The synthesis of chiral branched allylamines through dual photoredox/nickel catalysis

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Electronic supplementary information

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1. General info

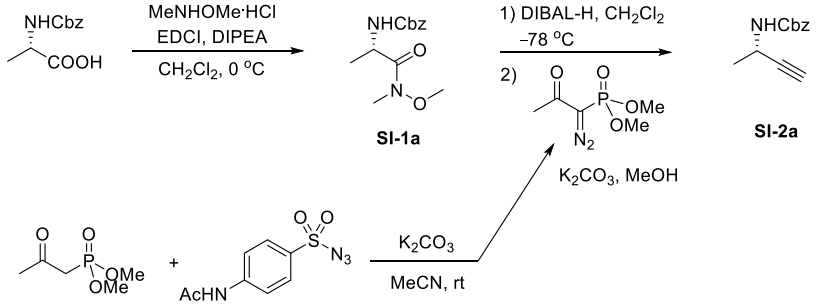
NMR Spectra (^{1}H, ^{13}C, ^{19}F, ^{31}P) were performed at 298 K. ^{1}H NMR spectra were referenced to residual chloroform (δ 7.26 ppm) in $CDCl_3$ and residual DMSO-d_5 (δ 2.50 ppm) in DMSO-d_6. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.2 ppm) and DMSO-d_6 (δ 39.5 ppm). Data is presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant *J* (Hz) and integration.

Reactions were monitored by TLC on silica gel plates (TLC Silica gel 60 F254, Aluminium sheets), HPLC and ^{1}H NMR spectra. TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using UV light, and $KMnO_4$ or cerium/molybdenium stains. Column

chromatography was performed by using silica gel from Merck (Silica gel 60, 40-63 μm). Flash chromatography was accomplished using an automated Reveleris X2 chromatograph, equipped with ELSD and UV (254 nm) detection, with silica cartridges (Merck, Silica gel 60, 40-63 μm). Solvents were purified by use of drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected. Optical rotation was recorded on Jasco P-2000 polarimeter.

2. Synthesis of enantioenriched propargylamines

N-Cbz (*S*)-but-3-yn-2-amine (SI-2a):



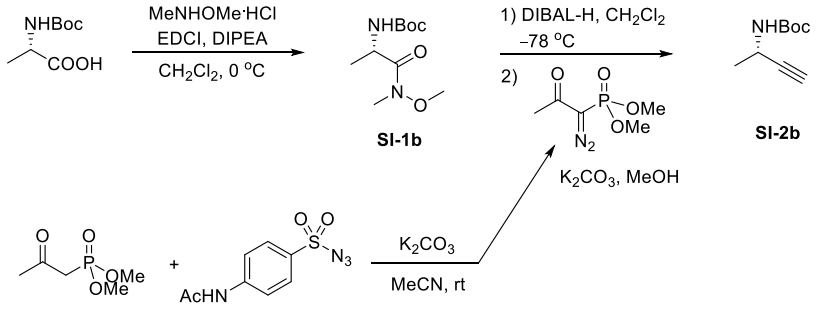
Step 1: *N*-Methoxy-*N*-methyl hydroxylamine hydrochloride (4.59 g, 47.0 mmol) was suspended in anhydr. toluene and the solvent was evaporated. This procedure was repeated three times to obtain white dry powder. Next, under argon the flask was charged with *N*-Cbz L-alanine (10.0 g, 44.8 mmol), anhydr. CH_2Cl_2 (200 mL) and *i*-Pr_2NEt (7.8 mL, 5.8 g, 44.8 mmol). The mixture was cooled to 0 °C, and a soln. of EDCI hydrochloride (7.3 g, 44.8 mmol) in anhydr. CH_2Cl_2 (50 mL) was added. The cooling bath was removed and the reaction mixture was stirred overnight at rt. Sat. NH_4Cl was added and layers were separated. Aqueous layer was washed three times with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and evaporated. The crude product was purified by silica gel column chromatography (40 to 70% AcOEt in hexanes) to give 11.0 g (41.1 mmol, 92% yield) of **SI-1a** as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 5.55 (s, 1H), 5.14 – 5.04 (m, *2*H), 4.78 – 4.71 (m, 1H), 3.76 (s, 3H), 3.20 (s, 3H), 1.34 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 155.7, 136.4, 128.4, 128.04, 127.97, 66.7, 61.6, 47.1, 32.2, 18.6.

Step 2: The Weinreb amide **SI-1a** (11.0 g, 41.1 mmol) was dissolved in anhydr. CH_2Cl_2 (200 mL) under argon and cooled down to −78 °C, followed by a dropwise addition of DIBAL-H

(1 M soln. in hexanes, 82.4 mL, 82.2 mmol) and stirred for 1 h. Next, MeOH (20 mL) was added dropwise, a cooling bath was removed and the resulting mixture was stirred vigorously. After reaching rt, the precipitate was filtered off through Celite pad and the filtrate was evaporated to dryness to give the crude amino aldehyde that was directly used in the next step without further purification.

Step 3: Anhydr. K_2CO_3 (17.3 g, 123.3 mmol) and 4-acetamidobenzenesulfonyl azide (14.8 g, 61.7 mmol) were suspended in anhydr. MeCN (400 mL) under argon. Dimethyl (2-oxopropyl)phosphonate (8.46 mL, 10.24 g, 61.7 mmol) was added dropwise and the resulting mixture was stirred for 3h at rt. Next, a solution of crude amino aldehyde from previous step in anhydr. MeOH (130mL) was added dropwise. The resulting suspension was stirred overnight at rt. Next, Et_2O and H_2O were added and the layers were separated, Aqueous one was washed twice with Et_2O, and combined organic layers were dried over Na_2SO_4, filtered and evaporated. The residue was purified by silica gel column chromatography (10% AcOEt in hexanes) to provide 4.85 g (23.8 mmol, 58%) of amine **SI-2a** as a white solid, m.p. 64.1 – 65.6 °C; $[\alpha]_D^{25}$ –58.9 (*c* 1.14, $CHCl_3$)[Lit.[1] –59.1 (*c* 0.23, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.29 (m, 5H), 5.12 (s, 2H), 5.02 – 4.93 (m, 1H), 4.62 – 4.50 (m, 1H), 2.28 (d, *J* = 2.3 Hz, 1H), 1.42 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 136.3, 128.5, 128.2, 128.1, 84.1, 70.6, 67.0, 38.9, 22.5; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{13}NO_2Na$ [$(M+Na)^+$] 226.0844; found: 226.0839; FTIR (film) ν: 3289, 3005, 2966, 2935, 1684, 1531, 1455, 1330, 1310, 1262, 1054, 651 cm^{-1}.

***N*-Boc (*S*)-but-3-yn-2-amine (SI-2b):**



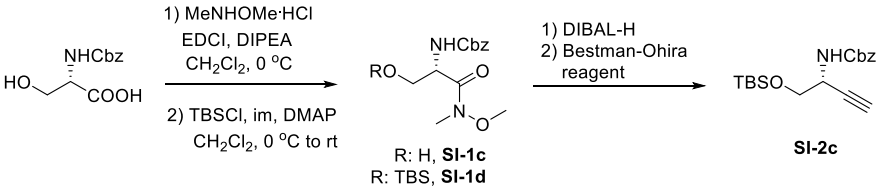
Step 1: Weinreb amide **SI-1b** was prepared following procedure for a preparation of amide **SI-1a** staring from 15.0 g (79.3 mmol) *N*-Boc L-alanine. Purification: column chromatography on silica gel (30 to 50% AcOEt in hexanes). Yield: 17.3 g (74.5 mmol, 94% yield) of **SI-1b**. White

solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (s, 1H), 4.67 (s, 1H), 3.75 (s, 3H), 3.19 (s, 3H), 1.42 (s, 9H), 1.30 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 155.2, 79.4, 61.5, 46.5, 32.2, 28.3, 18.6.

Step 2: The Weinreb amide **SI-1b** (10.0 g, 43.1 mmol) was reduced with DIBAL-H (86.1 mmol), as described above, to provide the corresponding amino aldehyde, which was used without further purification.

Step 3: Alkyne **SI-2b** was prepared following procedure of a preparation of alkyne **SI-2a**. Purification: column chromatography on silica gel (5-10% AcOEt in hexanes). Yield: 3.80 g (22.5 mmol, 52%) White solid, m.p. 91.5 – 92.5 °C; $[\alpha]_D^{25}$ –36.2 (*c* 1.12 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (s, 1H), 4.46 (s, 1H), 2.23 (d, *J* = 2.3 Hz, 1H), 1.43 (s, 9H), 1.38 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 84.6, 79.9, 70.1, 38.3, 28.3, 22.5; HRMS (ESI-TOF) *m/z* calcd for $C_9H_{15}NO_2Na$ [(M+Na)$^+$] 192.1000; found: 192.1001; FTIR (film) ν: 3328, 2977, 2932, 1680, 1525, 1448, 1253, 1165, 1026 cm^{-1}.

_N_-Cbz (_R_)-1-((_tert_-butyldimethylsilyl)oxy)but-3-yn-2-amine (SI-2c):



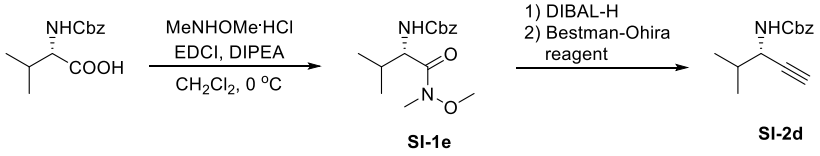
Step 1: Weinreb amide **SI-1c** was prepared following the procedure for a preparation of amide **SI-1a** staring from 1.9 g (7.94 mmol) *N*-Cbz L-serine. Purification: column chromatography on silica gel (50 to 80% AcOEt in hexanes). Yield: 2.1 g (7.44 mmol, 94% yield) of **SI-1c** as a white solid.

Step 2: The Weinreb amide **SI-1c** (2.1 g, 7.44 mmol), imidazole (1.01 g, 14.88 mmol) and DMAP (91 mg, 0.74 mmol) were dissolved in anhydr. CH_2Cl_2 (40 mL) under Ar atmosphere. After cooling to 0 °C, a solution of TBSCl (1.23 g, 8.18 mmol) in anhydr. CH_2Cl_2 (10 mL) was added dropwise. The cooling bath was removed and the resulting mixture was stirred for 2 h. Next, sat. NH_4Cl was added and the aqueous layer was washed with CH_2Cl_2 three times. The combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The crude product was purified by a column chromatography (SiO_2, 25% AcOEt in hexanes) to provide 2.52 g (6.34 mmol, 85 %) of **SI-1d** as a colourless oil.

Step 3: The Weinreb amide **SI-1d** (1 g, 2.79 mmol) was reduced with DIBAL-H (5.58 mmol), as described above, to provide the corresponding amino aldehyde, which was used without further purification.

Step 4: Alkyne **SI-2c** was prepared following procedure of a preparation of alkyne **SI-2a**. Purification: column chromatography on silica gel (5% AcOEt in hexanes). Yield 427.0 mg (1.28 mmol, 46% yield after 2 steps). Colourless oil; $[\alpha]_D^{25}$ –14.4 (*c* 1.44, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 5.21 – 5.02 (m, 3H), 4.54 (s, 1H), 3.80 – 3.72 (m, 2H), 2.25 (d, *J* = 2.3 Hz, 1H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 136.3, 128.5, 128.2(×2) 81.5, 71.4, 67.0, 65.3, 45.3, 25.8, 18.3, –5.37, –5.40; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{27}NO_3NaSi$ [$(M+Na)^+$] 356.1658; found: 356.1652; FTIR (film) ν: 3309, 3034, 2930, 2857, 1709, 1502, 1468, 1255, 1121, 1041, 839, 779 cm^{-1}.

_N_-Cbz (_S_)-4-methylpent-1-yn-3-amine (SI-2d):



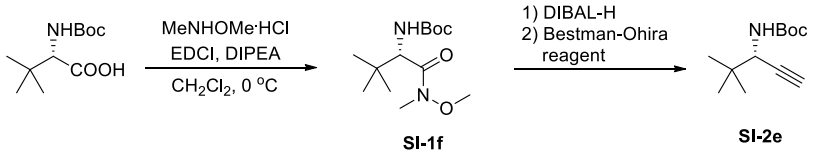
Step 1: Weinreb amide **SI-1e** was prepared following procedure for a preparation of amide **SI-1a** staring from 750 mg (2.98 mmol) *N*-Boc L-valine. Purification: column chromatography on silica gel (20 to 40% AcOEt in hexanes). Yield: 834 mg (2.83 mmol, 95%) of **SI-1e** as a white waxy solid.

Step 2: The Weinreb amide **SI-1e** (540 mg, 2.07 mmol) was reduced with DIBAL-H (4.14mmol), as described above, to provide the corresponding amino aldehyde, which was used without further purification.

Step 3: Alkyne **SI-2d** was prepared following procedure of a preparation of alkyne **SI-2a**. Purification: column chromatography on silica gel (5% AcOEt in hexanes). Yield 200 mg (1.01 mmol, 50%). White waxy solid; $[\alpha]_D^{25}$ –32.6 (*c* 0.45, $CHCl_3$)[Lit.[2] –2.7 (*c* 0.25, CH_2Cl_2] ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 5.12 (s, 2H), 4.99 (s, 1H), 4.45 – 4.32 (m, 1H), 2.27 (d, *J* = 2.4 Hz, 1H), 1.94 (hept, *J* = 6.8 Hz, 1H), 0.99 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.56, 136.3, 128.5, 128.2 (2×), 81.7, 72.1, 67.0, 49.2, 32.9, 18.6, 17.5; HRMS (ESI-TOF) *m/z* calcd for

$C_{14}H_{17}NO_2Na$ [$(M+Na)^+$] 254.1157; found: 254.1158; FTIR (film) ν: 3321, 3034, 2954, 1712, 1502, 1468, 1255, 1041 cm^{-1}.

***N*-Boc (*S*)-4,4-dimethylpent-1-yn-3-amine (SI-2e):**



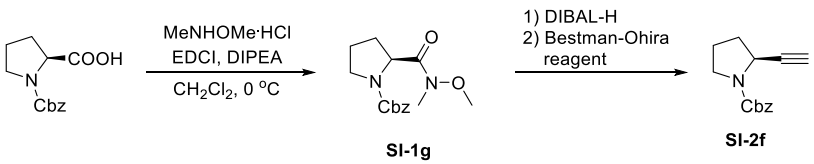
SI-1f **SI-2e**

Step 1: Weinreb amide **SI-1f** was prepared following procedure for a preparation of amide **SI-1a** staring from 750 mg (3.24 mmol) *N*-Boc *L*-tert-leucine. Purification: column chromatography on silica gel (20 to 30% AcOEt in hexanes). Yield: 700 mg (2.55 mmol, 79% yield) of **SI-1f** as a white solid.

Step 2: The Weinreb amide **SI-1f** (274 mg, 1.00 mmol) was reduced with DIBAL-H (2 mmol), as described above, to provide the corresponding amino aldehyde, which was used without further purification.

Step 3: Alkyne **SI-2e** was prepared following the procedure of a preparation of alkyne **SI-2a**. Purification: column chromatography on silica gel (5% AcOEt in hexanes). Yield 98.4 mg (0.47 mmol, 47%). White solid, m.p. 72–73 °C; $[\alpha]_D^{25}$ –68.0 (*c* 1.57, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (s, 1H), 4.25 – 4.18 (m, 1H), 2.23 (d, *J* = 2.4 Hz, 1H), 1.44 (s, 9H), 0.97 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 82.5, 79.7, 71.7, 52.1, 35.4, 28.3, 25.7; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{21}NO_2Na$ [$(M+Na)^+$] 234.1470; found: 234.1461; FTIR (film) ν: 3320, 2973, 2930, 1691, 1512, 1448, 1250, 1166, 1026 cm^{-1}.

***N*-Cbz (*S*)-2-ethynylpyrrolidine (SI-2f):**



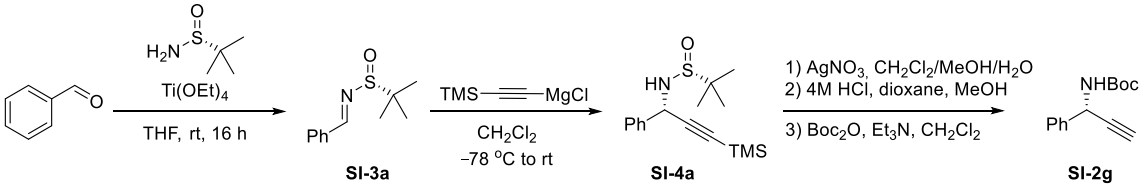
SI-1g **SI-2f**

Step 1: Weinreb amide **SI-1g** was prepared following procedure for a preparation of amide **SI-1a** staring from 750 mg (3.01 mmol) *N*-Cbz *L*-proline. Purification: column chromatography on silica gel (30 to 60% AcOEt in hexanes). Yield: 809 mg (2.77 mmol, 92% yield) of **SI-1g** as a colourless oil.

Step 2: The Weinreb amide **SI-1g** (646 mg, 2.21 mmol) was reduced with DIBAL-H (4.42 mmol), as described above, to provide the corresponding amino aldehyde, which was used without further purification.

Step 3: Alkyne **SI-2f** was prepared following the procedure of a preparation of alkyne **SI-2a**. Purification: column chromatography on silica gel (10-15% AcOEt in hexanes). Yield 275.3 mg (1.20 mmol, 54% yield). Colourless oil; $[\alpha]_D^{25}$ –108.1 (*c* 2.33, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ 7.47 – 7.27 (m, 5H), 5.24 – 5.08 (m, 2H), 4.64 – 4.48 (m, 1H), 3.61 – 3.47 (m, 1H), 3.44 – 3.33 (m, 1H), 2.29 – 2.23 (m, 1H), 2.17 – 2.00 (m, 3H), 1.98 – 1.87 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ 154.4, 136.8, 128.4, 127.9, 127.7, 83.7, 70.3, 66.9, 48.4 and 48.0, 46.1 and 45.8, 33.8 and 32.9, 24.4 and 23.5; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{15}NO_2Na$ $[(M+Na)^+]$ 252.1000; found: 252.0988; FTIR (film) ν: 3033, 2953, 1704, 1447, 1413, 1358, 1184. 1117, 1092 cm^{-1}.

***N*-Boc (*R*)-1-phenylprop-2-yn-1-amine (SI-2g):**



Step 1: (*R*)-*t*-Butyl sulfinamide (255 mg, 2.10 mmol) was dissolved in anhydr. THF (20 mL), followed by addition of benzaldehyde (212 mg, 204 μL, 2.00 mmol) and $Ti(OEt)_4$ (1.37 g, 1.26 mL, 6.00 mmol). The resulting mixture was stirred at rt overnight. Next sat. NaCl (20 mL) was added with vigorous stirring. The resulting precipitation was filtered off through Celite® pad and washed with Et_2O. Water was added to filtrate and layers were separated. Aqueous layer was washed with Et_2O twice. The combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The residue was purified by a silica gel chromatography (25% AcOEt in hexanes) to afford 356 mg (1.70 mmol, 85% yield) of **SI-3a** as a colourless oil; $[\alpha]_D^{25}$ –113.1 (*c* 1.55, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.89 – 7.79 (m, 2H), 7.51 – 7.39 (m, 3H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 134.1, 132.4, 129.4, 128.9, 57.7, 22.6.

Step 2: Trimethylsilylacetylene (418 mg, 589 μL, 4.25 mmol) was added dropwise to a cooled (0 °C) solution of *i*PrMgCl (2M in THF, 1.7 mL, 3.4 mmol). The resulting mixture was stirred 30 min at the same temperature and 15 min at rt. In a separate flask compound **SI-3a** (356 mg,

1.70 mmol) was dissolved in anhydr. CH_2Cl_2 (8.5 mL) and cooled down to –78 °C, followed by dropwise addition of prepared Grignard reagent. The resulting mixture was stirred at –78 °C for 2h, warmed to rt and stirred for additional 4h. Next, sat. NH_4Cl and Et_2O were added and layers were separated. Aqueous layer was washed with Et_2O twice. The combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The crude residue was purified by a silica gel chromatography (30% AcOEt in hexanes) to provide 411 mg (1.34 mmol, 79% yield) of **SI-4a** as a white solid; $[\alpha]_D^{25}$ –22.9 (*c* 0.62, $CHCl_3$)[Lit.[3] –18.4 (*c* 0.54, $CHCl_3$)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.38 – 7.29 (m, 3H), 5.23 (d, *J* = 5.4 Hz, 1H), 3.63 (d, *J* = 5.4 Hz, 1H), 1.20 (s, 9H), 0.19 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 128.6, 128.3, 127.9, 103.9, 92.2, 56.3, 51.0, 22.5, –0.2.

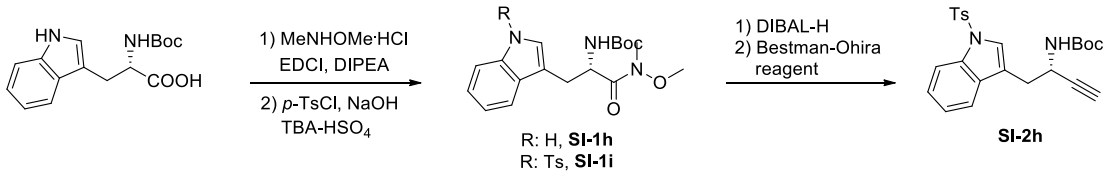
Step 3:[4] Compound **SI-4a** (355 mg, 1.15 mmol) was dissolved in 24 mL of mixture of CH_2Cl_2, MeOH and H_2O (7:4:1 *v*/*v*), followed by an addition of $AgNO_3$ (39.2 mg, 0.23 mmol). The reaction mixture was covered with a tinfoil and stirred overnight at rt. Next, sat. NH_4Cl and CH_2Cl_2 were added and layers were separated. Aqueous layer was washed with CH_2Cl_2 twice. The combined organic layers were dried over Na_2SO_4, filtered and evaporated. The residue was used in the next step without further purification.

Step 4: The residue from previous step was dissolved in anhydr. MeOH (3 mL), followed by addition of 4M HCl in dioxane (577 μL, 2.31 mmol). The resulting mixture was stirred at rt for 2h, then the volatiles were evaporated. The residue was used in the next step without further purification.

Step 5: The residue from previous step was dissolved in anhydr. CH_2Cl_2 (6 mL) and Et_3N (257 mg, 354 μL, 2.54 mmol) and cooled down to 0 °C, followed by addition of solution of Boc_2O (277 mg, 1.27 mmol) in anhydr. CH_2Cl_2 (1 mL). The resulting mixture was stirred at rt overnight. Next, 1 M HCl and CH_2Cl_2 were added and layers were separated. The aqueous layer was washed with CH_2Cl_2 twice. The combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The residue was purified by column chromatography (SiO_2, 5 – 10% AcOEt in hexanes) to give 212 mg (80% yield) of **SI-2g** as a white solid, m.p. 90.8 – 92.1 °C; $[\alpha]_D^{25}$ –18.4 (*c* 0.73, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.3 Hz, 2H), 7.40 – 7.27 (m, 3H), 5.66 (s, 1H), 5.08 (s, 1H), 2.49 (d, *J* = 2.4 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 138.8, 128.7, 128.1, 126.8, 82.2, 80.3, 72.9, 46.2, 28.34; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{17}NO_2Na$

[(M+Na)$^+$] 254.1157; found: 254.1160; FTIR (film) ν: 3349, 3031, 2979, 1688, 1499, 1454, 13067, 1311, 1243, 1165, 1020 cm^{-1}.

_t_-Butyl (_S_)-(1-(1-tosyl-1_H_-indol-3-yl)but-3-yn-2-yl)carbamate (SI-2h)



Step 1: Weinreb amide **SI-1h** was prepared following procedure for a preparation of amide **SI-1a** staring from 823 mg (2.70 mmol) *N*-Boc *L*-tryptophan. Purification: column chromatography on silica gel (30 to 70% AcOEt in hexanes). Yield: 888 mg (2.56 mmol, 95% yield) of **SI-1h** as a white solid.

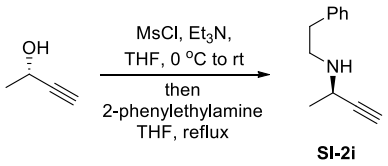
Step 2: The Weinreb amide **SI-1h** (630 mg, 1.81 mmol), NaOH (218 mg, 5.44 mmol) and tetrabutylammonium hydrogensulphate (30.7, 90 μmol) were suspended in anhydr. CH_2Cl_2 (11 mL), followed by an addition of *p*-TsCl (415 mg, 2.18 mmol) portionwise. The resulting reaction mixture was stirred at rt for 3 h. Next, w after was added and layers were separated. The aqueous layer was washed with CH_2Cl_2 twice. The combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The residue was purified by column chromatography (SiO_2, 40% AcOEt in hexanes) to provide 673 mg (1.34 mmol, 74% yield) of **SI-1i** as a white solid.

Step 3: The Weinreb amide **SI-1i** (650 mg, 1.30 mmol) was reduced with DIBAL-H (2.6 mmol), as described above, to provide the corresponding amino aldehyde, which was used without further purification.

Step 3: Alkyne **SI-2h** was prepared following the procedure of a preparation of alkyne **SI-2a**. Purification: column chromatography on silica gel (10% AcOEt in hexanes). Yield 290.1 mg (0.66 mmol, 51%). White solid, m.p. 116–117 °C; $[\alpha]_D^{25}$ –2.9 (*c* 0.92, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.50 (s, 1H), 7.33 – 7.16 (m, 4H), 4.80 – 4.62 (m, 2H), 3.11 – 3.00 (m, 2H), 2.32 (s, 3H), 2.25 (s, 1H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 144.8, 135.3, 135.1, 131.1, 129.8, 126.8, 124.9, 124.7, 123.2, 119.7, 117.5, 113.7, 82.7, 80.2, 72.2, 53.4, 31.4, 28.3, 21.5; HRMS (ESI-TOF) *m/z* calcd for $C_{24}H_{26}N_2O_4NaS$ [(M+Na)$^+$]

461.1511; found: 461.1523; FTIR (film) ν: 3402, 3053, 2978, 1707, 1598, 1496, 1449, 1367, 1247, 1173, 1122 cm^{-1}.

