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Supporting Information

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Supporting Information for:

Amphoteric Amino Aldehydes Enable Rapid Assembly of Complex Amino Alcohols

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Experimental Procedures:

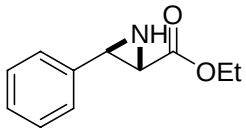
General Information: Anhydrous toluene and dimethylformamide (DMF) was purchased and used as received. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon. All other solvents were of reagent grade quality. Melting points were obtained on a MelTemp melting-point apparatus and are uncorrected.

Chromatography: Flash column chromatography was carried out using Silicycle 230-400 mesh silica gel and thin-layer chromatography (TLC) was performed on Macherey Nagel pre-coated glass backed TLC plates (SIL G/UV_{254}, 0.25 mm) and visualized using a UV lamp (254 nm) and Iodine stain.

Nuclear magnetic resonance spectra: ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Mercury 200, 300, or 400 MHz spectrometers. ^{1}H NMR spectra were referenced to TMS (0 ppm) and ^{13}C NMR spectra were referenced to $CDCl_3$ (77.23 ppm). Peak multiplicities are designated by the following abbreviations: s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet; ds, doublet of singlets; dd, doublet of doublets; ddd, doublet of doublet of doublets; bt, broad triplet; td, triplet of doublets; tdd, triplet of doublets of doublets.

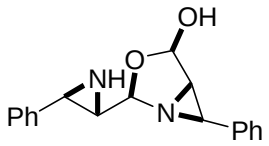
Mass Spectroscopy: High-resolution mass spectra were obtained on a VG 70-250S (double focusing) mass spectrometer at 70 eV or on an ABI/Sciex Qstar mass spectrometer with ESI source, MS/MS and accurate mass capabilities.

***trans*-3-Phenylaziridine-2-carboxylic acid ethyl ester**



To a mixture of 3-phenyloxirane-2-carboxylic acid ethyl ester (9.6 ml, 55 mmol) and 183 ml of EtOH in a flame-dried two-necked flask equipped with a water condenser and magnetic stirring rod was added NaN_3 (10.73 g, 165 mmol) and ammonium chloride (8.83 g, 165 mmol). The reaction mixture was brought to 65°C and stirred for 5 hours at which point GC analysis showed that the reaction was complete. The mixture was filtered and concentrated under reduced pressure. The crude ^{1}H NMR showed that the product of nucleophilic opening of the epoxide by azide was pure enough to carry over to the next step. In a flame-dried two-neck flask fitted with a water condenser and equipped with a magnetic stirring bar was added the product from above (12.93 g, 55 mmol) dissolved in 183 ml of acetonitrile. The reaction mixture was brought to 40°C, at which point PPh_3 (16g, 61 mmol) was added slow enough to avoid rapid evolution of N_2. The reaction was then brought to 83°C and stirred for 5 hours. The reaction mixture was then cooled and concentrated under reduced pressure. The crude mixture was then dissolved in 5% EtOAc in pentane and filtered. The filtrate was concentrated and subsequently dissolved in pentane and placed in the freezer overnight (-15°C). Any resulting precipitate that formed was filtered off and the filtrate was concentrated under reduced pressure and subjected to silica gel column chromatography (eluent 20% EtOAc in hexanes) to yield a pale yellow oil in 61% over two steps. ^{1}H NMR (200 MHz. $CDCl_3$) δ: 7.36-7.25 (m, 5H), 4.25 (qd, *J* = 7 Hz, 1.2 Hz, 2H), 3.25 (s, 1H), 2.58 (s, 1H), 1.89 (bs, 1H), 1.31 (t, *J* = 7 Hz, 3H) ppm. ^{13}C NMR (75 MHz. $CDCl_3$) δ: 171.6, 137.8, 128.3, 127.6, 126.1, 61.6, 40.2, 39.3, 14.0 ppm.

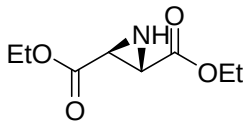
6-Phenyl-2-(3-phenylaziridin-2-yl)-3-oxa-1-azabicyclo[3.1.0]hexan-4-ol



In a flame dried 100 ml Schlenk tube equipped with a magnetic stirring bar was placed **1a** (4.78 g, 25 mmol) in 10 ml of toluene. The solution was cooled to -78°C and a 1.5M solution of DIBAL in toluene (33.3 ml, 50 mmol) was added dropwise along the wall of the vessel. Once the addition was complete, the reaction was allowed to stir at -78°C for another hour at which point ESI MS showed the disappearance of starting material. MeOH was slowly added along the wall of the vessel at -78°C. The reaction mixture was then allowed to stir for 30 minutes while warming to room temperature. Saturated Na_2SO_4 was then added and the solution was allowed to stir for another 15 minutes. The reaction was then filtered and water and ether was added. The organic later was extracted from the partition three times, washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting white solid may be recrystallized from EtOAc or MeOH to afford the title compound in 83% yield (3.05 g) as a white solid. ^{1}H NMR ($CDCl_3$, 200MHz) δ: 7.83 (d, *J* = 11.6 Hz, 1H), 7.40 – 7.10 (m, 10H), 4.51 (d, *J* = 11.8 Hz, 1H), 5.27 (s, 1H), 3.08 (dd, *J* = 7.4 Hz, 3.6 Hz, 1H), 2.90 – 2.80 (m, 2H), 2.49 (d, *J* = 3 Hz, 1H), 1.25 (bt, *J* = 7 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100MHz) δ: 137.4, 137.3, 128.9, 128.4, 127.9, 127.4, 126.3, 125.6, 96.8,

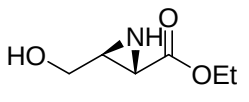
94.7, 53.1, 40.8, 36.3 ppm. HRMS (ESI) $[M+H]^+$ calcd. For $C_{18}H_{19}N_2O_2$ 294.1441 found 294.1444.

(2S,3S)-diethyl aziridine-2,3-dicarboxylate



In a round bottom flask equipped with a Teflon coated magnetic stirring bar and pressure equalizing addition funnel was placed L-diethyl-tartrate (17.73 g, 86 mmol). The reaction was cooled to 0°C and then $SOCl_2$ (7.3 ml, 100 mmol) was added dropwise through the addition funnel over a period of 15 minutes. After the addition was complete, 20 drops of anhydrous DMF was added to the reaction mixture and the vessel was first allowed to warm to room temperature, and then it was heated at 50°C for 30 minutes. The reaction was allowed to cool back to room temperature and N_2 was bubbled through for 1 hour in order to remove excess $SOCl_2$ and liberated acidic components. The mixture was then concentrated using rotary evaporator at 50°C to remove residual $SOCl_2$, then further concentrated under high vacuum to afford the cyclic sulfite as a pale yellow oil. The cyclic sulfite (21.67g, 86 mmol) was then dissolved in 50 ml of anhydrous DMF. NaN_3 (16.77g, 258 mmol) was then added to the solution and the reaction was allowed to stir for 24 hours. 50 ml of CH_2Cl_2 and 60 ml of water were then added to the reaction, and stirred for 2 hours. The aqueous phase was extracted three times with CH_2Cl_2 and the collected organic phases were dried over Na_2SO_4 and concentrated under reduced pressure to afford the azido alcohol in 95% yield (18.87 g, 81.7 mmol) over two steps as a yellow oil, which was pure by NMR and carried over to the next step. The azido alcohol (18.87 g, 81.7 mmol) was dissolved into 400 ml of anhydrous DMF and cooled to 0°C. PPh_3 (22.5g, 85.79 mmol) was added in portions over a period of 30 minutes. The reaction vessel was then allowed to warm to room temperature and stirred at this temperature of 90 minutes. The reaction vessel was then warmed to 85°C and stirred until completed by TLC (3:1 Et_2O/hexanes, R_f = 0.34). Water and Et_2O were added to the reaction mixture and the mixture was extracted 5 times using Et_2O. The combined organic layers were dried over Na_2SO_4, filtered and then concentrated under reduced pressure. The crude product was then purified by flash column chromatography (silica gel; gradient 9:1 – 7:3 hexanes/EtOAc) to afford the title compound as a pale yellow oil in 79% yield (12.1 g). ^{1}H NMR ($CDCl_3$, 400MHz) δ: 4.30 (m, 4H), 2.87 (dd, J = 9.2 Hz, 3.2 Hz, 2H), 1.82 (bt, J = 9.2 Hz, 1H), 1.31 (dt, J = 10.4 Hz, 7.2 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 50MHz) δ: 170.6, 168.9, 62.4, 61.8, 36.3, 35.5, 14.2 ppm.

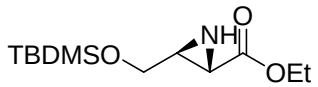
(2S,3S)-ethyl 3-(hydroxymethyl)aziridine-2-carboxylate



In a round bottom flask equipped with a magnetic stirring bar and a septum was placed (*S,S*) diethyl aziridine-2,3-dicarboxylate (1.87g, 10 mmol) dissolved into 30 ml of EtOH. The vessel was cooled to 0°C and $NaBH_4$ (302.6 mg, 8 mmol) was added slowly. The reaction mixture was allowed to stir at 0°C until the reaction was complete according to TLC (EtOAc, R_f = 0.66), which was approximately 2 hours. The reaction was quenched by the addition of pH 7 phosphate buffer, and extracted three times with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue

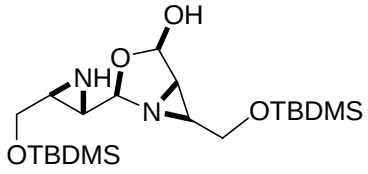
was purified by flash column chromatography (silica gel; gradient 8:2 EtOAc/hexanes – 100% EtOAc) to afford the title compound in 84% yield as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 200MHz) δ: 4.22 (q, *J* = 7.0 Hz, 2H), 3.82 (dd, *J* = 12.4 Hz, 2.8 Hz, 1H), 3.48 (dd, *J* =12 Hz, 4.8 Hz, 1H), 2.46 (m, 2H), 1.50 (bs, 1H), 1.31 (t, *J* = 7 .0 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 50MHz) δ: 172.2, 62.0, 61.5, 39.8, 32.7, 14.3 ppm. HRMS (ESI) $[M+H]^+$ calcd. for $C_6H_{12}NO_3$ 146.0817, found 146.0820.

(2S,3S)-ethyl 3-((tert-butyldimethylsilyloxy)methyl)aziridine-2-carboxylate



In a flame dried flask equipped with a magnetic stirring rod and a rubber septum with a N_2 inlet was added (*S,S*) 3-hydroxymethylaziridine-2-carboxylic acid ethyl ester (296 mg, 2.04 mmol) and 12 ml of CH_2Cl_2. The reaction vessel was cooled to 0^{o}C then TBDMSCl (377 mg, 2.50 mmol) and DMAP (623 mg, 5.1 mmol) was added. The reaction was allowed to stir for 1 hour at 0^{o}C then at room temperature until the reaction was completed according to TLC (R_f = 0.65; 7:3 hexanes/EtOAc). The reaction was diluted with CH_2Cl_2 then water was added. The organic layer was extracted three times, and the combined organic layers were washed first with saturated $NaHCO_3$, then water, then brine and dried over solid Na_2SO_4. The mixture was filtered and dried under reduced pressure to afford a pale yellow oil, which was subjected to flash column chromatography (silica gel; 8:2 hexanes/EtOAc) to afford the title compound as a thick colourless oil in 99% yield. ^{1}H NMR ($CDCl_3$, 400MHz) δ: 4.21 (q, *J* = 3.6 Hz, 2H), 3.66 (dd, *J* = 11.2 Hz, 5.2 Hz, 1H), 3.56 (dd, 10.8 Hz, 4.8 Hz, 1H), 2.42 (m, 2H), 1.37 (bt, 1H), 1.29 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100MHz) δ: 172.6, 64.8, 61.7, 40.3, 33.7, 26.1, 18.5, 14.4, -5.1 ppm. HRMS (ESI) $[M+H]^+$ calcd. for $C_{12}H_{25}NO_3Si$ 260.1676, found 260.1675.

