Supporting Information for:

Tunable, Chemoselective Amination *via* Silver Catalysis

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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 CaH_2 and freshly distilled prior to use. All other solvents were purified in accordance with "Purification of Laboratory Chemicals".[1] 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 F_{254} plates containing a fluorescent indicator, while preparative chromatography was performed using SilicaFlash P60 silica gel (230-400 mesh) via Still's method.[2] 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, $KMnO_4$, ceric ammonium molybdate (CAM stain) and iodine powder.

^{1}H NMR and ^{13}C NMR spectra were obtained using Bruker-300, Varian-400, Varian Inova-500, or Varian Unity-500 spectrometers. For ^{1}H NMR, chemical shifts are reported relative to residual protiated solvent peaks (δ 7.26, 2.49, 7.15 and 7.09 ppm for $CDCl_3$, $(CD_3)_2SO$, C_6D_6 and $CD_3C_6D_5$ respectively). ^{13}C NMR spectra were measured at either 125 MHz, 100 MHz or 75 MHz on the same instruments noted above for recording ^{1}H 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 $CDCl_3$, $(CD_3)_2SO$, C_6D_6, and $CD_3C_6D_5$, respectively). Chiral HPLC was carried out using an AD-H column at 40^{o}C (4.6 μm diameter × 258 mm) using one of three different

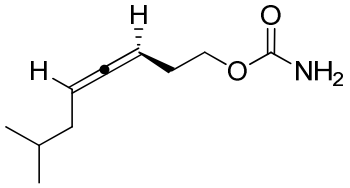
mobile phases: 98.8% hexanes/1.2% ^{i}PrOH at 0.6 mL/min, 99.0% hexanes/1.0% ^{i}PrOH at 0.6 mL/min or a gradient starting at 5% isopropyl alcohol in hexanes for 10 min (1.0 mL/min) and increasing to 30% isopropyl alcohol in hexanes. In this last case, the eluant was held at 30% isopropyl alcohol in hexanes until the run was completed. Detection of the signal was performed at both 215 and 225 nm. 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). The MALDI spectra were obtained using a Bruker ULTRAFLEX® III: Matrix-assisted laser desorption/ionization (MALDI), time-of-flight time-of-flight (TOF/TOF). The ULTRAFLEX is equipped with a SmartBeam® laser and anthracene was used as the matrix. The ULTRAFLEX purchase was partially funded by NIH NCRR 1S10RR024601-01 Award to the University of Wisconsin Department of Chemistry. 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 Homoallenic Carbamates

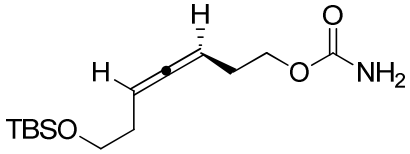
General procedure for the synthesis of allene carbamates. The allene alcohol (between 0.5 g and 3.0 g, 1 equiv) was dissolved in dichloromethane (0.3 M) and placed in an ice bath. Trichloroacetylisocyanate (1.2 equiv) was slowly added dropwise. The reaction was stirred with cooling in the ice bath until TLC indicated complete consumption of the starting material. The solvent was then removed and the crude reaction was dissolved in methanol (0.4 M). Potassium carbonate (0.5 equiv) was then added to the reaction and the mixture stirred at room temperature until TLC indicated complete consumption of the starting material. Water was added to the reaction and the mixture was extracted with three portions of dichloromethane. The organic

phase was dried with sodium sulfate and concentrated under reduced pressure. The crude products were purified by silica gel column chromatography.

Compounds 3a-3g and **3i** were synthesized according to previously reported procedures.[3-7]



Compound 3h. 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 90% yield from the corresponding homoallenic alcohol. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12-5.01 (m, 2H), 4.79 (br s, 2H), 4.12 (t, *J* = 6.8 Hz, 2H), 2.31 (qd, *J* = 6.8, 2.9 Hz, 2H), 1.91 (ddd, *J* = 14.1, 6.8, 2.7 Hz, 1H), 1.86 (ddd, *J* = 14.1, 6.8, 2.7 Hz, 1H), 1.65 (non, *J* = 6.8 Hz, 1H), 0.91 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 205.2, 157.1, 90.3, 85.9, 64.5, 38.3, 28.7, 28.4, 22.2, 22.1. HRMS (ESI) *m/z* calculated for $C_{10}H_{17}NO_2$ [M+Na^+] 206.1152, found 206.1156.



Compound 3j. 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 85% yield from the corresponding homoallenic alcohol. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.14 (qt, *J* = 6.9, 2.8 Hz, 1H), 5.07 (qt, *J* = 6.9, 2.8 Hz, 1H), 4.78 (br s, 2H), 4.11 (t, *J* = 6.8 Hz, 2H), 3.67 (t, *J* = 6.9 Hz, 2H), 2.31 (qd, *J* = 6.9, 2.8 Hz, 2H), 2.21 (qd, *J* = 6.8, 2.8 Hz, 2H), 0.90 (s, 9H), 0.06 (s,

6H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 205.5, 157.2, 88.5, 86.7, 64.5, 63.1, 32.7, 28.7, 26.1, 18.5, -5.1. HRMS (ESI) *m/z* calculated for $C_{14}H_{27}NO_3Si$ [$M+NH_4^+$] 303.2099, found 303.2090.

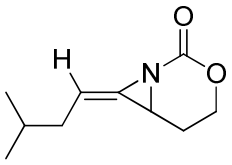
III. Synthesis of Bicyclic Methylene Aziridines

For best results, the silver to ligand ratio needs to be exact. Both silver triflate and phenanthroline are highly hydroscopic and will not give good results if they are not completely dry. Silver reagents should be stored in a dry box and phenanthroline 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.

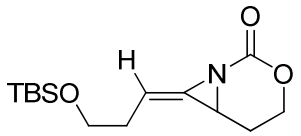
General procedure for Ag-catalyzed allene aziridination. A pre-dried reaction flask was charged with silver triflate (26.0 mg, 0.1 mmol, 0.20 equiv) and phenanthroline (23.0 mg, 0.125 mmol, 0.25 equiv). Dichloromethane (3 mL) was added and the mixture was stirred vigorously for 30 min. A solution of the homoallenic carbamate (0.5 mmol, 1 equiv) in dichloromethane (3 mL) was added to the reaction flask, followed by either 3Å or 4Å molecular sieves (1 mmol substrate/g of sieves or 0.25 mmol substrate/g of sieves). Iodosobenzene (220 mg, 1 mmol, 2 equiv) was added in one portion and the reaction mixture was allowed to stir at room temperature until TLC indicated complete consumption of the starting material (~14-16 h). The reaction mixture was filtered through a glass frit and the filtrate was concentrated under reduced pressure. The crude products were purified by silica gel column chromatography using a hexane/EtOAc gradient.

When Rh-based catalysis was used in the amination reactions for comparison to Ag-catalyzed reactions, the reader is referred to references 4-6 for details on the specific experimental conditions.

Compounds 4a-g, i were synthesized according to previously reported procedures.[6]



Compound 4h. The product was purified by column chromatography using a 0 → 20% gradient of EtOAc in hexanes with 5% increments. The resulting product was obtained in 57% yield as a 2.5:1 mixture of diastereomers. *E* diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (t, *J* = 8.0 Hz, 1H), 3.57 (td, *J* = 11.5, 2.0 Hz, 1H), 3.41 (dt, *J* = 10.5, 3.0 Hz, 1H), 2.59 (dd, *J* = 8.4, 6.9 Hz, 1H), 1.84-1.76 (m, 1H), 1.76-1.69 (m, 1H), 1.42 (sep, *J* = 6.8 Hz, 1H), 1.06-1.00 (m, 1H), 0.89-0.83 (m, 1H), 0.76 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 154.9, 126.9, 100.6, 67.9, 38.5, 37.4, 28.3, 23.5, 22.0, 21.9; HRMS (ESI) *m/z* calculated for $C_{10}H_{15}NO_2$ [M^+] 181.1098, found 181.1088.

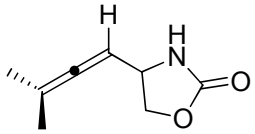


Compound 4j. The product was purified by column chromatography using a 0 → 30% gradient of EtOAc in hexanes with 6% increments. The product was obtained in 58% yield as a 1.7:1 mixture of diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 (t, *J* = 7.4 Hz, 1H), 3.54 (t, *J* = 11.1 Hz, 1H), 3.45-3.37 (m, 3H), 2.60 (dd, *J* = 8.3, 6.7 Hz, 1H), 2.11 (q, *J* = 7.4 Hz, 2H) 1.08-0.99 (m, 1H), 0.95 (s, 9H), 0.88-0.80 (m, 1H), 0.02 (s, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 153.5, 97.4, 66.7, 61.3, 37.4, 30.8, 24.8, 22.3, 17.0, -0.06, -1.46, -6.6; HRMS (ESI) *m/z* calculated for $C_{14}H_{25}NO_3Si$ [$M+H^+$] 284.1677, found 284.1678.

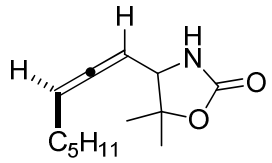
IV. Synthesis of Allenic C-H Insertion Products.

For reproducible results, these reactions are best performed under an inert atmosphere with dry, degassed dichloromethane.

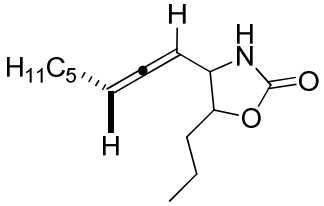
General procedure for Ag-catalyzed allenic C-H Insertion. A pre-dried reaction flask was charged with silver triflate (13.0 mg, 0.5 mmol, 0.1 equiv) and phenanthroline (26.0 mg, 0.15 mmol, 0.3 equiv). Dichloromethane (3 mL) was added to the flask and the mixture was stirred vigorously for 30 min. A solution of the homoallenic carbamate (0.5 mmol, 1 equiv) in dichloromethane (3 mL) was added to the reaction flask, followed by 3Å or 4Å molecular sieves (1 mmol substrate/g of sieves or 0.25 mmol substrate/g of sieves). Iodosobenzene (392 mg, 1.75 mmol, 3.5 equiv) was added in one portion and the reaction mixture was allowed to stir at room temperature until TLC indicated complete consumption of the starting material (~14-16 h). The reaction mixture was filtered through a glass frit and the filtrate concentrated under reduced pressure. The crude products were purified by silica gel column chromatography suing a hexanes/EtOAc gradient.



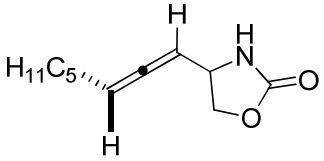
Compound 5a. The product was purified by column chromatography using a 0 → 50% gradient of EtOAc in hexanes with 10% increments. The product was obtained in 81% yield. The proton and carbon NMRs matched reported literature values.[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72 (s, 1H), 5.02 (m, 1H), 4.52 (t, J = 8.3, 1H), 4.32 (m, 1H), 4.15 (dd, J = 8.4, 5.7, 1H), 1.72 (m, 6H).



