**Supporting Information**

# Adapting Bower's Intramolecular Aziridination Reaction Allows for a Metal-Free Synthesis of N–H Aziridines

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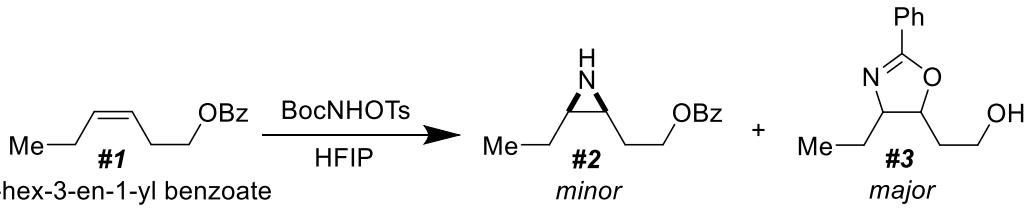
## I. General Considerations

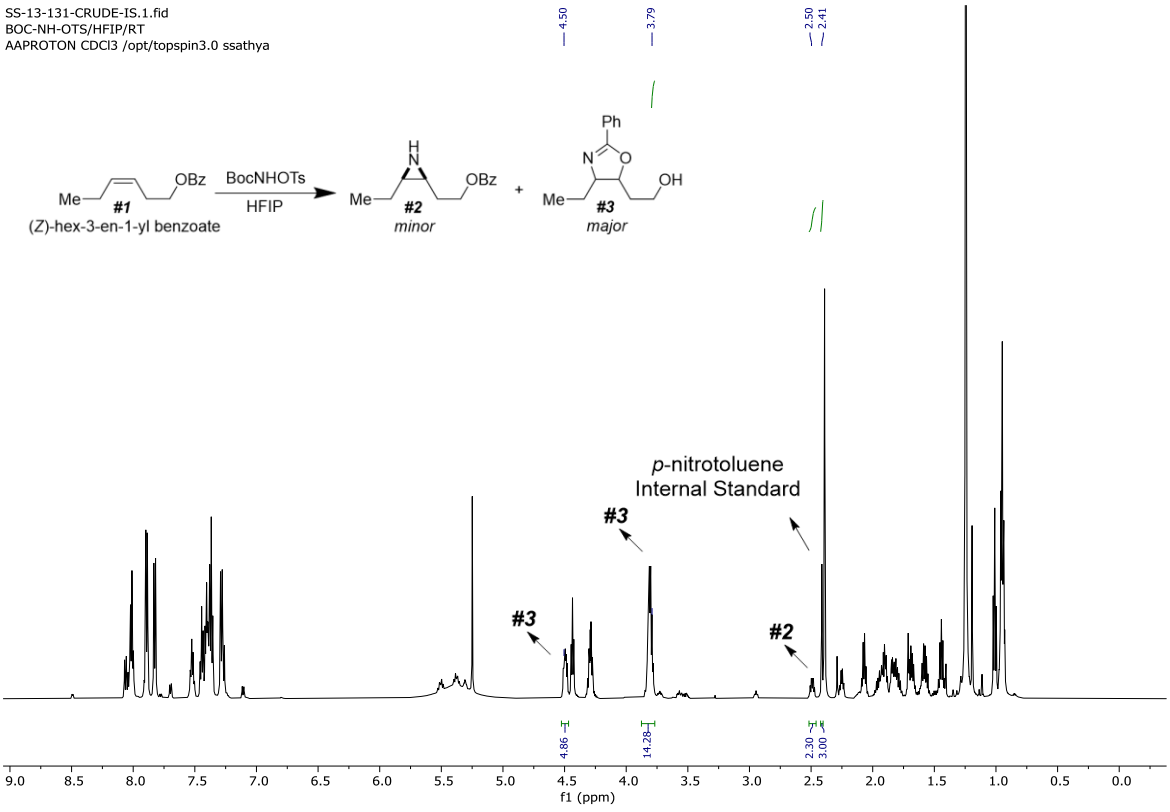
All reagents were obtained commercially unless otherwise noted. Solvents were purified by passage under 10 psi $N_2$ through activated alumina columns. Infrared (IR) spectra were recorded on a Thermo Scientific™ Nicolet™ iS™5 FT-IR Spectrometer; data are reported in frequency of absorption ($cm^{-1}$). $^1H$ NMR spectra were recorded at 400, 500, or 600 MHz. Data are recorded as: chemical shift in ppm referenced internally using residual solvent peaks, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances, qdd = quartet of doublet of doublets, tdt = triplet of doublet of triplets, dtq = doublet of triplet of quartets, qd = quartet of doublets, tdq = triplet of doublet of quartets), coupling constant (Hz), integration. $^{13}C$ NMR spectra were recorded at 101 or 126 MHz. Exact mass spectra were recorded using an electrospray ion source (ESI) either in positive mode or negative mode and with a time-of-flight (TOF) analyzer on a Waters LCT PremierTM mass spectrometer and are given in m/z. Thin Layer Chromatography (TLC) was performed on pre-coated glass plates (Merck) and visualized either with a UV lamp (254 nm) or by dipping into a solution of $KMnO_4$–$K_2CO_3$ in water followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) or Florisil (60-100 mesh). “Room temperature” refers to an ambient temperature of 23 – 25 °C.

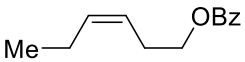
## II. Associated data for Manuscript Figure 1

The procedure used for the following reaction was disclosed by Jat and co-workers: Jat, J. L.; Chandra, D.; Kumar, P.; Singh, V.; Tiwari, B., Metal- and Additive-Free Intermolecular Aziridination of Olefins Using *N*-Boc-*O*-tosylhydroxylamine. *Synthesis* **2022**, *54*, 4513-4520.



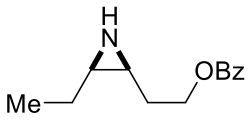

### Crude $^1$H NMR (600 MHz, $CDCl_3$) of the reaction with an internal standard



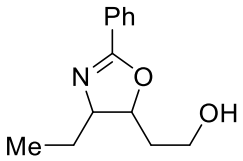

(*Z*)-hex-3-en-1-yl benzoate

**Compound 1**: commercially available




2-((2*S**,3*R**)-3-ethylaziridin-2-yl)ethyl benzoate

**Compound 2**: Previously characterized in *Science,* **2014***, 343*, 61 – 65.




2-(4-ethyl-2-phenyl-4,5-dihydrooxazol-5-yl)ethan-1-ol

**Compound 3**:

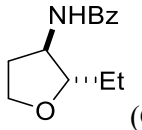
$^{1}$H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.49 – 7.44 (m, 1H), 7.40 (dd, *J* = 8.5, 7.0 Hz, 2H), 4.49 (ddd, *J* = 8.9, 6.4, 4.0 Hz, 1H), 3.90 – 3.87 (m, 2H), 3.85 (q, *J* = 6.4 Hz, 1H), 2.00 – 1.92 (m, 2H), 1.88 (dtd, *J* = 14.3, 6.5, 4.1 Hz, 1H), 1.78 – 1.70 (m, 1H), 1.63 (dp, *J* = 14.3, 7.3 Hz, 1H), 1.01 (t, *J* = 7.4 Hz, 3H).

$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 162.9, 131.3, 128.3, 128.2, 127.8, 81.7, 73.1, 58.7, 38.4, 28.3, 9.7.

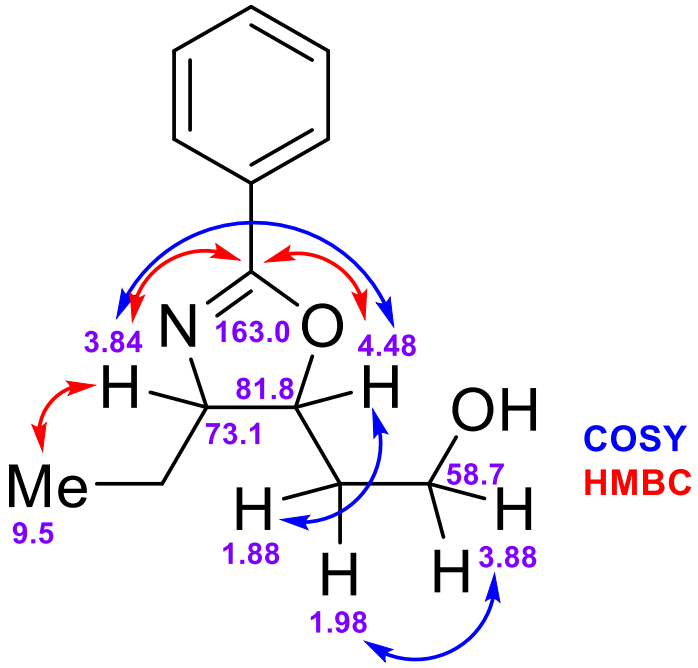
IR ν 3313, 2962, 1644, 1451, 1352, 1055 $cm^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{13}H_{18}NO_2^+$ 220.1332. Found 220.1323 (4.1 ppm error).

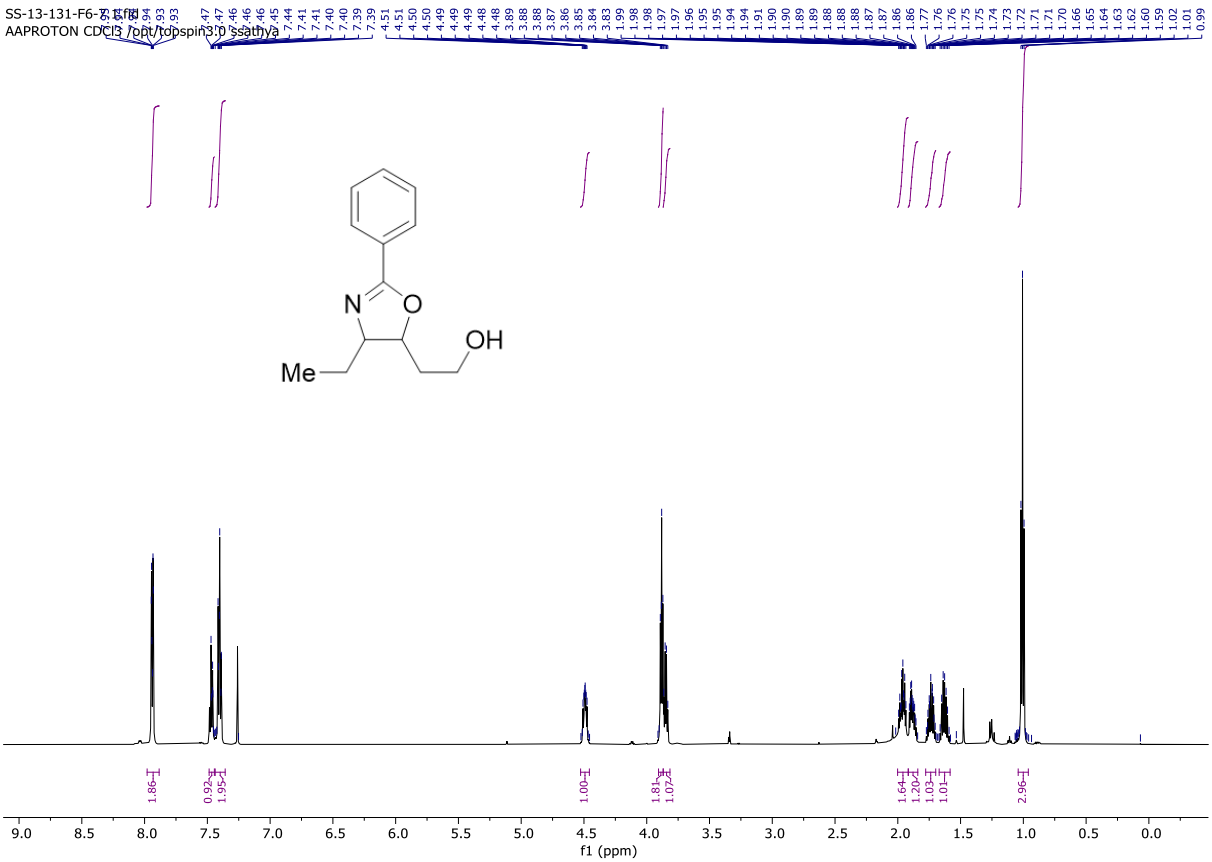
This compound was reported in *Science*, **2014**, *343*, 61 – 65, but the structure was misassigned as



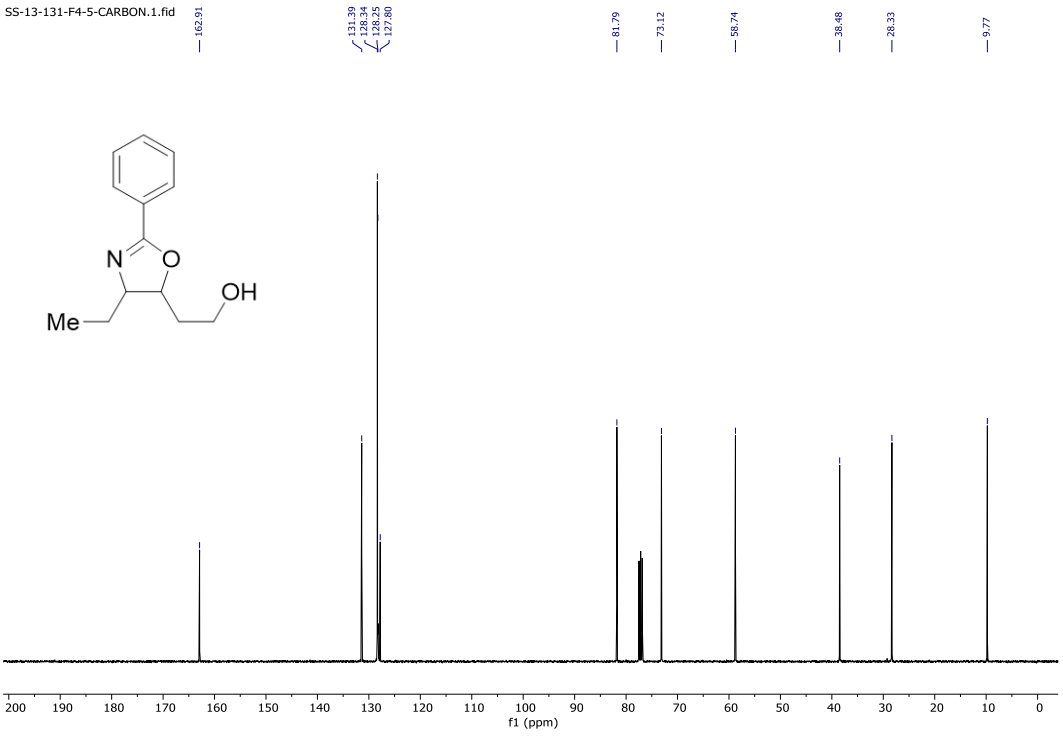

(Compound 10kk in the published manuscript). Our data matches what was tabulated.



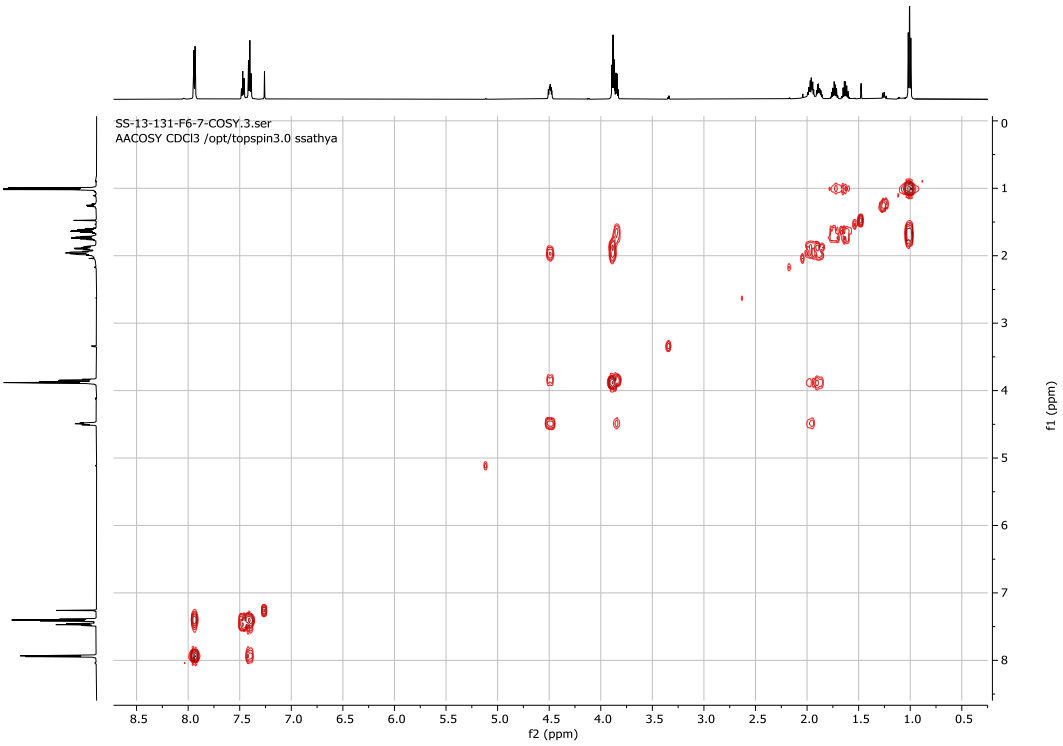

**$CDCl_3$, $^1H$ NMR: 600 MHz**



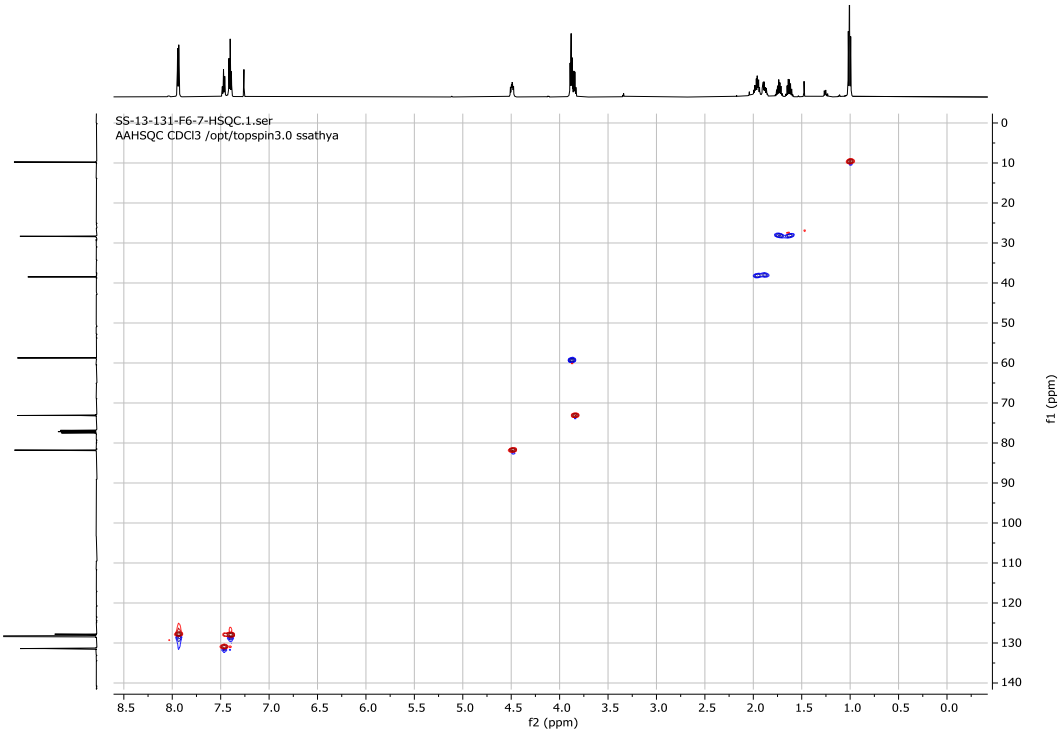
## $CDCl_3$, $^{13}C\{^1H\}$ NMR: 101 MHz



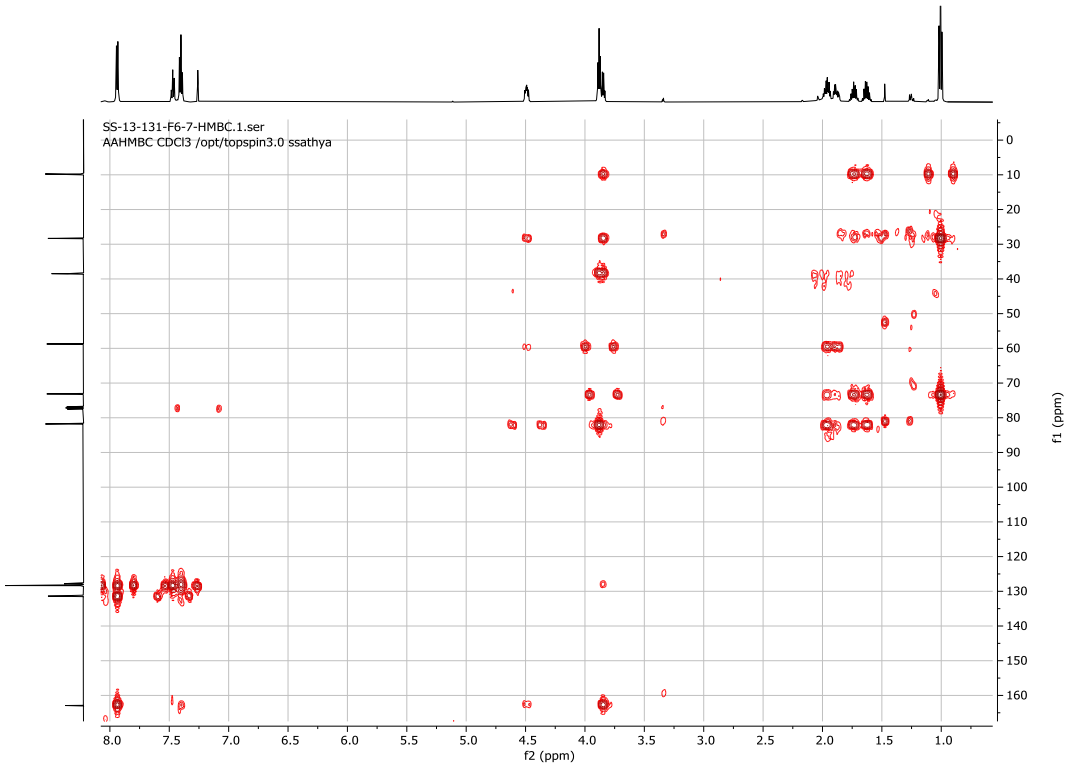

## $CDCl_3$, COSY



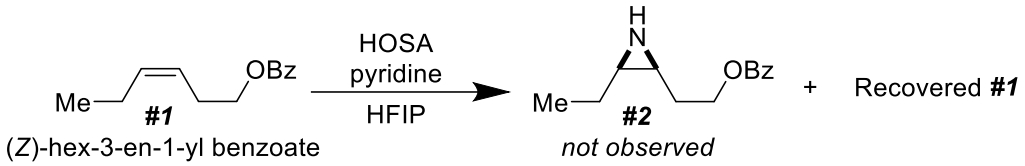
## $CDCl_3$, HSQC



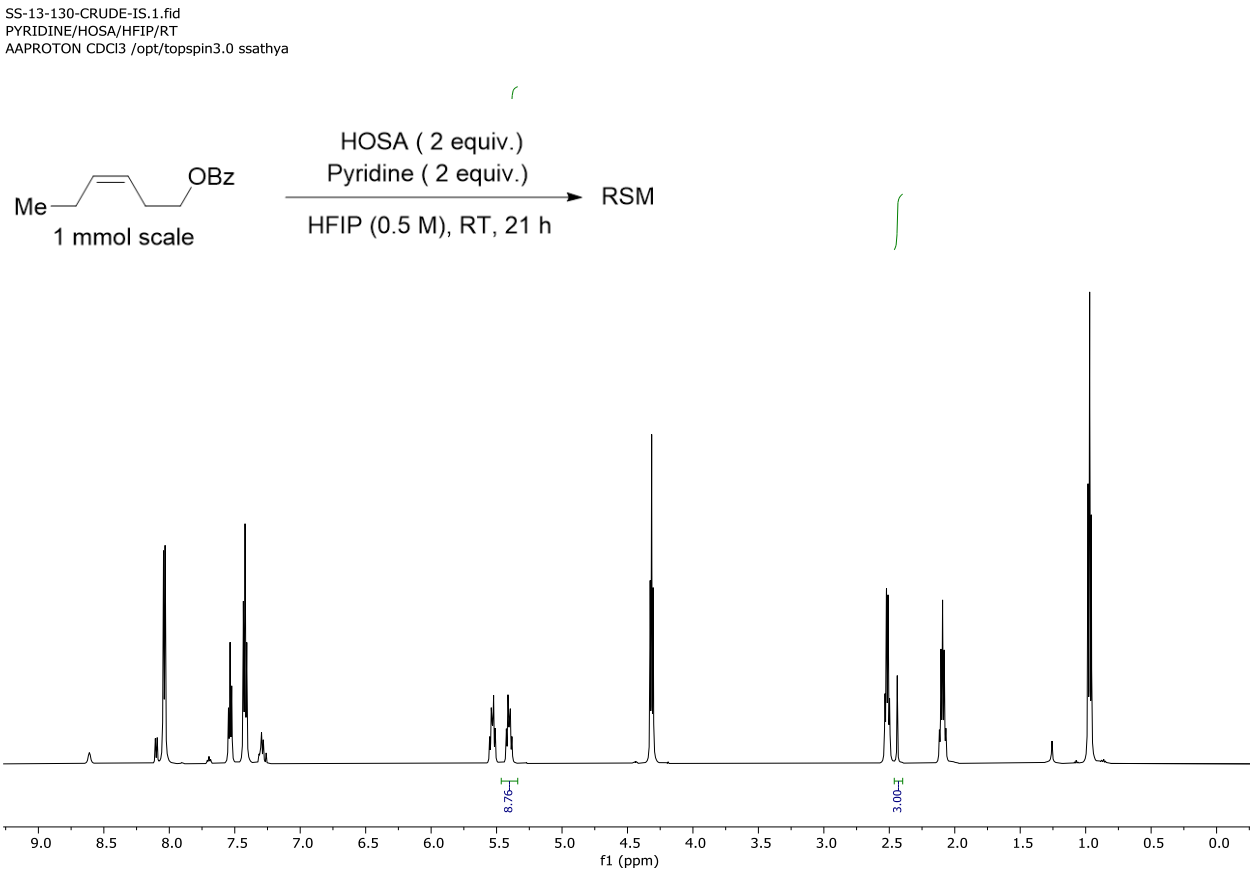

## $CDCl_3$, HMBC



The procedure used for the following reaction was disclosed by Wang and co-workers: Huang, Y.; Zhu, S.-Y.; He, G.; Chen, G.; Wang, H., Synthesis of N–H Aziridines from Unactivated Olefins Using Hydroxylamine-O-Sulfonic Acids as Aminating Agent. *J. Org. Chem.* **2024**, *89*, 6263-6273.

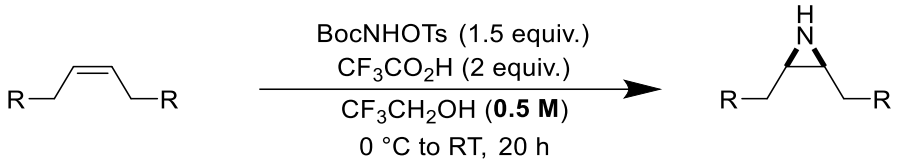



**Crude $^{1}$H NMR (600 MHz, $CDCl_3$) of the reaction with an internal standard (*p*-nitrotoluene)**



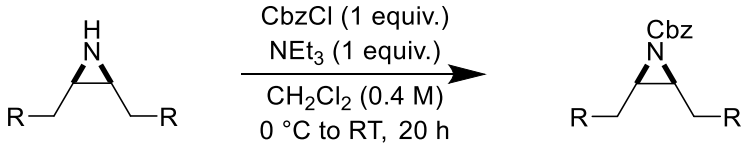
## III. General Procedures for N – H aziridination and Cbz protection

### General Procedure A, Part I



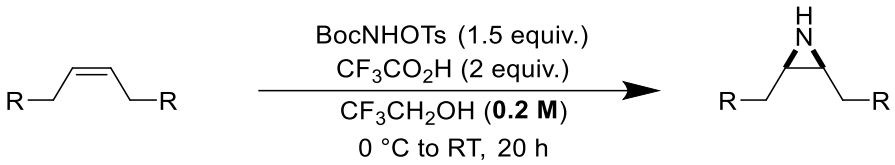

A 10 mL microwave vial equipped with a magnetic stir bar was charged with an alkene substrate (2.0 mmol), *N*-Boc-*O*-tosyl hydroxylamine (0.862 g, 3.0 mmol, 1.5 equiv.), and trifluoroethanol (2 mL). The stirring mixture was cooled to 0 °C using an ice-water bath. Trifluoroacetic acid (0.456 g, 4.0 mmol, 2 equiv.) in trifluoroethanol (2 mL) was slowly added to the reaction mixture (final reaction concentration = 0.5 M). The vial was sealed and removed from the ice-water bath. The stirring reaction mixture was warmed to room temperature over a period of 20 hours. Following this time, the seal was broken, and the contents of the flask were transferred to a separatory funnel with EtOAc (40 mL). The organic layer was washed with one portion of 1 M aqueous NaOH solution (30 mL), collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Prior to the next step, the residue was dissolved in $CH_2Cl_2$ (20 mL), filtered to remove unknown solid particles, and concentrated under reduced pressure.

### General Procedure A, Part II



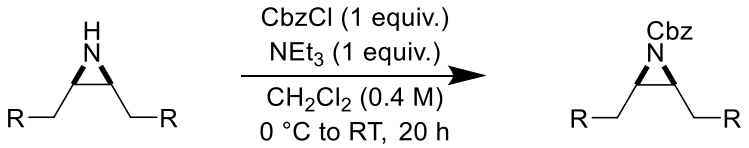

A 10 mL microwave vial equipped with a magnetic stir bar was charged with N-H aziridine substrate (crude from the previous step) and anhydrous $CH_2Cl_2$ (5 mL, reaction concentration = 0.4 M, based on the mmol of the alkene substrate from the previous step). The stirring reaction mixture was cooled to 0 °C using an ice-water bath. Benzyl chloroformate (0.290 mL, 0.35 g, 2.0 mmol, 1 equiv. based on the mmol of the alkene substrate from the previous step) and triethylamine (0.280 mL, 0.203 g, 2.0 mmol, 1 equiv. based on the mmol of the alkene substrate from the previous step) were added, and the vial was sealed. After five minutes, the stirring reaction mixture was removed from the ice-water bath and warmed to room temperature over a period of 20 hours. Following this time, the seal was broken, and the contents of the vial were transferred to a separatory funnel with $CH_2Cl_2$ (40 mL). The organic layer was washed once with 1 M aqueous HCl solution (20 mL), collected, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel (specific conditions are given with each product's characterization data).

**General Procedure B, Part I**



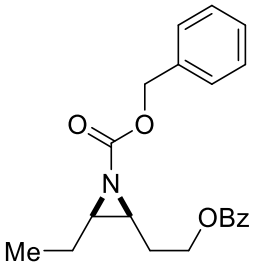

A 20 mL microwave vial equipped with a magnetic stir bar was charged with an alkene substrate (2.0 mmol), *N*-Boc-*O*-tosyl hydroxylamine (0.862 g, 3.0 mmol, 1.5 equiv.), and trifluoroethanol (5 mL). The stirring mixture was cooled to 0 °C using an ice-water bath. Trifluoroacetic acid (0.456 g, 4.0 mmol, 2 equiv.) in trifluoroethanol (5 mL) was slowly added to the reaction mixture (final reaction concentration = 0.2 M). The vial was sealed and removed from the ice-water bath. The stirring reaction mixture was warmed to room temperature over a period of 20 hours. Following this time, the seal was broken, and the contents of the flask were transferred to a separatory funnel with EtOAc (40 mL). The organic layer was washed with 1 M aqueous NaOH solution (30 mL) and brine (30 mL), collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Prior to the next step, the residue was dissolved in $CH_2Cl_2$ (20 mL), filtered to remove unknown solid particles, and concentrated under reduced pressure.

**General Procedure B, Part II**




A 10 mL microwave vial equipped with a magnetic stir bar was charged with N-H aziridine substrate (crude from the previous step) and anhydrous $CH_2Cl_2$ (5 mL, reaction concentration = 0.4 M, based on the mmol of the alkene substrate from the previous step). The stirring reaction mixture was cooled to 0 °C using an ice-water bath. Benzyl chloroformate (0.290 mL, 0.35 g, 2.0 mmol, 1 equiv. based on the mmol of the alkene substrate from the previous step) and triethylamine (0.280 mL, 0.203 g, 2.0 mmol, 1 equiv. based on the mmol of the alkene substrate from the previous step) were added, and the vial was sealed. After five minutes, the stirring reaction mixture was removed from the ice-water bath and warmed to room temperature over a period of 20 hours. Following this time, the seal was broken, and the contents of the vial were transferred to a separatory funnel with $CH_2Cl_2$ (40 mL). The organic layer was washed once with 1 M aqueous HCl solution (20 mL), collected, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel (specific conditions are given with each product's characterization data).

## IV. Procedures, characterization data, and spectra for Manuscript Figure 2 (Substrate Scope)




benzyl (2*S**,3*R**)-2-(2-(benzoyloxy)ethyl)-3-ethylaziridine-1-carboxylate

**Compound 4**: Synthesized using **General Procedure A** on a 2 mmol scale; Purified using a gradient of 0 to 30% EtOAc/hexanes on silica gel; Isolated and characterized as the single diastereomer shown; (colorless oil, 0.490 g, 1.39 mmol, 70% yield).

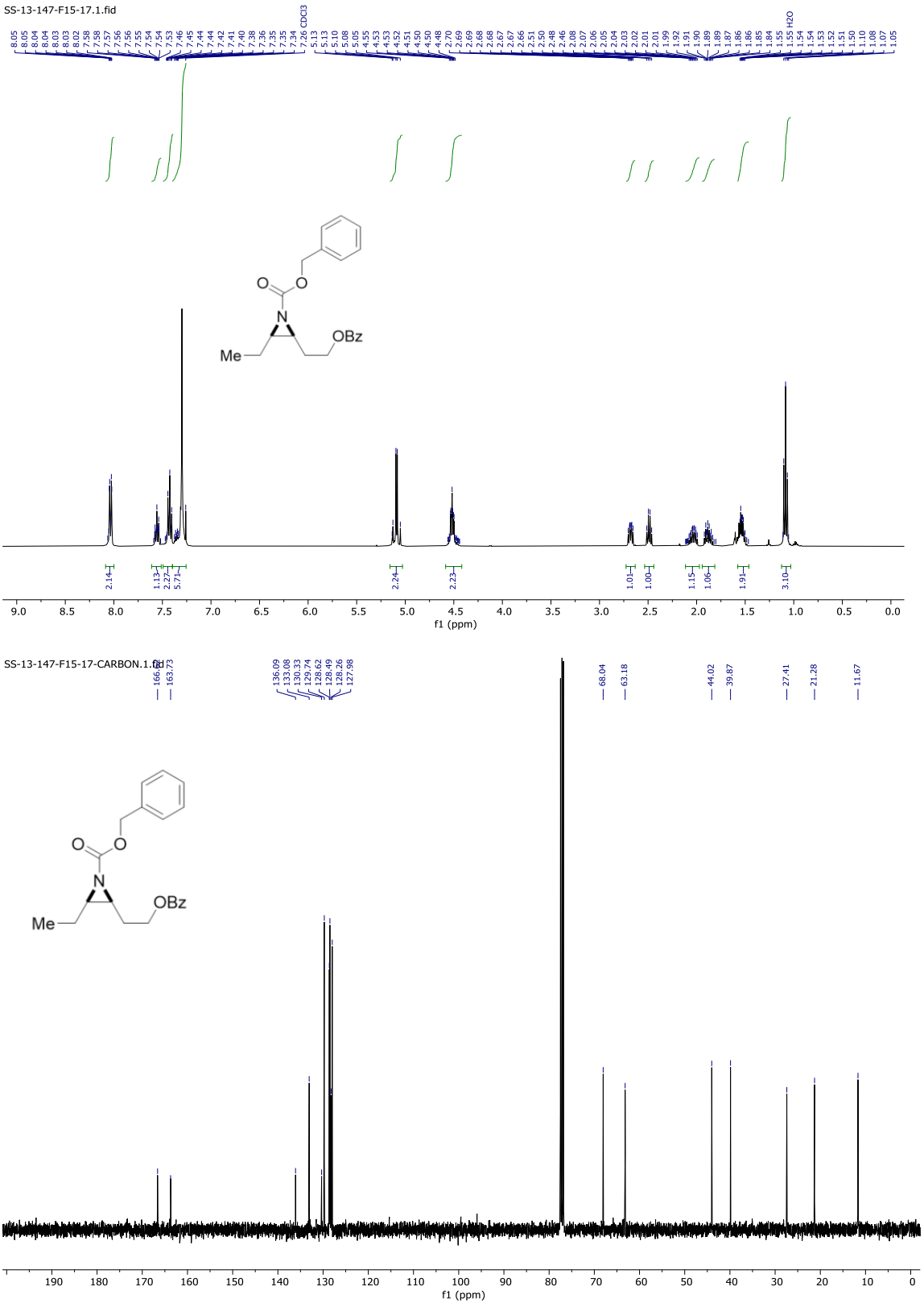
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 2H), 7.61 – 7.51 (m, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.27 (m, 5H), 5.11 (d, *J* = 12.4 Hz, 1H), 5.07 (d, *J* = 12.4 Hz, 1H), 4.58 – 4.43 (m, 2H), 2.68 (ddd, *J* = 8.1, 6.5, 5.1 Hz, 1H), 2.49 (q, *J* = 6.6 Hz, 1H), 2.04 (dtd, *J* = 14.2, 7.1, 5.1 Hz, 1H), 1.88 (ddt, *J* = 14.1, 8.0, 5.8 Hz, 1H), 1.66 – 1.40 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H).

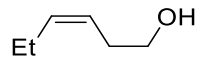
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 166.6, 163.7, 136.0, 133.0, 130.3, 129.7, 128.6, 128.4, 128.2, 127.9, 68.0, 63.1, 44.0, 39.8, 27.4, 21.2, 11.6.

IR ν 2967, 1721, 1452, 1379, 1273, 1220, 1112 $cm^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{21}H_{24}NO_4^+$ 354.1700. Found 354.1684 (4.5 ppm error).

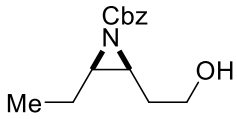
**Compound 4 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






(*Z*)-hex-3-en-1-ol

**Compound 5**: Commercially available.




benzyl (2*R**,3*S**)-2-ethyl-3-(2-hydroxyethyl)aziridine-1-carboxylate

**Compound 6**: Synthesized using **General Procedure B** on a 2 mmol scale; Purified using a gradient of 0 to 50% EtOAc/hexanes on silica gel; Isolated and characterized as the single diastereomer shown; (colorless oil, 0.221 g, 0.886 mmol, 44% yield).

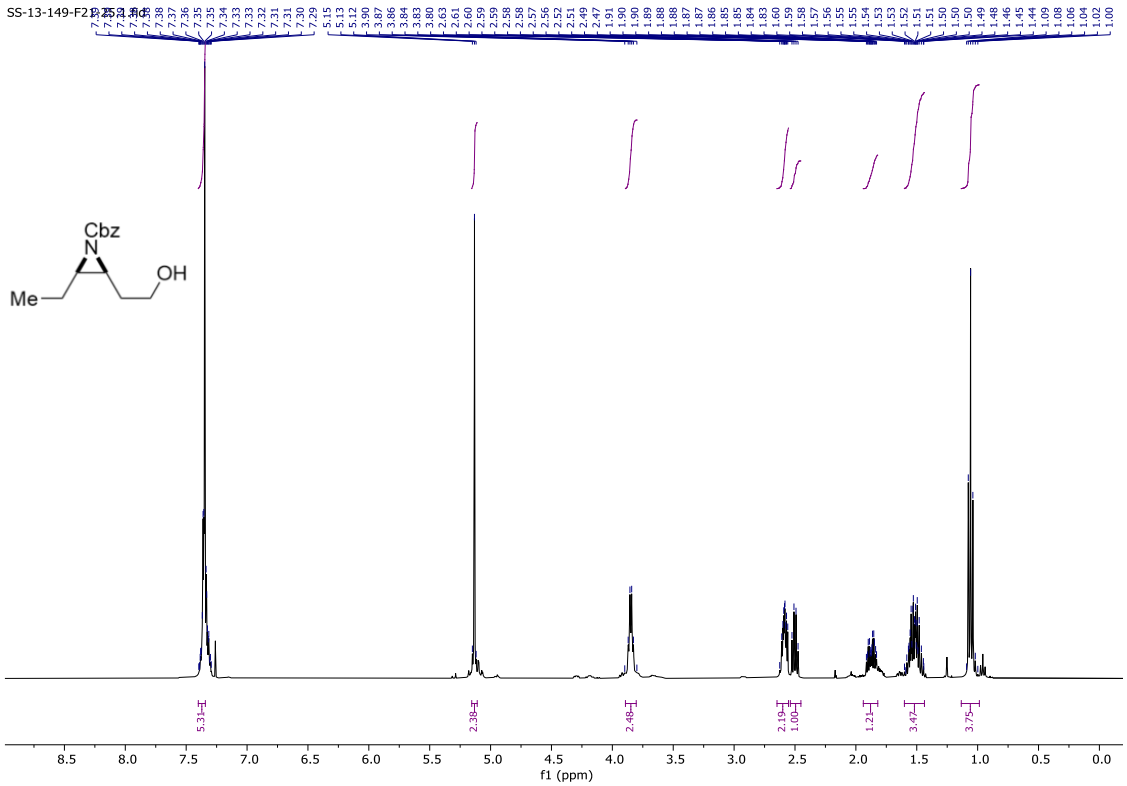
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 5H), 5.18 – 5.06 (m, 2H), 3.95 – 3.76 (m, 2H), 2.70 – 2.55 (m, 2H), 2.50 (q, *J* = 6.6 Hz, 1H), 1.88 (dtd, *J* = 14.1, 6.0, 4.0 Hz, 1H), 1.60 – 1.44 (m, 3H), 1.06 (t, *J* = 7.5 Hz, 3H).

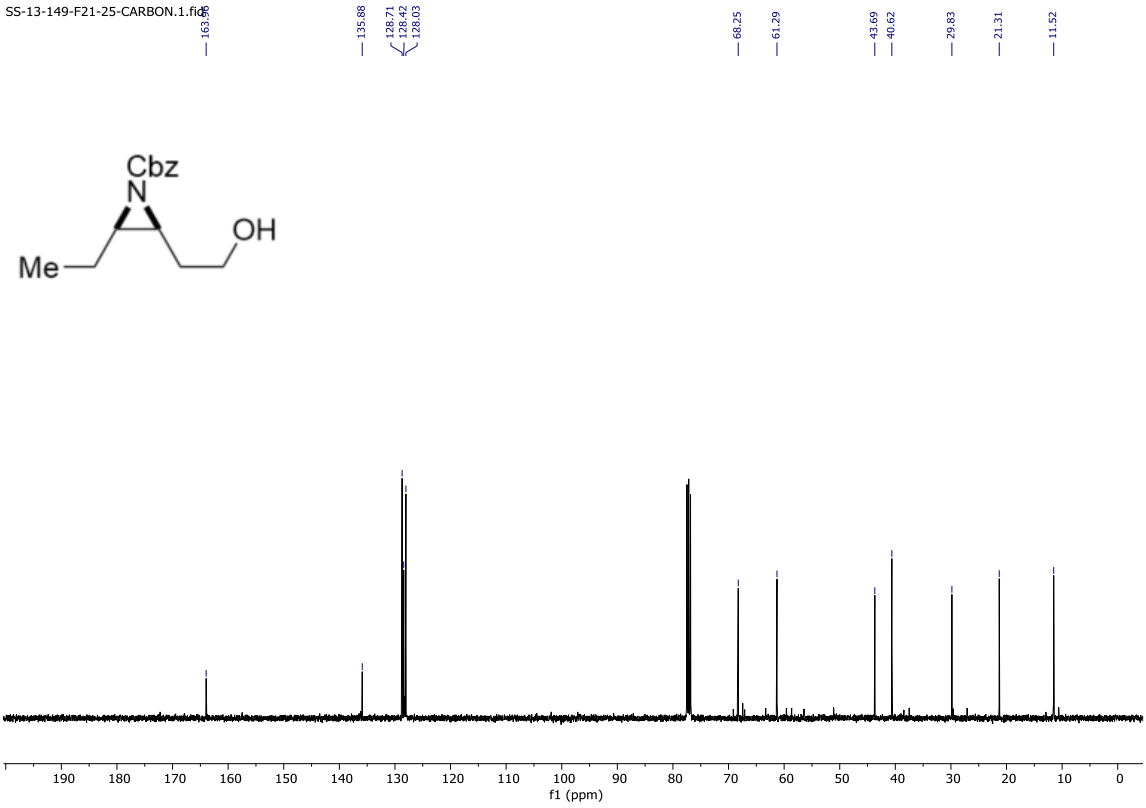
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 163.9, 135.8, 128.7, 128.4, 128.0, 68.2, 61.2, 43.6, 40.6, 29.8, 21.3, 11.5.

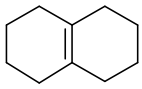
IR ν 3424, 2967, 1721, 1455, 1379, 1292, 1224, 1057 $cm^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{14}H_{19}NNaO_3^+$ 272.1257. Found 272.1240 (6.2 ppm error).

**Compound 6 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**

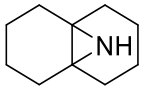




1,2,3,4,5,6,7,8-octahydronaphthalene

**Compound 7**: Commercially available.




octahydro-4a,8a-epiminonaphthalene

**Compound 8**: Synthesized using a modified version of **General Procedure B, Part I** on a 2 mmol scale (reaction solvent = 4:1 $CF_3CH_2OH/CH_2Cl_2$); (light yellow oil, 83% yield, estimated by $^1H$ NMR integration against an internal standard).

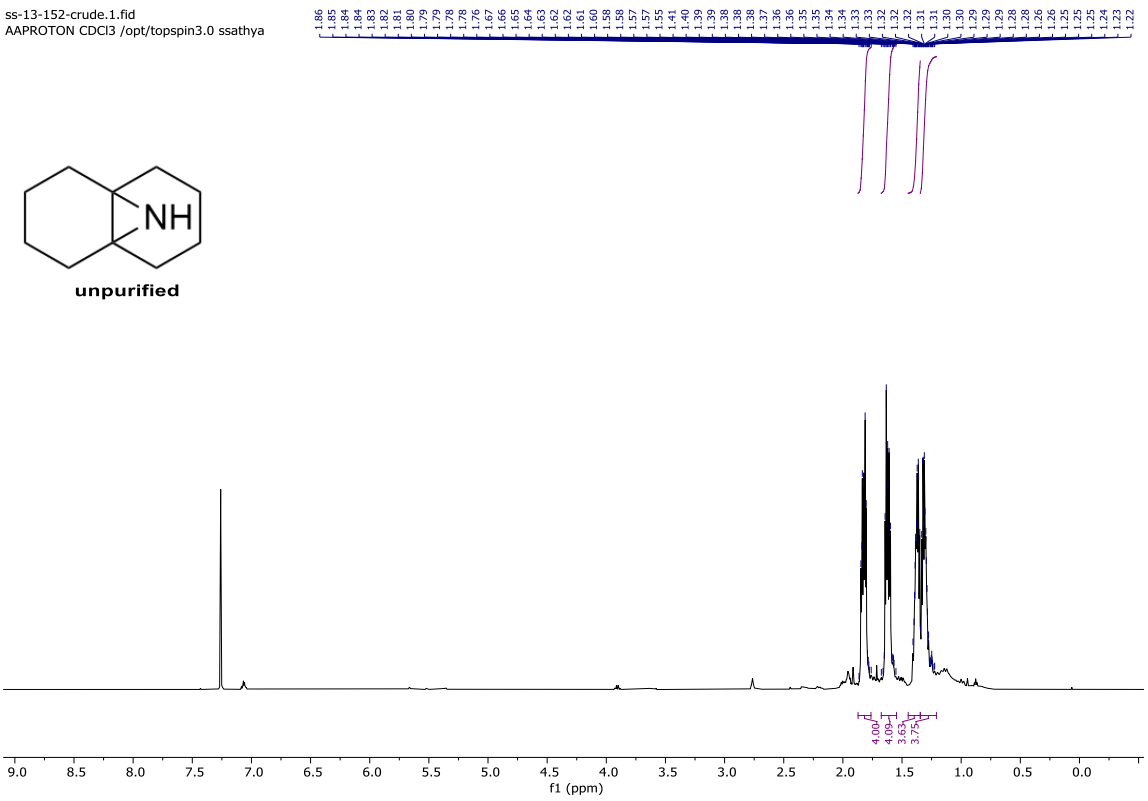
$^1H$ NMR (600 MHz, $CDCl_3$) δ 1.87 – 1.76 (m, 4H), 1.68 – 1.55 (m, 4H), 1.45 – 1.35 (m, 4H), 1.35 – 1.21 (m, 4H).

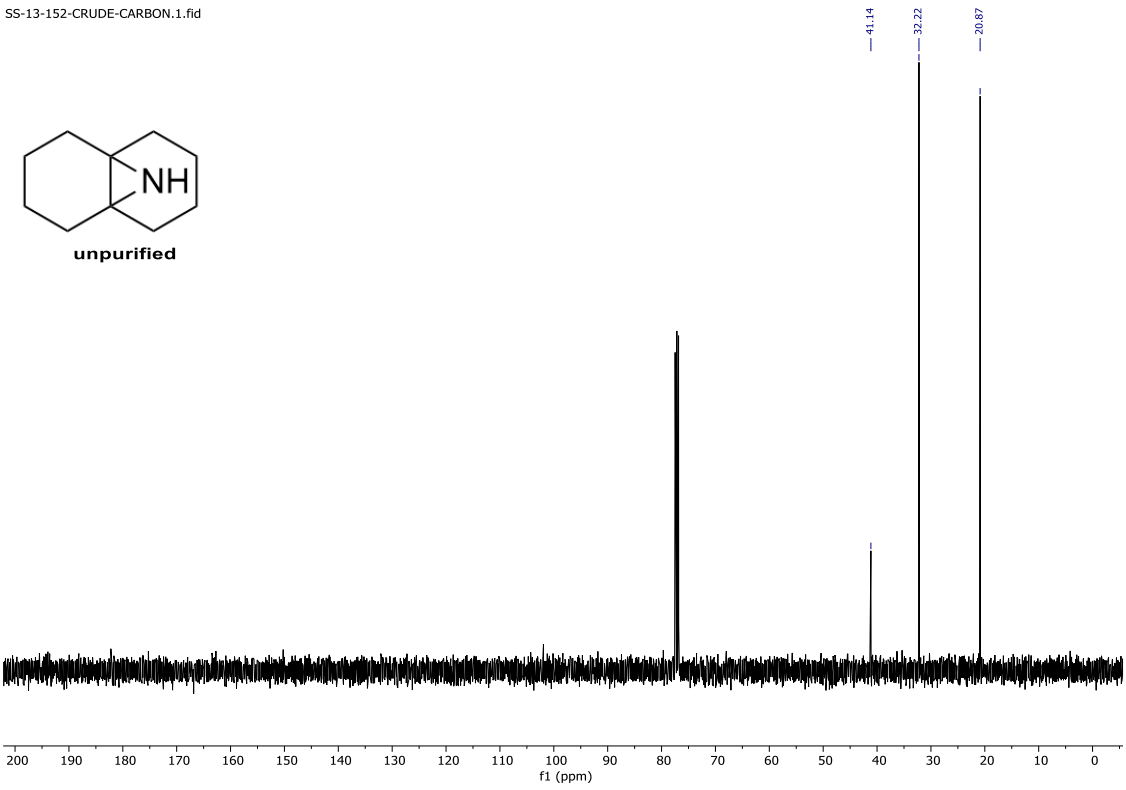
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 41.1, 32.2, 20.8.

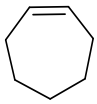
IR ν 2928, 2855, 1447, 945 $cm^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{10}H_{18}N^+$ 152.1434. Found 152.1434 (0 ppm error).

## Compound 8 ($CDCl_3$, $^1H$ NMR: 600 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)

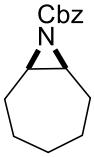




cycloheptene

**Compound 9**: Commercially available.




benzyl (1*R**,7*S**)-8-azabicyclo[5.1.0]octane-8-carboxylate

**Compound 10**: Synthesized using **General Procedure B** on a 2 mmol scale; Purified using a gradient of 0 to 1% acetone/$CH_2Cl_2$ on silica gel; Isolated and characterized as the single diastereomer shown; (colorless oil, 0.299 g, 1.22 mmol, 61% yield).

