Dimethylamine adducts of allylic triorganoboranes as effective reagents for Petasis-type homoallylation of primary amines with formaldehyde

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Supporting Information

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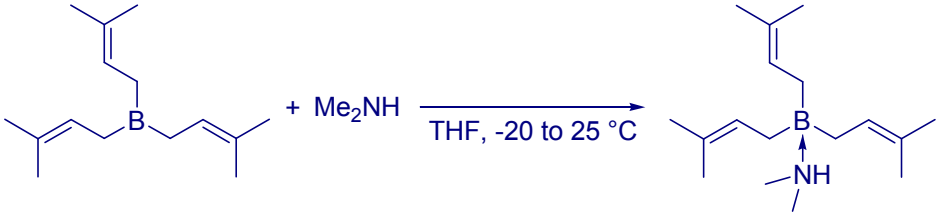
General. The manipulations with sensitive to air compounds were carried out under inert atmosphere of dry Ar. NMR spectra were recorded on Bruker Avance-400 instrument. Chemical shifts are reported in ppm with the solvent resonance as the internal standard: ^{1}H ($CHCl_3$, 7.26 ppm), ^{13}C ($CDCl_3$, 77.16 ppm), ^{1}H (C_6D_6, 7.16 ppm), ^{13}C (C_6D_6, 128.06 ppm), $^{11}B\{^{1}H\}$ NMR chemical shifts are reported in ppm relative to BF_3•OEt_2. Column chromatography was carried out using silica gel 60–230 mesh (Merck). Thin layer chromatography was run on AlugramSilG/UV_{254} (Macherey-Nagel). Melting points were measured on a Stuart SMP10 capillary melting point apparatus. Triallylborane [1], triprenylborane [2] and triallylborane-dimethylamine adduct [3] were prepared according to the described procedures.

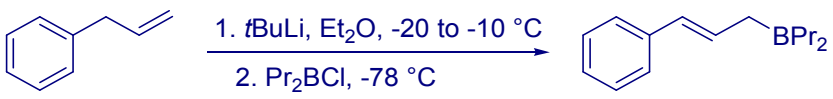
Triprenylborane-dimethylamine adduct (1b)



To 2M solution of Me_2NH in THF (8.5 ml, 17 mmol) was added dropwise with stirring triprenylborane (1.53 g, 1.95 ml, 7.0 mmol) at -20 °C. The cooling bath was removed and all volatiles were removed in vacuum, first with water-jet pump followed by oil-pump that furnished pure adduct **1b** (1.84 g, 100%) as colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ 5.49 (t, *J* = 8.0 Hz, 3H, 3CH=), 2.50 (br. s, 1H, NH), 1.77 (s, 9H, 3Me), 1.75 (s, 6H, Me_2N), 1.68 (s, 9H, 3Me), 1.20 (d, *J* = 8.1 Hz, 6H, $3CH_2$) ppm. ^{13}C NMR (101 MHz, C_6D_6): δ 128.69 3C, 125.47 3C, 37.56 2C, 26.63 3C, 22.76 br. 3C, 18.07 3C. ^{11}B NMR (128 MHz, C_6D_6): δ -1.47 ppm. $C_{17}H_{34}BN$ (263.27): calcd. C, 77.56; H, 13.02; N, 5.32; B, 4.11; found: C, 77.48; H, 12.94; N, 5.35; B, 4.00.

Synthesis of *trans*-cinnamyl(dipropyl)borane-dimethylamine adduct (1c)

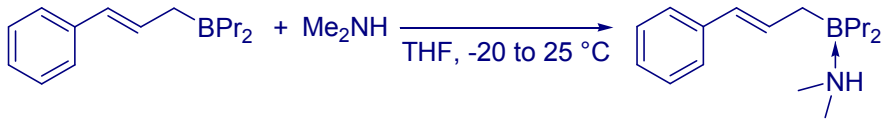
trans-Cinnamyl(dipropyl)borane



*t*BuLi (1.4M, 12.8 ml, 18mmol) was added to a stirred solution of allylbenzene (2.00 g, 16.0 mmol) in Et_2O (30 ml) at –70 to –60 °C and stirring was continued for 10 min and then for 40 min at –20 to –10 °C. The prepared solution of cinnamyllithium was added dropwise via syringe to a solution of Pr_2BCl (2.38 g, 18.0 mmol) in pentane (10 ml) at –78 °C. The reaction

mixture was then allowed to warm to room temperature before quenching with TMSCl (5.1 mL, 40.0 mmol). The solvents were removed under reduced pressure and the oily residue was stirred with *n*-hexane (10 mL) and supernatant was separated from the precipitate of LiCl. The *n*-hexane solution was concentrated, and vacuum distillation of the residue gave *trans*-cinnamyl(dipropyl)borane (2.78 g, 81%) as a colorless liquid, b.p. 94–96 °C (0.1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.28 (m, 4H), 7.20-7.17 (m, 1H, Ph), 6.41 (dt, *J* = 7.6, 15.7 Hz, 1H, CH=), 6.31 (d, *J* = 15.8 Hz, 1H, =CHPh), 2.33 (d, *J* =7.5 Hz, 2H, CH_2CH=), 1.53 (m., 4H, $2CH_2$), 1.31 (t, *J* = 7.7 Hz, 4H, $2CH_2B$), 0.97 (t, *J* = 7.3 Hz, 6H, $2CH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.58, 129.59, 128.58 2C, 128.31,126.50, 125.77 2C, 33.87 br., 31.18 br. 2C, 18.01 2C, 17.63 2C ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ 85.24 (s) ppm. **NMR spectra coincide with the literature data [4].**

trans-Cinnamyl(dipropyl)borane-dimethylamine adduct (1c)



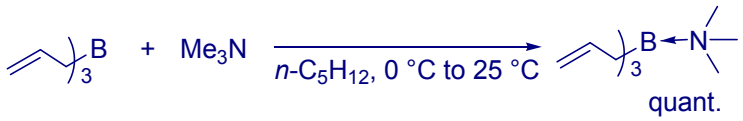
To 2M solution of Me_2NH in THF (8.0 ml, 16.0 mmol) was added *trans*-cinnamyl(dipropyl)borane (2.46 g, 11.5 mmol) dropwise with stirring at -20 °C. The cooling bath was removed and the solution was evaporated to dryness in vacuum to give adduct **1c** (4.00 g, 97%) as oil which was used without further purification. ^{1}H NMR (400 MHz, C_6D_6): δ 7.47 (d, *J* = 7.7 Hz, 2H, Ph), 7.29 (t, *J* = 7.5 Hz, 2H, Ph), 7.14 (t, *J* = 7.1 Hz, 1H, Ph), 6.80 (dt, *J* = 8.3, 15.7 Hz, 1H, CH=), 6.34 (d, *J* = 15.7 Hz, 1H, =CHPh), 2.31 (br. s, 1H, NH); 1.68-1.63 (d, *J* = 5.6 Hz, 3H), 1.50 (dt, *J* = 24.2, 12.2 Hz, 3H), 1.34 (t, *J* = 6.9 Hz, 3H), 0.47 (dd, *J* = 12.4, 7.8 Hz, 2H) ppm. ^{13}C NMR (101 MHz, C_6D_6): δ 139.78, 137.48, 128.89 2C, 126.06, 126.03, 125.64 2C, 36.94, 29.26 br., 25.80 br. 2C, 20.59 2C, 19.68 2C ppm. ^{11}B NMR (128 MHz, C_6D_6): δ -1.55 ppm. $C_{17}H_{30}BN$ (259.24): calcd. C, 78.76; H, 11.66; N, 5.40; found: C, 78.50; H, 11.50; N, 5.28.

Triallylborane-1,4-diazabicyclo[2.2.2]octane adduct (1d)

To a solution of dried and recrystallized DABCO (2.7 g, 24.1 mmol) in DCM (10 ml) was added triallylborane (3.23 g, 4.17 ml, 24.1 mmol) with stirring and cooling in an ice-bath. The solvent

was removed in vacuum to give adduct **1d** (5.93 g, 100%) as white crystalline solid, m.p. 58-59 °C (under Ar in a sealed capillary) which is not sensitive to air at ambient temperature (20 min exposure). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.11-6.00 (m, 3H, 3CH=), 4.78-4.70 (m, 6H, $3CH_2$=), 2.91 (s, 12H, $6CH_2N$), 1.32 (d, J = 7.9 Hz, 6H, $3CH_2$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.80 3C, 110.71 3C, 46.26 br. 6C, 29.10 br. 3C ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ 0.74 ppm. $C_{15}H_{27}BN_2$ (246.2): calcd. C, 73.18; H, 11.05; N, 11.38; B, 4.39; found: C, 73.21; H, 11.17; N, 11.31; B, 4.27.

Triallylborane-trimethylamine adduct (1e) [5]

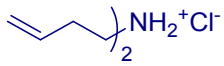


A current of dry trimethylamine (from Me_3NHCl and KOH) was passed through a solution of triallylborane (2.0 ml, 1.55 g, 11.6 mmol) in pentane (5 ml) upon cooling in an ice-bath. Then the solvent was evaporated under reduced pressure and the vessel was filled with argon to give the adduct **1e** (2.24 g, 100%) as colorless, moderately pyrophoric liquid. ^{1}H NMR (400 MHz, C_6D_6): δ 6.18-6.07 (m, 3H, 3CH=), 4.89-4.81 (m, 6H, $3CH_2$=), 1.95 (s, 9H, 3Me); 1.38 (d, J = 8.0 Hz, 6H, $3CH_2$) ppm. ^{13}C NMR (101 MHz, C_6D_6): δ 144.15 3C, 110.62 3C, 49.29 3C, 29.73 br. 3C ppm. ^{11}B NMR (128 MHz, C_6D_6): δ 0.98 ppm.

General procedure for homoallylation of primary amines with dimethylamine adducts of allylic triorganoboranes

To a solution of primary amine (1 mmol) in MeOH (0.5-0.8 ml) was added 37% solution of formaldehyde (74-81 µL, 1.0-1.1 mmol). The mixture was left for 20 min to ensure complete formation of an aminal, followed by addition of an allylborane-dimethylamine adduct. The reaction was stirred for 30 min at ambient temperature and 1 h at 40 °C. The progress of the reaction was monitored by TLC and NMR. After completion the reaction mixture was concentrated on the rotavapor under reduced pressure. In case of volatile amine equivalent amount of 6 M HCl solution was added before eveporation. The dry residue was treated with NaOH 20% and extracted with a mixture of Et_2O/n-C_5H_{12}, organic layer was washed with NaOH 10%, dried with K_2CO_3 and concentrated. The resulting oil was purified by FC to give corresponding homoallylamine derivative. Alternatevely amine was isolated as hydrochloride salt by treatment of its etheral solution with 4M HCl in dioxane.

N,N-Di(3-butenyl)amine hydrochloride (2a)



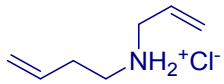
A solution of adduct **1a** (0.72 g, 4.0 mmol) in MeOH (2 ml) was combined with methanolic 7M NH_3 (2.0 ml, 14 mmol) followed by dropwise addition of 37% solution of formaldehyde (0.88 ml, 12.0 mmol) with stirring and external cooling with ice-bath. The obtained solution was heated on a water bath for 3 days at 55 °C, the progress of the reaction was monitored by ^{1}H and ^{11}B NMR. When the signal of ammonia adduct (δ ^{11}B -8.7 ppm) was disappeared 6M HCl (5 ml, 30 mmol) was added and the volatiles were removed on the rotavapor under reduced pressure. The dry solid residue was extracted with boiling $CHCl_3$ twice. Extracts were dried with $MgSO_4$, filtered and concentrated to give pure amine salt **2a** (0.68 g, 70%) as white solid, m.p. 251-252 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.60 (br. s, 2H, NH_2), 5.76 (ddt, *J* = 13.0, 10.5, 6.7 Hz, 2H, 2CH=), 5.17-5.10 (m, 4H, $2CH_2$=), 3.10–2.87 (m, 4H, $2NCH_2$), 2.67 (dd, *J* = 14.8, 6.8 Hz, 4H, $2C\underline{H}_2CH$=) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 132.56 2C, 118.64 2C, 47.05 2C, 30.09 2C ppm. Anal. Calcd for $C_8H_{16}ClN$ (161.67): C, 59.43; H, 9.98; N, 8.66; found: C, 59.42; H, 9.92; N, 8.70.

3-Butenylamine hydrochloride (2b)

4M HCl solution in dioxane (12 ml, 48.0 mmol) was added to MeOH (45 ml) followed by addition of methanolic 7M NH_3 (33.0 ml, 0.23 mol). To this mixture 37% solution of formaldehyde (0.88 ml, 12.0 mmol) was added dropwise with stirring. After then adduct **1a** (0.75 g, 4.2 mmol) was appended to the mixture and left for 3 days at 55 °C in a sealed vessel. The progress of the reaction was monitored by ^{1}H and ^{11}B NMR. When the signal of ammonia adduct (δ ^{11}B -8.7 ppm) was disappeared 6M HCl (30 ml, 0.18 mol) was added and the volatiles were removed on the rotavapor under reduced pressure. The dry solid residue was extracted with boiling $CHCl_3$ trice. Extracts were dried with $MgSO_4$, filtered and concentrated to give a mixture of mono- and dibutenylamine salts in molar ratio 4:1. The powder of hydrochlorides was covered with Et_2O/*n*-heptane (40 ml) and treated with 50% KOH. Organic extract was separated dried over pellets of KOH and distilled at atmospheric pressure. Distillate containing homoallylamine was cooled and treated with 4M HCl in dioxane (2.0 ml, 8.0 mmol) to give hydrochloride salt of homoallylamine (0.69 g, 54%) as white crystalls. ^{1}H NMR (400 MHz, DMSO-D_6): δ 8.21 (br.s, 3H, NH_3); 5.79 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, CH=); 5.15-5.05 (m, 2H, CH_2=); 2.83-2.76 (m,

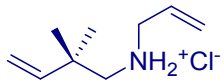
2H, C<u>H</u>$_2$NH$_3$), 2.34 (dd, *J* = 14.8, 6.9 Hz, 2H, C<u>H</u>$_2$CH=) ppm. **NMR spectra coincide with the literature data [6].**

N-Allyl-*N*-(3-butenyl)amine hydrochloride (2c)



To a solution of allylamine (0.46 g, 0.60 ml, 8.0 mmol) in MeOH (1.8 ml) was added 37% formaldehyde (0.37 ml, 5.0 mmol) and the solution was left for 20 min followed by the addition of **1a** adduct (0.32 g, 1.8 mmol). After 30 min, the reaction mixture was heated on the water bath for 1 h at 40 °C to complete the reaction. Dissolved amines were treated with 4M HCl in dioxane (2.5 ml, 10.0 mmol) to avoid loss of the product during evaporation. The volatiles were removed under reduced pressure and the residue was treated with 20% NaOH, extracted with Et_2O/*n*-pentane (3:1). The combined extracts were dried with K_2CO_3 and heated to evaporate allylamine at ambient pressure. The residual free amine was treated with 4.5M HCl in Et_2O, precipitate was collected by filtration, dried in vacuum to give hydrochloride salt **2c** (0.58 g, 78%), as white crystalline solid, m.p. 192-194 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.67 (br.s, 2H, NH_2), 6.10-6.01 (m, 1H, CH=), 5.77-5.68 (m, 1H, CH=), 5.48–5.41 (m, 2H, CH_2=), 5.15–5.08 (m, 2H, CH_2=), 3.58 (s, 2H, NC<u>H</u>$_2$CH=), 2.93 (s, 2H, NC<u>H</u>$_2$CH$_2$), 2.62–2.60 (m, 2H, NCH$_2$C<u>H</u>$_2$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 132.53, 127.78, 124.14, 118.60, 49.65, 45.61, 30.08 ppm. **NMR spectra coincide with the literature data [7].**

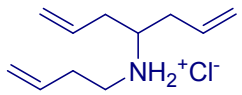
N-Allyl-*N*-(2,2-dimethyl-3-butenyl)amine hydrochloride (2d)



To a solution of allylamine (0.114 g, 0.15 ml, 2.0 mmol) in MeOH (0.6 ml) was added 37% formaldehyde (74 μL, 1.0 mmol) and the solution was left for 20 min followed by addition of **1b** adduct (0.105 g, 0.4 mmol). After 30 min, the reaction mixture was heated on the water bath for 1 h at 40 °C to complete the reaction. The volatiles were removed under reduced pressure and the residue was treated with 20% NaOH, extracted with Et_2O/*n*-pentane (3:1)., extracts were dried with K_2CO_3, evaporated and the product was dissolved in Et_2O and transferred to hydrochloride by addtion of 4M HCl in dioxane (0.3 ml, 1.2 mmol). The mixture was evaporated, triturated in Et_2O. The precipitate was filtered, washed with Et_2O and dried in vacuum to give **2d** (139 mg, 79%) as white powder, m.p. 135-136 °C. ^{1}H NMR (400 MHz,

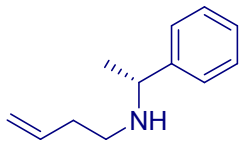
$CDCl_3$): δ 9.19 (br. s, 2H, NH_2), 6.07 (ddt, *J* = 14.2, 10.4, 7.0 Hz, 1H, $CH=_{allyl}$), 5.83 (dd, *J* = 17.4, 10.8 Hz, 1H, $CH=_{prenyl}$), 5.45–5.33 (m, 2H, $CH_2=_{allyl}$), 5.18–5.05 (m, 2H, $CH_2=_{prenyl}$), 3.62 (d, *J* = 6.8 Hz, 2H, CH_2N_{allyl}), 2.70 (s, 2H, CH_2N_{prenyl}), 1.19 (s, 6H, 2Me) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.98, 128.30, 124.29, 115.16, 55.87, 51.05, 36.42, 25.18 2C. Anal. Calcd for $C_9H_{18}ClN$ (175.7): C, 61.52; H, 10.33; N, 7.97; found: C, 61.48; H, 10.34; N, 7.93.

N-(But-3-enyl)hepta-1,6-dien-4-amine hydrochloride (2e)



The reaction was performed following the procedure described for **2d**. Hepta-1,6-dien-4-amine (0.56 g, 5.0 mmol), **1a** (0.39 g, 2.2 mmol), 37% CH_2O (0.48 g, 0.44 ml, 6.0 mmol) in MeOH (1.8 ml) that gave **2e** (0.81 g, 80%) as white powder, m.p. 72-73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (br. s, 2H, NH_2), 5.81 (ddt, *J* = 17.3, 10.4, 7.1 Hz, 2H, 2CH=), 5.71 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H, CH=), 5.19-5.15 (m, 4H, $2CH_2$=), 5.13-5.05 (m, 2H, CH_2=), 3.19 (s, 1H, CHN), 3.00 (s, 2H, CH_2N), 2.73–2.62 (m, 4H, $(C\underline{H}_2)_2CHN$), 2.53 (dt, *J* = 14.7, 7.4 Hz, 2H, $C\underline{H}_2CH_2N$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 132.79, 132.03 2C, 120.04 2C, 118.31, 57.14, 44.53, 34.53 2C, 30.10 ppm. Anal. Calcd for $C_{11}H_{20}ClN$ (201.74): C, 65.49; H, 9.99; N, 6.94; found: C, 65.51; H, 9.94; N, 6.97.

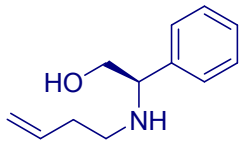
(*R*)-*N*-(-1-Phenylethyl)but-3-en-1-amine (2f)



To a solution (*R*)-1-phenylethylamine (0.121 g, 0.128 ml, 1.0 mmol) in MeOH (0.5 ml) was added 37% formaldehyde (81 μL, 1.1 mmol) and DABCO (0.11 g, 1.0 mmol) then the mixture was left for 20 min followed by the addition of adduct **1a** (68 mg, 0.38 mmol). The reaction mixture was stirred for 1 h at 25 °C and 1 h at 40 °C, the progress of the reaction was monitored by NMR. After completion all volatiles were removed under reduced pressure and the residue was treated with 20% NaOH, extracted with Et_2O/*n*-pentane (3:1), extracts were washed with water, dried with K_2CO_3, evaporated and the residual oil was subjected to chromatography (*n*-hexane/EtOAc, 1:1) that afford **2f** (0.146 g, 82%) as oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.29 (m, 4H, Ph), 7.28–7.21 (m, 1H, Ph), 5.76 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H, CH=), 5.14–4.98 (m, 2H, CH_2=), 3.77 (q, *J* = 6.6 Hz, 1H, CHPh), 2.63–2.47 (m, 2H, CH_2N), 2.24 (q, *J* = 6.7 Hz, 2H, CH_2CH=), 1.36 (d, *J* = 6.6 Hz, 4H, Me and NH) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ

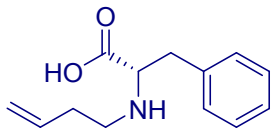
145.80, 136.60, 128.45 2C, 126.89, 126.60 2C, 116.35, 58.29, 46.75, 34.41, 24.41 ppm. **NMR spectra coincide with the literature data [8].**

(*R*)-2-(But-3-enylamino)-2-phenylethanol (2g)



To a solution of (*R*)-phenylglycinol (0.137 g, 1.0 mmol) in MeOH (0.5 ml) was added 37% formaldehyde (81 μL, 1.1 mmol) with stirring, after 2 min (before starting of precipitation) **1a** (68 mg, 0.38 mmol) was added. The reaction mixture was heated at 50 °C for 1h, and then evaporated under reduced pressure. To the oily residue 5% NaOH was added and extracted with *n*-hexane (5 ml x 3). The combined extracts were washed with 10% NaOH, dried with K_2CO_3 and evaporated to dryness to give pure amine **2g** (0.153 g, 80%) as oil, which was crystallized upon cooling, m.p. 55-56 °C, $[\alpha]_D^{25}$–63.9 (C, 1.5 in $CHCl_3$) [lit. **[9]** m.p. 46-48 °C, $[\alpha]_D^{25}$ –57.4 (C, 1.5 in $CHCl_3$); **[10]** m.p. 46 °C, $[\alpha]_D^{25}$ –64.9 (C, 0.5 in $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.34 (m, 2H, Ph), 7.34–7.27 (m, 3H, Ph), 5.78 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H, CH=), 5.14–5.03 (m, 2H, CH_2=), 3.80 (dd, *J* = 8.7, 4.3 Hz, 1H, CHN), 3.73 (dd, *J* = 10.8, 4.4 Hz, 1H, $C\underline{H}_AH_BOH$), 3.58 (dd, *J* = 10.8, 8.8 Hz, 1H, $CH_A\underline{H}_BOH$), 2.70–2.52 (m, 2H, CH_2N), 2.27 (q, *J* = 6.8 Hz, 2H, CH_2CH=) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.68, 136.35, 128.65, 127.60, 127.29, 116.59, 66.69, 64.66, 46.37, 34.34. **NMR spectra coincide with the literature data [9, 10].**

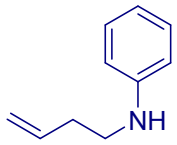
(*S*)-2-(But-3-enylamino)-3-phenylpropanoic acid (2h)



(*S*)-Phenylalanine (0.165 g, 1.0 mmol) was dissolved in MeOH (3.6 ml) containing MeONa (0.3 mmol) and Et_3N (0.21 g, 0.292 ml, 2.1 mmol), to this solution was added 37% formaldehyde (81 μL, 1.1 mmol) with stirring. After 10 min adduct **1a** (68 mg, 0.38 mmol) was added and the mixture was left for 3 h at 25 °C. Neutralization of excess of Et_3N was performed by addition of NH_4Cl solution, after that **2h** was precipitated of the solution. The precipitate was filtered washed successively with chilled aqueous MeOH and Et_2O to furnish pure aminoacid **2h** (0.208 g, 95%) as white crystals, m.p. 266 °C (sub.), $[\alpha]_D^{25}$ +28.9 (C, 1 in 6M HCl). ^{1}H NMR (400 MHz, D_2O/DCl): δ 6.75–6.53 (m, 5H, Ph), 5.09–5.00 (m, 1H, CH=), 4.48-4.41 (m, 2H, CH_2=),

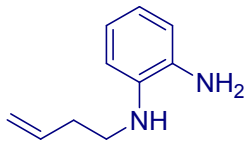
3.62 (t, J = 6.3 Hz, 1H, CHN), 2.65 (dd, J = 14.4, 5.8 Hz, 1H, C$\underline{H}_A$H$_B$Ph), 2.57 (dd, J = 14.3, 7.0 Hz, 1H, CH$_A$$\underline{H}_B$Ph), 2.46 (t, J = 7.3 Hz, 2H, CH$_2$N), 1.72 (q, J = 7.1 Hz, 2H, CH$_2$CH=) ppm. ^{13}C NMR (101 MHz, D$_2$O/DCl): δ 169.69, 132.98, 132.00, 128.86 2C, 128.64 2C, 127.52, 118.40, 60.24, 45.37, 34.21, 29.16 ppm. Anal. Calcd for $C_{13}H_{17}NO_2$ (219.28): C, 71.21; H, 7.81; N, 6.39; found: C, 71.25; H, 7.80; N, 6.39.

