Supporting Information

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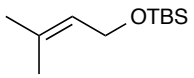
I. General experimental information

Dichloromethane, tetrahydrofuran, diethyl ether, and acetonitrile were dried by elution through alumina as described by Grubbs.[1] A 15 W blue light-emitting diode (LED) lamp (λ = 450 nm) purchased from Eagle Light was used for all reactions. Unless otherwise noted, chromatography was performed with Purasil 60 Å silica gel (230–400 mesh) and ^{13}C NMR data for all previously uncharacterized compounds were obtained using a Bruker Avance III 500 MHz spectrometer and are referenced to TMS (0.0 ppm) and $CDCl_3$ (77.16 ppm), respectively. ^{19}F data were obtained using a Bruker Avance III 400 MHz spectrometer and are referenced externally to the corresponding ^1H spectra. The NMR facilities at UW-Madison are funded by the NSF (CHE-1048642) and a generous gift from Paul J. Bender. IR spectral data were obtained using a Bruker Platinum-ATR spectrometer (neat). Melting points were obtained using a Stanford Systems DigiMelt apparatus and are uncorrected. Mass spectrometry was performed with a Waters (Micromass) Autospec®. These facilities are funded by the NSF (CHE-9974839, CHE-9304546) and the University of Wisconsin. All computational modeling was performed using the Phoenix supercomputer facility maintained by the UW-Madison Department of Chemistry and is funded in part by the NSF (CHE-0840494). Thin layer chromatography (TLC) was performed utilizing pre-coated silica gel F_{254} plates from SiliCycle Inc. containing a fluorescent indicator. Plates were visualized using either cerium ammonium molybdate (CAM), $KMnO_4$, or phosphomolybdic acid (PMA) stain.

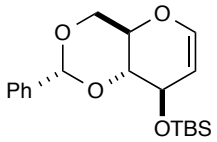
The catalyst complexes $Ru(dtbbpy)_3(PF_6)_2$,[2] $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$,[3] $Ir(ppy)_2(dtbbpy)(PF_6)$,[3] and $Ru(bpy)_3(PF_6)_2$ [4] were prepared as previously described. Cyclohexene, cyclooctene, cycloheptene, cyclopentene, dodecene, styrene, norbornene, trans-4-octene, cis-4-octene, trans-β-methylstyrene, *p*-chlorostyrene, tetramethylethylene, antheole, and benzofuran were purchased from Sigma-Aldrich and distilled immediately before use. Precursors to aziridine products **13**,[5] **14**,[6] **20**,[7] **17**,[8] **19**,[9] **16**,[7] and **26**[10] are known compounds and were prepared as previously described. Ethyl chloroformate and 2,2,2-

trichloroethyl chloroformate were purchased from Sigma-Aldrich. 2-Chloroethyl chloroformate was purchased from Acros.

II. Synthesis of alkene substrates



***tert*-Butyldimethyl((3-methylbut-2-en-1-yl)oxy)silane**. Prepared using a modification of a procedure reported by Waldmann.[11] To a 50 mL round-bottomed flask under an atmosphere of N_2 were added 3-methyl-2-butenol (1.00 mL, 10 mmol, 1 equiv.), CH_2Cl_2 (17 mL, 0.7 M), NEt_3 (1.70 mL, 12 mmol, 1.2 equiv), and 4-dimethylaminopyridine (48 mg, 0.39 mmol, 0.039 equiv). The solution was cooled to 0 °C, and TBSCl (1.81 g, 12 mmol, 1.2 equiv.) was added portionwise. The reaction was allowed to warm to room temperature and stirred overnight. After diluting with H_2O, the layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were concentrated after drying over Na_2SO_4, and the residue was purified by column chromatography to give the product as a clear oil (1.75 g, 88%). Spectral data were in complete agreement with reported values.[11]



4,6-O-Benzylidene-3-O-(tert-butyldimethyl)silyl-D-glucal. Prepared using to a modification of a procedure reported by Bennet.[12] To a 25 mL round-bottomed flask under an atmosphere of N_2 were added 1,5-anhydro-2-deoxy-4,6-O-benzylidene-D-arabino-hex-1-enitol (250 mg, 1.07 mmol, 1 equiv), [13] imidazole (95 mg, 1.39 mmol, 1.3 equiv) , and CH_2Cl_2 (10 mL, 0.1 M). The solution was cooled to 0 °C, and TBSCl (210 mg, 1.39 mmol, 1.3 equiv.) was added portionwise. The reaction was allowed to warm to room temperature and stirred overnight. The reaction was subsequently diluted with H_2O, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were concentrated *in vacuo*, and the residue was purified by flash chromatography to afford a clear oil (334 mg, 90%). Spectral data were in complete agreement with reported values.[14]

III. Synthesis of azidoformates

General procedure for the synthesis of azidoformates (3a-c): Based upon a procedure reported by Zhang.[15] To a rapidly stirring suspension of NaN_3 (1.5 equiv) in acetone (0.5 M) at 0 °C, freshly distilled chloroformate (1.0 equiv) was added dropwise. The reaction was allowed to warm to room temperature and stirred for 1 h. The reaction was subsequently diluted with H_2O and CH_2Cl_2, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was then purified by column chromatography (95:5 Hex:Et_2O) to afford pure azide.

Ethyl azidoformate (3a): Synthesized according to the general procedure using 500 mg ethyl chloroformate (4.61 mmol, 1 equiv.), 449 mg NaN_3 (6.91 mmol, 1.5 equiv), and 14 mL of acetone. The product was isolated as a clear liquid after chromatography (347 mg, 65%). Spectral data were in complete agreement with reported values.[16]

2-Chloroethyl azidoformate (3b): Synthesized according to the general procedure using 690 mg 2-chloroethyl chloroformate (4.83 mmol, 1 equiv.), 471 mg NaN_3 (7.24 mmol, 1.5 equiv.), and 10 mL

acetone. Product was isolated as a clear liquid after chromatography (745 mg, 103%). IR (neat) 2190, 2155, 2134, 1741, 1228, 1081 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 4.46 (t, J = 5.7 Hz), 3.72 (t, J = 5.7 Hz). ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 157.4, 67.7, 40.9; HRMS (ASAP) calculated for $[C_3H_5ClN_3O_2]^+$ requires *m/z* 150.0065, found *m/z* 150.0070.

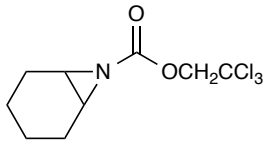
2,2,2-Trichloroethyl azidoformate (3c): Synthesized according to the general procedure using 2.53 g 2,2,2-trichloroethyl chloroformate (27.7 mmol, 1 equiv.), 2.70 g NaN_3 (41.5 mmol, 1.5 equiv.) and 54 mL acetone. Product was isolated as a clear liquid after chromatography (5.74 g, 95%). Spectral data were in complete agreement with reported values.[15]

IV. Aziridination of alkenes

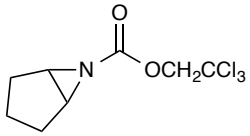
General procedure for synthesis of aziridines: An oven-dried 25 mL Schlenk tube containing a stir bar was charged with the alkene substrate (0.400 mmol, 1.00 equiv), $Ir(ppy)_2(dtbbpy)(PF_6)$ (2.2 mg, 0.010 mmol, 0.025 equiv) and CH_2Cl_2 (1 mL, 0.4 M). To the solution was added $TrocN_3$ (436 mg, 2.00 mmol, 5.00 equiv), and the mixture was submitted to three freeze-pump-thaw cycles, purged with N_2, and irradiated with a 15 W blue LED lamp (λ = 464 nm). Upon completion of the reaction, the reaction was concentrated *in vacuo*, and the residue was purified by flash chromatography on silica-9 (*vide infra*) to afford the pure aziridine.

The aziridine products were found to have varying degrees of stability on silica gel. The aliphatic aziridines were generally the most stable, while phenyl substituted aziridines decompose rapidly. The most reproducible method for isolation of all aziridines employed purification on silica-9, or basified silica gel with a pH of 9 in an aqueous solution (see below for preparation). Still, it is worthwhile to note that prolonged exposure to either silica or silica-9 lead to highly irreproducible isolation of material. Thus, relatively short (3" x 1") silica-9 columns were utilized to keep elution times below approximately 5 min in order to maximize reproducibility.

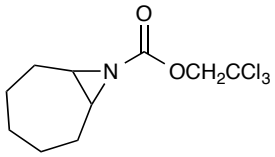
Silica-9 was prepared *via* a modified procedure described by Deli:[17] silica gel (200 g) was added to 2 L of saturated aqueous $NaHCO_3$. The resulting slurry was vigorously stirred for 2 h, at which point the mixture was diluted with 200 mL acetone and filtered. The silica gel was washed three times with a 1:1 H_2O/acetone mixture and once with acetone, and the filtrate was allowed to air dry overnight before use.



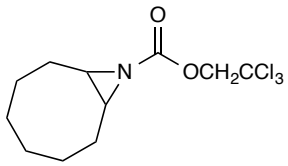
2,2,2-Trichloroethyl 2-cyclohexaneaziridine-1-carboxylate (4): Prepared according to the General Procedure using 32.9 mg (0.400 mmol) cyclohexene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using 95:5 hexanes:Et_2O to afford the aziridine as a white solid (mp = 30–34 °C). Experiment 1: 80 mg (73%) Experiment 2: 83 mg (75%) IR (neat) 3011, 2944, 2864, 1728, 1283, 1217 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 4.79 (s, 2H), 2.79–2.76 (m, 2H), 2.02–1.97 (m, 2H), 1.87–1.81 (m, 2H), 1.48–1.41 (m, 2H), 1.30–1.23 (m, 2H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 162.1, 95.2, 75.2, 37.7, 23.5, 19.7; HRMS (ESI) calculated for $[C_9H_{12}Cl_3NO_2]^+$ required 272.0007 *m/z* found 272.0006 *m/z*.



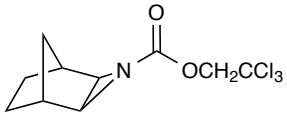
2,2,2-Trichloroethyl 2-cyclopentaneaziridine-1-carboxylate (5): Prepared according to the General Procedure using 28 mg (0.400 mmol) cyclopentene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using 97:3 hexanes:Et_2O to afford the aziridine as a clear oil. Experiment 1: 60 mg (58%); Experiment 2: 67 mg (65%). IR (neat) 2927, 2850, 1731, 1439, 1375, 1288, 1221, 1108, 1056 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 4.74 (s, 2H), 3.12 (s, 2H), 2.22–2.13 (m, 2H), 1.74–1.61 (m, 3H), 1.31–1.18 (m, 2H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 160.6, 95.2, 75.5, 43.9, 26.5, 19.4; HRMS (ESI) calculated for $[C_8H_{10}Cl_3NO_2]^+$ required 257.9850 *m/z* found 257.9849.



2,2,2-Trichloroethyl 2-cyclooctaneaziridine-1-carboxylate (6): Prepared according to the General Procedure using 39 mg (0.400 mmol) cycloheptene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using 97:3 hexanes:Et_2O to afford the aziridine as a clear oil. Experiment 1: 80 mg (70%); Experiment 2: 78 mg (68%). IR (neat) 2927, 2850, 1731, 1439, 1375, 1288, 1221, 1108, 1056 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 4.74 (s, 2H), 2.79–2.72 (m, 2H), 2.01–1.87 (m, 4H), 1.64–1.46 (m, 5H), 1.28–1.18 (m, 1H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 162.5, 95.4, 75.3, 42.7, 31.4, 28.9, 25.4; HRMS (ESI) calculated for $[C_{10}H_{14}Cl_3NO_2]^+$ required 286.0163 *m/z* found 286.0162 *m/z*.

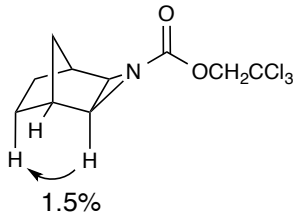


2,2,2-Trichloroethyl 2-cyclooctaneaziridine-1-carboxylate (7): Prepared according to the General Procedure using 44 mg (0.400 mmol) cyclooctene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using 97:3 hexanes:Et_2O to afford the aziridine as a clear oil and inseparable mixture of diastereomers (9:1 cis:trans). Experiment 1: 100 mg (83%); Experiment 2: 106 mg (88%). IR (neat) 2929, 2861, 1732, 1446, 1374, 1272, 1212, 1183, 1117 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 4.74 (s, 2H), 2.57–2.51 (m, 2H), 2.26 (dq, J = 14.2, 3.6 Hz, 2H), 1.71–1.52 (m, 4H), 1.53–1.39 (m, 4H), 1.37–1.23 (m, 2H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 161.9, 95.3, 75.3, 42.2, 26.7, 26.35, 26.1; HRMS (ESI) calculated for $[C_{11}H_{16}Cl_3NO_2]^+$ required 300.0319 *m/z* found 300.0319 *m/z*.

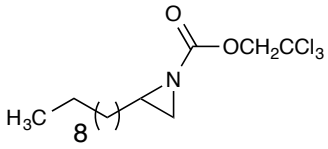


2,2,2-Trichloroethyl 3-azatricylo[3.2.1.$0^{2,4\text{-exo}}$]octane-3-carboxylate (8): Prepared according to the General Procedure using 37.7 mg (0.400 mmol) norbornene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using 95:5 hexanes:Et_2O to afford the aziridine as a white solid (mp = 51–53 °C). Experiment 1: 86 mg (76%) Experiment 2: 74 mg (65%) IR (neat) 2964, 2880, 1735,

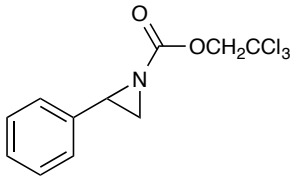
1387, 1302 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 4.74 (s, 2H), 2.73, (s, 2H), 2.56 (s, 2H) 1.52–1.48 (m, 2H) 1.38 (d, J = 10.7 Hz, 1H), 1.26–1.22 (m, 2H), 0.84 (d, J = 10.5 Hz, 1H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 160.0, 95.4, 75.3, 39.8, 36.0, 28.1, 25.8; HRMS (EI) calculated for $[C_{10}H_{12}Cl_3NO_2]^+$ required 284.0007 *m/z*, found 284.0009 *m/z*.



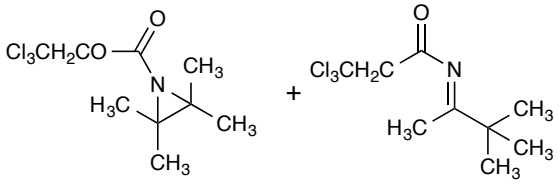
The relative stereochemistry of **10** was determined using NOESY1D spectroscopy.



2,2,2-Trichloroethyl 2-decylaziridine-1-carboxylate (9): Prepared according to the General Procedure using 67.2 mg (0.400 mmol) 1-dodecene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using 95:5 hexanes:Et_2O to afford the aziridine as a clear oil. Experiment 1: 89 mg (62%) Experiment 2: 89 mg (62%) IR (neat) 2927, 2855, 1739 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 4.77, 4.72 (ABq, J_{AB} = 12.0 Hz, 2H), 2.56 (qd, J = 5.8, 3.6, 1H), 2.44 (d, J = 6.0 Hz, 1H), 2.09 (d, J =3.9 Hz, 1H), 1.54–1.51 (m, 3H), 1.36–1.34 (m, 2H), 1.32–1.26 (m, 13H), 0.88 (t, J = 6.9, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 162.0, 95.2, 75.5, 39.3, 32.4, 32.3, 32.1, 29.8, 29.7, 29.7, 29.5, 29.3, 27.0, 22.8, 14.3; HRMS (EI) calculated for $[C_{15}H_{26}Cl_3NO_2]^+$ required 358.1102 *m/z,* found 358.1102 *m/z*.

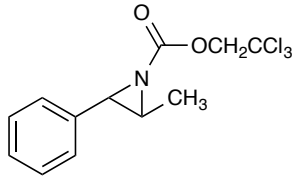


2,2,2-Trichloroethyl 2-phenylaziridine-1-carboxylate (10): Prepared according to the General Procedure using 41.6 mg (0.400 mmol) styrene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using 95:5 hexanes:Et_2O to afford the aziridine as a clear oil that solidified upon standing. Experiment 1: 73 mg (63%) Experiment 2: 69 mg (59%) All spectral data were in complete agreement with previously reported values.[19]

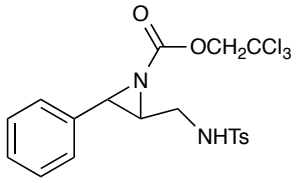


2,2,2-Trichloroethyl 2,2,3,3-tetramethylaziridine-1-carboxylate (11): Prepared according to the General Procedure using 33.7 mg (0.400 mmol) tetramethylethylene with an irradiation time of 20 h.

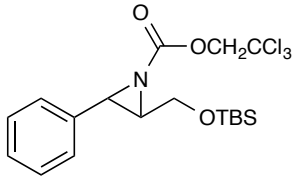
Purified by flash column chromatography on silica-9 using 98:2 hexanes:Et_2O to afford the aziridine product as a clear oil along with the imine product derived from methyl group migration (13:1). Experiment 1: 101 mg (91%); Experiment 2: 100 mg (91%). IR of mixture (neat) 3010, 2970, 1712, 1469, 1381, 1277, 1246 cm^{-1}. **Characterization data for 11**: ^1H NMR: (500.2 MHz, $CDCl_3$) δ 4.76 (s, 2H), 1.36 (s, 12H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 157.7, 95.4, 78.8, 46.4, 20.2; HRMS (ESI) calculated for $[C_9H_{14}Cl_3NO_2]^+$ required 274.0163 *m/z*, found 274.0164 *m/z*. **Characterization data for imine (2,2,2-trichloroethyl (3,3-dimethylbutan-2-imine)carbamate)**: ^1H NMR: (500.2 MHz, $CDCl_3$) δ 4.85 (s, 2H), 2.07 (s, 2H), 1.20 (s, 9H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 184.0, 161.6,
95.0, 40.5, 28.3, 18.2.



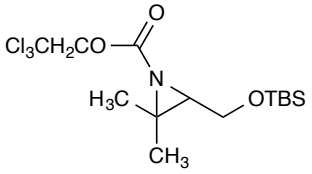
2,2,2-Trichloroethyl *trans*-2-phenyl-3-methylziridine-1-carboxylate (12): Prepared according to the General Procedure using 47.2 mg (0.400 mmol) *trans*-β-methylstyrene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using 95:5 hexanes:Et_2O to afford the aziridine as a clear oil and inseparable mixture of diastereomers (10:1 trans:cis). Experiment 1: 82 mg (72%); Experiment 2: 101 mg (82%). IR (neat) 3033, 3004, 2971, 1734, 1499, 1462, 1375 cm^{-1}. ^1H NMR of major diastereomer: (500.2 MHz, $CDCl_3$) δ 7.35–7.33 (m, 2H), 7.30–7.28 (m, 3H) 4.80, 4.75 (ABq, J_{AB} = 12.0 Hz, 2H), 3.34 (d, J = 3.2 Hz, 1H), 2.76 (qd, J = 5.6, 3.1 Hz, 1H), 1.52 (d, J = 5.6 Hz, 3H); ^{13}C NMR of major diastereomer: (125.8 MHz, $CDCl_3$) δ 159.7, 136.5, 128.7, 128.1, 126.4, 95.1, 75.6, 46.7, 44.2, 16.4; HRMS (EI) calculated for $[C_{12}H_{12}Cl_3NO_2]^+$ required 308.0007 *m/z,* found 308.0005 *m/z.*



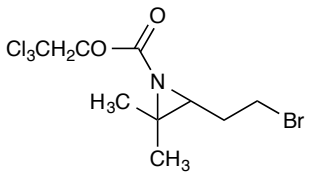
2,2,2-Trichloro *trans*-2-{[(4-methylphenyl)sulfonamido] methyl}-3-phenylaziridine-1-carboxylate (13): Prepared according to the General Procedure using 115 mg (0.400 mmol) 4-methyl-N-[(2E)-3-phenylprop-2-en-1-yl]benzene-1-sulfonamide with an irradiation time of 20 h. After the reaction was concentrated, the residue was passed through a short plug of silica-9 in 1:1 Et_2O:hexanes. Pure material was precipitated as a white solid by the addition of hexanes, and collected by vacuum filtration (mp = 109–116 °C). Experiment 1: 123 mg (65%) Experiment 2: 118 mg (62%) IR (neat) 3252, 2958, 2926, 1725. 1699, 1433, 1378, 1333 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.74 (d, J = 8.3 Hz, 2H), 7.34–7.29 (m, 5H), 7.23–7.20 (m, 2H), 5.35 (dd, J = 8.9, 4.4 Hz, 1H), 4.85, 4.55 (ABq, J_{AB} = 12.0 Hz, 2H), 3.69 (ddd, J = 14.0, 8.9, 3.2 Hz, 1H), 3.49 (d, J = 3.1 Hz, 1H), 2.97 (ddd, J = 13.9, 7.2, 4.4 Hz, 1H) 2.91 (dt, J = 6.9, 3.2 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 159.7, 143.9, 136.7, 134.5, 130.0, 128.8, 128.7, 127.2, 126.6, 94.8, 75.5, 45.4, 44.3, 43.7, 21.7; HRMS (EI) calculated for $[C_{19}H_{19}Cl_3N_2O_4S]^+$ required 477.0204 *m/z*, found 477.0209 *m/z*



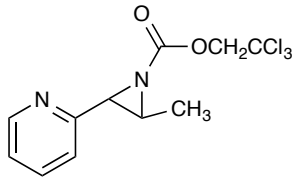
2,2,2-Trichloro *trans*-2-(*t*-butyldimethylsiloxy)methyl-3-phenylaziridine-1-carboxylate (14): Prepared according to the General Procedure using 115 mg (0.400 mmol) (*E*)-1-*tert*-butyldimethylsilyloxy-3-phenyl-2-propene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using 95:5 hexanes:Et_2O to afford the aziridine as a white solid and inseparable a mixture of diastereomers (14:1). (mp = 53–56 °C). Experiment 1: 127 mg (73%) Experiment 2: 140 mg (80%) IR (neat) 2955, 2931, 2859, 1733, 1472, 1318, 1180 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.54–7.43 (m, 5H), 4.91, 4.77 (ABq, J_{AB} = 12.0 Hz, 2H), 4.33, 4.26 (AB of ABXY, J_{AB} = 12.0 Hz, J_{AX} = 2.0 Hz, J_{BX} = 2.0 Hz, 2H), 3.89 (Y of ABXY, J_{XY} = 3.1 Hz, 1H), 2.95 (X of ABXY, J_{XY} = 3.1 Hz, J_{AX} = 2.0 Hz, J_{BX} = 2.0 Hz), 1.07 (s, 9H), 0.26 (s, 3H), 0.23 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 159.6, 136.5, 128.7, 128.0, 126.6, 95.0, 58.3, 48.2, 40.4, 25.94, 25.91, 18.4, –5.1, –5.4; HRMS (EI) calculated for $[C_{18}H_{26}Cl_3NO_3Si]^+$ required 438.0821 *m/z*, found 438.0823 *m/z*.



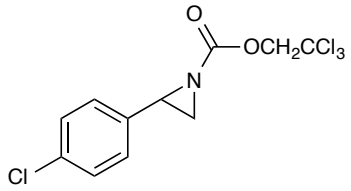
2,2,2-Trichloro 3-(t-butyldimethylsiloxy)methyl-2,2-dimethylazidine-1-carboxylate (15): Prepared according to the General Procedure using 115 mg (0.400 mmol) *tert*-butyldimethyl((3-methylbut-2-en-1-yl)oxy)silane with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using a gradient of 98:2 to 95:5 hexanes:Et_2O to afford the aziridine as a clear oil. Experiment 1: 127 mg (81%); Experiment 2 115 mg (74%): IR (neat) 2956, 2930, 2858, 1728, 1391, 1254 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 4.77, 4.73 (ABq, J_{AB} = 12.0 Hz, 2H), 3.93 (dd, *J* = 11.2, 5.2 Hz, 1H), 3.57 (dd, *J* = 11.2, 7.4, 1H), 2.57 (dd, *J* = 7.3, 5.2 Hz, 1H), 1.39 (s, 3H), 1.32 (s, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 159.9, 92.3, 75.4, 61.8, 49.0, 45.3, 25.99. 25.97, 23.7, 19.4, –5.1, –5.3; HRMS (EI) calculated for $[C_{18}H_{26}Cl_3NO_3Si]^+$ required 438.0821 *m/z* found 438.0823 *m/z*.



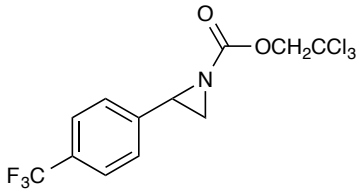
2,2,2-Trichloro 3-(2-bromoethyl)-2,2-dimethylaziridine-1-carboxylate (16): Prepared according to the General Procedure using 65.2 mg (0.400 mmol) 5-bromo-2-methyl-pent-2-ene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using 95:5 hexanes:Et_2O to afford the aziridine as a clear oil. Experiment 1: 120 mg (85%); Experiment 2: 117 mg (83%). IR (neat) 2971, 1727, 1245, 1382, 1136, 1104 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 4.79, 4.72 (ABq, J_{AB} = 12.0 Hz, 2H), 3.60–3.51 (m, 2H), 2.52 (dd, 7.7, *J* = 5.1 Hz, 1H), 2.18–2.03 (m, 2H), 1.40 (s, 3H), 1.32 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 159.7, 95.1, 75.3, 47.5, 45.4, 31.8, 30.1, 23.4, 19.7; HRMS (ASAP-MS) calculated for $[C_9H_{13}Cl_3BrNO_2]^+$ required 351.9268 *m/z* found 351.9268 *m/z*.



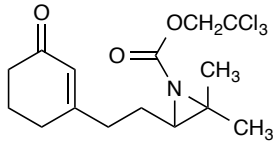
2,2,2-Trichloroethyl 2-methyl-3-(pyridin-2-yl)aziridine-1-carboxylate (17): Prepared according to the General Procedure using 47.6 mg (0.400 mmol) *trans*-1-(2-pyridyl)prop-1-ene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using a gradient of 9:1 hexanes:Et_2O to 8:2 hexanes:Et_2O to afford the aziridine as a white solid (mp = 56–60 °C). Experiment 1: 96 mg (78%); Experiment 2: 95 mg, (77%) IR (neat) 3155, 3107, 2975, 2933, 1730, 1594, 1463, 1377, 1308, 1184 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 8.52 (d, J = 4.9 Hz, 1H), 7.66 (td, J = 7.7, 1.8 Hz, 2H), 7.36 (d, J = 7.7 Hz, 2H), 7.18 (dd, J = 7.6, 4.8 Hz, 2H), 4.32, 4.26 (ABq, J_{AB}=12 Hz, 2H 3.43), (d, J = 3.0 Hz, 2H), 3.10 (qd, J = 5.6, 3.0 Hz, 2H), 1.51 (d, J = 5.6 Hz, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 159.7, 155.0, 149.6, 136.8, 122.9, 122.6, 94.8, 75.8, 47.2, 42.7, 16.8; HRMS (EI) calculated for $[C_{11}H_{11}Cl_3N_2O_2]^+$ required 308.9959 *m/z*, found 308.9964 *m/z*.



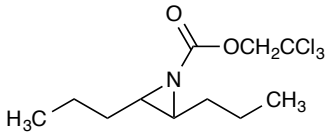
2,2,2-Trichloroethyl 2-(4-chlorophenyl)aziridine-1-carboxylate (18): Prepared according to the General Procedure using 55.4 mg (0.400 mmol) 4-chlorostyrene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using 98:2 hexanes:Et_2O to afford the aziridine as a white solid (mp = 39–42 °C). Experiment 1: 87 mg (66%); Experiment 2: 56 mg, (56%) All spectral data were in complete agreement with previously reported values.[18]



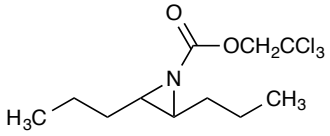
2,2,2-Trichloroethyl 2-(4-trifluoromethylphenyl) aziridine-1-carboxylate (19): Prepared according to the General Procedure using 69.0 mg (0.400 mmol) 4-(trifluoromethyl)styrene with an irradiation time of 30 h. Purified by flash chromatography on silica-9 using a gradient of 98:2 to 95:5 hexanes:Et_2O to afford the product as a white solid (42–45 °C). Experiment 1: 90 mg (62%); Experiment 2: 100 mg (69%). IR (neat) 3154, 3004, 2959, 1740, 1326, 1285, 1172 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 4.83, 4.77 (ABq, J_{AB} = 12 Hz, 2H) 3.67 (dd, J = 6.4, 3.6 Hz, 1H), 2.87 (d, J = 6.3 Hz, 1H), 2.41 (d, J = 3.5 Hz, 1H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 161.3, 140.6, 130.6 (q, J = 32.6 Hz), 126.8, 125.8 (q, J = 3.8 Hz), 124.1 (q, J = 272.1 Hz), 95.0, 75.7, 39.2, 35.7; ^{19}F NMR: (376.5 MHz, $CDCl_3$) δ –62.6; HRMS (ESI) calculated for $[C_{12}H_9Cl_3F_3NO_2]^+$ required 361.3724 *m/z*, found 361.9722 *m/z*.



2,2,2-Trichloroethyl 2,2-dimethyl-3-(2-(3-oxocyclohex-1-en-1-yl)ethyl)aziridine-1-carboxylate (20): Prepared according to the General Procedure using 71.2 mg (0.400 mmol) alkene with an irradiation time of 20 h. Purified by flash chromatography on silica-9 using 2:1 Et_2O:hexanes to yield the product as a clear oil. Experiment 1: 106 mg (72%); Experiment 2: 115 mg (78%). IR (neat) 2956, 2930, 2871, 1728, 1667, 1244 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 5.92 (s, 1H), 4.78, 4.71 (ABq, J_{AB} = 12.0 Hz, 2H), 2.52–2.40 (m, 2H), 2.39–2.32 (m, 5H), 2.01 (p, J = 6.1 Hz, 2H), 1.85–1.78 (m, 1H), 1.67–1.60 (m, 1H), 1.38 (s, 3H), 1.31 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 199.7, 164.9, 159.9, 125.7, 95.1, 75.3, 48.4, 45.5, 37.3, 35.5, 29.9, 25.8, 23.5, 22.7, 19.4; HRMS (ESI) calculated for $[C_{15}H_{20}Cl_3NO_3]^+$ required 368.0582 *m/z*, found 368.0582 *m/z*

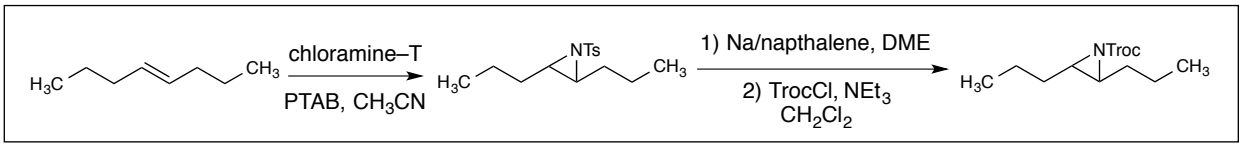


2,2,2-Trichloroethyl *trans*-2,3-dipropylaziridine-1-carboxylate (28): Prepared according to the General Procedure using 44.5 mg (0.400 mmol) trans-4-octene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using 98:2 hexanes:Et_2O to afford the aziridine product as a clear oil and inseparable mixture of diastereomers (3:1 trans:cis). Experiment 1: 104 mg (80%); Experiment 2: 104 mg (84%). IR (neat) 2962, 2933, 2874, 1726, 1451, 1374, 1297, 1102, 1057 cm^{-1}. ^1H NMR for trans: δ 4.76, 4.75 (ABq, J_{AB} = 12.0 Hz, 2H), 2.34–2.31 (m, 2H), 1.76 (ddt, J = 14.0, 8.9, 5.4 Hz, 2H), 1.60–1.45 (m, 4H), 1.29 (ddt, J = 13.3, 8.9, 6.5, 2H), 0.97 (t, J = 7.4 Hz, 6H); ^{13}C NMR for trans: (125.8 MHz, $CDCl_3$) δ 160.3, 95.3, 75.5, 44.9, 33.5, 20.4, 14.0.; ^1H NMR for cis: (500.2 MHz, $CDCl_3$) δ 4.72 (s, 2H), 2.60–2.55 (m, 2H), 1.65–1.42 (m, 8H), 1.01 (t, J = 7.0 Hz, 6H); ^{13}C NMR for cis (125.8 MHz, $CDCl_3$) δ 162.2, 95.1, 75.3, 43.1, 29.6, 20.6, 13.8. HRMS (ESI) calculated for $[C_{11}H_{18}Cl_3NO_2]^+$ required 302.0476 *m/z*, found 302.0475 *m/z*.