Compound 5b. The product was purified by column chromatography using a 0 → 30% gradient of EtOAc in hexanes with 6% increments. The product was obtained in 96% yield. The proton and carbon NMRs matched reported literature values.[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.35 (qt, J = 7.4, 2.2 Hz, 2H), 5.12 – 5.01 (m, 1H), 4.03 – 3.94 (m, 1H), 2.02 (qdd, J = 7.4, 4.6, 3.0 Hz, 2H), 1.48 (s, 3H), 1.45 – 1.23 (m, 9H), 0.89 (t, J = 6.7 Hz, 3H).

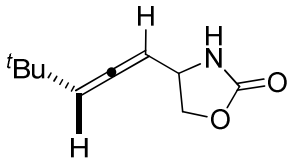


Compound 5c. The product was purified by column chromatography using a 0 → 50% gradient of EtOAc in hexanes with 10% increments. The product was obtained in 76% yield. The proton and carbon NMRs matched reported literature values.[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.54 (s, 1H), 5.52 (s, 1H), 5.34 (m, 1H), 5.10 (m, 1H), 4.63 minor isomer (m, 1H), 4.28 (m, 1H), 3.94 (m, 1H), 2.02 (m, 2H), 1.35 (m, 10H), 0.97 (t, J = 7.5 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H).

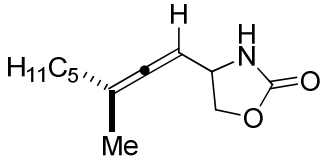


Compound 5d. The product was purified by column chromatography using a 0 → 30% gradient of EtOAc in hexanes with 6% increments. The product was obtained in 71% yield. The proton and carbon NMRs matched reported literature values.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.10-6.00

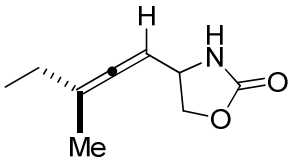
(two br s, 1H), 5.37 (app pd, J = 6.3, 1.3 Hz, 1H), 5.16 (m, 1H), 4.54 (t, J = 8.3 Hz, 1H), 4.38 (qd, J = 6.0, 2.0 Hz, 1H), 4.18 (dd, J = 8.6, 5.7 Hz, 1H), 2.02 (pd, J = 7.4, 2.7 Hz, 2H), 1.44-1.26 (m, 8H), 0.89 (t, J = 6.8 Hz, 3H).



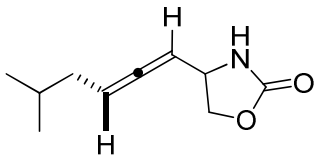
Compound 5e. The product was purified by column chromatography using a 0 → 50% gradient of EtOAc in hexanes with 10% increments. The product was obtained in 83% yield. The proton and carbon NMRs matched reported literature values.[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (br, 1H), 5.40 (dt, J = 6.2, 1.9 Hz, 1H), 5.24 (m, 1H), 4.53 (td, J = 8.3, 1.8 Hz, 1H), 4.36 (m, 1H), 4.19 (ddd, J = 8.5, 5.4, 3.2 Hz, 1H), 1.05 (d, J = 0.6 Hz, 9H).



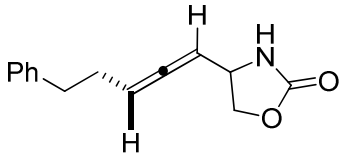
Compound 5f. The product was purified by column chromatography using a 0 → 50% gradient of EtOAc in hexanes with 10% increments. The product was obtained in 88% yield. The proton and carbon NMRs matched reported literature values.[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68 (br, 1H), 5.08 (m, 1H), 4.52 (td, J = 8.3, 2.7 Hz, 1H), 4.32 (m, 1H), 4.15 (ddd, J = 8.4, 5.7, 1.8 Hz, 1H), 1.95 (m, 2H), 1.70 (t, J = 2.6 Hz, 3H), 1.33 (m, 6H), 0.89 (m, 3H).



Compound 5g. The product was purified by column chromatography using a 0 → 50% gradient of EtOAc in hexanes with 10% increments. The product was obtained in 78% yield. The proton and carbon NMRs matched reported literature values.[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.60 (s, 1H), 5.13 (dq, *J* = 6.1 Hz, 1H), 4.52 (td, *J* = 8.2, 2.6 Hz, 1H), 4.32 (m, 1H), 4.16 (m, 1H), 1.98 (m, 2H), 1.72 (m, 3H), 0.98 (td, *J* = 7.4, 5.3 Hz, 3H).

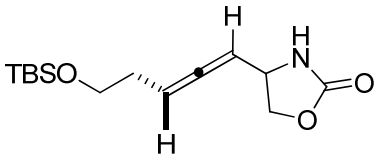


Compound 5h. The product was purified by column chromatography using a 0 → 30% gradient of EtOAc in hexanes with 6% increments. The product was obtained in 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.14-5.99 (br s, 1H), 5.32 (pd, *J* = 7.2, 1.5 Hz, 1H), 5.14 (qd, *J* = 6.4, 2.5 Hz, 1H), 4.54 (t, *J* = 8.5 Hz, 1H), 4.38 (q, *J* = 6.8 Hz, 1H), 4.18 (dd, *J* = 8.5, 5.8 Hz, 1H), 1.93 (qd, *J* = 6.8, 2.5 Hz, 2H), 1.67 (non of d, *J* = 6.8, 2.1 Hz, 1H), 0.92 (d, *J* = 2.1 Hz, 3H), 0.91 (d, *J* = 2.1 Hz, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 204.4, 204.3, 159.7, 159.7, 93.9, 93.8, 90.5, 90.5, 70.4, 52.3, 52.2, 37.9, 37.8, 28.3, 22.1. HRMS (ESI) *m/z* calculated for $C_{10}H_{15}NO_2$ [M+H$^+$] 182.1176, found 182.1169.



Compound 5i. The product was purified by column chromatography using a 0 → 30% gradient of EtOAc in hexanes with 6% increments. The product was obtained in 74% yield as a 1:1 mixture of diastereomers. The proton NMR matches literature values.[6] ^{1}H NMR (500 MHz,

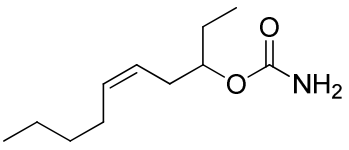
$CDCl_3$) δ 7.30 (td, *J* = 7.0, 2.3 Hz, 2H), 7.24-7.16 (m, 3H), 5.60-5.50 (2 br s, 1H), 5.37 (p, *J* = 7.4 Hz, 1H), 5.12-5.07 (m, 1H), 4.41 (t, *J* = 8.4 Hz, 0.5H), 4.36 (t, *J* = 8.4 Hz, 0.5H), 4.12 (p, *J* = 6.2 Hz, 1H), 4.02 (ddd, *J* = 13.1, 8.4, 5.6 Hz, 1H), 2.81-2.67 (m, 2H), 2.46-2.28 (m, 2H).



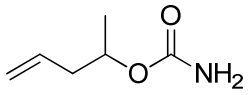
Compound 5j. The product was purified by column chromatography using a 0 → 40% gradient of EtOAc in hexanes with 8% increments. The product was obtained in 62% yield as a 1:1 mixture of diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.07 (br s, 0.5H), 5.95 (br s, 0.5H), 5.34 (dqd, *J* = 10.4, 6.3, 1.7 Hz, 1H), 5.11 (tt, *J* = 6.3, 2.7 Hz, 1H), 4.46 (td, *J* = 8.4, 1.5 Hz, 1H), 4.34-4.27 (m, 1H), 4.11 (dt, *J* = 8.4, 5.4 Hz, 1H), 3.66-3.58 (m, 2H), 2.18 (sd, *J* = 6.9, 2.7 Hz, 2H), 0.84 (d, *J* = 1.8 Hz, 9H), 0.01 (m, 6H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 204.4, 159.5, 92.4, 91.1, 70.3, 62.4, 52.0, 32.2, 25.9, 18.4, 18.3, -5.4. HRMS (ESI) *m/z* calculated for $C_{14}H_{25}NO_3Si$ [M+H$^+$] 284.1677, found 284.1686.

V. Synthesis of Homoallylic Carbamates.

Compounds **6a**, **6c**, and **6d** were synthesized according to published procedures.[8] The synthesis of the homoallylic carbamates was carried out according to the general procedure described for homoallenic carbamates.



Compound 6b. The product was purified by column chromatography using a 0 → 25% gradient of EtOAc in hexanes with 5% increments. The product was obtained in 90% yield as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.57 – 5.41 (m, 1H), 5.41 – 5.29 (m, 1H), 4.83 (s, 2H), 4.69 (dt, *J* = 11.8, 6.1, 6.1 Hz, 1H), 2.31 (t, *J* = 6.7, 6.7 Hz, 3H), 2.04 (q, *J* = 6.3, 6.3, 6.0 Hz, 2H), 1.69 – 1.44 (m, 2H), 1.40 – 1.25 (m, 4H), 0.97 – 0.82 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 132.8, 124.3, 76.2, 31.9, 31.7 27.2, 26.8, 22.5, 14.2, 9.8. HRMS (ESI) *m/z* calculated for $C_{11}H_{21}NO_2$ [M+NH_4^+] 217.1911, found 217.1909.

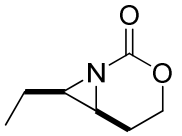


Compound 6e. The product was purified by column chromatography using a 0 → 25% gradient of EtOAc in hexanes with 5% increments. The product was obtained in 91% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.78 (ddt, 1H, *J* = 17.2, 10.3, 7.0 Hz), 5.16–5.03 (m, 2H), 4.84 (appt p, 1H, *J* = 6.3 Hz), 4.81–4.64 (m, 2H), 2.41–2.31 (m, 1H), 2.31–2.23 (m, 1H), 1.23 (d, 3H, *J* = 6.3 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 133.7, 117.7, 70.9, 40.4, 19.7. HRMS (EI) *m/z* calculated for $C_6H_{11}NO_2$ [M+] 129.0785, found 129.0782.

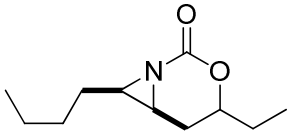
VI. Synthesis of Aziridines.

General procedure. A pre-dried reaction flask was charged with silver triflate (26.0 mg, 0.1 mmol, 0.2 equiv) and phenanthroline (23.0 mg, 0.125 mmol, 0.25 equiv). Dichloromethane (1 mL) was added to the flask and the mixture stirred vigorously for 30 min. A solution of the homoallylic carbamate (0.5 mmol, 1 equiv) in dichloromethane (1 mL) was added to the reaction flask, followed by 3Å or 4Å molecular sieves (1 mmol substrate/g of sieves or 0.25 mmol substrate/g of sieves). Iodosobenzene (220.0 mg, 1 mmol, 2 equiv) was added in one portion and

the reaction mixture was allowed to stir at room temperature until TLC indicated complete consumption of the starting material (~14 h). The reaction mixture was filtered through a glass frit and the filtrate was concentrated under reduced pressure. The crude products were purified by silica gel column chromatography using a hexanes/EtOAc gradient.

