Ligand-controlled, tunable silver-catalyzed C–H amination

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Table of Contents

I. General Information .................................................................................................................S1-2
II. Synthesis of Sulfamate Substrates .........................................................................................S1-3
III. Investigation of Counteranion Effects .................................................................................S1-27
IV. Synthesis of C–H insertion products ...................................................................................S1-27
V. Probing the Mechanism of Silver-Catalyzed Nitrene Transfer ........................................S1-49
VI. Hammett Plot .....................................................................................................................S1-60
VII. References .........................................................................................................................S1-61
I. General Information

All glassware was either oven-dried overnight at 130 °C or flame-dried under a stream of dry nitrogen prior to use. Unless otherwise specified, reagents were used as obtained from the vendor without further purification. Tetrahydrofuran and diethyl ether were freshly distilled from purple Na/benzophenone ketyl. Dichloromethane, acetonitrile and toluene were dried over CaH₂ and freshly distilled prior to use. All other solvents were purified in accordance with “Purification of Laboratory Chemicals”. Air- and moisture-sensitive reactions were performed using standard Schlenk techniques under an atmosphere of nitrogen. Analytical thin layer chromatography (TLC) was performed utilizing pre-coated silica gel 60 F₂₅₄ plates containing a fluorescent indicator, while preparative chromatography was performed using SilicaFlash P60 silica gel (230-400 mesh) via Still’s method. Unless otherwise stated, the mobile phases for column chromatography were mixtures of hexanes/ethyl acetate. Columns were typically run using a gradient method, beginning with 100% hexanes and gradually increasing the polarity using ethyl acetate. Various stains were used to visualize reaction products, including p-anisaldehyde, KMnO₄, ceric ammonium molybdate (CAM stain) and iodine powder.

¹H NMR and ¹³C NMR spectra were obtained using Bruker-300, Varian-300, Varian Inova-500, or Varian Unity-500 spectrometers. For ¹H NMR, chemical shifts are reported relative to residual protiated solvent peaks (δ 7.26, 2.49, 7.15 and 7.09 ppm for CDCl₃, (CD₃)₂SO, C₆D₆ and CD₃C₆D₅ respectively). ¹³C NMR spectra were measured at either 125 MHz or 75 MHz on the same instruments noted above for recording ¹H NMR spectra. Chemical shifts were again reported in accordance to residual protiated solvent peaks (δ 77.2, 39.5, 128.0 and 137.9 ppm for CDCl₃, (CD₃)₂SO, C₆D₆, and CD₃C₆D₅, respectively). High-pressure liquid chromatography (HPLC) analyses were performed at 215 and 225 nm using a Shimadzu HPLC, Model LC-20AB.
Further details are given in Section VII. Accurate mass measurements were acquired at the University of Wisconsin, Madison using a Micromass LCT (electrospray ionization, time-of-flight analyzer or electron impact methods) or a Waters Micromass Autospec (electron impact, high sector, direct probe). The NMR and Mass Spectrometry facilities are funded by the NSF (CHE-9974839, CHE-9304546, CHE-9208463, CHE-9629688) and the University of Wisconsin, as well as the NIH (RR08389-01).

II. Synthesis of Sulfamate Substrates

General procedure for synthesis of alcohols

A 250 mL round bottom flask with condenser was charged with 30 mL of diethyl ether and 0.97 g (40 mmol, 2 equiv) of Mg turnings. Alkyl bromide (40 mmol, 2 equiv) was added dropwise so as to keep a constant reflux, and the mixture was allowed to stir for 30 min. The reaction mixture was cooled to -78 °C in a dry ice/acetone bath and aldehyde (20 mmol, 1 equiv) in 30 mL of was added slowly via cannula. The reaction mixture was stirred 1 h at -78 °C, and was then quenched with gradual addition of aqueous 0.25 M HCl (60 mL). The layers were separated and the aqueous layer was extracted with two 30 mL portions of diethyl ether. The organic layers were combined, dried over MgSO₄, and concentrated in vacuo. The crude residue was purified via column chromatography with an ethyl acetate/hexane gradient to give the pure alcohol product.

Precursor for Compound 1: 5-methyl-1-phenylhexan-3-ol. The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments.
resulting colorless oil was obtained in 80% yield from 3-phenylpropionaldehyde. Characterization data was consistent with a previously reported synthesis.\textsuperscript{3} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.35 – 7.23 (m, 2H), 7.23 – 7.13 (m, 3H), 3.71 (tt, \(J = 8.8, 4.7\) Hz, 1H), 2.79 (ddd, \(J = 13.8, 9.9, 5.7\) Hz, 1H), 2.67 (ddd, \(J = 13.7, 9.8, 6.4\) Hz, 1H), 1.85 – 1.64 (m, 3H), 1.41 (ddd, \(J = 14.1, 8.8, 5.4\) Hz, 1H), 1.36 (s, 1H), 1.28 (ddd, \(J = 13.5, 8.8, 4.2\) Hz, 1H), 0.91 (t, \(J = 7.1\) Hz, 6H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 142.2, 128.4, 125.8, 69.5, 46.8, 39.7, 32.1, 24.6, 23.5, 22.1.

Precursor for Compound 13: 1-cyclopropyl-4-phenylbutan-2-ol. The alcohol was prepared from 1-phenyl-5-hexen-3-ol, which had been synthesized according to a previous procedure.\textsuperscript{4} A Schlenk flask was charged with 2.6 g (40 mmol, 3.1 equiv.) zinc powder and 3.9 g (40 mmol, 3.1 equiv.) copper(I) chloride. The flask was fitted with a condenser, sealed with a rubber septum, and flushed with N\textsubscript{2} to create an inert atmosphere. Diethyl ether (20 mL) was added and the suspension was stirred 30 min at reflux. 1-phenyl-5-hexen-3-ol (2.4 g, 13 mmol, 1 equiv.) was added, followed by 11 g (40 mmol, 3.1 equiv.) diiodomethane. The mixture was left to stir at reflux overnight. The mixture was filtered through Celite and concentrated \textit{in vacuo} to yield a dark oil. The product was purified by column chromatography using a 0\rightarrow30\% gradient of EtOAc in hexanes with 5\% increments. The resulting colorless oil was obtained in 42\% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.29 (t, \(J = 7.4\) Hz, 2H), 7.24 – 7.16 (m, 3H), 3.75 (tq, \(J = 8.3, 4.3\) Hz, 1H), 2.81 (ddd, \(J = 13.7, 9.7, 5.8\) Hz, 1H), 2.68 (ddd, \(J = 13.8, 9.7, 6.7\) Hz, 1H), 1.89 – 1.72 (m, 2H), 1.67 (d, \(J = 4.1\) Hz, 1H), 1.47 – 1.33 (m, 2H), 0.81 – 0.68 (m, 1H), 0.48 (tddd, \(J = 13.0, 6.5, 4.3\) Hz, 6H).
9.4, 8.2, 4.5 Hz, 2H), 0.13 (dtd, J = 9.4, 4.8, 3.4 Hz, 1H), 0.09 – 0.01 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.2, 128.4, 128.4, 125.8, 71.9, 42.3, 38.8, 32.1, 7.4, 4.5, 3.7. HRMS (EI) m/z calculated for C$_{13}$H$_{18}$O [M]$^+$ 190.1353, found 190.1357.

Precursor for Compound 14: 1-cyclobutyl-4-phenylbutan-2-ol. The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 73% yield from 3-phenylpropanaldehyde. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.34 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 3.59 (dp, J = 7.8, 4.0 Hz, 1H), 2.78 (ddd, J = 13.7, 9.9, 5.8 Hz, 1H), 2.65 (ddd, J = 13.7, 9.8, 6.6 Hz, 1H), 2.44 (hept, J = 7.9 Hz, 1H), 2.06 (dtd, J = 11.1, 8.0, 2.8 Hz, 2H), 1.93 – 1.61 (m, 6H), 1.61 – 1.56 (m, 2H), 1.31 (s, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.2, 128.4, 128.4, 125.8, 70.2, 44.8, 39.2, 32.9, 32.1, 29.0, 28.6, 18.9. HRMS (EI) m/z calculated for C$_{14}$H$_{18}$ [M-H$_2$O]$^+$ 186.1404, found 186.1407.

Precursor for Compound 15: 5-ethyl-1-phenylheptan-3-ol. The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 49% yield from 3-phenylpropanaldehyde. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.16 (m, 3H), 3.72 (tt, J = 7.9, 4.1 Hz, 1H), 2.80
(ddd, \(J = 13.8, 10.1, 5.7\) Hz, 1H), 2.67 (ddd, \(J = 13.7, 9.9, 6.4\) Hz, 1H), 1.86 – 1.66 (m, 2H), 1.45 – 1.21 (m, 8H), 0.85 (t, \(J = 7.4\) Hz, 3H), 0.85 (t, \(J = 7.4\) Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 142.2, 128.4, 125.8, 69.5, 41.4, 39.8, 36.7, 32.1, 25.9, 25.0, 10.8, 10.5. HRMS (EI) \(m/z\) calculated for C\(_{13}\)H\(_{24}\)O [M]\(^+\) 220.1822, found 220.1824.

Precursor to Compound 16: 1-cyclopentyl-4-phenylbutan-2-ol. The product was purified by column chromatography using a 0\(\rightarrow\)30\% gradient of EtOAc in hexanes with 5\% increments. The resulting colorless oil was obtained in 49\% yield from cyclohexylacetaldehyde. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) = 7.28 (t, \(J = 7.5\) Hz, 2H), 7.22 – 7.16 (m, 3H), 3.67 (tt, \(J = 8.3, 4.3\) Hz, 1H), 2.80 (ddd, \(J = 13.8, 10.0, 5.7\) Hz 1H), 2.67 (ddd, \(J = 13.7, 9.9, 6.4\) Hz 1H), 1.92 (tdd, \(J = 15.7, 8.6, 6.8\) Hz 1H), 1.85 – 1.69 (m, 4H), 1.60 (ddt, \(J = 13.5, 10.3, 4.5\) Hz 2H), 1.57 – 1.49 (m, 3H), 1.45 (ddd, \(J = 13.4, 8.4, 4.5\) Hz, 1H), 1.40 – 1.32 (m, 1H), 1.16 – 1.01 (m, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 142.2, 128.4, 128.4, 125.8, 70.8, 44.0, 39.5, 36.8, 33.2, 32.6, 32.1, 25.1, 24.9. HRMS (EI) \(m/z\) calculated for C\(_{13}\)H\(_{22}\)O [M]\(^+\) 218.1666, found 218.1667.

Precursor to Compound 17: 1-cyclohexyl-4-phenylbutan-2-ol. The product was purified by column chromatography using a 0\(\rightarrow\)30\% gradient of EtOAc in hexanes with 5\% increments. The resulting colorless oil was obtained in 77\% yield from 3-phenylpropionaldehyde. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.28 (t, \(J = 7.6\) Hz, 2H), 7.22 – 7.12 (m, 3H), 3.74 (tt, \(J = 8.3, 4.3\) Hz, 1H), 2.78
(ddd, J = 13.7, 9.9, 5.8 Hz, 1H), 2.66 (ddd, J = 13.7, 9.8, 6.5 Hz, 1H), 1.81 – 1.61 (m, 7H), 1.40 (ddddd, J = 27.3, 13.8, 8.5, 4.3 Hz, 3H), 1.30 (ddd, J = 13.6, 8.6, 4.2 Hz, 1H), 1.23 (ddt, J = 12.4, 9.2, 3.2 Hz, 2H), 1.20 – 1.08 (m, 1H), 0.99 – 0.89 (m, 1H), 0.84 (td, J = 12.4, 10.8, 3.3 Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.2, 128.4, 125.8, 68.8, 45.5, 39.7, 34.2, 34.1, 32.9, 32.1, 26.6, 26.4, 26.2. HRMS (EI) m/z calculated for C$_{16}$H$_{24}$O [M]$^+$ 232.1822, found 232.1813.

Precursor to Compound 18: 6-methyl-1-phenyl-5-(propan-2-yl)heptan-3-ol. The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was isolated in 48% yield from 3-isopropyl-4-methylpentanal (synthesized according to literature procedure).$^5$ $^1$H NMR (500 MHz, CDCl$_3$) δ 7.28 (dd, J = 8.0, 7.1 Hz, 2H), 7.23 – 7.16 (m, 3H), 3.65 (tdd, J = 8.4, 4.9, 3.8 Hz, 1H), 2.83 (ddd, J = 13.7, 10.2, 5.4 Hz, 1H), 2.67 (ddd, J = 13.7, 10.1, 6.4 Hz, 1H), 1.83 (dddd, J = 14.0, 10.3, 6.4, 3.8 Hz, 1H), 1.79 – 1.66 (m, 3H), 1.43 – 1.31 (m, 2H), 1.10 (dq, J = 6.4, 4.6 Hz, 1H), 0.89 (d, J = 6.9 Hz, 3H), 0.87 (d, J = 6.9 Hz, 3H), 0.85 (d, J = 6.9 Hz, 3H), 0.82 (d, J = 6.8 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.2, 128.4, 125.8, 71.4, 46.0, 39.7, 36.0, 32.3, 29.7, 29.0, 21.8, 21.2, 19.7, 19.0. HRMS (EI) m/z calculated for C$_{17}$H$_{28}$O [M]$^+$ 248.2140, found 248.2137.

Precursor to Compound 19: 2,8-dimethylnon-7-en-4-ol. The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The
resulting colorless oil was obtained in 78% yield from isovaleraldehyde. $^1$H NMR (500 MHz, CDCl$_3$) δ 5.20 – 5.08 (m, 1H), 3.68 (dq, $J = 8.1$, 4.0 Hz, 1H), 2.10 (dtt, $J = 22.0$, 14.7, 7.4 Hz, 2H), 1.85 – 1.72 (m, 1H), 1.70 (s, 3H), 1.63 (s, 3H), 1.54 – 1.47 (m, 1H), 1.47 – 1.42 (m, 1H), 1.42 – 1.37 (m, 1H), 1.36 (d, $J = 5.2$ Hz, 1H), 1.23 (ddd, $J = 13.7$, 8.8, 4.1 Hz, 1H), 0.92 (t, $J = 6.5$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 132.0, 124.2, 69.8, 46.8, 37.9, 25.7, 24.6, 24.4, 23.5, 22.1, 17.7. HRMS (EI) $m/z$ calculated for C$_{11}$H$_{22}$O [M]$^+$ 170.1666, found 170.1662.

