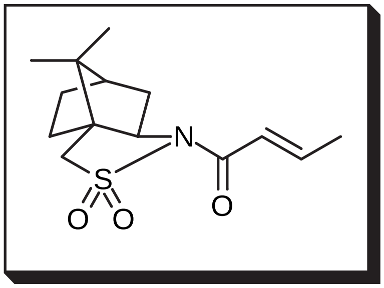
# EXPERIMENTAL

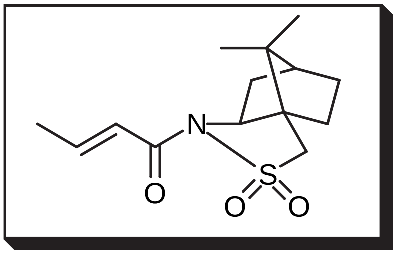
## *General Procedure*

All manipulations were conducted under an inert atmosphere (argon or nitrogen). All solvents were reagent grade (used in work–ups, columns and distillations) or HPLC grade (used as reaction solvent). Anhydrous tetrahydrofuran (THF) was distilled from sodium and benzophenone. The boiling point range of the hexane used was 38.0–55 °C. Methylene chloride ($CH_2Cl_2$) and toluene were distilled from calcium hydride ($CaH_2$). Organic acids and bases are reagent grade. All other reagents were commercial compounds of the highest purity available. Analytical thin–layer chromatography (TLC) was performed on EM Separations Tech./Merck silica gel (60–F254) plates (0.25 mm) precoated with a fluorescent indicator. Visualization was effected using ultraviolet light (254 nm), phosphomolybdic acid (7% w/v) in 95% ethanol. Melting points (mp) were determined with a Thomas–Hoover capillary melting point apparatus and are uncorrected. Proton and carbon magnetic resonance spectra ($^1$H–, $^{13}$C–NMR) were recorded on a Bruker AM–500 [500MHz] Fourier transform spectrometer, and chemical shifts were expressed in parts per million (ppm) relative to $CHCl_3$ as an internal reference (7.24 ppm for $^1$H and 77.0 for $^{13}$C). Multiplicities are designated as singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q) multiplet (m), and broad singlet (s). Infrared spectra (IR) were obtained on a Perkin–Elmer Model 1600 FT–IR spectrophotometer. Absorptions are reported in wavenumber (cm$^{-1}$). Optical rotations (in degrees) were measured with a Perkin–Elmer Model 341 polarimeter. High resolution mass spectra (HRMS) were obtained on either a VG 70–70HS, or a Micromass AutoSpect. Elemental Analyses were performed on a Perkin–Elmer 2400 Series II CHNS/O Analyzer at the University of Pennsylvania. Flash column chromatography was carried out on E. Merck silica gel 60 (240–400 mesh) using the solvent systems listed under individual experiments.

A solution of (-)-camphorsultam (**6**, 5.11 g, 24 mmol) in distilled toluene (120 mL) was treated with NaH (60% dispersion in mineral oil) (1.20 g, 30 mmol) at rt for 30 minutes, and *trans*-crotonyl chloride (2.80 mL, 29 mmol) was added dropwise. The reaction mixture was stirred at rt for 2h The reaction mixure was quenched by addition of 10% HCl. The resulting solution was concentrated *in vacuo*, and the residue was partitioned between EtOAc and 10% HCl. The organic phase was washed with 10% HCl, 5% $NaHCO_3$ and brine, then dried ($Na_2SO_4$), filtered, and concentrated. The residue was dissolved in toluene, and filtered through a silica gel bed. The solid was washed with toluene, the filtrate was concentrated *in vacuo* and the crude product was crystallized in MeOH to afford white crystals (**7**) (6.72 g, 85% yield).



**7:** $R_f$ 0.67 (30:70–ethyl acetate:petroleum ether); mp: 182-183 °C (Lit.[9] 186-187 °C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.00 (s, 3H), 1.20 (s, 3H), 1.35-1.50 (m, 2H), 1.85-1.95 (m, 2H), 1.96-1.98 (m, 4H), 2.05-2.20 (m, 2H), 3.45-3.55 (m, 2H), 3.92-3.96 (m, 1H), 6.54-6.58 (d, J=15.0 Hz, 1H), 7.05-7.12 (m, 1H); $^{13}$C NMR (250 MHz, $CDCl_3$) $\delta$ 18.3, 19.9, 20.8, 26.5, 32.9, 38.5, 44.7, 47.8, 48.4, 53.2, 65.1, 122.3, 146.1, 164.0; IR ($CHCl_3$) 2961, 1676, 1638, 1441, 1403, 1376, 1326, 1293, 1267, 1220, 1165, 1136, 1064 $cm^{-1}$; HRMS *m/z* calcd for $C_{14}H_{22}NO_3S$ (M+H): 284.1320, found 284.1312; Anal. Calcd for $C_{14}H_{21}NO_3S$: C, 59.34; H, 7.48, N, 4.95. Found: C, 59.52; H, 7.82, N, 4.71.

