Oxazaborinines from Vinylogous *N*-Allylic Amides: Reactivities of Underexplored Heterocyclic Building Blocks

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Supporting Information

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1 General Considerations

Unless otherwise noted, all reactions were performed in flame or oven-dried glassware fitted with rubber septa under a positive pressure of nitrogen using standard Schlenk techniques. Air- and moisture-sensitive liquids were transferred via syringe or stainless steel cannula through rubber septa. Solids were added under inert gas or were dissolved in appropriate solvents. Low temperature-reactions were carried out in a Dewar vessel filled with a cooling agent: acetone/dry ice (−78 °C), H_2O/ice (0 °C). Reaction temperatures above 23 °C were conducted in an oil bath or in a heated metal block (reactions conducted in vials). The reactions were magnetically stirred and monitored by NMR spectroscopy or analytical thin-layer chromatography (TLC), using glass plates precoated with silica gel (Silicycle Siliaplates, glass backed, extra hard layer, 60 Å, 250 µm thickness, F254 indicator). TLC plates were visualized by exposure to ultraviolet light (254 nm), were stained by submersion in aqueous potassium permanganate solution ($KMnO_4$) or ceric ammonium molybdate solution (CAM), and were developed by heating with a heat gun. Flash-column chromatography on silica gel was performed as described by Still et al.,[1] employing silica gel (Silicycle silica gel, 40–63 µm particle size). Organic solutions were concentrated under reduced pressure on a Heidolph temperature-controlled rotary evaporator equipped with a dry ice/isopropanol condenser. The yields refer to chromatographically and spectroscopically (^{1}H and ^{13}C NMR) pure material.

1.1 Materials

Unless noted below, commercial reagents were purchased from Sigma Aldrich, Acros Organics, Chem-Impex, Oakwood Chemical, Combi-blocks, TCI, and/or Alfa Aesar, and used without additional purification. Solvents were purchased from Fisher Scientific, Acros Organics, Alfa Aesar, and Sigma Aldrich. Tetrahydrofuran (THF), diethyl ether (Et_2O), acetonitrile (CH_3CN), benzene, toluene (PhMe), methanol (MeOH), and triethylamine (Et_3N) were sparged with argon and dried by passing through alumina columns using argon in a Glass Contour solvent purification system. Dichloromethane (CH_2Cl_2, DCM) was freshly distilled over calcium hydride under a N_2 atmosphere prior to each use.

1.2 NMR spectroscopy

NMR spectral data were obtained using deuterated solvents, obtained from Cambridge Isotope Laboratories, Inc. ^{1}H NMR and ^{13}C NMR data were recorded on Bruker AVB-400, AVQ-400, AV-500, DRX-500, AV-600 or AV-700 spectrometers operating at 400 MHz, 400 MHz, 500 MHz, 500 MHz, 600 MHz, 700 MHz for proton nuclei (100 MHz, 100 MHz, 125 MHz, 125 MHz, 150 MHz, 175 MHz for carbon nuclei), respectively. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.26). Carbon chemical shifts are expressed in parts per million (δ scale, assigned carbon atom) and are referenced to the carbon resonance of the NMR solvent ($CDCl_3$: δ 77.16). ^{19}F NMR spectra were acquired on the AVQ-400 spectrometer and internally referenced to $CFCl_3$ (δ 0.00). ^{11}B NMR spectra were acquired on the AV-600 spectrometer and chemical shifts were referenced to an external reference $BF_3{\cdot}OEt_2$ (δ 0.00). When ^{13}C signals appeared too weak and/or broad (such as all carbons directly bonded to boron, due to quadrupole relaxation), HSQC spectra were acquired to confirm signal authenticity. ^{1}H NMR spectroscopic data are reported as follows: Chemical shift in ppm (multiplicity, coupling constants *J* (Hz), integration) (e.g. "5.21 (t, ^3J = 7.3 Hz, 1H)"). The multiplicities are abbreviated with s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), p (pentet), se (sextet), h (heptet), m (multiplet) and app (apparent multiplicity). In case of combined multiplicities, the multiplicity with the larger coupling constant is stated first. Except for multiplets, the chemical shift of all signals, as well for centrosymmetric multiplets, is reported as the center of the resonance range. Data for ^{13}C, ^{19}F and

[1] Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923–2925.

^{11}B NMR spectroscopy are reported in terms of chemical shift (δ ppm). Additionally to 1D NMR experiments, 2D NMR techniques such as homonuclear correlation spectroscopy (COSY), heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond coherence (HMBC) and nuclear Overhauser enhancement spectroscopy (NOESY) were used to assist structure elucidation. All raw FID files were processed and the spectra analyzed using the program *MestReNOVA 11.0* from *Mestrelab Research S. L*.

Note: The AVB-400, AVQ-400, AV-500, DRX-500 and AV-600 instruments were partially supported by NIH grants SRR023679A, RR02424A-01, S10RR03353-01 and 1S10RR016634-01, and NSF grants CHE-9633007, CHE-8208992, CHE-0130862, and CHE-8703048. The AV-700 instrument was supported by the Berkeley College of Chemistry NMR facility.

1.3 Mass spectrometry

Mass spectral data were obtained from the Mass Spectral Facility at the University of California, Berkeley, on a Finnigan/Thermo LTQ-FT instrument (ESI). Data acquisition and processing were performed using the XcaliburTM software.

1.4 IR spectroscopy

IR spectroscopic data were recorded on a Bruker ALPHA FT-IR spectrophotometer using a diamond attenuated total reflectance (ATR) accessory. If required, substances were dissolved in dichloromethane prior to direct application on the ATR unit. Data are represented as follows: frequency of absorption (cm^{-1}), and intensity of absorption (s = strong, m = medium, w = weak, br = broad).

1.5 X-ray analysis

Single-crystal X-ray diffraction experiments were performed at the UC Berkeley CHEXRAY crystallographic facility. Measurements of all compounds were performed on a Rigaku XtaLAB P200 rotating anode equipped with a Pilatus 200K hybrid pixel array detector. Data were collected using Cu Kα radiation (λ = 1.54184 Å). Crystals were kept at 100(2) K throughout collection. Data collection was performed with CrysAlis^{Pro}.[2] Data processing was done using CrysAlis^{Pro} and included either a multi-scan absorption or face-indexed absorption correction applied using the SCALE3 ABSPACK scaling algorithm within CrysAlis^{Pro}. All structures were solved with SHELXT.[3] Structures were refined with SHELXL.[4] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were either included at the geometrically calculated positions and refined using a riding model or located as Q peaks in the Fourier difference map.

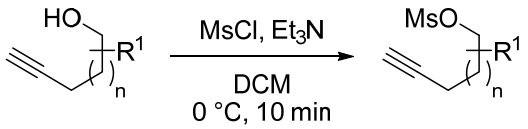
Note: The instruments are supported by an NIH Shared Instrumentation Grant S10-RR027172.

[2] Rigaku Oxford Diffraction, (2015), CrysAlisPro Software system, version 1.171.39.7a, Rigaku Corporation, Oxford, UK.
[3] Sheldrick, G. M. *Acta Crystallogr*. **2015**, *A71*, 3–8.
[4] Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112–122.

2 General Experimental Details

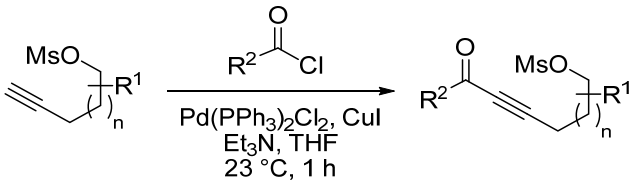
2.1 General Procedures A–G

A. General Procedure A: Preparation of alkyne-mesylates



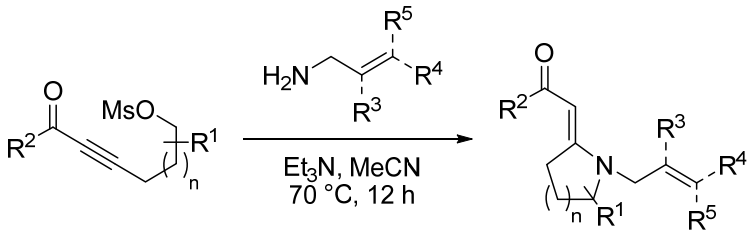
A solution of the alcohol (1 equiv) in dichloromethane (0.2 M) was sequentially treated with triethylamine (2.00 equiv) and methanesulfonyl chloride (1.10 equiv) at 0 °C. After 10 min, the mixture was diluted with saturated aqueous sodium bicarbonate solution. The layers were separated, the aqueous layer was extracted with dichloromethane and the combined organic extracts were washed with saturated aqueous sodium chloride solution. The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated to provide the crude alkyne-mesylate, which was used in the next step without further purification.

B. General Procedure B: Preparation of ynones



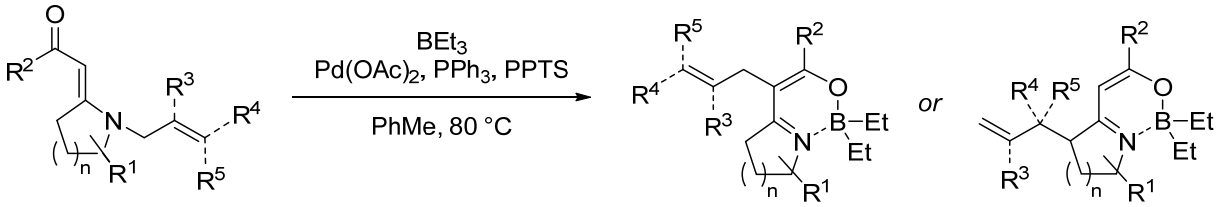
A solution of the crude alkyne-mesylate (1 equiv) in tetrahydrofuran–triethylamine (2:1 v/v, 0.60 M) was sequentially treated with bis(triphenylphosphine)palladium(II) dichloride (10 mol%) and copper(I) iodide (5 mol%) at 23 °C. The acid chloride (1.10 equiv) was added, and stirring was continued at 23 °C. After TLC analysis indicated complete consumption of the alkyne-mesylate (typically 1 h), the mixture was diluted with saturated aqueous sodium bicarbonate solution and ethyl acetate. The layers were separated, the aqueous layer was extracted with ethyl acetate and the combined organic extracts were washed with saturated aqueous sodium chloride solution. The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated to provide the ynone, which was used in the next step without further purification.

C. General Procedure C: Preparation of vinylogous amides



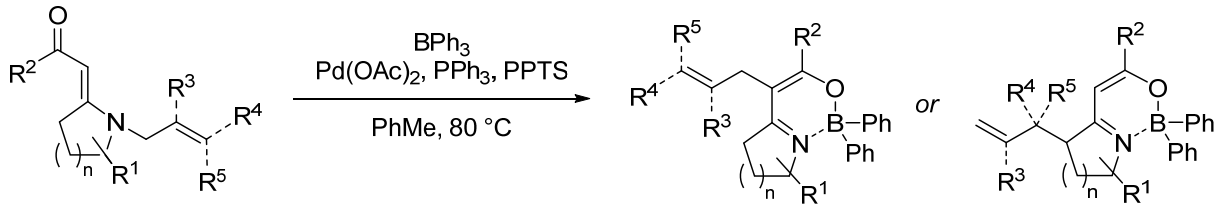
A mixture of the crude ynone (1 equiv), allylic amine (3.00–7.00 equiv), and triethylamine (1.20 equiv) in acetonitrile (1.0 M) was heated to 70 °C and held at this temperature for 12 h. The mixture was then cooled to 23 °C, concentrated in vacuo, and the residue was purified by flash chromatography on silica gel to provide the vinylogous amide.

D. General Procedure D: Preparation of diethyl oxazaborinines



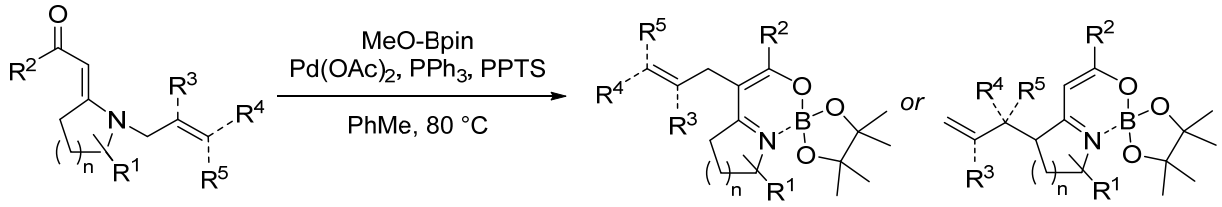
An oven-dried vial was charged with a magnetic stirring bar, vinylogous amide substrate (1 equiv), pyridinium *p*-toluenesulfonate (10 mol%), triphenylphosphine (10 mol%) and palladium(II) acetate (5 mol%). The vial was flushed with nitrogen and sealed with a septum cap. Toluene (0.2 M) and a solution of triethylborane (1 M in THF, 1.5 equiv) were added sequentially and the vial was placed in a preheated (80 °C) heating block. Stirring was continued at this temperature until TLC analysis indicated complete consumption of the vinylogous amide starting material (typically 1 h). The mixture was then cooled to 23 °C, concentrated in vacuo and the residue was purified by flash chromatography on silica gel to provide the oxazaborinine product.

E. General Procedure E: Preparation of diphenyl oxazaborinines



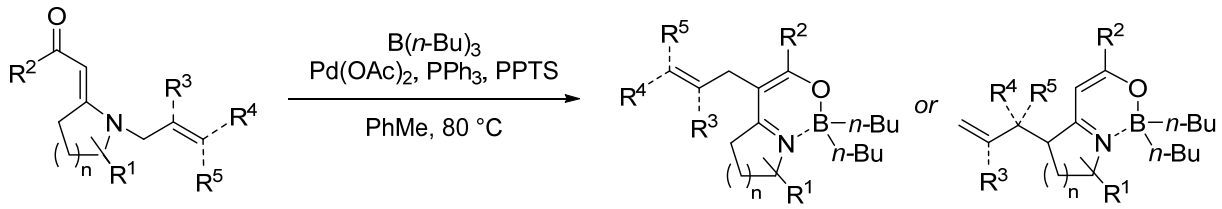
An oven-dried vial was charged with a magnetic stirring bar, vinylogous amide substrate (1 equiv), pyridinium *p*-toluenesulfonate (10 mol%), triphenylphosphine (10 mol%) palladium(II) acetate (5 mol%), and triphenylborane (1.2 equiv). The vial was flushed with nitrogen and sealed with a septum cap. Toluene (0.2 M) was added, and the vial was placed in a preheated (80 °C) heating block. Stirring was continued at this temperature until TLC analysis indicated complete consumption of the vinylogous amide starting material (typically 1 h). The mixture was then cooled to 23 °C, concentrated in vacuo and the residue was purified by flash chromatography on silica gel to provide the oxazaborinine product.

F. General Procedure F: Preparation of pinacol oxazaborinines



An oven-dried vial was charged with a magnetic stirring bar, vinylogous amide substrate (1 equiv), pyridinium *p*-toluenesulfonate (10 mol%), triphenylphosphine (10 mol%) and palladium(II) acetate (5 mol%). The vial was flushed with nitrogen and sealed with a septum cap. Toluene (0.2 M) and methoxyboronic acid pinacol ester (1.5 equiv) were added sequentially and the vial was placed in a preheated (80 °C) heating block. Stirring was continued at this temperature until TLC analysis indicated complete consumption of the vinylogous amide starting material (typically 1 h). The mixture was then cooled to 23 °C, concentrated in vacuo and the residue was purified by flash chromatography on silica gel to provide the oxazaborinine product.

G. General Procedure G: Preparation of di-*n*-butyl oxazaborinines



An oven-dried vial was charged with a magnetic stirring bar, vinylogous amide substrate (1 equiv), pyridinium *p*-toluenesulfonate (10 mol%), triphenylphosphine (10 mol%) and palladium(II) acetate (5 mol%). The vial was flushed with nitrogen and sealed with a septum cap. Toluene (0.2 M) and tributylborane (1.5 equiv) were added sequentially and the vial was placed in a preheated (80 °C) heating block. Stirring was continued at this temperature until TLC analysis indicated complete consumption of the vinylogous amide starting material (typically 1 h). The mixture was then cooled to 23 °C, concentrated in vacuo and the residue was purified by flash chromatography on silica gel to provide the oxazaborinine product.

2.2 Graphical Guide for Reaction Setup

Illustrated below is the reaction setup and General Procedure D (0.20 mmol scale experiment).

Figure S1. On a bench top, an oven-dried vial is charged with a magnetic stirring bar, vinylogous amide substrate, pyridinium *p*-toluenesulfonate, triphenylphosphine and palladium(II) acetate.

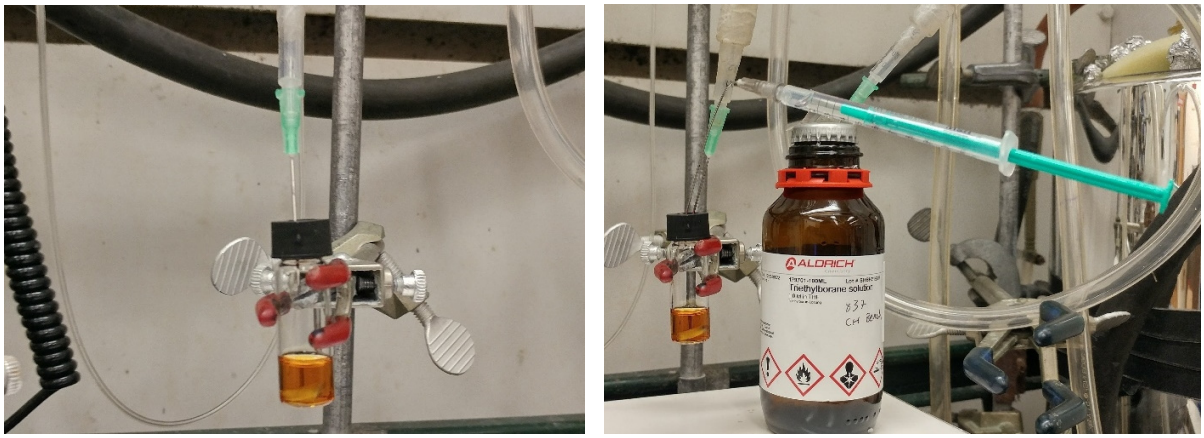


Figure S2. Using a Schlenk line, the vial is evacuated and backfilled with nitrogen. Toluene and triethylborane solution are then sequentially added *via* syringe.

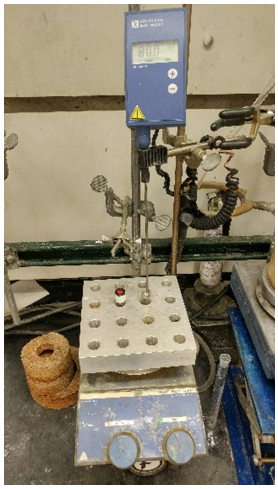


Figure S3. The vial is sealed with Teflon tape and placed in a preheated (80 °C) heating block.

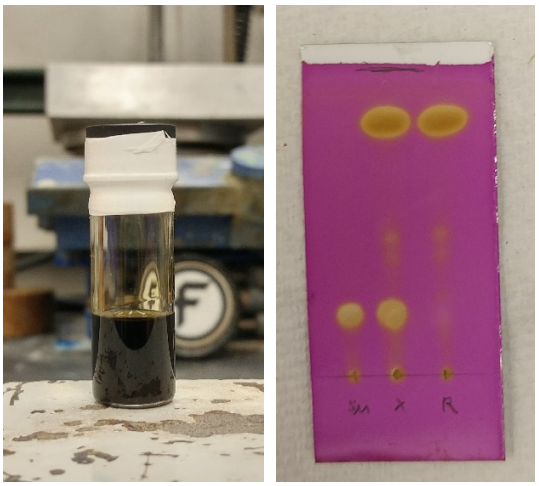
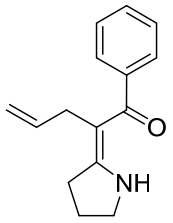


Figure S4. Reaction mixture after heating at 80 °C for 1 h, and TLC analysis ($KMnO_4$ stained).

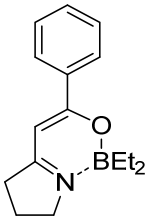
2.3 Reaction Development

The reaction development and control experiments were carried out, with variations as indicated (main manuscript Table 1), according to General Procedure D. The conversion of vinylogous amide **1** and product yields were determined by ^{1}H-NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard (except for entry 1 and 5, where isolated yields were obtained).
The characterization data of the rearranged product **3** and de-allyl oxazaborinine **4** are given here, the data of oxazaborinine **2a** is reported in Section 4.1.



3

TLC (60% ethyl acetate in hexanes): R_f = 0.38 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 11.04 (s, 1H), 7.43 – 7.37 (m, 2H), 7.35 – 7.29 (m, 3H), 5.84 – 5.77 (m, 1H), 5.01 – 4.93 (m, 2H), 3.67 (t, *J* = 7.2 Hz, 2H), 2.95 – 2.91 (m, 2H), 2.71 (t, *J* = 7.8 Hz, 2H), and 2.06 – 1.99 (m, 2H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 193.6, 170.6, 142.9, 138.8, 128.5, 127.9, 126.4, 114.2, 97.2, 48.1, 33.8, 31.7, and 21.3.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3240 (br), 3076 (w), 3052 (w), 2992 (w), 2971 (w), 2883 (w), 1599 (s), 1577 (w), 1516 (s), 1476 (w), 1290 (w), 1248 (m), and 670 (w) cm^{-1}.
HRMS (ESI): calcd for ([M], $C_{15}H_{17}NO)^{+}$: 228.1388, found: 228.1385.
mp: 61–69 °C (off-white solid).

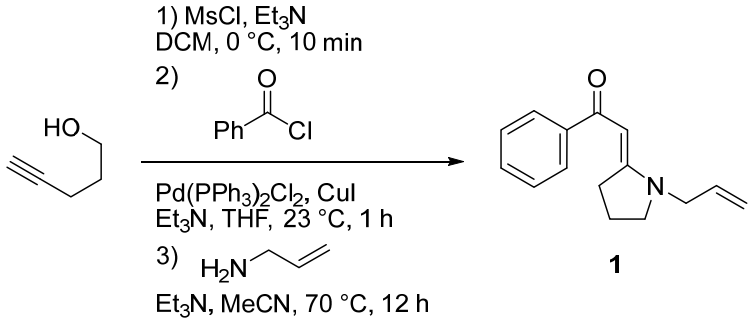


4

TLC (2% ethyl acetate in hexanes): R_f = 0.25 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 2H), 7.44 – 7.36 (m, 3H), 5.55 (s, 1H), 3.61 (t, *J* = 7.4 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.03 (p, *J* = 7.8 Hz, 2H), 0.81 (t, *J* = 7.7 Hz, 6H), and 0.49 – 0.39 (m, *J* = 7.3 Hz, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 172.3, 172.0, 136.0, 130.9, 128.4, 126.8, 86.6, 53.0, 35.3, 20.7, 14.0 (br), and 9.3.
^{11}B NMR (193 MHz, $CDCl_3$) δ 7.24.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2942 (m), 2902 (w), 2863 (m), 1623 (m), 1534 (s), 1491 (m), 1303 (w), 1089 (w), and 737 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{16}H_{23}BNO)^{+}$: 256.1873, found: 256.1866.
mp: 35–39 °C (bright yellow solid).

3 Synthesis of Vinylogous Amide Substrates

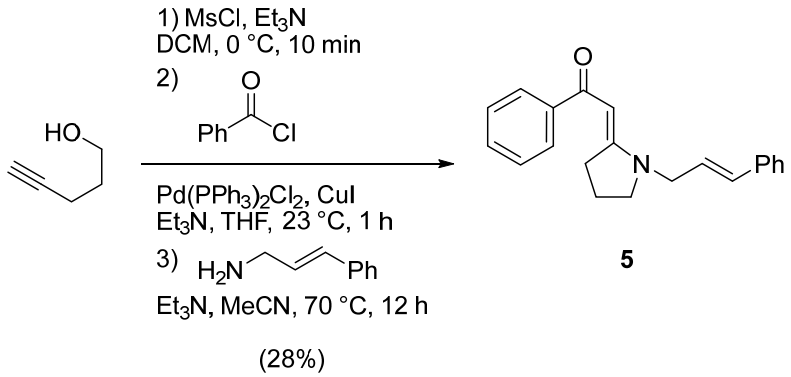
3.1 Synthesis of vinylogous amide 1



Following General Procedures A, B, and C, vinylogous amide **1** was prepared from pent-4-yn-1-ol (50.0 mmol). The crude residue was purified by flash-column chromatography on silica gel (50% → 70% ethyl acetate in hexanes) to provide vinylogous amide **1** (6.22 g, 51%) as an orange solid.

TLC (50% ethyl acetate in hexanes): R_f = 0.23 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 2H), 7.43 – 7.35 (m, 3H), 5.84 – 5.76 (m, 1H), 5.74 (s, 1H), 5.27 – 5.17 (m, 2H), 3.92 (d, *J* = 5.6 Hz, 2H), 3.49 – 3.40 (m, 4H), and 2.03 (app p, *J* = 7.6 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 187.9, 167.2, 142.1, 130.6, 130.4, 128.1, 127.3, 117.9, 86.8, 52.7, 49.2, 34.0, and 21.0.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3056 (w), 2981 (w), 2866 (w), 1624 (w), 1578 (m), 1535 (s), 1480 (m), 1301 (w), and 1215 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{15}H_{18}NO)^+$: 228.1388, found: 228.1398.
mp: 30–34 °C.

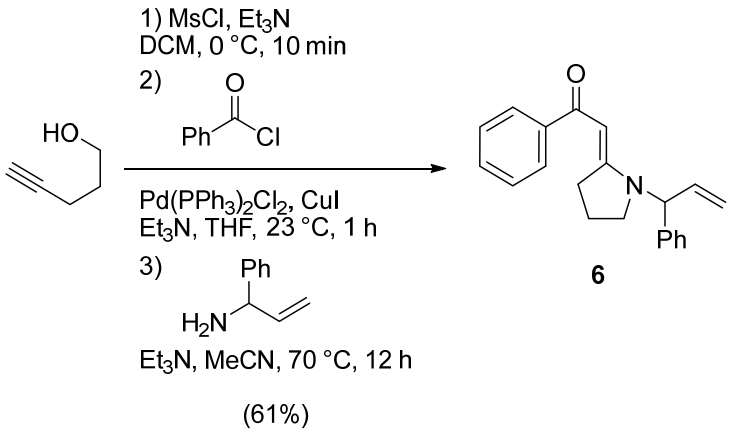
3.2 Synthesis of vinylogous amide 5



Following General Procedures A, B, and C, vinylogous amide **5** was prepared from pent-4-yn-1-ol (2.50 mmol). The crude residue was purified by flash-column chromatography on silica gel (60% → 80% ethyl acetate in hexanes) to provide vinylogous amide **5** (250 mg, 28%) as an orange oil.

TLC (80% ethyl acetate in hexanes): R_f = 0.35 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.43 – 7.36 (m, 5H), 7.35 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 6.58 – 6.53 (m, 1H), 6.18 (dt, *J* = 15.9, 6.1 Hz, 1H), 5.85 (s, 1H), 4.12 – 4.08 (m, 2H), 3.52 (t, *J* = 7.3 Hz, 2H), 3.47 (t, *J* = 7.8 Hz, 2H), and 2.06 (app p, *J* = 7.6 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 188.1, 167.2, 142.2, 136.2, 133.4, 130.5, 128.8, 128.2, 127.4, 126.6, 122.2, 87.0, 52.6, 48.8, 34.1, and 21.1.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3058 (w), 3024 (w), 2926 (w), 2866 (w), 1623 (w), 1576 (m), 1527 (s), 1478 (m), 1299 (w), 1213 (m), and 694 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{21}H_{22}NO)^+$: 304.1701, found: 304.1692.

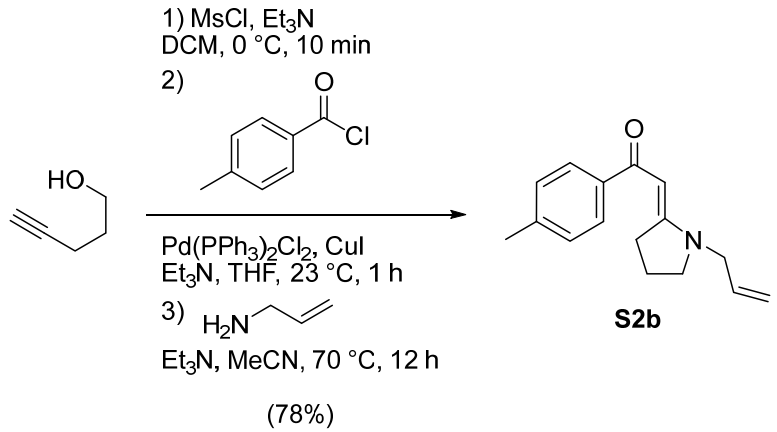
3.3 Synthesis of vinylogous amide 6



Following General Procedures A, B, and C, vinylogous amide **6** was prepared from pent-4-yn-1-ol (10.0 mmol). The crude residue was purified by flash-column chromatography on silica gel (30% → 60% ethyl acetate in hexanes) to provide vinylogous amide **6** (1.94 g, 61%) as a red oil.

TLC (50% ethyl acetate in hexanes): R_f = 0.36 (UV, $KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 2H), 7.41 – 7.31 (m, 6H), 7.28 – 7.25 (m, 2H), 6.08 (ddd, *J* = 16.8, 10.3, 6.1 Hz, 1H), 5.85 (s, 1H), 5.47 – 5.41 (m, 2H), 5.26 (d, *J* = 17.1 Hz, 1H), 3.53 – 3.42 (m, 2H), 3.41 – 3.35 (m, 1H), 3.19 – 3.13 (m, 1H), and 2.06 – 1.93 (m, 2H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 188.2, 167.1, 142.2, 137.7, 133.3, 130.4, 128.9, 128.2, 128.1, 127.8, 127.3, 118.9, 87.9, 61.6, 49.2, 34.0, and 21.2.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3058 (w), 3020 (w), 2978 (w), 2873 (w), 1623 (w), 1576 (w), 1526 (s), 1479 (m), 1289 (w), 1214 (m), 985 (w), and 698 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{21}H_{22}NO)^+$: 304.1701, found: 304.1713.

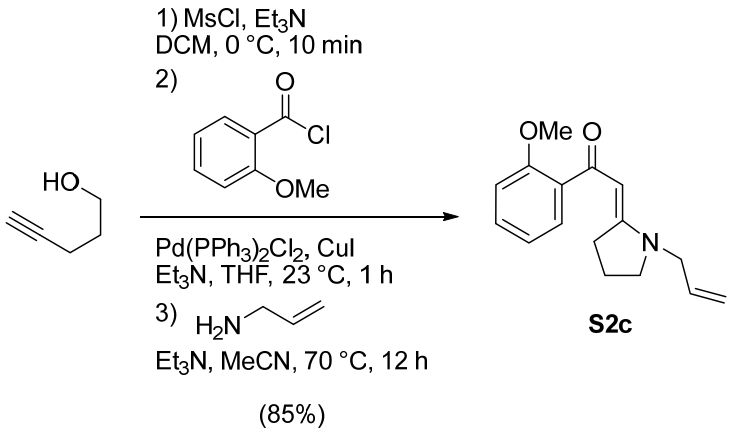
3.4 Synthesis of vinylogous amide S2b



Following General Procedures A, B, and C, vinylogous amide **S2b** was prepared from pent-4-yn-1-ol (5.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (50% → 70% ethyl acetate in hexanes) to provide vinylogous amide **S2b** (937 mg, 78%) as a yellow solid.

TLC (50% ethyl acetate in hexanes): R_f = 0.26 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 5.84 – 5.76 (m, 1H), 5.74 (s, 1H), 5.26 – 5.17 (m, 2H), 3.94 – 3.90 (m, 2H), 3.46 – 3.39 (m, 4H), 2.36 (s, 3H), and 2.02 (app p, *J* = 7.6 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 187.7, 166.8, 140.6, 139.4, 130.7, 128.8, 127.4, 117.8, 86.8, 52.6, 49.2, 33.9, 21.5, and 21.1.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3080 (w), 2975 (w), 2946 (w), 2918 (w), 2865 (w), 1606 (w), 1571 (m), 1537 (s), 1481 (m), 1299 (w), 1223 (m), 1176 (w), and 768 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{19}H_{20}NO)^+$: 242.1545, found: 242.1546.
mp: 53–57 °C.

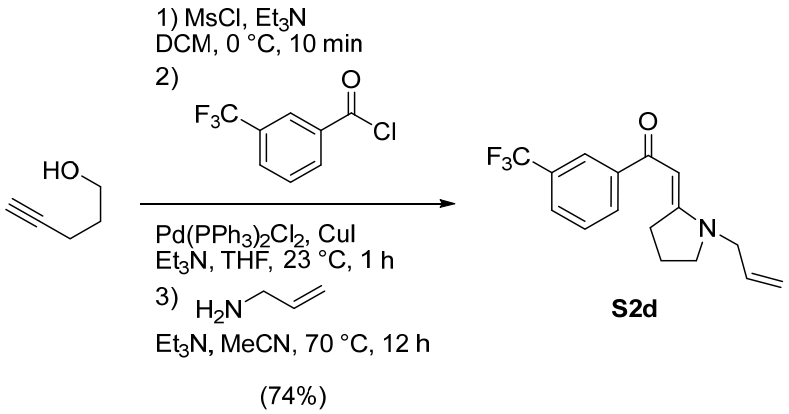
3.5 Synthesis of vinylogous amide S2c



Following General Procedures A, B, and C, vinylogous amide **S2c** was prepared from pent-4-yn-1-ol (2.50 mmol). The crude residue was purified by flash-column chromatography on silica gel (60% → 80% ethyl acetate in hexanes) to provide vinylogous amide **S2c** (544 mg, 85%) as an orange oil.

TLC (80% ethyl acetate in hexanes): R_f = 0.24 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.29 (ddd, *J* = 8.3, 7.4, 1.9 Hz, 1H), 6.94 (td, *J* = 7.4, 1.0 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 5.81 – 5.73 (m, 1H), 5.62 (s, 1H), 5.23 – 5.15 (m, 2H), 3.86 – 3.83 (m, 2H), 3.83 (s, 3H), 3.41 (t, *J* = 7.3 Hz, 2H), 3.38 (t, *J* = 7.7 Hz, 2H), and 2.00 (p, *J* = 7.5 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 188.7, 166.0, 156.9, 133.6, 130.8, 130.3, 129.6, 120.5, 117.8, 111.5, 91.8, 55.8, 52.4, 49.1, 33.9, and 21.1.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3070 (w), 2939 (w), 2870 (w), 2835 (w), 1619 (w), 1593 (m), 1527 (s), 1480 (s), 1335 (m), 1207 (m), 1022 (w), and 754 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{16}H_{20}NO_2)^+$: 258.1494, found: 258.1487.

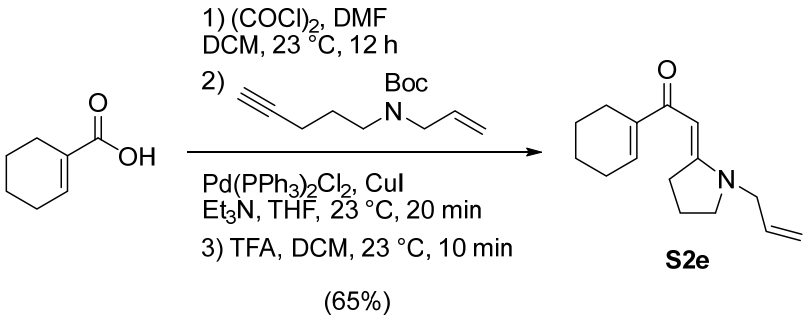
3.6 Synthesis of vinylogous amide S2d



Following General Procedures A, B, and C, vinylogous amide **S2d** was prepared from pent-4-yn-1-ol (2.50 mmol). The crude residue was purified by flash-column chromatography on silica gel (50% → 60% ethyl acetate in hexanes) to provide vinylogous amide **S2d** (547 mg, 74%) as a red oil.

TLC (60% ethyl acetate in hexanes): R_f = 0.41 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.49 (app t, *J* = 7.8 Hz, 1H), 5.83 – 5.76 (m, 1H), 5.70 (s, 1H), 5.29 – 5.18 (m, 2H), 3.96 – 3.93 (m, 2H), 3.48 (t, *J* = 7.3 Hz, 2H), 3.42 (t, *J* = 7.8 Hz, 2H), and 2.05 (app p, *J* = 7.7 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 185.9, 168.0, 142.9, 130.52 (q, *J* = 32.3 Hz), 130.50, 130.4, 128.7, 126.8 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.4 Hz), 124.2 (q, *J* = 4.0 Hz), 118.1, 86.4, 52.9, 49.3, 34.2, and 20.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ -61.77.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3080 (w), 2981 (w), 2944 (w), 2873 (w), 1625 (w), 1536 (s), 1481 (w), 1328 (m), 1208 (m), 1122 (m), 1071 (w), and 765 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{16}H_{17}F_3NO)^+$: 296.1262, found: 296.1259.

3.7 Synthesis of vinylogous amide S2e



A suspension of 1-cyclohexen-1-carboxylic acid (1.63 g, 12.9 mmol, 1 equiv) in dichloromethane (85 mL) and dimethylformamide (30 μL) was treated with oxalyl chloride (1.38 mL, 16.1 mmol, 1.25 equiv) at 0 °C, and the resulting mixture was warmed to 23 °C and held at this temperature for 12 h. The mixture was then concentrated in vacuo to provide the acid chloride which was used in the next step without further purification.

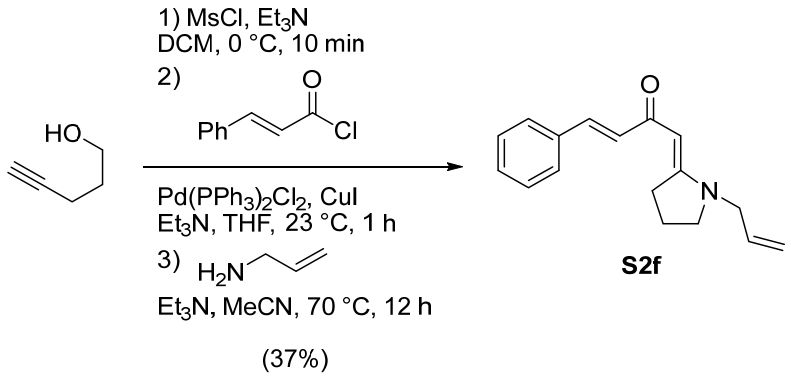
The crude acid chloride (assuming 12.9 mmol) was sequentially treated with a solution of *tert*-butyl allyl(pent-4-yn-1-yl)carbamate[5] (3.17 g, 14.2 mmol, 1.10 equiv) in triethylamine (35 mL), copper(I) iodide (246 mg, 1.30 mmol, 10 mol%), and bis(triphenylphosphine)palladium(II) dichloride (452 mg, 0.644 mmol, 5 mol%) at 0 °C. The resulting mixture was then allowed to warm to 23 °C. After 20 min, the mixture was diluted with diethyl ether (200 mL), and water (50 mL). The layers were separated, the organic layer was washed sequentially with water (2 x 50 mL) and saturated aqueous sodium chloride solution (50 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated to provide the ynone which was used in the next step without further purification.

A solution of the crude ynone (assuming 12.9 mmol) in dichloromethane (60 mL) was treated with trifluroacetic acid (10.5 mL, 137 mmol, 11.0 equiv) at 0 °C. After 10 min, the mixture was diluted with saturated aqueous sodium carbonate solution (150 mL). The layers were separated, the aqueous layer was extracted with dichloromethane (3 x 100 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (100 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (60% → 70% ethyl acetate in hexanes) to provide vinylogous amide **S2e** (1.93 g, 65%) as an orange solid.

TLC (7% methanol in dichloromethane): R_f = 0.37 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.58 – 6.54 (m, 1H), 5.79 – 5.71 (m, 1H), 5.39 (s, 1H), 5.22 – 5.12 (m, 2H), 3.83 (d, *J* = 5.5 Hz, 2H), 3.37 (t, *J* = 7.2 Hz, 2H), 3.28 (t, *J* = 7.8 Hz, 2H), 2.30 – 2.25 (m, 2H), 2.17 – 2.11 (m, 2H), 1.95 (app p, *J* = 7.6 Hz, 2H), 1.65 – 1.59 (m, 2H), and 1.59 – 1.53 (m, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 190.1, 165.9, 141.2, 131.8, 130.9, 117.6, 86.1, 52.4, 49.1, 33.7, 25.8, 24.6, 22.7, 22.1, and 21.1.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2925 (s), 2855 (m), 1609 (m), 1528 (s), 1480 (s), 1432 (m), 1294 (m), 1201 (s), 1164 (s), 1007 (m), 918 (m), and 769 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{15}H_{22}NO)^+$: 232.1701, found: 232.1710.
mp: 35–38 °C.

[5] Kumar, C. V. S.; Ramana, C. V. *Org. Lett.* **2014**, *16*, 4766–4769.

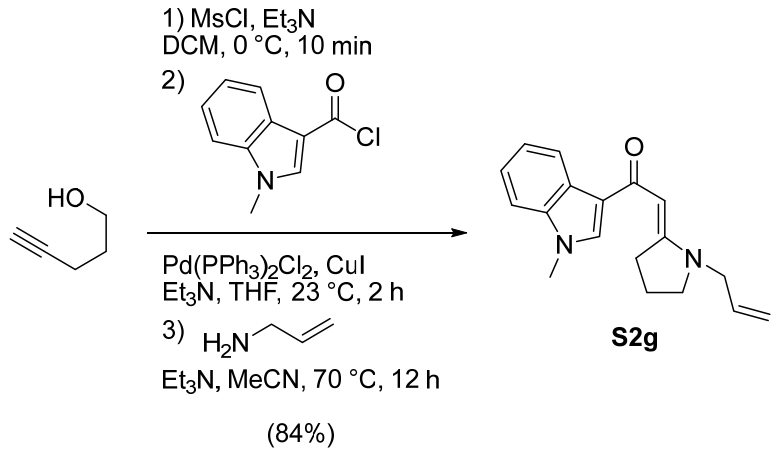
3.8 Synthesis of vinylogous amide S2f



Following General Procedure A, pent-4-yn-1-yl methanesulfonate was prepared from pent-4-yn-1-ol (5.00 mmol). The crude mesylate was used in the next step without further purification.
A solution of cinnamoyl chloride (1.00 g, 6.00 mmol, 1.20 equiv) in triethylamine (2.50 mL, 18.0 mmol, 3.50 equiv) and tetrahydrofuran (5.0 mL) was treated with bis(triphenylphosphine)palladium(II) dichloride (70.0 mg, 0.10 mmol, 2 mol%) at 23 °C. After 10 min, copper(I) iodide (38.0 mg, 0.20 mmol, 4 mol%) was added. After 10 min, a solution of the crude pent-4-yn-1-yl methanesulfonate (assuming 5.00 mmol) in tetrahydrofuran (5.0 mL) was added. After 2 h, the mixture was diluted with saturated aqueous sodium bicarbonate solution (10 mL). The layers were separated, the aqueous layer was extracted with diethyl ether (3 x 10 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (20 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated to provide the ynone, which was used in the next step without further purification.
Following General Procedure C, vinylogous amide **S2f** was prepared from the crude ynone (assuming 5.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (50% → 80% ethyl acetate in hexanes) to provide vinylogous amide **S2f** (462 mg, 37%) as an orange solid.

TLC (80% ethyl acetate in hexanes): R_f = 0.36 (UV, $KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.50 (d, *J* = 15.7 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 6.77 (d, *J* = 15.7 Hz, 1H), 5.82 – 5.74 (m, 1H), 5.25 – 5.16 (m, 3H), 3.90 – 3.87 (m, 2H), 3.43 (t, *J* = 7.3 Hz, 2H), 3.40 (t, *J* = 7.8 Hz, 2H), and 2.01 (app p, *J* = 7.6 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 185.4, 166.9, 137.3, 136.3, 130.6, 130.3, 128.9, 128.7, 127.9, 117.9, 91.3, 52.6, 49.1, 34.0, and 21.0.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3079 (w), 3023 (w), 2974 (w), 2937 (w), 2868 (w), 1595 (s), 1533 (s), 1481 (m), 1301 (m), 1114 (m), and 771 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{17}H_{20}NO)^+$: 254.1545, found: 254.1535.
mp: 57–61 °C.

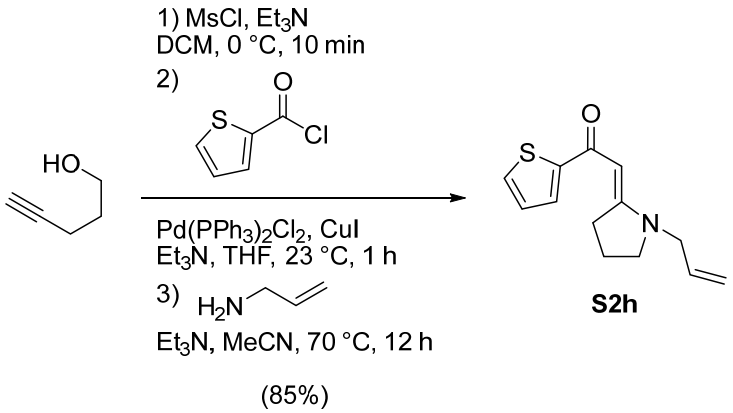
3.9 Synthesis of vinylogous amide S2g



Following General Procedures A, B, and C, vinylogous amide **S2g** was prepared from pent-4-yn-1-ol (5.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (70% → 100% ethyl acetate in hexanes) to provide vinylogous amide **S2g** (1.17 g, 84%) as a yellow solid.

TLC (90% ethyl acetate in hexanes): R_f = 0.19 (UV, $KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 – 8.35 (m, 1H), 7.59 (s, 1H), 7.30 – 7.27 (m, 1H), 7.26 – 7.20 (m, 2H), 5.88 – 5.80 (m, 1H), 5.68 (s, 1H), 5.27 – 5.20 (m, 2H), 3.93 – 3.90 (m, 2H), 3.77 (s, 3H), 3.47 – 3.43 (m, 2H), 3.41 (t, *J* = 7.1 Hz, 2H), and 2.01 (app p, *J* = 7.5 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 184.8, 164.6, 137.5, 132.3, 131.2, 126.8, 122.5, 122.2, 121.1, 119.6, 117.5, 109.4, 88.6, 52.3, 49.1, 33.6, 33.2, and 21.3.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3045 (w), 2974 (w), 2942 (w), 2910 (w), 2886 (w), 1605 (m), 1521 (s), 1466 (m), 1210 (m), 1092 (m), and 746 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{18}H_{21}N_2O)^+$: 281.1654, found: 281.1647.
mp: 88–93 °C.

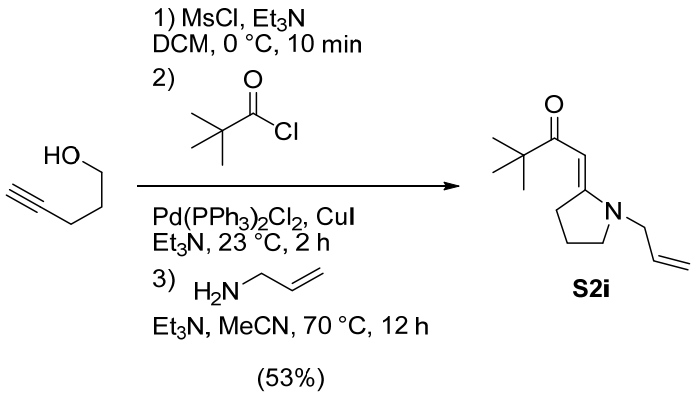
3.10 Synthesis of vinylogous amide S2h



Following General Procedures A, B, and C, vinylogous amide **S2h** was prepared from pent-4-yn-1-ol (5.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (50% → 70% ethyl acetate in hexanes) to provide vinylogous amide **S2h** (986 mg, 85%) as a yellow solid.

TLC (50% ethyl acetate in hexanes): R_f = 0.26 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.39 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.03 (dd, *J* = 4.9, 3.7 Hz, 1H), 5.82 – 5.75 (m, 1H), 5.65 (s, 1H), 5.26 – 5.18 (m, 2H), 3.92 – 3.89 (m, 2H), 3.44 (t, *J* = 7.3 Hz, 2H), 3.38 (t, *J* = 7.8 Hz, 2H), and 2.01 (app p, *J* = 7.6 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 180.3, 166.8, 149.3, 130.6, 129.5, 127.5, 127.4, 118.0, 86.3, 52.7, 49.2, 33.9, and 21.0.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3080 (w), 2978 (w), 2944 (w), 2913 (w), 2867 (w), 1605 (m), 1538 (s), 1481 (m), 1418 (w), 1302 (w), 1211 (m), and 765 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{13}H_{16}NOS)^+$: 234.0953, found: 234.0950.
mp: 53–56 °C.

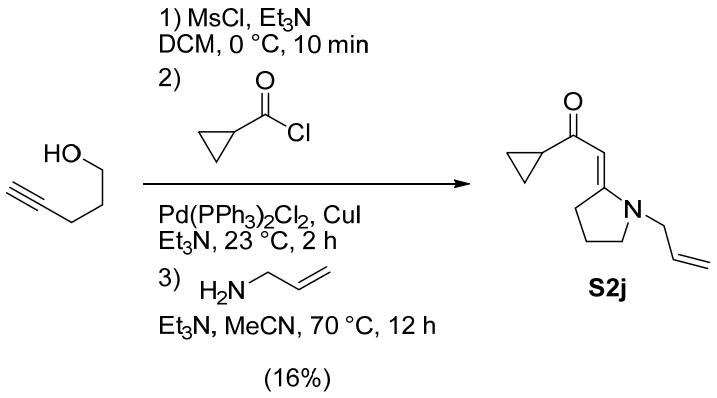
3.11 Synthesis of vinylogous amide S2i



Following General Procedure A, pent-4-yn-1-yl methanesulfonate was prepared from pent-4-yn-1-ol (5.00 mmol). The crude mesylate was used in the next step without further purification.
A mixture of the crude pent-4-yn-1-yl methanesulfonate (assuming 5.00 mmol) and pivaloyl chloride (0.74 mL, 6.00 mmol, 1.20 equiv) in triethylamine (10 mL, 0.5 M) was treated with bis(triphenylphosphine)palladium(II) dichloride (350 mg, 0.50 mmol, 10 mol%), and copper(I) iodide (48.0 mg, 0.25 mmol, 5 mol%) at 23 °C. After 2 h, the mixture was diluted with water (50 mL) and diethyl ether (200 mL). The layers were separated, the organic layer was washed sequentially with water (2 x 50 mL) and saturated aqueous sodium chloride solution (50 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the flltrate was concentrated to provide the ynone, which was used in the next step without further purification.
Following General Procedure C, the vinylogous amide was prepared from the crude ynone (assuming 5.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (40% → 60% ethyl acetate in hexanes) to provide vinylogous amide **S2i** (545 mg, 53%) as a yellow oil.

TLC (60% ethyl acetate in hexanes): R_f = 0.36 ($KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.77 – 5.69 (m, 1H), 5.24 (s, 1H), 5.21 – 5.11 (m, 2H), 3.82 – 3.78 (m, 2H), 3.36 – 3.32 (m, 2H), 3.24 – 3.19 (m, 2H), 1.93 (app p, *J* = 7.6 Hz, 2H), 1.10 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 203.0, 165.8, 130.9, 117.6, 85.4, 52.3, 49.1, 42.4, 33.5, 28.1, 21.1.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2950 (m), 2899 (w), 2865 (w), 1637 (m), 1541 (s), 1483 (m), 1302 (m), and 1108 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{13}H_{22}NO)^+$: 208.1701, found: 208.1693.

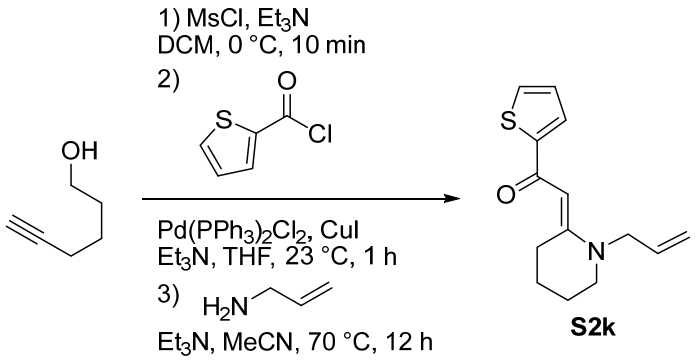
3.12 Synthesis of vinylogous amide S2j



Following General Procedure A, pent-4-yn-1-yl methanesulfonate was prepared from pent-4-yn-1-ol (5.00 mmol). The crude mesylate was used in the next step without further purification.
A mixture of the crude pent-4-yn-1-yl methanesulfonate (assuming 5.00 mmol) and cyclopropanecarbonyl chloride (620 mg, 6.00 mmol, 1.20 equiv) in triethylamine (10 mL, 0.5 M) was treated with bis(triphenylphosphine)palladium(II) dichloride (350 mg, 0.50 mmol, 10 mol%), and copper(I) iodide (47.0 mg, 0.25 mmol, 5 mol%) at 23 °C. After 2 h, the mixture was diluted with water (50 mL) and diethyl ether (200 mL). The layers were separated, the organic layer was washed sequentially with water (2 x 50 mL) and saturated aqueous sodium chloride solution (50 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the flltrate was concentrated to provide the ynone, which was used in the next step without further purification.
Following General Procedure C, vinylogous amide **S2j** was prepared from the crude ynone (assuming 5.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (60% → 70% ethyl acetate in hexanes) to provide vinylogous amide **S2j** (156 mg, 16%) as a yellow oil.

TLC (60% ethyl acetate in hexanes): R_f = 0.25 ($KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.78 – 5.70 (m, 1H), 5.22 (s, 1H), 5.21 – 5.11 (m, 2H), 3.83 – 3.79 (m, 2H), 3.37 – 3.32 (m, 2H), 3.22 (t, *J* = 7.8 Hz, 2H), 1.96 – 1.89 (m, 2H), 1.73 – 1.67 (m, 1H), 0.92 – 0.87 (m, 2H), and 0.66 – 0.61 (m, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 196.1, 164.5, 130.8, 117.6, 89.8, 52.2, 48.9, 33.5, 21.2, 21.1, and 8.7.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3084 (w), 3003 (w), 2981 (w), 2942 (w), 2873 (w), 1631 (w), 1537 (s), 1483 (m), 1301 (m), 1113 (m), 931 (m), and 767 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{12}H_{18}NO)^+$: 192.1388, found: 192.1378.

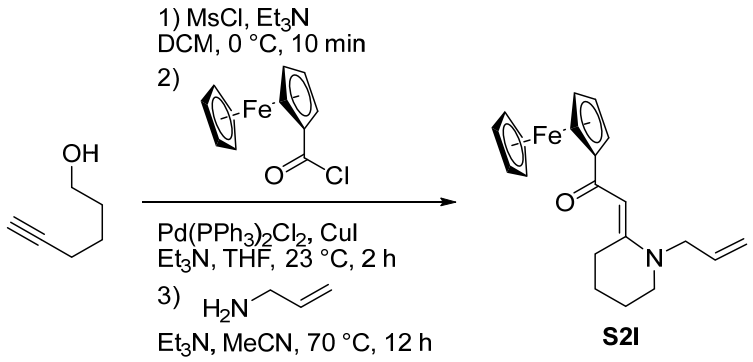
3.13 Synthesis of vinylogous amide S2k



Following General Procedures A, B, and C, vinylogous amide **S2k** was prepared from hex-5-yn-1-ol (4.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (50% ethyl acetate in hexanes) to provide vinylogous amide **S2k** (377 mg, 36%) as an orange solid.

TLC (50% ethyl acetate in hexanes): R_f = 0.44 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.47 (d, *J* = 3.7 Hz, 1H), 7.37 (d, *J* = 4.9 Hz, 1H), 7.03 – 7.00 (m, 1H), 5.88 – 5.81 (m, 1H), 5.70 (s, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 3.93 (d, *J* = 5.1 Hz, 2H), 3.36 – 3.30 (m, 4H), 1.84 – 1.78 (m, 2H), and 1.73 – 1.67 (m, 2H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 179.9, 164.5, 150.2, 130.6, 129.3, 127.5, 127.0, 117.6, 90.3, 55.2, 50.2, 28.5, 23.1, and 19.5.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3079 (w), 2944 (w), 2863 (w), 1596 (w), 1530 (s), 1482 (m), 1330 (w), 1214 (w), and 1172 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{14}H_{18}NOS)^+$: 248.1109, found: 248.1114.
mp: 41–46 °C.

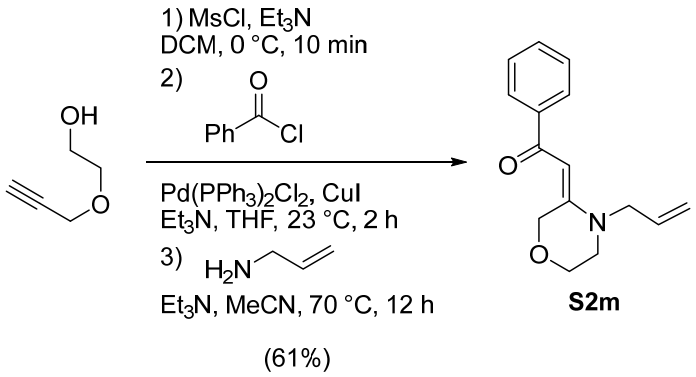
3.14 Synthesis of vinylogous amide S2l



Following General Procedures A, B, and C, vinylogous amide **S2l** was prepared from hex-5-yn-1-ol (3.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (40% → 70% ethyl acetate in hexanes) to provide vinylogous amide **S2l** (185 mg, 17%) as a red solid.

TLC (60% ethyl acetate in hexanes): R_f = 0.20 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 5.91 – 5.85 (m, 1H), 5.46 (s, 1H), 5.33 – 5.30 (m, 1H), 5.27 – 5.23 (m, 1H), 4.68 (t, *J* = 1.9 Hz, 2H), 4.30 (t, *J* = 1.9 Hz, 2H), 4.13 (s, 5H), 3.93 – 3.91 (m, 2H), 3.33 – 3.29 (m, 4H), 1.85 – 1.81 (m, 2H), and 1.73 – 1.68 (m, 2H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 190.7, 161.8, 131.0, 117.1, 92.2, 85.4, 70.4, 69.7, 68.8, 55.1, 50.1, 28.2, 23.4, and 19.8.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3089 (w), 2946 (w), 2866 (w), 1607 (w), 1530 (s), 1483 (m), 1330 (w), 1234 (m), and 1173 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{20}H_{24}FeNO)^+$: 350.1207, found: 350.1193.
mp: 48–56 °C.

3.15 Synthesis of vinylogous amide S2m



Following General Procedure A, 2-(prop-2-yn-1-yloxy)ethyl methanesulfonate was prepared from 2-(prop-2-yn-1-yloxy)ethan-1-ol[6] (5.00 mmol). The crude mesylate was used in the next step without further purification.

Based on a modified procedure for Sonogashira couplings,[7] a round-bottomed flask was charged with bis(triphenylphosphine)palladium(II) dichloride (73.0 mg, 0.10 mmol, 2 mol%), copper(I) iodide (40.0 mg, 0.21 mmol, 4 mol%) and tetrahydrofuran (20 mL) at 23 °C. Triethylamine (0.70 mL, 5.00, 1 equiv), a solution of the crude alkyne (assuming 5.00 mmol, 1 equiv) in tetrahydrofuran (5 mL) and benzoyl chloride (0.65 mL, 5.60 mmol, 1.10 equiv) were sequentially added at 23 °C. After 2 h, the mixture was diluted with saturated aqueous sodium bicarbonate solution (25 mL). The layers were separated, the aqueous layer was extracted with ethyl acetate (3 x 25 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (50 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated to provide the ynone, which was used in the next step without further purification.

Following General Procedure C, vinylogous amide **S2m** was prepared from the crude ynone (assuming 5.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (50% ethyl acetate in hexanes) to provide vinylogous amide **S2m** (700 mg, 61%) as a yellow oil.