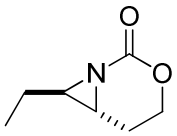


Compound 7a. The product was purified by column chromatography using a 0 → 50% gradient of EtOAc in hexanes with 10% increments. The product was obtained in 67% yield and the proton NMR matched the reported literature values.[8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.36 (m, 2H), 2.87 (ddd, *J* = 9.7, 6.9, 4.9 Hz, 1H), 2.61 (dt, *J* = 8.3, 5.1 Hz, 1H), 2.19 (ddt, *J* = 14.6, 6.9, 2.0 Hz, 1H), 1.87 (dqd, *J* = 13.8, 7.0, 6.6, 5.3 Hz, 1H), 1.48 (dddd, *J* = 14.4, 11.8, 9.0, 5.6 Hz, 1H), 1.23 (m, 1H), 1.11 (m, 3H).

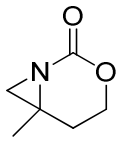


Compound 7b. The product was purified by column chromatography using a 0 → 2% gradient of MeOH in dichloromethane with 0.5% increments. The product was obtained in 89% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.38 (m, 1H), 2.83 (m, 1H), 2.65 (dt, *J* = 9.1, 5.1 Hz, 1H), 2.18 (m, 1H), 2.06 (m, minor isomer), 1.73 (m, 4H), 1.38 (d, *J* = 5.3 Hz, 3H), 1.15 (m, 2H), 1.04 (t, *J* = 9.3 Hz, 3H), 0.93 (t, *J* = 6.6 Hz, 3H). Major Isomer: ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 80.9, 43.7, 37.3, 28.9, 28.0, 25.2, 24.4, 22.6, 14.1, 9.4. Minor Isomer: ^{13}C NMR (126 MHz,

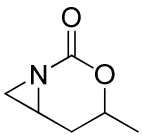
$CDCl_3$) δ 158.7, 81.0, 78.0, 43.5, 34.8, 28.8, 26.9, 24.9, 22.6, 21.5, 14.1. HRMS (ESI) *m/z* calculated for $C_{11}H_{19}NO_2$ [M+H$^+$] 198.1489, found 198.1494.



Compound 7c. The product was purified by column chromatography using a 0 → 100% gradient of EtOAc in hexanes with 20% increments. The product was obtained in 88% yield and the proton NMR matched the reported literature values.[8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.48 – 4.33 (m, 1H), 4.36 – 4.23 (m, 1H), 2.61 (ddd, *J* = 8.9, 6.3, 3.3 Hz, 1H), 2.37 (ddt, *J* = 14.6, 6.2, 1.9, Hz, 1H), 2.24 (td, *J* = 6.0, 3.3 Hz, 2H), 1.63 (p, *J* = 6.8 Hz, 2H), 1.40 (dddd, *J* = 14.5, 12.6, 8.7, 4.3 Hz, 1H), 1.06 (t, *J* = 7.4, 3H).



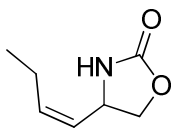
Compound 7d. The product was purified by column chromatography using a 0 → 50% gradient of EtOAc in hexanes with 10% increments. The product was obtained in 85% yield and the proton NMR matched the reported literature values.[8] ^{1}H NMR (300 MHz,) δ 4.45 (ddd, *J* = 12.4, 10.8, 1.9 Hz, 1H), 4.31 (ddd, *J* = 10.7, 4.1, 2.0 Hz, 1H), 2.39 (s, 1H), 2.19 (s, 1H), 2.12 (dt, *J* = 14.5, 1.9 Hz, 1H), 1.49 (m, 1H), 1.38 (s, 3H).



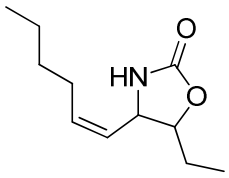
Compound 7e. The product was purified by column chromatography using a 0 → 50% gradient of EtOAc in hexanes with 10% increments. The aziridine was obtained in 51% yield, while the C-H insertion product was obtained in 19% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.64 (dqd, *J* = 11.0, 6.3, 6.3, 1.9 Hz, 1H), 2.76 (m, 1H), 2.56 (d, *J* = 4.3 Hz, 1H), 2.41 (ddd, *J* = 14.4, 6.1, 1.8 Hz, 1H), 2.07 (d, *J* = 3.7 Hz, 1H), 1.37 (d, *J* = 6.3 Hz, 3H), 1.05 (ddd, *J* = 14.4, 11.1, 8.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 76.1, 36.0, 33.7, 32.5, 20.6. HRMS (EI) *m/z* calculated for $C_6H_9NO_2$ [M+H$^+$] 128.0705, found 128.0705.

VII. Synthesis of Allylic C-H Insertion Products.

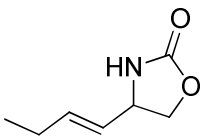
General procedure for Ag-catalyzed allylic C-H insertion. A pre-dried reaction flask was charged with silver triflate (13.0 mg, 0.5 mmol, 0.1 equiv) and phenanthroline (26.0 mg, 0.15 mmol, 0.3 equiv). Dichloromethane (3 mL) was added to the flask and the mixture was stirred vigorously for 30 min. A solution of the homoallylic carbamate (0.5 mmol, 1 equiv) in dichloromethane (3 mL) was added to the reaction flask, followed by 3Å or 4Å molecular sieves (1 mmol substrate/g of sieves or 0.25 mmol substrate/g of sieves). Iodosobenzene (392 mg, 1.75 mmol, 3.5 equiv) was added in one portion and the reaction mixture was allowed to stir at room temperature until TLC indicated complete consumption of the starting material (~14-16 h). The reaction mixture was filtered through a glass frit and the filtrate concentrated under reduced pressure. The crude products were purified by silica gel column chromatography using a hexanes/EtOAc gradient.



Compound 8a. The product was purified by column chromatography using a 0 → 50% gradient of EtOAc in hexanes with 10% increments. The product was obtained in 97% yield and the proton NMR matched the reported literature values.[8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82 (br, 1H), 5.64 (dtd, *J* = 10.9, 7.5, 1.1 Hz, 1H), 5.38 (ddt, *J* = 10.6, 8.9, 1.6 Hz, 1H), 4.74 (m, 1H), 4.52 (t, *J* = 8.5 Hz, 1H), 4.00 (dd, *J* = 8.5, 7.3 Hz, 1H), 2.08 (dddd, *J* = 11.9, 7.4, 5.7, 3.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H).

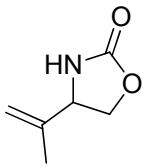


Compound 8b. The product was purified by column chromatography using a 0 → 50% gradient of EtOAc in hexanes with 10% increments. The product was obtained in 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.65 (m, 1H), 5.36 (m, 2H), minor 4.62 (dd, *J* = 9.7, 7.8 Hz, 1H), minor 4.52 (td, *J* = 8.3, 8.1, 4.7 Hz, 1H), major 4.32 (m, 1H), major 4.12 (td, *J* = 7.0, 5.6 Hz, 1H), 2.07 (m, 2H), 1.72 (m, 2H), 1.33 (m, 4H), 1.02 (m, 3H), 0.90 (m, 3H). Major isomer: ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 136.0, 127.4, 84.3, 54.9, 31.8, 27.5, 26.9, 22.5, 14.1, 9.5. Minor isomer: ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 136.1, 124.6, 81.9, 52.6, 31.8, 27.4, 23.7, 22.5, 14.1, 10.4. HRMS (EI) *m/z* calculated for $C_{11}H_{19}NO_2$ [M^+] 197.1411, found 197.1402.

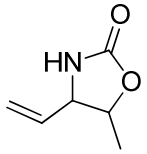


Compound 8c. The product was purified by column chromatography using a 0→25% gradient of EtOAc in hexanes with 5% increments. Obtained in 84% yield combined. Proton matched

reported literature values.[8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (dtd, J = 15.3, 6.3, 0.8 Hz, 1H), 5.66 (s, 1H), 5.41 (ddt, *J* = 15.3, 7.9, 1.6 Hz, 1H), 4.51 (t, *J* = 8.4 Hz, 1H), 4.35 (q, *J* = 7.6 Hz, 1H), 4.03 (dd, *J* = 8.4, 6.9 Hz, 1H), 2.02-2.12 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

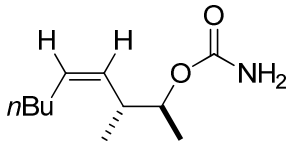


Compound 8d. The product was purified by column chromatography using a 0 → 50% gradient of EtOAc in hexanes with 10% increments. The product was obtained in 66% yield and the proton NMR matched the reported literature values.[8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.10 (s, 1H), 5.03 (bd, *J* = 0.9 Hz, 1H), 4.95 (bs, 1H), 4.54 (t, *J* = 8.7 Hz, 1H), 4.38 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.09 (dd, *J* = 8.4, 6.0 Hz, 1H), 1.76 (s, 3H).

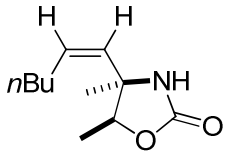


Compound 8e. The product was purified by column chromatography using a 0 → 50% gradient of EtOAc in hexanes with 10% increments. The product was obtained in 68% yield. An analytical sample of the major isomer was obtained as it eluted prior to mixture of isomers. Major: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.92 (s, 1H), 5.79 (ddd, *J* = 17.3, 10.1, 7.5 Hz, 1H), 5.33 (dt, *J* = 17.1, 1.0 Hz, 1H), 5.26 (dt, *J* = 10.2, 0.9 Hz, 1H), 4.33 (dq, *J* = 7.4, 6.3 Hz, 1H), 3.90 (tq, *J* = 7.4, 1.0 Hz, 1H), 1.44 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 135.2, 119.1, 78.8, 62.9, 18.9. Minor: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (m, 2H), 5.34 (m, 2H), 4.83 (m, 1H), 4.31 (m, 1H), 1.31 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 133.0, 119.4, 76.3, 58.5, 16.0. HRMS (EI) *m/z* calculated for $C_6H_9NO_2$ [M^+] 127.0628, found 127.0624.

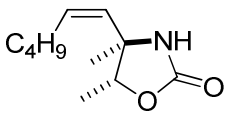
VIII. Mechanistic Studies.



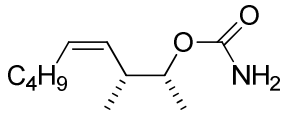
Compound 9. The product was purified by column chromatography using a 0 → 30% gradient of EtOAc in hexanes with 6% increments. The product was obtained in 91% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.43 (dt, *J* = 10.0, 7.0 Hz, 1H), 5.21 (t, *J* = 10.0 Hz, 1H), 4.72 (app p, *J* = 5.2 Hz, 1H), 4.56 (br s, 2H), 2.69-2.61 (m, 1H), 2.11-1.98 (m, 2H), 1.38-1.28 (m, 4H), 1.18 (d, *J* = 6.4 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 156.8, 131.1, 130.8, 74.8, 36.6, 32.0, 27.2, 22.4, 17.5, 16.9, 14.0.



Compound 10. The procedure for Ag-catalyzed C-H insertion was used. The product was purified by column chromatography using a 0 → 40% gradient of EtOAc in hexanes with 8% increments. The product was obtained in 86% yield as a clear oil when BHT was added to the reaction mixture. ^{1}H NMR (500.0 MHz, $CDCl_3$) δ 6.20 (br s, 1H), 5.48 (dt, *J* = 11.9, 7.5 Hz, 1H), 5.28 (dt, *J* = 11.9, 1.4 Hz, 1H), 4.51 (q, *J* = 6.8 Hz, 1H), 2.30-2.16 (m, 2H), 1.41-1.29 (overlapping m, 11H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 158.9, 134.8, 130.4, 82.0, 61.0, 31.9, 27.8, 22.7, 22.3, 14.1, 14.0.



