 7.30 – 7.21 (m, 2H), 7.18 (dd, J = 8.1, 1.9 Hz, 1H), 7.11 (d, J = 1.8 Hz, 1H), 6.50 (d, J = 15.8 Hz, 1H), 6.28 (dt, J = 15.8, 6.4 Hz, 1H), 3.87 (s, 2H), 4.00-3.70 (br s, 1H), 3.45 (d, J = 6.4 Hz, 2H), 2.90 (dd, J = 9.1, 4.2 Hz, 2H), 2.54 – 2.45 (m, 1H), 2.45 – 2.36 (m, 1H), 2.28 (td, J = 10.8, 4.3 Hz, 1H), 2.14-1.92 (m, 3H), 1.67 – 1.37 (m, 6H), 0.91 (s, 3H).  
$^{13}$C NMR (126 MHz, Chloroform-d) δ 221.2, 139.7, 138.8, 137.0, 134.8, 132.9, 128.9, 127.8, 127.4, 126.3, 126.0, 124.2, 55.9, 50.9, 50.9, 48.4, 44.8, 38.5, 36.2, 32.0, 29.8, 26.0, 21.9, 22.0, 14.2.  
HRMS (ESI) m/z calculated for C$_{28}$H$_{34}$NO [M+H]+: 400.2640, found 400.2629. $[\alpha]^{22}_D = +84.9^\circ$ (c = 1.0, CHCl$_3$)  

α-Methyl benzylamine-tocopherol conjugate (+)-33. The reaction was performed according to the general procedure using Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2.5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (+)-Allylated-δ-Tocopherol derivative (S39) (85.3 mg, 0.2 mmol, 1.0 equiv) and (-)-(S)-1,1,1-trifluoro-N-(1-(4-nitrophenyl)ethyl)methanesulfonamide (S27) (59.6 mg, 0.2 mmol, 1.0 equiv) for 72 hours. The reaction mixture purified by flash column chromatography (column 1: 50 mL silica gel, 0% => 5% acetone in hexanes; column 2: 50 mL silica gel, 10% => 50% CH$_3$Cl in hexanes) to provide pure desired product (+)-33 as a yellow oil. Run 1: (112.4 mg, 77.7% yield); Run 2: (112.9 mg, 78.1% yield); Run 3: (110.7 mg, 76.5% yield). Average: 77% yield ± 0.8%.  
With 5% Pd(OAc)$_2$ and (+)-MeO-SOX ligand (L-5): Run 1: (92.0 mg, 63.6% yield); Run 2: (93.1 mg, 64.4% yield); Average: 64% yield  

$^1$H NMR (500 MHz, Chloroform-d) δ 8.20 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 6.73 (s, 1H), 6.61 (s, 1H), 6.08 (d, J = 15.7 Hz, 1H), 5.54 (s, 1H), 5.41-5.32 (m, 1H), 4.09-3.85 (m, 2H), 2.75-2.58 (m, 2H), 2.11 (s, 3H), 1.81 (d, J = 7.1, 3H), 1.79-1.70 (m, 2H), 1.62-1.02 (m, 24H), 0.92-0.81 (m, 12H).  
$^{13}$C NMR (125 MHz, CDCl$_3$) δ 152.84, 147.74, 146.07, 134.72, 128.97, 126.73, 126.43, 126.31, 125.41, 123.88, 120.65, 120.52, 120.07 (q, 321.3 Hz), 76.65, 56.68, 48.68, 40.35, 39.51, 37.58, 37.55, 37.41, 32.93, 32.82, 32.01, 29.32, 28.12, 24.94, 24.59, 24.32, 22.86, 22.77, 22.30, 21.10, 19.89, 19.79, 16.15. (one peak missing probably due to overlapping). $^{19}$F NMR (470 MHz, CDCl$_3$) δ-76.17. HRMS (ESI) m/z calculated for C$_{30}$H$_{37}$N$_2$O$_3$S$_3$ [M+H]+: 722.3940, found 722.3926. $[\alpha]^{23}_D = +37.8^\circ$ (c = 0.5, CHCl$_3$)  
Complete stereoretention for this cross-coupling was determined by chiral HPLC analysis. (Product from reaction using (-)-(S)-1,1,1-trifluoro-N-(1-(4-nitrophenyl)ethyl)methanesulfonamide (S27) versus product from reaction using known mixture of 62% (-)-(S)-1,1,1-trifluoro-N-(1-(4-nitrophenyl)ethyl)methanesulfonamide (S27) and 38% (+)-(R)-1,1,1-trifluoro-N-(1-(4-nitrophenyl)ethyl)methanesulfonamide). Chiralpak AD-RH column, 0.5 mL/min, 10% EtOH in H$_2$O, λ = 254nm (4nm). tR(major) = 22.401 min.
Gramine-tocopherol conjugate (+)-34. The reaction was performed according to the general procedure using Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (+)-Allylated-δ-Tocopherol derivative (S39) (85.3 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-((1-methyl-1H-indol-3-yl) methyl) methanesulfonamide (S30) (58.2 mg, 0.2 mmol, 1.0 equiv) for 24 hours. The reaction mixture was purified by flash column chromatography (50 mL silica gel, 10% => 30% CH$_2$Cl$_2$ in hexanes) to provide pure desired product (+)-34 as a colorless oil. Run 1: (100.8 mg, 70.3% yield); Run 2: (101.6 mg, 70.9% yield); Run 3: (102.2 mg, 71.3% yield). **Average: 71% yield ± 0.5%**.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.76 (dd, J = 8.0, 1.0 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.30 (ddd, J = 8.2, 6.8, 1.1 Hz, 1H), 7.20 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.11 (s, 1H), 6.97 (br s, 1H), 6.89 (br s, 1H), 6.33 (d, J = 15.7 Hz, 1H), 5.89 (dt, J = 15.7, 7.0 Hz, 1H), 4.76 (br s, 2H), 4.02 (br s, 2H), 3.80 (s, 3H), 2.84-2.71 (m, 2H), 2.20 (s, 3H), 1.86 (dt, J = 13.8Hz, 6.9 Hz, 1H), 1.79 (dt, J = 13.3Hz, 6.5 Hz, 1H), 1.64-1.01 (m, 24H), 0.98-0.81 (m, 12H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 152.80, 137.15, 135.95, 129.72, 127.44, 126.76, 126.73, 126.68, 125.56, 122.33, 120.71, 120.29 (q, 322.8 Hz), 120.00, 119.23, 118.92, 109.62, 107.53, 76.63, 49.36, 42.45, 40.29, 39.52, 37.58, 37.58, 37.42, 33.05, 32.94, 32.84, 31.29, 28.13, 24.96, 24.60, 24.41, 22.88, 22.78, 22.44, 21.13, 19.91, 19.81, 16.26. $^{19}$F NMR (470 MHz, CDCl$_3$) δ -76.40. **HRMS (ESI) m/z calculated for C$_{41}$H$_{60}$N$_2$O$_3$F$_3$S [M+H]$^+$: 717.4277, found 717.4265. [$\alpha$]$^2_D = +7.3^\circ$ (c = 0.51, CHCl$_3$)

Tyrosine-tocopherol conjugate (-)-35. The reaction was performed according to the general procedure using Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (+)-Allylated-δ-Tocopherol derivative (S39) (85.3 mg, 0.2 mmol, 1.0 equiv) and methyl-((S)-2-((trifluoromethyl)sulfonyl)oxy) phenyl propanoate (S29) (91.9 mg, 0.2 mmol, 1.0 equiv) for 72 hours. The reaction mixture was purified by flash column chromatography (column 1: 50 mL silica gel, 0% => 5% acetone in hexanes; column 2: 50 mL silica gel, 10% => 50% CH$_2$Cl$_2$ in hexanes) to provide pure desired product (-)-35 as a colorless oil. Run 1: (136.7 mg, 77.3% yield); Run 2: (135.4 mg, 76.6% yield); Run 3: (139.8 mg, 79.1% yield). **Average: 78% yield ± 1.3%**.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.30 (d, J = 8.7 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.98 (br s, 1H), 6.89 (br s, 1H), 6.43 (d, J = 15.8 Hz, 1H), 5.88 (dt, J = 15.8, 7.1 Hz, 1H), 4.71 (br s, 1H), 4.20 (br s, 2H), 3.69 (s, 3H), 3.50 (dd, J = 14.3, 8.0 Hz, 1H), 3.09 (dd, J = 14.2, 7.0 Hz, 1H), 2.79-2.68 (m, 2H), 2.16 (s, 3H), 1.83 (m, 1H), 1.76 (m, 1H), 1.62-0.99 (m, 24H), 0.88-0.82 (m, 12H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 169.42, 153.10, 148.80, 136.88, 135.83, 131.41, 126.86, 126.82, 126.54, 125.77, 121.60, 120.85, 119.92, 119.91(q, J = 323.1Hz), 118.95 (q, 320.8 Hz), 76.75,
Leelamine-tocopherol conjugate (+)-36. The reaction was performed according to the general procedure using Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (+)-Allylated-δ-Tocopherol derivative (S39) (85.3 mg, 0.2 mmol, 1.0 equiv) and (+)-N-triflyl protected dihydroabietylamine (S28) (83.5 mg, 0.2 mmol, 1.0 equiv) for 72 hours. The reaction mixture purified by flash column chromatography (50 mL silica gel, 0% → 10% acetone in hexanes) to provide pure desired product (+)-36 as a colorless oil. Run 1: (100.2 mg, 59.5% yield); Run 2: (98.9 mg, 58.7% yield); Run 3: (100.8 mg, 59.8% yield). Average: 59% yield ± 0.6%.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.17 (d, J = 8.2 Hz, 1H), 7.01 (s, 2H), 6.92 (dd, J = 9.2, 2.1 Hz, 2H), 6.46 (d, J = 15.7 Hz, 1H), 5.93 (dt, J = 15.1, 7.1 Hz, 1H), 4.33 (br s, 1H), 4.17 (br s, 1H), 3.46 (d, J = 14.9 Hz, 1H), 3.24-3.16 (m, 1H), 2.97-2.88 (m, 2H), 2.84 (p, J = 6.9 Hz, 1H), 2.80-2.73 (m, 2H), 2.35-2.29 (m, 1H), 2.19 (s, 3H), 1.91-1.66 (m, 6H), 1.64-1.03 (m, 40H), 0.93-0.83 (m, 12H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 152.95, 147.23, 145.86, 136.85, 134.44, 126.99, 126.82, 126.72, 126.49, 125.71, 124.03, 123.98, 120.73, 120.54 (q, J = 325.3 Hz) 118.51, 76.66, 57.69, 53.61, 46.31, 40.28, 39.52, 39.34, 38.14, 37.79, 37.58, 37.55, 37.42, 33.60, 32.94, 32.83, 31.24, 29.88, 28.13, 25.78, 24.96, 24.59, 24.41, 24.15, 24.11, 22.88, 22.79, 22.40, 21.12, 19.91, 19.80, 19.42, 18.65, 16.25. (48 peaks in total, one peak missing probably due to overlapping). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -74.31 HRMS (ESI) m/z calculated for C$_{51}$H$_{79}$NO$_3$F$_3$S [M+H]$^+$: 842.5733, found 842.5709. $[a]^{23}_{D}$ = +42.7° (c = 0.50, CHCl$_3$)
**Synthetic examples**