TLC (30% ethyl acetate in hexanes): R_f = 0.10 (UV/$KMnO_4$).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.81 – 7.78 (m, 2H), 7.43 – 7.35 (m, 3H), 5.88 – 5.81 (m, 1H), 5.79 (s, 1H), 5.31 (d, *J* = 10.4 Hz, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.21 (s, 2H), 3.96 (d, *J* = 5.2 Hz, 2H), 3.88 (t, *J* = 5.4 Hz, 2H), and 3.38 (t, *J* = 5.4 Hz, 2H).

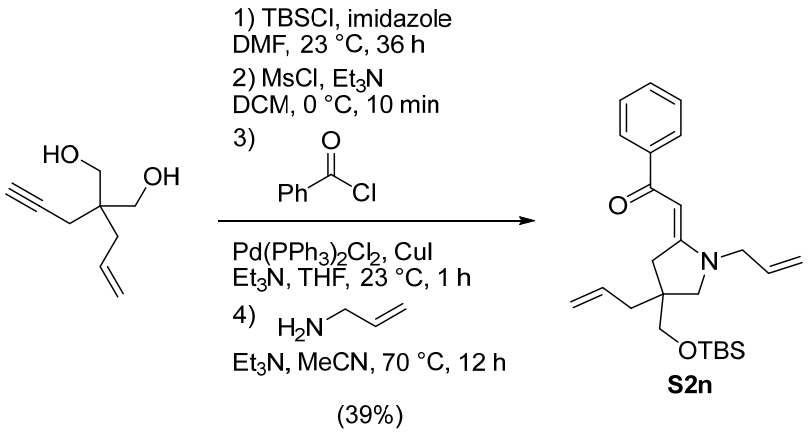
^{13}C NMR (175 MHz, $CDCl_3$) δ 187.7, 161.1, 141.9, 130.6, 129.8, 128.2, 127.3, 118.0, 89.5, 68.8, 63.5, 54.7, and 47.9.

IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3083 (w), 2980 (w), 2922 (w), 2869 (w), 1532 (s), 1478 (w), 1345 (w), 1214 (m), and 1107 (w) cm^{-1}.

HRMS (ESI): calcd for ([M+H], $C_{15}H_{18}NO_2$)$^+$: 244.1338, found: 244.1344.

[6] Bucher, J.; Wurm, T.; Nalivela, K. S.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Angew. Chem. Int. Ed.* **2014**, *53*, 3854–3858.
[7] Karpov, A. S.; Müller, T. J. J. *Org. Lett.* **2003**, *5*, 3451–3454.

3.16 Synthesis of vinylogous amide S2n



A solution of 2-allyl-2-(prop-2-yn-1-yl)propane-1,3-diol[8] (460 mg, 3.00 mmol, 1 equiv) in dimethylformamide (3 mL) was treated with imidazole (618 mg, 9.10 mmol, 3.00 equiv) and *tert*-butyldimethylsilyl chloride (470 mg, 3.10 mmol, 1.00 equiv) at 0 °C. After 10 min, the mixture was warmed to 23 °C. After 36 h, the mixture was diluted with saturated aqueous ammonium chloride solution (5 mL) and diethyl ether (10 mL). The layers were separated, the aqueous layer was extracted with diethyl ether (3 x 10 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (20 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated to provide the mono-TBS ether, which was used in the next step without further purification.

Following General Procedure A, the alkyne-mesylate was prepared from the crude mono-TBS ether (assuming 3.00 mmol). The crude alkyne-mesylate was used in the next step without further purification.

Based on a modified procedure for Sonogashira couplings,[7] a round-bottomed flask was charged with bis(triphenylphosphine)palladium(II) dichloride (40.0 mg, 0.06 mmol, 2 mol%), copper(I) iodide (24.0 mg, 0.13 mmol, 4 mol%), and tetrahydrofuran (10 mL). Triethylamine (0.42 mL, 3.00 mmol, 1 equiv), followed by a solution of the crude alkyne-mesylate (assuming 3.00 mmol, 1 equiv) and benzoyl chloride (0.40 mL, 3.44 mmol, 1.10 equiv) in tetrahydrofuran (5 mL) were added at 23 °C. After 1 h, the mixture was diluted with saturated aqueous sodium bicarbonate solution (15 mL). The layers were separated, the aqueous layer was extracted with ethyl acetate (3 x 15 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (25 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated to provide the ynone, which was used in the next step without further purification.

Following General Procedure C, vinylogous amide **S2n** was prepared from the crude ynone (assuming 3.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (20% ethyl acetate in hexanes) to provide vinylogous amide **S2n** (790 mg, 39%) as a yellow oil.

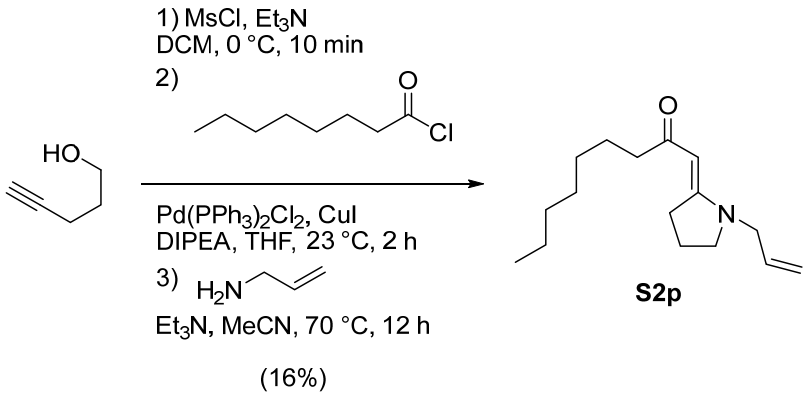
TLC (25% ethyl acetate in hexanes): R_f = 0.60 (UV/$KMnO_4$).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 2H), 7.42 – 7.36 (m, 3H), 5.82 – 5.75 (m, 2H), 5.72 (s, 1H), 5.27 – 5.20 (m, 2H), 5.12 – 5.07 (m, 2H), 3.92 – 3.83 (m, 2H), 3.49 – 3.40 (m, 3H), 3.30 – 3.17 (m, 3H), 2.30 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.23 (dd, *J* = 13.8, 7.3 Hz, 1H), 0.88 (s, 9H), 0.04 (s, 3H), and 0.03 (s, 3H).

[8] Tap, A.; Lecourt, C.; Dhambri, S.; Arnould, M.; Galvani, G.; VanBuu, O. N.; Jouanneau, M.; Férézou, J.-P.; Ardisson, J.; Lannou, M.-I.; Sorin, G. *Chem. Eur. J.* **2016**, *22*, 4938–4944.

^{13}C NMR (175 MHz, $CDCl_3$) δ 187.7, 166.5, 142.0, 133.9, 130.6, 130.4, 128.1, 127.3, 118.6, 118.1, 86.8, 67.2, 59.0, 49.2, 43.9, 41.9, 40.1, 26.0, 18.3, -5.40, and -5.43.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2955 (w), 2929 (w), 2889 (w), 2856 (w), 1628 (w), 1579 (m), 1540 (s), 1480 (w), 1213 (m), 1094 (w), and 814 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{25}H_{38}NO_2Si)^+$: 412.2672, found: 412.2682.

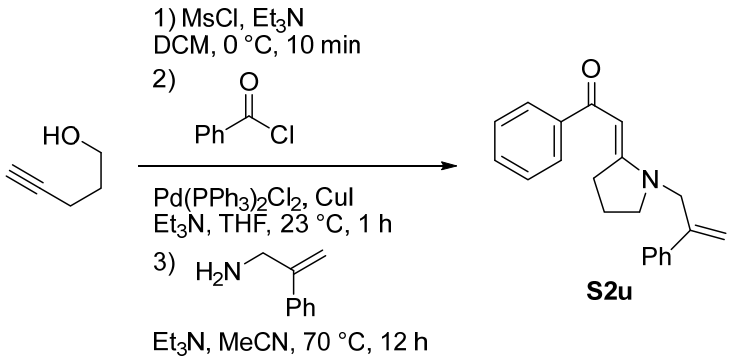
3.17 Synthesis of vinylogous amide S2p



Following General Procedure A, pent-4-yn-1-yl methanesulfonate was prepared from pent-4-yn-1-ol (5.00 mmol). The crude mesylate was used in the next step without further purification.
A mixture of the crude pent-4-yn-1-yl methanesulfonate (assuming 5.00 mmol), diisopropylethylamine (2.18 mL, 12.5 mmol, 2.50 equiv), bis(triphenylphosphine)palladium(II) dichloride (350 mg, 0.50 mmol, 10 mol%), and copper(I) iodide (47.0 mg, 0.25 mmol, 5 mol%) in tetrahydrofuran (10 mL) was treated dropwise with octanoyl chloride (0.94 mL, 5.50 mmol, 1.10 equiv) at 23 °C. After 2 h, the mixture was diluted with saturated aqueous sodium bicarbonate solution (25 mL). The layers were separated, the aqueous layer was extracted with diethyl ether (3 x 25 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (50 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated to provide the ynone, which was used in the next step without further purification.
Following General Procedure C, vinylogous amide **S2p** was prepared from the crude ynone (assuming 5.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (40% → 50% ethyl acetate in hexanes) to provide vinylogous amide **S2p** (204 mg, 16%) as a yellow oil.

TLC (50% ethyl acetate in hexanes): R_f = 0.26 ($KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.74 – 5.66 (m, 1H), 5.18 – 5.08 (m, 2H), 5.01 (s, 1H), 3.78 – 3.75 (m, 2H), 3.32 (t, *J* = 7.2 Hz, 2H), 3.20 (t, *J* = 7.8 Hz, 2H), 2.24 – 2.20 (m, 2H), 1.91 (app p, *J* = 7.5 Hz, 2H), 1.57 – 1.49 (m, 2H), 1.28 – 1.16 (m, 8H), and 0.84 – 0.80 (m, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 197.5, 165.0, 130.7, 117.5, 89.4, 52.1, 48.9, 43.7, 33.4, 31.8, 29.6, 29.3, 26.1, 22.7, 21.0, and 14.1.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2923 (m), 2853 (w), 1640 (w), 1544 (s), 1484 (m), 1301 (m), and 927 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{16}H_{28}NO)^+$: 250.2171, found: 250.2164.

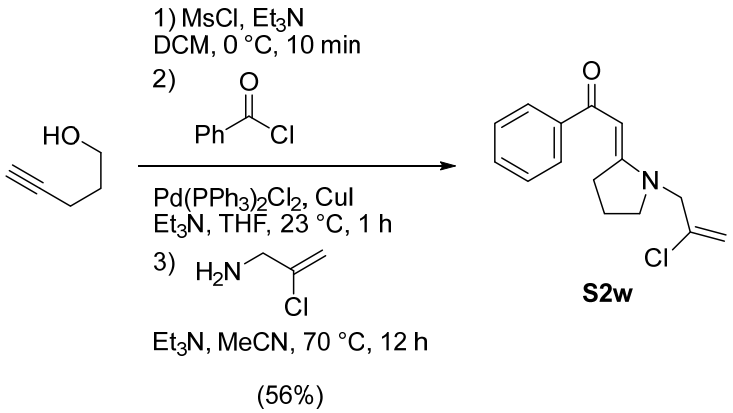
3.18 Synthesis of vinylogous amide S2u



Following General Procedures A, B, and C, vinylogous amide **S2u** was prepared from pent-4-yn-1-ol (4.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (50% ethyl acetate in hexanes) to provide vinylogous amide **S2u** (854 mg, 67%) as an orange solid.

TLC (50% ethyl acetate in hexanes): R_f = 0.27 (UV, $KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 2H), 7.43 – 7.31 (m, 8H), 5.83 (s, 1H), 5.53 (s, 1H), 5.15 (s, 1H), 4.32 (s, 2H), 3.46 – 3.41 (m, 4H), and 1.99 (app p, *J* = 7.5 Hz, 2H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 188.1, 167.4, 142.1, 140.8, 138.6, 130.5, 128.7, 128.4, 128.1, 127.4, 126.0, 114.1, 87.2, 52.8, 50.6, 33.9, and 21.2.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3055 (w), 2977 (w), 2866 (w), 1624 (w), 1577 (m), 1536 (s), 1480 (m), 1300 (w), 1214 (m), and 704 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{21}H_{22}NO)^+$: 304.1701, found: 304.1709.
mp: 60–65 °C.

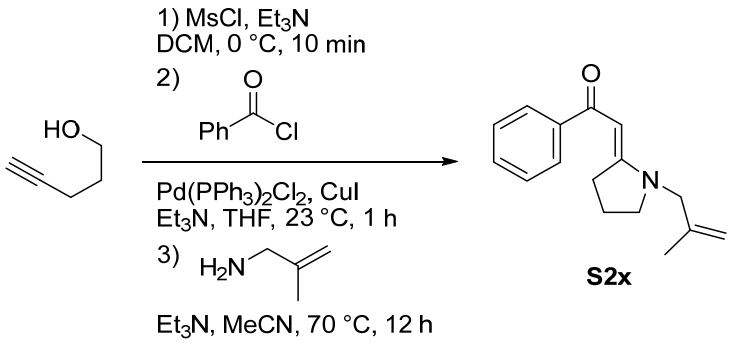
3.19 Synthesis of vinylogous amide S2w



Following General Procedures A, B, and C, vinylogous amide **S2w** was prepared from pent-4-yn-1-ol (7.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (50% → 70% ethyl acetate in hexanes) to provide vinylogous amide **S2w** (1.13 g, 56%) as a dark orange solid.

TLC (60% ethyl acetate in hexanes): R_f = 0.31 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 2H), 7.44 – 7.37 (m, 3H), 5.78 (s, 1H), 5.42 – 5.39 (m, 1H), 5.31 – 5.28 (m, 1H), 4.06 (s, 2H), 3.53 – 3.49 (m, 2H), 3.45 – 3.40 (m, 2H), and 2.06 (app p, *J* = 7.4 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 188.4, 166.8, 141.8, 135.3, 130.7, 128.2, 127.4, 113.9, 87.8, 53.1, 52.7, 33.6, and 21.3.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3056 (w), 2974 (w), 2946 (w), 2875 (w), 1627 (w), 1578 (m), 1532 (s), 1479 (m), 1300 (w), 1214 (m), 1019 (w), and 705 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{15}H_{17}ClNO)^+$: 262.0999, found: 262.0993.
mp: 29–33 °C.

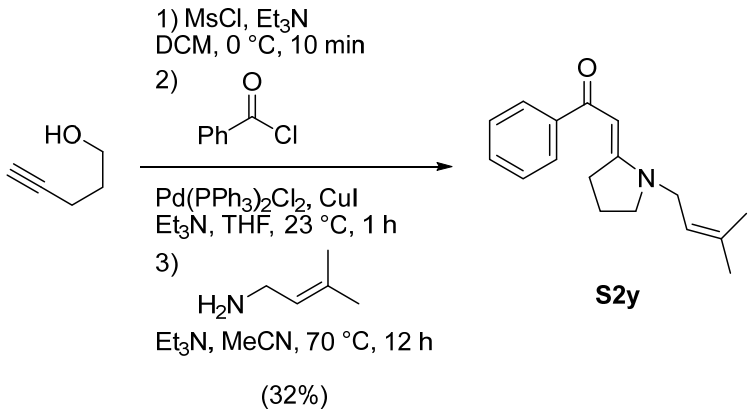
3.20 Synthesis of vinylogous amide S2x



Following General Procedures A, B, and C, vinylogous amide **S2x** was prepared from pent-4-yn-1-ol (3.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (50% ethyl acetate in hexanes) to provide vinylogous amide **S2x** (434 mg, 54%) as an orange solid.

TLC (50% ethyl acetate in hexanes): R_f = 0.25 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.42 – 7.35 (m, 3H), 5.74 (s, 1H), 4.94 – 4.92 (m, 1H), 4.82 – 4.80 (m, 1H), 3.83 (s, 2H), 3.46 – 3.41 (m, 4H), 2.03 (app p, *J* = 7.6 Hz, 2H), and 1.74 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 188.0, 167.5, 142.2, 138.6, 130.4, 128.1, 127.3, 112.5, 86.9, 53.1, 52.7, 33.9, 21.2, and 20.3.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3078 (w), 2972 (w), 2937 (w), 2911 (w), 2867 (w), 1624 (w), 1577 (m), 1531 (s), 1480 (m), 1301 (w), 1212 (m), and 707 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{16}H_{20}NO)^+$: 242.1545, found: 242.1545.
mp: 35–38 °C.

3.21 Synthesis of vinylogous amide S2y

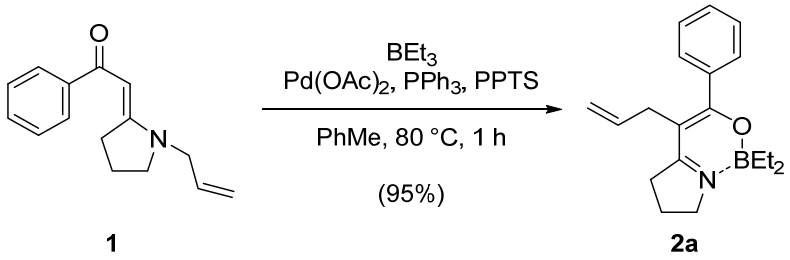


Following General Procedures A, B, and C, vinylogous amide **S2y** was prepared from pent-4-yn-1-ol (3.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (25% → 50% ethyl acetate in hexanes) to provide vinylogous amide **S2y** (270 mg, 32%) as a brown oil.

TLC (50% ethyl acetate in hexanes): R_f = 0.24 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.42 – 7.36 (m, 3H), 5.75 (s, 1H), 5.21 – 5.17 (m, 1H), 3.89 (d, *J* = 7.0 Hz, 2H), 3.45 – 3.38 (m, 4H), 2.00 (app p, *J* = 7.6 Hz, 2H), 1.76 (s, 3H), and 1.74 (s, 3H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 187.7, 167.1, 142.3, 137.2, 130.3, 128.1, 127.3, 117.7, 86.5, 52.4, 44.5, 34.1, 25.8, 20.9, and 18.1.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2969 (w), 2913 (w), 2857 (w), 1624 (w), 1578 (m), 1536 (s), 1480 (m), 1300 (w), and 1219 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{17}H_{22}NO)^+$: 256.1701, found: 256.1694.

4 Synthesis of Oxazaborinines

4.1 Synthesis of oxazaborinine 2a

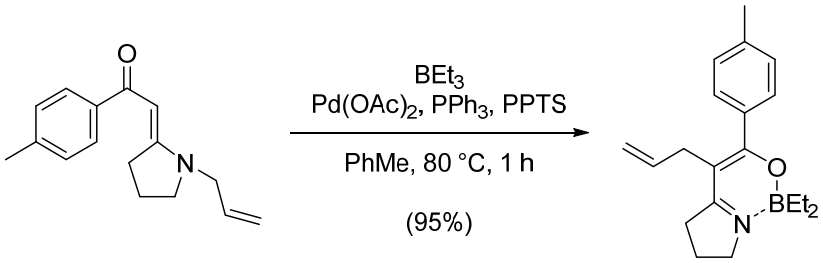


1 **2a**

Following General Procedure D, oxazaborinine **2a** was prepared from vinylogous amide **1** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (3% ethyl acetate in hexanes) to provide oxazaborinine **2a** (56.0 mg, 95%) as a bright yellow oil.

TLC (5% ethyl acetate in hexanes): R_f = 0.36 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 2H), 7.37 – 7.32 (m, 3H), 5.93 – 5.87 (m, 1H), 5.16 – 5.10 (m, 2H), 3.65 (t, *J* = 7.5 Hz, 2H), 2.90 – 2.87 (m, 2H), 2.80 (t, *J* = 7.9 Hz, 2H), 2.01 (app p, *J* = 7.8 Hz, 2H), 0.87 (t, *J* = 7.8 Hz, 6H), and 0.44 (q, *J* = 7.7 Hz, 4H).
^{13}C NMR (175 MHz, $CDCl_3$) δ f174.3, 172.5, 138.2, 137.6, 129.4, 128.1, 127.7, 115.3, 97.3, 53.6, 34.1, 32.3, 20.6, 14.2 (br), and 9.44.
^{11}B NMR (193 MHz, $CDCl_3$) δ 6.78.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2941 (m), 2901 (w), 2863 (m), 1620 (m), 1516 (s), 1485 (s), 1454 (m), 1303 (w), 1200 (w), 912 (w), and 705 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{19}H_{27}BNO)^+$: 296.2186, found: 296.2192.

4.2 Synthesis of oxazaborinine 2b

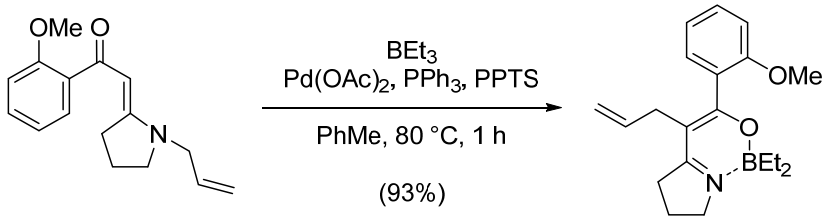


S2b **2b**

Following General Procedure D, oxazaborinine **2b** was prepared from vinylogous amide **S2b** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (3% ethyl acetate in hexanes) to provide oxazaborinine **2b** (59.0 mg, 95%) as a bright yellow solid.

TLC (3% ethyl acetate in hexanes): R_f = 0.29 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.18 – 7.14 (m, 2H), 5.95 – 5.87 (m, 1H), 5.17 – 5.09 (m, 2H), 3.67 – 3.62 (m, 2H), 2.93 – 2.89 (m, 2H), 2.81 – 2.76 (m, 2H), 2.36 (s, 3H), 2.00 (d, *J* = 7.7 Hz, 2H), 0.87 (t, *J* = 7.8 Hz, 6H), 0.44 (q, *J* = 7.8 Hz, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 174.2, 172.6, 139.4, 138.3, 134.8, 128.7, 127.8, 115.2, 97.2, 53.5, 34.1, 32.4, 21.5, 20.7, 14.1 (br), and 9.4.
^{11}B NMR (193 MHz, $CDCl_3$) δ 6.62.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2938 (m), 2901 (w), 2862 (m), 1618 (m), 1525 (m), 1491 (s), 1469 (w), 1454 (m), 1303 (w), and 911 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{20}H_{29}BNO)^+$: 310.2342, found: 310.2341.
mp: 45–50 °C.

4.3 Synthesis of oxazaborinine 2c

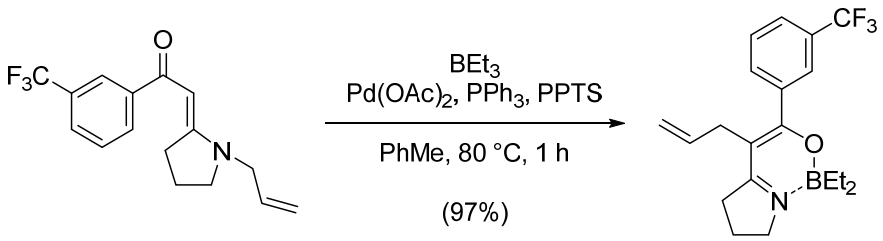


S2c **2c**

Following General Procedure D, oxazaborinine **2c** was prepared from vinylogous amide **S2c** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (15% ethyl acetate in hexanes) to provide oxazaborinine **2c** (60.0 mg, 93%) as a bright orange oil.

TLC (15% ethyl acetate in hexanes): R_f = 0.47 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 1H), 7.22 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.93 (app td, *J* = 7.4, 1.0 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 5.75 – 5.67 (m, 1H), 5.02 – 4.93 (m, 2H), 3.80 (s, 3H), 3.66 – 3.61 (m, 2H), 2.83 – 2.77 (m, 2H), 2.69 – 2.64 (m, 2H), 2.00 (app p, *J* = 7.8 Hz, 2H), 0.89 (t, *J* = 7.7 Hz, 6H), and 0.49 – 0.38 (m, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.9, 171.4, 156.4, 138.1, 130.0, 129.1, 127.1, 120.5, 114.5, 111.5, 99.2, 55.7, 53.4, 34.1, 32.3, 20.5, 14.2 (br), and 9.2.
^{11}B NMR (193 MHz, $CDCl_3$) δ 7.09.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2937 (m), 2900 (w), 2863 (m), 1621 (m), 1602 (w), 1518 (s), 1487 (s), 1452 (m), 1248 (w), and 753 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{20}H_{29}BNO_2$)$^+$: 326.2291, found: 326.2291.

4.4 Synthesis of oxazaborinine 2d

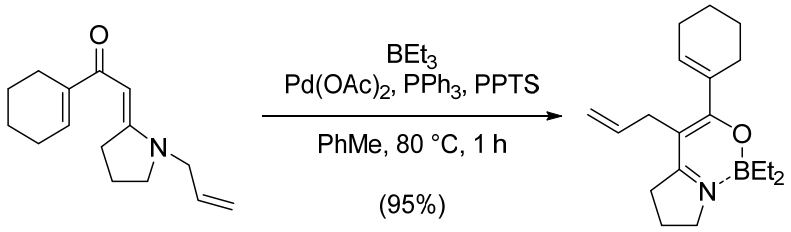


S2d **2d**

Following General Procedure D, oxazaborinine **2d** was prepared from vinylogous amide **S2d** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (5% ethyl acetate in hexanes) to provide oxazaborinine **2d** (71.0 mg, 97%) as a bright yellow oil.

TLC (5% ethyl acetate in hexanes): R_f = 0.43 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.76 (m, 1H), 7.71 – 7.68 (m, 1H), 7.63 – 7.60 (m, 1H), 7.50 – 7.46 (m, 1H), 5.94 – 5.87 (m, 1H), 5.16 (t, *J* = 2.0 Hz, 1H), 5.14 (dq, *J* = 8.4, 1.9 Hz, 1H), 3.70 – 3.66 (m, 2H), 2.87 – 2.84 (m, 2H), 2.84 – 2.80 (m, 2H), 2.03 (app p, *J* = 7.8 Hz, 2H), 0.87 (t, *J* = 7.7 Hz, 6H), and 0.45 (q, *J* = 7.8 Hz, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 174.4, 170.5, 138.3, 137.7, 131.2, 130.5 (q, *J* = 32.4 Hz), 128.7, 126.1 (q, *J* = 3.9 Hz), 124.7 (q, *J* = 4.0 Hz), 124.1 (q, *J* = 272.4 Hz), 115.6, 97.9, 53.8, 34.2, 32.2, 20.6, 14.1 (br), and 9.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -61.9.
^{11}B NMR (193 MHz, $CDCl_3$) δ 6.97.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2941 (m), 2903 (w), 2864 (m), 1625 (m), 1519 (s), 1434 (w), 1350 (m), 1322 (s), 1309 (m), 1167 (m), 1128 (s), 1074 (m), and 911 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{20}H_{26}BF_3NO)^+$: 364.2060, found: 364.2053.

4.5 Synthesis of oxazaborinine 2e

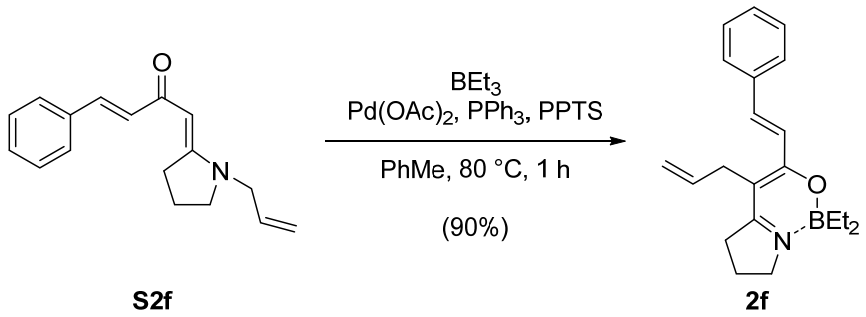


S2e **2e**

Following General Procedure D, oxazaborinine **2e** was prepared from vinylogous amide **S2e** (2.50 mmol). The crude residue was purified by flash-column chromatography on silica gel (4% ethyl acetate in hexanes) to provide oxazaborinine **2e** (708 mg, 95%) as a bright yellow oil.

TLC (10% ethyl acetate in hexanes): R_f = 0.67 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.87 – 5.79 (m, 2H), 5.05 – 4.99 (m, 2H), 3.60 – 3.53 (m, 2H), 2.92 – 2.87 (m, 2H), 2.76 – 2.70 (m, 2H), 2.22 – 2.14 (m, 2H), 2.10 – 2.04 (m, 2H), 1.98 – 1.91 (m, 2H), 1.69 – 1.62 (m, 2H), 1.62 – 1.53 (m, 2H), 0.78 (t, *J* = 7.7 Hz, 6H), and 0.34 (q, *J* = 7.7 Hz, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 175.7, 174.0, 138.7, 135.3, 127.5, 114.6, 96.3, 53.4, 34.1, 32.4, 26.2, 25.0, 22.4, 21.9, 20.6, 14.1 (br), and 9.4.
^{11}B NMR (193 MHz, $CDCl_3$) δ 6.50.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2933 (m), 2901 (w), 2860 (m), 1614 (m), 1502 (s), 1455 (w), 1427 (w), 1302 (w), and 911 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{19}H_{31}BNO)^+$: 300.2499, found: 300.2492.

4.6 Synthesis of oxazaborinine 2f

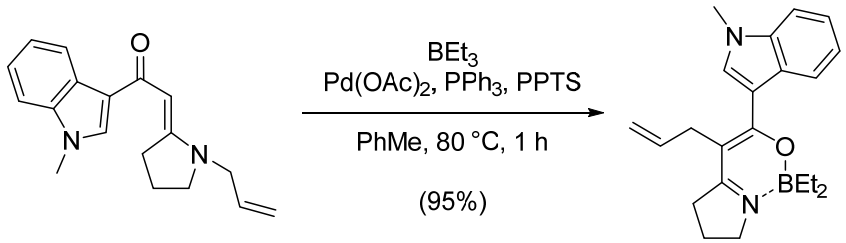


S2f **2f**

Following General Procedure D, oxazaborinine **2f** was prepared from vinylogous amide **S2f** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (3% ethyl acetate in hexanes) to provide oxazaborinine **2f** (58.0 mg, 90%) as a bright orange solid.

TLC (3% ethyl acetate in hexanes): R_f = 0.29 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 3H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 6.86 (d, *J* = 15.3 Hz, 1H), 5.94 – 5.86 (m, 1H), 5.12 – 5.04 (m, 2H), 3.69 – 3.63 (m, 2H), 3.07 – 3.03 (m, 2H), 2.79 – 2.74 (m, 2H), 2.03 – 1.96 (m, 2H), 0.83 (t, *J* = 7.8 Hz, 6H), and 0.48 – 0.36 (m, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 166.5, 137.6, 137.4, 136.6, 128.9, 128.8, 127.8, 120.9, 115.2, 100.0, 53.8, 33.9, 31.0, 20.6, 13.8, and 9.3.
^{11}B NMR (193 MHz, $CDCl_3$) δ 5.99.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2938 (m), 2902 (w), 2862 (m), 1634 (w), 1598 (m), 1503 (s), 1491 (m), 1454 (m), 1304 (w), and 762 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{21}H_{29}BNO)^+$: 322.2342, found: 322.2333.
mp: 58–70 °C.

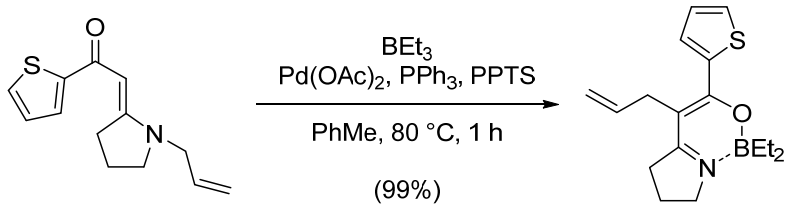
4.7 Synthesis of oxazaborinine 2g



Following General Procedure D, oxazaborinine **2g** was prepared from vinylogous amide **S2g** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (15% ethyl acetate in hexanes) to provide oxazaborinine **2g** (66.0 mg, 95%) as a bright yellow solid.
Recrystallization (ethyl acetate/hexanes) of the product gave crystals suitable for X-ray diffraction (see Section 7).

TLC (15% ethyl acetate in hexanes): R_f = 0.39 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 1H), 7.39 (s, 1H), 7.31 – 7.25 (m, 2H), 7.23 (ddd, *J* = 8.0, 6.4, 1.8 Hz, 1H), 6.08 – 6.01 (m, 1H), 5.25 (app dq, *J* = 17.2, 2.0 Hz, 1H), 5.19 (app dq, *J* = 10.2, 1.9 Hz, 1H), 3.77 (s, 3H), 3.68 – 3.63 (m, 2H), 3.17 – 3.13 (m, 2H), 2.82 – 2.76 (m, 2H), 2.04 – 1.97 (m, 2H), 0.94 (t, *J* = 7.7 Hz, 6H), and 0.61 – 0.47 (m, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.2, 169.1, 137.9, 136.9, 130.9, 127.8, 123.1, 122.5, 120.9, 115.4, 111.9, 109.2, 95.7, 53.3, 34.0, 33.3, 32.7, 20.7, 14.3, and 9.7.
^{11}B NMR (193 MHz, $CDCl_3$) δ 6.46.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2937 (m), 2900 (w), 2861 (m), 1605 (w), 1534 (m), 1497 (s), 1467 (m), 1386 (m), 1298 (w), and 744 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{22}H_{30}BN_2O)^+$: 349.2451, found: 349.2443.
mp: 124–130 °C.

4.8 Synthesis of oxazaborinine 2h

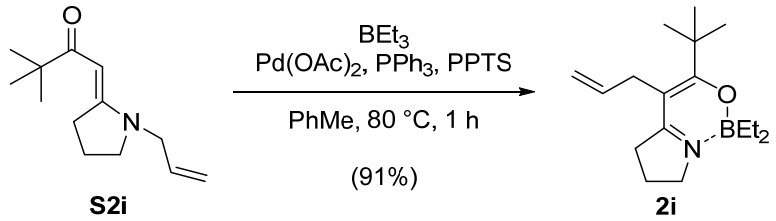


S2h **2h**

Following General Procedure D, oxazaborinine **2h** was prepared from vinylogous amide **S2h** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (3% ethyl acetate in hexanes) to provide oxazaborinine **2h** (60.0 mg, 99%) as a bright orange solid.

TLC (3% ethyl acetate in hexanes): R_f = 0.26 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.05 – 7.02 (m, 1H), 6.04 – 5.96 (m, 1H), 5.21 – 5.12 (m, 2H), 3.70 – 3.63 (m, 2H), 3.21 – 3.16 (m, 2H), 2.84 – 2.78 (m, 2H), 2.01 (app p, *J* = 7.9 Hz, 2H), 0.84 (t, *J* = 7.7 Hz, 6H), and 0.48 – 0.38 (m, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.9, 164.0, 141.0, 136.6, 129.0, 128.9, 127.3, 115.6, 97.0, 53.7, 34.2, 32.2, 20.6, 13.6 (br), and 9.3.
^{11}B NMR (193 MHz, $CDCl_3$) δ 6.31.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2940 (m), 2901 (w), 2862 (m), 1614 (m), 1527 (m), 1498 (s), 1468 (w), 1453 (m), 1426 (w), 1302 (w), 1229 (w), 854 (w), and 711 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+Na], $C_{17}H_{24}BNNaOS)^+$: 324.1569, found: 324.1560.
mp: 33–35 °C.

4.9 Synthesis of oxazaborinine 2i

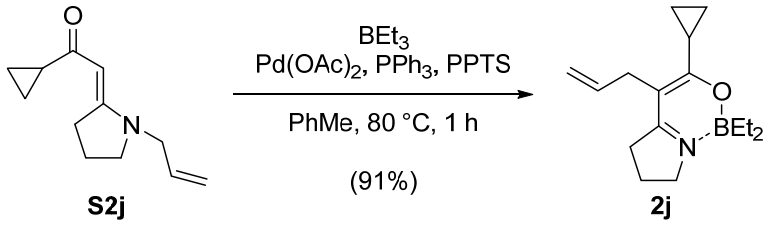


S2i **2i**

Following General Procedure D, oxazaborinine **2i** was prepared from vinylogous amide **S2i** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (3% ethyl acetate in hexanes) to provide oxazaborinine **2i** (50.0 mg, 91%) as a yellow oil.

TLC (3% ethyl acetate in hexanes): R_f = 0.52 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.91 – 5.82 (m, 1H), 5.08 – 5.02 (m, 2H), 3.55 – 3.50 (m, 2H), 3.08 – 3.04 (m, 2H), 2.72 – 2.67 (m, 2H), 1.93 – 1.87 (m, 2H), 1.20 (s, 9H), 0.76 (t, *J* = 7.7 Hz, 6H), and 0.36 – 0.28 (m, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 182.7, 174.5, 138.5, 115.1, 95.7, 53.0, 39.3, 34.0, 31.7, 29.1, 20.6, 13.7 (br), and 9.4.
^{11}B NMR (193 MHz, $CDCl_3$) δ 5.73.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2941 (m), 2903 (w), 2863 (m), 1613 (m), 1490 (s), 1454 (m), 1304 (w), and 911 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{17}H_{31}BNO)^+$: 276.2499, found: 276.2496.

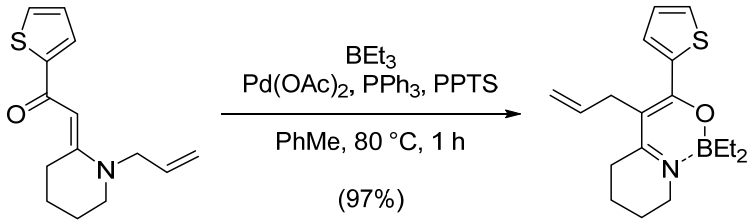
4.10 Synthesis of oxazaborinine 2j



Following General Procedure D, oxazaborinine **2j** was prepared from vinylogous amide **S2j** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (5% ethyl acetate in hexanes) to provide oxazaborinine **2j** (47.0 mg, 91%) as a yellow oil.

TLC (5% ethyl acetate in hexanes): R_f = 0.65 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.92 – 5.84 (m, 1H), 5.06 (app dq, *J* = 17.1, 1.9 Hz, 1H), 5.01 (app dq, *J* = 10.1, 1.8 Hz, 1H), 3.54 – 3.49 (m, 2H), 3.01 – 2.97 (m, 2H), 2.70 – 2.66 (m, 2H), 1.92 (app p, *J* = 7.7 Hz, 2H), 1.70 – 1.64 (m, 1H), 1.07 – 1.03 (m, 2H), 0.74 – 0.68 (m, 8H), and 0.26 (q, *J* = 7.7 Hz, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.2, 171.8, 137.6, 114.4, 96.3, 53.1, 33.6, 31.1, 20.7, 13.6 (br), 12.8, 9.3, and 7.9.
^{11}B NMR (193 MHz, $CDCl_3$) δ 6.03.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2941 (m), 2900 (w), 2862 (m), 1615 (m), 1507 (s), 1472 (w), 1381 (w), 1300 (w), and 894 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{16}H_{27}BNO)^+$: 260.2186, found: 260.2179.

4.11 Synthesis of oxazaborinine 2k

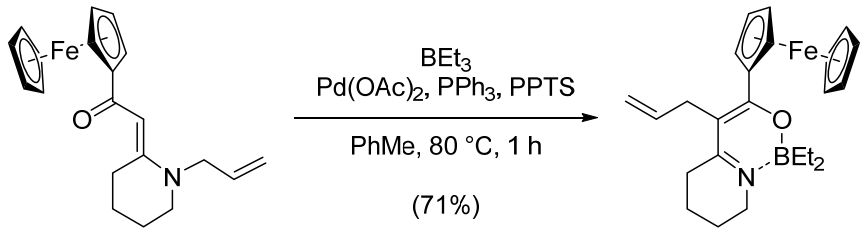


S2k **2k**

Following General Procedure D, oxazaborinine **2k** was prepared from vinylogous amide **S2k** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (10% ethyl acetate in hexanes) to provide oxazaborinine **2k** (61.0 mg, 97%) as a bright yellow oil.

TLC (10% ethyl acetate in hexanes): R_f = 0.57 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 2H), 7.03 – 7.00 (m, 1H), 6.02 – 5.96 (m, 1H), 5.21 – 5.15 (m, 2H), 3.35 – 3.31 (m, 2H), 3.23 – 3.19 (m, 2H), 2.54 – 2.49 (m, 2H), 1.73 – 1.69 (m, 4H), 0.85 (t, *J* = 7.8 Hz, 6H), and 0.44 (q, *J* = 7.8 Hz, 4H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 168.8, 161.9, 141.6, 137.3, 128.8, 128.6, 127.2, 115.9, 101.4, 45.1, 31.3, 26.8, 21.5, 18.9, 12.6 (br), and 9.5.
^{11}B NMR (193 MHz, $CDCl_3$) δ 5.97.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2939 (m), 2902 (w), 2862 (m), 1615 (m), 1527 (m), 1500 (s), 1447 (m), 1417 (m), 1210 (w), 881 (w), and z710 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{18}H_{27}BNOS)^+$: 316.1906, found: 316.1909.

4.12 Synthesis of oxazaborinine 2l

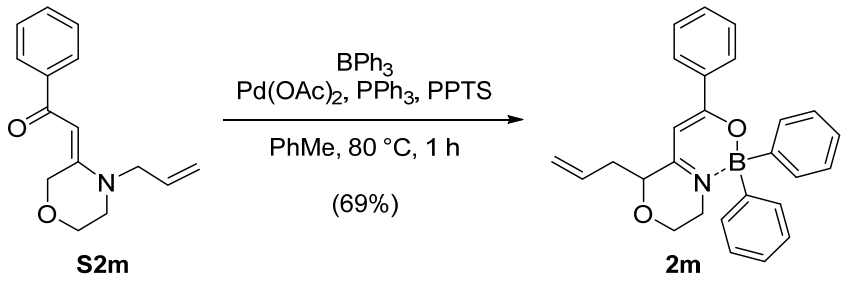


S2l **2l**

Following General Procedure D, oxazaborinine **2l** was prepared from vinylogous amide **S2l** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (5% ethyl acetate in hexanes) to provide oxazaborinine **2l** (59.0 mg, 71%) as a bright red solid.
Recrystallization (ethyl acetate/hexanes) of the product gave crystals suitable for X-ray diffraction (see Section 7).

TLC (5% ethyl acetate in hexanes): R_f = 0.40 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 6.02 – 5.95 (m, 1H), 5.19 – 5.13 (m, 2H), 4.69 (t, *J* = 1.9 Hz, 2H), 4.29 (t, *J* = 1.9 Hz, 2H), 4.19 (s, 5H), 3.28 – 3.24 (m, 2H), 3.20 – 3.17 (m, 2H), 2.46 – 2.42 (m, 2H), 1.71 – 1.66 (m, 4H), 0.87 (t, *J* = 7.7 Hz, 6H), and 0.44 (q, *J* = 7.7 Hz, 4H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 170.6, 167.7, 138.4, 115.4, 100.9, 80.8, 70.6, 69.8, 69.7, 44.7, 31.0, 26.4, 21.6, 19.0, 12.6 (br), and 9.6.
^{11}B NMR (193 MHz, $CDCl_3$) δ 5.51.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2941 (m), 2903 (w), 2862 (m), 1612 (m), 1505 (s), 1442 (m), 1420 (m), 1214 (m), 910 (w) and 821 (w) cm^{-1}.
HRMS (ESI): calcd for ([M], $C_{24}H_{32}BFeNO)^+$: 417.1926, found: 417.1934.
mp: 108–113 °C.

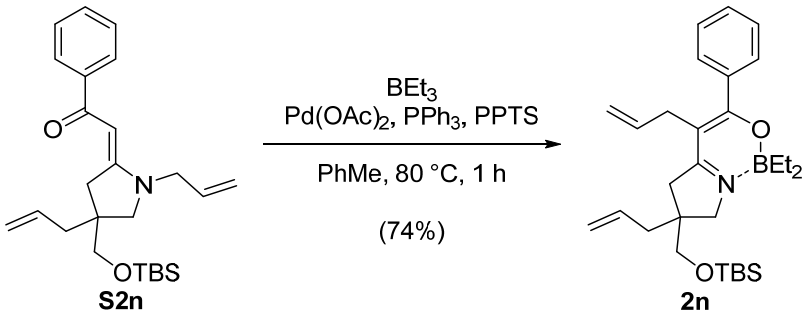
4.13 Synthesis of oxazaborinine 2m



Following General Procedure E, oxazaborinine **2m** was prepared from vinylogous amide **S2m** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (15% ethyl acetate in hexanes) to provide oxazaborinine **2m** (55.0 mg, 69%) as an off-white solid.

TLC (25% ethyl acetate in hexanes): R_f = 0.50 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 2H), 7.48 – 7.43 (m, 5H), 7.42 – 7.38 (m, 2H), 7.31 – 7.26 (m, 4H), 7.26 – 7.22 (m, 2H), 5.94 – 5.86 (m, 1H), 5.83 (s, 1H), 5.26 – 5.19 (m, 2H), 4.60 – 4.57 (m, 1H), 4.04 – 3.99 (m, 1H), 3.79 – 3.73 (m, 1H), 3.32 – 3.26 (m, 1H), 3.17 – 3.12 (m, 1H), and 2.77 – 2.63 (m, 2H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 171.3, 168.3, 134.7, 133.2, 133.0, 132.7, 131.7, 128.6, 127.31, 127.29, 127.1, 126.6, 126.5, 119.1, 91.1, 74.1, 61.9, 45.7, and 37.9.
^{11}B NMR (193 MHz, $CDCl_3$) δ 4.52.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3067 (w), 3043 (w), 3005 (w), 2975 (w), 2925 (w), 2855 (w), 1621 (w), 1523 (s), 1489 (m), 1340 (w), 746 (w), and 703 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{27}H_{27}BNO_2)^+$: 408.2135, found: 408.2130.
mp: 213–218 °C.

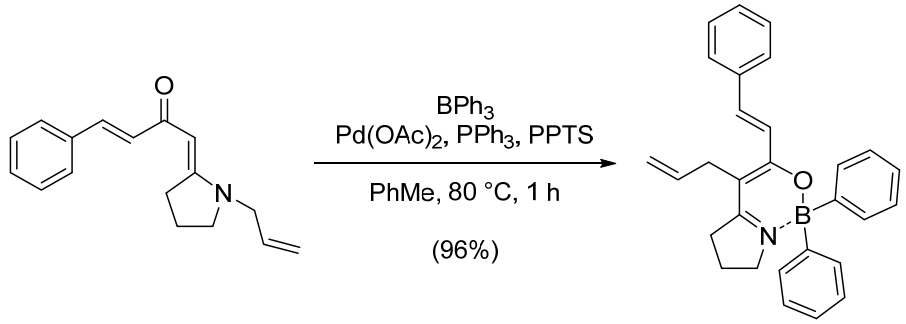
4.14 Synthesis of oxazaborinine 2n



Following General Procedure D, oxazaborinine **2n** was prepared from vinylogous amide **S2n** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (3% ethyl acetate in hexanes) to provide oxazaborinine **2n** (70.0 mg, 74%) as a bright yellow oil.

TLC (3% ethyl acetate in hexanes): R_f = 0.52 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.36 – 7.32 (m, 3H), 5.93 – 5.85 (m, 1H), 5.77 – 5.69 (m, 1H), 5.17 – 5.10 (m, 4H), 3.55 (d, *J* = 14.1 Hz, 1H), 3.46 – 3.42 (m, 2H), 3.39 (d, *J* = 14.2 Hz, 1H), 2.86 – 2.83 (m, 2H), 2.73 (d, *J* = 18.1 Hz, 1H), 2.57 (d, *J* = 18.1 Hz, 1H), 2.29 – 2.21 (m, 2H), 0.91 (s, 9H), 0.88 (d, *J* = 7.8 Hz, 3H), 0.86 (t, *J* = 7.8 Hz, 3H), 0.45 – 0.38 (m, 4H), and 0.08 – 0.05 (m, 6H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 173.6, 172.6, 138.2, 137.6, 133.5, 129.4, 128.1, 127.7, 119.2, 115.4, 97.3, 66.6, 59.9, 44.5, 41.4, 40.2, 32.2, 26.0, 18.4, 14.1 (br), 9.44, 9.43, -5.38, and -5.41.
^{11}B NMR (193 MHz, $CDCl_3$) δ 6.91.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2930 (m), 2899 (w), 2860 (m), 1622 (m), 1514 (s), 1484 (s), 1448 (m), 1203 (w), 1099 (s), 837 (s), 776 (m), and 670 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{29}H_{47}BNO_2Si)^+$: 480.3469, found: 480.3474.

4.15 Synthesis of oxazaborinine 2o

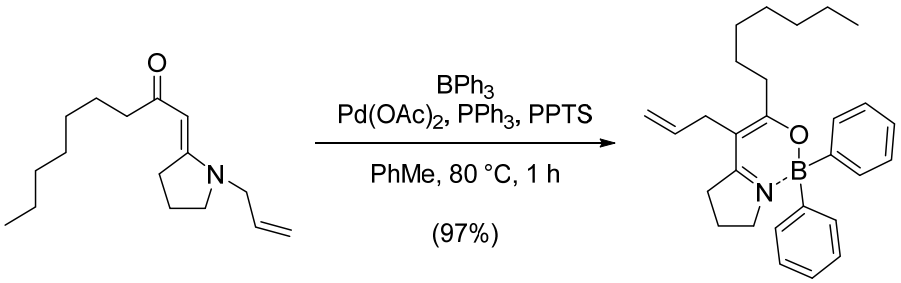


S2f **2o**

Following General Procedure E, oxazaborinine **2o** was prepared from vinylogous amide **S2f** (0.25 mmol). The crude residue was purified by flash-column chromatography on silica gel (20% ethyl acetate in hexanes) to provide oxazaborinine **2o** (100 mg, 96%) as an orange solid.

TLC (20% ethyl acetate in hexanes): R_f = 0.45 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 15.3 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 4H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.26 (m, 4H), 7.24 – 7.20 (m, 2H), 6.90 (d, *J* = 15.3 Hz, 1H), 5.92 – 5.85 (m, 1H), 5.05 – 5.01 (m, 1H), 4.98 – 4.93 (m, 1H), 3.68 (t, *J* = 7.6 Hz, 2H), 3.11 – 3.08 (m, 2H), 2.91 (t, *J* = 8.0 Hz, 2H), and 2.05 (app p, *J* = 7.8 Hz, 2H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 173.6, 166.0, 139.1, 136.7, 136.3, 134.8, 132.8, 131.2, 129.3, 128.8, 128.1, 127.9, 127.1, 126.2, 120.1, 115.6, 102.1, 55.7, 34.2, 31.0, and 20.7.
^{11}B NMR (193 MHz, $CDCl_3$) δ 3.34.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3066 (w), 3044 (w), 3002 (w), 2974 (w), 2930 (w), 2880 (w), 1631 (w), 1594 (m), 1503 (s), 1302 (w), 1188 (w), 743 (w), and 703 (m) cm^{-1}.
HRMS (ESI): calcd for ([M], $C_{29}H_{28}BNO)^+$: 417.2264, found: 417.2273.
mp: 134–140 °C.

4.16 Synthesis of oxazaborinine 2p

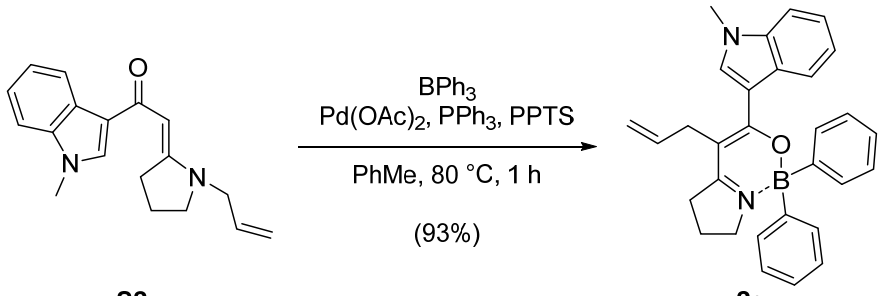


S2p **2p**

Following General Procedure E, oxazaborinine **2p** was prepared from vinylogous amide **S2p** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (10% ethyl acetate in hexanes) to provide oxazaborinine **2p** (80.0 mg, 97%) as a colorless oil.

TLC (10% ethyl acetate in hexanes): R_f = 0.40 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 4H), 7.29 (t, *J* = 7.3 Hz, 4H), 7.25 – 7.22 (m, 2H), 5.87 – 5.80 (m, 1H), 5.04 – 5.00 (m, 1H), 4.99 – 4.94 (m, 1H), 3.57 (t, *J* = 7.6 Hz, 2H), 2.97 – 2.93 (m, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 2.03 (d, *J* = 7.8 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.32 – 1.26 (m, 2H), 1.26 – 1.16 (m, 6H), and 0.90 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 177.3, 173.4, 136.8, 132.7, 127.1, 126.1, 115.0, 99.3, 55.1, 34.0, 33.3, 31.9, 31.4, 29.5, 29.3, 26.7, 22.8, 20.6, and 14.2.
^{11}B NMR (193 MHz, $CDCl_3$) δ 3.35.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3066 (w), 3046 (w), 3002 (w), 2955 (w), 2926 (w), 2855 (w), 1614 (m), 1509 (s), 1430 (w), 1301 (w), 1186 (w), 1145 (w), 874 (w), 740 (m), and 702 (s) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{28}H_{37}BNO)^+$: 414.2968, found: 414.2961.

4.17 Synthesis of oxazaborinine 2q

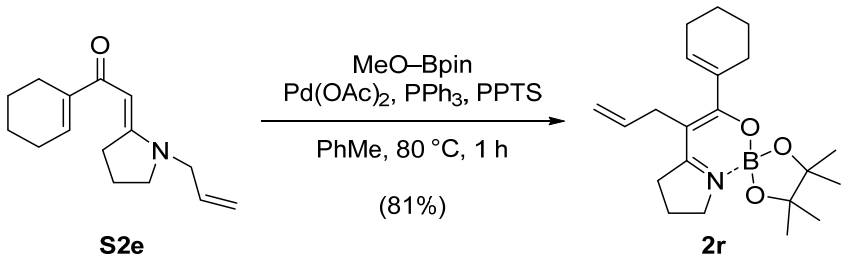


S2g **2q**

Following General Procedure E, oxazaborinine **2q** was prepared from vinylogous amide **S2g** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (10% → 20% ethyl acetate in hexanes) to provide oxazaborinine **2q** (83.0 mg, 93%) as an orange solid.

TLC (20% ethyl acetate in hexanes): R_f = 0.26 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 – 8.26 (m, 1H), 7.59 – 7.56 (m, 4H), 7.44 (s, 1H), 7.36 – 7.31 (m, 4H), 7.29 – 7.24 (m, 4H), 7.17 (ddd, *J* = 8.1, 5.6, 2.5 Hz, 1H), 6.06 – 5.98 (m, 1H), 5.19 – 5.11 (m, 2H), 3.71 (s, 3H), 3.69 – 3.64 (m, 2H), 3.29 – 3.25 (m, 2H), 2.96 (t, *J* = 8.1 Hz, 2H), and 2.10 – 2.04 (m, 2H).
^{13}C NMR (150z MHz, $CDCl_3$) δ 173.5, 168.2, 136.78, 136.77, 133.1, 132.3, 127.6, 127.1, 127.0, 126.0, 123.5, 122.6, 121.3, 115.8, 111.4, 109.2, 97.8, 54.8, 34.2, 33.3, 32.8, and 20.7.
^{11}B NMR (193 MHz, $CDCl_3$) δ 3.81.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3066 (w), 3044 (w), 3000 (w), 2975 (w), 2913 (w), 1599 (w), 1530 (m), 1497 (s), 1466 (s), 1387 (m), 1296 (w), 1192 (w), 744 (m), and 704 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{30}H_{30}BN_2O)^+$: 445.2451, found: 445.2442.
mp: 163–167 °C.

4.18 Synthesis of oxazaborinine 2r

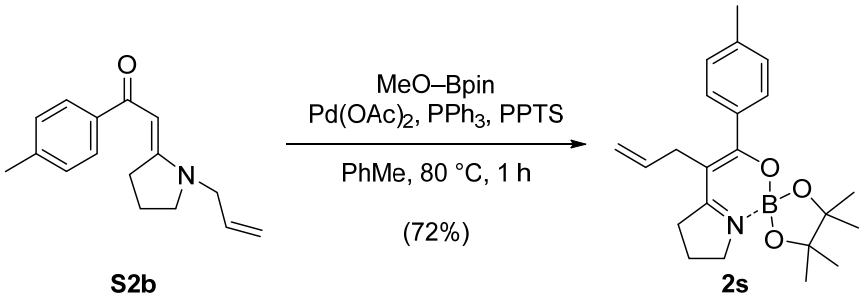


S2e **2r**

Following General Procedure F, oxazaborinine **2r** was prepared from vinylogous amide **S2e** (1.00 mmol). The crude residue was purified by flash-column chromatography on silica gel (60% → 70% ethyl acetate in hexanes) to provide oxazaborinine **2r** (290 mg, 81%) as an off-white solid.

TLC (70% ethyl acetate in hexanes): R_f = 0.27 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.00 – 5.96 (m, 1H), 5.83 – 5.75 (m, 1H), 5.02 – 4.97 (m, 1H), 4.96 – 4.90 (m, 1H), 3.95 (t, *J* = 7.6 Hz, 2H), 2.99 – 2.95 (m, 2H), 2.79 (t, *J* = 8.2 Hz, 2H), 2.25 – 2.19 (m, 2H), 2.10 – 2.05 (m, 2H), 1.97 (app p, *J* = 8.0 Hz, 2H), 1.66 – 1.60 (m, 2H), 1.60 – 1.54 (m, 2H), 1.27 (s, 6H), and 1.18 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.1, 174.6, 137.8, 134.2, 130.7, 115.3, 98.1, 79.8, 53.1, 34.6, 32.4, 26.2, 26.1, 26.0, 25.3, 22.5, 21.8, and 20.4.
^{11}B NMR (193 MHz, $CDCl_3$) δ 5.03.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2967 (m), 2926 (m), 2859 (w), 1603 (m), 1507 (s), 1359 (w), 1297 (w), 1179 (w), 1082 (s), and 1022 (s) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{21}H_{33}BNO_3$)$^+$: 358.2553, found: 358.2560.
mp: 80–92 °C.

4.19 Synthesis of oxazaborinine 2s

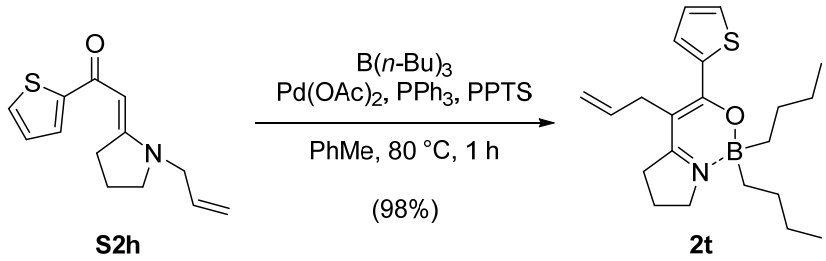


S2b **2s**

Following General Procedure F, oxazaborinine **2s** was prepared from vinylogous amide **S2b** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (50% → 70% ethyl acetate in hexanes) to provide oxazaborinine **2s** (53.0 mg, 72%) as an off-white solid.

TLC (60% ethyl acetate in hexanes): R_f = 0.22 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.95 – 5.87 (m, 1H), 5.14 – 5.10 (m, 1H), 5.09 – 5.04 (m, 1H), 4.03 (t, *J* = 7.6 Hz, 2H), 3.01 – 2.97 (m, 2H), 2.86 (t, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 2.02 (app p, *J* = 7.9 Hz, 2H), 1.31 (s, 6H), and 1.22 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.4, 171.9, 140.1, 137.5, 133.6, 128.61, 128.56, 115.8, 98.7, 80.0, 53.2, 34.7, 32.2, 26.3, 26.2, 21.5, and 20.5.
^{11}B NMR (193 MHz, $CDCl_3$) δ 5.17.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2966 (m), 2925 (w), 1608 (w), 1525 (m), 1496 (s), 1471 (w), 1181 (w), 1086 (s), 1032 (m), 1019 (w), and 835 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{22}H_{31}BNO_3$)$^+$: 368.2397, found: 368.2390.
mp: 140–144 °C.

