Iron-Catalyzed Intramolecular Allylic C—H Amination

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General Information

The following commercially obtained reagents for the C—H amination were used as received: iron(III) phthalocyanine chloride ([FePc]Cl, Sigma-Aldrich), 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine iron(III) chloride (Fe(TPP)Cl, Strem), silver hexafluoroantimonate ($AgSbF_6$, Strem), (diacetoxyiodo)benzene ($PhI(OAc)_2$, Sigma-Aldrich), bis(*tert*-butylcarbonyloxy)iodobenzene ($PhI(OPiv)_2$, Sigma-Aldrich), and rhodium(II) acetate dimer ($Rh_2(OAc)_4$, Sigma-Aldrich). All starting materials for the sulfamate ester formation were either commercially available or synthesized according to literature procedures (see end of Supporting Information for synthetic sequences and references). All 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. Solid reagents were stored in a dessicator or glovebox, and anhydrous solvents were purified by passage through a bed of activated alumina immediately prior to use (Glass Countour, Laguna Beach, California). Deuterochloroform was stored over 3Å molecular sieves in a secondary container with drierite. Fe(*R,R*-PDP)$(SbF_6)_2$ and Fe(*R,R*-salen)Cl were prepared according to methods described in the literature[1,2] and stored at 4°C. Chlorosulfonyl isocyanate ($ClSO_2NCO$, Sigma-Aldrich or TCI America) was transferred to a Schlenk-type flask and stored at 4°C under an inert atmosphere.[3] Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm) and visualized with UV and ethanolic anisaldehyde or potassium permanganate stains. Flash chromatography was performed as described by Still[4] using American International ZEOprep 60 ECO silica gel (230-400 mesh). Achiral gas chromatographic (GC) analysis was performed on an Agilent 6890N Series instrument equipped with FID detectors using a HP-5 (5%-Phenyl)-methylpolysiloxane column (30m, 0.32mm, 0.25mm).

^{1}H-NMR spectra were recorded on a Varian Inova-500 (500 MHz) or Varian Unity-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, spt = 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) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm). Diastereoselectivity and product selectivity ratios for the intramolecular allylic C—H amination reaction were determined by ^{1}H-NMR analysis of the crude product mixture when possible. IR spectra were recorded as thin films on NaCl plates on a Mattson Galaxy Series FTIR 5000 and are reported in frequency of absorption (cm^{-1}). 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: $[\alpha]_\lambda T^oC$ (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 Ultima spectrometer, and electron ionization (EI) and field desorption (FD) spectra were performed on a Micromass 70-VSE spectrometer.

Preparation of Sulfamate Ester Starting Materials

General procedure for preparation of sulfamate ester substrates[5]

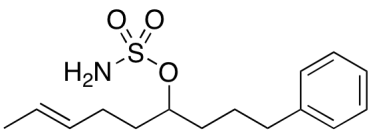
Method A:

Preparation of $ClSO_2NH_2$ solution (2M in MeCN): A 25 mL round-bottom flask equipped with stir bar and rubber septum was charged with $ClSO_2NCO$ (653 μL, 7.50 mmol, 1.5 equiv). The flask was cooled to 0°C, and then neat formic acid (283 μL, 7.50 mmol, 1.5 equiv) was added dropwise. After vigorously stirring for 5 min at 0°C, MeCN (3.8 mL, 2M) was added, and the reaction stirred vigorously at 0°C (1 h) then room temp (~20°C) overnight.

Sulfamate ester formation: A 50 mL round-bottom flask equipped with stir bar and rubber septum was charged with 95% NaH (139 mg, 5.50 mmol, 1.1 equiv) and 5 mL DMF and cooled to 0°C. The alcohol starting material (5.00 mmol, 1.0 equiv) in 4 mL DMF was slowly added. The reaction was stirred at room temp. for 1 h, after which it was cooled again to 0°C. The freshly prepared 2M MeCN solution of $ClSO_2NH_2$ (*vide supra*) was then added dropwise via syringe, and the reaction stirred at room temp. for 2-4 h. Upon complete consumption of starting material as monitored by TLC, the reaction was quenched with H_2O until the mixture turned clear (~8 mL). The reaction mixture was partitioned between 15 mL H_2O and 60 mL Et_2O and separated. The aqueous layer was then extracted with 2x30 mL Et_2O. The organic layers were combined, dried over $MgSO_4$ and concentrated under reduced pressure. Following purification of the crude product via flash column chromatography, the pure product was dissolved in CH_2Cl_2 and filtered through a short silica plug, then twice dissolved in benzene and concentrated under reduced pressure to remove trace H_2O, then stored in a dessicator until use.

Method B:

A 50 mL round-bottom flask equipped with stir bar and rubber septum was charged with $ClSO_2NCO$ (653 μL, 7.50 mmol, 1.5 equiv). The flask was cooled to 0°C, and then neat formic acid (283 μL, 7.50 mmol, 1.5 equiv) was added dropwise. After vigorously stirring for 5 min at 0°C, CH_2Cl_2 (3.8 mL, 2M) was added, and the reaction stirred vigorously at 0°C (1 h) then room temp. overnight. After cooling the reaction flask back to 0°C, the alcohol starting material (5.00 mmol, 1.0 equiv) with Et_3N (1.05 mL, 7.50 mmol, 1.5 equiv) in 7 mL CH_2Cl_2 was slowly added via syringe. After complete addition, the reaction warmed back to room temp. and stirred for 4-6 h. If conversion is low after 3-4 h, additional Et_3N (1-2 equiv) can be added. Upon complete consumption of starting material as monitored by TLC, the reaction was quenched with H_2O until the mixture turned clear (~8 mL). The reaction mixture was partitioned between 15 mL H_2O and 30 mL CH_2Cl_2 and separated. The aqueous layer was then extracted with 2x30 mL CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$ and concentrated under reduced pressure. Following purification of the crude product via flash column chromatography, the pure product was dissolved in CH_2Cl_2 and filtered through a short silica plug, then twice dissolved in benzene and concentrated under reduced pressure to remove trace H_2O, then stored in a dessicator until use.

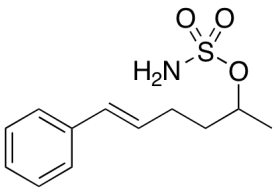


(±)-(*E*)-1-phenylnon-7-en-4-yl sulfamate (Table 1).

Prepared according to method **A**. 1.092 g (5.00 mmol) of (±)-(*E*)-1-phenylnon-7-en-4-ol **S1** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes:EtOAc as eluent gave 1.264 g (4.25

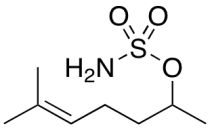
mmol) of pure product as a colorless oil (>20:1 *E:Z*, 85% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.21-7.17 (m, 3H), 5.44 (dq, *J* = 15.5, 6.0 Hz, 1H), 5.39 (dt, *J* = 15.0, 6.0 Hz, 1H), 4.61 (br. s, 3H), 2.65-2.64 (m, 2H), 2.07-2.05 (m, 2H), 1.80-1.70 (m, 6H), 1.64 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.9, 129.8, 128.6 (2 peaks), 126.2, 126.1, 84.7, 35.6, 33.9, 33.5, 28.1, 26.5, 18.0; IR (film, cm^{-1}) 3381, 3284, 3026, 2933, 2856, 1554, 1496, 1452, 1358, 1180, 914; HRMS (ESI) *m/z* calculated for $C_{15}H_{23}NO_3SNa$ $[M+Na]^+$: 320.1296, found 320.1299.

(±)-(*E*)-6-phenylhex-5-en-2-yl sulfamate (Table 2).



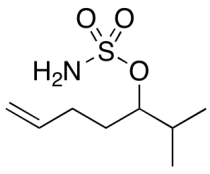
Prepared according to method **A**. 881 mg (5.00 mmol) of (±)-(*E*)-6-phenylhex-5-en-2-ol[6] were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes:EtOAc as eluent gave 919 mg (3.60 mmol) of pure product as a white solid (>20:1 *E:Z*, 72% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 4H), 7.23-7.20 (m, 1H), 6.43 (d, *J* = 15.5 Hz, 1H), 6.19 (dt, *J* = 15.5, 7.0 Hz, 1H), 4.80-1.73 (m, 1H), 4.64 (br. s, 2H), 2.37-2.33 (m, 2H), 1.97-1.90 (m, 1H), 1.82-1.76 (m, 1H), 1.47 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 137.5, 131.1, 129.1, 128.7, 127.3, 126.2, 81.1, 36.2, 28.7, 20.8; IR (film, cm^{-1}) 3383, 3292, 3026, 2980, 2937, 1554, 1446, 1361, 1182, 922; HRMS (ESI) *m/z* calculated for $C_{12}H_{17}NO_3SNa$ $[M+Na]^+$: 278.0827, found 278.0837.

(±)-6-methylhept-5-en-2-yl sulfamate (Table 2).



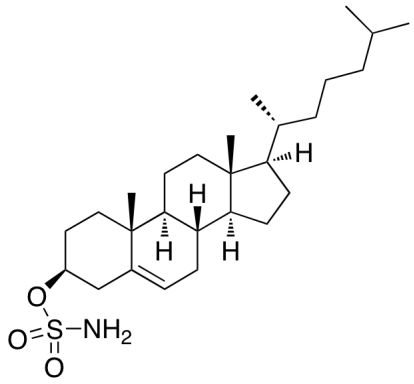
Prepared according to method **A**. 641 mg (5.00 mmol) of (±)-6-methylhept-5-en-2-ol were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes:EtOAc as eluent gave 800 mg (3.86 mmol) of pure product as a colorless oil (77% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.10-5.07 (m, 1H), 4.80 (br. s, 2H), 4.70 (app sxt, *J* = 6.5 Hz, 1H), 2.15-2.03 (m, 2H), 1.77 (ddt, *J* = 14.0, 9.0, 6.5 Hz, 1H), 1.69 (s, 3H), 1.66-1.59 (m, 1H), 1.61 (s, 3H), 1.43 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 132.9, 123.0, 81.5, 36.6, 25.8, 23.8, 20.7, 17.9; IR (film, cm^{-1}) 3379, 3288, 2972, 2929, 2858, 1562, 1450, 1358, 1182, 1126 924; HRMS (ESI) *m/z* calculated for $C_8H_{17}NO_3SNa$ $[M+Na]^+$: 230.0827, found 230.0828.

(±)-2-methylhept-6-en-3-yl sulfamate (Table 2).



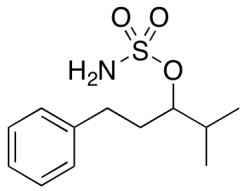
Prepared according to method **A**. 641 mg (5.00 mmol) of (±)-2-methylhept-6-en-3-ol **S2** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes:EtOAc as eluent gave 674 mg (3.25 mmol) of pure product as a colorless oil (65% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.81 (ddt, *J* = 16.5, 10.0, 6.0 Hz, 1H), 5.07 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.01 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.75 (br. s, 2H), 4.47 (dt, *J* = 7.5, 4.5 Hz, 1H), 2.24-2.09 (m, 3H), 1.86-1.71 (m, 2H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 137.6, 115.6, 89.4, 31.1, 29.6, 29.5, 17.7 (2 peaks); IR (film, cm^{-1}) 3381, 3288, 2968, 2879, 1641, 1556, 1468, 1363, 1182, 918; HRMS (ESI) *m/z* calculated for $C_8H_{17}NO_3SNa$ $[M+Na]^+$: 230.0827, found 230.0826.

(-)-3β-cholest-5-enyl sulfamate (Table 2).



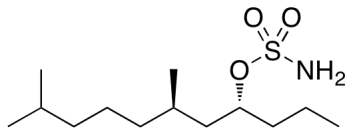
Prepared according to method **A**. 1.934 g (5.00 mmol) of 3β-hydroxycholesterol were used. Due to its insolubility in DMF, cholesterol was dissolved in $CHCl_3$ (4 mL) instead prior to addition to NaH solution; the general procedure was otherwise exactly followed. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 9:1 hexanes:EtOAc as eluent followed by recrystallization from ether (in place of the normal silica plug filtration) gave 1.514 g (3.25 mmol) of pure product as a white solid (65% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.42 (app. d, J = 5.0 Hz, 1H), 4.64 (br. s, 1H), 4.45 (dddd, J = 11.5, 11.5, 11.0, 11.0 Hz, 1H), 2.57-2.52 (m, 2H), 2.10-2.07 (m, 1H), 2.04-1.96 (m, 2H) 1.90 (dt, J = 13.5, 3.8 Hz, 1H), 1.87-1.74 (m, 2H), 1.60-1.43 (m, 7H), 1.38-1.31 (m, 3H), 1.27-1.25 (m, 1H), 1.18-1.05 (m, 7H), 1.05 (s, 3H), 1.01-0.93 (m, 2H), 0.92 (d, J = 6.5 Hz, 3H), 0.87 (dd, J = 6.5, 2.5 Hz, 6H), 0.68 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 139.0, 123.8, 83.5, 56.8, 56.3, 50.2, 42.5, 39.9, 39.7, 38.9, 37.1, 36.6, 36.3, 35.9, 32.1, 32.0, 28.7, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.2, 19.4, 18.9, 12.0; IR (film, cm^{-1}) 3373, 3273, 2951, 2883, 1545, 1468, 1350, 1196, 1163, 980, 958, 928; $[\alpha]^{25}_D$ = -36.7^o (c = 1.2, $CHCl_3$); HRMS (CI) *m/z* calculated for $C_{27}H_{47}NO_3SNa$ $[M+Na]^+$: 488.3174, found 488.3184.

(±)-1-phenyl-4-methylpentan-3-yl sulfamate (Table 2).



Prepared according to method **A**. 891 mg (5.00 mmol) of (±)-1-phenyl-5-methylpentan-3-ol **S3** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes:EtOAc as eluent gave 901 mg (3.50 mmol) of pure product as a colorless oil (70% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.30 (t, J = 7.5 Hz, 2H), 7.22-7.19 (m, 3H), 4.73 (br. s, 2H), 4.50 (dt, J = 7.5, 4.5 Hz, 1H), 2.83-2.77 (m, 1H), 2.74-2.68 (m, 1H), 2.20-2.13 (m, 1H), 2.07-1.94 (m, 2H), 1.00 (d, J = 6.5 Hz, 3H), 0.97 (d, J = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.4, 128.7, 128.5, 126.2, 89.4, 32.0, 31.7, 31.2, 17.9, 17.5; IR (film, cm^{-1}) 3388, 3284, 3087, 3064, 3028, 2966, 2937, 2877, 1603, 1554, 1496, 1454, 1360, 1182, 922; HRMS (ESI) *m/z* calculated for $C_{12}H_{19}NO_3SNa$ $[M+Na]^+$: 280.0983, found 280.0985.

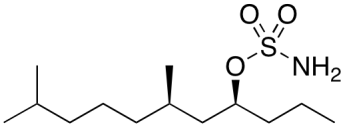
(-)-(*4R, 6R*)-6,10-dimethylundecan-4-yl sulfamate (Table 2).



Prepared according to method **A**. 777 mg (3.92 mmol) of a 97:3 *anti:syn* mixture of (-)-(*4R, 6R*)-6,10-dimethylundecan-4-ol **S4** were used, along with NaH (109 mg, 4.31 mmol, 1.1 equiv), DMF (4 + 3 mL), $ClSO_2NCO$ (511 μL, 5.88 mmol, 1.5 equiv), formic acid (222 μL, 5.88 mmol, 1.5 equiv) and MeCN (3 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 9:1 hexanes:EtOAc as eluent gave 771 mg (2.76 mmol) of pure product as a colorless oil (70% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.73-4.68 (m, 3H), 1.78-1.67 (m, 3H), 1.62-1.60 (m, 1H), 1.54-1.49 (m, 1H), 1.45-1.40 (m, 2H), 1.38-1.30 (m, 2H), 1.29-1.21 (m, 2H), 1.16-1.11 (m, 3H), 0.95 (t, J = 7.3 Hz, 3H), 0.93 (d, J = 6.5 Hz,

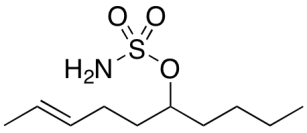
3H), 0.86 (d, J = 6.5 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 84.1, 41.8, 39.4, 37.6, 37.1, 29.2, 28.1, 24.7, 22.8, 22.7, 19.7, 18.3, 14.1; IR (film, cm^{-1}) 3369, 3284, 2956, 2929, 2873, 1556, 1466, 1360, 1184, 920; $[\alpha]^{27}_D$ = -11.0° (c = 1.0, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{13}H_{29}NO_3SNa$ $[M+Na]^+$: 302.1766, found 302.1768.

(-)-(*4R, 6S*)-6,10-dimethylundecan-4-yl sulfamate (Table 2).



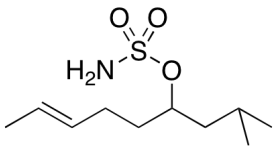
Prepared according to method **A**. 770 mg (3.88 mmol) of a 5:95 *anti:syn* mixture of (-)-(*4R, 6S*)-6,10-dimethylundecan-4-ol **S4** were used, along with NaH (108 mg, 4.27 mmol, 1.1 equiv), DMF (4 + 3 mL), $ClSO_2NCO$ (507 μL, 5.82 mmol, 1.5 equiv), formic acid (220 μL, 5.82 mmol, 1.5 equiv) and MeCN (3 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 9:1 hexanes:EtOAc as eluent gave 642 mg (2.30 mmol) of pure product as a colorless oil (60% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.72-4.67 (m, 3H), 1.74-1.65 (m, 2H), 1.64-1.59 (m, 2H), 1.58-1.39 (m, 4H), 1.38-1.20 (m, 3H), 1.18-1.07 (m, 3H), 0.95 (t, J = 7.5 Hz, 3H), 0.91 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 6.5 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 84.3, 41.7, 39.3, 37.3, 36.4, 29.5, 28.1, 24.6, 22.8, 22.8, 22.7, 19.9, 18.1, 14.1; IR (film, cm^{-1}) 3371, 3290, 2956, 2929, 2873, 1466, 1363, 1184, 922; $[\alpha]^{27}_D$ = -7.4° (c = 1.0, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{13}H_{29}NO_3SNa$ $[M+Na]^+$: 302.1766, found 302.1772.

(±)-(*E*)-dec-8-en-5-yl sulfamate (Table 3, entries 1-2).



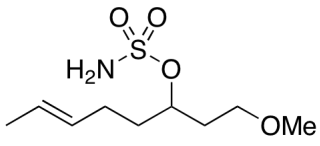
Prepared according to method **A**. 781 mg (5.00 mmol) of (±)-(*E*)-dec-8-en-5-ol **S5** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes:EtOAc as eluent gave 941 mg (4.00 mmol) of pure product as a colorless oil (>20:1 *E:Z*, 80% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.49 (dq, J = 15.5, 6.0 Hz, 1H), 5.41 (dt, J = 15.0, 6.5 Hz, 1H), 4.74 (br. s, 2H), 4.62 (p, J = 6.0 Hz, 1H), 2.11-2.09 (m, 2H), 1.84-1.71 (m, 4H), 1.66 (d, J = 6.0 Hz, 3H), 1.41-1.32 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 130.0, 126.1, 85.2, 34.0, 33.8, 28.1, 27.0, 22.7, 18.0, 14.1; IR (film, cm^{-1}) 3363, 3292, 2958, 2862, 1556, 1452, 1365, 1182, 916; HRMS (ESI) *m/z* calculated for $C_{10}H_{21}NO_3SNa$ $[M+Na]^+$: 258.1140, found 258.1138.

(±)-(*E*)-2-methylnon-7-en-4-yl sulfamate (Table 3, entries 3-4).



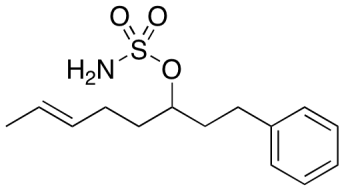
Prepared according to method **A**. 781 mg (5.00 mmol) of (±)-(*E*)-2-methylnon-7-en-4-ol **S6** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes:EtOAc as eluent gave 1.153 g (4.90 mmol) of pure product as a colorless oil (>20:1 *E:Z*, 98% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.48 (dq, J = 15.5, 6.5 Hz, 1H), 5.41 (dt, J = 15.0, 6.5 Hz, 1H), 4.86 (br. s, 2H), 4.67 (p, J = 6.0 Hz, 1H), 2.10 (q, J = 7.0 Hz, 2H), 1.81-1.65 (m, 4H), 1.66 (d, J = 6.0 Hz, 3H), 1.49-1.44 (m, 1H), 0.94 (t, J = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.9, 126.1, 83.8, 43.3, 34.4, 27.9, 24.5, 22.9, 22.5, 18.0; IR (film, cm^{-1}) 3391, 3290, 2958, 2871, 1562, 1450, 1360, 1182, 924; HRMS (ESI) *m/z* calculated for $C_{10}H_{21}NO_3SNa$ $[M+Na]^+$: 258.1140, found 258.1131.

(±)-(*E*)-1-methoxyoct-6-en-3-yl sulfamate (Table 3, entries 5-6).



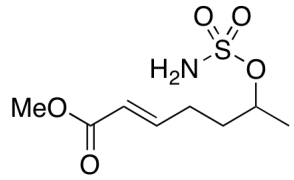
Prepared according to method **A**. 791 mg (5.00 mmol) of (±)-(*E*)-1-methoxyoct-6-en-3-ol **S7** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes:EtOAc as eluent gave 818 mg (3.45 mmol) of pure product as a colorless oil (>20:1 *E:Z*, 69% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.49 (dq, *J* = 15.5, 6.0 Hz, 1H), 5.41 (dt, *J* = 15.5, 6.0 Hz), 4.96 (br. s, 2H), 4.74 (p, *J* = 6.0 Hz, 1H), 3.58 (dt, *J* = 10.0, 6.5 Hz, 1H), 3.49 (dt, *J* = 10.0, 5.5 H, 1H), 3.35 (s, 3H), 2.12 (q, *J* = 7.0 Hz, 2H), 1.97 (q, *J* = 6.0 Hz, 2H), 1.88-1.72 (m, 2H), 1.66 (d, *J* = 5.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.8, 126.2, 82.1, 68.6, 58.6, 34.9, 34.1, 28.0, 18.0; IR (film, cm^{-1}) 3357, 3280, 2924, 2854, 1452, 1367, 1178, 1107, 910; HRMS (ESI) *m/z* calculated for $C_9H_{19}NO_4SNa$ $[M+Na]^+$: 260.0932, found 260.0928.

(±)-(*E*)-1-phenyloct-6-en-3-yl sulfamate (Table 3, entries 7-8).



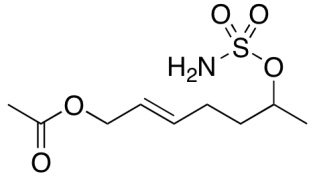
Prepared according to method **A**. 1.022 g (5.00 mmol) of (±)-(*E*)-1-phenyloct-6-en-3-ol **S8** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes:EtOAc as eluent gave 1.261 g (4.45 mmol) of pure product as a colorless oil (>20:1 *E:Z*, 89% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.22-7.19 (m, 3H), 5.47 (dq, *J* = 15.5, 6.0 Hz, 1H), 5.39 (dt, *J* = 15.5, 6.0 Hz, 1H), 4.68 (br. s, 2H), 4.65 (p, *J* = 6.0 Hz, 1H), 2.78-2.69 (m, 2H), 2.10 (q, *J* = 7.0 Hz, 2H), 2.05 (q, *J* = 7.0 Hz, 2H), 1.91-1.76 (m, 2H), 1.65 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.2, 129.8, 128.7, 128.5, 126.3 (2 peaks), 84.3, 35.7, 34.0, 31.2, 28.0, 18.0; IR (film, cm^{-1}) 3377, 3292, 3028, 2939, 2856, 1554, 1496, 1454, 1358, 1182, 920; HRMS (ESI) *m/z* calculated for $C_{14}H_{21}NO_3SNa$ $[M+Na]^+$: 306.1140, found 306.1147.