Precursor to Compound 20. 4-Decyn-1-ol was prepared from tert-butyl-dimethyl-pent-4-ynylosilsilane, which was synthesized according to a previously reported procedure. An oven-dried, 500 mL roundbottom flask was purged with N$_2$ and allowed to cool to rt. The flask was then charged with 5 ml (21.2 mmol, 1 equiv) of tert-butyl-dimethyl-pent-4-ynylosilsilane and 106 ml of THF. The flask was then cooled to -78 ºC using a dry ice/acetone bath and a CC-100 ThermoNESLAB chiller. A solution of 2.27 M $n$-butyllithium in hexanes (11.2 mL, 25.4 mmol, 1.2 equiv) was injected dropwise, followed by 4.15 mL (31.8 mmol, 1.5 equiv) of iodopentane and 8.4 mL (70.0 mmol, 3.3 equiv) of 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone. The reaction was stirred for 24 h and then quenched with 100 mL of saturated NH$_4$Cl. The aqueous phase was extracted 3x with 100 mL portions of ethyl acetate, the organic phases combined and concentrated under reduced pressure. The residue was diluted with 92 mL of THF and treated with 27.6 ml of 1 M Bu$_4$NF in THF. After 6 h, the reaction mixture was quenched with 100 mL of H$_2$O. The aqueous phase was extracted 3x with 50 mL portions of CH$_2$Cl$_2$, the organic phases combined and concentrated under reduced pressure. The product was purified by column
chromatography using a 0-25% gradient of ethyl acetate in hexanes in 5% increments to afford a colorless oil (1.94 g, 55%). $^1$H NMR (400 MHz, CDCl$_3$) δ 3.76 (t, $J = 6.1$ Hz, 2H), 2.28 (tt, $J = 6.9$, 2.4 Hz, 2H), 2.14 (tt, $J = 7.2$, 2.4 Hz, 2H), 1.79 – 1.68 (m, 3H), 1.55 – 1.43 (m, 2H), 1.34 (ddt, $J = 11.5$, 8.6, 4.3 Hz, 4H), 0.90 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 81.4, 79.5, 62.3, 31.8, 31.3, 29.0, 22.4, 18.9, 15.7, 14.2. The spectral data is consistent with previously reported data.\(^7\)

A 250 mL, 2-neck roundbottom flask was purged with nitrogen. The flask was charged with 2.71 g (17.5 mmol, 1.0 equiv) of 4-decyn-1-ol, 11.2 mL (157.8 mmol, 9.0 equiv) of dry dimethylsulfoxide and 17 mL (122 mmol, 7.0 equiv) of triethylamine. The mixture was cooled to 0 ºC, and 5.57 g (35 mmol, 2.0 equiv) of pyridine*SO$_3$ complex was added portionwise. After 5 h, the reaction was quenched with 20 mL of 1 M HCl solution. The aqueous phase was extracted 3x with 20 mL portions of CH$_2$Cl$_2$. The organic phases were combined, dried over sodium sulfate and concentrated under reduced pressure. The product was purified by column chromatography using a 0-5% gradient of EtOAc in hexane in 1% increments to afford a colorless, pungent liquid. This material was then reacted with the appropriate Grignard reagent to provide the secondary alcohol. The product was purified by column chromatography using a 0-14% gradient of EtOAc in hexanes with 2% increments. The resulting colorless liquid was obtained in 46% yield (1.70 g). $^1$H NMR (500 MHz, CDCl$_3$) δ 3.84 (tq, $J = 8.5$, 4.2 Hz, 1H), 2.37 – 2.24 (m, 2H), 2.14 (tt, $J = 7.1$, 2.4 Hz, 2H), 1.83 – 1.76 (m, 1H), 1.75 (s, 1H), 1.64 (dtd, $J = 14.3$, 7.2, 3.5 Hz, 1H), 1.55 (ddd, $J = 13.7$, 6.9, 1.9 Hz, 1H), 1.52 – 1.46 (m, 2H), 1.42 (ddd, $J = 14.1$, 8.8, 5.5 Hz, 1H), 1.38 – 1.27 (m, 4H), 1.23 (ddd, $J = 13.5$, 8.7, 4.3 Hz, 1H), 0.93 (d, $J = 3.0$ Hz, 3H), 0.92 (d, $J = 2.9$ Hz, 3H), 0.89 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ
HRMS (EI) m/z calculated for C_{14}H_{26}O [M]^+ 210.1979, found 210.1979.

Precursor to Compound 21: 2-Methyloctan-4-ol. Prepared according to a previous synthesis. The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 60% yield from valeraldehyde. Characterization data was consistent with the previously reported synthesis.

Precursor to Compound 22: 1-Cyclohexyl-4-methylpentan-2-ol. The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 78% yield from isovaleraldehyde. Characterization data was consistent with the previously reported synthesis.

Precursor to Compound 23: 2-Methyl-6-phenylheptan-4-ol. The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The
resulting colorless oil was obtained in as a 1.2:1 mixture of diastereomers in 64% yield from 3-phenylbutyraldehyde. $^1$H NMR (500 MHz, CDCl$_3$): δ 7.30 (t, $J = 7.6$ Hz, 2H), 7.24 – 7.16 (m, 3H), 3.69 (tt, $J = 8.5$, 4.3 Hz, 0.45H), 3.44 – 3.38 (m, 0.55H), 3.00 (dqd, $J = 10.1$, 7.0, 4.8 Hz, 0.55H), 2.91 (h, $J = 7.1$ Hz, 0.45H), 1.79 – 1.61 (m, 3H), 1.35 (dddd, $J = 16.9$, 14.1, 8.6, 5.5 Hz, 1H), 1.27 (dd, $J = 7.0$, 4.6 Hz, 3H), 1.19 (ddd, $J = 13.5$, 8.3, 4.7 Hz, 1H), 0.91 (d, $J = 6.7$ Hz, 1H), 0.86 (d, $J = 6.6$ Hz, 1H), 0.81 (ddd, $J = 6.6$, 1.6 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 147.7, 146.9, 128.7, 128.6, 127.2, 127.0, 126.3, 126.2, 68.5, 68.0, 47.5, 47.2, 47.0, 46.3, 36.9, 36.6, 29.9, 24.8, 24.7, 23.7, 23.5, 23.3, 22.4, 22.2, 22.1. HRMS (EI) m/z calculated for C$_{14}$H$_{20}$ [M-H$_2$O]$^+$ 188.1560, found 188.1566.

**Precursor to Compound 24: 5-Methyl-1-(2-methylphenyl)hexan-3-ol.** The product was purified by column chromatography using a 0→25% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 80% yield from 3-(2-methylphenyl)propanal. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.21 – 7.07 (m, 4H), 3.78 – 3.72 (m, 1H), 2.79 (ddd, $J = 13.8$, 10.6, 5.5 Hz, 1H), 2.65 (ddd, $J = 13.8$, 10.4, 6.0 Hz, 1H), 2.32 (s, 3H), 1.83 – 1.62 (m, 3H), 1.43 (ddd, $J = 14.0$, 8.8, 5.4 Hz, 1H), 1.30 (ddd, $J = 13.8$, 8.8, 4.2 Hz, 1H), 0.92 (dd, $J = 6.7$, 4.6 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.6, 136.0, 130.4, 128.9, 126.1, 69.9, 46.9, 38.6, 29.6, 24.8, 22.3, 19.4. HRMS (EI) m/z calculated for C$_{14}$H$_{22}$O [M]$^+$ 206.1666, found 206.1663.
Precursor to Compound 25: 1-(4-Methoxyphenyl)-5-methylhexan-3-ol. The product was purified by column chromatography using a 10→25% EtOAc in hexanes using 5% increments. The resulting product was isolated in 48% yield from 3-(4-methoxyphenyl)propanal. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.12 (d, $J = 8.7$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 3H), 3.70 (tt, $J = 8.4$, 4.4 Hz, 1H), 2.79 – 2.56 (m, 2H), 1.84 – 1.65 (m, 3H), 1.47 – 1.35 (m, 1H), 1.33 – 1.22 (m, 2H), 0.91 (dd, $J = 6.6$, 4.6 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 157.7, 134.2, 129.3, 129.3, 113.8, 113.8, 76.8, 69.5, 55.3, 46.8, 39.9, 31.1, 30.9, 24.6, 23.5, 22.1. HRMS (ESI) $m/z$ calculated for C$_{14}$H$_{22}$O$_2$ [M + NH$_4$]$^+$ 240.1959, found 240.1966.

Precursor to Compound 26: 5-Methyl-1-(4-methylphenyl)hexan-3-ol. The product was purified by column chromatography using a 10→25% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was isolated in 50% yield from 3-(4-methylphenyl)propanal. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.09 (s, 4H), 3.71 (tt, $J = 8.4$, 4.2 Hz, 1H), 2.75 (ddd, $J = 13.7$, 9.8, 5.9 Hz, 1H), 2.63 (dd, $J = 13.7$, 9.7, 6.5 Hz, 1H), 2.32 (s, 3H), 1.85 – 1.63 (m, 3H), 1.41 (ddd, $J = 14.1$, 8.7, 5.4 Hz, 1H), 1.31 – 1.24 (m, 2H), 0.91 (t, $J = 6.4$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 139.2, 135.4, 129.2, 128.4, 69.7, 46.9, 39.9, 31.8, 31.1, 24.8, 23.6, 22.3, 21.1. HRMS (ESI) $m/z$ calculated for C$_{14}$H$_{20}$ [M-H$_2$O]$^+$ 188.1560, found 188.1561.
Precursor to Compound 27: 1-(4-Bromophenyl)-5-methylhexan-3-ol. The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 6% increments. The resulting colorless oil was isolated in 73% yield from 3-(4-bromophenyl)propanal. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J = 8.3$ Hz, 2H), 7.08 (d, $J = 8.3$ Hz, 2H), 3.72 – 3.64 (m, 1H), 2.75 (ddd, $J = 13.8$, 9.9, 5.7 Hz, 1H), 2.64 (tdd, $J = 13.8$, 9.5, 7.0 Hz, 1H), 1.81 – 1.64 (m, 3H), 1.45 – 1.38 (m, 1H), 1.27 (ddd, $J = 13.9$, 8.7, 4.2 Hz, 1H), 0.91 (dd, $J = 8.4$, 6.6 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 141.3, 131.6, 130.3, 119.6, 69.4, 47.0, 39.6, 31.6, 24.8, 23.6, 22.2. HRMS (ESI) $m/z$ calculated for C$_{13}$H$_{18}$BrO [M-H]$^+$ 269.0536, found 269.0535.

![Precursor to Compound 27: 1-(4-Bromophenyl)-5-methylhexan-3-ol](image)

Precursor to Compound 28: 5-Methyl-1-[4-(trifluoromethyl)phenyl]hexan-3-ol. The product was purified by column chromatography using a 0→25% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was isolated in 69% yield from 3-[4-(trifluoromethyl)phenyl]propanal. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 7.9$ Hz, 2H), 3.71 (dp, $J = 8.4$, 3.8 Hz, 1H), 2.87 (ddd, $J = 13.8$, 10.0, 5.6 Hz, 1H), 2.74 (ddd, $J = 13.8$, 9.9, 6.5 Hz, 1H), 1.83 – 1.66 (m, 3H), 1.43 (ddd, $J = 14.0$, 8.8, 5.4 Hz, 1H), 1.34 – 1.22 (m, 2H), 0.92 (dd, $J = 8.3$, 6.6 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 146.6, 128.9, 128.3 (q, $J = 32.4$ Hz), 125.4 (q, $J = 3.6$ Hz), 124.5 (q, $J = 271.8$ Hz), 69.4, 47.1, 39.5, 32.0, 24.8, 23.6, 22.2. HRMS (EI) $m/z$ calculated for C$_{14}$H$_{17}$F$_3$ [M-H$_2$O]$^+$ 242.1277, found 242.1273.

![Precursor to Compound 28: 5-Methyl-1-[4-(trifluoromethyl)phenyl]hexan-3-ol](image)
Precursor for Compound 29: 1-(4-Methoxyphenyl)-5-phenylpentan-3-ol. The product was purified by column chromatography using a 0→25% gradient of EtOAc in hexanes with 5% increments. The resulting white solid was isolated in 59% yield from 3-(4-methoxyphenyl)propanal. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.31 – 7.26 (m, 2H), 7.19 (dt, $J = 6.0$, 1.7 Hz, 3H), 7.10 (d, $J = 8.5$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 3H), 3.66 (tt, $J = 8.2$, 4.4 Hz, 1H), 2.82 – 2.59 (m, 4H), 1.87 – 1.70 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 157.9, 142.2, 134.2, 129.4, 128.6, 128.6, 127.4, 126.0, 114.0, 114.0, 71.0, 55.4, 39.6, 39.4, 32.2, 31.3. HRMS (EI) m/z calculated for C$_{18}$H$_{22}$O$_2$ [M]$^+$ 270.1615, found 270.1626.

![Diagram of 1-(4-Methoxyphenyl)-5-phenylpentan-3-ol]

Precursor for Compound 30: 1-(4-Methylphenyl)-5-phenylpentan-3-ol. The product was purified by column chromatography using a 0→25% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was isolated in 61% yield from 3-(4-methylphenyl)propanal. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.28 (dd, $J = 8.2$, 7.0 Hz, 2H), 7.21 – 7.17 (m, 3H), 7.09 (d, $J = 1.6$ Hz, 4H), 3.73 – 3.60 (m, 1H), 2.77 (dddd, $J = 20.4$, 13.7, 9.6, 6.0 Hz, 2H), 2.65 (dddd, $J = 16.2$, 13.7, 9.6, 6.6 Hz, 2H), 2.32 (s, 3H), 1.87 – 1.71 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.2, 139.1, 135.5, 129.3, 128.6, 128.6, 128.4, 125.9, 71.0, 39.5, 39.4, 32.2, 31.8, 21.1. HRMS (ESI) m/z calculated for C$_{18}$H$_{26}$NO [M+NH$_4$]$^+$ 272.2009, found 272.2017.

![Diagram of 1-(4-Methylphenyl)-5-phenylpentan-3-ol]
Precursor for Compound 31: 1-(4-Bromophenyl)-5-phenylpentan-3-ol. The product was purified by column chromatography using a 0→25% gradient of EtOAc in hexanes with 5% increments. The resulting white solid was isolated in 80% yield from 3-(4-bromophenyl)propanal. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.39 (d, $J = 8.4$ Hz, 2H), 7.31 – 7.26 (m, 2H), 7.19 (tt, $J = 7.9, 1.4$ Hz, 3H), 7.05 (d, $J = 8.3$ Hz, 2H), 3.68 – 3.59 (m, 1H), 2.76 (dddd, $J = 19.5, 13.7, 9.4, 6.0$ Hz, 2H), 2.65 (dddd, $J = 22.9, 13.8, 9.4, 6.9$ Hz, 2H), 1.86 – 1.69 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.0, 141.1, 131.6, 130.3, 128.6, 128.5, 126.1, 119.7, 70.7, 39.4, 39.2, 32.2, 31.6. HRMS (EI) calculated for C$_{17}$H$_{17}$Br [M-H$_2$O]$^+$ 300.0509, found 300.0518.

![Chemical structure of precursor for Compound 31 (1-(4-Bromophenyl)-5-phenylpentan-3-ol)](image)

Precursor for Compound 32: 1-Phenyl-5-[4-(trifluoromethyl)phenyl]pentan-3-ol. The product was purified by column chromatography using a 0→25% gradient of EtOAc in hexanes with 5% increments. The resulting white solid was isolated in 53% yield from 3-[4-(trifluoromethyl)phenyl]propanal. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.53 (d, $J = 8.0$ Hz, 2H), 7.31 – 7.26 (m, 4H), 7.23 – 7.15 (m, 3H), 3.65 (tq, $J = 8.5, 4.5$ Hz, 1H), 2.91 – 2.62 (m, 4H), 1.88 – 1.73 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 146.4, 141.9, 128.9, 128.6, 128.5, 126.1, 125.5 (q, $J = 3.6$ Hz), 124.5 (q, $J = 271.4$ Hz), 70.7, 39.4, 39.0, 32.2, 32.0. HRMS (EI) m/z calculated for C$_{18}$H$_{17}$F$_3$ [M-H$_2$O]$^+$ 290.1277, found 290.1267.