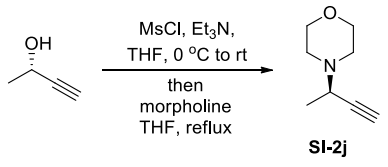
(*R*)-*N*-phenethylbut-3-yn-2-amine (SI-2i)



SI-2i

To a solution of (*S*)-3-butyn-2-ol (Acros Organics, 98% *ee*) (200 mg, 224 µL, 2.85 mmol) and Et_3N (722 mg, 1 mL, 7.13 mmol) in anhydr. THF (15 mL) was added MsCl (392 mg, 265 µL, 3.42 mmol) at 0 °C. After stirring for 1 h at rt, 2-phenylethylamine (865 mg, 899 µL, 7.13 mmol) was added in a one portion and the reaction mixture was stirred at reflux overnight. After cooling down to rt the reaction mixture was filtered through Celite® and washed with Et_2O. The solvent was evaporated and the crude residue was purified by column chromatography (SiO_2, 50% AcOEt in hexanes + 1% Et_3N) to give 224 mg (1.29 mmol, 45%) of **SI-2i** as a colourless oil. $[\alpha]_D^{25}$ +5.3 (*c* 0.58, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 3.52 (qd, *J* = 6.8, 2.1 Hz, 1H), 3.19 – 3.07 (m, 1H), 2.93 – 2.73 (m, 3H), 2.24 (d, *J* = 2.1 Hz, 1H), 1.35 (d, *J* = 6.8 Hz, 3H) [N-**H** proton signal is not visible]; ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 128.7, 128.5, 126.2, 86.3, 70.5, 48.5, 45.0, 36.3, 22.3; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{16}N$ [$(M+H)^+$] 174.1283; found: 174.1284; FTIR (film) ν: 3297, 3027, 2931, 2099, 1603, 1453, 1139, 1122, 699 cm^{-1}.

(*R*)-4-(but-3-yn-2-yl)morpholine (SI-2j)

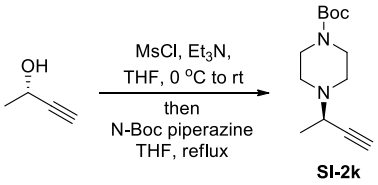


SI-2j

To a solution of (*S*)-3-butyn-2-ol (Acros Organics, 98% *ee*) (200 mg, 224 µL, 2.85 mmol) and Et_3N (1.43 g, 2 mL, 14.3 mmol) in anhydr. THF (15 mL) was added MsCl (654 mg, 442 µL, 5.71 mmol) at 0 °C. After stirring for 1 h at rt, morpholine (746 mg, 746 µL, 8.56 mmol) was added in one portion and the reaction mixture was stirred at reflux overnight. After cooling down to rt the reaction mixture was filtered through Celite® and washed with Et_2O. The solvent was evaporated and the crude residue was purified by column chromatography (SiO_2, 20%

AcOEt in hexanes + 1% Et_3N) to give 189 mg (1.36 mmol, 48% yield) of **SI-2j** as a colourless oil. $[\alpha]_D^{25}$ +40.4 (*c* 0.53, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 3.81 – 3.66 (m, 4H), 3.44 (qd, *J* = 7.0, 2.2 Hz, 1H), 2.70 – 2.61 (m, 2H), 2.53 – 2.43 (m, 2H), 2.29 (d, *J* = 2.2 Hz, 1H), 1.34 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.0, 72.9, 67.0, 51.9, 49.3, 18.9; HRMS (ESI-TOF) *m/z* calcd for $C_8H_{14}NO$ $[(M+H)^+]$ 140.1075; found: 140.1072; FTIR (film) ν: 2958, 2096, 1140, 1118 cm^{-1}.

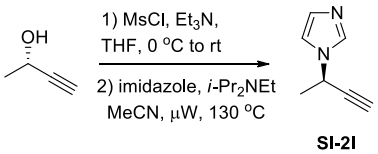
_t_-Butyl (_R_)-4-(but-3-yn-2-yl)piperazine-1-carboxylate (SI-2k):



SI-2k

To a solution of (*S*)-3-but-yn-2-ol (Acros Organics, 98% *ee*) (200 mg, 224 µL, 2.85 mmol) and Et_3N (1.43 g, 2 mL, 14.3 mmol) in anhydr. THF (15 mL) was added MsCl (654 mg, 442 µL, 5.71 mmol) at 0 °C. After stirring for 1 h at rt, *N*-Boc piperazine (1.59 g, 8.56 mmol) was added in one portion and the reaction mixture was stirred at reflux overnight. After cooling down to rt the reaction mixture was filtered through Celite® and washed with Et_2O. The solvent was evaporated and the crude residue was purified by column chromatography (SiO_2, 10 – 15% AcOEt in hexanes + 1% Et_3N) to give 302 mg (1.27 mmol, 44% yield) of **SI-2k** as a colourless oil. $[\alpha]_D^{25}$ +28.9 (*c* 0.74, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 3.55 – 3.37 (m, 5H), 2.64 – 2.55 (m, 2H), 2.46 – 2.36 (m, 2H), 2.27 (d, *J* = 2.2 Hz, 1H), 1.45 (s, 9H), 1.35 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 81.9, 79.6, 72.9, 51.7, 48.7, 28.4, 24.9, 19.1; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{22}N_2O_2Na$ $[(M+Na)^+]$ 261.1579; found: 261.1571; FTIR (film) ν: 2979, 2097, 1695, 1456, 1422, 1249, 1171, 1126, 1034 cm^{-1}.

(_R_)-1-(but-3-yn-2-yl)-1_H_-imidazole (SI-2l)



SI-2l

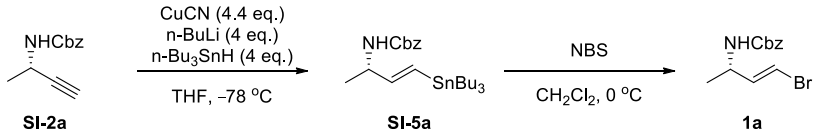
Step 1: To a solution of (*S*)-but-3-yn-2-ol (Acros Organics, 98% *ee*) (1 g, 1.12 mL, 14.3 mmol) and Et_3N (3.61 g, 5 mL, 35.7 mmol) in anhydr. THF (75 mL) was added MsCl (1.96 g, 1.33 mL, 17.1 mmol) at 0 °C. After stirring for 1 h at rt, sat. aqueous $NaHCO_3$ was added. Layers were

separated and aqueous layer was washed with Et_2O twice. Combined organic layers were dried over Na_2SO_4, filtered and evaporated to give crude (*S*)-but-3-yn-2-yl methanesulfonate which was used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (qd, *J* = 6.7, 2.1 Hz, 1H), 3.11 (s, 3H), 2.69 (d, *J* = 2.1 Hz, 1H), 1.66 (d, *J* = 6.7 Hz, 3H).

Step 2: The crude (*S*)-but-3-yn-2-yl methanesulfonate from previous step (300 mg, 2.03 mmol), DIPEA (314 mg, 423 µL, 2.43 mmol) and imidazole (152 mg, 2.23 mmol) were dissolved in anhydr. MeCN (7 mL). The resulting mixture was stirred under microwave irradiation (200 MW, 130 °C, 1h). Solvent was removed and the crude residue was purified using column chromatography (10% *i*PrOH in hexanes) to to give 119 mg (0.99 mmol, 49% yield) of **SI-2l** as a colourless oil. $[\alpha]_D^{25}$ - 1.3 (*c* 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.05 (s, 2H), 4.99 (qd, *J* = 7.0, 2.4 Hz, 1H), 2.53 (d, *J* = 2.4 Hz, 1H), 1.71 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6, 129.6, 117.2, 81.0, 73.8, 44.4, 24.0; HRMS (EI) *m/z* calcd for $C_7H_8N_2$ [M] 120.0687; found: 120.0691; FTIR (film) ν: 3289, 2989, 2116, 1615, 1496, 1449, 1227, 1110, 1074, 693 cm^{-1}.

3. Synthesis of vinyl bromides

N-Cbz (*S*,*E*)-4-bromobut-3-en-2-amine (1a):



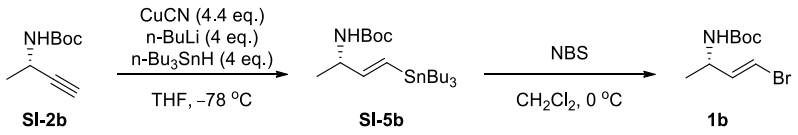
SI-2a SI-5a 1a

Step 1: A round-bottom flask was charged with CuCN (1.76 g, 19.7 mmol) and evacuated, then backfilled with argon three times. Next, anhydr. THF (130 mL) was added and the resulting suspension was cooled down to –78 °C. Next, *n*-BuLi (2.5 M soln. in hexanes, 16.5 mL, 41.3 mmol) was added over 10 min and the resulting mixture was stirred for additional 30 min. Next, *n*-Bu_3SnH (11.1 mL, 12.03 g, 41.3 mmol) was added dropwise over 15 min. After an additional 30 min, a solution of propargylic amine **SI-2a** (2 g, 9.84 mmol) in anhydr. THF (15 mL) was added dropwise over 15 min and the resulting mixture was stirred for 60 min. Next, sat. NH_4Cl was added and the cooling bath was removed. Once reaction mixture reached rt, AcOEt was added. An aqueous layer was washed twice with AcOEt. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered and evaporated. The

crude product was purified by silica gel column chromatography (1 to 3% AcOEt in hexanes) to provide vinyl stannane **SI-5a** in 95% yield (4.63 g).

Step 2: Vinyl stannane **SI-5a** (4.62 g, 9.37 mmol) was dissolved in anhydr. CH_2Cl_2 (40 mL). After cooling to 0 °C, NBS (1.67 g, 9.37 mmol) was added in a one portion. The reaction mixture was stirred for 3 h at rt. Next, sat. $NaHCO_3$ was added and layers were separated. Aquoeus layer was washed twice with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and evaporated. The residue was purified by silca gel column chromatography (5% to 10% AcOEt in hexanes) to provide 2.46 g (8.67 mmol, 93% yield (88% after two steps)) of vinyl bromide **1a** as a white solid. M.p. 48.5–49.5 °C; $[\alpha]_D^{25}$ –36.2 (*c* 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 5H), 6.26 (d, *J* = 13.7 Hz, 1H), 6.14 (dd, *J* = 13.7, 6.2 Hz, 1H), 5.15 – 4.99 (m, 3H), 4.37 – 4.25 (m, 1H), 1.22 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 138.9, 136.4, 128.6, 128.21, 128.15, 107.0, 66.8, 48.8, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{14}NO_2NaBr$ [$(M+Na)^+$] 306.0106; found: 306.0097; FTIR (film) ν: 3319, 3033, 2975, 1696, 1622, 1528, 1453, 1247, 1049, 936, 697 cm^{-1}.

***N*-Boc (*S*,*E*)-4-bromobut-3-en-2-amine (1b):**

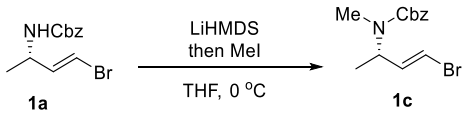


SI-2b **SI-5b** **1b**

Step 1: The vinyl stannane **SI-5b** was prepared following procedure for the synthesis of **SI-3a**. Yield: 1.60 g (85%, 3.48 mmol) starting from propargylic amine **SI-2b** (695 mg, 4.11 mmol). Purification: column chromatography on silica gel (1–2% AcOEt in hexanes).

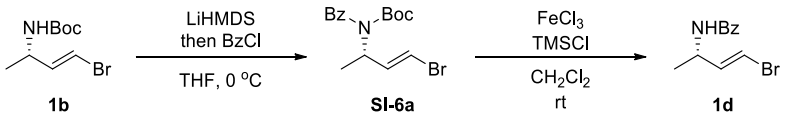
Step 2: The vinyl bromide **1b** was prepared following procedure for synthesis of **1a**. Yield: 788 mg (3.15 mmol, 92% (78% after two steps)). Purification: column chromatography on silica gel (5–10% AcOEt in hexanes; white solid, m.p. 41.7 – 42.8; $[\alpha]_D^{25}$ –50.0 (*c* 1.05 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23 (d, *J* = 13.6 Hz, 1H), 6.13 (dd, *J* = 13.6, 6.0 Hz, 1H), 4.58 – 4.46 (m, 1H), 4.27 – 4.13 (m, 1H), 1.42 (s, 9H), 1.20 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 139.4, 106.5, 79.7, 48.2, 28.4, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_9H_{16}NO_2BrNa$ [$(M+Na)^+$] 272.0262; found: 272.0262; FTIR (film) ν: 3331, 2977, 1690, 1622, 1520, 1367, 1248, 1170, 1049 cm^{-1}.

***N*-Cbz (*S*,*E*)-4-bromo-*N*-methylbut-3-en-2-amine (1c):**



A solution of **1a** (142 mg, 0.50 mmol) in anhydr. THF (3 mL) was cooled to 0 °C and 1M soln. of LiHMDS in THF (0.53 mL, 0.53 mmol) was added dropwise over 10 min. Next, MeI (37 μL, 85 mg, 0.60 mmol) was added and the resulting mixture was stirred overnight at rt. Next, sat. NH_4Cl and Et_2O was added. Aqueous layer was washed twice with Et_2O, the combined organic layers were dried over Na_2SO_4, filtered and evaporated. The residue was purified by column chromatography (SiO_2, 5% AcOEt in hexanes) to provide 93.5 mg (0.31 mmol, 63%) of **1c** as a colorless oil. $[\alpha]_D^{25}$ –64.3 (*c* 0.72 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 6.27 – 6.14 (m, 2H), 5.14 (s, 2H), 4.97 – 4.69 (m, 1H), 2.78 (s, 3H), 1.24 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 137.5, 136.7, 128.5, 128.0, 127.9, 107.7, 67.3, 52.5, 28.4, 16.6; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{16}NO_2NaBr$ [(M+Na)$^+$] 320.0262; found: 320.0254; FTIR (film) ν: 3032, 2975, 1698, 1618, 1453, 1399, 1314, 1150, 698 cm^{-1}.

(*S*,*E*)-*N*-(4-Bromobut-3-en-2-yl)benzamide (1d):

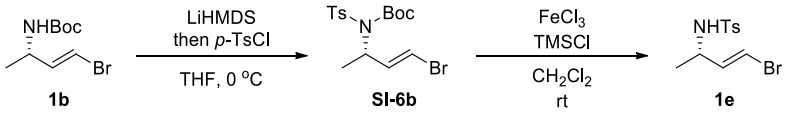


Step 1: A solution of **1b** (107 mg, 0.43 mmol) in anhydr. THF (2.5 mL) was cooled to 0 °C, and 1M soln. of LiHMDS in THF (0.45 mL, 0.45 mmol) was added. After 10 min., benzoyl chloride (59 μL, 72 mg, 0.51 mmol) was added and mixture was stirred overnight at rt. Next, sat. NH_4Cl and Et_2O was added. An aqueous layer was washed twice with Et_2O, and the combined organic layers were dried over Na_2SO_4, filtered and evaporated. The crude residue was used directly in the next step.

Step 2:[5] The residue from the previous step was dissolved in CH_2Cl_2 (2 mL), $FeCl_3$ (35 mg, 0.21 mmol) and TMSCl (54 μL, 46 mg, 0.43 mmol) were added and the reaction mixture was stirred for 1 h. Water was added and aqueous layer was washed with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and evaporated. The residue was purified by a column chromatography (SiO_2, 15% AcOEt in hexanes) to provide 63.8 mg (0.25 mmol, 58% yield) of **1d** as a white solid, m.p. 73.1 – 74.0 °C; $[\alpha]_D^{25}$ –10.7 (*c* 1.02 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.51 – 7.45 (m, 1H), 7.39 (dd, *J* = 8.2, 6.7 Hz, 2H), 6.38 (d, *J* = 7.6 Hz,

1H), 6.31 (dd, *J* = 13.7, 1.1 Hz, 1H), 6.23 (dd, *J* = 13.7, 5.9 Hz, 1H), 4.81 – 4.69 (m, 1H), 1.34 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 138.6, 134.2, 131.6, 128.6, 127.0, 107.4, 47.3, 20.1; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{12}NONaBr$ [(M+Na)$^+$] 276.0000; found: 275.9993; FTIR (film) ν: 3322, 3036, 2972, 1702, 1618, 1452, 1085 cm^{-1}.

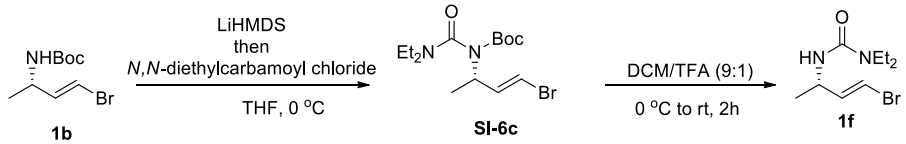
_N_-Ts (_S_,_E_)-4-bromobut-3-en-2-amine (1e):



Step 1: A solution of **1b** (107 mg, 0.43 mmol) in anhydr. THF (2.5 mL) was cooled to 0 °C, and 1M soln. of LiHMDS in THF (0.45 mL, 0.45 mmol) was added. After 10 min., *p*-TsCl (97 mg, 0.51 mmol) was added and mixture was stirred overnight at rt. Next, sat. NH_4Cl and Et_2O was added. An aqueous layer was washed twice with Et_2O, and the combined organic layers were dried over Na_2SO_4, filtered and evaporated. The crude residue was used directly in the next step.

Step 2:[5] The residue from the previous step was dissolved in CH_2Cl_2 (2 mL), $FeCl_3$ (35 mg, 0.21 mmol) and TMSCl (54 μL, 46 mg, 0.43 mmol) were added and the reaction mixture was stirred for 1 h. Water was added and aqueous layer was washed with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and evaporated. The residue was purified by a column chromatography (SiO_2, 15% AcOEt in hexanes) to provide 97.2 mg (0.33 mmol, 75% yield) of **1e** as a white solid, m.p. 73.1 – 74.0 °C; $[\alpha]_D^{25}$ –14.8 (*c* 0.84 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.12 (dd, *J* = 13.7, 1.2 Hz, 1H), 5.90 (dd, *J* = 13.7, 6.9 Hz, 1H), 4.80 (d, *J* = 7.7 Hz, 1H), 3.91 (m, 1H), 2.42 (s, 3H), 1.18 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 138.0, 137.7, 129.7, 127.2, 107.7, 51.6, 21.5, 21.3; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{14}NO_2NaSBr$ [(M+Na)$^+$] 325.9826; found: 325.9820; FTIR (film) ν: 3298, 2972, 1619, 1430, 1094 cm^{-1}.

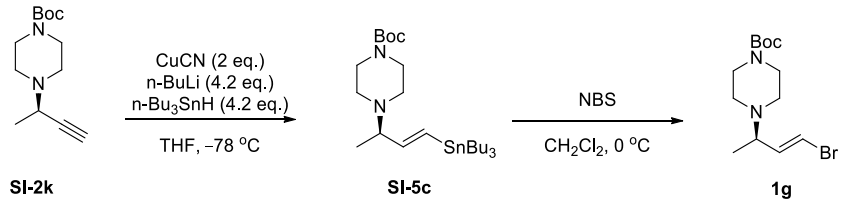
(_S_,_E_)-3-(4-Bromobut-3-en-2-yl)-1,1-diethylurea (1f):



Step 1: A solution of **1b** (80 mg, 0.48 mmol) in anhydr. THF (2 mL) was cooled to 0 °C, and 1M soln. of LiHMDS in THF (0.32 mL, 0.32 mmol) was added. After 10 min., *N,N*-diethylcarbamoyl chloride (52 mg, 49 μL, 0.38 mmol) was added and mixture was stirred overnight at rt. Next, sat. NH_4Cl and Et_2O was added. An aqueous layer was washed twice with Et_2O, and the combined organic layers were dried over Na_2SO_4, filtered and evaporated. The crude residue was used directly in the next step.

Step 2: The residue from the previous step was dissolved in CH_2Cl_2 (1.8 mL), cooled down to 0 °C, followed by addition of TFA (0.2 mL). The cooling bath was removed and the resulting mixture was stirred for 2 h. Next, sat. Na_2CO_3 was added and aqueous layer was washed with CH_2Cl_2 twice. The combined organic layers were dried over Na_2SO_4, filtered and evaporated. The residue was purified by a column chromatography (SiO_2, 25% AcOEt in hexanes) to provide 46.0 mg (0.18 mmol, 58%) of **1f** as a colourless oil; $[\alpha]_D^{25}$ –12.9 (*c* 2.14 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28 – 6.15 (m, 2H), 4.54 – 4.44 (m, 1H), 4.18 (d, *J* = 8.0 Hz, 1H), 3.24 (q, *J* = 7.2 Hz, 4H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 140.2, 106.3, 47.9, 41.2, 20.8, 13.9; HRMS (ESI-TOF) *m/z* calcd for $C_9H_{17}N_2ONaBr$ [(M+Na)$^+$] 248.0524; found: 248.0528; FTIR (film) ν: 3336, 2974, 1690, 1618, 1451, 1150 cm^{-1}.

***tert*-Butyl (*R*,*E*)-4-(4-bromobut-3-en-2-yl)piperazine-1-carboxylate (1g):**



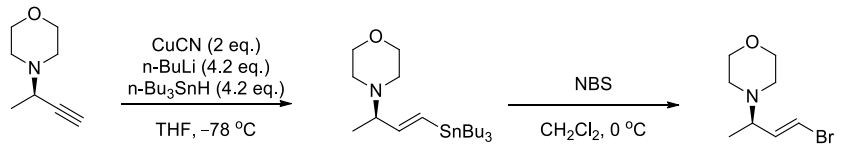
SI-2k **SI-5c** **1g**

Step 1: The vinyl stannane **SI-5c** was prepared following the procedure for the synthesis of **SI-5a**. Yield: 298.2 mg (56% yield, 0.56 mmol) starting from propargylic amine **SI-2k** (238.3 mg, 1.00 mmol). Purification: column chromatography on silica gel (1-2% AcOEt in hexanes).

Step 2: The vinyl bromide **1g** was prepared following the procedure for the synthesis of **1a**. Yield: 161.4 mg (0.51 mmol, 92% (51% after two steps)). Purification: column chromatography on silica gel (15% AcOEt in hexanes); colourless oil; $[\alpha]_D^{25}$ +21.0 (*c* 0.66 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 – 6.07 (m, 2H), 3.39 (t, *J* = 4.9 Hz, 4H), 3.07 – 2.95 (m, 1H), 2.50 – 2.33 (m, 4H), 1.43 (s, 9H), 1.15 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 139.2, 106.4, 79.6, 62.1, 49.2,

28.4, 16.9; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{23}N_2O_2NaBr$ [(M+Na)$^+$] 341.0841; found: 341.0825; FTIR (film) ν: 2926, 1706, 1619, 1449, 1141, 1119 cm^{-1}.

(*R*,*E*)-4-(4-bromobut-3-en-2-yl)morpholine (1h):

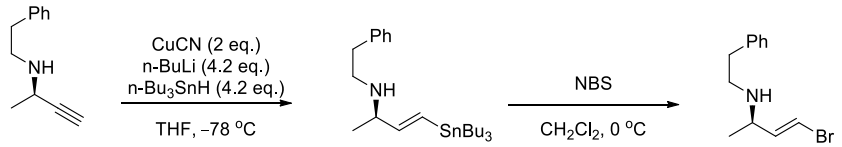


SI-2j **SI-5d** **1h**

Step 1: The vinyl stannane **SI-5d** was prepared following the procedure for the synthesis of **SI-5a**. Yield: 160.0 mg (49%, 0.37 mmol) starting from propargylic amine **SI-2j** (105.0 mg, 0.75 mmol). Purification: column chromatography on silica gel (3% AcOEt in hexanes).

Step 2: The vinyl bromide **1h** was prepared following the procedure for the synthesis of **1a**. Yield: 61.5 mg (0.28 mmol, 75% (37% after two steps)). Purification: column chromatography on silica gel (25% AcOEt in hexanes); colourless oil; $[\alpha]_D^{25}$ +41.5 (*c* 0.39 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 – 6.09 (m, 2H), 3.69 (t, *J* = 4.6 Hz, 4H), 2.94 (p, *J* = 6.5 Hz, 1H), 2.48 (m, 4H), 1.16 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 106.4, 67.1, 62.5, 50.1, 17.0; HRMS (ESI-TOF) *m/z* calcd for $C_8H_{15}NOBr$ [(M+H)$^+$] 220.0337; found: 220.0342; FTIR (film) ν: 2959, 2854, 1610, 1451, 1265, 1119 cm^{-1}.

(*R*,*E*)-4-bromo-*N*-phenethylbut-3-en-2-amine (1i):



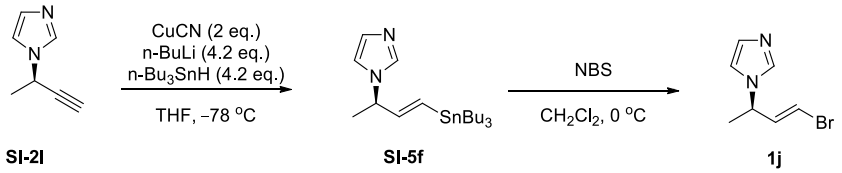
SI-2i **SI-5e** **1i**

Step 1: The vinyl stannane **SI-5e** was prepared following the procedure for the synthesis of **SI-5a**. Yield: 245.0 mg (70% yield, 0.53 mmol) starting from propargylic amine **SI-2i** (129.9 mg, 0.75 mmol). Purification: column chromatography on silica gel (5% AcOEt in hexanes).

Step 2: The vinyl bromide **1i** was prepared following the procedure for the synthesis of **1a**. Yield: 78.2 mg (0.31 mmol, 59% yield (41% after two steps)). Purification: column chromatography on silica gel (50% AcOEt in hexanes); colourless oil; $[\alpha]_D^{25}$ +7.0 (*c* 0.46 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.16 (m, 5H), 6.15 (d, *J* = 13.6 Hz, 1H), 6.02 (dd, *J* = 13.6,

8.0 Hz, 1H), 3.21 (m, 1H), 2.92 – 2.73 (m, 4H), 1.14 (d, *J* = 6.5 Hz, 3H) [N-**H** proton signal not visible]; ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 139.8, 128.7, 128.5, 126.2, 105.5, 56.1, 48.6, 36.5, 21.4; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{17}NBr$ [(M+H)$^+$] 254.0544; found: 254.0539; FTIR (film) ν: 3311, 3026, 2926, 1619, 1453, 1196, 1119, 939, 699 cm^{-1}.

