Supporting Information for:

Chemoselective Allene Aziridination *via* Ag(I) 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.

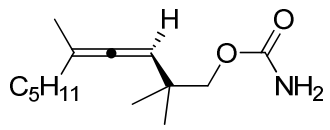
^1H NMR and ^{13}C NMR spectra were obtained using Bruker-300, Varian-300, Varian Inova-500, or Varian Unity-500 spectrometers. For ^1H NMR, chemical shifts are reported relative to residual protiated solvent peaks (δ 7.26, 2.49, 7.15 and 7.09 ppm for $CDCl_3$, $(CD_3)_2SO$, C_6D_6 and $CD_3C_6D_5$ respectively). ^{13}C 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 $CDCl_3$, $(CD_3)_2SO$, C_6D_6, and $CD_3C_6D_5$, 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). 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).

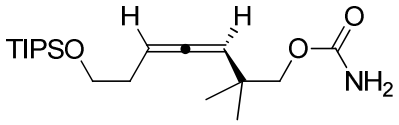
II. Preparation of Allene Substrates.

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 (0 → 30% EtOAc in hexanes, 6% increments). All allenes were stored in a freezer at -78 ^{o}C.

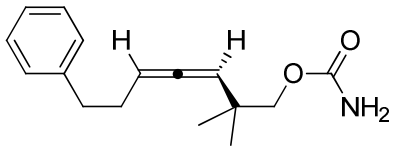
Compounds 4a, 4b, 7a, and 7h-7k. These desired allenic carbamates were prepared from their corresponding alcohols according to literature procedures.[3]



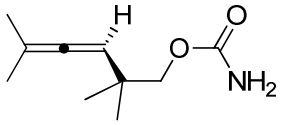
Compound 7b. Obtained in 76% yield as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 (m, 1H), 4.72 (s, 2H), 3.84 (s, 2H) 1.92 (ddd, *J* = 8.9, 6.2, 2.7 Hz, 2H), 1.68 (d, *J* = 2.9 Hz, 3H), 1.47-1.22 (m, 6H), 1.02 (s, 6H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.61, 101.99, 97.52, 73.33, 35.74, 33.98, 31.62, 27.30, 25.02, 25.00, 22.57, 19.38, 14.10. HRMS (ESI) *m/z* calculated for $C_{14}H_{25}NO_2$ [M+NH_4^+] 257.2224, found 257.2217. IR (cm^{-1}, CH_2Cl_2) 3530, 3420, 2931, 1731, 1584, 1468, 1397, 1377, 1331, 1271, 1068.



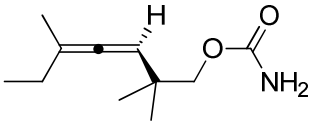
Compound 7c. Obtained as a clear oil from the corresponding homoallenic alcohol in 49% yield. ^{1}H-NMR (300.1 MHz, $CDCl_3$) δ 5.24 (q, *J* = 6.4 Hz, 1H), 5.07 (dt, *J* = 6.4, 3.1 Hz, 1H), 4.68-4.50 (br s, 2H), 3.86 (s, 2H), 3.74 (t, *J* = 7.0 Hz, 2H), 2.26 (qd, *J* = 7.0,3.1 Hz, 2H), 1.14-0.99 (m, 27H); ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 203.21, 157.20, 98.37, 90.13, 73.39, 63.47, 35.55, 33.11, 25.04, 18.24, 12.23; HRMS (ESI) *m/z* calculated for $C_{19}H_{37}NO_3Si$ [M+H^+] 356.2616, found 356.2622. IR (cm^{-1}, CH_2Cl_2) 3535, 3424, 2968, 1728, 1585, 1454, 1399, 1378, 1331, 1271, 1068.



Compound 7d. Obtained from the corresponding homoallenic alcohol as a clear, colorless oil in 75% yield. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32-7.23 (m, 2H), 7.22-7.14 (m, 3H), 5.25 (q, *J* = 6.1 Hz, 1H), 5.09 (dt, *J* = 6.1, 3.1 Hz, 1H), 4.83-4.64 (br s, 2H), 3.84 (s, 2H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.40-2.25 (m, 2H), 1.01 (s, 6H); ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 157.29, 141.96, 128.65, 128.52, 126.07, 99.07, 92.92, 73.31, 35.60, 30.87, 25.04; HRMS (ESI) *m/z* calculated for $C_{16}H_{21}NO_2$ [M+H$^+$] 260.1646, found 260.1656. IR (cm^{-1}, CH_2Cl_2) 3537, 3426, 2949, 1732, 1602, 1589, 1464, 1404, 1382, 1332, 1101.