General procedure for the synthesis of sulfamates. Formic acid (0.49 mL, 13 mmol, 2.5 equiv) was added dropwise to chlorosulfonyl isocyanate (3.0 equiv) cooled in an ice bath with
vigorous stirring. Gas was evolved and the reaction mixture solidified within 5 min. To the resulting solid was added 10.4 mL of CH₃CN and the clear solution stirred in an ice bath for 30 min, allowed to warm to rt and stirred for an additional 4 h. The flask was placed in an ice bath and cooled to 0 °C. To the cold solution was added 5.2 mmol alcohol substrate in 8.7 mL of dimethylacetamide. The solution was warmed to rt and the mixture was stirred for 1 h. The reaction was quenched by the addition of 10 mL of H₂O and the aqueous layer was extracted with 3 x 50 mL portions of Et₂O. The combined organic layers were washed with 5 x 20 mL portions of H₂O, 1 x 25 mL saturated aqueous sodium chloride, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude products were purified by silica gel column chromatography using a hexane/EtOAc gradient.

Compounds 29, 30, and 32 were synthesized according to previously reported procedures.⁹

![Chemical structure of Compound 1]

**Compound 1.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting yellow oil was obtained in 76% yield from the corresponding alcohol. ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.23 (m, 2H), 7.19 (d, J = 7.3 Hz, 3H), 4.91 (bs, 2H), 4.69 (dq, J = 7.0, 5.6 Hz, 1H), 2.83 – 2.63 (m, 2H), 2.15 – 1.93 (m, 2H), 1.82 – 1.65 (m, 2H), 1.49 (hept, J = 5.6 Hz, 1H), 0.92 (dd, J = 9.2, 6.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 141.3, 128.6, 128.5, 126.2, 83.5, 43.3, 36.1, 31.1, 24.5, 22.8, 22.6. HRMS (ESI) m/z calculated for C₁₃H₂₅N₂O₃S [M+NH₄]⁺ 289.1581, found 289.1581.
**Compound 13.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting clear oil was obtained in 25% yield from the corresponding alcohol. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.29 (td, $J = 7.1, 1.6$ Hz, 2H), 7.23 – 7.16 (m, 3H), 4.89 (s, 2H), 4.70 (dddd, $J = 6.4$, 5.9 Hz, 1H), 2.78 (dd, $J = 13.8$, 9.7, 6.9 Hz, 1H), 2.78 (ddd, $J = 14.2$, 9.7, 6.2 Hz, 1H), 2.17 – 2.06 (m, 2H), 1.76 – 1.62 (m, 2H), 0.76 (ddd, $J = 15.1$, 10.1, 5.1, 2.3 Hz, 1H), 0.50 (dq, $J = 8.0$, 1.2 Hz, 2H), 0.12 (qdd, $J = 11.3$, 4.8, 2.0 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.1, 128.5, 128.4, 128.4, 126.1, 84.9, 38.9, 35.6, 31.3, 6.8, 4.6, 4.5. HRMS (ESI) $m/z$ calculated for C$_{13}$H$_{23}$N$_2$O$_3$S [M+NH$_4$]$^+$ 287.1424, found 287.1414.

**Compound 14.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting clear oil was obtained in 27% yield from the corresponding alcohol. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.29 (dd, $J = 8.2$, 7.0 Hz, 2H), 7.20 (td, $J = 5.8$, 5.4, 2.4 Hz, 3H), 4.59 (s, 1H), 4.57 (p, $J = 6.0$ Hz, 2H), 2.84 – 2.63 (m, 2H), 2.44 (hept, $J = 7.9$ Hz, 1H), 2.14 – 2.03 (m, 2H), 2.01 (td, $J = 8.0$, 5.8 Hz, 2H), 1.97 – 1.77 (m, 4H), 1.68 (dp, $J = 12.1$, 9.0 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.1, 128.5, 128.4, 126.1, 83.6, 41.1,
35.7, 32.1, 31.2, 28.8, 28.5, 18.7. HRMS (ESI) \( m/z \) calculated for \( \text{C}_{14}\text{H}_{25}\text{N}_{2}\text{O}_{3}\text{S} \) [M+NH₄]⁺ 301.1581, found 301.1581.

**Compound 15.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting clear oil was obtained in 27% yield from the corresponding alcohol. \(^1\)H NMR (500 MHz, CDCl₃) δ 7.33 – 7.24 (m, 2H), 7.24 – 7.16 (m, 3H), 4.73 (p, \( J = 6.2 \) Hz, 1H), 4.59 (s, 2H), 2.85 – 2.67 (m, 2H), 2.14 – 1.97 (m, 2H), 1.78 (dt, \( J = 14.4, 6.2 \) Hz, 1H), 1.58 (dt, \( J = 14.4, 6.3 \) Hz, 1H), 1.34 (dd, \( J = 19.1, 11.3 \) Hz, 1H), 0.86 (m, 6H). \(^{13}\)C NMR (126 MHz, CDCl₃) δ 141.1, 128.5, 128.4, 126.1, 83.6, 37.7, 36.5, 36.0, 31.1, 25.2, 10.5, 10.4. HRMS (ESI) \( m/z \) calculated for \( \text{C}_{15}\text{H}_{29}\text{N}_{2}\text{O}_{3}\text{S} \) [M+NH₄]⁺ 317.1894, found 317.1895.

**Compound 16.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting clear oil was obtained in 56% yield from the corresponding alcohol. \(^1\)H NMR (500 MHz, CDCl₃) δ 7.33 – 7.24 (m, 2H), 7.22 – 7.17 (m, 3H), 4.75 (s, 2H), 4.66 (p, \( J = 6.0 \) Hz, 1H), 2.80 – 2.69 (m, 2H), 2.13 – 1.98 (m, 2H), 1.95 – 1.80 (m, 3H), 1.80 – 1.66 (m, 2H), 1.66 – 1.57 (m, 2H), 1.56 – 1.47 (m, 2H), 1.11 (t, \( J = 12.2 \) Hz, 3H).
Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.1, 128.5, 128.4, 126.1, 84.4, 40.4, 36.1, 35.9, 32.9, 32.7, 31.1, 25.1, 24.9. HRMS (ESI) m/z calculated for C$_{15}$H$_{27}$N$_2$O$_3$S [M+NH$_4$]$^+$ 315.1737, found 315.1729.

![Compound 17](image1.png)

**Compound 17.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting clear oil was obtained in 71% yield from the corresponding alcohol. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.31 – 7.26 (m, 2H), 7.20 (d, $J = 7.0$ Hz, 3H), 4.79 – 4.70 (m, 3H), 2.82 – 2.65 (m, 2H), 2.04 (tq, $J = 6.7, 2$ Hz, 2H), 1.82 – 1.61 (m, 6H), 1.52 (ddd, $J = 13.9, 7.2, 6.0$ Hz, 1H), 1.41 (dt, $J = 14.1, 6.7, 3.3$ Hz, 1H), 1.28 – 1.09 (m, 3H), 1.00 – 0.84 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.1, 128.4, 126.1, 82.9, 41.8, 36.1, 33.8, 33.4, 33.2, 31.0, 26.4, 26.1. HRMS (ESI) m/z calculated for C$_{16}$H$_{29}$N$_2$O$_3$S [M+NH$_4$]$^+$ 329.1894, found 329.1889.

![Compound 18](image2.png)

**Compound 18.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting clear oil was obtained in 75% yield from the corresponding alcohol.$^1$H NMR (500 MHz, CDCl$_3$) δ 7.30 (td, $J = 7.3, 1.5$ Hz, 2H), 7.23 –
7.17 (m, 3H), 4.76 – 4.66 (m, 1H), 4.66 – 4.53 (m, 2H), 2.87 – 2.68 (m, 2H), 2.11 (dddd, J = 14.6, 9.8, 6.3, 4.9 Hz, 1H), 2.03 (ddt, J = 14.4, 9.8, 6.3 Hz, 1H), 1.82 – 1.70 (m, 3H), 1.54 (ddd, J = 14.7, 6.4, 5.4 Hz, 1H), 1.10 (p, J = 5.2 Hz, 1H), 0.90 (d, J = 2.8 Hz, 3H), 0.89 (d, J = 2.7 Hz, 3H), 0.86 (d, J = 1.7 Hz, 3H), 0.85 (d, J = 1.7 Hz, 3H). $^1$C NMR (126 MHz, CDCl$_3$) δ 141.2, 128.5, 128.4, 126.1, 85.4, 45.6, 36.0, 32.6, 31.1, 29.4, 29.1, 21.4, 19.3, 19.2. HRMS (ESI) $m/z$ calculated for C$_{17}$H$_{33}$N$_2$O$_3$S [M+NH$_4$]$^+$ 345.2207, found 345.2210.

**Compound 19.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting clear oil was obtained in 50% yield from the corresponding alcohol. $^1$H NMR (500 MHz, CDCl$_3$) δ 5.16 – 5.04 (m, 1H), 4.73 (s, 2H), 4.67 (dq, J = 7.5, 5.7 Hz, 1H), 2.08 (h, J = 7.8 Hz, 2H), 1.83 – 1.66 (m, 7H), 1.61 (d, J = 1.3 Hz, 3H), 1.46 (dd, J = 14.0, 7.7, 5.4 Hz, 1H), 0.94 (dd, J = 1.6, 1.9 Hz, 6H). $^1$C NMR (126 MHz, CDCl$_3$) δ 132.7, 123.0, 83.9, 43.1, 34.5, 25.7, 24.4, 23.4, 22.8, 22.4, 17.8. HRMS (ESI) $m/z$ calculated for C$_{11}$H$_{27}$N$_2$O$_3$S [M+NH$_4$]$^+$ 267.1737, found 267.1738.

![Compound 19](image1.png)

**Compound 20.** The general procedure for the formation of sulfamates was employed and the crude product was purified by column chromatography using a 0-20% gradient of EtOAc in hexanes with 5% increments. The resulting clear oil was obtained in 50% yield from the corresponding alcohol. $^1$H NMR (500 MHz, CDCl$_3$) δ 5.16 – 5.04 (m, 1H), 4.73 (s, 2H), 4.67 (dq, J = 7.5, 5.7 Hz, 1H), 2.08 (h, J = 7.8 Hz, 2H), 1.83 – 1.66 (m, 7H), 1.61 (d, J = 1.3 Hz, 3H), 1.46 (dd, J = 14.0, 7.7, 5.4 Hz, 1H), 0.94 (dd, J = 1.6, 1.9 Hz, 6H). $^1$C NMR (126 MHz, CDCl$_3$) δ 132.7, 123.0, 83.9, 43.1, 34.5, 25.7, 24.4, 23.4, 22.8, 22.4, 17.8. HRMS (ESI) $m/z$ calculated for C$_{11}$H$_{27}$N$_2$O$_3$S [M+NH$_4$]$^+$ 267.1737, found 267.1738.

![Compound 20](image2.png)
hexanes with 4% increments. The resulting clear liquid was obtained in 80% yield from the corresponding alcohol. $^1$H NMR (500 MHz, CDCl$_3$) δ 4.82 (p, $J = 6.3$ Hz, 1H), 4.78 (s, 2H), 2.32 (tt, $J = 7.0$, 2.4 Hz, 2H), 2.15 (tt, $J = 7.2$, 2.4 Hz, 2H), 1.87 (q, $J = 6.8$ Hz, 2H), 1.74 (ddt, $J = 13.6$, 10.9, 6.7 Hz, 2H), 1.55 – 1.43 (m, 3H), 1.39 – 1.28 (m, 4H), 0.97 (d, $J = 6.3$ Hz, 3H), 0.94 (d, $J = 6.3$ Hz, 3H), 0.90 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 82.7, 82.2, 78.5, 43.5, 33.5, 31.1, 28.7, 24.5, 22.6, 22.5, 22.2, 18.6, 15.0, 14.0. HRMS (ESI) m/z calculated for C$_{14}$H$_{27}$NO$_3$S [M+NH$_4$]$^+$ 307.2050, found 307.2047.

**Compound 21.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting clear oil was obtained in 76% yield from the corresponding alcohol. $^1$H NMR (500 MHz, CDCl$_3$) δ 4.76 (s, 2H), 4.67 (dq, $J = 7.4$, 5.7 Hz, 1H), 1.71 (dddd, $J = 22.1$, 13.9, 7.9, 6.3 Hz, 4H), 1.44 (ddd, $J = 13.7$, 7.7, 5.3 Hz, 1H), 1.41 – 1.28 (m, 4H), 0.97 – 0.88 (m, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 84.2, 43.2, 34.2, 26.8, 24.4, 22.9, 22.6, 22.4, 13.9. HRMS (ESI) m/z calculated for C$_9$H$_{25}$N$_2$O$_3$S [M+NH$_4$]$^+$ 241.1581, found 241.1584.

**Compound 22.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting clear oil was obtained in 71% yield from
the corresponding alcohol. $^1$H NMR (500 MHz, CDCl$_3$) δ 4.81 (s, 2H), 4.75 (ddd, $J = 12.7, 7.1, 5.6$ Hz, 1H), 1.86 – 1.78 (m, 1H), 1.79 – 1.60 (m, 7H), 1.46 (qdd, $J = 14.6, 9.4, 4.7$ Hz, 3H), 1.30 – 1.10 (m, 3H), 1.01 – 0.85 (m, 8H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 82.5, 43.8, 42.3, 33.8, 33.4, 33.2, 26.4, 26.1, 26.1, 24.5, 22.7, 22.5. HRMS (ESI) $m/z$ calculated for C$_{12}$H$_{29}$N$_2$O$_3$S [M+NH$_4$]$^+$ 281.1894, found 281.1892.

**Compound 23.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 6% increments. The resulting yellow oil was obtained in 77% yield from the corresponding alcohol as a 1.2:1 mixture of diastereomers. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.31 (t, $J = 7.6$ Hz, 2H), 7.24 – 7.18 (m, 3H), 4.55 – 4.45 (m, 2H), 4.43 (bs, 2H), 2.97 (dp, $J = 8.9, 6.9$ Hz, 0.55H), 2.85 (dp, $J = 8.9, 6.8$ Hz, 0.45H), 2.19 (dd, $J = 14.1, 8.8, 6.5$ Hz, 0.45H), 2.05 – 1.94 (m, 0.1H), 1.88 (dt, $J = 14.2, 6.3$ Hz, 0.55H), 1.76 – 1.61 (m, 2H), 1.51 – 1.41 (m, 1H), 1.28 (dd, $J = 11.0, 7.0$ Hz, 4H), 0.91 (dd, $J = 11.5, 6.4$ Hz, 3H), 0.82 (d, $J = 6.4$ Hz, 1H), 0.77 (d, $J = 6.2$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 146.3, 146.2, 128.8, 128.7, 127.3, 127.2, 126.6, 82.8, 82.7, 43.9, 43.7, 42.8, 42.7, 36.9, 36.3, 24.7, 24.4, 23.4, 23.1, 22.9, 22.4, 22.3. HRMS (ESI) $m/z$ calculated from C$_{14}$H$_{27}$N$_2$O$_3$S [M+NH$_4$]$^+$ 303.1737, found 303.1731.
**Compound 24.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting white solid was obtained in 78% yield from the corresponding alcohol. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.17 – 7.08 (m, 4H), 4.79 – 4.73 (m, 1H), 4.70 (bs, 2H), 2.79 – 2.66 (m, 2H), 2.32 (s, 3H), 2.07 – 1.92 (m, 2H), 1.82 – 1.71 (m, 2H), 1.56 – 1.48 (m, 1H), 0.96 (dd, $J = 10.5$, 6.3 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 139.5, 137.0, 136.0, 130.5, 128.9, 126.3, 83.8, 43.3, 35.0, 28.5, 24.7, 22.9, 22.6, 19.4. HRMS (ESI) $m/z$ calculated for C$_{14}$H$_{27}$N$_2$O$_3$S [M+NH$_4$]$^+$ 303.1737, found 303.1729.

