

Supporting Information

Table of Contents

1. General Experimental Methods	2
2. Experimental Procedures	3
2.1. Synthesis of boroxines	3
2.2. Synthesis of imines.....	7
2.3. Synthesis of homoallylic amines.....	14
3. ¹H and ¹³C NMR Spectra	33
4. References	76

1. General Experimental Methods

All reactions were performed using flame-dried microwave vial under atmosphere of dry argon unless otherwise stated. All solvents using in reaction were dried and distilled using standard procedure. All reagents were used as supplied without further purification.

Flash column chromatography (FCC) was performed using Breckland Scientific silica gel 60, particle size 40-63 nm under air pressure and Biotage Isolera™ Prime. All solvents except triethyl amine (Et₃N) used for chromatography purification were distilled prior to use. Triethyl amine used for chromatography were purchased from Sigma Aldrich and used without further purification. Thin layer chromatography (TLC) was performed using silica gel 60 F254 pre-coated glass backed plates and visualized by potassium permanganate and/or phosphomolybdic acid (PMA) as appropriate.

Quantities are reported to 3 significant figures and are rounded accordingly. Isolated yields are reported to 0 decimal places and 'quant.' as an indication of a yield of 99.5% or higher.

All homoallylic amines and azetidines isolated are racemic. The diastereomeric ratios were determined by analysis of ¹H NMR spectra of the isolated products.

¹H NMR spectra were recorded on a Bruker DRX-600 (600 MHz). Chemical shifts are reported in ppm with the resonance resulting from incomplete deuteration of the solvent as the internal standard (CDCl₃: .26 ppm). ¹³C NMR spectra were recorded on a Bruker DRX-600 (151 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (¹³CDCl₃: 77.16 ppm, t). All ¹H and ¹³C spectra were recorded at 298 K unless otherwise specified. Data are reported as follows: chemical shift δ /ppm (multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet or combinations thereof). ¹³C signals are singlets unless otherwise stated), coupling constants *J* Hz, integration (1H only), assignment). Spectra are assigned as fully as possible, using 1H-COSY, HSQC and NOESY where appropriate to facilitate structural determination. Signals that cannot be unambiguously assigned are reported with all possible assignments separated by a slash (e.g. H¹/H²). Multiple signals arising from diastereotopic or (pseudo-)axial/equatorial positions are suffixed alphabetically (e.g. H1a, H1b). Signals arising from mixtures of stereoisomers are suffixed with maj (major isomer) or min (minor isomer). Overlapping signals that cannot be resolved are reported with their assignments denoted in list format (e.g. H¹, H², H³). ¹H NMR signals are reported to 2 decimal points. and ¹³C NMR signals are reported to 1 decimal point unless signals are very close.

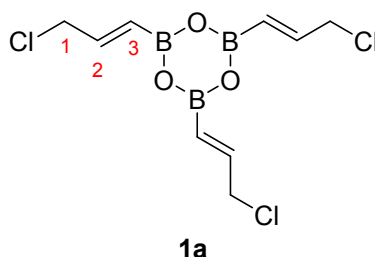
High resolution mass spectrometry (HRMS) was performed on a Waters LCT Premier spectrometer using electrospray ionization, time-of-flight analysis and Masslynx version 4.0 software. Mass values are reported up to 4 decimal points and are within the error limits of ± 5 ppm.

Infrared spectra were recorded neat as thin films on a Perkin-Elmer Spectrum One FTIR spectrometer and only selected peaks are reported (s = strong, m = medium, w = weak, b = broad, s = sharp).

2. General Experimental Procedures

2.1. Synthesis of Boroxines

To a flame-dried 25-mL round bottom flask connecting to a Dean-Stark apparatus was added vinyl boronic acid (1 g) and dry toluene (12.5 mL). The system was then flushed with dry argon. The reaction mixture was heated under reflux at 110 °C for 7 hr under argon. Upon cooled to room temperature, the solvent was evaporated under reduced pressure to yield the title compounds.



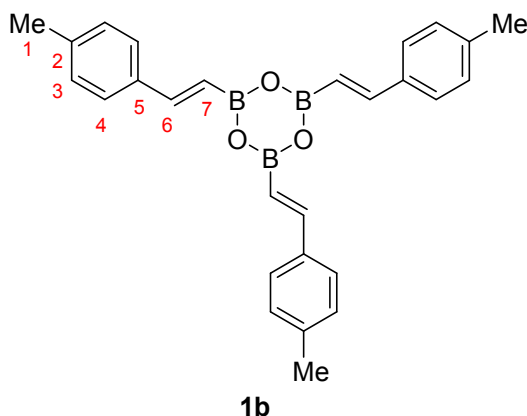
2,4,6-tris((*E*)-3-chloroprop-1-en-1-yl)-1,3,5,2,4,6-trioxatriborinane (1a): Following the general procedure for the synthesis of boroxine using *E*-2-chloromethylvinylboronic acid (1.0 g, 8.3 mmol) provided the title compound as an off-white solid (850 mg, 2.8 mmol, quant.) without further purification.

¹H NMR (600 MHz, CDCl₃): δ 6.98 (dt, *J* = 17.4, 5.9 Hz, 3H, H₂), 5.86 (dt, *J* = 17.5, 1.5 Hz, 3H, H₃), 4.19 (dd, *J* = 5.9, 1.5 Hz, 6H, H₁).

¹³C NMR (151 MHz, CDCl₃): δ 150.1 (C₂), 124.6 (br, C₃), 45.6 (C₁).

FTIR (ν_{max}, cm⁻¹): 2333 (w), 1637 (w), 1415(w), 1358 (s), 1303 (w), 1260 (m), 1175 (w), 1152 (w), 993 (m), 932 (w), 774 (w), 707 (m).

HRMS (ESI): calculated for C₉H₁₂B₃Cl₃O₃ [M+H]⁺ 307.0209, found: 307.0215.



2,4,6-tris((*E*)-4-methylstyryl)-1,3,5,2,4,6-trioxatriborinane (1b): Following the general procedure for the synthesis of boroxine using *E*-2-(4-methylphenyl)vinylboronic acid (1.0 g, 6.2 mmol) provided the title compound as an off-white solid (888 mg, 2.1 mmol, 99 %) without

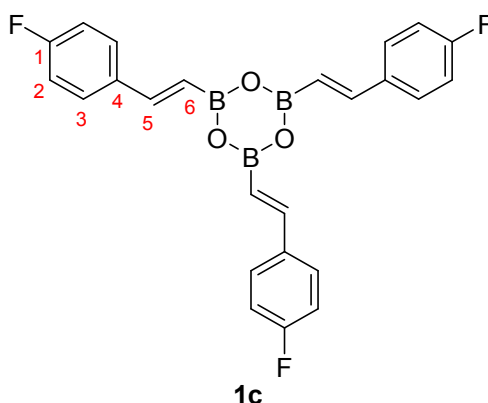
further purification.

¹H NMR (600 MHz, CDCl₃): δ 7.76 (d, *J* = 18.0 Hz, 3H, H₆), 7.53 (d, *J* = 7.9 Hz, 6H, H₄), 7.22 (d, *J* = 7.9 Hz, 6H, H₃), 6.30 (d, *J* = 18.0 Hz, 3H, H₇), 2.40 (s, 9H, H₁).

¹³C NMR (151 MHz, CDCl₃): δ 152.1 (C₆), 139.6 (C₂), 134.5 (C₅), 129.4 (C₃), 127.5 (C₄), 118.2 (C₇), 21.4 (C₁).

FTIR (ν_{max}, cm⁻¹): 1621 (m), 1568 (w), 1509 (w), 1410 (w), 1339 (s), 1294 (m), 1271 (m), 1205 (w), 1180 (m), 1109 (w), 1018 (w), 993 (m), 887 (w), 801 (m), 720 (w), 680 (w).

HRMS (ESI): calculated for C₂₇H₂₇B₃O₃ [M+H]⁺ 433.2318, found: 433.2311.



1c

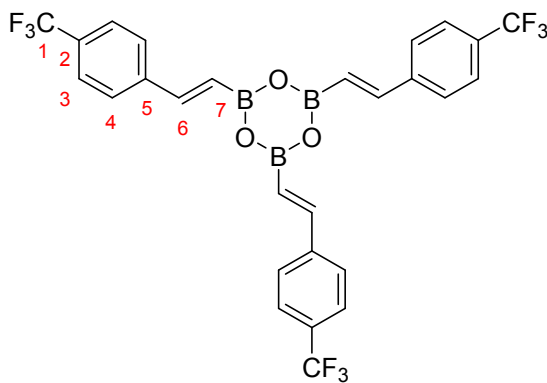
2,4,6-tris((*E*)-4-fluorostyryl)-1,3,5,2,4,6-trioxatriborinane (1c): Following the general procedure for the synthesis of boroxine using *E*-2-(4-fluorophenyl)vinylboronic acid (1.0 g, 6.0 mmol) provided the title compound as a white solid (890 mg, 2.0 mmol, quant.) without further purification.

¹H NMR (600 MHz, CDCl₃): δ 7.74 (d, *J* = 18.1 Hz, 3H, H₅), 7.63 – 7.58 (m, 6H, H₂), 7.13 – 7.08 (m, 6H, H₃), 6.26 (d, *J* = 18.1 Hz, 3H, H₆).

¹³C NMR (151 MHz, CDCl₃): δ 162.7 (C₅), 151.0 (C₄), 133.4 (d, *J* = 7.6 Hz, C₁), 129.3 (C₃), 119.0 (C₆), 115.8 (C₂).

FTIR (ν_{max}, cm⁻¹): 1620 (w), 1600 (w), 1508 (m), 1414 (w), 1349 (s), 1270 (m), 1225 (m), 1202 (m), 1180 (m), 1155 (m), 1093 (w), 1013 (w), 996 (m), 954 (w), 941 (w), 888 (w), 862 (w), 851 (w), 810 (s), 767 (m), 721 (w), 674 (w).

HRMS (ESI): calculated for C₂₄H₁₈B₃F₃O₃ [M+H]⁺ 445.1565, found: 445.1569.



1d

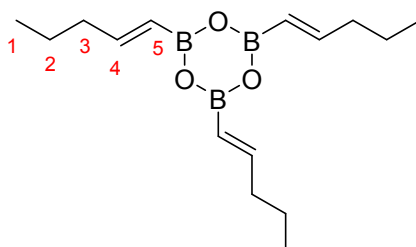
2,4,6-tris((*E*)-4-(trifluoromethyl)styryl)-1,3,5,2,4,6-trioxatriborinane (1d): Following the general procedure for the synthesis of boroxine using *E*-2-(4-trifluoromethylphenyl)vinylboronic acid (1.0 g, 4.6 mmol) provided the title compound as a white solid (915 mg, 1.5 mmol, quant.) without further purification.

¹H NMR (600 MHz, CDCl₃): δ 7.80 (d, *J* = 18.1 Hz, 3H, H6), 7.72 (d, *J* = 8.2 Hz, 6H, H4), 7.67 (d, *J* = 8.2 Hz, 6H, H3), 6.45 (d, *J* = 18.1 Hz, 3H, H7).

¹³C NMR (151 MHz, CDCl₃): δ 150.7 (C6), 140.2 (C2), 131.0 (C5), 127.7 (C4), 125.7 (q, *J* = 3.0 Hz, C1), 124.9 (C3), 122.4 (C7).

FTIR (ν_{max}, cm⁻¹): 1625 (w), 1578 (w), 1417 (w), 1356 (m), 1320 (s), 1275 (m), 1209 (w), 1192 (w), 1180 (w), 1154 (m), 1119 (m), 1107 (s), 1065 (s), 1015 (w), 996 (m), 949 (w), 887 (w), 817 (s), 741 (w), 690 (w).

HRMS (ESI): calculated for C₂₇H₁₈B₃F₉O₃ [M+H]⁺ 594.1391, found: 594,1387.



1e

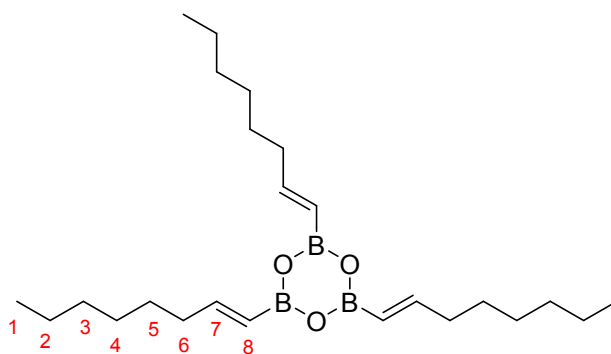
2,4,6-tri((*E*)-pent-1-en-1-yl)-1,3,5,2,4,6-trioxatriborinane (1e): Following the general procedure for the synthesis of boroxine using *E*-1-penten-1-ylboronic acid (1.0 g, 8.8 mmol) provided the title compound as a transparent oil (840 mg, 2.9 mmol, quant.) without further purification.

¹H NMR (600 MHz, CDCl₃): δ 6.97 (dt, *J* = 17.6, 6.7 Hz, 3H, H4), 5.55 (dt, *J* = 17.6, 1.6 Hz, 3H, H5), 2.21 (dtd, *J* = 7.9, 6.7, 1.6 Hz, 6H, H3), 1.50 (q, *J* = 7.3 Hz, 6H, H2), 0.94 (t, *J* = 7.3 Hz, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 157.6 (C4), 122.5 (C5), 37.7 (C3), 21.37 (C2), 13.7 (C1).

FTIR (ν_{max}, cm⁻¹): 2960 (w), 2931 (w), 2874 (w), 1632 (m), 1458 (w), 1347 (s), 1334 (s), 1303 (m), 1269 (w), 1235 (m), 1197 (w), 1106 (w), 1044 (w), 996 (m), 841 (w), 807 (w), 767 (w), 742 (w), 729 (w), 688 (w).

HRMS (ESI): calculated for C₁₅H₂₇B₃O₃ [M+H]⁺ 289.2318, found: 289.2322.



1f

2,4,6-tri(*E*-oct-1-en-1-yl)-1,3,5,2,4,6-trioxatriborinane (1f): Following the general procedure for the synthesis of boroxine using *E*-1-penten-1-ylboronic acid (1.0 g, 6.4 mmol) provided the title compound as a transparent oil (884 mg, 2.1 mmol, quant.) without further purification.

¹H NMR (600 MHz, CDCl₃): δ 6.97 (dt, *J* = 17.6, 6.5 Hz, 3H, H7), 5.54 (dt, *J* = 17.6, 1.6 Hz, 3H, H8), 2.29 – 2.14 (m, 6H, H6), 1.46 (p, *J* = 7.5 Hz, 6H, H5), 1.31 (dtdd, *J* = 14.5, 9.5, 5.7, 2.7 Hz, 18H, H2-H4), 0.90 (t, *J* = 6.9 Hz, 9H, H1).

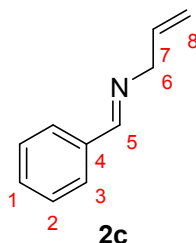
¹³C NMR (151 MHz, CDCl₃): δ 157.8 (C7), 121.9 (C8), 35.7 (C6), 31.7 (C5), 28.9 (C4), 28.15 (C3), 22.6 (C2), 14.1 (C1).

FTIR (ν_{max}, cm⁻¹): 2957 (w), 2925 (m), 2856 (w), 1642 (m), 1467 (w), 1347 (s), 1304 (m), 1228 (m), 1107 (w), 1051 (w), 999 (m), 822 (w), 789 (w), 750 (w), 735 (w), 692 (w).

HRMS (ESI): calculated for C₂₄H₄₅B₃O₃ [M+H]⁺ 415.3726, found: 415.3731.

2.2. Synthesis of Imines

To a flame-dried 25-mL round bottom flask was charged aldehyde (5 mmol, 1.0 equiv.), amine (5 mmol, 1.0 equiv.), Na₂SO₄ (2 g) and CH₂Cl₂ (15 mL). The flask was then flushed with argon for 5 mins and left stirring at room temperature overnight under argon. The solution was filtered and concentrated under reduced pressure to yield the title compounds.

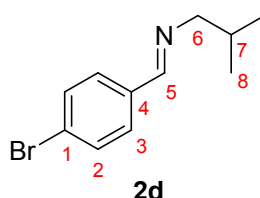


***E-N*-allyl-1-phenylmethanimine (2c):** Following the general procedure for the synthesis of imine using benzaldehyde (0.531 g, 5.00 mmol) and allylamine (0.290 g, 5.00 mmol), provided the title compound as a yellow oil without further purification (0.588 g, 4.05 mmol, 81 %).

¹H NMR (600 MHz, CDCl₃): δ 8.31 (d, *J* = 1.5 Hz, 1H, H5), 7.83 – 7.70 (m, 2H, H3), 7.48 – 7.38 (m, 3H, H1 and H2), 6.09 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H, H7), 5.25 (dq, *J* = 17.1, 1.6 Hz, 1H, H8a), 5.17 (dq, *J* = 10.3, 1.6 Hz, 1H, H8b), 4.28 (dq, *J* = 5.7, 1.6 Hz, 2H, H6).

HRMS (ESI): calculated for C₁₀H₁₁N [M+H]⁺ 146.0970, found 146.0974.

Data is consistent with a reported example.¹



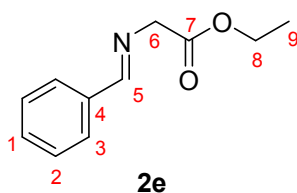
***E*-1-(4-bromophenyl)-*N*-isobutylmethanimine (2d):** Following the general procedure for the synthesis of imine using 4-bromobenzaldehyde (0.925 g, 5.00 mmol) and *iso*-butylamine (0.366 g, 5.00 mmol), provided the title compound as a yellow oil without further purification (1.05 g, 4.41 mmol, 88 %).

¹H NMR (600 MHz, CDCl₃): δ 8.19 (d, *J* = 1.5 Hz, 1H, H5), 7.61 (d, *J* = 8.3 Hz, 2H, H3), 7.54 (d, *J* = 8.4 Hz, 2H, H2), 3.42 (dd, *J* = 6.7, 1.3 Hz, 2H, H6), 2.01 (dt, *J* = 13.3, 6.7 Hz, 1H, H7), 0.95 (d, *J* = 6.7 Hz, 6H, H8).

HRMS (ESI): calculated for C₁₁H₁₄N⁷⁹Br [M+H]⁺ 240.0388, found 240.0381.

calculated for C₁₁H₁₄N⁸¹Br [M+H]⁺ 242.0388, found 242.0389.

Data is consistent with a reported example.²

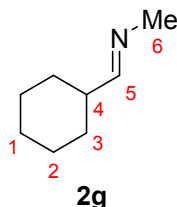


Ethyl *E*-2-(benzylideneamino)acetate (2e): Following the general procedure for the synthesis of imine using benzaldehyde (0.501 g, 5.00 mmol), Et₃N (0.506 g, 5.00 mmol) and glycine ethyl ester hydrochloride (0.698 g, 5.00 mmol), provided the title compound as a colourless oil after aqueous work-up (0.910 g, 4.75 mmol, 95 %).

¹H NMR (600 MHz, CDCl₃): δ 8.31 (d, *J* = 1.4 Hz, 1H, H5), 7.97 – 7.71 (m, 2H, H3), 7.62 – 7.34 (m, 3H, H1 and H2), 4.41 (d, *J* = 1.4 Hz, 2H, H6), 4.25 (q, *J* = 7.1 Hz, 2H, H8), 1.31 (t, *J* = 7.1 Hz, 3H, H9).

HRMS (ESI): calculated for C₁₁H₁₃NO₂ [M+H]⁺ 192.1025, found 192.1031.

Data is consistent with a reported example.³

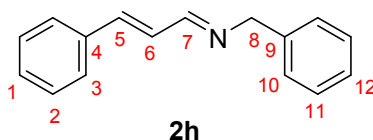


***E*-1-cyclohexyl-*N*-methylmethanimine (2g):** Following the general procedure for the synthesis of imine using cyclohexanecarboxaldehyde (0.561 g, 5.00 mmol) and methylamine (0.155 g, 5.00 mmol), provided the title compound as a yellow oil without further purification (0.582 g, 4.65 mmol, 93 %).

¹H NMR (600 MHz, CDCl₃): δ 7.53 – 7.47 (m, 1H, H5), 3.25 (s, 3H, H6), 2.13 (m, 1H, H4), 1.84 – 1.71 (m, 4H, H2a and H3a), 1.71 – 1.63 (m, 1H, H1a), 1.36 – 1.11 (m, 5H, H1b, H2b and H3b).

HRMS (ESI): calculated for C₈H₁₅N [M+H]⁺ 126.1282, found 126.276.

Data is consistent with a reported example.⁴



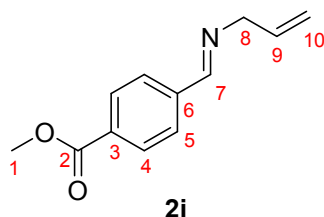
(1*E*,2*E*)-*N*-benzyl-3-phenylprop-2-en-1-imine (2h): Following the general procedure for the synthesis of imine using *E*-cinnamaldehyde (0.661 g, 5.00 mmol) and benzylamine (0.538 g, 5.00 mmol), provided the title compound as a brown oil without further purification (0.844 g, 3.77 mmol, 75 %).

¹H NMR (600 MHz, CDCl₃): δ 8.16 (dq, *J* = 6.5, 1.5 Hz, 1H, H5), 7.52 – 7.47 (m, 2H, H3), 7.40 – 7.30 (m, 9H, H1, H2, H10 and H12), 7.30 – 7.25 (m, 2H, H11), 7.01 – 6.98 (m, 2H, H5 and

H6), 4.73 (d, $J = 1.2$ Hz, 2H, H8).

HRMS (ESI): calculated for $C_{16}H_{15}N$ $[M+H]^+$ 222.1283, found 222.1277.

Data is consistent with a reported example.⁵

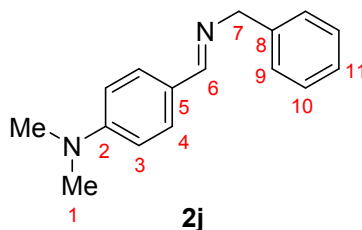


Methyl *E*-4-((allylimino)methyl)benzoate (2i): Following the general procedure for the synthesis of imine using methyl 4-formylbenzoate (0.821 g, 5.00 mmol) and allylamine (0.285 g, 5.00 mmol), provided the title compound as a yellow oil without further purification (0.986 g, 4.83 mmol, 97 %).

¹H NMR (600 MHz, $CDCl_3$): δ 8.35 (d, $J = 1.4$ Hz, 1H, H7), 8.11 – 8.07 (m, 2H, H5), 7.85 – 7.81 (m, 2H, H4), 6.08 (ddt, $J = 17.1, 10.2, 5.8$ Hz, 1H, H9), 5.25 (dq, $J = 17.1, 1.7$ Hz, 1H, H10a), 5.19 (dq, $J = 10.2, 1.5$ Hz, 1H, H10b), 4.30 (dq, $J = 5.7, 1.6$ Hz, 2H, H8), 3.94 (s, 3H, H1).

HRMS (ESI): calculated for $C_{12}H_{13}NO_2$ $[M+H]^+$ 204.1025, found 204.1022.

Data is consistent with a reported example.⁶

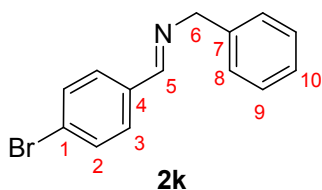


***E*-4-((benzylimino)methyl)-*N,N*-dimethylaniline (2j):** Following the general procedure for the synthesis of imine using 4-dimethylamino benzaldehyde (0.746 g, 5.00 mmol) and benzylamine (0.540 g, 5.00 mmol), provided the title compound as a yellow oil without further purification (0.985 g, 4.14 mmol, 83 %).

¹H NMR (400 MHz, $CDCl_3$): δ 8.27 (t, $J = 1.3$ Hz, 1H, H6), 7.66 (dd, $J = 8.4, 1.3$ Hz, 2H, H4), 7.33 (dd, $J = 4.4, 0.8$ Hz, 5H, H9-H11), 6.75 – 6.66 (m, 2H, H3), 4.77 (d, $J = 1.3$ Hz, 2H, H7), 3.02 (d, $J = 0.9$ Hz, 6H, H1).

HRMS (ESI): calculated for $C_{16}H_{18}N_2$ $[M+H]^+$ 239.1548, found 239.1544.

Data is consistent with a reported example.⁷



***E-N*-benzyl-1-(4-bromophenyl)methanimine (2k):** Following the general procedure for the

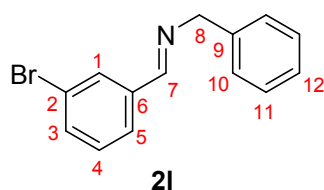
synthesis of imine using 4-bromobenzaldehyde (0.925 g, 5.00 mmol) and benzylamine (0.536 g, 5.00 mmol), provided the title compound as a yellow oil without further purification (1.33 g, 4.87 mmol, 97 %).

¹H NMR (600 MHz, CDCl₃): δ 8.35 (s, 1H, H5), 7.71 – 7.62 (m, 3H, H3 and H10), 7.56 (d, *J* = 8.3 Hz, 2H, H8), 7.38 – 7.32 (m, 4H, H2 and H9), 4.83 (s, 2H, H6).

HRMS (ESI): calculated for C₁₄H₁₂N⁷⁹Br [M+H]⁺ 274.0231, found 274.0237.

calculated for C₁₄H₁₂N⁸¹Br [M+H]⁺ 276.0231, found 274.0241.

Data is consistent with a reported example.⁸



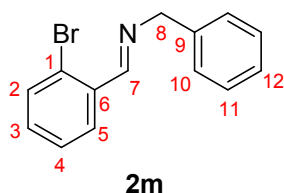
***E-N*-benzyl-1-(3-bromophenyl)methanimine (2l):** Following the general procedure for the synthesis of imine using 3-bromobenzaldehyde (0.925 g, 5.00 mmol) and benzylamine (0.536 g, 5.00 mmol), provided the title compound as a yellow oil without further purification (1.35 g, 4.93 mmol, 99 %).

¹H NMR (600 MHz, CDCl₃): δ 8.34 (s, 1H, H7), 7.99 (t, *J* = 1.8 Hz, 1H, H1), 7.67 (dt, *J* = 7.7, 1.3 Hz, 1H, H3/H5), 7.61 – 7.53 (m, 1H, H3/H5), 7.39 – 7.32 (m, 4H, H10 and H11), 7.32 – 7.24 (m, 2H, H4 and H12), 4.84 (d, *J* = 1.3 Hz, 2H, H8).

HRMS (ESI): calculated for C₁₄H₁₂N⁷⁹Br [M+H]⁺ 274.0231, found 274.0233.

calculated for C₁₄H₁₂N⁸¹Br [M+H]⁺ 276.0231, found 274.0234.

Data is consistent with a reported example.⁹



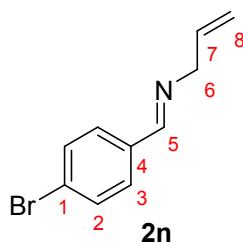
***E-N*-benzyl-1-(2-bromophenyl)methanimine (2m):** Following the general procedure for the synthesis of imine using 2-bromobenzaldehyde (0.925 g, 5.00 mmol) and benzylamine (0.536 g, 5.00 mmol), provided the title compound as a yellow oil without further purification (1.24 g, 4.52 mmol, 91 %).

¹H NMR (600 MHz, CDCl₃): δ 8.79 (d, *J* = 1.5 Hz, 1H, H8), 8.09 (dd, *J* = 7.8, 1.8 Hz, 1H, H5), 7.59 (dd, *J* = 8.0, 1.2 Hz, 1H, H1), 7.40 – 7.32 (m, 5H, H10-H12), 7.29 (ddd, *J* = 11.4, 6.3, 2.5 Hz, 2H, H3 and H4), 4.88 (d, *J* = 1.4 Hz, 2H, H8).

HRMS (ESI): calculated for C₁₄H₁₂N⁷⁹Br [M+H]⁺ 274.0231, found 274.0228.

calculated for C₁₄H₁₂N⁸¹Br [M+H]⁺ 276.0231, found 274.0236.

Data is consistent with a reported example.¹⁰



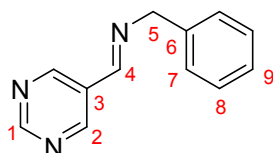
***E-N*-allyl-1-(4-bromophenyl)methanimine (2n):** Following the general procedure for the synthesis of imine using 4-bromobenzaldehyde (0.925 g, 5.00 mmol) and allylamine (0.285 g, 5.00 mmol), provided the title compound as a yellow oil without further purification (1.11 g, 4.94 mmol, 99 %).

¹H NMR (600 MHz, CDCl₃): δ 8.25 (t, *J* = 1.4 Hz, 1H, H5), 7.67 – 7.60 (m, 2H, H3), 7.58 – 7.53 (m, 2H, H2), 6.06 (ddt, *J* = 17.1, 10.2, 5.7 Hz, 1H, H7), 5.28 – 5.13 (m, 2H, H8), 4.26 (dq, *J* = 5.7, 1.6 Hz, 2H, H6).

HRMS (ESI): calculated for C₁₀H₁₀N⁷⁹Br [M+H]⁺ 224.0075, found 224.0077.

calculated for C₁₄H₁₂N⁸¹Br [M+H]⁺ 226.0075, found 226.0065.

Data is consistent with a reported example.¹¹

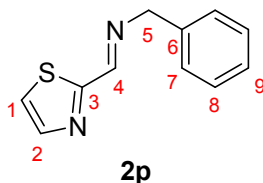


***E-N*-benzyl-1-(pyrimidin-5-yl)methanimine (2o):** Following the general procedure for the synthesis of imine using 5-pyrimidinecarboxaldehyde (0.541 g, 5.00 mmol) and benzylamine (0.538 g, 5.00 mmol), provided the title compound as a yellow oil without further purification (0.894 g, 4.53 mmol, 91 %).

¹H NMR (600 MHz, CDCl₃): δ 9.26 (s, 1H, H1), 9.10 (s, 2H, H2), 8.41 (t, *J* = 1.5 Hz, 1H, H3), 7.41 – 7.29 (m, 5H, H7-H9), 4.89 (d, *J* = 1.4 Hz, 2H, H4).

HRMS (ESI): calculated for C₁₂H₁₁N₃ [M+H]⁺ 198.1031, found 198.1025.

Data is consistent with a reported example.¹²

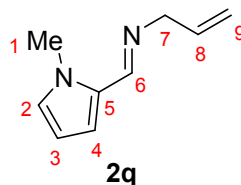


***E-N*-benzyl-1-(thiazol-2-yl)methanimine (2p):** Following the general procedure for the synthesis of imine using 2-thiazolecarboxylic aldehyde (0.566 g, 5.00 mmol) and benzylamine (0.538 g, 5.00 mmol), provided the title compound as a red oil without further purification (0.856 g, 4.24 mmol, 85 %).

¹H NMR (600 MHz, CDCl₃): δ 8.54 (q, *J* = 1.4 Hz, 1H, H4), 7.93 (d, *J* = 3.2 Hz, 1H, H2), 7.42 (dd, *J* = 3.1, 1.0 Hz, 1H, H1), 7.40 – 7.27 (m, 5H, H6-H8), 4.89 (d, *J* = 1.5 Hz, 2H, H5).

HRMS (ESI): calculated for C₁₁H₁₀N₂S [M+H]⁺ 203.0643, found 203.0639.

Data is consistent with a reported example.¹³

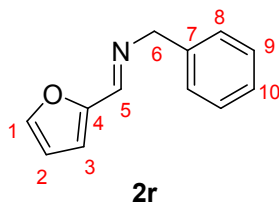


***E*-N-allyl-1-(1-methyl-1H-pyrrol-2-yl)methanimine (2q):** Following the general procedure for the synthesis of imine using 1-Methyl-2-pyrrolicarboxylic aldehyde (0.546 g, 5.00 mmol) and allylamine (0.285 g, 5.00 mmol), provided the title compound as a yellow oil without further purification (0.582 g, 3.93 mmol, 79 %).

¹H NMR (600 MHz, CDCl₃): δ 8.14 (d, *J* = 1.3 Hz, 1H, H6), 6.71 (t, *J* = 2.2 Hz, 1H, H2), 6.50 (dd, *J* = 3.9, 1.8 Hz, 1H, H4), 6.14 (dd, *J* = 3.8, 2.5 Hz, 1H, H3), 6.05 (ddt, *J* = 17.1, 10.6, 5.4 Hz, 1H, H8), 5.21 (dd, *J* = 17.2, 1.8 Hz, 1H, H9a), 5.12 (dd, *J* = 10.3, 1.7 Hz, 1H, H9b), 4.15 (dt, *J* = 5.5, 1.6 Hz, 2H, H7), 3.96 (s, 3H, H1).

HRMS (ESI): calculated for C₉H₁₂N₂ [M+H]⁺ 149.1079, found 149.1081.

Data is consistent with a reported example.¹⁴

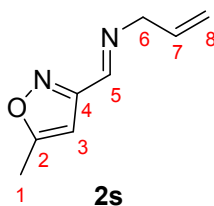


***E*-N-benzyl-1-(furan-2-yl)methanimine (2r):** Following the general procedure for the synthesis of imine using furfural (0.560 g, 4.99 mmol) and benzylamine (0.536 g, 5.00 mmol), provided the title compound as a red oil without further purification (0.917 g, 4.95 mmol, 99 %).

¹H NMR (600 MHz, CDCl₃): δ 8.18 (d, *J* = 1.5 Hz, 1H, H5), 7.53 (d, *J* = 1.6 Hz, 1H, H1), 7.34 (h, *J* = 5.9 Hz, 4H, H8 and H9), 7.30 – 7.24 (m, 1H, H10), 6.79 (d, *J* = 3.3 Hz, 1H, H3), 6.49 (dd, *J* = 3.4, 1.8 Hz, 1H, H2), 4.80 (d, *J* = 1.3 Hz, 2H, H6).

HRMS (ESI): calculated for C₁₂H₁₁NO [M+H]⁺ 186.0919, found 186.0913.

Data is consistent with a reported example.¹⁵



***E-N*-allyl-1-(5-methylisoxazol-3-yl)methanimine (2s):** Following the general procedure for the synthesis of imine using 5-methylisoxazole-3-carboxaldehyde (0.555 g, 5.00 mmol) and allylamine (0.285 g, 5.00 mmol), provided the title compound as a yellow oil without further purification (0.687 g, 4.57 mmol, 91 %).

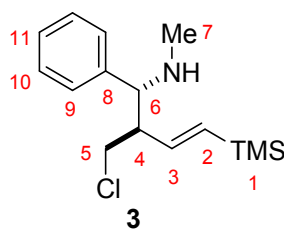
¹H NMR (600 MHz, CDCl₃): δ 8.38 (t, *J* = 1.5 Hz, 1H, H5), 6.42 (d, *J* = 1.1 Hz, 1H, H3), 6.04 (ddt, *J* = 17.1, 10.2, 5.8 Hz, 1H, H7), 5.29 – 5.14 (m, 2H, H8), 4.29 (dq, *J* = 5.8, 1.6 Hz, 2H, H6), 2.46 (d, *J* = 0.9 Hz, 3H, H1).

HRMS (ESI): calculated for C₈H₁₀N₂O [M+H]⁺ 151.0871, found 151.0877.

Data is consistent with a reported example.¹⁶

2.3. Synthesis of homoallylic amines

To a flame-dried 2-mL microwave vial was added boroxine (0.125 mmol, 1.5 equiv. w.r.t monomer) and imine (0.25 mmol, 1.0 equiv.). The microwave vial was sealed with cap and backfilled with argon and evacuated (3 times), before addition of dry toluene (1 mL) under argon atmosphere. The vial was left stirring at room temperature for 5 mins until all the solid dissolved. TMSCHN₂ (2M in hexane, 0.2 mL) was added to the solution as drops and the solution was heated at 85 °C for 6 hr. The solution was then cooled to room temperature and concentrated under reduced pressure to yield the reaction crude as brown oil which was purified by flash column chromatography (EtOAc/hexane/Et₃N) to yield the title compounds.



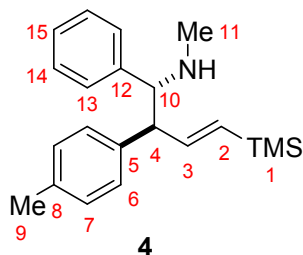
(E)-2-(chloromethyl)-N-methyl-1-phenyl-4-(trimethylsilyl)but-3-en-1-amine (3): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1a**) (38.4 mg, 0.125 mmol) and *N*-benzylidenemethylamine (**2a**) (29.8 mg, 0.250 mmol), purified by flash column chromatography (eluent: 15% EtOAc/ 84% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (66.3 mg, 0.235 mmol, 94 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.37 – 7.26 (m, 5H, H9-11), 6.09 – 5.89 (m, 2H, H2 and H3), 3.60 (d, *J* = 8.3 Hz, 1H, H6), 3.46 (dd, *J* = 10.8, 5.1 Hz, 1H, H5a), 3.24 (dd, *J* = 10.8, 5.1 Hz, 1H, H5b), 2.67 – 2.55 (m, 1H, H4), 2.22 (s, 3H, H7), 0.11 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 143.7(C2), 140.8(C8), 136.8(C3), 128.4(C9), 128.0(C10), 127.5(C11), 65.5(C6), 55.2(C4), 46.5(C5), 34.6(C7), -1.3(C1).

FTIR (ν_{max}, cm⁻¹): 2952 (w), 2897 (w), 2850 (w), 2794 (w), 1740 (w), 1613 (w), 1443 (w), 1247 (m), 1130 (w), 993(w), 862 (s), 834 (s), 729 (m), 700 (s).

HRMS (ESI): calculated for C₁₅H₂₄ClNSi [M+H]⁺ 282.1445, found: 282.1443.



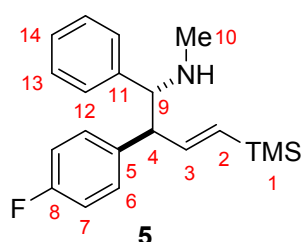
(E)-N-methyl-1-phenyl-2-(p-tolyl)-4-(trimethylsilyl)but-3-en-1-amine (4): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1b**) (51.6 mg, 0.13 mmol) and *N*-benzylidenemethylamine (**2a**) (29.8 mg, 0.250 mmol), purified by flash column chromatography (eluent: 10% EtOAc/ 89% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (69.6 mg, 0.215 mmol, 86 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.21 – 7.12 (m, 3H, H15 and H13/H14), 7.12 – 7.09 (m, 2H, H13/H14), 6.98 (d, *J* = 7.8 Hz, 2H, H6), 6.89 (d, *J* = 8.0 Hz, 2H, H7), 6.30 (dd, *J* = 18.4, 8.7 Hz, 1H, H3), 5.88 (d, *J* = 18.4 Hz, 1H, H2), 3.71 (d, *J* = 8.7 Hz, 1H, H10), 3.47 (apparent t, *J* = 8.8 Hz, 1H, H4), 2.26 (s, 3H, H9), 2.25 (s, 3H, H11), 0.09 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 146.4 (C3), 141.3 (C8), 138.3 (C5), 135.6 (C12), 133.7 (C2), 128.8 (C7), 128.3 (C13/14), 128.1 (C6), 127.7 (C13/14), 126.7 (C15), 69.6 (C10), 61.0 (C4), 34.7 (C9), 21.0 (C11), -1.2 (C1).

FTIR (ν_{max}, cm⁻¹): 3210 (br), 2955 (w), 2685 (w), 2499 (w), 1607 (w), 1514 (w), 1458 (w), 1400 (w), 1349 (w), 1246 (w), 1193 (w), 1138 (w), 1005 (w), 984 (w), 926 (w), 871 (m), 838 (m), 802 (m), 755 (m), 727 (m), 699 (s).

HRMS (ESI): calculated for C₂₁H₂₉NSi [M+H]⁺ 324.2148, found: 324.2144.



(E)-2-(4-fluorophenyl)-N-methyl-1-phenyl-4-(trimethylsilyl)but-3-en-1-amine (5):

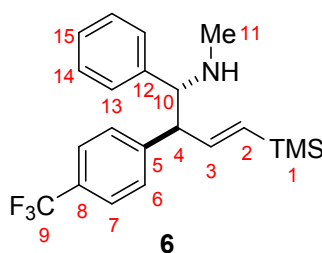
Following the general procedure for the synthesis of homoallylic amine using boroxine (**1c**) (38.4 mg, 0.250 mmol) and *N*-benzylidenemethylamine (**2a**) (29.8 mg, 0.250 mmol), purified by flash column chromatography (eluent: 20% EtOAc/ 79% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (61.4 mg, 0.188 mmol, 75 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.20 – 7.11 (m, 3H, H13 and H14), 7.10 – 7.06 (m, 2H, H12), 6.93 (dd, *J* = 8.7, 5.5 Hz, 2H, H7), 6.88 – 6.81 (m, 2H, H6), 6.30 (dd, *J* = 18.4, 8.8 Hz, 1H, H3), 5.92 (dd, *J* = 18.4, 0.9 Hz, 1H, H2), 3.69 (d, *J* = 8.8 Hz, 1H, H9), 3.50 (apparent t, *J* = 8.8 Hz, 1H, H4), 2.26 (s, 3H, H10), 1.92 (s, 1H, NH), 0.11 (d, *J* = 4.4 Hz, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 161.3 (d, *J* = 256.7 Hz, C8), 146.1 (C3), 141.1 (C5), 137.1 (C11), 134.1 (C2), 129.7 (d, *J* = 15.1 Hz, C7), 128.2 (C13/C12), 127.8 (C13/C12), 126.9 (C14), 114.9 (d, *J* = 19.6 Hz, C6), 69.7 (C9), 60.5 (C4), 34.7 (C10), -1.2 (C1).

FTIR (ν_{max}, cm⁻¹): 3026 (w), 2953 (w), 2896 (w), 2849 (w), 2790 (w), 1604 (w), 1509 (m), 1475 (w), 1454 (w), 1444 (w), 1296 (w), 1248 (m), 1223 (m), 1159 (w), 1331 (w), 1098 (w), 1074 (w), 992 (w), 877 (m), 860 (m), 837 (s), 734 (w), 700 (m).

HRMS (ESI): calculated for C₂₀H₂₆FNSi [M+H]⁺ 328.1897, found: 328.1896.



(E)-N-methyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)-4-(trimethylsilyl)but-3-en-1-amine

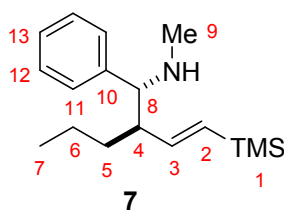
(6): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1d**) (74.2 mg, 0.125 mmol) and *N*-benzylidenemethylamine (**2a**) (29.8 mg, 0.250 mmol), purified by flash column chromatography (eluent: 20% EtOAc/ 79% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (76.4 mg, 0.203 mmol, 81 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.39 (d, *J* = 8.1 Hz, 2H, H7), 7.18 – 7.13 (m, 3H, H14 and H15), 7.10 – 7.03 (m, 4H, H6 and H13), 6.27 (dd, *J* = 18.4, 8.8 Hz, 1H, H3), 5.93 (d, *J* = 18.4 Hz, 1H, H2), 3.73 (d, *J* = 8.8 Hz, 1H, H10), 3.55 (apparent t, *J* = 8.8 Hz, 1H, C4), 2.26 (s, 3H, H11), 0.10 (d, *J* = 1.7 Hz, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 145.6 (C5), 145.2 (C3), 140.7 (C8), 135.0 (C2), 129.2 (C7), 128.6 (C6), 128.1 (C13), 127.9 (C14), 127.1 (C15), 124.96 (q, *J* = 3.0 Hz, C9), 124.94 (C12), 69.4 (C10), 61.2 (C4), 34.6 (C11), -1.3 (C1).

FTIR (ν_{max}, cm⁻¹): 2955 (w), 2790 (w), 1610 (w), 1494 (w), 1475 (w), 1445 (w), 1418 (w), 1325 (s), 1249 (w), 1164 (m), 1125 (m), 1070 (m), 1019 (w), 992 (w), 838 (m), 756 (w), 700 (m).

HRMS (ESI): calculated for C₁₅H₂₄ClNSi [M+H]⁺ 378.1865, found: 378.1859.



***N*-methyl-1-phenyl-2-((E)-2-(trimethylsilyl)vinyl)pentan-1-amine (7):** Following the general procedure for the synthesis of homoallylic amine using boroxine (**1f**) (110.97 mg, 0.250 mmol) and *N*-benzylidenemethylamine (**2a**) (29.8 mg, 0.250 mmol), purified by flash column chromatography (eluent: 30% EtOAc/ 69% Hexane/ 1% Et₃N) provided the title compound as an inseparable mixture of diastereomers (3:1) as a colourless oil (45.4 mg, 0.165 mmol, 66 %, 3:1 dr).