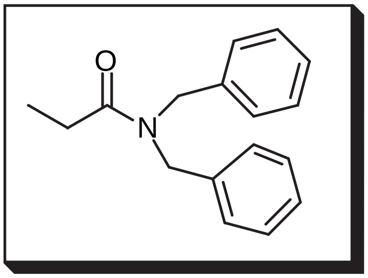


Procedure as above. Starting with (+)-camphorsultam (**10**).

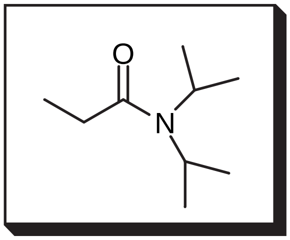
**11:** 90% yield; white crystals; $R_f$ 0.57 (30:70–ethyl acetate:petroleum ether); mp: 179-181 °C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.99 (s, 3H), 1.19

(s, 3H), 1.38-1.44 (m, 2H), 1.88-1.95 (m, 6H), 2.03-2.15 (m, 2H), 3.44-3.47 (d, J=13.8 Hz, 1H) and 3.51-3.53 (d, J=13.8 Hz, 1H), 3.92-3.95 (m, 1H), 6.58-6.59 (d, J=15.0 Hz, 1H), 7.07-7.14 (m, 1H); $^{13}$C NMR (250 MHz, $CDCl_3$) $\delta$ 18.3, 19.8, 20.8, 26.5, 32.8, 38.5, 44.7, 47.7, 48.4, 53.1, 65.1, 122.3, 146.0, 164.0; IR ($CHCl_3$) 3011, 2962, 2877, 1676, 1638, 1442, 1403, 1376, 1327, 1293, 1221, 1165, 1064 cm$^{-1}$; HRMS *m/z* calcd for $C_{14}H_{22}NO_3S$ (M+H): 284.1320, found 284.1326; $[\alpha]^{20}_{D}$ +99.94 (c 0,93, $CHCl_3$); Anal. Calcd for $C_{14}H_{21}NO_3S$: C, 59.34; H, 7.48, N, 4.95. Found: C, 59.79; H, 7.72, N, 4.83.

Propionyl chloride (10 mL, 0.115 mol) was added to a solution of dibenzylamine in $CH_2Cl_2$(250 mL), and the mixture was cooled in an ice/salt bath, at a rate sufficient to maintain a gentle reflux. After the addition was completed, the mixture was heated in an oil bath at reflux for 1 to 1.5h. The mixture was cooled to rt, poured into 10% HCl, and separated. The organic phase was washed 5% $NaHCO_3$ and brine, then dried ($Na_2SO_4$), filtered, and concentrated. The crude product was purified by column chromatography eluting with ethyl acetate:hexane (10:90 to 30:70) to afford a colorless oil (20.19 g, 70% yield).



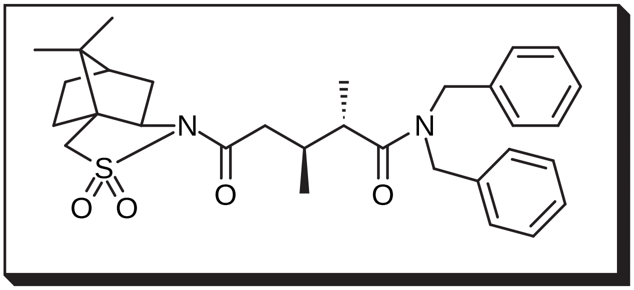
R$_f$ 0.40 (30:70–ethyl acetate:hexane); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.18-1.21 (t, J=7.4 Hz, 3H), 2.41-2.46 (q, J=7.4 Hz, 2H), 4.44 (s, 2H) and 4.61 (s, 2H), 7.13-7.14 (d, J=7.5 Hz, 2H) and 7.20-7.22 (d, J=7.3 Hz, 2H), 7.23-7.31 (m, 2H), 7.33-7.36 (m, 4H); $^{13}$C NMR (250 MHz, $CDCl_3$) $\delta$ 9.6, 26.4, 48.2, 49.8, 126.3, 127.3, 127.5, 128.3, 128.5,128.9, 136.6, 137.5, 174.3; IR ($CHCl_3$) 3062, 3029, 2979, 2937, 1651, 1495, 1466, 1452, 1421, 1362, 1214 cm$^{-1}$; Anal. Calcd for $C_{17}H_{19}NO$: C, 80.59; H, 7.56, N, 5.53. Found: C, 80.14; H, 7.75, N, 5.42.



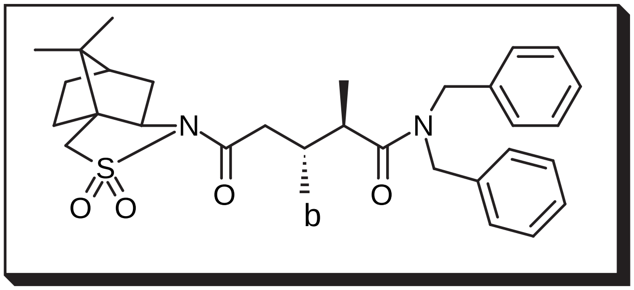
Procedure as above. Propionyl chloride reacted with diisopropylamine.

