A Manganese Catalyst for Highly Reactive Yet Chemoselective Intramolecular C(sp^3)—H Amination

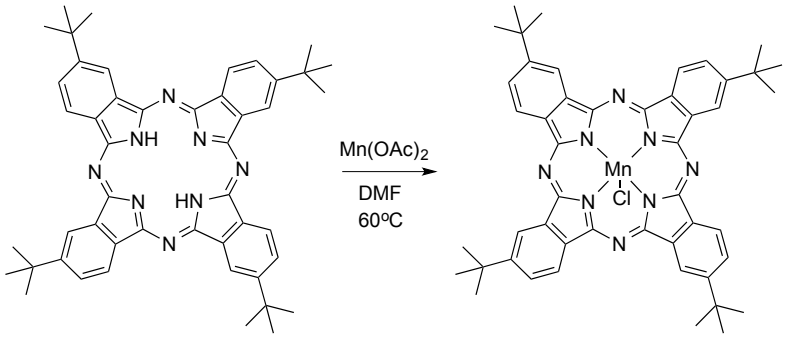
Contents

General Information

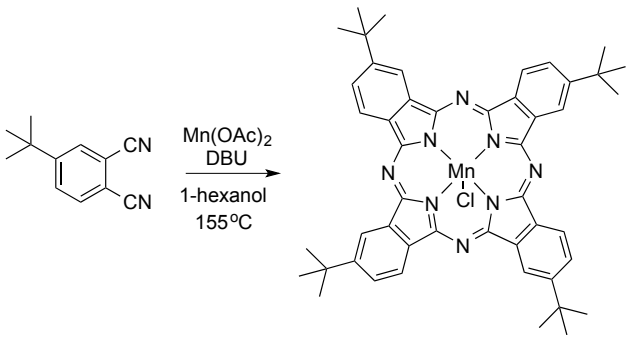
The following commercially obtained reagents were used as received: iron(III) phthalocyanine chloride ([FePc]Cl, Sigma-Aldrich), manganese(III) phthalocyanine chloride ([MnPc]Cl, Sigma-Aldrich), 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine iron(III) chloride (Fe(TPP)Cl, Strem), 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine manganese(III) chloride (Mn(TPP)Cl, Strem), Mn(*R,R*-salen)Cl (Sigma-Aldrich), silver hexafluoroantimonate ($AgSbF_6$, Strem), and bis (*tert*-butylcarbonyloxy)iodobenzene ($PhI(OPiv)_2$, Sigma-Aldrich).[1] 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). Chloroform-*d* was stored over 3Å molecular sieves in a secondary container with drierite. Fe(*R,R*-PDP)$(SbF_6)_2$,[2] Mn(*R,R*-PDP)$(SbF_6)_2$, and Fe(*R,R*-salen)Cl[3] were prepared according to methods described in the literature 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.[4] 4Å MS beads were crushed with a mortar and pestle until fine, then activated in a 180°C oven for at least 48h and stored in a dessicator or glovebox. 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[5] 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), and chiral GC analysis using a CycloSil-B column (30m, 0.25mm, 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). Kinetic isotope effect analyses were recorded on a Varian Inova-600 (600 MHz) spectrometer. IR spectra were recorded as thin films on NaCl plates or by ATR on a Perkin Elmer Frontier FTIR 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. Elemental analysis was performed by Robertson Microlit Laboratories.

Preparation of [Mn^{III}(^{t}BuPc)]



[Mn(^{t}BuPc)]Cl from ligand: The following procedure was adapted from a literature preparation.[6] 2,9,16,23-Tetra-*tert*-butyl-29*H*,31*H*-phthalocyanine (250 mg, 0.338 mmol, 1.0 equiv, Sigma-Aldrich) was taken up in degassed DMF (16 mL) in a 50 mL round-bottom flask equipped with stir bar and septum (the flask and stir bar should be free of trace metal impurities). $Mn(OAc)_2$ (58.5 mg, 0.338 mmol, 1.0 equiv, Sigma-Aldrich) was added under a stream of N_2, then reaction was warmed to 60°C and stirred for 12h. Upon completion, the reaction cooled to rt, then was diluted with water (10 mL), transferred to a separatory funnel, and the aqueous layer was washed with hexanes (20 mL) to remove unreacted ligand. Brine (15 mL) was added, and then complex was extracted with chloroform (3x30 mL). The combined organic layers were dried over Na_2SO_4 and filtered. Neutral alumina (15 mL) was added to the solution of crude complex and concentrated to dryness. The adsorbed catalyst-alumina powder was then applied to a flash column with dry neutral alumina (45 mm column, 100 mm Al_2O_3). Remaining uncomplexed ligand, which is a bright turquoise color, was eluted with 9:1 hex/EtOAc (ca. 1.5L). Once ligand fully eluted, **3**, which is a dark evergreen color, was eluted with neat EtOAc (ca. 1L). Pure product was isolated as a flaky dark green solid in 89% yield.

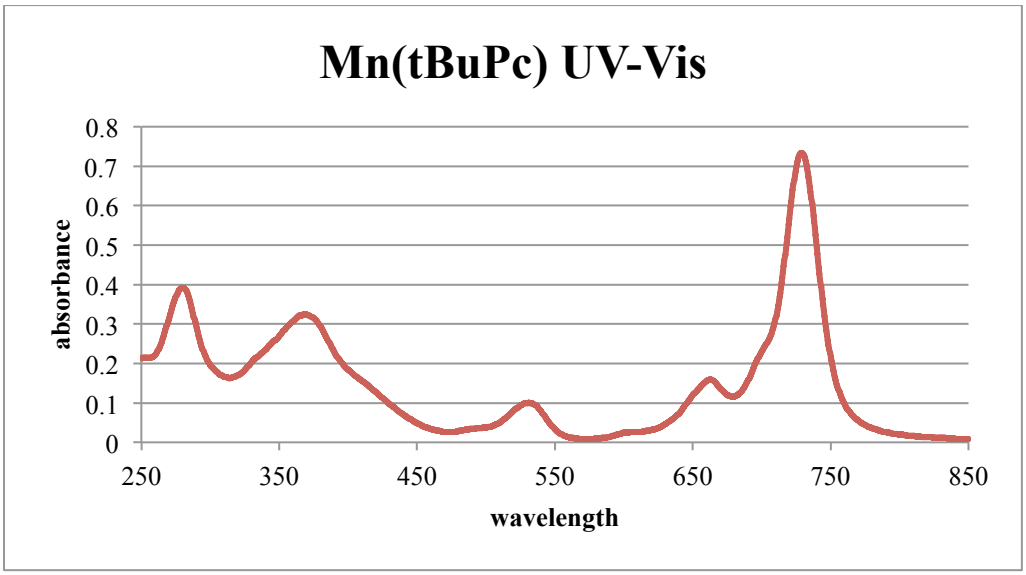


[Mn(^{t}BuPc)]Cl from phthalonitrile: A flame dried 100 mL round-bottom flask equipped with a stir bar and reflux condenser (the flask and stir bar should be free of trace metal impurities) was sequentially charged with 4-*tert*-butyl-phthalonitrile (2.211 g, 12.0 mmol, 4.0 equiv, TCI America), 1-hexanol (24 mL, freshly distilled over $MgSO_4$ and degassed), $Mn(OAc)_2$ (519 mg, 3.00 mmol, 1.0 equiv, Sigma-Aldrich) and DBU (3.59 mL, 24.0 mmol, 8.0 equiv, Sigma-Aldrich). Reaction flask was evacuated under vacuum and refilled with N_2 three times, then heated to 155ºC. The reaction mixture changed from colorless to turquoise green over 10 min. After stirring at 155ºC overnight (12-15h), the heat was ceased and the condenser was removed. Brine (15 mL) was cautiously added into the reaction dropwise via a pasteur pipette while the

reaction temperature was maintained over 100ºC, then the reaction was stirred open to air while cooling to room temp for 1h. Brine and chloroform were added to the flask and the mixture was extracted with chloroform 3 times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated by rotatory evaporation. The remaining solution was transferred to a round-bottom flask equipped with stir bar and short path distillation head, placed under high vac, and then heated to ~60-80ºC until crude material was a sticky solid (~2-3 days). The crude catalyst was taken up in CH_2Cl_2 with 50 mL neutral alumina (Brockmann Type I, Alfa Aesar), then concentrated to dryness and applied to a plug of 200 mL neutral Al_2O_3 (50 mm fritted glass column) pre-wetted with 5% EtOAc/hexanes. Nonpolar impurities were eluted with 10% EtOAc/hexanes → 20% EtOAc/hexanes (~2L) until eluting solution turned green. [Mn(^{t}BuPc)]Cl was eluted as a separate dark green fraction by flushing with EtOAc (~2-4L). The solution was concentrated by rotatory evaporation and was dried under high vac overnight to afford 971 mg (1.17 mmol) of **3** as a dark green powder (39% yield). Catalyst obtained by this method contains a minor unknown impurity (visible in IR at 1711 cm^{-1}), which has no observable impact on reactivity or reaction rate for any of the substrate classes examined. Due to the convenience and economy of this procedure, this was the standard method for preparing the catalyst used in this report. [Mn(^{t}BuPc)]Cl prepared in this way can be made analytically pure by column chromatography on silica using a gradient of 10% → 20% → 30% → 50% → 100% EtOAc/hexanes.

UV-Vis ($CHCl_3$, λ_{max} = nm, ε = $M^{-1}cm^{-1}$): 729 (ε = 73400), 662 (ε = 15900), 531 (ε = 10100), 369 (ε = 32400), 280 (ε = 39200); IR (ATR, cm^{-1}) 2955, 2865, 1612, 1506, 1482, 1459, 1394, 1363, 1328, 1280, 1255, 1199, 1147, 1075, 932, 893, 828, 763, 746; HRMS (ESI) *m/z* calculated for $C_{48}H_{48}MnN_8$ $[M\text{-}Cl]^+$: 791.3382, found 791.3380. LRMS (FD) *m/z* 792.9 (Mn(^{t}BuPc)+H), 827.8 (M^+). Anal. calculated for $C_{48}H_{48}ClMnN_8$ (FW = 827.36), C 69.68, H 5.85, N 13.54, Mn 6.64; found C 70.07, H 6.05, N 13.21, Mn 6.62.

UV-Vis Studies: 4.2 mg (0.005 mmol) of [Mn^{III}(^{t}BuPc)] was taken up in $CHCl_3$ to 5 mL solution (1.0 mM). 100 µL of this solution was diluted to 10 mL (10.0 µM). UV-Vis was taken from 850-250 nm in a quartz cuvette (path length = 1 cm).



Preparation of Sulfamate Ester Starting Materials

General procedure for preparation of sulfamate ester substrates[7,8]

Method A:

Preparation of $ClSO_2NH_2$ solution (2M in MeCN): A round-bottom flask equipped with stir bar and rubber septum was charged with $ClSO_2NCO$ (1.5 equiv) and MeCN (2M relative to isocyanate). The flask was cooled to 0°C, and then neat formic acid (1.5 equiv) was added dropwise. 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 (1.1 equiv) and 5 mL DMF (1M relative to starting material) and cooled to 0°C. The alcohol starting material (1.0 equiv) in DMF was slowly added. The reaction was stirred at room temp for 1h, 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 H_2O (15 mL) and Et_2O (60 mL) and separated. The aqueous layer was then extracted with Et_2O (2x30 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Although the sulfamate esters were generally pure by NMR after a single column, as a precaution they were subjected to a second column to remove minor NMR-silent impurities that have been shown to inhibit the amination reaction. Following purification, sulfamate esters were thrice dissolved in benzene and concentrated under reduced pressure to remove trace H_2O, then stored in a dessicator until use.

Method B:

A round-bottom flask equipped with stir bar and rubber septum was charged with $ClSO_2NCO$ (2.0 equiv) and CH_2Cl_2 (2M relative to isocyanate). The flask was cooled to 0°C, and then neat formic acid (2.0 equiv) was added dropwise. The reaction stirred vigorously at 0°C (1 h) then room temp (~20°C) overnight. After cooling the reaction flask back to 0°C, the alcohol starting material (1.0 equiv) with Et_3N (2.0 equiv) in CH_2Cl_2 (0.75M relative to starting material) 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 H_2O (15 mL) and CH_2Cl_2 (30 mL) and separated. The aqueous layer was then extracted with CH_2Cl_2 (2x30 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Although the sulfamate esters were generally pure by NMR after a single column, as a precaution they were subjected to a second column to remove minor NMR-silent impurities that have been shown to inhibit the amination reaction. Following purification, sulfamate esters were thrice dissolved in benzene and concentrated under reduced pressure to remove trace H_2O, then stored in a dessicator until use.

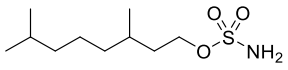
Method C:

A round-bottom flask equipped with stir bar and rubber septum was charged with $ClSO_2NCO$ (1.5 equiv). The flask was cooled to 0ºC, and then neat formic acid (1.5 equiv) was added dropwise. After vigorously stirring for 5 min at 0ºC, MeCN (2M relative to isocyanate) was added, and the reaction stirred vigorously at 0ºC (1 h) then room temp (~20ºC) overnight. After cooling the reaction flask back to 0ºC, the phenol (1.0 equiv) in *N,N*-dimethylacetamide (DMA,

1.6M) was slowly added via syringe. After complete addition, the reaction warmed back to room temp and stirred for 4-6 h. Upon complete consumption of starting material as monitored by TLC, the reaction was quenched with H_2O (~5 mL). The reaction mixture was partitioned between H_2O (15 mL) and Et_2O (30 mL) and separated. The aqueous layer was then extracted with Et_2O (2x30 mL). The organic layers were combined, dried over $MgSO_4$, filtered, 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 desiccator until use.

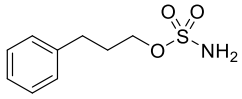
NOTE: Some sulfamate esters exhibited suboptimal reactivity after storing for more than a month (although some are bench stable for much longer); repurification usually restored reactivity in these cases.

(±)-3,7-dimethyloctyl sulfamate [4].



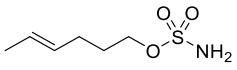
Prepared according to method **A**. 4.75 g (30.0 mmol) of (±)-3,7-dimethyloctanol were used, along with NaH (834 mg, 33.0 mmol, 1.1 equiv), DMF (30 + 15 mL), $ClSO_2NCO$ (3.92 mL, 45.0 mmol, 1.5 equiv), formic acid (1.70 mL, 45.0 mmol, 1.5 equiv) and MeCN (23 mL). Flash column chromatography on silica (45 mm fritted glass column, 200 mm SiO_2) using 4:1 hexanes/EtOAc as eluent gave 5.835 g (24.6 mmol) of pure product as a colorless oil (82% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.71 (br. s, 2H), 4.29-4.22 (m, 2H), 1.82-1.76 (m, 1H), 1.64-1.48 (m, 3H), 1.34-1.22 (m, 3H), 1.20-1.10 (m, 3H), 0.92 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 6.5 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 70.3, 39.3, 37.1, 35.8, 29.5, 28.1, 24.7, 22.8, 22.7, 19.4; IR (film, cm^{-1}) 3392, 3294, 2953, 2870, 1556, 1468, 1367, 1180, 1034, 953, 766; HRMS (ESI) *m/z* calculated for $C_{10}H_{23}NO_3SNa$ $[M+Na]^+$: 260.1296, found 260.1297.

(±)-3-phenylpropan-1-yl sulfamate [46].



Prepared according to method **A**. 1.634 g (12.0 mmol) of 3-phenyl-1-propanol were used, along with NaH (333 mg, 13.2 mmol, 1.1 equiv), DMF (12 mL + 9 mL), $ClSO_2NCO$ (1.57 mL, 18.0 mmol, 1.5 equiv), formic acid (679 µL, 18.0 mmol, 1.5 equiv) and MeCN (9 mL). Flash column chromatography on silica (100 mL SiO_2) using 2:1 hexanes/EtOAc as eluent gave 1.592 g (7.40 mmol) of pure product as a white solid (62% 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). These data are in agreement with that previously reported in the literature.[7]

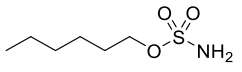
(*E*)-hex-4-en-1-yl sulfamate [S1].



Prepared according to method **A**. 500 mg (5.00 mmol) of (*E*)-hex-4-en-1-ol were used, along with NaH (138 mg, 5.50 mmol, 1.1 equiv), DMF (8.9 mL), $ClSO_2NCO$ (651 µL, 7.50 mmol, 1.5 equiv), formic acid (283 µL, 7.50 mmol, 1.5 equiv) and MeCN (3.8 mL). Flash column chromatography on silica (100 mL SiO_2) using 4:1 hexanes/EtOAc → 3:1 hexanes/EtOAc as eluent gave 613 mg (3.40 mmol) of pure product as a colorless oil (68% yield).

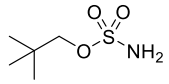
^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.52-5.45 (m, 1H), 5.42-5.35 (m, 1H), 4.73 (s, 2H), 4.21 (t, *J* = 6.5 Hz, 2H), 2.13-2.08 (m, 2H), 1.80 (tt, *J* = 7.3, 6.6 Hz, 2H), 1.65 (ddd, *J* = 6.3, 2.3, 1.2 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.3, 126.7, 71.1, 28.7, 28.4, 18.0. These data are in agreement with that previously reported in the literature.[9]

Hexyl sulfamate [S2].



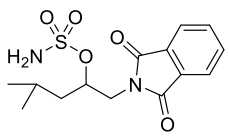
Prepared according to method **A**. 1.88 mL (15.0 mmol) of 1-hexanol were used, along with NaH (417 mg, 16.5 mmol, 1.1 equiv), DMF (15 + 12 mL), $ClSO_2NCO$ (1.96 mL, 22.5 mmol, 1.5 equiv), formic acid (849 μL, 22.5 mmol, 1.5 equiv) and MeCN (11 mL). Flash column chromatography on silica (45 mm fritted glass column, 170 mm SiO_2) using 2:1 hexanes/EtOAc as eluent gave 2.533 g (14.0 mmol) of pure product as a white solid (93% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.81 (br. s, 2H), 4.21 (t, *J* = 6.5 Hz, 2H), 1.74 (app. p, *J* = 7.0 Hz, 2H), 1.43-1.37 (m, 2H), 1.34-1.28 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 71.8, 31.4, 28.9, 25.3, 22.6, 14.1; IR (ATR, cm^{-1}) 3263, 2963, 2936, 2875, 1421, 1359, 1234, 1188, 1137, 1088, 1029, 996, 941, 861, 782; HRMS (ESI) *m/z* calculated for $C_6H_{15}NO_3SNa$ $[M+Na]^+$: 204.0670, found 204.0671.

Neopentyl sulfamate [S3].



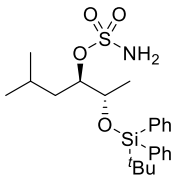
Prepared according to method **B**. 2,2-dimethylpropan-1-ol (440 mg, 5.00 mmol) was used, along with $ClSO_2NCO$ (653 μL, 7.50 mmol, 1.5 equiv), formic acid (283 μL, 7.50 mmol, 1.5 equiv), Et_3N (1.05 mL, 7.50 mmol, 1.5 equiv) and CH_2Cl_2 (3.8 mL + 7.0 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 15% EtOAc/hexanes → 40% EtOAc/hexanes as eluent gave 728 mg (4.35 mmol) of pure product as a white solid (87% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.69 (br, s, 2H), 3.88 (s, 2H), 1.00 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 80.5, 31.7, 26.2; IR (ATR, cm^{-1}) 3364, 3274, 2958, 2872, 1552, 1477, 1465, 1355, 1191, 1170, 979, 919, 832; HRMS (ESI) *m/z* calculated for $C_5H_{13}NaNO_3S$ $[M+Na]^+$: 190.0514, found 190.0510.

(±)-1-(1,3-dioxoisoindolin-2-yl)-4-methylpentan-2-yl sulfamate [S4].



Prepared according to method **B**. 1.446 g (5.85 mmol) of (±)-2-(2-hydroxy-4-methylpentyl)isoindoline-1,3-dione were used, along with Et_3N (1.63 mL, 11.7 mmol, 2.0 equiv), $ClSO_2NCO$ (1.02 mL, 11.7 mmol, 2.0 equiv), formic acid (2441 μL, 11.7 mmol, 2.0 equiv) and CH_2Cl_2 (6 mL + 8 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes/EtOAc → 1:1 hexanes/EtOAc as eluent gave 976 mg (2.99 mmol) of pure product as a white solid (51% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.89-7.85 (m, 2H), 7.77-7.73 (m, 2H), 5.03 (br. s, 2H), 4.92-4.88 (m, 1H), 4.08 (dd, *J* = 15.0, 3.0 Hz, 1H), 3.91 (dd, *J* = 15.0, 5.0 Hz, 1H), 1.89-1.81 (m, 1H), 1.68 (ddd, *J* = 14.5, 9.5, 5.0 Hz, 1H), 1.47 (ddd, *J* = 13.5, 8.5, 4.5 Hz, 1H), 0.98 (d, *J* = 6.5 Hz, 3H), 0.97 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 168.8, 134.4, 132.0, 123.7, 79.8, 41.7, 41.5, 24.3, 23.1, 21.9; IR (ATR, cm^{-1}) 3381, 3279, 2964, 2936, 2877, 1770, 1705, 1552, 1466, 1428, 1402, 1360, 1314, 1180, 1070, 987, 976, 866, 796, 770, 747, 722, 713, 694; HRMS (ESI) *m/z* calculated for $C_{14}H_{19}N_2O_5S$ $[M+H]^+$: 327.1015, found 327.1014.

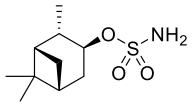
(-)-(2*S*,3*R*)-2-((*tert*-butyldiphenylsilyl)oxy)-5-methylhexan-3-yl sulfamate [S5].



Prepared according to method **B**. 518 mg (1.40 mmol) of (2*S*,3*R*)-2-((*tert*-butyldiphenylsilyl)oxy)-5-methylhexan-3-ol were used, along with Et_3N (391 µL, 2.80 mmol, 2.0 equiv), $ClSO_2NCO$ (244 µL, 2.80 mmol, 2.0 equiv), formic acid (106 µL, 2.80 mmol, 2.0 equiv) and CH_2Cl_2 (1.4 mL + 2.8 mL). Flash column chromatography on silica (35 mm fritted glass column, 130 mm SiO_2) using 9:1 hexanes/EtOAc → 4:1 hexanes/EtOAc as eluent gave 204 mg (0.454 mmol) of pure product as a white solid (32% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.73-7.66 (m, 4H), 7.48-7.39 (m, 6H), 4.53 (dt, *J* = 9.0, 4.0 Hz, 1H), 4.17 (dq, *J* = 6.5, 4.0 Hz, 1H), 4.09 (br. s, 2H), 1.79-1.71 (m, 1H), 1.66-1.56 (m, 2H), 1.15 (d, *J* = 6.5 Hz, 3H), 1.07 (s, 9H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.91 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 136.2, 136.0, 133.8 (2 peaks), 130.2, 130.0, 128.0, 127.8, 83.6, 68.6, 36.6, 27.1, 23.9 (d, $J_{C\text{-}Si}$ = 10.9 Hz), 21.7, 19.3, 16.9; IR (ATR, cm^{-1}) 3289, 2959, 2859, 1472, 1428, 1367, 1187, 1112, 1078, 923, 822, 740, 702; $[\alpha]^{25}_D$ = -19.3° (*c* = 1.1, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{23}H_{35}NO_4SSiNa$ $[M+Na]^+$: 472.1954, found 472.1956.

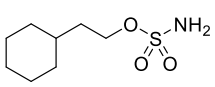
(-)-(1*S*,2*S*,3*S*,5*R*)-isopinocamheyl sulfamate [S6].



Prepared according to method **B**. 1.543 g (10.0 mmol) of (+)-isopinocampheol were used, along with Et_3N (2.79 mL, 20.0 mmol, 2.0 equiv), $ClSO_2NCO$ (1.74 mL, 20.0 mmol, 2.0 equiv), formic acid (755 µL, 20.0 mmol, 2.0 equiv) and CH_2Cl_2 (10 + 10 mL). Flash column chromatography on silica (45 mm fritted glass column, 170 mm SiO_2) using 4:1 hexanes/EtOAc as eluent gave 580 mg (2.49 mmol) of pure product as a white solid (25% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.90 (ddd, *J* = 9.5, 5.5, 4.5 Hz, 1H), 4.72 (s, 2H), 2.68-2.62 (m, 1H), 2.40 (dtd, *J* = 10.0, 6.0, 2.5 Hz, 1H), 2.28 (qdd, *J* = 7.5, 5.5, 2.0 Hz, 1H), 2.11 (ddd, *J* = 14.5, 4.5, 3.0 Hz, 1H), 1.98 (tt, *J* = 6.0, 3.0 Hz, 1H), 1.85 (td, *J* = 6.0, 2.0 Hz, 1H), 1.23 (s, 3H), 1.18 (d, *J* = 7.5 Hz, 3H), 1.08 (d, *J* = 10.0 Hz, 1H), 0.94 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 84.3, 47.6, 44.2, 44.1, 38.4, 36.2, 33.8, 27.4, 24.1, 20.2; IR (ATR, cm^{-1}); $[\alpha]^{26}_D$ = -24.1° (*c* = 0.5, $CHCl_3$); HRMS (EI) *m/z* calculated for $C_{10}H_{19}NO_3S$ $[M]^+$: 233.1086, found 233.1087.

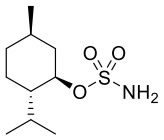
2-cyclohexylethyl sulfamate [S7].



Prepared according to method **A**. 1.145 g (8.93 mmol) of cyclohexylethanol were used, along with NaH (248 mg, 9.82 mmol, 1.1 equiv), DMF (9 + 7 mL), $ClSO_2NCO$ (1.17 mL, 13.4 mmol, 1.5 equiv), formic acid (505 µL, 13.4 mmol, 1.5 equiv) and MeCN (7 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave 1.702 g (8.21 mmol) of pure product as a colorless oil (91% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.88 (br. s, 2H), 4.25 (t, *J* = 6.5 Hz, 2H), 1.74-1.66 (m, 5H), 1.64 (app. q, *J* = 7.0 Hz, 2H), 1.48-1.39 (m, 1H), 1.29-1.10 (m, 3H), 0.93 (app. dq, *J* = 12.0, 3.0 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 69.9, 36.1, 34.0, 33.1, 26.5, 26.2; IR (ATR, cm^{-1}) 3369, 3289, 2916, 2844, 1539, 1450, 1376, 1353, 1189, 1097, 1028, 999, 966, 917, 888, 849, 787, 746; HRMS (ESI) *m/z* calculated for $C_8H_{17}NO_3SNa$ $[M+Na]^+$: 230.0827, found 230.0835.

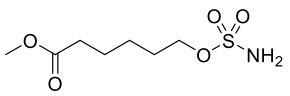
(-)-(1*R*,2*S*,5*R*)-menthyl sulfamate [S8].



Prepared according to method **A**. 1.563 g (10.0 mmol) of (-)-menthol were used, along with NaH (278 mg, 11.0 mmol, 1.1 equiv), DMF (10 mL + 8 mL), $ClSO_2NCO$ (1.31 mL, 15.0 mmol, 1.5 equiv), formic acid (566 μL, 15.0 mmol, 1.5 equiv) and MeCN (7.5 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc as eluent, followed by recrystallization from CH_2Cl_2 layered with hexanes, gave 1.821 g (7.70 mmol) of pure product as a crystalline white solid (77% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.71 (br. s, 2H), 4.43 (dt, *J* = 11.0, 4.5 Hz, 1H), 2.38-2.34 (m, 1H), 2.12 (ddt, *J* = 14.0, 7.0, 2.0 Hz, 1H), 1.74-1.66 (m, 2H), 1.51-1.38 (m, 2H), 1.26 (app. q, *J* = 11.8 Hz, 1H), 1.04 (dq, *J* = 13.0, 3.5 Hz, 1H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 7.5 Hz, 3H), 0.89-0.86 (m, 1H), 0.83 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 84.9, 47.7, 41.6, 33.9, 31.8, 25.7, 23.2, 22.1, 21.0, 15.9; IR (film, cm^{-1}) 3361, 3253, 2945, 2872, 1560, 1454, 1358, 1186, 1169, 916; $[\alpha]^{25}_D$ = -82.1° (*c* = 1.0, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{10}H_{21}NO_3SNa$ $[M+Na]^+$: 258.1140, found 258.1139.

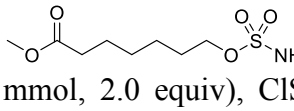
Methyl 6-(sulfamoyloxy)hexanoate [S9].



Prepared according to method **B**. 1.385 g (9.47 mmol) of methyl 6-hydroxyhexanoate[10] were used, along with Et_3N (2.64 mL, 18.9 mmol, 2.0 equiv), $ClSO_2NCO$ (1.65 mL, 18.9 mmol, 2.0 equiv), formic acid (713 μL, 18.9 mmol, 2.0 equiv) and CH_2Cl_2 (9 mL + 10 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:2 hexanes/EtOAc as eluent gave 1.520 g (6.75 mmol) of pure product as a white solid (71% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.84 (br. s, 2H), 4.22 (t, *J* = 6.5 Hz, 2H), 3.67 (s, 3H), 2.34 (t, *J* = 7.0 Hz, 2H), 1.77 (dt, *J* = 13.5, 7.0 Hz, 2H), 1.70-1.64 (m, 2H), 1.49-1.43 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 174.4, 71.0, 51.8, 33.8, 28.4, 25.0, 24.2; IR (ATR, cm^{-1}) 3352, 3328, 3268, 3226, 2955, 2875, 1735, 1712, 1547, 1475, 1435, 1414, 1399, 1359, 1305, 1242, 1108, 1040, 970, 924, 820, 735; HRMS (ESI) *m/z* calculated for $C_7H_{16}NO_5S$ $[M+H]^+$: 226.0749, found 226.0748.

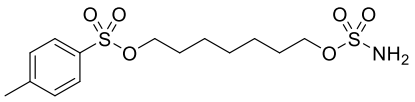
Methyl 7-(sulfamoyloxy)heptanoate [S10].



Prepared according to method **B**. 1.556 g (9.71 mmol) of methyl 7-hydroxyheptanoate[11] were used, along with Et_3N (2.71 mL, 19.4 mmol, 2.0 equiv), $ClSO_2NCO$ (1.69 mL, 19.4 mmol, 2.0 equiv), formic acid (732 μL, 19.4 mmol, 2.0 equiv) and CH_2Cl_2 (10 mL + 10 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:2 hexanes/EtOAc as eluent gave 1.655 g (6.91 mmol) of pure product as a colorless oil (71% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.96 (br. s, 2H), 4.21 (t, *J* = 6.5 Hz, 2H), 3.67 (s, 3H), 2.32 (t, *J* = 7.3 Hz, 2H), 1.75 (dt, *J* = 15.0, 5.5 Hz, 2H), 1.64 (dt, *J* = 17.0, 5.5 Hz, 2H), 1.47-1.33 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 174.5, 71.3, 51.7, 33.9, 28.6, 28.5, 25.2, 24.7; IR (ATR, cm^{-1}) 3363, 3283, 2950, 2865, 1738, 1698, 1549, 1472, 1430, 1376, 1339, 1304, 1235, 1099, 1011, 986, 961, 915, 882, 845, 792, 742, 722; HRMS (ESI) *m/z* calculated for $C_8H_{18}NO_5S$ $[M+H]^+$: 240.0906, found 240.0905.

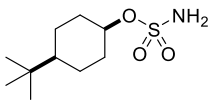
7-(tosyloxy)heptyl sulfamate [S11].



Prepared according to method **B**. 1.989 g (6.94 mmol) of 7-(tosyloxy)heptan-1-ol were used, along with Et_3N (1.94 mL, 13.9 mmol, 2.0 equiv), $ClSO_2NCO$ (1.21 mL, 13.9 mmol, 2.0 equiv), formic acid (524 μL, 13.9 mmol, 2.0 equiv) and CH_2Cl_2 (7 mL + 8 mL). Flash column chromatography on silica (45 mm fritted glass column, 170 mm SiO_2) using 3:2 hexanes/EtOAc → 1:1 hexanes/EtOAc as eluent gave 1.491 g (4.08 mmol) of pure product as a colorless oil (59% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 6.5 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.83 (br. s, 2H), 4.19 (t, J = 6.5 Hz, 2H), 4.02 (t, J = 6.3 Hz, 2H), 2.45 (s, 3H), 1.74-1.69 (m, 2H), 1.67-1.62 (m, 2H), 1.41-1.27 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 144.9, 133.1, 130.0, 128.0, 71.3, 70.7, 28.7, 28.6, 28.2, 25.3, 25.2, 21.8; IR (ATR, cm^{-1}) 3376, 3285, 2937, 2861, 1598, 1561, 1465, 1349, 1097, 916, 814, 769, 662; HRMS (ESI) *m/z* calculated for $C_{14}H_{24}NO_6S_2$ $[M+H]^+$: 366.1045, found 366.1037.

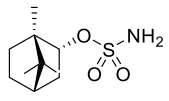
(±)-*cis*-4-(tert-butyl)cyclohexyl sulfamate [S12].



Prepared according to method **A**. 1.563 g (10.0 mmol) of *cis*-4-(*tert*-butyl)cyclohexanol were used, along with NaH (278 mg, 11.0 mmol, 1.1 equiv), DMF (10 + 8 mL), $ClSO_2NCO$ (1.31 mL, 15.0 mmol, 1.5 equiv), formic acid (566 μL, 15.0 mmol, 1.5 equiv) and MeCN (7.5 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc as eluent, followed by recrystallization from CH_2Cl_2 layered with hexanes, gave 1.821 g (7.70 mmol) of pure product as a crystalline white solid (77% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.89-4.88 (m, 1H), 4.67 (br. s, 2H), 2.21-2.18 (m, 2H), 1.64-1.61 (m, 2H), 1.57-1.51 (m, 2H), 1.37 (app. dq, J = 13.0, 3.5 Hz, 2H), 1.03 (tt, J = 12.0, 3.0 Hz, 1H), 0.86 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 84.3, 43.3, 34.3, 26.9, 23.0, 22.7, 22.5, 14.1; IR (ATR, cm^{-1}) 3386, 3293, 2952, 2868, 1560, 1440, 1373, 1358, 1347, 1305, 1237, 1193, 1176, 1161, 1106, 1031, 875, 808, 756; HRMS (ESI) *m/z* calculated for $C_{10}H_{21}NO_3SNa$ $[M+Na]^+$: 258.1140, found 258.1143.

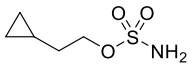
(-)-(1*S*,2*R*,4*S*)-borneyl sulfamate [S13].



Prepared according to method **A**. 1.543 g (10.0 mmol) of (-)-borneol were used, along with NaH (278 mg, 11.0 mmol, 1.1 equiv), DMF (10 + 8 mL), $ClSO_2NCO$ (1.31 mL, 15.0 mmol, 1.5 equiv), formic acid (566 μL, 15.0 mmol, 1.5 equiv) and MeCN (7.5 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc as eluent, followed by recrystallization from Et_2O layered with hexanes, gave 1.353 g (5.80 mmol) of pure product as a crystalline white solid (58% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.73 (ddd, J = 10.0, 3.4, 2.1 Hz, 1H), 4.64 (br. s, 2H), 2.37 (ddt, J = 14.0, 10.1, 4.0 Hz, 1H), 1.91 (ddd, J = 14.6, 9.9, 4.4 Hz, 1H), 1.80-1.72 (m, 2H), 1.55 (s, 1H), 1.40 (dd, J = 14.0, 3.5 Hz, 1H), 1.36-1.25 (m, 2H), 0.93 (s, 3H), 0.89 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 89.1, 76.9, 49.7, 47.9, 44.8, 36.3, 28.0, 26.7, 19.8, 18.9, 13.3; IR (ATR, cm^{-1}) 3344, 3274, 2961, 2887, 1562, 1459, 1394, 1350, 1326, 1184, 1141, 1113, 1007, 989, 974, 956, 941, 906, 871, 838, 809, 784, 744; $[\alpha]^{26}_D$ = -27.9° (c = 1.0, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{10}H_{19}NO_3SNa$ $[M+Na]^+$: 256.0983, found 256.0992.

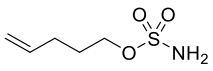
2-cyclopropylethyl sulfamate [S14].



Prepared according to method **B**. 431 mg (5.00 mmol) of 2-cyclopropylethan-1-ol were used, along with $ClSO_2NCO$ (653 µL, 7.50 mmol, 1.5 equiv), formic acid (283 µL, 7.50 mmol, 1.5 equiv), Et_3N (1.05 mL, 7.50 mmol, 1.5 equiv) and CH_2Cl_2 (3.8 mL + 7 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 20% → 25% EtOAc/hexanes as eluent gave 478 mg (2.89 mmol) of pure product as a colorless oil (58% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.71 (br. s, 2H), 4.28 (td, *J* = 6.7, 1.4 Hz, 2H), 1.73-1.61 (app. q, 2H), 0.82-0.74 (m, 1H), 0.52-0.49 (m, 2H), 0.13-0.10 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 71.7, 33.9, 7.3, 4.3; IR (ATR, cm^{-1}): 3384, 3283, 3082, 3004, 1557, 1467, 1428, 1352, 1172, 1079, 1050, 1018, 916, 802, 765; HRMS (ESI) *m/z* calculated for $C_5H_{11}NO_3SNa$ $[M+Na]^+$: 188.0357, found 188.0357.

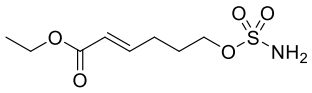
Pent-4-en-1-yl sulfamate [S15].



Prepared according to method **A**. 1.03 g (12.0 mmol) of 4-penten-1-ol were used, along with NaH (333 mg, 13.2 mmol, 1.1 equiv), DMF (21.4 mL), $ClSO_2NCO$ (2.2 mL, 25.5 mmol, 1.5 equiv), formic acid (959 µL, 25.5 mmol, 1.5 equiv) and MeCN (12.8 mL). Flash column chromatography on silica (45 mm fritted glass column, 170 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave 1.60 g (9.70 mmol) of pure product as a colorless oil (81% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.07 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.03 (dd, *J* = 10.2, 1.3 Hz, 1H), 4.81 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 2H), 2.23 - 2.14 (m, 2H), 1.86 (tt, *J* = 7.4, 6.5 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 137.0, 116.2, 71.0, 29.7, 28.1. These data are in agreement with that previously reported in the literature.[12]

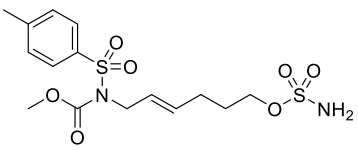
Ethyl (*E*)-6-(sulfamoyloxy)hex-2-enoate [S16].



Prepared according to method **B**. 949 mg (6.00 mmol) of ethyl (*E*)-6-hydroxyhex-2-enoate were used, along with Et_3N (1.74 mL, 9.00 mmol, 1.5 equiv), $ClSO_2NCO$ (783 µL, 9.00 mmol, 1.5 equiv), formic acid (340 µL, 9.00 mmol, 1.5 equiv) and CH_2Cl_2 (4.5 + 8.6 mL). Flash column chromatography on silica (45 mm fritted glass column, 200 mm SiO_2) using 25% acetone/hexanes → 30% acetone/hexanes as eluent gave 968 mg (4.08 mmol) of pure product as a colorless oil (68% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.93 (dt, *J* = 15.6, 7.0 Hz, 1H), 5.87 (dt, *J* = 15.7, 1.6 Hz, 1H), 4.93 (br. s, 2H), 4.23 (t, *J* = 6.2 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.36 (qd, *J* = 7.2, 1.6 Hz, 2H), 1.93 (tt, *J* = 7.5, 6.2 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.7, 147.0, 122.7, 70.3, 60.6, 28.2, 27.3, 14.4. These data are in agreement with that previously reported in the literature.[12]

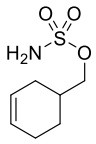
(*E*)-6-((*N*-(methoxycarbonyl)-4-methylphenyl)sulfonamido)hex-4-en-1-yl sulfamate [S17].



Prepared according to method **B**. 1.15 g (3.50 mmol) of methyl (*E*)-(6-hydroxyhex-2-en-1-yl)(tosyl)carbamate were used, along with Et_3N (731 µL, 5.3 mmol, 1.5 equiv), $ClSO_2NCO$ (461 µL, 5.3 mmol, 1.5 equiv), formic acid (198 µL, 5.3 mmol, 1.5 equiv) and CH_2Cl_2 (5 + 2.6 mL). Flash column chromatography on silica (45

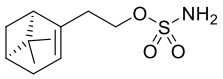
mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/acetone as eluent gave 810 mg (1.99 mmol) of pure product as a white solid (57% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 5.77 (dt, *J* = 15.2, 7.0 Hz, 1H), 5.67-5.61 (m, 1H), 4.82 (s, 2H), 4.41 (d, *J* = 6.1 Hz, 2H), 4.21 (t, *J* = 6.3 Hz, 2H), 3.70 (s, 3H), 2.44 (s, 3H), 2.23 (dd, *J* = 13.6, 7.0 Hz, 2H), 1.88 (p, *J* = 6.6 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ152.7, 144.9, 136.1, 133.3, 129.4, 128.3, 126.1, 70.0, 54.0, 48.6, 27.9, 27.7, 21.6; IR (film, cm^{-1}) 3378, 3283, 2959, 1736, 1596, 1559, 1495, 1447, 1359, 1244, 1127, 974, 928, 816, 768, 737, 677, 578, 547; HRMS (ESI) *m/z* calculated for $C_{15}H_{23}N_2O_7S_2$ $[M+H]^+$: 407.0947, found 407.0941.

(±)-cyclohex-3-en-1-ylmethyl sulfamate [S18].



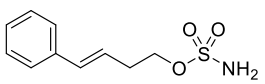
Prepared according to method **A**. 841 mg (875 µL, 7.50 mmol) of 3-cyclohexene -1-methanol were used, along with Et_3N (1.57 mL, 11.3 mmol, 1.5 equiv), $ClSO_2NCO$ (984 µL, 11.3 mmol, 1.5 equiv), formic acid (426 µL, 11.3 mmol, 1.5 equiv) and CH_2Cl_2 (5.7 + 10.7 mL). Flash column chromatography on silica (45 mm fritted glass column, 200 mm SiO_2) using 4:1 hexanes/EtOAc → 3:1 hexanes/EtOAc as eluent gave 1.07 g (5.60 mmol) of pure product as a colorless oil (75% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.71-5.64 (m, 2H), 4.80 (br. s, 2H), 4.11 (d, *J* = 6.6 Hz, 2H), 2.19-2.03 (m, 1H), 2.11-2.04 (m, 3H), 1.86-1.78 (m, 2H), 1.37 (dddd, *J* = 12.9, 10.8, 8.8, 7.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 127.2, 125.1, 75.4, 33.2, 27.7, 24.9, 24.2. These data are in agreement with that previously reported in the literature.[12]

(-)-2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl sulfamate [S19].



Prepared according to method **A**. 1.25 g (1.3 mL, 7.50 mmol) of (-)-(*1R*)-nopol were used, along with NaH (208 mg, 8.30 mmol, 1.1 equiv), DMF (13.4 mL), $ClSO_2NCO$ (984 µL, 11.3 mmol, 1.5 equiv), formic acid (426 µL, 11.3 mmol, 1.5 equiv) and MeCN (5.6 mL). Flash column chromatography on silica (35 mm fritted glass column, 170 mm SiO_2) using 4:1 hexanes/EtOAc as eluent gave 1.30 g (5.30 mmol) of pure product as a white solid (71% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.36 (app tt, *J* = 3.0, 1.5 Hz, 1H), 4.71 (br. s, 2H), 4.21 (td, *J* = 7.2, 1.9 Hz, 2H), 2.54-2.36 (m, 3H), 2.29-2.17 (m, 2H), 2.10 (app tdt, *J* = 6.9, 4.0, 1.9 Hz, 1H), 2.04 (td, *J* = 5.6, 1.5 Hz, 1H), 1.28 (s, 3H), 1.15 (d, *J* = 8.6 Hz, 1H), 0.83 (s, 3H).; ^{13}C-NMR (125 MHz, $CDCl_3$) δ142.8, 119.9, 69.7, 45.7, 40.7, 38.2, 36.1, 31.7, 31.5, 26.3, 21.3; IR (film, cm^{-1}) 3371, 3288, 2989, 2928, 2875, 1542, 1467, 1443, 1341, 1190, 1067, 1056, 969, 955, 912, 837, 769, 698; $[\alpha]_D^{25}$ = -25.0° (*c* = 1.0, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{11}H_{19}NO_3SNa$ $[M+Na]^+$: 268.0983, found 268.0987.

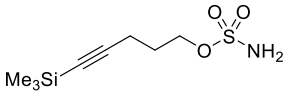
(*E*)-4-phenylbut-3-en-1-yl sulfamate [S20].



Prepared according to method **B**. 727 mg (4.90 mmol) of (*E*)-4-phenylbut-3-en-1-ol were used, along with Et_3N (1.03 mL, 7.36 mmol, 1.5 equiv), $ClSO_2NCO$ (639 µL, 7.36 mmol, 1.5 equiv), formic acid (278 µL, 7.36 mmol, 1.5 equiv) and CH_2Cl_2 (3.7 + 7.0 mL). Flash column chromatography on silica (150 mL SiO_2) using 3:1 hexanes/EtOAc as eluent gave 830 mg (3.65 mmol) of pure product as a white solid (75% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.37-7.28 (m, 4H), 7.26-7.21 (m, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.17 (dt, *J* = 15.8, 7.0 Hz, 1H), 4.71 (br. s, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 2.67 (qd, *J* = 6.7, 1.5

Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 137.0, 133.5, 128.7, 127.7, 126.3, 124.1, 70.6, 32.5. These data are in agreement with that previously reported in the literature.[13]

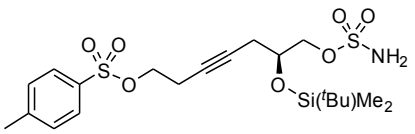
(±)-5-(trimethylsilyl)pent-4-yn-1-yl sulfamate [S21].



Prepared according to method **B**. 782 mg (5.00 mmol) of 5-(trimethylsilyl)pent-4-yn-1-ol were used, along with Et_3N (1.05 mL, 7.50 mmol, 1.5 equiv), $ClSO_2NCO$ (653 μL, 7.50 mmol, 1.5 equiv), formic acid (283 μL, 7.50 mmol, 1.5 equiv) and CH_2Cl_2 (3.8 + 7.1 mL). Flash column chromatography on silica (45 mm fritted glass column, 150 mm SiO_2) using 5% Et_2O/hexanes → 10% Et_2O/hexanes → 15% Et_2O/hexanes as eluent gave 605 mg (2.57 mmol) of pure product as a clear oil (51% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.82 (br. s, 2H), 4.34 (t, J = 6.1 Hz, 2H), 2.39 (t, J = 6.9 Hz, 2H), 1.95 (p, J = 6.4 Hz, 2H), 0.15 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 105.0, 86.4, 69.9, 27.8, 16.3, 0.2; IR (film, cm^{-1}) 3383, 3284, 2960, 2175, 1557, 1359, 1249, 1177, 1070, 1017, 979, 929, 759, 698; HRMS (ESI) *m/z* calculated for $C_8H_{18}O_3SSi$ $[M+H]^+$: 236.0777, found 236.0779.

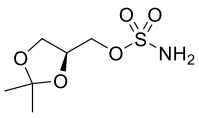
(+)-(*S*)-2-((*tert*-butyldimethylsilyl)oxy)-7-(tosyloxy)hept-4-yn-1-yl sulfamate [S22].



Prepared according to method **B**. 940 mg (2.30 mmol) of (*S*)-6-((*tert*-butyldimethylsilyl)oxy)-7-hydroxyhept-3-yn-1-yl 4-methylbenzene sulfonate were used, along with Et_3N (488 μL, 3.50 mmol, 1.5 equiv), $ClSO_2NCO$ (304 μL, 3.50 mmol, 1.5 equiv), formic acid (132 μL, 3.50 mmol, 1.5 equiv) and CH_2Cl_2 (1.75 + 3.3 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc → 2:1 hexanes/EtOAc as eluent gave 688 mg (1.40 mmol) of pure product as a pale yellow oil (61% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 5.03 (s, 2H), 4.33 (dd, J = 10.2, 3.7 Hz, 1H), 4.15 (dd, J = 10.2, 5.9 Hz, 1H), 4.08-4.01 (m, 3H), 2.51 (tt, J = 6.5, 2.4 Hz, 2H), 2.46 (s, 3H), 2.38 (dt, J = 6.6, 2.4 Hz, 2H), 0.88 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 145.3, 132.7, 130.1, 128.1, 78.1, 77.5, 73.3, 69.3, 68.4, 25.8, 24.5, 21.8, 20.0, 18.2, -4.6, -4.8; IR (film, cm^{-1}) 3378, 3288, 2929, 2857, 1598, 1558, 1463, 1358, 1255, 1120, 1096, 971, 903, 808, 775, 663; $[\alpha]_D^{25}$ = +8.21° (c = 0.56, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{20}H_{34}NO_7S_2Si$ $[M+H]^+$: 492.1546, found 492.1542.

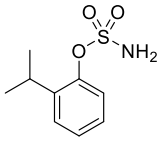
(-)-(*S*)-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl sulfamate [S23].



Prepared according to method **B**. 661 mg (622 μL, 5.00 mmol) of (*R*)-glycerol acetonide were used, along with Et_3N (1.05 mL, 7.50 mmol, 1.5 equiv), $ClSO_2NCO$ (651 μL, 7.50 mmol, 1.5 equiv), formic acid (282.9 μL, 7.5 mmol, 1.5 equiv) and CH_2Cl_2 (3.8 + 7.1 mL). Flash column chromatography on silica (150 mL SiO_2) using 2:1 hexanes/EtOAc as eluent gave 704 mg (3.30 mmol) of pure product as a clear oil (67% yield).

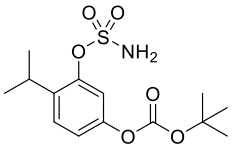
^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.20 (s, 2H), 4.41 (p, J = 5.7 Hz, 1H), 4.23 (dd, J = 10.7, 6.1 Hz, 1H), 4.18 (dd, J = 10.7, 4.8 Hz, 1H), 4.11 (dd, J = 8.8, 6.5 Hz, 1H), 3.83 (dd, J = 8.8, 5.4 Hz, 1H), 1.45 (s, 3H), 1.37 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 110.4, 73.2, 70.6, 65.7, 26.6, 25.2. These data are in agreement with that previously reported in the literature.[14]

2-isopropylphenyl sulfamate [S24].



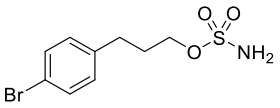
Prepared according to method **C**. 681 mg (5.00 mmol) of 2-isopropylphenol were used, along with $ClSO_2NCO$ (653 µL, 7.50 mmol, 1.5 equiv), formic acid (283 µL, 7.50 mmol, 1.5 equiv), MeCN (3.8 mL, 2M), DMA (3.0 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave 877 mg (4.07 mmol) of pure product as a white solid (81% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.30-7.26 (m, 1H), 7.23-7.19 (m, 1H), 5.14 (br. s, 2H), 3.39 (hept, *J* = 6.9 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 147.7, 141.7, 127.6, 127.5, 127.0, 121.7, 27.0, 23.4; IR (ATR, cm^{-1}): 3374, 3279, 2986, 2928, 1540, 1488, 1445, 1379, 1359, 1201, 1182, 1151, 1077, 1033, 945, 928, 900, 873, 860; HRMS (ESI) *m/z* calculated for $C_9H_{13}NNaO_3S$ $[M+Na]^+$: 238.0514, found 238.0512.

5-((*tert*-butoxycarbonyl)oxy)-2-isopropylphenyl sulfamate [S25].



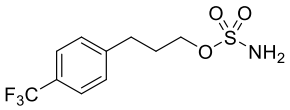
Prepared according to method **C**. 1.030 g (4.08 mmol) of *tert*-butyl (3-hydroxy-4-isopropylphenyl) carbonate was used, along with $ClSO_2NCO$ (533 µL, 6.12 mmol, 1.5 equiv), formic acid (231 µL, 6.12 mmol, 1.5 equiv), 3.1 mL MeCN and 6 mL DMA. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 15% EtOAc/hexanes → 30% EtOAc /hexanes as eluent gave 1.113 g (3.36 mmol) of pure product as a yellowish oil (82% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.6 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.11 (dd, *J* = 8.6, 2.4 Hz, 1H), 4.97 (br. s, 2H), 3.36 (hept, *J* = 7.0 Hz, 1H), 1.56 (s, 9H), 1.23 (d, *J* = 6.9 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 151.9, 149.0, 147.3, 139.4, 127.8, 120.4, 115.2, 84.4, 27.8, 26.8, 23.3; IR (ATR, cm^{-1}): 3389, 3242, 3081, 2970, 1725, 1589, 1562, 1498, 1417, 1399, 1370, 1294, 1264, 1244, 1184, 1154, 1131, 1084, 964, 887, 870, 813, 778; HRMS (ESI) *m/z* calculated for $C_{14}H_{21}NO_6SNa$ $[M+Na]^+$: 354.0987, found 354.0992.

3-(4-bromophenyl)propyl sulfamate [S26].



Prepared according to method **B**. 1.617 g (7.52 mmol) of 3-(4-bromophenyl)propan-1-ol were used, along with $ClSO_2NCO$ (982 µL, 11.28 mmol, 1.5 equiv), formic acid (425 µL, 11.28 mmol, 1.5 equiv), Et_3N (1.57 mL, 11.28 mmol, 1.5 equiv) and CH_2Cl_2 (5.7 mL + 10.5 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 25% EtOAc/hexanes → 30% EtOAc/hexanes as eluent gave 1.493 g (5.08 mmol) of pure product as a white solid (68% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 1H), 4.67 (br. s, 2H), 4.21 (t, *J* = 6.2 Hz, 1H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.12-2.00 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 139.5, 131.7, 130.4, 120.2, 70.4, 31.1, 30.3; IR (ATR, cm^{-1}): 3357, 3270, 2977, 1548, 1487, 1471, 1350, 1183, 1164, 1072, 1010, 967, 917, 829, 790; HRMS (ESI) *m/z* calculated for $C_9H_{11}NO_3SBr$ $[M-H]^-$: 291.9643, found 291.9644.

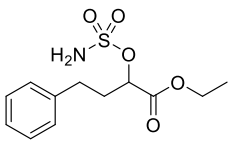
3-(4-(trifluoromethyl)phenyl)propyl sulfamate [S27].



Prepared according to method **B**. 1.865 g (9.13 mmol) of 3-(4-trifluoromethyl)propan-1-ol were used, along with $ClSO_2NCO$ (1.19 mL, 13.70 mmol, 1.5 equiv), formic acid (517 µL, 13.70 mmol, 1.5 equiv), Et_3N (1.92 mL, 13.70 mmol, 1.5 equiv) and CH_2Cl_2 (6.9 mL +

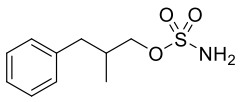
12.8 mL). Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 25% EtOAc/hexanes → 45% EtOAc /hexanes as eluent gave 1.989 g (7.02 mmol) of pure product as a white solid (77% yield).
^{1}H-NMR (500 MHz, Acetonitrile-d_3) δ 7.61 (d, J = 7.9 Hz, 2H), 7.42 (d, J = 7.9 Hz, 2H), 5.66 (br. s, 2H), 4.12 (t, J = 6.3 Hz, 2H), 2.80 (t, J = 7.7 Hz, 2H), 2.06-2.01 (m, 2H); ^{13}C-NMR (125 MHz, Acetonitrile-d_3) δ 146.9, 130.1, 128.6 (q, J = 32.0 Hz), 126.1 (q, J = 3.9 Hz), 125.5 (q, J = 270.1 Hz), 70.2, 32.0, 30.8; ^{19}F-NMR (470 MHz, Acetonitrile-d_3) δ -62.45; IR (ATR, cm^{-1}): 3370, 3270, 1619, 1544, 1357, 1324, 1162, 1111, 1068, 1009, 931, 846, 833, 816; HRMS (EI) *m/z* calculated for $C_{10}H_{12}NO_3SF_3$ [M^+]: 283.0490, found 283.0497.

(±)-ethyl 4-phenyl-2-(sulfamoyloxy)butanoate [S28].



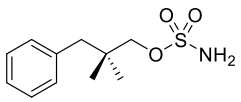
Prepared according to method **B**. 1.553 g (7.46 mmol) of (±)-ethyl 4-phenyl-2-(hydroxy)butanoate were used, along with Et_3N (1.56 mL, 11.2 mmol, 1.5 equiv), $ClSO_2NCO$ (973 µL, 11.2 mmol, 1.5 equiv), formic acid (422 µL, 11.2 mmol, 1.5 equiv) and CH_2Cl_2 (6 mL + 7 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc → 2:1 hexanes/EtOAc as eluent gave 611 mg (2.16 mmol) of pure product as a white solid (29% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.31 (t, J = 7.3 Hz, 2H), 7.24-7.20 (m, 3H), 5.13 (br. s, 2H), 4.95 (dd, J = 8.0, 4.0 Hz, 1H), 4.22 (q, J = 7.0 Hz, 2H), 2. 79 (t, J = 7.8 Hz, 2H), 2.30-2.17 (m, 2H), 1.30 (t, J = 7.3 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 170.5, 139.9, 128.8, 128.7, 126.6, 79.2, 62.5, 33.5, 31.0, 14.2. These data are in agreement with that previously reported in the literature.[8]

(±)-2-methyl-3-phenylpropyl sulfamate [S29].



Prepared according to method **A**. 719 mg (4.79 mmol) of (±)-2-methyl-3-phenylpropan-1-ol were used, along with NaH (133 mg, 5.27 mmol, 1.1 equiv), DMF (5.0 + 4.0 mL), $ClSO_2NCO$ (625 µL, 7.19 mmol, 1.5 equiv), formic acid (271 µL, 7.19 mmol, 1.5 equiv) and MeCN (3.6 mL). Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 3:2 hexanes/EtOAc as eluent gave 954 mg (4.16 mmol) of pure product as a colorless oil (87% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 2H), 7.27-7.21 (m, 1H), 7.20-7.16 (m, 2H), 5.20 (br. s, 2H), 4.06 (qd, J = 9.4, 5.8 Hz, 2H), 2.79 (dd, J = 13.6, 6.4 Hz, 1H), 2.51 (dd, J = 13.6, 8.0 Hz, 1H), 2.25-2.15 (m, 1H), 0.99 (d, J = 6.8 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 139.4, 129.2, 128.5, 126.3, 75.1, 39.1, 34.7, 16.3; IR (ATR, cm^{-1}): 3360, 3275, 2920, 1544, 1497, 1453, 1391, 1330, 1260, 1177, 971, 951, 924, 887, 820, 805; HRMS (ESI) *m/z* calculated for $C_{10}H_{16}NO_3S$ [M+H]$^+$: 230.0851, found 230.0855.

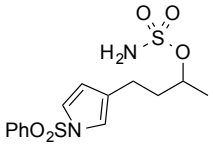
2,2-dimethyl-3-phenylpropyl sulfamate [S30].



Prepared according to method **A**. 821 mg (5.00 mmol) of 2,2-dimethyl-3-phenylpropan-1-ol[15] were used, along with NaH (139 mg, 5.50 mmol, 1.1 equiv), DMF (5.0 mL + 4.0 mL), $ClSO_2NCO$ (653 µL, 7.50 mmol, 1.5 equiv), formic acid (293 µL, 7.50 mmol, 1.5 equiv) and MeCN (3.8 mL). Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 35% EtOAc/hexanes as eluent gave 726 mg (2.98 mmol) of pure product as a white solid (60% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 7.25-7.21 (m, 1H), 7.16-7.14 (m, 2H), 4.90 (br. s, 2H), 3.86 (s, 2H), 2.62 (s, 2H), 0.97 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 137.5, 130.7,

128.2, 126.5, 78.2, 44.6, 35.3, 24.2; IR (ATR, cm^{-1}): 3327, 3238, 2975, 1602, 1561, 1494, 1452, 1471, 1395, 1353, 1194, 1161, 1007, 975, 930, 921, 906, 844, 826; HRMS (ESI) *m/z* calculated for $C_{11}H_{18}NO_3S$ $[M+H]^+$: 244.1007, found 244.1003.

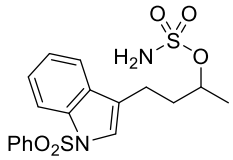
(±)-4-(1-(phenylsulfonyl)-1*H*-pyrrol-3-yl)butan-2-yl sulfamate [S31].



Prepared according to method **B**. 838 mg (3.00 mmol) 4-(1-(phenylsulfonyl)-1*H*-pyrrol-3-yl) butan-2-ol were used, along with Et_3N (455 µL, 4.50 mmol, 1.5 equiv), CH_2Cl_2 (2.25 mL + 4.5 mL), $ClSO_2NCO$ (391 µL, 4.50 mmol, 1.5 equiv), formic acid (170 µL, 4.50 mmol, 1.5 equiv). Flash column chromatography on silica (45 mm fritted glass column, 180 mm SiO_2) using 9:1 hexanes/acetone → 3:2 hexanes/acetone as eluent gave 751 mg (2.10 mmol) of pure product as a white solid (70% yield).

^1H NMR (5^1H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.29 (dd, *J* = 3.5, 1.7 Hz, 1H), 6.22 (t, *J* = 3.4 Hz, 1H), 6.04-6.03 (m, 1H), 4.87 (s, 2H), 4.77-4.70 (m, 1H), 2.80 (dd, *J* = 9.2, 6.5 Hz, 2H), 1.97 – 1.92 (m, 2H), 1.41 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 134.2, 134.1, 129.7, 126.9, 122.8, 112.8, 111.8, 80.4, 35.8, 23.0, 20.8; HRMS (ESI) *m/z* calculated for $C_{14}H_{19}N_2O_5S_2$ $[M+H]^+$: 359.0735, found 359.0734.

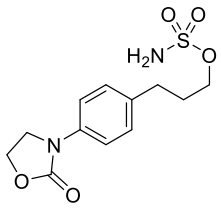
(±)-4-(1-(phenylsulfonyl)-1*H*-indol-3-yl)butan-2-yl sulfamate [S32].



Prepared according to method **B**. 988 mg (3.00 mmol) 4-(1-(phenylsulfonyl)-1*H*-indol-3-yl)butan-2-ol were used, along with Et_3N (455 µL, 4.5 mmol, 1.5 equiv), CH_2Cl_2 (2.25 mL + 4.5 mL), $ClSO_2NCO$ (392 µL, 4.50 mmol, 1.5 equiv), formic acid (170 µL, 4.50 mmol, 1.5 equiv). Flash column chromatography on silica (45 mm fritted glass column, 200 mm SiO_2) using 9:1 hexanes/EtOAc → 3:2 hexanes/EtOAc as eluent gave 897 mg (2.20 mmol) of pure product as an off-white solid (73% yield).

^1H NMR (500 MHz, $CDCl_3$) δ 7.99-7.97 (m, 1H), 7.88-7.86 (m, 2H), 7.52-7.39 (m, 5H), 7.33-7.30 (m, 1H), 7.24-7.21 (m, 1H), 4.96 (s, 2H), 4.77-4.71 (m, 1H), 2.83-2.73 (m, 2H), 2.12-2.05 (m, 1H), 1.99-1.92 (m, 1H), 1.44 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 135.5, 133.9, 130.8, 129.4, 126.9, 125.0, 123.4, 123.1, 122.1, 119.5, 114.0, 80.6, 35.7, 20.8, 20.7; HRMS (ESI) *m/z* calculated for $C_{18}H_{20}N_2O_5S_2Na$ $[M+Na]^+$: 431.0711, found 431.0709.

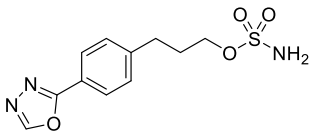
3-(4-(2-oxooxazolidin-3-yl)phenyl)propyl sulfamate [S33].



Prepared according to method **B**. 487 mg (2.20 mmol) 3-(4-(3-hydroxypropyl)phenyl)oxazolidin-2-one were used, along with Et_3N (614 µL, 4.40 mmol, 2.0 equiv), DCM (2 mL + 4ml), $ClSO_2NCO$ (383 µL, 4.40 mmol, 2.0 equiv), formic acid (166 µL, 4.40 mmol, 2.0 equiv). Flash column chromatography on silica (45 mm fritted glass column, 200 mm SiO_2) using 10% EtOAc/hexanes → 80% EtOAc/hexanes as eluent gave 390 mg (1.30 mmol) of pure product as an off white solid (59% yield).

^1H NMR (500 MHz, Acetone-d_6) δ 7.55 – 7.53 (m, 2H), 7.26-7.25 (m, 2H), 6.63 (s, 2H), 4.49 (dd, *J* = 9.5, 7.0 Hz, 2H), 4.16-4.11 (m, 4H), 2.72 (dd, *J* = 8.5, 6.7 Hz, 2H), 2.09-1.99 (m, 2H); ^{13}C NMR (125 MHz, Acetone) δ 155.9, 138.2, 137.1, 129.7, 119.0, 69.7, 62.3, 45.9, 31.6, 31.5; HRMS (ESI) *m/z* calculated for $C_{12}H_{17}N_2O_5S$ $[M+H]^+$: 301.0858, found 301.0857.

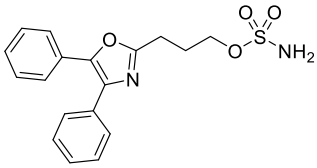
3-(4-(1,3,4-oxadiazol-2-yl)phenyl)propyl sulfamate [S34].