2,2,2-Trichloroethyl *trans*-2,3-dipropylaziridine-1-carboxylate (28): Prepared according to the General Procedure using 44.5 mg (0.400 mmol) cis-4-octene with an irradiation time of 20 h. Purified by flash column chromatography on silica-9 using 98:2 hexanes:Et_2O to afford the aziridine as a clear oil as an inseparable mixture of diastereomers (2.2:1). Experiment 1: 93 mg (77%) Experiment 2: 88 mg, (73%) IR (neat) 2962, 2933, 2874, 1726, 1451, 1374, 1297, 1102, 1057 cm^{-1}. ^1H NMR for trans: δ 4.76, 4.75 (ABq, J_{AB} = 12.0 Hz, 2H), 2.34–2.31 (m, 2H), 1.76 (ddt, J = 14.0, 8.9, 5.4 Hz, 2H), 1.60–1.45 (m, 4H), 1.29 (ddt, J = 13.3, 8.9, 6.5, 2H), 0.97 (t, J= 7.4 Hz, 6H); ^{13}C NMR for trans: (125.8 MHz, $CDCl_3$) δ 160.3, 95.3, 75.5, 44.9, 33.5, 20.4, 14.0.; ^1H NMR for cis: (500.2 MHz, $CDCl_3$) δ 4.72 (s, 2H), 2.60–2.55 (m, 2H), 1.65–1.42 (m, 8H), 1.01 (t, J = 7.0 Hz, 6H); ^{13}C NMR for cis (125.8 MHz, $CDCl_3$) δ 162.2, 95.1, 75.3, 43.1, 29.6, 20.6, 13.8; HRMS (ESI) calculated for $[C_{11}H_{18}Cl_3NO_2]^+$ required 302.0476 *m/z*, found 302.0475 *m/z*.

Assignment of ^{1}H NMR signals for *cis*- and *trans*-**28** was aided *via* analysis of pure samples prepared by stereospecific aziridination of both cis- and tras-4-octene *via* the method of Sharpless,[19] tosyl group removal *via* the method of Morgan,[20] and installation of the Troc group.



Representative procedure follows for synthesis of **2,2,2-trichloroethyl *trans*-2,3-dipropylaziridine-1-carboxylate:** In a dry 25 mL round-bottomed flask under an atmosphere of N_2 was placed a solution of *trans*-4-octene (416 mg, 2.67 mmol, 1.0 equiv.) and chloramine-T (729 mg, 3.20 mmol, 1.2 equiv.) in CH_3CN (13 mL, 0.2 M). Phenyltrimethylammonium tribromide (100 mg, 0.267 mmol, 0.1 equiv.) was added, and the reaction was stirred for 24 h. The mixture was concentrated, and the residue was isolated by column chromatography on silica gel using 9:1 Hex:EtOAc as eluent, yielding 627 mg (79%) of *trans*-1-(4-methylphenylsulfonyl)-2,3-dipropylaziridine as a yellow oil. Spectral data were in complete agreement with reported values.[21]

This material was placed in a 50 mL round-bottomed flask, dissolved in degassed DME (8 mL) under positive N_2 pressure, and cooled to –78 °C. To a separate 25 mL Schlenk tube containing degassed DME (19 mL) were added freshly cut sodium metal (437 mg, 19 mmol) and napthalene (2.68 g, 20.9 mmol) under positive N_2 pressure. After stirring 2 h at room temperature, this freshly prepared sodium napthalenide solution was added dropwise to the aziridine until the solution maintained a green color (~18 mL, 18 mmol, 8.5 equiv). The reaction was diluted with ether (50 mL) and washed with H_2O (50 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo* to give the crude product as an oil that was carried directly onto the next step. The crude was dissolved in CH_2Cl_2 (6 mL) and cooled to 0 °C. To this was added NEt_3 (0.585 mL, 4.20 mmol) and 2,2,2-trichloroethyl chloroformate (0.288 mL, 2.11 mmol), and the reaction was allow to warm to RT and stir overnight. The reaction was washed with H_2O (5 mL), dried over $MgSO_4$, and concentrated. The product was isolated after chromatography on silica-9 using a gradient of hexanes to 9:1 hexanes:Et_2O yielding 220 mg (33% over two steps).

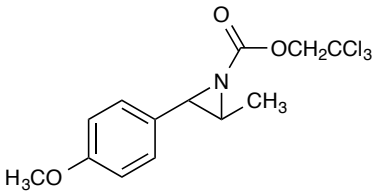
Representative NMR data for **2,2,2-trichloroethyl *trans*-2,3-dipropylaziridine-1-carboxylate:** ^{1}H NMR: (500.2 MHz, $CDCl_3$) δ 4.76, 4.75 (ABq, J_{AB} = 12.0 Hz, 2H), 2.34–2.31 (m, 2H), 1.76 (ddt, J = 14.0, 8.9, 5.4 Hz, 2H), 1.60–1.45 (m, 4H), 1.29 (ddt, J = 13.3, 8.9, 6.5, 2H), 0.97 (t = 7.4 Hz, 6H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 160.3, 95.3, 75.5, 44.9, 33.5, 20.4, 14.0.

Synthesis of **2,2,2-trichloroethyl *cis*-2,3-dipropylaziridine-1-carboxylate** was performed in an identical manner as above starting from cis-4-octene.

Representative NMR data for **2,2,2-trichloroethyl *cis*-2,3-dipropylaziridine-1-carboxylate:** ^{1}H NMR: (500.2 MHz, $CDCl_3$) δ 4.72 (s, 2H), 2.60–2.55 (m, 2H), 1.65–1.42 (m, 8H), 1.01 (t, J = 7.0 Hz, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 162.2, 95.1, 75.3, 43.1, 29.6, 20.6, 13.8.

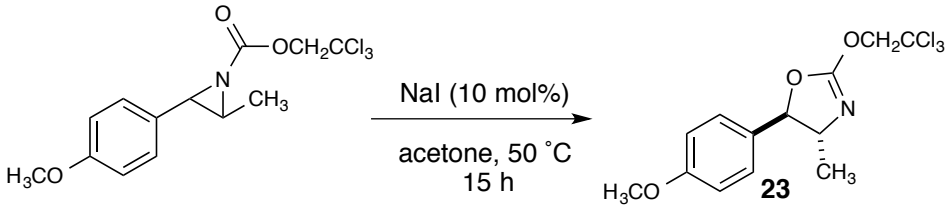
V. Reactions involving electron-rich alkenes

Reactions were carried out in an identical manner to the General Procedure outlined for synthesis of aziridines above.

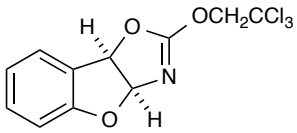


2,2,2-Trichloro *trans*-2-(4-methoxyphenyl)-3-phenylaziridine-1-carboxylate (22): Prepared according to the General Procedure using 59.3 mg (0.400 mmol) anethole, 16.6 mg (0.0748 mmol, 0.187 equiv) 1,4-bis(trimethylsilyl)benzene added as an internal standard, and an irradiation time of 20 h. Analysis of the reaction mixture by ^{1}H NMR resulted in identification of both aziridine product and oxazoline product. Attempts to isolate the aziridine product resulted in significant decomposition and poor mass recovery. Yields are determined from ^{1}H NMR analysis of the unpurified reaction mixture using a relaxation delay of 10 s and 1,4-bis(trimethylsilyl)benzene as an internal standard. Experiment 1: 0.280 mmol (70%) **22**, 0.0320 mmol (8%) **23**; Experiment 2: 0.288 mmol (72%) **22**, 0.0320 mmol (8%) **23**. Characterization data of **25** from the unpurified sample are as follows: ^{1}H NMR (500.2 MHz, $CDCl_3$) δ 7.21 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 4.79, 4.73 (ABq, J_{AB} = 12.0 Hz, 2H), 3.80 (s, 3H), 3.30 (d, J = 3.2, 1H), 2.75 (qd, J = 5.6, 3.2 Hz, 1H), 1.50 (d, J = 5.6 Hz, 3H). Characterization data of **26** from on resolved peaks in the ^{1}H NMR of the reaction mixture are as follows: ^{1}H NMR (500.2 MHz, $CDCl_3$) δ 5.10 (d, J = 7.6 Hz, 1H), 4.91, 4.87 (ABq, J_{AB} = 12.0 Hz, 2H), 4.04 (p, 6.6 Hz, 1H), 1.37 (d, J = 6.4 Hz, 3H).

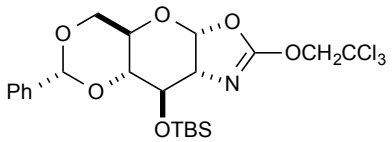
Identity of the oxazoline product **5-(4-methoxyphenyl)-4-methyl-2-(2,2,2-trichloroethoxy)-4,5-dihydrooxazole** (**23)** was confirmed by subjecting aziridine **22** to the Heine rearrangement.[22]



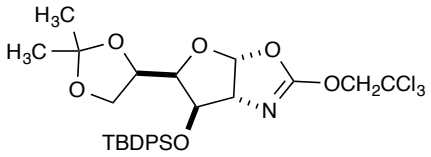
The unpurified reaction mixture from above was concentrated *in vacuo* and dissolved in acetone (2 mL, 0.2 M) in a 3 dram vial. NaI (6 mg, 0.0400 mmol, 0.1 equiv) was added, and the vial was flushed with N_2, capped, and heated to 50 °C for 15 h. After cooling to RT, the reaction was diluted with H_2O and extracted three times with CH_2Cl_2. The combined organics were dried over $MgSO_4$ and concentrated *in vacuo*. Attempted chromatography on the residue resulted in rapid decomposition of the product. ^{1}H NMR analysis of the reaction mixture showed peaks consistent with product **23** observed above in 93% yield vs.1,4-bis(trimethylsilyl)benzene with a relaxation delay of 10 s. Characterization of **23** from the unpurified sample is consistent with that reported for the aziridination reaction (*vide supra*).



2-(2,2,2-Trichloroethoxy)-dihydrobenzofuro[2,3-*d*]oxazole (24): Prepared according to the General Procedure using 47.2 mg (0.400 mmol) benzofuran and an irradiation time of 20 h. Purified by flash chromatography on silica-9 using 95:5 hexanes:Et_2O to yield the product as a white solid (111–116 °C). Experiment 1: 107 mg (87%); Experiment 2: 109 mg (89%). IR (neat) 3154, 2981, 1756, 1653, 1478, 1406, 1348 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.44 (d, J = 7.5 Hz, 1H), 7.35 (t, J = 7.7 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.49 (d, J = 6.4 Hz, 1H), 6.19 (d, J = 6.4 Hz, 1H), 4.98, 4.81 (ABq, J_{AB} = 12.0 Hz, 2H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 165.7, 159.5, 132.6, 127.1, 122.0, 121.8, 111.5, 101.5, 93.6, 85.5, 80.3. HRMS (ESI) calculated for $[C_{11}H_8Cl_3NO_3]^+$ required 307.9643 *m/z*, found 307.9641 *m/z*.

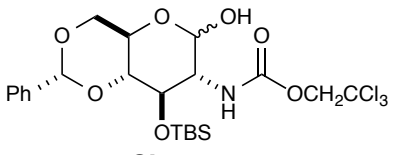


9-((*tert*-Butyldimethylsilyl)oxy)-7-phenyl-2-(2,2,2-trichloroethoxy)-hexahydro-[1,3]dioxino [4',5':5,6]pyrano[3,2-*d*]oxazole (25): Prepared according to the General Procedure using 139 mg (0.400 mmol) 4,6-O-benzylidene-3-O-(*tert*-butyldimethyl)silyl-D-glucal, 20.1 mg 1,4- bis(trimethylsilyl) benzene (0.0905 mmol, 0.226 equiv.), and an irradiation time of 20 h. Attempted purification by flash chromatography on silica-9 lead to clean hydrolysis to the amino-alcohol **SI-1** (*vide infra*). A yield of 65% for **26** of the major diastereomer was determined vs. 1,4- bis(trimethylsilyl)benzene by ^1H NMR analysis of the unpurified mixture using a relaxation delay of 10 s. Characterization of resolved peaks of **26** from the unpurified sample is as follows: ^1H NMR (500.2 MHz, $CDCl_3$) δ 7.48–7.26 (m, 2H), 7.37–7.35 (m, 3H), 6.11 (d, J = 7.2 Hz, 1H), 5.57 (s, 1H), 4.39 (dd, J = 10.1, 4.9 Hz, 1H), 3.94 (dd, J = 7.2, 4.8 Hz, 1H), 3.76 (dd, J = 9.6, 4.8 Hz, 1H), 3.71 (t, J = 10.1 Hz, 1H), 3.58 (t, J = 9.0 Hz, 1H), 0.90 (s, 9H), 0.13 (s, 3H), 0.06 (s, 3H).



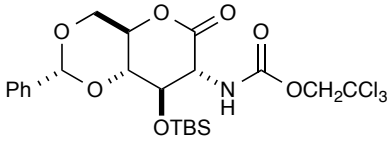
6-((*tert*-Butyldiphenylsilyl)oxy)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-(2,2,2-trichloroethoxy)-tetrahydrofuro[3,2-*d*]oxazole (26): Prepared according to the General Procedure using 170 mg (0.400 mmol) (R)-4-((2S,3R)-3-(*tert*-butyldiphenylsilyloxy)-2,3-dihydrofuran-2-yl)-2,2-dimethyl-1,3-dioxolane and an irradiation time of 20 h. Purified by flash chromatography on silica-9 using 95:5 hexanes:Et_2O to yield the product as a white solid (51–55 °C). Experiment 1: 200 mg (81%); Experiment 2: 109 mg (79%). IR (neat) 3073, 2989, 2958, 1668, 1402, 1333 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.45 (t, J = 7.4 Hz, 2H), 7.42–7.37 (m, 4H), 6.12 (d, J = 4.8 Hz, 1H), 4.72, 4.66 (ABq, J_{AB} = 12 Hz, 2H), 4.51 (d, J = 2.6 Hz, 1H), 4.47 (dt, J = 7.9, 5.9 sHz, 1H), 4.16 (dd, J = 8.5, 6.3 Hz, 1H), 4.13 (d, J = 4.8 Hz, 1H), 4.03 (dd, J = 8.5, 5.6 Hz, 1H), 3.86 (dd, J = 7.9, 2.6 Hz,

1H), 1.4 (s, 3H), 1.34 (s, 3H), 1.10 (s, 9H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 162.0, 136.2, 135.9, 134.1, 132.7, 130.13, 130.11, 128.0, 127.9, 109.3, 108.5, 94.0, 83.7, 79.3, 76.5, 75.7, 72.2, 67.7, 27.0, 26.9, 25.4, 19.5; HRMS (ESI) calculated for $[C_{28}H_{34}Cl_3NO_6Si]^+$ required 614.1294 *m/z*, found 614.1299 *m/z.*



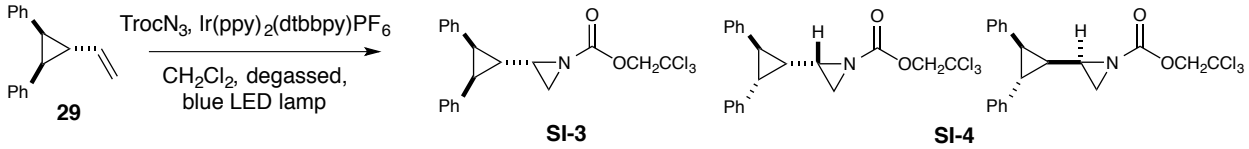
D-Glucopyranoside-methyl-2-(2,2,2-trichloroaminocarboxylate)-2-deoxy-3-*O*-[(1,1 dimethylethyl) dimethylsilyl]-4,6-*O*-[phenylmethylene] (SI-1): The most reproducible method for the hydrolysis of **26** was *via* a method described by Carreira[23]: silica-gel (500 mg), Celite® (500 mg), and 15 mL pentane were added to the unpurified reaction mixture of **26** and the resulting slurry was rapidly stirred for 30 min before filtering through a silica plug, using Et_2O as the eluent. The eluent was concentrated and purified on silica gel using 7:3 hexanes:Et_2O to afford 145 mg (67% over two steps) of a white solid (82–88 °C) as a mixture of diastereomers (*vide infra*). IR (neat) of the mixture 3155, 2953, 2930, 2859, 1740, 1517, 1464, 1381 cm^{-1}. ^{1}H NMR of the major diastereomer: (500.2 MHz, $CDCl_3$) δ 7.44–7.49–7.47 (m, 2H), 7.37–7.35 (m, 3H), 5.53 (s, 1H), 5.29 (t, *J* = 3.5 Hz, 1H) 5.22 (d, –NH, *J* = 9.2 Hz, 1H), 4.73, 4.53 (ABq, J_{AB} = 12 Hz, 2H), 4.25 (dd, *J* = 10.3, 4.9 Hz, 1H), 4.05 (td, *J* = 9.9, 4.9 Hz, 1H), 3.98–3.90 (m, 2H), 3.74 (t, *J* = 10.3 Hz, 1H), 3.54 (t, *J* = 8.9 Hz, 1H), 2.92 (d, –OH, *J* = 2.2 Hz, 1H), 0.82 (s, 9H), 0.05 (s, 3H), –0.02, (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 154.4, 137.3, 129.2, 126.3, 126.4, 102.1, 95.3, 93.2, 82.6, 75.1, 70.5, 69.1, 63.1, 56.8, 25.9, 18.3, –4.0, –4.9. HRMS (ESI) calculated for $[C_{22}H_{32}Cl_3NO_7Si]^+$ required 556.1087 *m/z*, found 556.1089 *m/z*

To determine the diastereomeric ratio at the 2-position, **S1-1** was oxidized to the lactone **SI-2** in an analogous fashion to the method reported by Carreira.[23]



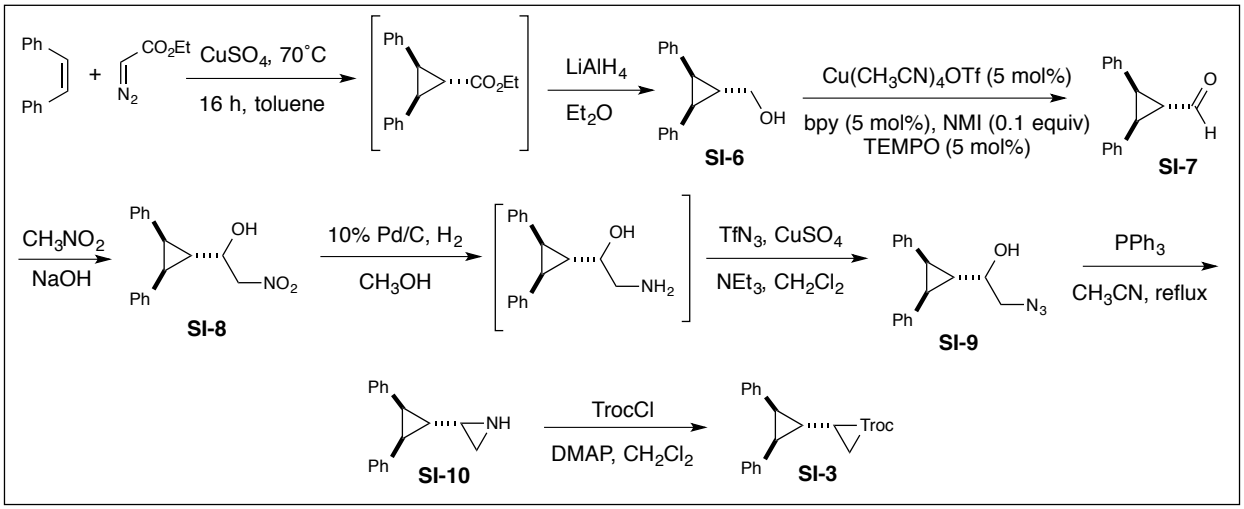
2,2,2-Trichloroethyl(8-((*tert*-butyldimethylsilyl)oxy)-6-oxo-2-phenylhexahydropyrano[3,2-*d*][1,3]dioxin-7-yl)carbamate (SI-2): To a solution of **SI-1** (20 mg, 0.0359 mmol, 1 equiv.) in CH_2Cl_2 (0.36 mL, 0.1M) under a N_2 atmosphere was added Dess–Martin periodinane (17 mg, 0.0395, 1.1 equiv). After stirring for 2 h, the reaction was concentrated to a clear oil, which was purified by flash chromatography on silica in 7:3 pentanes:Et_2O to give 18 mg (90%) of a clear oil that consisted of an inseparable mixture of diastereomers (13:1). IR (neat) of the mixture 2958, 2931, 1764, 1736, 1513, 1376, 1221, 1095 cm^{-1}. ^{1}H NMR of the major diastereomer: (500.2 MHz, $CDCl_3$) δ 7.50–7.48 (m, 2H), 7.40–7.39 (m, 3H), 5.89 (d, –NH, *J* = 7.5 Hz, 1H), 5.60 (s, 1H), 4.88, 4.68 (ABq, J_{AB} = 12 Hz, 2H), 4.49 (dd, *J* = 10.6, 5.2 Hz, 1H), 4.39 (td, *J* = 10.0, 5.2 Hz, 1H), 4.34 (dd, *J* = 9.6, 8.4 Hz, 1H), 3.87 (dd, *J* = 8.2, 7.7 Hz, 1H), 3.84 (t, *J* = 10.5 Hz, 1H), 3.80 (t, *J* = 9.6 Hz, 1H), 0.86 (s, 9H), 0.06 (s, 3H), 0.00 (s, 3H). ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 168.0, 154.7, 136.6, 129.5, 128.4, 126.4, 102.1, 95.0, 79.2, 75.1, 72.2, 68.3, 68.0, 60.1, 25.8, 18.2, –4.13, –4.76. HRMS (ESI) calculated for $[C_{22}H_{30}Cl_3NO_7Si + NH_4]^+$ required 571.1196 *m/z*, found 571.1196 *m/z*.

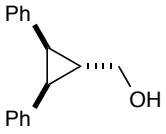
VI. Cyclopropyl alkene radical probe experiments



A radical probe experiment was carried out using the General Procedure for the aziridine synthesis in Section III with 88.0 mg **29** (0.400 mmol), 1,4-bis(trimethylsilyl)benzene (24.0 mg, 0.108 mmol, 0.27 equiv) as an internal standard, and an irradiation time of 20 h. Attempted isolation of the aziridine products resulted in rapid decomposition and poor mass recovery. ^{1}H NMR analysis of the unpurified material resulted in identification of three aziridine products as inseparable mixture of diastereomers (4.0:2.4:1, 64% yield). The assignments of *trans*-phenyl and *cis*-phenyl diastereomers were confirmed *via* independent synthesis (*vide infra*), however the identity of the major *trans*-phenyl diastereomer could not be unambiguously determined.

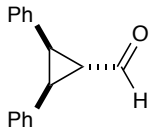
Independent synthesis of SI-3:



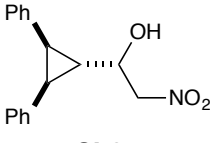


(*cis*-2,3-Diphenylcyclopropyl)methanol (SI-6): To a flame-dried 3-necked flask under a N_2 atmosphere were added *cis*-stilbene (2.00 g, 11.1 mmol, 1 equiv.), anhydrous $CuSO_4$ (106 mg, 0.666 mmol, 0.06 equiv) and toluene (13.3 mL, 0.8 M). The mixture was heated to 75 ºC, and ethyl diazoacetate (3.4 mL, 27.8 mmol 2.5 equiv.) was added dropwise over a 4 h period. After stirring overnight, the reaction was allowed to cool completely before concentrating *in vacuo* to a brown oil. This residue was taken up in 5 mL Et_2O and added dropwise to a rapidly stirred suspension of LiAlH4 (3.00 g, 79.1 mmol, 7.1 equiv.) in 100 mL dry ether under a N_2 atmosphere cooled to 0 °C. After addition was completed, the ice bath was removed, and the reaction was refluxed for 2 h. Following this period, the mixture was cooled to ambient temperature and slowly quenched with iPrOH. To resulting slurry were sequentially added 3 mL H_2O, 3 mL 15% NaOH solution, and 9 mL H_2O. The reaction was then filtered through a pad of Celite® and concentrated to afford a yellow oil. Purification by flash chromatography in 85:15 hexanes:EtOAc yielded

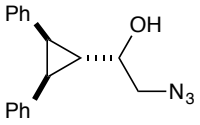
880 mg (35% over two steps) of **SI-6**, with all spectra in complete agreement with previously reported values.[24]



***cis*-2,3-Diphenylcyclopropane-1-carbaldehyde (SI-7)**: To a rapidly stirred solution of **SI-6** (400 mg, 1.78 mmol 1 equiv.) in CH_3CN (9 mL, 0.2 M) were added $Cu(CH_3CN)_4(OTf)_2$ (33 mg, 0.089 mmol, 0.05 equiv.), bpy (14.5 mg, 0.089 mmol, 0.05 equiv.), TEMPO (14.5 mg, 0.089 mmol, 0.05 equiv.), and 1-methylimidazole (14.5 µL, 0.178 mmol, 0.1 equiv), resulting in a dark red solution. The flask was sealed with a rubber septum, fitted with balloon of O_2, and stirred until a green color persisted (~20 min). The reaction was concentrated *in vacuo* and purified by flash chromatography in 95:5 hexanes:EtOAc to give 350 mg (89%) of **SI-7** as a clear oil. All spectral data were in complete agreement with previously reported values.[25]



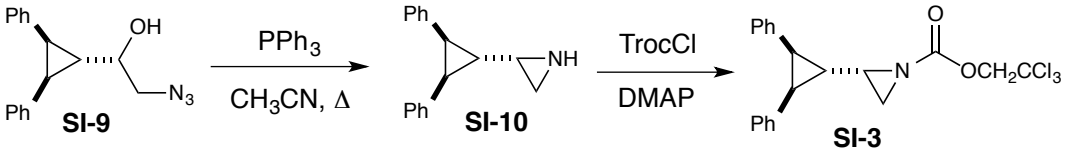
1-(*cis*-2,3-Diphenylcyclopropyl)-2-nitroethan-1-ol (SI-8): To a stirred solution of **SI-7** (230 mg, 1 mmol, 1 equiv.) and nitromethane (56 µL, 1.00 mmol, 1 equiv.) in MeOH (2 mL, 0.5 M) at 0 ºC was added dropwise a 2.7 M aq. NaOH solution (0.5 mL, 1.35 mmol, 1 equiv). The resulting mixture was stirred for 1 h before the addition of AcOH (77 µL, 1.35 mmol, 1 equiv.) The mixture was transferred to a separatory funnel and extracted with Et_2O (3x), dried over $MgSO_4$, and concentrated *in vacuo* to give a yellow oil. Purification of the residue by flash chromatography in 8:2 hexanes:EtOAc yielded 240 mg (82%) as a yellow oil in approximately 90% purity, which was carried on without further purification. IR (neat) 3429, 3058, 3025, 2975, 1603, 1553, 1498, 1386, 1266 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.17 – 7.05 (m, 6H), 6.95 – 6.91 (m, 4H), 6.91 – 6.87 (m, 2H), 4.74 – 4.62 (m, 2H), 4.27 (td, J = 7.7, 3.5 Hz, 1H), 2.72 (br. s, 1H), 2.65 (dd, J = 9.8, 5.7 Hz, 1H), 2.55 (dd, J = 9.8, 5.7 Hz, 1H), 1.92 (dt, J = 7.0, 5.7 Hz, 1H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 136.4, 136.2, 139.1, 128.8, 128.1, 129.1, 126.4, 126.5 80.1, 71.3, 29.4, 28.5, 28.0; HRMS (ASAP) calculated for $[C_{17}H_{17}NO_3+NH_4]^+$ required 301.1536 *m/z*, found 301.15467 *m/z*.



2-Azido-1-(*cis*-2,3-diphenylcyclopropyl)ethan-1-ol (SI-9): (Caution! This reaction sequence involves the generation of trifyl azide, and should be performed behind a blast shield with a partner). In a dry 10 mL round-bottomed flask was placed **SI-8**, (100 mg, 0.353 mmol, 1 equiv.), MeOH (1.5 mL, 0.24 M), and 10% Pd/C (15 mg). The flask was fitted with a balloon of H_2 and stirred for 12 h, at which point TLC analysis showed the reaction to be complete. The mixture was diluted with CH_2Cl_2, filtered through Celite®, and concentrated to give the crude amino alcohol product, which was carried on directly to the next step.

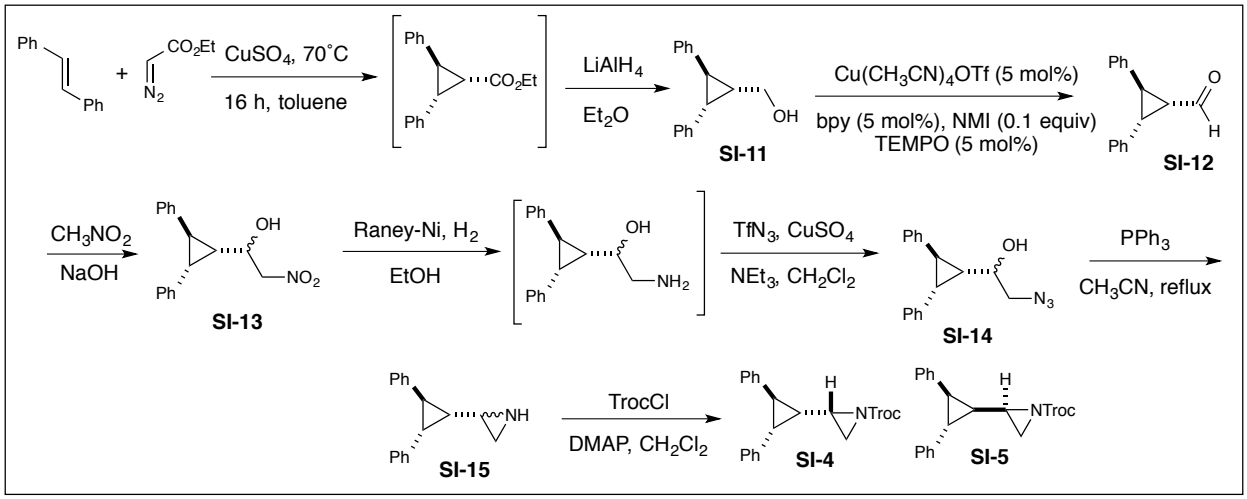
To a mixture of NaN_3 (368 mg, 5.66 mmol, 16.9 equiv) in H_2O (1 mL) and CH_2Cl_2 (0.5 mL) at 0 ºC behind a blast shield was added dropwise freshly distilled Tf_2O (158 µL, 0.938 mmol, 2.8 equiv.). The resulting mixture was stirred for 3 h, maintaining a temperature of 0 ºC. To the reaction containing the

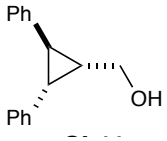
freshly generated triflyl azide was added 0.25 mL H_2O, and the organic layer was extracted using a syringe. The organic layer was washed with aq. $NaHCO_3$ and subsequently used without further purification. To a solution of the crude amino alcohol product in CH_2Cl_2 (0.5 mL, 0.67 M) was added NEt_3 (140 μL, 1 mmol, 3 equiv.) and an aqueous 0.1 M solution of $CuSO_4$ (0.1 mL, 0.01 mmol, 0.03 equiv.) The freshly prepared solution of triflyl azide was added followed by the addition of 0.25 mL MeOH. After 2 h, the reaction was diluted with CH_2Cl_2 and washed with sat. aq. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo* to give a green oil. Purification by flash chromatography using a gradient of 92:8 to 85:15 hexanes:EtOAc yielded 68 mg of (69% over two steps) of a clear oil. IR (neat) 3395, 3060, 3027, 2923, 2102, 1605, 1397, 1443, 1284 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.16–7.04 (m, 6H), 6.96–6.87 (m, 4H), 3.71 – 3.59 (m, 2H), 3.54 (dd, J = 12.3, 7.0 Hz, 1H), 2.56 (dd, J = 9.7, 5.7 Hz, 1H), 2.46 (dd, J = 9.7, 5.7 Hz, 1H), 2.18 (br. s, 1H), 1.95 (q, J = 6.1 Hz, 1H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 137.0, 136.7, 129.0, 129.0, 128.0, 128.0, 126.2, 126.2, 74.0, 56.6, 29.3, 28.9, 28.8; HRMS (ASAP) calculated for $[C_{17}H_{17}NO_3+NH_4]^+$ required 297.1710 *m/z*, found 297.1700 *m/z*.



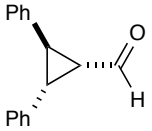
2,2,2-Trichloroethyl 2-(*cis*-2,3-diphenylcyclopropyl)aziridine-1-carboxylate (SI-3): A solution of **SI-9** (50 mg, 0.180 mmol, 1 equiv.) in CH_3CN (1.2 mL, 0.15 M) in a 4 mL vial was treated with PPh_3 (71 mg, 0.270 mmol, 1.5 equiv.), resulting in rapid N_2 evolution. After 1 h, the vial was sealed with a Teflon-coated cap and heated to 70 °C. After 15 h, the reaction was cooled to ambient temperature and concentrated. Repeated chromatography yielded 7 mg (16%) of N–H aziridine **SI-10** that was partially separated from triphenyl phosphine oxide. This material was carried on directly to the next step. To a solution of aziridine in CH_2Cl_2 (0.3 mL, 0.1 M) at –20 °C were added DMAP (4 mg, 0.0330 mmol, 1.1 equiv.) and TrocCl (4.5 μL, 0.0330 mmol, 1.1 equiv). After 30 min, the reaction was warmed to ambient temperature, diluted with pentanes, and filtered through a pad of Celite with excess pentanes. The mixture was concentrated to yield a clear oil. Due to instability of the product towards silica gel, the aziridine was partially characterized from the unpurified reaction mixture. ^1H NMR: (500.2 MHz, C_6D_6) δ 7.02–6.88 (m, 6H), 6.87–6.81 (m, 4H), 4.56, 4.38 (ABq, J = 12.0 Hz, 2H), 2.58 (dt, J = 6.0, 3.6 Hz, 1H), 2.50 (dd, J = 9.7, 5.7 Hz, 1H), 2.40 (dd, J = 9.7, 5.7 Hz, 1H), 2.11 (d, J = 6.0 Hz, 1H), 1.79 (d, J = 3.8 Hz, 1H), 1.76 (td, J = 5.7, 3.4 Hz, 1H); HRMS (ESI) calculated for $[C_{20}H_{18}Cl_3NO_2]^+$ required 410.0476 *m/z*, found 410.0477 *m/z*.