![Compound 24](image)

**Compound 25.** The product was purified by column chromatography using a 10→25% gradient EtOAc in hexanes with 5% increments. The resulting white solid was obtained in 69% yield from the corresponding alcohol. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.12 (d, $J = 8.5$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 4.70 (dq, $J = 7.2$, 5.6 Hz, 1H), 4.64 (bs, 2H), 3.79 (s, 3H), 2.74 – 2.63 (m, 2H), 2.07 – 1.98 (m, 2H), 1.81 – 1.69 (m, 2H), 1.50 (hept, $J = 5.6$ Hz, 1H), 0.93 (dd, $J = 12.1$, 6.2 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 158.1, 133.2, 129.4, 114.1, 83.6, 55.4, 43.4, 36.4, 30.3, 24.6, 22.9, 22.6. HRMS (ESI) $m/z$ calculated for C$_{14}$H$_{27}$N$_2$O$_4$S [M+NH$_4$]$^+$ 319.1687, found 319.1687.
Compound 26. The product was purified by column chromatography using a 10→25% gradient of EtOAc in hexanes with 5% increments. The resulting yellow oil was obtained in 69% yield from the corresponding alcohol. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.09 (s, 4H), 4.78 (bs, 2H), 4.70 (dt, $J$ = 7.1, 5.7 Hz, 1H), 2.69 (m, 2H), 2.31 (s, 3H), 2.02 (dtd, $J$ = 11.0, 5.9, 3.1 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.50 (hept, $J$ = 5.7 Hz, 1H), 0.93 (dd, $J$ = 11.0, 6.2 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 138.1, 135.7, 129.3, 128.4, 83.6, 43.3, 36.3, 30.7, 24.6, 22.9, 22.6, 21.1 HRMS (ESI) m/z calculated for C$_{14}$H$_{27}$N$_2$O$_3$S [M+NH$_4$]$^+$ 303.1737, found 303.1732.

Compound 27. The product was purified by column chromatography using a 10→25% gradient of EtOAc in hexanes with 5% increments. The resulting white solid was obtained in 60% yield from the corresponding alcohol. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.40 (d, $J$ = 8.3 Hz, 2H), 7.08 (d, $J$ = 8.3 Hz, 2H), 4.79 (s, 2H), 4.69 (dt, $J$ = 7.1, 5.6 Hz, 1H), 2.76 – 2.63 (m, 2H), 2.09 – 1.93 (m, 2H), 1.80 – 1.68 (m, 2H), 1.54 – 1.44 (m, 1H), 0.93 (dd, $J$ = 12.3, 6.2 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.2, 131.7, 130.3, 120.0, 83.2, 43.3, 36.1, 30.5, 24.6, 22.9, 22.6. HRMS (ESI) m/z calculated for C$_{13}$H$_{25}$BrN$_2$O$_3$S [M+NH$_4$]$^+$ 367.0686, found 367.0696.
**Compound 28.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 6% increments. The resulting white solid was obtained in 71% yield from the corresponding alcohol. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.55 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 4.76 – 4.69 (m, 1H), 4.66 (s, 2H), 2.81 (dt, $J = 9.3$, 6.2 Hz, 2H), 2.12 – 1.99 (m, 2H), 1.81 – 1.70 (m, 2H), 1.54 – 1.46 (m, 1H), 0.94 (dd, $J = 13.2$, 6.3 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 145.4, 129.1, 128.8, 128.7 (q, $J = 32.8$ Hz), 125.6 (q, $J = 3.7$ Hz), 124.4 (q, $J = 271.7$ Hz) 83.1, 43.3, 36.0, 30.9, 24.7, 22.8, 22.6. HRMS (ESI) m/z calculated for C$_{14}$H$_{24}$F$_3$N$_2$O$_3$S [M+NH$_4$]$^+$ 357.1455, found 357.1465.

**Compound 29.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 6% increments. The resulting oil was obtained in 69% yield from the corresponding alcohol. Characterization was consistent with a previously reported synthesis.$^9$
Compound 30. The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 6% increments. The resulting white solid was obtained in 83% yield from the corresponding alcohol. Characterization was consistent with a previously reported synthesis.\(^9\)

![Compound 30](image)

Compound 31. The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 6% increments. The resulting white solid was obtained in 87% yield from the corresponding alcohol. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.40 (d, \(J = 8.3\) Hz, 2H), 7.32 – 7.27 (m, 2H), 7.23 – 7.15 (m, 3H), 7.05 (d, \(J = 8.4\) Hz, 2H), 4.69 – 4.62 (m, 1H), 4.58 (bs, 2H), 2.81 – 2.61 (m, 4H), 2.19 – 1.96 (m, 4H). \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 140.9, 139.9, 131.8, 130.3, 128.7, 128.5, 126.4, 120.1, 83.7, 35.8, 35.8, 31.3, 30.6. HRMS (ESI) \(m/z\) calculated for C\(_{17}\)H\(_{24}\)BrN\(_2\)O\(_3\)S \([\text{M+NH}_4]^+\) 415.0686, found 415.0688.

![Compound 31](image)

Compound 32. The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 6% increments. The resulting colorless oil was obtained in 76% yield
from the corresponding alcohol. Characterization data was consistent with a previously reported synthesis. 

III. Investigation of Counteranion Effects

![Diagram]

| entry | counteranion (X) | Ligand (L) | 2a:2b | yield |
|-------|-----------------|------------|-------|-------|
| 1     | OTf             | 1Bubipy    | 1:2.8 | 76%   |
| 2     | OTf             | tpa        | 2.4:1 | 84%   |
| 3     | NO₃             | 1Bubipy    | 1:3.3 | 68%   |
| 4     | NO₃             | tpa        | 2.4:1 | 82%   |
| 5     | OAc             | 1Bubipy    | 1:2.3 | 76%   |
| 6     | OAc             | tpa        | 2.5:1 | 85%   |
| 7     | BF₄             | 1Bubipy    | 1:1.6 | 59%   |
| 8     | BF₄             | tpa        | 2.4:1 | 89%   |
| 9     | CO₂CF₃          | 1Bubipy    | 1:2.8 | 76%   |
| 10    | CO₂CF₃          | tpa        | 2.4:1 | 68%   |

*10 mol% AgX, 30 mol% 1Bubipy, 3.5 equiv PhIO, 4 Å MS, 0.05 M CH₂Cl₂, *10 mol% AgX, 12.5 mol% tpa, 3.5 equiv PhIO, 4 Å MS, 0.05 M CH₂Cl₂, *Total NMR yield, mesitylene internal standard.

IV. Synthesis of C-H Insertion Products.

For best results, the silver to ligand ratio needs to be exact. Both silver triflate and phenanthroline are highly hygroscopic and will not give good results if they are not completely dry. Silver reagents should be stored in a dry box and the ligands in a standard dessicator. Alternatively, the reaction can be carried out in a glove box, although this is not necessary as long as the quality of the reagents is properly maintained.

General procedure for Ag-catalyzed C–H amination. A pre-dried reaction flask was charged with silver triflate (6.6 mg, 0.025 mmol, 0.1 equiv) and ligand (20.1 mg 1Bubipy, 0.075 mmol, 0.3 equiv or 9.1 mg tpa, 0.031 mmol, 0.125 equiv). Dichloromethane (2.5 mL) was added and
the mixture was stirred vigorously for 30 minutes. Then, 4Å molecular sieves (1 mmol substrate/g of sieves) were added, followed by a solution of the sulfamate substrate (0.25 mmol, 1 equiv) in dichloromethane (2.5 mL). Iodosobenzene (194 mg, 0.88 mmol, 3.5 equiv) was added in one portion and the reaction mixture was allowed to stir at room temperature for 30 minutes. The reaction mixture was filtered through a glass frit with dichloromethane and the filtrate was concentrated under reduced pressure. The crude products were purified by silica gel column chromatography using an EtOAc/hexane gradient (0→30% EtOAc/hexane unless otherwise specified). The reported yields were from the higher-yielding conditions for each product.

**Compound 2a.** The product was obtained in 60% yield using (tpa)AgOTf, while 2b was produced in 24% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 – 7.29 (m, 5H), 4.94 (dddd, $J = 11.3, 8.9, 4.2, 2.2$ Hz, 1H), 4.80 (ddd, $J = 12.2, 9.3, 2.9$ Hz, 1H), 4.31 (d, $J = 9.4$ Hz, 1H), 2.03 (dt, $J = 14.3, 2.6$ Hz, 1H), 1.96 – 1.84 (m, 2H), 1.78 (ddd, $J = 14.4, 8.9, 5.6$ Hz, 1H), 1.43 (ddd, $J = 13.9, 8.5, 4.2$ Hz, 1H), 0.96 (dd, $J = 9.3, 6.6$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.3, 129.3, 128.9, 126.5, 82.9, 58.4, 44.3, 36.8, 23.9, 23.0, 21.9. HRMS (ESI) $m/z$ calculated for C$_{13}$H$_{23}$N$_2$O$_3$S [M+NH$_4$]$^+$ 287.1424, found 287.1427.
Compound 2b. The product was isolated in 56% yield using the (4'-Bubipy)$_2$AgOTf catalyst, while 2a was produced in 19% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.31 (t, $J$ = 7.5 Hz, 2H), 7.24 – 7.17 (m, 3H), 4.88 – 4.78 (m, 1H), 4.03 (bs, 1H), 2.85 (ddd, $J$ = 14.5, 9.6, 5.2 Hz, 1H), 2.75 (ddd, $J$ = 13.8, 9.2, 7.2 Hz, 1H), 2.06 (dtd, $J$ = 14.2, 9.1, 5.3 Hz, 1H), 1.96 – 1.82 (m, 1H), 1.63 (d, $J$ = 6.3 Hz, 2H), 1.47 (s, 3H), 1.30 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.46, 128.47, 126.29, 80.19, 55.88, 41.56, 37.10, 32.00, 30.76, 25.13. HRMS (ESI) $m/z$ calculated for C$_{13}$H$_{23}$N$_2$O$_3$S [M+NH$_4^+$] 287.1424, found 287.1430.

![Chemical Structure of Compound 2b](image)

Compound 13a. The product was isolated in 63% yield using the (tpa)AgOTf catalyst, while no 13b was noted. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.45 – 7.32 (m, 5H), 4.97 (dtd, $J$ = 11.7, 6.3, 2.1 Hz, 1H), 4.82 (ddd, $J$ = 12.2, 9.3, 2.8 Hz, 1H), 4.17 (d, $J$ = 9.3 Hz, 1H), 2.17 (ddd, $J$ = 14.3, 2.8, 2.1 Hz, 1H), 1.95 (dt, $J$ = 14.3, 12.0 Hz, 1H), 1.83 (dt, $J$ = 13.8, 6.6 Hz, 1H), 1.53 (ddd, $J$ = 14.0, 7.5, 6.0 Hz, 1H), 0.89 – 0.77 (m, 1H), 0.60 – 0.49 (m, 2H), 0.17 (ddd, $J$ = 10.6, 4.8, 2.0 Hz, 1H), 0.11 (ddd, $J$ = 12.3, 4.8, 2.1 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 138.1, 129.2, 128.9, 126.3, 84.6, 58.3, 40.1, 36.0, 6.4, 4.5, 4.5. HRMS (ESI) $m/z$ calculated for C$_{13}$H$_{23}$N$_2$O$_3$S [M+NH$_4^+$] 285.1268, found 285.1274.

![Chemical Structure of Compound 13a](image)

S1-29
Compound 14a. The product was isolated in 64% yield using (tpa)AgOTf and 21% of 14b was produced. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.41 – 7.36 (m, 2H), 7.36 – 7.31 (m, 3H), 4.90 – 4.67 (m, 2H), 4.42 (d, $J = 9.5$ Hz, 1H), 2.49 (hept, $J = 8.0$ Hz, 1H), 2.09 (dtt, $J = 19.1$, 7.9, 4.0 Hz, 2H), 1.98 (dt, $J = 14.3$, 2.7 Hz, 1H), 1.96 – 1.77 (m, 4H), 1.77 – 1.60 (m, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 138.1, 129.1, 128.7, 126.3, 83.3, 58.3, 42.2, 36.2, 31.6, 28.5, 28.4, 18.7. HRMS (ESI) m/z calculated for C$_{14}$H$_{23}$N$_2$O$_3$S [M+NH$_4$]$^+$ 299.1424, found 299.1419.

Compound 14b. The product was obtained in 30% yield using (4'-Bubipy)$_2$AgOTf, while 27% of 14a was produced. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.31 (t, $J = 7.5$ Hz, 2H), 7.25 – 7.16 (m, 3H), 4.73 (dddd, $J = 12.2$, 8.6, 4.0, 1.9 Hz, 1H), 4.17 (s, 1H), 2.85 (dd, $J = 14.5$, 9.7, 5.3 Hz, 1H), 2.74 (dd, $J = 13.8$, 9.4, 7.0 Hz, 1H), 2.59 – 2.45 (m, 1H), 2.13 – 1.95 (m, 6H), 1.91 (ddddd, $J = 14.1$, 9.6, 7.1, 4.0 Hz, 1H), 1.87 – 1.79 (m, 1H), 1.66 (dd, $J = 13.9$, 11.8, 1.6 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.5, 128.6, 128.5, 126.3, 80.8, 58.9, 39.2, 36.9, 34.1, 31.9, 30.8, 14.9. HRMS (ESI) m/z calculated for C$_{14}$H$_{23}$N$_2$O$_3$S [M+NH$_4$]$^+$ 299.1424, found 299.1423.

Compound 15a. The product was isolated in 65% yield using (tpa)AgOTf and 22% of 15b was produced. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.43 – 7.33 (m, 5H), 4.95 (ddddd, $J = 10.9$, 8.7, 4.0, 2.1 Hz, 1H), 4.81 (dd, $J = 12.2$, 9.2, 2.9 Hz, 1H), 4.13 (d, $J = 9.2$ Hz, 1H), 2.06 (dt, $J = 14.3$, 2.5 Hz, 1H), 1.91 (d, $J = 10.9$, 8.7, 4.0, 2.1 Hz, 1H). HRMS (ESI) m/z calculated for C$_{14}$H$_{23}$N$_2$O$_3$S [M+NH$_4$]$^+$ 299.1424, found 299.1423.
Hz, 1H), 1.90 (dt, $J = 14.3$, 11.8 Hz, 1H), 1.81 (t, $J = 8.8$ Hz, 1H), 1.58 – 1.49 (m, 2H), 1.48 – 1.26 (m, 4H), 0.87 (td, $J = 7.4$, 1.3 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 138.1, 129.2, 128.9, 126.3, 82.8, 58.3, 38.9, 36.9, 35.7, 25.4, 24.7, 10.6, 10.3. HRMS (ESI) $m/z$ calculated for C$_{15}$H$_{27}$N$_2$O$_3$S [M+NH$_4$]$^+$ 315.1737, found 315.1729.