**Abamines:**

Scheme S7. 2-step synthesis of abamine core

\[(E)-N-(3-(3,4-dimethoxyphenyl)allyl)-1,1,1-trifluoro-N-(4-fluorobenzyl) methane sulfonamide (S43)\]. To a 1 dram vial equipped with a stir bar was added Pd(OAc)\(_2\) (5.6 mg, 0.025 mmol, 0.025 equiv), \((\pm)\)-MeO-SOX ligand (L-5) (8.6 mg, 0.025 mmol, 0.025 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (150 mg, 1.1 mmol, 1.1 equiv), methyl eugenol (178.2 mg, 1.0 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-(4-fluorobenzyl)methanesulfonamide (S24) (257.2 mg, 1.0 mmol, 1.0 equiv). Toluene (1.0 mL, 1.0 M) was added and the vial was capped and heated at 45 °C for 48 hours (monitored by TLC). The vial was allowed to cool to room temperature and diluted with acetone (1 mL). The reaction mixture was plug filtered a ½ inch pipette silica plug and concentrated under reduced pressure. The crude mixture was diluted with 10 mL CDCl\(_3\) and an internal standard (trifluorotoluene 73 mg, 0.5 mmol, 0.5 equiv) was added for crude \(^1\)H NMR. The mixture was concentrated under reduced pressure and subjected to flash column chromatography (column 1: 100 mL silica gel 10% => 30% acetone in hexanes; column 2: 100 mL silica gel, 10% => 100% CH\(_2\)Cl\(_2\) in hexanes) to provide pure desired product S43 as white solid. Run 1: (371.6 mg, 85.7% yield); Run 2: (374.1 mg, 86.3 % yield). **Average:** 86% yield.

\(^1\)H NMR (500 MHz, Chloroform-d) δ 7.32 (dd, \(J = 8.4, 5.2\) Hz, 2H), 7.07 (t, \(J = 8.4\) Hz, 2H), 6.87 (dd, \(J = 8.3, 1.8\) Hz, 1H), 6.85-6.81 (m, 2H), 6.34 (d, \(J = 15.7\) Hz, 1H), 5.84 (dt, \(J = 15.0, 7.1\) Hz, 1H), 4.52 (br s, 2H), 4.01 (br s, 2H), 3.90 (s, 3H), 3.89 (s, 3H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 162.8 (d, \(J = 247.6\) Hz), 149.7, 149.2, 136.1, 130.5 (d, \(J = 8.3\) Hz), 130.2 (d, \(J = 3.1\) Hz), 128.6, 120.2 (q, \(J = 322.8\) Hz (124.0, 121.4, 118.9, 116.3)), 120.1, 119.5, 116.0 (d, \(J = 21.6\) Hz), 111.2, 108.9, 56.0, 55.9, 50.3, 50.0.

\(^{19}\)F NMR (470 MHz, CDCl\(_3\)) δ -76.26, -113.55.

HRMS (ESI) \(m/z\) calculated for C\(_{19}\)H\(_{20}\)NO\(_4\)F\(_4\)S [M+H]\(^+\): 434.1049, found 434.1042.
(E)-3-(3,4-dimethoxyphenyl)-N-(4-fluorobenzyl)prop-2-en-1-amine (37). An oven-dried 25 ml flask was charged with a stir bar, S43 (216.7 mg, 0.5 mmol, 1.0 equiv) and toluene (10 ml, 0.05 M). The reaction was cooled to 0 °C and Red-Al (3.5 M in toluene) (sodium bis(2-methoxyethoxy)aluminohydride) (5.0 mmol, 1.42 mL) was added dropwise and the reaction was allowed to warm up to room temperature and stirred at room temperature for 16 hours. Upon completion, the reaction was cooled to 0 °C and 5% NH₄Cl was added. Layers were separated and the aqueous layer was further extracted with CH₂Cl₂ (30 ml x 3). The organic layers were combined and dried over Na₂SO₄, filtered, concentrated under vacuum and subjected to a flash column chromatography (100 mL silica gel, 0% => 10% MeOH in CH₂Cl₂) to provide pure product (37). Run 1: (138.9 mg, 92.2% yield); Run 2: (139.5 mg, 92.6% yield) Average: 92% yield.

1H NMR (500 MHz, Chloroform-d) δ 7.31 (dd, J = 8.4, 5.6 Hz, 2H), 7.01 (t, J = 8.7 Hz, 2H), 6.93 (d, J = 1.9 Hz, 1H), 6.89 (dd, J = 8.2, 2.0 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 6.47 (d, J = 15.8 Hz, 1H), 6.17 (dt, J = 15.6, 6.4 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.80 (s, 2H), 3.41 (d, J = 6.4 Hz, 2H), 2.18 (br s, 1H). Spectral data for S42 was consistent with previously literature report.

(E)-N-benzyl-1,1,1-trifluoro-N-(3-(4-(trifluoromethyl)phenyl)allyl)methanesulfonamide (38). Pd(OAc)₂ (2.2 mg, 0.01 mmol, 0.05 equiv), (±)-MeO-SOX ligand (L-5) (3.4 mg, 0.01 mmol, 0.05 equiv), 2.5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), 1-allyl-4-(trifluoromethyl)benzene (37.2 mg, 0.2 mmol) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol) were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (50 mL silica gel, 10% => 30% CH₂Cl₂ in hexanes) provided pure product 38 as a colorless oil. Run 1: (67.9 mg, 80.1% yield); Run 2: (68.0 mg, 80.3% yield); Run 3: (67.6 mg, 79.8% yield). Average: 80% yield ± 0.3%.

1H NMR (500 MHz, Chloroform-d) δ 7.59 (d, J = 8.1 Hz, 2H), 7.43-7.37 (m, 5H), 7.37-7.34 (m, 2H), 6.44 (d, J = 15.8 Hz, 1H), 6.10 (dt, J = 15.8, 7.0 Hz, 1H), 4.57 (br s, 2H), 4.07 (br s, 2H). 13C NMR (126 MHz, Chloroform-d) δ 139.2, 134.6, 134.1, 130.33 (q, J = 32.4 Hz), 129.2, 128.8, 128.7, 126.9, 125.9 (d, J = 260.2 Hz), 125.8 (q, J = 3.8 Hz), 124.9, 120.2 (q, J = 322.7 Hz), 51.6, 49.7. 19F NMR (470 MHz, Chloroform-d) δ -63.02, -76.20. HRMS (ESI) m/z calculated for C₁₈H₁₅NO₂F₆SnNa [M+Na]⁺: 446.0625, found 446.0649.

Methyl-(E)-4-(3-(N-benzyl-1,1,1-trifluoromethyl)sulfonamido)prop-1-en-1-yl)benzoate (39). Pd(OAc)₂ (2.2 mg, 0.01 mmol, 0.05 equiv), (±)-MeO-SOX ligand (L-5) (3.4 mg, 0.01 mmol, 0.05 equiv), 2.5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), Methyl 4-allylbenzoate (35.2 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 2.5% => 15% acetone in hexanes, column 2: 50 mL silica gel, 10% => 50% CH₂Cl₂ in hexanes) provided pure product 39 as a colorless oil. Run 1: (78.0 mg, 94.3% yield); Run 2: (78.6 mg, 95.1% yield); Run 3: (79.1 mg, 95.7% yield). Average: 95% yield ± 0.7%.
**Chloroform**

1H NMR (500 MHz, Chloroform-d) δ 8.00 (d, J = 8.1 Hz, 2H), 7.43-7.31 (m, 7H), 6.43 (d, J = 15.8 Hz, 1H), 6.11 (dt, J = 15.8, 7.0 Hz, 1H), 4.56 (br s, 2H), 4.06 (br s, 2H), 3.93 (s, 3H). 13C NMR (126 MHz, Chloroform-d) δ 166.9, 140.2, 135.2, 134.2, 130.3, 130.1, 129.3, 128.9, 128.9, 126.7, 124.8, 120.33 (q, J = 322.9 Hz), 52.4, 51.6, 49.9. 19F NMR (470 MHz, Chloroform-d) δ -76.19. HRMS (ESI) m/z calculated for C19H19NO4F3S [M+H]+: 414.0987, found 414.0974.

(E)-N-benzyl-1,1,1-trifluoro-N-(3-(4-formylphenyl)allyl)methanesulfonamide (40). Pd(OAc)$_2$ (2.2 mg, 0.01 mmol, 0.05 equiv), (±)-MeO-SOX ligand (L-5) (3.4 mg, 0.01 mmol, 0.05 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), 4-allylbenzaldehyde (29.2 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 2.5% acetone in hexanes, column 2: 50 mL silica gel, 10% => 50% CH2Cl$_2$ in hexanes) provided pure product 40 as a colorless oil. Run 1: (62.0 mg, 80.9% yield); Run 2: (60.9 mg, 79.4% yield); Run 3: (61.5 mg, 80.2% yield). Average: 80% yield ± 0.8%.