Independent synthesis of SI-4 and SI-5:

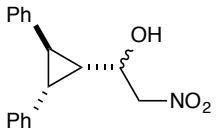




(*trans*-2,3-Diphenylcyclopropyl)methanol (SI-11): Prepared according to the procedure for **SI-6** using *trans*-stilbene (4.00 g, 22.2 mmol) yielding 2.02 g (42%) of **SI-11**. All spectra were in complete agreement with previously reported values.[26]

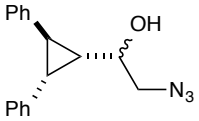


***trans*-2,3-Diphenylcyclopropane-1-carbaldehyde (SI-12):** Prepared according to the procedure for **SI-7** using **SI-11** (1.00 g, 4.46 mmol) yielding 0.82 g (82%) of product. IR (neat) 3062, 3031, 2932, 2839, 1700, 1607, 1499, 1451, 1145, 1075 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 8.94 (d, J = 6.3 Hz, 1H), 7.42–7.36 (m, 2H), 7.36–7.30 (m, 4H), 7.28–7.24 (m, 4H), 3.35 (dd, J = 6.9, 4.8 Hz, 1H), 3.18 (dd, J = 9.1, 6.9 Hz, 1H), 2.47 (ddd, J = 9.2, 6.2, 4.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.8, 138.1, 135.0, 128.8, 128.4, 128.3, 127.0, 126.8, 126.4, 39.5, 34.6, 29.5; HRMS (ASAP) calculated for $[C_{16}H_{15}O]^+$ required 223.1118 *m/z*, found 223.1120 *m/z*.



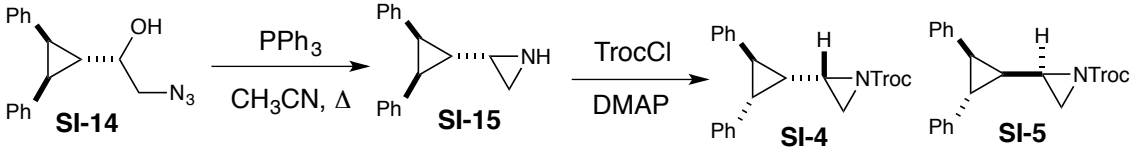
1-(*trans*-2,3-Diphenylcyclopropyl)-2-nitroethan-1-ol (SI-13): Prepared according to the procedure for **SI-8** using **SI-12** (230 mg, 1.04 mmol) yielding 244 mg (83%) of **SI-13** as a 1.5:1 mixture of diastereomers. IR (neat) 3429, 3062, 3030, 2920, 1602, 1543, 1497, 1447, 1383, 1276, 1200 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.41–7.23 (m, 14H), 7.25–7.23 (m, 4H), 7.18–7.16 (m, 2H) 4.63–4.49 (m, 2H), 4.33 (dd, J = 13.2, 8.4 Hz, 1H), 4.22 (dd, J = 13.1, 2.7 Hz, 1H), 3.86–3.75 (m, 2H), 2.80 (t, J = 5.6 Hz, 1H), 2.76 (dd, J = 9.2, 5.8 Hz, 1H), 2.64 (dd, J = 9.4, 6.0 Hz, 1H), 2.44 (t, J = 5.6 Hz, 2H), 2.22 (br. s,

1H), 1.72 (td, *J* = 9.6, 5.3 Hz, 1H), 1.62 (td, *J* = 9.2, 5.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 139.9, 136.3, 136.1, 129.02, 129.01, 129.0, 128.9, 128.7, 128.3, 127.3, 127.26, 126.73, 126.71, 126.6, 126.4, 80.2, 79.3, 66.79, 66.76, 31.9, 31.6, 31.2, 30.9, 26.3, 26.0; HRMS (ASAP) calculated for [C17H17NO3+NH4]$^+$ required 301.15467 *m/z*, found 301.1536 *m/z*.

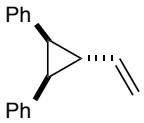


2-azido-1-(*trans*-2,3-Diphenylcyclopropyl)ethan-1-ol (SI-14): **(Caution! This reaction sequence involves the generation of triflyl azide, and should be performed behind a blast shield with a partner)** A solution of **SI-13** (100 mg, 0.353 mmol, 1 equiv.) in EtOH (2 mL, 0.18 M) was placed in a 10 mL round-bottomed flask. Raney nickel (100 mg in 1 mL EtOH, measured by displacement of EtOH in a graduated cylinder) was added to flask, the vessel was sealed with a rubber septum, and a H_2 balloon was attached. After 4 h the reaction was diluted with EtOH, filtered through a pipette of Celite®, and concentrated to give a residue that was carried on directly to the next step.

To a mixture of NaN_3 (368 mg, 5.0 mmol, 16.9 equiv) in H_2O (1 mL) and CH_2Cl_2 (0.5 mL) at 0 ºC behind a blast shield was added dropwise freshly distilled Tf_2O (139 µL, 0.829 mmol, 2.8 equiv.). The resulting mixture was stirred for 3 h, maintaining a temperature of 0 ºC. To the reaction containing the freshly generated triflyl azide was added 0.25 mL H_2O, and the organic layer was extracted using a syringe. The organic layer was washed with aq. $NaHCO_3$ and subsequently used without further purification. To a solution of the crude amino alcohol product in CH_2Cl_2 (0.5 mL) was added NEt_3 (123 µL, 0.888 mmol, 3 equiv.) and an aqueous 0.1 M solution of $CuSO_4$ (0.1 mL, 0.01 mmol, 0.03 equiv.) The freshly prepared solution of triflyl azide was added followed by the addition of 0.25 mL MeOH. After 2 h, the reaction was diluted with CH_2Cl_2 and washed with sat. aq. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo* to give a green oil. Purification by flash chromatography using a gradient of 92:8 to 85:15 hexanes:EtOAc yielded 55 mg of **SI-14** as a 1.5:1 mixture of diastereomers (55% over two steps) as a clear oil. IR (neat) 3399, 3057, 3028, 2920, 2105, 1604, 1499, 1455, 1264, 1080 cm^{-1}. ^{1}H NMR: (500.2 MHz, $CDCl_3$) δ 7.42–7.17 (m, 20H), 3.51–3.41 (m, 2H), 3.32 (m, 2H), 3.24 (dd, *J* = 12.5, 3.1 Hz, 1H), 3.18 (dd, *J* = 12.5, 6.6 Hz, 1H), 2.73 (t, *J* = 5.6 Hz, 1H), 2.68 (dd, *J* = 9.2, 5.7 Hz, 1H), 2.61 (dd, *J* = 9.4, 5.9 Hz, 1H), 2.42 (t, *J* = 5.5 Hz, 1H), 1.78–1.67 (m, 4H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 141.1, 140.6, 137.0, 136.9, 128.89 , 128.88 , 128.8, 128.7, 128.5, 127.1, 126.9, 126.63, 126.55, 126.51, 126.4, 71.0, 70.7, 56.5, 56.1, 36.8 32.8, 32.3, 31.4, 31.2, 26.1, 26.1; HRMS (ASAP) calculated for [$C_{17}H_{17}NO_3$+NH_4]$^+$ required 302.12638 *m/z*, found 302.1252 *m/z*.



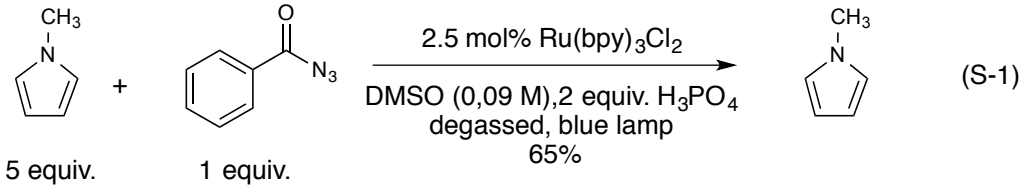
2,2,2-Trichloroethyl-2-(*trans*-2,3-diphenylcyclopropyl)aziridine-1-carboxylate (SI-4 and SI-5): Prepared according to the procedure for **SI-3** using **SI-14**. Due to instability of the product on silica gel, the aziridine diastereomers was partially characterized from the crude reaction. ^{1}H NMR (500.2 MHz, C_6D6) δ 7.22–6.94 (m, 20H), 4.56, 4.52 (ABq, *J* = 14 Hz, 2H), 4.46, 4.42 (ABq, *J* = 12 Hz, 2H), 2.76 (t, *J* = 5.6 Hz, 1H), 2.50 (dd, *J* = 9.2, 5.8 Hz, 1H), 2.42 (dd, *J* = 9.3, 6.1 Hz, 1H), 2.13 (t, *J* = 5.6 Hz, 1H), 2.09–2.06 (m, 1H), 2.03 (ddd, *J* = 7.9, 6.0, 3.7 Hz, 1H), 1.91 (d, *J* = 6.1 Hz, 1H), 1.86 (d, *J* = 5.8 Hz, 1H), 1.82 – 1.79 (m, 2H), 1.39 (ddd, *J* = 9.2, 6.7, 5.4 Hz, 1H), 1.03 (ddd, *J* = 9.3, 7.9, 5.1 Hz, 1H). HRMS (ESI) calculated for [$C_{20}H_{18}Cl_3NO_2$]$^+$ required 410.0476 *m/z*, found 410.0464 *m/z*.



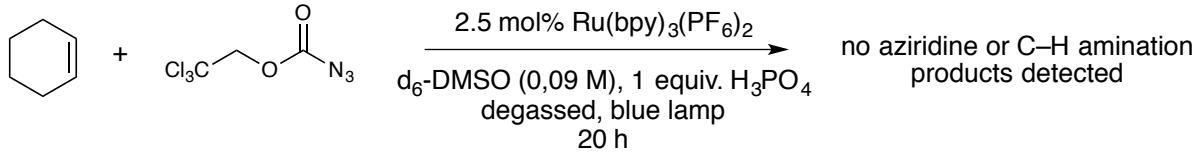
(*cis*-3-Vinylcyclopropane-1,2-diyl)dibenzene (29): To a flame-dried RBF containing THF (10 mL, 0.15M) was added NaHMDS (316 mg, 1.73 mmol, 1.1 equiv.) and Ph_3PCH_3Br (618 mg, 1.73 mmol, 1.1 equiv.) under N_2. The mixture was stirred for 1 h before addition of **SI-7** (350 mg, 1.57 mmol, 1.0 equiv.) in 1 mL of THF. After 1 h the reaction was concentrated and passed through a short plug of silica in hexanes to give pure **29**, 250 mg (71%). IR (neat) 3064, 3031, 2990, 1638, 1602, 1497, 1448, 1078 cm^{-1}. ^1H NMR (500.2 MHz, $CDCl_3$) δ 7.21–7.01 (m, 6H), 6.97 – 6.90 (m, 4H), 5.81 (ddd, J = 17.1, 10.3, 7.9 Hz, 1H), 5.27 (d, J = 17.0 Hz, 1H), 5.06 (dd, J = 10.3, 1.4 Hz, 1H), 2.54 (d, J = 5.6 Hz, 2H), 2.36 (dt, J = 7.95, 5.65, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.2, 137.6, 129.0, 127.9, 125.9, 113.4, 32.9, 29.9. HRMS (ASAP) calculated for $[C_{17}H_{17}]^+$ required 221.1325 *m/z*, found 221.1335 *m/z*.

VII. Control Reactions

Conditions developed by König and coworkers[27] (see eq. S-1) for C–H amination of N-methyl pyrrole were evaluated in our system under three sets of conditions.

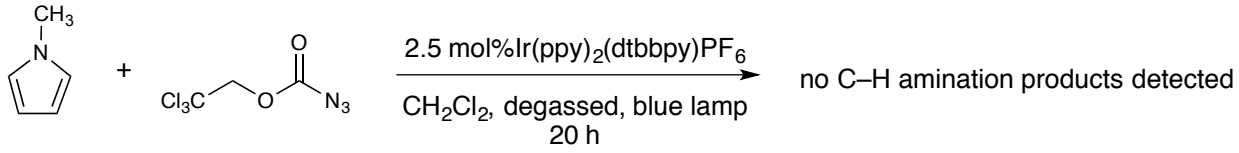


a) Evaluation of König's reaction conditions to promote aziridination of cyclohexene with $TrocN_3$.



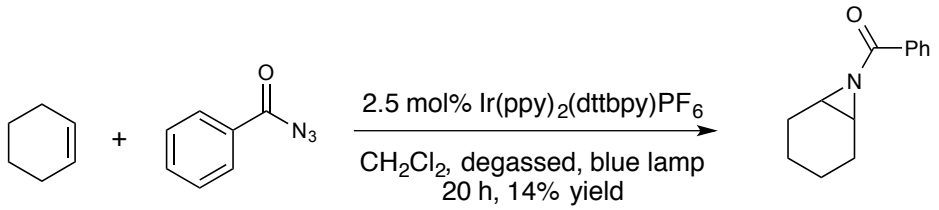
Procedure: Reactions were run according to a modified procedure to König. To an oven-dried 25 mL Schlenk tube was added $TrocN_3$ (13µL, 0.100 mmol, 1 equiv.), cyclohexene (50 µL, 0.500 mmol, 5 equiv.), H_3PO_4 (20 mg, 0.200 mmol, 2 equiv.), $Ru(bpy)_3(PF_6)_2$ (2.1 mg, 0.0025 mmol, 0.025 equiv.) and d6-DMSO (0.09 M). The vessel was degassed *via* three freeze-pump-thaw cycles, backfilled with N_2, and irradiated with a 15 W blue LED lamp for 20 h. An aliquot was taken from the reaction and diluted with addition d6–DMSO and analyzed *via* ^1H NMR. No peaks consistent with aziridine or allylic C–H amination were observed.

b) Evaluation of *N*-methyl pyrrole under our optimal reaction conditions.



Procedure: To an oven-dried 25 mL Schlenk tube was added *N*-methyl pyrrole (9 µL, 0.100 mmol, 1 equiv.), $TrocN_3$ (65 µL, 0.500 mmol, 5 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 0.0025 mmol, 0.025 equiv.), CH_2Cl_2 (0.25 mL, 0.4 M), and 1,4-bis(trimethylsilyl)benzene (11.6 mg, 0.0523 mmol) as an internal standard. The vessel was degassed *via* three freeze-pump-thaw cycles, backfilled with N_2, and irradiated with a 15 W blue LED lamp for 20 h. The reaction was concentrated and analyzed *via* ^1H NMR. No C–H amination products analogous to those found by König and coworkers were observed.

c) Evaluation of benzoyl azide under our optimal reaction conditions.



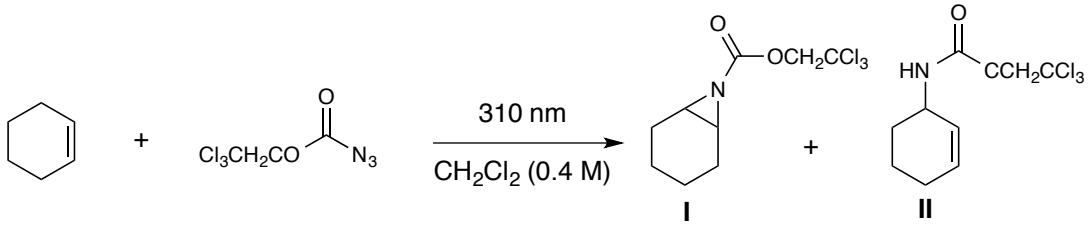
Procedure: To an oven-dried 25 mL Schlenk tube was added cyclohexene (10 µL, 0.100 mmol, 1 equiv.), benzoyl azide (75 mg, 0.500 mmol, 5 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 0.0025 mmol, 0.025 equiv.), CH_2Cl_2 (0.25 mL, 0.4 M), and 1,4-bis(trimethylsilyl)benzene (6.8 mg, 0.0306 mmol) as an internal standard. The vessel was degassed *via* three freeze-pump-thaw cycles, backfilled with N_2, and irradiated with a 15 W blue LED lamp for 20 h. The reaction was concentrated and analyzed *via* ^1H NMR and yielded 14% yield of aziridine product consistent with previously reported shifts.[28]

d) UV-irradiation of $TrocN_3$ at 310 nm with cyclohexene.

The selectivity of allylic C–H amination versus alkene aziridination using $TrocN_3$ as the nitrene source was examined *via* direct photolysis using a Rayonet RPR-200 photoreactor equipped with 310 nm bulbs. Selectivity was found to favor ~1:1 allylic amination to aziridination when excess alkene was used. Interestingly, when alkene was the limiting reagent, similar selectivity was seen at a minimal conversion, however, the allylic amination product was consumed under the reaction conditions such that at prolonged reaction times only aziridine product was observed.

General procedure for direct photolysis: For amounts of each reagent, see Table SI-1 below. To an oven-dried 25 mL Schlenk tube with a stir bar was added the cyclohexene and CH_2Cl_2 (0.5 mL, 0.4 M). To the solution was added $TrocN_3$ and the mixture was submitted to three freeze-pump-thaw cycles, left under a static vacuum, and irradiated at 310 nm for the designated time. The vessel was then opened to air, and phenanthrene was added as an external standard. The mixture was concentrated and the residue was taken up in $CDCl_3$ for direct analysis by ^1H NMR. The identity of the allylic amination product (**II**) was confirmed based on reported literature spectra.[29]

Table SI-1.



entry	time (h)	cyclohexene (mmol)	$TrocN_3$ (mmol)	Aziridine yield (**I**) (%)	Amidation yield (**II**) (%)
1	0.15	0.20	1.0	5	6
2	4	0.20	1.0	50	0
3	4	1.0	0.20	24	22

VIII. Flow Chemistry

The flow reactor setup consisted of Shimano LC-10AT HPLC pump, a home-made injection loop with an 4-way PEEK "diagonal" flow valve and 4-way PEEK "L" flow valve (IDEX Health Sciences, V-100D and V-100L respectively), a 100 psi back-pressure regulator (BPR) assembly (IDEX Health Sciences, U-607), and FEP tubing (fluorinated ethylene polymer, IDEX Health Sciences, outer diameter (OD) 1/16 in, inner diameter (ID) 0.03 in). The tubed was wrapped in a coil shaped and secured with copper wire such that a total reactor volume of 1.9 mL was irradiated using a 15 W blue light-emitting diode (LED) lamp (λ = 464 nm) purchased from Eagle Light.

Figure SI-1. Flow reactor assembly with injection loop

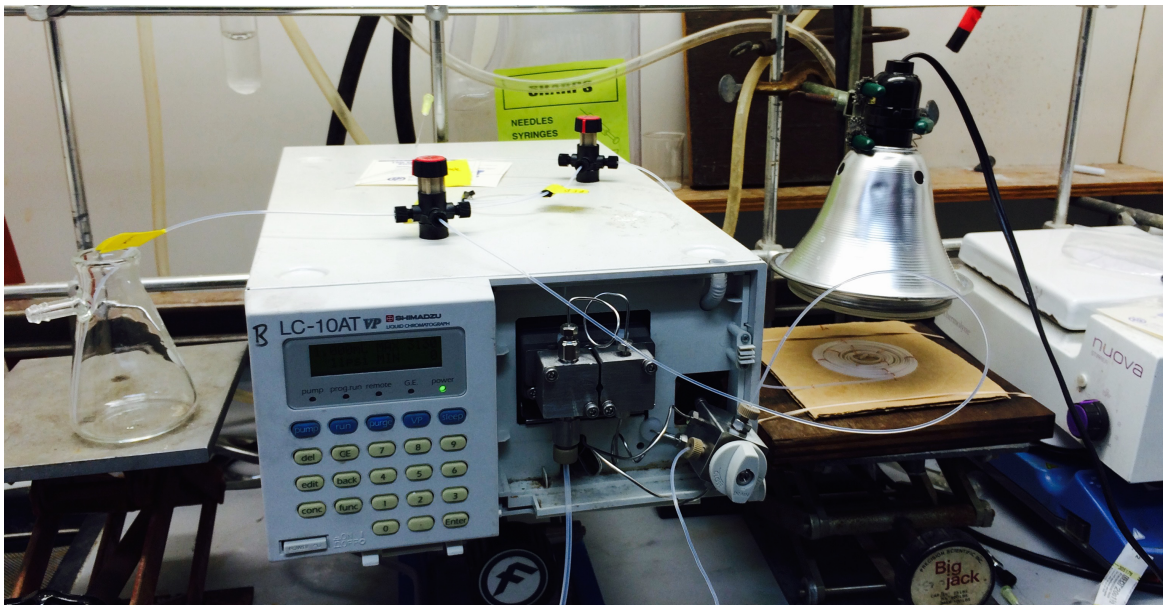
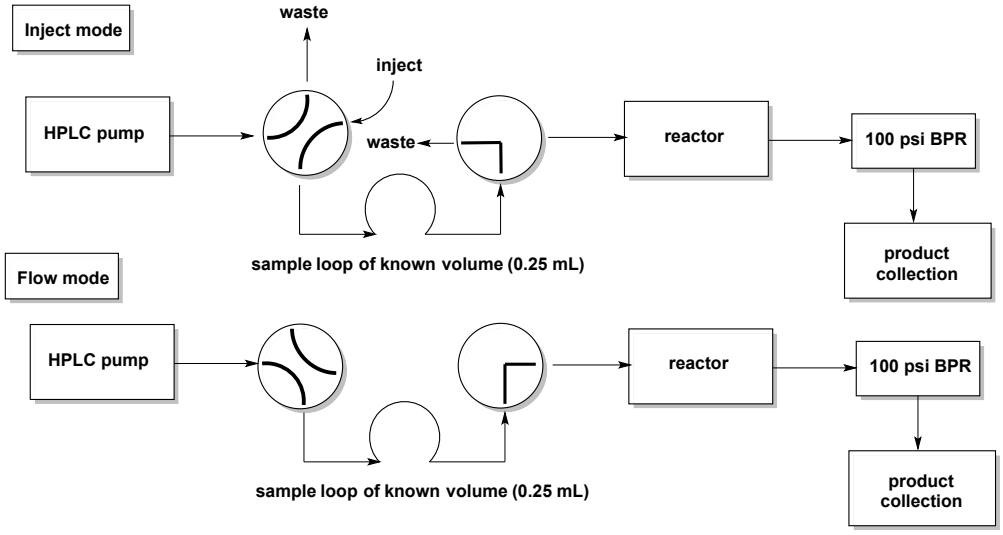


Figure SI-2. Schematic of inject and flow modes.



General procedure for evaluation of aziridination in flow under the standard reaction conditions: To a vial was added cyclohexene (1.00 equiv), $Ir(ppy)_2(dtbbpy)(PF_6)$ (0.025 equiv), CH_2Cl_2 (0.4 M), $TrocN_3$ (variable equivalents, see below), and 1,4-bis(trimethylsilyl)benzene as an internal standard. The mixture was loaded into a 0.25 mL sample loop using inject mode (Fig. SI-2) (the reactor was always filled with CH_2Cl_2 prior to injecting the sample so a constant pressure was maintained during the reaction). Both 4-way PEEK valves were changed to flow mode simultaneously and the reaction mixture was flowed through the reactor into a collection flask (variable flow rate, see below) with the HPLC pump drawing from a CH_2Cl_2 reservoir. To measure the yield of aziridine, a middle fraction of the reaction was collected to avoid issues pertaining to reaction dilution, concentrated, and evaluated by ^1H NMR.

entry	equiv. $TrocN_3$	t_R (h)	flow rate (mL/min)	yield aziridine
1	5	2.3	0.014	72%
2	1	8	0.0040	70%

For reaction scale-up the flow reactor was operated as a continuous flow reactor. When operated in continuous flow, the HPLC pump was connected directly to the reactor, bypassing the injection loop.

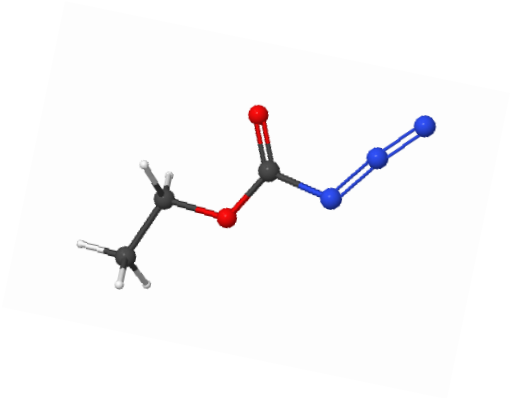
General procedure for scale-up *via* continuous flow operation: In a 25 mL round-bottomed flask were placed cyclohexene (417 μL, 4.125 mmol, 1.00 equiv), $Ir(ppy)_2(dtbbpy)(PF_6)$ (95 mg, 0.103 mmol, 0.025 equiv), CH_2Cl_2 (10.3 mL, 0.4 M), and $TrocN_3$ (4.50 g, 20.6 mmol, 5 equiv.). The flask was sealed with a septum fitted with a N_2 inlet. An HPLC inlet line was inserted in the reaction, and the pump was primed. The reactor outlet was fed back into the reaction flask and the reaction was circulated for 16 h at a flow rate of 0.1 mL/min. To prevent evaporative loss of volatile cyclohexene, the collection vessel was maintained at 5 °C over the course of the reaction. Upon completion of the reaction, the HPLC inlet line

was placed in a fresh beaker of CH_2Cl_2 and the reaction was flushed from the system into the collection flask. The reaction was subsequently concentrated and purified *via* silica gel chromatography on silica-9 in 98:2 hexanes/Et_2O to yield 0.785 g of aziridine (70% yield), with all spectral data matching those reported above.

IX. Molecular modeling of the S_0–T_1 gap for ethyl azidoformate

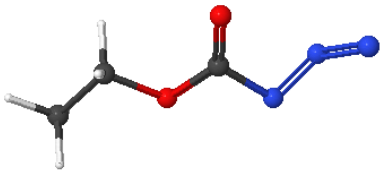
The adiabatic S_0–T_1 gap for ethyl azidoformate was determined *via* the energy difference of the optimized singlet ground state structure and the first excited triplet structure. All ground state and triplet state geometries were optimized using the B3LYP density functional with 6-31G(d) basis set. All calculations were performed using the Gaussian09 software package.[30] Structures were confirmed to be a minimum on the potential energy surface *via* harmonic frequency calculations. Additionally, single point energy calculations were performed on the optimized structures using CCSD with 6-31G(d) basis set.

Optimized structure for S_0



RB3LYP energy: -431.980911264 Hartree
CCSD energy: -430.77909346 Hartree

Optimized structure for T_1



UB3LYP energy: -431.893433475 Hartree
CCSD energy: -430.69741151 Hartee

S_o–T_1 energy (B3LYP/UB3LYP): 0.08921637 Hartrees (54.9 kcal/mol)
S_o–T_1 energy (CCSD): 0.08168195 Hartrees (51.2 kcal/mol)

Standard orientation for S_0:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.642515	-1.375671	0.000000
2	6	0	-1.706501	-2.890319	0.000000
3	1	0	-2.752979	-3.213496	0.000000
4	1	0	-1.217258	-3.302597	0.887884
5	1	0	-1.217258	-3.302597	-0.887884
6	8	0	-0.240459	-1.005201	0.000000
7	6	0	0.000000	0.307556	0.000000
8	7	0	1.412749	0.476804	0.000000
9	7	0	1.777879	1.669238	0.000000
10	7	0	2.242856	2.702066	0.000000
11	8	0	-0.824208	1.194382	0.000000
12	1	0	-2.117731	-0.940452	0.884577
13	1	0	-2.117731	-0.940452	-0.884577

Standard orientation for T_1:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.064812	0.452886	-0.042650
2	6	0	-3.310432	-0.408848	-0.079798
3	1	0	-4.194053	0.230882	-0.176698
4	1	0	-3.407746	-0.996080	0.838351
5	1	0	-3.286403	-1.095900	-0.931163
6	8	0	-0.924095	-0.441443	0.090080
7	6	0	0.269760	0.148397	0.096273
8	7	0	1.266092	-0.858963	0.295943
9	7	0	2.453421	-0.545919	-0.409187
10	7	0	3.265838	0.173297	0.069490
11	8	0	0.501411	1.334442	0.020003
12	1	0	-2.058240	1.141270	0.807871
13	1	0	-1.936642	1.042323	-0.955703

X. References

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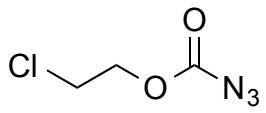
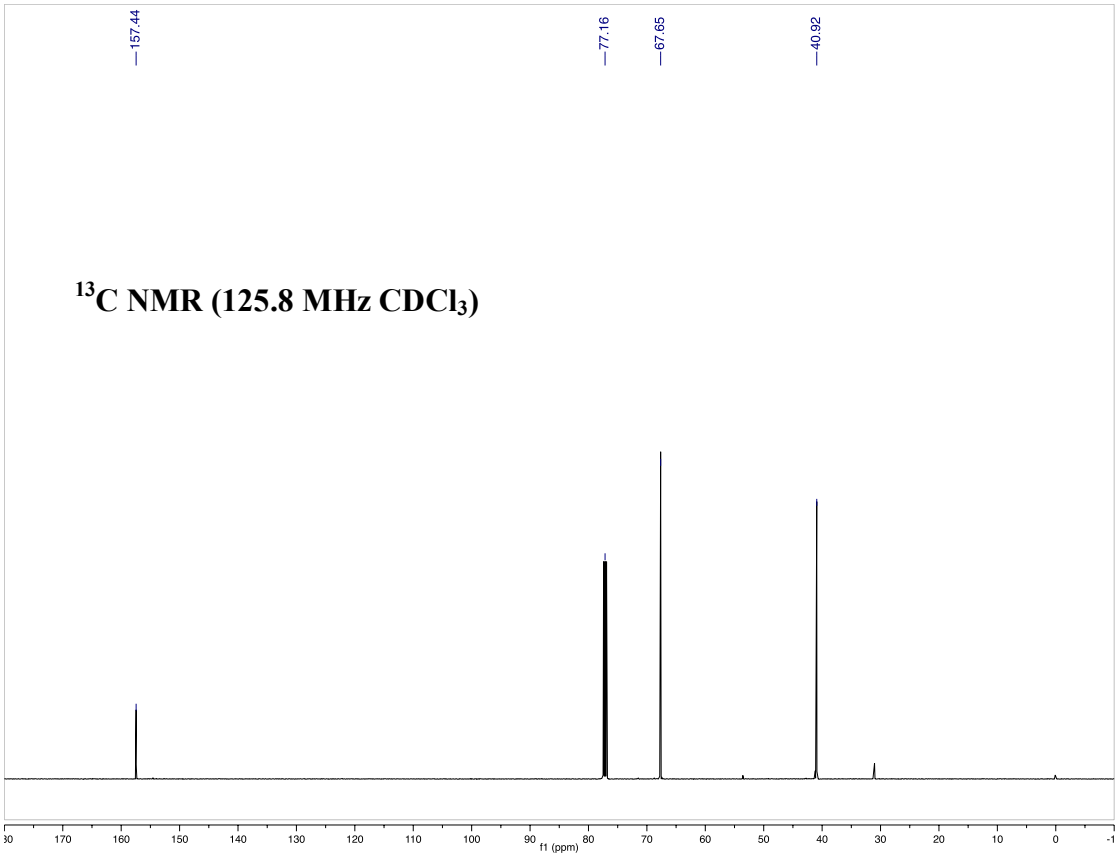
2-Chloroethyl azidoformate (3b)
^{1}H NMR (500.2 MHz $CDCl_3$)