Compound 11. The procedure for Ag-catalyzed C-H insertion was used, with compound **12** as the substrate. The product was purified by column chromatography using a 0 → 40% gradient of EtOAc in hexanes with 8% increments. The product was obtained in 73% yield as a clear oil when BHT was added to the reaction mixture. Traces (<10%) of the *trans*-alkene were present, but no trace of compound **10** was detected. ^{1}H NMR: (500.0 MHz, $CDCl_3$) δ 5.84 (br s, 1H), 5.54 (dt, J = 12.2, 4.3 Hz, 1H), 5.21 (d, J = 12.2 Hz, 1H), 4.42 (q, J = 6.6 Hz, 1H), 2.15 (qd, J = 7.3, 1.5 Hz, 2H), 1.46 (s, 3H), 1.31-1.41 (m, 4H), 1.28 (d, J = 7.3 Hz, 3H), 0.91 (t, J = 7.0 Hz, 3H);^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 158.30, 134.43, 128.05, 82.93, 61.40, 31.89, 28.35, 27.93, 22.24, 16.38, 13.83; HRMS (EI) *m/z* calculated for $C_{11}H_{19}NO_2$ [M+H$^+$] 198.1489, found 198.1491.



Compound 12. The product was purified by column chromatography using a 0 → 30% gradient of EtOAc in hexanes with 6% increments. The product was obtained in 86% yield as a white solid. Traces (<10%) of the trans alkene were present. ^{1}H NMR: (500.0 MHz, $CDCl_3$) δ 5.41 (dt, *J* = 11.2, 7.2 Hz, 1H), 5.18 (t, *J* = 11.2 Hz, 1H), 4.87 (br s, 2H), 4.61 (p, *J* = 6.7 Hz, 1H), 2.65 (dp, *J* = 9.8, 6.7 Hz, 1H), 1.97-2.11 (m, 2H), 1.24-1.39 (m, 4H), 1.18 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H);^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 158.43, 134.57, 128.18, 83.06, 61.53, 32.02, 28.48, 28.06, 22.37, 16.52, 13.96. HRMS (EI) *m/z* calculated for $C_{11}H_{21}NO_2$ [M+NH_4^+] 217.191, found 217.1909.

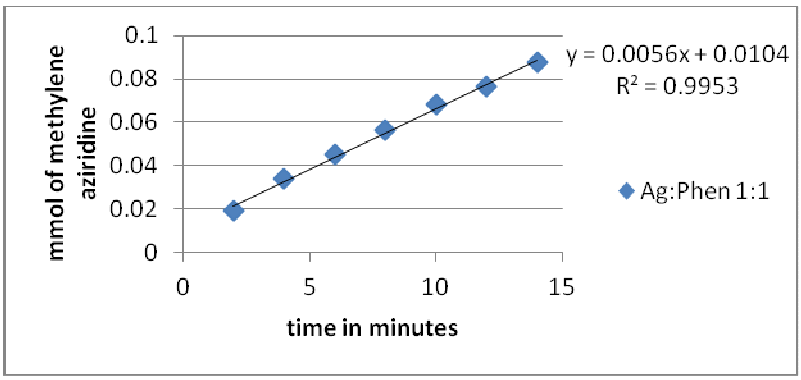
General procedure for Ag-catalyzed allenic C-H insertion using BHT as a radical inhibitor. A pre-dried reaction flask was charged with silver triflate (13.0 mg, 0.5 mmol, 0.1 equiv) and

phenanthroline (26.0 mg, 0.15 mmol, 0.3 equiv). Dichloromethane (3 mL) was added to the flask and the mixture stirred vigorously for 30 min. A solution of the homoallylic carbamate (0.5 mmol, 1 equiv) in dichloromethane (3 mL) was added to the reaction flask, followed by 3Å or 4Å molecular sieves (1 mmol substrate/g of sieves or 0.25 mmol substrate/g of sieves). Butylated hydroxytoluene was added in a single portion, followed by iodosobenzene (392 mg, 1.75 mmol, 3.5 equiv) and the reaction mixture was allowed to stir at room temperature until TLC indicated complete consumption of the starting material (~8-12 h). The reaction mixture was filtered through a glass frit and the filtrate concentrated under reduced pressure. The crude products were purified by silica gel column chromatography using a hexanes/EtOAc gradient.

Exploring the effect of BHT on the rate of aziridination.

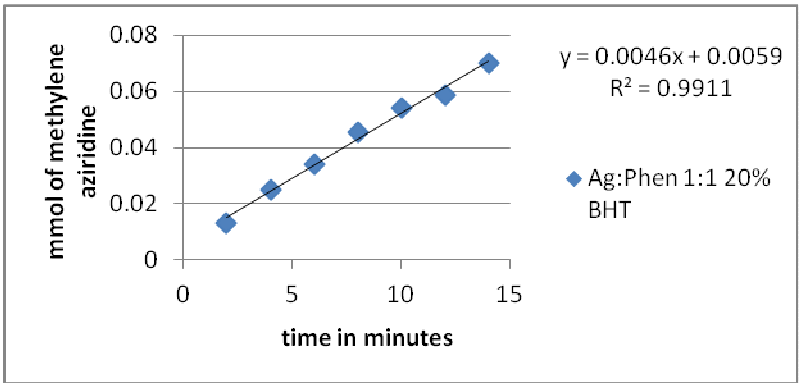
19 **20**

Initial Rates of aziridination using a 1:1.25 ratio of AgOTf:phen. The homoallenic carbamate **19** (0.25 mmol) was added as a solution in dichloromethane (1.7 mL) to a pre-stirred mixture (15 minutes) of silver triflate (20 mol %) and phenanthroline (25 mol %) in 1.7 mL of dichloromethane. Mesitylene (0.0719 mmol) was added as an internal standard. Dried molecular sieves (0.150 g) were then added, followed by PhIO (2 equiv, 0.5 mmol). The reaction was sampled every 2 minutes and the product distribution (**20**) analyzed by ^{1}H NMR.



(2 Trials) Average rate = 5.9×10^{-3} mmol/(min*mL)

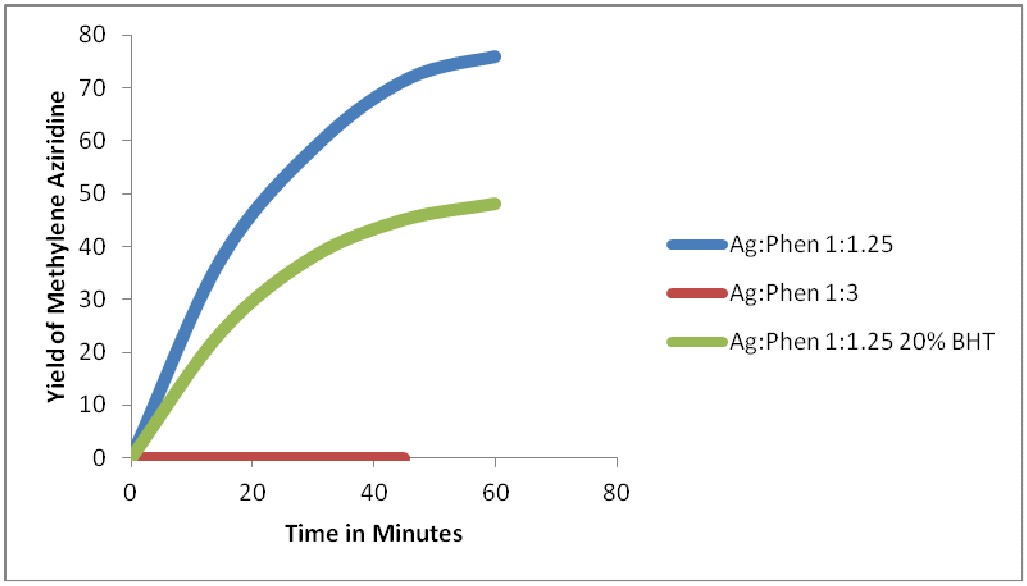
Initial Rates of aziridination using a 1:1.25 ratio of AgOTf:phen and 20 mol% BHT. The homoallenic carbamate **19** (0.25 mmol) was added as a solution in dichloromethane (1.7 mL) to a pre-stirred mixture (15 minutes) of silver triflate (20 mol %), phenanthroline (25 mol %) and BHT (20 mol %) in 1.7 mL of dicholoromethane. Mesitylene (0.0719 mmol) was added as an internal standard. Molecular sieves (0.150 g) were then added, followed by PhIO (2 equiv, 0.5 mmol). The reaction was sampled every 2 minutes and the product distribution (**20**) analyzed by ^{1}H NMR.

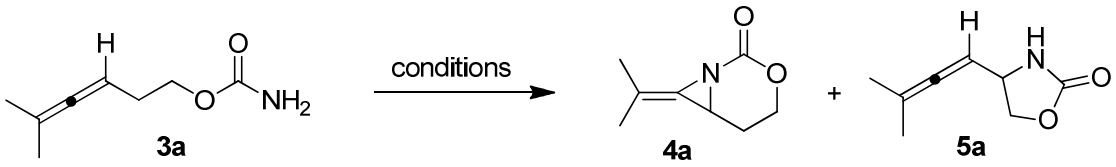


(2 Trials) Average rate = 4.3×10^{-3} mmol/(min*mL)

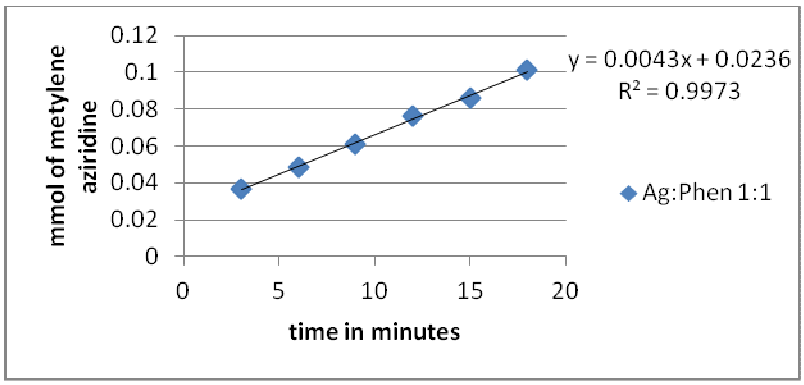
Initial Rates of aziridination using a 1:3 ratio of AgOTf:phen. The homoallenic carbamate **9** (0.25 mmol) was added as solution in dichloromethane (1.7 mL) to a pre-stirred mixture (15 minutes) of silver triflate (20 mol %) and phenanthroline (60 mol %) in 1.7 mL of

dichloromethane. Mesitylene (0.0719 mmol) was added as an internal standard. Molecular sieves (0.150 g) were then added, followed by PhIO (2 equiv, 0.5 mmol). The reaction was sampled every 15 minutes and the progress monitored by ^{1}H NMR. No reaction occurred.