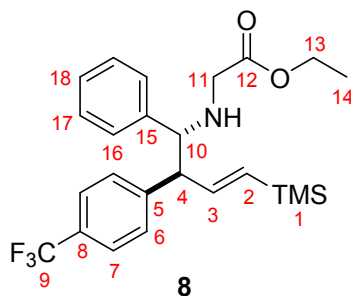
¹H NMR (600 MHz, CDCl₃): δ 7.41 – 7.30 (m, 1.5H, H11 of diastereomer B), 7.29 – 7.25 (m, 2.5H, H12 of diastereomer B and H13), 7.25 – 7.21 (m, 0.6H, H11 of diastereomer A), 7.16 – 7.13 (m, 0.6H, H12 of diastereomer A), 5.87 – 5.57 (m, 2H, H2 and H3), 3.48 and 3.21 (d, *J* = 5.2 Hz and *J* = 8.7 Hz, 1H, H8), 2.45 – 2.35 (m, 0.3H, H4 of diastereomer A), 2.26 (s, 1H, H9 of diastereomer A), 2.25 – 2.21 (m, 0.7H, H4 of diastereomer B), 2.18 (s, 2.2H, H9 of diastereomer B), 1.48 – 1.39 (m, 0.3H, H5a of diastereomer A), 1.36 – 1.11 (m, 2.2H, H5b and H6 of diastereomer A, H5a and H6a of diastereomer B), 1.09 – 0.98 (m, 1.5H, H5b and H6b of diastereomer B), 0.85 and 0.73 (two t, *J* = 7.1 Hz, 3H, H7), 0.09 and 0.00 (two s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 148.4 and 147.3 (C3), 142.5 and 141.2 (C10), 134.3 and 132.6 (C2), 128.4 and 128.2 (C12), 128.1 and 127.7 (C11), 127.0 and 126.7 (C13), 69.0 and 68.4 (C8), 54.3 and 52.6 (C4), 34.7 and 34.4 (C9), 33.6 and 33.1 (C5), 20.6 and 20.3 (C6), 14.1 and 13.9 (C7), -1.1 and -1.2 (C1).

FTIR (ν_{max}, cm⁻¹): 3063 (w), 3026 (w), 2955 (w), 2872 (w), 2786 (w), 1612 (w), 1493 (w), 1475 (w), 1454 (w), 1443 (w), 1378 (w), 1355 (w), 1247 (m), 1185 (w), 1132 (w), 1072 (w), 1029 (w),

996 (w), 863 (s), 834 (s), 741 (m), 722 (m), 700 (s).

HRMS (ESI): calculated for $C_{17}H_{29}NSi$ $[M+H]^+$ 276.2148, found: 276.2140.



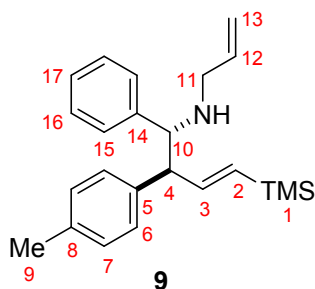
Ethyl ((E)-1-phenyl-2-(4-(trifluoromethyl)phenyl)-4-(trimethylsilyl)but-3-en-1-yl)glycinate (8): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1d**) (74.2 mg, 0.125 mmol) and imine (**2e**) (47.8 mg, 0.250 mmol), purified by flash column chromatography (eluent: 2% EtOAc/ 97% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (70.8 mg, 0.158 mmol, 63 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.37 (d, J = 8.1 Hz, 2H, H7), 7.15 – 7.12 (m, 3H, H17 and H18), 7.08 – 7.03 (m, 4H, H6 and H16), 6.35 (dd, J = 18.4, 9.0 Hz, 1H, H3), 6.03 (d, J = 18.4 Hz, 1H, H2), 4.17 (q, J = 7.2 Hz, 2H, H13), 3.89 (d, J = 9.0 Hz, 1H, H10), 3.53 (apparent t, J = 9.0 Hz, 1H, H4), 3.28 (d, J = 17.7 Hz, 1H, H11a), 3.09 (d, J = 17.7 Hz, 1H, H11b), 1.24 (t, J = 7.2 Hz, 3H, H14), 0.12 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 172.4 (C12), 145.4 (C5), 145.1 (C3), 140.1 (C15), 135.4 (C2), 129.0 (C18), 128.5 (C16), 128.2 (C7), 128.0 (C6), 127.3 (C17), 124.9 (q, J = 4.5 Hz, C9), 123.3 (C8), 66.3 (C10), 61.5 (C4), 60.6 (C13), 48.5 (C11), 14.2 (C14), -1.3 (C1).

FTIR ($\nu_{\max}$, cm⁻¹): 2984 (w), 2955 (w), 2905 (w), 1737 (m), 1612 (w), 1469 (w), 1455 (w), 1418 (w), 1372 (2), 1325 (s), 1248 (w), 1196 (w), 1164 (m), 1124 (m), 1113 (m), 1069 (m), 1019 (w), 991 (w), 913 (w), 880 (w), 864 (m), 838 (m), 752 (w), 701 (w).

HRMS (ESI): calculated for $C_{24}H_{30}F_3NO_2Si$ $[M+H]^+$ 450.2076, found: 450.2085.



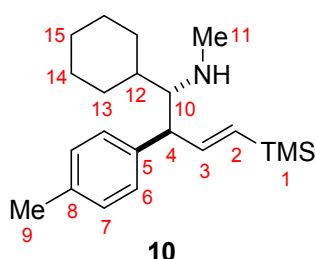
(E)-N-allyl-1-phenyl-2-(p-tolyl)-4-(trimethylsilyl)but-3-en-1-amine (9): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1b**) (54.0 mg, 0.125 mmol) and imine (**2c**) (36.3 mg, 0.250 mmol), purified by flash column chromatography (eluent: 5% EtOAc/ 94% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (58.6 mg, 0.168 mmol, 67 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.15 (m, 2H, H15), 7.13 – 7.11 (m, 1H, H17), 7.10 – 7.08 (m, 2H, H16), 6.95 (d, *J* = 7.8 Hz, 2H, H6), 6.87 (d, *J* = 8.0 Hz, 2H, H7), 6.30 (dd, *J* = 18.4, 8.9 Hz, 1H, H3), 5.89 (d, *J* = 18.4 Hz, 1H, H2), 5.87 – 5.80 (m, 1H, H12), 5.15 – 5.00 (m, 2H, H13), 3.86 (d, *J* = 8.9 Hz, 1H, H10), 3.46 (apparent t, *J* = 8.9 Hz, 1H, H4), 3.14 – 3.07 (m, 1H, H11a), 2.95 (ddd, *J* = 14.4, 6.7, 1.3 Hz, 1H, H11b), 2.24 (s, 3H, H9), 1.73 (s, 1H, NH), 0.08 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 146.7 (C3), 141.6 (C8), 138.2 (C12), 136.9 (C5), 135.5 (C14), 133.5 (C2), 128.7 (C7), 128.3 (C6), 128.1 (C16), 127.7 (C15), 126.7 (C17), 115.4 (C13), 66.5 (C10), 60.8 (C4), 49.9 (C11), 21.0 (C9), -1.2 (C1).

FTIR (ν_{max}, cm⁻¹): 3028 (w), 2954 (w), 2897 (w), 1725 (w), 1643 (w), 1608 (w), 1514 (w), 1492 (w), 1454 (w), 1416 (w), 1247 (m), 1174 (w), 1112 (w), 1070 (w), 1022 (w), 992 (m), 917 (w), 876 (m), 859 (s), 836 (s), 811 (m), 758 (m), 733 (m), 700 (s).

HRMS (ESI): calculated for C₂₃H₃₁NSi [M+H]⁺ 350.2304, found: 350.2298.



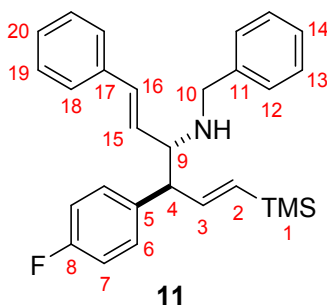
(E)-1-cyclohexyl-N-methyl-2-(p-tolyl)-4-(trimethylsilyl)but-3-en-1-amine (10): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1b**) (51.6 mg, 0.119 mmol) and imine (**2g**) (40.3 mg, 0.250 mmol), purified by flash column chromatography (eluent: 30% EtOAc/ 69% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (66.7 mg, 0.203 mmol, 81 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.19 – 7.04 (m, 4H, H6 and H7), 6.25 (dd, *J* = 18.4, 8.7 Hz, 1H, H3), 5.72 (d, *J* = 18.4 Hz, 1H, H2), 3.33 (apparent t, *J* = 8.7 Hz, 1H, H4), 2.39 (s, 3H, H11), 2.34 (m, 4H, H9 and H10), 1.71 – 1.65 (m, 2H, H14a), 1.65 – 1.60 (m, 2H, H14b), 1.60 – 1.51 (m, 2H, H13a), 1.35 – 1.24 (m, 1H, H15a), 1.18 (dt, *J* = 11.7, 8.6, 3.2 Hz, 1H, H12), 1.14 – 0.99 (m, 3H, H13b and H15b), 0.05 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 148.2 (C3), 140.1 (C8), 135.5 (C5), 131.6 (C2), 129.2 (C6/C7), 127.8 (C6/C7), 69.1 (C10), 56.8 (C4), 40.3 (C12), 38.4 (C9), 31.2 (C15), 27.0 (C14), 26.7 (C13), 26.6 (C14), 26.4 (C13), 21.0 (C11), -1.2 (C1).

FTIR (ν_{max}, cm⁻¹): 2923 (m), 2851 (m), 2796 (w), 1609 (w), 1513 (w), 1449 (w), 1299 (w), 1247 (m), 1123 (w), 991 (w), 857 (m), 837 (s), 814 (w), 758 (w), 691 (w), 666 (w).

HRMS (ESI): calculated for C₂₁H₃₅NSi [M+H]⁺ 330.2617, found: 330.2622.



(1E,5E)-N-benzyl-4-(4-fluorophenyl)-1-phenyl-6-(trimethylsilyl)hexa-1,5-dien-3-amine

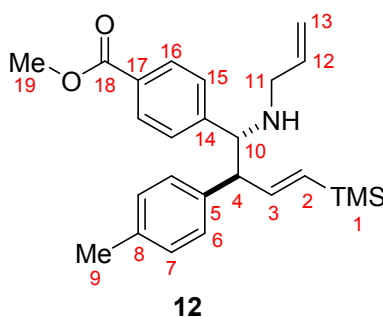
(11): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1c**) (55.5 mg, 0.128 mmol) and imine (**2h**) (55.3 mg, 0.250 mmol), purified by flash column chromatography (eluent: 15% EtOAc/ 84% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (74.1 mg, 0.173 mmol, 69 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.34 (dd, *J* = 8.0, 6.8 Hz, 2H, H14 and H20), 7.29 – 7.26 (m, 4H, H12 and H13), 7.26 – 7.20 (m, 4H, H18 and H19), 7.11 (dd, *J* = 8.6, 5.4 Hz, 2H, H6), 6.94 (t, *J* = 8.7 Hz, 2H, H7), 6.27 (d, *J* = 15.8 Hz, 1H, H16), 6.17 (dd, *J* = 18.5, 8.2 Hz, 1H, H3), 5.91 – 5.82 (m, 2H, H2 and H15), 3.91 (d, *J* = 13.5 Hz, 1H, H10a), 3.68 (d, *J* = 13.6 Hz, 1H, H10b), 3.48 – 3.36 (m, 2H, H4 and H9), 0.08 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 161.4 (d, *J* = 243 Hz, C8), 146.2 (C3), 140.3 (C11), 137.0 (C5), 133.8 (C15), 132.5 (C2), 130.4 (C16), 129.8 (d, *J* = 7.6 Hz, C6), 128.5 (C19), 128.4 (C13), 128.0 (C18), 127.3 (C20), 126.9 (C12) (C14), 126.2, 115.1 (d, *J* = 21 Hz, C7), 63.5 (C9), 58.1 (C4), 51.1 (C10), -1.3 (C1).

FTIR (ν_{max}, cm⁻¹): 3027 (w), 2955 (w), 2899 (w), 1603 (s), 1508 (m), 1495 (w), 1453 (w), 1416 (w), 1296 (w), 1247 (m), 1222 (m), 1158 (w), 1098 (w), 1073 (w), 1029 (w), 1015 (w), 992 (w), 966 (w), 859 (m), 834 (s), 736 (m), 692 (s)

HRMS (ESI): calculated for C₂₈H₃₂FNsSi, [M+H]⁺ 430.2366, found: 430.2360.



Methyl 4-((E)-1-(allylamino)-2-(p-tolyl)-4-(trimethylsilyl)but-3-en-1-yl)benzoate (12):

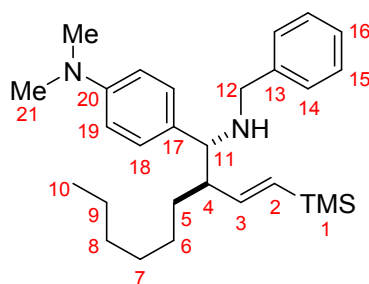
Following the general procedure for the synthesis of homoallylic amine using boroxine (**1b**) (56.1 mg, 0.130 mmol) and imine (**2i**) (50.8 mg, 0.250 mmol), purified by flash column chromatography (eluent: 10% EtOAc/ 89% Hexane/ 1% Et₃N) provided the title compound as an inseparable mixture of diastereomers (2:1) as a yellow oil (82.5 mg, 0.203 mmol, 81 %, 2:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 8.00 and 7.82 (two d, *J* = 8.3 Hz, 2H, H16), 7.38 (d, *J* = 8.3 Hz, 1H, H15 of diastereomer A), 7.21 – 7.12 (m, 4H, H15 of diastereomer B, H6 and H7 of diastereomer A), 6.94 (d, *J* = 7.8 Hz, 2H, H6 of diastereomer B), 6.89 – 6.81 (m, 2H, H7 of diastereomer B), 6.28 (dd, *J* = 18.4, 8.9 Hz, 1H, H3 of diastereomer B), 5.95 – 5.86 (m, 1.6H, H2 of diastereomer B and H3 of diastereomer A), 5.82 and 5.64 (two dddd, *J* = 18.0, 9.5, 6.7, 5.0 Hz, 1H, H12), 5.25 (d, *J* = 18.4 Hz, 0.6H, H2 of diastereomer A), 5.12 – 5.04 (m, 3H, H13 of diastereomer A and H13a of diastereomer B), 5.02 – 4.89 (m, 1H, H13b of diastereomer B), 4.01 – 3.90 (m, 4H, H4 and H19 of diastereomer A and H10 of diastereomer B), 3.87 (s, 3H, H19 of diastereomer B), 3.43 (m, 1.6H, H4), 3.07 and 3.02 (two dd, *J* = 14.5, 5.1 Hz, 1H, H11a), 2.93 and 2.83 (ddt, *J* = 14.5, 7.1, 1.2 Hz, 1H, H11b), 2.36 and 2.24 (two s, 3H, H9), 0.08 and -0.15 (two s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 167.13 and 167.11 (C18), 147.8 and 147.5 (C17), 146.2 and 145.9 (C3), 137.8 and 137.7 (C8), 136.6 and 136.5 (C12), 135.8 (C14), 134.1 and 132.4 (C2), 129.5 and 129.1 (C16), 129.3 and 128.9 (C15), 129.0 and 128.6 (C5), 128.6 and 128.3 (C7), 128.2 and 128.0 (C6), 115.8 and 115.7 (C13), 66.3 and 66.2 (C10), 60.7 and 60.1 (C4), 52.0 and 51.9 (C19), 49.9 and 49.8 (C11), 21.1 and 21.0 (C9), -1.2 and -1.5 (C1).

FTIR (ν_{max}, cm⁻¹): 2953 (w), 1724 (s), 1611 (w), 1513 (w), 1436 (w), 1416 (w), 1278 (s), 1248 (m), 1191 (w), 1113 (m), 1019 (w), 992 (w), 920 (w), 861 (m), 838 (m), 756 (w), 709 (w)

HRMS (ESI): calculated for C₂₅H₃₃NO₂Si [M+H]⁺ 408.2353, found: 408.2348.



13

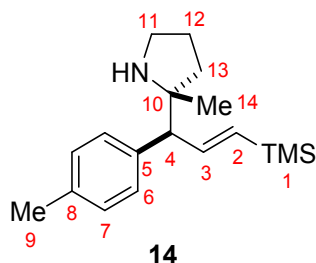
4-(1-(benzylamino)-2-((E)-2-(trimethylsilyl)vinyl)octyl)-N,N-dimethylaniline (13): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1f**) (51.8 mg, 0.125 mmol) and imine (**2j**) (59.6 mg, 0.250 mmol), purified by flash column chromatography (eluent: 10% EtOAc/ 89% Hexane/ 1% Et₃N) provided the title compound as a colourless oil (105 mg, 0.240 mmol, 96 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.33 (t, *J* = 7.5 Hz, 2H, H14), 7.25 (t, *J* = 7.5 Hz, 1H, H16), 7.20 (d, *J* = 8.0 Hz, 4H, H15 and H19), 6.77 (d, *J* = 8.4 Hz, 2H, H18), 5.86 (d, *J* = 18.6 Hz, 1H, H2), 5.70 (dd, *J* = 18.6, 8.9 Hz, 1H, H3), 3.67 (d, *J* = 13.6 Hz, 1H, H12a), 3.41 (d, *J* = 13.7 Hz, 1H, H12b), 3.22 (d, *J* = 9.2 Hz, 1H, H11), 2.99 (s, 6H, H21), 2.29 – 2.17 (m, 1H, H4), 1.37 – 0.96 (m, 10H, H5-H9), 0.84 (t, *J* = 7.3 Hz, 3H, H10), 0.12 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 149.7 (C20), 149.6 (C3), 141.0 (13), 133.8 (C2), 130.2 (C17), 129.2 (C15/C19), 128.3 (C14), 128.1 (C15/C19), 126.6 (C6), 112.4 (C18), 64.4 (C11), 54.5 (C4), 51.0 (C12), 40.7 (C21), 31.8 (C6/C8), 30.9 (C6/C8), 29.0 (C5), 27.2 (C9), 22.6 (C7), 14.1 (C10), -1.0 (C1).

FTIR (ν_{max} , cm^{-1}): 2955 (m), 2928 (m), 2856 (m), 2801 (w), 1614 (m), 1569 (w), 1521 (m), 1495 (w), 1456 (w), 1347 (w), 1247 (m), 1183 (w), 1163 (w), 1125 (w), 1060 (w), 1029 (w), 997 (w), 948 (w), 866 (s), 837 (s), 818 (m), 746 (w), 699 (m)

HRMS (ESI): calculated for $\text{C}_{28}\text{H}_{44}\text{N}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 437.3347, found: 437.3339.



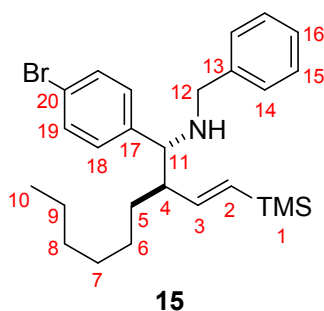
2-methyl-2-(1-(p-tolyl)-3-(trimethylsilyl)allyl)pyrrolidine (14): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1b**) (51.6 mg, 0.119 mmol) and 3,4-dihydro-5-methyl-2H-Pyrrole (20.8 mg, 0.250 mmol), refluxed 12 hrs instead of 6 hrs, purified by flash column chromatography (eluent: 30% EtOAc/ 69% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (64.0 mg, 0.223 mmol, 89 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.18 (d, J = 8.0 Hz, 2H, H₆), 7.11 (d, J = 7.9 Hz, 2H, H₇), 6.48 (dd, J = 18.4, 8.8 Hz, 1H, H₃), 5.74 (d, J = 18.4 Hz, 1H, H₂), 3.29 (d, J = 8.8 Hz, 1H, H₄), 2.98 (ddd, J = 10.7, 7.7, 6.0 Hz, 1H, H_{11a}), 2.95 – 2.88 (ddd, J = 10.7, 7.7, 6.0 Hz, 1H, H_{11b}), 2.33 (s, 3H, H₉), 1.80 (m, 1H, H_{13a}), 1.79 – 1.66 (m, 2H, H₁₂), 1.37 (ddd, J = 12.0, 8.0, 5.3 Hz, 1H, H_{13b}), 1.08 (s, 3H, H₁₄), 0.07 (s, 9H, H₁).

¹³C NMR (151 MHz, CDCl₃): δ 146.5 (C₃), 139.0 (C₈), 135.7 (C₅), 132.8 (C₂), 129.1 (C₆/C₇), 128.8 (C₆/C₇), 64.2 (C₁₀), 62.0 (C₄), 45.8 (C₁₁), 36.0 (C₁₃), 25.5 (C₁₄), 25.2 (C₁₂), 21.0 (C₉), -1.1 (C₁).

FTIR (ν_{max} , cm^{-1}): 2955 (m), 2925 (w), 2897 (w), 2869 (w), 1609 (w), 1513 (w), 1448 (w), 1405 (w), 1371 (w), 1300 (w), 1247 (m), 1116 (w), 995 (w), 866 (m), 837 (s), 757 (w), 692 (w)

HRMS (ESI): calculated for $\text{C}_{18}\text{H}_{29}\text{NSi}$ $[\text{M}+\text{H}]^+$ 288.2148, found: 288.2159



N-benzyl-1-(4-bromophenyl)-2-((E)-2-(trimethylsilyl)vinyl)octan-1-amine (15): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1f**) (51.8 mg, 0.125 mmol) and imine (**2k**) (68.5 mg, 0.250 mmol), purified by flash column chromatography (eluent: 2% EtOAc/ 97% Hexane/ 1% Et₃N) provided the title compound as an inseparable mixture of diastereomers (6:1) as a colourless oil (95.7 mg, 0.203 mmol, 81 %, 3:1 dr).

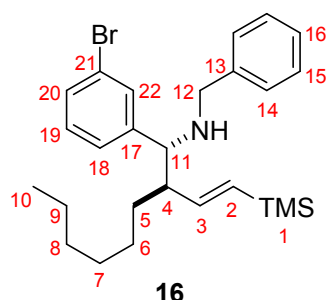
¹H NMR (600 MHz, CDCl₃): δ 7.49 – 7.44 (two d, *J* = 8.3 Hz, 2H, H19), 7.30 (m, 2H, H15), 7.26 – 7.22 (m, 1H, H16), 7.22 – 7.19 (m, 2H, H18), 7.17 – 7.13 and 7.10 (two d, *J* = 8.4 Hz, 2H, H13), 5.79 (d, *J* = 18.6 Hz, 0.7H, C2 of diastereomer B), 5.65 (dd, *J* = 18.6, 8.8 Hz, 0.7H, C3 of diastereomer B), 5.60 (dd, *J* = 18.7, 7.9 Hz, 0.3H, C3 of diastereomer A), 5.54 (d, *J* = 18.7 Hz, 0.3H, C2 of diastereomer A), 3.67 (d, *J* = 13.4 Hz, 0.3H, H12a of diastereomer A), 3.64 – 3.57 (m, 1H, H11), 3.48 (d, *J* = 13.4 Hz, 0.3H, H12b of diastereomer A), 3.35 (d, *J* = 13.6 Hz, 0.8H, H12a of diastereomer B), 3.28 (d, *J* = 8.9 Hz, 0.8H, H12b of diastereomer B), 2.29 (dd, *J* = 8.3, 4.3 Hz, 0.2H, H4 of diastereomer A), 2.15 (dq, *J* = 15.9, 8.1, 7.1 Hz, 0.8H, H4 of diastereomer B), 1.33 – 0.94 (m, 10H, H5-H9), 0.86 and 0.82 (two t, *J* = 7.3 Hz, 3H, H10), 0.08 and -0.01 (two s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 148.4 and 147.1 (C3), 141.8 (C13) and 140.5 (C17), 134.5 and 132.7 (C2), 131.2 and 130.9 (C19), 130.2 and 130.0 (C15), 128.3 and 128.3 (C18), 128.03 and 127.97 (C14), 126.82 and 126.80 (C16), 121.4 and 120.7 (C20), 64.9 and 64.6 (C11), 54.2 and 52.7 (C4), 51.21 and 51.16 (C12), 31.7 and 31.6 (C6/C8), 30.8 and 30.5 (C5), 29.2 and 28.9 (C6/C8), 27.3 and 27.0 (C9), 22.6 and 22.5 (C7), 14.04 and 14.01 (C10), -1.1 and -1.2 (C1).

FTIR (ν_{max}, cm⁻¹): 3026 (w), 2954 (w), 2926 (w), 2856 (w), 1611 (w), 1486 (w), 1156 (w), 1405 (w), 1430 (w), 1247 (m), 1113 (w), 1071 (w), 1029 (w), 1011 (m), 997 (w), 864 (s), 836 (s), 741 (m), 723 (m), 697 (m)

HRMS (ESI): calculated for C₂₆H₃₈⁷⁹BrNSi [M+H]⁺ 472.2035, found: 472.2039.

calculated for C₂₆H₃₈⁸¹BrNSi [M+H]⁺ 474.2035, found: 474.2042.



***N*-benzyl-1-(3-bromophenyl)-2-((*E*)-2-(trimethylsilyl)vinyl)octan-1-amine (16):** Following the general procedure for the synthesis of homoallylic amine using boroxine (**1f**) (51.8 mg, 0.125 mmol) and imine (**2i**) (68.5 mg, 0.250 mmol), purified by flash column chromatography (eluent: 2% EtOAc/ 97% Hexane/ 1% Et₃N) provided the title compound as an inseparable mixture of diastereomers (3:1) as a colourless oil (74.4 mg, 0.158 mmol, 63 %, 6:1 dr).

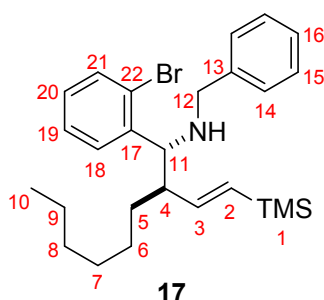
¹H NMR (600 MHz, CDCl₃): δ 7.52 (s, 1H, H20), 7.44 – 7.37 (m, 1H, H22), 7.36 – 7.30 (m, 2H, H14), 7.29 – 7.15 (m, 5H, H15, H16, H18 and H19), 5.79 (d, *J* = 18.6 Hz, 0.7H, H2 of diastereomer B), 5.68 (dd, *J* = 18.6, 8.8 Hz, 0.7H, H3 of diastereomer B), 5.62 (dd, *J* = 18.7, 8.0 Hz, 0.3H, H3 of diastereomer A), 5.55 (d, *J* = 18.7 Hz, 0.3H, H2 of diastereomer A), 3.71 and 3.64 (two d, *J* = 13.6 Hz, 1H, H12a), 3.59 (d, *J* = 8.6 Hz, 0.3H, H11 of diastereomer A), 3.51 and 3.38 (two d, *J* = 13.6 Hz, 1H, H12b), 3.31 (d, *J* = 8.6 Hz, 0.7H, H11 of diastereomer B), 2.42 – 2.12 (m, 1H, H4), 1.55 – 0.96 (m, 10H, H5-H9), 0.88 and 0.84 (two t, *J* = 7.3 Hz, 3H, H10), 0.10 and 0.02 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 148.3 and 147.1 (C3), 145.4 and 144.7 (C17), 140.48 and 140.45 (C13), 134.6 and 132.8 (C2), 131.4 and 131.3 (C22), 130.2 and 129.8 (C19), 129.7 and 129.4 (C20), 128.4 and 128.3 (C18), 128.1 and 128.0 (C15), 127.3 and 126.9 (C14), 126.9 and 126.8 (C16), 122.4 and 122.2 (C21), 65.2 and 64.9 (C11), 54.2 and 52.8 (C4), 51.30 and 51.28 (C12), 31.8 and 31.6 (C6/C8), 30.8 and 30.6 (C5), 29.2 and 28.9 (C6/C8), 27.3 and 27.1 (C9), 22.6 and 22.5 (C7), 14.1 and 14.0 (C10), -1.1 and -1.2 (C1).

FTIR (ν_{max}, cm⁻¹): 2954 (w), 2927 (w), 2856 (w), 1611 (w), 1593 (w), 1570 (w), 1495 (w), 1458 (w), 1426 (w), 1321 (w), 1247 (w), 1195 (w), 1113 (w), 1070 (w), 1029 (w), 997 (w), 864 (s), 837 (s), 784 (w), 748 (m), 697 (m)

HRMS (ESI): calculated for C₂₆H₃₈⁷⁹BrNSi [M+H]⁺ 472.2035, found: 472.2034.

calculated for C₂₆H₃₈⁸¹BrNSi [M+H]⁺ 474.2035, found: 472.2039.



N-benzyl-1-(2-bromophenyl)-2-((E)-2-(trimethylsilyl)vinyl)octan-1-amine (17): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1f**) (51.8 mg, 0.125 mmol) and imine (**2m**) (68.5 mg, 0.250 mmol), purified by flash column chromatography (eluent: 2% EtOAc/ 97% Hexane/ 1% Et₃N) provided the title compound as an inseparable mixture of diastereomers (9:1) as a colourless oil (86.2 mg, 0.183 mmol, 73 %, 6:1 dr).

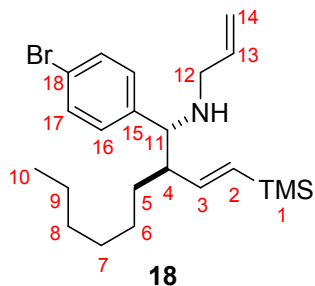
¹H NMR (600 MHz, CDCl₃): δ 7.55 (dd, *J* = 8.0, 1.3 Hz, 2H, H21 and H19), 7.36 – 7.29 (m, 3H, H14 and H16), 7.26 – 7.21 (m, 3H, H15 and H18), 7.16 – 7.09 (m, 1H, H20), 5.77 (dd, *J* = 18.6, 8.4 Hz, 1H, H3, H18 and H), 5.69 (d, *J* = 18.6 Hz, 1H, H2), 4.12 – 4.06 (m, 1H, H11), 3.61 (d, *J* = 13.5 Hz, 1H, H12a), 3.44 (d, *J* = 13.5 Hz, 1H, H12b), 2.25 (m, 1H, H4), 1.46 – 0.87 (m, 10H, H5-H9), 0.84 (t, *J* = 7.3 Hz, 3H, H10), 0.07 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 147.9 (C3), 142.0 (C13), 141.9 (C17), 140.6 (C18), 135.3 (C2), 134.3 (C20), 132.4 (C19), 128.3 (C15), 128.2 (C16), 128.2 (C14), 127.5 (C22), 126.8 (C), 62.9 (C11), 54.1 (C4), 51.3 (C12), 31.7 (C6/C8), 30.4 (C5), 28.9 (C6/C8), 27.2 (C9), 22.6 (C7), 14.1 (C10), -1.1 (C1).

FTIR (ν_{max}, cm⁻¹): 3215 (br), 3064 (w), 2956 (w), 2928 (m), 2856 (m), 1614 (w), 1567 (w), 1496 (w), 1456 (w), 1248 (m), 1022 (w), 997 (w), 866 (s), 837 (s), 749 (m), 698 (m), 665 (w)

HRMS (ESI): calculated for C₂₆H₃₈⁷⁹BrNSi [M+H]⁺ 472.2035, found: 472.2033.

calculated for C₂₆H₃₈⁸¹BrNSi [M+H]⁺ 474.2035, found: 472.2027.



***N*-allyl-1-(4-bromophenyl)-2-((*E*)-2-(trimethylsilyl)vinyl)octan-1-amine (18):** Following the general procedure for the synthesis of homoallylic amine using boroxine (**1f**) (51.8 mg, 0.125 mmol) and imine (**2n**) (56.0 mg, 0.250 mmol), purified by flash column chromatography (eluent: 5% EtOAc/ 94% Hexane/ 1% Et₃N) provided the title compound as a colourless oil (105.6 mg, 0.250 mmol, quant. >20:1 dr).

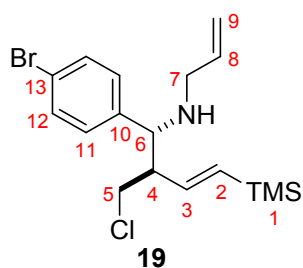
¹H NMR (600 MHz, CDCl₃): δ 7.47 – 7.41 (m, 2H, H17), 7.19 – 7.15 (m, 2H, H16), 5.81 (d, *J* = 18.6 Hz, 1H, H2), 5.79 – 5.74 (m, 1H, H13), 5.71 (dd, *J* = 18.6, 8.7 Hz, 1H, H3), 5.08 – 5.00 (m, 2H, H14), 3.35 (d, *J* = 8.7 Hz, 1H, H11), 3.01 (ddt, *J* = 14.4, 5.1, 1.6 Hz, 1H, H12a), 2.86 (ddt, *J* = 14.4, 6.9, 1.3 Hz, 1H, H12b), 2.15 (apparent dd, *J* = 8.6, 6.2 Hz, 1H, H4), 1.34 – 0.86 (m, 10H, H5-H9), 0.83 (t, *J* = 7.3 Hz, 3H), 0.09 (s, 9H).

¹³C NMR (151 MHz, CDCl₃): δ 148.2 (C3), 141.9 (C15), 136.8 (C13), 134.7 (C2), 131.2 (C17), 130.1 (C16), 120.6 (C18), 115.5 (C14), 65.2 (C11), 54.3 (C4), 49.9 (C12), 31.7 (C6/C8), 30.7 (C5), 28.9 (C6/C8), 27.1 (C9), 22.5 (C7), 14.0 (C10), -1.1 (C1).

FTIR (ν_{max}, cm⁻¹): 2956 (w), 2928 (w), 2856 (w), 1644 (w), 1614 (w), 1486 (w), 1459 (w), 1405 (w), 1248 (m), 1113 (w), 1071 (w), 1011 (w), 995 (w), 918 (w), 864 (s), 837 (s), 743 (w), 723 (w), 692 (w)

HRMS (ESI): calculated for C₂₂H₃₆⁷⁹BrNSi [M+H]⁺ 422.1873, found: 422.1870.

calculated for C₂₂H₃₆⁸¹BrNSi [M+H]⁺ 424.1873, found: 424.1879.



(*E*)-*N*-allyl-1-(4-bromophenyl)-2-(chloromethyl)-4-(trimethylsilyl)but-3-en-1-amine (19): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1a**) (38.4 mg, 0.125 mmol) and imine (**2n**) (56.0 mg, 0.250 mmol), purified by flash column chromatography (eluent: 5% EtOAc/ 94% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (90.9 mg, 0.235 mmol, 94 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.51 – 7.44 (m, 2H, H12), 7.25 – 7.22 (m, 2H, H11), 6.02 – 5.89 (m, 2H, H2 and H3), 5.84 – 5.73 (m, 1H, H8), 5.11 – 5.04 (m, 2H, H9), 3.75 (d, *J* = 8.2 Hz, 1H, H6), 3.46 (dd, *J* = 10.9, 4.2 Hz, 1H, H5a), 3.22 (dd, *J* = 10.9, 5.7 Hz, 1H, H5b), 3.04 (ddt, *J* =

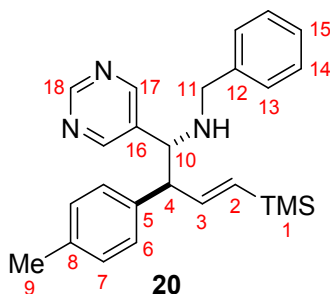
14.3, 5.1, 1.4 Hz, 1H, H7a), 2.90 (ddt, $J = 14.3, 6.7, 1.4$ Hz, 1H, H7b), 2.52 (tdd, $J = 8.2, 5.7, 4.2$ Hz, 1H, H4), 1.56 (s, 1H, NH), 0.10 (s, 9H, H1).

^{13}C NMR (151 MHz, CDCl_3): δ 143.4 (C3), 140.4 (C13), 137.1 (C2), 136.5 (C8), 131.6 (C12), 129.8 (C11), 121.2 (C10), 115.8 (C9), 61.7 (C6), 55.1 (C4), 49.8 (C7), 46.3 (C5), -1.3 (C1).

FTIR (ν_{max} , cm^{-1}): 2957 (w), 1615 (w), 1487 (w), 1461 (w), 1406 (w), 1248 (m), 1073 (w), 1011 (w), 994 (w), 920 (w), 865 (s), 840 (s), 747 (w)

HRMS (ESI): calculated for $\text{C}_{17}\text{H}_{25}^{79}\text{BrCINSi}$ $[\text{M}+\text{H}]^+$ 386.0701, found: 386.0697.

calculated for $\text{C}_{17}\text{H}_{25}^{81}\text{BrCINSi}$ $[\text{M}+\text{H}]^+$ 386.0701, found: 386.0705.



(E)-N-benzyl-1-(pyrimidin-5-yl)-2-(p-tolyl)-4-(trimethylsilyl)but-3-en-1-amine (20):

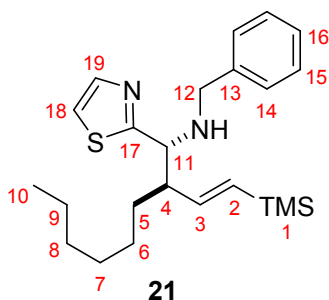
Following the general procedure for the synthesis of homoallylic amine using boroxine (**1b**) (51.6 mg, 0.119 mmol) and imine (**2o**) (49.3 mg, 0.250 mmol), purified by flash column chromatography (eluent: 30% EtOAc/ 69% Hexane/ 1% Et₃N) provided the title compound as an inseparable mixture of diastereomers (2:1) as a yellow oil (67.3 mg, 0.168 mmol, 67 %, 1.5:1 dr).

^1H NMR (600 MHz, CDCl_3): δ 9.12 and 8.98 (two s, 1H, H18), 8.66 and 8.43 (two s, 2H, H17), 7.36 – 7.31 (m, 1H, H14 of diastereomer A), 7.27 (d, $J = 4.2$ Hz, 2.5H, H7 of diastereomer B and H15 of diastereomer A), 7.25 (d, $J = 4.8$ Hz, 1H, H15 of diastereomer B), 7.16 (t, $J = 6.9$ Hz, 3H, H14 of diastereomer B and H13 of diastereomer A), 7.09 – 7.06 (m, 2H, H13 of diastereomer B), 6.98 (d, $J = 6.4$ Hz, 2H, H6 of diastereomer B), 6.96 (d, $J = 7.8$ Hz, 1H, H7 of diastereomer A), 6.78 (d, $J = 8.0$ Hz, 1H, H6 of diastereomer A), 6.20 (dd, $J = 18.5, 8.8$ Hz, 1H, H3 of diastereomer A), 5.91 (d, $J = 18.4, 0.5$ Hz, H2 of diastereomer A), 5.83 (dd, $J = 18.4, 8.4$ Hz, 1H, H3 of diastereomer B), 5.27 (d, $J = 18.4, 1$ Hz, H2 of diastereomer B), 3.84 and 3.81 (two d, $J = 9.4$ Hz, 1H, H10), 3.69 and 3.63 (d, $J = 13.9$ Hz, 1H, H11a), 3.45 (d, $J = 13.9$ Hz, 0.5H, H11b of diastereomer A), 3.43 – 3.37 (m, 1H, H4), 3.35 (d, $J = 13.9$ Hz, 1H, H11b of diastereomer B), 2.37 and 2.23 (two s, 3H, H9), 0.08 and -0.14 (two s, 9H, H1).

^{13}C NMR (151 MHz, CDCl_3): δ 157.8 and 157.5 (C18), 157.4 and 156.9 (C17), 145.3 and 144.9 (C3), 139.5 and 139.3 (C12), 137.0 and 136.8 (C5), 136.7 and 136.5 (C16), 135.5 and 135.0 (C8), 134.9 and 134.2 (C2), 129.7 and 129.4 (C7), 128.5 and 128.4 (C14), 127.94 and 127.92 (C6), 127.91 and 127.89 (C13), 127.2 and 127.1 (C15), 62.1 and 61.8 (C10), 60.53 and 60.48 (C11), 51.6 and 51.3 (C4), 21.1 and 20.9 (C9), -1.3 and -1.6 (C1).

FTIR (ν_{max} , cm^{-1}): 3027 (w), 2955 (w), 1616 (w), 1563 (m), 1514 (w), 1496 (w), 1355 (w), 1405 (m), 1248 (m), 1116 (w), 1030 (w), 992 (w), 860 (s), 838 (s), 731 (m), 699 (m)

HRMS (ESI): calculated for $\text{C}_{25}\text{H}_{31}\text{N}_3\text{Si}$ $[\text{M}+\text{H}]^+$ 402.2366, found: 402.2364.



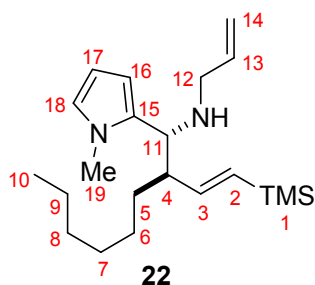
N-benzyl-1-(thiazol-2-yl)-2-((E)-2-(trimethylsilyl)vinyl)octan-1-amine (21): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1f**) (51.8 mg, 0.125 mmol) and imine (**2p**) (50.6 mg, 0.250 mmol), purified by flash column chromatography (eluent: 5% EtOAc/ 94% Hexane/ 1% Et₃N) provided the title compound as an inseparable mixture of diastereomers (1.5:1) as a yellow oil (100.2 mg, 0.250 mmol, quant., 1.5:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.73 (m, 1H, H19), 7.34 – 7.29 (m, 2.6H, H18 of diastereomer B, H14), 7.28 – 7.22 (m, 3.4H, H18 of diastereomer A, H15 and H16), 5.80 – 5.73 (m, 1H, H3 of diastereomer A and H2 of diastereomer B), 5.71 – 5.58 (m, 1H, H2 of diastereomer A and H3 of diastereomer B), 4.11 – 3.87 (two d, *J* = 5.6 and *J* = 13.3 Hz, H11), 3.80 (two d, *J* = 13.3 Hz, 1H, H12a), 3.60 (two d, *J* = 13.4 Hz, 1H, H12b), 2.51 – 2.26 (two m, 1H, H4), 1.63 – 0.94 (m, 10H, H5-H9), 0.84 (two t, *J* = 7.2 Hz, 3H, H10), 0.03 (two s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 176.3 and 175.1 (C17), 147.1 and 146.4 (C3), 142.1 and 141.9 (C19), 140.0 and 139.9 (C13), 135.2 and 133.1 (C2), 128.4 and 128.3 (C15), 128.17 and 128.15 (C14), 127.01 and 126.98 (C16), 119.1 and 118.5 (C18), 63.4 and 63.1 (C11), 54.7 and 52.6 (C4), 52.0 and 51.90 (C12), 31.7 and 31.6 (C6/C8), 30.6 and 30.2 (C5), 29.1 and 28.9 (C6/C8), 27.2 and 27.0 (C9), 22.6 and 22.5 (C7), 14.1 and 14.0 (C10), -1.2 and -1.3 (C1).

FTIR (ν_{max}, cm⁻¹): 2954 (w), 2926 (w), 2856 (w), 1611 (w), 1496 (w), 1455 (w), 1315 (w), 1247 (m), 1184 (w), 1116 (w), 1053 (w), 1029 (w), 996 (w), 864 (s), 837 (s), 723 (m), 698 (m)

HRMS (ESI): calculated for C₂₃H₃₆N₂SSi [M+H]⁺ 401.2447, found: 401.2445.



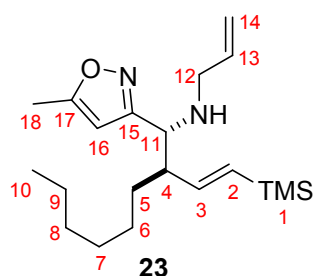
N-allyl-1-(1-methyl-1H-pyrrol-2-yl)-2-((E)-2-(trimethylsilyl)vinyl)octan-1-amine (22): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1f**) (51.8 mg, 0.125 mmol) and imine (**2q**) (37.1 mg, 0.250 mmol), purified by flash column chromatography (eluent: 10% EtOAc/ 89% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (84.9 mg, 0.245 mmol, 98 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 6.53 (t, *J* = 2.3 Hz, 1H, H18), 6.06 (t, *J* = 3.1 Hz, 1H, H17), 5.99 (dd, *J* = 3.6, 1.8 Hz, 1H, H16), 5.83 (d, *J* = 18.6 Hz, 1H, H2), 5.81 – 5.76 (m, 1H, H13), 5.73 (dd, *J* = 18.6, 8.6 Hz, 1H, H3), 5.12 – 4.98 (m, 2H, H14), 3.66 (s, 3H, H19), 3.58 (d, *J* = 9.1 Hz, 1H, H11), 3.10 (ddt, *J* = 14.3, 5.1, 1.7 Hz, 1H, H12a), 2.96 (ddt, *J* = 14.3, 6.6, 1.3 Hz, 1H, H12b), 2.37 (apparent qd, *J* = 9.1, 3.5 Hz, 1H, H4), 1.44 – 0.99 (m, 10H, H5–H9), 0.85 (t, *J* = 7.2 Hz, 3H, H10), 0.09 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 149.0 (C3), 137.3 (C13), 134.0 (C2), 132.4 (C15), 122.1 (C18), 115.2 (C14), 108.5 (C16), 106.4 (C17), 58.3 (C11), 53.1 (C4), 49.6 (C12), 34.4 (C19), 31.7 (C6/C8), 30.9 (C6/C8), 29.0 (C5), 27.1 (C9), 22.5 (C7), 14.0 (C10), -1.1 (C1).

FTIR (ν_{max}, cm⁻¹): 2957 (s), 2926 (s), 2856 (m), 1615 (w), 1498 (w), 1461 (w), 1415 (w), 1296 (w), 1248 (m), 1089 (w), 996 (w), 917 (w), 865 (s), 838 (s), 748 (w), 707 (m)

HRMS (ESI): calculated for C₂₁H₃₈N₂Si [M+H]⁺ 347.2877, found: 347.2870.