Prepared according to method **A**. 600 mg (2.90 mmol) of 3-(4-(1,3,4-oxadiazol-2-yl)phenyl)propan-1-ol were used, along with NaH (81 mg, 3.20 mmol, 1.1 equiv), DMF (5.8 mL), $ClSO_2NCO$ (500 µL, 5.80 mmol, 2.0 equiv), formic acid (220 µL, 5.80 mmol, 2.0 equiv) and MeCN (2.9 mL). Flash column chromatography on silica (45 mm fritted glass column, 200 mm SiO_2) using 20% acetone/hexanes → 60% acetone/hexanes as eluent gave 390 mg (1.38 mmol) of pure product as a white solid (48% yield).

^{1}H NMR (500 MHz, Acetone-d_6) δ 8.96 (s, 1H), 8.01 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 6.67 (s, 2H), 4.19 (t, J = 6.3 Hz, 2H), 2.88-2.83 (m, 2H), 2.11-2.09 (m, 2H); ^{13}C NMR (125 MHz, Acetone-d_6) δ 165.2, 154.5, 146.7, 130.4, 127.9, 122.8, 69.7, 32.5, 31.2; HRMS (ESI) *m/z* calculated for $C_{11}H_{14}N_3O_4S$ $[M+H]^+$: 284.0705, found 284.0699.

3-(4,5-diphenyloxazol-2-yl)propyl sulfamate [S35].

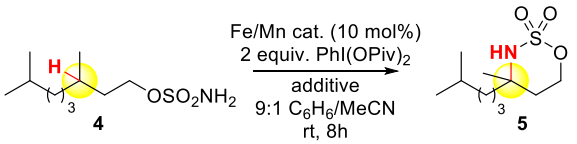


Prepared according to method **A**. 1.310 g (4.70 mmol) 3-(4,5-diphenyloxazol-2-yl)propan-1-ol were used, along with NaH (130 mg, 5.12 mmol, 1.1 equiv), DCM (3.6 mL), $ClSO_2NCO$ (617 µL, 7.10 mmol, 1.5 equiv), formic acid (268 µL, 7.10 mmol, 1.5 equiv) and DMF (7 mL). Flash column chromatography on silica (45 mm fritted glass column, 200 mm SiO_2) using 20% EtOAc/hexanes → 70% EtOAc/hexanes as eluent gave 1.090 g (3.00 mmol) of pure product as a white solid (64% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.60 (m, 2H), 7.57 (dt, J = 6.9, 2.3 Hz, 2H), 7.40-7.32 (m, 6H), 5.16 (s, 2H), 4.40 (td, J = 5.9, 0.9 Hz, 2H), 3.05 (t, J = 6.9 Hz, 2H), 2.32-2.27 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 145.8, 135.1, 132.2, 128.8, 128.8, 128.8, 128.4, 128.0, 126.6, 69.8, 26.3, 24.2; HRMS (ESI) *m/z* calculated for $C_{18}H_{19}N_2O_4S$ $[M+H]^+$: 359.1066, found 359.1060.

Optimization of Mn-catalyzed Intramolecular C—H Amination

Table S1. Development of the Mn-catalyzed intramolecular C—H amination.



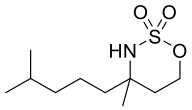
entry	catalyst	additive	% yield (% rsm)
1	[FePc]Cl (**1**) + $AgSbF_6$	-	29 (32)
2	[MnPc]Cl (**2**) + $AgSbF_6$	-	43 (27)
3	Fe(TPP)Cl + $AgSbF_6$	-	4 (85)
4	Mn(TPP)Cl + $AgSbF_6$	-	18 (62)
5	Fe(*R,R*-salen)Cl + $AgSbF_6$	-	<1 (85)
6	Mn(*R,R*-salen)Cl + $AgSbF_6$	-	4 (78)
7	Fe(*R,R*-PDP)$(SbF_6)_2$	-	<1 (91)
8	Mn(*R,R*-PDP)$(SbF_6)_2$	-	7 (82)
9	[MnPc]Cl (**2**) + $AgSbF_6$	4Å MS	60 (11)
10	[MnPc]Cl (**2**) + $AgSbF_6$	4Å MS	58 (20)*
11	[Mn(^{t}BuPc)]Cl (**3**) + $AgSbF_6$	4Å MS	75 (<5)
12	[Fe(^{t}BuPc)]Cl + $AgSbF_6$	4Å MS	29 (34)
13	[Mn(^{t}BuPc)]Cl (**3**) + $AgSbF_6$	4Å MS	72 (14)*
14	[Mn(^{t}BuPc)]Cl (**3**) + $AgSbF_6$	4Å MS	71 (13)†
15	[Mn(^{t}BuPc)]Cl (**3**) + $AgSbF_6$	4Å MS	68 (16)*,‡

Isolated yields are average of three runs. * Used 5 mol% each Mn catalyst and $AgSbF_6$. † Used 2.5 mol% each Mn catalyst and $AgSbF_6$. ‡ Used 1.2 equiv $PhI(OPiv)_2$.

General procedure for catalyst and optimization studies (entries 1-15)

Into a 10 mL round-bottom flask was added $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), catalyst (0.040 mmol, 0.10 equiv), crushed 4Å MS (100 mg, if using) 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. (±)-3,7-dimethyloctyl sulfamate **4** (94.9 mg, 0.400 mmol, 1.0 equiv) dissolved in 9:1 C_6H_6/MeCN (800 µL, 0.5M) was added via syringe, followed by $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) in a single portion. The reaction stirred for 8h at room temp (~23°C), and then was applied directly to a silica column (35 mm fritted glass column, 150 mm SiO_2). The product and starting material were eluted with 5:1 hexanes/EtOAc and isolated separately.

(±)-4-methyl-4-(4-methylpentyl)-1,2,3-oxathiazinane 2,2-dioxide [5].



Isolated as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.71-4.61 (m, 2H), 4.29 (br. s, 1H), 1.82-1.67 (m, 3H), 1.54 (app. spt, J = 7.0 Hz, 1H), 1.45-1.41 (m, 2H), 1.38 (s, 3H), 1.30-1.24 (m, 1H), 1.20-1.15 (m, 2H), 0.87 (d, J = 6.5 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 69.1, 59.1, 41.3, 39.1, 34.7, 27.3, 24.7,

22.7, 22.6, 20.8; IR (film, cm^{-1}) 3271, 2954, 2872, 1466, 1421, 1360, 1252, 1188, 1155, 1113, 1070, 1014, 987, 933, 870, 783; HRMS (ESI) *m/z* calculated for $C_{10}H_{22}NO_3S$ $[M+H]^+$: 236.1320, found 236.1315.

Entry 1. (±)-3,7-dimethyloctyl sulfamate (94.9 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 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used.
Run 1: (27.1 mg, 0.115 mmol, 29%), (12.3 mg alcohol, 0.078 mmol, 19%), (24.9 mg rsm, 0.262 mmol, 26%). Run 2: (28.0 mg, 0.119 mmol, 30%), (32.8 mg rsm, 0.138 mmol, 35%). Run 3: (26.6 mg, 0.113 mmol, 28%), (33.7 mg rsm, 0.142 mmol, 36%). **Average: 29% yield ± 0.8, 32% rsm ± 4.5.**

Entry 2. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), [MnPc]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 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used.
Run 1: (39.2 mg, 0.167 mmol, 42%), (22.3 mg rsm, 0.094 mmol, 23%). Run 2: (39.4 mg, 0.167 mmol, 42%), (27.1 mg rsm, 0.114 mmol, 29%). Run 3: (41.8 mg, 0.178 mmol, 44%), (26.7 mg rsm, 0.113 mmol, 28%). **Average: 43% yield ± 0.9, 27% rsm ± 2.6.**

Entry 3. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), Fe(TPP)Cl (28.2 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 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used.
Run 1: (4.0 mg, 0.017 mmol, 4%), (80.1 mg rsm, 0.338 mmol, 84%). Run 2: (2.9 mg, 0.012 mmol, 3%), (82.3 mg rsm, 0.347 mmol, 87%). Run 3: (3.5 mg, 0.015 mmol, 4%), (79.5 mg rsm, 0.335 mmol, 84%). **Average: 4% yield ± 0.5, 85% rsm ± 1.4.**

Entry 4. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), Mn(TPP)Cl (28.2 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 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used.
Run 1: (15.6 mg, 0.066 mmol, 17%), (51.8 mg rsm, 0.218 mmol, 55%). Run 2: (16.8 mg, 0.072 mmol, 18%), (63.1 mg rsm, 0.266 mmol, 67%). Run 3: (17.4 mg, 0.074 mmol, 18%), (61.4 mg rsm, 0.259 mmol, 65%). **Average: 18% yield ± 0.5, 62% rsm ± 5.3.**

Entry 5. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), Fe(R,R-salen)Cl (22.8 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 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used.
Run 1: <1% yield, (784.6 mg rsm, 0.357 mmol, 89%). Run 2: <1% yield, (77.9 mg rsm, 0.328 mmol, 82%). Run 3: <1% yield, (79.1 mg rsm, 0.333 mmol, 83%). **Average: <1% yield, 85% rsm ± 3.1.**

Entry 6. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), Mn(R,R-salen)Cl (22.8 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 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used.
Run 1: (4.0 mg, 0.016 mmol, 4%), (72.5 mg rsm, 0.306 mmol, 76%). Run 2: (4.1 mg, 0.017 mmol, 4%), (78.0 mg rsm, 0.329 mmol, 82%). Run 3: (5.1 mg, 0.022 mmol, 5%), (73.2 mg rsm, 0.309 mmol, 77%). **Average: 4% yield ± 0.5, 78% rsm ± 2.6.**

Entry 7. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), Fe(*R,R*-PDP)$(SbF_6)_2$ (33.6 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used.
Run 1: <1% yield, (87.9 mg rsm, 0.370 mmol, 93%). Run 2: <1% yield, (87.7 mg rsm, 0.370 mmol, 92%). Run 3: <1% yield, (84.7 mg rsm, 0.357 mmol, 89%). **Average: <1% yield, 91% rsm ± 1.7.**

Entry 8. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), Mn(*R,R*-PDP)$(SbF_6)_2$ (33.6 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used.
Run 1: (7.0 mg, 0.030 mmol, 7%), (78.3 mg rsm, 0.330 mmol, 83%). Run 2: (6.2 mg, 0.026 mmol, 7%), (73.7 mg rsm, 0.311 mmol, 78%). Run 3: (6.7 mg, 0.028 mmol, 7%), (79.4 mg rsm, 0.335 mmol, 84%). **Average: 7% yield ± 0.0, 82% rsm ± 2.2.**

Entry 9. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), [MnPc]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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used.
Run 1: (56.1 mg, 0.238 mmol, 60%), (10.6 mg rsm, 0.045 mmol, 11%). Run 2: (54.3 mg, 0.231 mmol, 58%), (10.5 mg rsm, 0.044 mmol, 11%). Run 3: (58.2 mg, 0.247 mmol, 62%), (10.9 mg rsm, 0.046 mmol, 11%). **Average: 60% yield ± 1.6, 11% rsm ± 0.1.**

Entry 10. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), [MnPc]Cl (12.0 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used.
Run 1: (56.3 mg, 0.239 mmol, 60%), (21.6 mg rsm, 0.091 mmol, 23%). Run 2: (51.3 mg, 0.218 mmol, 55%), (15.0 mg rsm, 0.063 mmol, 16%). Run 3: (56.0 mg, 0.238 mmol, 59%), (20.3 mg rsm, 0.086 mmol, 21%). **Average: 58% yield ± 2.2, 20% rsm ± 2.9.**

Entry 11. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.2 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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used.
Run 1: (71.3 mg, 0.303 mmol, 76%), <5% rsm. Run 2: (70.4 mg, 0.299 mmol, 75%), <5% rsm. Run 3: (70.1 mg, 0.298 mmol, 74%), <5% rsm. **Average: 75% yield ± 0.8, <5% rsm.**

Entry 12. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), [Fe(^{t}BuPc)]Cl (33.2 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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used.
Run 1: (26.0 mg, 0.111 mmol, 28%), (26.3 mg rsm, 0.111 mmol, 28%). Run 2: (28.0 mg, 0.119 mmol, 30%), (29.2 mg rsm, 0.123 mmol, 31%). Run 3: (26.2 mg, 0.111 mmol, 28%), (41.2 mg rsm, 0.174 mmol, 43%). **Average: 29% yield ± 0.9, 34% rsm ± 6.6.**

Entry 13. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used.
Run 1: (68.1 mg, 0.289 mmol, 72%), (12.2 mg rsm, 0.051 mmol, 12%). Run 2: (68.8 mg, 0.292 mmol, 73%), (16.6 mg rsm, 0.070 mmol, 17%). Run 3: (67.8 mg, 0.288 mmol, 72%), (13.1 mg rsm, 0.055 mmol, 14%). **Average: 72% yield ± 0.5, 14% rsm ± 2.1.**

Entry 14. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (8.3 mg, 0.010 mmol, 0.025 equiv), $AgSbF_6$ (3.4 mg, 0.010 mmol, 0.025 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. *Note: reactions run at these low catalyst loadings were less reproducible at 0.400 mmol scale, likely due to increased effect of balance error in weighing catalysts.*
Run 1: (65.6 mg, 0.279 mmol, 70%), (16.5 mg rsm, 0.070 mmol, 17%). Run 2: (67.0 mg, 0.284 mmol, 71%), (11.8 mg rsm, 0.050 mmol, 12%). Run 3: (66.6 mg, 0.283 mmol, 71%), (10.1 mg rsm, 0.043 mmol, 11%). **Average: 71% yield ± 0.5, 13% rsm ± 2.6.**

Entry 15. (±)-3,7-dimethyloctyl sulfamate (94.9 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (195 mg, 0.480 mmol, 1.2 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used.
Run 1: (64.2 mg, 0.273 mmol, 68%), (12.9 mg rsm, 0.054 mmol, 14%). Run 2: (64.1 mg, 0.272 mmol, 68%), (15.9 mg rsm, 0.067 mmol, 17%). Run 3: (63.8 mg, 0.271 mmol, 68%), (16.8 mg rsm, 0.071 mmol, 18%). **Average: 68% yield ± 0.2, 16% rsm ± 1.7.**

Substrate Scope for Mn-catalyzed Intramolecular C—H Amination

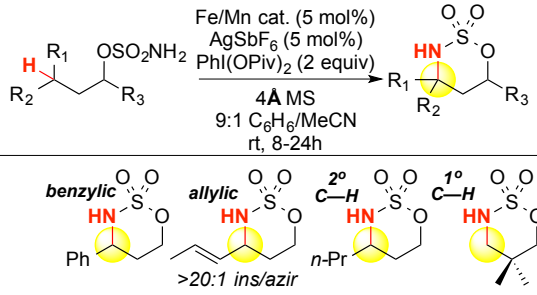
General procedure for [MnPc] and [Mn(^{t}BuPc)]-mediated C—H amination

Into a 10 mL round-bottom flask was added $AgSbF_6$ (0.05 equiv or 0.10 equiv), [Mn(^{t}BuPc)]Cl (0.05 equiv or 0.10 equiv), crushed 4Å MS, 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. Sulfamate ester (1.0 equiv), 9:1 C_6H_6/MeCN (0.5M), and, lastly, $PhI(OPiv)_2$ (2.0 equiv) were then added under an inert atmosphere; 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 dark red solution gradually turned dark brown. The reaction stirred for 8h at room temperature unless otherwise specified (~20°C). Upon completion, the reaction mixture was applied directly to a silica column for purification. Alternatively, the reaction can be concentrated under reduced pressure, and the remaining dark brown residue suspended in Et_2O and filtered through a small pad of Celite. Upon removal of solvent under reduced pressure, the brown residue was taken up in minimal CH_2Cl_2 and applied to a column. Any variation of these reaction conditions is noted for individual substrates.

General procedure for [FePc]-mediated intramolecular C—H amination[7]

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 8h at room temperature unless otherwise specified (~20°C). Upon completion, the reaction mixture was applied directly to a silica column (35 mm fritted glass column, 150 mm SiO_2) for purification. Alternatively, the reaction can be concentrated under reduced pressure, and the remaining dark brown residue suspended in Et_2O and filtered through a small pad of Celite. Upon removal of solvent under reduced pressure, the brown residue was taken up in minimal CH_2Cl_2 and applied to a column. Any variation of these reaction conditions is noted for individual substrates.

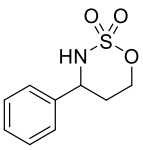
Table S2. Catalyst comparison across C—H bond types.



catalyst	6	7	8	9
[FePc]*	22%	10%	5%†	3%†
[MnPc]	71%	61%	39%†	37%†
[Mn(^{t}BuPc)]	74%	61%	57%†	64%†

Isolated yields are average of three runs. * Conditions: 5 mol% [FePc]Cl, 5 mol% $AgSbF_6$, 2 equiv. $PhI(OPiv)_2$, 4:1 PhMe/MeCN (0.5M), rt, 8h. † Used 10 mol% catalyst.

(±)-4-phenyl-1,2,3-oxathiazinane 2,2-dioxide [6].



In all cases, material was purified via flash column chromatography on silica (25 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc as eluent, affording oxathiazinane product and starting material separately.

FePc conditions: 3-phenylpropyl sulfamate **46** (86.5 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (12.0 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), and 4:1 PhMe/MeCN (800 μL, 0.5M) were used.

Run 1: (18.5 mg, 0.086 mmol, 22%), (54.9 mg rsm, 0.254 mmol, 63%). Run 2: (19.0 mg, 0.089 mmol, 22%), (58.2 mg rsm, 0.269 mmol, 67%). Run 3: (17.8 mg, 0.083 mmol, 21%), (56.2 mg rsm, 0.260 mmol, 65%). **Average: 22% yield ± 0.5, 65% rsm ± 1.6.**

MnPc conditions: 3-phenylpropyl sulfamate **46** (86.5 mg, 0.400 mmol, 1.0 equiv), [MnPc]Cl (12.0 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used.

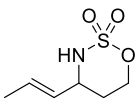
Run 1: (59.1 mg, 0.276 mmol, 69%), (<5% rsm). Run 2: (59.8 mg, 0.279 mmol, 70%), (<5% rsm). Run 3: (62.6 mg, 0.292 mmol, 73%), (<5% rsm). **Average: 71% yield ± 1.7, <5% rsm.**

Mn(^{t}BuPc) conditions: 3-phenylpropyl sulfamate **46** (86.5 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used.

Run 1: (63.0 mg, 0.294 mmol, 74%), (<5% rsm). Run 2: (65.2 mg, 0.304 mmol, 76%), (<5% rsm). Run 3: (61.5 mg, 0.287 mmol, 72%), (<5% rsm). **Average: 74% yield ± 1.6, <5% rsm.**

Pure product was isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.43-7.35 (m, 5H), 4.90-4.85 (m, 2H), 4.66 (ddd, J = 11.5, 5.0, 1.5 Hz, 1H), 4.35 (br. d, J = 9.0 Hz, 1H), 2.30-2.21 (m, 1H), 2.05-2.00 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 137.7, 129.0, 128.7, 126.1, 71.8, 58.7, 30.0. These data are in agreement with that previously reported in the literature.[7]

(±)-(*E*)-4-(prop-1-en-1-yl)-1,2,3-oxathiazinane 2,2-dioxide [7].



In all cases, material was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc, affording a mixture of product and starting material; yields were determined based on ^{1}H NMR ratios. Pure product could be obtained by eluting with 10% hexanes/CH_2Cl_2 → CH_2Cl_2 → 2% Et_2O/CH_2Cl_2. Ins./azir. ratios determined by ^{1}H NMR of the crude reaction mixture. Pure product was isolated as a white solid.

FePc conditions: (*E*)-hex-4-en-1-yl sulfamate **S1** (71.7 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (12.1 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), and 4:1 PhMe/MeCN (800 μL, 0.5M) were used.

Run 1: (8.2 mg, 0.046 mmol, 11%), (54.3 mg rsm, 0.303 mmol, 76%). Run 2: (7.6 mg, 0.043 mmol, 11%), (55.0 mg rsm, 0.307 mmol, 77%). Run 3: (6.7 mg, 0.038 mmol, 9%), (54.8 mg rsm, 0.306 mmol, 76%). **Average: 10% yield ± 0.9 (ins./azir. crude = >20:1), 76% rsm ± 0.5.**

MnPc conditions: (*E*)-hex-4-en-1-yl sulfamate **S1** (71.7 mg, 0.400 mmol, 1.0 equiv), [MnPc]Cl (12.1 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used.

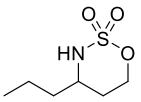
Run 1: (43.1 mg, 0.243 mmol, 61%). Run 2: (43.6 mg, 0.246 mmol, 61%). Run 3: (42.7 mg, 0.241 mmol, 60%) **Average: 61% yield ± 0.5 (ins./azir. crude = >20:1).**

Mn(^{t}BuPc) conditions: (*E*)-hex-4-en-1-yl sulfamate **S1** (71.7 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used.

Run 1: (45.0 mg, 0.254 mmol, 63%). Run 2: (40.9 mg, 0.231 mmol, 58%). Run 3: (44.3 mg, 0.250 mmol, 62%) **Average: 61% yield ± 2.2 (ins./azir. crude = >20:1).**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.78 (dqd, *J* = 14.3, 6.5, 1.3 Hz, 1H), 5.43 (dd, *J* = 15.4, 5.9 Hz, 1H), 4.74 (dt, *J* = 12.0, 2.7 Hz, 1H), 4.55 (dd, *J* = 11.6, 5.0 Hz, 1H), 4.30-4.24 (m, 1H), 4.00 (br. d, *J* = 10.0 Hz, 1H), 1.91-1.77 (m, 2H), 1.73 (dd, *J* = 6.5, 1.4 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.6, 128.1, 71.8, 56.9, 29.8, 17.9; ^{13}C-NMR (125 MHz, $CDCl_3$) δ 129.6, 128.1, 71.8, 56.9, 29.8, 17.9. These data are in agreement with that previously reported in the literature.[9]

(±)-4-propyl-1,2,3-oxathiazinane 2,2-dioxide [8].



In all cases, material was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc, affording a mixture of product and starting material; yields were determined based on ^{1}H NMR ratios. Pure product could be obtained by eluting with CH_2Cl_2 → 2% Et_2O/CH_2Cl_2.

FePc conditions: Hexyl sulfamate **S2** (72.5 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, 0.5M) were used.

Run 1: (3.7 mg, 0.021 mmol, 5%), (53.3 mg rsm, 0.294 mmol, 74%). Run 2: (3.3 mg, 0.018 mmol, 5%), (56.2 mg rsm, 0.310 mmol, 77%). Run 3: (2.7 mg, 0.015 mmol, 4%), (55.6 mg rsm, 0.307 mmol, 77%). **Average: 5% yield ± 0.8, 76% rsm ± 1.4.**

MnPc conditions: Hexyl sulfamate **S2** (72.5 mg, 0.400 mmol, 1.0 equiv), [MnPc]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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used.

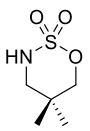
Run 1: (26.1 mg, 0.146 mmol, 36%), (27.2 mg rsm, 0.150 mmol, 38%). Run 2: (29.1 mg, 0.162 mmol, 41%), (23.9 mg rsm, 0.132 mmol, 33%). Run 3: (28.1 mg, 0.157 mmol, 39%), (23.9 mg rsm, 0.132 mmol, 33%). **Average: 39% yield ± 2.1, 35% rsm ± 2.4.**

Mn(^{t}BuPc) conditions: Hexyl sulfamate **S2** (72.5 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.2 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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used.

Run 1: (40.8 mg, 0.228 mmol, 57%), (14.5 mg rsm, 0.080 mmol, 20%). Run 2: (42.2 mg, 0.235 mmol, 59%), (11.2 mg rsm, 0.062 mmol, 16%). Run 3: (40.1 mg, 0.224 mmol, 56%), (13.2 mg rsm, 0.073 mmol, 18%). **Average: 57% yield ± 1.2, 18% rsm ± 1.6.**

Product was isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.74-4.66 (m, 1H), 4.52 (dt, *J* = 11.0, 3.3 Hz, 1H), 4.20 (br. d, *J* = 10.5 Hz, 1H), 3.74-3.66 (m, 1H), 1.73-1.69 (m, 2H), 1.53-1.35 (m, 4H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 72.2, 55.9, 37.2, 29.9, 18.4, 13.7; IR (ATR, cm^{-1}) 3367, 3285, 2919, 2858, 1539, 1470, 1343, 1178, 1063, 1032, 973, 922, 850, 792, 742, 717; HRMS (ESI) *m/z* calculated for $C_6H_{14}NO_3S$ $[M+H]^+$: 180.0694, found 180.0698.

5,5-dimethyl-1,2,3-oxathiazinane 2,2-dioxide [9].



In all cases, the reaction was stirred at rt for 24h. The crude reaction mixture was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 15% EtOAc/hexanes → 20% EtOAc/hexanes with 0.5% AcOH as eluent.

FePc conditions: Neopentyl sulfamate **S3** (66.9 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24.2 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. Product and recovered starting material were isolated as a mixture after column purification.

Run 1: (2.0 mg, 0.012 mmol, 3% yield), (50.2 mg, 0.300 mmol, 75% rsm). Run 2: (2.4 mg, 0.015 mmol, 4% yield), (48.0 mg, 0.287 mmol, 72% rsm). Run 3: (2.1 mg, 0.013 mmol, 3% yield), (52.2 mg, 0.312 mmol, 78% rsm). **Average: 3% yield ± 0.6, 75% rsm ± 3.0.**

MnPc conditions: Neopentyl sulfamate **S3** (66.9 mg, 0.400 mmol, 1.0 equiv), [MnPc]Cl (24.2 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), crushed 4Å MS (100 mg), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (800 μL) were used. Product and starting material were isolated separately.

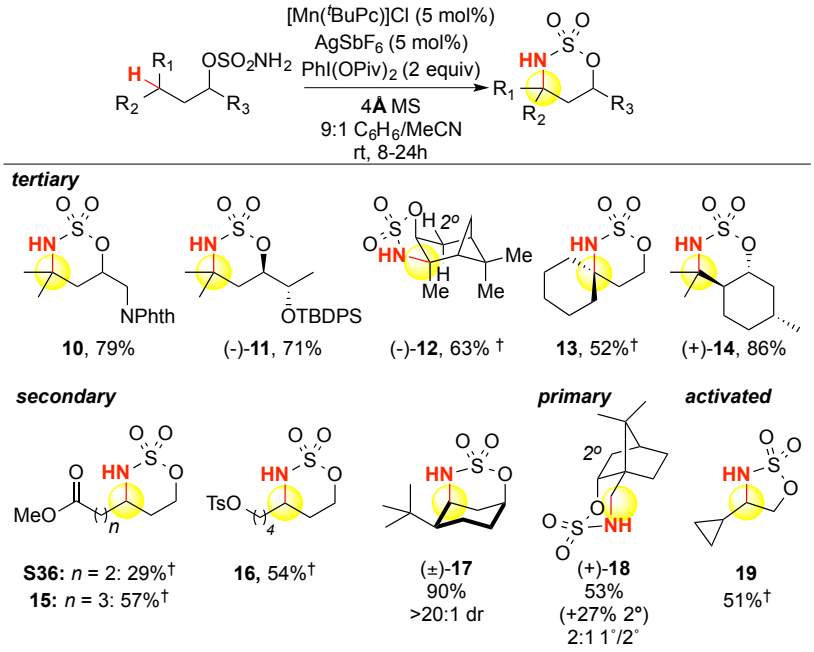
Run 1: (24.8 mg, 0.150 mmol, 38% yield), (25.9 mg, 0.155 mmol, 39% rsm). Run 2: (22.1 mg, 0.134 mmol, 33% yield), (27.0 mg, 0.161 mmol, 40% rsm). Run 3: (26.8 mg, 0.162 mmol, 41% yield), (29.5 mg, 0.176 mmol, 44% rsm). **Average: 37% yield ± 4.0, 41% rsm ± 2.6.**

Mn(^{t}BuPc) conditions: Neopentyl sulfamate **S3** (66.9 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.2 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), crushed 4Å MS (100 mg), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (800 μL) were used. Product and starting material were isolated separately.

Run 1: (42.6 mg, 0.258 mmol, 64% yield), (6.0 mg, 0.036 mmol, 9% rsm). Run 2: (41.3 mg, 0.250 mmol, 63% yield), (10.4 mg, 0.062 mmol, 16% rsm). Run 3: (42.6 mg, 0.258 mmol, 64% yield), (8.6 mg, 0.051 mmol, 13% rsm). **Average: 64% yield ± 0.6, 13% rsm ± 3.5.**

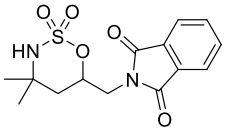
Product was isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.69 (br. s, 1H), 4.27 (s, 2H), 3.27 (d, J = 7.5 Hz, 2H), 1.07 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 81.7, 55.4, 29.1, 21.9; IR (ATR, cm^{-1}): 3315, 2967, 1425, 1399, 1350, 1336, 1314, 1282, 1183, 1046, 954, 930, 922, 910, 844; HRMS (ESI) *m/z* calculated for $C_5H_{12}NO_3S$ $[M+H]^+$: 166.0538, found 166.0535.

Table S3. Aliphatic C—H bond substrate scope.



Isolated yields are average of three runs. *Conditions: 5 mol% [FePc]Cl, 5 mol% $AgSbF_6$, 2 equiv. $PhI(OPiv)_2$, 4:1 PhMe/MeCN (0.5M), rt, 8h. † Used 10 mol% catalyst.

(±)-2-((4,4-dimethyl-2,2-dioxido-1,2,3-oxathiazinan-6-yl)methyl)isoindoline-1,3-dione [10].

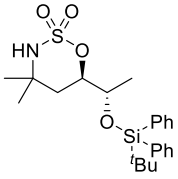


(±)-1-(1,3-dioxoisoindolin-2-yl)-4-methylpentan-2-yl sulfamate **S4** (131.0 mg, 0.400 mmol, 1.0 equiv), [Mn(*t*BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:2 hexanes/EtOAc. Pure product was isolated as a white solid.

Run 1: (104.0 mg, 0.320 mmol, 80%), 0% rsm. Run 2: (100.1 mg, 0.308 mmol, 77%), 0% rsm. Run 3: (103.7 mg, 0.319 mmol, 80%), 0% rsm. **Average: 79% yield ± 1.4, 0% rsm.**

^{1}H-NMR (500 MHz, acetone-d_6) δ 7.91-7.86 (m, 4H), 6.01 (br. s, 1H), 5.13 (dddd, J = 12.0, 7.0, 5.0, 2.0 Hz, 1H), 4.02 (dd, J = 14.5, 7.0 Hz, 1H), 3.88 (dd, J = 14.5, 5.0 Hz, 1H), 2.01 (dd, J = 14.5, 2.0 Hz, 1H), 1.72 (dd, J = 14.5, 12.0 Hz, 1H), 1.46 (s, 3H), 1.36 (s, 3H); ^{13}C-NMR (125 MHz, acetone-d_6) δ 168.6, 135.4, 133.1, 124.2, 78.3, 56.5, 42.2, 39.4, 31.6, 25.6; IR (thin film, cm^{-1}) 3228, 2981, 2950, 1713, 1468, 1433, 1393, 1360, 1272, 1193, 1160, 1061, 1026, 995, 943, 869; HRMS (ESI) *m/z* calculated for $C_{14}H_{17}N_2O_5S$ $[M+H]^+$: 325.0858, found 325.0859.

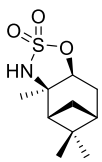
(-)-(*R*)-6-((*S*)-1-((*tert*-butyldiphenylsilyl)oxy)ethyl)-4,4-dimethyl-1,2,3-oxathiazinane 2,2-dioxide [11].



(-)-(2*S*,3*R*)-2-((*tert*-butyldiphenylsilyl)oxy)-5-methylhexan-3-yl sulfamate **S5** (89.9 mg, 0.200 mmol, 1.0 equiv), [Mn(*t*BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv), 50 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (400 µL, 0.5M) were used. Product was purified via flash column chromatography on silica (35

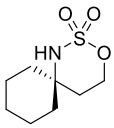
mm fritted glass column, 100 mm SiO_2) using 9:1 hexanes/EtOAc. Pure product was isolated as a white solid.
Run 1: (58.7 mg, 0.131 mmol, 66%), <10% rsm. Run 2: (66.5 mg, 0.149 mmol, 74%), <10% rsm. Run 3: (65.4 mg, 0.146 mmol, 73%), <10% rsm. **Average: 71% yield ± 3.6, <10% rsm.**
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.68-7.65 (m, 4H), 7.47-7.43 (m, 2H), 7.41-7.38 (m, 4H), 4.68 (ddd, *J* = 12.0, 4.5, 2.0 Hz, 1H), 3.96 (qd, *J* = 12.5, 4.5 Hz, 1H), 3.91 (s, 1H), 1.70 (dd, *J* = 14.5, 12.5 Hz, 1H), 1.57 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.44 (s, 3H), 1.28 (s, 3H), 1.13 (d, *J* = 6.5 Hz, 3H), 1.07 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 136.0, 133.7, 133.2, 130.2, 130.0, 127.9, 127.8, 82.8, 69.7, 55.8, 36.0, 32.3, 27.1, 25.0, 19.4, 18.3; IR (ATR, cm^{-1}) 3269, 3072, 2962, 2933, 2859, 1473, 1428, 1390, 1375, 1353, 1266, 1196, 1141, 1111, 1029, 934, 875, 822, 740, 703; $[\alpha]^{25}_D$ = -23.2° (*c* = 1.1, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{23}H_{33}NO_4SSiNa$ $[M+Na]^+$: 470.1797, found 470.1798.

(-)-(3*R*,4*R*,6*R*,7*S*)-3,5,5-trimethylhexahydro-3*H*-4,6-methanobenzo[*d*][1,2,3]oxathiazole 2,2-dioxide [12].



(-)-(1*S*,2*S*,3*S*,5*R*)-isopinocampheyl sulfamate **S6** (93.3 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.2 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. By crude ^{1}H NMR, ratio of 3° to other products (most likely 2° and 1° C—H amination products, but could not be isolated pure to confirm assignment) was >10:1. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 7:1 hexanes/EtOAc → 4:1 hexanes/EtOAc. Pure product was isolated as a white solid.
Run 1: (57.1 mg, 0.247 mmol, 62%), <5% rsm. Run 2: (59.1 mg, 0.256 mmol, 64%), <5% rsm. Run 3: (57.5 mg, 0.249 mmol, 62%), <5%. **Average: 63% yield ± 0.9, <5% rsm.**
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.67 (dd, *J* = 8.5, 2.0 Hz, 1H), 4.24 (s 1H), 2.49-2.43 (m, 1H), 2.34 (dtd, *J* = 11.0, 6.0, 2.0 Hz, 1H), 2.16-2.11 (m, 1H), 2.06 (dd, *J* = 6.0, 1.5 Hz, 2H), 1.63 (s, 3H), 1.47 (d, *J* = 11.0 Hz, 1H), 1.33 (s, 3H), 0.94 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 82.1, 66.0, 51.1, 39.6, 39.0, 32.7, 28.2, 27.3, 26.1, 24.4; IR (ATR, cm^{-1}) 3244, 3005, 2985, 2959, 2941, 2926, 2912, 1479, 1450, 1393, 1381, 1318, 1281, 1181, 1131, 1085, 1062, 1029, 972, 959, 944, 893, 865, 852, 815, 753; $[\alpha]^{26}_D$ = -48.7° (*c* = 1.0, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{10}H_{17}NO_3SNa$ $[M+Na]^+$: 254.0827, found 254.0830.

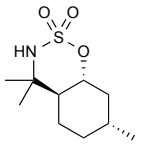
3-oxa-2-thia-1-azaspiro[5.5]undecane 2,2-dioxide [13].



2-cyclohexylethyl sulfamate **S7** (82.9 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.2 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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. Reaction stirred for 20h. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using CH_2Cl_2 → 2% Et_2O/CH_2Cl_2 → 5% Et_2O/CH_2Cl_2. Pure product was isolated as a white solid.
Run 1: (41.0 mg, 0.200 mmol, 50%), (13.1 mg rsm, 0.063 mmol, 16%). Run 2: (41.1 mg, 0.200 mmol, 50%), (17.6 mg rsm, 0.085 mmol, 21%). Run 3: (45.2 mg, 0.220 mmol, 55%), (13.8 mg rsm, 0.067 mmol, 17%). **Average: 52% yield ± 2.4, 18% rsm ± 2.2.**
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.64 (t, *J* = 5.5 Hz, 2H), 4.26 (s, 1H), 2.01 (d, *J* = 13.0 Hz, 2H), 1.75 (t, *J* = 5.5 Hz, 2H), 1.69-1.59 (m, 3H), 1.49-1.42 (m, 4H), 1.33-1.24 (m, 1H); ^{13}C-NMR

(125 MHz, $CDCl_3$) δ 68.7, 58.6, 36.3, 34.9, 25.7, 20.9; IR (ATR, cm^{-1}) 3247, 2930, 2860, 1466, 1445, 1417, 1357, 1341, 1279, 1186, 1153, 1111, 1023, 996, 945, 933, 926, 900, 871, 849, 739; HRMS (ESI) *m/z* calculated for $C_8H_{16}NO_3S$ $[M+H]^+$: 206.0851, found 206.0850.

(+)-(4*R*,7*S*,8*S*)-4,4,7-trimethyloctahydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide [14].

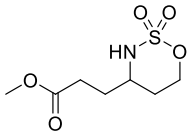


(-)-(1*R*,2*S*,5*R*)-menthyl sulfamate **S8** (94.1 mg, 0.400 mmol, 1.0 equiv), [Mn(*t*BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc. Pure product was isolated as a white solid.

Run 1: (81.9 mg, 0.351 mmol, 88%), 0% rsm. Run 2: (79.9 mg, 0.342 mmol, 86%), 0% rsm. Run 3: (79.0 mg, 0.339 mmol, 85%), 0% rsm. **Average: 86% yield ± 1.2, 0% rsm.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.58 (dt, *J* = 10.5, 4.5 Hz, 1H), 4.54 (br. s, 1H), 2.10-2.07 (m, 1H), 1.79-1.73 (m, 2H), 1.59-1.51 (m, 1H), 1.47 (dt, *J* = 11.3, 3.0 Hz, 1H), 1.36 (s, 3H), 1.24 (s, 3H), 1.08-1.00 (m, 1H), 0.96 (d, *J* = 6.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 82.4, 59.1, 48.7, 40.4, 34.1, 31.4, 29.4, 25.2, 21.9, 21.2; IR (film, cm^{-1}) 3280, 2958, 2922, 2862, 1460, 1410, 1389, 1373, 1336, 1225, 1200, 1184, 1161, 1137, 1086, 1012, 991, 920, 903, 885, 860, 818; $[\alpha]^{25}_D$ = +23.5° (*c* = 1.0, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{10}H_{20}NO_3S$ $[M+H]^+$: 234.1164, found 234.1164.

(±)-methyl 3-(2,2-dioxido-1,2,3-oxathiazinan-4-yl)propanoate [S36].

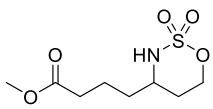


Methyl 6-(sulfamoyloxy)hexanoate **S9** (90.1 mg, 0.400 mmol, 1.0 equiv), [Mn(*t*BuPc)]Cl (33.2 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. Reaction stirred at rt for 17h. Material was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes/EtOAc. Starting material and product were isolated as a mixture; yields were determined based on ^{1}H NMR ratios. Pure product could be isolated by eluting with 5% Et_2O/CH_2Cl_2 → 10% Et_2O/CH_2Cl_2. Pure product was isolated as a white solid.

Run 1: (26.0 mg, 0.116 mmol, 29%), (37.1 mg rsm, 0.165 mmol, 41%). Run 2: (24.6 mg, 0.110 mmol, 28%), (42.2 mg rsm, 0.187 mmol, 47%). Run 3: (26.3 mg, 0.118 mmol, 30%), (32.0 mg rsm, 0.142 mmol, 36%). **Average: 29% yield ± 0.8, 41% rsm ± 4.1.**

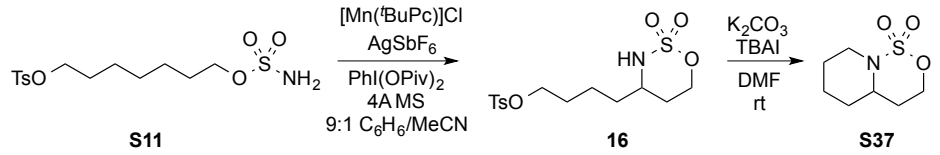
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.74-4.68 (m, 1H), 4.54 (dt, *J* = 11.0, 3.0 Hz, 1H), 4.22 (d, *J* = 10.7 Hz, 1H), 3.78-3.71 (m, 1H), 3.69 (s, 3H), 2.49 (td, *J* = 7.1, 1.5 Hz, 2H), 1.94 (dtd, *J* = 14.5, 7.2, 4.5 Hz, 1H), 1.86-1.73 (m, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.6, 71.8, 55.9, 52.1, 30.2, 29.8, 29.7; IR (ATR, cm^{-1}) 3273, 2960, 2942, 1735, 1433, 1386, 1355, 1337, 1319, 1269, 1252, 1228, 1203, 1170, 1104, 1081, 1056, 1009, 982, 937, 906, 895, 856, 775; HRMS (ESI) *m/z* calculated for $C_7H_{14}NO_5S$ $[M+H]^+$: 224.0593, found 224.0592.

(±)-methyl 4-(2,2-dioxido-1,2,3-oxathiazinan-4-yl)butanoate [15].

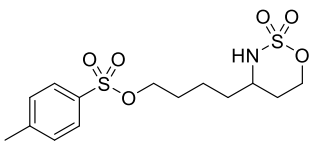


Methyl 7-(sulfamoyloxy)heptanoate **S10** (95.7 mg, 0.400 mmol, 1.0 equiv), [Mn(*t*BuPc)]Cl (33.2 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. Reaction stirred at rt for 17h.

Product was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 5% Et_2O/CH_2Cl_2 → 10% Et_2O/CH_2Cl_2. Pure product was isolated as a colorless oil with a minor amount (~6%) of an unidentified product-like impurity; reported yields are corrected to reflect amount of desired product isolated.
Run 1: (53.9 mg, 0.227 mmol, 57%), (20.4 mg rsm, 0.085 mmol, 21%). Run 2: (54.2 mg, 0.228 mmol, 57%), (17.1 mg rsm, 0.071 mmol, 18%). Run 3: (53.9 mg, 0.227 mmol, 57%), (17.9 mg rsm, 0.075 mmol, 19%). **Average: 57% yield ± 0.0, 19% rsm ± 1.2.**
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.74-4.69 (m, 1H), 4.54 (ddd, J = 11.5, 4.5, 2.0 Hz, 1H), 4.08 (br. d, J = 10.5 Hz, 1H), 3.76-3.69 (m, 1H), 3.68 (s, 3H), 2.35 (dt, J = 7.3, 2.0 Hz, 2H), 1.84-1.51 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.8, 72.1, 55.9, 51.8, 34.3, 33.3, 29.9, 20.6; IR (ATR, cm^{-1}) 3249, 2956, 1718, 1422, 1357, 1237, 1084, 1012, 987, 938, 917, 890, 862, 774, 731; HRMS (ESI) *m/z* calculated for $C_8H_{16}NO_5S$ $[M+H]^+$: 238.0749, found 238.0750.

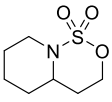


(±)-4-(2,2-dioxido-1,2,3-oxathiazinan-4-yl)butyl 4-methylbenzenesulfonate [16].



7-(tosyloxy)heptyl sulfamate **S11** (146 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.2 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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. Reaction stirred for 17h. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 5% Et_2O/CH_2Cl_2 → 10% Et_2O/CH_2Cl_2. Pure product was isolated as a colorless oil.
Run 1: (78.1 mg, 0.215 mmol, 54%), <10% rsm. Run 2: (79.2 mg, 0.218 mmol, 54%), <10% rsm. Run 3: (77.9 mg, 0.214 mmol, 54%), <10% rsm. **Average: 54% yield ± 0.0, <10% rsm.**
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 6.5 Hz, 2H), 7.36 (d, J = 6.0 Hz, 2H), 4.70 (dt, J = 12.0, 3.5 Hz, 1H), 4.53 (ddd, J = 11.5, 4.5, 2.0 Hz, 1H), 4.04 (t, J = 6.0 Hz, 2H), 3.87 (br. d, J = 10.5 Hz, 1H), 3.70-3.62 (m, 1H), 2.46 (s, 3H), 1.73-1.63 (m, 4H), 1.54-1.40 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 145.1, 133.0, 130.1, 128.0, 71.9, 70.0, 56.0, 34.5, 30.2, 28.4, 21.8, 21.3; HRMS (ESI) *m/z* calculated for $C_{14}H_{22}NO_6S_2$ $[M+H]^+$: 364.0889, found 364.0887.

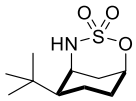
(±)-hexahydro-3*H*-pyrido[1,2-*c*][1,2,3]oxathiazine 1,1-dioxide [S37].



Cyclization procedure was modified from a similar procedure reported in the literature.[16] **17** (50.0 mg, 0.138 mmol, 1.0 equiv) was taken up in DMF (2.76 mL, 0.05M) in a 2 dram vial. K_2CO_3 (28.6 mg, 0.207 mmol, 1.5 equiv) and *n*-Bu_4NI (5.2 mg, 0.014 mmol, 0.10 equiv) were added, and then vial was capped and reaction stirred vigorously at rt for 15h (no precautions were taken to remove oxygen or water). Upon completion, reaction was quenched with H_2O (1 mL), then diluted with EtOAc (15 mL) and H_2O (5 mL). After separating, the aqueous layer was extracted twice more with EtOAc (2x10 mL). Organic layers were combined and washed with H_2O (10 mL) and brine (2x10 mL), then dried over $MgSO_4$ and filtered. Flash column chromatography on silica (35 mm fritted glass column, 70 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave 21.1 mg (0.110 mmol) of pure product as a colorless oil (80% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.71 (ddd, *J* = 13.5, 11.0, 2.5 Hz, 1H), 4.46 (ddd, *J* = 11.5, 5.5, 1.5 Hz, 1H), 3.58 (ddt, *J* = 11.5, 7.0, 3.0 Hz, 1H), 3.47-3.42 (m, 1H), 2.95 (ddd, *J* = 11.5, 9.0, 4.0 Hz, 1H), 2.19 (dddd, *J* = 14.5, 13.5, 12.0, 5.5 Hz, 1H), 1.85-1.80 (m, 1H), 1.75-1.64 (m, 3H), 1.58-1.44 (m, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 71.9, 57.4, 44.6, 31.2, 28.1, 24.6, 21.5; IR (ATR, cm^{-1}) 2974, 2957, 2939, 2867, 1468, 1445, 1427, 1360, 1343, 1300, 1282, 1254, 1208, 1107, 1089, 1047, 1030, 1011, 985, 959, 900, 872, 862, 799, 704; HRMS (ESI) *m/z* calculated for $C_7H_{14}NO_3S$ $[M+H]^+$: 192.0694, found 192.0699.

(±)-6-(tert-butyl)-2-oxa-3-thia-4-azabicyclo[3.3.1]nonane 3,3-dioxide [17].

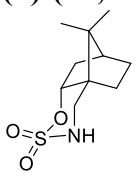


(±)-*cis*-4-(tert-butyl)cyclohexyl sulfamate **S12** (94.1 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes/EtOAc. Pure product was isolated as a white solid.

Run 1: (83.0 mg, 0.356 mmol, 89%), 0% rsm. Run 2: (83.6 mg, 0.358 mmol, 90%), 0% rsm. Run 3: (84.9 mg, 0.364 mmol, 91%), 0% rsm. **Average: 90% yield ± 0.8, 0% rsm.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.93-4.92 (m, 1H), 4.56 (br. s, 1H), 3.71-3.67 (m, 1H), 2.43-2.39 (m, 1H), 2.03 (ddd, *J* = 12.5, 6.0, 3.0 Hz, 1H), 1.71-1.64 (m, 2H), 1.59 (app. q, *J* = 12.5 Hz, 1H), 1.33-1.25 (m, 1H), 1.03-0.98 (m, 1H), 0.89 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 84.0, 58.5, 45.1, 32.5, 29.9, 27.8, 27.4, 20.3; IR (ATR, cm^{-1}) 3227, 2955, 2871, 1393, 1376, 1358, 1340, 1315, 1229, 1181, 1093, 996, 976, 952, 884, 870, 792, 760, 707, 692; HRMS (ESI) *m/z* calculated for $C_{10}H_{20}NO_3S$ $[M+H]^+$: 234.1164, found 234.1168.

(+)-(7*S*,8α*R*)-9,9-dimethylhexahydro-5*H*-4α,7-methanobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide [18].

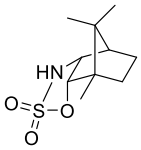


(-)-(1*S*,2*R*,4*S*)-borneyl sulfamate **S13** (93.3 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc. Both 1° and 2° products were isolated separately as white solids.

Run 1: (47.3 mg 1°, 0.204 mmol, 51%), (25.4 mg 2°, 0.110 mmol, 27%), (15.4 mg rsm, 0.065 mmol, 17%). Run 2: (48.9 mg 1°, 0.211 mmol, 53%), (27.2 mg 2°, 0.118 mmol, 29%), (12.1 mg rsm, 0.052 mmol, 13%). Run 3: (49.5 mg 1°, 0.214 mmol, 54%), (24.4 mg 2°, 0.105 mmol, 26%), (12.6 mg rsm, 0.054 mmol, 14%). **Average: 53% yield 1° ± 1.2, 27% yield 2° ± 1.2, 14% rsm ± 1.2.**

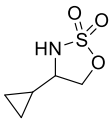
^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.13 (ddd, *J* = 11.0, 5.0, 2.5 Hz, 1H), 4.41 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.58 (dd, *J* = 14.0, 11.0 Hz, 1H), 3.08 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.34-2.27 (m, 2H), 1.86-1.80 (m, 2H), 1.51-1.45 (m, 1H), 1.41-1.36 (m, 1H), 1.26 (dd, *J* = 14.0, 5.0 Hz, 1H), 0.97 (s, 3H), 0.95 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 87.5, 47.6, 46.4, 45.8, 45.8, 32.6, 27.9, 24.0, 20.0, 18.9; IR (ATR, cm^{-1}) 3312, 2967, 2893, 1463, 1446, 1428, 1349, 1306, 1180, 1137, 1073, 1019, 989, 968, 922, 873, 840, 815, 797, 753; $[\alpha]^{26}_D$ = +37.9° (*c* = 1.0, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{10}H_{18}NO_3S$ $[M+H]^+$: 232.1007, found 232.1008.

(-)-(3α*R*,4*R*,7*R*,7α*S*)-7,8,8-trimethylhexahydro-3*H*-4,7-methanobenzo[*d*][1,2,3]oxathiazole 2,2-dioxide [S38].



^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.72 (dd, *J* = 9.0, 2.0 Hz, 1H), 4.28 (br. s, 1H), 4.26-4.21 (m, 1H), 1.99 (dd, *J* = 4.5, 4.0 Hz, 1H), 1.87 (ddd, *J* = 14.0, 9.0, 5.0 Hz, 1H), 1.74-1.63 (m, 2H), 1.39 (dddd, *J* = 13.5, 11.5, 6.0, 2.0 Hz, 1H), 1.01 (s, 3H), 1.00 (s, 3H), 0.96 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 88.4, 56.4, 49.6, 48.5, 48.4, 26.5, 20.5, 19.4, 18.3, 14.3; IR (ATR, cm^{-1}) 3325, 2967, 2923, 1475, 1388, 1378, 1342, 1327, 1283, 1262, 1125, 1075, 1024, 1001, 982, 964, 906, 883, 853, 823, 759, 709; $[\alpha]^{26}_D$ = -38.7° (*c* = 1.6, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{10}H_{18}NO_3S$ $[M+H]^+$: 232.1007, found 232.1007.

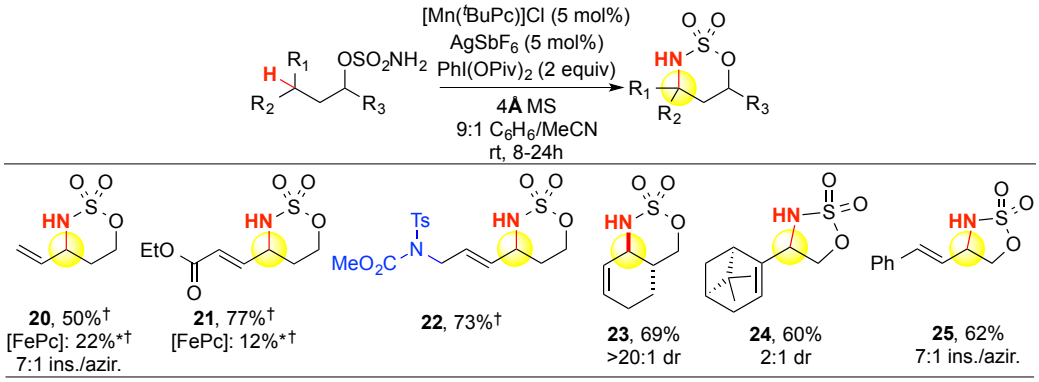
(±)-4-cyclopropyl-1,2,3-oxathiazolidine 2,2-dioxide [19].



2-cyclopropylethyl sulfamate **S14** (66.1 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.2 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), crushed 4Å MS (100 mg), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. The reaction was stirred for 24h at rt (~20ºC). Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 20% EtOAc/hexanes → 30% EtOAc/hexanes with 0.5% AcOH as eluent gave product as colorless oil. Run 1: (33.1 mg, 0.203 mmol, 51%), (7.4 mg rsm, 0.045 mmol, 11%). Run 2: (34.1 mg, 0.209 mmol, 52%), (11.1 mg rsm, 0.067 mmol, 17%). Run 3: (32.9 mg, 0.202 mmol, 50%), (10.0 mg rsm, 0.060 mmol, 15%). **Average: 51% yield ± 1.0, 14% rsm ± 3.1.**

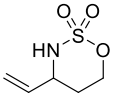
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.83 (br. d, *J* = 8.0 Hz, 1H), 4.64 (dd, *J* = 8.5, 6.4 Hz, 1H), 4.34 (t, *J* = 8.2 Hz, 1H), 3.32 (app. p, *J* = 7.4 Hz, 1H), 1.04 (qt, *J* = 8.5, 4.7 Hz, 1H), 0.71 - 0.61 (m, 2H), 0.44 (dq, *J* = 9.7, 5.0 Hz, 1H), 0.31 (dq, *J* = 10.1, 5.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 74.6, 61.5, 12.6, 3.3, 2.6; IR (thin film, cm^{-1}): 3267, 3011, 1391, 1339, 1189, 1054, 966, 832, 789; HRMS (ESI) *m/z* calculated for $C_5H_9NO_3SNa$ $[M+Na]^+$: 186.0201, found 186.0208.

Table S4. Allylic C—H bond substrate scope



Isolated yields are average of three runs. * Conditions: 5 mol% [FePc]Cl, 5 mol% $AgSbF_6$, 2 equiv. $PhI(OPiv)_2$, 4:1 PhMe/MeCN (0.5M), rt, 8h. † Used 10 mol% catalyst.

(±)-4-vinyl-1,2,3-oxathiazinane 2,2-dioxide [20].



In both cases, product was purified via flash column chromatography on silica (35 mm fritted glass column, 120 mm SiO_2) using 3:1 hexanes/EtOAc and collected as a

mixture of sulfamate ester and product and yields determined by ^{1}H NMR. Additional column purification using 10% hexanes/CH_2Cl_2 → CH_2Cl_2 → 2% Et_2O/CH_2Cl_2 affords pure product as a pale yellow oil. Ins./azir. ratios determined by ^{1}H NMR of the crude reaction mixture.

FePc conditions: Pent-4-en-1-yl sulfamate **S15** (66.1 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, 0.5M) were used.

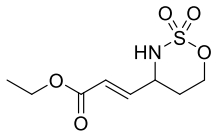
Run 1: (13.5 mg, 0.083 mmol, 21%), (15.7 mg rsm, 0.095 mmol, 24%). Run 2: (14.2 mg, 0.087 mmol, 22%), (15.7 mg rsm, 0.095 mmol, 24%). Run 3: (15.5 mg, 0.095 mmol, 24%), (18.2 mg rsm, 0.110 mmol, 28%). **Average: 22% yield ± 1.5 (ins./azir. crude = 7:1), 25% rsm ± 2.3.**

Mn(^{t}BuPc) conditions: Pent-4-en-1-yl sulfamate **S15** (66.1 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.2 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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used.

Run 1: (33.7 mg, 0.207 mmol, 52%), (12.6 mg rsm, 0.076 mmol, 19%). Run 2: (32.0 mg, 0.196 mmol, 49%), (10.6 mg rsm, 0.064 mmol, 16%). Run 3: (31.2 mg, 0.191 mmol, 48%), (8.1 mg rsm, 0.050 mmol, 12%). **Average: 50% yield ± 1.9 (ins./azir. crude = 7:1), 16% rsm ± 3.5.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.82 (ddd, J = 17.1, 10.6, 4.9 Hz, 1H), 5.36-5.25 (m, 2H), 4.81-4.72 (m, 1H), 4.57 (ddd, J = 11.9, 4.6, 2.2 Hz, 1H), 4.38-4.30 (m, 1H), 4.19 (d, J = 8.7 Hz, 1H), 1.94-1.80 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 135.0, 117.5, 71.8, 57.0, 29.2. These data are in agreement with that previously reported in the literature.[12]

(±)-ethyl (*E*)-3-(2,2-dioxido-1,2,3-oxathiazinan-4-yl)acrylate [21].



In both cases, reaction stirred at rt for 12 h. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 120 mm SiO_2) using 20% acetone/hexanes → 30% acetone/hexanes → 40% acetone/hexanes.

FePc conditions: ethyl (*E*)-6-(sulfamoyloxy)hex-2-enoate **S16** (94.9 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, 0.5M) were used.

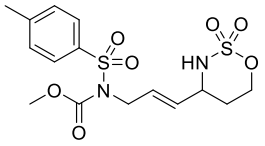
Run 1: (10.4 mg, 0.044 mmol, 11%), (55.1 mg rsm, 0.232 mmol, 58%). Run 2: (14.8 mg, 0.063 mmol, 16%), (48.4 mg rsm, 0.204 mmol, 51%). Run 3: (9.2 mg, 0.039 mmol, 10%), (66.4 mg rsm, 0.280 mmol, 70%). **Average: 12% yield ± 2.6, 60% rsm ± 7.8.**

Mn(^{t}BuPc) conditions: Ethyl (*E*)-6-(sulfamoyloxy)hex-2-enoate **S16** (94.9 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.2 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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used.

Run 1: (71.3 mg, 0.303 mmol, 76%), <10% rsm. Run 2: (71.6 mg, 0.305 mmol, 76%) <10% rsm. Run 3: (72.7 mg, 0.309 mmol, 77%) <10% rsm. **Average: 77% yield ± 0.5, <10% rsm.**

Product was isolated as a yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.84 (dd, J = 15.9, 4.7 Hz, 1H), 6.04 (dd, J = 15.6, 1.8 Hz, 1H), 4.82-4.77 (m, 1H), 4.61 (ddd, J = 11.8, 3.4, 2.5 Hz, 1H), 4.56-4.50 (m, 1H), 4.23 (q, J = 7.1 Hz, 2H), 4.15 (br. d, J = 10.5 Hz, 1H), 1.94-1.89 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 165.8, 143.1, 123.0, 71.6, 61.2, 55.8, 28.9, 14.3. These data are in agreement with that previously reported in the literature.[12]

(±)-Methyl (*E*)-(3-(2,2-dioxido-1,2,3-oxathiazinan-4-yl)allyl)(tosyl)carbamate [22].

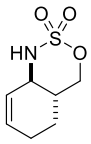


(*E*)-6-((*N*-(methoxycarbonyl)-4-methylphenyl)sulfonamido)hex-4-en-1-yl sulfamate **S17** (81.3 mg, 0.200 mmol, 1.0 equiv), [Mn(*t*BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 4:1 PhMe/MeCN (400 μL, 0.5M) were used. Reaction stirred at rt for 12 h. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 120 mm SiO_2) using 2:1 hexane/EtOAc →1:1 hexanes/EtOAc. Pure product was isolated as a white solid.

Run 1: (58 mg, 0.144 mmol, 72%), <5% rsm. Run 2: (59 mg, 0.146 mmol, 73%), <5% rsm. Run 3: (60 mg, 0.149 mmol, 76%), <5% rsm. **Average: 73% yield ± 1.5, <5% rsm.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.86 (dt, *J* = 15.6, 5.7 Hz, 1H), 5.76 (dd, *J* = 15.6, 5.2 Hz, 1H), 4.76 (td, *J* = 11.7, 11.0, 4.4 Hz, 1H), 4.60-4.56 (m, 1H), 4.46 (d, *J* = 5.5 Hz, 2H), 4.38 (tt, *J* = 10.2, 5.0 Hz, 1H), 3.96 (d, *J* = 10.3 Hz, 1H), 3.71 (s, 3H), 2.45 (s, 3H), 1.95-1.82 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 152.6, 145.1, 136.2, 130.9, 129.6, 128.5, 128.1, 71.8, 56.3, 54.2, 47.9, 29.4, 21.8; IR (film, cm^{-1}) 3255, 2960, 1736, 1596, 1443, 1359, 1242, 1170, 1089, 1011, 973, 937, 910, 866, 771, 736, 673, 579, 546; HRMS (ESI) *m/z* calculated for $C_{15}H_{21}N_2O_7S_2$ $[M+H]^+$: 405.0790, found 405.0786.

(±)-hexahydrobenzo[*d*][1,2,3]oxathiazine 2,2-dioxide [23].

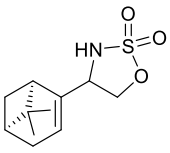


(±)-cyclohex-3-en-1-ylmethyl sulfamate **S18** (76.5 mg, 0.400 mmol, 1.0 equiv), [Mn(*t*BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 120 mm SiO_2) using 5:1 hexanes/EtOAc. Pure product was isolated as a white solid as a single diastereomer.

Run 1: (50.8 mg, 0.268 mmol, 67%), <5% rsm. Run 2: (54.4 mg, 0.287 mmol, 72%), <5% rsm. Run 3: (51.5 mg, 0.272 mmol, 68%), <5% rsm. **Average: 69% yield ± 2.2, <5% rsm.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.06-6.02 (m, 1H), 5.75-5.72 (m, 1H), 4.96 (dd, *J* = 11.8, 3.1 Hz, 1H), 4.35 (dd, *J* = 11.8, 1.4 Hz, 1H), 4.32-4.28 (m, 1H), 4.05 (br. d, *J* = 11.2 Hz, 1H), 2.31-2.12 (m, 2H), 1.92 (tdd, *J* = 14.1, 11.2, 5.9 Hz, 1H), 1.72-1.67 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 133.6, 123.7, 76.8, 52.4, 31.1, 25.0, 20.0. These data are in agreement with that previously reported in the literature.[12]

4-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-1,2,3-oxathiazolidine 2,2-dioxide [24].



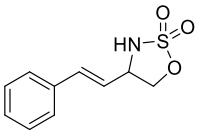
(-)-2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl sulfamate **S19** (98.1 mg, 0.400 mmol, 1.0 equiv), [Mn(*t*BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 120 mm SiO_2) using 5:1 hexanes/EtOAc. Pure product was isolated as a white solid and a 2:1 mixture of inseparable diastereomers.

Run 1: (57.3 mg, 0.235 mmol, 59%), <5% rsm. Run 2: (59.7 mg, 0.245 mmol, 61%), <5% rsm. Run 3: (58.4 mg, 0.240 mmol, 60%), <5% rsm. **Average: 60% yield ± 1.3, <5% rsm**.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.72-5.70 (m, 1H-D_{maj} + 1H-D_{min}), 4.58-4.46 (m, 2H-D_{maj} + 2H-D_{min}), 4.32 (s, 1H-D_{maj} + 1H-D_{min}), 4.20 (t, *J* = 8.4 Hz, 1H-D_{min}), 4.16 (t, *J* = 8.1 Hz, 1H-D_{maj}), 2.48 (dq, *J* = 8.9, 5.7 Hz, 1H-D_{maj} + 1H-D_{min}), 2.40-2.22 (m, 3H-D_{maj} + 3H-D_{min}), 2.18-2.12 (m,

1H-D_{maj} + 1H-D_{min}), 1.32 (s, 3H-D_{maj} + 3H-D_{min}), 1.16 (d, J = 8.9 Hz, 1H-D_{maj}), 1.13 (d, J = 8.9 Hz, 1H-D_{min}), 0.83 (s, 3H-D_{min}), 0.79 (s, 3H-D_{maj}); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.2, 141.1, 124.7, 124.1, 72.5, 72.2, 60.1, 60.0, 41.6, 41.4, 40.6, 40.6, 38.1, 31.6, 31.4, 31.4, 26.0, 25.9, 21.3, 21.2; IR (film, cm^{-1}) 3281, 2918, 2832, 1721, 1469, 1384, 1347, 1287, 1064, 973, 922, 886, 796, 773, 658, 637, 513, 487; HRMS (ESI) *m/z* calculated for $C_{11}H_{17}NO_3SNa$ $[M+Na]^+$: 266.0827, found 266.0827.

(±)-(*E*)-4-styryl-1,2,3-oxathiazolidine 2,2-dioxide [25].