(2R,4R,5S,6S)-6-((tert-butyldimethylsilyloxy)methyl)-2-((2S,3S)-3-((tert-butyldimethylsilyloxy)methyl)aziridin-2-yl)-3-oxa-1-aza-bicyclo[3.1.0]hexan-4-ol



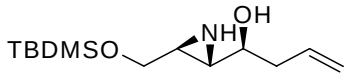
In a flame dried 100 ml Schlenk tube equipped with a magnetic stirring bar was placed **1e** (400 mg, 1.54 mmol) in 6 ml of toluene. The solution was cooled to -78^{o}C and a 1.5M solution of DIBAL in toluene (2.2 ml, 3.3 mmol) was added dropwise along the wall of the vessel. Once the addition was complete, the reaction was allowed to stir at -78^{o}C for another hour at which point TLC showed the lack of starting material. MeOH was slowly added along the wall of the vessel at -78^{o}C. The reaction mixture was then allowed to stir for 30 minutes while warming to room temperature. Saturated Na_2SO_4 was then added and the solution was allowed to stir for another 15 minutes. The reaction was then filtered and water and ether were added. The organic layer was extracted three times, washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting clear oil was pure by NMR analysis and was used in subsequent transformations. TLC (7:3, hexanes/EtOAc R_f = 0-0.55 streaking. ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.20 – 8.05 (bs, 1H) 5.29 (bs, 1H),

4.95 (s, 1H), 3.86 – 3.85 (m, 2H), 3.65 (dd, *J* = 11.2 Hz, 6 Hz, 1H), 3.56 (dd, *J* = 11.6 Hz, 5.6 Hz, 1H), 2.53 (d, *J* = 2.8 Hz, 1H), 2.39 (bs, 1H), 2.13 (bs, 1H), 1.65 (sextet, *J* = 2.8 Hz), 1.20 (bs, 1H), 0.89 (s, 9H), 0.87 (s, 9H), 0.07 (ds, 6 H), 0.04 (ds, 6H) ppm ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 96.5, 94.7, 64.0, 58.4, 48.5, 40.3, 34.0, 33.5, 26.1, 26.0, 18.6, 18.5, -4.9, -5.0, -5.3, -5.4 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{20}H_{43}N_2O_4Si_2$ 431.2755, found 431.2749.

General Procedure for aziridine alcohol synthesis:

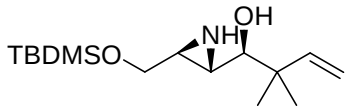
In a vial equipped with a stirring-bar and a screw-cap lid was dissolved aziridine aldehyde (0.1 mmol) in 1 ml of a 1:1 (v/v) mixture of H_2O and THF. Indium (0.22 mmol) then allyl bromide (0.22 mmol) was added and the reaction mixture was stirred for one hour. Water and EtOAc were then added to the reaction and the mixture was extracted 3 times with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and then concentrated under reduced pressure. The crude product was then purified using flash column chromatography on silica eluting with 100% EtOAc.

(S)-1-((2S,3S)-3-((tert-butyldimethylsilyloxy)methyl)aziridin-2-yl)but-3-en-1-ol



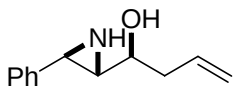
R_f = 0.21; 40 % EtOAc in hexanes. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 5.86 (tdd, *J* = 17.6 Hz, 10.4 Hz, 7.2 Hz, 1H), 5.17-5.04 (m, 2H), 3.79 (d, *J* = 2.4 Hz, 2H), 3.33 (dd, *J* = 12.4 Hz, 6.8 Hz, 1H), 2.35 (m, 2H), 2.05 (dd, *J* = 6.4 Hz, 3.2 Hz, 1H), 1.98 (m, 1H), 1.40-1.00 (bs, 2H), 0.88 (s, 9H), 0.05 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.6, 117.6, 71.7, 60.4, 40.5, 37.2, 36.1, 26.0, 18.5, -5.3 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{13}H_{28}NO_2Si$ 257.1889, found 257.1892.

(S)-1-((2S,3S)-3-((tert-butyldimethylsilyloxy)methyl)aziridin-2-yl)-2,2-dimethylbut-3-en-1-ol



R_f = 0.34; 50 % EtOAc in hexanes. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 5.93 (dd, *J* = 17.2 Hz, 10.8 Hz, 1H), 5.09-5.04 (m, 1H), 5.03 (dd, *J* = 9.2 Hz, 1.2 Hz, 1H), 3.78 (d, *J* = 3.2 Hz, 2H), 3.00 (d, *J* = 6.4 Hz, 1H), 2.09 (dd, *J* = 6.0 Hz, 3.2 Hz, 1H), 1.95-1.92 (m, 1H), 1.08 (s, 6H), 0.87 (s, 9H), 0.05 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ:145.2, 112.7, 77.7, 60.4, 41.6, 36.9, 33.8, 26.0, 23.5, 22.8, 18.4, -5.3 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{15}H_{32}NO_2Si$ 286.2203, found 286.2196.

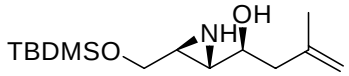
1-(3-phenylaziridin-2-yl)but-3-en-1-ol



R_f = 0.15; EtOAc. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 7.38-7.18 (m, 5H), 5.55 (m, 1H), 5.20-5.10 (m, 2H), 3.61 (dd, *J* = 6.4 Hz, 12 Hz, 1H), 2.91 (d, *J* = 3.2 Hz, 1H), 2.41 (m, 2H), 2.30 (bs, 1H), 2.20-1.40 (bs,

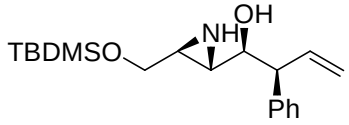
2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.4, 134.2, 128.8, 127.5, 125.9, 118.3, 71.1, 45.0, 40.7, 37.4 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{12}H_{16}NO$ 190.1232, found 190.1234.

(S)-1-((2S,3S)-3-((tert-butyldimethylsilyloxy)methyl)aziridin-2-yl)-3-methylbut-3-en-1-ol



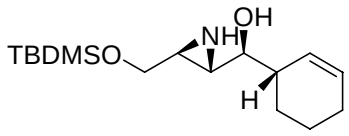
R_f = 0.24; 50 % EtOAc in hexanes. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 4.85 (s, 1H), 4.80 (s, 1H), 3.79 (m, 2H), 3.50 (dd, *J* = 13.6 Hz, 6.0 Hz, 1H), 2.30 (m, 2H), 2.07-2.01 (m, 1H), 2.01-1.98 (m, 1H), 1.77 (s, 3H), 0.88 (s, 9H), 0.05 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.4, 113.4, 69.9, 44.4, 36.0, 26.0, 22.8, 18.5, -5.2 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{14}H_{30}NO_2Si$ 272.2044, found 272.2040.

(1S,2S)-1-((2S,3S)-3-((tert-butyldimethylsilyloxy)methyl)aziridin-2-yl)-2-phenylbut-3-en-1-ol



R_f = 0.24; 50 % EtOAc in hexanes. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 6.09 (ddd, *J* = 16.8, 10.4 Hz, 8.8 Hz, 1H), 5.20-5.11 (m, 2H), 3.78 (dd, *J* = 10.8 Hz, 2.4 Hz, 1H), 3. 71 (dd, *J* = 10.8 Hz, 2.4 Hz, 2H), 3.65 (dd, *J* = 7.6 Hz, 5.6 Hz, 1H), 3.51 (t, *J* = 8.0 Hz, 1H), 2.14 (dd, *J* = 5.6 Hz, 3.2 Hz, 1H), 1.95 (dd, *J* = 5.6 Hz, 2.4 Hz, 1H), 1.80-1.30 (bs, 2H), 0.87 (s, 9H), 0.03 (s, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.0, 138.0, 128.9, 128.6, 127.0, 117.1, 74.2, 56.5, 36.4, 26.0, 18.4, -5.2 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{19}H_{32}NO_2Si$ 334.2203, found 334.2210.

(S)-((2S,3S)-3-((tert-butyldimethylsilyloxy)methyl)aziridin-2-yl)((S)-cyclohex-2-enyl)methanol



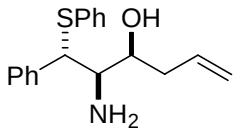
R_f = 0.31; 50 % EtOAc in hexanes. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 5.80 (s, 2H), 3.80 (d, *J* = 2.8 Hz, 2H), 3.13 (t, *J* = 6.0 Hz, 1H), 2.39-2.29 (m, 1H), 2.10 (dd, *J* = 5.6 Hz, 3.2 Hz, 1H), 2.03-1.04 (m, 2H), 1.87-1.74 (m, 2H), 1.60-1.34 (m, 3H), 0.88 (s, 9H), 0.05 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 129.0, 128.0, 75.2, 55.3, 41.3, 46.3, 26.0, 25.5, 25.4, 21.9, 18.5, -5.2 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{16}H_{32}NO_2Si$ 298.2202, found 298.2207.

General Procedure for thio amino alcohol synthesis:

In a vial equipped with a stirring-bar and a screw-cap lid was dissolved aziridine aldehyde (0.1 mmol) in 1 ml of a 1:1 (v/v) mixture of H_2O and THF (0.1M solution). Indium (0.22 mmol) then allyl bromide (0.22 mmol) were added and the mixture and the reaction was stirred for one hour. Thiol (0.2 mmol) was then added and the reaction was heated to 60^{o}C for one hour. The reaction was then cooled to room temperature and water and EtOAc was then added and the mixture was extracted 3 times with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and then concentrated under

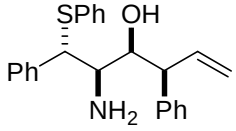
reduced pressure. The crude product was then purified using flash column chromatography.

2-amino-1-phenyl-1-(phenylthio)hex-5-en-3-ol



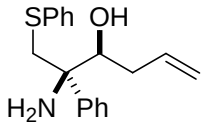
R_f = 0.48; EtOAc. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 7.18-7.26 (m, 10H), 5.88 (ddd, *J* = 17.2 Hz, 10.4 Hz, 6.8 Hz, 1H), 5.18-5.08 (m, 2H), 4.29 (d, *J* = 8 Hz, 1H), 4.05 (td, *J* = 6.4 Hz, 3.2 Hz, 1H), 3.09 (dd, *J* = 8 Hz, 3.6 Hz, 1H), 2.38 (t, *J* = 6.4 Hz, 2H) 1.80-1.00 (bs, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.8, 135.0, 132.7, 129.0, 128.9, 128.8, 127.8, 127.5, 117.9, 70.0, 57.8, 57.3, 39.7 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{18}H_{22}NOS$ 300.1422, found 300.1424.

2-amino-1,4-diphenyl-1-(phenylthio)hex-5-en-3-ol



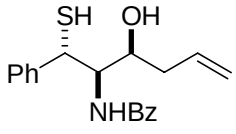
R_f = 0.57; 50% EtOAc in hexanes. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 7.40-7.10 (m, 15H), 6.08 (ddd, *J* = 16.8 Hz, 10.0 Hz, 8.8 Hz, 1H), 5.22-5.12 (m, 2H), 4.50 (dd, *J* = 8.8 Hz, 1.6 Hz, 1H), 4.29 (d, *J* = 9.0 Hz, 1H), 3.64 (t, *J* = 9.2 Hz, 1H), 3.33 (dd, *J* = 9.2 Hz, 2.0 Hz, 1H), 1.80-0.80 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.5, 140.5, 138.9, 134.7, 132.7, 129.1, 128.9, 128.9, 128.8, 128.8, 127.6, 127.4, 127.1, 116.9, 73.0, 57.8, 55.8, 54.8 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{24}H_{26}NOS$ 376.1729, found 376.1741.