N-(But-3-enyl)benzenamine (2i)



To a solution of aniline (0.14 g, 1.5 mmol) in MeOH (0.6 ml) was added 37% solution of formaldehyde (0.118 ml, 0.129 g, 1.6 mmol), DABCO (0.17 g, 1.5 mmol) and after 20 min adduct **1a** (97 mg, 0.54 mmol) was added to the solution. The mixture was left for 30 min at 25 °C, and 1 h at 40 °C, after then evaporated under reduced pressure. The resulting oil was treated with 10% NaOH and extracted with *n*-pentane (5 ml x 3), dried with K_2CO_3, evaporated and purified by FC (R_f = 0.67, *n*-C_6H_{14}/EtOAc, 4:1) to give amine **2i** (0.196 g, 89%) as yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (t, J = 7.9 Hz, 1H, Ph), 6.80 (t, J = 7.3 Hz, 1H, Ph), 6.70 (d, J = 8.0 Hz, 1H, Ph), 5.92 (ddt, J = 17.0, 10.1, 6.8 Hz, 1H, CH=), 5.26-5.19 (m, 2H, CH$_2$=), 3.74 (br. s, 1H, NH), 3.26 (t, J = 6.7 Hz, 2H, CH$_2$N), 2.47 (q, J = 6.7 Hz, 1H, C$\underline{H}_2$CH=) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.33, 135.88, 129.32 2C, 117.42, 117.15, 112.96 2C, 42.86, 33.70 ppm. **NMR spectra coincide with the literature data [11].**

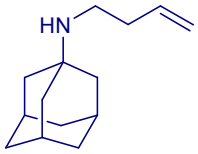
N-(But-3-enyl)benzene-1,2-diamine (2j)



The reaction was performed following the procedure described for **2f**. *o*-Phenylenediamine (0.108 g, 1.0 mmol), 37% formaldehyde (81 μL, 1.1 mmol), DABCO (0.11 g, 1.0 mmol), **1a** (68 mg, 0.38 mmol) and MeOH (0.6 ml). According to ^{1}H NMR the reaction mixture consisted of **2j**:1,2-di(homoallylamine)-derivative in ratio 4.2:1. The mixture was separated by FC (R_f = 0.21, *n*-C_6H_{14}/EtOAc, 4:1) to give **2j** (97 mg, 60%) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96–6.89 (m, 1H, Ph), 6.82–6.73 (m, 3H, Ph), 5.94 (ddt, J = 17.0, 10.2, 6.8 Hz, 1H, CH=), 5.31–5.16 (m, 2H, CH$_2$=), 3.39 (br. s, 3H, NH$_2$ and NH), 3.24 (t, J = 6.8 Hz, 2H, CH$_2$N), 2.50 (q,

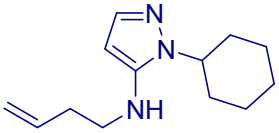
J = 6.7 Hz, 2H, C$\underline{H}_2$CH=) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.71, 135.98, 134.21, 120.60, 118.50, 116.91, 116.38, 111.71, 43.06, 33.74 ppm. **NMR spectra coincide with the literature data [12].**

N-(3-Butenyl)-1-adamantanamine (2k)



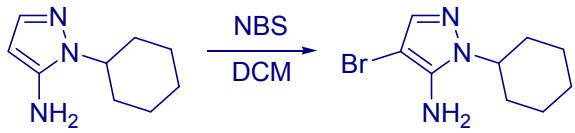
The reaction was performed following the procedure described for **2f**. 1-Adamantaneamine (0.151 g, 1.0 mmol), 37% formaldehyde (81 μL, 1.1 mmol), DABCO (0.11 g, 1.0 mmol), **1a** (68 mg, 0.38 mmol) and MeOH (0.6 ml). The mixture was separated by FC in EtOAc to give **2k** (80 mg, 39%) as oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.74 (ddt, J = 17.2, 10.2, 6.8 Hz, 1H, CH=), 5.07 (dd, J = 17.2, 1.6 Hz, 1H, C$\underline{H}_A$H$_B$=), 5.00 (dd, J = 10.3, 0.8 Hz, 1H, CH$_A\underline{H}_B$=), 2.62 (t, J = 7.0 Hz, 2H, CH_2N), 2.19 (q, J = 7.0 Hz, 2H, CH_2CH=), 2.03 (s, 3H, 3CH(Ad)), 1.69–1.52 (m, 12H, 6CH_2(Ad)), 1.06 (br. s, NH) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.85, 116.33, 50.33, 42.87 3C, 39.47, 36.86 3C, 35.22, 29.67 3C ppm. Anal. Calcd for $C_{14}H_{23}N$ (205.34): C, 81.89; H, 11.29; N, 6.82; found: C, 81.85; H, 11.42; N, 6.69.

N-(But-3-en-1-yl)-1-cyclohexyl-1*H*-pyrazol-5-amine (2l)



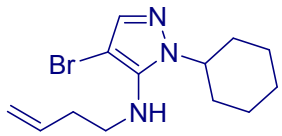
The reaction was performed following the procedure described for **2f**. 1-Cyclohexyl-1*H*-pyrazol-5-amine (0.165 g, 1.0 mmol), 37% formaldehyde (81 μL, 1.1 mmol), DABCO (0.11 g, 1.0 mmol), **1a** (68 mg, 0.38 mmol) and MeOH (0.6 ml). The mixture was separated by FC (*n*-C_6H_{14}/EtOAc, 1:1) to give **2l** (0.136 g, 62%) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 1H, Pyr), 5.80 (ddt, J = 17.1, 10.2, 6.9 Hz, 1H, CH=), 5.44 (s, 1H, Pyr), 5.16–5.07 (m, 2H, CH_2=), 3.73 (ddd, J = 15.1, 9.9, 5.1 Hz, 1H, CHN), 3.31 (s, 1H, NH), 3.12 (q, J = 6.3 Hz, 2H, CH_2N), 2.37 (q, J = 6.4 Hz, 2H, CH_2CH=), 1.93–1.78 (m, 6H, 3CH_2), 1.68 (d, J = 12.5 Hz, 1H, C$\underline{H}_A$H$_B$), 1.42–1.16 (m, 3H, CH$_A\underline{H}_B$ and CH_2) ppm. Several signals are broaden and splitted, because of dynamic process in the molecule, ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.62, (138.11, 137.98), 135.56, 117.38, 88.33, (55.95, 55.85), 45.03, 33.71, 32.26 2C, 25.78 br. 2C, 25.36 ppm. Anal. Calcd for $C_{13}H_{21}N_3$ (219.33): C, 71.19; H, 9.65; N, 19.16; found: C, 71.00; H, 9.71; N, 18.99.

4-Bromo-1-cyclohexyl-1*H*-pyrazol-5-amine



To a chilled to 0 °C solution of 1-cyclohexyl-1*H*-pyrazol-5-amine (1.39 g, 8.45 mmol) in DCM (25 ml) NBS (1.58 g, 8.87 mmol) was added portionwise. The mixture was stirred for 2 h at rt. The reaction mixture was concentrated, dissolved in Et_2O/*n*-hexane and stirred with 10% NaOH (6 ml). Organic layer was washed with water and dried with K_2CO_3 and evaporated that give rise to solid residue which was recrystallized from EtOAc/*n*-hexane mixture to give bromopyrazole (1.47 g, 71%) as beige transparent crystals, m.p. 111-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (br. s, 1H, CH= Pyr), 3.90 (br. s, 1H, CH), 3.62 (br. s, 2H, NH_2), 1.90-1.73 (br. m, 7H, c-hexyl), 1.36 (br. m, 3H, c-hexyl) ppm. Several signals are broaden and splitted ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.05, (137.51 and 137.40), 78.49, 57.25, 32.13 br. 2C, 25.68 br. 2C, 25.25 br. ppm. Anal. Calcd for $C_9H_{14}BrN_3$ (244.13): C, 44.28; H, 5.78; N, 17.21; found: C, 44.39; H, 5.84; N, 17.18.

4-Bromo-*N*-(but-3-en-1-yl)-1-cyclohexyl-1*H*-pyrazol-5-amine (2m)



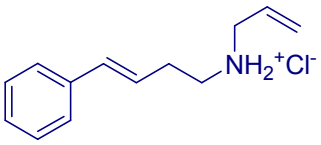
The reaction was performed following the procedure described for **2f**. 4-Bromo-1-cyclohexyl-1*H*-pyrazol-5-amine (0.794 g, 3.25 mmol), 37% formaldehyde (0.239 ml, 3.25 mmol), DABCO (0.39 g, 3.5 mmol), **1a** (0.21 g, 1.17 mmol) and MeOH (1.8 ml). The mixture was separated by FC (*n*-C_6H_{14}/EtOAc, 5:1) to give **2m** (0.268 g, 28%) as yellow oil and starting bromopyrazol (0.46 g, 58%) as solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 1H, Pyr), 5.81 (ddt, J = 17.1, 10.2, 6.8 Hz, 1H, CH=), 5.18-5.11 (m, 2H, CH_2=), 4.06 (tt, J = 10.4, 5.0 Hz, 1H, CHN), 3.14–2.99 (m, 3H, CH_2N and NH), 2.31 (q, J = 6.4 Hz, 2H, C$\underline{H}_2$CH=), 1.93–1.77 (m, 6H, 3CH_2), 1.69 (d, J = 12.4 Hz, 1H,C$\underline{H}_A$H$_B$), 1.44–1.16 (m, 3H, CH$_A\underline{H}_B$ and CH_2) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.30, 138.09, 135.36, 117.55, 84.22, 56.84, 48.10, 34.73, 32.72 2C, 25.83 2C, 25.30. Anal. Calcd for $C_{13}H_{20}BrN_3$ (298.23): C, 52.36; H, 6.76; N, 14.09; found: C, 52.64; H, 6.77; N, 13.97.

Synthesis of 2m through the bromination of 2l.

To a solution of *N*-butenylpyrazol **2l** (0.118 g, 0.54 mmol) in DCM (3 ml) cooled in an ice bath NBS (96 mg, 0.54 mmol) was added at 5 °C, after then cooling bath was removed and the

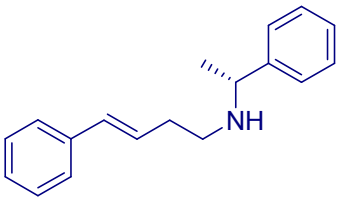
mixture was stirred at rt for 5 min. The progress of the reaction was monitored by TLC (EtOAc/*n*-C_6H_{14}, 1:5). In order to remove succinimide 20% NaOH was added and the mixture was vigorously stirred for 15 min. Organic layer was separated, washed with water, dried with K_2CO_3, evaporated and purified by FC to give bromide **2m** (0.148 g, 92%) as yellow oil.

trans-*N*-Allyl-4-phenylbut-3-en-1-amine hydrochloride (2n)

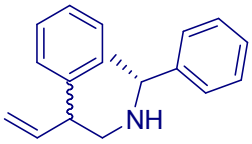


The reaction was performed following the procedure described for **2d**. Allylamine (0.114 g, 0.15 ml, 2.0 mmol), 37% formaldehyde (81 µL, 1.1 mmol), **1c** (0.285 g, 1.1 mmol) and MeOH (0.6 ml), the reaction mixture was stirred for 30 min at rt, after then evaporated under reduced pressure. The product was extracted with *n*-hexane, the combined extracts were washed with 20% NaOH, dried with K_2CO_3, evaporated. The residue was taken up in Et_2O (4 ml) and treated with HCl 3M in Et_2O (0.4 ml, 1.2 mmol), the separated oil gradually crystallized that give 2n (0.182 g, 74%) as white powder, m.p. 168-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (s, 2H, NH_2), 7.48–7.12 (m, 5H, Ph), 6.51 (dd, *J* = 15.8, 3.5 Hz, 1H, PhCH=), 6.29–5.98 (m, 2H, CH=$_{allyl}$and C<u>H</u>=CHPh), 5.62–5.39 (m, 2H, CH_2=), 3.64-3.61 (m, 2H, CH_2N_{allyl}), 3.04 (s, 2H, CH_2N), 2.82 (s, 2H, CH_2CH=) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.70, 133.60, 128.61 2C, 127.77, 127.65, 126.34 2C, 124.19, 123.92, 49.68, 45.97, 29.54 ppm. Anal. Calcd for $C_{13}H_{18}ClN$ (223.74): C, 69.79; H, 8.11; N, 6.26; found: C, 69.64; H, 7.94; N, 6.34.

(*R*,*E*)-4-Phenyl-*N*-(1-phenylethyl)but-3-en-1-amine (2o)



and a mixture of (2*S*)- and (2*R*)-2-phenyl-*N*-[(1*R*)-1-phenylethyl]-3-buten-1-amines (2p)



To a solution of (*R*)-1-phenylethylamine (0.121 g, 0.128 ml, 1.0 mmol) in MeOH (0.8 ml) was added 37% formaldehyde (81 µL, 1.1 mmol) and DABCO (0.11 g, 1.0 mmol) the mixture was

stirred for 20 min at rt, after then cooled to -20 °C followed by the addition of adduct **1c** (0.285 g, 1.1 mmol) with stirring for 1 h. All volatiles were removed under reduced pressure and the residue was treated with 10% NaOH, extracted with *n*-hexane, the combined extracts were washed with 3% NaOH, dried with K_2CO_3, evaporated and the residual oil was subjected to chromatography (EtOAc) that afford in upper fraction a mixture of diastereomers (2.5:1) **2p** (0.136 g, 54%) as oil, R_f = 0.6 (EtOAc) and in lower fraction amine **2o** (55 mg, 22%) as oil, R_f = 0.39 (EtOAc).

2o: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.22 (m, 10H, 2Ph), 6.48 (d, *J* = 15.9 Hz, 1H, PhCH=), 6.19 (dt, *J* = 15.9, 7.0 Hz, 1H, $CH_2C\underline{H}$=), 3.84 (q, *J* = 6.6 Hz, 1H, MeCH), 2.68 (ddd, *J* = 18.2, 11.5, 5.7 Hz, 1H, $C\underline{H}_AH_BN$), 2.64 (ddd, *J* = 18.2, 11.4, 5.8 Hz, 1H $CH_A\underline{H}_BN$), 2.43 (q, *J* = 6.7 Hz, 2H), 1.98 (br. s, 1H, NH), 1.41 (d, *J* = 6.6 Hz, 3H, Me) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): 145.57, 137.57, 131.66, 128.57 br. 4C, 128.29, 127.10 br. 4C, 126.71 br., 126.10 br., (58.44, 58.36), 47.12, 33.67, (24.61, 24.37, 24.12) ppm. HRMS (ESI): calcld for $C_{18}H_{21}N$ $[M+H]^+$ 252.1747; found: 252.1751.

2p: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.11 (m, 10H, 2Ph), 6.12–5.79 (m, 1H, CH=) 5.25–5.00 (m, 2H, CH_2=), 3.93–3.70 (m, 1H, PhCHN), 3.67–3.41 (m, 1H, PhCH), 2.92–2.68 (m, 2H, CH_2), 1.65 (br. s, 1H, NH), 1.38–1.35 (m, 3H, Me) ppm. HRMS (ESI): calcld for $C_{18}H_{21}N$ $[M+H]^+$ 252.1747; found: 252.1751.