(±)-(*E*)-methyl 6-(sulfamoyloxy)hept-2-enoate (Table 3, entry 9).



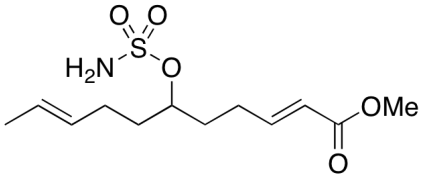
Prepared according to method **B**. 790 mg (5.00 mmol) of (±)-(*E*)-methyl 6-hydroxyhept-2-enoate **S9** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 1:1 hexanes:EtOAc as eluent gave 795 mg (3.35 mmol) of pure product as a colorless oil (67% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.95 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.87 (dt, *J* = 15.5, 1.5 Hz, 1H), 5.10 (br. s, 2H), 4.73-4.66 (m, 1H), 3.72 (s, 3H), 2.39-2.31 (m, 2H), 1.91-1.84 (m, 1H), 1.81-1.73 (m, 1H), 1.43 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 167.3, 148.0, 121.8, 80.2, 51.7, 34.8, 27.9, 20.8; IR (film, cm^{-1}) 3356, 3248, 3118, 2985, 2954, 2850, 1711, 1658, 1566, 1441, 1360, 1294, 1221, 1178, 1130, 1045, 985, 930, 796; HRMS (ESI) *m/z* calculated for $C_8H_{16}NO_5S$ $[M+H]^+$: 238.0749, found 238.0738.

(±)-(*E*)-6-(sulfamoyloxy)hept-2-en-1-yl acetate (Table 3, entry 10).

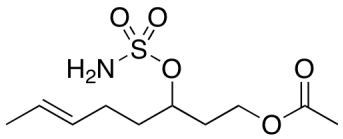


Prepared according to method **B**. 861 mg (5.00 mmol) of (±)-(*E*)-6-hydroxyhept-2-en-1-yl acetate **S10** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes:EtOAc as eluent gave 667 mg (2.65 mmol) of pure product as a colorless oil (53% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.75 (dt, *J* = 15.5, 6.5 Hz, 1H), 5.60 (ddt, *J* = 15.5, 6.0, 1.5 Hz, 1H), 4.98 (br. s, 2H), 4.67 (app sxt, *J* = 6.5 Hz, 1H), 4.51 (d, *J* = 6.5 Hz, 2H), 2.19 (app q, *J* = 7.0 Hz, 2H), 2.06 (s, 3H), 1.84 (app dq, *J* = 14.5, 7.0 Hz, 1H) 1.74-1.67 (m, 1H), 1.42 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.3, 134.7, 125.1, 80.5, 65.2, 35.6, 27.9, 21.2, 20.7; IR (film, cm^{-1}) 3354, 3271, 3118, 2981, 2943, 1720, 1566, 1448, 1365, 1259, 1180, 1028, 922; HRMS (ESI) *m/z* calculated for $C_9H_{17}NO_5SNa$ $[M+Na]^+$: 274.0725, found 274.0730.

(±)-(2*E*,9*E*)-methyl 6-(sulfamoyloxy)undeca-2,9-dienoate (Table 3, entry 11).

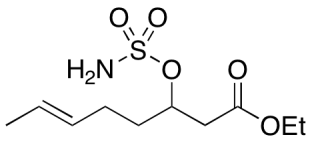


Prepared according to method **B**. 1.061 g (5.00 mmol) of (±)-(2*E*,9*E*)-methyl 6-hydroxyundeca-2,9-dienoate **S11** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes:EtOAc as eluent gave 1.004 g (3.45 mmol) of pure product as a colorless oil (69% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.95 (dt, *J* = 16.0, 6.5 Hz, 1H), 5.87 (d, *J* = 15.5 Hz, 1H), 5.47 (dq, *J* = 15.5, 6.5 Hz, 1H), 5.38 (dt, *J* = 15.5, 6.5 Hz, 1H), 4.94 (br. s, 2H), 4.61 (app p, *J* = 6.0 Hz, 1H), 3.73 (s, 3H), 2.35 (app q, *J* = 7.5 Hz, 2H), 2.09 (app q, *J* = 7.0 Hz, 2H), 1.89-1.80 (m, 3H), 1.72 (app dq, *J* = 14.5, 7.5 Hz, 1H), 1.64 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 167.3, 148.0, 129.6, 126.4, 121.8, 83.5, 51.7, 34.0, 32.4, 28.0, 27.6, 18.0; IR (film, cm^{-1}) 3367, 3271, 3113, 3022, 2953, 2856, 1705, 1657, 1564, 1439, 1362, 1290, 1182, 1041, 970, 918, 752; HRMS (ESI) *m/z* calculated for $C_{12}H_{22}NO_5S$ $[M+H]^+$: 292.1219, found 292.1218.



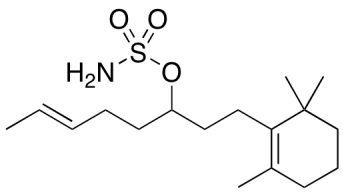
(±)-(*E*)-3-(sulfamoyloxy)oct-6-en-1-yl acetate (Table 3, entry 12). Prepared according to method **B**. 931 mg (5.00 mmol) of (±)-(*E*)-3-hydroxyoct-6-en-1-yl acetate **S12** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes:EtOAc as eluent gave 703 mg (2.65 mmol) of pure product as a colorless oil (53% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.47 (dq, *J* = 15.0, 6.0 Hz, 1H), 5.39 (ddt, *J* = 15.0, 6.5, 1.5 Hz, 1H), 5.03 (br. s, 2H), 4.71-4.66 (m, 1H), 4.34-4.29 (m, 1H), 4.15-4.10 (m, 1H), 2.12-1.95 (m, 4H), 2.07 (s, 3H), 1.89-1.82 (m, 1H), 1.79-1.71 (m, 1H), 1.64 (dd, *J* = 6.5, 1.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.6, 129.5, 126.4, 81.2, 60.3, 34.4, 33.1, 27.9, 21.1, 18.1; IR (film, cm^{-1}) 3346, 3269, 3116, 3024, 2962, 2937, 2856, 1724, 1564, 1450, 1369, 1257, 1182, 1045, 968, 928, 739; HRMS (ESI) *m/z* calculated for $C_{10}H_{19}NO_5SNa$ $[M+Na]^+$: 288.0882, found 288.0885.

(±)-(*E*)-ethyl 3-(sulfamoyloxy)oct-6-enoate (Table 3, entry 13).



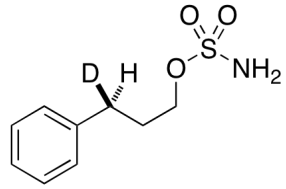
Prepared according to method **B**. 931 mg (5.00 mmol) of (±)-(*E*)-ethyl 3-hydroxyoct-6-enoate **S13** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes:EtOAc as eluent gave 796 mg (3.00 mmol) of pure product as a colorless oil (60% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.48 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.39 (ddt, *J* = 15.5, 6.0, 1.0 Hz, 1H), 5.02 (br. s, 2H), 4.98-4.93 (m, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 2.80 (dd, *J* = 17.0, 8.0 Hz, 1H), 2.63 (dd, *J* = 17.0, 4.5 Hz, 1H), 2.10 (app q, *J* = 7.5 Hz, 2H), 1.86 (app dq, *J* = 14.8, 7.0 Hz, 1H), 1.80-1.73 (m, 1H), 1.64 (dd, *J* = 6.0, 1.5 Hz, 3H), 1.74 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.2, 129.3, 126.5, 79.7, 61.4, 39.2, 34.7, 27.9, 18.0, 14.2; IR (film, cm^{-1}) 3367, 3280, 3114, 2981, 2939, 2858, 1724, 1562, 1448, 1369, 1321, 1188, 1028, 968, 930, 777; HRMS (ESI) *m/z* calculated for $C_{10}H_{20}NO_5S$ $[M+H]^+$: 266.1062, found 266.1062.

(±)-(*E*)-1-(2,6,6-trimethylcyclohex-1-en-1-yl)oct-6-en-3-yl sulfamate (Table 3, entry 14).



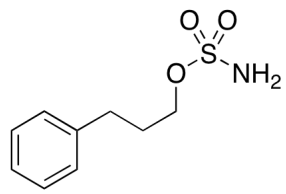
Prepared according to method **A**. 1.252 g (5.00 mmol) of (±)-(*E*)-1-(2,6,6-trimethylcyclohex-1-en-1-yl)oct-6-en-3-ol **S14** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes:EtOAc as eluent gave 1.400 g (4.25 mmol) of pure product as a colorless oil (85% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.48 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.42 (dt, *J* = 15.0, 6.5 Hz, 1H), 4.70 (br. s, 2H), 4.60 (app p, *J* = 6.0 Hz, 1H), 2.15-2.07 (m, 3H), 2.05-1.99 (m, 1H), 1.90 (t, *J* = 6.5 Hz, 2H), 1.87-1.72 (m, 4H), 1.65 (d, *J* = 6.0 Hz, 3H), 1.59 (s, 3H), 1.59-1.54 (m, 2H), 1.42-1.40 (m, 2H), 0.98 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 136.2, 129.9, 127.9, 126.2, 85.6, 39.9, 35.1, 34.5, 33.8, 32.9, 28.7 (2 peaks), 28.3, 23.8, 19.9, 19.6, 18.1; IR (film, cm^{-1}) 3375, 3286, 2929, 2866, 1556, 1473, 1452, 1358, 1184, 966, 922; HRMS (ESI) *m/z* calculated for $C_{17}H_{31}NO_3SNa$ $[M+Na]^+$: 352.1922, found 352.1926.

(±)-3-deuterio-3-phenylpropan-1-yl sulfamate [18].



Prepared according to method **A**. 686 mg (5.00 mmol) of 3-deuterio-3-phenylpropan-1-ol were used (contained ~20% of an unreactive impurity).[7] Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes:EtOAc as eluent gave 693 mg (3.20 mmol) of pure product as a white solid (64% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.23-7.19 (m, 3H), 4.81 (br s, 2H), 4.22 (t, *J* = 6.5 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 1H), 2.07 (dt, *J* = 7.0, 6.5 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 140.5, 128.7, 128.6, 126.4, 70.7, 31.3 (1:1:1 triplet), 30.3; IR (film, cm^{-1}) 3379, 3292, 3028, 2960, 2927, 1554, 1496, 1452, 1365, 1180, 931; HRMS (ESI) *m/z* calculated for $C_9H_{12}DNO_3SNa$ $[M+Na]^+$: 239.0577, found 239.0577.

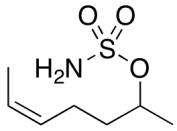
(±)-3-phenylpropan-1-yl sulfamate.



Prepared according to method **A**. 686 mg (5.00 mmol) of 3-phenylpropan-1-ol were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes:EtOAc as eluent gave 907 mg (4.20 mmol) of pure product as a white solid (84%

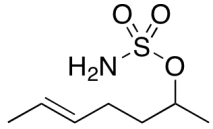
yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.23-7.19 (m, 3H), 4.75 (br s, 2H), 4.22 (t, *J* = 6.5 Hz, 2H), 2.76 (dd, *J* = 7.5 Hz, 2H), 2.08 (dt, *J* = 7.5, 7.0 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 140.6, 128.7, 128.6, 126.4, 70.7, 31.7, 30.4; IR (film, cm^{-1}) 3381, 3276, 3028, 2960, 2939, 2864, 1554, 1496, 1454, 1365, 1180, 939; HRMS (ESI) *m/z* calculated for $C_9H_{13}NO_3SNa$ $[M+Na]^+$: 238.0514, found 238.0516.

(±)-(*Z*)-hept-5-en-2-yl sulfamate [20].



Prepared according to method **A**. 571 mg (5.0 mmol) of (±)-(*Z*)-hept-6-en-3-ol **S15** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes:EtOAc as eluent gave 715 mg (3.70 mmol) of pure product as a colorless oil (74% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.49 (dq, *J* = 11.0, 7.0 Hz, 1H), 5.36 (dt, *J* = 11.0, 7.0 Hz, 1H), 4.79 (br. s, 2H), 4.71 (app. sxt, *J* = 6.5 Hz, 1H), 2.19-2.11 (m, 2H), 1.85-1.78 (m, 1H), 1.69-1.65 (m, 1H), 1.62 (dd, *J* = 6.5, 1.5 Hz, 3H), 1.44 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) 130.0, 125.3, 81.4, 36.3, 22.7, 20.7, 13.0; IR (film, cm^{-1}) 3381, 3278, 3014, 2981, 2939, 2866, 1562, 1448, 1358, 1176, 1124, 1039, 930; HRMS (ESI) *m/z* calculated for $C_7H_{15}NO_3SNa$ $[M+Na]^+$: 216.0670, found 216.0675.

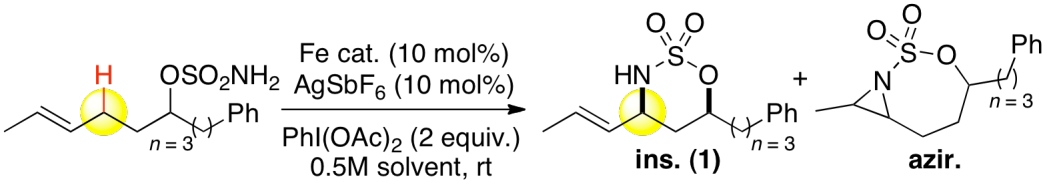
(±)-(*E*)-hept-5-en-2-yl sulfamate.



Prepared according to method **A**. 571 mg (5.0 mmol) of (±)-(*E*)-hept-6-en-3-ol **S16** were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes:EtOAc as eluent gave 733 mg (4.00 mmol) of pure product as a colorless oil (80% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.47 (dq, *J* = 15.5, 6.0 Hz, 1H), 5.40 (dt, *J* = 15.0, 6.5 Hz, 1H), 4.75 (br. s, 2H), 4.70 (app. sxt, *J* = 6.5 Hz, 1H), 2.12-2.05 (m, 2H), 1.85-1.77 (m, 1H), 1.68-1.60 (m, 1H), 1.65 (dd, *J* = 6.0, 1.0 Hz, 3H), 1.42 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) 129.7, 126.3, 81.3, 36.4, 28.3, 20.7, 18.1; IR (film, cm^{-1}) 3377, 3286, 2981, 2939, 2920, 2856, 1562, 1450, 1358, 1182, 1124, 926; HRMS (ESI) *m/z* calculated for $C_7H_{15}NO_3SNa$ $[M+Na]^+$: 216.0670, found 216.0674.

Optimization of Fe-catalyzed Intramolecular C—H Amination

Table 1. Development of the Fe-catalyzed Intramolecular Allylic C—H Amination.

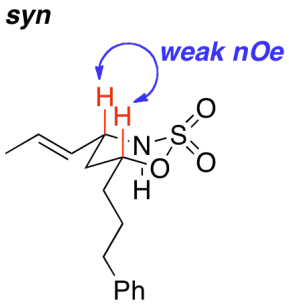


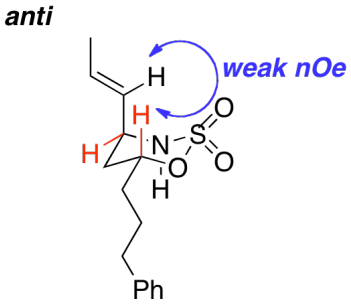
entry	catalyst	AgX	solvent	% yield[a]	ins./azir.[b]
1	Fe(*R,R*-PDP)	-	CH_3CN[c]	10 (58)[d]	>20:1
2	Fe(TPP)Cl	-	CH_3CN[c]	21 (41)[d]	>20:1
3	Fe(*R,R*-salen)Cl	-	CH_3CN[c]	0 (87)	-
4	[FePc]Cl	-	CH_3CN	34 (22)	15:1
5	[FePc]Cl	$AgSbF_6$	CH_3CN	39 (14)	16:1
6	[FePc]Cl	$AgSbF_6$	4:1 PhMe:CH_3CN	52 (7)	>20:1
7	[FePc]Cl[e]	$AgSbF_6$	4:1 PhMe:CH_3CN	68 (<5)	>20:1
8	[FePc]Cl[e]	-	4:1 PhMe:CH_3CN	58 (7)	>20:1
9	[FePc]Cl[e,f]	$AgSbF_6$	4:1 PhMe:CH_3CN	68 (<5)	>20:1

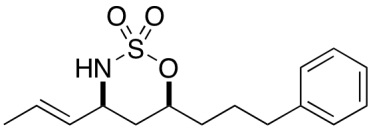
[a] Isolated (yield is sum of *syn* + *anti*; dr ~ 3-4:1 *syn*:*anti*); % rsm in parentheses. [b] Determined by ^{1}H-NMR analysis of crude reaction mixture. [c] concentration = 0.1M. [d] dr = 1:1. [e] $PhI(OPiv)_2$ was used as oxidant. [f] [FePc]Cl and $AgSbF_6$ were added together in 3x3.3 mol% portions at 2h intervals.

(±)-4-((1*E*)-1-propenyl)-6-(3-phenylpropyl)tetrahydro-1,2,3-oxathiazine-2,2-dioxide [1]. In general, the *syn* and *anti* oxathiazinanes can be isolated pure via flash column chromatography directly from the crude reaction mixture. The minor (*anti*) diastereomer co-elutes with starting material under hexanes/EtOAc eluent conditions, but can be easily separated in cases of incomplete conversion when CH_2Cl_2/hexanes is instead used as the eluent system. See general procedure for single catalyst addition for specific experimental details (*vide infra*). All products were obtained with an olefin geometry of >20:1 *E/Z*.

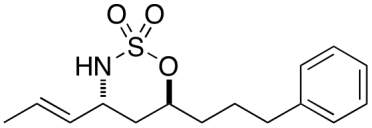
The relative stereochemistry of the oxathiazinanes was confirmed via nOe NMR experiments (500 MHz, $CDCl_3$) in which the C4 and C6 protons for each diastereomer were irradiated (irradiated protons are highlighted in red). *Syn* oxathiazinanes have a characteristic weak nOe between the C4 and C6 pseudo-axial hydrogens. Conversely, the C4 and C6 hydrogens in the *anti* oxathiazinane fall on opposite sides of the ring and therefore experience no observable nOe. Instead, for *anti* allylic C—H amination products a weak nOe can be observed between the C3 vinylic hydrogen of the pseudo-axial propenyl group and the pseudo-axial C6 hydrogen. All products described in this paper are assumed to have the same relative stereochemistry as **1** by analogy. The experimental data are consistent with previously reported studies in the literature.[8]





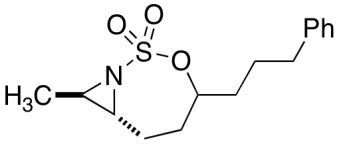


***Syn* (major) diastereomer:** Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.21-7.16 (m, 3H), 5.76 (dq, *J* = 15.5, 6.5 Hz, 1H), 5.39 (dd, *J* = 15.5, 5.5 Hz, 1H), 4.77-4.73 (m, 1H), 4.21-4.18 (m, 1H), 3.78 (br. d, *J* = 10.0 Hz, 1H), 2.65 (t, *J* = 7.0 Hz, 2H), 1.88-1.63 (m, 8H), 1.51 (app. q, *J* = 12.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.5, 129.5, 128.6, 128.5, 128.2, 126.2, 83.9, 56.1, 35.8, 35.4, 34.8, 26.3, 17.9; IR (film, cm^{-1}) 3265, 3028, 2924, 2856, 1416, 1360, 1188, 872; HRMS (ESI) *m/z* calculated for $C_{15}H_{22}NO_3S$ $[M+H]^+$: 296.1320, found 296.1325.



***Anti* (minor) diastereomer:** Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.3 Hz, 2H), 7.21-7.17 (m, 3H), 5.80 (ddd, *J* = 15.5, 6.5, 1.5 Hz, 1H), 5.70 (dq, *J* = 15.5, 6.0 Hz, 1H), 4.88-4.83 (m, 1H), 4.38 (br. d, *J* = 7.0 Hz, 1H), 4.17 (app. p, *J* = 6.0 Hz, 1H), 2.66 (dt, *J* = 7.5, 2.0 Hz, 2H), 1.99-1.85 (m, 3H), 1.83-1.79 (m, 1H), 1.73 (d, *J* = 6.5 Hz, 3H), 1.74-1.60 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.6, 129.2, 128.6, 128.5, 128.4, 126.1, 82.7, 55.0, 35.4, 34.1, 33.9, 26.7, 17.9; IR (film, cm^{-1}) 3280, 3028, 2937, 2860, 1496, 1452, 1419, 1367, 1184, 966, 874; HRMS (ESI) *m/z* calculated for $C_{15}H_{21}NO_3SNa$ $[M+Na]^+$: 318.1140, found 318.1142.

(±)-*trans*-4-(3-phenylpropyl)-8-methyl-3-oxa-2-thia-1-azabicyclo[5.1.0]octane-2,2-dioxide. In general, the aziridine is formed in only trace quantities under the standard Fe-catalyzed C—H amination conditions. The trace aziridine is more polar than the insertion products and is easily separated from the desired oxathiazinane products via flash column chromatography on silica. Most of the aziridine side products from substrates described in this paper share a characteristic peak near δ = 3.0 ppm (1H), which was used to determine ins./azir. ratios in the crude ^{1}H-NMR. ^{1}H-NMR spectra showing the 2.5-5.5 ppm region for crude reaction mixtures of each olefin-containing substrate in this paper are presented in a separate supporting information document.



Prepared as a standard using Rh-catalyzed C—H amination conditions (*vide infra*). Purified via flash column chromatography on silica using 4:1 → 2:1 hexanes/EtOAc as the eluent system. Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.20-7.15 (m, 3H), 4.33-4.28 (m, 1H), 2.99 (app. p, *J* = 5.5 Hz, 1H), 2.66-2.59 (m, 3H), 2.49-2.38 (m, 2H), 1.83-1.78 (m, 2H), 1.75-1.64 (m, 4H), 1.60-1.55 (m, 1H), 1.34 (d, *J* = 5.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.6, 128.5 (2 peaks), 126.1, 83.7, 47.2, 38.6, 35.3, 34.0, 32.3, 27.2, 24.7, 17.1; IR (film, cm^{-1}) 3060, 3026, 2929, 2862, 1496, 1454, 1373, 1261, 1180, 999, 901; HRMS (ESI) *m/z* calculated for $C_{15}H_{22}NO_3S$ $[M+H]^+$: 296.1320, found 296.1314.

General procedure for single catalyst addition (entries 1-8)
Into a 10 mL round-bottom flask was added $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv, entries 5-7), catalyst (0.040 mmol, 0.10 equiv), and a stir bar in a glovebox. The flask was then sealed with a rubber septum, covered in aluminum foil (when $AgSbF_6$ was used), and taken out of the box. (±)-(*E*)-1-phenylnon-7-en-4-yl sulfamate (119 mg, 0.400 mmol, 1.0 equiv) dissolved in solvent was added via syringe, followed by $PhI(O_2CR)_2$ (0.800 mmol, 2.0 equiv) in a single portion. After addition of oxidant, the dark turquoise solution gradually turned dark brown. The reaction stirred for 6h at room temp (~20°C), and then concentrated under reduced pressure. The remaining dark brown residue was suspended in Et_2O and filtered through a pad of Celite. Upon removal of solvent under reduced pressure, flash column chromatography on silica allowed separate isolation of each component as colorless oils. When reaction gave <5% recovered starting material (rsm), the column conditions were as follows: (35 mm fritted glass column, 150 mm SiO_2), 5:1 hexanes/EtOAc. For incomplete conversion of starting material, column conditions were as follows: 35 mm fritted glass column, 110 mm SiO_2, 4:1 CH_2Cl_2/hex (600 mL) → 9:1 CH_2Cl_2/hexanes (350 mL) → 100% CH_2Cl_2.