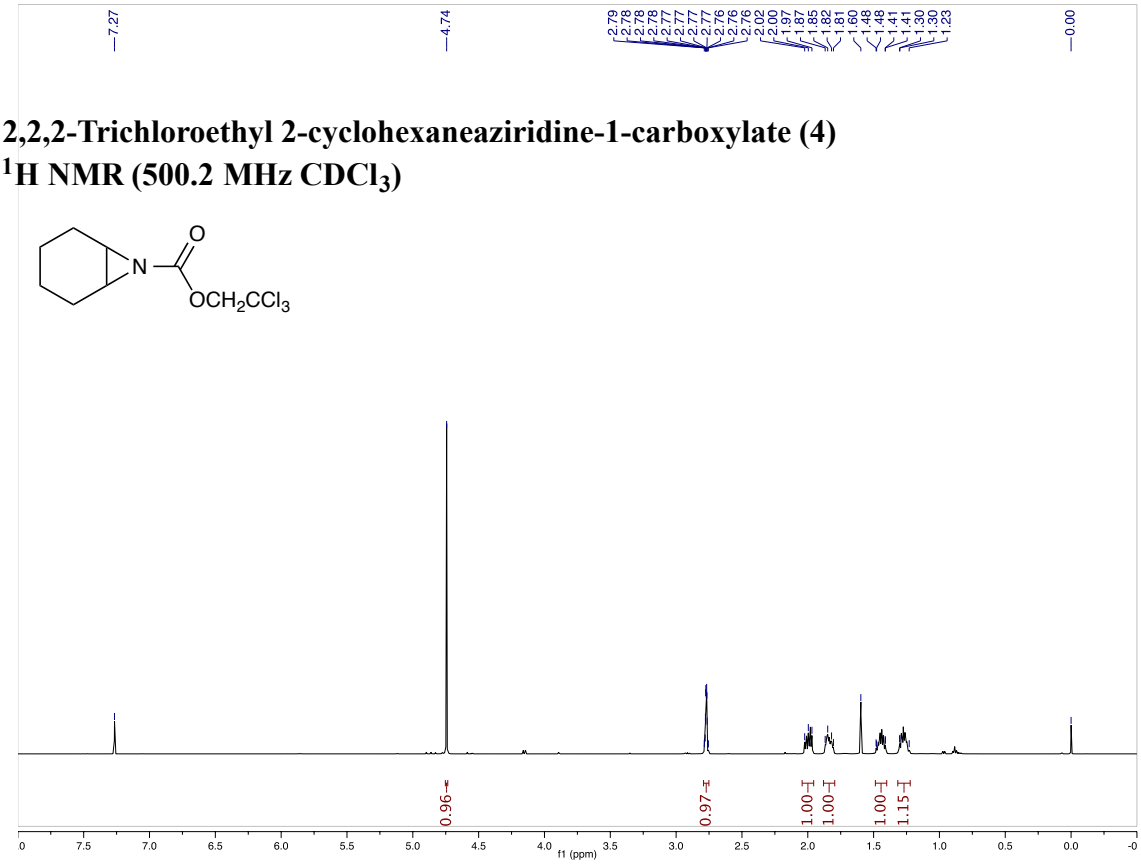


^{13}C NMR (125.8 MHz $CDCl_3$)

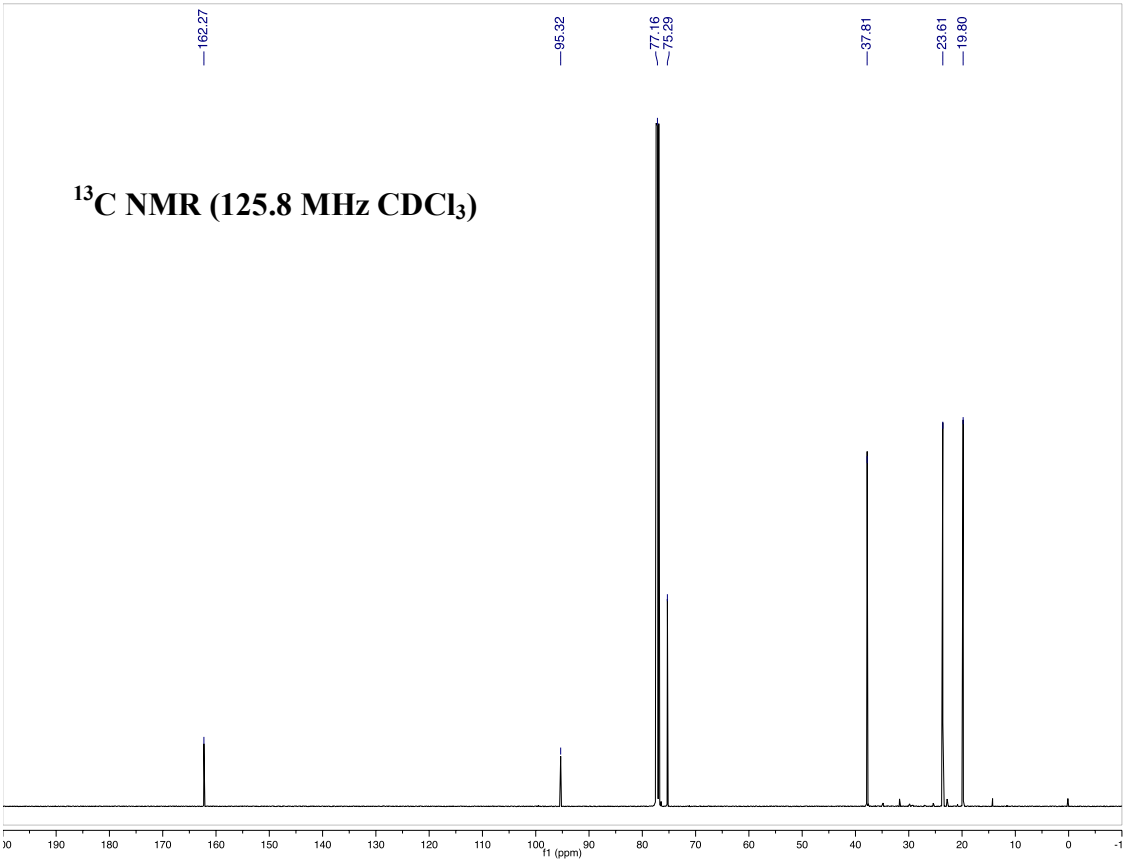


2,2,2-Trichloroethyl 2-cyclohexaneaziridine-1-carboxylate (4)

^{1}H NMR (500.2 MHz $CDCl_3$)

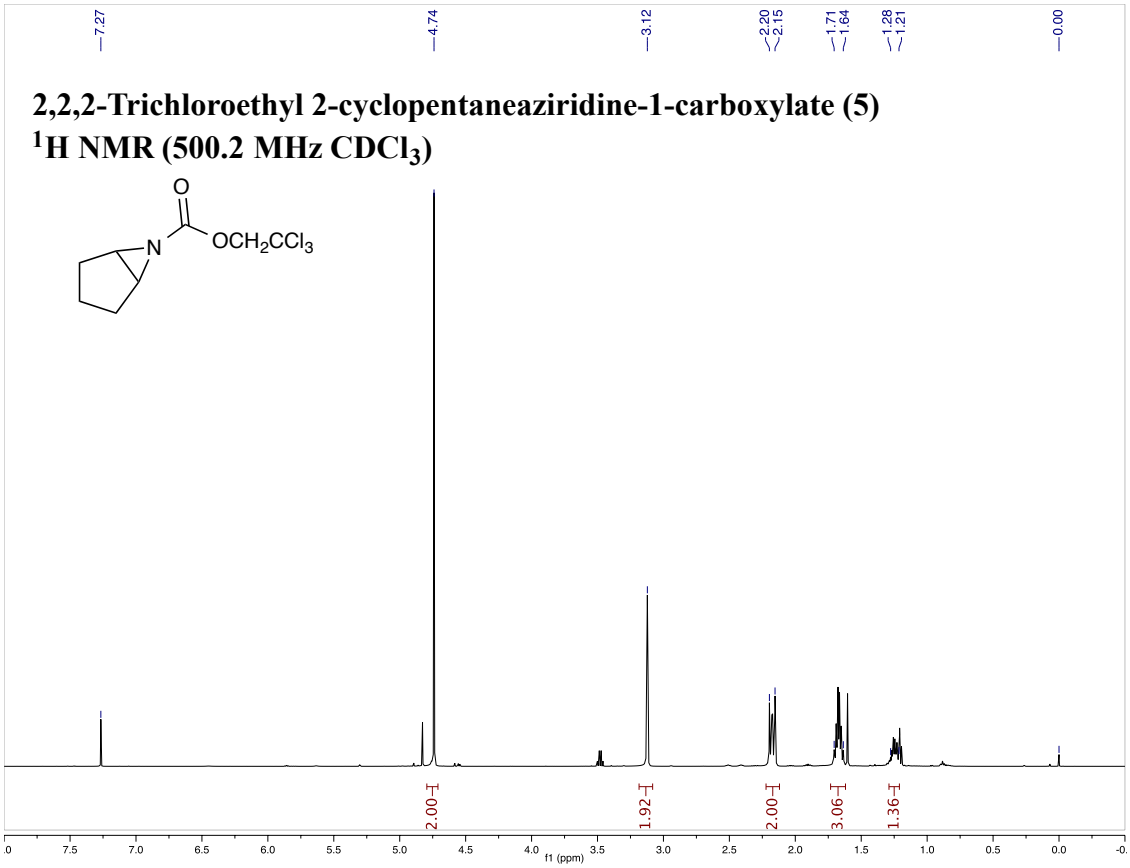


^{13}C NMR (125.8 MHz $CDCl_3$)

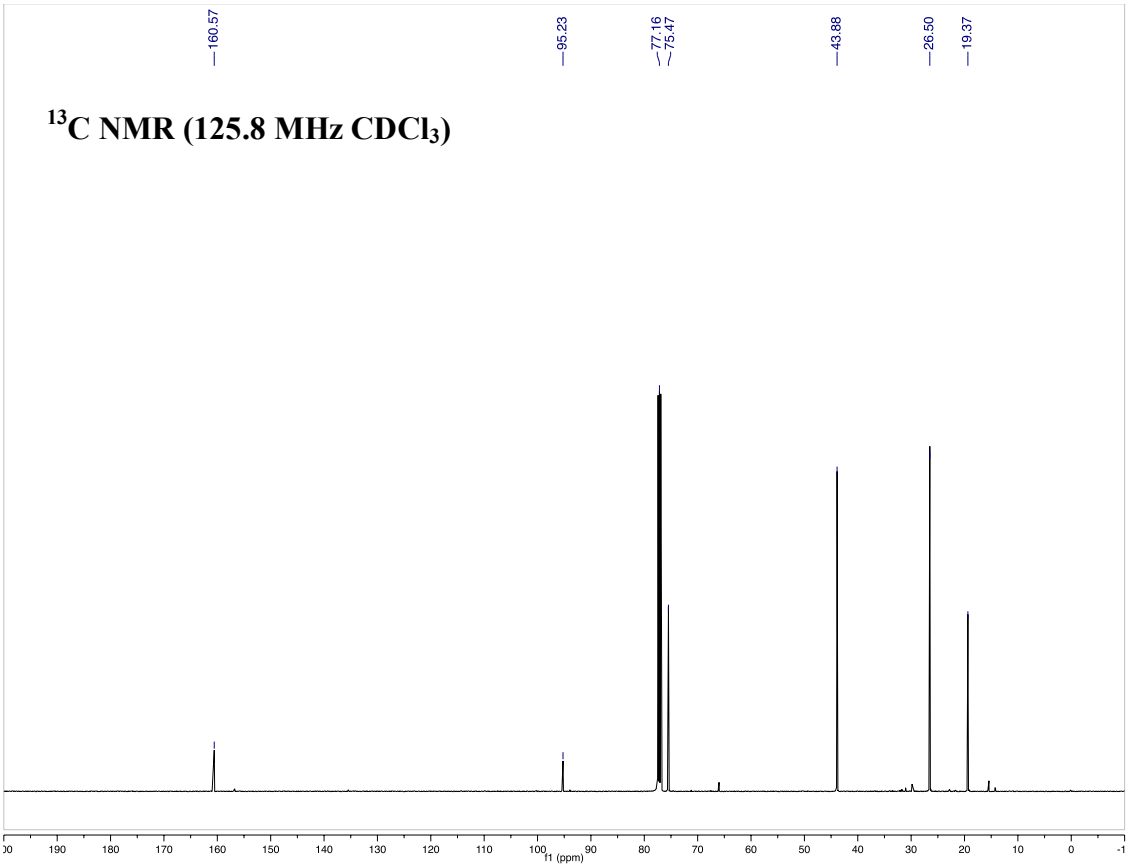


2,2,2-Trichloroethyl 2-cyclopentaneaziridine-1-carboxylate (5)

^{1}H NMR (500.2 MHz $CDCl_3$)

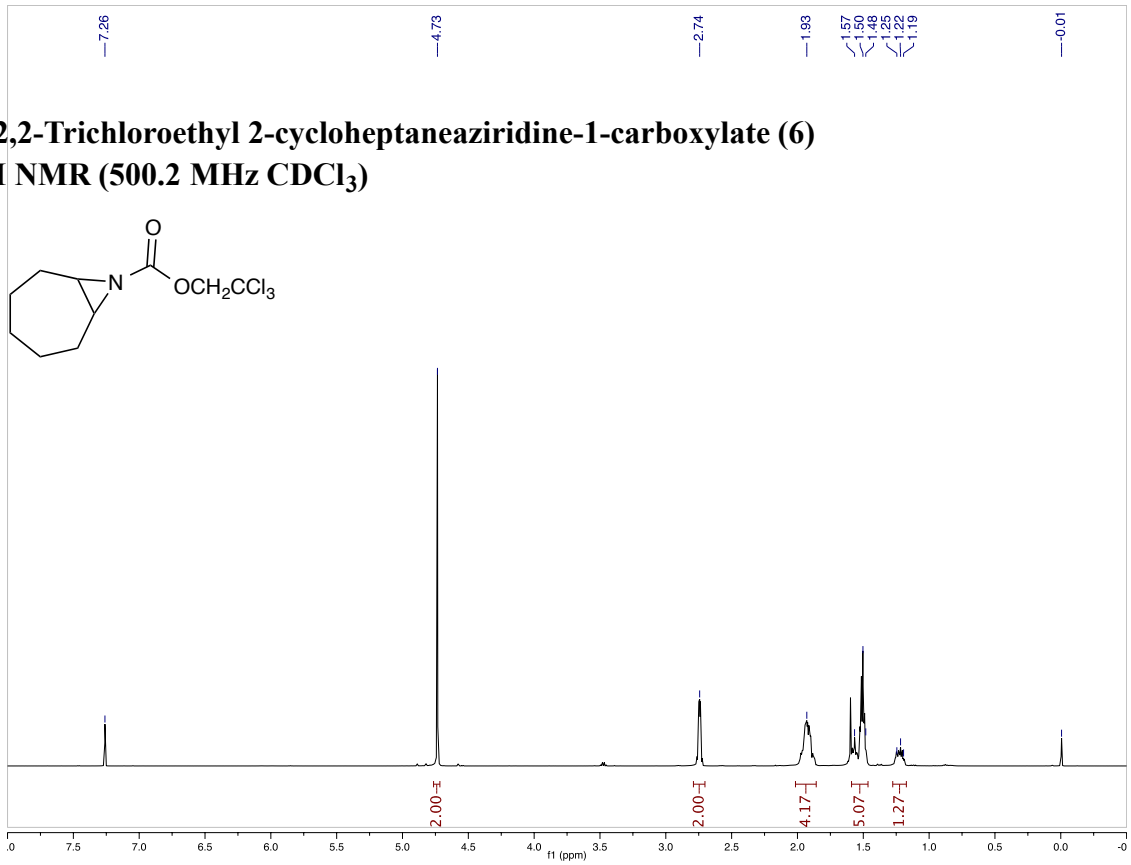


^{13}C NMR (125.8 MHz $CDCl_3$)

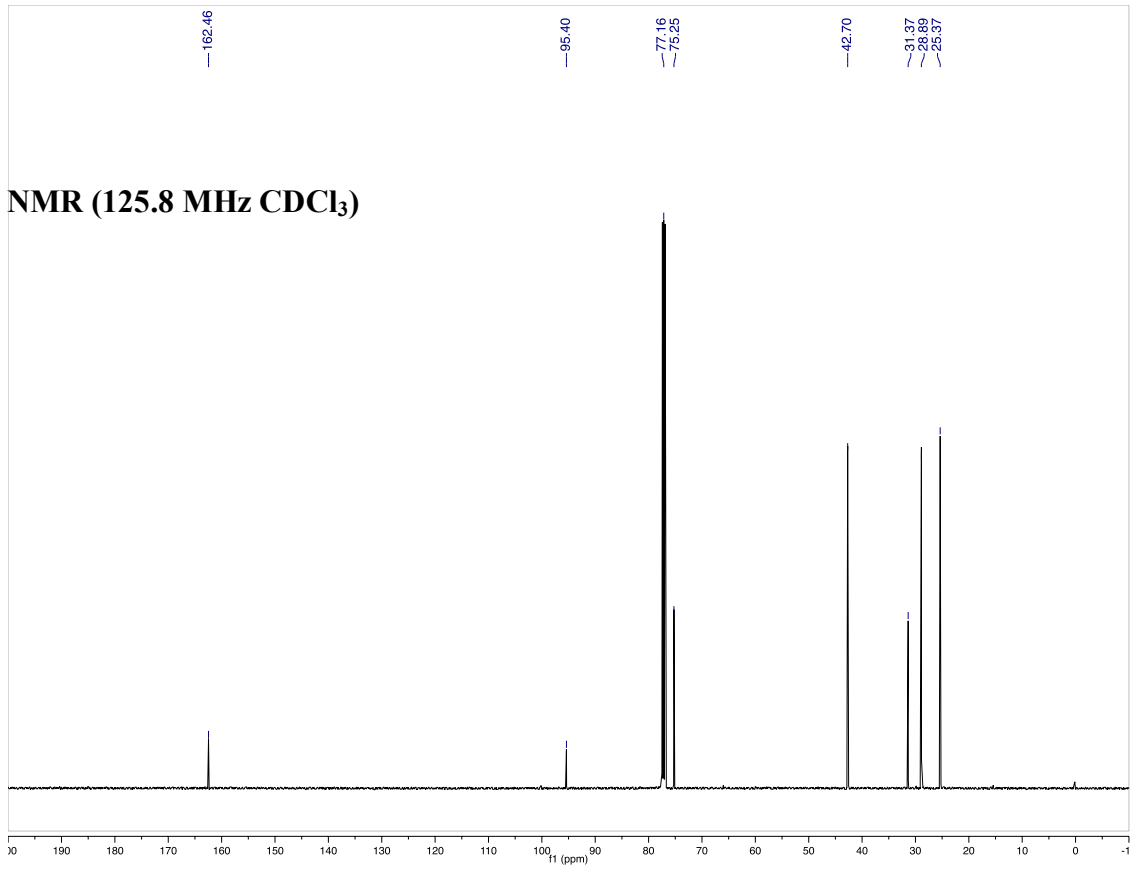


2,2,2-Trichloroethyl 2-cycloheptaneaziridine-1-carboxylate (6)

^{1}H NMR (500.2 MHz $CDCl_3$)

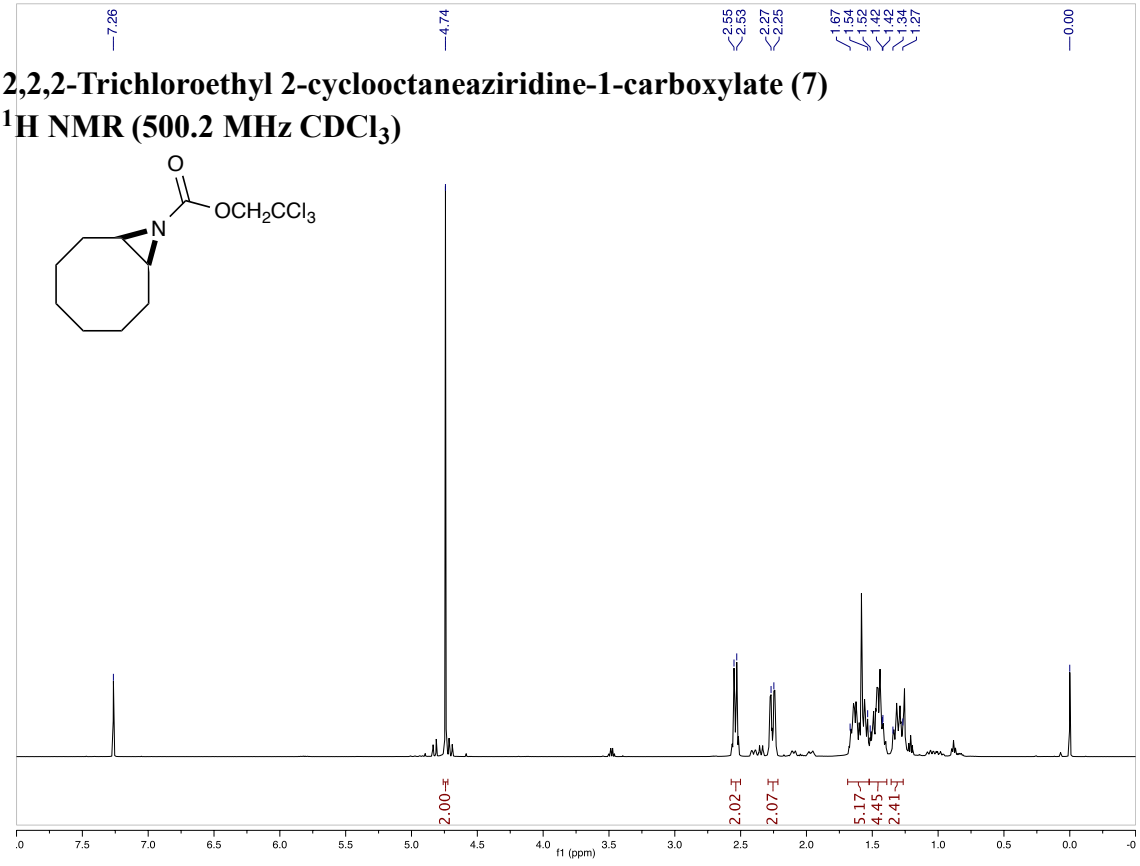


^{13}C NMR (125.8 MHz $CDCl_3$)

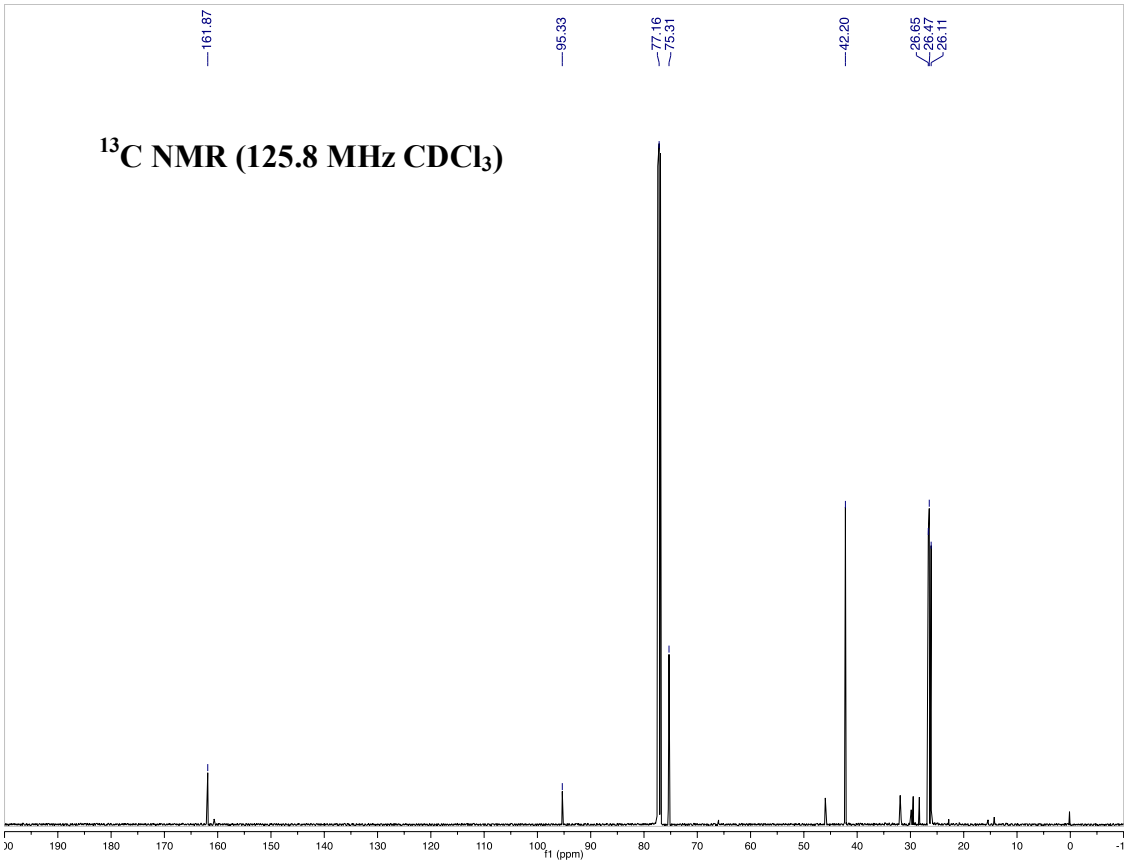


2,2,2-Trichloroethyl 2-cyclooctaneaziridine-1-carboxylate (7)

^{1}H NMR (500.2 MHz $CDCl_3$)

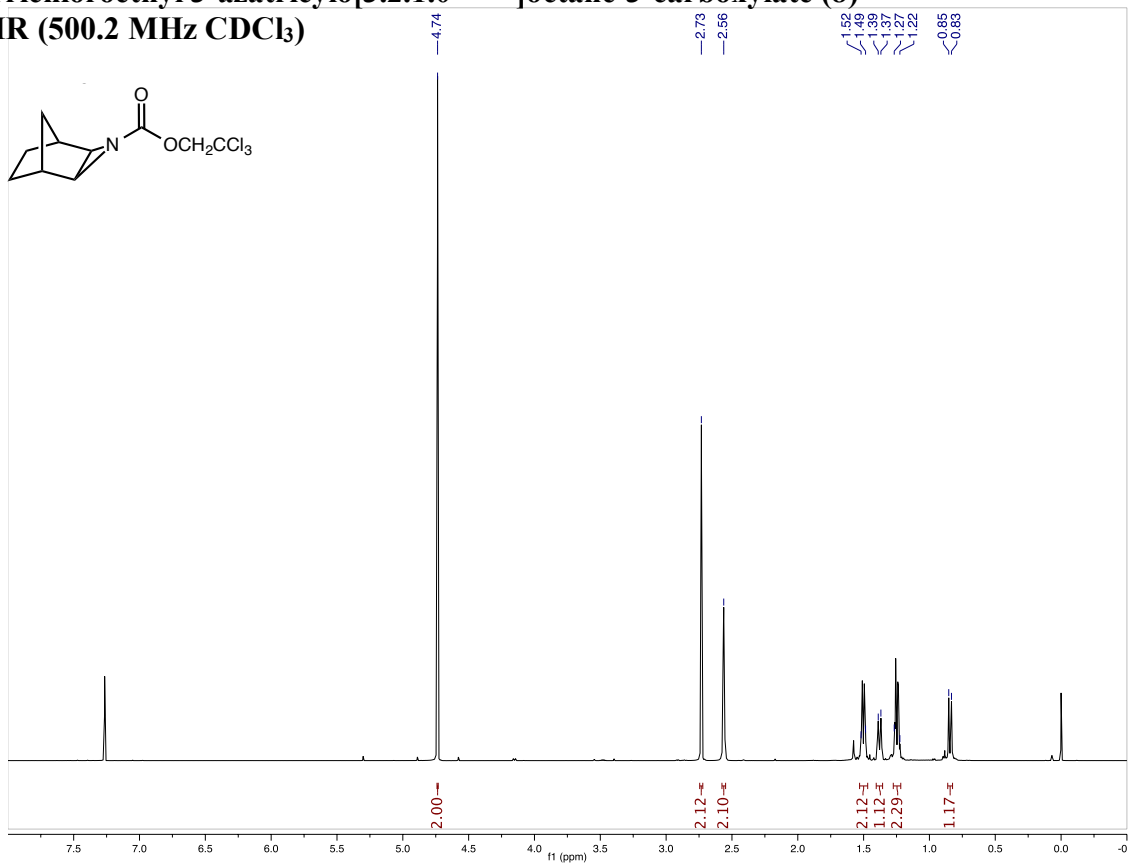


^{13}C NMR (125.8 MHz $CDCl_3$)

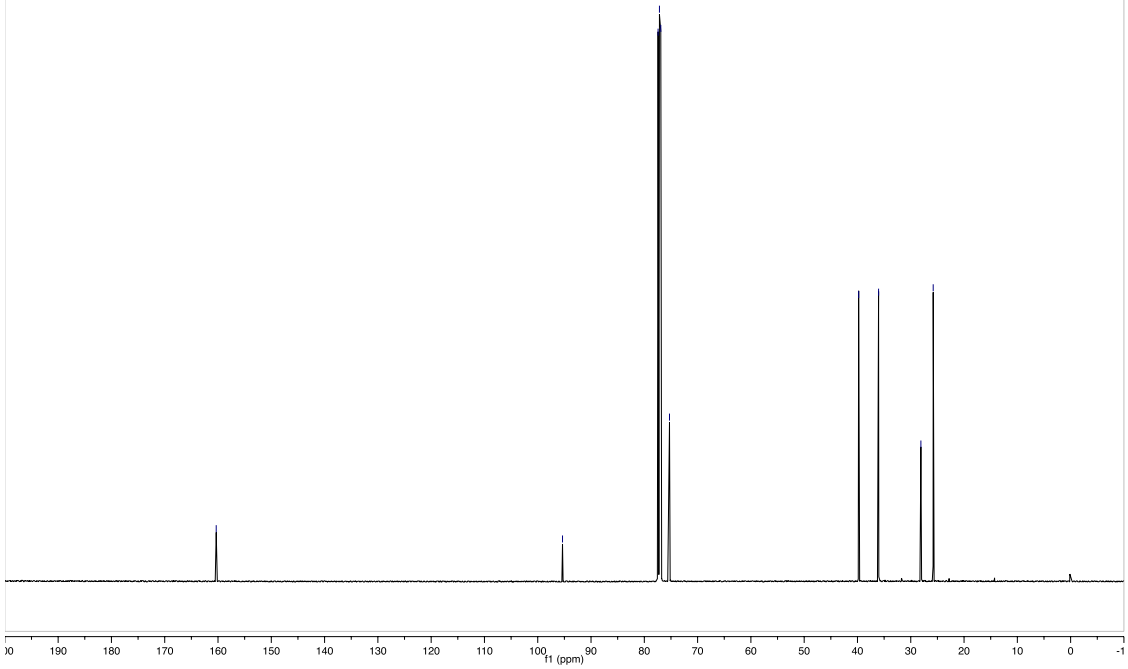


2,2,2-Trichloroethyl 3-azatricylo[3.2.1.0$^{2,4\text{-exo}}$]octane-3-carboxylate (8)

^{1}H NMR (500.2 MHz $CDCl_3$)

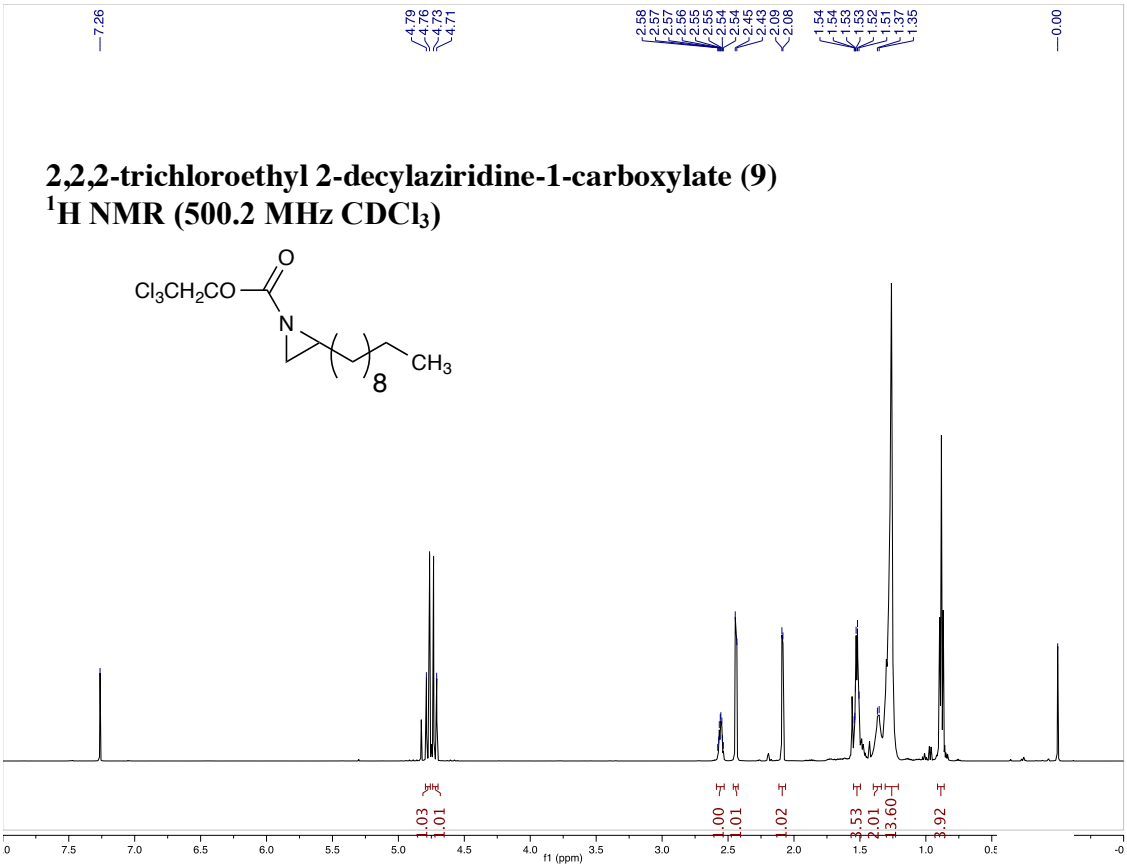


^{13}C NMR (125.8 MHz $CDCl_3$)