1H NMR (500 MHz, Chloroform-d) δ 10.00 (s, 1H), 7.87-7.82 (m, 2H), 7.48-7.32 (m, 7H), 6.44 (d, J = 15.8 Hz, 1H), 6.15 (dt, J = 15.8, 7.0, 1H), 4.56 (br s, 2H), 4.07 (br s, 2H). 13C NMR (126 MHz, Chloroform-d) δ 191.8, 141.7, 136.2, 134.9, 134.2, 130.4, 129.3, 129.0, 128.9, 127.4, 125.9, 120.3 (q, J = 322.7 Hz), 51.8, 49.9. 19F NMR (470 MHz, Chloroform-d) δ -76.16. HRMS (ESI) m/z calculated for C19H17NO4F3S [M+H]^+: 384.0880, found 384.0880.

(E)-N-benzyl-N-(3-(4-bromophenyl)allyl)-1,1,1-trifluoromethanesulfonamide (41). Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), 1-allyl-4-bromobenzene (39.4 mg, 0.2 mmol) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol) were reacted according to general procedure for 24 hours. Purification by flash column chromatography (50 mL silica gel, 2.5% => 15% acetone in hexanes) provided pure product 41 as a colorless oil. Run 1: (78.2 mg, 90.0% yield); Run 2: (79.0 mg, 91.0% yield); Run 3: (61.5 mg, 79.0% yield). Average: 90% yield ± 0.6%.

1H NMR (500 MHz, Chloroform-d) δ 7.46 (d, J = 8.4 Hz, 2H), 7.43-7.35 (m, 3H), 7.35-7.31 (m, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.34 (d, J = 15.8 Hz, 1H), 6.00 (dt, J = 15.8, 7.0 Hz, 1H), 4.55 (br s, 2H), 4.02 (br s, 2H). 13C NMR (126 MHz, Chloroform-d) δ 135.0, 134.7, 134.1, 132.0, 129.1, 128.8, 128.7, 128.2, 122.8, 122.5, 120.2 (q, J = 322.8 Hz), 51.3, 49.8. 19F NMR (470 MHz, Chloroform-d) δ -76.23. HRMS (EI) m/z calculated for C19H15NO2F3SBr [M]^+: 432.9959, found 432.9951.
(E)-N-benzyl-1,1,1-trifluoro-N-(3-(4-(hydroxymethyl)phenyl)allyl)methanesulfonamide (42). Pd(OAc)$_2$ (2.2 mg, 0.01 mmol, 0.05 equiv), (+)-MeO-SOX ligand (L-5) (3.4 mg, 0.01 mmol, 0.05 equiv), 2.5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (4-allylphenyl)methanol (29.6 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 2.5% => 15% acetone in hexanes, column 2: 50 mL silica gel, 10% => 50% CH$_2$Cl$_2$ in hexanes) provided pure product 42 as a white solid. Run 1: (68.1 mg, 88.3% yield); Run 2: (67.5 mg, 87.6% yield); Run 3: (69.6 mg, 90.3% yield). **Average: 89% yield ± 1.4%**.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.44-7.30 (m, 9H), 6.41 (d, J = 15.8 Hz, 1H), 6.02 (dt, J = 15.7, 7.1 Hz, 1H), 4.70 (s, 2H), 4.56 (br s, 2H), 4.03 (br s, 2H), 1.77 (s, 1H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 141.3, 136.0, 135.1, 134.2, 129.1, 128.7, 128.7, 127.4, 126.9, 121.8, 120.2 (q, J = 322.7 Hz), 65.0, 51.1, 49.8. $^{19}$F NMR (470 MHz, Chloroform-d) δ -76.26. HRMS (EI) m/z calculated for C$_{18}$H$_{18}$NO$_3$F$_3$S [M$^+$]: 385.0960, found 385.0959.

Methyl (E)-4-(3-(benzylamino)prop-1-en-1-yl)benzoate (43).

Pd(OAc)$_2$ (6.7 mg, 0.03 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (10.2 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2,5-dimethylbenzoquinone) (45 mg, 0.33 mmol, 1.1 equiv), Methyl 4-allylbenzoate (51.3 mg, 0.3 mmol, 1.0 equiv) and 4-nitro-N-phenethylbenzenesulfonamide (91.8 mg, 0.3 mmol, 1.0 equiv) were reacted according to the general procedure in dioxane (0.3 mL, 1.0 M) for 72 hours. The mixture was concentrated under reduced pressure, diluted with 2 mL CDCl$_3$ and analyzed by crude $^1$H NMR with internal standard (trifluorotoluene 24.3 mg, 0.166 mmol, 0.555 equiv): about 71% NMR yield (see spectrum). Purification by flash column chromatography (100 mL silica gel, 0% => 15% acetone in hexanes provided a mixture of product 43 with 4-nitro-N-phenethylbenzenesulfonamide.

To a 20 mL vial was added a stir bar, mixture from last step, Cs$_2$CO$_3$ (325.8 mg, 1.0 mmol), DMF (1 mL) and PhSH (307.3µL, 3.0 mmol). The reaction was heated to 45 °C for 2 hours. The vial was allowed to cool to room temperature, diluted with 10 mL Et$_2$O and added 5% aq. NaHCO$_3$. Layers were separated, aqueous layer was extracted with Et$_2$O. Organic layers were combined, dried over anhydrous MgSO$_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica plug (50 mL silica gel, 100 mL 2% MeOH/ CH$_2$Cl$_2$ then switch to 4% MeOH/CH$_2$Cl$_2$ to give pure product.

Run 1: (56.3 mg, 66.7% yield); Run 2: (57.5 mg, 68.1% yield); Run 3: (54.6 mg, 64.7% yield). **Average: 67% yield ± 1.7%** over two steps.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.98 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.37 – 7.32 (m, 4H), 7.29 – 7.25 (m, 1H), 6.59 (d, J = 15.9 Hz, 1H), 6.44 (dt, J = 15.9, 6.1 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 2H), 3.47 (d, J = 6.1 Hz, 2H), 2.19 – 1.98 (br s, 1H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 167.0, 141.7, 139.9, 131.2, 130.7, 130.0, 129.0, 128.6, 128.4, 127.3, 126.3, 53.4, 52.2, 51.1. HRMS (EI) m/z calculated for C$_{18}$H$_{26}$NO$_3$ [M$^+$]: 282.1494, found 282.1493.

tert-Butyl (E)-benzyl(3-(4-formylphenyl)allyl)carbamate (44).
Pd(OAc)$_2$ (6.7 mg, 0.03 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (10.2 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2,5-dimethylbenzoquinone) (45 mg, 0.33 mmol, 1.1 equiv), 4-allylbenzaldehyde (43.8 mg, 0.23 mmol, 1.0 equiv) and 4-nitro-N-phenethylbenzenesulfonamide (91.8 mg, 0.3 mmol, 1.0 equiv) were reacted according to the general procedure in dioxane (0.3 mL, 1.0 M) for 72 hours. The mixture was concentrated under reduced pressure, diluted with 2 mL CDCl$_3$ and analyzed by crude $^1$H NMR with internal standard (trifluorotoluene 21.8 mg, 0.149 mmol, 0.498 equiv): about 63% NMR yield (see spectrum). Purification by flash column chromatography (100 mL silica gel, 0% => 15% Acetone in hexanes provided a mixture of product 44 with 4-nitro-N-phenethylbenzenesulfonamide.

To a 20 mL vial was added a stir bar, mixture from last step, Cs$_2$CO$_3$ (325.8 mg, 1.0 mmol), DMF (1 mL) and PhSH (307.3 µL, 3.0 mmol). The reaction was heated to 45 °C for 2 hours. The vial was allowed to cool to room temperature for 2 hours and concentrated under reduced pressure. The crude mixture was stirred at room temperature for 2 hours and concentrated under reduced pressure. The crude mixture was purified by flash silica plug (50 mL silica gel, 100 mL 2% MeOH/CH$_2$Cl$_2$ then switch to 4% MeOH/CH$_2$Cl$_2$ to collect pure amine product (not stable under room temperature, carried through the next step).

To a 20 mL vial was added a stir bar, amine product from last step, di-tert-butyldicarbonate (Boc$_2$O) (65.5 mg, 0.3 mmol), Et$_3$N (46.0 µL, 0.33 mmol) and CH$_2$Cl$_2$ (1 mL, 0.33 M). The reaction was stirred at room temperature for 2 hours and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (100 mL silica gel, 0% acetone/hexanes => 10% acetone/hexanes) to give pure product as a colorless oil.

Run 1: (58.1 mg, 55.1% yield); Run 2: (57.1 mg, 54.1% yield); Run 3: (58.9 mg, 55.9% yield). **Average: 55% yield ± 2.5%** over three steps.

$^1$H NMR (500 MHz, Chloroform-d) δ 9.98 (s, 1H), 7.82 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 7.9 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.22 (m, 3H), 6.45 (d, J = 15.9 Hz, 1H), 6.28 (s, 1H), 4.48 (s, 2H), 4.00 (s, 2H), 1.50 (s, 8H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 191.6, 155.8, 143.0, 138.3, 135.7, 130.9, 130.2, 129.7, 128.7, 127.8, 127.5, 127.0, 80.3, 50.2, 48.5, 28.6. HRMS (EI) m/z calculated for C$_{22}$H$_{26}$NO$_3$ [M+H]$: 352.1913, found 352.1914.

(E)-N-benzyl-N-(3-((tert-butyl(dimethyl)silyl)oxy)phenyl)allyl)-1,1,1-trifluoromethanesulfonamide (45). Pd(ÔAc)$_2$ (2.2 mg, 0.01 mmol, 0.05 equiv), (+)-MeO-SOX ligand (L-5) (3.4 mg, 0.01 mmol, 0.05 equiv), 2.5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), (2-allylphenoxy)(tert-butyl)dimethylsilane (49.7 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 10% => 30% CH$_2$Cl$_2$ in hexanes) provided pure product 45 as a colorless oil. Run 1: (79.0 mg, 81.3% yield); Run 2: (78.7 mg, 81.0% yield); Run 3: (79.3 mg, 81.7% yield). **Average: 81% yield ± 0.4%**.