4.20 Synthesis of oxazaborinine 2t

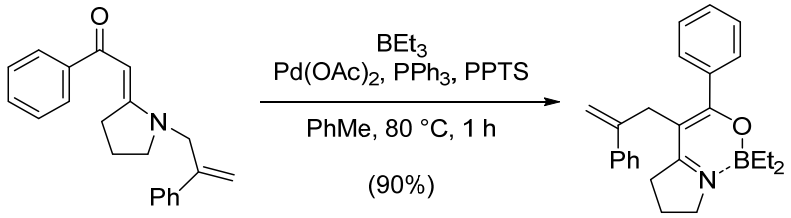


S2h **2t**

Following General Procedure G, oxazaborinine **2t** was prepared from vinylogous amide **S2h** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (4% ethyl acetate in hexanes) to provide oxazaborinine **2t** (70.0 mg, 98%) as a bright yellow solid.

TLC (4% ethyl acetate in hexanes): R_f = 0.42 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.05 – 7.02 (m, 1H), 6.04 – 5.96 (m, 1H), 5.22 – 5.13 (m, 2H), 3.69 – 3.63 (m, 2H), 3.21 – 3.17 (m, 2H), 2.82 – 2.77 (m, 2H), 2.00 (app p, *J* = 7.7 Hz, 2H), 1.37 – 1.24 (m, 6H), 1.24 – 1.13 (m, 2H), 0.94 – 0.83 (m, 6H), and 0.50 – 0.38 (m, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.5, 163.7, 141.1, 136.7, 129.0, 128.9, 127.3, 115.6, 97.1, 53.8, 34.2, 32.2, 28.2, 26.9, 22.5 (br), 20.6, and 14.5.
^{11}B NMR (193 MHz, $CDCl_3$) δ 6.13.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2951 (m), 2906 (m), 2869 (w), 1615 (m), 1527 (m), 1498 (s), 1467 (m), 1425 (w), 1303 (w), 1232 (m), and 710 (w) cm^{-1}.
HRMS (ESI): calcd for ([M], $C_{21}H_{32}BNOS)^+$: 357.2298, found: 357.2304.
mp: 33–38 °C.

4.21 Synthesis of oxazaborinine 2u

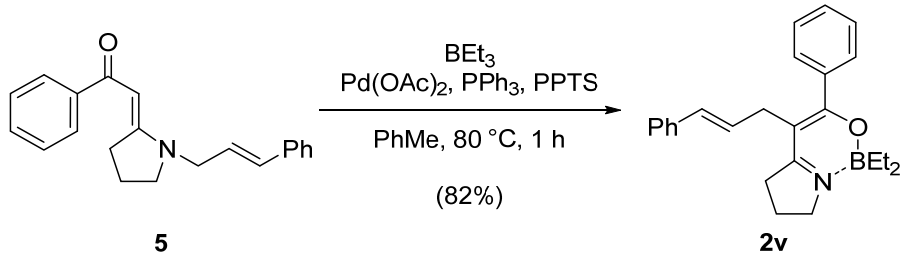


S2u **2u**

Following General Procedure D, oxazaborinine **2u** was prepared from vinylogous amide **S2u** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (7% ethyl acetate in hexanes) to provide oxazaborinine **2u** (69.0 mg, 90%) as a bright yellow oil.

TLC (7% ethyl acetate in hexanes): R_f = 0.50 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.37 – 7.27 (m, 8H), 5.51 (s, 1H), 5.28 (s, 1H), 3.67 (t, *J* = 7.5 Hz, 2H), 3.28 (s, 2H), 2.78 (t, *J* = 7.9 Hz, 2H), 2.00 (app p, *J* = 7.8 Hz, 2H), 0.89 (t, *J* = 7.7 Hz, 6H), and 0.45 (q, *J* = 7.7 Hz, 4H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 174.5, 172.7, 148.1, 141.5, 137.5, 129.5, 128.5, 128.2, 127.9, 127.6, 125.9, 113.2, 97.3, 53.7, 34.3, 34.1, 20.7, 14.2 (br), and 9.5.
^{11}B NMR (193 MHz, $CDCl_3$) δ 6.77.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2927 (m), 2902 (w), 2861 (w), 1620 (m), 1515 (s), 1485 (s), 1453 (m), 1072 (w), and 700 (s) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{25}H_{31}BNO)^+$: 372.2499, found: 372.2494.

4.22 Synthesis of oxazaborinine 2v

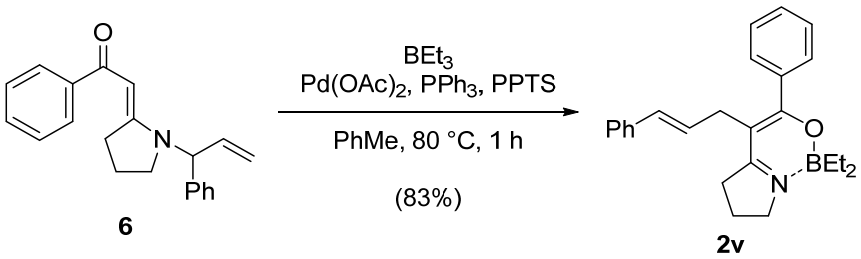


5 **2v**

Following General Procedure D, oxazaborinine **2v** was prepared from vinylogous amide **5** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (7% ethyl acetate in hexanes) to provide oxazaborinine **2v** (60.9 mg, 82%) as an orange oil.

TLC (10% ethyl acetate in hexanes): R_f = 0.60 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.39 – 7.31 (m, 7H), 7.25 – 7.21 (m, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.29 (dt, *J* = 15.9, 5.0 Hz, 1H), 3.66 (t, *J* = 7.5 Hz, 2H), 3.06 (d, *J* = 4.7 Hz, 2H), 2.83 (t, *J* = 7.8 Hz, 2H), 2.00 (app p, *J* = 7.8 Hz, 2H), 0.90 (t, *J* = 7.7 Hz, 6H), and 0.46 (q, *J* = 7.8 Hz, 4H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 174.3, 172.6, 137.5, 130.4, 130.1, 129.4, 128.8, 128.2, 127.8, 127.4, 126.3, 97.7, 53.7, 34.3, 31.6, 20.6, 14.2 (br), and 9.5.
^{11}B NMR (193 MHz, $CDCl_3$) δ 7.01.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2938 (m), 2903 (w), 2869 (w), 1682 (w), 1619 (m), 1518 (s), 1485 (s), 1448 (s), 1346 (w), 1303 (m), and 698 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{25}H_{31}BNO)^+$: 372.2499, found: 372.2497.

Alternatively, the same oxazaborinine **2v** could be obtained starting from (isomeric) vinylogous amide **6** (see main manuscript Scheme 3).

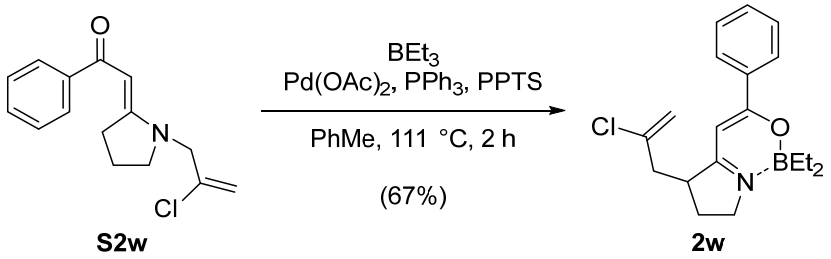


6 **2v**

Following General Procedure D, oxazaborinine **2v** was prepared from vinylogous amide **6** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (7% ethyl acetate in hexanes) to provide oxazaborinine **2v** (61.6 mg, 83%) as an orange oil.

The characterization data for oxazaborinine **2v** were in full agreement with the values reported above.

4.23 Synthesis of oxazaborinine 2w

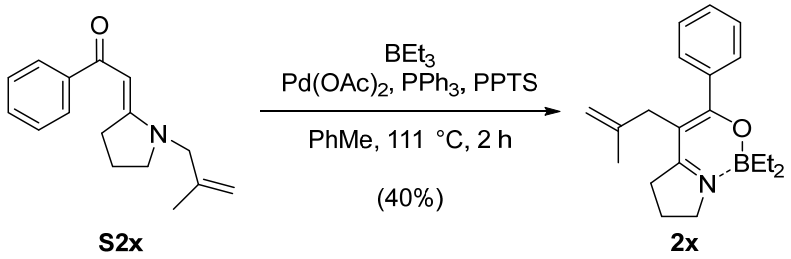


S2w **2w**

Following the slightly modified General Procedure D (reaction conducted at 111 °C instead of 80 °C), oxazaborinine **2w** was prepared from vinylogous amide **S2w** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (2% ethyl acetate in hexanes) to provide oxazaborinine **2w** (44.0 mg, 67%) as a yellow solid.

TLC (2% ethyl acetate in hexanes): R_f = 0.24 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.47 – 7.37 (m, 3H), 5.55 (s, 1H), 5.31 (d, *J* = 1.5 Hz, 1H), 5.28 – 5.26 (m, 1H), 3.65 – 3.53 (m, 2H), 3.37 – 3.30 (m, 1H), 2.82 – 2.76 (m, 1H), 2.39 (dd, *J* = 14.4, 10.0 Hz, 1H), 2.26 – 2.19 (m, 1H), 1.78 – 1.71 (m, 1H), 0.83 (app td, *J* = 7.7, 2.2 Hz, 6H), and 0.51 – 0.39 (m, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.29, 173.27, 139.6, 135.8, 131.1, 128.4, 126.9, 115.0, 85.6, 51.3, 45.0, 41.8, 26.7, 14.1 (br), 9.26, and 9.23.
^{11}B NMR (193 MHz, $CDCl_3$) δ 7.46.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2942 (m), 2902 (w), 2862 (m), 1620 (m), 1530 (s), 1490 (m), 1460 (w), 1315 (w), 889 (w), and 739 (w) cm^{-1}.
HRMS (ESI): calcd for ([M], $C_{19}H_{25}BClNO)^+$: 329.1718, found: 329.1720.
mp: 47–54 °C.

4.24 Synthesis of oxazaborinine 2x

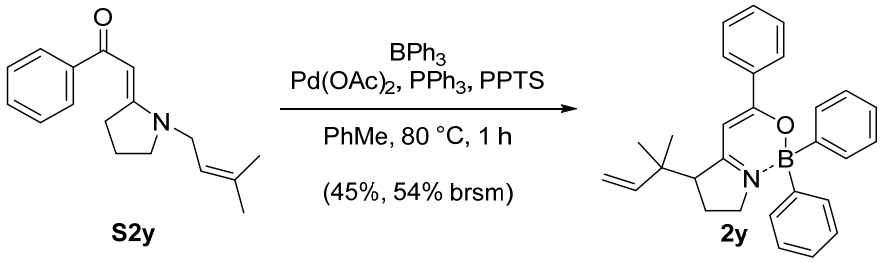


S2x **2x**

Following the slightly modified General Procedure D (reaction conducted at 111 °C instead of 80 °C), oxazaborinine **2x** was prepared from vinylogous amide **S2x** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (100% hexanes) to provide oxazaborinine **2x** (27.0 mg, 40%) as a bright yellow oil.

TLC (2% ethyl acetate in hexanes): R_f = 0.24 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.36 – 7.32 (m, 3H), 4.87 (d, *J* = 10.3 Hz, 2H), 3.65 (t, *J* = 7.6 Hz, 2H), 2.79 – 2.75 (m, 4H), 1.99 (app p, *J* = 7.8 Hz, 2H), 1.70 (s, 3H), 0.87 (t, *J* = 7.8 Hz, 6H), and 0.44 (q, *J* = 7.8 Hz, 4H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 174.5, 172.4, 145.8, 137.6, 129.3, 128.1, 127.7, 110.7, 97.9, 53.6, 36.6, 34.0, 23.1, 20.6, 14.2 (br), and 9.44.
^{11}B NMR (193 MHz, $CDCl_3$) δ 6.91.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2938 (m), 2900 (w), 2861 (m), 1653 (m), 1516 (s), 1485 (s), 1447 (m), 1304 (w), 889 (w), and 708 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{20}H_{29}BNO)^+$: 310.2342, found: 310.2335.

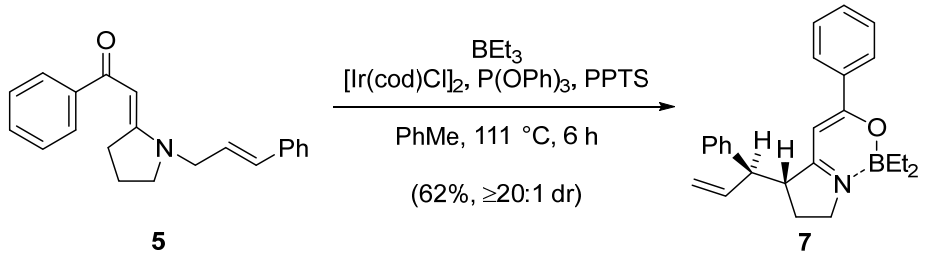
4.25 Synthesis of oxazaborinine 2y



Following General Procedure E, oxazaborinine **2y** was prepared from vinylogous amide **S2y** (0.20 mmol). The crude residue was purified by flash-column chromatography on silica gel (3% ethyl acetate in hexanes) to provide oxazaborinine **2y** (38.0 mg, 45%, 54% based on recovered starting material) as a yellow solid. Recrystallization (ethyl acetate/hexanes) of the product gave crystals suitable for X-ray diffraction (see Section 7).

TLC (15% ethyl acetate in hexanes): R_f = 0.54 (UV/$KMnO_4$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.50 – 7.39 (m, 7H), 7.32 – 7.27 (m, 4H), 7.27 – 7.22 (m, 2H), 6.12 (s, 1H), 5.94 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.18 – 5.10 (m, 2H), 3.58 – 3.47 (m, 2H), 3.11 – 3.06 (m, 1H), 2.21 – 2.12 (m, 1H), 2.04 – 1.96 (m, 1H), 1.19 (s, 3H), and 1.15 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.3, 170.5, 146.5, 135.2, 132.8, 131.3, 128.5, 127.23, 127.18, 127.1, 126.3, 126.2, 112.9, 90.7, 57.1, 53.5, 40.5, 26.5, 24.5, and 23.5.
^{11}B NMR (193 MHz, $CDCl_3$) δ 4.25.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3067 (w), 3043 (w), 3002 (w), 2966 (w), 2933 (w), 2877 (w), 1611 (w), 1527 (s), 1489 (m), 1187 (w), 738 (w), and 703 (w) cm^{-1}.
HRMS (ESI): calcd for ([M], $C_{29}H_{30}BNO)^+$: 420.2499, found: 420.2493.
mp: 132–138 °C.

4.26 Synthesis of oxazaborinine 7 and X-ray derivative S18



5 **7**

An oven-dried vial was charged with a magnetic stirring bar, vinylogous amide **5** (60.6 mg, 0.20 mmol, 1 equiv), pyridinium *p*-toluenesulfonate (5.0 mg, 0.02 mmol, 10 mol%) and bis(1,5-cyclooctadiene)diiridium(I) dichloride (5.4 mg, 0.008 mmol, 4 mol%). The vial was flushed with nitrogen and sealed with a septum cap. Toluene (1.00 mL), triphenylphosphite (9.9 mg, 0.03 mmol, 16 mol%) and a solution of triethylborane (1 M in THF, 0.30 mL, 0.30 mmol, 1.5 equiv) were added sequentially and the vial was placed in a preheated (111 °C) heating block. After 6 h, the mixture was cooled to 23 °C, concentrated in vacuo and the crude residue was purified by flash-column chromatography on silica gel (2% ethyl acetate in hexanes) to provide oxazaborinine **7** (46.0 mg, 62%, ≥20:1 dr) as a yellow solid.

Data for 7

TLC (10% ethyl acetate in hexanes): R_f = 0.61 (UV/$KMnO_4$).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.41 – 7.32 (m, 5H), 7.31 – 7.27 (m, 3H), 6.02 (ddd, *J* = 16.9, 10.3, 8.2 Hz, 1H), 5.22 – 5.19 (m, 1H), 5.17 – 5.12 (m, 1H), 5.06 (s, 1H), 3.59 (t, *J* = 7.8 Hz, 1H), 3.54 – 3.50 (m, 2H), 3.41 – 3.36 (m, 1H), 2.18 – 2.11 (m, 1H), 2.05 – 1.98 (m, 1H), 0.83 (t, *J* = 7.7 Hz, 3H), 0.80 (t, *J* = 7.7 Hz, 3H), and 0.48 – 0.38 (m, 4H).

^{13}C NMR (175 MHz, $CDCl_3$) δ 172.9, 171.9, 141.7, 137.7, 136.0, 130.8, 129.0, 128.3, 128.2, 127.1, 126.8, 117.9, 87.3, 52.3, 51.9, 51.5, 25.4, 13.9, 9.34, and 9.24.

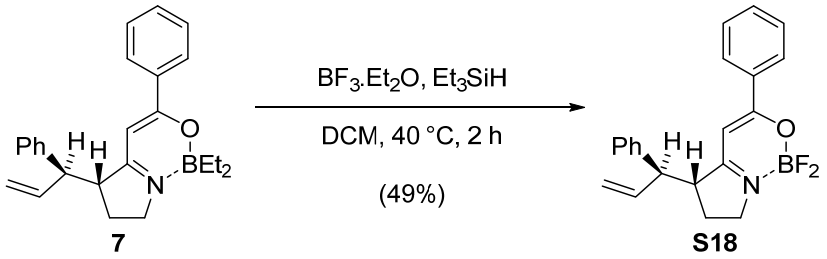
^{11}B NMR (193 MHz, $CDCl_3$) δ 7.29.

IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2941 (m), 2902 (w), 2864 (m), 1616 (w), 1531 (s), 1490 (m), 1460 (w), 1303 (w), 1092 (w), 921 (w), and 700 (w) cm^{-1}.

HRMS (ESI): calcd for ([M+H], $C_{25}H_{31}BNO)^+$: 372.2499, found: 372.2514.

mp: 42–50 °C.

In order to determine the relative stereochemistry of oxazaborinine **7**, it was converted to the corresponding difluoro oxazaborinine **S18**. The structure of **S18** could then be unambiguously confirmed by single-crystal X-ray analysis (see Section 7).



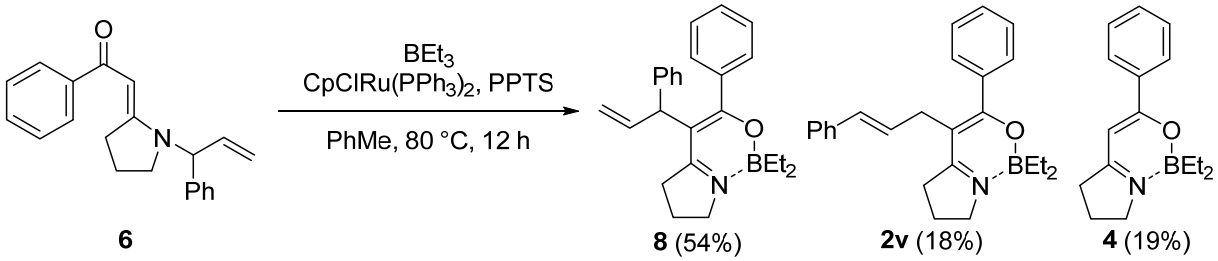
7 **S18**

A solution of oxazaborinine **7** (65.0 mg, 0.18 mmol, 1 equiv) in dichloromethane (2 mL) was treated with triethylsilane (30.7 μL, 0.19 mmol, 1.10 equiv) and boron trifluoride diethyl etherate (64.8 μL, 0.53 mmol, 3.00 equiv) at 23 °C and the resulting mixture was warmed to 40 °C. After 2 h, the mixture was cooled to 23 °C and concentrated in vacuo. The residue was purified by flash-column chromatography on silica gel

(15% → 25% ethyl acetate in hexanes) to provide difluoro oxazaborinine **S18** (30.0 mg, 49%) as an off-white solid.
Recrystallization (ethyl acetate/hexanes) of the product gave crystals suitable for X-ray diffraction (see Section 7).

Data for S18
TLC (30% ethyl acetate in hexanes): R_f = 0.48 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.47 – 7.43 (m, 1H), 7.42 – 7.31 (m, 5H), 7.28 – 7.25 (m, 2H), 6.02 (ddd, *J* = 17.4, 10.2, 7.7 Hz, 1H), 5.42 (s, 1H), 5.22 (d, *J* = 10.2 Hz, 1H), 5.16 (d, *J* = 17.0 Hz, 1H), 3.93 – 3.88 (m, 2H), 3.59 – 3.53 (m, 2H), 2.36 – 2.29 (m, 1H), and 2.18 – 2.12 (m, 1H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 176.4, 170.5, 141.0, 137.7, 133.5, 132.0, 129.2, 128.6, 128.2, 127.5, 127.3, 118.0, 90.0, 52.4, 52.3, 50.0, and 26.1.
^{11}B NMR (193 MHz, $CDCl_3$) δ 0.91 (t, *J* = 15.7 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -136.21 – -136.48 (m).
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3067 (w), 2959 (w), 2924 (m), 2853 (w), 1616 (w), 1538 (s), 1493 (m), 1454 (w), 1362 (w), 1302 (w), 1091 (m), 1056 (m), 991 (w), 766 (m), and 700 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{21}H_{21}BF_2NO)^+$: 352.1684, found: 352.1690.
mp: 153–157 °C.

4.27 Synthesis of oxazaborinine 8



An oven-dried vial was charged with a magnetic stirring bar, vinylogous amide **6** (68.0 mg, 0.22 mmol, 1 equiv), pyridinium *p*-toluenesulfonate (5.6 mg, 0.02 mmol, 10 mol%) and chlorocyclopentadienyl-bis(triphenylphosphine)ruthenium(II) (8.1 mg, 0.01 mmol, 5 mol%). The vial was flushed with nitrogen and sealed with a septum cap. Toluene (1.20 mL) and a solution of triethylborane (1 M in THF, 0.33 mL, 0.33 mmol, 1.5 equiv) were added sequentially and the vial was placed in a preheated (80 °C) heating block. After 12 h, the mixture was cooled to 23 °C and concentrated in vacuo. Analysis of the crude reaction mixture by ^{1}H-NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard indicated the formation of three products: oxazaborinie **8** (54%), oxazaborinine **2v** (18%) and de-allyl derivative **4** (19%). An analytically pure sample of **8** was obtained by purification of the product mixture by flash chromatography on silica gel (2% ethyl acetate in hexanes), to provide oxazaborinine **8** as a bright yellow oil.

Data for oxazaborinine 8

TLC (2% ethyl acetate in hexanes): R_f = 0.30 (UV/$KMnO_4$).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.40 – 7.36 (m, 3H), 7.34 – 7.27 (m, 4H), 7.24 – 7.20 (m, 1H), 6.36 (ddd, *J* = 16.6, 10.2, 5.7 Hz, 1H), 5.41 – 5.37 (m, 1H), 5.25 – 5.21 (m, 1H), 4.58 (d, *J* = 5.7 Hz, 1H), 3.61 – 3.48 (m, 2H), 2.60 – 2.54 (m, 1H), 1.96 – 1.89 (m, 1H), 1.88 – 1.73 (m, 2H), 0.96 (t, *J* = 7.7 Hz, 3H), 0.91 (t, *J* = 7.7 Hz, 3H), and 0.52 – 0.46 (m, 4H).

^{13}C NMR (175 MHz, $CDCl_3$) δ 174.2, 173.5, 143.4, 138.8, 137.9, 129.4, 128.5, 128.3, 127.64, 127.61, 126.2, 117.2, 102.2, 52.9, 46.5, 35.6, 21.1, 14.1 (br), 9.44, and 9.36.

^{11}B NMR (193 MHz, $CDCl_3$) δ 6.84.

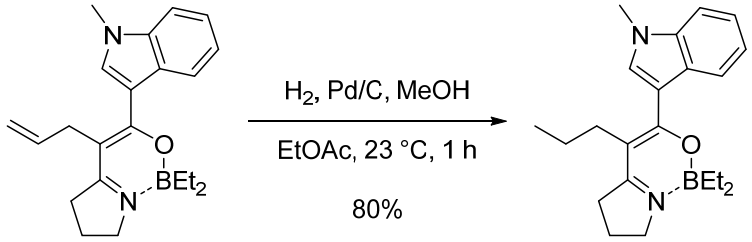
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2940 (m), 2903 (w), 2862 (m), 1612 (m), 1510 (s), 1482 (s), 1453 (m), 1303 (w), 919 (w), and 700 (w) cm^{-1}.

HRMS (ESI): calcd for ([M+H], $C_{25}H_{31}BNO)^{+}$: 372.2499, found: 372.2497.

The characterization data for oxazaborinine **2v** and de-allyl derivative **4** were in full agreement with the values reported above.

5 Oxazaborinine Derivatization

5.1 Synthesis of oxazaborinine 9

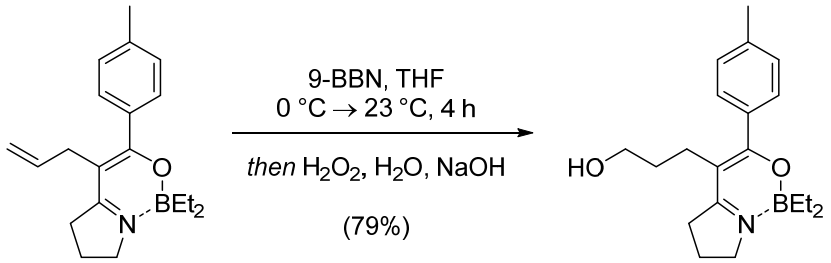


2g **9**

To a solution of oxazaborinine **9** (15 mg, 0.04 mmol, 1 equiv) in methanol–ethyl acetate (2:1 v/v, 1.50 mL) was added palladium on carbon (5 wt.%, tip of a spatula) at 23 °C. An atmosphere of hydrogen was maintained by sparging with a stream of pure hydrogen gas through a stainless steel needle for 5 min, and vigorous stirring of the suspension was then continued under hydrogen atmosphere at 23 °C. After 2 h, the mixture was diluted with ethyl acetate (3 mL) and filtered through a short pad of silica gel. The filtrate was concentrated and the residue was purified by flash-column chromatography on silica gel (15% ethyl acetate in hexanes) to provide oxazaborinine **9** (12.0 mg, 80%) as a yellow solid.

TLC (15% ethyl acetate in hexanes): R_f = 0.43 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.27 – 7.24 (m, 1H), 7.21 – 7.17 (m, 1H), 3.81 (s, 3H), 3.65 (t, *J* = 7.5 Hz, 2H), 2.85 (t, *J* = 7.9 Hz, 2H), 2.36 – 2.32 (m, 2H), 2.03 (app p, *J* = 7.7 Hz, 2H), 1.49 – 1.42 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 7.7 Hz, 6H), and 0.54 – 0.41 (m, 4H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 172.9, 167.6, 136.8, 130.7, 127.8, 123.1, 122.4, 120.8, 112.6, 109.2, 100.9, 53.3, 34.2, 33.4, 30.7, 24.5, 20.9, 13.96, 13.86 (br) and 9.8.
^{11}B NMR (193 MHz, $CDCl_3$) δ 5.83.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2935 (m), 2900 (w), 2863 (m), 1603 (w), 1533 (m), 1496 (s), 1466 (s), 1385 (m), 1301 (m), 1086 (w), and 744 (m) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{22}H_{32}BN_2O)^+$: 351.2608, found: 351.2606.
mp: 78–85 °C.

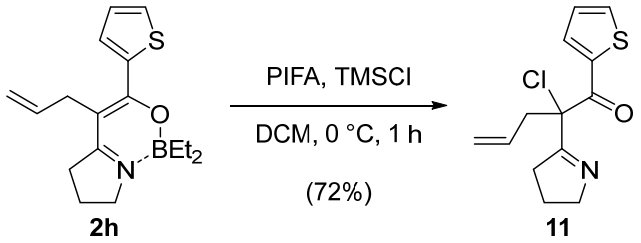
5.2 Synthesis of alcohol 10



A solution of oxazaborinine **2b** (58.0 mg, 0.20 mmol, 1 equiv) in tetrahydrofuran (0.5 mL) was treated with 9-borabicyclo[3.3.1]nonane solution (0.50 M in THF, 0.90 mL, 0.45 mmol, 2.20 equiv) at 0 °C and the resulting mixture was gradually warmed to 23 °C. After 4 h, the mixture was treated with water (35.0 μL, 1.90 mmol, 10.0 equiv), sodium hydroxide solution (3.00 M in H_2O, 0.20 mL), and hydrogen peroxide solution (50.0 wt. % in H_2O, 60.0 μL). After 5 min, the mixture was diluted with saturated aqueous sodium bicarbonate solution (5 mL) and ethyl acetate (5 mL). The layers were separated, the aqueous layer was extracted with dichloromethane (3 x 5 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (20 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (50% ethyl acetate in hexanes) to provide alcohol **10** (48.0 mg, 79%) as a yellow oil.

TLC (25% ethyl acetate in hexanes): R_f = 0.17 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 3.66 (t, *J* = 7.6 Hz, 2H), 3.48 (t, *J* = 6.3 Hz, 2H), 2.86 (t, *J* = 7.9 Hz, 2H), 2.36 (s, 3H), 2.26 (t, *J* = 7.6 Hz, 2H), 2.04 (app p, *J* = 7.8 Hz, 2H), 1.52 (app p, *J* = 6.7 Hz, 2H), 0.83 (t, *J* = 7.8 Hz, 6H), and 0.41 (q, *J* = 7.7 Hz, 4H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 173.7, 172.1, 139.2, 134.9, 129.0, 128.0, 100.5, 61.8, 53.6, 34.3, 34.2, 23.9, 21.5, 20.8, 13.7 (br), and 9.5.
^{11}B NMR (193 MHz, $CDCl_3$) δ 6.46.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3386 (br), 2939 (m), 2901 (w), 2862 (m), 1611 (m), 1525 (m), 1491 (s), 1453 (m), 1303 (w), and 1055 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{20}H_{31}BNO_2$)$^+$: 328.2448, found: 328.2445.

5.3 Synthesis of imine 11

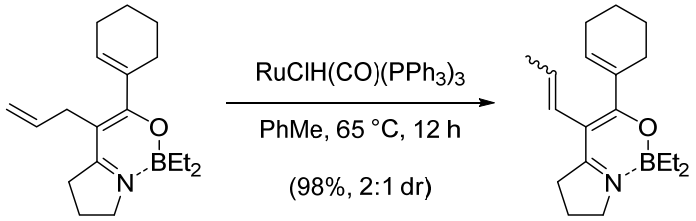


2h **11**

A solution of oxazaborinine **2h** (26.0 mg, 0.08 mmol, 1 equiv) in dichloromethane (1.20 mL) was treated with chlorotrimethylsilane (30.0 μL, 0.24 mmol, 3.00 equiv) and [bis(trifluoroacetoxy)iodo]benzene (48.0 mg, 0.11 mmol, 1.30 equiv) at 0 °C. After 1 h, the mixture was diluted with saturated aqueous sodium bicarbonate solution (5 mL) and ethyl acetate (5 mL). The layers were separated, the aqueous layer was extracted with ethyl acetate (3 x 5 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (10 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (25% ethyl acetate in hexanes) to provide imine **11** (16.0 mg, 72%) as a colorless oil.

TLC (30% ethyl acetate in hexanes): R_f = 0.30 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.82 (d, *J* = 3.9 Hz, 1H), 7.63 (d, *J* = 5.0 Hz, 1H), 7.07 (app t, *J* = 4.4 Hz, 1H), 5.91 – 5.83 (m, 1H), 5.16 – 5.08 (m, 2H), 4.00 – 3.89 (m, 2H), 3.22 – 3.17 (m, 1H), 3.15 – 3.10 (m, 1H), 2.66 – 2.60 (m, 2H), and 1.99 – 1.86 (m, 2H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 185.4, 175.2, 140.1, 134.7, 134.6, 131.7, 128.1, 119.8, 74.8, 61.5, 43.5, 35.8, and 23.3.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3080 (w), 2954 (w), 2920 (w), 2865 (w), 1666 (s), 1640 (w), 1410 (s), 1353 (w), 1244 (m), 924 (w), and 724 (m) cm^{-1}.
HRMS (ESI): calcd for ([M], $C_{13}H_{14}ClNOS)^+$: 268.0563, found: 268.0555.

5.4 Synthesis of isomerized product 12

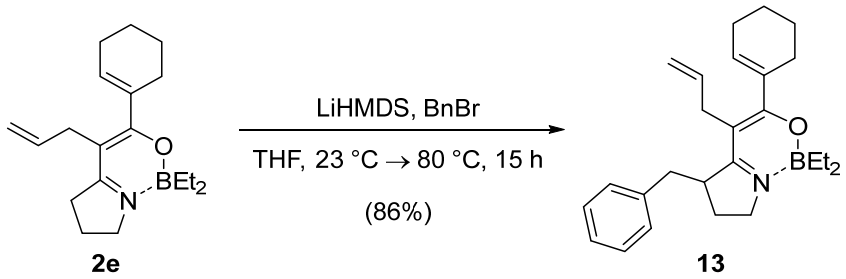


2e **12**

A mixture of oxazaborinine **2e** (60.0 mg, 0.20 mmol, 1 equiv) and $RuClH(CO)(PPh_3)_3$ (10.0 mg, 0.01 mmol, 5 mol%) in toluene (1.30 mL) was heated to 65 °C. After 12 h, the mixture was concentrated in vacuo and the residue was purified by flash-column chromatography on silica gel (4% ethyl acetate in hexanes) to provide isomerized oxazaborinine **12** (59.0 mg, 98%, 2:1 dr) as a yellow oil.

TLC (3% ethyl acetate in hexanes): R_f = 0.47 (UV/$KMnO_4$).
In cases where the proton or carbon atoms show a double set of signals, the signal of the second diastereomer is marked with an asterisk.
^{1}H NMR (700 MHz, $CDCl_3$) δ 6.14 – 6.11* (m, 1H), 6.01 – 5.98 (m, 1H), 5.97 – 5.92 (m, 1H), 5.52 – 5.46* (m, 1H), 5.39 – 5.33 (m, 1H), 3.62 – 3.56 (m, 2H), 2.85 (t, *J* = 7.9 Hz, 2H), 2.65* (t, *J* = 7.8 Hz, 2H), 2.22 – 2.07 (m, 4H), 1.99 – 1.92 (m, 2H), 1.74 – 1.71 (m, 3H), 1.69 – 1.56 (m, 4H), 1.55 – 1.52* (m, 3H), 0.80* (t, *J* = 7.8 Hz, 6H), 0.76 (t, *J* = 7.8 Hz, 6H), and 0.42 – 0.30 (m, 4H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 175.0, 173.6*, 172.9*, 172.6, 135.9, 132.5*, 131.8, 127.2*, 126.3, 125.4*, 123.6, 101.1, 98.0*, 85.9*, 53.3*, 53.2, 35.7, 34.7*, 26.1, 25.6*, 25.4, 22.7*, 22.5, 22.0, 20.8, 20.7*, 18.9, 15.0*, 13.6 (br), 9.4*, and 9.3.
^{11}B NMR (193 MHz, $CDCl_3$) δ 5.95.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2932 (s), 2862 (m), 1601 (s), 1528 (w), 1483 (s), 1451 (s), 1306 (m), 1272 (w), 1081 (w), and 866 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{19}H_{31}BNO)^+$: 300.2499, found: 300.2498.

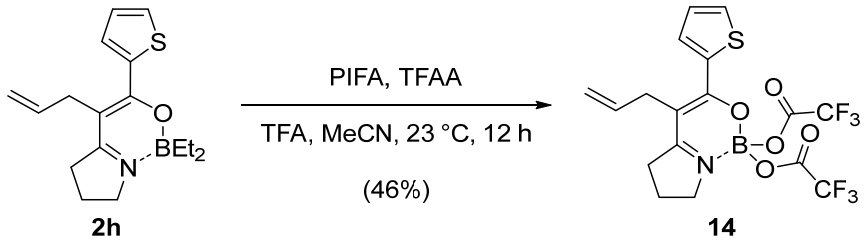
5.5 Synthesis of γ–alkylated oxazaborinine 13



A solution of oxazaborinine **2e** (15.0 mg, 0.05 mmol, 1 equiv) and benzyl bromide (13.0 mg, 0.08 mmol, 1.50 equiv) in tetrahydrofuran (0.50 mL) was treated with lithium bis(trimethylsilyl)amide solution (1.00 M in THF, 0.10 mL, 0.10 mmol, 2.00 equiv) at 23 °C. The resulting mixture was then heated to 80 °C. After 15 h, the mixture was diluted with saturated aqueous sodium bicarbonate solution (3 mL) and diethyl ether (5 mL). The layers were separated, the aqueous layer was extracted with diethyl ether (3 x 5 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (10 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (2.5% ethyl acetate in hexanes) to provide the γ–alkylated oxazaborinine **13** (17.0 mg, 86%) as a yellow oil.

TLC (2.5% ethyl acetate in hexanes): R_f = 0.26 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.29 – 7.23 (m, 1H), 7.19 – 7.16 (m, 2H), 5.93 – 5.86 (m, 1H), 5.85 – 5.82 (m, 1H), 5.09 (app dq, *J* = 17.1, 1.9 Hz, 1H), 5.04 (app dq, *J* = 10.2, 1.8 Hz, 1H), 3.51 – 3.38 (m, 2H), 3.31 – 3.26 (m, 1H), 3.19 – 3.12 (m, 1H), 2.97 (dd, *J* = 14.0, 3.9 Hz, 1H), 2.91 (app ddt, *J* = 17.6, 5.8, 1.8 Hz, 1H), 2.53 (dd, *J* = 14.1, 10.3 Hz, 1H), 2.26 – 2.14 (m, 2H), 2.13 – 2.06 (m, 2H), 1.93 – 1.85 (m, 1H), 1.82 – 1.77 (m, 1H), 1.70 – 1.65 (m, 2H), 1.64 – 1.58 (m, 2H), 0.83 – 0.75 (m, 6H), and 0.42 – 0.29 (m, 4H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 177.1, 175.9, 139.2, 139.0, 135.4, 129.0, 128.8, 127.7, 126.8, 114.8, 96.1, 51.1, 47.7, 36.9, 31.7, 26.44, 26.36, 25.0, 22.4, 21.9, 13.8 (br) and 9.41.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2934 (m), 2905 (w), 2900 (w), 2880 (w), 2860 (w), 1607 (m), 1495 (s), 1454 (m), 1308 (w), 910 (w), and 700 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{26}H_{37}BNO)^+$: 390.2968, found: 390.2972.

5.6 Synthesis of bis-trifluoroacetate oxazaborinine 14

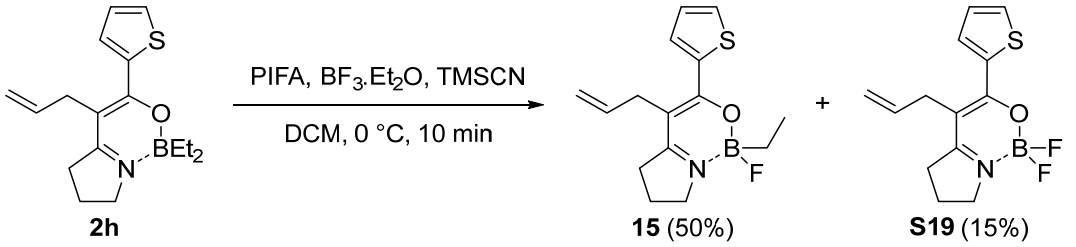


2h **14**

A mixture of [bis(trifluoroacetoxy)iodo]benzene (74.0 mg, 0.17 mmol, 1.30 equiv) in acetonitrile–trifluoroacetic acid (1:1 v/v, 1.00 mL) was treated with trifluoroacetic anhydride (28.0 μL, 0.20 mmol, 1.50 equiv) at 23 °C. After 15 min, the mixture was cooled to 0 °C, and oxazaborinine **2h** (40.0 mg, 0.13 mmol, 1 equiv) was added. The resulting mixture was then slowly warmed to 23 °C. After 12 h, the mixture was diluted with saturated aqueous sodium bicarbonate solution (5 mL) and ethyl acetate (5 mL). The layers were separated, the aqueous layer was extracted with ethyl acetate (3 x 5 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (10 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (25% ethyl acetate in hexanes) to provide bis-trifluoroacetate oxazaborinine **14** (28.0 mg, 46%) as a yellow solid.

TLC (30% ethyl acetate in hexanes): R_f = 0.33 (UV/$KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.66 (d, *J* = 3.9 Hz, 1H), 7.60 (d, *J* = 5.0 Hz, 1H), 7.10 (app t, *J* = 4.5 Hz, 1H), 6.09 – 6.02 (m, 1H), 5.32 (d, *J* = 17.2 Hz, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 3.84 (t, *J* = 7.7 Hz, 2H), 3.42 – 3.37 (m, 2H), 3.05 (t, *J* = 8.0 Hz, 2H), and 2.18 (app p, *J* = 7.8 Hz, 2H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 180.6, 163.4, 157.5 (q, *J* = 41.4 Hz), 136.4, 133.9, 132.6, 132.4, 128.2, 117.1, 114.9 (q, *J* = 286 Hz), 101.3, 52.5, 34.4, 32.1, 20.6.
^{11}B NMR (193 MHz, $CDCl_3$) δ 1.71.
^{19}F NMR (376 MHz, $CDCl_3$) δ -75.37.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3013 (w), 2978 (w), 2923 (w), 1776 (m), 1759 (m), 1526 (m), 1509 (s), 1391 (w), 1214 (m), 1156 (s), 1005 (w), 966 (w), and 724 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+Na], $C_{17}H_{14}BF_6NNaO_5S)^+$: 492.0488, found: 492.0490.
mp: 104–111 °C.

5.7 Synthesis of fluoro oxazaborinines 15 and S19



A solution of [bis(trifluoroacetoxy)iodo]benzene (114 mg, 0.27 mmol, 2.00 equiv) in dichloromethane (1 mL) was treated with boron trifluoride diethyl etherate (66.0 μL, 0.53 mmol, 4.00 equiv) and trimethylsilyl cyanide (50.0 μL, 0.40 mmol, 3.00 equiv) at 23 °C. After 30 min, the mixture was cooled to 0 °C, and a solution of oxazaborinine **2h** (35.0 mg, 0.12 mmol, 1 equiv) in dichloromethane (2.70 mL) was added. After 10 min, the mixture was diluted with saturated aqueous sodium bicarbonate solution (5 mL) and diethyl ether (5 mL). The layers were separated, the aqueous layer was extracted with diethyl ether (3 x 5 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (10 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (25% ethyl acetate in hexanes) to provide, in order of elution, fluoro oxazaborinine **15** (17.0 mg, 50%) as a yellow oil, and difluoro oxazaborinine **S19** (5.00 mg, 15%) as a white solid.

Data for fluoro oxazaborinine 15

TLC (30% ethyl acetate in hexanes): R_f = 0.38 (UV/$KMnO_4$).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.55 (d, *J* = 3.8 Hz, 1H), 7.50 (d, *J* = 5.0 Hz, 1H), 7.07 (app t, *J* = 4.4 Hz, 1H), 6.03 – 5.97 (m, 1H), 5.18 – 5.10 (m, 2H), 4.05 – 3.98 (m, 1H), 3.88 – 3.81 (m, 1H), 3.33 – 3.23 (m, 2H), 2.98 – 2.88 (m, 2H), 2.17 – 2.04 (m, 2H), 0.86 (t, *J* = 7.8 Hz, 3H), 0.64 – 0.56 (m, 1H), and 0.55 – 0.45 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 175.3, 162.8, 139.5, 135.7, 130.3, 130.2, 127.6, 116.2, 98.8, 53.3, 34.4, 32.3, 20.6, 8.41, 8.37.

^{11}B NMR (193 MHz, $CDCl_3$) δ 5.70 (br).

^{19}F NMR (376 MHz, $CDCl_3$) δ -145.27 (br s).

IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2977 (w), 2947 (w), 2909 (w), 2871 (w), 1612 (w), 1527 (m), 1503 (s), 1420 (w), 1302 (w), and 1048 (w) cm^{-1}.

HRMS (ESI): calcd for ([M+Na], $C_{15}H_{19}BFNNaOS)^+$: 314.1162, found: 314.1161.

Data for difluoro oxazaborinine S19

TLC (30% ethyl acetate in hexanes): R_f = 0.23 (UV/$KMnO_4$).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.62 (d, *J* = 3.9 Hz, 1H), 7.56 (d, *J* = 5.0 Hz, 1H), 7.09 (app t, *J* = 4.5 Hz, 1H), 6.03 – 5.96 (m, 1H), 5.21 – 5.16 (m, 1H), 5.15 – 5.09 (m, 1H), 4.05 (t, *J* = 7.7 Hz, 2H), 3.34 – 3.30 (m, 2H), 2.98 (t, *J* = 8.1 Hz, 2H), 2.17 (app p, *J* = 7.8 Hz, 2H).

^{13}C NMR (175 MHz, $CDCl_3$) δ 177.9, 162.9, 138.0, 135.0, 131.3, 131.2, 127.8, 116.6, 99.6, 52.4, 34.5, 32.1, 20.6.

^{11}B NMR (193 MHz, $CDCl_3$) δ 0.38 (app t, *J* = 15.4 Hz).

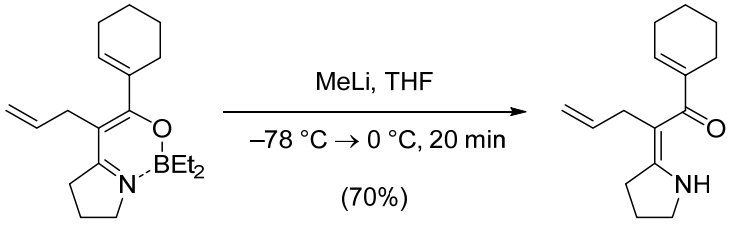
^{19}F NMR (376 MHz, $CDCl_3$) δ -137.76 (app dd, *J* = 30.9, 15.1 Hz).

IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2954 (w), 2930 (w), 2876 (w), 1609 (w), 1525 (m), 1507 (s), 1418 (w), 1239 (w), 1099 (w), 1049 (w), and 737 (w) cm^{-1}.

HRMS (ESI): calcd for ([M+Na], $C_{13}H_{14}BF_2NNaOS)^+$: 304.0755, found: 304.0753.

mp: 155–163 °C.

5.8 Synthesis of vinylogous amide 16

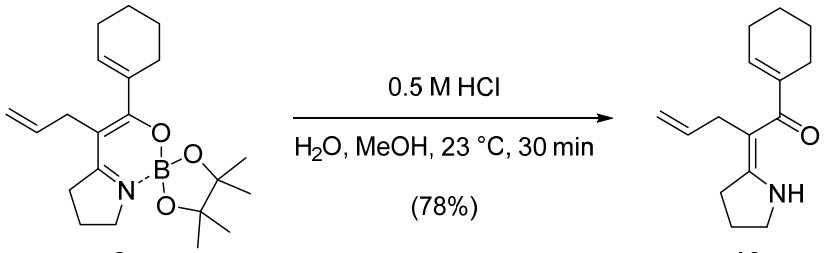


2e **16**

A solution of oxazaborinine **2e** (40.0 mg, 0.13 mmol, 1 equiv) in tetrahydrofuran (1 mL) was treated with methyllithium solution (1.60 M in Et_2O, 0.33 mL, 0.53 mmol, 4.00 equiv) at –78 °C. The mixture was slowly warmed to 0 °C, and after 20 min, was diluted with saturated aqueous sodium bicarbonate solution (3 mL) and dichloromethane (3 mL). The layers were separated, the aqueous layer was extracted with dichloromethane (3 x 5 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (10 mL). The organic phase was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (50% ethyl acetate in hexanes) to provide vinylogous amide **16** (17.0 mg, 70%) as an off-white solid.

TLC (60% ethyl acetate in hexanes): R_f = 0.43 ($KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 10.80 (br s, 1H), 5.83 – 5.76 (m, 1H), 5.70 – 5.65 (m, 1H), 4.96 – 4.91 (m, 2H), 3.60 (t, *J* = 7.2 Hz, 2H), 3.02 – 2.98 (m, 2H), 2.66 (t, *J* = 7.9 Hz, 2H), 2.20 – 2.16 (m, 2H), 2.08 – 2.03 (m, 2H), 1.98 (app p, *J* = 7.5 Hz, 2H), and 1.69 – 1.56 (m, 4H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 196.8, 169.8, 140.2, 139.3, 124.4, 113.8, 96.9, 47.9, 33.9, 31.6, 26.2, 24.8, 22.6, 22.1, and 21.4.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 3249 (br), 2925 (m), 2856 (w), 2834 (w), 1593 (s), 1510 (s), 1479 (m), 1424 (w), 1282 (m), 1214 (m), 915 (w), and 700 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{15}H_{22}NO)^+$: 232.1701, found: 232.1698.
mp: 37–42 °C.

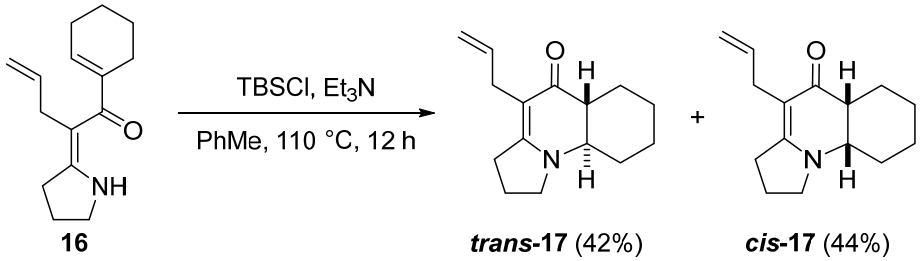
Alternatively, the same vinylogous amide **16** could be obtained via hydrolysis of pinacol derivative **2r**.



2r **16**

A solution of oxazaborinine **2r** (15.0 mg, 0.04 mmol, 1 equiv) in methanol (0.5 mL) was treated with hydrochloric acid solution (1 M in H_2O, 0.5 mL) at 23 °C. After 30 min, the mixture was diluted with saturated aqueous sodium bicarbonate solution (3 mL) and ethyl acetate (3 mL). The layers were separated, the aqueous layer was extracted with ethyl acetate (4 x 3 mL) and the combined organic extracts were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue was purified by flash-column chromatography on silica gel (50% ethyl acetate in hexanes) to provide vinylogous amide **16** (7.6 mg, 78%) as an off-white solid.
The characterization data for vinylogous amide **16** were in full agreement with the values reported above.

5.9 Synthesis of tricycles *trans*-17 and *cis*-17



16 ***trans*-17** (42%) ***cis*-17** (44%)

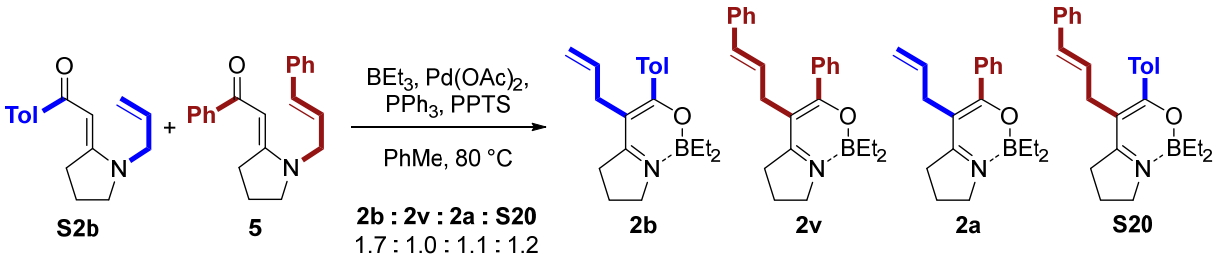
A mixture of vinylogous amide **16** (50.0 mg, 0.22 mmol, 1 equiv), *tert*-butyldimethylsilyl chloride (49.0 mg, 0.33 mmol, 1.50 equiv), and triethylamine (75.0 μL, 0.54 mmol, 2.50 equiv) in toluene (1.20 mL) was heated to 110 °C. After 12 h, the mixture was concentrated in vacuo and the residue was purified by flash-column chromatography on silica gel (50% → 60% ethyl acetate in hexanes) to provide, in order of elution, *trans*-tricycle ***trans*-17** (21.0 mg, 42%) as a white solid, and *cis*-tricycle ***cis*-17** (22.0 mg, 44%) as a colorless oil.

Data for *trans*-tricycle ***trans*-17**
TLC (60% ethyl acetate in hexanes): R_f = 0.58 ($KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 5.81 – 5.73 (m, 1H), 4.92 (app dq, *J* = 17.0, 1.8 Hz, 1H), 4.86 (app dq, *J* = 9.9, 1.7 Hz, 1H), 3.59 (app td, *J* = 8.7, 1.5 Hz, 1H), 3.02 – 2.95 (m, 2H), 2.93 – 2.84 (m, 2H), 2.78 (ddd, *J* = 17.5, 9.2, 2.0 Hz, 1H), 2.63 – 2.55 (m, 1H), 2.42 – 2.37 (m, 1H), 2.14 – 2.08 (m, 1H), 2.06 – 1.99 (m, 2H), 1.97 – 1.89 (m, 1H), 1.84 – 1.78 (m, 2H), 1.46 – 1.39 (m, 1H), 1.32 – 1.16 (m, 2H), and 1.11 – 1.03 (m, 1H).
^{13}C NMR (175 MHz, $CDCl_3$) δ 191.9, 166.3, 137.7, 113.2, 103.8, 61.3, 50.2, 48.2, 31.1, 30.4, 29.7, 25.4, 25.1, 24.5, and 20.9.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2928 (m), 2856 (w), 1627 (m), 1585 (s), 1447 (w), 1370 (w), 1249 (m), 1200 (m), and 1163 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{15}H_{22}NO)^+$: 232.1701, found: 232.1694.
mp: 52–57 °C.

Data for *cis*-tricycle ***cis*-17**
TLC (60% ethyl acetate in hexanes): R_f = 0.22 ($KMnO_4$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 5.81 – 5.73 (m, 1H), 4.91 (app dq, *J* = 17.0, 1.8 Hz, 1H), 4.86 (app dq, *J* = 9.9, 1.7 Hz, 1H), 3.55 (app ddd, *J* = 9.2, 8.1, 3.6 Hz, 1H), 3.49 – 3.45 (m, 1H), 3.12 (q, *J* = 8.4 Hz, 1H), 2.96 (app ddt, *J* = 15.7, 6.1, 1.7 Hz, 1H), 2.87 (app ddt, *J* = 15.6, 6.0, 1.7 Hz, 1H), 2.72 (ddd, *J* = 17.4, 9.2, 4.2 Hz, 1H), 2.67 – 2.60 (m, 1H), 2.35 – 2.28 (m, 1H), 2.08 – 2.01 (m, 1H), 2.02 – 1.96 (m, 1H), 1.94 – 1.86 (m, 1H), 1.77 – 1.41 (m, 6H), and 1.38 – 1.30 (m, 1H).
^{13}C NMR (*Note: **cis*-17** shows signal broadening in the ^{13}C NMR spectrum*) (175 MHz, $CDCl_3$) δ 193.1 (br), 166.1, 137.8, 113.0, 102.1, 56.5, 50.3, 46.7, 30.6, 29.4, 26.2 (br), 25.2, 24.3, 21.9 (br), and 21.1.
IR (Diamond-ATR, neat) $\tilde{\nu}_{max}$: 2929 (m), 2853 (w), 1626 (m), 1575 (s), 1459 (w), 1238 (m), 1219 (m), and 902 (w) cm^{-1}.
HRMS (ESI): calcd for ([M+H], $C_{15}H_{22}NO)^+$: 232.1701, found: 232.1693.

6 Crossover Experiment

To probe the intermediacy of the proposed π-allyl palladium complex (main manuscript Scheme 1c), a crossover experiment was conducted using vinylogous amides **S2b** and **5** (Scheme S1). Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy and high-resolution mass spectrometry revealed that oxazaborinines **2b** and **2v**, as well as crossover products **2a** and **S20** were formed in an approximate 1.7:1.0:1.1:1.2 ratio. This experiment corroborates the reaction proceeding via a π-allyl palladium complex that is dissociated from the parent vinylogous amide, leading to *intermolecular* allylic alkylation.



Scheme S1. Crossover experiment of vinylogous amides **S2b** and **5**.

Experimental Procedure:

An oven-dried vial was charged with a magnetic stirring bar, vinylogous amide **S2b** (36.2 mg, 0.15 mmol, 0.5 equiv), vinylogous amide **5** (45.5 mg, 0.15 mmol, 0.5 equiv), pyridinium *p*-toluenesulfonate (7.5 mg, 0.03 mmol, 10 mol%), triphenylphosphine (7.9 mg, 0.03 mmol, 10 mol%) and palladium(II) acetate (3.4 mg, 0.015 mmol, 5 mol%). The vial was flushed with nitrogen and sealed with a septum cap. Toluene (1.5 mL) and a solution of triethylborane (1 M in THF, 0.45 mL, 0.45 mmol, 1.5 equiv) were added sequentially and the resulting mixture was placed in a preheated (80 °C) heating block. After 1 h, the mixture was cooled to 23 °C, concentrated in vacuo and the residue was filtered through a pad of silica gel to provide a mixture of the oxazaborinine products **2b**, **2v**, **2a** and **S20** (89.0 mg) as a yellow oil.

Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy revealed that oxazaborinines **2b**, **2v**, **2a** and **S20** were formed in an approximate 1.7:1.0:1.1:1.2 ratio.

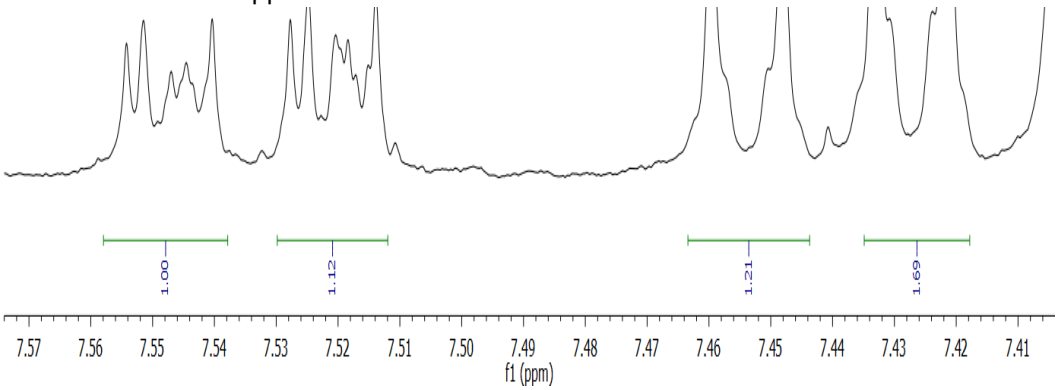


Figure S5. ^{1}H NMR analysis (7.57–7.41 ppm range) of the crude reaction mixture of the crossover experiment.

Furthermore, analysis of the crude reaction mixture by high-resolution mass spectrometry confirmed the formation of all four oxazaborinines:

HRMS (ESI): calcd for (**2b**, [M+H], $C_{20}H_{29}BNO)^+$: 310.2342, found: 310.2352.
HRMS (ESI): calcd for (**2v**, [M+H], $C_{25}H_{31}BNO)^+$: 372.2499, found: 372.2499.
HRMS (ESI): calcd for (**2a**, [M+H], $C_{19}H_{27}BNO)^+$: 296.2186, found: 296.2192.
HRMS (ESI): calcd for (**S20**, [M+H], $C_{26}H_{33}BNO)^+$: 386.2655, found: 386.2664.