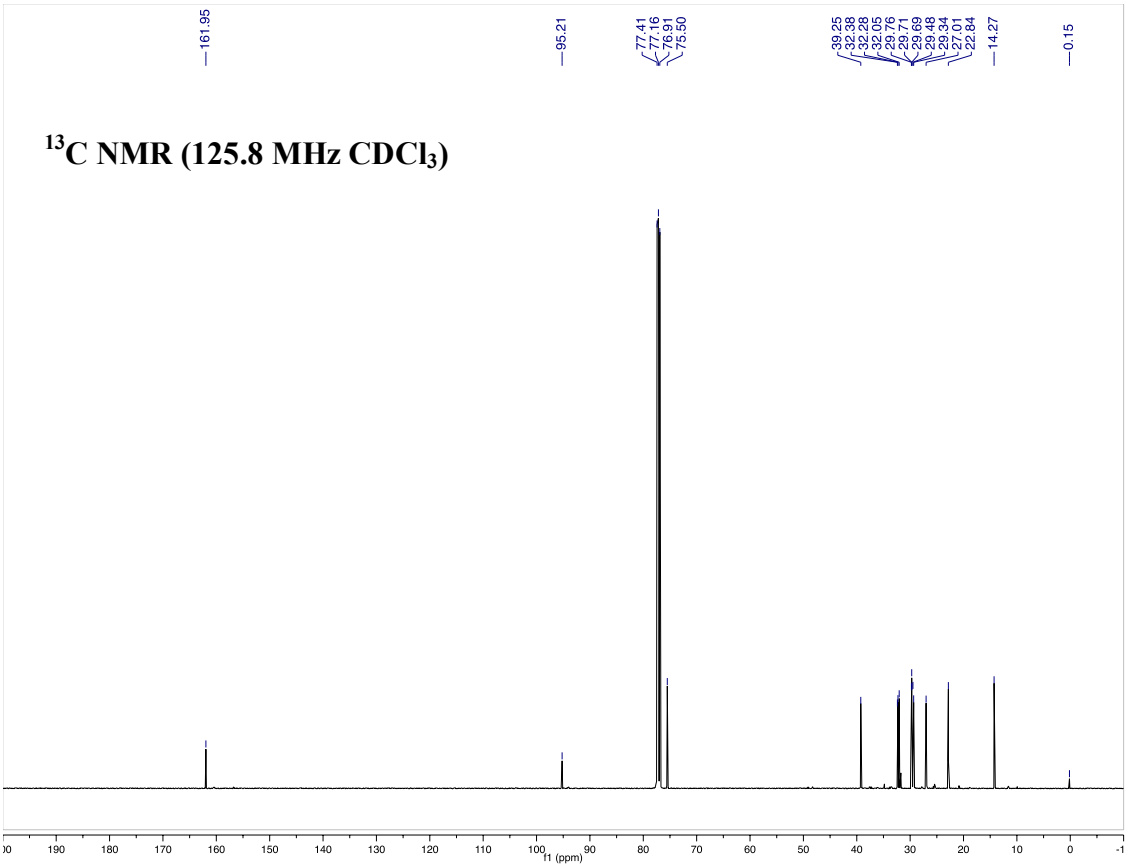


2,2,2-trichloroethyl 2-decylaziridine-1-carboxylate (9)

^{1}H NMR (500.2 MHz $CDCl_3$)

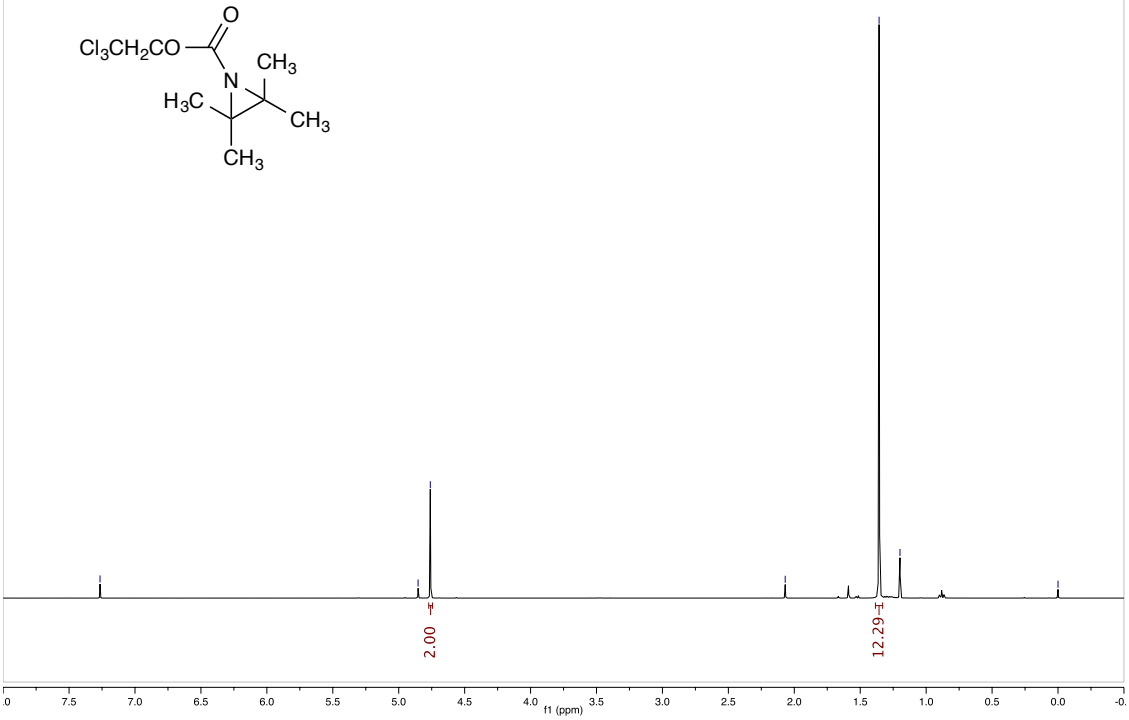


^{13}C NMR (125.8 MHz $CDCl_3$)

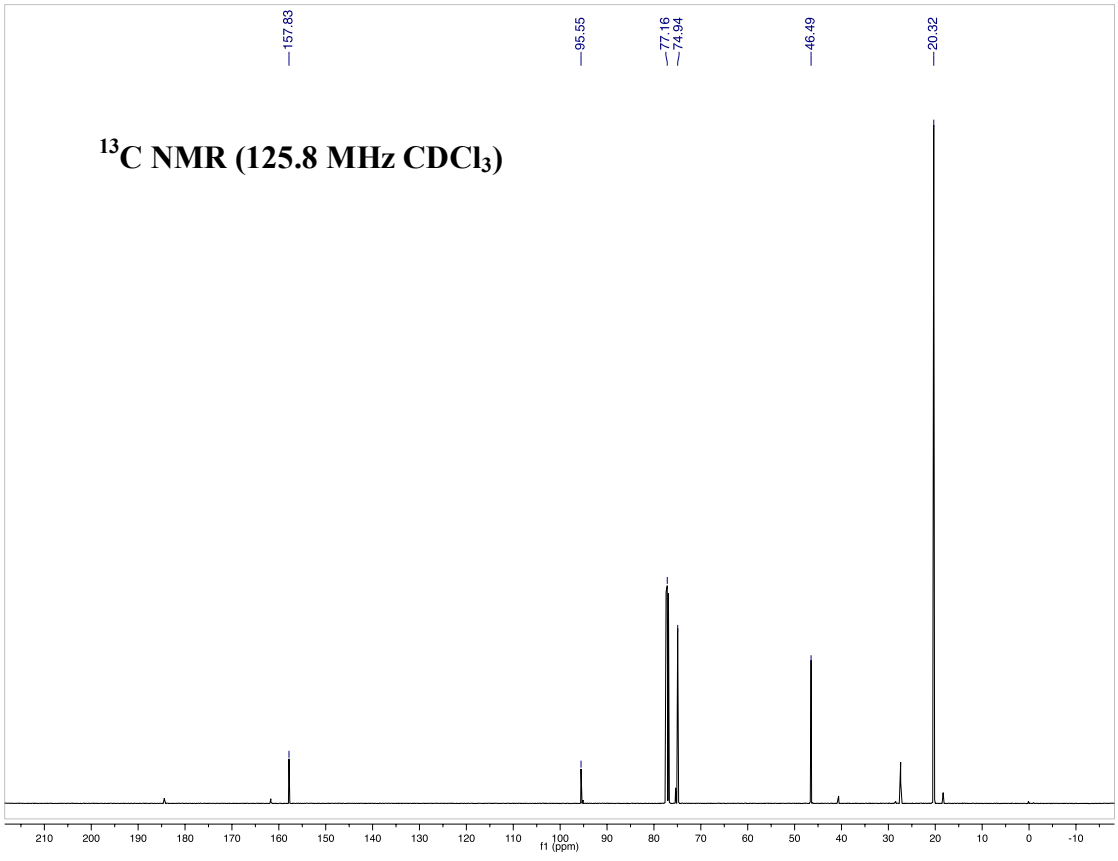


2,2,2-Trichloroethyl 2,2,3,3-tetramethylaziridine-1-carboxylate (11)

^{1}H NMR (500.2 MHz $CDCl_3$)

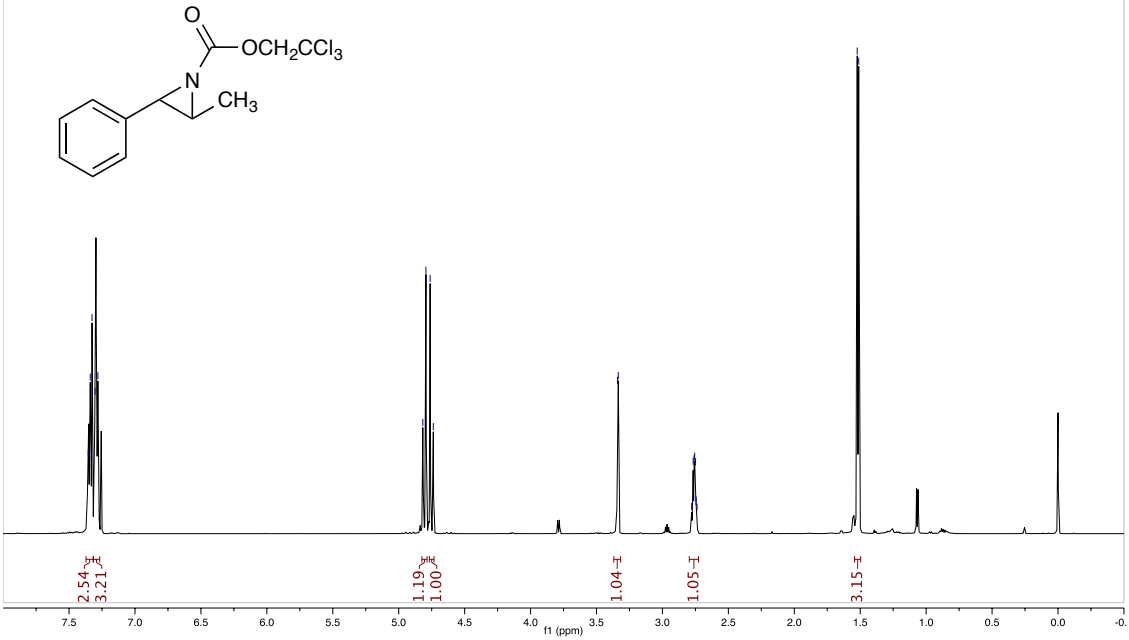


^{13}C NMR (125.8 MHz $CDCl_3$)

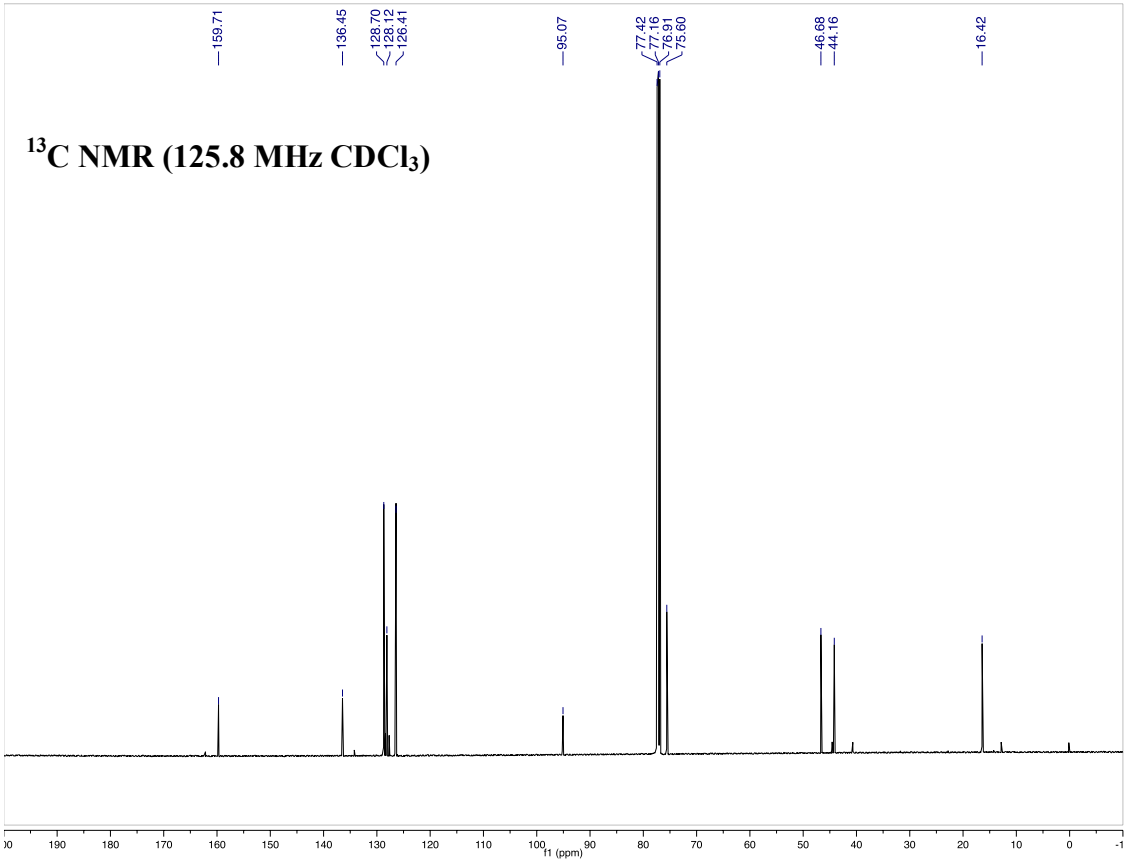


2,2,2-Trichloroethyl *trans*-2-phenyl-3-methylziridine-1-carboxylate (12)

^{1}H NMR (500.2 MHz $CDCl_3$)

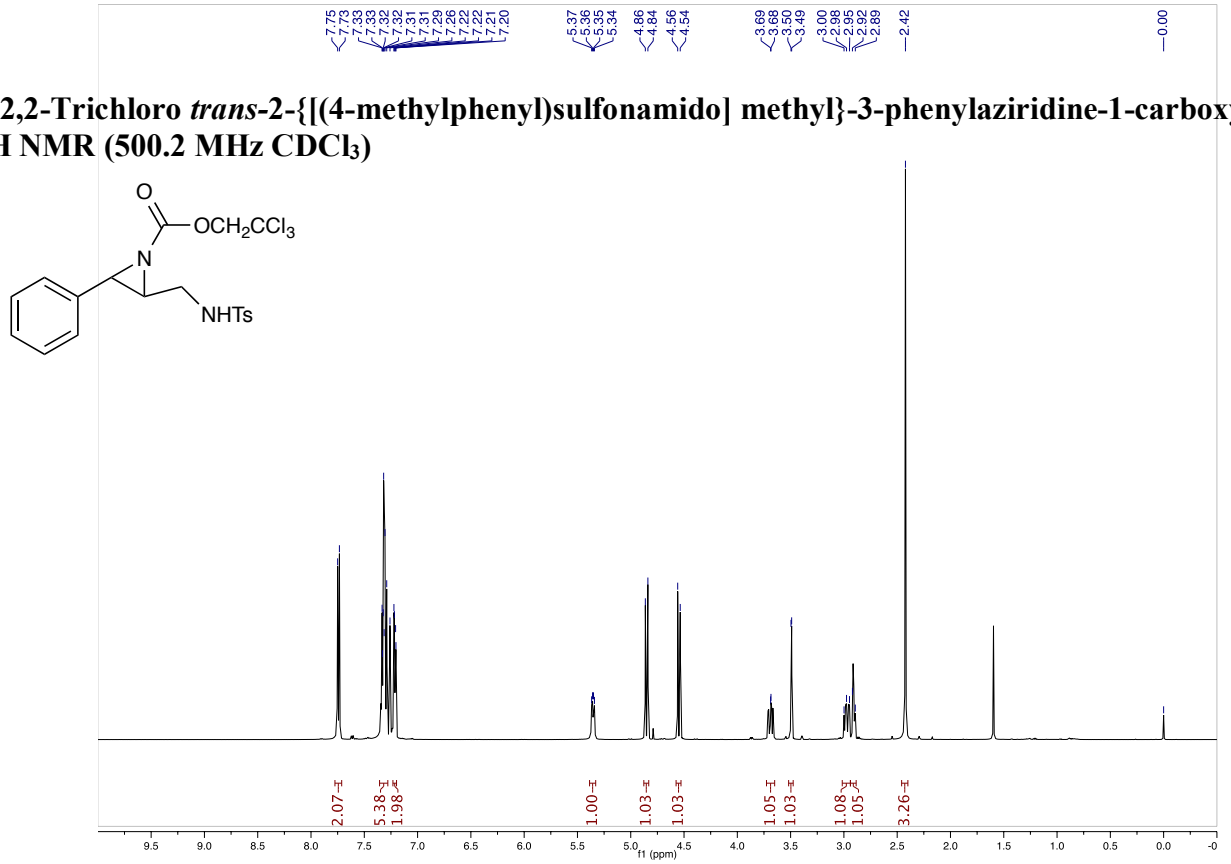


^{13}C NMR (125.8 MHz $CDCl_3$)

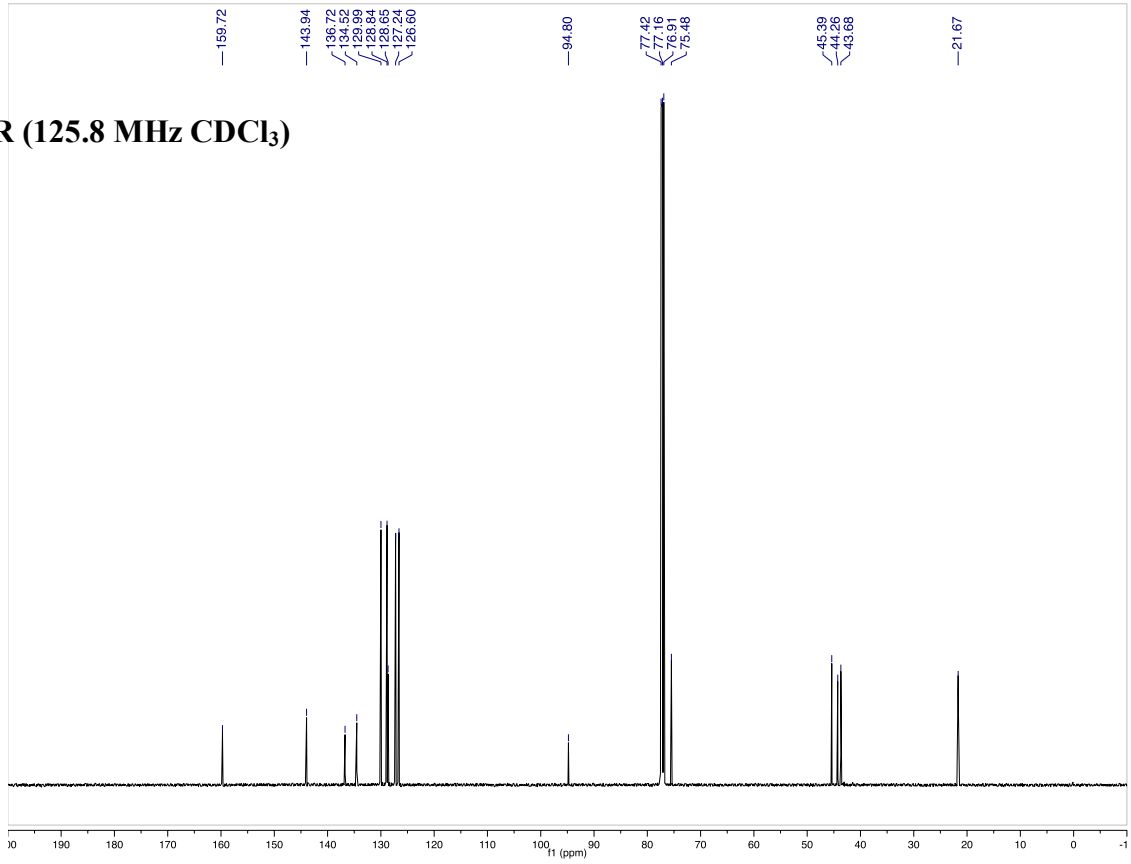


2,2,2-Trichloro *trans*-2-{[(4-methylphenyl)sulfonamido] methyl}-3-phenylaziridine-1-carboxylate (13):

^{1}H NMR (500.2 MHz $CDCl_3$)

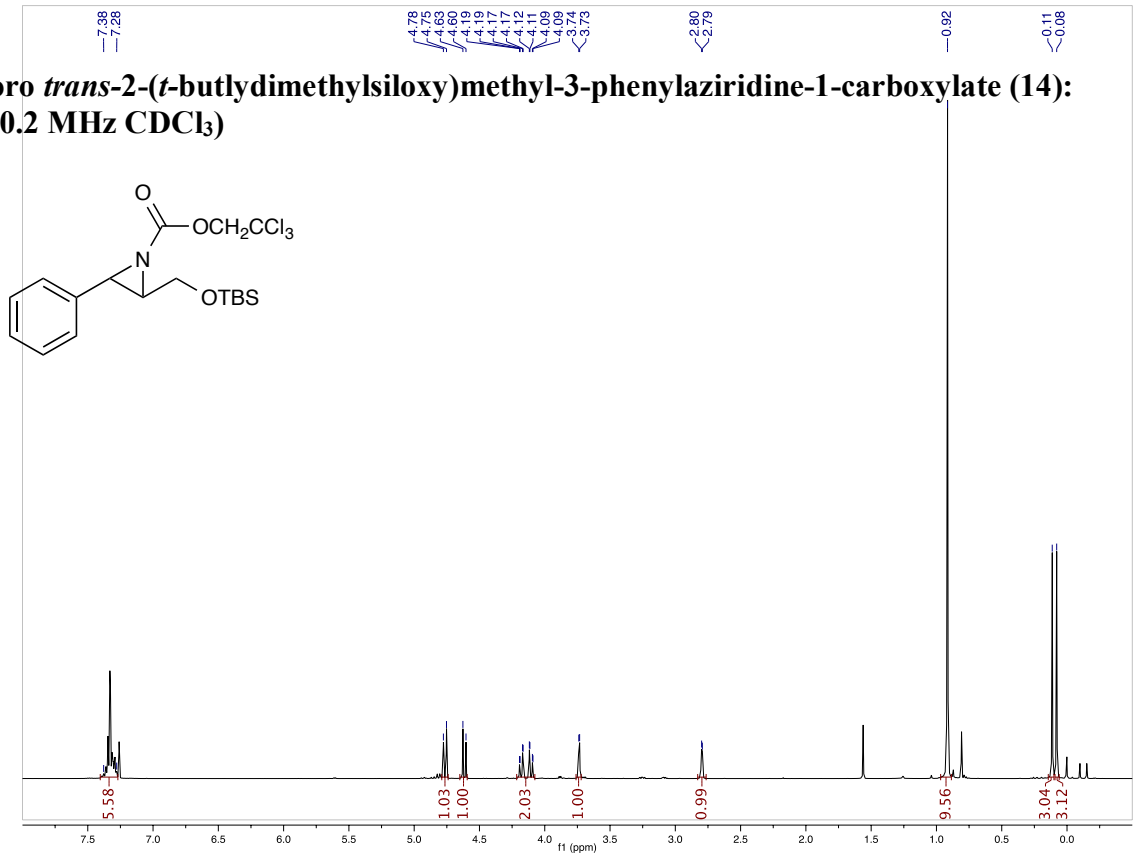


^{13}C NMR (125.8 MHz $CDCl_3$)

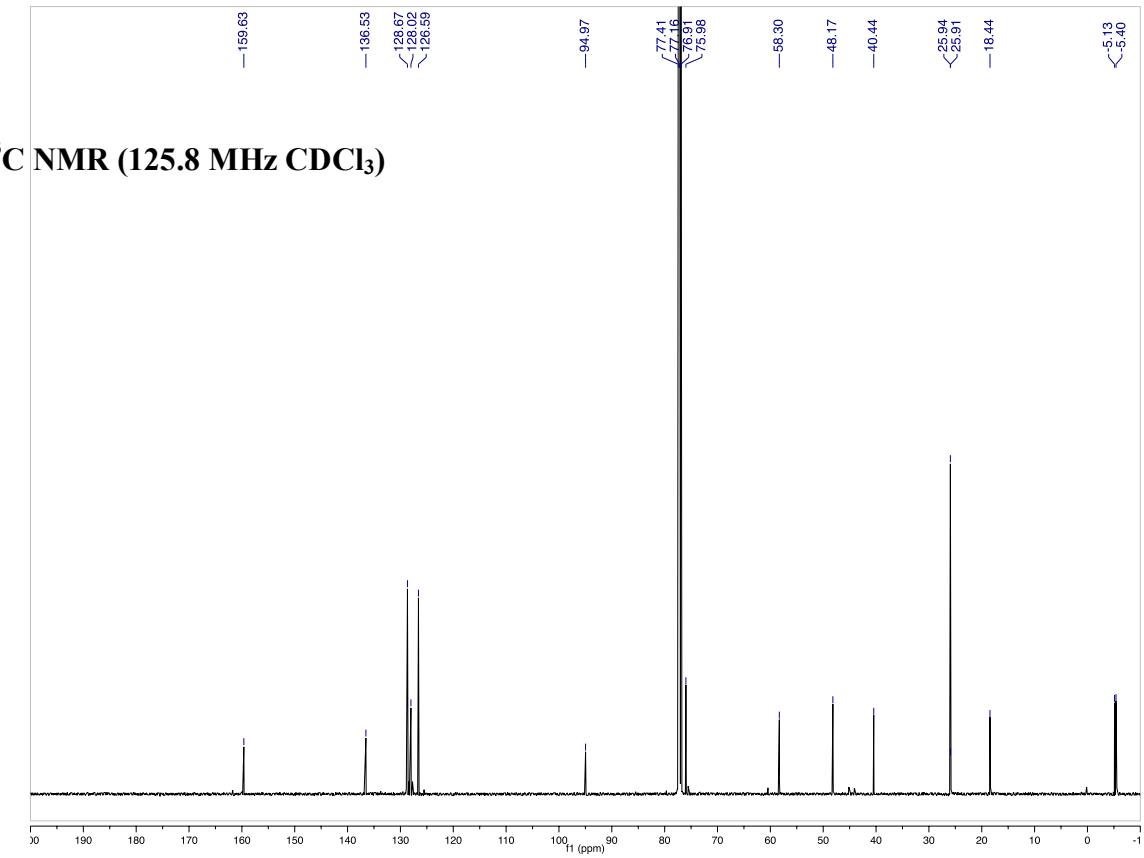


2,2,2-Trichloro *trans*-2-(*t*-butlydimethylsiloxy)methyl-3-phenylaziridine-1-carboxylate (14):

^{1}H NMR (500.2 MHz $CDCl_3$)

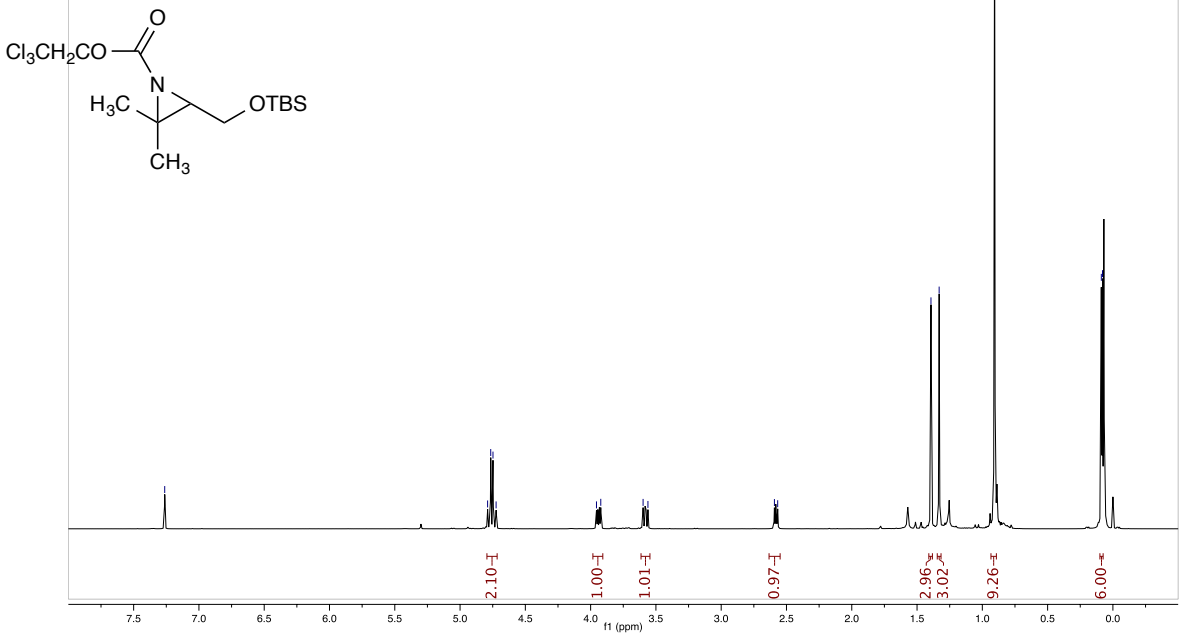


^{13}C NMR (125.8 MHz $CDCl_3$)

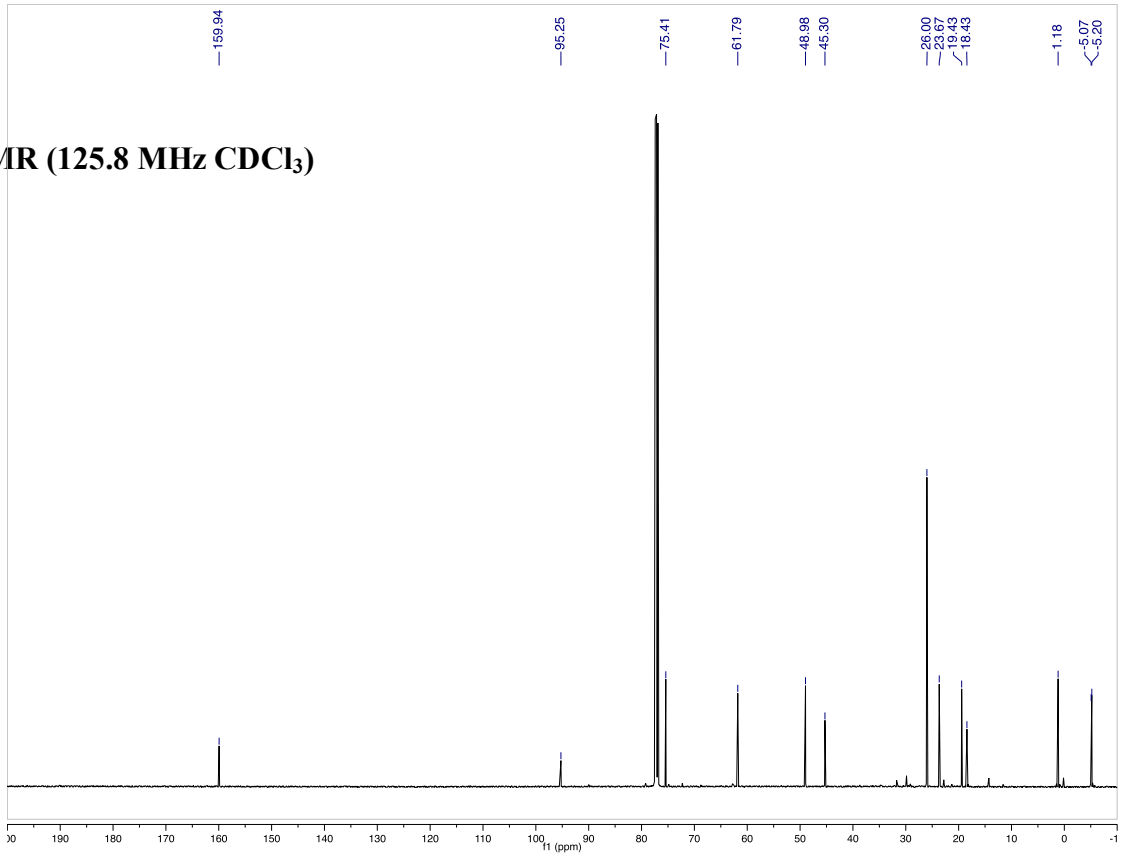


2,2,2-Trichloro 3-(t-butyldimethylsiloxy)methyl-2,2-dimethylazidine-1-carboxylate (15):