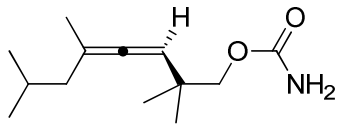


Compound 7e. Obtained in 72% yield as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.90 (m, 1H), 4.65 (br s, 2h), 3.84 (s, 2H), 1.69 (d, *J* = 2.9 Hz, 6H), 1.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.46, 157.30, 97.57, 96.44, 73.45, 35.95, 25.19, 20.90. HRMS (ESI) *m/z* calculated for $C_{10}H_{17}NO_2$ [M-H$^+$] 182.1176, found 182.1169. IR (cm^{-1}, CH_2Cl_2) 3535, 3422, 2969, 1731, 1584, 1377, 1331, 1270, 1261, 1068.

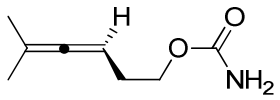


Compound 7f. Obtained in 68% yield as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.98 (m, 1H), 4.52 (s, 2H), 3.81 (s, 2H), 1.90 (qd, *J* = 7.4, 3.3 Hz, 2H), 1.65 (d, *J* = 2.9 Hz, 3H), 0.98 (s, 6H), 0.95 (t, *J* = 7.5, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.46, 157.56, 103.85, 98.48, 73.48,

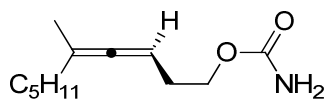
35.90, 27.06, 25.20, 19.53, 12.44. HRMS (ESI) *m/z* calculated for $C_{11}H_{19}NO_2$ [M^+] 197.1411, found 197.1412. IR (cm^{-1}, CH_2Cl_2) 3533, 3425, 2968, 1733, 1583, 1459, 1399, 1378, 1328, 1065.



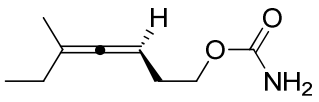
Compound 7g. Obtained in 67% yield as a thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23-4.57 (m, 3H), 3.84 (s, 2H), 1.93-1.68 (m, 3H), 1.65 (d, *J* = 2.9 Hz, 3H), 1.02 (s, 1H), 0.90 (dd, *J* = 6.4, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.39, 157.39, 100.61, 96.77, 73.31, 43.86, 35.80, 26.36, 25.05, 24.99, 22.72, 22.57, 19.28. HRMS (ESI) *m/z* calculated for $C_{13}H_{23}NO_2$ [$M+H^+$] 226.1802, found 226.1804. IR (cm^{-1}, CH_2Cl_2) 3536, 3425, 2963, 2879, 1728, 1584, 1465, 1397, 1378, 1323, 1071.



Compound 4a. Obtained in 53% yield as a thick oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.94 (m, 1H), 4.58 (br s, 2H), 4.11 (t, *J* = 6.8 Hz, 2H), 2.27 (q, *J* = 6.6 Hz, 2H), 1.68 (d, *J* = 2.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.66, 157.48, 96.06, 84.56, 64.65, 28.98, 20.72. HRMS (ESI) *m/z* calculated for $C_8H_{13}NO_2$ [$M+Na^+$] 178.0839, found 178.0842. IR (cm^{-1}, CH_2Cl_2) 3537, 3424, 2987, 1730, 1585, 1422, 1337, 1265 1159, 1093.

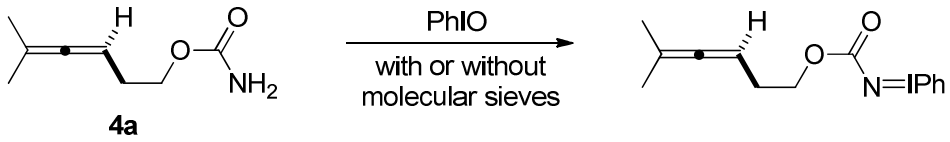


Compound 7l. Obtained in 78% yield as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03-4.94 (m, 1H), 4.81 (br s, 2H), 4.10 (t, *J* = 6.8 Hz, 2H), 2.28 (q, *J* = 6.8 Hz, 2H), 1.91 (td, *J* = 7.5, 3.0 Hz, 2H), 1.66 (d, *J* = 2.9 Hz, 3H), 1.47-1.20 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.00, 157.11, 100.38, 85.63, 64.63, 33.87, 31.52, 29.01, 27.17, 22.56, 19.17, 14.11. HRMS (ESI) *m*/*z* calculated for $C_{12}H_{21}NO_2$ [M+Na^+] 234.1465, found 234.1473. IR (cm^{-1}, CH_2Cl_2) 3538, 3424, 2987, 1730, 1585, 1422, 1337, 1265, 1115, 1093.