(*R*,*E*)-1-(4-bromobut-3-en-2-yl)-1*H*-imidazole (1j):

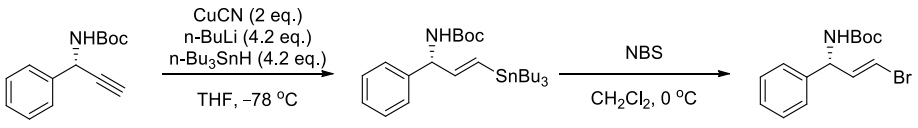


SI-2l **SI-5f** **1j**

Step 1: The vinyl stannane **SI-5f** was prepared following the procedure for the synthesis of **SI-5a**. Yield: 302.0 mg (86%, 0.73 mmol) starting from propargylic amine **SI-2l** (103.0 mg, 0.86 mmol). Purification: column chromatography on silica gel (50% AcOEt in hexanes).

Step 2: The vinyl bromide **1j** was prepared following the procedure for the synthesis of **1a**. Yield: 120.3 mg (0.60 mmol, 82% (71% after two steps)). Purification: column chromatography on silica gel (AcOEt); colourless oil; $[\alpha]_D^{25}$ -6.2 (*c* 0.89 $CHCl_3$); ^{1}H NMR (500 MHz, DMSO-d_6, 90 °C) δ 7.64 (s, 1H), 7.17 (s, 1H), 6.92 (s, 1H), 6.49 (m, 2H), 4.99 – 4.90 (m, 1H), 1.53 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6, 90 °C) δ 138.1, 135.4, 128.2, 117.0, 108.1, 53.3, 20.0; HRMS (ESI-TOF) *m/z* calcd for $C_7H_{10}N_2Br$ [(M+H)$^+$] 201.0027; found: 201.0037; FTIR (film) ν: 3372, 2980, 1622, 1495, 1227, 1079, 939, 664 cm^{-1}.

***N*-Boc (*E*)-3-Bromo-1-phenylprop-2-en-1-amine (1k):**



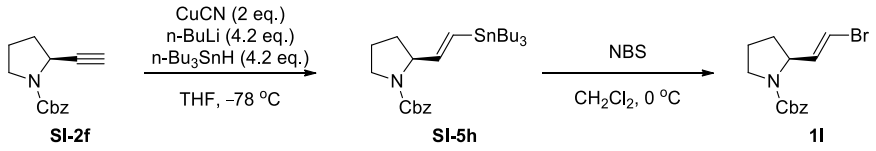
SI-2g **SI-5g** **1k**

Step 1: The vinyl stannane **SI-5g** was prepared following the procedure for the synthesis of **SI-3a**. Yield: 241.1 mg (85%, 0.46 mmol) starting from propargylic amine **SI-2g** (125.0 mg, 0.54 mmol). Purification: column chromatography on silica gel (1–2% AcOEt in hexanes).

Step 2: The vinyl bromide **1k** was prepared following procedure for synthesis of **1a**. Yield: 121.4 mg (0.39 mmol, 84% (71% after two steps)). Purification: column chromatography on silica gel (5% AcOEt in hexanes); white solid, m.p. 90.8 – 92.1 °C; $[\alpha]_D^{25}$ –4.3 (*c* 0.83 $CHCl_3$) ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 5H), 6.35 (dd, *J* = 13.6, 6.1 Hz, 1H), 6.26 (d, *J* = 13.6 Hz, 1H), 5.26 (s, 1H), 4.89 (s, 1H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 139.7, 137.4, 128.9, 127.9, 126.8, 108.3, 80.1, 56.6, 28.3; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{17}NO_2Na$ [(M+Na)$^+$] 254.1157; found: 254.1160; FTIR (film) ν: 3349, 3031, 2978, 1668, 1499, 1454, 1367, 1311, 1243, 1165 cm^{-1}.

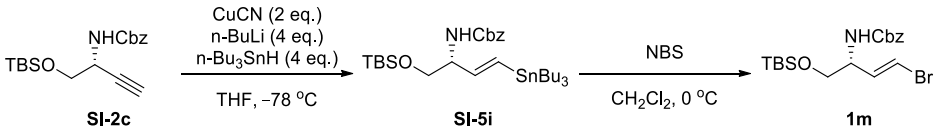
_N_-Cbz (_S_,_E_)-2-(2-Bromovinyl)pyrrolidine (1l):



Step 1: The vinyl stannane **SI-5h** was prepared following the procedure for the synthesis of **SI-3a**. Yield: 52.8 mg (89%, 1.02 mmol) starting from propargylic amine **SI-2f** (264.1 mg, 1.15 mmol). Purification: column chromatography on silica gel (2–5% AcOEt in hexanes).

Step 2: The vinyl bromide **1l** was prepared following the procedure for the synthesis of **1a**. Yield: 303.5 mg (0.98 mmol, 96% (85% after two steps)). Purification: column chromatography on silica gel (10–15% AcOEt in hexanes); colourless oil; $[\alpha]_D^{25}$ –64.5 (*c* 2.21 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ 7.40 – 7.23 (m, 5H), 6.29 – 6.02 (m, 2H), 5.22 – 4.99 (m, 2H), 4.45 – 4.29 (m, 1H), 3.54 – 3.36 (m, 2H), 2.05 – 1.95 (m, 1H), 1.94 – 1.83 (m, 2H), 1.81 – 1.70 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of 2 rotamers) δ 154.7, 137.7 and 137.1, 136.7, 128.5, 128.0 (×2), 107.1 and 106.9, 67.0, 59.0 and 58.8, 46.6 and 46.2, 31.9 and 30.9, 23.6 and 22.8; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{16}NO_2BrNa$ [(M+Na)$^+$] 332.0262; found: 332.0260; FTIR (film) ν: 3033, 2953, 1702, 1621, 1448, 1410, 1363, 1179, 1099 cm^{-1}.

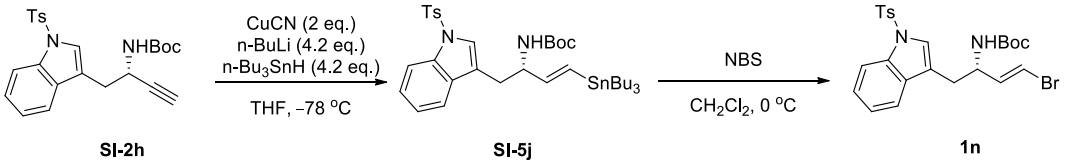
_N_-Cbz (_R_,_E_)-4-Bromo-1-((*tert*-butyldimethylsilyl)oxy)but-3-en-2-amine (1m)



Step 1: The vinyl stannane **SI-5i** was prepared following the procedure for the synthesis of **SI-5a**. Yield: 715 mg (83%, 1.14 mmol) starting from propargylic amine **SI-2c** (458 mg, 1.37 mmol). Purification: column chromatography on silica gel (1–2% AcOEt in hexanes). Colourless oil.

Step 2: The vinyl bromide **1m** was prepared following the procedure for the synthesis of **1a**. Yield: 466 mg (1.12 mmol, 98% (81% after two steps)). Purification: column chromatography on silica gel (5% AcOEt in hexanes); colourless oil; $[\alpha]_D^{25}$ –13.6 (*c* 2.21 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 6.34 (d, *J* = 13.8 Hz, 1H), 6.21 (dd, *J* = 13.8, 6.7 Hz, 1H), 5.20 – 5.05 (m, 3H), 4.24 (s, 1H), 3.70 (dd, *J* = 10.1, 4.2 Hz, 1H), 3.64 (dd, *J* = 10.1, 3.6 Hz, 1H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 136.3, 135.4, 128.6, 128.21, 128.17, 108.4, 67.0, 64.7, 54.6, 25.8, 18.3, –5.46, –5.48; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{28}NO_3BrNaSi$ [(M+Na)$^+$] 436.0920; found: 436.0908; FTIR (film) ν: 3325, 3033, 2954, 2857, 1704, 1623, 1500, 1464, 1254, 1115, 837, 777 cm^{-1}.

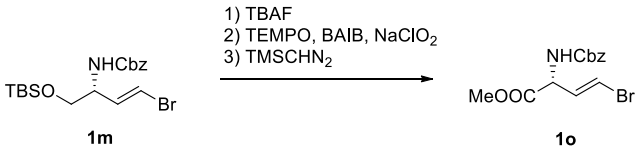
_t_-Butyl (_S_,_E_)-(4-bromo-1-(1-tosyl-1_H_-indol-3-yl)but-3-en-2-yl)carbamate (1n):



Step 1: The vinyl stannane **SI-5j** was prepared following the procedure for the synthesis of **SI-5a**. Yield: 397.5 mg (88% yield, 0.54 mmol) starting from propargylic amine **SI-2h** (270.0 mg, 0.62 mmol). Purification: column chromatography on silica gel (1–4% AcOEt in hexanes).

Step 2: The vinyl bromide **1n** was prepared following the procedure for the synthesis of **1a**. Yield: 163.7 mg (0.32 mmol, 58% (51% after two steps)). Purification: column chromatography on silica gel (5-10% AcOEt in hexanes); white waxy solid; $[\alpha]_D^{25}$ –3.2 (*c* 0.72 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.38 (s, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.19 (m, 3H), 6.16 – 6.02 (m, 2H), 4.60 – 4.40 (m, 2H), 2.96 (dd, *J* = 14.6, 5.6 Hz, 1H), 2.87 (dd, *J* = 14.6, 7.2 Hz, 1H), 2.33 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 144.9, 137.0, 135.2, 135.1, 130.8, 129.9, 126.8, 124.9, 124.5, 123.3, 119.6, 117.7, 113.8, 107.8, 80.0, 59.1, 30.7, 28.3, 21.6; HRMS (ESI-TOF) *m/z* calcd for $C_{24}H_{27}N_2O_4BrNaS$ [(M+Na)$^+$] 541.0773; found: 541.0767; FTIR (film) ν: 3400, 3062, 2977, 1701, 1622, 1598, 1504, 1448, 1227, 1173, 1122, 1092 cm^{-1}.

***N*-Cbz Methyl (*R*,*E*)-2-amino-4-bromobut-3-enoate (1o):**

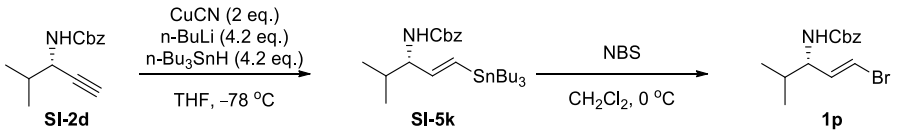


Step 1: Vinyl bromide **1m** (268.0 mg, 0.65 mmol) was dissolved in anhydr. THF (4 mL) and the solution was cooled down to 0 °C, followed by a dropwise addition of TBAF (1M solution in THF, 0.71 mL, 0.71 mmol). After 1h, sat. NH_4Cl was added and layers were separated. An aqueous layer was washed with three times with AcOEt. The combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The crude residue was purified by column chromatography (SiO_2, 40% AcOEt in hexanes) to provide 190.6 mg (0.64 mmol, 98%) of intermediate amino alcohol.

Step 2: The amino alcohol from previous step (100 mg, 0.33 mmol) was dissolved in MeCN (1 mL) and phosphate buffer pH 6.8 (1 mL) and cooled down to 0 °C, followed by an addition of TEMPO (10.4 mg, 0.067 mmol), bis(acetoxy)iodobenzene (10.7 mg, 0.033 mmol) and $NaClO_2$ (80% purity, 113 mg, 1.00 mmol). The reaction mixture was stirred vigorously at rt overnight. Next, water and AcOEt were added and layers were separated. An aqueous layer was washed with AcOEt (×6). The combined organic layers were dried over Na_2SO_4, filtered and evaporated to dryness to give the crude residue that was used directly in the next step without further purification.

Step 3: The crude aminoacid from previous step was dissolved in anhydr. MeOH (2 mL), followed by a dropwise addition of (trimethylsilyl)diazomethane (2M solution in Et_2O, 0.5 mL, 1.0 mmol). After 30 min the reaction mixture was evaporated and the residue was purified by a column chromatography (SiO_2, 10% AcOEt in hexanes) to provide 63.9 mg (0.19 mmol, 58%) of vinyl bromide **1o** as white waxy solid; $[\alpha]_D^{25}$ −46.8 (*c* 0.64 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 5H), 6.47 (d, *J* = 13.7 Hz, 1H), 6.22 (dd, *J* = 13.7, 6.5 Hz, 1H), 5.61 – 5.54 (m, 1H), 5.12 (s, 2H), 4.94 – 4.85 (m, 1H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 155.4, 135.9, 131.6, 128.6, 128.3, 128.2, 110.7, 67.4, 55.9, 53.1; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{14}NO_4BrNa$ [$(M+Na)^+$] 350.0004; found: 349.9998; FTIR (film) ν: 3330, 3033, 2963, 1747, 1721, 1623, 1521, 1454, 1331, 1283, 1212, 1054 cm^{-1}.

***N*-Cbz (*S*,*E*)-1-Bromo-4-methylpent-1-en-3-amine (1p):**

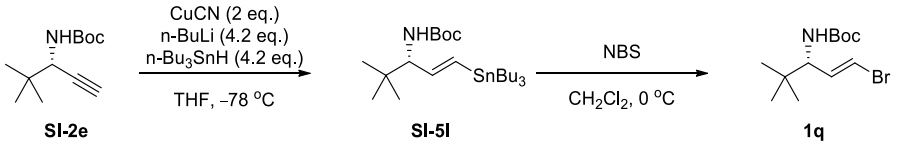


SI-2d SI-5k 1p

Step 1: The vinyl stannane **SI-5k** was prepared following the procedure for synthesis of **SI-5a**. Yield: 183.6 mg (88% yield, 0.35 mmol) starting from propargylic amine **SI-2d** (92 mg, 0.40 mmol). Purification: column chromatography on silica gel (1–2% AcOEt in hexanes).

Step 2: The vinyl bromide **1p** was prepared following the procedure for synthesis of **1a**. Yield: 98.5 mg (0.32 mmol, 90% (79% after two steps)). Purification: column chromatography on silica gel (5% AcOEt in hexanes); white waxy solid; $[\alpha]_D^{25}$ –15.8 (*c* 1.39 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 5.2 Hz, 5H), 6.27 (d, *J* = 13.6 Hz, 1H), 6.08 (dd, *J* = 13.6, 7.2 Hz, 1H), 5.10 (s, 2H), 4.77 (s, 1H), 4.02 (s, 1H), 1.79 (hept, *J* = 6.8 Hz, 1H), 0.92 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 136.3 (×2), 128.6, 128.22, 128.15, 107.7, 67.0, 58.7, 32.2, 18.6, 18.3; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{18}NO_2BrNa$ [(M+Na)$^+$] 334.0419; found: 334.0413; FTIR (film) ν: 3321, 2973, 1690, 1622, 1511, 1363, 1247, 1170, 1050 cm^{-1}.

***N*-Boc (*S*,*E*)-1-Bromo-4,4-dimethylpent-1-en-3-amine (1q):**

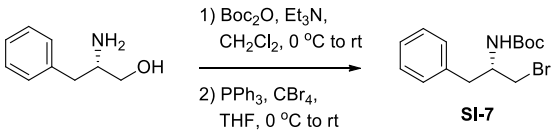


Step 1: The vinyl stannane **SI-5l** was prepared following the procedure for the synthesis of **SI-5a**. Yield: 149.4 mg (77%, 0.30 mmol) starting from propargylic amine **SI-2e** (81.5 mg, 0.39 mmol). Purification: column chromatography on silica gel (1–2% AcOEt in hexanes).

Step 2: The vinyl bromide **1q** was prepared following the procedure for the synthesis of **1a**. Yield: 76.4 mg (0.26 mmol, 88% (68% after two steps)). Purification: column chromatography on silica gel (5% AcOEt in hexanes); white solid, m.p. 69.2 – 71.1; $[\alpha]_D^{25}$ –34.7 (*c* 1.31 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.23 (d, *J* = 13.5 Hz, 1H), 6.12 (dd, *J* = 13.5, 7.5 Hz, 1H), 4.58 – 4.49 (m, 1H), 3.89 (s, 1H), 1.43 (s, 9H), 0.90 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 135.5, 107.7, 79.6, 61.3, 34.3, 28.4, 26.2; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{22}NO_2BrNa$ [(M+Na)$^+$] 314.0732; found: 314.0729; FTIR (film) ν: 3298, 2965, 1676, 1622, 1534, 1476, 1454, 1366, 1311, 1251, 1173, 1062 cm^{-1}.

4. Synthesis of alkyl bromides

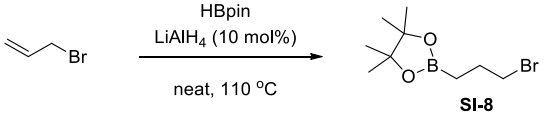
***t*-Butyl (*S*)-(1-bromo-3-phenylpropan-2-yl)carbamate (SI-7):**



SI-7

A soln. of Boc_2O (7.6 g, 34.7 mmol) in 20 mL of anhydr. CH_2Cl_2 was added to the cooled (0 °C) solution of L-phenylalaninol (5 g, 33.0 mmol) and Et_3N (5.1 mL, 3.7 g, 36.3 mmol) in anhydr. CH_2Cl_2 (60 mL) under Ar. The mixture was adjusted to rt and stirred overnight. Next, water was added and organic layer was separated and washed with sat. $NaHCO_3$ twice, dried over Na_2SO_4, filtered and evaporated. The residue was dissolved in anhydr. THF (150 mL) under argon followed by addition of PPh_3 (13.0 g, 49.6 mmol). After cooling to 0 °C, CBr_4 (16.5 g, 49.6 mmol) was added in one portion and the mixture was adjusted to rt and stirred for 2 h. The resulting suspension was filtered through short Celite pad and washed with cold THF. The filtrate was concentrated and the residue was purified by a column chromatography on silica gel (5% AcOEt in hexanes). Yield 6.3 g (61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.20 (m, 5H), 4.79 (s, 1H), 4.08 – 4.00 (m, 1H), 3.52 (dd, *J* = 10.5, 4.2 Hz, 1H), 3.36 (dd, *J* = 10.5, 3.4 Hz, 1H), 2.94 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.86 (dd, *J* = 13.6, 8.3 Hz, 1H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 137.1, 129.3, 128.7, 126.8, 79.8, 51.5, 38.9, 37.3, 28.3.

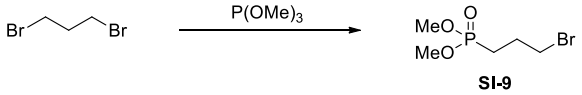
2-(3-Bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (SI-8):



SI-8

Young's flask was charged with $LiAlH_4$ (78 mg, 2.07 mmol), allyl bromide (1.79 mL, 2.5 g, 20.7 mmol) and HBpin (4.5 mL, 3.9 mg, 31.0 mmol) under Ar (**Caution:** gas evolution may occur during reaction set-up). The mixture was stirred at 110 °C for 3h. After cooling to rt, CH_2Cl_2 was added and the mixture was filtered through short pad of silica gel. After concentration, the residue was purified by a column chromatography on silica gel (10% AcOEt in hexanes). Yield 2.9 g (56 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.43 (t, *J*= 7.7Hz, 2H), 2.02 –1.95 (m, 2H), 1.26 (s, 12H), 0.93 (t, *J*= 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.2, 36.2, 27.5, 24.8 (carbon α to boron not visible); ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.6.

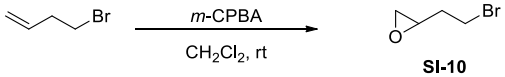
Dimethyl (3-bromopropyl)phosphonate (SI-9):



SI-9

A mixture of $P(OMe)_3$ (2.6 mL, 2.77 g, 22.2 mmol) and 1,3-dibromopropane (7.6 mL, 15.0 g, 74.3 mmol) was stirred at 150 °C for 30 min. After cooling to rt, the impurities were removed under reduced pressure. Yield 4.8 g (93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (d, J_{H-P} = 10.8 Hz, 6H), 3.45 (td, *J* = 6.5, 1.1 Hz, 2H), 2.20 – 2.07 (m, 2H), 1.97 – 1.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 52.42 and 52.35 (d, J_{C-P} 6.3 Hz), 33.5 and 33.3 (d, J_{C-P} 18.9 Hz), 25.83 and 25.78 (d, J_{C-P} 4.4 Hz), 24.1 and 22.7 (d, J_{C-P} 142.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.1.

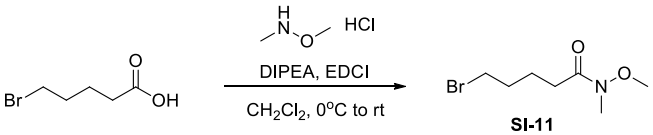
2-(2-Bromoethyl)oxirane (SI-10):



SI-10

Homoallyl bromide (2.0 mL, 2.66 g, 19.7 mmol) was dissolved in anhydr. CH_2Cl_2 (40 mL) and *m*-CPBA (77% purity, 6.6 g, 29.6 mmol) was added. After stirring at rt overnight, sat. $NaHCO_3$ was added. An organic layer was washed twice with sat. $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated. Yield 2.8 g (94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50 (t, *J* = 6.7 Hz, 2H), 3.11 – 3.04 (m, 1H), 2.82 (t, *J* = 4.4 Hz, 1H), 2.56 (dd, *J* = 4.4, 2.7 Hz, 1H), 2.20 – 1.98 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 50.7, 47.0, 35.7, 28.9.

5-Bromo-*N*-methoxy-*N*-methylpentanamide (SI-11):

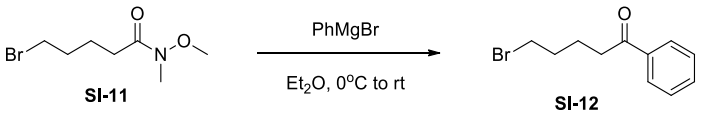


SI-11

5-Bromovaleric acid (800 mg, 4.42 mmol) and N,O-dimethylhydroxylamine hydrochloride (474 mg, 4.86 mmol) was dissolved in anhydr. DCM (20 mL), followed by addition of DIPEA (628 mg, 847 µL, 4.86 mmol). The mixture was cooled down to 0 °C, followed by addition of solution of EDCI (932 mg, 4.86 mmol) in anhydr. DCM (10 mL). The resulting mixture was stirred at rt overnight. Next, sat. aqueous NH_4Cl was added and layers were separated. Aqueous layer was washed with DCM twice. The combined organic layers were dried with anhydr. Na_2SO_4, filtered and evaporated. The crude residue was purified using a silica gel column chromatography (40% AcOEt in hexanes) to give 812 mg (82% yield) of **SI-11** as a

colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (s, 3H), 3.38 (t, *J* = 6.7 Hz, 2H), 3.13 (s, 3H), 2.41 (t, *J* = 7.2 Hz, 2H), 1.92 – 1.69 (m, 4H).

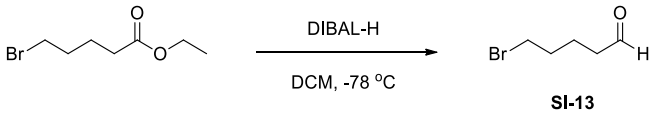
5-Bromo-1-phenylpentan-1-one (SI-12):



SI-11 **SI-12**

5-Bromo-*N*-methoxy-*N*-methylpentanamide **SI-11** (300 mg, 1.34 mmol) was dissolved in anhydr. Et_2O (5 mL) and cooled down to 0 °C, followed by dropwise addition of phenylmagnesium bromide (3 M solution in Et_2O, 0.58 mL, 1.74 mmol). The resulting mixture was stirred at rt for 2 h, followed by addition of sat. aqueous NH_4Cl and layers were separated. The aqueous layer was washed with Et_2O twice. The combined organic layers were dried with anhydr. Na_2SO_4, filtered and evaporated. The crude residue was purified using a silica gel column chromatography (20% AcOEt in hexanes) to give 303.4 mg (94%) of **SI-12** as a white waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 2H), 3.43 (t, *J* = 6.0 Hz, 2H), 3.00 (t, *J* = 6.2 Hz, 2H), 2.01 – 1.84 (m, 4H).

5-Bromo-1-phenylpentan-1-one (SI-13):

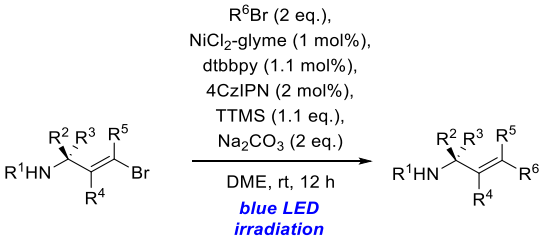


SI-13

Ethyl 5-bromovaleriate (1.32 g, 1.0 mL, 6.3 mmol) was dissolved in anhydr. DCM (40 mL) and cooled down to -78 °C, followed by dropwise addition of DIBAL-H (1 M solution in hexane, 6.3 mL, 6.3 mmol). After 1 h, 10% aqueous HCl was added and the mixture was warmed to rt. Layers were separated and aqueous layer was washed with DCM twice. The combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The resulting mixture was distilled (4.5 torr, 82 °C) to give 920 mg (88%) of **SI-13** as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.5 Hz, 1H), 3.43 – 3.36 (m, 2H), 2.48 (td, *J* = 7.1, 1.5 Hz, 2H), 1.93 – 1.85 (m, 2H), 1.82 – 1.74 (m, 2H).

5. Photochemical and Ni-catalyzed coupling of vinyl bromides

5.1. Photoredox/Ni-catalyzed coupling of vinyl bromides with alkyl bromides (Method A):



General procedure: A 8 mL reaction vial was charged with $NiCl_2$-glyme (0.55 mg, 1 mol%) and dtbbpy (0.74 mg, 1.1 mol%). Next, anhydr. DME (0.5 mL) is added under an argon atmosphere and the solution in stirred for 10 min. To a second vial, 4CzIPN photocatalyst (3.9 mg, 2 mol%), vinyl bromide **4** (71 mg, 0.25 mmol), Na_2CO_3 (54 mg, 2 eq.), and alkyl bromide (if solid, 2 eq.) were added. Next, anhydr. DME (2 mL), alkyl bromide (if liquid and not volatile, 2 eq.) and TTMS (68 mg, 85 μL) were added sequentially under an argon atmosphere. Finally, the nickel complex from the first vial was transferred into second one and the reaction mixture was flushed with argon for 10 min. In case of volatile alkyl bromides, it was added after the argon flush. Next, the resulting mixture was stirred vigorously and irradiated with two Higrow 36W LED bulb overnight (18×2W LEDs in each lamp, 450-460 nm) (vial was placed ca. 7 cm away from each lamp) (Figure 1). The vial was cooled with a cooling fan to avoid overheating (ca. 25 °C). When vinyl bromide was consumed according to TLC analysis ($KMnO_4$ stain) reaction mixture concentrated in vacuo and the residue was purified by column chromatography.