$^1$H NMR (500 MHz, Chloroform-d) δ 7.48–7.32 (m, 6H), 7.24–7.17 (m, 1H), 6.97 (td, J = 7.5, 1.3 Hz, 1H), 6.90–6.79 (m, 2H), 6.04 (ddd, J = 15.9, 7.9, 6.4 Hz, 1H), 4.57 (br s, 2H), 4.07 (br s, 2H), 1.02 (s, 9H), 0.25 (s, 6H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 153.2, 134.3, 131.5, 129.5, 129.0, 128.7, 128.6, 127.0, 126.7, 121.6, 121.4, 120.2 (q, J = 322.9 Hz), 119.7, 50.7, 50.0, 25.9, 18.5, 4.0.
\(^{19}\text{F}\) NMR (470 MHz, Chloroform-\(d\)) \(\delta -76.33\). HRMS (EI) \textit{m/z} calculated for C\(_{25}\)H\(_{31}\)NO\(_3\)F\(_3\)SSi [M+H]\(^+\): 486.1746, found 486.1732.

\((E)-N\)-benzyl-1,1,1-trifluoro-N-(3-(3-(trifluoromethyl)phenyl)allyl)methanesulfonamide (46). Pd(OAc)\(_2\) (2.2 mg, 0.01 mmol, 0.05 equiv), (\(\pm\))-MeO-SOX ligand (L-5) (3.4 mg, 0.01 mmol, 0.05 equiv), 2.5 DMBQ (2.5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), 1-allyl-3-(trifluoromethyl)benzene (37.2 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 10% => 30% CH\(_2\)Cl\(_2\) in hexanes) provided pure product 46 as a colorless oil. Run 1: (71.4 mg, 84.3% yield); Run 2: (72.5 mg, 85.7% yield); Run 3: (72.2 mg, 85.3% yield). \textbf{Average: 85\% yield \pm 0.7\%.}

\(^1\text{H}\) NMR (500 MHz, Chloroform-\(d\)) \(\delta 7.54\) (d, \(J = 6.9\) Hz, 1H), 7.52-7.45 (m, 3H), 7.43-7.33 (m, 5H), 6.43 (d, \(J = 15.8\) Hz, 1H), 6.06 (dt, \(J = 15.7, 7.0\) Hz, 1H), 4.56 (br s, 2H), 4.07 (br s, 2H). \(^{13}\text{C}\) NMR (126 MHz, Chloroform-\(d\)) \(\delta 136.6, 134.5, 134.2, 131.3\) (q, \(J = 32.3\) Hz), 129.8, 129.3, 129.2, 128.8, 128.8, 125.1 (q, \(J = 3.8\) Hz), 124.2, 124.1 (q, \(J = 272.3\) Hz), 123.5 (q, \(J = 3.8\) Hz), 120.2 (q, \(J = 322.7\) Hz), 51.7, 49.8. \(^{19}\text{F}\) NMR (470 MHz, Chloroform-\(d\)) \(\delta -76.20, -76.18\). HRMS (ESI) \textit{m/z} calculated for C\(_{18}\)H\(_{15}\)NO\(_3\)F\(_6\)SnNa [M+Na]\(^+\): 446.0625, found 446.0618.

\((E)-N\)-benzyl-1,1,1-trifluoro-N-(3-(4-hydroxy-3-methoxyphenyl)allyl)methanesulfonamide (47). Pd(OAc)\(_2\) (4.4 mg, 0.02 mmol, 0.1 equiv), (\(\pm\))-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2.5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), eugenol (32.8 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol) were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 10% => 30% CH\(_2\)Cl\(_2\) in hexanes) provided pure product 47 as a yellow oil. Run 1: (72.4 mg, 90.2% yield); Run 2: (71.7 mg, 89.3% yield); Run 3: (72.8 mg, 90.7% yield). \textbf{Average: 90\% yield \pm 0.7\%.}

\(^1\text{H}\) NMR (500 MHz, Chloroform-\(d\)) \(\delta 7.44-7.31\) (m, 5H), 6.89 (d, \(J = 8.0\) Hz, 1H), 6.86-6.81 (m, 2H), 6.33 (d, \(J = 15.7\) Hz, 1H), 5.85 (dt, \(J = 15.7, 7.2\) Hz, 1H), 5.74 (s, 1H), 4.56 (br s, 2H), 4.02 (br s, 2H), 3.92 (s, 3H). \(^{13}\text{C}\) NMR (126 MHz, Chloroform-\(d\)) \(\delta 146.8, 146.3, 136.3, 134.3, 129.1, 128.7, 128.6, 128.3, 120.8, 120.2\) (q, \(J = 322.8\) Hz), 119.3, 116.4, 114.6, 56.0, 51.0, 50.0. \(^{19}\text{F}\) NMR (470 MHz, Chloroform-\(d\)) \(\delta -76.25\). HRMS (ESI) \textit{m/z} calculated for C\(_{18}\)H\(_{19}\)NO\(_3\)F\(_3\)S [M+H]\(^+\): 402.0987, found 402.0998.

\((E)-N\)-benzyl-N-(3-(3,4-dimethoxyphenyl)allyl)-1,1,1-trifluoromethanesulfonamide (48). Pd(OAc)\(_2\) (4.4 mg, 0.02 mmol, 0.1 equiv), (\(\pm\))-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1
equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), 4-allyl-1,2-dimethoxybenzene (35.6 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 2.5% => 10% acetone in hexanes; column 2: 50 mL silica gel, 30% => 60% CH₂Cl₂ in hexanes) provided pure product 48 as a colorless oil. Run 1: (71.9 mg, 86.5% yield); Run 2: (74.9 mg, 90.1% yield); Run 3: (73.9 mg, 89.0% yield). **Average: 88% yield ± 1.8%**.

**1H NMR** (500 MHz, Chloroform-d) δ 7.44-7.32 (m, 5H), 6.88 (dd, J = 8.2, 2.0 Hz, 1H), 6.83 (d, J = 8.4 Hz, 2H), 6.34 (d, J = 15.7 Hz, 1H), 5.86 (dt, J = 15.7, 7.1 Hz, 1H), 4.56 (br s, 2H), 4.03 (br s, 2H), 3.91 (s, 3H), 3.90 (s, 3H).

**13C NMR** (126 MHz, Chloroform-d) δ 149.6, 149.2, 136.1, 134.3, 129.0, 128.8, 128.7, 128.6, 120.2 (q, J = 322.8 Hz), 120.1, 119.7, 111.2, 108.9, 56.0, 56.0, 51.0, 50.0. **19F NMR** (470 MHz, Chloroform-d) δ -76.25. **HRMS (EI) m/z** calculated for C₁₉H₂₀NO₄F₃S [M+Na]^+: 415.10651, found 415.10659.

![Diagram of N-cinnamyl-1,1,1-trifluoro-N-(4-fluorobenzyl) methanesulfonamide](image_url)

**N-cinnamyl-1,1,1-trifluoro-N-(4-fluorobenzyl)methanesulfonamide (49).** Pd(OAc)_2 (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allylbenzene (23.6 mg, 0.2 mmol, 1.0 equiv) and 1,1,1-trifluoro-N-(4-fluorobenzyl)methanesulfonamide (S24) (51.4 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (50 mL silica gel, 10% => 20% CH₂Cl₂ in hexanes) provided pure product 49 as a colorless oil. Run 1: (66.1 mg, 88.5% yield); Run 2: (66.8 mg, 89.4% yield); Run 3: (66.6 mg, 89.2% yield). **Average: 89% yield ± 0.5%**.

**1H NMR** (500 MHz, Chloroform-d) δ 7.40-7.29 (m, 7H), 7.09 (t, J = 8.6 Hz, 2H), 6.43 (d, J = 15.8 Hz, 1H), 6.03 (dt, J = 15.8, 7.1 Hz, 1H), 4.51 (br s, 2H), 4.03 (br s, 2H). **13C NMR** (126 MHz, Chloroform-d) δ 162.9 (d, J = 247.7 Hz), 136.5, 135.6, 130.6 (d, J = 8.3 Hz), 130.0 (d, J = 3.2 Hz), 128.9, 128.7, 126.7, 121.7, 120.2 (q, J = 322.6 Hz), 116.1 (d, J = 21.6 Hz), 50.3, 49.8. **19F NMR** (470 MHz, Chloroform-d) δ -76.30, -113.45. **HRMS (EI) m/z** calculated for C₁₇H₁₅NO₂F₃SNa [M+Na]^+: 396.0657, found 396.0647.

![Diagram of N-cinnamyl-N-(4-(dimethylamino)benzyl)-1,1,1-trifluoromethanesulfonamide](image_url)

**N-cinnamyl-N-(4-(dimethylamino)benzyl)-1,1,1-trifluoromethanesulfonamide** (50). Pd(OAc)_2 (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), allylbenzene (23.6 mg, 0.2 mmol, 1.0 equiv) and N-(4-(dimethylamino)benzyl)-1,1,1-trifluoromethanesulfonamide (S26) (56.5 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (50 mL silica gel, 2% => 4% Ethyl acetate in hexanes) provided pure product 50 as a white solid. Run 1: (68.0 mg, 85.3% yield); Run 2: (68.7 mg, 86.2% yield); Run 3: (67.5 mg, 84.7% yield). **Average: 85% yield ± 0.8%**.

**1H NMR** (500 MHz, Chloroform-d) δ 7.34 (app d, J = 4.3 Hz, 4H), 7.32-7.27 (m, 1H), 7.20 (d, J = 8.2 Hz, 2H), 6.73 (app s, 2H), 6.43 (d, J = 15.8, 1H), 6.02 (dt, J = 15.8, 7.0 Hz, 1H), 4.44 (br s, 2H), 4.00 (br s, 2H), 2.97 (s, 6H). **13C NMR** (126 MHz, Chloroform-d) δ 150.7, 136.0, 135.9,
130.1, 128.8, 128.4, 126.7, 122.3, 121.1, 120.3 (q, J = 322.8 Hz), 112.6, 50.8, 49.1, 40.6. \(^{19}\text{F NMR}\) (470 MHz, Chloroform-\(d\)) \(\delta\) -76.42. \(\text{HRMS (ESI)}\) \(m/z\) calculated for \(\text{C}_{19}\text{H}_{22}\text{N}_{2}\text{O}_{5}\text{F}_{3}\text{S}\) [\(\text{M+H}\)]\(^{+}\): 399.1354, found 399.1349.