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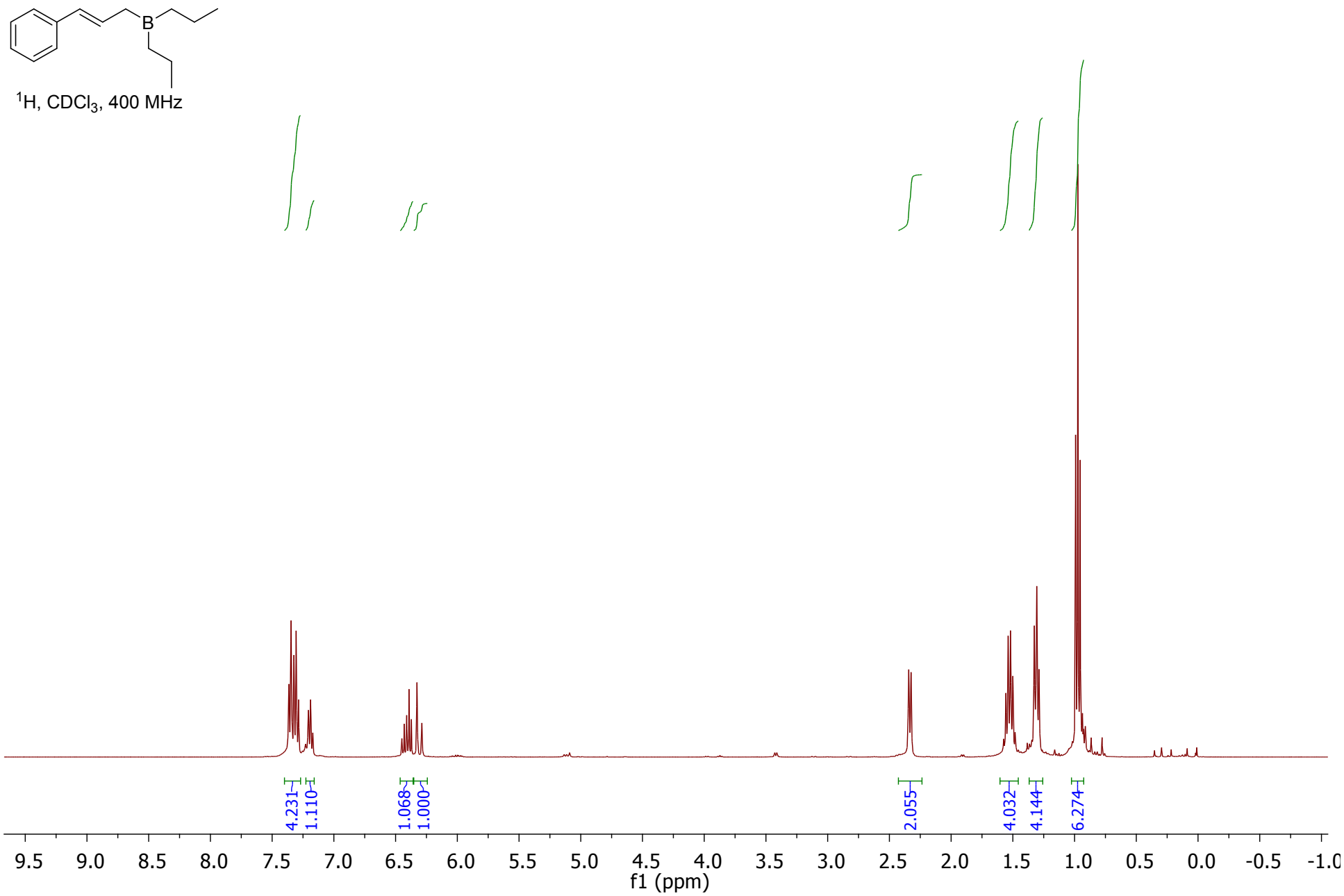
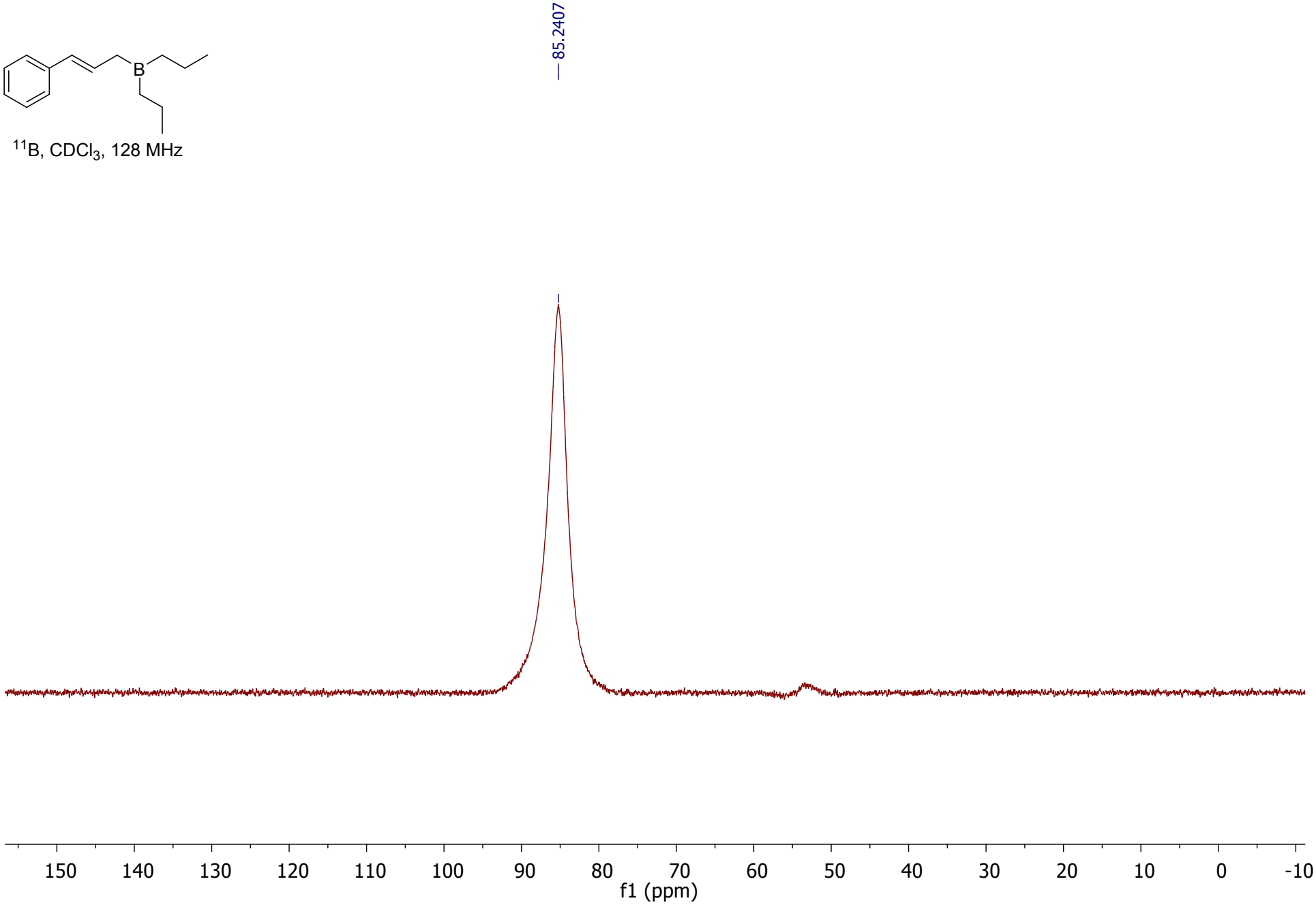
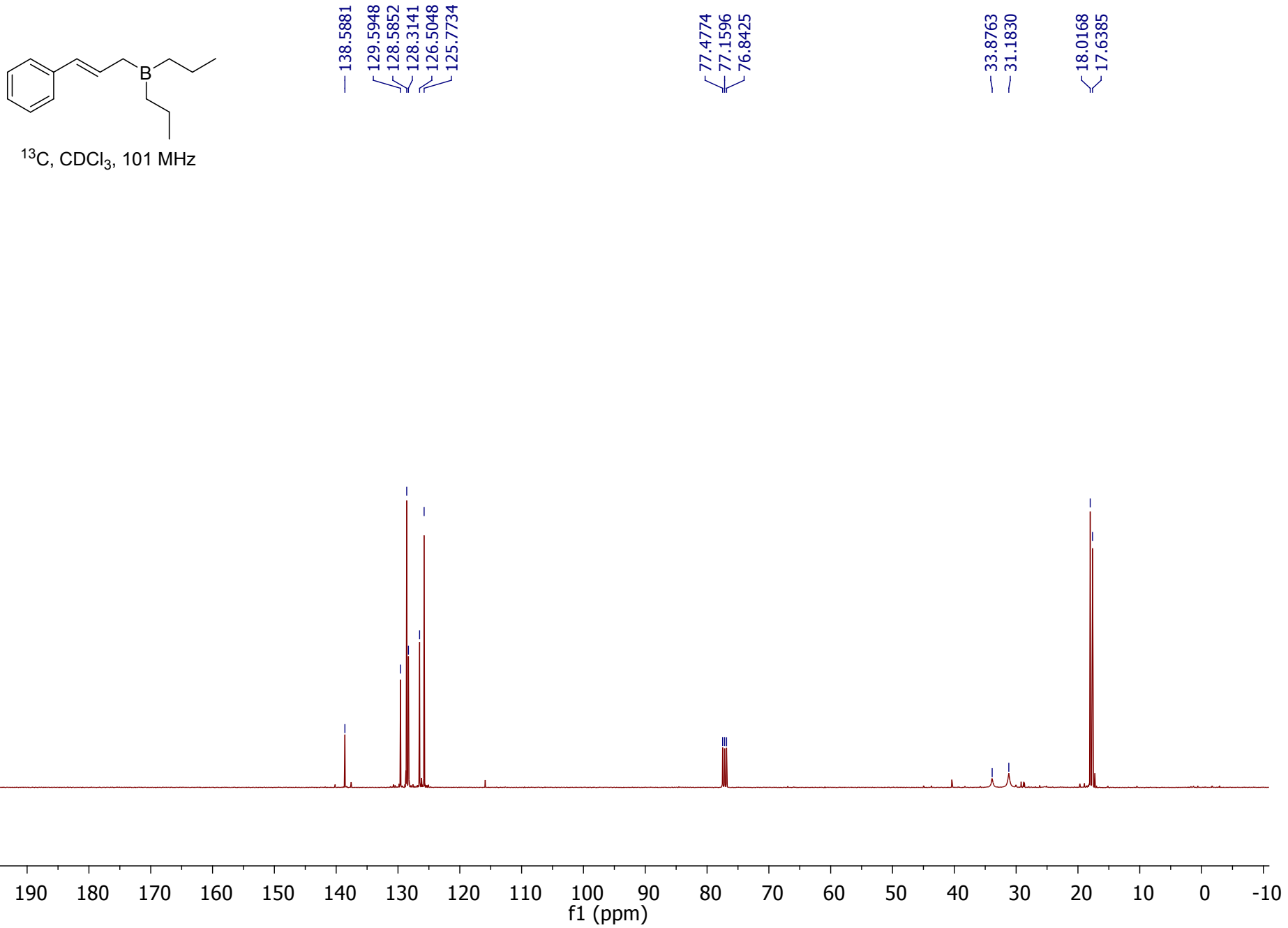

B
1H, CDCl3, 400 MHz
4.231
1.110
1.068
1.000
2.055
4.032
4.144
6.274
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



^{11}B, $CDCl_3$, 128 MHz


B
138.5881
129.5948
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128.3141
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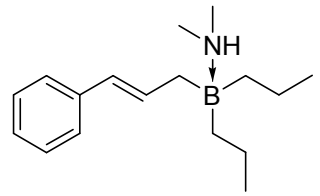
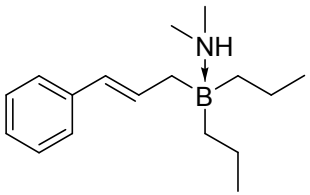
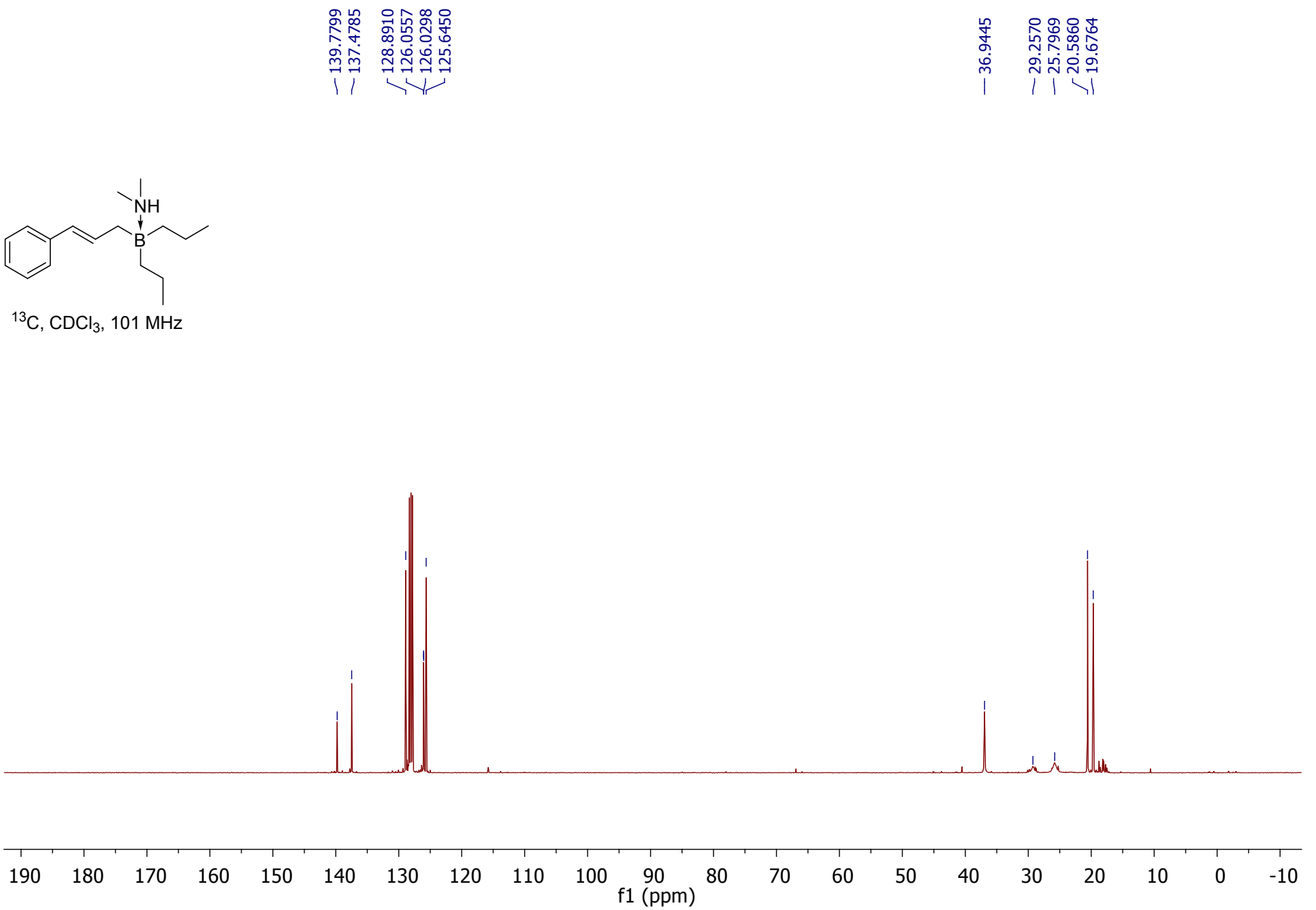
125.7734
77.4774
77.1596
76.8425
33.8763
31.1830
18.0168
17.6385
^{13}C, $CDCl_3$, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

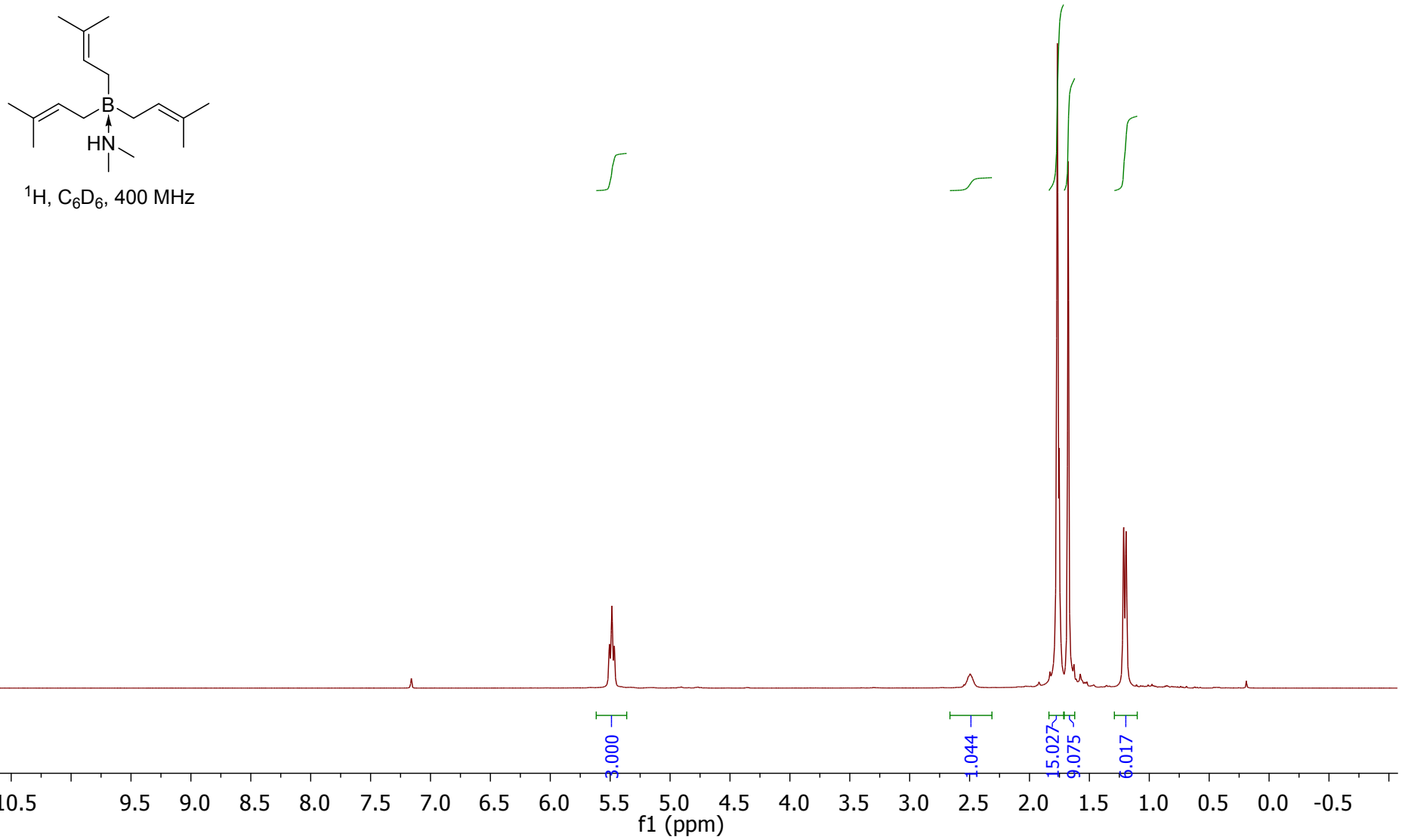


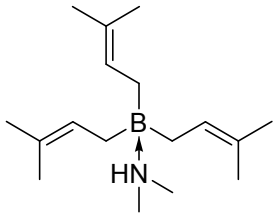
^{1}H, $CDCl_3$, 400 MHz



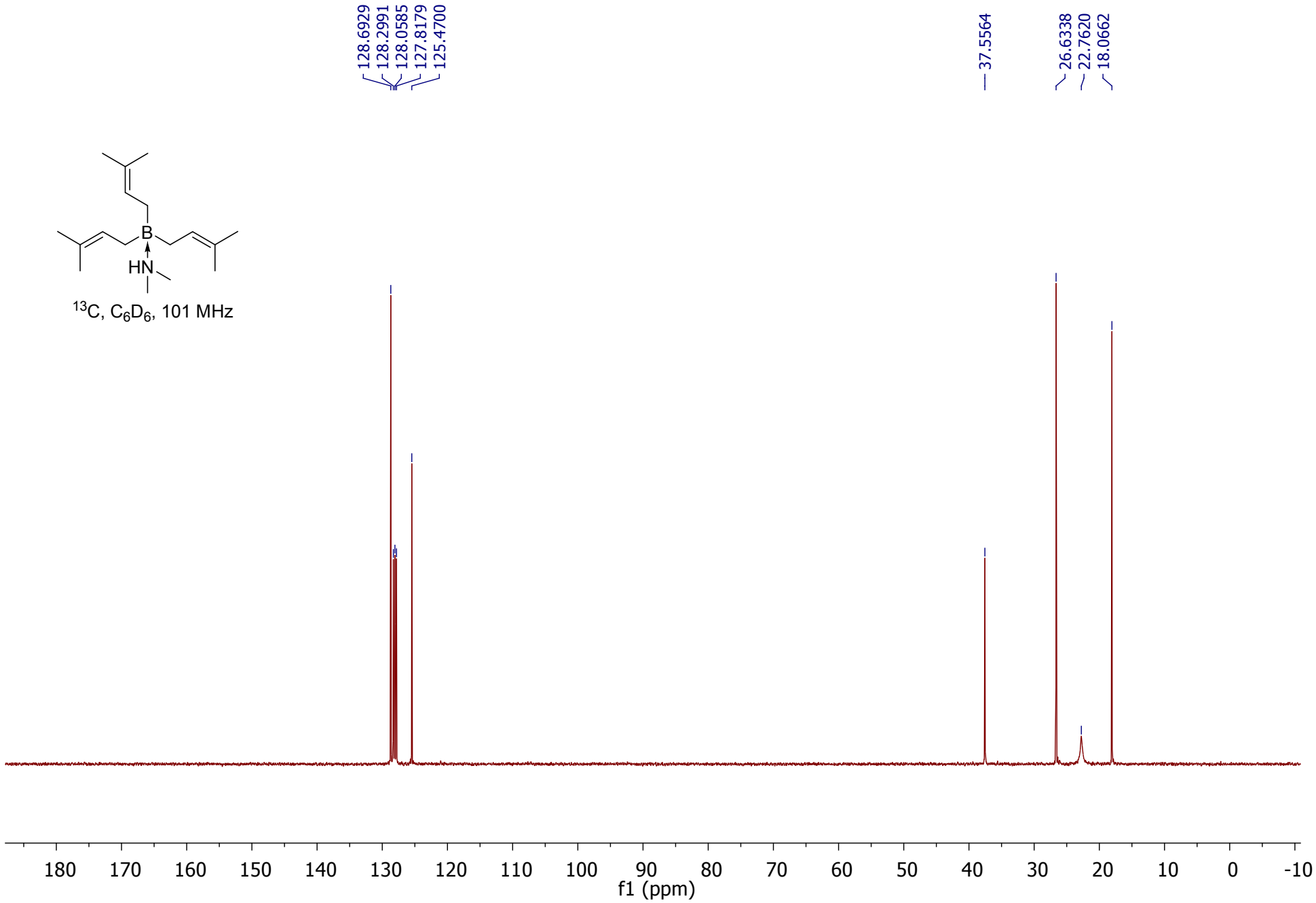
^{11}B, $CDCl_3$, 128 MHz

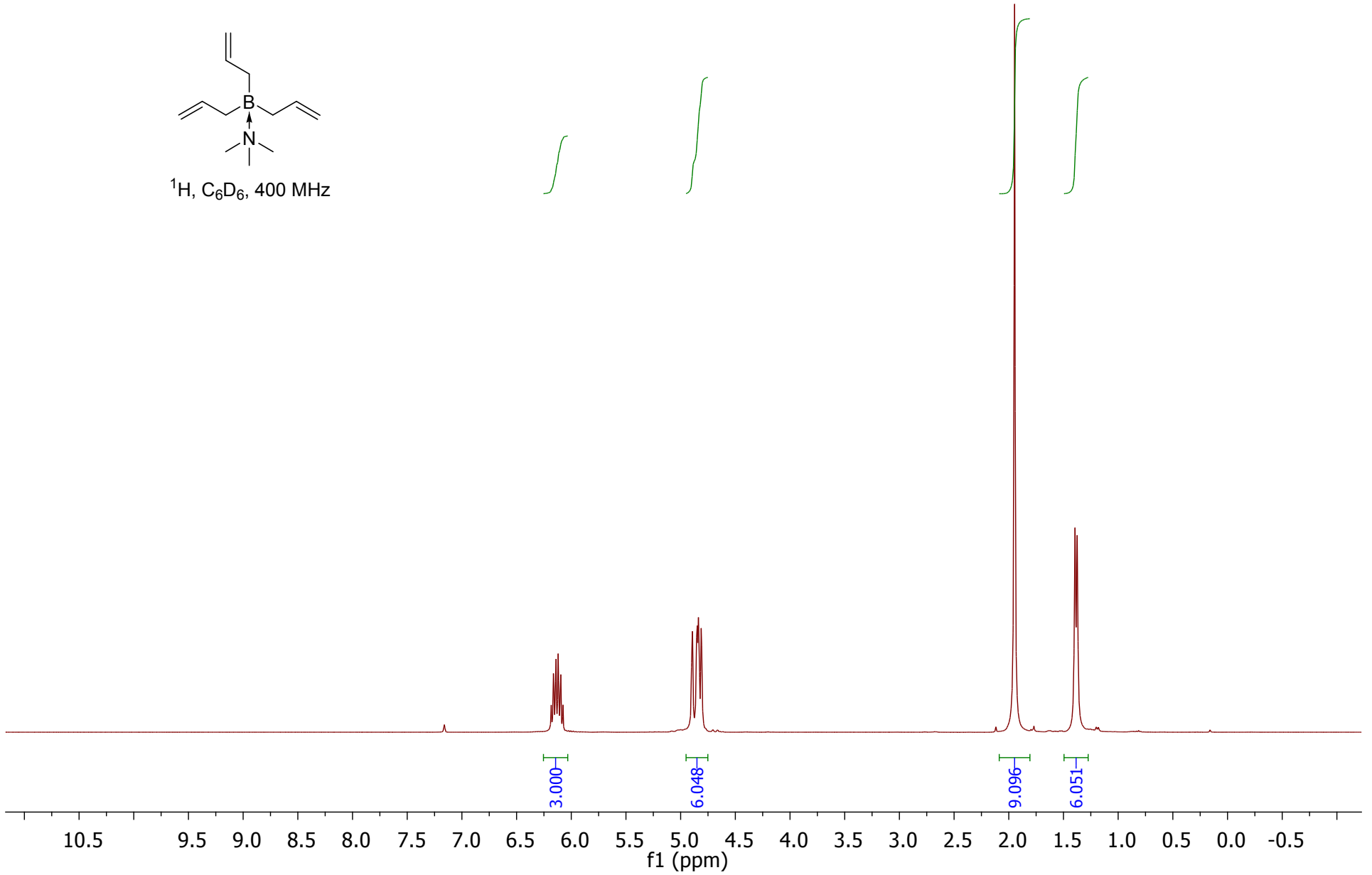

139.7799
137.4785
128.8910
126.0557
126.0298
125.6450
36.9445
29.2570
25.7969
20.5860
19.6764
NH
B
13C, CDCl3, 101 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