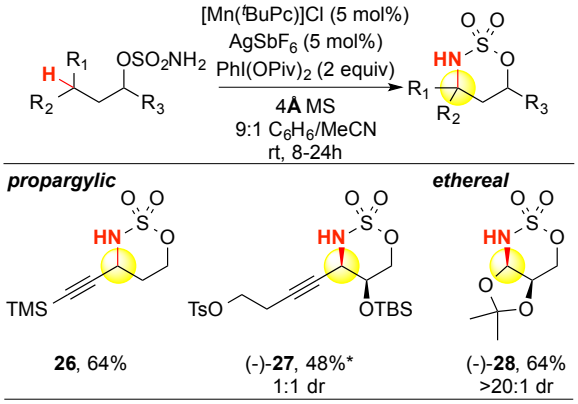


(*E*)-4-phenylbut-3-en-1-yl sulfamate **S20** (90.0 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc. Pure product was isolated as a white solid. Insertion to aziridination ratio was determined from ^{1}H NMR of the crude mixture.

Run 1: (57.7 mg, 0.256 mmol, 64%), <5% rsm. Run 2: (55.1 mg, 0.245 mmol, 61%), <5% rsm. Run 3: (54.6 mg, 0.242 mmol, 61%), <5% rsm. **Average: 62% yield ± 1.7 (ins./azir. crude = 7:1), <5% rsm.**

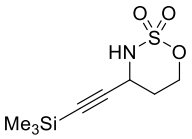
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.42-7.30 (m, 5H), 6.75 (d, J = 15.8 Hz, 1H), 6.13 (dd, J = 15.8, 7.8 Hz, 1H), 4.77-4.64 (m, 2H), 4.46 (br. d, J = 6.6 Hz, 1H), 4.36 (t, J = 8.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 136.7, 135.0, 129.2, 129.0, 127.0, 122.1, 74.0, 58.7. These data are in agreement with that previously reported in the literature.[17]

Table S5. Propargylic and ethereal C—H bond substrate scope.



Isolated yields are average of three runs. * Used 10 mol% cat.

(±)-4-((trimethylsilyl)ethynyl)-1,2,3-oxathiazinane 2,2-dioxide [26].



5-(trimethylsilyl)pent-4-yn-1-yl sulfamate **S21** (94.13 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc. Pure product was isolated as a white solid.

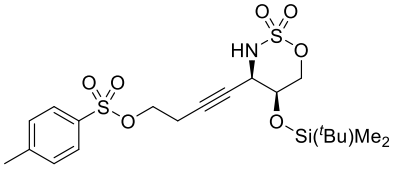
Run 1: (60.0 mg, 0.257 mmol, 64%), <5% rsm. Run 2: (58.2 mg, 0.249 mmol, 62%), <5% rsm. Run 3: (60.0 mg, 0.257 mmol, 64%), <5% rsm. **Average: 64% yield ± 1.1, <5% rsm.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.70 (ddd, *J* = 12.7, 11.8, 2.5 Hz, 1H), 4.58-4.51 (m, 2H), 4.30 (d, *J* = 10.1 Hz, 1H), 2.10 (dddd, *J* = 14.8, 12.6, 11.6, 4.9 Hz, 1H), 2.01-1.97 (m, 1H), 0.17 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 100.1, 91.6, 71.4, 48.1, 30.9, -0.3; IR (film, cm^{-1}) 3233, 2962, 2901, 2193, 1717, 1463, 1430, 1358, 1254, 1190, 1170, 1077, 1061, 997, 941, 922, 876, 780, 757, 710, 665; HRMS (ESI) *m/z* calculated for $C_8H_{16}NO_3SiS$ $[M+H]^+$: 234.0620, found 234.0623.

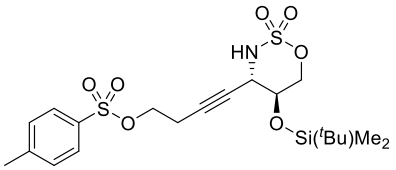
(-)-4-((4*S*,5*S*)-5-((*tert*-butyldimethylsilyl)oxy)-2,2-dioxido-1,2,3-oxathiazinan-4-yl)but-3-yn-1-yl 4-methylbenzenesulfonate [27].

(*S*)-2-((*tert*-butyldimethylsilyl)oxy)-7-(tosyloxy)hept-4-yn-1-yl sulfamate **S22** (98.3 mg, 0.200 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 50 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. Reaction stirred at rt for 12 hours. Product was purified via flash column chromatography on silica (75 mL SiO_2) using 5:1 hexanes/EtOAc → 4:1 hexanes/EtOAc. Product was isolated as a clear oil as a 1:1 mixture of diastereomers. Additional column purification using a gradient of 10% hexanes/CH_2Cl_2 → CH_2Cl_2 → 1% Et_2O/CH_2Cl_2 allowed separation of diastereomers.

Run 1: (45.7 mg, 0.093 mmol, 47%), <5% rsm. Run 2: (47.9 mg, 0.098 mmol, 49%), <5% rsm. Run 3: (46.5 mg, 0.095 mmol, 48%), <5% rsm. **Average: 48% yield ± 1, <5% rsm.**

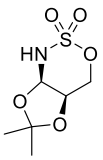


Syn diastereomer: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 4.65-4.54 (m, 3H), 4.28 (dd, *J* = 12.3, 1.9 Hz, 1H), 4.07 (td, *J* = 6.9, 1.0 Hz, 2H), 3.67 (dt, *J* = 2.1, 1.0 Hz, 1H), 2.58 (td, *J* = 6.8, 1.7 Hz, 2H), 2.47 (s, 3H), 0.92 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 145.4, 132.8, 130.1, 128.1, 81.4, 76.9, 75.9, 67.1, 64.0, 53.4, 25.7, 21.8, 19.8, 18.2, -4.6, -4.7; IR (film, cm^{-1}) 3257, 2929, 2857, 1422, 1364, 1257, 1176, 1137, 1074, 1028, 986, 904, 864, 838, 776, 664, 553, 480, 459; $[\alpha]_D^{25}$= -18.2° (*c* = 1.28, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{20}H_{32}NO_7S_2Si$ $[M+H]^+$: 490.1389, found 490.1386.



Anti diastereomer: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 4.55 (d, *J* = 8.7 Hz, 1H), 4.45 (dd, *J* = 11.7, 4.0 Hz, 1H), 4.31 (dd, *J* = 11.6, 8.2 Hz, 1H), 4.22 (ddt, *J* = 9.6, 7.8, 2.2 Hz, 1H), 4.11 (t, *J* = 6.6 Hz, 2H), 3.79 (td, *J* = 7.9, 4.0 Hz, 1H), 2.61 (td, *J* = 6.7, 2.0 Hz, 2H), 2.47 (s, 3H), 0.89 (s, 9H), 0.12 (s, 3H), 0.12 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 145.4, 132.9, 130.1, 128.0, 82.4, 77.3, 73.1, 67.3, 66.4, 53.3, 25.6, 21.8, 20.0, 18.1, -4.5, -4.6; IR (film, cm^{-1}) 3257, 2929, 2857, 1719, 1598, 1432, 1369, 1259, 1190, 1133, 1046, 904, 840, 782, 664, 618, 555, 492; $[\alpha]_D^{25}$ = -38.1° (*c* = 0.54, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{20}H_{32}NO_7S_2Si$ $[M+H]^+$: 490.1389, found 490.1388.

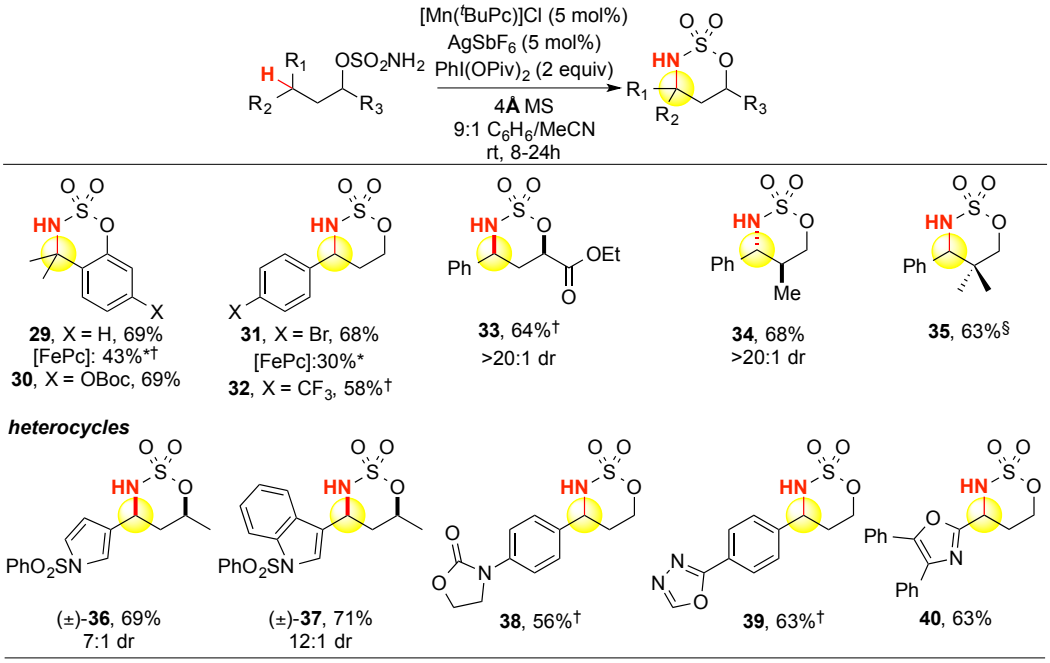
(-)-(4*R*,7*R*)-6,6-dimethyltetrahydro-[1,3]dioxolo[4,5-*d*][1,2,3]oxathiazine 2,2-dioxide [28].



(-)-(*S*)-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl sulfamate **S23** (84.49 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 120 mm SiO_2) using 3:1 hexanes/EtOAc → 2:1 hexanes/EtOAc. Pure product was isolated as a pale yellow solid.

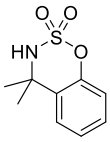
Run 1: (55.5 mg, 0.265 mmol, 66%), <5% rsm. Run 2: (52.6 mg, 0.251 mmol, 63%), <5% rsm. Run 3: (52.9 mg, 0.253 mmol, 63%), <5% rsm. **Average: 64% yield ± 1.4, <5% rsm.**
^{1}H-NMR (500 MHz, CD_3OD) δ 5.41 (d, J = 5.1 Hz, 1H), 4.59-4.58 (m, 2H), 4.30 (dt, J = 5.2, 1.6 Hz, 1H), 1.54 (s, 3H), 1.34 (s, 3H); ^{13}C-NMR (125 MHz, CD_3OD) δ 111.5, 85.6, 71.7, 71.5, 26.9, 25.6. $[\alpha]_D^{25}$= -36.7° (c = 0.71, acetone). These data are in agreement with that previously reported in the literature.[14]

Table S6. Benzylic C—H bond substrate scope.



Isolated yields are average of three runs. * Conditions: 5 mol% [FePc]Cl, 5 mol% $AgSbF_6$, 2 equiv. $PhI(OPiv)_2$, 4:1 PhMe/MeCN (0.5M), rt, 8h. † Used 10 mol% catalyst. § 10% of 1° C—H amination also isolated.

4,4-dimethyl-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide [29].

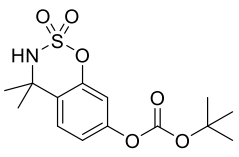


In both cases, material was purified *via* flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 15% EtOAc/hexanes with 0.5% AcOH as eluent.

FePc conditions: 2-isopropylphenyl sulfamate **S24** (86.1 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24.2 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. The reaction was stirred for 6h at rt (~20ºC). Product and recovered starting material were isolated as a mixture after column chromatography.
Run 1: (35.5 mg, 0.167 mmol, 42%), (18.7 mg rsm, 0.087 mmol, 22%). Run 2: (37.7 mg, 0.177 mmol, 44%), (20.1 mg rsm, 0.093 mmol, 23%). Run 3: (37.0 mg, 0.174 mmol, 43%), (17.2 mg rsm, 0.080 mmol, 20%). **Average: 43% yield ± 1.0, 22% rsm ± 1.5.**
Mn(*t*BuPc) conditions: 2-isopropylphenyl sulfamate **S24** (86.1 mg, 0.400 mmol, 1.0 equiv), [Mn(tBuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), crushed 4Å MS (100 mg), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (800 µL) were used. The reaction was stirred for 17h at rt (~20ºC).

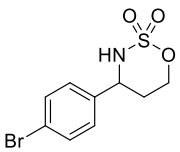
Run 1: (61.2 mg, 0.287 mmol, 72%), 0% rsm. Run 2: (59.0 mg, 0.277 mmol, 69%), 0% rsm. Run 3: (55.9 mg, 0.262 mmol, 66%), 0% rsm. **Average: 69% yield ± 3.0, 0% rsm.**
Product was isolated as an off-white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.31-7.18 (m, 3H), 7.01-6.97 (m, 1H), 4.74 (br. s, 1H), 1.73 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 149.4, 129.3, 128.0, 126.6, 125.8, 119.3, 60.3, 30.8. IR (ATR, cm^{-1}): 3267, 2983, 2937, 1610, 1578, 1483, 1446, 1430, 1417, 1386, 1362, 1353, 1284, 1211, 1170, 1117, 1085, 1038, 989, 889, 845; HRMS (ESI) *m/z* calculated for $C_9H_{12}NO_3S$ $[M+H]^+$: 214.0538, found 214.0534.

***tert*-butyl (4,4-dimethyl-2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-7-yl) carbonate [30].**



5-((tert-butoxycarbonyl)oxy)-2-isopropylphenyl sulfamate **S25** (99.4 mg, 0.300 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (12.4 mg, 0.015 mmol, 0.05 equiv), $AgSbF_6$ (5.2 mg, 0.015 mmol, 0.05 equiv), crushed 4Å MS (75 mg), $PhI(OPiv)_2$ (244 mg, 0.600 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (600 μL) were used. The reaction was stirred for 17h at rt (~20ºC). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 15% EtOAc/hexanes → 20% EtOAc/hexanes with 0.5% AcOH as eluent afforded product as white solid.
Run 1: (69.1 mg, 0.210 mmol, 70%), <5% rsm. Run 2: (68.7 mg, 0.209 mmol, 70%), <5% rsm. Run 3: (65.9 mg, 0.200 mmol, 67%), <5% rsm. **Average: 69% yield ± 1.7, <5% rsm.**
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J = 8.5 Hz, 1H), 7.05 (dd, J = 8.5, 2.5 Hz, 1H), 6.90 (t, J = 1.8 Hz, 1H), 4.64 (br. s, 1H), 1.71 (s, 6H), 1.56 (s, 9H).;^{13}C-NMR (125 MHz, $CDCl_3$) δ 151.3, 150.9, 149.6, 127.2, 125.4, 118.9, 112.4, 84.6, 60.1, 30.8, 27.7; IR (ATR, cm^{-1}): 3237, 2984, 1734, 1498, 1435, 1417, 1392, 1365, 1288, 1247, 1205, 1175, 1139, 1119, 1090, 961, 887, 856, 811; HRMS (ESI) *m/z* calculated for $C_{14}H_{19}NO_6SNa$ $[M+Na]^+$: 352.0831, found 352.0831.

(±)-4-(4-bromophenyl)-1,2,3-oxathiazinane 2,2-dioxide [31].

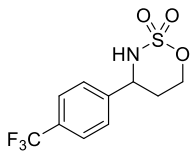


In both cases, the reaction was stirred for 12h at rt (~20ºC). Crude material was purified *via* flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 25% EtOAc/hexanes → 30% EtOAc/hexanes with 0.5% AcOH as eluent.

FePc conditions: 2,3-(4-bromophenyl)propyl sulfamate **S26** (118.0 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (12.1 mg, 0.02 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 PhMe/MeCN (800 μL) were used. Product and recovered starting material were isolated as a mixture.
Run 1: (30.4 mg, 0.104 mmol, 26%), (48.7 mg rsm, 0.166 mmol, 41%). Run 2: (39.2 mg, 0.134 mmol, 34%), (51.9 mg rsm, 0.176 mmol, 44%). Run 3: (36.1 mg, 0.123 mmol, 31%), (50.5 mg rsm, 0.172 mmol, 43%). **Average: 30% yield ± 4.0, 43% rsm ± 1.5.**
Mn(^{t}BuPc) conditions: 3-(4-bromophenyl)propyl sulfamate **S26** (118.0 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), crushed 4Å MS (100 mg), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (800 μL) were used.
Run 1: (80.1 mg, 0.274 mmol, 69%), 0% rsm. Run 2: (77.2 mg, 0.264 mmol, 66%), 0% rsm. Run 3: (79.1 mg, 0.271 mmol, 68%), 0% rsm. **Average: 68% yield ± 1.5, 0% rsm.**
Product was isolated as a white solid. ^{1}H-NMR (500 MHz, acetone-d_6) δ 7.59 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 6.40 (br. d, J = 9.9 Hz, 1H), 4.92-4.83 (m, 1H), 4.79 (td, J = 12.0,

2.5 Hz, 1H), 4.69 (ddd, J = 12.0, 4.8, 1.8 Hz, 1H), 2.30-2.18 (m, 1H), 2.14 (m, 1H); ^{13}C-NMR (500 MHz, acetone-d_6) δ 139.5, 132.6, 129.6, 122.4, 72.7, 59.3, 30.8; IR (ATR, cm^{-1}): 3258, 2961, 1490, 1406, 1434, 1420, 1297, 1235, 1193, 1184, 1174, 1063, 1018, 1007, 937, 904, 868, 833, 806; HRMS (ESI) *m/z* calculated for $C_9H_9NO_3SBr$ [M-H]$^-$: 289.9487, found 289.9489.

(±)-4-(4-(trifluoromethyl)phenyl)-1,2,3-oxathiazinane 2,2-dioxide [32].

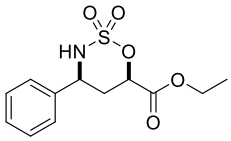


3-(4-trifluoromethyl)propyl sulfamate **S27** (113.3 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.1 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), crushed 4Å MS (100 mg), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (800 μL) were used. The reaction was stirred for 12h at rt (~20ºC). Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 25% EtOAc/hexanes → 35% EtOAc/hexanes with 0.5% AcOH as eluent afforded product as white solid.

Run 1: (67.3 mg, 0.239 mmol, 60%), <5% rsm. Run 2: (64.2 mg, 0.228 mmol, 57%), <5% rsm. Run 3: (65.4 mg, 0.233 mmol, 58%), <5% rsm. **Average: 58% yield ± 1.5, <5% rsm.**

^{1}H-NMR (500 MHz, Acetonitrile-d_3) δ 7.73 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.1 Hz, 2H), 5.60 (br. d, J = 10.0 Hz, 1H), 4.91 (ddd, J = 12.6, 10.1, 3.0 Hz, 1H), 4.77 (td, J = 12.1, 2.5 Hz, 1H), 4.67 (ddd, J = 11.6, 5.0, 1.8 Hz, 1H), 2.21-2.14 (m, 1H), 2.09-2.05 (m, 1H); ^{13}C-NMR (125 MHz, Acetonitrile-d_3) δ 144.0, 130.6 (q, J = 32.3 Hz), 128.3, 126.5 (q, J = 3.9 Hz), 125.2 (q, J = 271.3 Hz), 73.3, 59.3, 30.3; ^{19}F-NMR (470 MHz, Acetonitrile-d_3) δ -62.82; IR (ATR, cm^{-1}): 3232, 1623, 1444, 1412, 1364, 1350, 1326, 1249, 1187, 1159, 1115, 1067, 1018, 946, 915, 870, 845, 816; HRMS (EI) *m/z* calculated for $C_{10}H_{10}NO_3SF_3$ [M$^+$]: 281.03335, found 281.03377.

(±)-ethyl-4-phenyl-1,2,3-oxathiazinane-6-carboxylate 2,2-dioxide [33].

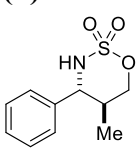


(±)-ethyl 4-phenyl-2-(sulfamoyloxy)butanoate **S28** (114.9 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.2 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc. Pure product was isolated as a white solid as a single diastereomer.

Run 1: (74.9 mg, 0.263 mmol, 66%), <5% rsm. Run 2: (74.0 mg, 0.259 mmol, 65%), <5% rsm. Run 3: (70.1 mg, 0.246 mmol, 61%), <5% rsm. **Average: 64% yield ± 2.2, <5% rsm.**

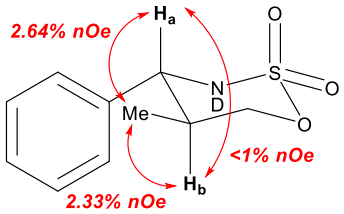
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.44-7.37 (m, 5H), 5.33 (dd, J = 12.5, 2.5 Hz, 1H), 4.88 (ddd, J= 12.5, 10.0, 3.0 Hz, 1H), 4.69 (br. d, J = 9.5 Hz, 1H), 4.29 (q, J = 7.0 Hz, 2H), 2.41 (dt, J = 14.0, 3.0 Hz, 1H), 2.29 (dt, J = 14.5, 12.0 Hz, 1H), 1.31 (t, J = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 167.4, 137.5, 129.3, 129.2, 126.7, 78.8, 62.9, 58.5, 32.4, 14.1. These data are in agreement with that previously reported in the literature.[8]

(±)-*trans*-5-methyl-4-phenyl-1,2,3-oxathiazinane 2,2-dioxide [34].



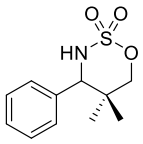
(±)-2-methyl-3-phenylpropyl sulfamate **S29** (91.7 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), crushed 4Å MS (100 mg), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (800 μL) were used. The reaction was stirred for 8h at rt

(~20ºC). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 20% EtOAc/hexanes → 30% EtOAc/hexanes with 0.5% AcOH as eluent gave product as white solid as a single diastereomer.
Run 1: (64.8 mg, 0.285 mmol, 71%), 0% rsm. Run 2: (59.1 mg, 0.260 mmol, 65%), 0% rsm. Run 3: (61.5 mg, 0.271 mmol, 68%), 0% rsm. **Average: 68% yield ± 3.0, 0% rsm.**
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.43-7.34 (m, 3H), 7.34-7.29 (m, 2H), 4.70 (d, *J* = 8.9 Hz, 1H), 4.52-4.44 (m, 2H), 4.34 (dd, *J* = 11.0, 9.0 Hz, 1H), 2.42-2.31 (m, 1H), 0.69 (d, *J* = 6.7 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 137.1, 129.3, 129.2, 127.4, 76.7, 65.6, 34.0, 12.0; IR (ATR, cm^{-1}): 3260, 2983, 2940, 1459, 1424, 1354, 1193, 1175, 1088, 1072, 1016, 968, 923, 887; HRMS (ESI) *m/z* calculated for $C_{10}H_{14}NO_3S$ $[M+H]^+$: 228.0694, found 228.0691.

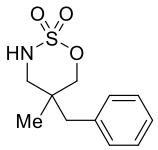


Stereochemistry Assignment: To avoid potential proton peak overlap with the exchangeable NH proton, D_2O was added into NMR sample to saturate the NH peak. ^{1}H-NMR (500 MHz, $CDCl_3$, D_2O) δ 7.43-7.34 (m, 3H), 7.34-7.29 (m, 2H), 4.52-4.44 (m, 2H), 4.34 (d, *J* = 11.0 Hz, 1H), 2.42-2.31 (m, 1H), 0.69 (dd, *J* = 6.9, 1.3 Hz, 3H). Notably the coupling pattern of benzylic proton H_a (4.34 ppm) changed from dd (*J* = 11.0, 9.0 Hz) to d (*J* = 11.0 Hz).
A series of 1D nOe difference experiments were conducted to assign the relative stereochemistry of the structure. When H_a was irradiated, 2.64% nOe was observed on corresponding methyl peak while only 0.94% nOe was observed on H_b peak. Similarly, when H_b was irradiated, 2.33% nOe of methyl was observed while H_a only gave 0.09% nOe. These results indicate H_a and H_b are in an *anti*-configuration.

(±)-5,5-dimethyl-4-phenyl-1,2,3-oxathiazinane 2,2-dioxide [35].

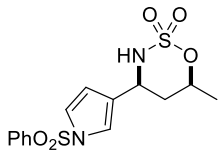


2,2-dimethyl-3-phenylpropyl sulfamate **S30** (97.3 mg, 0.400 mmol, 1.0 equiv), [Mn(*t*BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), crushed 4Å MS (100 mg), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. The reaction was stirred for 17h at rt (~20ºC). Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 15% EtOAc/hexanes → 20% EtOAc/hexanes with 0.5% AcOH as eluent gave product as white solid. Minor 1° C—H amination product **S39** was also isolated separately as white solid.
Run 1: (59.7 mg benzylic, 0.247 mmol, 62%), (8.8 mg 1°, 0.036 mmol, 9%), 0% rsm. Run 2: (58.8 mg benzylic, 0244 mmol, 61%), (9.3 mg 1°, 0.039 mmol, 10%), 0% rsm. Run 3: (63.3 mg benzylic, 0.262 mmol, 66%), (10.7 mg 1°, 0.045 mmol, 11%), 0% rsm. **Average: 63% benzylic ± 2.6, 10% 1° ± 1.0, 0% rsm.**
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.41-7.33 (m, 3H), 7.24-7.17 (m, 2H), 5.11 (d, *J* = 7.9 Hz, 1H), 4.62 (d, *J* = 7.4 Hz, 1H), 4.60 (d, *J* = 3.9 Hz, 1H), 4.10 (d, *J* = 11.4 Hz, 1H), 1.09 (s, 3H), 0.80 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 135.1, 128.8, 128.5, 128.0, 82.5, 67.3, 34.0, 21.5, 17.4; IR (ATR, cm^{-1}): 3272, 2974, 1711, 1469, 1459, 1428, 1365, 1349,1188, 1047, 1013. 960, 908, 851, 803; HRMS (ESI) *m/z* calculated for $C_{11}H_{16}NO_3S$ $[M+H]^+$: 242.0851, found 242.0847.



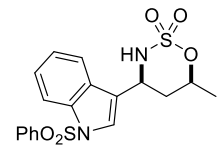
(±)-5-benzyl-5-methyl-1,2,3-oxathiazinane 2,2-dioxide [S39].
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.36 -7.27 (m, 3H), 7.17-7.11 (m, 2H), 4.76 (t, *J* = 7.5 Hz, 1H), 4.35 (d, *J* = 11.8 Hz, 1H), 4.23 (d, *J* = 11.6 Hz, 1H), 3.39-3.28 (m, 2H), 2.82 (d, *J* = 13.4 Hz, 1H), 2.60 (d, *J* = 13.4 Hz, 1H), 0.94 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 135.4, 130.5, 128.7, 127.2, 79.7, 54.1, 40.6, 32.5, 19.1; IR (ATR, cm^{-1}): 3280, 2925, 1496, 1446, 1418,1391, 1356, 1337, 1174, 1155, 1028, 951, 931, 854; HRMS (ESI) *m/z* calculated for $C_{11}H_{16}NO_3S$ $[M+H]^+$: 242.0851, found 242.0845.

(±)-6-methyl-4-(1-(phenylsulfonyl)-1*H*-pyrrol-3-yl)-1,2,3-oxathiazinane 2,2-dioxide [36].



4-(1-(phenylsulfonyl)-1*H*-pyrrole-3-yl)butan-2-yl sulfamate **S31** (143 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. By ^{1}H NMR analysis of the crude mixture, the d.r. was determined to be 7:1 *syn:anti*. Flash column chromatography on silica (35 mm fritted glass column, 150mm SiO_2) using 10% EtOAc/hexanes → 60% EtOAc/hexanes as eluent gave oxathiazinane product as a ~7:1 *syn:anti* mixture of diastereomers. Pure *syn* diastereomer can be isolated using flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 9:1 hexanes/EtOAc → 1:1 hexanes/EtOAc. *Anti* diastereomer always eluted with *syn* diastereomer and trace rsm.
Run 1: (96.3 mg (6.8:1 *syn:anti*), 0.270 mmol, 68%), <5% rsm. Run 2: (101.1 mg (6.9:1 *syn:anti*), 0.284 mmol, 71%), <5% rsm. Run 3: (99.8 mg (7.1:1 *syn:anti*), 0.280 mmol, 70%), <5% rsm. **Average: 69% yield ± 1.7 (7:1 *syn*:*anti*), <5% rsm.**
Syn diastereomer: Pure product was isolated as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.6, 1.8, Hz, 2H), 7.64-7.60 (m, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.42-7.41 (m, 1H), 6.31-6.30 (m, 1H), 6.27 (t, *J* = 3.4 Hz, 1H), 5.44 (ddd, *J* = 12.5, 10.2, 2.6 Hz, 1H), 4.95 (dqd, *J* = 12.5, 6.3, 1.9 Hz, 1H), 3.69-3.67 (m, 1H), 2.08 (dt, *J* = 14.2, 2.4 Hz, 1H), 1.84 (dt, *J* = 14.4, 11.9 Hz, 1H), 1.45 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 134.5, 131.3, 129.5, 127.8, 124.3, 113.5, 111.4, 80.5, 50.5, 37.0, 21.2; HRMS (ESI) *m/z* calculated for $C_{14}H_{17}N_2O_5S$ $[M+H]^+$: 357.0579, found 357.0576.

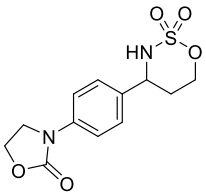
(±)-6-methyl-4-(1-(phenylsulfonyl)-1*H*-indol-3-yl)-1,2,3-oxathiazinane2,2-dioxide [37].



4-(1-(phenylsulfonyl)-1*H*-indol-3-yl)butan-2-yl sulfamate **S32** (164 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL) were used. By ^{1}H NMR analysis of the crude mixture, the d.r. was determined to be 12:1 *syn:anti*. Flash column chromatography on silica (25 mm fritted glass column, 150 mm SiO_2) using 9:1 hexanes/EtOAc → 3:2 hexanes/EtOAc as eluent gave oxathiazinane product as a ~12:1 *syn:anti* mixture of diastereomers. Pure *syn* diastereomer can be isolated using flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc as eluent.
Run 1: (115.8 mg, 0.285 mmol, 71%), <5% rsm. Run 2: (112.9 mg, 0.278 mmol, 70%), <5% rsm. Run 3: (119.3mg, 0.294 mmol, 73%), <5% rsm. **Average: 71% yield ± 1.2 (12:1 *syn:anti*), <5% rsm.**

Syn diastereomer: Pure product was isolated as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.90-7.88 (m, 2H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.58-7.53 (m, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.38-7.35 (m, 1H), 7.29-7.26 (m, 1H), 5.08-5.03 (m 2H), 4.14 (d, *J* = 10.3 Hz, 1H), 2.23 (dt, *J* = 14.1, 2.5 Hz, 1H), 2.02 (dt, *J* = 14.2, 11.9 Hz, 1H), 1.52 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 135.3, 134.4, 129.6, 128.4, 127.0, 125.9, 123.9, 123.2, 120.6, 120.1, 113.8, 80.6, 51.5, 36.0, 21.3; HRMS (ESI) *m/z* calculated for $C_{18}H_{19}N_2O_5S_2$ $[M+H]^+$: 407.0735, found 407.0731.

(±)-3-(4-(2,2-dioxido-1,2,3-oxathiazinan-4-yl)phenyl)oxazolidin-2-one [38].

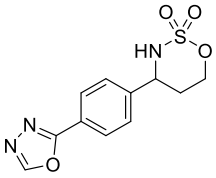


3-(4-(2-oxooxazolidin-3-yl)phenyl)propyl sulfamate **S33** (60.0 mg, 0.200 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 2:1:1 C_6H_6/Acetone/MeCN (600 μL, 0.33M) were used. Reaction stirred at 45^{o}C for 18h. Flash column chromatography on silica (35 mm fritted glass column, 75 mm SiO_2) using 30% EtOAc/hexanes → 75% EtOAc/hexanes as eluent gave oxathiazinane product as a white solid.

Run 1: (33.5 mg, 0.112 mmol, 56%), <5% rsm. Run 2: (32.1 mg, 0.108 mmol, 54%), <5% rsm. Run 3: (35.3 mg, 0.118 mmol, 59%), <5% rsm. **Average: 56% yield ± 2.1, <5% rsm.**

^{1}H NMR (500 MHz, Acetone-d_6) δ 7.67-7.64 (m, 2H), 7.52-7.50 (m, 2H), 6.32 (d, *J* = 10.1 Hz, 1H), 4.87-4.76 (m, 2H), 4.69 (ddd, *J* = 11.5, 5.0, 1.7 Hz, 1H), 4.52-4.48 (m, 2H), 4.17-4.14 (m, 2H), 2.30-2.21 (m, 1H), 2.12-2.08 (m, 1H); ^{13}C NMR (125 MHz, Acetone-d_6) δ 155.9, 139.9, 135.0, 128.0, 118.8, 72.7, 62.3, 59.4, 45.7, 31.0; HRMS (ESI) *m/z* calculated for $C_{12}H_{15}N_2O_5S$ $[M+H]^+$: 299.0702, found 299.0702.

(±)-4-(4-(1,3,4-oxadiazol-2-yl)phenyl)-1,2,3-oxathiazinane 2,2-dioxide [39].

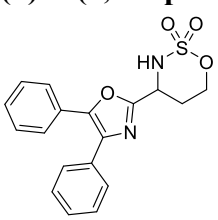


(4-(1,3,4-oxadiazol-2-yl)phenyl)propyl sulfamate **S34** (113 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.2 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 4:1 CH_2Cl_2/MeCN (1.2 mL, 0.33M) were used. The reaction stirred at rt for 18h. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 30% EtOAc/hexanes → 90% EtOAc/hexanes as eluent gave oxathiazinane product.

Run 1: (72.9 mg, 0.259 mmol, 65%), <5% rsm. Run 2: (70.1mg, 0.249 mmol, 62%), <5% rsm. Run 3: (71.2 mg, 0.253 mmol, 63%), <5% rsm. **Average: 63% yield ± 1.3, <5% rsm.**

^{1}H NMR (500 MHz, CD_3OD) δ 9.04 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 4.93 (dd, *J* = 11.9, 3.1 Hz, 1H), 4.81 (td, J=12.0, 2.6 Hz, 1H), 4.68 (ddd, *J* = 11.5, 4.8, 1.8 Hz, 1H), 2.24-2.10 (m, 2H); ^{13}C-NMR (125 MHz, CD_3OD) δ165.8, 155.5, 144.9, 128.6, 124.3, 73.1, 59.7, 31.0; HRMS (ESI) *m/z* calculated for $C_{11}H_{12}N_3O_4S$ $[M+H]^+$: 282.0549, found 282.0541.

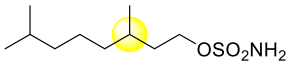
(±)-4-(4,5-diphenyloxazol-2-yl)-1,2,3-oxathiazinane 2,2-dioxide [40].



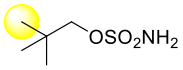
3-(4,5-diphenyloxazol-2-yl) propyl sulfamate **S35** (143 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. The reaction stirred at rt for 12h. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 30% EtOAc/hexanes → 80% EtOAc/hexanes gave oxathiazinane

product. Significant EtOAc remains on the product after prolonged vacuum; the peaks corresponding to EtOAc are labeled in the provided spectrum and yields reported account for this by integration in ^{1}H NMR.
Run 1: (87.4 mg, 0.245 mmol, 61%), <5% rsm. Run 2: (89.8 mg, 0.252 mmol, 63%), <5% rsm. Run 3: (90.2 mg, 0.253 mmol, 63%), <5% rsm. **Average: 63% yield ± 1.1, <5% rsm.**
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.63 (m, 2H), 7.61-7.58 (m, 2H), 7.43-7.36 (m, 6H), 5.15 (ddd, J = 11.9, 10.3, 3.2 Hz, 1H), 4.98-4.90 (m, 2H), 4.70 (ddd, J = 11.8, 5.0, 2.0 Hz, 1H), 2.38 (dddd, J = 14.8, 12.6, 11.8, 4.9 Hz, 1H), 2.25-2.20 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 146.7, 135.6, 131.6, 129.4, 129.0, 128.9, 128.8, 128.2, 128.0, 71.4, 53.1, 28.9; HRMS (ESI) *m/z* calculated for $C_{18}H_{17}N_2O_4S$ $[M+H]^+$: 357.0909, found 357.0910.

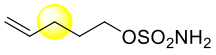
Effect of silver salt additive on reactivity:
Control experiments have demonstrated that $AgSbF_6$ itself is not a catalyst for the reaction, with only starting material recovered when the phthalocyanine catalyst is not present in the reaction. However, inclusion of $AgSbF_6$ is important for optimal reactivity, likely via an *in situ* metathesis that generates a cationic metal phthalocyanine complex. The magnitude to which $AgSbF_6$ impacts the overall reactivity increases as the substrate becomes more challenging (e.g. aliphatic C—H bonds, substrates without biasing groups). Below are reactivity comparisons under the optimized reaction conditions with and without $AgSbF_6$.



optimized conditions: 73% yield
without $AgSbF_6$: 22% yield



optimized conditions: 64% yield
without $AgSbF_6$: 36% yield



optimized conditions: 50% yield
without $AgSbF_6$: 13% yield

Hammett Study

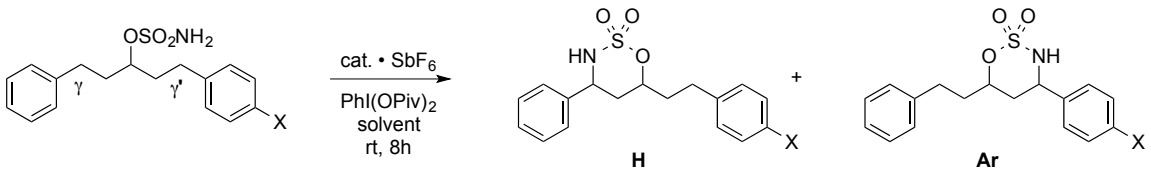
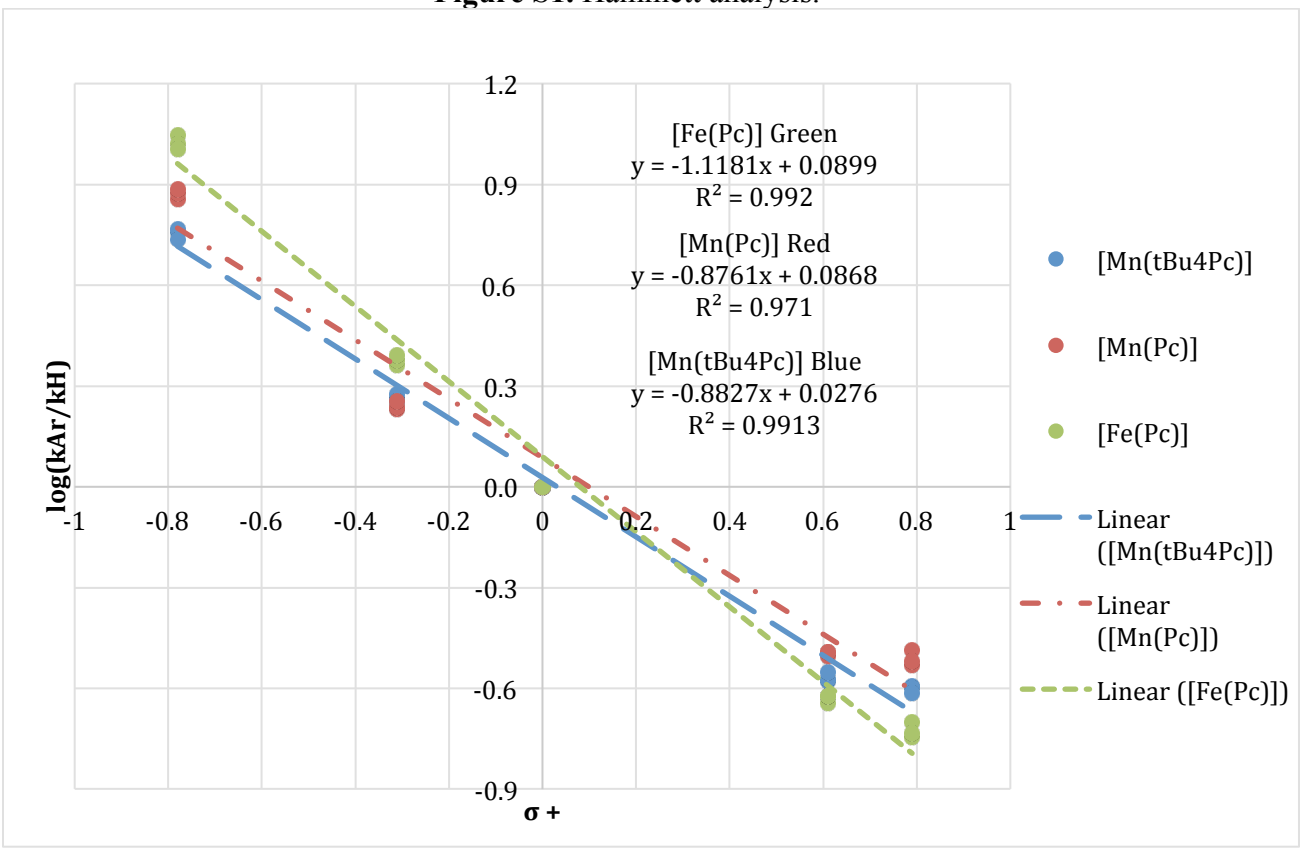


Figure S1. Hammett analysis.



Least Squared (LS) Regression was performed on each catalyst with 13 data point sets (3 runs for each of the 4 substrates and (0,0)). Analysis of the Hammett ρ values is listed in the following table. These data were obtained in Excel with LINEST function.

Catalyst	ρ from LS	SD (ρ)	ρ Value
[Mn(^{t}BuPc)]	-0.883	0.025	-0.883 ± 0.025
[MnPc]	-0.876	0.046	-0.876 ± 0.046
[FePc]	-1.118	0.030	-1.118 ± 0.030

Table S7. Raw data for [FePc].

Substrate	σ +	γ:γ'	k_{Ar}/k_H	$\log(k_{Ar}/k_H)$
NO_2	0.79	5.02:1	0.1992	-0.7007
NO_2	0.79	5.58:1	0.1792	-0.7466
NO_2	0.79	5.41:1	0.1848	-0.7332
CF_3	0.61	4.4:1	0.2273	-0.6435
CF_3	0.61	4.2:1	0.2381	-0.6232
CF_3	0.61	4.2:1	0.2381	-0.6232
Me	-0.31	1:2.30	2.3000	0.3617
Me	-0.31	1:2.37	2.3700	0.3747
Me	-0.31	1:2.47	2.4700	0.3927
OMe	-0.78	1:11.1	11.1000	1.0453
OMe	-0.78	1:10.5	10.5000	1.0212
OMe	-0.78	1:10.1	10.1000	1.0043
H	0	1.00:1	1.0000	0.0000

Table S8. Raw data for [MnPc].

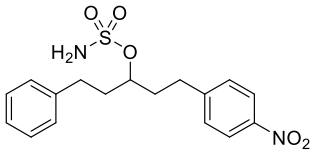
Substrate	σ +	γ:γ'	k_{Ar}/k_H	$\log(k_{Ar}/k_H)$
NO_2	0.79	3.07:1	0.3257	-0.4871
NO_2	0.79	3.4:1	0.2941	-0.5315
NO_2	0.79	3.31:1	0.3021	-0.5198
CF_3	0.61	3.1:1	0.3226	-0.4914
CF_3	0.61	3.2:1	0.3125	-0.5051
CF_3	0.61	3.1:1	0.3226	-0.4914
Me	-0.31	1:1.7	1.7000	0.2304
Me	-0.31	1:1.72	1.7200	0.2355
Me	-0.31	1:1.8	1.8000	0.2553
OMe	-0.78	1:7.2	7.2000	0.8573
OMe	-0.78	1:7.5	7.5000	0.8751
OMe	-0.78	1:7.7	7.7000	0.8865
H	0	1.00:1	1.0000	0.0000

Table S9. Raw data for [Mn(^{t}BuPc)].

Substrate	σ +	γ:γ'	k_{Ar}/k_H	$\log(k_{Ar}/k_H)$
NO_2	0.79	3.93:1	0.2545	-0.5944
NO_2	0.79	3.97:1	0.2519	-0.5988
NO_2	0.79	4.11:1	0.2433	-0.6138
CF_3	0.61	3.80:1	0.2632	-0.5798
CF_3	0.61	3.75:1	0.2667	-0.5740

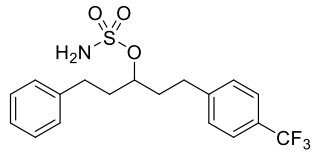
CF_3	0.61	3.57:1	0.2801	-0.5527
Me	-0.31	1:1.79	1.7900	0.2529
Me	-0.31	1:1.83	1.8300	0.2625
Me	-0.31	1:1.88	1.8800	0.2742
OMe	-0.78	1:5.74	5.7400	0.7589
OMe	-0.78	1:5.86	5.8600	0.7679
OMe	-0.78	1:5.44	5.4400	0.7356
H	0	1.00:1	1.0000	0.0000

(±)-1-(4-nitrophenyl)-5-phenylpentan-3-yl sulfamate [S40].



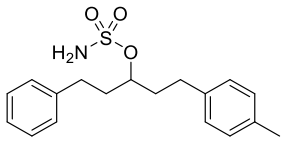
Prepared according to method **B**. 1.997 g (7.00 mmol) (±)-1-(4-nitrophenyl)-5-phenylpentan-3-ol were used, along with Et_3N (1.9 mL, 14.0 mmol, 2.0 equiv), CH_2Cl_2 (7 mL + 14 mL), $ClSO_2NCO$ (1.22 mL, 14.0 mmol, 2.0 equiv), formic acid (530 µL, 14.0 mmol, 2.0 equiv). Flash column chromatography on silica (45 mm fritted glass column, 200 mm SiO_2) using 4:1 hexanes/EtOAc → 3:2 hexanes/EtOAc as eluent gave 1.79 g (4.92 mmol) of pure product as a yellow solid (70% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 9.0 Hz, 2H), 7.34-7.28 (m, 4H), 7.23-7.18 (m, 3H), 4.73-4.65 (m, 3H), 2.90-2.81 (m, 2H), 2.80-2.72 (m, 2H), 2.19-2.03 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 146.4, 140.5, 129.1, 128.5, 128.2, 126.2, 123.7, 83.0, 35.4, 35.2, 31.1, 30.8; HRMS (ESI) *m/z* calculated for $C_{17}H_{20}N_2O_5SNa$ $[M+Na]^+$: 387.0991, found 387.0986. These data agree with that previously reported in the literature.[12]

(±)-1-phenyl-5-(4-(trifluoromethyl)phenyl)pentan-3-yl sulfamate [S41].



Prepared according to method **A**. 1.634 g (5.30 mmol) of (±)-1-phenyl-5-(4-(trifluoromethyl)phenyl)pentan-3-ol were used, along with NaH (148 mg, 5.84 mmol, 1.1 equiv), DMF (5 mL + 4 mL), $ClSO_2NCO$ (696 µL, 7.95 mmol, 1.5 equiv), formic acid (300 µL, 9.75 mmol, 1.5 equiv) and MeCN (4 mL). Flash column chromatography on silica (45 mm fritted glass column, 175 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave 1.250 g (3.23 mmol) of pure product as a white solid (61% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 2H), 7.31-7.28 (m, 4H), 7.23-7.17 (m, 3H), 4.70-4.64 (m, 3H), 2.83-2.73 (m, 4H), 2.17-2.03 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 145.2, 140.8, 128.8, 128.7, 128.5, 126.4, 125.6 (q, $J_{C\text{-}F}$ = 3.9 Hz), 83.6, 35.7, 35.6, 31.3, 31.0. These data agree with that previously reported in the literature.[12]

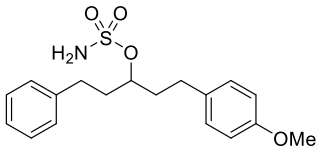
(±)-1-phenyl-5-(p-tolyl)pentan-3-yl sulfamate [S42].



Prepared according to method **A**. 3.200 g (12.6 mmol) of (±)-1-phenyl-5-(*p*-tolyl)pentan-3-ol were used, along with NaH (350 mg, 13.9 mmol, 1.1 equiv), DMF (13 + 10 mL), $ClSO_2NCO$ (1.7 mL, 19.1 mmol, 1.5 equiv), formic acid (712 µL, 19.1 mmol, 1.5 equiv) and MeCN (10.4 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc → 2:1 hexanes/EtOAc as eluent gave 2.01 g (6.03 mmol) of pure product as a white solid (48% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.22-7.18 (m, 3H), 7.11-7.06 (m, 4H), 4.68 (app. p, *J* = 6.5 Hz, 1H), 4.54 (br. s, 2H), 2.79-2.66 (m, 4H), 2.32 (s, 3H), 2.15-2.01 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.1, 137.9, 135.8, 129.4, 128.7, 128.5, 128.4, 126.3, 84.8, 35.9, 35.8, 31.2, 30.8, 21.1. These data agree with that previously reported in the literature.[12]

(±)-1-(4-methoxyphenyl)-5-phenylpentan-3-yl sulfamate [S43].



Prepared according to method **A**. 1.351 g (5.00 mmol) (±)-1-(4-methoxyphenyl)-5-phenylpentan-3-ol were used, along with NaH (140 mg, 5.50 mmol, 1.1 equiv), MeCN (5 mL), $ClSO_2NCO$ (870 µL, 10.0 mmol, 2 equiv), formic acid (380 µL, 10.0 mmol, 2 equiv) and DMF (10 mL). Flash column chromatography on silica (45 mm fritted glass column, 200 mm SiO_2) using 4:1 hexanes/EtOAc → 3:2 hexanes/EtOAc as eluent gave 1.290 g (3.69 mmol) of pure product as a pale yellow oil (74% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.23 (m, 3H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 5.19 (br. s, 2H), 4.72 (p, *J* = 5.9 Hz, 1H), 3.82 (s, 3H), 2.83-2.69 (m, 4H), 2.15-2.04 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8, 141.1, 133.1, 129.3, 128.5, 128.4, 126.1, 113.9, 83.8, 55.2, 35.9, 35.6, 31.0, 30.1. These data agree with that previously reported in the literature.[12]

***Para*-nitrophenyl versus phenyl.**

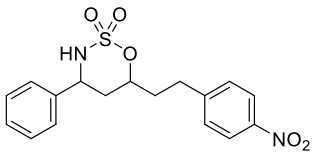
In all cases, the product ratio was established by HPLC analysis of the crude reaction mixture (reaction aliquots were filtered through a short silica plug with ^{i}PrOH into a HPLC vial. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 9:1 hexanes/EtOAc → 3:2 hexanes/EtOAc as eluent gave oxathiazinane product as a mixture of constitutional isomers. Each pure constitutional isomer can be isolated using flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 9:1 hexanes/EtOAc → 2:1 hexanes/EtOAc. Products retained EtOAc after prolonged drying in vacuo; this mass was accounted for when calculating yields. Additionally, free Pc ligand co-elutes with the minor products and its peaks are labeled and its mass accounted for in yields.

FePc conditions: 1-(4-nitrophenyl)-5-phenylpentan-3-yl sulfamate **S40** (73.0 mg, 0.200 mmol, 1.0 equiv), [FePc]Cl (12.0 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 4:1 PhMe/MeCN (400 µL, 0.5M) were used. By HPLC analysis of the crude product, γ:γ' was **5.34 ± 0.29 : 1**.
Run 1: (39.1 mg, 0.108 mmol, 54%), (12.3 mg rsm, 0.034 mmol, 17%), γ:γ' = 5.02:1. Run 2: (38.4 mg, 0.106 mmol, 53%), (11.6 mg rsm, 0.032 mmol, 16%), γ:γ' = 5.58:1. Run 3: (37.0 mg, 0.102 mmol, 51%), (10.1 mg rsm, 0.028 mmol, 14%), γ:γ' = 5.41:1. **Average: 53% yield ± 1.5, 16% rsm ± 1.5.**

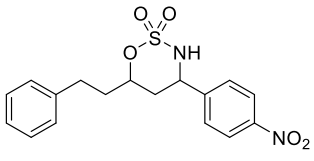
MnPc conditions: 1-(4-nitrophenyl)-5-phenylpentan-3-yl sulfamate **S40** (73.0 mg, 0.200 mmol, 1.0 equiv), [MnPc]Cl (12.0 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 4:1 PhMe/MeCN (400 µL, 0.5M) were used. By HPLC analysis of the crude product, γ:γ' was **3.26 ± 0.17 : 1**.
Run 1: (48.5 mg, 0.134 mmol, 67%), <5% rsm, γ:γ' = 3.07:1. Run 2: (46.4 mg, 0.128 mmol, 64%), <5% rsm, γ:γ' = 3.40:1. Run 3: (45.7 mg, 0.126 mmol, 63%), <5% rsm, γ:γ' = 3.31:1. **Average: 65% yield ± 2.1, <5% rsm.**

Mn(^{t}BuPc) conditions: 1-(4-nitrophenyl)-5-phenylpentan-3-yl sulfamate **S40** (73.0 mg, 0.200 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020

mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (400 μL, 0.5M) were used. By HPLC analysis of the crude product, γ:γ' was **4.00 ± 0.09 : 1**.
Run 1: (59.4 mg, 0.164 mmol, 82%), <5% rsm, γ:γ' = 4.11:1. Run 2: (61.6 mg, 0.170 mmol, 85%), <5% rsm, γ:γ' = 3.97:1. Run 3: (63.4 mg, 0.175 mmol, 88%), <5% rsm, γ:γ' = 3.93:1. **Average: 85% yield ± 3.0, <5% rsm.**



(±)-4-(4-nitrophenyl)-6-phenethyl-1,2,3-oxathiazinane 2,2-dioxide [S44]: Product was isolated as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 9.0 Hz, 2H), 7.43-7.36 (m, 5H), 7.34-7.32 (m, 2H), 4.85-4.76 (m, 2H), 4.21 (d, *J* = 9.1 Hz, 1H), 3.01 (ddd, *J* = 14.1, 9.3, 4.9 Hz, 1H), 2.91 (dt, *J* = 14.0, 8.3 Hz, 1H), 2.19-2.14 (m, 1H), 2.08-1.93 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 146.9, 137.8, 129.6, 129.4, 129.2, 126.4, 124.1, 82.6, 58.3, 36.5, 36.4, 30.7. These data agree with that previously reported in the literature.[12]

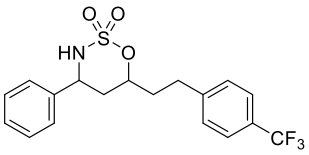


(±)-6-(4-nitrophenethyl)-4-phenyl-1,2,3-oxathiazinane 2,2-dioxide [S45]: Product was isolated as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.0 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.34-7.31 (m, 2H), 7.26-7.20 (m, 3H), 4.90 (dtt, *J* = 11.7, 5.9, 3.4 Hz, 2H), 4.18 (d, *J* = 9.2 Hz, 1H), 2.89 (ddd, *J* = 14.0, 8.9, 5.2 Hz, 1H), 2.80 (dt, *J* = 13.9, 8.2 Hz, 1H), 2.21-2.09 (m, 2H), 2.02-1.89 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 140.1, 134.5, 128.9, 128.7, 127.5, 126.6, 124.5, 83.1, 57.6, 37.1, 36.1, 30.7; HRMS (ESI) *m/z* calculated for $C_{17}H_{18}N_2O_5SNa$ $[M+Na]^+$: 385.0834, found 385.0830.

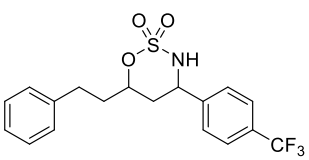
***Para*-(trifluoromethyl)phenyl versus phenyl.**
In all cases, the product ratio was established by HPLC analysis of the crude reaction mixture (reaction aliquots were filtered through a short silica plug with ^{i}PrOH into a HPLC vial. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc as eluent gave oxathiazinane product as a mixture of constitutional isomers. Each pure constitutional isomer can be isolated using flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 9:1 hexanes/EtOAc → 4:1 hexanes/EtOAc.
FePc conditions: (±)-1-phenyl-5-(4-(trifluoromethyl)phenyl)pentan-3-yl sulfamate **S41** (77.5 mg, 0.200 mmol, 1.0 equiv), [FePc]Cl (12.0 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 4:1 PhMe/MeCN (400 μL, 0.5M) were used. By HPLC analysis of the crude product, γ:γ' was **4.27 ± 0.12 : 1**.
Run 1: (88.1 mg , 0.229 mmol, 57%), (>5% rsm), γ:γ' = 4.4:1. Run 2: (84.8 mg, 0.220 mmol, 55%), (>5% rsm), γ:γ' = 4.2:1. Run 3 (80.7 mg, 0.209 mmol, 52%), (>5% rsm), γ:γ' = 4.2:1. **Average: 55% yield ± 2.4, <5% rsm.**
MnPc conditions: (±)-1-phenyl-5-(4-(trifluoromethyl)phenyl)pentan-3-yl sulfamate **S41** (77.5 mg, 0.200 mmol, 1.0 equiv), [MnPc]Cl (12.0 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 4:1 PhMe/MeCN (400 μL, 0.5M) were used. By HPLC analysis of the crude product, γ:γ' was **3.13 ± 0.06 : 1**.
Run 1: (108.3 mg, 0.281 mmol, 70%), (>5% rsm), γ:γ' = 3.1:1. Run 2: (102.4 mg, 0.266 mmol, 66%), (>5% rsm), γ:γ' = 3.2:1. Run 3: (106.2 mg, 0.276 mmol, 69%), (>5% rsm), γ:γ' = 3.1. **Average: 69% yield ± 1.9, <5% rsm.**
Mn(^{t}BuPc) conditions: (±)-1-phenyl-5-(4-(trifluoromethyl)phenyl)pentan-3-yl sulfamate **S41** (77.5 mg, 0.200 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 9:1

C_6H_6/MeCN (400 μL, 0.5M) were used. By HPLC analysis of the crude product, γ:γ' was **3.71 ± 0.12 : 1**.

Run 1: (56.7 mg, 0.147 mmol, 73%), <5% rsm, γ:γ' = 3.75:1. Run 2: (52.4 mg, 0.136 mmol, 68%), <5% rsm, γ:γ' = 3.57:1. Run 3: (55.1 mg, 0.143 mmol, 72%), <5% rsm, γ:γ' = 3.80:1. **Average: 71% yield ± 2.6, <5% rsm.**

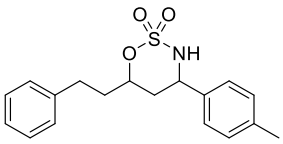


4-phenyl-6-(4-(trifluoromethyl)phenethyl)-1,2,3-oxathiazinane 2,2-dioxide [S46]. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 8.0 Hz, 2H), 7.40-7.30 (m, 7H), 4.86-4.76 (m, 2H), 4.42-4.37 (m, 1H), 2.95-2.80 (m, 2H), 2.16-2.12 (m, 1H), 2.04-1.93 (m, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 144.6, 138.0, 129.2, 129.0, 126.4, 125.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 83.0, 58.4, 36.6, 36.2, 30.5. These data agree with that previously reported in the literature.[12]



6-phenethyl-4-(4-(trifluoromethyl)phenyl)-1,2,3-oxathiazinane 2,2-dioxide [S47]. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.31 (dd, J = 8.0, 7.0 Hz, 2H), 7.25-7.19 (m, 3H), 4.90-4.81 (m, 2H), 4.45 (d, J = 9.0 Hz, 1H), 2.89-2.74 (m, 2H), 2.19-2.11 (m, 1H), 2.07-1.91 (m, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.8, 140.2, 128.8, 128.6, 126.3 (q, $J_{C\text{-}F}$ = 3.8 Hz), 83.3, 57.9, 37.0, 36.2, 30.7; IR (thin film, cm^{-1}): 3262, 3029, 2931, 1623, 1497, 1437, 1419, 1365, 1327, 1191, 1127, 1070, 1018, 918, 879, 756; HRMS (ESI) *m/z* calculated for $C_{18}H_{19}F_3NO_3S$ $[M+H]^+$: 386.1038, found 386.1039.

***Para*-methylphenyl versus phenyl.**



In all cases, the product ratio was determined by ^{1}H NMR analysis of the crude product mixture after reaction work-up. Flash column chromatography on silica (35 mm fritted glass column, 75 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave oxathiazinane product as a mixture of constitutional isomers. Pure constitutional isomers cannot be isolated and as such the ^{1}H NMR spectrum of the mixture is provided but not tabulated.

FePc conditions: 1-phenyl-5-(p-tolyl)pentan-3-yl sulfamate **S42** (67 mg, 0.200 mmol, 1.0 equiv), [FePc]Cl (12.0 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 4:1 PhMe/MeCN (400 μL, 0.5M) were used. By ^{1}H NMR analysis of the crude product, γ:γ' was **1 : 2.38 ± 0.09**.

Run 1: (38.0 mg, 0.115 mmol, 57%), <5% rsm, γ:γ' = 1:2.30. Run 2: (39.7 mg 0.120 mmol, 60%), <5% rsm, γ:γ' = 1:2.37. Run 3: (40.7 mg 0.123 mmol, 61%), <5% rsm, γ:γ' = 1:2.47. **Average: 59% yield ± 2.0, <5% rsm.**

MnPc conditions: 1-phenyl-5-(*p*-tolyl)pentan-3-yl sulfamate **S42** (67 mg, 0.200 mmol, 1.0 equiv), [MnPc]Cl (12.0 mg, 0.020 mmol, 0.1 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.1 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 4:1 PhMe/MeCN (400 μL, 0.5M) were used. By ^{1}H NMR analysis of the crude product, γ:γ' was **1 : 1.74 ± 0.05**.

Run 1: (41.0 mg, 0.124 mmol, 62%), <5% rsm, γ:γ' = 1:1.7. Run 2: (43.3 mg 0.131 mmol, 65%), <5% rsm, γ:γ' = 1:1.72. Run 3: (43.9 mg 0.132 mmol, 66%), <5% rsm, γ:γ' = 1:1.8. **Average: 64% yield ± 2.0, <5% rsm.**

Mn(^{t}BuPc) conditions: 1-phenyl-5-(*p*-tolyl)pentan-3-yl sulfamate **S42** (67 mg, 0.200 mmol, 1.0 equiv), Mn(^{t}BuPc)Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (400 μL, 0.5M) were used. By ^{1}H NMR analysis of the product mixture, γ:γ' was **1 : 1.83 ± 0.05**.

Run 1: (45.5 mg, 0.137 mmol, 69%), <5% rsm, γ:γ' = 1:1.88. Run 2: (44.2 mg, 0.133 mmol, 67%), <5% rsm, γ:γ' = 1:1.83. Run 3: (50.0 mg, 0.151 mmol, 76%), <5% rsm, γ:γ' = 1:1.79. **Average: 70% yield ± 4.6, <5% rsm.**

***Para*-methoxyphenyl versus phenyl.**

In all cases, the product ratio was established by HPLC analysis of the crude reaction mixture (reaction aliquots were filtered through a short silica plug with ^{i}PrOH into a HPLC vial). Flash column chromatography on silica (35 mm fritted glass column, 75 mm SiO_2) using 30% EtOAc/hexanes as eluent gave oxathiazinane product as a mixture of constitutional isomers. Pure major constitutional isomer can be isolated as a white solid using flash column chromatography on silica (35 mm fritted glass column, 75 mm SiO_2) using 9:1 hexanes/EtOAc → 3:1 hexanes/EtOAc as eluent. The minor constitutional isomer was always isolated as a mixture with the major product.

FePc conditions: 1-(4-methoxyphenyl)-5-phenylpentan-3-yl sulfamate **S43** (70.0 mg, 0.200 mmol, 1.0 equiv), [FePc]Cl (12.0 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv), and 4:1 PhMe/MeCN (400 μL, 0.5M) were used. By HPLC analysis of the crude product, γ:γ' was **1 : 10.57± 0.50**.

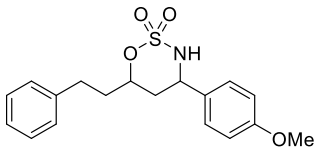
Run 1: (38.4 mg, 0.111 mmol, 55%), <5% rsm, γ:γ' = 1:11.1. Run 2: (39.2 mg, 0.113 mmol, 56%), <5% rsm, γ:γ' = 1:10.5. Run 3: (40.2 mg, 0.116 mmol, 58%), <5% rsm, γ:γ' = 1:10.1. **Average: 56% yield ± 1.2, <5% rsm.**

MnPc conditions: 1-(4-methoxyphenyl)-5-phenylpentan-3-yl sulfamate **S43** (70.0 mg, 0.200 mmol, 1.0 equiv), [MnPc]Cl (12.0 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv), and 9:1 C_6H_6/MeCN (400 μL, 0.5M) were used. By HPLC analysis of the crude product, γ:γ' was **1 : 7.47 ± 0.25**.

Run 1: (41.1 mg, 0.118 mmol, 59%), <5% rsm, γ:γ' = 1:7.2. Run 2: (42.9 mg, 0.123 mmol, 62%), <5% rsm, γ:γ' = 1:7.7. Run 3: (44.8 mg, 0.129 mmol, 64%), <5% rsm, γ:γ' = 1:7.5. **Average: 62% yield ± 2.5, <5% rsm.**

Mn(^{t}BuPc) conditions: 1-(4-methoxyphenyl)-5-phenylpentan-3-yl sulfamate **S43** (70.0 mg, 0.200 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (400 μL, 0.5M) were used. By HPLC analysis of the crude product, γ:γ' was **1 : 5.68 ± 0.22**.