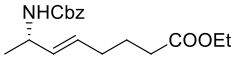
Figure 1. Photoredox reaction set-up.

5.2. Decarboxylative photoredox/Ni-catalyzed coupling of vinyl bromides with alkyl carboxylic acids (Method B):

General procedure: A vial was charged with $NiCl_2$-glyme (5.49 mg, 10 mol%) and bpy (5.86 mg, 15 mol%), 4CzIPN photocatalyst (4.9 mg, 3 mol%), vinyl bromide **4** (71 mg, 0.25 mmol),

Cs_2CO_3 (164 mg, 1.5 eq.), and carboxylic acid (1.5 eq.). Vial was purged with argon and anhydr. DMF (2 mL) was added. The resulting mixture was stirred vigorously and irradiated with two Higrow 36W LED bulb overnight (18x2W LEDs, 450-460 nm) (vial was placed ca. 7 cm away from each lamp) (Figure 1). The vial was cooled with a cooling fan to avoid overheating (ca. 25 °C). When vinyl bromide was consumed (TLC analysis, $KMnO_4$ stain) Et_2O and brine were added to reaction mixture. The organic phase was washed twice with brine and dried over Na_2SO_4. After removal of solvents, the residue was purified by a column chromatography.

(*S*,*E*)-Ethyl 7-((benzyloxycarbonyl)amino)oct-5-enoate (2a):

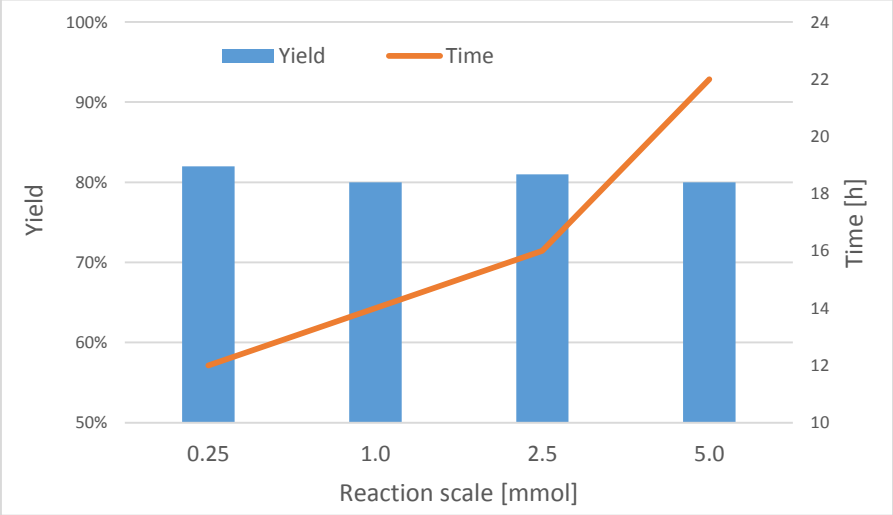


Method A: Yield: 79.0 mg (82%) starting from 85.8 mg (0.30 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-30% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –11.4 (*c* 1.09, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 5.54 (dt, *J* = 15.5, 6.6 Hz, 1H), 5.42 (dd, *J* = 15.5, 5.5 Hz, 1H), 5.08 (s, 2H), 4.76 – 4.64 (m, 1H), 4.27 – 4.18 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.26 (t, *J* = 7.5 Hz, 2H), 2.03 (m, 2H), 1.68 (p, *J* = 7.5 Hz, 2H), 1.27 – 1.18 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 155.5, 136.7, 132.5, 129.4, 128.5, 128.0 (2x), 66.6, 60.2, 48.2, 33.6, 31.5, 24.3, 21.2, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{25}NO_4Na$ $[(M+Na)^+]$ 342.1681; found: 342.1673; FTIR (film) ν: 3330, 3033, 2938, 1725, 1525, 1454, 1233, 1059, 1028, 966 cm^{-1}.

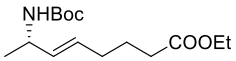
Large-scale synthesis of product 2a:

Vinyl bromide **1a**	$NiCl_2$-glyme (1 mol%)	dtbbpy (1.1 mol%)	4CzIPN (2 mol%)	DME	Time	Yield of **2a**
0.25 mmol (71 mg)[a]	0.55 mg	0.74 mg	3.9 mg	2.5 mL	12 h	82%
1 mmol (285 mg)[b]	2.2 mg	3 mg	15.5 mg	10 mL	14 h	80%
2.5 mmol (700 mg)[c]	5.5 mg	7.5 mg	40 mg	25 mL	16 h	81%
5 mmol (1.4 g)[d]	11 mg	15 mg	80 mg[e]	50 mL	22 h	80%

[a] 8 mL vial (Ø 1 cm, h 12 cm); [b] 30 mL vial (Ø 2.1 cm, h 9 cm); [c] 40 mL test tube (Ø 2.1 cm, h 12 cm); [d] 60 mL test tube (Ø 2.3 cm, h 15 cm); [e] To compare 5 mmol scale cross-coupling reaction of **1a** with ethyl 4-bromobutyrate catalyzed by $(Ir[dF(CF_3)ppy]_2(dtbby))PF_6$ complex (MW 1121.91 g/mol) would require 112 mg of this catalyst.

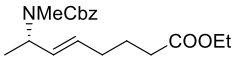


(*S*,*E*)-Ethyl 7-((*tert*-butoxycarbonyl)amino)oct-5-enoate (3):



Method A: Yield: 48.8 mg (71%) starting from 60 mg (0.24 mmol) of vinyl bromide **1b**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-25% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –15.1 (*c* 1.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 – 5.46 (m, 1H), 5.39 (dd, *J* = 15.5, 5.5 Hz, 1H), 4.41 (s, 1H), 4.10 (m, 3H), 2.26 (t, *J* = 7.5 Hz, 2H), 2.03 (m, 2H), 1.67 (p, *J* = 7.5 Hz, 2H), 1.42 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 155.1, 133.0, 128.9, 79.1, 60.2, 47.6, 33.6, 31.5, 28.4, 24.4, 21.2, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{27}NO_4Na$ $[(M+Na)^+]$ 308.1838; found: 308.1841; FTIR (film) ν: 3330, 2978, 1721, 1454, 1236, 1059, 1031 cm^{-1}.

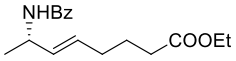
(*S*,*E*)-Ethyl 7-(((benzyloxy)carbonyl)(methyl)amino)oct-5-enoate (4):



Method A: Yield: 60.5 mg (65%) starting from 83.0 mg (0.28 mmol) vinyl bromide **1c**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-25% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –38.2 (*c* 0.89, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.55 – 5.39 (m, 2H), 5.14 (s, 2H), 4.90 – 4.70 (m, 1H), 4.12 (q, *J*

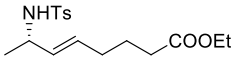
= 7.1 Hz, 2H), 2.73 (s, 3H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.06 (m, 2H), 1.69 (p, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.19 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 156.1, 137.1, 130.8, 130.8, 128.4, 127.84, 127.75, 67.0, 60.2, 56.5, 51.67 33.6, 31.7, 24.4, 21.5, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{27}NO_4Na$ [(M+Na)$^+$] 356.1836; found: 356.1838; FTIR (film) ν: 3031, 2977, 1734, 1699, 1452, 1400, 1316, 1146, 1028, 698 cm^{-1}.

(*S*,*E*)-Ethyl 7-benzamidooct-5-enoate (5):



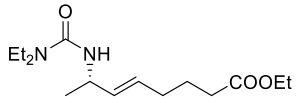
Method A: Yield: 52.4 mg (73%) starting from 63.0 mg (0.25 mmol) of vinyl bromide **1d**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-30% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ −9.6 (*c* 0.70, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 2H), 7.50 – 7.43 (m, 1H), 7.42 – 7.37 (m, 2H), 6.13 (d, *J* = 8.2 Hz, 1H), 5.67 – 5.47 (m, 2H), 4.78 – 4.64 (m, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.10 – 2.02 (m, 2H), 1.69 (p, *J* = 7.5 Hz, 2H), 1.30 (d, *J* = 6.8 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 166.5, 134.8, 132.2, 131.3, 129.8, 128.5, 126.9, 60.2, 46.7, 33.7, 31.6, 24.3, 20.8, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{23}NO_3Na$ [(M+Na)$^+$] 312.1576; found: 312.1575; FTIR (film) ν: 3312, 3060, 2978, 1733, 1637, 1533, 1490, 1333, 1247, 1179, 1159, 1030, 970, 713, 696 cm^{-1}.

(*S*,*E*)-Ethyl 7-(4-methylphenylsulfonamido)oct-5-enoate (6):



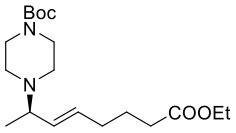
Method A: yield: 55.0 mg (77%) starting from 64.0 mg (0.21 mmol) of vinyl bromide **1e**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-35% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ −16.5 (*c* 0.41, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 5.38 (dtd, *J* = 15.4, 6.7, 1.2 Hz, 1H), 5.21 (ddt, *J* = 15.4, 6.4, 1.4 Hz, 1H), 4.50 (d, *J* = 7.5 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.85 (m, 1H), 2.41 (s, 3H), 2.19 (t, *J* = 7.5 Hz, 2H), 1.89 (m, 2H), 1.55 (p, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.15 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 143.2, 138.2, 131.7, 130.5, 129.5, 127.2, 60.2, 51.3, 33.6, 31.3, 24.1, 22.1, 21.5, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{25}NO_4NaS$ [(M+Na)$^+$] 362.1402; found: 362.1408; FTIR (film) ν: 3277, 2979, 1732, 1599, 1452, 1428, 1329, 1160, 1094, 664, 552 cm^{-1}.

Ethyl (*S*,*E*)-7-(3,3-diethylureido)oct-5-enoate (7):



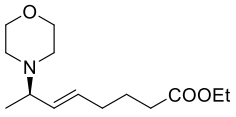
Method A: Yield: 33.8 mg (73%) starting from 40.6 mg (0.16 mmol) of vinyl bromide **1f**; purification: flash column chromatography on silica gel (12 g column cartridge, 10-45% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –2.1 (*c* 1.30, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.58 – 5.42 (m, 2H), 4.49 – 4.36 (m, 1H), 4.11 (q, *J* = 7.2 Hz, 3H), 3.24 (q, *J* = 7.1 Hz, 4H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.09 – 2.00 (m, 2H), 1.69 (p, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.20 (d, *J* = 6.7 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 156.5, 133.9, 128.5, 60.2, 47.2, 41.1, 33.7, 31.6, 24.4, 21.5, 14.2, 13.9; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{28}N_2O_3Na$ $[(M+Na)^+]$ 307.1998; found: 307.1993; FTIR (film) ν: 3342, 2974, 1734, 1624, 1525, 1452, 1375, 1267, 1189, 969 cm^{-1}.

***Tert*-butyl (*R*,*E*)-4-(8-ethoxy-8-oxooct-3-en-2-yl)piperazine-1-carboxylate (8):**



Method A: Yield: 32.8 mg (49%) starting from 60.6 mg (0.19 mmol) of vinyl bromide **1g**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +7.7 (*c* 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ ^1H NMR (400 MHz, $CDCl_3$) δ 5.47 (dt, *J* = 15.4, 6.4 Hz, 1H), 5.37 (dd, *J* = 15.4, 6.6 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.40 (t, *J* = 5.0 Hz, 4H), 2.88 (p, *J* = 6.6 Hz, 1H), 2.49 – 2.31 (m, 4H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.05 (m, 2H), 1.69 (p, *J* = 7.5 Hz, 2H), 1.44 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.12 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 154.7, 132.4, 131.0, 79.5, 62.2, 60.2, 49.5, 33.7, 31.7, 30.9, 28.4, 24.5, 17.7, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{35}N_2O_4$ $[(M+H)^+]$ 355.2591; found: 355.2588; FTIR (film) ν: 2958, 1715, 1451, 1145, 1119 cm^{-1}.

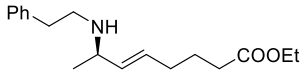
Ethyl (*R*,*E*)-7-morpholinooct-5-enoate (9):



Method A: Yield: 26.5 mg (49%) starting from 46.3 mg (0.21 mmol) of vinyl bromide **1h**; purification: flash column chromatography on silica gel (12 g column cartridge, 10-40% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +16.6 (*c* 0.63, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.48 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.37 (dd, *J* = 15.3, 6.6 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.70 (t, *J* = 4.7 Hz, 4H), 2.81 (p, *J* = 6.6 Hz, 1H), 2.47 (m, 4H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.06 (m, 2H), 1.70 (p, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$)

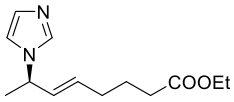
δ 173.5, 132.9, 131.1, 67.2, 62.7, 60.2, 50.5, 33.7, 31.7, 24.6, 17.8, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{26}NO_3$ [(M+H)$^+$] 256.1913; found: 256.1913; FTIR (film) ν: 2958, 1736, 1451, 1373, 1119 cm^{-1}.

Ethyl (*R*,*E*)-7-(phenethylamino)oct-5-enoate (10):



Method A: Yield: 15.6 mg (42%) starting from 32.8 mg (0.13 mmol) of vinyl bromide **1i**; purification: flash column chromatography on silica gel (12 g column cartridge, 20-80% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +3.9 (*c* 0.71, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.23 – 7.15 (m, 3H), 5.51 – 5.40 (dt, *J* = 15.3, 6.8 Hz, 1H), 5.27 (dd, *J* = 15.3, 6.6 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.14 (p, *J* = 6.6 Hz, 1H), 2.88 – 2.75 (m, 4H), 2.28 (t, *J* = 7.6 Hz, 2H), 2.07 – 2.00 (m, 2H), 1.69 (p, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 6.4 Hz, 3H) [N-**H** proton signal not visible]; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 135.3, 129.7, 128.7, 128.4, 126.1, 60.2, 55.7, 48.7, 36.5, 33.7, 31.6, 24.6, 22.0, 14.2 [one signal in aromatic region is missing, propably due to overlapping]; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{28}NO_2$ [(M+H)$^+$] 290.2120; found: 290.2124; FTIR (film) ν: 3327, 3026, 2928, 1735, 1603, 1453, 1371, 1162, 1031, 700 cm^{-1}.

Ethyl (*R*,*E*)-7-(1*H*-imidazol-1-yl)oct-5-enoate (11):

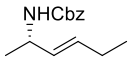


Method A: Yield: 34.3 mg (72%) starting from 40.3 mg (0.20 mmol) of vinyl bromide **1j**; purification: flash column chromatography on silica gel (12 g column cartridge, 20-100% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ -9.1 (*c* 0.83, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) 7.49 (s, 1H), 7.03 (s, 1H), 6.90 (s, 1H), 5.63 – 5.47 (m, 2H), 4.67 (p, *J* = 6.7 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.26 (t, *J* = 7.5 Hz, 2H), 2.11 – 2.02 (m, 2H), 1.69 (p, *J* = 7.5 Hz, 2H), 1.54 (d, *J* = 6.7 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 135.6, 131.8, 131.2, 129.2, 117.2, 60.3, 54.5, 33.5, 31.3, 24.1, 21.3, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{20}N_2O_2Na$ [(M+Na)$^+$] 259.1422; found: 259.1430; FTIR (film) ν: 3377, 3110, 2979, 1731, 1601, 1495, 1452, 1375, 1225, 1164 cm^{-1}.

Benzyl (*S*,*E*)-pent-3-en-2-yl carbamate (2b):

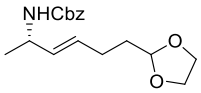
Method A: Yield: 34.8 mg (63%) starting from 71.0 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0–20% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 77.9–79.3 °C; $[\alpha]_D^{25}$ –14.5 (*c* 0.77, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 5.60 (dq, *J* = 15.0, 6.3 Hz, 1H), 5.46 – 5.38 (dd, *J* = 15.0 Hz, 6.4 Hz 1H), 5.14 – 5.06 (m, 2H), 4.69 (s, 1H), 4.27 – 4.19 (m, 1H), 1.67 (d, *J* = 6.4 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 136.7, 132.7, 128.5, 128.07, 128.03, 125.4, 66.5, 48.3, 21.2, 17.6; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{17}NO_2Na$ $[(M+Na)^+]$ 242.1157; found: 242.1150; FTIR (film) ν: 3316, 3033, 2975, 1683, 1540, 1453, 1271, 1050, 967, 697 cm^{-1}.

(*S*,*E*)-Benzyl hex-3-en-2-ylcarbamate (2c)



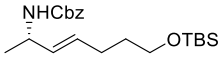
Method A: Yield: 46.9 mg (78%) starting from 72.8 mg (0.26 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0–15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 53.9–54.7 °C; $[\alpha]_D^{25}$ –11.4 (*c* 0.52, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.63 (dt, *J* = 15.4, 7.0 Hz, 1H), 5.40 (dd, *J* = 15.4, 5.7 Hz, 1H), 5.10 (s, 2H), 4.67 (s, 1H), 4.29 – 4.19 (m, 1H), 2.02 (p, *J* = 7.0 Hz, 2H), 1.22 (d, *J* = 6.8 Hz, 3H), 0.97 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 136.7, 132.3, 130.4, 128.5, 128.07, 128.05, 66.5, 48.3, 25.2, 21.3, 13.4; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{19}NO_2Na$ $[(M+Na)^+]$ 256.1313; found: 256.1307; FTIR (film) ν: 3319, 3033, 2961, 1683, 1542, 1455, 966 cm^{-1}.

(*S*,*E*)-Benzyl (6-(1,3-dioxolan-2-yl)hex-3-en-2-yl)carbamate (2d):



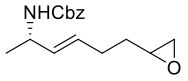
Method A: yield: 83.4 mg (87%) starting from 89.3 mg (0.31 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0–30% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –13.0 (*c* 0.88, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 5H), 5.60 (dt, *J* = 15.7, 6.7 Hz, 1H), 5.44 (dd, *J* = 15.7, 5.4 Hz, 1H), 5.09 (s, 2H), 4.84 (s, 1H), 4.73 (s, 1H), 4.29 – 4.20 (m, 1H), 3.94 (s, 2H), 3.82 (s, 2H), 2.16 – 2.11 (m, 2H), 1.79 – 1.64 (m, 2H), 1.20 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 136.7, 132.0, 129.6, 128.5, 128.0 (x2), 104.0, 66.6, 64.9, 48.2, 33.4, 26.6, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{23}NO_4Na$ $[(M+Na)^+]$ 328.1525; found: 328.1516; FTIR (film) ν: 3354, 3031, 2920, 1699, 1606, 1496, 1453, 1208, 1020, 736, 698 cm^{-1}.

Benzyl (*S*,*E*)-(7-((*t*-butyldimethylsilyl)oxy)hept-3-en-2-yl)carbamate (2e):



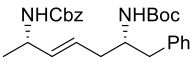
Method A: Yield: 71.4 mg (76%) starting from 71.0 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –9.7 (*c* 0.67, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 5.59 (dt, *J* = 15.5, 6.6 Hz, 1H), 5.42 (dd, *J* = 15.5, 5.8 Hz, 1H), 5.10 (s, 2H), 4.66 (s, 1H), 4.29 – 4.20 (m, 1H), 3.59 (t, *J* = 6.4 Hz, 2H), 2.11 – 2.05 (m, 2H), 1.64 – 1.53 (m, 2H), 1.21 (d, *J* = 6.8 Hz, 3H), 0.90 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 136.7, 131.7, 130.3, 128.5, 128.0 (×2), 66.6, 62.4, 48.3, 32.3, 28.4, 26.0, 21.2, 18.3, -5.3; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{35}NO_3NaSi$ [(M+Na)$^+$] 400.2284; found: 400.2293; FTIR (film) ν: 3327, 3033, 2930, 2857, 1701, 1527, 1453, 1330, 1250, 1101, 1049, 837, 776 cm^{-1}.

(2*S*,*E*)-Benzyl (5-(3,4-dimethoxyphenyl)pent-3-en-2-yl)carbamate (2f):



Method A: Yield: 43.5 mg (63%) starting from 71.0 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-25% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 5H), 5.60 (dt, *J* = 15.5, 6.7 Hz, 1H), 5.45 (dd, *J* = 15.5, 5.7 Hz, 1H), 5.09 (s, 2H), 4.69 (s, 1H), 4.28 – 4.19 (m, 1H), 2.89 (tt, *J* = 6.1, 2.6 Hz, 1H), 2.72 (td, *J* = 4.4, 2.1 Hz, 1H), 2.45 (dd, *J* = 5.0, 2.6 Hz, 1H), 2.25 – 2.09 (m, 2H), 1.66 – 1.51 (m, 2H), 1.21 (d, *J* = 6.7 Hz, 3H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 136.6, 132.4, 129.3, 128.5, 128.1 (2x), 66.6, 51.7, 48.1, 47.1, 32.1, 28.6, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{21}NO_3Na$ [(M+Na)$^+$] 298.1419; found: 298.1414; FTIR (film) ν: 3325, 3033, 2939, 1703, 1527, 1451, 1238, 1042, 967 cm^{-1}.

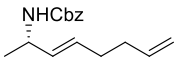
***N*^{2}-Cbz *N*^{6}-Boc (2*S*,6*S*,*E*)-7-phenylhept-3-en-2,6-diamine (2g):**



Method A: Yield: 82.1 mg (74%) starting from 72.3 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 130.0–131.7 °C; $[\alpha]_D^{25}$ –23.3 (*c* 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.13 (m, 10H), 5.57 (dt, *J* = 15.5, 6.2 Hz, 1H), 5.45 (dd, *J* = 15.5, 5.8 Hz, 1H), 5.09 (d, *J* = 5.7 Hz, 2H), 4.71 (s, 1H), 4.45 (s, 1H), 4.24 (q, *J* = 6.9 Hz, 1H), 3.96 – 3.78 (m, 1H), 2.83 – 2.63 (m, 2H), 2.21 (dt, *J* = 14.1, 6.2 Hz, 1H), 2.07 (dt, *J* = 14.1, 6.9 Hz, 1H), 1.40 (s, 9H), 1.21 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 155.4, 138.1, 136.1, 134.9, 129.4, 128.5, 128.4, 128.1

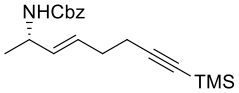
(2x), 126.4, 126.3, 79.1, 66.6, 51.2, 48.4, 40.1, 36.5, 28.4, 21.1; HRMS (ESI-TOF) *m/z* calcd for $C_{26}H_{34}N_2O_4Na$ [(M+Na)$^+$] 461.2416; found: 461.2409; FTIR (film) ν: 3350, 3062, 3032, 2936, 1686, 1531, 1445, 1307, 1238, 1173, 1053, 985 cm^{-1}.

(*S*,*E*)-Benzyl octa-3,7-dien-2-ylcarbamate (2h)



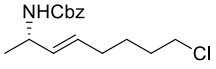
Method A: Yield: 55.4 mg (84%) starting from 72.2 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 40.2–41.3 °C; $[\alpha]_D^{25}$ –13.8 (*c* 0.77, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 5.79 (tdd, *J* = 16.0, 7.8, 4.9 Hz, 1H), 5.63 – 5.54 (m, 1H), 5.43 (dd, *J* = 15.4, 5.7 Hz, 1H), 5.10 (s, 2H), 5.04 – 4.93 (m, 2H), 4.67 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 1H), 2.14 – 2.07 (m, 4H), 1.21 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 138.0, 136.7, 132.0, 129.9, 128.5, 128.0 (x2), 114.8, 66.6, 48.2, 33.3, 31.5, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{21}NO_2Na$ [(M+Na)$^+$] 282.1470; found: 282.1461; FTIR (film) ν: 3322, 3033, 2939, 1686, 1643, 1535, 1452, 1240, 1028, 966 cm^{-1}.

(*S*,*E*)-Benzyl (8-(trimethylsilyl)oct-3-en-7-yn-2-yl)carbamate (2i):



Method A: yield: 57.2 mg (63%) starting from 77.8 mg (0.27 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); colorless oil; $[\alpha]_D^{25}$ –13.1 (*c* 0.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 5.61 (dt, *J* = 15.5, 6.2 Hz, 1H), 5.48 (dd, *J* = 15.5, 5.5 Hz, 1H), 5.10 (s, 2H), 4.66 (s, 1H), 4.33 – 4.21 (m, 1H), 2.29 – 2.17 (m, 4H), 1.23 (d, *J* = 6.7 Hz, 3H), 0.14 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 136.6, 132.9, 128.49, 128.47, 128.1 (x2), 106.5, 85.0, 66.6, 48.2, 31.3, 21.2, 19.9, 0.1; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{27}NO_2NaSi$ [(M+Na)$^+$] 352.1709; found: 352.1706; FTIR (film) ν: 3324, 3033, 2958, 2174, 1699, 1529, 1454, 1249, 1052, 966, 843, 759, 697 cm^{-1}.

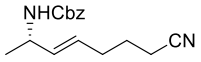
(*S*,*E*)-Benzyl (8-chlorooct-3-en-2-yl)carbamate (2j):



Method A: Yield: 66.2 mg (86%) starting from 73.6 mg (0.26 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartdridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); colorless oil; $[\alpha]_D^{25}$ –16.0 (*c* 0.49, $CHCl_3$); ^{1}H NMR

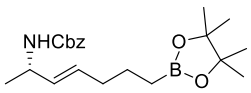
(400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 5.56 (dt, *J* = 15.5, 7.1 Hz, 1H), 5.42 (dd, *J* = 15.5, 5.7 Hz, 1H), 5.10 (s, 2H), 4.68 (s, 1H), 4.29 – 4.18 (m, 1H), 3.51 (t, *J* = 7.1 Hz, 2H), 2.04 (q, *J* = 7.1 Hz, 2H), 1.75 (p, *J* = 7.1 Hz, 2H), 1.50 (p, *J* = 7.1 Hz, 2H), 1.21 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 136.7, 132.2, 129.9, 128.5, 128.1 (2×), 66.6, 48.2, 44.9, 32.0, 31.3, 26.3, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{23}NO_2Cl$ [(M+H)$^+$] 296.1417; found: 296.1406; FTIR (film) ν: 3335, 3034, 2945, 1726, 1516, 1454, 1282, 1197, 1167, 1028 cm^{-1}.