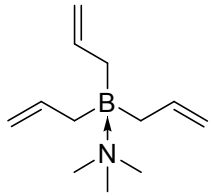

B
HN
1H, C6D6, 400 MHz
3.000
1.044
15.027
9.075
6.017
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



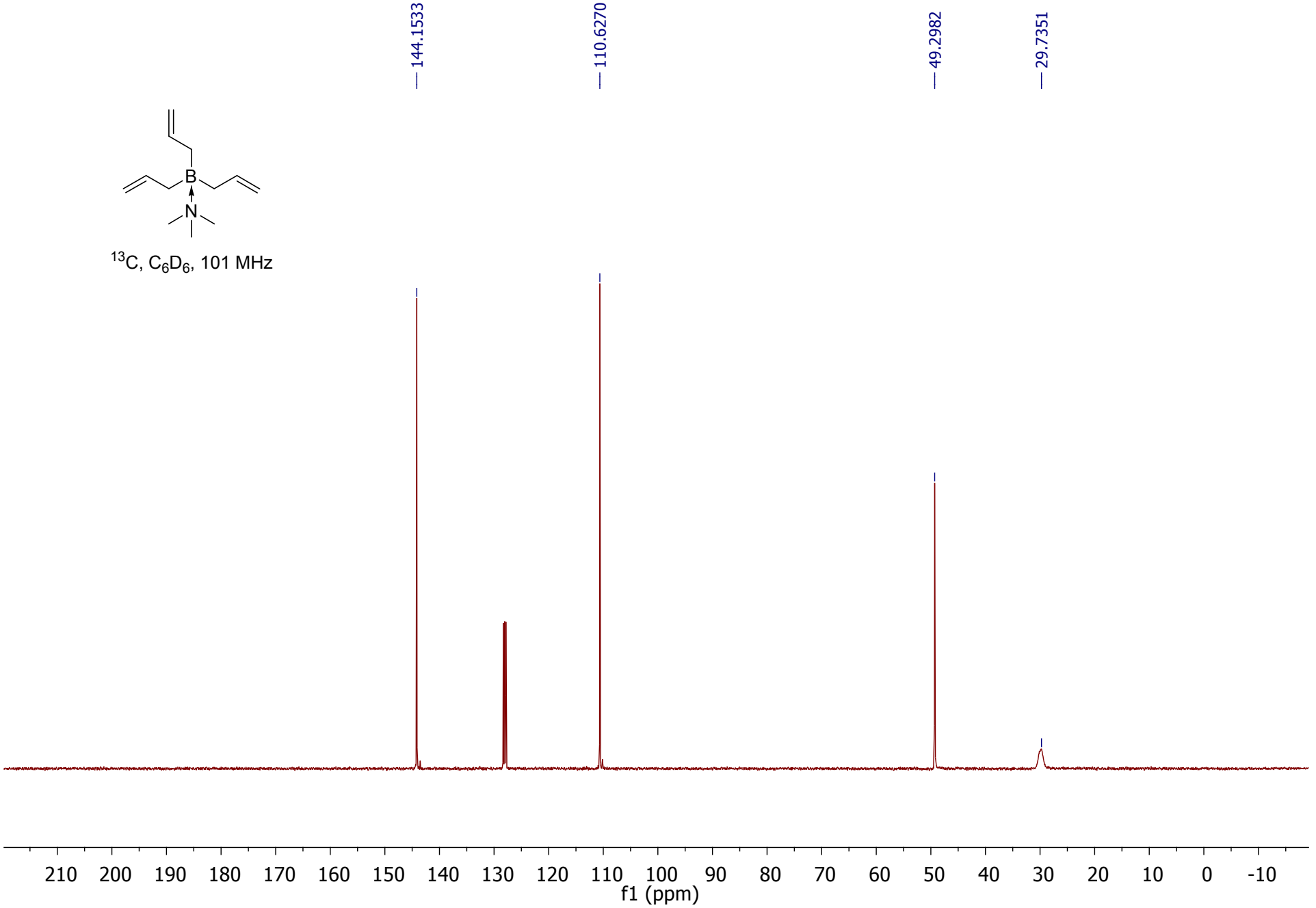
^{11}B, C_6D_6, 128 MHz

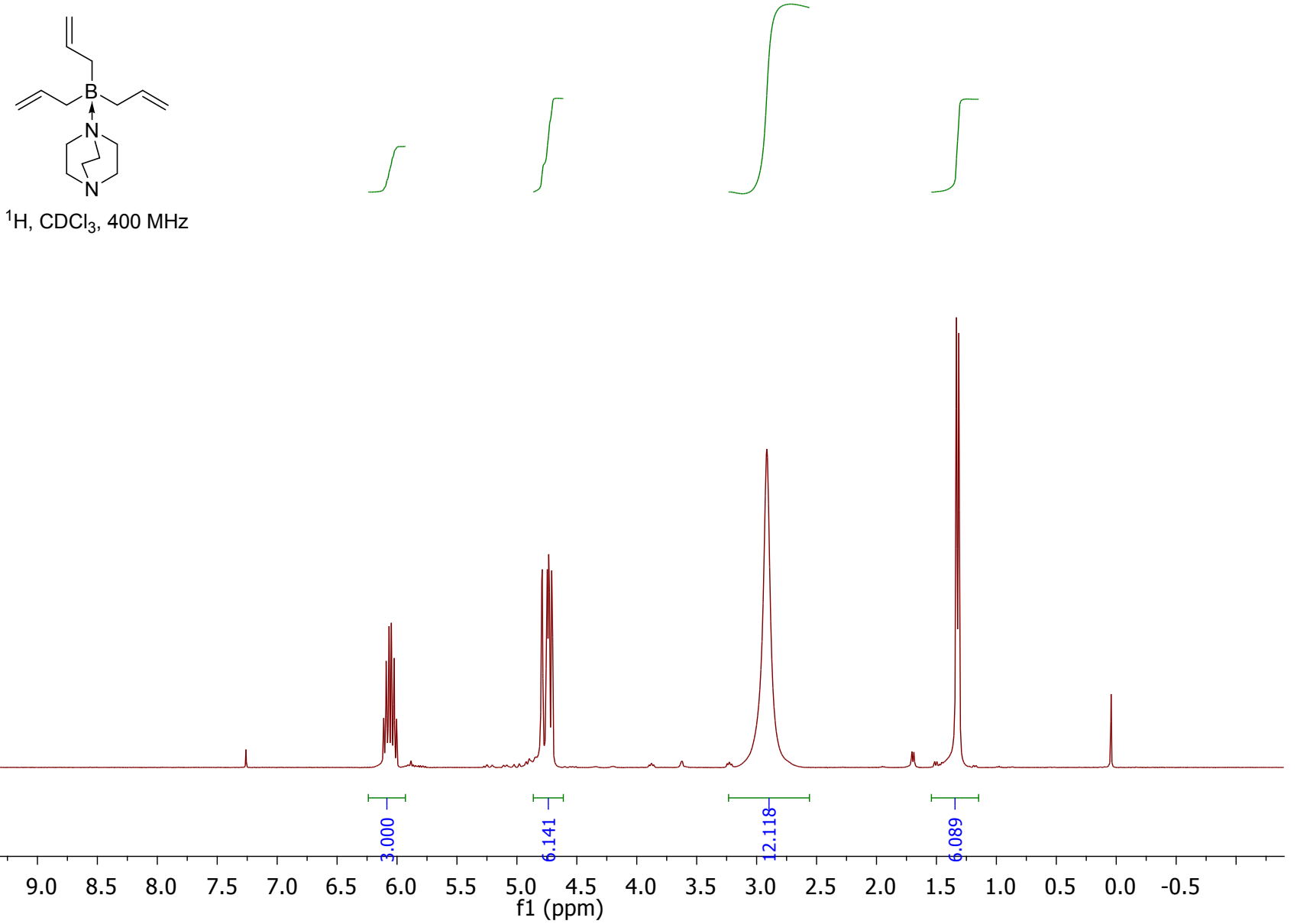

128.6929
128.2991
128.0585
127.8179
125.4700
37.5564
26.6338
22.7620
18.0662
B
HN
^{13}C, C_6D_6, 101 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

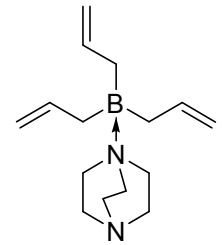

B
N
^{1}H, C_6D_6, 400 MHz
3.000
6.048
9.096
6.051
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



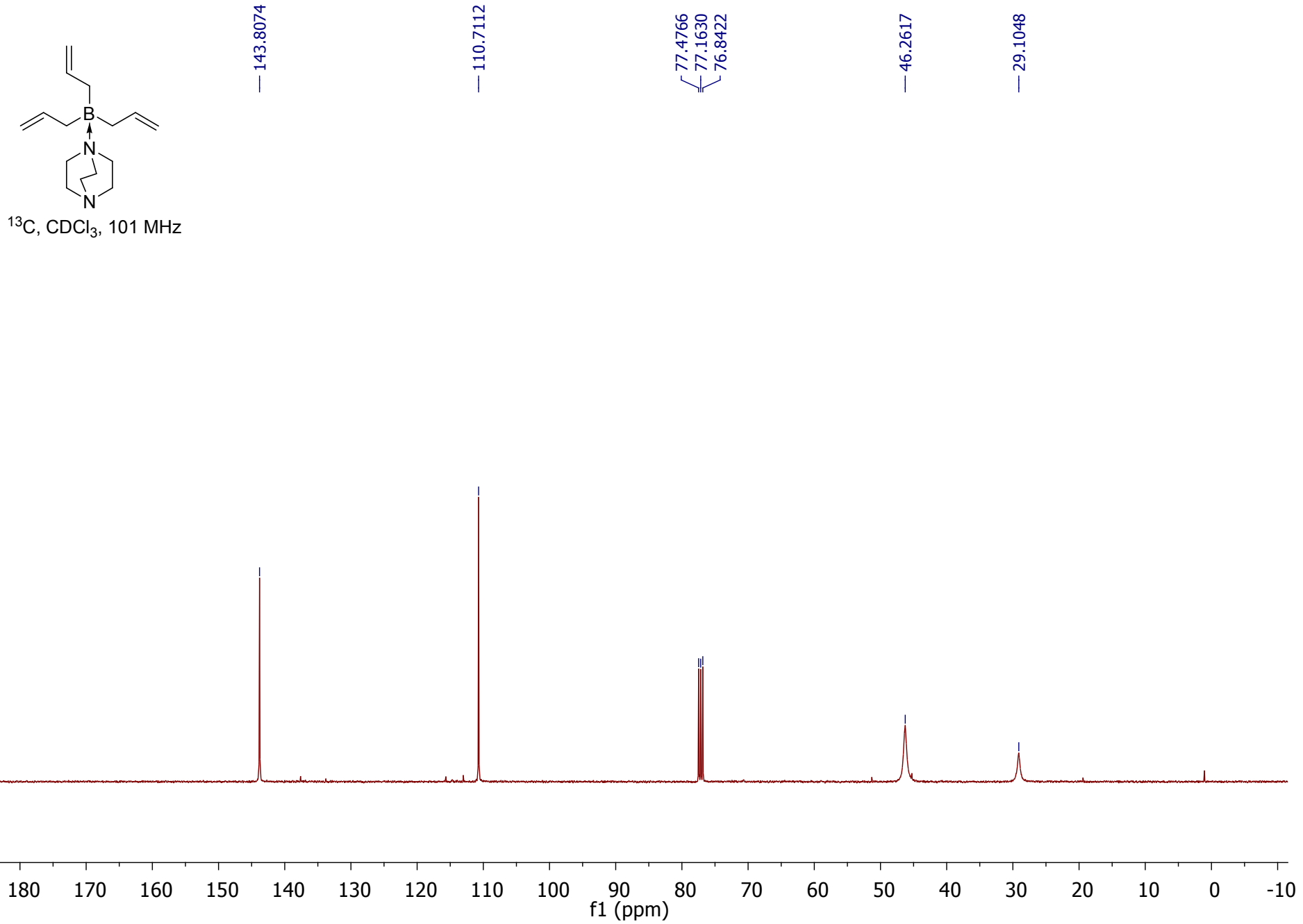
^{11}B, C_6D_6, 128 MHz

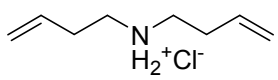

144.1533
110.6270
49.2982
29.7351
B
N
^{13}C, C_6D_6, 101 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


B
N
N
^{1}H, CDCl$_3$, 400 MHz
3.000
6.141
12.118
6.089
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

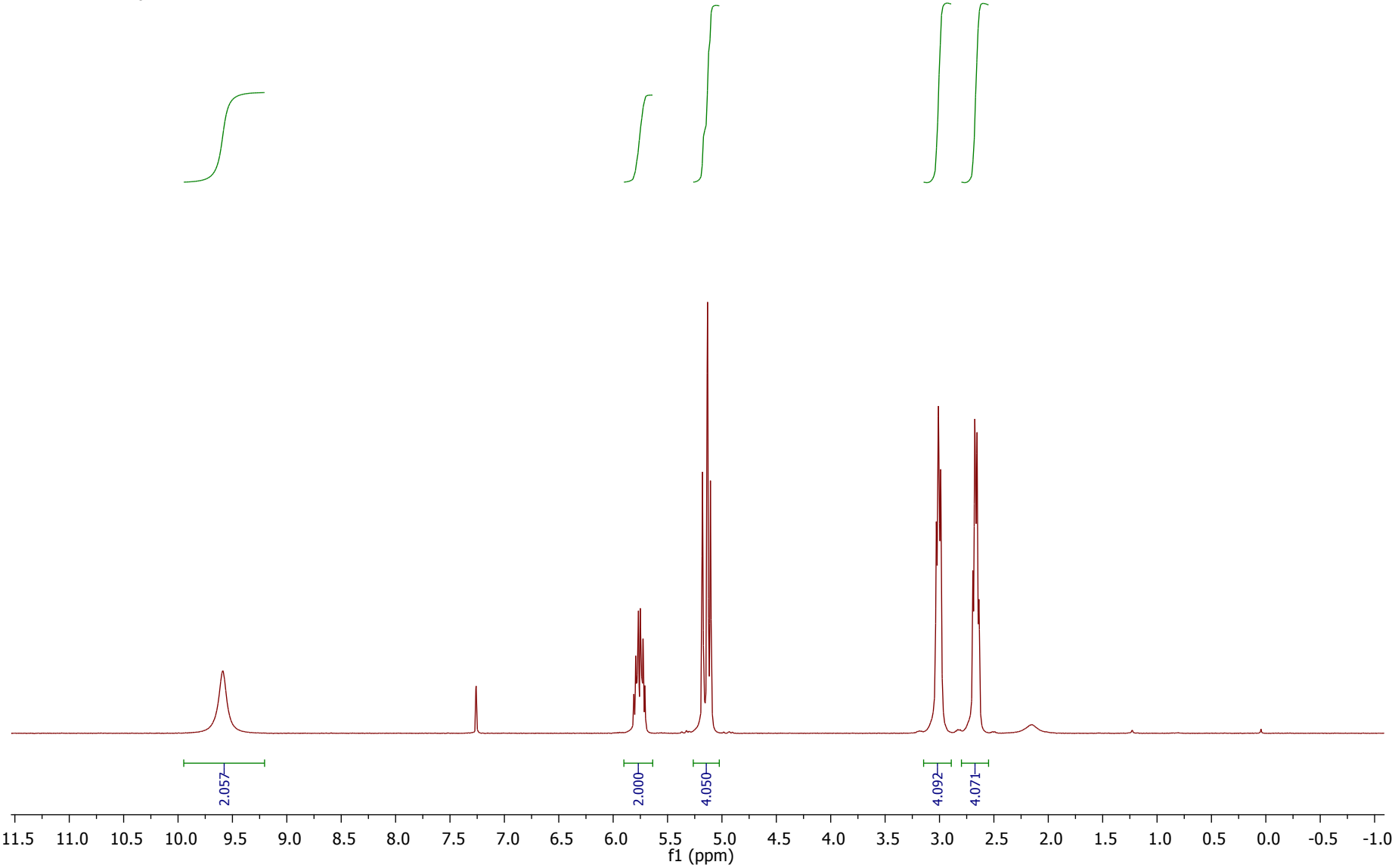


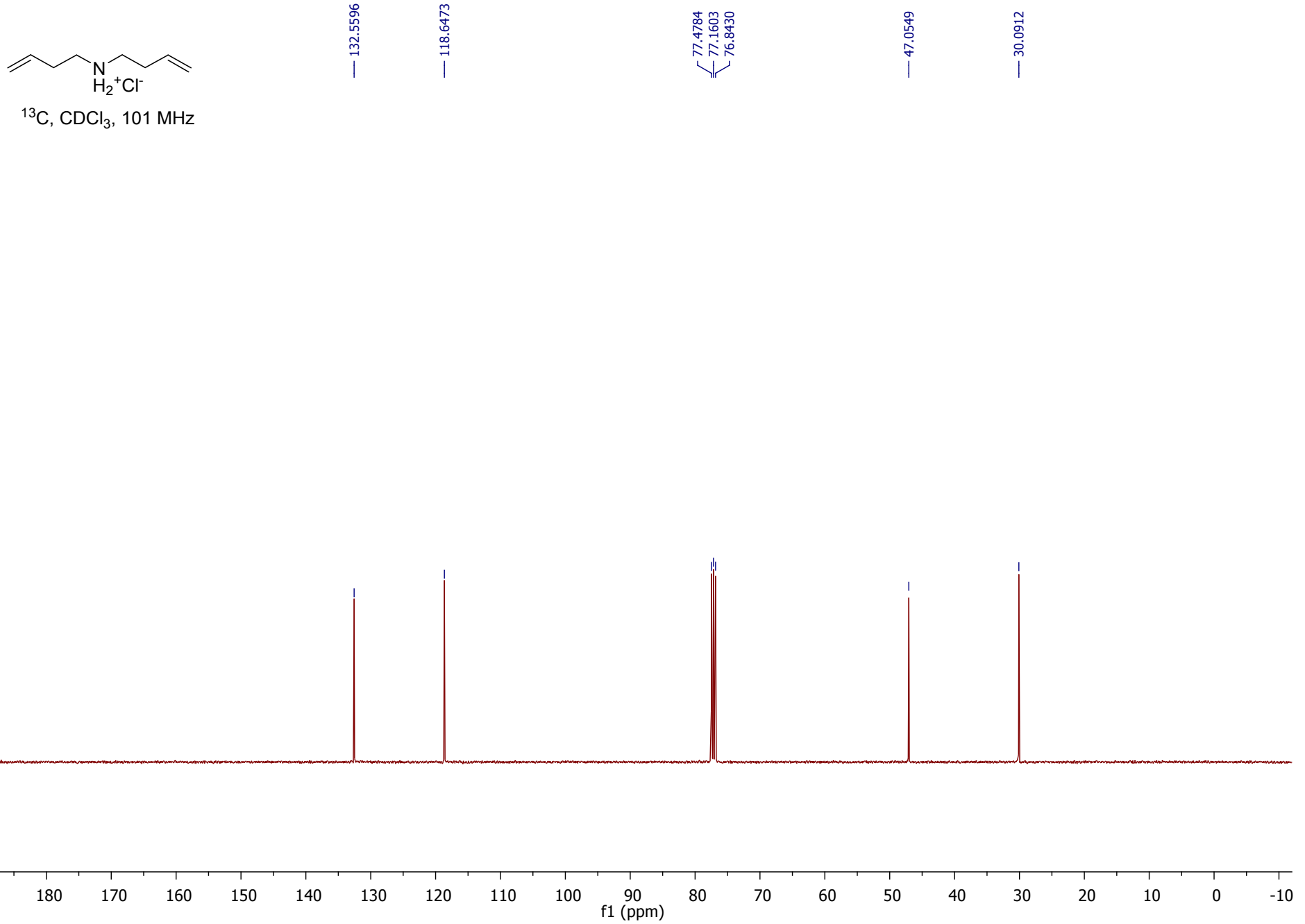
^{11}B, $CDCl_3$, 128 MHz

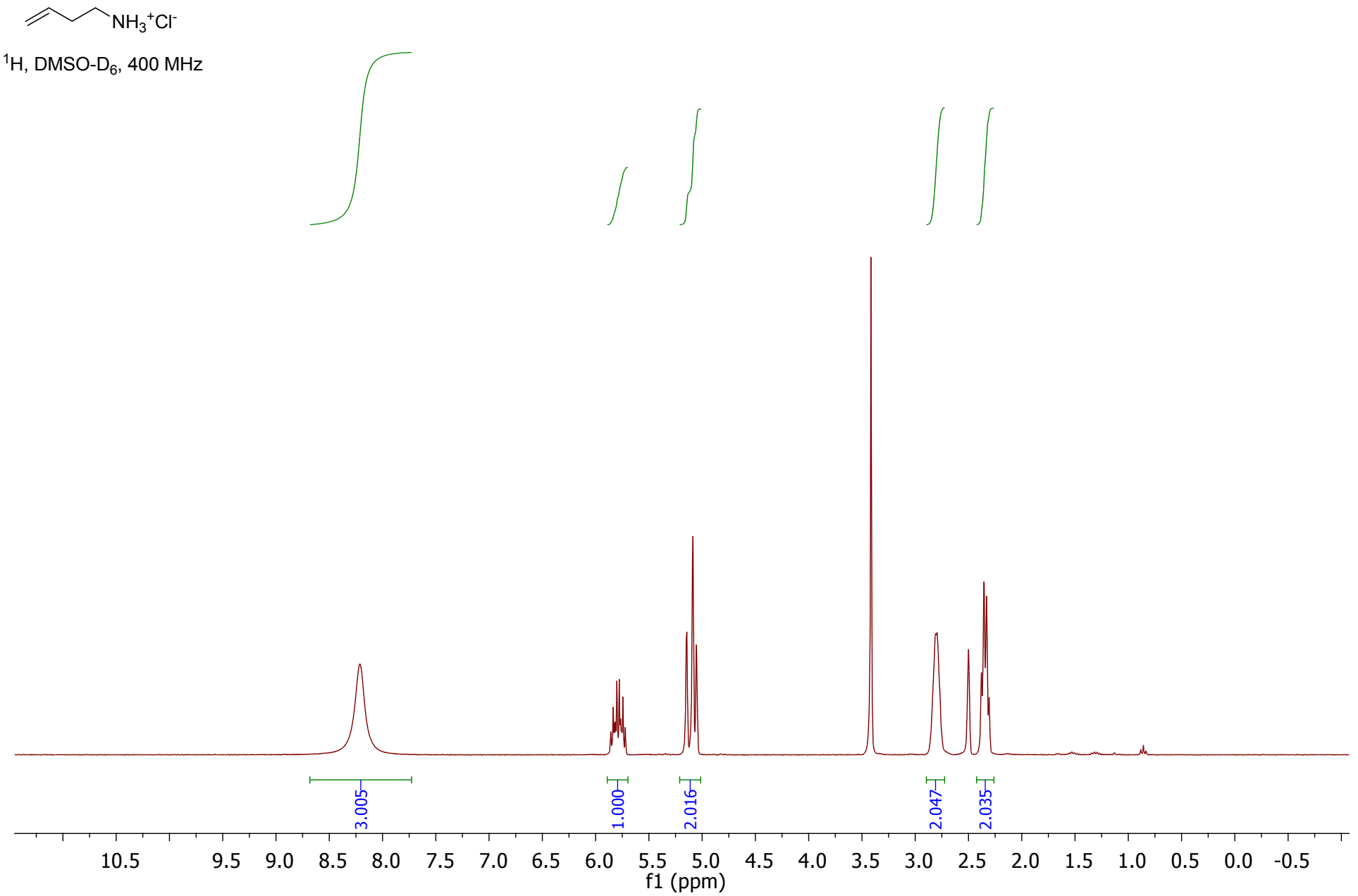

143.8074
110.7112
77.4766
77.1630
76.8422
46.2617
29.1048
B
N
N
^{13}C, $CDCl_3$, 101 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