2-amino-2-phenyl-1-(phenylthio)hex-5-en-3-ol



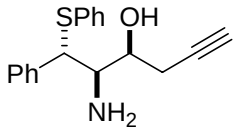
R_f = 0.56; 50 % EtOAc in hexanes. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 7.45-7.15 (m, 10H), 5.75 (tdd, *J* = 16.8 Hz, 10.0 Hz, 7.6 Hz, 1H), 5.02 (m, 2H), 3.87 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 3.63 (dd, *J* = 24.0 Hz, 12.8 Hz, 2H), 2.40 – 1.60 (bs, 3H), 1.95-1.87 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.9, 137.3, 135.7, 129.9, 129.0, 128.6, 127.4, 126.3, 126.2, 118.0, 76.2, 62.2, 47.3, 36.8 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{18}H_{22}NOS$ 300.1422, found 300.1430.

N-(3-hydroxy-1-mercapto-1-phenylhex-5-en-2-yl)benzamide



R_f = 0.63; 40% EtOAc in hexanes. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 7.48-7.18 (m, 10 H), 6.38 (m, 1H), 5.83 (dddd, *J* = 16.8 Hz, 10 Hz, 7.6 Hz, 6.4 Hz, 1H), 5.18-5.09 (m, 2H), 4.45 (d, *J* = 6.8 Hz, 2H), 4.39 (dd, *J* = 8.8 Hz, 4.8 Hz, 1H), 2.40-2.19 (m, 2H), 1.90-1.60 (bs, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.9, 141.7, 134.6, 134.2, 131.7, 129.0, 128.8, 128.7, 127.9, 127.8, 127.0, 119.1, 69.3, 58.8, 45.4, 39.9 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{19}H_{22}NO_2S$ 328.1372, found 328.1380.

2-amino-1-phenyl-1-(phenylthio)hex-5-yn-3-ol

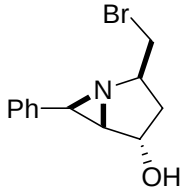


R_f = 0.30; 70% EtOAc in hexanes. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 7.31-7.14 (m, 10H), 4.26 (m, 2H), 3.28 (dd, *J* = 8.4 Hz, 2.8 Hz, 1H), 2.61 (ddd, *J* = 16.8 Hz, 6.4 Hz, 2.4 Hz, 1H), 2.48 (ddd, *J* = 16.8 Hz, 6.4 Hz, 2.8 Hz, 1H), 2.05 (t, *J* = 2.8 Hz, 1H), 1.60-0.90 (bs, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.7, 134.3, 132.9, 129.0, 129.0, 128.9, 127.8, 127.6, 81.1, 71.0, 69.1, 57.2, 57.1, 25.2 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{18}H_{20}NOS$ 298.1266, found 298.1259.

General Procedure for pyrrolidinol synthesis:

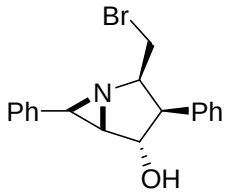
In a vial equipped with a stirring-bar and a screw-cap lid was put a solution of aziridine aldehyde (0.1 mmol) dissolved in 1 ml of a 1:1 (v/v) mixture of H_2O and THF (0.1M solution). Indium (0.22 mmol) then allyl bromide (0.22 mmol) was added and the reaction mixture was stirred for one hour. The reaction was then diluted with 1ml of THF and cooled to 0^{o}C. *N*-bromo succunimide (0.22 mmol) was added slowly in 3 portions over a period of two minutes. The reaction was then allowed to warm to 0^{O}C and stirred at this temperature for another 2 hours. At the completion of the reaction, a saturated solution of $NaSO_3$ was added and the mixture turns and remains colourless. Water and ether were then added and the mixture was extracted 3 times with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and then concentrated *at room temperature* (decomposition occured when using heat) under reduced pressure. The crude product was then purified using flash column chromatography.

2-(bromomethyl)-6-phenyl-1-aza-bicyclo[3.1.0]hexan-4-ol



R_f = 0.51; 50% EtOAc in hexanes. ^{1}H NMR (400 MHz,$CDCl_3$) δ:5.03 (td, *J* = 3.2 Hz, 4.8 Hz, 1H), 3.71 (m, 1H), 3.54 (dd, *J* = 4.4 Hz, 10.4 Hz, 1H), 3.42 (dd, *J* = 7.2 Hz, 10 Hz, 1H), 2.70 (dd, *J* = 2.8 Hz, 4.0 Hz, 1H), 2.23 (ddd, *J* = 1.6 Hz, 8.4 Hz, 14 Hz, 1H), 1.86 (dt, *J* = 8 Hz, 14.4 Hz, 1H), 1.88-1.78 (bs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.8, 128.5, 127.7, 126.4, 72.4, 65.8, 54.1, 40.1, 38.1, 35.5 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{19}H_{31}NO_2SiBr$ 268.0331, found 268.0328.

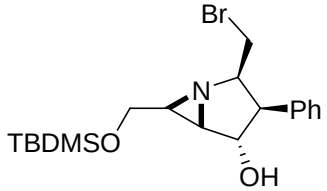
2-(bromomethyl)-3,6-diphenyl-1-aza-bicyclo[3.1.0]hexan-4-ol



R_f = 0.51; 40% EtOAc in hexanes. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 7.45-7.2 (m, 10H), 5.40-5.30 (m, 1H), 3.87 (m, 1H), 3.45 (t, *J* = 8,4 Hz, 1H), 3.6 (m, 2H), 3.10 (dd, *J* = 10.8

Hz, 6.8 Hz, 1H), 2.84 (dd, *J* = 4.8 Hz, 2.8 Hz, 1H), 1.98 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.0, 135.8, 129.1, 128.8, 128.8, 128.6, 127.4, 126.7, 75.2, 68.4, 53.3, 52.8, 40.7, 35.9 ppm. HRMS (ESI) $[MH]^+$ calcd. For $C_{18}H_{19}NOBr$ 344.0644, found 344.0637.

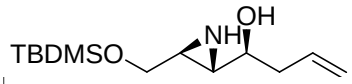
(2R,3R,4S,5S,6S)-2-(bromomethyl)-6-((tert-butyldimethylsilyloxy)methyl)-3-phenyl-1-aza-bicyclo[3.1.0]hexan-4-ol

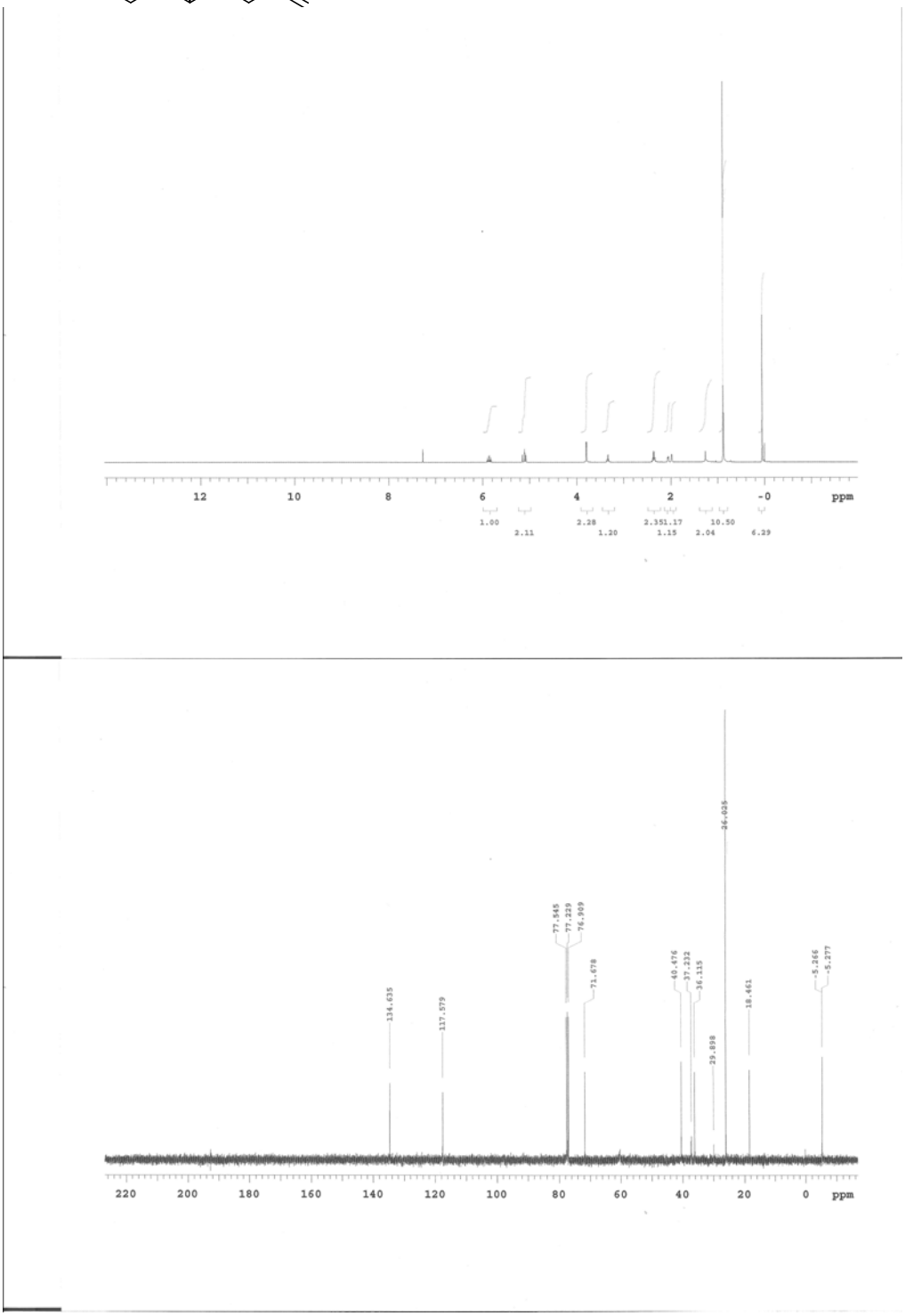


R_f = 0.38; 10% EtOAc in hexanes. ^{1}H NMR (400 MHz,$CDCl_3$) δ: 7.32-7.20 (m, 5H), 5.20 (m, 1H), 3.71 (dd, *J* = 11.2 Hz, 5.6 Hz, 1H), 3.69 (m, 1H), 3.63 (dd, *J* = 10.8 Hz, 5.2 Hz, 1H), 3.26 (m, 2H), 3.02 (dd, *J* = 10.8 Hz, 7.2 Hz, 1H), 2.62 (dd, *J* = 4.8 Hz, 2.8 Hz, 1H), 2.52 (ddd, *J* = 5.6 Hz, 5.6 Hz, 2.8 Hz, 1H), 1.79 (d, *J* = 4.4 Hz, 1H), 0.92 (s, 9H), 0.11 (d, *J* = 1.2 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.8, 129.1, 128.9, 127.5, 74.5, 67.9, 65.3, 52.5, 47.3, 40.3, 35.9, 26.2, 18.6, -4.8, -4.9 ppm.
HRMS (ESI) $[MH]^+$ calcd. For $C_{19}H_{31}NO_2SiBr$ 412.1301, found 412.1299.