Compound 7m. Obtained in 69% yield as a thick oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.03 (m, 1H), 4.96 (br s, 2H), 4.10 (t, *J* = 6.9 Hz, 2H), 2.28 (q, *J* = 6.9 Hz, 2H), 1.93 (qd, *J* = 7.3, 3.0 Hz, 2H), 1.68 (d, *J* = 2.8 Hz, 3H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.73, 157.46, 102.35, 86.58, 64.73, 29.16, 27.01, 19.28, 12.36. HRMS (ESI) *m*/*z* calculated for $C_9H_{15}NO_2$ [M+Na^+] 192.0995, found 192.0999. IR (cm^{-1}, CH_2Cl_2) 3537, 3424, 2987, 1730, 1585, 1422, 1398, 1337, 1265, 1160, 1093.

III. Attempts to form an iodinane from homoallenic carbamate 4a. Our poor results using Cu catalysts prompted us to try to pre-form the iodinane and then subject it to Cu catalysis.



4a

No literature precedent exists for the formation of such a species, in contrast to the use of sulfonamides as nitrogen sources.[4] Treatment of homoallenic carbamate **4a** with PhIO in the absence of a catalyst in both CH_2Cl_2 and acetonitrile as the solvent resulted in only recovered starting material. A procedure reported by Dodd and Dauben for the conversion of sulfonamides to iminoiodinanes was also attempted. This involved stirring the carbamate with $PhI(OAc)_2$ and KOMe, but only starting material was recovered. The same procedure, followed by the addition of a CuOTf catalyst, still resulted in only the recovery of the starting material.

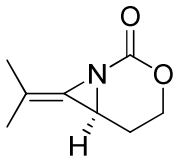
Slightly better results were obtained when a homoallenic carbamate was stirred for 1 h with PhIO, followed by addition of 20 mol % $Cu(MeCN)_4PF_6$, a catalyst known to promote C-N bond formation using sulfamates or carbamates containing an activated benzylic C-H bond.[5] Under these conditions, a 13% yield of the bicyclic methylene aziridine **5a** and 4% of the C-H insertion product **6a**, along with 28% of the starting material **4a**. Traces of unidentified products were also formed, with only 45% of the total mass corresponding to identifiable products. However, both the poor mass balance and the lowered chemoselectivity compared to the use of the Ag-based system were discouraging.

It is not clear why the presumed iodinane could not be isolated. It may be a result of the instability of the proposed intermediate, or the catalyst might be necessary in order to access the iodinane itself. Further efforts to employ Cu catalysts for allene amination are on-going, but are focusing on nitrene precursors other than carbamates.

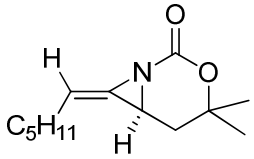
IV. Allene aziridination promoted by Ag(I) catalysts.

General procedure for Ag-catalyzed allene aziridination. Silver triflate (26 mg, 0.1 mmol, 0.2 equiv) and phenanthroline (23 mg, 0.125 mmol, 0.25 equiv) were charged into a pre-dried

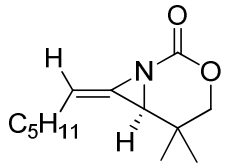
reaction flask. Dichloromethane (1 mL) was added to the flask. The mixture was stirred vigorously for 30 min, then a solution of the homoallenic carbamate (0.5 mmol, 1 equiv) in dichloromethane (1 mL) was added to the reaction flask, followed by 3Å or 4Å molecular sieves (1 mmol substrate/g of sieves or 0.25 mmol substrate/g of sieves). Iodosobenzene (220 mg, 1 mmol, 2 equiv) was then 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 then filtered through a glass frit and the filtrate was concentrated under reduced pressure. The crude products were then purified by silica gel column chromatography (0 → 30% EtOAc in hexanes, 6% increments).



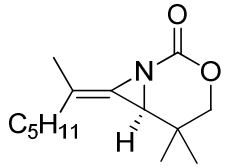
Compound 6a. Obtained in a 79% yield as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.50 (m, 1H), 4.33 (m, 1H), 3.38 (t, J = 7.4 Hz, 1H), 2.35 (m, 1H), 1.98 (s, 3H), 1.80 (s, 3H), 1.60 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.84, 120.37, 108.25, 68.52, 40.05, 24.36, 19.76, 18.53. HRMS (ESI) m/z calculated for $C_8H_{11}NO_2$ [M+H$^+$] 154.0863, found 154.0858. IR (cm^{-1}, CH_2Cl_2) 2983, 2904, 1793, 1718, 1471, 1384, 1094.