Entry 1. Single addition protocol was followed, except product was isolated as a diastereomeric mixture with starting material under the hexanes/EtOAc column conditions. (±)-(*E*)-9-phenylnon-2-en-6-yl sulfamate (119 mg, 0.400 mmol, 1.0 equiv), Fe(*R,R*-PDP)$(SbF_6)_2$ (33.6 mg, 0.040 mmol, 0.10 equiv), $PhI(OAc)_2$ (257 mg, 0.800 mmol, 2.0 equiv) and MeCN (4.0 mL, 0.1M) were used. By ^{1}H-NMR analysis of the crude product, ins./azir. was >20:1 and d.r. was ~1:1 (*syn:anti*).
Run 1: (13 mg of 1.1:1 *syn:anti* mixture, 0.044 mmol, 11%), (68 mg rsm, 0.228 mmol, 57%). Run 2: (9 mg of 1.2:1 *syn:anti* mixture, 0.032 mmol, 8%), (70 mg rsm, 0.236 mmol, 59%). **Average: 10% yield, 58% rsm.**

Entry 2. Single addition protocol was followed, except product was isolated as a diastereomeric mixture with starting material under the hexanes/EtOAc column conditions. (±)-(*E*)-9-phenylnon-2-en-6-yl sulfamate (119 mg, 0.400 mmol, 1.0 equiv), Fe(TPP)Cl (28.2 mg, 0.040 mmol, 0.10 equiv), $PhI(OAc)_2$ (257 mg, 0.800 mmol, 2.0 equiv) and MeCN (4.0 mL, 0.1M) were used. By ^{1}H-NMR analysis of the crude product, ins./azir. was >20:1 and d.r. was ~1:1 (*syn:anti*).
Run 1: (24 mg of 1:1 *syn:anti* mixture, 0.081 mmol, 20%), (53 mg rsm, 0.178 mmol, 45%). Run 2: (26 mg of 1.1:1 *syn:anti* mixture, 0.088 mmol, 22%), (44 mg rsm, 0.148 mmol, 37%). **Average: 21% yield, 41% rsm.**

Entry 3. Single addition protocol was followed; starting material was reisolated via flash column (35 mm fritted glass column, 110 mm SiO_2) using 4:1 hexanes/EtOAc. (±)-(*E*)-9-phenylnon-2-en-6-yl sulfamate (119 mg, 0.400 mmol, 1.0 equiv), Fe(R,R-salen)Cl (22.8 mg, 0.040 mmol, 0.10 equiv), $PhI(OAc)_2$ (257 mg, 0.800 mmol, 2.0 equiv) and MeCN (4.0 mL, 0.1M) were used. ^{1}H-NMR analysis of the crude product indicated formation of neither the desired insertion product nor aziridine. Due to the presence of an unidentified impurity after column

chromatography, recovery of starting material was determined via ^{1}H-NMR analysis using $PhNO_2$ as an internal standard (delay = 60 s).
Run 1: (0 mg, 0 mmol, 0% yield), (107 mg rsm, 0.360 mmol, 90%). Run 2: (0 mg, 0 mmol, 0% yield), (99 mg rsm, 0.333 mmol, 83%). **Average: 0% yield, 87% rsm.**

Entry 4. Single addition protocol was followed. (±)-(*E*)-9-phenylnon-2-en-6-yl sulfamate (119 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24 mg, 0.040 mmol, 0.10 equiv), $PhI(OAc)_2$ (257 mg, 0.800 mmol, 2.0 equiv) and MeCN (800 μL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, ins./azir. was 18:1 and d.r. was 2.3:1 (*syn:anti*).
Run 1: (31.8 mg *syn* + 10.9 mg *anti* (2.9:1 d.r.), 0.145 mmol, 36%), (26.3 mg rsm, 0.088 mmol, 22%). Run 2: (29.8 mg *syn* + 11.1 mg *anti* (2.7:1 d.r.), 0.138 mmol, 35%), (24.4 mg rsm, 0.082 mmol, 21%). Run 3: (26.8 mg *syn* + 10.0 mg *anti* (2.7:1 d.r.), 0.125 mmol, 31%), (26.1 mg rsm, 0.088 mmol, 22%). **Average: 34% yield, 22% rsm.**

Entry 5. Single addition protocol was followed. (±)-(*E*)-9-phenylnon-2-en-6-yl sulfamate (119 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OAc)_2$ (257 mg, 0.800 mmol, 2.0 equiv) and MeCN (800 μL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, ins./azir. was 16:1 and d.r. was 2.3:1 (*syn:anti*).
Run 1: (36.6 mg *syn* + 10.0 mg *anti* (3.7:1 d.r.), 0.158 mmol, 39%), (18.6 mg rsm, 0.063 mmol, 16%). Run 2: (38.8 mg *syn* + 9.6 mg *anti* (4:1 d.r.), 0.164 mmol, 41%), (12.7 mg rsm, 0.043 mmol, 11%). Run 3: (35.0 mg *syn* + 9.3 mg *anti* (3.7:1 d.r.), 0.150 mmol, 38%), (19.6 mg rsm, 0.066 mmol, 16%). **Average: 39% yield, 14% rsm.**

Entry 6. Single addition protocol was followed. (±)-(*E*)-9-phenylnon-2-en-6-yl sulfamate (119 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OAc)_2$ (257 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, ins./azir. was >20:1 and d.r. was 3.1:1 (*syn:anti*).
Run 1: (48 mg *syn* + 10.4 mg *anti* (4.6:1 d.r.), 0.198 mmol, 49%), (12 mg rsm, 0.040 mmol, 10%). Run 2: (53.4 mg *syn* + 9.6 mg *anti* (5.5:1 d.r.), 0.213 mmol, 53%), (8 mg rsm, 0.027 mmol, 7%). Run 3: (53.6 mg *syn* + 9.8 mg *anti* (5.4:1 d.r.), 0.215 mmol, 54%), (4.1 mg rsm, 0.014 mmol, 3%). **Average: 52% yield, 7% rsm.**

Entry 7. Single addition protocol was followed. (±)-(*E*)-9-phenylnon-2-en-6-yl sulfamate (119 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, ins./azir. was >20:1 and d.r. was 4.0:1 (*syn:anti*). The crude material was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 6:1 hexanes/EtOAc + 1% AcOH as eluent (the AcOH additive prevents streaking of PivOH and allows it to be more easily separated from the desired products).

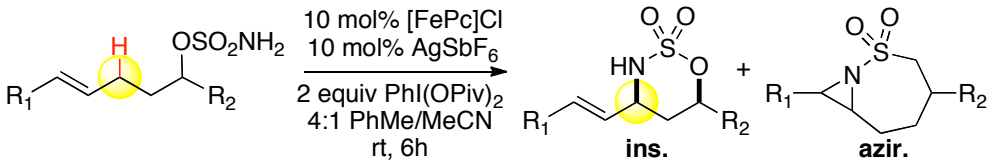
Run 1: (62.4 mg *syn* + 14.8 mg *anti* (4.2:1 d.r.), 0.262 mmol, 65%), <5% rsm. Run 2: (67.4 mg *syn* + 13.2 mg *anti* (5:1 d.r.), 0.273 mmol, 68%), <5% rsm. Run 3: (69.4 mg *syn* + 13.7 mg *anti* (5:1 d.r.), 0.282 mmol, 70%), <5% rsm. **Average: 68% yield, <5% rsm.**

Entry 8. Single addition protocol was followed. (±)-(*E*)-9-phenylnon-2-en-6-yl sulfamate (119 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, ins./azir. was >20:1 and d.r. was 3:1 (*syn:anti*). The crude material was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 6:1 hexanes/EtOAc + 1% AcOH as eluent.
Run 1: (47.7 mg *syn* + 19.7 mg *anti* (2.4:1 d.r.), 0.228 mmol, 57%), (8.7 mg rsm, 0.028 mmol, 7%). Run 2: (50.0 mg *syn* + 16.1 mg *anti* (3.1:1 d.r.), 0.224 mmol, 56%), (7.5 mg rsm, 0.025 mmol, 6%). **Average: 57% yield, 7% rsm.**

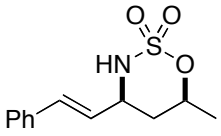
Entry 9. $AgSbF_6$ (3x4.5 mg, 0.040 mmol, 0.10 equiv) and [FePc]Cl (3x8 mg, 0.040 mmol, 0.10 equiv) were weighed out into three separate ½-dram borosilicate vials in a glovebox, sealed, covered in aluminum foil, taken out of the box and temporarily stored in a dessicator. A 10 mL round-bottom flask covered in aluminum foil and equipped with a stir bar and rubber septum was charged with (±)-(*E*)-9-phenylnon-2-en-6-yl sulfamate (119 mg, 0.400 mmol, 1.0 equiv) dissolved in 4:1 PhMe:MeCN (800 μL, 0.5M), and then $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv). The contents of one vial were quickly added to the reaction flask under a stream of N_2, and then the rubber septum was replaced. After stirring for 2h at rt, a second portion was added in the same manner; this was then repeated once more in 2h intervals for a total of three catalyst additions. The reaction stirred for 2h more at room temp after addition of the final portion for a total reaction time of 6h, then the reaction was concentrated under reduced pressure. Work-up and purification were performed in a manner identical to that described in the single catalyst addition protocol (*vide supra*). By ^{1}H-NMR analysis of the crude product, ins./azir. was >20:1 and d.r. was 3.5:1 (*syn:anti*). The crude material was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 6:1 hexanes/EtOAc + 1% AcOH as eluent.
Run 1: (66.2 mg *syn* + 14.9 mg *anti* (4.4:1 d.r.), 0.275 mmol, 69%), <5% rsm. Run 2: (62.8 mg *syn* + 15.0 mg *anti* (4.2:1 d.r.), 0.263 mmol, 66%), <5% rsm. Run 3: (66.5 mg *syn* + 15.0 mg *anti* (4.4:1 d.r.), 0.276 mmol, 69%), <5% rsm. **Average: 68% yield, <5% rsm.**

Olefin and Substrate Scope for Fe-catalyzed Intramolecular C—H Amination

Table 2. Scope of Fe-catalyzed C—H Amination.

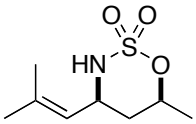


styrenyl



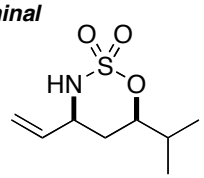
(±)-**2**
70% yield (0% rsm)[a]
d.r. = 3.5:1 *syn*:*anti*[b]
E:*Z* >20:1
ins./azir. >20:1[b]

trisubstituted



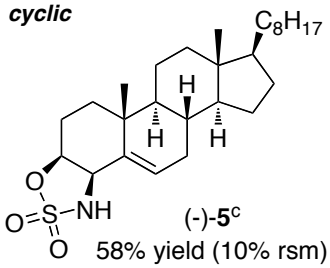
(±)-**3**[c]
53% yield (<10% rsm)
d.r. = 2.7:1 *syn*:*anti*
ins./azir. > 20:1

terminal



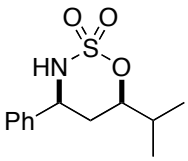
(±)-**4**[c]
52% yield (10% rsm)
d.r. = 3:1 *syn*:*anti*
ins./azir. = 12:1

cyclic



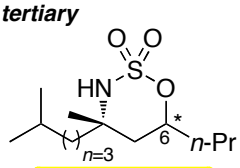
(-)-**5**[c]
58% yield (10% rsm)
d.r. >20:1 *syn*:*anti*
ins./azir. >20:1

benzylic



(±)-**6**
66% yield (<5% rsm)
d.r. = 17:1 *syn*:*anti*

tertiary



stereospecific

(+)-(6*R*)-**7**/(-)-(6*S*)-**7**[c]
(6*R*): 45% yield (27% rsm)
d.r. = 97:3 *syn*:*anti*[d]
(6*S*): 42% yield (22% rsm)
d.r. = 5:95 *syn*:*anti*[e]

[a] All yields are isolated (*syn* + *anti*; rsm in parentheses). [b] All product ratios determined by ^{1}H-NMR analysis of crude reaction mixture. [c] Conditions: 4x(0.03 equiv [FePc]Cl, 0.03 equiv $AgSbF_6$), 2 equiv $PhI(OPiv)_2$, 4:1 PhMe/MeCN, rt, 8h. [d] Determined by GC analysis of crude mixture; starting d.r. = 97:3. [e] Determined by GC analysis of crude mixture; starting d.r. = 5:95.

Single catalyst addition protocol for [FePc]Cl-mediated intramolecular amination

Into a 10 mL round-bottom flask was added $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), [FePc]Cl (24.0 mg, 0.040 mmol, 0.10 equiv), and a stir bar in a glovebox. The flask was then sealed with a rubber septum, covered in aluminum foil, and taken out of the box. 4:1 PhMe:MeCN (800 µL, 0.5M), sulfamate ester (0.400 mmol, 1.0 equiv), and $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) were then added sequentially; if sulfamate ester was an oil, it was taken up in the solvent mixture and added to the flask via syringe. After addition of oxidant, the deep violet solution gradually turned dark brown. The reaction stirred for 6h at room temp (~20°C), then the reaction was concentrated under reduced pressure. The remaining dark brown residue was suspended in Et_2O and filtered through a pad of Celite. Upon removal of solvent under reduced pressure, flash column chromatography on silica allowed separate isolation of each component.

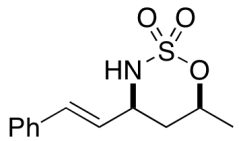
Iterative catalyst addition protocol for [FePc]Cl-mediated intramolecular amination

$AgSbF_6$ (4x4.5 mg, 0.053 mmol, 0.13 equiv) and [FePc]Cl (4x8 mg, 0.053 mmol, 0.13 equiv) were weighed out into four separate ½-dram borosilicate vials in a glovebox, sealed, covered in aluminum foil, taken out of the box and temporarily stored in a dessicator. A 10 mL round-bottom flask covered in aluminum foil and equipped with a stir bar and rubber septum was charged with 4:1 PhMe:MeCN (800 μL, 0.5M), sulfamate ester (0.400 mmol, 1.0 equiv), and $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv); if sulfamate ester is an oil, it was taken up in the solvent mixture and added to the flask via syringe. The contents of one vial were quickly added to the reaction flask under a stream of N_2, and then the rubber septum was replaced. After stirring for 2h at room temp, a second portion was added in the same manner; this was then repeated twice more in 2h intervals for a total of four catalyst additions. The reaction stirred for 2h more at room temp after addition of the final portion for a total reaction time of 8h, then the solvent was removed under reduced pressure. Work-up and purification were performed in a manner identical to that described in the single catalyst addition protocol (*vide supra*). The iterative addition protocol was used for substrates that did not react to completion under the standard single catalyst addition reaction conditions. While simply increasing catalyst loading under standard reaction conditions with less reactive substrates did not result in improved reactivity, iterative addition of the precatalyst mixture had a beneficial effect on overall reactivity and yield of the desired product.

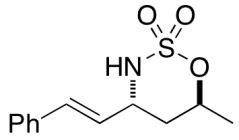
(±)-4-(*E*-styrenyl)-6-methyl-tetrahydro-1,2,3-oxathiazine-2,2-dioxide [2].

Single catalyst addition protocol for Fe conditions was followed. (±)-(*E*)-6-phenylhex-5-en-2-yl sulfamate (102 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24.0 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product, *E:Z* was >20:1, d.r. was 3.5:1 *syn*:*anti*, and ins./azir. was >20:1. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes:EtOAc + 1% AcOH as eluent gave pure *syn* and *anti* allylic oxathiazinanes separately.

Run 1: (60.3 mg *syn* + 11.9 mg *anti* (5:1 d.r.), 0.286 mmol, 71%), 0% rsm. Run 2: (59.6 mg *syn* + 10.4 mg *anti* (5.7:1 d.r.), 0.278 mmol, 69%), 0% rsm. Run 3: (58.4 mg *syn* + 11.2 mg *anti* (5.2:1 d.r.), 0.276 mmol, 69%), 0% rsm. **Average: 70% yield, 0% rsm.**



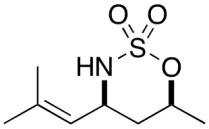
***Syn* (major) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.10 (dd, *J* = 16.0, 6.0 Hz, 1H), 4.99-4.93 (m, 1H), 4.49-4.44 (m, 1H), 3.90 (br. d, *J* = 10.0 Hz, 1H), 2.02 (dt, *J* = 14.0, 2.0 Hz, 1H), 1.66 (dt, *J* = 14.0 12.0 Hz, 1H), 1.48 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 136.0, 133.1, 129.2, 128.9, 127.0, 126.2, 80.8, 56.6, 37.6, 21.5; IR (film, cm^{-1}) 3259, 3028, 2985, 2935, 1728, 1495, 1415, 1360, 1188, 1066, 866; HRMS (ESI) *m/z* calculated for $C_{12}H_{16}NO_3S$ $[M+H]^+$: 254.0851, found 254.0857.



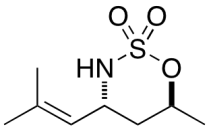
***Anti* (minor) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 6.60 (d, *J* = 16.5 Hz, 1H), 6.53 (dd, *J* = 16.5, 6.5 Hz, 1H), 5.13-5.07 (m, 1H), 4.54 (br. d, *J* = 6.5 Hz, 1H), 4.43 (app. p, *J* = 5.5 Hz, 1H), 2.06-1.96 (m, 2H), 1.53 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 136.0, 132.7, 128.8, 128.5, 128.4, 126.8,

126.7, 79.2, 55.2, 35.4, 21.0; IR (film, cm^{-1}) 3269, 3027, 2983, 2931, 1416, 1365, 1184, 1074, 968, 885; HRMS (ESI) *m/z* calculated for $C_{12}H_{15}NO_3SNa$ $[M+Na]^+$: 276.0670, found 276.0674.

(±)-4-(2-methylprop-1-en-1-yl)-6-methyltetrahydro-1,2,3-oxathiazine-2,2-dioxide [3].
Iterative catalyst addition protocol for Fe conditions was followed. (±)-2-methylhept-6-en-3-yl sulfamate (82.8 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (4x8 mg, 0.053 mmol, 0.13 equiv), $AgSbF_6$ (4x4.5 mg, 0.053 mmol, 0.13 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product, d.r. was 2.7:1 *syn*:*anti* and ins./azir. was >20:1. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 9:1 CH_2Cl_2/hexanes (300 mL) → 19:1 CH_2Cl_2/hexanes as eluent gave *syn* and *anti* allylic oxathiazinanes separately.
Run 1: (35.1 mg *syn* + 11.3 mg *anti* (3.1:1 d.r.), 0.228 mmol, 57%), <10% rsm. Run 2: (32.3 mg *syn* + 9.8 mg *anti* (3.3:1 d.r.), 0.205 mmol, 51%), <10% rsm. Run 3: (31.1 mg *syn* + 9.6 mg *anti* (3.2:1 d.r.), 0.198 mmol, 50%), <10% rsm. **Average: 53% yield, <10% rsm.**

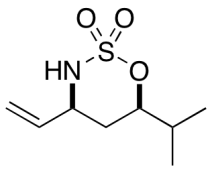


***Syn* (major) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.96 (dt, *J* = 8.0, 1.5 Hz, 1H), 4.91-4.85 (m, 1H), 4.43-4.37 (m, 1H), 3.86 (br. d, *J* = 9.5 Hz, 1H), 1.76 (dt, *J* = 14.5, 2.5 Hz, 1H), 1.74 (s, 3H), 1.73 (d, *J* = 1.0 Hz, 3H), 1.49 (dt, *J* = 14.0, 12.0 Hz, 1H), 1.41 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 139.8, 121.7, 80.5, 53.2, 37.8, 25.7, 21.3, 18.7; IR (film, cm^{-1}) 3269, 2983, 2935, 2920, 1419, 1354, 1186, 1066, 931, 916, 866, 820, 791; HRMS (ESI) *m/z* calculated for $C_8H_{15}NO_3SNa$ $[M+Na]^+$: 228.0670, found 228.0673.



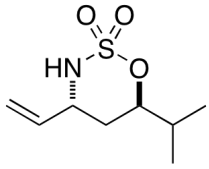
***Anti* (minor) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.57 (dt, *J* = 8.5, 1.0 Hz, 1H), 5.06-4.99 (m, 1H), 4.47-4.40 (m, 2H), 1.87 (ddd, *J* = 14.0, 9.0, 5.0 Hz, 1H), 1.77-1.73 (m, 1H), 1.75 (app s, 3H), 1.68 (d, *J* = 1.0 Hz, 3H), 1.50 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 137.4, 121.7, 79.4, 51.3, 35.8, 25.8, 20.9, 18.2; IR (film, cm^{-1}) 3271, 2981, 2937, 2920, 2885, 1421, 1371, 1354, 1290, 1238, 1182, 1136, 1065, 964, 908, 883, 833, 791; HRMS (ESI) *m/z* calculated for $C_8H_{15}NO_3SNa$ $[M+Na]^+$: 228.0670, found 228.0670.

(±)-4-vinyl-6-(1-methylethyl)tetrahydro-1,2,3-oxathiazine-2,2-dioxide [4].
Iterative catalyst addition protocol for Fe conditions was followed. (±)-2-methylhept-6-en-3-yl sulfamate (82.8 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (4x8 mg, 0.053 mmol, 0.13 equiv), $AgSbF_6$ (4x4.5 mg, 0.053 mmol, 0.13 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product, d.r. was 3:1 *syn*:*anti* and ins./azir. was 12:1. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 6:1 hexanes/EtOAc + 1% AcOH (300 mL) → 4:1 hexanes/EtOAc + 1% AcOH as eluent gave *syn* and *anti* allylic oxathiazinanes separately.
Run 1: (35.5 mg *syn* + 7.8 mg *anti* (4.5:1 d.r.), 0.211 mmol, 53%), <10% rsm. Run 2: (33.2 mg *syn* + 7.8 mg *anti* (4.3:1 d.r.), 0.200 mmol, 50%), <10% rsm. Run 3: (35.1 mg *syn* + 7.8 mg *anti* (4.5:1 d.r.), 0.209 mmol, 52%), <10% rsm. **Average: 52% yield, <10% rsm.**



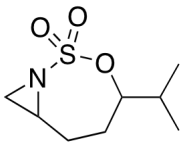
***Syn* (major) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.82 (ddd, *J* = 15.5, 10.5, 5.0 Hz, 1H), 5.32 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.28 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.54 (ddd, *J* = 12.0, 6.0, 2.0 Hz, 1H), 4.30-4.23 (m, 1H), 3.84 (br. d, *J* = 10.0 Hz, 1H), 1.93 (app. sxt, *J* = 6.5 Hz,

1H), 1.89 (dt, *J* = 14.0, 2.0 Hz, 1H), 1.54 (dt, *J* = 14.5, 12.0 Hz, 1H), 1.03 (d, *J* = 6.5 Hz, 3H), 1.01 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 135.3, 117.4, 88.7, 56.3, 32.7, 32.3, 18.0, 17.7; IR (film, cm^{-1}) 3261, 2968, 2927, 2881, 1470, 1419, 1360, 1190, 918, 879, 818; HRMS (ESI) *m/z* calculated for $C_8H_{15}NO_3SNa$ $[M+Na]^+$: 228.0670, found 228.0671.