^{1}H NMR (500.2 MHz $CDCl_3$)

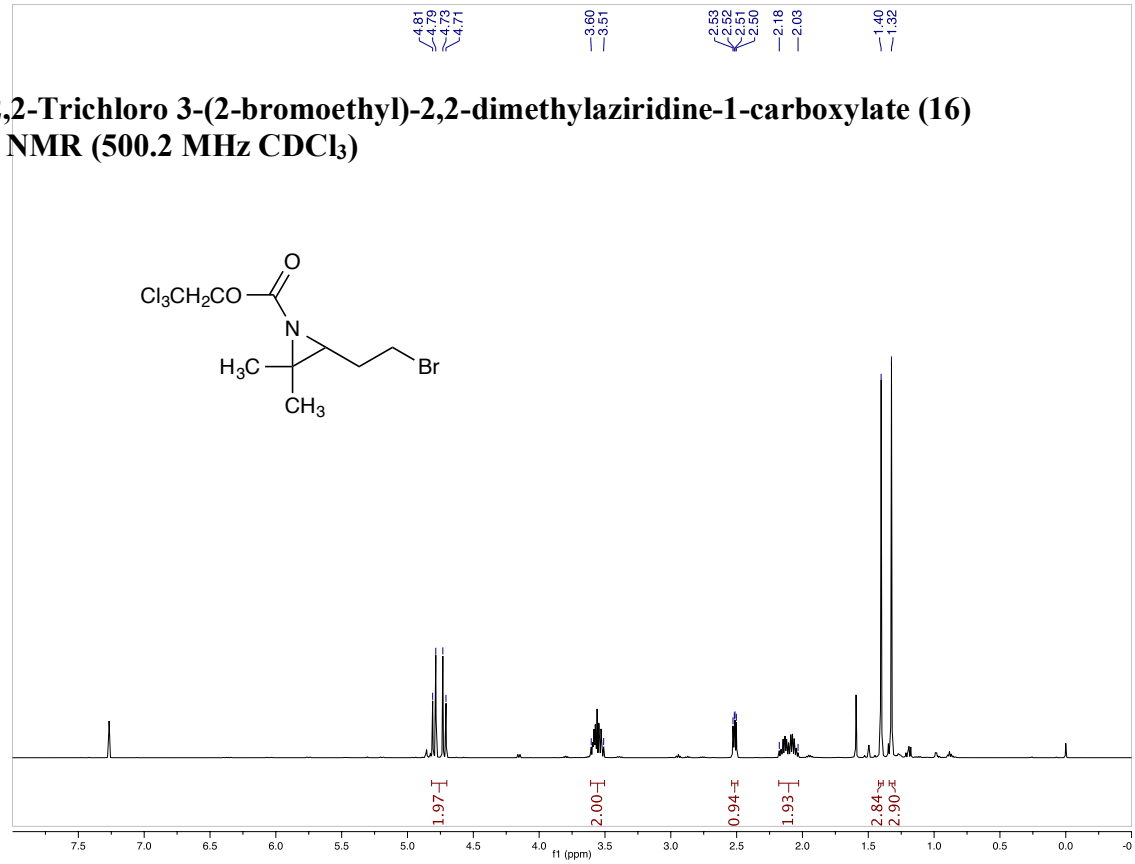


^{13}C NMR (125.8 MHz $CDCl_3$)

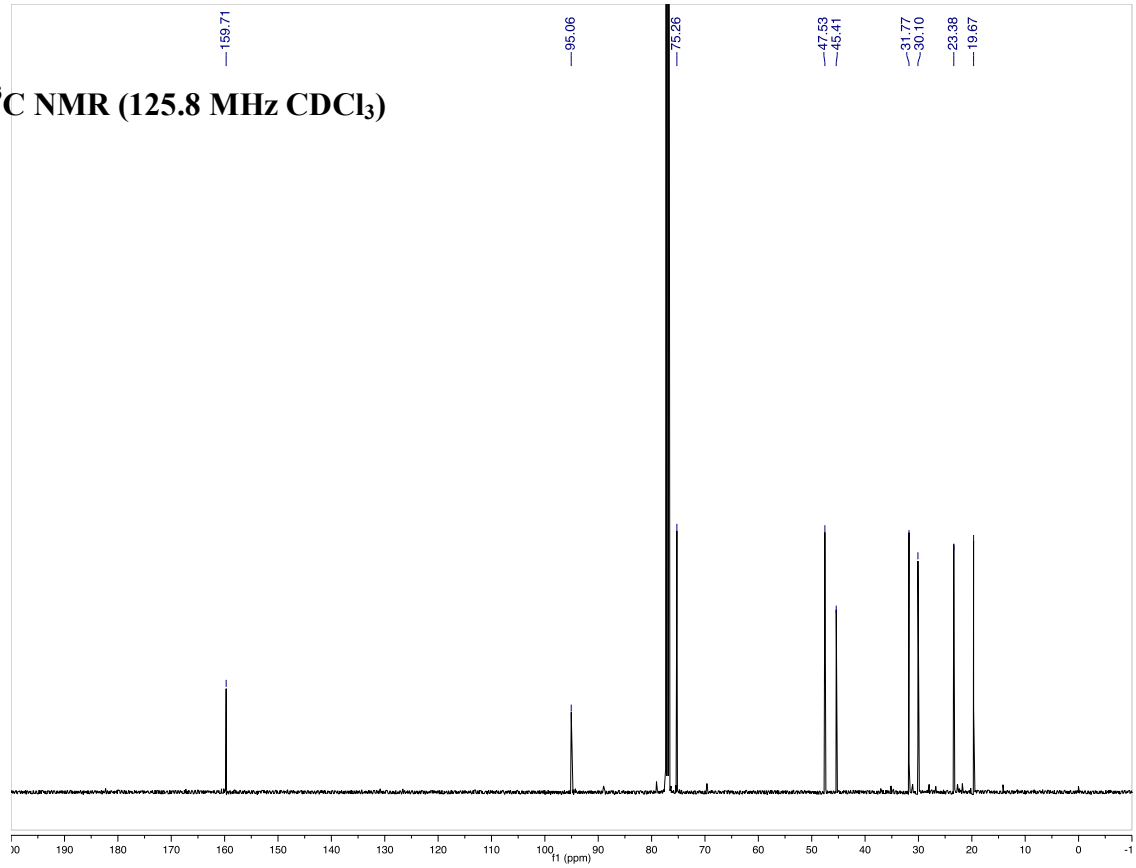


2,2,2-Trichloro 3-(2-bromoethyl)-2,2-dimethylaziridine-1-carboxylate (16)

^{1}H NMR (500.2 MHz $CDCl_3$)

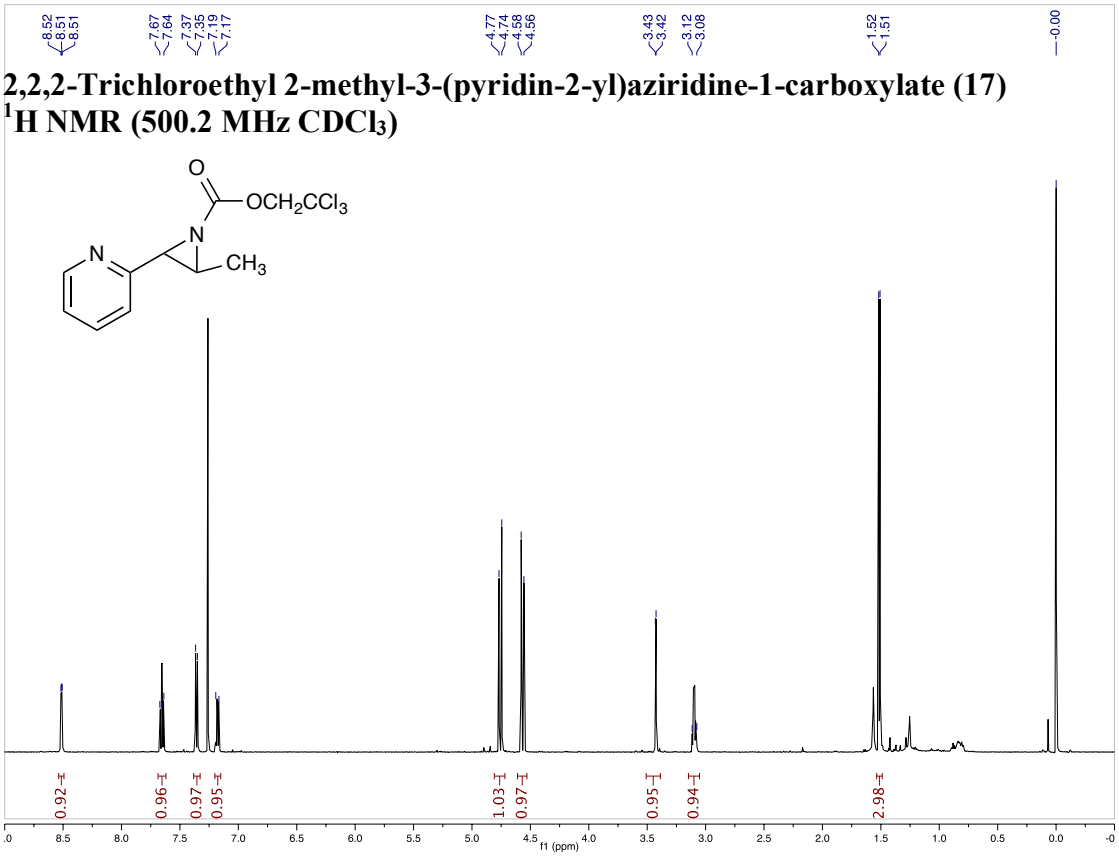


^{13}C NMR (125.8 MHz $CDCl_3$)

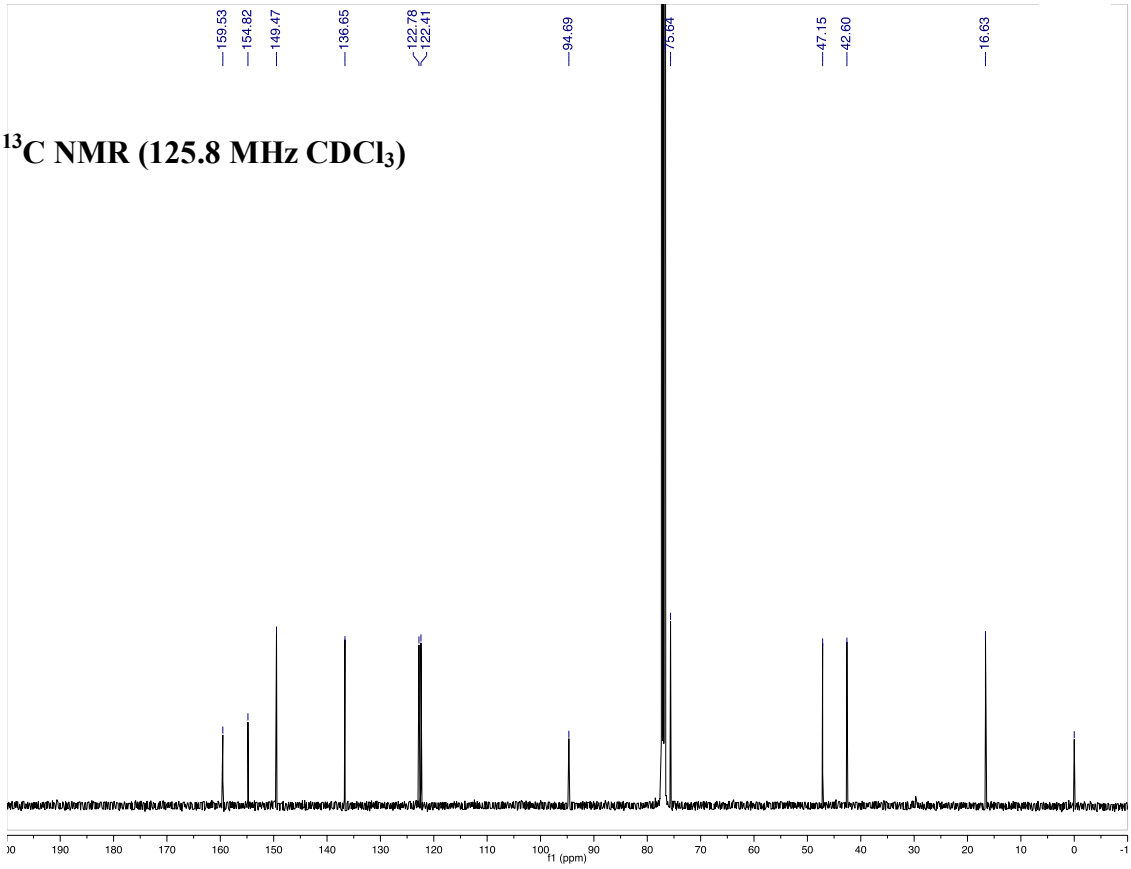


2,2,2-Trichloroethyl 2-methyl-3-(pyridin-2-yl)aziridine-1-carboxylate (17)

^{1}H NMR (500.2 MHz $CDCl_3$)

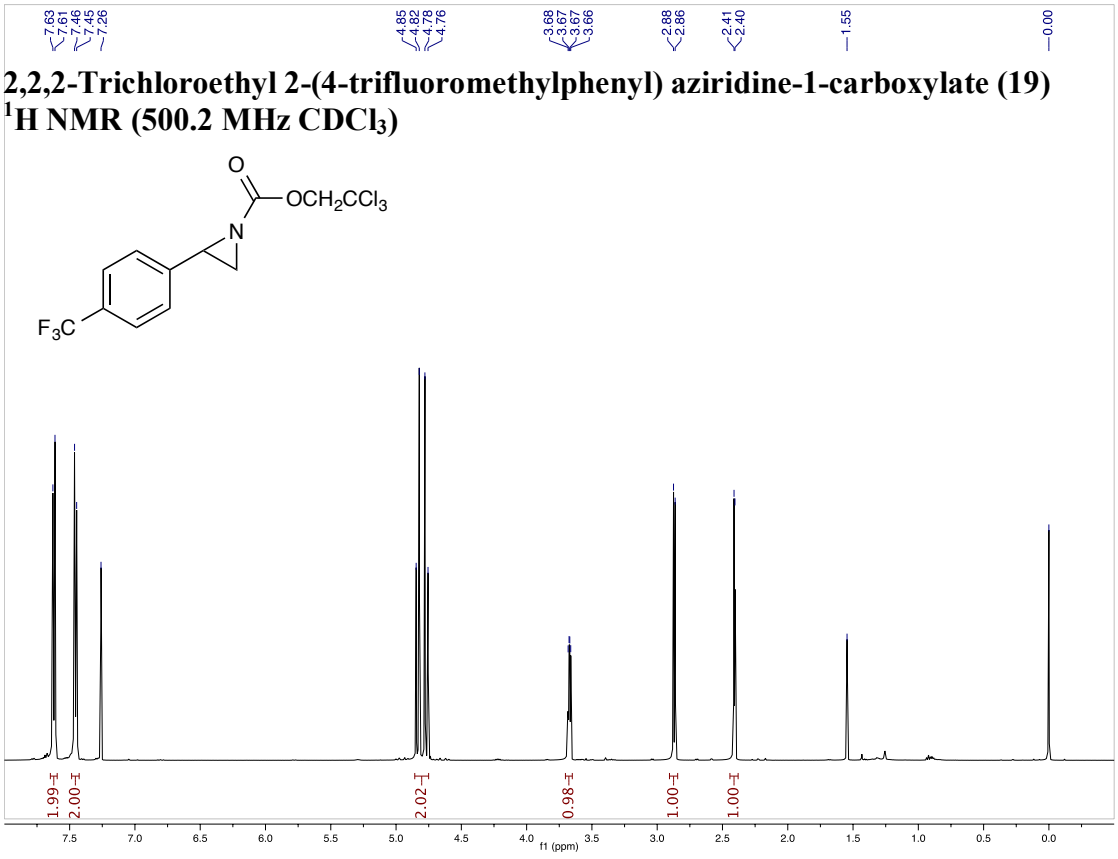


^{13}C NMR (125.8 MHz $CDCl_3$)

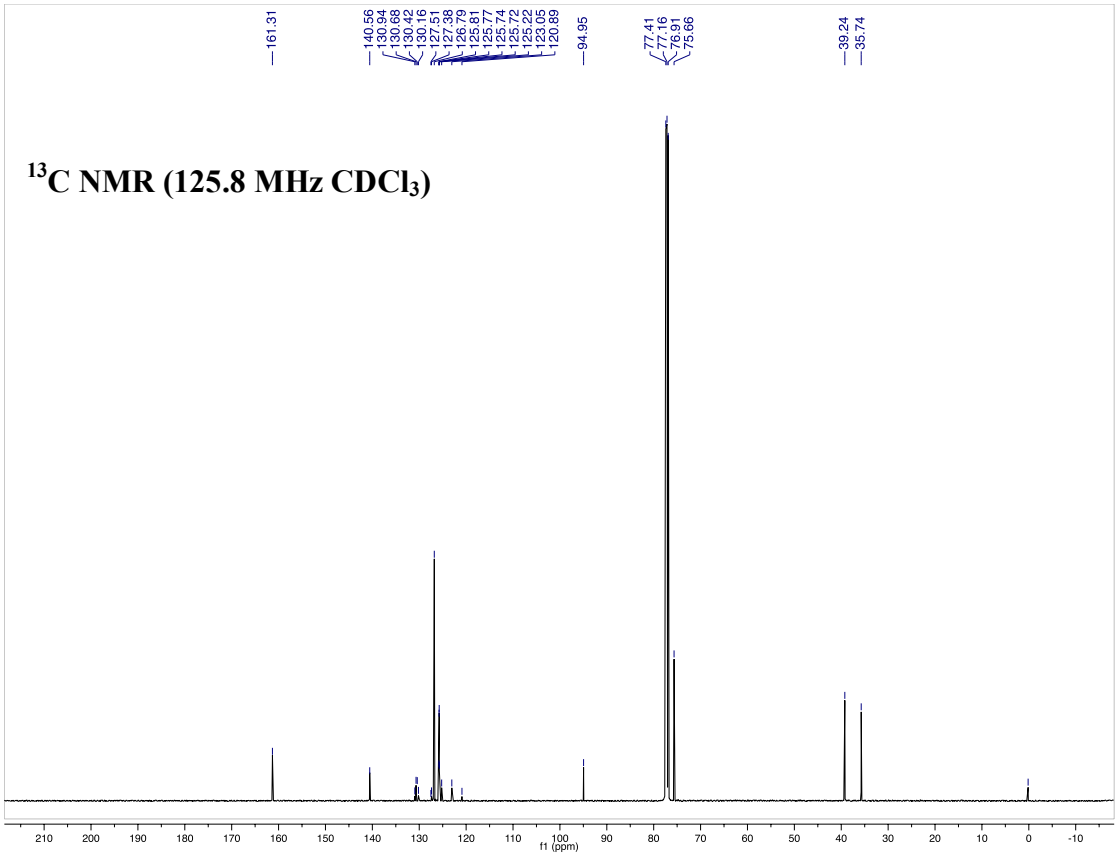


2,2,2-Trichloroethyl 2-(4-trifluoromethylphenyl) aziridine-1-carboxylate (19)

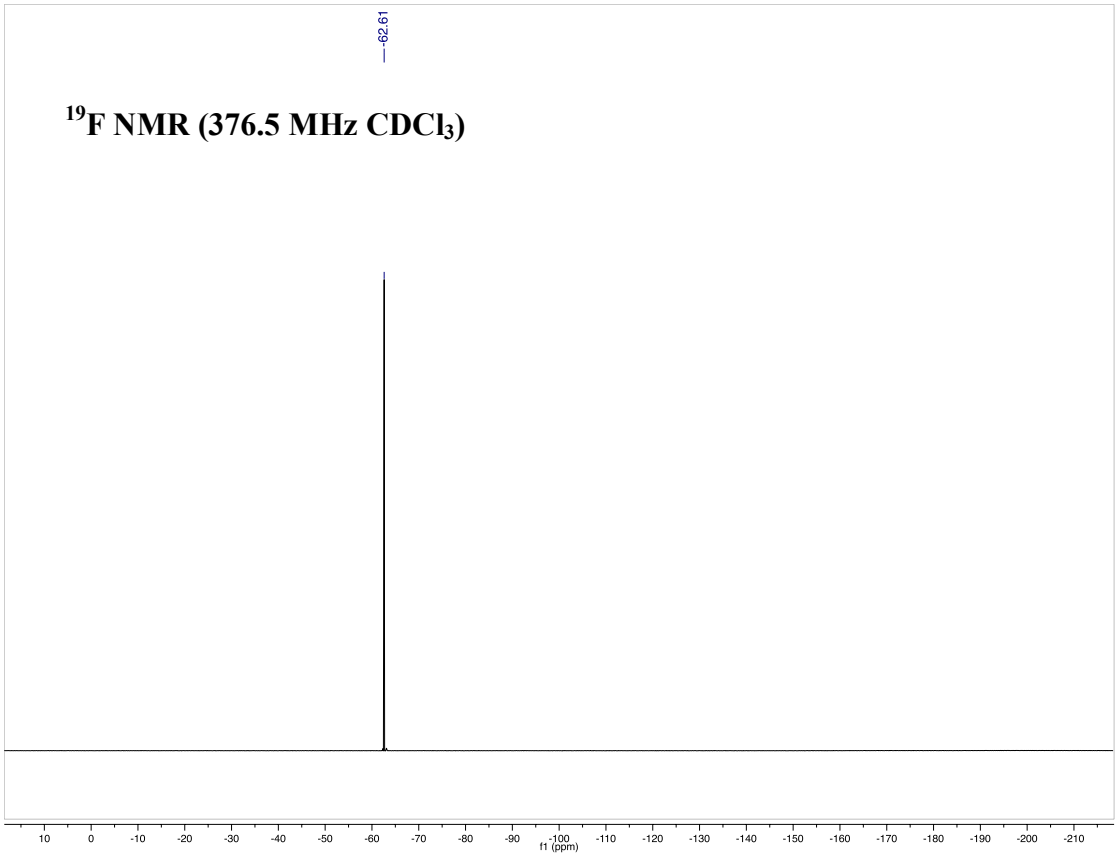
^{1}H NMR (500.2 MHz $CDCl_3$)



^{13}C NMR (125.8 MHz $CDCl_3$)

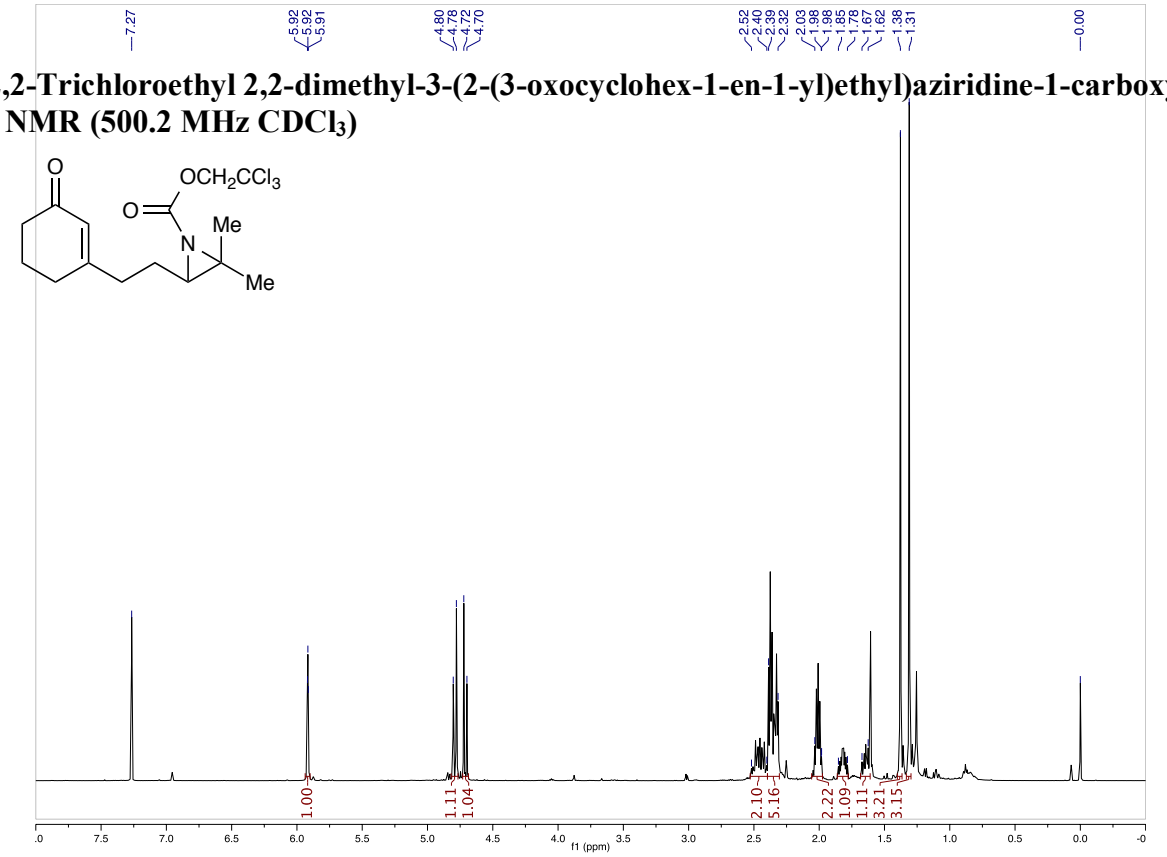


^{19}F NMR (376.5 MHz $CDCl_3$)

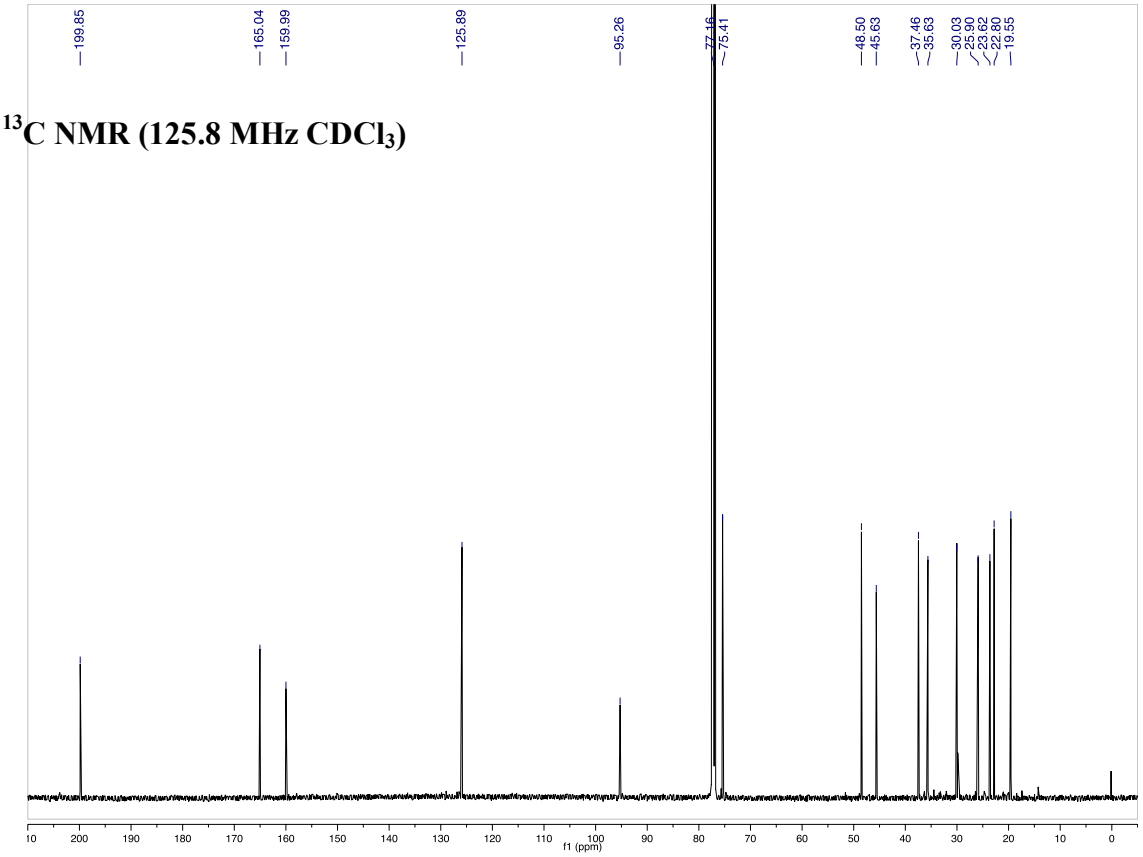


2,2,2-Trichloroethyl 2,2-dimethyl-3-(2-(3-oxocyclohex-1-en-1-yl)ethyl)aziridine-1-carboxylate (20):

^{1}H NMR (500.2 MHz $CDCl_3$)

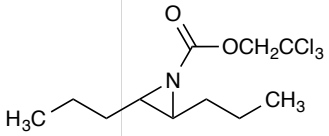


^{13}C NMR (125.8 MHz $CDCl_3$)

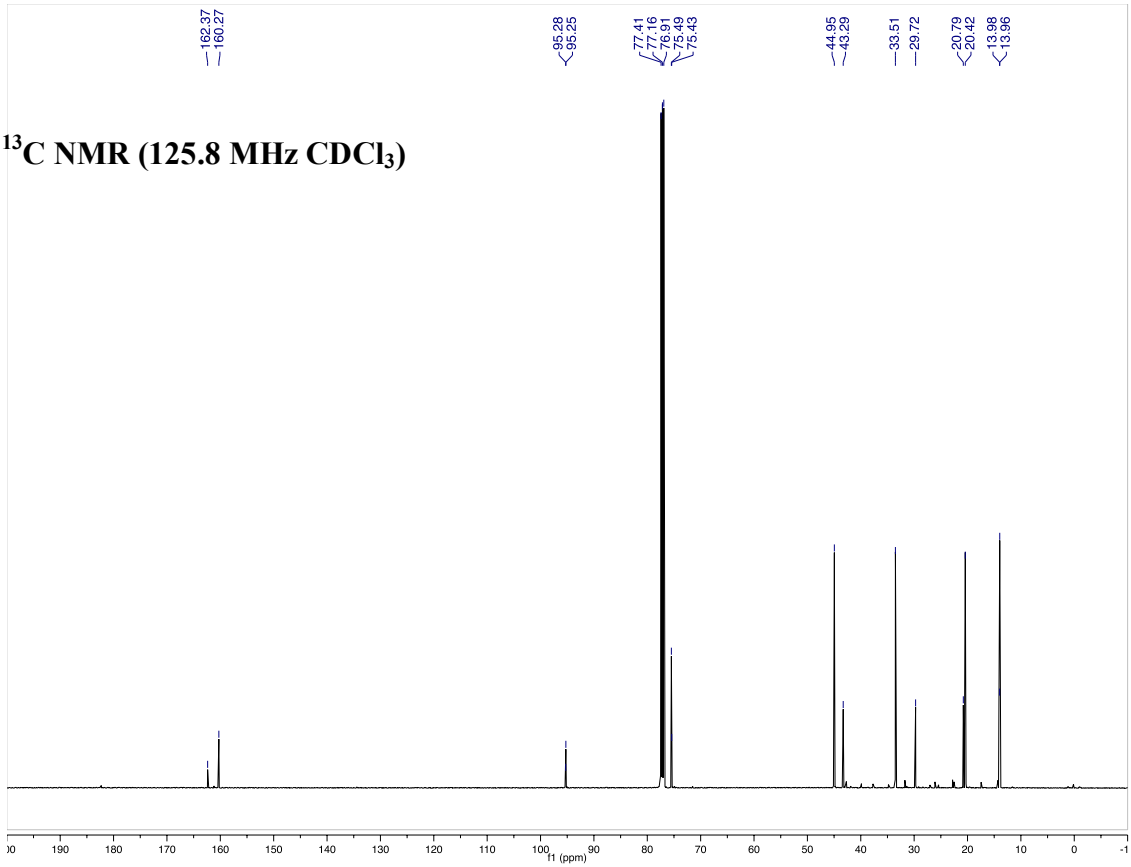


2,2,2-Trichloroethyl *trans*-2,3-dipropylaziridine-1-carboxylate (28)