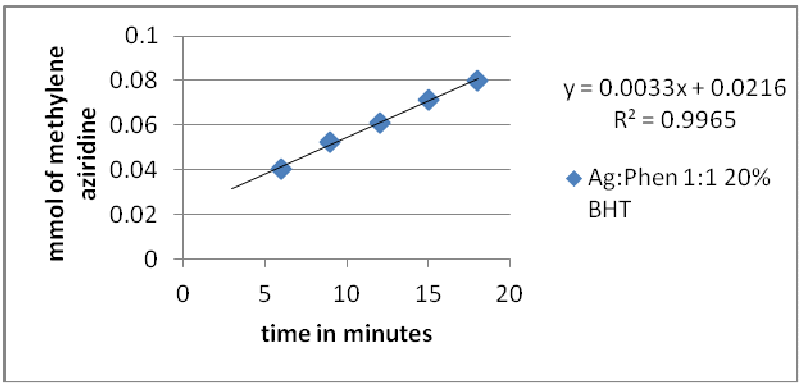
Initial Rates of aziridination using a 1:1.25 ratio of AgOTf:phen. The homoallenic carbamate **3a** (0.25 mmol) was added as a solution in dichloromethane (1.7 mL) to a pre-stirred mixture (15 minutes) of silver triflate (20 mol %) and phenanthroline (25 mol %) in 1.7 mL of dichloromethane. Mesitylene (0.0719 mmol) was added as an internal standard. Dried molecular sieves (0.150 g) were then added, followed by PhIO (2 equiv, 0.5 mmol). The reaction was sampled every 3 minutes and the product distribution analyzed by ^{1}H NMR.



(3 Trials) Average rate = 1.3×10^{-3} mmol/(min*mL)

Standard deviation = 0.06×10^{-3}

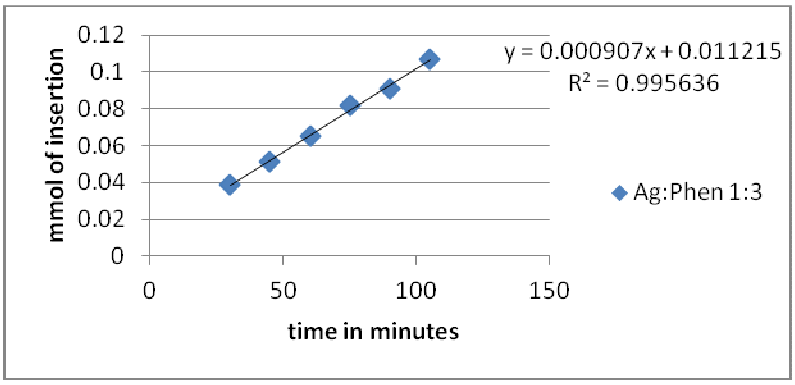
Initial Rates of aziridination using a 1:1.25 ratio of AgOTf:phen and 20 mol% BHT. The homoallenic carbamate **3a** (0.25 mmol) was added as a solution in dichloromethane (1.7 mL) to a pre-stirred mixture (15 minutes) of silver triflate (20 mol %), phenanthroline (25 mol %) in 1.7 mL of dicholoromethane. BHT (20 mol %) and mesitylene (0.0719 mmol) were added. Molecular sieves (0.150 g) were then added, followed by PhIO (2 equiv, 0.5 mmol). The reaction was sampled every 3 minutes and the product distribution analyzed by ^{1}H NMR.



(3 Trials) Average rate = 9.6×10^{-4} mmol/(min*mL)

Standard deviation = 0.2×10^{-4}

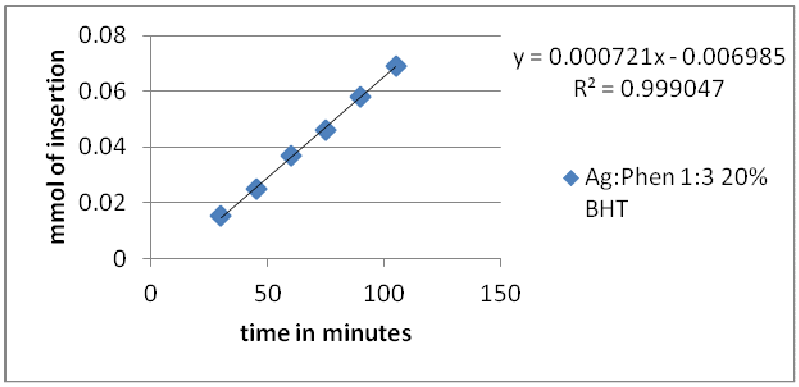
Initial Rates of aziridination using a 1:3 ratio of AgOTf:phen. The homoallenic carbamate **3a** (0.25 mmol) was added as solution in dichloromethane (1.7 mL) to a pre-stirred mixture of silver triflate (20 mol %) and phenanthroline (60 mol %) in 1.7 mL of dichloromethane. Mesitylene (0.0719 mmol) was added as an internal standard. Molecular sieves (0.150 g) were then added, followed by PhIO (2 equiv, 0.5 mmol). The reaction was sampled every 15 minutes and the progress monitored by ^{1}H NMR. No reaction occurred.



(3 Trials) Average rate = 2.7×10^{-4} mmol/(min*mL)

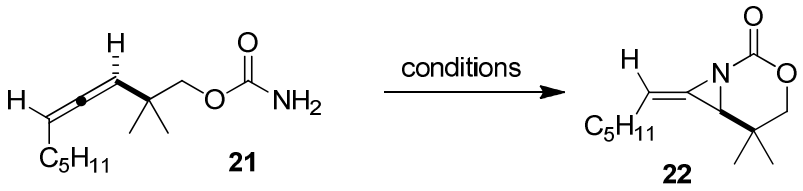
Standard deviation = 0.1×10^{-4}

Initial Rates of aziridination using a 1:3 ratio of AgOTf:phen with 20% BHT. The homoallenic carbamate **3a** (0.25 mmol) was added as solution in dichloromethane (1.7 mL) to a pre-stirred mixture of silver triflate (20 mol %) and phenanthroline (60 mol %) in 1.7 mL of dichloromethane. BHT (20 mol %) and mesitylene (0.0719 mmol) were added. Molecular sieves (0.150 g) were then added, followed by PhIO (2 equiv, 0.5 mmol). The reaction was sampled every 15 minutes and the progress monitored by ^{1}H NMR. No reaction occurred.

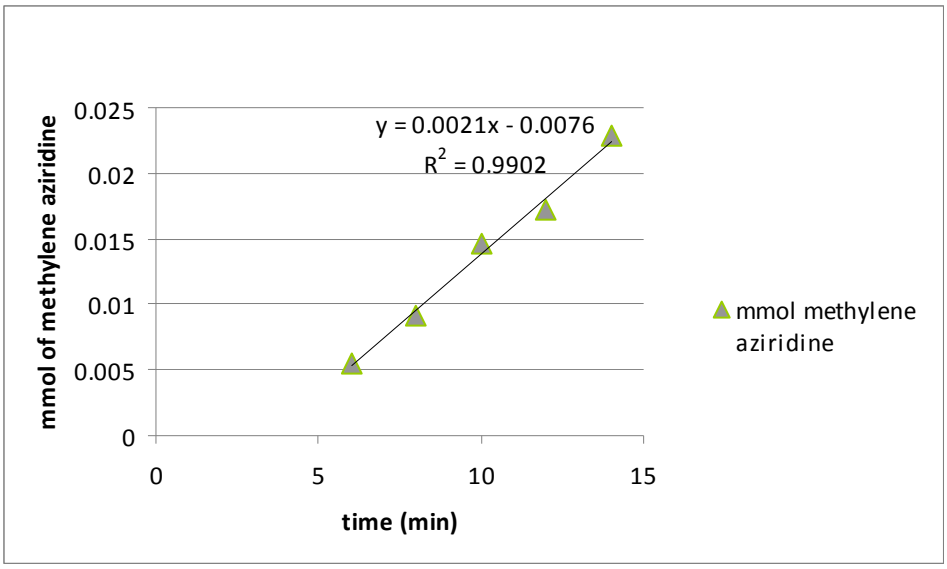


(3 trials) Average rate = 2.0×10^{-4} mmol/(min*mL)

Standard deviation = 0.2×10^{-4}



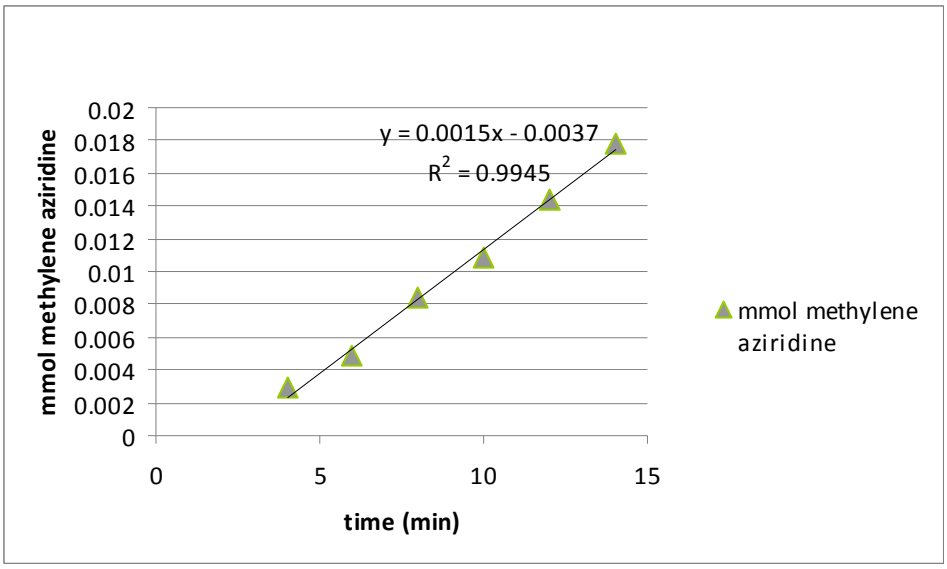
Initial Rates of aziridination using a 1:1.25 ratio of AgOTf:phen. A mixture of silver triflate (11.3 mg, 0.0444 mmol) and phenanthroline (10.0 mg, 0.0555 mmol) was stirred in 1.1 mL of dichloromethane. After 25 minutes, 4A molecular sieves were added, followed by mesitylene (10 µl, 0.0719 mmol) after 28 total minutes. After 30 minutes of total stirring, the homoallenic carbamate **21** (50 mg, 0.222 mmol) was added in 1.1 ml dichloromethane. After 32 minutes total stirring, PhIO (97 mg, 0.444 mmol) was added in a single portion. The reaction was sampled every 2 minutes (4 min-14 min from addition of PhIO) and the progress monitored by ^{1}H NMR.