***N*-allyl-1-(5-methylisoxazol-3-yl)-2-((*E*)-2-(trimethylsilyl)vinyl)octan-1-amine (23):**

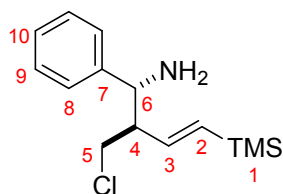
Following the general procedure for the synthesis of homoallylic amine using boroxine (**1f**) (51.8 mg, 0.125 mmol) and imine (**2s**) (37.5 mg, 0.250 mmol), purified by flash column chromatography (eluent: 10% EtOAc/ 89% Hexane/ 1% Et₃N) provided the title compound as an inseparable mixture of diastereomers (2:1) as a yellow oil (81.9 mg, 0.235 mmol, 94 %, 2:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 6.00 – 5.64 (m, 4H, H2, H3, H13 and H16), 5.24 – 5.02 (m, 2H, H14), 3.79 and 3.60 (d, *J* = 9.0 Hz, 1H, H11), 3.15 (ddt, *J* = 14.1, 5.6, 1.6 Hz, 0.7H, H12a of diastereomer B), 3.08 (dtt, *J* = 11.1, 6.2, 1.4 Hz, 1H, H12a of diastereomer A and H12b of diastereomer B), 2.98 (dd, *J* = 14.3, 6.6 Hz, 0.3H, H12b of diastereomer A), 2.43 – 2.35 (m, 3.7H, H18 and H4 of diastereomer B), 2.25 – 2.19 (m, 0.3H, H4 of diastereomer A), 1.70 – 1.43 (m, 4H, H6 and H8), 1.41 – 1.02 (m, 6H, H5, H7 and H9), 0.84 (m, 3H, H10), 0.07 and 0.02 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 169.2 and 168.7 (C17), 166.0 and 164.8 (C15), 147.2 and 146.5 (C3), 136.5, 136.3 (C2), 135.3 and 133.7 (C13), 115.9 and 115.9 (C14), 100.5 and 99.5 (C16), 57.3 and 57.3 (C11), 52.1 and 51.3 (C4), 49.9 and 49.8 (C12), 31.7 and 31.6 (C6/C8), 31.0 and 30.7 (C6/C8), 29.1 and 28.9 (C5), 27.1 and 26.9 (C9), 22.6 and 22.5 (C7), 14.02 and 14.01 (C10), 12.4 and 12.3 (C18), -1.2 and -1.3 (C1).

FTIR (ν_{max}, cm⁻¹): 2956 (m), 2927 (m), 2857 (w), 1608 (w), 1458 (w), 1411 (w), 1248 (m), 1109 (w), 994 (w), 919 (w), 865 (s), 839 (s), 749 (w)

HRMS (ESI): calculated for C₂₀H₃₆N₂OSi [M+H]⁺ 349.2670, found: 349.2666.



24

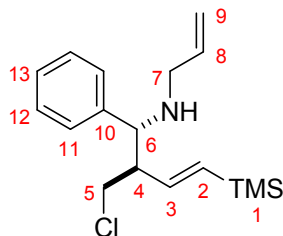
(E)-2-(chloromethyl)-1-phenyl-4-(trimethylsilyl)but-3-en-1-amine (24): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1a**) (38.4 mg, 0.125 mmol) and *N*-trimethylsilylbenzaldimine (44.3 mg, 0.250 mmol), purified by flash column chromatography (eluent: 5% EtOAc/ 94% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (43.5 mg, 0.163 mmol, 65 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.35 (d, *J* = 5.6 Hz, 4H, H8 and H9), 7.30 – 7.26 (m, 1H, H10), 6.00 (dd, *J* = 18.6, 7.9 Hz, 1H, H3), 5.90 (d, *J* = 18.6 Hz, 1H, H2), 4.10 (d, *J* = 7.9 Hz, 1H, H6), 3.50 (dd, *J* = 10.9, 4.8 Hz, 1H, H5a), 3.31 (dd, *J* = 10.9, 6.0 Hz, 1H, H5b), 2.63 – 2.55 (m, 1H, H4), 1.75 (s, 1H, NH), 0.10 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 143.3 (C3), 136.4 (C2), 128.5 (C7), 128.5 (C8), 127.5 (C10), 127.1 (C9), 56.0 (C6), 55.9 (C4), 46.3 (C5), -1.3 (C1).

FTIR (ν_{max}, cm⁻¹): 2955 (w), 2895 (w), 1612 (w), 1493 (w), 1545 (w), 1437 (w), 1301 (w), 1247 (m), 1150 (w), 1057 (w), 1028 (w), 993 (w), 955 (w), 863 (s), 836 (s), 761 (m), 740 (m), 700 (s).

HRMS (ESI): calculated for C₁₄H₂₂ClNSi [M+H]⁺ 268.1288, found: 268.1275.



25

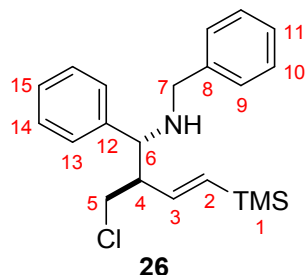
(E)-N-allyl-2-(chloromethyl)-1-phenyl-4-(trimethylsilyl)but-3-en-1-amine (25): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1a**) (38.4 mg, 0.125 mmol) and imine (**2c**) (44.3 mg, 0.250 mmol), purified by flash column chromatography (eluent: 5% EtOAc/ 94% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (56.2 mg, 0.183 mmol, 73 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.34 (m, 4H, H11 and H12), 7.31 – 7.26 (m, 1H, H13), 6.06 – 5.90 (m, 2H, H2 and H3), 5.81 (dddd, *J* = 17.1, 10.3, 6.7, 5.2 Hz, 1H, H8), 5.13 – 5.02 (m, 2H, H9), 3.77 (d, *J* = 8.4 Hz, 1H, H6), 3.47 (dd, *J* = 10.8, 4.2 Hz, 1H, H5a), 3.25 (dd, *J* = 10.8, 6.1 Hz, 1H, H5b), 3.07 (ddt, *J* = 14.3, 5.2, 1.5 Hz, 1H, H7a), 2.94 (ddt, *J* = 14.3, 6.7, 1.5 Hz, 1H, H7b), 2.60 (tdd, *J* = 8.4, 6.1, 4.2 Hz, 1H, H4), 0.11 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 143.9 (C3), 141.1 (C19), 136.7 (C8 and C2), 128.4 (C11/C12), 128.0 (C11/C12), 127.5 (C13), 115.7 (C9), 62.4 (C6), 55.2 (C4), 49.8 (C7), 46.4 (C5), -1.3 (C1).

FTIR (ν_{max} , cm^{-1}): 2955 (w), 1643 (w), 1615 (w), 1493 (w), 1343 (w), 1418 (w), 1302 (w), 1248 (m), 1149 (w), 1111 (w), 1071 (w), 1028 (w), 992 (m), 956 (w), 917 (w), 863 (s), 835 (s), 774 (w), 738 (m), 722 (m), 700 (s).

HRMS (ESI): calculated for $\text{C}_{23}\text{H}_{31}\text{NSi}$ $[\text{M}+\text{H}]^+$ 308.1601, found: 308.1603.



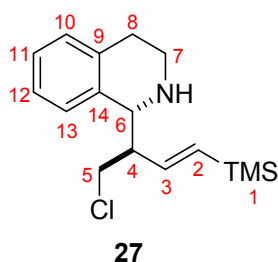
(E)-N-benzyl-2-(chloromethyl)-1-phenyl-4-(trimethylsilyl)but-3-en-1-amine (26): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1a**) (38.4 mg, 0.125 mmol) and *N*-benzylidenebenzylamine (48.8 mg, 0.250 mmol), purified by flash column chromatography (eluent: 3% EtOAc/ 96% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (49.0 mg, 0.190 mmol, 76 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.40 (d, J = 4.3 Hz, 4H, H9 and H10), 7.33 (t, J = 7.6 Hz, 3H, H13 and H11), 7.29 – 7.25 (m, 1H, H15), 7.24 – 7.21 (m, 2H, H14), 6.01 – 5.91 (m, 2H, H2 and H3), 3.73 (d, J = 8.5 Hz, 1H, H6), 3.67 (d, J = 13.4 Hz, 1H, H7), 3.48 – 3.43 (m, 2H, H5a and H7), 3.24 (dd, J = 10.9, 6.4 Hz, 1H, H5b), 2.67 – 2.60 (m, 1H, H4), 1.95 (s, 1H, NH), 0.14 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 144.1 (C3), 141.2 (C12), 140.4 (C8), 136.6 (C2), 128.5 (C9/C10), 128.4 (C13), 128.2 (C9/C10), 128.0 (C14), 127.6 (C11), 126.9 (C15), 62.3 (C6), 55.3 (C4), 51.3 (C7), 46.4 (C5), -1.2 (C1).

FTIR (ν_{max} , cm^{-1}): 3063 (w), 3027 (w), 2955 (w), 2893 (w), 1614 (w), 1494 (w), 1454 (w), 1304 (w), 1248 (m), 1116 (w), 1073 (w), 1028 (w), 994 (w), 954 (w), 865 (s), 837 (s), 745 (m), 700 (s).

HRMS (ESI): calculated for $\text{C}_{21}\text{H}_{28}\text{ClNSi}$ $[\text{M}+\text{H}]^+$ 358.1758, found: 358.1757.



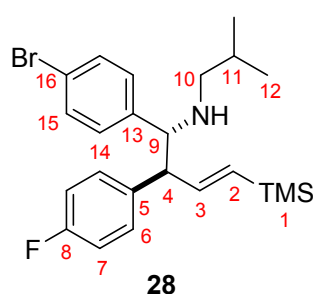
1-((E)-1-chloro-4-(trimethylsilyl)but-3-en-2-yl)-1,2,3,4-tetrahydroisoquinoline (27): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1a**) (51.8 mg, 0.125 mmol) and 3,4-dihydroisoquinoline (32.8 mg, 0.250 mmol), purified by flash column chromatography (eluent: 15% EtOAc/ 84% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (30.1 mg, 0.103 mmol, 41 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.18 – 7.15 (m, 2H, H10 and H12), 7.13 (m, 1H, H11), 7.07 (d, *J* = 7.4 Hz, 1H, H13), 5.80 (dd, *J* = 19.1, 7.1 Hz, 1H, H3), 5.62 (d, *J* = 19.1, 1H, H2), 4.44 (d, *J* = 4.2 Hz, 1H, H6), 3.84 (dd, *J* = 10.9, 8.3 Hz, 1H, H5a), 3.74 (dd, *J* = 10.9, 5.9 Hz, 1H, H5b), 3.22 (dt, *J* = 12.4, 4.9 Hz, 1H, H7a), 3.05 – 2.99 (m, 1H, H4), 2.94 (ddd, *J* = 12.8, 8.5, 4.8 Hz, 1H, H7b), 2.72 (dt, *J* = 15.2, 5.0 Hz, 2H, H8), 2.55 – 2.27 (br s, 1H, NH), -0.06 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 142.6 (C3), 136.9 (C14), 136.2 (C9), 135.0 (C2), 129.0 (C13), 126.3 (C11), 125.9 (C12), 125.8 (C10), 55.4 (C6), 53.0 (C4), 45.8 (C5), 41.57 (C7), 30.1 (C8), -1.5 (C1).

FTIR (ν_{max}, cm⁻¹): 2953 (w), 1611 (w), 1493 (w), 1454 (w), 1430 (w), 1377 (w), 1302 (w), 1247 (m), 1128 (w), 992 (w), 863 (m), 835 (s), 741 (s), 692 (m)

HRMS (ESI): calculated for C₁₆H₂₄ClNSi [M+H]⁺ 294.1445, found: 294.1445.



(E)-1-(4-bromophenyl)-2-(4-fluorophenyl)-N-isobutyl-4-(trimethylsilyl)but-3-en-1-amine

(28): Following the general procedure for the synthesis of homoallylic amine using boroxine (**1c**) (55.5 mg, 0.125 mmol) and imine (**2d**) (60.0 mg, 0.250 mmol), purified by flash column chromatography (eluent: 5% EtOAc/ 94% Hexane/ 1% Et₃N) provided the title compound as a yellow oil (53.8 mg, 0.120 mmol, 48 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.29 – 7.21 (m, 2H, H15), 6.95 – 6.91 (m, 2H, H14), 6.88 (dd, *J* = 8.7, 5.6 Hz, 2H, H6), 6.84 (t, *J* = 8.7 Hz, 2H, H7), 6.24 (dd, *J* = 18.4, 8.8 Hz, 1H, H3), 5.93 (d, *J* = 18.4 Hz, 1H, H2), 3.66 (d, *J* = 9.3 Hz, 1H, H9), 3.34 (apparent t, *J* = 9.3 Hz, 1H, H4), 2.16 (d, *J* = 6.6 Hz, 2H, H10), 1.68 (apparent dq, *J* = 13.3, 6.6 Hz, 1H, H11), 0.85 (d, *J* = 6.6 Hz, 6H, H12), 0.09 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 162.3 (d, *J* = 244.6 Hz, C8), 146.0 (C3), 141.1 (C5), 136.8 (d, C16), 134.3 (C2), 130.8 (C15), 129.8 (C14), 129.5 (C6), 120.4 (C13), 115.1 (C7), 66.9 (C9), 60.7 (C4), 55.6 (C10), 28.1 (C11), 20.6 (C12), -1.3 (C1).

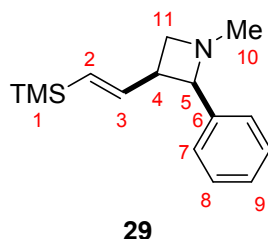
FTIR (ν_{max}, cm⁻¹): 2955 (m), 2899 (w), 2808 (w), 1608 (w), 1509 (m), 1486 (w), 1470 (w), 1404 (w), 1387 (w), 1368 (w), 1335 (w), 1295 (w), 1248 (m), 1228 (m), 1159 (w), 1116 (w), 1097 (w), 1071 (w), 1011 (m), 992 (w), 860 (m), 838 (s), 750 (w), 736 (w), 708 (w).

HRMS (ESI): calculated for C₂₃H₃₁⁷⁹BrFNSi [M+H]⁺ 448.1471, found: 448.1465.

calculated for C₂₃H₃₁⁷⁹BrFNSi [M+H]⁺ 450.1471, found: 450.1465.

2.4. Synthesis of Azetidines

To a 2-mL microwave vial was charged homoallylic amine (1 equiv.), Et₃N (1 equiv.) and MeCN (1 mL). The vial was sealed with microwave cap and heat to 70°C for 14 hr. The solution was cooled to room temperature and partitioned between H₂O (10 mL) and EtOAc (10 mL). The aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layer was washed with brine (30 mL), dried over MgSO₄ and concentrated under reduced pressure to yield the title compounds.



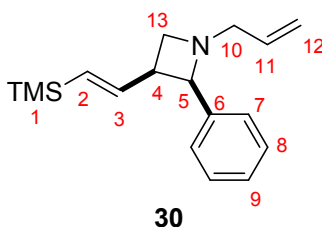
N-methyl-2-phenyl-3-(E-2-(trimethylsilyl)vinyl)azetidine (29): Following the general procedure of synthesis of azetidines using homoallylic amine **3** (141 mg, 0.50 mmol) and Et₃N (50.6 mg, 0.50 mmol), aqueous work-up provided the title compound as a dark red oil (123 mg, 0.496 mmol, 99 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.32 – 7.28 (m, 2H, H8), 7.28 – 7.24 (m, 2H, H7), 7.22 – 7.18 (m, 1H, H9), 6.02 (dd, *J* = 18.7, 7.9 Hz, 1H, H3), 5.56 (d, *J* = 18.7 Hz, 1H, H2), 4.22 (d, *J* = 6.9 Hz, 1H, H5), 3.42 (dd, *J* = 11.8, 4.8 Hz, 1H, H11a), 3.25 – 3.10 (m, 2H, H4 and H11b), 2.40 (s, 3H, H10), -0.12 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 146.2 (C3), 139.6 (C6), 131.7 (C2), 127.8 (C7), 127.0 (C8), 126.7 (C9), 73.9 (C5), 57.5 (C11), 44.3 (C10), 42.8 (C4), -1.4 (C1).

FTIR (ν_{max}, cm⁻¹): 3062 (w), 3026 (w), 2953 (w), 2826 (w), 2774 (w), 1686 (w), 1612 (w), 1492 (w), 1472 (w), 1450 (w), 1354 (w), 1326 (w), 1295 (w), 1247 (m), 1224 (w), 1207 (w), 1160 (w), 1136 (w), 1072 (w), 1029 (w), 989 (m), 936 (w), 911 (w), 863 (s), 834 (s), 754 (m), 729 (s), 698 (s)

HRMS (ESI): calculated for C₁₅H₂₃NSi [M+H]⁺ 246.2678, found: 246.2669.



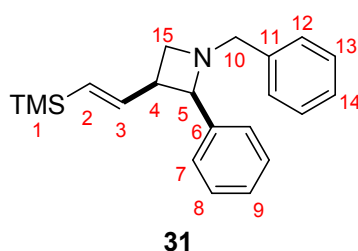
N-allyl-2-phenyl-3-(E-2-(trimethylsilyl)vinyl)azetidine (30): Following the general procedure of synthesis of azetidines using homoallylic amine **30** (130 mg, 0.42 mmol) and Et₃N (51.3 mg, 0.42 mmol), aqueous work-up provided the title compound as a yellow oil (114 mg, 0.415 mmol, 99 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.31 – 7.26 (m, 4H, H7 and H8), 7.21 – 7.16 (m, 1H, H9), 5.99 (dd, *J* = 18.7, 7.8 Hz, 1H, H3), 5.83 (ddt, *J* = 17.0, 10.2, 6.3 Hz, 1H, H11), 5.52 (d, *J* = 18.5 Hz, 1H, H2), 5.20 (dd, *J* = 17.1, 1.6 Hz, 1H, H12a), 5.06 (d, *J* = 11.0 Hz, 1H, H12b), 4.36 (d, *J* = 7.0 Hz, 1H, C5), 3.38 (d, *J* = 5.2 Hz, 1H, H13a), 3.30 (dd, *J* = 13.4, 6.3 Hz, 1H, H10a), 3.16 (m, 2H, H4 and H13b), 3.05 (dd, *J* = 13.4, 6.3 Hz, 1H, H10b), -0.14 (s, 9H, H1).

¹³C NMR (151 MHz, CDCl₃): δ 146.4 (C3), 139.8 (C5), 134.7 (C11), 131.7 (C2), 127.7 (C7), 127.2 (C8), 126.6 (C9), 117.0 (H12), 71.8 (C5), 61.0 (C10), 55.4 (C13), 42.6 (C4), -1.4 (C1).

FTIR (ν_{max}, cm⁻¹): 3064 (w), 2953 (w), 2826 (w), 1723 (w), 1643 (w), 1614 (w), 1493 (w), 1451 (w), 1419 (w), 1327 (w), 1302 (w), 1247 (m), 1204 (w), 1181 (w), 1055 (w), 1028 (w), 990 (m), 920 (w), 864 (s), 837 (s), 762 (w), 737 (m), 699 (m)

HRMS (ESI): calculated for C₁₇H₂₅NSi [M+H]⁺ 272.1835, found: 272.1842.



***N*-benzyl-2-phenyl-3-(*E*-2-(trimethylsilyl)vinyl)azetidine (31):** Following the general procedure of synthesis of azetidines using homoallylic amine **31** (116 mg, 0.32 mmol) and Et₃N (36.1 mg, 0.32 mmol), aqueous work-up provided the title compound as a dark yellow oil (103 mg, 0.315 mmol, 98 %, >20:1 dr).

¹H NMR (600 MHz, CDCl₃): δ 7.37 (d, *J* = 8.2 Hz, 2H, H7), 7.33 (ddd, *J* = 7.9, 4.8, 1.5 Hz, 4H, H8 and H13), 7.31 – 7.24 (m, 3H, H14 and H12), 7.19 (td, *J* = 7.2, 1.4 Hz, 1H, H9), 6.07 – 5.95 (m, 1H, H3), 5.51 (d, *J* = 18.7 Hz, 1H, H2), 4.48 (d, *J* = 6.5 Hz, 1H, H5), 3.91 (d, *J* = 13.2 Hz, 1H, H10a), 3.47 (d, *J* = 13.3 Hz, 1H, H10b), 3.30 (d, *J* = 4.7 Hz, 1H, H15a), 3.17 (q, *J* = 4.3, 2.3 Hz, 2H, H4 and H15b), -0.14 (d, *J* = 1.8 Hz, 9H, H1).

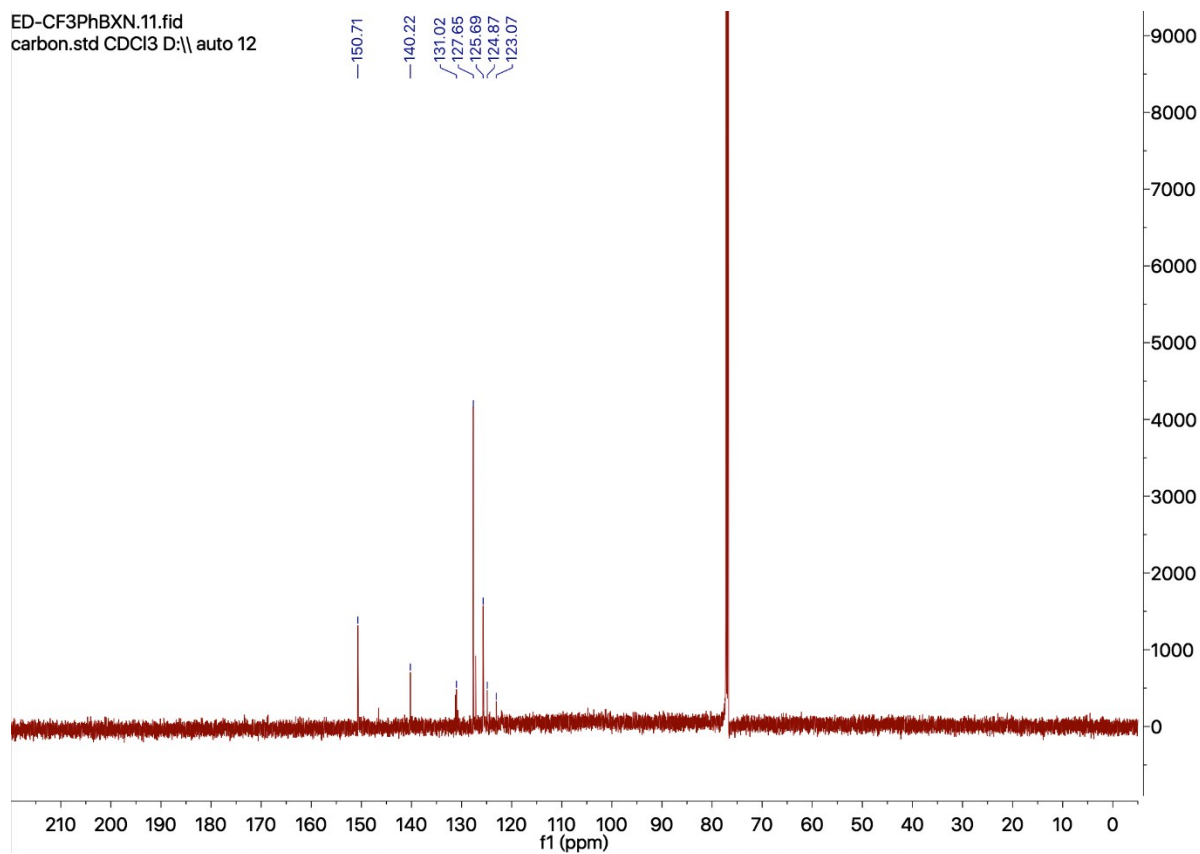
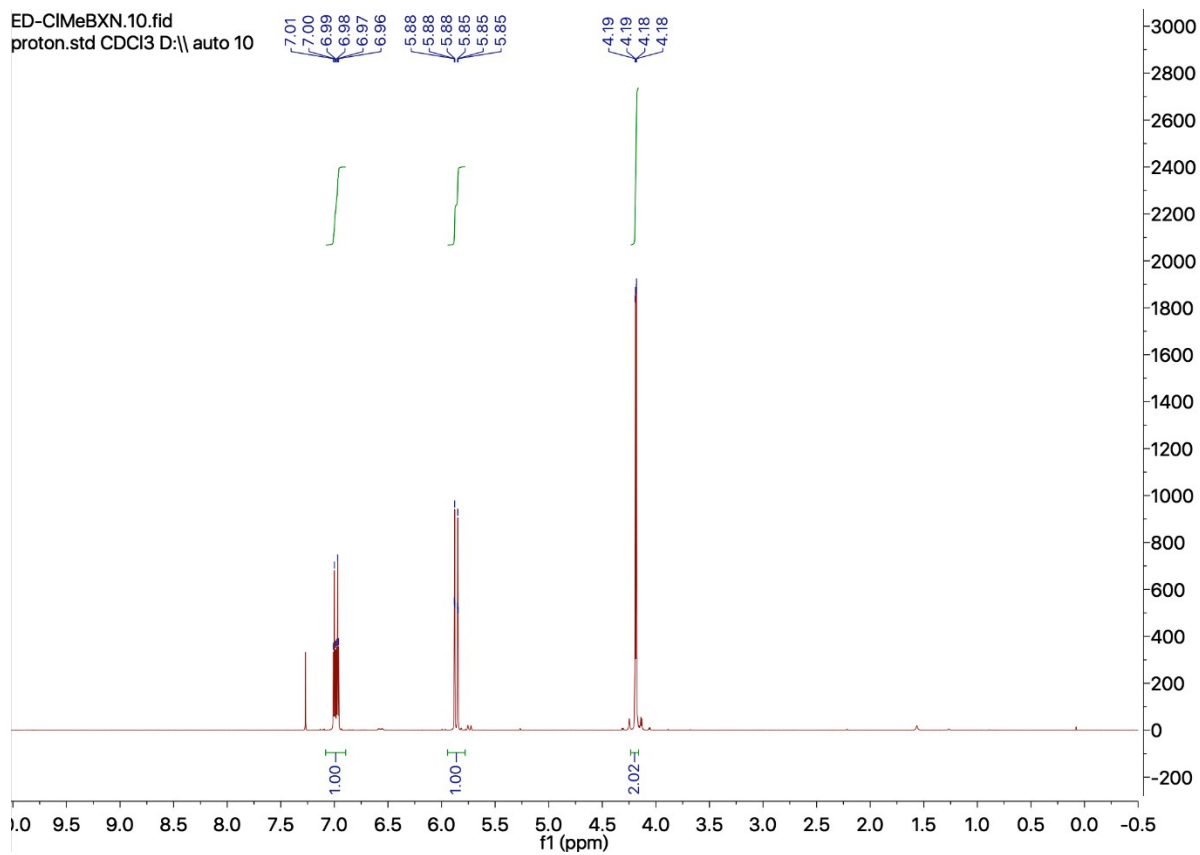
¹³C NMR (151 MHz, CDCl₃): δ 146.4 (C3), 139.6 (C6), 138.2 (C11), 131.7 (C2), 128.8 (C8), 128.2 (C12), 127.7 (C13), 127.2 (C7), 126.9 (C14), 126.7 (C9), 71.4 (C5), 61.3 (C10), 55.4 (C15), 42.9 (C4), -1.4 (C1).

FTIR (ν_{max}, cm⁻¹): 3062 (w), 3027 (w), 2953 (w), 2827 (w), 1614 (w), 1494 (w), 1452 (w), 1350 (w), 1327 (w), 1302 (w), 1276 (w), 1260 (w), 1246 (w), 1211 (w), 1177 (w), 1111 (w), 1073 (w), 1051 (w), 1028 (w), 989 (w), 932 (w), 863 (m), 835 (m), 764 (m), 748 (m), 696 (s)

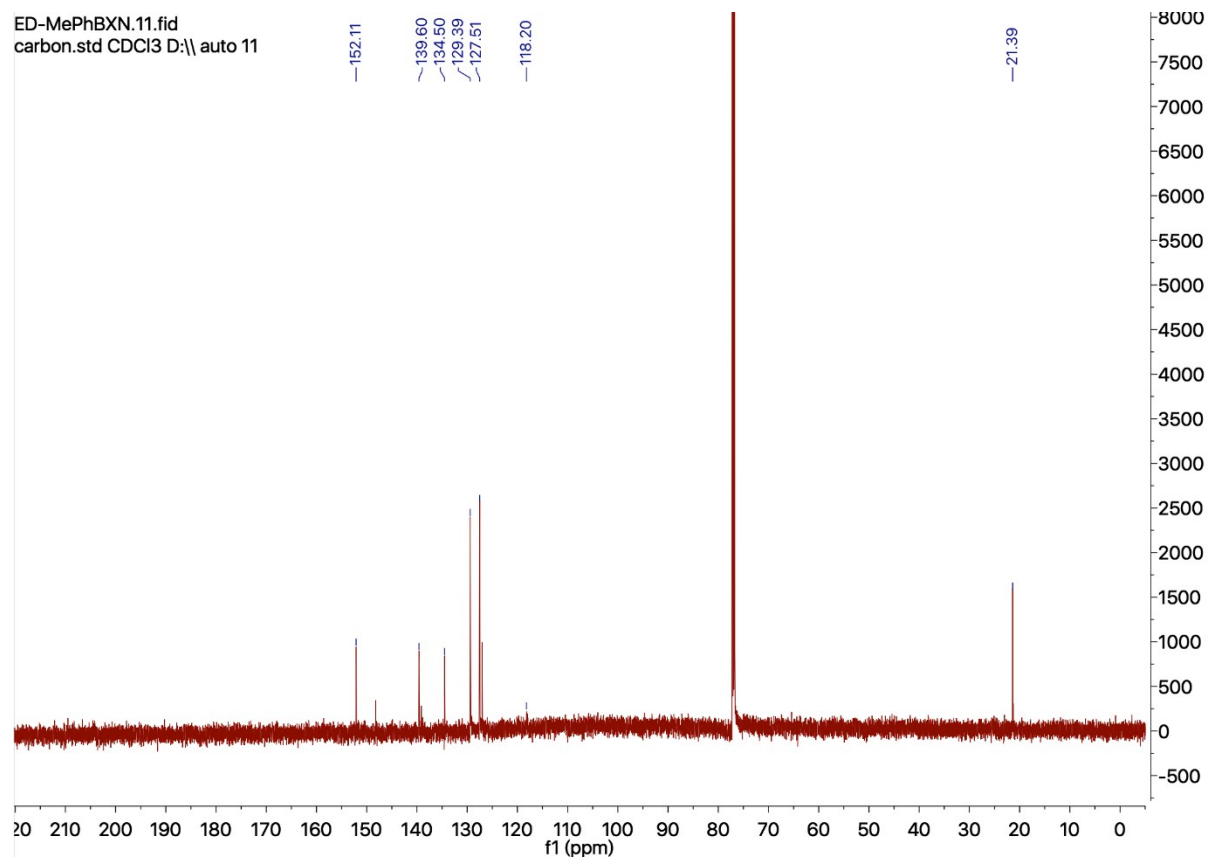
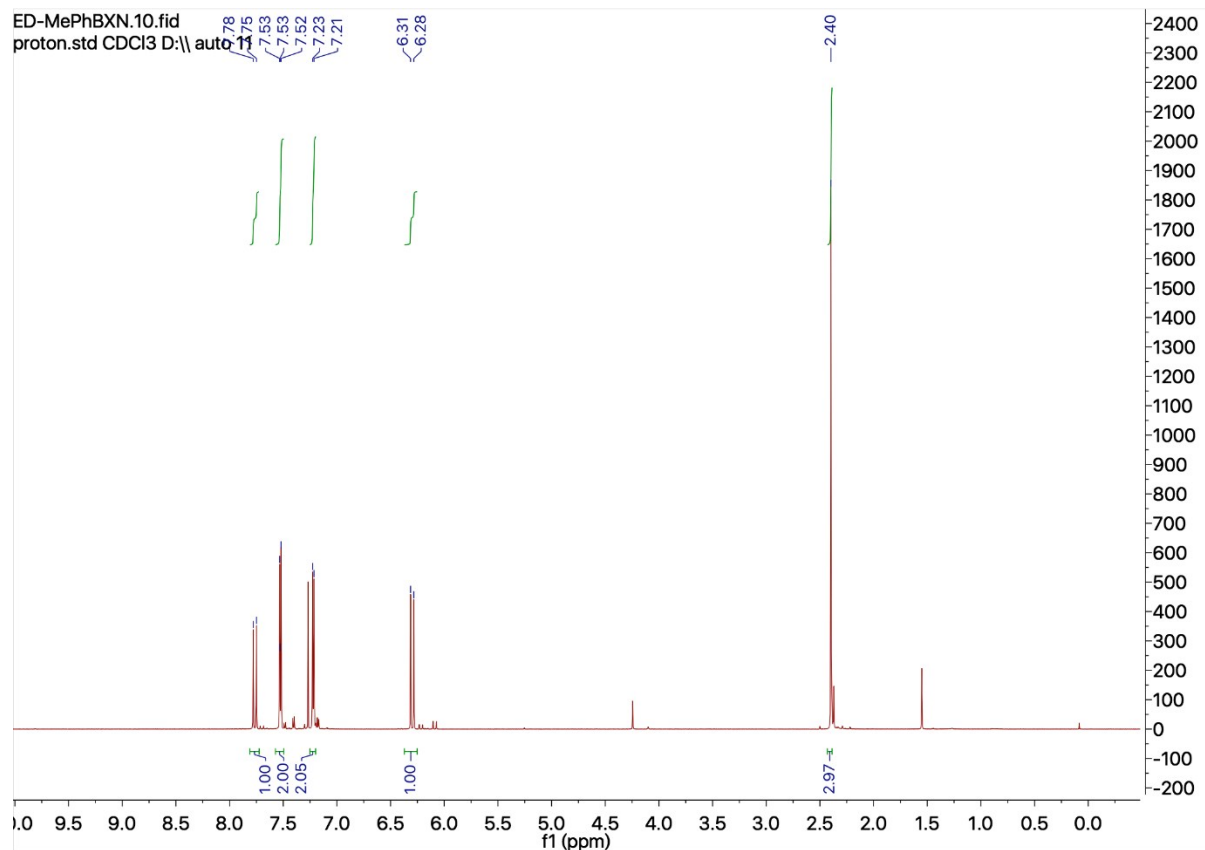
HRMS (ESI): calculated for C₂₁H₂₇NSi [M+H]⁺ 322.1991, found: 322.1985.

3. ^1H and ^{13}C NMR Spectra

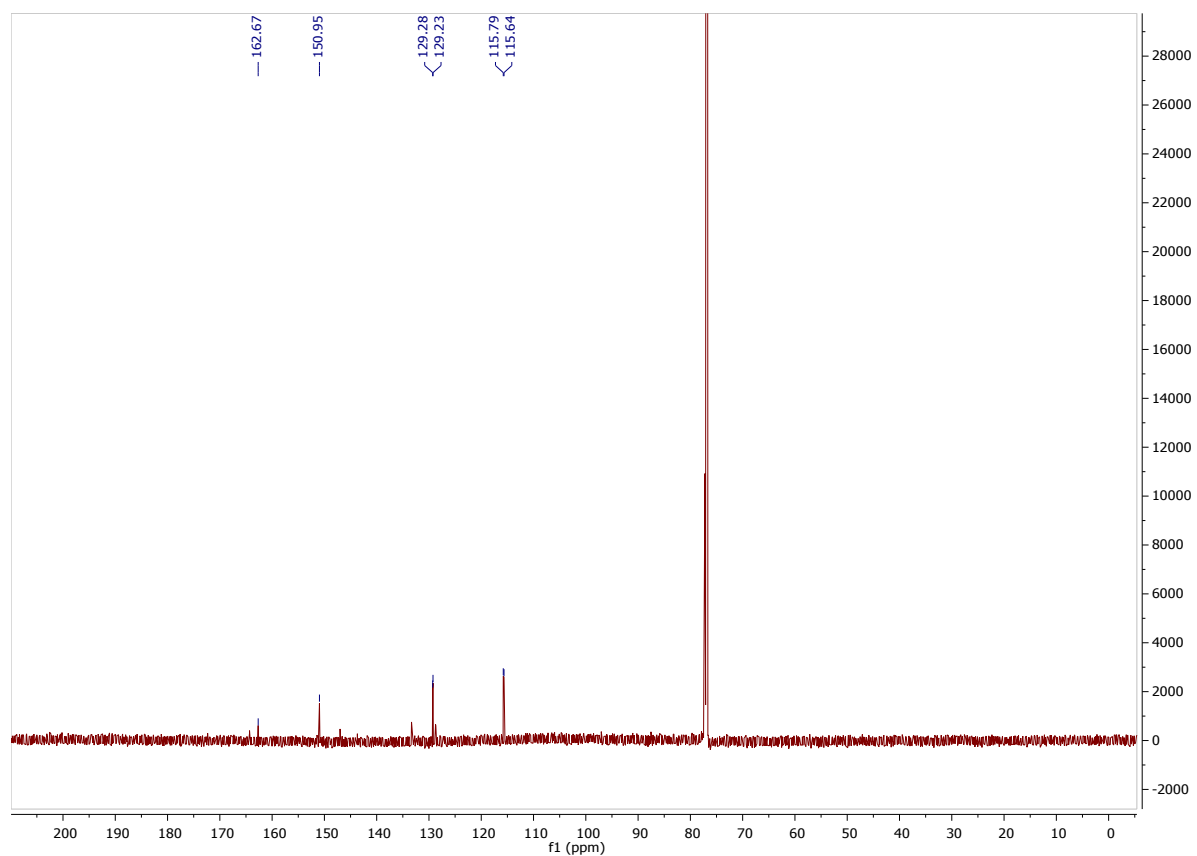
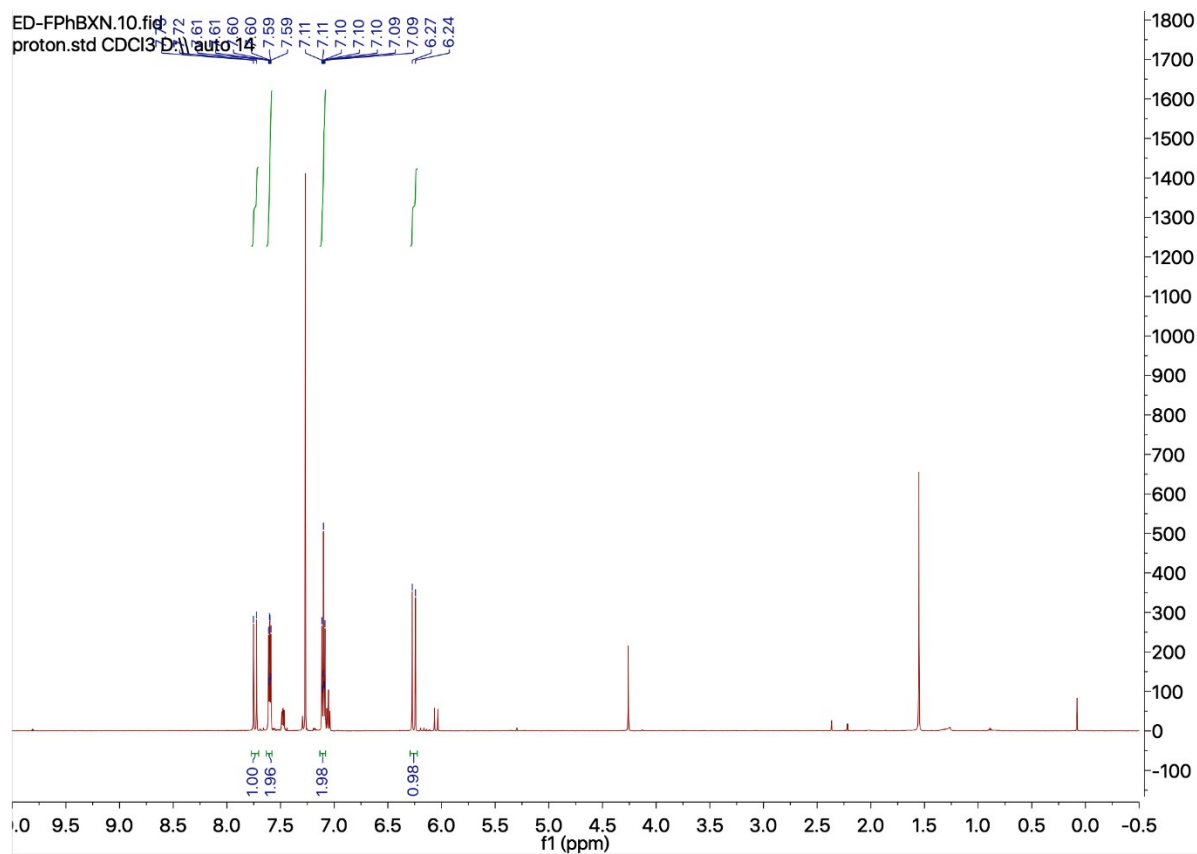
2,4,6-tris((*E*)-3-chloroprop-1-en-1-yl)-1,3,5,2,4,6-trioxatriborinane (1a):



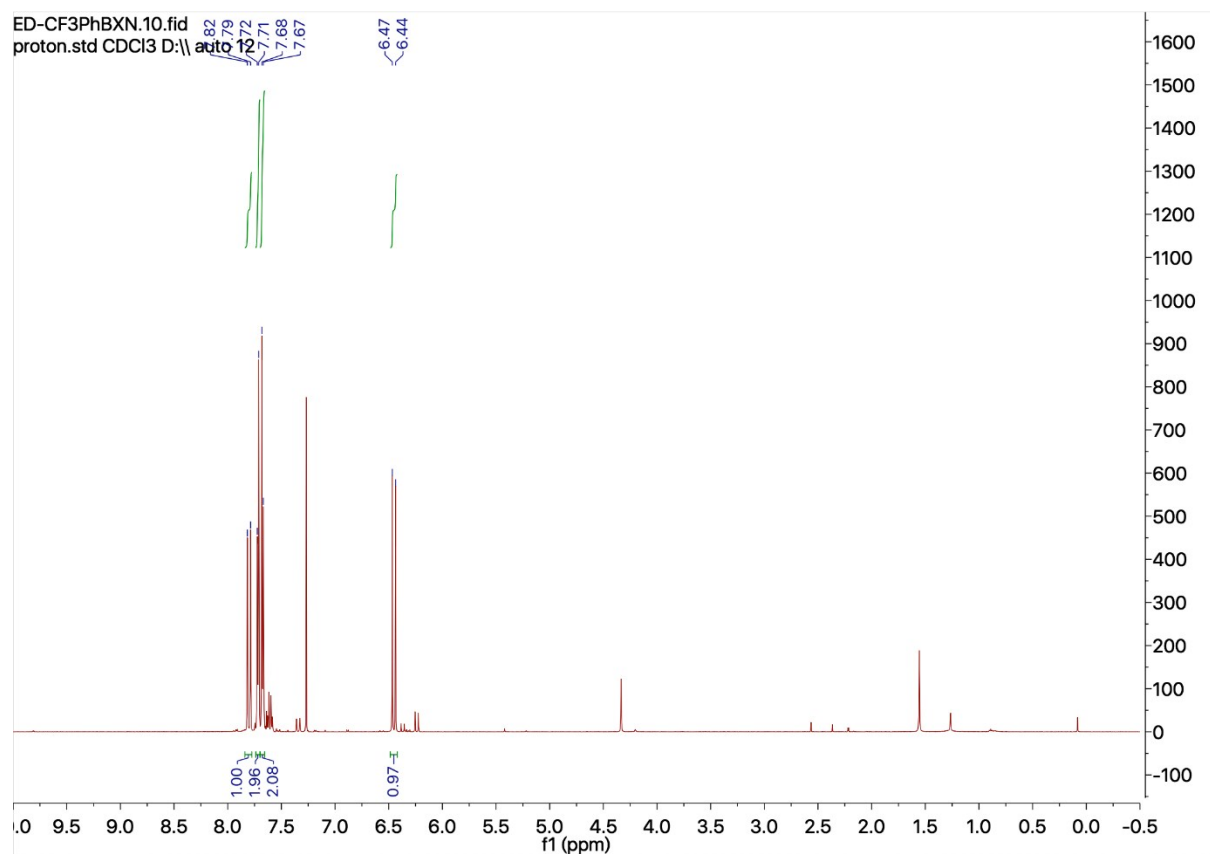
2,4,6-tris((E)-4-methylstyryl)-1,3,5,2,4,6-trioxatriborinane (1b):