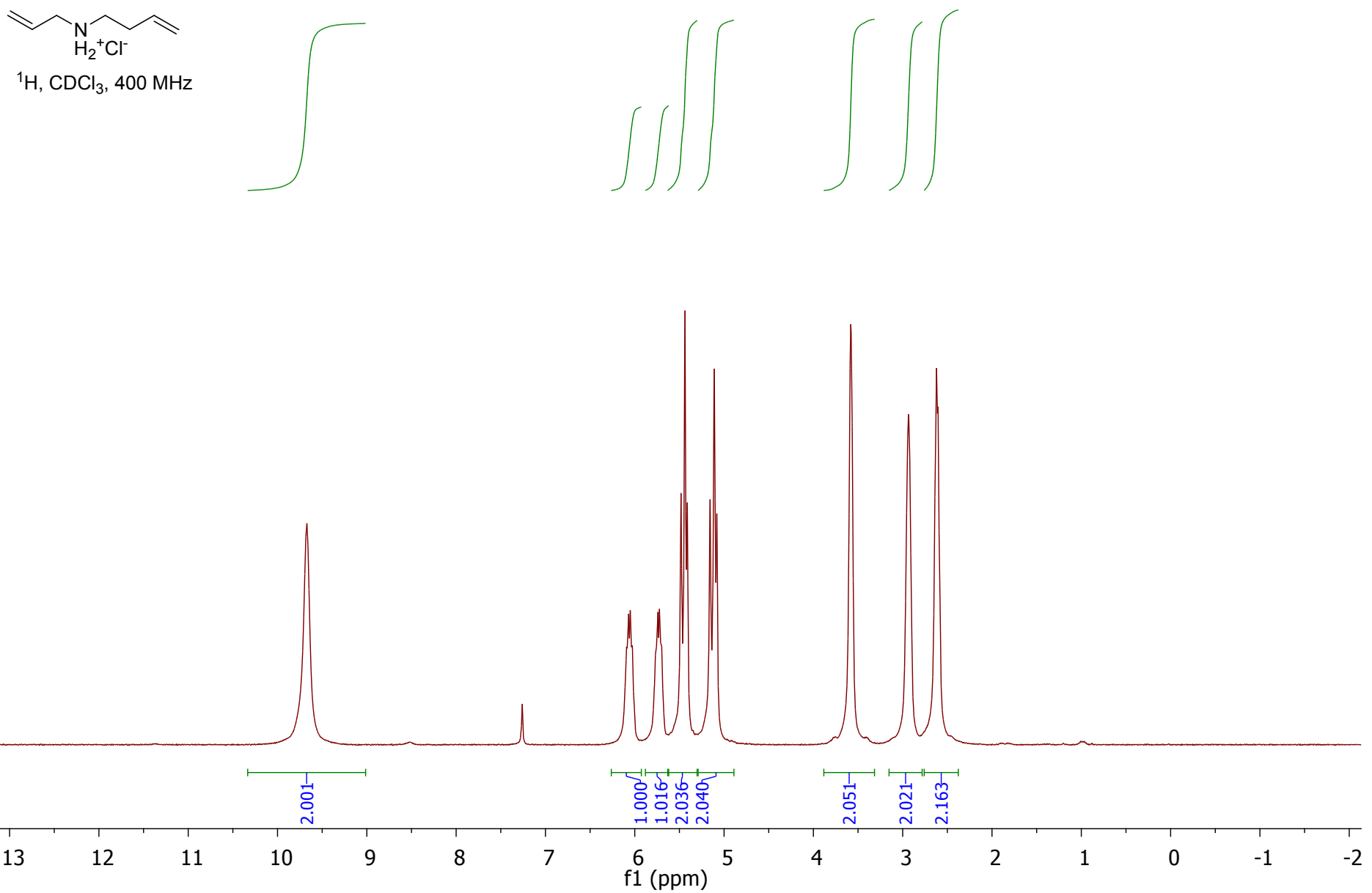


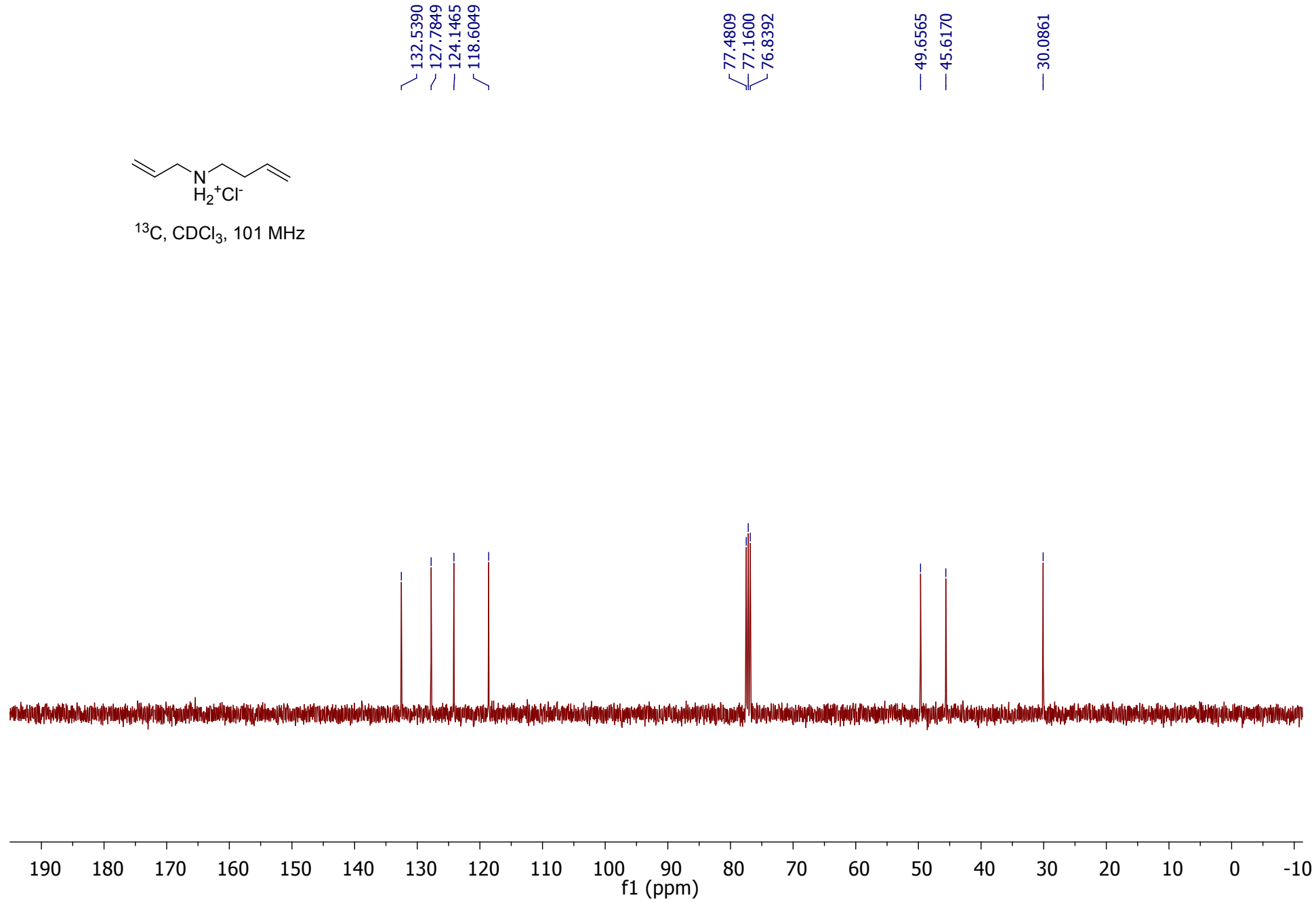
^1H, $CDCl_3$, 400 MHz

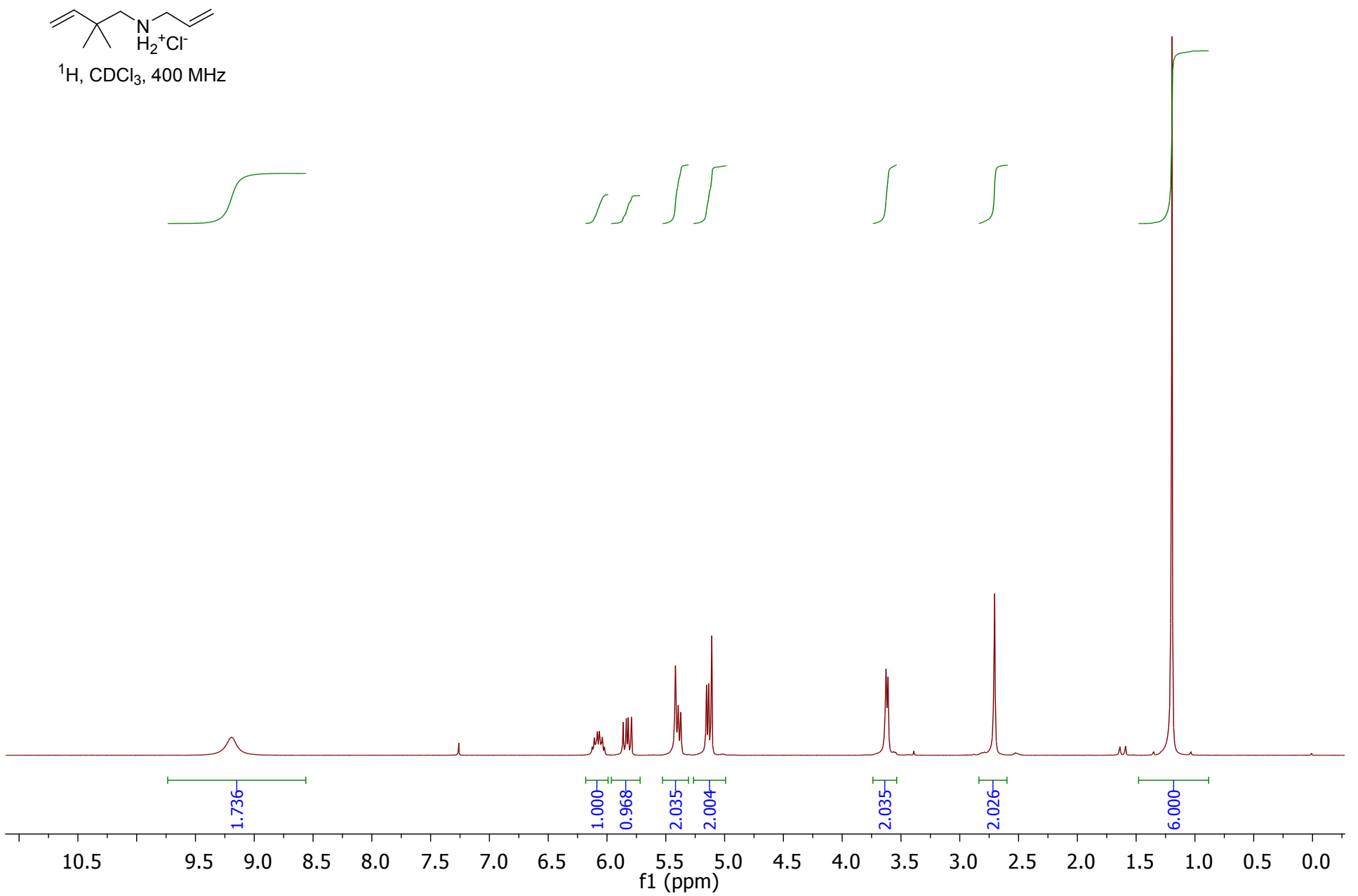


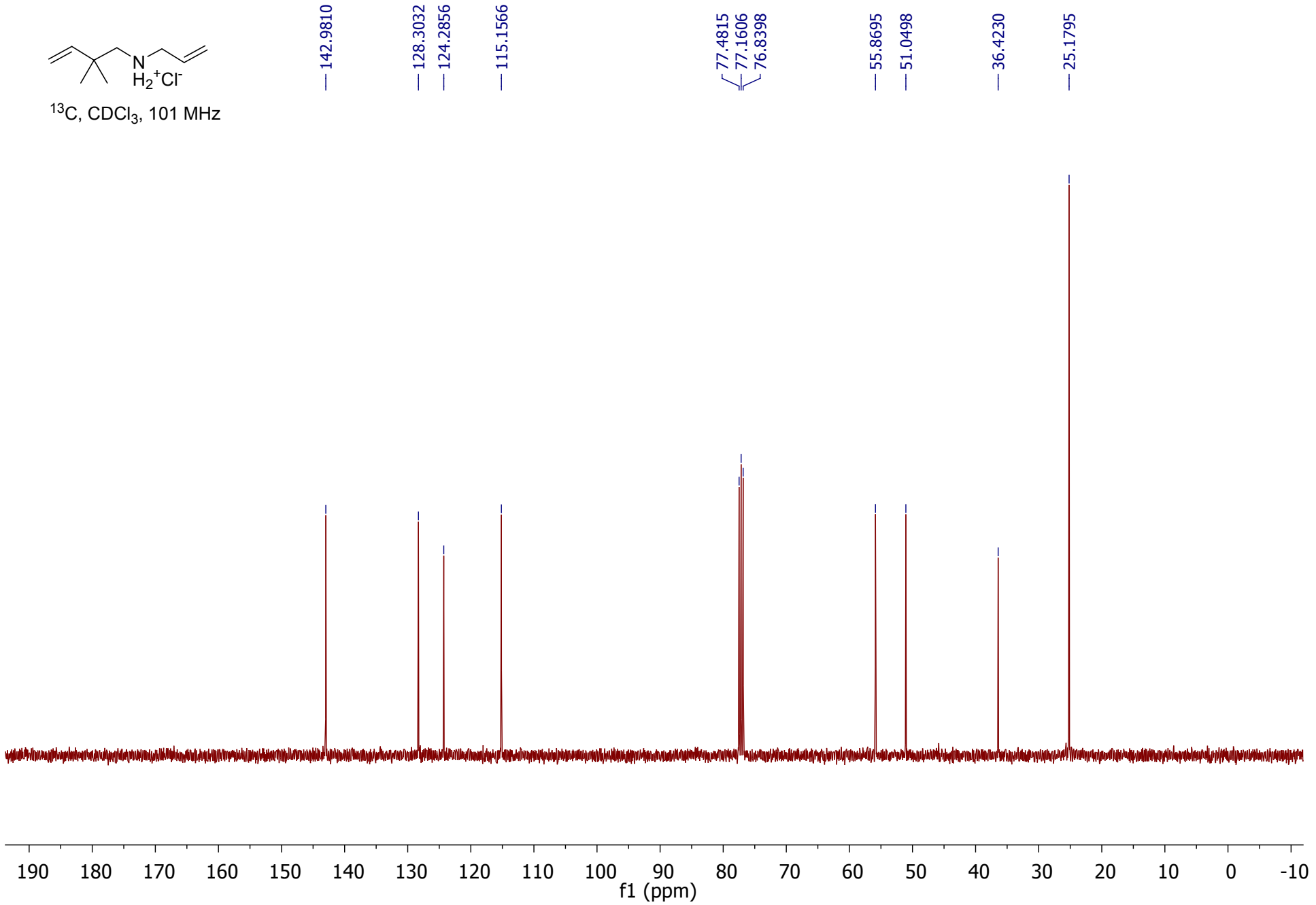

N
H2+Cl-
13C, CDCl3, 101 MHz
132.5596
118.6473
77.4784
77.1603
76.8430
47.0549
30.0912
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

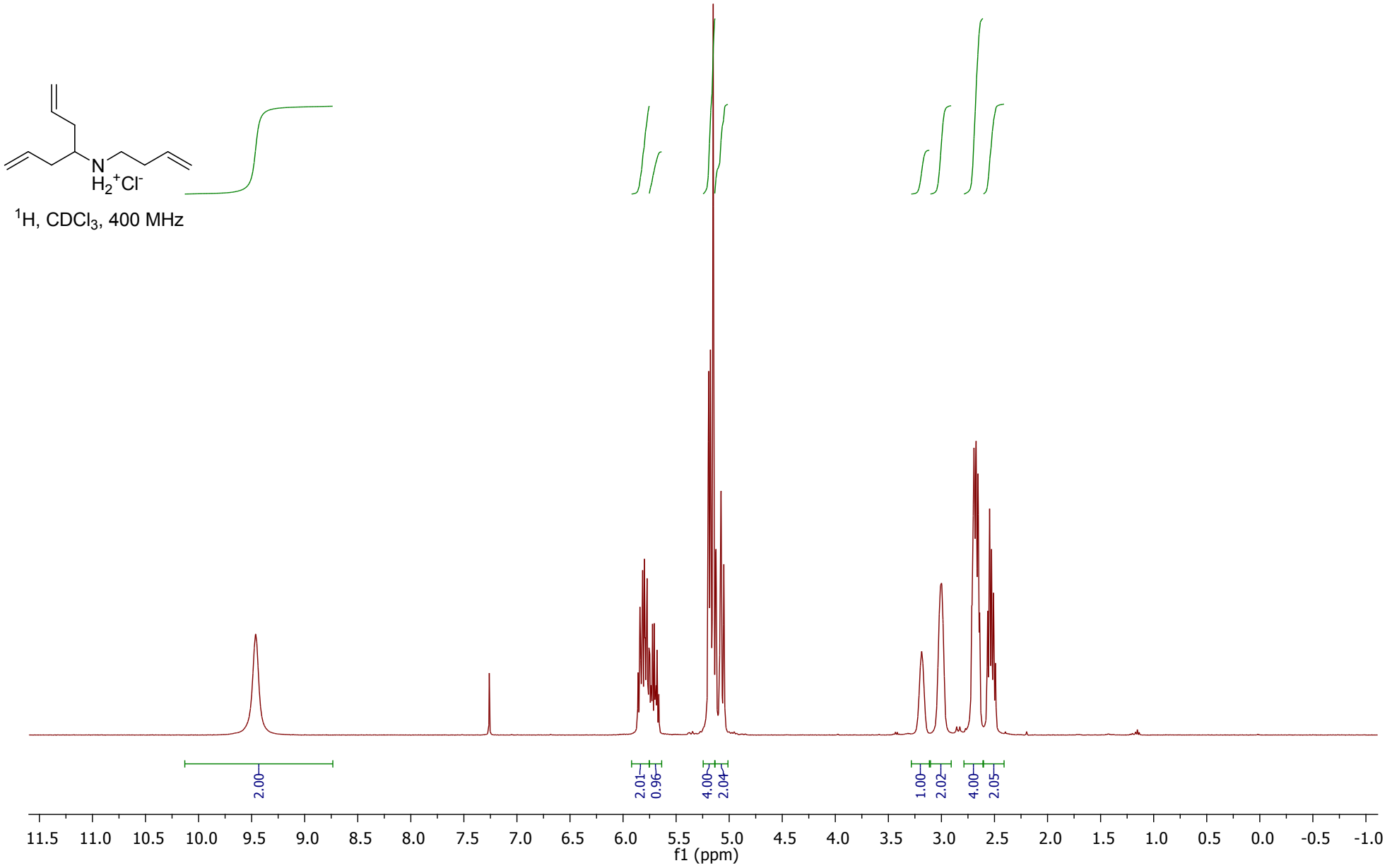

NH3+Cl-
1H, DMSO-D6, 400 MHz
3.005
1.000
2.016
2.047
2.035
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

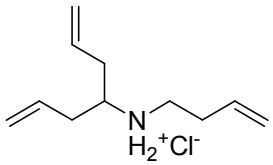

N
H2+Cl-
1H, CDCl3, 400 MHz
2.001
1.000
1.016
2.036
2.040
2.051
2.021
2.163
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)


132.5390
127.7849
124.1465
118.6049
77.4809
77.1600
76.8392
49.6565
45.6170
30.0861
N
H2+Cl-
13C, CDCl3, 101 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