R*f* 0.38 (30:70–ethyl acetate:hexane); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.97-1.00 (t, J=7.4 Hz, 3H), 1.06-1.08 (d, J=6.3 Hz, 6H) and 1.24-1.25 (d, J=6.3 Hz, 6H), 2.15-2.20 (q, J=7.4 Hz, 2H), 3.35 (b, 2H) and 3.81 (m, 1H); $^{13}$C NMR (250 MHz, $CDCl_3$) $\delta$ 9.3, 20.5, 20.7, 28.1, 45.2, 47.9, 172.3; IR ($CHCl_3$) 3566, 3486, 2999, 2967, 2935, 2876, 1641, 1474, 1441, 1371, 1344, 1291 $cm^{-1}$.

**General procedure for Michael addition**: A solution of diisopropylamine (2.1 eq.) in distilled THF was cooled to 0 °C, and n-BuLi (1.6 M in hexane, 2.1 eq.) was added to this solution. The mixture was stirred at 0 °C for 30 min and cooled to -78 °C. Dibenzylpropylamide (2 eq.) was dissolved in distilled THF, cooled to -78 °C, and cannulated into the above mixture. The reaction was stirred at -78 °C for 1h. *N*-*trans*-crotonyl camphorsultam (1 eq.) was dissolved in distilled THF and cannulated into the above enolate solution. The reaction mixture was stirred at -78 °C for 45 min and then quenched by addition of saturated $NH_4Cl$ solution at -78 °C. The resulting solution was then warmed to rt, and concentrated *in vacuo*. The residue was diluted with water, and extracted with EtOAc 3 times. The organic phase was washed with 10% HCl, 5% $NaHCO_3$ and brine, then dried ($Na_2SO_4$), filtered, and concentrated. The crude product was purified by column chromatography eluting with ethyl acetate:hexane (10:90 to 30:70) to afford two compounds as white foams. Recrystallization from ether/hexane afforded two compounds as white crystals.

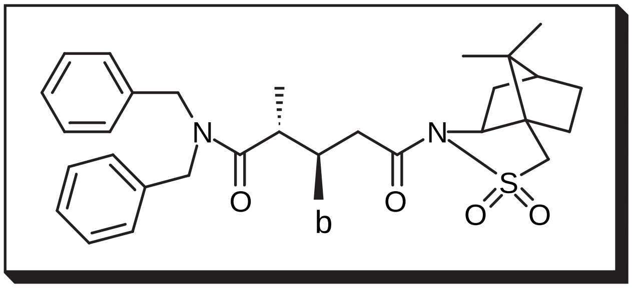


**8:** 19% yield; $R_f$ 0.26 (30:70–ethyl acetate:hexane); mp: 103-104 °C $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.94 (s, 3H) and 0.96-0.97 (d, J=6.4 Hz, 3H), 1.12-1.14 (m, 6H), 1.22-1.39 (m, 2H), 1.83-1.88 (m, 3H), 2.00-2.06 (m, 2H), 2.48-2.56 (m, 2H), 2.68-2.72 (m, 1H), 2.92-2.96 (m, 1H), 3.37-3.39 (d, J=13.8 Hz, 1H) and 3.44-3.46 (d, J=13.7 Hz, 1H), 3.82-3.85 (dd, $J_1$=7.3 Hz, $J_2$=5.0 Hz, 1H), 4.36-4.55 (m, 3H) and 4.71-4.74 (d, J=14.7 Hz, 1H), 7.12-7.34 (m, 10H); $^{13}$C NMR (250 MHz, $CDCl_3$) $\delta$ 15.2, 18.8, 19.9, 20.8, 26.4, 32.8, 32.9, 38.5, 38.9, 40.4, 44.6, 47.7, 48.2, 49.8, 53.0, 65.2, 126.5, 127.2, 127.5, 128.3, 128.5, 128.8, 136.8, 137.6, 171.1, 176.4; IR ($CHCl_3$) 2961, 1696, 1638, 1496, 1452, 1420, 1329, 1272, 1212, 1165, 1133 cm$^{-1}$; HRMS *m/z* calcd for $C_{31}H_{40}N_2O_4SNa$ (M+Na): 559.2607, found 559.2625; $[\alpha]_D^{20}$ – 59.2 (c 1.06, $CHCl_3$); Anal. Calcd for $C_{31}H_{40}N_2O_4S$: C, 69.37; H, 7.52, N, 5.22. Found: C, 69.69; H, 7.70, N, 5.08.