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\begin{align*}
\text{N-cinnamyl-N-(3,4-dimethoxybenzyl)-1,1,1-trifluoromethanesulfonamide (51).} & \quad \text{Pd(OAc)}_{2} (4.4 \text{ mg, 0.02 mmol, 0.1 equiv}), (\pm)-\text{MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv)}, 2.5 \text{ DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv)}, \text{allylbenzene (23.6 mg, 0.2 mmol, 1.0 equiv)} \text{ and N-(3,4-dimethoxybenzyl)-1,1,1-trifluoromethanesulfonamide (S25) (59.9 mg, 0.2 mmol, 1.0 equiv)} \text{ were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (50 mL silica gel, 2.5% \(\rightarrow\) 5% acetone in hexanes) provided pure product 51 as a colorless oil. Run 1: (71.6 mg, 86.2% yield); Run 2: (72.6 mg, 87.4% yield); Run 3: (73.3 mg, 88.2% yield). Average: 87% yield \(\pm\) 1%.} \\
\text{\(^{1}\text{H NMR}\) (500 MHz, Chloroform-\(d\)) \(\delta\) 7.38-7.27 (m, 5H), 6.87 (app s, 1H), 6.85 (app s, 2H), 6.43 (d, \(J = 15.7, 1\text{H})\), 6.04 (dt, \(J = 15.7, 7.1 \text{ Hz, 1H})\), 4.48 (br s, 2H), 4.10-3.93 (m, 2H), 3.89 (s, 3H), 3.86 (s, 3H).} \text{\(^{13}\text{C NMR}\) (126 MHz, Chloroform-\(d\)) \(\delta\) 149.5, 149.3, 136.2, 135.7, 128.9, 128.6, 126.7, 126.4, 121.9, 121.5, 120.2 (q, \(J = 322.7 \text{ Hz})\), 111.5, 111.1, 56.0, 56.0, 50.9, 49.5.} \text{\(^{19}\text{F NMR}\) (470 MHz, Chloroform-\(d\)) \(\delta\) -76.30. \(\text{HRMS (ESI)}\) \(m/z\) calculated for \(\text{C}_{19}\text{H}_{21}\text{NO}_{4}\text{F}_{3}\text{S}\) [\(\text{M+H}\)]\(^{+}\): 416.1143, found 416.1130.} \\
\end{align*}
\]

\[
\begin{align*}
\text{(E)-N-benzyl-1,1,1-trifluoro-N-(3-phenylbut-2-en-1-yl)methanesulfonamide (52).} & \quad \text{Pd(OAc)}_{2} (4.4 \text{ mg, 0.02 mmol, 0.1 equiv}), (\pm)-\text{MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv)}, 2.5 \text{ DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv)}, \text{but-3-en-2-ylbenzene}^{26} (26.4 mg, 0.2 mmol) \text{ and 1,1,1-trifluoro-N-phenylmethanesulfonamide (S12) (47.8 mg, 0.2 mmol)} \text{ were reacted according to the general procedure for 72 hours. Purification by flash column chromatography (column1: 50 mL silica gel, 2.5% \(\rightarrow\) 5% acetone in hexanes; column2: 50 mL silica gel, 10% \(\rightarrow\) 20% CH\(_2\)Cl\(_2\) in hexanes) provided product 52 as a colorless oil (E:Z = 15:1). E:Z selectivity was measured by \(^{1}\text{H NMR}\): triplet of doublet at 5.65 ppm (E isomer) and triplet at 5.46 (Z isomer). Run 1: (51.9 mg, 70.2% yield, 15:1 E:Z, 66.2% yield for E); Run 2: (51.2 mg, 69.3% yield, 15:1 E:Z, 64.8% yield for E isomer); Run 3: (51.7 mg, 70.0% yield, 15:1 E:Z, 65.4% yield for E isomer). Average: 65% yield \(\pm\) 0.7%.} \quad \text{Further purification column chromatography was applied to afford pure E isomer (>20:1 E:Z).} \\
\text{For E isomer:} \\
\text{\(^{1}\text{H NMR}\) (500 MHz, Chloroform-\(d\)) \(\delta\) 7.43-7.27 (m, 10H), 5.65 (td, \(J = 7.1, 1.6 \text{ Hz, 1H})\), 4.57 (br s, 2H), 4.10 (br s, 2H), 1.82 (d, \(J = 1.3 \text{ Hz, 3H})\).} \text{\(^{13}\text{C NMR}\) (126 MHz, CDCl\(_3\)) \(\delta\) 142.5, 141.2, 134.4, 129.1, 128.7, 128.6, 128.5, 127.9, 125.9, 120.4, 120.3 (q, \(J = 322.8 \text{ Hz})\), 51.5, 45.9, 16.2. \(^{19}\text{F NMR}\) (470 MHz, Chloroform-\(d\)) \(\delta\) -76.22. \(\text{HRMS (ESI)}\) \(m/z\) calculated for \(\text{C}_{18}\text{H}_{18}\text{NO}_{2}\text{F}_{3}\text{SNa}\) [\(\text{M+Na}\)]\(^{+}\): 392.0908, found 392.0910.} \\
\text{E/Z configuration assignment is based on \(^{13}\text{C NMR}\) analogy to similar compounds (the chemical shifts of the methyl group attached to olefin, geranyl acetate(E, 16.4 ppm) and neryl acetate(Z, 18.4 ppm).} \\
\end{align*}
\]

S 56
23.5 ppm)) from previous literature\textsuperscript{28,28}. In addition to \textsuperscript{13}C NMR, in NOESY-1D, no NOE to the olefin proton was observed when irradiating the methyl group; larger NOE observed between olefin proton and the aryl proton and the neighboring methylene, but not to the methyl group (tiny peak), which are consistent with an \textit{E} isomer.

\chemfig{[N-\{-3-(3-(benzo[\textit{b}]thiophen-5-yl)allyl)-1,1,1-trifluoro-N-(naphthalen-1-ylmethyl)methanesulfonamide (54). Pd(OAc)\textsubscript{2} (4.4 mg, 0.02 mmol, 0.1 equiv), (\pm)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), 5-allylbenzo[\textit{b}]thiophene (34.9 mg, 0.2 mmol, 1.0 equiv) and and 1,1,1-trifluoro-N-(naphthalen-1-ylmethyl)methanesulfonamide (S13) (57.9 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (50 mL silica gel, 0\% => 30\% CH\textsubscript{2}Cl\textsubscript{2} in hexanes) provided pure product (54) as a colorless oil. Run 1: (81.1 mg, 87.9\% yield); Run 2: (83.0 mg, 89.9\% yield); Run 3: (82.5 mg, 89.4\% yield). Average: \textbf{89}\% yield \pm 1.0\%.

\textbf{1H NMR} (500 MHz, Chloroform-d) \(\delta\) 8.17 (d, \(J = 8.5\) Hz, 1H), 7.90 (t, \(J = 9.2\) Hz, 2H), 7.80 (d, \(J = 8.4\) Hz, 1H), 7.62-7.50 (m, 5H), 7.47 (d, \(J = 5.4\) Hz, 1H), 7.31 (dd, \(J = 5.5, 0.8\) Hz, 1H), 7.19 (dd, \(J = 8.4, 1.7\) Hz, 1H), 6.29 (d, \(J = 15.7\) Hz, 1H), 6.00 (dt, \(J = 15.7, 7.0\) Hz, 1H), 5.11 (br s, 2H), 4.09 (br s, 2H). \textbf{13C NMR} (126 MHz, CDCl\textsubscript{3}) \(\delta\) 140.0, 139.7, 136.2, 134.0, 132.1, 131.6, 129.7, 129.2, 129.1, 127.5, 127.3, 127.1, 126.3, 125.3, 124.0, 123.0, 122.7, 122.5, 122.1, 121.4, 120.4 (q, \(J = 323.6\) Hz), 50.2, 49.3. \textbf{19F NMR} (470 MHz, CDCl\textsubscript{3}) \(\delta\) -75.4. \textbf{HRMS (ESI)} \(m/z\) calculated for C\textsubscript{23}H\textsubscript{18}NO\textsubscript{2}F\textsubscript{3}S\textsubscript{2} [M+\textsuperscript{+}]: 461.0731, found 461.0721.
(+)-(S,E)-1,1,1-trifluoro-N-(1-(4-nitrophenyl)ethyl)-N-(3-(2-oxo-2H-chromen-6-yl)allyl) methanesulfonamide (55). Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (6.9 mg, 0.02 mmol, 0.1 equiv), 2.5 DMBQ (2,5-dimethylbenzoxazine) (30 mg, 0.22 mmol, 1.1 equiv), 6-allyl-2H-chromen-2-one (S38) (37.2 mg, 0.2 mmol, 1.0 equiv) and (S)-1,1,1-trifluoro-N-(1-(4-nitrophenyl)ethyl)methanesulfonamide (S27) (59.6 mg, 0.2 mmol, 1.0 equiv) were reacted according to the general procedure for 24 hours. Purification by flash column chromatography (column 1: 50 mL silica gel, 2.5% => 30% acetone in hexanes provided pure product (+)-55 as a yellow oil. Run 1: (85.8 mg, 88.9% yield); Run 2: (87.3 mg, 90.5% yield); Run 3: (88.2 mg, 91.4% yield). **Average**: 88% yield ± 1.3%.

**1H NMR** (500 MHz, Chloroform-$d$) $\delta$ 8.19 (d, $J = 8.0$ Hz, 2H), 7.70-7.53 (m, 3H), 7.34-7.11 (m, 3H), 6.41 (d, $J = 9.4$ Hz, 1H), 6.23 (d, $J = 15.7$ Hz, 1H), 5.78 (br s, 1H), 5.39 (q, $J = 7.1$ Hz, 1H), 4.08-3.93 (m, 2H), 1.82 (d, $J = 7.0$ Hz, 3H).