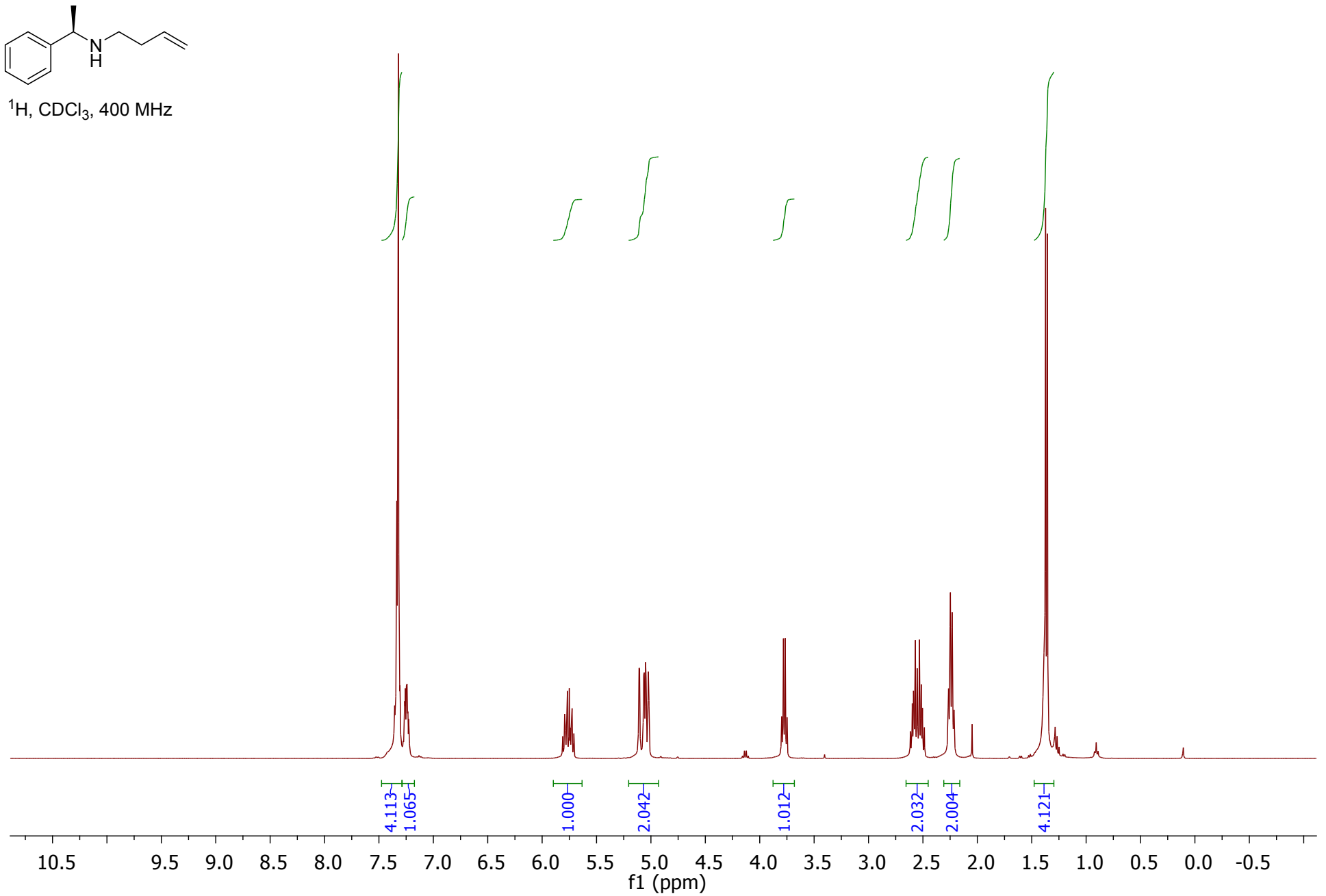

N
H2+Cl-
1H, CDCl3, 400 MHz
1.736
1.000
0.968
2.035
2.004
2.035
2.026
6.000
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

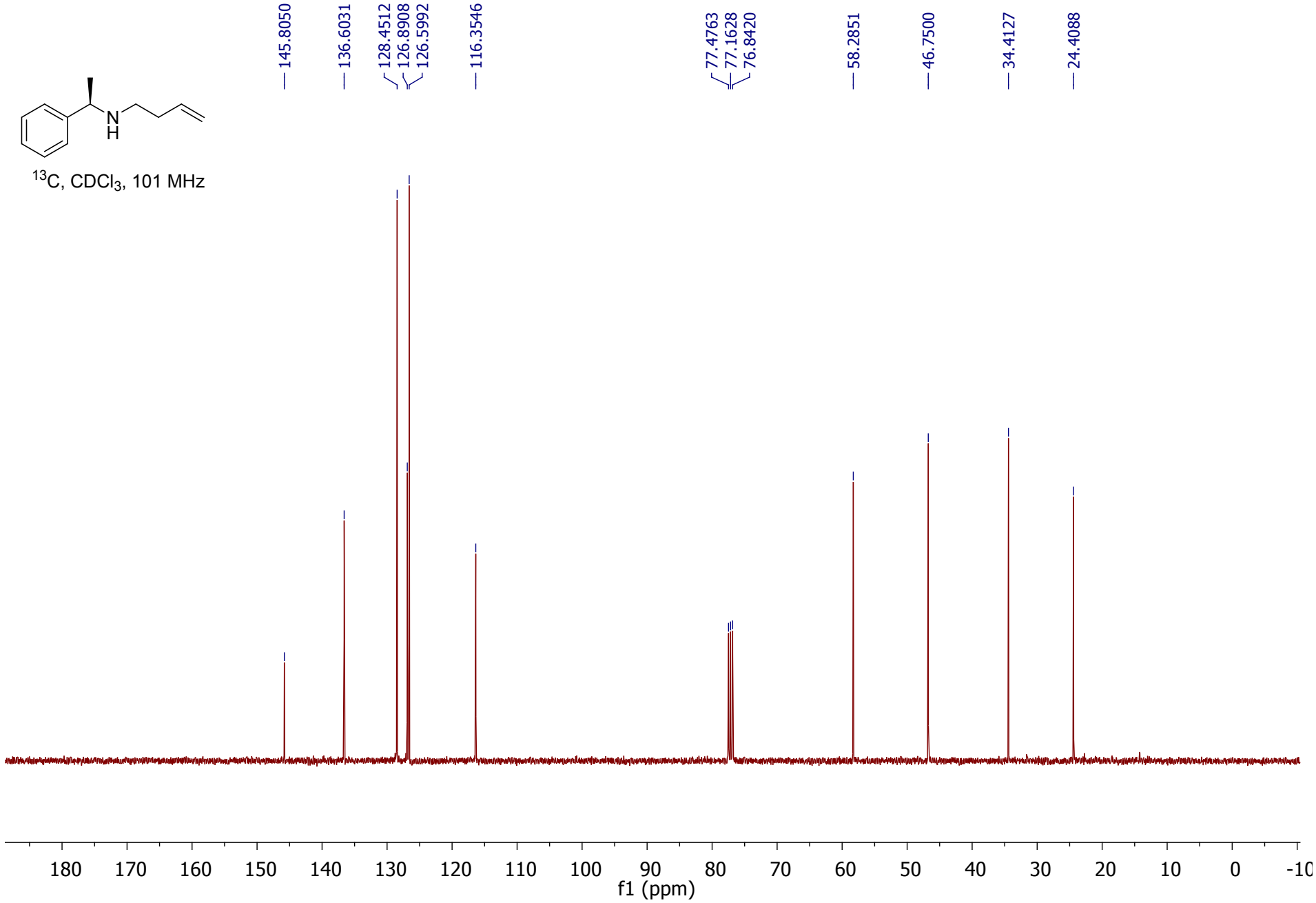

142.9810
128.3032
124.2856
115.1566
77.4815
77.1606
76.8398
55.8695
51.0498
36.4230
25.1795
N
H2+Cl-
13C, CDCl3, 101 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

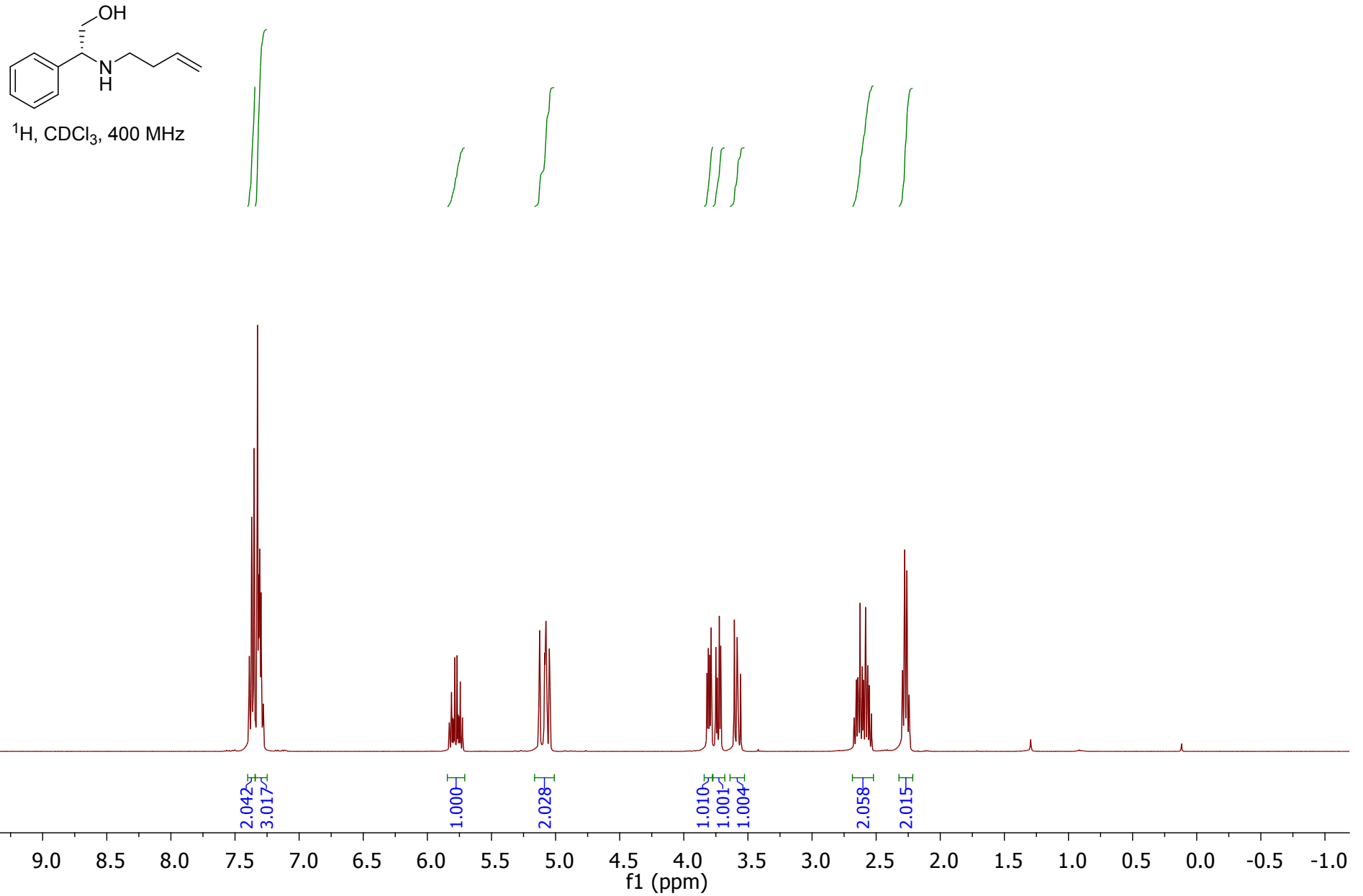

N
H2+Cl-
1H, CDCl3, 400 MHz
2.00
2.01
0.96
4.00
2.04
1.00
2.02
4.00
2.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

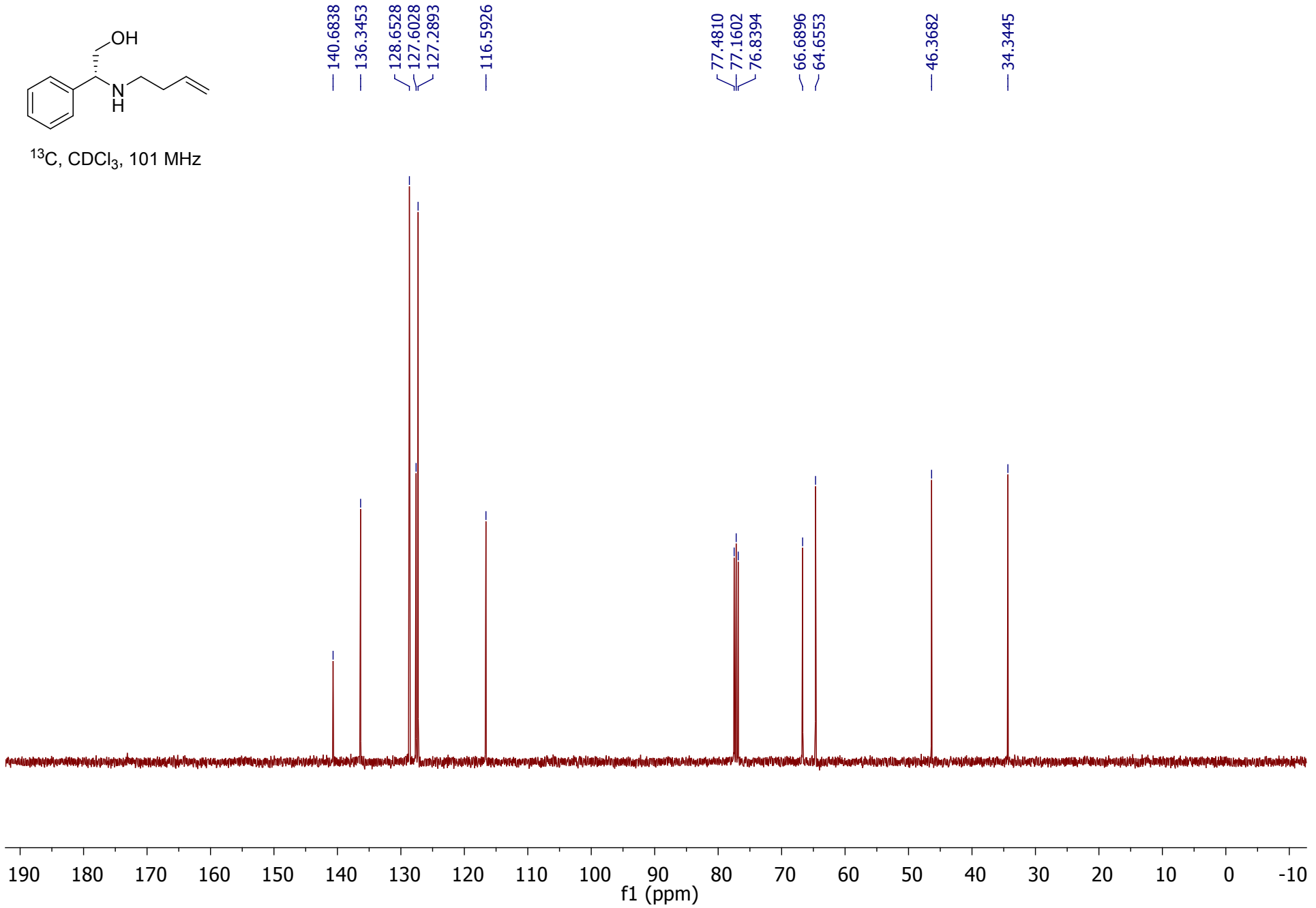


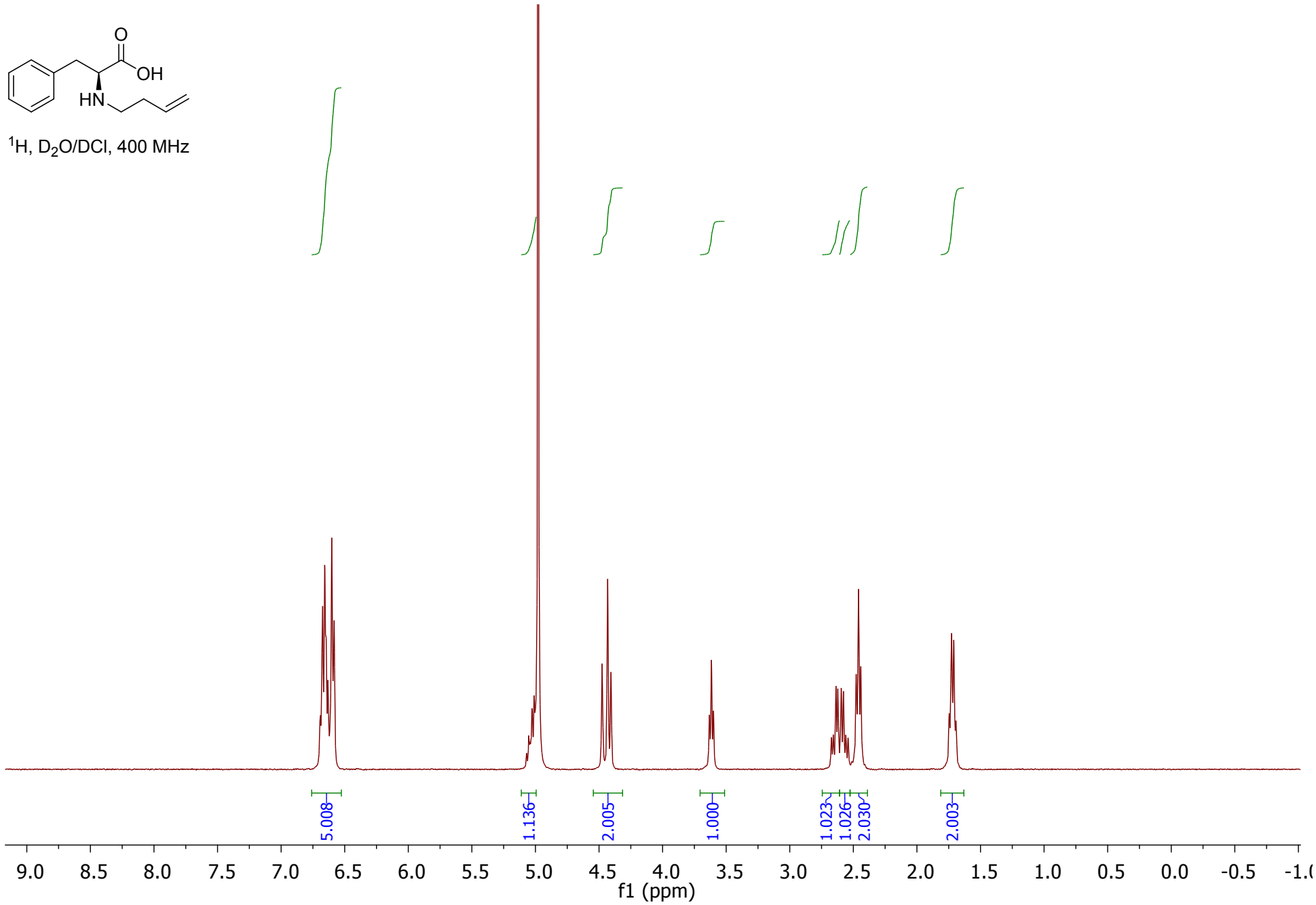
^{13}C, $CDCl_3$, 101 MHz

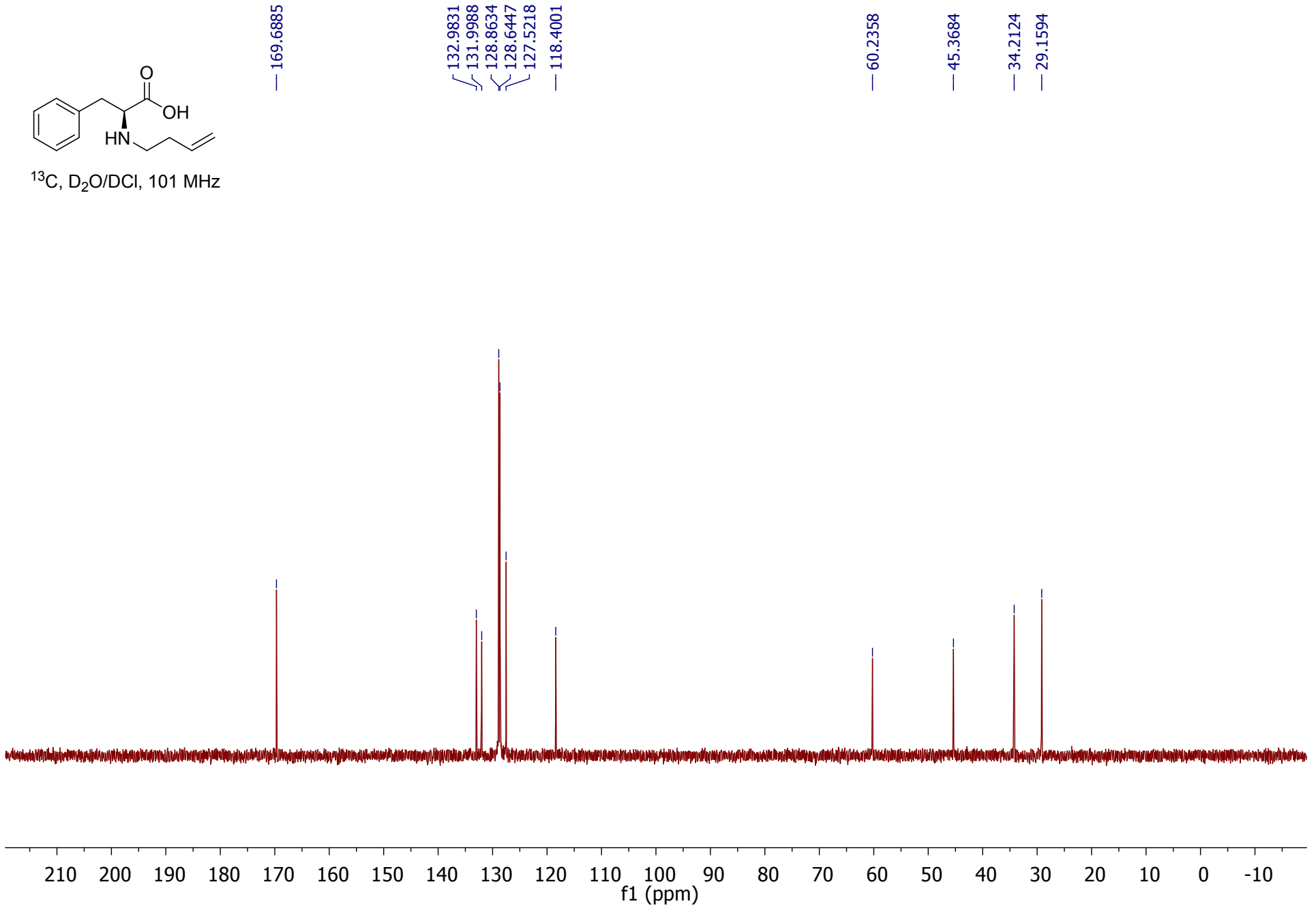

N
H
1H, CDCl3, 400 MHz
4.113
1.065
1.000
2.042
1.012
2.032
2.004
4.121
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


145.8050
136.6031
128.4512
126.8908
126.5992
116.3546
77.4763
77.1628
76.8420
58.2851
46.7500
34.4127
24.4088
N
H
^{13}C, CDCl$_3$, 101 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