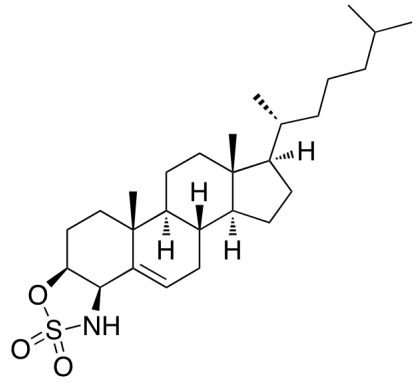
***Anti* (minor) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.19 (ddd, *J* = 16.5, 10.5, 5.5 Hz, 1H), 5.29 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.26 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.61-4.56 (m, 2H), 4.24-4.19 (m, 1H), 2.06-1.98 (m, 2H), 1.88 (dt, *J* = 14.5, 3.5 Hz, 1H), 1.03 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 136.1, 117.3, 86.8, 55.3, 32.4, 30.6, 18.1, 17.8; IR (film, cm^{-1}) 3282, 2970, 2933, 2879, 1470, 1410, 1363, 1182 1032, 993, 883, 831; HRMS (ESI) *m/z* calculated for $C_8H_{15}NO_3SNa$ $[M+Na]^+$: 228.0670, found 228.0669.

(±)-4-(1-methylethyl)-3-oxa-2-thia-1-azabicyclo[5.1.0]octane-2,2-dioxide.



Prepared as a standard using general protocol for Rh conditions. Purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc as eluent system. Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.32 (dt, *J* = 8.0, 5.0 Hz, 1H), 2.72 (d, *J* = 4.5 Hz, 1H), 2.64 (d, *J* = 5.0 Hz, 1H), 2.63-2.58 (m, 1H), 2.49-2.34 (m, 1H), 2.05-1.90 (m, 4H), 1.02 (d, *J* = 7.0 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 91.5, 40.1, 39.2, 32.5, 29.3, 27.1, 18.9, 17.9; IR (film, cm^{-1}) 2968, 2931, 2881, 1470, 1360, 1269, 1173, 1014, 985, 960, 899, 860; HRMS (ESI) *m/z* calculated for $C_8H_{15}NO_3SNa$ $[M+Na]^+$: 228.0670, found 228.0670.

(-)-4,5β-(cholest-5-enyl)-1,2,3-oxathiazole-2,2-dioxide [5].



Iterative catalyst addition protocol for Fe conditions was followed, with the exception that a small amount of toluene (2-3 mL) was added to the Et_2O suspension prior to Celite filtration in order to improve solubility of starting material and product. (-)-3β-cholest-5-enyl sulfamate (186 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (4x8 mg, 0.053 mmol, 0.10 equiv), $AgSbF_6$ (4x4.5 mg, 0.053 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product ins./azir. was >20:1, and d.r. was >20:1 *syn*:*anti*. Flash column chromatography on silica (35 mm fritted glass column, 110 mm SiO_2) using 9:1 hexanes:EtOAc + 1% AcOH as eluent gave pure *syn* product as a white solid (% rsm was determined based on crude ratios). Run 1: (105 mg, 0.227 mmol, 57%), (20.3 mg rsm, 0.044 mmol, 11%). Run 2: (102.9 mg, 0.222 mmol, 56%), (20.8 mg rsm, 0.045 mmol, 11%). Run 3: (112.3 mg, 0.243 mmol, 61%), (17.0 mg rsm, 0.037 mmol, 9%). **Average: 58% yield, 10% rsm.**

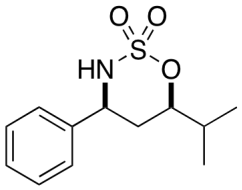
^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.82 (app t, *J* = 2.5 Hz, 1H), 4.74 (dt, *J* = 10.5, 6.0 Hz, 1H), 4.53 (t, *J* = 5.0 Hz, 1H), 4.34 (d, *J* = 5.0 Hz, 1H), 2.27 (dq, *J* = 3.0, 14.0 Hz, 1H), 2.14 (dt, *J* = 18.0, 4.5 Hz, 1H), 2.08-2.02 (m, 2H), 1.91 (dt, *J* = 14.0, 4.0 Hz, 1H), 1.87-1.81 (m, 1H), 1.65-1.43 (m, 7H), 1.41-1.24 (m, 5H), 1.20 (s, 3H), 1.18-1.05 (m, 6H), 1.02-0.89 (m, 2H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.86 (dd, *J* = 7.0, 2.5 Hz, 6H), 0.69 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 135.8, 133.9, 84.3, 62.4, 56.9, 56.2, 49.4, 42.5, 39.6 (2 peaks), 36.3, 36.2, 35.9, 33.6, 32.3, 31.6, 28.3, 28.2,

24.3, 23.9, 23.8, 23.0, 22.7, 21.3, 20.7, 18.8, 12.0; IR (film, cm^{-1}) 3292, 2953, 2937, 2866, 1466, 1379, 1338, 1281, 1192, 989, 970; $[\alpha]^{25}_{D}$ = -67.7° (*c* = 1.0, $CHCl_3$); HRMS (EI) *m/z* calculated for $C_{27}H_{45}NO_3S$ $[M]^+$: 463.3120, found 463.3139.

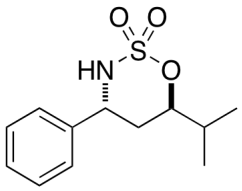
(±)-4-phenyl-6-(1-methylethyl)-tetrahydro-1,2,3-oxathiazine-2,2-dioxide [6].

Single catalyst addition protocol for Fe conditions was followed. (±)-1-phenyl-5-methylpentan-3-yl sulfamate (103 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24.0 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. Flash column chromatography on silica (35 mm fritted glass column, 110 mm SiO_2) using 4:1 hexanes:EtOAc + 1% AcOH as eluent gave pure *syn* and *anti* oxathiazinanes separately.

Run 1: (65.8 mg *syn* + 4.0 mg *anti* (16:1 d.r.), 0.274 mmol, 68%), <5% rsm. Run 2: (63.8 mg *syn* + 3.8 mg *anti* (17:1 d.r.), 0.262 mmol, 65%), <5% rsm. Run 3: (63.9 mg *syn* + 3.8 mg *anti* (17:1 d.r.), 0.265 mmol, 66%), <5% rsm. **Average: 66% yield, <5% rsm.**

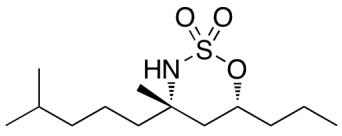


***Syn* (major) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.43-7.34 (m, 5H), 4.78 (ddd, *J* = 12.0, 9.0, 3.0 Hz, 1H), 4.65 (ddd, *J* = 11.5, 6.5, 2.0 Hz, 1H), 4.15 (br. d, *J* = 8.5 Hz, 1H), 2.06 (dt, *J* = 14.0, 2.5 Hz, 1H), 1.99 (app. sxt, *J* = 7.0 Hz, 1H), 1.91 (dt, *J* = 14.0, 12.0 Hz, 1H), 1.06 (d, *J* = 6.5 Hz, 3H), 1.03 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.4, 129.3, 129.1, 126.5, 89.0, 58.4, 33.6, 32.8, 18.1, 17.8; IR (film, cm^{-1}) 3267, 2968, 2935, 2879, 1456, 1416, 1363, 1190, 874; HRMS (ESI) *m/z* calculated for $C_{12}H_{18}NO_3S$ $[M+H]^+$: 256.1007, found 256.1010.



***Anti* (minor) diastereomer:** Isolated as a white waxy solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.41-7.39 (m, 4H), 7.37-7.33 (m, 1H), 4.83 (dt, *J* = 8.0, 5.5 Hz, 1H), 4.58 (br. d, *J* = 8.0 Hz, 1H), 4.50 (dt, *J* = 7.5, 4.5 Hz, 1H), 2.36-2.22 (m, 3H), 1.11 (d, *J* = 6.5 Hz, 3H), 1.00 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.2, 129.1, 128.5, 126.5, 88.1, 55.5, 31.6, 31.4, 18.6, 18.5; IR (film, cm^{-1}) 3284, 2968, 2935, 2902, 2875, 1450, 1423, 1360, 1176, 891; HRMS (ESI) *m/z* calculated for $C_{12}H_{17}NO_3SNa$ $[M+Na]^+$: 278.0827, found 278.0829.

(+)-(4*S, 6R*)-4-methyl 4-(4-methylpentyl)-6-propyl-tetrahydro-1,2,3-oxathiazine-2,2-dioxide [*syn*-7].

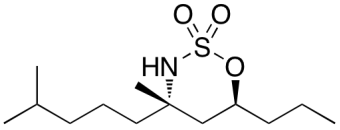


Iterative catalyst addition protocol for Fe conditions was followed. (-)-(*4R, 6R*)-6,10-dimethylundecan-4-yl sulfamate (112 mg, 0.400 mmol, 1.0 equiv, 97:3 *anti:syn*), [FePc]Cl (4x8 mg, 0.053 mmol, 0.13 equiv), $AgSbF_6$ (4x4.5 mg, 0.053 mmol, 0.13 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By achiral GC analysis of the crude reaction mixture, d.r. was 97:3 *syn:anti* (the diastereomers in this case are based on the oxathiazinane ring rather than the 1,3 relationship between the oxygen and chiral methyl substituent). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 9:1 hexanes:EtOAc + 1% AcOH as eluent gave oxathiazinane product as a ~40:1 *syn:anti* mixture of diastereomers. If desired, the diastereomers could be readily separated under the stated purification conditions; the pure *syn* oxathiazinane was isolated as a white solid in this case.

Run 1: (49.6 mg (39:1 *syn:anti*), 0.179 mmol, 45%), (32.0 mg rsm, 0.114 mmol, 29%). Run 2: (51.1 mg (40:1 *syn:anti*), 0.184 mmol, 46%), (30.6 mg rsm, 0.109 mmol, 27%). Run 3: (47.8 mg (40:1 *syn:anti*), 0.172 mmol, 43%), (28.4 mg rsm, 0.101 mmol, 25%). **Average: 45% yield, 27% rsm.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.85 (ddt, *J* = 11.0, 7.0, 4.0 Hz, 1H), 4.01 (br. s, 1H), 1.76-1.71 (m, 1H), 1.61-1.49 (m, 5H), 1.49-1.27 (m, 5H), 1.46 (s, 3H), 1.16 (q, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.88 (d, *J* = 6.5 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 80.8, 58.5, 45.2, 40.6, 39.1, 37.5, 28.0, 22.7 (2 peaks), 22.6, 20.5, 18.0, 13.8; IR (film, cm^{-1}) 3257, 2956, 2872, 1466, 1419, 1383, 1356, 1190, 877; $[\alpha]^{26}_D$ = +11.1^o (*c* = 1.0, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{13}H_{27}NO_3SNa$ $[M+Na]^+$: 300.1609, found 300.1610.

(-)-(4*S, 6S*)-4-methyl 4-(4-methylpentyl)-6-propyl-tetrahydro-1,2,3-oxathiazine-2,2-dioxide [*anti*-7].



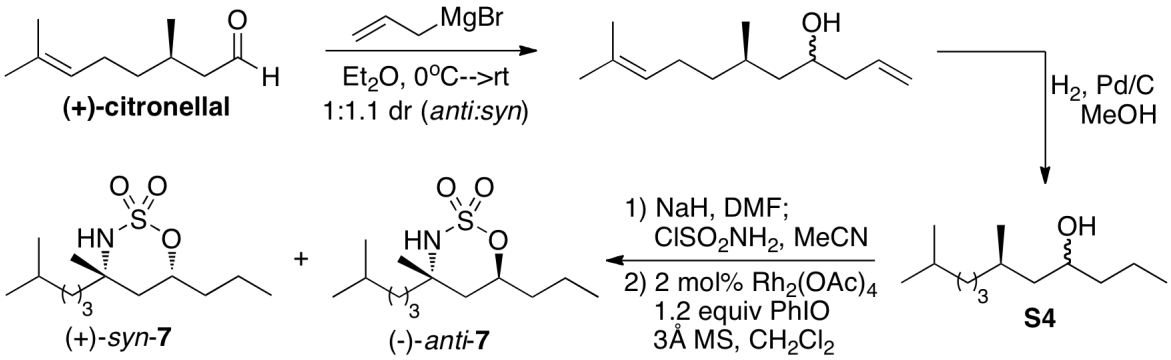
Iterative catalyst addition protocol for Fe conditions was followed. (+)-(*4R, 6R*)-6,10-dimethylundecan-4-yl sulfamate (112 mg, 0.400 mmol, 1.0 equiv, 97:3 *anti:syn*), [FePc]Cl (4x8 mg, 0.053 mmol, 0.13 equiv), $AgSbF_6$ (4x4.5 mg, 0.053 mmol, 0.13 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By achiral GC analysis of the crude reaction mixture, d.r. was 5:95 *syn:anti* (the diastereomers in this case are based on the oxathiazinane ring rather than the 1,3 relationship between the oxygen and chiral methyl substituent). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 9:1 hexanes:EtOAc + 1% AcOH as eluent gave oxathiazinane product as a ~1:X *syn:anti* mixture of diastereomers. If desired, the diastereomers could be readily separated under the stated purification conditions; the pure *anti* oxathiazinane was isolated as a white solid in this case.

Run 1: (47.4 mg (1:19 *syn:anti*), 0.172 mmol, 43%), (27.5 mg rsm, 0.098 mmol, 25%). Run 2: (48.1 mg (1:19 *syn:anti*), 0.172 mmol, 43%), (23.6 mg rsm, 0.084 mmol, 21%). Run 3: (44.3 mg (1:19 *syn:anti*), 0.160 mmol, 40%), (22.3 mg rsm, 0.080 mmol, 20%). **Average: 42% yield, 22% rsm.**

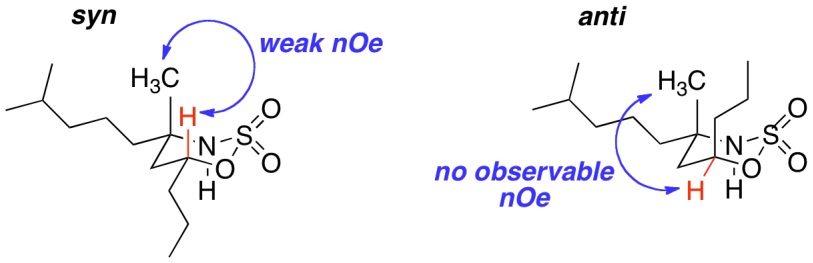
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.86-4.81 (m, 1H), 3.91 (br. s, 1H), 2.14-2.09 (m, 1H), 1.76-1.67 (m, 2H), 1.59-1.37 (m, 7H), 1.28-1.14 (m, 3H), 1.23 (s, 3H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.88 (d, *J* = 2.0 Hz, 3H), 0.87 (d, *J* = 2.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 80.6, 58.5, 41.4, 39.2, 37.4, 36.8, 28.9, 27.9, 22.7, 21.6, 18.0, 13.8; IR (film, cm^{-1}) 3269, 2956, 2872, 1466, 1421, 1383, 1354, 1190, 1157, 876; $[\alpha]^{26}_D$ = -35.5^o (*c* = 0.5, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{13}H_{27}NO_3SNa$ $[M+Na]^+$: 300.1609, found 300.1607.

Confirmation of Stereoretention in a Stereochemically Defined 3° C—H Bond

In order to confirm the configuration of the tertiary center in **7** following C—H amination under [FePc]·SbF_6 catalysis, standards representing each diasteromeric configuration were prepared. A diastereomeric mixture, resulting from the non-selective addition of allylmagnesium bromide to chirally pure (+)-citronellal, was carried forward for use as a standard for quantitative analysis (*vide infra*). Authentic standards of each oxathiazinane product, (+)-*syn*-**7** and (-)-*anti*-**7**, were prepared under Rh-catalyzed C—H amination conditions. These products are readily separated via flash column chromatography, allowing for full characterization of pure samples of each possible diastereomer that could be formed under the [FePc]·SbF_6-catalyzed C—H amination conditions. *NOTE:* the standard that was prepared for the minor diastereomer in each case has the opposite enantiomeric configuration to that which would be formed in the case of epimerization at the reacting tertiary C—H center of **7** (if the correct enantiomer is desired, (-)-citronellal can instead be used as the starting material).



The relative configurations of (+)-*syn*-**7** and (-)-*anti*-**7** were confirmed based on nOe ^{1}H-NMR experiments (500 MHz, $CDCl_3$). The ethereal proton peaks at δ = 4.85 ppm and δ = 4.85-4.81 ppm, respectively, were irradiated in each case, and the resulting observed relationships are illustrated below (irradiated protons are highlighted in red). (+)-*syn*-**7** gave a characteristic nOe between the pseudo-axial ethereal proton and the axial methyl group. Conversely, (-)-*anti*-**7** gave no measurable nOe for these two groups, as the ethereal proton in this case is in a pseudo-equatorial position, placing it on the opposite side of the ring from the axial methyl group.

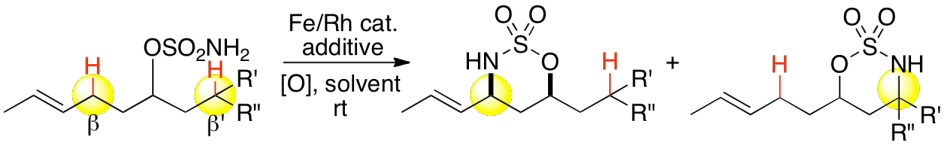


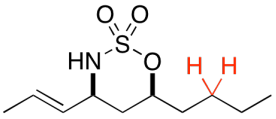
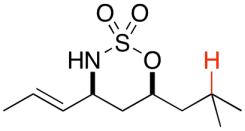
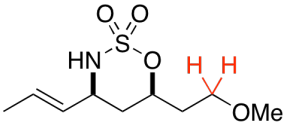
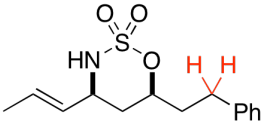
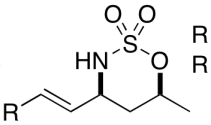
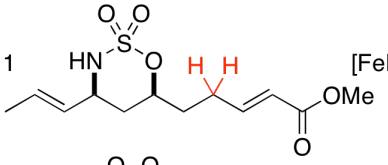
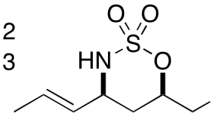
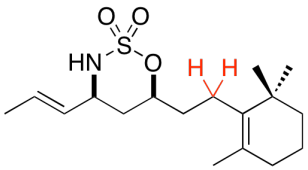
Quantitative determination of stereoretention was accomplished via achiral GC analysis. Hydrogenation of the Grignard addition product gave compound **S4** as a mixture of diastereomers, which was used as a standard to establish a baseline separation of the

diastereomers by GC. The corresponding diastereomerically enriched (-)-*anti*-**S4** or (+)-*anti*-**S4** were subjected to GC analysis to establish the initial diastereomeric ratio of the starting material that would be subjected to the [FePc]$^{\cdot}SbF_6$-catalyzed C—H amination reaction. The diastereomeric mixture of (+)-*syn*-**7** and (-)-*anti*-**7**, prepared by the synthetic pathway illustrated above, was used as a standard to establish a baseline separation of the oxathiazinane diastereomers by GC. Following standard work-up protocol for the [FePc]$^{\cdot}SbF_6$-catalyzed C—H amination reaction, the crude reaction mixture was subjected to GC analysis in triplicate runs using the optimized method established by the standard mixture. The stereoretention under the reaction was then determined by comparing the diastereomeric ratio of the starting material with that of oxathiazinane product **7**. No loss of d.r. suggests that the purported carbon-centered radical intermediate has a lifetime shorter than $1x10^{-9}$s, whereas a change in d.r. would indicate that the radical is sufficiently long-lived to at least partially racemize a stereodefined tertiary center.

Competition studies for Allylic C—H amination

Table 3. Competition Studies for Allylic C—H Amination.



entry	major product	catalyst	ins./azir.[a]	β/β'[a]	% yield major[b]
	C—H reactivity trends				
1		[FePc]SbF_6[c]	>20:1	>20:1	**8**, 64 (<5)
2		$Rh_2(OAc)_4$[d]	4:1	>20:1	63 (<5)
3		[FePc]SbF_6[c]	>20:1	>20:1	**9**, 72 (<5)
4		$Rh_2(OAc)_4$[d]	6:1	1.3:1	43 (0)
5		[FePc]SbF_6[c]	>20:1	7:1	**10**, 71 (0)
6		$Rh_2(OAc)_4$[d]	4:1	4:1	45 (<5)
7		[FePc]SbF_6[c]	>20:1	5:1	**11**, 62 (0)
8		$Rh_2(OAc)_4$[d]	4:1	2:1	50 (0)
	electronic trends				
9	 R = CO_2Me	[FePc]SbF_6[e]	>20:1	-	**12**, 39 (18)
10	R = CH_2OAc	[FePc]SbF_6[e]	>20:1	-	**13**, 47 (13)
11		[FePc]SbF_6[e]	>20:1	14:1	**14**, 55 (0)
12	 R = CH_2OAc	[FePc]SbF_6[e]	>20:1	-	**15**, 61 (0)
13	R = CO_2Et	[FePc]SbF_6[c]	>20:1	-	**16**, 69 (0)
	steric trends				
14		[FePc]SbF_6[e]	>20:1	7:1	**17**, 53 (0)

[a] Determined by ^{1}H-NMR analysis of crude reaction mixture (d.r. ~3:1 unless noted). [b] Isolated (*syn* + *anti*; *E/Z* >20:1 in all cases); rsm in parentheses. [c] Conditions: 0.10 equiv [FePc]Cl, 0.10 equiv $AgSbF_6$, 2 equiv $PhI(OPiv)_2$, 4:1 PhMe/MeCN, rt, 6h. [d] Conditions: 0.02 equiv $Rh_2(OAc)_4$, 1.1 equiv $PhI(OAc)_2$, 2.3 equiv MgO, CH_2Cl_2, rt, 4h. [e] Conditions: 4x(0.03 equiv [FePc]Cl, 0.03 equiv $AgSbF_6$), 2 equiv $PhI(OPiv)_2$, 4:1 PhMe/MeCN, rt, 8h.

General procedure for $Rh_2(OAc)_4$-mediated intramolecular amination[9]

A 10 mL round bottom flask equipped with a stir bar and rubber septum was charged with sulfamate ester (0.400 mmol, 1.0 equiv), CH_2Cl_2 (2.6 mL, 0.15M), magnesium oxide (37.1 mg, 0.920 mmol, 2.3 equiv), $PhI(OAc)_2$ (142 mg, 0.440 mmol, 1.1 equiv), and $Rh_2(OAc)_4$ (3.5 mg, 0.008 mmol, 0.02 equiv) sequentially (if sulfamate ester is an oil, it was taken up in solvent and added to the flask via syringe). The reaction stirred at room temp for 4h. Upon completion, the mint green reaction mixture was filtered through a small pad of $MgSO_4$ over Celite and rinsed with CH_2Cl_2. Upon removal of solvent under reduced pressure, flash column chromatography on silica allowed separate isolation of each component.

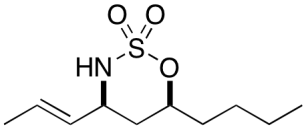
(±)-4-((1*E*)-1-propenyl)-6-butyltetrahydro-1,2,3-oxathiazine-2,2-dioxide [8].