**13C NMR** (126 MHz, Chloroform-$d$) $\delta$ 160.4, 153.8, 147.9, 145.7, 143.1, 132.5, 129.5, 125.0, 125.6, 125.2, 123.9, 119.9, 119.0, 117.3, 56.9, 47.7, 17.1. **19F NMR** (470 MHz, Chloroform-$d$) $\delta$ -76.13. **HRMS** (ESI) $m/z$ calculated for C$_{21}$H$_{18}$N$_2$O$_6$F$_3$S [M+H]$^+$: 483.0838, found 483.0834. [α]$^\text{D}_{22}$ = +8.2° ($c = 0.55$, CHCl$_3$)

**(S,S)-Reboxetine:**

**Scheme S8. 5-step synthesis of (S,S)-Reboxetine**

$\text{NaH}$

DMF

91% yield (2 steps)

$\text{NaH}$

DMF

91% yield (2 steps)

**N-(2-bromoethyl)-N-cinnamyl-1,1,1-trifluoromethanesulfonamide (56).** To a 25 mL round bottom flask equipped with a stir bar was added Pd(OAc)$_2$ (67 mg, 0.3 mmol, 0.1 equiv), (+)-MeO-SOX ligand (L-5) (102.9 mg, 0.3 mmol, 0.1 equiv), 2.5 DMBQ (2,5-dimethylbenzoxazine) (450 mg, 33 mmol, 1.1 equiv), allylbenzene (354.5 mg, 3.0 mmol, 1.0 equiv) and N-(2-bromoethyl)-1,1,1-trifluoromethanesulfonamide (S18) (768.1 mg, 3.0 mmol, 1.0 equiv). Toluene (3.0 mL, 1.0 M) was added and the flask was capped and heated at 45 °C for 72 hours (monitored by TLC). The
vial was allowed to cool to room temperature and diluted with acetone (10 mL). The reaction mixture was filtered through a ½ pipette silica plug into a 100 mL vial using acetone (30 mL), concentrated under reduced pressure and subjected to flash column chromatography (200 mL silica gel, 10% => 30% CH₂Cl₂ in hexanes) to provide pure desired product 56 as a colorless oil. Run 1: (962.1 mg, 86.2% yield); Run 2: (970.5 mg, 86.9% yield; Run 3: (951.1 mg, 85.2% yield) Average: 86% yield ± 0.9%. The reaction has also been run under smaller scale (0.3 mmol) using Pd(OAc)₂ (6.7 mg, 0.03 mmol, 0.1 equiv), ligand 5 (10.3 mg, 0.03 mmol, 0.1 equiv), 2,5-dimethylbenzoquinone (2.5 DMBQ) (45.0 mg, 3.3 mmol, 1.1 equiv), allylbenzene (35.5 mg, 0.3 mmol, 1.0 equiv) and N-(2-bromoethyl)-1,1,1-trifluoromethanesulfonamide (S18) (76.8 mg, 0.3 mmol, 1.0 equiv). Toluene (0.3 mL, 1.0 M), the reaction gave comparable result: 100.6 mg, 90% yield.

**N-(2-bromoethyl)-N-((2S,3S)-2,3-dihydroxy-3-phenylpropyl)-1,1,1-trifluoromethanesulfonamide (S44).** To a 50 mL round bottom flask equipped with a stir bar was added S2 (744.4 mg, 2 mmol, 1 equiv), t-BuOH (10 mL) and H₂O (10 mL). The reaction was cooled to 0 °C. AD-mix-α (2.8 g), additional (DHQ)₂PHAL (75 mg, 0.096 mmol, 0.048 equiv) and K₂OsO₄·H₂O (10.2 mg, 0.028 mmol, 0.014 equiv) were added. The reaction was stirred at 0 °C until all solid was fully dissolved and two clear phases were produced. MeSO₂NH₂ (190 mg, 2.0 mmol, 1.0 equiv) was added and the reaction was slowly warmed up to room temperature and stirred under room temperature for 24 hours (monitored by TLC). Upon completion, the reaction was cooled to 0 °C and Na₂SO₄ (3 g) was added. The reaction mixture was allowed to warm up to room temperature over 30 mins. The reaction was diluted with ethyl acetate (30 mL) and the layers were separated. The aqueous layer was extracted with ethyl acetate (20 mL x 3). Combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The mixture was filtered through a short silica plug (ethyl acetate/hexane), concentrated under reduced pressure to provide the product S44 without further purification.

**(S)-phenyl((S)-4-((trifluoromethyl)sulfonyl)morpholin-2-yl)methanol (57).** To an oven-dried 25 mL round bottom flask under N₂, S44 (carried through from last step) was added as a solution in DMF (14 mL 0.13M). The reaction was cooled to 0 °C, then NaH (120 mg, 5 mmol, 2.5 equiv) was added in one portion. The reaction was stirred for 1 hour at 0 °C and slowly quenched with H₂O (20 ml) at 0 °C. Ethyl acetate (20 mL) was added, and the layers were separated. The aqueous layer was extracted with ethyl acetate (20 mL x 3). And the combined organic layers were dried
over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The crude mixture was purified via flash column chromatography (100 mL silica gel, 30% ethyl acetate in hexanes) to afford the desired product 57 as a white solid. Run 1: (588.8 mg, 90.5% yield); Run 2: (595.9 mg, 91.6% yield) \textbf{Average: 91% yield over two steps.}

\textbf{1H NMR} (500 MHz, Chloroform-d) δ 7.45-7.26 (m, 5H), 4.55 (d, J = 6.7 Hz, 1H), 4.07 (dd, J = 11.7, 3.3 Hz, 1H), 3.70 (br d, J = 15.2 Hz, 1H), 3.68-3.62 (m, 2H), 3.45 (br d, J = 12.8 Hz, 1H), 3.22 (br t, J = 11.9 Hz, 1H), 3.01 (br t, J = 11.7 Hz, 1H), 2.85 (br s, 1H). \textbf{13C NMR} (125 MHz, CDCl₃) δ 138.5, 129.0, 126.8, 131.1, 75.43. \textbf{HRMS} (ESI) \textit{m/z} calculated for C₁₂H₁₄NO₅F₃SNa [M+Na]⁺: 348.0493, found 348.0494.

\textbf{(S)-2-((S)-(2-ethoxyphenoxy)(phenyl)methyl)morpholine (S45).} To an oven-dried sealed tube under N₂ equipped with a stir bar was added alcohol 57 (325.3 mg, 1.0 mmol, 1.0 equiv), Cul (57.1 mg, 0.30 mmol, 0.3 equiv), 4-methyl-1,10-phenanthroline (141.8 mg, 0.60 mmol, 0.6 equiv), Cs₂CO₃ (651.6 mg, 2.0 mmol, 2.0 equiv), 1-ethoxy-2-iodo-benzene (372.1 mg, 1.5 mmol, 1.5 equiv) and toluene (0.5 mL, 2.0 M), the tube was sealed and heated to 100 °C for 96 hours. The reaction was cooled to room temperature, diluted with ethyl ether (5 mL), and filtered through a silica plug. The mixture was concentrated under reduced pressure and purified via flash column chromatography (100 mL silica gel, 0% => 15% ethyl acetate in hexanes) to afford the desired product S44 as a colorless oil. Run 1: (278.3 mg, 62.5% yield; 101.2 mg recover alcohol 57, 31.1%); Run 2: (284.2 mg, 63.8% yield; 100.6 mg recover alcohol 57, 30.9%); \textbf{Average: 63% yield.}

\textbf{1H NMR} (500 MHz, Chloroform-d) δ 7.45-7.40 (m, 2H), 7.39-7.30 (m, 3H), 6.94-6.84 (m, 2H), 6.79-6.69 (m, 2H), 5.19 (d, J = 4.4 Hz, 1H), 4.11-4.03 (m, 3H), 3.95 (ddd, J = 10.6, 4.4, 2.6 Hz, 1H), 3.86 (d, J = 12.9 Hz, 1H), 3.70 (dd, J = 12.9, 1.5 Hz, 1H), 3.64 (td, J = 11.8, 2.8 Hz, 1H), 3.32-3.18 (m, 2H), 1.47 (t, J = 7.0 Hz, 3H). \textbf{13C NMR} (125 MHz, CDCl₃) δ 150.3, 147.2, 136.9, 128.5, 128.4, 127.5, 123.2, 120.8, 120.1 (q, J = 323.4), 119.3, 113.8, 81.9, 78.1, 66.7, 64.5, 47.6, 46.1, 15.0. \textbf{19F NMR} (470 MHz, CDCl₃) δ -75.43. \textbf{HRMS} (ESI) \textit{m/z} calculated for C₂₀H₂₂NO₅F₃SNa [M+Na]⁺: 468.1068, found 468.1060.

\textbf{(S, S)-Reboxetine.} To an oven-dried 50 mL round bottom flask equipped with a stir bar and condenser under N₂ was added S45 (222.8 mg, 0.50 mmol, 0.5 equiv), dioxane (20 ml, 0.025 M) and LAH (190 mg, 5.0 mmol, 10 equiv). The reaction was heated up to 100 °C for 1 hour, then cooled to 0 °C. Sequentially, 0.5 mL of H₂O, 0.5 mL of 15% NaOH solution and 1.5 mL of H₂O were added dropwise, followed by anhydrous MgSO₄. The mixture was filtered through a celite plug, concentrated under reduced pressure and purified via flash column chromatography (100 mL
silica gel, 0% => 7% MeOH in CH$_2$Cl$_2$) to afford the (S, S)-Reboxetine as a colorless oil. Run 1: (152.9 mg, 97.6% yield); Run 2: (154.5 mg, 98.5% yield). **Average: 98% yield.**