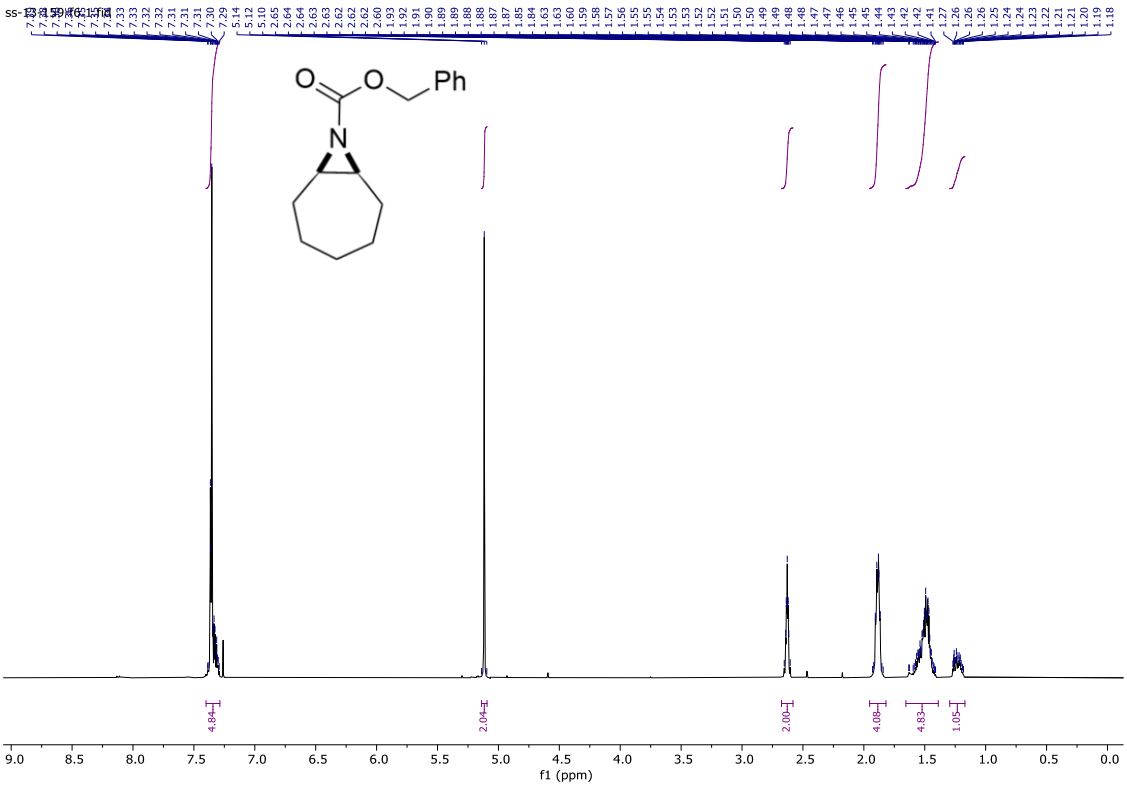
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.15 – 5.07 (m, 2H), 2.63 (ddd, *J* = 5.0, 3.2, 1.9 Hz, 2H), 1.97 – 1.82 (m, 4H), 1.65 – 1.39 (m, 5H), 1.29 – 1.17 (m, 1H).

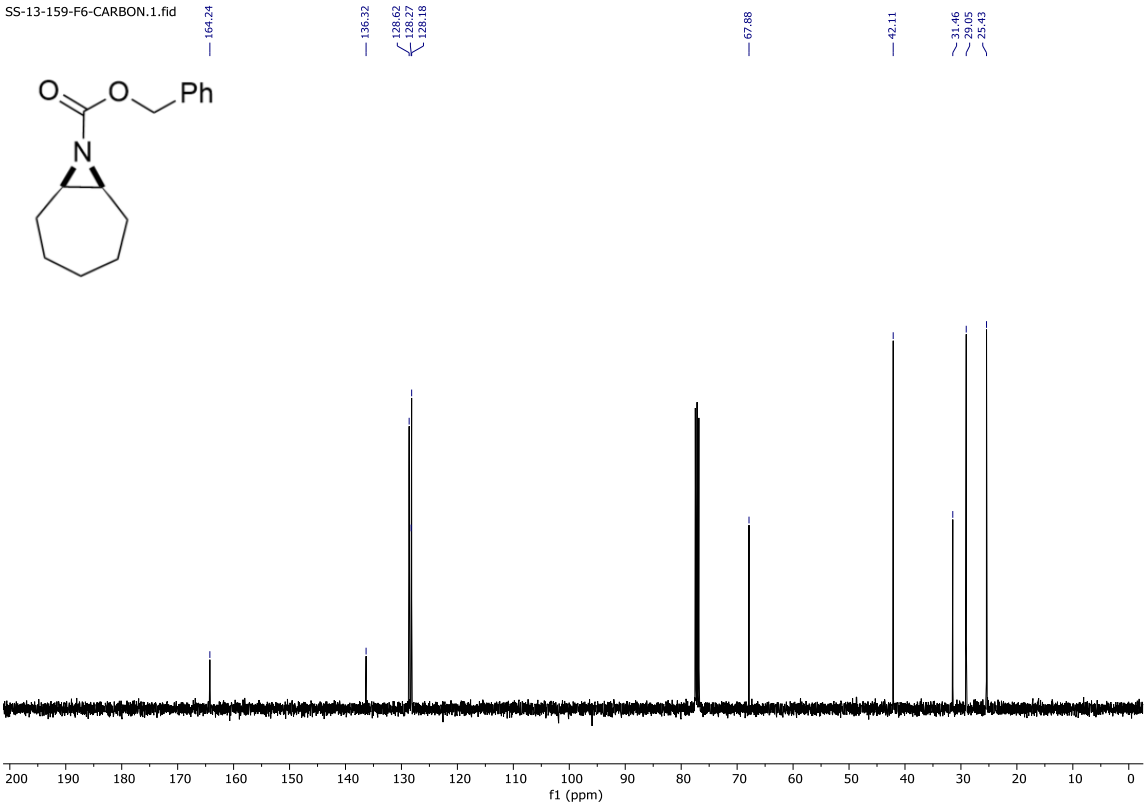
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 164.2, 136.3, 128.6, 128.2, 128.1, 67.8, 42.1, 31.4, 29.0, 25.4.

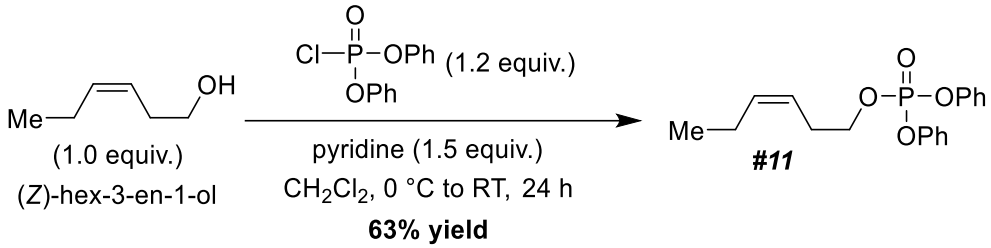
IR ν 2941, 1721, 1458, 1384, 1286, 1241, 1217, 1088 cm$^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{15}H_{19}NNaO_2^+$ 268.1308. Found 268.1323 (5.6 ppm error).

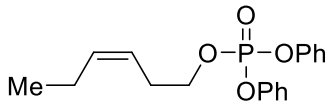
**Compound 10 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






A round-bottom flask equipped with a magnetic stir bar was charged with (*cis*)-3-hexen-1-ol (2.0 g, 20 mmol, 1.0 equiv.) and dichloromethane (20 mL, reaction concentration = 1 M). The stirring solution was cooled to 0 °C using an ice-water bath. Pyridine (2.41 ml, 2.37 g, 30 mmol, 1.5 equiv.) followed by diphenyl phosphoryl chloride (4.96 mL, 6.43 g, 24 mmol, 1.2 equiv.) were added slowly. The reaction mixture warmed to room temperature with stirring over a period of 24 h. Following this time, the reaction mixture was transferred to a separatory funnel and diluted with dichloromethane (50 mL). The organic layer was washed once with 1 M aqueous HCl solution (50 mL), collected, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude residue by silica gel flash column chromatography using a gradient of 0 to 80% ethyl acetate in hexanes afforded compound **11** (colorless oil, 4.18 g, 12.6 mmol, 63% yield).




(*Z*)-hex-3-en-1-yl diphenyl phosphate

**Compound 11**:

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.25 – 7.15 (m, 6H), 5.57 – 5.45 (m, 1H), 5.34 – 5.23 (m, 1H), 4.23 (dt, *J* = 8.0, 7.0 Hz, 2H), 2.53 – 2.40 (m, 2H), 2.02 (pd, *J* = 7.5, 1.6 Hz, 2H), 0.95 (t, *J* = 7.6 Hz, 3H).

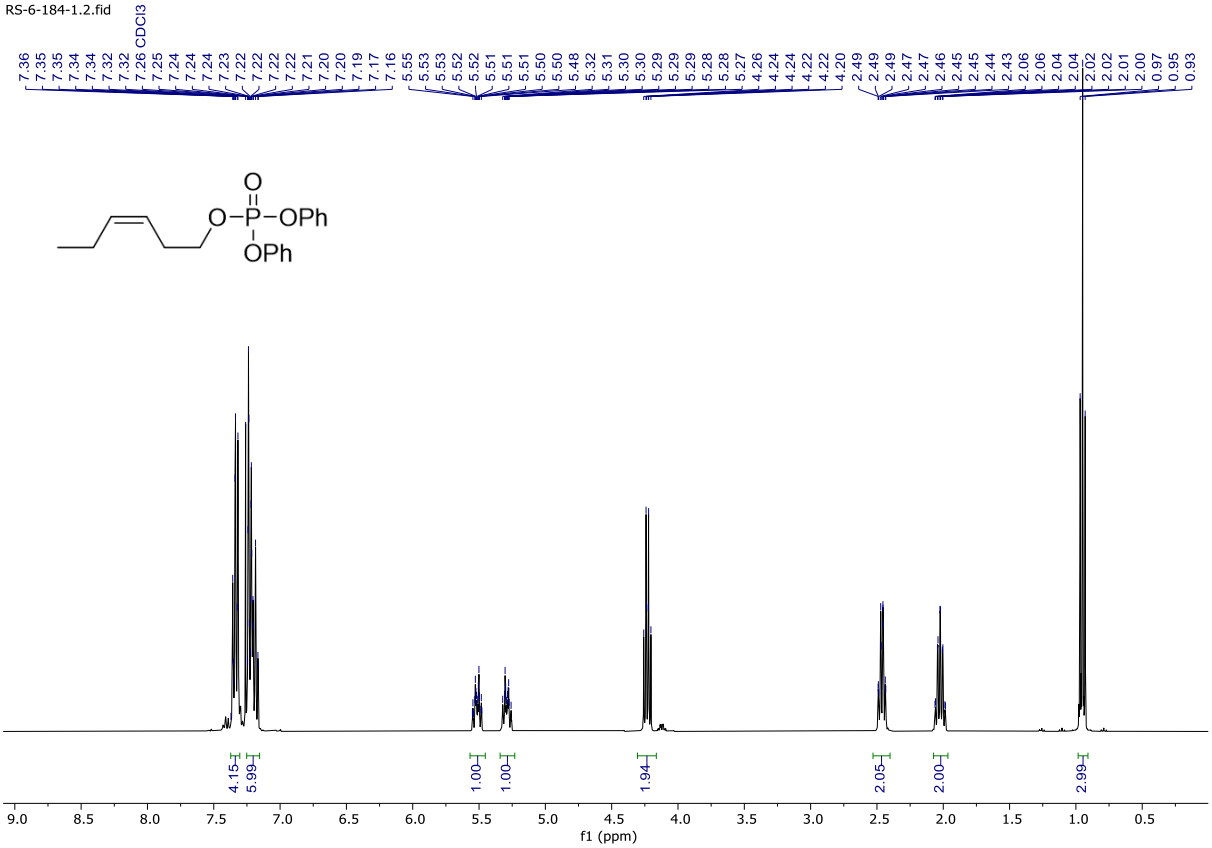
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 150.7 (d, *J* = 7.3 Hz), 135.3, 129.8, 125.3, 122.6, 120.1 (d, *J* = 5.1 Hz), 68.7 (d, *J* = 6.6 Hz), 28.3 (d, *J* = 6.7 Hz), 20.7, 14.2.

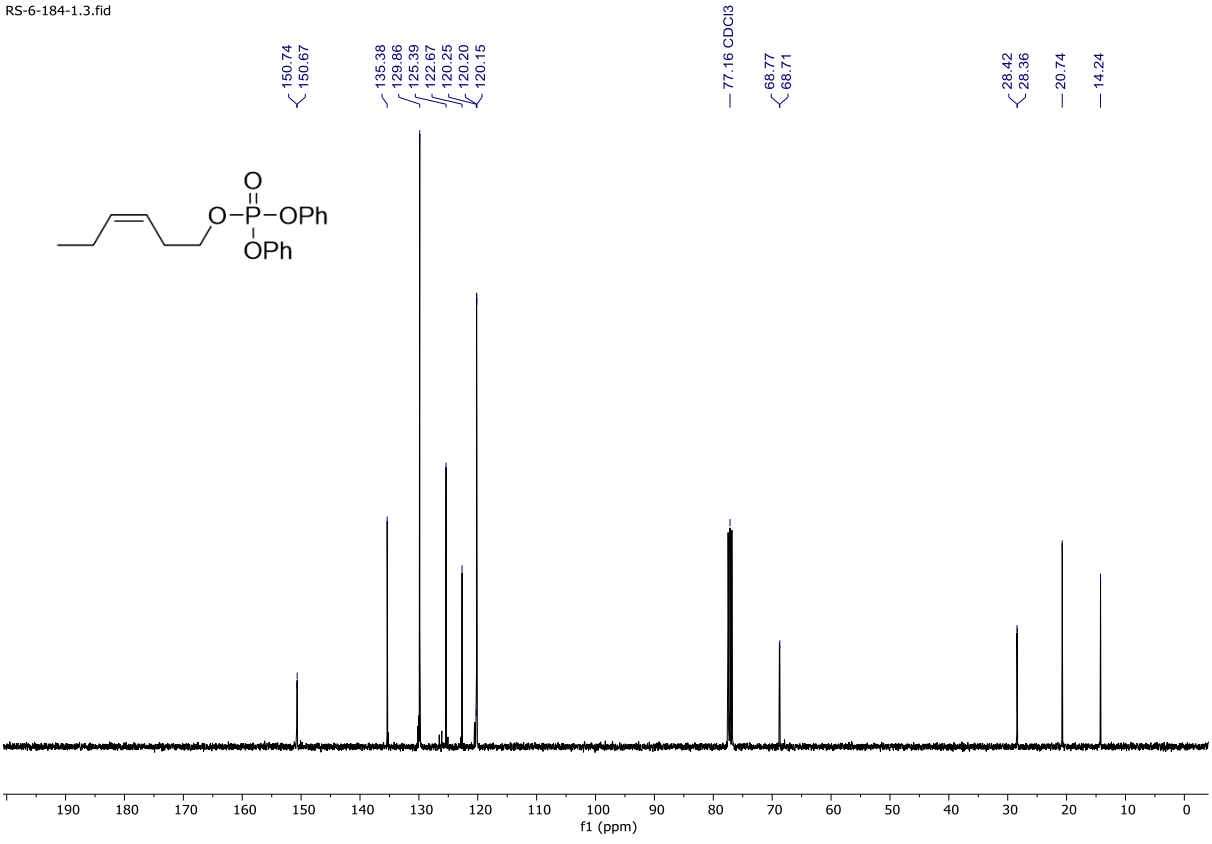
$^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$) δ -11.9.

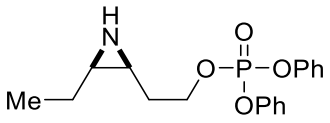
IR ν 2966, 1591, 1489, 1265, 1191, 1024, 955, 740 $cm^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{18}H_{21}O_4PNa^+$ 355.1075. Found 355.1046 (8.2 ppm error).

**Compound 11 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**





2-((2*S**,3*R**)-3-ethylaziridin-2-yl)ethyl diphenyl phosphate

**Compound 12**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; Purified by flash column chromatography on Florisil (60 – 100 mesh) using a gradient of 0 to 50% ethyl acetate in hexanes, followed by flushing with 100% methanol; Isolated and characterized as the single diastereomer shown; (colorless oil, 0.347 g, 1.0 mmol, 50% yield).

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 4H), 7.25 – 7.17 (m, 6H), 4.45 – 4.30 (m, 2H), 2.24 – 2.13 (m, 1H), 2.09 – 1.99 (m, 1H), 1.98 – 1.84 (m, 1H), 1.75 – 1.54 (m, 1H), 1.45 – 1.32 (m, 2H), 0.98 (t, $J$ = 7.5 Hz, 3H).

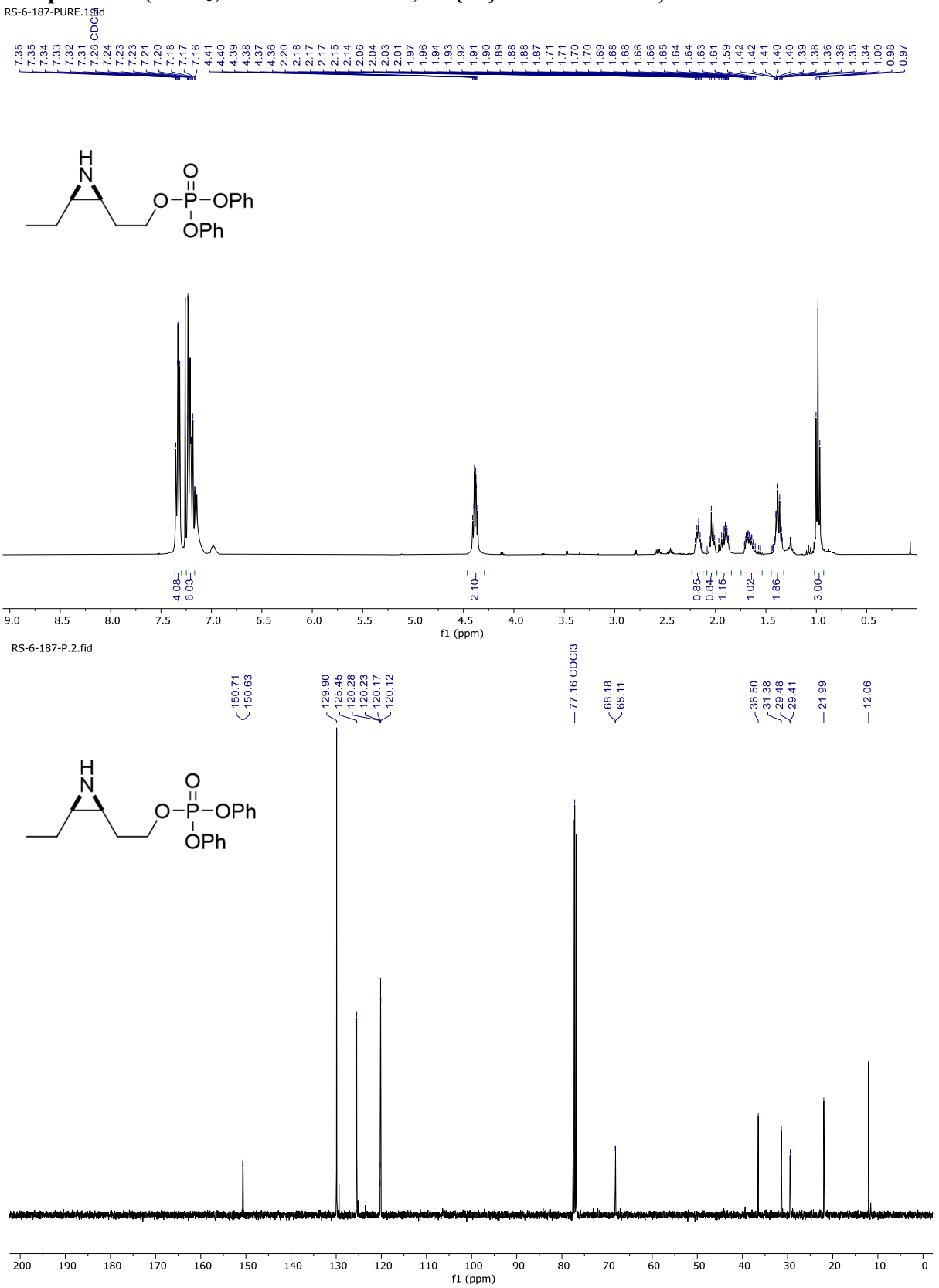
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 150.6 (d, $J$ = 7.3 Hz), 129.9, 125.4, 120.32 – 120.00 (m), 68.1 (d, $J$ = 6.4 Hz), 36.5, 31.3, 29.4 (d, $J$ = 7.0 Hz), 21.9, 12.0.

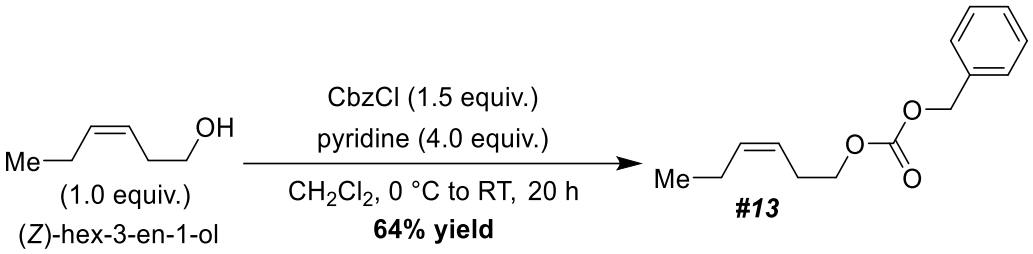
$^{31}$P{$^{1}$H} NMR (162 MHz, $CDCl_3$) δ -11.9.

IR ν 3302, 2966, 1684, 1590, 1489, 1275, 1191, 954, 753, 688 cm$^{-1}$.

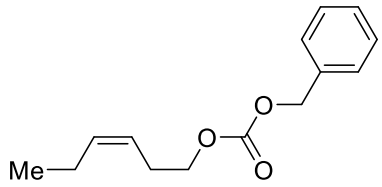
HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{18}H_{23}NO_4P^+$ 348.1365. Found 348.1365 (0.0 ppm error).

**Compound 12 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






A round-bottom flask equipped with a magnetic stir bar was charged with *(cis)*-3-hexen-1-ol (2.0 g, 20 mmol, 1.0 equiv.) and dichloromethane (20 mL, reaction concentration = 1 M). The stirring solution was cooled to 0 °C using an ice-water bath. Pyridine (6.4 mL, 6.3 g, 80 mmol, 4 equiv.) followed by benzyl chloroformate (4.3 mL, 5.2 g, 30 mmol, 1.5 equiv.) were added slowly. The stirring reaction mixture was warmed to room temperature over a period of 20 hours. Following this time, the reaction mixture was transferred to a separatory funnel and diluted with dichloromethane (50 mL). The organic layer was washed once with 1 M aqueous HCl solution (50 mL), collected, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude residue by silica gel flash column chromatography using a gradient of 0 to 50% ethyl acetate in hexanes afforded compound **13** (colorless oil, 2.99 g, 12.8 mmol, 64% yield).




(*Z*)-benzyl hex-3-en-1-yl carbonate

**Compound 13:**

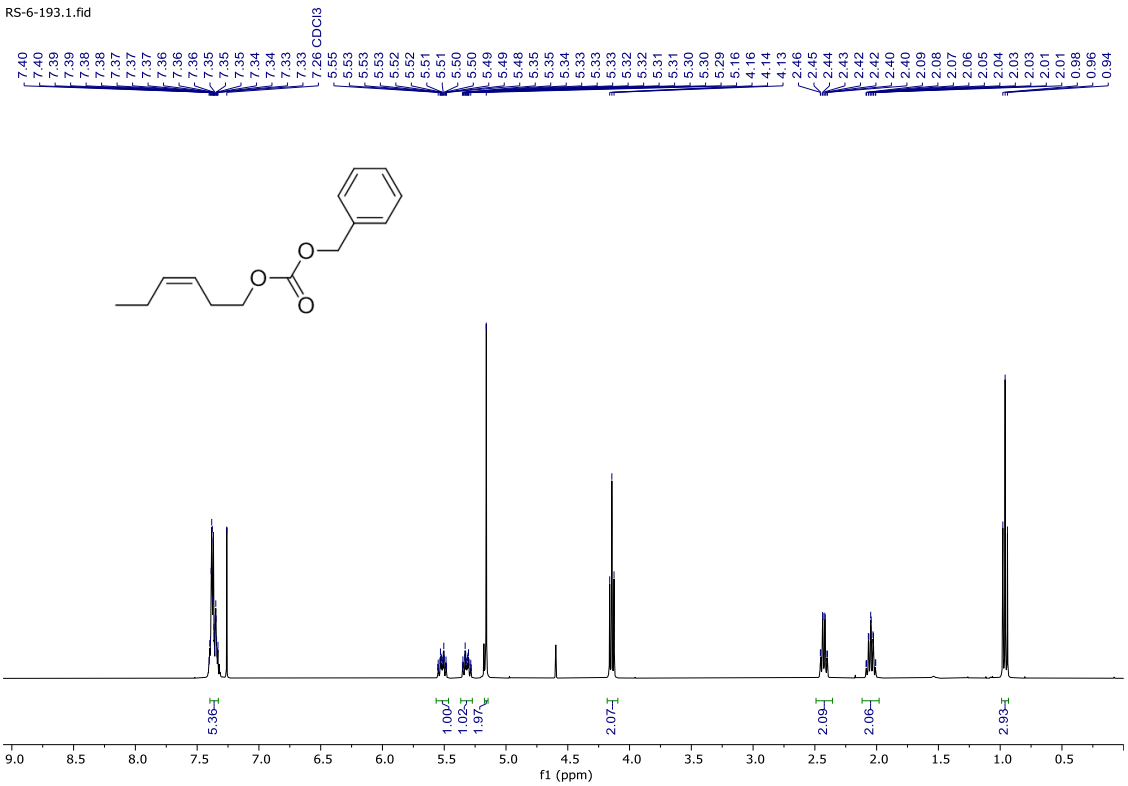
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 5H), 5.57 – 5.47 (m, 1H), 5.37 – 5.27 (m, 1H), 5.16 (s, 2H), 4.14 (t, *J* = 7.0 Hz, 2H), 2.43 (qd, *J* = 7.1, 1.5 Hz, 2H), 2.05 (pd, *J* = 7.5, 1.5 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H).

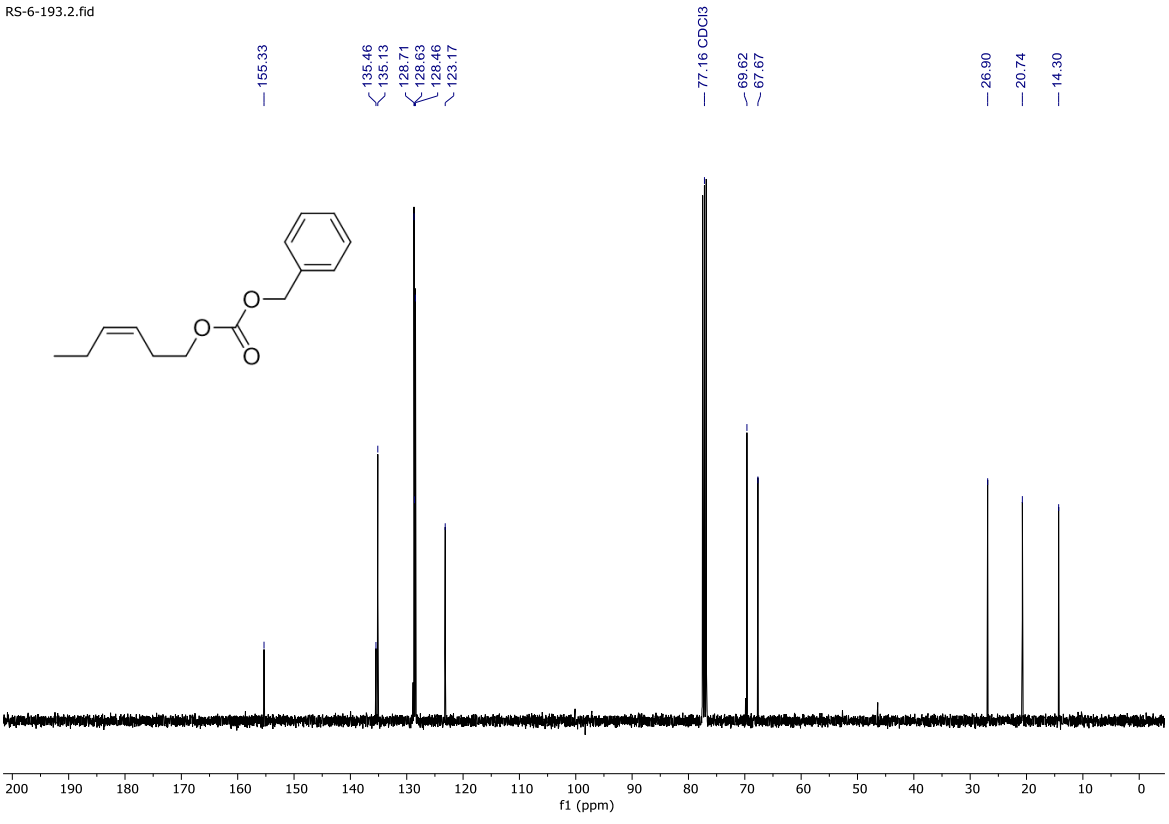
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 155.3, 135.4, 135.1, 128.7, 128.6, 128.4, 123.1, 69.6, 67.6, 26.9, 20.7, 14.3.

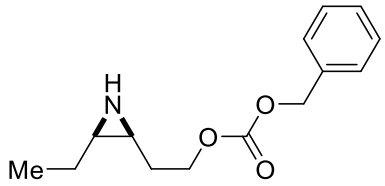
IR ν 3054, 2965, 2305, 1745, 1395, 1265, 742 cm$^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{14}H_{19}O_3^+$ 235.1334. Found 235.1321 (5.5 ppm error).

**Compound 13 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**





benzyl (2-((2*S**,3*R**)-3-ethylaziridin-2-yl)ethyl) carbonate

**Compound 14**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; Purified by column chromatography on Florisil (60 – 100 mesh) using a gradient of 0 to 50% ethyl acetate in hexanes, followed by flushing with 100% methanol; Isolated and characterized as the single diastereomer shown; (pale yellow oil, 0.264 g, 1.06 mmol, 53% yield).

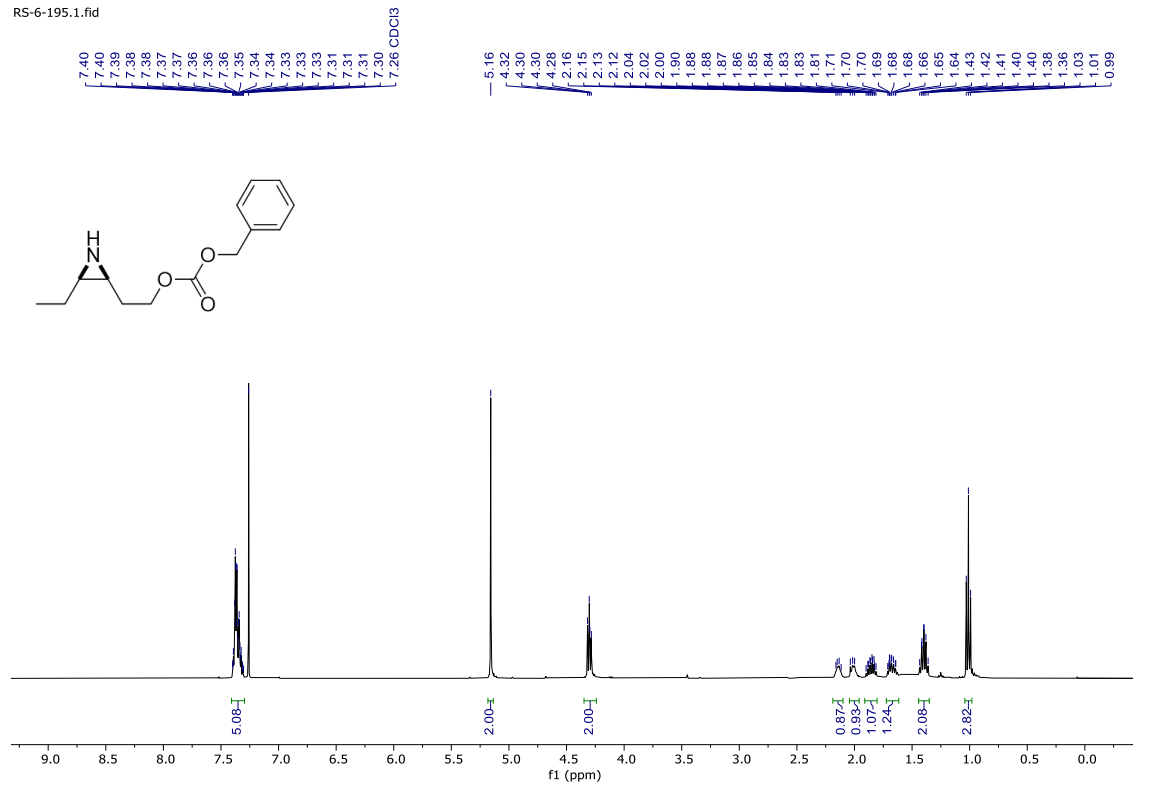
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 5H), 5.18 – 5.14 (m, 2H), 4.34 – 4.24 (m, 2H), 2.19 – 2.10 (m, 1H), 2.04 – 1.96 (m, 1H), 1.85 (dtd, *J* = 13.9, 7.2, 5.5 Hz, 1H), 1.72 – 1.62 (m, 1H), 1.44 – 1.35 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H).

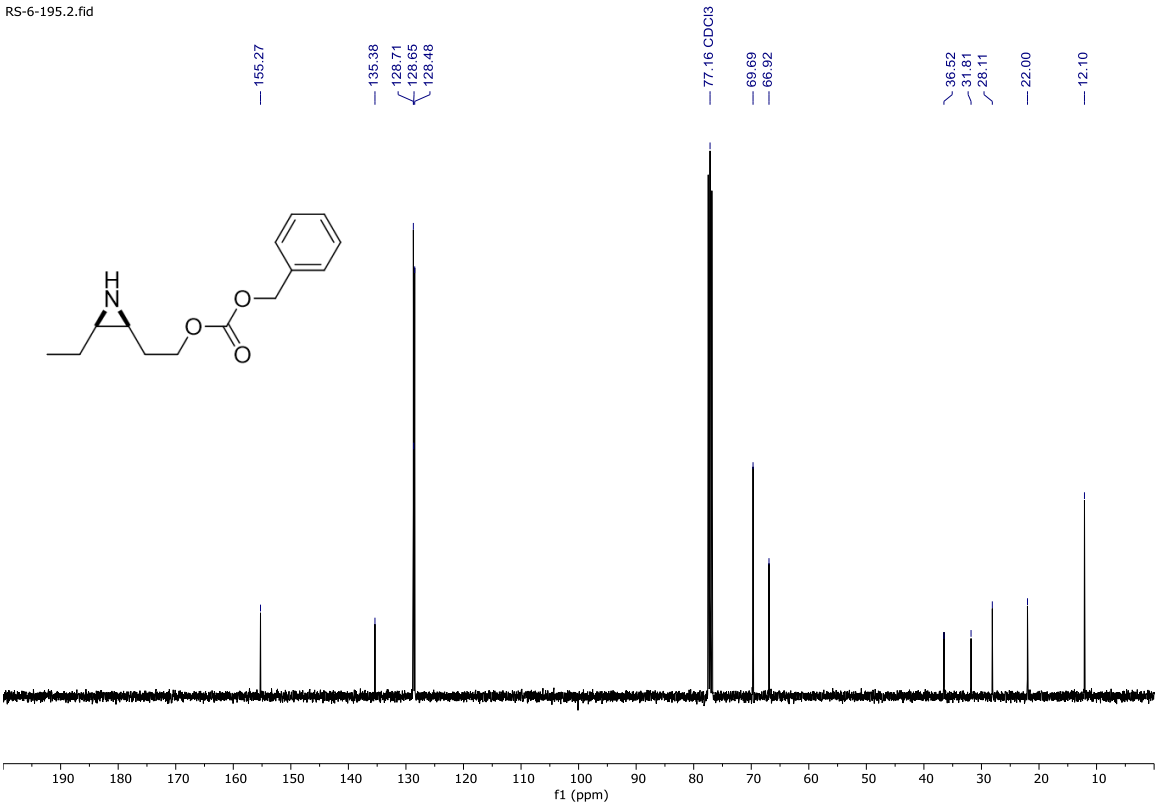
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 155.2, 135.3, 128.7, 128.6, 128.4, 69.6, 66.9, 36.5, 31.8, 28.1, 22.0, 12.1.

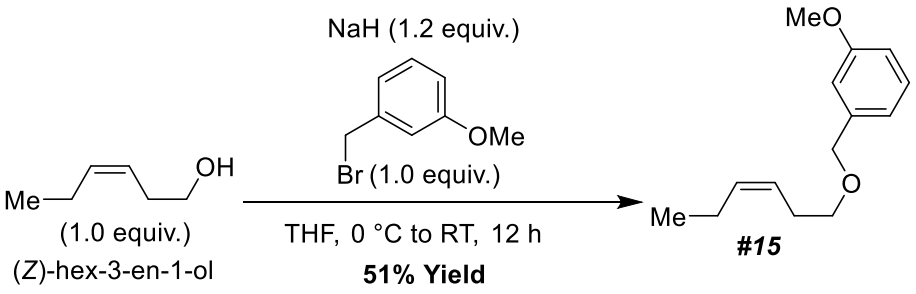
IR ν 3054, 2986, 2306, 1746, 1265, 895, 704 cm$^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{14}H_{19}NO_3Na^+$ 272.1263. Found 272.1272 (3.3 ppm error).

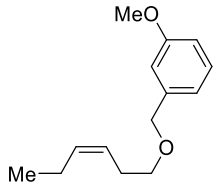
**Compound 14 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






A round-bottom flask equipped with a magnetic stir bar was charged with *(cis)*-3-hexen-1-ol (2.0 g, 20 mmol, 1.0 equiv.) and tetrahydrofuran (10 mL, reaction concentration = 2 M). The solution was cooled to 0 °C using an ice-water bath, and dry sodium hydride (0.574 g, 24 mmol, 1.2 equiv.) was added in portions. The reaction mixture was stirred at 0 °C for 30 minutes. 3-methoxybenzyl bromide (2.8 mL, 4.02 g, 20 mmol, 1.0 equiv.) was added dropwise. The stirring reaction mixture was warmed to room temperature over a period of 12 hours. Following this time, the reaction was quenched with saturated aqueous $NH_4Cl$ solution (20 mL) and transferred to a separatory funnel. The mixture was diluted with ethyl acetate (50 mL), and the layers were shaken vigorously. The organic layer was collected, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude residue by silica gel column chromatography using a gradient of 0 to 40% ethyl acetate in hexanes afforded compound **15** (pale yellow oil, 2.24 g, 10.2 mmol, 51% yield).




(*Z*)-1-((hex-3-en-1-yloxy)methyl)-3-methoxybenzene

**Compound 15**:

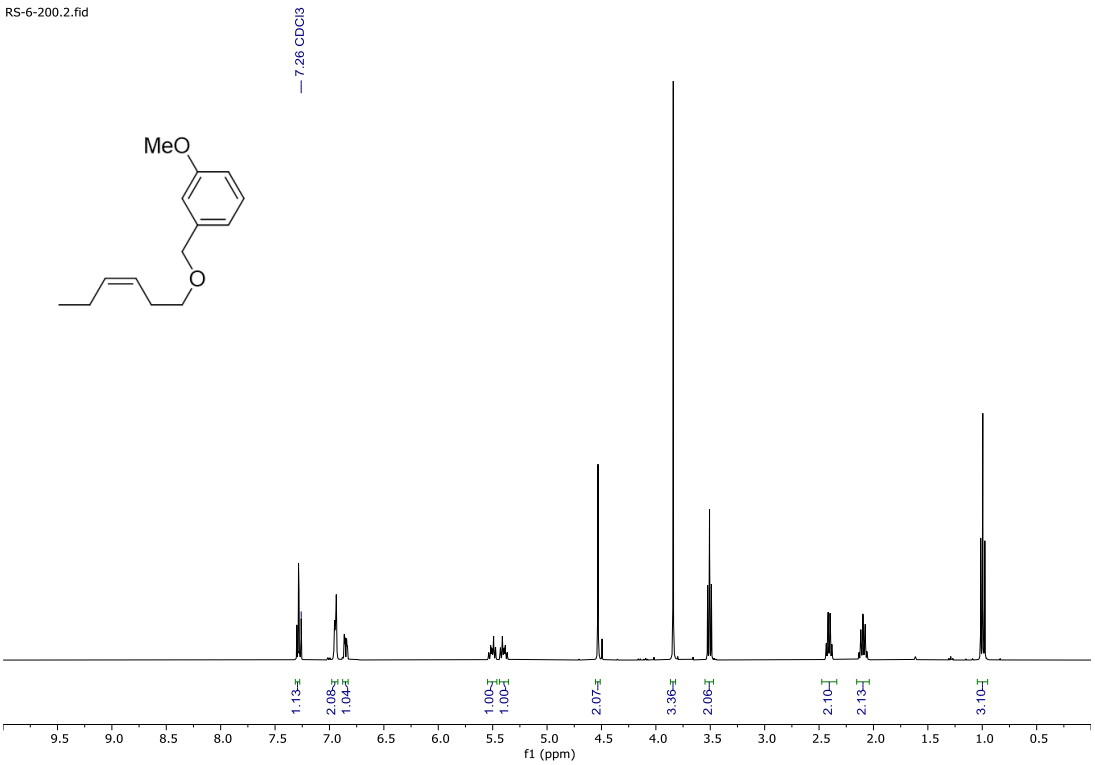
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.85 (ddd, *J* = 8.1, 2.8, 1.0 Hz, 1H), 5.55 – 5.46 (m, 1H), 5.44 – 5.36 (m, 1H), 4.53 (s, 2H), 3.84 (s, 3H), 3.51 (t, *J* = 7.0 Hz, 2H), 2.41 (qd, *J* = 7.1, 1.5 Hz, 2H), 2.10 (pd, *J* = 7.5, 1.4 Hz, 2H), 1.00 (t, *J* = 7.6 Hz, 3H).

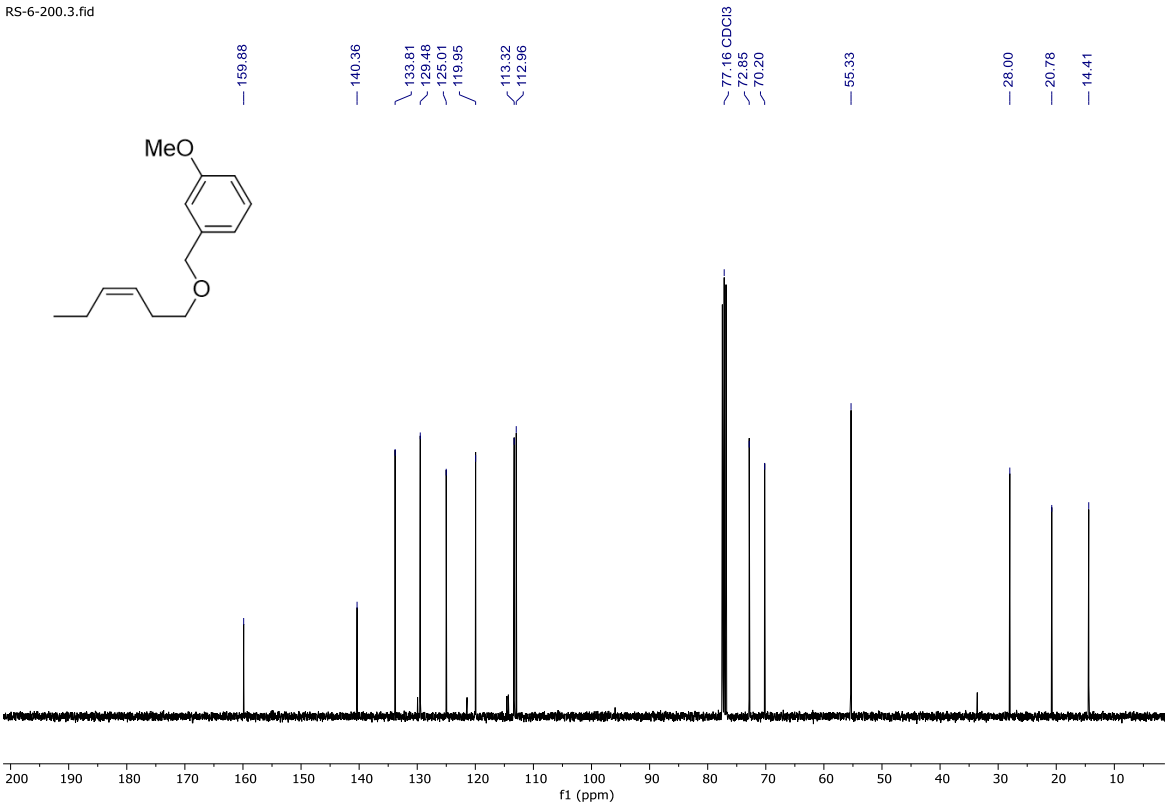
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 159.8, 140.3, 133.8, 129.4, 125.0, 119.9, 113.3, 112.9, 72.8, 70.2, 55.3, 28.0, 20.7, 14.4.

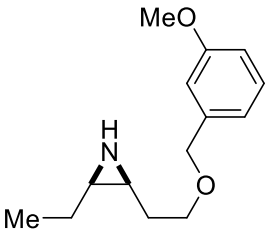
IR ν 3054, 2305, 1601, 1265, 742 cm$^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{14}H_{21}O_2^+$ 221.1542. Found 221.1523 (8.6 ppm error).

**Compound 15 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






(2*R**,3*S**)-2-ethyl-3-(2-((3-methoxybenzyl)oxy)ethyl)aziridine

**Compound 16**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; Purified by column chromatography on Florisil (60 – 100 mesh) using a gradient of 0 to 50% ethyl acetate in hexanes, followed by flushing with 100% methanol; Isolated and characterized as the single diastereomer shown; (pale yellow oil, 0.291 g, 1.24 mmol, 62% yield).

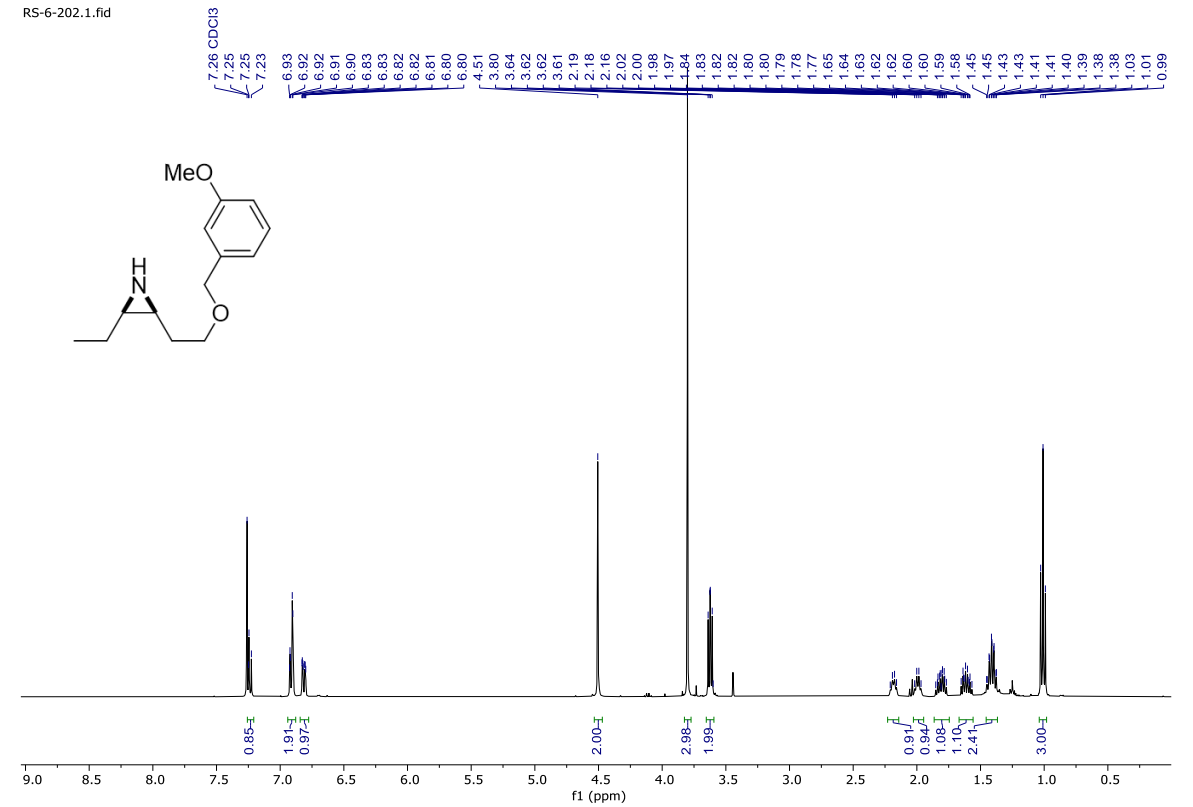
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.6 Hz, 1H), 6.94 – 6.87 (m, 2H), 6.84 – 6.78 (m, 1H), 4.54 – 4.47 (m, 2H), 3.80 (s, 3H), 3.65 – 3.59 (m, 2H), 2.22 – 2.14 (m, 1H), 2.04 – 1.95 (m, 1H), 1.81 (dtd, *J* = 14.0, 7.0, 5.2 Hz, 1H), 1.61 (ddt, *J* = 13.9, 7.9, 5.9 Hz, 1H), 1.47 – 1.38 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

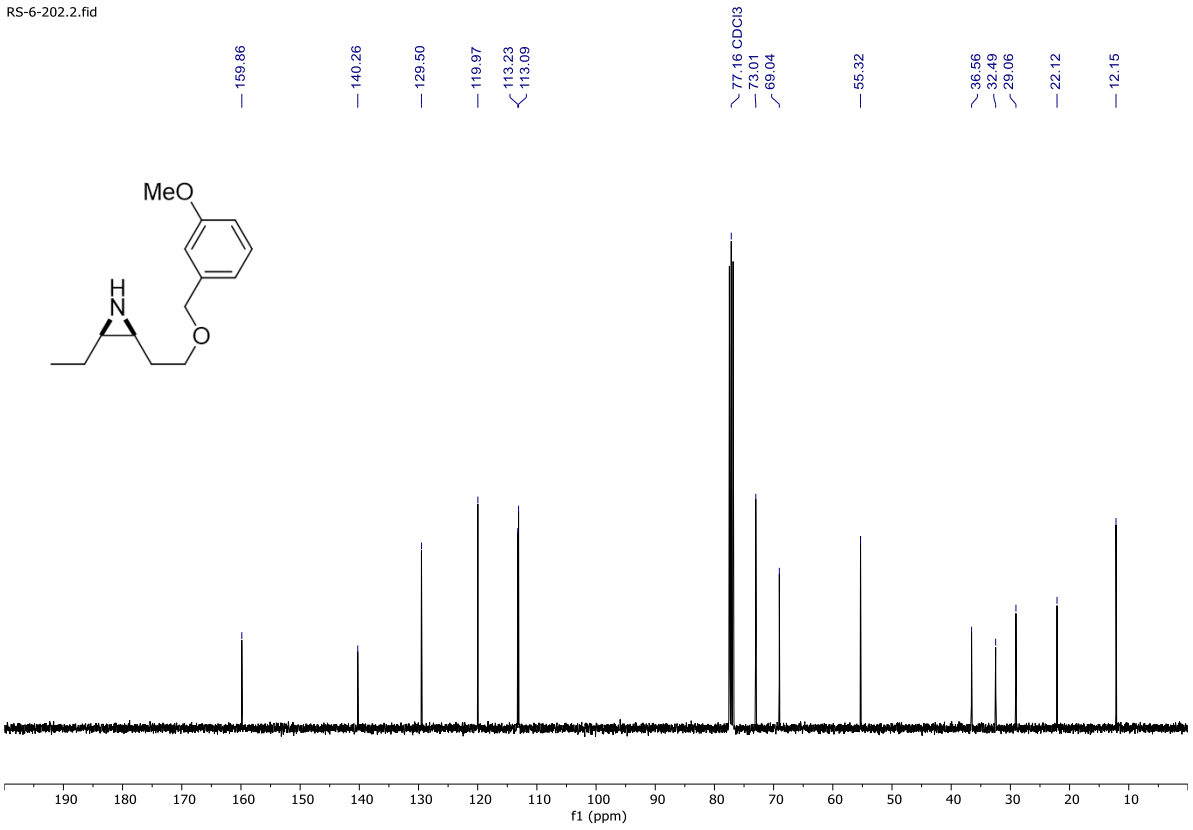
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 159.8, 140.2, 129.5, 119.9, 113.2, 113.0, 73.0, 69.0, 55.3, 36.5, 32.4, 29.0, 22.1, 12.1.