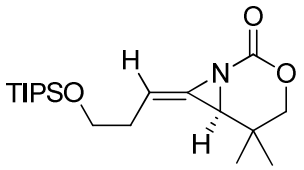
Compound 6b. Obtained in 80% yield as an oil. The identity of this product was verified by comparison of NMR spectra with reported literature.[3]



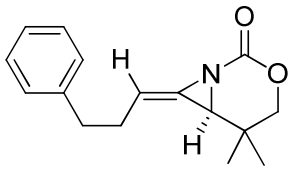
Compound 8a. Obtained in 88% yield as an oil. The identity of this product was verified by comparison of NMR spectra with reported literature.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.61 (t of d, 1H, *J* = 7.3, 0.9 Hz), 4.23 (d, 1H, *J* = 10.5 Hz), 3.81 (d, 1H, *J* = 9.8 Hz), 3.72 (s, 1H), 2.11 (dd, 2H, *J* = 14.1, 7.1 Hz), 1.54 (m, 2H), 1.42-1.29 (br m, 7H total), 0.87 (2 overlapping signals, 6H total).



Compound 8b. Obtained in a 81% yield as a mixture of *E* and *Z* isomers *E* isomer: ^{1}H NMR (300 MHz, C_6D_6) δ 3.56 (d, *J* = 9.8 Hz, 1H), 3.19 (d, *J* = 9.8 Hz, 1H), 2.61 (s, 1H), 2.08 (s, 3H), 1.88 (m, 2H), 1.24 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H), 0.54 (s, 3H), 0.51 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6) δ 155.93, 119.55, 112.54, 77.46, 49.35, 34.82, 32.26, 29.71, 27.58, 23.75, 23.19, 20.58, 17.10, 14.55. HRMS (ESI) *m*/*z* calculated for $C_{14}H_{23}NO_2$ [M+H$^+$] 238.1802, found 238.1805. *Z* isomer: ^{1}H NMR (300 MHz, C_6D_6) δ 3.52 (d, *J* = 10.4 Hz, 1H), 3.17 (d, *J* = 10.4 Hz, 1H), 2.59 (m, 1H), 2.53 (s, 1H), 1.88 (m, 1H), 1.53 (s, 3H), 1.23 (m, 6H), 0.91 (t, *J* = 6.8 Hz, 3H), 0.51 (s, 3H), 0.49 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6) δ 155.80, 119.79, 112.04, 77.32, 48.73, 33.02, 32.19, 29.57, 28.23, 23.81, 23.31, 20.46, 17.85, 14.67. HRMS (ESI) *m*/*z* calculated for $C_{14}H_{23}NO_2$ [M+H$^+$] 238.1802, found 238.1805. IR (cm^{-1}, CH_2Cl_2) 2987, 1730, 1422, 1378, 1334, 1265, 1155, 1110.

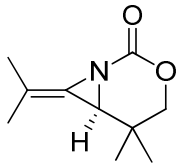


Compound 8c. Obtained from carbamate **7c** in 87% yield and 3:1 *E*:*Z* mixture of isomers as a clear oil. *E* isomer: ^{1}H-NMR (300 MHz, C_6D_6) δ 5.58 (t, *J* = 7.5 Hz, 1H), 3.61-3.49 (m, 3H), 3.15 (d, *J* = 10.9 Hz, 1H), 2.56 (s, 1H), 2.33-2.10 (m, 2H), 1.14-0.98 (m, 21H), 0.53 (s, 3H), 0.46 (s, 3H); ^{13}C NMR (75.4 MHz, C_6D_6) δ 155.19, 126.06, 100.16, 77.71, 63.53, 48.48, 33.42, 29.32, 23.76, 20.79, 18.61, 12.66; HRMS (ESI) *m/z* calculated for $C_{19}H_{35}NO_3Si$ [M+H$^+$] 354.2459, found 354.2457. IR (cm^{-1}, CH_2Cl_2) 2971, 1727, 1586, 1406, 1377, 1332, 1270, 1070 cm^{-1} *Z* isomer: ^{1}H NMR (300 MHz, C_6D_6) δ 5.49 (t, *J* = 7.6 Hz, 1H), 3.79 (dt, *J* = 9.8, 6.0 Hz, 1H), 3.73 (ddd, *J* = 9.8, 6.7, 5.5 Hz, 1H), 3.48 (d, *J* = 10.6 Hz, 1H), 3.14 (d, *J* = 10.6 Hz, 1H), 2.98-2.79 (m, 2H), 2.54 (s, 1H), 1.15-1.06 (m, 21H), 0.52 (s, 3H), 0.41 (s, 3H); 13C NMR (75.4 MHz, C_6D_6) δ 155.09, 125.17, 101.98, 77.31, 64.20, 48.73, 31.97, 28.99, 23.62, 20.66, 18.64, 12.68; HRMS (ESI) *m/z* calculated for $C_{19}H_{35}NO_3Si$ [M+H$^+$] 354.2459, found 354.2457. IR (cm^{-1}, CH_2Cl_2) 2971, 1731, 1592, 1502, 1382, 1331, 1070.