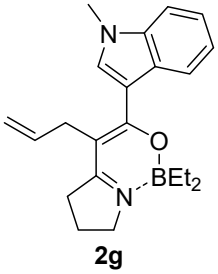
7 X-Ray Crystallographic Data

X-ray crystallographic data for oxazaborinines **2g**, **2l**, **2y** and **S18** (along with their .cif files) are provided along with this supporting information. The ORTEP renderings shown below were visualized using Mercury.[9] The X-ray structures in the main manuscript were visualized using CYLview.[10]

	2g	**2l**	**2y**	**S18**
Chemical formula	$C_{22}H_{29}BN_2O$	$C_{24}H_{32}BFeNO$	$C_{29}H_{30}BNO$	$C_{21}H_{20}BF_2NO$
Formula weight	348.28	417.16	419.35	351.19
Color, habit	Yellow, block	Red, block	Yellow, block	Colorless, block
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	P 21/n	P 21/c	Pbcn	P 21/c
a (Å)	10.66570(10)	7.45390(10)	32.9474(2)	9.90690(10)
b (Å)	13.42650(10)	13.7173(2)	7.27590(10)	14.74580(10)
c (Å)	13.50690(10)	20.1136(2)	19.8175(2)	12.25850(10)
α (°)	90	90	90	90
β (°)	90.4060(10)	98.3980(10)	90	99.9110(10)
γ (°)	90	90	90	90
V (Å^3)	1934.18(3)	2034.51(5)	4750.69(9)	1764.06
Z	4	4	8	4
Densitiy (Mg m^{-3})	1.196	1.362	1.173	1.322
F(000)	752	888	1792	736
Radiation Type	CuK_α	CuK_α	CuK_α	CuK_α
μ (mm^{-1})	0.556	6.035	0.530	0.774
Crystal size (mm^3)	0.14 x 0.17 x 0.22	0.13 x 0.18 x 0.24	0.08 x 0.12 x 0.20	0.10 x 0.15 x 0.18
Meas. Refl.	39914	22120	49414	37742
Indep. Refl.	3958	4311	5047	3762
R(int)	0.0432	0.0341	0.0508	0.0393
Final R indices [I > 2σ(I)]	R = 0.0370 R_w = 0.0941	R = 0.0331 R_w = 0.0900	R = 0.0685 R_w = 0.1633	R = 0.0505 R_w = 0.01240
Goodness-of-fit	1.050	1.106	1.052	1.053
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, -0.19	0.34, -0.40	0.83, -0.32	0.92, -0.36
CCDC	1815589	1815588	1815591	1815590

[9] Mercury 3.10, The Cambridge Structural Database (CSD), 2017 (http://www.ccdc.cam.ac.uk/mercury)
[10] CYLview, 1.0b, Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org).

a) Oxazaborinine **2g**



2g

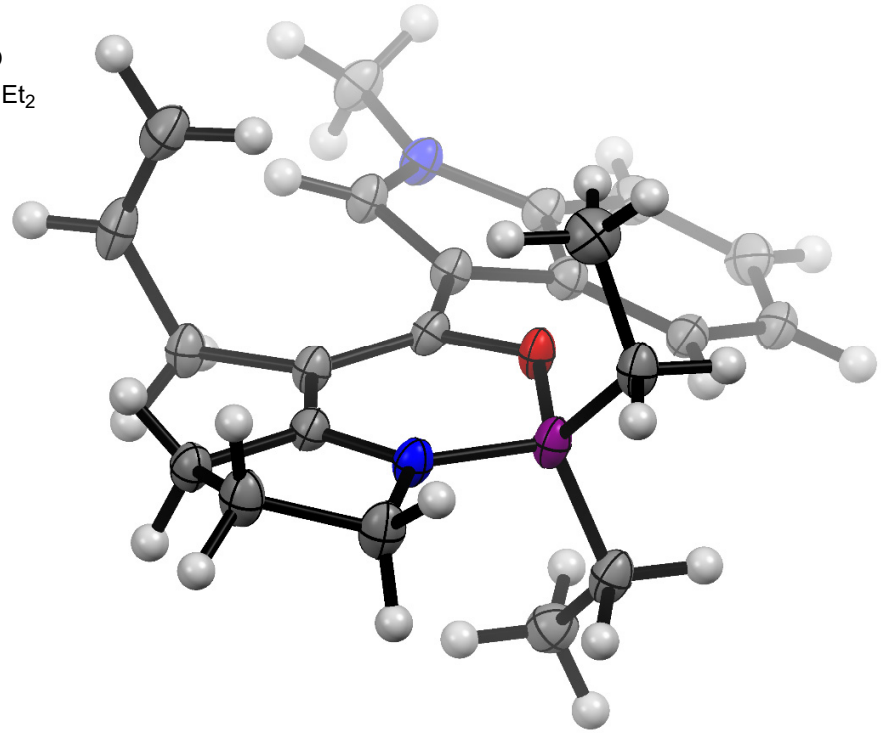
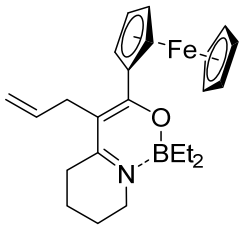


Figure S6. ORTEP rendering of oxazaborinine **2g** with ellipsoids at 50% probability.

This crystal structure has been deposited at the Cambridge Crystallographic Data Center under **CCDC 1815589**.

b) Oxazaborinine **2l**



2l

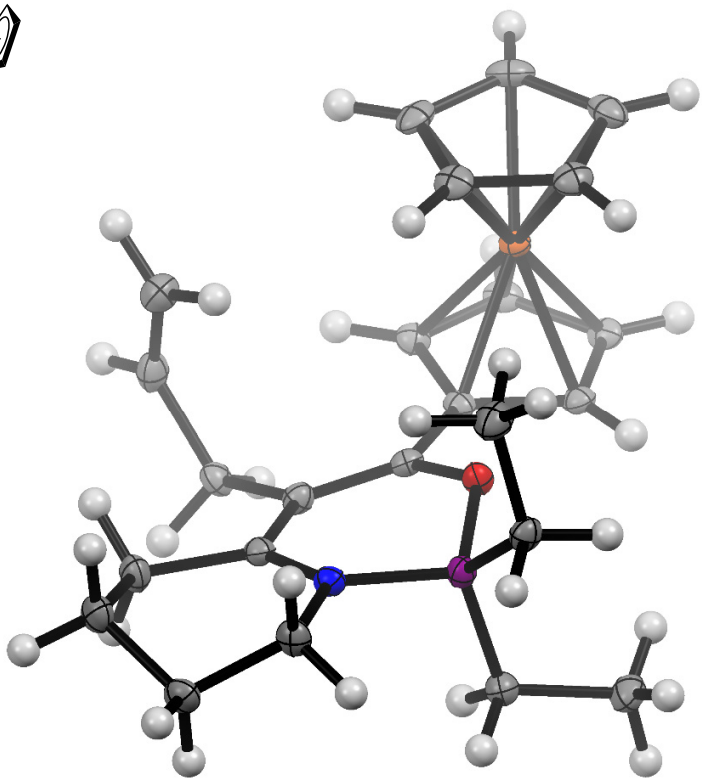


Figure S7. ORTEP rendering of oxazaborinine **2l** with ellipsoids at 50% probability.

This crystal structure has been deposited at the Cambridge Crystallographic Data Center under **CCDC 1815588**.

c) Oxazaborinine **2y**

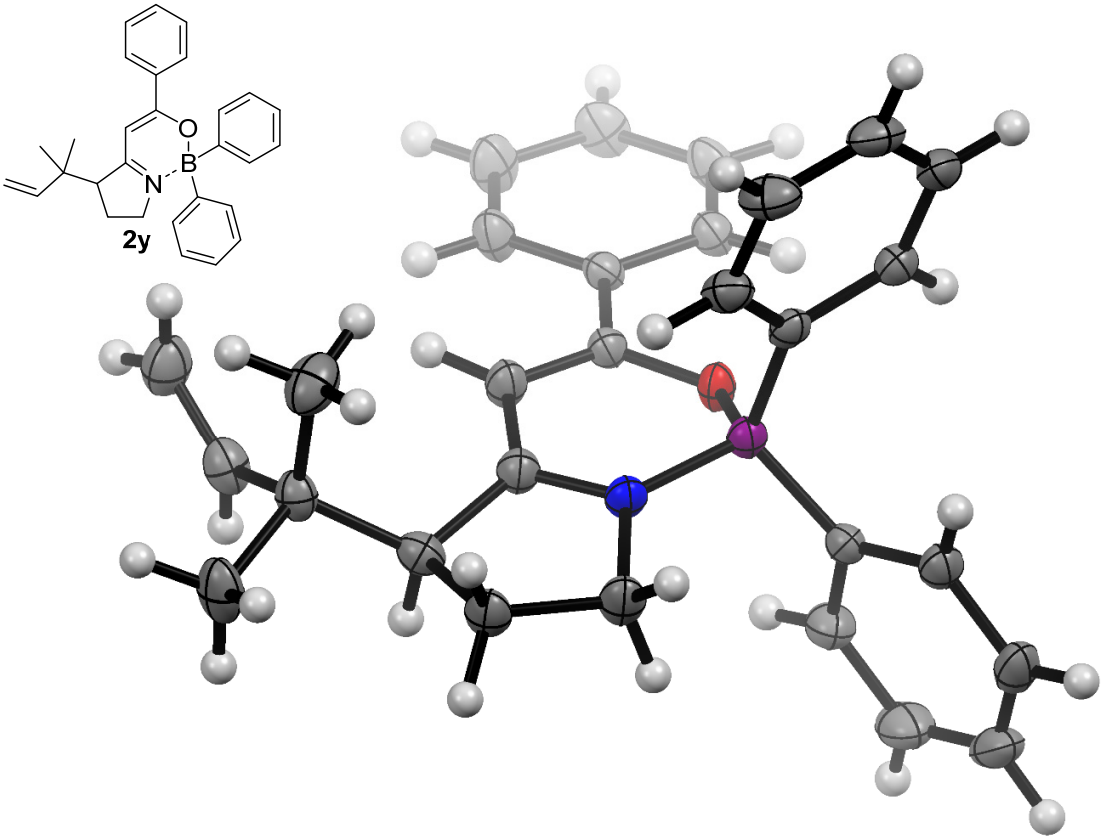
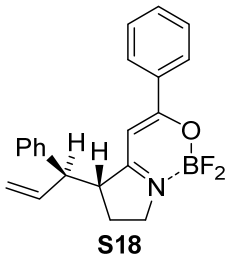


Figure S8. ORTEP rendering of oxazaborinine **2y** with ellipsoids at 50% probability.

This crystal structure has been deposited at the Cambridge Crystallographic Data Center under **CCDC 1815591**.

d) Oxazaborinine **S18**



S18

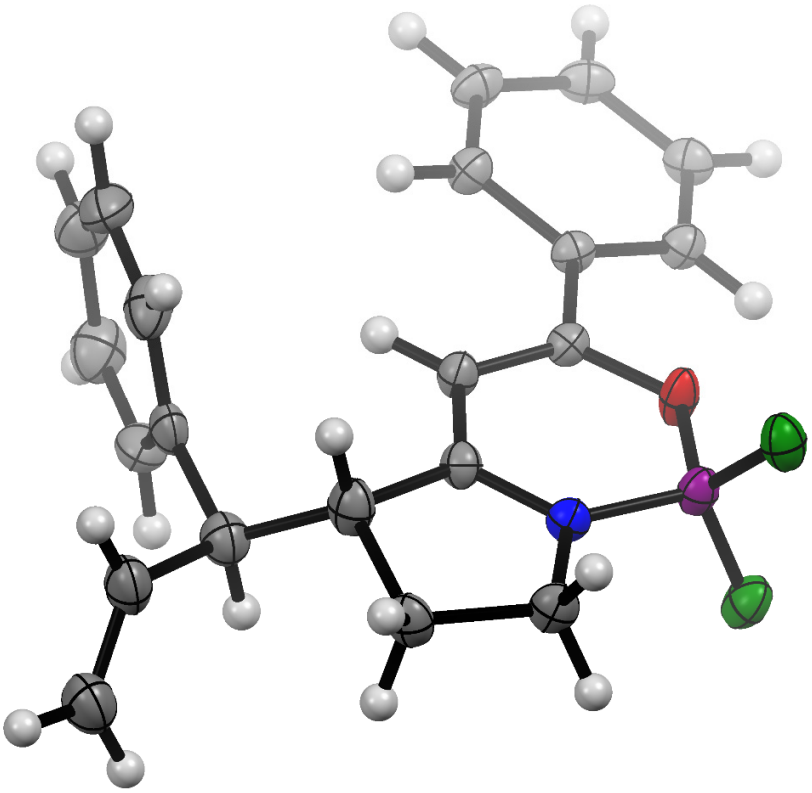


Figure S9. ORTEP rendering of oxazaborinine **S18** with ellipsoids at 50% probability.

This crystal structure has been deposited at the Cambridge Crystallographic Data Center under **CCDC 1815590**.

8 DFT Calculations

DFT calculations were performed at the Molecular Graphics and Computational Facility at UC Berkeley (*Supported by NIH S10OD023532*) using Gaussian16.[11] The computed structures shown below were visualized using CYLview.[10]

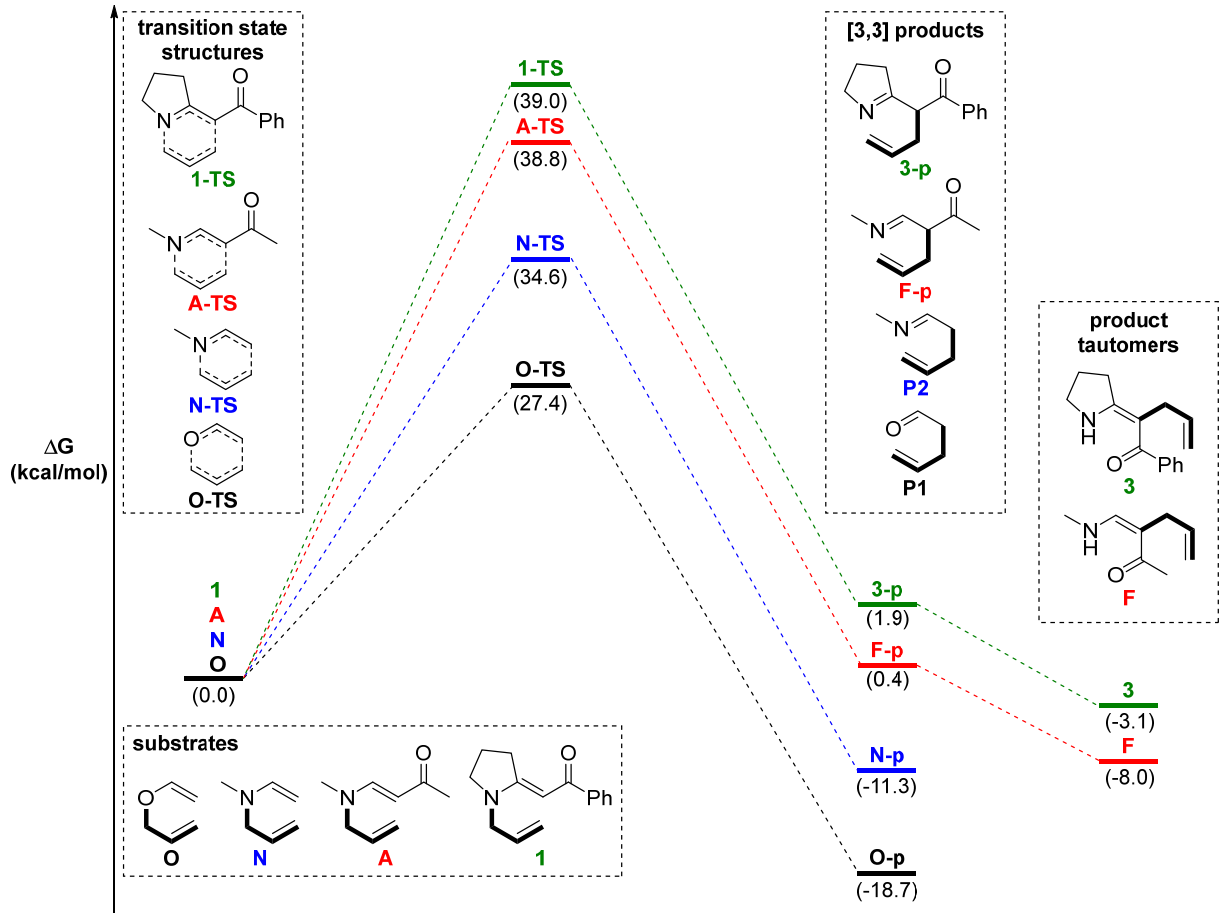


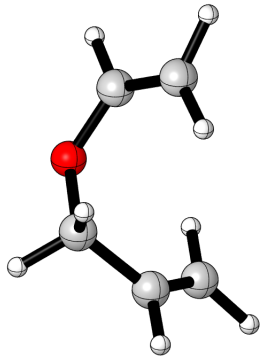
Figure S10. Activation barriers for [3,3] sigmatropic rearrangements. Computed at the B3LYP/6-31+G(d,p) level of theory in the gas phase.

Structures were optimized at the B3LYP/6-31+G(d,p) level of theory at 298 K and 1 atm in the gas phase. Frequency calculations were performed to verify the nature of the stationary points and obtain free energies.[12]

[11] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[12] For selected previous reports of $\Delta G^{\ddagger}$ values for the [3,3] rearrangement of allyl vinyl ether and related sytems, see: a) Schuler, F. W.; Murphy, G. W. *J. Am. Chem. Soc.* **1950**, *72*, 3155; b) Jolidon, S.; Hansen, H.-J. *Helv. Chim. Acta* **1977**, *60*, 978; c) Gilbert, J. C.; Cousins, K. R. *Tetrahedron* **1994**, *50*, 10671; d) Yamabe, S.; Okumoto, S.; Hayashi, T. *J. Org. Chem.* **1996**, *61*, 6218; e) Aviyente, V.; Yoo, H. Y.; Houk, K. N. *J. Org. Chem.* **1997**, *62*, 6121.

i) O

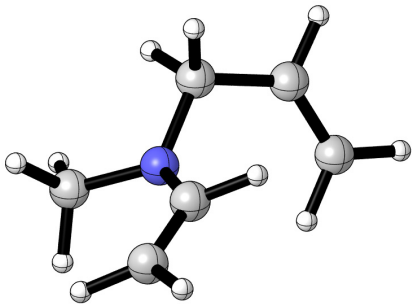


B3LYP SCF Energy: -270.451773
B3LYP Free Energy: -270.429354

Cartesian coordinates

Atom	X	Y	Z
C	-4.904820	-1.244860	0.828150
H	-4.547930	-2.253590	0.827820
H	-5.276830	-0.997830	-0.144210
O	-3.833670	-0.360380	1.167590
C	-4.309980	0.987960	1.168210
H	-4.039090	1.649470	0.372010
C	-5.103280	1.430820	2.173750
H	-5.377520	0.773980	2.972660
H	-5.456600	2.440800	2.168760
C	-6.036610	-1.101120	1.862550
H	-7.053690	-1.246510	1.563690
C	-5.748840	-0.791110	3.150050
H	-4.733700	-0.644540	3.454850
H	-6.539490	-0.692580	3.864240

ii) N

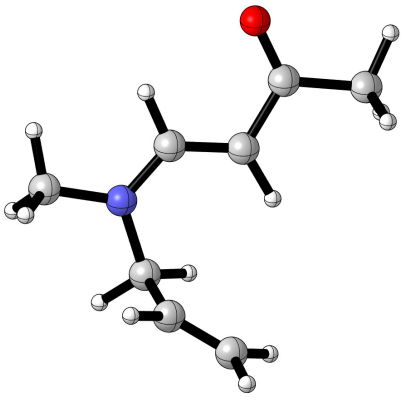


B3LYP SCF Energy: -289.949804
B3LYP Free Energy: -289.842639

Cartesian coordinates

Atom	X	Y	Z
N	-4.180790	1.271190	0.000000
C	-3.690780	1.964140	-1.200250
H	-4.048890	1.460760	-2.073900
H	-4.046000	2.973460	-1.199370
H	-2.620780	1.962610	-1.201130
C	-3.693000	-0.115520	-0.001340
H	-4.052870	-0.619350	-0.874010
H	-2.623010	-0.117230	-0.004280
C	-3.688590	1.962590	1.200250
H	-2.635910	2.057500	1.366890
C	-4.563510	2.480210	2.096440
H	-5.617300	2.388440	1.935220
H	-4.199260	2.982400	2.968230
C	-4.204040	-0.840670	1.257470
H	-4.466260	-1.876790	1.206410
C	-4.322790	-0.171020	2.429660
H	-4.062120	0.865160	2.486880
H	-4.678440	-0.680230	3.300930

iii) A

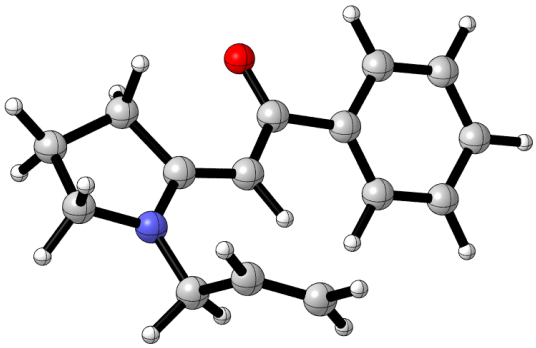


B3LYP SCF Energy: -442.589463
B3LYP Free Energy: -442.472473

Cartesian coordinates

Atom	X	Y	Z
N	-2.809600	0.055680	0.870560
C	-2.593350	1.507350	0.788040
H	-3.441760	2.017960	1.193470
H	-1.718880	1.769960	1.345930
C	-2.404280	1.915270	-0.684860
H	-2.885840	1.357340	-1.460570
C	-1.628000	2.980890	-0.998560
H	-1.146440	3.538820	-0.222860
H	-1.496640	3.264320	-2.021940
C	-1.644020	-0.645810	0.313580
C	-0.413650	-0.083030	0.391210
H	-0.290620	0.871920	0.857940
C	0.807440	-0.817920	-0.192290
O	0.662750	-1.941020	-0.741190
C	2.205590	-0.178400	-0.104070
H	2.377960	0.423340	-0.971880
H	2.263170	0.433770	0.771620
H	2.947070	-0.947980	-0.050650
C	-4.010970	-0.305100	0.104110
H	-3.879610	-0.021680	-0.919270
H	-4.168380	-1.361760	0.164180
H	-4.859390	0.205500	0.509540
H	-1.767050	-1.600760	-0.153150

iv) 1

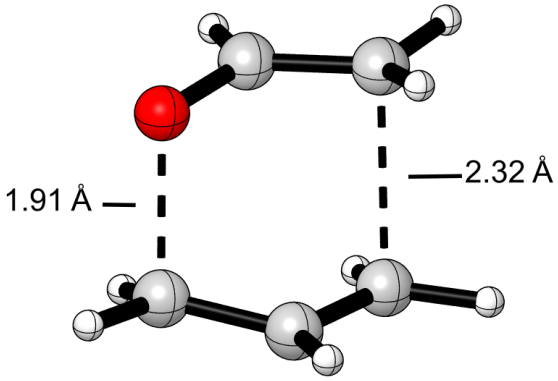


B3LYP SCF Energy: -711.744386
B3LYP Free Energy: -711.563757

Cartesian coordinates

Atom	X	Y	Z
C	-1.001960	1.863890	-0.622550
C	-0.617100	4.092980	-0.100950
C	-1.142860	3.248810	-1.254720
H	-1.242590	1.059070	-1.285310
H	-1.634520	1.789790	0.237260
H	-1.331690	4.121640	0.694950
H	-0.383670	5.100610	-0.374990
H	-2.136420	3.509380	-1.554470
H	-0.509930	3.323410	-2.114210
N	0.430200	1.877730	-0.230240
C	1.291520	1.712120	-1.409900
H	1.119530	0.749750	-1.844820
H	1.064600	2.473260	-2.126890
C	2.767990	1.828260	-0.987830
H	3.310060	0.954570	-0.691620
C	3.380750	3.037010	-0.991580
H	2.838680	3.910700	-1.287800
H	4.406610	3.117700	-0.698330
C	0.592200	3.247540	0.326660
C	1.632030	3.677550	1.081920
H	2.429780	3.007240	1.325210
C	1.665490	5.130930	1.590010
O	0.727280	5.919260	1.303870
C	2.847110	5.619580	2.448260
C	3.891940	4.741670	2.766900
C	2.877560	6.942160	2.910610
C	4.967210	5.186340	3.547910
H	3.868690	3.731850	2.413880
C	3.952840	7.386830	3.691620
H	2.079820	7.612470	2.667320
C	4.997660	6.508920	4.010270
H	5.764960	4.516040	3.791210
H	3.976090	8.396650	4.044640
H	5.818660	6.848440	4.606590

v) O-TS

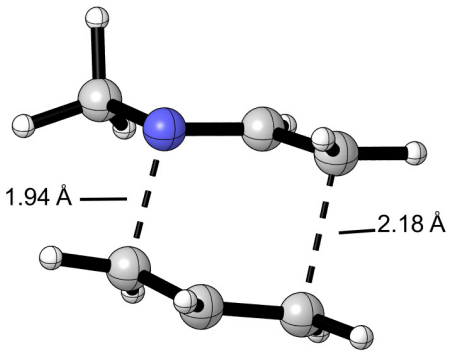


B3LYP SCF Energy: -270.354907
B3LYP Free Energy: -270.385757

Cartesian coordinates

Atom	X	Y	Z
C	-1.709650	-1.481230	-0.007170
C	-0.243060	-1.424440	-0.096900
C	0.407380	-0.157410	-0.302940
C	-0.446410	1.089610	1.463600
C	-1.863020	0.946220	1.257070
H	1.525980	-0.191400	-0.240230
H	0.632670	-2.121910	-0.039710
H	-2.173280	-0.461750	-0.071140
H	-2.089300	-2.534720	0.042840
H	-0.002860	0.131370	1.842270
H	-0.070390	2.143750	1.401610
H	-2.165290	1.955280	0.873700
H	-0.365490	0.655500	-0.302330
O	-2.466170	-0.390720	1.361760

vi) N-TS

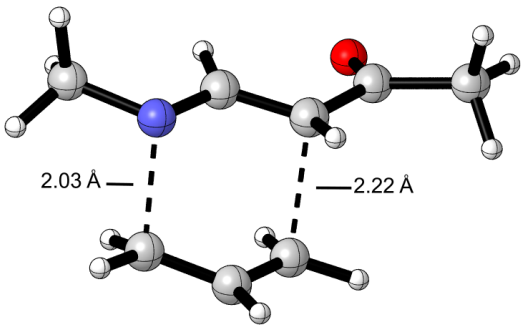


B3LYP SCF Energy: -289.724580
B3LYP Free Energy: -289.787495

Cartesian coordinates

Atom	X	Y	Z
C	-1.709650	-1.481230	-0.007170
C	-0.243060	-1.424440	-0.096900
C	0.407380	-0.157410	-0.302940
C	-0.446410	1.089610	1.463600
C	-1.863020	0.946220	1.257070
H	1.525980	-0.191400	-0.240230
H	0.632670	-2.121910	-0.039710
H	-2.173280	-0.461750	-0.071140
H	-2.089300	-2.534720	0.042840
H	-0.002860	0.131370	1.842270
H	-0.070390	2.143750	1.401610
H	-2.165290	1.955280	0.873700
H	-0.365490	0.655500	-0.302330
N	-2.466170	-0.390720	1.361760
C	-3.843870	0.100180	1.213880
H	-3.860160	0.912880	0.518070
H	-4.467550	-0.690840	0.853050
H	-4.206700	0.435820	2.162880

vii) A-TS

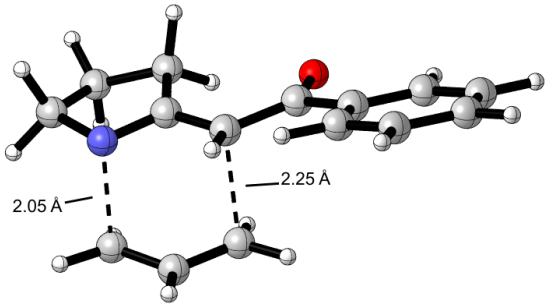


B3LYP SCF Energy: -442.554198
B3LYP Free Energy: -442.410608

Cartesian coordinates

Atom	X	Y	Z
N	-2.668400	0.543190	-0.834930
C	-2.889890	1.867300	0.508010
H	-3.540460	2.532900	-0.049030
H	-3.406780	1.166810	1.157340
C	-1.607610	2.331570	0.895330
H	-1.204830	3.213230	0.400900
C	-0.709290	1.403880	1.430700
H	-1.068120	0.577180	2.036040
H	0.320410	1.692640	1.618200
C	-1.725970	-0.346050	-0.433730
C	-0.405880	0.148710	-0.237890
H	-0.147300	1.007160	-0.840680
C	0.687580	-0.712390	0.234690
O	0.479730	-1.758080	0.857140
H	-2.107980	-1.292810	-0.113400
C	2.141020	-0.265140	-0.008350
H	2.330700	-0.225270	-1.060650
H	2.291900	0.704470	0.418250
H	2.810340	-0.963880	0.448470
C	-3.945440	-0.178660	-0.929880
H	-4.237600	-0.516040	0.042600
H	-4.696560	0.475290	-1.321090
H	-3.831690	-1.020670	-1.580250

viii) 1-TS

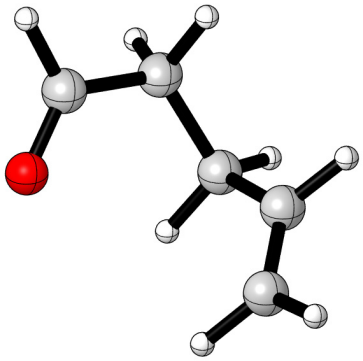


B3LYP SCF Energy: -711.646149
B3LYP Free Energy: -711.501598

Cartesian coordinates

Atom	X	Y	Z
C	-1.001960	1.863890	-0.622550
C	-0.617100	4.092980	-0.100950
C	-1.142860	3.248810	-1.254720
H	-1.242590	1.059070	-1.285310
H	-1.634520	1.789790	0.237260
H	-1.331690	4.121640	0.694950
H	-0.383670	5.100610	-0.374990
H	-2.136420	3.509380	-1.554470
H	-0.509930	3.323410	-2.114210
N	0.344620	1.894180	-0.113030
C	1.377090	1.695670	-1.527100
H	1.205100	0.733300	-1.962020
H	1.150170	2.456810	-2.244090
C	2.767990	1.828260	-0.987830
H	3.310060	0.954570	-0.691620
C	3.109950	3.136200	-0.670500
H	2.567890	4.009880	-0.966710
H	4.135820	3.216890	-0.377250
C	0.592200	3.247540	0.326660
C	1.902820	3.578360	0.760830
H	2.700570	2.908050	1.004130
C	1.936280	5.031740	1.268920
O	0.998070	5.820070	0.982790
C	3.117900	5.520390	2.127170
C	4.162730	4.642480	2.445820
C	3.148360	6.842970	2.589530
C	5.238000	5.087150	3.226830
H	4.139480	3.632660	2.092790
C	4.223630	7.287640	3.370540
H	2.350610	7.513280	2.346230
C	5.268450	6.409730	3.689190
H	6.035750	4.416850	3.470120
H	4.246880	8.297460	3.723560
H	6.089450	6.749250	4.285510

ix) O-p

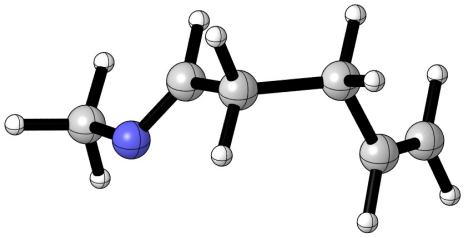


B3LYP SCF Energy: -270.528874
B3LYP Free Energy: -270.459197

Cartesian coordinates

Atom	X	Y	Z
C	-5.418130	-1.533280	0.513770
H	-4.401810	-1.735090	0.780740
H	-5.790850	-1.837870	-0.441840
O	-3.272250	-0.052520	1.453030
C	-3.968420	0.980720	1.630070
H	-3.762640	1.867340	1.067530
C	-5.116540	0.969090	2.656360
H	-4.743820	1.273690	3.611980
H	-5.883810	1.644870	2.340860
C	-6.233270	-0.891910	1.385980
H	-7.249590	-0.690110	1.119020
C	-5.696830	-0.453530	2.761360
H	-4.929570	-1.129300	3.076850
H	-6.494550	-0.461600	3.474430

x) N-p

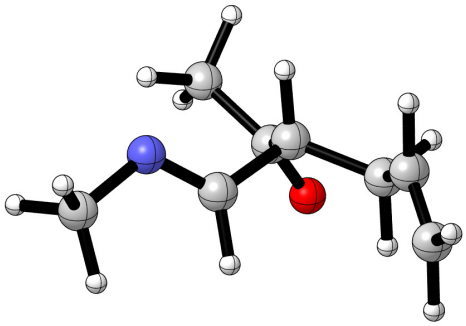


B3LYP SCF Energy: -289.965028
B3LYP Free Energy: -289.860605

Cartesian coordinates

Atom	X	Y	Z
N	-4.376810	1.901530	-0.278260
C	-3.686150	2.339610	-1.499720
H	-3.906040	1.660550	-2.296850
H	-4.019220	3.321170	-1.765250
H	-2.630440	2.356000	-1.326150
C	-3.515980	-0.899170	0.410690
H	-3.735880	-1.578240	-0.386440
H	-2.579550	-0.381830	0.429790
C	-3.862840	2.154670	0.881560
H	-2.934990	2.682930	0.951800
C	-4.586390	1.695730	2.161180
H	-5.642090	1.679340	1.987610
H	-4.366500	2.374790	2.958310
C	-4.423500	-0.694330	1.396090
H	-5.359930	-1.211660	1.376990
C	-4.107010	0.283020	2.543360
H	-3.051310	0.299410	2.716930
H	-4.609740	-0.035850	3.432450

xi) F-p

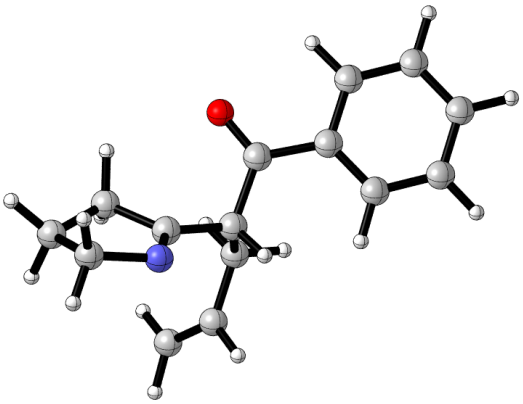


B3LYP SCF Energy: -442.606143
B3LYP Free Energy: -442.471788

Cartesian coordinates

Atom	X	Y	Z
N	2.046450	-1.141780	1.346020
C	2.672000	3.259870	-0.804640
H	3.445460	3.852580	-0.362630
H	2.534040	3.265350	-1.865690
C	1.867120	2.502250	-0.020580
H	2.005080	2.496770	1.040470
C	0.753930	1.649190	-0.656740
H	1.051820	1.349710	-1.639830
H	-0.146210	2.224570	-0.716570
C	1.803080	-0.429070	0.294250
C	0.507540	0.399040	0.208140
H	0.209660	0.698510	1.191240
C	-0.605650	-0.454020	-0.428010
O	-0.313250	-1.348210	-1.263780
C	-2.076680	-0.212790	-0.041380
H	-2.504000	0.514120	-0.700090
H	-2.621460	-1.130270	-0.121070
H	-2.126650	0.145380	0.965650
C	3.283100	-1.932250	1.428210
H	3.580990	-2.231730	0.445120
H	4.056550	-1.339540	1.870220
H	3.111910	-2.800870	2.029140
H	2.501920	-0.414930	-0.515890

xii) 3-p

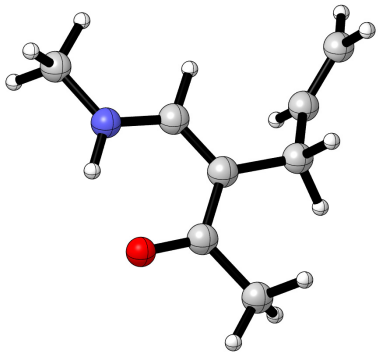


B3LYP SCF Energy: -711.761469
B3LYP Free Energy: -711.560754

Cartesian coordinates

Atom	X	Y	Z
C	-1.319520	1.929080	-0.130260
C	-0.550830	4.103990	-0.232920
C	-1.322740	3.121120	-1.074530
H	-1.625370	1.027190	-0.618050
H	-1.964980	2.094340	0.706980
H	-1.130430	4.468360	0.589390
H	-0.203090	4.948620	-0.790230
H	-2.293240	3.455370	-1.376690
H	-0.766500	2.882510	-1.956890
N	0.102620	1.916170	0.324450
C	2.029490	1.683640	-2.029300
H	2.054500	0.679610	-2.398340
H	1.291960	2.368750	-2.392040
C	2.931920	2.087570	-1.102460
H	3.669450	1.402460	-0.739720
C	2.895930	3.532630	-0.571320
H	2.517940	4.183000	-1.332260
H	3.885050	3.837760	-0.300330
C	0.556770	3.163310	0.274970
C	1.980370	3.602470	0.664990
H	2.358360	2.952090	1.425940
C	1.944380	5.047530	1.196130
O	1.077000	5.853270	0.769520
C	2.969870	5.506540	2.249350
C	3.935820	4.609240	2.724440
C	2.937120	6.821540	2.732690
C	4.869020	5.026940	3.682880
H	3.960830	3.605210	2.355400
C	3.870310	7.239240	3.691130
H	2.199590	7.506650	2.369950
C	4.836270	6.341940	4.166220
H	5.606540	4.341830	4.045620
H	3.845310	8.243280	4.060170
H	5.548780	6.660870	4.898000

xiii) F

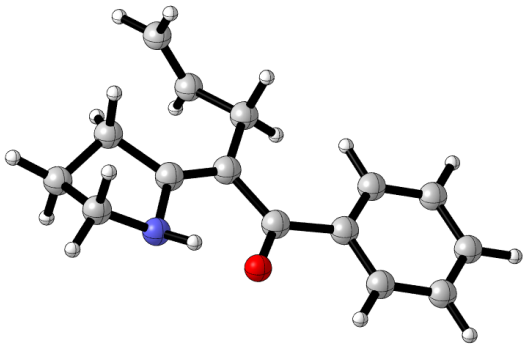


B3LYP SCF Energy: -442.605277
B3LYP Free Energy: -442.485236

Cartesian coordinates

Atom	X	Y	Z
C	2.559560	2.883510	-0.202280
H	3.347950	3.432230	0.269150
H	2.640450	2.610060	-1.233580
C	1.458560	2.534870	0.506830
H	1.377660	2.808310	1.538130
C	0.323860	1.745130	-0.171680
H	0.286680	1.996120	-1.211160
H	-0.609160	1.994390	0.289010
C	1.856900	-0.227730	0.058040
C	0.585520	0.235410	-0.017160
C	-0.597570	-0.748020	0.051900
O	-0.383750	-1.981670	0.178170
N	2.106670	-1.668830	0.205540
H	1.369850	-2.181650	-0.235050
C	-2.042320	-0.221720	-0.033550
H	-2.667020	-0.965760	-0.481960
H	-2.400360	-0.001160	0.950350
H	-2.063420	0.667430	-0.628430
C	3.388490	-2.011270	-0.427380
H	3.351310	-1.760290	-1.466860
H	4.176880	-1.462560	0.044050
H	3.570290	-3.060240	-0.320010
H	2.678920	0.455560	0.010060

xiv) 3

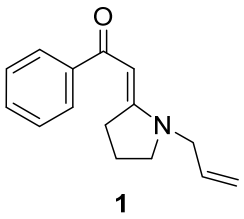


B3LYP SCF Energy: -711.640685
B3LYP Free Energy: -711.568713

Cartesian coordinates

Atom	X	Y	Z
C	-1.179690	2.113480	-1.000790
C	-0.877520	4.248100	-0.143220
C	-1.538200	3.562340	-1.331110
H	-1.476110	1.412570	-1.752950
H	-1.637200	1.826730	-0.077010
H	-1.435600	4.063330	0.750830
H	-0.774840	5.306900	-0.258460
H	-2.586580	3.761840	-1.408540
H	-1.079790	3.850210	-2.254090
C	-0.680320	6.256710	1.024790
H	-1.355060	6.940330	0.553300
H	-1.029100	5.613600	1.805600
C	0.616000	6.205410	0.633020
H	0.964780	6.848520	-0.147790
C	1.587120	5.221510	1.311600
H	1.282420	5.061240	2.324700
H	2.576220	5.629380	1.296920
C	0.449510	3.476770	-0.087280
C	1.573210	3.881260	0.553230
C	2.836220	3.000660	0.522700
O	2.824860	1.905490	-0.097000
C	4.113160	3.460320	1.250550
C	4.125820	4.679950	1.940670
C	5.262500	2.658970	1.222780
C	5.287820	5.098240	2.603010
H	3.248260	5.291790	1.961880
C	6.424510	3.077260	1.885120
H	5.252840	1.727760	0.695850
C	6.437170	4.296890	2.575240
H	5.297490	6.029450	3.129930
H	7.302060	2.465420	1.863910
H	7.324390	4.616260	3.080950
N	0.295620	2.211950	-0.856190
H	0.703890	1.413930	-0.412930

9 NMR Spectra

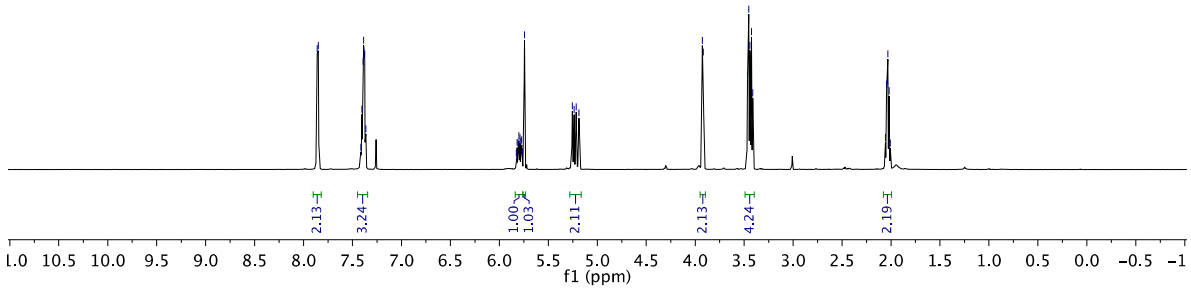


1

Solvent $CDCl_3$

MHz 600

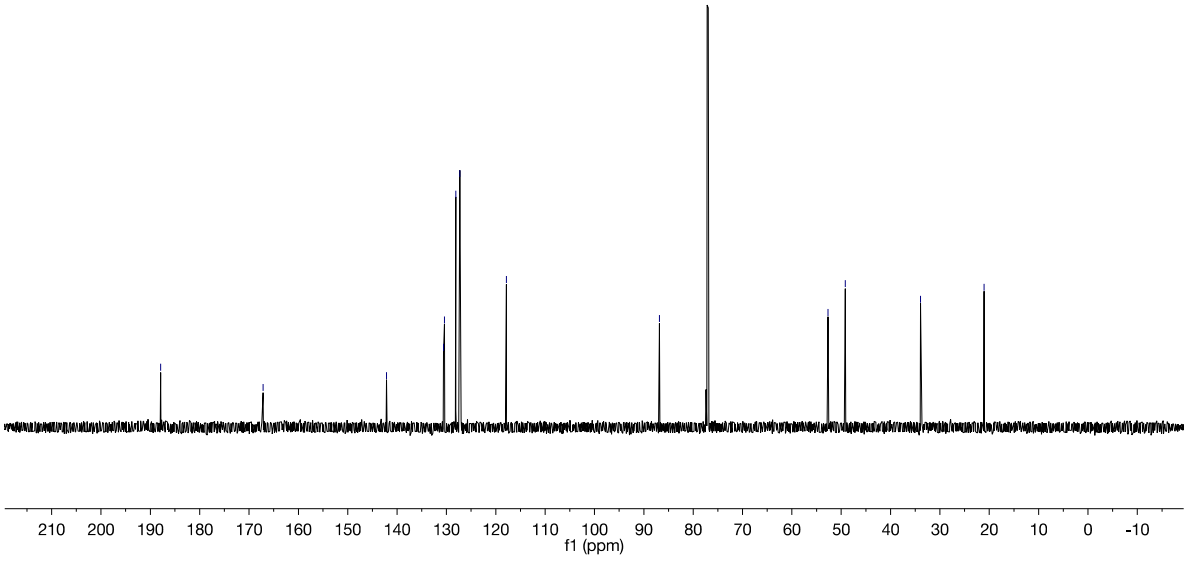
Nucleus 1H

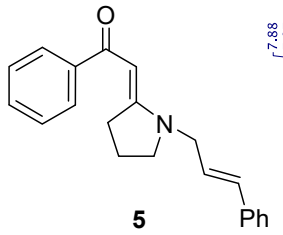


Solvent $CDCl_3$

MHz 150

Nucleus 13C



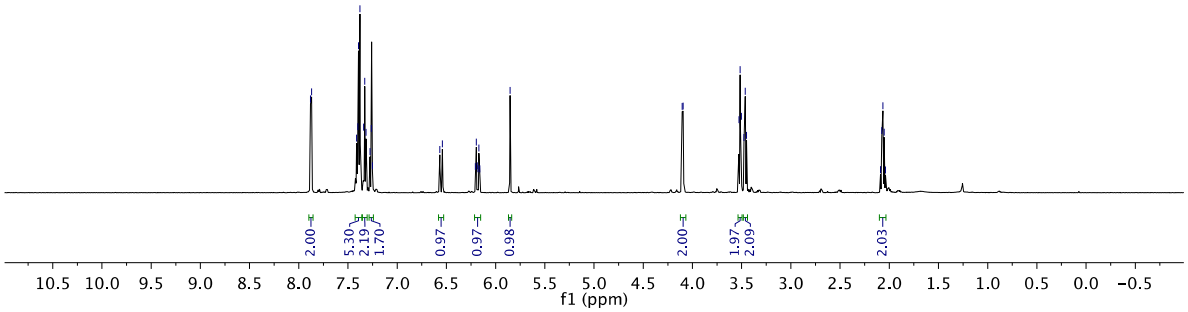


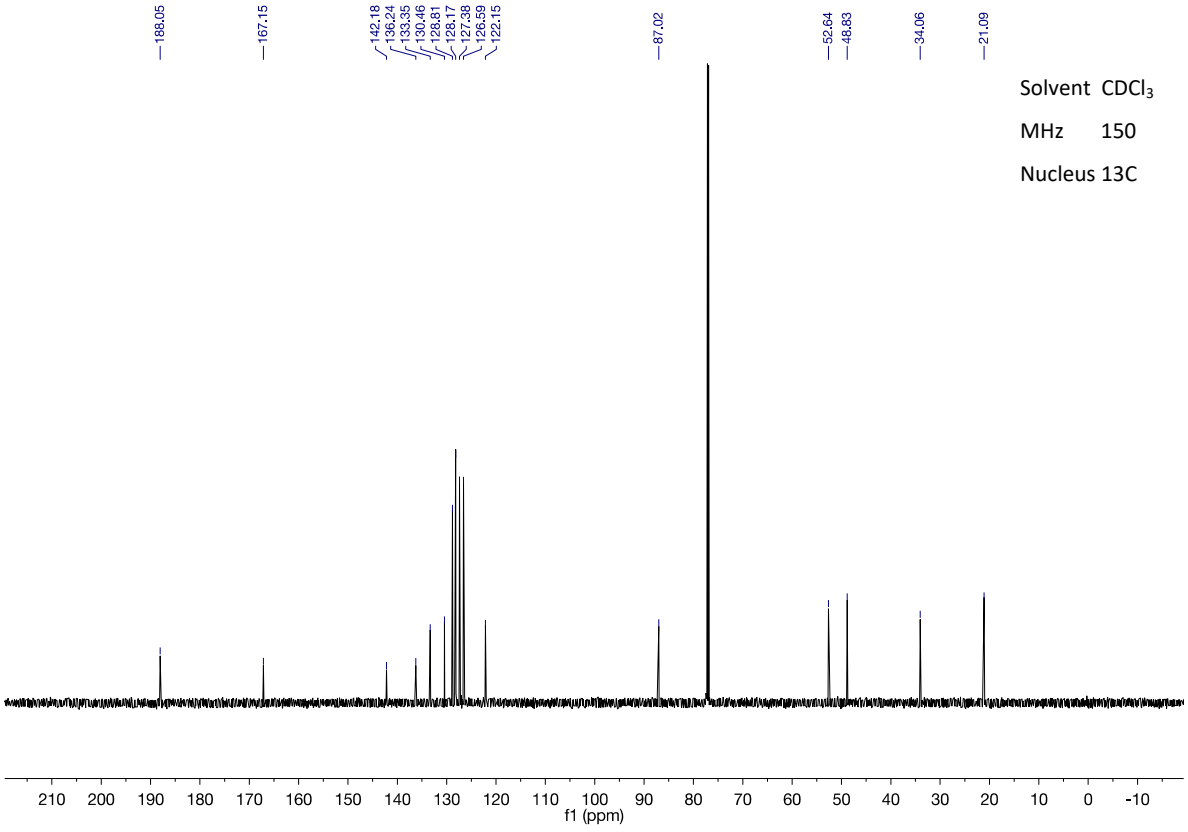
5

Solvent $CDCl_3$

MHz 600

Nucleus 1H

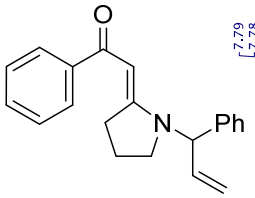




Solvent $CDCl_3$

MHz 150

Nucleus 13C

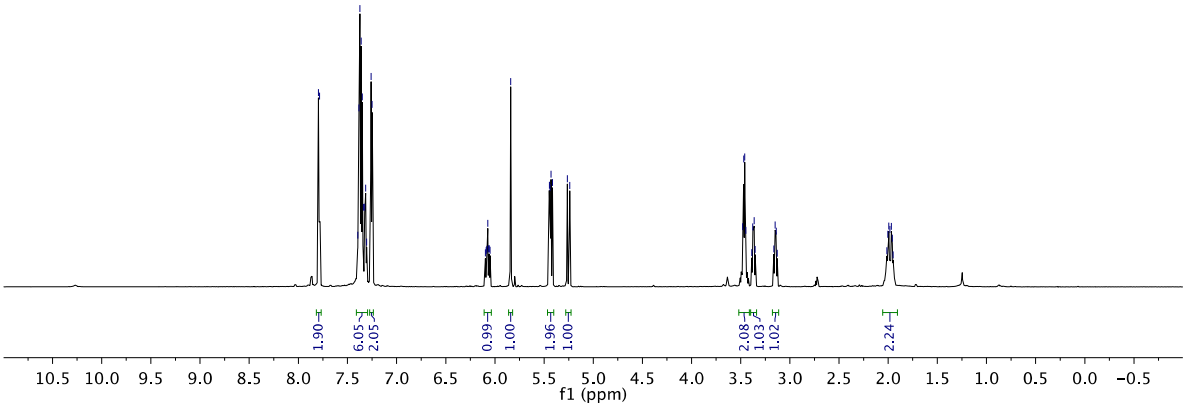


6

Solvent $CDCl_3$

MHz 700

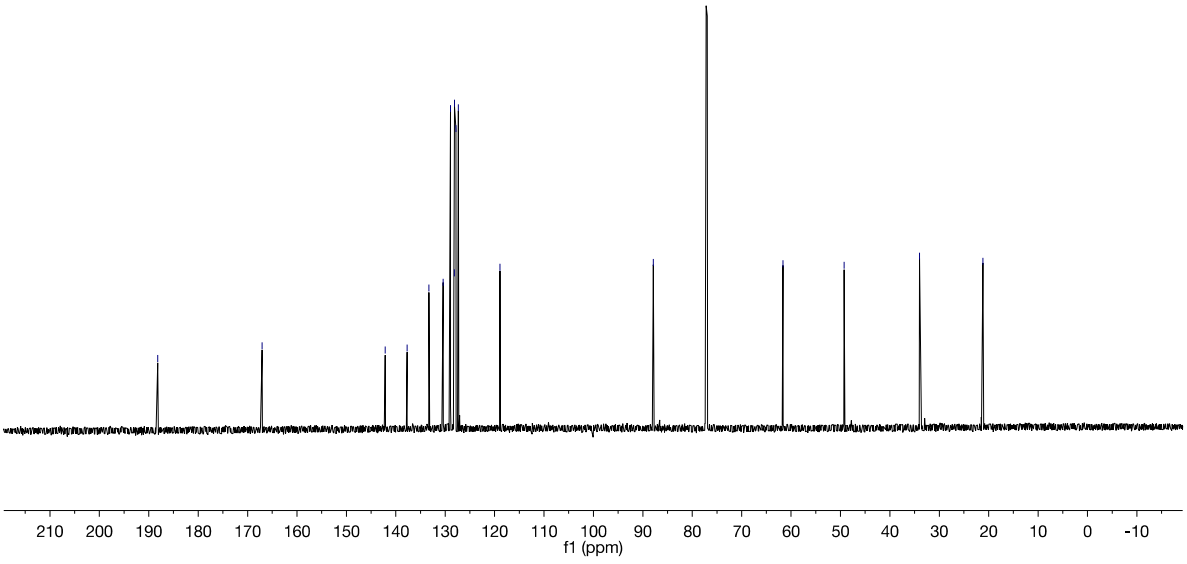
Nucleus 1H

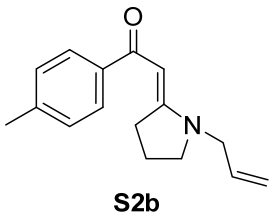


Solvent $CDCl_3$

MHz 175

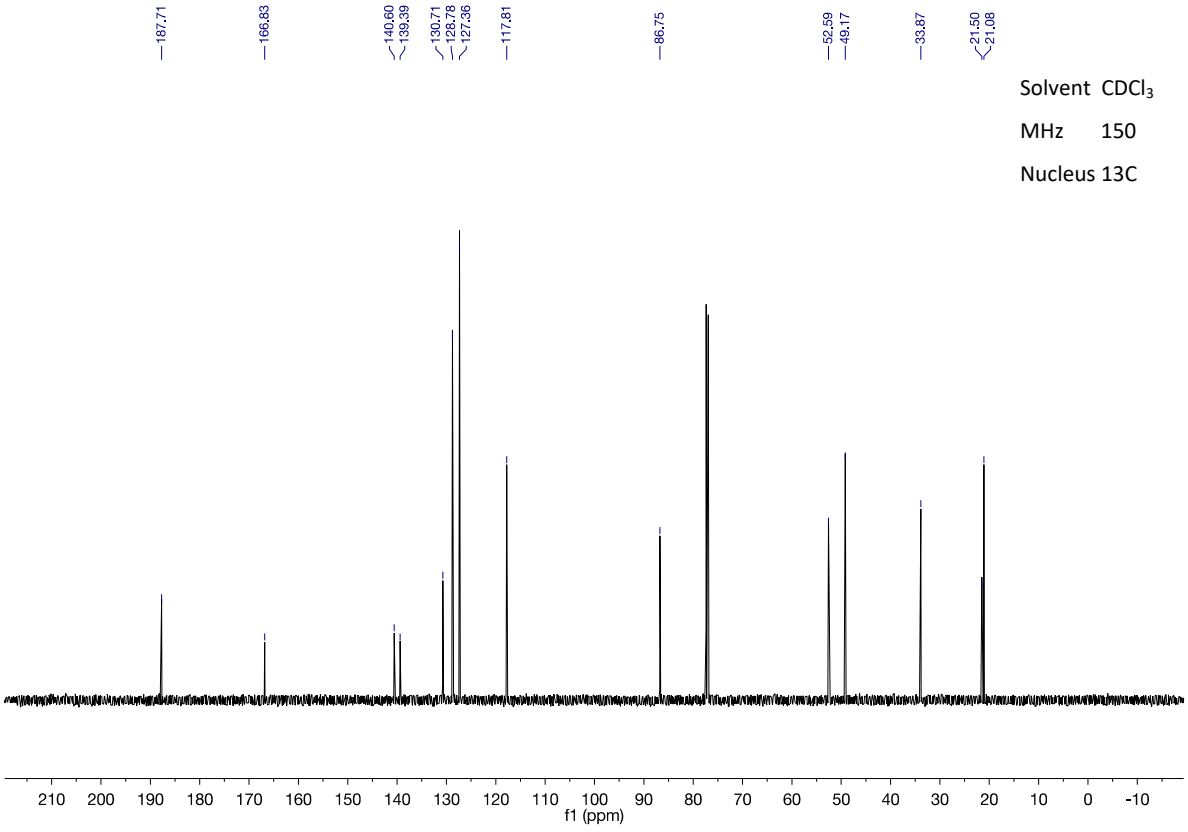
Nucleus 13C

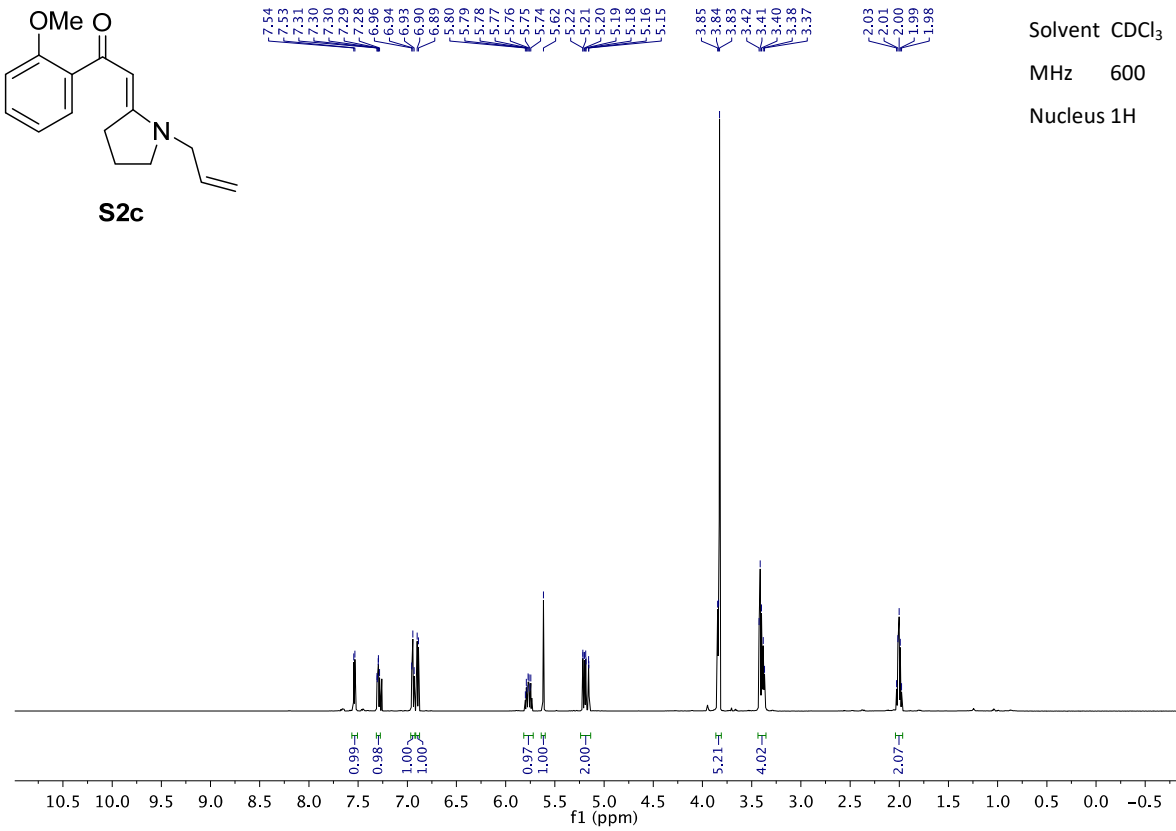


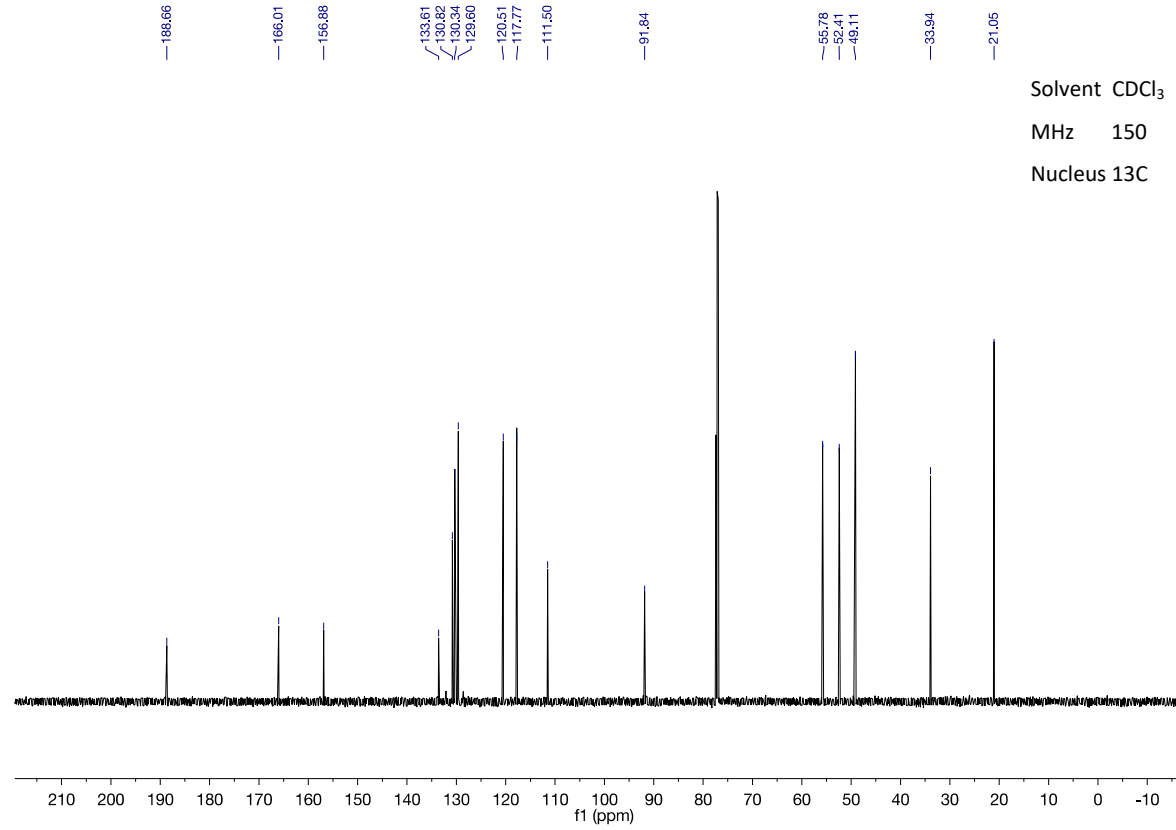


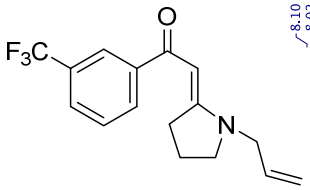
S2b

7.77
7.76
7.18
7.17
5.83
5.82
5.81
5.80
5.79
5.78
5.77
5.76
5.74
5.25
5.23
5.21
5.18
3.92
3.91
3.45
3.44
3.43
3.42
3.40
2.36
2.05
2.03
2.02
2.01
2.00
Solvent CDCl3
MHz 600
Nucleus 1H
1.93
1.93
1.00
0.89
1.92
2.01
3.98
3.00
2.18
f1 (ppm)