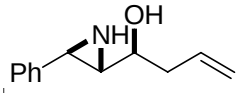
^{1}H and ^{13}C NMR spectra:

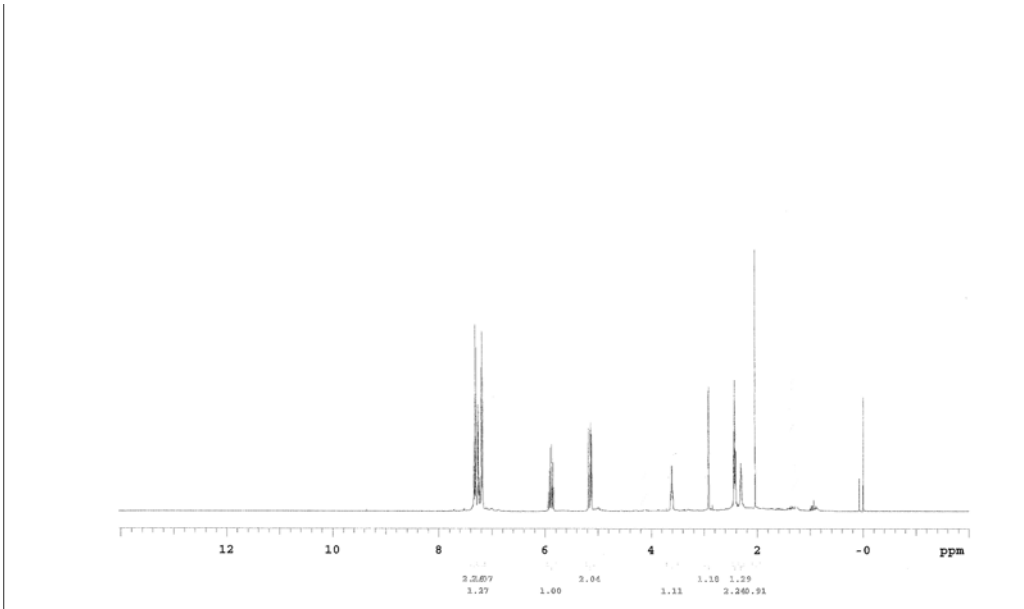
(S)-1-((2S,3S)-3-((tert-butyldimethylsilyloxy)methyl)aziridin-2-yl)but-3-en-1-ol

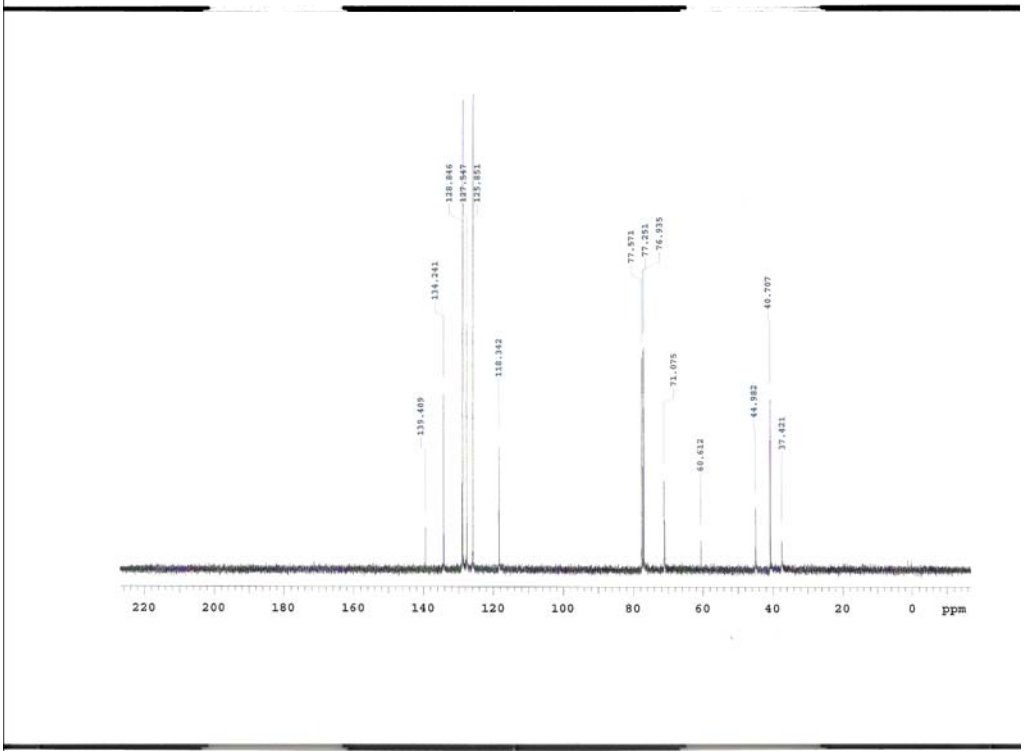




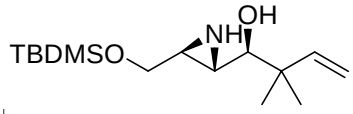
1-(3-phenylaziridin-2-yl)but-3-en-1-ol

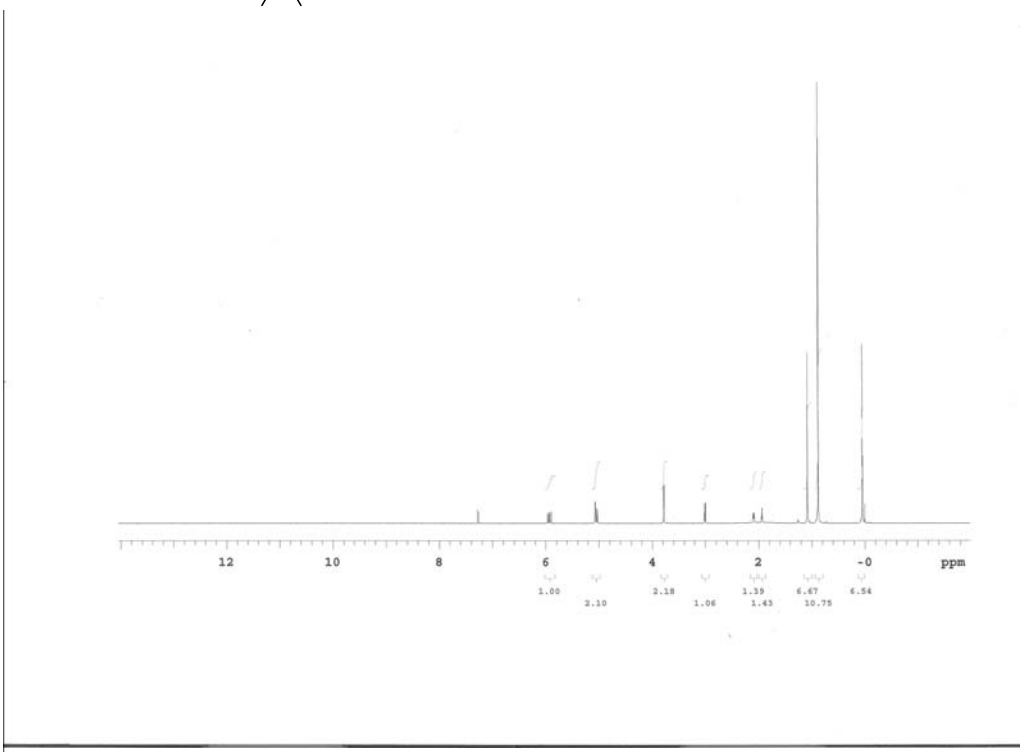


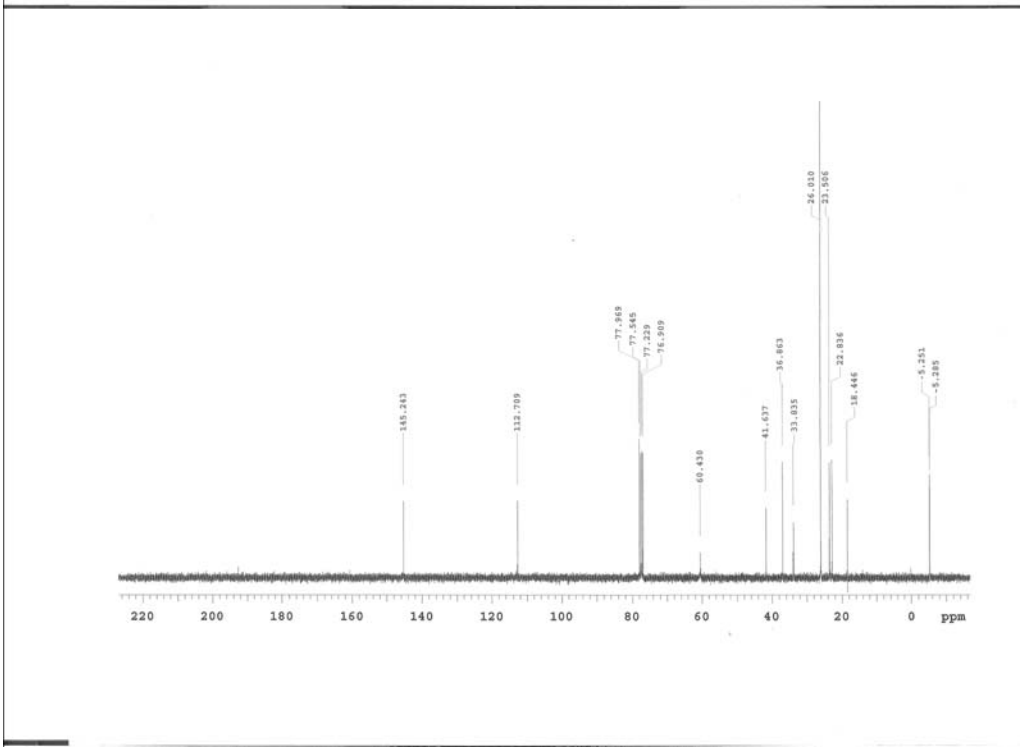




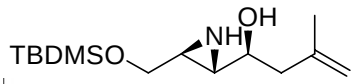
(S)-1-((2S,3S)-3-((tert-butyldimethylsilyloxy)methyl)aziridin-2-yl)-2,2-dimethylbut-3-en-1-ol