Entry 1: Single catalyst addition protocol for Fe conditions was followed. (±)-(*E*)-dec-8-en-5-yl sulfamate (94.0 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24.0 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product, β:β' was >20:1, ins./azir. was >20:1, and d.r. was 3.8:1 *syn*:*anti*. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 6:1 hexanes/EtOAc + 1% AcOH as eluent gave pure *syn* and *anti* oxathiazinanes separately; the olefin maintained a >20:1 *E/Z* geometry in each case.

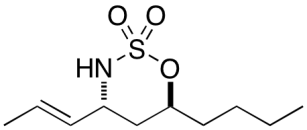
Run 1: (42.5 mg *syn* + 13.8 mg *anti* (3.1:1 d.r. – this was 2.9:1 in crude), 0.242 mmol, 61%), <5% rsm. Run 2: (51.0 mg *syn* + 10.8 mg *anti* (4.7:1 d.r.), 0.264 mmol, 66%), <5% rsm. Run 3: (50.2 mg *syn* + 11.3 mg *anti* (4.4:1 d.r.), 0.264 mmol, 66%), <5% rsm. **Average: 64% yield allylic, <5% rsm.**

Entry 2: General protocol for Rh conditions was followed. (±)-(*E*)-dec-8-en-5-yl sulfamate (94.0 mg, 0.400 mmol, 1.0 equiv), $Rh_2(OAc)_4$ (3.5 mg, 0.008 mmol, 0.02 equiv), MgO (37.1 mg, 0.920 mmol, 2.3 equiv), $PhI(OAc)_2$ (142 mg, 0.440 mmol, 1.1 equiv), CH_2Cl_2 (2.6 mL, 0.15M) were used. By ^{1}H-NMR analysis of the crude product, β:β' was >20:1, ins./azir. was 4:1, and d.r. was 4:1. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 5:1 hexanes/EtOAc (400 mL) → 3:1 hexanes/EtOAc as eluent gave pure *syn* and *anti* oxathiazinanes and aziridine separately; the olefin maintained a >20:1 *E/Z* geometry in each case.

Run 1: (48.0 mg *syn* + 8.9 mg *anti* (5:1 d.r.), 0.245 mmol, 61%), (15.6 mg aziridine (3.6:1 ins/azir), 0.067 mmol, 17%), <5% rsm. Run 2: (51.8 mg *syn* + 10.1 mg *anti* (5:1 d.r.), 0.267 mmol, 66%), (16.5 mg aziridine (3.8:1 ins/azir), 0.067 mmol, 17%), <5% rsm. Run 3: (49.3 mg *syn* + 8.7 mg *anti* (5.7:1 d.r.), 0.247 mmol, 62%), (17.4 mg mg aziridine (3.3:1 ins/azir), 0.074 mmol, 19%), <5% rsm. **Average: 63% yield allylic, <5% rsm.**

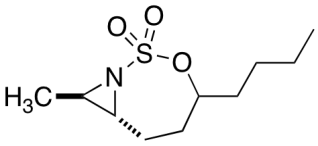


***Syn* (major) diastereomer:** Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.77 (dq, *J* = 15.0, 7.0 Hz, 1H), 5.41 (dd, *J* = 15.5, 6.0 Hz, 1H), 4.76-4.71 (m, 1H), 4.23-4.18 (m, 1H), 3.83 (br. d, *J* = 9.0 Hz, 1H), 1.84 (dt, *J* = 14.5, 2.5 Hz, 1H), 1.78-1.71 (m, 1H), 1.72 (d, *J* = 6.5 Hz, 3H), 1.66-1.59 (m, 1H), 1.57-1.31 (m, 5H), 0.91 (t, *J* = 7.3 Hz, 3H) ; ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.6, 128.6, 84.5, 56.5, 36.1, 35.3, 27.0, 22.6, 18.1, 14.2; IR (film, cm^{-1}) 3261, 2937, 2872, 1417, 1362, 1188, 870; HRMS (ESI) *m/z* calculated for $C_{10}H_{20}NO_3S$ $[M+H]^+$: 234.1164, found 234.1161.



***Anti* (minor) diastereomer:** Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.81 (ddd, *J* = 15.0, 6.5, 1.5 Hz, 1H), 5.71 (dq, *J* = 15.5, 6.0 Hz, 1H), 4.87-4.82 (m, 1H), 4.40 (br. d, *J* = 7.0 Hz, 1H), 4.19 (app. p, *J* = 5.5 Hz, 1H), 1.95-1.88 (m, 2H), 1.84 (ddd, *J* = 14.5, 5.0, 3.5 Hz, 1H), 1.73 (d, *J* = 6.5 Hz, 3H), 1.65-1.59 (m, 1H), 1.50-1.46 (m, 1H), 1.40-1.31 (m, 3H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.1, 128.5, 83.0, 55.0, 34.4, 33.9, 27.1, 22.4, 17.9, 14.0; IR (film, cm^{-1}) 3375, 2958, 2935, 2872, 1421, 1367, 1184, 874; HRMS (ESI) *m/z* calculated for $C_{10}H_{19}NO_3SNa$ $[M+Na]^+$: 256.0983, found 256.0984.

(±)-*trans*-4-butyl-8-methyl-3-oxa-2-thia-1-azabicyclo[5.1.0]octane-2,2-dioxide.



Isolated under Rh conditions (entry 2). Purified via flash column chromatography on silica using 4:1 hexanes/EtOAc → 2:1 hexanes/EtOAc as the eluent system. Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.31-4.26 (m, 1H), 3.00 (app. p, *J* = 5.5 Hz, 1H), 2.65-2.62 (m, 1H), 2.51-2.39 (m, 2H), 1.87-1.82 (m, 1H), 1.76-1.63 (m, 2H), 1.58-1.52 (m, 1H), 1.46-1.25 (m, 4H), 1.35 (d, *J* = 5.5 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 84.0, 47.2, 38.6, 34.4, 32.4, 27.7, 24.8, 22.4, 17.1, 14.0; IR (film, cm^{-1}) 2956, 2932, 2870, 1437, 1373, 1180, 1003, 901, 837; HRMS (ESI) *m/z* calculated for $C_{10}H_{20}NO_3S$ $[M+H]^+$: 234.1164, found 234.1168.

(±)-4-((1*E*)-1-propenyl)-6-(2-methylpropyl)tetrahydro-1,2,3-oxathiazine-2,2-dioxide [9].

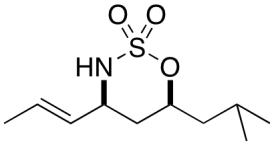
Entry 3: Single catalyst addition protocol for Fe conditions was followed. (±)-(*E*)-2-methylnon-7-en-4-yl sulfamate (94.0 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24.0 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product, β:β' was >20:1, ins./azir. was >20:1, and d.r. was 3.7:1 *syn*:*anti*. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 6:1 hexanes:EtOAc + 1% AcOH as eluent gave pure *syn* and *anti* oxathiazinanes separately; the olefin maintained a >20:1 *E/Z* geometry in each case.

Run 1: (54.6 mg *syn* + 12.1 mg *anti* (4.5:1 d.r.), 0.286 mmol, 72%), <5% rsm. Run 2: (56.0 mg *syn* + 11.1 mg *anti* (5:1 d.r.), 0.288 mmol, 72%), <5% rsm. Run 3: (56.3 mg *syn* + 11.2 mg *anti* (5:1 d.r.), 0.290 mmol, 73%), <5% rsm. **Average: 72% yield allylic, <5% rsm.**

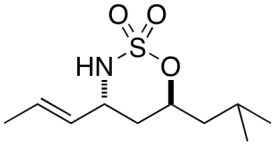
Entry 4: General protocol for Rh conditions was followed. (±)-(*E*)-2-methylnon-7-en-4-yl sulfamate (94.0 mg, 0.400 mmol, 1.0 equiv), $Rh_2(OAc)_4$ (3.5 mg, 0.008 mmol, 0.02 equiv), MgO (37.1 mg, 0.920 mmol, 2.3 equiv), $PhI(OAc)_2$ (142 mg, 0.440 mmol, 1.1 equiv), CH_2Cl_2 (2.6 mL, 0.15M) were used. By ^{1}H-NMR analysis of the crude product, β:β' was 1.3:1, ins./azir. was 6:1, and d.r. was 4:1. Flash column chromatography on silica (35 mm fritted glass column, 110 mm SiO_2) using 4:1 hexanes:EtOAc as eluent gave *syn* and *anti* oxathiazinanes separately, along with product of 3^o insertion (the allylic minor diasteromer and 3^o products co-eluted) and aziridine; the olefin maintained a >20:1 *E/Z* geometry in each case.

Run 1: (32.3 mg *syn* + 5.1 mg *anti* (6:1 d.r.), 0.161 mmol, 40%), (28.1 mg tertiary (β:β' = 1.3:1), 0.121 mmol, 30%), (10.1 mg aziridine (6:1 ins/azir), 0.043 mmol, 11%), 0% rsm. Run 2: (35.2 mg *syn* + 6.4 mg *anti* (5.5:1 d.r.), 0.179 mmol, 45%), (31.7 mg tertiary (β:β' = 1.3:1), 0.136 mmol, 34%), (9.3 mg aziridine (8:1 ins/azir), 0.040 mmol, 10%), 0% rsm. Run 3: (33.0 mg *syn* + 7.5 mg *anti* (4.4:1 d.r.), 0.174 mmol, 44%), (37.5 mg tertiary (β:β' = 1.1:1), 0.136 mmol, 34%),

(15.0 mg aziridine (5:1 ins/azir), 0.065 mmol, 16%), 0% rsm. **Average: 43% yield allylic, 0% rsm.**

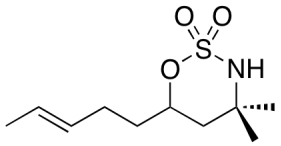


***Syn* (major) diastereomer:** Isolated as a waxy solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.78 (dq, *J* = 15.5, 6.5 Hz, 1H), 5.41 (dd, *J* = 15.5, 6.0 Hz, 1H), 4.85-4.80 (m, 1H), 4.25-4.20 (m, 1H), 3.79 (br. d, *J* = 9.5 Hz, 1H), 1.90-1.83 (m, 1H), 1.82 (dt, *J* = 14.0, 2.0 Hz, 1H), 1.75-1.69 (m, 1H), 1.73 (d, *J* = 5.5 Hz, 3H), 1.55-1.47 (m, 1H), 1.38 (ddd, *J* = 12.5, 8.5, 4.0 Hz, 1H), 0.94 (t, *J* = 6.8 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.4, 128.4, 82.7, 56.2, 44.4, 36.3, 24.0, 23.0, 22.0, 17.84; IR (film, cm^{-1}) 3261, 2958, 2873, 1416, 1365, 1188, 876; HRMS (ESI) *m/z* calculated for $C_{10}H_{19}NO_3SNa$ $[M+Na]^+$: 256.0983, found 256.0984.



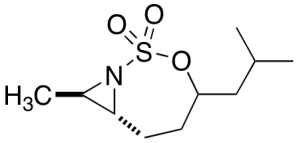
***Anti* (minor) diastereomer:** Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.83 (ddd, *J* = 15.5, 6.5, 1.5 Hz, 1H), 5.72 (dq, *J* = 15.5, 6.5 Hz, 1H), 4.95 (app. spt, *J* = 4.5 Hz, 1H), 4.25 (br. d, *J* = 7.0 Hz, 1H), 4.19 (app. p, *J* = 5.5 Hz, 1H), 1.95-1.81 (m, 4H), 1.75 (d, *J* = 6.5 Hz, 3H), 1.38-1.33 (m, 1H), 0.95 (t, *J* = 6.0 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.2, 128.5, 81.2, 55.1, 43.5, 34.3, 24.1, 23.0, 21.9, 17.9; IR (film, cm^{-1}) 3275, 2960, 2873, 1421, 1369, 1184, 1012, 996, 874; HRMS (ESI) *m/z* calculated for $C_{10}H_{19}NO_3SNa$ $[M+Na]^+$: 256.0983, found 256.0983.

(±)-4-((3*E*)-3-pentenyl)-6,6-dimethyltetrahydro-1,2,3-oxathiazine-2,2-dioxide.



Isolated under Rh conditions (entry 4). Purified via flash column chromatography on silica (35 mm fritted glass column, 110 mm SiO_2) using 6:1 hexanes/EtOAc as eluent system. Isolated as a colorless oil; the olefin maintained a >20:1 *E/Z* geometry. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.48 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.38 (ddt, *J* = 15.5, 6.5, 1.5 Hz, 1H), 4.82 (ddt, *J* = 11.0, 5.0, 4.5 Hz, 1H), 4.18 (br. s, 1H), 2.17-2.09 (m, 2H), 1.84-1.77 (m, 1H), 1.65 (dd, *J* = 6.0, 1.5 Hz, 3H), 1.66-1.58 (m, 3H), 1.48 (s, 3H), 1.29 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.2, 126.8, 80.7, 56.0, 41.5, 35.1, 32.0, 27.7, 25.2, 18.0; IR (film, cm^{-1}) 3267, 2972, 2939, 2922, 2856, 1421, 1389, 1352, 1192, 1157, 968, 941, 872; HRMS (ESI) *m/z* calculated for $C_{10}H_{19}NO_3SNa$ $[M+Na]^+$: 256.0983, found 256.0983.

(±)-*trans*-4-butyl-8-methyl-3-oxa-2-thia-1-azabicyclo[5.1.0]octane-2,2-dioxide.



Isolated under Rh conditions (entry 4). Purified via flash column chromatography on silica (35 mm fritted glass column, 110 mm SiO_2) using 6:1 hexanes/EtOAc → 2:1 hexanes/EtOAc as the eluent system. Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.36 (ddt, *J* = 11.5, 4.0, 2.0 Hz, 1H), 3.00 (app. p, *J* = 5.5 Hz, 1H), 2.65-2.63 (m, 1H), 2.53-2.40 (m, 2H), 1.84-1.70 (m, 2H), 1.68-1.61 (ddd, *J* = 14.5, 9.5, 5.0 Hz, 1H), 1.35 (d, *J* = 5.5 Hz, 3H), 1.29-1.24 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 82.3, 47.2, 43.5, 38.6, 32.9, 24.8, 24.7, 23.1, 21.6, 17.1; IR (film, cm^{-1}) 2960, 2931, 2873, 1439, 1375, 1180, 1003, 903, 764; HRMS (ESI) *m/z* calculated for $C_{10}H_{19}NO_3SNa$ $[M+Na]^+$: 256.0983, found 256.0981.

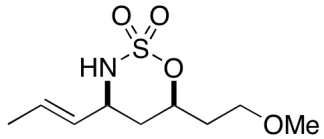
(±)-4-((1*E*)-1-propenyl)-6-(2-methoxyethyl)tetrahydro-1,2,3-oxathiazine-2,2-dioxide [10].

Entry 5: Single catalyst addition protocol for Fe conditions was followed. (±)-(*E*)-1-methoxyoct-6-en-3-yl sulfamate (94.8 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product, β:β' was 7:1, ins./azir. was >20:1, and d.r. was 3.8:1 *syn*:*anti*. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave pure *syn* and *anti* oxathiazinanes separately; the olefin maintained a >20:1 *E/Z* geometry in each case. Due to the instability of the ethereal product on silica, product ratios in this case were based solely on the crude ^{1}H-NMR integrations.

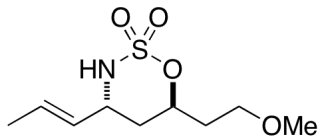
Run 1: (53.6 mg *syn* + 13.7 mg *anti* (4:1 d.r.), 0.286 mmol, 72%), 0% rsm. Run 2: (54.5 mg *syn* + 11.9 mg *anti* (4.5:1 d.r.), 0.283 mmol, 71%), 0% rsm. Run 3: (54.4 mg *syn* + 11.8 mg *anti* (4.6:1 d.r.), 0.282 mmol, 70%), 0% rsm. **Average: 71% yield allylic, 0% rsm.**

Entry 6: General protocol for Rh conditions was followed. (±)-(*E*)-1-methoxyoct-6-en-3-yl sulfamate (94.8 mg, 0.400 mmol, 1.0 equiv), $Rh_2(OAc)_4$ (3.5 mg, 0.008 mmol, 0.02 equiv), MgO (37.1 mg, 0.920 mmol, 2.3 equiv), $PhI(OAc)_2$ (142 mg, 0.440 mmol, 1.1 equiv), CH_2Cl_2 (2.6 mL, 0.15M) were used. By ^{1}H-NMR analysis of the crude product, β:β' was 4:1 and ins./azir. was 4:1 (only the ethereal and aziridine products gave clear peaks in the crude ^{1}H-NMR, so product ratios were based on these peaks and isolated yields). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes:EtOAc + 2% Et_3N (500 mL) → 1:1 hexanes/EtOAc as eluent gave *syn* and *anti* allylic oxathiazinanes and aziridine separately; the olefin maintained a >20:1 *E/Z* geometry in each case. In one case (Run 3), the crude material was purified using Davisil grade 643 silica gel in order to confirm the crude ratios for the ethereal product (the ethereal product is acid-sensitive and decomposes on normal silica, precluding quantitative isolation); 3:1 hexanes/EtOAc (300 mL) → 2:1 hexanes/EtOAc (300 mL) → 1:1 hexanes/EtOAc was used as the eluent.

Run 1: (35.4 mg *syn* + 8.5 mg *anti* (4:1 d.r.), 0.188 mmol, 47%), (14.3 mg aziridine (3.5:1 ins./azir.), 0.060 mmol, 15%), <5% rsm. Run 2: (35.3 mg *syn* + 8.9 mg *anti* (4:1 d.r.), 0.188 mmol, 47%), (14.9 mg aziridine (3.7:1 ins/azir), 0.064 mmol, 16%), <5% rsm. Run 3: (30.0 mg *syn* + 7.6 mg *anti* (3.9:1 d.r.), 0.160 mmol, 40%), (11.0 mg ethereal (β:β' = 3.4:1), 0.047 mmol, 12% yield), (13.4 mg aziridine (3.6:1 ins/azir), 0.057 mmol, 14%), 0% rsm. **Average: 45% yield allylic, <5% rsm.**



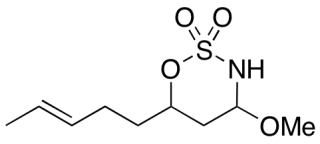
***Syn* (major) diastereomer:** Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.79 (dq, *J* = 15.5, 6.5 Hz, 1H), 5.42 (dd, *J* = 15.5, 6.0 Hz, 1H), 4.96-4.91 (m, 1H), 4.23-4.19 (m, 1H), 3.90-3.83 (m, 1H), 3.55-3.48 (m, 2H), 3.35 (s, 3H), 2.01-1.89 (m, 3H), 1.74 (d, *J* = 6.5 Hz, 3H), 1.57 (dt, *J* = 14.0, 12.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.5, 128.2, 81.6, 67.6, 59.0, 56.2, 35.9, 35.7, 17.9; IR (film, cm^{-1}) 3259, 3174, 2934, 2881, 1421, 1360, 1188, 1117, 864; HRMS (ESI) *m/z* calculated for $C_9H_{17}NO_4SNa$ $[M+Na]^+$: 258.0776, found 258.0778.



***Anti* (minor) diastereomer:** Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.78 (dd, *J* = 15.5, 6.0 Hz, 1H), 5.72 (dq, *J* = 16.0, 6.0 Hz, 1H), 5.05 (app. spt, *J* = 4.5 Hz, 1H), 4.35 (br. d, *J* = 7.5 Hz, 1H), 4.21 (app. p, *J* = 6.0 Hz, 1H), 3.57-3.48 (m, 2H), 3.35 (s, 3H), 2.24-2.18 (m, 1H), 1.97-1.87 (m, 3H), 1.73 (d, *J* = 6.0 Hz, 3H); ^{13}C-

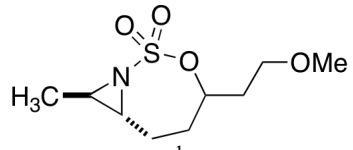
NMR (125 MHz, $CDCl_3$) δ 129.3, 128.4, 80.4, 67.9, 59.0, 54.8, 34.7, 33.9, 17.9; IR (film, cm^{-1}) 3273, 2924, 2885, 1423, 1369, 1186, 1119, 968 870; HRMS (ESI) *m/z* calculated for $C_9H_{17}NO_4SNa$ $[M+Na]^+$: 258.0776, found 258.0775.

(±)-4-((3*E*)-3-pentenyl)-6-methoxytetrahydro-1,2,3-oxathiazine-2,2-dioxide.



Due to its instability under silica-based flash column chromatography conditions, the minor ethereal product could not be isolated in a quantitative manner. However, a sufficient amount was isolated pure for the purposes of characterization, to ensure use of appropriate ^{1}H-NMR peaks for product ratio determination in the crude reaction mixture. Isolated as a colorless oil; the olefin maintained a >20:1 *E/Z* geometry. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.49 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.37 (ddt, *J* = 15.0, 7.0, 1.5 Hz, 1H), 4.73 (dt, *J* = 10.0, 3.0 Hz, 1H), 4.61-4.56 (m, 1H), 3.76 (br. d, *J* = 10.0 Hz, 1H), 3.52 (s, 3H), 2.19-2.10 (m, 2H), 2.09 (dt, *J* = 14.0, 2.5 Hz, 1H), 1.87-1.80 (m, 1H), 1.71-1.65 (m, 1H), 1.65 (d, *J* = 6.0 Hz, 3H), 1.60-1.53 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 128.9, 127.1, 87.9, 80.0, 56.9, 37.0, 34.8, 27.6, 18.1; IR (film, cm^{-1}) 3246, 2922, 2852, 1450, 1416, 1365, 1192, 968, 866; HRMS (ESI) *m/z* calculated for $C_9H_{17}NO_4SNa$ $[M+Na]^+$: 258.0776, found 258.0774.

(±)-*trans*-4-(2-methoxyethyl)-8-methyl-3-oxa-2-thia-1-azabicyclo[5.1.0]octane-2,2-dioxide.



Isolated under Rh conditions (entry 6). Purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc (300 mL) → 2:1 hexanes/EtOAc (500 mL) → 1:1 hexanes/EtOAc as the eluent system. Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.49-4.44 (m, 1H), 3.49-3.42 (m, 2H), 3.33 (s, 3H), 3.01 (app. p, *J* = 5.5 Hz, 1H), 2.64 (dt, *J* = 4.5, 2.0 Hz, 1H), 2.53-2.40 (m, 2H), 1.91-1.71 (m, 4H), 1.35 (d, *J* = 5.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 81.2, 68.4, 59.0, 47.2, 38.7, 34.9, 32.5, 24.8, 17.1; IR (film, cm^{-1}) 2974, 2924, 2879, 1439, 1373, 1180, 1003, 903; HRMS (ESI) *m/z* calculated for $C_9H_{18}NO_4S$ $[M+H]^+$: 236.0957, found 236.0957.

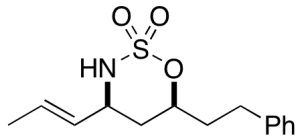
(±)-4-((1*E*)-1-propenyl)-6-(2-phenylethyl)tetrahydro-1,2,3-oxathiazine-2,2-dioxide [11].