187.71
166.83
140.60
139.39
130.71
128.78
127.36
117.81
86.75
52.59
49.17
33.87
21.50
21.08
Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)


OMe O
N
S2c
Solvent CDCl3
MHz 600
Nucleus 1H
f1 (ppm)


Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)

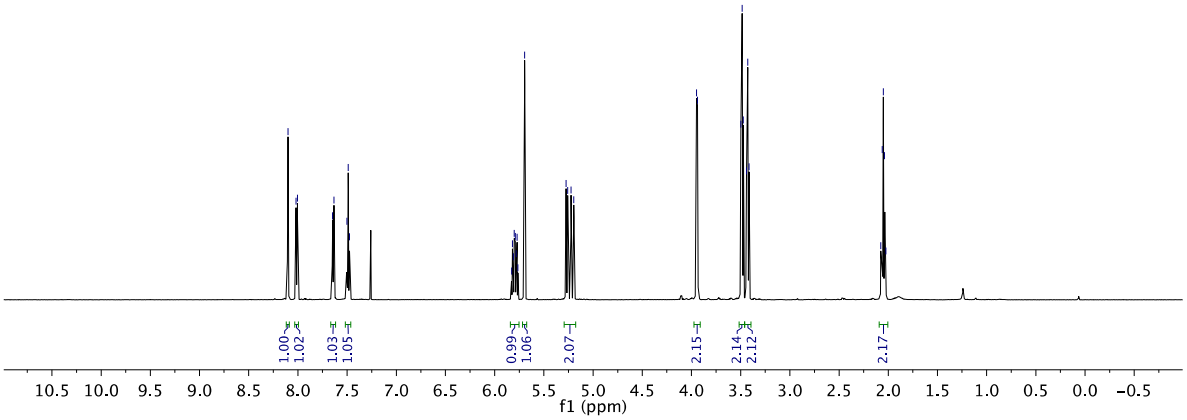


S2d

Solvent $CDCl_3$

MHz 600

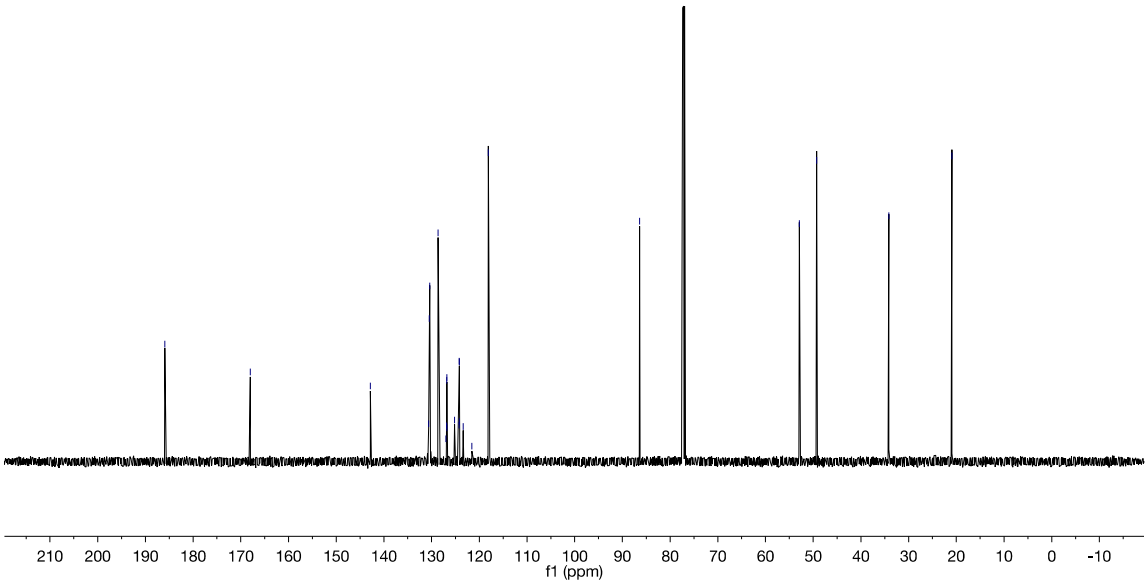
Nucleus 1H

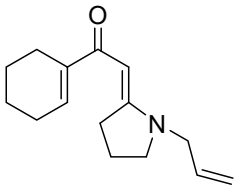


Solvent $CDCl_3$

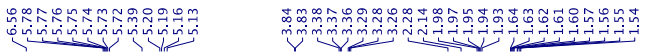
MHz 150

Nucleus 13C





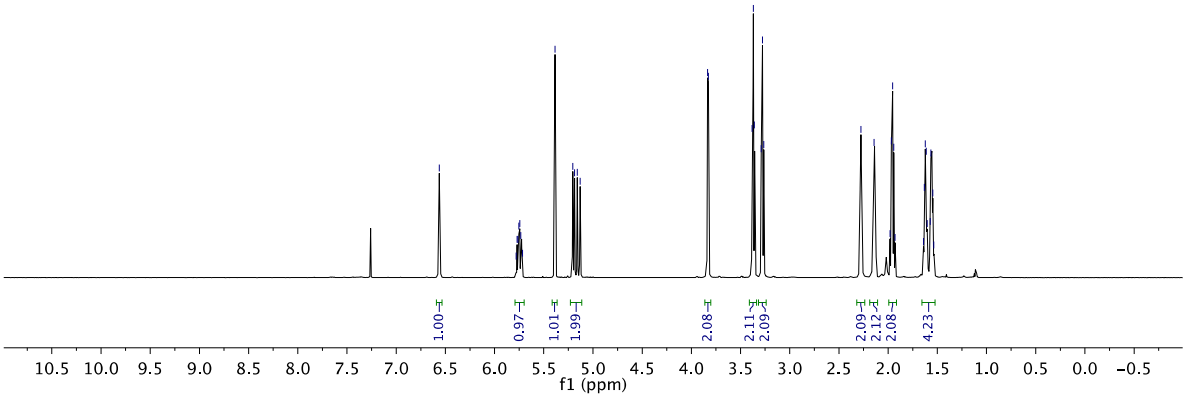
S2e



Solvent $CDCl_3$

MHz 600

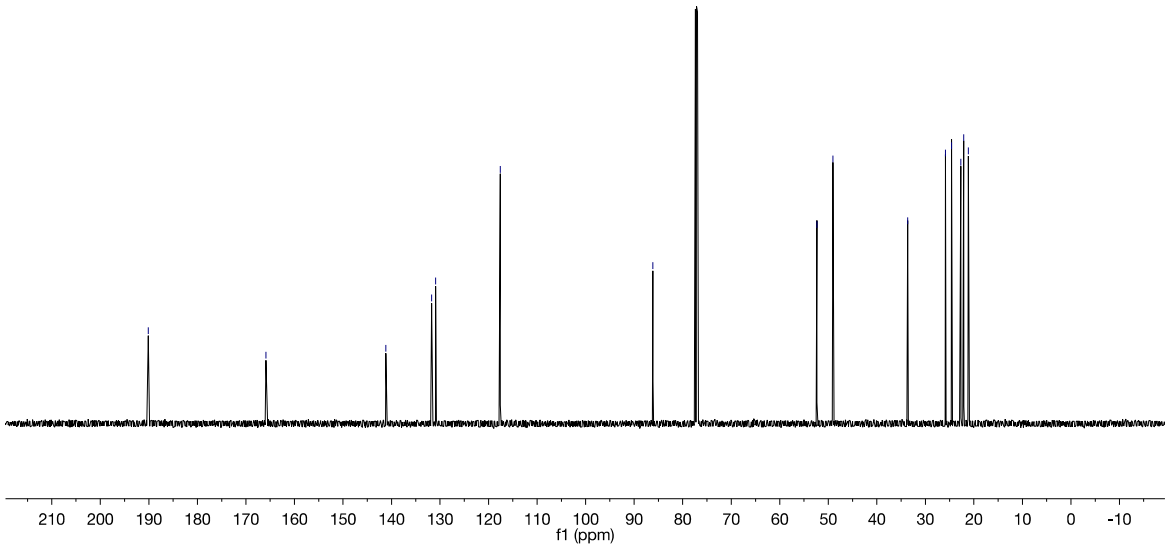
Nucleus 1H

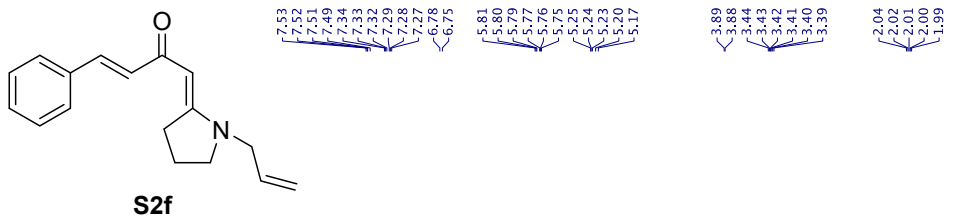


Solvent $CDCl_3$

MHz 150

Nucleus 13C



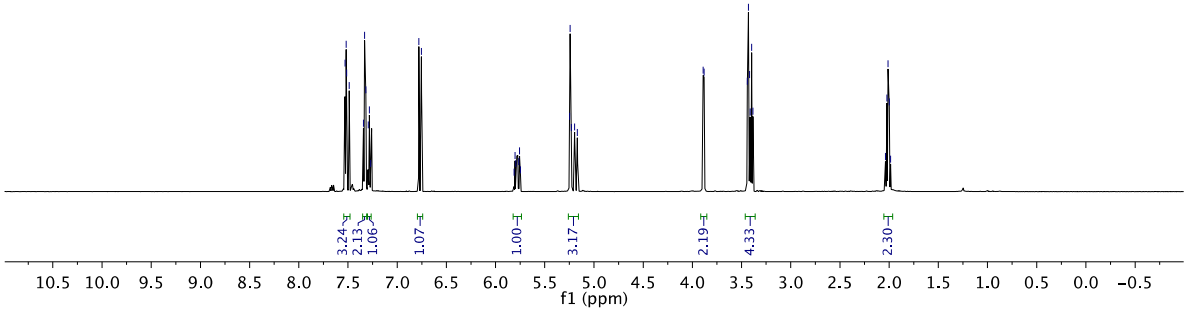


S2f

Solvent $CDCl_3$

MHz 600

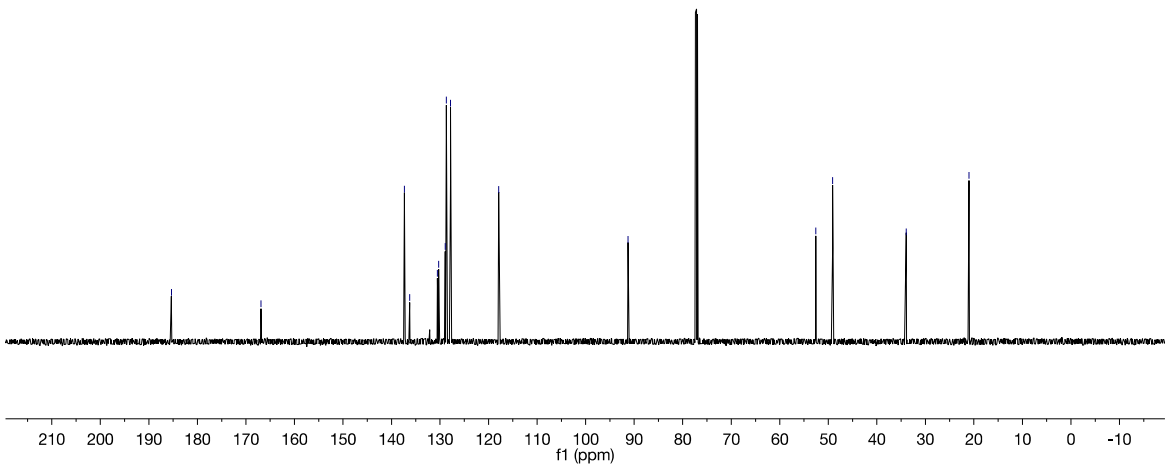
Nucleus 1H

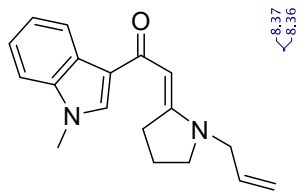


Solvent $CDCl_3$

MHz 150

Nucleus 13C



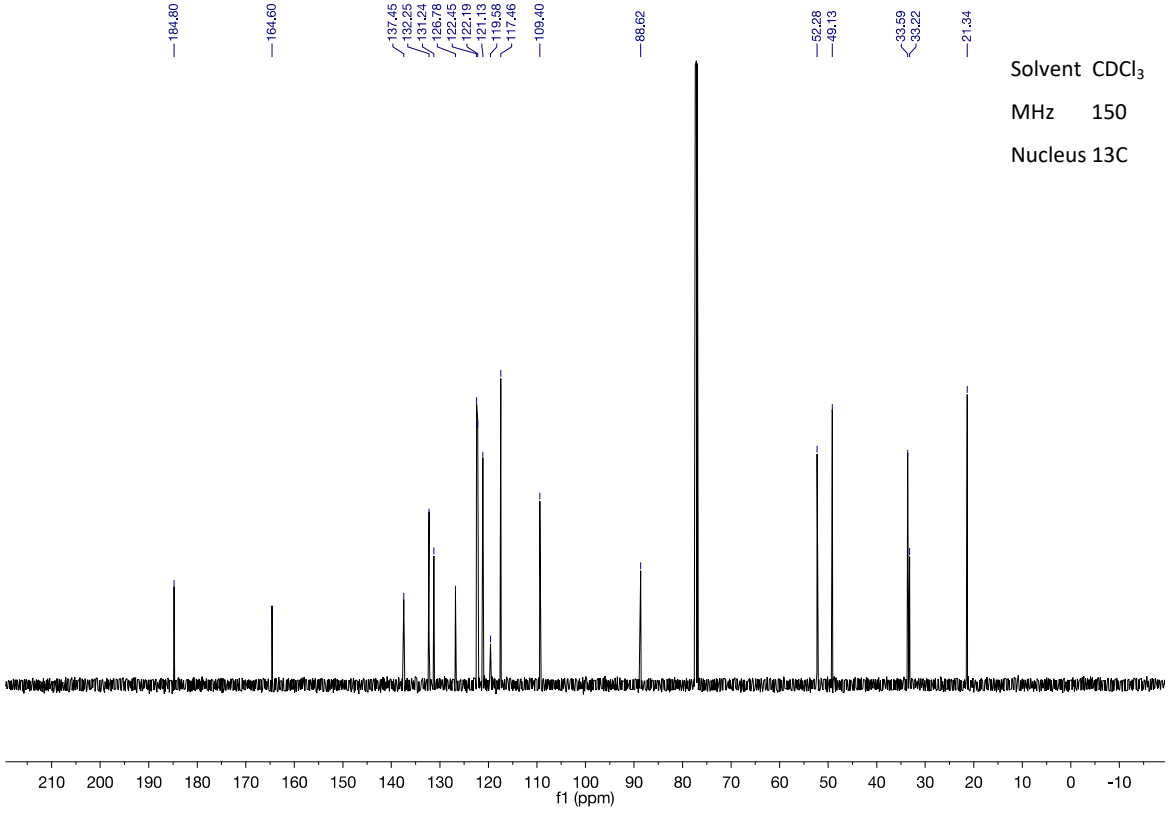


S2g

Solvent $CDCl_3$

MHz 600

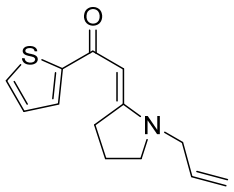
Nucleus 1H



Solvent $CDCl_3$

MHz 150

Nucleus 13C

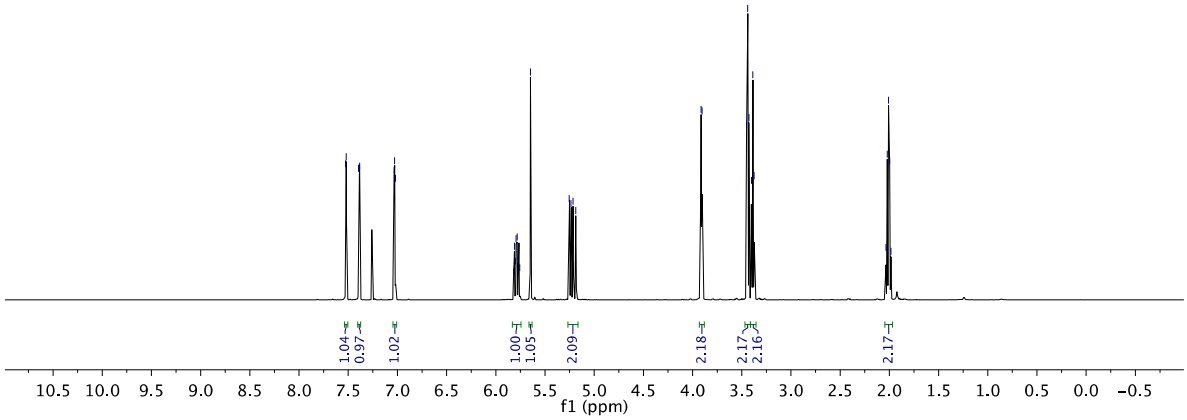


S2h

Solvent $CDCl_3$

MHz 600

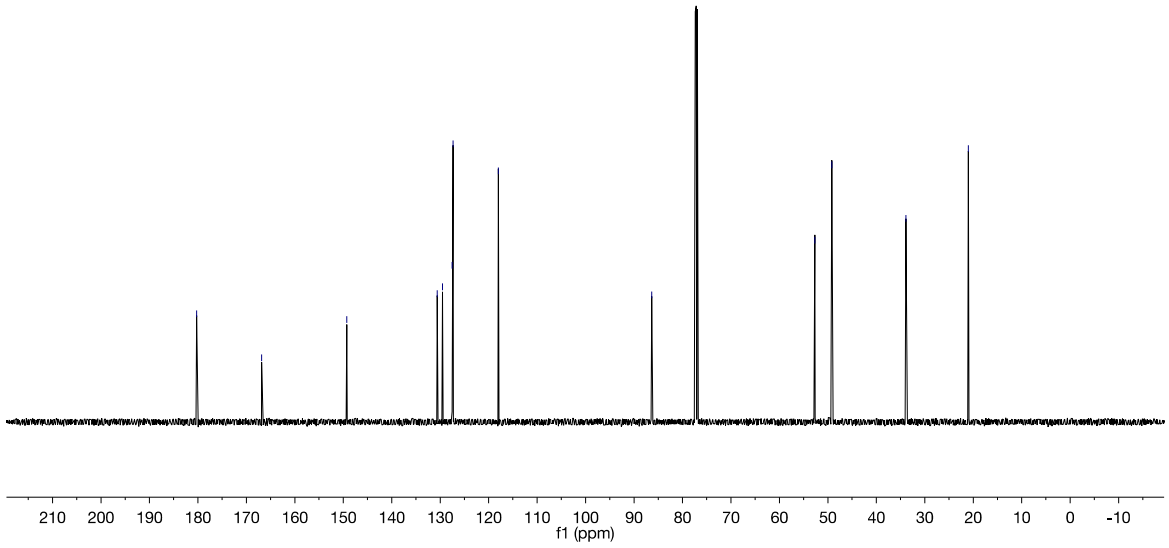
Nucleus 1H

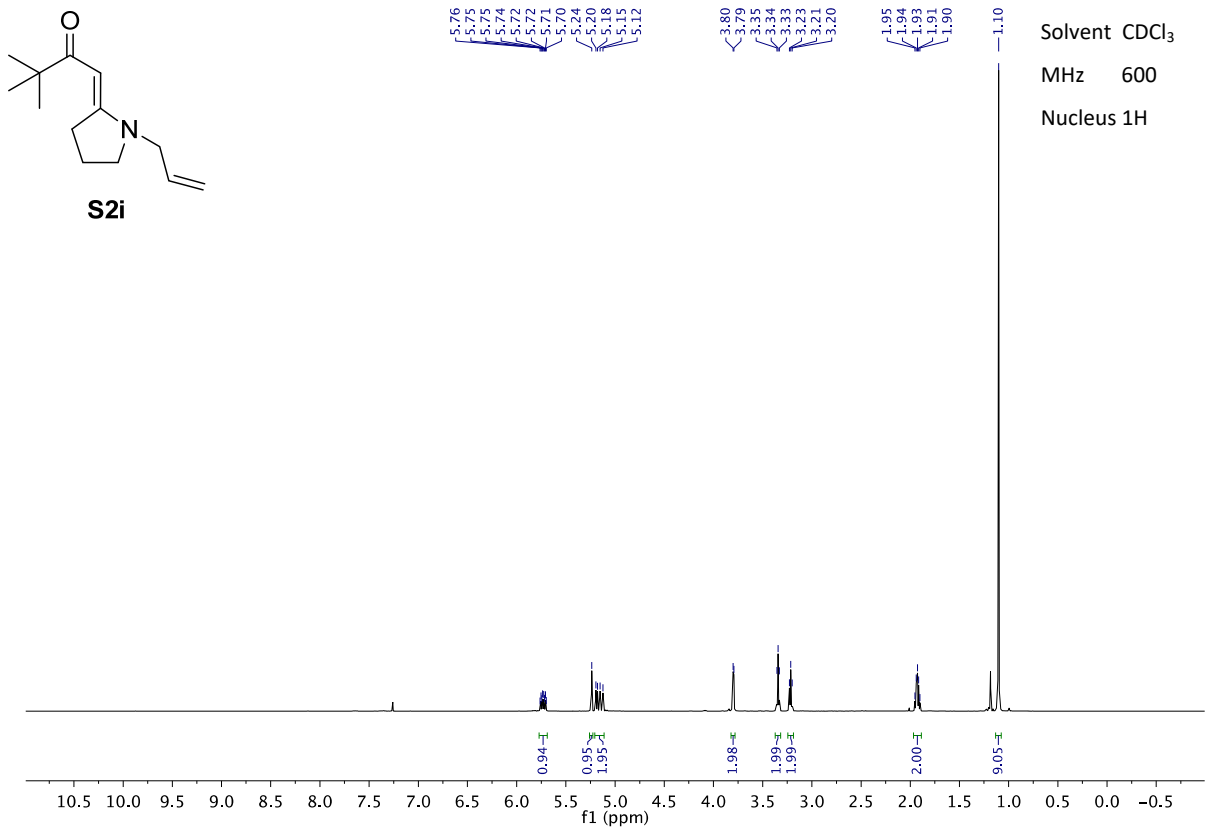


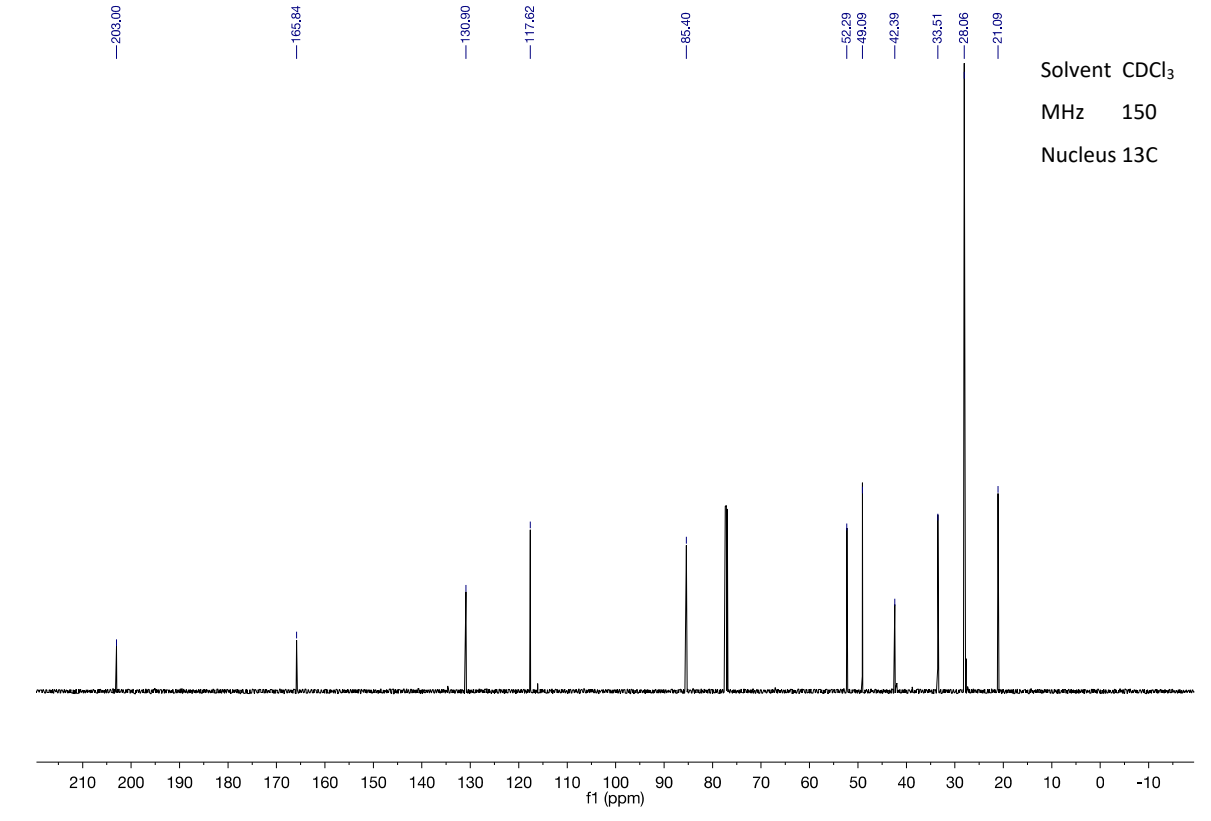
Solvent $CDCl_3$

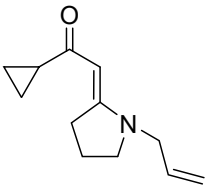
MHz 150

Nucleus 13C




S2i
Solvent CDCl3
MHz 600
Nucleus 1H
f1 (ppm)


Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)

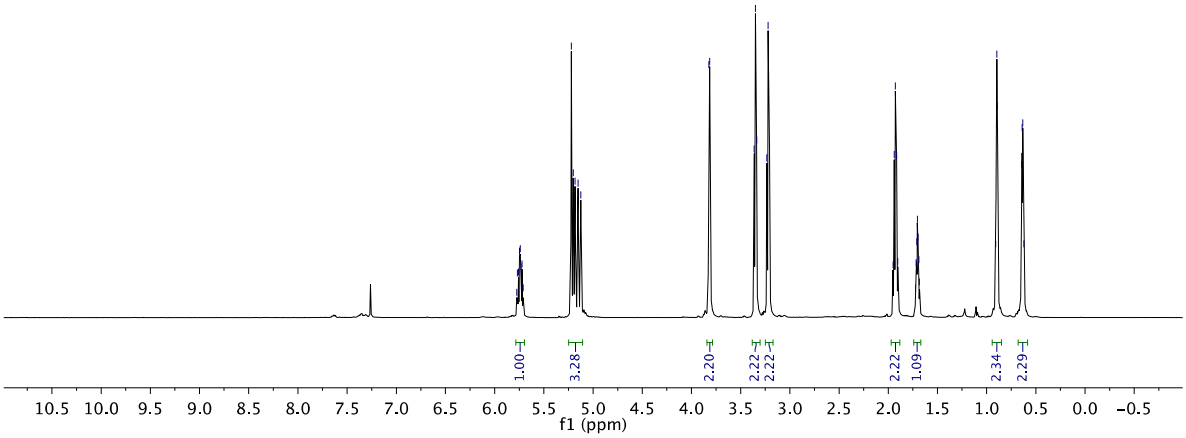


S2j

Solvent $CDCl_3$

MHz 600

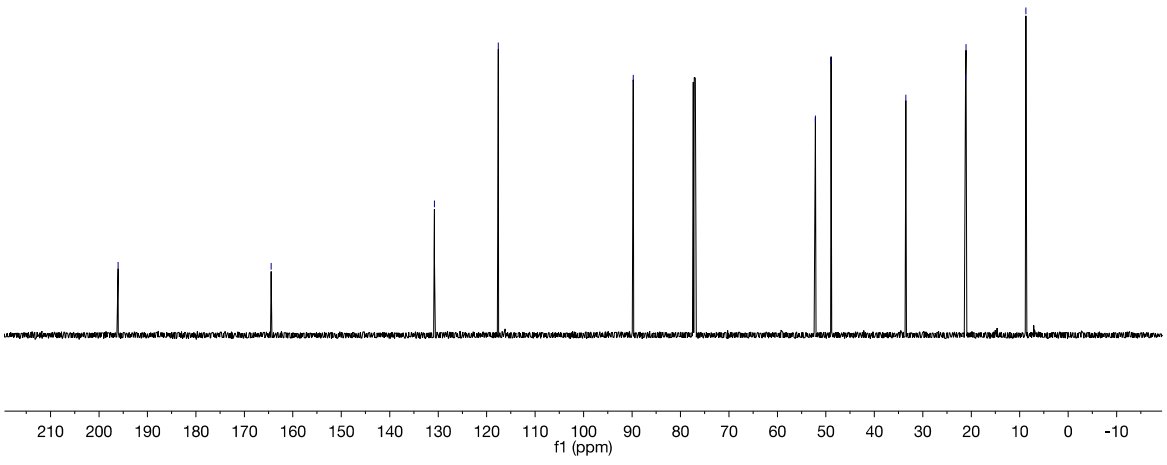
Nucleus 1H

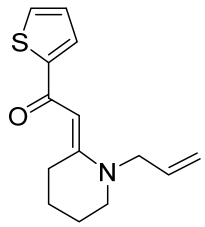


Solvent $CDCl_3$

MHz 150

Nucleus 13C



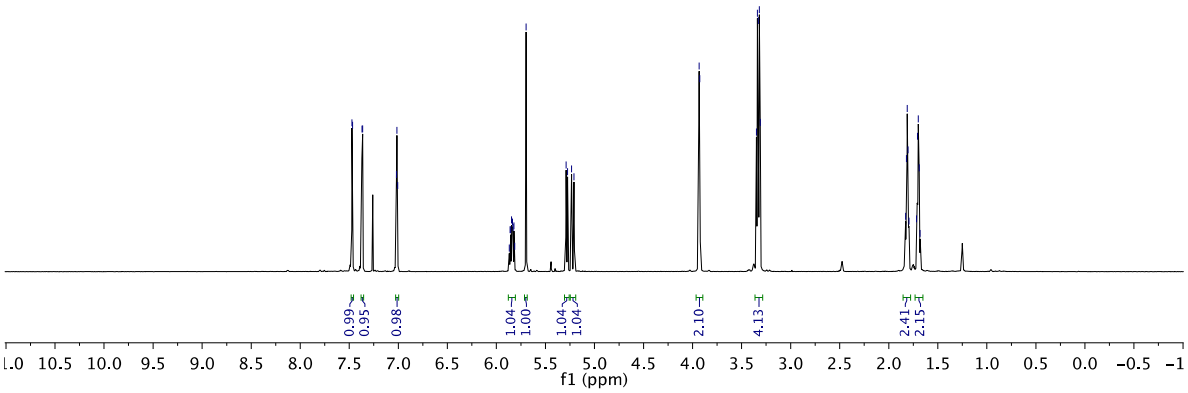


S2k

Solvent $CDCl_3$

MHz 700

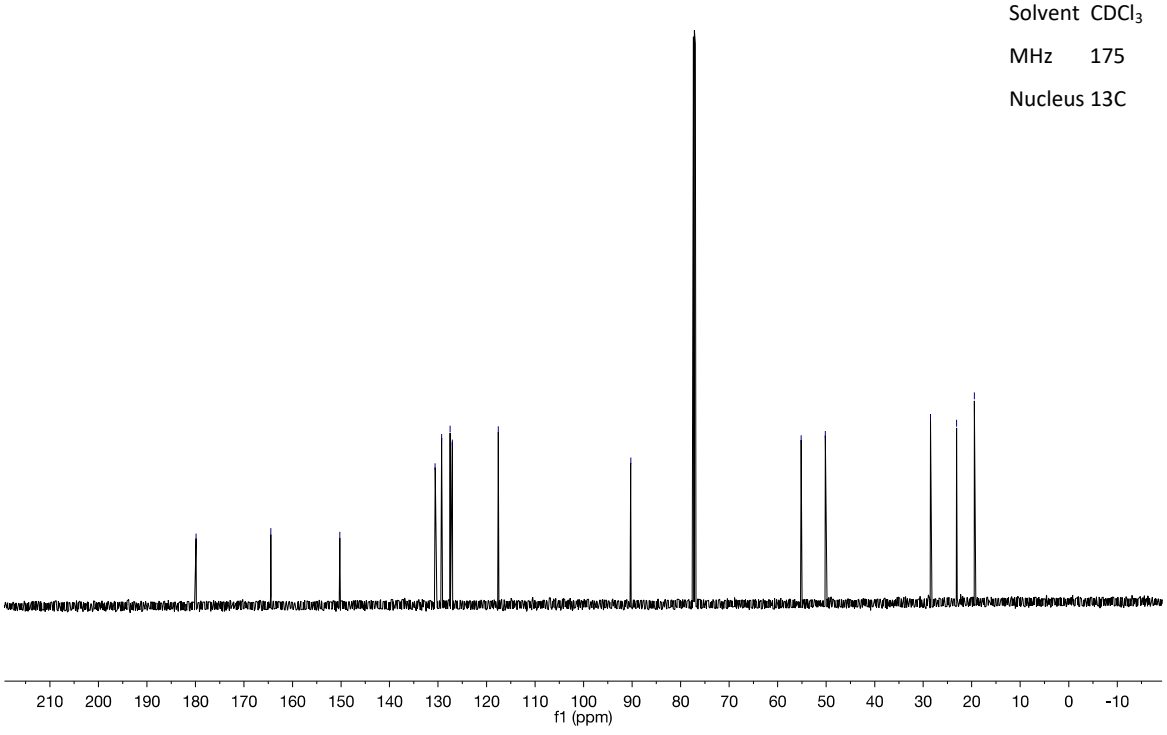
Nucleus 1H

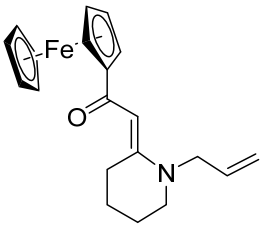


Solvent $CDCl_3$

MHz 175

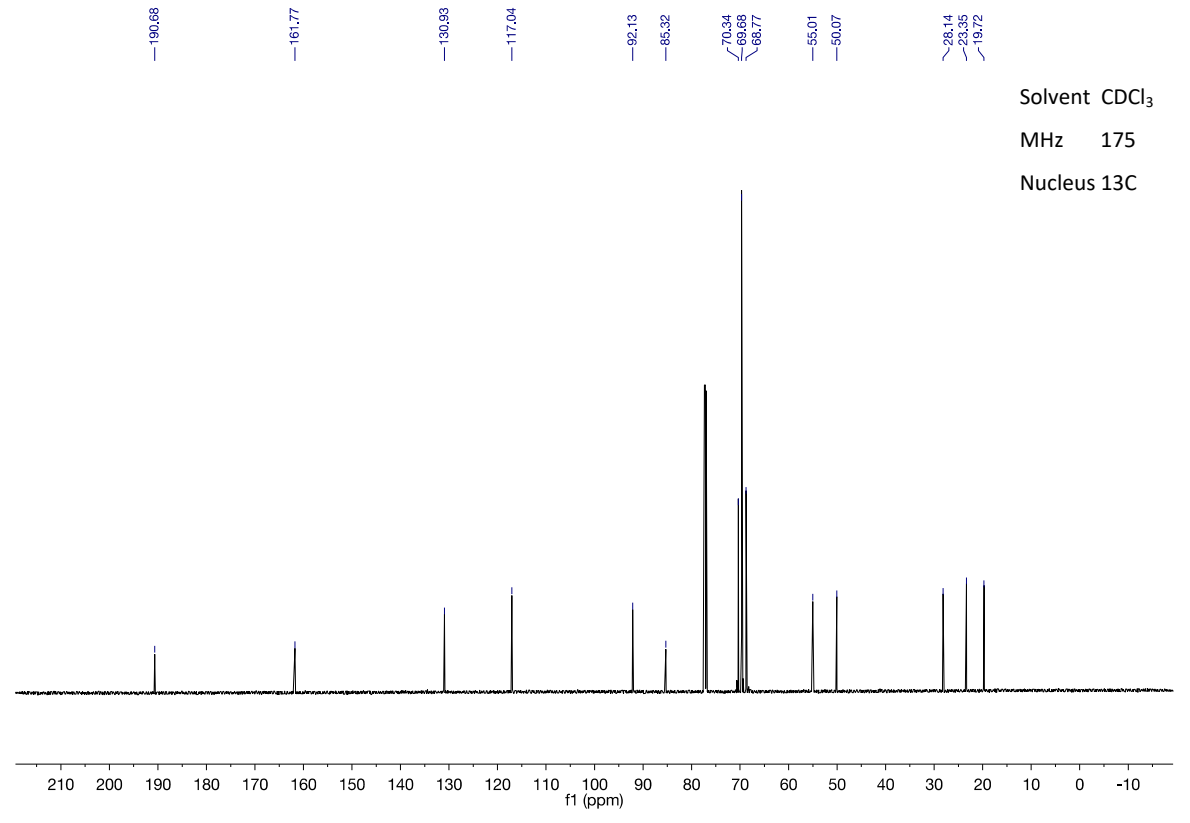
Nucleus 13C

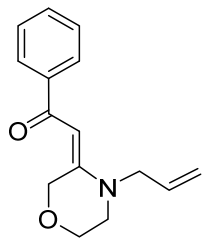



Fe
O
N

S2l

5.89
5.88
5.88
5.87
5.86
5.85
5.84
5.84
5.45
5.31
5.29
5.25
5.22
4.67
4.29
4.12
3.91
3.90
3.30
3.29
3.29
1.83
1.82
1.81
1.80
1.79
1.70
1.69
1.69
1.68
1.67
Solvent CDCl3
MHz 700
Nucleus 1H
1.07
1.01
1.04
1.00
1.96
2.06
4.79
2.00
3.91
2.00
2.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


190.68
161.77
130.93
117.04
92.13
85.32
70.34
69.68
68.77
55.01
50.07
28.14
23.35
19.72
Solvent CDCl3
MHz 175
Nucleus 13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

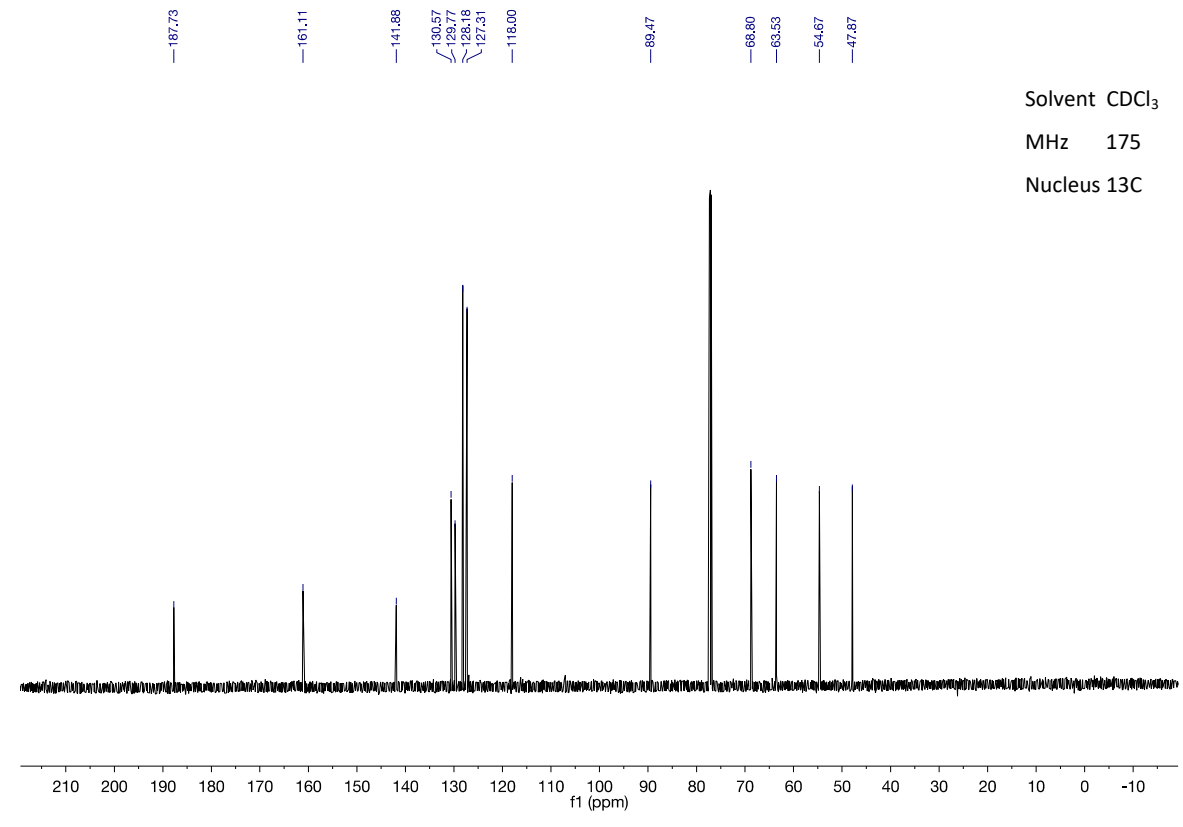


S2m

Solvent $CDCl_3$

MHz 700

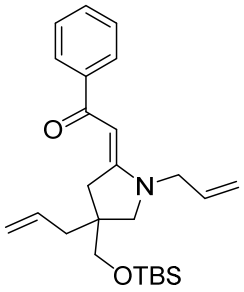
Nucleus 1H



Solvent $CDCl_3$

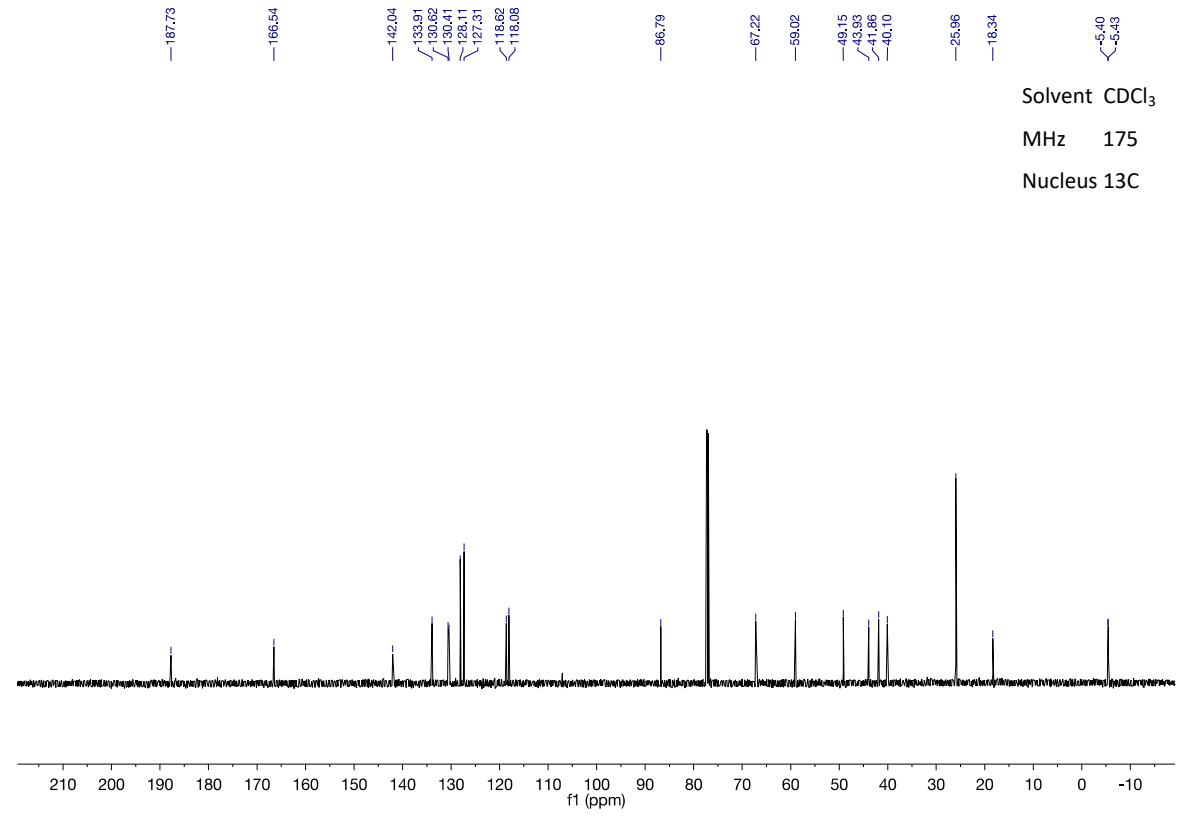
MHz 175

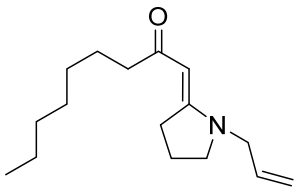
Nucleus 13C


O
N
OTBS

S2n

Solvent CDCl3
MHz 700
Nucleus 1H
f1 (ppm)


Solvent CDCl3
MHz 175
Nucleus 13C
f1 (ppm)

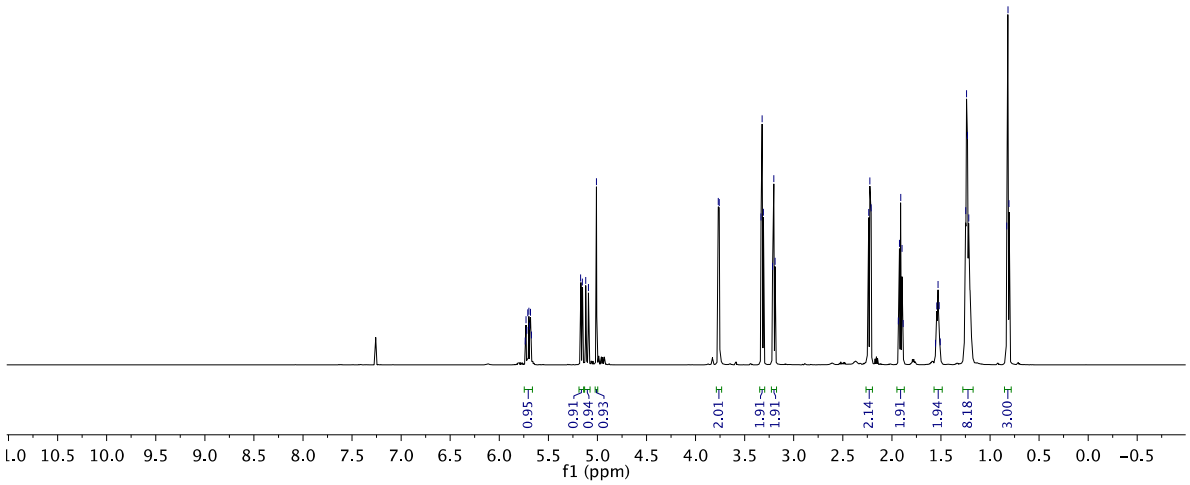


S2p

Solvent $CDCl_3$

MHz 600

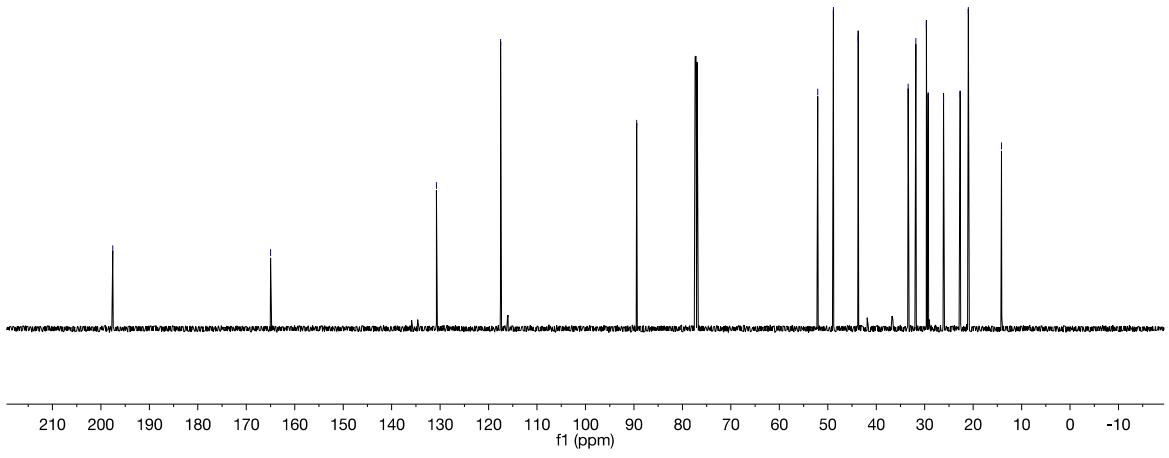
Nucleus 1H

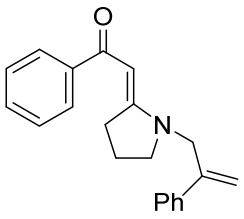


Solvent $CDCl_3$

MHz 150

Nucleus 13C



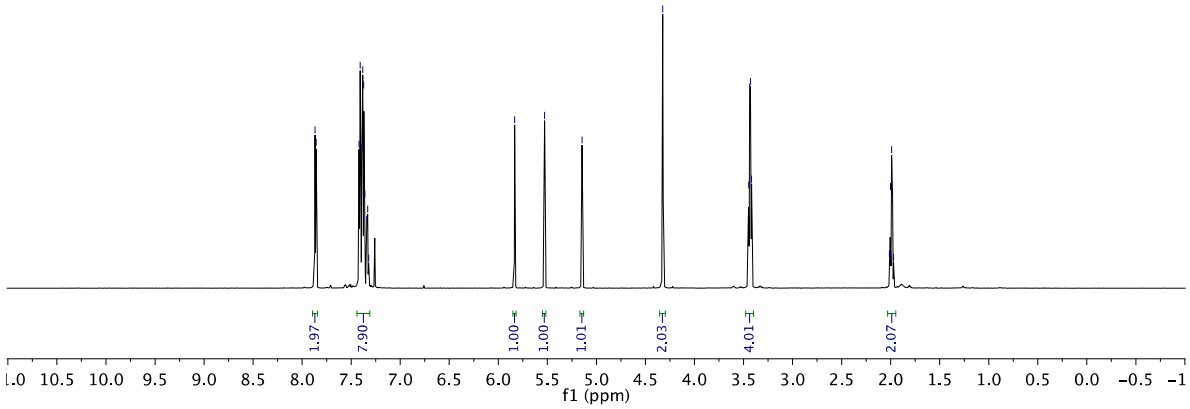


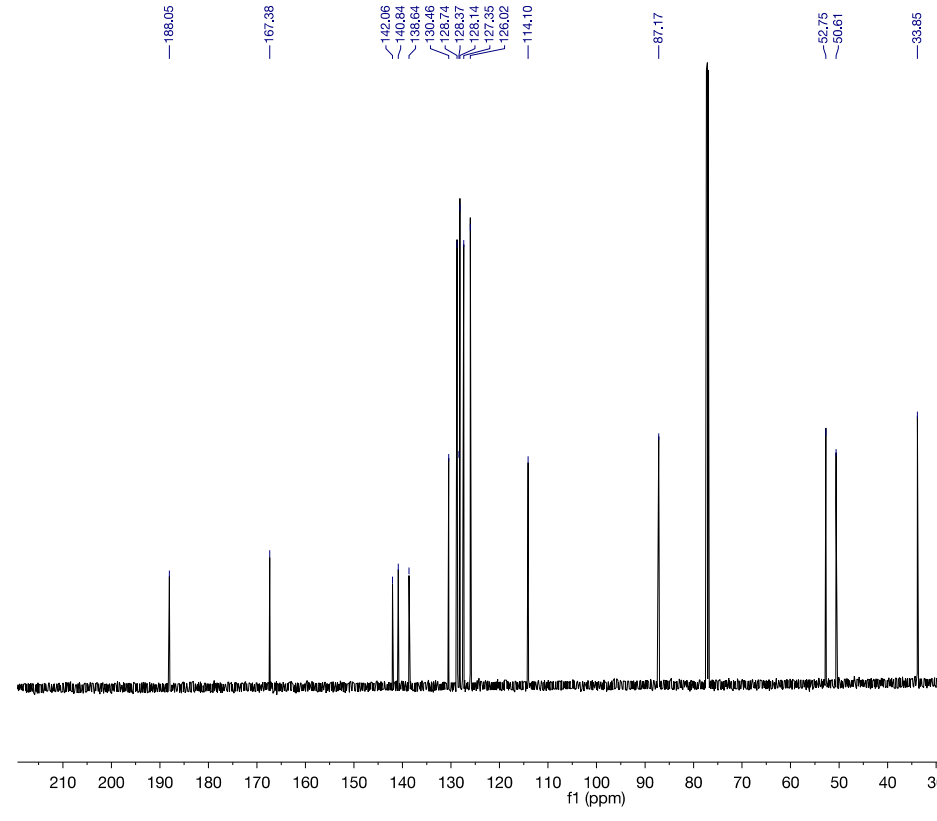
S2u

Solvent $CDCl_3$

MHz 700

Nucleus 1H

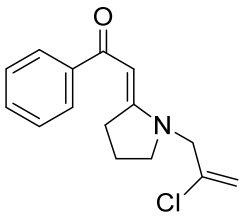




Solvent $CDCl_3$

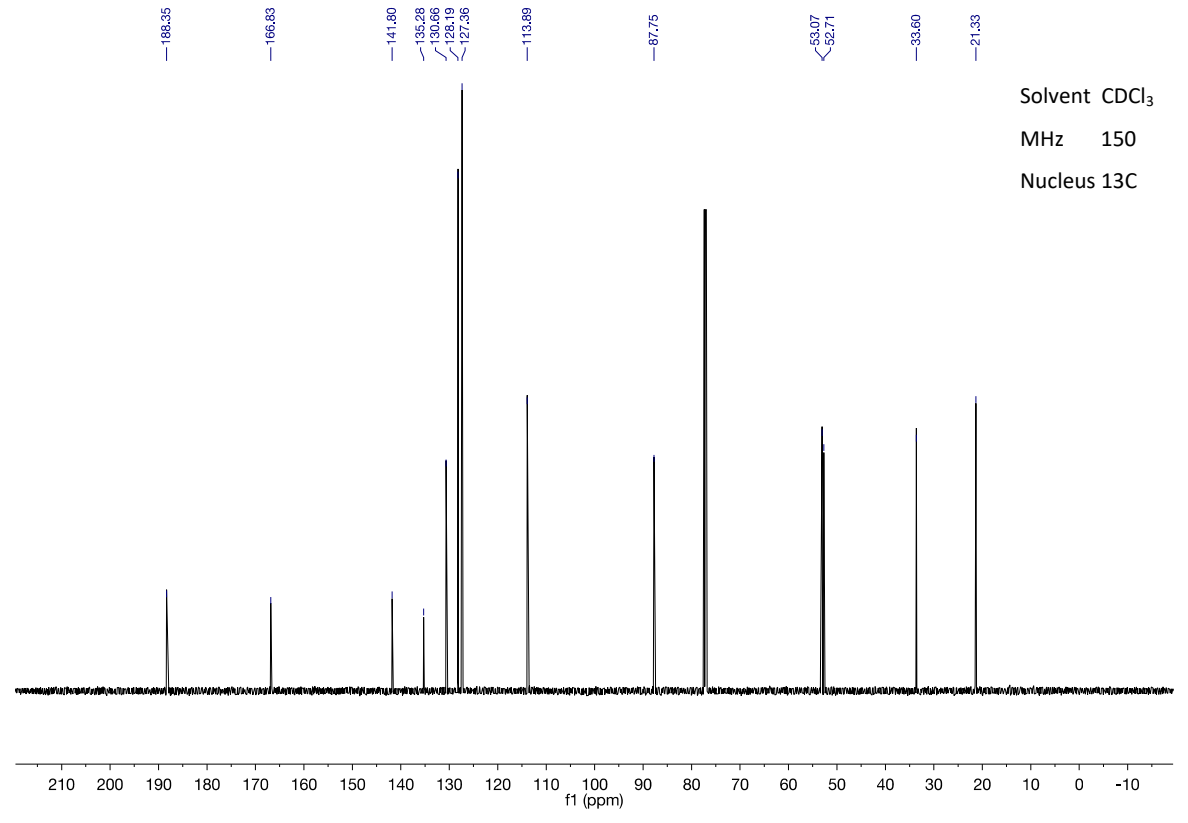
MHz 175

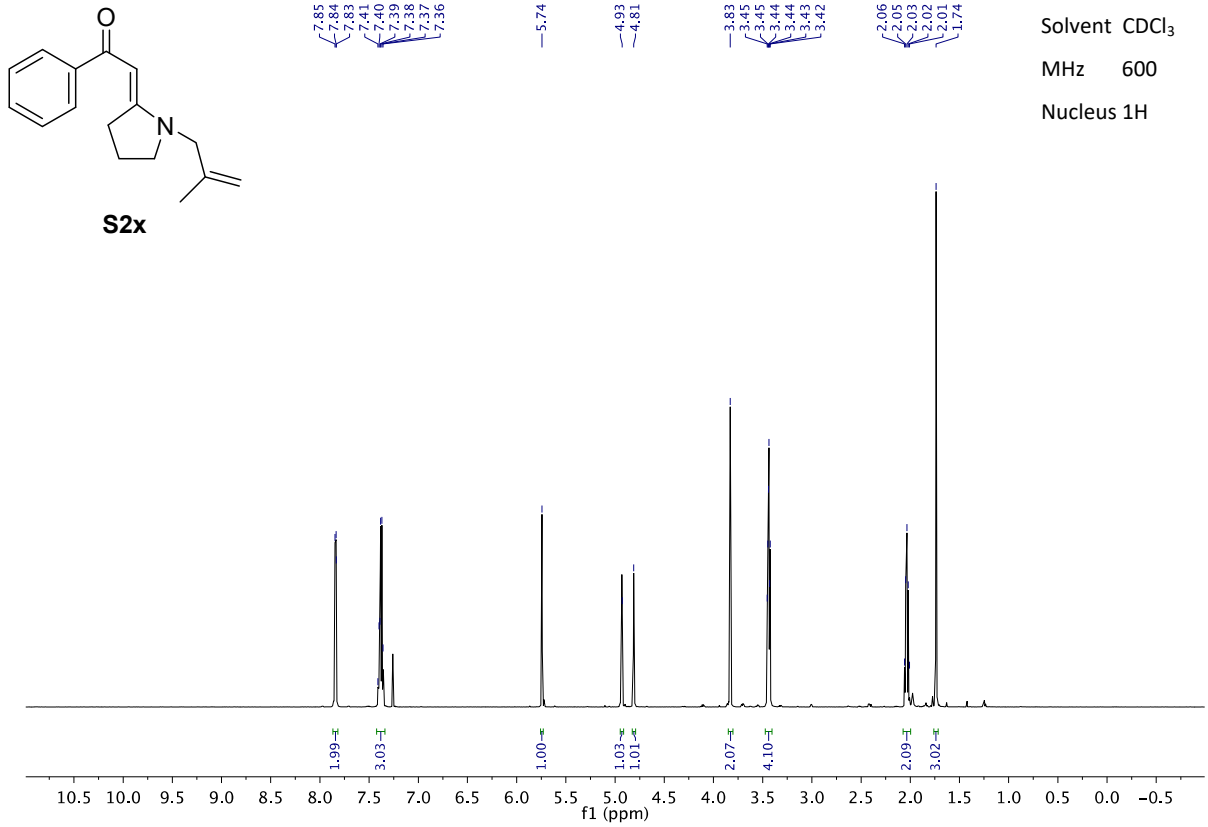
Nucleus 13C

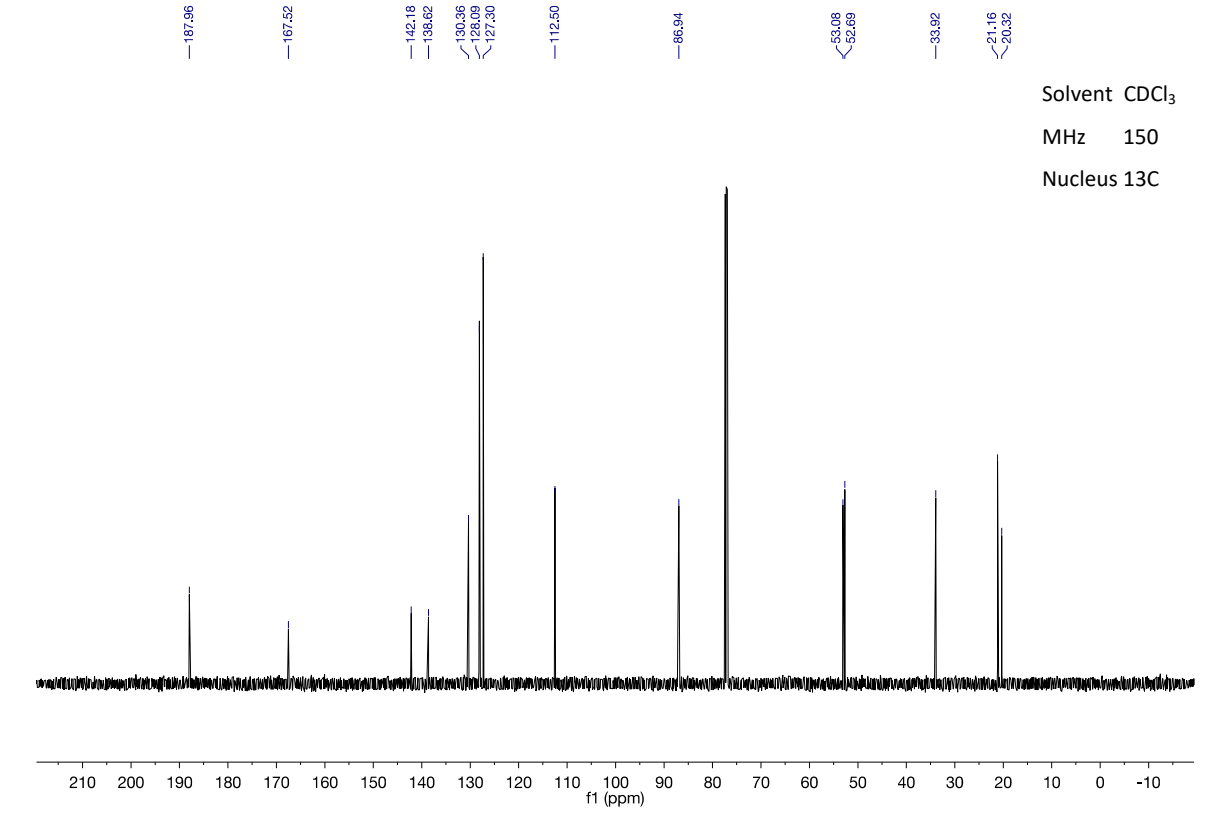

O
N
Cl

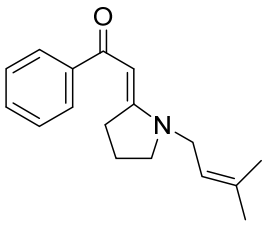
S2w

7.85
7.84
7.43
7.42
7.41
7.40
7.39
7.37
5.78
5.40
5.29
4.06
3.52
3.51
3.50
3.44
3.43
3.41
2.08
2.07
2.06
2.05
2.03
Solvent CDCl3
MHz 600
Nucleus 1H
1.95
2.98
1.00
1.00
1.00
2.04
2.02
2.01
2.15
f1 (ppm)