(*S*,*E*)-Benzyl (7-cyanohept-3-en-2-yl)carbamate (2k):



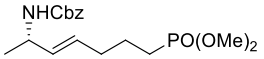
Method A: Yield: 66.1 mg (89%) starting from 76.7 mg (0.27 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-30% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –10.6 (*c* 1.22, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 5H), 5.54 – 5.42 (m, 2H), 5.08 (s, 2H), 4.74 (s, 1H), 4.28 – 4.18 (m, 1H), 2.28 (t, *J* = 7.1 Hz, 2H), 2.19 – 2.11 (m, 2H), 1.70 (p, *J* = 7.1 Hz, 2H), 1.21 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 136.6, 134.0, 128.5, 128.1 (2×), 127.7, 119.6, 66.6, 48.2, 30.8, 24.7, 21.1, 16.3; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{20}N_2O_2Na$ [(M+Na)$^+$] 295.1422; found: 295.1416; FTIR (film) ν: 3329, 3033, 2939, 2246, 1702, 1527, 1453, 1235, 1057, 968 cm^{-1}.

(*S*,*E*)-Benzyl (7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-3-en-2-yl)carbamate (2l):



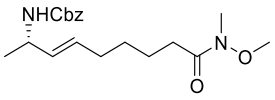
Method A: Yield: 70.7 mg (76%) starting from 71.1 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-25% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –10.0 (*c* 0.98, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 5.56 (dt, *J* = 15.4, 6.7 Hz, 1H), 5.39 (dd, *J* = 15.4, 5.7 Hz, 1H), 5.09 (s, 2H), 4.67 (s, 1H), 4.29 – 4.16 (m, 1H), 2.05 – 1.97 (m, 2H), 1.46 (p, *J* = 7.9 Hz, 2H), 1.23 (s, 15H), 0.75 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 136.7, 131.6, 130.6, 128.5, 128.1, 128.0, 82.9, 66.5, 48.2, 34.7, 24.8, 23.6, 21.2 (carbon α to boron not visible); ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.9; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{32}NO_4BNa$ [(M+Na)$^+$] 396.2322; found: 396.2316; FTIR (film) ν: 3334, 3033, 2978, 2934, 1705, 1525, 1454, 1377, 1319, 1233, 1145, 1027, 966 cm^{-1}.

(*S*,*E*)-Benzyl (7-(dimethoxyphosphoryl)hept-3-en-2-yl)carbamate (2m):



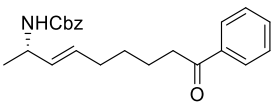
Method A: Yield: 75.3 mg (85%) starting from 71.2 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-3% MeOH in AcOEt, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –8.3 (*c* 0.91, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 5H), 5.56 – 5.33 (m, 2H), 5.05 (s, 2H), 4.80 (s, 1H), 4.25 – 4.15 (m, 1H), 3.68 (d, J_{H-P} = 10.6 Hz, 6H), 2.09 – 2.02 (m, 2H), 1.74 – 1.58 (m, 4H), 1.18 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 136.6, 133.0, 128.8, 128.5, 128.0 (2×), 66.5, 52.3 and 52.2 (d, J_{C-P} = 6.5 Hz), 48.2, 32.8 and 32.6 (d, J_{C-P} = 16.8 Hz), 24.6 and 23.2 (d, J_{C-P} = 141.3 Hz), 21.83 and 21.78 (d, J_{C-P} = 4.9 Hz), 21.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.8; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{26}NO_5NaP$ [(M+Na)$^+$] 378.1446; found: 378.1436; FTIR (film) ν: 3275, 3033, 2953, 1715, 1535, 1455, 1237, 1334, 840 cm^{-1}.

Benzyl (*S*,*E*)-(9-(methoxy(methyl)amino)-9-oxonon-3-en-2-yl)carbamate (2n):



Method A: Yield: 60.7 mg (70%) starting from 71.0 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 10-40% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –10.6 (*c* 0.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 5H), 5.56 (dt, *J* = 15.4, 6.5 Hz, 1H), 5.40 (dd, *J* = 15.4, 5.6 Hz, 1H), 5.08 (s, 2H), 4.72 (s, 1H), 4.26 – 4.15 (m, 1H), 3.65 (s, 3H), 3.15 (s, 3H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.05 – 1.99 (m, 2H), 1.61 (p, *J* = 7.5 Hz, 2H), 1.39 (p, *J* = 7.7 Hz, 2H), 1.19 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 155.5, 136.7, 131.7, 130.3, 128.5, 128.04, 127.99, 66.5, 61.2, 48.2, 32.2, 31.9, 31.7, 28.9, 24.1, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{28}N_2O_4Na$ [(M+Na)$^+$] 371.1947; found: 371.1939; FTIR (film) ν: 3320, 3033, 2934, 1717, 1658, 1527, 1454, 1239, 1110, 1049 cm^{-1}.

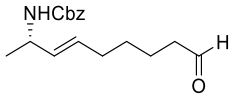
Benzyl (*S*,*E*)-(9-oxo-9-phenylnon-3-en-2-yl)carbamate (2o):



Method A: Yield: 54.8 mg (60%) starting from 71.0 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-25% AcOEt in hexanes, flow 15 mL/min, 30 min); white waxy solid; $[\alpha]_D^{25}$ –9.3 (*c* 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.37 – 7.23 (m, 5H), 5.58 (dt, *J* = 15.5, 6.4 Hz, 1H), 5.42 (dd, *J* = 15.5, 5.5 Hz, 1H), 5.09 (s, 2H), 4.70 (s, 1H), 4.29

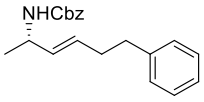
– 4.19 (m, 1H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.09 – 2.02 (m, 2H), 1.73 (p, *J* = 7.5 Hz, 2H), 1.45 (p, *J* = 7.5 Hz, 2H), 1.21 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 155.5, 137.1, 136.7, 132.9, 131.9, 130.2, 128.6, 128.5, 128.0 (×2), 66.5, 48.3, 38.4, 32.0, 28.8, 23.8, 21.2 [one of aromatic carbon signal is missing due to overlapping]; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{27}NO_3Na$ [(M+Na)$^+$] 388.1889; found: 388.1881; FTIR (film) ν: 3337, 3032, 2931, 1715, 1687, 1597, 1523, 1451, 1234, 1049 cm^{-1}.

Benzyl (*S*,*E*)-(9-oxonon-3-en-2-yl)carbamate (2p):



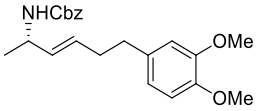
Method A: Yield: 37.8 mg (51%) starting from 71.0 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –7.9 (*c* 0.51, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (t, *J* = 1.7 Hz, 1H), 7.38 – 7.26 (m, 5H), 5.56 (dt, *J* = 15.5, 6.1 Hz, 1H), 5.41 (dd, *J* = 15.5, 5.6 Hz, 1H), 5.09 (s, 2H), 4.61 (s, 1H), 4.28 – 4.20 (m, 1H), 2.41 (td, *J* = 7.5, 1.7 Hz, 2H), 2.08 – 2.01 (m, 2H), 1.62 (p, *J* = 7.5 Hz, 2H), 1.41 (p, *J* = 7.5 Hz, 2H), 1.21 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 154.7, 136.6, 132.1, 129.9, 128.5, 128.1 (x2), 66.6, 48.2, 43.7, 31.8, 28.6, 21.5, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{23}NO_3Na$ [(M+Na)$^+$] 312.1576; found: 312.1572; FTIR (film) ν: 3327, 3032, 2930, 2859, 2747, 1711, 1589, 1452, 1333, 1240, 1051 cm^{-1}.

(*S*,*E*)-Benzyl (6-phenylhex-3-en-2-yl)carbamate (2q)



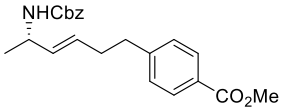
Method A: Yield: 62.1 mg (76%) starting from 74.6 mg (0.26 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 75.5–76.5 °C; $[\alpha]_D^{25}$ –19.0 (*c* 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 7H), 7.22 – 7.14 (m, 3H), 5.64 (dt, *J* = 15.5, 7.4 Hz, 1H), 5.42 (dd, *J* = 15.5, 5.8 Hz, 1H), 5.12 (s, 2H), 4.67 – 4.62 (m, 1H), 4.31 – 4.20 (m, 1H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.34 (q, *J* = 7.4 Hz, 2H), 1.21 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 141.7, 136.7, 132.2, 129.7, 128.51, 128.48, 128.3, 128.1(2×), 125.9, 66.6, 48.3, 35.6, 34.0, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{23}NO_2Na$ [(M+Na)$^+$] 332.1626; found: 332.1218; FTIR (film) ν: 3323, 3029, 2939, 1698, 1528, 1453, 1239, 1043, 966, 698 cm^{-1}.

(*S*,*E*)-Benzyl (6-(3,4-dimethoxyphenyl)hex-3-en-2-yl)carbamate (2r):



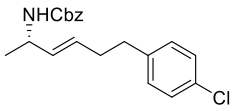
Method A: yield: 86.1 mg (91%) starting from 73.0 mg (0.26 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 126.7-128.3 °C; $[\alpha]_D^{25}$ –13.2 (*c* 0.51, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.72 – 6.66 (m, 2H), 5.62 (dt, *J* = 15.5, 6.5 Hz, 1H), 5.46 – 5.38 (m, 1H), 5.10 (s, 2H), 4.67 (s, 1H), 4.28 – 4.19 (m, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.61 (t, 2H), 2.30 (q, *J* = 7.3 Hz, 2H), 1.20 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 148.8, 147.3, 136.7, 134.4, 132.2, 129.8, 128.5, 128.1 (×2), 120.3, 111.9, 111.3, 66.6, 55.9, 55.8, 48.3, 35.2, 34.2, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{27}NO_4Na$ [(M+Na)$^+$] 392.1838; found: 392.1822; FTIR (film) ν: 3339, 3032, 2936, 1704, 1607, 1516, 1454, 1261, 1230, 1156, 1142, 1029 cm^{-1}.

Methyl (*S*,*E*)-4-(5-(((benzyloxy)carbonyl)amino)hex-3-en-1-yl)benzoate (2s)



Method A: Yield: 76.6 mg (83%) starting from 71.0 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white waxy solid; $[\alpha]_D^{25}$ –19.9 (*c* 0.64, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.27 (m, 5H), 7.20 (d, *J* = 8.1 Hz, 2H), 5.59 (dt, *J* = 15.5, 6.7 Hz, 1H), 5.39 (dd, *J* = 15.5, 5.8 Hz, 1H), 5.09 (s, 2H), 4.69 (s, 1H), 4.28 – 4.19 (m, 1H), 3.88 (s, 3H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.35 – 2.28 (m, 2H), 1.18 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 155.5, 147.2, 136.7, 132.7, 129.7, 129.1, 128.52, 128.49, 128.1 (×2), 127.9, 66.6, 51.9, 48.2, 35.6, 33.5, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{25}NO_4Na$ [(M+Na)$^+$] 390.1681; found: 390.1673; FTIR (film) ν: 3347, 3033, 2951, 1720, 1609, 1524, 1454, 1281, 1243, 1111, 1051 cm^{-1}.

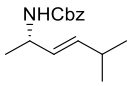
Benzyl (*S*,*E*)-(6-(4-chlorophenyl)hex-3-en-2-yl)carbamate (2t):



Method A: Yield: 79.5 mg (92%) starting from 71.0 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-20% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 94.1–96.4 °C; $[\alpha]_D^{25}$ –15.7 (*c* 0.77, $CHCl_3$);

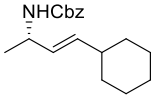
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 5.59 (dt, *J* = 15.5, 6.7 Hz, 1H), 5.40 (dd, *J* = 15.5, 5.8 Hz, 1H), 5.11 (s, 2H), 4.70 – 4.61 (m, 1H), 4.29 – 4.21 (m, 1H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.32 – 2.26 (m, 2H), 1.19 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 140.1, 136.7, 132.6, 131.6, 129.8, 129.3, 128.5, 128.4, 128.1(×2), 66.6, 48.3, 34.9, 33.8, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{22}NO_2NaCl$ [(M+Na)$^+$] 366.1237; found: 366.1223; FTIR (film) ν: 3321, 3033, 2977, 2931, 1685, 1540, 1492, 1454, 1256, 1051 cm^{-1}.

(*S*,*E*)-Benzyl (5-methylhex-3-en-2-yl)carbamate (2u):



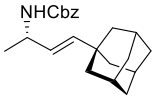
Method A: Yield: 56.5 mg (88%) starting from 73.7 mg (0.26 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 70.8–72.1 °C; $[\alpha]_D^{25}$ –14.8 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.55 (dd, *J* = 15.5, 6.5 Hz, 1H), 5.35 (dd, *J* = 15.5, 5.7 Hz, 1H), 5.10 (s, 2H), 4.67 (s, 1H), 4.31 – 4.19 (m, 1H), 2.33 – 2.19 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 137.7 (×2), 136.7, 128.5, 128.06, 128.03, 66.6, 48.2, 30.6, 22.31, 22.28, 21.3; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{21}NO_2Na$ [(M+Na)$^+$] 270.1470; found: 270.1464; FTIR (film) ν: 3319, 3030, 2956, 1683, 1542, 1465, 1294, 1024, 969 cm^{-1}.

(*S*,*E*)-Benzyl (5-methylhex-3-en-2-yl)carbamate (2v):



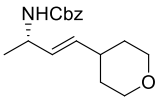
Method A: Yield: 68.8 mg (82%) starting from 83.0 mg (0.29 mmol) of vinyl bromide **1a**; Method B: Yield 67 mg (81%); Purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 70.1–71.8 °C; $[\alpha]_D^{25}$ –17.3 (*c* 0.98, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 5.52 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.35 (dd, *J* = 15.6, 5.6 Hz, 1H), 5.10 (s, 2H), 4.66 (s, 1H), 4.31 – 4.19 (m, 1H), 1.92 (tdt, *J* = 10.7, 6.6, 3.3 Hz, 1H), 1.78 – 1.59 (m, 5H), 1.31 – 0.98 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 136.7, 136.5, 128.9, 128.5, 128.06, 128.02, 66.5, 48.3, 40.2, 32.9, 32.8, 26.2, 26.0 (×2), 21.3; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{25}NO_2Na$ [(M+Na)$^+$] 310.1783; found: 310.1779; FTIR (film) ν: 3311, 3033, 2917, 2850, 1685, 1536, 1442, 1291, 1261, 1242, 1023 cm^{-1}.

Benzyl ((*S*,*E*)-4-(adamantan-2-yl)but-3-en-2-yl)carbamate (2w):



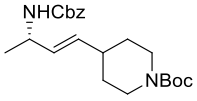
Method A: Yield: 33.2 mg (39%) starting from 71.0 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white waxy solid; $[\alpha]_D^{25}$ –14.0 (*c* 0.62, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.44 (d, *J* = 15.9 Hz, 1H), 5.24 (dd, *J* = 15.9, 5.6 Hz, 1H), 5.10 (s, 2H), 4.63 (s, 1H), 4.31 – 4.19 (m, 1H), 1.97 (q, *J* = 3.4 Hz, 3H), 1.71 (d, *J* = 11.6 Hz, 3H), 1.63 (d, *J* = 12.2 Hz, 3H), 1.58 – 1.52 (m, 6H), 1.21 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 141.9, 136.7, 128.5, 128.06, 128.03, 126.2, 66.5, 48.4, 42.22 (x3), 36.9 (x3), 34.5, 28.4 (x3), 21.4; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{35}NO_3NaSi$ [(M+Na)$^+$] 400.2284; found: 400.2293; FTIR (film) ν: 3327, 3033, 2930, 2857, 1701, 1527, 1453, 1330, 1250, 1101, 1049, 837, 776 cm^{-1}.

(*S*,*E*)-Benzyl (4-(tetrahydro-2*H*-pyran-4-yl)but-3-en-2-yl)carbamate (2x):



Method A: Yield: 58.9 mg (79%) starting from 73.4 mg (0.26 mmol) of vinyl bromide **1a**; Method B: 57 mg (78%); Purification: flash column chromatography on silica gel (12 g column cartridge, 0-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 80.1–80.8 °C; $[\alpha]_D^{25}$ –14.7 (*c* 0.53, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 5.52 (dd, *J* = 15.7, 6.3 Hz, 1H), 5.40 (dd, *J* = 15.7, 5.5 Hz, 1H), 5.09 (s, 2H), 4.71 (s, 1H), 4.29 – 4.22 (m, 1H), 3.94 (ddd, *J* = 11.7, 4.4, 2.0 Hz, 2H), 3.38 (td, *J* = 11.7, 2.2 Hz, 2H), 2.21 – 2.10 (m, 1H), 1.60 – 1.53 (m, 2H), 1.47 – 1.35 (m, 2H), 1.21 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 136.6, 134.5, 130.1, 128.5, 128.1 (2x), 67.7, 66.6, 48.1, 37.5, 32.5, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{23}NO_3Na$ [(M+Na)$^+$] 312.1566; found: 312.1566; FTIR (film) ν: 3306, 3033, 2957, 2841, 1683, 1544, 1281, 1245, 1094, 1030 cm^{-1}.

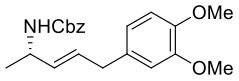
(*S*,*E*)-*t*-Butyl 4-(3-(((benzyloxy)carbonyl)amino)but-1-en-1-yl)piperidine-1-carboxylate (2y):



Method A: Yield: 76.8 mg (79%) starting from 71.0 mg (0.25 mmol) of vinyl bromide **1a**; Method B: 78 mg (81%); Purification: flash column chromatography on silica gel (12 g column cartridge, 0-30% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –14.0 (*c* 0.84, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 5H), 5.51 (dd, *J* = 15.7, 6.3 Hz, 1H), 5.39 (dd, *J*

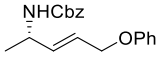
= 15.7, 5.5 Hz, 1H), 5.08 (s, 2H), 4.69 (s, 1H), 4.29 – 4.19 (m, 1H), 4.05 (s, 2H), 2.70 (t, *J* = 12.8 Hz, 2H), 2.12 – 2.00 (m, 1H), 1.61 (d, *J* = 12.8 Hz, 2H), 1.44 (s, 9H), 1.29 – 1.15 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 154.8, 136.6, 134.3, 130.3, 128.5, 128.06 (2x), 79.3, 66.6, 48.2, 43.9, 38.4, 31.2, 28.5, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{32}N_2O_4Na$ [(M+Na)$^+$] 411.2260; found: 411.2253; FTIR (film) ν: 3322, 2937, 1694, 1531, 1425, 1366, 1238, 1171, 1022, 969 cm^{-1}.

(*S*,*E*)-Benzyl (5-(3,4-dimethoxyphenyl)pent-3-en-2-yl)carbamate (2aa):



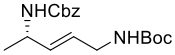
Method B: Yield: 76.3 mg (86%) starting from 71.0 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 68.5–69.9 °C; $[\alpha]_D^{25}$ –15.5 (*c* 0.77, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.72 – 6.66 (m, 2H), 5.73 (dt, *J* = 15.4, 6.7 Hz, 1H), 5.48 (dd, *J* = 15.4, 5.6 Hz, 1H), 5.09 (s, 2H), 4.71 (s, 1H), 4.35 – 4.26 (m, 1H), 3.85 (s, 6H), 3.29 (d, *J* = 6.7 Hz, 2H), 1.23 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 149.0, 147.5, 136.6, 132.8, 132.7, 129.5, 128.5, 128.1 (×2), 120.4, 112.0, 111.4, 66.6, 56.0, 55.8, 48.2, 38.1, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{25}NO_4Na$ [(M+Na)$^+$] 378.1681; found: 378.1675; FTIR (film) ν: 3329, 3000, 2937, 1689, 1590, 1538, 1518, 1452, 1266, 1237, 1159, 1138, 1029 cm^{-1}.

Benzyl (*S*,*E*)-(5-phenoxypent-3-en-2-yl)carbamate (2ab):



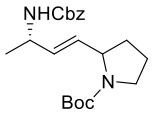
Method B: yield: 76.3 mg (86%) starting from 71.0 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 97.1–99.0 °C; $[\alpha]_D^{25}$ –13.1 (*c* 1.51, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.18 (m, 7H), 7.00 – 6.84 (m, 3H), 5.89 – 5.80 (m, 2H), 5.11 (s, 2H), 4.74 – 7.63 (m, 1H), 4.57 – 4.48 (m, 2H), 4.42 – 4.31 (m 1H), 1.27 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 155.5, 136.5, 135.1, 129.5, 128.5, 128.1(x2), 125.1, 120.9, 114.7, 67.8, 66.7, 47.9, 20.8; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{21}NO_3Na$ [(M+Na)$^+$] 334.1419; found: 334.1412; FTIR (film) ν: 3379, 3034, 2977, 1700, 1599, 1532, 1496, 1445, 1244, 1046 cm^{-1}.

N^4-Benzyl N^1-*t*-butyl pent-2-ene-1,4-diyl(*S*,*E*)-dicarbamate (2ac):



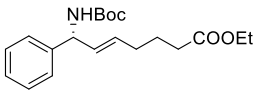
Method B: Yield: 83.6 mg (63%) starting from 113.7 mg (0.40 mmol) of vinyl bromide **4**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 119.5–121.2 °C; $[\alpha]_D^{25}$ –6.3 (*c* 0.78, $CHCl_3$); ^1H NMR (400 MHz, (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 5.60 – 5.52 (m, 2H), 5.08 (s, 2H), 4.74 (s, 1H), 4.57 (s, 1H), 4.27 (s, 1H), 3.69 (s, 2H), 1.43 (d, *J* = 1.8 Hz, 9H), 1.21 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 155.7, 136.5, 133.4, 128.5, 128.08, 128.04, 126.7, 79.4, 66.6, 47.8, 40.8, 28.4, 20.9; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{26}N_2O_4Na$ [(M+Na)$^+$] 357.1790; found: 357.1783; FTIR (film) ν: 3337, 3032, 2971, 1689, 1520, 1449, 1352, 1169, 1019 cm^{-1}.

t-Butyl 2-((*S*,*E*)-3-(((benzyloxy)carbonyl)amino)but-1-en-1-yl)pyrrolidine-1-carboxylate (2ad):



Method B: Yield: 78.5 mg (84%) starting from 70.9 mg (0.25 mmol) of vinyl bromide **1a**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-30% AcOEt in hexanes, flow 15 mL/min, 30 min); colorless oil; Mixture of diastereoisomers in ratio 1:1; ^1H NMR (400 MHz, DMSO-d_6) δ 7.39 – 7.25 (m, 5H), 5.44 – 5.34 (m, 2H), 4.98 (s, 2H), 4.25 – 3.98 (m, 2H), 3.29 (s, 1H), 3.22 (t, *J* = 7.2 Hz, 2H), 2.02 – 1.82 (m, 1H), 1.71 (t, *J* = 7.0 Hz, 2H), 1.59 – 1.53 (m, 1H), 1.34 (s, 9H), 1.10 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.6, 153.9, 137.3, 132.4, 129.9, 128.8, 128.2 (2x), 78.5, 65.5, 58.3, 48.0, 46.4, 32.3, 28.6, 22.9, 21.5; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{30}N_2O_4Na$ [(M+Na)$^+$] 397.2103; found: 397.2095; FTIR (film) ν: 3330, 3032, 2973, 1723, 1694, 1517, 1453, 1338, 1232, 1169, 1096, 1024 cm^{-1}.

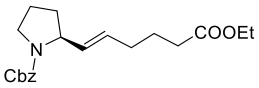
Ethyl (*R*,*E*)-7-(((*t*-butyloxy)carbonyl)amino)-7-phenylhept-5-enoate (2ae):



Method A: Yield: 77 mg (81%) starting from 78 mg (0.25 mmol) of vinyl bromide **1k**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-25% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –10.4 (*c* 0.55, $CHCl_3$); HPLC (Chiralpak IB, hexanes : *i*-PrOH 99:1, 1 mL/min, det. 210 nm): racemic sample: R_t = 11.19 min (*R*), R_t = 12.93 min (*S*), enantioenriched sample: R_t = 11.17 min, *ee* >99%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 5H), 5.63 – 5.52 (m, 2H), 5.21 (s, 1H), 4.87 (s, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.28 (t, *J* = 7.5 Hz,

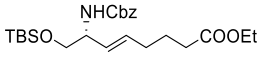
2H), 2.13 – 2.06 (m, 2H), 1.71 (p, *J* = 7.5 Hz, 2H), 1.42 (s, 9H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 155.0, 141.8, 131.1, 131.0, 128.6, 127.3, 126.8, 79.6, 60.2, 56.1, 33.6, 31.5, 28.4, 24.3, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{29}NO_4Na$ [(M+Na)$^+$] 370.1994; found: 370.1998; FTIR (film) ν: 3361, 3030, 2978, 1713, 1513, 1453, 1367, 1247, 1171, 1019 cm^{-1}.

Benzyl (*S*,*E*)-2-(6-ethoxy-6-oxohex-1-en-1-yl)pyrrolidine-1-carboxylate (2af):



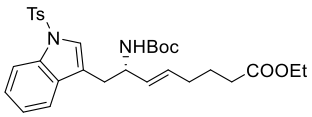
Method A: Yield: 63.0 mg (73%) starting from 77.5 mg (0.25 mmol) of vinyl bromide **1l**; purification: flash column chromatography on silica gel (12 g column cartridge, 10-40% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –32.1 (*c* 1.28, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 – 7.21 (m, 5H), 5.35 (s, 2H), 5.10 – 4.92 (m, 2H), 4.28 – 4.18 (m, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.39 – 3.26 (m, 2H), 2.27 – 2.13 (m, 2H), 1.99 – 1.86 (m, 3H), 1.81 – 1.73 (m, 2H), 1.66 – 1.43 (m, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.2, 154.2, 137.7, 131.9, 129.3, 128.7, 128.1, 127.8, 66.0, 60.1, 58.6, 46.9, 33.2, 32.5, 31.1, 24.5, 22.8, 14.6; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{27}NO_4Na$ [(M+Na)$^+$] 368.1838; found: 368.1837; FTIR (film) ν: 3032, 2975, 1733, 1703, 1448, 1412, 1352, 1181, 1098 cm^{-1}.