Entry 7: Single catalyst addition protocol for Fe conditions was followed. (±)-(*E*)-1-phenyloct-6-en-3-yl sulfamate (113 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product, ins./azir. was >20:1 and d.r. was 3.5:1 *syn*:*anti* (for benzylic product, d.r. was >20:1 *syn*:*anti*). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 9:1 hexanes/EtOAc + 1% AcOH (180 mL) → 6:1 hexanes/EtOAc + 1% AcOH (180 mL) → 4:1 hexanes/EtOAc + 1% AcOH as eluent gave pure benzylic and *syn* and *anti* allylic oxathiazinanes separately; the olefin maintained a >20:1 *E/Z* geometry in each case. Due to overlapping peaks in crude reaction mixture, β:β' was calculated based on isolated yields of the allylic and benzylic products after column purification; β:β' = 5:1.

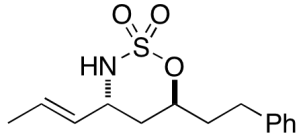
Run 1: (56.2 mg *syn* + 10.8 mg *anti* (5.2:1 d.r.), 0.238 mmol, 60%), (13.0 mg benzylic (5:1 allylic/benzylic), 0.046 mmol, 12%), 0% rsm. Run 2: (53.2 mg *syn* + 13.8 mg *anti* (3.9:1 d.r.), 0.238 mmol, 60%), (14.5 mg benzylic (4.6:1 allylic/benzylic), 0.052 mmol, 13%), 0% rsm. Run 3: (61.6 mg *syn* + 12.8 mg *anti* (4.8:1 d.r.), 0.264 mmol, 66%), (9.6 mg benzylic (7:1 allylic/benzylic), 0.036 mmol, 9%). **Average: 62% yield allylic, 0% rsm.**

Entry 8: General protocol for Rh conditions was followed. (±)-(*E*)-1-phenyloct-6-en-3-yl sulfamate (113 mg, 0.400 mmol, 1.0 equiv), $Rh_2(OAc)_4$ (3.5 mg, 0.008 mmol, 0.02 equiv), MgO (37.1 mg, 0.920 mmol, 2.3 equiv), $PhI(OAc)_2$ (142 mg, 0.440 mmol, 1.1 equiv), CH_2Cl_2 (2.6 mL, 0.15M) were used. Due to significant overlap of relevant peaks, ^{1}H-NMR analysis of the crude product was not possible. Flash column chromatography on silica (35 mm fritted glass column, 110 mm SiO_2) using 6:1 hexanes/EtOAc (500 mL) → 3:1 hexanes/EtOAc (250 mL) → 2:1 hexanes/EtOAc as eluent gave benzylic, *syn* and *anti* allylic oxathiazinanes and aziridine separately; the olefin maintained a >20:1 *E/Z* geometry in each case. β:β', ins./azir. and d.r. were calculated based on isolated yields of the allylic and benzylic products after column purification; β:β' = 2:1, ins./azir. = 4:1, d.r. = 5:1.

Run 1: (46.2 mg *syn* + 9.4 mg *anti* (5:1 d.r.), 0.199 mmol, 50%), (26.0 mg benzylic (β:β' = 2:1), 0.093 mmol, 23%), (18.9 mg aziridine (4:1 ins./azir.), 0.068 mmol, 17%), 0% rsm. Run 2: (43.3 mg *syn* + 10.2 mg *anti* (4:1 d.r.), 0.191 mmol, 48%), (24.1 mg benzylic (β:β' = 2:1), 0.086 mmol, 22%), (17.6 mg aziridine (4:1 ins/azir), 0.063 mmol, 16%), 0% rsm. Run 3: (50.2 mg *syn* + 9.3 mg *anti* (5.4:1 d.r.), 0.213 mmol, 53%), (22.3 mg benzylic (β:β' = 2.6:1), 0.080 mmol, 20%), (13.9 mg aziridine (6:1 ins/azir), 0.050 mmol, 12%), 0% rsm. **Average: 50% yield allylic, 0% rsm.**

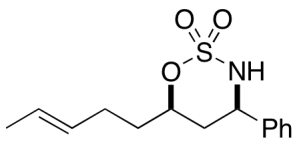


***Syn* (major) diastereomer:** Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.23-7.18 (m, 3H), 5.76 (dq, *J* = 15.5, 6.5 Hz, 1H), 5.40 (dd, *J* = 15.5, 6.5 Hz, 1H), 4.77-4.72 (m, 1H), 4.22-4.16 (m, 1H), 3.81 (d, *J* = 10.0 Hz, 1H), 2.87-2.81 (m, 1H), 2.77-2.71 (m, 1H), 2.11-2.03 (m, 1H), 1.94-1.87 (m, 1H), 1.82 (dt, *J* = 14.0, 2.5 Hz, 1H), 1.72 (d, *J* = 7.0 Hz, 3H), 1.57 (dt, *J* = 14.0, 12.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 140.5, 129.5, 128.8, 128.7, 128.2, 126.5, 83.0, 56.1, 37.2, 35.8, 30.8, 17.9; IR (film, cm^{-1}) 3263, 3028, 2922, 2856, 1417, 1360, 1186, 870; HRMS (ESI) *m/z* calculated for $C_{14}H_{19}NO_3SNa$ $[M+Na]^+$: 304.0983, found 304.0978.



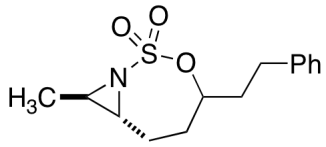
***Anti* (minor) diastereomer:** Isolated as a colorless waxy oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.23-7.20 (m, 3H), 5.76 (dd, *J* = 15.5, 6.0 Hz, 1H), 5.70 (dq, *J* = 15.5, 6.0 Hz, 1H), 4.85 (app. spt, *J* = 4.5 Hz, 1H), 4.28 (br. d, *J* = 7.5 Hz, 1H), 4.22 (app. p, *J* = 6.0 Hz, 1H), 2.88 (ddd, *J* = 14.0, 9.0, 5.0 Hz, 1H), 2.74 (ddd, *J* = 13.5, 9.0, 7.0 Hz, 1H), 2.33 (ddt, *J* = 9.0, 5.5, 14.5 Hz, 1H), 1.95-1.82 (m, 3H), 1.72 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 140.6, 129.3, 128.7 (2 peaks), 128.3, 126.4, 82.0, 54.9, 36.4, 34.0, 31.2, 17.9; IR (film, cm^{-1}) 3286, 3271, 3028, 2922, 2856, 1419, 1367, 1186, 1038, 996, 876; HRMS (ESI) *m/z* calculated for $C_{14}H_{19}NO_3SNa$ $[M+Na]^+$: 304.0983, found 304.0984.

(±)-4-((3*E*)-3-pentenyl)-4-phenyltetrahydro-1,2,3-oxathiazine-2,2-dioxide.



Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.43-7.33 (m, 5H), 5.51 (dq, *J* = 15.5, 6.0 Hz, 1H), 5.39 (dt, *J* = 15.0, 6.5 Hz, 1H), 4.91-4.86 (m, 1H), 4.80 (ddd, *J* = 12.0, 9.5, 2.5 Hz, 1H), 4.14-4.12 (br. m, 1H), 2.22-2.13 (m, 2H), 2.07 (dt, *J* = 14.5, 2.5 Hz, 1H), 1.94-1.85 (m, 2H), 1.75-1.69 (m, 1H), 1.67 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.2, 129.3, 129.1, 129.0, 127.1, 126.4, 83.7, 58.3, 36.3, 35.2, 27.6, 18.1; IR (film, cm^{-1}) 3261, 3024, 2960, 2937, 2920, 2856, 1456, 1416, 1360, 1186, 1053, 864; HRMS (ESI) *m/z* calculated for $C_{14}H_{20}NO_3S$ $[M+H]^+$: 282.1164, found 282.1162.

(±)-*trans*-4-(2-phenylethyl)-8-methyl-3-oxa-2-thia-1-azabicyclo[5.1.0]octane-2,2-dioxide.

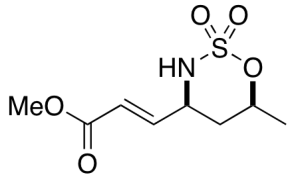


Isolated under Rh conditions (entry 8). Purified via flash column chromatography on silica (35 mm fritted glass column, 110 mm SiO_2) using 9:1 hexanes/EtOAc → 4:1 hexanes/EtOAc → 2:1 hexanes/EtOAc as eluent system. Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.0 Hz, 2H), 7.22-7.17 (m, 3H), 4.32-4.27 (m, 1H), 3.03 (app. p, *J* = 5.5 Hz, 1H), 2.82 (ddd, *J* = 14.0, 9.5, 5.5 Hz, 1H), 2.72-2.67 (m, 1H), 2.65-2.63 (m, 1H), 2.50-2.39 (m, 2H), 2.02-1.95 (m, 1H), 1.87-1.74 (m, 3H), 1.37 (d, *J* = 5.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 128.7 (2 peaks), 126.4, 121.8, 82.8, 47.1, 38.7, 36.6, 32.5, 31.8, 24.6, 17.1; IR (film, cm^{-1}) 3026, 2929, 2864, 1496, 1454, 1373, 1180, 1036, 997, 901; HRMS (ESI) *m/z* calculated for $C_{14}H_{20}NO_3S$ $[M+H]^+$: 282.1164, found 282.1164.

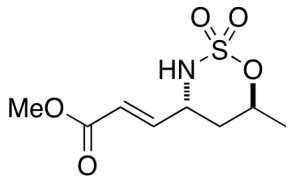
(±)-(*E*)-methyl 3-(6-methyl-2,2-dioxido-1,2,3-oxathiazinan-4-yl)acrylate [12]; entry 9.

Iterative catalyst addition protocol for Fe conditions was followed. (±)-(*E*)-methyl 6-(sulfamoyloxy)hept-2-enoate (94.9 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (4x8 mg, 0.053 mmol, 0.13 equiv), $AgSbF_6$ (4x4.5 mg, 0.053 mmol, 0.13 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product, d.r. was 3:1 *syn*:*anti* and ins./azir. was >20:1. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes/EtOAc as eluent gave *syn* allylic oxathiazinane, recovered starting material and *anti* allylic oxathiazinane separately.

Run 1: (30.6 mg *syn* + 8.2 mg *anti* (3.7:1 d.r.), 0.165 mmol, 41%), (21.7 mg rsm, 0.091 mmol, 23%). Run 2: (31.2 mg *syn* + 5.9 mg *anti* (5.2:1 d.r.), 0.158 mmol, 39%), (14.8 mg rsm, 0.062 mmol, 16%). Run 3: (26.4 mg *syn* + 7.5 mg *anti* (3.5:1 d.r.), 0.144 mmol, 36%), (14.8 mg rsm, 0.062 mmol, 16%). **Average: 39% yield, 18% rsm.**



***Syn* (major) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.84 (dd, *J* = 16.0, 5.0 Hz, 1H), 6.04 (dd, *J* = 16.0, 2.0 Hz, 1H), 4.92 (dddd, *J* = 12.0, 10.5, 6.5, 2.0 Hz, 1H), 4.49-4.42 (m, 1H), 4.31 (br. d, *J* = 10.5 Hz, 1H), 3.76 (s, 3H), 1.96 (dt, *J* = 14.5, 2.5 Hz, 1H), 1.57 (dt, *J* = 14.0, 12.0 Hz, 1H), 1.45 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.1, 143.4, 122.5, 80.5, 55.2, 52.2, 36.4, 21.2; IR (film, cm^{-1}) 3244, 2985, 2956, 1712, 1664, 1439, 1363, 1323, 1286, 1254, 1188, 1124, 1076, 1028, 980, 941, 866, 796; HRMS (ESI) *m/z* calculated for $C_8H_{13}NO_5SNa$ $[M+Na]^+$: 258.0412, found 258.0413.

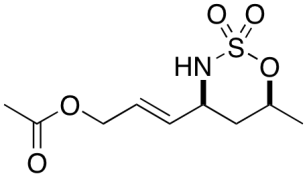


***Anti* (minor) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 16.0, 5.0 Hz, 1H), 6.08 (dd, *J* = 16.0, 2.0 Hz, 1H), 5.00 (dddd, *J* = 16.0, 9.5, 6.5, 3.5 Hz, 1H), 4.56 (br. d, *J* = 6.5 Hz, 1H), 4.42-4.37 (m, 1H), 3.77 (s, 3H), 2.02 (ddd, *J* = 15.0, 9.5, 5.5 Hz, 1H), 1.95 (dt, *J* = 14.5, 3.5 Hz, 1H), 1.50 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.2, 144.3, 123.5, 78.7, 53.9, 52.1, 34.3, 21.1; IR (film, cm^{-1}) 3251, 2993, 2953, 1712, 1662, 1437, 1369, 1321, 1282, 1182, 1072, 885, 862, 808; HRMS (ESI) *m/z* calculated for $C_8H_{13}NO_3SNa$ $[M+Na]^+$: 258.0412, found 258.0410.

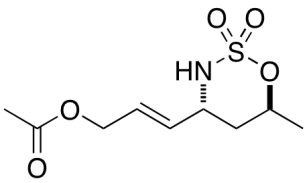
(±)-(*E*)-3-(6-methyl-2,2-dioxido-1,2,3-oxathiazinan-4-yl)allyl acetate [13]; entry 10.

Iterative catalyst addition protocol for Fe conditions was followed. (±)-(*E*)-6-(sulfamoyloxy)hept-2-en-1-yl acetate (101 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (4x8 mg, 0.053 mmol, 0.13 equiv), $AgSbF_6$ (4x4.5 mg, 0.053 mmol, 0.13 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product, d.r. was 3:1 *syn*:*anti* and ins./azir. was >20:1. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 19:1 CH_2Cl_2/EtOAc (800 mL) → 9:1 CH_2Cl_2/EtOAc (150 mL) → 6:1 CH_2Cl_2/EtOAc as eluent gave *syn* and *anti* allylic oxathiazinanes plus recovered starting material separately.

Run 1: (39.4 mg *syn* + 10.5 mg *anti* (3.8:1 d.r.), 0.200 mmol, 50%), (12.5 mg rsm, 0.050 mmol, 12%). Run 2: (36.2 mg *syn* + 8.0 mg *anti* (4.5:1 d.r.), 0.177 mmol, 44%), (12.3 mg rsm, 0.049 mmol, 12%). Run 3: (37.2 mg *syn* + 10.6 mg *anti* (3.5:1 d.r.), 0.191 mmol, 48%), (16.4 mg rsm, 0.065 mmol, 16%). **Average: 47% yield, 13% rsm.**



***Syn* (major) diastereomer:** Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.83 (ddt, *J* = 16.0, 5.5, 1.5 Hz, 1H), 5.70 (dd, *J* = 16.0, 5.5 Hz, 1H), 4.86 (dddd, *J* = 12.5, 10.5, 6.5, 2.0 Hz, 1H), 4.55 (d, *J* = 5.5 Hz, 2H), 4.33-4.24 (m, 1H), 4.31 (br. d, *J* = 10.5 Hz, 1H), 2.05 (s, 3H), 1.87 (dt, *J* = 14.5, 2.5 Hz, 1H), 1.54 (dt, *J* = 14.0, 12.0 Hz, 1H), 1.41 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 170.8, 130.6, 127.3, 80.5, 63.7, 55.6, 36.7, 21.2, 20.9; IR (film, cm^{-1}) 3244, 2985, 2939, 1736, 1425, 1363, 1238, 1188, 1111, 1066, 1030, 970, 933, 864, 796; HRMS (ESI) *m/z* calculated for $C_9H_{15}NO_5SNa$ $[M+Na]^+$: 272.0569, found 272.0569.

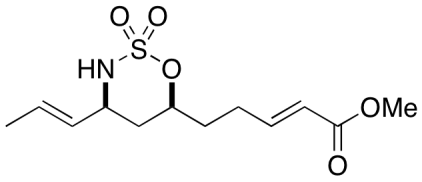


***Anti* (minor) diastereomer:** Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.10 (ddt, *J* = 15.5, 5.5, 1.5 Hz, 1H), 5.82 (ddt, *J* = 16.0, 6.0, 2.0 Hz, 1H), 5.02 (dddd, *J* = 16.0, 10.0, 6.5, 3.5 Hz, 1H), 4.60 (d, *J* = 6.0 Hz, 2H), 4.52 (br. d, *J* = 6.5 Hz, 1H), 4.28 (app p, *J* = 5.3 Hz, 1H), 2.08 (s, 3H), 1.95 (ddd, *J* = 14.5, 9.0, 5.0 Hz, 1H), 1.89 (dt, *J* = 14.5, 4.0 Hz, 1H), 1.50 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 170.9, 131.5, 127.3, 78.9, 64.0, 54.3, 34.8, 21.0 (2 peaks); IR (film, cm^{-1}) 3261, 2985, 2939, 1738, 1425, 1367, 1240, 1184, 1095, 1061, 1030, 970, 883, 837, 796; HRMS (ESI) *m/z* calculated for $C_9H_{15}NO_5SNa$ $[M+Na]^+$: 272.0569, found 272.0570.

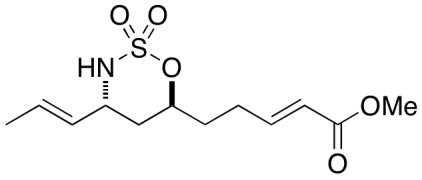
(±)-(*E*)-methyl 5-(2,2-dioxido-4-((*E*)-prop-1-en-1-yl)-1,2,3-oxathiazinan-6-yl)pent-2-enoate [14]; entry 11.

Iterative catalyst addition protocol for Fe conditions was followed. (±)-(2*E*,9*E*)-methyl 6-(sulfamoyloxy)undeca-2,9-dienoate (117 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (4x8 mg, 0.053 mmol, 0.13 equiv), $AgSbF_6$ (4x4.5 mg, 0.053 mmol, 0.13 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product, ins./azir. was >20:1. By GC analysis of the crude product, β:β' = 14:1 and d.r. = 4:1 *syn*:*anti*. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave *syn* ester allylic oxathiazinane plus *syn* and *anti* methyl allylic oxathiazinanes separately.

Run 1: (50.3 mg *syn* + 12.4 mg *anti* (4.0:1 d.r.), 0.216 mmol, 54%), 0% rsm. Run 2: (50.1 mg *syn* + 11.9 mg *anti* (4.2:1 d.r.), 0.214 mmol, 53%), 0% rsm. Run 3: (52.6 mg *syn* + 13.7 mg *anti* (3.8:1 d.r.), 0.229 mmol, 57%), 0% rsm. **Average: 55% yield, 0% rsm.**

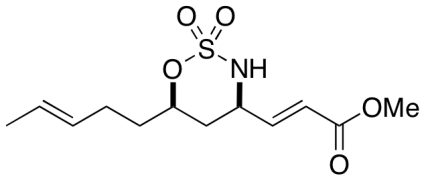


***Syn* (major) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.90 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.85 (dt, *J* = 15.5, 1.5 Hz, 1H), 5.75 (dq, *J* = 15.5, 6.5 Hz, 1H), 5.41-5.37 (m, 1H), 4.74-4.69 (m, 1H), 4.19-4.18 (m, 2H), 3.71 (s, 3H), 2.45-2.38 (m, 1H), 2.36-2.28 (m, 1H), 1.91-1.73 (m, 3H), 1.70 (d, *J* = 6.5 Hz, 3H), 1.59-1.51 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.9, 147.0, 129.5, 127.9, 122.2, 82.8, 56.1, 51.6, 35.5, 33.5, 27.2, 17.9; IR (film, cm^{-1}) 3236, 2953, 2922, 2856, 1722, 1657, 1437, 1362, 1323, 1286, 1188, 1049, 968, 868; HRMS (ESI) *m/z* calculated for $C_{12}H_{19}NO_5SNa$ $[M+Na]^+$: 312.0882, found 312.0883.



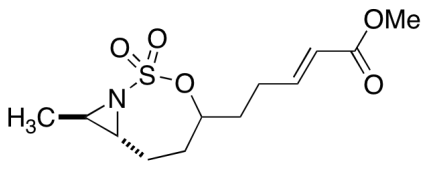
***Anti* (minor) diastereomer:** Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.93 (dt, *J* = 16.0, 6.5 Hz, 1H), 5.88 (d, *J* = 16.0 Hz, 1H), 5.80-5.68 (m, 2H), 4.84 (app spt, *J* = 4.5 Hz, 1H), 4.51 (br. d, *J* = 7.0 Hz, 1H), 4.21 (app p, *J* = 5.8 Hz, 1H), 3.73 (s, 3H), 2.50-2.43 (m, 1H), 2.38-2.31 (m, 1H), 2.12 (ddd, *J* = 14.5, 9.5, 5.0 Hz, 1H), 1.92 (ddd, *J* = 14.5, 8.5, 5.5 Hz, 1H), 1.84 (ddd, *J* = 14.5, 5.5, 4.0 Hz, 1H), 1.77-1.67 (m, 1H), 1.73 (d, *J* = 5.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 167.0, 147.1, 129.4, 128.2, 122.3, 81.7, 54.8, 51.7, 33.8, 32.9, 27.6, 17.9; IR (film, cm^{-1}) 3257, 2951, 2931, 2854, 1722, 1658, 1437, 1367, 1286, 1184, 1043, 968, 872; HRMS (ESI) *m/z* calculated for $C_{12}H_{19}NO_5SNa$ $[M+Na]^+$: 312.0882, found 312.0884.

(±)-(*E*)-methyl 3-(2,2-dioxido-6-((*E*)-pent-3-en-1-yl)-1,2,3-oxathiazinan-4-yl)acrylate:



Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.83 (dd, *J* = 16.0, 5.0 Hz, 1H), 6.03 (dd, *J* = 16.0, 2.0 Hz, 1H), 5.48 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.36 (ddt, *J* = 15.0, 6.5, 1.5 Hz, 1H), 4.82-4.77 (m, 1H), 4.48-4.42 (m, 1H), 4.27 (br. d, *J* = 10.5 Hz, 1H), 3.76 (s, 3H), 2.19-2.08 (m, 2H), 1.92 (dt, *J* = 14.5, 2.0 Hz, 1H), 1.88-1.79 (m, 1H), 1.73-1.65 (m, 1H), 1.65 (d, *J* = 5.5 Hz, 3H), 1.57 (dt, *J* = 14.0, 12.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.1, 143.4, 128.9, 127.1, 122.5, 83.4, 55.2, 52.2, 35.1, 34.9, 27.5, 18.0; IR (film, cm^{-1}) 3236, 3024, 2995, 2953, 2920, 2856, 1712, 1664, 1439, 1365, 1323, 1284, 1259, 1188, 1126, 970, 868, 821; HRMS (ESI) *m/z* calculated for $C_{12}H_{19}NO_5SNa$ $[M+Na]^+$: 312.0882, found 312.0883.

(±)-(*E*)-methyl 5-(8-methyl-2,2-dioxido-3-oxa-2-thia-1-azabicyclo[5.1.0]octan-4-yl)pent-2-enoate.



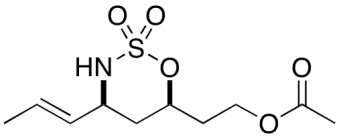
Prepared as a standard using general protocol for Rh conditions. Purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc (400 mL) → 2:1 hexanes/EtOAc (200 mL) → 1:1 hexanes/EtOAc as eluent system. Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.89 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.85 (dd, *J* = 16.0, 1.5 Hz, 1H), 4.30-4.25 (m, 1H), 3.72 (s, 3H), 3.00 (app p, *J* = 5.3 Hz, 1H), 2.65-2.63 (m, 1H), 2.51-2.36 (m, 3H), 2.33-2.26 (m, 1H), 1.86-1.67 (m, 4H), 1.35 (d, *J* = 5.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.9, 147.0, 122.3, 82.6, 51.6, 47.2, 38.7, 33.0, 32.4, 28.2, 24.7, 17.1; IR (film, cm^{-1})

2953, 2931, 2852, 1722, 1658, 1439, 1373, 1273, 1180, 1041, 1001, 901, 837, 687, 631; HRMS (ESI) *m/z* calculated for $C_{12}H_{19}NO_5SNa$ $[M+Na]^+$: 312.0882, found 312.0884.