188.35
166.83
141.80
135.28
130.66
128.19
127.36
113.89
87.75
53.07
52.71
33.60
21.33
Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)

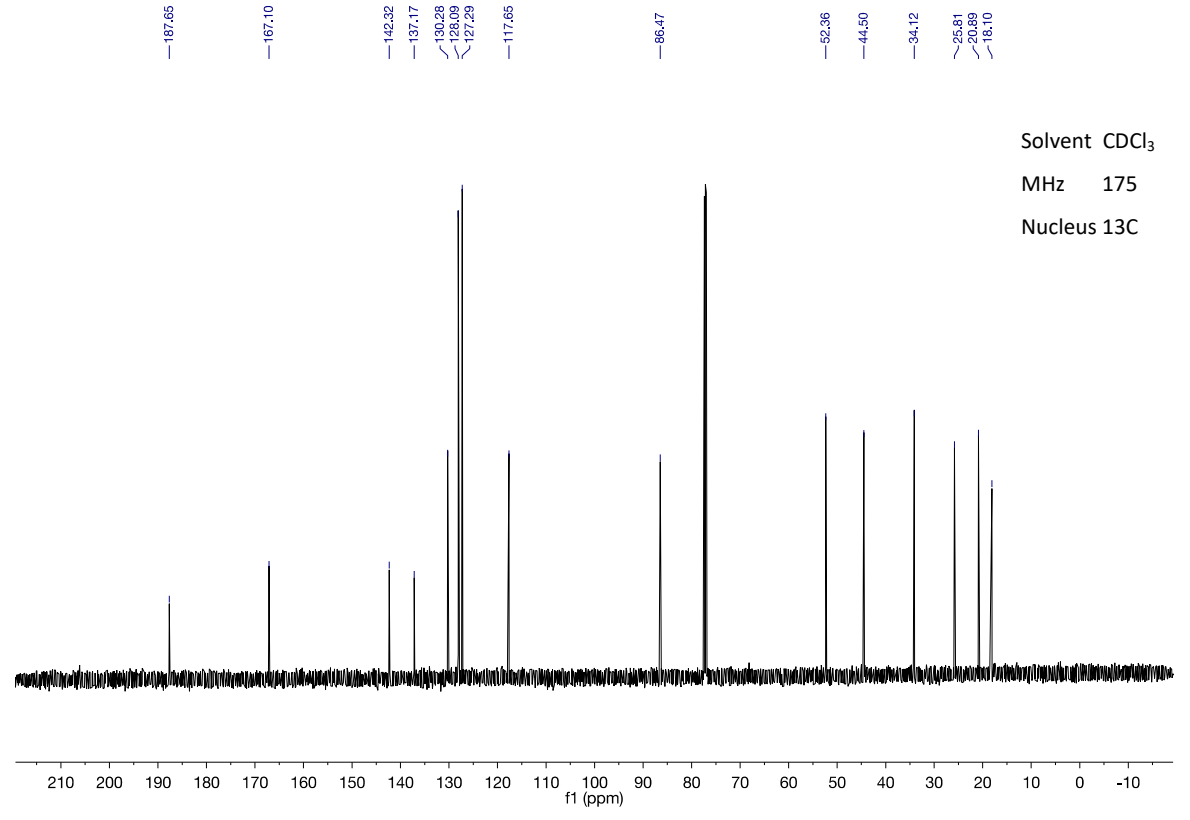

S2x
Solvent CDCl3
MHz 600
Nucleus 1H
f1 (ppm)

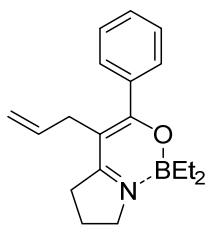

Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)



S2y

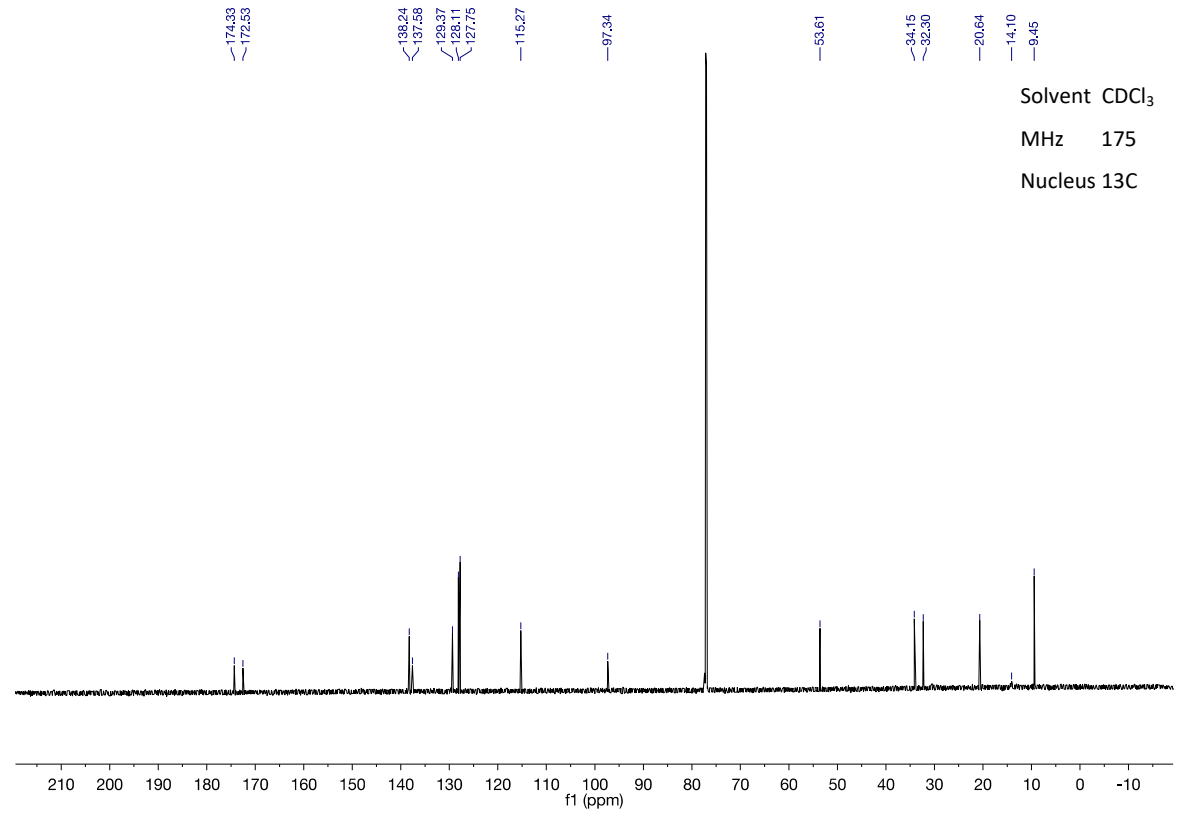
7.87
7.86
7.41
7.39
7.38
7.37
5.75
5.20
5.19
5.18
3.89
3.88
3.44
3.43
3.42
3.41
3.39
2.02
2.01
2.00
1.99
1.98
1.76
1.74
Solvent CDCl3
MHz 700
Nucleus 1H
1.98
3.15
1.00
0.99
2.09
4.13
2.16
5.91
f1 (ppm)

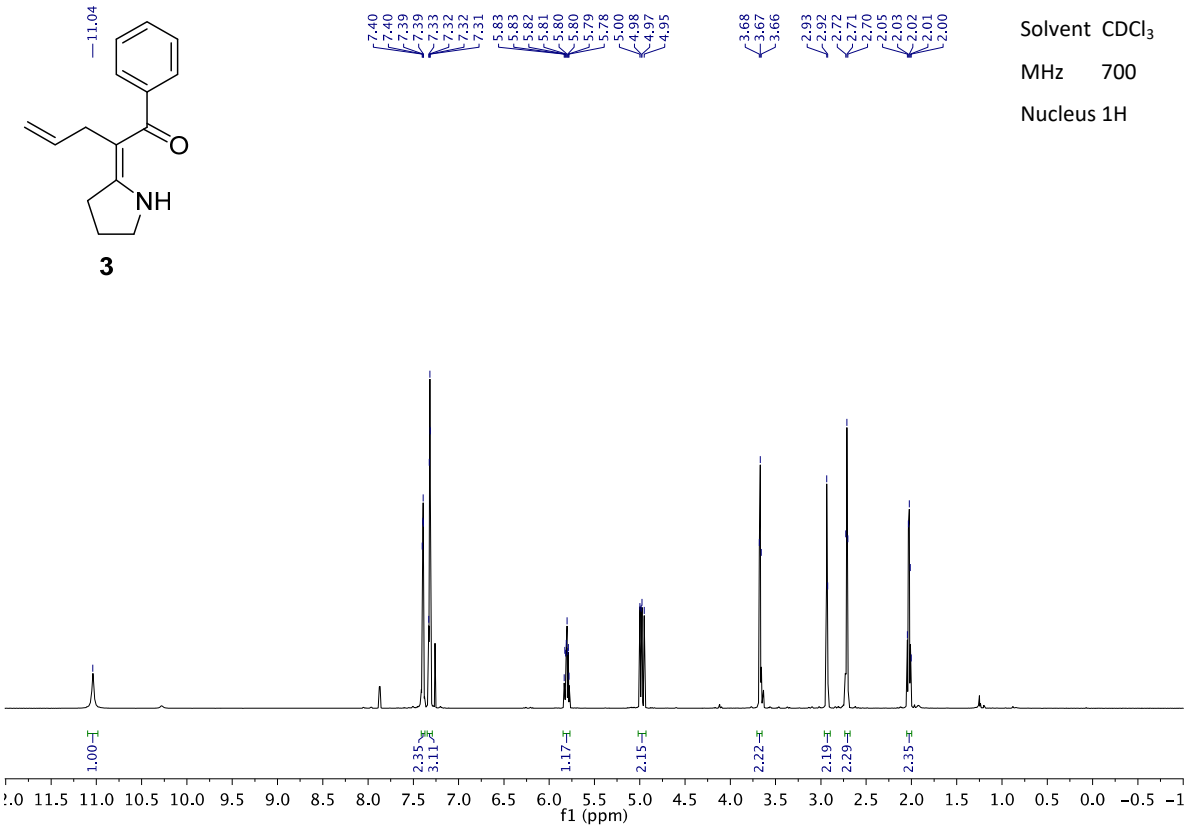

187.65
167.10
142.32
137.17
130.28
128.09
127.29
117.65
86.47
52.36
44.50
34.12
25.81
20.89
18.10
Solvent CDCl3
MHz 175
Nucleus 13C
f1 (ppm)

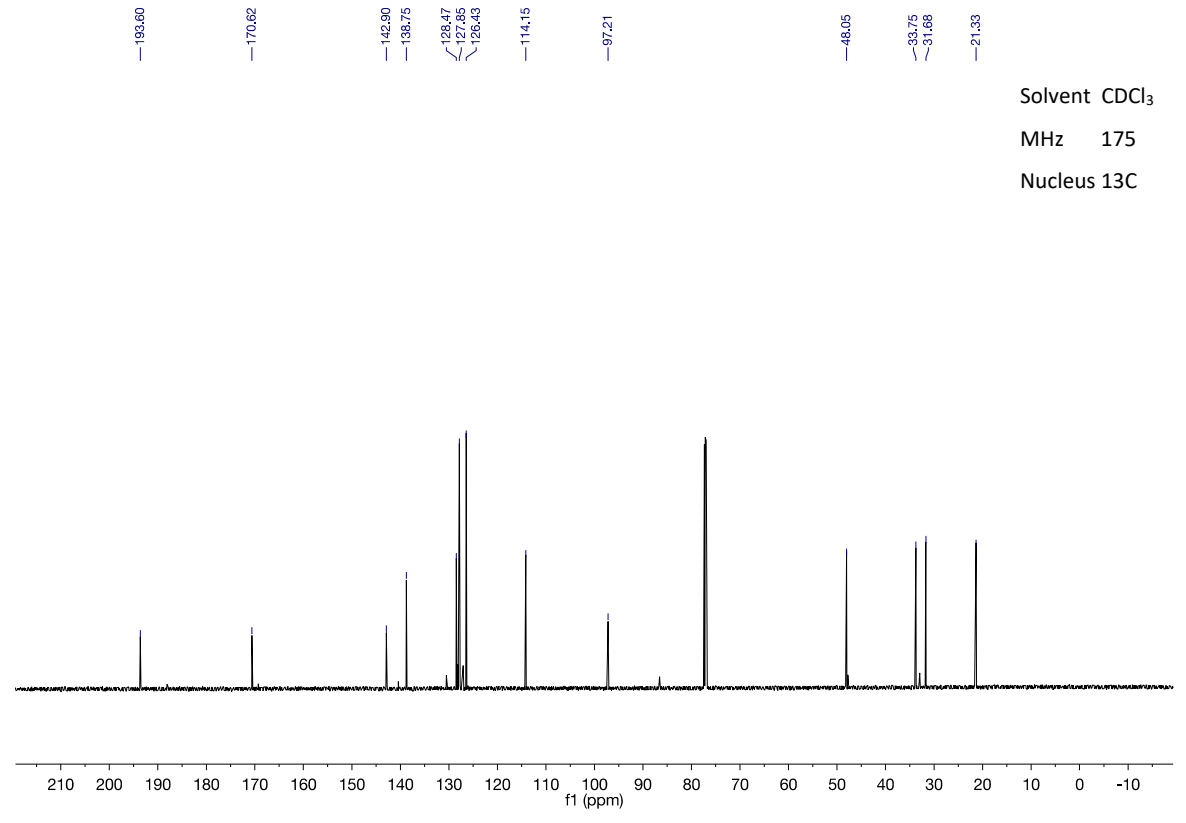

O
BEt2
N

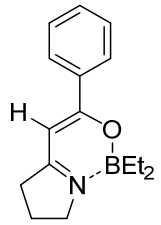
2a

Solvent CDCl3
MHz 700
Nucleus 1H
f1 (ppm)


Solvent CDCl3
MHz 175
Nucleus 13C
f1 (ppm)

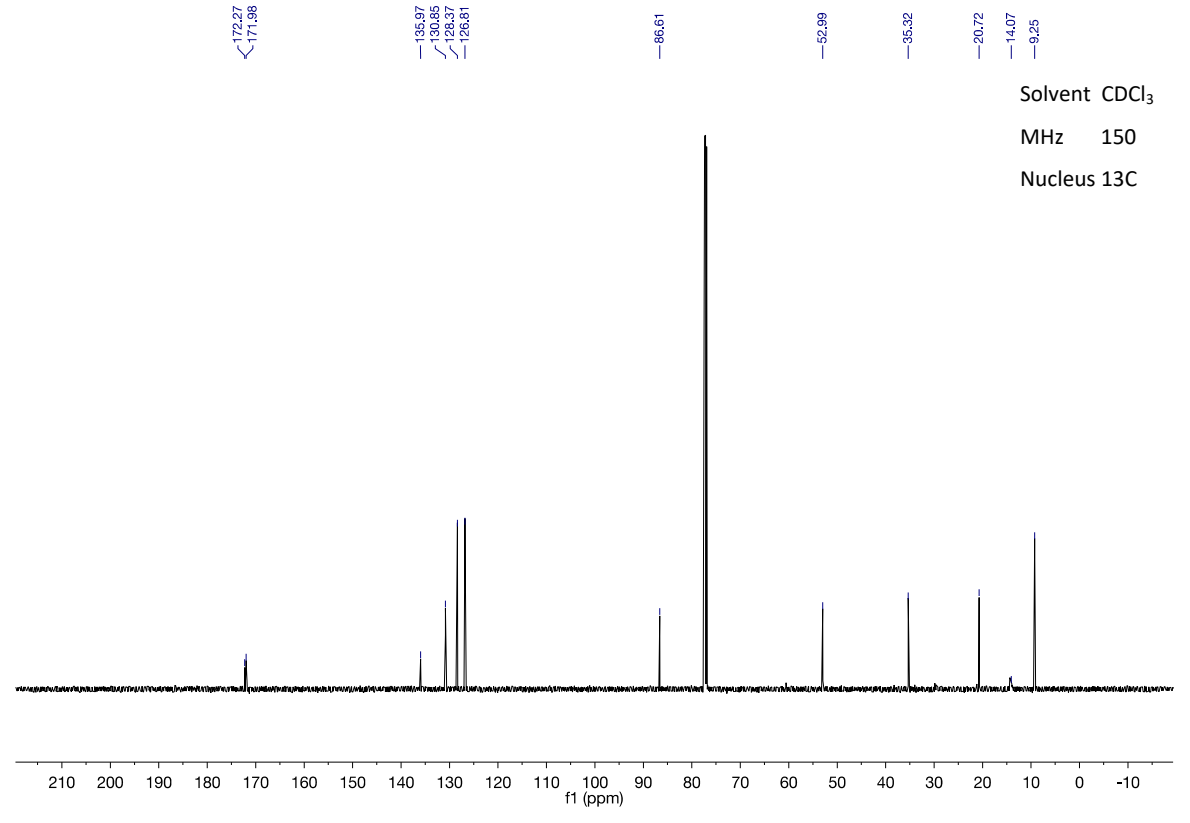

11.04
7.40
7.40
7.39
7.39
7.33
7.32
7.32
7.31
5.83
5.83
5.82
5.81
5.80
5.80
5.79
5.78
5.00
4.98
4.97
4.95
3.68
3.67
3.66
2.93
2.92
2.72
2.71
2.70
2.05
2.03
2.02
2.01
2.00
O
NH
3
Solvent CDCl3
MHz 700
Nucleus 1H
1.00
2.35
3.11
1.17
2.15
2.22
2.19
2.29
2.35
f1 (ppm)

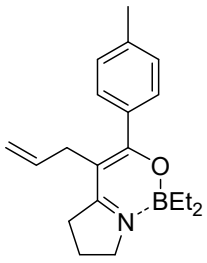

193.60
170.62
142.90
138.75
128.47
127.85
126.43
114.15
97.21
48.05
33.75
31.68
21.33
Solvent CDCl3
MHz 175
Nucleus 13C
f1 (ppm)


H
O
BEt2
N

4

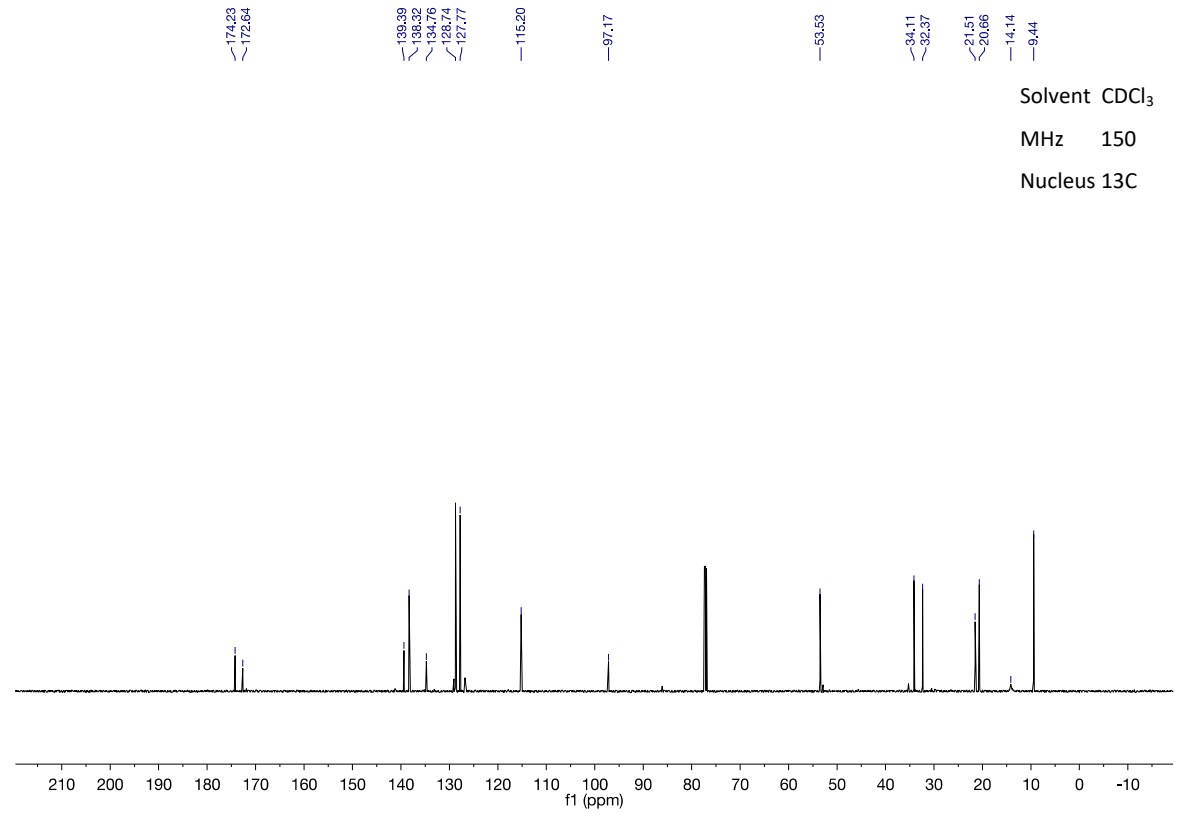
7.82
7.81
7.43
7.42
7.41
7.40
7.39
7.38
5.55
3.63
3.61
3.60
2.78
2.77
2.76
2.05
2.04
2.03
2.02
2.01
0.82
0.81
0.80
0.48
0.47
0.46
0.45
0.44
0.43
0.42
0.41
0.40
Solvent CDCl3
MHz 700
Nucleus 1H
1.90
3.06
1.00
2.16
2.19
2.32
5.71
4.31
f1 (ppm)

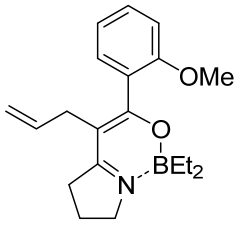

172.27
171.98
135.97
130.85
128.37
126.81
86.61
52.99
35.32
20.72
14.07
9.25
Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)


O
BEt2
N

2b

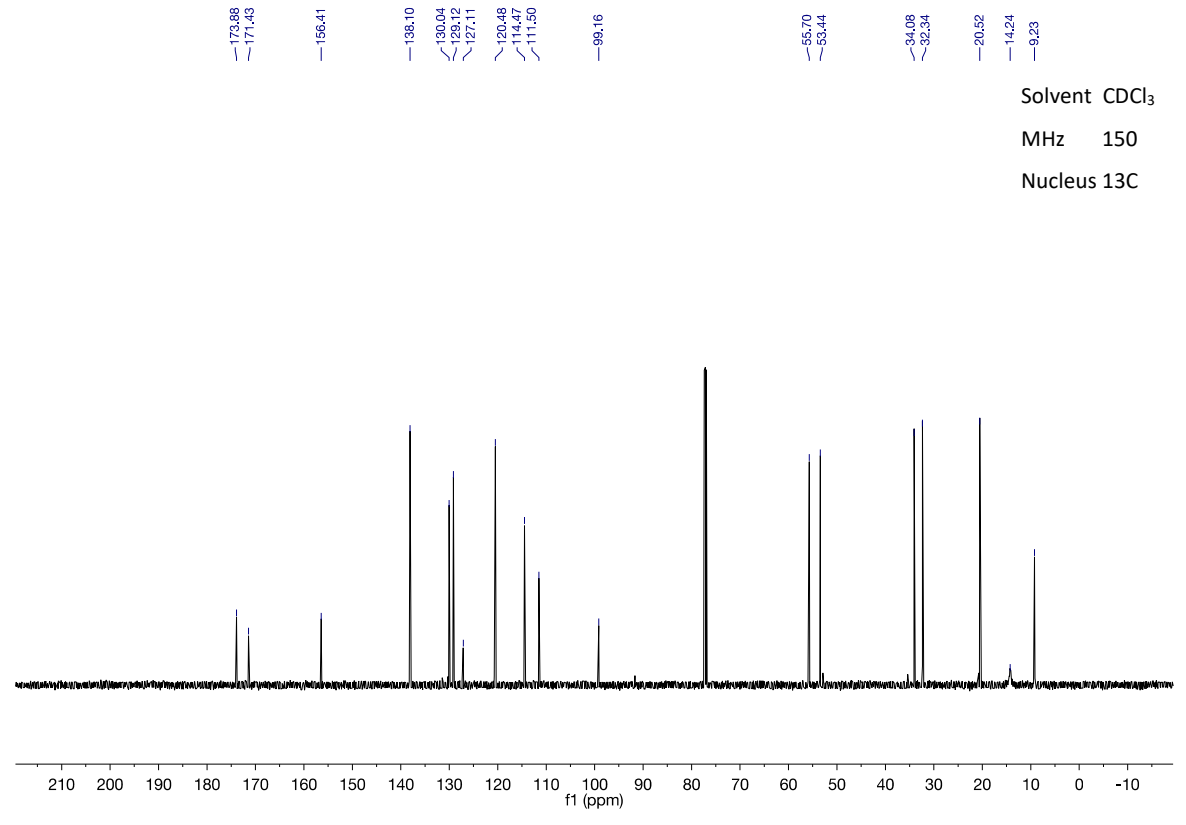
7.42
7.40
7.17
7.15
5.94
5.93
5.92
5.92
5.90
5.90
5.89
5.88
5.16
5.15
5.13
5.13
5.12
5.11
5.10
3.66
3.65
3.63
2.92
2.91
2.91
2.90
2.80
2.79
2.78
2.36
2.03
2.01
2.00
1.99
1.97
0.88
0.87
0.85
0.46
0.44
0.43
0.42
Solvent CDCl3
MHz 600
Nucleus 1H
1.89
1.90
0.93
2.02
1.99
2.03
2.01
2.99
2.12
6.00
4.29
f1 (ppm)

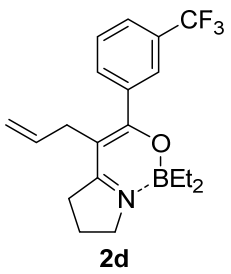

174.23
172.64
139.39
138.32
134.76
128.74
127.77
115.20
97.17
53.53
34.11
32.37
21.51
20.66
14.14
9.44
Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)


OMe
O
BEt2
N

2c

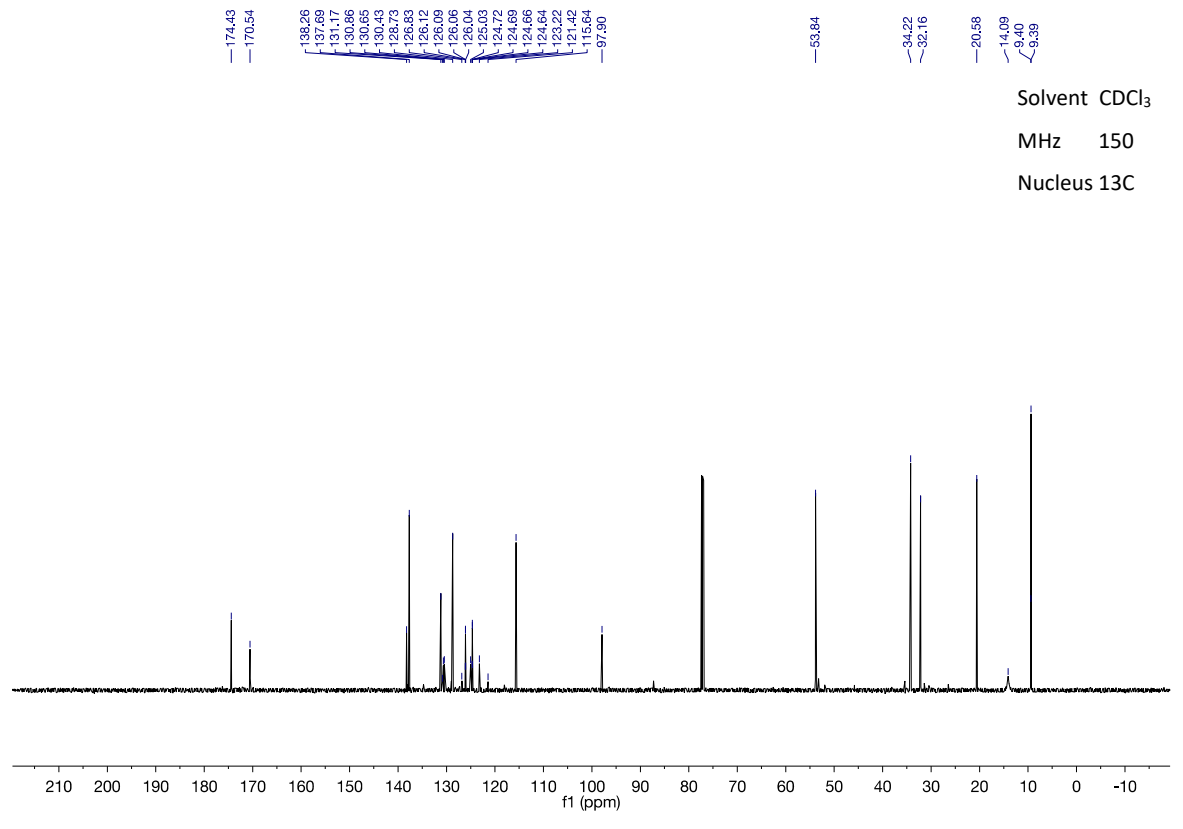
7.31
7.29
7.28
7.22
7.21
6.95
6.93
6.92
6.90
6.89
5.74
5.73
5.73
5.72
5.71
5.70
5.69
5.68
5.01
4.98
4.96
4.94
3.80
3.65
3.64
3.62
2.81
2.80
2.79
2.67
2.66
2.02
2.01
2.00
1.99
1.97
0.90
0.89
0.88
0.48
0.47
0.46
0.44
0.43
0.42
0.40
0.39
0.38
Solvent CDCl3
MHz 600
Nucleus 1H
0.97
0.96
1.01
0.99
0.96
2.00
3.06
2.05
2.00
1.97
2.08
6.12
4.27
f1 (ppm)

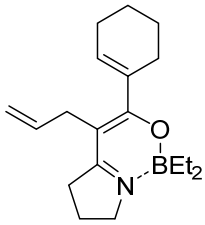

173.88
171.43
156.41
138.10
130.04
129.12
127.11
120.48
114.47
111.50
99.16
55.70
53.44
34.08
32.34
20.52
14.24
9.23
Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)


CF3
O
BEt2
N

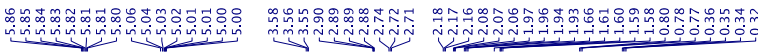
2d

7.77
7.70
7.69
7.63
7.61
7.50
7.48
7.47
5.94
5.93
5.92
5.91
5.90
5.89
5.89
5.88
5.17
5.16
5.15
5.13
3.69
3.68
3.66
2.86
2.86
2.85
2.85
2.84
2.83
2.82
2.81
2.06
2.04
2.03
2.02
2.00
0.88
0.87
0.86
0.47
0.46
0.44
0.43
Solvent CDCl3
MHz 600
Nucleus 1H
0.86
0.93
0.90
0.95
0.91
2.00
1.96
3.95
2.02
5.93
4.14
f1 (ppm)


174.43
170.54
138.26
137.69
131.17
130.86
130.65
130.43
128.73
126.83
126.12
126.09
126.06
126.04
125.03
124.72
124.69
124.66
124.64
123.22
121.42
115.64
97.90
53.84
34.22
32.16
20.58
14.09
9.40
9.39
Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)



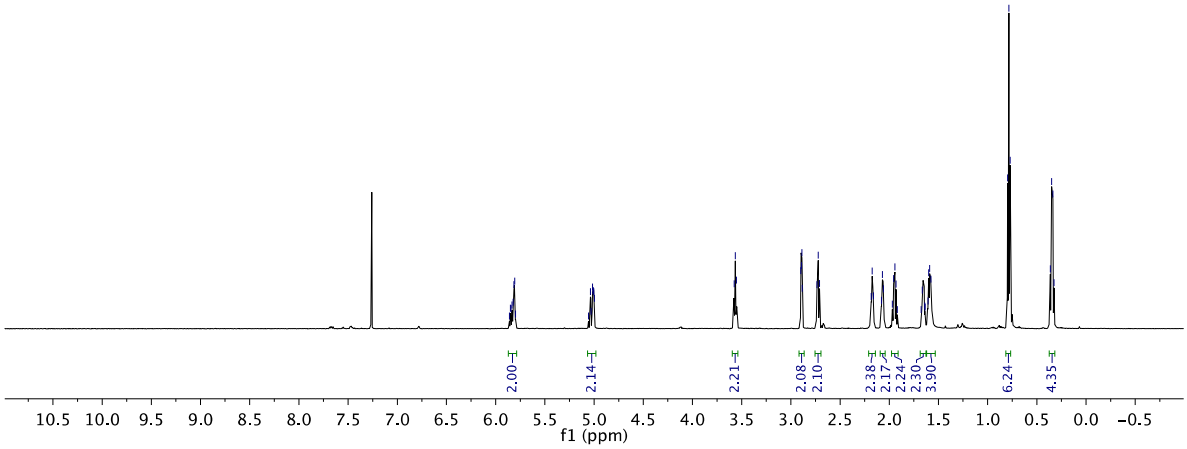
2e



Solvent $CDCl_3$

MHz 600

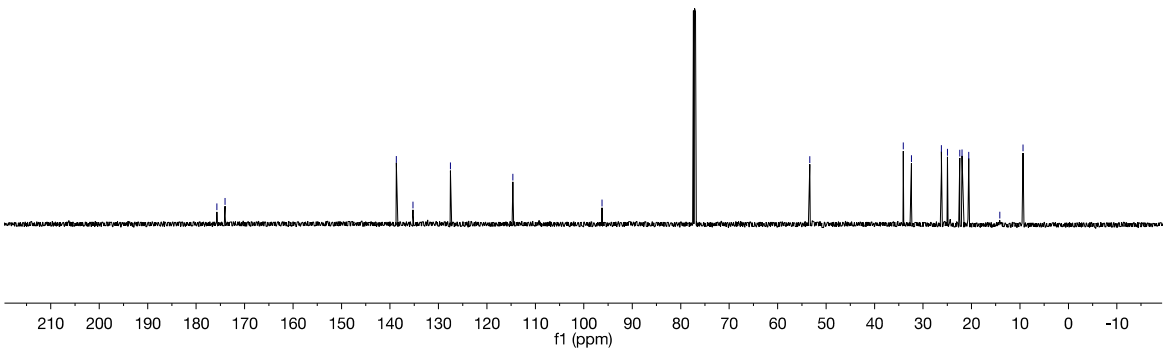
Nucleus 1H

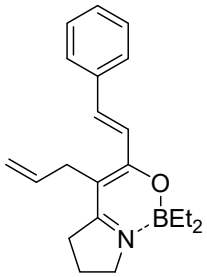


Solvent $CDCl_3$

MHz 150

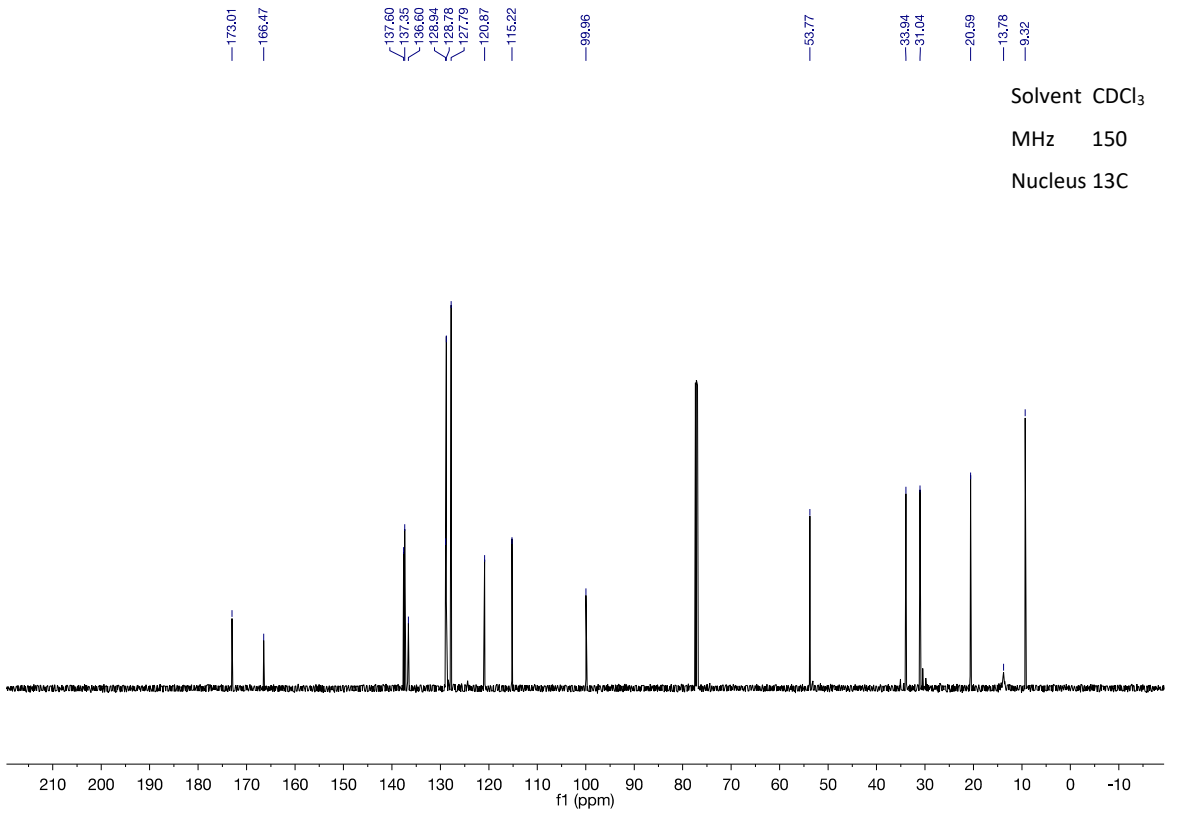
Nucleus 13C

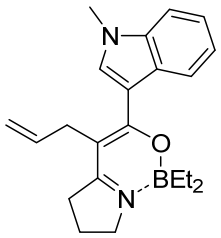



O
BEt2
N

2f

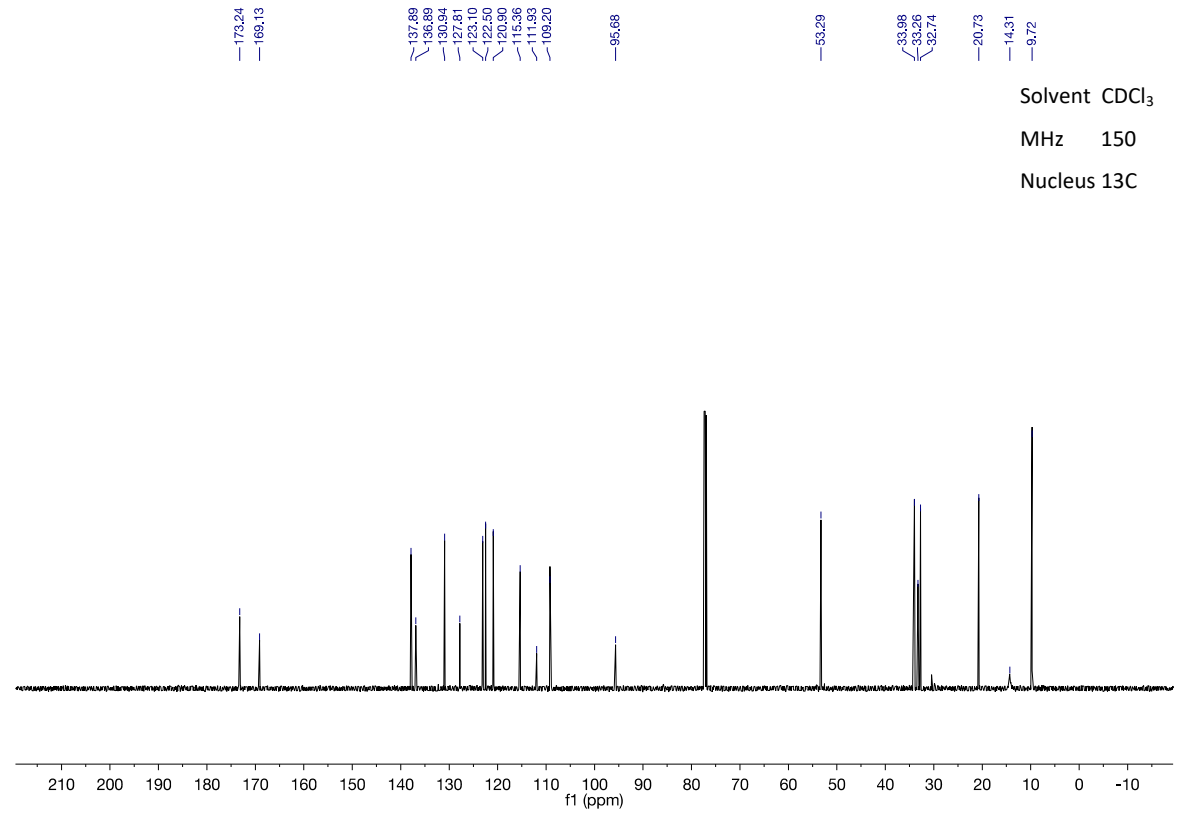
Solvent CDCl3
MHz 600
Nucleus 1H
f1 (ppm)

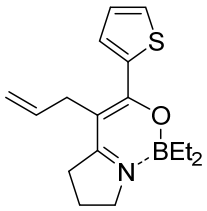

Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)


N
O
BEt2
N

2g

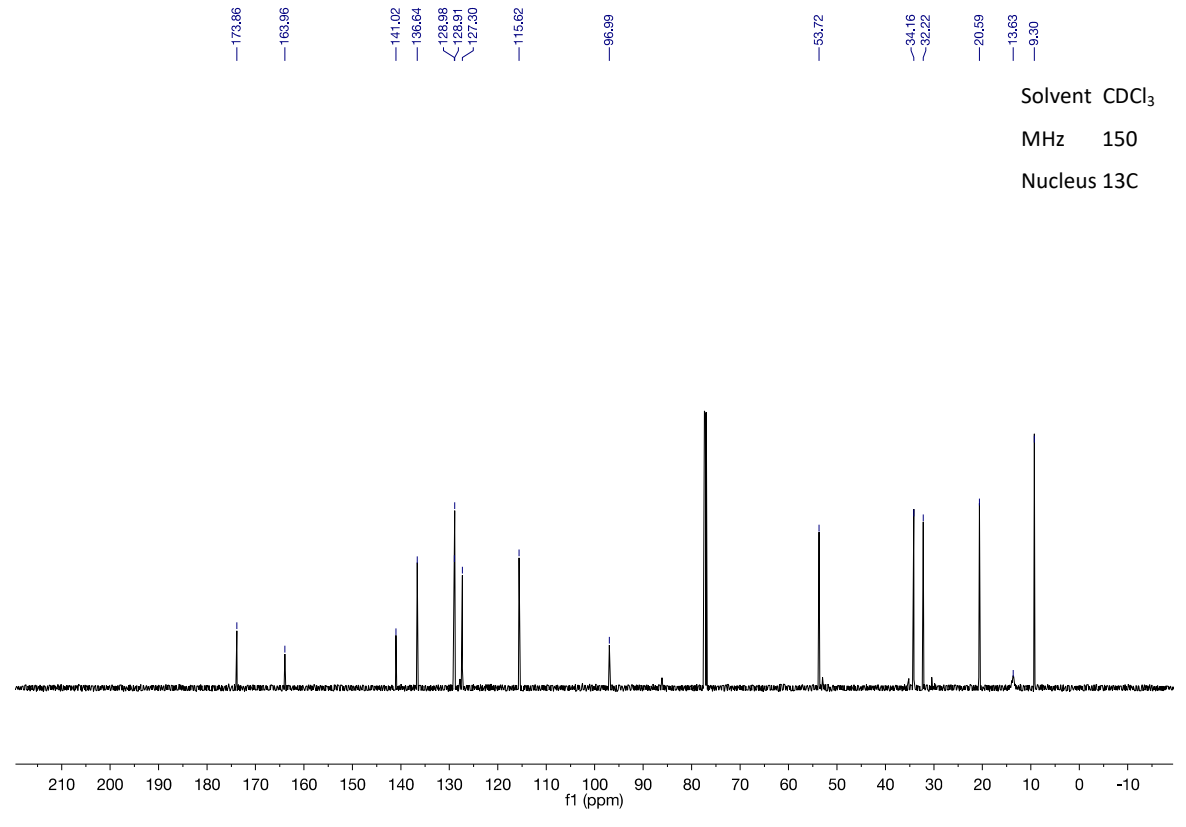
Solvent CDCl3
MHz 600
Nucleus 1H
f1 (ppm)

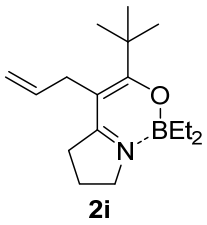

Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)


S
O
BEt2
N

2h

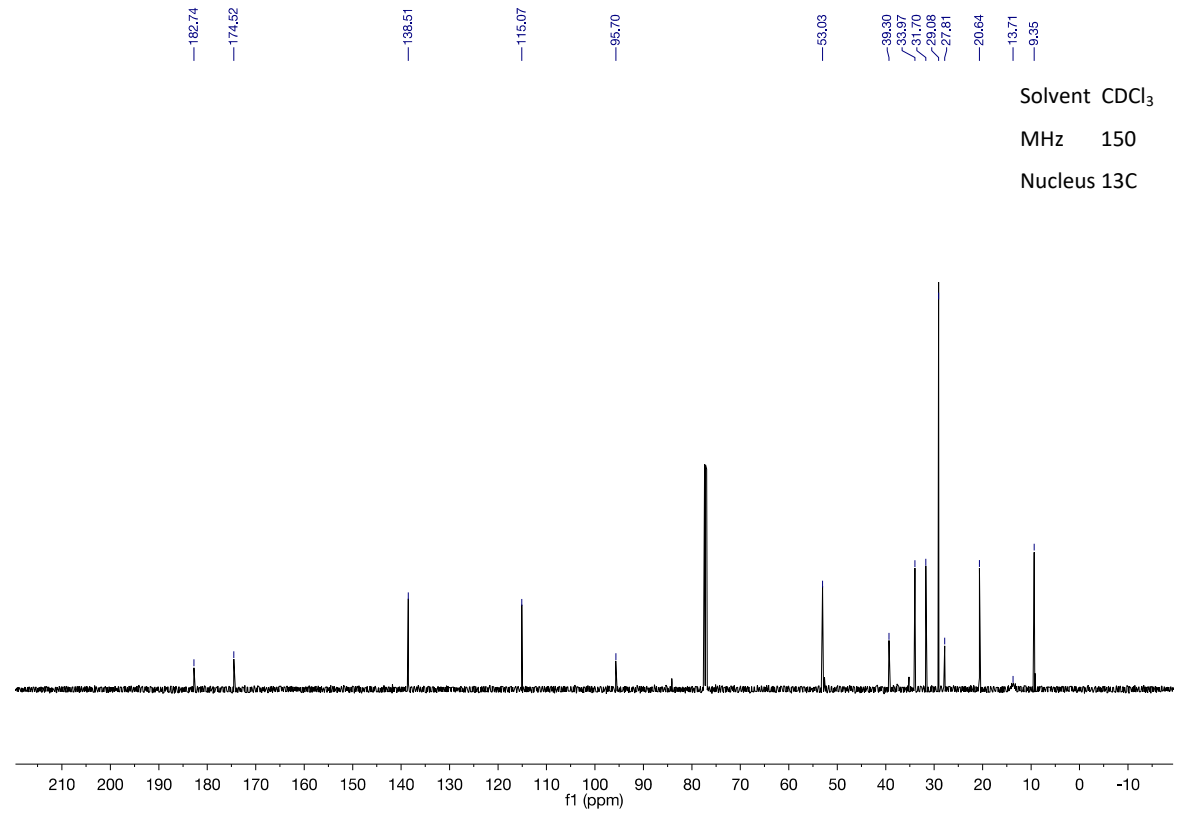
7.44
7.43
7.42
7.04
7.03
7.02
6.03
6.02
6.01
6.00
5.99
5.98
5.97
5.96
5.19
5.17
5.16
5.15
5.13
3.67
3.66
3.65
3.19
3.18
3.17
2.82
2.80
2.79
2.03
2.02
2.01
1.99
1.98
0.85
0.84
0.83
0.47
0.46
0.45
0.43
0.42
0.41
0.40
0.39
Solvent CDCl3
MHz 600
Nucleus 1H
1.86
0.90
0.94
2.00
1.99
1.99
1.98
2.15
6.14
4.28
f1 (ppm)

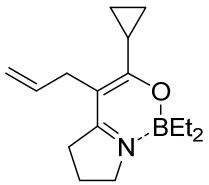

173.86
163.96
141.02
136.64
128.98
128.91
127.30
115.62
96.99
53.72
34.16
32.22
20.59
13.63
9.30
Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)


O
BEt2
N

2i

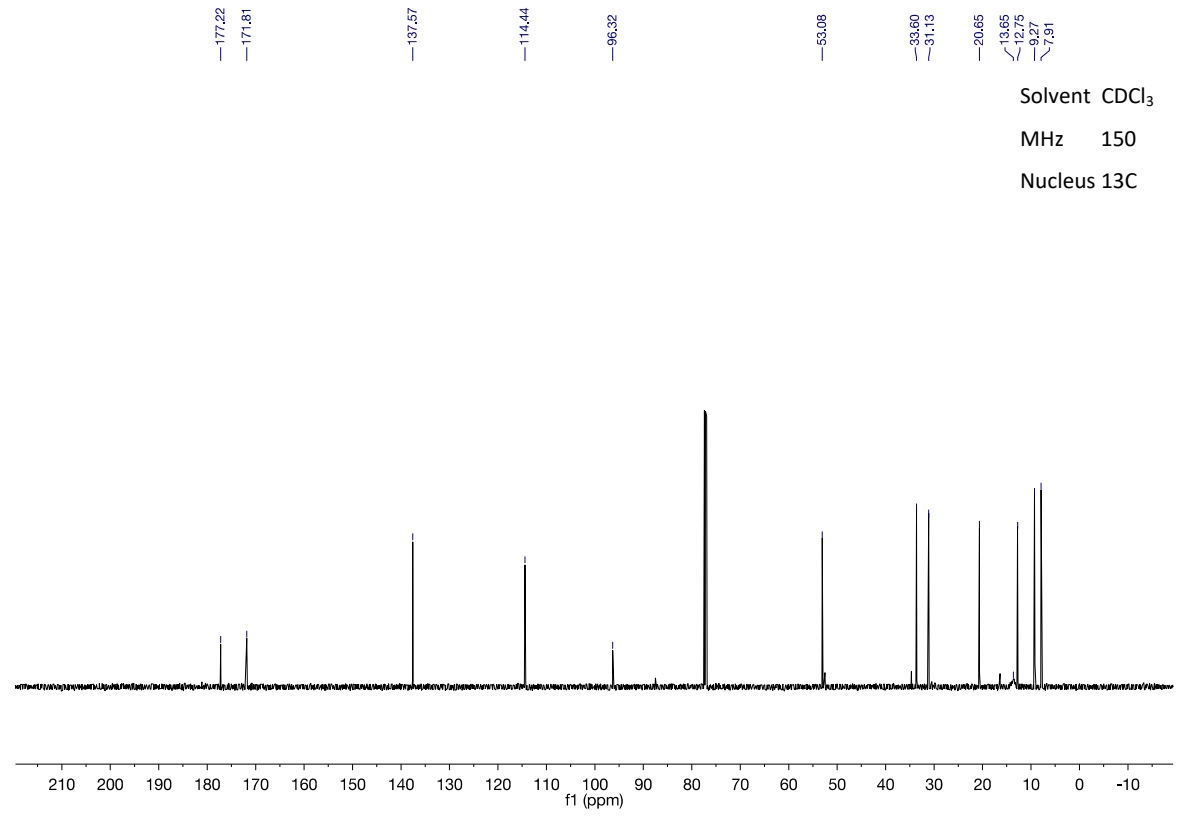
Solvent CDCl3
MHz 600
Nucleus 1H
f1 (ppm)

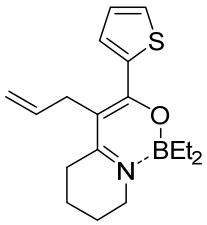

Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)


O
BEt2
N

2j

Solvent CDCl3
MHz 600
Nucleus 1H
f1 (ppm)


Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)