**Compound 15b.** The product was isolated in 68% yield using (4'-Bubipy)$_2$AgOTf and 13% of 15a was also produced. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.30 (t, $J = 7.5$ Hz, 2H), 7.25 – 7.16 (m, 3H), 4.83 (dddd, $J = 11.1$, 8.7, 4.0, 2.2 Hz, 1H), 3.84 (s, 1H), 2.85 (ddd, $J = 14.4$, 9.5, 5.3 Hz, 1H), 2.74 (ddd, $J = 13.8$, 9.2, 7.1 Hz, 1H), 2.13 (dq, $J = 14.4$, 7.2 Hz, 1H), 2.06 (ddd, $J = 14.2$, 9.8, 5.2 Hz, 1H), 1.88 (dddd, $J = 13.9$, 9.4, 7.2, 3.9 Hz, 1H), 1.64 (dd, $J = 14.4$, 2.1 Hz, 1H), 1.61 – 1.48 (m, 3H), 1.41 (dt, $J = 14.0$, 7.4 Hz, 1H), 0.89 (td, $J = 7.5$, 1.4 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.5, 128.6, 128.5, 126.3, 79.8, 61.2, 38.5, 37.2, 32.5, 30.8, 25.3, 7.5, 7.0. HRMS (ESI) $m/z$ calculated for C$_{15}$H$_{27}$N$_2$O$_3$S [M+NH$_4$]$^+$ 315.1737, found 315.1734.

**Compound 16a.** The product was isolated in 54% yield with (tpa)AgOTf and 38% 16b was isolated. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.39 (dd, $J = 8.4$, 6.1 Hz, 2H), 7.36 – 7.32 (m, 3H), 4.89 (dddd, $J = 10.8$, 8.3, 4.7, 2.1 Hz, 1H), 4.79 (dddd, $J = 12.3$, 9.4, 2.9 Hz, 1H), 4.38 (d, $J = 9.5$ Hz,
1H), 2.05 (dt, $J = 14.4$, 2.6 Hz, 1H), 2.03 – 1.95 (m, 1H), 1.95 – 1.83 (m, 3H), 1.79 (td, $J = 11.6$, 6.8 Hz, 1H), 1.69 – 1.57 (m, 3H), 1.54 (dp, $J = 8.3$, 4.7, 4.2 Hz, 2H), 1.11 (dp, $J = 12.1$, 8.2 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 138.2, 129.1, 128.8, 126.3, 84.1, 58.3, 41.4, 36.6, 35.6, 32.8, 32.4, 25.0, 24.8. HRMS (ESI) $m/z$ calculated for C$_{15}$H$_{25}$N$_2$O$_3$S [M+NH$_4$]$^+$ 313.1581, found 313.1591.

**Compound 16b.** The product was obtained in 67% yield using (4'-Bubipy)$_2$AgOTf and 14% of 16a was produced. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.30 (t, $J = 7.5$ Hz, 2H), 7.23 – 7.15 (m, 3H), 4.78 (ddddd, $J = 12.2$, 8.7, 4.1, 1.8 Hz, 1H), 4.27 (s, 1H), 2.84 (dddd, $J = 14.6$, 9.6, 5.3 Hz, 1H), 2.73 (dd, $J = 13.8$, 9.4, 7.0 Hz, 1H), 2.44 (dd, $J = 13.5$, 8.4, 4.7 Hz, 1H), 2.05 (dt, $J = 14.3$, 9.1, 5.3 Hz, 1H), 1.94 – 1.84 (m, 2H), 1.83 – 1.73 (m, 2H), 1.73 – 1.63 (m, 4H), 1.60 (dd, $J = 14.3$, 1.9 Hz, 1H), 1.55 (dt, $J = 14.0$, 7.8 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.5, 128.6, 128.5, 126.2, 81.4, 66.4, 42.4, 39.7, 37.1, 35.3, 30.7, 24.1, 22.4. HRMS (ESI) $m/z$ calculated for C$_{15}$H$_{25}$N$_2$O$_3$S [M+NH$_4$]$^+$ 313.1581, found 313.1583.

**Compound 17a.** The product was isolated in 73% yield using (tpa)AgOTf and 20% of 17b was produced. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.47 – 7.31 (m, 5H), 4.99 (ddddd, $J = 11.3$, 9.0, 4.2, 2.1 Hz, 1H), 4.81 (dd, $J = 12.1$, 9.2, 2.9 Hz, 1H), 4.11 (d, $J = 9.2$ Hz, 1H), 2.10 – 2.00 (m, 1H),
1.94 – 1.64 (m, 7H), 1.58 (ddt, $J = 11.5, 5.4, 3.0$ Hz, 1H), 1.47 (ddd, $J = 14.2, 8.4, 4.2$ Hz, 1H), 1.26 (dddd, $J = 14.8, 11.6, 8.9, 2.8$ Hz, 2H), 1.15 (qt, $J = 12.8, 3.5$ Hz, 1H), 1.02 – 0.86 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 138.1, 129.2, 128.9, 126.3, 82.3, 58.2, 42.9, 36.8, 33.6, 33.0, 32.6, 26.3, 26.1, 25.9. HRMS (ESI) m/z calculated for C$_{16}$H$_{27}$N$_2$O$_3$S [M+NH$_4$]$^+$ 327.1737, found 327.1737.

**Compound 17b.** The product was obtained in 72% yield with (4'-Bubipy)$_2$AgOTf and 9% 17a was produced. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.30 (t, $J = 7.5$ Hz, 2H), 7.24 – 7.16 (m, 3H), 4.92 – 4.76 (m, 1H), 3.91 (s, 1H), 2.84 (ddd, $J = 14.4, 9.6, 5.2$ Hz, 1H), 2.78 – 2.69 (m, 1H), 2.40 (d, $J = 13.1$ Hz, 1H), 2.05 (dtd, $J = 14.2, 8.9, 5.4$ Hz, 1H), 1.87 (dtt, $J = 13.7, 7.1, 4.0$ Hz, 1H), 1.72 – 1.59 (m, 4H), 1.57 (d, $J = 4.1$ Hz, 1H), 1.49 (dd, $J = 31.0, 11.3, 4.7$ Hz, 4H), 1.39 – 1.22 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.5, 128.6, 128.5, 126.3, 79.4, 57.9, 41.3, 40.5, 37.2, 32.8, 30.8, 25.5, 21.1, 20.8. HRMS (ESI) m/z calculated for C$_{16}$H$_{27}$N$_2$O$_3$S [M+NH$_4$]$^+$ 327.1737, found 327.1742.

**Compound 18a.** The product was obtained in 63% yield using (tpa)AgOTf; no formation of 18b was noted. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.43 – 7.38 (m, 2H), 7.38 – 7.32 (m, 3H), 4.88 (dddd, $J = 10.9, 8.3, 4.8, 2.0$ Hz, 1H), 4.78 (dddd, $J = 12.1, 9.2, 2.8$ Hz, 1H), 4.22 (d, $J = 9.3$ Hz, 1H),
2.10 (dt, J = 14.3, 2.5 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.82 – 1.70 (m, 3H), 1.54 (ddd, J = 14.9, 6.5, 4.8 Hz, 1H), 1.24 (dq, J = 6.3, 4.8 Hz, 1H), 0.91 (d, J = 6.8 Hz, 6H), 0.89 (d, J = 6.8 Hz, 3H), 0.85 (d, J = 6.8 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 138.2, 129.1, 128.8, 126.3, 84.8, 58.3, 45.0, 36.8, 33.8, 29.3, 28.9, 21.5, 21.2, 19.5, 18.9. HRMS (ESI) m/z calculated for C$_{17}$H$_{31}$N$_2$O$_3$S [M+NH$_4$]$^+$ 343.2050, found 343.2058.

**Compound 18b.** Compound isolated by column chromatography on silica gel using a 0 → 6% gradient of EtOAc in hexanes. The product was obtained in 54% yield using (4'-Bubipy)$_2$AgOTf and 21% of 18a was also produced. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.30 (t, J = 7.5 Hz, 2H), 7.23 – 7.16 (m, 3H), 4.77 (ddt, J = 10.1, 8.1, 3.9 Hz, 1H), 3.99 (s, 1H), 2.87 (ddd, J = 14.6, 9.6, 5.3 Hz, 1H), 2.74 (ddd, J = 13.9, 9.4, 7.0 Hz, 1H), 2.54 (hept, J = 7.1 Hz, 1H), 2.11 (dt, J = 14.2, 8.9, 5.3 Hz, 1H), 1.99 – 1.86 (m, 2H), 1.78 – 1.71 (m, 2H), 1.09 (d, J = 6.8 Hz, 3H), 0.98 (d, J = 6.9 Hz, 6H), 0.95 (d, J = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.5, 128.6, 128.4, 126.3, 80.1, 65.9, 37.3, 34.3, 32.4, 32.2, 30.9, 18.4, 18.3, 17.9, 17.5. HRMS (ESI) m/z calculated for C$_{17}$H$_{31}$N$_2$O$_3$S [M+NH$_4$]$^+$ 343.2050, found 343.2039.

![Compound 18b structure](image)

**Compound 19a.** The product was obtained in 74% yield as the syn isomer using (tpa)AgOTf as the catalyst, with 8% yield of 19b produced. $^1$H NMR (500 MHz, CDCl$_3$) δ 4.96 (dp, J = 8.1, 1.5
Hz, 1H), 4.83 (dddd, J = 11.4, 9.0, 4.2, 2.1 Hz, 1H), 4.42 (dtd, J = 11.8, 8.6, 3.0 Hz, 1H), 3.79 (d, J = 9.6 Hz, 1H), 1.95 – 1.81 (m, 1H), 1.75 (s, 6H), 1.74 – 1.67 (m, 2H), 1.49 (dt, J = 14.5, 11.8 Hz, 1H), 1.36 (ddd, J = 14.2, 8.6, 4.2 Hz, 1H), 0.94 (dd, J = 8.0, 6.6 Hz, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 139.7, 139.6, 121.7, 82.5, 53.1, 44.2, 36.7, 36.6, 25.5, 23.7, 22.9, 21.8, 18.6. HRMS (ESI) \(m/z\) calculated for C\(_{11}\)H\(_{21}\)NO\(_3\)S \([\text{M+NH}_4]^+\) 265.1581, found 265.1578.

**Compound 19b.** The product was isolated in 30% yield using (4'-Bubipy)\(_2\)AgOTf as the catalyst, with 28% of 19a also produced. \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 5.58 (dp, J = 8.4, 1.4 Hz, 1H, anti), 5.13 – 5.01 (m, 1H, 3°), 4.95 (tt, J = 9.0, 4.0 Hz, 1H, anti), 4.81 (tt, J = 8.9, 4.7 Hz, 1H, 3°), 4.56 (d, J = 6.9 Hz, 1H, anti), 4.42 (dq, J = 12.6, 5.6 Hz, 1H, anti), 4.27 (s, 1H, 3°), 2.15 (q, J = 7.5 Hz, 2H, 3°), 1.99 – 1.80 (m, 4H), 1.77 (s, 4H), 1.74 – 1.67 (m, 7H), 1.63 (s, 4H), 1.49 (s, 3H), 1.30 (s, 3H), 0.95 (dd, J = 6.5, 4.0 Hz, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 137.2, 133.4, 122.3, 121.7, 81.3, 80.7, 55.8, 51.3, 43.4, 41.4, 35.3, 34.7, 31.8, 25.7, 25.6, 25.1, 24.0, 23.1, 22.9, 21.7, 18.2, 17.7. HRMS (ESI) \(m/z\) calculated for C\(_{11}\)H\(_{21}\)NO\(_3\)S \([\text{M+NH}_4]^+\) 265.1581, found 265.1580.

**Compound 20a.** The product was isolated in 37% yield using (tpa)AgOTf and 26% of 20b was also produced. Major isomer (syn): \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 4.77 (ddddd, J = 11.4, 9.0, 4.3,
2.1 Hz, 1H), 4.48 (ddt, J = 12.3, 7.2, 2.5, 2.5 Hz, 1H), 4.04 (d, J = 10.4 Hz, 1H), 2.18 (td, J = 7.2, 7.1, 2.1 Hz, 2H), 1.99 (ddd, J = 14.5, 3.0, 2.1 Hz, 1H), 1.92 – 1.81 (m, 1H), 1.76 – 1.67 (m, 2H), 1.54 – 1.45 (m, 2H), 1.42 – 1.27 (m, 5H), 0.94 (d, J = 4.5 Hz, 3H), 0.93 (d, J = 4.6 Hz, 3H), 0.90 (t, J = 7.2, 7.0 Hz, 3H). 13C NMR (126 MHz, CDCl3) δ 86.9, 82.1, 75.6, 47.2, 43.9, 37.5, 30.9, 27.9, 23.7, 22.8, 22.1, 21.8, 18.5, 13.9. HRMS (ESI) m/z calculated for C14H29N2O3S [M+NH4]+ 305.1894, found 305.1897. The minor isomer (anti) coelutes with 26b and was identified based on peak patterns observed in the crude NMR for 26b.

**Compound 20b.** The product was obtained in 51% yield using (4’-Bubipy)2AgOTf and 21% of 20a was also produced. The compound co-elutes with minor isomer of 20a, and an amount sufficient for characterization was isolated in 95% purity with a gradient of 0→30% ethyl acetate/hexanes on silica impregnated with AgNO3 as a 5% solution in acetonitrile. 1H NMR (500 MHz, CDCl3) δ 5.00 (dddd, J = 12.2, 8.3, 4.4, 2.0 Hz, 1H), 3.99 (s, 1H), 2.35 (tdt, J = 6.3, 4.2, 2.4 Hz, 2H), 2.14 (tt, J = 7.1, 2.4 Hz, 2H), 1.98 – 1.89 (m, 1H), 1.77 (dtd, J = 14.1, 7.6, 4.5 Hz, 1H), 1.70 (dd, J = 14.3, 2.0 Hz, 1H), 1.63 – 1.55 (m, 2H), 1.52 (s, 3H), 1.47 (p, J = 7.2 Hz, 2H), 1.40 – 1.27 (m, 3H), 1.31 (s, 3H), 0.90 (t, J = 7.0 Hz, 3H). 13C NMR (126 MHz, CDCl3) δ 81.8, 79.9, 77.7, 55.9, 41.3, 34.5, 32.0, 31.1, 28.7, 25.1, 22.2, 18.7, 14.4, 14.0. HRMS (ESI) m/z calculated for C14H29N2O3S [M+NH4]+ 305.1894, found 305.1897.
**Compound 21b.** The product was obtained in 94% yield using (tpa)AgOTf. $^1$H NMR (500 MHz, CDCl$_3$) δ 4.82 (dd, $J = 11.5, 7.9, 4.7, 2.2$ Hz, 1H), 3.92 (bs, 1H), 1.75 (dd, $J = 14.5, 9.8, 7.9, 5.0$ Hz, 1H), 1.70-1.54 (m, 3H), 1.50 (s, 3H), 1.45-1.31 (m, 4H), 1.30 (s, 3H), 0.92 (t, $J=7.2$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 81.2, 55.8, 41.6, 34.9, 32.1, 26.7, 25.1, 22.3, 13.9. HRMS (ESI) $m/z$ calculated for C$_9$H$_{19}$NO$_3$S [M+NH$_4$]$^+$ 239.1424, found 239.1416.