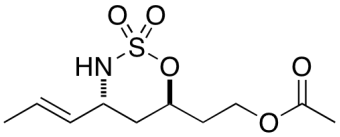
(±)-2-(2,2-dioxido-4-((*E*)-prop-1-en-1-yl)-1,2,3-oxathiazinan-6-yl)ethyl acetate [15]; entry 12.

Iterative catalyst addition protocol for Fe conditions was followed. (±)-(*E*)-3-(sulfamoyloxy)oct-6-en-1-yl acetate (106 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (4x8 mg, 0.053 mmol, 0.13 equiv), $AgSbF_6$ (4x4.5 mg, 0.053 mmol, 0.13 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product, d.r. was 3:1 *syn*:*anti* and ins./azir. was >20:1. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes/EtOAc as eluent gave *syn* and *anti* allylic oxathiazinanes separately.

Run 1: (52.1 mg *syn* + 11.9 mg *anti* (4.4:1 d.r.), 0.244 mmol, 61%), 0% rsm. Run 2: (53.1 mg *syn* + 12.3 mg *anti* (4.3:1 d.r.), 0.249 mmol, 62%), 0% rsm. Run 3: (50.3 mg *syn* + 12.2 mg *anti* (4.1:1 d.r.), 0.238 mmol, 60%), 0% rsm. **Average: 61% yield, 0% rsm.**

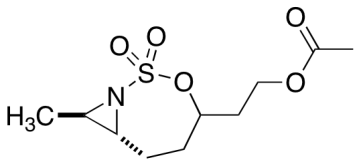


***Syn* (major) diastereomer:** Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.75 (dq, *J* = 15.5, 6.5 Hz, 1H), 5.39 (ddd, *J* = 15.5, 6.0, 1.5 Hz, 1H), 4.88-4.82 (m, 1H), 4.26 (br. d, *J* = 10.0 Hz, 1H), 4.23-4.12 (m, 3H), 2.05-1.94 (m, 2H), 2.04 (s, 3H), 1.84 (dt, *J* = 14.0, 2.5 Hz, 1H), 1.70 (d, *J* = 7.0 Hz, 3H), 1.57 (dt, *J* = 14.0, 12.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.1, 129.6, 127.9, 80.7, 59.5, 56.2, 35.4, 34.3, 21.0, 17.9; IR (film, cm^{-1}) 3255, 2966, 2939, 2922, 2858, 1728, 1425, 1367, 1248, 1188, 1136, 1095, 1051, 970, 866, 823, 769; HRMS (ESI) *m/z* calculated for $C_{10}H_{17}NO_5SNa$ $[M+Na]^+$: 286.0725, found 286.0722.



***Anti* (minor) diastereomer:** Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.80-5.69 (m, 2H), 4.99 (app spt, *J* = 4.5 Hz, 1H), 4.49 (br. d, *J* = 7.0 Hz, 1H), 4.28-4.17 (m, 3H), 2.30 (ddt, *J* = 15.0, 9.0, 5.0 Hz, 1H), 2.06 (s, 3H), 2.00-1.87 (m, 3H), 1.74 (d, *J* = 5.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.1, 129.5, 128.2, 79.6, 60.0, 54.7, 33.6 (2 peaks), 21.0, 17.9; IR (film, cm^{-1}) 3255, 2962, 2920, 1738, 1425, 1367, 1246, 1186, 1099, 1047, 968, 870, 766; HRMS (ESI) *m/z* calculated for $C_{10}H_{17}NO_5SNa$ $[M+Na]^+$: 286.0725, found 286.0725.

(±)-2-(8-methyl-2,2-dioxido-3-oxa-2-thia-1-azabicyclo[5.1.0]octan-4-yl)ethyl acetate.

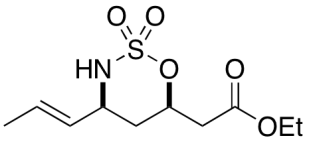


Prepared as a standard using general protocol for Rh conditions. Purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes/EtOAc (600 mL) → 1:1 hexanes/EtOAc as eluent system. Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.45-4.40 (m, 1H), 4.19 (dt, *J* = 11.5, 5.5 Hz, 1H), 4.22-4.11 (m, 2H), 3.01 (app p, *J* = 5.3 Hz, 1H), 2.66-2.64 (m, 1H), 2.53-2.42 (m, 2H), 2.05 (s, 3H), 1.99-1.91 (m, 2H), 1.90-1.84 (m, 1H), 1.81-1.72 (m, 1H), 1.35 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.0, 80.4, 60.3, 47.1, 38.8, 33.7, 32.3, 24.7, 21.0, 17.1; IR (film, cm^{-1}) 2970, 2931, 1739, 1439, 1373, 1248, 1180, 1047, 1005, 903, 754, 687; HRMS (ESI) *m/z* calculated for $C_{10}H_{17}NO_5SNa$ $[M+Na]^+$: 286.0725, found 286.0722.

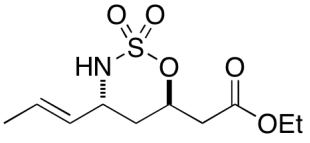
(±)-ethyl 2-(2,2-dioxido-4-((*E*)-prop-1-en-1-yl)-1,2,3-oxathiazinan-6-yl)acetate [16]; entry 13.

Single catalyst addition protocol for Fe conditions was followed. (±)-(*E*)-ethyl 3-(sulfamoyloxy)oct-6-enoate (106 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24.0 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product, d.r. was 3:1 *syn*:*anti* and ins./azir. was >20:1. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave *syn* and *anti* allylic oxathiazinanes separately.

Run 1: (58.4 mg *syn* + 18.2 mg *anti* (3.2:1 d.r.), 0.292 mmol, 73%), 0% rsm. Run 2: (57.3 mg *syn* + 15.1 mg *anti* (3.8:1 d.r.), 0.276 mmol, 69%), 0% rsm. Run 3: (53.1 mg *syn* + 14.8 mg *anti* (3.6:1 d.r.), 0.259 mmol, 65%), 0% rsm. **Average: 69% yield, 0% rsm.**

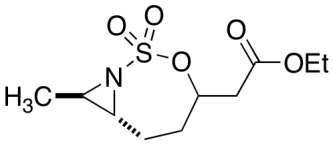


***Syn* (major) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ; 5.77 (dq, *J* = 15.5, 6.5 Hz, 1H), 5.41-5.38 (m, 1H), 5.13 (ddt, *J* = 15.0, 6.5, 2.0 Hz, 1H), 4.23-4.22 (m, 2H), 4.16 (q, *J* = 7.0 Hz, 2H), 2.78 (dd, *J* = 16.3, 6.8 Hz, 1H), 2.63 (dd, *J* = 16.3, 6.3 Hz, 1H), 1.97 (app d, *J* = 14.5 Hz, 1H), 1.70 (d, *J* = 6.5 Hz, 3H), 1.63-1.54 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 169.0, 129.6, 127.8, 79.7, 61.3, 56.1, 40.1, 35.0, 17.9, 14.2; IR (film, cm^{-1}) 3257, 2983, 2941, 2920, 1736, 1423, 1365, 1311, 1219, 1188, 1047, 10128, 941, 870, 791; HRMS (ESI) *m/z* calculated for $C_{10}H_{18}NO_5S$ $[M+H]^+$: 264.0906, found 264.0914.



***Anti* (minor) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.78-5.71 (m, 2H), 5.30-5.25 (m, 1H), 4.53 (br. d, *J* = 7.5 Hz, 1H), 4.23-4.21 (m, 1H), 4.17 (q, *J* = 7.0 Hz, 2H), 2.99 (dd, *J* = 16.5, 6.5 Hz, 1H), 2.78 (dd, *J* = 16.5, 7.5 Hz, 1H), 2.04-1.93 (m, 2H), 1.73 (d, *J* = 4.0 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 169.4, 129.4, 128.0, 78.5, 61.4, 54.5, 39.1, 32.8, 18.0, 14.2; IR (film, cm^{-1}) 3267, 2983, 2939, 2922, 1732, 1425, 1371, 1309, 1186, 1034, 968, 881, 787; HRMS (ESI) *m/z* calculated for $C_{10}H_{18}NO_3S$ $[M+H]^+$: 264.0906, found 264.0900.

(±)-ethyl *trans*-2-(8-methyl-2,2-dioxido-3-oxa-2-thia-1-azabicyclo[5.1.0]octan-4-yl)acetate.

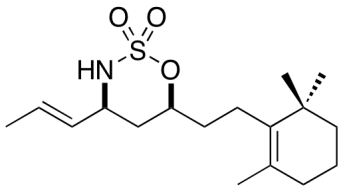


Prepared as a standard using general protocol for Rh conditions. Purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes/EtOAc as eluent system. Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.73-4.68 (m, 1H), 4.21-4.11 (m, 2H), 3.03 (app p, *J* = 5.5 Hz, 1H), 2.73 (dd, *J* = 16.0, 6.5 Hz, 1H), 2.67-2.65 (m, 1H), 2.58 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.52 (d, *J* = 12.5 Hz, 1H), 2.48-2.42 (m, 1H), 1.98-1.93 (m, 1H), 1.86-1.78 (m, 1H), 1.35 (d, *J* = 6.0 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 169.1, 79.2, 61.3, 47.1, 39.6, 38.9, 31.9, 24.6, 17.1, 14.2; IR (film, cm^{-1}) 2981, 2931, 1738, 1443, 1375, 1298, 1265, 1221, 1180, 1034, 1016, 908, 771; HRMS (ESI) *m/z* calculated for $C_{10}H_{18}NO_3S$ $[M+H]^+$: 264.0906, found 264.0905.

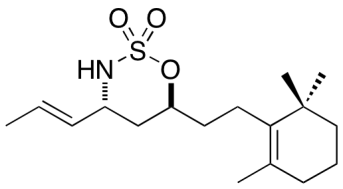
(±)-4-((*E*)-prop-1-en-1-yl)-6-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)ethyl)-1,2,3-oxathiazinane 2,2-dioxide [17]; entry 14.

Iterative catalyst addition protocol for Fe conditions was followed. (±)-(*E*)-1-(2,6,6-trimethylcyclohex-1-en-1-yl)oct-6-en-3-yl sulfamate (132 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (4x8 mg, 0.053 mmol, 0.13 equiv), $AgSbF_6$ (4x4.5 mg, 0.053 mmol, 0.13 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By ^{1}H-NMR analysis of the crude product, d.r. was 3.5:1 *syn*:*anti*, ins./azir. was >20:1 and β:β' was 7:1. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 19:1 hexanes/EtOAc + 1% AcOH as eluent gave *syn* methyl allylic oxathazinane separately; the *anti* methyl and *syn* tetrasubstituted allylic oxathiazinanes were isolated as a mixture.

Run 1: (51.6 mg *syn* + 13.3 mg *anti* (3.9:1 d.r.), 0.198 mmol, 50%), (6.6 mg *syn*-tetrasubstituted (β:β' = 9.8:1), 0.020 mmol, 5%), 0% rsm. Run 2: (59.7 mg *syn* + 13.1 mg *anti* (4.6:1 d.r.), 0.220 mmol, 55%), (8.9 mg *syn*-tetrasubstituted (β:β' = 8.2:1), 0.027 mmol, 7%), 0% rsm. Run 3: (59.1 mg *syn* + 13.3 mg *anti* (4.4:1 d.r.), 0.221 mmol, 55%), (8.3 mg *syn*-tetrasubstituted (β:β' = 8.7:1), 0.025 mmol, 6%), 0% rsm. **Average: 53% yield, 0% rsm.**

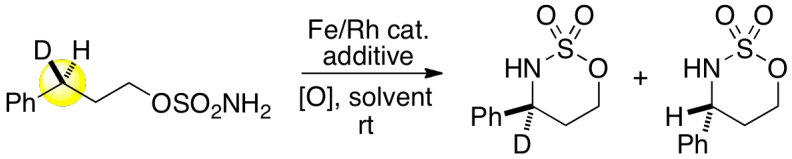


***Syn* (major) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.77 (ddq, *J* = 15.5, 6.5, 1.5 Hz, 1H), 5.41 (ddd, *J* = 15.5, 5.5, 1.5 Hz, 1H), 4.76-4.71 (m, 1H), 4.23-4.18 (m, 1H), 3.97 (br. d, *J* = 10.0 Hz, 1H), 2.23 (dt, *J* = 13.5, 5.0 Hz, 1H), 2.01 (dt, *J* = 13.0, 5.0 Hz, 1H), 1.89 (t, *J* = 6.5 Hz, 2H), 1.84 (dt, *J* = 14.5, 2.5 Hz, 1H), 1.80-1.75 (m, 1H), 1.73-1.66 (m, 1H), 1.72 (dt, *J* = 7.0, 1.5 Hz, 3H), 1.57-1.52 (m, 3H), 1.57 (s, 3H), 1.41-1.39 (m, 2H), 0.97 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 135.8, 129.4, 128.2, 128.1, 84.7, 56.2, 39.8, 35.9, 35.5, 35.1, 32.8, 28.6, 23.6, 19.9, 19.5, 17.9; IR (film, cm^{-1}) 3261, 2956, 2927, 2866, 2831, 1473, 1419, 1360, 1188, 1057, 966, 912, 870, 818, 735; HRMS (ESI) *m/z* calculated for $C_{17}H_{29}NO_3SNa$ $[M+Na]^+$: 350.1766, found 350.1765.



***Anti* (minor) diastereomer:** Isolated as a colorless oil by resubjecting the product mixture from above to flash column chromatography (25 mm fritted glass column, 140 mm SiO_2) in 3:1 CH_2Cl_2/hex (the β' product could not be isolated, even after flushing column). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.83 (ddd, *J* = 15.5, 6.5, 1.5 Hz, 1H), 5.72 (dq, *J* = 15.5, 6.0 Hz, 1H), 4.87-4.83 (m, 1H), 4.34 (br. d, *J* = 6.5 Hz, 1H), 4.19 (app p, *J* = 5.8 Hz, 1H), 2.29-2.23 (m, 1H), 2.04-1.93 (m, 3H), 1.90 (t, *J* = 6.3 Hz, 2H), 1.85 (app dt, *J* = 14.0, 4.0 Hz, 1H), 1.75 (d, *J* = 6.0 Hz, 3H), 1.72-1.63 (m, 1H) 1.59-1.54 (m, 2H), 1.59 (s, 3H), 1.42-1.40 (m, 2H), 0.99 (s, 3H), 0.98 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 135.9, 129.3, 128.5, 128.2, 83.4, 55.1, 39.9, 35.4, 35.1, 33.9, 32.9, 28.7 (2 peaks), 24.2, 20.0, 19.6, 18.0; IR (film, cm^{-1}) 3273, 2947, 2927, 2864, 1423, 1367, 1186, 1051, 966, 874; HRMS (ESI) *m/z* calculated for $C_{17}H_{30}NO_3S$ $[M+H]^+$: 328.1946, found 328.1946.

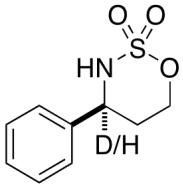
Intramolecular Kinetic Isotope Effect Study



(±)-**18** (±)-**19**(D) (±)-**19**(H)

$Rh_2(OAc)_4$	*1.8*	:	*1*
[FePc]·SbF_6	*2.5*	:	*1*

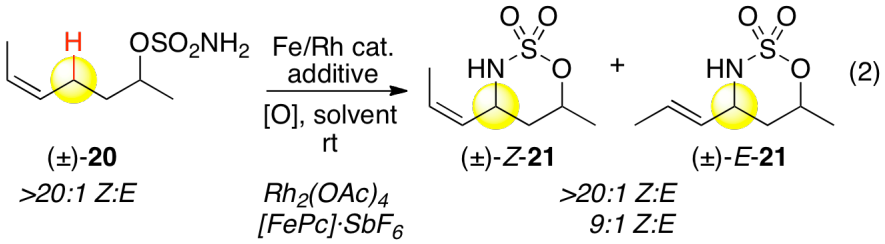
(±)-4-deuterio-4-phenyl-tetrahydro-1,2,3-oxathiazine-2,2-dioxide [19].
Rh conditions: General protocol for Rh conditions was followed, at a scale of 0.250 mmol for the sulfamate ester. (±)-3-deuterio-3-phenylprop-1-yl sulfamate **18** (53.8 mg, 0.250 mmol, 1.0 equiv), $Rh_2(OAc)_4$ (2.2 mg, 0.005 mmol, 0.02 equiv), MgO (23.0 mg, 0.570 mmol, 2.3 equiv), $PhI(OAc)_2$ (90.2 mg, 0.280 mmol, 1.1 equiv), CH_2Cl_2 (1.6 mL, 0.15M) were used, and reaction stirred at room temp for 6h. Flash column chromatography on silica (35 mm fritted glass column, 110 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave 46.2 mg of the deuterated and protonated oxathiazinanes as a mixture (0.218 mmol, 87% yield, <5% rsm). This sample was used as a control to confirm the KIE determination method. **KIE = 1.8±0.2** (1.9, 1.9, 1.6); this is in good agreement with that reported by Du Bois and co-workers for the same substrate (1.9±0.2).[9]
Fe conditons: Iterative catalyst addition protocol for Fe conditions was followed, at a scale of 0.600 mmol for the sulfamate ester. (±)-3-deuterio-3-phenylprop-1-yl sulfamate **18** (130 mg, 0.600 mmol, 1.0 equiv), [FePc]Cl (4x12.1 mg, 0.080 mmol, 0.13 equiv), $AgSbF_6$ (4x6.8 mg, 0.080 mmol, 0.13 equiv), $PhI(OPiv)_2$ (487 mg, 1.20 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (1.2 mL) were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc + 1% AcOH as eluent gave the deuterated and protonated oxathiazinanes as a mixture, and the recovered starting material separately.
Run 1: (33.0 mg, 0.153 mmol, 26%), (47.0 mg rsm, 0.217 mmol, 36%), KIE = 2.5±0.1 (2.4, 2.4, 2.6). Run 2: (35.8 mg, 0.167 mmol, 28%), (39.5 mg rsm, 0.182 mmol, 30%), KIE = 2.7±0.2 (2.7, 2.5, 2.8). Run 3: (32.8 mg, 0.153 mmol, 25%), (42.0 mg rsm, 0.194 mmol, 32%), KIE = 2.4±0.1 (2.5, 2.3, 2.4). **Average: 26% yield, 33% rsm, KIE = 2.5±0.2.**



^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.43-7.35 (m, 5H), 4.90-4.85 (m, 2H – protonated), 4.87 (ddd, *J* = 13.0, 11.5, 2.0 Hz, 1H – deuterated), 4.66 (ddd, *J* = 11.5, 5.0, 1.5 Hz, 1H), 4.35 (br. s, 1H – deuterated), 4.35 (br. d, *J* = 9.0 Hz, 1H – protonated), 2.30-2.21 (m, 1H), 2.05-2.00 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 137.7 (protonated), 137.7 (deuterated), 129.0, 128.7, 126.1, 71.8, 58.7 (protonated), 58.4 (deuterated – 1:1:1 triplet), 30.0 (protonated) 29.9 (deuterated); IR (film, cm^{-1}) 3261, 3062, 3033, 2964, 2926, 2852, 1728, 1498, 1450, 1410, 1354, 1190, 1024, 995, 930, 874, 779; HRMS (ESI) *m/z* calculated for $C_9H_{10}DNO_3SNa$ $[M+Na]^+$: 237.0420, found 237.0419; HRMS (ESI) *m/z* calculated for $C_9H_{11}NO_3SNa$ $[M+Na]^+$: 236.0357, found 237.0355.

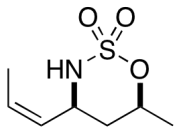
Method for KIE Determination: The column-purified product mixture **19** (35-40 mg in 700 μL $CDCl_3$, in a straight-walled NMR tube) was analyzed by ^{13}C-NMR.[8,10] In order to obtain an accurately integratable ^{13}C-NMR, the experiment was run under inverse-gated decoupling conditions (decoupling switched off during the relaxation delay; for Varian, the command is *dm='nny'*). A delay of 5 s was used, with sufficient scans to obtain a signal-to-noise (S/N) ratio of >30:1 on the deuterated peak. The KIE was reported as the area of the deuterated peak over that of the protonated peak. Three identical experiments were run and an average value was calculated with measurement error.
Alternative Method: 15 mg $Cr(acac)_3$ was added to the NMR sample; this additive significantly reduces relaxation time for ^{13}C-NMR and allows for more accurate integration than inverse-gated decoupling alone.[11] Experimental conditions were otherwise identical to the standard method. It was found that for both the Rh- and Fe-catalyzed C—H amination reactions, the calculated KIEs were noticeably higher, although the trend remains the same. The following KIEs were determined: **Rh conditions – 3.5±0.4 (3.7, 3.7, 3.1); Fe conditions – 4.8±0.3 (4.7, 5.1, 4.7)**.

Evidence of Olefin Isomerization in Fe-catalyzed C-H Amination

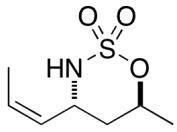


(±)-4-((1*Z*)-1-propenyl)-6-methyl-tetrahydro-1,2,3-oxathiazine-2,2-dioxide [*Z*-21].
Rh conditions: General protocol for Rh conditions was followed. (±)-(*Z*)-hept-5-en-2-yl sulfamate **20** (77.3 mg, 0.400 mmol, 1.0 equiv), $Rh_2(OAc)_4$ (3.5 mg, 0.008 mmol, 0.02 equiv), MgO (37.0 mg, 0.920 mmol, 2.3 equiv), $PhI(OAc)_2$ (142 mg, 0.440 mmol, 1.1 equiv), CH_2Cl_2 (2.6 mL, 0.15M) were used, and reaction stirred at room temp for 4h. By GC analysis of the crude product, *Z:E* was >30:1. By ^{1}H-NMR analysis, d.r. was 4:1 *syn*:*anti*, and ins./azir. was 2.7:1. Flash column chromatography on silica (35 mm fritted glass column, 110 mm SiO_2) using 4:1 hexanes/EtOAc as eluent gave pure *syn* and *anti* oxathiazinanes and aziridine separately: (42.1 mg *syn* + 10.4 mg *anti* (4:1 d.r.), 0.275 mmol, **69% yield**), (17.4 mg aziridine (3:1 ins./azir.), 0.091 mmol, 23%).
Fe Conditions: Single catalyst addition protocol for Fe conditions was followed. (±)-(*Z*)-hept-5-en-2-yl sulfamate **20** (77.3 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24.0 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe:MeCN (800 μL) were used. By GC analysis of the crude product, *Z:E* was 9:1 (this ratio was confirmed by subjecting column-purified Z/E mixtures of products to GC analysis). By ^{1}H-NMR analysis, d.r. was 3:1 *syn*:*anti*, and ins./azir. was >10:1. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 9:1 CH_2Cl_2/hexanes (500 mL) → 19:1 CH_2Cl_2/hexanes as eluent gave *syn* and *anti* oxathiazinanes as a mixture. This mixture was further purified by flash column chromatography using 4:1 hexanes:EtOAc + 1% AcOH as eluent; this gave pure *syn* and *anti* allylic oxathiazinanes separately (as *E/Z* mixtures).