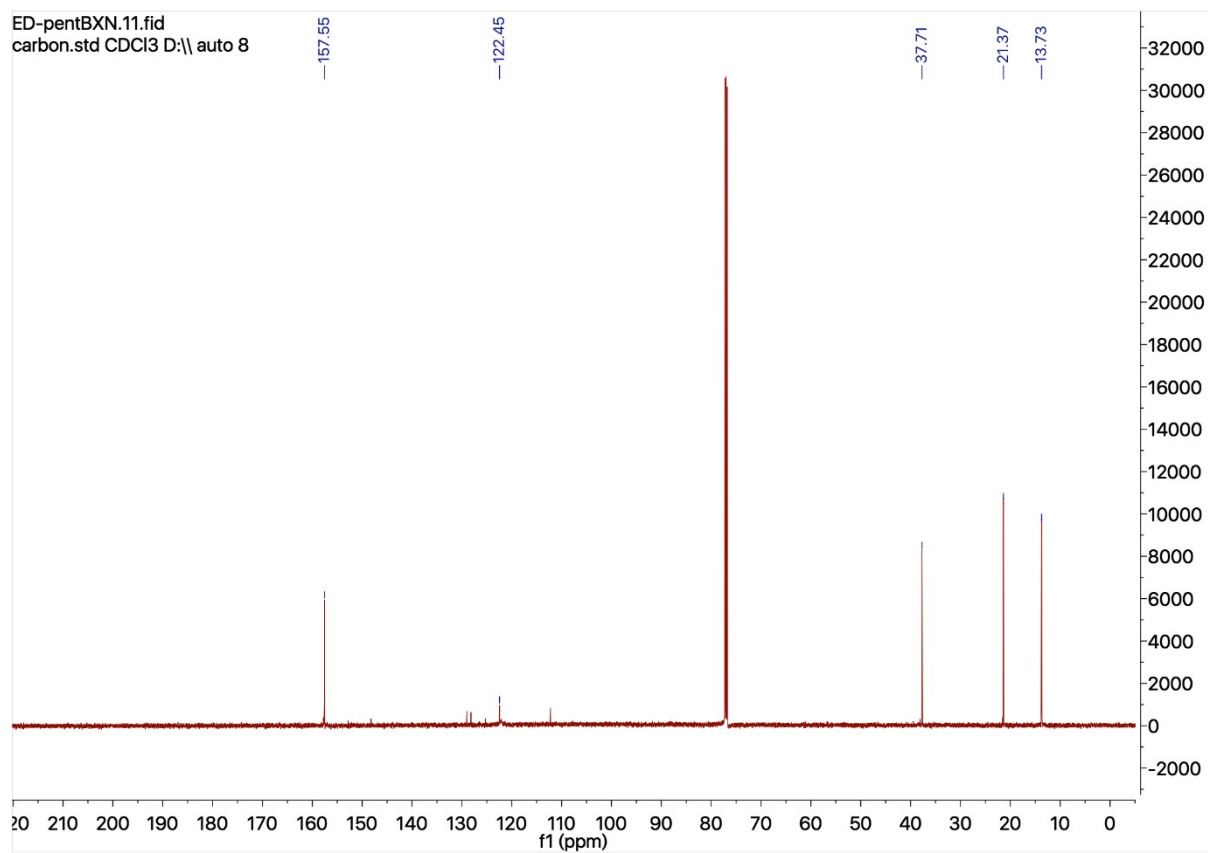
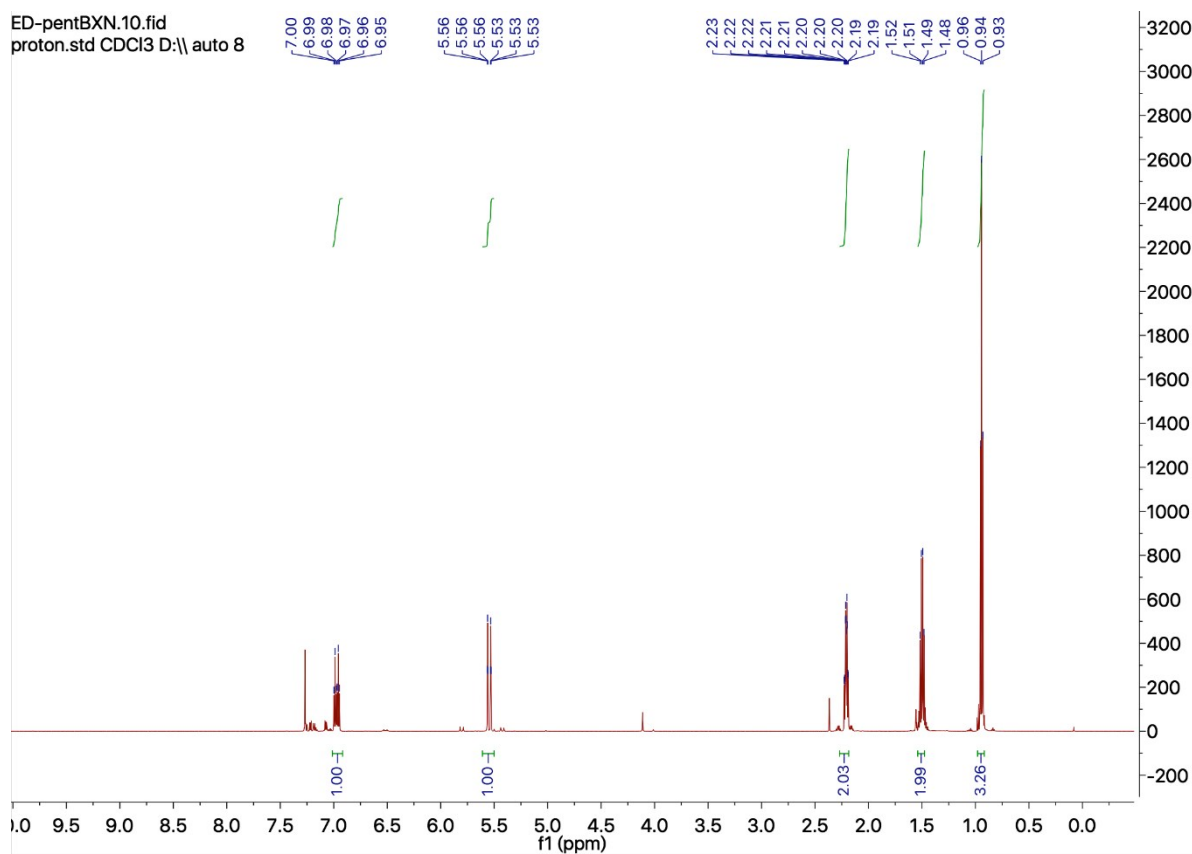
2,4,6-tris((*E*)-4-fluorostyryl)-1,3,5,2,4,6-trioxatriborinane (1c):



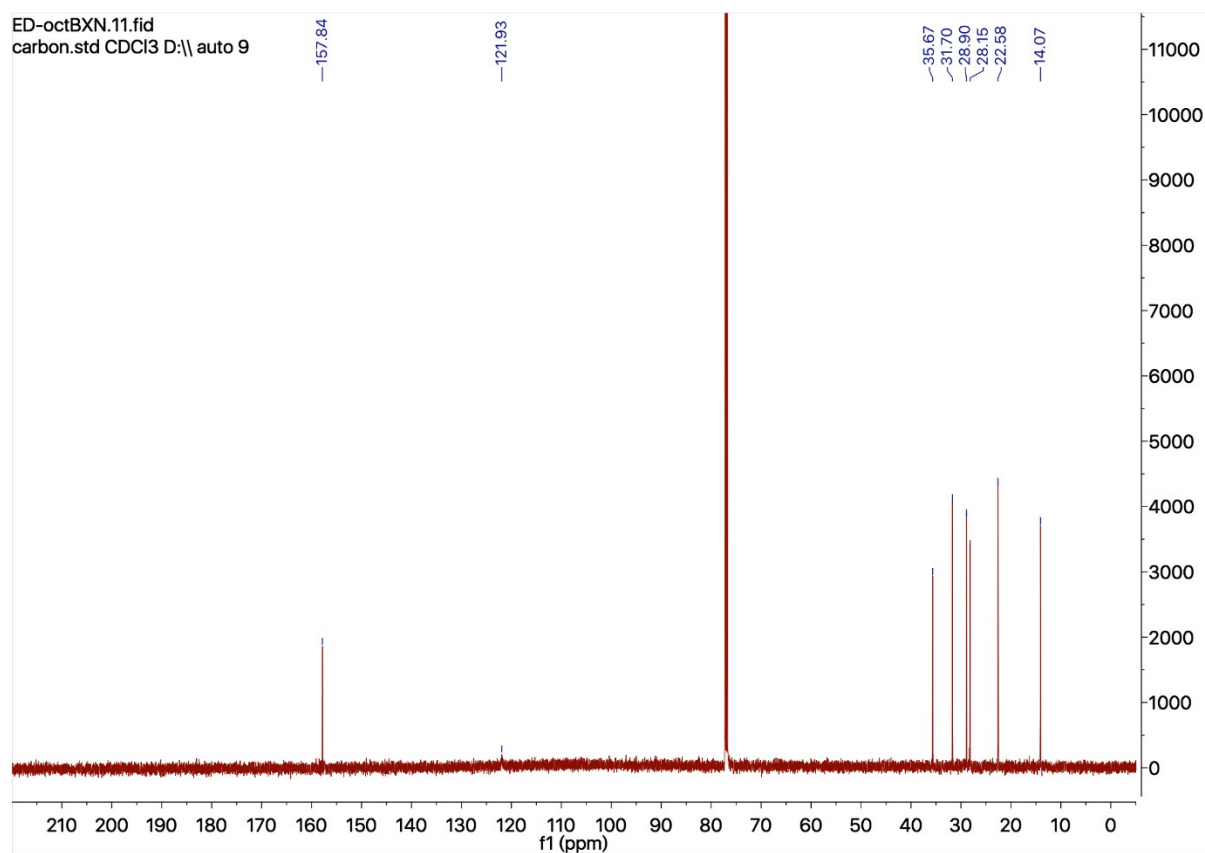
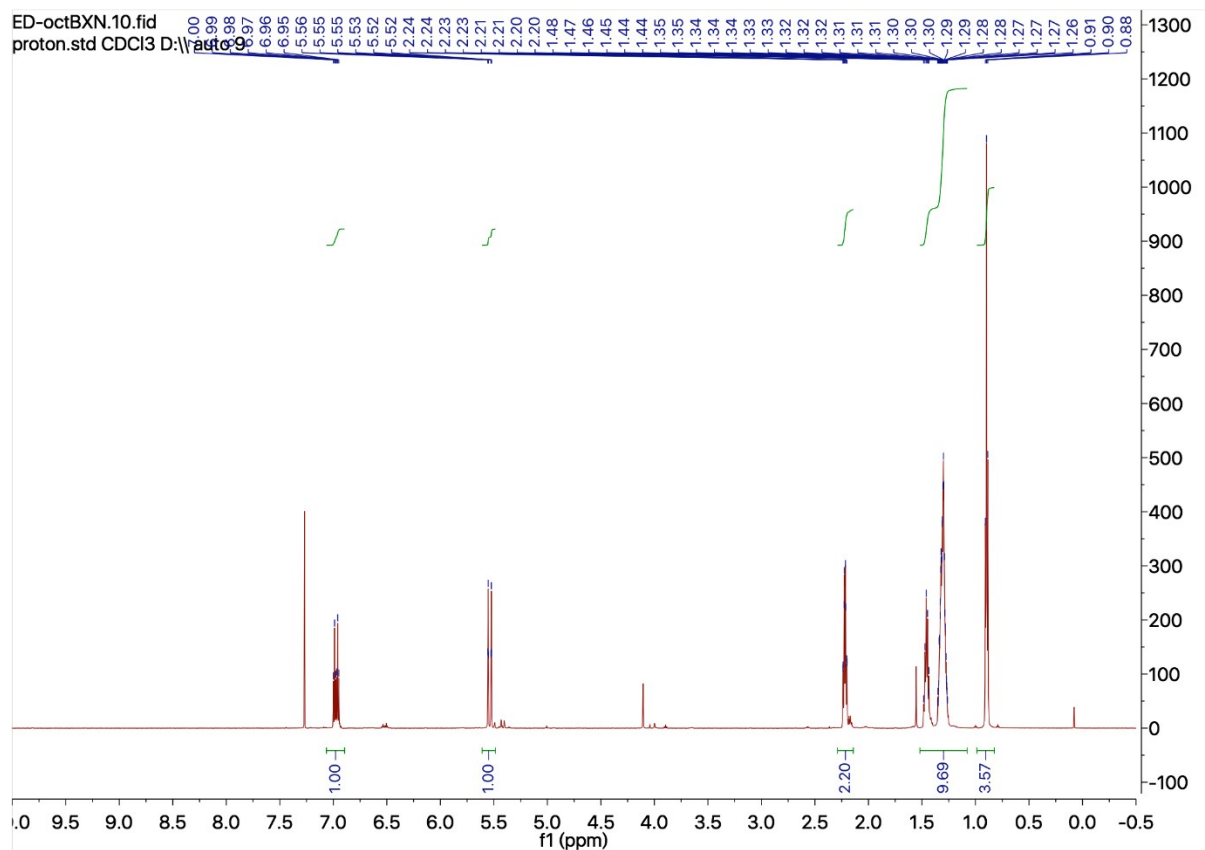
2,4,6-tris((*E*)-4-(trifluoromethyl)styryl)-1,3,5,2,4,6-trioxatriborinane (1d):



2,4,6-tri((E)-pent-1-en-1-yl)-1,3,5,2,4,6-trioxatriborinane (1e):



2,4,6-tri((E)-oct-1-en-1-yl)-1,3,5,2,4,6-trioxatriborinane (1f):



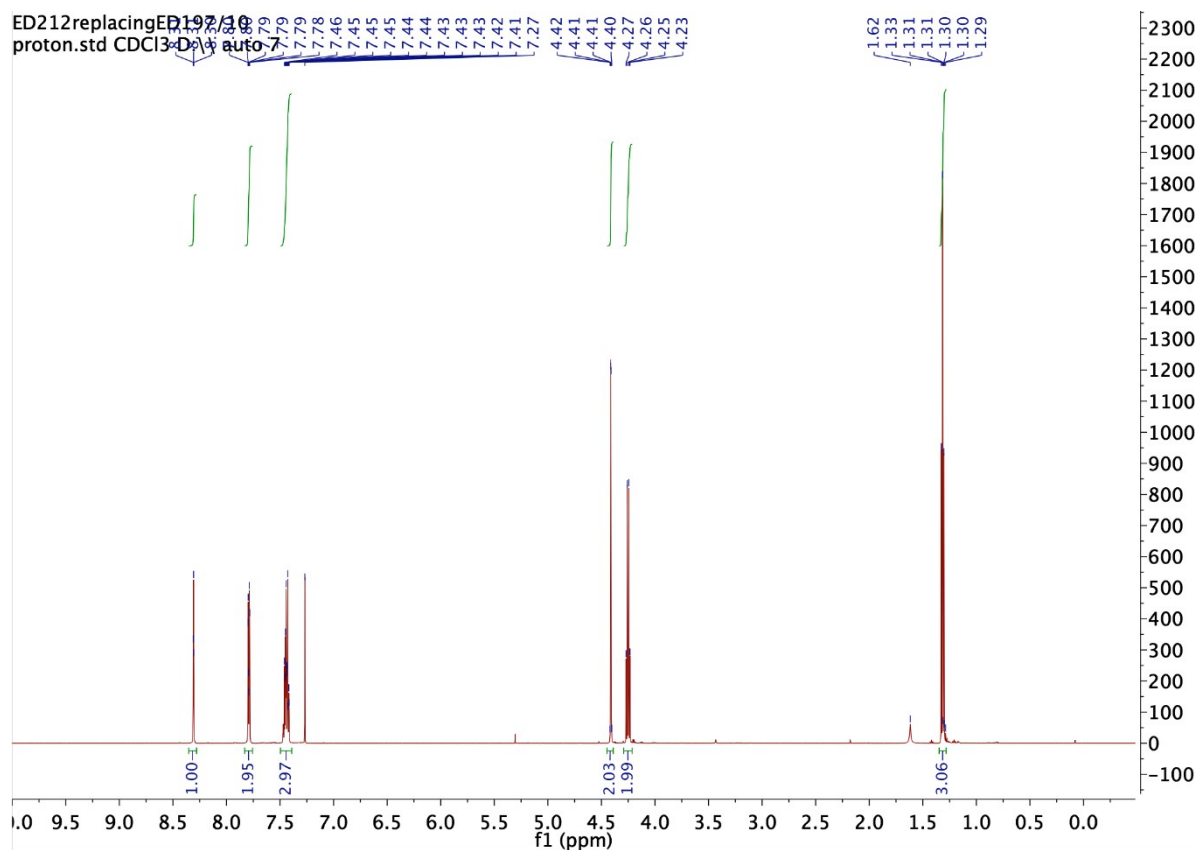
1H NMR spectrum of compound 10 in CDCl₃. The x-axis is chemical shift (f1) in ppm, ranging from -0.5 to 10.0. The y-axis is intensity. The spectrum shows several peaks: a multiplet at ~8.4 ppm (1.00H), a multiplet at ~7.8 ppm (1.98H), a multiplet at ~7.4 ppm (3.08H), a multiplet at ~6.1 ppm (0.96H), a multiplet at ~5.1 ppm (1.07H), a multiplet at ~4.9 ppm (1.02H), and a multiplet at ~4.2 ppm (2.09H). Integration values are shown below the peaks.

ED177/10
proton.std CDCI3 D:\auto 6

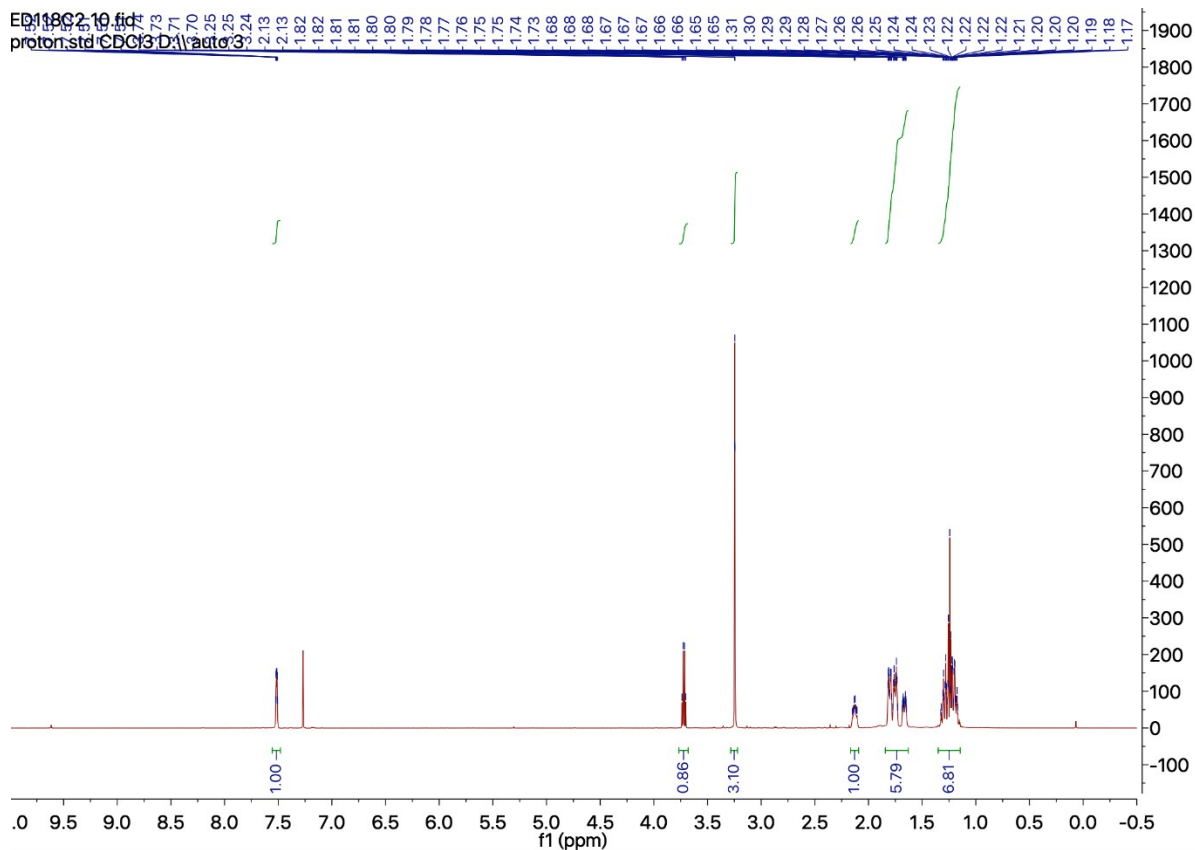
1.00
1.90
2.07
2.04
0.98
6.04

8.19
8.19
8.01
7.60
7.55
7.54
7.54
7.27
3.43
3.43
3.42
3.42
2.03
2.02
2.01
2.00
1.98
0.96
0.95

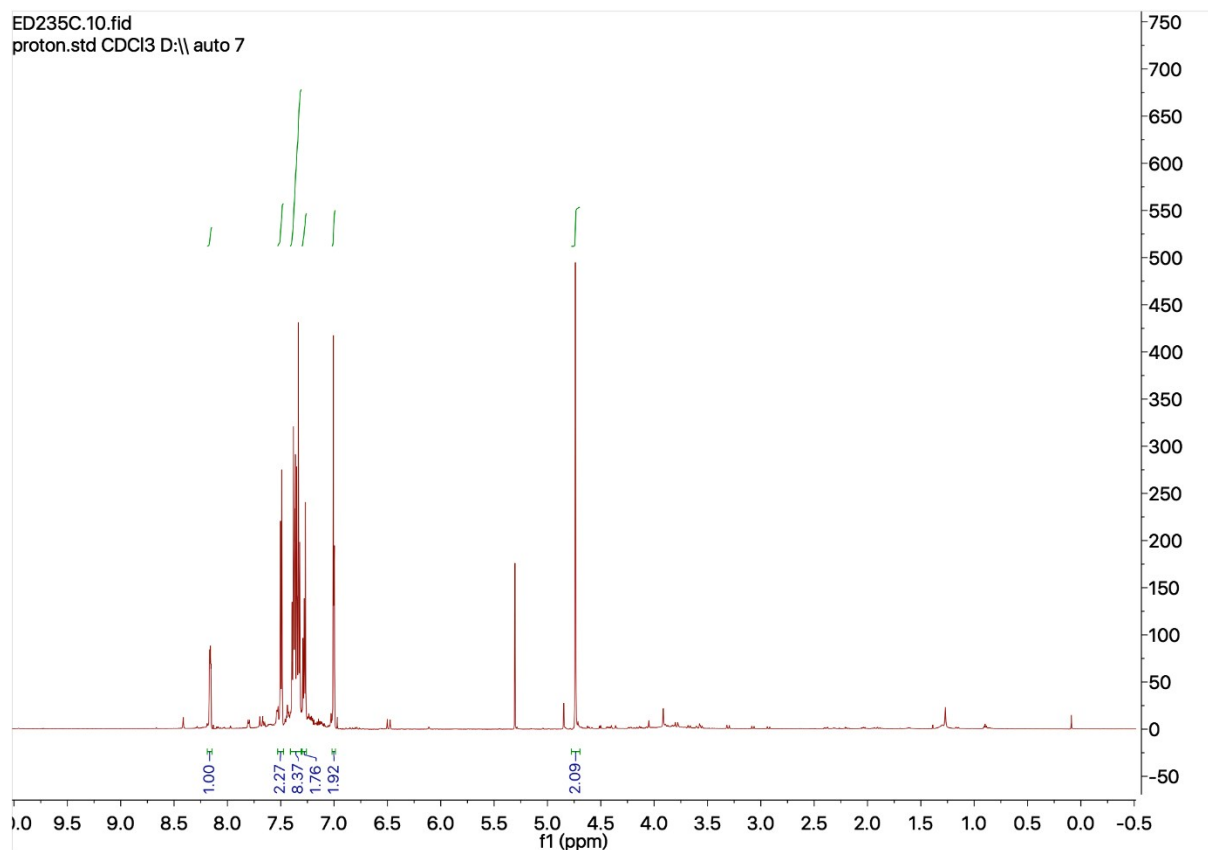
Ethyl *E*-2-(benzylideneamino)acetate (2e):



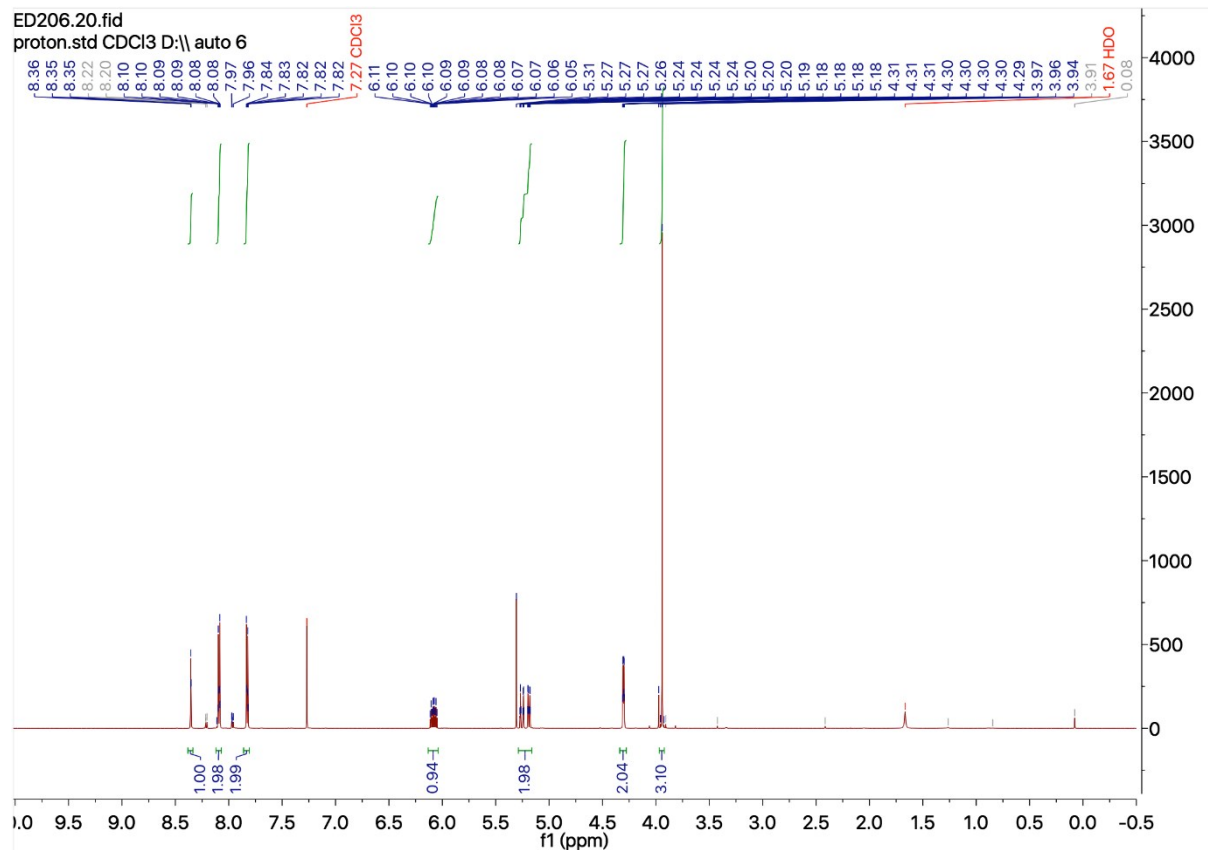
***E*-1-cyclohexyl- *N*-methylmethanimine (2g):**



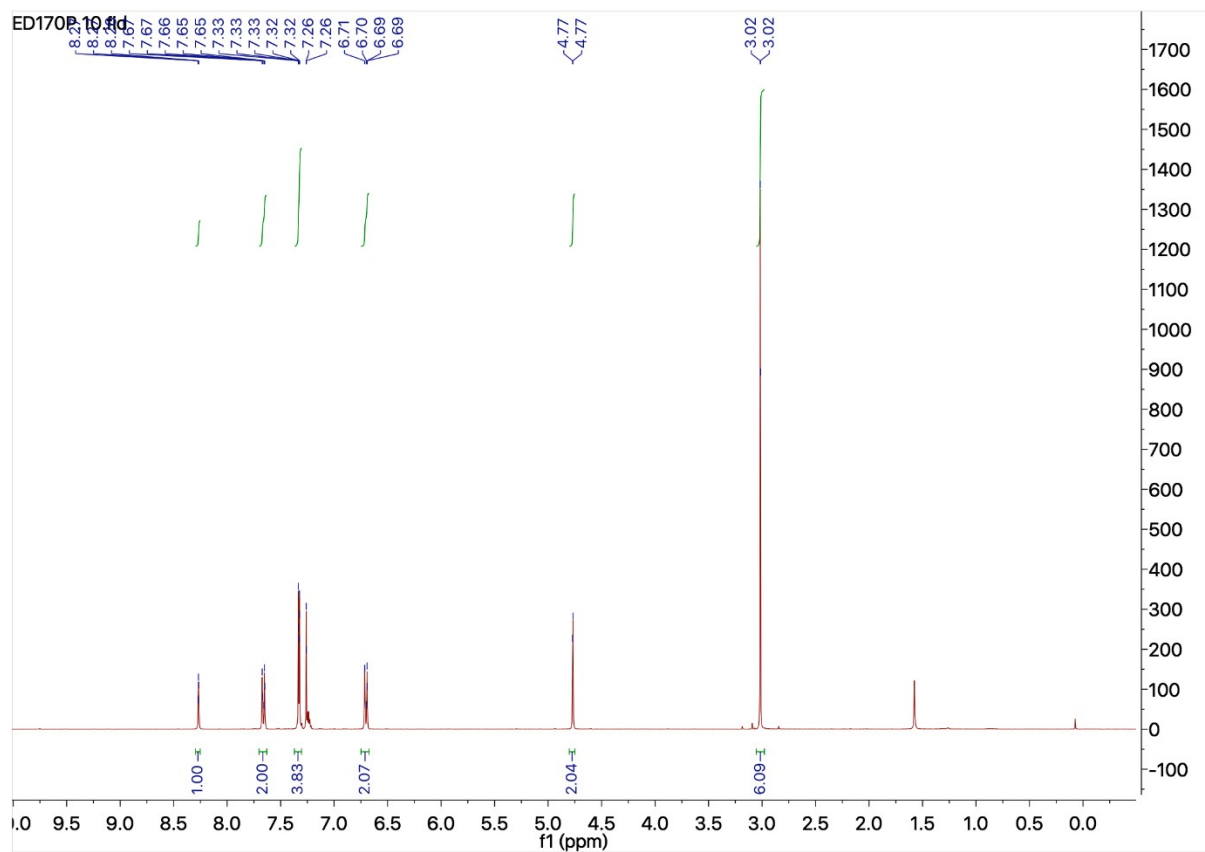
(1*E*,2*E*)-*N*-benzyl-3-phenylprop-2-en-1-imine (2h):



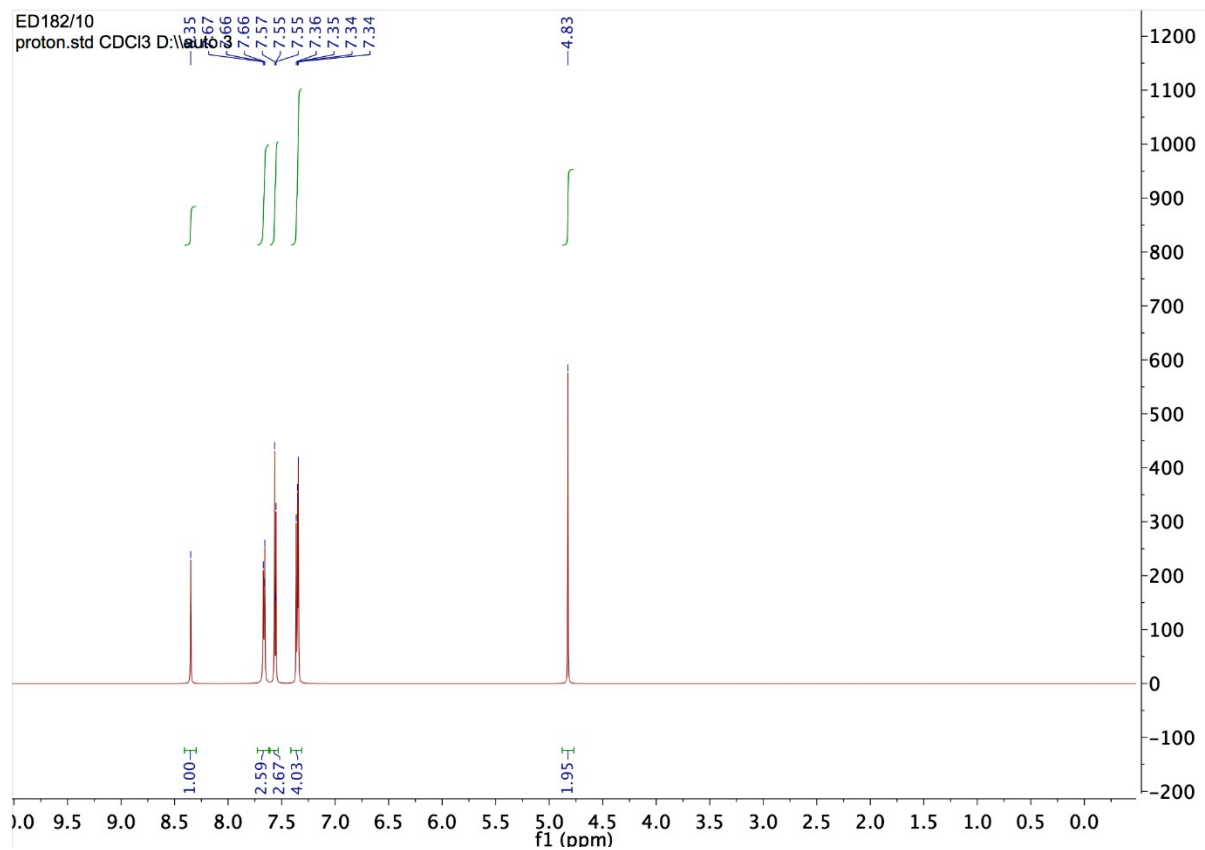
Methyl *E*-4-((allylimino)methyl)benzoate (2i):



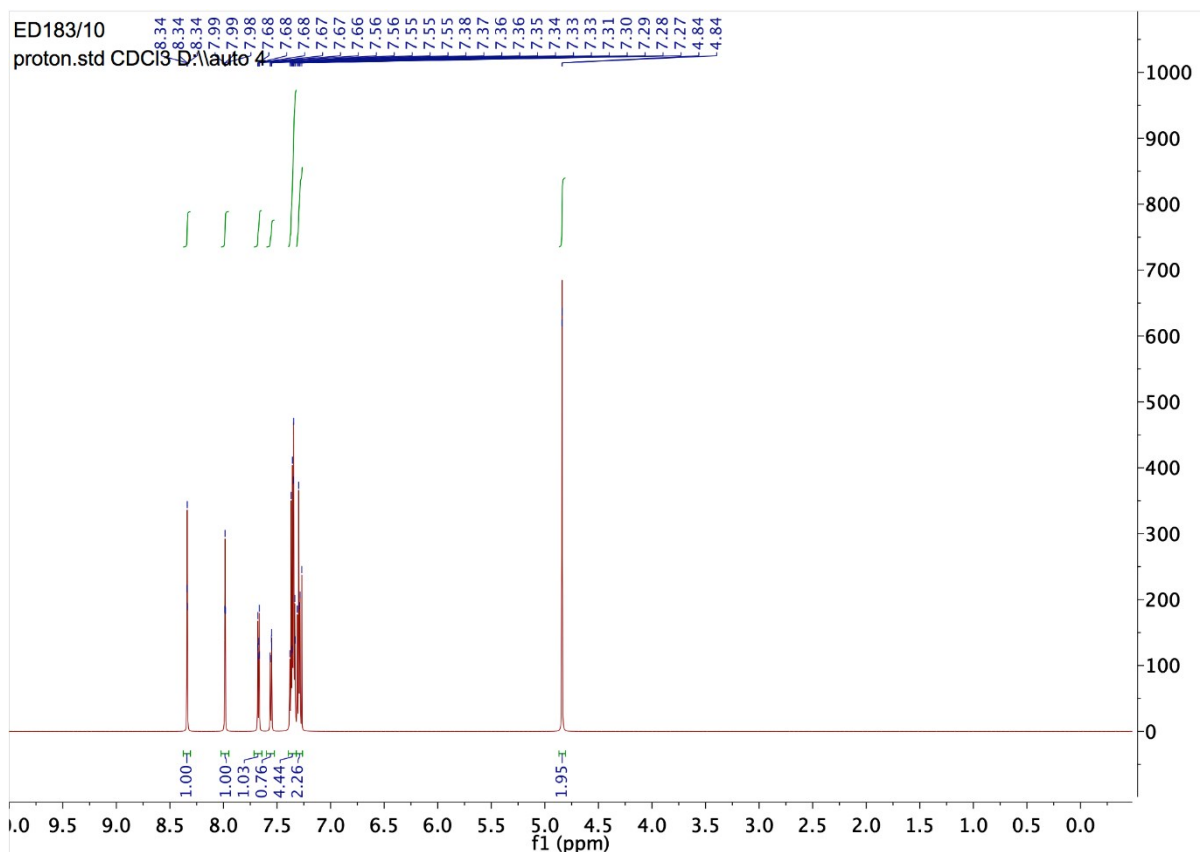
***E*-4-((benzylimino)methyl)- *N,N*-dimethylaniline (2j):**



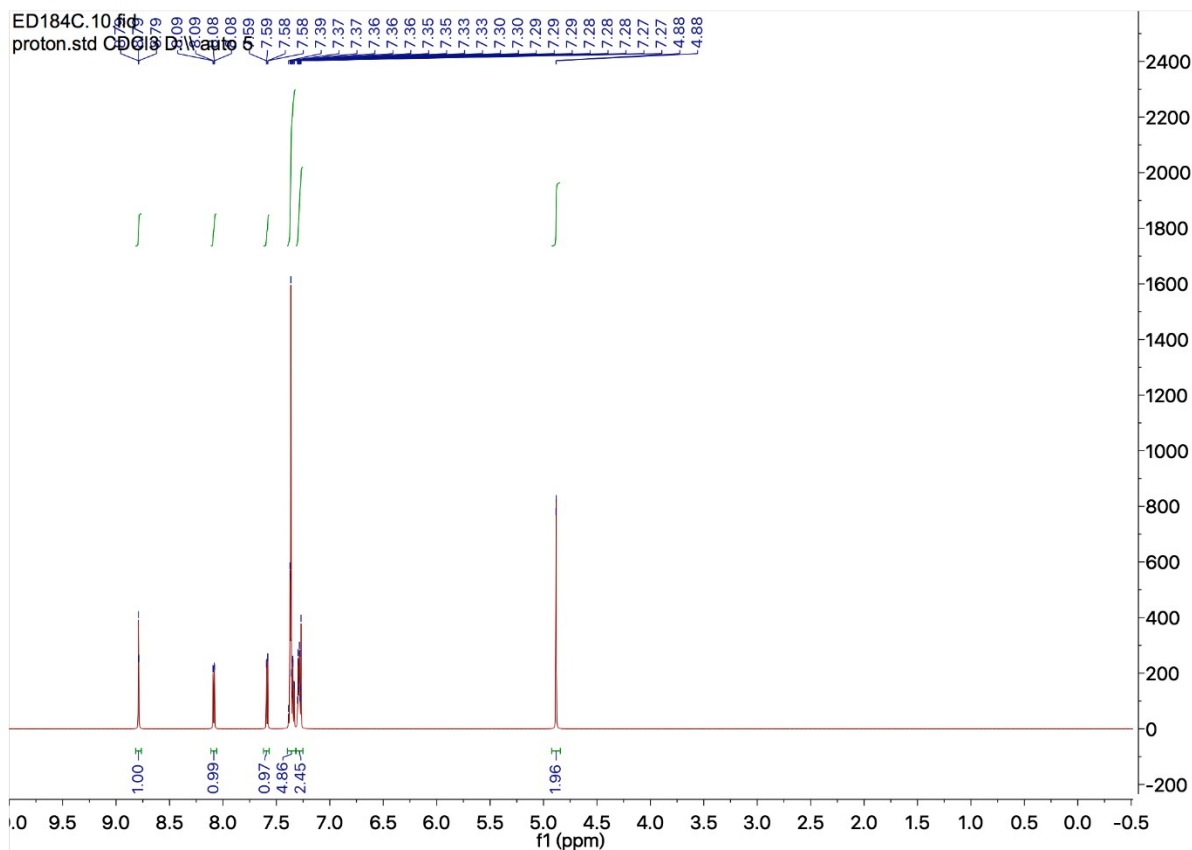
***E*-*N*-benzyl-1-(4-bromophenyl)methanimine (2k):**



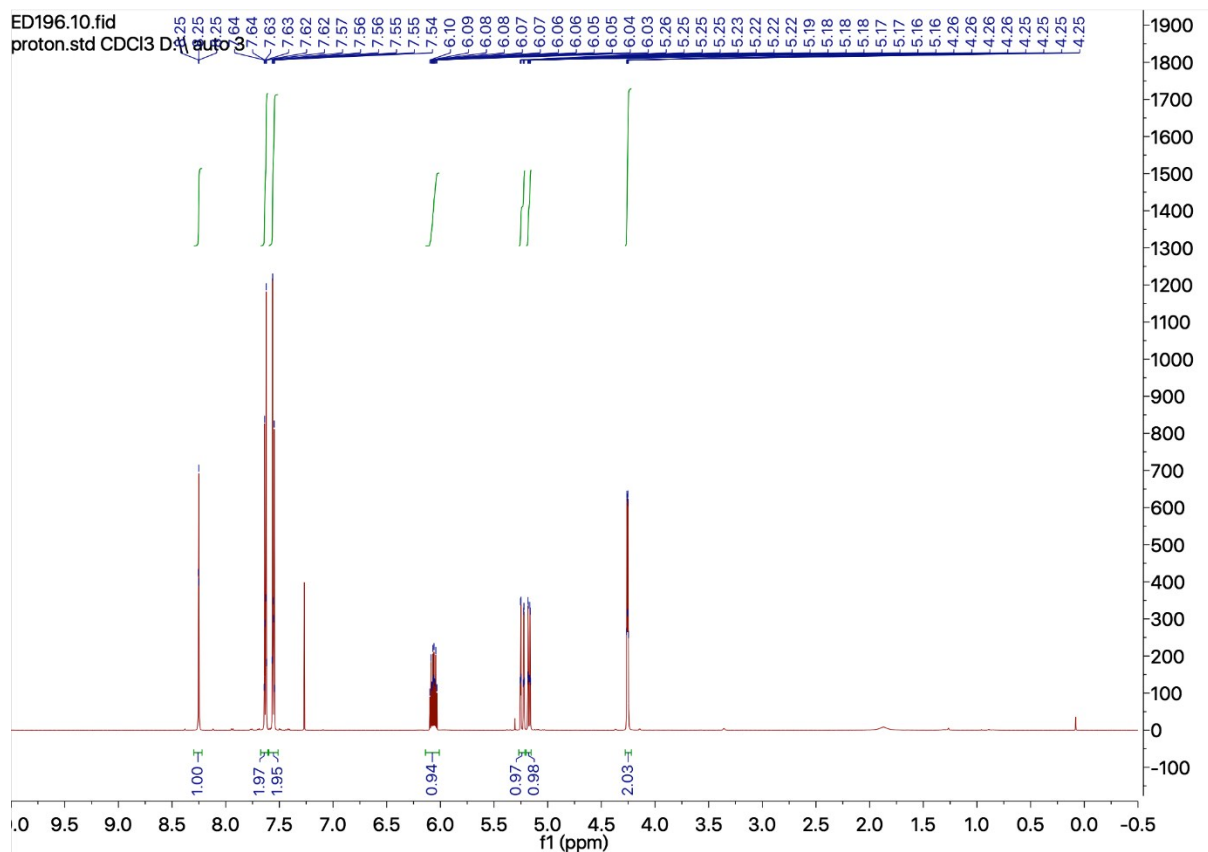
***E-N*-benzyl-1-(3-bromophenyl)methanimine (2l):**



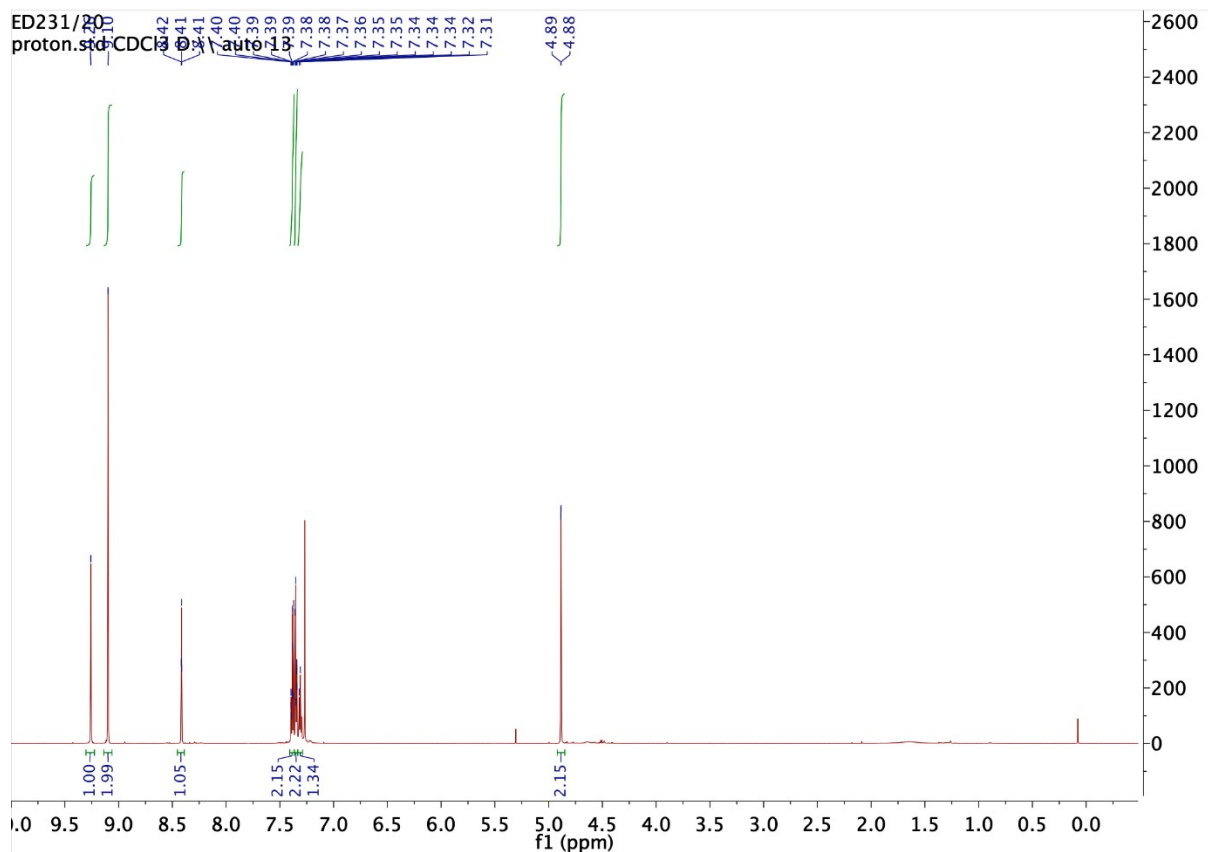
***E-N*-benzyl-1-(2-bromophenyl)methanimine (2m):**