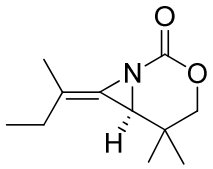


Compound 8d. Obtained from carbamate **7d** to give the methylene aziridine **8d** in 83% yield as a 2.8:1 *E*:*Z* mixture of diastereomers. *E* isomer: ^{1}H NMR (300 MHz, C_6D_6) δ 7.12 (d, *J* = 7.8 Hz, 2H), 7.08-7.01 (m, 1H), 6.95 (d, *J* = 7.4 Hz, 1H), 5.52 (t, *J* = 7.0 Hz, 1H), 3.45 (d, *J* = 10.5 Hz, 1H), 3.07 (d, *J* = 10.5 Hz, 1H), 2.42 (t, *J* = 7.3 Hz, 2H), 2.37 (s, 1H), 2.10 (non, *J* = 7.3 Hz, 2H), 0.41 (s, 3H), 0.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.24, 140.86, 133.24, 129.61,

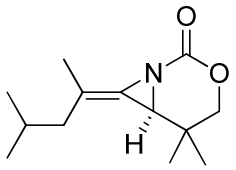
126.36, 75.01, 72.99, 59.40, 54.91, 34.04, 32.39, 31.21, 25.18, 20.44; HRMS (ESI) *m/z* calculated for $C_{16}H_{19}NO_2$ [M+H$^+$] 258.1489, found 258.1494. IR (cm^{-1}, CH_2Cl_2) 2971, 1728, 1589, 1402, 1380, 1344, 1070. *Z* isomer: ^{1}H NMR (300 MHz, C_6D_6) δ 7.15-7.10 (m, 4H), 7.09-7.00 (m, 1H), 4.99 (t, *J* = 7.2 Hz, 1H), 3.42 (d, *J* = 10.4 Hz, 1H), 3.05 (d, *J* = 10.4 Hz, 1H), 2.93 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.77 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.67 (t, *J* = 7.2 Hz, 1H), 2.43 (s, 1H), 0.39 (s, 3H), 0.38 (s, 3H); ^{13}C NMR (75.4 MHz, C_6D_6) δ 155.06, 142.06, 129.40, 129.05, 126.59, 124.72, 103.69, 77.18, 48.62, 36.87, 29.78, 28.90, 23.64, 20.56; HRMS (ESI) *m/z* calculated for $C_{16}H_{19}NO_2$ [M+NH_4^+] 275.1755, found 275.1747. IR (cm^{-1}, CH_2Cl_2) 2971, 1731, 1592,, 1502, 1382, 1331, 1070 cm^{-1}.



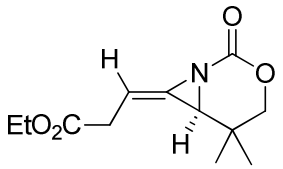
Compound 8e. Obtained in a 98% yield as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.20 (d, *J* = 10.6 Hz, 1H), 3.81 (d, *J* = 10.6 Hz, 1H), 3.11 (s, 1H), 1.99 (s, 3H), 1.79 (s, 3H), 1.25 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.58, 118.66, 108.95, 77.42, 49.40, 29.76, 24.11, 20.54, 20.08, 18.47. HRMS (ESI) *m/z* calculated for $C_{10}H_{15}NO_2$ [M+H$^+$] 182.1176, found 182.1173. IR (cm^{-1}, CH_2Cl_2) 2975, 1730, 1472, 1404, 1375, 1345, 1298, 1265, 1216, 1185, 1093, 1018.