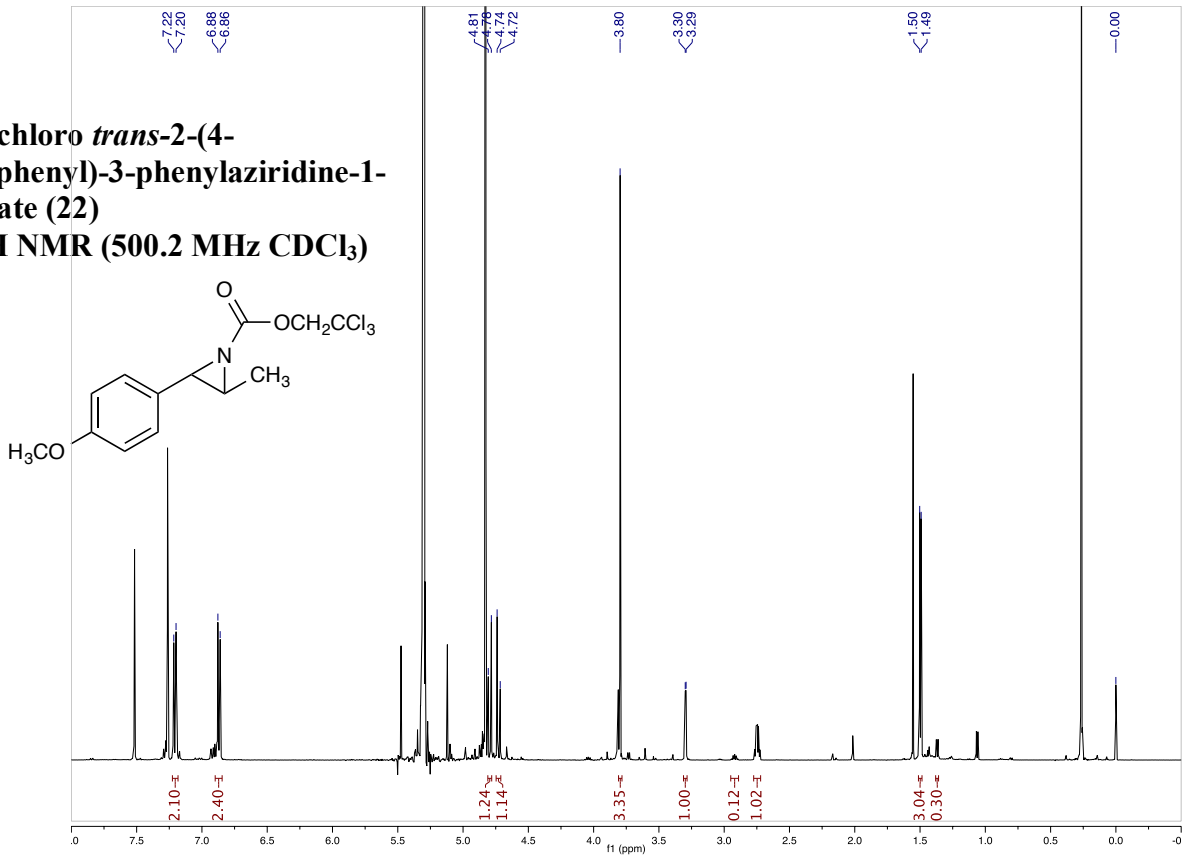
^{1}H NMR (500.2 MHz $CDCl_3$)



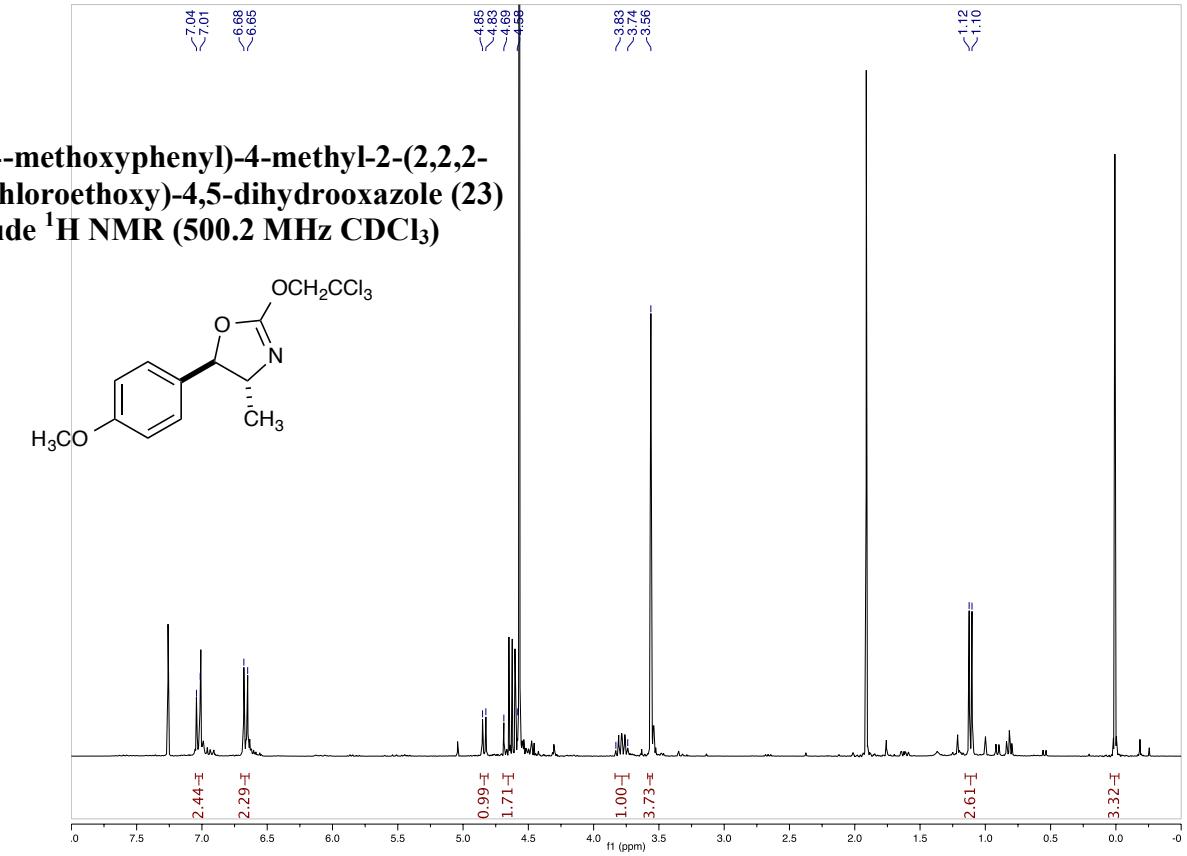
^{13}C NMR (125.8 MHz $CDCl_3$)



2,2,2-Trichloro *trans*-2-(4-methoxyphenyl)-3-phenylaziridine-1-carboxylate (22)
Crude ^{1}H NMR (500.2 MHz $CDCl_3$)

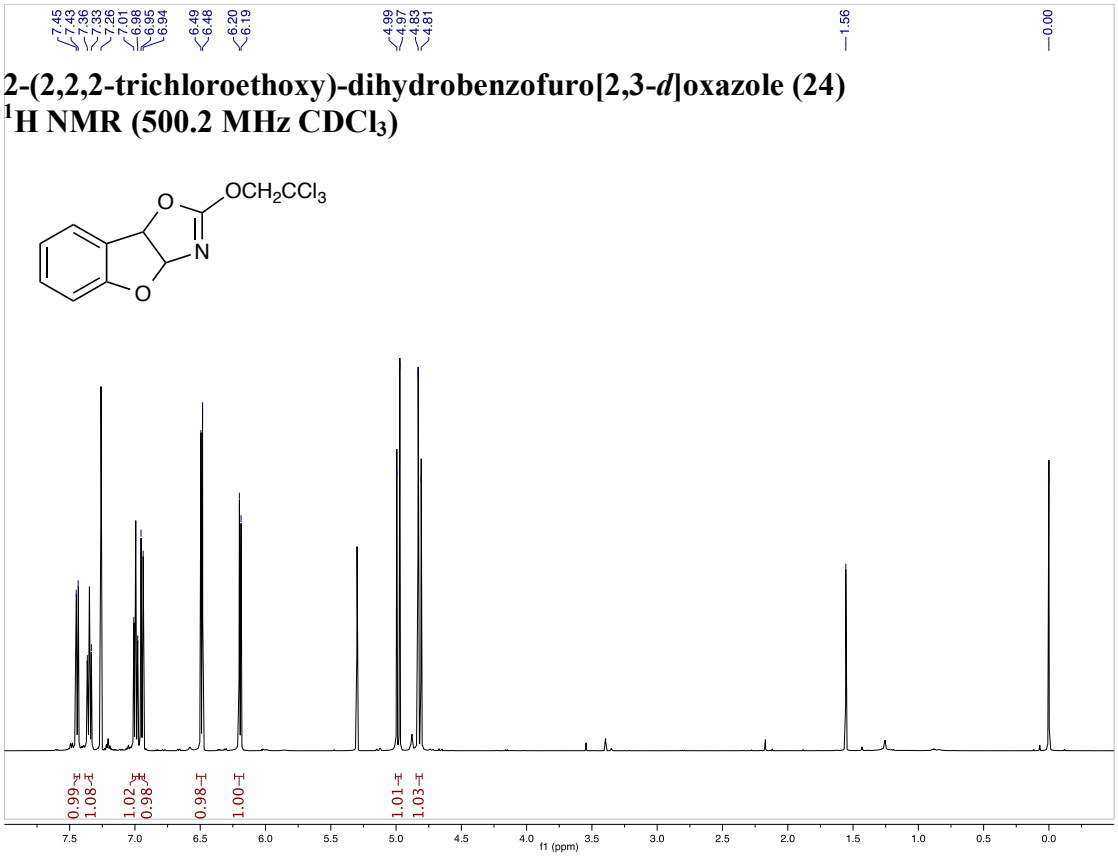


5-(4-methoxyphenyl)-4-methyl-2-(2,2,2-trichloroethoxy)-4,5-dihydrooxazole (23)
Crude ^{1}H NMR (500.2 MHz $CDCl_3$)

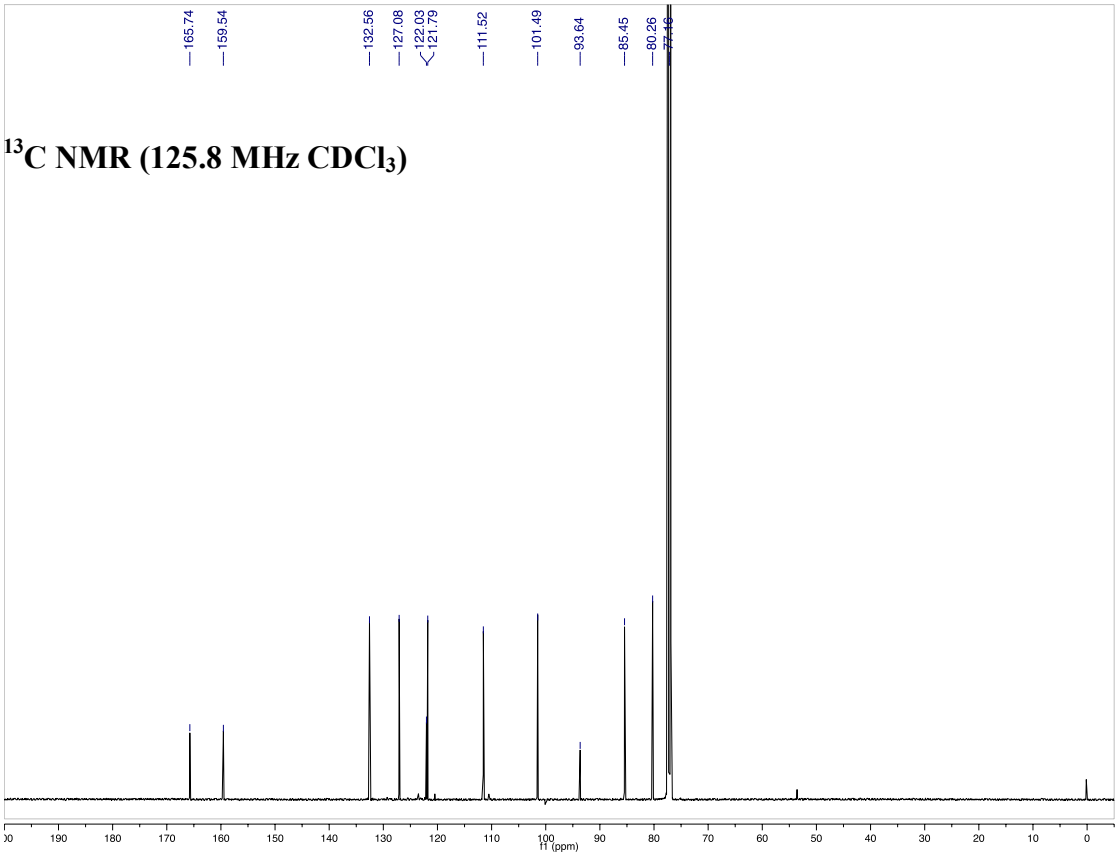


2-(2,2,2-trichloroethoxy)-dihydrobenzofuro[2,3-*d*]oxazole (24)

^{1}H NMR (500.2 MHz $CDCl_3$)

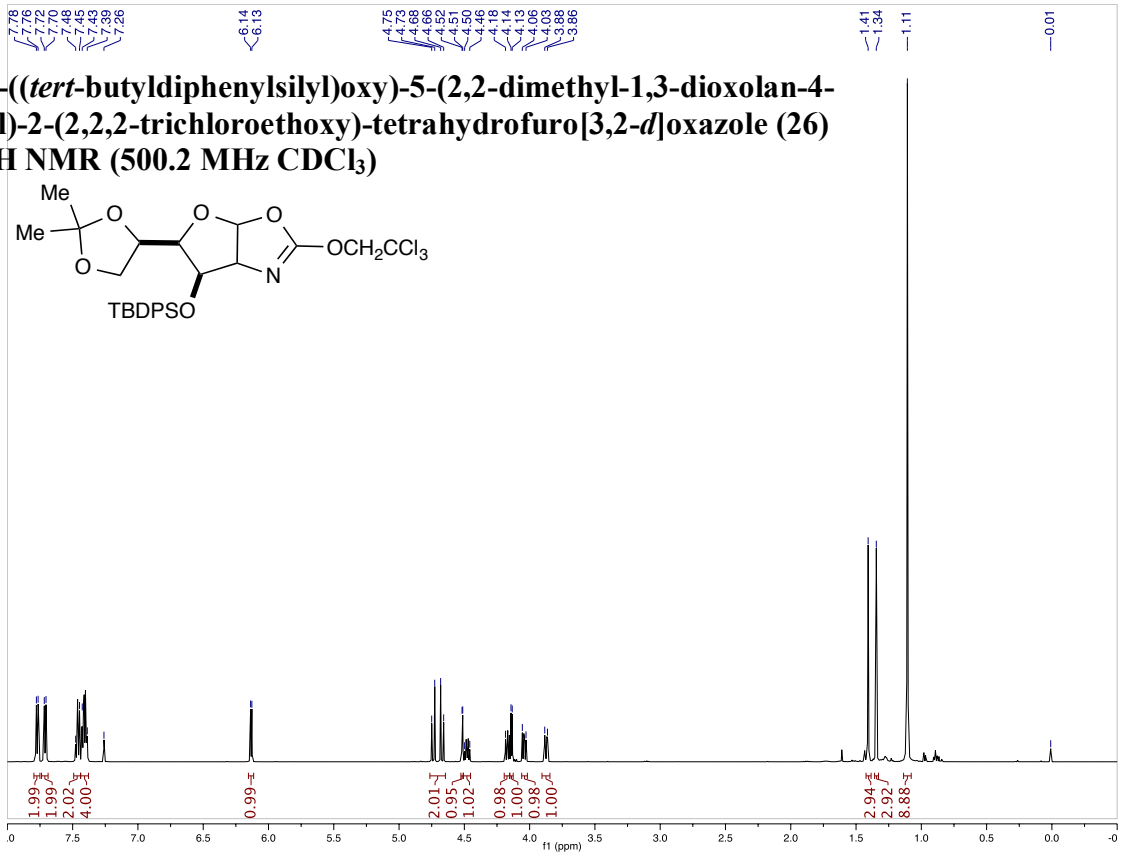


^{13}C NMR (125.8 MHz $CDCl_3$)

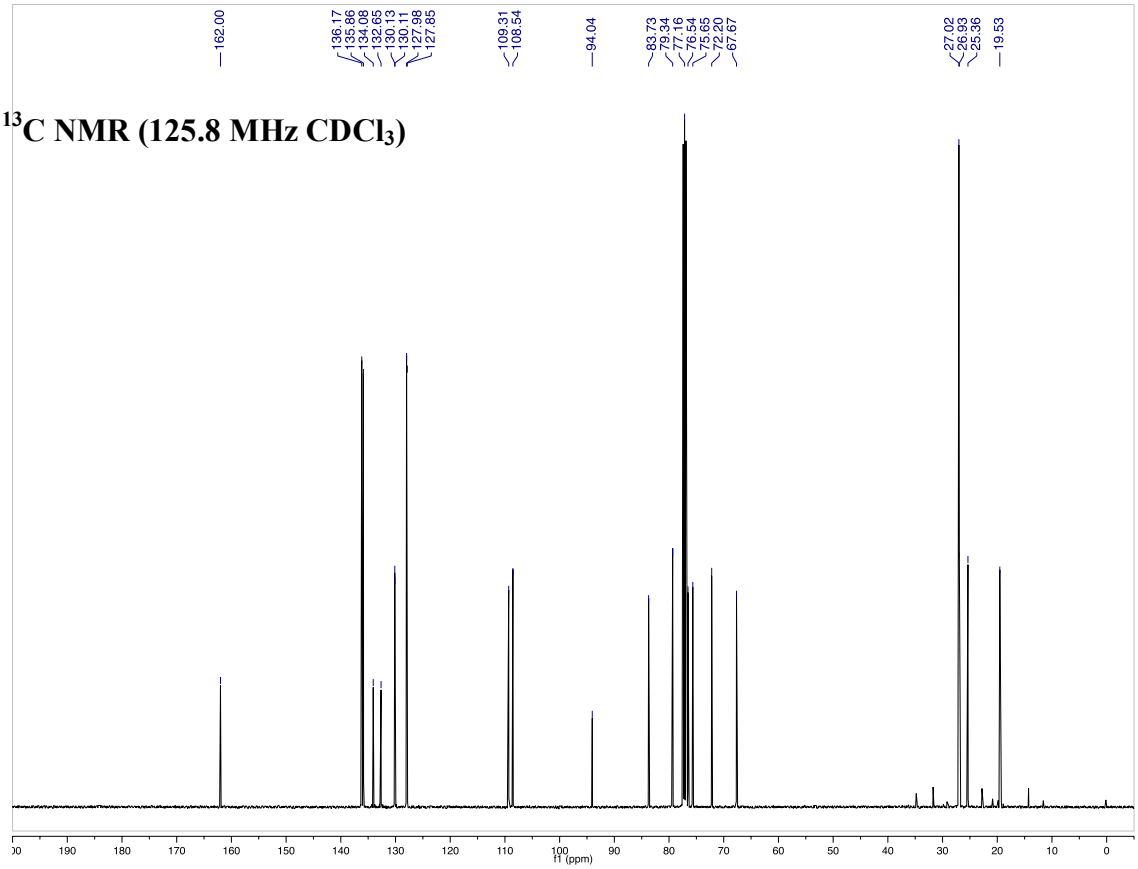


6-((*tert*-butyldiphenylsilyl)oxy)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-(2,2,2-trichloroethoxy)-tetrahydrofuro[3,2-*d*]oxazole (26)

^{1}H NMR (500.2 MHz $CDCl_3$)

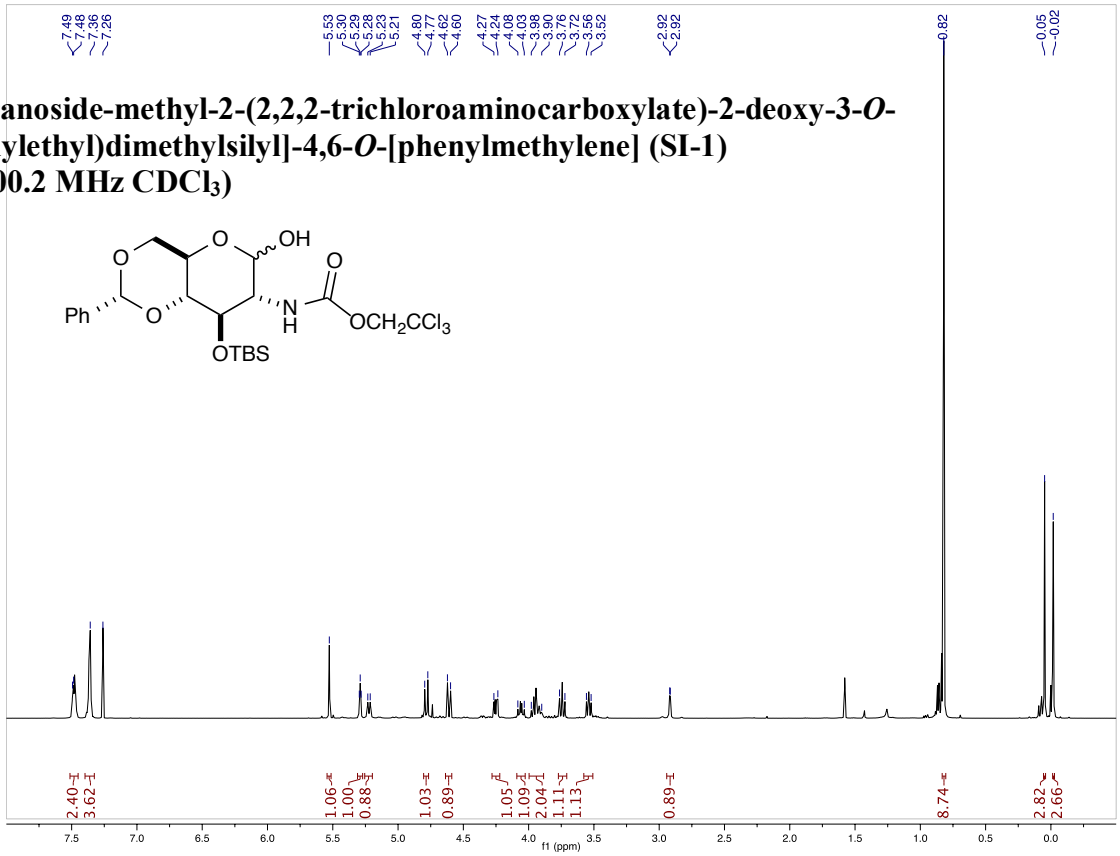


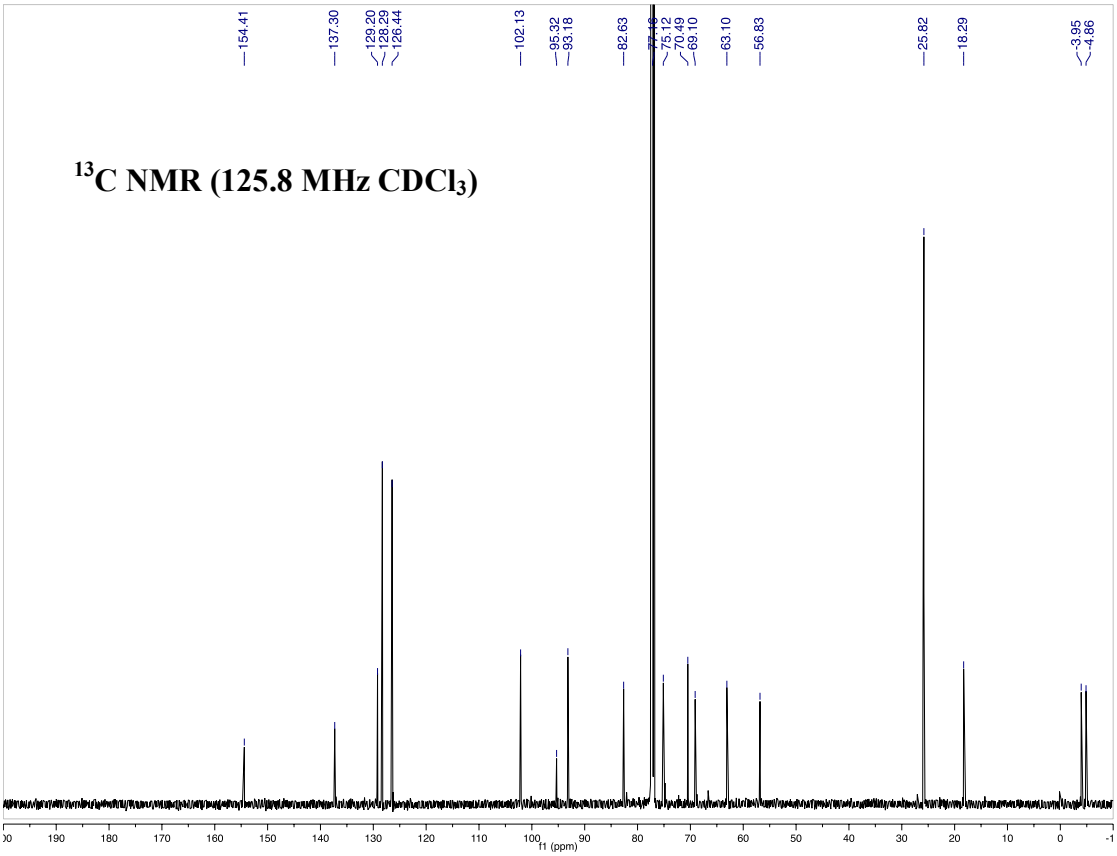
^{13}C NMR (125.8 MHz $CDCl_3$)



D-Glucopyranoside-methyl-2-(2,2,2-trichloroaminocarboxylate)-2-deoxy-3-*O*-[(1,1 dimethylethyl)dimethylsilyl]-4,6-*O*-[phenylmethylene] (SI-1)

^{1}H NMR (500.2 MHz $CDCl_3$)

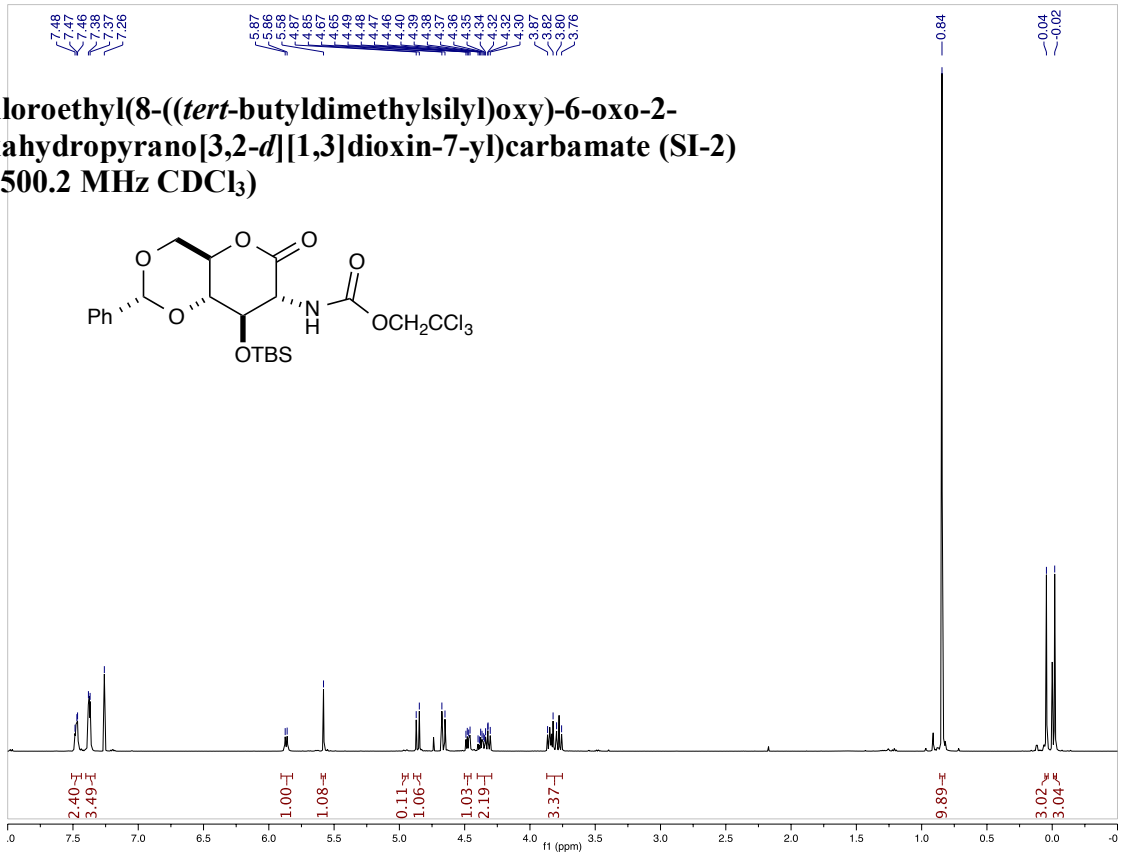


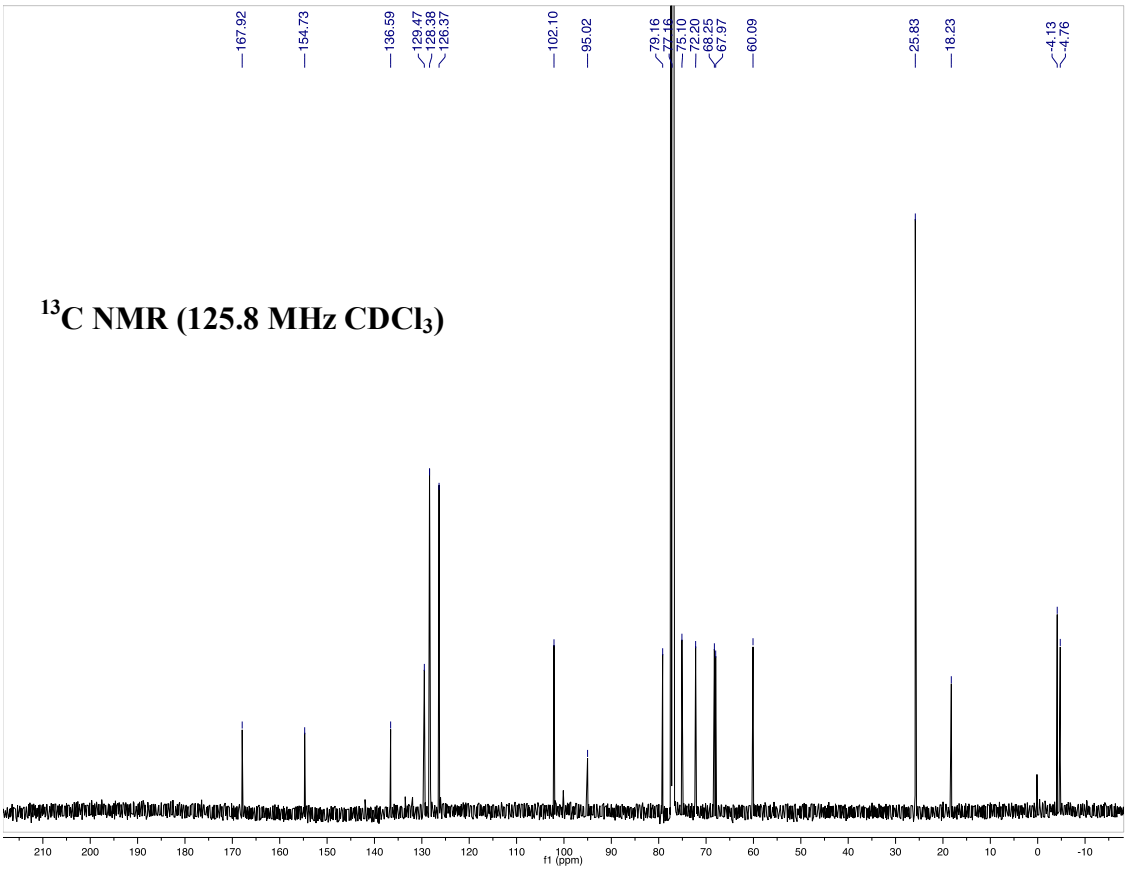


^{13}C NMR (125.8 MHz $CDCl_3$)

2,2,2-trichloroethyl(8-((*tert*-butyldimethylsilyl)oxy)-6-oxo-2-phenylhexahydropyrano[3,2-*d*][1,3]dioxin-7-yl)carbamate (SI-2)