Ethyl (*R*,*E*)-7-(((benzyloxy)carbonyl)amino)-8-((*t*-butyldimethylsilyl)oxy)oct-5-enoate (2ag):



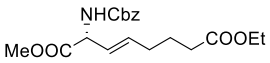
Method A: Yield: 35.8 mg (60%) starting from 55.3 mg (0.13 mmol) of vinyl bromide **1m**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-20% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +4.8 (*c* 1.42, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 5.61 (dt, *J* = 15.5, 6.6 Hz, 1H), 5.45 (dd, *J* = 15.5, 6.6 Hz, 1H), 5.17 – 4.95 (m, 3H), 4.18 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.68 (dd, *J* = 10.0, 4.3 Hz, 1H), 3.59 (dd, *J* = 10.0, 4.1 Hz, 1H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.12 – 2.03 (m, 2H), 1.69 (p, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 9H), 0.03 (s, 6H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 155.8, 136.6, 131.3, 128.8, 128.5, 128.09, 128.05, 66.7, 65.5, 60.2, 54.2, 33.6, 31.6, 25.8, 24.3, 18.3, 14.2, -5.5; HRMS (ESI-TOF) *m/z* calcd for $C_{24}H_{39}NO_5NaSi$ [(M+Na)$^+$] 472.2495; found: 472.2476; FTIR (film) ν: 3347, 3033, 2952, 2857, 1731, 1502, 1465, 1252, 1110, 1055, 838 cm^{-1}.

Ethyl (*S*,*E*)-7-((*t*-butoxycarbonyl)amino)-8-(1-tosyl-1*H*-indol-3-yl)oct-5-enoate (2ah):



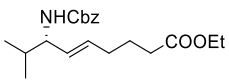
Method A: yield: 108.5 mg (78%) starting from 129.9 mg (0.25 mmol) of vinyl bromide **1n**; purification: flash column chromatography on silica gel (12 g column cartridge, 10-40% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +5.7 (*c* 0.82, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.35 (s, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.23 – 7.16 (m, 3H), 5.45 (dt, *J* = 15.5, 6.4 Hz, 1H), 5.35 (dd, *J* = 15.5, 5.8 Hz, 1H), 4.53 (s, 1H), 4.39 (s, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.96 – 2.80 (m, 2H), 2.30 (s, 3H), 2.19 (t, *J* = 7.5 Hz, 2H), 2.02 – 1.91 (m, 2H), 1.59 (q, *J* = 7.5 Hz, 2H), 1.41 (s, 9H), 1.23 (t, *J* = 7.2 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 155.1, 144.8, 135.3, 135.2, 131.2, 130.8, 130.5, 129.8, 126.7, 124.6, 124.2, 123.1, 119.8, 118.8, 113.7, 79.5, 60.2, 51.9, 33.5, 31.5, 31.1, 28.4, 24.2, 21.5, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{38}N_2O_6NaS$ [$(M+Na)^+$] 577.2348; found: 577.2346; FTIR (film) ν: 3375, 2978, 1711, 1505, 1448, 1367, 1246, 1173, 1121, 1019 cm^{-1}.

8-Ethyl 1-methyl (*R*,*E*)-2-(((benzyloxy)carbonyl)amino)oct-3-enedioate (2ai):



Method A: yield: 41.1 mg (68%) starting from 54.6 mg (0.17 mmol) of vinyl bromide **1o**; purification: flash column chromatography on silica gel (12 g column cartridge, 10-40% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –23.6 (*c* 1.06, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 5H), 5.74 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.49 (dd, *J* = 15.6, 6.2 Hz, 1H), 5.42 – 5.33 (m, 1H), 5.11 (s, 2H), 4.84 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 2.26 (t, *J* = 7.5 Hz, 2H), 2.16 – 2.02 (m, 2H), 1.70 (p, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 171.4, 155.5, 136.2, 133.8, 128.5, 128.2, 128.1, 125.0, 67.1, 60.3, 55.6, 52.6, 33.5, 31.4, 24.0, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{25}NO_6Na$ [$(M+Na)^+$] 386.1580; found: 386.1574; FTIR (film) ν: 3351, 3033, 2953, 1729, 1519, 1453, 1328, 1212, 1046 cm^{-1}.

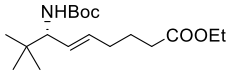
Ethyl (*S*,*E*)-7-(((benzyloxy)carbonyl)amino)-8-methylnon-5-enoate (2aj):



Method A: Yield: 32.1 mg (71%) starting from 40.7 mg (0.13 mmol) of vinyl bromide **1p**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-25% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +1.4 (*c* 0.72, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 5.54 (dt, *J* = 15.4, 7.0 Hz, 1H), 5.34 (dd, *J* = 15.4, 6.6 Hz, 1H), 5.10 (s,

2H), 4.69 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 1H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.11 – 2.06 (m, 2H), 1.80 – 1.66 (m, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.88 (2×d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 155.9, 136.7, 131.0, 129.6, 128.5, 128.1 (x2), 66.7, 60.2, 58.2, 33.6, 32.5, 31.6, 24.4, 18.6, 18.2, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{29}NO_4Na$ [(M+Na)$^+$] 370.1994; found: 370.1985; FTIR (film) ν: 3344, 3033, 2959, 1729, 1527, 1455, 1231, 1025 cm^{-1}.

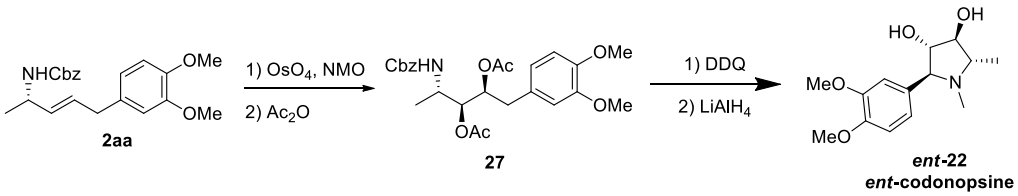
Ethyl (*R*,*E*)-7-((*tert*-butoxycarbonyl)amino)-8,8-dimethylnon-5-enoate (2ak):



Method A: yield: 48.8 mg (60%) starting from 72.9 mg (0.25 mmol) of vinyl bromide **1q**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-20% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –4.6 (*c* 1.36, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (dt, *J* = 15.5, 6.6 Hz, 1H), 5.43 – 5.34 (dd, *J* = 15.5, 6.0 Hz, 1H), 4.47 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 1H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.10 – 2.04 (m, 2H), 1.69 (p, *J* = 7.5 Hz, 2H), 1.42 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.86 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 155.5, 131.2, 128.7, 79.0, 60.8, 60.2, 34.3, 33.6, 31.7, 28.4, 26.3, 24.5, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{33}NO_4Na$ [(M+Na)$^+$] 350.2307; found: 350.2312; FTIR (film) ν: 3376, 2967, 1715, 1515, 1366, 1243, 1173 cm^{-1}.

6. Functionalization of selected products

6.1. Synthesis of *ent*-codonopsine (*ent*-22)



Step 1:[6] Allylamine **2aa** (76.3 mg, 0.21 mmol) and *N*-methyl morpholine oxide (37.7 mg, 0.32 mmol) were dissolved in a mixture of acetone (1 mL) and water (0.25 mL). The mixture was cooled to 0 °C, followed by an addition of OsO_4 (4% soln. in water, 13.6 μL, 2.2 μmol) and the resulting mixture was stirred at rt overnight. Sat. aqueous $Na_2S_2O_3$ and CH_2Cl_2 were added. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic layers were dried over Na_2SO_4, filtered and evaporated. The residue was purified using silica gel flash column chromatography (24 g column cartridge, 20–60% ethyl acetate in hexanes, flow 20 mL/min, 60 min). The main diastereoisomer eluted first, providing 41.5 mg (0.11 mmol, 50% yield) of **26** as a white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 6.79 (d, *J* = 8.6 Hz,

1H), 6.77 – 6.72 (m, 2H), 5.11 (d, *J* = 12.2 Hz, 1H), 5.07 (d, *J* = 12.2 Hz, 1H), 4.96 (d, *J* = 8.7 Hz, 1H), 3.88 – 3.72 (m, 8H), 3.14 (m, 2H), 2.80 (m, 2H), 2.48 (s, 1H), 1.23 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 149.0, 147.7, 136.2, 130.7, 128.6, 128.3, 128.1, 121.4, 112.8, 111.4, 75.5, 71.2, 67.1, 55.92, 55.89, 49.4, 39.0, 17.3; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{27}NO_6Na$ [$(M+Na)^+$] 412.1736; found: 412.1724; FTIR (film) ν: 3389, 3346, 3033, 2936, 1693, 1590, 1515, 1453, 1261, 1236, 1156, 1141, 1029 cm^{-1}.

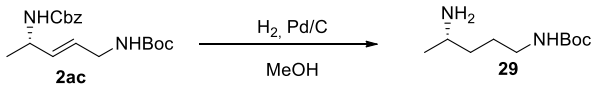
Step 2: 26 (41.5 mg, 0.11 mmol) and DMAP (0.65 mg, 5.32 µmol) were dissolved in anhydr. CH_2Cl_2 (1 mL), followed by addition of Et_3N (52 µL, 38 mg, 0.37 mmol). The resulting solution was cooled down to 0 °C before addition of Ac_2O (30 µL, 33 mg, 0.32 mmol). The resulting mixture was stirred at rt for 2 h, before addition of sat. $NaHCO_3$. Layers were separated and the aqueous layer was washed with CH_2Cl_2 twice. Combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The crude residue was purified using silica gel flash column chromatography (4 g column cartridge, 10-30% ethyl acetate in hexanes, flow 8 mL/min, 30 min) to provide 43.2 mg (0.09 mmol, 86%) of **27** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 5H), 6.76 (d, *J* = 8.6 Hz, 1H), 6.71 – 6.66 (m, 2H), 5.23 (td, *J* = 6.9, 3.8 Hz, 1H), 5.06 (s, 2H), 4.90 (dd, *J* = 5.8, 3.8 Hz, 1H), 4.81 (d, *J* = 9.3 Hz, 1H), 4.13 – 4.02 (m, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.83 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.73 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.13 (s, 3H), 2.02 (s, 3H), 1.10 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 170.1, 155.5, 148.9, 147.9, 136.4, 132.9, 128.5, 128.10, 128.06, 121.5, 112.6, 111.3, 74.7, 72.8, 66.8, 55.8 (×2), 46.9, 36.8, 21.0, 20.8, 16.7.

Step 3: 27 (43.2 mg, 0.09 mmol) and DDQ (22.8 mg, 0.10 mmol) were dissolved in 0.5 mL of anhydr. MeCN and heated in reflux overnight. Next, reaction mixture was quenched with Et_3N and evaporated. The crude residue was purified using silica gel flash column chromatography (4 g column cartridge, 10-30% ethyl acetate in hexanes, flow 8 mL/min, 30 min) to provide 38.6 mg (0.08 mmol, 90% yield) of **28** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ 7.39 – 7.07 (m, 4H), 6.91 – 6.64 (m, 4H), 5.20 – 4.74 (m, 5H), 4.37 – 4.21 (m, 1H), 3.90 – 3.72 (m, 6H), 2.14 (d, *J* = 3.0 Hz, 2.5H), 2.09 (s, 0.5H), 2.03 (s, 0.5H), 1.83 (s, 2.5H), 1.61 – 1.46 (m, 3H).

Step 4: 28 (38.6 mg, 0.08 mmol) was dissolved in anhydr. THF, followed by dropwise addition of $LiAlH_4$ (1M solution in THF, 0.41 mL, 0.41 mmol), The resulting solution was heated in reflux for 5 h. After cooling to rt, reaction was quenched with water. The resulting suspension was

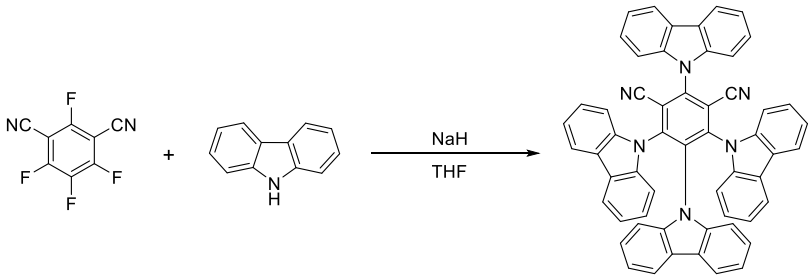
filtered and the filtrate was dried over anhydr. Na_2SO_4, filtered and evaporated. The resulting crude residue was purified using silica gel flash chromatography (4 g column cartridge, 0-5% MeOH in ethyl acetate) to give *ent*-codonopsine (12.3 mg, 56% yield) as a white solid, m.p. 148.2 – 149.8 °C (Lit.[7] 149 – 150 °C); $[\alpha]_D^{25}$ +16.5 (*c* 0.92, MeOH)(Lit.[7] -16.0, c=1.2, MeOH (for opposite enantiomer)); ^{1}H NMR (400 MHz, CD_3OD) δ 7.01 (s, 1H), 6.90 (s, 2H), 3.93 (dd, *J* = 6.3, 3.8 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.68 (t, *J* = 3.8 Hz, 1H), 3.53 (d, *J* = 6.3 Hz, 1H), 3.15 (qd, *J* = 6.8, 3.8 Hz, 2H), 2.05 (s, 3H), 1.18 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 148.7, 133.1, 121.1, 111.5, 111.4, 85.0, 83.5, 73.6, 64.3, 55.1, 55.0, 33.1, 12.0; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{22}NO_4$ $[(M+H)^+]$ 268.1549; found: 268.1543; FTIR (film) ν: 3376, 2965, 1592, 1261, 1234, 1142, 1027 cm^{-1}.

6.2. Synthesis of *t*-butyl (*S*)-(4-aminopentyl)carbamate (29)



Allylamine **2ac** (53.0 mg, 0.16 mmol) was dissolved in anhydr. MeOH (2 mL) in a Schlenk flask. The flask was gently evacuated and backfilled with hydrogen three times. Next, 5 mg of Pd/C (10%) was added and reaction mixture was stirred overnight. Next, the mixture was filtered through Celite® and the filtrate was evaporated. The residue was purified using silica gel column chromatography (30% MeOH in AcOEt with 1% of Et_3N) to give analytically pure diamine **29** (28.2 mg, 0.14 mmol, 88%) as a colourless oil. $[\alpha]_D^{25}$ +8.7 (*c* 2.82, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 (s, 1H), 4.20 (s, 2H), 3.09 (t, *J* = 6.4 Hz, 2H), 3.02 – 2.93 (m, 1H), 1.57 – 1.39 (m, 13H), 1.13 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 79.0, 46.8, 40.4, 35.5, 28.4, 26.6, 22.4. Analytical data in agreement with reported one for racemic compound.[8]

7. Synthesis of 4CzIPN photocatalyst



A solution[9] of carbazole (25 mmol, 4.18 g, 5 eq.) in 20 mL of anhydr. THF was added slowly to a stirred suspension of NaH (60% dispersion in mineral oil, 1.5 g, 37.5 mmol) in anhydr. THF (80 mL). After stirring for 30 min at rt. Next tetrafluoroisophtalonitrile (1g, 5 mmol) was added

and mixture was stirred at rt overnight. Yellow precipitate was obtained. Water (5 mL) was cautiously added to destroy an excess of NaH. Solvent was evaporated and and the resulting solid was washed with water and EtOH. The crude product was dissolved in small amount of CH_2Cl_2 followed by an addition of pentane. The resulting precipitation was filtered off and dried under vacuum to give 4CzIPN (3.19 g, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (dt, *J* = 7.7, 1.0 Hz, 2H), 8.19 (d, *J* = 8.3 Hz, 2H), 7.87 –7.84 (m, 4H), 7.76 –7.72 (m, 6H), 7.55 –7.44 (m, 6H), 7.19 – 7.05 (m, 8H), 6.83 – 6.79 (m, 2H), 6.72 – 6.68 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 144.8, 139.9, 138.5, 137.6, 136.4, 126.8, 125.4, 124.1, 123.6, 123.2, 122.8, 121.9, 121.3, 121.0, 120.5, 120.1, 119.4, 116.7, 112.2, 111.1, 110.9, 110.8.

8. References

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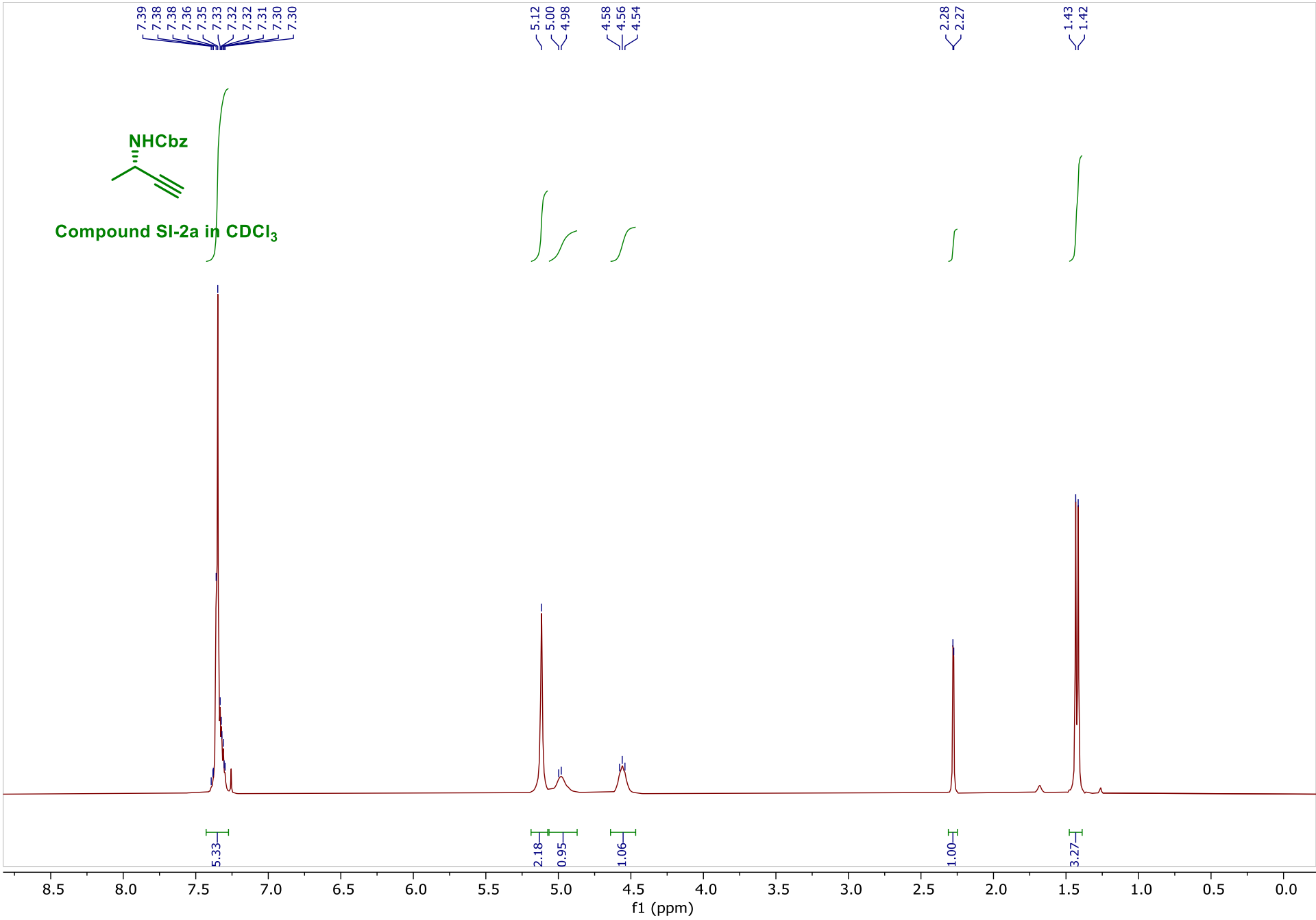
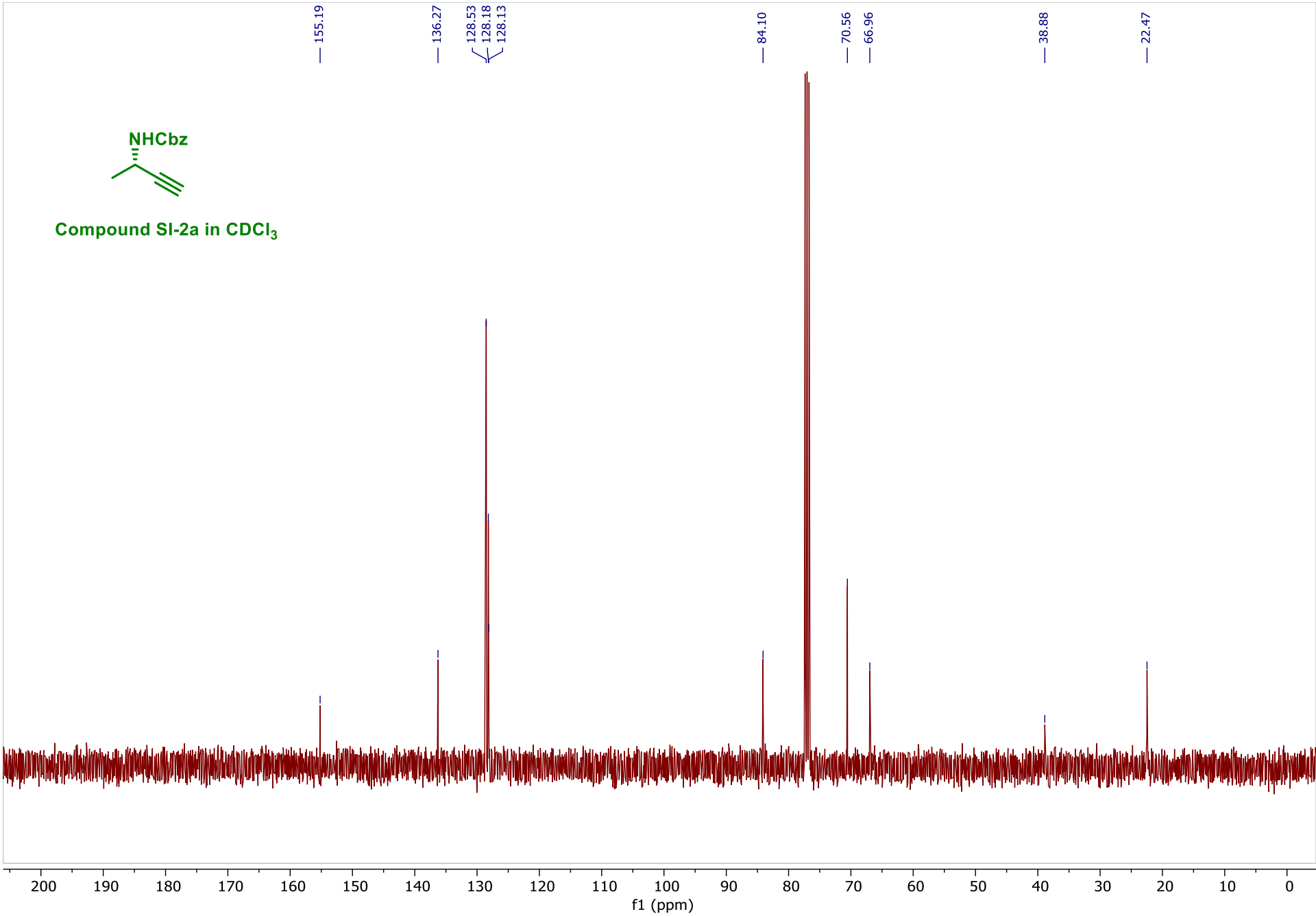
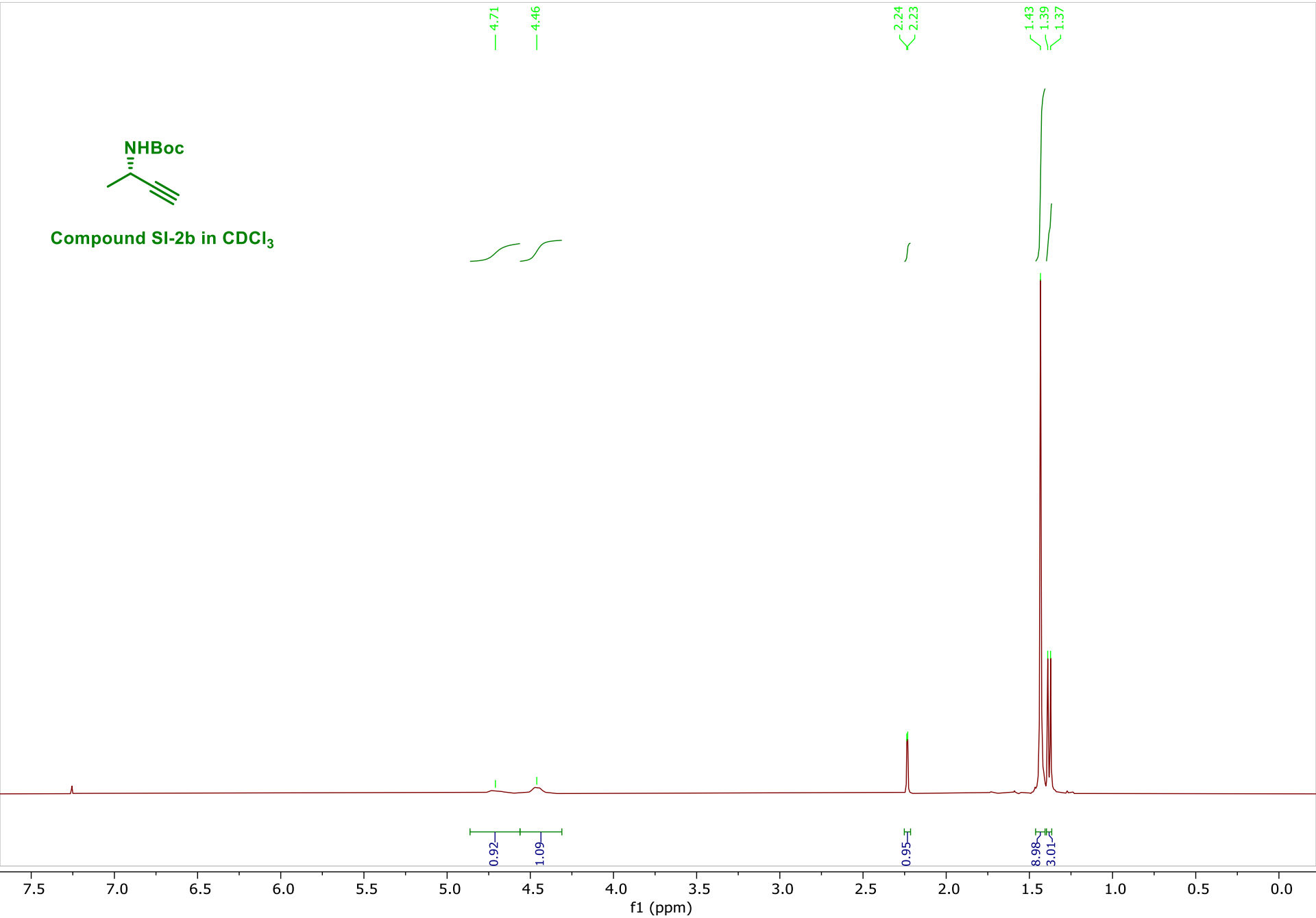
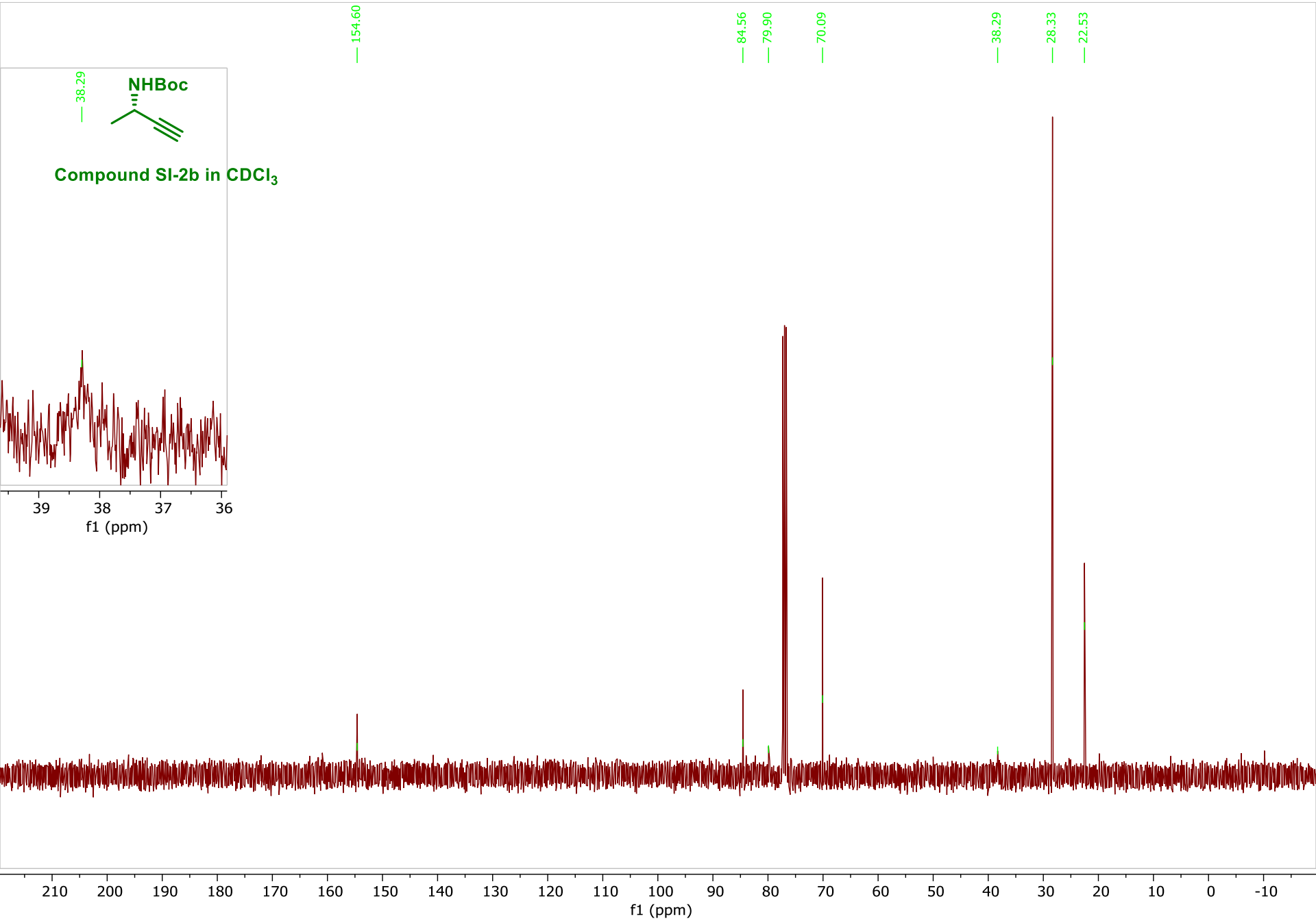
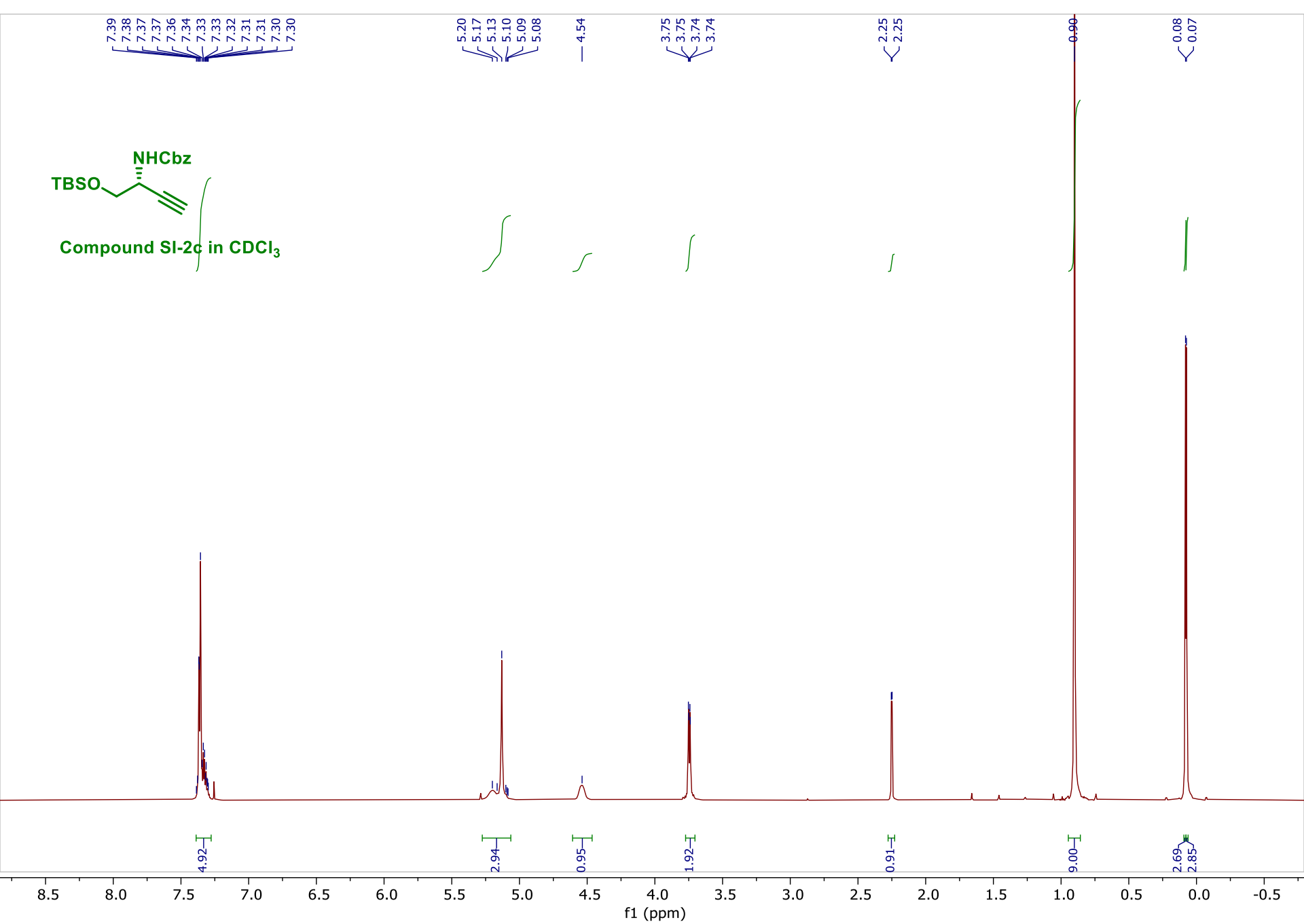
9. ^{1}H, ^{11}B, ^{13}C, ^{31}P NMR spectra and HPLC chromatograms