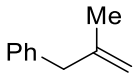
IR ν 3311, 3054, 2982, 2306, 1601, 1265, 746 $cm^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{14}H_{21}NO_2Na^+$ 258.1470. Found 258.1483 (5.0 ppm error).

**Compound 16 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**

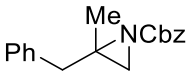





(2-methylallyl)benzene

**Compound 17**: Commercially available.




benzyl 2-benzyl-2-methylaziridine-1-carboxylate

**Compound 18**: Synthesized using **General Procedure B** on a 2 mmol scale; Purified using 100% $CH_2Cl_2$ on silica gel and preparative thin-layer chromatography (30% acetone/hexanes); (light yellow oil, 0.226 g, 0.803 mmol, 40% yield).

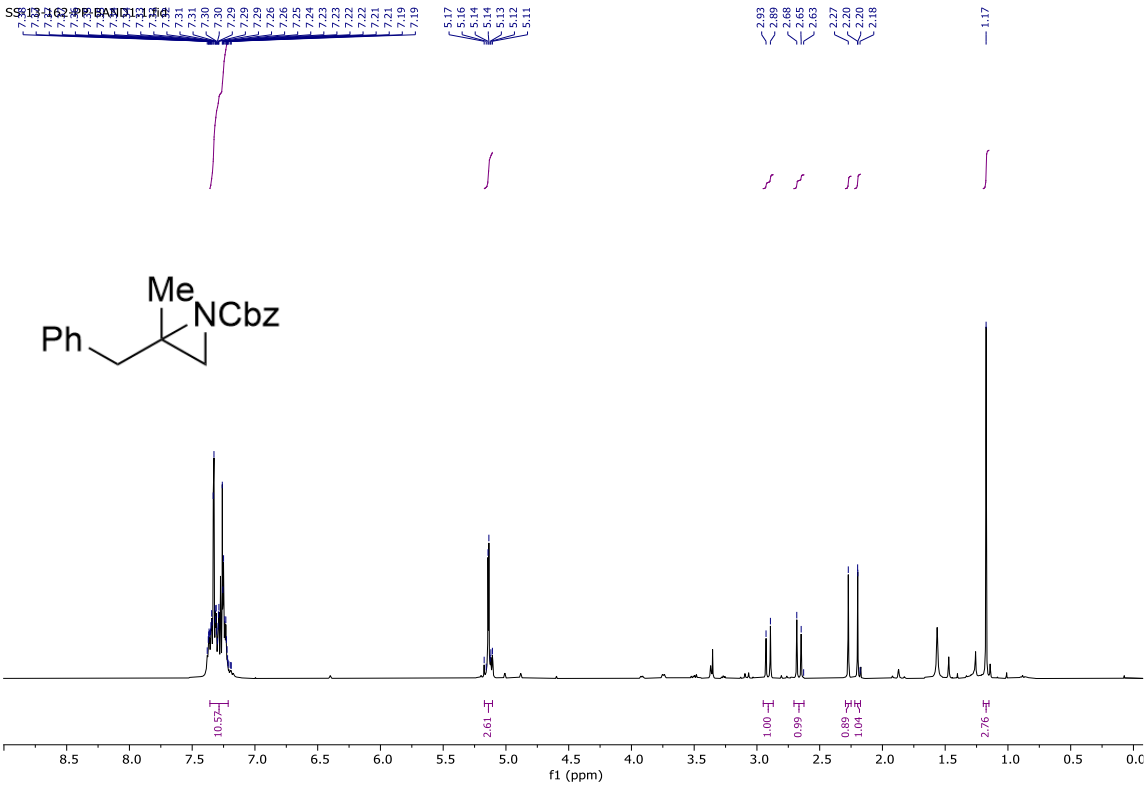
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 10H), 5.17 – 5.11 (m, 2H), 2.91 (d, *J* = 14.0 Hz, 1H), 2.67 (d, *J* = 14.0 Hz, 1H), 2.27 (s, 1H), 2.20 (s, 1H), 1.17 (s, 3H).

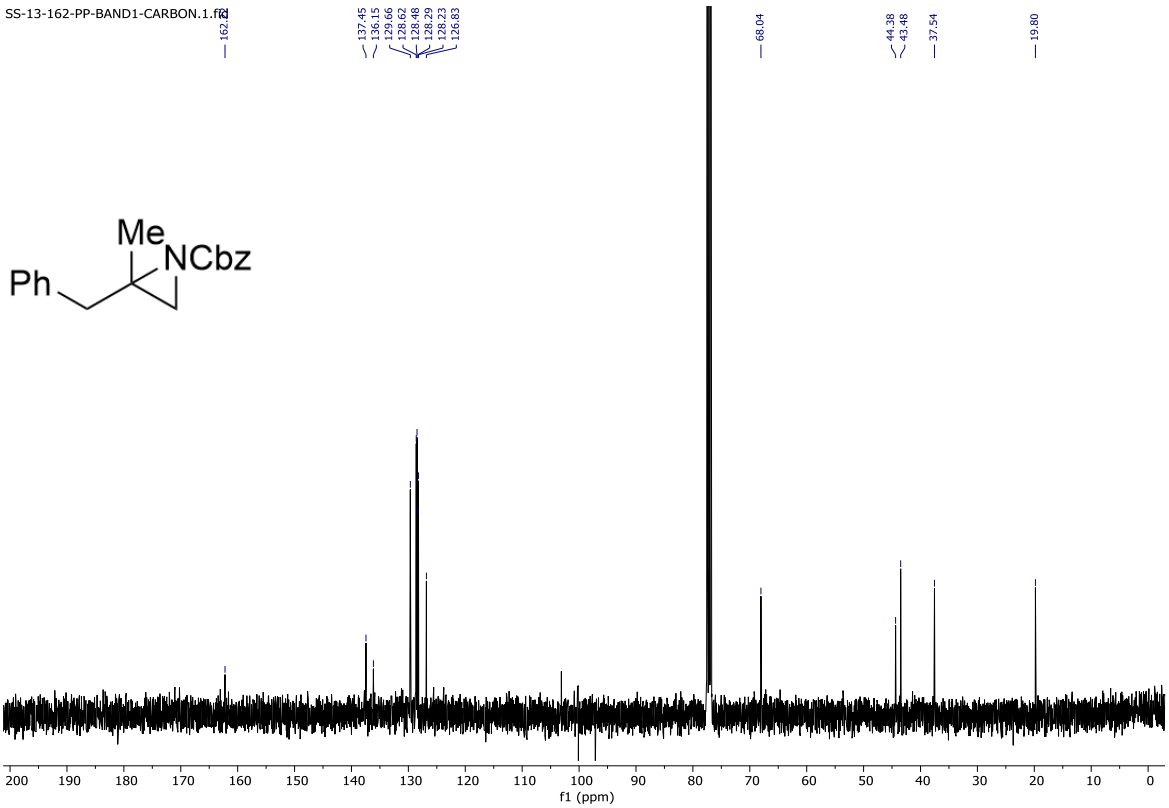
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 162.2, 137.4, 136.1, 129.6, 128.6, 128.4, 128.3, 128.2, 126.8, 68.0, 44.3, 43.4, 37.5, 19.8.

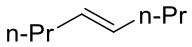
IR ν 2972, 1715, 1452, 1378, 1247, 749 $cm^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{18}H_{19}NNaO_2^+$ 304.1308. Found 304.1318 (3.3 ppm error).

**Compound 18 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**

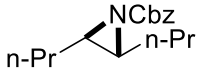





(*E*)-oct-4-ene

**Compound 19**: Commercially available.




benzyl (2*R**,3*R**)-2,3-dipropylaziridine-1-carboxylate

**Compound 20**: Synthesized using **General Procedure B** on a 2 mmol scale; Purified using 100% $CH_2Cl_2$ on silica gel; Isolated and characterized as the single diastereomer shown; (colorless oil, 0.385 g, 1.47 mmol, 74% yield).

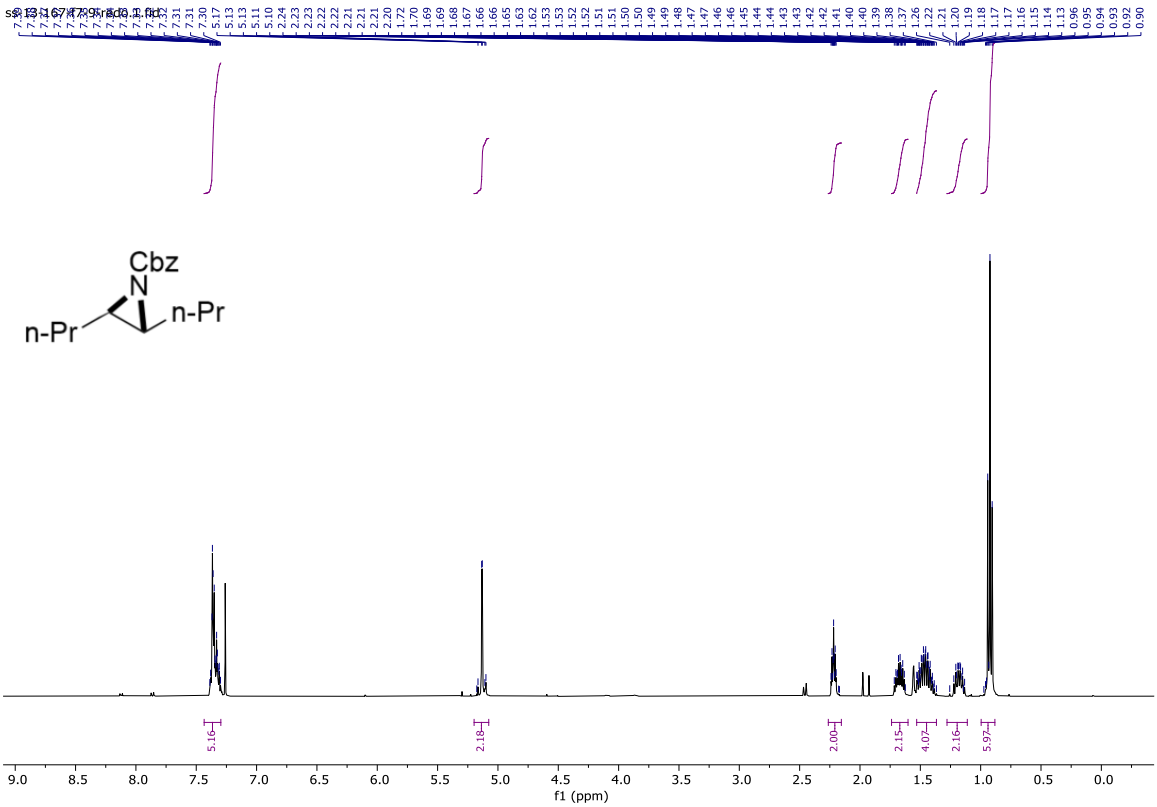
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 5H), 5.20 – 5.08 (m, 2H), 2.26 – 2.15 (m, 2H), 1.67 (ddt, *J* = 14.0, 9.2, 5.3 Hz, 2H), 1.53 – 1.37 (m, 4H), 1.18 (ddt, *J* = 13.3, 8.9, 6.6 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 6H).

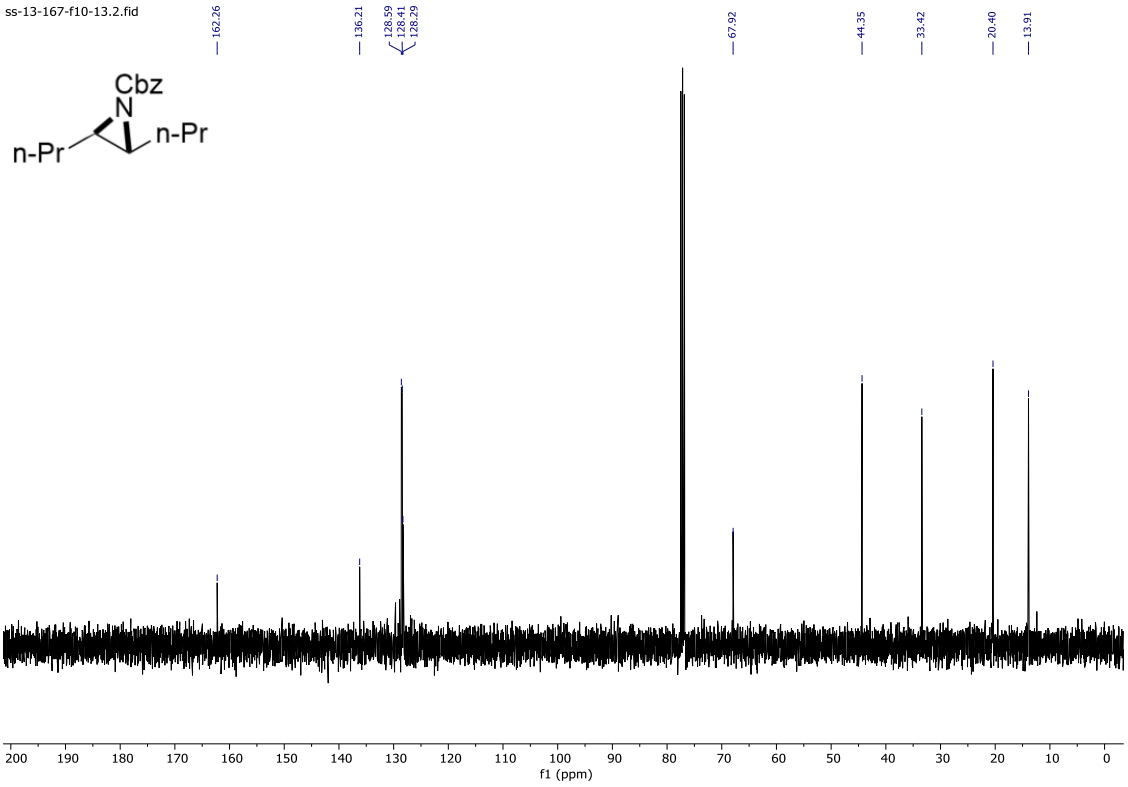
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 162.2, 136.2, 128.5, 128.4, 128.2, 67.9, 44.3, 33.4, 20.4, 13.9.

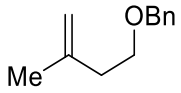
IR ν 2959, 2932, 1716, 1455, 1379, 1305, 1193, 1063 $cm^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{16}H_{23}NNaO_2^+$ 284.1621. Found 284.1604 (6 ppm error).

**Compound 20 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**

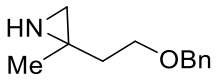





(((3-methylbut-3-en-1-yl)oxy)methyl)benzene

**Compound 21**: This compound has been synthesized and characterized in *Org. Lett.* **2019**, *21*, 9759–9762.




2-(2-(benzyloxy)ethyl)-2-methylaziridine

**Compound 22**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; Purified using sequential flushes of EtOAc, acetone, and methanol on Florisil (60 – 100 mesh); (yellow oil, 0.252 g, 1.32 mmol, 66% yield).

$^{1}$H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.24 (m, 5H), 4.54 – 4.45 (m, 2H), 3.60 – 3.58 (m, 2H), 1.82 – 1.71 (m, 2H), 1.62 (s, 1H), 1.52 (s, 1H), 1.24 (s, 3H), 0.58 (br s, 1 H).

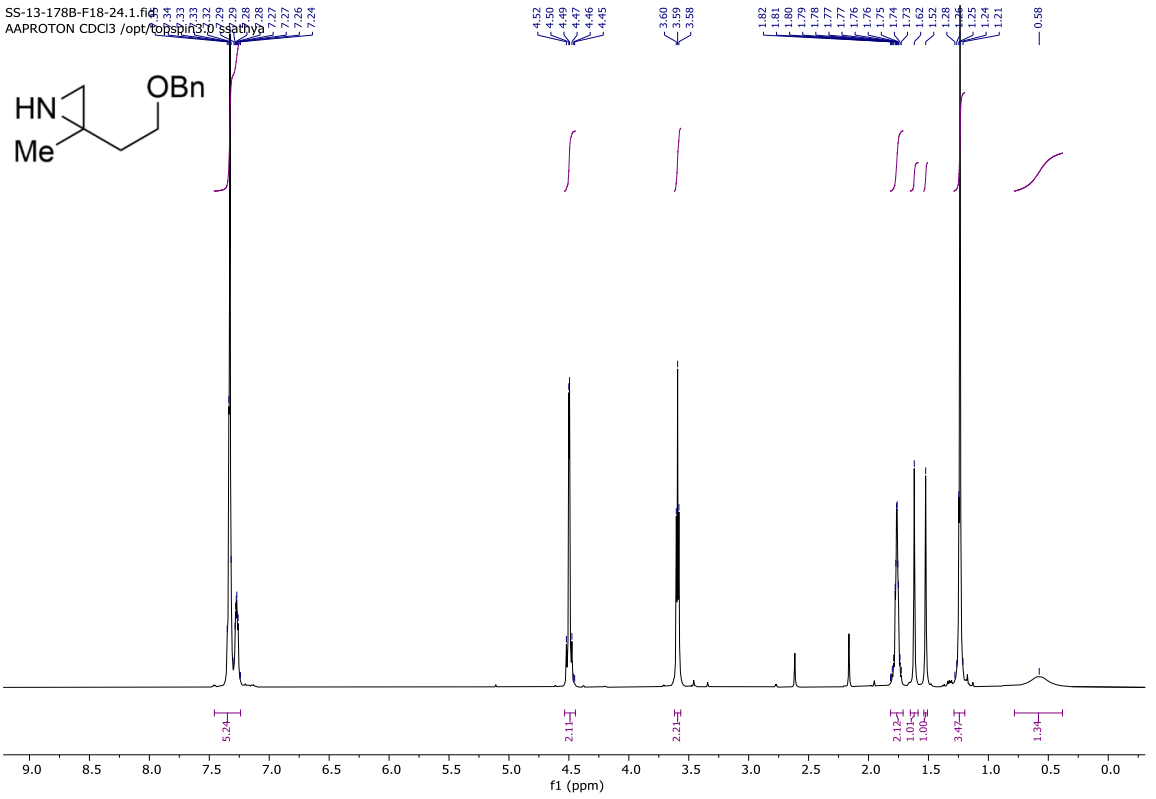
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 138.4, 128.4, 127.68, 127.66, 73.1, 67.8, 38.4, 33.1, 32.7, 23.4.

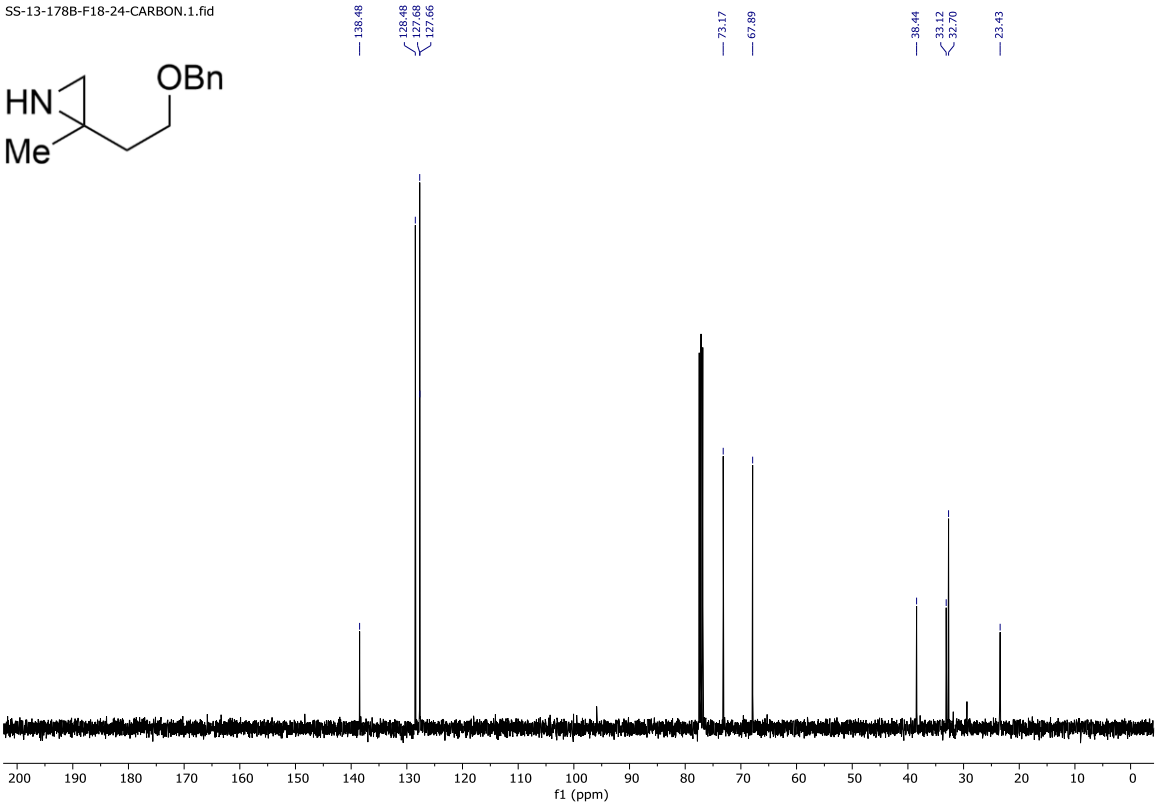
IR ν 3292, 2862, 1698, 1454, 1363, 1201, 1104 $cm^{-1}$.

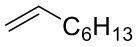
HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{12}H_{18}NO^+$ 192.1383. Found 192.1392 (4.7 ppm error).

Our data matches what has been reported in *Angew. Chem. Int. Ed.*, **2017**, *56*, 12654 – 12657.

**Compound 22 ($CDCl_3$, $^1H$ NMR: 600 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**

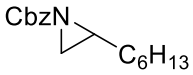





oct-1-ene

**Compound 23**: Commercially available.




benzyl 2-hexylaziridine-1-carboxylate

**Compound 24**: Synthesized using **General Procedure B** on a 2 mmol scale; Purified using 100% $CH_2Cl_2$ on silica gel; (colorless oil, 0.356 g, 1.36 mmol, 68% yield).

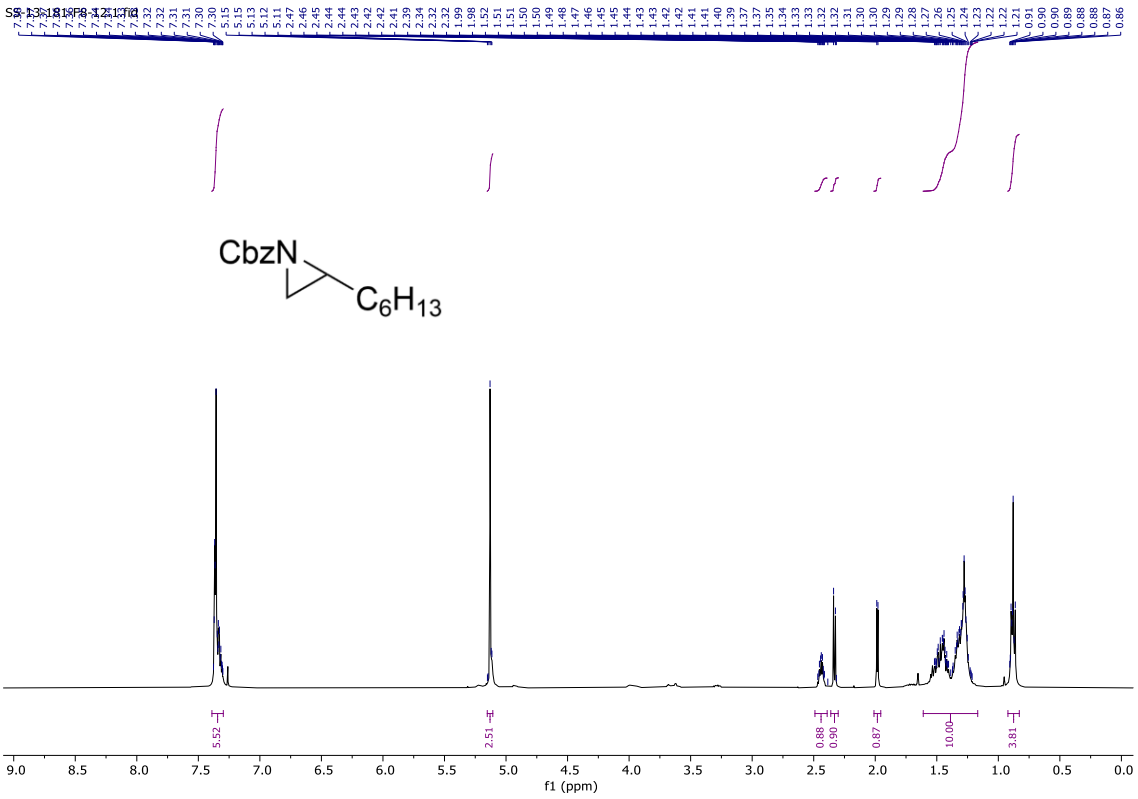
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 5H), 5.18 – 5.10 (m, 2H), 2.43 (td, *J* = 6.2, 3.8 Hz, 1H), 2.33 (d, *J* = 6.1 Hz, 1H), 1.98 (d, *J* = 3.8 Hz, 1H), 1.61 – 1.17 (m, 10H), 0.92 – 0.83 (m, 3H).

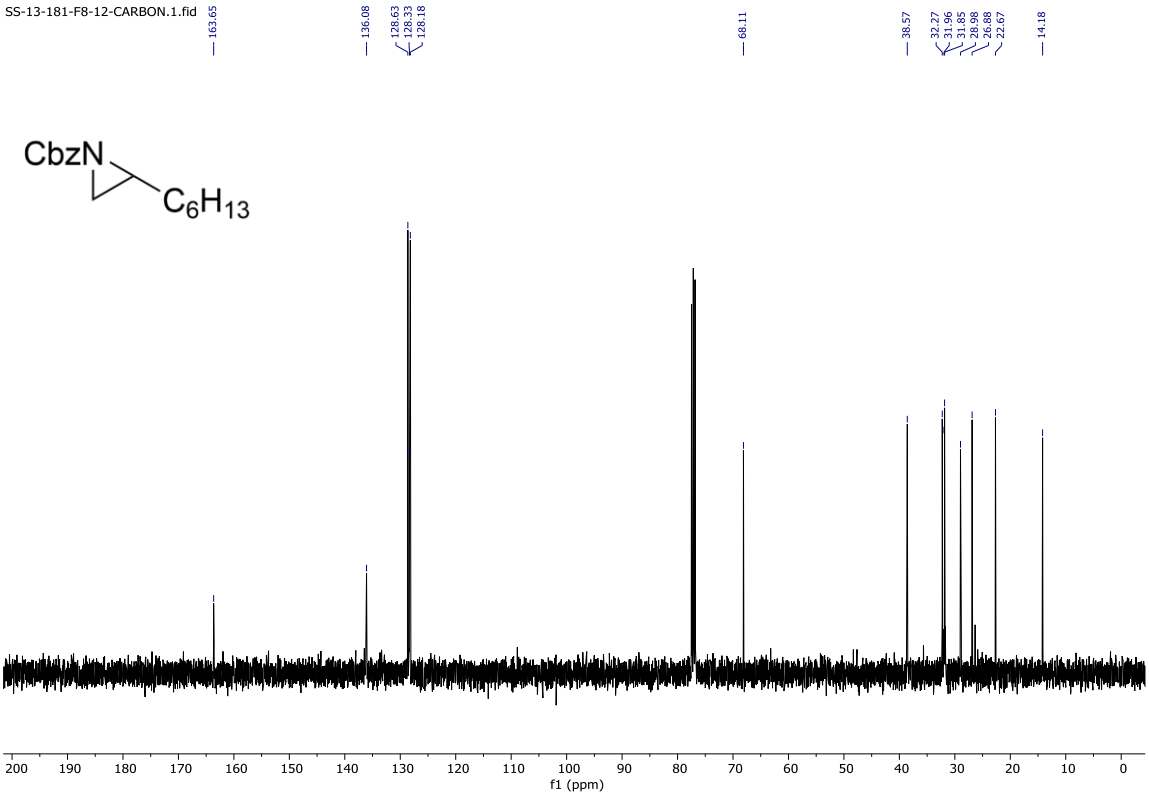
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 163.6, 136.0, 128.6, 128.3, 128.1, 68.1, 38.5, 32.2, 31.9, 31.8, 28.9, 26.8, 22.6, 14.1.

IR ν 2929, 1723, 1467, 1414, 1380, 1297, 1209, 1150 $cm^{-1}$.

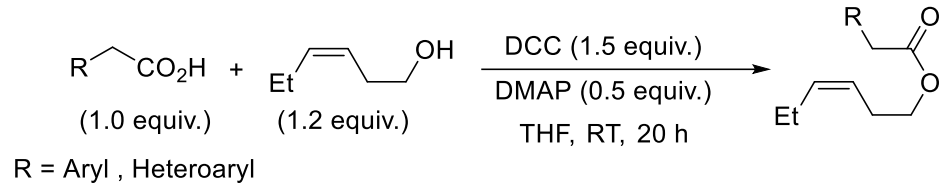
HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{16}H_{24}NO_2^+$ 262.1802. Found 262.1803 (0.4 ppm error).

**Compound 24 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**

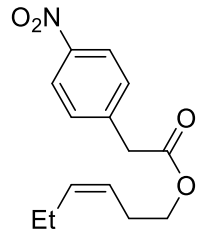


**General Procedure C (Starting Material Preparation)**




A round-bottom flask equipped with a magnetic stir bar was charged with the aryl or heteroaryl acetic acid (10.0 mmol, 1.0 equiv.), *(cis)*-3-hexen-1-ol (1.2 g, 12 mmol, 1.2 equiv.), N,N'-dicyclohexylcarbodiimide (DCC) (3.1 g, 15 mmol, 1.5 equiv.), and THF (37 mL, reaction concentration = 0.27 M). 4-Dimethylaminopyridine (DMAP) (0.610 g, 5 mmol, 0.5 equiv.) was then added at room temperature, and the reaction mixture was stirred for 20 hours. Following this time, the reaction mixture was transferred to a separatory funnel and diluted with ethyl acetate (100 mL). The organic layer was washed once with 1 M aqueous HCl solution (100 mL), collected, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (specific elution conditions are provided in the characterization data for each compound).




(*Z*)-hex-3-en-1-yl 2-(4-nitrophenyl)acetate

**Compound 25**: Synthesized using **General Procedure C** on a 10 mmol scale; Purified using a gradient of 0 to 50% EtOAc/hexanes on silica gel; (yellow solid, 1.36 g, 5.2 mmol, 52% yield).

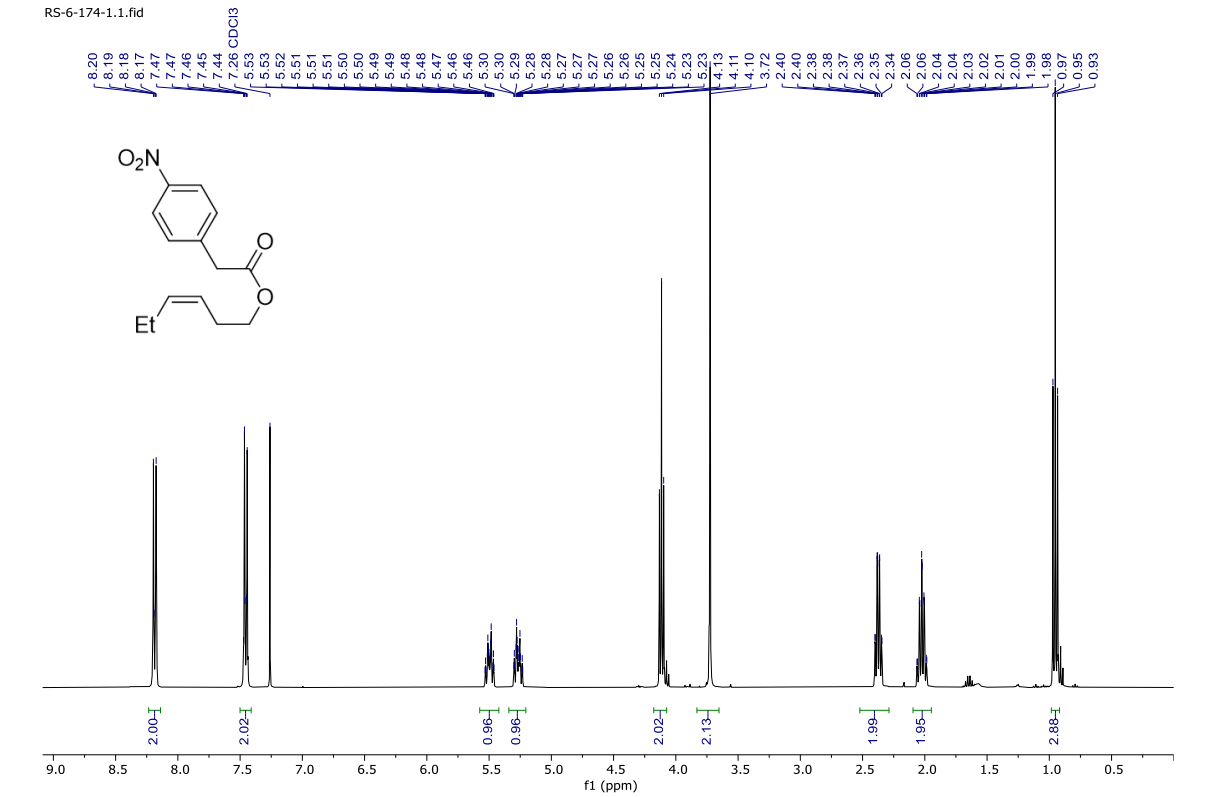
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.14 (m, 2H), 7.50 – 7.41 (m, 2H), 5.58 – 5.42 (m, 1H), 5.34 – 5.20 (m, 1H), 4.11 (t, *J* = 6.9 Hz, 2H), 3.72 (s, 2H), 2.37 (qd, *J* = 7.2, 1.5 Hz, 2H), 2.02 (pd, *J* = 7.5, 1.6 Hz, 2H), 0.95 (t, *J* = 7.6 Hz, 3H).

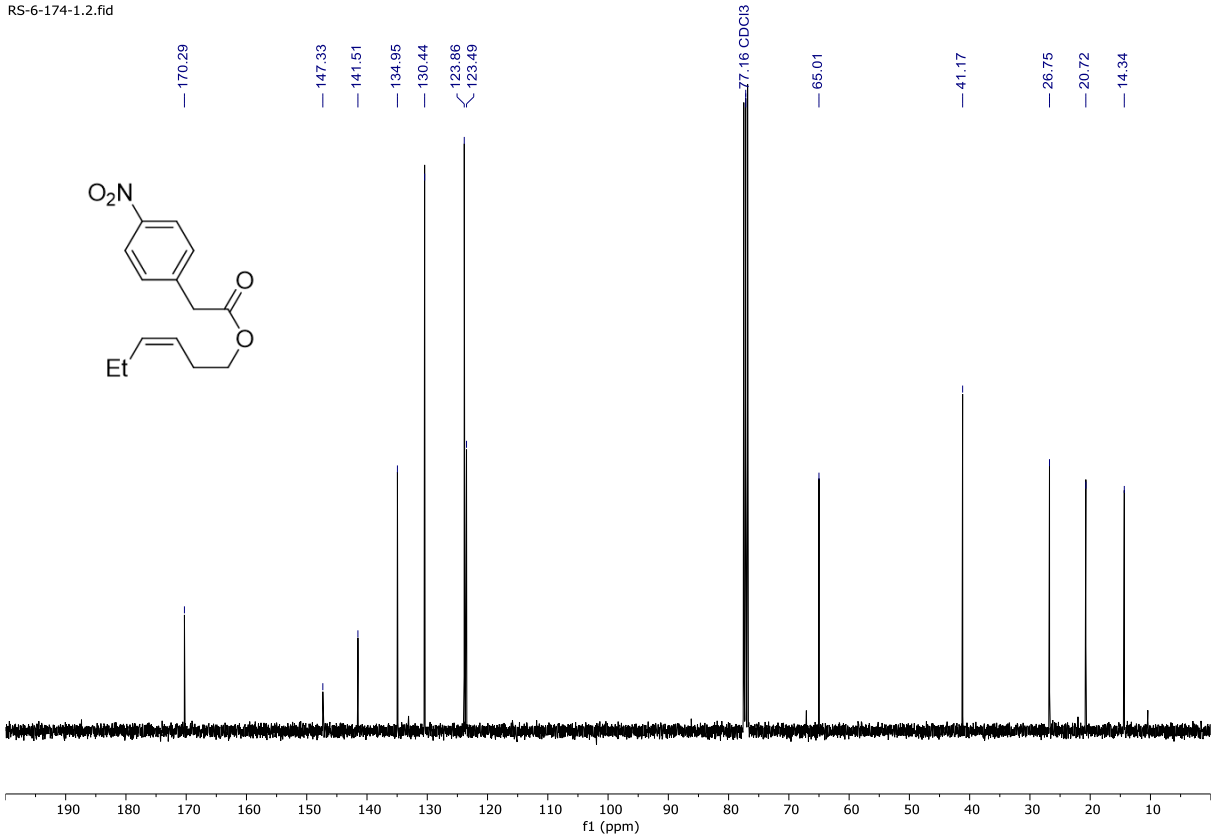
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.2, 147.3, 141.5, 134.9, 130.4, 123.8, 123.4, 65.0, 41.1, 26.7, 20.7, 14.3.

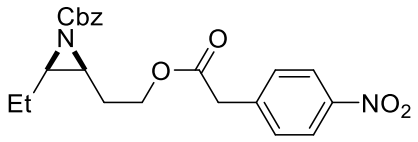
IR ν 2965, 2333, 1734, 1608, 1522, 1349, 1265, 1164, 739 $cm^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{14}H_{17}NO_4Na^+$ 286.1055. Found 286.1029 (9.1 ppm error).

**Compound 25 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






benzyl (2*R**,3*S**)-2-ethyl-3-(2-(2-(4-nitrophenyl)acetoxy)ethyl)aziridine-1-carboxylate

**Compound 26**: Synthesized using **General Procedure B** on a 2 mmol scale; Purified using a gradient of 0 to 50% EtOAc/hexanes on silica gel; Isolated and characterized as the single diastereomer shown; (colorless oil, 0.247 g, 0.6 mmol, 30% yield).

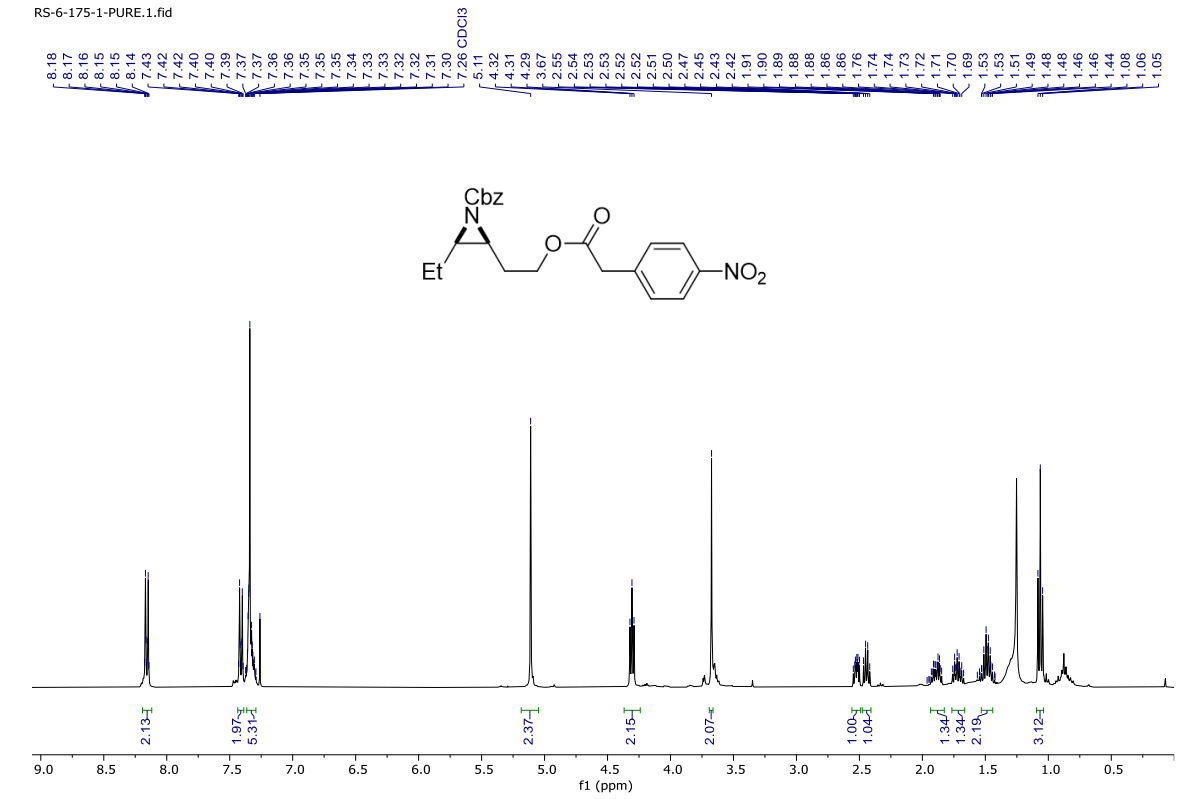
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.12 (m, 2H), 7.44 – 7.39 (m, 2H), 7.36 – 7.29 (m, 5H), 5.18 – 5.04 (m, 2H), 4.37 – 4.24 (m, 2H), 3.72 – 3.64 (m, 2H), 2.52 (ddd, *J* = 8.3, 6.5, 4.7 Hz, 1H), 2.47 – 2.39 (m, 1H), 1.89 (dtd, *J* = 14.0, 6.8, 4.6 Hz, 1H), 1.72 (ddt, *J* = 14.4, 8.3, 6.0 Hz, 1H), 1.54 – 1.44 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H).

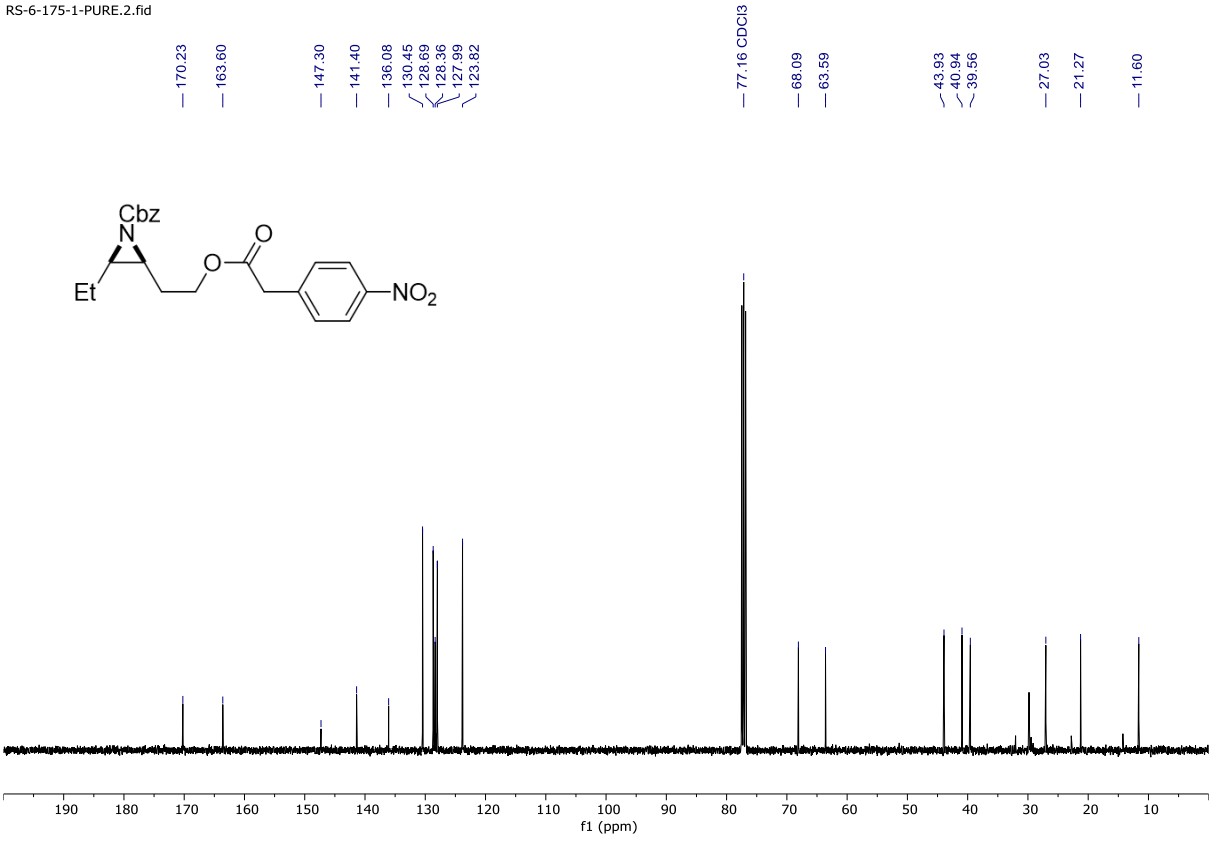
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.2, 163.6, 147.3, 141.4, 136.0, 130.4, 128.6, 128.3, 127.9, 123.8, 68.0, 63.5, 43.9, 40.9, 39.5, 27.0, 21.2, 11.6.

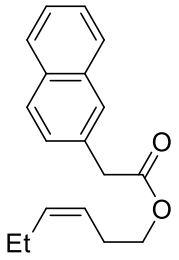
IR ν 3054, 2986, 2306, 1733, 1522, 1265, 704 $cm^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{22}H_{24}N_2O_6Na^+$ 435.1532. Found 435.1524 (1.8 ppm error).

**Compound 26 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






(*Z*)-hex-3-en-1-yl 2-(naphthalen-2-yl)acetate

**Compound 27**: Synthesized using **General Procedure C** on a 10 mmol scale; Purified using a gradient of 0 to 60% EtOAc/hexanes on silica gel; (pale yellow oil, 1.82 g, 6.8 mmol, 68% yield).

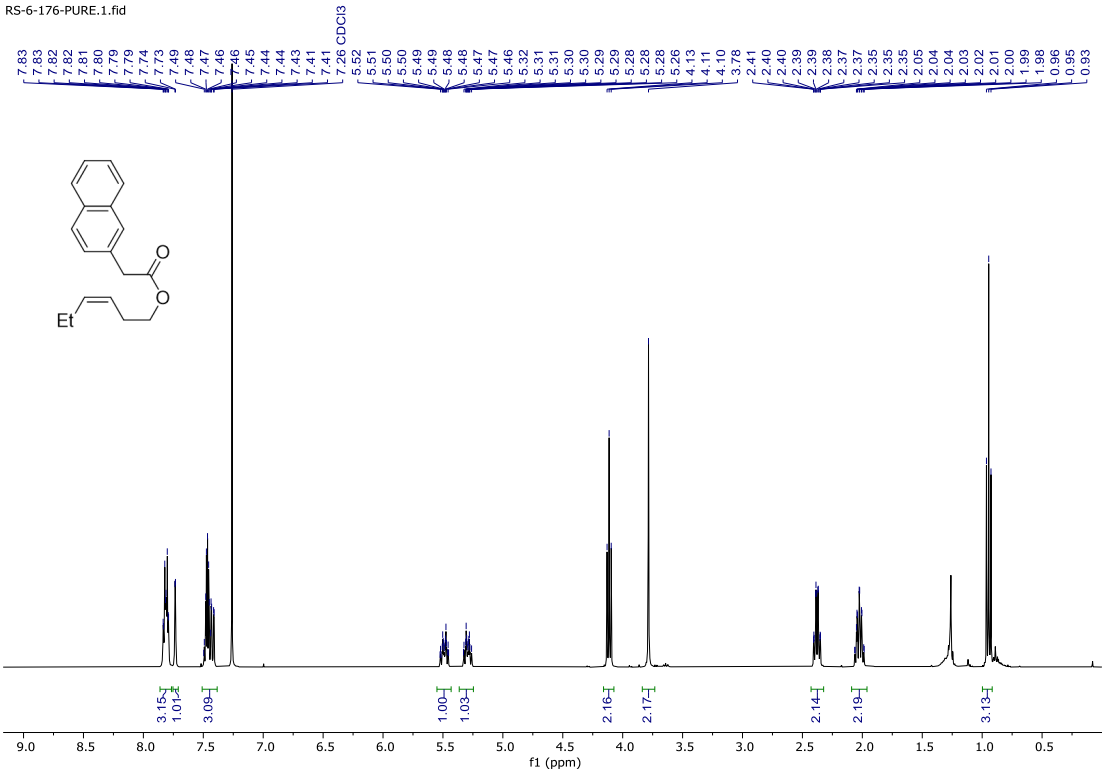
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 3H), 7.73 (d, *J* = 1.7 Hz, 1H), 7.51 – 7.38 (m, 3H), 5.55 – 5.43 (m, 1H), 5.36 – 5.25 (m, 1H), 4.11 (t, *J* = 6.9 Hz, 2H), 3.78 (s, 2H), 2.43 – 2.32 (m, 2H), 2.09 – 1.96 (m, 2H), 0.95 (t, *J* = 7.6 Hz, 3H).

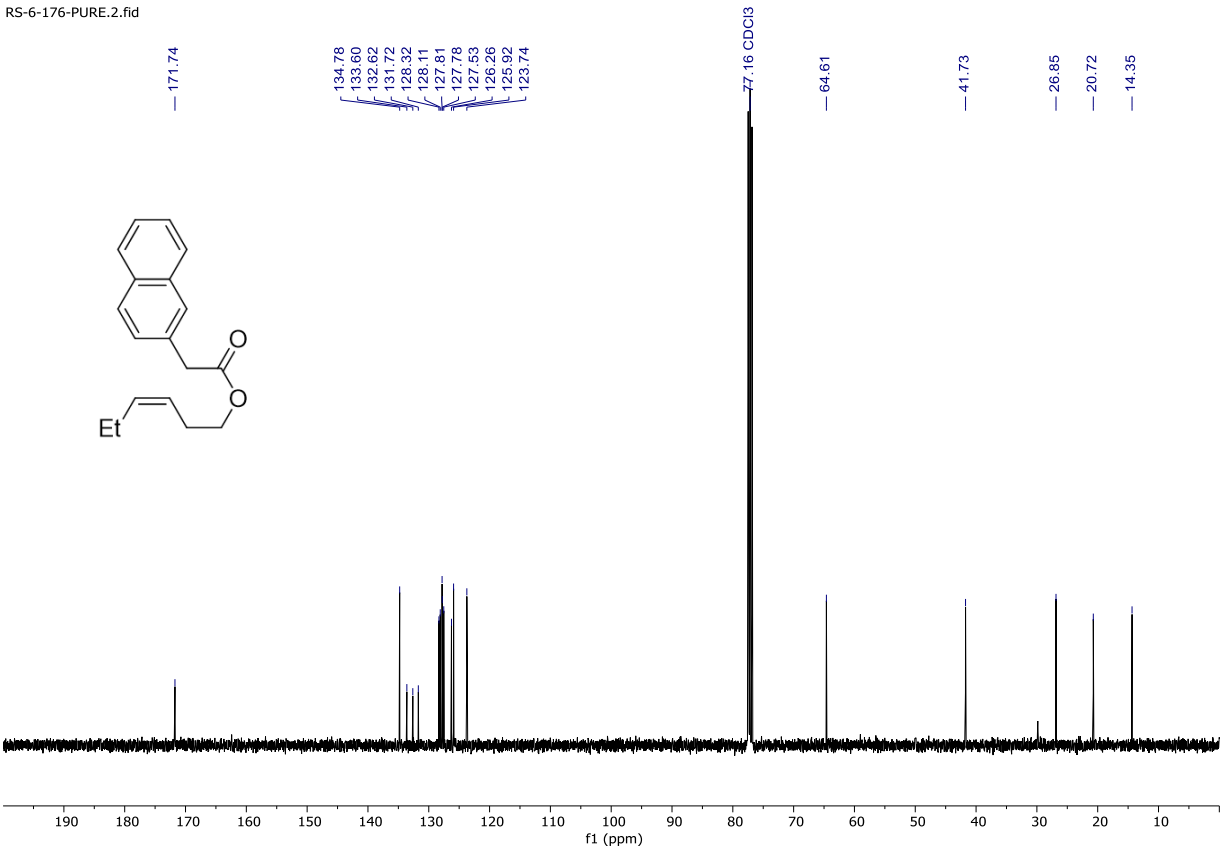
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.7, 134.7, 133.6, 132.6, 131.7, 128.3, 128.1, 127.8, 127.7, 127.5, 126.2, 125.9, 123.7, 64.6, 41.7, 26.8, 20.7, 14.3.