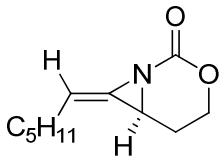
Compound 8f. The product was obtained in a 90% yield as a mixture of *E* and *Z* isomers. *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.22 (d, *J* = 10.7 Hz, 1H), 3.81 (d, *J* = 10.7 Hz, 1H), 3.13 (s, 1H), 2.14 (m, 2H), 1.99 (s, 3H), 1.24 (s, 3H), 1.07 (t, *J* = 7.5 Hz, 3H), 0.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.17, 117.53, 114.18, 77.22, 49.12, 29.41, 27.10, 23.55, 20.11, 16.09, 11.69. HRMS (ESI) *m*/*z* calculated for $C_{11}H_{17}NO_2$ [M+H$^+$] 196.1333, found 196.1330. *Z* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.20 (d, *J* = 10.7 Hz, 1H), 3.81 (d, *J* = 10.7 Hz, 1H), 3.09 (s, 1H), 2.43 (m, 2H), 1.78 (s, 3H), 1.25 (s, 3H), 1.09(t, *J* = 7.6 Hz, 3H), 0.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.17, 117.59, 113.86, 77.00, 48.55, 29.35, 25.51, 23.70, 20.05, 16.89, 12.36. HRMS (ESI) *m*/*z* calculated for $C_{11}H_{17}NO_2$ [M+H$^+$] 196.1333, found 196.1330. IR (cm^{-1}, CH_2Cl_2) 2972, 1728, 1472, 1404, 1376, 1297, 1245, 1215, 1157, 1096 cm^{-1}.



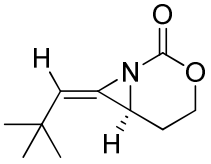
Compound 8g. Obtained in a 97% yield as a mixture of *E* and *Z* isomers. *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.20 (d, *J* = 10.6 Hz, 1H), 3.82 (d, *J* = 10.6 Hz, 1H), 3.10 (s, 1H), 1.98 (m, 2H), 1.96 (s, 3H), 1.88 (m, 1H), 1.25 (m, 3H), 0.89 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.55, 119.34, 112.48, 77.40, 49.64, 43.57, 29.82, 26.00, 24.11, 22.93, 22.22, 20.70, 16.49. HRMS (ESI) *m*/*z* calculated for $C_{13}H_{21}NO_2$ [M+H$^+$] 224.1646, found 224.1649. *Z* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.19 (d, *J* = 10.6 Hz, 1H), 3.82 (d, *J* = 10.6 Hz, 1H), 3.10 (s, 1H), 2.29 (d, *J* = 7.5 Hz, 2H), 1.88 (m, 1H), 1.75 (s, 3H), 1.26 (s, 3H), 0.89 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.32, 119.26, 112.04, 77.34, 49.05, 41.35, 29.67, 26.07, 24.11, 22.54, 22.22, 20.66, 17.82. HRMS (ESI) *m*/*z* calculated for $C_{13}H_{21}NO_2$ [M+H$^+$] 224.1646, found 224.1649. IR (cm^{-1}, CH_2Cl_2) 2962, 1730, 1472, 1404, 1377, 1341, 1299, 1265, 1214, 1159 cm^{-1}.



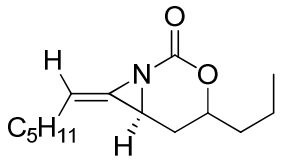
Compound 8h. Obtained 86% yield as a 2.2:1 *E*:*Z* mixture of diastereomers. The *Z* isomer was previously characterized.[3] *E* isomer: ^{1}H NMR (300 MHz) δ 5.67 (t, *J* = 6.7 Hz, 1H), 3.87 (q, *J* = 7.4 Hz, 2H), 3.49 (d, *J* = 10.0 Hz, 1H), 3.16 (d, *J* = 10.0 Hz, 1H), 2.72 (qd, *J* = 16.9, 7.8 Hz, 2H), 2.50 (s, 1H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.50 (s, 3H), 0.46 (s, 3H); ^{13}C NMR (75.4 MHz, C_6D_6) δ 170.42, 154.83, 127.46, 96.27, 61.00, 48.55, 34.62, 29.26, 23.56, 20.52, 14.47. HRMS (ESI) *m/z* calculated for $C_{12}H_{17}NO_4$ [M+H$^+$] 240.1231, found 240.1223. IR (cm^{-1}, CH_2Cl_2) 2968, 1728, 1580, 1402, 1380, 1332, 1071.



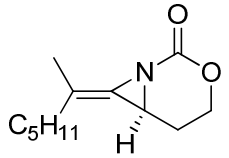
Compound 8i. Bipyridine was used as the ligand instead of phenanthroline. Obtained in 72% yield as an oil. The identity of this product was verified by comparison of NMR spectra with reported literature.[3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.55 (dd, 1H, *J* = 7.3, 6.8 Hz), 4.50 (dd, 1H, *J* = 11.3, 2.1 Hz), 4.33 (ddd, 1H, *J* = 11.0, 4.0, 2.6 Hz), 3.40 (dd, 1H, *J* = 8.0, 6.5 Hz), 2.34 (m, 2H), 2.13 (ddd, 2H, *J* = 8.5, 7.2, 1.6 Hz), 1.59-1.2 (m, 6H), 0.85 (t, 3H, *J* = 8.0 Hz).