7.39
7.38
7.38
7.36
7.35
7.33
7.32
7.32
7.31
7.30
7.30
5.12
5.00
4.98
4.58
4.56
4.54
2.28
2.27
1.43
1.42
NHCbz
Compound SI-2a in CDCl3
5.33
2.18
0.95
1.06
1.00
3.27
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)


155.19
136.27
128.53
128.18
128.13
84.10
70.56
66.96
38.88
22.47
NHCbz
Compound SI-2a in CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4.71
4.46
2.24
2.23
1.43
1.39
1.37
NHBoc
Compound SI-2b in CDCl3
0.92
1.09
0.95
8.98
3.01
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)


154.60
84.56
79.90
70.09
38.29
28.33
22.53
38.29
NHBoc
Compound SI-2b in CDCl3
39
38
37
36
f1 (ppm)
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)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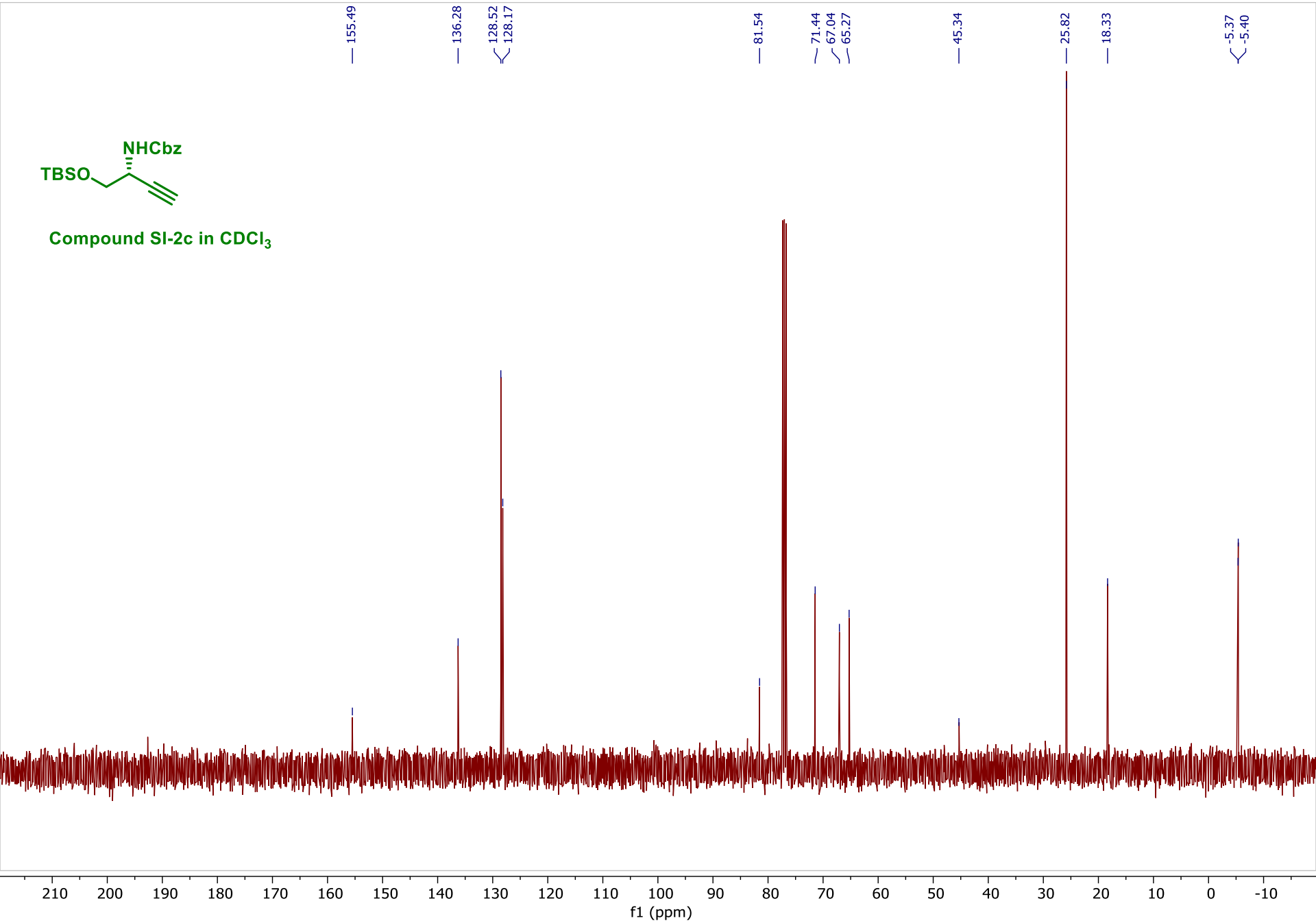
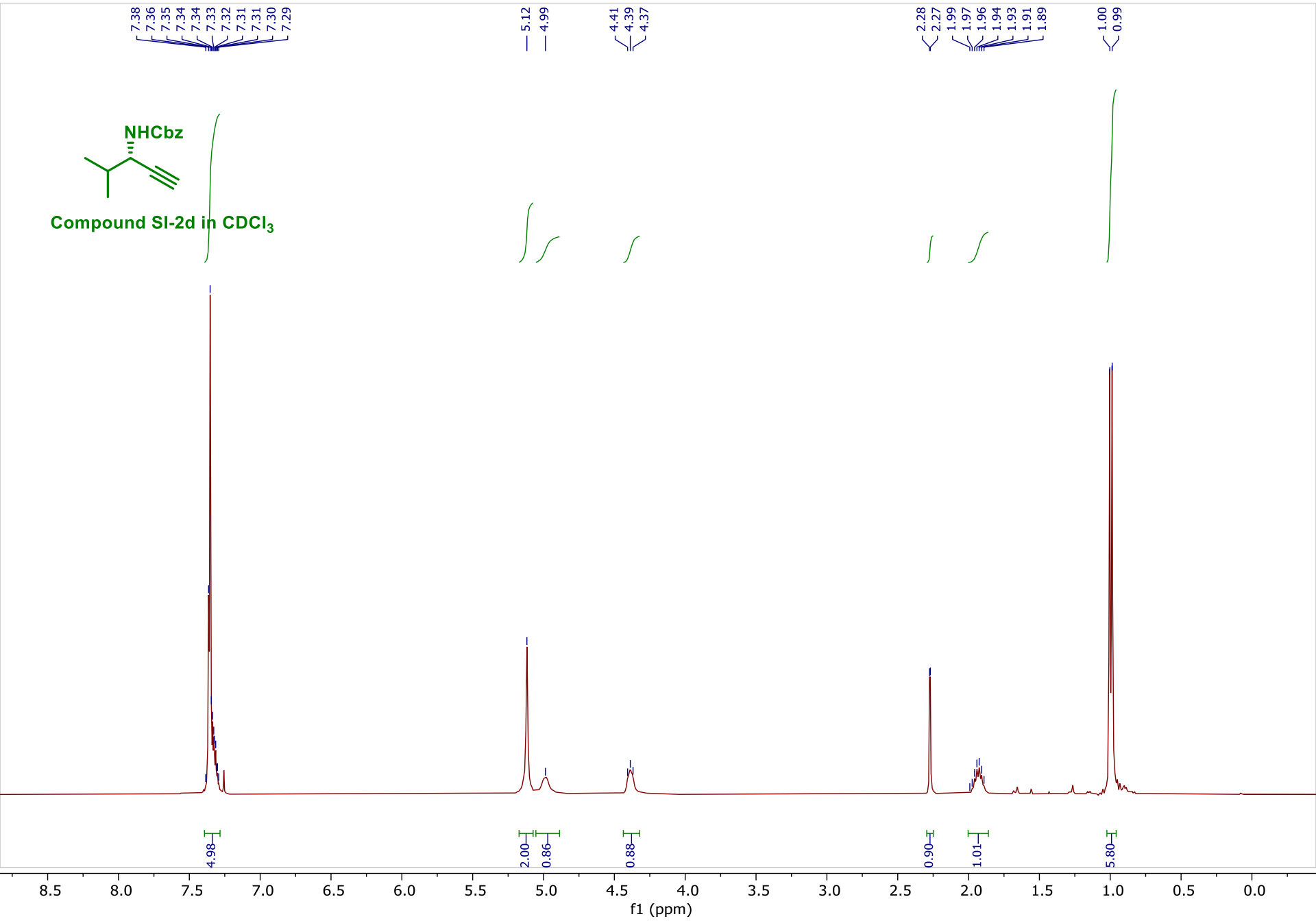
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
5.20
5.17
5.13
5.10
5.09
5.08
4.54
3.75
3.75
3.74
3.74
2.25
2.25
0.90
0.08
0.07
NHCbz
TBSO
Compound SI-2c in CDCl3
4.92
2.94
0.95
1.92
0.91
9.00
2.69
2.85
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


155.49
136.28
128.52
128.17
81.54
71.44
67.04
65.27
45.34
25.82
18.33
-5.37
-5.40
NHCbz
TBSO
Compound SI-2c in CDCl3
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)


7.38
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.29
5.12
4.99
4.41
4.39
4.37
2.28
2.27
1.99
1.97
1.96
1.94
1.93
1.91
1.89
1.00
0.99
NHCbz
Compound SI-2d in CDCl3
4.98
2.00
0.86
0.88
0.90
1.01
5.80
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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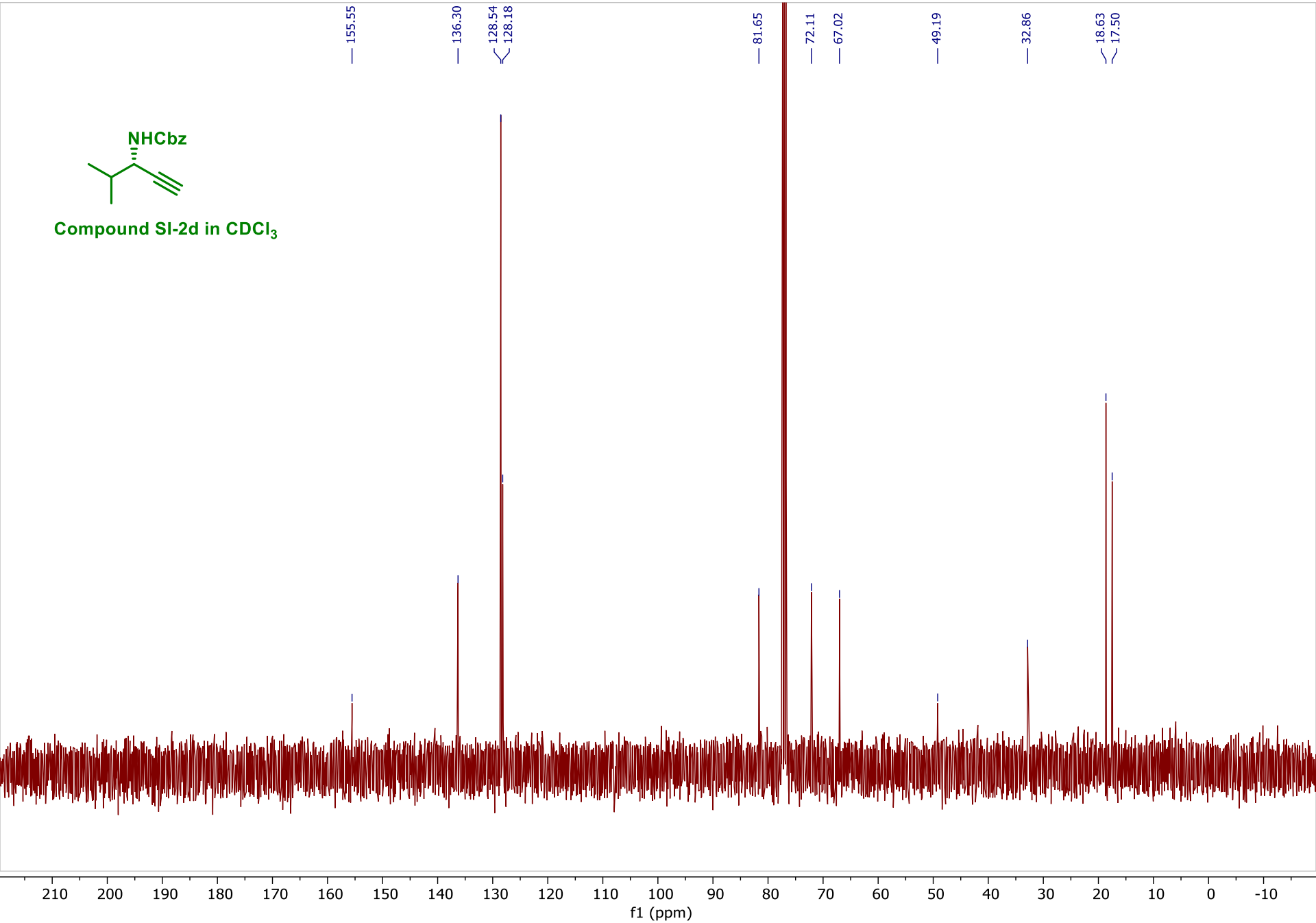
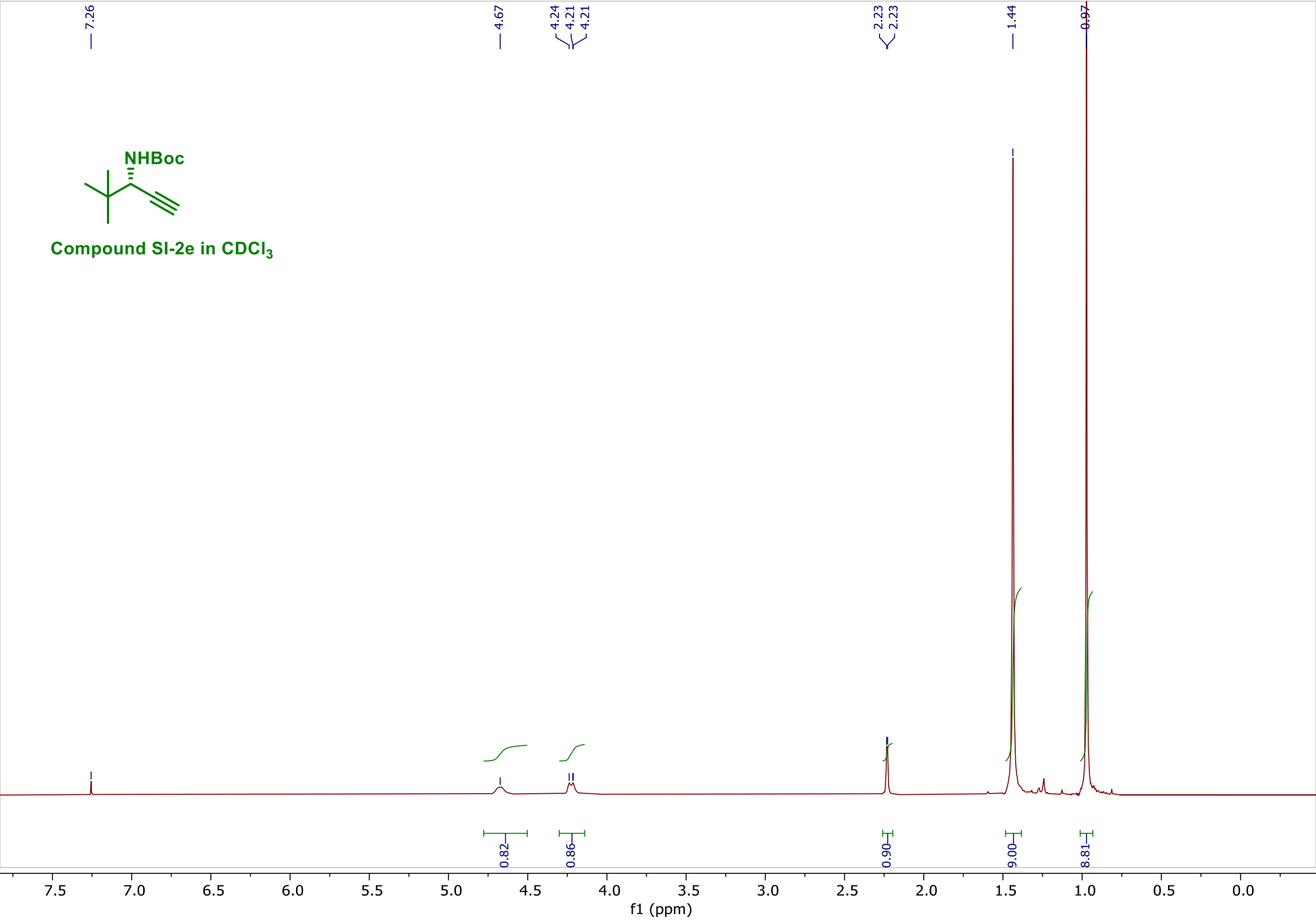
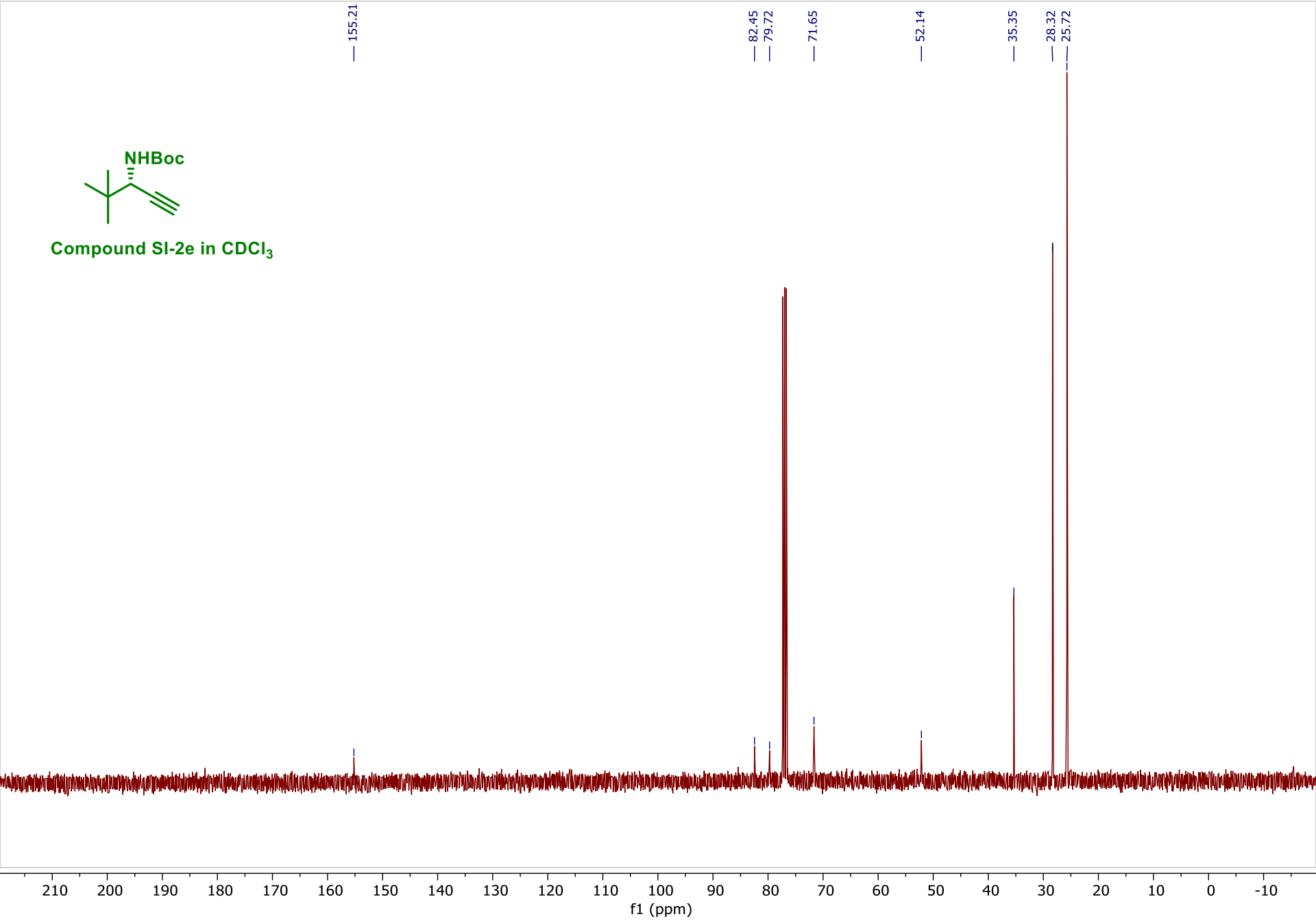
1.0
0.5
0.0
f1 (ppm)