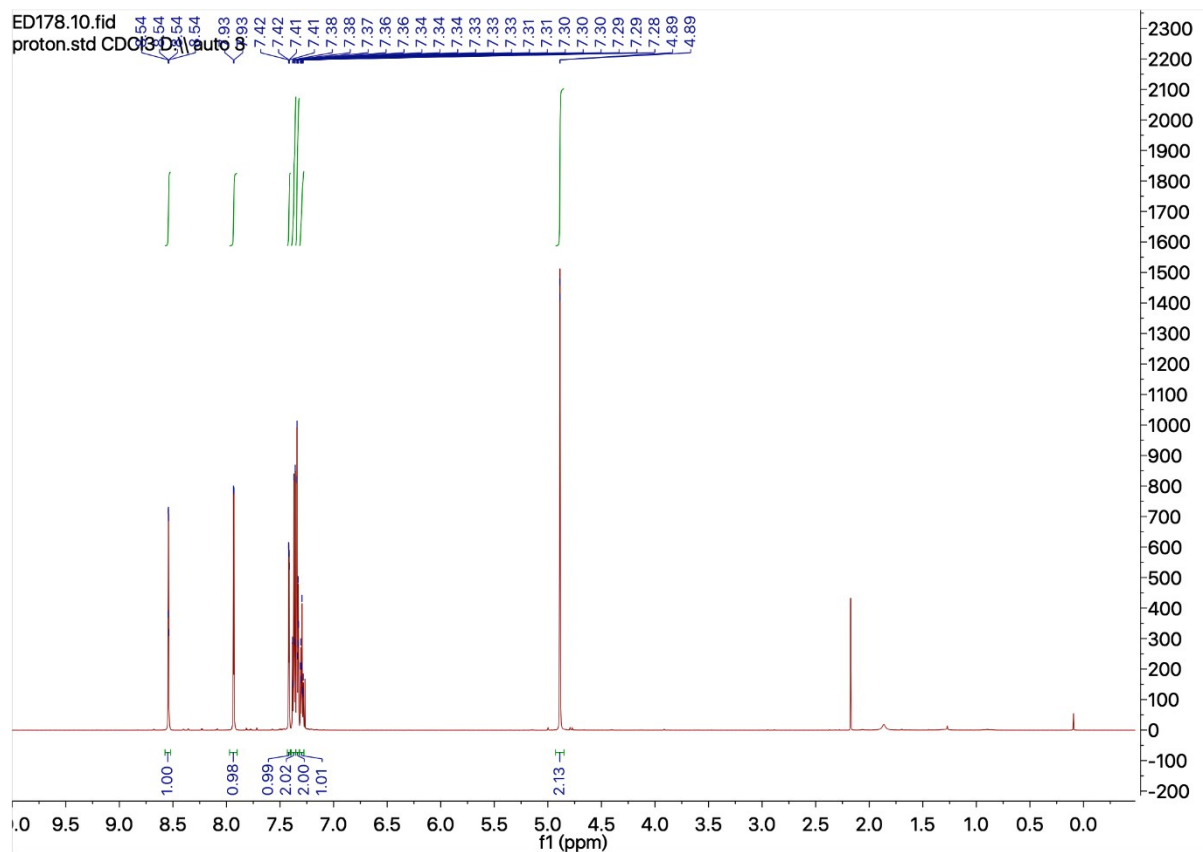
***E-N*-allyl-1-(4-bromophenyl)methanimine (2n):**



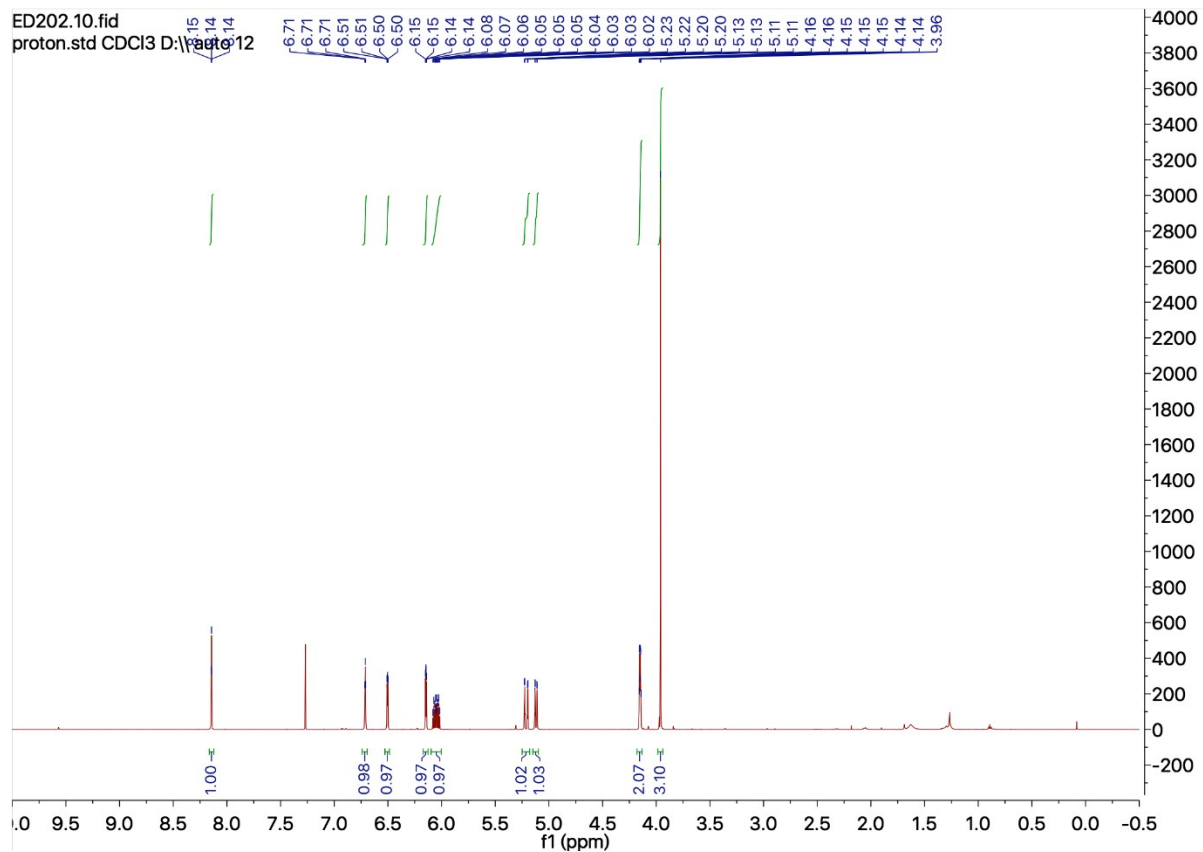
***E-N*-benzyl-1-(pyrimidin-5-yl)methanimine (2o):**



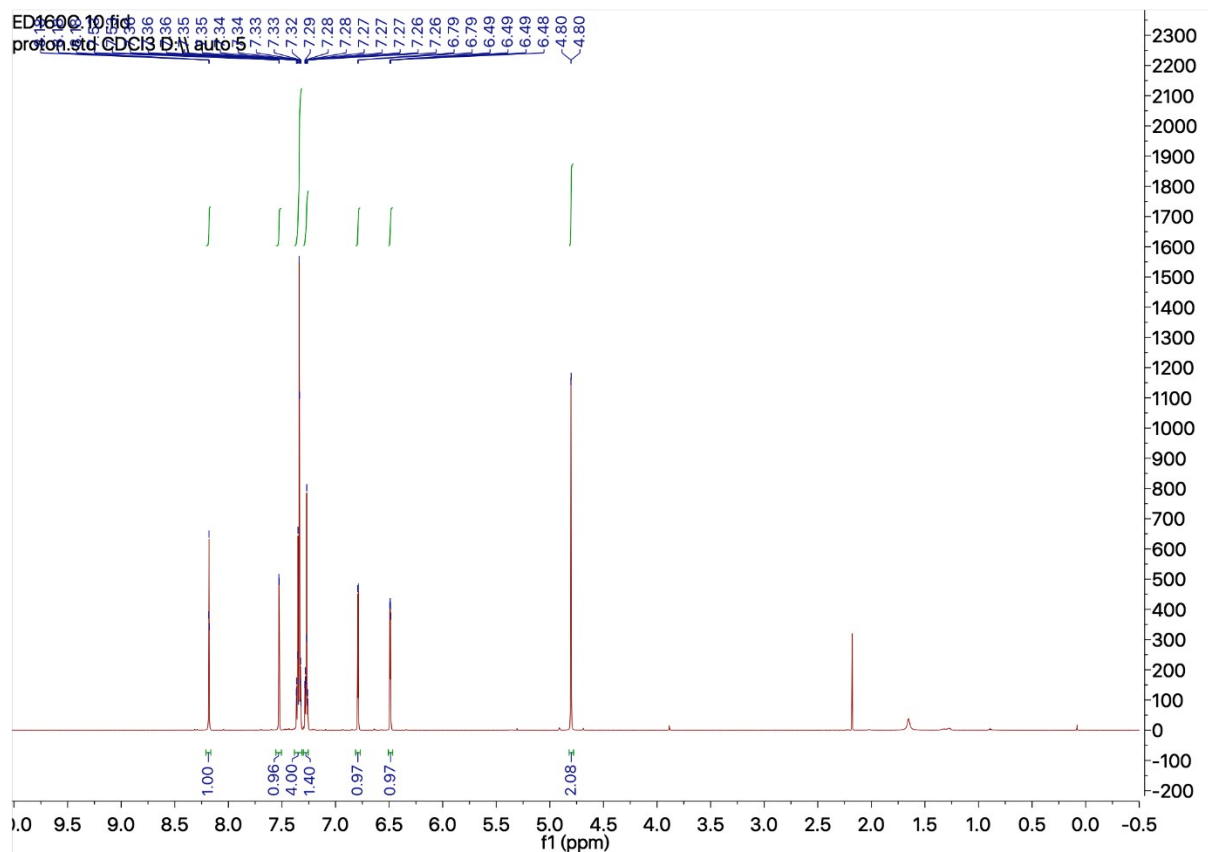
***E-N*-benzyl-1-(thiazol-2-yl)methanimine (2p):**



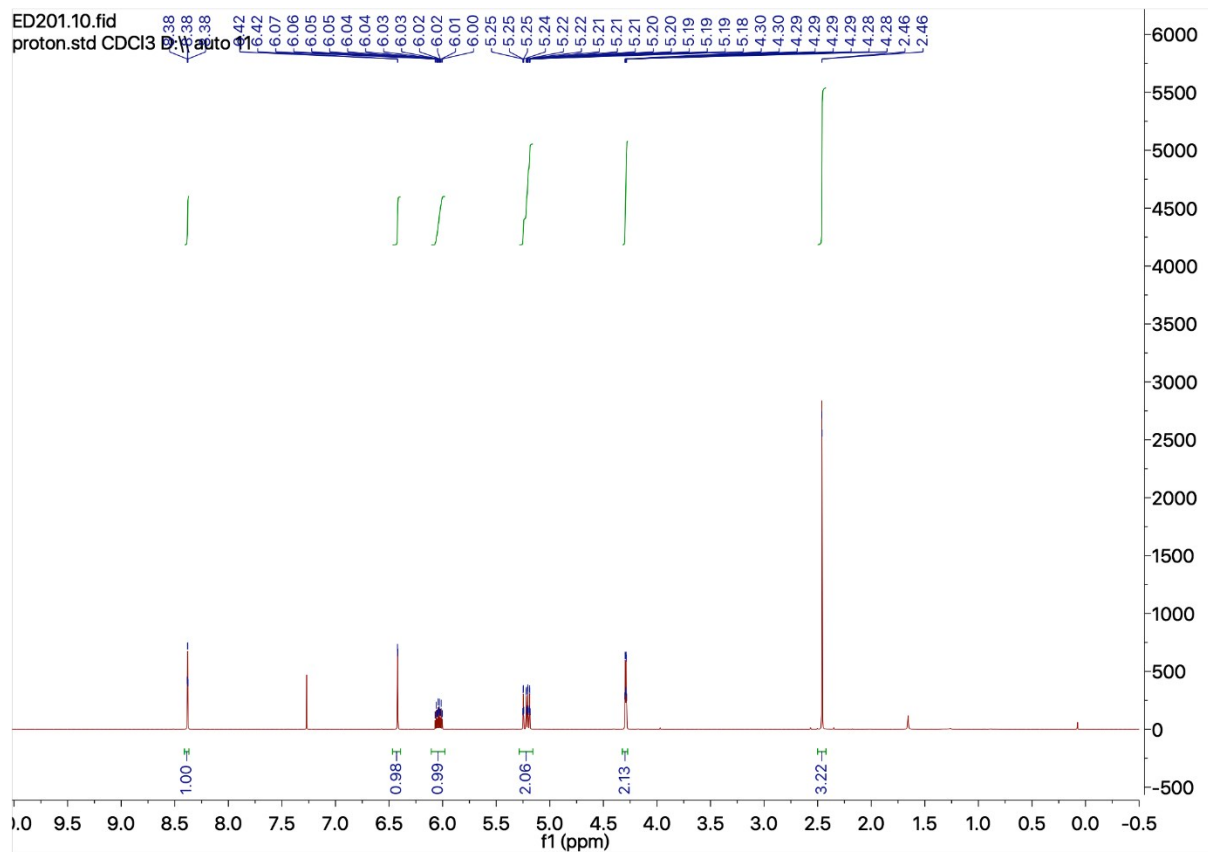
***E-N*-allyl-1-(1-methyl-1 H-pyrrol-2-yl)methanimine (2q):**



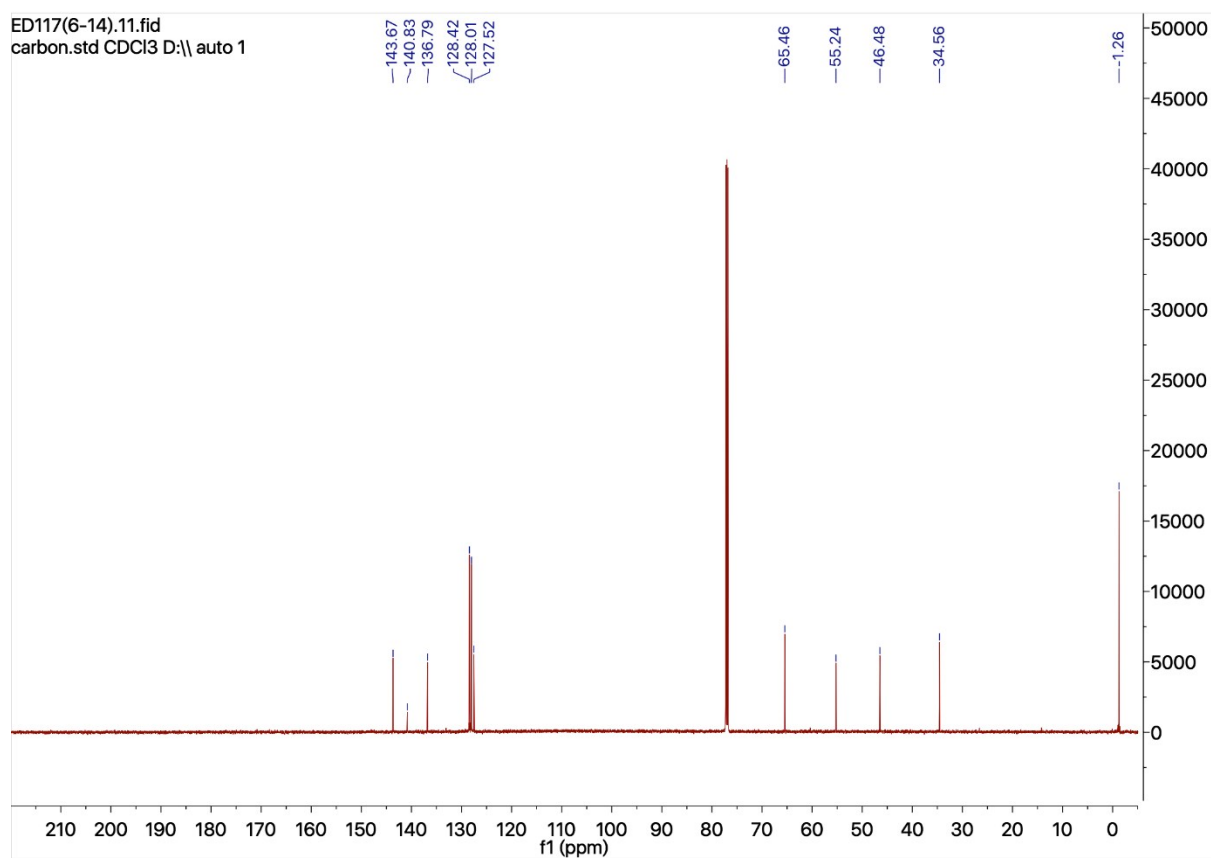
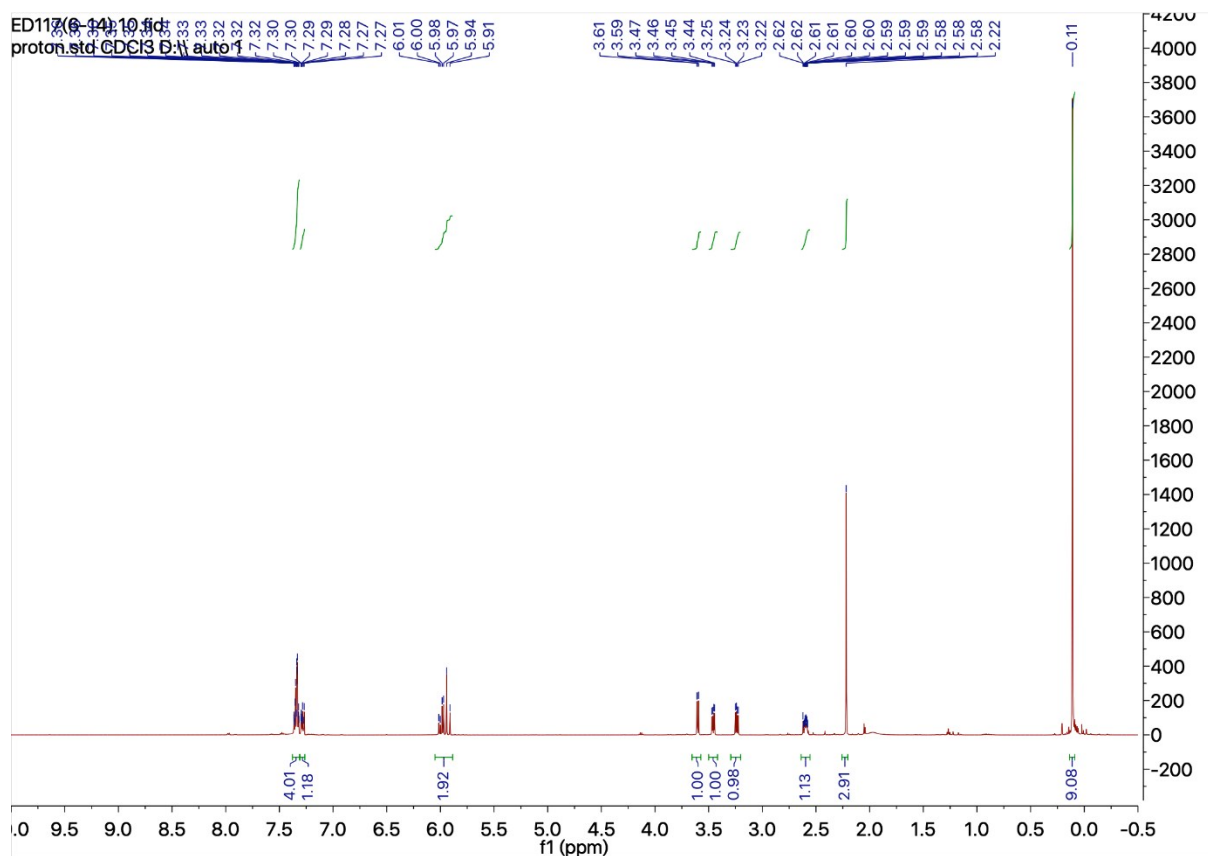
***E-N*-benzyl-1-(furan-2-yl)methanimine (2r):**



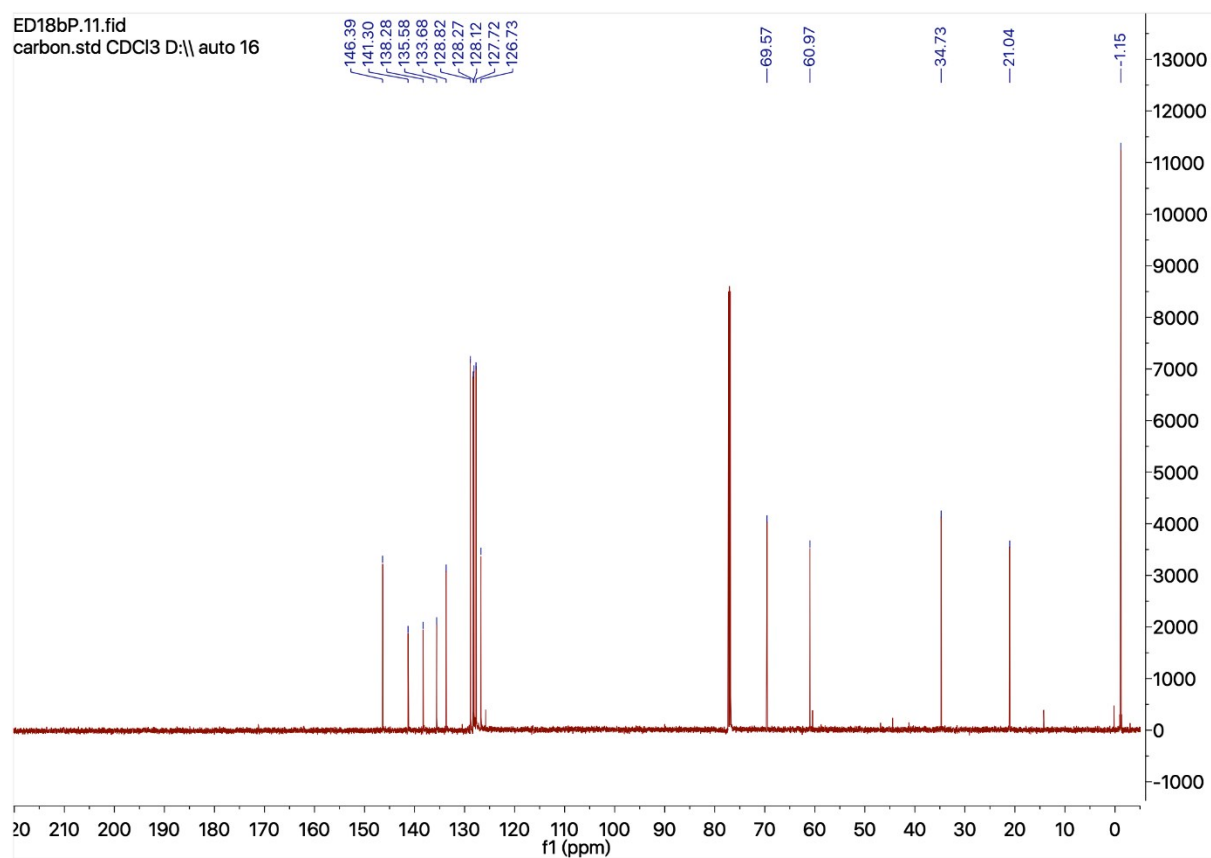
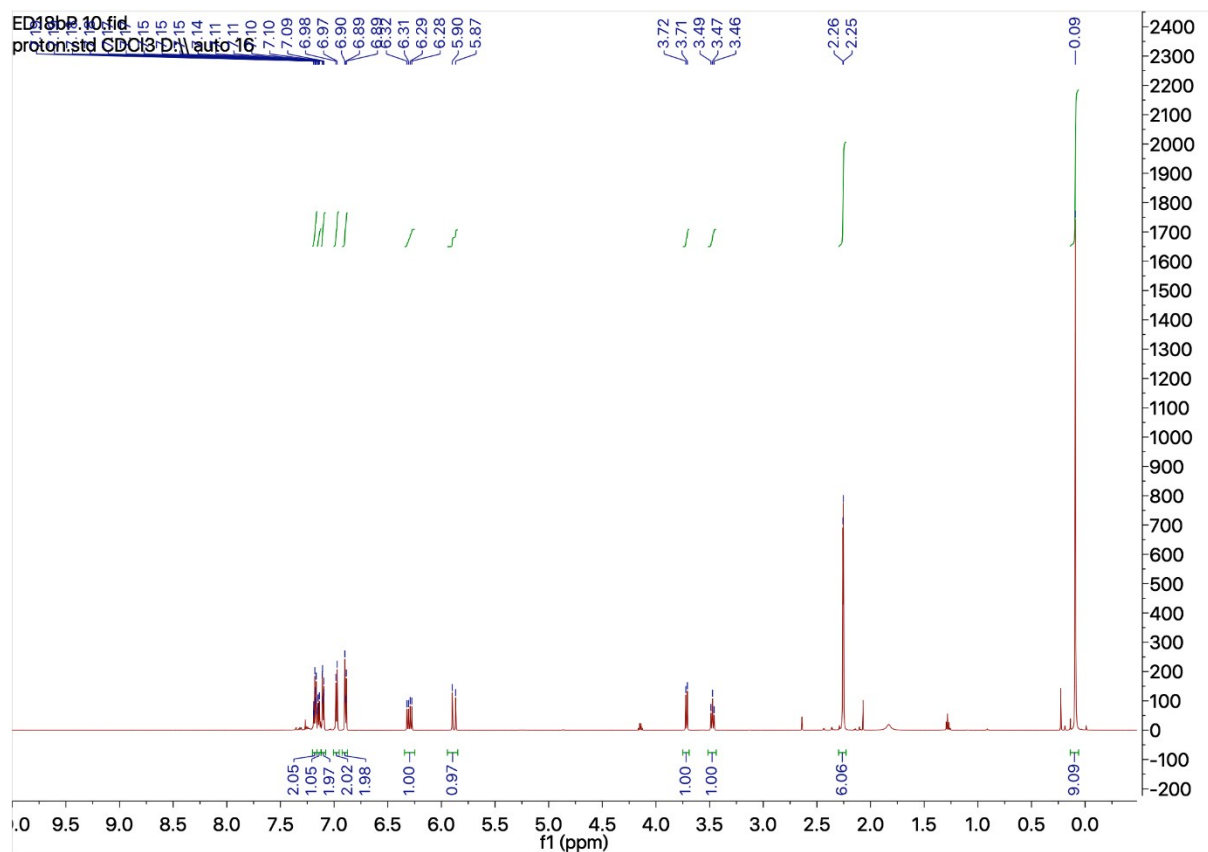
***E-N*-allyl-1-(5-methylisoxazol-3-yl)methanimine (2s):**



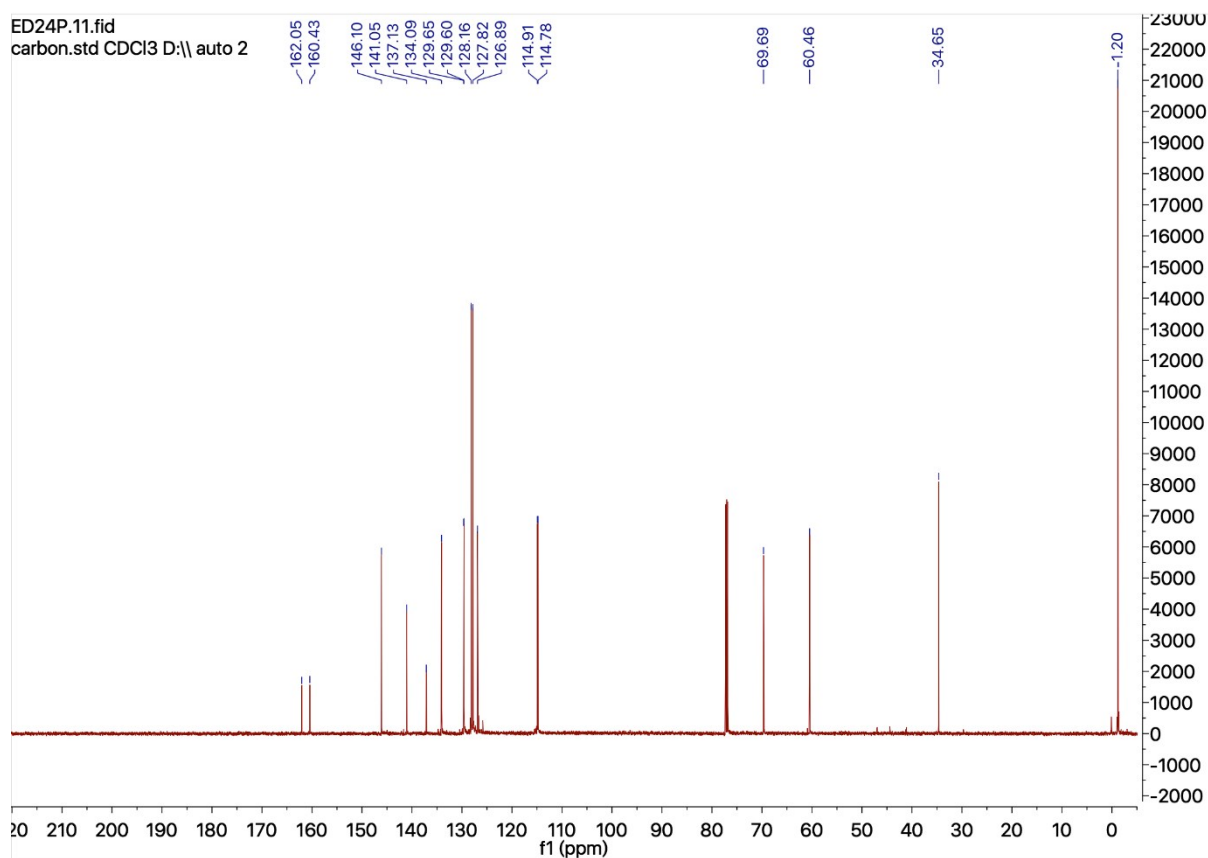
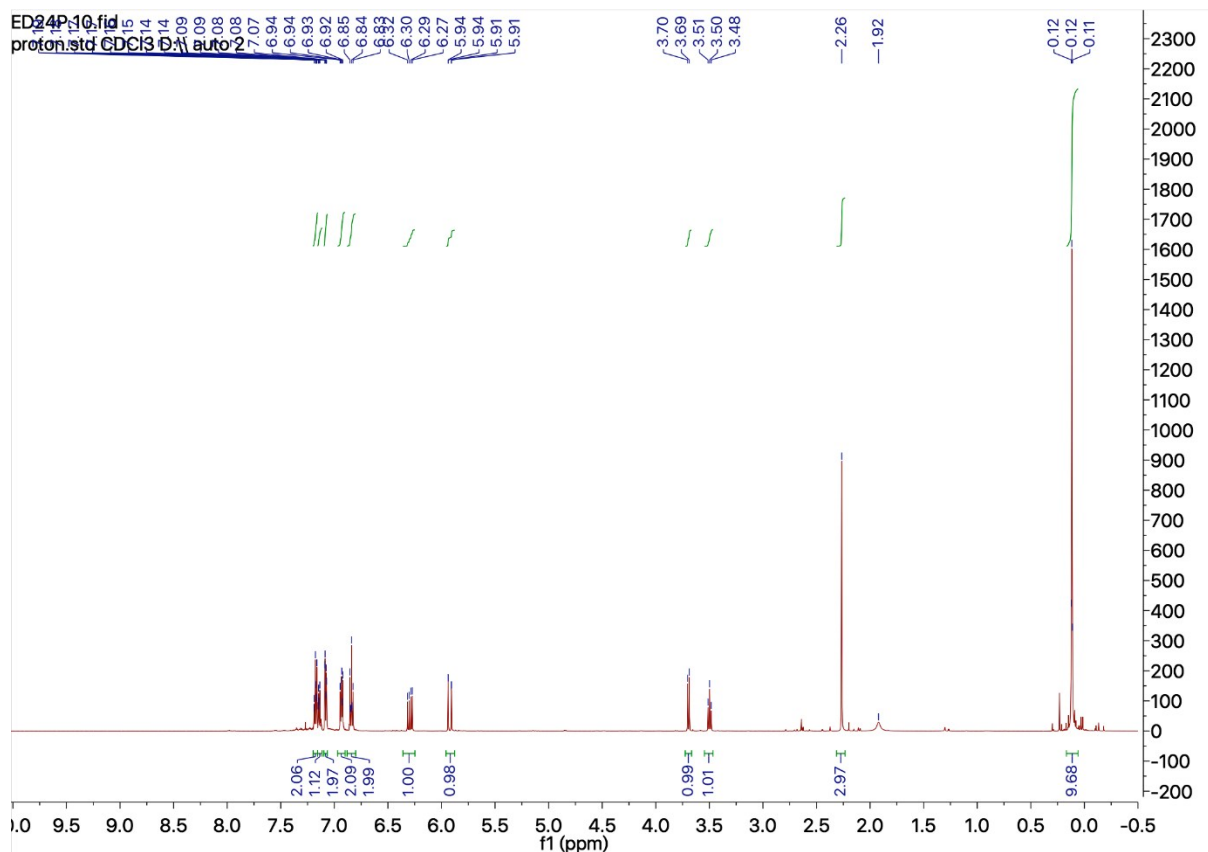
(E)-2-(chloromethyl)-N-methyl-1-phenyl-4-(trimethylsilyl)but-3-en-1-amine (3):



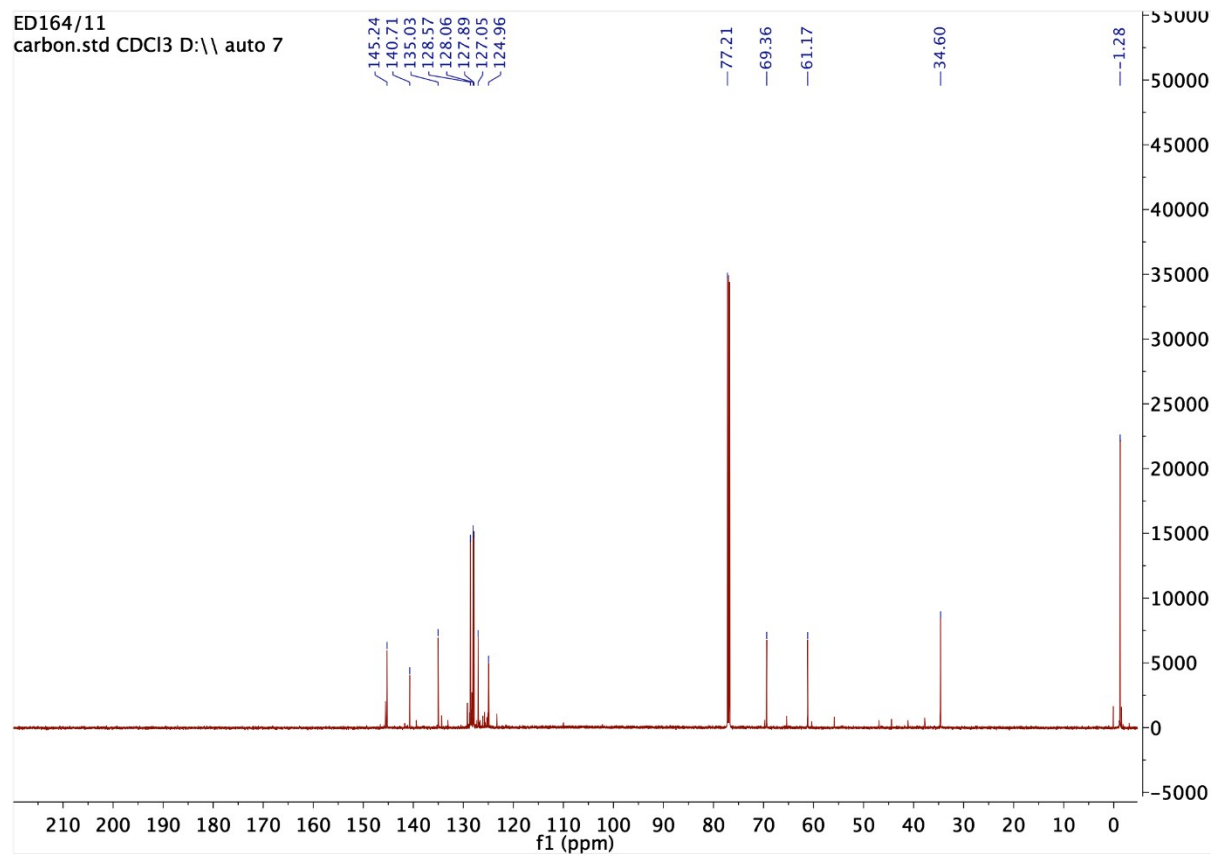
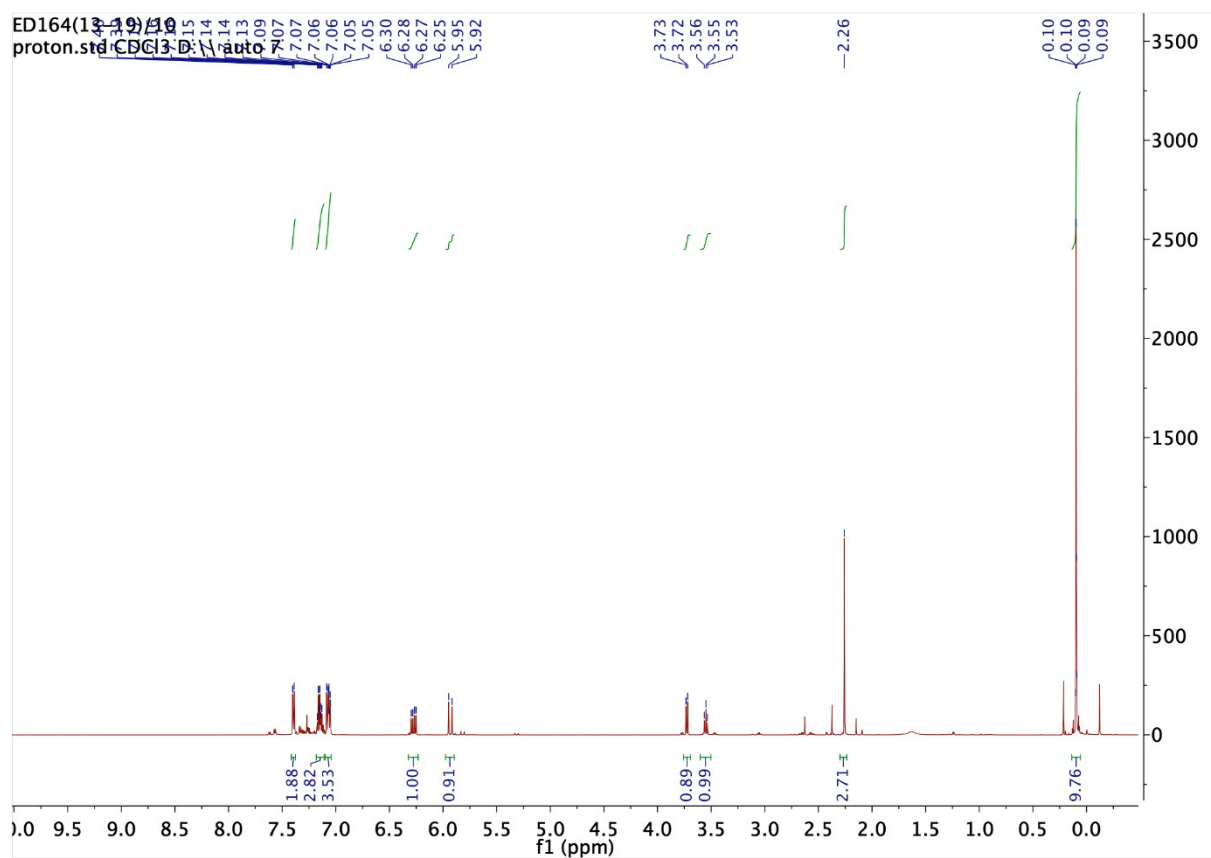
(E)-N-methyl-1-phenyl-2-(p-tolyl)-4-(trimethylsilyl)but-3-en-1-amine (4):



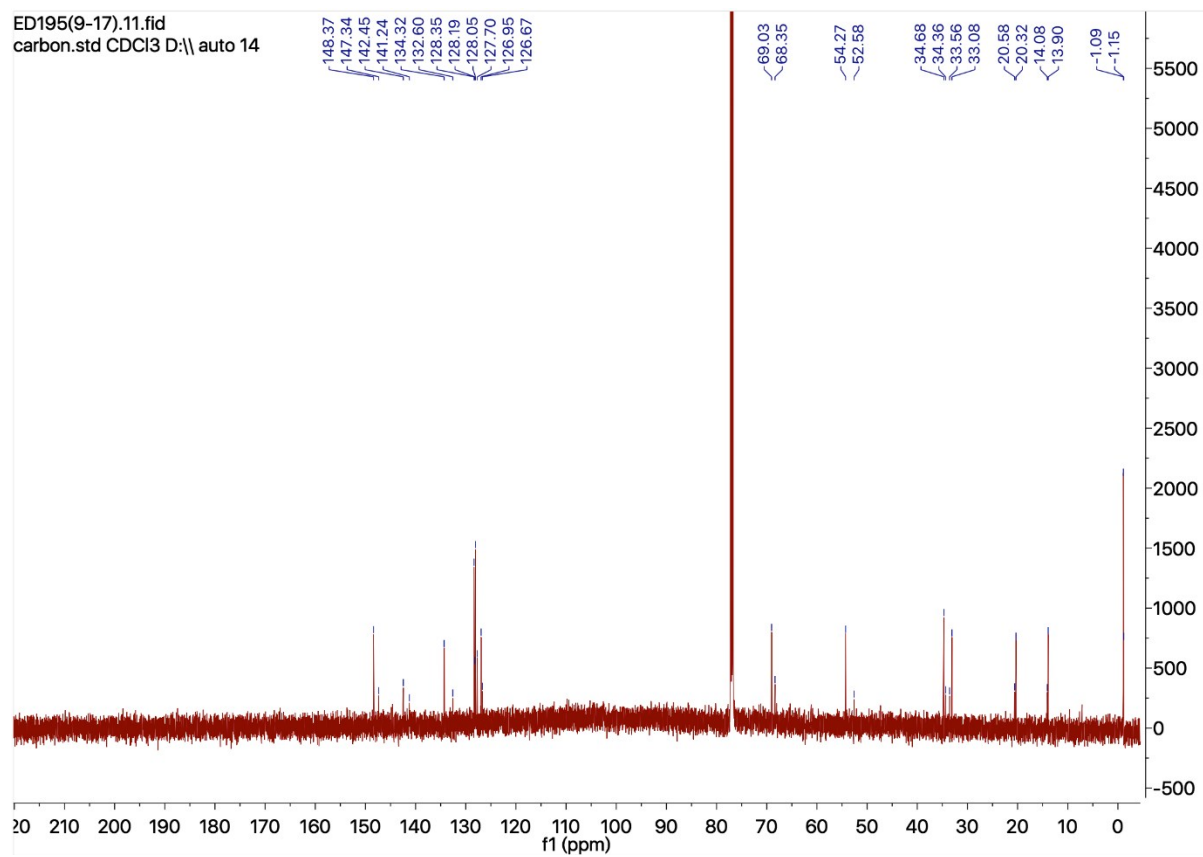
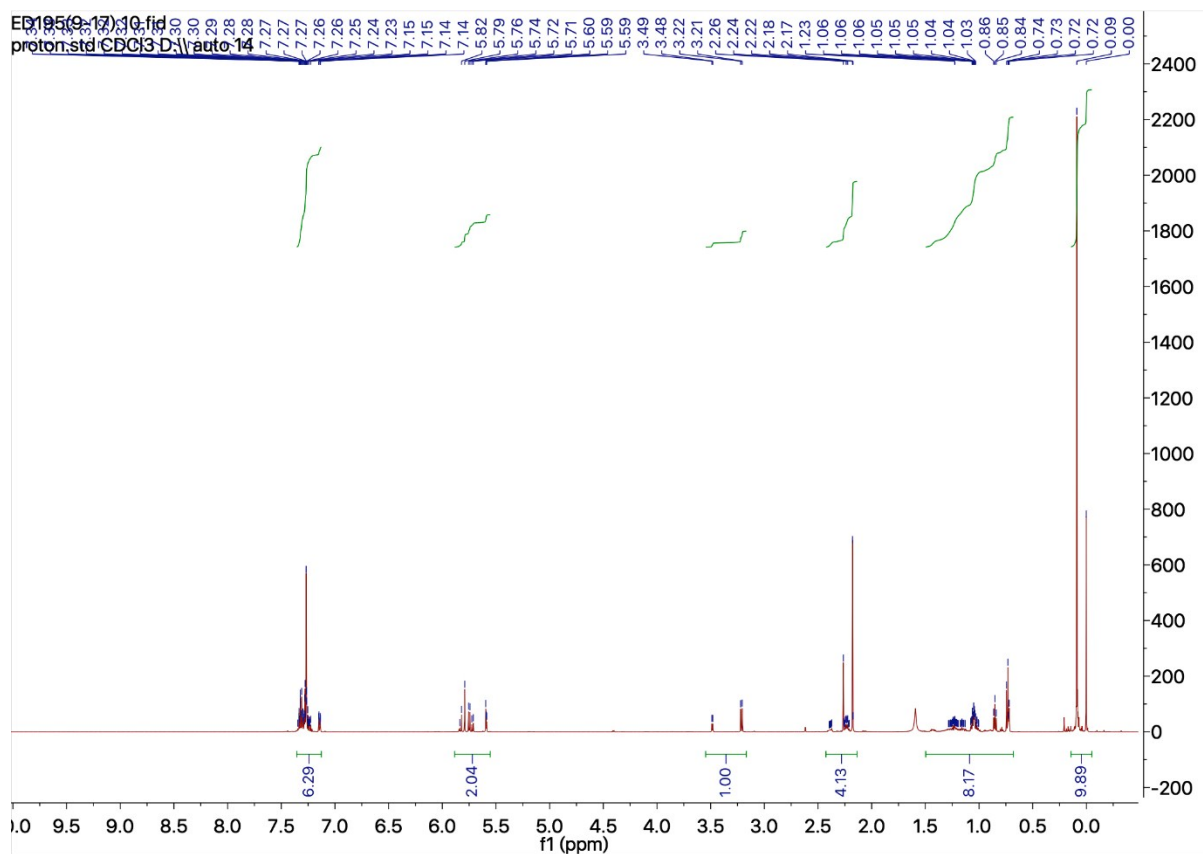
(E)-2-(4-fluorophenyl)-N-methyl-1-phenyl-4-(trimethylsilyl)but-3-en-1-amine (5):