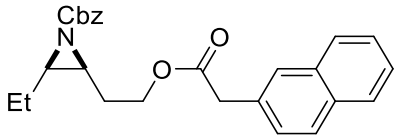
IR ν 2965, 2117, 1735, 1508, 1265, 746 $cm^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{18}H_{20}O_2Na^+$ 291.1361. Found 291.1370 (3.1 ppm error).

**Compound 27 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






Benzyl (2*R**,3*S**)-2-ethyl-3-(2-(2-(naphthalen-2-yl)acetoxy)ethyl)aziridine-1-carboxylate

**Compound 28**: Synthesized using **General Procedure B** on a 2 mmol scale; Purified using a gradient of 0 to 40% EtOAc/hexanes on silica gel; Isolated and characterized as the single diastereomer shown; (colorless oil, 0.417 g, 1.0 mmol, 50% yield).

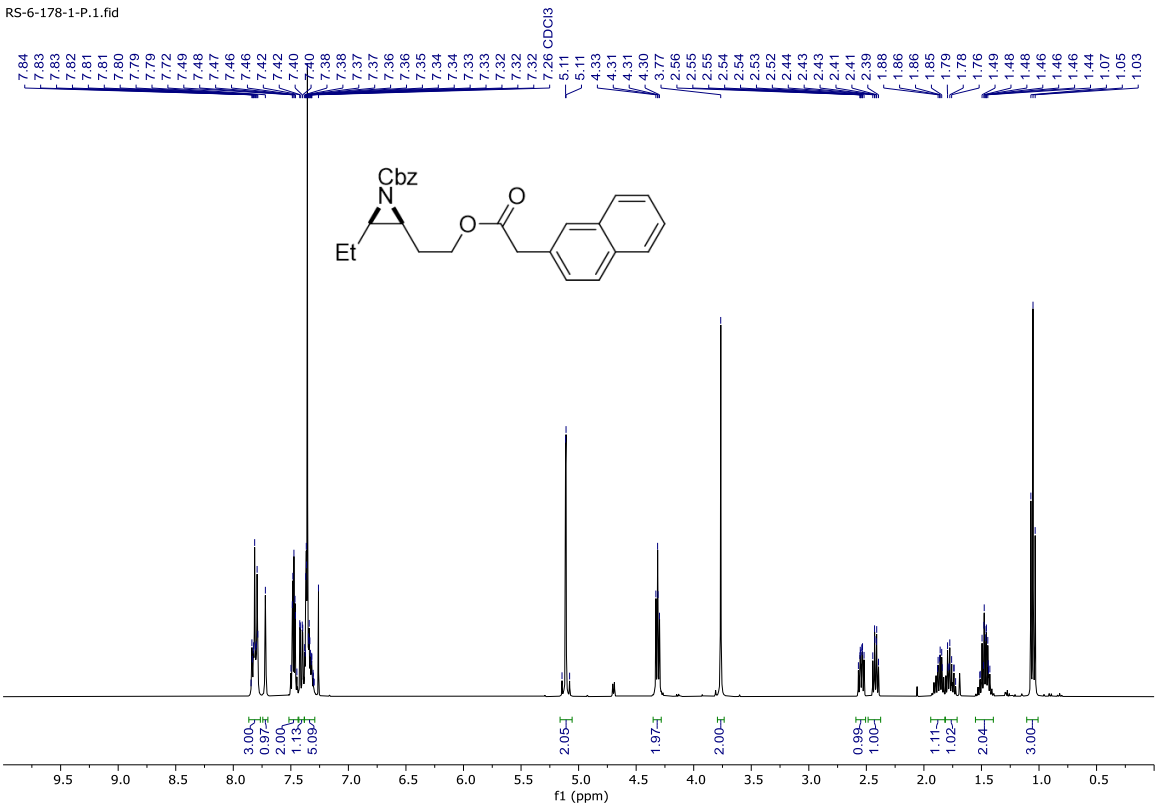
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 3H), 7.72 (s, 1H), 7.52 – 7.44 (m, 2H), 7.41 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.38 – 7.29 (m, 5H), 5.16 – 5.06 (m, 2H), 4.35 – 4.29 (m, 2H), 3.81 – 3.73 (m, 2H), 2.54 (ddd, *J* = 7.8, 6.5, 5.3 Hz, 1H), 2.42 (dt, *J* = 7.3, 6.2 Hz, 1H), 1.94 – 1.82 (m, 1H), 1.81 – 1.71 (m, 1H), 1.55 – 1.40 (m, 2H), 1.05 (t, *J* = 7.5 Hz, 3H).

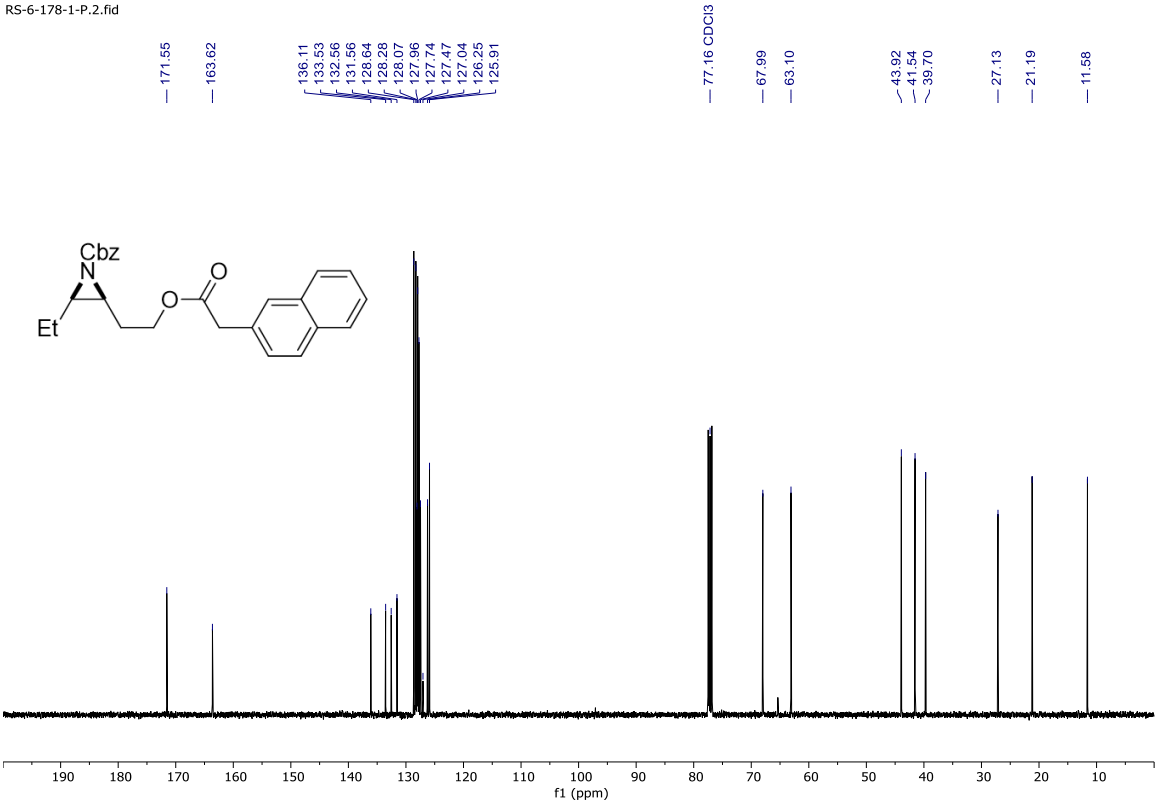
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 171.5, 163.6, 136.1, 133.5, 132.5, 131.5, 128.6, 128.2, 128.0, 127.9, 127.7, 127.4, 127.0, 126.2, 125.9, 67.9, 63.1, 43.9, 41.5, 39.7, 27.1, 21.1, 11.5.

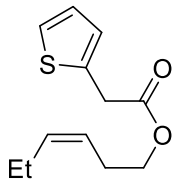
IR ν 3054, 2970, 1723, 1455, 1380, 1265, 1221, 749 $cm^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{26}H_{28}NO_4^+$ 418.2018. Found 418.2009 (2.2 ppm error).

**Compound 28 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






(*Z*)-hex-3-en-1-yl 2-(thiophen-2-yl)acetate

**Compound 29**: Synthesized using **General Procedure C** on a 10 mmol scale; Purified using a gradient of 0 to 50% EtOAc/hexanes on silica gel; (colorless oil, 1.41 g, 6.3 mmol, 63% yield).

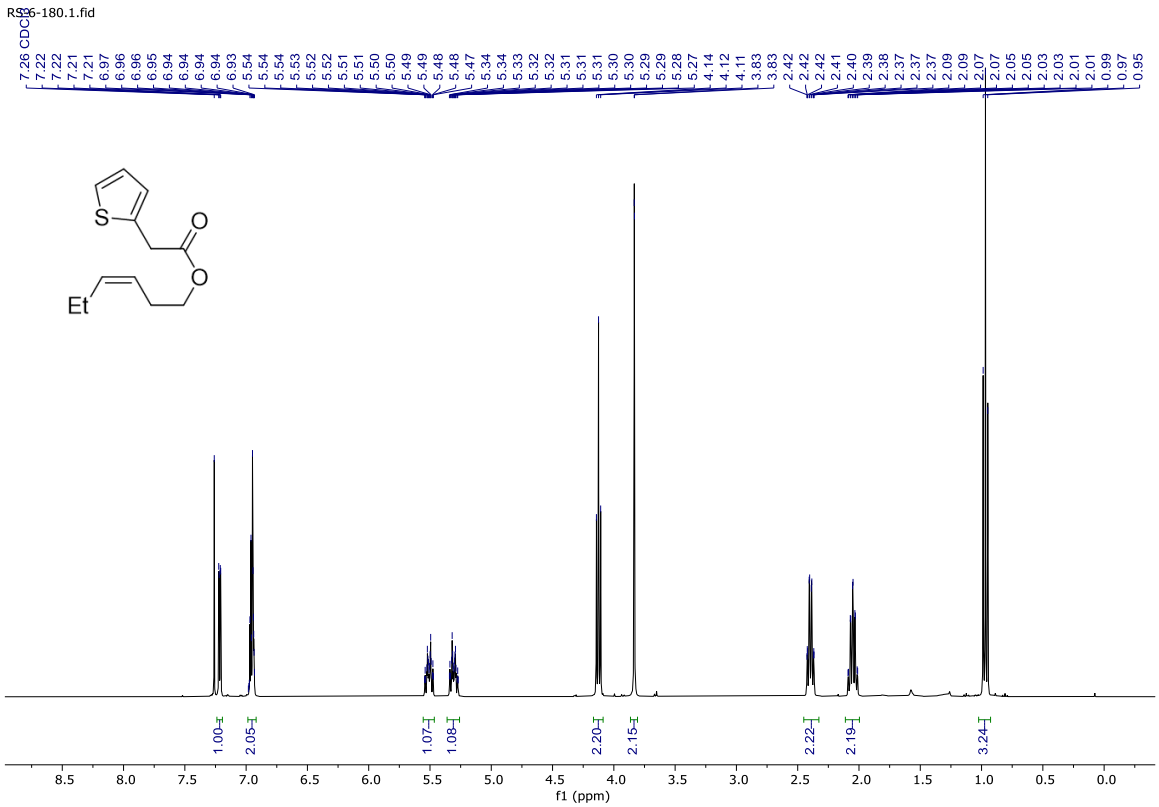
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 4.9, 1.5 Hz, 1H), 6.99 – 6.92 (m, 2H), 5.56 – 5.46 (m, 1H), 5.36 – 5.26 (m, 1H), 4.12 (t, *J* = 6.9 Hz, 2H), 3.83 (d, *J* = 0.9 Hz, 2H), 2.40 (qd, *J* = 7.2, 1.9 Hz, 2H), 2.05 (pd, *J* = 7.5, 1.5 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H).

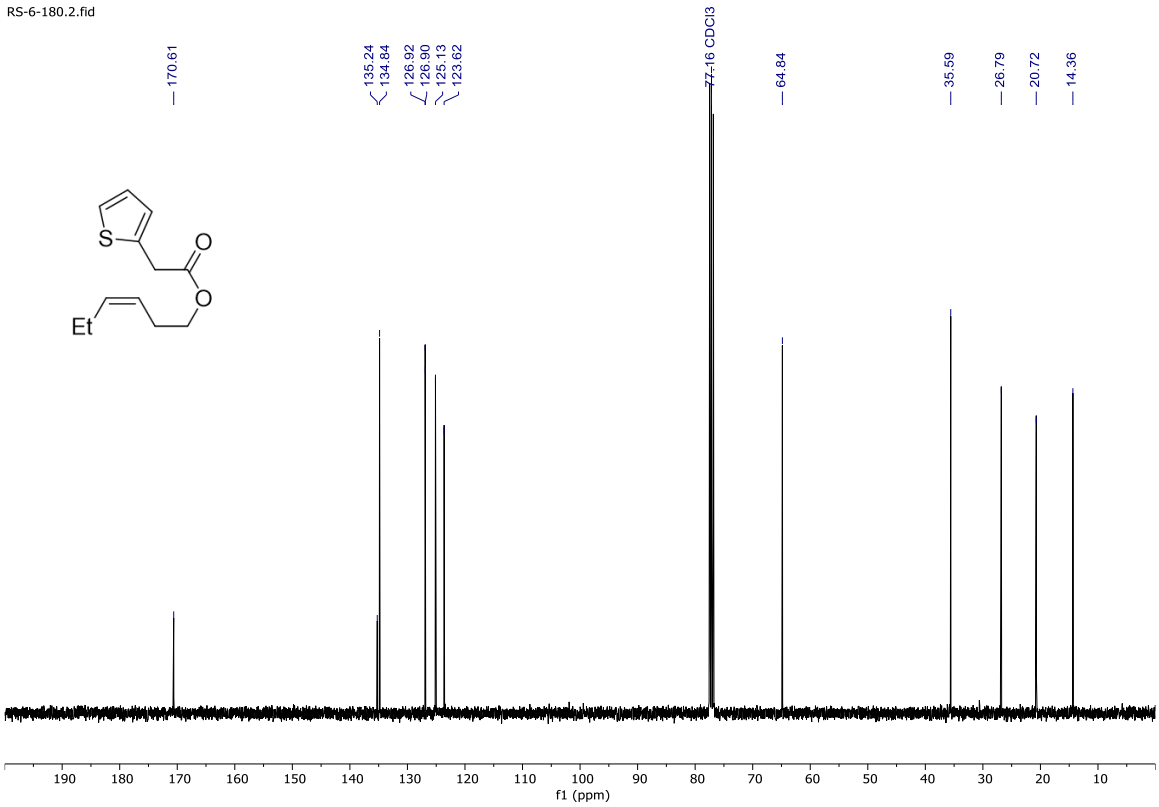
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.6, 135.2, 134.8, 126.92, 126.90, 125.1, 123.6, 64.8, 35.5, 26.7, 20.7, 14.3.

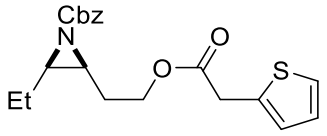
IR ν 3054, 2966, 2306, 1735, 1265, 1172, 742 $cm^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{12}H_{17}O_2S^+$ 225.0949. Found 225.0950 (0.4 ppm error).

**Compound 29 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






benzyl (2*R**,3*S**)-2-ethyl-3-(2-(2-(thiophen-2-yl)acetoxy)ethyl)aziridine-1-carboxylate

**Compound 30**: Synthesized using **General Procedure B** on a 2 mmol scale; Purified using a gradient of 0 to 10% EtOAc/hexanes on silica gel; Isolated and characterized as the single diastereomer shown; (colorless oil, 0.388 g, 1.04 mmol, 52% yield).

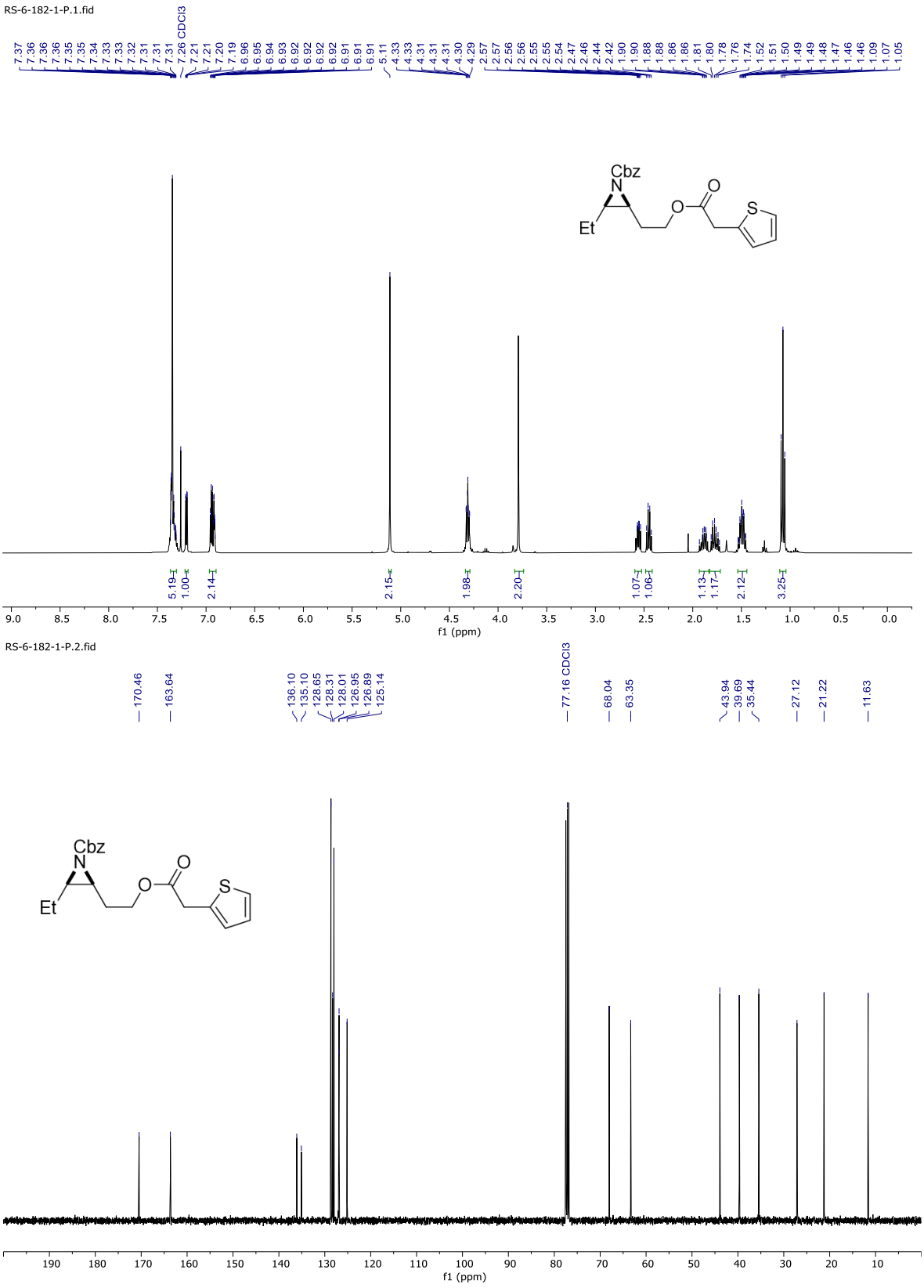
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 7.20 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.97 – 6.90 (m, 2H), 5.12 – 5.09 (m, 2H), 4.34 – 4.28 (m, 2H), 3.83 – 3.74 (m, 2H), 2.59 – 2.53 (m, 1H), 2.48 – 2.41 (m, 1H), 1.93 – 1.83 (m, 1H), 1.83 – 1.72 (m, 1H), 1.54 – 1.44 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H).

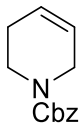
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.4, 163.6, 136.1, 135.1, 128.6, 128.3, 128.0, 126.9, 126.8, 125.1, 68.0, 63.3, 43.9, 39.6, 35.4, 27.1, 21.2, 11.6.

IR ν 2970, 2306, 1719, 1267, 1219, 749 cm$^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{20}H_{23}NO_4SNa^+$ 396.1246. Found 396.1212 (8.6 ppm error).

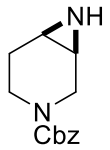
**Compound 30 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






benzyl 3,6-dihydropyridine-1(2*H*)-carboxylate

**Compound 31**: Commercially available.




benzyl (1*S**,6*R**)-3,7-diazabicyclo[4.1.0]heptane-3-carboxylate

**Compound 32**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; Purified using sequential flushes of $CH_2Cl_2$, EtOAc, acetone, and methanol on Florisil (60 – 100 mesh); isolated and characterized as the single diastereomer shown; (colorless oil, 0.175 g, 0.753 mmol, 38% yield).

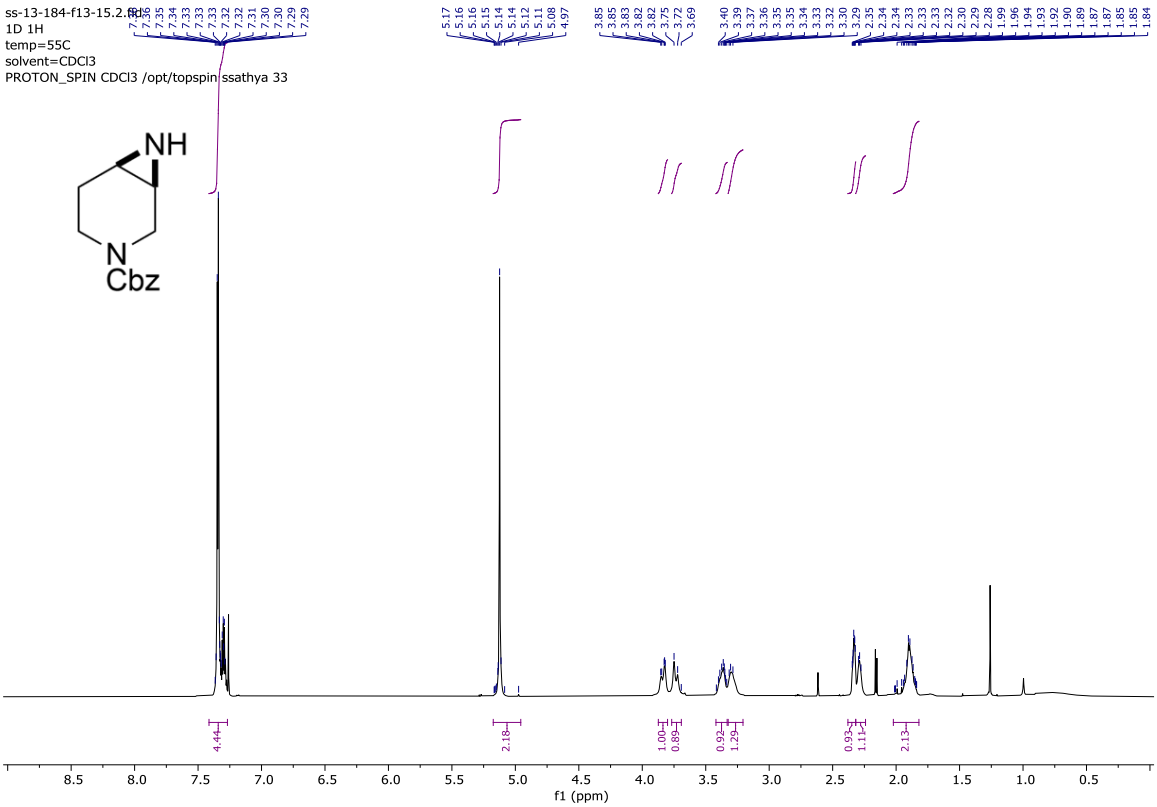
$^1$H NMR (500 MHz, $CDCl_3$, 55 °C) δ 7.41 – 7.27 (m, 5H), 5.24 – 5.03 (m, 2H), 3.87 – 3.80 (m, 1H), 3.74 (d, $J$ = 14.1 Hz, 1H), 3.42 – 3.33 (m, 1H), 3.32 – 3.21 (m, 1H), 2.33 (ddd, $J$ = 6.0, 3.8, 1.9 Hz, 1H), 2.32 – 2.24 (m, 1H), 2.02 – 1.82 (m, 2H).

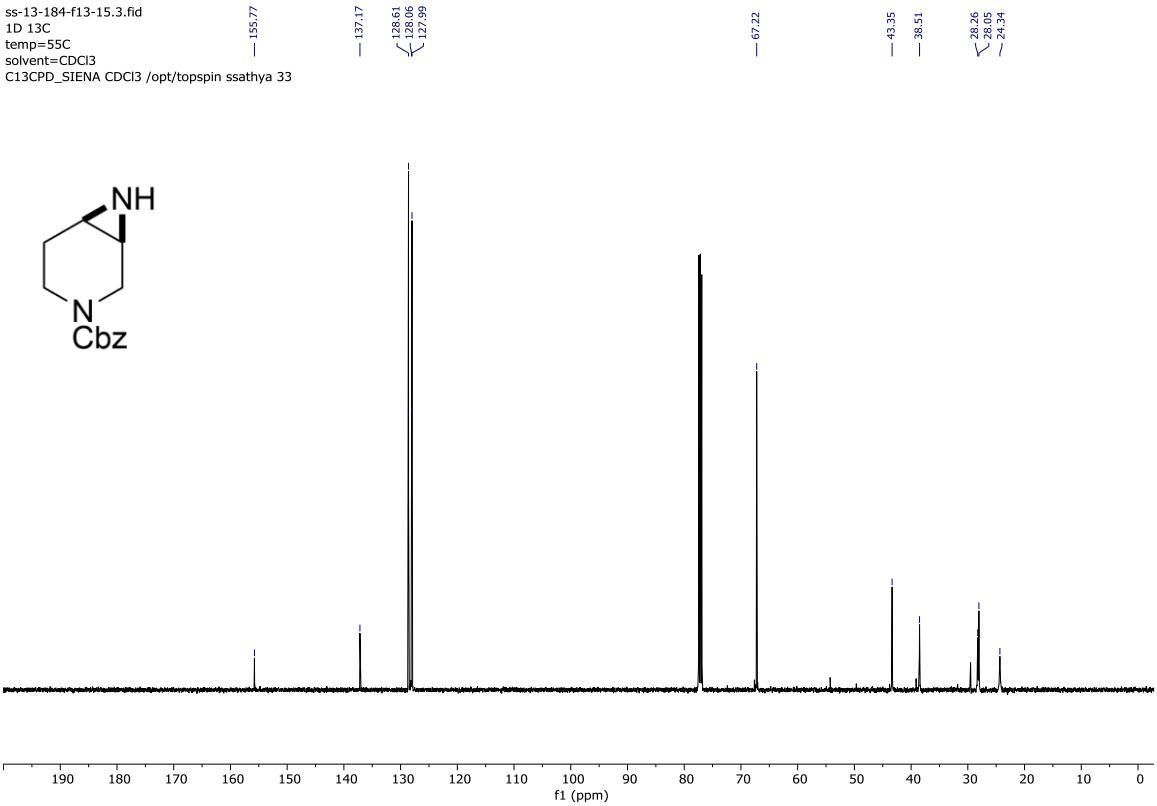
$^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$, 55 °C) δ 155.7, 137.1, 128.6, 128.0, 127.9, 67.2, 43.3, 38.5, 28.2, 28.0, 24.3.

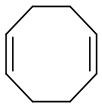
IR ν 3302, 2922, 1697, 1431, 1363, 1249, 1130 cm$^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{13}H_{17}N_2O_2^+$ 233.1285. Found 233.1264 (9 ppm error).

**Compound 32 ($CDCl_3$, $^1H$ NMR: 500 MHz, $^{13}C\{^1H\}$ NMR: 126 MHz, 55 °C)**

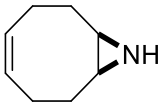




(1*Z*,5*Z*)-cycloocta-1,5-diene

**Compound 33**: Commercially available.




(1*R**,8*S**,*Z*)-9-azabicyclo[6.1.0]non-4-ene

**Compound 34**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; Purified using sequential flushes of $CH_2Cl_2$, EtOAc, acetone, and methanol on Florisil (60 – 100 mesh); isolated and characterized as the single diastereomer shown; (colorless oil, 0.143 g, 1.16 mmol, 58% yield).

$^1$H NMR (400 MHz, $CDCl_3$) δ 5.61 – 5.50 (m, 2H), 2.40 – 2.27 (m, 2H), 2.19 – 1.88 (m, 6H), 1.73 – 1.60 (m, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 129.3, 34.6, 29.2, 25.1.

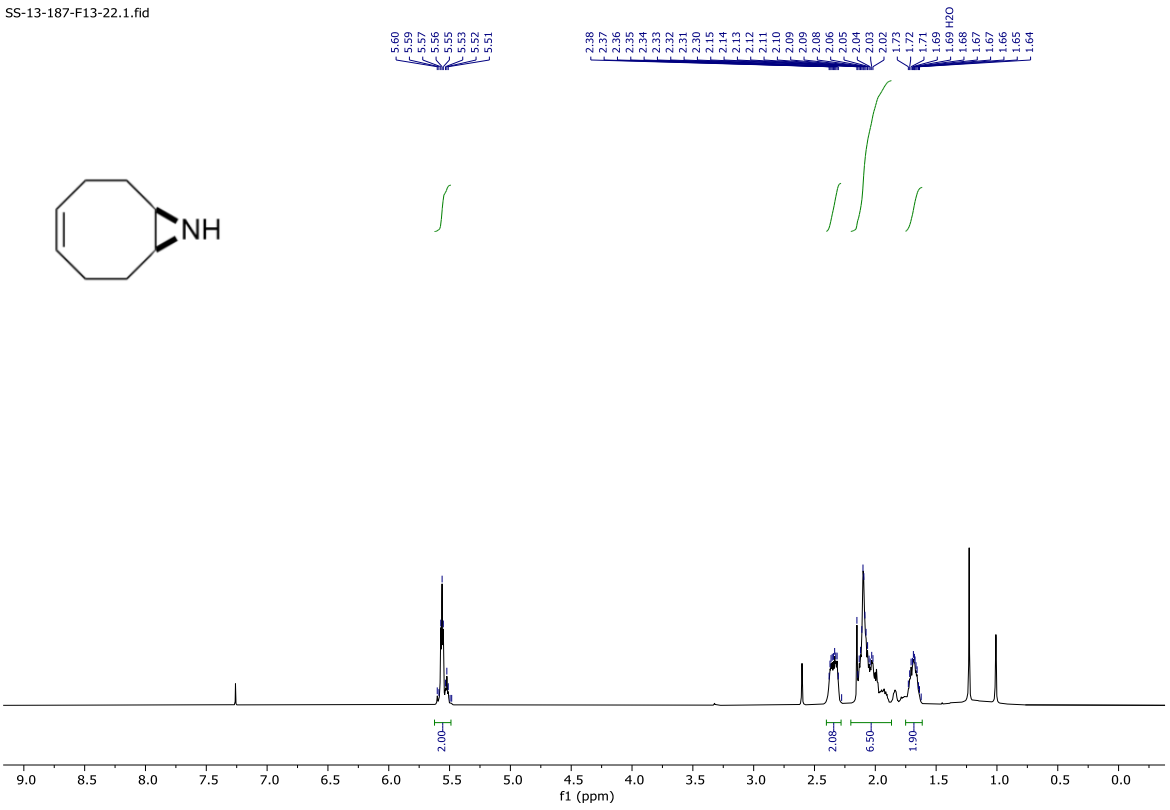
IR ν 3232, 2931, 1699, 1482, 1437, 1200, 937 $cm^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_8H_{14}N^+$ 124.1121. Found 124.1119 (1.6 ppm error).

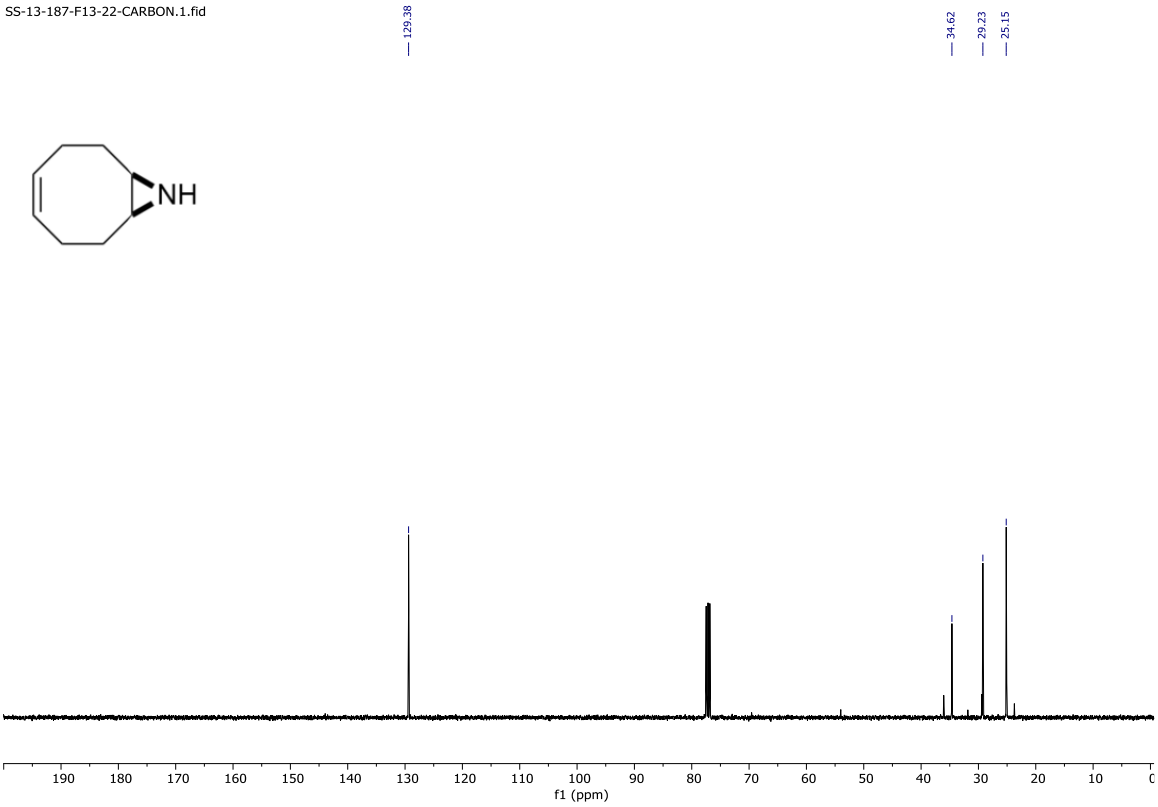
Our data agrees with what has been reported in *J. Org. Chem.* **2024**, *89*, 6263 – 6273.

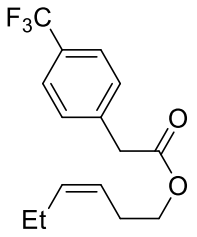
## Compound 34 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)

SS-13-187-F13-22.1.fid




SS-13-187-F13-22-CARBON.1.fid






(*Z*)-hex-3-en-1-yl 2-(4-(trifluoromethyl)phenyl)acetate

**Compound 35**: Synthesized using **General Procedure C** on a 10 mmol scale; Purified using a gradient of 0 to 60% EtOAc/hexanes on silica gel; (colorless oil, 1.60 g, 5.59 mmol, 56% yield).

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.45 – 7.36 (m, 2H), 5.55 – 5.44 (m, 1H), 5.32 – 5.20 (m, 1H), 4.11 (t, *J* = 6.9 Hz, 2H), 3.67 (s, 2H), 2.43 – 2.31 (m, 2H), 2.10 – 1.96 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H).

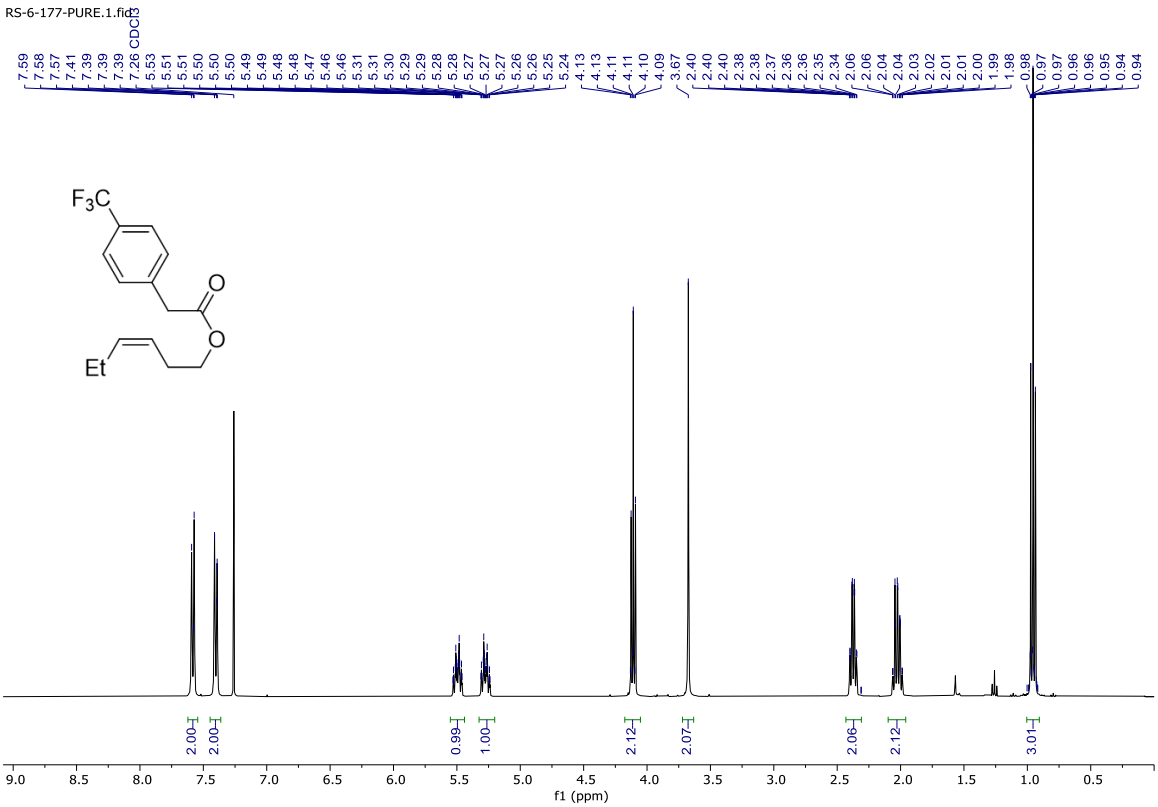
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.9, 138.1, 134.8, 129.8, 129.6 (q, *J* = 32.3 Hz), 125.6 (q, *J* = 3.9 Hz), 123.6, 123.2 (q, *J* = 264.6 Hz), 64.8, 41.2, 26.8, 20.7, 14.3.

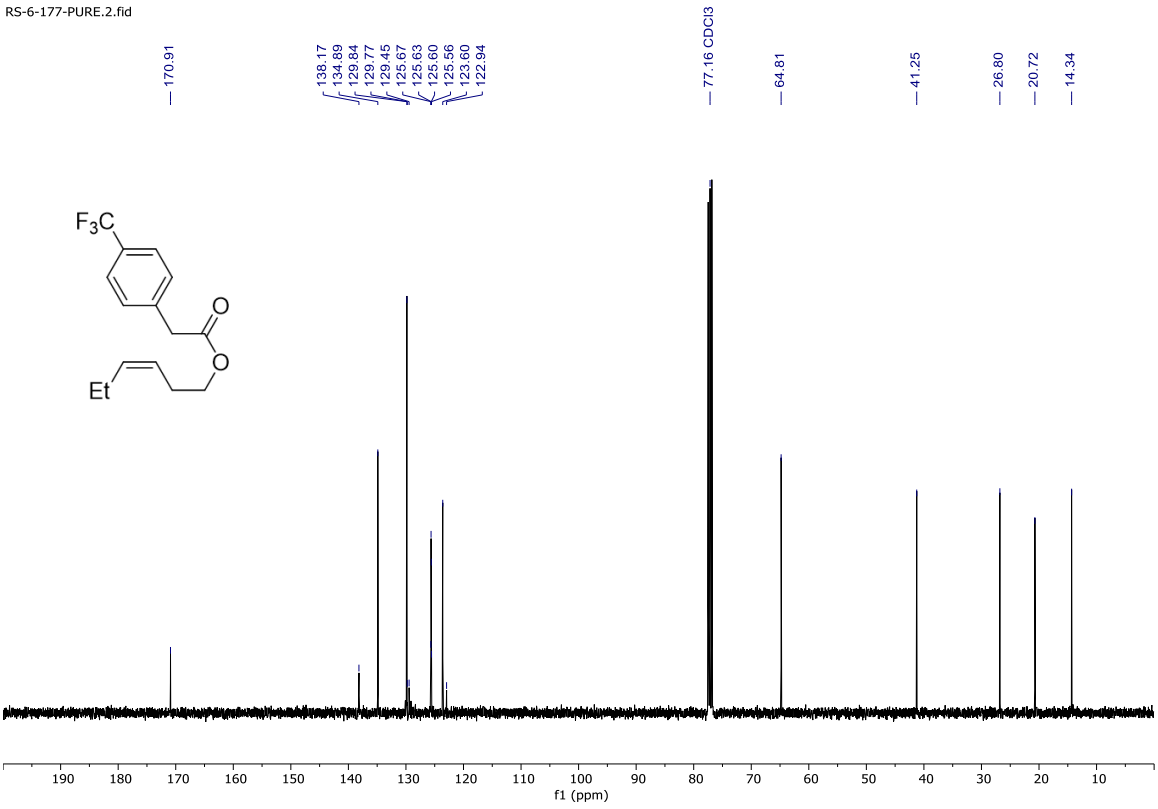
$^{19}$F{$^{1}$H} NMR (377 MHz, $CDCl_3$) δ -62.5.

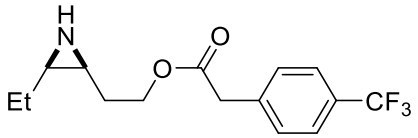
IR ν 3055, 2966, 2319, 1735, 1620, 1420, 1327, 1265, 1067, 742 $cm^{-1}$.

HRMS (ESI) m/z = $[M - H]^-$ Calcd $C_{15}H_{16}F_3O_2^-$ 285.1102. Found 285.1100 (0.7 ppm error).

**Compound 35 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






2-((2*S**,3*R**)-3-ethylaziridin-2-yl)ethyl 2-(4-(trifluoromethyl)phenyl)acetate

**Compound 36**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; Purified by column chromatography on Florisil (60 – 100 mesh) using a gradient of 0 to 50% ethyl acetate in hexanes, followed by flushing with 100% methanol; Isolated and characterized as the single diastereomer shown; (white solid, 0.421 g, 1.4 mmol, 70% yield).

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 4.32 – 4.07 (m, 2H), 3.72 – 3.48 (m, 2H), 2.02 – 1.92 (m, 1H), 1.91 – 1.84 (m, 1H), 1.73 (dq, *J* = 13.0, 5.9 Hz, 1H), 1.56 (dq, *J* = 13.7, 6.5 Hz, 1H), 1.38 – 1.23 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.81 (broad s, 1H).

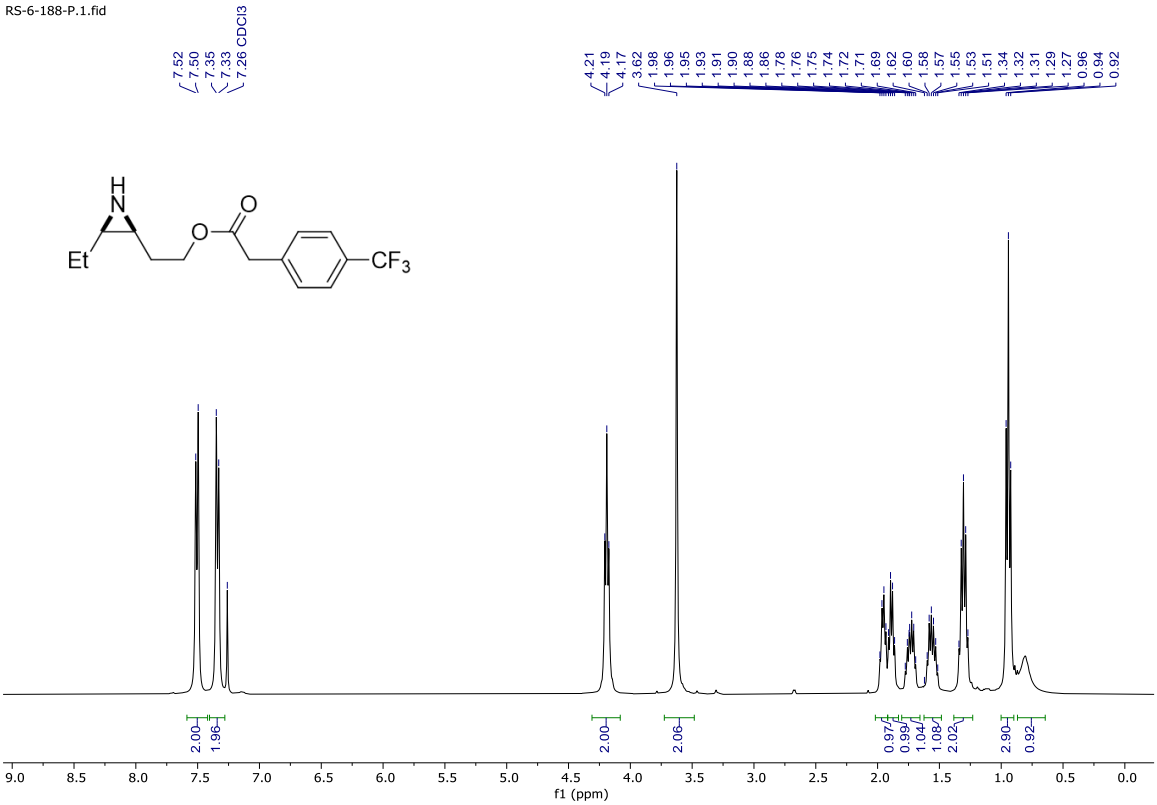
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.7, 138.0, 129.6, 129.3 (q, *J*= 32.3 Hz), 125.3 (q, *J* = 3.7 Hz), 122.7 (q, *J* = 272.7 Hz), 63.9, 40.9, 36.0, 31.6, 27.9, 21.9, 11.9.

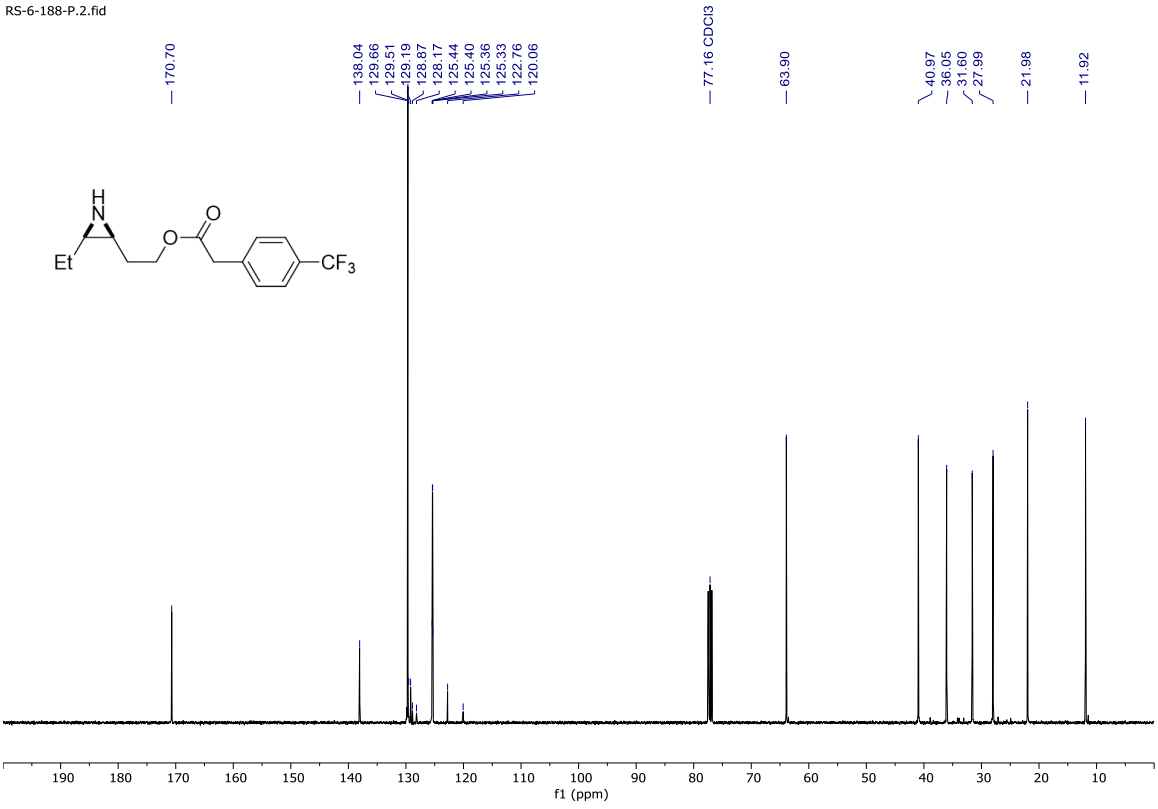
$^{19}$F{$^{1}$H} NMR (377 MHz, $CDCl_3$) δ -62.6.

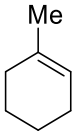
IR ν 2968, 2307, 1735, 1421, 1326, 1265, 1067, 1020, 739 $cm^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{15}H_{19}F_3NO_2^+$ 302.1368. Found 302.1360 (2.6 ppm error).

**Compound 36 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**

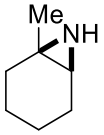





1-methylcyclohex-1-ene

**Compound 37**: Commercially available.




(1*R**,6*S**)-1-methyl-7-azabicyclo[4.1.0]heptane

**Compound 38**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; (light yellow oil, 55% yield, estimated by $^{1}$H NMR integration against an internal standard).

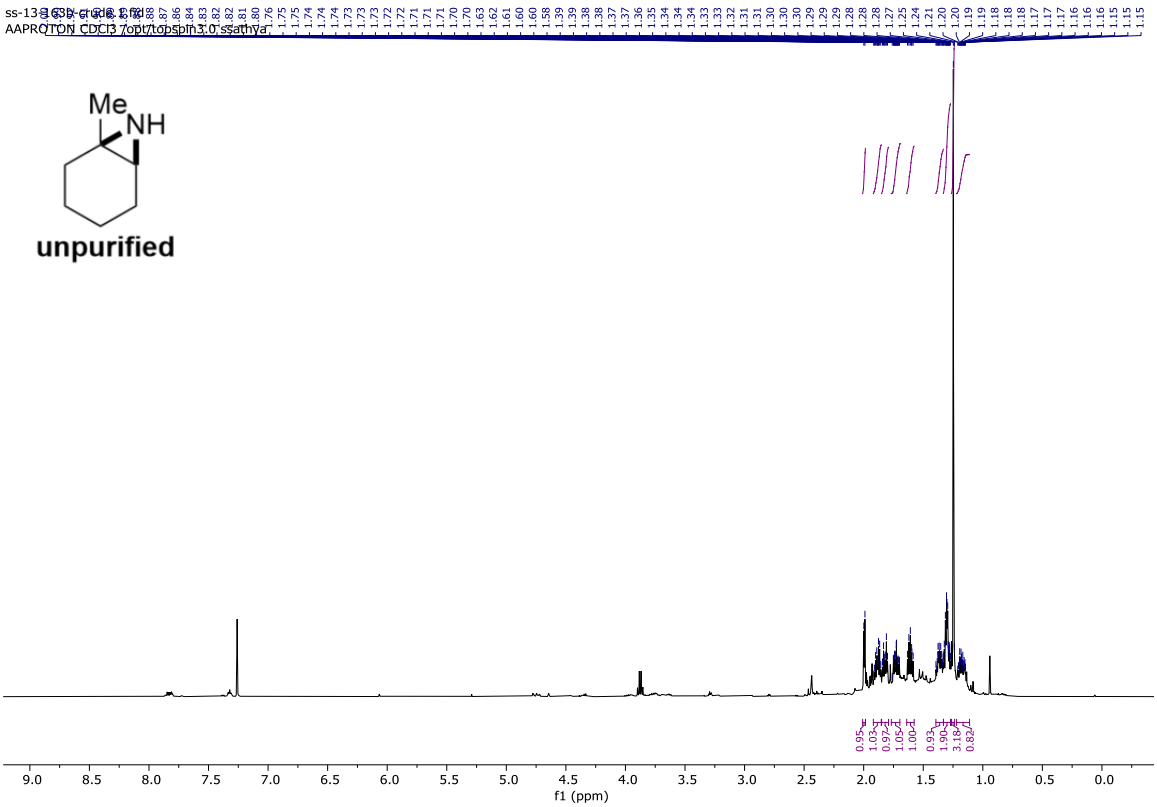
$^{1}$H NMR (600 MHz, $CDCl_3$) δ 1.99 (d, *J* = 5.6 Hz, 1H), 1.88 (dq, *J* = 14.5, 5.9 Hz, 1H), 1.82 (dt, *J* = 14.2, 5.4 Hz, 1H), 1.73 (dddd, *J* = 14.6, 8.9, 5.9, 1.2 Hz, 1H), 1.61 (dt, *J* = 14.2, 7.4 Hz, 1H), 1.39 – 1.33 (m, 1H), 1.33 – 1.27 (m, 2H), 1.25 (s, 3H), 1.22 – 1.11 (m, 1H).