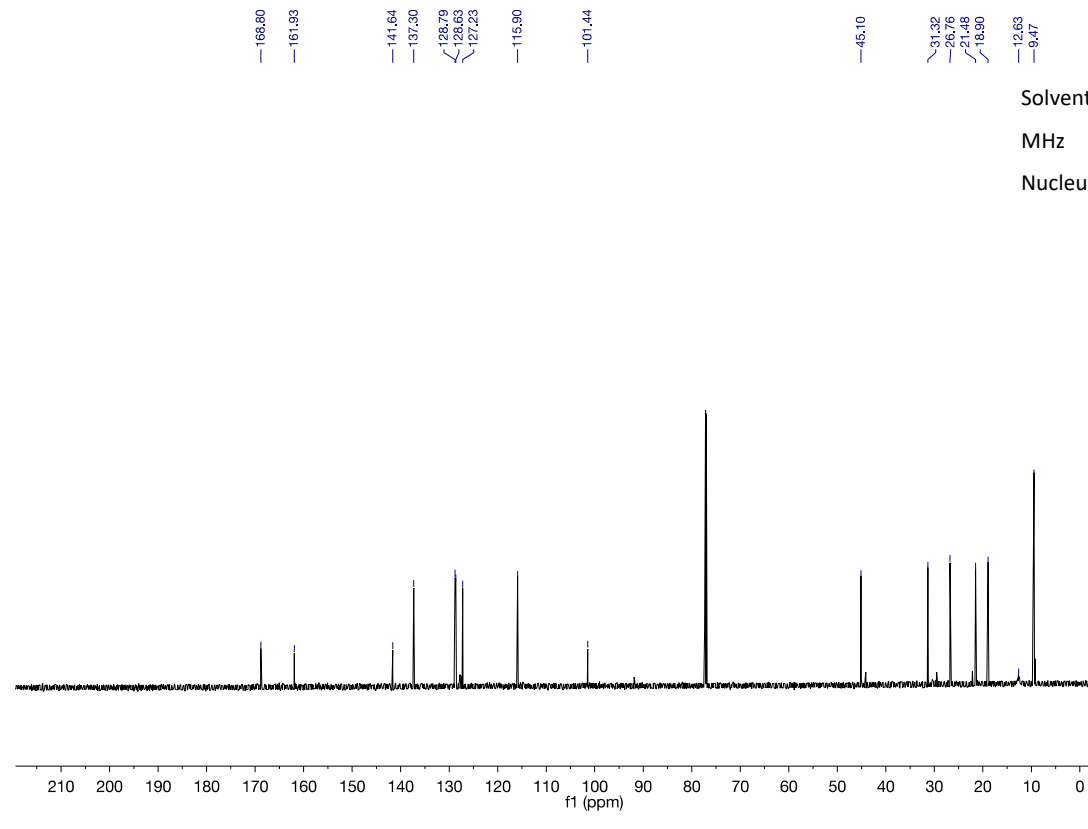


2k

Solvent $CDCl_3$

MHz 700

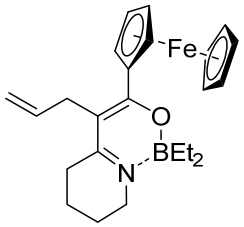
Nucleus 1H



Solvent $CDCl_3$

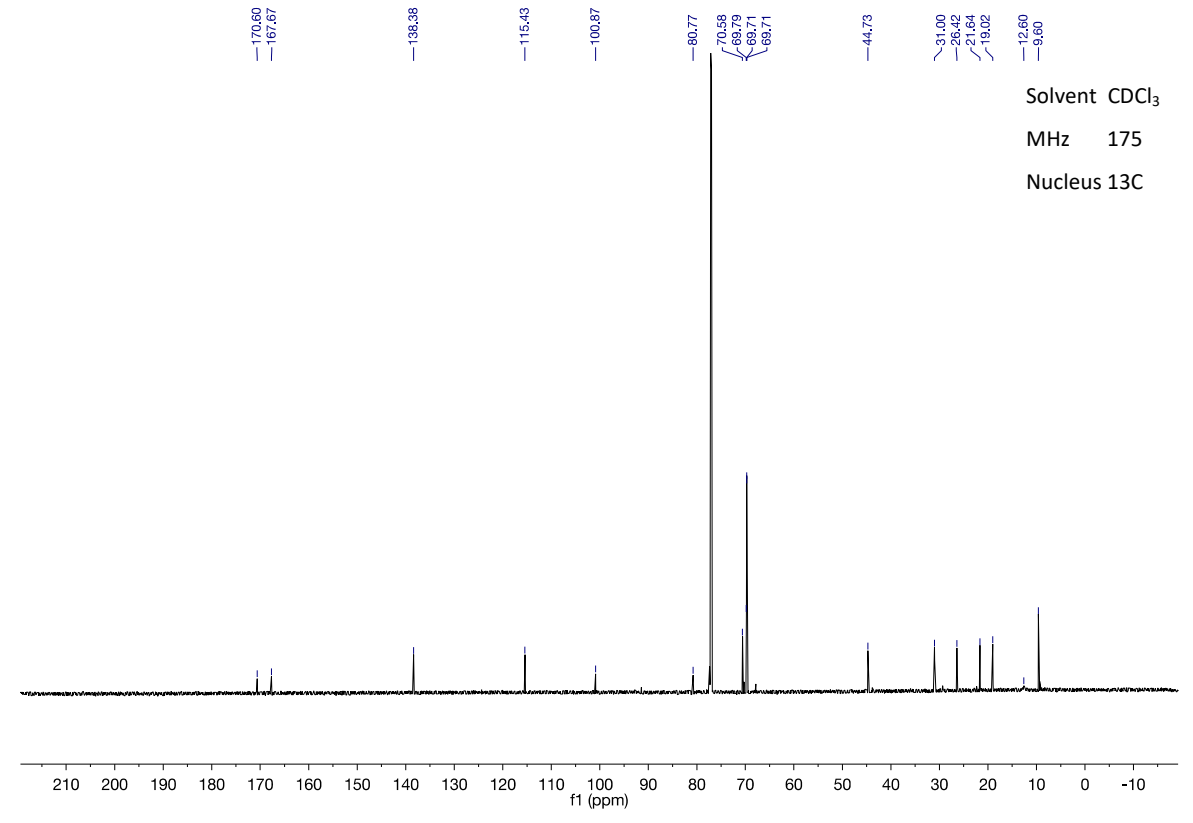
MHz 175

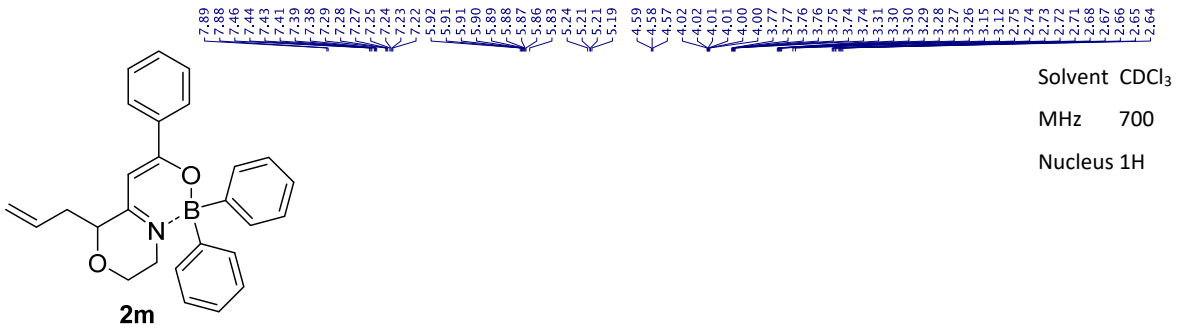
Nucleus 13C

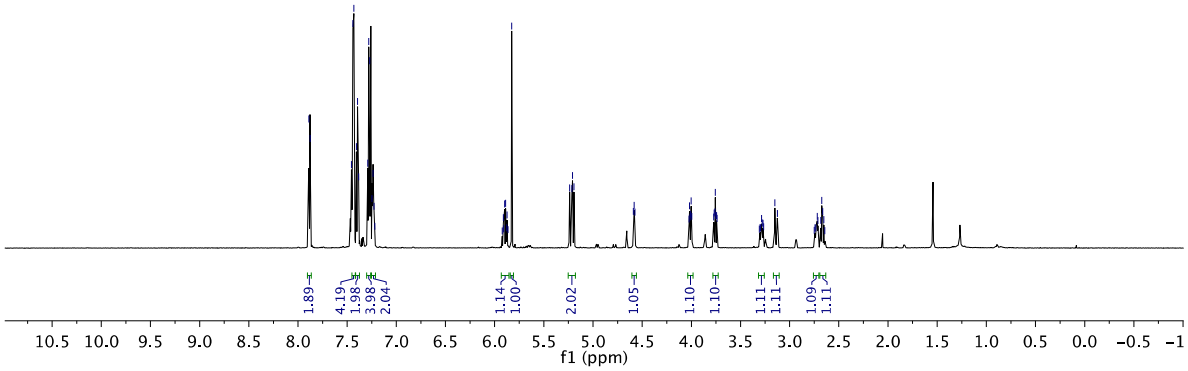

Fe
O
BEt2
N

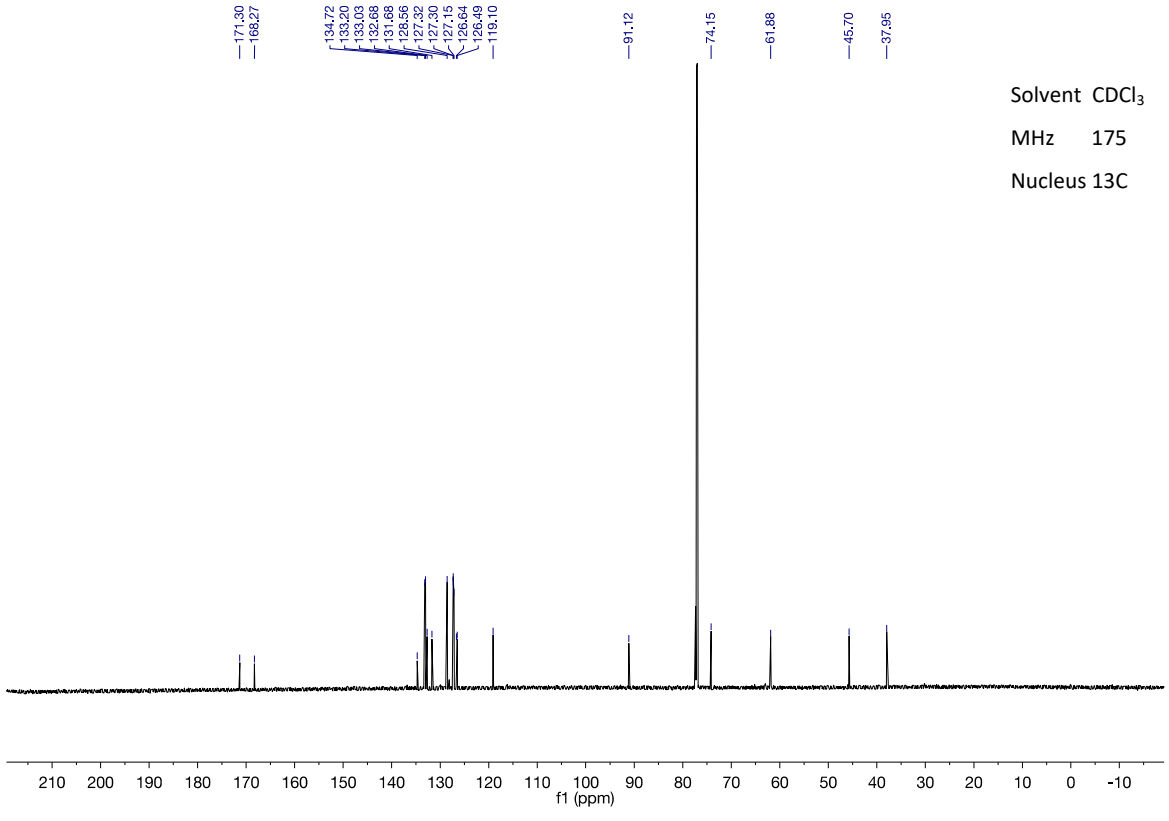
2l

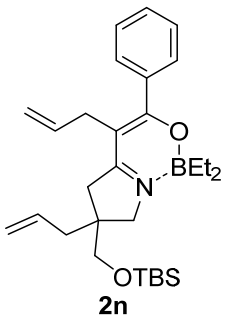
6.01
6.00
5.99
5.99
5.98
5.98
5.97
5.96
5.96
5.17
5.17
5.16
5.15
5.15
4.69
4.29
4.19
3.26
3.19
2.45
2.44
2.43
1.69
1.68
0.88
0.87
0.86
0.45
0.44
0.43
0.42
Solvent CDCl3
MHz 700
Nucleus 1H
1.22
2.00
1.87
1.87
4.82
2.08
2.19
2.09
4.34
5.69
4.07
f1 (ppm)


170.60
167.67
138.38
115.43
100.87
80.77
70.58
69.79
69.71
69.71
44.73
31.00
26.42
21.64
19.02
12.60
9.60
Solvent CDCl3
MHz 175
Nucleus 13C
f1 (ppm)


7.89
7.88
7.46
7.44
7.43
7.41
7.39
7.38
7.29
7.28
7.27
7.25
7.24
7.23
7.22
5.92
5.91
5.91
5.90
5.89
5.88
5.87
5.86
5.83
5.24
5.21
5.21
5.19
4.59
4.58
4.57
4.02
4.02
4.01
4.01
4.00
4.00
3.77
3.77
3.76
3.76
3.75
3.74
3.74
3.31
3.30
3.30
3.29
3.28
3.27
3.26
3.15
3.12
2.75
2.74
2.73
2.72
2.71
2.68
2.67
2.66
2.65
2.64
O
B
N
O
2m
Solvent CDCl3
MHz 700
Nucleus 1H

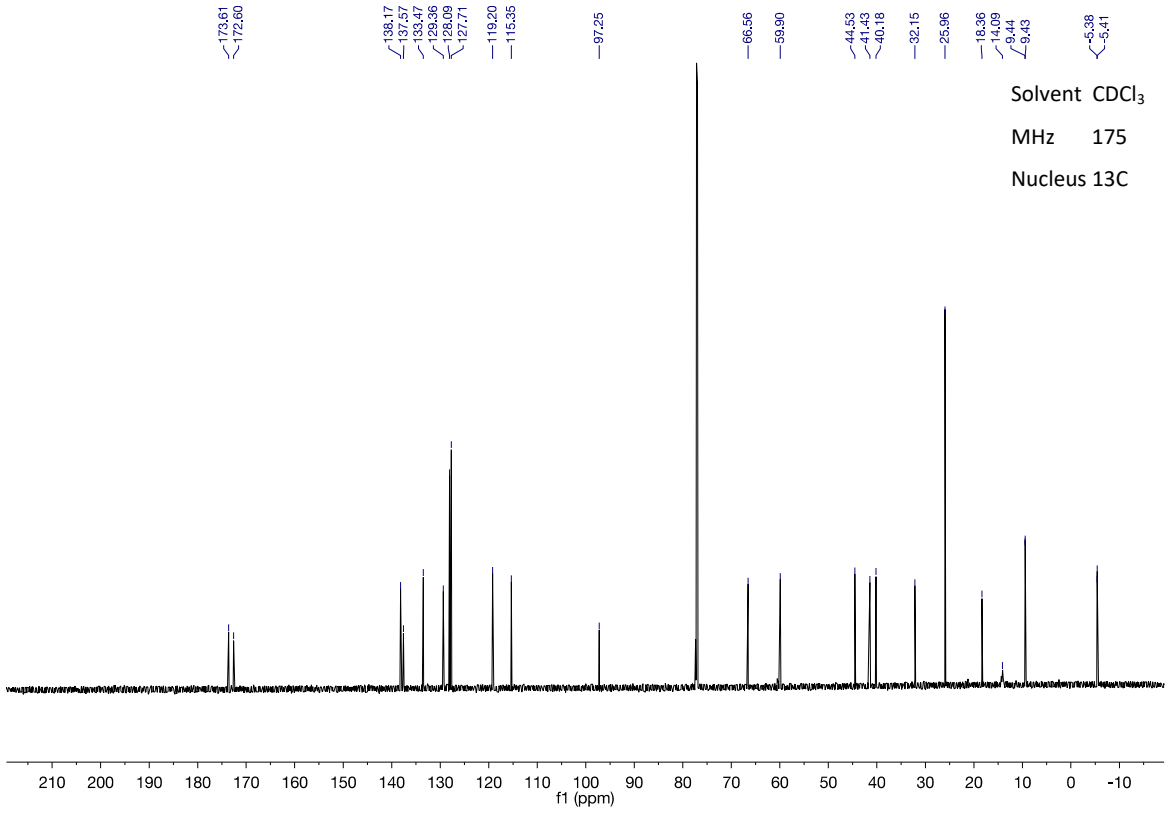

1.89
4.19
1.98
3.98
2.04
1.14
1.00
2.02
1.05
1.10
1.10
1.11
1.11
1.09
1.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

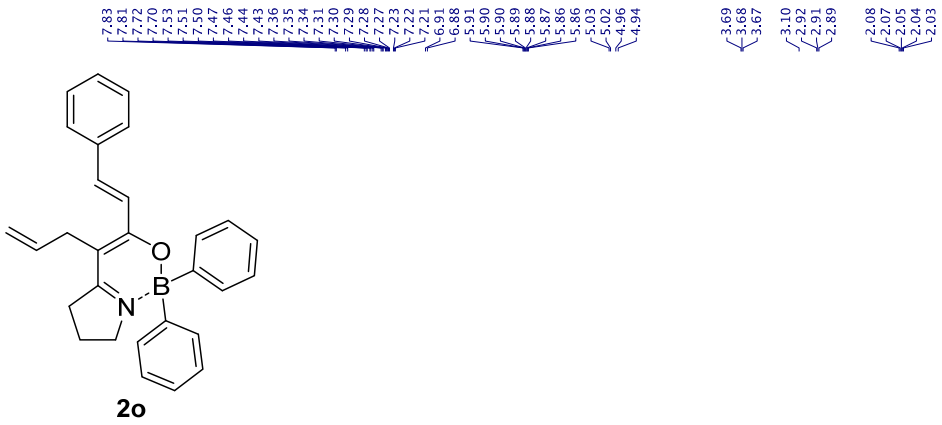

171.30
168.27
134.72
133.20
133.03
132.68
131.68
128.56
127.32
127.30
127.15
126.64
126.49
119.10
91.12
74.15
61.88
45.70
37.95
Solvent CDCl3
MHz 175
Nucleus 13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
BEt2
N
OTBS

2n

Solvent CDCl3
MHz 700
Nucleus 1H
f1 (ppm)

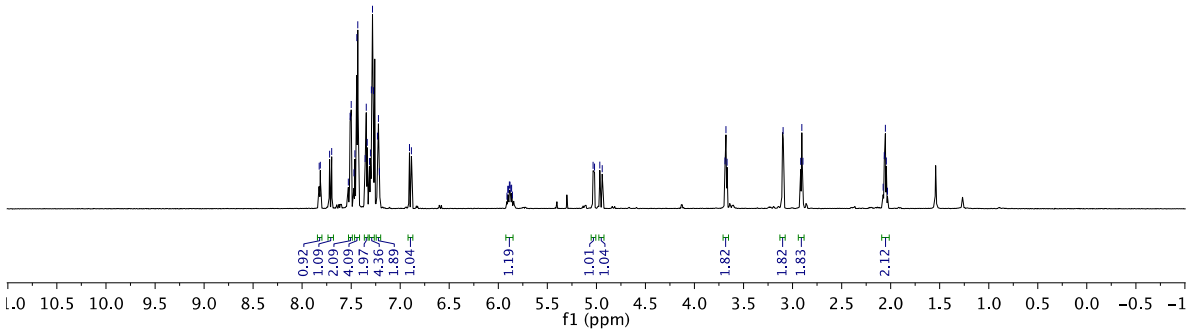

Solvent CDCl3
MHz 175
Nucleus 13C
f1 (ppm)



Solvent $CDCl_3$

MHz 700

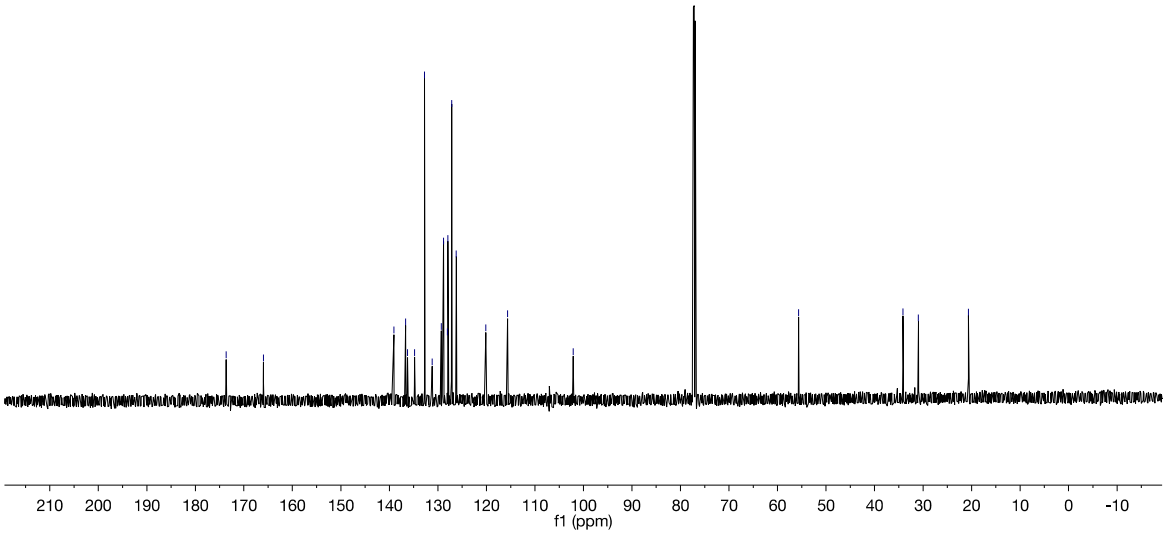
Nucleus 1H

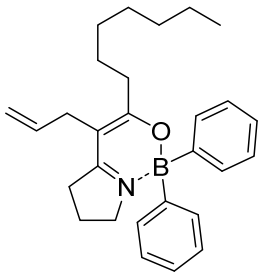


Solvent $CDCl_3$

MHz 175

Nucleus 13C



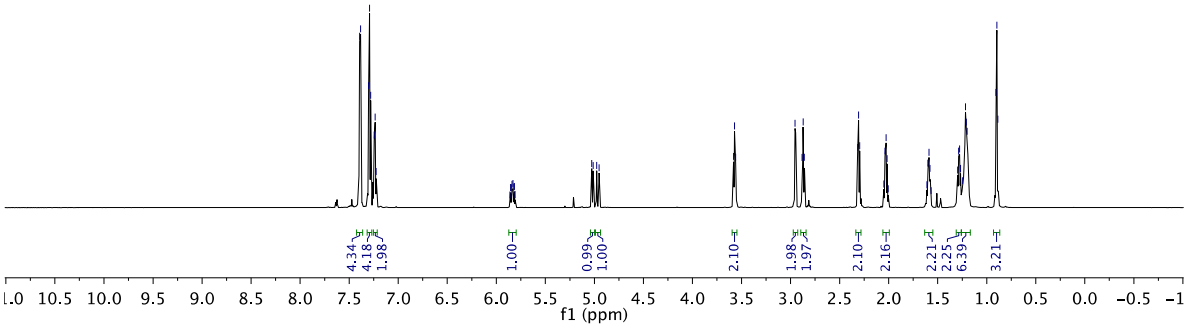


2p

Solvent $CDCl_3$

MHz 700

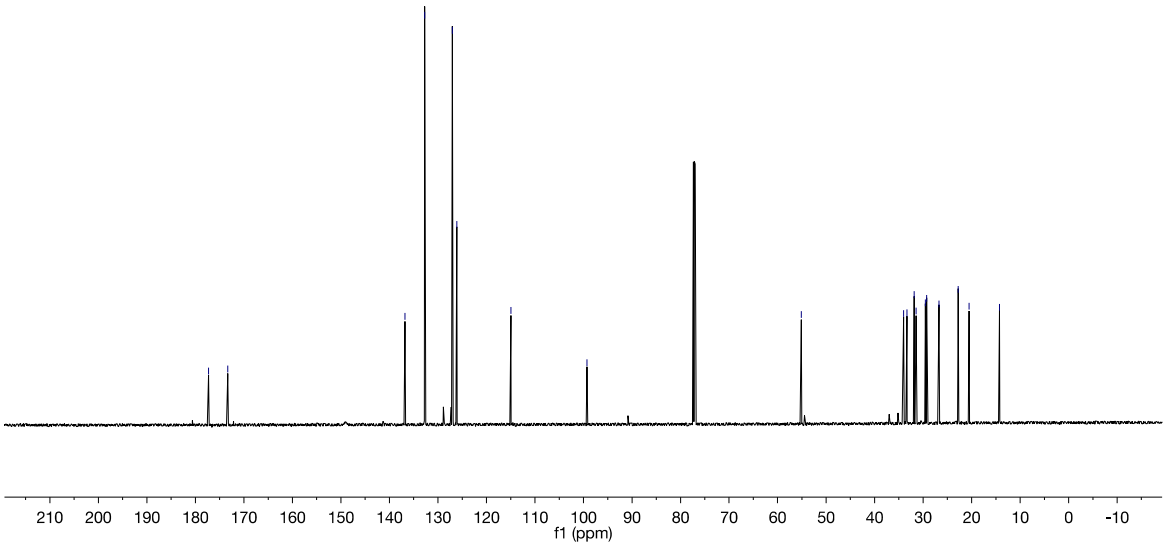
Nucleus 1H

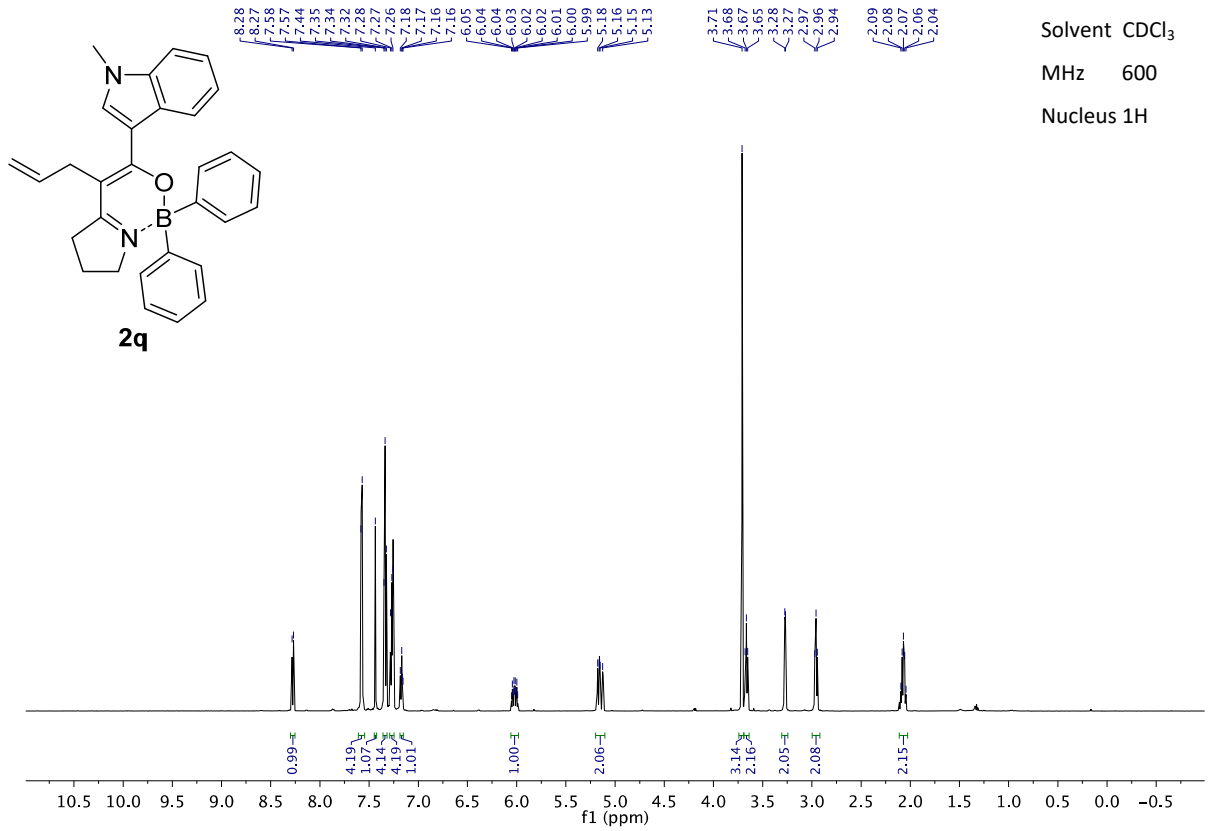


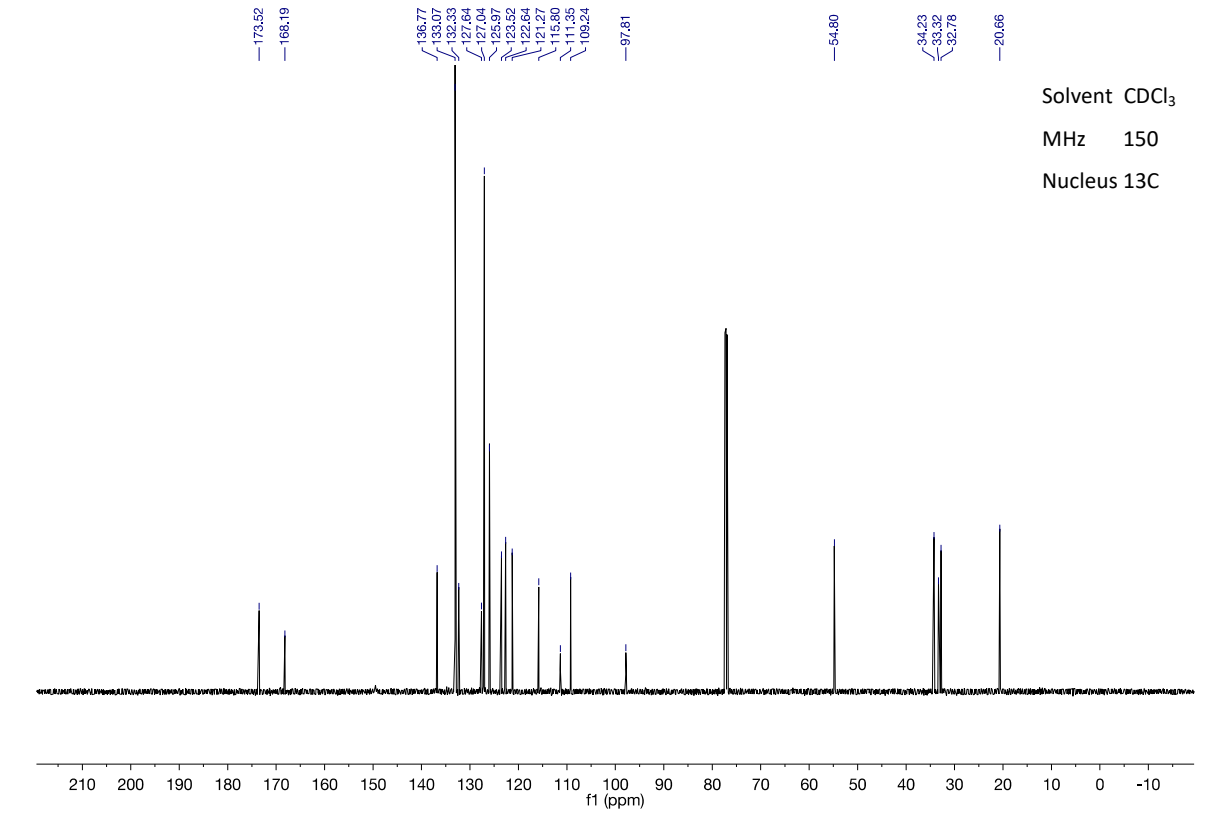
Solvent $CDCl_3$

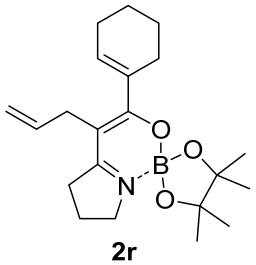
MHz 175

Nucleus 13C



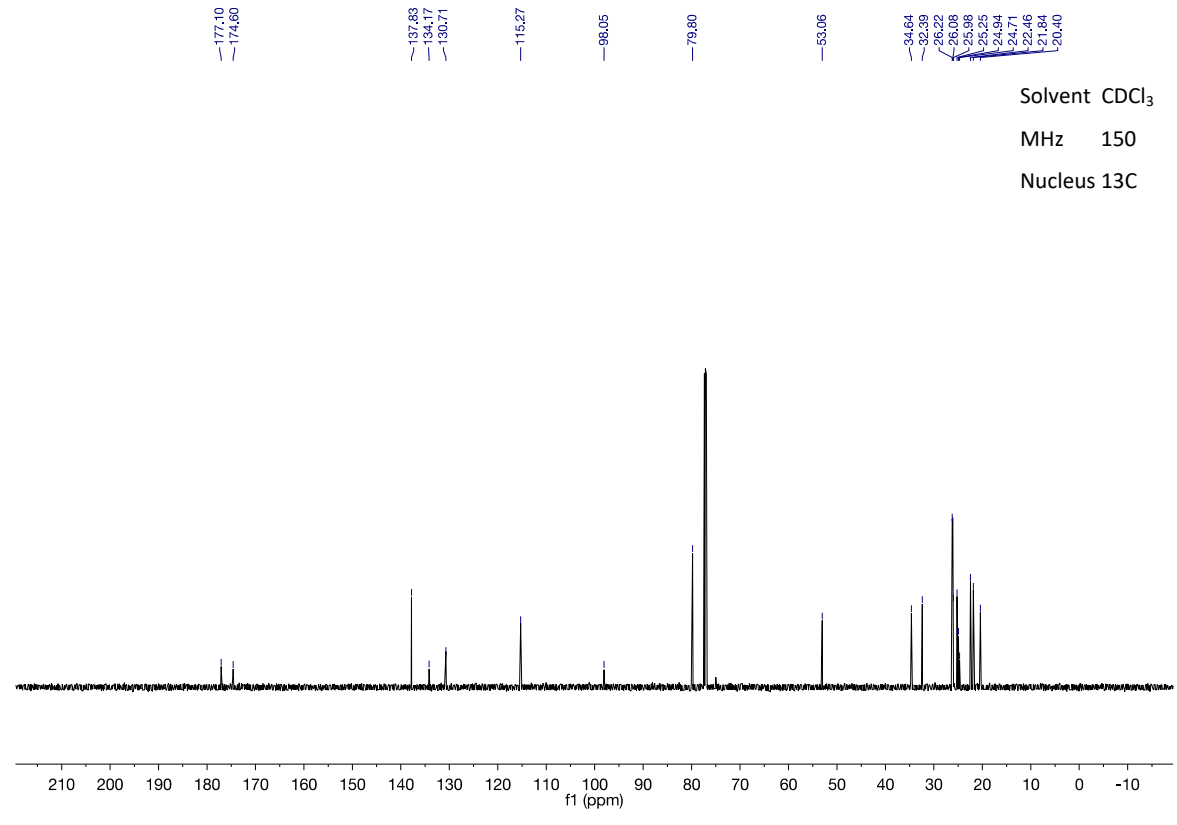

8.28
8.27
7.58
7.57
7.44
7.35
7.34
7.32
7.28
7.27
7.26
7.18
7.17
7.16
7.16
6.05
6.04
6.04
6.03
6.02
6.02
6.02
6.01
6.00
5.99
5.18
5.16
5.15
5.13
3.71
3.68
3.67
3.65
3.28
3.27
2.97
2.96
2.94
2.09
2.08
2.07
2.06
2.04
Solvent CDCl3
MHz 600
Nucleus 1H
N
O
B
N
2q
0.99
4.19
1.07
4.14
4.19
1.01
1.00
2.06
3.14
2.16
2.05
2.08
2.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

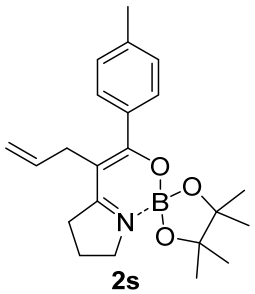

173.52
168.19
136.77
133.07
132.33
127.64
127.04
125.97
123.52
122.64
121.27
115.80
111.35
109.24
97.81
54.80
34.23
33.32
32.78
20.66
Solvent CDCl3
MHz 150
Nucleus 13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



2r

Solvent CDCl3
MHz 600
Nucleus 1H
f1 (ppm)


Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)

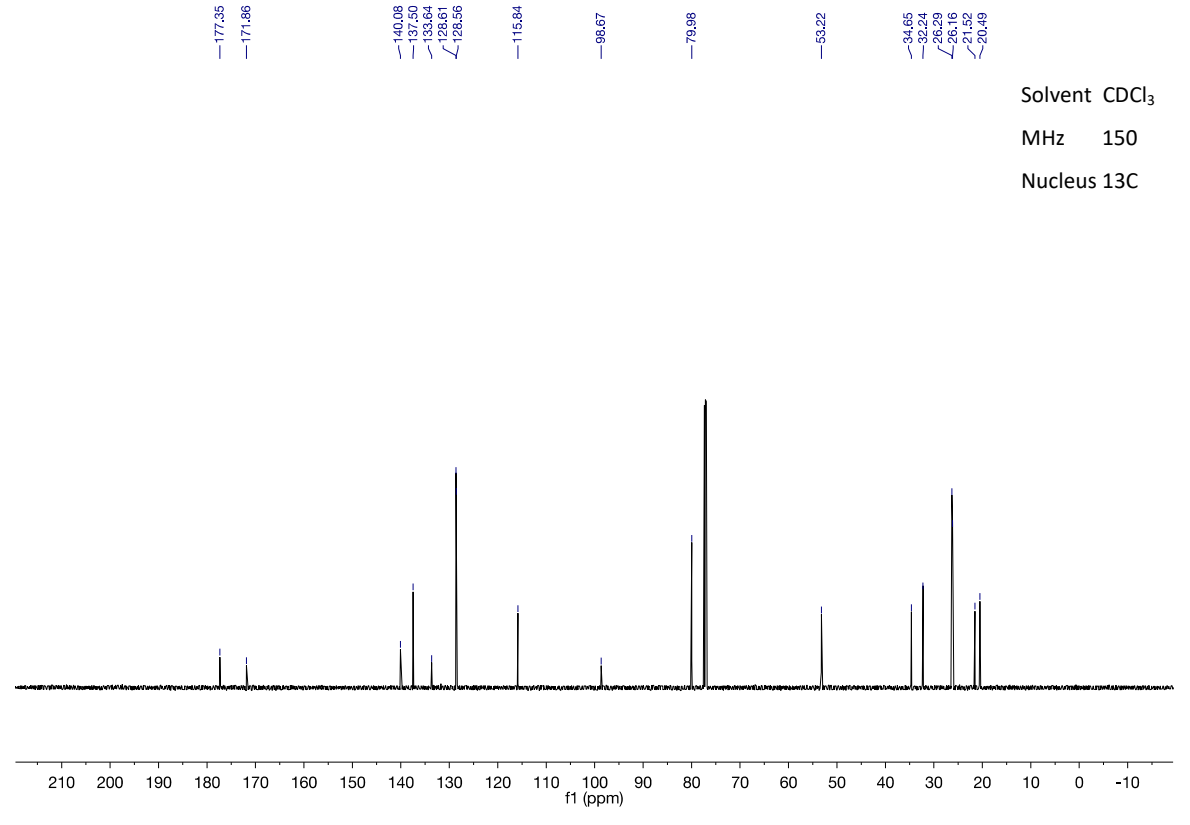


2s

Solvent $CDCl_3$

MHz 600

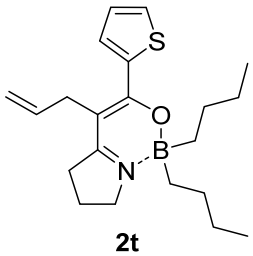
Nucleus 1H



Solvent $CDCl_3$

MHz 150

Nucleus 13C

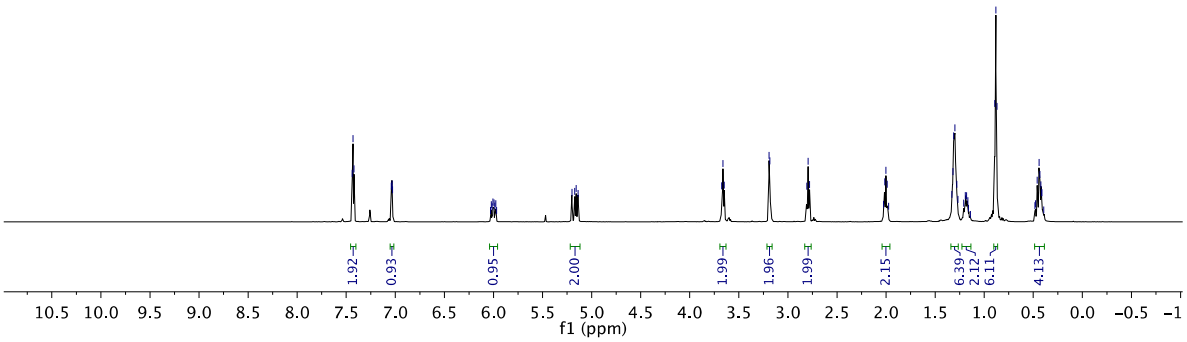


2t

Solvent $CDCl_3$

MHz 600

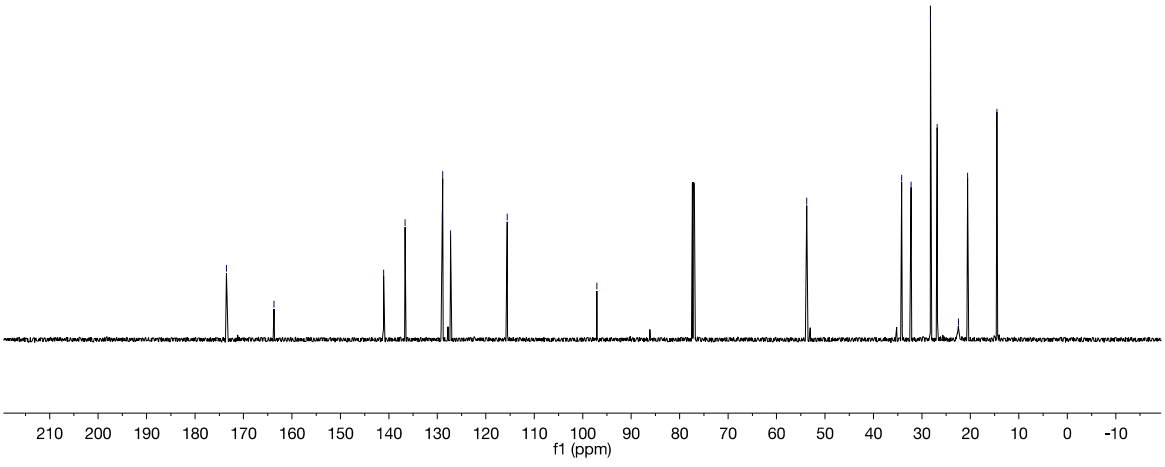
Nucleus 1H

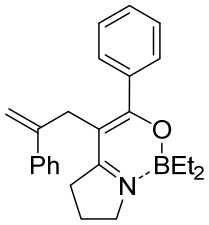


Solvent $CDCl_3$

MHz 150

Nucleus 13C



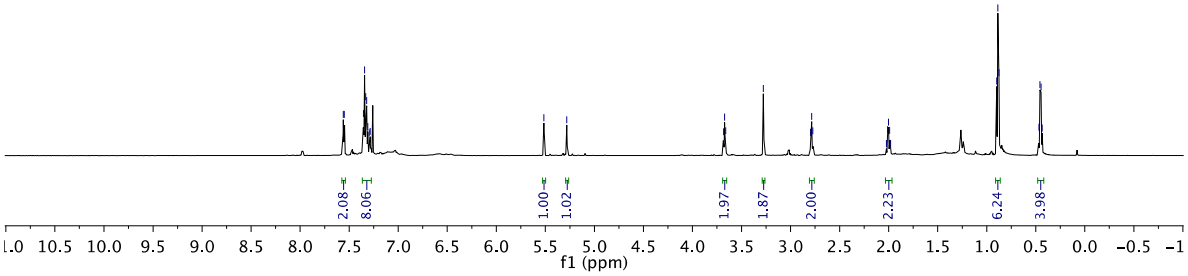


2u

Solvent $CDCl_3$

MHz 700

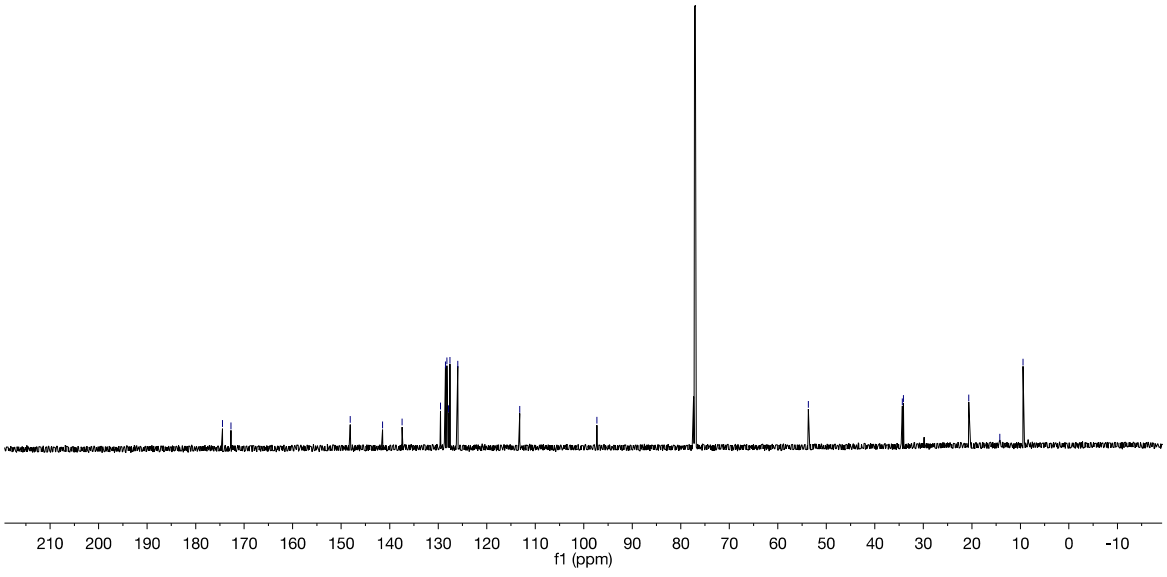
Nucleus 1H

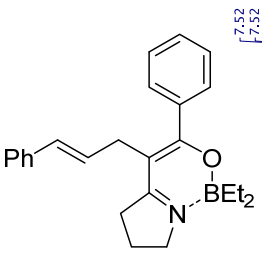


Solvent $CDCl_3$

MHz 175

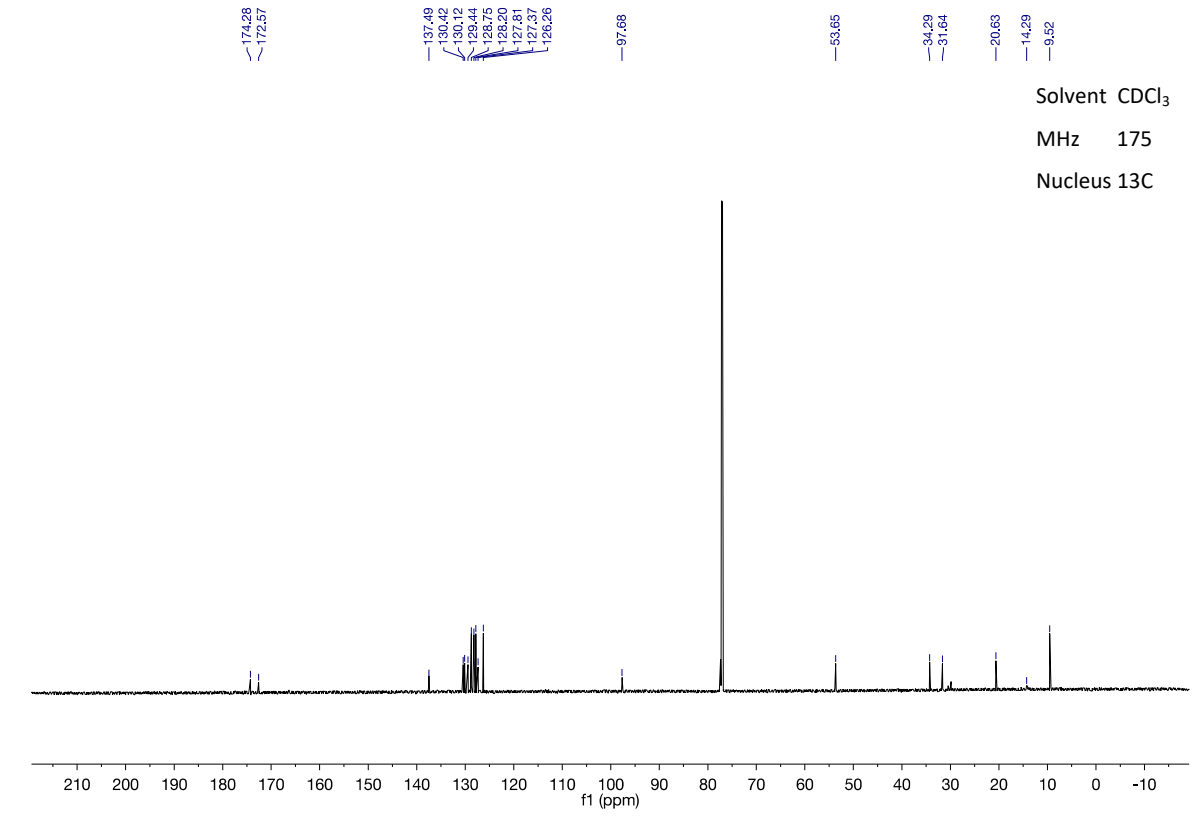
Nucleus 13C

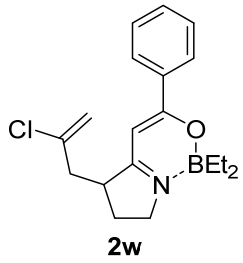



Ph
O
BEt2
N

2v

Solvent CDCl3
MHz 700
Nucleus 1H
f1 (ppm)


Solvent CDCl3
MHz 175
Nucleus 13C
f1 (ppm)

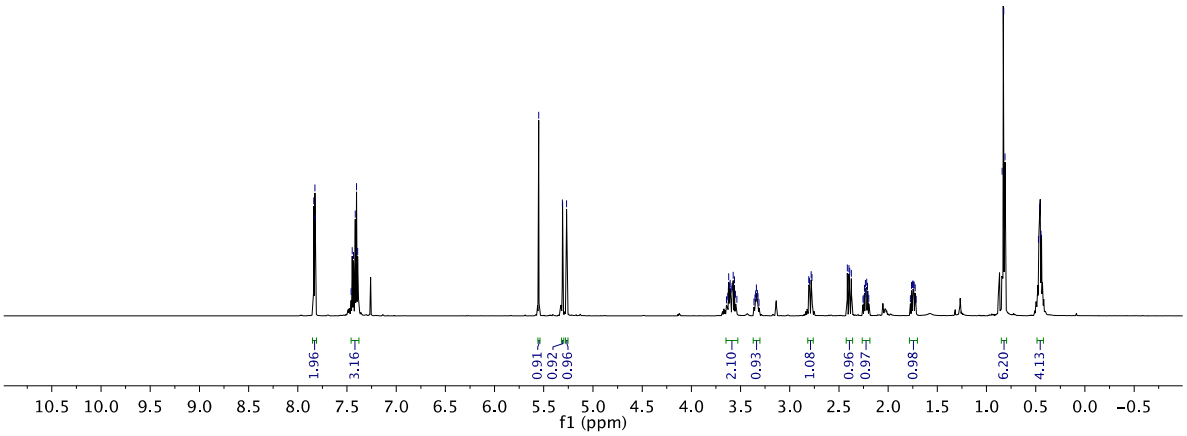


2w

Solvent $CDCl_3$

MHz 600

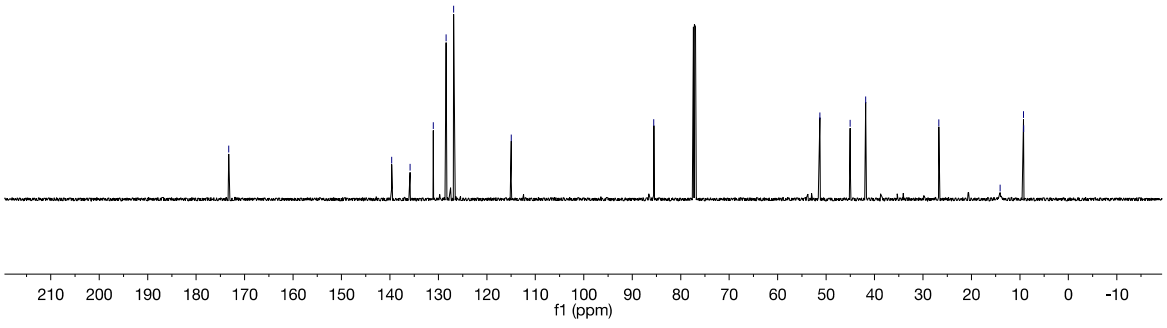
Nucleus 1H

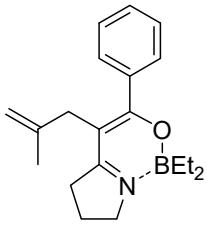


Solvent $CDCl_3$

MHz 150

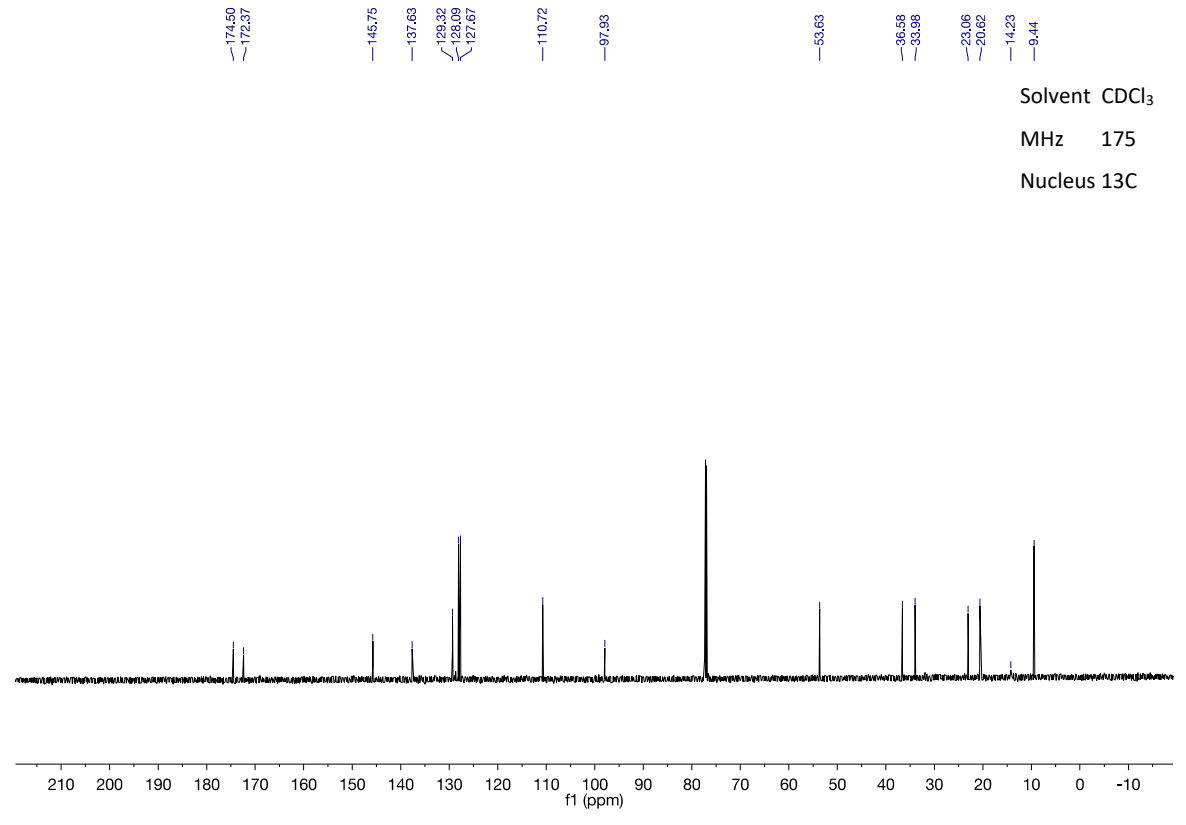
Nucleus 13C

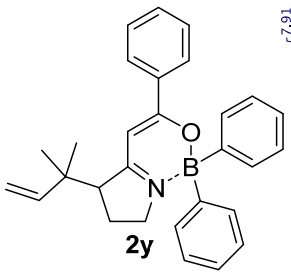



O
BEt2
N

2x

7.50
7.49
7.34
7.34
4.87
4.86
3.66
3.65
3.64
2.78
2.77
2.76
2.01
2.00
1.99
1.98
1.97
1.70
0.88
0.87
0.86
0.45
0.44
0.43
0.42
Solvent CDCl3
MHz 700
Nucleus 1H
2.00
2.89
2.11
2.10
4.17
2.25
3.14
6.33
4.30
f1 (ppm)


174.50
172.37
145.75
137.63
129.32
128.09
127.67
110.72
97.93
53.63
36.58
33.98
23.06
20.62
14.23
9.44
Solvent CDCl3
MHz 175
Nucleus 13C
f1 (ppm)