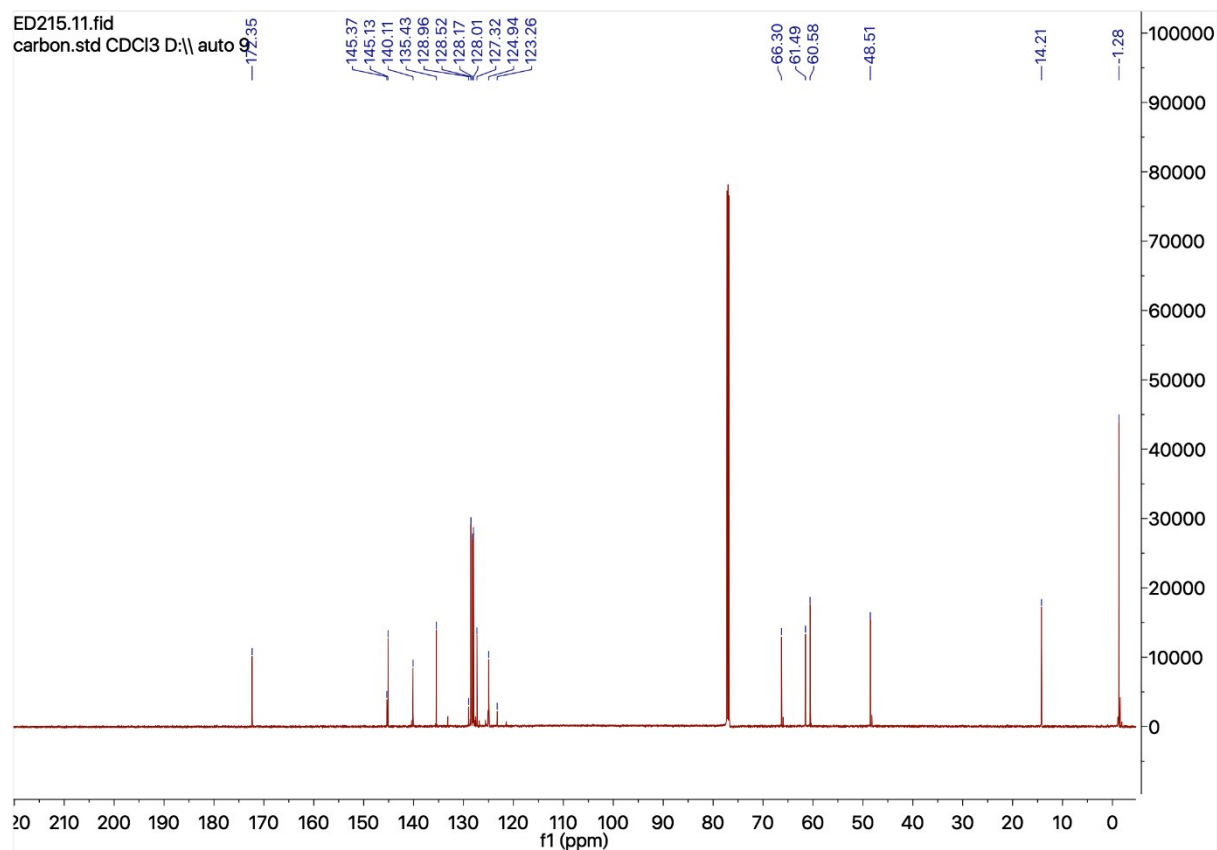
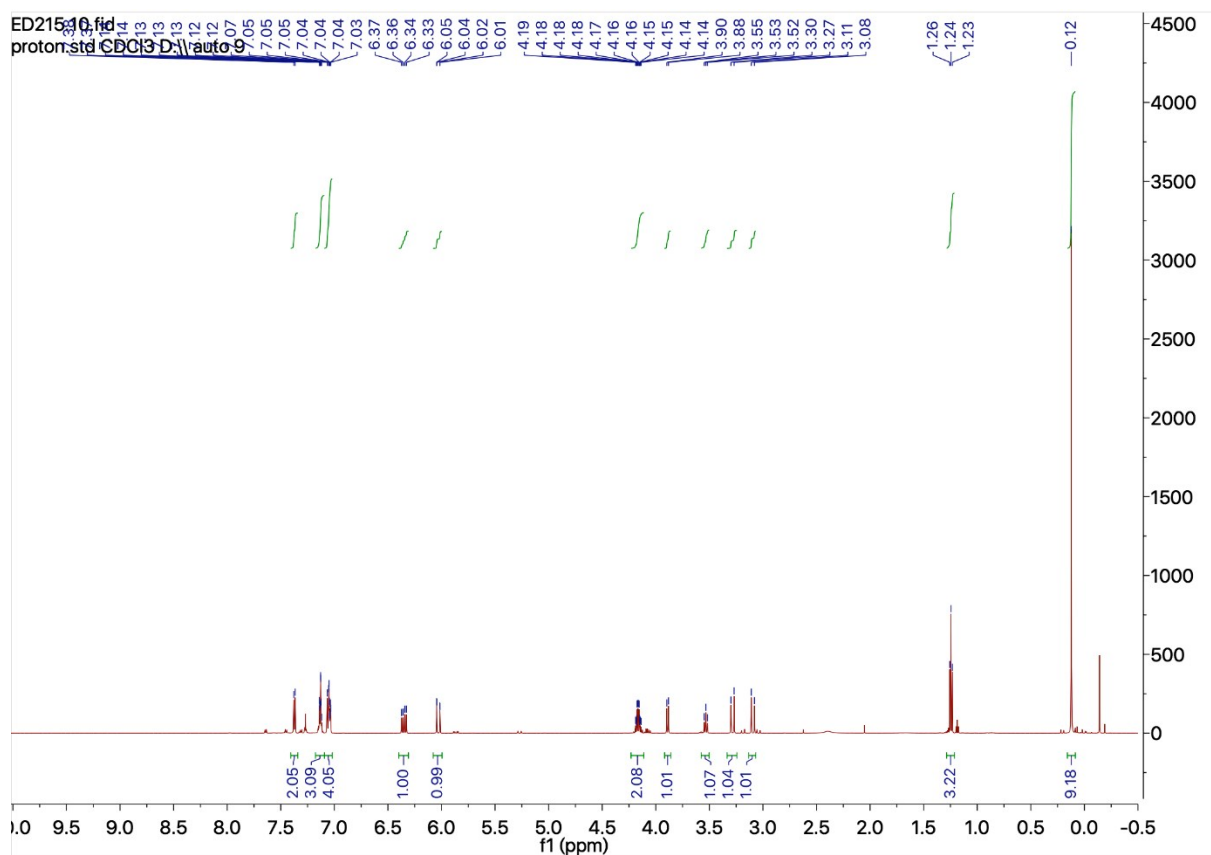
(E)-N-methyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)-4-(trimethylsilyl)but-3-en-1-amine
(6):



***N*-methyl-1-phenyl-2-((*E*)-2-(trimethylsilyl)vinyl)pentan-1-amine (7):**



Ethyl ((*E*)-1-phenyl-2-(4-(trifluoromethyl)phenyl)-4-(trimethylsilyl)but-3-en-1-yl)glycinate (8):

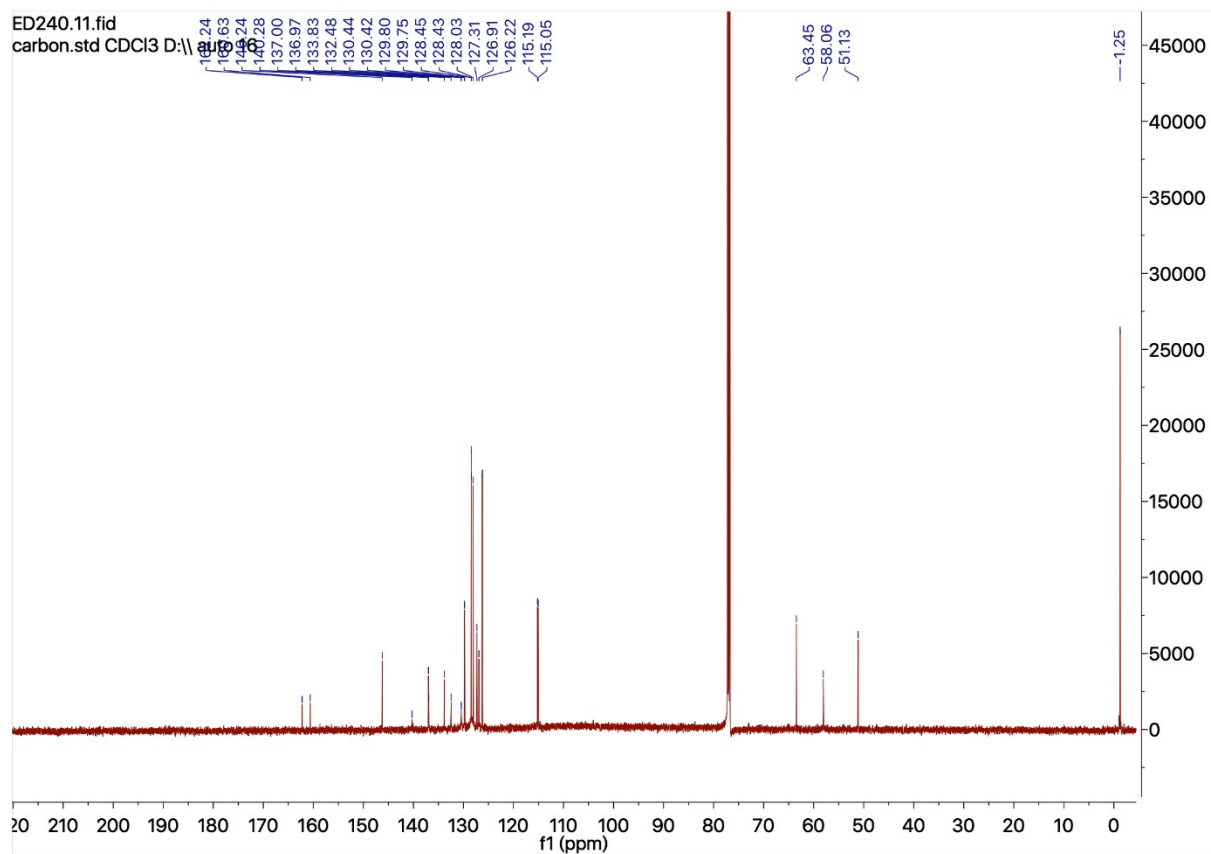
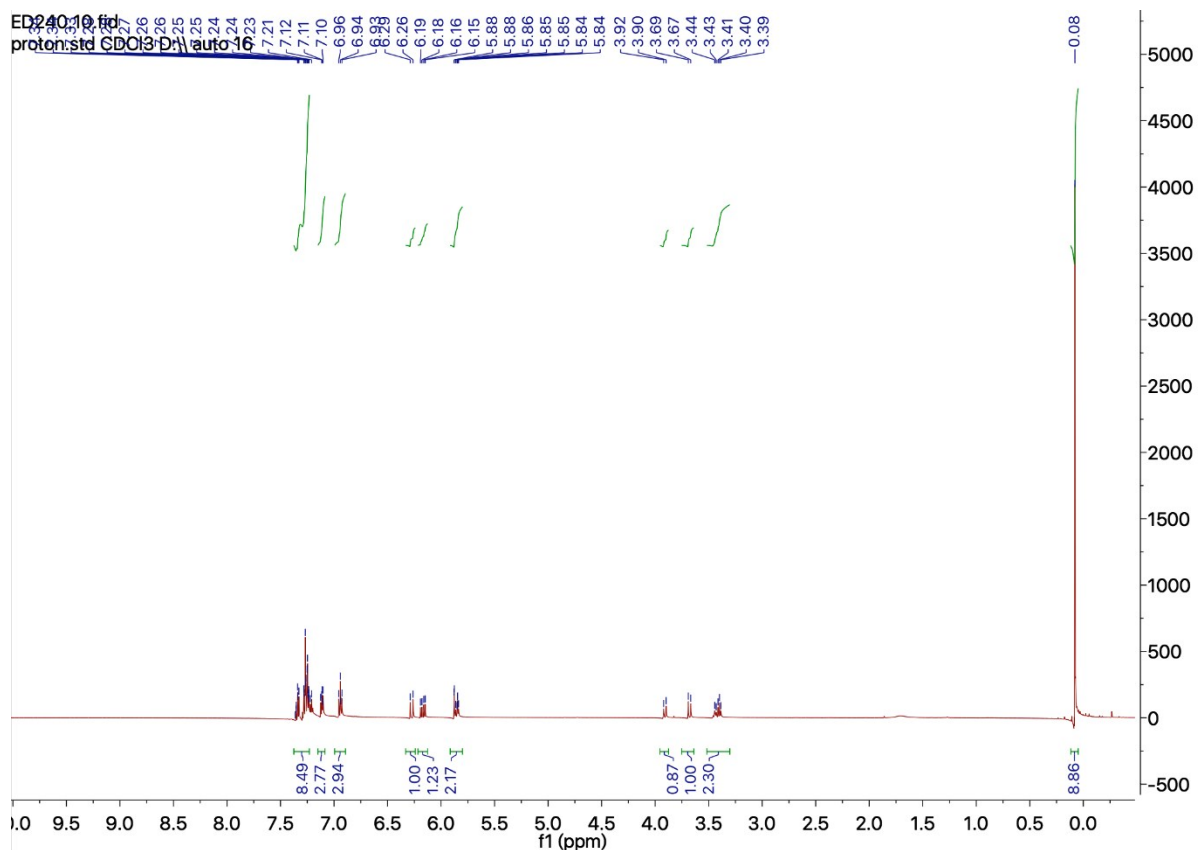


[illegible]

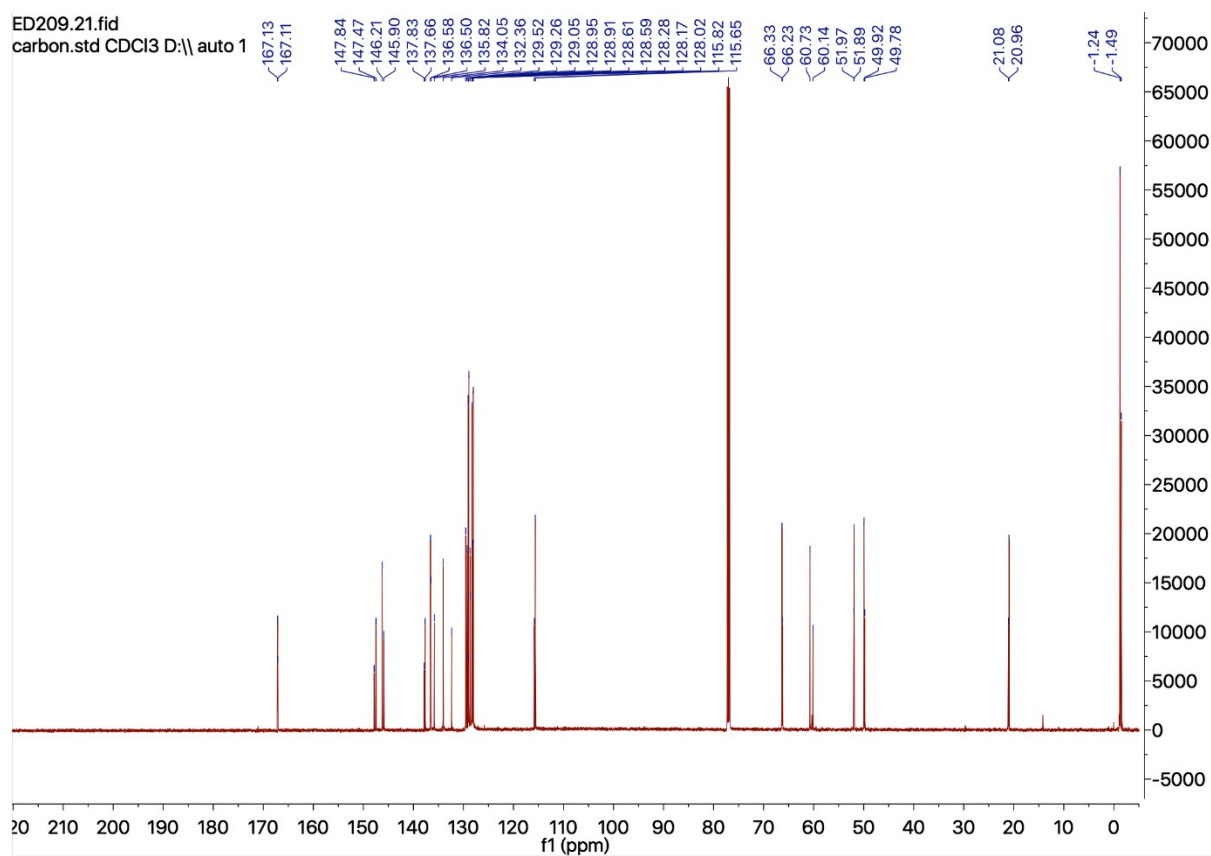
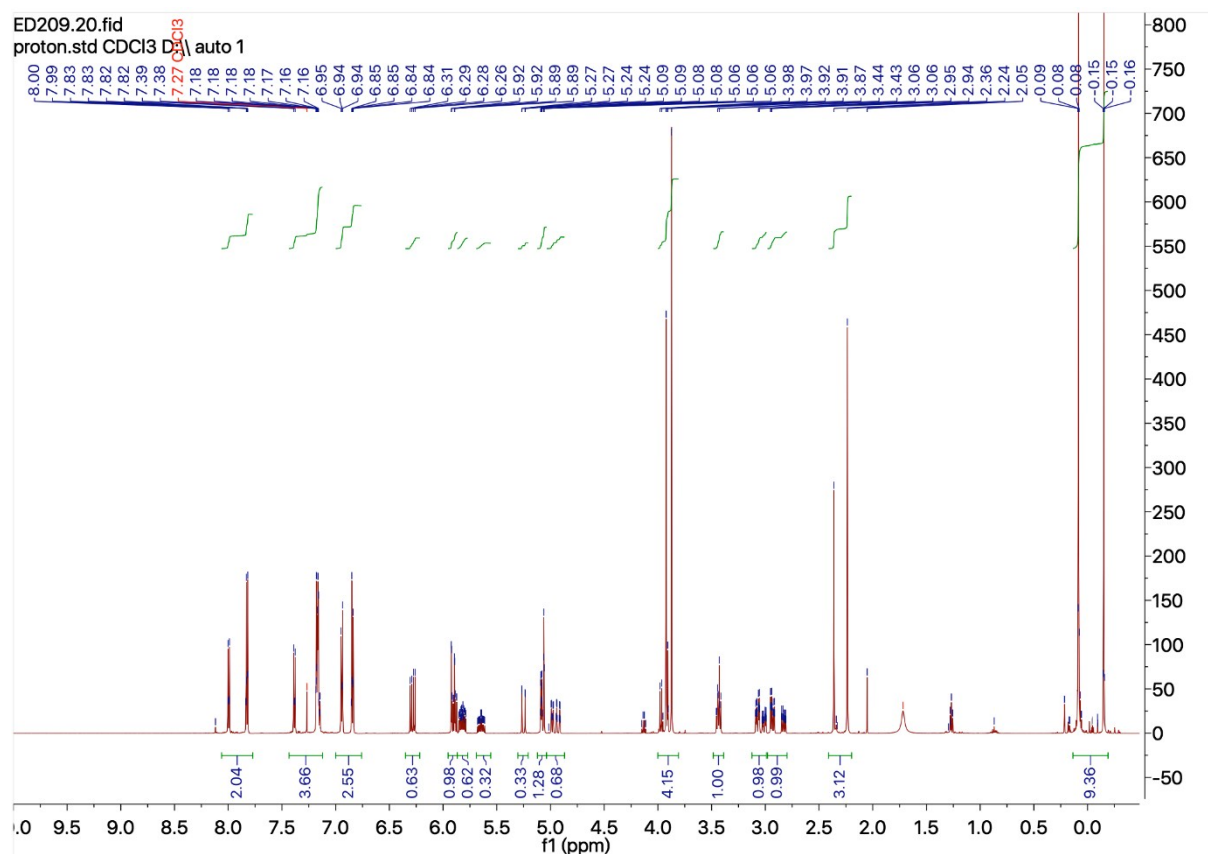
ED146011-15310 f1
proton std CDC13-D4 auto 11



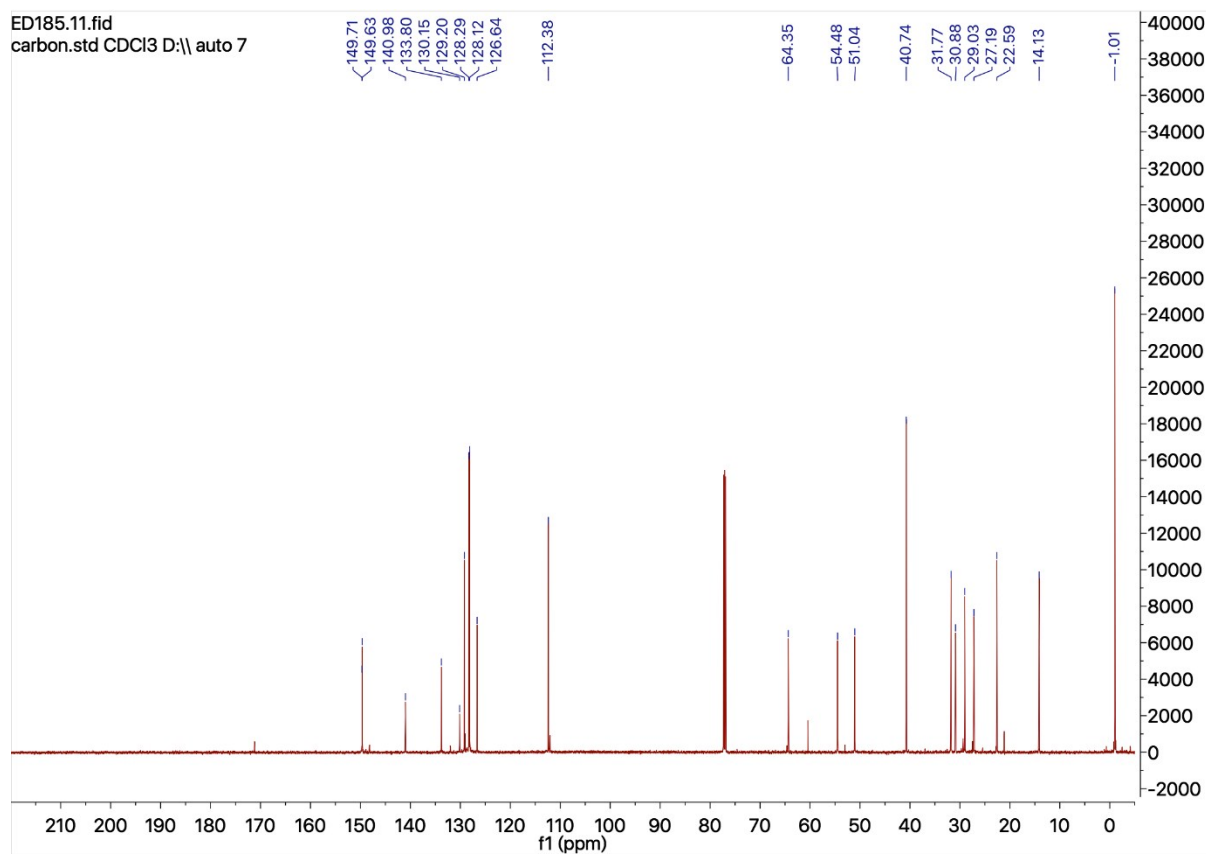
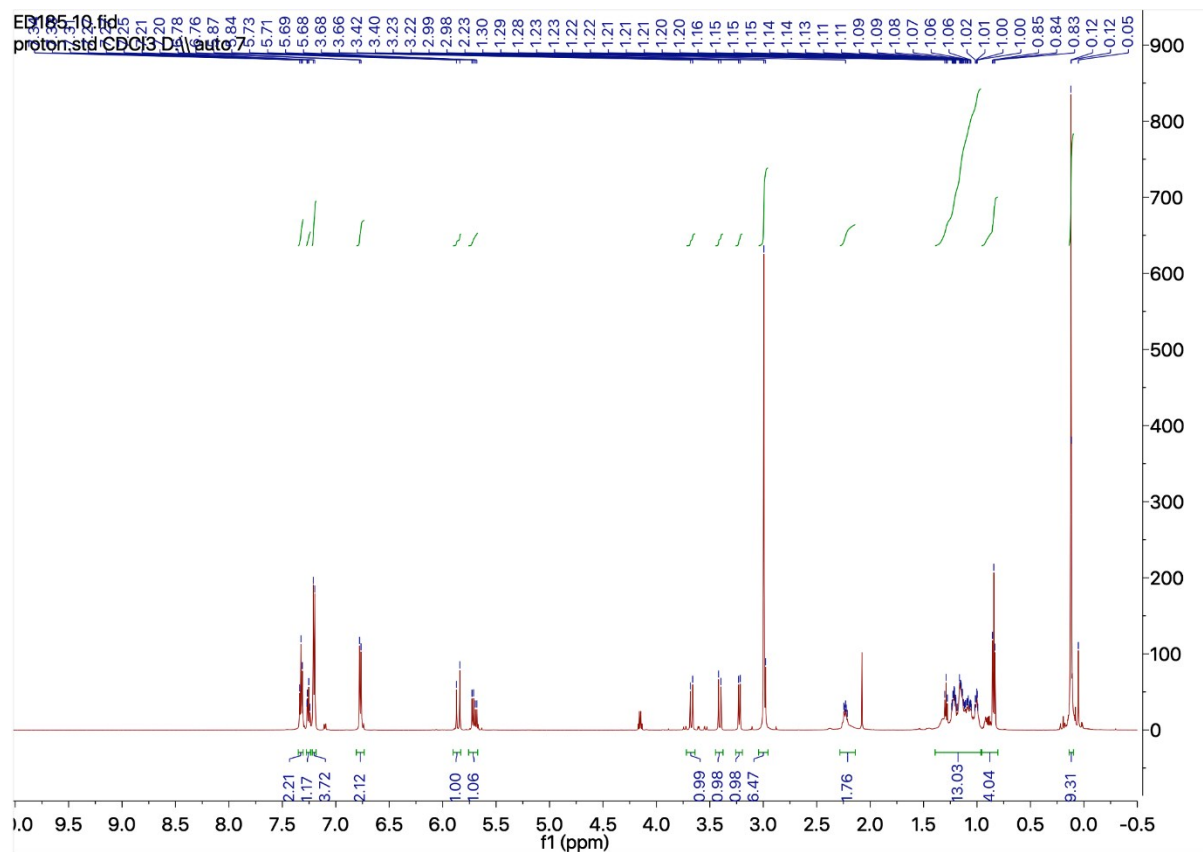
**(1E,5E)-N-benzyl-4-(4-fluorophenyl)-1-phenyl-6-(trimethylsilyl)hexa-1,5-dien-3-amine
(11):**



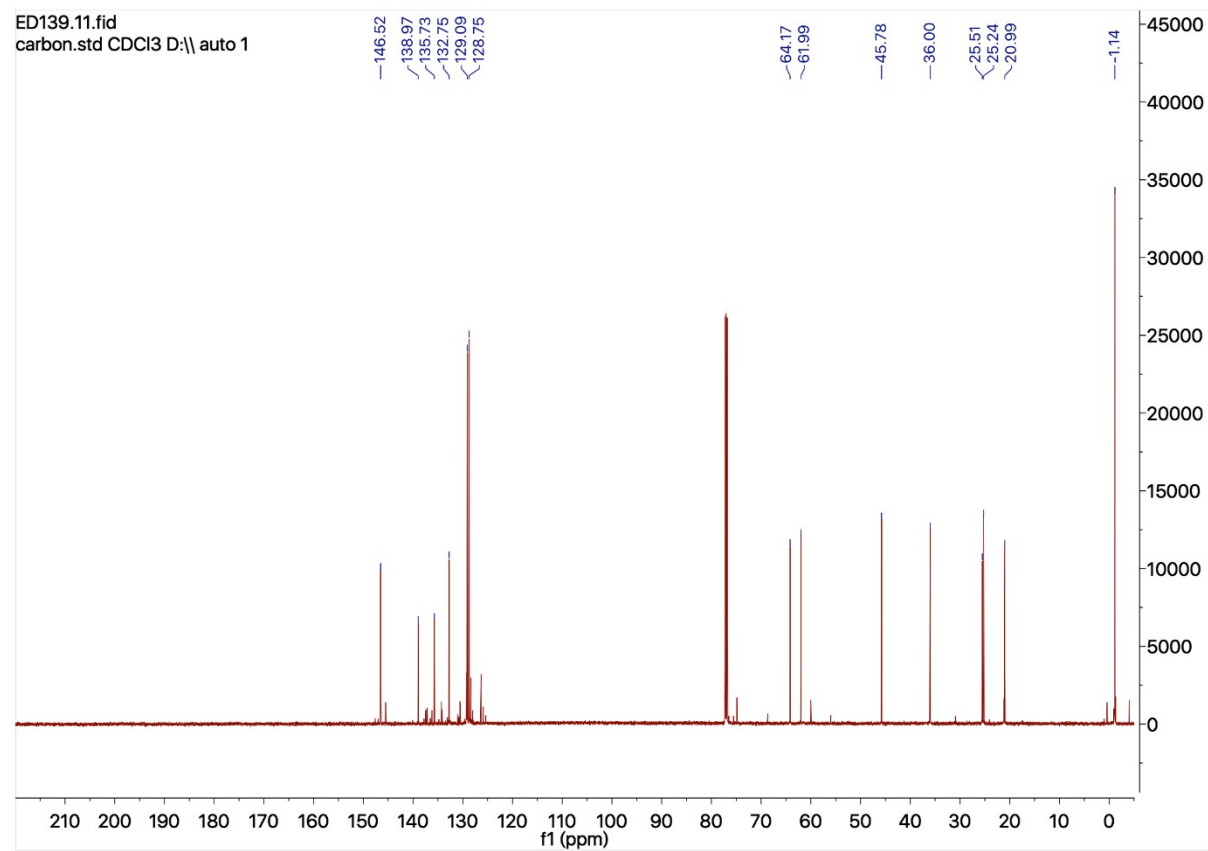
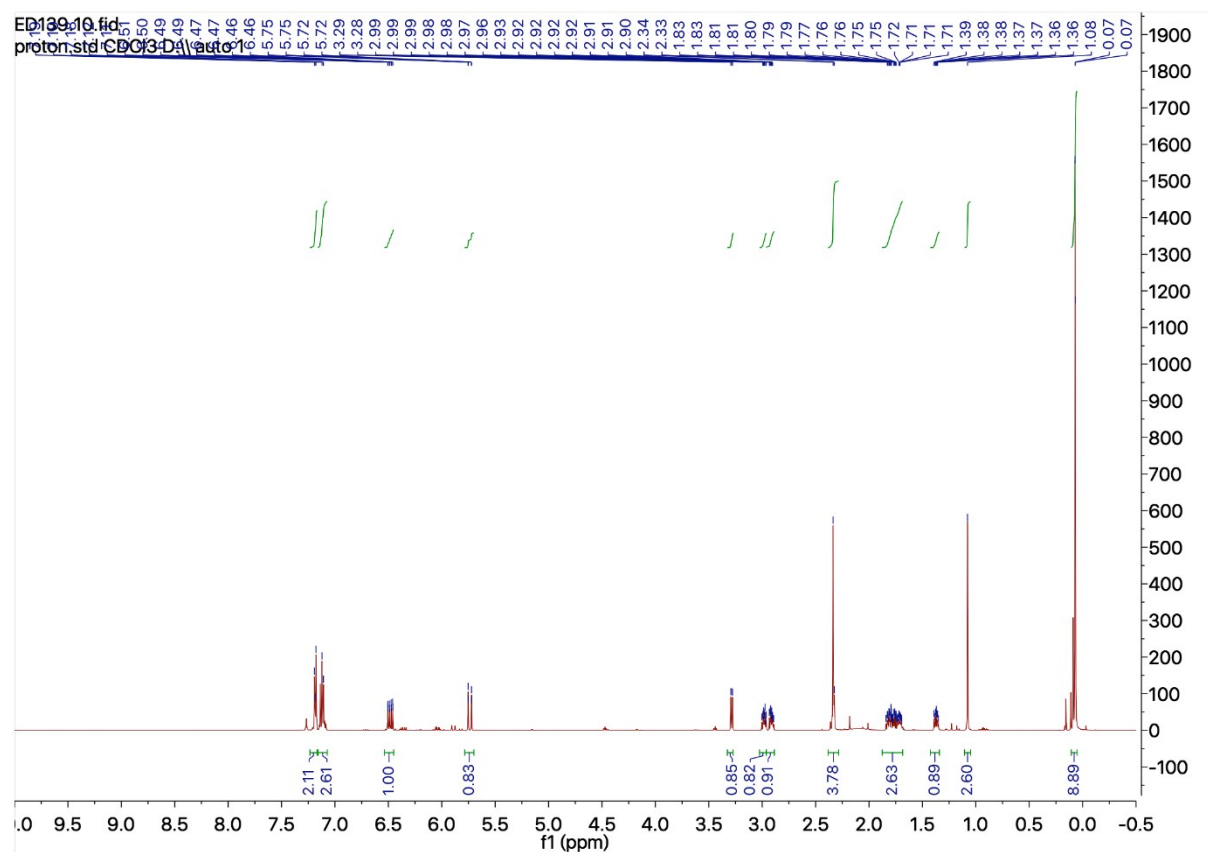
Methyl 4-((*E*)-1-(allylamino)-2-(*p*-tolyl)-4-(trimethylsilyl)but-3-en-1-yl)benzoate (12):



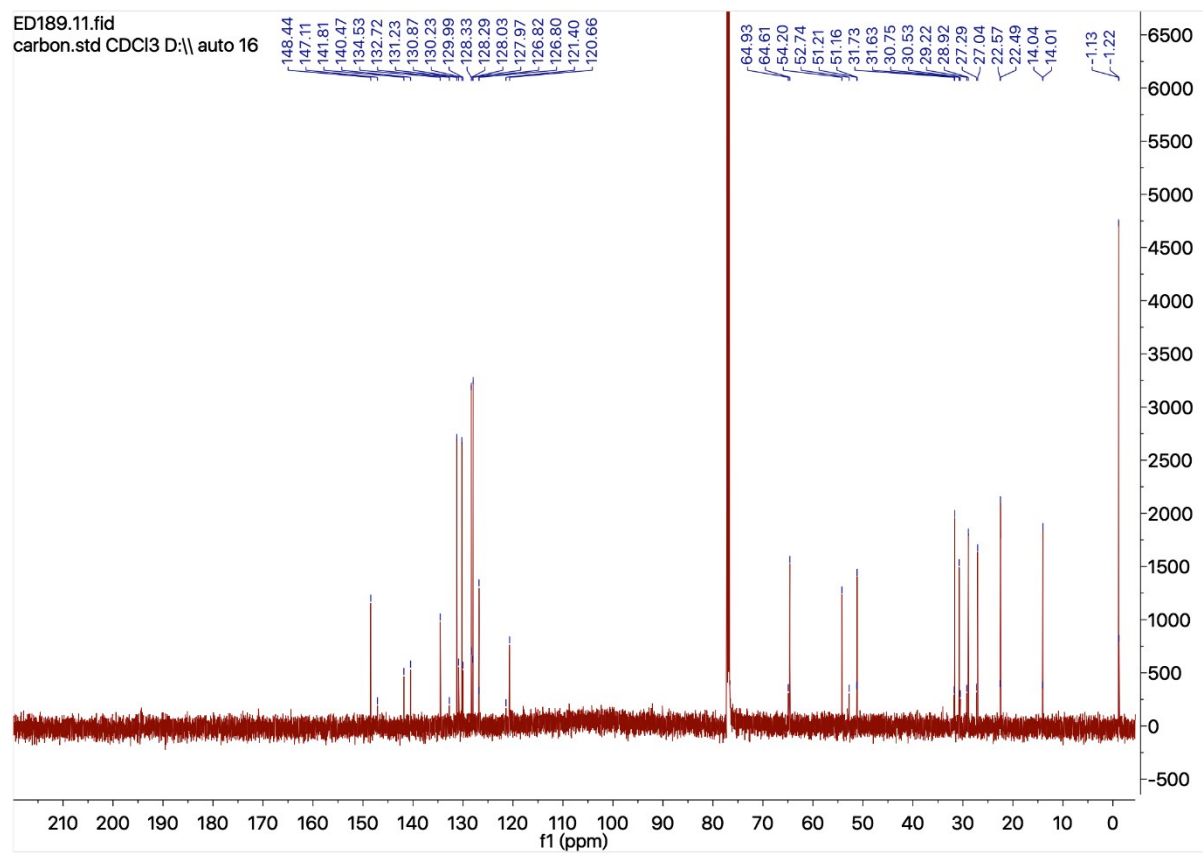
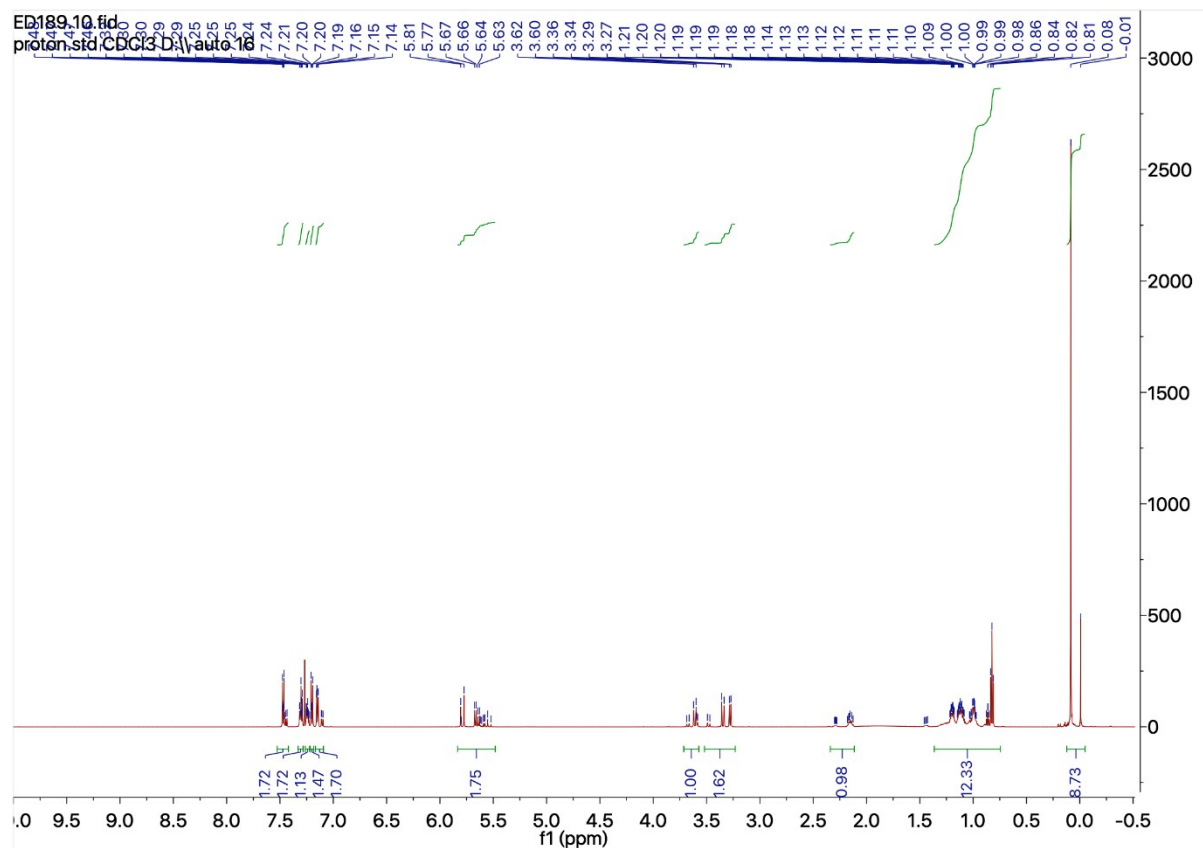
4-(1-(benzylamino)-2-((E)-2-(trimethylsilyl)vinyl)octyl)-N,N-dimethylaniline (13):



2-methyl-2-(1-(p-tolyl)-3-(trimethylsilyl)allyl)pyrrolidine (14):