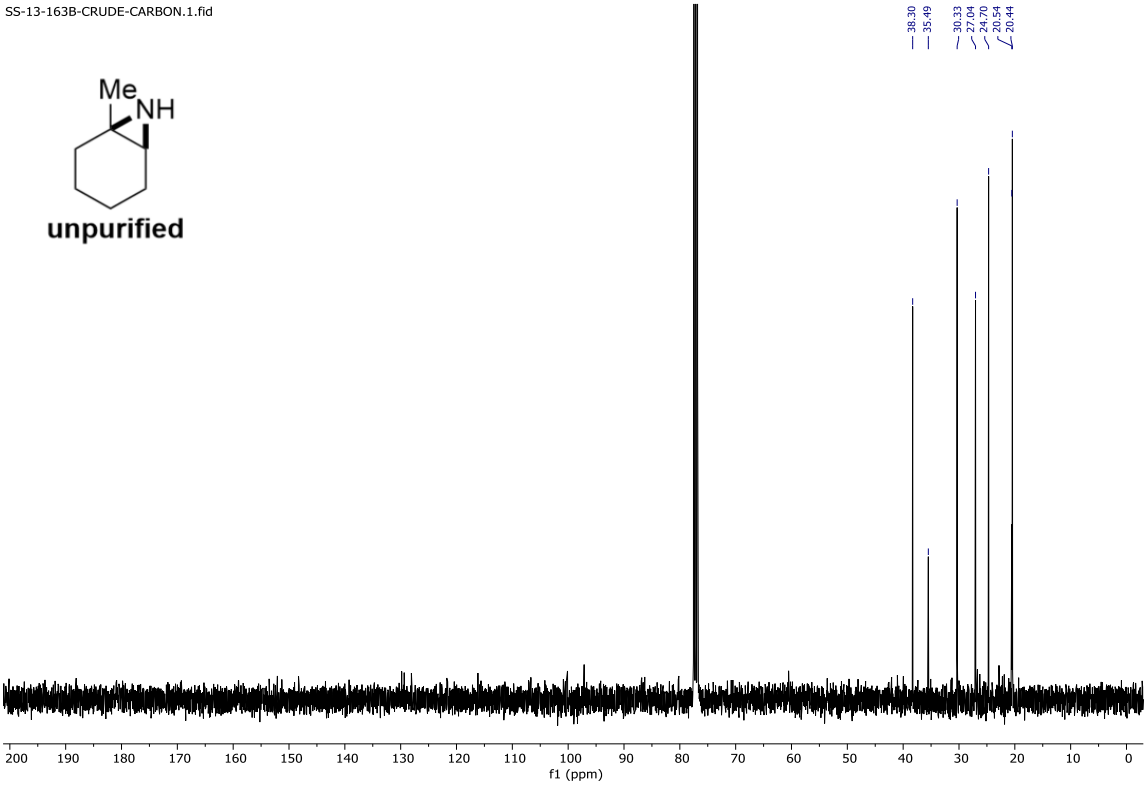
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 38.3, 35.4, 30.3, 27.0, 24.7, 20.5, 20.4.

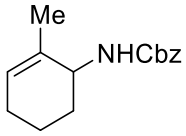
IR ν 2932, 1451, 1279, 1158 $cm^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_7H_{14}N^+$ 112.1121. Found 112.1144 (2.3 mmu error).

**Compound 38 ($CDCl_3$, $^1H$ NMR: 600 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






benzyl (2-methylcyclohex-2-en-1-yl)carbamate

**Compound 39**: Synthesized using **General Procedure B** on a 2 mmol scale; Purified using 100% $CH_2Cl_2$ on silica gel; (light yellow solid, 0.156 g, 0.636 mmol, 32% yield).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 5H), 5.55 (d, *J* = 3.8 Hz, 1H), 5.14 – 5.08 (m, 2H), 4.75 (d, *J* = 9.4 Hz, 1H), 4.09 (dt, *J* = 9.5, 4.7 Hz, 1H), 1.99 – 1.92 (m, 2H), 1.77 – 1.71 (m, 2H), 1.69 (s, 3H), 1.64 – 1.54 (m, 1H), 1.52 – 1.44 (m, 1H).

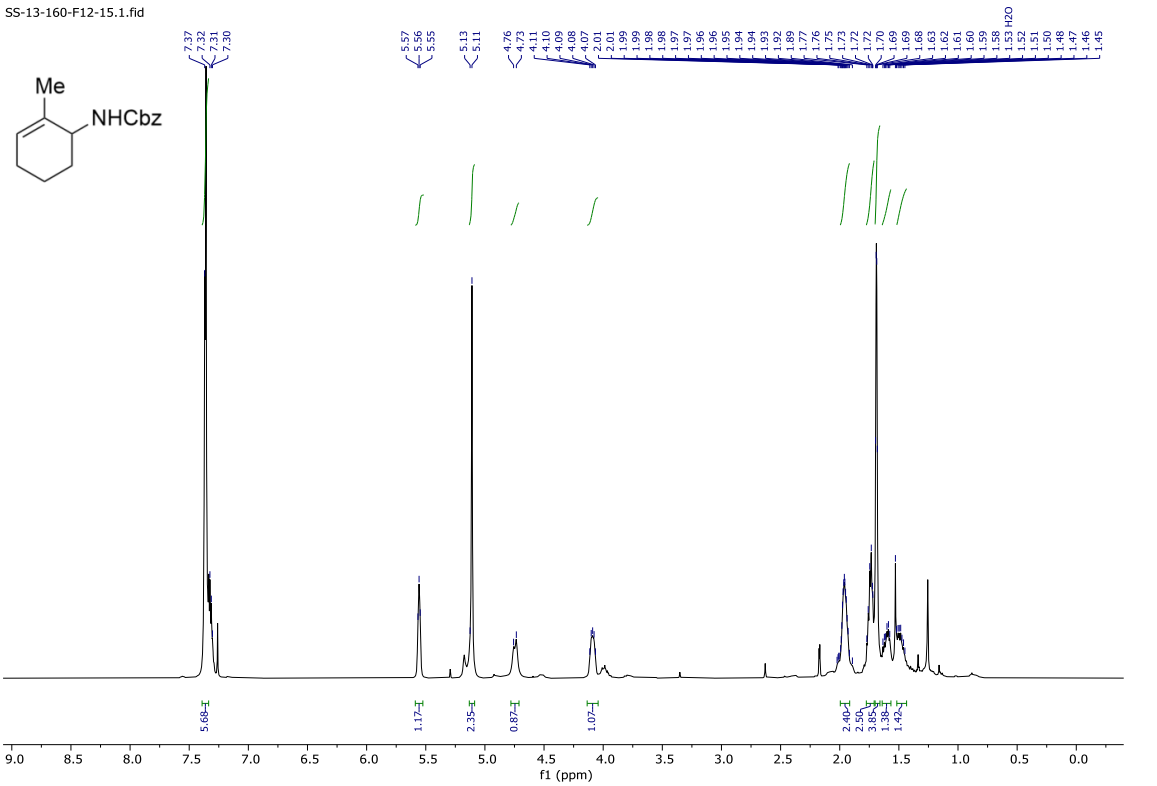
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 156.0, 136.7, 133.2, 128.5, 128.0, 126.1, 66.6, 49.3, 30.0, 25.1, 20.9, 18.5.

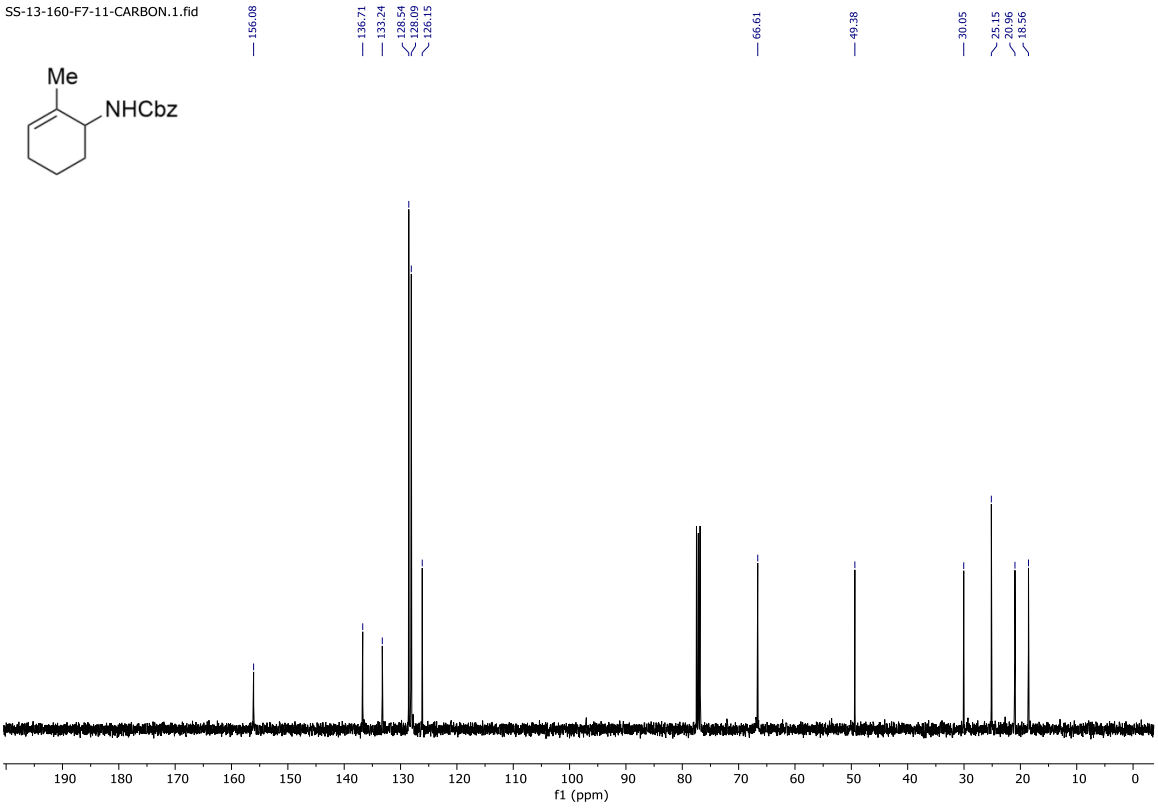
IR ν 3325, 2935, 1697, 1526, 1455, 1329, 1237, 1028 cm$^{-1}$.

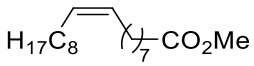
HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{15}H_{19}NNaO_2^+$ 268.1308. Found 268.1289 (7.1 ppm error).

This compound has been previously characterized in *ACS Catal.* **2023**, *13*, 4369–4375, and our data matches.

**Compound 39 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**

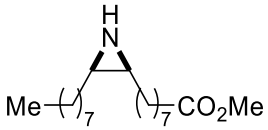




methyl oleate

**Compound 40**: Commercially available.



methyl 8-((2*S**,3*R**)-3-octylaziridin-2-yl)octanoate

**Compound 41**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; Purified using sequential flushes of $CH_2Cl_2$, EtOAc, acetone, 10% acetone/methanol, 100% methanol on Florisil (60 – 100 mesh); isolated and characterized as the single diastereomer shown; (white solid, 0.568 g, 1.82 mmol, 91% yield).

$^1$H NMR (400 MHz, $CDCl_3$) δ 3.64 (s, 3H), 2.32 – 2.22 (m, 2H), 1.98 – 1.89 (m, 2H), 1.66 – 1.55 (m, 2H), 1.53 – 1.13 (m, 24H), 0.85 (t, $J$ = 6.6 Hz, 3H).

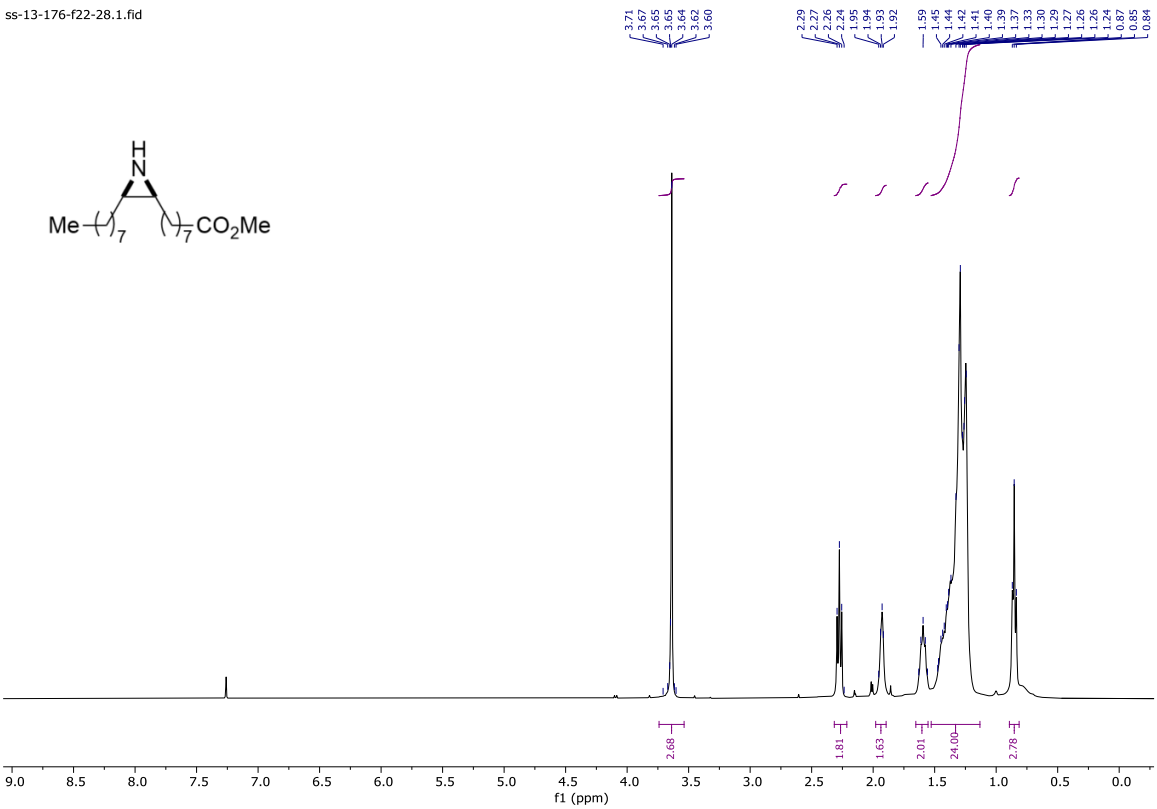
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 174.3, 51.5, 35.1, 35.0, 34.1, 31.9, 29.7 (2C), 29.5, 29.38, 29.35, 29.1, 29.0, 28.9, 28.2, 28.1, 25.0, 22.7, 14.2.

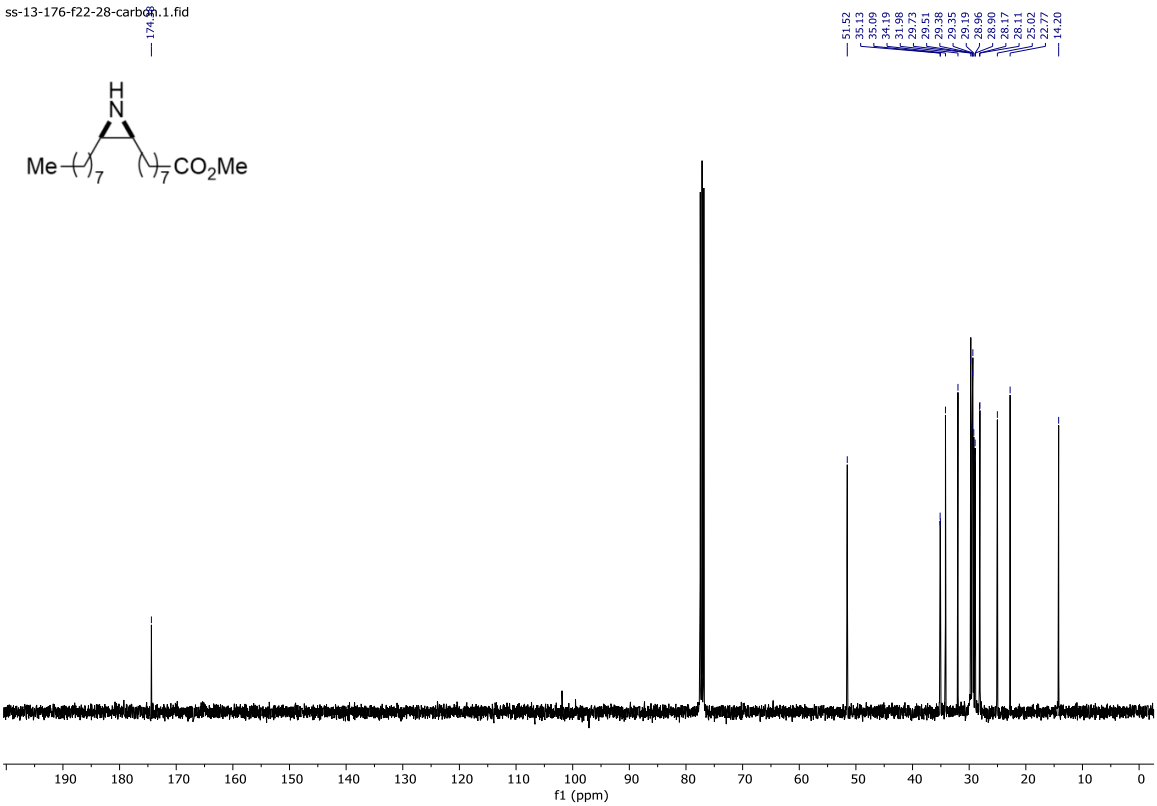
IR ν 3158, 2939, 2916, 2848, 1744, 1470, 1174 cm$^{-1}$.

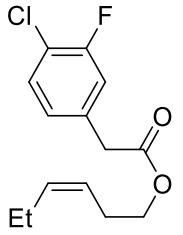
HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{19}H_{38}NO_2^+$ 312.2897. Found 312.2891 (1.9 ppm error).

Our data and spectra match what has been reported in *Synthesis*, **2022**, *54*, 4513 – 4520.

**Compound 41 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






(*Z*)-hex-3-en-1-yl 2-(4-chloro-3-fluorophenyl)acetate

**Compound 42**: Synthesized using **General Procedure C** on a 10 mmol scale; Purified using a gradient of 0 to 50% EtOAc/hexanes on silica gel; (colorless oil, 2.19 g, 8.0 mmol, 80% yield).

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.9 Hz, 1H), 7.10 (dd, *J* = 9.8, 2.0 Hz, 1H), 7.00 (dd, *J* = 7.9, 1.9 Hz, 1H), 5.55 – 5.45 (m, 1H), 5.27 (dtd, *J* = 9.0, 7.3, 3.7 Hz, 1H), 4.10 (t, *J* = 6.9 Hz, 2H), 3.58 (s, 2H), 2.37 (qd, *J* = 7.1, 1.7 Hz, 2H), 2.03 (pd, *J* = 7.4, 1.6 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H).

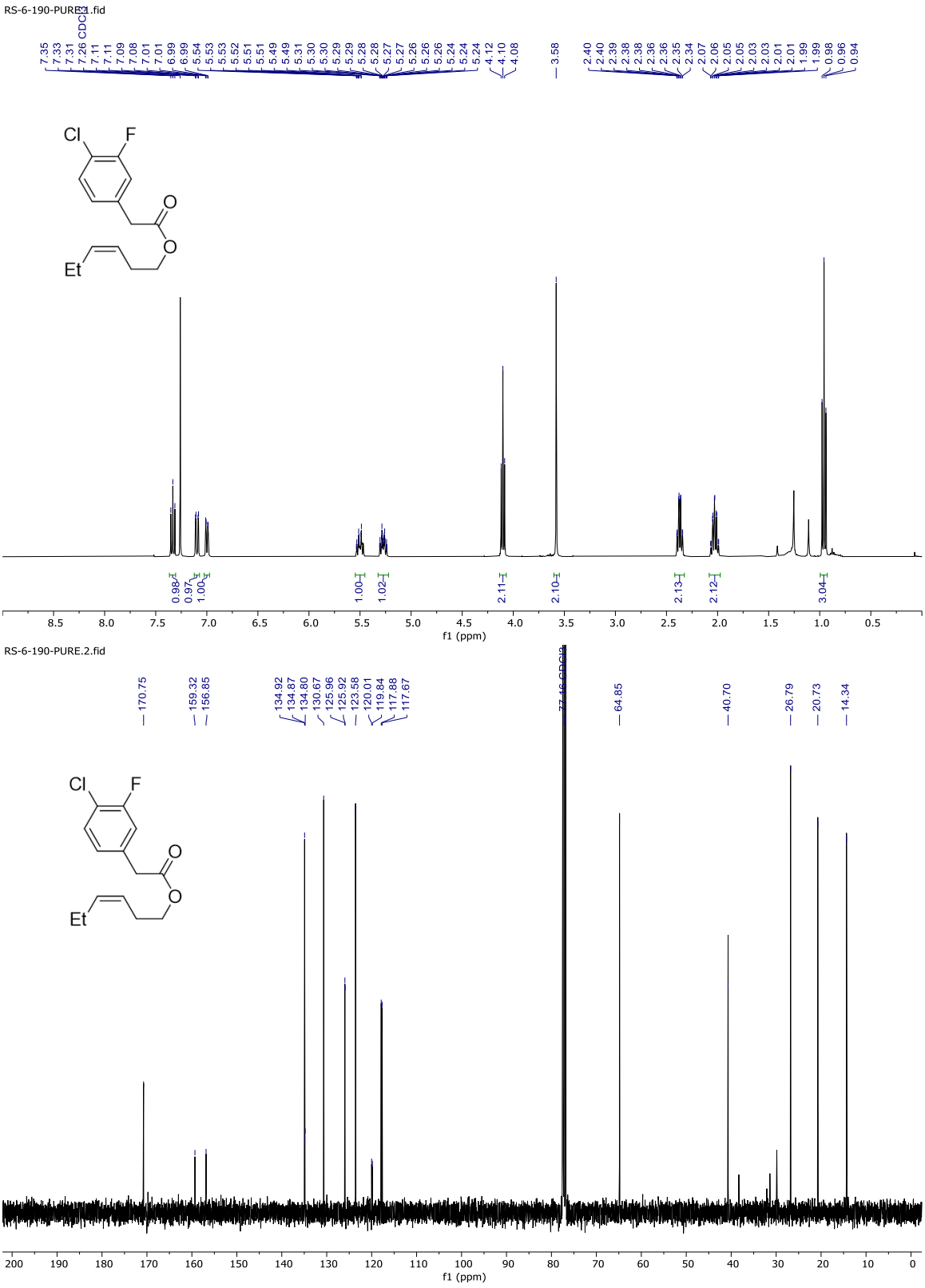
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.7, 158.0 (d, *J* = 247 Hz), 134.9, 134.8 (d, *J* = 7.0 Hz), 130.6, 125.9 (d, *J* = 4.0 Hz), 123.5, 119.9 (d, *J* = 17.1 Hz), 117.7 (d, *J* = 21.4 Hz), 64.8, 40.7, 26.7, 20.7, 14.3.

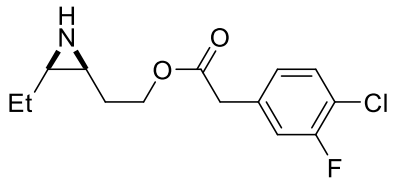
$^{19}$F{$^{1}$H} NMR (377 MHz, $CDCl_3$) δ -115.3

IR ν 3054, 2935, 2118, 1735, 1492, 1428, 1265, 1156, 742 $cm^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{14}H_{16}ClFO_2Na^+$ 293.0721. Found 293.0726 (1.7 ppm error).

**Compound 42 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






2-((2*S**,3*R**)-3-ethylaziridin-2-yl)ethyl 2-(4-chloro-3-fluorophenyl)acetate

**Compound 43**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; Purified by column chromatography on Florisil (60 – 100 mesh) using a gradient of 0 to 50% ethyl acetate in hexanes, followed by flushing with 100% methanol; Isolated and characterized as the single diastereomer shown; (colorless oil, 0.291 g, 1.02 mmol, 51% yield).

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.9 Hz, 1H), 7.08 (dd, *J* = 9.8, 2.1 Hz, 1H), 7.01 – 6.95 (m, 1H), 4.29 – 4.16 (m, 2H), 3.63 – 3.52 (m, 2H), 2.04 – 1.87 (m, 2H), 1.78 (dtd, *J* = 14.2, 7.0, 5.2 Hz, 1H), 1.60 (ddt, *J* = 14.0, 7.7, 6.1 Hz, 1H), 1.41 – 1.30 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

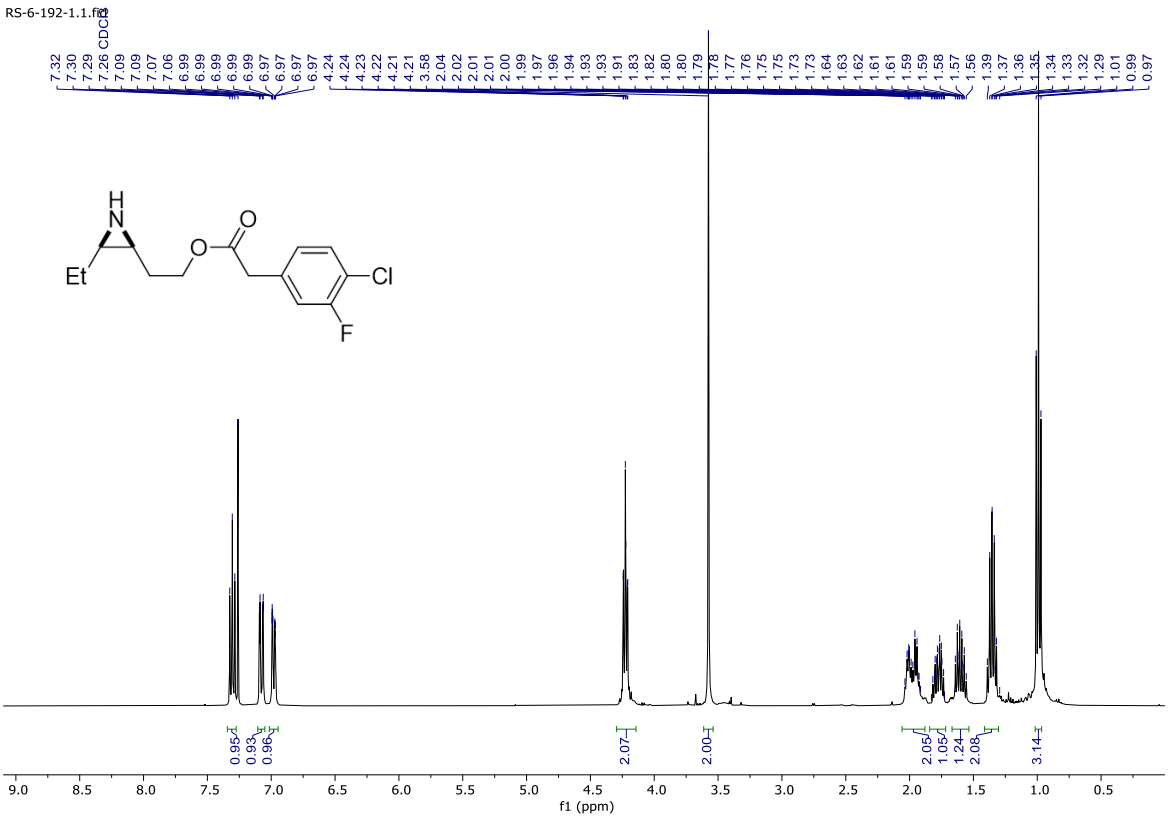
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.6, 157.9 (d, *J* = 250.4 Hz), 134.7 (d, *J* = 7.0 Hz), 130.6, 125.8 (d, *J* = 3.6 Hz), 119.8 (d, *J* = 18.1 Hz), 117.6 (d, *J* = 21.4 Hz), 64.0, 40.5, 36.2, 31.7, 28.0, 22.1, 12.0.

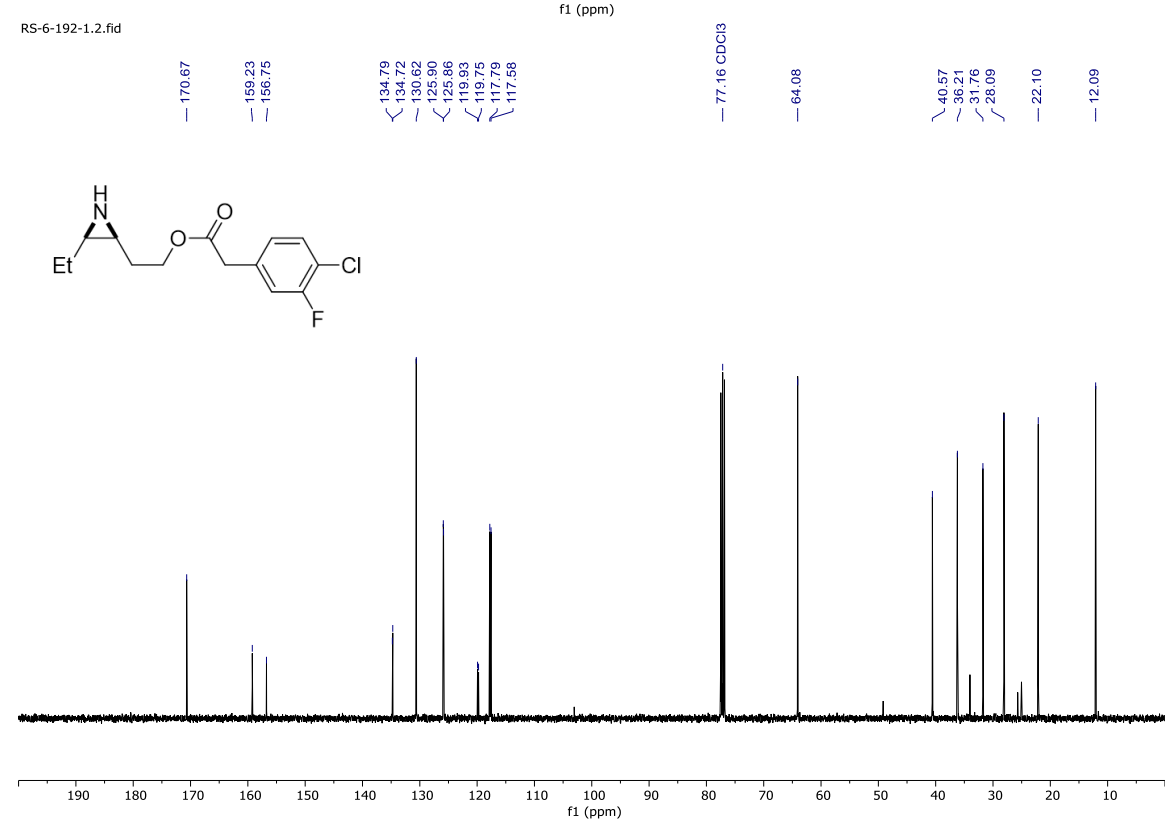
$^{19}$F{$^{1}$H} NMR (377 MHz, $CDCl_3$) δ -115.2.

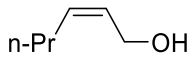
IR ν 3054, 2968, 1735, 1492, 1265, 1156, 740 cm$^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{14}H_{17}ClFNO_2Na^+$ 308.0830. Found 308.0801 (9.4 ppm error).

**Compound 43 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**

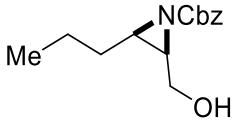





(*Z*)-hex-2-en-1-ol

**Compound 44**: Commercially available.




benzyl (2*R**,3*R**)-2-(hydroxymethyl)-3-propylaziridine-1-carboxylate

**Compound 45**: Synthesized using **General Procedure B** on a 2 mmol scale; Purified using a gradient of 0 to 50% EtOAc/hexanes on silica gel; Isolated and characterized as the single diastereomer shown; (colorless oil, 0.152 g, 0.6 mmol, 30% yield).

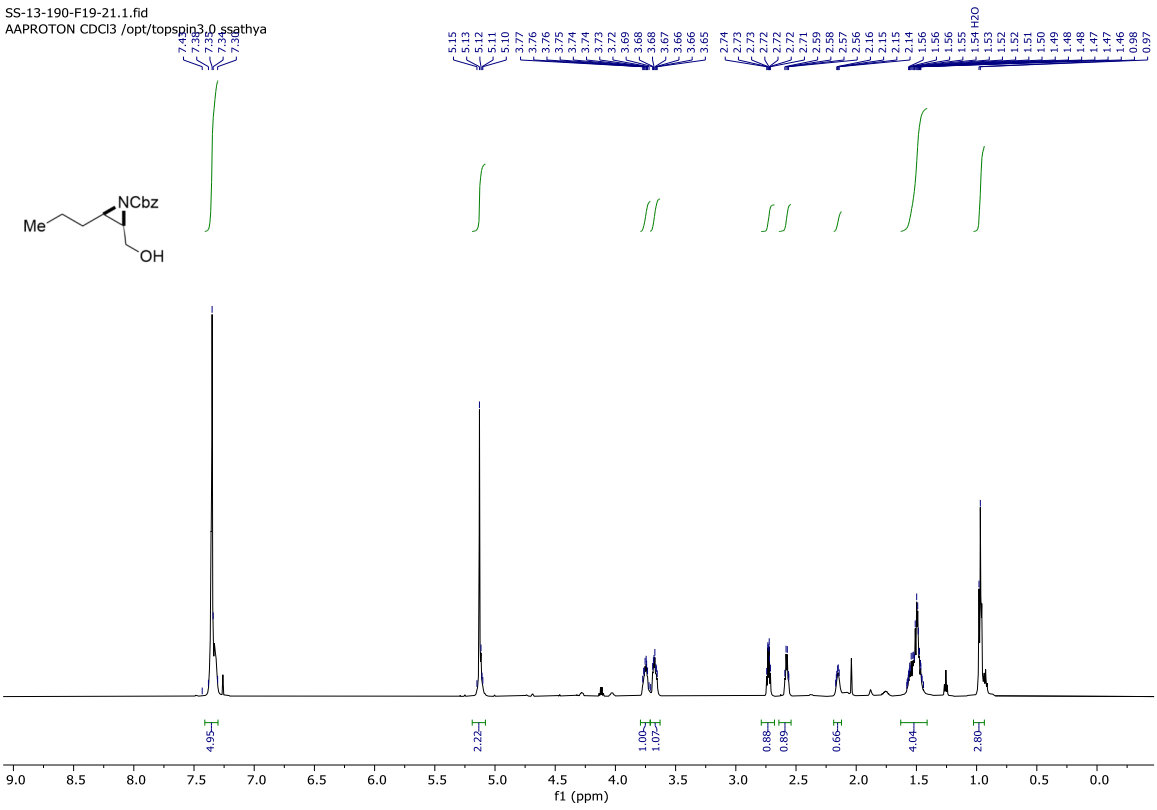
$^{1}$H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 5H), 5.19 – 5.07 (m, 2H), 3.79 – 3.71 (m, 1H), 3.67 (ddd, *J* = 11.7, 7.0, 4.1 Hz, 1H), 2.79 – 2.68 (m, 1H), 2.58 (q, *J* = 6.1 Hz, 1H), 2.19 – 2.12 (broad m, 1H), 1.63 – 1.41 (m, 4H), 0.97 (t, *J* = 6.7 Hz, 3H).

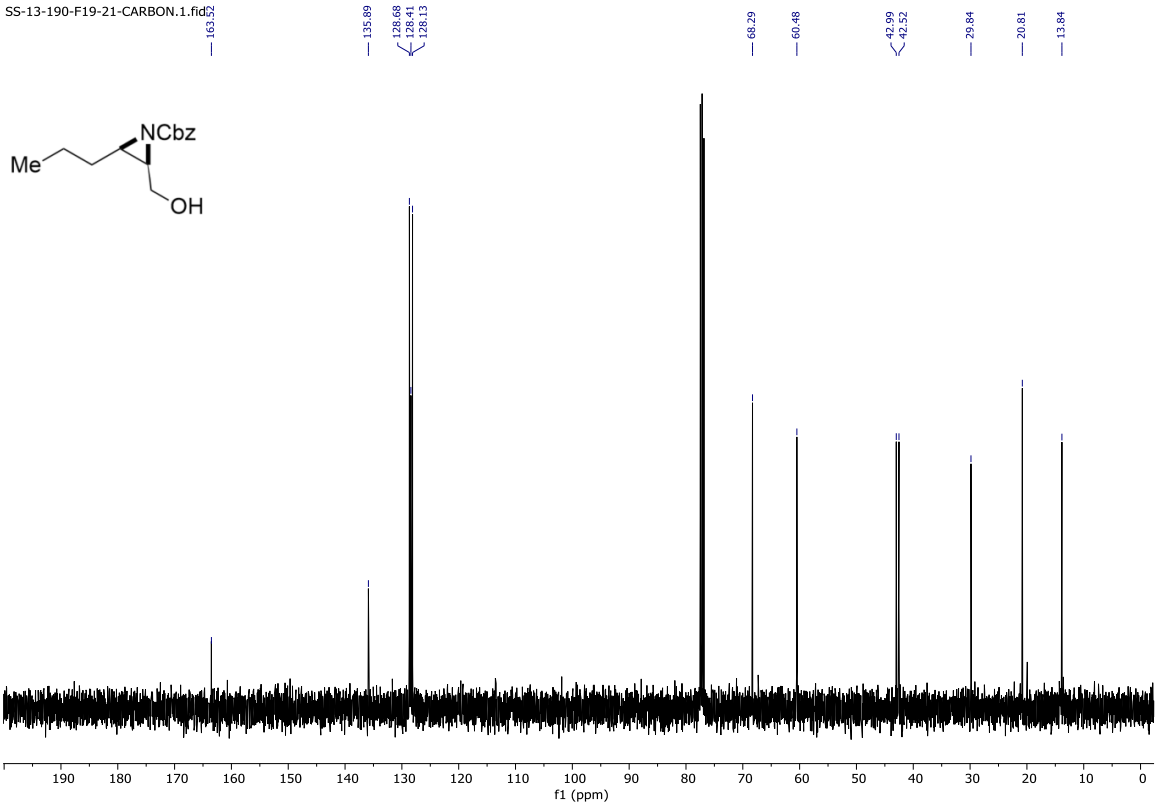
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 163.5, 135.8, 128.6, 128.4, 128.1, 68.2, 60.4, 42.9, 42.5, 29.8, 20.8, 13.8.

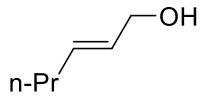
IR ν 3423, 2959, 1722, 1455, 1381, 1292, 1218, 1038 $cm^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{14}H_{20}NO_3^+$ 250.1438. Found 250.1418 (8 ppm error).

## Compound 45 ($CDCl_3$, $^1H$ NMR: 600 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)

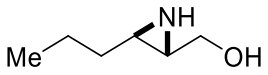





(*E*)-hex-2-en-1-ol

**Compound 46**: Commercially available.




((2*S**,3*R**)-3-propylaziridin-2-yl)methanol

**Compound 47**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; Purified using sequential flushes of $CH_2Cl_2$, EtOAc, acetone, and methanol on Florisil (60 – 100 mesh); isolated and characterized as the single diastereomer shown; (colorless oil, 0.071 g, 0.62 mmol, 31% yield).

$^1$H NMR (600 MHz, $CDCl_3$) δ 3.90 – 3.67 (m, 1H), 3.35 (dt, *J* = 13.3, 6.6 Hz, 1H), 2.06 – 1.90 (m, 1H), 1.89 – 1.71 (m, 1H), 1.52 – 1.33 (m, 4H), 0.92 (t, *J* = 6.9 Hz, 3H).

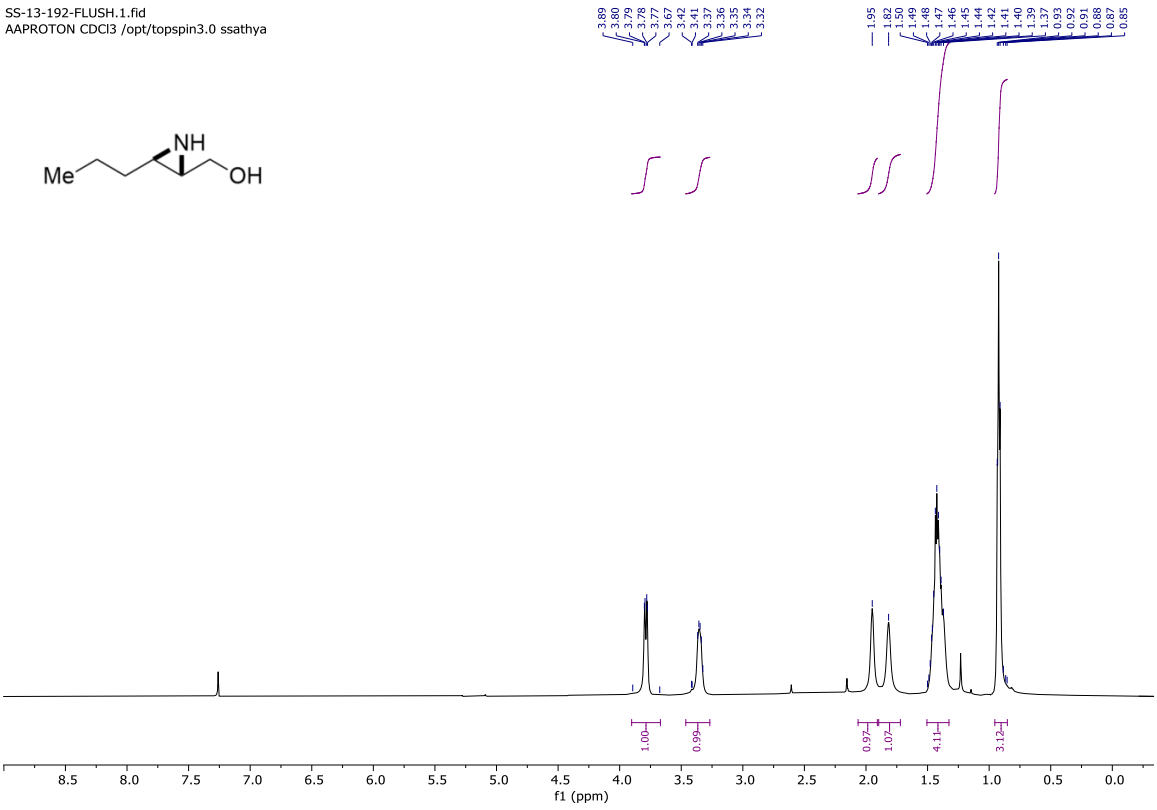
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 63.1, 38.6, 36.0, 35.0, 20.9, 13.9.

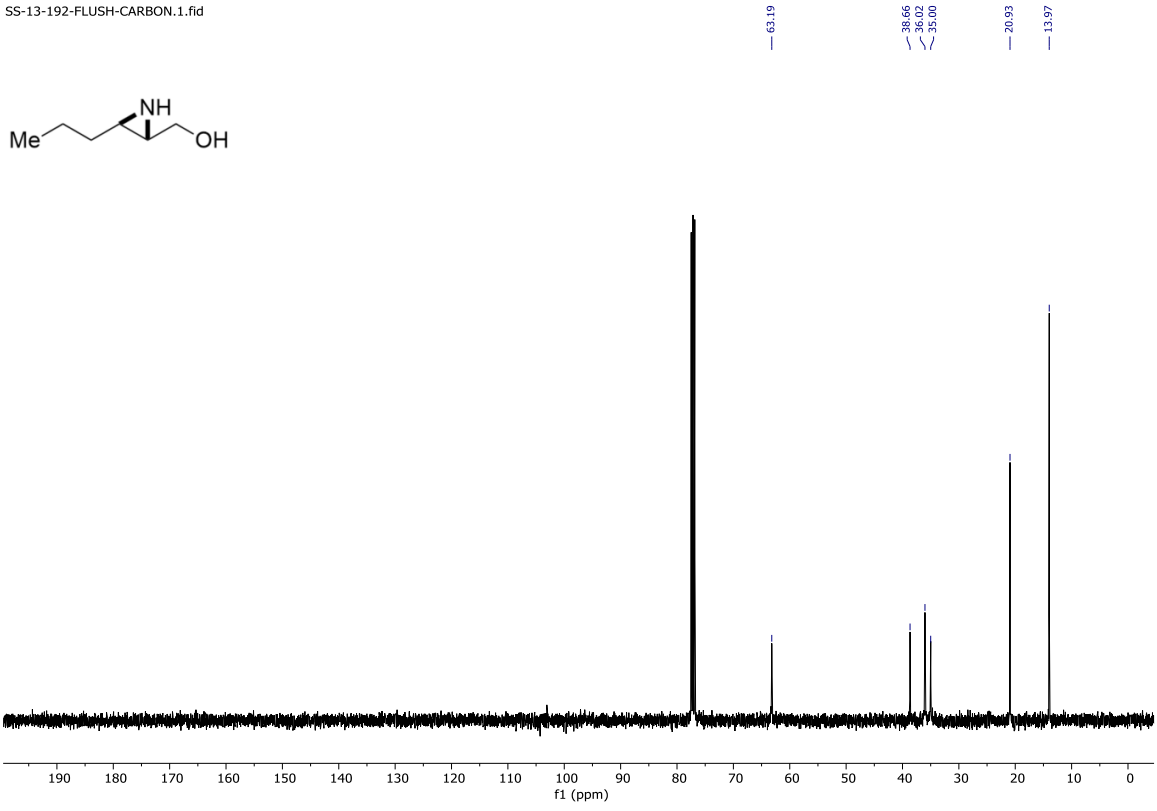
IR ν 3268, 2959, 1465, 1138, 1043, 913 cm$^{-1}$.

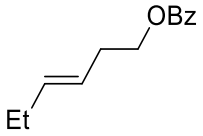
HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_6H_{14}NO^+$ 116.1070. Found 116.1078 (6.9 ppm error).

Our data agrees with what has been reported in *ACS Catal.* **2020***, 10,* 556 – 561.

## Compound 47 ($CDCl_3$, $^1H$ NMR: 600 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)

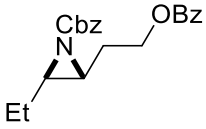





(*E*)-hex-3-en-1-yl benzoate

**Compound 48**: Previously synthesized in *J. Org. Chem.* **2013**, *78*, 1682 – 1686.




benzyl (2*R**,3*R**)-2-(2-(benzoyloxy)ethyl)-3-ethylaziridine-1-carboxylate

**Compound 49**: Synthesized using **General Procedure B** on a 2 mmol scale; Purified using a gradient of 0 to 1% acetone/$CH_2Cl_2$ on silica gel; Isolated and characterized as the single diastereomer shown; (colorless oil, 0.343 g, 0.97 mmol, 49% yield).

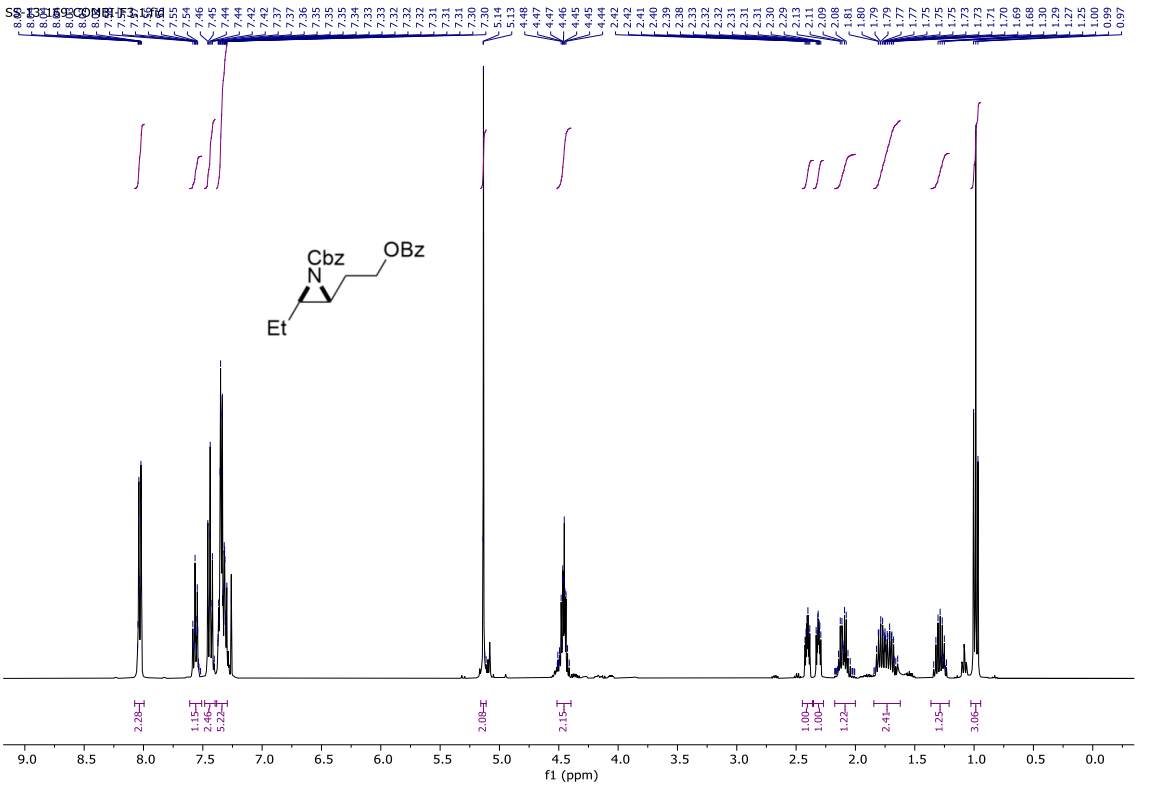
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.61 – 7.51 (m, 1H), 7.48 – 7.40 (m, 2H), 7.38 – 7.29 (m, 5H), 5.17 – 5.12 (m, 2H), 4.52 – 4.40 (m, 2H), 2.40 (td, *J* = 6.4, 3.3 Hz, 1H), 2.31 (ddd, *J* = 6.8, 5.5, 3.2 Hz, 1H), 2.10 (dq, *J* = 14.5, 5.8 Hz, 1H), 1.84 – 1.62 (m, 2H), 1.36 – 1.21 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H).

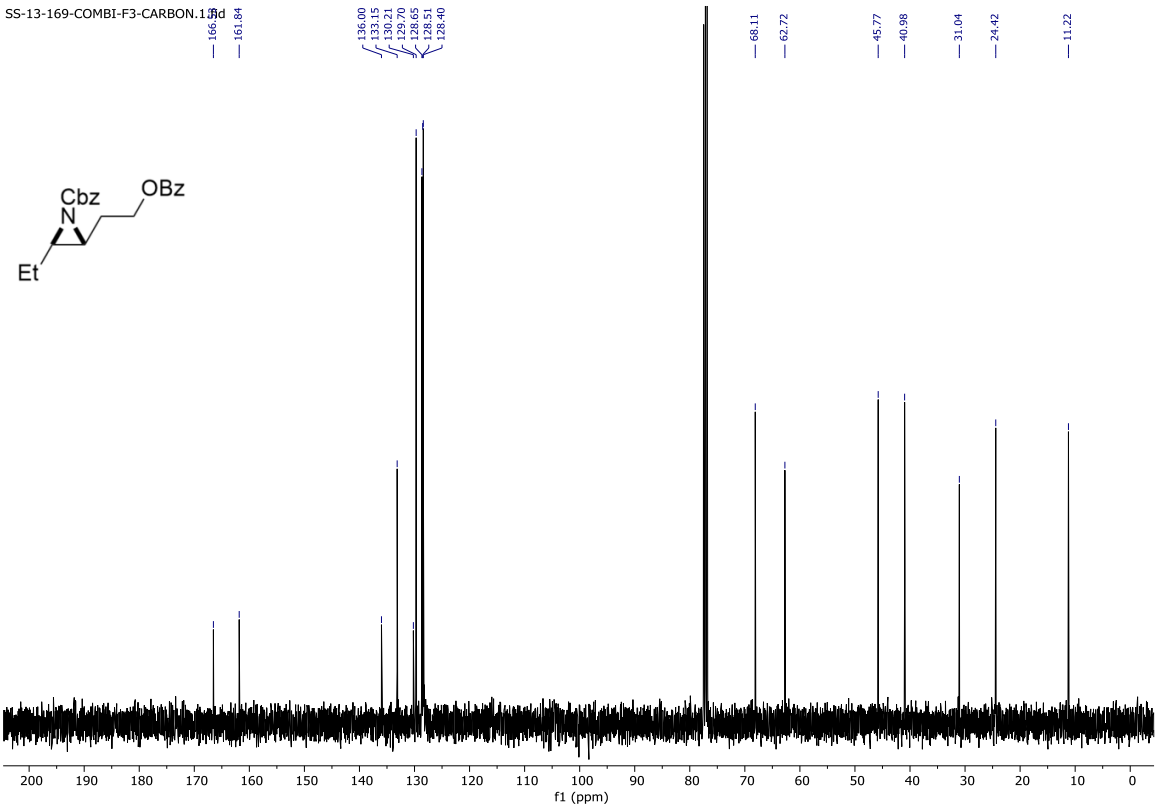
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 166.5, 161.8, 136.0, 133.1, 130.2, 129.7, 128.6, 128.5, 128.4, 68.1, 62.7, 45.7, 40.9, 31.0, 24.4, 11.2.