Although the reaction did not go to complete conversion, the remaining starting material was not isolated under the given purification conditions.
Run 1: (21.3 mg *syn* + 7.2 mg *anti* (3:1 d.r.), 0.149 mmol, 37%). Run 2: (18.1 mg *syn* + 5.8 mg *anti* (3.1:1 d.r.), 0.125 mmol, 31%), 0% rsm. Run 3: (17.9 mg *syn* + 5.7 mg *anti* (3.1:1 d.r.), 0.123 mmol, 31%). **Average: 33% yield.**

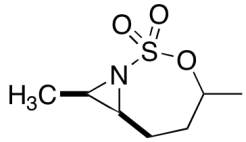


***Syn* (major) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.72 (ddq, *J* = 10.5, 6.5, 1.0 Hz, 1H), 5.21 (ddd, *J* = 10.5, 6.5, 1.5 Hz, 1H), 4.91 (ddt, *J* = 12.0, 6.5, 2.0 Hz, 1H), 4.56-4.49 (m, 1H), 3.99 (br. d, *J* = 9.5 Hz, 1H), 1.76 (dt, *J* = 14.5, 2.5 Hz, 1H), 1.73 (dd, *J* = 7.0, 2.0 Hz, 3H), 1.53 (dt, *J* = 14.5, 12.0 Hz, 1H), 1.42 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 130.6, 127.1, 80.6, 52.0, 37.5, 21.2, 13.7; IR (film, cm^{-1}) 3234, 3033, 2983, 2943, 2852, 1429, 1385, 1346, 1296, 1171, 1078, 947, 910, 864; HRMS (ESI) *m/z* calculated for $C_7H_{13}NO_3SNa$ $[M+Na]^+$: 214.0514, found 214.0515.



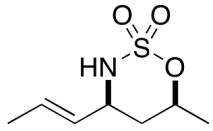
***Anti* (minor) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.88 (ddd, *J* = 10.5, 7.0, 1.5 Hz, 1H), 5.69 (ddq, *J* = 11.0, 7.0, 1.0 Hz, 1H), 5.04 (dddd, *J* = 15.5, 9.0, 6.5, 3.0 Hz, 1H), 4.56-4.51 (m, 1H), 4.48 (br. d, *J* = 6.0 Hz, 1H), 1.91 (ddd, *J* = 14.5, 9.5, 5.5 Hz, 1H), 1.77 (ddd, *J* = 14.5, 4.0, 3.5 Hz, 1H), 1.69 (dd, *J* = 7.0, 1.5 Hz, 3H), 1.50 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 128.6, 127.4, 79.2, 50.3, 35.7, 21.0, 13.3; IR (film, cm^{-1}) 3280, 3026, 2983, 2935, 2860, 1425, 1402, 1379, 1358, 1184, 1080, 957, 904, 883, 835, 796 750; HRMS (ESI) *m/z* calculated for $C_7H_{13}NO_3SNa$ $[M+Na]^+$: 214.0514, found 214.0517.

(±)-*cis*-4,8-dimethyl-3-oxa-2-thia-1-azabicyclo[5.1.0]octane-2,2-dioxide.



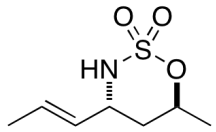
Purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc → 3:1 hexanes/EtOAc as eluent system. Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.84-4.82 (m, 1H), 3.00 (app q, *J* = 6.0 Hz, 1H), 2.88 (app. p, *J* = 6.0 Hz, 1H), 2.50-2.44 (m, 1H), 2.27-2.20 (m, 1H), 2.08-2.01 (m, 1H), 1.83 (dd, *J* = 14.5, 9.0 Hz, 1H), 1.60 (d, *J* = 6.5 Hz, 3H), 1.33 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 78.7, 45.2, 41.9, 29.7, 20.9, 18.2, 9.3; IR (film, cm^{-1}) 3284, 2983, 2943, 2877, 1448, 1371, 1298, 1176, 1146, 1117, 1076, 1005, 962, 893, 839, 785, 768; HRMS (ESI) *m/z* calculated for $C_7H_{13}NO_3SNa$ $[M+Na]^+$: 214.0514, found 214.0513.

(±)-4-((1*E*)-1-propenyl)-6-methyl-tetrahydro-1,2,3-oxathiazine-2,2-dioxide [*E*-21].
Prepared as a standard under the Rh conditions described above: (±)-(*E*)-hept-5-en-2-yl sulfamate **20** (77.3 mg, 0.400 mmol, 1.0 equiv), $Rh_2(OAc)_4$ (3.5 mg, 0.008 mmol, 0.02 equiv), MgO (37.0 mg, 0.920 mmol, 2.3 equiv), $PhI(OAc)_2$ (142 mg, 0.440 mmol, 1.1 equiv), CH_2Cl_2 (2.6 mL, 0.15M) were used, and reaction stirred at room temp for 4h. Flash column chromatography on silica (35 mm fritted glass column, 110 mm SiO_2) using 4:1 hexanes/EtOAc as eluent gave pure *syn* and *anti* oxathiazinanes separately. These compounds were used in order to confirm Z/E ratios by GC analysis.



***Syn* (major) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.76 (ddq, *J* = 15.0, 6.5, 1.5 Hz, 1H), 5.39 (ddd, *J* = 15.5, 6.0, 1.5 Hz, 1H), 4.86 (ddt, *J* = 12.0, 6.0, 2.0 Hz, 1H), 4.22-4.16 (m, 1H), 4.03 (br. d, *J* = 10.0 Hz, 1H), 1.84 (dt, *J* = 14.5, 2.5 Hz, 1H), 1.71 (d, *J* = 6.5 Hz, 3H), 1.52 (dt, *J* = 14.5, 12.0 Hz, 1H), 1.41 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.4,

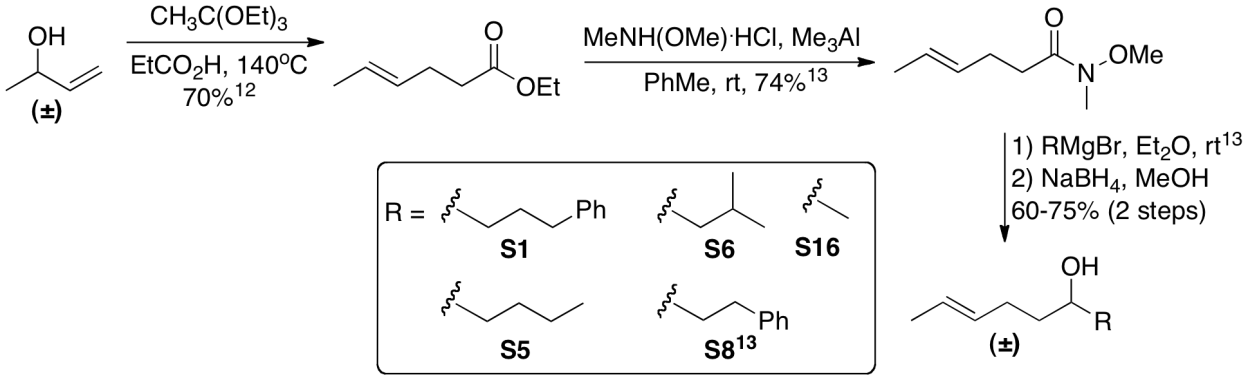
128.1, 80.6, 56.2, 37.1, 21.2, 17.9; IR (film, cm^{-1}) 3263, 2983, 2939, 2922, 2858, 1421, 1360, 1186, 1136, 1093, 1061, 966, 945, 914, 866, 796; HRMS (ESI) *m/z* calculated for $C_7H_{13}NO_3SNa$ $[M+Na]^+$: 214.0514, found 214.0513.



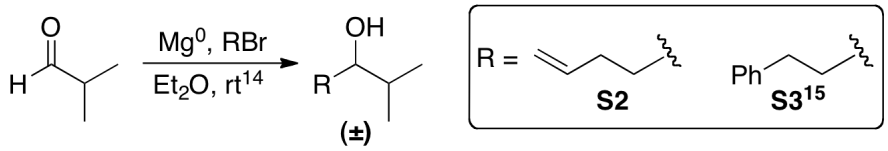
***Anti* (minor) diastereomer:** Isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.82 (ddd, *J* = 15.5, 6.5, 1.5 Hz, 1H), 5.72 (ddq, *J* = 15.0, 6.5, 1.0 Hz, 1H), 5.03 (ddd, *J* = 6.5, 6.5, 1.5 Hz, 1H), 4.34 (br. d, *J* = 7.0 Hz, 1H), 4.21 (app. p, *J* = 6.0 Hz, 1H), 1.93-1.83 (m, 2H), 1.74 (dd, *J* = 6.5, 1.5 Hz, 3H), 1.51 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.3, 128.6, 79.3, 55.0, 35.4, 21.0, 18.0; IR (film, cm^{-1}) 3267, 2985, 2964, 2922, 2856, 1429, 1360, 1327, 1236, 1182, 1136, 1092, 1051, 964, 879, 862; HRMS (ESI) *m/z* calculated for $C_7H_{13}NO_3SNa$ $[M+Na]^+$: 214.0514, found 214.0518.

Synthesis of Starting Materials

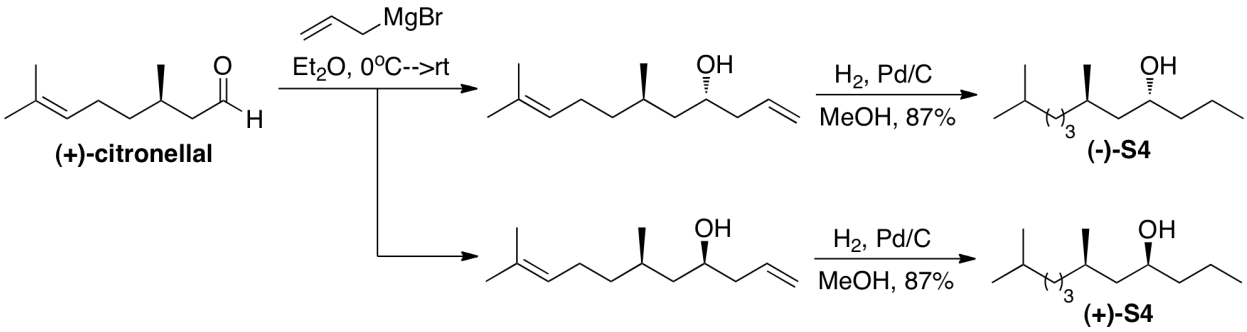
Synthesis of alcohols S1, S5, S6, S8 and S16 for optimization substrate, secondary, tertiary and benzylic competition substrates, and *E*-methyl olefin substrate[12,13]



Synthesis of alcohols S2 and S3 for terminal olefin and benzylic substrates[14,15]



Synthesis of alcohol S4 for 3° C—H stereoretention substrate[16]

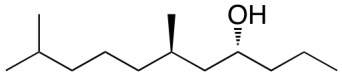


6,10-dimethylundeca-1,9-dien-4-ol.
This compound was prepared according to the methods described in the literature.[16] The initial product was isolated as a 1:1 *anti:syn* mixture of diastereomers following flash column chromatography on silica using 9:1 hexanes/EtOAc as eluent. It was diastereomerically enriched via MPLC purification with a 240 g basic alumina column (Activity II-III) using neat CH_2Cl_2 as eluent (the order of elution was the *anti* diastereomer first, then *syn*). After 4-6 iterations in which fractions containing only one diastereomer were removed each time, the pure products were isolated as a >20:1 mixture (as determined by ^{1}H-NMR analysis). This compound has been previously reported in the literature as a diastereomeric mixture.[16]

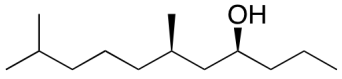
^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.83 (ddt, *J* = 16.5, 9.5, 7.0 Hz, 1H), 5.15-5.08 (m, 3H), 3.77-3.72 (m, 1H), 2.27 (dt, *J* = 14.0, 4.5 Hz, 1H), 2.15 (dt, *J* = 14.0, 8.0 Hz, 1H), 2.04-1.93 (m, 2H), 1.68-1.64 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.52-1.46 (m, 2H), 1.35-1.27 (m, 1H), 1.23-1.16 (m, 2H), 0.95 (d, *J* = 6.5 Hz, 3H – *syn*), 0.91 (d, *J* = 6.5 Hz, 3H - *anti*). This data is in agreement with the literature.[25]

6,10-dimethylundecan-4-ol [S4].

6,10-dimethylundeca-1,9-dien-4-ol (1.0 equiv) was dissolved in MeOH (0.1M) in a flask equipped with a stir bar. Activated 30% Pd/C (10 mg per mmol of substrate) was added, and then the flask was sealed with a rubber septum. A balloon of H_2 was placed over the flask, and H_2 was bubbled through the reaction mixture with stirring until complete disappearance of olefins was observed, as monitored by ^{1}H-NMR analysis. Upon completion, the reaction mixture was filtered through a short silica plug, which was washed with additional MeOH. The filtrate was dried over Na_2SO_4 and concentrated *in vacuo*. No further purification was necessary.

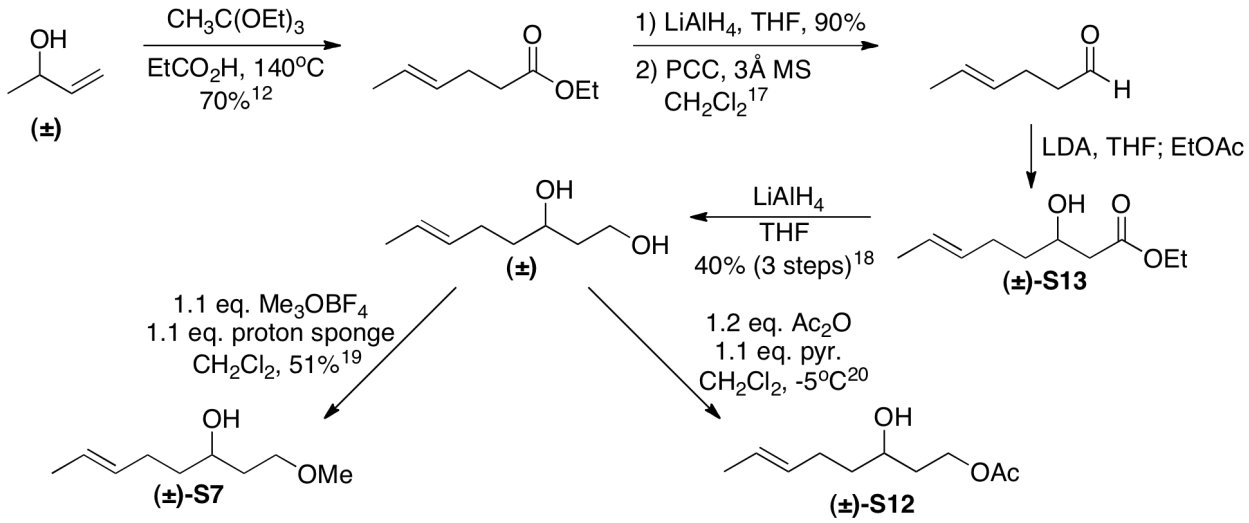


(-)-(4*R*,6*R*)-6,10-dimethylundecan-4-ol: The diastereomeric ratio was quantitatively established by achiral GC analysis in triplicate, and was found to be 97:3 *anti:syn*. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.72-3.67 (m, 1H), 1.66-1.59 (m, 1H), 1.56-1.48 (m, 1H), 1.47-1.38 (m, 3H), 1.38-1.20 (m, 6H), 1.19-1.10 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) 69.5, 45.2, 40.7, 39.4, 38.3, 29.4, 28.1, 24.9, 22.8 (2 peaks), 19.4, 10.0, 14.3; IR (film, cm^{-1}) 3350, 2956, 2927, 2872, 1466, 1379, 1367, 1146, 1122, 1066, 1024; $[\alpha]^{25}_D$ = -10.1° (*c* = 1.0, $CHCl_3$); HRMS (EI) *m/z* calculated for $C_{13}H_{26}$ $[M-H_2O]^+$: 182.20345, found 182.20253 (ESI failed for this compound, and the the peak resulting from alcohol elimination was the dominant peak in the EI spectrum, the minor peak being extrusion of H^+ – no M+ peak was observed under ESI, EI, or FD methods).

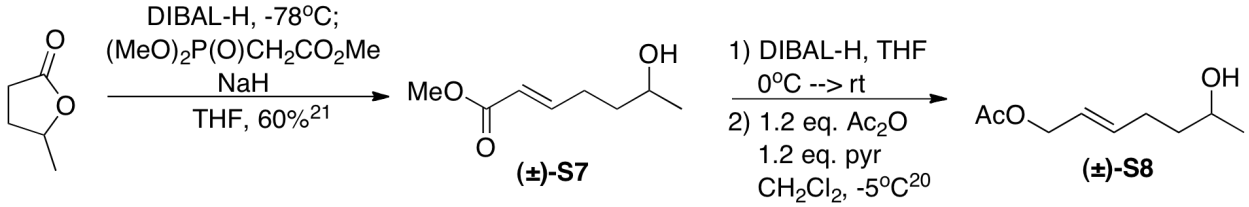


(+)-(4*R*,6*S*)-6,10-dimethylundecan-4-ol: The diastereomeric ratio was quantitatively established by achiral GC analysis in triplicate, and was found to be 5:95 *anti:syn*. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.70 (m, 1H), 1.62-1.18 (m, 12H), 1.17-1.10 (m, 2H), 1.09-1.02 (m, 1H), 0.93 (t, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) 69.9, 45.5, 40.1, 39.5, 37.0, 29.8, 28.1, 24.7, 22.9, 22.7, 20.5, 18.9, 14.3; IR (film, cm^{-1}) 3338, 2956, 2927, 2872, 1466, 1379, 1367, 1124, 1005; $[\alpha]^{25}_D$ = +6.7° (*c* = 1.0, $CHCl_3$).

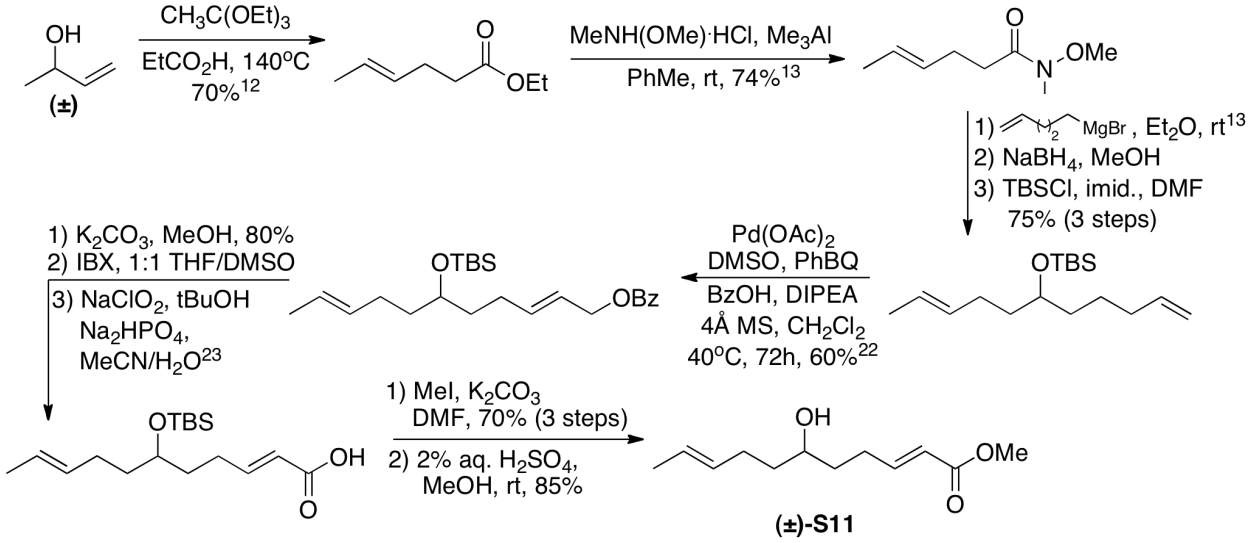
Synthesis of alcohols S7, S12 and S13 for ethereal competition substrate and β-functionalized substrates[12,17,18,19,20]



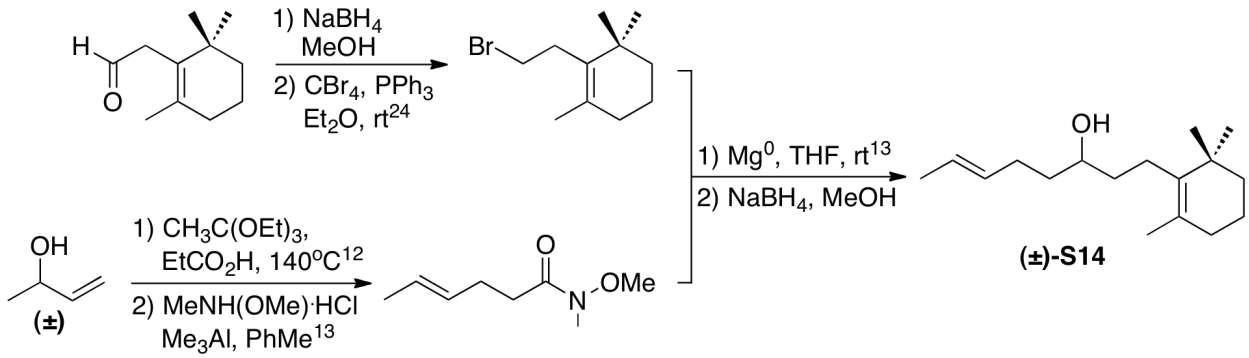
Synthesis of alcohols S9 and S10 for electron-poor olefin substrates[20,21]



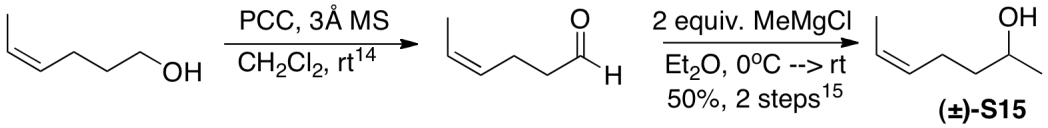
Synthesis of alcohol S11 for olefin electronic competition substrate[12,13,22,23]



Synthesis of alcohol S14 for olefin steric competition substrate[12,13,24]



Synthesis of alcohol S15 for *Z*-olefin isomerization substrate[14,15]



See separate supporting information file for ^{1}H and ^{13}C-NMR spectra of all sulfamate ester starting materials, *syn* and *anti* oxathiazinanes, and aziridines, as well as labeled, integrated ^{1}H-NMR spectra of crude reaction mixtures, labeled, integrated ^{13}C-NMR spectra of purified H/D mixtures for the KIE study, relevant nOe NMR spectra, GC traces of standards and enriched substrates for the stereoretention and olefin isomerization experiments, and GC traces of crude reaction mixtures for the stereoretention, olefin competition and olefin isomerization experiments.

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[2] Preparation of Fe(*R,R*-salen)Cl: Salomão, G.C.; Olsen, M.H.N.; Drago, V.; Fernandes, C.; Filho, L.C.; Antunes, O.A.C. *Cat. Commun.* **2007**, *8*, 69. No characterization data is reported in the literature, but successful preparation of the catalyst was confirmed via low-resolution field desorption (LR-FD) mass spectrometry: *m/z* = 600.4 ($C_{36}H_{52}N_2O_2Fe$, 5%), 635.3 ($C_{36}H_{52}N_2O_2ClFe$, 100%).

[3] Caution: $ClSO_2NCO$ reacts violently with water, so the transfer should be done under an inert atmosphere, preferably in a glovebox. Because of its propensity for freezing glass stopcocks, $ClSO_2NCO$ should be stored in a flask with Teflon stopcocks.

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[17] Due to volatility of this compound, removal of solvents under reduced pressure was performed at 0°C.
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