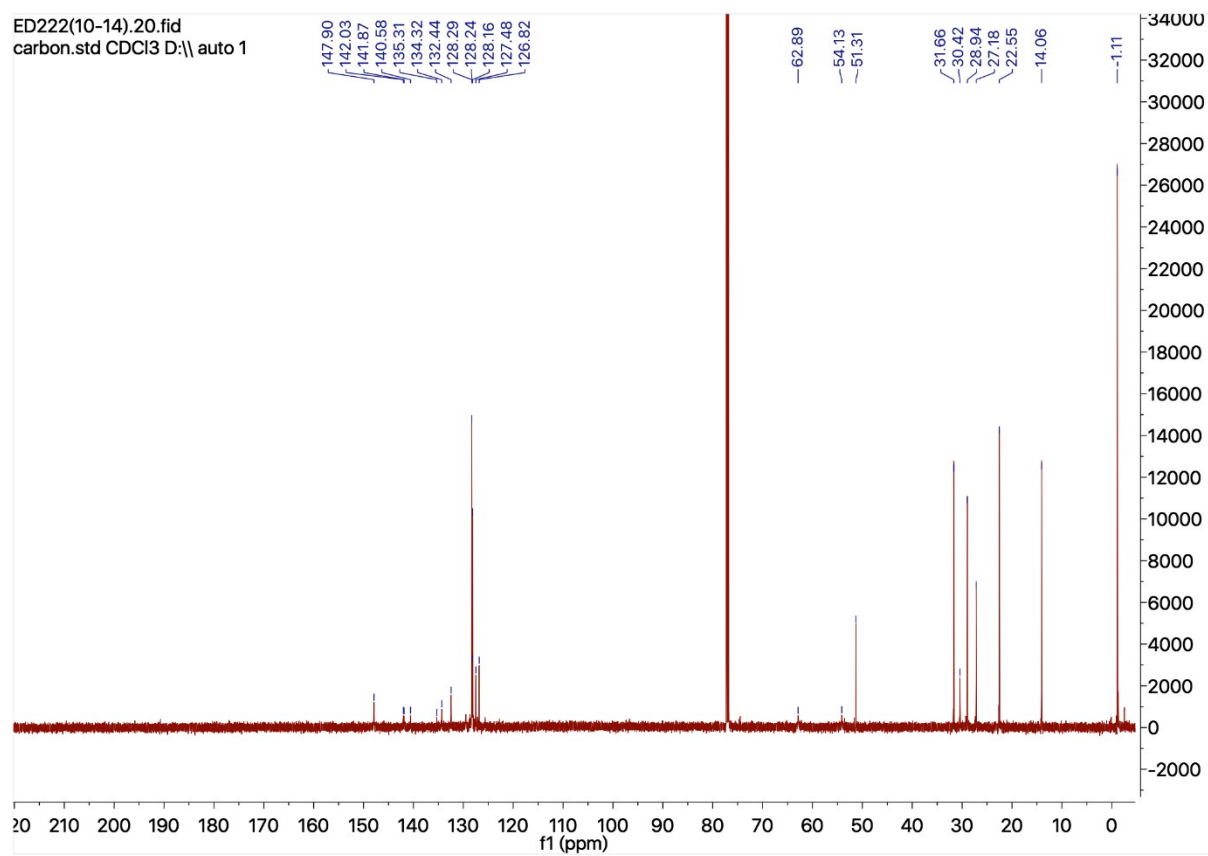
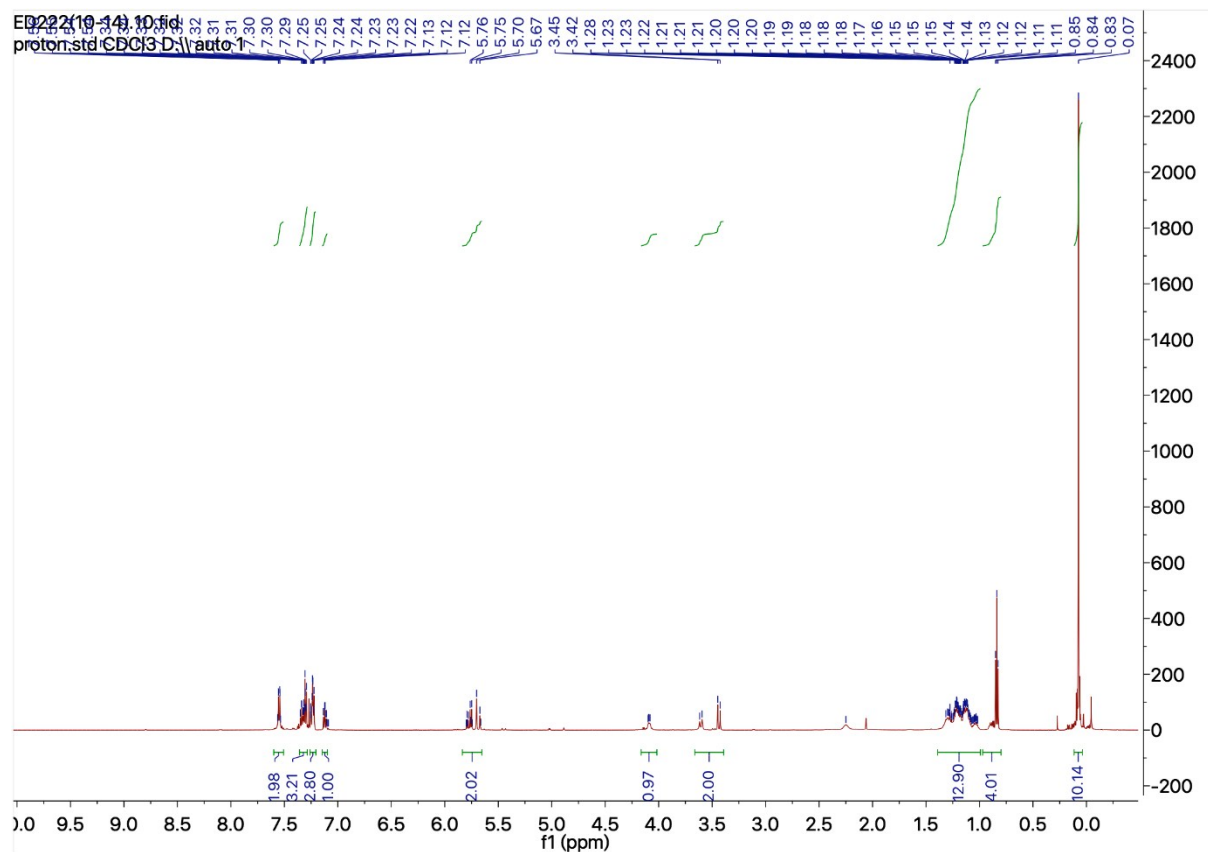
***N*-benzyl-1-(4-bromophenyl)-2-((*E*)-2-(trimethylsilyl)vinyl)octan-1-amine (15):**



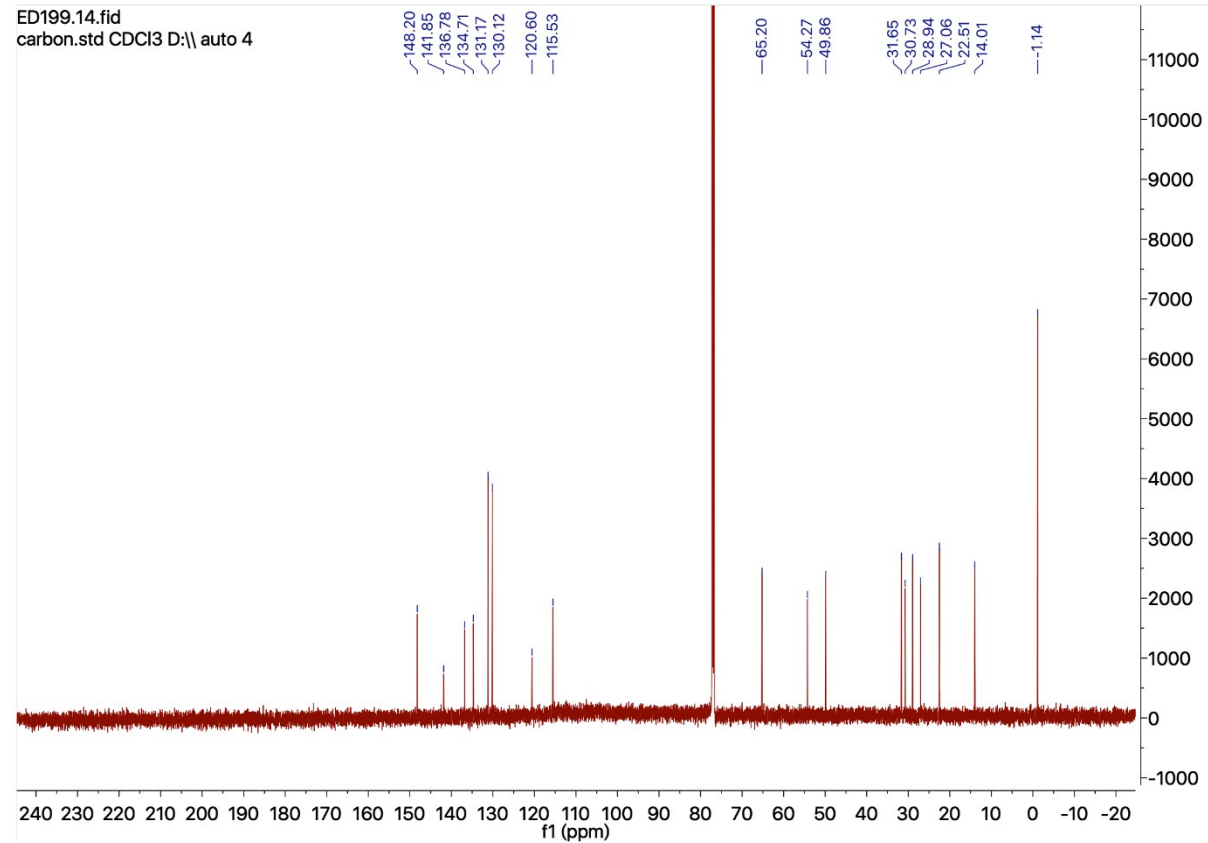
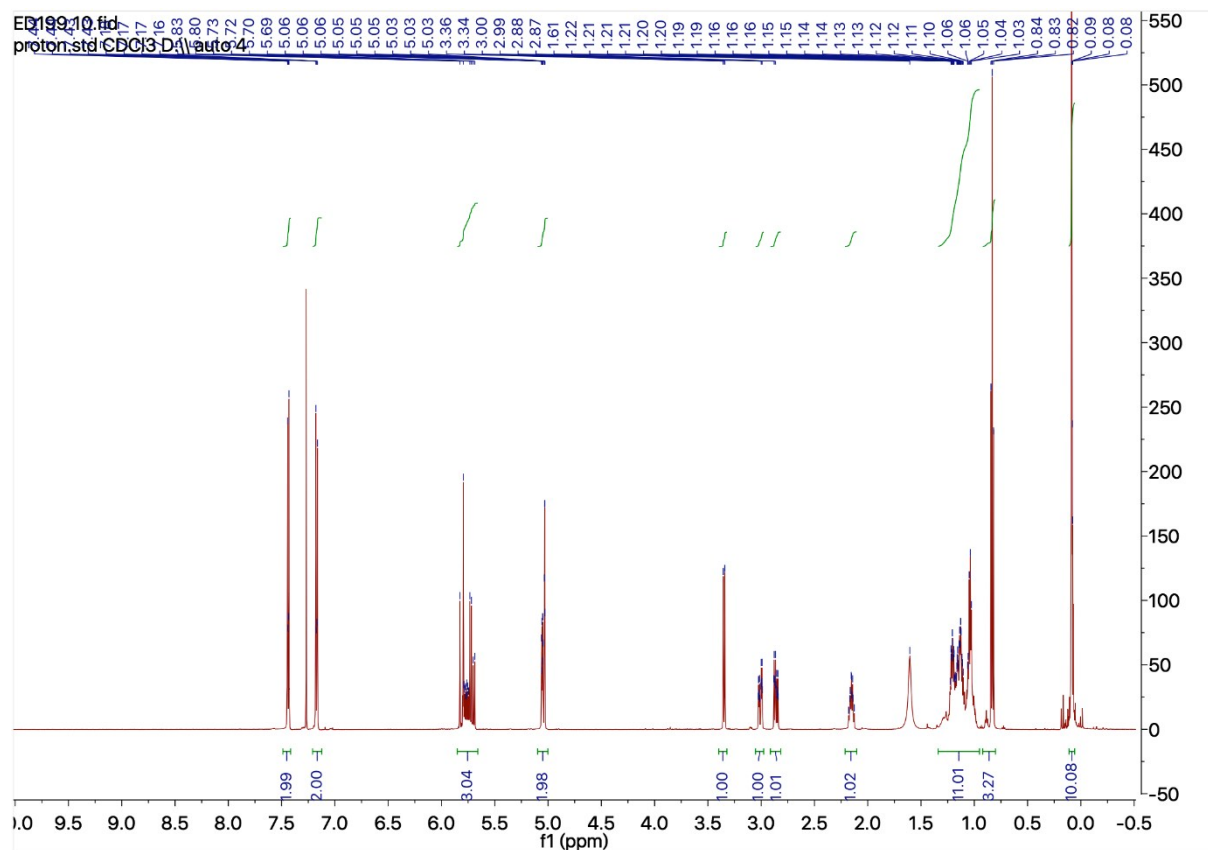
13C NMR spectrum of compound 10b (proton std CDC13 D₂O auto 13). The x-axis represents the chemical shift in ppm (f1), ranging from 0.0 to 10.0. The y-axis represents the intensity, ranging from -100 to 1300. The spectrum shows several peaks, with the most prominent ones at approximately 0.1 ppm (TMS), 0.8 ppm, 1.0 ppm, 1.2 ppm, 1.4 ppm, 1.6 ppm, 1.8 ppm, 2.0 ppm, 2.2 ppm, 2.4 ppm, 2.6 ppm, 2.8 ppm, 3.0 ppm, 3.2 ppm, 3.4 ppm, 3.6 ppm, 3.8 ppm, 4.0 ppm, 4.2 ppm, 4.4 ppm, 4.6 ppm, 4.8 ppm, 5.0 ppm, 5.2 ppm, 5.4 ppm, 5.6 ppm, 5.8 ppm, 6.0 ppm, 6.2 ppm, 6.4 ppm, 6.6 ppm, 6.8 ppm, 7.0 ppm, 7.2 ppm, 7.4 ppm, 7.6 ppm, 7.8 ppm, 8.0 ppm, 8.2 ppm, 8.4 ppm, 8.6 ppm, 8.8 ppm, 9.0 ppm, 9.2 ppm, 9.4 ppm, 9.6 ppm, 9.8 ppm, and 10.0 ppm. The peaks are labeled with their corresponding chemical shifts and integration values.



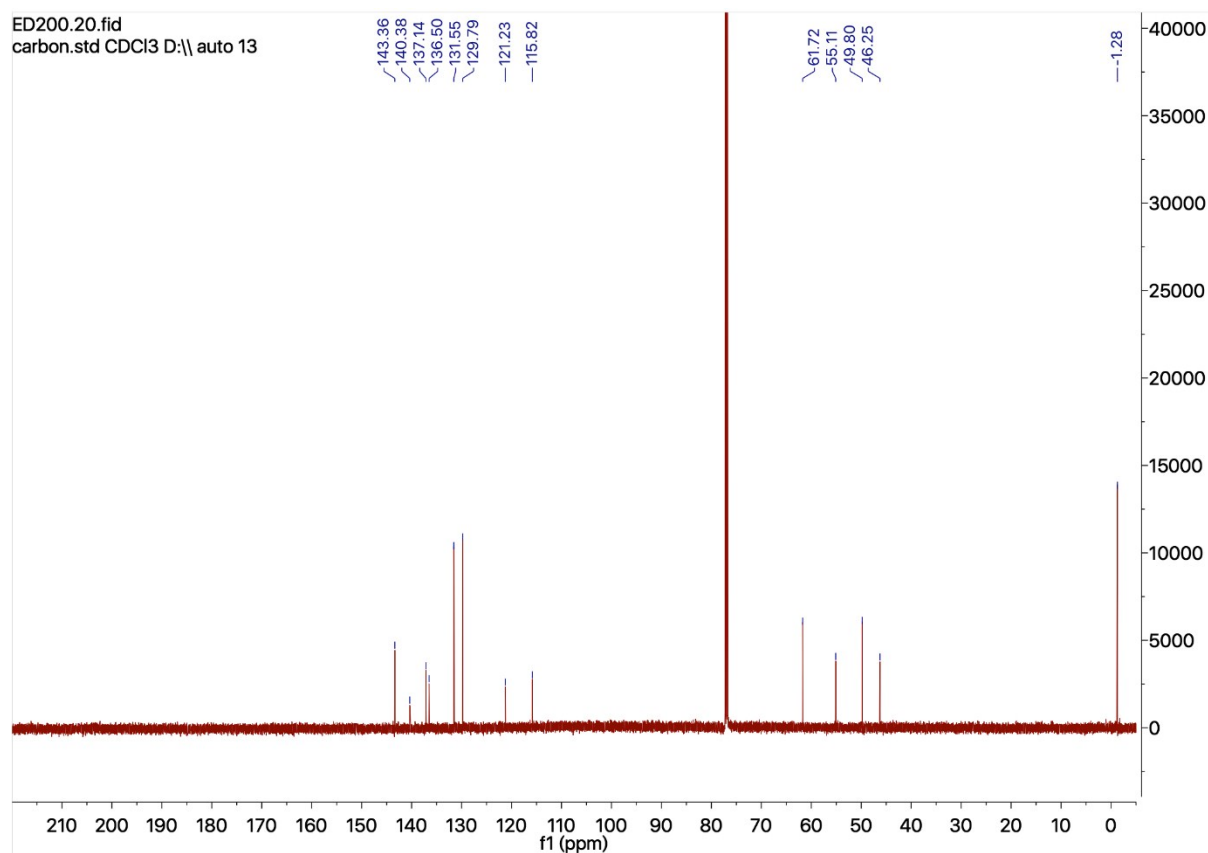
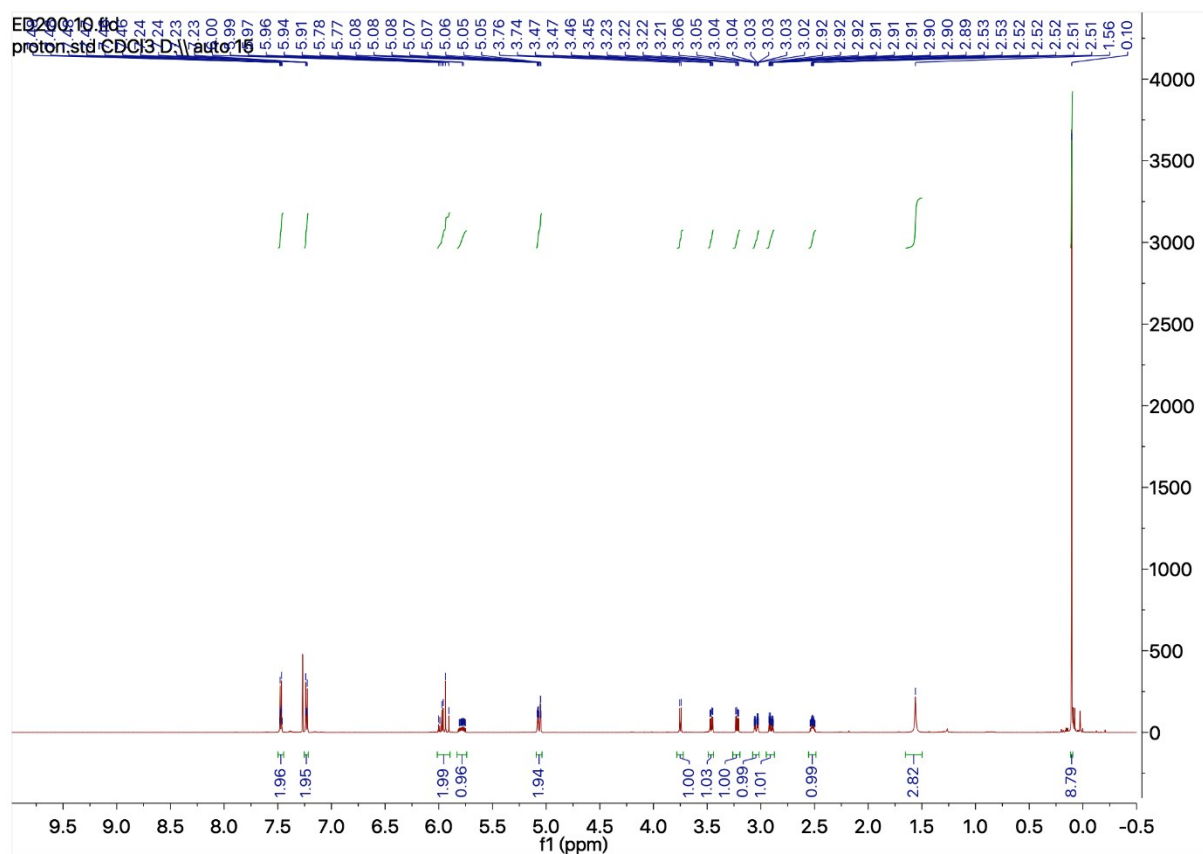
***N*-benzyl-1-(2-bromophenyl)-2-((*E*)-2-(trimethylsilyl)vinyl)octan-1-amine (17):**



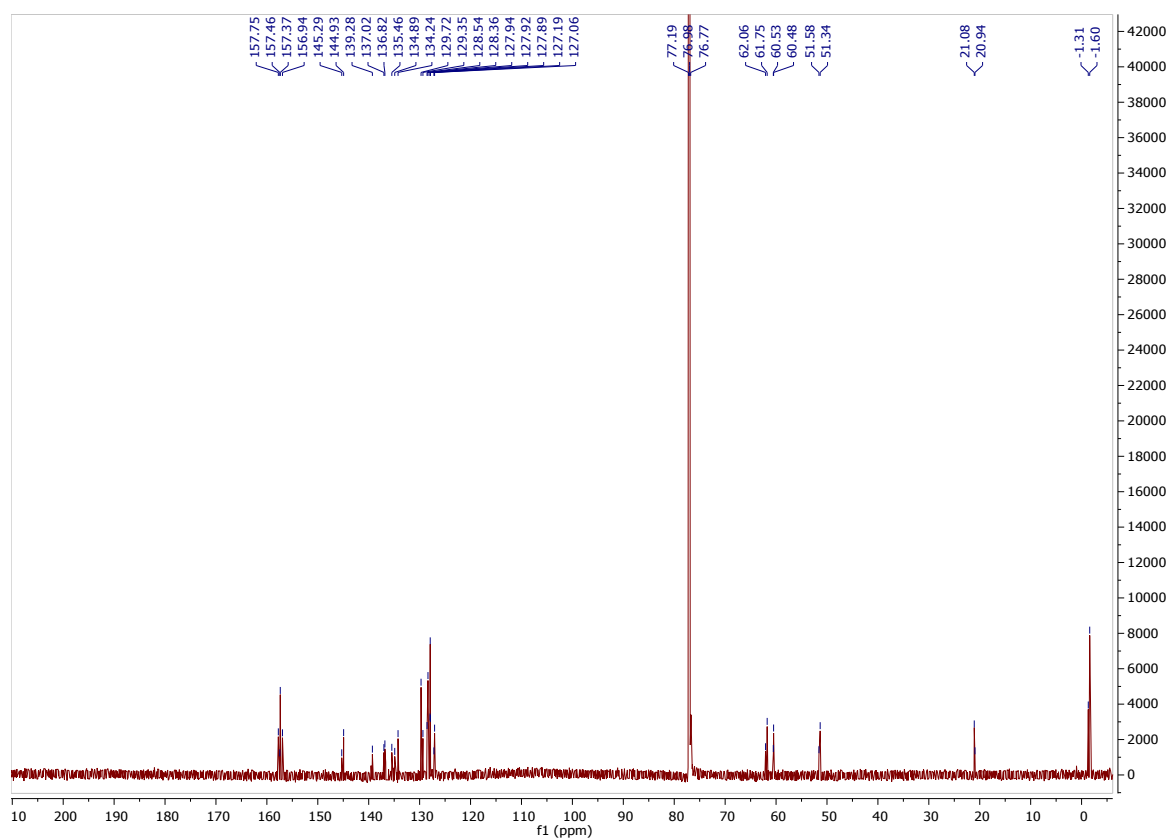
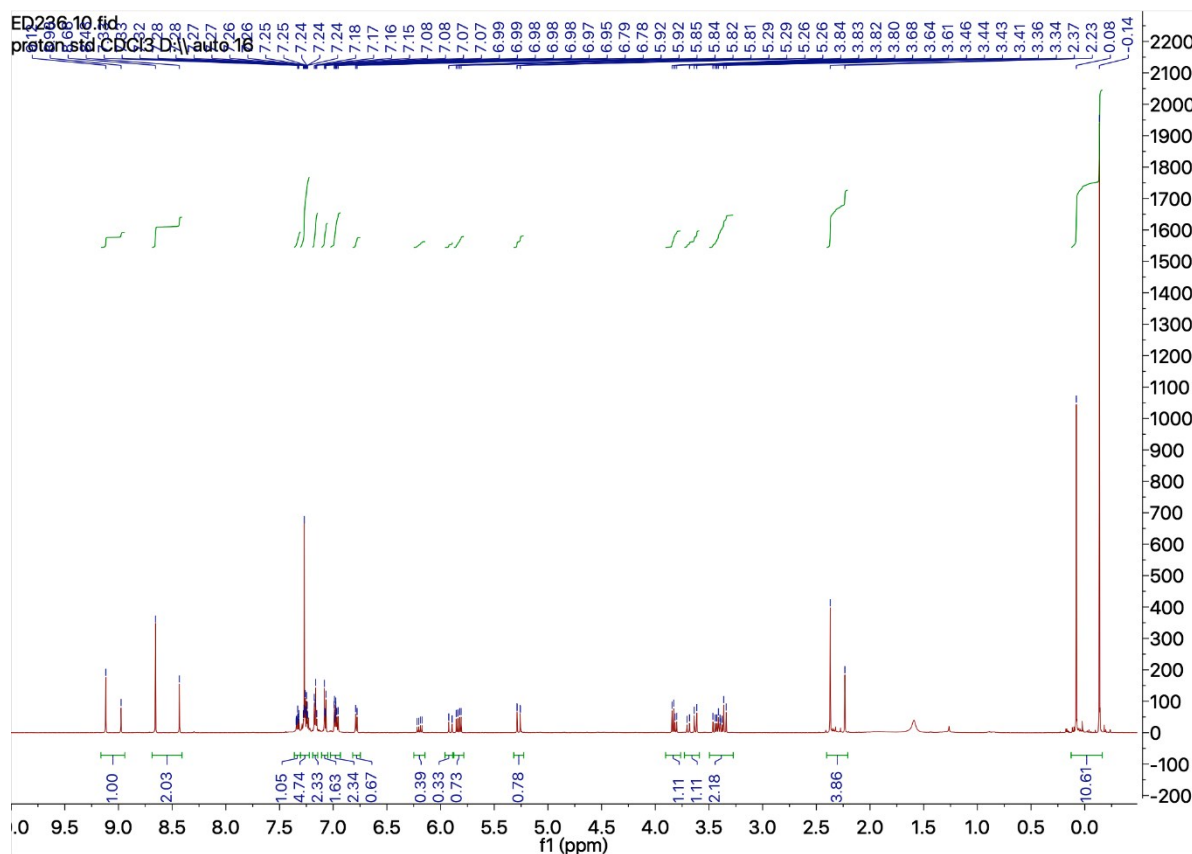
N-allyl-1-(4-bromophenyl)-2-((E)-2-(trimethylsilyl)vinyl)octan-1-amine (18):



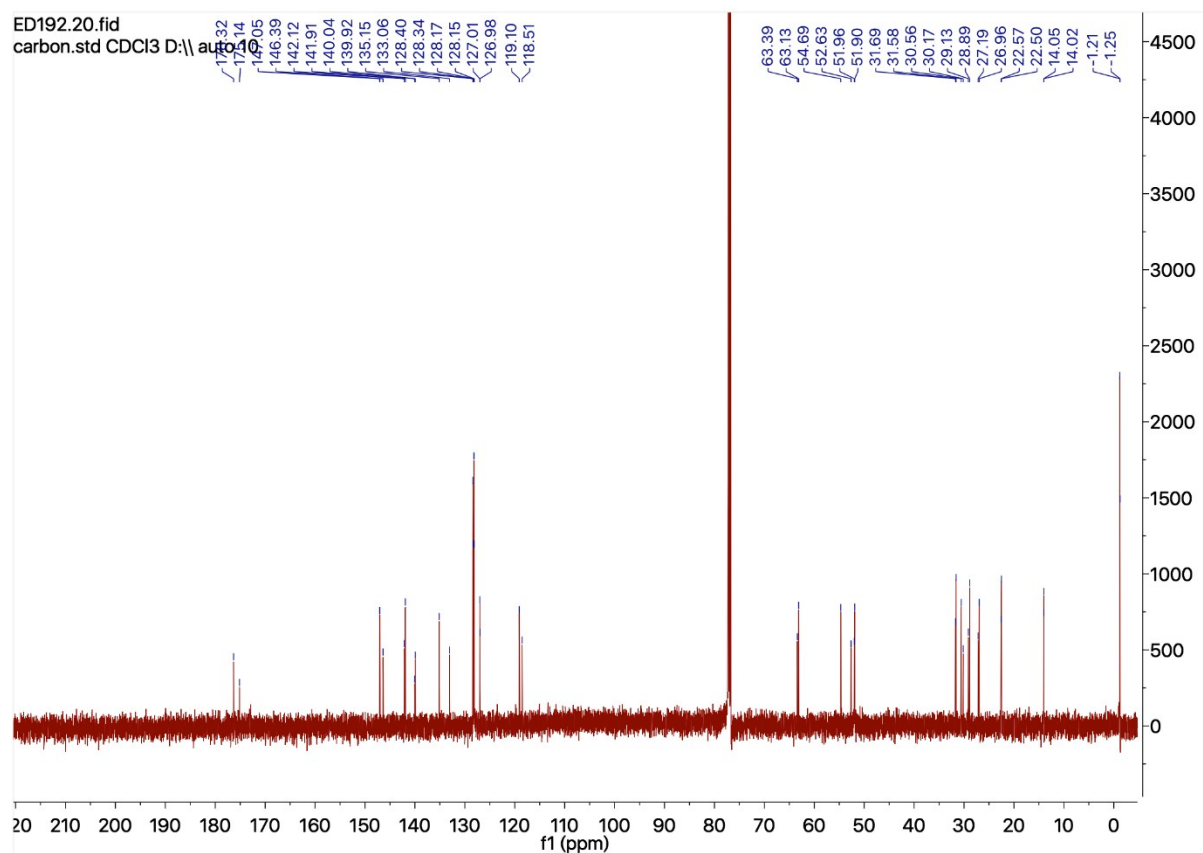
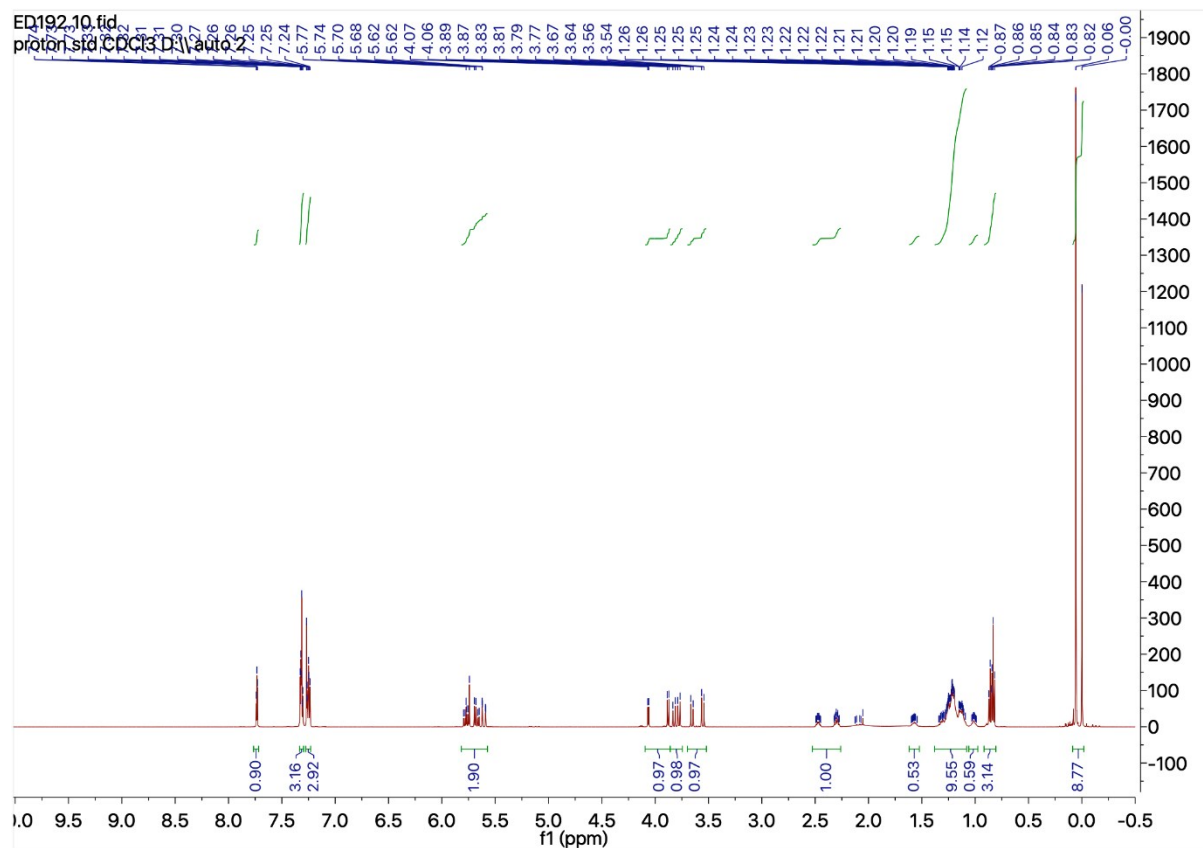
(E)-N-allyl-1-(4-bromophenyl)-2-(chloromethyl)-4-(trimethylsilyl)but-3-en-1-amine (19):



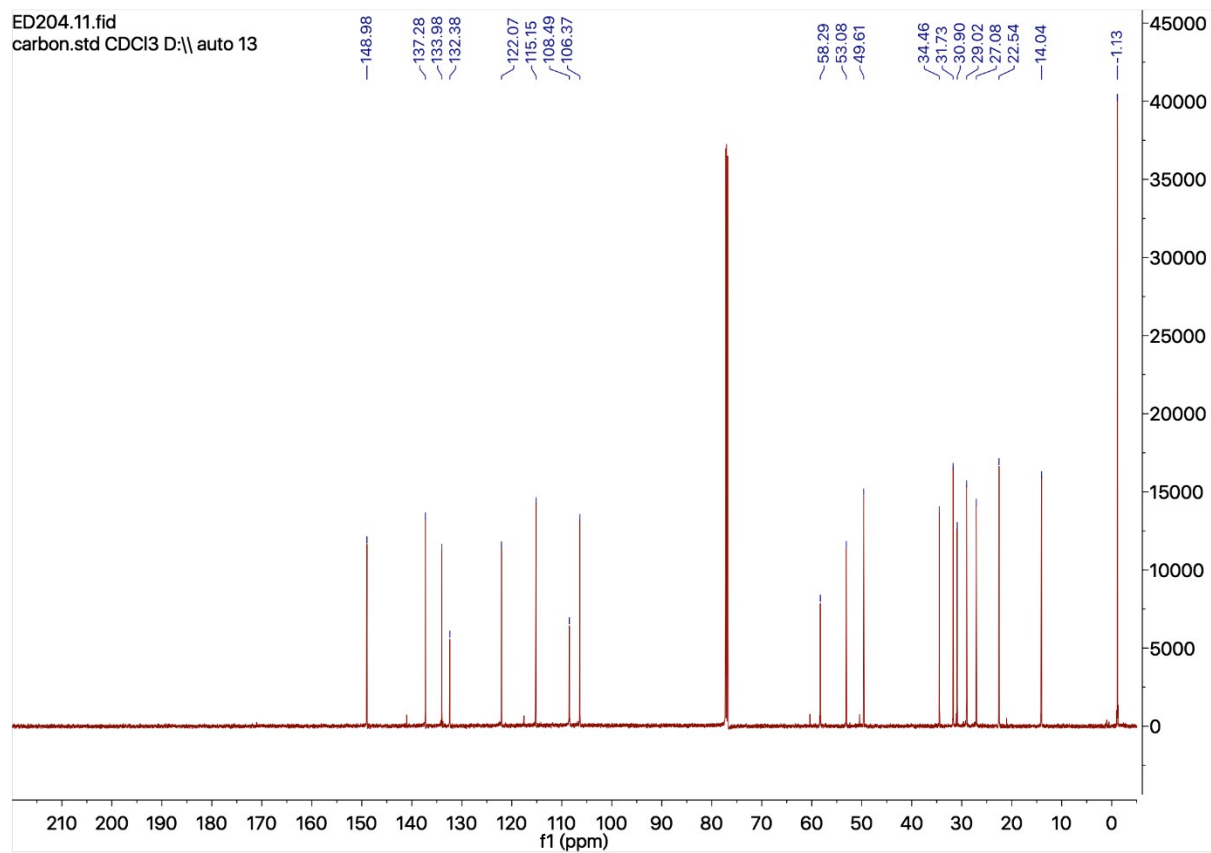
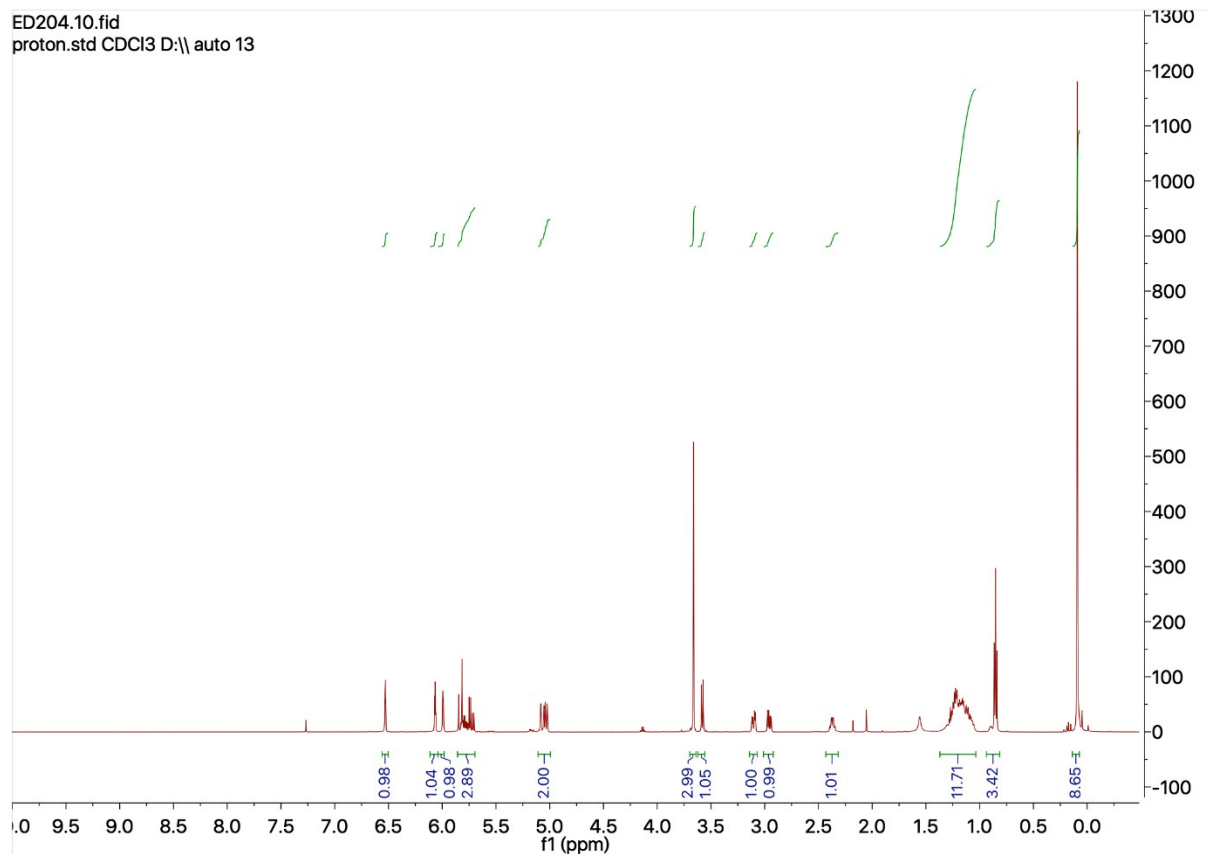
(E)-N-benzyl-1-(pyrimidin-5-yl)-2-(p-tolyl)-4-(trimethylsilyl)but-3-en-1-amine (20):



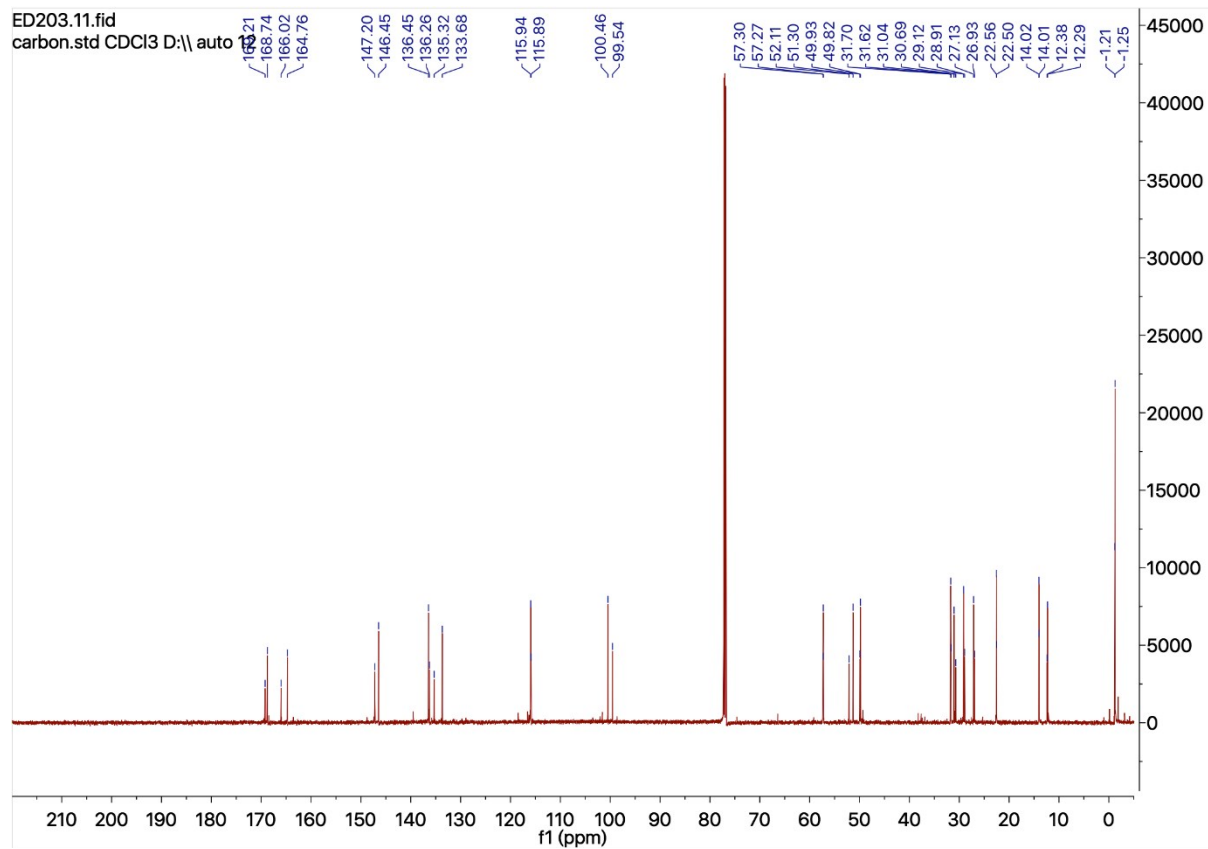
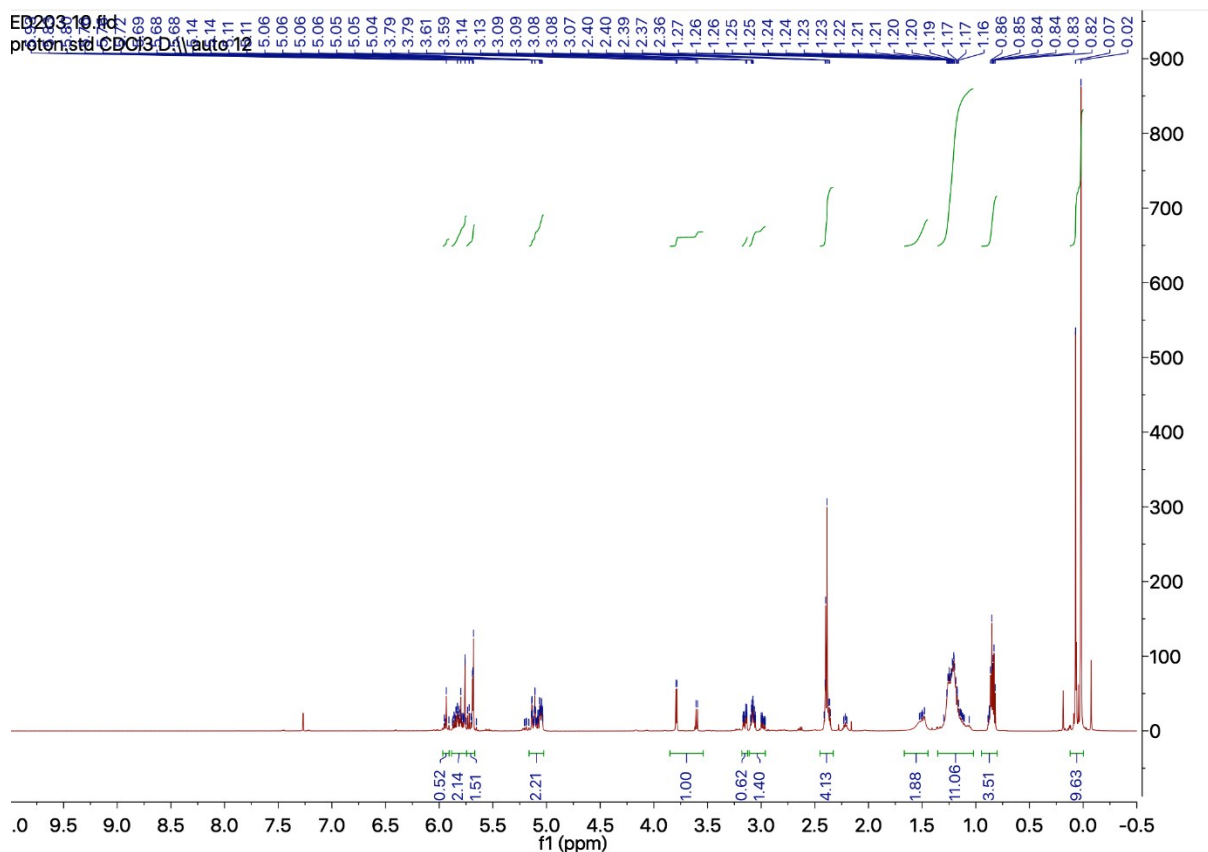
***N*-benzyl-1-(thiazol-2-yl)-2-((*E*)-2-(trimethylsilyl)vinyl)octan-1-amine (21):**