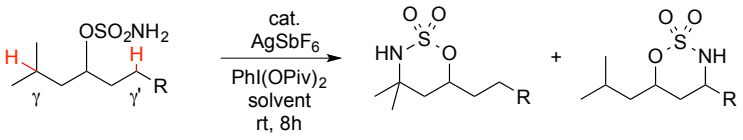
Run 1: (57.7 mg, 0.166 mmol, 83%), <5% rsm, γ:γ' = 1:5.44. Run 2: (56.6 mg, 0.163 mmol, 82%), <5% rsm, γ:γ' = 1:5.86. Run 3: (52.5 mg, 0.151 mmol, 75%), <5% rsm, γ:γ' = 1:5.74. **Average: 80% yield ± 4.0, <5% rsm.**

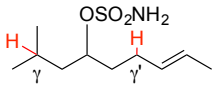
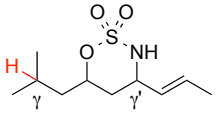
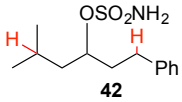
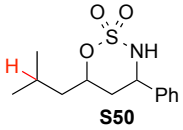
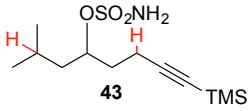
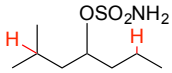
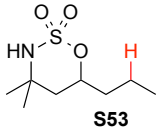


(±)-6-(4-methoxyphenethyl)-4-phenyl-1,2,3-oxathiazinane 2,2-dioxide [S48]: Product was isolated as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.30 (m, 2H), 7.26-7.20 (m, 5H), 6.92-6.90 (m, 2H), 4.87-4.82 (m, 1H), 4.72 (ddd, *J* = 12.0, 8.7, 2.8 Hz, 1H), 4.13 (d, *J* = 9.2 Hz, 1H), 3.81 (s, 3H), 2.87 (ddd, *J* = 14.1, 9.1, 5.2 Hz, 1H), 2.77 (ddd, *J* = 13.9, 8.9, 7.6 Hz, 1H), 2.18-2.10 (m, 1H), 2.02-1.91 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 140.4, 130.2, 128.8, 128.7, 127.7, 126.5, 114.6, 83.2, 57.8, 55.5, 37.2, 36.4, 30.8. These data agree with that previously reported in the literature.[12]

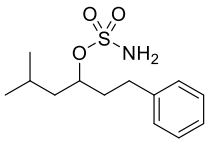
C—H Bond Reactivity Trends

Table S10. C—H bond reactivity trends for Fe and Mn catalysts.



Substrate	Major Product	Catalyst	γ/γ'
 **41**		*[FePc]* *[MnPc]* *[Mn(tBuPc)]*	<1:20 <1:20 <1:20
 **42**	 **S50**	*[FePc]* *[MnPc]* *[Mn(tBuPc)]*	1:14 1:3 1:3
 **43**	 **S52**	*[FePc]* *[MnPc]* *[Mn(tBuPc)]*	1:3 1:2 1:2
 **44**	 **S53**	*[FePc]* *[MnPc]* *[Mn(tBuPc)]*	>20:1 5:1 5:1

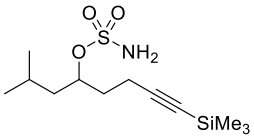
(±)-5-methyl-1-phenylhexan-3-yl sulfamate [42].



Prepared according to method **A**. 1.600 g (8.56 mmol) of (±)-5-methyl-1-phenylhexan-3-ol were used, along with NaH (237 mg, 9.4 mmol, 1.1 equiv), DMF (8.5 mL + 6.8 mL), $ClSO_2NCO$ (1.11 mL, 12.8 mmol, 1.5 equiv), formic acid (483 µL, 12.8 mmol, 1.5 equiv) and MeCN (6.5 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 9:1 hexanes/EtOAc → 4:1 hexanes/EtOAc as eluent gave 1.720 g (6.34 mmol) of pure product as a white solid (74% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.22-7.19 (m, 3H), 4.76-4.69 (m, 3H), 2.75 (td, J = 8.5, 3.0 Hz, 2H), 2.11-2.00 (m, 2H), 1.79-1.72 (m, 2H), 1.51 (ddd, J = 16.0, 10.0, 5.5 Hz, 1H), 0.95 (d, J = 6.0 Hz, 3H), 0.93 (d, J = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.3, 128.6, 128.5, 126.2, 83.5, 43.3, 36.2, 31.1, 24.6, 22.9, 22.6. These data are in agreement with that previously reported in the literature.[9]

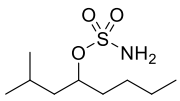
(±)-2-methyl-8-(trimethylsilyl)oct-7-yn-4-yl sulfamate [43].



Prepared according to method **B**. 2.655 g (12.5 mmol) of (±)-2-methyl-8-(trimethylsilyl)oct-7-yn-4-ol were used, along with Et_3N (3.5 mL, 25 mmol, 2.0 equiv), CH_2Cl_2 (13 mL + 36 mL), $ClSO_2NCO$ (2.18 mL, 25 mmol, 2.0 equiv), formic acid (943 µL, 25 mmol, 2.0 equiv). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2)

using 9:1 hexanes/EtOAc → 4:1 hexanes/EtOAc as eluent gave 2.290 g (7.85 mmol) of pure product as a white solid (63% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.84-4.80 (m, 2H), 2.40 (t, *J* = 6.8 Hz, 2H), 1.92-1.88 (m, 2H), 1.77-1.71 (m, 2H), 1.53-1.47 (m, 1H), 0.96 (d, *J* = 6.0 Hz, 3H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.16 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 106.0, 86.7, 82.5, 43.6, 33.0, 24.6, 22.7, 22.6, 16.9, 0.2; IR (ATR, cm^{-1}) 3370, 3284, 2960, 2873, 2175, 1559, 1470, 1359, 1250, 1183, 923, 844, 761; HRMS (ESI) *m/z* calculated for $C_{12}H_{26}NO_3SSi$ $[M+H]^+$: 292.1403, found 292.1406.

(±)-2-methyloctan-4-yl sulfamate [44].



Prepared according to method **A**. 1.863 g (12.9 mmol) of (±)-2-methyloctan-4-ol were used, along with NaH (359 mg, 14.2 mmol, 1.1 equiv), DMF (13 mL + 10 mL), $ClSO_2NCO$ (1.69 mL, 19.4 mmol, 1.5 equiv), formic acid (731 μL, 19.4 mmol, 1.5 equiv) and MeCN (10 mL). Flash column chromatography on silica (45 mm fritted glass column, 170 mm SiO_2) using 9:1 hexanes/EtOAc → 4:1 hexanes/EtOAc as eluent gave 2.017 g (9.03 mmol) of pure product as a colorless oil (70% yield). *This sulfamate ester generated precipitate rapidly and was repurified if not used within a week.*
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.75 (br. s, 2H), 4.67 (app. dq, *J* = 7.5, 5.5 Hz, 1H), 1.79-1.66 (m, 4H), 1.47-1.29 (m, 5H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 84.3, 43.3, 34.3, 26.9, 24.5, 23.0, 22.7, 22.5, 14.1; HRMS (ESI) *m/z* calculated for $C_9H_{21}NO_3SNa$ $[M+Na]^+$: 246.1140, found 246.1139.

Tertiary C—H versus Allylic C—H.
In all cases, 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. Data for [FePc]Cl has been previously reported.[7]
MnPc conditions: (±)-(*E*)-2-methylnon-7-en-4-yl sulfamate **41** (94.0 mg, 0.400 mmol, 1.0 equiv), [MnPc]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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, γ:γ' was <1:20, ins./azir. was >20:1, and d.r. was 3:1 *syn*:*anti*.
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 ± 0.5 (γ:γ' crude = <1:20), <5% rsm.**
Mn(^{t}BuPc) conditions: (±)-(*E*)-2-methylnon-7-en-4-yl sulfamate **41** (94.0 mg, 0.400 mmol, 1.0 equiv), Mn(^{t}BuPc)Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, γ:γ' was <1:20, ins./azir. was >20:1, and d.r. was 4:1 *syn*:*anti*.
Run 1: (55.0 mg *syn* + 13.8 mg *anti* (4:1 d.r.), 0.296 mmol, 74%), 0% rsm. Run 2: (51.9 mg *syn* + 14.0 mg *anti* (3.7:1 d.r.), 0.284 mmol, 71%), 0% rsm. Run 3: (55.6 mg *syn* + 15.9 mg *anti* (3.5:1 d.r.), 0.308 mmol, 77%), 0% rsm. **Average: 74% yield allylic ± 2.4 (γ:γ' crude = <1:20), 0% rsm.**

Tertiary C—H versus Benzylic C—H.

In all cases, material was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 10% EtOAc/hexanes → 15% EtOAc/hexanes → 20% EtOAc/hexanes, isolating the 3° and benzylic products and starting material separately.

FePc conditions: 5-methyl-1-phenylhexan-3-yl sulfamate **42** (109 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, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, γ:γ' was 1:14.

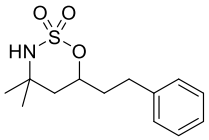
Run 1: (56.2 mg benzylic, 0.208 mmol, 52%), (5.5 mg 3° (10:1 benzylic/3°), 0.020 mmol, 5%), (14.5 mg rsm, 0.053 mmol, 13% rsm). Run 2: (53.9 mg benzylic, 0.200 mmol, 50%), (5.7 mg 3° (10:1 benzylic/3°), 0.021 mmol, 5%), (12.4 mg rsm, 0.046 mmol, 11%). Run 3: (55.5 mg benzylic, 0.206 mmol, 51%), (5.8 mg 3° (10:1 benzylic/3°), 0.021 mmol, 5%), (13.4 mg rsm, 0.049 mmol, 12%). **Average: 51% yield benzylic ± 0.8 (γ:γ' crude = 1:14), 12% rsm ± 0.8.**

MnPc conditions: 5-methyl-1-phenylhexan-3-yl sulfamate **42** (109 mg, 0.400 mmol, 1.0 equiv), [MnPc]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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, γ:γ' was 1:3.

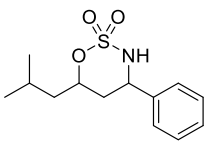
Run 1: (66.8 mg benzylic, 0.247 mmol, 62%), (23.0 mg 3° (2.9:1 benzylic/3°), 0.085 mmol, 21%), 0% rsm. Run 2: (65.6 mg benzylic, 0.242 mmol, 61%), (19.9 mg 3° (2.8:1 benzylic/3°), 0.073 mmol, 18%), 0% rsm. Run 3: (64.7 mg benzylic, 0.240 mmol, 60%), (20.5 mg 3° (2.8:1 benzylic/3°), 0.076 mmol, 19%), 0% rsm. **Average: 61% yield benzylic ± 0.8 (γ:γ' crude = 1:3), 0% rsm.**

Mn(^{t}BuPc) conditions: 5-methyl-1-phenylhexan-3-yl sulfamate **42** (109 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, γ:γ' was 1:3.

Run 1: (66.0 mg benzylic, 0.244 mmol, 61%), (22.8 mg 3° (2.9:1 benzylic/3°), 0.084 mmol, 21%), 0% rsm. Run 2: (62.6 mg benzylic, 0.232 mmol, 58%), (18.0 mg 3° (2.7:1 benzylic/3°), 0.067 mmol, 17%), 0% rsm. Run 3: (63.0 mg benzylic, 0.233 mmol, 58%), (20.7 mg 3° (2.8:1 benzylic/3°), 0.077 mmol, 19%), 0% rsm. **Average: 59% yield benzylic ± 1.4 (γ:γ' crude = 1:3), 0% rsm.**



4,4-dimethyl-6-phenethyl-1,2,3-oxathiazinane 2,2-dioxide [S49]. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 12.5, 7.5 Hz, 2H), 7.23-7.19 (m, 3H), 4.84-4.82 (m, 1H), 4.34 (br. s, 1H), 2.84 (ddd, *J* = 15.5, 9.5, 5.0 Hz, 1H), 2.78-2.72 (m, 1H), 2.06 (dtd, *J* = 14.5, 9.0, 5.5 Hz, 1H), 1.89 (dddd, *J* = 13.5, 9.5, 7.5, 4.0 Hz, 1H), 1.68-1.60 (m, 2H), 1.47 (s, 3H), 1.30 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 140.6, 128.7, 128.6, 126.4, 80.4, 56.0, 41.5, 37.2, 31.9, 30.9, 25.2. These data agree with that previously reported in the literature.[9]



6-isobutyl-4-phenyl-1,2,3-oxathiazinane 2,2-dioxide [S50]. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.42-7.33 (m, 5H), 4.95 (dddd, *J* = 11.5, 9.0, 4.5, 2.0 Hz, 1H), 4.81 (ddd, *J* = 12.0, 9.0, 3.0 Hz, 1H), 4.21 (br. d, *J* = 9.0 Hz, 1H), 2.04 (dt, *J* = 14.5, 3.0 Hz, 1H), 1.94-1.86 (m, 2H), 1.79 (ddd, *J* = 9.0, 6.0 Hz, 1H), 1.44 (ddd, *J* = 12.5, 8.5, 4.0 Hz, 1H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.2, 129.3, 129.0, 126.4, 83.9, 58.4, 44.3, 36.8, 23.9, 23.0, 22.0. These data agree with that previously reported in the literature.[9]

Tertiary C—H versus Propargylic C—H.

In all cases, material was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 10% EtOAc/hexanes → 15% EtOAc/hexanes, isolating product and starting material separately.

FePc conditions: 2-methyl-8-(trimethylsilyl)oct-7-yn-4-yl sulfamate **43** (116.6 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, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, γ:γ' was 1:3.

Run 1: (61.1 mg propargylic, 0.211 mmol, 53%), (21.7 mg 3°, 0.075 mmol, 19%), 0% rsm. Run 2: (64.7 mg propargylic, 0.223 mmol, 56%), (23.6 mg 3°, 0.081 mmol, 20%), 0% rsm. Run 3: (61.7 mg propargylic, 0.213 mmol, 53%), (26.1 mg 3°, 0.090 mmol, 23%), 0% rsm. **Average: 54% yield ± 1.7 propargylic (γ:γ' crude = 1:3), 0% rsm.**

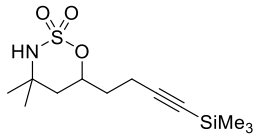
MnPc conditions: 2-methyl-8-(trimethylsilyl)oct-7-yn-4-yl sulfamate **43** (116.6 mg, 0.400 mmol, 1.0 equiv), [MnPc]Cl (24.0 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, γ:γ' was 1:2.

Run 1: (61.0 mg propargylic, 0.210 mmol, 53%), (34.8 mg tertiary, 0.120 mmol, 30%). Run 2: (69.9 mg propargylic, 0.241 mmol, 60%), (36.4 mg tertiary, 0.126 mmol, 31%). Run 3: (65.1 mg propargylic, 0.225 mmol, 56%), (37.9 mg tertiary, 0.131 mmol, 33%). **Average: 56% yield ± 3.5 propargylic (γ:γ' crude = 1:2), 0% rsm.**

Mn(^{t}BuPc) conditions: 2-methyl-8-(trimethylsilyl)oct-7-yn-4-yl sulfamate **43** (116.6 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 μL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, γ:γ' was 1:2.

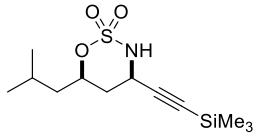
Run 1: (81.6 mg propargylic, 0.282 mmol, 70%), (30.8 mg tertiary, 0.106 mmol, 27%). Run 2: (78.4 mg propargylic, 0.271 mmol, 68%), (28.7 mg tertiary, 0.099 mmol, 25%). Run 3: (80.0 mg propargylic, 0.276 mmol, 69%), (32.5 mg tertiary, 0.112 mmol, 28%). **Average: 69% yield ± 0.8 propargylic (γ:γ' crude = 1:2), 0% rsm.**

4,4-dimethyl-6-(4-(trimethylsilyl)but-3-yn-1-yl)-1,2,3-oxathiazinane 2,2-dioxide [S51].

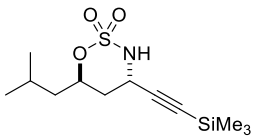


^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.00-4.96 (m, 1H), 4.28 (br. s, 1H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.99-1.92 (m, 1H), 1.84-1.77 (m, 1H), 1.70-1.59 (m, 2H), 1.50 (s, 3H), 1.30 (s, 3H), 0.14 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 134.5, 123.7, 104.9, 86.3, 79.8, 56.0, 41.2, 33.9, 31.9, 25.2, 15.6, 0.1; (ATR, cm^{-1}) 3269, 2960, 1730, 1423, 1389, 1374, 1354, 1250, 1194, 1164, 944, 908, 844, 873, 760; HRMS (ESI) *m/z* calculated for $C_{12}H_{24}NO_3SSi$ $[M+H]^+$: 290.1246, found 290.1238.

6-isobutyl-4-((trimethylsilyl)ethynyl)-1,2,3-oxathiazinane 2,2-dioxide [S52].



Syn diastereomer: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.77 (dddd, *J* = 11.6, 9.0, 4.3, 2.1 Hz, 1H), 4.50 (ddd, *J* = 12.0, 10.4, 3.0 Hz, 1H), 4.12 (d, *J* = 10.4 Hz, 1H), 2.02 (dt, *J* = 14.6, 2.6 Hz, 1H), 1.90-1.81 (m, 1H), 1.82-1.66 (m, 2H), 1.38 (ddd, *J* = 14.2, 8.5, 4.4 Hz, 1H), 0.94 (d, *J* = 4.5 Hz, 3H), 0.93 (d, *J* = 4.8 Hz, 3H), 0.17 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 100.4, 91.5, 82.4, 47.6, 44.1, 37.2, 23.9, 23.0, 22.1, -0.2; (ESI) *m/z* calculated for $C_{12}H_{24}NO_3SSi$ $[M+H]^+$: 290.1246, found 290.1244.



Anti diastereomer: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.19-5.14 (m, 1H), 4.67 (d, *J* = 6.0 Hz, 1H), 4.49-4.46 (m, 1H), 2.02-1.77 (m, 4H), 1.44-1.39 (m, 1H), 0.97 (d, *J* = 6.4 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.18 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 101.1, 91.6, 81.4, 46.1, 43.3, 35.2, 24.1, 22.7, 22.0, 0.0; (ATR, cm^{-1}) 3278, 2960, 2874, 1470, 1422, 1371, 1251, 1189, 1097, 1015, 867, 845, 791, 761; (ESI) *m/z* calculated for $C_{12}H_{24}NO_3SSi$ $[M+H]^+$: 290.1246, found 290.1252.

Tertiary C—H *versus* Secondary C—H.

In all cases, material was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc, isolating product and starting material separately. The 3° + 2° products could not be separated by any column conditions and were thus isolated as a mixture.

FePc conditions: (±)-2-methyloctan-4-yl sulfamate **44** (89.3 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, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, γ:γ' was >20:1.

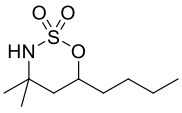
Run 1: (26.5 mg 3°, 0.120 mmol, 30%), (27.5 mg rsm, 0.123 mmol, 31%). Run 2: (28.3 mg 3°, 0.128 mmol, 32%), (33.6 mg rsm, 0.151 mmol, 38%). Run 3: (27.1 mg 3°, 0.122 mmol, 31%), (33.4 mg rsm, 0.150 mmol, 37%). **Average: 31% yield 3° ± 0.8 (γ:γ' crude = >20:1), 35% rsm ± 3.1**.

MnPc conditions: (±)-2-methyloctan-4-yl sulfamate **44** (89.3 mg, 0.400 mmol, 1.0 equiv), [MnPc]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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, γ:γ' was 5:1.

Run 1: (55.8 mg 3°, 0.252 mmol, 63%), 0% rsm. Run 2: (57.2 mg 3°, 0.259 mmol, 65%), 0% rsm. Run 3: (59.0 mg 3°, 0.267 mmol, 67%), 0% rsm. **Average: 65% yield 3° ± 1.6 (γ:γ' crude = 5:1), 0% rsm.**

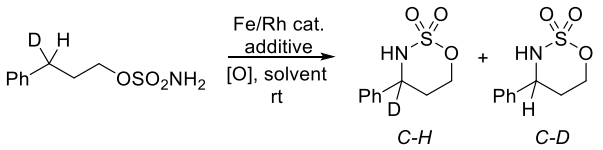
Mn(^{t}BuPc) conditions: (±)-2-methyloctan-4-yl sulfamate **44** (89.3 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.05 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. By ^{1}H-NMR analysis of the isolated product, γ:γ' was 5:1.

Run 1: (70.6 mg 3°, 0.319 mmol, 80%), 0% rsm. Run 2: (71.1 mg 3°, 0.321 mmol, 80%), 0% rsm. Run 3: (74.3 mg 3°, 0.336 mmol, 84%), 0% rsm. **Average: 81% yield 3° ± 1.9 (γ:γ' = 5:1), 0% rsm.**



6-butyl-4,4-dimethyl-1,2,3-oxathiazinane 2,2-dioxide [S53]. Product was isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.84-4.79 (m, 1H), 4.06 (s, 1H), 1.77-1.71 (m, 1H), 1.66-1.56 (m, 3H), 1.51-1.31 (m, 4H), 1.48 (s, 3H), 1.30 (s, 3H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 81.4, 56.0, 41.7, 35.1, 32.1, 26.8, 25.3, 22.4, 14.0; IR (ATR, cm^{-1}) 3264, 2974, 2953, 2931, 2874, 1472, 1456, 1429, 1418, 1388, 1374, 1345, 1271, 1190, 1179, 1152, 1043, 1008, 988, 952, 890, 822, 766, 728; HRMS (ESI) *m/z* calculated for $C_9H_{19}NO_3SNa$ $[M+Na]^+$: 244.0983, found 244.0982.

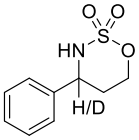
Intramolecular Kinetic Isotope Effect Study



Method for KIE Determination: The column-purified product mixture **S54** (ca. 30 mg in 700 µL $CDCl_3$) was analyzed by ^{13}C-NMR (600 MHz instrument).[7,9,18] $Cr(acac)_3$ (15 mg) was added directly to the solution in the NMR tube immediately prior to running the NMR study; this helps to significantly reduce delay times needed to obtain accurate integrations. The experiment was run under inverse-gated decoupling conditions without sample spinning. The following parameters were used for the experiment, listed as Varian commands:
temp=23
dm='nny' (inverse-gated decoupling)
d1=5 (initial delay)
at=0.5 (acquisition time)
setsw(180,0) (spectral width, in ppm)
bs=64 (block size for FID)
nt=2944 (number of scans)
pw=pw90=7.0 (pulse width, 90° pulse width)

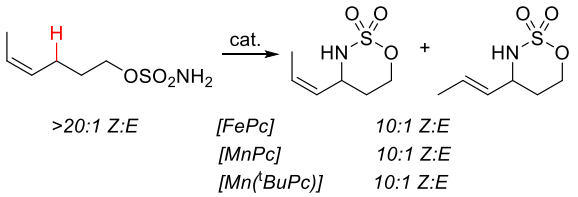
The KIE was reported as the area of the deuterated peak over that of the protonated peak. Three identical NMR experiments were run and an average value was calculated with error reported as a standard deviation.
[FePc]Cl: *C—H/C—D* = 4.8 ± 0.1 (5.0, 4.6, 4.8)
[MnPc]Cl: *C—H/C—D* = 4.5 ± 0.1 (4.6, 4.4, 4.4)
[Mn(^{t}BuPc)]Cl: *C—H/C—D* = 4.2 ± 0.1 (4.2, 4.1, 4.4)
$Rh_2(OAc)_4$: *C—H/C—D* = 3.8 ± 0.1 (3.8, 4.0, 3.7)

(±)-4-deuterio-4-phenyl-tetrahydro-1,2,3-oxathiazine-2,2-dioxide [S54].

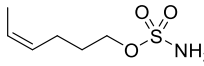


(±)-3-deuterio-3-phenylprop-1-yl sulfamate **45** (86.5 mg, 0.400 mmol, 1.0 equiv), [MnPc]Cl (24.0 mg, 0.040 mmol, 0.10 equiv), $AgSbF_6$ (13.7 mg, 0.040 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) and 9:1 C_6H_6:MeCN (800 µL) were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave the deuterated and protonated oxathiazinanes as a mixture.
Run 1: (58.4 mg, 0.1273 mmol, 68%), <5% rsm. Run 2: (55.7 mg, 0.260 mmol, 65%), <5% rsm. Run 3: (55.1 mg, 0.257 mmol, 64%), <5% rsm. **Average: 66% yield ± 1.7, <5% rsm.**
Characterization data are in agreement with that previously reported in the literature.[7]

Olefin Isomerization Study

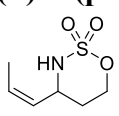


(*Z*)-hex-4-en-1-yl sulfamate [47].



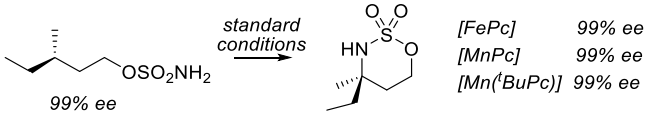
Prepared according to method **A**. 500 mg (584 µL, 5.0 mmol) of *cis*-4-hexene-1-ol were used, along with NaH (138 mg, 5.5 mmol, 1.1 equiv), DMF (8.9 mL), $ClSO_2NCO$ (651 µL, 7.5 mmol, 1.5 equiv), formic acid (283 µL, 7.5 mmol, 1.5 equiv) and MeCN (3.8 mL). Flash column chromatography on silica (100 mL SiO_2) using 4:1 hexanes/EtOAc → 3:1 hexanes/EtOAc as eluent gave 756 mg (4.2 mmol) of pure product as a colorless oil (84% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.56-5.49 (m, 1H), 5.38-5.32 (m, 1H), 4.79 (br. s, 2H), 4.22 (t, *J* = 6.5 Hz, 2H), 2.18 (q, *J* = 7.3 Hz, 2H), 1.82 (tt, *J* = 7.3, 6.6 Hz, 2H), 1.62 (ddd, *J* = 6.8, 1.7, 0.9 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 128.6, 125.9, 71.2, 28.8, 22.9, 13.0. These data are in agreement with that previously reported in the literature.[9]

Procedure for olefin isomerization experiments:
In all cases, crude material was purified via flash column chromatography on silica (35 mm fritted glass column, 120 mm SiO_2) using 9:1 CH_2Cl_2/hexanes → 19:1 CH_2Cl_2/hexanes as eluent, affording pure oxathiazinane as a white solid.
[FePc] Conditions: (*Z*)-hex-4-en-1-yl sulfamate **47** (71.7 mg, 0.400 mmol, 1.0 equiv), [FePc]Cl (24.2 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, *Z*/*E* was 10:1 (this ratio was confirmed by subjecting column-purified *Z*/*E* mixtures of products to ^{1}H-NMR analysis).
[MnPc] Conditions: (*Z*)-hex-4-en-1-yl sulfamate **47** (71.7 mg, 0.400 mmol, 1.0 equiv), [MnPcCl (24.1 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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, *Z*/*E* was 10:1 (this ratio was confirmed by subjecting column-purified *Z*/*E* mixtures of products to ^{1}H-NMR analysis).
[Mn(^{t}BuPc)] Conditions: (*Z*)-hex-4-en-1-yl sulfamate **47** (71.7 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.2 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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. By ^{1}H-NMR analysis of the crude product, *Z*/*E* was 10:1 (this ratio was confirmed by subjecting column-purified *Z*/*E* mixtures of products to ^{1}H-NMR analysis).
(*Z*)-4-(prop-1-en-1-yl)-1,2,3-oxathiazinane 2,2-dioxide [*Z*-7].

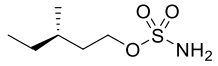


^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.77 (dqd, *J* = 10.8, 7.0, 1.2 Hz, 1H), 5.27 (ddq, *J* = 10.1, 8.1, 1.9 Hz, 1H), 4.81 (ddd, *J* = 12.8, 11.7, 2.4 Hz, 1H), 4.66-4.60 (m, 1H), 4.57 (ddd, *J* = 11.7, 5.0, 1.7 Hz, 1H), 4.01 (br. d, *J* = 9.3 Hz, 1H), 1.90 (dddd, *J* = 14.6, 12.8, 11.7, 5.0 Hz, 1H), 1.80-1.71 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 130.8, 127.1, 71.9, 52.8, 30.1, 13.8. These data are in agreement with that previously reported in the literature.[9]

Stereoretention Study

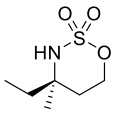


(+)-(*R*)-3-methylpentyl sulfamate [48].



Prepared according to method **A**. 1.00 mL (8.12 mmol) of (+)-(*R*)-3-methyl-1-pentanol were used, along with NaH (226 mg, 8.93 mmol, 1.1 equiv), DMF (8 mL + 6 mL), $ClSO_2NCO$ (1.06 mL, 12.2 mmol, 1.5 equiv), formic acid (460 µL, 12.2 mmol, 1.5 equiv) and MeCN (6 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave 1.385 g (7.64 mmol) of pure product as a colorless oil (94% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.96 (br. s, 2H), 4.28-4.21 (m, 2H), 1.83-1.74 (m, 1H), 1.57-1.49 (m, 2H), 1.41-1.33 (m, 1H), 1.20 (dp, J = 14.0, 7.0 Hz, 1H), 0.91 (d, J = 6.5 Hz, 3H), 0.88 (t, J = 7.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 70.3, 35.3, 31.0, 29.4, 18.9, 11.3; $[\alpha]^{25}_D$ = +5.8^o (c = 2.0, $CHCl_3$). These data agree with that previously reported in the literature.[8]

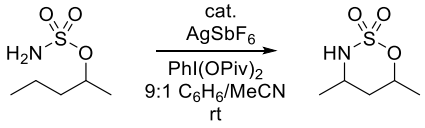
(+)-(*R*)-4-ethyl-4-methyl-1,2,3-oxathiazinane 2,2-dioxide [49].



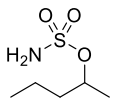
In all cases, material was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using CH_2Cl_2 → 2% Et_2O/CH_2Cl_2, affording pure product (starting material was not collected). Enantiopurity was established by chiral GC analysis using a CycloSil-B column with an isocratic method at 160°C.
Racemic product: t_r (*R*) = 22.51 min, t_r (*S*) = 24.35 min
Enantioenriched product: t_r (*R*) = 22.51 min
FePc conditions: (+)-(*R*)-3-methylpentyl sulfamate **48** (72.5 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, 0.5M) were used. By chiral GC analysis, product was 99% ee.
Run 1: (14.2 mg product, 0.079 mmol, 20%). Run 2: (13.7 mg product, 0.076 mmol, 19%). Run 3: (13.6 mg product, 0.076 mmol, 19%). **Average: 19% yield ± 0.5.**
MnPc conditions: (+)-(*R*)-3-methylpentyl sulfamate **48** (72.5 mg, 0.400 mmol, 1.0 equiv), [MnPc]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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. By chiral GC analysis, product was 99% ee.
Run 1: (33.3 mg product, 0.186 mmol, 46%). Run 2: (36.4 mg product, 0.203 mmol, 51%). Run 3: (34.4 mg product, 0.192 mmol, 48%). **Average: 48% yield ± 2.1.**
Mn(^{t}BuPc) conditions: (+)-(*R*)-3-methylpentyl sulfamate **48** (72.5 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (33.2 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), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. By chiral GC analysis, product was 99% ee.
Run 1: (44.3 mg product, 0.247 mmol, 62%). Run 2: (43.2 mg product, 0.241 mmol, 60%). Run 3: (40.4 mg product, 0.225 mmol, 56%). **Average: 59% yield ± 2.5.**
Pure product is isolated as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.77-4.63 (m, 2H), 4.10 (br. s, 1H), 1.86 (dq, J = 14.5, 7.5 Hz, 1H), 1.79 (ddd, J = 14.5, 8.0, 4.0 Hz, 1H), 1.71 (ddd, J = 15.0, 6.5, 4.0 Hz, 1H), 1.52 (dq, J = 14.0, 7.3 Hz, 1H), 1.37 (s, 3H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C-

NMR (125 MHz, $CDCl_3$) δ 69.1, 59.2, 34.4, 33.7, 24.3, 7.6; $[\alpha]^{26}_D = +7.6^o$ (*c* = 1.8, $CHCl_3$). These data agree with that previously reported in the literature.[8]

Kinetic Analysis of C—H Amination Reactions

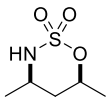


(±)-pentan-2-yl sulfamate [S55].

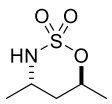


Prepared according to method **A**. 1.30 g (1.63 mL, 15.0 mmol) of pentan-2-ol were used, along with NaH (417 mg, 16.5 mmol, 1.1 equiv), DMF (27 mL), $ClSO_2NCO$ (1.95 mL, 22.5 mmol, 1.5 equiv), formic acid (850 µL, 22.5 mmol, 1.5 equiv) and MeCN (11.3 mL). Flash column chromatography on silica (100 mL SiO_2) using 4:1 hexanes:EtOAc as eluent gave 2.00 g (11.7 mmol) of pure product as a colorless oil (80% yield). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.76-4.70 (m, 3H), 1.79-1.71 (m, 1H), 1.60 (ddt, *J* = 13.9, 9.7, 5.8 Hz, 1H), 1.51-1.38 (m, 2H), 1.44 (d, *J* = 6.2 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 81.7, 38.7, 20.7, 18.5, 13.9. These data are in agreement with that previously reported in the literature.[19]

(±)-4,6-dimethyl-1,2,3-oxathiazinane 2,2-dioxide [S56].



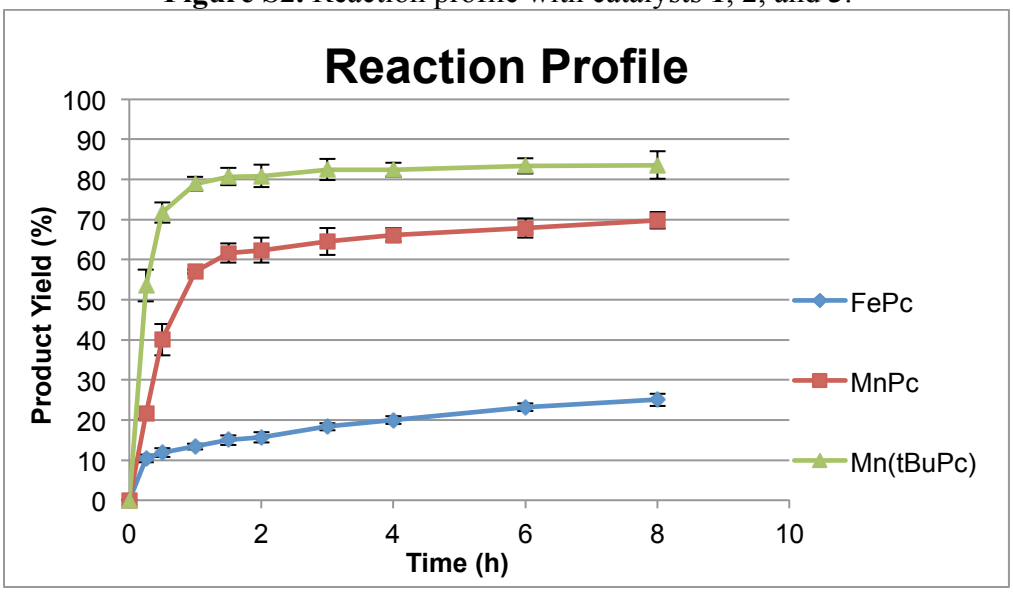
***Syn* diastereomer:** Isolated as a white sold. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.89 (dqd, *J* = 12.5, 6.3, 2.2 Hz, 1H), 3.87-3.78 (m, 1H), 3.65 (br. d, *J* = 10.6 Hz, 1H), 1.84 (dt, *J* = 14.3, 2.5 Hz, 1H), 1.44 (d, *J* = 6.2 Hz, 3H), 1.38 (dt, *J* = 14.4, 11.8 Hz, 1H), 1.29 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 81.0, 51.2, 38.8, 21.1, 20.7. These data are in agreement with that previously reported in the literature.[19]



***Anti* diastereomer:** Isolated as a white solid with ~20% of *syn* diastereomer. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.04 (dqd, *J* = 9.8, 6.4, 3.3 Hz, 1H), 4.37 (d, *J* = 7.8 Hz, 1H), 3.84 (dtd, *J* = 14.5, 7.3, 4.7 Hz, 1H), 1.87-1.78 (m, 1H), 1.71-1.66 (m, 1H), 1.50 (d, *J* = 6.5 Hz, 3H), 1.46 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 78.8, 77.4, 77.2, 76.9, 49.4, 36.0, 20.8, 19.7. These data are in agreement with that previously reported in the literature.[19]

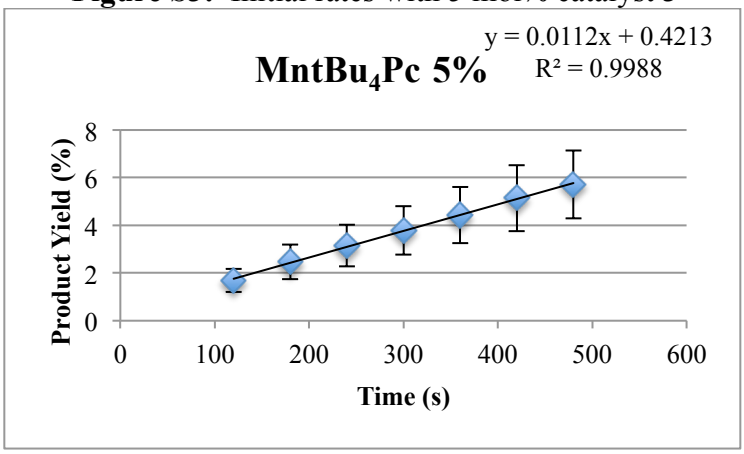
General procedure for reaction profile studies: Into a 1 dram vial was added $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), catalyst (0.020 mmol, 0.10 equiv), and a stir bar in a glovebox. The vial was then sealed with a septum-lined cap, covered in aluminum foil, taken out of the box, and topped with a balloon of argon. Pentan-2-yl sulfamate **S55** (33.4 mg, 0.200 mmol, 1.0 equiv) was taken up in 9:1 C_6H_6/MeCN (400 µL, 0.5M) and added via syringe, followed by internal standard (decane, 19.5 µL, 0.500 equiv). After stirring for 10-15 min, a 10 µL aliquot was removed (as a t_0 timepoint), then $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv) was added under an inert atmosphere and reaction stirred at room temp (~23°C) for 8h. 10 µL aliquots were removed by syringe at 15 min, 30 min, 1h, 1.5h, 2h, 3h, 4h, 6h, and 8h; aliquots were filtered through a short plug of silica (glass wool lined pipette, 1-2 mm SiO_2) with 1 mL Et_2O directly into a GC vial. Yields of **S56** were established by GC analysis based on a standard curve. Each catalyst was run in triplicate; reported values are averages of three runs with error bars denoting standard deviation.

Figure S2. Reaction profile with catalysts **1**, **2**, and **3**.



General Procedure for Initial Rate Analysis
5 mol% Conditions:
In order to obtain accurate initial rate data, all reactions for rate analysis were run at room temperature and at 0.25 M concentration. Into a flame-dried 1 dram vial was added $AgSbF_6$ (3.4 mg, 0.010 mmol, 0.05 equiv), [Mn(^{t}BuPc)]Cl (8.3 mg, 0.010 mmol, 0.05 equiv), and a stir bar in a glovebox. The vial was then sealed with a septum-lined cap, covered in aluminum foil, taken out of the box, and topped with a balloon of argon. Pentan-2-yl sulfamate **S55** (33.4 mg, 0.2 mmol, 1.0 equiv) and internal standard decane (0.08 mmol, 40 mol%), were dissolved in 9:1 C_6H_6/MeCN (400 µL, 0.5M) and added to the 1 dram vial. PhI(OPiv)$_2$ (163 mg, 0.400 mmol, 2.0 equiv) was dissolved in 9:1 C_6H_6/MeCN (400 µL, 0.5M), and added directly to the reaction. The vial was then sealed and placed to stir at rt. Aliquots (10 µL) were taken at the corresponding times from the reaction flask, and filtered through a silica pad with 600 µL of diethyl ether for GC analysis. The yield was determined by integration of the product peaks relative to the decane internal standard. Yields of **S56** are reported as the average of three runs with error bars denoting standard deviation.

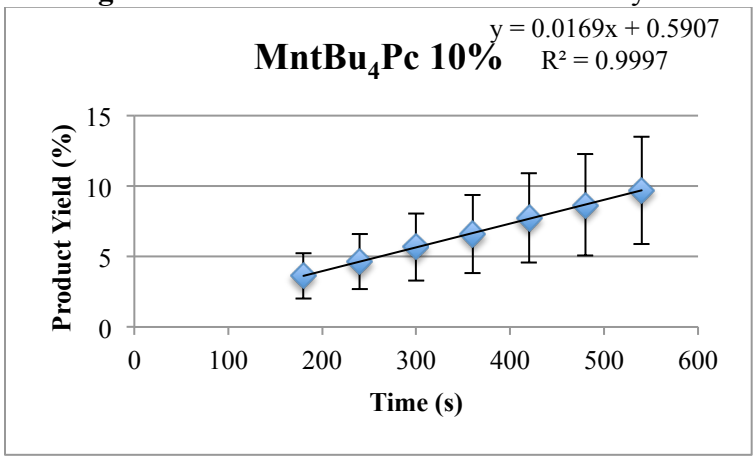
Figure S3: Initial rates with 5 mol% catalyst **3**



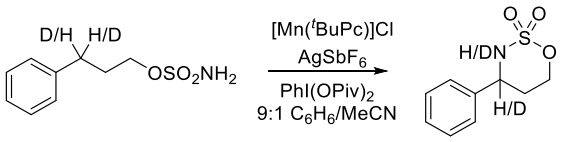
10 mol% Conditions:

In order to obtain accurate initial rate data, all reactions for rate analysis were run at room temperature and 0.25 M concentration. Into a flame-dried 1 dram vial was added $AgSbF_6$ (6.8 mg, 0.020 mmol, 0.10 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), and a stir bar in a glovebox. The vial was then sealed with a septum-lined cap, covered in aluminum foil, taken out of the box, and topped with a balloon of argon. Pentan-2-yl sulfamate **S55** (33.4 mg, 0.2 mmol, 1.0 equiv) and internal standard decane (0.08 mmol, 40 mol%.), were dissolved in 9:1 C_6H_6:MeCN (400 µL, 0.5M) and added to the 1 dram vial. $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) was dissolved in 9:1 C_6H_6/MeCN (400 µL, 0.5M), and added directly to the reaction. The vial was then sealed and placed to stir at room temperature. Aliquots (10 µL) were taken at the corresponding times from the reaction flask, and filtered through a silica pad with 600 µL of diethyl ether for GC analysis. The yield was determined by integration of the product peaks relative to the decane internal standard. Yields of **S56** are reported as the average of three runs with error bars denoting standard deviation.

Figure S4: Initial rates with 10 mol% catalyst **3**

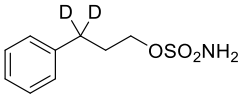


Determination of Kinetic Isotope Effect via Initial Rates



General Procedure for Initial Rate Analysis at 5 mol%: *In order to obtain accurate initial rate data, all reactions for rate analysis were run at room temperature and at 0.25 M concentration.* To a 1 dram flame-dried borosilicate vial containing a Teflon stir bar was added catalyst (0.010 mmol, 0.05 equiv) and $AgSbF_6$ (3.4 mg, 0.010 mmol, 0.05 equiv). 3-phenylpropyl sulfamate **46** or 3-phenylpropyl-3,3-d_2 sulfamate **46**-d_2 (33.4 mg, 0.2 mmol, 1.0 equiv) and internal standard 1-fluoro-2-nitrobenzene (0.08 mmol, 40 mol%), were dissolved in 9:1 C_6H_6/MeCN (400 µL, 0.5M) and added to the 1 dram vial. $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) was dissolved in 9:1 C_6H_6/MeCN (400 µL, 0.5M), and added directly to the reaction. The vial was then sealed and placed to stir at rt. Aliquots (10 µL) were taken at the corresponding times from the reaction flask, and filtered through a silica pad with 600 µL of isopropanol for HPLC (Zorbax CN, 4.6 x 250 nm) analysis. The yield was determined by integration of the product peaks relative to the 1-fluoro-2-nitrobenzene internal standard and comparison to a standard curve. Yields are reported as the average of three runs with error bars denoting standard deviation. Initial rates were determined for formation of **7** (Figures S5 and S6). Error for kinetic isotopes was calculated via propagation of the standard error of the mean for each set of rates.

(±)-3-phenylpropyl-3,3-d_2 sulfamate [46-d_2].



^{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), 2.08 (dt, J = 7.5, 7.0 Hz, 2H).

[Mn(tBuPc)]Cl: k_H/k_D= 0.0052 / 0.0030= 1.7 ± 0.1
[MnPc]Cl: k_H/k_D= 0.0034 / 0.0018= 1.9 ± 0.2

Figure S5: Initial rates with **46** and 5 mol% catalyst **3**

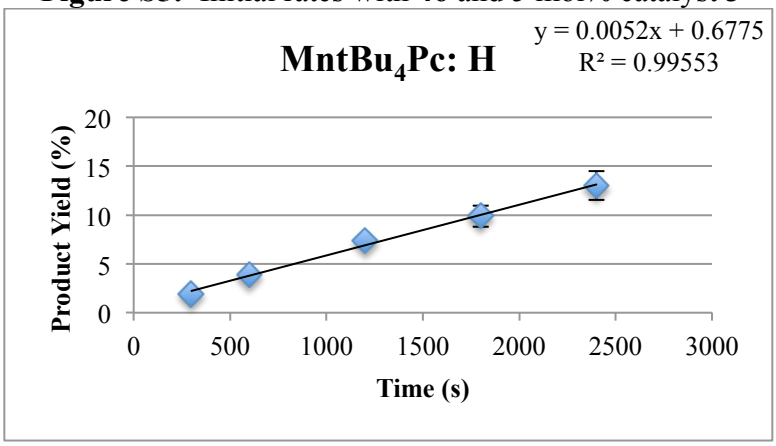


Figure S7: Initial rates with **46**-d_2 and 5 mol% catalyst **3**

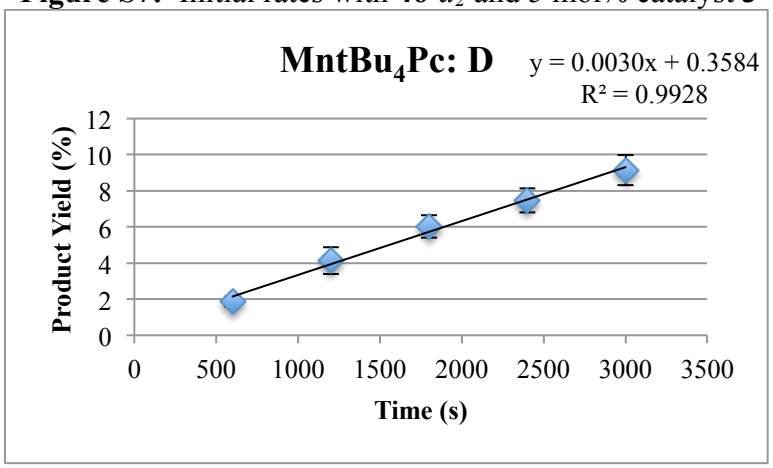


Figure S8: Initial rates with **46** and 5 mol% catalyst **2**

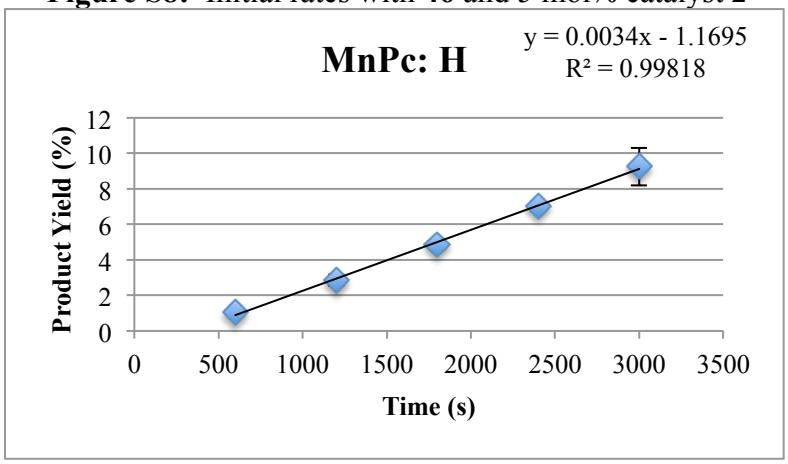
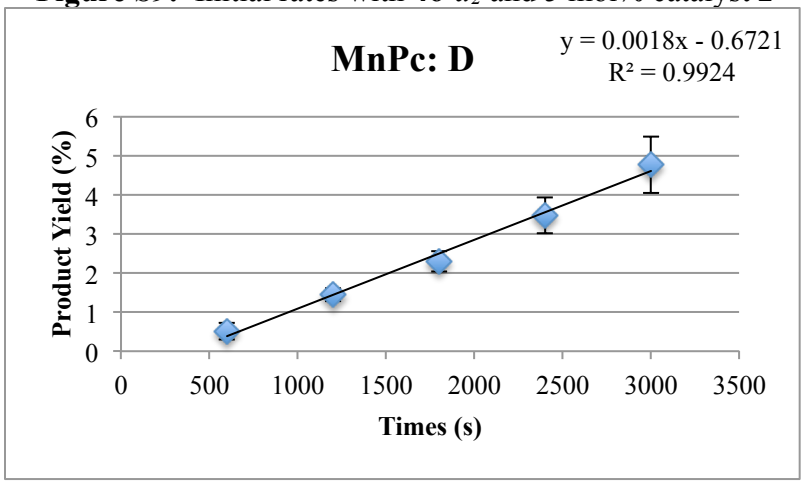


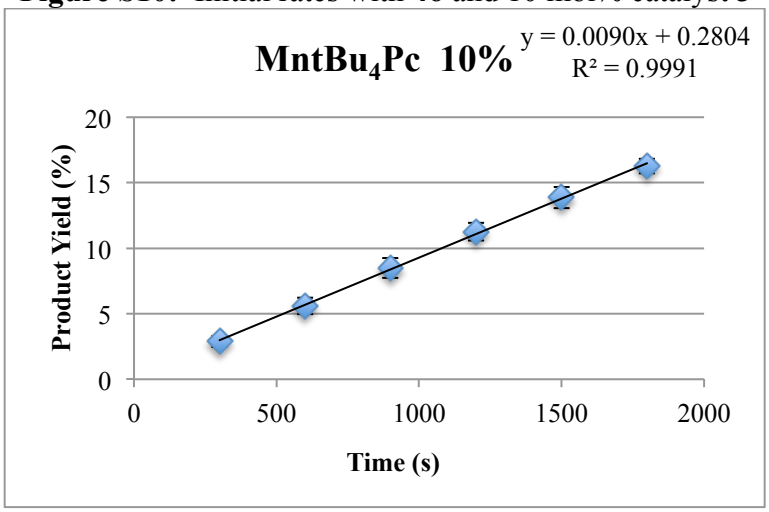
Figure S9: Initial rates with **46**-d_2 and 5 mol% catalyst **2**



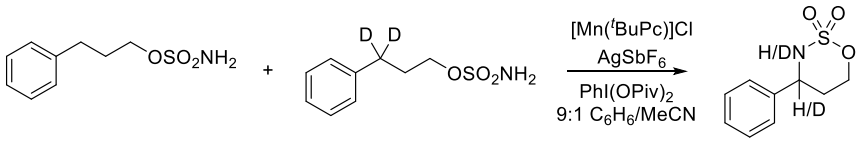
General Procedure for Initial Rate Analysis at 10 mol%*: In order to obtain accurate initial rate data, all reactions for rate analysis were run at room temperature and at 0.25 M concentration.* Into a flame-dried 1 dram vial was added $AgSbF_6$ (6.7 mg, 0.02 mmol, 0.10

equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.02 mmol, 0.10 equiv), and a stir bar in a glovebox. The vial was then sealed with a septum-lined cap, covered in aluminum foil, taken out of the box, and topped with a balloon of argon. 3-phenylpropyl sulfamate **46** (43.1 mg, 0.2 mmol, 1.0 equiv) and internal standard 1-fluoro-2-nitrobenzene (0.08 mmol, 40 mol%), were dissolved in 9:1 C_6H_6/MeCN (400 µL, 0.5M) and added to the 1 dram vial. $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) was dissolved in 9:1 C_6H_6/MeCN (400 µL, 0.5M), and added directly to the reaction. The vial was then sealed and placed to stir at rt. Aliquots (10 µL) were taken at the corresponding times from the reaction flask, and filtered through a silica pad with 600 µL of isopropanol for HPLC (Zorbax CN, 4.6 x 250 nm) analysis. The yield was determined by integration of the product peaks relative to the 1-fluoro-2-nitrobenzene internal standard and comparison to a standard curve. Yields are reported as the average of three runs with error bars denoting standard deviation.

Figure S10: Initial rates with **46** and 10 mol% catalyst **3**



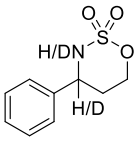
Intermolecular Kinetic Isotope Effect Study



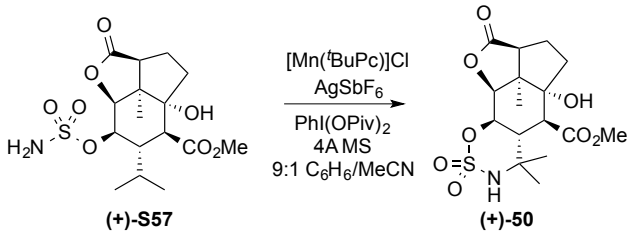
Method for KIE Determination: The column-purified product mixture **S54** (ca. 30 mg in 700 µL $CDCl_3$) was analyzed by ^{13}C-NMR (600 MHz instrument).[7,9,18] $Cr(acac)_3$ (15 mg) was added directly to the solution in the NMR tube immediately prior to running the NMR study; this helps to significantly reduce delay times needed to obtain accurate integrations. The experiment was run under inverse-gated decoupling conditions without sample spinning. The following parameters were used for the experiment, listed as Varian commands:
temp=23
dm='nny' (inverse-gated decoupling)
d1=5 (initial delay)
at=0.5 (acquisition time)
setsw(180,0) (spectral width, in ppm)
bs=64 (block size for FID)
nt=4416 (number of scans)
pw=7.0 (pulse width)
pw90=7.0 (90° pulse width)

The KIE was reported as the area of the protonated peak over that of the deuterated peak. The experiment was run in triplicate and each was analyzed by NMR. An average value was calculated with error reported as a standard deviation.
[Mn(^{t}BuPc)]Cl: k_H/k_D = 1.62 ± 0.06 (1.56, 1.67, 1.64).
[MnPc]Cl: k_H/k_D= 1.90 ± 0.09 (2.00, 1.81, 1.90).

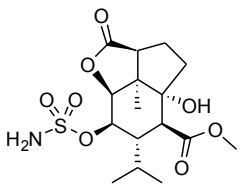
(±)-4-deuterio-4-phenyl-tetrahydro-1,2,3-oxathiazine-2,2-dioxide [S54].



3-phenylpropyl sulfamate **46** (43.1 mg, 0.200 mmol, 1.0 equiv), 3-phenylpropyl-3,3-d_2 sulfamate **46**-d_2 (43.5 mg, 0.200 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (162.5 mg, 0.400 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (400 µL, 0.5M) were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave the deuterated and protonated oxathiazinanes as a mixture. Characterization data are in agreement with that previously reported in the literature.[7]

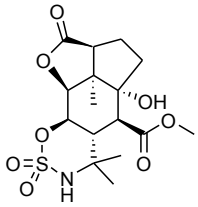


(+)-tetrahydropicrotoxin-(3-sulfamoyloxy)-15-methyl ester [S57].

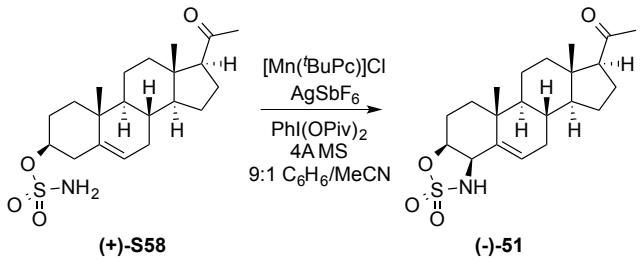


Prepared according to method **B**. 1.328 g (4.25 mmol) of (+)-tetrahydropicrotoxin-(3-hydroxy)-15-methyl ester[20] were used, along with Et_3N (1.48 mL, 10.6 mmol, 2.5 equiv), $ClSO_2NCO$ (923 µL, 10.6 mmol, 2.5 equiv), formic acid (400 µL, 10.6 mmol, 2.5 equiv) and CH_2Cl_2 (6 mL + 6 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 30% acetone/hexanes → 40% acetone/hexanes as eluent gave 590 mg (1.50 mmol) of pure product as a white solid (35% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.95 (br. s, 2H), 4.80 (d, *J* = 3.5 Hz, 1H), 4.71 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.75 (s, 3H), 2.79 (d, *J* = 7.5 Hz, 1H), 2.65 (d, *J* = 12.5 Hz, 1H), 2.36 (ddd, *J* = 12.5, 11.0, 2.0 Hz, 1H), 2.22 – 2.07 (m, 3H), 1.95 (td, *J* = 14.0, 6.5 Hz, 1H), 1.86-1.80 (m, 1H), 1.58 (dd, *J* = 14.0, 5.5 Hz, 1H), 1.34 (s, 3H), 1.10 (d, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 179.5, 172.3, 83.2, 81.3, 78.7, 54.9, 53.1, 52.3, 52.1, 39.3, 37.7, 29.1, 27.6, 21.3, 19.7, 16.8; IR (ATR, cm^{-1}) 3254, 2960, 1760, 1720, 1566, 1438, 1371, 1236, 1015, 965, 931, 825, 796; $[\alpha]^{25}_D$ = +78.1° (*c* = 1.0, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{16}H_{26}NO_8S$ $[M+H]^+$: 392.1379, found 392.1383.

(+)-tetrahydropicrotoxin-3-(2,2-dioxido-1,2,3-oxathiazinan-3-yl)-15-methyl ester [50].

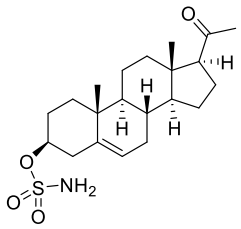


(+)-tetrahydropicrotoxin-(3-sulfamoyloxy)-15-methyl ester **S57** (78.3 mg, 0.200 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv), 50 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. Reaction stirred at rt for 17h. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 35% acetone/hexanes. Pure product was isolated as a white solid.
Run 1: (47.6 mg, 0.122 mmol, 61%), <10% rsm. Run 2: (44.6 mg, 0.115 mmol, 57%), <10% rsm. Run 3: (42.9 mg, 0.110 mmol, 55%), <10% rsm. **Average: 57% yield ± 2.1, <10% rsm.**
^{1}H-NMR (500 MHz, acetone-d_6) δ 6.28 (s, 1H), 4.96 (dd, *J* = 11.5, 3.5 Hz, 1H), 4.69 (d, *J* = 3.5 Hz, 1H), 4.15 (br. s, 1H), 3.71 (s, 3H), 2.86 (d, *J* = 7.5 Hz, 1H), 2.76 (d, *J* = 12.0 Hz, 1H), 2.31 (t, *J* = 12.0 Hz, 1H), 2.21-2.13 (m, 1H), 1.92-1.81 (m, 3H), 1.51 (s, 3H), 1.46 (s, 3H), 1.24 (s, 3H); ^{13}C-NMR (125 MHz, acetone-d_6) δ 179.2, 173.0, 83.8, 82.9, 79.0, 59.5, 55.3, 52.4, 52.2, 51.6, 40.5, 38.3, 30.9, 27.8, 21.3, 19.2; IR (ATR, cm^{-1}) 3582, 3190, 2954, 1777, 1711, 1443, 1397, 1363, 1289, 1224, 1196, 1154, 1092, 1049, 993, 975, 938, 920, 903, 865, 839, 732, 707; $[\alpha]^{23}_D$ = +66.7° (*c* = 0.5, acetone); HRMS (ESI) *m/z* calculated for $C_{16}H_{24}NO_8S$ $[M+H]^+$: 390.1223, found 390.1218.



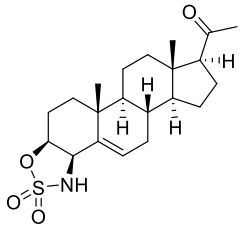
(+)-S58 (-)-51

(+)-pregnenolyl sulfamate [S58].

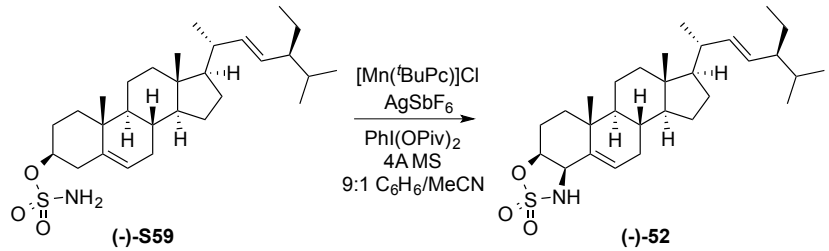


Prepared according to method **B**. 1.58 g (5.00 mmol) of (+)-pregnenolone were used, along with Et_3N (1.05 mL, 7.50 mmol, 1.5 equiv), $ClSO_2NCO$ (653 µL, 7.50 mmol, 1.5 equiv), formic acid (283 µL, 7.50 mmol, 1.5 equiv) and CH_2Cl_2 (3.8 mL + 7.1 mL). Flash column chromatography on silica (45 mm fritted glass column, 170 mm SiO_2) using 3:1 hexanes/EtOAc as eluent gave 967 mg (2.44 mmol) of pure product as a white solid (49% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.42 (dt, *J* = 5.0, 2.0 Hz, 1H), 4.72 (br. s, 2H), 4.44 (tt, *J* = 11.2, 5.3 Hz, 1H), 2.57-2.45 (m, 3H), 2.22- 1.99 (m, 7H), 1.92 (dt, *J* = 13.6, 3.7 Hz, 1H), 1.80-1.44 (m, 8H), 1.26-1.12 (m, 3H), 1.02 (s, 3H), 0.98 (dd, *J* = 11.3, 4.9 Hz, 1H), 0.63 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 209.9, 139.0, 123.5, 83.1, 63.8, 56.9, 49.9, 44.1, 38.8, 38.8, 37.0, 36.5, 31.9, 31.7, 28.6, 24.6, 22.9, 21.2, 19.3, 13.4; IR (film, cm^{-1}) 3421, 3239, 3102, 2937, 1683, 1580, 1470, 1451, 1376, 1352, 1174, 978, 937, 857, 820, 729; $[\alpha]_D^{25}$ = +19.4° (*c* = 0.62, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{21}H_{34}NO_4S$ $[M+H]^+$: 396.2209, found 396.2208.

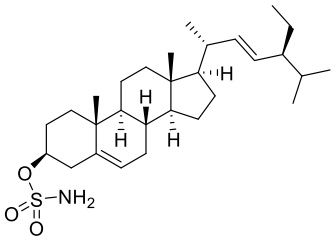
(-)-3,4-(2,2-dioxido-1,2,3-oxathiazinan-3-yl)-pregnenolone [51].



Pregenolyl sulfamate **S58** (79.1 mg, 0.200 mmol, 1.0 equiv), [Mn(*t*BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 4:1 C_6H_6/MeCN (400 µL, 0.5M) were used. Reaction stirred at rt for 12 h. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 120 mm SiO_2) using 20% EtOAc/hexanes → 30% EtOAc/hexanes → 40% EtOAc/hexanes. Pure product was isolated as a white solid.
Run 1: (41.9 mg, 0.106 mmol, 53%), <5% rsm. Run 2: (45.5 mg, 0.116 mmol, 58%), <5% rsm. Run 3: (42.3 mg, 0.107 mmol, 54%), <5% rsm. **Average: 55% yield ± 2.2, <5% rsm.**
^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.82 (dd, *J* = 4.8, 2.3 Hz, 1H), 4.75 (dt, *J* = 11.5, 6.0 Hz, 1H), 4.54 (t, *J* = 5.5 Hz, 1H), 4.38 (d, *J* = 5.0 Hz, 1H), 2.53 (t, *J* = 8.8 Hz, 1H), 2.33-2.14 (m, 3H), 2.13 (s, 3H), 2.11-2.04 (m, 2H), 1.92 (dt, *J* = 14.0, 4.0 Hz, 1H), 1.71-1.57 (m, 5H), 1.49-1.41 (m, 2H), 1.28-1.22 (m, 2H), 1.21 (s, 3H), 1.20-1.09 (m, 2H), 1.02-0.96 (m, 1H), 0.64 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 209.5, 135.9, 133.3, 84.0, 63.6, 62.1, 56.9, 49.2, 44.0, 38.6, 36.2, 33.6, 32.1, 31.6, 31.5, 24.5, 23.8, 22.9, 21.2, 20.7, 13.4; IR (film, cm^{-1}) 3252, 2944, 1698, 1454, 1339, 1291, 1174, 966, 941, 754, 667, 587, 479; $[\alpha]_D^{25}$ = -23.6° (*c* = 0.68, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{21}H_{32}NO_4S$ $[M+H]^+$: 394.2052, found 394.2053.