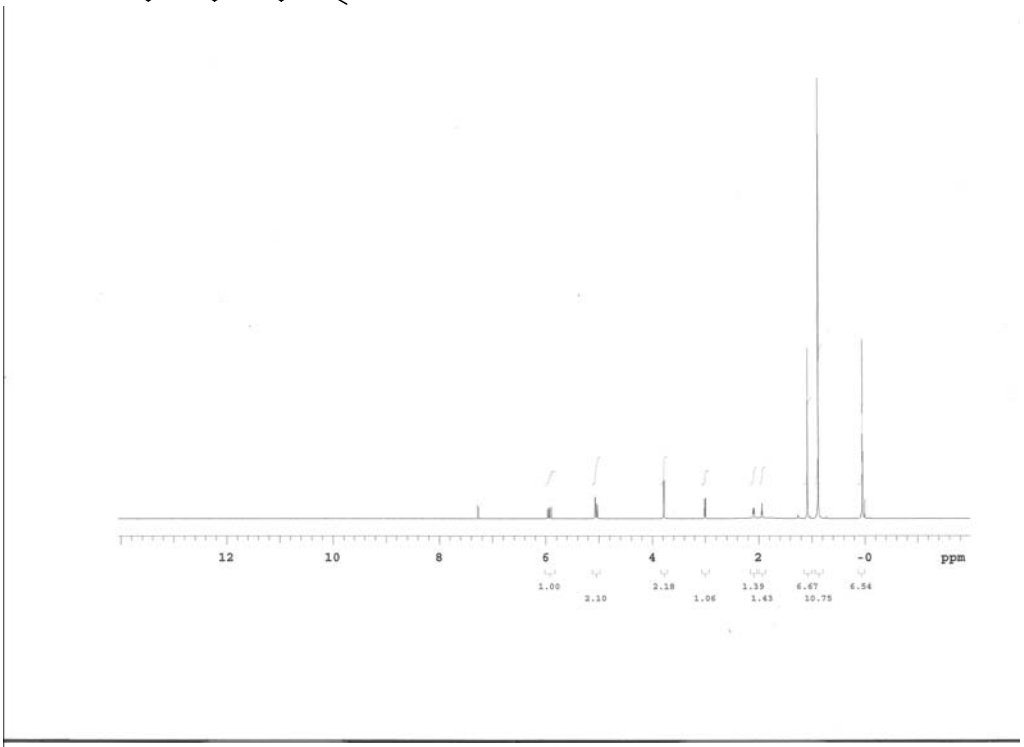


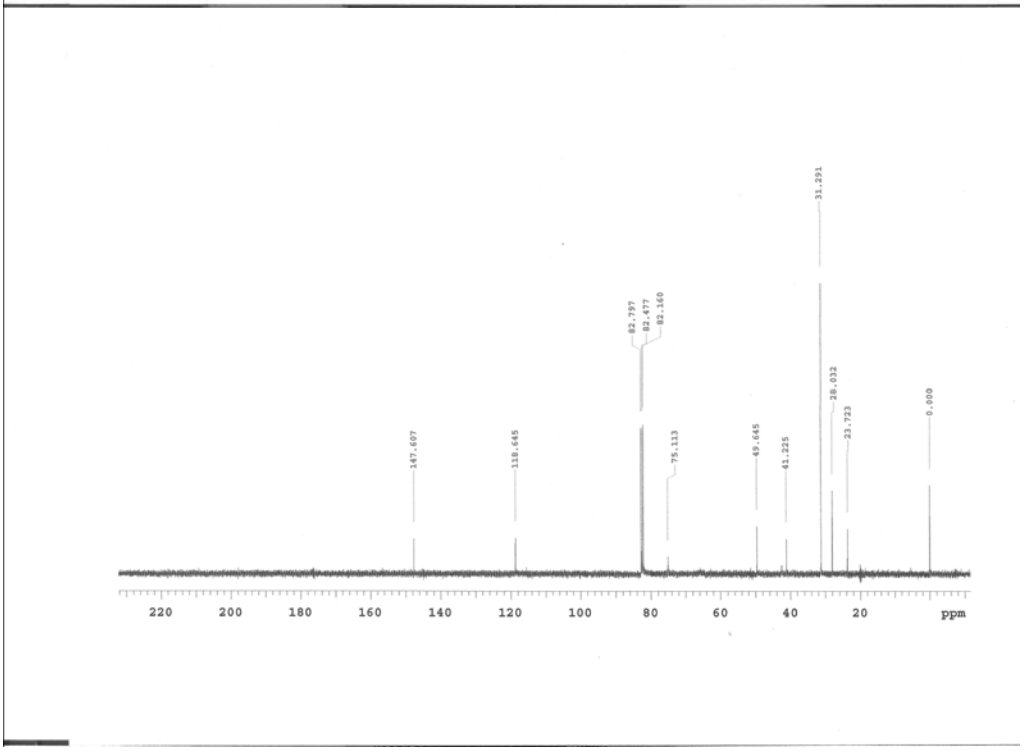




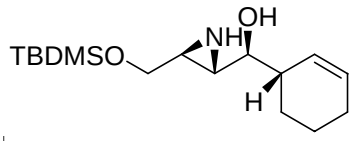
(S)-1-((2S,3S)-3-((tert-butyldimethylsilyloxy)methyl)aziridin-2-yl)-3-methylbut-3-en-1-ol

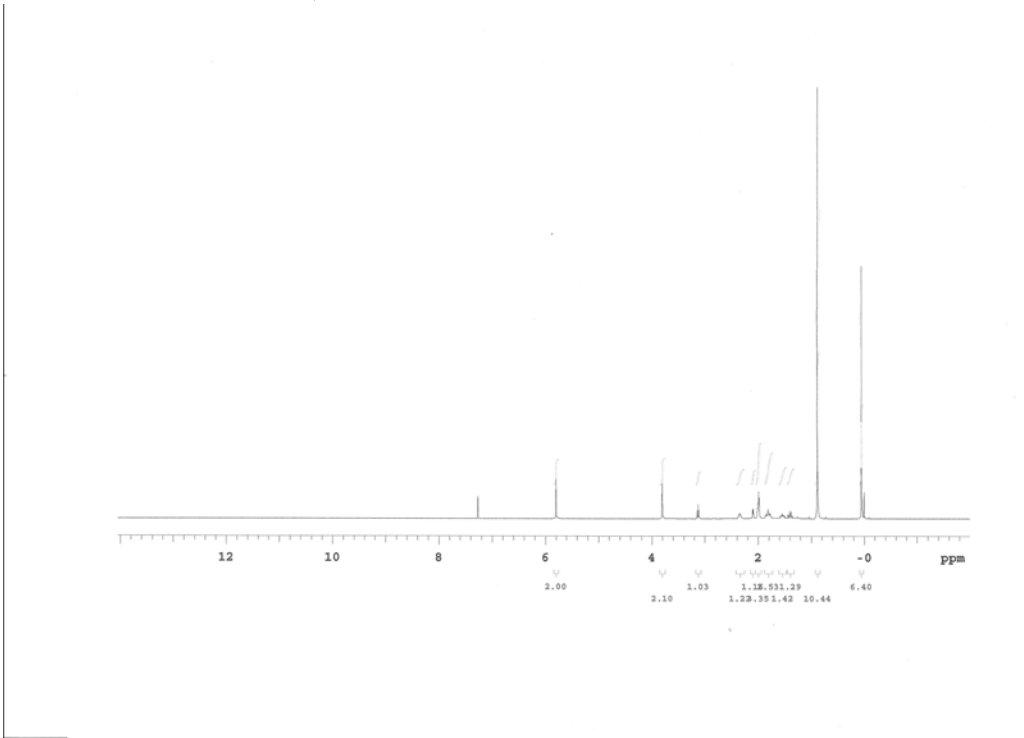


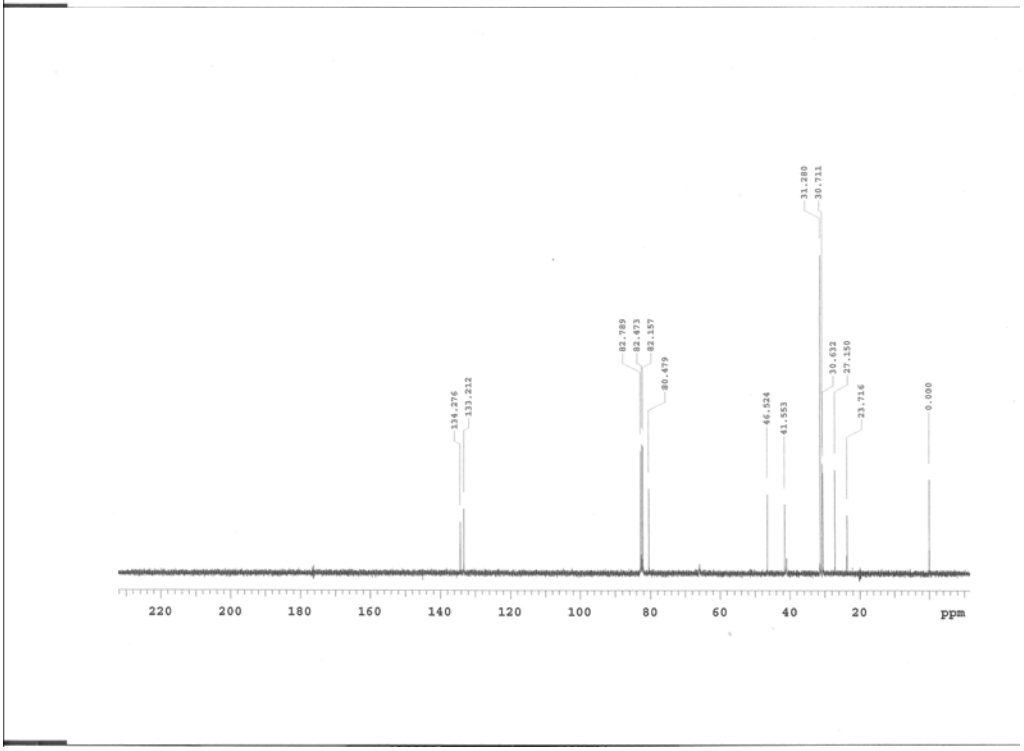




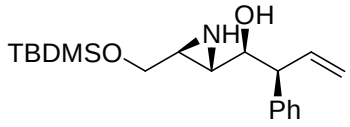
(S)-((2S,3S)-3-((tert-butyldimethylsilyloxy)methyl)aziridin-2-yl)((S)-cyclohex-2-enyl)methanol

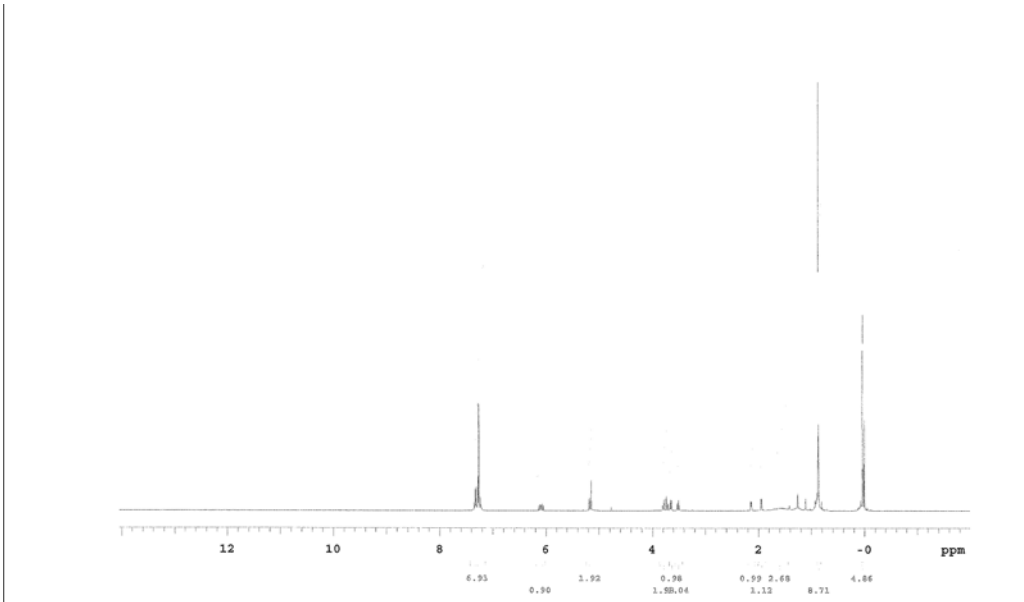


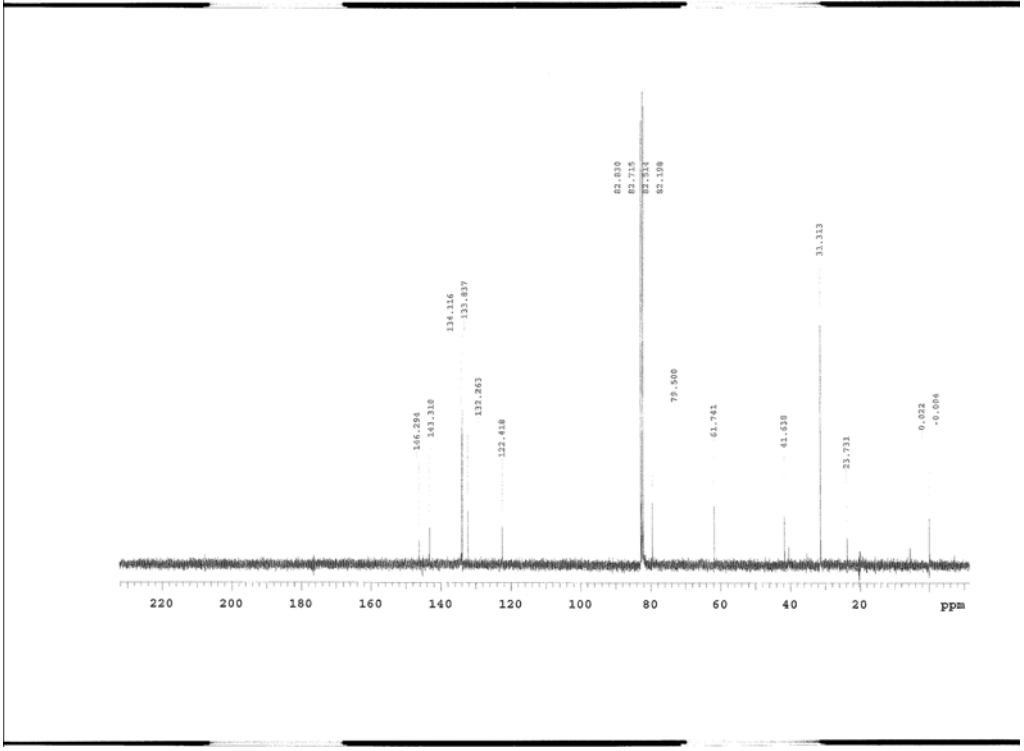




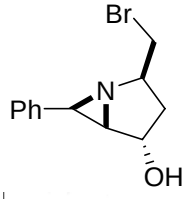
(1S,2S)-1-((2S,3S)-3-((tert-butyldimethylsilyloxy)methyl)aziridin-2-yl)-2-phenylbut-3-en-1-ol