$^1$H NMR (500 MHz, Methanol-d4) $\delta$ 7.40-7.36 (m, 2H), 7.28 (t, $J = 7.4$ Hz, 2H), 7.25-7.21 (m, 1H), 6.86 (dd, $J = 7.9, 1.6$ Hz, 1H), 6.82-6.76 (m, 2H), 6.67 (ddd, $J = 8.5, 7.3, 1.6$ Hz, 1H), 5.16 (d, $J = 6.0$ Hz, 1H), 4.09-3.96 (m, 2H), 3.94-3.86 (m, 2H), 3.60 (ddd, $J = 11.9, 7.9, 6.1$ Hz, 1H), 2.74 (dd, $J = 6.3, 2.0$ Hz, 2H), 2.67-2.54 (m, 2H), 1.39 (t, $J = 6.9$ Hz, 3H). $^{13}$C NMR (125 MHz, CD$_3$OD) $\delta$ 150.9, 149.0, 139.0, 129.2, 129.1, 128.5, 123.2, 122.0, 118.6, 115.5, 83.7, 79.8, 68.2, 65.7, 47.6, 45.9, 15.4. $[^{25}]$$\alpha$D = +15.73° ($c = 1.03$, CHCl$_3$); **HRMS (ESI) m/z calculated for C$_{19}$H$_{24}$NO$_3$ [M+H]$^+$: 314.1756, found 314.1755.** These data are in agreement with that previously reported in the literature$^{29}$. The enantiomeric excess was determined to be 96% by chiral HPLC analysis (Chiralpak IB3 column, 1.0 mL/min, 10% Isopropanol in hexanes (0.2% Et$_2$NH), $\lambda = 215$nm (4nm). tR(minor) = 9.868 min, tR(major) = 11.308 min.
Preparation of (±)-MeO-SOX SOX ligand (L5)/Pd(OAc)$_2$

To a 1-dram vial was added Pd(OAc)$_2$ (22.5 mg, 0.1 mmol, 1.0 equiv) and (±)-MeO-SOX ligand (L5) (34.3 mg, 0.1 mmol, 1.0 equiv) and 1.0 mL toluene (0.1 M), the mixture was stirred at 45 °C for 30 min. Upon completion, the complex was separated from the reaction mixture by filtration as a light green powder (51.8 mg, 93% yield).

$^1$H NMR (500 MHz, Chloroform-$d$) δ 8.08 – 8.04 (m, 3H), 7.37 (d, $J = 2.6$ Hz, 1H), 7.34 (dd, $J = 8.8, 2.6$ Hz, 1H), 7.30 – 7.31 (m, 1H), 7.30 – 7.29 (m, 1H), 4.22 (d, $J = 8.5$ Hz, 1H), 3.96 (s, 3H), 3.85 (d, $J = 8.5$ Hz, 1H), 2.41 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H), 1.47 (s, 3H), 1.38 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.3, 177.7, 163.4, 161.1, 145.2, 139.3, 130.1, 128.8, 128.4, 127.2, 124.6, 118.6, 117.6, 81.9, 71.4, 56.4, 27.0, 26.8, 23.6, 22.3, 21.8. HRMS (FAB) m/z calculated for C$_{21}$H$_{24}$NO$_5$SPd [M-OAc]$^+$: 508.04101, found 508.04103.

The complex was not bench-stable and has to be stored in the glove box (stable for at least a month). Reactions using the complex gave comparable yields to reactions using (±)-MeO-SOX ligand and Pd(OAc)$_2$.

X-ray Crystal structure analysis of (±)-MeO-SOX ligand (L5)/Pd(OAc)$_2$

A suitable crystal was mounted with Paratone-N oil (Exxon) on a 0.3 mm cryo-loop (Hampton Research) and transferred to the goniometer of a Bruker D8 Venture/Photon 100 diffractometer. Data was collected at 100 K utilizing a cold stream of N$_2$(g). Microfocus sealed tube Mo $K_{\alpha}$ radiation ($\lambda = 0.71073$ Å) was used. The structure was phased by intrinsic methods with SHELXT (v2014/4) and refined by full-matrix least-squares refinement on $F^2$ using SHELXL (v2014/7). The intensities were corrected for Lorentz and polarization effects by integration using SADABS (v2014/5). All non-hydrogen atoms were refined anisotropically. Methyl H atom positions, R-CH$_3$, were optimized by rotation about R-C bonds with idealized C-H, R--H and H--H distances.
Remaining H atoms were included as riding idealized contributors. Methyl H atom U's were assigned as 1.5 times $U_{eq}$ of the carrier atom; remaining H atom U's were assigned as 1.2 times carrier $U_{eq}$. Details of the crystal data and a summary of the intensity data for ($\pm$)-MeO-SOX (L5)/Pd(OAc)$_2$ are listed in Table S2. CCDC: 1819815

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Mechanistic Studies

Determination of Kinetic Isotope Effect

1-decene-d2 (58-d2). To a flamed-dried 25 mL flask under N₂ was added a stir bar, Nonanal (1.42g, 10 mmol, 1.0 equiv), 4-dimethylaminopyridine (122.2mg, 1 mmol, 0.1 equiv), D₂O (2.5 mL, 4.0 M), and was heated to 100 °C for 2 h. The reaction was cooled to room temperature and diluted with CH₂Cl₂ (25 mL). The layers were separated and the organic layer was washed with 1N HCl (10 mL x 2) and brine, dried over anhydrous MgSO₄, filtered through a short silica gel plug and concentrated under reduced pressure at 0 °C. The yellow oil was then re-subject to the same reaction condition again to achieve Nonanal-d₂ with >95% D incorporation (1.07 g, 7.42 mmol). The Nonanal-d₂ was carried through next step without further purification. To a flamed-dried 100 mL flask under N₂ was added Nonanal-d₂ (750 mg, 5.2 mmol, 1.0 equiv), methyltriphenylphosphonium bromide (3.25 g, 8.8 mmol, 1.7 equiv) and diethyl ether (20 mL). The reaction was cooled to 0 °C and added KOt-Bu (953 mg, 7.8 mmol, 1.5 equiv). The reaction was allowed to warm up to room temperature and stirred for additional 3 h. Upon completion, the reaction was quenched with sat. aq. NH₄Cl. Layers were separated and the aqueous layer was extracted with diethyl ether (25 mL x 3). The combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered and carefully concentrated under reduced pressure at 0 °C. The resulting mixture was purified via flash column chromatography (100 mL silica gel, pentane) to afford the 1-decene-d₂ (58- d₂) in 89% yield as a colorless oil (696.3mg, 4.89 mmol) with 97% D incorporation (See ¹H NMR).

1-decene-d₁ (59). To a flamed-dried 50 mL flask under N₂ was added a stir bar, LAD (lithium aluminum deuteride, 252 mg, 6.0 mmol, 1.0 equiv) and THF (6.0 mL). The reaction was cooled to 0 °C and octanal (937µL, 6.0 mmol) in THF (12 mL) was added dropwise. The reaction was allowed to warm up to room temperature and stirred for additional 1 h, then cooled to 0 °C. Sequentially, 0.25 mL of H₂O, 0.35 mL of 15% NaOH solution and 0.75 mL of H₂O were added dropwise, followed by anhydrous MgSO₄. The mixture was filtered, concentrated under reduced pressure and purified via flash column chromatography (100 mL silica gel, pentane) to afford the alcohol (762.1 mg, 5.5 mmol, 92% yield) as a colorless oil.

To a flamed-dried 50 mL flask under N₂ was added a stir bar, PPh₃ (1.57 g, 6.0 mmol, 1.2 equiv.), Et₂O (15 mL), imidazole (546 mg, 8.0 mmol, 1.5 equiv.) and iodine (2.0 g, 7.8 mmol, 1.3 equiv.). A solution of alcohol from last step (693 mg, 5.0 mmol, 1.0 equiv) in Et₂O (10 mL) was added to the resulting mixture. The reaction was stirred at room temperature overnight. The mixture was filtered, concentrated under reduced pressure and purified via flash silica plug to gave pure alkyl iodide as colorless oil (988.7 mg, 4.1 mmol, 82% yield).

To a flamed-dried 50 mL flask under N₂ was added a stir bar, CuI (1.142 g, 6.0 mmol, 1.5 equiv.), alkyl iodide (964.6, 4.0 mmol, 1.0 equiv) in THF (8 mL). The reaction was cooled to 0 °C.
and vinyl magnesium bromide (1.0 M, 5.2 mL, 1.3 equiv) was added dropwise and the reaction was allowed to warm to room temperature for 2 hours. The reaction was quenched by addition of sat. aq. NH₄Cl, extracted with Et₂O, dried over anhydrous MgSO₄ and concentrated under reduced pressure (low temperature). The crude mixture was purified by flash column chromatography (100 mL silica gel, 100% pentane) to give 156.8 mg (1.1 mmol) 59 in 27.5% yield as a colorless oil with 98% D incorporation (See ¹H NMR).

\((E)\)-N-benzyl-N-(dec-2-en-1-yl)-1,1,1-trifluoromethanesulfonamide (61).

¹H NMR (500 MHz, Chloroform-d) δ 7.41 – 7.29 (m, 5H), 5.62 – 5.52 (m, 1H), 5.39 – 5.30 (m, 1H), 4.50 (br s, 2H), 3.82 (br s, 2H), 2.04 (app q, J = 7.0 Hz, 2H), 1.39 – 1.23 (m, 10H), 0.90 (t, J = 6.9 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 138.8, 134.2, 128.9, 128.5, 128.4, 122.1, 120.1 (q, J = 322.8 Hz), 50.4, 49.3, 32.2, 31.8, 29.1, 28.9, 22.7, 14.1. (one peak missing probably due to overlapping) ¹⁹F NMR (470 MHz, Chloroform-d) δ -76.04. HRMS (EI) m/z calculated for C₁₈H₂₆NO₂F₃Na [M+Na]⁺: 400.1525, found 400.1534.