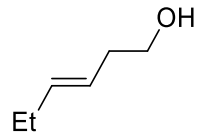
IR ν 2965, 1717, 1452, 1382, 1275, 1197, 1114 cm$^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{21}H_{23}NNaO_4^+$ 376.1519. Found 376.1511 (2.1 ppm error).

**Compound 49 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**

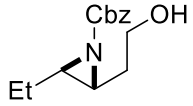





(*E*)-hex-3-en-1-ol

**Compound 50**: Commercially available.




benzyl (2*R**,3*R**)-2-ethyl-3-(2-hydroxyethyl)aziridine-1-carboxylate

**Compound 51**: Synthesized using **General Procedure B** on a 2 mmol scale; Purified using a gradient of 0 to 50% EtOAc/hexanes on silica gel; Isolated and characterized as the single diastereomer shown; (colorless oil, 0.275 g, 1.10 mmol, 55% yield).

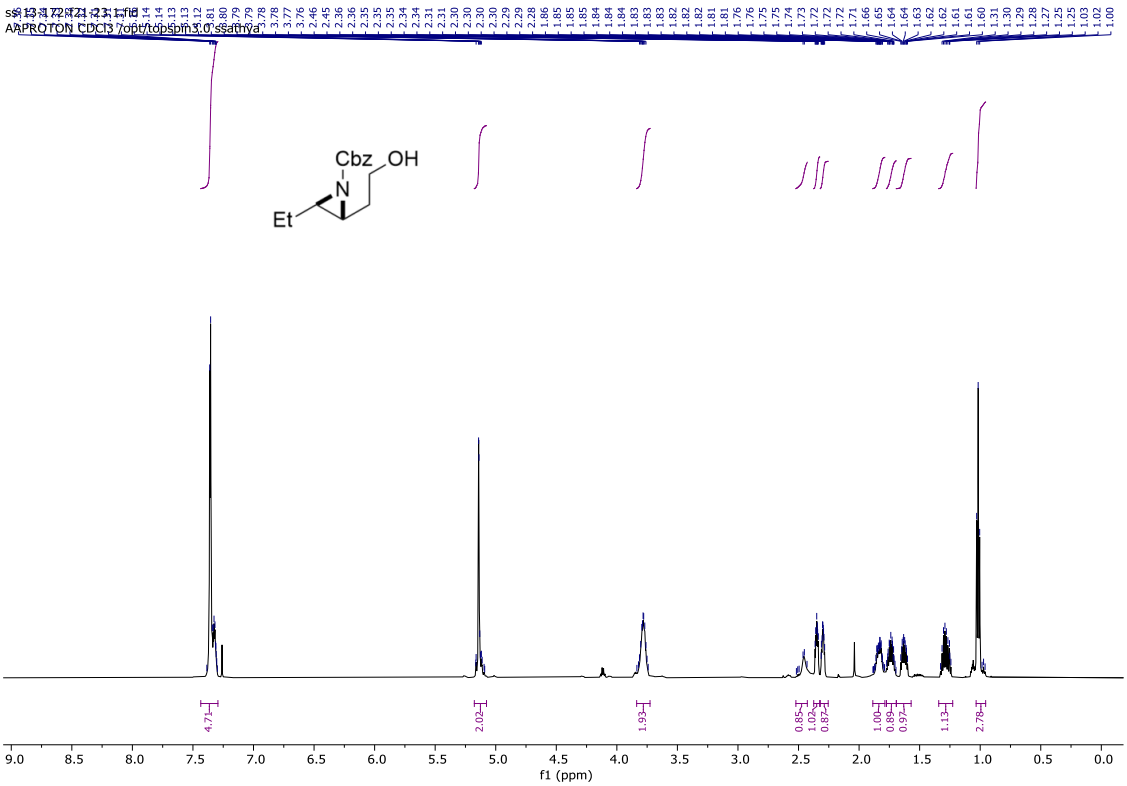
$^{1}$H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 5H), 5.18 – 5.08 (m, 2H), 3.84 – 3.73 (m, 2H), 2.52 – 2.43 (broad m, 1H), 2.35 (ddd, *J* = 7.8, 4.9, 3.4 Hz, 1H), 2.30 (ddd, *J* = 6.9, 5.5, 3.4 Hz, 1H), 1.89 – 1.79 (m, 1H), 1.77 – 1.69 (m, 1H), 1.63 (dtd, *J* = 14.2, 7.0, 5.1 Hz, 1H), 1.35 – 1.24 (m, 1H), 1.02 (t, *J* = 7.5 Hz, 3H).

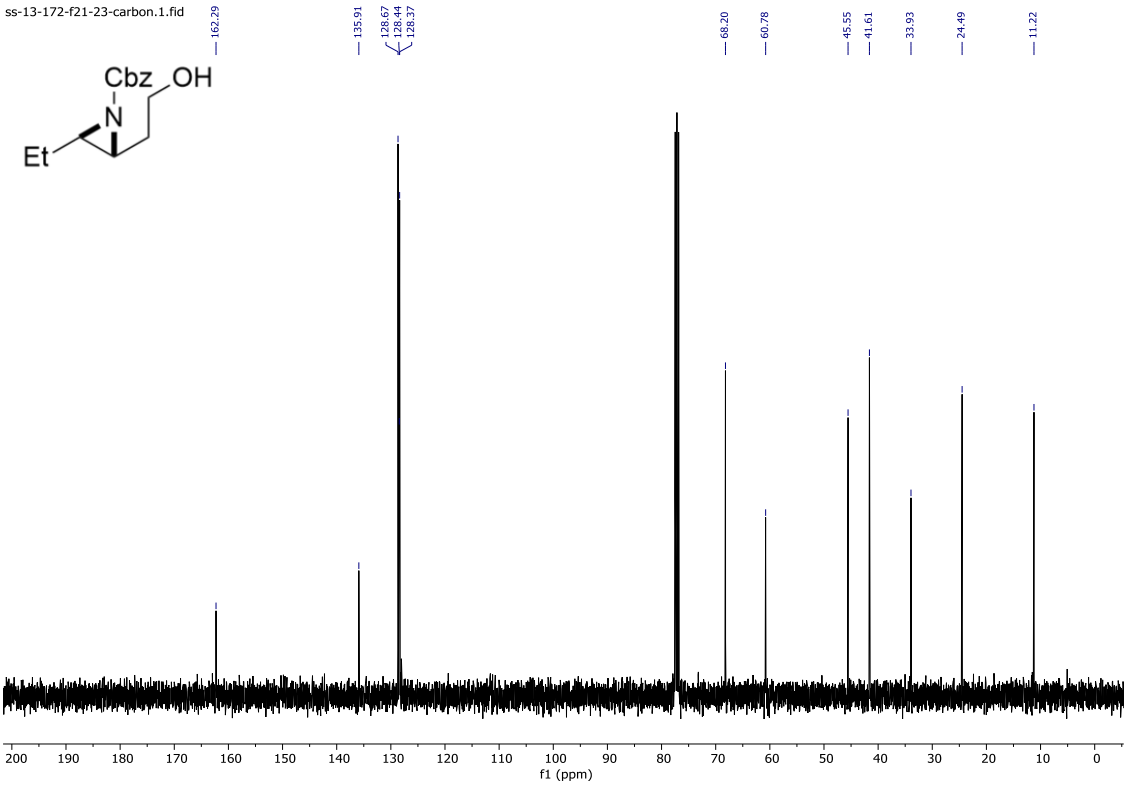
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 162.2, 135.9, 128.6, 128.4, 128.3, 68.2, 60.7, 45.5, 41.6, 33.9, 24.4, 11.2.

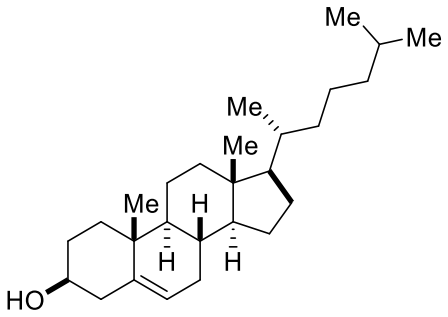
IR ν 3417, 2965, 1713, 1455, 1382, 1317, 1197, 1059 $cm^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{14}H_{20}NO_3^+$ 250.1438. Found 250.1428 (4 ppm error).

**Compound 51 ($CDCl_3$, $^1H$ NMR: 600 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**

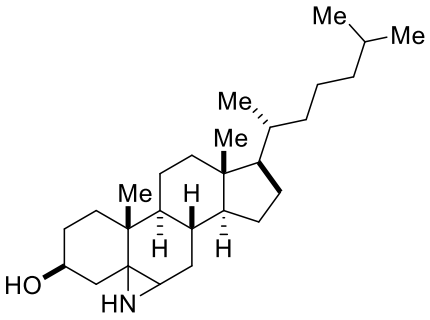





cholesterol

**Compound 52**: Commercially available.




(3*S**,6a*S**,6b*S**,9*R**,9a*R**,11a*S**,11b*R**)-9a,11b-dimethyl-9-((*R**)-6-methylheptan-2-yl)hexadecahydro-2*H*-cyclopenta[1,2]phenanthro[8a,9-*b*]azirin-3-ol

**Compound 53**: Synthesized using a modified version of **General Procedure B, Part I** on a 2 mmol scale (reaction solvent was 7 mL of $CF_3CH_2OH$ and 3 mL of $CH_2Cl_2$); Purified by column chromatography on Florisil (60 – 100 mesh) using a gradient of 0 to 50% ethyl acetate in hexanes, followed by flushing with 100% methanol; Isolated and characterized as a 2:1 mixture of diastereomers; (brown solid, 0.490 g, 1.22 mmol, 61% yield).

$^1$H NMR (400 MHz, $CDCl_3$) δ 3.81 – 3.59 (m, 1.38H), 2.23 – 2.07 (m, 1.73H), 2.05 – 1.67 (m, 8.59H), 1.65 – 1.41 (m, 5.43H), 1.39 – 1.13 (m, 13.22H), 1.12 – 0.74 (m, 30.81H), 0.60 (s, 1.38H), 0.56 (s, 3H).

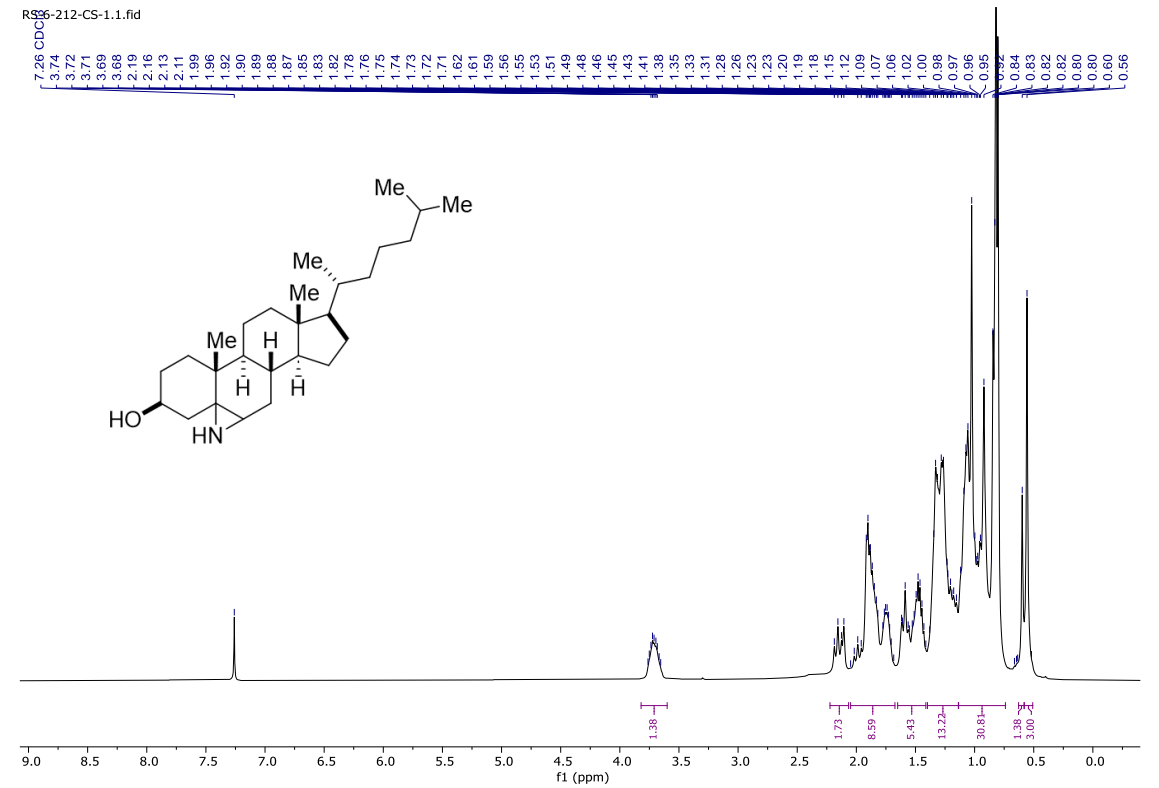
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 68.8, 68.5, 57.1, 56.6, 56.3, 55.9, 51.2, 46.1, 45.2, 42.8, 42.6, 42.4, 42.3, 40.0, 39.5, 37.5, 37.0, 36.2, 35.8, 35.7, 34.4, 34.1, 32.6, 32.3, 31.4, 31.0, 30.2, 30.0, 28.7, 28.23, 28.1, 28.0, 24.2, 24.0, 23.9, 23.8, 22.8, 22.6, 22.3, 20.9, 18.7, 18.7, 16.4, 11.9.

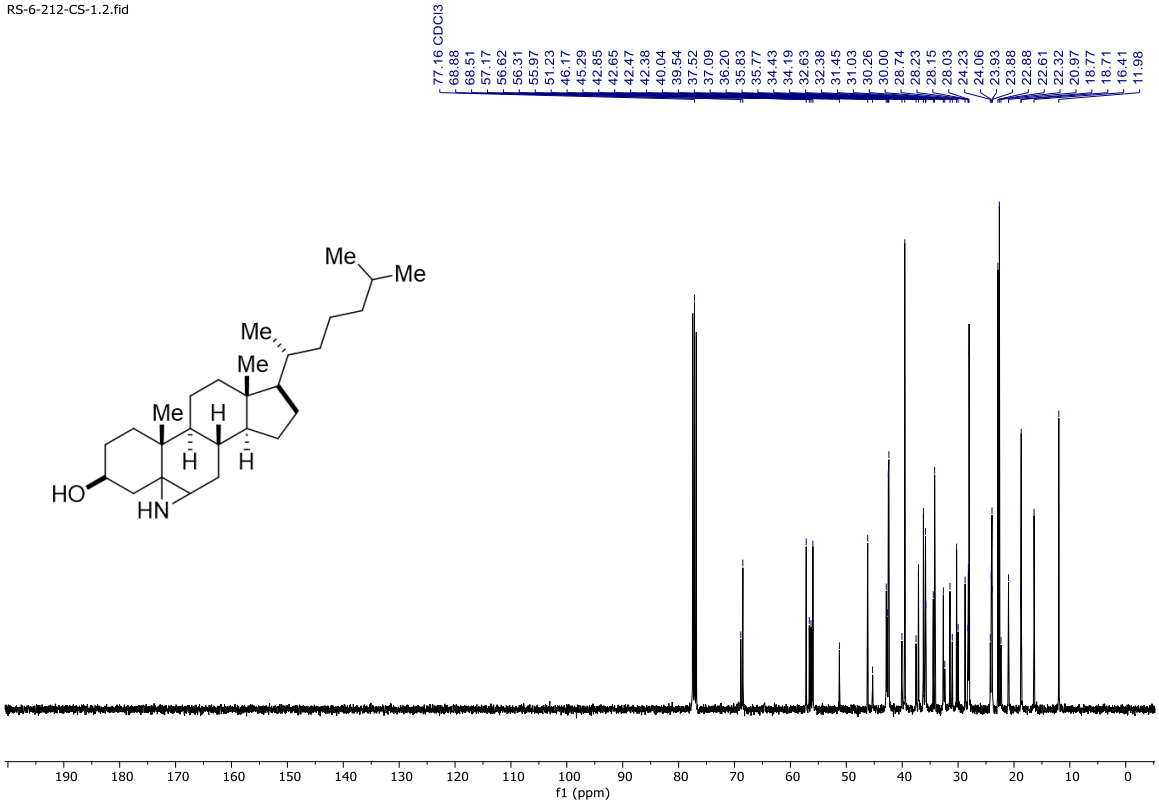
IR ν 3313, 3054, 2953, 2306, 1265, 763 cm$^{-1}$.

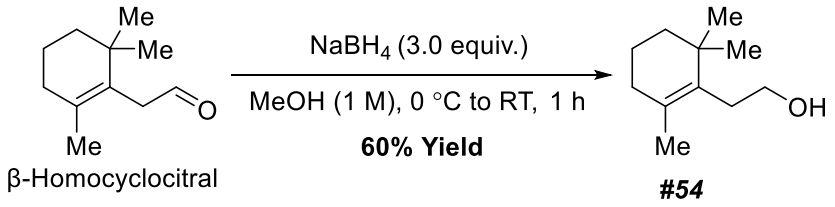
HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{27}H_{48}NO^+$ 402.3736. Found 402.3747 (2.7 ppm error).

This compound has previously been reported in *Science*, **2014**, *343*, 61 – 65, and our spectra match.

**Compound 53 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**



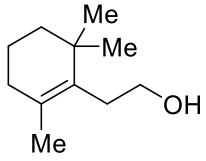






β-Homocyclocitral

***#54***

A 25 mL round-bottom flask equipped with a magnetic stir bar was charged with β-homocyclocitral (2.0 g, 12.0 mmol, 1.0 equiv.) and methanol (12 mL, reaction concentration = 1.0 M). The solution was cooled to 0 °C using an ice-water bath, and sodium borohydride (1.365 g, 36.0 mmol, 3.0 equiv.) was added in portions. The reaction mixture was stirred at 0 °C for 30 minutes, and then the ice-water bath was removed. The mixture was stirred for an additional 30 minutes. The reaction was then quenched with saturated aqueous ammonium chloride solution (4 mL). Methanol was removed under reduced pressure, and the resulting crude residue was diluted with ethyl acetate (50 mL) and transferred to a separatory funnel. The organic layer was washed with water (10 mL) and collected. The aqueous layer was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with brine (20 mL), collected, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using a gradient of 0 to 70% ethyl acetate in hexanes to afford compound **54** (white solid, 1.210 g, 7.19 mmol, 60% yield).




2-(2,6,6-trimethylcyclohex-1-en-1-yl)ethan-1-ol

**Compound 54**:

$^1$H NMR (400 MHz, $CDCl_3$) δ 3.65 – 3.56 (m, 2H), 2.39 – 2.29 (m, 2H), 1.91 (t, *J* = 6.3 Hz, 2H), 1.78 – 1.67 (broad m, 1H), 1.62 (s, 3H), 1.60 – 1.52 (m, 2H), 1.45 – 1.38 (m, 2H), 0.98 (s, 6H).

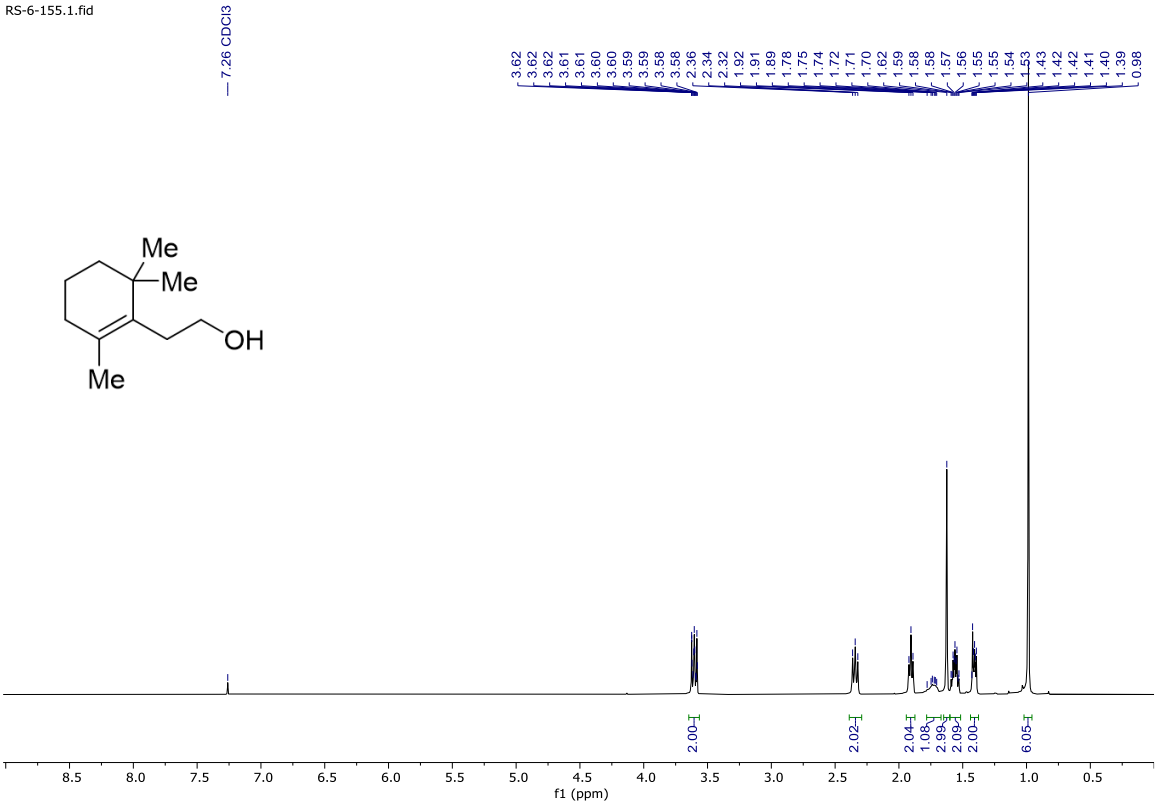
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 132.9, 129.7, 62.6, 39.8, 34.8, 32.9, 32.3, 28.6, 20.2, 19.5.

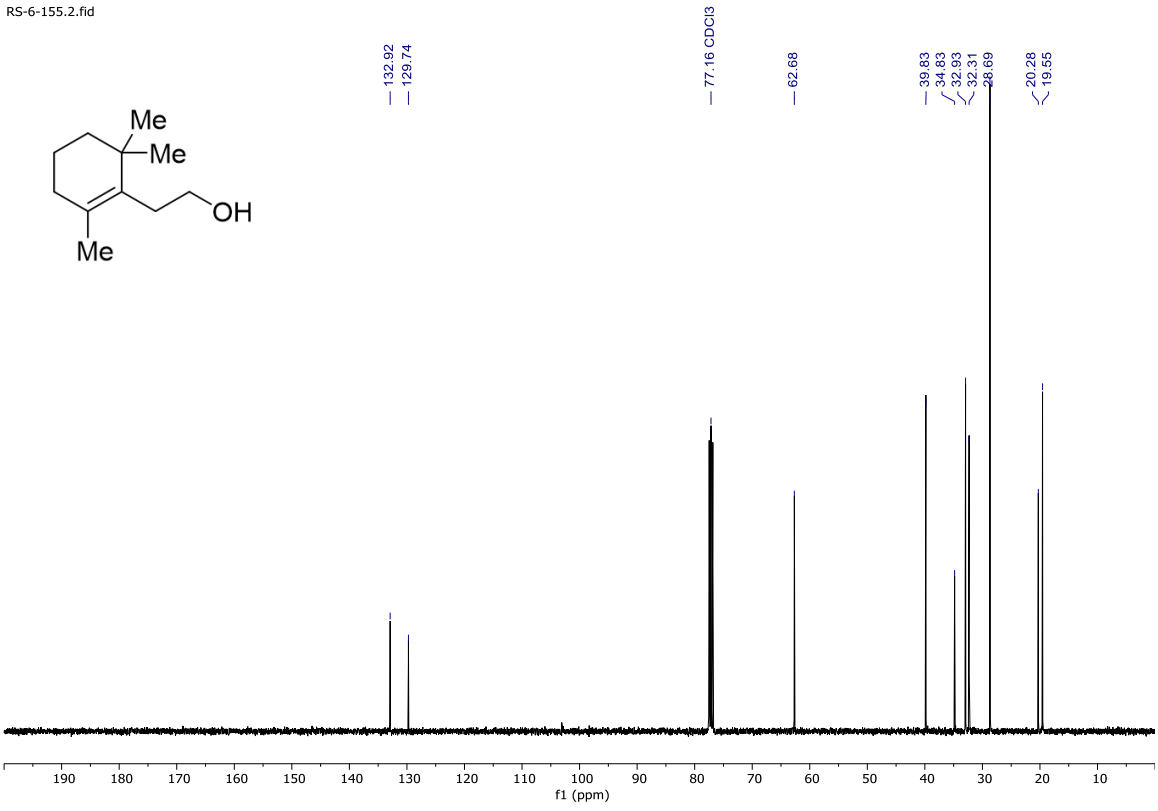
IR ν 3503, 3019, 2400, 1275, 1215, 767, 669 cm$^{-1}$.

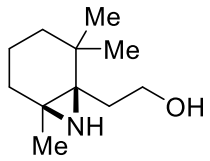
HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{11}H_{21}O^+$ 169.1592. Found 169.1603 (6.5 ppm error).

This compound has been previously characterized in *J. Am. Chem. Soc.* **2014**, *136*, 1222–1225, and our data matches.

## Compound 54 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)






2-((1*R**,6*S**)-2,2,6-trimethyl-7-azabicyclo[4.1.0]heptan-1-yl)ethan-1-ol

**Compound 55**: Synthesized using **General Procedure B, Part I** on a 1.8 mmol scale; Purified by column chromatography on Florisil (60 – 100 mesh) using a gradient of 0 to 50% ethyl acetate in hexanes, followed by flushing with 100% methanol; Isolated and characterized as a single diastereomer; (white solid, 0.181 g, 0.99 mmol, 55% yield).

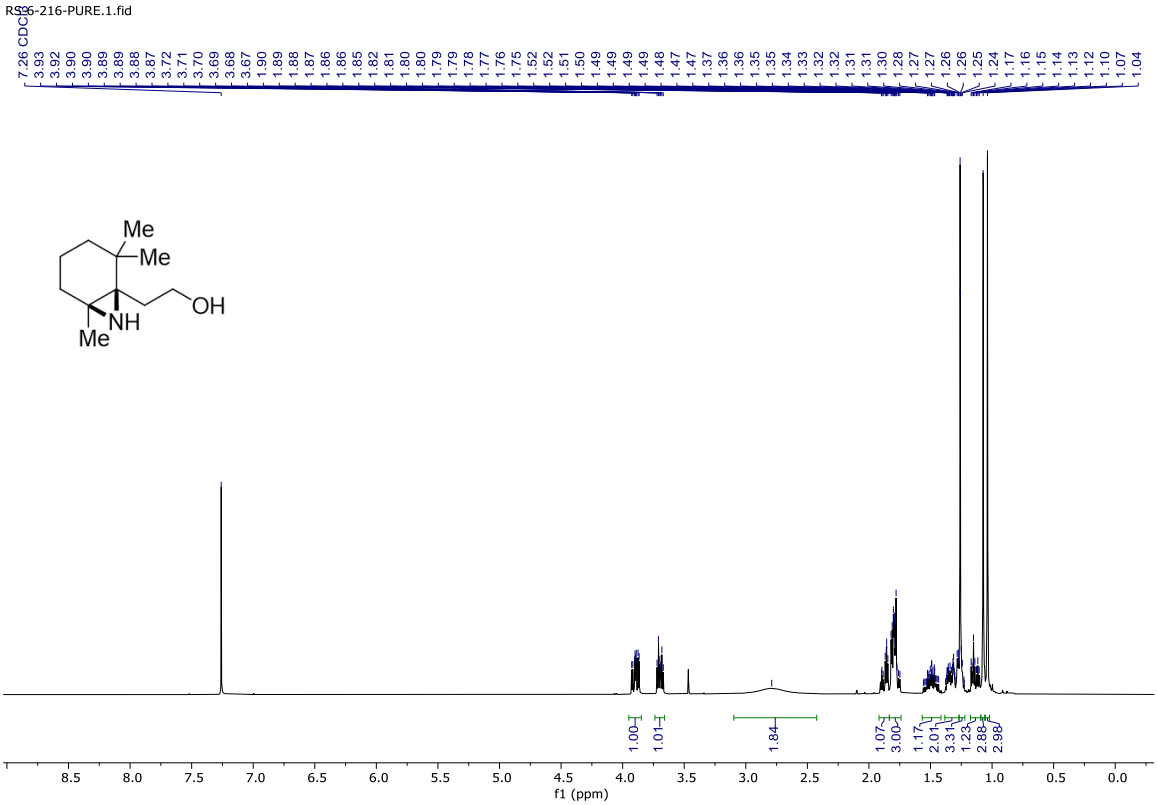
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 3.90 (ddd, *J* = 11.0, 9.5, 3.7 Hz, 1H), 3.70 (dt, *J* = 11.1, 4.6 Hz, 1H), 3.08 – 2.51 (broad m, 2H), 1.92 – 1.83 (m, 1H), 1.83 – 1.74 (m, 3H), 1.49 (dtdd, *J* = 12.9, 10.6, 8.3, 4.4 Hz, 1H), 1.38 – 1.27 (m, 2H), 1.26 (s, 3H), 1.18 – 1.09 (m, 1H), 1.07 (s, 3H), 1.04 (s, 3H).

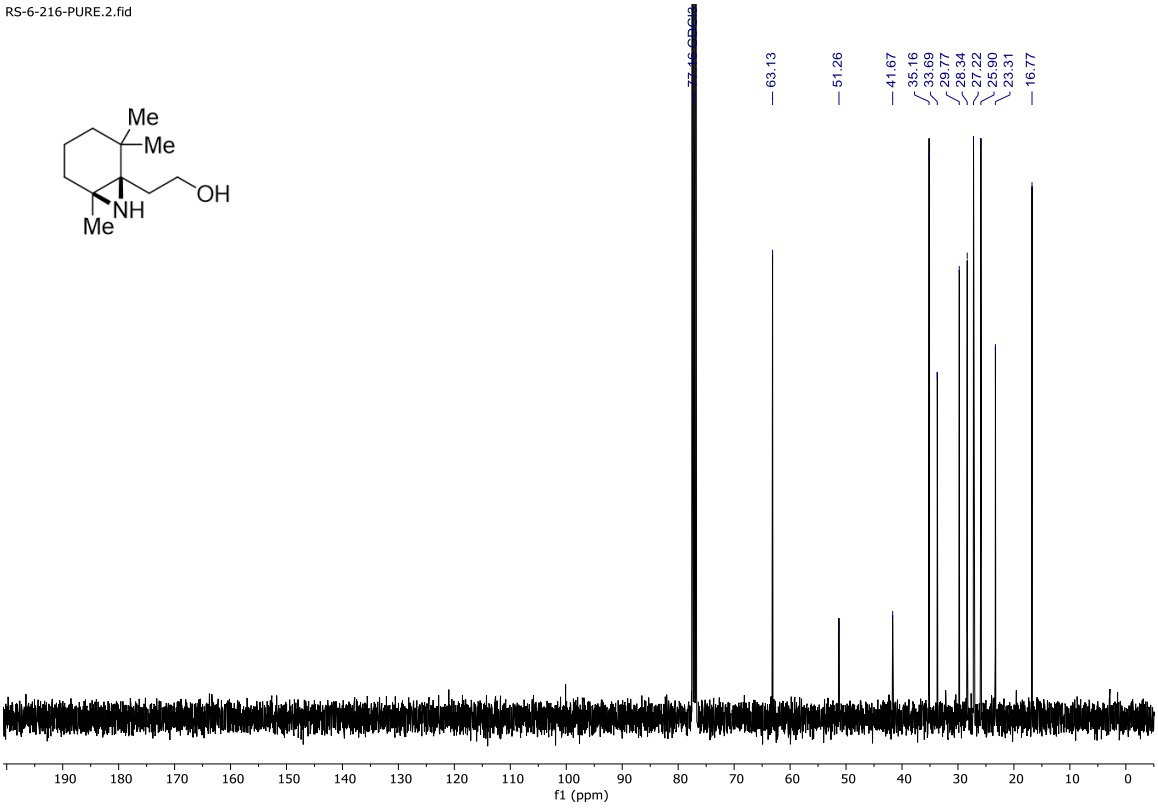
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 63.1, 51.2, 41.6, 35.1, 33.6, 29.7, 28.3, 27.2, 25.9, 23.3, 16.7.

IR ν 3324, 3058, 2953, 2305, 1465, 1265, 1060, 739 $cm^{-1}$.

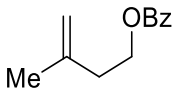
HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{11}H_{21}NONa^+$ 206.1521. Found 206.1503 (8.7 ppm error).

**Compound 55 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**



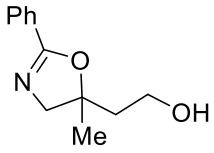



## V. Associated data for Manuscript Figure 3 (Interesting Results and Poor Performers)




3-methylbut-3-en-1-yl benzoate

**Compound 56**: Previously synthesized and characterized in *J. Org. Chem.* **2024**, *89*, 6263 – 6273.




2-(5-methyl-2-phenyl-4,5-dihydrooxazol-5-yl)ethan-1-ol

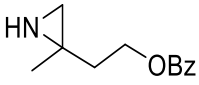
**Compound 57**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; Purified using a gradient of 0 to 100% EtOAc/hexanes on silica gel; (colorless oil, 0.200 g, 0.974 mmol, 49% yield).

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.51 – 7.44 (m, 1H), 7.43 – 7.35 (m, 2H), 3.91 (d, *J* = 14.7 Hz, 1H), 3.88 – 3.77 (m, 2H), 3.74 (d, *J* = 14.5 Hz, 1H), 2.53 – 2.31 (broad m, 1H), 2.06 – 1.96 (m, 2H), 1.48 (s, 3H).

$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 163.2, 131.4, 128.4, 128.1, 128.0, 85.7, 66.0, 58.7, 42.5, 25.9.

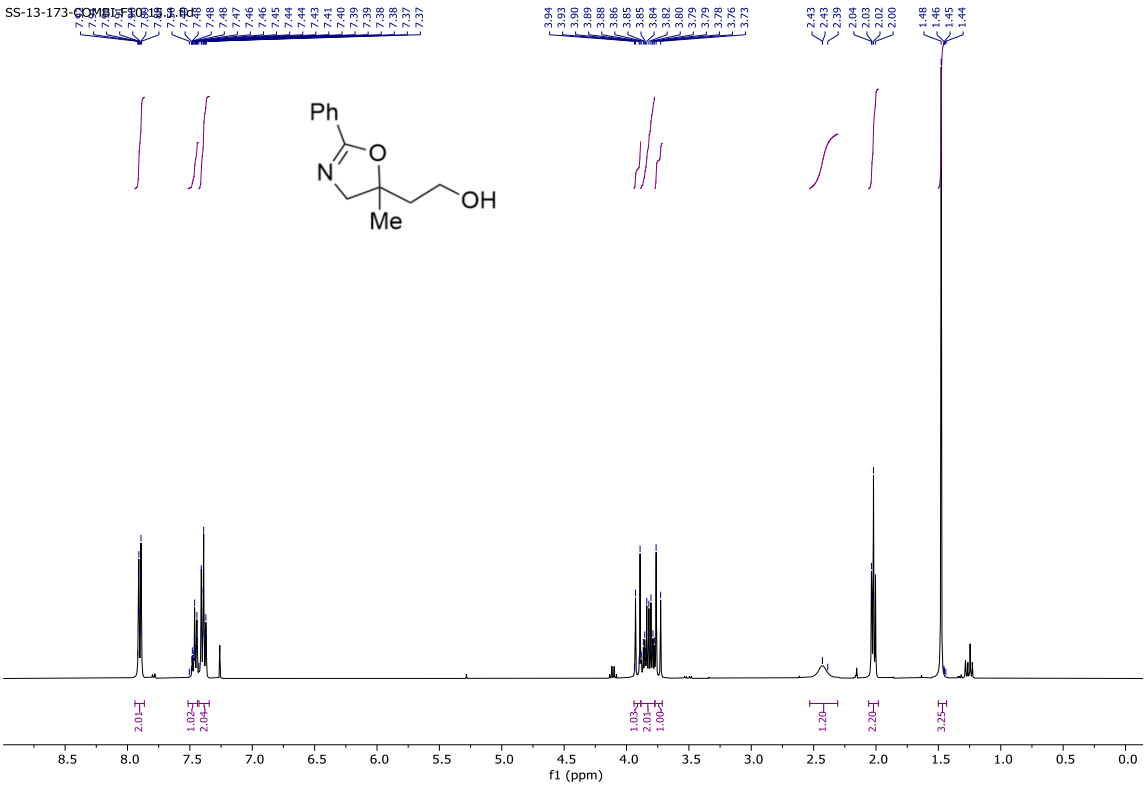
IR ν 3299, 2931, 1643, 1359, 1277, 1066, 1027 $cm^{-1}$.

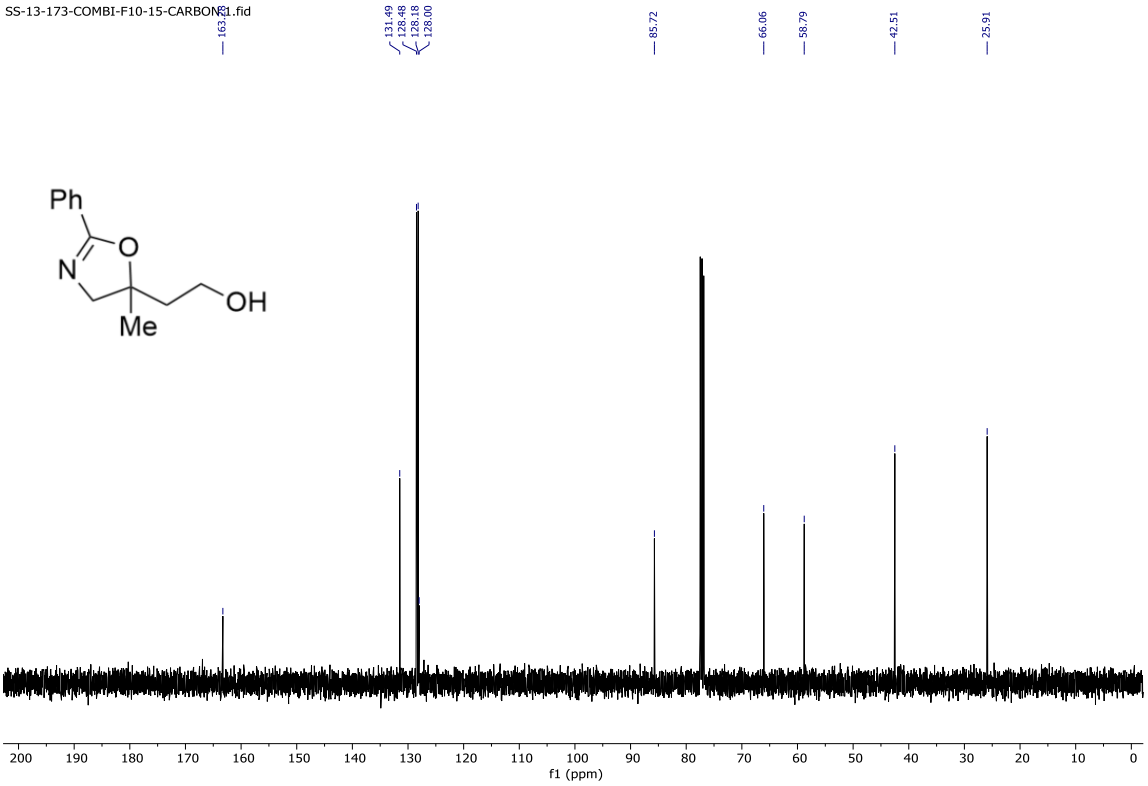
HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{12}H_{16}NO_2^+$ 206.1176. Found 206.1164 (5.8 ppm error).

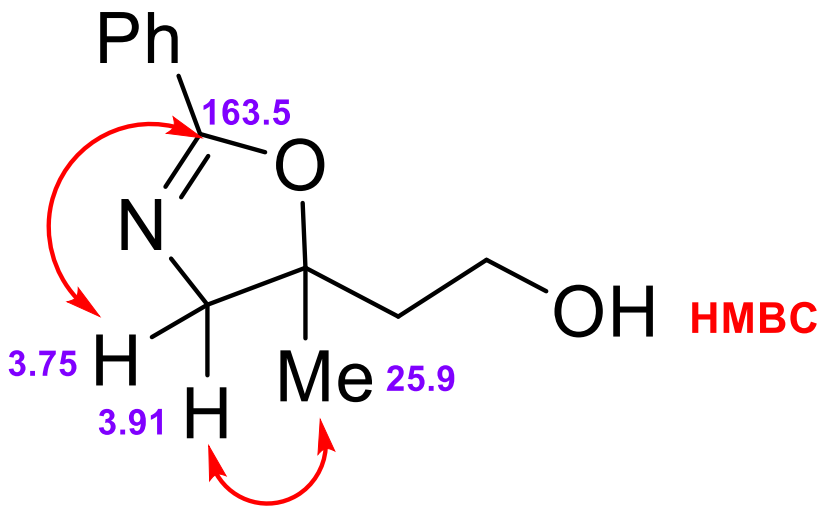
This compound was synthesized in *J. Org. Chem.* **2024***, 89,* 6263–6273, but the structure was misassigned as 

. Our data matches what was tabulated.

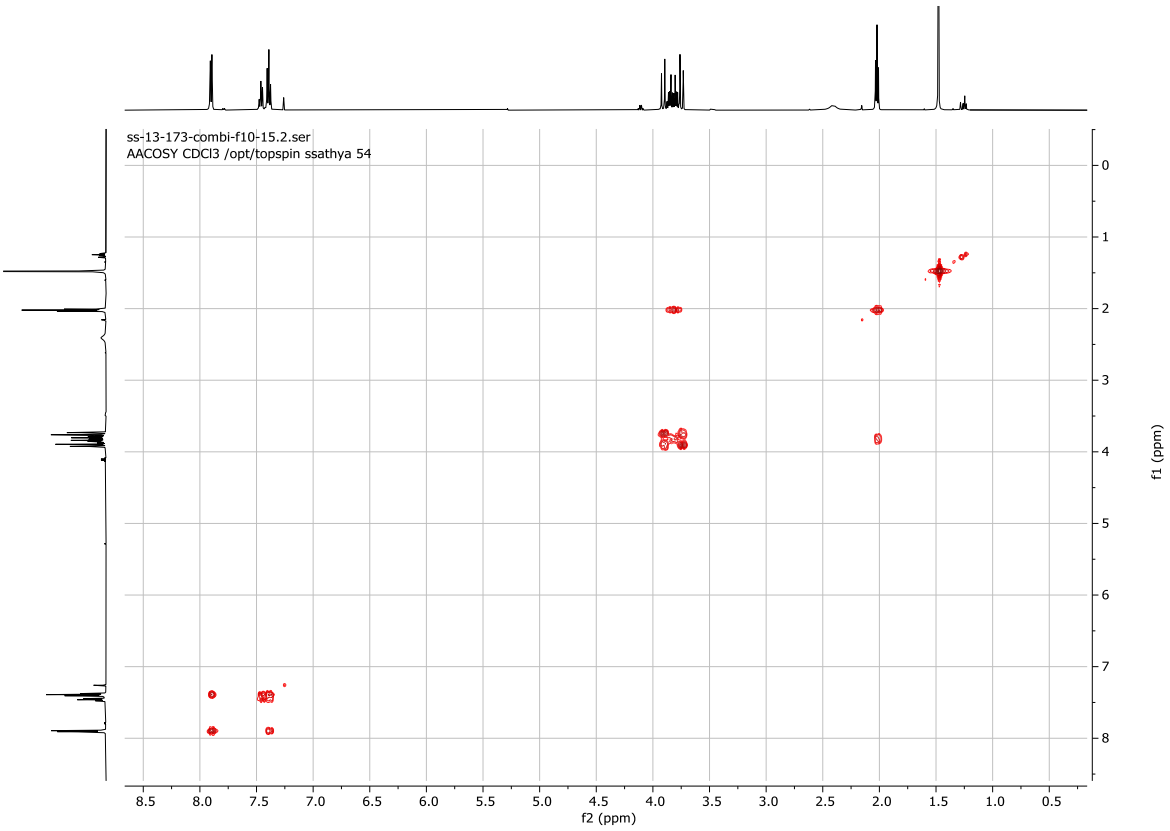
**Compound 57 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**



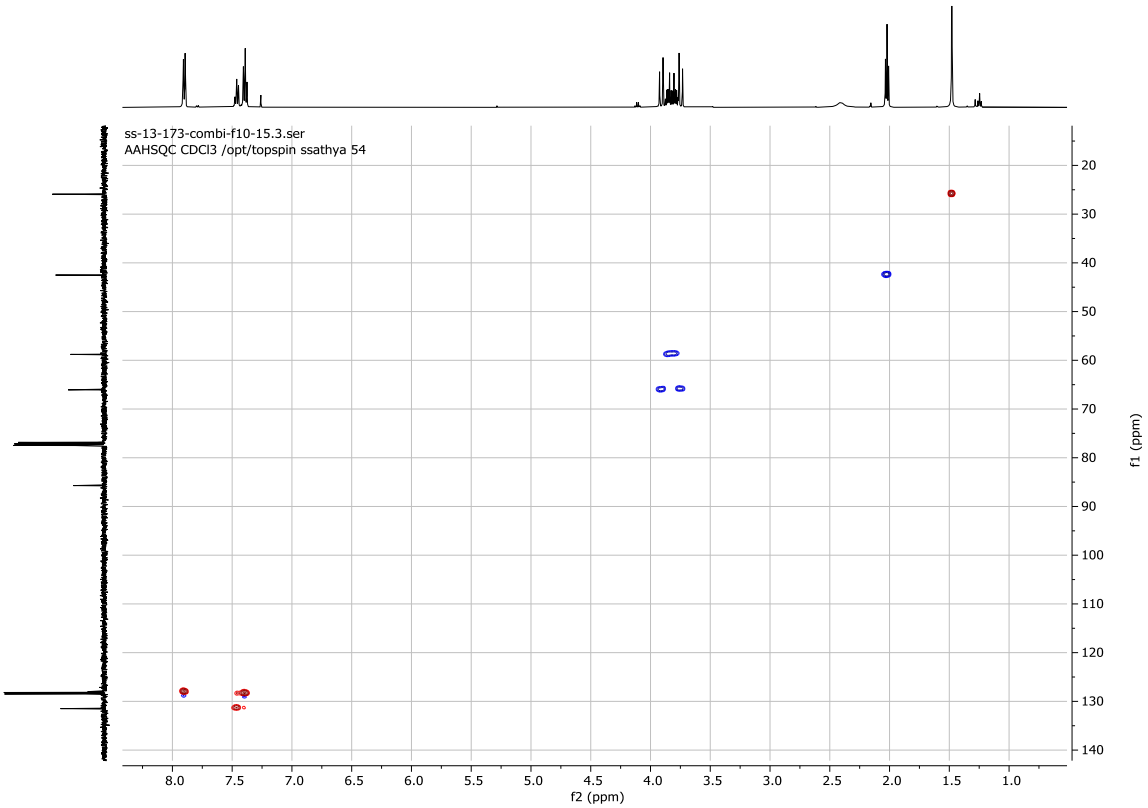




Ph
163.5
O
N
OH
HMBC
3.75
H
Me
25.9
3.91
H

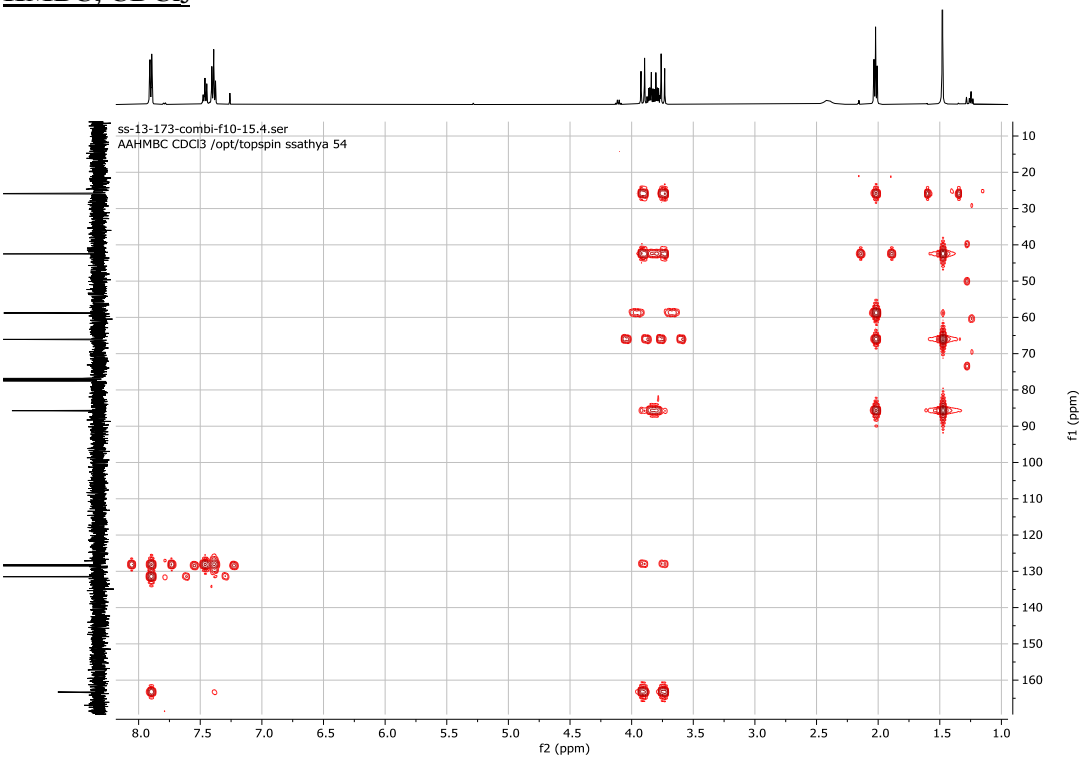
**COSY, $CDCl_3$**

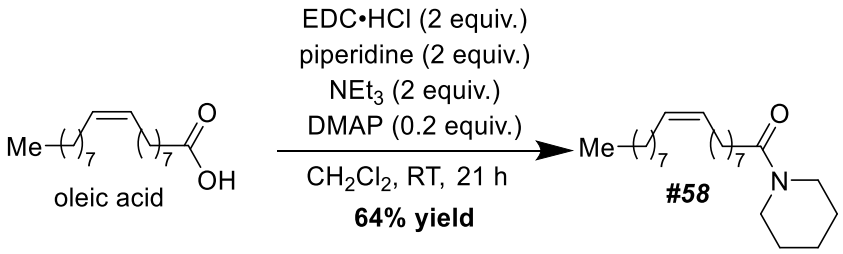

ss-13-173-combi-f10-15.2.ser
AACOSY CDCl3 /opt/topspin ssathya 54
f2 (ppm)
f1 (ppm)

## HSQC, $CDCl_3$

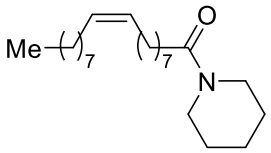



## HMBC, $CDCl_3$






A 100 mL round-bottom flask equipped with a magnetic stir bar was charged with oleic acid (2.03 g, 7.19 mmol, 1 equiv.), $CH_2Cl_2$ (35 mL, reaction concentration = 0.2 M), EDC•HCl (2.71 g, 14.1 mmol, 2 equiv.), piperidine (1.4 mL, 1.21 g, 14.2 mmol, 2 equiv.), $NEt_3$ (2 mL, 1.45 g, 14.3 mmol, 2 equiv.), and DMAP (0.170 g, 1.4 mmol, 0.2 equiv.). The reaction mixture was stirred at ambient temperature for 21 hours. Following this time, the mixture was transferred to a separatory funnel with $CH_2Cl_2$ (40 mL) and quenched by the addition of 1 M aqueous HCl solution (40 mL) and brine (40 mL). The layers were vigorously shaken and allowed to separate. The organic layer was collected, and the aqueous layer was extracted with $CH_2Cl_2$ (2 x 40 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel (gradient of 0 to 100% EtOAc/hexanes) to give **58** (colorless oil, 1.60 g, 4.58 mmol, 64% yield).