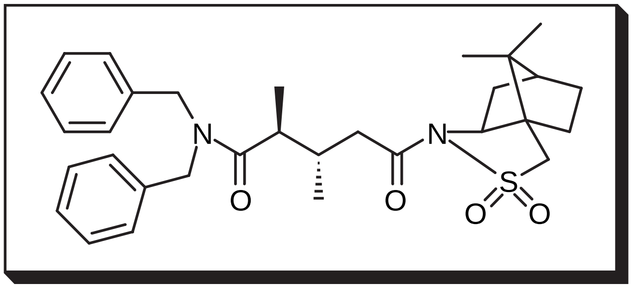


**9:** 76% yield; $R_f$ 0.21 (30:70–ethyl acetate:hexane); mp: 137-138 °C $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.94-0.98 (m, 6H), 1.12-1.14 (m, 6H), 1.24-1.43 (m, 2H), 1.83-1.89 (m, 3H), 2.02-2.06 (m, 2H), 2.52 (b, 1H) and 2.59-2.66 (m, 1H), 2.67-2.71 (m, 1H), 2.79-2.83 (m, 1H), 3.38-3.41 (d, J=13.8 Hz, 1H) and 3.44-3.47 (d, J=13.7 Hz, 1H), 3.84-3.86 (t, J=6.1 Hz, 1H), 4.36-4.56 (m, 3H) and 4.77-4.80 (d, J=14.6 Hz, 1H), 7.13-7.35 (m, 10H); $^{13}$C NMR (250 MHz, $CDCl_3$) $\delta$ 15.7, 18.5, 19.9, 20.8, 26.4, 32.9, 33.8, 38.7, 38.9, 40.4, 44.7, 47.7, 48.3, 50.0, 53.1, 65.3, 126.5, 127.3, 127.5, 128.3, 128.6, 128.9, 136.8, 137.6, 171.2, 176.4; IR ($CHCl_3$) 2963, 1694, 1644, 1495, 1453, 1328, 1273, 1211, 1133, 1165, 1069 cm$^{-1}$; HRMS *m/z* calcd for $C_{31}H_{40}N_2O_4SNa$ (M+Na):

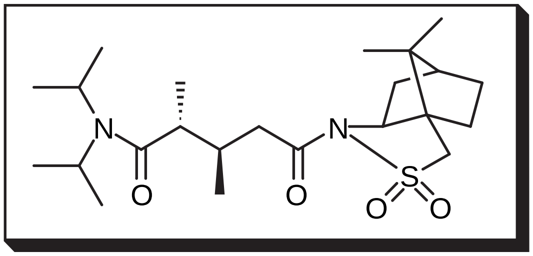
559.2607, found 559.2602; $[\alpha]_D^{20}$ – 42.8 (c 0.80, $CHCl_3$); Anal. Calcd for $C_{31}H_{40}N_2O_4S$: C, 69.37; H, 7.52, N, 5.22. Found: C, 69.87; H, 7.57, N, 5.19.



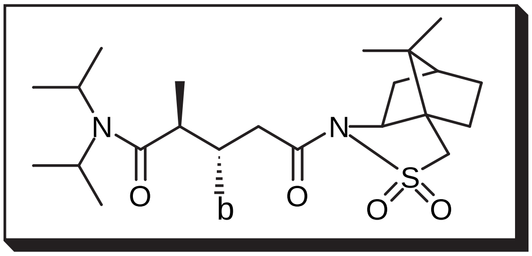
**12:** 72% yield; $R_f$ 0.29 (30:70–ethyl acetate:hexane); mp: 52-53 °C $^{1}H$ NMR (500 MHz, $CDCl_3$) δ 0.94-0.97 (m, 6H), 1.12-1.20 (m, 6H), 1.29-1.38 (m, 2H), 1.83-1.90 (m, 3H), 2.02-2.06 (m, 2H), 2.46-2.55 (m, 2H), 2.70-2.73 (t, J=7.0 Hz, 1H), 2.92-2.97 (m, 1H), 3.37-3.48 (m, 2H), 3.84-3.85 (dd, $J_1$=7.5 Hz, $J_2$=5.1 Hz, 1H), 4.37-4.55 (m, 3H) and 4.71-4.74 (d, J=14.7 Hz, 1H), 7.13-7.35 (m, 10H); $^{13}C$ NMR (250 MHz, $CDCl_3$) δ 15.2, 18.8, 19.9, 20.8, 26.5, 32.9, 38.5, 38.9, 40.4, 44.7, 47.7, 48.3, 49.8, 53.0, 65.2, 126.5, 127.3, 127.5, 128.3, 128.6, 128.9, 136.8, 137.7, 171.1, 176.5; IR ($CHCl_3$) 2961, 2878, 1693, 1641, 1494, 1452, 1421, 1328, 1272, 1212, 1165, 1133, 1060 cm$^{-1}$; HRMS *m/z* calcd for $C_{31}H_{40}N_2O_4SNa$ (M+Na): 559.2607, found 559.2623; $[\alpha]_D^{20}$ +60.2 (c 0.83, $CHCl_3$); Anal. Calcd for $C_{31}H_{40}N_2O_4S$: C, 69.14; H, 7.69, N, 5.22. Found: C, 69.14; H, 7.69, N, 5.16.