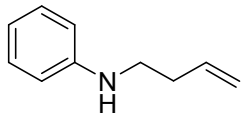

OH
N
H
^{1}H, $CDCl_3$, 400 MHz
2.042
3.017
1.000
2.028
1.010
1.001
1.004
2.058
2.015
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


OH
N
H
^{13}C, $CDCl_3$, 101 MHz
140.6838
136.3453
128.6528
127.6028
127.2893
116.5926
77.4810
77.1602
76.8394
66.6896
64.6553
46.3682
34.3445
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

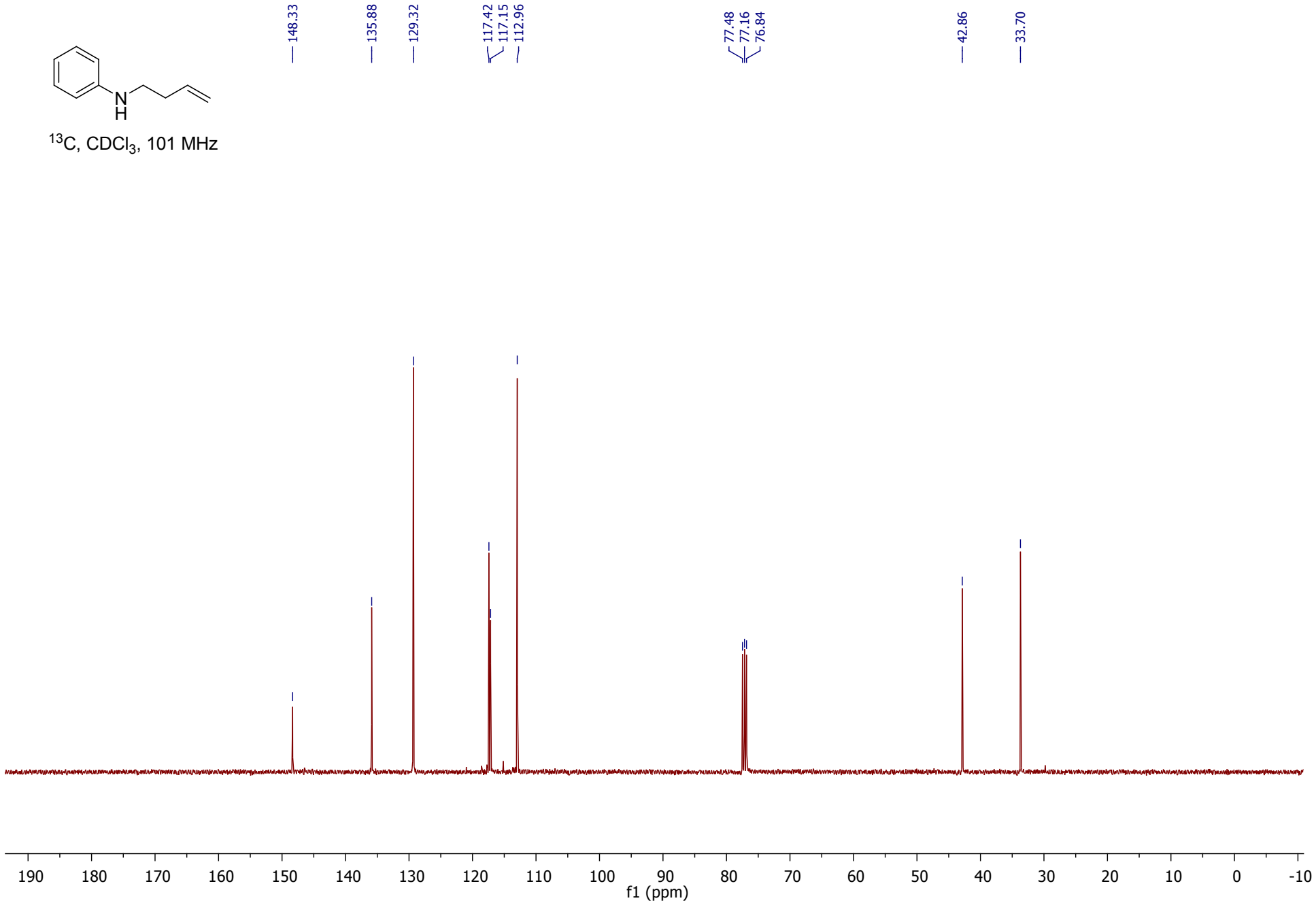

O
OH
HN
1H, D2O/DCl, 400 MHz
5.008
1.136
2.005
1.000
1.023
1.026
2.030
2.003
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

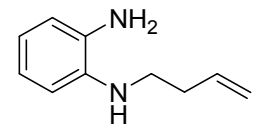


^{13}C, D_2O/DCl, 101 MHz

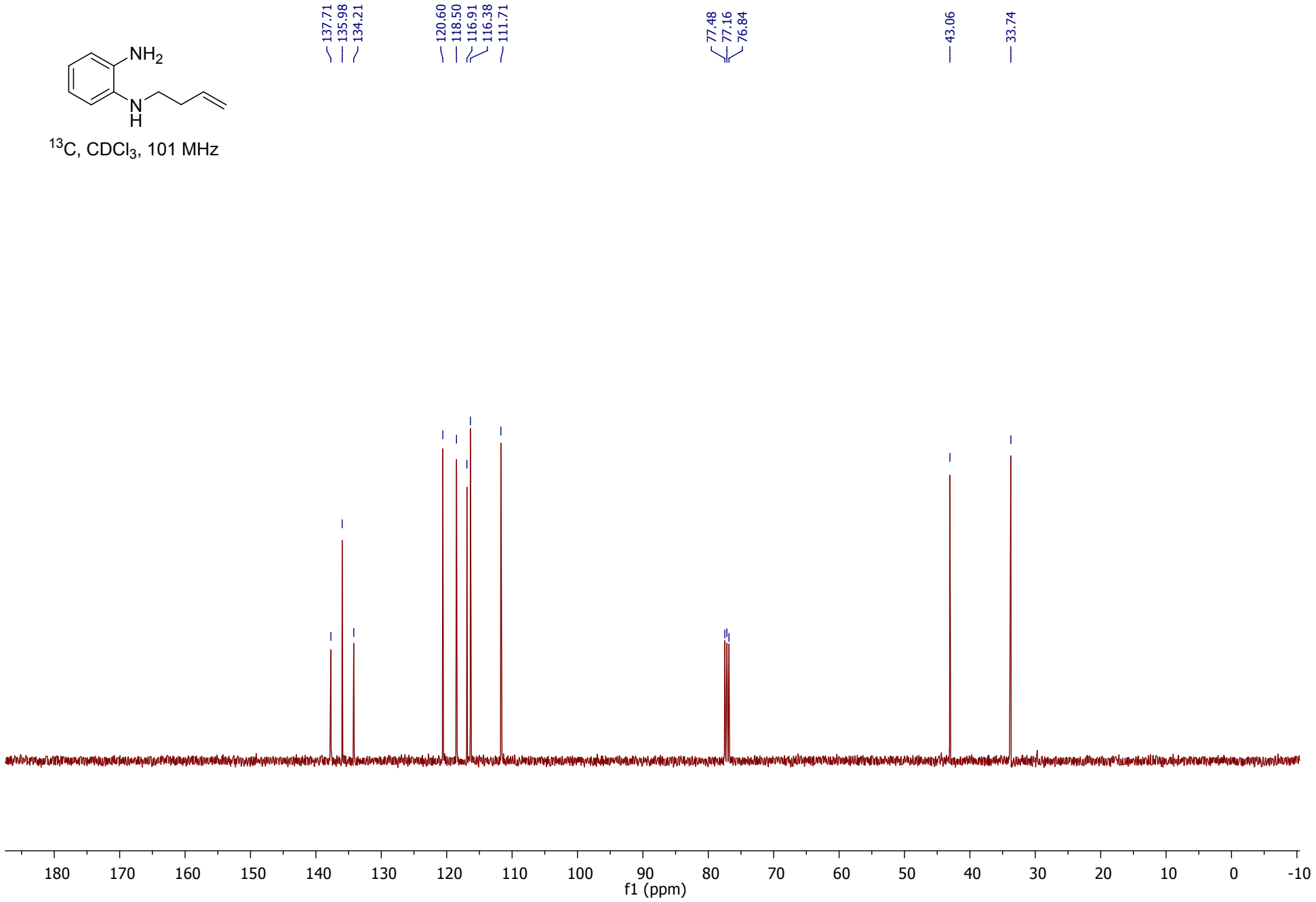


^1H, $CDCl_3$, 400 MHz

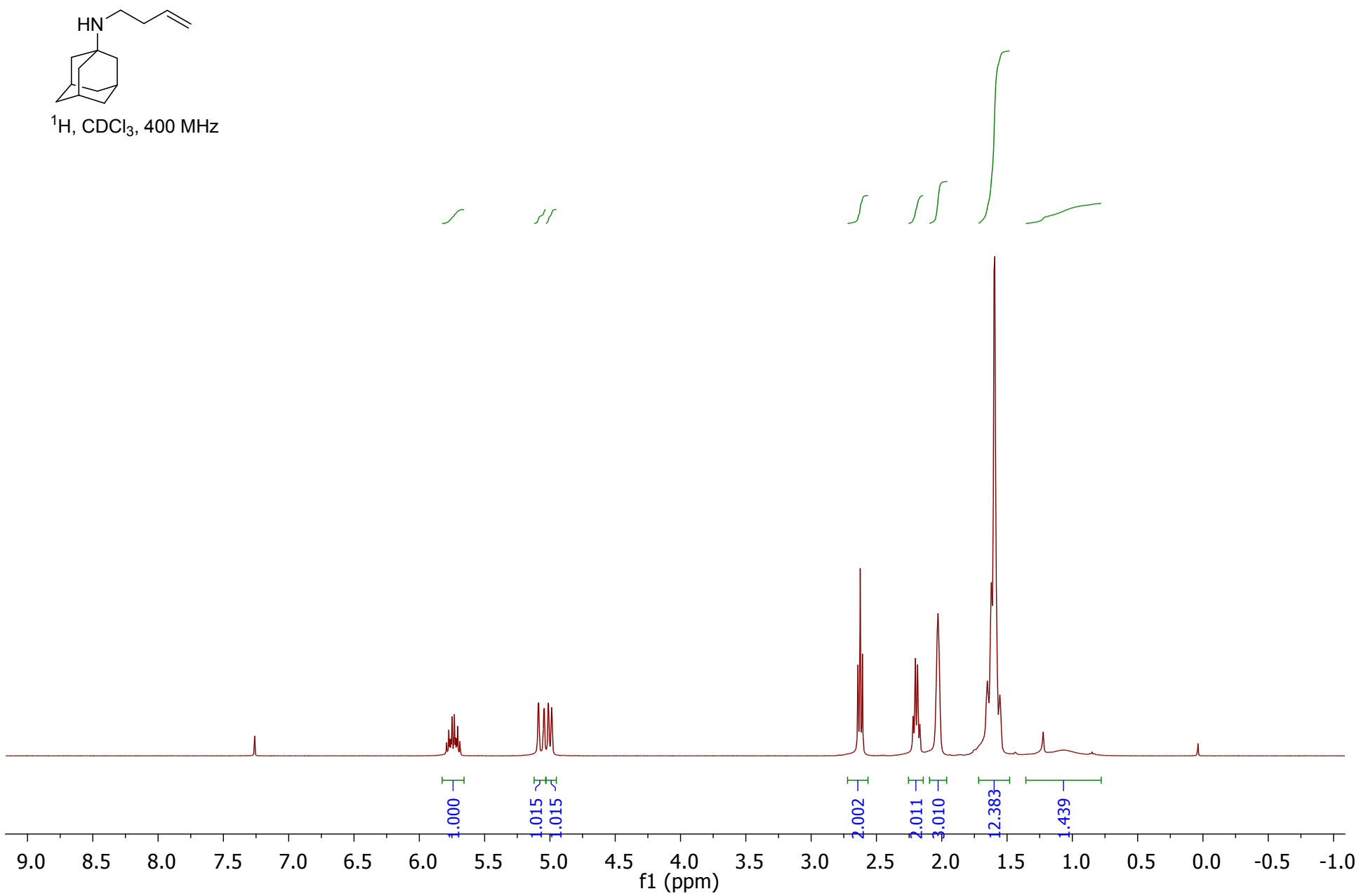

148.33
135.88
129.32
117.42
117.15
112.96
77.48
77.16
76.84
42.86
33.70
N
H
^{13}C, $CDCl_3$, 101 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

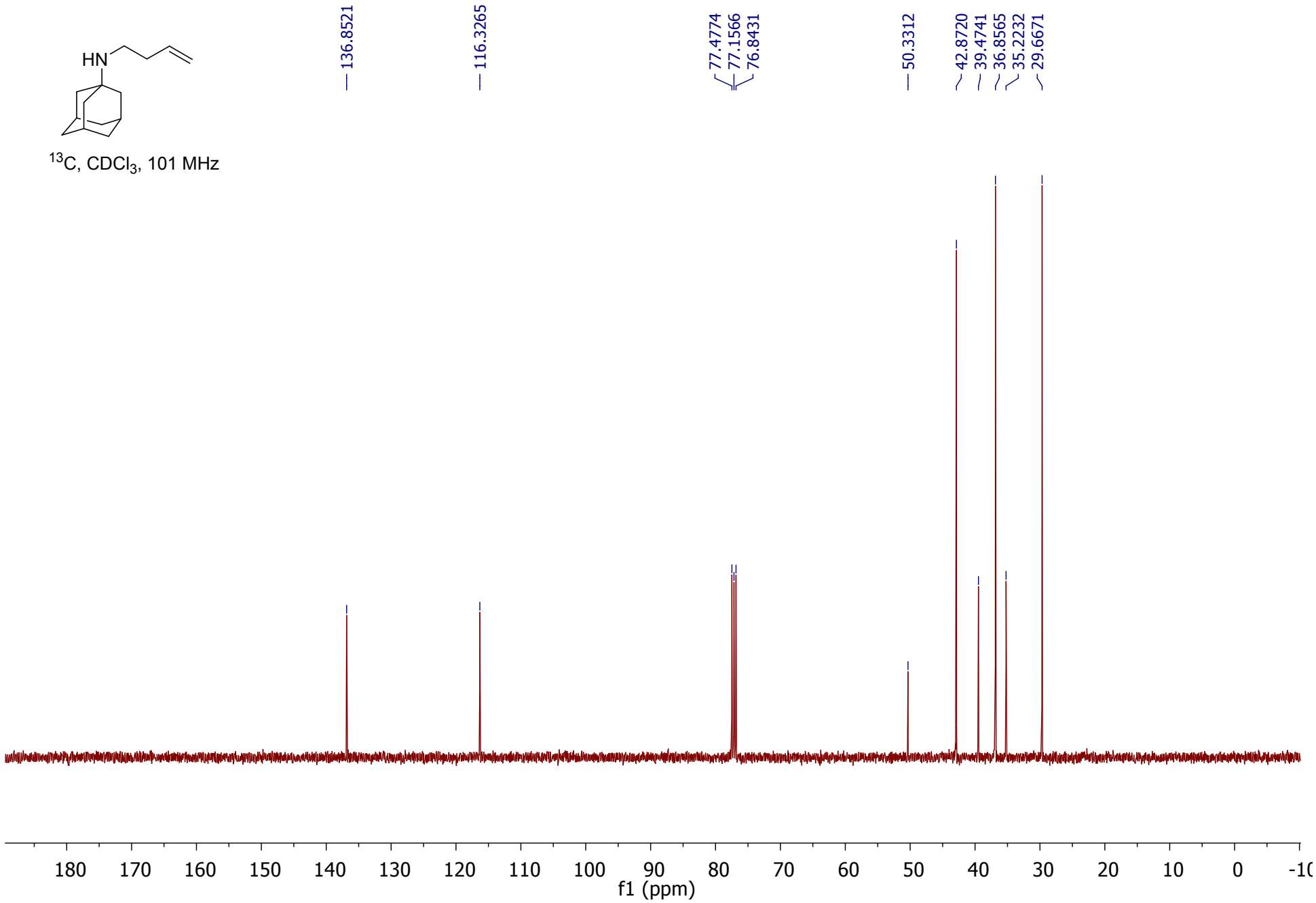


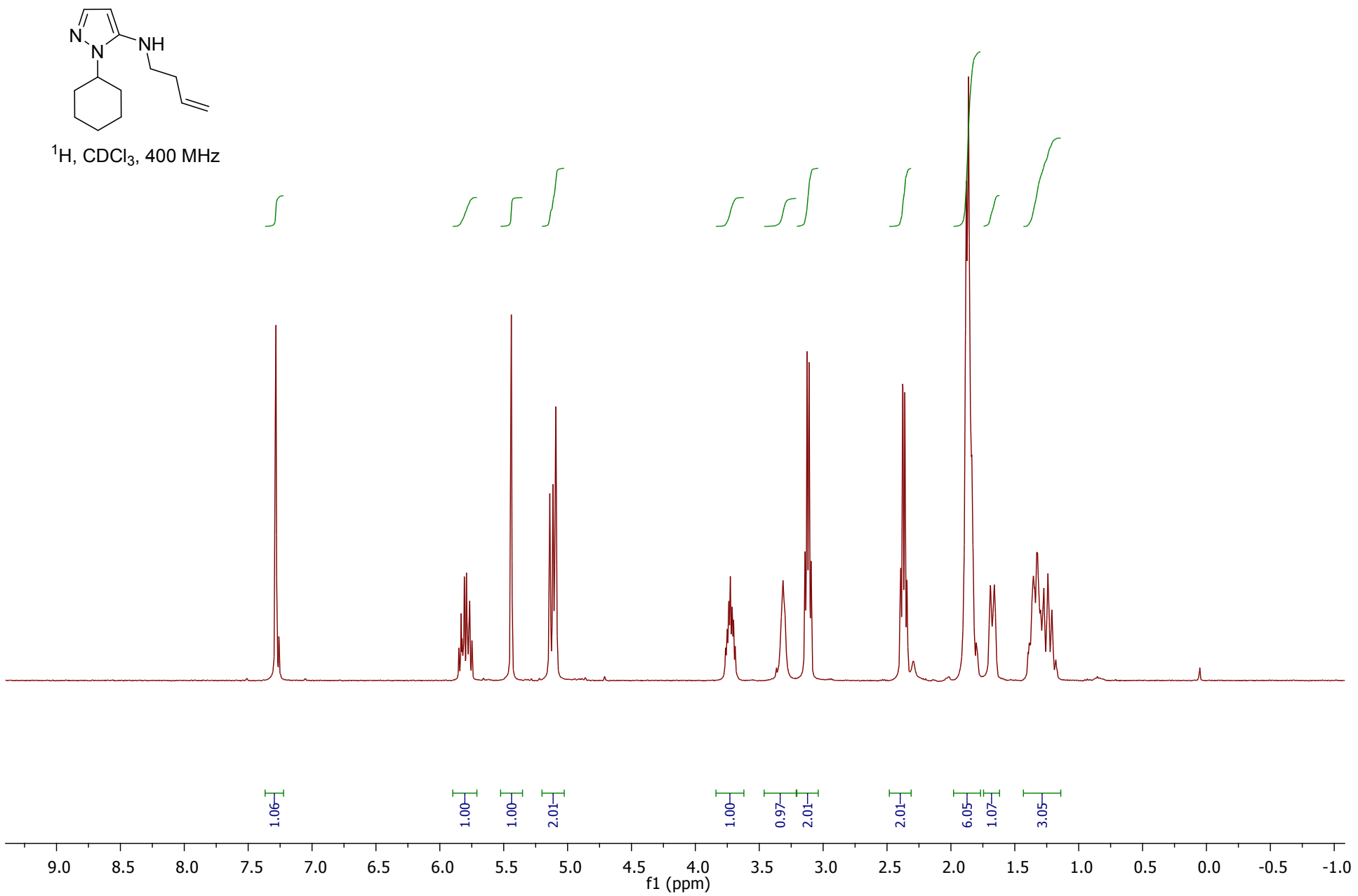
^{1}H, $CDCl_3$, 400 MHz

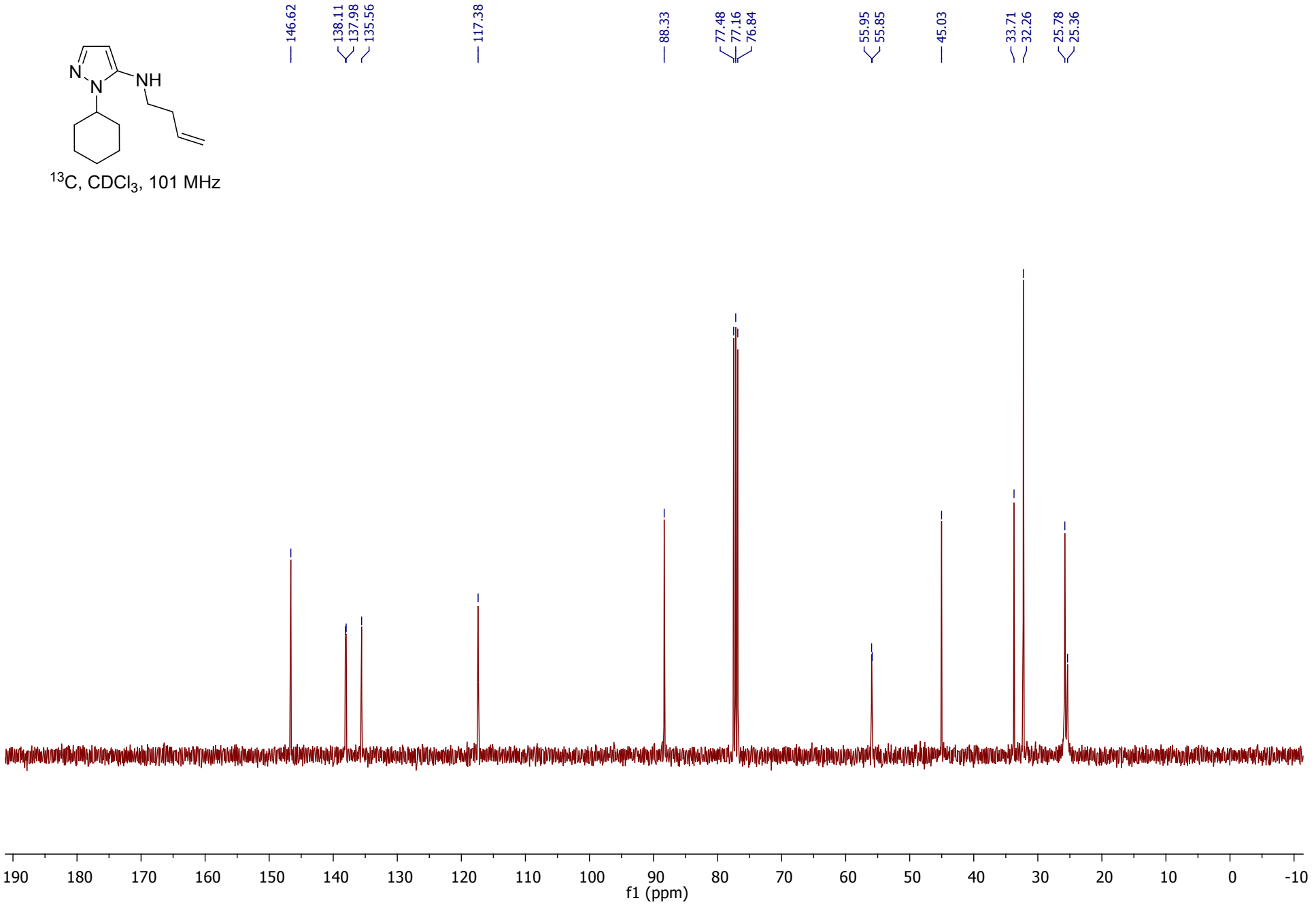


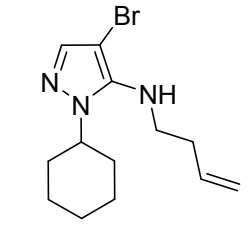
^{13}C, $CDCl_3$, 101 MHz


HN
1H, CDCl3, 400 MHz
1.000
1.015
1.015
2.002
2.011
3.010
12.383
1.439
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