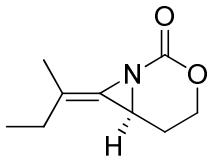
Compound 8j. Bipyridine was used as the ligand instead of phenanthroline. Obtained in 67% yield as a white solid. The identity of this product was verified by comparison of NMR spectra with reported literature.[3] ^{1}H NMR (500 MHz, C_6D_6) δ 5.56 (br s, NH), 3.61 (ddd, *J* = 14.1, 11.7, 2.5 Hz, 1H), 3.45 (ddd, *J* = 10.5, 4.0, 2.4 Hz, 1H), 2.65 (dd, *J* = 8.4, 6.3 Hz, 1H), 1.09 (ddt, *J* = 14.5, 6.3, 2.1 Hz, 1H), 0.89 (s, 9H), 0.83-0.76 (m, 1H).



Compound 8k. Obtained in 80% yield as an oil. The identity of this product was verified by comparison of NMR spectra with reported literature.[6] ^{1}H NMR (500 MHz, C_6D_6) δ 5.57 (t, *J* = 7.0 Hz, 0.83H), 5.18 (t, *J* = 7.5 Hz, 0.34H), 3.84 (m, 1.32H), 2.66 (m, 1.98H), 1.94 (q, *J* = 7.3 Hz, 2.00H), 1.47 (m, 0.83H), 1.02-1.37 (m, 13.64H), 0.91 (m, 5.71H), 0.72 (m, 5.57H).



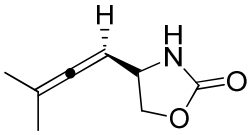
Compound 8l. Obtained in a 87% yield as a mixture of *E* and *Z* isomers. *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.50 (ddd, *J* = 11.6, 10.7, 2.2 Hz, 1H), 4.33 (ddd, *J* = 10.8, 3.9, 2.7 Hz, 1H), 3.38 (dd, *J* = 8.3, 6.1 Hz, 1H), 2.35 (dddd, *J* = 14.4, 6.1, 2.8, 2.2 Hz, 1H), 2.16-2.06 (m, 2H), 1.97 (s, 3H), 1.68-1.39 (m, 4H), 1.29 (m, 4H), 0.90 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.86, 120.29, 112.48, 68.44, 40.30, 34.29, 31.81, 26.99, 24.71, 22.64, 16.86, 14.18. HRMS (ESI) *m*/*z* calculated for $C_{12}H_{19}NO_2$ [M+H$^+$] 210.1489, found 210.1479.



Compound 8m. Obtained in a 70% yield as a mixture of *E* and *Z* isomers. *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.51 (m, 1H), 4.34 (m, 1H), 3.38 (m, 1H), 2.38 (m, 1H), 2.15 (m, 2H), 1.98 (s, 3H), 1.62 (m, 1H), 1.07 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.79, 119.94, 113.86, 68.45, 40.42, 27.42, 24.79, 16.98, 12.14. HRMS (ESI) *m/z* calculated for $C_{11}H_{17}NO_2$ [M+H$^+$] 196.1333, found 196.1330. *Z* isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.51 (m, 1H), 4.34 (m, 1H), 3.38 (m, 1H), 2.38 (m, 3H), 1.98 (s, 3H), 1.62 (m, 1H), 1.07 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.74, 130.29, 113.44, 68.49, 39.68, 25.81, 24.39, 16.87, 12.63. HRMS (ESI) *m/z* calculated for $C_{11}H_{17}NO_2$ [M+H$^+$] 196.1333, found 196.1330. IR (cm^{-1}, CH_2Cl_2) 2971, 1728, 1475, 1390, 1265, 1164, 1092, 1002 cm^{-1}.

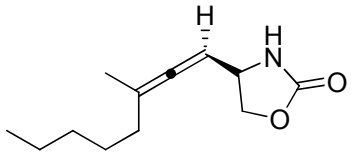
V. Synthesis of C-H insertion products.

Compounds 6b, and 9i-9k. These compounds were synthesized by established methods[3,6] and the characterization data from these methods[3,6] were used to evaluate and determine the ratio of methylene azridine to C-H insertion products from crude reaction mixtures using the Ag system.