**13:** 24% yield; $R_f$ 0.24 (30:70–ethyl acetate:petroleum ether); mp: 54-55°C; $^{1}H$ NMR (500 MHz, $CDCl_3$) δ 0.94 -1.02 (m, 6H), 1.09-1.20 (m, 6H), 1.30-1.40 (m, 2H), 1.83-1.91 (m, 3H), 2.02-2.09 (m, 2H), 2.49-2.51 (m, 1H) and 2.53-2.64 (m, 1H), 2.66-2.71 (m, 1H), 2.79-2.83 (dd, $J_1$=15.8 Hz, $J_2$=3.7 Hz, 1H), 3.38-3.49 (m, 2H), 3.84-3.86 (t, J=6.3 Hz, 1H), 4.36-4.56 (m, 3H) and 4.77-4.80 (d, J=14.7 Hz, 1H), 7.12-7.37 (m, 10H); $^{13}C$ NMR (250 MHz, $CDCl_3$) δ 16.1, 18.9, 20.3, 21.3, 26.9, 33.3, 34.2, 39.1, 39.3, 40.9, 45.1, 48.1, 48.7, 50.3, 53.5, 65.8, 126.9, 127.7, 128.0, 128.7, 129.0, 129.3, 137.3, 138.1, 171.6, 176.8; IR ($CHCl_3$) 2961, 2878, 1686, 1639, 1452, 1420, 1328, 1273, 1213, 1165, 1134, 1060 cm$^{-1}$; HRMS *m/z* calcd for $C_{31}H_{40}N_2O_4SNa$ (M+Na): 559.2607, found 559.2619; $[\alpha]_D^{20}$ +40.8 (c 0.62, $CHCl_3$); Anal. Calcd for $C_{31}H_{40}N_2O_4S$: C, 69.37; H, 7.52, N, 5.22. Found: C, 69.54; H, 7.75, N, 5.22.

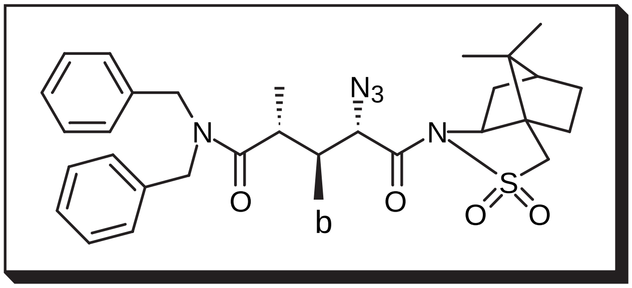


**14:** 71% yield; R$_f$ 0.40 (30:70 –acetone:hexane); $^1$H NMR (500 MHz, $CDCl_3$) δ 0.93 (s, 6H), 1.04-1.05 (d, J=6.7 Hz, 3H), 1.12 (m, 3H), 1.17-1.18 (d, J=6.5 Hz, 6H), 1.31-1.38 (m, 8H), 1.82-1.87 (m, 3H), 2.00-2.06 (m, 2H), 2.40-2.45 (m, 1H), 2.46-2.58 (m, 2H), 2.85-2.91 (m, 1H), 3.36-3.39 (d, J=13.8 Hz, 1H) and 3.43-3.46 (d, J=13.8 Hz, 1H), 3.82-3.85 (t, J=6.3 Hz, 10H), 4.0 (s, 6H); $^{13}$C NMR (250 MHz, $CDCl_3$) δ 15.4, 18.6, 19.8, 20.8, 21.3, 21.5, 26.4, 32.8, 33.0, 38.5, 39.2, 41.7, 44.7, 45.6, 47.7, 47.9, 48.2, 53.0, 65.1, 171.4, 174.9; IR ($CHCl_3$) 3462, 2964, 2880, 1695, 1633, 1456, 1440, 1373, 1330, 1271, 1237, 1209, 1166, 1134, 1060 cm$^{-1}$; HRMS *m/z* calcd for $C_{23}H_{40}N_2O_4SNa$ (M+Na): 463.2607, found 463.2620; $[\alpha]_D^{20}$ + 52.1 (c 0.75, $CHCl_3$); Anal. Calcd for $C_{23}H_{40}N_2O_4S$: C, 62.69; H, 9.16, N, 6.36. Found: C, 62.82; H, 9.59, N, 6.29.



**15:** 3% yield; R$_f$ 0.34 (30:70 –acetone:hexane) $^1$H NMR (500 MHz, $CDCl_3$) δ 0.88-0.92 (m, 6H), 1.02-1.053 (d, J=6.8 Hz, 3H), 1.10 (s, 3H), 1.15-1.17 (d, J=6.7 Hz, 6H), 1.26-1.40 (m, 8H), 1.78-1.86 (m, 3H), 2.03-2.05 (m, 2H), 2.38-2.41 (m, 1H), 2.52-2.58 (m, 2H), 2.71-2.75 (m, 1H), 3.36-3.39 (d, J=13.8 Hz, 1H) and 3.42-3.45 (d, J=13.8 Hz, 1H), 3.80-3.83 (t, J=6.3 Hz, 10H), 4.0 (s, 3H) and 4.3 (s, 3H); $^{13}$C NMR (250 MHz, $CDCl_3$) δ 15.5, 18.2, 18.6, 20.8, 21.2, 26.4, 32.8, 33.6, 38.6, 38.9, 41.5, 44.6, 45.6, 47.6, 48.2, 50.3, 53.0, 65.3, 171.3, 174.7; IR ($CHCl_3$) 3250, 2964, 2881, 1694, 1633, 1455, 1373, 1330, 1273, 1208, 1165, 1135, 1061 cm$^{-1}$; HRMS *m/z* calcd for $C_{23}H_{40}N_2O_4SNa$ (M+Na): 463.2607, found 463.2620.