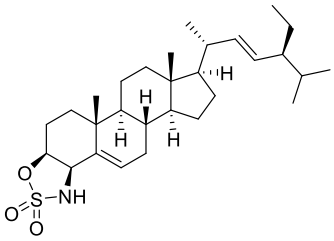
(-)-stigmasteryl sulfamate [S59].



Prepared according to method **B**. 2.06 g (5.00 mmol) of (-)-stigmasterol were used, along with Et_3N (1.38 mL, 10.0 mmol, 2.0 equiv), $ClSO_2NCO$ (870 µL, 10.0 mmol, 2.0 equiv), formic acid (377 µL, 10.0 mmol, 2.0 equiv) and CH_2Cl_2 (5.0 mL + 7.1 mL). Flash column chromatography on silica (45 mm fritted glass column, 170 mm SiO_2) using 4:1 hexanes/acetone as eluent gave 1.40 g (2.85 mmol) of pure product as a white solid (57% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.42-5.40 (m, 1H), 5.15 (dd, *J* = 15.2, 8.6 Hz, 1H), 5.02 (dd, *J* = 15.2, 8.5 Hz, 1H), 4.83 (br. s, 2H), 4.43 (tt, *J* = 11.0, 5.3 Hz, 1H), 2.56-2.46 (m, 2H), 2.11-1.95 (m, 4H), 1.91 (dt, *J* = 13.5, 3.7 Hz, 1H), 1.81-1.67 (m, 2H), 1.56-1.40 (m, 9H), 1.28-0.91 (m, 13H), 0.85-0.79 (m, 9H), 0.70 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.9, 138.4, 129.5, 123.8, 83.5, 56.9, 56.1, 51.4, 50.1, 42.3, 40.7, 39.7, 38.9, 37.1, 36.6, 32.0, 31.9, 29.1, 28.7, 25.6, 24.5, 21.4, 21.3, 21.2, 19.4, 19.1, 12.4, 12.2; IR (film, cm^{-1}) 3323, 3262, 2962, 2937, 2893, 2866, 1569, 1458, 1381, 1328, 1189, 968, 869, 807, 737; $[\alpha]_D^{25}$ = -50.8° (*c* = 0.5, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{29}H_{49}NO_3SNa$ $[M+Na]^+$: 514.3331, found 514.3333.

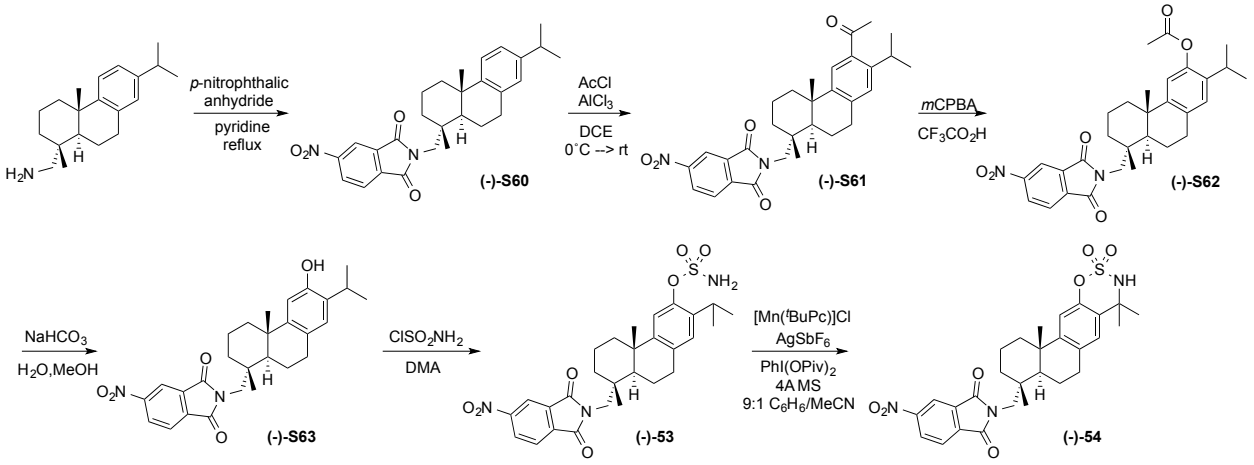
(-)-3,4-(2,2-dioxido-1,2,3-oxathiazinan-3-yl)-stigmasterol [52].



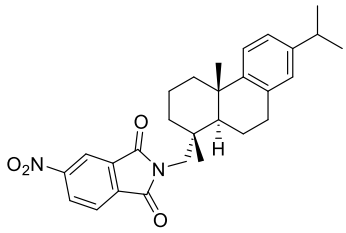
Stigmasteryl sulfamate **S59** (98.4 mg, 0.200 mmol, 1.0 equiv), Mn(*t*BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 4:1 C_6H_6/MeCN (400 µL, 0.5M) were used. Reaction stirred for 12 h. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 120 mm SiO_2) using 10% acetone/hexanes → 15% acetone/hexanes. Pure product was isolated as a white solid.

Run 1: (61 mg, 0.125 mmol, 63%), <5% rsm. Run 2: (64 mg, 0.131 mmol, 66%), <5% rsm. Run 3: (67 mg, 0.137 mmol, 69%), <5% rsm. **Average: 66% yield ± 2.1, <5% rsm.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.82 (dd, *J* = 4.7, 2.2 Hz, 1H), 5.15 (dd, *J* = 15.1, 8.6 Hz, 1H), 5.02 (dd, *J* = 15.1, 8.6 Hz, 1H), 4.74 (dt, *J* = 10.7, 6.0 Hz, 1H), 4.53 (t, *J* = 5.6 Hz, 1H), 4.29 (d, *J* = 5.3 Hz, 1H), 2.27 (tdd, *J* = 13.9, 10.8, 3.5 Hz, 1H), 2.14 (dt, *J* = 17.2, 4.5 Hz, 1H), 2.08-1.99 (m, 3H), 1.91 (dt, *J* = 14.0, 4.0, 1H), 1.72 (dtd, *J* = 13.6, 9.4, 5.9 Hz, 1H), 1.63-1.39 (m, 10H), 1.28-1.25 (m, 2H), 1.23- 0.99 (m, 10H), 0.93-0.90 (m, 2H), 0.88-0.75 (m, 9H), 0.71 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.3, 135.9, 133.9, 129.7, 84.4, 62.4, 57.1, 56.1, 51.5, 49.5, 42.4, 40.7, 39.6, 36.3, 33.7, 32.3, 32.1, 31.7, 29.1, 27.3, 25.6, 24.5, 23.9, 21.4, 21.3, 20.8, 19.2, 12.5, 12.3; IR (film, cm^{-1}) 3326, 2955, 2867, 1456, 1369, 1321, 1190, 1173, 1021, 987, 940, 925, 820, 790, 752, 688; $[\alpha]_D^{25}$ = -60.1° (*c* = 0.62, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{29}H_{48}NO_3S$ $[M+H]^+$: 490.3355, found 490.3362.



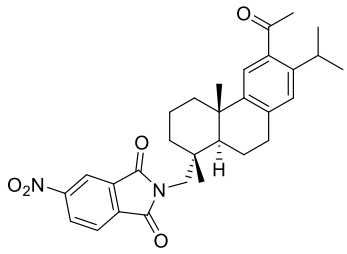
(-)-(*N*-nitroisoindolyl)dihydroabietylamine [S60].



(+)-Dehydroabietylamine (2.89 g, 90% purity) was dissolved in 21 mL pyridine. 4-nitrophthalic anhydride (2.145 g, 11.1 mmol) was added and the reaction was allowed to stir under reflux overnight. Upon completion, the reaction was poured into 80 mL ice and extracted with Et_2O (3x50 mL). The combined organic layer was washed with 2M HCl (2x30 mL), H_2O (2x30 mL) and brine (30 mL), then dried over $MgSO_4$. The product was loaded on celite and was purified *via* MPLC separation (Silica 40g Gold column, 40 mL/min, hexanes → 5% EtOAc/hexanes) to give 2.301 g (5.0 mmol) **S60**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.9 Hz, 1H), 8.59 (dd, *J* = 8.1, 2.0 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 6.97 (dd, *J* = 7.9, 2.1 Hz, 1H), 6.94-6.92 (s, 1H), 3.76 (d, *J* = 13.8 Hz, 1H), 3.56 (d, *J* = 13.8 Hz, 1H), 3.06-2.96 (m, 2H), 2.82 (hept, *J* = 6.9 Hz, 1H), 2.25 (ddt, *J* = 12.0, 8.2, 3.2 Hz, 2H), 1.84 (m, 1H), 1.68 (m, 2H), 1.52 (dt, *J* = 13.4, 3.5 Hz, 1H), 1.44-1.38 (m, 1H), 1.36-1.25 (m, 2H), 1.24 (s, 3H), 1.22 (d, *J* = 7.0 Hz, 6H), 1.08 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 167.2, 166.9, 151.7, 147.1, 145.7, 136.4, 134.9, 133.4, 129.2, 127.1, 124.5, 123.8 (2 peaks), 118.7, 49.5, 45.1, 39.7, 38.1, 37.6, 37.0, 33.4, 30.0, 25.9, 24.1, 24.0, 19.5, 19.2, 18.5; IR (film, cm^{-1}): 2958, 2955, 2872, 1780, 1722, 1543, 1496, 1437, 1383, 1344, 1092, 910; $[\alpha]^{27}_D$ = -66.3° (*c* = 0.63, $CHCl_3$); HRMS (ESI) m/z calculated for $C_{28}H_{33}N_2O_4$ $[M+H]^+$: 461.2440, found 461.2452.

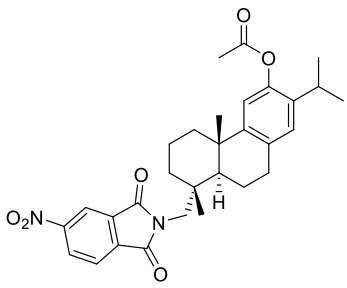
(-)-12-acetyl-(*N*-nitroisoindolyl)dihydroabietylamine [S61].



S60 (1.842 g, 4.00 mmol, 1.0 equiv) was dissolved in 25 mL $(CHCl)_2$ in a flame dried 100 mL recovery flask. Acetyl chloride (1.099 g, 14.0 mmol, 3.5 equiv) and $AlCl_3$ (1.600 g, 12.0 mmol, 3.0 equiv) was added at 0ºC. The reaction was allowed to warm up slowly to rt and stirred for 22h. The reaction mixture was poured into 30 mL cold 6M HCl and extracted with Et_2O (3x50 mL). The combined organic layers were washed by brine and dried over $CaCl_2$. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO_2) using 10% EtOAc/hexanes → 15% EtOAc/hexanes as eluent gave 1.889 g (3.76 mmol) product as a pale yellow solid (94% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 2.0 Hz, 1H), 8.59 (dd, *J* = 8.1, 2.0 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.35 (s, 1H), 7.08 (s, 1H), 3.76 (d, *J* = 13.9 Hz, 1H), 3.56 (d, *J* = 13.9 Hz, 1H), 3.44 (hept, *J* = 6.8 Hz, 1H), 3.02 (dd, *J* = 9.0, 4.5 Hz, 2H), 2.51 (s, 3H), 2.29-2.25 (m, 2H), 1.89 - 1.80 (m, 1H), 1.78-1.64 (m, 2H), 1.55-1.51 (m, 1H), 1.43-1.26 (m, 3H), 1.24 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 3H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.08 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 203.3, 167.3, 167.0, 151.8, 146.8, 145.0, 139.1, 136.4, 136.3, 133.4, 129.3, 127.3, 124.6, 124.1, 118.8, 49.5, 45.1, 39.7, 38.1, 37.6, 37.0, 30.6, 30.1, 28.8, 26.0, 24.3, 24.2, 19.4, 19.3, 18.5. IR (ATR, cm^{-1}): 2929, 1781, 1719, 1678, 1539, 1435, 1384, 1338, 1262, 1232, 1194, 1088; $[\alpha]^{26}_D$ = -23.8^o (*c* = 1.0, $CHCl_3$); HRMS (ESI) m/z calculated for $C_{30}H_{35}N_2O_5$ $[M+H]^+$: 503.2546, found 503.2527.

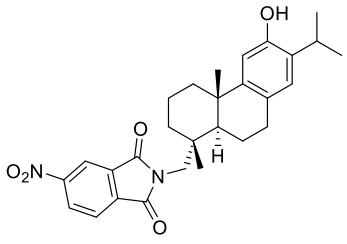
(-)-12-acetoxy-(*N*-nitroisoindolyl)dihydroabietylamine [S62].



S61 (1.898 g, 3.76 mmol, 1.0 equiv.) was dissolved in 10 mL anhydrous CH_2Cl_2. *m*CPBA (2.292 g, 9.30 mmol, 2.5 equiv, 70% in H_2O) was added at 0ºC followed by dropwise addition of CF_3CO_2H (429 mg, 3.76 mmol, 1.0 equiv.). The reaction was allowed to warm up to rt and stir for 24h. The reaction was sequentially washed by 10% Na_2SO_3 (10 mL), H_2O (10 mL), saturated aq. $NaHCO_3$ (10 mL), H_2O (10 mL), then organic layer was dried over $CaCl_2$. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 10% EtOAc/hexanes → 15% EtOAc/hexanes as eluent gave 1.622 g (3.13 mmol) product as white solid (83% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64-8.63 (m, 1H), 8.59 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.01 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.97 (s, 1H), 6.76 (s, 1H), 3.78 (d, *J* = 13.9, 1H), 3.51 (d, *J* = 13.8, 1H), 3.0 - 2.97 (m, 2H), 2.89 (hept, *J* = 6.8 Hz, 1H), 2.30-2.23 (m, 1H), 2.28 (s, 3H), 2.15-2.12 (m, 1H), 1.85-1.80 (m, 1H), 1.71-1.59 (m, 2H), 1.51 (dq, *J* = 13.5, 2.7 Hz, 1H), 1.37 (dd, *J* = 12.2, 2.0 Hz, 1H), 1.30 (ddd, *J* = 21.0, 12.8, 4.1 Hz, 2H), 1.22 (s, 3H), 1.19 (d, *J* = 6.8 Hz, 3H), 1.15 (d, *J* = 7.0 Hz, 3H), 1.07 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 170.1, 167.3, 167.0, 151.8, 148.4, 146.1, 137.0, 136.5, 133.5, 133.2, 129.3, 127.3, 124.6, 118.9, 117.6, 49.4, 44.5, 39.8, 38.1, 37.7, 37.1, 29.5, 27.2, 25.9, 23.1 (2 peaks), 21.1, 19.5, 19.3, 18.5; IR (ATR, cm^{-1}): 2931, 1756, 1719, 1622, 1540, 1497, 1435, 1397, 1383, 1339, 1205, 1164, 1087, 1060, 1041, 1017, 941, 911; $[\alpha]^{26}_D$ = -23.7^o (*c* = 0.94, $CHCl_3$); HRMS (ESI) m/z calculated for $C_{30}H_{35}N_2O_6$ $[M+H]^+$: 519.2495, found 519.2488.

(-)-12-hydroxy-(*N*-nitroisoindolyl)dihydroabietylamine [S63].

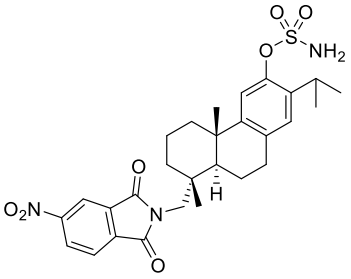


S62 (1.540 g, 2.97 mmol, 1.0 equiv) was taken up in 8 mL MeOH. $NaHCO_3$ (1.072 g, 12.8 mmol, 4.3 equiv) was added into the mixture followed by 1 drop of H_2O. The reaction was stirred at rt for 24h then 40ºC for 72h. Upon completion as determined by TLC, CH_2Cl_2 (20 mL) and H_2O (20 mL) were added and the mixture was acidified with 3M H_2SO_4 to pH~5. The aqueous layer was extracted with TBME (3x30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO_2) using 20% EtOAc/hexanes as eluent gave 896 mg (1.88 mmol) product as an orange solid (63% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.8 Hz, 1H), 8.58 (dd, *J* = 8.2, 1.8 Hz, 1H), 8.01 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.87 (s, 1H), 6.59 (s, 1H), 4.63 (br. s, 1H), 3.75 (dd, *J* = 13.9, 1.6 Hz, 1H),

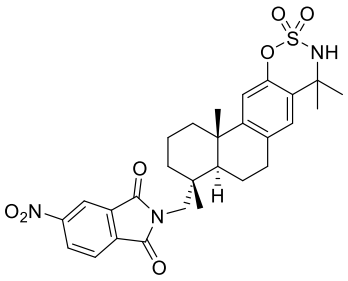
3.57 (dd, *J* = 13.8, 1.6 Hz, 1H), 3.10 (hept, *J* = 6.8 Hz, 1H), 2.99-2.88 (m, 2H), 2.24-2.19 (m, 1H), 2.17-2.13 (m, 1H), 1.85-1.76 (m, 1H), 1.75-1.60 (m, 2H), 1.51 (dq, *J* = 13.5, 2.7 Hz, 1H), 1.38 (dd, *J* = 12.2, 2.0 Hz, 1H), 1.30 (ddd, *J* = 21.0, 12.8, 4.1 Hz, 2H), 1.25-1.19 (m, 9H), 1.07 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 167.3, 167.0, 151.9, 150.8, 148.2, 136.5, 133.5, 131.8, 129.3, 127.2, 127.0, 124.6, 118.8, 110.7, 49.7, 45.3, 39.8, 38.2, 37.7, 37.2, 29.4, 26.9, 25.8, 22.8, 22.7, 19.7, 19.3, 18.6; IR (thin film, cm^{-1}): 2960, 2935, 2892, 1780, 1720, 1620, 1543, 1466, 1437, 1416, 1398, 1385, 1344, 1165, 1090, 910; $[\alpha]^{26}_D$ = -41.6° (*c* = 0.93, $CHCl_3$); HRMS (ESI) m/z calculated for $C_{28}H_{33}N_2O_5$ $[M+H]^+$: 477.2389, found 477.2388.

(-)-12-sulfamoyloxy-(*N*-nitroisoindolyl)dihydroabietylamine [53].



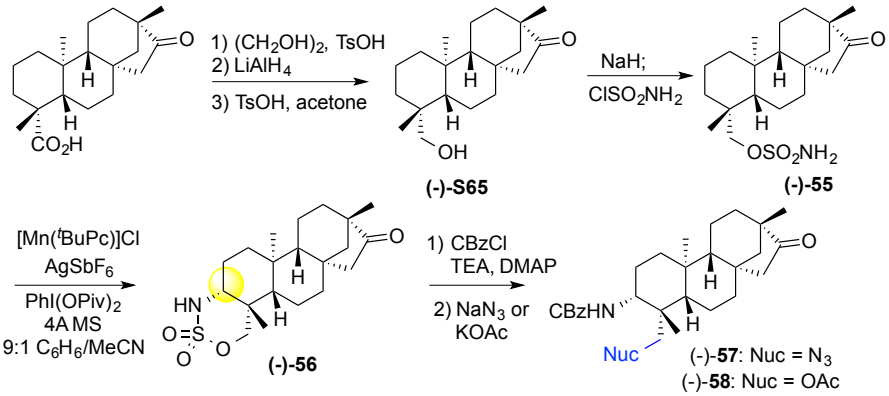
Prepared according to method **C**. **S63** (238 mg, 0.50 mmol, 1.0 equiv), $ClSO_2NCO$ (65 µL, 0.75 mmol, 1.5 equiv), formic acid (28 µL, 0.75 mmo, 1.5 equiv), MeCN (1 mL) and DMA (1 mL) were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 20% EtOAc/hexanes as eluent gave 189 mg (0.34 mmol) of pure product as a white solid (68% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.59 (dd, *J* = 8.2, 1.9 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.16 (s, 1H), 7.00 (s, 1H), 4.85 (br. s, 2H), 3.75 (d, *J* = 13.8 Hz, 1H), 3.55 (d, *J* = 13.8 Hz, 1H), 3.26 (hept, *J* = 7.5, 7.0 Hz, 1H), 2.98 (dd, *J* = 8.9, 4.5 Hz, 2H), 2.28-2.17 (m, 2H), 1.82 (ddd, *J* = 18.0, 12.8, 9.0 Hz, 1H), 1.67 (dtd, *J* = 18.4, 10.3, 4.0 Hz, 2H), 1.56-1.50 (m, 1H), 1.36-1.14 (m, 12H), 1.07 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 167.4, 167.0, 151.8, 148.7, 145.7, 138.2, 136.4, 134.6, 133.4, 129.4, 127.7, 124.7, 118.9, 117.2, 49.5, 44.8, 39.7, 38.0, 37.8, 36.9, 29.5, 26.6, 25.8, 23.5, 23.4, 19.4, 19.3, 18.4; IR (thin film, cm^{-1}): 3402, 3383, 3296, 3107, 2964, 2937, 2870, 1780, 1722, 1624, 1543, 1495, 1464, 1437, 1385, 1344, 1248, 1190, 1153, 1088, 933; $[\alpha]^{25}_D$ = -23.1° (*c* = 0.86, $CHCl_3$); HRMS (ESI) m/z calculated for $C_{28}H_{34}N_3O_7S$ $[M+H]^+$: 556.2117, found 556.2128.

(-)-12,15-(2,2-dioxido-1,2,3-oxathiazinan-3-yl)-(*N*-nitroisoindolyl)dihydroabietylamine [54].

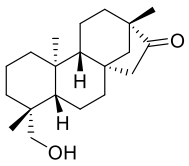


53 (111.1 mg, 0.200 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), crushed 4Å MS (50 mg), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (400 µL) were used. The reaction was stirred for 24h at rt (~20ºC). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 20% EtOAc/hexanes → 30% EtOAc/hexanes with 0.5% AcOH as eluent gave product as slightly yellow solid.
Run 1: (77.7 mg, 0.140 mmol, 70%), 0% rsm. Run 2: (75.8 mg, 0.137 mmol, 68%), 0% rsm. Run 3: (79.1 mg, 0.143 mmol, 72%), 0% rsm. **Average: 70% yield ± 2.0, 0% rsm.**
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 2.0 Hz, 1H), 8.59 (dd, *J* = 8.1, 2.0 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 6.88 (s, 1H), 6.80 (s, 1H), 4.50 (d, *J* = 4.2 Hz, 1H), 3.75 (d, *J* = 13.8 Hz, 1H), 3.54 (d, *J* = 13.9 Hz, 1H), 2.97 (dd, *J* = 9.1, 4.6 Hz, 2H), 2.27 (dtd, *J* = 11.5, 4.7, 2.4 Hz, 1H), 2.16-2.13 (m, 1H), 1.82 (tt, *J* = 13.0, 9.1 Hz, 1H), 1.73-1.63 (m, 1H), 1.69 (s, 3H), 1.67 (s, 3H), 1.54-1.51 (m, 1H), 1.34-1.24 (m, 4H), 1.21 (s, 3H), 1.07 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 167.3, 167.0, 151.9, 151.5, 147.4, 136.4, 133.4, 132.9, 129.4, 126.8, 125.0, 124.7, 118.9, 114.4, 60.1, 49.4, 44.6, 39.7, 38.0, 37.9, 36.9, 31.0, 30.9, 29.3, 25.7, 19.4, 19.3, 18.4; IR (thin film, cm^{-1}): 3267, 2933, 2870, 1780, 1720, 1624, 1541, 1493, 1429, 1400, 1387, 1344, 1207, 1173,

1155, 1092, 910; $[\alpha]^{25}_D$ = -43.6° (*c* = 0.66, $CHCl_3$); HRMS (ESI) m/z calculated for $C_{28}H_{32}N_3O_7S$ $[M+H]^+$: 554.1961, found 554.1968.



(-)-18-hydroxy-13-methyl-17-norkauran-16-one [S65].

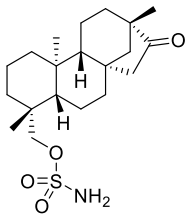


(-)-Isosteviol (2.229 g, 7.00 mmol, 1.0 equiv) was suspended in benzene (6 mL, ~1.2M) in a 25 mL round-bottom flask equipped with stir bar. Ethylene glycol (429 uL, 7.70 mmol, 1.1 equiv) and *p*-TSA (6.1 mg, 0.035 mmol, 0.005 equiv) were added, then flask was fitted with a Dean-Stark trap and condenser. Reaction stirred under reflux for 48h. Upon completion, reaction was cooled to rt, diluted with CH_2Cl_2, and washed with H_2O (5 times). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. Crude material was carried forward without additional purification.

$LiAlH_4$ (531 mg, 14.0 mmol, 2.0 equiv) was suspended in THF (35 mL) in a 250 mL multineck flask equipped with stir bar and reflux condenser. Isosteviol ketal from previous step was dissolved in remaining THF (35 mL) and added dropwise. Reaction was then heated to reflux and stirred 48h. Upon completion, reaction was cooled to rt, diluted with Et_2O (100 mL), carefully quenched with dropwise addition of H_2O, then poured into a 500 mL Erylenmeyer flask containing sat. aq. Rochelle salt solution (150 mL). Once layers became clear, material was extracted with Et_2O (3x50 mL), then organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The resulting residue was suspended in acetone (14 mL, 0.5M) in a 50 mL round-bottom flask. *p*-TSA (12.1 mg, 0.070 mmol, 0.01 equiv) was added, then reaction stirred for 48h at room temp. Upon completion, reaction was diluted with Et_2O (50 mL) and washed with H_2O (4x15 mL). Organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes/EtOAc as eluent gave 1.037 g (3.41 mmol) of pure **S65** as a white solid (49% yield over three steps).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.74 (d, *J* = 11.0 Hz, 1H), 3.44 (d, *J* = 10.5 Hz, 1H), 2.64 (dd, *J* = 18.5, 3.8 Hz, 1H), 1.82-1.73 (m, 2H), 1.71-1.61 (m, 5H), 1.57-1.48 (m, 3H), 1.43-1.20 (m, 7H), 1.07-1.05 (m, 2H), 0.99 (s, 3H), 0.97 (s, 3H), 0.96-0.88 (m, 1H), 0.86 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 222.9, 65.6, 57.0, 55.6, 54.6, 48.8 (2 peaks), 41.8, 39.6, 39.5, 38.6, 37.7, 37.5, 35.6, 27.2, 20.4, 20.3, 20.0, 18.1, 15.6; IR (ATR, cm^{-1}) 3536, 2927, 2843, 1737, 1715, 1454, 1400, 1253, 1115, 1090, 1070, 1033, 975, 852; $[\alpha]^{25}_D$ = -40.7° (*c* = 1.0, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{20}H_{33}O_2$ $[M+H]^+$: 305.2481, found 305.2479.

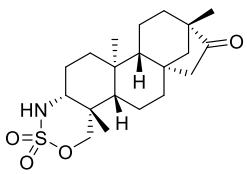
(-)-18-sulfamoyloxy-13-methyl-17-norkauran-16-one [55].



Prepared according to method **A**. 1.037 g (3.41 mmol) of **S65** were used, along with NaH (94.6 mg, 3.75 mmol, 1.1 equiv), DMF (3 mL + 2 mL), $ClSO_2NCO$ (445 µL, 5.11 mmol, 1.5 equiv), formic acid (193 µL, 5.11 mmol, 1.5 equiv) and MeCN (2.5 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes/EtOAc as eluent, followed by recrystallization from EtOAc layered with hexanes, gave 685 mg (1.79 mmol) of pure product as a white solid (52% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.67 (br. s, 2H), 4.35 (d, *J* = 9.5 Hz, 1H), 3.97 (d, *J* = 9.5 Hz, 1H), 2.63 (dd, *J* = 18.5, 4.0 Hz, 1H), 1.83-1.62 (m, 7H), 1.59-1.36 (m, 6H), 1.30 (dq, *J* = 13.0, 3.5 Hz, 1H), 1.27-1.18 (m, 2H), 1.12 (dd, *J* = 12.5, 1.5 Hz, 1H), 1.09-1.02 (m, 1H), 1.04 (s, 3H), 0.98 (s, 3H), 0.94-0.88 (m, 1H), 0.88 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 223.0, 74.3, 56.8, 55.5, 54.4, 48.9, 48.7, 41.5, 39.5, 39.2, 37.6, 37.4, 37.3, 35.7, 27.4, 20.3 (2 peaks), 20.0, 17.9, 15.7; IR (film, cm^{-1}) 3363, 3228, 2927, 2873, 2846, 1728, 1568, 1454, 1377, 1367, 1169, 1109, 1092, 962, 914, 837; $[\alpha]^{25}_D$ = -40.9^o (*c* = 1.0, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{20}H_{34}NO_4S$ $[M+H]^+$: 384.2209, found 384.2208.

(-)-3,18-(2,2-dioxido-1,2,3-oxathiazinan-3-yl)-13-methyl-17-norkauran-16-one [56].



Preparative-scale C—H amination: (-)-18-sulfamoyloxy-13-methyl-17-norkauran-16-one **55** (76.7 mg, 0.200 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (8.3 mg, 0.010 mmol, 0.05 equiv), $AgSbF_6$ (3.4 mg, 0.010 mmol, 0.05 equiv), $PhI(OPiv)_2$ (325 mg, 0.800 mmol, 2.0 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. Product was purified via flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2:1 hexanes/EtOAc. Pure product was isolated as a white solid. X-ray quality crystals were obtained *via* diffusion crystallization from EtOAc with pentane.

Run 1: (71.2 mg, 0.187 mmol, 93%), 0% rsm. Run 2: (70.4 mg, 0.185 mmol, 92%), 0% rsm. Run 3: (70.1 mg, 0.184 mmol, 92%), 0% rsm. **Average: 92% yield ± 0.5, 0% rsm.**

Reduced catalyst and oxidant loadings: (-)-18-sulfamoyloxy-13-methyl-17-norkauran-16-one **55** (147 mg, 0.400 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (8.3 mg, 0.010 mmol, 0.025 equiv), $AgSbF_6$ (3.4 mg, 0.010 mmol, 0.025 equiv), $PhI(OPiv)_2$ (244 mg, 0.600 mmol, 1.5 equiv), 100 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (800 µL, 0.5M) were used. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 2% Et_2O/CH_2Cl_2 → 5% Et_2O/CH_2Cl_2 → Et_2O gave 116.0 mg (0.304 mmol) of pure product as a white solid (76% yield). *This yield is identical to that obtained when the reaction is run on a larger scale.*

Gram-scale C—H amination: (-)-18-sulfamoyloxy-13-methyl-17-norkauran-16-one **55** (1.00 g, 2.61 mmol, 1.0 equiv), [Mn(^{t}BuPc)]Cl (54.0 mg, 0.065 mmol, 0.025 equiv), $AgSbF_6$ (22.1 mg, 0.065 mmol, 0.025 equiv), $PhI(OPiv)_2$ (1.590 mg, 3.92 mmol, 1.5 equiv), 650 mg crushed 4Å MS, and 9:1 C_6H_6/MeCN (5.2 mL, 0.5M) were used. Product was purified via flash column chromatography on silica (45 mm fritted glass column, 200 mm SiO_2) using 5% Et_2O/CH_2Cl_2 → Et_2O. Pure product was isolated as a white solid.

Run 1: (768 mg, 2.01 mmol, 77%), (155 mg rsm, 0.404 mmol, 16%). Run 2: (730 mg, 1.91 mmol, 73%), (145 mg rsm, 0.378 mmol, 15%). Run 3: (738 mg, 1.93 mmol, 74%), (130 mg rsm, 0.339 mmol, 13%). **Average: 75% yield ± 1.7, 15% rsm ± 0.9.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.31 (d, *J* = 3.5 Hz, 1H), 5.02 (d, *J* = 11.5 Hz, 1H), 3.95 (d, *J* = 12.0 Hz, 1H), 2.96 (d, *J* = 12.0 Hz, 1H), 2.60 (dd, *J* = 19.0, 3.5 Hz, 1H), 2.53 (app. q, *J* = 12.8

Hz, 1H), 1.79-1.50 (m, 9H), 1.41-1.33 (m, 2H), 1.33 (s, 3H), 1.27-1.12 (m, 5H), 0.96 (s, 3H), 0.94 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 222.2, 75.4, 63.7, 55.2, 54.9, 54.2, 48.8, 48.6, 41.1, 39.2, 37.5, 37.1 (2 peaks), 35.8, 24.5, 23.6, 20.2, 19.9, 19.8, 15.5; IR (film, cm^{-1}) 3242, 2949, 2929, 2850, 1726, 1454, 1437, 1371, 1360, 1180, 947, 785, 773; $[\alpha]^{25}_D$ = -4.5° (*c* = 1.0, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{20}H_{32}NO_4S$ $[M+H]^+$: 382.2052, found 382.2055.

Scheme S1. Crystal structure of (-)-(18,18-dioxido-1,2,3-oxathiazinan-3-yl)-13-methyl-17-norkauran-16-one (**56**)

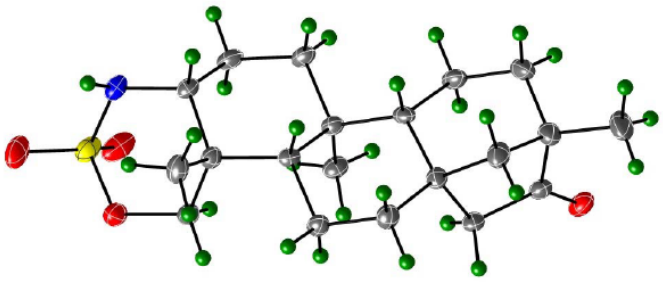


Table S11. Crystal data and structure refinement for **56**.

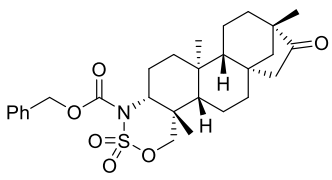
Identification code	cm72isa	
Empirical formula	C20 H31 N O4 S	
Formula weight	381.52	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 12.1565(17) Å	α= 90°.
	b = 13.8036(19) Å	β= 90.433(4)°.
	c = 34.595(4) Å	γ = 90°.
Volume	5805.0(13) $Å^3$	
Z	12	
Density (calculated)	1.310 Mg/m^3	
Absorption coefficient	0.192 mm^{-1}	
F(000)	2472	
Crystal size	0.685 x 0.536 x 0.12 mm^3	
Theta range for data collection	1.588 to 25.460°.	
Index ranges	-14<=h<=14, -16<=k<=16, -41<=l<=27	
Reflections collected	93497	
Independent reflections	21440 [R(int) = 0.0637]	
Completeness to theta = 25.242°	100.0 %	

Absorption correction	Integration
Max. and min. transmission	0.98024 and 0.89778
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	21440 / 38 / 1441
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.0996
R indices (all data)	R1 = 0.0537, wR2 = 0.1060
Absolute structure parameter	-0.01(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.472 and -0.465 e.Å^{-3}

The associated B level alerts are present regarding Hirshfeld test differences. This means that the displacement parameters along the bond pair are larger than the parameters perpendicular to the bond. These alerts can occur when the atoms are misidentified. This is not the case in this structure. These problems can also occur between the heaviest atom and its bond pairs. There are 6 identical molecules in the asymmetric unit with one molecule having suspect Hirshfeld test differences because it is vibrating a little more than the rest of the molecules. Because there are 5 other molecules to compare the chiral structure to, we are confident that the structure solution is correct.

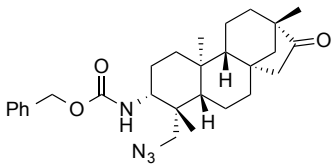
CCDC #1421220 (**56**) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

(-)-*N*-benzylcarbamoyl-3,18-(2,2-dioxido-1,2,3-oxathiazinan-3-yl)-13-methyl-17-norkauran-16-one [S66].



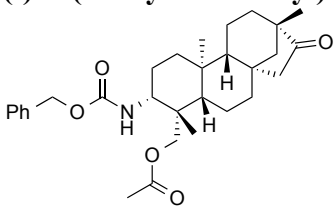
(-)-3,18-(2,2-dioxido-1,2,3-oxathiazinan-3-yl)-13-methyl-17-norkauran-16-one **56** (76.2 mg, 0.200 mmol, 1.0 equiv) was taken up in THF (870 µL). 4-dimethylaminopyridine (24.0 mg, 0.200 mmol, 1.0 equiv), Et_3N (557 µL, 4.00 mmol, 20 equiv), and benzyl chloroformate (275 µL, 1.90 mmol, 9.5 equiv) were added and reaction was stirred for 2h. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 4:1 hexanes/EtOAc → 2:1 hexanes/EtOAc as eluent gave 85.3 mg (0.170 mmol) of pure product as a white solid (83% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.34-7.32 (m, 1H), 5.33 (dd, J = 12.5, 17.5 Hz, 2H), 4.85 (d, J = 12.0 Hz, 1H), 4.13 (d, J = 11.9 Hz, 2H), 2.64 (dd, J = 18.5, 3.8 Hz, 1H), 2.24 (qd, J = 13.6, 13.1, 3.2 Hz, 1H), 1.83-1.54 (m, 9H), 1.404-1.39 (m, 2H), 1.31 (s, 3H), 1.29-1.17 (m, 4H), 1.03 (dd, J = 13.9, 3.9 Hz, 1H), 0.99 (s, 3H), 0.97 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 221.6, 152.4, 134.9, 128.8, 128.5, 127.7, 75.9, 69.5, 67.2, 55.2, 54.6, 54.2, 48.8, 48.7, 40.9, 39.2, 38.1, 37.2, 37.1 (2 peaks), 26.9, 23.7, 20.3, 20.2, 19.9, 14.3; IR (thin film, cm^{-1}) 2935, 2852, 1736, 1456, 1392, 1290, 1174, 976, 813, 751; $[\alpha]^{25}_D$ = -50.7^o (c = 1.2, $CHCl_3$); HRMS (ESI) m/z calculated for $C_{28}H_{38}NO_6S$ [M+H]+: 516.2420, found 516.2421.

(-)-3-(benzylcarbamoyl)-18-azido-13-methyl-17-norkauran-16-one [57].

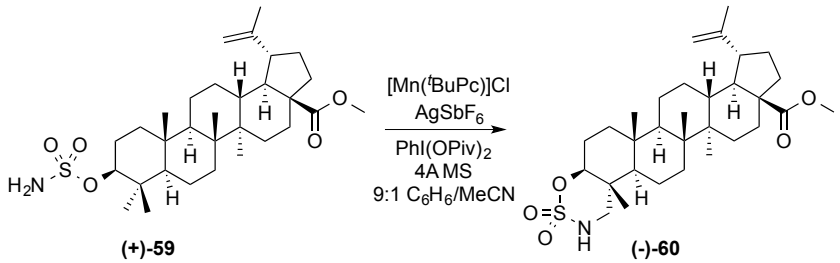


CBz-protected (-)-3,18-(2,2-dioxido-1,2,3-oxathiazinan-3-yl)-13-methyl-17-norkauran-16-one **S66** (103 mg, 0.200 mmol, 1.0 equiv) was taken up in DMF (500 µL) in a 1-dram vial. Sodium azide (26.0 mg, 0.400 mmol, 2.0 equiv) was added, then vial was sealed with a Teflon-lined cap and reaction stirred at 40°C for 48h. After cooling to rt, reaction was diluted with 1.5 mL Et_2O and 0.5 mL 10% aq. HCl, then stirred for 30 min. This mixture was poured into 15 mL brine, then extracted with Et_2O (3x15 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. Flash column chromatography on silica (35 mm fritted glass column, 120 mm SiO_2) using 4:1 hexanes/EtOAc as eluent gave 53.3 mg (0.111 mmol) of product as a white solid (56% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.36-7.29 (m, 5H), 5.68 (d, *J* = 9.0 Hz, 1H), 5.12 (d, *J* = 12.5 Hz, 1H), 5.05 (d, *J* = 12.5 Hz, 1H), 3.71 (d, *J* = 13.0 Hz, 1H), 3.36 (ddd, *J* = 12.5, 8.5, 4.0 Hz, 1H), 3.22 (d, *J* = 13.0 Hz, 1H), 2.59 (dd, *J* = 18.8, 3.8 Hz, 1H), 1.80-1.06 (m, 17H), 1.14 (s, 3H), 0.97 (s, 3H), 0.83 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 222.2, 156.3, 136.8, 128.6, 128.2, 128.1, 66.6, 59.6, 57.2, 55.4, 54.4, 54.0, 48.8, 48.5, 41.8, 41.3, 39.3, 38.3, 37.3 (2 peaks), 37.2, 25.3, 23.6, 20.5, 20.2, 19.9, 15.8; IR (thin film, cm^{-1}) 3408, 2935, 2850, 2101, 1733, 1512, 1455, 1246, 1072, 1047, 1016, 755; $[\alpha]^{25}_D$ = -28.0^o (*c* = 2.3, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{28}H_{39}N_4O_3$ $[M+H]^+$: 479.3026, found 479.3022.

(-)-3-(benzylcarbamoyl)-18-acetoxy-13-methyl-17-norkauran-16-one [58].

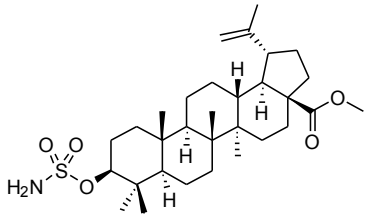


CBz-protected (-)-3,18-(2,2-dioxido-1,2,3-oxathiazinan-3-yl)-13-methyl-17-norkauran-16-one **S66** (103 mg, 0.200 mmol, 1.0 equiv) was taken up in DMF (500 µL) in a 1-dram vial. Potassium acetate (58.9 mg, 0.600 mmol, 3.0 equiv) was added and reaction was stirred at 80^o C for 48h. Additional KOAc (9.8 mg, 0.100 mmol, 0.5 equiv) was added at this point, then reaction continued to stir at 80^{o}C for 24h more. After cooling to rt, reaction was diluted with Et_2O (1.5 mL) and 10% aq. HCl (0.5 mL), then stirred for 30 min. This mixture was poured into brine (15 mL), then extracted with Et_2O (3x15 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 5% Et_2O in DCM as eluent gave 74.9 mg (0.15 mmol) of pure product as a white solid (76% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 5H), 5.33 (d, *J* = 9.3 Hz, 1H), 5.09 (s, 2H), 4.21-4.09 (m, 2H), 3.39 (ddd, *J* = 13.0, 9.3, 4.1 Hz, 1H), 2.59 (dd, *J* = 18.5, 3.7 Hz, 1H), 2.01 (s, 3H), 1.77-1.49 (m, 10H), 1.42-1.31 (m, 3H), 1.25-1.08 (m, 4H), 1.05 (s, 3H), 0.96 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 222.2, 170.8, 156.3, 136.9, 128.5, 128.1, 127.9, 66.5, 65.2, 59.0, 57.2, 55.2, 54.2, 48.8, 48.5, 41.5, 41.3, 39.3, 38.4, 37.2, 37.2, 25.5, 22.7, 21.1, 20.5, 20.3, 19.9, 15.5; IR (thin film, cm^{-1}): 3445, 3349, 2936, 2850, 1737, 1520, 1455, 1399, 1375, 1317, 1246, 1126, 1072, 1047, 1017, 754; $[\alpha]^{25}_D$ = -25.5^o (*c* = 1.6, $CHCl_3$); HRMS (ESI) m/z calculated for $C_{30}H_{42}NO_5$ [M+H]+: 496.3063, found 496.3070.



(+)-59 (-)-60

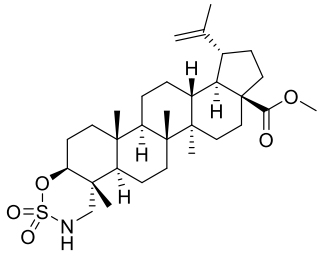
(+)-3-(sulfamoyloxy) betulinic acid methyl ester [59].



Prepared according to method **B**. Betulinic acid methyl ester[21] (304 mg, 0.645 mmol, 1.0 equiv) was used, along with $ClSO_2NCO$ (169 µL, 1.94 mmol, 3.0 equiv), formic acid (73 µL, 1.94 mmol, 3.0 equiv), Et_3N (273 µL, 1.94 mmol, 3.0 equiv) and CH_2Cl_2 (1.0 mL + 2.0 mL). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 20% acetone/hexanes as eluent afforded 196 mg (0.357 mmol) of pure product as a white solid (55% yield). *NOTE: the product should be stored and transferred under an Ar atmosphere.*

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.00 (br. d, *J* = 8.7 Hz, 2H), 4.72 (d, *J* = 2.5 Hz, 1H), 4.62 - 4.55 (br. s, 1H), 4.18 (dd, *J* = 12.1, 4.6 Hz, 1H), 3.65 (s, 3H), 2.97 (td, *J* = 10.9, 4.5 Hz, 1H), 2.26-2.13 (m, 2H), 2.05-1.97 (m, 1H), 1.93-1.78 (m, 3H), 1.75-1.64 (m, 2H), 1.67 (s, 3H), 1.56 (t, *J* = 11.4 Hz, 1H), 1.52-1.46 (m, 1H), 1.45-1.30 (m, 8H), 1.30-1.18 (m, 2H), 1.16-1.10 (m, 1H), 1.06-0.79 (m, 2H), 1.00 (s, 3H), 0.94 (s, 3H), 0.89 (s, 3H), 0.83 (s, 3H), 0.82 (s, 3H), 0.79-0.73 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 176.8, 150.6, 109.8, 91.9,56.6, 55.7, 51.4, 50.5, 49.5, 47.1, 42.5, 40.7, 38.8, 38.6, 38.3, 37.1, 37.1, 34.3, 32.2, 30.7, 29.7, 28.1, 25.5, 24.5, 21.0, 19.5, 18.4, 16.3, 16.2, 16.0, 14.8; IR (ATR, cm^{-1}):3269, 2947, 2868, 1728, 1642, 1449, 1328, 1186, 1136, 929, 903, 874, 846; $[\alpha]^{27}_D$ = +14.2° (*c* = 1.1, $CHCl_3$); HRMS (ESI) *m/z* calculated for $C_{31}H_{52}NO_5S$ $[M+H]^+$: 550.3566, found 550.3571.

(-)-3,23-(2,2-dioxido-1,2,3-oxathiazinan-3-yl)-24-methyl betulinic acid methyl ester [60].

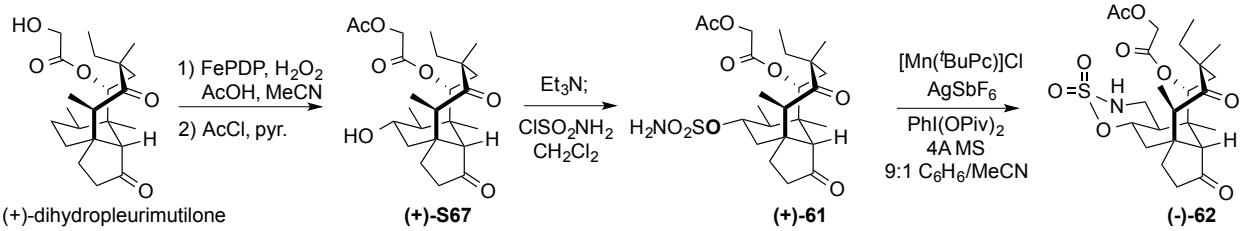


59 (110.0 mg, 0.200 mmol, 1.0 equiv), [Mn(*t*BuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), 50 mg crushed 4Å MS, $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (600 µL, 0.33 M) were used. The reaction was stirred for 24h at rt (~20ºC). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 10% acetone/hexanes → 15% acetone/hexanes with 0.5% AcOH as eluent afforded product as white solid. We observed a minor product resulting from epoxidation of the aminated product (confirmed by ^{1}H NMR and HRMS), likely due to the presence of exogenous water or oxygen. This normally accounted for an additional ~5% of the total C—H amination, although in some cases accounted for 10-15% yield if special precautions were not taken.

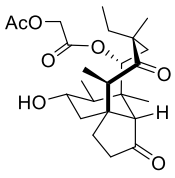
Run 1: (78.9 mg, 0.144 mmol, 72%), 0% rsm. Run 2: (83.5 mg, 0.152 mmol, 76%), 0% rsm. Run 3: (86.6 mg, 0.158 mmol, 79%), 0% rsm. **Average: 76% yield ± 3.5, 0% rsm.**

^{1}H NMR (500 MHz, acetone-d_6) δ 6.53 (dd, *J* = 9.8, 5.0 Hz, 1H), 4.73 (d, *J* = 2.4 Hz, 1H), 4.60 (d, *J* = 2.3 Hz, 1H), 4.50 (dd, *J* = 12.2, 4.1 Hz, 1H), 3.65 (s, 3H), 3.25 (dd, *J* = 13.8, 5.0 Hz, 1H), 3.15 (dd, *J* = 13.8, 9.5 Hz, 1H), 3.02 (td, *J* = 11.0, 5.0 Hz, 1H), 2.28 (ddd, *J* = 12.9, 11.4, 3.6 Hz, 1H), 2.23-2.18 (m, 1H), 1.92-1.76 (m, 4H), 1.76-1.57 (m, 3H), 1.70 (s, 3H), 1.55-1.10 (m, 14H),

1.09 (s, 3H), 1.05-1.00 (m, 1H), 1.04 (s, 3H), 0.96 (s, 3H), 0.95 (s, 3H); ^{13}C-NMR (125 MHz, Acetone-d_6) δ 176.8, 151.5, 110.3, 91.0, 57.3, 56.6, 52.6, 51.7, 51.2, 50.2, 48.1, 43.4, 41.8, 39.6, 39.1, 38.5, 37.5, 37.0, 34.7, 32.8, 31.4, 30.6, 26.3, 24.5, 21.7, 19.6, 18.8, 17.7, 16.5, 15.2, 11.5; IR (ATR, cm^{-1}): 3285, 2946, 2870, 1723, 1642, 1450, 1432, 1359, 1184, 1153, 1134, 1044, 938, 881, 843, 825; $[\alpha]^{26}_D$ = -12.4^o (*c* = 1.05, $CHCl_3$); HRMS (ESI) m/z calculated for $C_{31}H_{50}NO_5S$ $[M+H]^+$: 548.3410, found 548.3414.



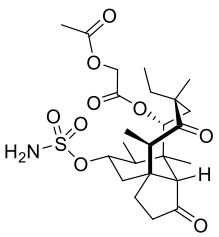
(+)-(7*S*)-hydroxy-dihydropleuromutilone-acetate [S67].



(-)-(7*S*)-hydroxy-dihydropleuromutilone[22] (25.0 mg, 0.063 mmol, 1.0 equiv.) was dissolved in 0.2 mL pyridine. Acetyl chloride (45.0 mg, 0.063 mmol, 1.0 equiv.) was added at 0ºC. The reaction was allowed to stir at 0ºC for 3h. The reaction was diluted with 10 mL CH_2Cl_2, washed with 1M HCl (2x5 mL), H_2O (5 mL) and dried over Na_2SO_4. Flash column chromatography on silica (35 mm fritted glass column, 30 mL SiO_2) using 30% EtOAc/hexanes → 50% EtOAc/hexanes as eluent gave 19.9 mg (0.0456 mmol) product as white solid (72% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 (d, *J* = 8.8 Hz, 1H), 4.61-4.51 (ab q., 2H), 3.86 (td, *J* = 11.0, 4.6 Hz, 1H), 3.41 (q, *J* = 6.6 Hz, 1H), 2.31-2.16 (m, 4H), 2.18 (s, 3H), 2.10-2.03 (m, 1H), 1.99 (dd, *J* = 15.8, 8.8 Hz, 1H), 1.64-1.63 (m, 1H), 1.57-1.46 (m, 4H), 1.49 (s, 3H), 1.35 (d, *J* = 15.8 Hz, 1H), 1.14 (d, *J* = 6.4 Hz, 3H), 1.11-1.03 (m, 1H), 0.98 (s, 3H), 0.95 (d, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 7.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 217.4, 216.1, 170.4, 167.1, 70.7, 69.3, 61.5, 58.5, 51.6, 45.8, 44.5, 43.7, 43.4, 43.2, 39.2, 34.5, 29.9, 24.4, 22.1, 20.6, 15.1, 13.0, 12.1, 9.2; IR (ATR, cm^{-1}): 3497, 2972, 2942, 1735, 1693, 1454, 1421, 1377, 1282, 1242, 1199, 1080, 1029, 972, 958, 916; $[\alpha]^{25}_D$ = +9.9^o (*c* = 1.11, $CHCl_3$); HRMS (ESI) m/z calculated for $C_{24}H_{37}O_7$ $[M+H]^+$: 437.2539, found 437.2540.

(+)-(7*S*)-sulfamoyloxy-dihydropleuromutilone-acetate [61].

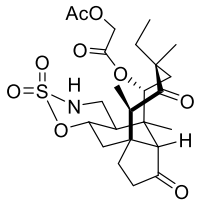


Prepared according to method **B**. **S67** (258.9 mg, 0.59 mmol) was used, along with $ClSO_2NCO$ (154 µL, 1.77 mmol, 3.0 equiv), formic acid (69 µL, 1.77 mmol, 3.0 equiv), Et_3N (247 µL, 1.77 mmol, 3.0 equiv) and CH_2Cl_2 (1.0 mL + 1.0 mL). Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 30% EtOAc/hexanes → 50% EtOAc/hexanes as eluent gave 145.3 mg (0.28 mmol) of pure product as a white solid (48% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.07 (d, *J* = 8.4 Hz, 1H), 4.82 (br. s, 2H), 4.68 - 4.62 (m, 2H), 4.44 (d, *J* = 16.2 Hz, 1H), 3.44 (q, *J* = 6.6 Hz, 1H), 2.47 (ddd, *J* = 14.1, 4.6, 2.3 Hz, 1H), 2.30-2.18 (m, 3H), 2.17 (s, 3H), 2.00 (dd, *J* = 15.9, 8.5 Hz, 1H), 1.82 (dq, *J* = 11.4, 7.1 Hz, 1H), 1.64 (d, *J* = 2.5 Hz, 1H), 1.60-1.45 (m, 3H), 1.50 (s, 3H), 1.42-1.32 (m, 2H), 1.16 (d, *J* = 6.5 Hz, 3H), 1.03 (d, *J* = 7.1 Hz, 3H), 0.99 (s, 3H), 0.81 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ

216.9, 215.5, 171.0, 167.6, 81.2, 70.5, 61.6, 58.4, 51.5, 46.0, 44.1, 43.6, 43.1, 42.1, 37.0, 34.4, 29.8, 24.5, 22.0, 20.6, 15.2, 13.0, 12.0, 9.2; IR (ATR, cm^{-1}): 3273, 2973, 1735, 1694, 1563, 1455, 1376, 1284, 1199, 1182, 1080, 973, 956m 918, 863; $[\alpha]^{25}_D$ = +34.4° (*c* = 0.95, $CHCl_3$); HRMS (ESI) m/z calculated for $C_{24}H_{37}NO_9SNa$ $[M+Na]^+$: 538.2087, found 538.2083.

(-)-7,16-(2,2-dioxido-1,2,3-oxathiazinan-3-yl)-dihydropleuromutilone-acetate [62].



61 (103.1 mg, 0.200 mmol, 1.0 equiv), [Mn(ᵗBuPc)]Cl (16.6 mg, 0.020 mmol, 0.10 equiv), $AgSbF_6$ (6.9 mg, 0.020 mmol, 0.10 equiv), crushed 4Å MS (50 mg), $PhI(OPiv)_2$ (163 mg, 0.400 mmol, 2.0 equiv) and 9:1 C_6H_6/MeCN (400 µL, 0.5M) were used. The reaction was stirred for 24h at rt (~20ºC). Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 20% EtOAc/hexanes → 30% EtOAc/hexanes with 0.5% AcOH as eluent gave product as colorless oil.

Run 1: (82.2 mg, 0.160 mmol, 80%), <5% rsm. Run 2: (88.6 mg, 0.172 mmol, 86%), <5% rsm. Run 3: (89.0 mg, 0.173 mmol, 87%), <5% rsm. **Average: 84% yield ± 3.8, <5% rsm.**

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72 (d, *J* = 8.7 Hz, 1H), 5.05 (td, *J* = 11.4, 4.9 Hz, 1H), 4.76 (dd, *J* = 10.6, 4.2 Hz, 1H), 4.59 (s, 2H), 3.45 (dt, *J* = 14.0, 3.3 Hz, 1H), 3.37 (q, *J* = 6.5 Hz, 1H), 3.28 (dt, *J* = 14.3, 11.2 Hz, 1H), 2.37-2.12 (m, 5H), 2.16 (s, 3H), 1.93-1.84 (m, 2H), 1.75 (d, *J* = 2.5 Hz, 1H), 1.57-1.49 (m, 2H), 1.51 (s, 3H), 1.39 (d, *J* = 15.9 Hz, 1H), 1.30-1.23 (m, 1H), 1.13 (d, *J* = 6.5 Hz, 3H), 0.96 (s, 3H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 216.6, 215.5, 170.5, 166.7, 81.4, 70.4, 61.4, 58.1, 51.5, 45.6, 45.2, 44.6, 43.3, 42.8, 42.4, 35.4, 34.2, 29.7, 23.9, 22.0, 20.5, 14.1, 13.0, 9.2. IR (ATR, cm^{-1}): 3262, 2969, 1736, 1693, 1420, 1368, 1283, 1183, 1072, 1038, 978, 960, 921, 865, 824; $[\alpha]^{25}_D$ = -7.8° (*c* = 0.83, $CHCl_3$); HRMS (ESI) m/z calculated for $C_{24}H_{36}NO_9S$ $[M+H]^+$: 514.2111, found 514.2109.

See separate supporting information file for ^{1}H and ^{13}C-NMR spectra of all reported compounds, as well as labeled, integrated ^{13}C-NMR spectra of purified H/D mixtures for the KIE study, GC traces of standards and enriched substrates for the stereoretention experiments, and nOE and 2D NMR spectra for the betulinic acid and pleuromutilone substrates.

References

[1] Alternatively, this reagent can be prepared using the following procedure: Fiori, K.W.; Du Bois, J. *J. Am. Chem. Soc.* **2007**, *129*, 562.