(2 trials) Average rate = 9.9×10^{-4} mmol/(min*mL)

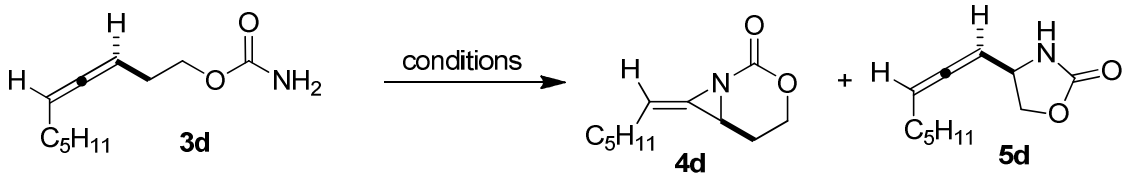
Standard deviation = 0.2×10^{-4}

Initial Rates of aziridination using a 1:1.25 ratio of AgOTf:phen and 20 mol % BHT. A mixture of silver triflate (11.3 mg, 0.0444 mmol), phenanthroline (10.0 mg, 0.0555 mmol), and BHT (9.8 mg, 0.0444 mmol) was stirred in 1.1 mL of dichloromethane. After 25 minutes, 4A molecular sieves were added, followed by mesitylene (10 µl, 0.0719 mmol) after 28 total minutes. After 30 minutes of total stirring, the homoallenic carbamate (43.8 mg, 0.222 mmol) was added in 1.1 ml dichloromethane. After 32 minutes total stirring, PhIO (97 mg, 0.444 mmol) was added in a single portion. The reaction was sampled every 3 minutes (6 min-21 min from addition of PhIO) and the progress monitored by ^{1}H NMR.

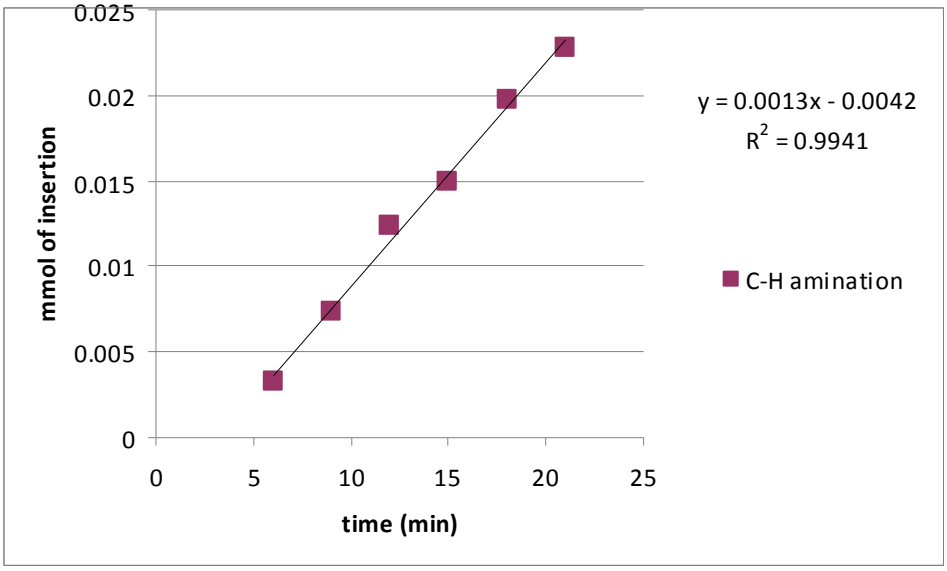


(2 trials) Average rate = 6.2×10^{-4} mmol/(min*mL)

Standard deviation = 0.5×10^{-4}



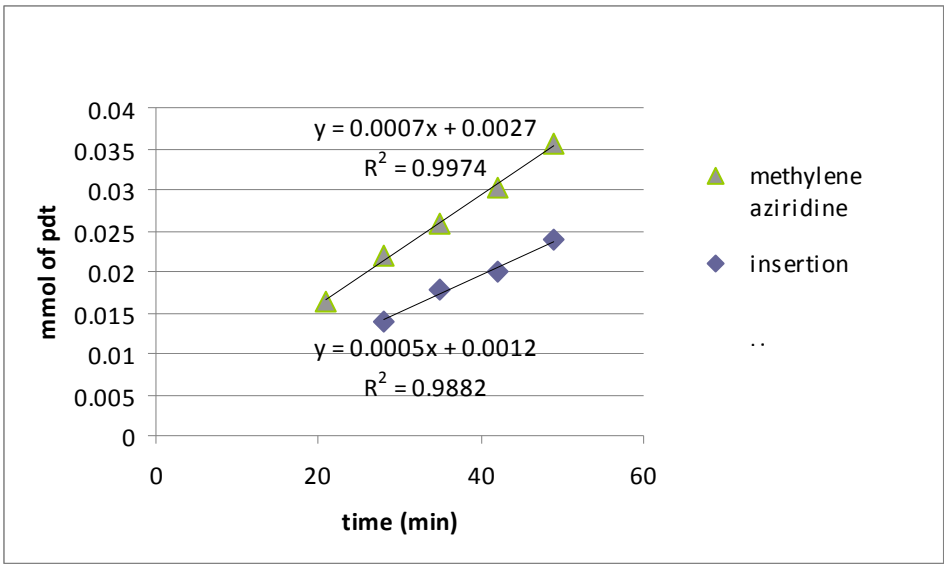
Initial Rates of aziridination using a 1:1.25 ratio of AgOTf:phen. A mixture of silver triflate (11.3 mg, 0.0444 mmol) and phenanthroline (10.0 mg, 0.0555 mmol) was stirred in 1.1 mL of dichloromethane. After 25 minutes, 4A molecular sieves were added, followed by mesitylene (10 µl, 0.0719 mmol) after 28 total minutes. After 30 minutes of total stirring, the homoallenic carbamate **3d** (43.8 mg, 0.222 mmol) was added in 1.1 ml dichloromethane. After 32 minutes total stirring, PhIO (97 mg, 0.444 mmol) was added in a single portion. The reaction was sampled every 3 minutes (6 min-21 min from addition of PhIO) and the progress monitored by ^{1}H NMR.



(2 trials) Average rate = 5.73×10^{-4} mmol/(min*mL)

Standard deviation = 0.15×10^{-4}

Initial Rates of aziridination using a 1:1.25 ratio of AgOTf:phen and 20 mol% BHT. A mixture of silver triflate (10.4 mg, 0.0404 mmol) and phenanthroline (9.2 mg, 0.0506 mmol) was stirred in 1.0 mL of dichloromethane. After 20 minutes, BHT (8.9 mg, 0.0404 mmol) was added. After 25 minutes total stirring, 4A molecular sieves were added, followed by mesitylene (10 µl, 0.0719 mmol) after 28 total minutes. After 30 minutes of total stirring, the homoallenic carbamate (43.8 mg, 0.222 mmol) was added in 1.1 ml dichloromethane. After 40 minutes total stirring, PhIO (97 mg, 0.444 mmol) was added in a single portion. The reaction was sampled every 7 minutes (14 min-56 min from addition of PhIO) and the progress monitored by ^{1}H NMR.



(2 trials) Average rate aziridination = 3.31 x10^{-4} mmol/(min*mL)

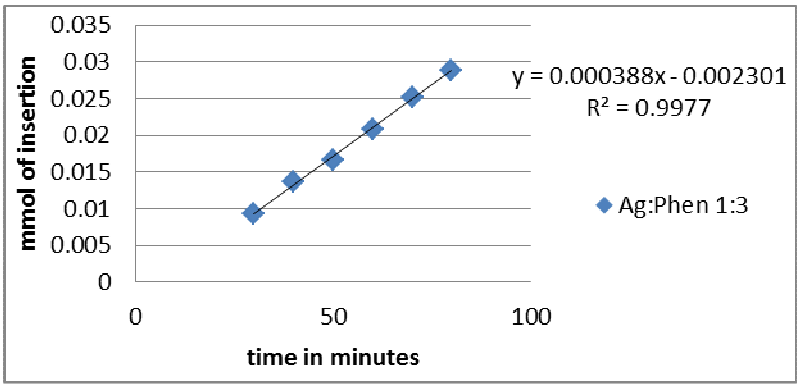
Standard deviation = 0.02.x10^{-4}

(2 trials) Average rate aziridination = 2.31 x10^{-4} mmol/(min*mL)

Standard deviation = 0.04 x10^{-4}

Initial Rates of insertion using a 1:3 ratio of AgOTf:phen.

The homoallenic carbamate **3d** (0.25 mmol) was added as solution in dichloromethane (1.25 mL) to a pre-stirred mixture of silver triflate (20 mol %) and phenanthroline (60 mol %) in 1.25 mL of dichloromethane. Mesitylene (0.0719 mmol) and molecular sieves (0.150 g) were added, followed by PhIO (3.5 equiv, 0.875 mmol). The reaction was sampled every 10 minutes and the progress monitored by ^{1}H NMR.

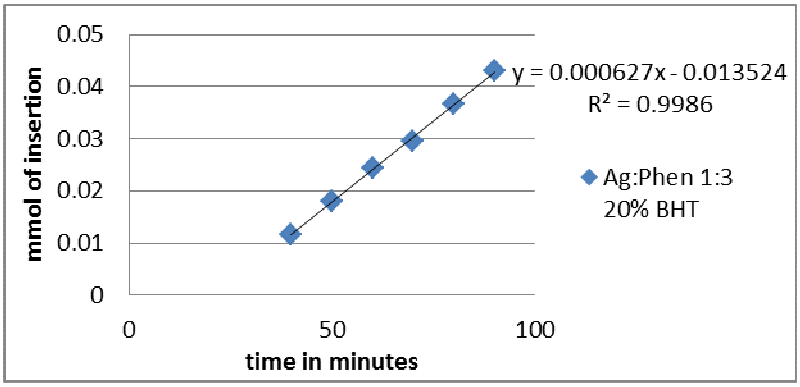


(3 trials) Average rate=1.6×10^{-4} mmol/(min*mL)

Standard deviation=0.1×10^{-4}

Initial Rates of insertion using a 1:3 ratio of AgOTf:phen and 20 mol% BHT.

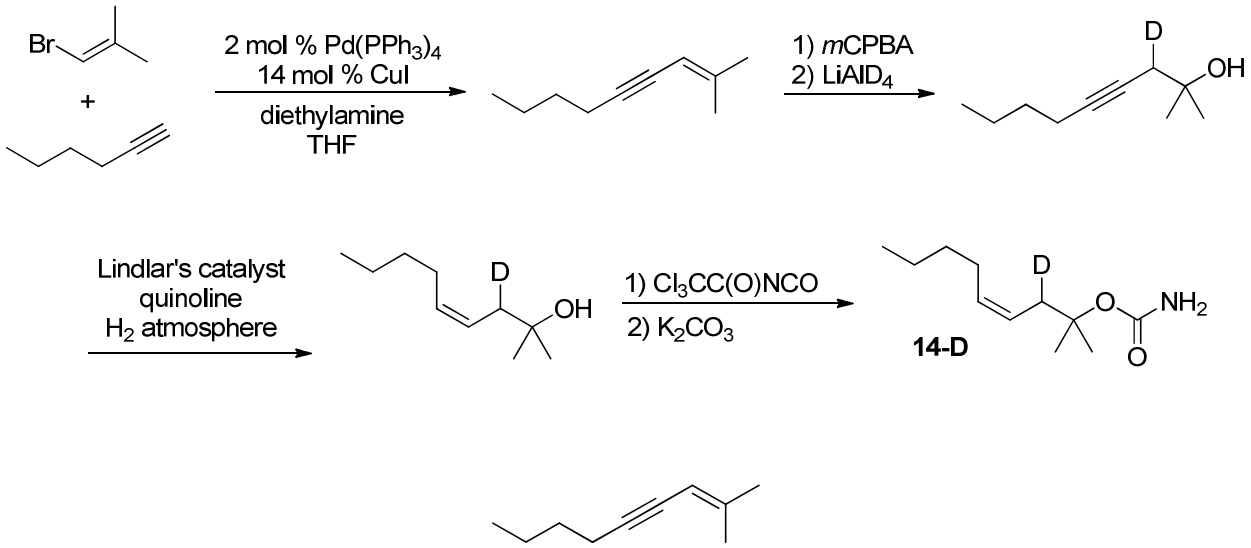
The homoallenic carbamate **3d** (0.25 mmol) was added as solution in dichloromethane (1.25 mL) to a pre-stirred mixture of silver triflate (20 mol %) and phenanthroline (60 mol %) in 1.25 mL of dichloromethane. Mesitylene (0.0719 mmol) and molecular sieves (0.150 g) were added. BHT (20 mol %) was then added, followed by PhIO (3.5 equiv, 0.875 mmol). The reaction was sampled every 10 minutes and the progress monitored by ^{1}H NMR.