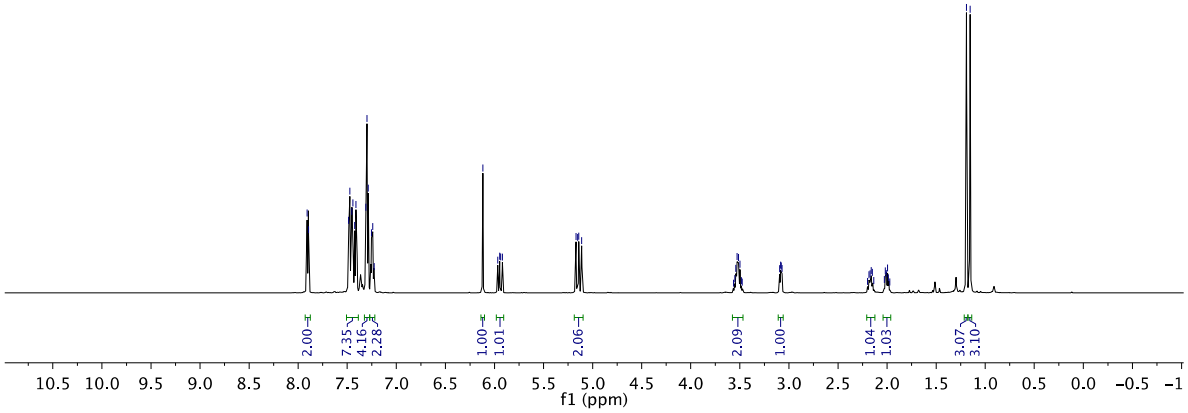


2y

Solvent $CDCl_3$

MHz 600

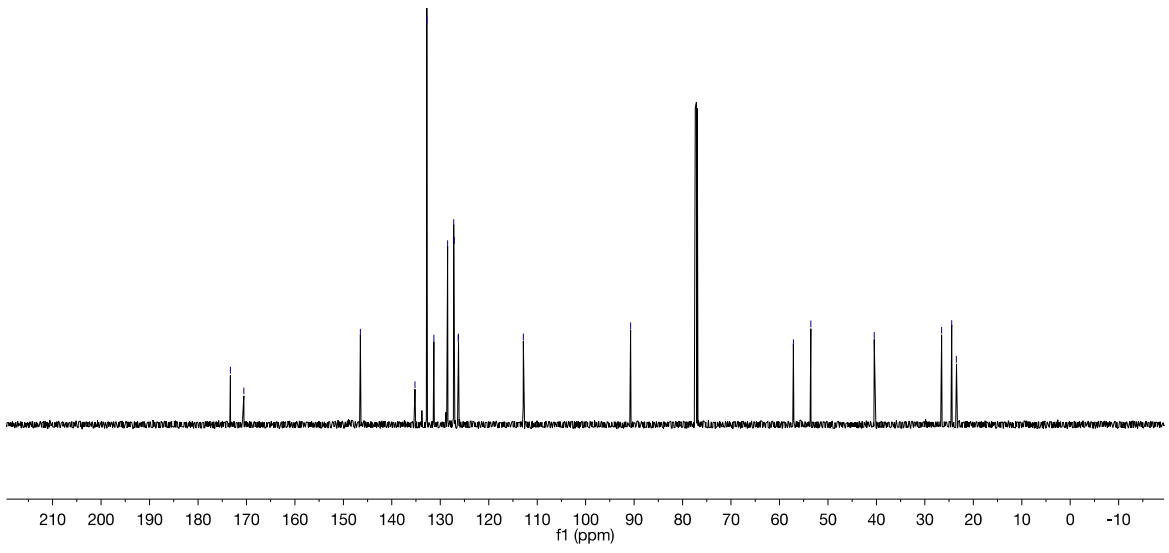
Nucleus 1H

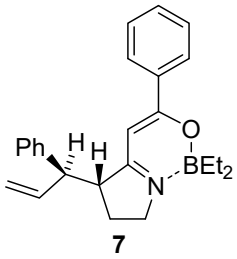


Solvent $CDCl_3$

MHz 150

Nucleus 13C



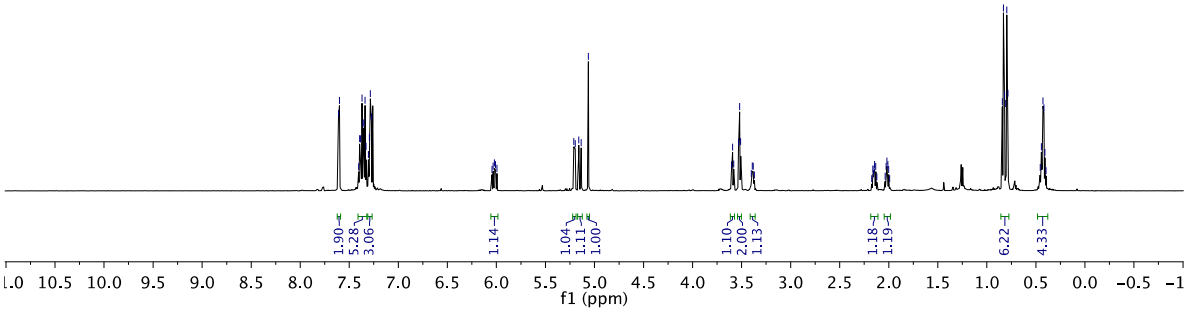


7

Solvent $CDCl_3$

MHz 700

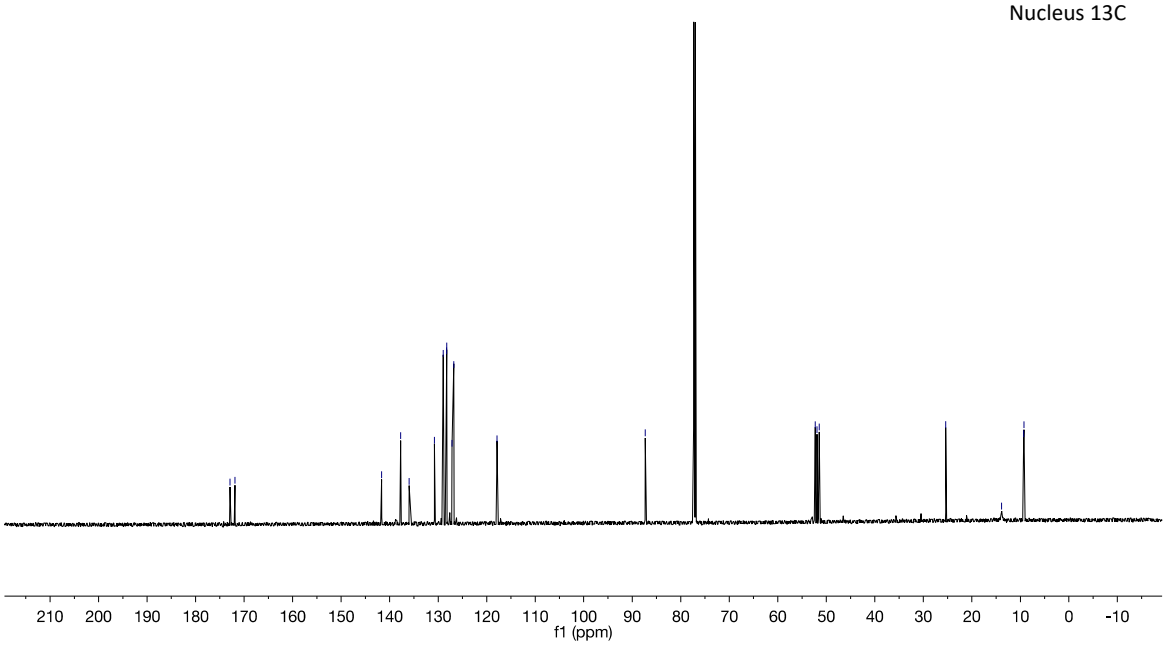
Nucleus 1H

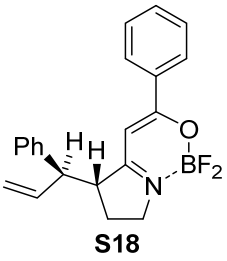


Solvent $CDCl_3$

MHz 175

Nucleus 13C



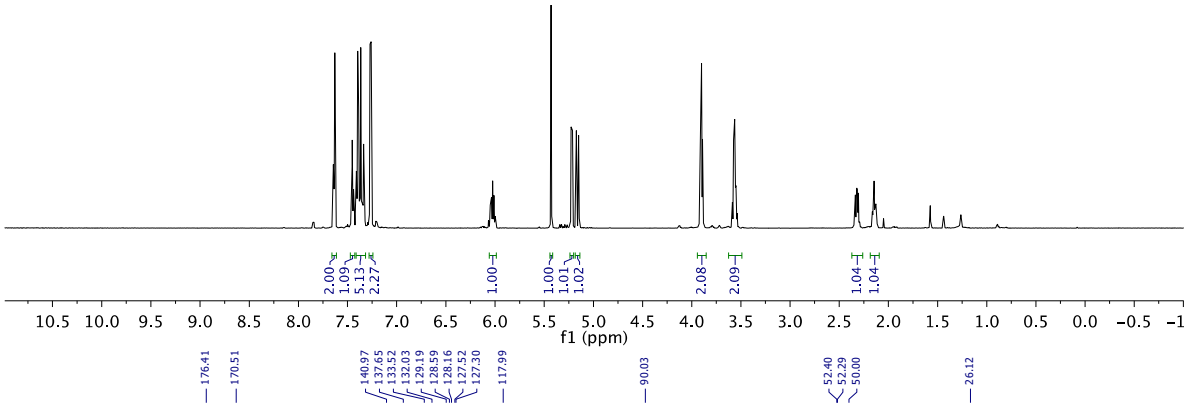


S18

Solvent $CDCl_3$

MHz 700

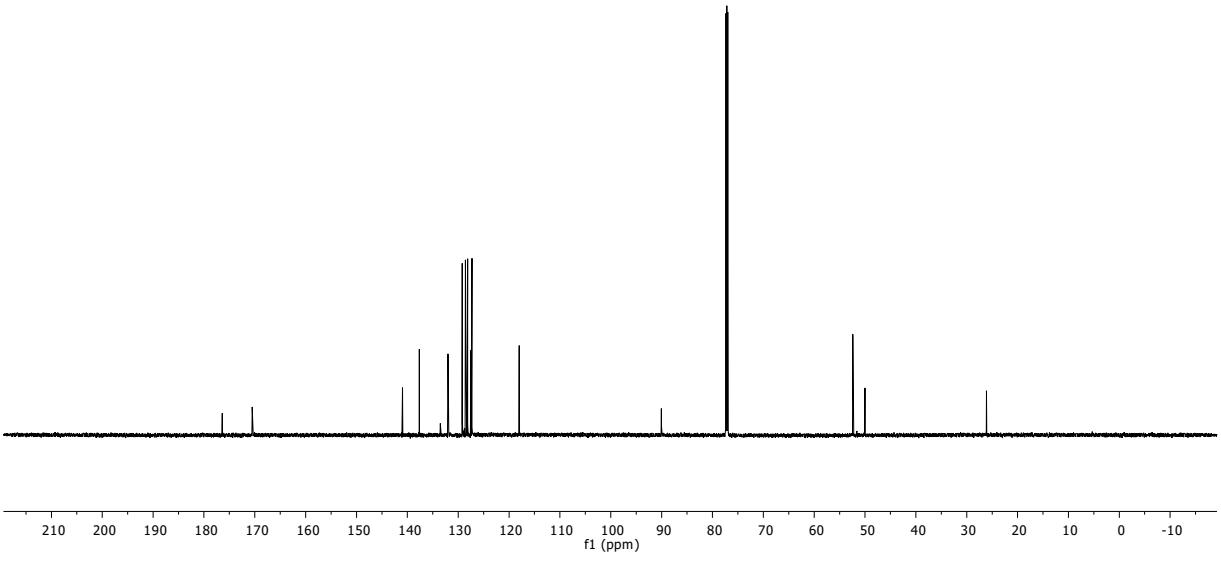
Nucleus 1H

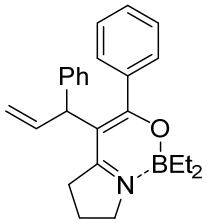


Solvent $CDCl_3$

MHz 175

Nucleus 13C



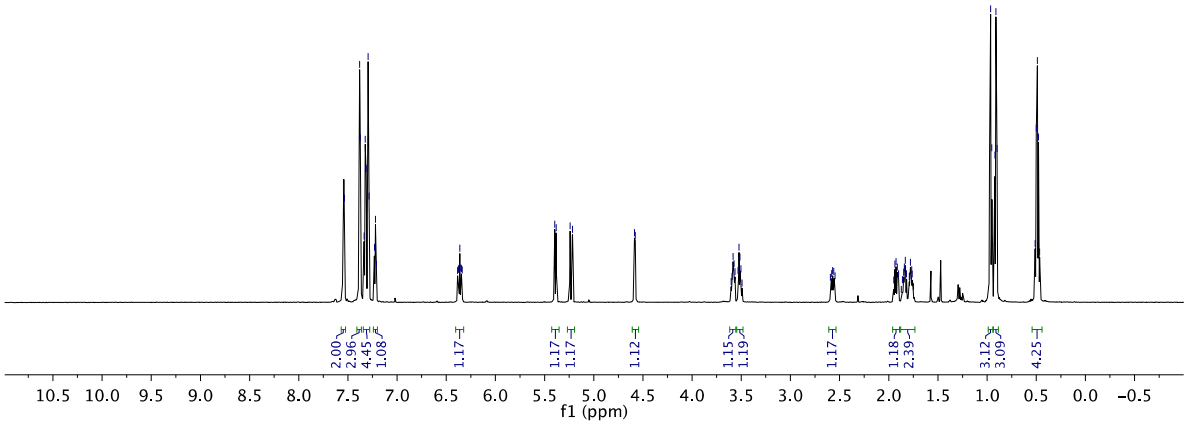


8

Solvent $CDCl_3$

MHz 700

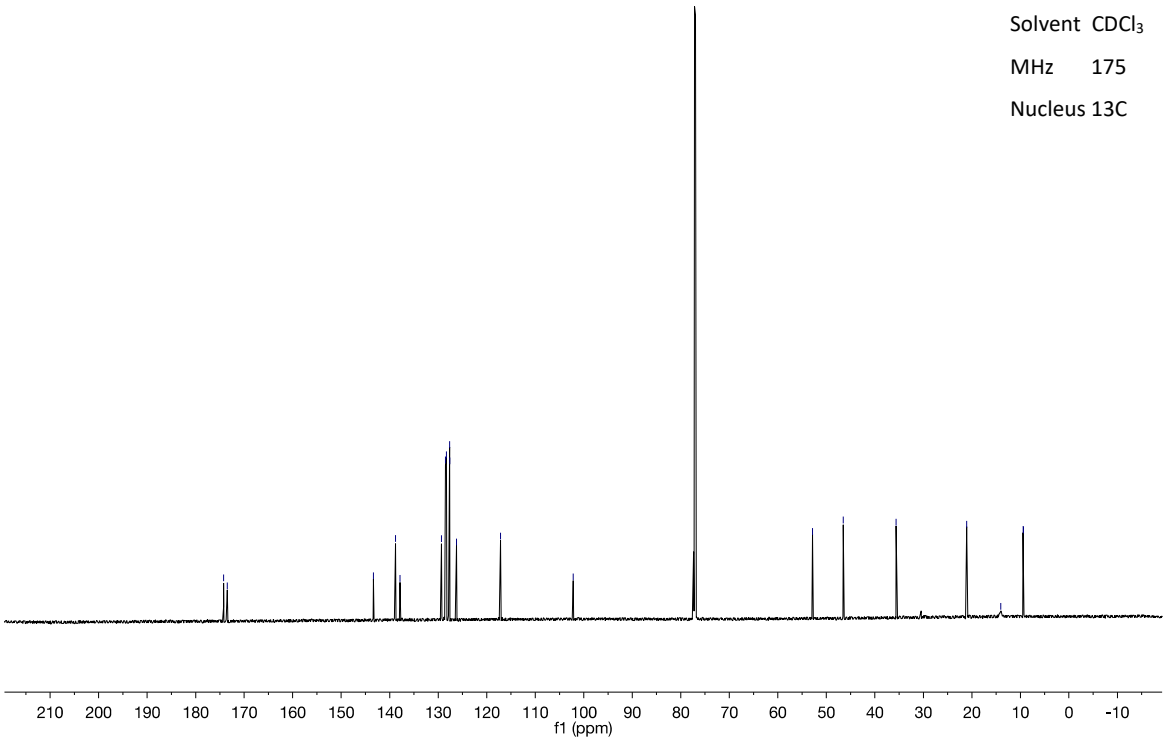
Nucleus 1H

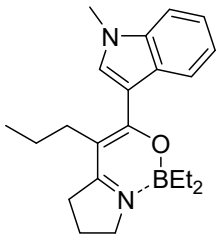


Solvent $CDCl_3$

MHz 175

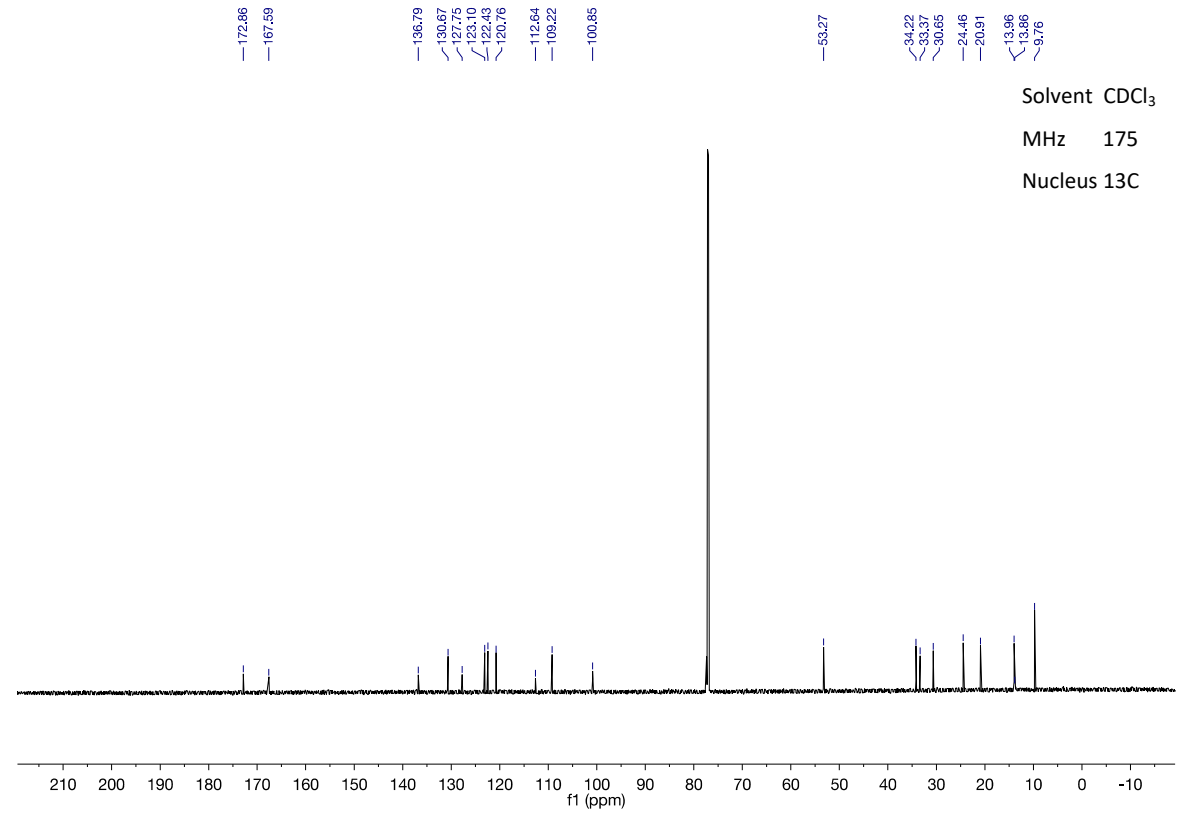
Nucleus 13C

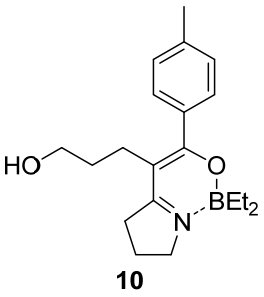



N
O
BEt2
N

9

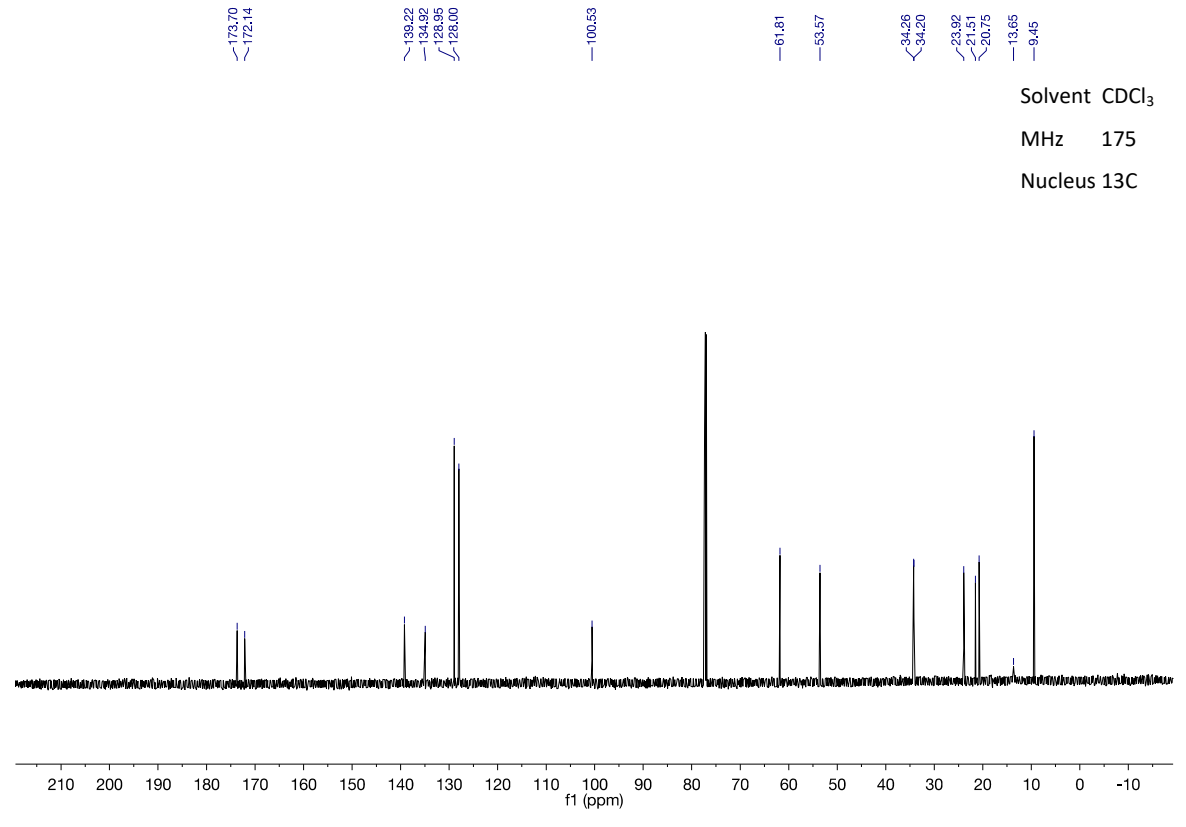
8.10
8.09
7.30
7.29
7.26
7.20
7.19
7.18
3.81
3.66
3.65
3.64
2.86
2.85
2.84
2.35
2.34
2.33
2.04
2.03
2.02
1.47
1.46
1.45
1.44
0.92
0.91
0.89
0.88
0.87
0.86
0.52
0.51
0.50
0.49
0.47
0.45
0.44
Solvent CDCl3
MHz 700
Nucleus 1H
0.96
1.81
1.37
1.00
2.67
1.88
1.85
1.87
1.99
2.26
2.91
5.68
3.99
f1 (ppm)

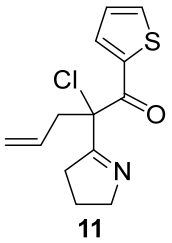

172.86
167.59
136.79
130.67
127.75
123.10
122.43
120.76
112.64
109.22
100.85
53.27
34.22
33.37
30.65
24.46
20.91
13.96
13.86
9.76
Solvent CDCl3
MHz 175
Nucleus 13C
f1 (ppm)


HO
O
BEt2
N

10

7.35
7.34
7.18
7.17
3.67
3.66
3.64
3.48
3.48
3.47
2.87
2.86
2.85
2.36
2.27
2.26
2.25
2.06
2.05
2.04
2.03
2.02
1.53
1.53
1.52
1.51
1.50
0.84
0.83
0.82
0.43
0.41
0.40
0.39
Solvent CDCl3
MHz 700
Nucleus 1H
1.86
1.80
2.00
1.90
1.89
2.81
1.89
2.02
2.02
5.84
3.91
f1 (ppm)


173.70
172.14
139.22
134.92
128.95
128.00
100.53
61.81
53.57
34.26
34.20
23.92
21.51
20.75
13.65
9.45
Solvent CDCl3
MHz 175
Nucleus 13C
f1 (ppm)

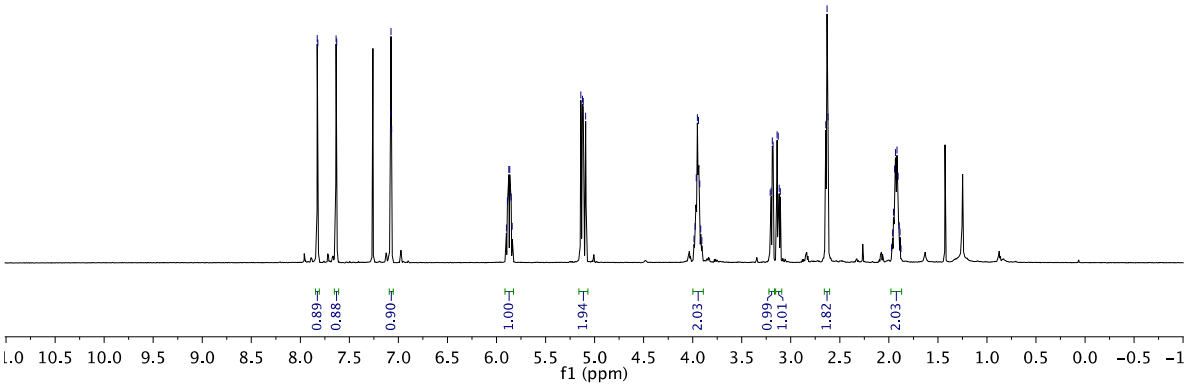


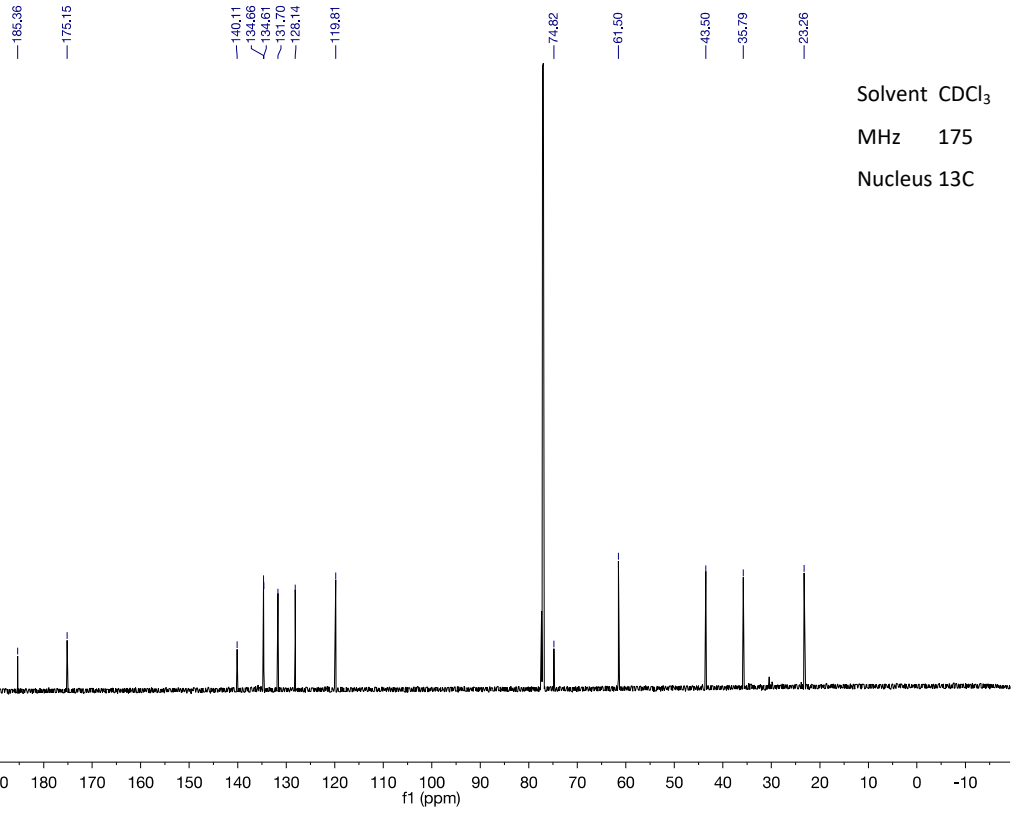
11

Solvent $CDCl_3$

MHz 700

Nucleus 1H

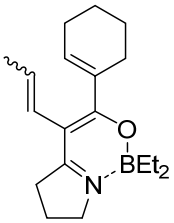




Solvent $CDCl_3$

MHz 175

Nucleus 13C

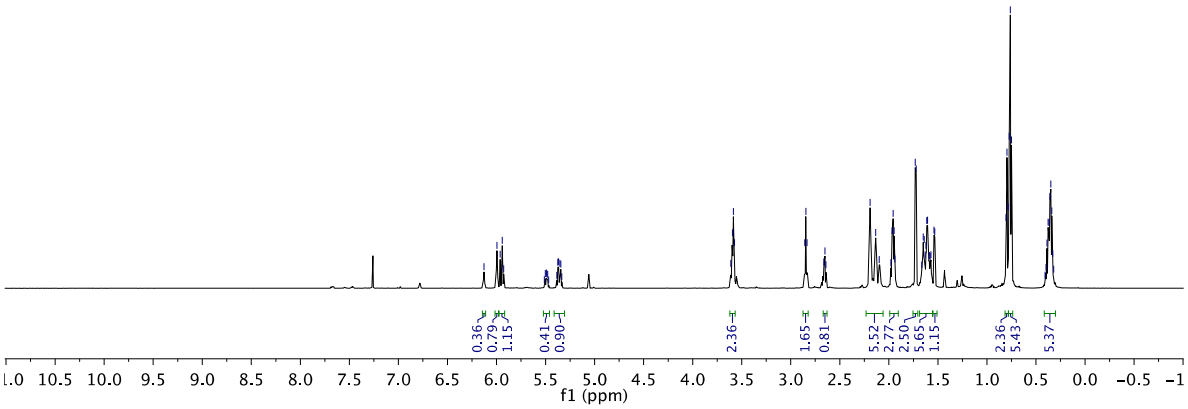


12

Solvent $CDCl_3$

MHz 700

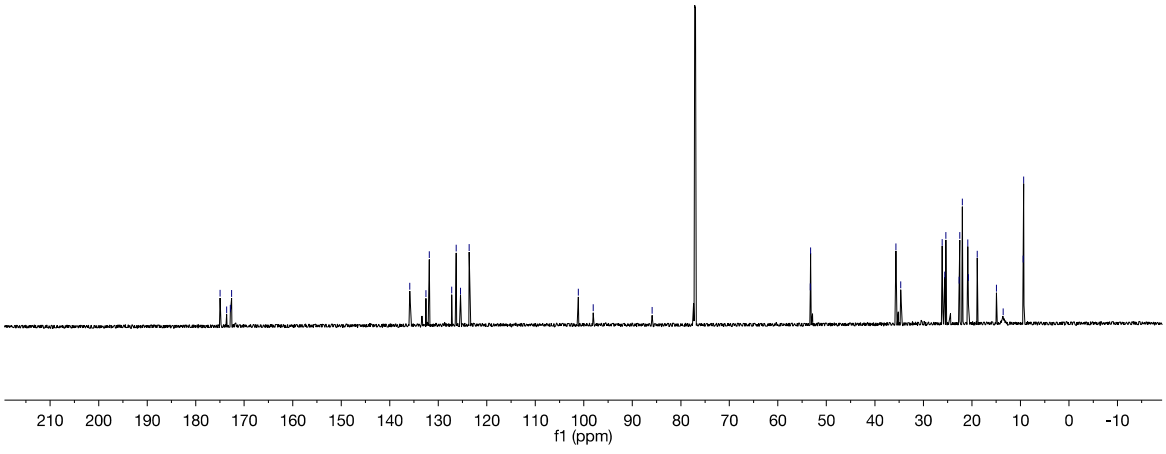
Nucleus 1H

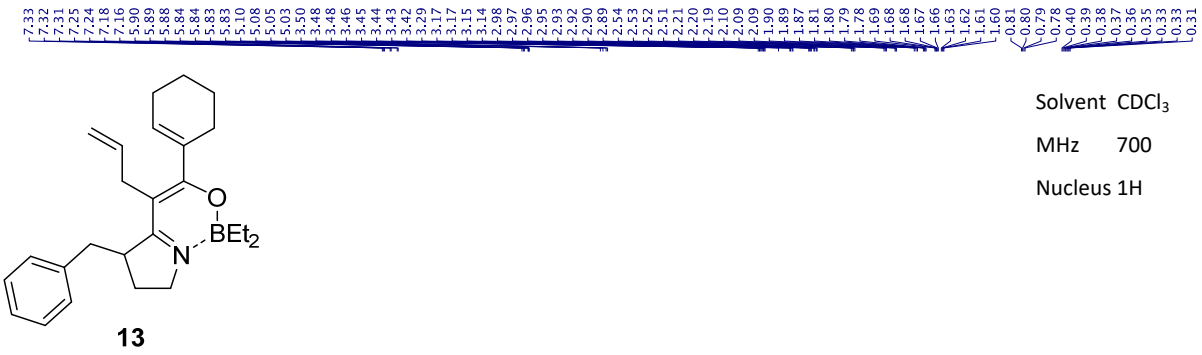


Solvent $CDCl_3$

MHz 175

Nucleus 13C



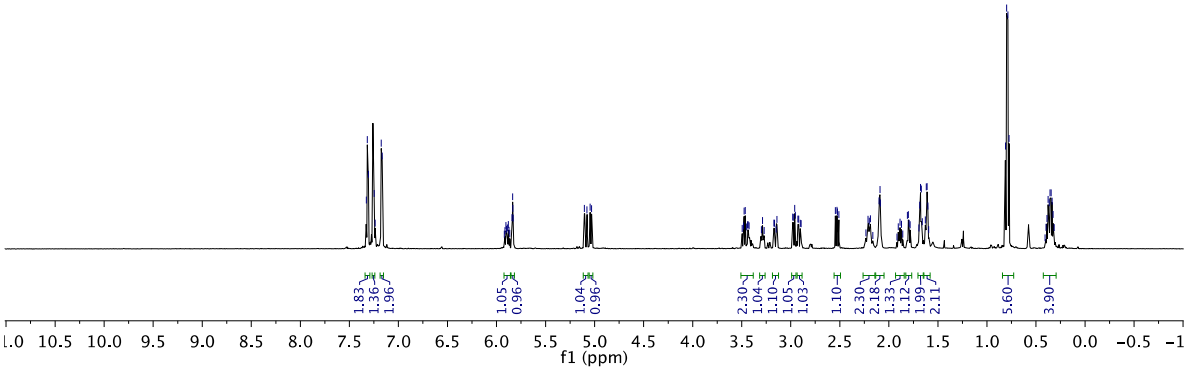


13

Solvent $CDCl_3$

MHz 700

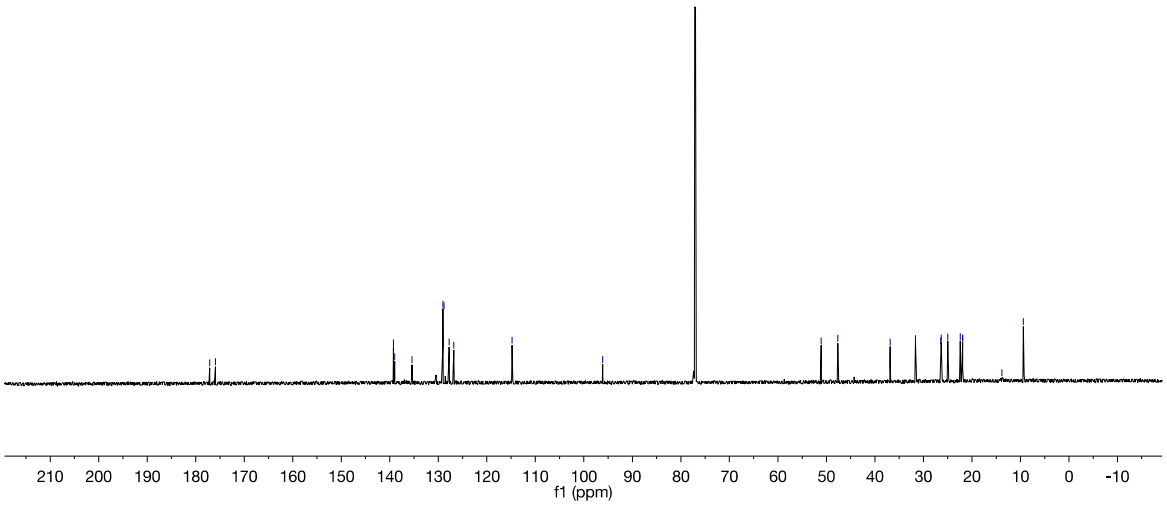
Nucleus 1H

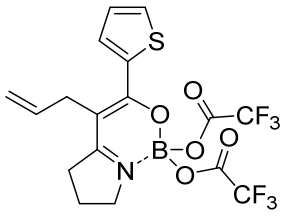


Solvent $CDCl_3$

MHz 175

Nucleus 13C



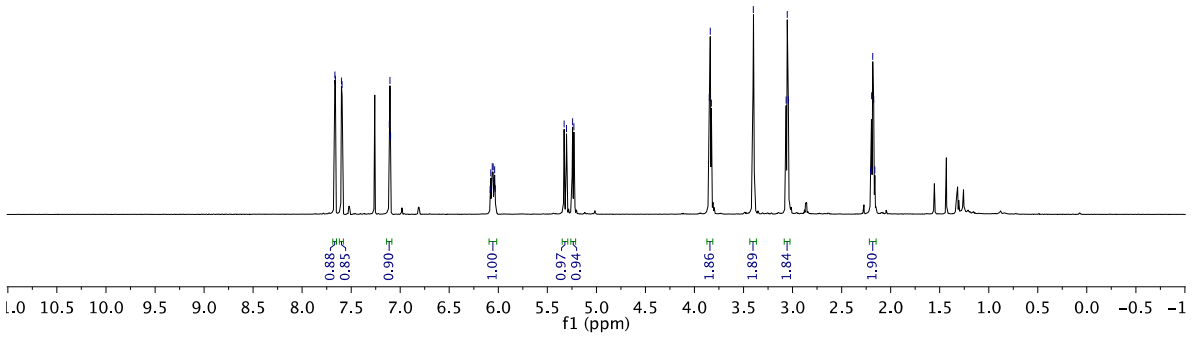


14

Solvent $CDCl_3$

MHz 700

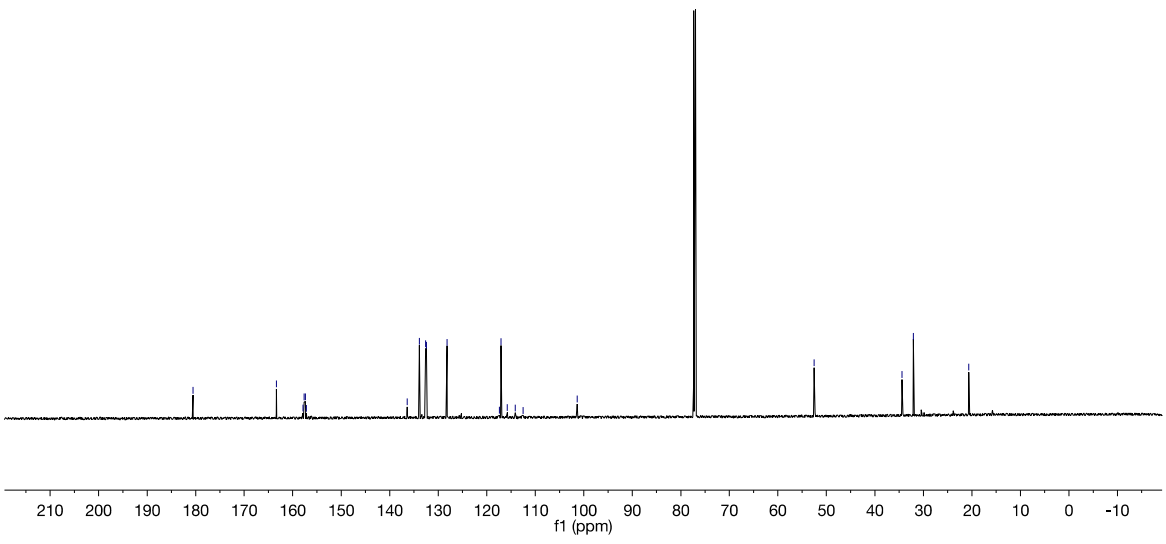
Nucleus 1H

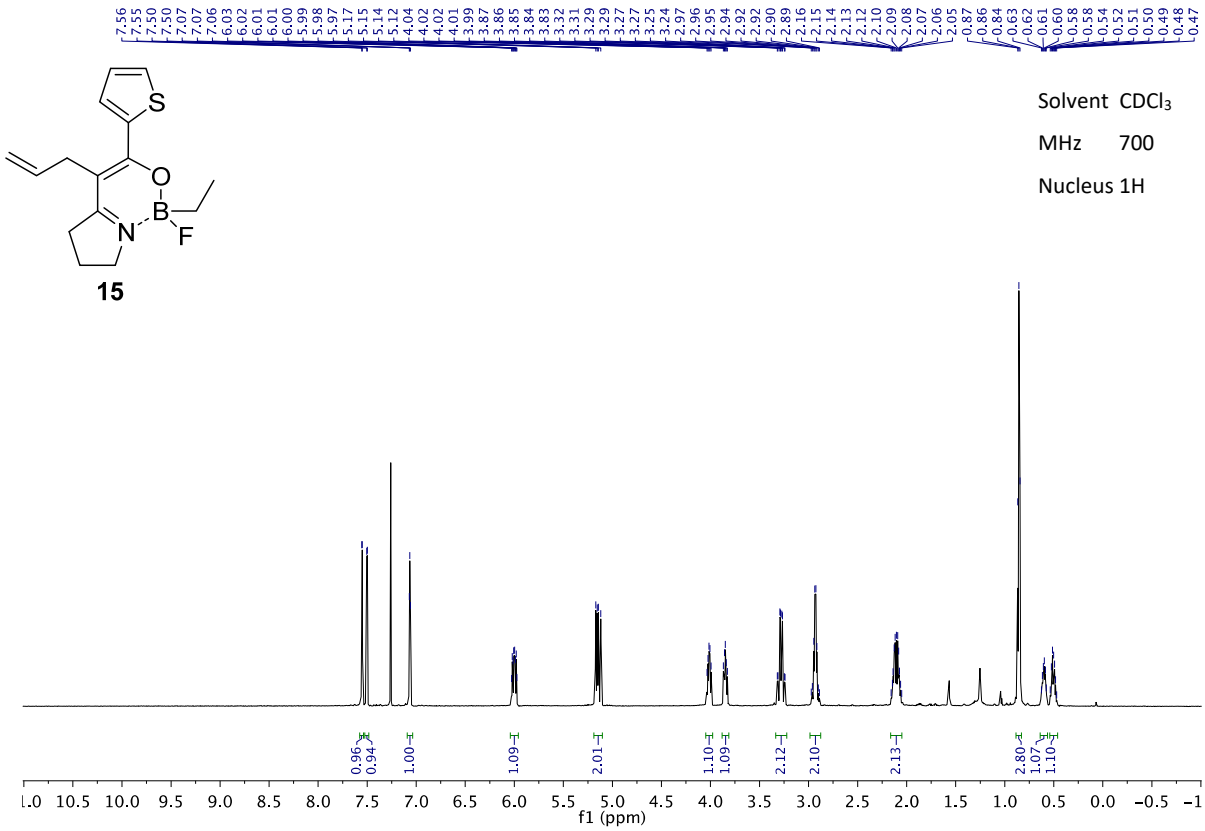


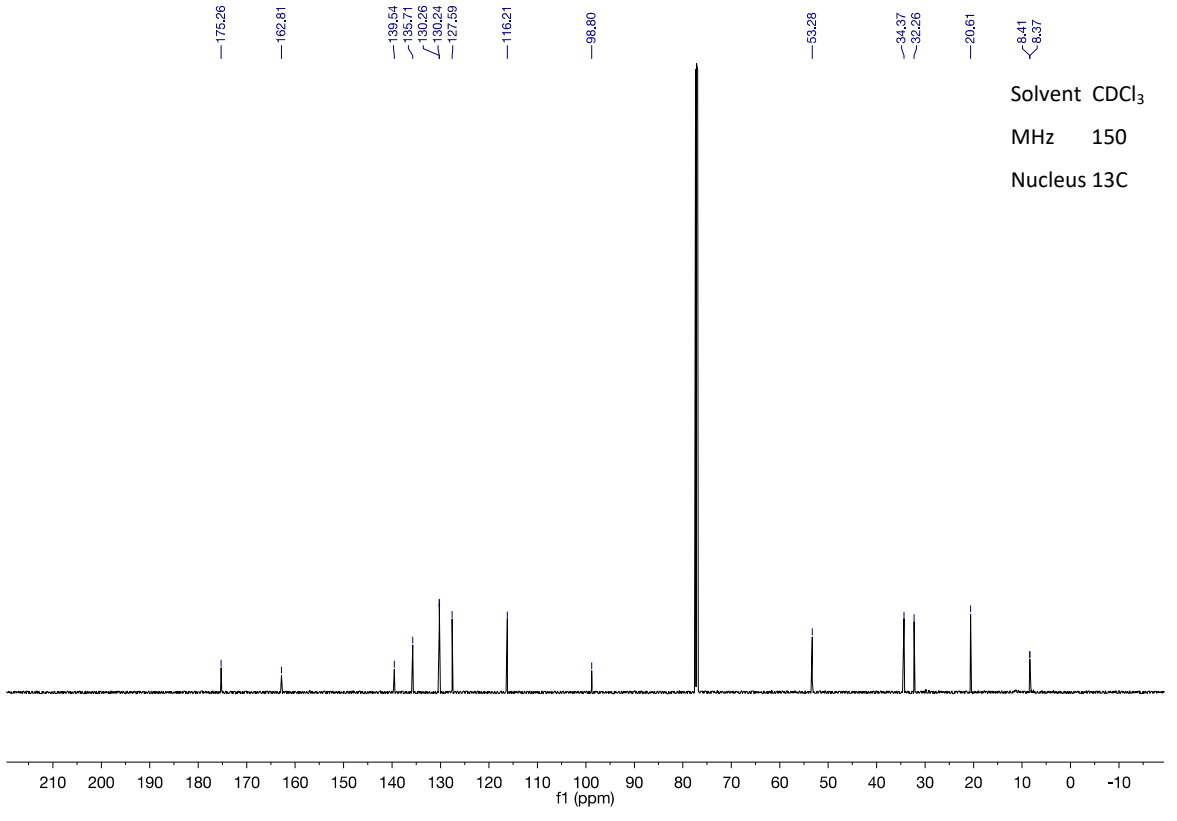
Solvent $CDCl_3$

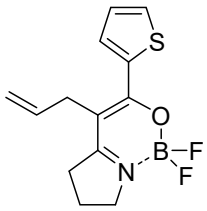
MHz 175

Nucleus 13C




Solvent CDCl3
MHz 700
Nucleus 1H
15
f1 (ppm)


Solvent CDCl3
MHz 150
Nucleus 13C
f1 (ppm)

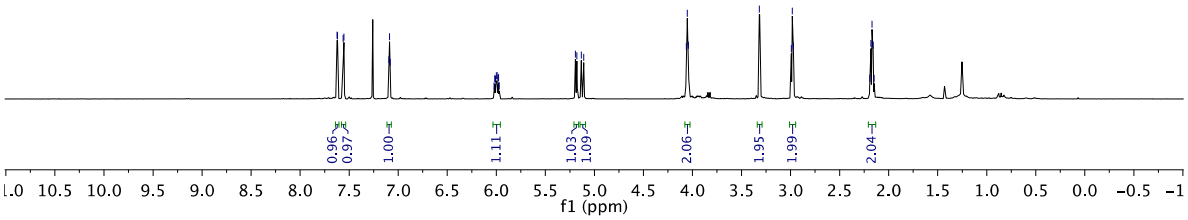


S19

Solvent $CDCl_3$

MHz 700

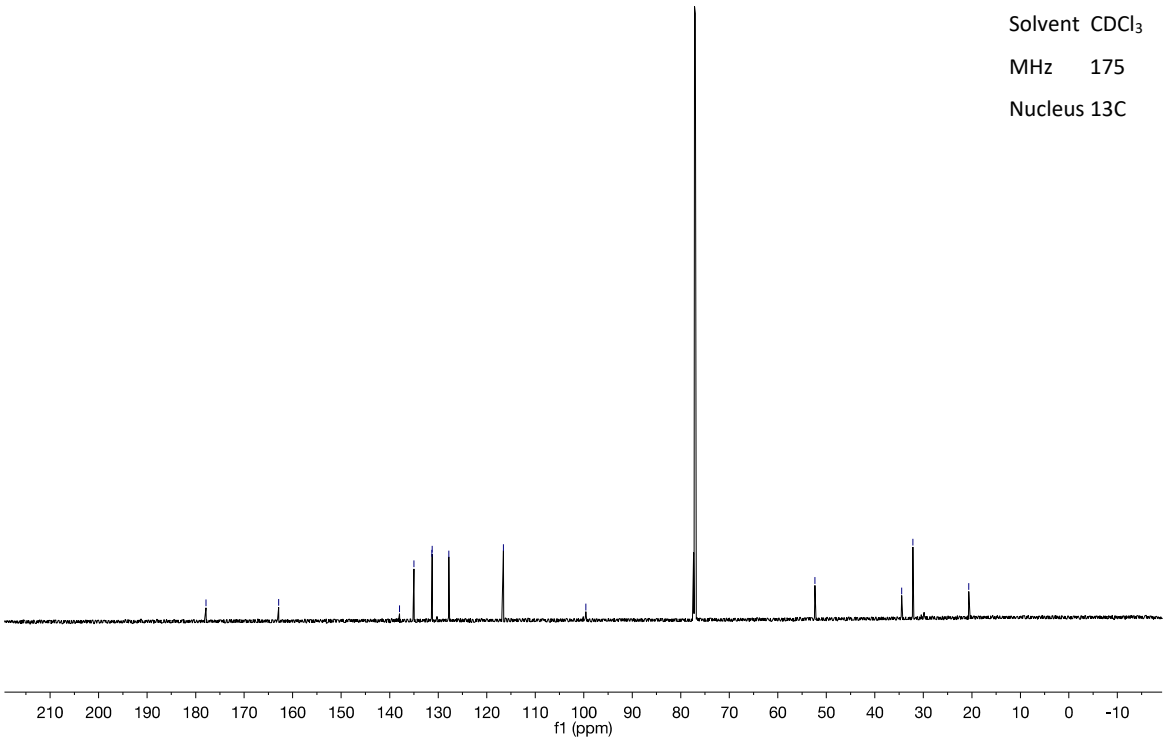
Nucleus 1H

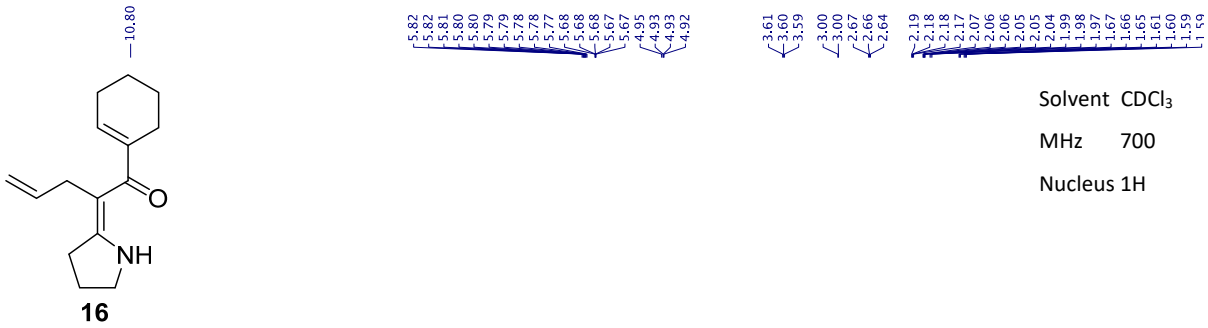


Solvent $CDCl_3$

MHz 175

Nucleus 13C



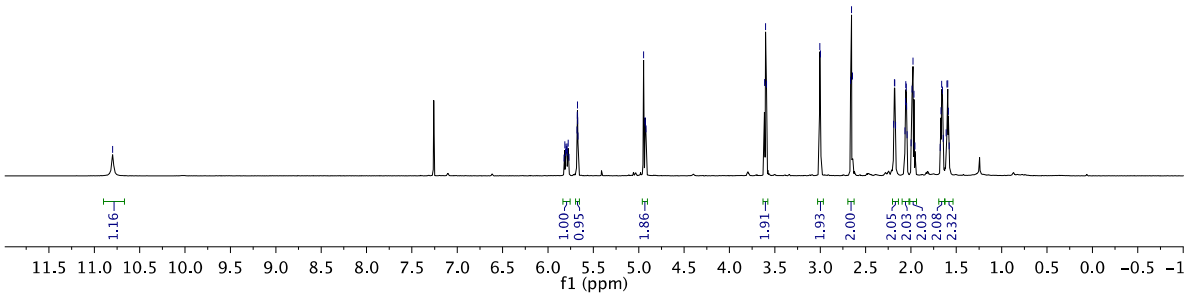


16

Solvent $CDCl_3$

MHz 700

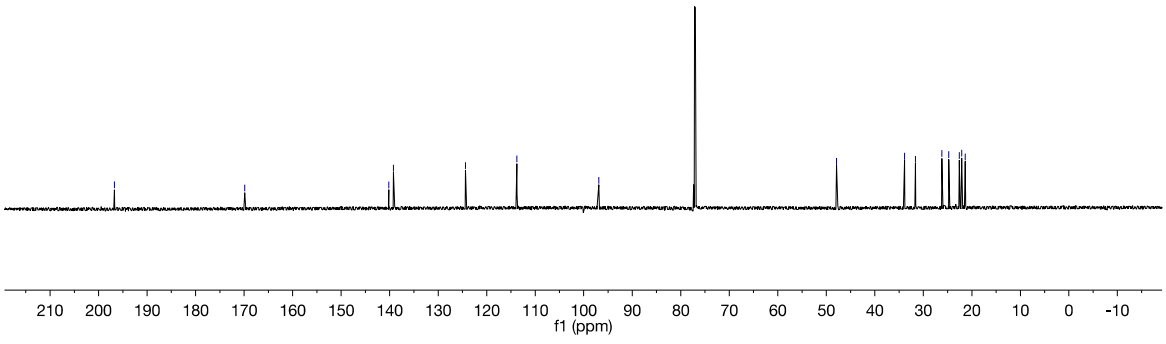
Nucleus 1H

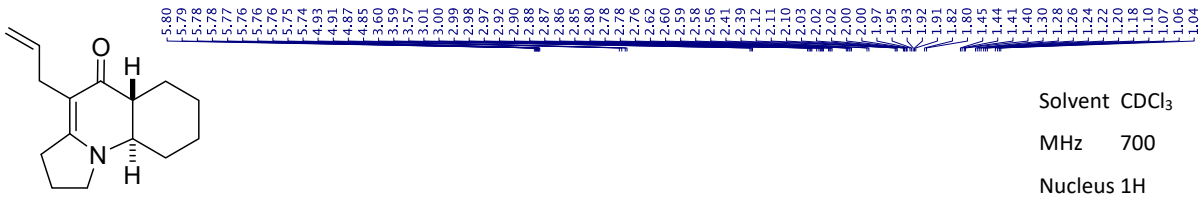


Solvent $CDCl_3$

MHz 175

Nucleus 13C



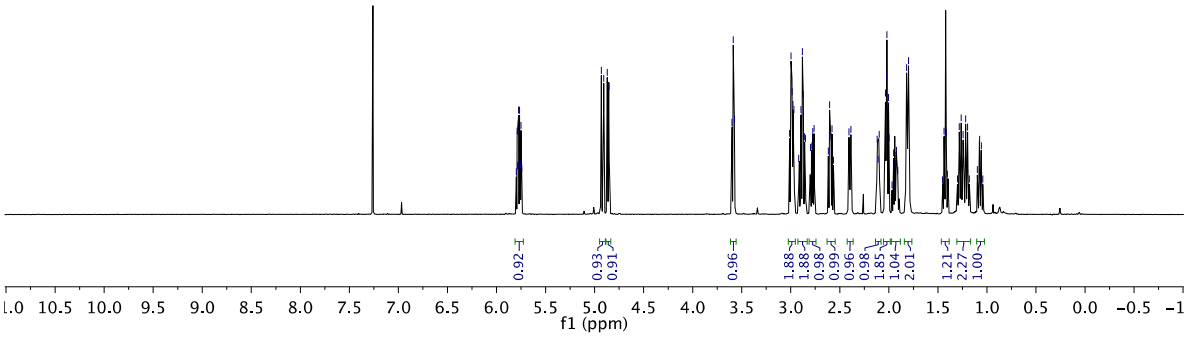


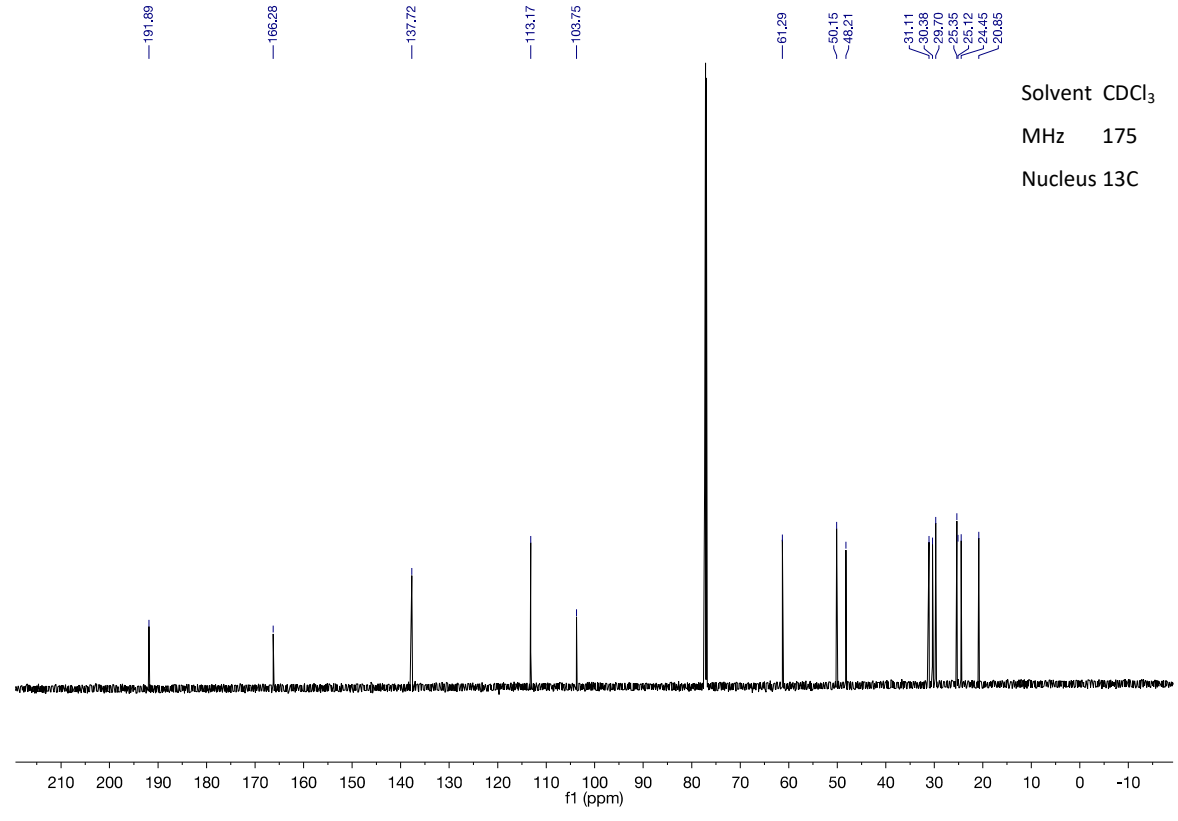
***trans*-17**

Solvent $CDCl_3$

MHz 700

Nucleus 1H

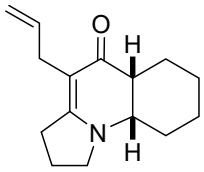




Solvent $CDCl_3$

MHz 175

Nucleus 13C

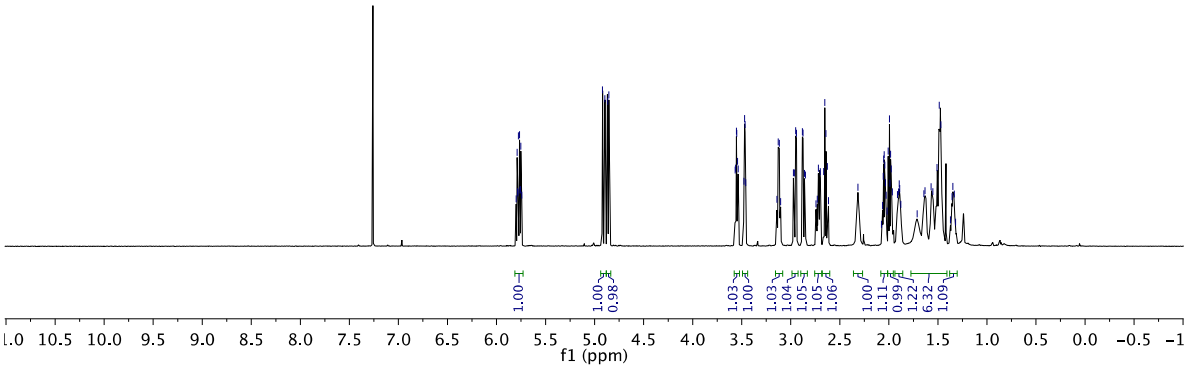


***cis*-17**

Solvent $CDCl_3$

MHz 700

Nucleus 1H



Solvent $CDCl_3$

MHz 175

Nucleus 13C