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[4] 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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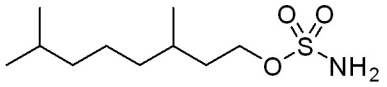

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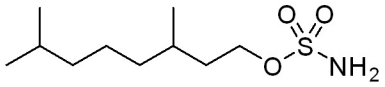

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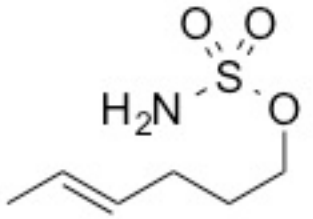

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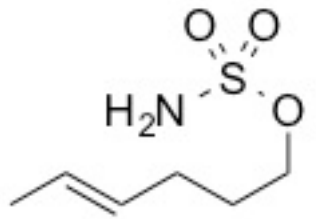

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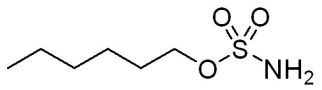

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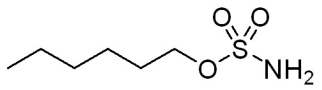

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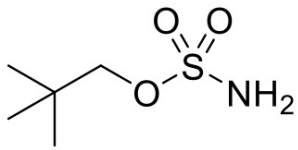

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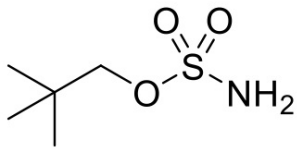

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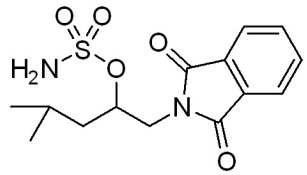

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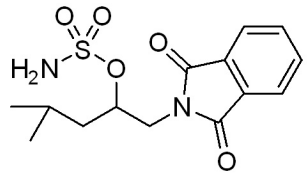

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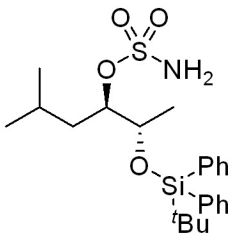

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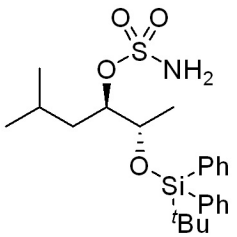
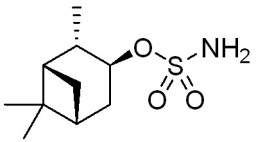
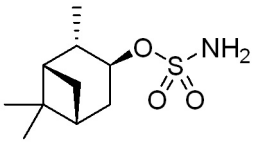
20	Acquired Size	32768
21	Spectral Size	65536



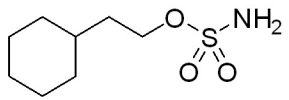
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	58
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-07-30T18:16:53
15	Modification Date	2014-07-30T18:16:55
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1012.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



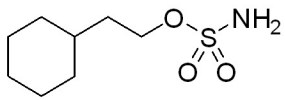
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	400
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-07-30T18:31:38
15	Modification Date	2014-07-30T18:31:40
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1270.8
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



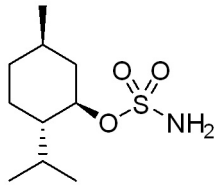
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	26
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-05-26T08:56:55
15	Modification Date	2014-05-26T08:56:56
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1499.6
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



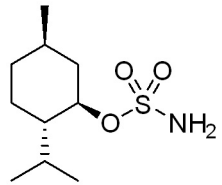
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	72
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-07-28T12:45:22
15	Modification Date	2014-07-28T12:48:12
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1274.9
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



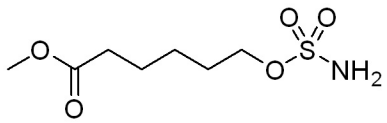
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	52
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-01-23T15:40:42
15	Modification Date	2014-01-23T15:41:10
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1012.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



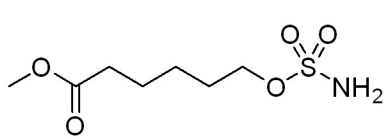
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	254
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-01-23T15:43:20
15	Modification Date	2014-01-23T15:52:59
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1271.3
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



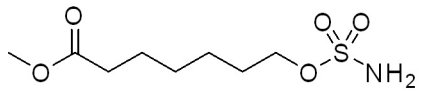
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	42
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-10-03T15:12:40
15	Modification Date	2014-10-03T15:12:44
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1511.1
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



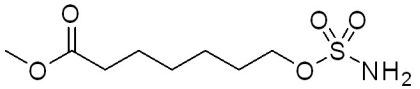
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	216
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-03T17:03:20
15	Modification Date	2014-10-03T17:11:05
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1275.0
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536

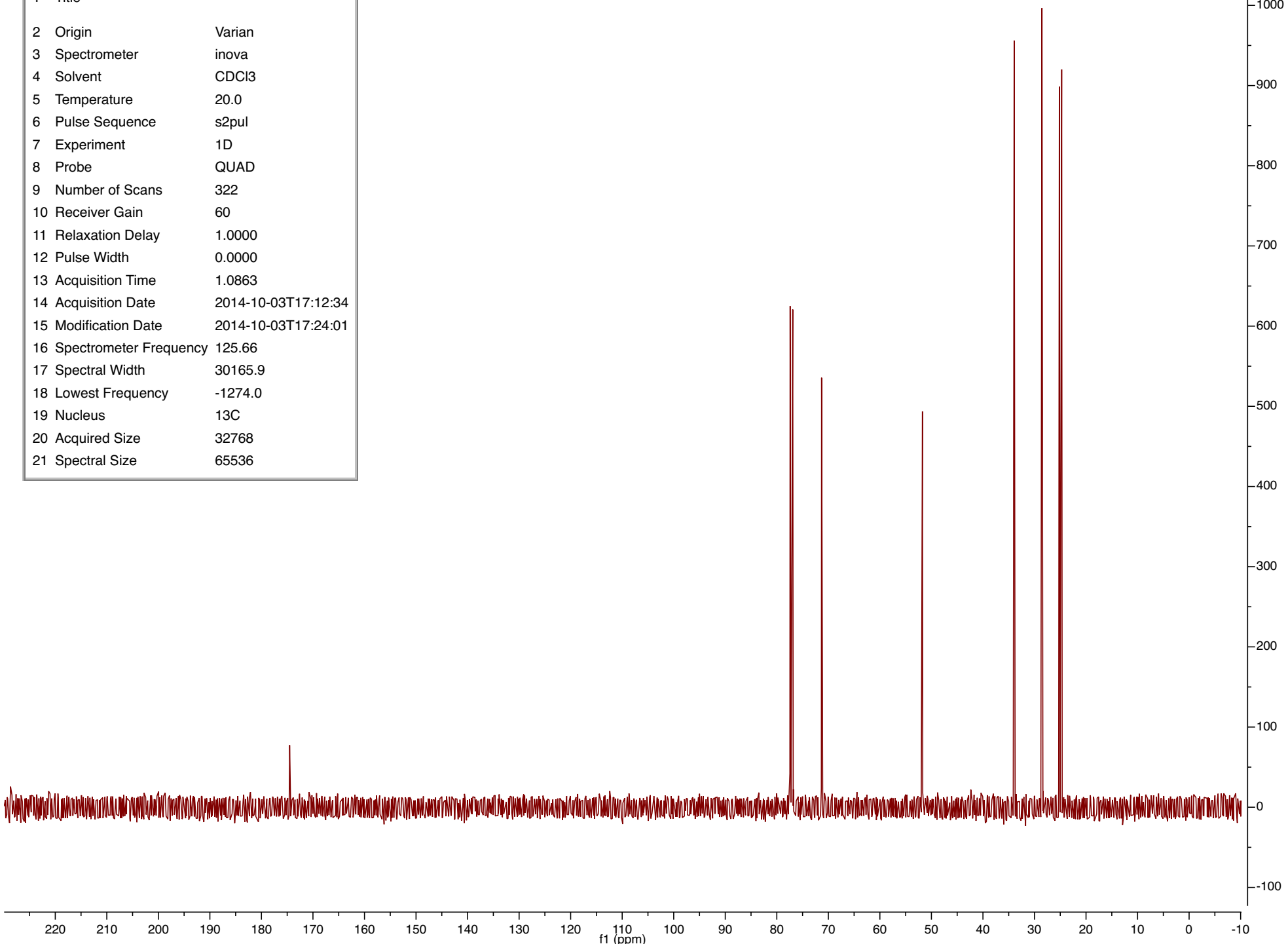


	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	30
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-10-03T15:15:50
15	Modification Date	2014-10-03T15:15:53
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1510.6
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536

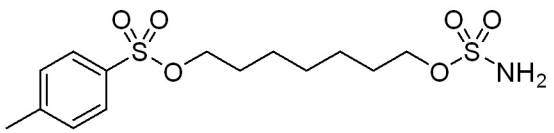


	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	322
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-03T17:12:34
15	Modification Date	2014-10-03T17:24:01
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1274.0
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536

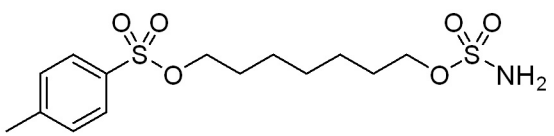




	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	32
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-10-01T08:32:56
15	Modification Date	2014-10-01T08:33:01
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1510.6
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	226
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-08T14:29:01
15	Modification Date	2014-10-08T14:37:13
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1273.8
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536

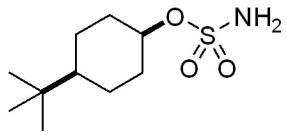


650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50

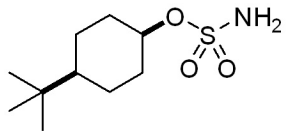
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

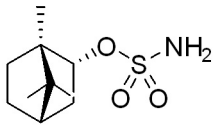
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	42
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-05-13T08:45:26
15	Modification Date	2014-05-13T08:45:28
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1499.6
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



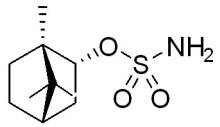
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	22.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	400
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-05-21T10:47:31
15	Modification Date	2014-05-21T10:47:33
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1272.3
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



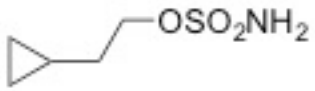
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	22.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	48
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2013-10-24T11:26:08
15	Modification Date	2013-10-24T11:26:10
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1499.6
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



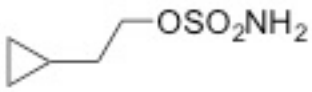
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	274
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-07-28T12:50:02
15	Modification Date	2014-07-28T12:59:53
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1271.1
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



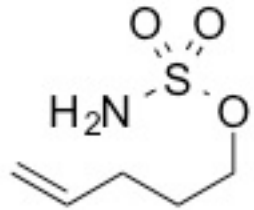
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	hcn
Number of Scans	8
Relaxation Delay	10.0000
Pulse Width	0.0000
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



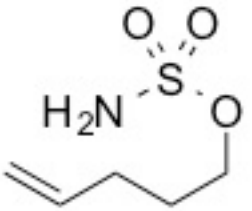
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	481
Relaxation Delay	2.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1274.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



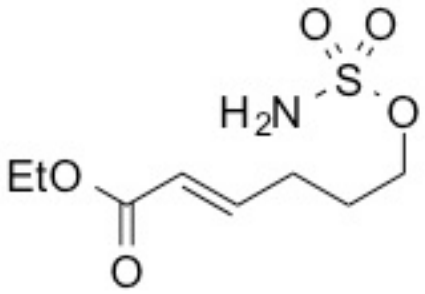
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	34
Relaxation Delay	5.0000
Pulse Width	0.0000
Modification Date	2014-05-20T12:06:25
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1499.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



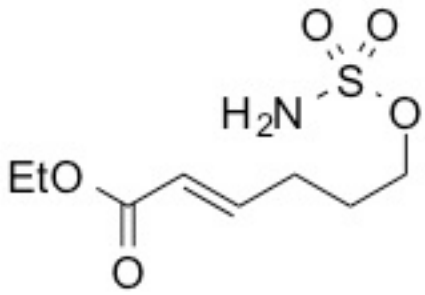
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	22.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	1064
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-05-21T19:39:15
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1260.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



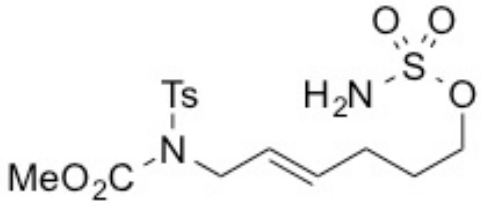
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	40
Relaxation Delay	5.0000
Pulse Width	0.0000
Modification Date	2014-05-20T12:01:12
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1511.1
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



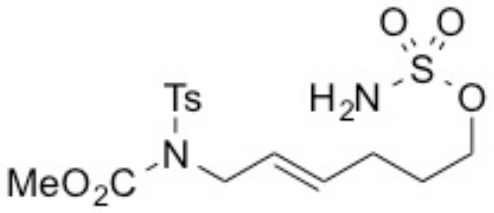
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	22.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	632
Receiver Gain	60
Relaxation Delay	3.0000
Pulse Width	0.0000
Modification Date	2014-05-20T13:54:20
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1271.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



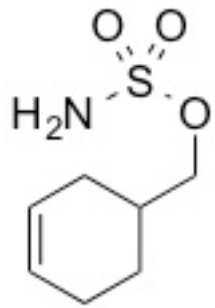
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	48
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-10-09T10:02:44
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1499.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



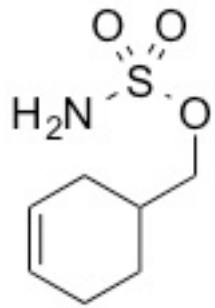
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	42
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-10-09T10:50:55
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1260.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



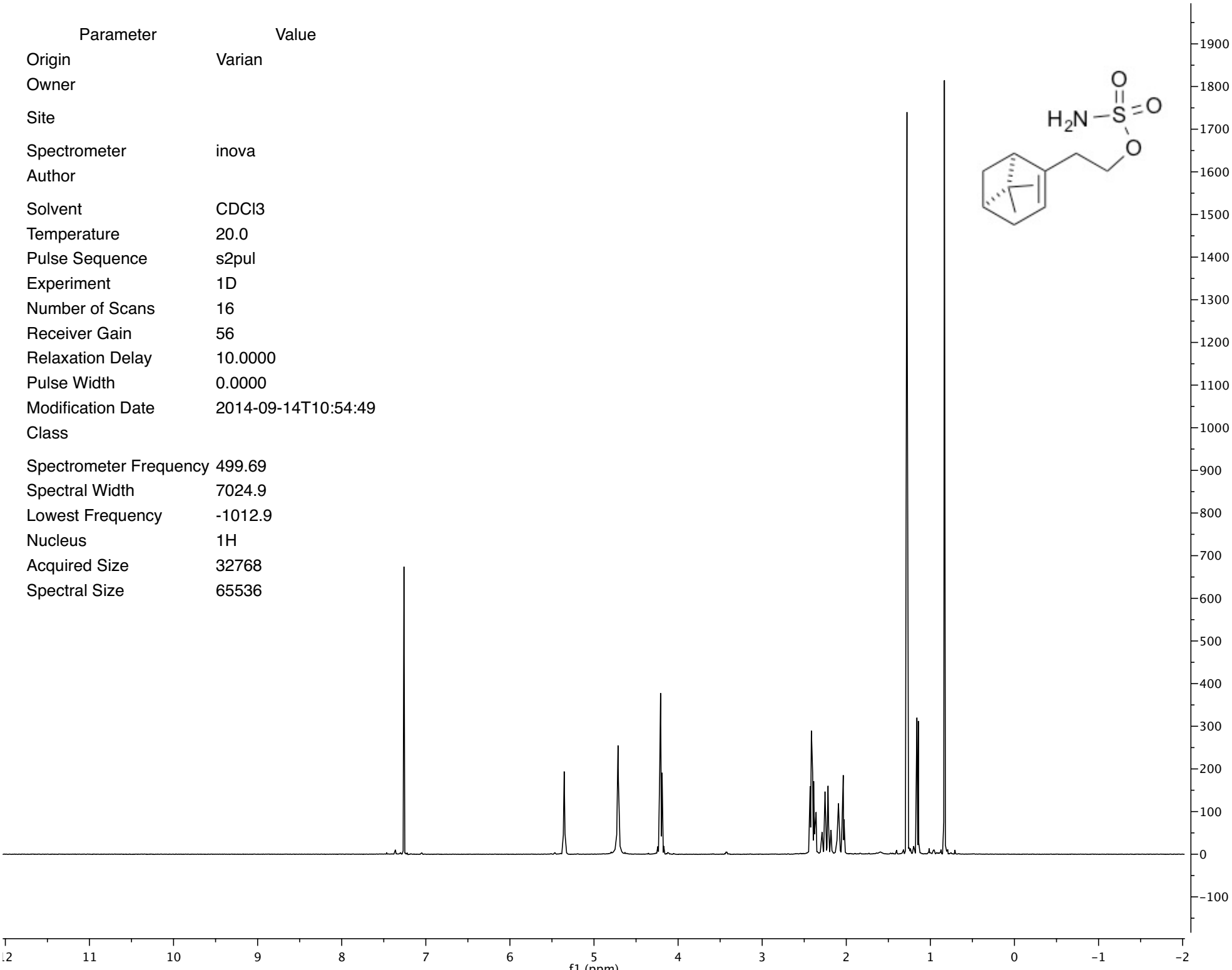
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	54
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-09-14T10:40:26
Class	
Spectrometer Frequency	499.69
Spectral Width	7024.9
Lowest Frequency	-1012.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



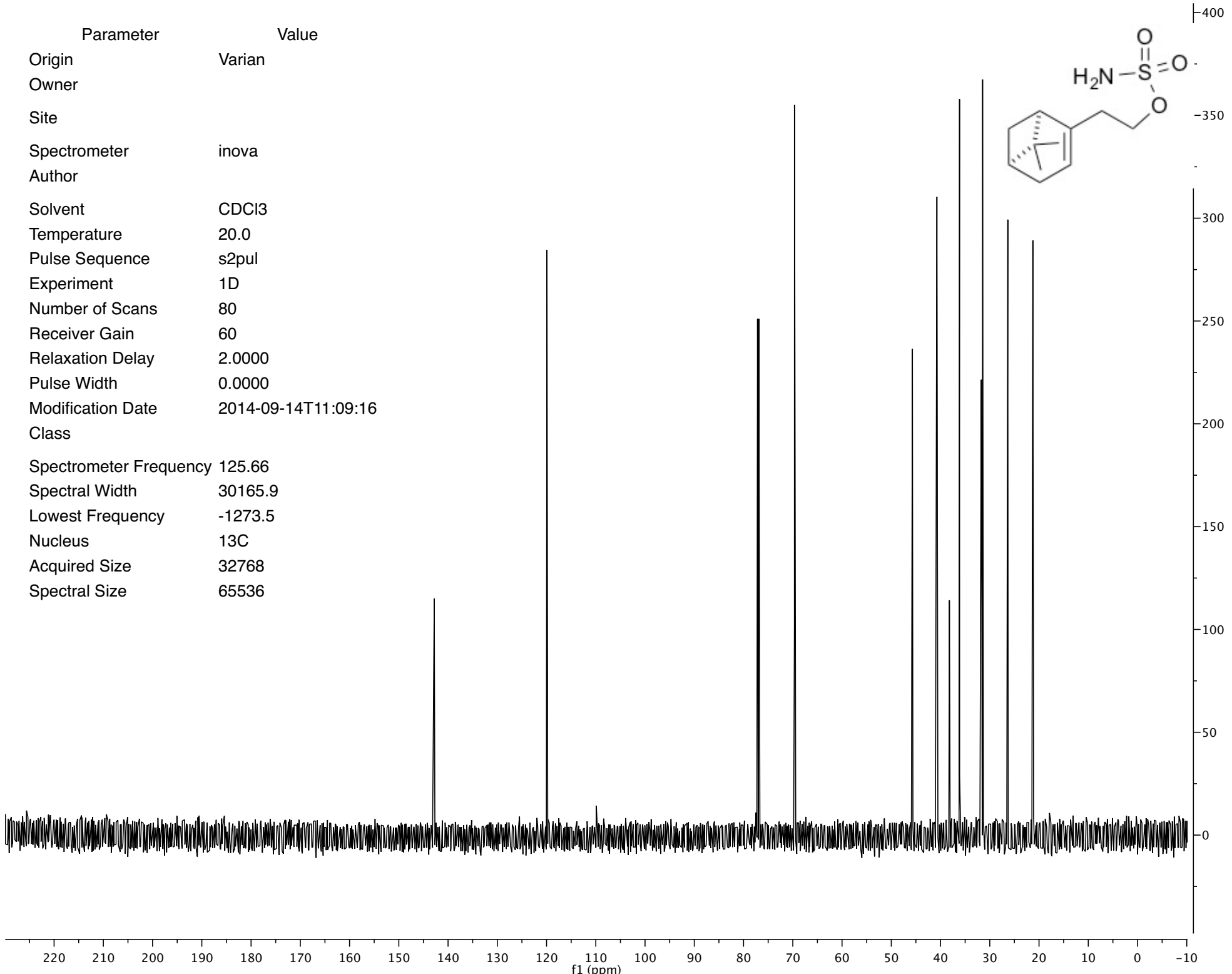
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	52
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-09-14T11:14:36
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1276.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



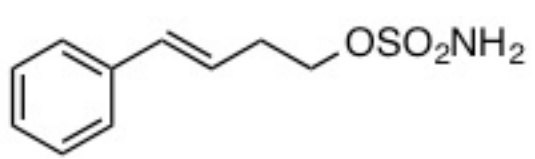
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	56
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-09-14T10:54:49
Class	
Spectrometer Frequency	499.69
Spectral Width	7024.9
Lowest Frequency	-1012.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



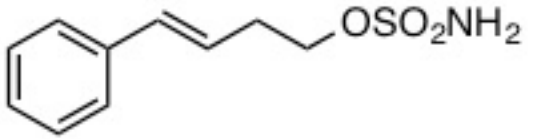
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	80
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-09-14T11:09:16
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1273.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



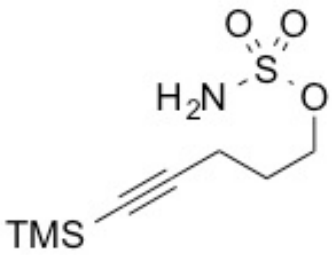
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	42
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-12-19T11:00:39
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



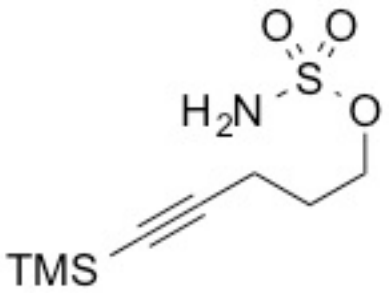
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	64
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-12-19T11:33:10
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1274.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

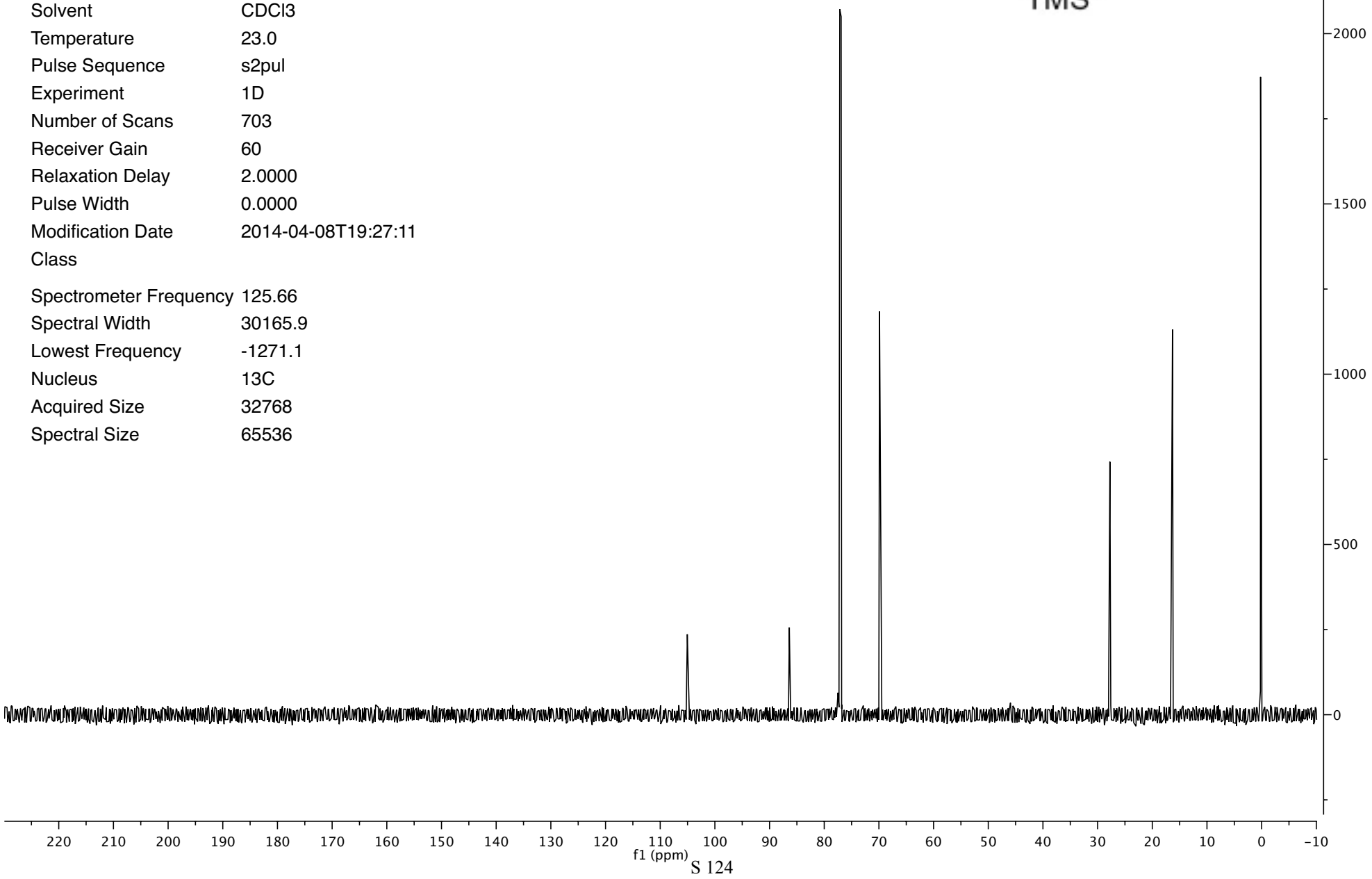


Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	32
Relaxation Delay	3.0000
Pulse Width	0.0000
Modification Date	2014-04-08T18:59:42
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1499.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

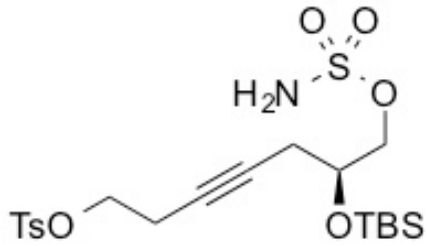


Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	23.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	703
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-04-08T19:27:11
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1271.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

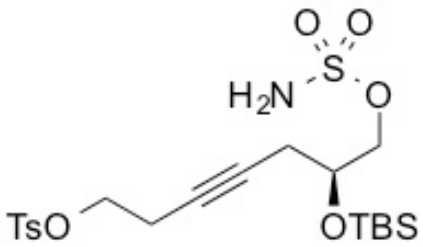




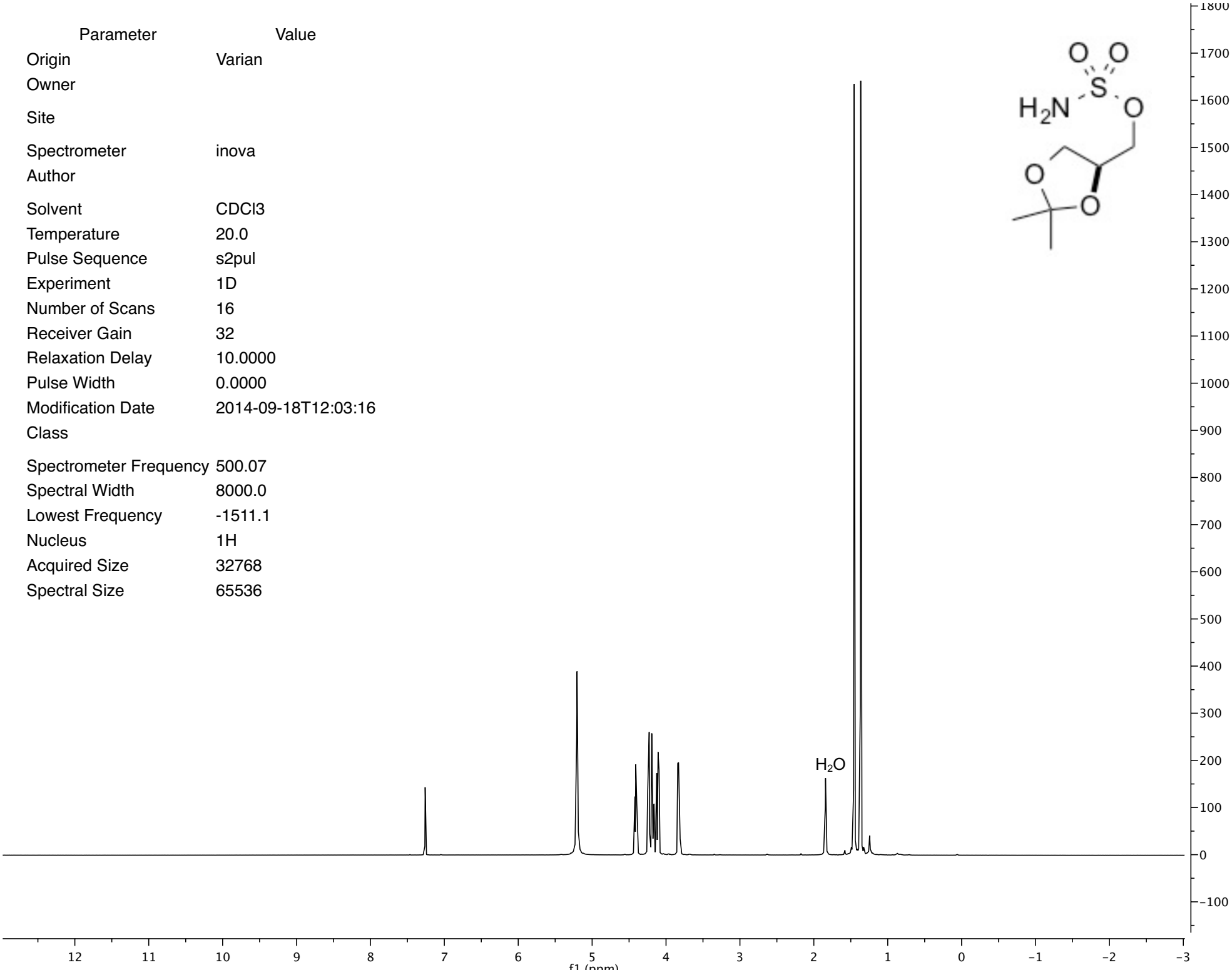
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	32
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-08-07T11:14:30
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1499.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



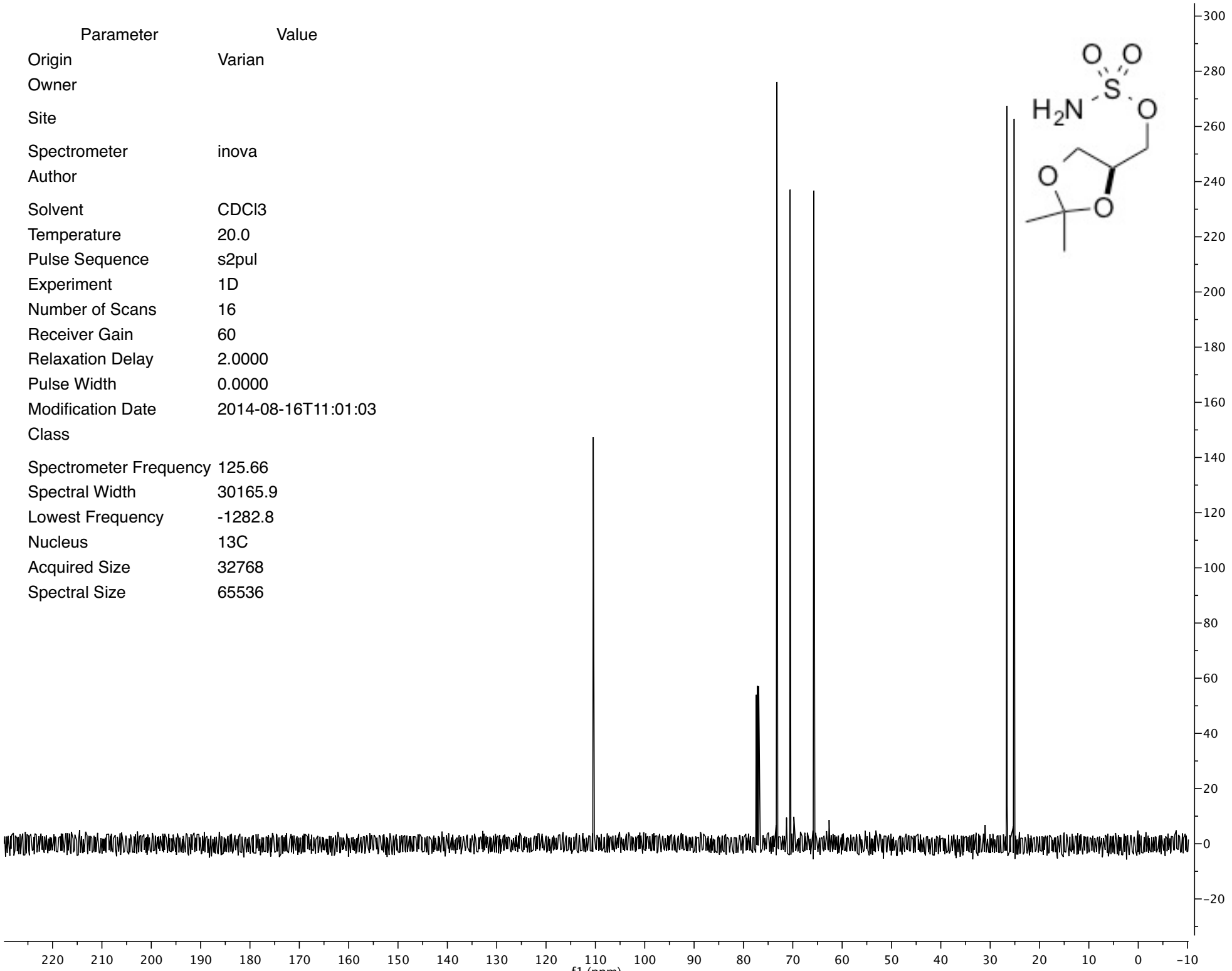
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	805
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-08-07T12:44:37
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1260.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



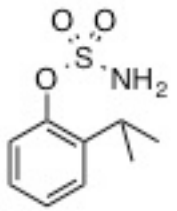
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	32
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-09-18T12:03:16
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1511.1
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



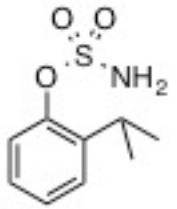
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-08-16T11:01:03
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1282.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



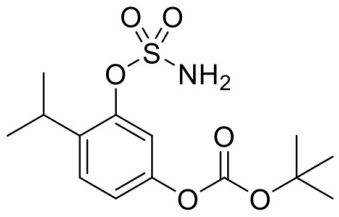
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUADG
Number of Scans	4
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.43
Spectral Width	8000.0
Lowest Frequency	-1507.2
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



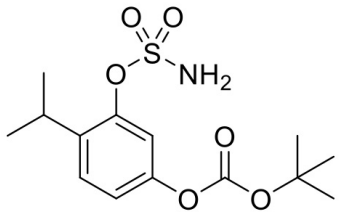
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUADG
Number of Scans	221
Relaxation Delay	5.0000
Pulse Width	0.0000
Spectrometer Frequency	125.60
Spectral Width	32000.0
Lowest Frequency	-2200.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



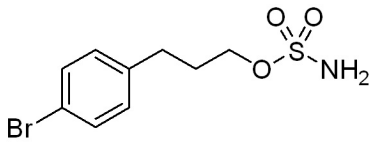
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	hcn
Number of Scans	8
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1511.1
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



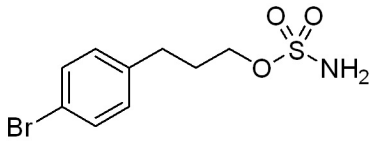
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	512
Relaxation Delay	2.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1272.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



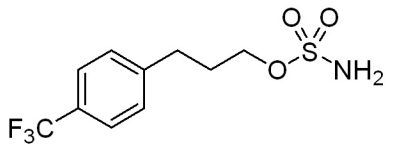
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	hcn
Number of Scans	8
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



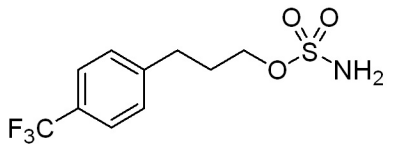
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	512
Relaxation Delay	1.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1275.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



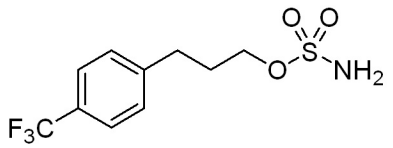
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CD3CN
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	2
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.70
Spectral Width	7024.9
Lowest Frequency	-1023.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

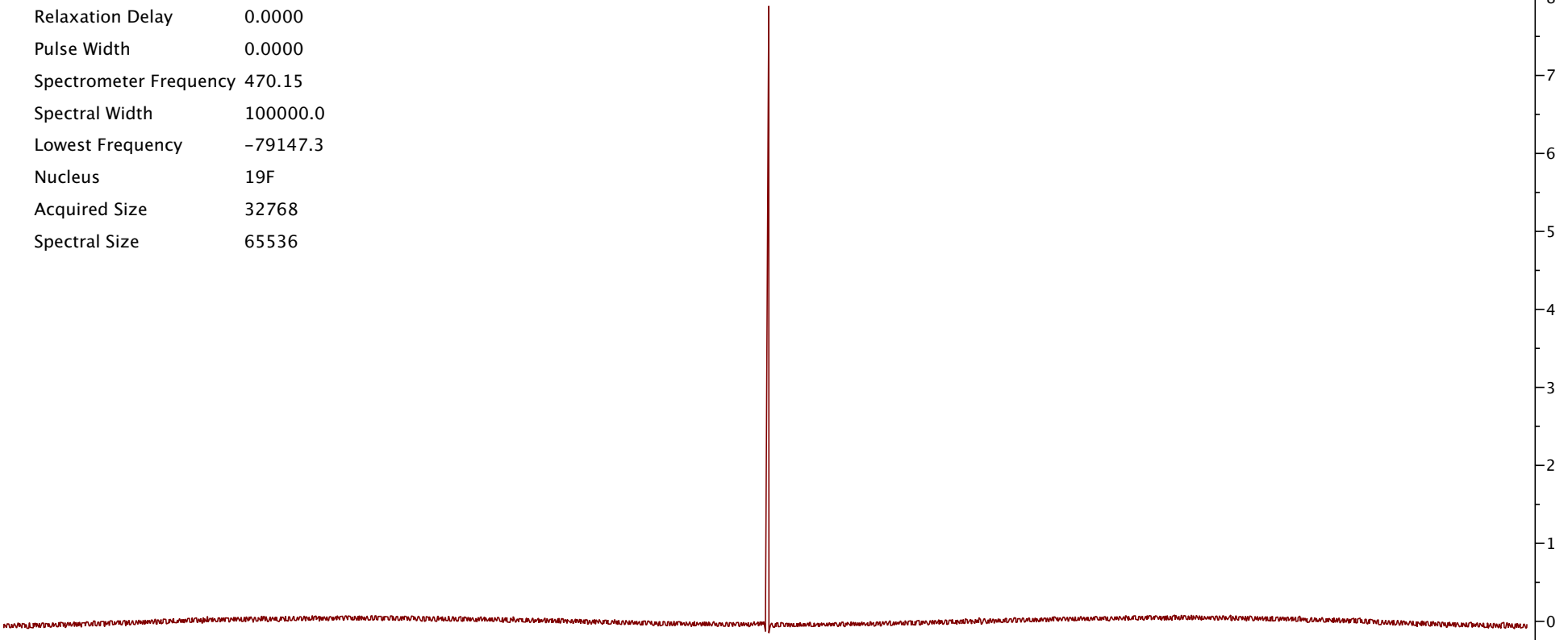


Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CD3CN
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	942
Relaxation Delay	5.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1178.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CD3CN
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	16
Relaxation Delay	0.0000
Pulse Width	0.0000
Spectrometer Frequency	470.15
Spectral Width	100000.0
Lowest Frequency	-79147.3
Nucleus	19F
Acquired Size	32768
Spectral Size	65536





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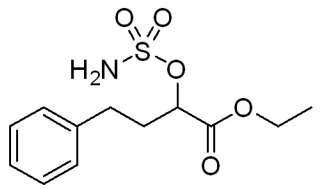
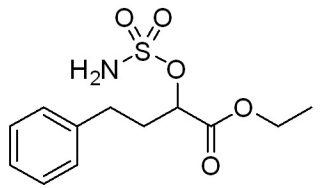
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160

f1 (ppm)

	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	60
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-07-29T18:58:46
15	Modification Date	2014-07-29T18:58:47
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1012.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	175
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-07-30T12:43:25
15	Modification Date	2014-07-30T12:49:44
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1273.3
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536

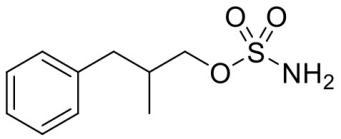


650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50

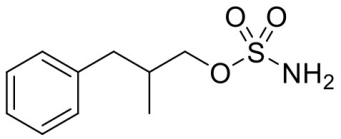
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

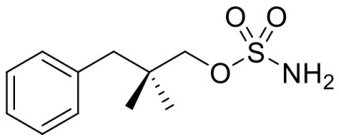
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	8
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.69
Spectral Width	7024.9
Lowest Frequency	-1012.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



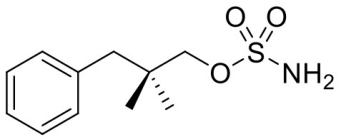
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	340
Relaxation Delay	1.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1291.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



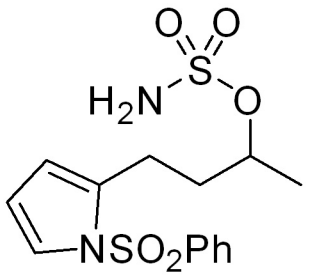
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	8
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.69
Spectral Width	7024.9
Lowest Frequency	-1012.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



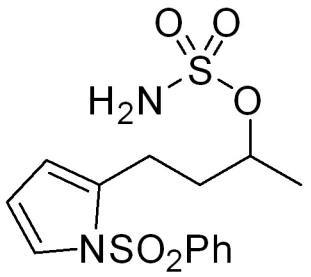
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	1024
Relaxation Delay	1.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1274.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



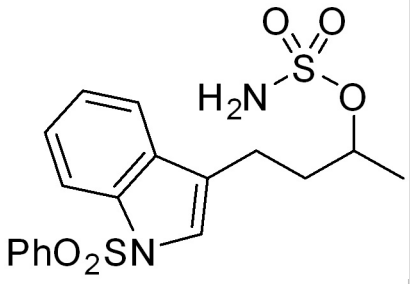
	Parameter	Value
1	Title	
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	8
9	Receiver Gain	32
10	Relaxation Delay	10.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-10-16T17:22:26
14	Modification Date	2014-10-16T17:23:24
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1511.1
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



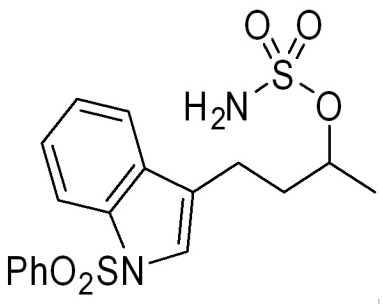
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUADG
9	Number of Scans	864
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0240
14	Acquisition Date	2014-10-16T18:42:28
15	Modification Date	2014-10-16T19:12:06
16	Spectrometer Frequency	125.60
17	Spectral Width	32000.0
18	Lowest Frequency	-2188.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



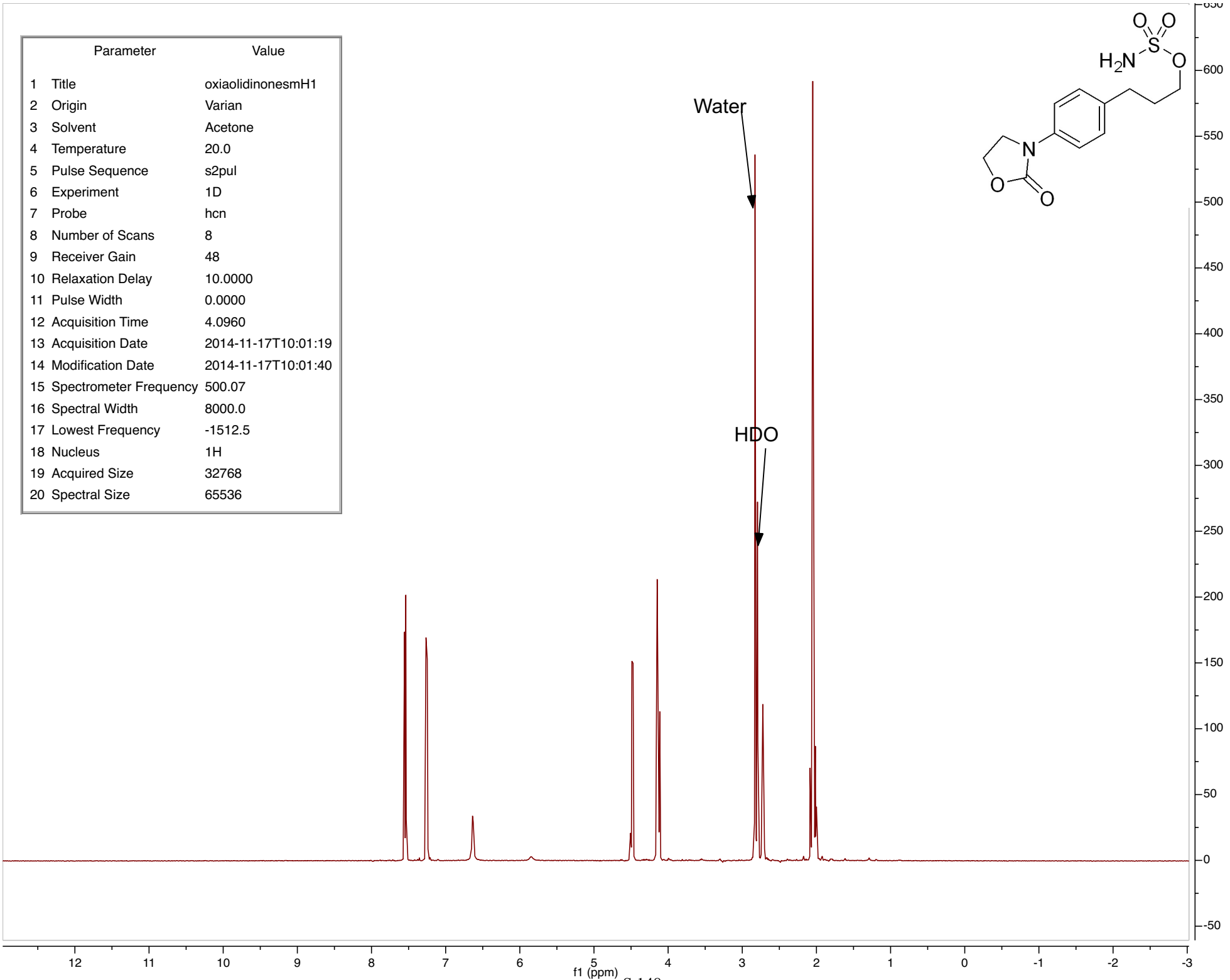
	Parameter	Value
1	Title	
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	8
9	Receiver Gain	32
10	Relaxation Delay	10.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-10-16T17:18:07
14	Modification Date	2014-10-16T17:18:58
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1511.1
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



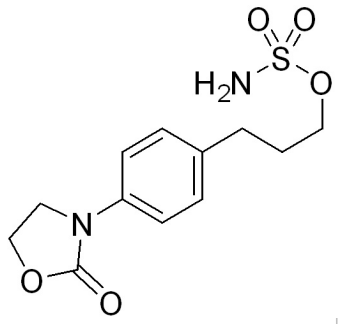
	Parameter	Value
1	Title	
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	944
9	Receiver Gain	60
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.0863
13	Acquisition Date	2014-10-29T14:03:34
14	Modification Date	2014-10-29T14:36:43
15	Spectrometer Frequency	125.66
16	Spectral Width	30165.9
17	Lowest Frequency	-1260.2
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536



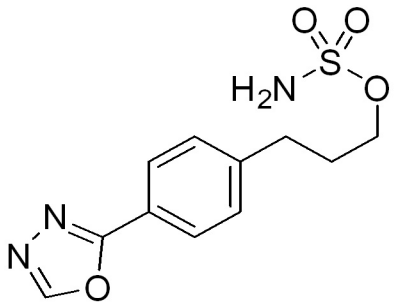
	Parameter	Value
1	Title	oxiaolidinonesmH1
2	Origin	Varian
3	Solvent	Acetone
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	8
9	Receiver Gain	48
10	Relaxation Delay	10.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-11-17T10:01:19
14	Modification Date	2014-11-17T10:01:40
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1512.5
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536

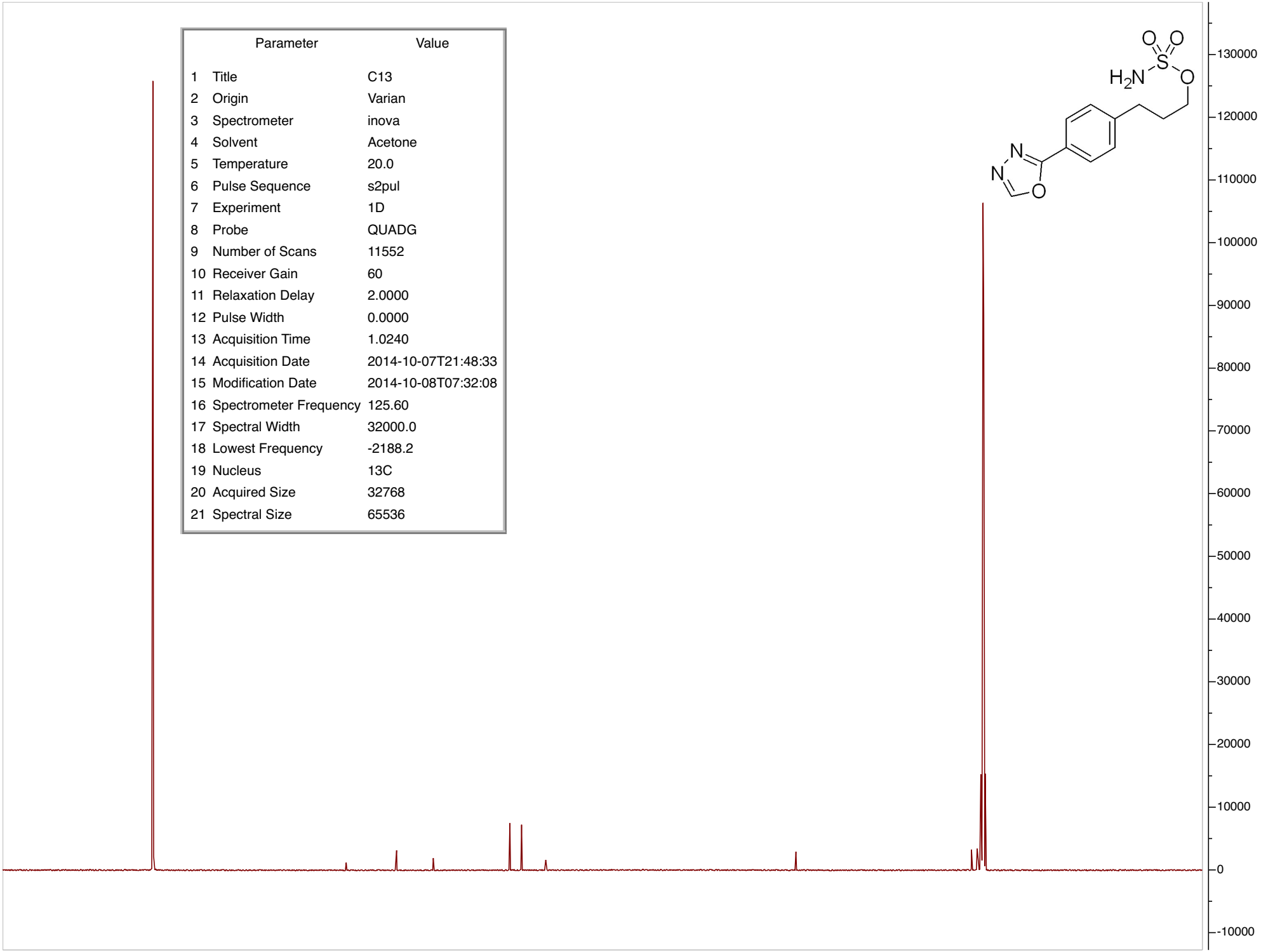


	Parameter	Value
1	Title	oxizolidinonesmc13C13
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	Acetone
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUADG
9	Number of Scans	22408
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0240
14	Acquisition Date	2014-11-18T19:31:50
15	Modification Date	2014-11-19T08:09:14
16	Spectrometer Frequency	125.60
17	Spectral Width	32000.0
18	Lowest Frequency	-2188.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536

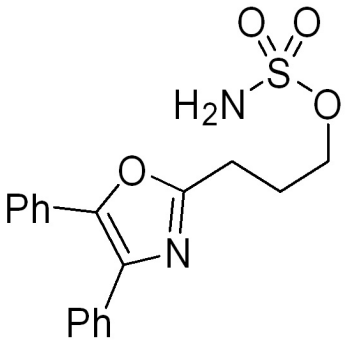


	Parameter	Value
1	Title	H1
2	Origin	Varian
3	Solvent	Acetone
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	8
9	Receiver Gain	48
10	Relaxation Delay	20.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-10-06T15:13:31
14	Modification Date	2014-10-06T15:17:22
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1512.5
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536

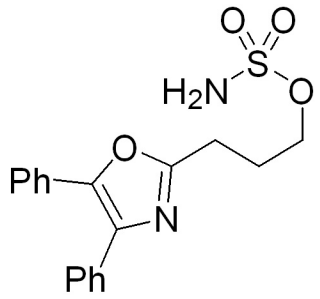



Parameter Value
1 Title C13
2 Origin Varian
3 Spectrometer inova
4 Solvent Acetone
5 Temperature 20.0
6 Pulse Sequence s2pul
7 Experiment 1D
8 Probe QUADG
9 Number of Scans 11552
10 Receiver Gain 60
11 Relaxation Delay 2.0000
12 Pulse Width 0.0000
13 Acquisition Time 1.0240
14 Acquisition Date 2014-10-07T21:48:33
15 Modification Date 2014-10-08T07:32:08
16 Spectrometer Frequency 125.60
17 Spectral Width 32000.0
18 Lowest Frequency -2188.2
19 Nucleus 13C
20 Acquired Size 32768
21 Spectral Size 65536
O
O
S
H2N
O
N
N
O
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

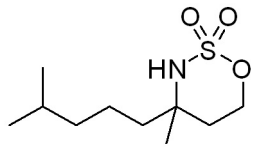
	Parameter	Value
1	Title	H1
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	56
10	Relaxation Delay	10.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-10-05T16:32:41
14	Modification Date	2014-10-05T16:33:06
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1511.6
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



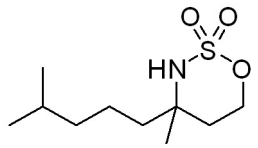
	Parameter	Value
1	Title	C13
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	11152
10	Receiver Gain	60
11	Relaxation Delay	2.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-07T22:02:59
15	Modification Date	2014-10-08T07:37:17
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1270.4
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



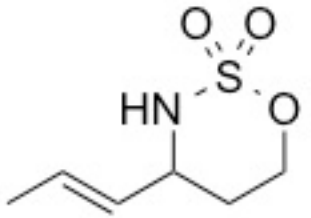
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	36
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2013-10-29T10:34:21
15	Modification Date	2013-10-29T10:34:23
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1012.4
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536

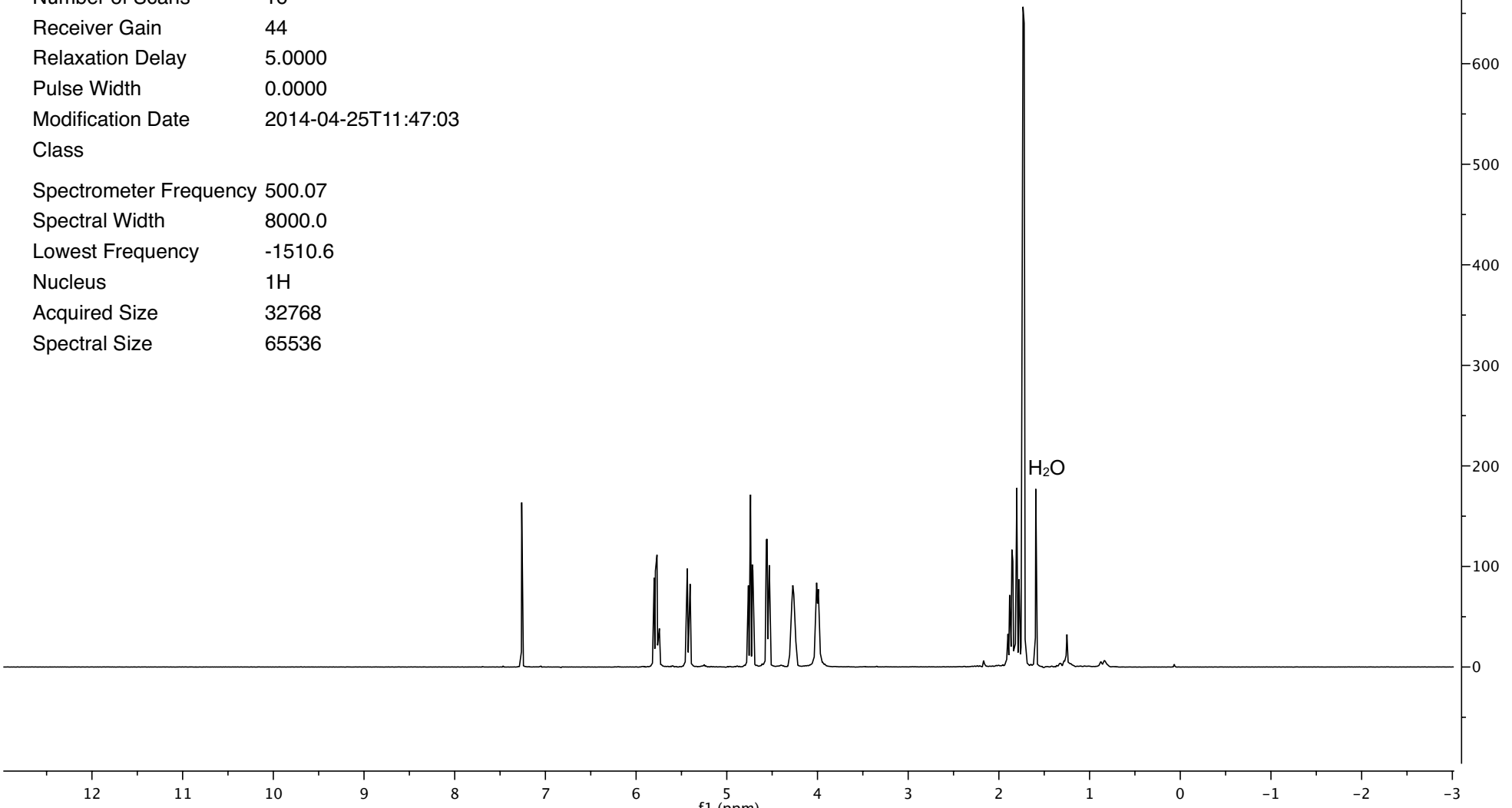


	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	98
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2013-10-29T10:36:47
15	Modification Date	2013-10-29T10:40:34
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536

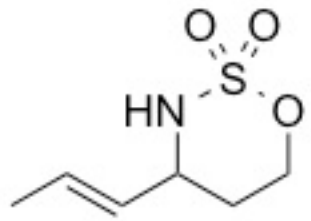


Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	44
Relaxation Delay	5.0000
Pulse Width	0.0000
Modification Date	2014-04-25T11:47:03
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

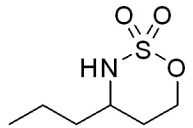




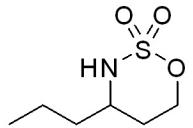
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	50.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	672
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-04-25T15:53:09
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1260.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



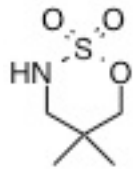
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	28
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-07-29T14:15:41
15	Modification Date	2014-07-29T14:15:42
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1511.1
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



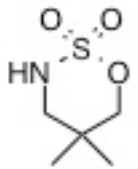
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	119
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-07-29T15:31:15
15	Modification Date	2014-07-29T15:35:36
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1279.0
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



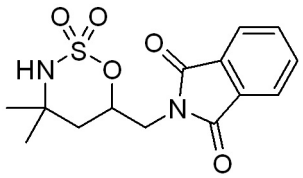
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	8
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.69
Spectral Width	7024.9
Lowest Frequency	-1012.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



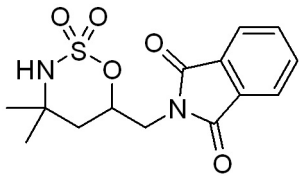
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	924
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-30T13:53:02
15	Modification Date	2014-10-30T14:28:24
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



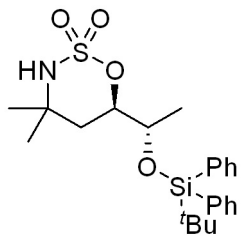
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	Acetone
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	8
10	Receiver Gain	58
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2015-01-20T11:21:43
15	Modification Date	2015-01-20T11:21:49
16	Spectrometer Frequency	499.70
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



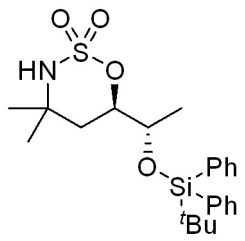
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	Acetone
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	642
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2015-01-20T11:22:20
15	Modification Date	2015-01-20T11:44:56
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



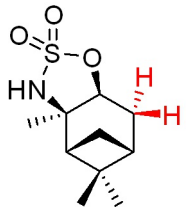
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	44
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-12-15T15:01:22
15	Modification Date	2014-12-15T15:01:24
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1510.6
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



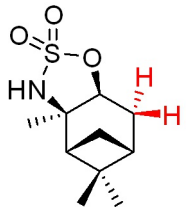
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	316
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-12-15T16:03:54
15	Modification Date	2014-12-15T16:15:11
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1273.1
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



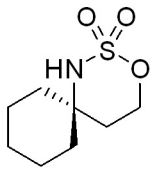
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	52
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-12-01T14:45:29
15	Modification Date	2014-12-01T14:46:22
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1012.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



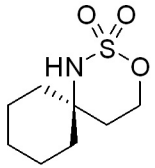
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	329
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-12-01T14:46:34
15	Modification Date	2014-12-01T14:58:16
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1271.5
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



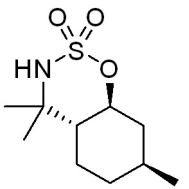
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	20
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-07-30T11:14:09
15	Modification Date	2014-07-30T11:14:10
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1511.1
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



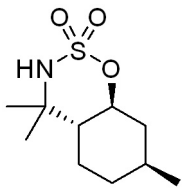
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	146
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-07-30T12:52:31
15	Modification Date	2014-07-30T12:57:52
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



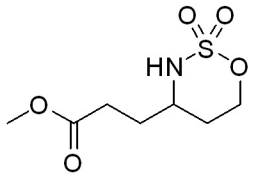
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	16
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-01-21T14:32:17
15	Modification Date	2014-01-21T14:32:19
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1510.6
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



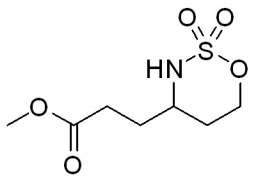
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	116
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-01-21T16:46:29
15	Modification Date	2014-01-21T16:51:19
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1278.0
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



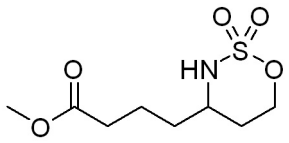
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	46
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-12-01T14:27:25
15	Modification Date	2014-12-01T14:28:02
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1012.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



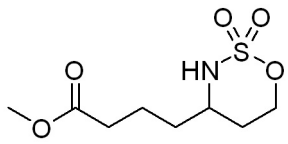
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	400
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-12-01T14:42:19
15	Modification Date	2014-12-01T14:42:27
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1272.4
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



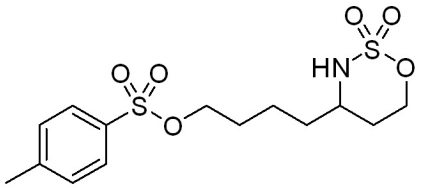
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	32
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-10-28T18:58:16
15	Modification Date	2014-10-28T18:58:18
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1510.6
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



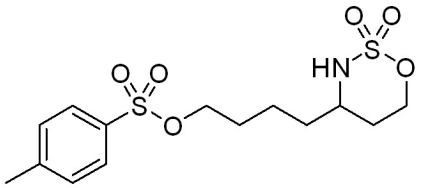
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	114
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-29T10:00:01
15	Modification Date	2014-10-29T10:04:22
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



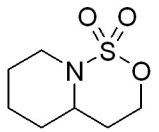
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	58
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-10-31T14:16:22
15	Modification Date	2014-10-31T14:16:42
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1012.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



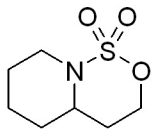
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	600
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-31T14:37:56
15	Modification Date	2014-10-31T14:38:33
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1271.8
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



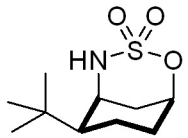
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	50
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-11-17T10:30:18
15	Modification Date	2014-11-17T10:30:33
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1012.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



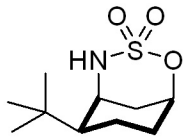
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	268
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-11-17T10:30:57
15	Modification Date	2014-11-17T10:40:38
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1272.0
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



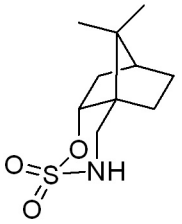
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	48
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-05-21T09:11:26
15	Modification Date	2014-05-21T09:12:26
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1511.1
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



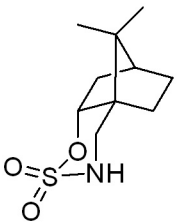
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	22.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	132
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-05-21T18:17:29
15	Modification Date	2014-05-21T18:22:41
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	36
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-07-30T18:34:44
15	Modification Date	2014-07-30T18:34:46
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1012.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	82
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-07-30T18:35:47
15	Modification Date	2014-07-30T18:38:55
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536

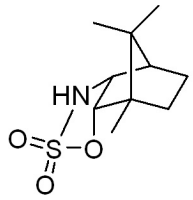


600 550 500 450 400 350 300 250 200 150 100 50 0 -50

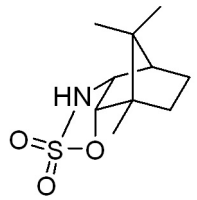
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

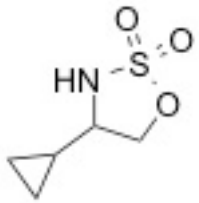
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	48
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-10-28T19:01:27
15	Modification Date	2014-10-28T19:01:33
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1499.6
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



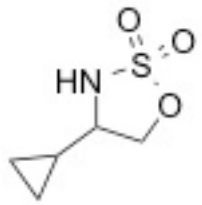
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	336
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-29T10:06:29
15	Modification Date	2014-10-29T10:18:34
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1272.6
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536

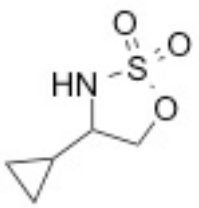


Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	8
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.69
Spectral Width	7024.9
Lowest Frequency	-1011.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	512
Relaxation Delay	2.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1276.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

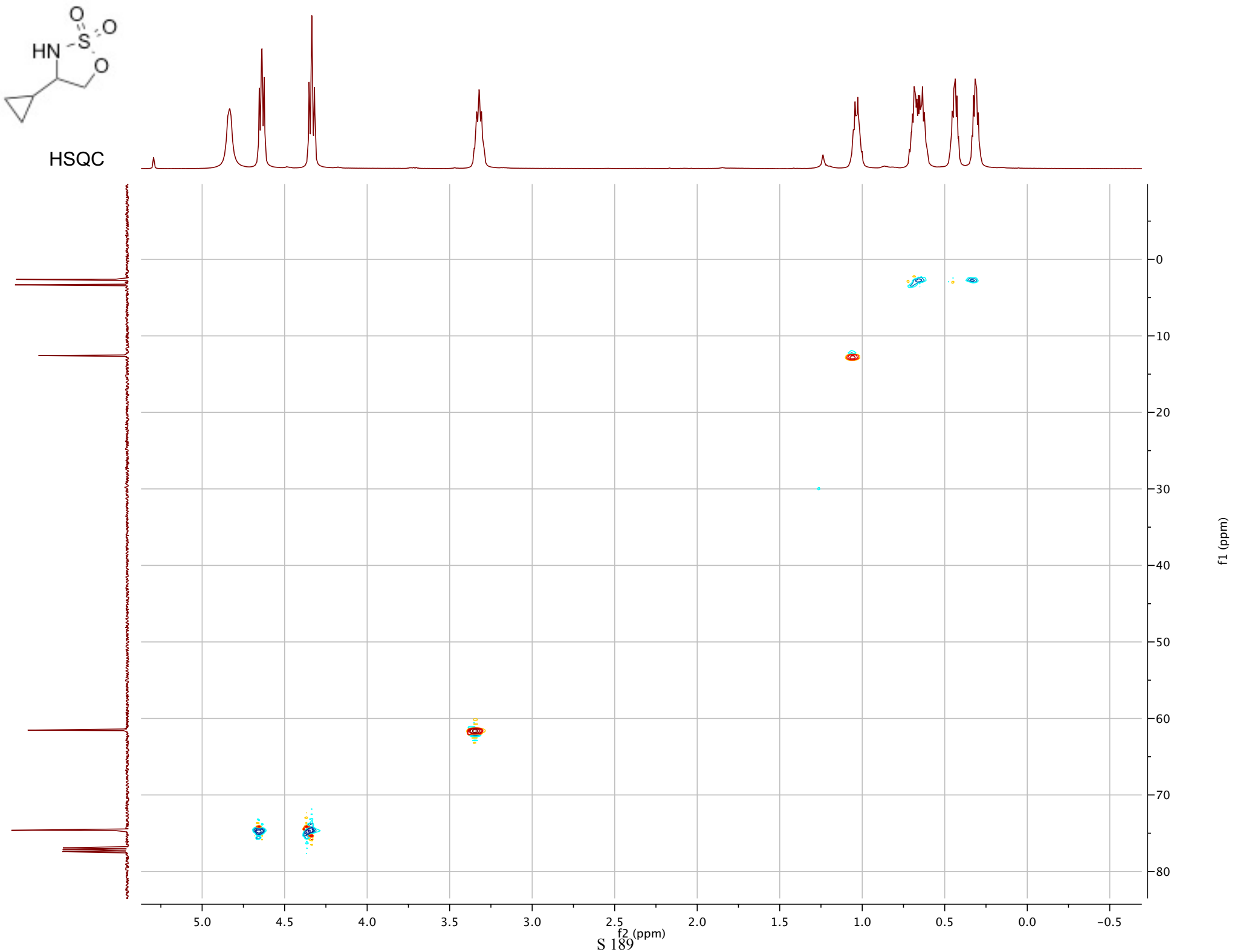




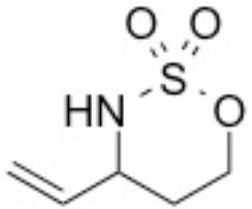
COSY

f2 (ppm)

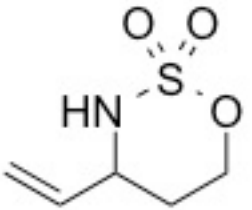
f1 (ppm)


HSQC
f2 (ppm)
f1 (ppm)

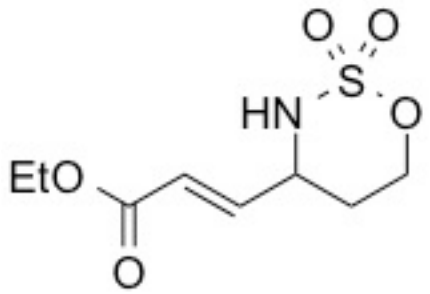
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	56
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-08-09T09:44:48
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1511.1
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