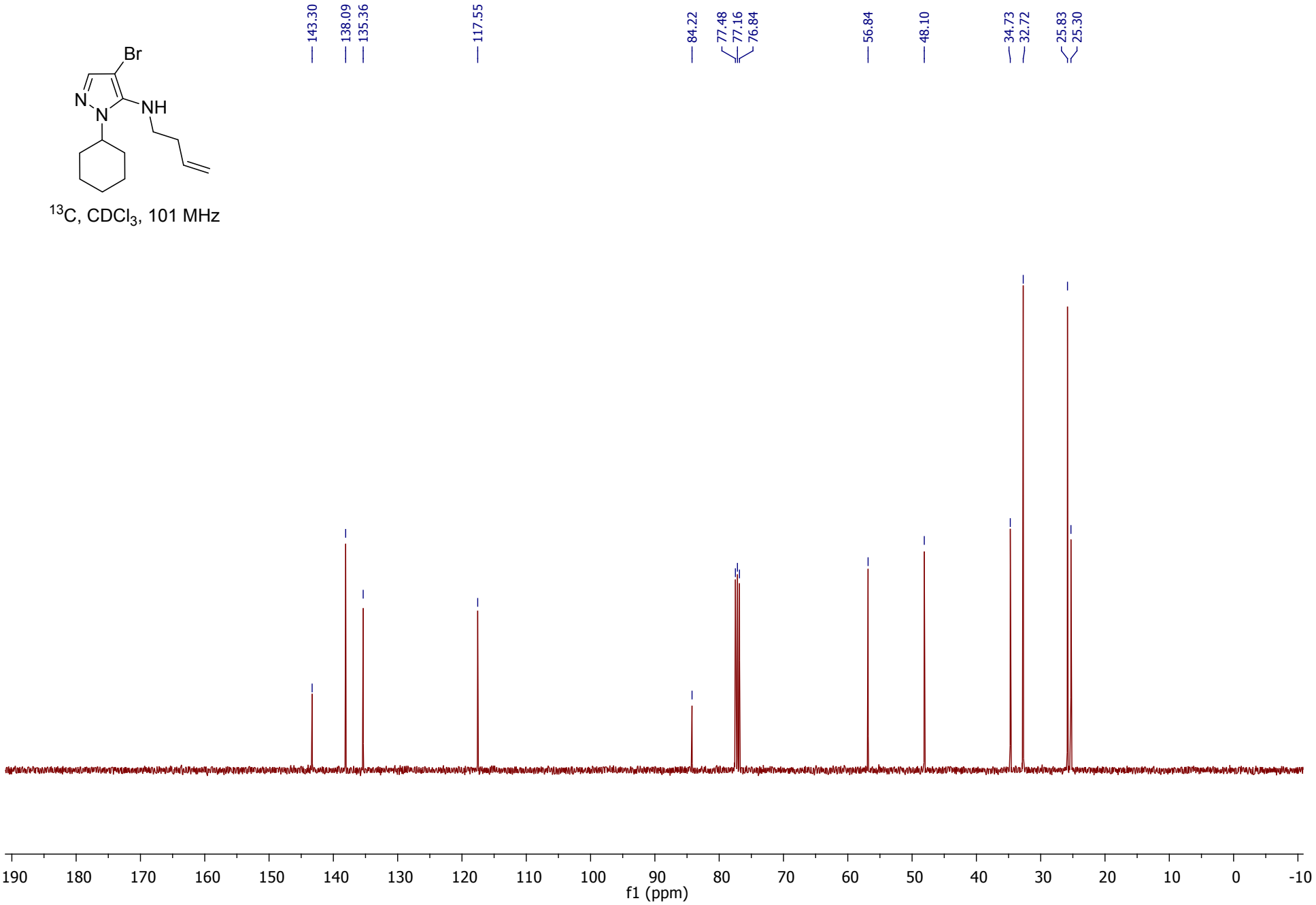

HN
^{13}C, CDCl$_3$, 101 MHz
136.8521
116.3265
77.4774
77.1566
76.8431
50.3312
42.8720
39.4741
36.8565
35.2232
29.6671
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
N
NH
^{1}H, CDCl$_3$, 400 MHz
1.06
1.00
1.00
2.01
1.00
0.97
2.01
2.01
6.05
1.07
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

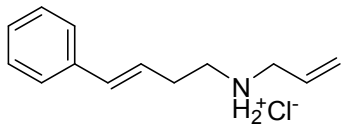

146.62
138.11
137.98
135.56
117.38
88.33
77.48
77.16
76.84
55.95
55.85
45.03
33.71
32.26
25.78
25.36
N
N
NH
13C, CDCl3, 101 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



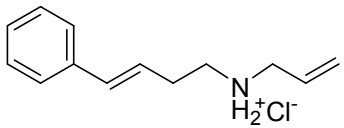
^{1}H, $CDCl_3$, 400 MHz



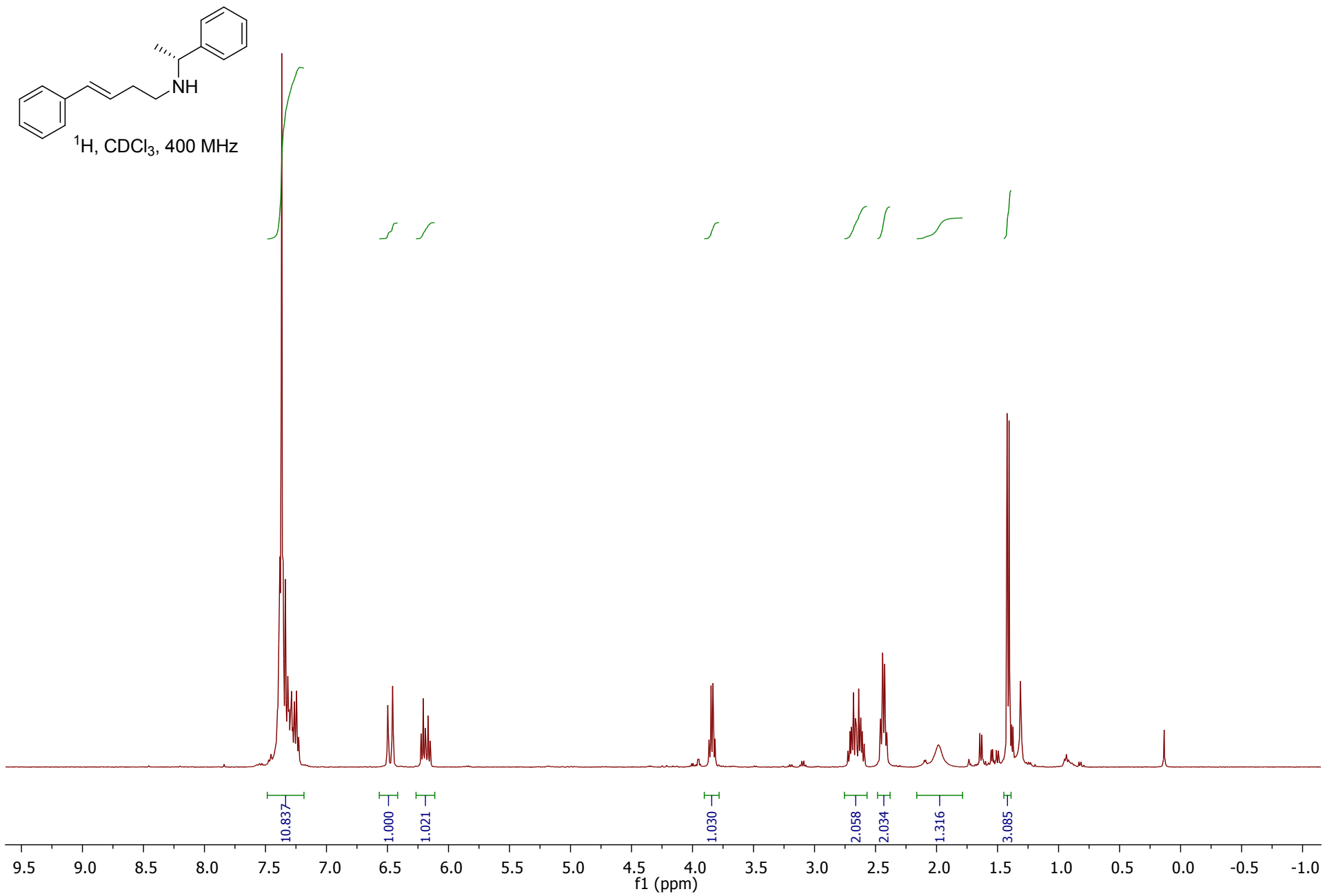
^{13}C, $CDCl_3$, 101 MHz

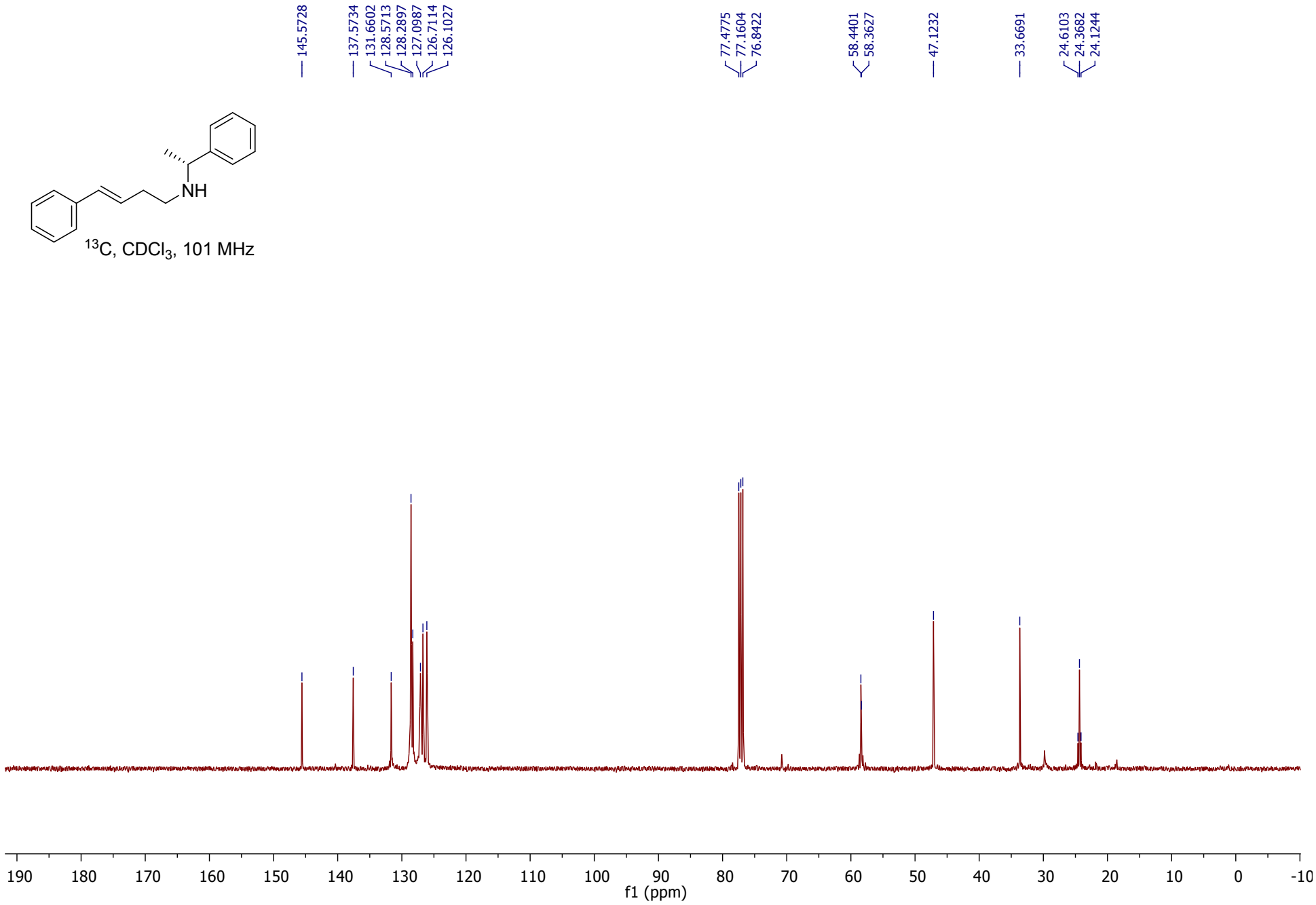


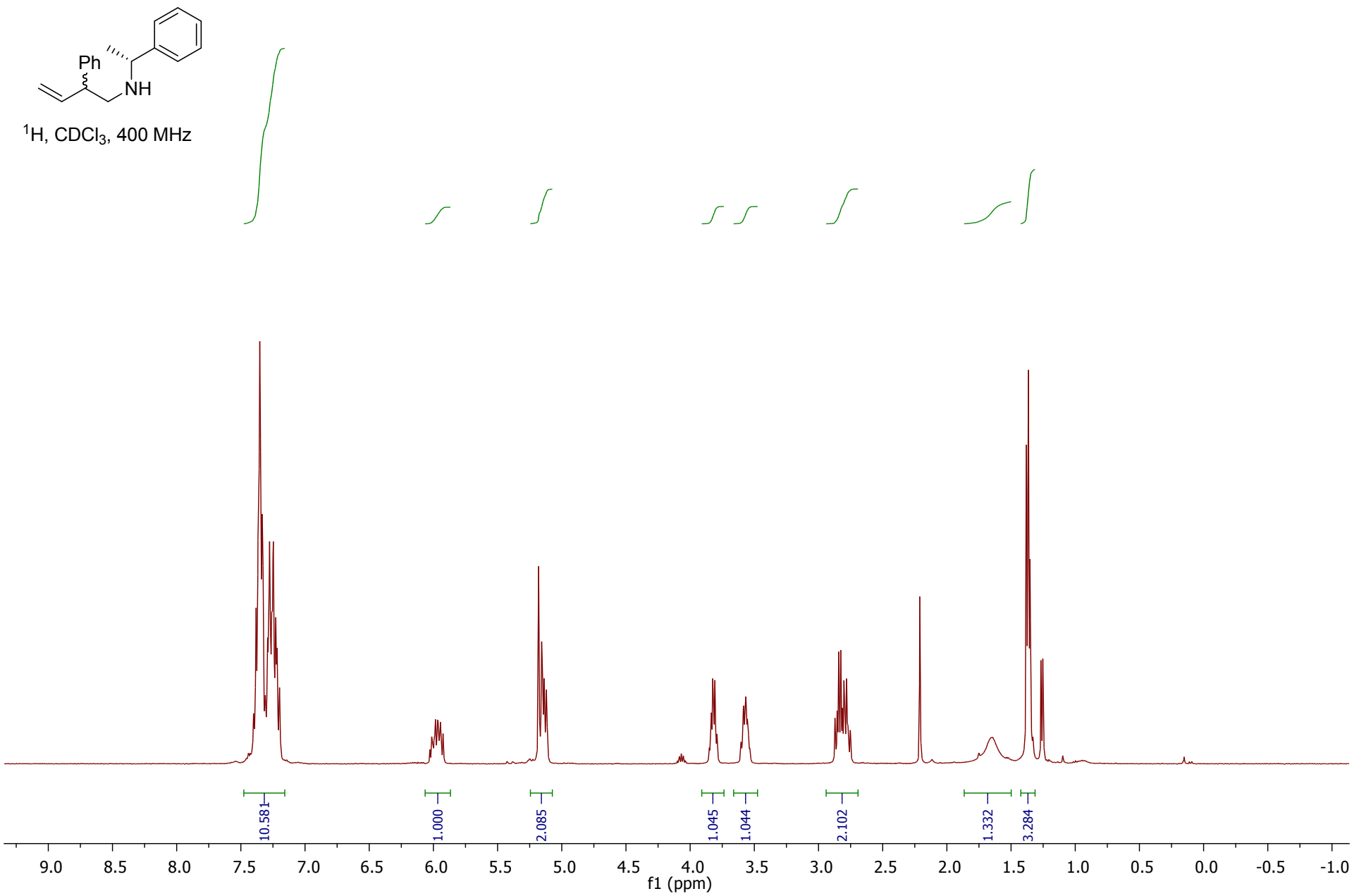
^1H, $CDCl_3$, 400 MHz

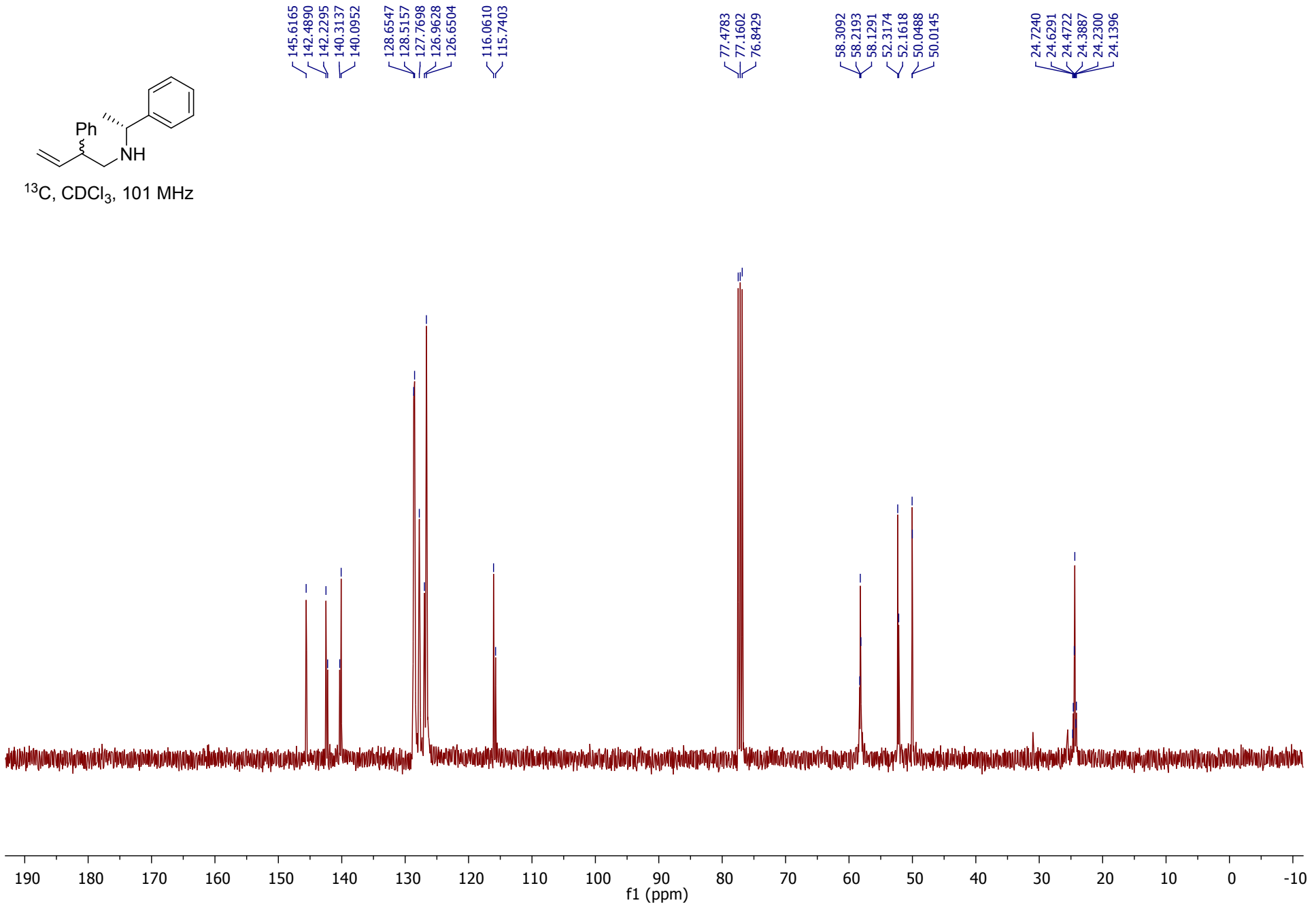


^{13}C, $CDCl_3$, 101 MHz


NH
^{1}H, $CDCl_3$, 400 MHz
10.837
1.000
1.021
1.030
2.058
2.034
1.316
3.085
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


145.5728
137.5734
131.6602
128.5713
128.2897
127.0987
126.7114
126.1027
77.4775
77.1604
76.8422
58.4401
58.3627
47.1232
33.6691
24.6103
24.3682
24.1244
NH
13C, CDCl3, 101 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ph
NH
^{1}H, $CDCl_3$, 400 MHz
10.581
1.000
2.085
1.045
1.044
2.102
1.332
3.284
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


145.6165
142.4890
142.2295
140.3137
140.0952
128.6547
128.5157
127.7698
126.9628
126.6504
116.0610
115.7403
77.4783
77.1602
76.8429
58.3092
58.2193
58.1291
52.3174
52.1618
50.0488
50.0145
24.7240
24.6291
24.4722
24.3887
24.2300
24.1396
Ph
NH
13C, CDCl3, 101 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)