**Compound 22a.** The product was purified by column chromatography using a 5$\rightarrow$20% gradient of EtOAc in hexanes, using 5% increments. The product was isolated in 74% yield using (4-‘Bubipy)$_2$AgOTf as the catalyst and 21% of 22b was also produced. $^1$H NMR (500 MHz, CDCl$_3$) δ 4.91 (dd, $J = 11.8, 8.9, 4.3, 1.9$ Hz, 1H), 3.76 (bs, 1H), 2.45 (dd, $J = 11.4, 6.9$ Hz, 1H), 1.94 – 1.81 (m, 1H), 1.78 – 1.56 (m, 5H), 1.56 – 1.45 (m, 5H), 1.35 (qdd, $J = 16.4, 10.5, 3.1$ Hz, 3H), 0.95 (d, $J = 6.6$ Hz, 3H), 0.93 (d, $J = 6.7$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 78.7, 57.9, 44.2, 40.6, 32.9, 25.6, 23.8, 22.9, 21.9, 21.1, 20.8. HRMS (ESI) $m/z$ calculated for C$_{12}$H$_{27}$N$_2$O$_3$S [M+NH$_4$]$^+$ 279.1737, found 279.1745.
**Compound 22b.** The product was isolated in 50% yield with (tpa)AgOTf and 36% of 22a was also produced. $^1$H NMR (500 MHz, CDCl$_3$) δ 4.93 (dddd, $J = 10.7, 8.9, 4.2, 2.9$ Hz, 1H), 4.08 (bs, 1H), 1.81 (ddt, $J = 12.1, 4.8, 2.2$ Hz, 1H), 1.73 – 1.62 (m, 5H), 1.62 – 1.59 (m, 2H), 1.50 (s, 3H), 1.42 – 1.35 (m, 2H), 1.29 (s, 3H), 1.25 (dddd, $J = 13.1, 11.6, 8.7, 4.5$ Hz, 2H), 1.19 – 1.11 (m, 1H), 1.01 – 0.84 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 79.1, 55.9, 42.9, 42.0, 33.6, 33.0, 32.6, 31.9, 30.6, 26.4, 26.1, 26.0, 25.2. HRMS (ESI) $m/z$ calculated for C$_{12}$H$_{23}$NO$_3$S [M+NH$_4$]$^+$ 279.1737, found 279.1745.

![Compound 22b](image)

**Compound 23a.** The product was purified by column chromatography using a 0→25% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 48% yield using (tpa)AgOTf as a mixture of diastereomers with $dr$ (2.5:1). A 51% yield of 23b was also observed. Major diastereomer: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.46 – 7.38 (m, 4H), 7.35 – 7.31 (m, 1H), 5.07 (dddd, $J = 11.2, 9.0, 4.1, 2.0$ Hz, 1H), 4.28 (s, 1H), 2.14 (dd, $J = 14.1, 2.0$ Hz, 1H), 2.08 – 2.01 (m, 1H), 1.95 (dddd, $J = 15.2, 12.2, 7.7, 6.1$ Hz, 1H), 1.86 – 1.82 (m, 1H), 1.81 (d, $J = 0.8$ Hz, 3H), 1.47 (ddd, $J = 14.1, 8.6, 4.1$ Hz, 1H), 0.99 (dd, $J = 13.7, 6.6$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 146.1, 129.2, 128.3, 124.1, 79.3, 60.8, 44.4, 40.4, 27.4, 23.9, 23.1, 22.0. HRMS (ESI) $m/z$ calculated for C$_{14}$H$_{25}$N$_2$O$_3$S [M+NH$_4$]$^+$ 301.1581, found 301.1574. Minor diastereomer: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.50 – 7.46 (m, 2H), 7.41 – 7.36 (m, 2H), 7.33 – 7.28 (m, 1H), 4.71 (dddd, $J = 11.6, 8.7, 4.6, 1.5$ Hz, 1H), 4.38 (s, 1H), 2.65 (dd, $J = 15.0, 1.5$ Hz, 1H), 1.92 – 1.81 (m, 2H), 1.76 (ddd, $J = 14.5, 8.7, 6.0$ Hz, 1H), 1.48 (s, 3H), 1.47 – 1.42 (m, 1H), 0.92 (dd, $J = 13.1, 6.6$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 161.1, 149.2, 141.4, 128.7,
127.8, 125.7, 120.9, 118.4, 80.2, 61.7, 44.3, 40.1, 35.5, 30.8, 24.0, 23.0, 22.1 HRMS (ESI) m/z calculated for C$_{14}$H$_{25}$N$_2$O$_3$S [M+NH$_4$]$^+$ 301.1581, found 301.1583.

**Compound 23b.** The product was purified by column chromatography using a 0→25% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 58% yield using (4′-Bubipy)$_2$AgOTf as a mixture of diastereomers with $dr$ (2.1:1). Compound 23a was also produced in 35% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.35 – 7.29 (m, 3H), 7.25 – 7.17 (m, 4H), 4.82 (dddd, $J$ = 11.7, 8.5, 5.0, 2.0 Hz, 0.4H), 4.60 – 4.52 (m, 1H), 3.96 (s, 0.4H), 3.93 (s, 1H), 3.07 (ddq, $J$ = 13.6, 6.8, 3.4, 2.5 Hz, 1H), 3.04 – 2.96 (m, 0.4H), 2.09 (ddd, $J$ = 14.5, 8.5, 6.3 Hz, 0.4H), 2.02 (ddd, $J$ = 14.1, 9.5, 4.5 Hz, 1H), 1.81 – 1.76 (m, 0.4H), 1.73 (ddd, $J$ = 14.1, 10.6, 3.3 Hz, 1H), 1.66 (dd, $J$ = 14.3, 2.0 Hz, 0.4H), 1.46 – 1.41 (m, 2H), 1.39 (s, 1H), 1.33 (d, $J$ = 2.2 Hz, 3H), 1.31 (d, $J$ = 3.3 Hz, 2H), 1.29 (d, $J$ = 4.9 Hz, 3H), 1.24 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 146.1, 145.3, 128.9, 127.3, 126.8, 126.8, 126.7, 79.6, 79.2, 56.0, 55.9, 44.4, 43.6, 42.0, 41.8, 35.4, 34.9, 32.2, 32.1, 30.8, 25.2, 22.4, 21.2. HRMS (ESI) m/z calculated for C$_{14}$H$_{25}$N$_2$O$_3$S [M+NH$_4$]$^+$ 301.1581, found 301.1582.

**Compound 24a.** The product was purified by column chromatography using a 0→30% gradient of EtOAc in hexanes with 5% increments. The resulting white solid was obtained in 65% yield.
using (tpa)AgOTf and 24b was produced in 20% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.32 – 7.17 (m, 4H), 4.96 (dddt, \(J = 15.8, 8.9, 4.2, 2.4\) Hz, 2H), 4.13 (d, \(J = 9.8\) Hz, 1H), 2.43 (s, 3H), 2.03 (dt, \(J = 14.3, 11.7\) Hz, 1H), 1.96 – 1.84 (m, 2H), 1.80 (ddd, \(J = 14.5, 9.0, 5.6\) Hz, 1H), 1.45 (ddd, \(J = 14.1, 8.5, 4.2\) Hz, 1H), 0.96 (dd, \(J = 12.3, 6.6\) Hz, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 136.9, 135.9, 131.3, 128.8, 126.7, 124.8, 82.9, 54.8, 44.3, 35.5, 23.9, 23.0, 21.9, 19.2: HRMS (ESI) \(m/z\) calculated for C\(_{14}\)H\(_{25}\)N\(_2\)O\(_3\)S \([\text{M+NH}_4]^+\) 301.1581, found 301.1571.

**Compound 24b.** The product was purified by column chromatography using a 0\(\rightarrow\)30% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 45% yield using (4-’Bubipy)\(_2\)AgOTf and 24a was produced in 32% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.17 – 7.10 (m, 4H), 4.86 (dtd, \(J = 8.6, 7.0, 3.8\) Hz, 1H), 4.13 (s, 1H), 2.86 (ddd, \(J = 13.9, 10.1, 5.0\) Hz, 1H), 2.71 (ddd, \(J = 14.0, 9.9, 6.7\) Hz, 1H), 2.32 (s, 3H), 2.06 – 1.95 (m, 1H), 1.84 (ddddd, \(J = 14.1, 10.3, 6.7, 3.8\) Hz, 1H), 1.64 (d, \(J = 6.3\) Hz, 2H), 1.49 (s, 3H), 1.30 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 138.8, 136.0, 130.6, 129.1, 126.6, 126.3, 80.6, 56.0, 41.7, 35.9, 32.1, 28.2, 25.3, 19.4. HRMS (ESI) \(m/z\) calculated for C\(_{14}\)H\(_{25}\)N\(_2\)O\(_3\)S \([\text{M+NH}_4]^+\) 301.1581, found 301.1573.

**Compound 25a.** The product was purified by column chromatography using a 0\(\rightarrow\)25% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 70% yield.

S1-40
based on NMR integrations using mesitylene as an internal standard with (tpa)AgOTf as the catalyst. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.30 – 7.23 (m, 2H), 6.95 – 6.87 (m, 2H), 4.93 (dddd, $J$ = 11.2, 8.9, 4.2, 2.1 Hz, 1H), 4.75 (ddd, $J$ = 12.1, 9.2, 2.9 Hz, 1H), 4.13 (d, $J$ = 9.2 Hz, 1H), 3.81 (s, 3H), 2.03 – 1.97 (m, 1H), 1.95 – 1.83 (m, 2H), 1.79 (ddd, $J$ = 14.5, 9.0, 5.6 Hz, 1H), 1.43 (ddd, $J$ = 14.2, 8.6, 4.2 Hz, 1H), 0.96 (dd, $J$ = 9.8, 6.6 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.9, 130.2, 127.6, 114.4, 82.7, 57.8, 55.4, 44.2, 36.7, 23.8, 22.9, 21.9. HRMS (ESI) $m/z$ calculated for C$_{14}$H$_{21}$NO$_4$S [M+NH$_4$]$^+$ 317.1530, found 317.1533.

**Compound 25b.** The product was purified by column chromatography using a 0→25% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 38% yield based on NMR integrations using mesitylene as an internal standard using (4-Bubipy)$_2$AgOTf as the catalyst. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.29 – 7.23 (m, 2H), 6.91 (d, $J$ = 8.8 Hz, 2H), 4.93 (dddd, $J$ = 11.2, 8.9, 4.2, 2.1 Hz, 1H), 4.75 (ddd, $J$ = 12.1, 9.1, 2.9 Hz, 1H), 4.13 (d, $J$ = 9.2 Hz, 1H), 3.81 (s, 3H), 2.05 – 1.97 (m, 1H), 1.95 – 1.86 (m, 2H), 1.79 (ddd, $J$ = 14.5, 9.0, 5.6 Hz, 1H), 1.43 (ddd, $J$ = 14.1, 8.5, 4.2 Hz, 1H), 0.96 (dd, $J$ = 9.8, 6.6 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 157.0, 131.4, 128.4, 112.9, 79.1, 66.9, 54.9, 54.2, 40.5, 36.3, 30.9, 28.8, 24.6, 24.1. HRMS (ESI) $m/z$ calculated for C$_{14}$H$_{21}$NO$_4$S [M+NH$_4$]$^+$ 317.1530, found 317.1534.
**Compound 26a.** The product was purified by column chromatography using a 0→20% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 66% yield based on NMR integrations using mesitylene as an internal standard using (tpa)AgOTf as the catalyst. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.24 – 7.19 (m, 4H), 4.94 (dddd, $J = 11.4, 9.0, 4.2, 2.1$ Hz, 1H), 4.78 (ddd, $J = 12.2, 9.2, 2.9$ Hz, 1H), 4.06 (d, $J = 9.2$ Hz, 1H), 2.36 (s, 3H), 2.03 (ddd, $J = 14.4, 2.9, 2.1$ Hz, 1H), 1.94 – 1.86 (m, 2H), 1.84 – 1.76 (m, 1H), 1.43 (ddd, $J = 14.1, 8.6, 4.2$ Hz, 1H), 0.97 (dd, $J = 9.2, 6.6$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 138.9, 135.3, 129.9, 126.3, 82.9, 58.2, 44.3, 36.9, 23.9, 23.1, 22.0, 21.3. HRMS (ESI) $m/z$ calculated for C$_{14}$H$_{25}$N$_2$O$_3$S [M+NH$_4$]$^+$ 301.1581, found 301.1578.

**Compound 26b.** The product was purified by column chromatograph using a 0→20% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 52% yield based on NMR integrations using mesitylene as an internal standard using (4-tBubipy)$_2$AgOTf as the catalyst. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.13 – 7.05 (m, 4H), 4.83 (dtd, $J = 8.6, 6.9, 3.9$ Hz, 1H), 4.10 (s, 1H), 2.80 (ddt, $J = 14.3, 9.6, 4.6$ Hz, 1H), 2.70 (ddd, $J = 13.8, 9.2, 7.1$ Hz, 1H), 2.32 (s, 3H), 2.04 (dtd, $J = 14.2, 9.0, 5.3$ Hz, 1H), 1.89 – 1.81 (m, 1H), 1.62 (d, $J = 6.8$ Hz, 2H), 1.46 (s, 3H), 1.29 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 137.5, 135.9, 129.4, 128.5, 80.4, 56.0, 41.7, 37.4, 32.1, 30.4, 25.3, 21.1. HRMS (ESI) $m/z$ calculated for C$_{14}$H$_{25}$N$_2$O$_3$S [M+NH$_4$]$^+$ 301.1581, found 301.1584.
Compound 27a. The product was purified by column chromatography using a 0\(\rightarrow\)25% gradient of EtOAc in hexanes with 5% increments. The resulting white solid was obtained in 55% yield based on NMR integrations using mesitylene as an internal standard using (tpa)AgOTf as the catalyst. \(^1\text{H} \text{NMR (500 MHz, CDCl}_3\) \(\delta\) 7.53 (d, \(J = 8.4\) Hz, 2H), 7.23 (d, \(J = 8.4\) Hz, 2H), 4.93 (dddd, \(J = 11.3, 9.0, 4.2, 2.1\) Hz, 1H), 4.77 (dddd, \(J = 12.2, 9.3, 2.8\) Hz, 1H), 4.29 (d, \(J = 9.3\) Hz, 1H), 2.02 (dt, \(J = 14.3, 2.4\) Hz, 1H), 1.92 – 1.83 (m, 2H), 1.83 – 1.74 (m, 1H), 1.43 (dd, \(J = 3.0, 8.5\) Hz, 1H), 0.96 (dd, \(J = 10.0, 6.6\) Hz, 6H). \(^{13}\text{C} \text{NMR (126 MHz, CDCl}_3\) \(\delta\) 137.2, 132.4, 128.2, 123.0, 82.9, 57.9, 44.2, 36.6, 23.9, 23.0, 21.9. HRMS (ESI) \(m/z\) calculated for \(\text{C}_{13}\text{H}_{22}\text{BrN}_2\text{O}_3\text{S [M+NH}_4^+}\) 365.0530, found 365.0527.

Compound 27b. The product was purified by column chromatography using a 0\(\rightarrow\)25% gradient of EtOAc in hexanes with 5% increments. The resulting white solid was obtained in 44% yield based on NMR integrations using mesitylene as an internal standard and (4-\(^{1}\text{Bubipy})_2\text{AgOTf as the catalyst.} \(^1\text{H} \text{NMR (500 MHz, CDCl}_3\) \(\delta\) 7.42 (d, \(J = 8.3\) Hz, 2H), 7.07 (d, \(J = 8.3\) Hz, 2H), 4.80 (ddddd, \(J = 9.2, 7.7, 6.0, 3.6\) Hz, 1H), 4.01 (s, 1H), 2.81 (dd, \(J = 14.3, 9.5, 5.1\) Hz, 1H), 2.71 (dd, \(J = 13.9, 9.1, 7.4\) Hz, 1H), 2.03 (dt, \(J = 14.2, 9.1, 5.1\) Hz, 1H), 1.84 (ddd, \(J = 14.3, 9.4, 7.4, 3.6\) Hz, 1H), 1.63 (d, \(J = 1.8\) Hz, 1H), 1.57 (s, 1H), 1.47 (s, 3H), 1.30 (s, 3H). \(^{13}\text{C} \text{NMR (126}\)
MHz, CDCl$_3$ $\delta$ 139.5, 131.9, 130.4, 120.3, 79.9, 56.0, 41.7, 37.0, 32.2, 30.3, 25.3. HRMS (ESI) $m/z$ calculated for C$_{13}$H$_{22}$BrN$_2$O$_3$S [M+NH$_4$]$^+$ 365.0530, found 365.0530.