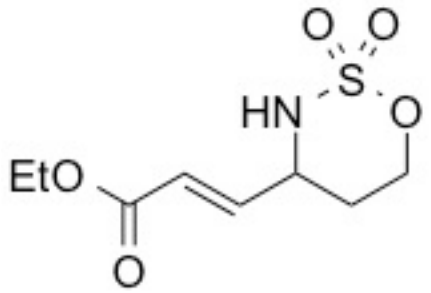
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	166
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-08-09T10:16:10
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1273.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



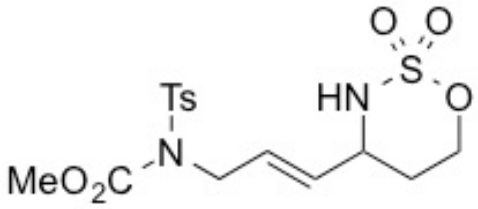
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	48
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-07-13T08:56:42
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1511.1
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



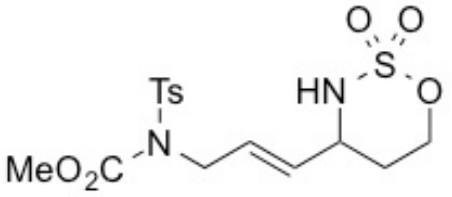
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	960
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-07-13T09:22:16
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1275.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



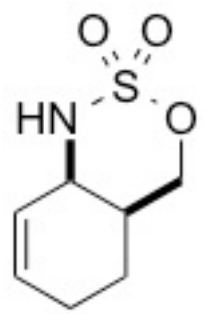
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	48
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-10-09T09:55:59
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

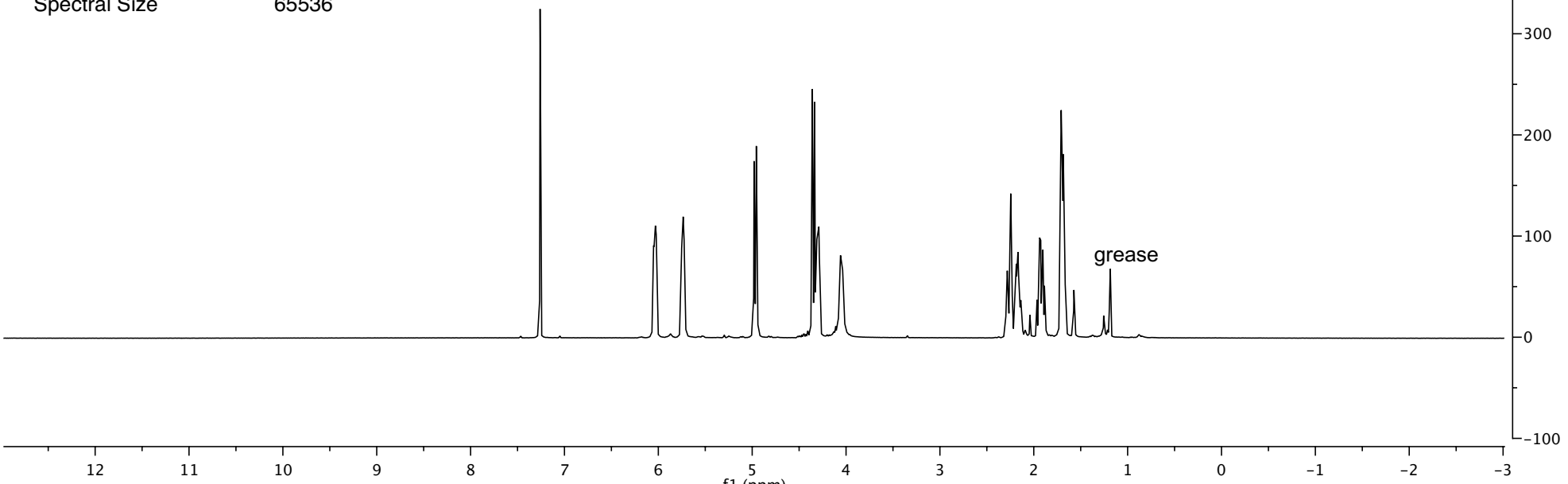


Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	176
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-10-09T10:45:00
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1277.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

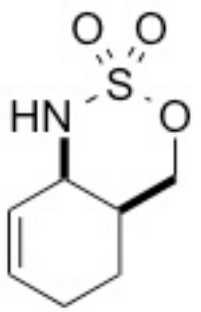


Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	38
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-10-05T07:54:36
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

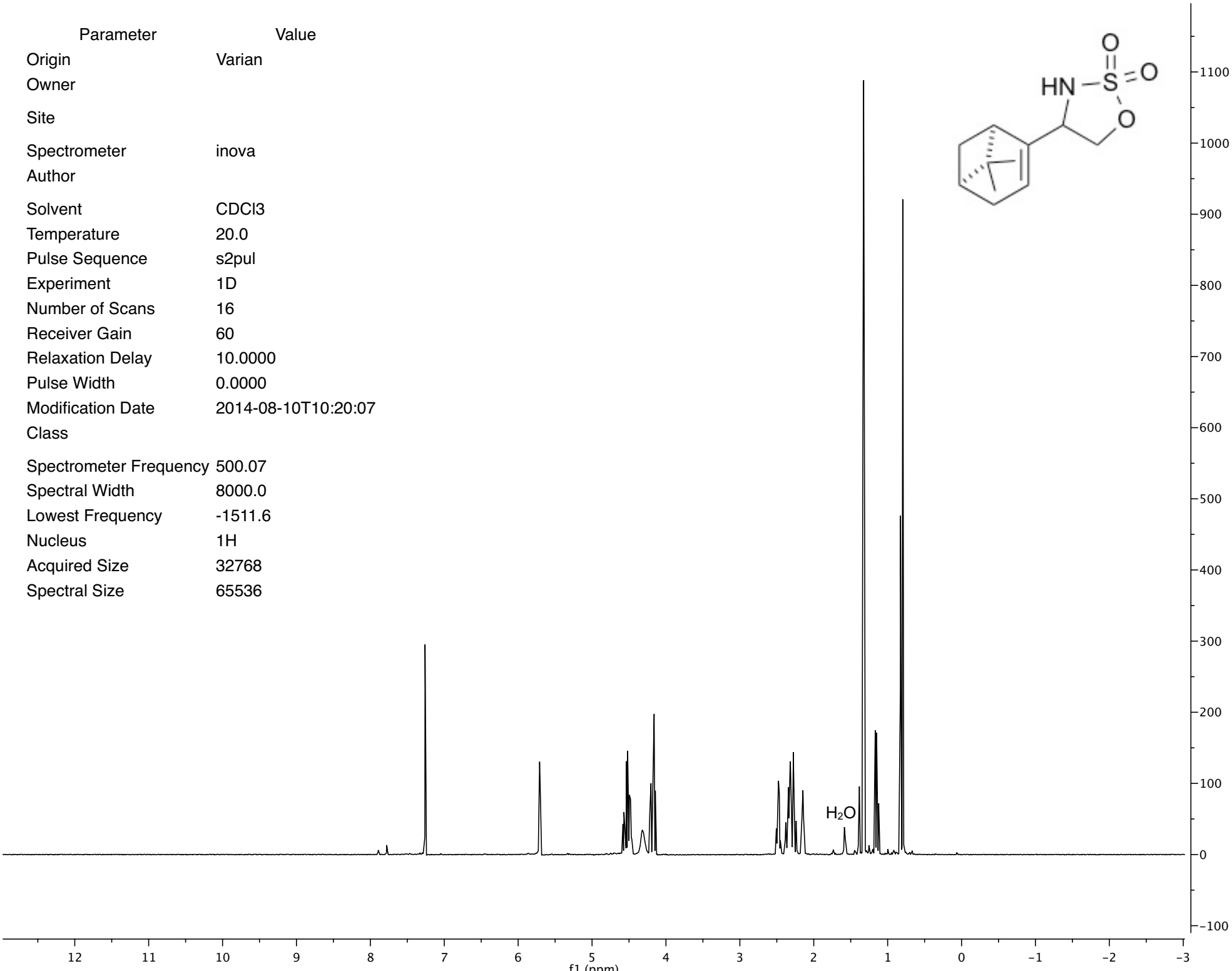




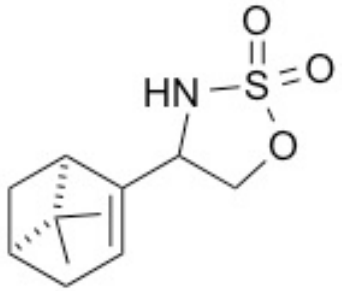
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	48
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-10-05T09:41:11
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1280.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



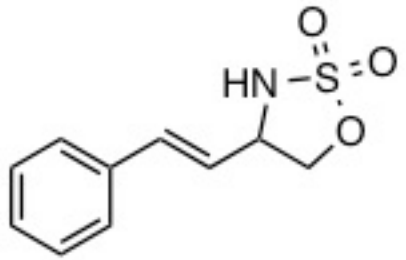
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	60
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-08-10T10:20:07
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1511.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

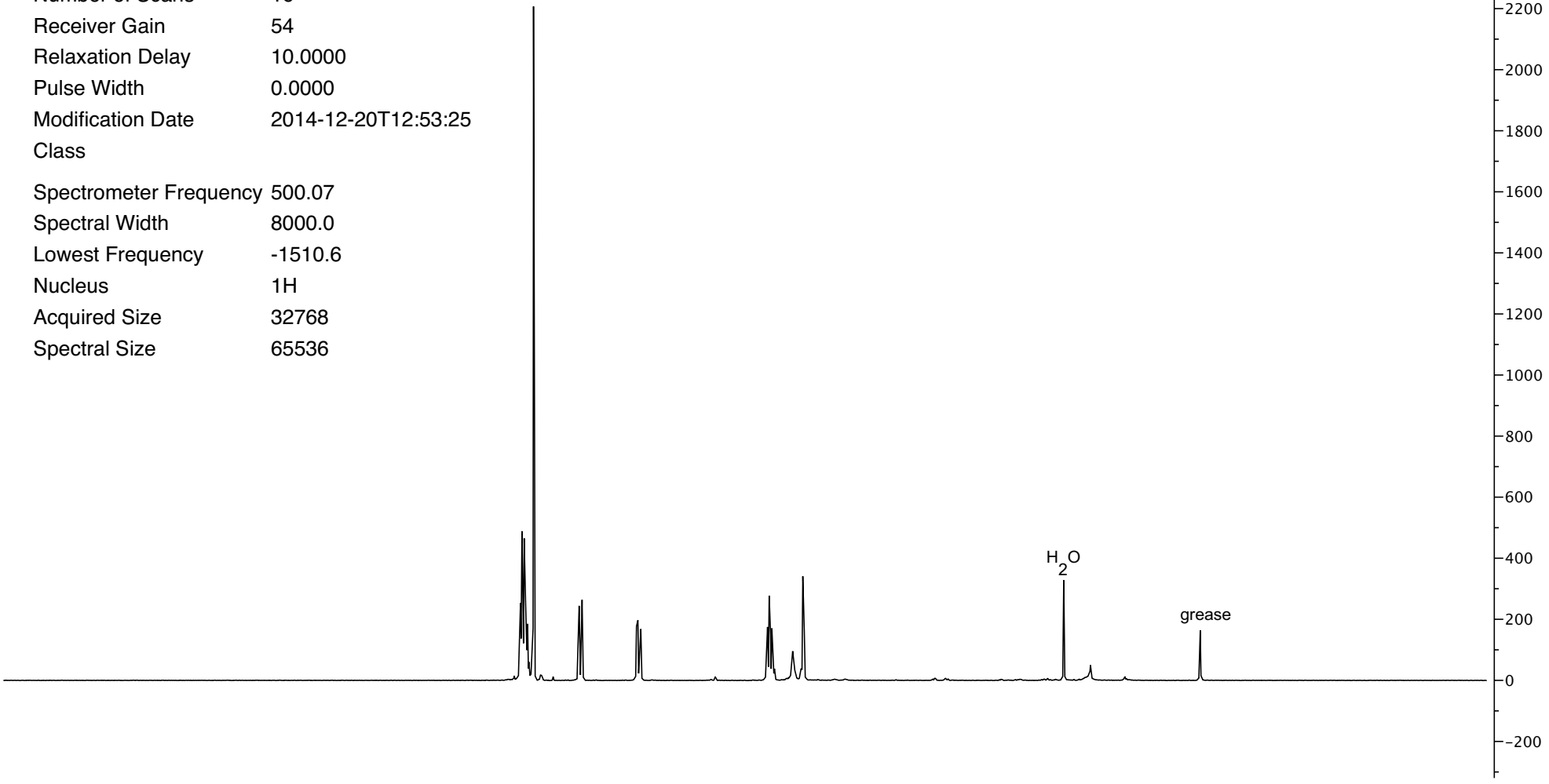


Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	128
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-08-11T10:33:26
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1279.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

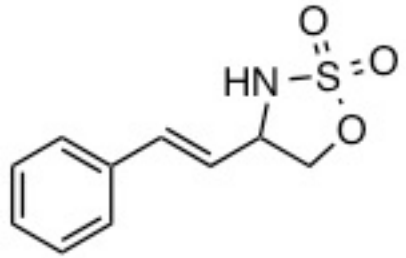


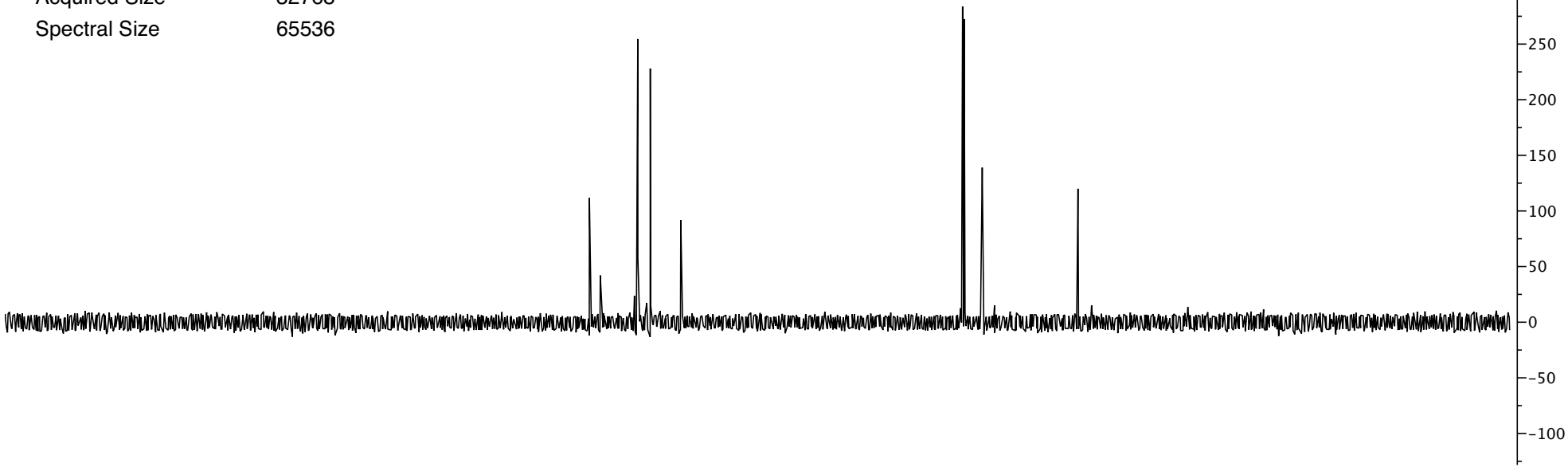
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	54
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-12-20T12:53:25
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



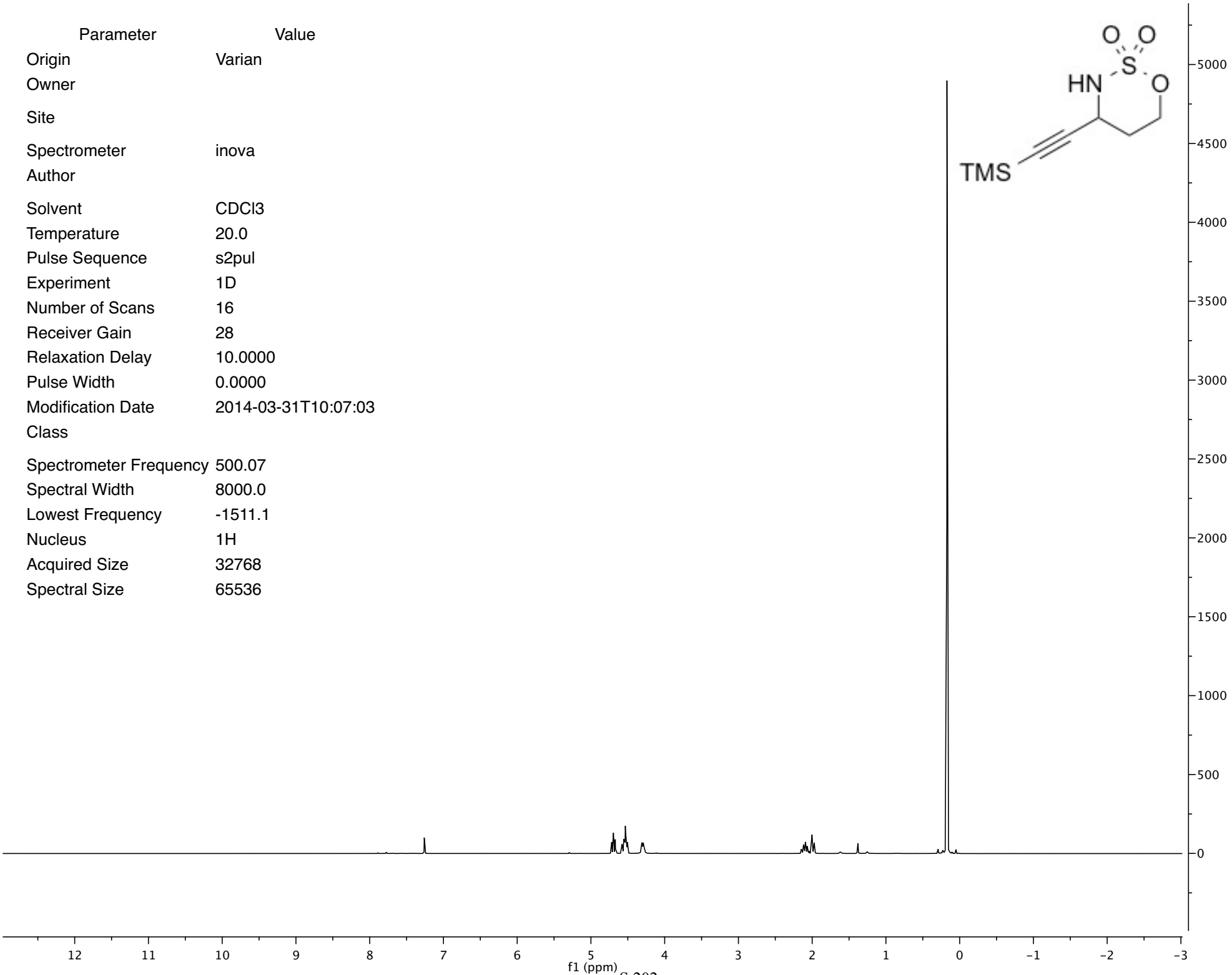


Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	80
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-12-20T13:04:21
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1272.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

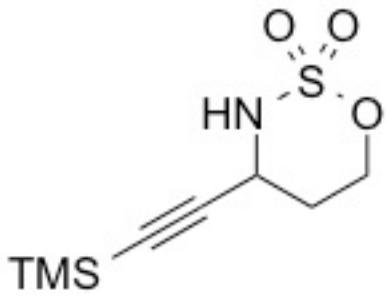




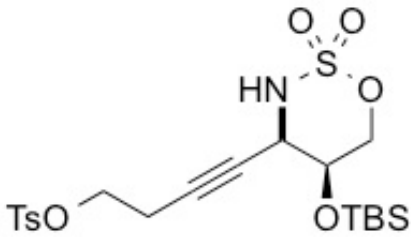
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	28
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-03-31T10:07:03
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1511.1
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

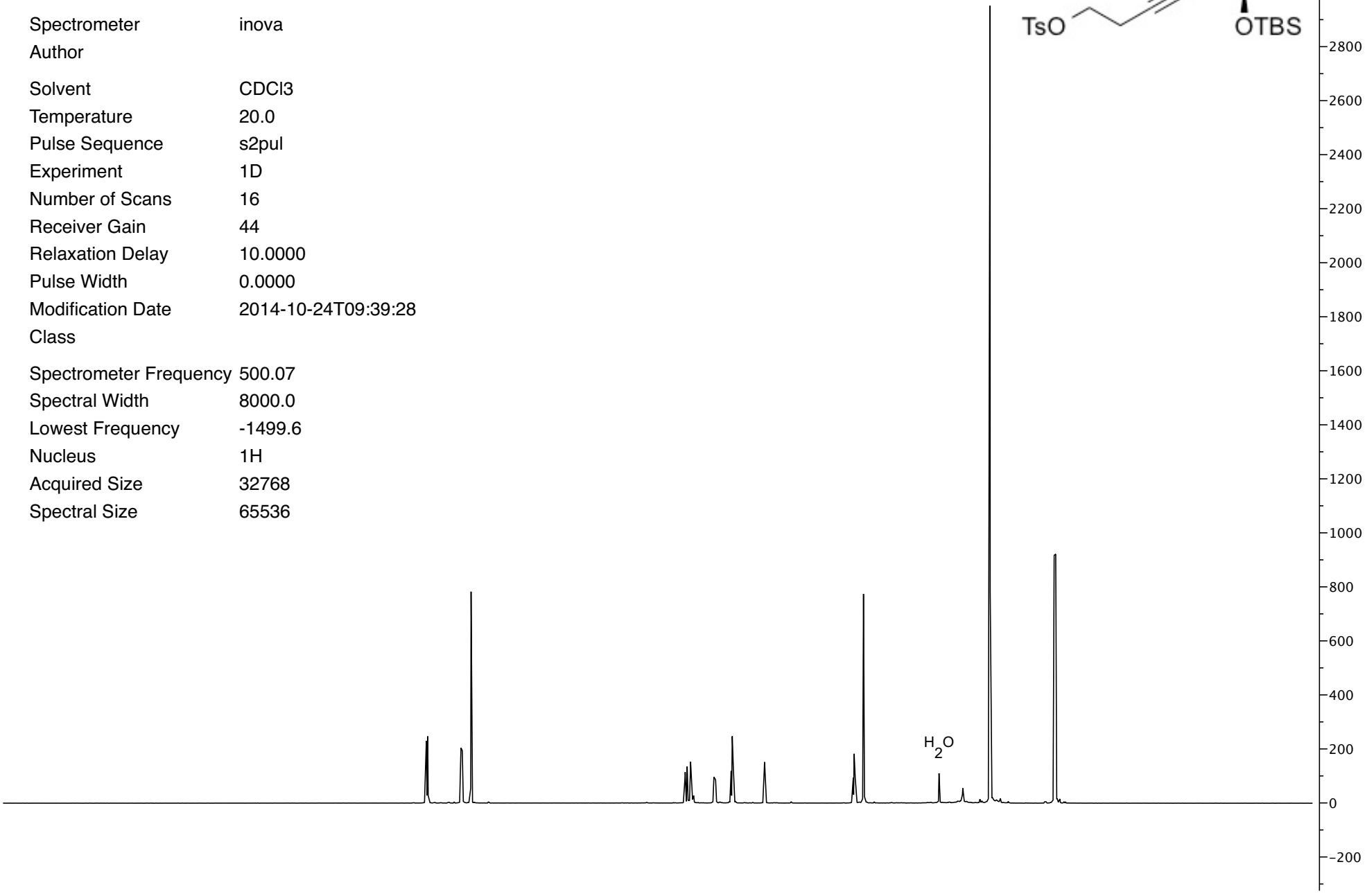


Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	704
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-03-31T09:24:50
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1274.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

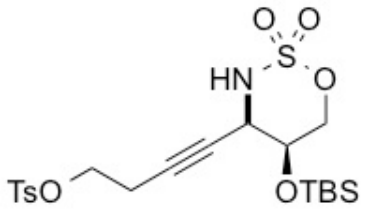


Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	44
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-10-24T09:39:28
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1499.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

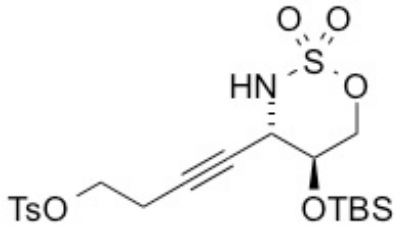




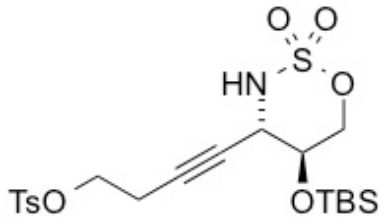
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	801
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-10-19T10:39:41
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1260.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



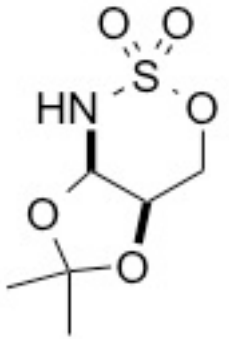
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	48
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-10-24T09:31:14
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1499.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



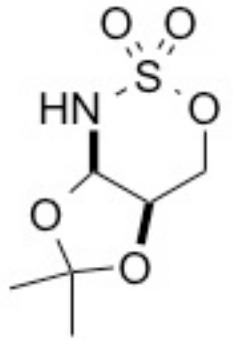
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	1290
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-10-19T11:48:43
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1260.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



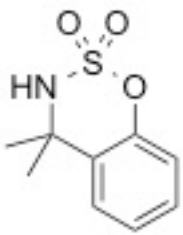
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CD3OD
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	52
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-12-12T09:30:54
Class	
Spectrometer Frequency	499.70
Spectral Width	7024.9
Lowest Frequency	-1016.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



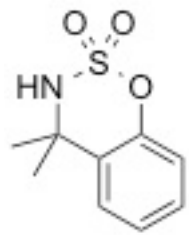
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CD3OD
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	64
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-12-12T09:37:54
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1116.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



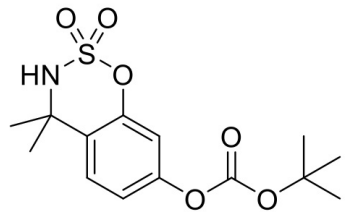
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	8
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.69
Spectral Width	7024.9
Lowest Frequency	-1012.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



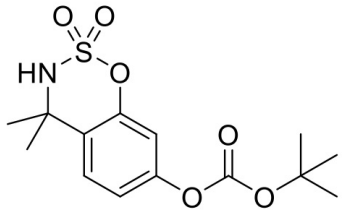
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	968
Relaxation Delay	1.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1275.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



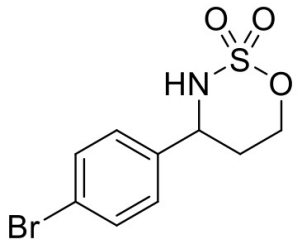
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	16.0
Pulse Sequence	s2pul
Experiment	1D
Probe	hcn
Number of Scans	16
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



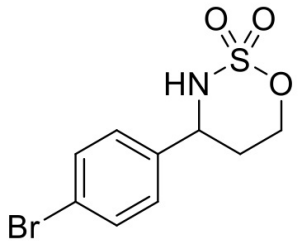
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	512
Relaxation Delay	2.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1275.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



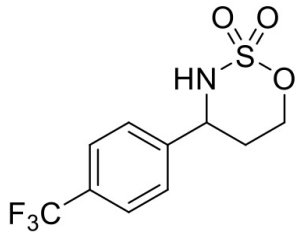
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	Acetone
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	8
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.70
Spectral Width	7024.9
Lowest Frequency	-1013.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



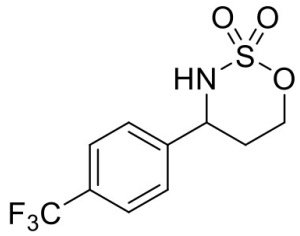
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	Acetone
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	834
Relaxation Delay	1.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1180.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



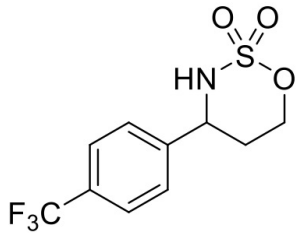
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CD3CN
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	2
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.70
Spectral Width	7024.9
Lowest Frequency	-1023.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



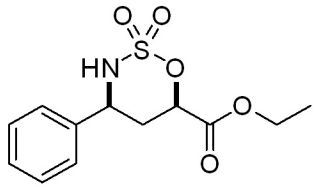
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CD3CN
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	8192
Relaxation Delay	5.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1174.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CD3CN
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	4
Relaxation Delay	0.0000
Pulse Width	0.0000
Spectrometer Frequency	470.15
Spectral Width	100000.0
Lowest Frequency	-79162.6
Nucleus	19F
Acquired Size	32768
Spectral Size	65536



	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	42
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-10-02T11:40:01
15	Modification Date	2014-10-02T11:40:03
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1499.6
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



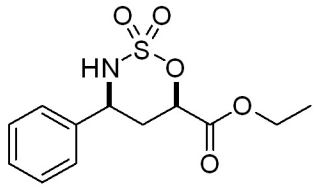
EtOAc

EtOAc

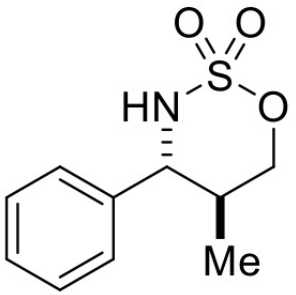
EtOAc

f1 (ppm)

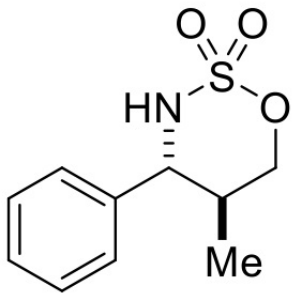
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	195
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-02T18:17:17
15	Modification Date	2014-10-02T18:24:21
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1275.5
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



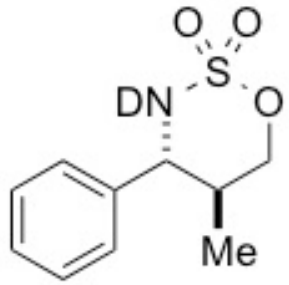
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	4
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.69
Spectral Width	7024.9
Lowest Frequency	-1012.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

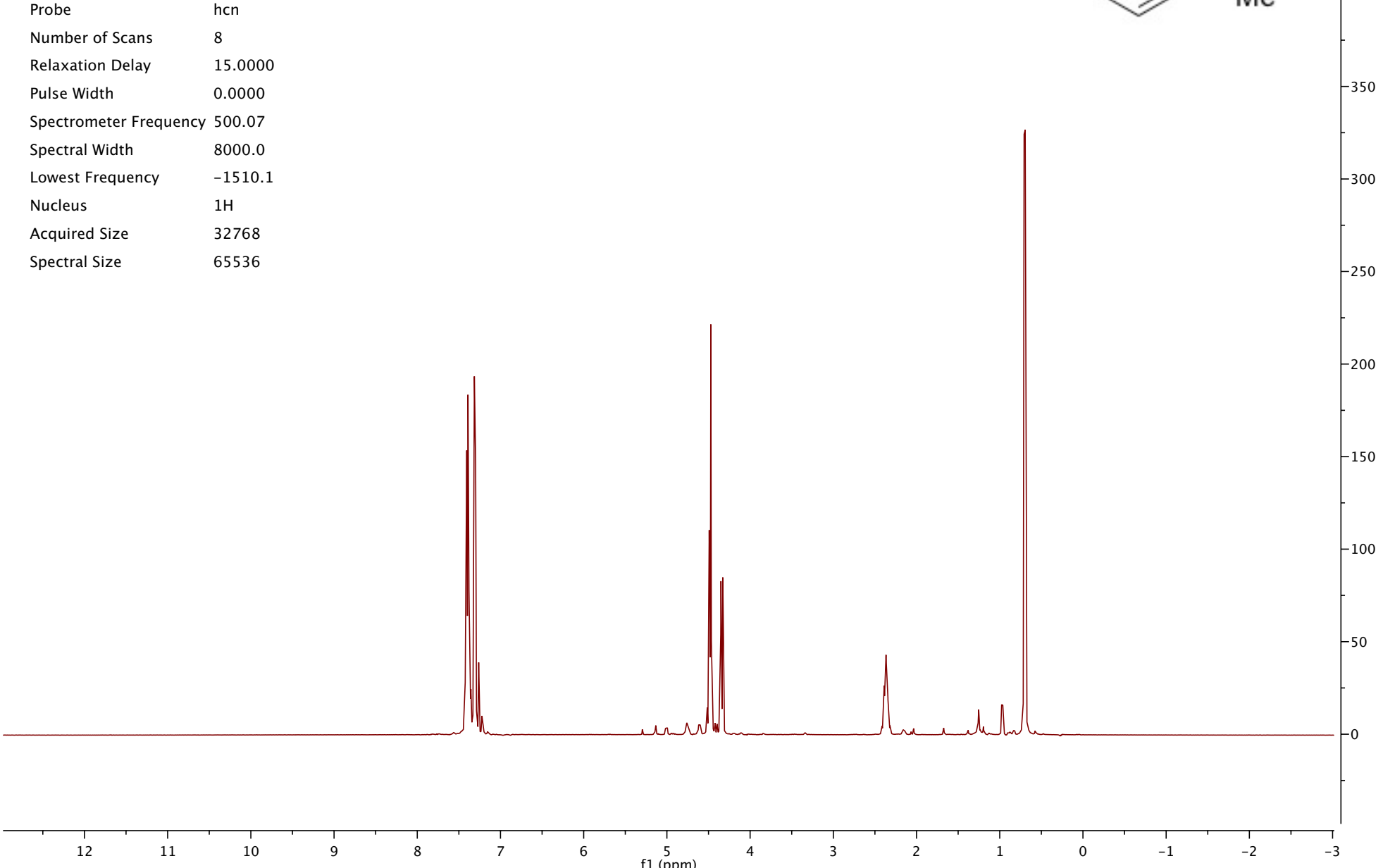


Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	54
Relaxation Delay	1.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1279.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

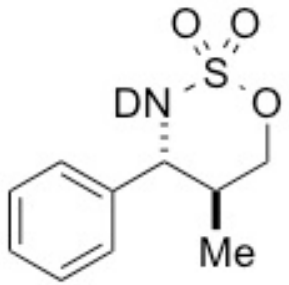


Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	hcn
Number of Scans	8
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.1
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



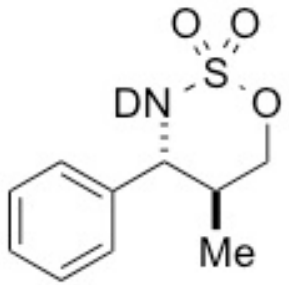


Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	cyclenoe
Experiment	1D
Probe	hcn
Number of Scans	32
Relaxation Delay	0.0000
Pulse Width	0.0000
Spectrometer Frequency	500.07
Spectral Width	5323.0
Lowest Frequency	-570.4
Nucleus	1H
Acquired Size	21803
Spectral Size	65536



NOE

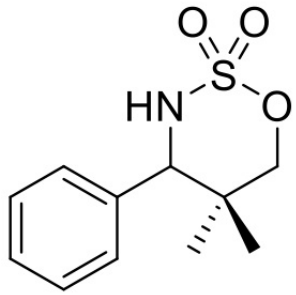
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	cyclenoe
Experiment	1D
Probe	hcn
Number of Scans	32
Relaxation Delay	0.0000
Pulse Width	0.0000
Spectrometer Frequency	500.07
Spectral Width	5353.7
Lowest Frequency	-590.6
Nucleus	1H
Acquired Size	21929
Spectral Size	65536



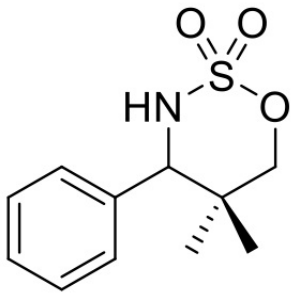
NOE

f1 (ppm)

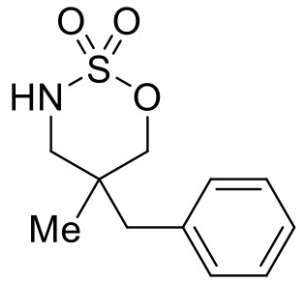
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	8
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.69
Spectral Width	7024.9
Lowest Frequency	-1012.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



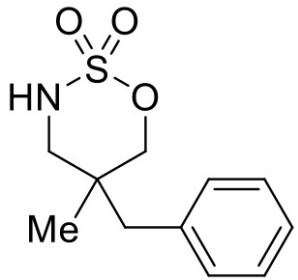
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	1024
Relaxation Delay	1.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1276.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



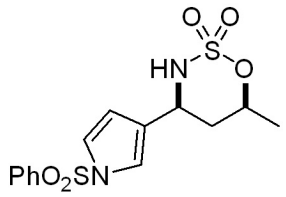
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	8
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.69
Spectral Width	7024.9
Lowest Frequency	-1012.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



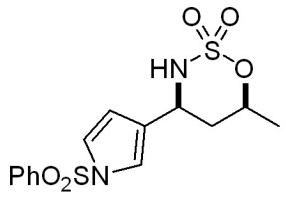
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	512
Relaxation Delay	2.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1274.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



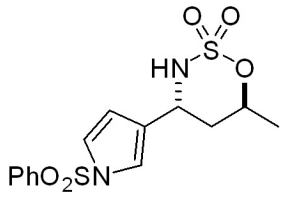
	Parameter	Value
1	Title	H1
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	8
9	Receiver Gain	32
10	Relaxation Delay	10.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-10-16T17:27:27
14	Modification Date	2014-10-16T17:28:48
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1499.6
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



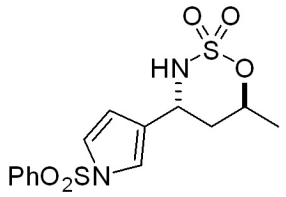
	Parameter	Value
1	Title	
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	17712
9	Receiver Gain	60
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.0863
13	Acquisition Date	2014-10-16T21:40:30
14	Modification Date	2014-10-17T07:57:01
15	Spectrometer Frequency	125.66
16	Spectral Width	30165.9
17	Lowest Frequency	-1272.5
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536



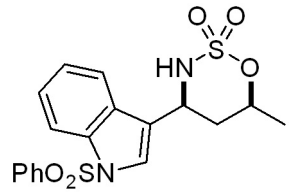
	Parameter	Value
1	Title	H1
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	54
10	Relaxation Delay	10.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-10-16T17:34:10
14	Modification Date	2014-10-16T17:34:44
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1499.6
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



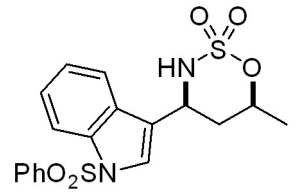
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUADG
9	Number of Scans	18720
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0240
14	Acquisition Date	2014-10-21T21:21:56
15	Modification Date	2014-10-22T07:54:22
16	Spectrometer Frequency	125.60
17	Spectral Width	32000.0
18	Lowest Frequency	-2188.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



	Parameter	Value
1	Title	
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	38
10	Relaxation Delay	10.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-10-28T17:02:36
14	Modification Date	2014-10-28T17:03:36
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1499.6
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



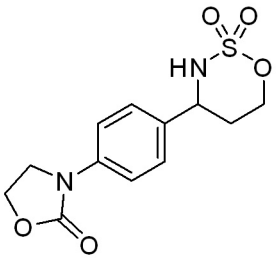
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	944
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-28T17:33:45
15	Modification Date	2014-10-28T18:06:56
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



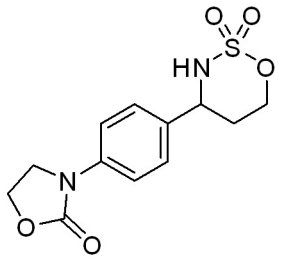
grease

f1 (ppm)

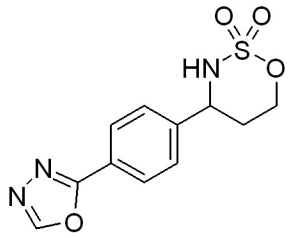
	Parameter	Value
1	Title	OxizolidinoneH1Final
2	Origin	Varian
3	Solvent	Acetone
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	42
10	Relaxation Delay	10.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-11-18T15:04:33
14	Modification Date	2014-11-18T15:04:45
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1512.5
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



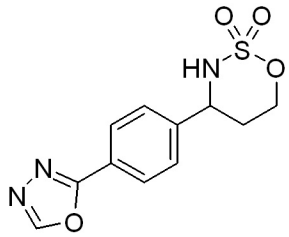
	Parameter	Value
1	Title	oxizolidinonePC13
2	Origin	Varian
3	Solvent	Acetone
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	1072
9	Receiver Gain	60
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.0863
13	Acquisition Date	2014-11-18T16:13:12
14	Modification Date	2014-11-18T16:51:00
15	Spectrometer Frequency	125.66
16	Spectral Width	30165.9
17	Lowest Frequency	-1179.5
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536



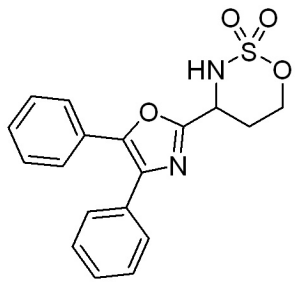
	Parameter	Value
1	Title	H1
2	Origin	Varian
3	Solvent	CD3OD
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	50
10	Relaxation Delay	20.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-10-08T10:09:48
14	Modification Date	2014-10-08T10:10:06
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1505.5
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



	Parameter	Value
1	Title	C13
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CD3OD
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16816
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-08T21:51:39
15	Modification Date	2014-10-09T07:37:15
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1110.1
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



	Parameter	Value
1	Title	H1
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	8
10	Receiver Gain	44
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-10-08T10:19:48
15	Modification Date	2014-10-08T10:21:17
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1511.1
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



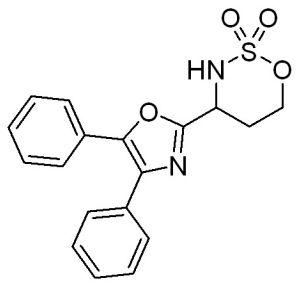
EtOAc

EtOAc

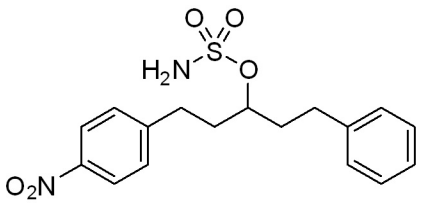
EtOAc

f1 (ppm)

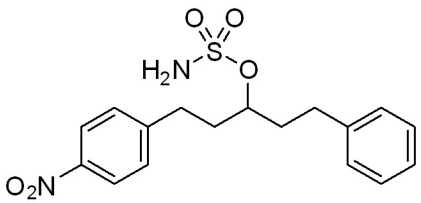
	Parameter	Value
1	Title	C13
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	11560
10	Receiver Gain	60
11	Relaxation Delay	2.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-09T21:47:31
15	Modification Date	2014-10-10T07:42:40
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



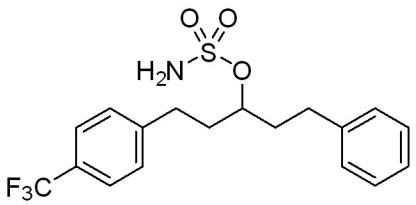
	Parameter	Value
1	Title	H1
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	8
9	Receiver Gain	38
10	Relaxation Delay	10.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-10-16T17:13:42
14	Modification Date	2014-10-16T17:14:01
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1511.1
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



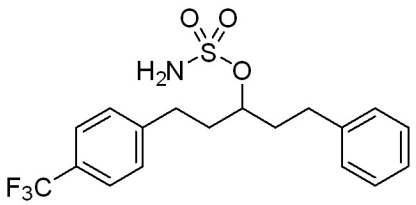
	Parameter	Value
1	Title	C13
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	1216
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-16T18:05:03
15	Modification Date	2014-10-16T18:47:58
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



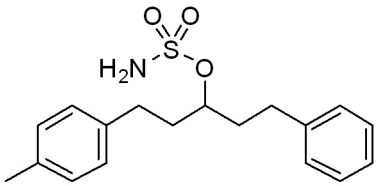
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	56
11	Relaxation Delay	4.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-12-03T16:53:50
15	Modification Date	2014-12-20T15:02:30
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



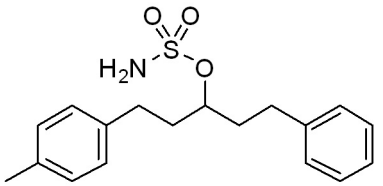
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	224
10	Receiver Gain	60
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-12-03T17:33:23
15	Modification Date	2014-12-20T15:02:32
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1273.0
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



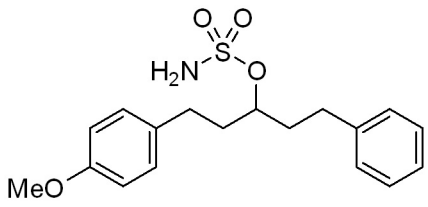
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	58
11	Relaxation Delay	2.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-10-08T16:25:18
15	Modification Date	2014-12-20T15:13:38
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



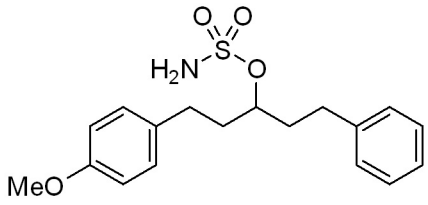
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	1872
10	Receiver Gain	60
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-12-15T17:42:37
15	Modification Date	2014-12-20T15:13:38
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



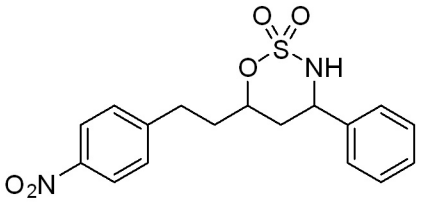
	Parameter	Value
1	Title	
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	16
9	Receiver Gain	14
10	Relaxation Delay	5.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-11-06T17:01:06
14	Modification Date	2014-11-06T17:01:32
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1499.6
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



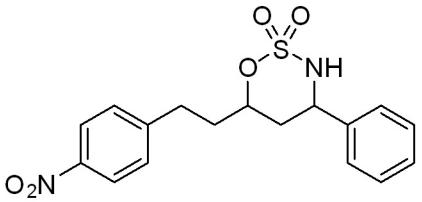
	Parameter	Value
1	Title	
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	48
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.0863
13	Acquisition Date	2014-11-06T17:09:22
14	Modification Date	2014-11-06T17:12:18
15	Spectrometer Frequency	125.66
16	Spectral Width	30165.9
17	Lowest Frequency	-1304.4
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536



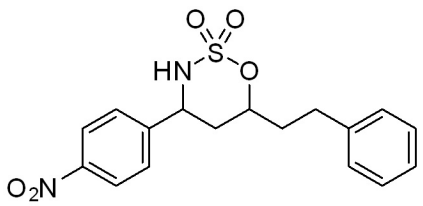
	Parameter	Value
1	Title	H1
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	8
10	Receiver Gain	48
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-10-08T10:15:36
15	Modification Date	2014-10-08T10:15:50
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1499.6
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



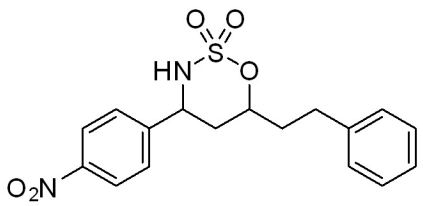
	Parameter	Value
1	Title	
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	20728
9	Receiver Gain	60
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.0863
13	Acquisition Date	2014-10-28T19:54:43
14	Modification Date	2014-10-29T07:56:06
15	Spectrometer Frequency	125.66
16	Spectral Width	30165.9
17	Lowest Frequency	-1270.5
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536



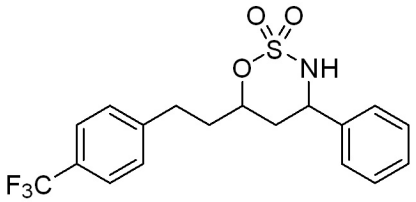
	Parameter	Value
1	Title	H1
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	8
9	Receiver Gain	56
10	Relaxation Delay	10.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-10-08T10:24:50
14	Modification Date	2014-10-08T10:25:28
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1499.6
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



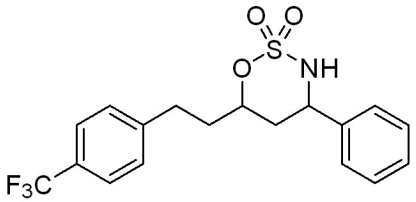
	Parameter	Value
1	Title	
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	11376
9	Receiver Gain	60
10	Relaxation Delay	2.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.0863
13	Acquisition Date	2014-10-13T22:03:44
14	Modification Date	2014-10-14T07:49:38
15	Spectrometer Frequency	125.66
16	Spectral Width	30165.9
17	Lowest Frequency	-1269.9
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536



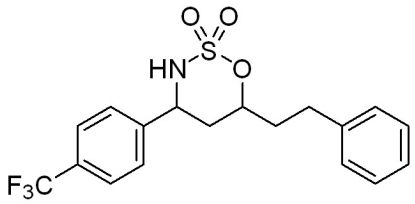
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	8
10	Receiver Gain	46
11	Relaxation Delay	4.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-10-17T16:40:45
15	Modification Date	2014-12-20T15:13:40
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



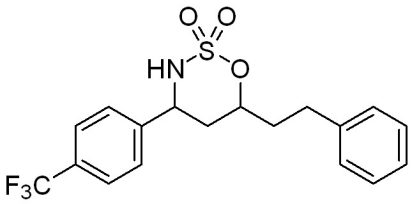
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	60
10	Receiver Gain	60
11	Relaxation Delay	2.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-09-27T14:38:51
15	Modification Date	2014-12-20T15:13:40
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1279.8
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



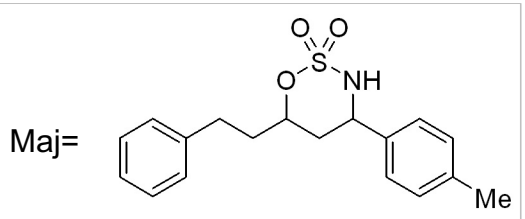
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	8
10	Receiver Gain	46
11	Relaxation Delay	4.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-10-17T16:45:09
15	Modification Date	2014-12-20T15:13:40
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536

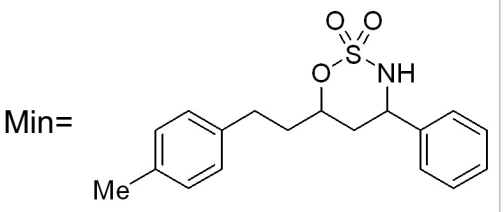


	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	180
10	Receiver Gain	60
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-17T16:47:29
15	Modification Date	2014-12-20T15:13:38
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536

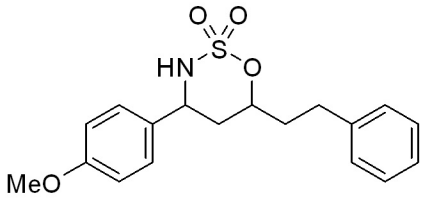


	Parameter	Value
1	Title	ch3majmin
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	4
9	Receiver Gain	32
10	Relaxation Delay	10.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-11-03T10:55:25
14	Modification Date	2014-11-03T10:57:44
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1499.6
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536

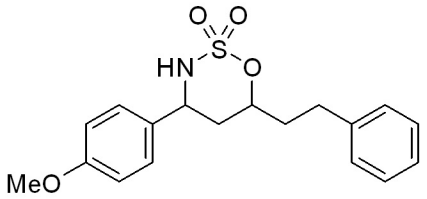




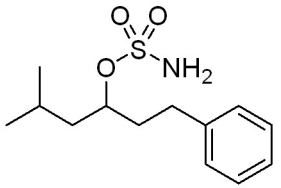
	Parameter	Value
1	Title	
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	hcn
8	Number of Scans	8
9	Receiver Gain	42
10	Relaxation Delay	10.0000
11	Pulse Width	0.0000
12	Acquisition Time	4.0960
13	Acquisition Date	2014-11-03T16:52:52
14	Modification Date	2014-11-03T16:53:42
15	Spectrometer Frequency	500.07
16	Spectral Width	8000.0
17	Lowest Frequency	-1499.6
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



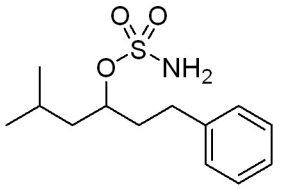
	Parameter	Value
1	Title	
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	520
9	Receiver Gain	60
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.0863
13	Acquisition Date	2014-11-03T16:59:09
14	Modification Date	2014-11-03T17:17:44
15	Spectrometer Frequency	125.66
16	Spectral Width	30165.9
17	Lowest Frequency	-1260.2
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536



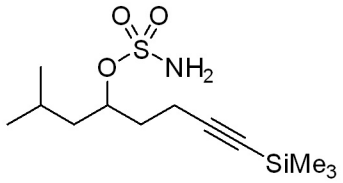
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	28
11	Relaxation Delay	4.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-12-06T11:08:59
15	Modification Date	2014-12-06T12:16:34
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1499.6
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



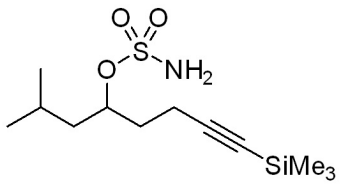
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	96
10	Receiver Gain	60
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-12-06T11:23:47
15	Modification Date	2014-12-06T12:16:52
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



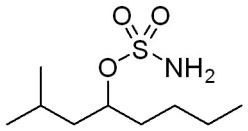
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	54
11	Relaxation Delay	2.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-10-08T16:14:53
15	Modification Date	2015-01-14T15:31:32
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



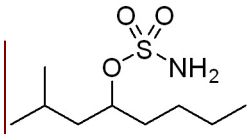
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	90
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-08T16:18:43
15	Modification Date	2015-01-14T15:31:32
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



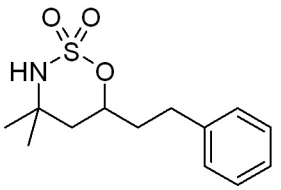
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	22.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	41
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-05-21T18:26:54
15	Modification Date	2014-05-21T18:26:56
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



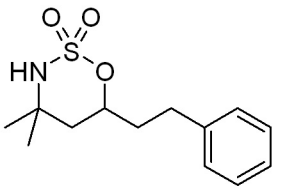
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	22.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	180
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-05-21T18:30:18
15	Modification Date	2014-05-21T18:36:49
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	41
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-07-03T08:47:18
15	Modification Date	2015-01-14T15:38:44
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



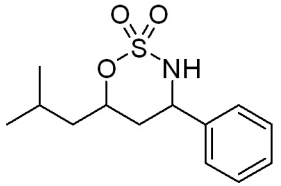
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	60
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-07-03T08:48:28
15	Modification Date	2015-01-14T15:38:44
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



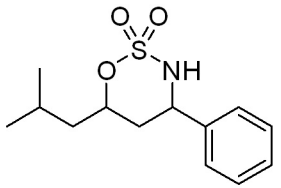
Pc ligand

f1 (ppm)

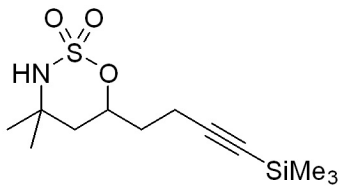
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	1
10	Receiver Gain	52
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-06-02T11:14:16
15	Modification Date	2015-01-14T15:38:44
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



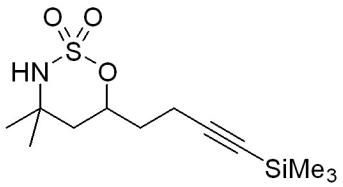
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	160
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-06-02T11:19:11
15	Modification Date	2015-01-14T15:38:44
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



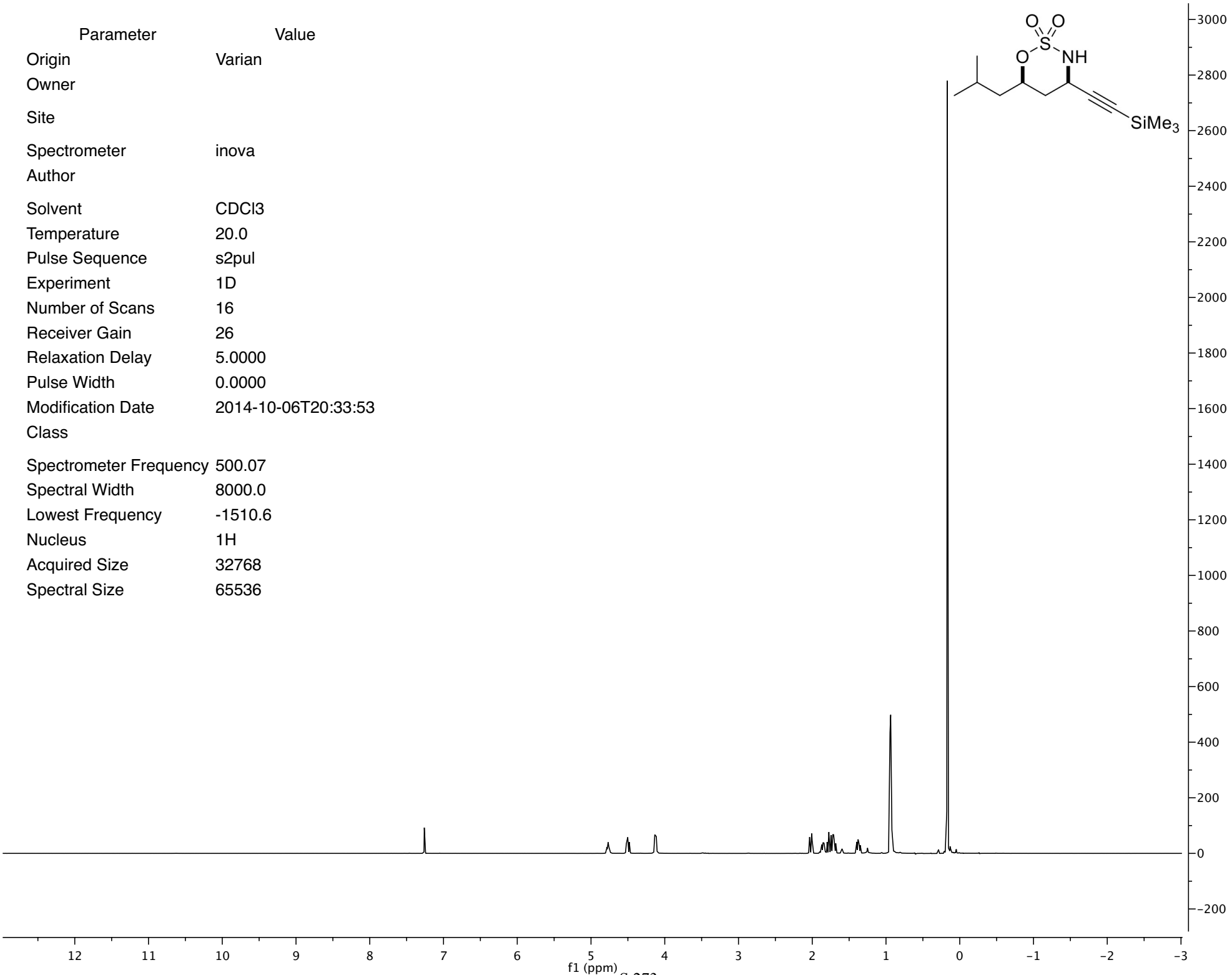
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	60
11	Relaxation Delay	4.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-11-19T15:42:05
15	Modification Date	2014-12-03T20:53:28
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



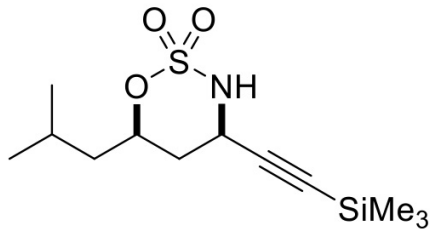
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	96
10	Receiver Gain	60
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-11-19T15:43:57
15	Modification Date	2014-12-03T20:53:28
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1274.0
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



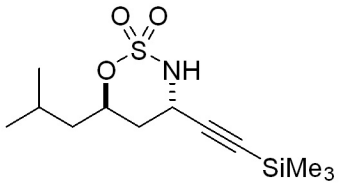
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	26
Relaxation Delay	5.0000
Pulse Width	0.0000
Modification Date	2014-10-06T20:33:53
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



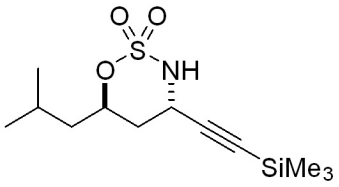
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	590
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-07-12T10:02:13
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1260.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



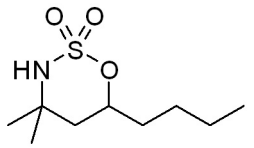
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	36
11	Relaxation Delay	4.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-12-03T16:06:17
15	Modification Date	2014-12-03T20:53:28
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



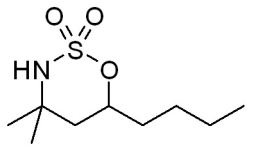
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	64
10	Receiver Gain	60
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-12-03T16:08:01
15	Modification Date	2014-12-03T20:53:28
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



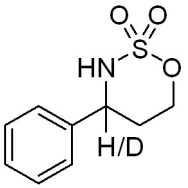
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	46
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-10-31T14:03:11
15	Modification Date	2014-10-31T14:03:13
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



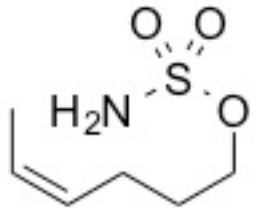
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	263
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-31T14:03:47
15	Modification Date	2014-10-31T14:13:14
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



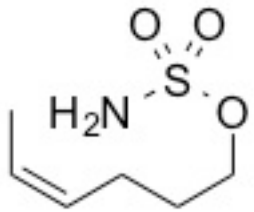
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	23.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	autox
9	Number of Scans	2944
10	Receiver Gain	60
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	0.5000
14	Acquisition Date	2014-12-16T12:14:06
15	Modification Date	2014-12-16T12:42:08
16	Spectrometer Frequency	150.82
17	Spectral Width	24883.4
18	Lowest Frequency	0.2
19	Nucleus	13C
20	Acquired Size	12442
21	Spectral Size	131072



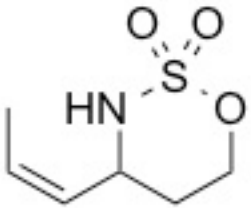
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	22.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	52
Relaxation Delay	5.0000
Pulse Width	0.0000
Modification Date	2014-04-14T13:54:14
Class	
Spectrometer Frequency	499.69
Spectral Width	7024.9
Lowest Frequency	-1012.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



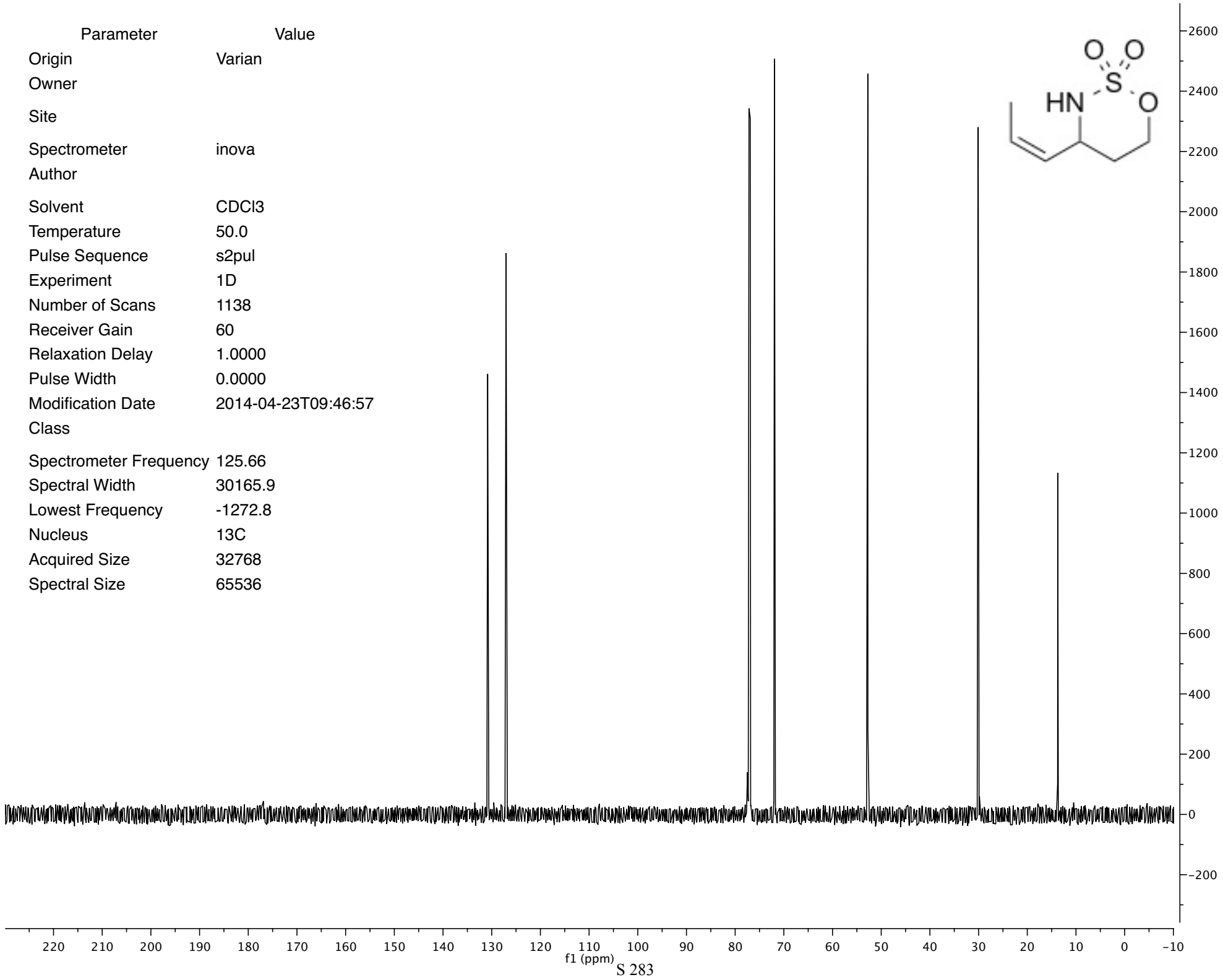
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	22.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	725
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-04-14T15:26:15
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1275.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