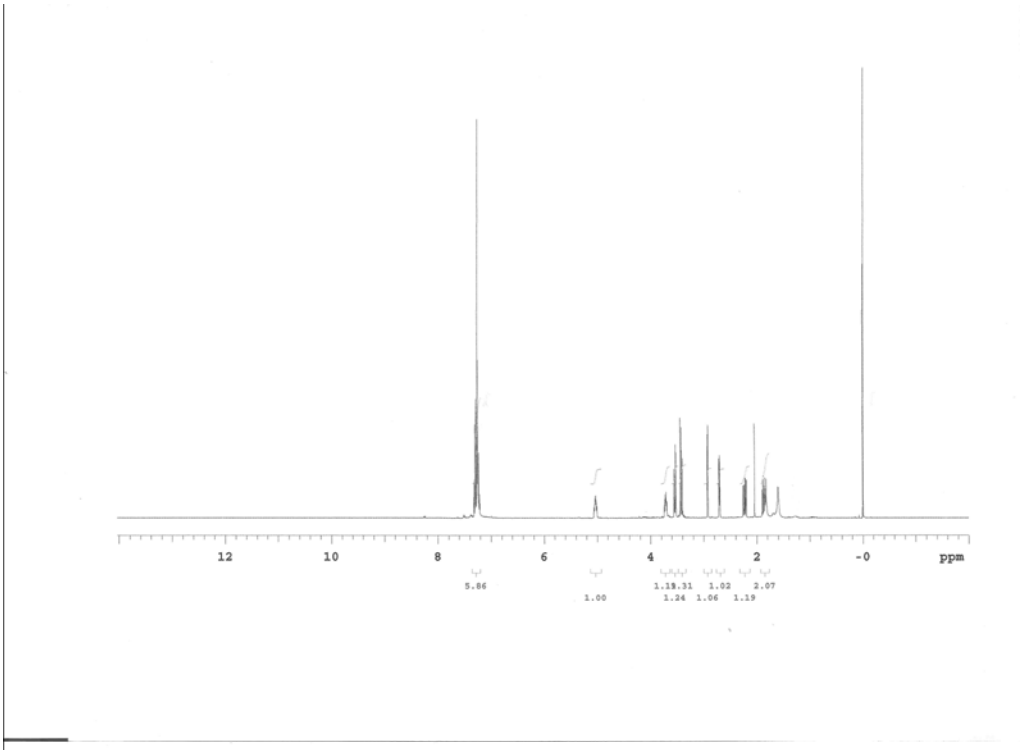


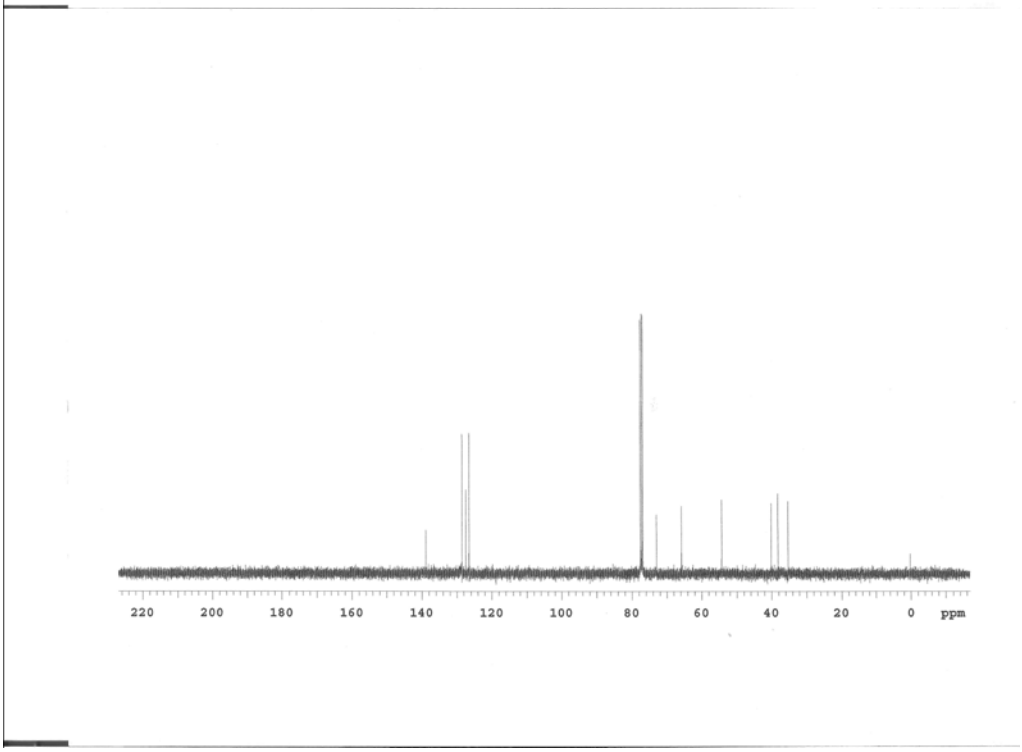




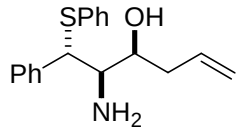
2-(bromomethyl)-6-phenyl-1-aza-bicyclo[3.1.0]hexan-4-ol

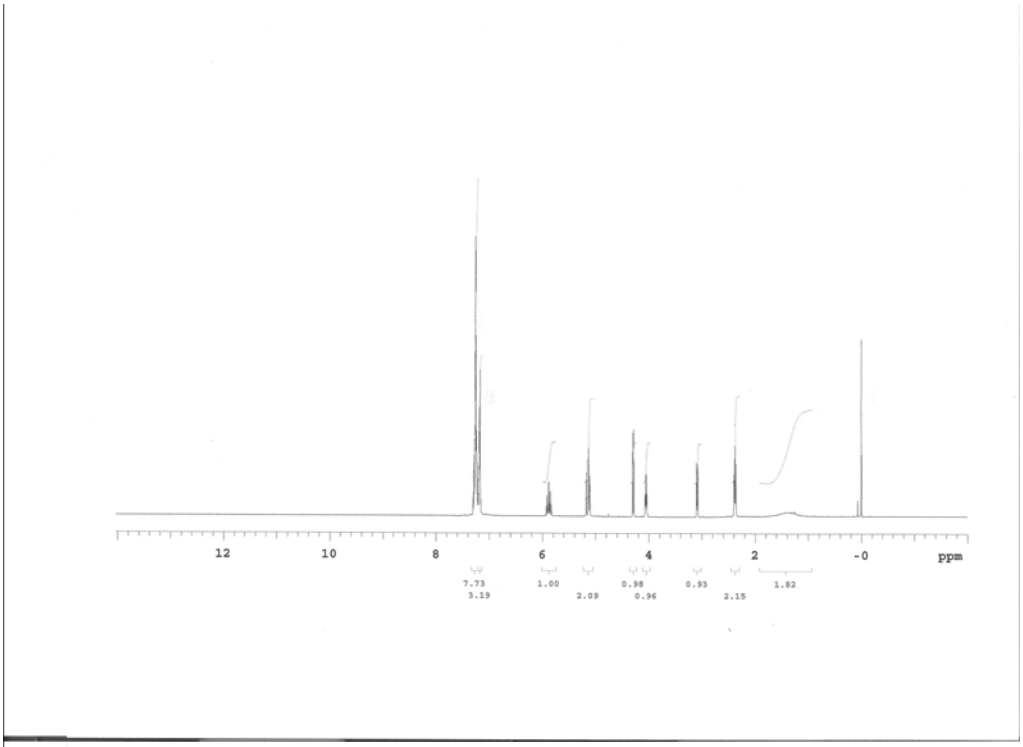


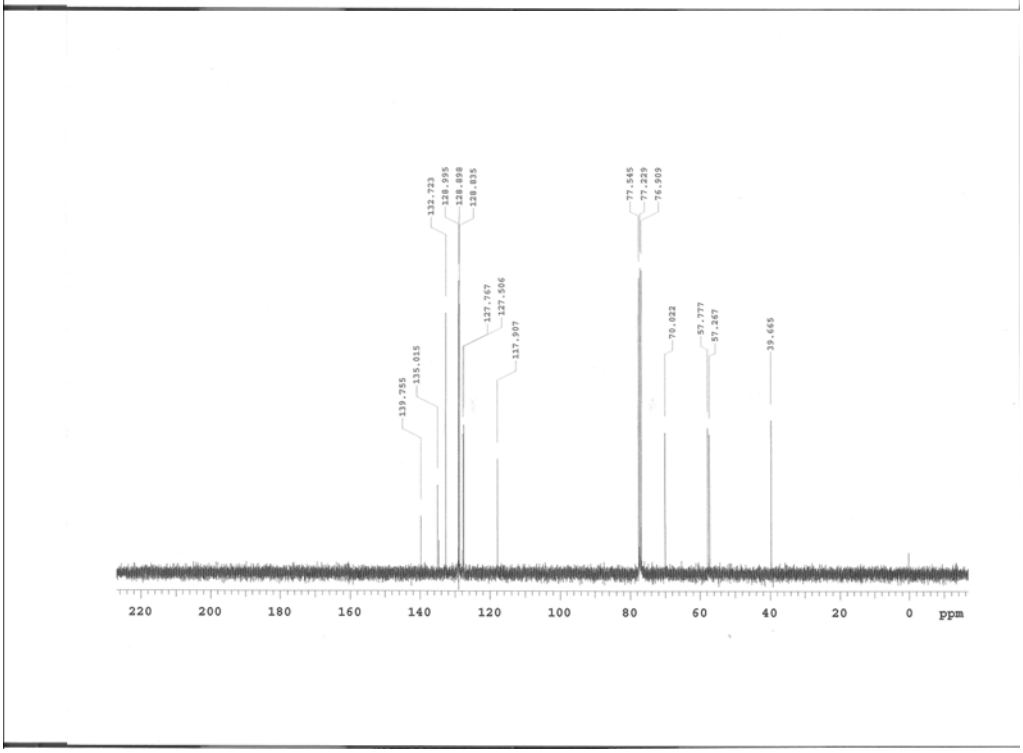




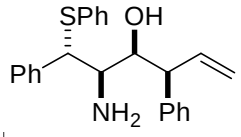
2-amino-1-phenyl-1-(phenylthio)hex-5-en-3-ol