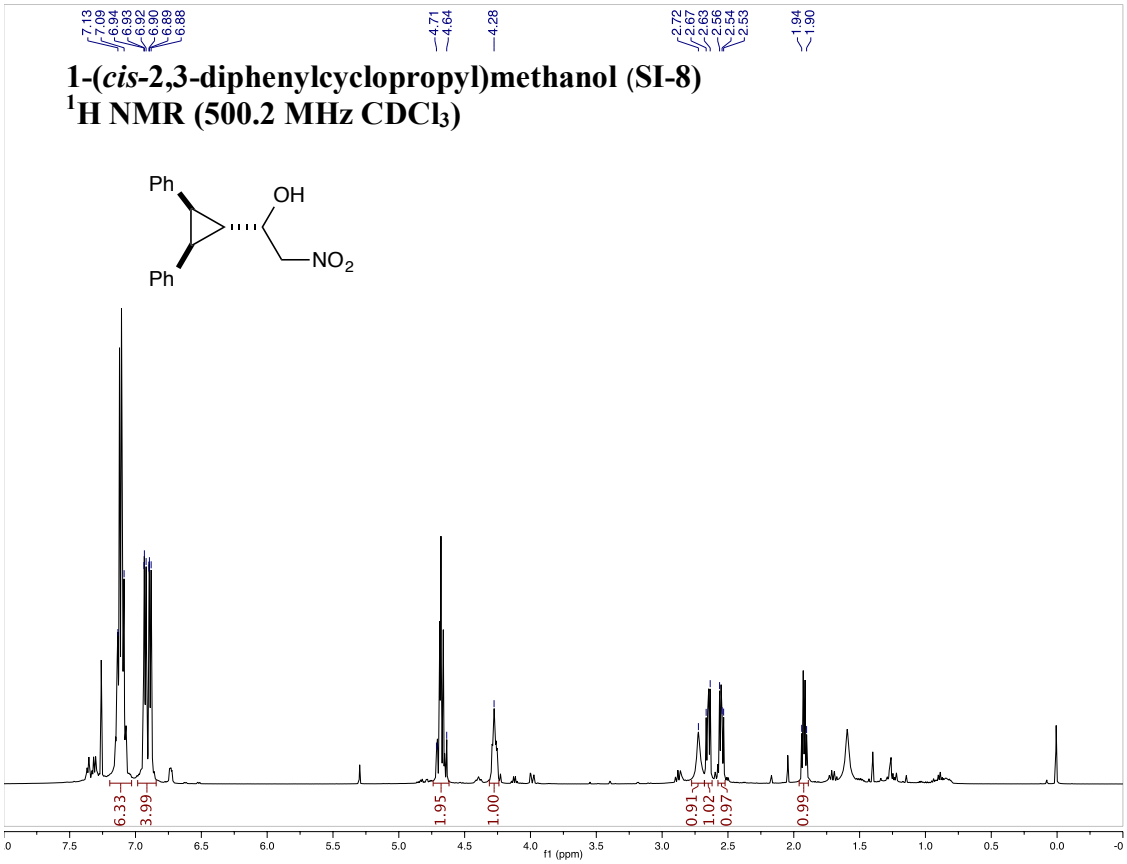
^{1}H NMR (500.2 MHz $CDCl_3$)



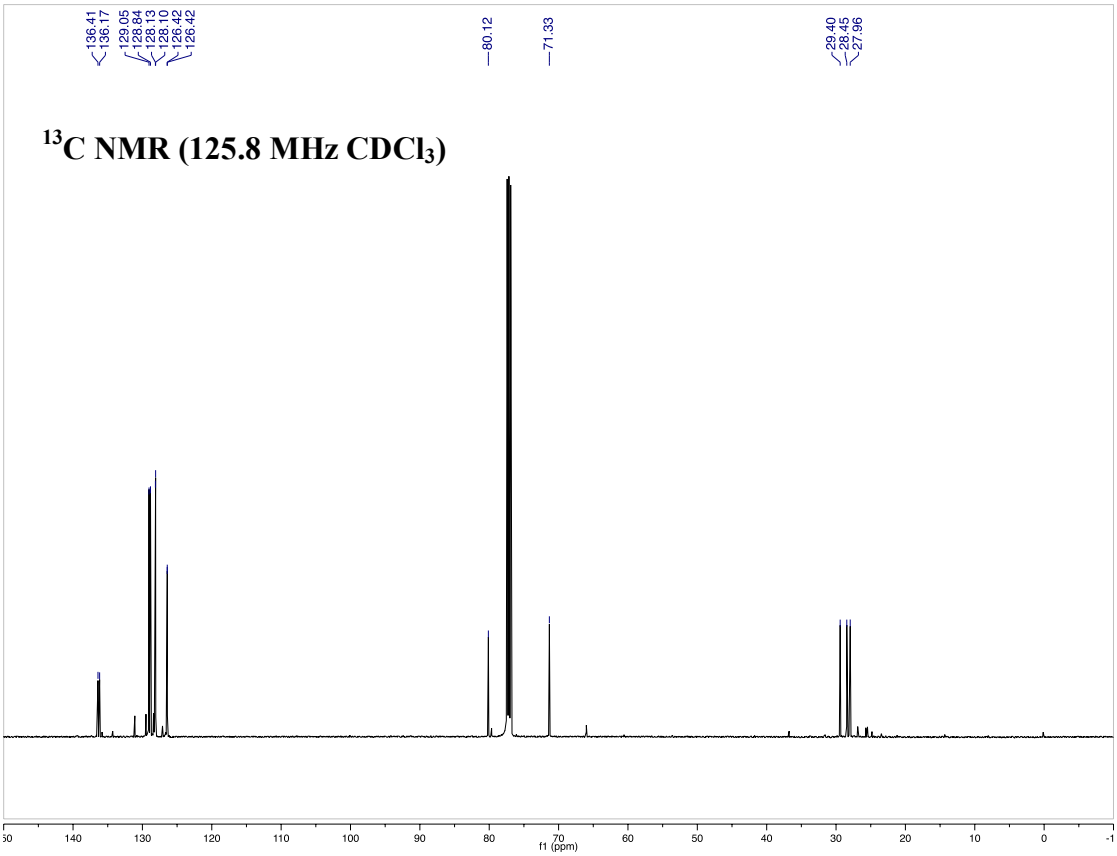


^{13}C NMR (125.8 MHz $CDCl_3$)

1-(*cis*-2,3-diphenylcyclopropyl)methanol (SI-8)
^{1}H NMR (500.2 MHz $CDCl_3$)

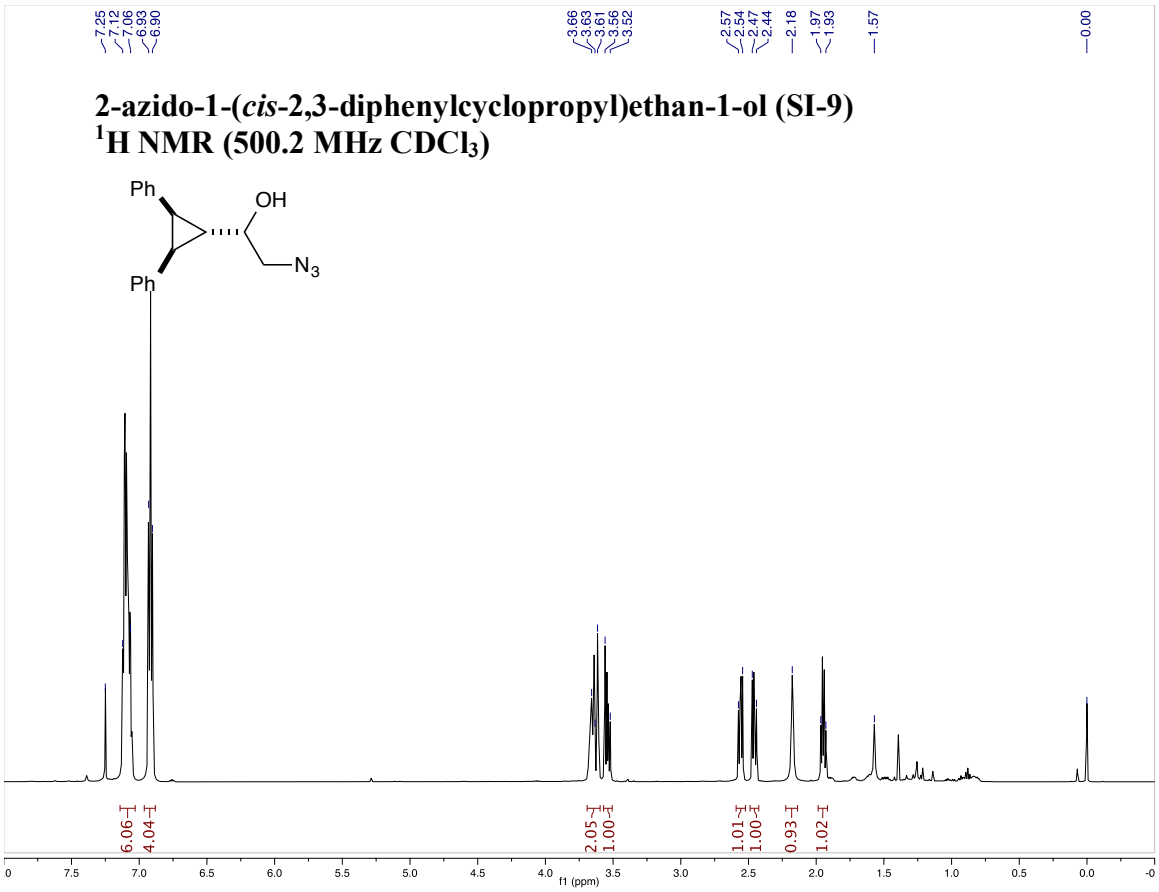


^{13}C NMR (125.8 MHz $CDCl_3$)

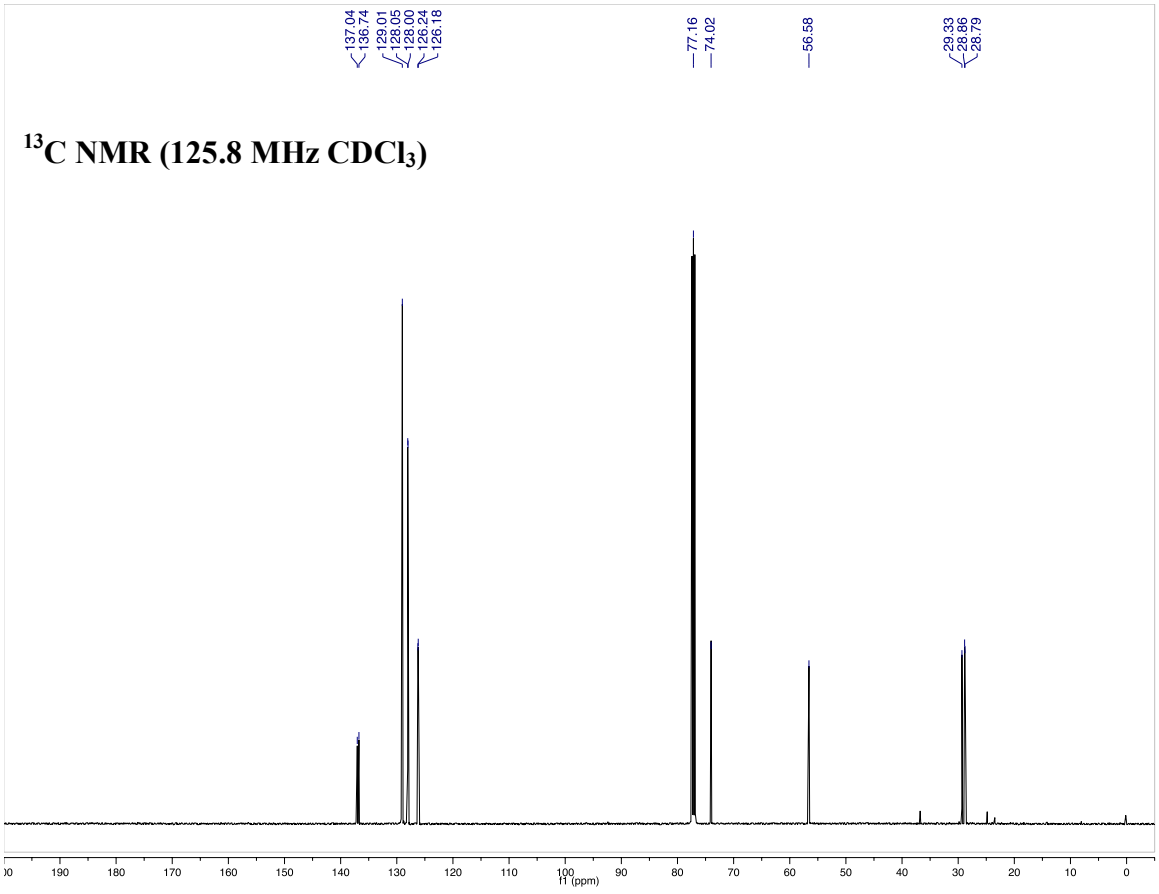


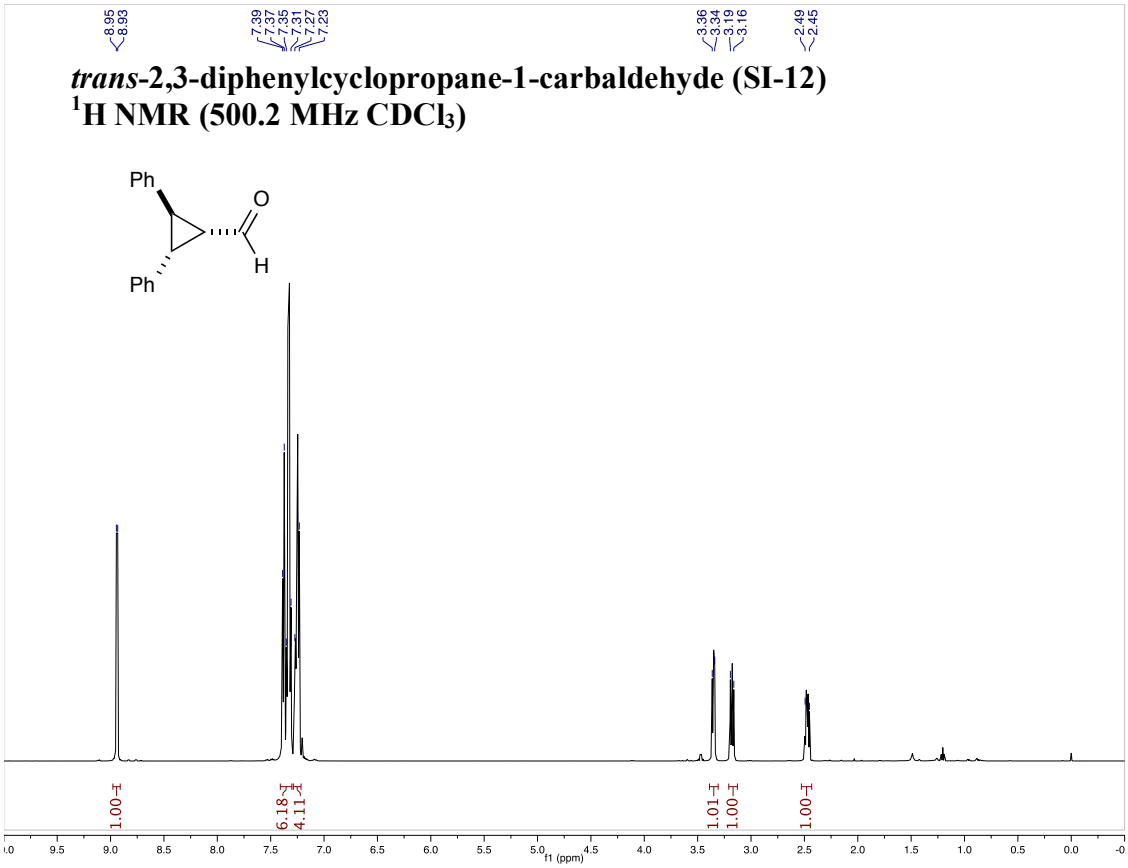
2-azido-1-(*cis*-2,3-diphenylcyclopropyl)ethan-1-ol (SI-9)

^{1}H NMR (500.2 MHz $CDCl_3$)

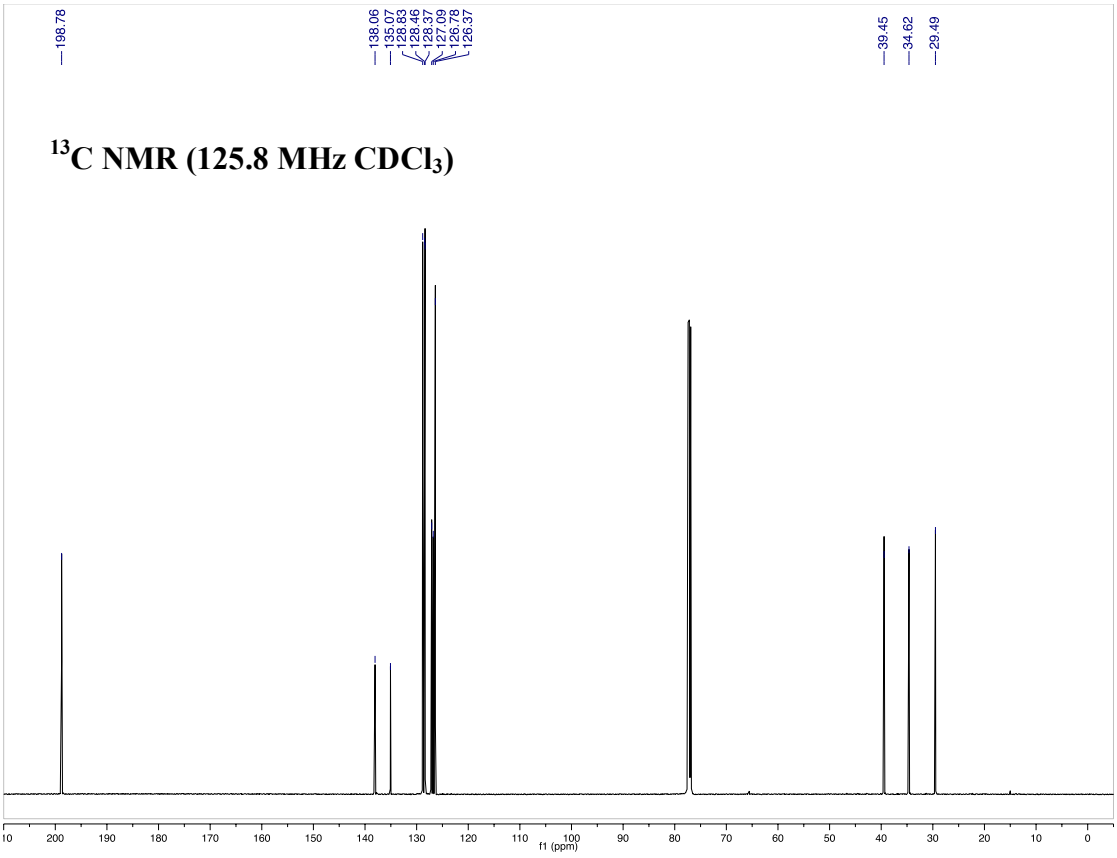


^{13}C NMR (125.8 MHz $CDCl_3$)





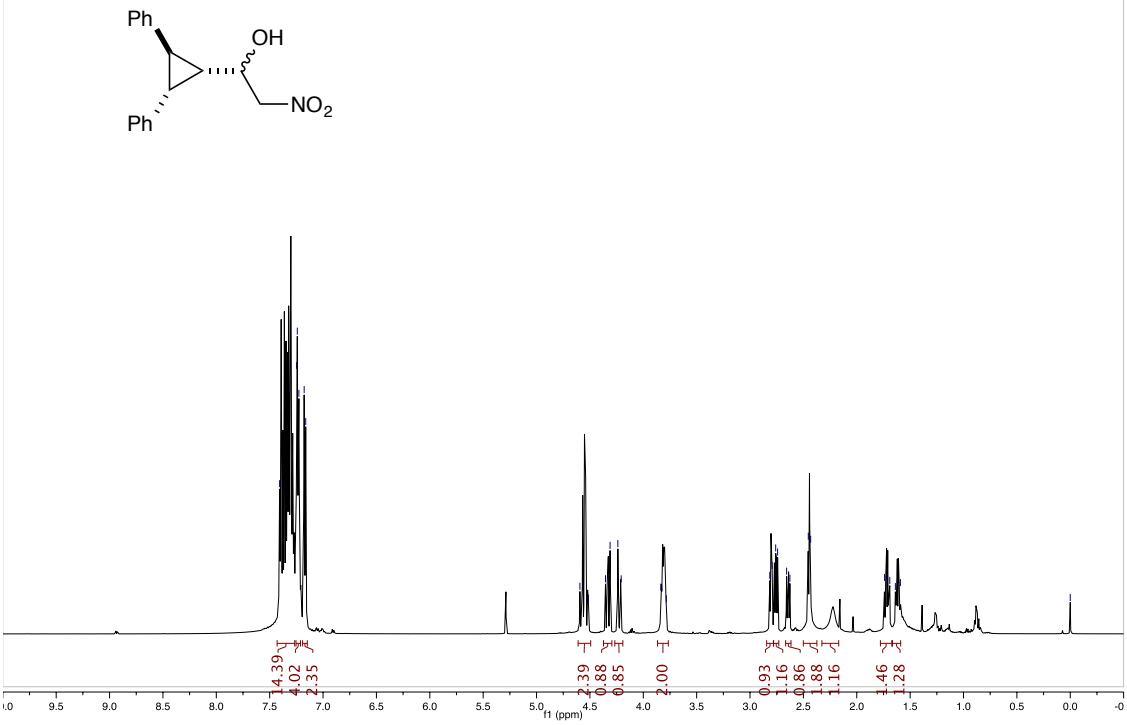
trans-2,3-diphenylcyclopropane-1-carbaldehyde (SI-12)
^{1}H NMR (500.2 MHz $CDCl_3$)



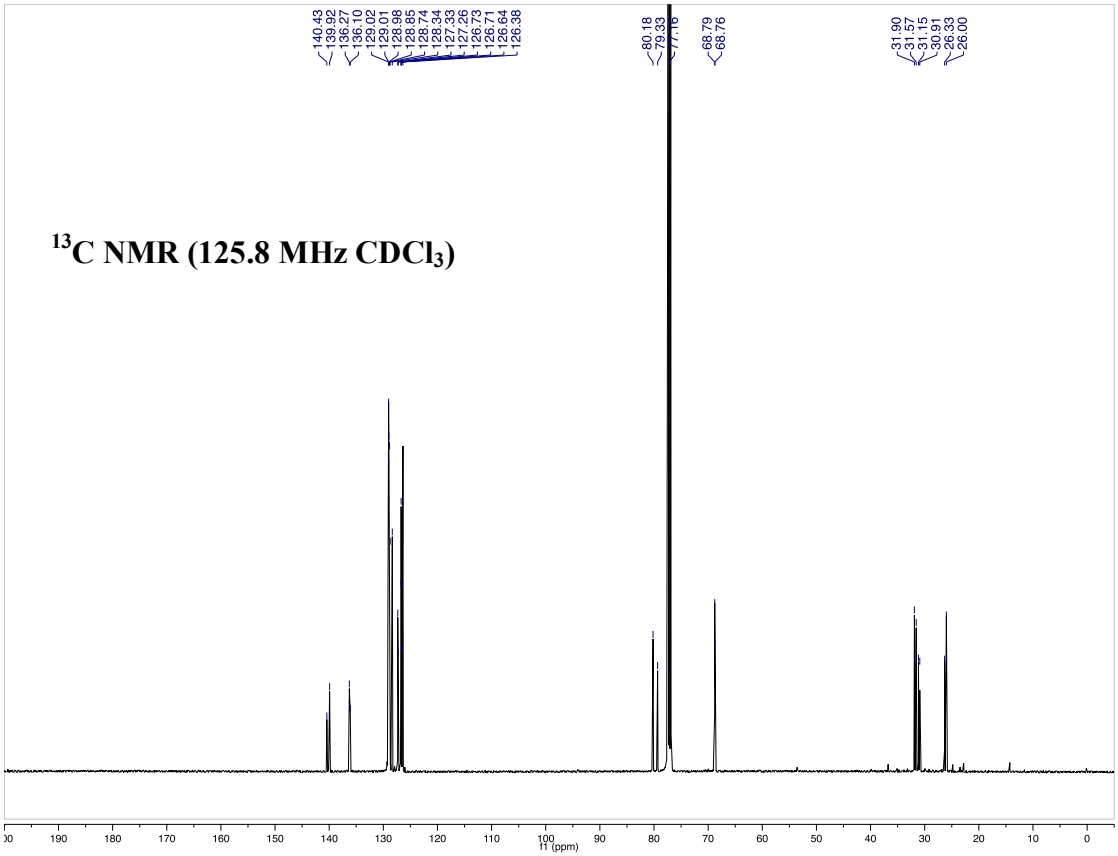
^{13}C NMR (125.8 MHz $CDCl_3$)

1-(*trans*-2,3-diphenylcyclopropyl)-2-nitroethan-1-ol (SI-13)

^{1}H NMR (500.2 MHz $CDCl_3$)

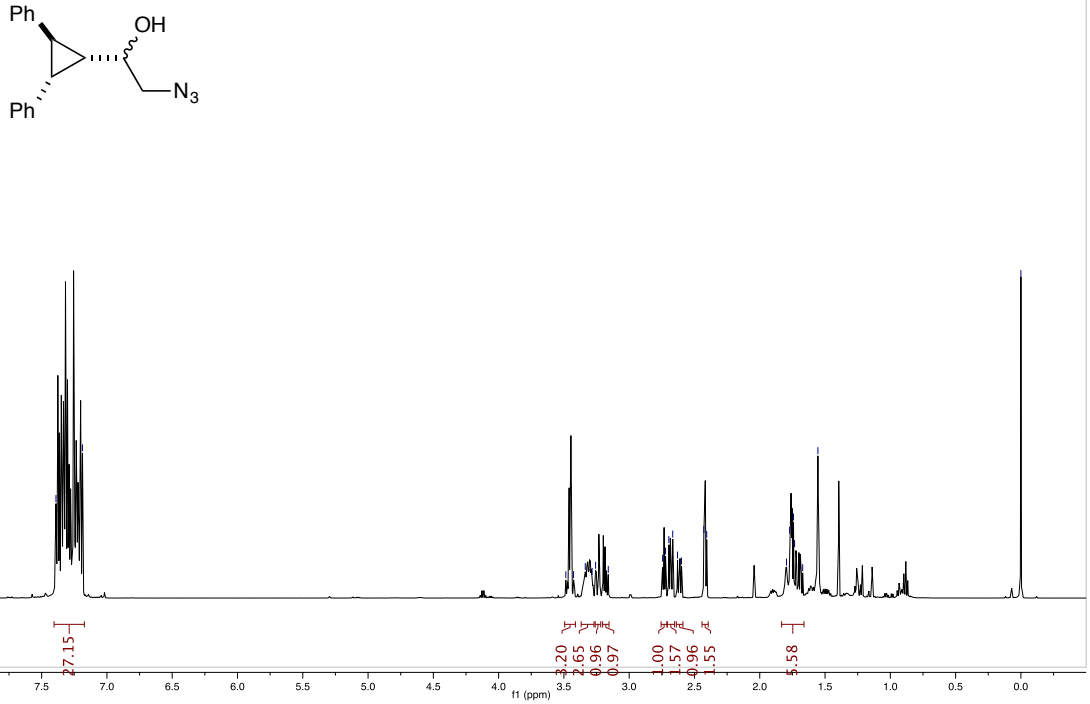


^{13}C NMR (125.8 MHz $CDCl_3$)

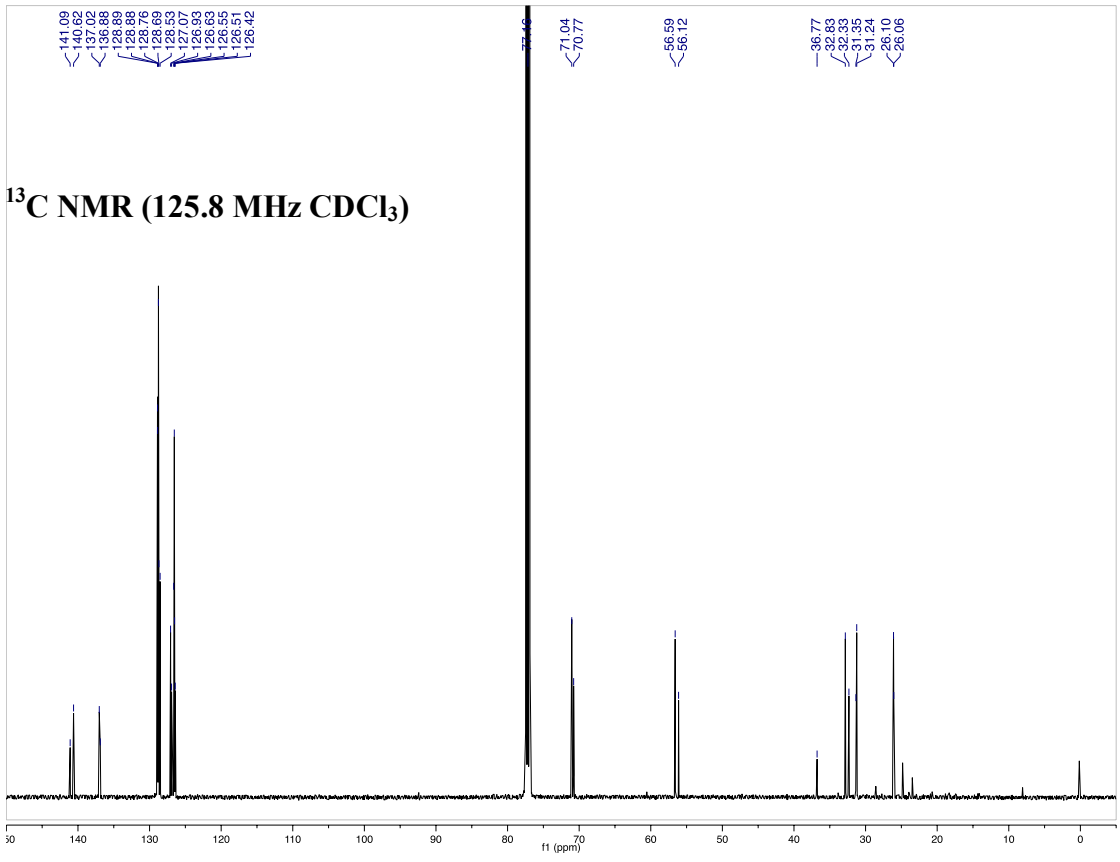


2-azido-1-(*trans*-2,3-diphenylcyclopropyl)ethan-1-ol (SI-14)

^{1}H NMR (500.2 MHz $CDCl_3$)

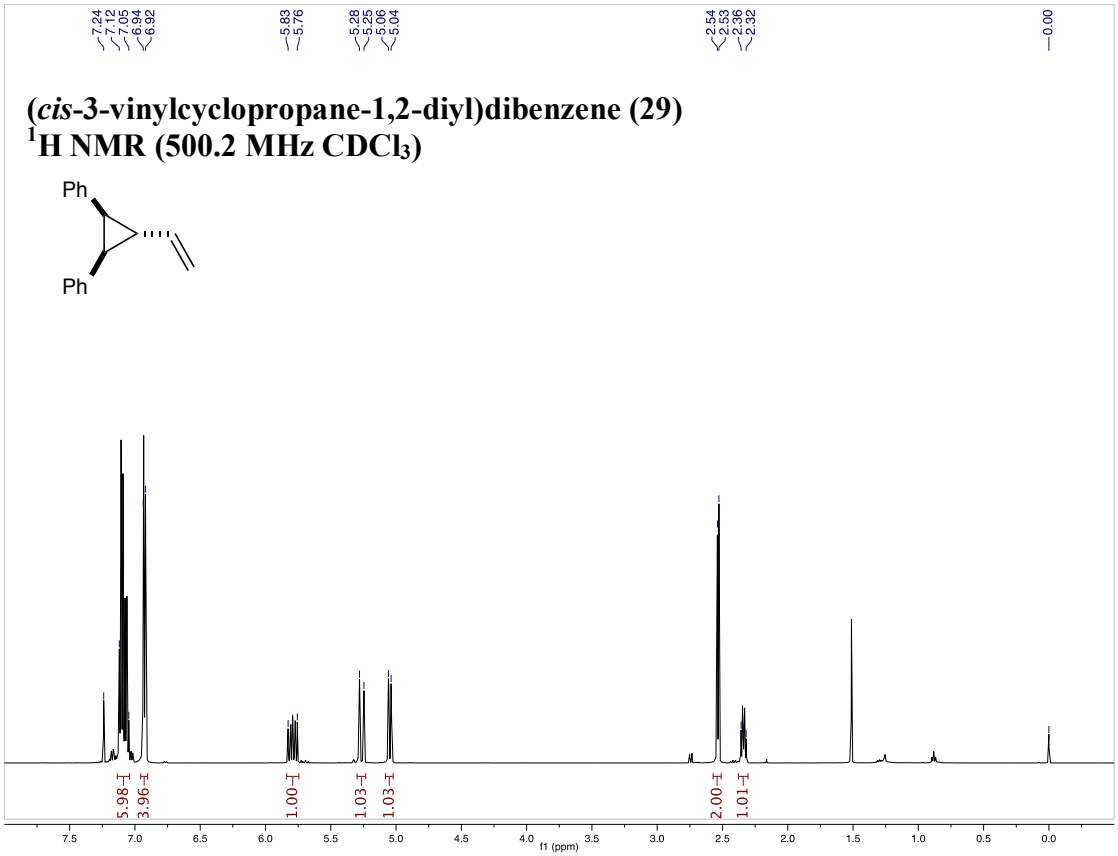


^{13}C NMR (125.8 MHz $CDCl_3$)



(*cis*-3-vinylcyclopropane-1,2-diyl)dibenzene (29)

^{1}H NMR (500.2 MHz $CDCl_3$)



^{13}C NMR (125.8 MHz $CDCl_3$)