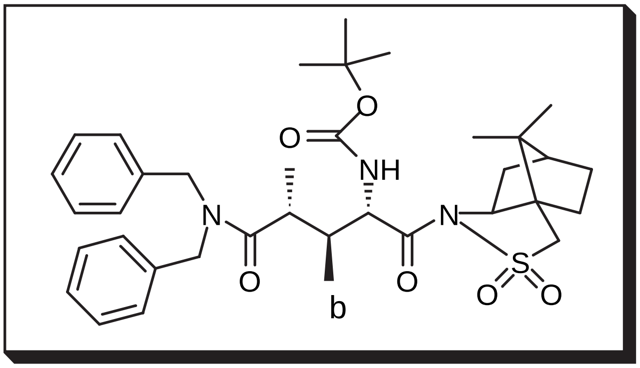
To a cooled (-78 °C) 0.2 M solution of KHMDS (0.5 M in toluene, 1.2 eq.) in distilled THF was added via cannula a cooled (-78 °C) solution (0.3 M in THF) of the major Michael adduct (**12**, 1.0 eq.). After an enolization time of ca. 30 min, a cooled solution (-78 °C) of 2,4,6-triisopropylbenzenesulfonyl azide (trisyl azide)[12] (1.2 eq., 0.3 M in THF) was added via cannula, and after1-2 min, glacial acetic acid (6 eq.) was added in one portion. After slow warming to rt, the reaction mixture was gently heated to 30 °C and stirred for 2h. The resulting solution was then concentrated *in vacuo*, and the residue was diluted with water, extracted with EtOAc 3 times. The organic phase was washed with 5% $NaHCO_3$ and brine, then dried ($Na_2SO_4$), filtered, and concentrated. The crude product was purified by column chromatography eluting with ethyl acetate:hexane (10:90 to 25:75) to afford a white foam. Recrystallization from ethyl acetate afforded a white crystal (**16**, 78% yield).



**16:** $R_f$ 0.28 (30:70–ethyl acetate : hexane); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.96 (s, 3H) and 1.18 (s, 3H), 1.12-1.13 (d, J=6.9 Hz, 3H) and 1.20-1.21 (d, J=6.9 Hz, 3H), 1.31-1.43 (m, 2H), 1.85-1.95 (m, 3H), 2.05-2.09 (m, 1H) and 2.13-2.18 (m, 1H), 2.36-2.41 (m, 1H), 3.08-3.13 (m, 1H), 3.44-3.46 (d, J=13.8 Hz, 1H) and 3.52-3.55 (d, J=13.8 Hz, 1H), 3.89-3.92 (m, 1H), 4.22-4.43 (m, 3H) and 4.71-4.74 (d, J=16.9 Hz, 1H), 4.99-5.02 (d, J=14.8 Hz, 1H), 7.15-7.35 (m, 10H); $^{13}$C NMR (250 MHz, $CDCl_3$) $\delta$ 13.2, 16.8, 19.8, 20.8, 26.4, 32.8, 35.9, 38.3, 38.5, 44.5, 47.9, 48.3, 48.6, 49.9, 53.0, 64.1, 65.2, 126.7, 127.2, 127.5, 128.3, 128.6, 128.8, 136.9, 137.4, 167.8, 175.3; IR ($CHCl_3$) 3090-3390(b), 2964, 2110, 1691, 1642, 1452, 1386, 1332, 1278, 1206, 1163, 1127, 1073, 1031 cm$^{-1}$; HRMS *m/z* calcd for $C_{31}H_{39}N_5O_4SNa$ (M+Na): 600.2620, found 600.2640; $[\alpha]^{20}_{D}$

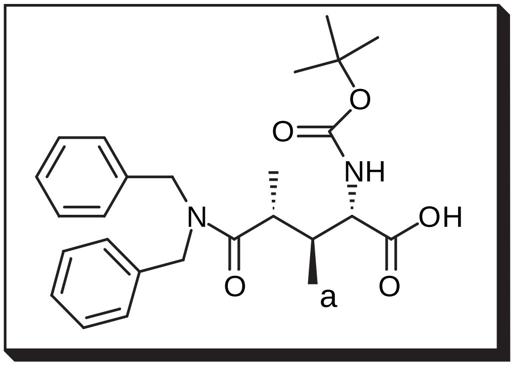
+76.5 (c 0.60, $CHCl_3$); Anal. Calcd for $C_{31}H_{39}N_5O_4S$: C, 64.51; H, 6.81, N, 12.13. Found: C, 64.51; H, 6.70, N, 12.03.

To a cooled (0 °C) solution of $SnCl_2•2H_2O$ (4 eq.) in dioxane/$H_2O$ (2:1) under argon was added a solution of compound **16** (1.0 eq.) in dioxane. The ice-bath was removed and the reaction was stirred at rt overnight. Then $Boc_2O$ (5 eq.) and $NaHCO_3$ (5 eq.) in water were added and the mixture stirred at rt for 3h. The resulting solution was then concentrated *in vacuo*, and the residue was diluted with water, acidified with 1N $KHSO_4$ to pH 3, and extracted with EtOAc 3 times. The organic phase was dried ($Na_2SO_4$), filtered, and concentrated. The crude product was purified by column chromatography eluting with ethyl acetate:hexane (10:90 to 25:75) to afford a white foam (**17**, one-pot 93% yield).