**Compound 28a.** The product was purified by column chromatography using a 0$\rightarrow$30% gradient of EtOAc in hexanes with 6% increments. The resulting white solid was obtained in 42% yield based on NMR integrations using mesitylene as an internal standard using (tpa)AgOTf as the catalyst. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.67 (d, $J = 8.1$ Hz, 2H), 7.49 (d, $J = 8.1$ Hz, 2H), 4.96 (dddd, $J = 11.3$, 9.0, 4.2, 2.1 Hz, 1H), 4.88 (ddd, $J = 12.2$, 9.4, 2.8 Hz, 1H), 4.47 (d, $J = 9.4$ Hz, 1H), 2.06 (dt, $J = 14.3$, 2.5 Hz, 1H), 1.94 – 1.83 (m, 2H), 1.79 (ddd, $J = 14.4$, 9.0, 5.6 Hz, 1H), 1.44 (ddd, $J = 14.1$, 8.5, 4.1 Hz, 1H), 0.96 (dd, $J = 11.8$, 6.6 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 141.9, 131.2 (q, $J = 32.7$ Hz), 126.9, 126.3 (q, $J = 3.8$ Hz), 123.9 (q, $J = 272.2$ Hz), 83.0, 58.0, 44.2, 36.6, 23.9, 22.9, 21.9. HRMS (ESI) $m/z$ calculated for C$_{14}$H$_{22}$F$_3$N$_2$O$_3$S [M+NH$_4$]$^+$ 355.1298, found 355.1300.

**Compound 28b.** The product was purified by column chromatography using a 0$\rightarrow$30% gradient of EtOAc in hexanes with 6% increments. The resulting white solid was obtained in 69% yield based on NMR integrations using mesitylene as an internal standard using (4'-Bubipy)$_2$AgOTf as
the catalyst. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.56 (d, \(J = 8.0\) Hz, 2H), 7.31 (d, \(J = 7.9\) Hz, 2H), 4.82 (ddt, \(J = 10.4, 9.1, 3.5\) Hz, 1H), 4.24 (s, 1H), 2.92 (ddd, \(J = 14.4, 9.7, 5.1\) Hz, 1H), 2.81 (ddd, \(J = 13.9, 9.3, 7.2\) Hz, 1H), 2.06 (dt, \(J = 14.3, 9.2, 5.1\) Hz, 1H), 1.94 – 1.85 (m, 1H), 1.70 – 1.59 (m, 2H), 1.47 (s, 3H), 1.31 (s, 3H). \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 144.7, 128.9, 128.6 (q, \(J = 32.4\) Hz), 125.7 (q, \(J = 3.52\) Hz), 124.4 (q, \(J = 271.81\) Hz), 80.0, 56.0, 41.6, 36.8, 31.9, 30.7, 25.3. HRMS (ESI) \(m/z\) calculated for C\(_{14}\)H\(_{22}\)F\(_{3}\)N\(_2\)O\(_3\)S [M+NH\(_4^+\)]\(^+\) 355.1298, found 355.1308.

**Compound 29a.** The product was purified by column chromatography using 10% EtOAc in hexanes. The resulting colorless oil was obtained in 51% yield based on NMR integrations using mesitylene as an internal standard and (tpa)AgOTf as the catalyst. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.35 – 7.28 (m, 2H), 7.26 – 7.18 (m, 5H), 6.91 (d, \(J = 8.8\) Hz, 2H), 4.88 – 4.81 (m, 1H), 4.72 (ddd, \(J = 12.0, 9.1, 3.0\) Hz, 1H), 4.08 (d, \(J = 9.1\) Hz, 1H), 3.81 (s, 3H), 2.87 (ddd, \(J = 14.2, 9.2, 5.2\) Hz, 1H), 2.78 (ddd, \(J = 13.9, 8.9, 7.6\) Hz, 1H), 2.14 (dt, \(J = 14.1, 8.8, 5.0\) Hz, 1H), 2.01 (dt, \(J = 14.4, 2.6\) Hz, 1H), 1.98 – 1.87 (m, 2H). \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 160.1, 140.5, 130.2, 128.8, 128.7, 127.7, 126.5, 114.6, 83.2, 57.8, 55.5, 37.2, 36.4, 30.8, 29.9. HRMS (ESI) \(m/z\) calculated for C\(_{18}\)H\(_{25}\)N\(_2\)O\(_4\)S [M+NH\(_4^+\)]\(^+\) 365.1530, found 365.1527.
**Compound 29b.** The product was purified by column chromatography using 10% EtOAc in hexanes. The resulting colorless oil was obtained in 23% yield based on NMR integrations using mesitylene as an internal standard and (4-Bubipy)$_2$AgOTf as the catalyst. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.43–7.34 (m, 3H), 7.34–7.30 (m, 2H), 7.13 (d, $J$ = 8.5 Hz, 2H), 6.86 (d, $J$ = 8.6 Hz, 2H), 4.85 (tdd, $J$ = 9.0, 3.9, 1.9 Hz, 1H), 4.78 (ddd, $J$ = 12.1, 9.2, 2.9 Hz, 1H), 4.13 (dd, $J$ = 8.2, 6.7 Hz, 1H), 3.80 (s, 3H), 2.81 (ddd, $J$ = 14.0, 8.9, 5.2 Hz, 1H), 2.73 (dt, $J$ = 14.0, 8.1 Hz, 1H), 2.12 (dtdd, $J$ = 14.0, 8.7, 5.1 Hz, 1H), 2.06–2.01 (m, 1H), 1.98–1.88 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 158.3, 138.1, 132.4, 129.6, 129.3, 129.1, 126.4, 114.2, 83.2, 58.3, 55.4, 37.4, 36.5, 29.9. HRMS (ESI) $m/z$ calculated for C$_{18}$H$_{25}$N$_2$O$_4$S [M+NH$_4$]$^+$ 365.1530, found 365.1526.

![Image of compound 29b]

**Compound 30a and 30b.** The product mixture was inseparable by column chromatography using (tpa)AgOTf as the catalyst. The yields were based on NMR integrations using mesitylene as an internal standard. Compound 30a formed in 45% yield and 30b formed in 31% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.42–7.34 (m, 3H), 7.34–7.29 (m, 3H), 7.25–7.17 (m, 5H), 7.11 (q, $J$ = 8.1 Hz, 4H), 4.86 (dddd, $J$ = 11.3, 8.7, 3.8, 2.3 Hz, 1.8H), 4.75 (dddd, $J$ = 17.0, 12.2, 9.2, 3.0 Hz, 1.8H), 4.17 (d, $J$ = 9.3 Hz, 1H), 4.13 (d, $J$ = 9.3 Hz, 0.8H), 2.91–2.70 (m, 4H), 2.35 (s, 2.4H), 2.33 (s, 3H), 2.13 (dtdd, $J$ = 14.0, 8.7, 6.8, 5.2 Hz, 2H), 2.02 (ddt, $J$ = 15.4, 10.2, 2.7 Hz, 2H), 1.98–1.88 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.5, 139.0, 138.1, 137.3, 136.0, 135.2, 129.9, 129.5, 129.4, 129.3, 129.1, 128.8, 128.7, 128.6, 126.5, 126.4, 126.3, 83.3, 83.2,
77.2, 58.3, 58.1, 37.3, 37.2, 36.4. HRMS (ESI) m/z calculated for C_{18}H_{25}N_{2}O_{3}S [M+NH_{4}]^{+} 349.1581, found 349.1587.

**Compound 31a.** The product was purified by column chromatography using 10% EtOAc in hexanes. The resulting colorless oil was obtained in 34% yield based on NMR integrations using mesitylene as an internal standard and (4'-Bubipy)_{2}AgOTf as the catalyst. \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.53 (d, J = 8.4 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.25 – 7.18 (m, 5H), 4.89 – 4.81 (m, 1H), 4.74 (ddd, J = 12.1, 9.2, 2.8 Hz, 1H), 4.19 (d, J = 9.2 Hz, 1H), 2.87 (ddd, J = 14.0, 9.0, 5.1 Hz, 1H), 2.77 (dt, J = 13.8, 8.2 Hz, 1H), 2.14 (ddt, J = 14.1, 8.8, 5.2 Hz, 1H), 2.05 – 2.00 (m, 1H), 2.00 – 1.85 (m, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 140.3, 137.1, 132.5, 128.8, 128.7, 128.1, 126.6, 123.1, 83.2, 57.7, 37.1, 36.2, 30.7. HRMS (ESI) m/z calculated for C\(_{17}\)H\(_{23}\)BrN\(_{2}\)O\(_{3}\)S [M+NH\(_{4}\)]\(^{+}\) 413.0530, found 413.0535.

**Compound 31b.** The product was purified by column chromatography using 10% EtOAc in hexanes. The resulting colorless oil was obtained in 58% yield based on NMR integrations using mesitylene as an internal standard and (tpa)AgOTf as the catalyst. \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.43 (d, J = 8.3 Hz, 2H), 7.41 – 7.30 (m, 5H), 7.08 (d, J = 8.3 Hz, 2H), 4.87 – 4.80 (m, 1H), 4.77 (ddd, J = 12.1, 9.3, 3.1 Hz, 1H), 4.23 (d, J = 9.3 Hz, 1H), 2.83 (ddd, J = 14.0, 9.1, 5.0 Hz, 1H), 2.74 (dt, J = 13.9, 8.2 Hz, 1H), 2.11 (ddt, J = 14.1, 8.9, 5.0 Hz, 1H), 2.02 (dt, J = 14.3, 2.5 Hz,
1H), 1.97 – 1.86 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 139.3, 138.0, 131.9, 130.4, 129.3, 129.1, 126.4, 120.3, 82.9, 58.3, 36.9, 36.4, 30.2. HRMS (ESI) m/z calculated for C$_{17}$H$_{22}$BrN$_2$O$_3$S [M+NH$_4$]$^+$ 413.0530, found 413.0528.

![Compound 32a](image)

**Compound 32a.** The product was purified by column chromatography using 10% EtOAc in hexanes. The resulting colorless oil was obtained in 21% yield based on NMR integrations using mesitylene as an internal standard and (4'-Bubipy)$_2$AgOTf as the catalyst. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.60 (d, $J$ = 8.1 Hz, 2H), 7.40 (d, $J$ = 8.1 Hz, 2H), 7.25 (dd, $J$ = 8.2, 6.8 Hz, 2H), 7.18 – 7.12 (m, 3H), 4.86 – 4.74 (m, 2H), 4.17 (d, $J$ = 9.2 Hz, 1H), 2.81 (ddd, $J$ = 14.0, 9.0, 5.1 Hz, 1H), 2.72 (dt, $J$ = 13.8, 8.2 Hz, 1H), 2.09 (dt, $J$ = 14.1, 8.8, 5.2 Hz, 1H), 2.00 (dt, $J$ = 14.2, 2.5 Hz, 1H), 1.95 – 1.81 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.8, 140.2, 131.4 (q, $J$=32.7 Hz), 128.9, 128.7, 126.9, 126.6, 126.3 (q, $J$=3.7 Hz), 123.8 (q, $J$=272.1 Hz), 83.2, 57.8, 37.1, 36.3, 30.7. HRMS (ESI) m/z calculated for C$_{18}$H$_{22}$F$_3$N$_2$O$_3$S [M+NH$_4$]$^+$ 403.1298, found 403.1302.

![Compound 32b](image)

**Compound 32b.** The product was purified by column chromatography using 10% EtOAc in hexanes. The resulting colorless oil was obtained in 61% yield based on NMR integrations using mesitylene as an internal standard using (tpa)AgOTf as the catalyst. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.57 (d, $J$ = 8.0 Hz, 2H), 7.43 – 7.35 (m, 3H), 7.35 – 7.30 (m, 4H), 4.84 (ddt, $J$ = 11.8, 9.2, 3.0
4.78 (ddd, J = 12.2, 9.3, 3.1 Hz, 1H), 4.28 (d, J = 9.3 Hz, 1H), 2.94 (ddd, J = 14.1, 9.2, 5.0 Hz, 1H), 2.84 (dt, J = 13.9, 8.3 Hz, 1H), 2.14 (ddt, J = 14.2, 9.0, 5.0 Hz, 1H), 2.03 (dt, J = 14.3, 2.8 Hz, 1H), 2.00 – 1.91 (m, 2H). ^13^C NMR (126 MHz, CDCl$_3$) δ 144.5, 137.9, 129.4, 129.1, 129.0, 126.4, 125.7 (q, J = 3.8 Hz), 124.4 (q, J = 272 Hz), 82.9, 58.3, 36.8, 36.4, 30.6. HRMS (ESI) m/z calculated for C$_{18}$H$_{22}$F$_3$N$_2$O$_3$S [M+NH$_4$]$^+$ 403.1298, found 403.1298.

V. Probing the Mechanism of Silver-Catalyzed Nitrene Transfer.

**Precursor for Compound 33:** (6-Z)-Oct-6-en-3-ol. The product was purified by column chromatography using a 0  30% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 10% yield from 4-hexen-1-al, which was used crude from a Swern oxidation of (Z)-4-hexen-1-ol. ^1^H NMR (500 MHz, CDCl$_3$) δ 5.52 – 5.44 (m, 1H), 5.41 (dtd, J = 10.7, 7.0, 1.6 Hz, 1H), 3.55 (tt, J = 8.0, 4.5 Hz, 1H), 2.24 – 2.08 (m, 2H), 1.66 – 1.60 (m, 3H), 1.58 – 1.41 (m, 4H), 1.40 (s, 1H), 0.95 (t, J = 7.5 Hz, 3H). ^13^C NMR (126 MHz, CDCl$_3$) δ 130.2, 124.4, 73.1, 36.6, 30.2, 23.2, 12.8, 9.9. HRMS (EI) m/z calculated for C$_8$H$_{17}$O [M+H]$^+$ 129.1279, found 129.1282.

**Compound 33.** The product was purified by column chromatography using a 0  30% gradient of EtOAc in hexanes with 5% increments. The resulting clear oil was obtained in 25% yield from the corresponding alcohol. ^1^H NMR (500 MHz, CDCl$_3$) δ 5.56 – 5.43 (m, 1H), 5.37 (dtq, J =
10.7, 7.2, 1.8 Hz, 1H), 4.63 (s, 2H), 4.61–4.55 (m, 1H), 2.16 (p, $J = 7.6$ Hz, 2H), 1.87–1.68 (m, 4H), 1.62 (ddt, $J = 6.9$, 1.9, 1.0 Hz, 3H), 0.99 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 128.9, 125.1, 86.1, 33.2, 26.9, 22.4, 12.8, 9.1. HRMS (ESI) $m/z$ calculated for C$_8$H$_{21}$N$_2$O$_3$S [M+NH$_4$]$^+$ 225.1268, found 225.1262.