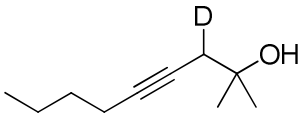
(5 trials) Average rate=2.9×10^{-4} mmol/(min*mL)

Standard deviation=0.4×10^{-4}

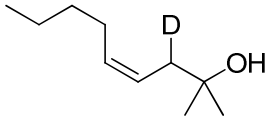
Kinetic Isotope Study and Synthesis of 14-D.



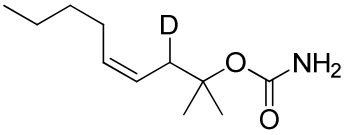
Compound 14-Da. A dry flask was charged with $Pd(PPh_3)_4$ (70.0 mg, 0.12 mmol, 0.02 equiv) and CuI (70.0 mg, 0.72 mmol, 0.14 equiv). Freshly distilled diethylamine (12 mL) was added to the flask. A solution of hexyne (3.0 mL, 26 mmol, 1 equiv) and 1-bromo-2-methyl-1-propene (3.3 mL, 65 mmol, 2.5 equiv) in a solution of THF (30 mL) was added slowly to the reaction flask. The reaction was left to stir overnight. The reaction was quenched with water (100 mL) and the mixture was extracted with diethyl ether (150 mL). The organic layer was washed with 1M HCl (4 x 50 mL). The combined organics was dried with sodium sulfate and concentrated via evaporation. Any resulting precipitate was filtered out of the crude mixture and the filtrate concentrated under reduced pressure. The crude oil was then carefully distilled at 20 mmHg and 75 ºC to yield 0.41 g of an oil for a 12% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.24 (m, 1H), 2.37–2.31 (m, 2H), 1.87 (s, 3H), 1.79–1.75 (m, 3H), 1.57–1.48 (m, 2H), 1.48–1.39 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 105.4, 92.1, 78.4, 31.2, 24.6, 22.0, 20.7, 19.2, 13.6. HRMS (EI) *m/z* calculated for $C_{10}H_{16}$ [M+] 136.1247, found 136.1250.



Compound 14-Db. Compound **14-Da** (390.0 mg, 2.86 mmol, 1 equiv) was dissolved in dichloromethane (3 mL) and placed in an ice bath. A solution of *m*CPBA (1.55 g, 6.29 mmol, 2.2 equiv) in dichloromethane (16 mL) was added in a dropwise fashion through an addition funnel over a period of 1 h. The ice bath was removed and the reaction stirred vigorously until complete by TLC. The reaction was quenched with 10% sodium thiosulfate (30 mL) and extracted with diethyl ether. The combined organic layers were then washed with a saturated solution of sodium bicarbonate (3 x 30 mL). The organic phase was dried with sodium sulfate and carefully concentrated under reduced pressure. The crude material was further purified using silica gel chromatography (0 → 10% EtOAc in hexanes with 2% increments) to give the epoxide in 60% yield. The epoxide was subsequently dissolved in dry THF and slowly added to a suspension of $LiAlD_4$ (148.0 mg, 1.90 mmol, 2.2 equiv relative to epoxide used) in dry THF (3 mL) cooled to 0 ºC in an ice bath. The reaction mixture was warmed to room temperature and stirred overnight, then re-cooled using an ice bath. Water (0.150 mL) was carefully added in a dropwise fashion, followed by 15% NaOH (0.150 mL), and another portion of water (0.45 mL). Diethyl ether (6 mL) was added, the mixture was stirred vigorously for 2 h and then filtered. After concentration, the crude oil was purified using silica gel chromatography (0 → 20% EtOAc in hexanes with 4% increments) to give a clear oil in 59% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.35–2.27 (m, 1H), 2.19 (td, J = 7.0, 2.3 Hz, 3H), 1.93 (s, 1H), 1.54–1.45 (m, 2H), 1.41 (d, J = 8.0 Hz, 1H), 1.29 (s, 7H), 0.91 (t, J = 7.2 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 83.7, 76.2 (d, J = 1.8 Hz), 69.8, 34.2 (t, J = 21.0 Hz), 31.1, 28.5, 22.0, 18.4, 13.6. HRMS (EI) *m/z* calculated for $C_{10}H_{17}DO$ [M-HOD] 136.1247, found 136.1248.

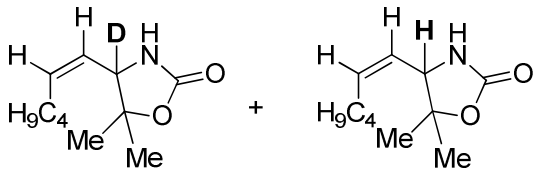


Compound 14-Dc. Compound **14-Db** (147.0 mg, 0.947 mmol, 1 equiv) was added to suspension of Lindlar's catalyst (14.6 mg, 10% by weight) in THF (3.1 mL). Quinoline (0.023 mL) was added and the reaction was placed under a hydrogen atmosphere. The reaction was monitored by NMR until complete (90 min). The reaction was filtered through a pad of Celite and washed with portions of diethyl ether. The organic phase was washed with 1M HCl (3 x 25 mL), dried with sodium sulfate and concentrated under reduced pressure to give a light yellow oil in 85% yield. No further purification was required. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.59 (dtd, *J* = 11.2, 7.2, 1.4 Hz, 1H), 5.46 (ddt, *J* = 11.4, 8.1, 1.6 Hz, 1H), 2.24–2.19 (m, 1H), 2.11–2.02 (m, 2H), 1.45 (s, 1H), 1.33 (m, 4H), 1.23 (s, 6H), 0.92–0.88 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.8, 124.4, 71.0, 40.8 (t, *J* = 19.2 Hz), 31.9, 29.1, 27.1, 22.4, 14.0. HRMS (EI) *m/z* calculated for $C_{10}H_{19}DO$ [M+] 157.1572, found 157.1563.



Compound 14-D. The same procedure previously described for the synthesis of the homoallylic carbamates was employed to obtain **14-D** as a white solid in 87% yield. The crude material was purified using silica gel chromatography (0 → 20% EtOAc in hexanes with 4% increments). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.52 (dtd, *J* = 11.0, 7.3, 1.7 Hz, 1H), 5.42–5.34 (m, 1H), 4.47 (s, 2H), 2.50 (dd, *J* = 7.6, 2.9 Hz, 1H), 2.05 (m, 2H), 1.44 (s, 6H), 1.33 (m, 4H), 0.90 (m, 3H). ^{13}C NMR

(126 MHz, $CDCl_3$) δ 156.1, 132.9, 124.0, 81.7, 38.0 (t, J = 20.4 Hz), 31.8, 27.1, 26.0, 22.4, 14.0. HRMS (EI) *m/z* calculated for $C_{11}H_{20}DN0_2$ [M-$DCNO_2$] 139.1482, found 139.1489.

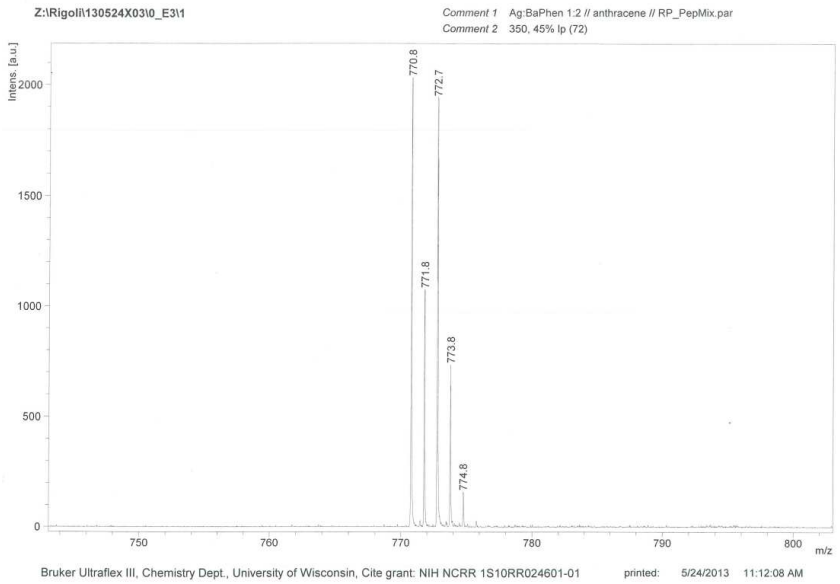


Compound 15-D and 15-H. The procedure described for the Ag-catalyzed C-H insertion was used. The kinetic isotope effect (KIE) was determined using proton signals from the crude reaction mixtures using quantitative NMR. The products were isolated using silica gel chromatography (0 → 50% gradient of EtOAc in hexanes with 10% increments) to give a clear oil in 97% combined yield of the mixture of protonated and deuterated products. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74–5.64 (m, 1H), 5.40–5.31 (m, 1H), 5.17 (s, 1H), 4.37 (d, J = 9.8 Hz, 1H, D insertion product), 2.15–1.98 (m, 2H), 1.47 (s, 3H), 1.40–1.29 (m, 7H), 0.91 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 136.4, 124.7, 124.7, 84.1, 84.0, 58.6, 58.2 (t, J = 23.9 Hz), 31.7, 27.3, 27.2, 27.25, 22.6, 22.3, 13.9. HRMS (ESI) *m/z* calculated for $C_{11}H_{19}NO_2$ [M+H+] 198.1489, found 198.1481.

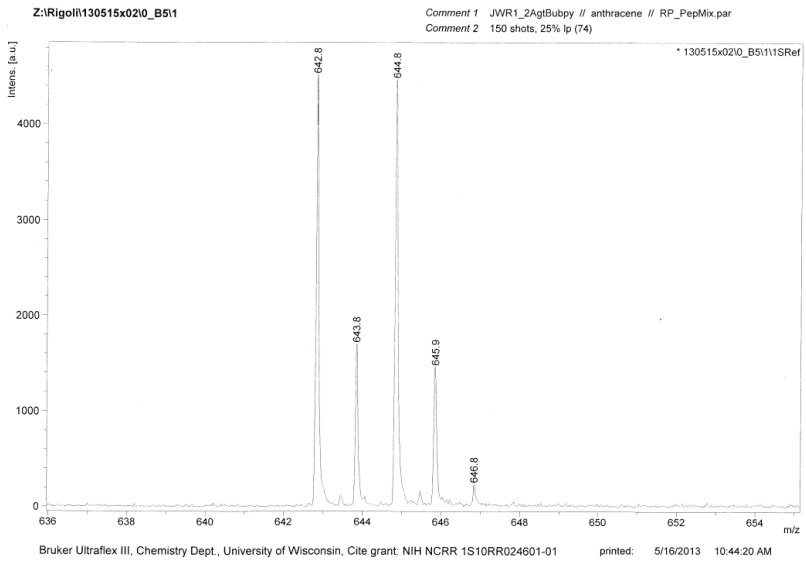
IX. Structure Analysis of Catalytic Species

MALDI data for 1:2 complexes of AgOTf:ligand.