**Intermolecular Kinetic isotope effect via initial rates:**

**Scheme S9. Kinetic Isotope Effect via Initial Rates**

General procedure for initial rate analysis

*In order to obtain accurate initial rate data, all reactions were run at 0.5M concentration.* To a ½ dram vial was added a stir bar, Pd(OAc)₂ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX L5 (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), N-benzyl-1,1,1-trifluoromethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv) and 1,4-di-tert-butylbenzene (15.2 mg, 0.8 mmol, 0.4 equiv) as internal standard. Toluene (0.4 mL, 0.5 M) was added and the vial was capped and heated to 45 °C then 1-decene or 1-decene-d₂ (0.2 mmol, 1.0 equiv) was added by injection through the screw-cap. Aliquots (15µL) were taken at the corresponding times from the reaction vial, and filtered through a silica plug with diethyl ether (0.6 mL) for HPLC analysis (Ellipse XDB C-8, 75% MeCN / 25% H₂O, 1 mL/min). The yield was determined by integration of the product peak (22.8 min) relative to the 1,4-di-tert-butylbenzene internal standard peak (9.8 min) and corrected by a standard curve. Yields are reported as the average of three runs with error bars denoting standard deviation. Error for kinetic isotopes was calculated via propagation of the standard error of the mean for each set of rates.

\[ k_{H}/k_D = 0.0231 / 0.0095 = 2.4 \pm 0.1 \]
**Intramolecular Kinetic isotope effect:**

To a ½ dram vial was added a stir bar, Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX L5 (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), N-benzyl-1,1,1-trifluoromethanesulfonamide (S12) (47.8 mg, 0.2 mmol, 1.0 equiv), 1-decene-$d_1$ (28.3 mg, 0.2 mmol, 1.0 equiv) and Toluene (0.4 mL, 0.4 M) was added. The vial was capped and heated to 45 °C for 72 hours. The vial was allowed to cool to room temperature and diluted with 1 mL acetone. The reaction mixture was filtered through a pipette silica plug into a 20mL vial with acetone. The mixture was concentrated under reduced pressure, diluted with 2 mL CDCl$_3$ and analyzed by crude $^1$H NMR with internal standard (trifluorotoluene 14.6 mg, 0.1 mmol, 0.5 equiv). The mixture was then concentrated under reduced pressure and subjected to flash column chromatography (0% => 20% CH$_2$Cl$_2$ in hexanes) to provide allylic amine mixture as a colorless oil. The column-purified product mixture was analyzed by $^1$H NMR (500 MHz instrument). The KIE was reported as the area of the protonated peak over that of the deuterated peak (See spectrum). The experiment was run in triplicate and each was analyzed by NMR. An average value was calculated with error reported as a standard deviation.

$$k_H/k_D = 4.0 \pm 0.1 \ (4.0, 4.0, 3.9)$$
Effect of N-triflyl amine on standard Pd(II)/bis-sulfoxide C—H amination

Scheme S11. Effect of N-triflyl amine on standard Pd(II)/bis-sulfoxide C—H amination

<table>
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<th>Equiv. (S10)</th>
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<td>0</td>
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</table>

a. Control experiment (without S10):
Following the reported procedure.22 To a ½ dram vial was added a stir bar, 1,2-Bis(phenylsulfinyl)ethane palladium(II) acetate (10.0 mg, 0.02 mmol, 0.10 equiv), benzoquinone (43.3 mg, 0.4 mmol, 2.0 equiv) and methyl tosylcarbamate (91.7 mg, 0.4 mmol, 2.0 equiv). Allylcyclohexane (30.9 mg, 0.2 mmol, 1.0 equiv) and t-butyl methyl ether (0.30 mL) and N,N-diisopropylethylamine (2.09 µL, 0.012 mmol, 0.06 equiv) was sequentially added. The vial was fitted with a Teflon cap, and heated to 45 °C for 72 h. The reaction was allowed to cool to room temperature, and thoroughly rinsed into a 125 mL separatory funnel with diethyl ether (30 mL). The organic phase was washed with 5% aq. K_2CO_3 (6 x 10 mL), and the aqueous rinses back-extracted with ether (2 x 30 mL). The combined organic extracts were dried over MgSO_4, filtered through a 1:1 mixture of Celite/silica gel, and concentrated under reduced pressure. The crude product was purified by flash chromatograph on silica gel (100 mL silica gel, 2.5% EthOAc/hexanes) to afford a colorless oil.

Run 1 (58.8 mg, 0.167 mmol, 83.6% yield); run 2 (59.9 mg, 0.169 mmol, 85.2% yield); run 3 (57.5 mg, 0.164 mmol, 81.7% yield). Average yield: 84% (>20:1 linear : branched >20 : 1 E : Z).

Spectroscopic data for the amination product matched that which was reported previously.

b. Inhibition experiment (with 1.0 equiv. S10):
Following the same reported procedure.22 To a ½ dram vial was added a stir bar, 1,2-Bis(phenylsulfinyl)ethane palladium(II) acetate (10.0 mg, 0.02 mmol, 0.10 equiv), benzoquinone (43.3 mg, 0.4 mmol, 2.0 equiv) and methyl tosylcarbamate (91.7 mg, 0.4 mmol, 2.0 equiv). Allylcyclohexane (30.9 mg, 0.2 mmol, 1.0 equiv) and t-butyl methyl ether (0.30 mL) and N-(2-Phenylethyl)trifluoromethanesulfonamide (S10) (50.6 mg, 0.2 mmol, 1.0 equiv) was added. The vial was heated to 45 °C for 72 h. Upon completion, the same work-up and purification procedure from controlled experiments was followed.

Run 1 (21.7 mg, 0.0617 mmol, 30.8% yield); run 2 (23.3 mg, 0.0663 mmol, 33.1% yield); run 3 (23.1 mg, 0.0657 mmol, 33.0% yield). Average yield: 32% (>20:1 linear : branched >20 : 1 E : Z). No N-triflyl amine product 1 was detected. Spectroscopic data for the amination product matched that which was reported previously.22
Stoichiometric Pd π–allyl study to evaluate functionalization

Scheme S12. Stoichiometric Pd π–allyl study to evaluate functionalization

a. “Mock catalytic” condition with SOX Ligand
To a 1-dram vial under N\textsubscript{2} was added a stirred bar, π–allyl Pd chloride dimer\textsuperscript{21} (28.2 mg, 0.05 mmol, 1.0 equiv), AgOAc (16.7 mg, 0.1 mmol, 2.0 equiv, 1.0 equiv to Pd) and CDCl\textsubscript{3} (0.4 mL). The vial was capped, wrapped with aluminum foil and stirred at 45 °C for 10 min., (±)-MeO-SOX L5 (34.3 mg, 0.1 mmol, 2.0 equiv (1.0 equiv to Pd)) was added, the reaction was stirred at 45 °C for another 10 min. Reaction was filtered by a pipette filled with glass wool into a NMR tube with additional 0.3 mL CDCl\textsubscript{3}. \textsuperscript{1}H NMR was taken under both room temperature and -20 °C, complexation between Pd metal and SOX ligand was observed. The solution was transferred back into the 1-dram vial and N-benzyl-1,1,1-trifluoromethanesulfonamide (S12) (239 mg, 1.0 mmol, 20 equiv (10 equiv to Pd) was added, the reaction was stirred at 45 °C for 2 hours. The vial was allowed to cool to room temperature and diluted with 1 mL acetone. The reaction mixture was filtered through a pipette silica plug into a 20 mL vial with acetone. The mixture was concentrated under reduced pressure, diluted with 2 mL CDCl\textsubscript{3} and analyzed by crude \textsuperscript{1}H NMR with internal standard (trifluorotoluene 14.6 mg, 0.1 mmol, 1.0 equiv). The mixture was then concentrated under reduced pressure and subjected to flash column chromatography (50 mL silica gel. 10\%=>15\% CH\textsubscript{2}Cl\textsubscript{2}/hexanes) to afford pure product 61 as a colorless oil. Run 1 (24.7 mg, 65.4\% yield); run 2 (25.3 mg, 67.1\% yield). Average yield: 66\% (>20:1 linear : branched >20 : 1 E : Z).

b. “Mock catalytic” condition with bis-sulfoxide Ligand
Follow same procedure, but switching (±)-MeO-SOX L5 to bis-sulfoxide ligand (27.8 mg, 0.1 mmol, 2.0 equiv (1.0 equiv to Pd). No complexation between Pd metal and bis-sulfoxide was observed and no aminated product 61 was detected by TLC or Crude \textsuperscript{1}H NMR. No product could be isolated by flash column chromatography.

Additional control experiments were conducted without any ligand. The reactions provided no aminated product 61.

Additional control experiments were conducted with 2,5 DMBQ instead of SOX or bisulfoxide ligand. The reactions provided no aminated product 61.

c. Catalytic condition with SOX ligand.
Following the general procedure for Table 2 in 0.2 mmol scale in CDCl$_3$. Run 1 (44.1 mg, 0.117 mmol, 58.4% yield); run 2 (44.8 mg, 0.119 mmol, 59.3% yield); run 3 (45.6 mg, 0.121 mmol, 60.5% yield). Average yield: 59% ± 1.1%. (>20:1 linear: branched >20 : 1 E : Z).

**Exploratory studies on internal olefins**

**General procedure (same as table S1):** The following procedure was used with no effort to exclude air or moisture. To a ½ dram vial was added a stir bar, Pd(OAc)$_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-SOX-Ligand 5 (L5) (6.3 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (30 mg, 0.22 mmol, 1.1 equiv), olefin (0.2 mmol, 1.0 equiv) and N-(2-Phenylethyl)trifluoromethanesulfonamide (50.6 mg, 0.2 mmol, 1.0 equiv). Toluene (0.2 mL, 1.0 M) was added and the vial was capped and heated to 45 °C for 72 hours. The vial was allowed to cool to room temperature and diluted with 1 mL acetone. The reaction mixture was filtered through a pipette silica plug into a 20mL vial with acetone. The mixture was concentrated under reduced pressure, diluted with 2 mL CDCl$_3$ and analyzed by crude $^1$H NMR with internal standard (trifluorotoluene 14.6 mg, 0.1 mmol, 0.5 equiv).

Following the general procedure using $(E)$-prop-1-ene-1,3-diyl dibenzene (38.9 mg 0.2 mmol, 1.0 equiv). Curde H$^1$ NMR showed 60% remaining olefin starting material (volatility / side reactions), 98% remaining unreacted N-(2-Phenylethyl)trifluoromethanesulfonamide, no aminated product was observed.

Following the general procedure using trans-β-methylstyrene (23.6 mg 0.2 mmol, 1.0 equiv). Curde H$^1$ NMR showed 36% remaining olefin starting material (volatility / side reactions), 98% remaining unreacted N-(2-Phenylethyl)trifluoromethanesulfonamide, no aminated product was observed.

See separate supporting information file for $^1$H, $^{13}$C NMR, $^{19}$F NMR spectra of all reported compounds, GC and HPLC traces of standards and enriched substrates for the stereoretention experiments.
References:


30. Sheldrick, G.M. Acta Cryst. 2015, A71, 3-8

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