(*Z*)-1-(piperidin-1-yl)octadec-9-en-1-one

**Compound 58**:

$^1$H NMR (600 MHz, $CDCl_3$) δ 5.39 – 5.31 (m, 2H), 3.59 – 3.46 (m, 2H), 3.45 – 3.27 (m, 2H), 2.30 (td, *J* = 8.0, 2.8 Hz, 2H), 2.05 – 1.93 (m, 4H), 1.69 – 1.57 (m, 4H), 1.55 – 1.48 (m, 4H), 1.42 – 1.10 (m, 20H), 0.87 (td, *J* = 7.0, 2.5 Hz, 3H).

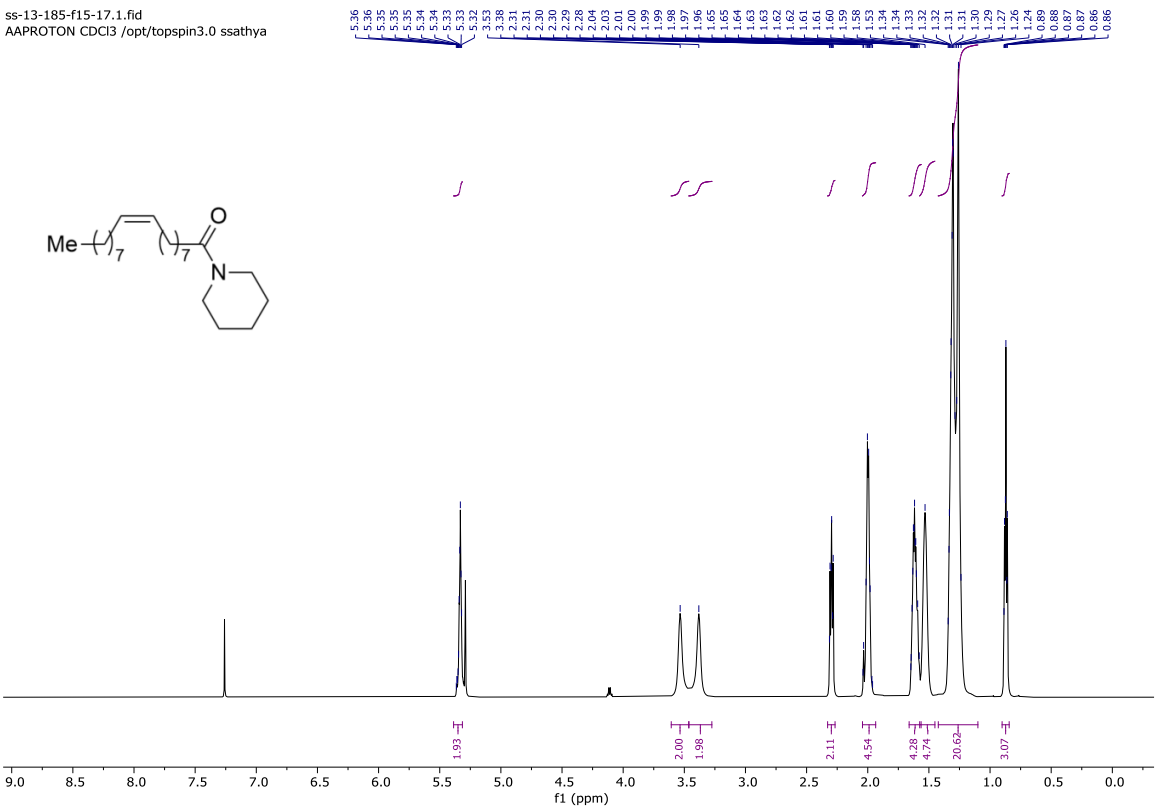
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 171.5, 129.9, 129.8, 46.7 (broad), 42.5 (broad), 33.5, 31.9, 29.8, 29.7, 29.5, 29.4, 29.3, 29.1, 27.22, 27.20, 26.6 (broad), 25.6 (broad), 25.5, 24.6, 22.6, 14.1.

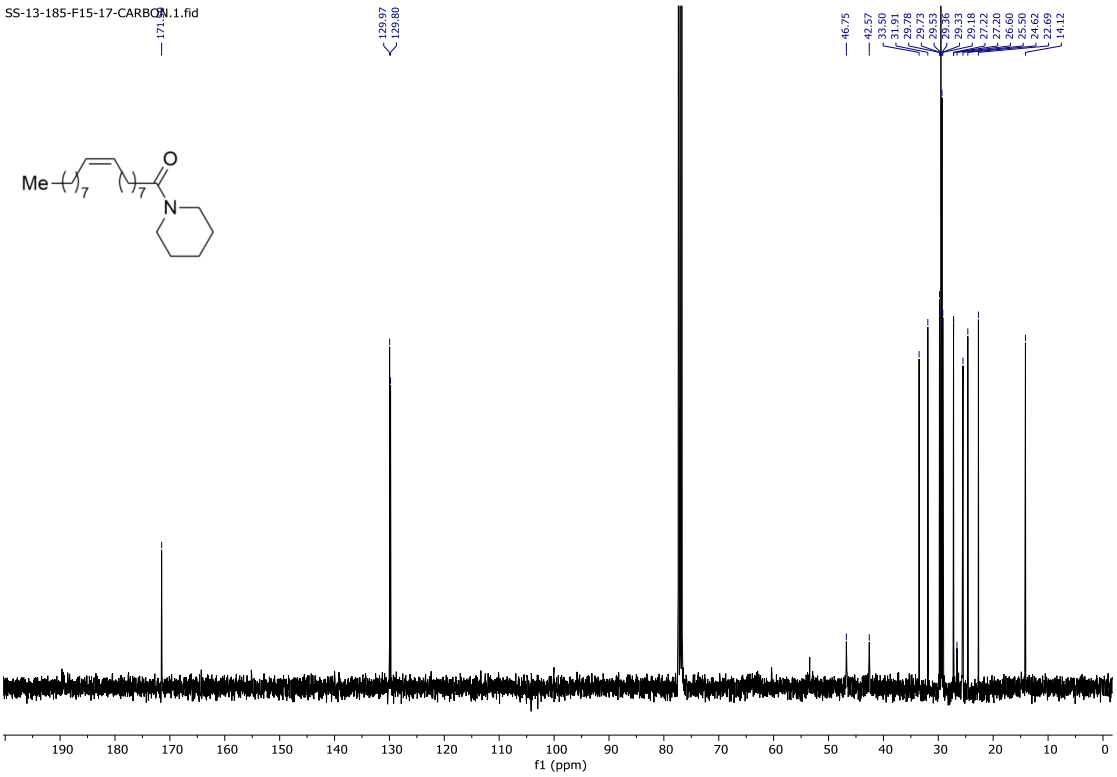
IR ν 2925, 2853, 1649, 1465, 1432, 1253, 1220 cm$^{-1}$.

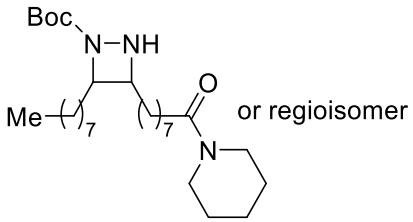
HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{23}H_{44}NO^+$ 350.3417. Found 350.3409 (2.3 ppm error).

Our data has reasonable concordance with what has been reported in *Green Chem.*, **2015**, *17*, 3157 – 3163.

## Compound 58 ($CDCl_3$, $^1H$ NMR: 600 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)






*tert*-butyl 4-octyl-3-(8-oxo-8-(piperidin-1-yl)octyl)-1,2-diazetidine-1-carboxylate

**Compound 59**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; Purified using a gradient of 0 to 100% EtOAc/hexanes on silica gel; (colorless oil, ~20% yield estimated by $^{1}$H NMR integration against an internal standard).

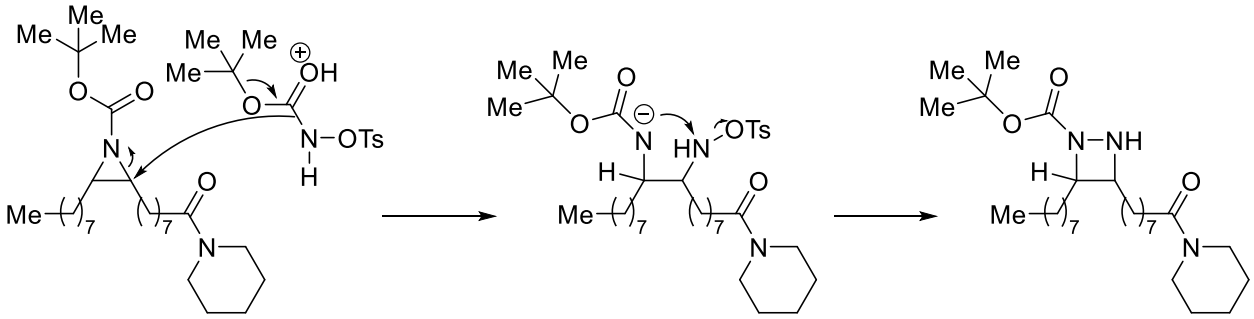
$^{1}$H NMR (600 MHz, $CDCl_3$) δ 7.51 (broad s, 1H), 3.58 – 3.48 (m, 2H), 3.43 – 3.33 (m, 2H), 2.51 – 2.42 (m, 2H), 2.32 – 2.24 (m, 2H), 1.65 – 1.56 (m, 4H), 1.55 – 1.48 (m, 4H), 1.47 – 1.37 (m, 8H), 1.36 – 1.31 (m, 8H), 1.30 – 1.19 (m, 17H), 0.86 (t, $J$ = 6.9 Hz, 3H).

$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 171.5, 167.2, 81.7, 46.8, 43.8, 43.7, 42.7, 33.5, 31.9, 29.6, 29.53, 29.49, 29.40, 29.3, 27.7, 27.68, 27.59, 27.51, 26.7, 26.3, 25.7, 25.4, 24.7, 22.7, 14.2.

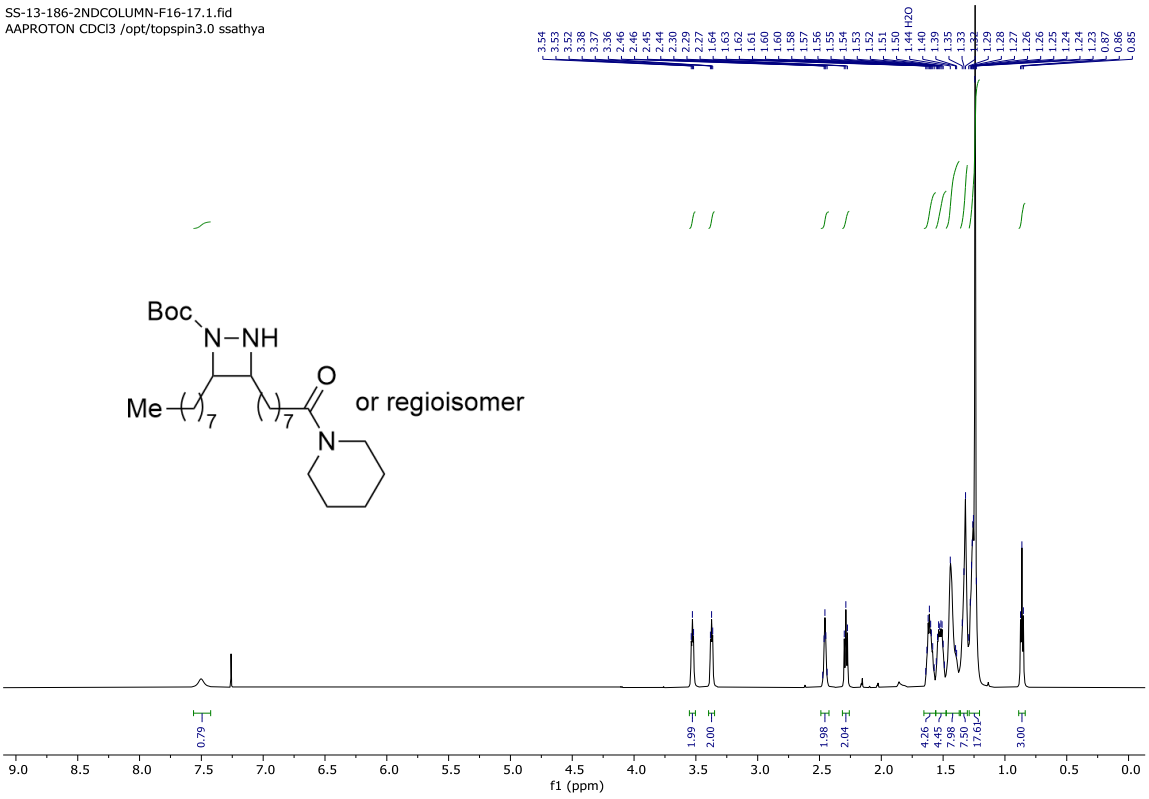
IR ν 3226, 2927, 2854, 1715, 1629, 1466, 1365, 1275, 1189 cm$^{-1}$.

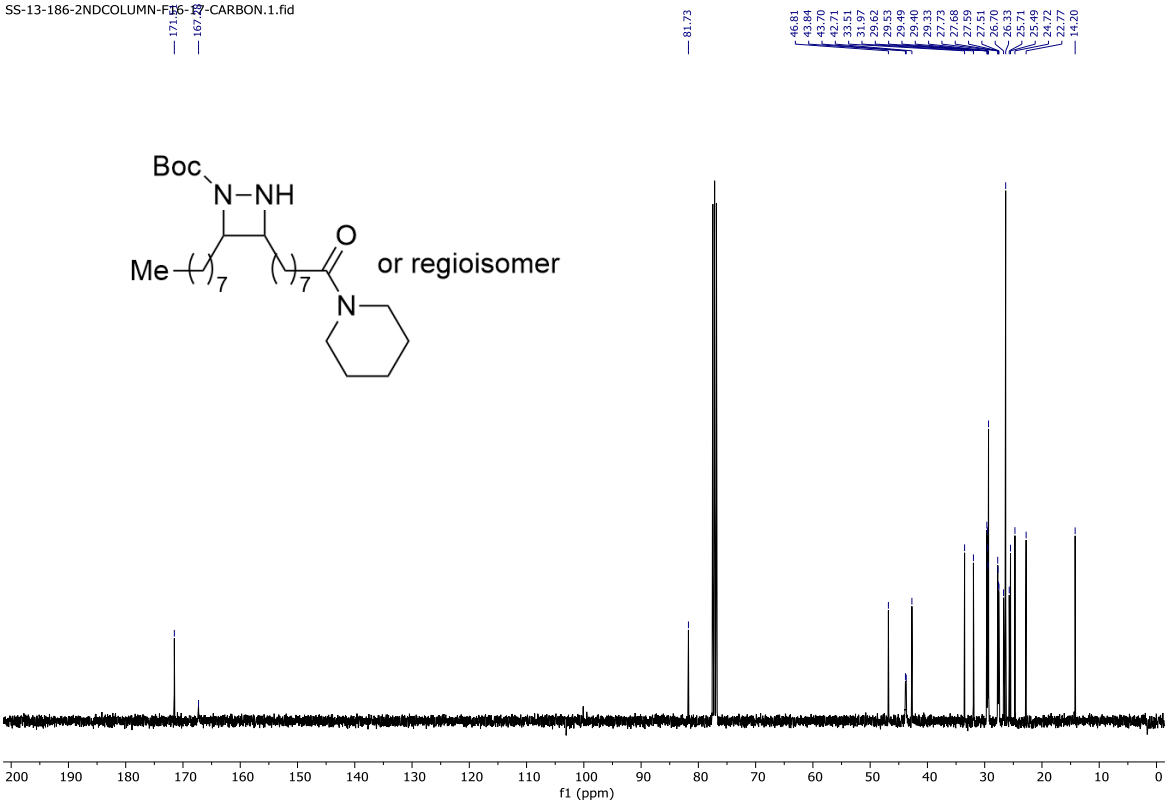
HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{28}H_{54}N_3O_3^+$ 480.4160. Found 480.4134 (5.4 ppm error).

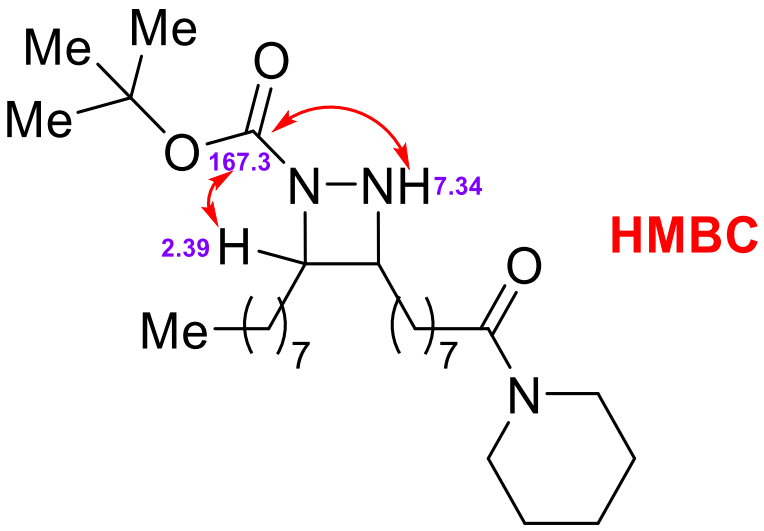
**Possible mechanism of formation**



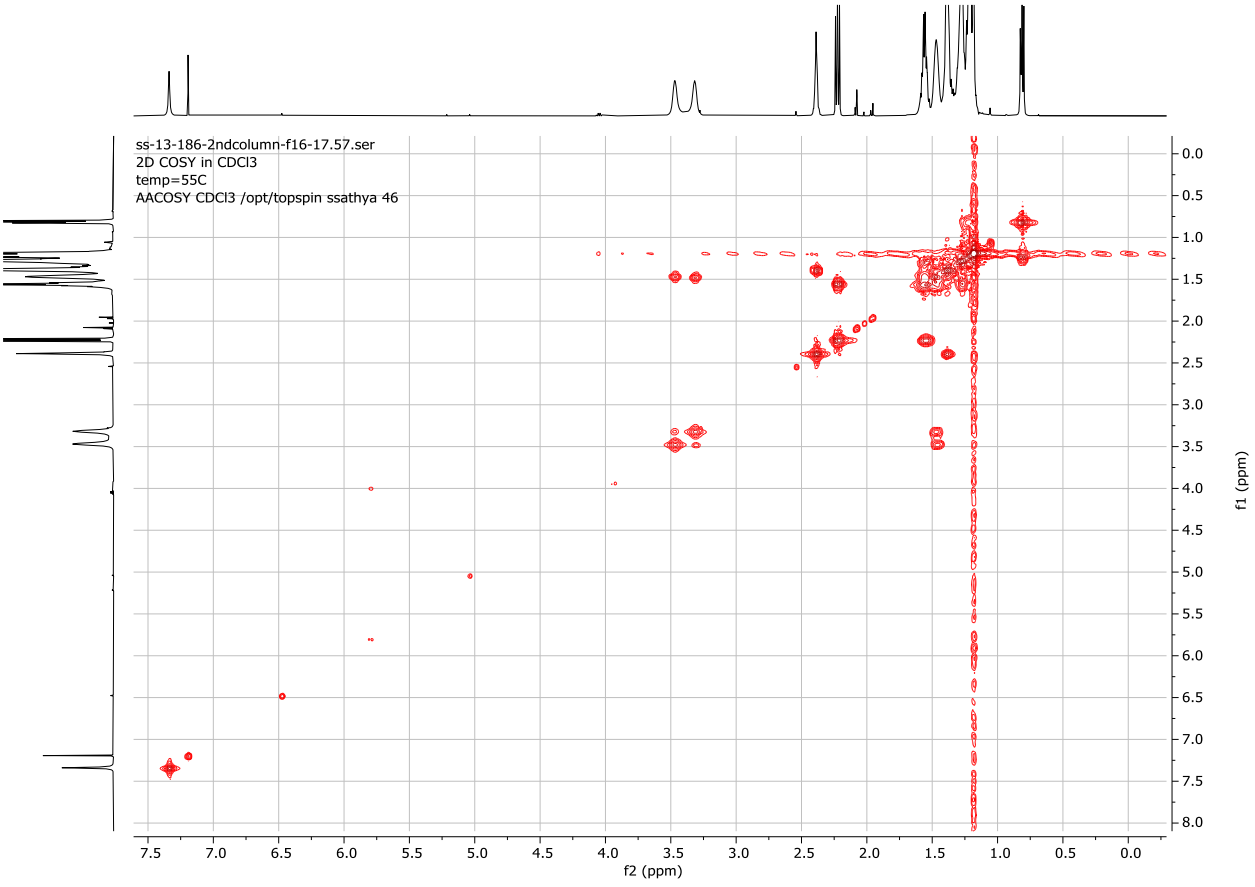
## Compound 59 ($CDCl_3$, $^1H$ NMR: 600 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)



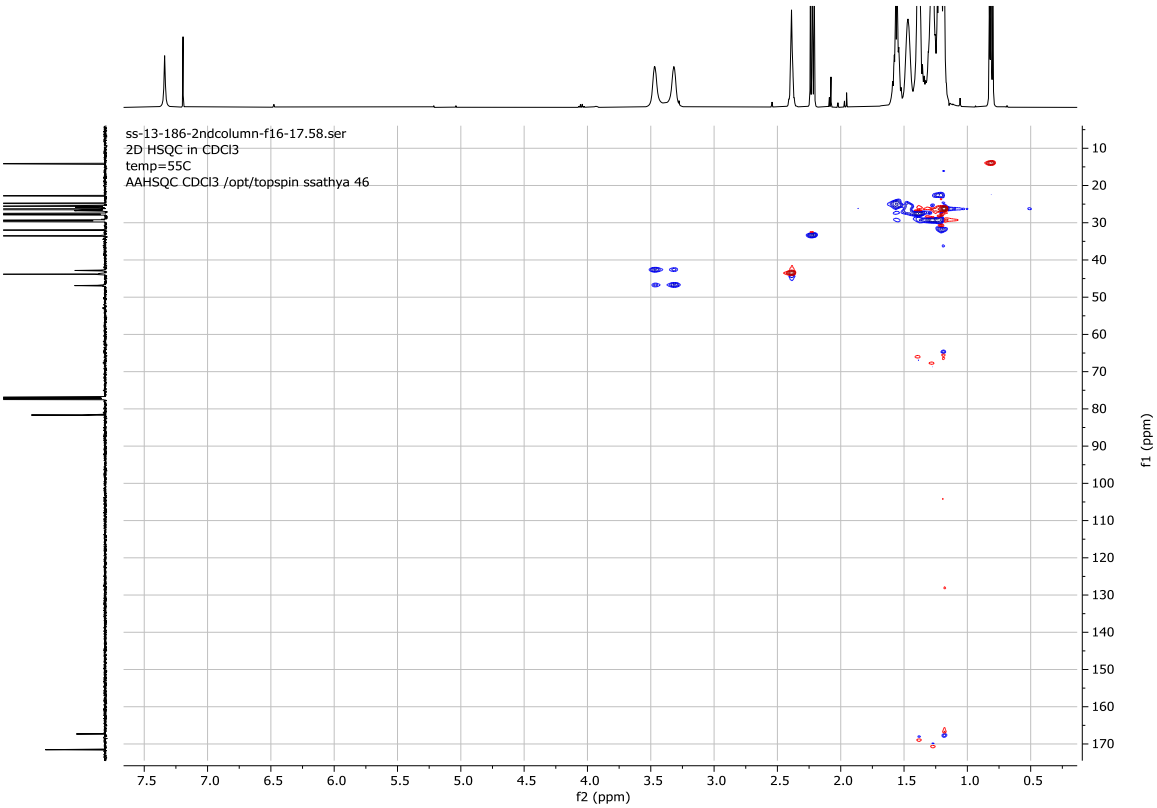





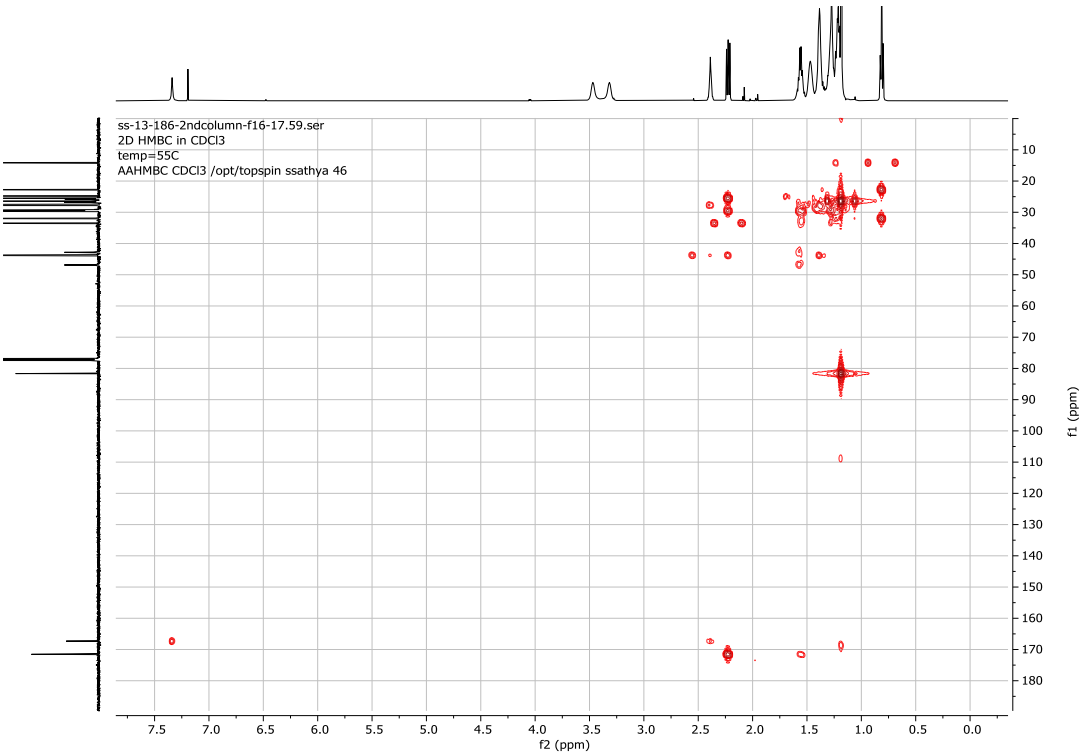

**COSY, $CDCl_3$, 55 °C**

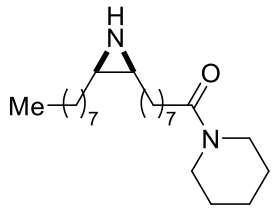


## HSQC, $CDCl_3$, 55 °C




## HMBC, $CDCl_3$, 55 °C





8-((2*S**,3*R**)-3-octylaziridin-2-yl)-1-(piperidin-1-yl)octan-1-one

**Compound 60**: Synthesized using **General Procedure B, Part I** on a 2 mmol scale; Purified using sequential flushes of $CH_2Cl_2$, EtOAc, acetone, and methanol on Florisil (60 – 100 mesh); isolated and characterized as the single diastereomer shown; (colorless oil, ~10% yield estimated by $^1$H NMR integration against an internal standard).

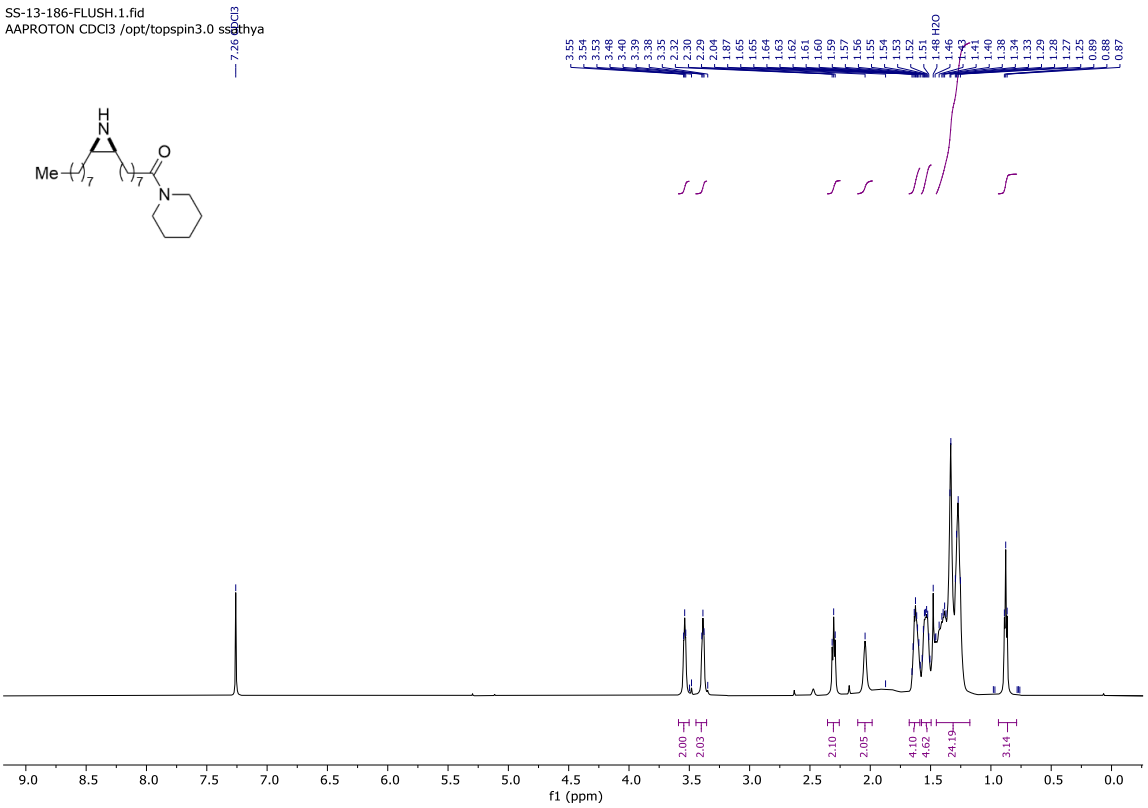
$^1$H NMR (600 MHz, $CDCl_3$) δ 3.57 – 3.50 (m, 2H), 3.41 – 3.35 (m, 2H), 2.35 – 2.26 (m, 2H), 2.11 – 1.98 (m, 2H), 1.69 – 1.58 (m, 4H), 1.58 – 1.50 (m, 4H), 1.45 – 1.17 (m, 24H), 0.88 (t, *J* = 6.9 Hz, 3H).

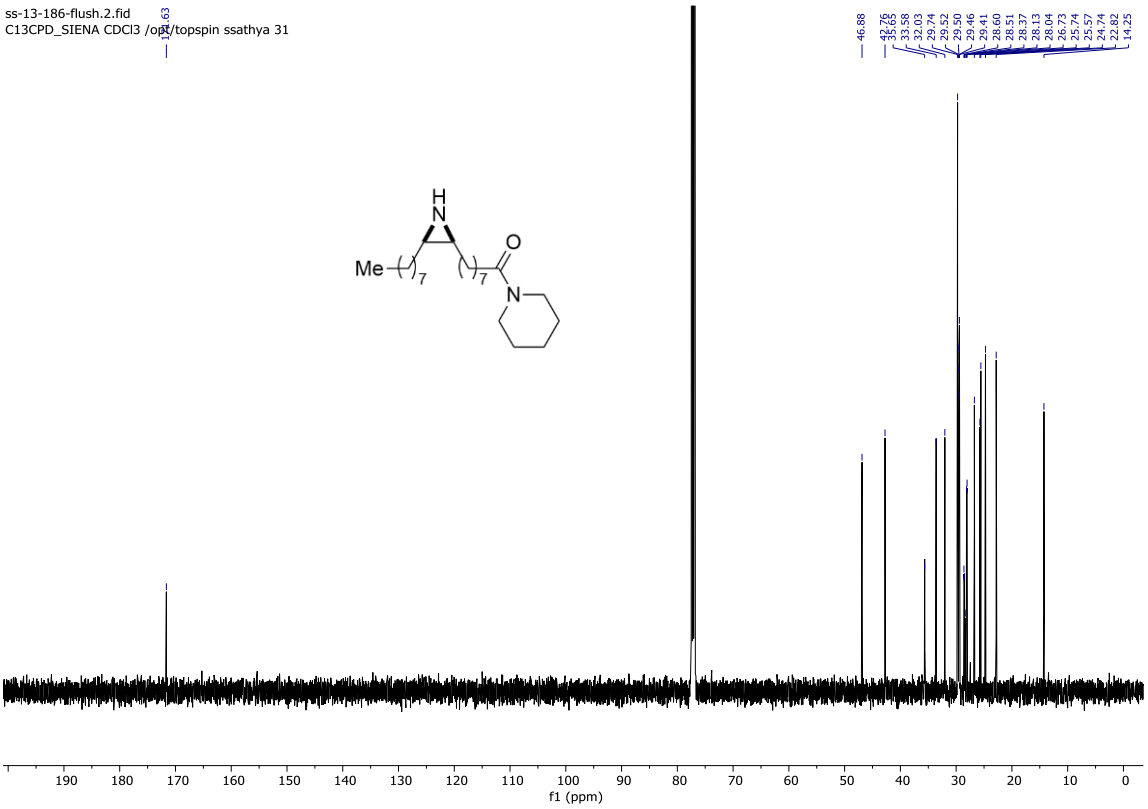
$^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) δ 171.6, 46.8, 42.7, 35.6, 33.5, 32.0, 29.7, 29.52, 29.50, 29.46, 29.41, 28.6, 28.5, 28.3, 28.1, 28.0, 26.7, 25.7, 25.5, 24.7, 22.8, 14.2.

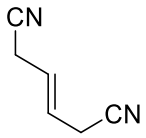
IR ν 2925, 2853, 1643, 1435, 1256 cm$^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{23}H_{45}N_2O^+$ 365.3526. Found 365.3535 (2.5 ppm error).

## Compound 60 ($CDCl_3$, $^1H$ NMR: 600 MHz, $^{13}C\{^1H\}$ NMR: 126 MHz)

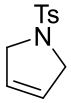





(*E*)-hex-3-enedinitrile

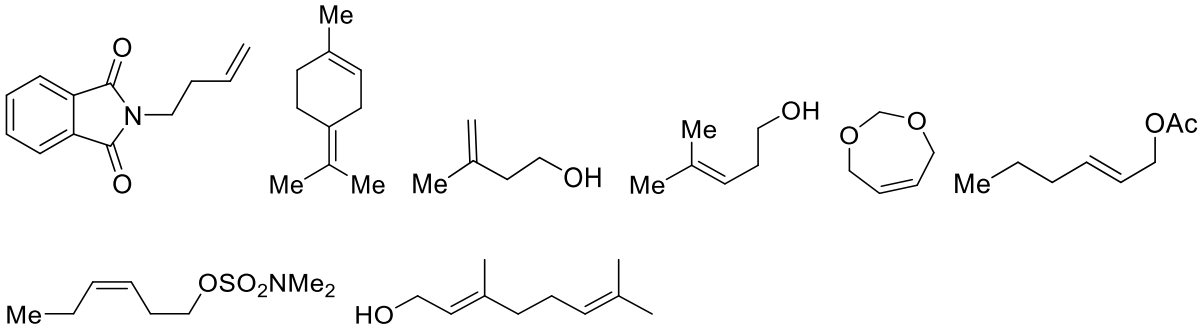
**Compound 61**: Commercially available.




1-tosyl-2,5-dihydro-1*H*-pyrrole

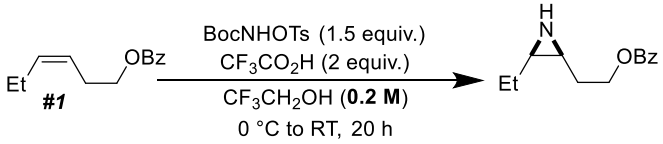
**Compound 62**: Commercially available.

Other substrates that did not give appreciable aziridine product include:



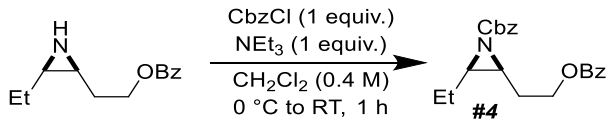
## VI. Procedures, characterization data, and spectra for Manuscript Figure 5

### Scale-up Procedure, Part I

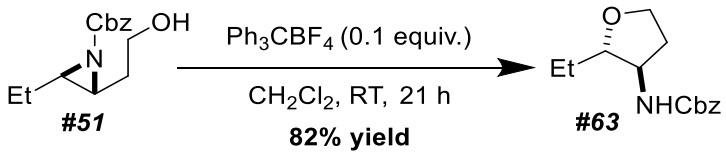



A 100 mL round-bottom flask equipped with a magnetic stir bar was charged with **1** (2.04 g, 10.0 mmol, 1 equiv.), *N*-Boc-*O*-tosyl hydroxylamine (4.31 g, 15.0 mmol, 1.5 equiv.), and trifluoroethanol (40 mL). The stirring mixture was cooled to 0 °C using an ice-water bath. Trifluoroacetic acid (2.28 g, 20.0 mmol, 2 equiv.) in trifluoroethanol (10 mL) was slowly added to the reaction mixture (final reaction concentration = 0.2 M). The flask was sealed and removed from the ice-water bath. The stirring reaction mixture was warmed to room temperature over a period of 20 hours. Following this time, the seal was broken, and the contents of the flask were transferred to a separatory funnel with EtOAc (50 mL). The organic layer was washed with 1 M aqueous NaOH solution (50 mL) and brine (50 mL), collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Prior to the next step, the residue was dissolved in $CH_2Cl_2$ (50 mL), filtered to remove unknown solid particles, and concentrated under reduced pressure.

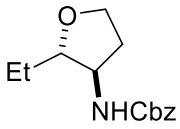
### Scale-up Procedure, Part II




A 100 mL round-bottom flask equipped with a magnetic stir bar was charged with N-H aziridine substrate (crude from the previous step) and HPLC grade $CH_2Cl_2$ (25 mL, reaction concentration = 0.4 M, based on the mmol of the alkene substrate from the previous step). The stirring reaction mixture was cooled to 0 °C using an ice-water bath. Benzyl chloroformate (1.4 mL, 1.68 g, 9.8 mmol, ~1 equiv. based on the mmol of the alkene substrate from the previous step) and triethylamine (1.4 mL, 1.02 g, 10.0 mmol, 1 equiv. based on the mmol of the alkene substrate from the previous step) were added, and the flask was sealed. After five minutes, the stirring reaction mixture was removed from the ice-water bath and warmed to room temperature over a period of 1 hour. Following this time, the seal was broken, and the contents of the vial were transferred to a separatory funnel with $CH_2Cl_2$ (40 mL). The organic layer was washed once with 1 M aqueous HCl solution (20 mL), collected, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel (gradient of 0 to 50% EtOAc/hexanes) to give **4** (colorless oil, 2.23 g, 6.31 mmol, 63% yield over 2 steps).




A scintillation vial was charged with a stir bar, **51** (0.240 g, 0.963 mmol, 1 equiv.), and anhydrous $CH_2Cl_2$ (5 mL, reaction concentration = 0.2 M). Triphenylcarbenium tetrafluoroborate (0.032 g, 0.096 mmol, 0.1 equiv.) was added in one bolus. The vial was sealed, and the reaction was stirred for 21 hours at room temperature, over which time the reaction hue changed from bright yellow to orange. Following this time, the seal was broken, and the contents of the reaction flask were transferred to a separatory funnel with $CH_2Cl_2$ (40 mL). The organic layer was washed once with saturated aqueous $NaHCO_3$ solution (40 mL), collected, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (gradient of 0 to 50% EtOAc/hexanes) to give **63** (light yellow oil, 0.199 g, 0.798 mmol, 82% yield).




benzyl ((2*S**,3*R**)-2-ethyltetrahydrofuran-3-yl)carbamate

**Compound 63**:

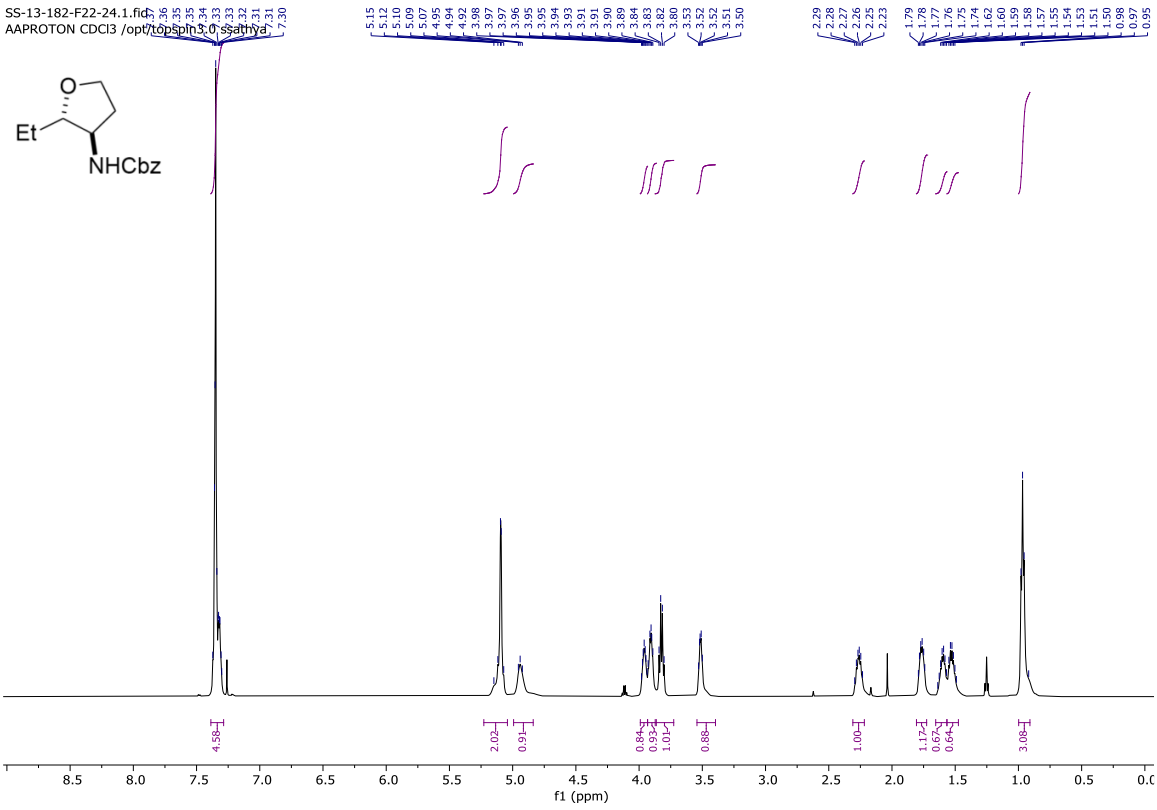
$^1$H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 5.19 – 5.06 (m, 2H), 4.99 – 4.86 (m, 1H), 3.96 (dp, *J* = 9.2, 5.1 Hz, 1H), 3.93 – 3.86 (m, 1H), 3.82 (q, *J* = 7.9 Hz, 1H), 3.52 (dt, *J* = 10.6, 5.1 Hz, 1H), 2.26 (dq, *J* = 15.6, 8.2 Hz, 1H), 1.77 (h, *J* = 5.2 Hz, 1H), 1.60 (hept, *J* = 7.1 Hz, 1H), 1.52 (dq, *J* = 14.2, 7.2 Hz, 1H), 0.97 (t, *J* = 7.5 Hz, 3H).

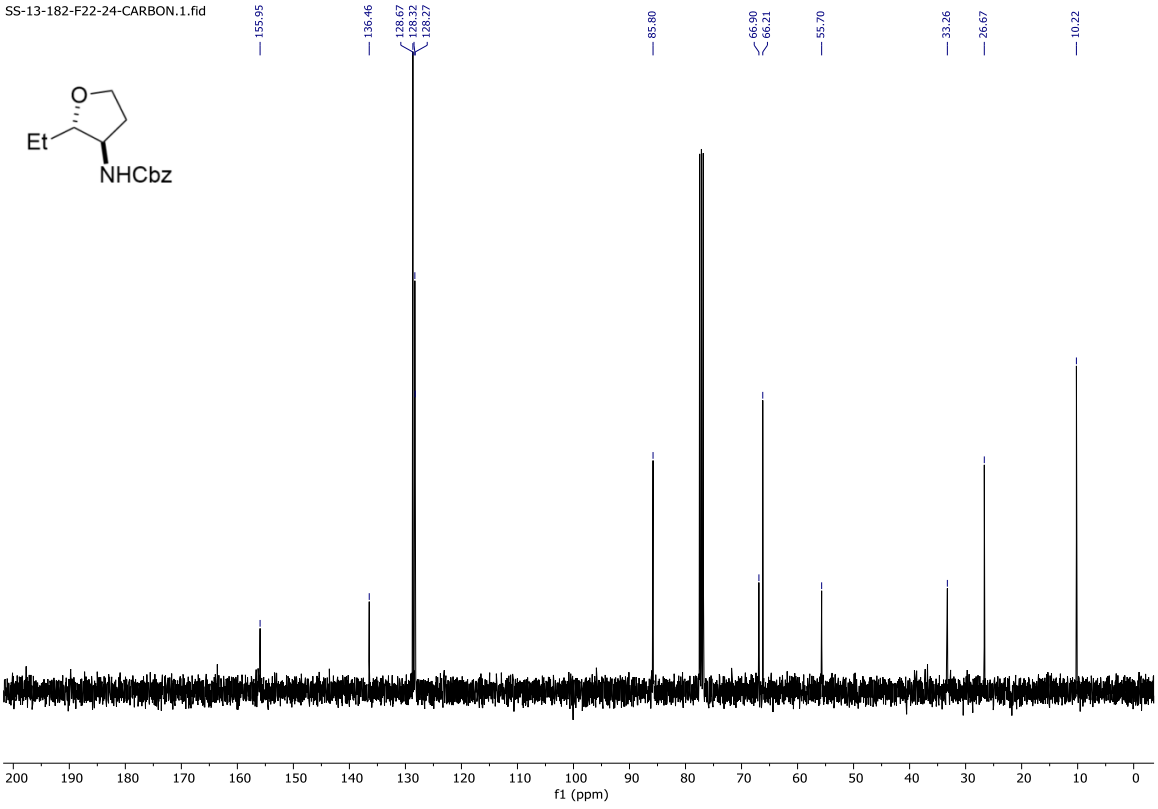
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 155.9, 136.4, 128.6, 128.3, 128.2, 85.8, 66.9, 66.2, 55.7, 33.2, 26.6, 10.2.

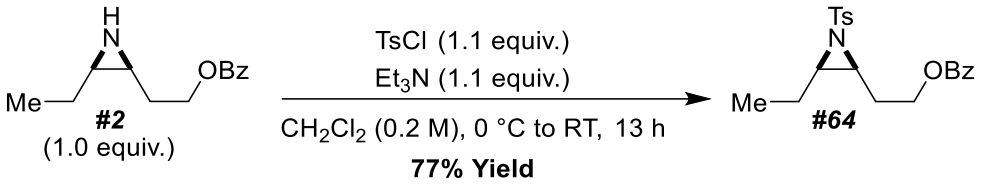
IR ν 3318, 2964, 1697, 1537, 1455, 1236, 1071 cm$^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{14}H_{19}NNaO_3^+$ 272.1257. Found 272.1255 (0.7 ppm error).

**Compound 63 ($CDCl_3$, $^1H$ NMR: 600 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**

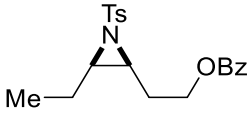





A round-bottom flask equipped with a magnetic stir bar was charged with compound **2** (0.500 g, 2.28 mmol, 1.0 equiv.) and dichloromethane (11 mL, reaction concentration = 0.2 M). The resulting solution was cooled to 0 °C using an ice-water bath. Triethylamine (0.348 mL, 0.253 g, 2.50 mmol, 1.1 equiv.) was added dropwise, followed by the portionwise addition of tosyl chloride (0.478 g, 2.50 mmol, 1.1 equiv.). The stirring reaction mixture was warmed to room temperature over a period of 13 hours. Following this time, the reaction mixture was diluted with dichloromethane (40 mL) and transferred to a separatory funnel. The organic layer was washed with 1 M aqueous HCl solution (10 mL), collected, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude residue by silica gel column chromatography using a gradient of 0 to 60% ethyl acetate in hexanes afforded compound **64** (colorless oil, 0.659 g, 1.76 mmol, 77% yield).

*Note: Compound 2 was synthesized from cis-3-hexen-1-yl benzoate using General Procedure B, Part I and was purified by column chromatography on Florisil (60 – 100 mesh) using a gradient of 0 to 50% ethyl acetate/hexanes followed by flushing with 100% methanol.*




2-((2*S**,3*R**)-3-ethyl-1-tosylaziridin-2-yl)ethyl benzoate

**Compound 64**:

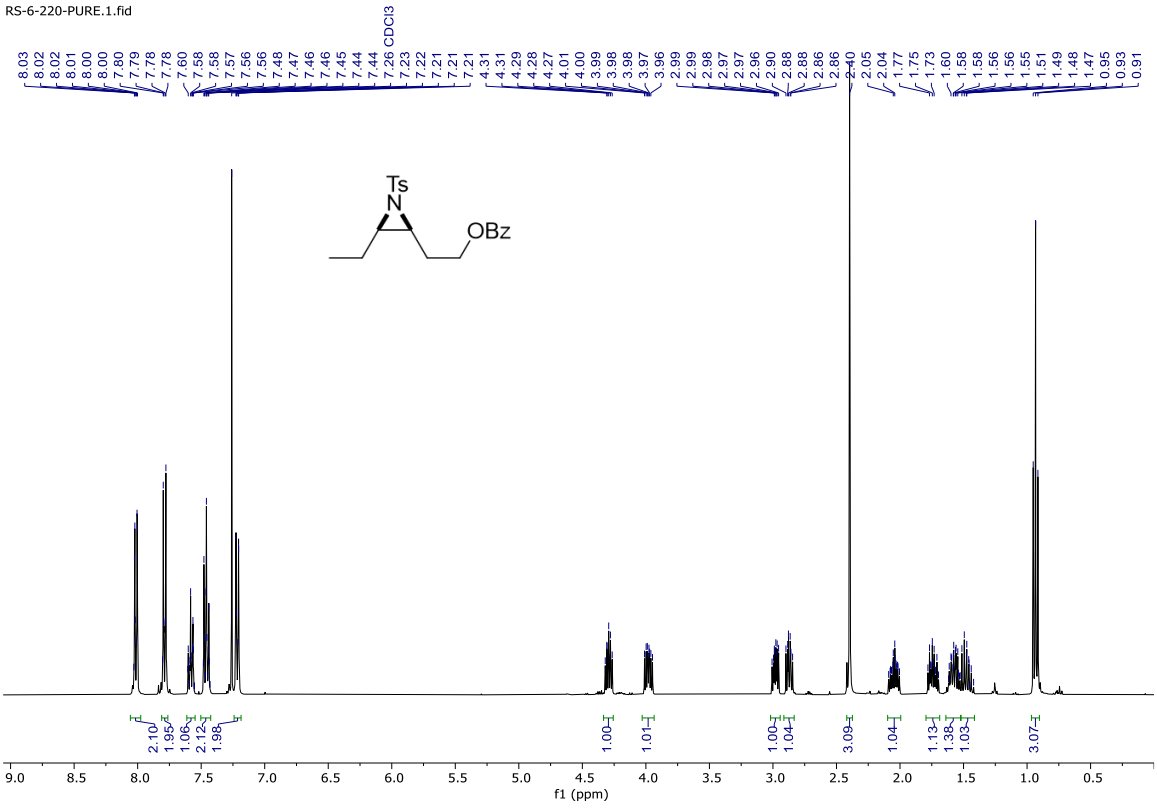
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 2H), 7.81 – 7.76 (m, 2H), 7.61 – 7.55 (m, 1H), 7.50 – 7.43 (m, 2H), 7.24 – 7.19 (m, 2H), 4.33 – 4.26 (m, 1H), 3.98 (ddd, *J* = 11.1, 8.9, 5.1 Hz, 1H), 2.98 (ddd, *J* = 8.7, 7.3, 4.7 Hz, 1H), 2.87 (td, *J* = 7.8, 5.5 Hz, 1H), 2.40 (s, 3H), 2.05 (dddd, *J* = 14.8, 8.9, 5.9, 4.7 Hz, 1H), 1.80 – 1.69 (m, 1H), 1.57 (dtd, *J* = 15.0, 7.5, 5.5 Hz, 1H), 1.47 (ddd, *J* = 15.4, 14.3, 7.5 Hz, 1H), 0.93 (t, *J* = 7.4 Hz, 3H).