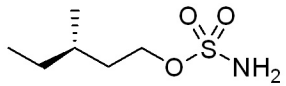
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	38
Relaxation Delay	5.0000
Pulse Width	0.0000
Modification Date	2014-04-22T11:10:02
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1511.1
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



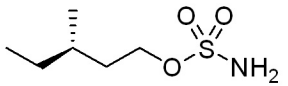
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	50.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	1138
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	0.0000
Modification Date	2014-04-23T09:46:57
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1272.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



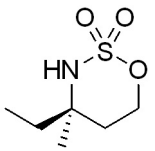
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	41
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-10-18T14:03:29
15	Modification Date	2014-10-18T14:03:44
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



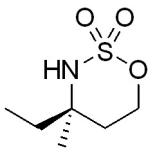
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	22.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	108
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-02-11T18:40:03
15	Modification Date	2014-02-11T18:44:05
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



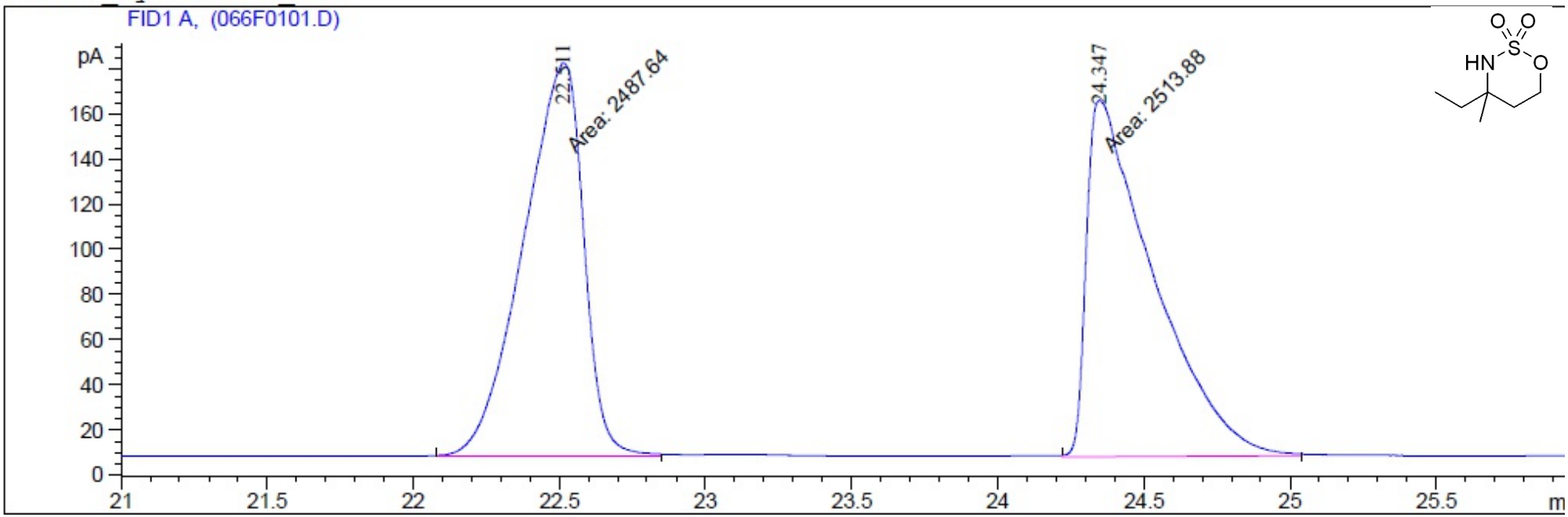
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	50
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-10-18T14:13:20
15	Modification Date	2014-10-18T14:13:23
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1012.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



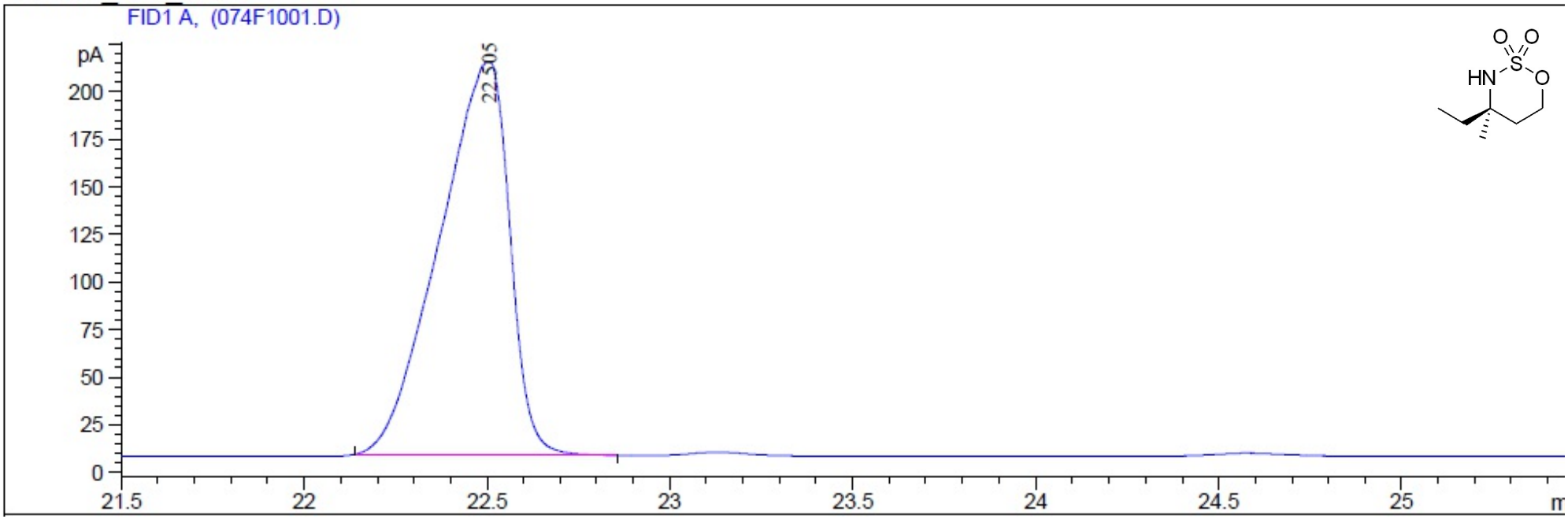
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	296
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-18T14:13:38
15	Modification Date	2014-10-18T14:24:14
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



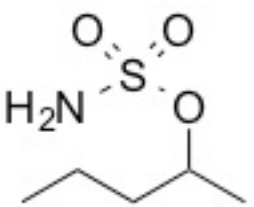
Chiral_Cyclosil-B_160



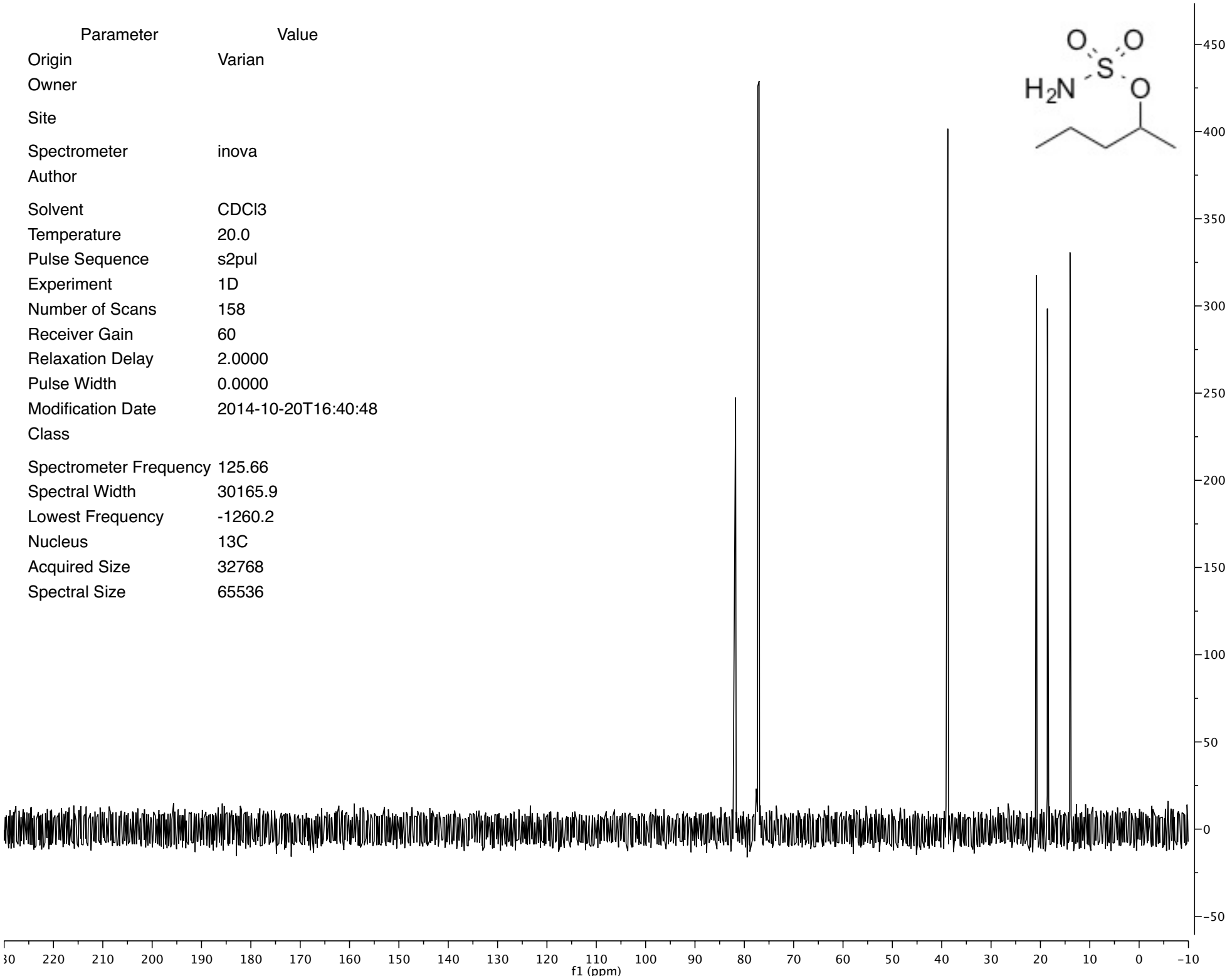
Chiral_CSB_bake



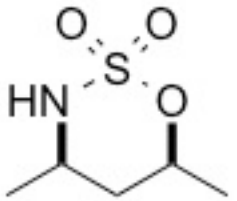
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	38
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-10-19T08:59:43
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1499.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



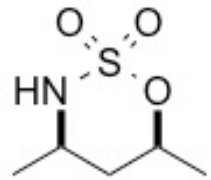
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	158
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-10-20T16:40:48
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1260.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



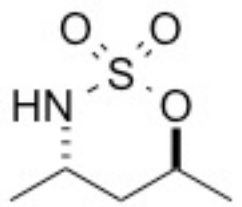
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	60
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-10-14T09:25:39
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1499.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



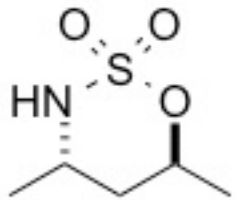
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	22
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-10-14T10:07:33
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1260.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



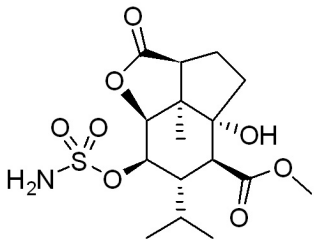
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	32
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-11-16T08:39:48
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1499.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



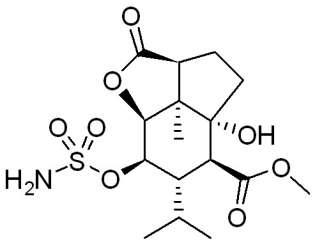
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	210
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-11-16T09:18:50
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1260.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



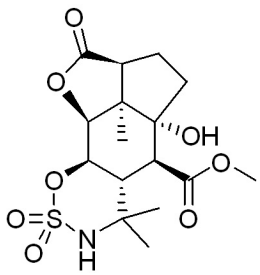
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	60
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-09-15T17:44:47
15	Modification Date	2014-09-15T17:44:48
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1012.4
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



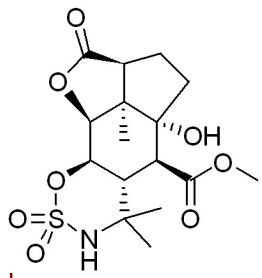
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	278
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-09-30T11:19:19
15	Modification Date	2014-09-30T11:29:21
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



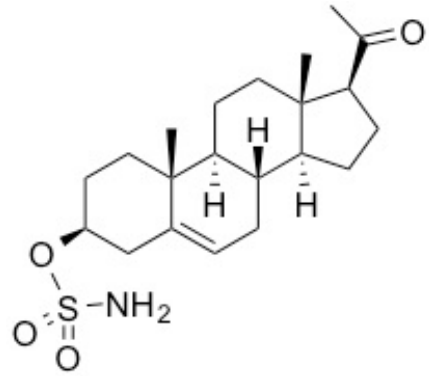
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	Acetone
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	44
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-10-10T10:54:17
15	Modification Date	2014-10-10T10:54:20
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1499.5
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



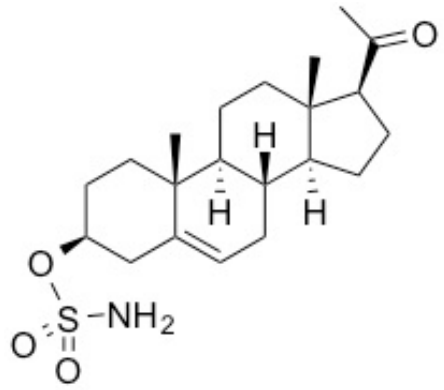
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	Acetone
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	2413
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-10-16T19:59:41
15	Modification Date	2014-10-16T21:24:06
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1165.3
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



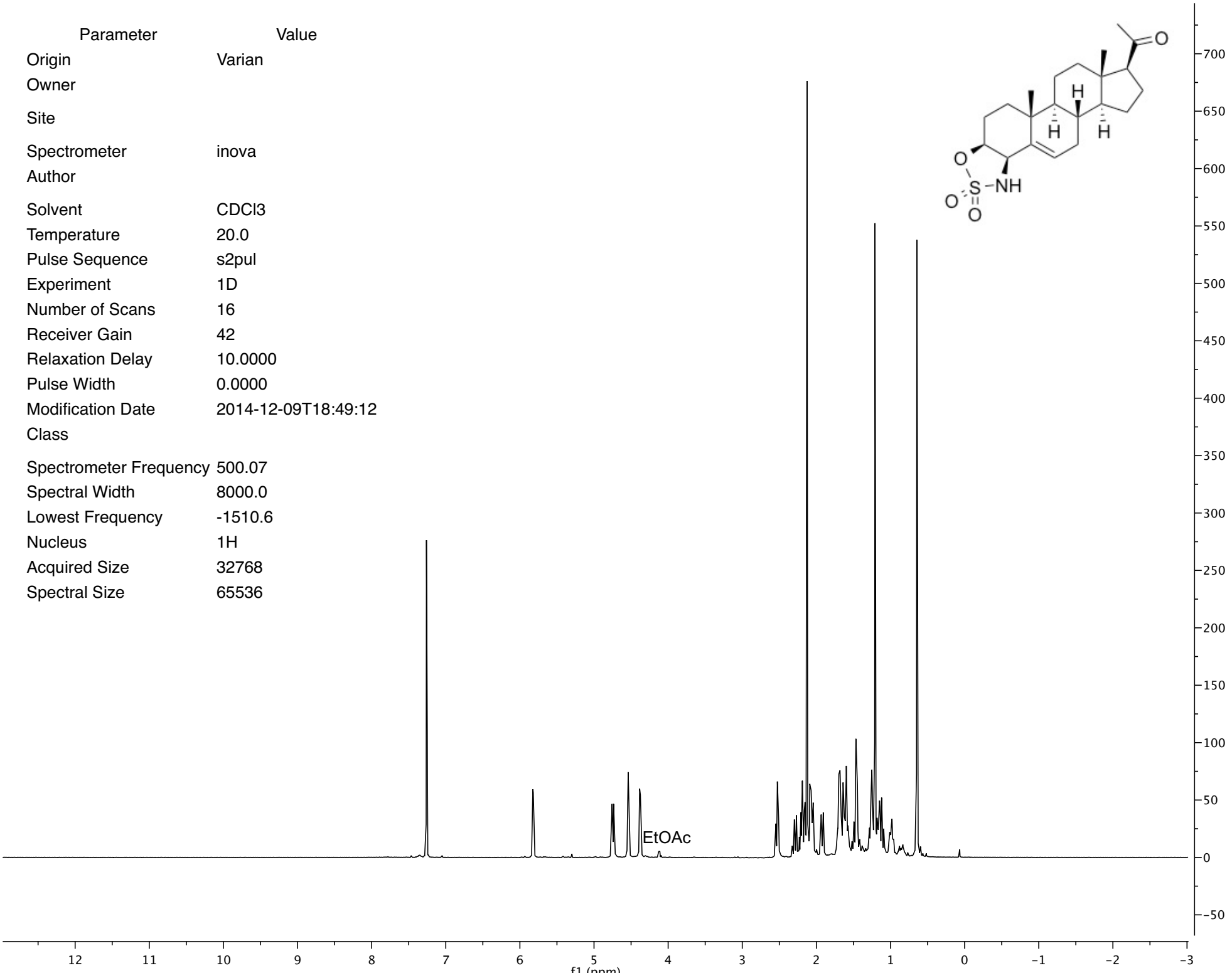
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	42
Relaxation Delay	5.0000
Pulse Width	0.0000
Modification Date	2014-05-20T11:49:15
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



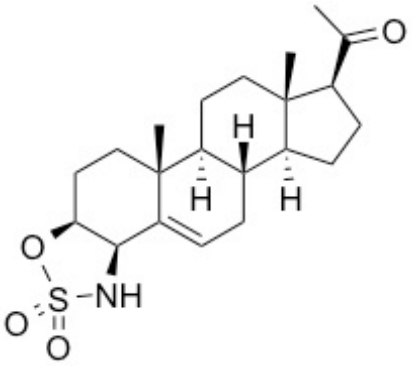
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	915
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-07-13T10:12:38
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1274.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



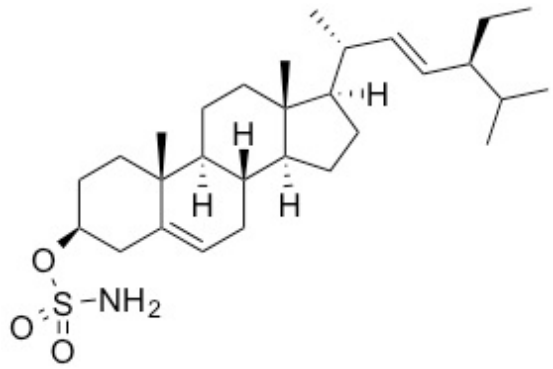
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	42
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-12-09T18:49:12
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



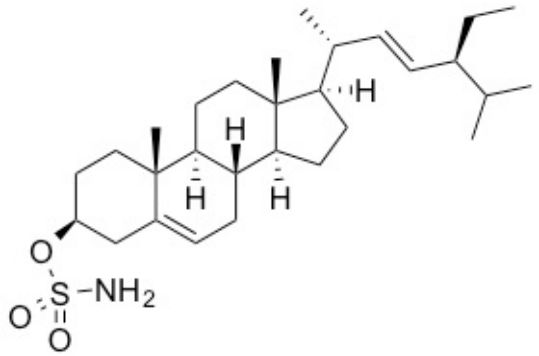
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	22.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	1021
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-05-23T14:53:09
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1276.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



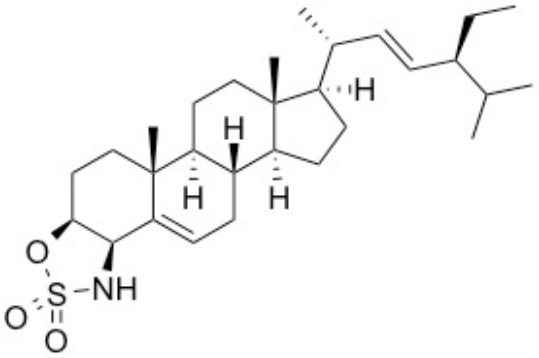
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	36
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-06-25T14:13:55
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



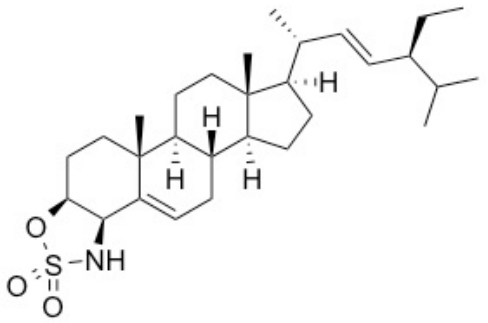
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	822
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-07-12T15:44:50
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1260.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



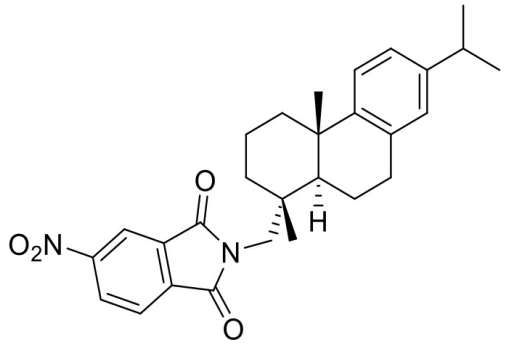
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	48
Relaxation Delay	10.0000
Pulse Width	0.0000
Modification Date	2014-10-05T07:47:06
Class	
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1511.1
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



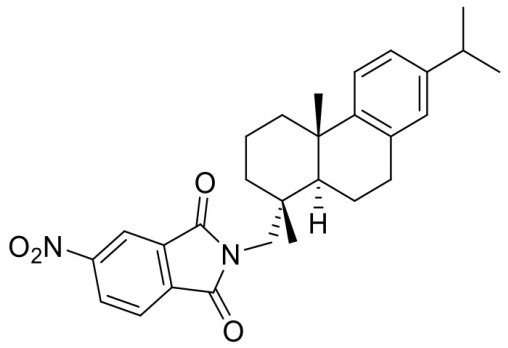
Parameter	Value
Origin	Varian
Owner	
Site	
Spectrometer	inova
Author	
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	740
Receiver Gain	60
Relaxation Delay	2.0000
Pulse Width	0.0000
Modification Date	2014-07-12T11:24:59
Class	
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1260.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



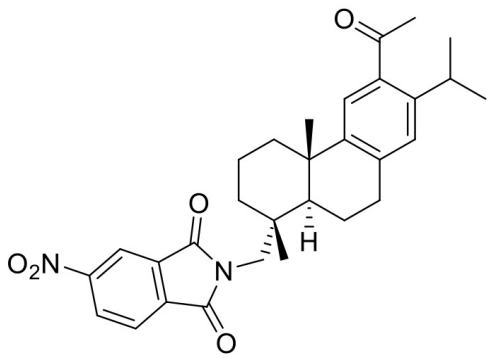
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	hcn
Number of Scans	32
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



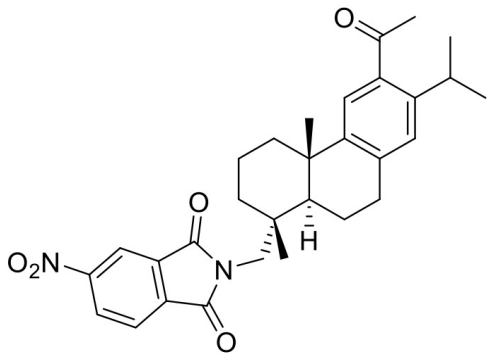
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	512
Relaxation Delay	5.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1291.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



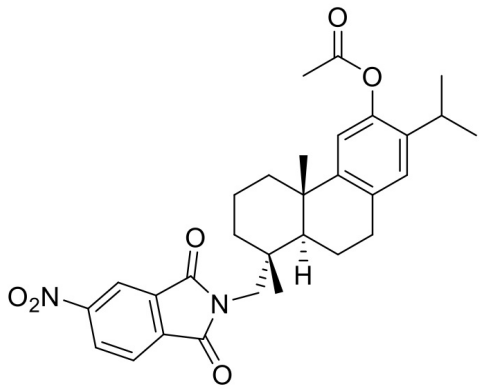
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	32
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.69
Spectral Width	7024.9
Lowest Frequency	-1012.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



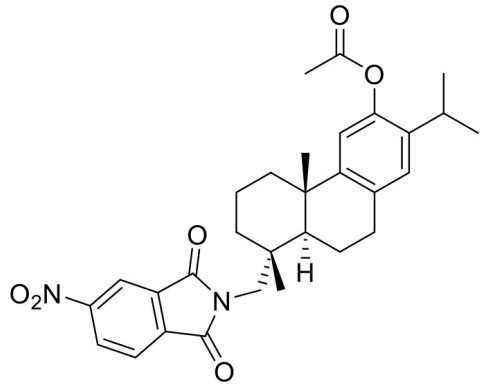
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	1025
Relaxation Delay	5.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1275.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



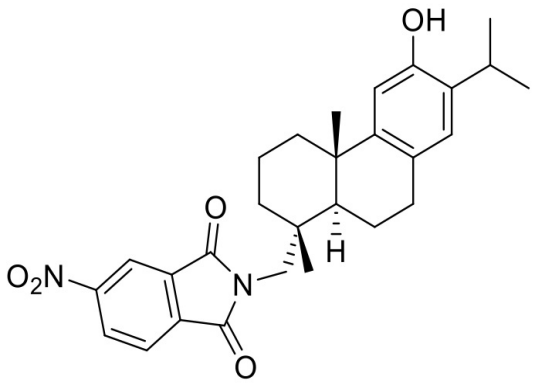
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUADG
Number of Scans	32
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.43
Spectral Width	8000.0
Lowest Frequency	-1508.7
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



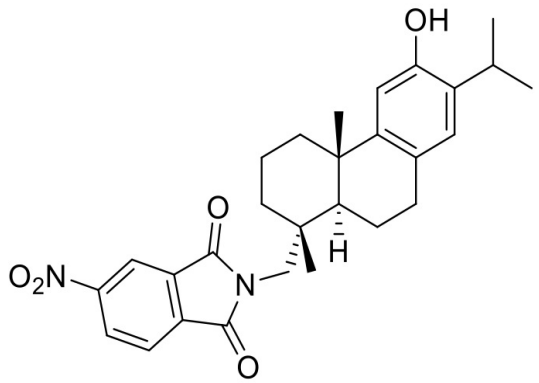
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUADG
Number of Scans	2048
Relaxation Delay	2.0000
Pulse Width	0.0000
Spectrometer Frequency	125.60
Spectral Width	32000.0
Lowest Frequency	-2202.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



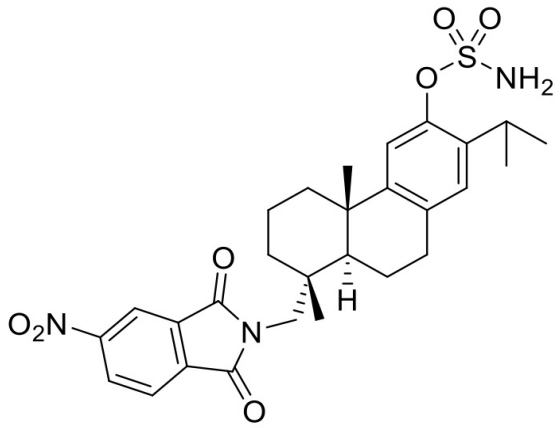
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUADG
Number of Scans	32
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.43
Spectral Width	8000.0
Lowest Frequency	-1508.7
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



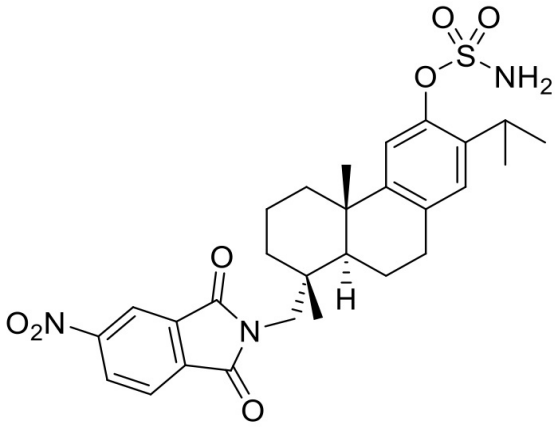
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUADG
Number of Scans	2048
Relaxation Delay	2.0000
Pulse Width	0.0000
Spectrometer Frequency	125.60
Spectral Width	32000.0
Lowest Frequency	-2200.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



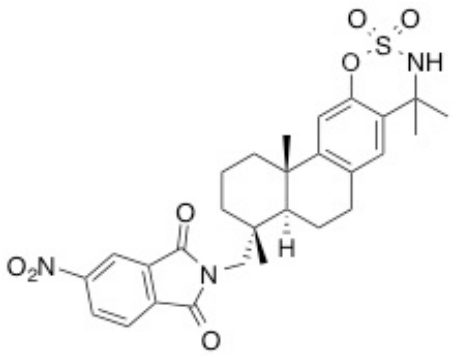
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	hcn
Number of Scans	16
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



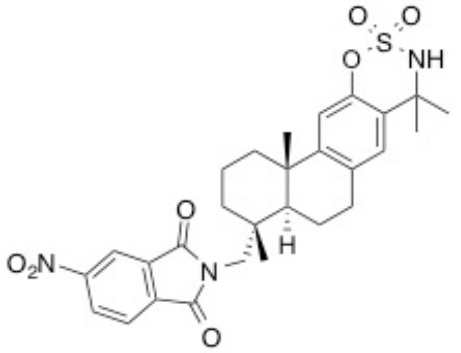
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	1024
Relaxation Delay	2.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1275.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



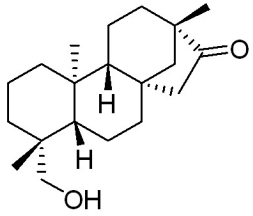
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	hcn
Number of Scans	32
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1511.1
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



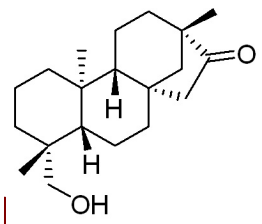
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	1024
Relaxation Delay	1.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1273.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



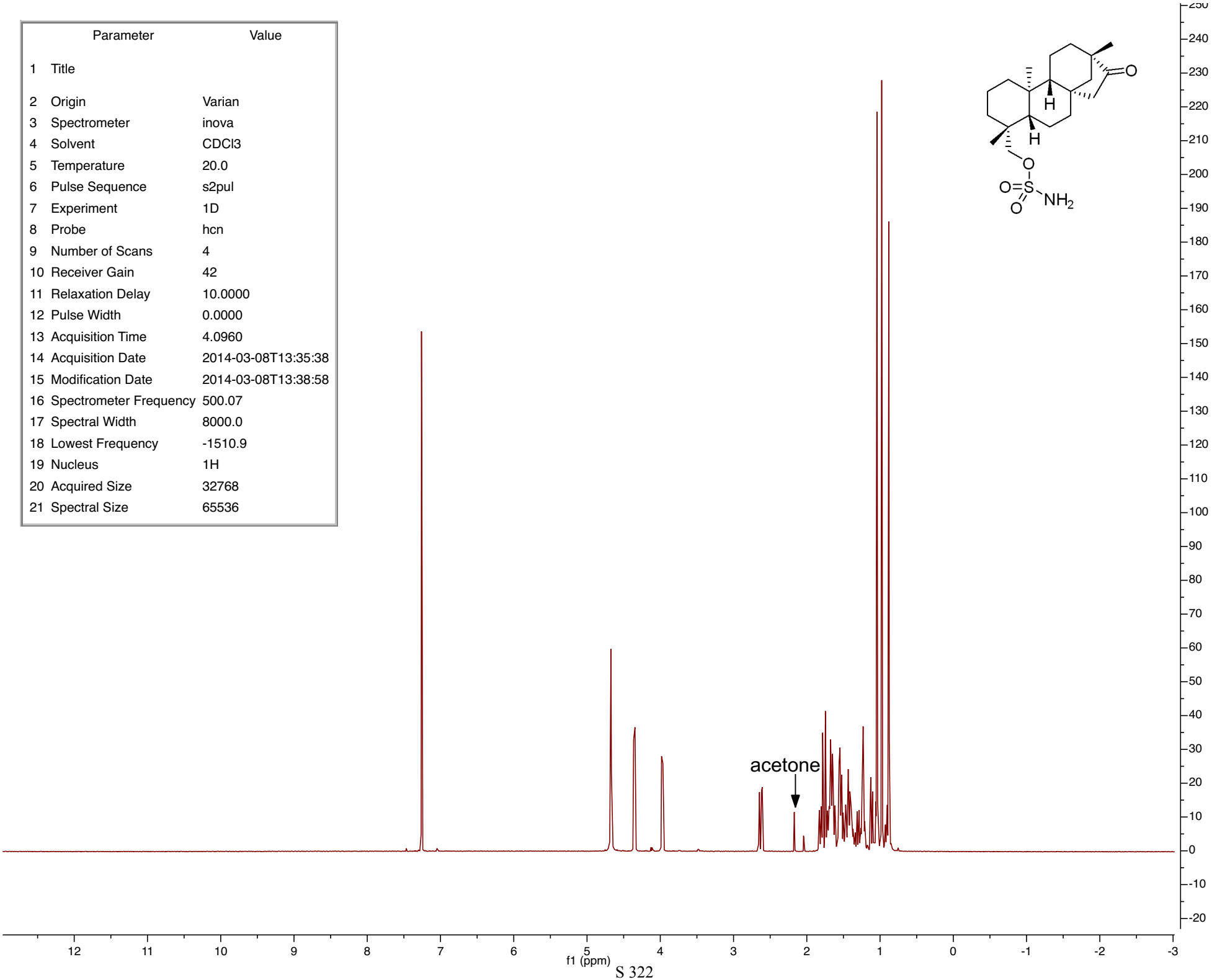
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	54
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-02-27T16:15:51
15	Modification Date	2014-02-27T16:15:53
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1499.6
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



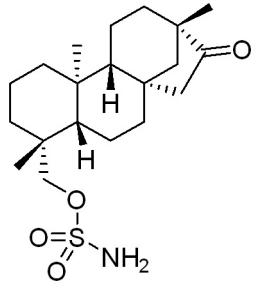
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	382
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-07-28T13:05:35
15	Modification Date	2014-07-28T13:19:10
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1273.4
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



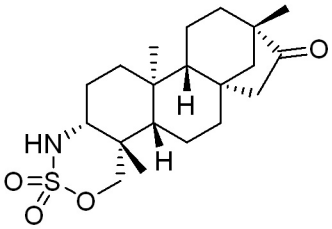
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	4
10	Receiver Gain	42
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.0960
14	Acquisition Date	2014-03-08T13:35:38
15	Modification Date	2014-03-08T13:38:58
16	Spectrometer Frequency	500.07
17	Spectral Width	8000.0
18	Lowest Frequency	-1510.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



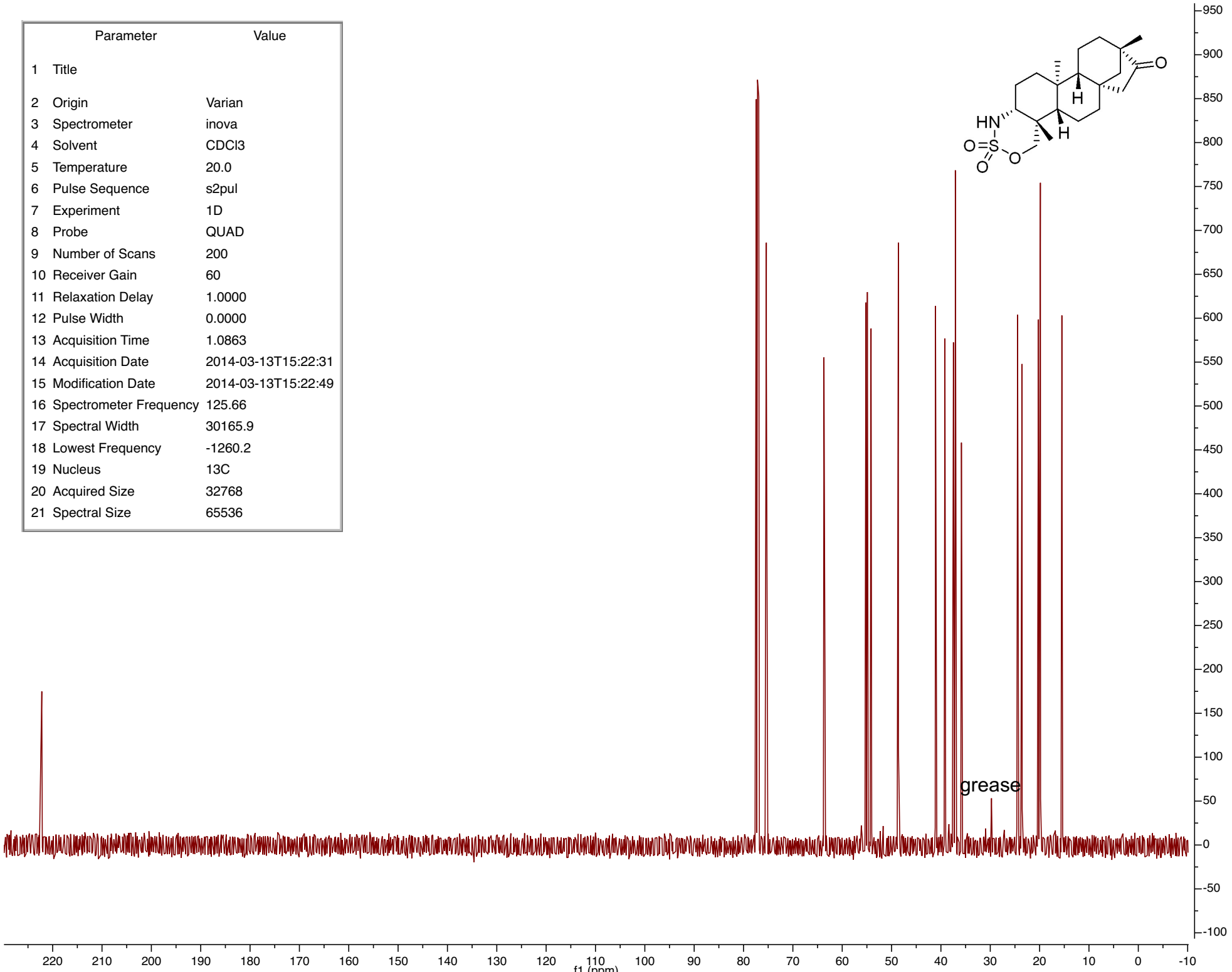
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	153
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-03-15T10:48:08
15	Modification Date	2014-03-15T10:53:49
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



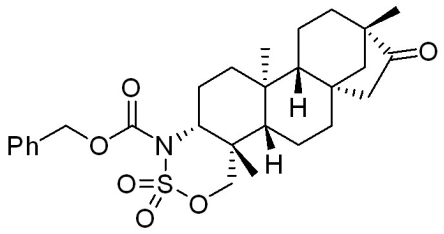
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	32
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2014-03-13T15:11:02
15	Modification Date	2014-03-13T15:11:04
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



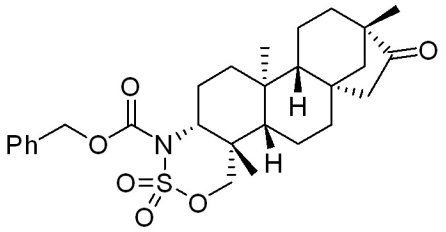
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	200
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2014-03-13T15:22:31
15	Modification Date	2014-03-13T15:22:49
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



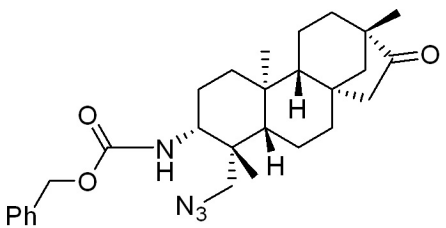
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	46
11	Relaxation Delay	4.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2015-01-17T08:08:30
15	Modification Date	2015-01-17T11:14:36
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



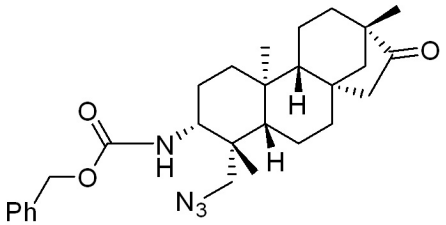
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	480
10	Receiver Gain	60
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2015-01-17T08:10:28
15	Modification Date	2015-01-17T11:14:36
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



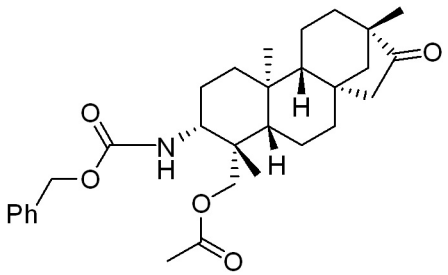
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	41
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2015-01-12T10:42:23
15	Modification Date	2015-01-12T10:42:25
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



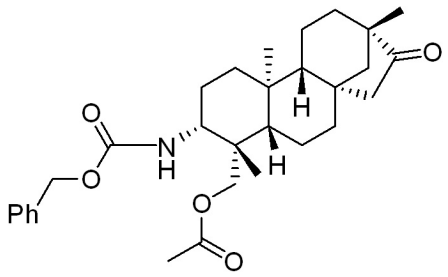
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	325
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2015-01-12T10:42:47
15	Modification Date	2015-01-12T10:54:34
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



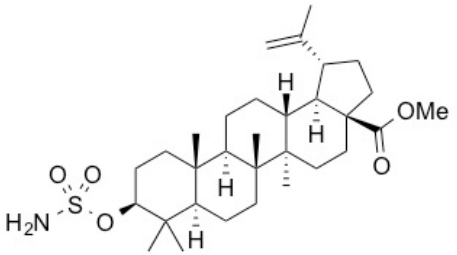
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16
10	Receiver Gain	36
11	Relaxation Delay	2.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2015-01-29T16:21:51
15	Modification Date	2015-01-30T10:33:30
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



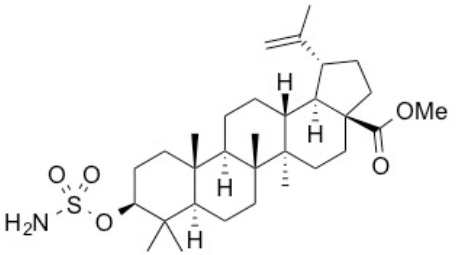
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	176
10	Receiver Gain	60
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.0863
14	Acquisition Date	2015-01-29T16:23:39
15	Modification Date	2015-01-30T10:33:48
16	Spectrometer Frequency	125.66
17	Spectral Width	30165.9
18	Lowest Frequency	-1260.2
19	Nucleus	13C
20	Acquired Size	32768
21	Spectral Size	65536



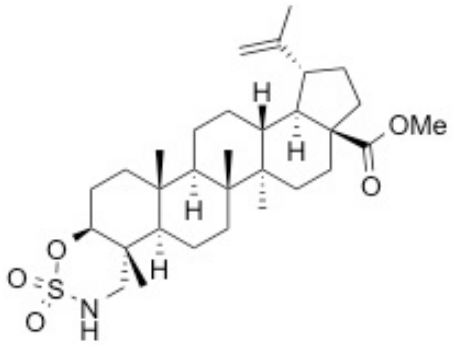
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	8
Relaxation Delay	15.0000
Pulse Width	0.0000
Spectrometer Frequency	499.69
Spectral Width	7024.9
Lowest Frequency	-1012.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



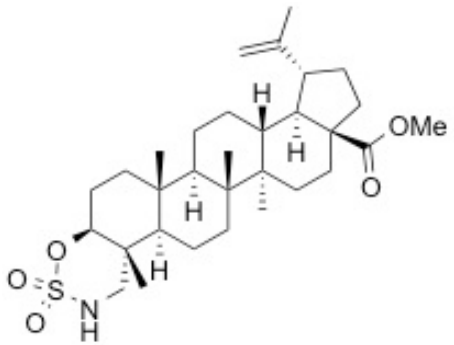
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	1024
Relaxation Delay	3.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1275.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

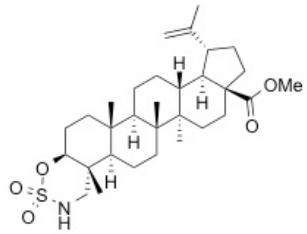


Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	Acetone
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	1
Relaxation Delay	0.0000
Pulse Width	0.0000
Spectrometer Frequency	499.70
Spectral Width	7024.9
Lowest Frequency	-1013.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	Acetone
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	1024
Relaxation Delay	1.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1161.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536




OMe
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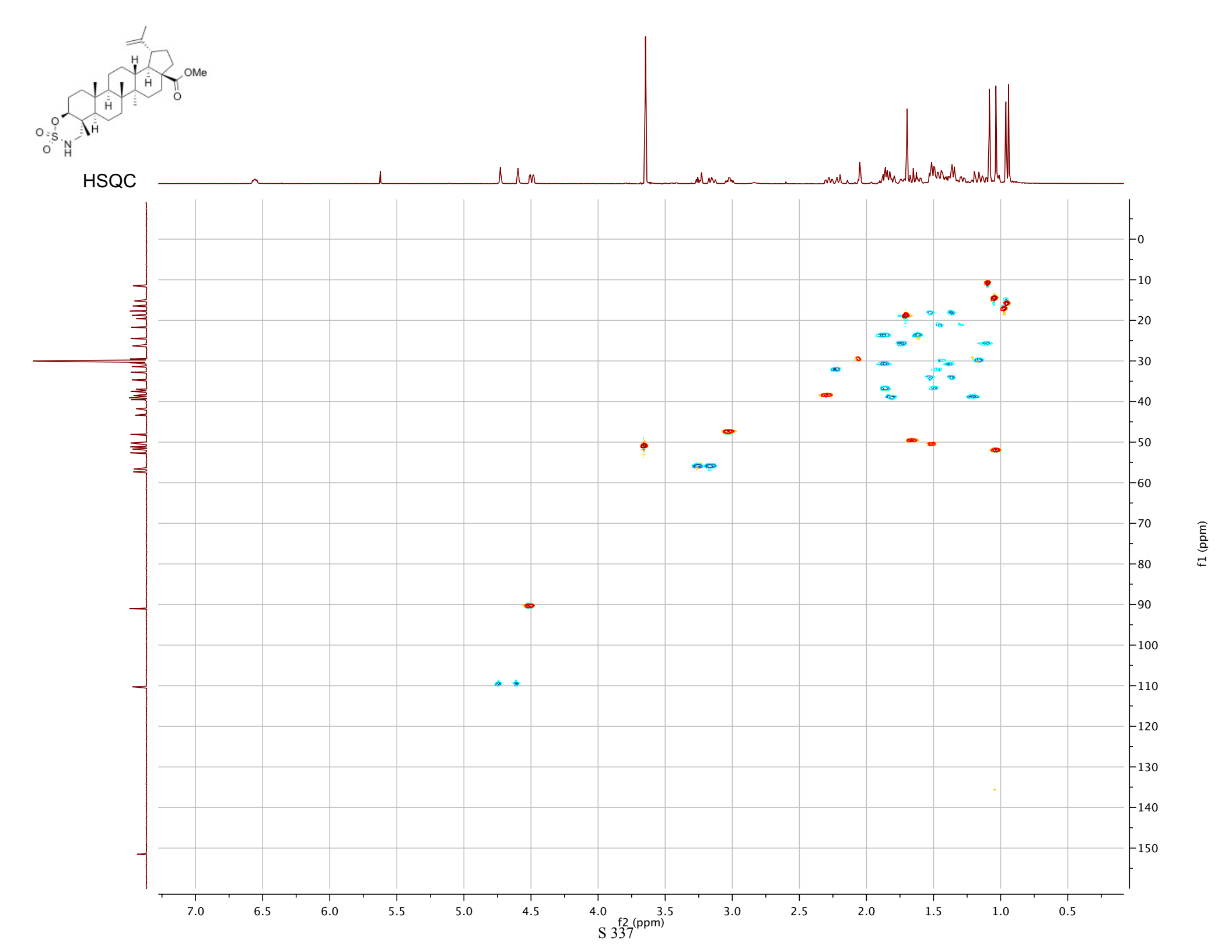
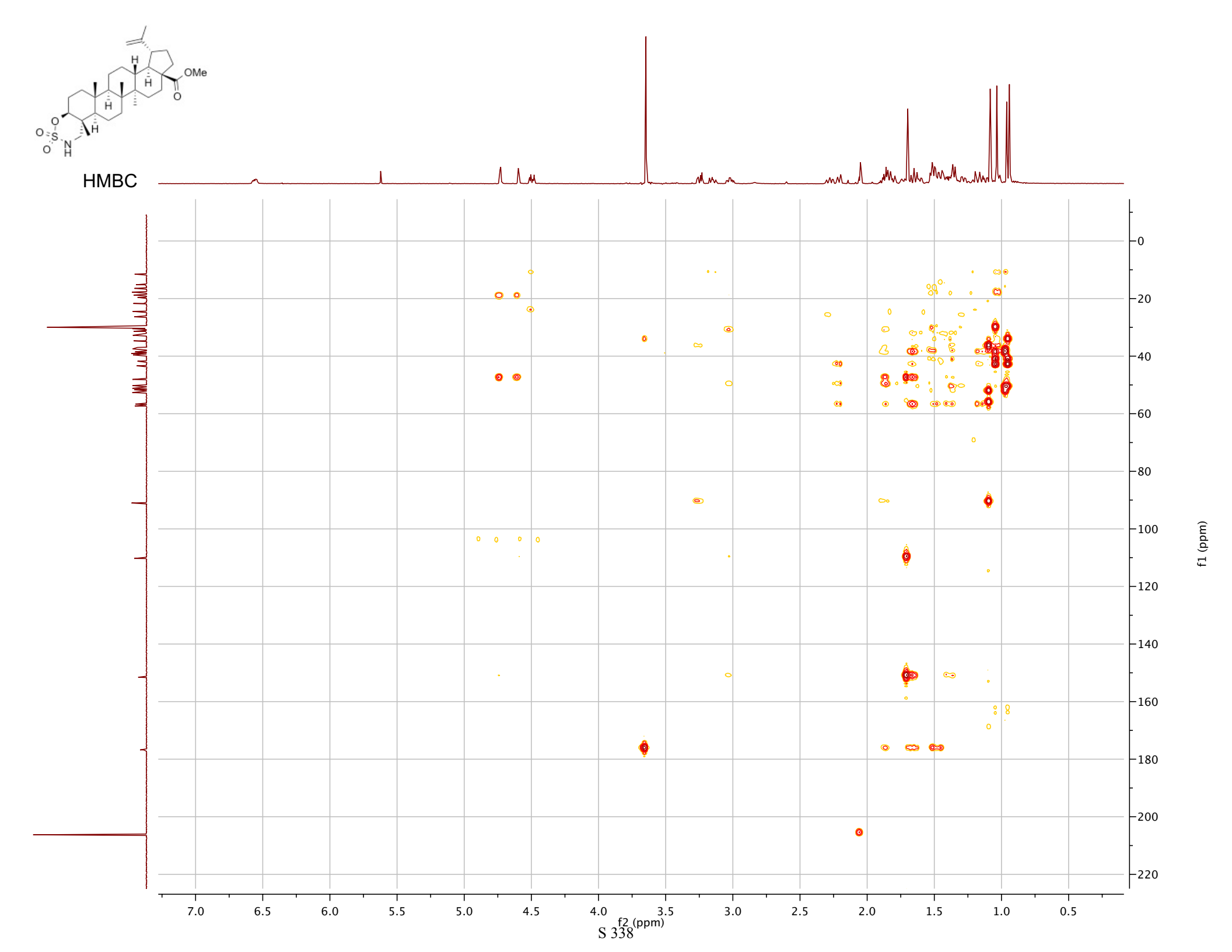
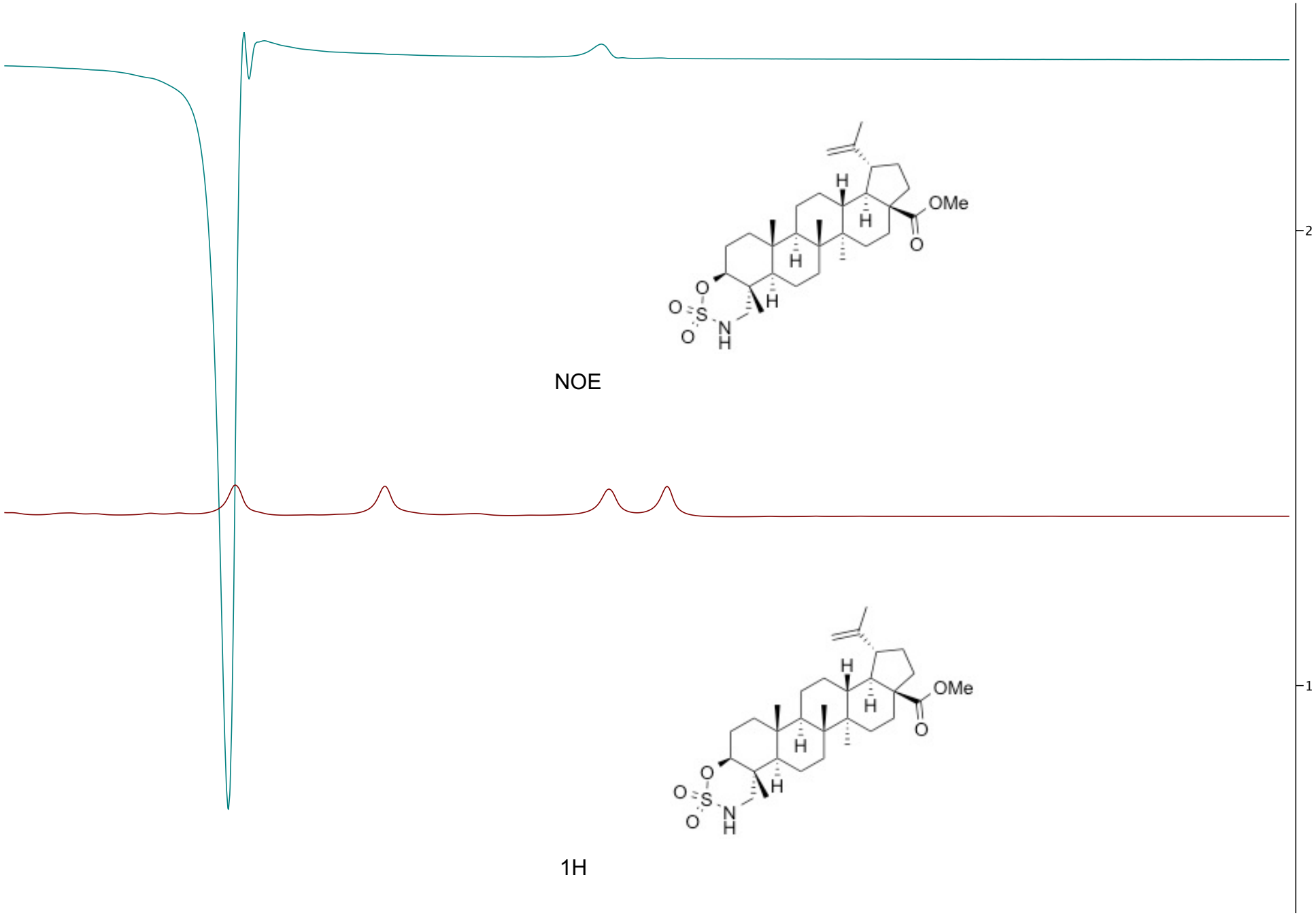
COSY

7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
f1 (ppm)


HSQC
OMe
f2 (ppm)
f1 (ppm)


HMBC
OMe
f2 (ppm)
f1 (ppm)


OMe
O
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NOE
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1.10
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1.06
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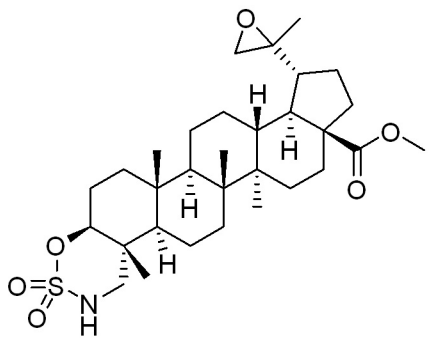
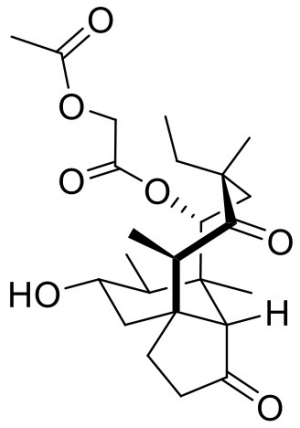
1.02
1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
0.82
0.80
0.78
0.76
f1 (ppm)

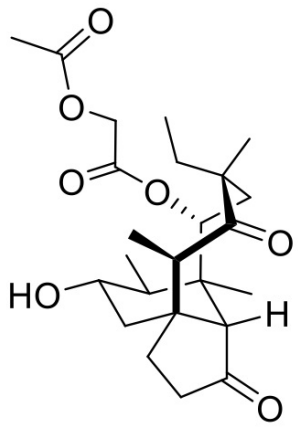
	Parameter	Value
1	Title	
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	46
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	4.6645
14	Acquisition Date	2015-01-29T13:10:54
15	Modification Date	2015-01-29T13:10:55
16	Spectrometer Frequency	499.69
17	Spectral Width	7024.9
18	Lowest Frequency	-1011.9
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536



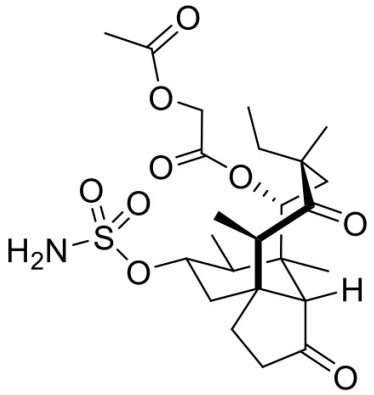
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	hcn
Number of Scans	32
Relaxation Delay	10.0000
Pulse Width	0.0000
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



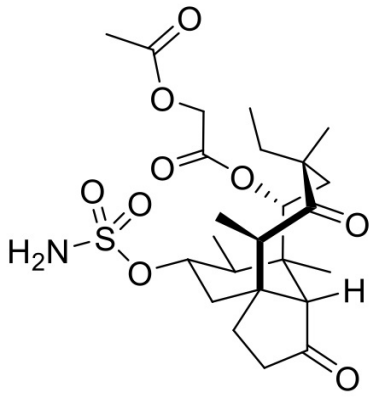
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	953
Relaxation Delay	1.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1272.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



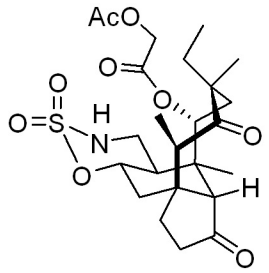
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	hcn
Number of Scans	16
Relaxation Delay	10.0000
Pulse Width	0.0000
Spectrometer Frequency	500.07
Spectral Width	8000.0
Lowest Frequency	-1510.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



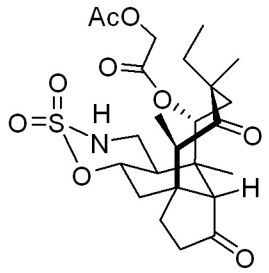
Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUADG
Number of Scans	1024
Relaxation Delay	2.0000
Pulse Width	0.0000
Spectrometer Frequency	125.60
Spectral Width	32000.0
Lowest Frequency	-2200.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	hcn
Number of Scans	8
Relaxation Delay	4.0000
Pulse Width	0.0000
Spectrometer Frequency	500.07
Spectral Width	3846.9
Lowest Frequency	-40.3
Nucleus	1H
Acquired Size	15757
Spectral Size	65536



Parameter	Value
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Probe	QUAD
Number of Scans	909
Relaxation Delay	2.0000
Pulse Width	0.0000
Spectrometer Frequency	125.66
Spectral Width	30165.9
Lowest Frequency	-1275.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

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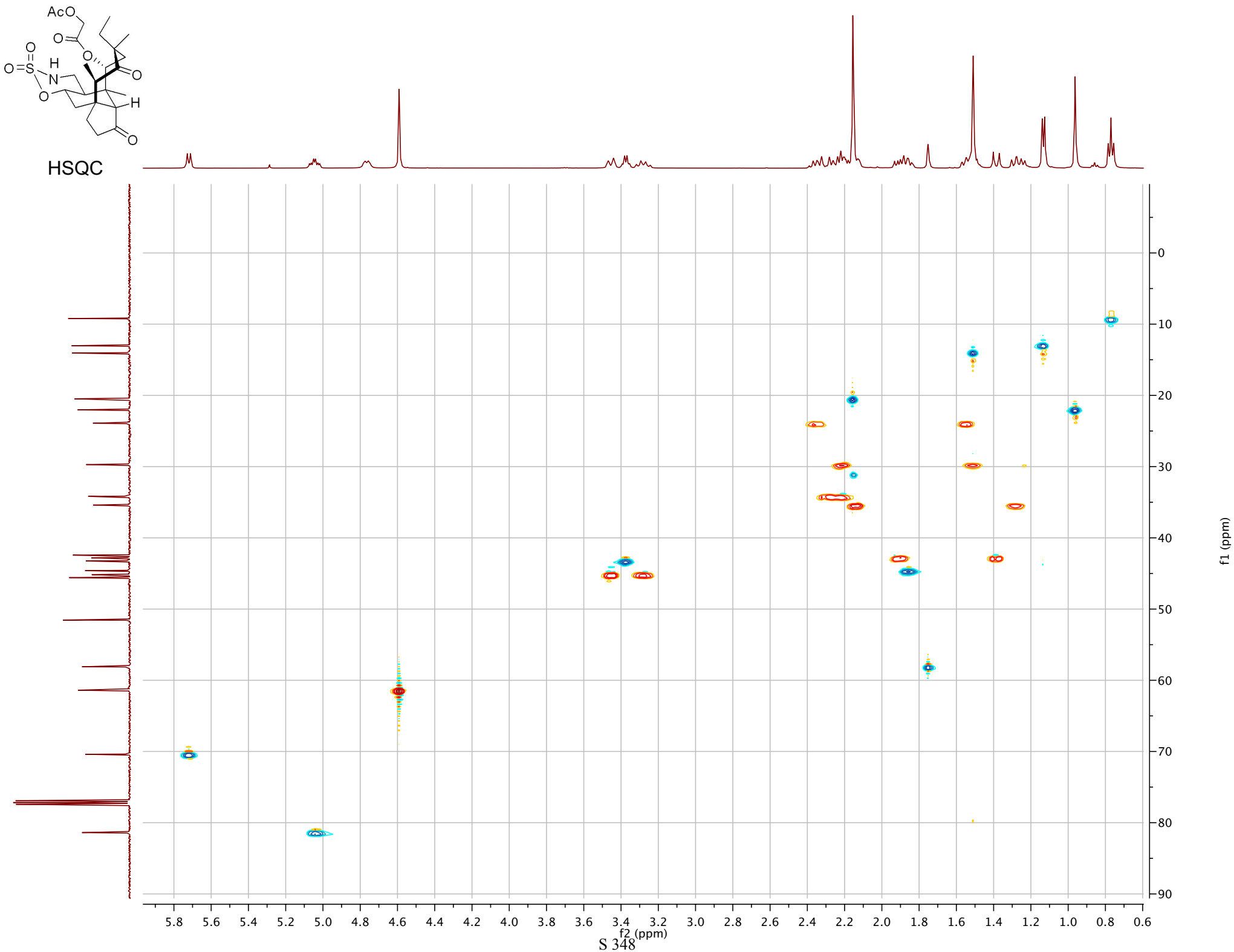
COSY
f2 (ppm)
f1 (ppm)


AcO
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HSQC
f2 (ppm)
f1 (ppm)


AcO
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O=S
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H
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HMBC
f2 (ppm)
f1 (ppm)