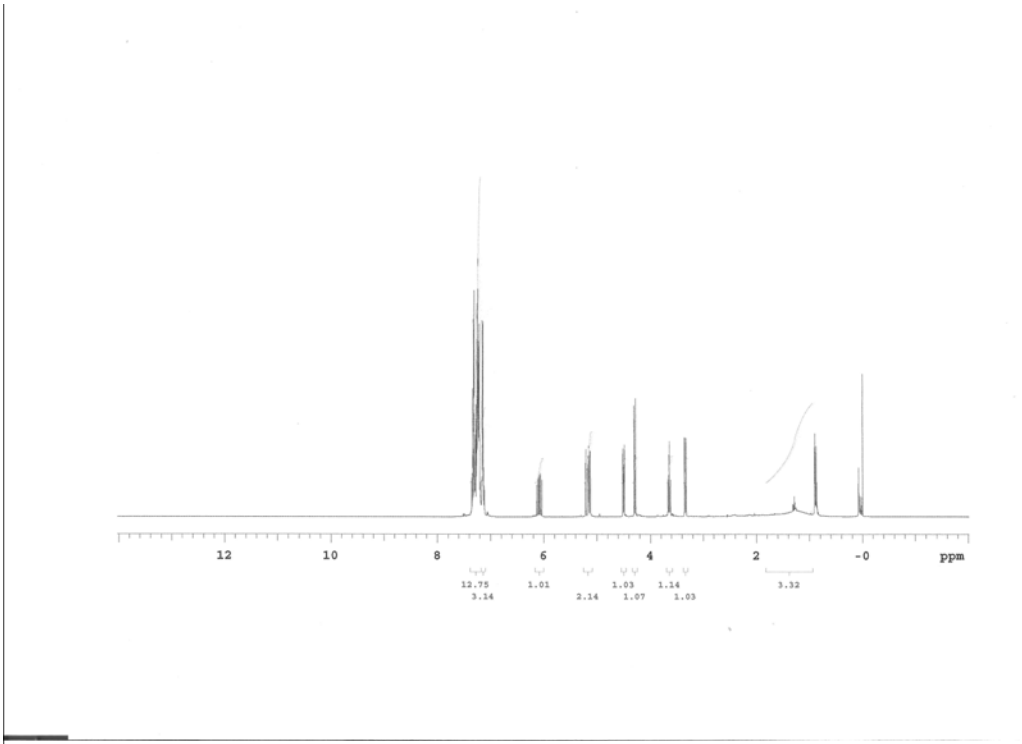


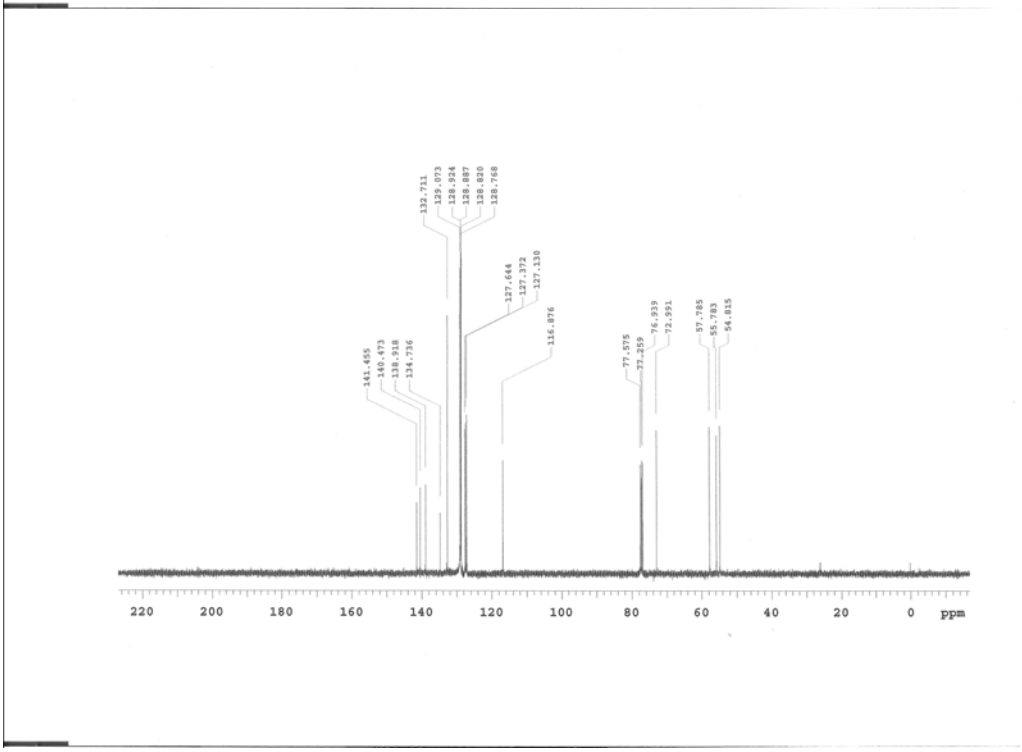




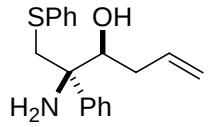
2-amino-1,4-diphenyl-1-(phenylthio)hex-5-en-3-ol

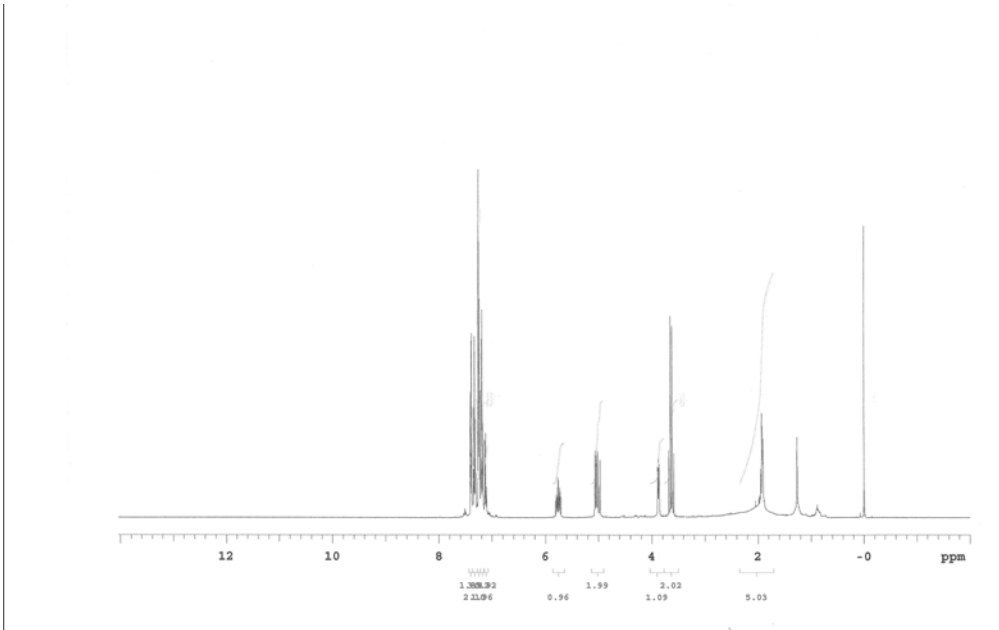


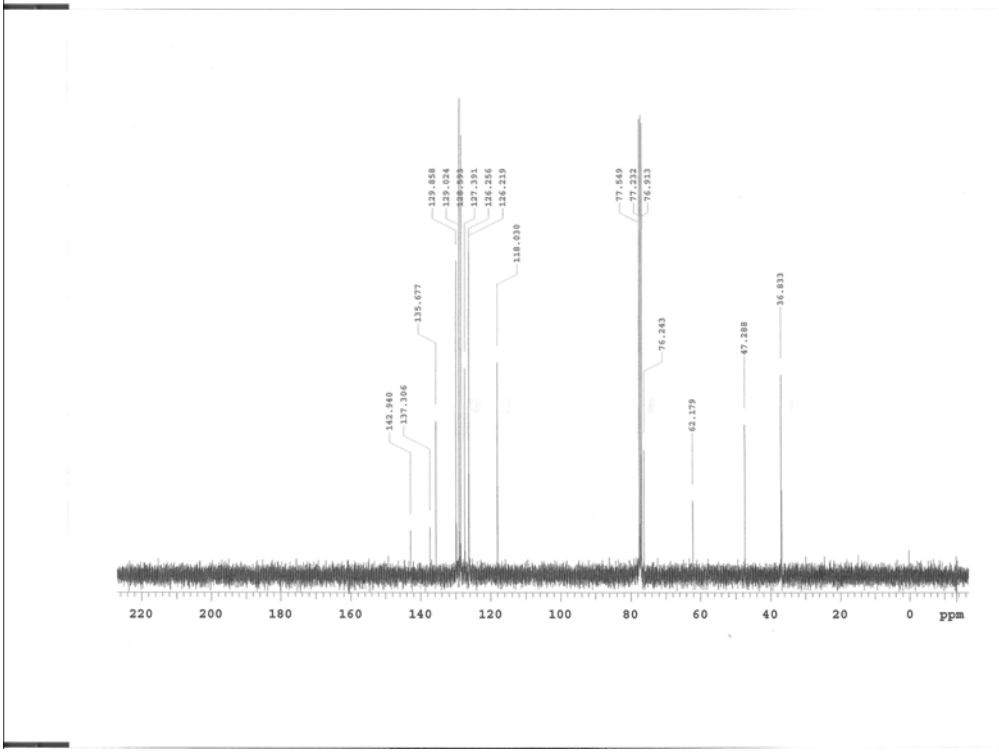




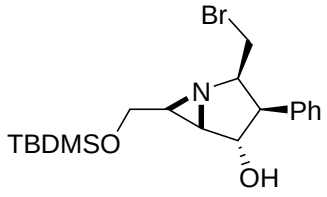
2-amino-2-phenyl-1-(phenylthio)hex-5-en-3-ol

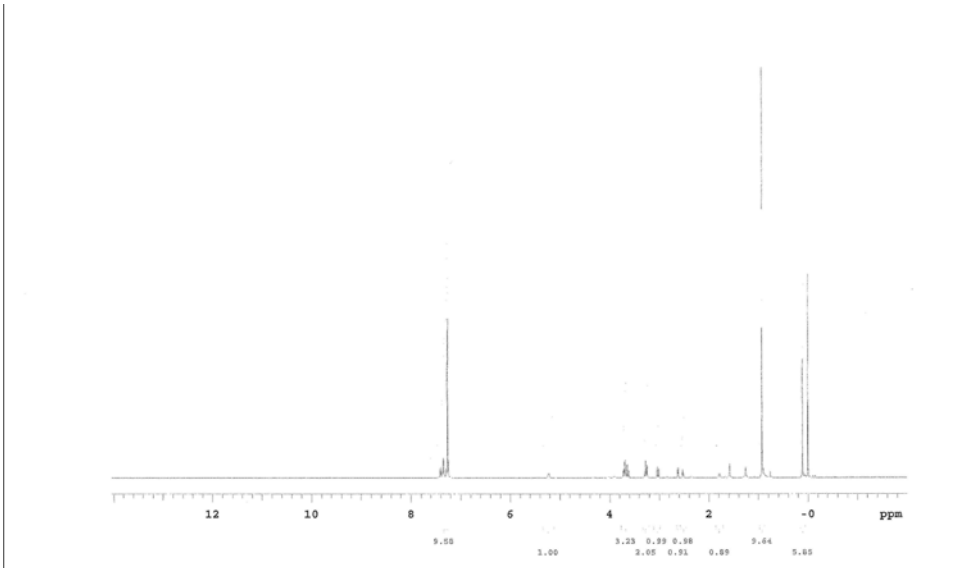


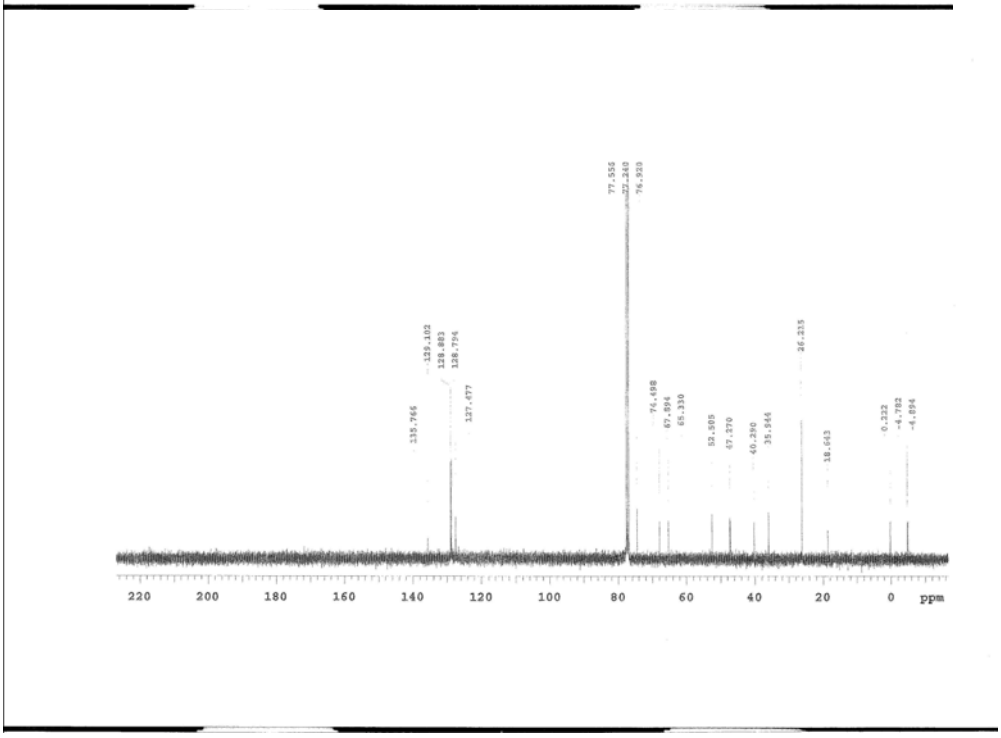




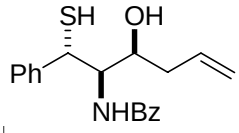
(2R,3R,4S,5S,6S)-2-(bromomethyl)-6-((tert-butyldimethylsilyloxy)methyl)-3-phenyl-1-aza-bicyclo[3.1.0]hexan-4-ol