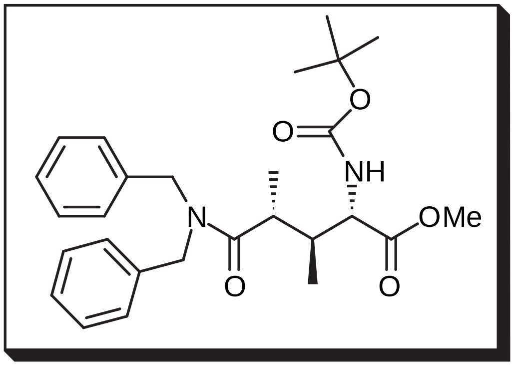
**17:** $R_f$ 0.22 (30:70–ethyl acetate : hexane); $^1H$ NMR (500 MHz, $CDCl_3$) δ 0.93 (s, 3H) and 1.13 (s, 3H), 1.12-1.13 (d, J=6.9 Hz, 3H) and 1.16-1.17 (d, J=6.9 Hz, 3H), 1.21-1.34 (m, 2H), 1.40 (s, 9H), 1.83-1.90 (m, 3H), 1.99-2.04 (m, 1H) and 2.10-2.12 (m, 1H), 2.39-2.43 (m, 1H), 2.98-3.01 (m, 1H), 3.35-3.38 (d, J=13.7 Hz, 1H) and 3.43-3.45 (d, J=13.7 Hz, 1H), 3.91 (s, 1H), 4.33-4.39 (m, mH) and 4.56-4.61 (m, 2H), 4.80-4.83 (d, J=14.7 Hz, 1H), 5.54 (b, 1H), 7.13-7.33 (m, 10H); $^{13}C$ NMR (250 MHz, $CDCl_3$) δ 14.1, 16.7, 19.9, 20.7, 25.2, 28.2, 31.8, 36.9, 38.4, 38.7, 44.7, 47.7, 48.1, 48.6, 50.0, 52.8, 56.9, 65.2, 79.8, 126.8, 127.5, 127.6, 128.3, 128.5, 128.8, 136.7, 137.4, 155.0, 171.2, 176.4; IR ($CHCl_3$) 3320(b), 2966(b), 2883, 1704, 1678, 1634, 1496, 1454, 1392, 1366, 1340, 1269, 1237, 1214, 1167, 1135, 1079 $cm^{-1}$; HRMS *m/z* calcd for $C_{36}H_{49}N_3O_6SNa$ (M+Na): 674.3240, found 674.3218; $[\alpha]_D^{20}$ +26.7 (c 0.79, $CHCl_3$); Anal. Calcd for $C_{36}H_{49}N_3O_6S$: C, 66.33; H, 7.58, N, 6.45. Found: C, 66.07; H, 7.47, N, 6.07.

To a cooled (0 °C) solution of compound **17** (35 mg, 0.054 mmol) in THF/$H_2O$ (2:1, 0.6 mL) was added LiOH•$H_2O$ (11.3 mg, 0.27 mmol). The reaction was stirred at 0 °C for 3h, and warmed to rt overnight. Then the mixture was washed with $CH_2Cl_2$ (3 x 2 mL) and the layers were separated. The organic layer was concentrated to recover the chiral auxiliary. The aqueous layer was acidified to pH 2 with 1N $KHSO_4$, and extracted with EtOAc 3 times. The organic phase was dried ($Na_2SO_4$), filtered, and concentrated to give a white foam (**3**, 22.0 mg, 90% yield).



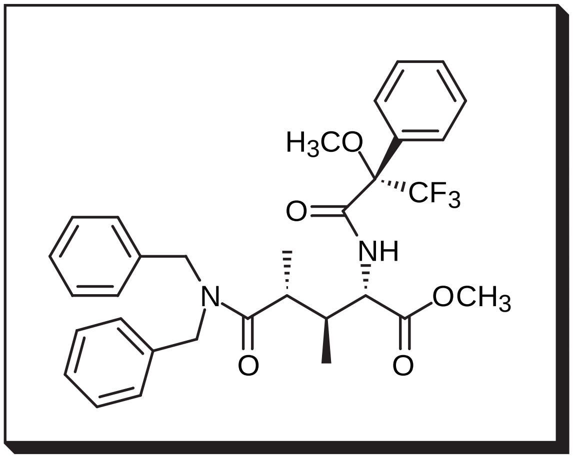
**3:** $R_f$ 0.05 (30:70–ethyl acetate:hexane) $^{1}$H NMR (500 MHz, $CDCl_3$) δ 0.96-0.98 (d, J=6.8 Hz, 3H), 1.10-1.12 (d, J=6.5 Hz, 3H), 1.42 (s, 9H), 2.30-2.37 (m, 1H), 2.82-2.98 (m, 1H), 4.35-4.56 (m, 4H), 4.62-4.80 (m, 1H), 5.46 (b, 1H), 7.08-7.35 (m, 10H); $^{13}$C NMR (250 MHz, $CDCl_3$) δ 15.2, 15.6, 28.3, 38.4, 39.6, 54.8, 55.0, 62.8, 79.8, 126.8, 127.4, 127.6, 128.3, 128.6, 128.9, 136.5, 137.2, 155.2, 174.0, 177.1; IR (KBr, $CHCl_3$) 3430, 3260(b), 2966, 2884, 1713, 1631, 1491, 1455, 1390, 1361, 1296, 1243, 1214, 1132, 1079 cm$^{-1}$; HRMS *m/z* calcd for $C_{26}H_{34}N_2O_5Na$ (M+Na): 477.2365, found 477.2363.