**Compound 34.** The product was obtained in 71% yield (5.5:1 syn:anti) using (tpa)AgOTf as the catalyst and in 50% yield (3.3:1 syn:anti) using (4-tBubipy)$_2$AgOTf as the catalyst. Major isomer:$^1$H NMR (500 MHz, CDCl$_3$) δ 5.74 (dqd, $J = 10.8$, 7.0, 1.2 Hz, 1H), 5.22 (ddq, $J = 10.4$, 8.4, 1.8 Hz, 1H), 4.72 (ddddd, $J = 12.2$, 7.3, 5.1, 2.1 Hz, 1H), 4.60–4.48 (m, 1H), 3.90 (d, $J = 9.7$ Hz, 1H), 1.83–1.65 (m, 6H), 1.53 (dt, $J = 14.4$, 11.9 Hz, 1H), 1.02 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 130.6, 127.0, 85.4, 51.8, 35.5, 28.4, 13.6, 9.0. HRMS (ESI) $m/z$ calculated for C$_8$H$_{19}$N$_2$O$_3$S [M+NH$_4$]$^+$ 223.1111, found 223.1114.

**Synthesis of the Products 36a and 36b from the stereochemical probe 35.** The stereochemical probe containing a defined 3˚C–H bond 35 was synthesized from (-)-citronellal as described above.$^{10}$ The same synthesis was completed starting from racemic citronellol after oxidation to the aldehyde. The Grignard addition resulted in a 1.2:1 mixture of diastereomers that was confirmed by both $^1$H NMR and HPLC analysis, and the two diastereomers could be separated via column chromatography.
Precursor to compound 35: (4S)-4,8-dimethyl-1-phenylnonan-2-ol. The alcohol was purified by column chromatography using a 0→10% gradient of EtOAc in hexanes with 2% increments. The resulting colorless oil was isolated in 93% yield and 1.2:1 dr. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.36 – 7.28 (m, 4H), 7.25 – 7.20 (m, 7H), 3.99 – 3.84 (m, 2H), 2.84 (dd, $J = 13.7, 4.0$ Hz, 2H), 2.80 (dd, $J = 13.6, 4.3$ Hz, 2H), 2.66 (dd, $J = 13.6, 8.4$ Hz, 1H), 2.60 (dd, $J = 13.6, 8.6$ Hz, 1H), 1.73 – 1.61 (m, 2H), 1.58 – 1.47 (m, 6H), 1.47 – 1.38 (m, 4H), 1.38 – 1.20 (m, 8H), 1.20 – 1.04 (m, 7H), 0.93 (d, $J = 6.7$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 4H), 0.86 (dd, $J = 6.6, 1.8$ Hz, 13H).$^{13}$C NMR (126 MHz, CDCl$_3$) δ 138.8, 138.8, 129.6, 129.6, 128.7, 126.6, 126.6, 126.6, 126.6, 70.9, 70.5, 45.0, 44.7, 44.5, 44.4, 39.4, 39.4, 38.2, 36.9, 29.8, 29.4, 28.1, 24.9, 24.7, 22.9, 22.9, 22.8, 22.7, 20.5, 19.4. HRMS (ESI) $m/z$ calculated for $C_{17}H_{32}NO$ [M+NH$_4$]$^+$ 266.2479, found 266.2472.

Compound 35. The product was purified by column chromatography using a 0→25% gradient of EtOAc in hexanes with 5% increments. The resulting colorless oil was obtained in 81% yield.
from the corresponding alcohol as an inseparable mixture of diastereomers (1.2:1 \textit{dr}). $^1$H NMR (500 MHz, CDCl$_3$) \(\delta\) 7.37 – 7.31 (m, 5H), 7.29 – 7.26 (m, 5H), 4.87 (major, dddd, \(J = 8.6, 7.3, 5.8, 4.1\) Hz, 1.2H), 4.84 – 4.78 (minor, m, 1H), 3.97 (major, s, 2.4H), 3.91 (minor, s, 2H), 3.07 – 2.98 (m, 3H), 2.92 (dd, \(J = 14.1, 8.2\) Hz, 1H), 1.79 (major, dddd, \(J = 14.2, 8.7, 4.5\) Hz, 1.2H), 1.66 (tdd, \(J = 11.2, 8.1, 5.3\) Hz, 4H), 1.51 (dtd, \(J = 13.3, 6.7, 4.5\) Hz, 2H), 1.39 (dtd, \(J = 14.2, 9.1, 4.0\) Hz, 1H), 1.35 – 1.19 (m, 5H), 1.19 – 1.06 (m, 7H), 0.95 (minor, d, \(J = 6.1\) Hz, 3H), 0.92 (major, d, \(J = 6.5\) Hz, 3.7H), 0.86 (dd, \(J = 6.6, 3.2\) Hz, 13H). $^{13}$C NMR (126 MHz, CDCl$_3$) \(\delta\) 137.5, 137.5, 129.9, 128.8, 127.2, 84.9, 84.7, 42.4, 42.2, 41.8, 41.1, 39.3, 39.3, 37.7, 37.0, 29.5, 29.1, 28.1, 24.7, 24.5, 22.8, 22.8, 22.7, 19.9, 19.5. HRMS (ESI) \(m/z\) calculated for C$_{17}$H$_{33}$N$_2$O$_3$S [M+NH$_4$]$^+$ 345.2207, found 345.2205.

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\text{Compound 36a.} \text{ The reaction was run using (4-`}Bubipy)$_2$AgOTf as the catalyst. The product was purified by column chromatography using a 0\(\rightarrow\)25\% gradient of EtOAc in hexanes with 5\% increments. The resulting white solid was the minor diastereomer obtained in 38\% yield and 95\% ee from the corresponding sulfamate. Similar results were obtained using (tpa)AgOTf as the catalyst. $^1$H NMR (500 MHz, CDCl$_3$) \(\delta\) 7.32 (dd, \(J = 8.0, 6.5\) Hz, 2H), 7.30 – 7.23 (m, 1H), 7.23 – 7.19 (m, 2H), 5.06 (dtd, \(J = 9.9, 6.4, 3.1\) Hz, 1H), 3.95 (s, 1H), 3.12 (dd, \(J = 14.1, 6.3\) Hz, 1H), 2.90 (dd, \(J = 14.1, 6.5\) Hz, 1H), 1.61 – 1.48 (m, 3H), 1.45 – 1.40 (m, 5H), 1.40 – 1.23 (m, 2H), 1.15 (q, \(J = 7.0\) Hz, 2H), 0.87 (d, \(J = 6.6\) Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) \(\delta\) 135.3, 129.6, 128.9, 127.3, 80.9, 58.5, 45.3, 41.7, 39.9, 39.1, 27.9, 22.7, 22.7, 22.6, 20.4. HRMS (ESI) \(m/z\) calculated for C$_{17}$H$_{27}$NO$_3$S [M+NH$_4$]$^+$ 343.2050, found 343.2049.

S1-52
Compound 36b. The reaction was run using (4-tBubipy)$_2$AgOTf as the catalyst. The product was purified by column chromatography using a 0→25% gradient of EtOAc in hexanes with 5% increments. The resulting white solid was the major diastereomer, obtained in 47% yield and 95% ee from the corresponding sulfamate. Similar results were obtained using (tpa)AgOTf as the catalyst. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32 (dd, $J$ = 8.1, 6.6 Hz, 2H), 7.26 (t, $J$ = 3.6 Hz, 1H), 7.23 – 7.19 (m, 2H), 5.04 (dd, $J$ = 12.0, 6.5, 1.9 Hz, 1H), 3.93 (s, 1H), 3.13 (dd, $J$ = 14.0, 6.2 Hz, 1H), 2.88 (dd, $J$ = 14.0, 6.8 Hz, 1H), 2.05 (ddd, $J$ = 13.7, 11.2, 4.0 Hz, 1H), 1.67 (dd, $J$ = 14.4, 1.9 Hz, 1H), 1.59 – 1.40 (m, 3H), 1.38 – 1.30 (m, 1H), 1.22 – 1.07 (m, 6H), 0.84 (dd, $J$ = 6.5, 1.3 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 135.3, 129.6, 128.9, 127.3, 80.7, 58.5, 41.7, 40.6, 39.1, 36.6, 28.9, 27.9, 22.7, 22.7, 21.5. HRMS (ESI) $m/z$ calculated for C$_{17}$H$_{27}$NO$_3$S [M+NH$_4$]$^+$ 343.2050, found 343.2047.

The relative configurations of the products were confirmed based on nOe $^1$H NMR experiments (500 MHz, CDCl$_3$) and matched previously published nOe data for a similar citronellol-derived substrate.$^{10}$
Quantitative determination of stereoretention was accomplished via achiral HPLC analysis. Racemic citronellol was used to determine the initial enantioselectivity of (-)-citronellal after it had been reduced to the alcohol and was measured to be 95% ee. The racemic version of substrate 35 was subjected to the standard reaction conditions with 'Bubipy or tpa and the diastereomers at the ether position were first separated via column chromatography. Each diastereomer and its enantiomer were resolved via achiral HPLC analysis and used as a baseline separation for the enantoienriched products.

After the enantoienriched substrate was subjected to the standard reaction conditions, the diastereomers of the product (36a and 36b) were separated via column chromatography and then run on the HPLC to determine if any enantiomer was present in either of the two HPLC traces. If the stereochemistry at the 3° position was destroyed, the enantiomer would be present in the other diastereomer’s HPLC trace. The reactions were performed twice and an average enantioselectivity was reported for each transformation. Sample HPLC traces are shown on the pages following this discussion. The small differences in enantioselectivity between substrate 35 and the products 36a and 36b are within experimental error and suggest there are no long-lived radical intermediates in the reaction pathway.

**HPLC Traces.**

| Citronellol:          |                  |
|----------------------|------------------|

S1-54
Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiracel OJ-H column. Flow rate: 0.5 mL/min.; Oven temp: 25.0 °C; Solvent: isocratic 1.0% iPrOH in hexanes; Detector: UV @ 215 nm
Compound 36a:

Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiracel AD-H column. Flow rate: 1.0 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 3% iPrOH in hexanes; Detector: UV @ 215 nm
Compound 36b:

(racemic)

**Conditions:** Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiracel AD-H column. Flow rate: 1.0 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 3% iPrOH in hexanes; Detector: UV @ 215 nm
Precursor for Compound 37: 1-(1-Hydroxycylopropyl)-2-(2,2-diphenylcyclopropyl)ethane.

A 50 mL roundbottom flask equipped with a condenser under a flow of N\textsubscript{2} was charged with 2.88 g (22.4 mmol) ethyl-4-pentenoate and 5 mL benzene. Diazodiphenylmethane (30 mmol) in 10 mL benzene was added via syringe pump overnight (1.5 mL/h) to the ester solution at reflux. The solution was then cooled to rt and diluted with 60 mL of hexane to precipitate any undesired side products. The mixture was filtered, the filtrate concentrated and diluted with 20 mL of EtOH. The mixture was filtered again and the filtrate concentrated in vacuo to yield 1.32 g crude ethyl-3-(2,2-diphenylcyclopropyl)propanoate. The residue was carried on to the next step without further purification.

Titanium isopropanoxide (0.14 mL, 0.46 mmol) was added to the crude ester in 15 mL diethyl ether under N\textsubscript{2} at rt. A solution of 6.1 mL of 1.5 M ethylmagnesium bromide in diethyl ether was added dropwise over 1 h; the solution darkened over the course of the addition. The mixture was stirred for an additional 15 min and then poured into 50 mL of ice cold 5\% H\textsubscript{2}SO\textsubscript{4}. The aqueous mixture was extracted with 3 x 15 mL diethyl ether and the combined organic layers were washed with 25 mL brine, and then dried with MgSO\textsubscript{4}, filtered, and concentrated in vacuo. The product was purified by column chromatography using 1\% MeOH in CH\textsubscript{2}Cl\textsubscript{2} to yield the alcohol in 9\% yield over the 2 steps. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.34 – 7.28 (m, 4H), 7.25 – 7.16 (m, 6H), 1.77 – 1.56 (m, 5H), 1.25 – 1.19 (m, 2H), 1.13 – 1.00 (m, 1H), 0.71 – 0.59 (m, 2H), 0.41 – 0.34 (m, 1H), 0.34 – 0.26 (m, 1H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 147.3, 141.6, 130.5, 128.2, 127.8, 126.3, 125.6, 55.6, 38.0, 35.6, 27.2, 26.1, 20.6, 13.7, 13.5. HRMS (EI) m/z calculated for C\textsubscript{20}H\textsubscript{22}O [M]+ 278.1664, found 278.1668.
**Compound 37.** The product was purified by column chromatography using a 10→40% gradient of Et₂O in hexanes in two portions. The resulting colorless oil was obtained in 66% yield from the corresponding alcohol. ¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.10 (m, 10H), 4.45 (s, 2H), 1.97 (ddd, J = 15.6, 10.8, 5.3 Hz, 1H), 1.89 (s, 1H), 1.72 – 1.61 (m, 1H), 1.58 – 1.43 (m, 1H), 1.35 – 1.13 (m, 7H), 0.93 – 0.78 (m, 1H), 0.62 – 0.47 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 147.06, 141.64, 130.50, 128.22, 128.20, 128.05, 126.26, 125.81, 71.50, 67.18, 35.75, 35.10, 26.61, 25.71, 20.01, 11.80, 11.79. HRMS (EI) m/z calculated for C₂₀H₂₃NO₅S [M + NH₄]⁺ 375.1737, found 375.1743.

**Compound 38.** The compound was isolated as an approximately 1:1 mixture of diastereomers using both (tpa)AgOTf and (4-tBubipy)₂AgOTf as catalysts. The product was purified via column chromatography with a gradient of 0-50% ethyl acetate/hexane. The mixture was isolated in 43% total yield using (4-tBubipy)₂AgOTf as the catalyst (1.9:1 dr) and 64% yield using (tpa)AgOTf (1.1:1 dr). ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.47 (m, 2H), 7.35 – 7.29 (m, 3H), 7.29 – 7.19 (m, 14H), 7.18 – 7.12 (m, 1H), 4.31 (d, J = 9.8 Hz, 1H), 4.22 (d, J = 10.3 Hz, 1H), 3.08 (dtt, J = 10.9, 9.8, 3.2 Hz, 1H), 2.91 – 2.80 (m, 1H), 2.41 – 2.23 (m, 2H), 1.80 – 1.66 (m, 3H), 1.42 (d, J = 9.1, 5.1 Hz, 1H), 1.37 (t, J = 3.2 Hz, 1H), 1.33 (t, J = 3.1 Hz, 1H), 1.30 – 1.26 (m, 2H), 1.25 – 1.19 (m, 2H), 1.16 – 1.05 (m, 2H), 1.04 – 0.95 (m, 1H), 0.91 – 0.85 (m,
1H), 0.71 – 0.53 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.36, 144.06, 138.92, 138.57, 129.31, 128.44, 127.60, 127.51, 127.49, 127.45, 127.42, 126.83, 126.31, 126.07, 125.59, 125.36, 64.94, 64.77, 55.72, 55.34, 35.85, 35.62, 35.26, 34.76, 28.68, 28.47, 27.73, 16.59, 16.46, 11.69, 11.33, 10.07, 9.87. HRMS (El) $m/z$ calculated for C$_{20}$H$_{21}$NO$_3$S [M + NH$_4$]$^+$ 373.1581, found 373.1582.

VI. Hammett Plot.
VII. References.

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