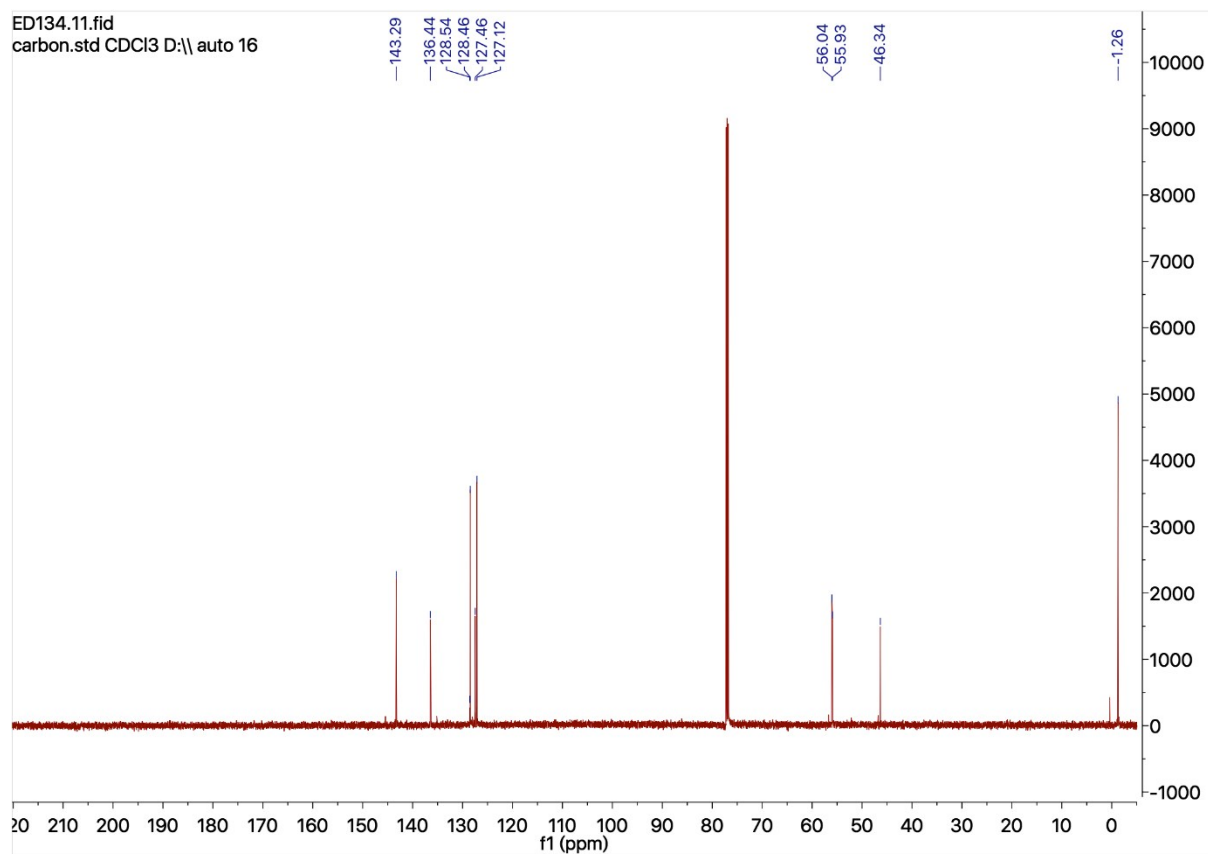
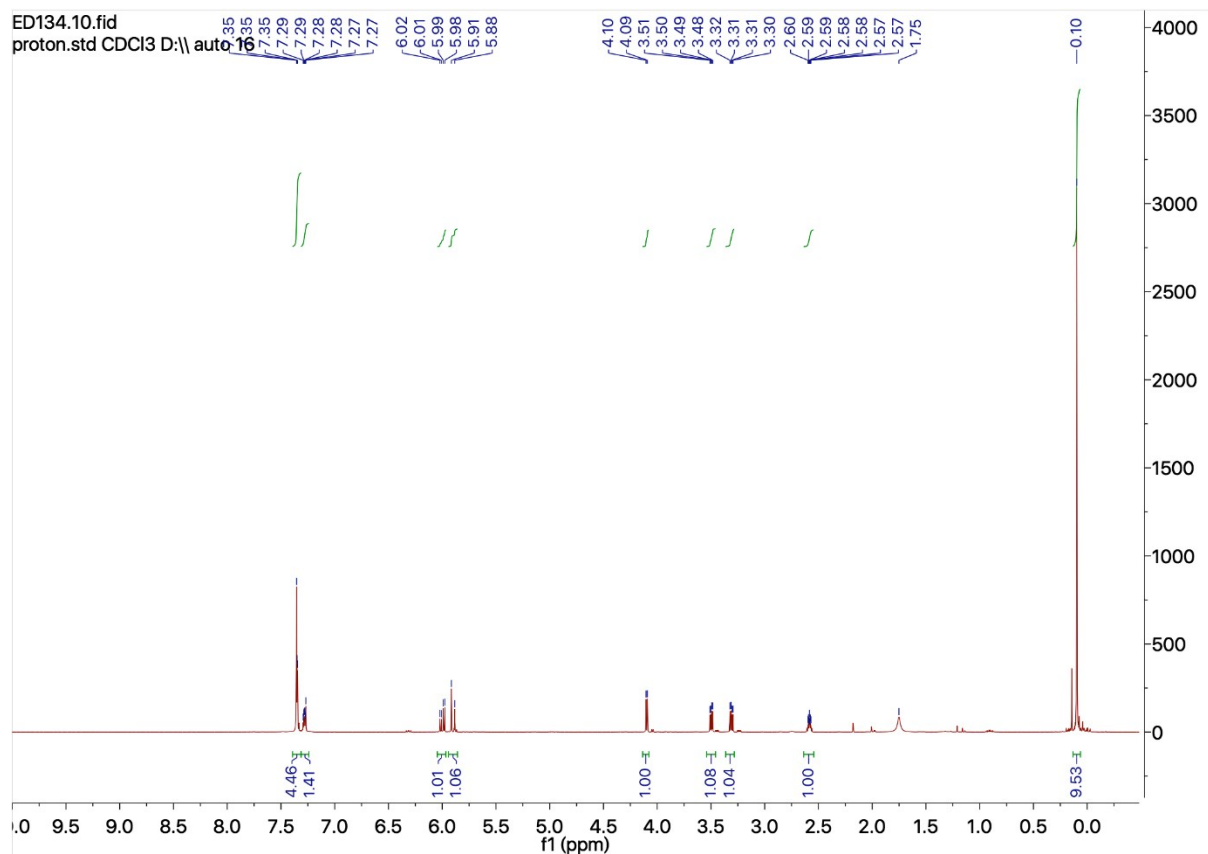
***N*-allyl-1-(1-methyl-1H-pyrrol-2-yl)-2-((*E*)-2-(trimethylsilyl)vinyl)octan-1-amine (22):**



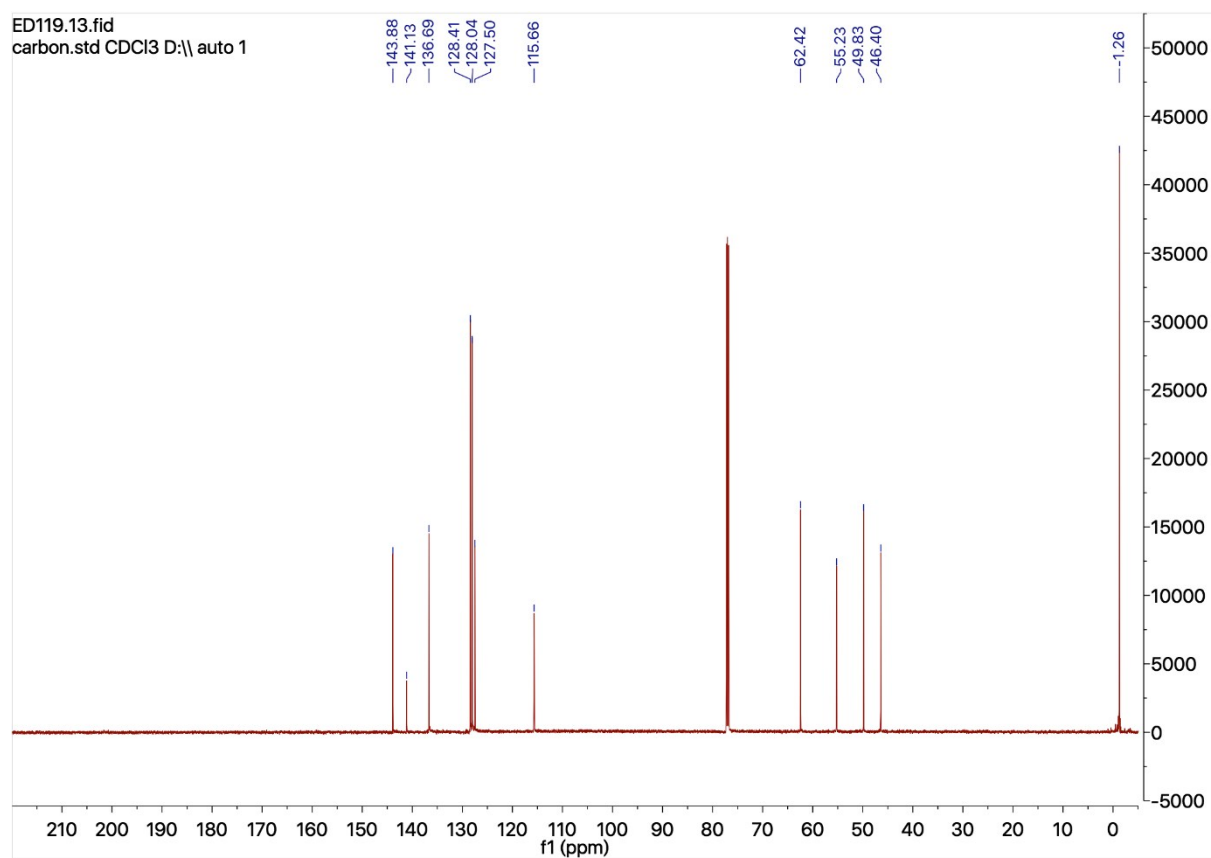
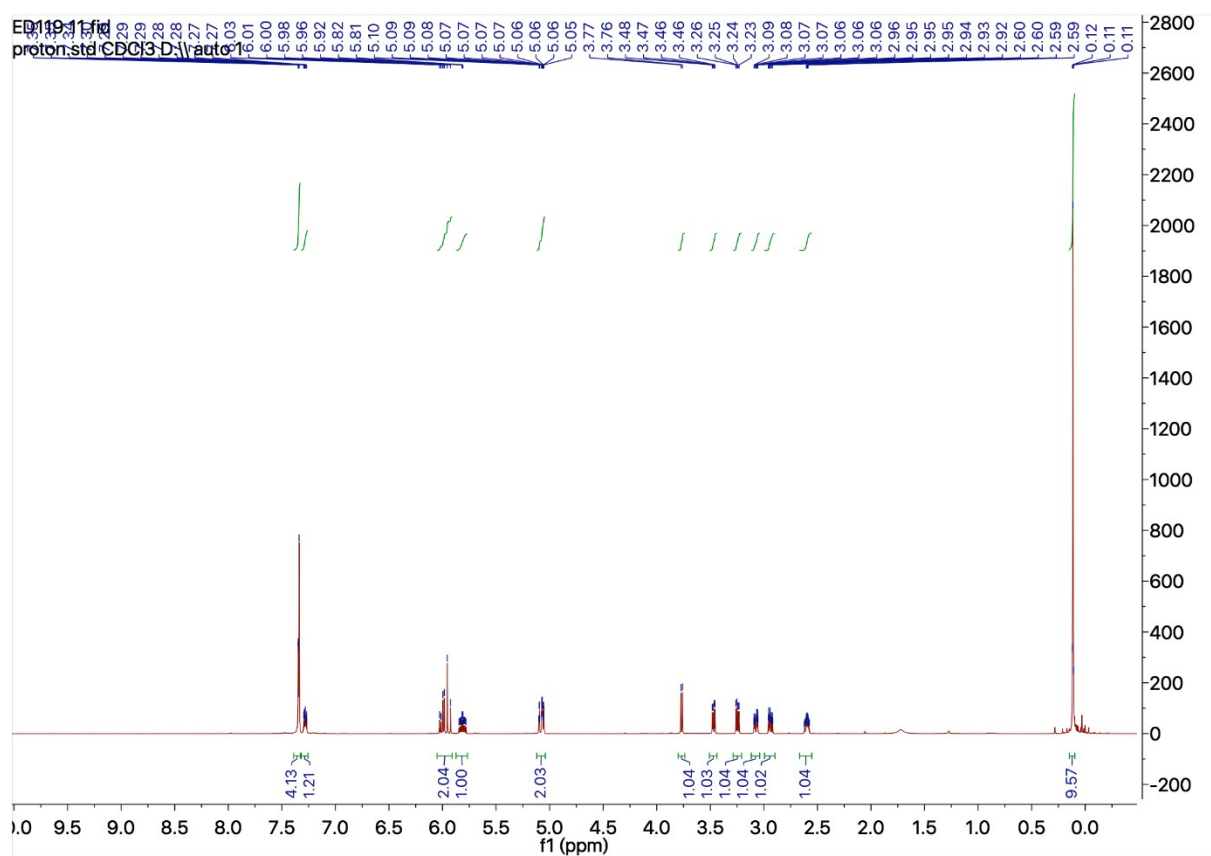
***N*-allyl-1-(5-methylisoxazol-3-yl)-2-((*E*)-2-(trimethylsilyl)vinyl)octan-1-amine (23):**



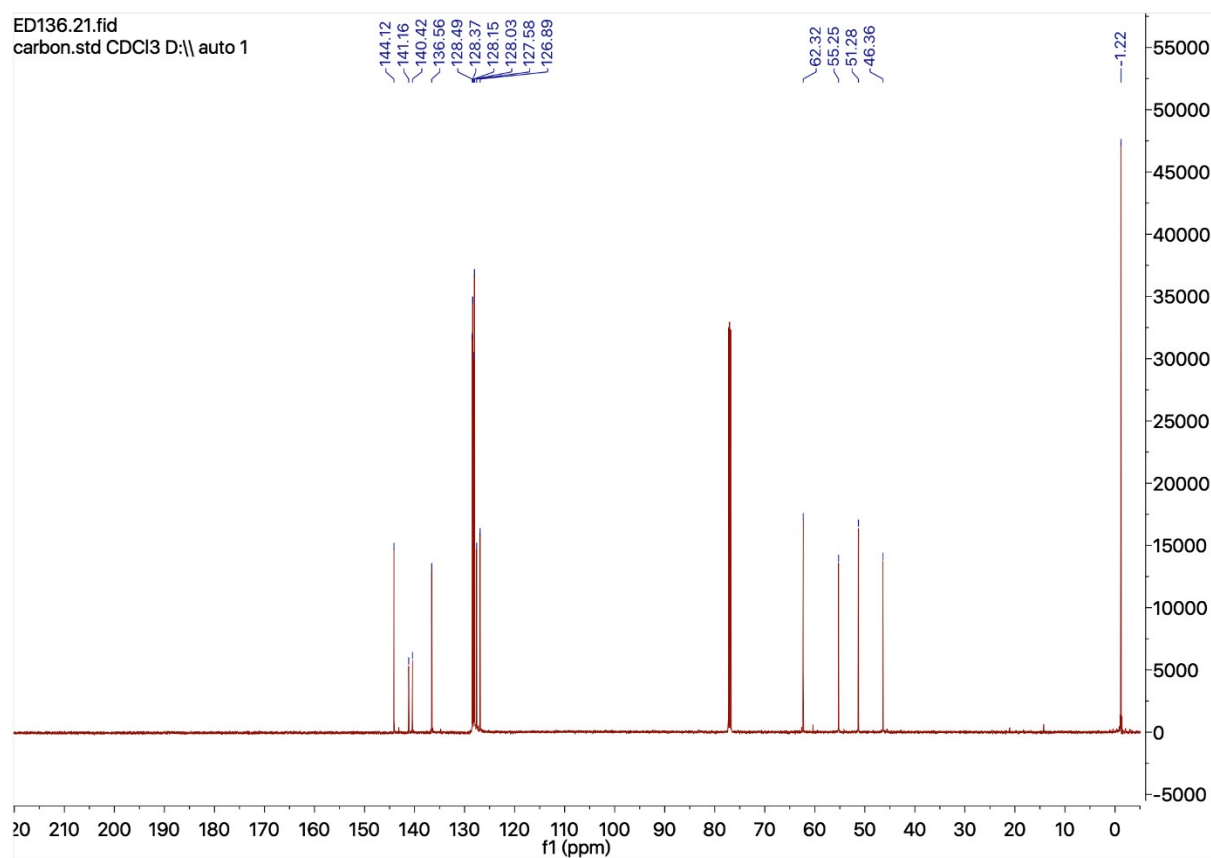
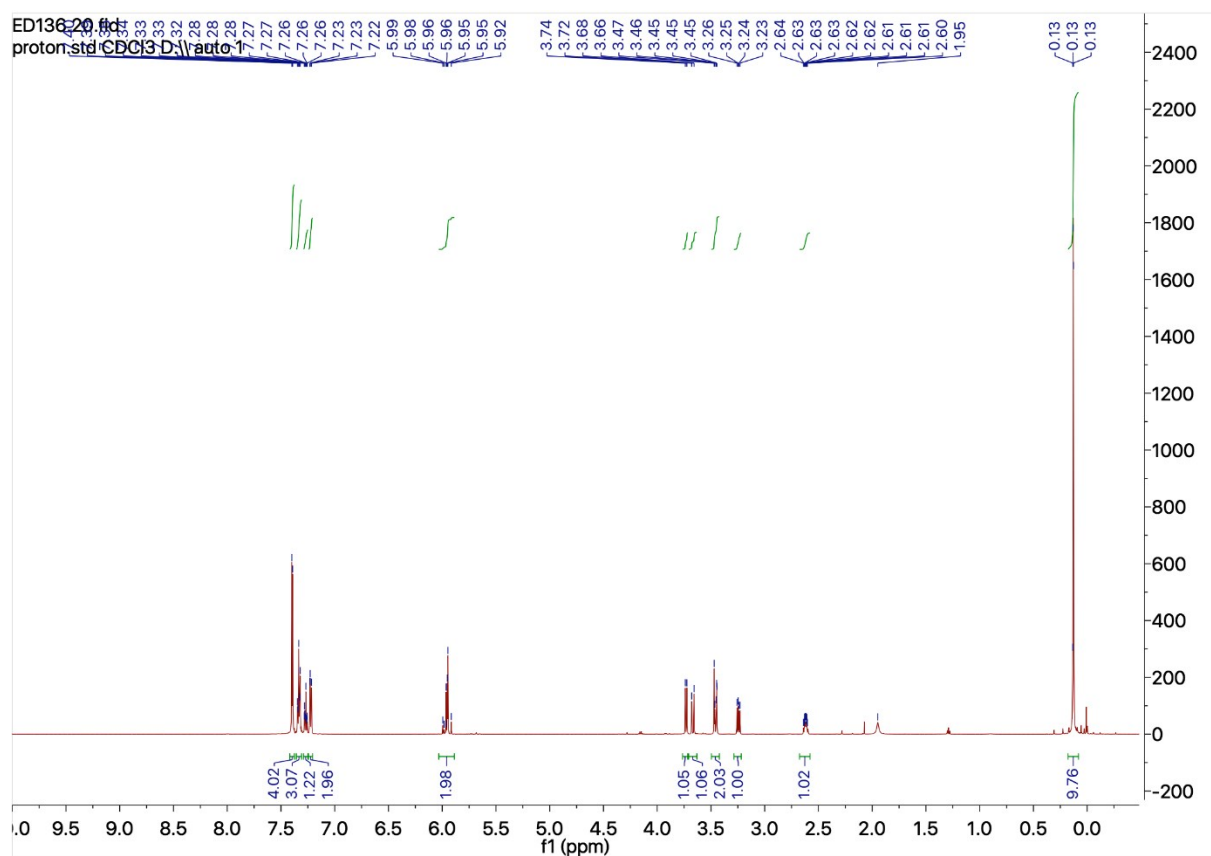
(E)-2-(chloromethyl)-1-phenyl-4-(trimethylsilyl)but-3-en-1-amine (24):



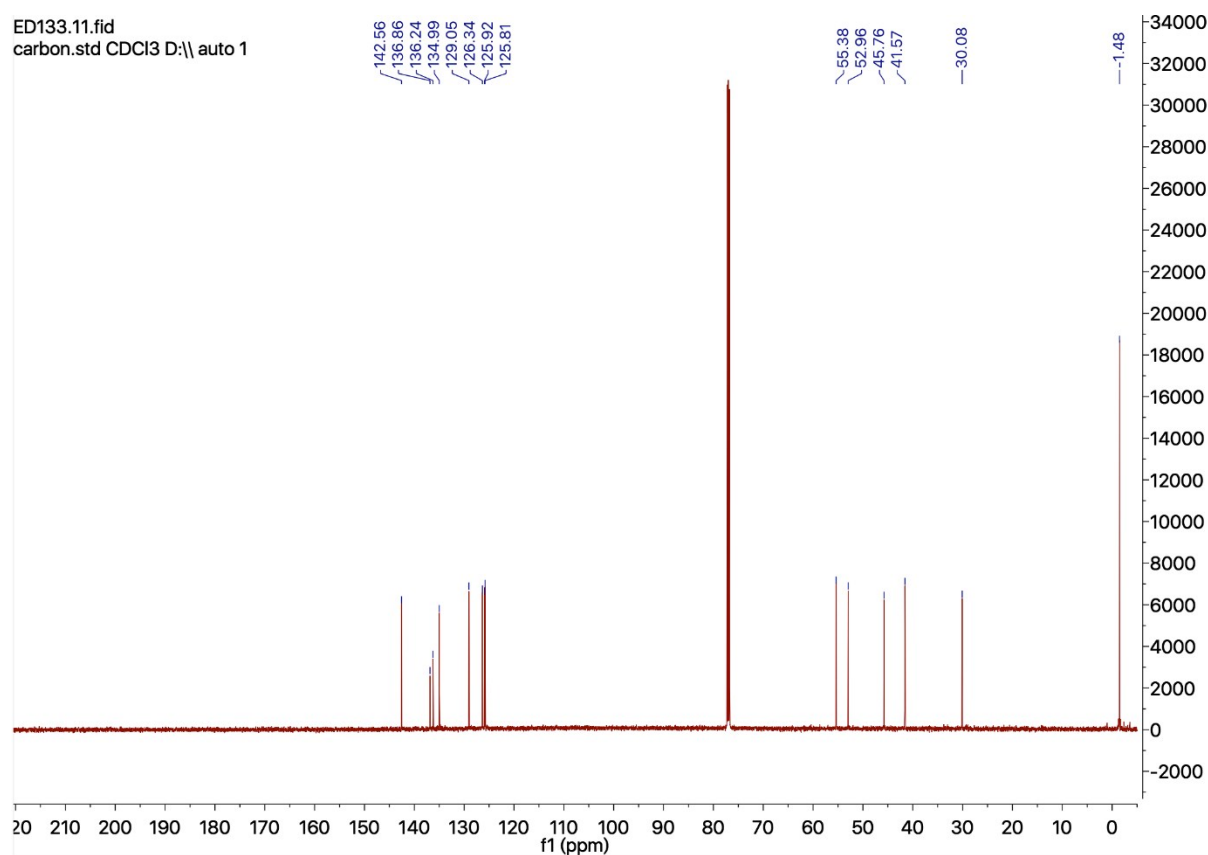
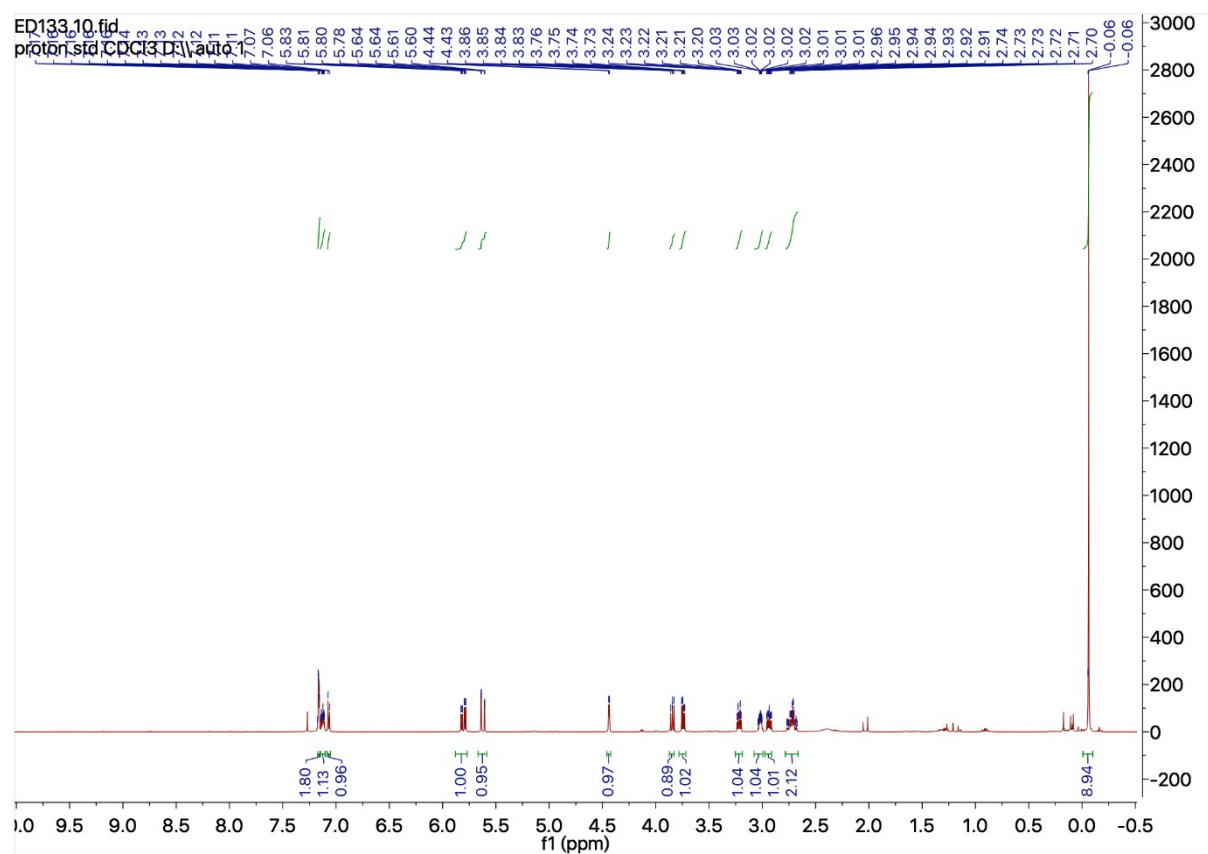
(E)-N-allyl-2-(chloromethyl)-1-phenyl-4-(trimethylsilyl)but-3-en-1-amine (25):



(E)-N-benzyl-2-(chloromethyl)-1-phenyl-4-(trimethylsilyl)but-3-en-1-amine (26):

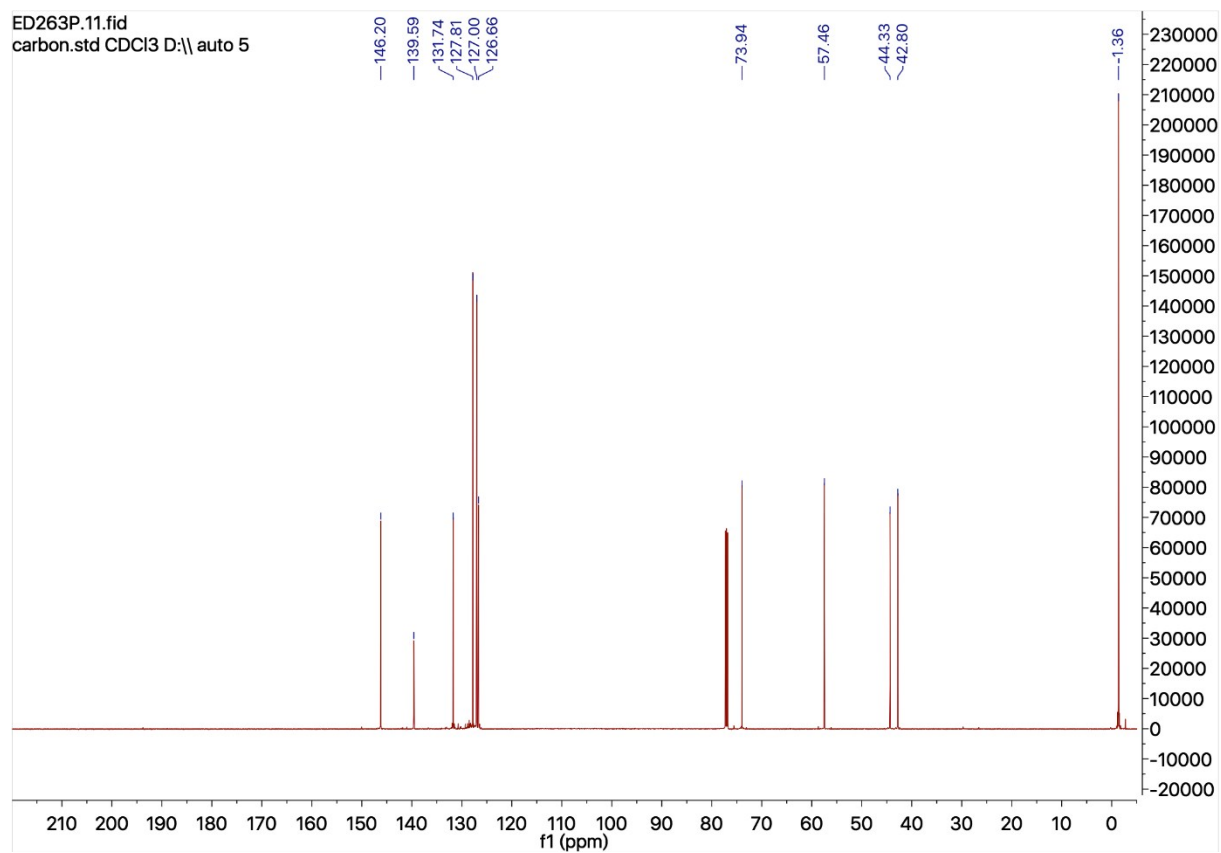
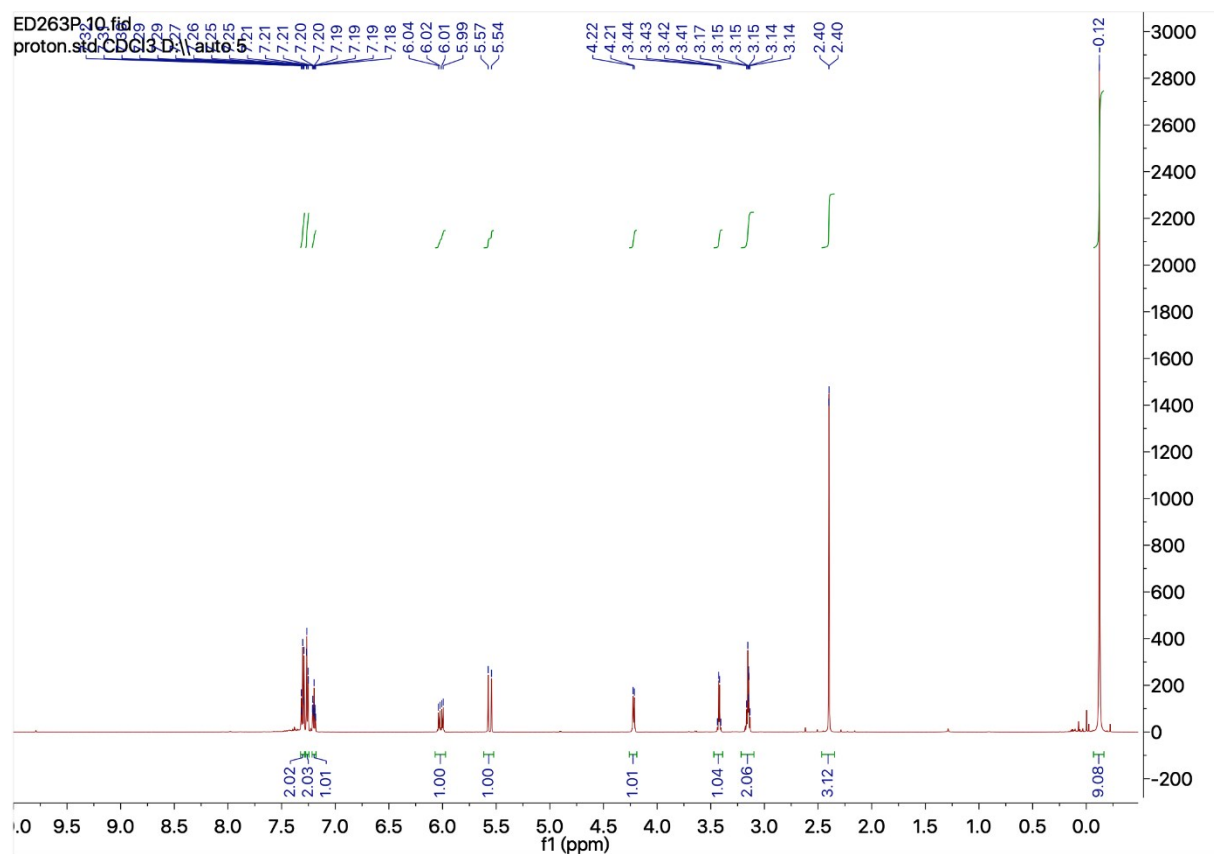


1-((*E*)-1-chloro-4-(trimethylsilyl)but-3-en-2-yl)-1,2,3,4-tetrahydroisoquinoline (27):

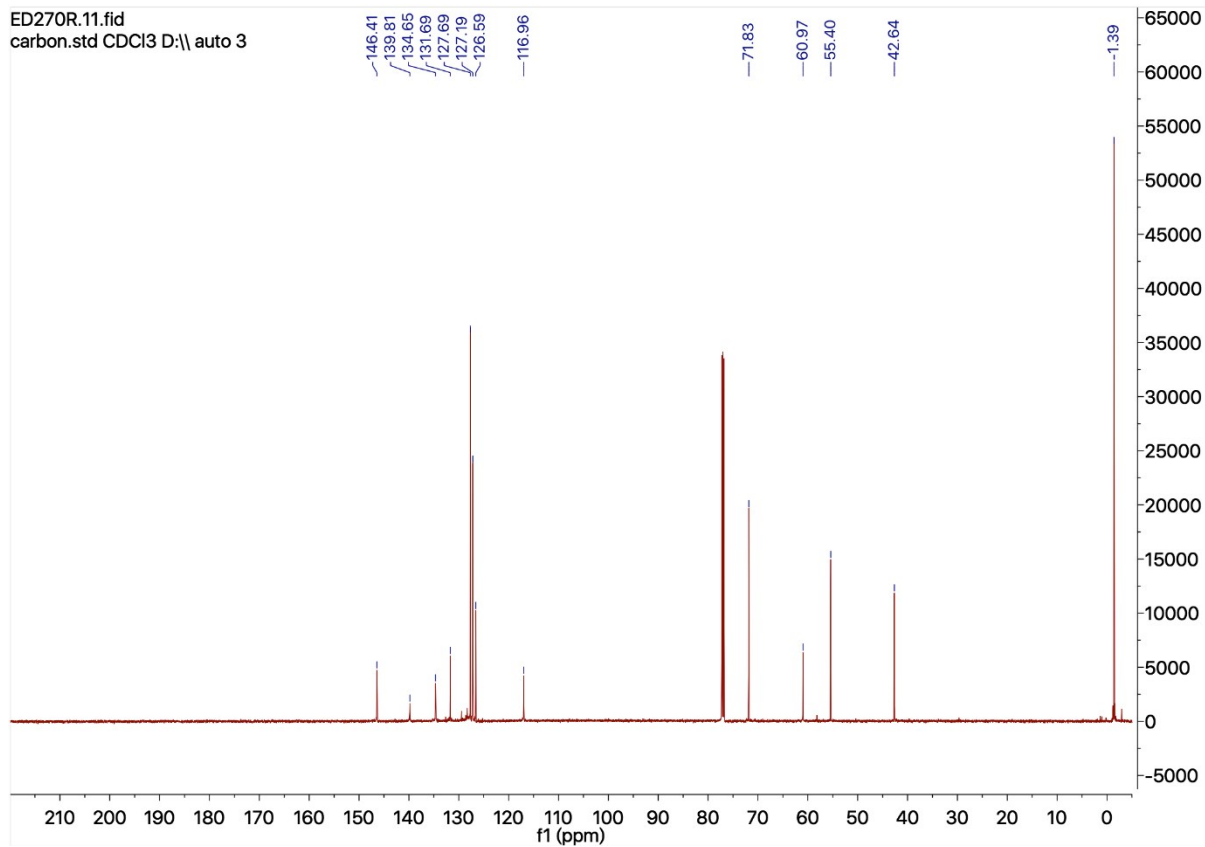
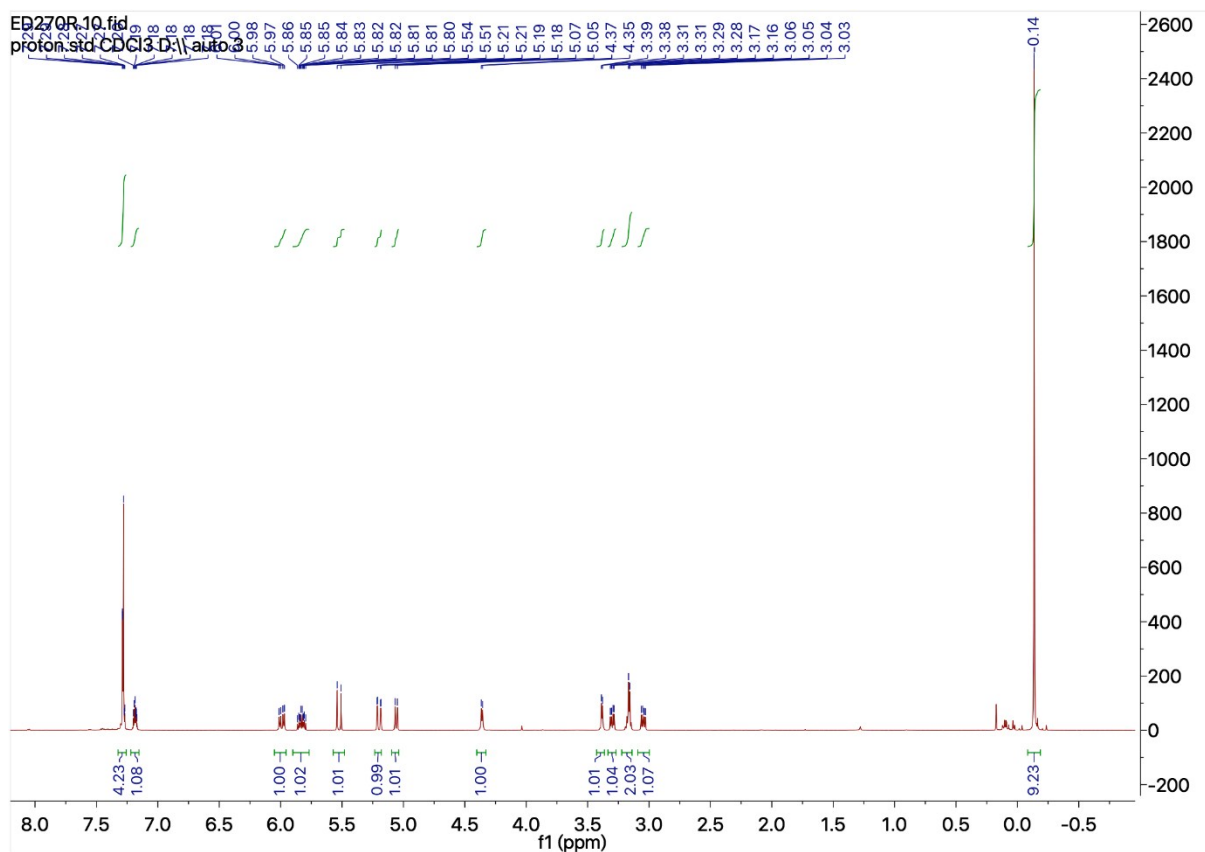


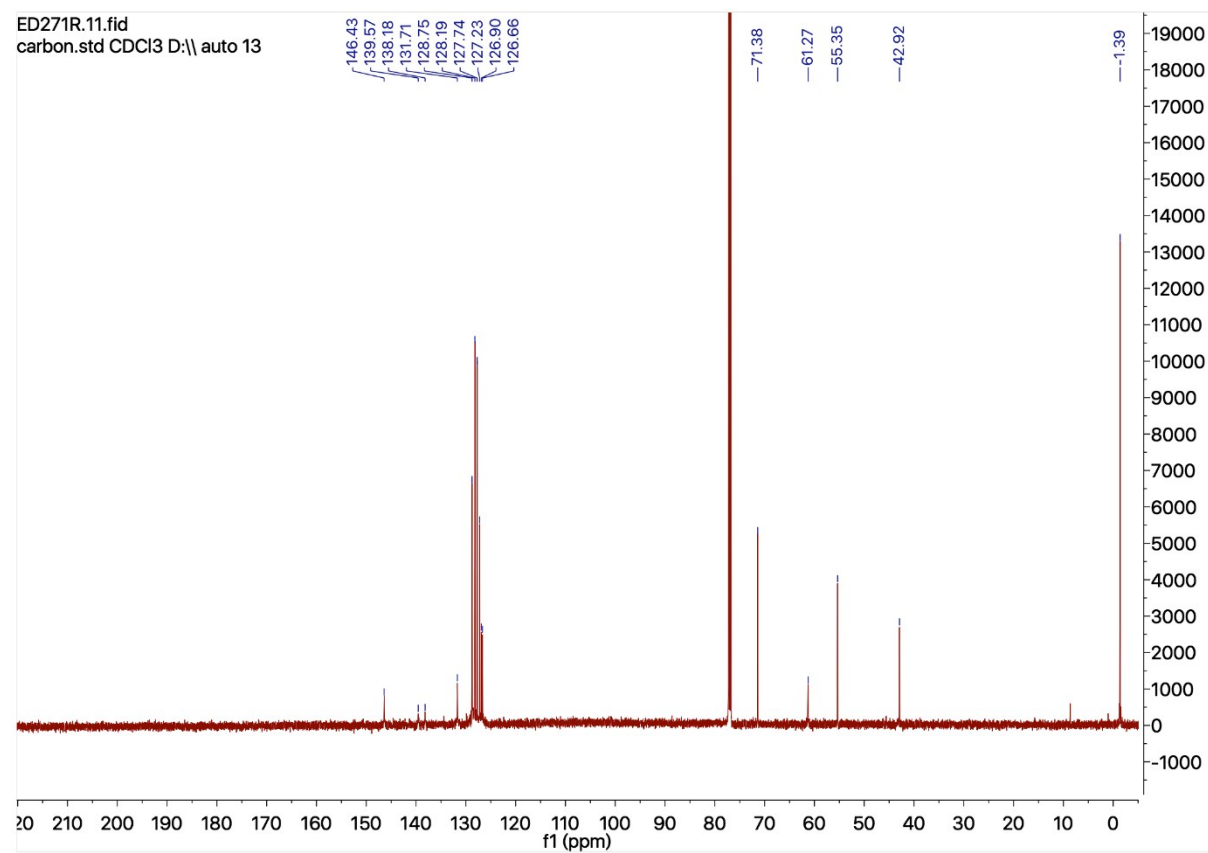
[illegible]

***N*-methyl-2-phenyl-3-(*E*-2-(trimethylsilyl)vinyl)azetidine (29):**



***N*-allyl-2-phenyl-3-(*E*-2-(trimethylsilyl)vinyl)azetidine (30):**





4. References

1. J. Wei, Y. Li and X. Jiang, *Org. Lett.*, 2016, **18**, 340–343.
2. R. E. Erickson, P. J. Andrus, J. C. Collins, M. L. Lungle and G. D. Mercer, *J. Org. Chem.*, 1969, **34**, 2961–2966.
3. K. A. Gonzalez, L. J. Wilson, W. Wu and G. H. Nancollas, *Bioorg. Med. Chem.*, 2002, **10**, 1991–1997.
4. J.-K. Xu, S.-J. Li, H.-Y. Wang, W.-C. Xu and S.-K. Tian, *Chem. Commun.*, 2017, **53**, 1708–1711.
5. T. N. Danks and S. E. Thomas, *J. Chem. Soc. Perkin Trans. 1*, 1990, 761.
6. A. R. Ickes, S. C. Ensign, A. K. Gupta and K. L. Hull, *J. Am. Chem. Soc.*, 2014, **136**, 11256–11259.
7. O. Cifuentes, R. Contreras, A. Laguna and O. Crespo, *Inorganica Chimica Acta*, 2011, **379**, 81–89.
8. L. Han, P. Xing and B. Jiang, *Org. Lett.*, 2014, **16**, 3428–3431.
9. T. K. Achar, S. Maiti and P. Mal, *RSC Adv.*, 2014, **4**, 12834–12839.
10. T. Nguyen, W. Chiu, X. Wang, M. O. Sattler and J. A. Love, *Org. Lett.*, 2016, **18**, 5492–5495.
11. A. R. Ickes, S. C. Ensign, A. K. Gupta and K. L. Hull, *J. Am. Chem. Soc.*, 2014, **136**, 11256–11259.
12. R.S. Vardanyan, G. G. Danagulyan, A. D. Mkrtchyan and V. J. Hruby, *Heterocycl. Commun.*, 2011, **17**, 129–133.
13. T. K. Olszewski and B. Boduszek, *Tetrahedron*, 2010, **66**, 8661–8666.
14. C. K. Govindan and G. Taylor, *J. Org. Chem.*, 1983, **48**, 5348–5354.
15. H. Tian, X. Yu, Q. Li, J. Wang and Q. Xu, *Adv. Synth. Catal.*, 2012, **354**, 2671–2677.
16. R. Parella and S. A. Babu, *J. Org. Chem.*, 2017, **82**, 6550–6567.