To a solution of the acid (**3**, 0.0225 g, 0.050 mmol) in redistilled DMF was added anhydrous $K_2CO_3$ (0.007 g, 0.052 mmol), $Bu_4NI$ (0.004 g, 0.01 mmol) and MeI (0.012 mL, 0.20 mmol). The reaction was stirred at rt for 1h, and the mixture was diluted with $H_2O$, and extracted with EtOAc 3 times. The organic phase was washed with 10% HCl, 5% $NaHCO_3$, and brine sequentially. The organic layer was dried ($Na_2SO_4$), filtered, and concentrated. The crude product was purified by column chromatography eluting with ethyl acetate:hexane (10:90 to 25:75) to afford a colorless oil (0.0210 g, 91% yield).



R$_f$ 0.27 (30:70–ethyl acetate:hexane) $^1$H NMR (500 MHz, $CDCl_3$) δ 0.78-0.79 (d, J=6.8 Hz, 3H), 1.25-1.27 (d, J=6.6 Hz, 3H), 1.42 (s, 9H), 2.31-2.35 (m, 1H), 2.74-2.80 (m, 1H), 3.51 (s, 3H), 4.43 (s, 3H) and 4.49-4.51 (d, J=14.7 Hz, 1H), 4.76-4.79 (d, J=14.6 Hz, 1H), 5.33-5.34 (d, J=6.1 Hz, 1H), 7.12-7.35 (m, 10H); $^{13}$C NMR (250 MHz, $CDCl_3$) δ 15.2, 16.3, 28.3, 38.5, 40.3, 50.0, 54.8, 55.1, 62.9, 79.8, 126.3, 127.4, 127.6, 128.3, 128.6, 128.9, 136.9, 137.5, 155.0, 171.9, 176.4; IR (KBr, $CHCl_3$) 3272, 2960, 2884, 1743, 1715, 1636, 1496, 1454, 1300, 1247, 1212, 1137, 1077 cm$^{-1}$; HRMS *m/z* calcd for $C_{27}H_{36}N_2O_5Na$ (M+Na): 491.2522, found 491.2541.

To a solution of the methyl ester (0.0160 g, 0.034 mmol) in distilled $CH_2Cl_2$ (1 mL), was added trifluoroacetic acid (1 mL). The reaction was stirred at rt for 1h, and concentrated *in vacuo*. The TFA residue was azotroped with toluene. The crude residue was suspended in distilled $CH_2Cl_2$ (0.10 mL), followed by addition of $Et_3N$ (0.014 mL, 0.10 mmol) and (*R*)-(–)-α-(trifluomethyl)phenylacetic acid chloride [ (–) MTPA-Cl, 0.010 mL, 0.051 mmol]. The reaction was stirred at rt for 3h, after which the mixture was diluted with $H_2O$, extracted with $CH_2Cl_2$ 3 times. The organic phase was washed with 10% HCl, 5% $NaHCO_3$, and brine sequentially. The organic layer was dried ($Na_2SO_4$), filtered, and concentrated to give a brown oil. After purification by column chromatography eluting with acetone : hexane(5:95 to 20:80), a white solid (0.0155 g, 78% yield) was obtained.



**(–) Mosher amide:** $R_f$ 0.45 (30:70–acetone:hexane) $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.76-0.77 (d, J=7.0 Hz, 3H), 1.15-1.16 (d, J=6.9 Hz, 3H), 2.35-2.40 (m, 1H), 2.70-2.75 (m, 1H), 3.52 (s, 3H), 3.56 (s, 3H), 4.31-4.42 (m, 3H) and 4.81-4.84 (d, J=14.6 Hz, 1H), 4.65-4.66 (dd, J=2.4, 4.3 Hz, 1H), 7.07-7.55 (m, 15H), 7.82-7.84 (d, J=7.3 Hz, 1H); $^{19}F$ NMR (500 MHz, $CDCl_3$) $\delta$ -69.4; IR (KBr, $CHCl_3$) 3256, 2953, 1743, 1693, 1635, 1496, 1452, 1436, 1358, 1270, 1220, 1136, 1078, 1000 $cm^{-1}$; HRMS *m/z* calcd for $C_{32}H_{35}N_2F_3O_5Na$ (M+Na): 607.2396, found 607.2420.