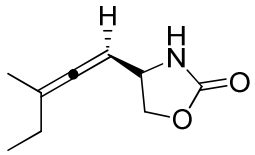
Compound 6a. Allene carbamate **4a** (0.05 g, 0.322 mmol, 1 equiv) was dissolved in dichloromethane (3 mL). 4A molecular sieves (0.2g) was added to the reaction mixture followed by $Rh_2(esp)_2$ (7.3 mg, 0.0096 mmol), 0.03 equiv) and was allowed to stir for 10 min. Iodosobenzene (0.142 g, 0.644 mmol, 2 equiv) was added in one portion and the reaction was

stirred at room temperature until complete by TLC. The reaction mixture filtered and the filtrate was concentrated by vacuum. The crude was subjected to silica gel column chromatography (0 → 30% EtOAc in hexanes, 6% increments). Methylene aziridine **5a** eluted first (35% yield) followed by **6a** in 21% yield as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.34 (br s, 1H), 5.02 (m, 1H), 4.53 (t, *J* = 8.6 Hz, 1H), 4.32 (m, 1H), 4.15 (dd, *J* = 8.6, 5.7 Hz, 1H), 1.72 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.94, 159.46, 100.27, 89.32, 70.64, 52.46, 20.61, 20.53. HRMS (ESI) *m*/*z* calculated for $C_8H_{11}NO_2$ [M+NH_4^+] 171.1129, found 171.1124. IR (cm^{-1}, CH_2Cl_2) 3460, 2986, 1757, 1477, 1387, 1265, 1094.



Compound 9l. Allene carbamate **7l** (0.05 g, 0.237 mmol, 1 equiv) was dissolved in dichloromethane (2 mL). 4A molecular sieves (0.2 g) was added to the reaction mixture followed by $Rh_2(esp)_2$ (5.1 mg, 0.0071 mmol), 0.03 equiv) and was allowed to stir for 10 min. Iodosobenzene (0.104 g, 0.473 mmol, 2 equiv) was added in one portion and the reaction was stirred at room temperature until complete by TLC. The reaction mixture filtered and the filtrate was concentrated by vacuum. The crude was subjected to silica gel column chromatography (0 → 30% EtOAc in hexanes, 6% increments). Methylene aziridine **8l** eluted first (34% yield) followed by **9l** in 44% yield as an oil. Both diastereomers: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.35 (br s, 1H), 5.08 (m, 1H), 4.53 (m, 1H), 4.32 (m, 1H), 4.15 (m, 1H), 1.96 (m, 2H), 1.71 (m, 3H), 0.89 (t, *J* = 6.4 Hz, 3H). Diastereomer 1: ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.41, 159.40, 104.71, 90.52, 70.70, 52.53, 33.82, 31.60, 27.23, 22.67, 19.07, 14.26. Diastereomer 2: ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.53, 159.40, 104.88, 90.57, 70.76, 52.68, 33.85, 31.60, 27.26. HRMS (ESI)

m/*z* calculated for $C_{12}H_{19}NO_2$ [M+NH_4^+] 227.1755, found 227.1754. IR (cm^{-1}, CH_2Cl_2) 3460, 2930, 1757, 1468, 1386, 1265, 1229, 1094.



Compound 9m. Allene carbamate **7m** (0.05 g, 0.295 mmol, 1 equiv) was dissolved in dichloromethane (3 mL). To this solution was added 4Å molecular sieves (0.2 g), followed by $Rh_2(esp)_2$ (6.7 mg, 0.009 mmol), 0.03 equiv) and the reaction mixture was allowed to stir for 10 min. Iodosobenzene (0.129 g, 0.6 mmol, 2 equiv) was added in one portion and the reaction was stirred at room temperature until complete by TLC. The reaction mixture filtered and the filtrate was concentrated by vacuum. The crude was subjected to silica gel column chromatography (0 → 30% EtOAc in hexanes, 6% increments). Methylene aziridine **8m** eluted first (32% yield) followed by **9m** in 33% yield as an oil. Both diastereomers: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50 (br s, 1H), 5.13 (m, 1H), 4.53 (m, 1H), 4.33 (m, 1H), 4.16 (m, 1H), 1.98 (m, 2H), 1.72 (m, 3H), 0.98 (m, 3H). Diastereomer 1: ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.99, 159.56, 106.51, 91.31, 70.68, 52.42, 26.85, 19.05, 12.28. Diastereomer 2: ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.15, 194,94, 159.56, 106.81, 91.42, 70.78, 52.60, 26.92, 19.15, 12.30. HRMS (ESI) *m*/*z* calculated for $C_9H_{13}NO_2$ [M+NH_4^+] 185.1285, found 185.1280. IR (cm^{-1}, CH_2Cl_2) 3459, 2985, 1757, 1472, 1387, 1265, 1094.

VI. References

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