1:2 AgOTf:bathophenanthroline



1:2 AgOTf:^{t}Bu-bipyridine

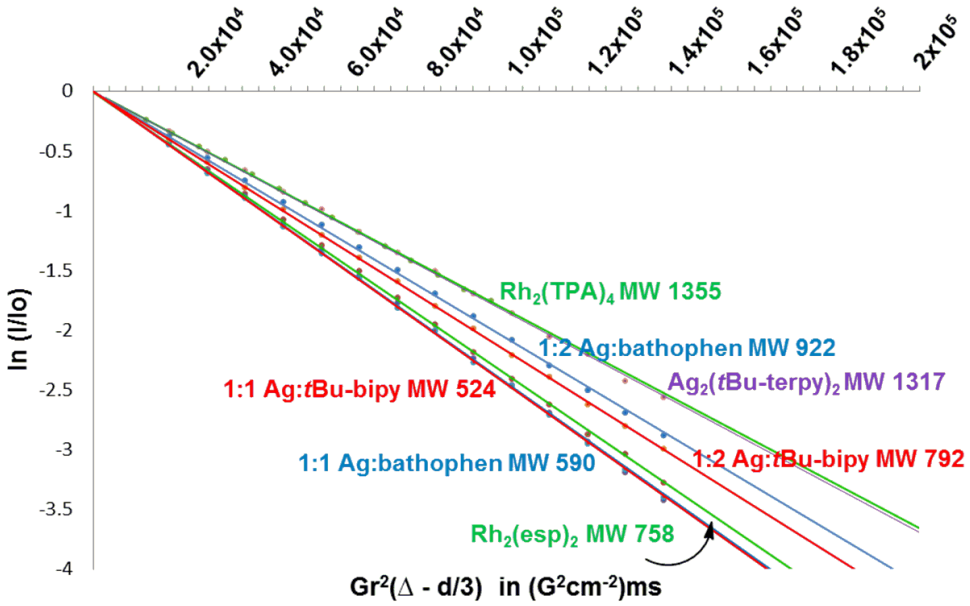


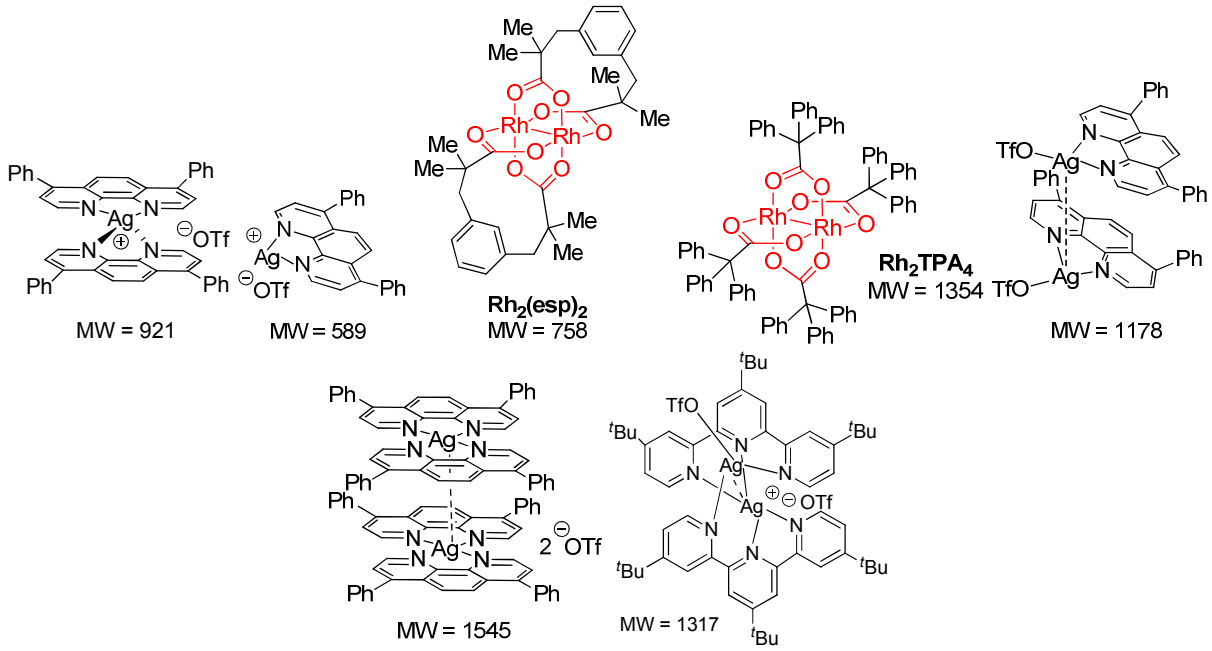
Pulse gradient spin echo experiments.

More insight into the nature of the silver species in solution was obtained using pulse gradient spin echo (PGSE) NMR. The PGSE experiment measures the translational motion of molecules and weakly associated complexes through a solution, permitting the extraction of diffusion coefficients for individual compounds.[9] As these coefficients are inversely related to the hydrodynamic volume of the complexes, they can be used to probe monomer-dimer equilibria in solution and yield information about the relative molecular weights of species that cannot be isolated in the solid state.[9,10a-b] In our studies, $Rh_2(TPA)_4$ (TPA = triphenylacetate) and $Rh_2(esp)_2$ were used as reference compounds due to their similar molecular weights and reactivities as compared to the silver complexes under investigation (see figures below). Bathophen and ^{t}Bu-bipy were substituted for phen in the PGSE experiment due to their better solubility; both ligands exhibited the same behavior in chemoselective aminations as phen. The 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine ligand, shown by the He group to adopt a $Ag_2(^t$Bu-terpy$)_2$ structure in the solid state with $AgNO_3$ as the silver source,[11] was also explored. The PGSE data in Figure 2 showed that combining an equivalent of AgOTf with an equivalent of bathophen (1:1 blue line) or ^{t}Bu-bipy (1:1 red line), resulted in the formation of complexes with diffusion coefficients slightly higher than $Rh_2(esp)_2$, indicating they are behaving as monomeric species in solution. In contrast, a 1:1 mixture of AgOTf:4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine (^{t}Bu-terpy, purple line), exhibited a diffusion coefficient similar to $Rh_2(TPA)_4$, suggesting a dimeric $Ag_2(^t$Bu-terpy$)_2(OTf)_2$ species in solution.

It is clear from the PGSE data that dimeric Ag_2L_4 complexes are not present in solution, with the exception of $Ag_2(^t$Bu-terpy$)_2(OTf)_2$, as the diffusion coefficients would be lower than the value observed for $Rh_2(TPA)_4$. However, other possible species that may arise from the

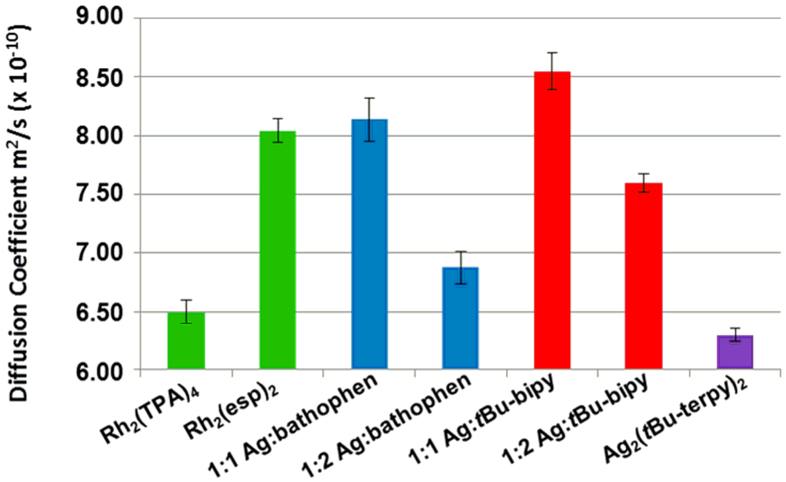
combination of one equivalent of AgOTf with two equivalents of bathophen or ^{t}Bu-bipy include AgL_2 and Ag_2L_2 complexes. The presence of Ag_2L_2 was ruled out by carrying out MALDI experiments on 1:2 mixtures of both AgOTf:bathophen and AgOTf: ^{t}Bu-bipy; the results showed molecular weights consistent with $Ag(bathophen)_2$ and $Ag(^{t}Bu\text{-}bipy)_2$ complexes. Taken together, experimental evidence indicates that bathophen and bipy-based ligands interact with AgOTf to adopt monomeric 1:1 or 1:2 metal:ligand complexes in solution depending on the metal:ligand stoichiometry



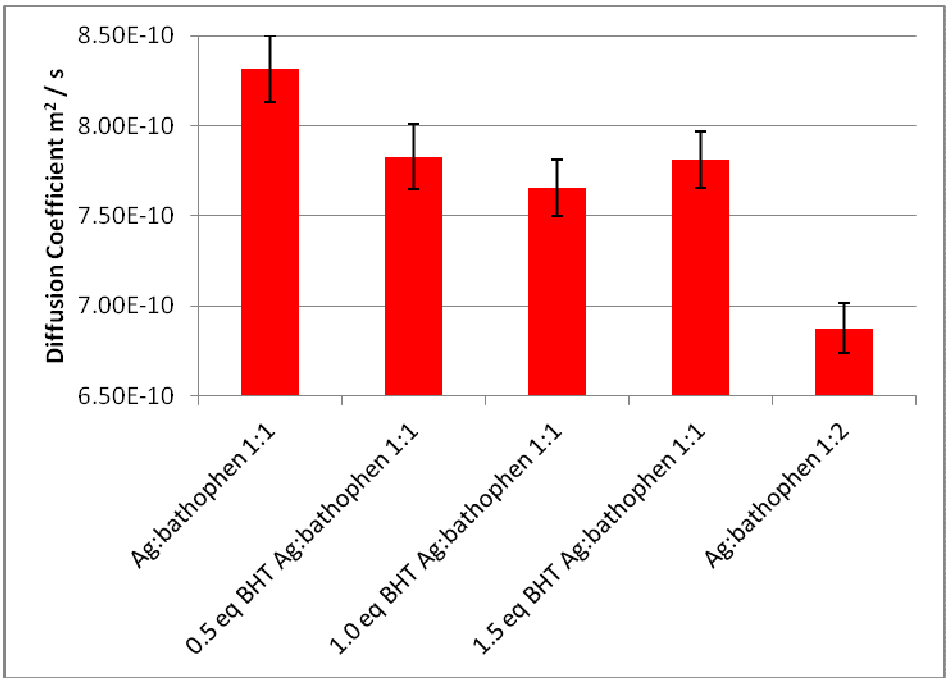


Examples of Plausible Structures

Diffusion Coefficients of Analyzed Structures



Effect of BHT on structure:



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