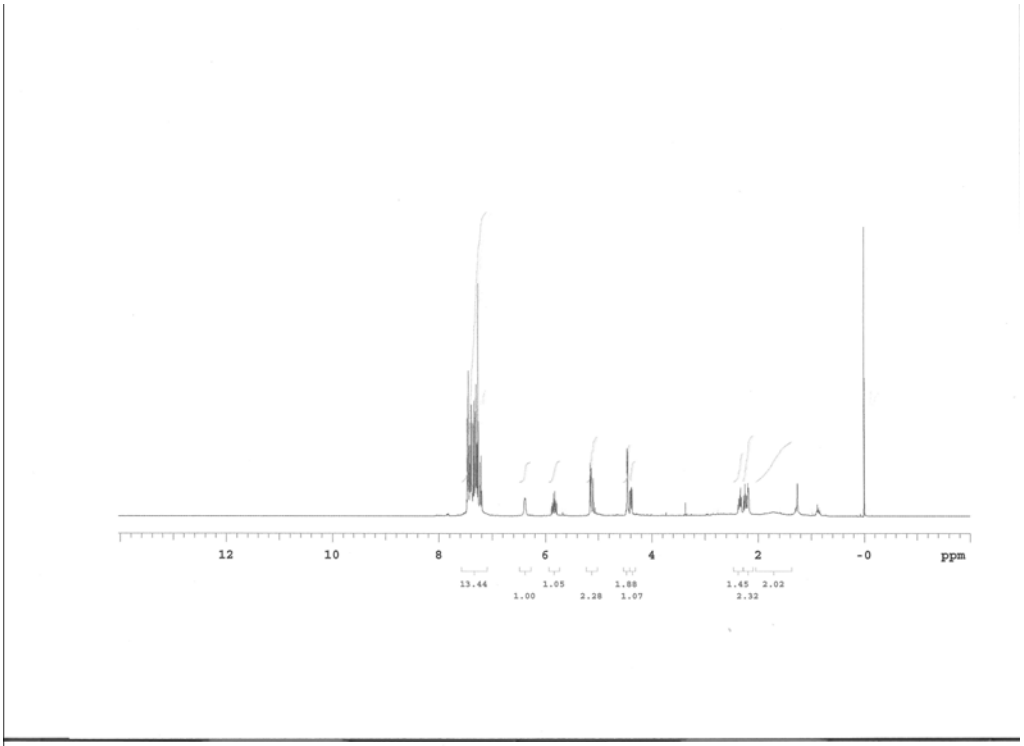


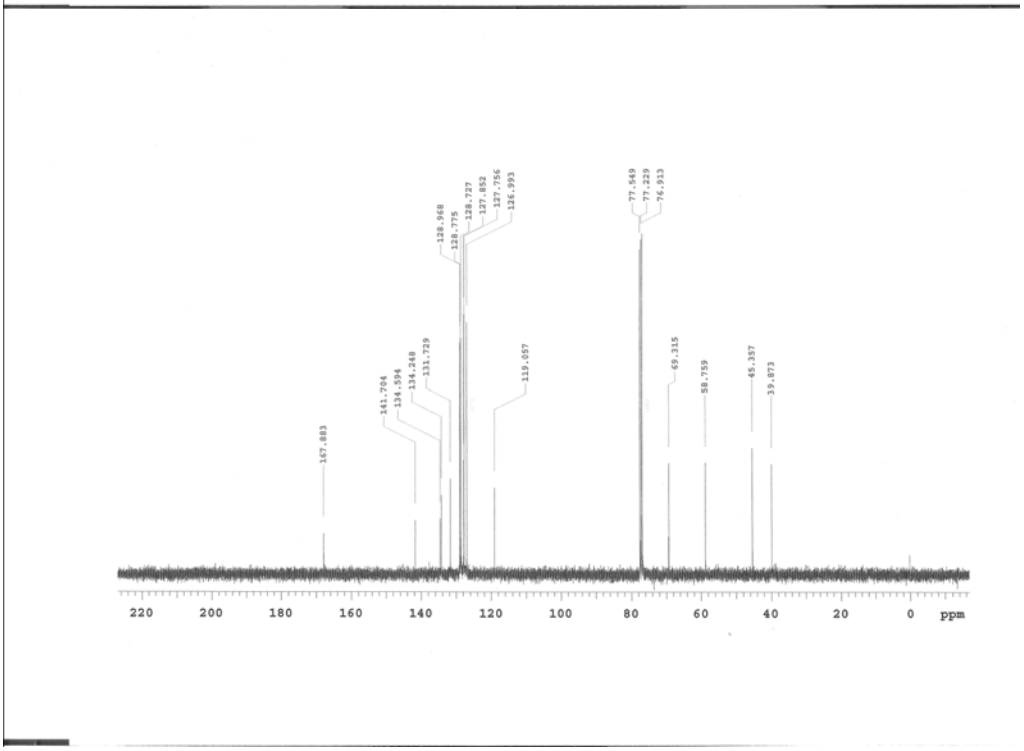




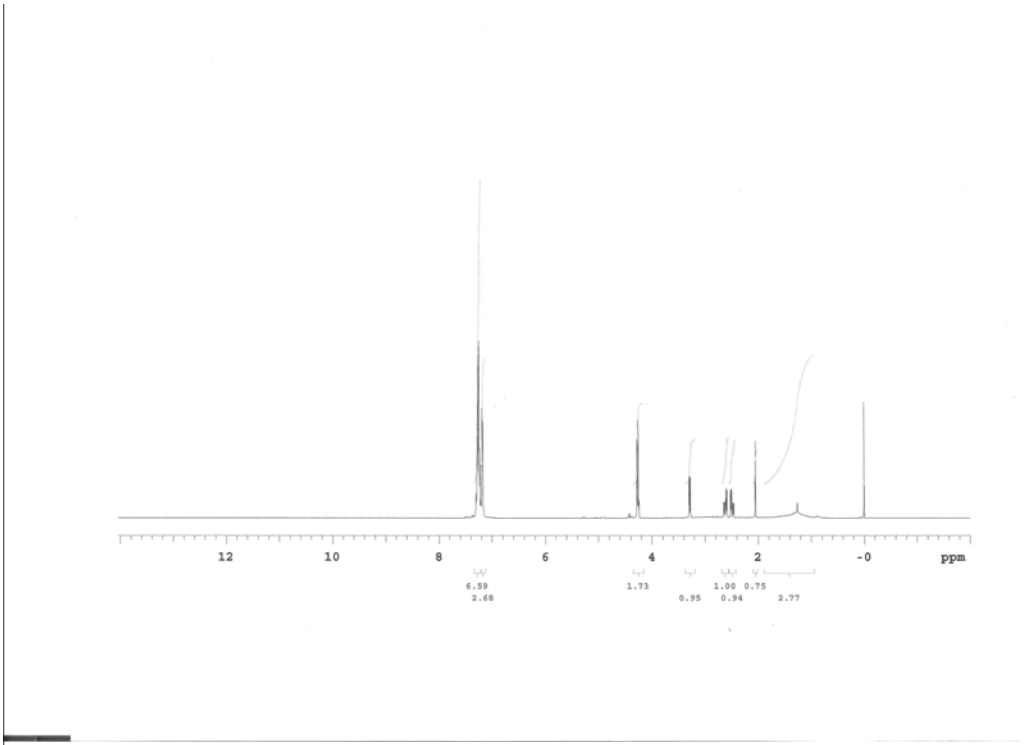
N-(3-hydroxy-1-mercapto-1-phenylhex-5-en-2-yl)benzamide

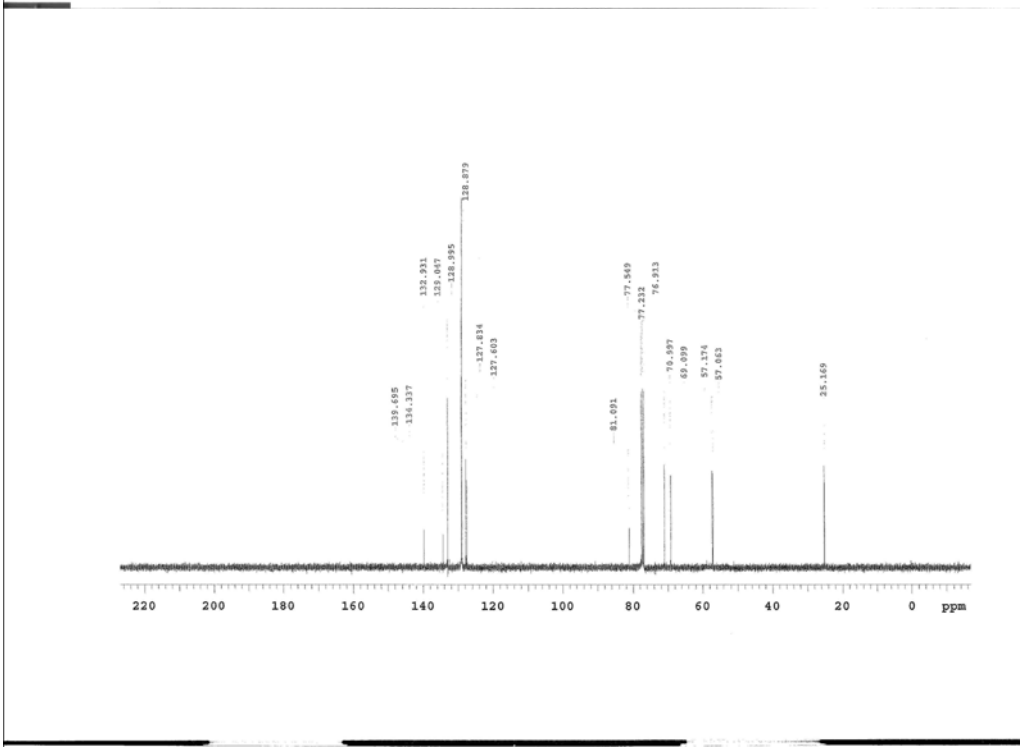






2-amino-1-phenyl-1-(phenylthio)hex-5-yn-3-ol





2-(bromomethyl)-3,6-diphenyl-1-aza-bicyclo[3.1.0]hexan-4-ol