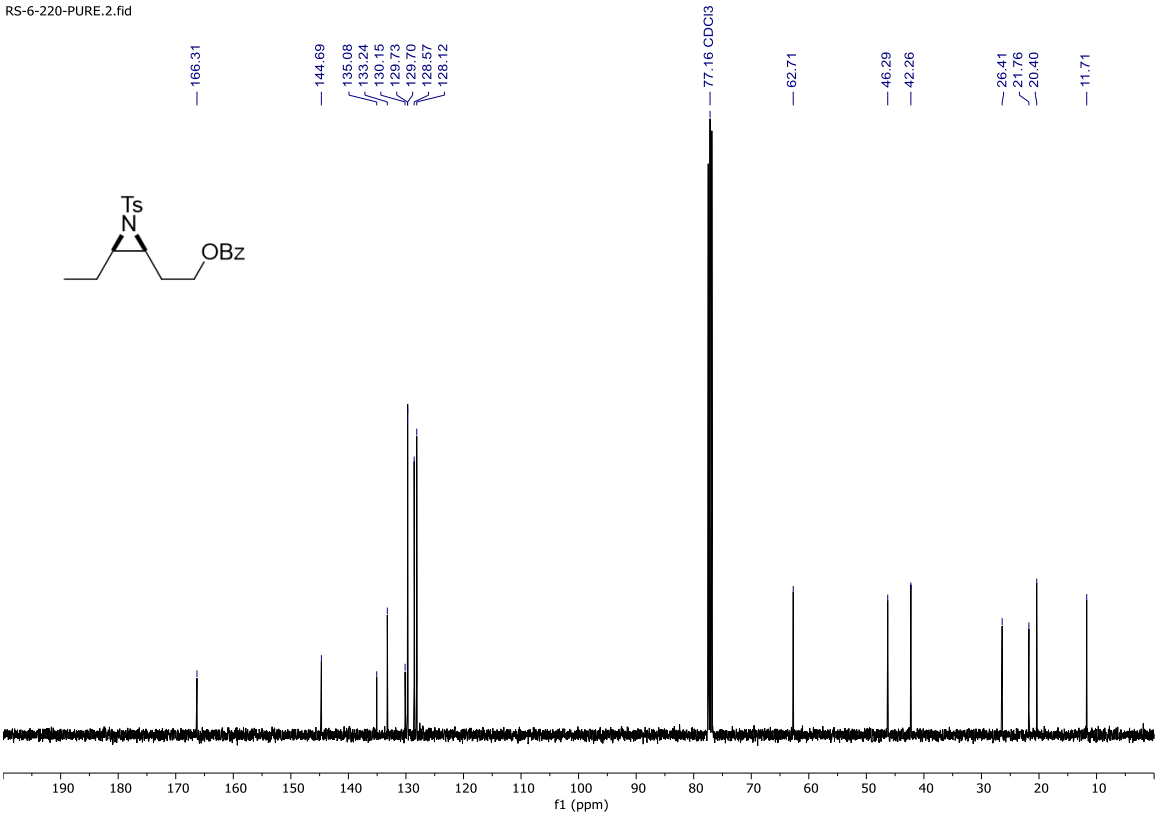
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 166.3, 144.6, 135.0, 133.2, 130.1, 129.73, 129.70, 128.5, 128.1, 62.7, 46.2, 42.2, 26.4, 21.7, 20.4, 11.7.

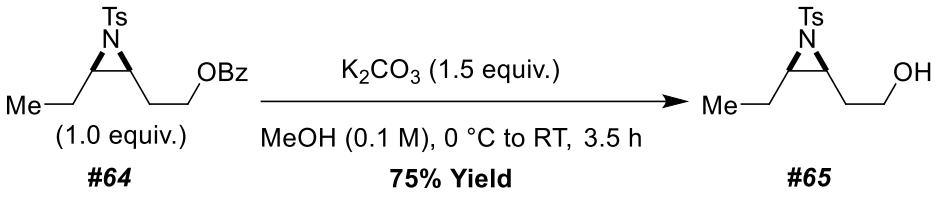
IR ν 3054, 2968, 2312, 1716, 1265, 1118, 743 cm$^{-1}$.

HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{20}H_{23}NO_4SNa^+$ 396.1246. Found 396.1261 (3.8 ppm error).

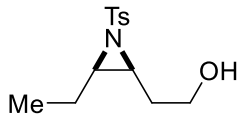
**Compound 64 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






A round-bottom flask equipped with a magnetic stir bar was charged with compound **64** (0.515 g, 1.38 mmol, 1.0 equiv.) and methanol (14 mL, reaction concentration = 0.1 M). The solution was cooled to 0 °C using an ice-water bath. Potassium carbonate (0.285 g, 2.06 mmol, 1.5 equiv.) was added in one portion. The stirring reaction mixture was warmed to room temperature over a period of 3.5 hours. Following this time, the reaction was quenched with saturated aqueous $NH_4Cl$ solution (5 mL) and transferred to a separatory funnel. The mixture was extracted with ethyl acetate (30 mL), and the organic layer was collected. The aqueous layer was further extracted with ethyl acetate (2 x 30 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude residue by silica gel column chromatography using a gradient of 0 to 100% ethyl acetate in hexanes afforded compound **65** (colorless oil, 0.278 g, 1.03 mmol, 75% yield).




2-((2*S**,3*R**)-3-ethyl-1-tosylaziridin-2-yl)ethan-1-ol

**Compound 65**:

$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.77 (m, 2H), 7.38 – 7.29 (m, 2H), 3.79 – 3.61 (m, 2H), 2.98 (ddd, *J* = 9.4, 7.3, 4.1 Hz, 1H), 2.73 (ddd, *J* = 8.2, 7.3, 5.5 Hz, 1H), 2.44 (s, 3H), 2.28 – 2.05 (broad m, 1H), 1.90 (dddd, *J* = 14.3, 7.2, 5.1, 4.2 Hz, 1H), 1.58 – 1.46 (m, 2H), 1.45 – 1.32 (m, 1H), 0.82 (t, *J* = 7.4 Hz, 3H).

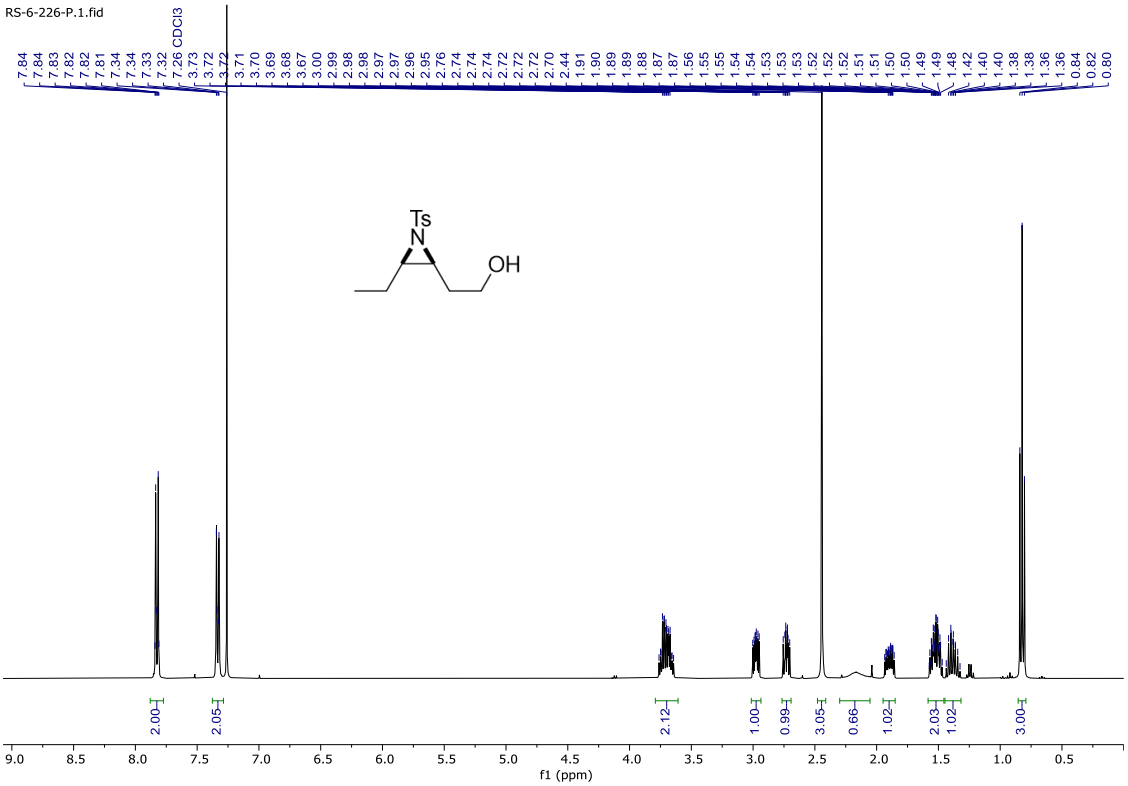
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.7, 134.9, 129.7, 128.2, 60.9, 47.0, 42.1, 29.2, 21.8, 20.3, 11.6.

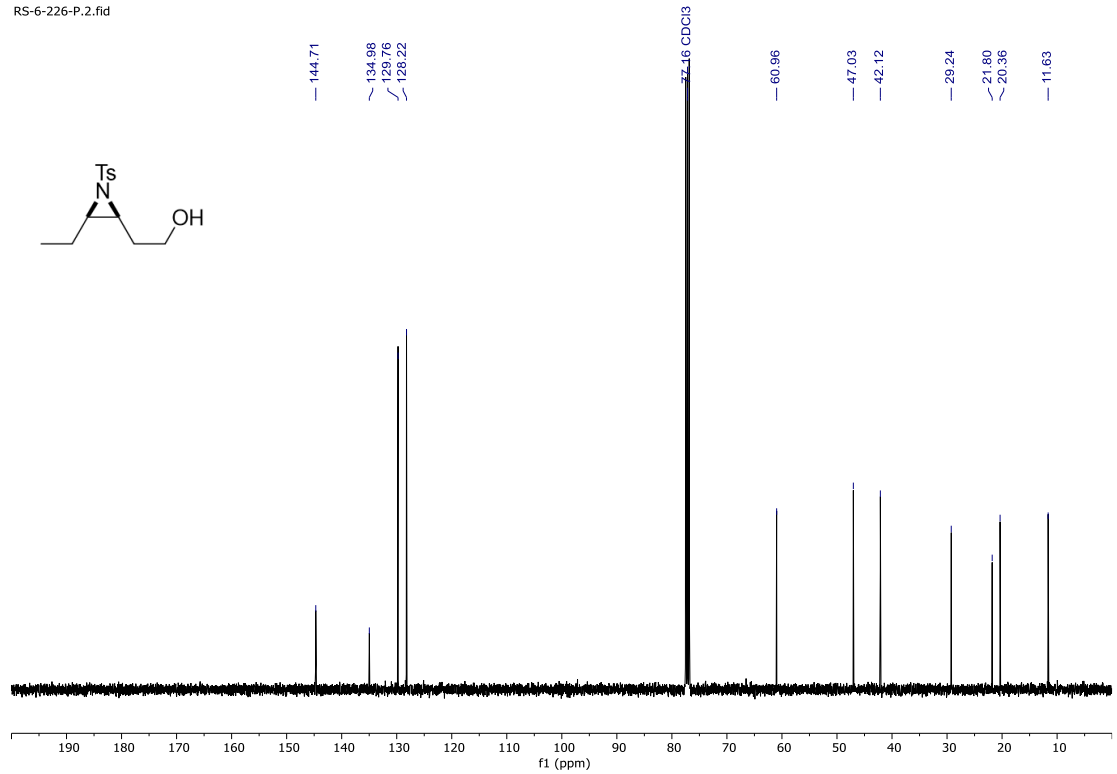
IR ν 3502, 2944, 2254, 1375, 1027, 918, 749 $cm^{-1}$.

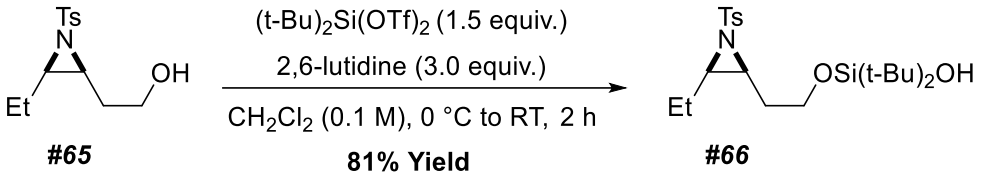
HRMS (ESI) m/z = $[M + Na]^+$ Calcd $C_{13}H_{19}NO_3SNa^+$ 292.0983. Found 292.0956 (9.2 ppm error).

Our data matches what has been reported in *J. Org. Chem.* **2023**, *88*, 15989–16006.

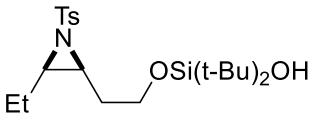
**Compound 65 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






A round-bottom flask equipped with a magnetic stir bar was charged with anhydrous dichloromethane (3 mL) and cooled to 0 °C using an ice-water bath. Di-tert-butylsilyl bis(trifluoromethanesulfonate) (0.292 mL, 0.395 g, 0.90 mmol, 1.5 equiv.) was added, followed by 2,6-lutidine (0.208 mL, 0.192 g, 1.80 mmol, 3.0 equiv.). The reaction mixture was stirred at 0 °C for 10 minutes. A solution of compound **65** (0.161 g, 0.60 mmol, 1.0 equiv.) in anhydrous dichloromethane (3 mL; final reaction concentration = 0.1 M) was then added slowly at 0 °C. The stirring reaction mixture was warmed to room temperature over a period of 2 hours. Upon completion, the reaction was quenched with saturated aqueous $NaHCO_3$ solution (10 mL) and transferred to a separatory funnel. The organic layer was collected. The aqueous layer was extracted with dichloromethane (30 mL), and the combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude residue by silica gel column chromatography using a gradient of 0 to 40% ethyl acetate in hexanes afforded compound **66** (colorless oil, 0.207 g, 0.484 mmol, 81% yield).




di-*tert*-butyl(2-((2*S**,3*R**)-3-ethyl-1-tosylaziridin-2-yl)ethoxy)silanol

**Compound 66**:

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.34 – 7.29 (m, 2H), 3.91 – 3.82 (m, 2H), 3.16 (ddd, *J* = 9.7, 7.4, 3.7 Hz, 1H), 2.74 (td, *J* = 7.9, 5.5 Hz, 1H), 2.44 (s, 3H), 1.92 (dddd, *J* = 14.2, 8.8, 6.3, 3.7 Hz, 1H), 1.57 – 1.29 (m, 3H), 1.03 (s, 9H), 1.02 (s, 9H), 0.79 (t, *J* = 7.4 Hz, 3H).

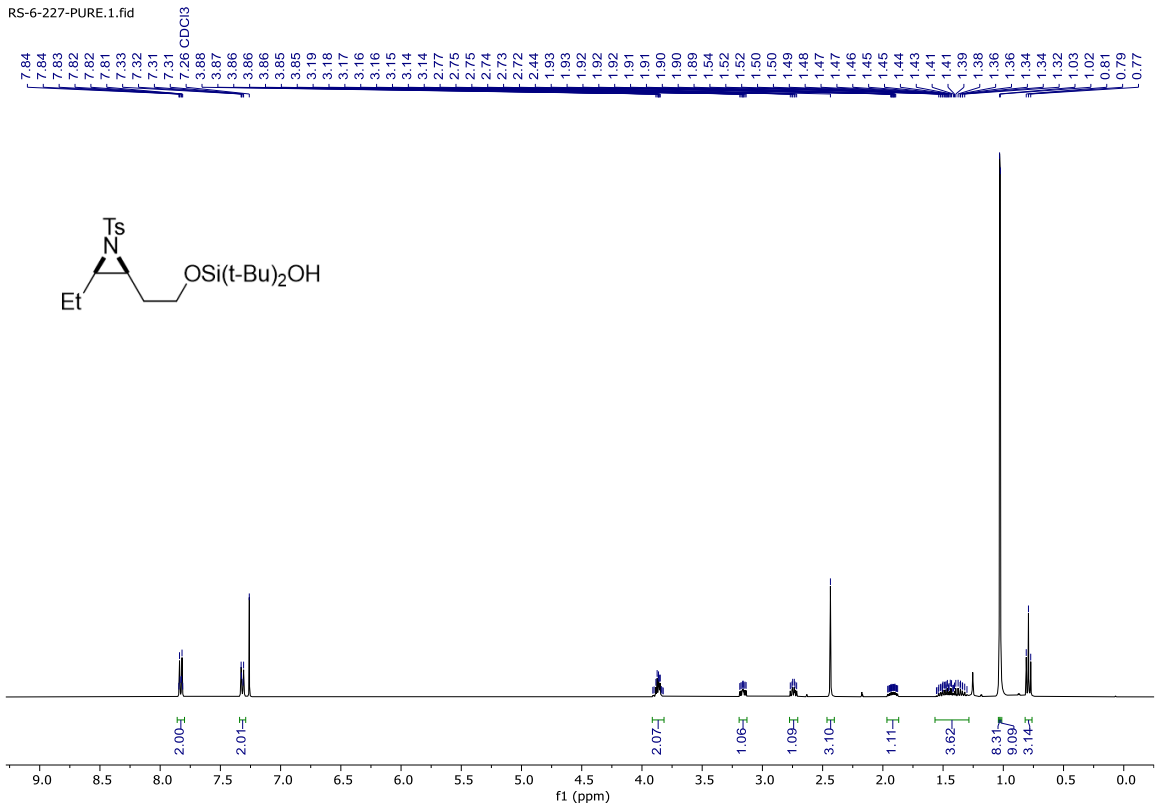
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 144.5, 135.3, 129.7, 128.1, 61.2, 47.5, 42.2, 30.1, 27.8, 27.6, 21.7, 20.7, 20.5, 20.3, 11.6.

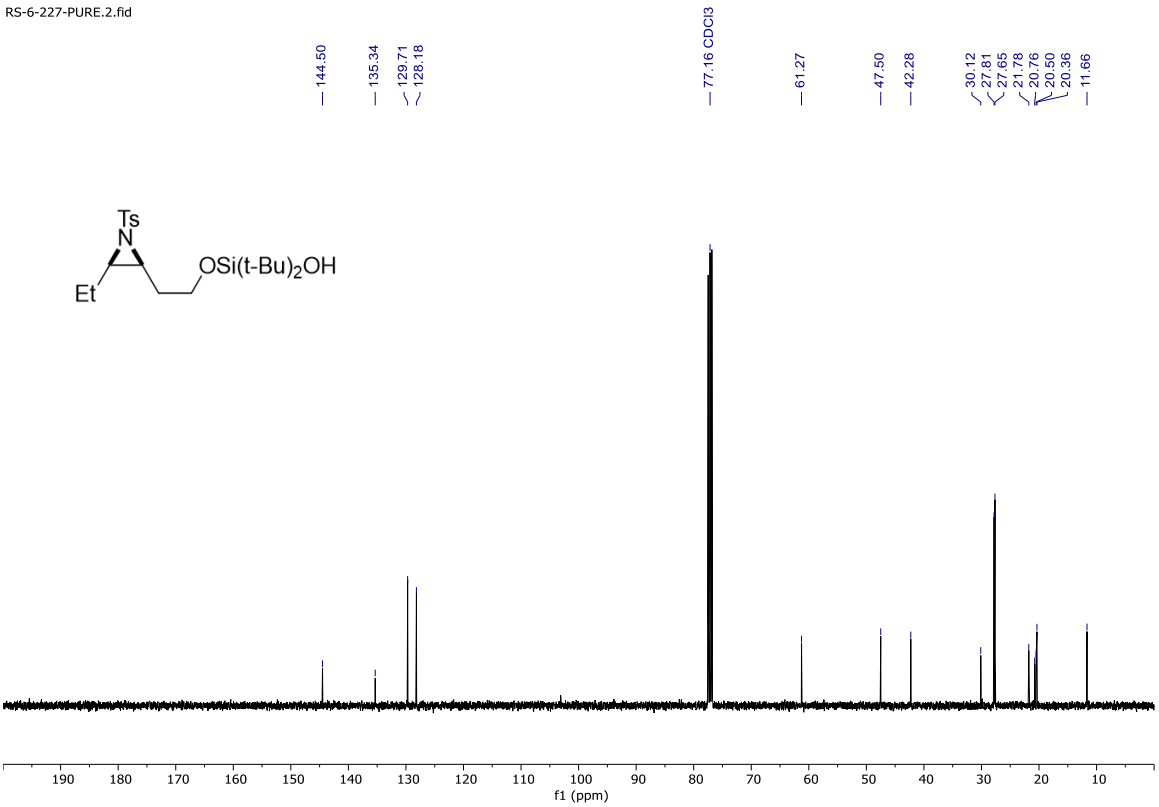
IR ν 3375, 2943, 2254, 1434, 1033, 739 cm$^{-1}$.

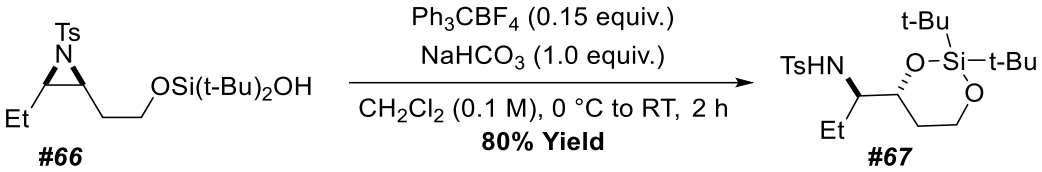
HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{21}H_{38}NO_4SSi^+$ 428.2291. Found 428.2296 (1.2 ppm error).

Our data matches what has been reported in *Org. Lett.* **2022**, *24*, 6202–6207.

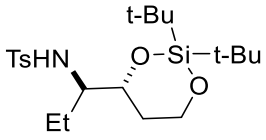
**Compound 66 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






**Compound 67**: For the benefit of readers, analytical data are provided herein. This compound was previously synthesized and fully characterized in *Org. Lett.* **2022**, *24*, 6202–6207 (See Cyclization Procedure A and Compound 42 in the Supporting Information of this reference).




*N*-((*R**)-1-((*R**)-2,2-di-*tert*-butyl-1,3,2-dioxasilinan-4-yl)propyl)-4-methylbenzenesulfonamide

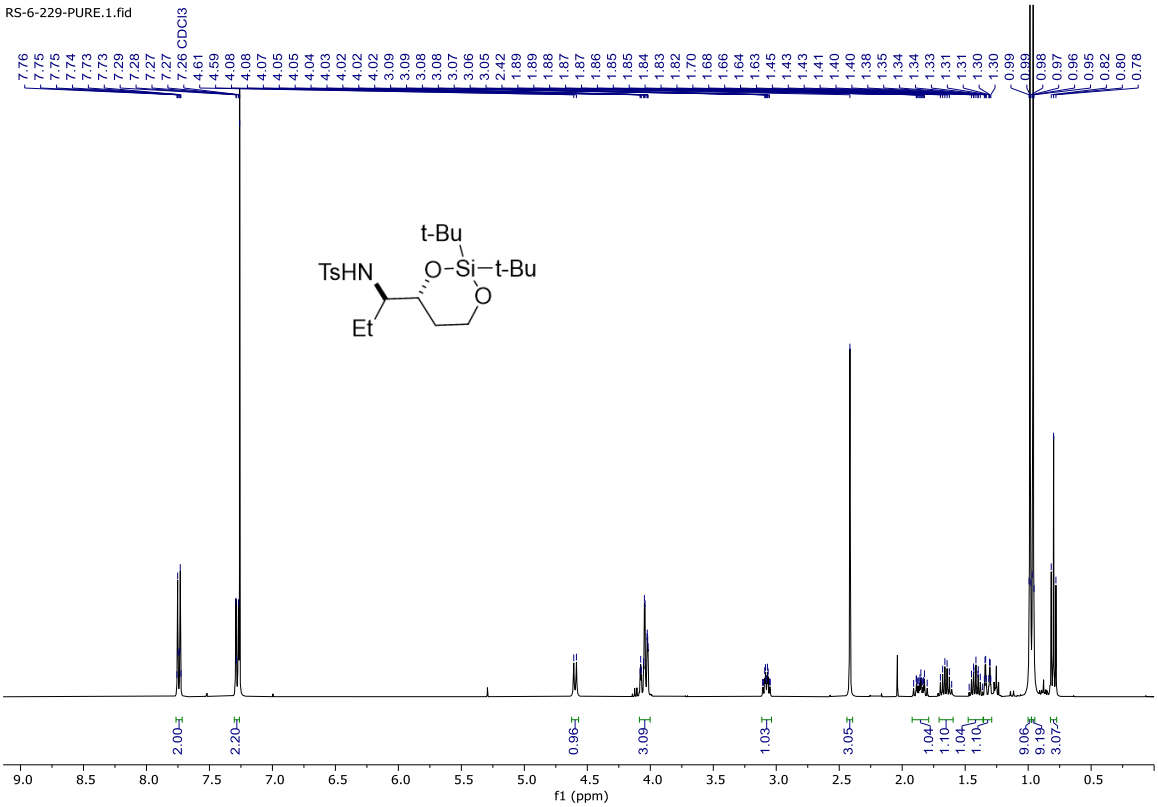
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 4.60 (d, *J* = 8.5 Hz, 1H), 4.09 – 4.00 (m, 3H), 3.08 (dtd, *J* = 9.1, 6.7, 2.5 Hz, 1H), 2.42 (s, 3H), 1.86 (ddt, *J* = 14.3, 11.3, 8.7 Hz, 1H), 1.65 (dq, *J* = 14.6, 7.2 Hz, 1H), 1.41 (tt, *J* = 13.9, 7.4 Hz, 1H), 1.32 (dq, *J* = 14.3, 2.1 Hz, 1H), 0.99 (s, 9H), 0.96 (s, 9H), 0.80 (t, *J* = 7.5 Hz, 3H).

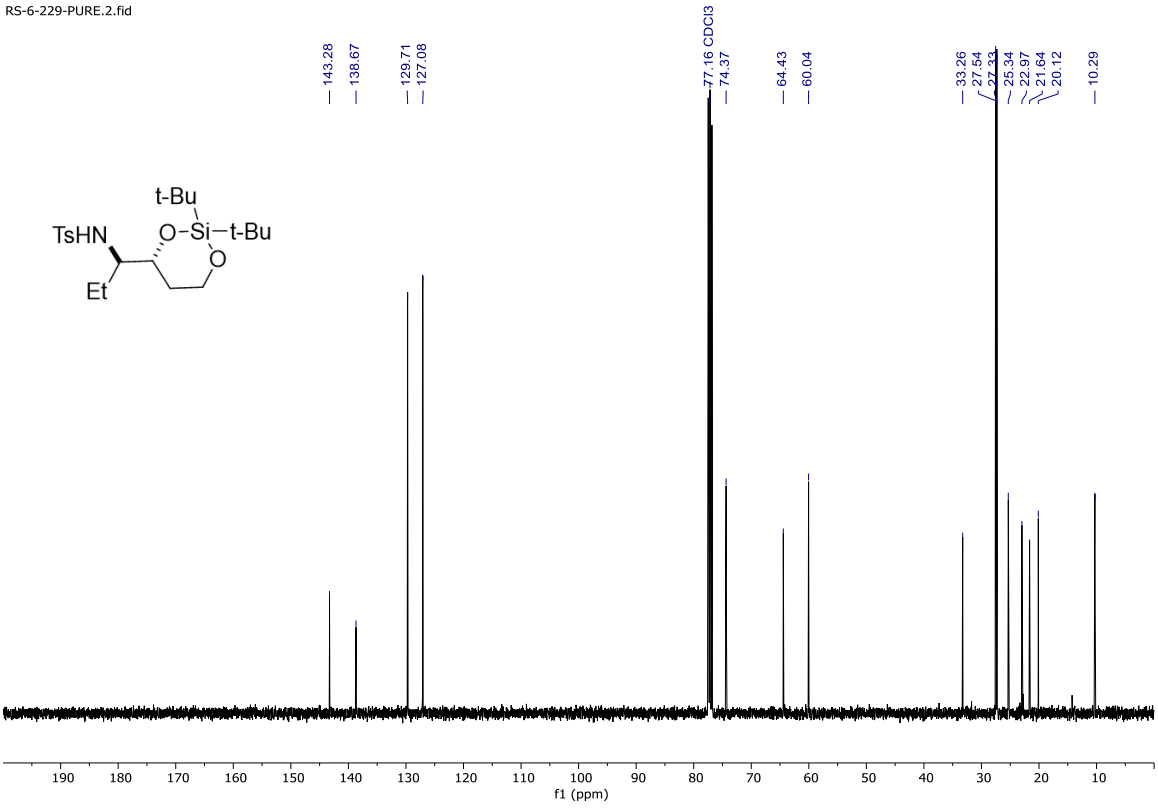
$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 143.2, 138.6, 129.7, 127.0, 74.3, 64.4, 60.0, 33.2, 27.5, 27.3, 25.3, 22.9, 21.6, 20.1, 10.2.

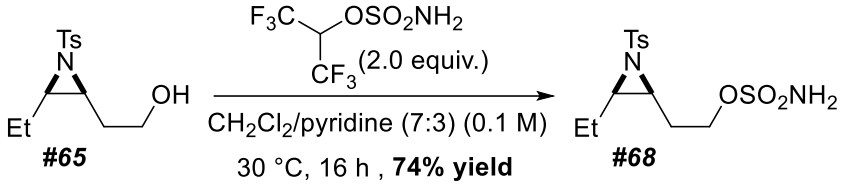
IR ν 3164, 2943, 2292, 2253, 1375, 1039, 917, 749 $cm^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{21}H_{38}NO_4SSi^+$ 428.2291. Found 428.2296 (1.2 ppm error).

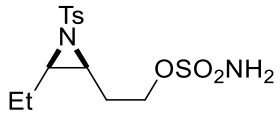
**Compound 67 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






**Compound 68**: For the benefit of readers, analytical data are provided herein. This compound was previously synthesized and fully characterized in *J. Org. Chem.* **2023**, *88*, 22, 15989–16006 (See General Procedure A and Compound 1 in this reference).




2-((2*S**,3*R**)-3-ethyl-1-tosylaziridin-2-yl)ethyl sulfamate

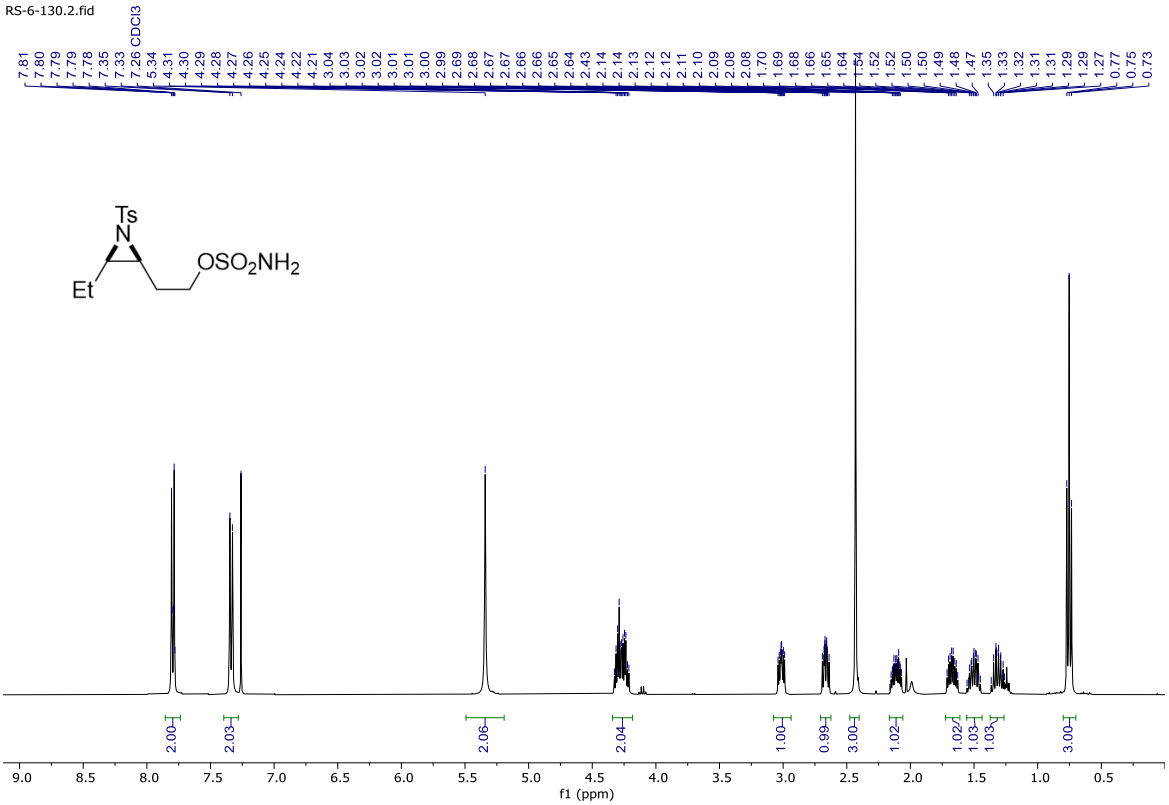
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.74 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.34 (broad s, 2H), 4.34 – 4.18 (m, 2H), 3.01 (ddd, *J* = 9.3, 7.3, 3.8 Hz, 1H), 2.67 (ddd, *J* = 8.4, 7.3, 5.2 Hz, 1H), 2.43 (s, 3H), 2.11 (dddd, *J* = 14.6, 9.1, 5.2, 3.9 Hz, 1H), 1.67 (ddt, *J* = 14.4, 9.4, 4.6 Hz, 1H), 1.50 (dqd, *J* = 14.9, 7.4, 5.2 Hz, 1H), 1.37 – 1.26 (m, 1H), 0.75 (t, *J* = 7.4 Hz, 3H).

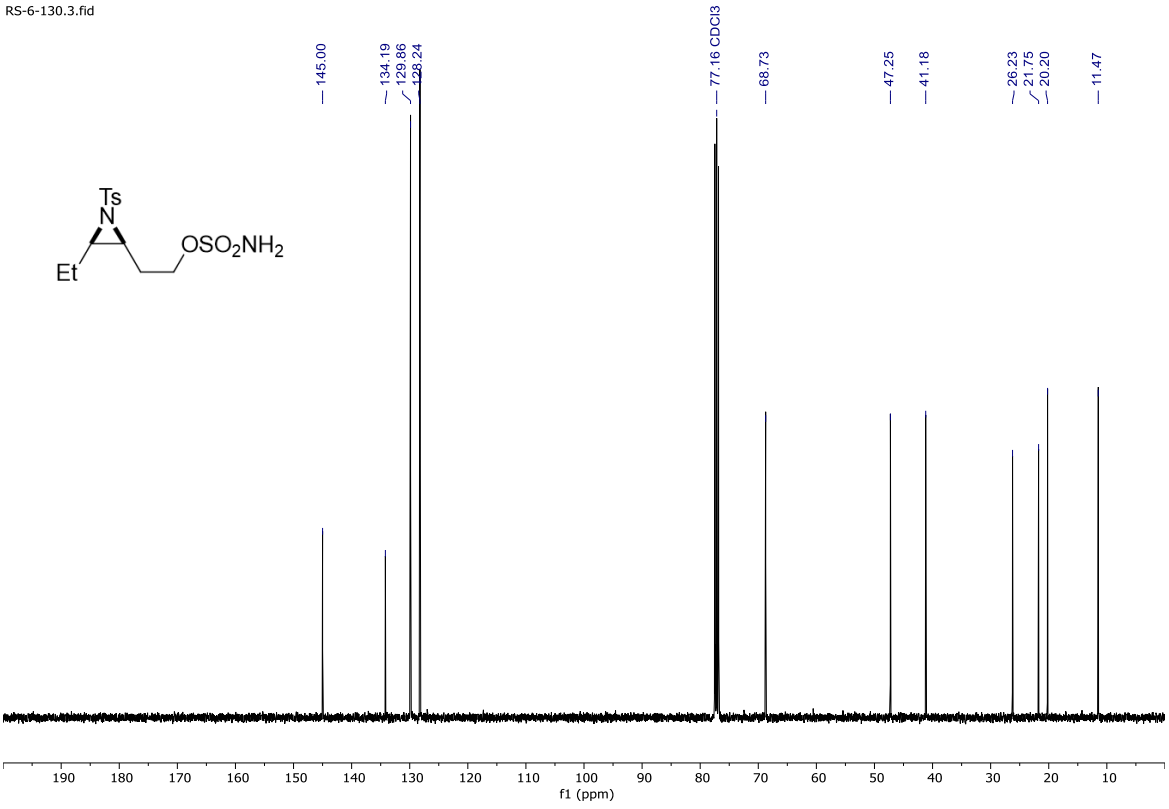
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 145.0, 134.1, 129.8, 128.2, 68.7, 47.2, 41.1, 26.2, 21.7, 20.2, 11.4.

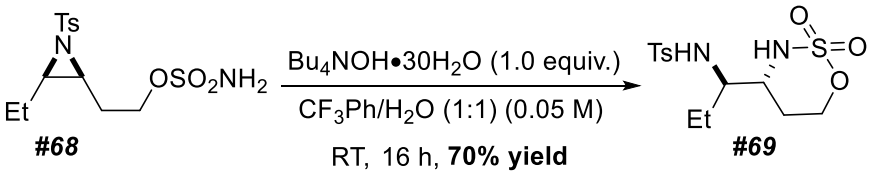
IR ν 3420, 3054, 2986, 2305, 1261, 1159, 896, 762, 574 $cm^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{13}H_{21}N_2O_5S_2^+$ 349.0892. Found 349.0891 (0.3 ppm error).

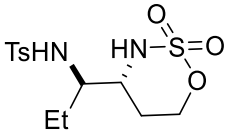
**Compound 68 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**






**Compound 69**: For the benefit of readers, analytical data are provided herein. This compound was previously synthesized and fully characterized in *J. Org. Chem.* **2023**, *88*, 22, 15989–16006 (See General Procedure G and Compound 2 in this reference).




*N*-((*R**)-1-((*R**)-2,2-dioxido-1,2,3-oxathiazinan-4-yl)propyl)-4-methylbenzenesulfonamide

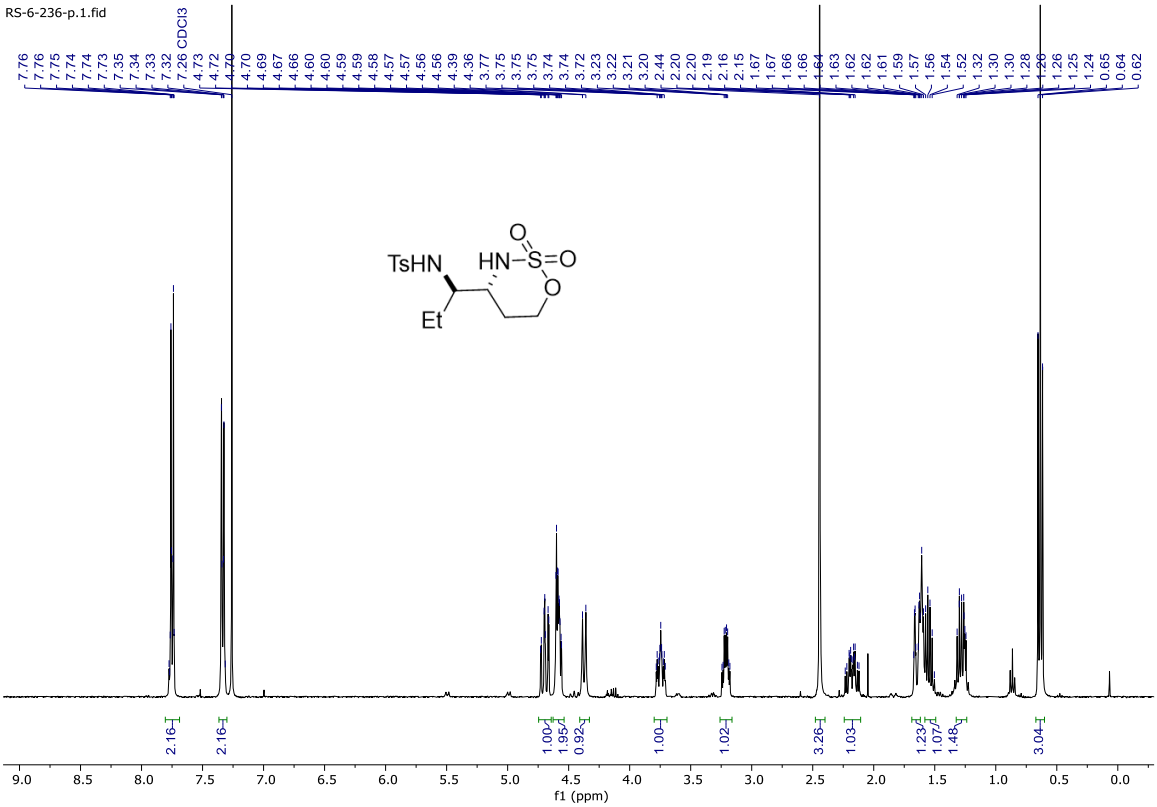
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.69 (m, 2H), 7.37 – 7.30 (m, 2H), 4.70 (ddd, *J* = 13.3, 11.6, 2.4 Hz, 1H), 4.63 – 4.54 (m, 2H), 4.37 (d, *J* = 11.0 Hz, 1H), 3.80 – 3.69 (m, 1H), 3.21 (qd, *J* = 7.3, 3.6 Hz, 1H), 2.44 (s, 3H), 2.18 (dtd, *J* = 14.7, 12.7, 5.2 Hz, 1H), 1.65 (dq, *J* = 14.4, 2.1 Hz, 1H), 1.54 (dt, *J* = 14.5, 7.2 Hz, 1H), 1.32 – 1.24 (m, 1H), 0.64 (t, *J* = 7.4 Hz, 3H).

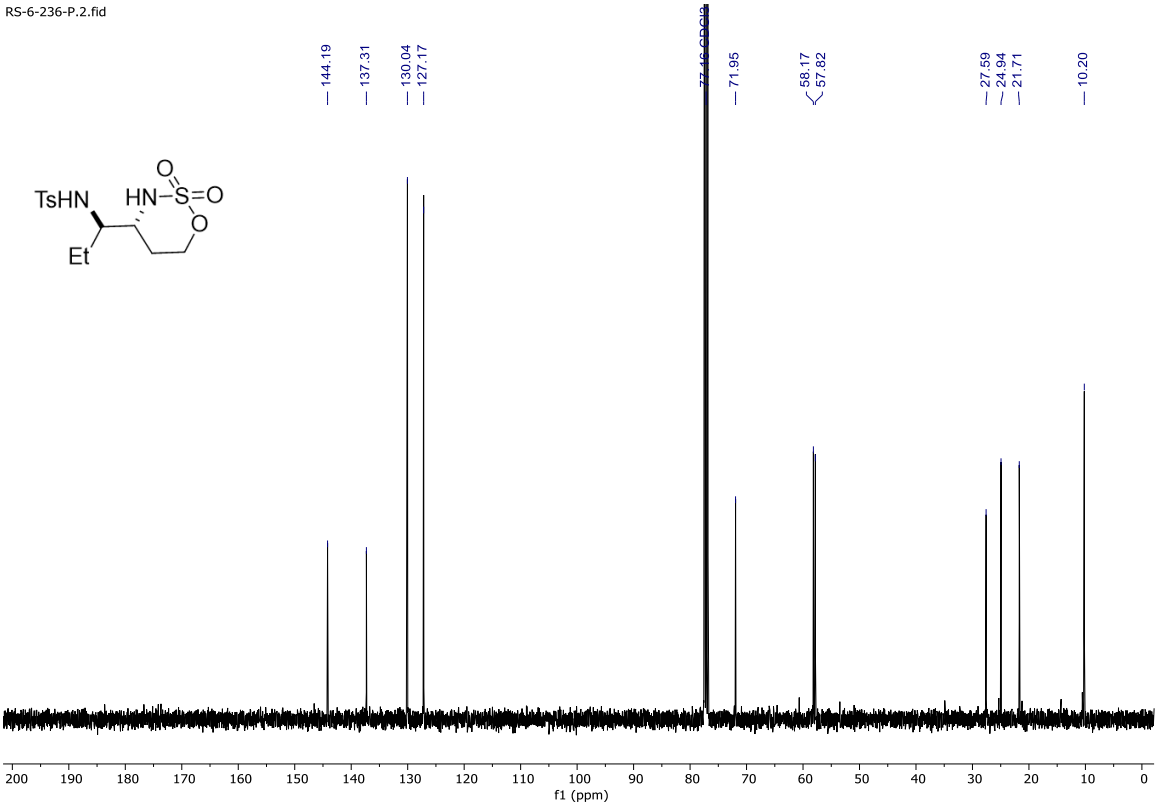
$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 144.1, 137.3, 130.0, 127.1, 71.9, 58.1, 57.8, 27.5, 24.9, 21.7, 10.2.

IR ν 3266, 2970, 1715, 1189, 1011, 749, 668, 549 $cm^{-1}$.

HRMS (ESI) m/z = $[M + H]^+$ Calcd $C_{13}H_{21}N_2O_5S_2^+$ 349.0892. Found 349.0908 (4.6 ppm error).

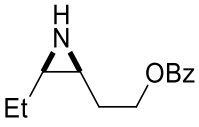
**Compound 69 ($CDCl_3$, $^1H$ NMR: 400 MHz, $^{13}C\{^1H\}$ NMR: 101 MHz)**



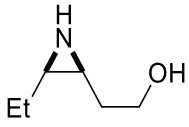



## VII. Structural Reasoning

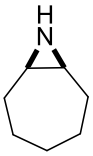
The following aziridines are known compounds in the literature:



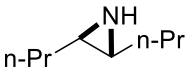
*Science,* **2014***, 343*, 61 – 65.



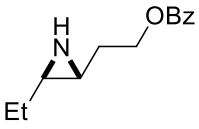
*J. Org. Chem.,* **2024**, *89*, 6263 – 6273.



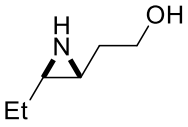
*J. Org. Chem.,* **2024**, *89*, 6263 – 6273.



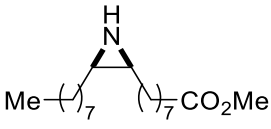
*Angew. Chem. Int. Ed.* **2017**, *56*, 9886 – 9890.



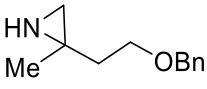
*Science,* **2014***, 343*, 61 – 65.



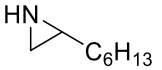
*Angew. Chem. Int. Ed.* **2017**, *56*, 9886 – 9890.



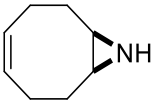
*Synthesis*, **2022**, *54*, 4513 – 4520.



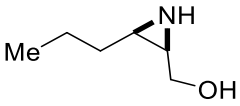
*Angew. Chem. Int. Ed.*, **2017**, *56*, 12654 – 12657.



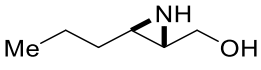
*J. Org. Chem.,* **2024**, *89*, 6263 – 6273.



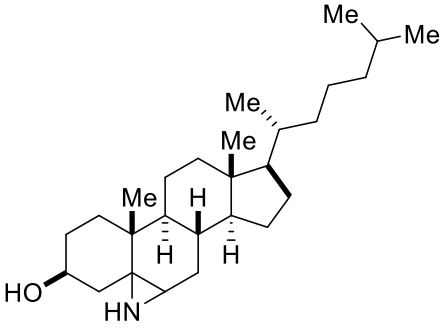
*J. Org. Chem.,* **2024**, *89*, 6263 – 6273.



*J. Org. Chem.,* **2024**, *89*, 6263 – 6273.



*ACS Catal.* **2020**, *10*, 556 – 561.



*Science,* **2014***, 343*, 61 – 65.

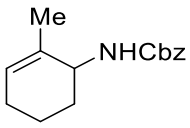
While in some cases we have not purified these N – H aziridines and have directly converted them into N – Cbz aziridines for the purposes of isolation and characterization, in all cases, we have carefully analyzed the crude NMRs of these compounds and compared them to the literature reports.

## VIII. X-Ray Crystallographic Data

SCXRD data for **39** was collected on a Rigaku Synergy diffractometer with a Hypix area detector using Cu-Kα radiation from a microfocus source (Rigaku-Oxford Diffraction, Lake of the Woods, TX, USA). The crystal was cooled to the collection temperature under a stream of cold $N_2$ gas using a Cryostream 1000 cryostat (Oxford Cryosystems, Long Hanborough, UK). A hemisphere of unique data was collected using strategies of scans about the omega, phi, and chi axes. CrysAlisPro was used for data collection, data reduction, absorption correction, and space group determination.[i]

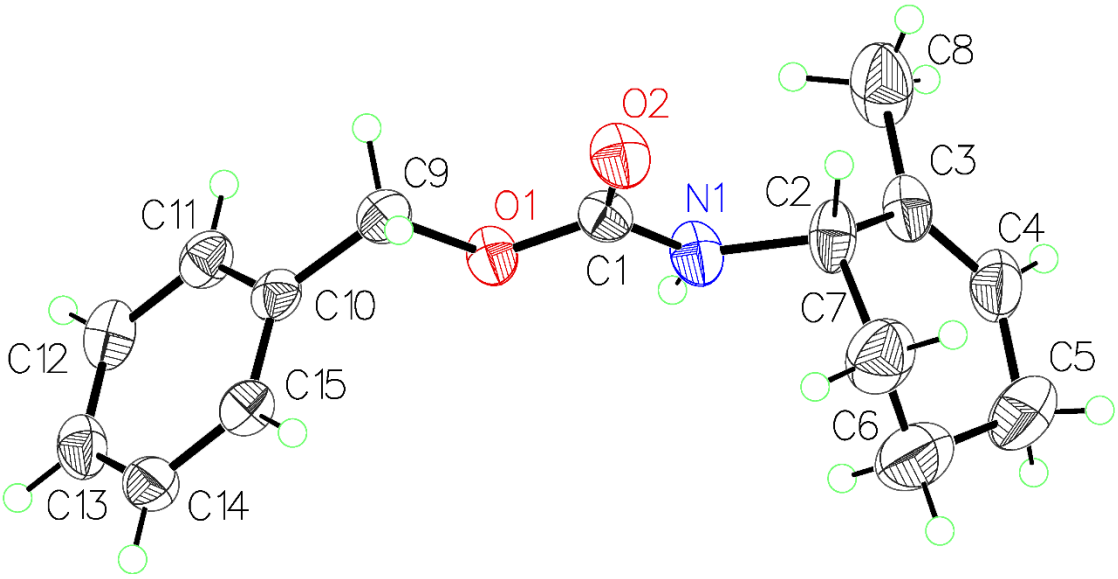
The crystal structure was solved by direct methods as implemented in SHELXS[ii] and refined by full-matrix least squares refinement against $F^2$ using SHELXL v.2019/3.[iii] Non-hydrogen atoms were located from the difference map and refined anisotropically. Both enantiomorphs are substitutionally disordered throughout the crystal. The disorder was modeled using geometric restraints to keep chemically equivalent bonds and angles in both parts the same, and the occupancies were refined with a constraint to sum to 100%. The occupancy values converge 50.6(5) and 49.4(5)%, or essentially complete random substitution. The amide hydrogen atom was located from the difference map, and its coordinates were refined while its thermal parameter was constrained to ride on the carrier atom. Hydrogen atoms bonded to carbon were placed in idealized, calculated positions, and their coordinates and thermal parameters were constrained to ride on the carrier atoms.

### Compound 39




**CCDC 2517258**

Crystals grown from ethanol.




50% probability ellipsoid plot of the formula unit of **CCDC 2517258**. Disorder omitted for clarity.

Table S1. Crystal data and structure refinement for **CCDC 2517258**.

| | | |
|---|---|---|
| Identification code | s1 | |
| Empirical formula | C15 H19 N O2 | |
| Formula weight | 245.31 | |
| Temperature | 100(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 21.1835(3) Å | α= 90°. |
| | b = 4.85638(4) Å | β= 103.0712(12)°. |
| | c = 13.24574(16) Å | γ = 90°. |
| Volume | 1327.35(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.228 $Mg/m^3$ | |
| Absorption coefficient | 0.645 $mm^{-1}$ | |
| F(000) | 528 | |
| Crystal size | 0.18 x 0.15 x 0.05 $mm^3$ | |
| Theta range for data collection | 4.285 to 80.371°. | |
| Index ranges | -27<=h<=26, -4<=k<=6, -16<=l<=16 | |
| Reflections collected | 39326 | |
| Independent reflections | 2894 [R(int) = 0.0389] | |
| Completeness to theta = 67.679° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000 and 0.83673 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2894 / 15 / 232 | |
| Goodness-of-fit on $F^2$ | 1.019 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0609, wR2 = 0.1658 | |
| R indices (all data) | R1 = 0.0635, wR2 = 0.1686 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.558 and -0.653 $e.Å^{-3}$ | |


[i]. CrysAlisPro (2018) Oxford Diffraction Ltd.
[ii]. Sheldrick, G. M. SHELXS, v.2013-1, 2013.
[iii]. Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C. Struct. Chem.* **2015**, *71*, 3-8.