155.55
136.30
128.54
128.18
81.65
72.11
67.02
49.19
32.86
18.63
17.50
NHCbz
Compound SI-2d in CDCl3
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)


7.26
4.67
4.24
4.21
4.21
2.23
2.23
1.44
0.97
NHBoc
Compound SI-2e in CDCl3
0.82
0.86
0.90
9.00
8.81
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)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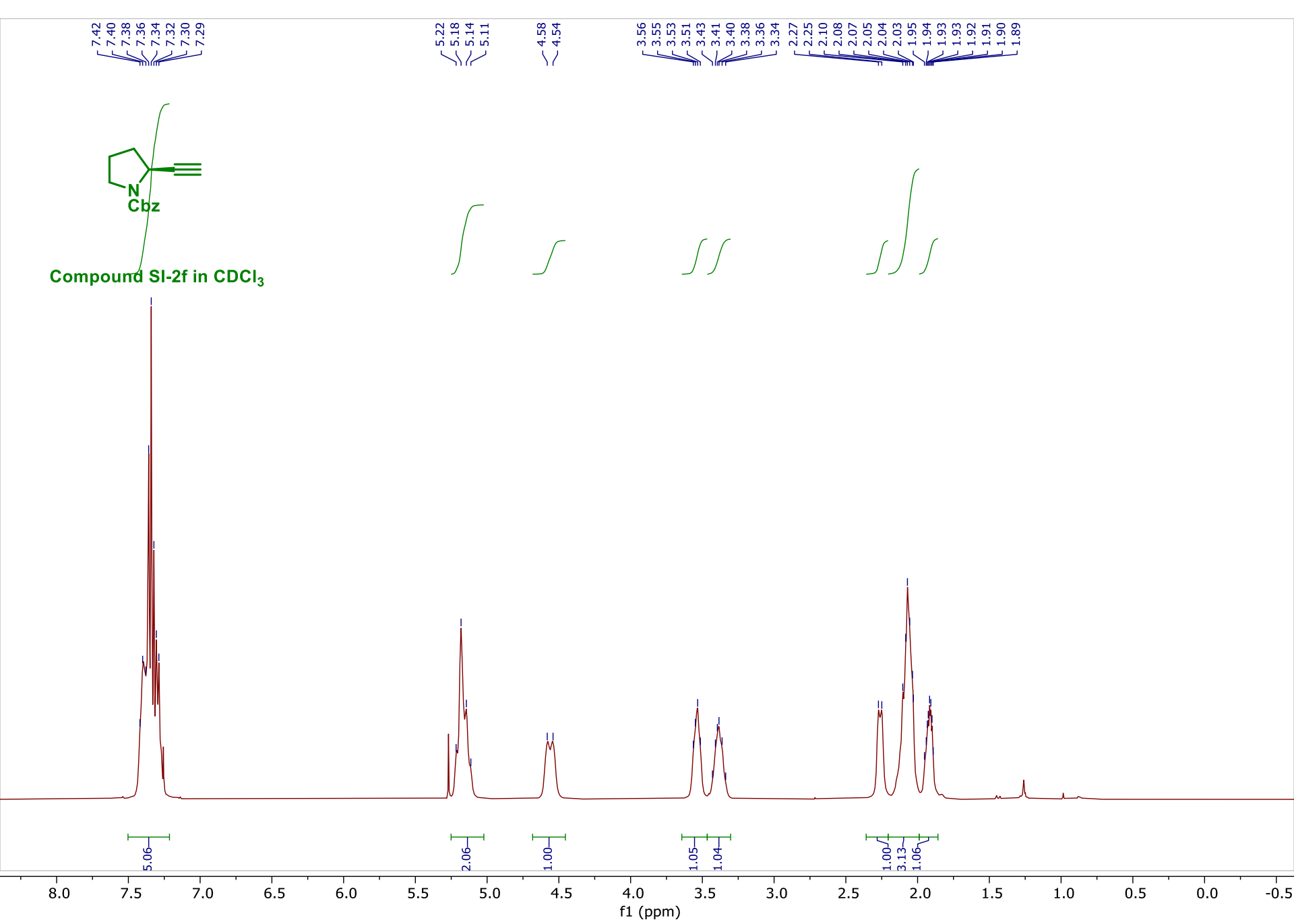
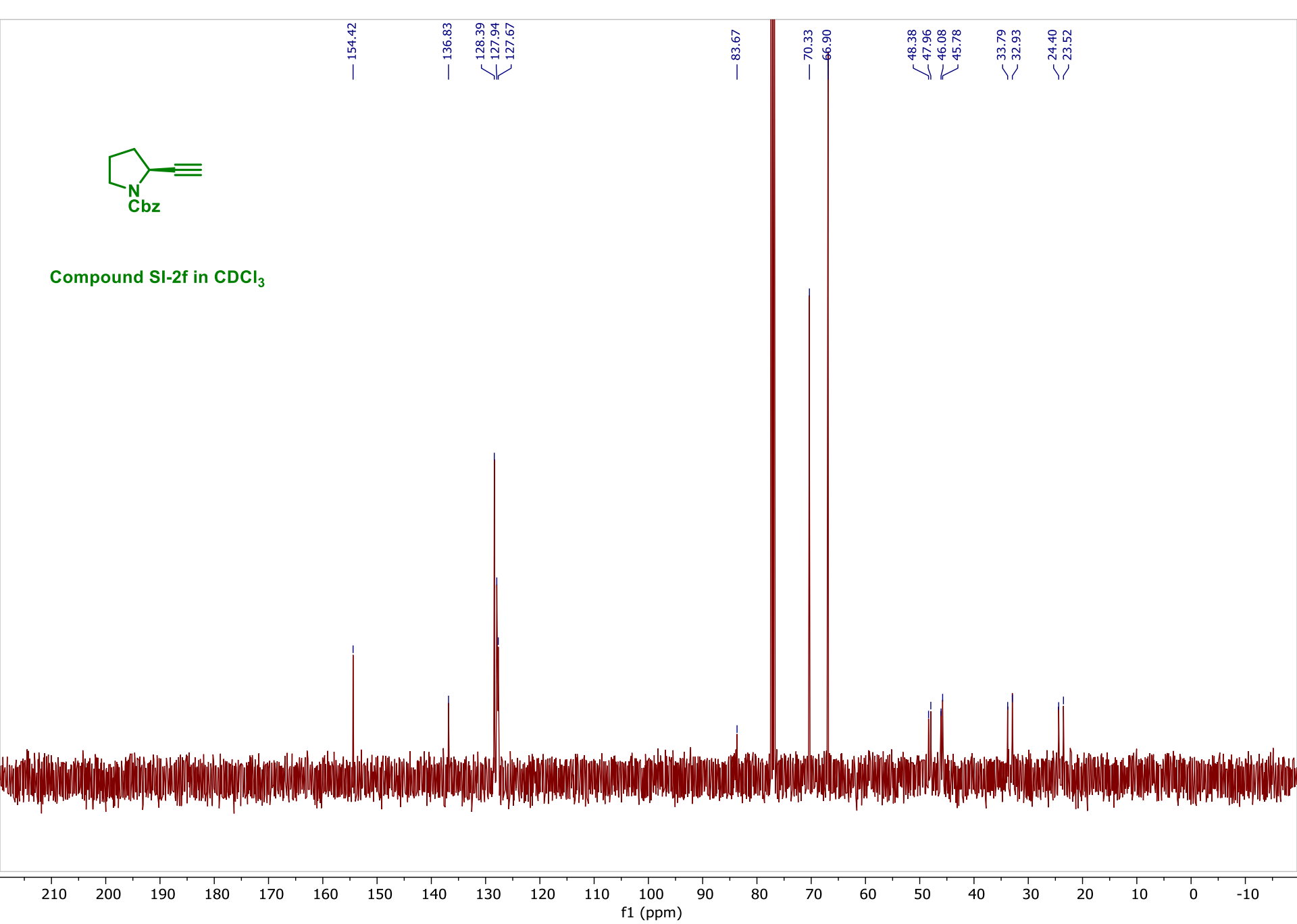
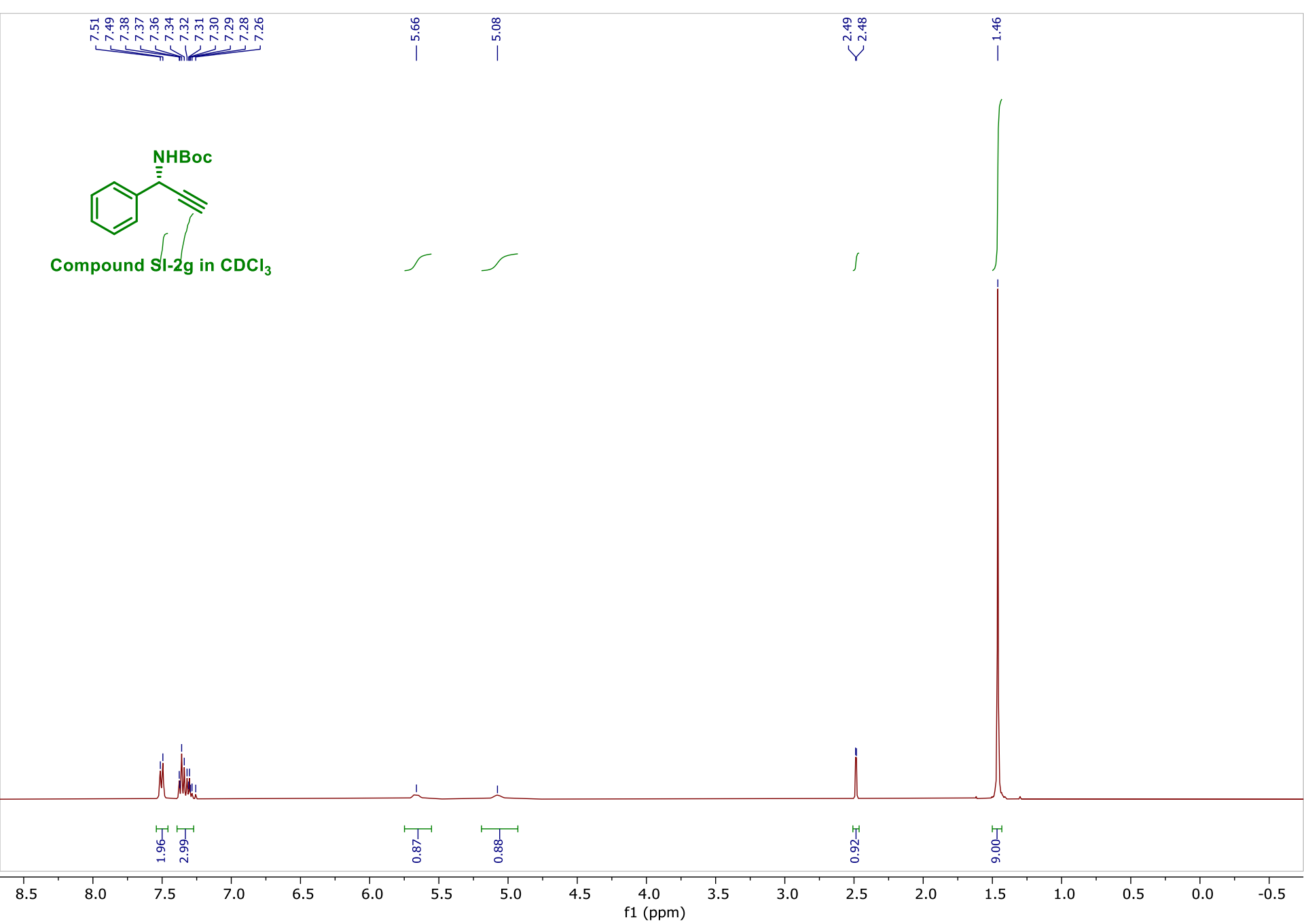
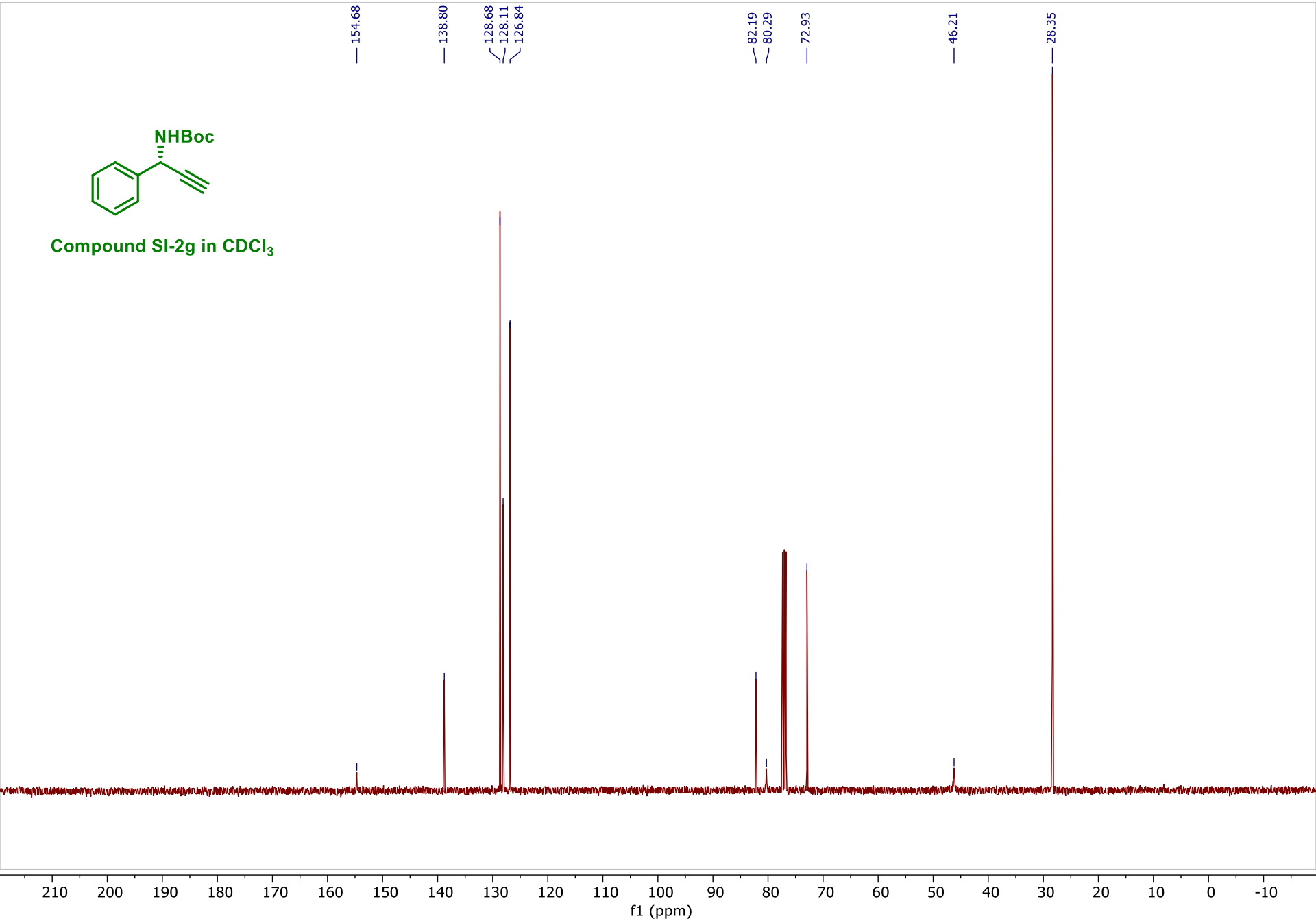
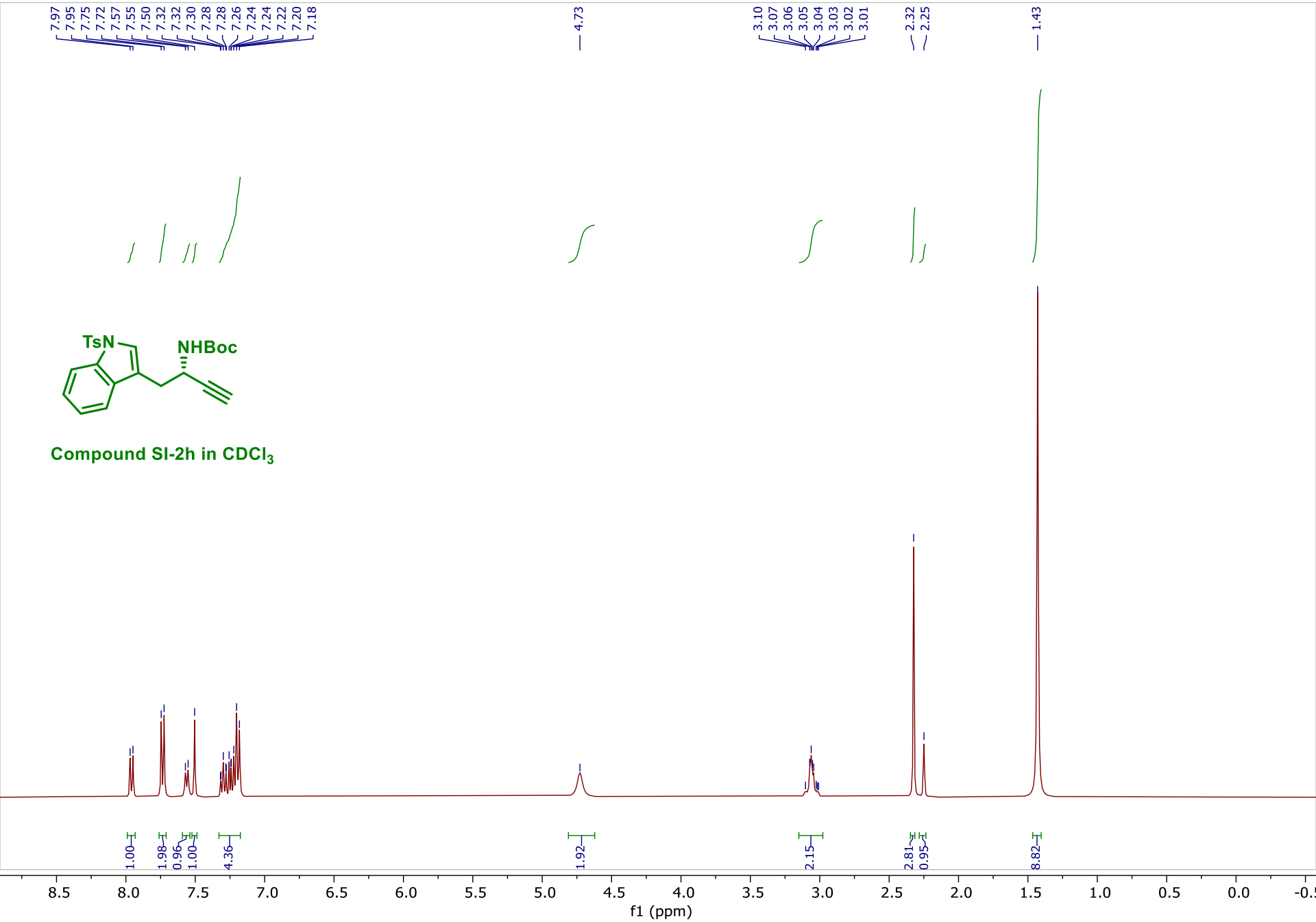
71.65
52.14
35.35
28.32
25.72
NHBoc
Compound SI-2e in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.42
7.40
7.38
7.36
7.34
7.32
7.30
7.29
5.22
5.18
5.14
5.11
4.58
4.54
3.56
3.55
3.53
3.51
3.43
3.41
3.40
3.38
3.36
3.34
2.27
2.25
2.10
2.08
2.07
2.05
2.04
2.03
1.95
1.94
1.93
1.93
1.92
1.91
1.90
1.89
N
Cbz
Compound SI-2f in CDCl3
5.06
2.06
1.00
1.05
1.04
1.00
3.13
1.06
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)

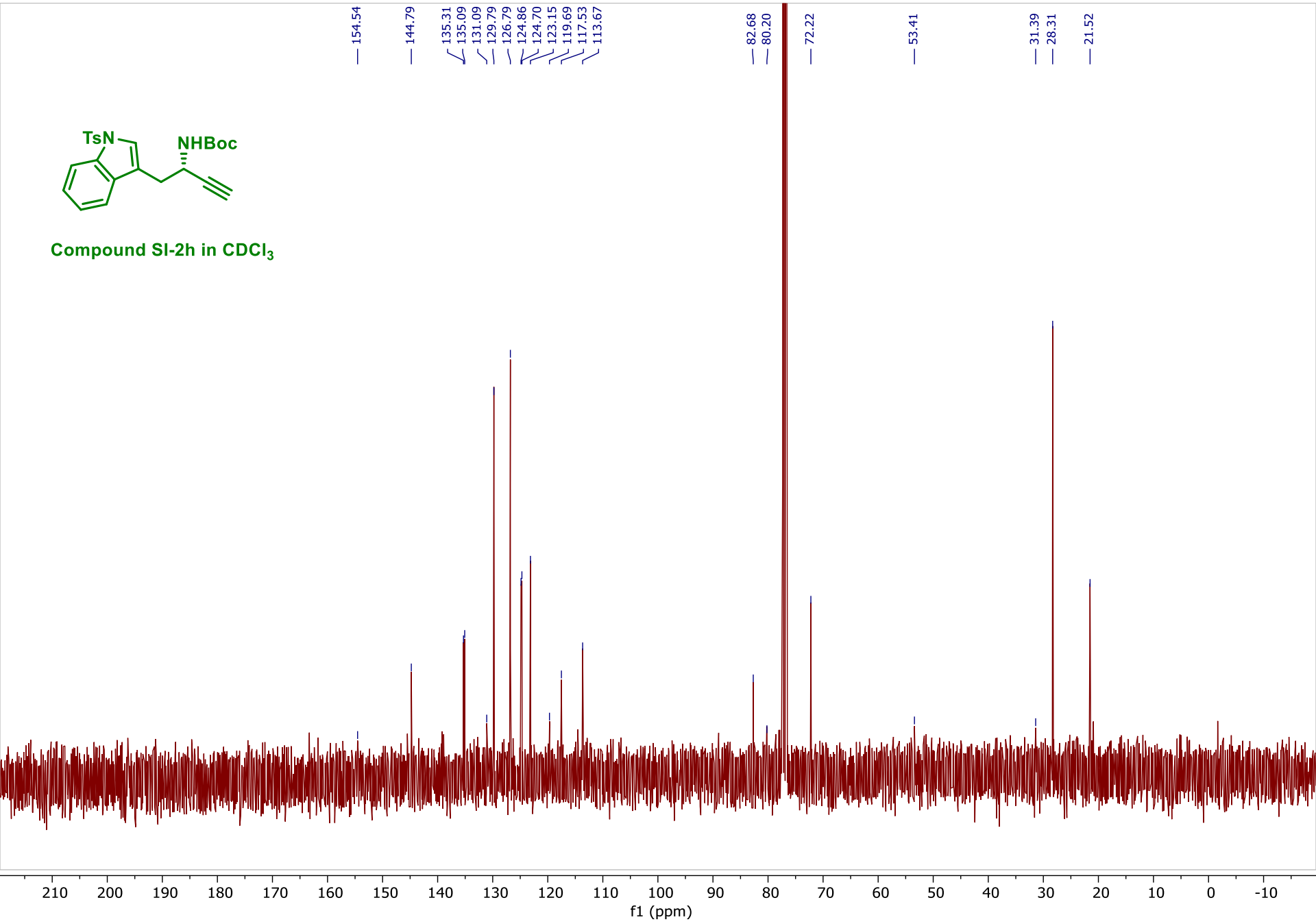

154.42
136.83
128.39
127.94
127.67
83.67
70.33
66.90
48.38
47.96
46.08
45.78
33.79
32.93
24.40
23.52
N
Cbz
Compound SI-2f in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

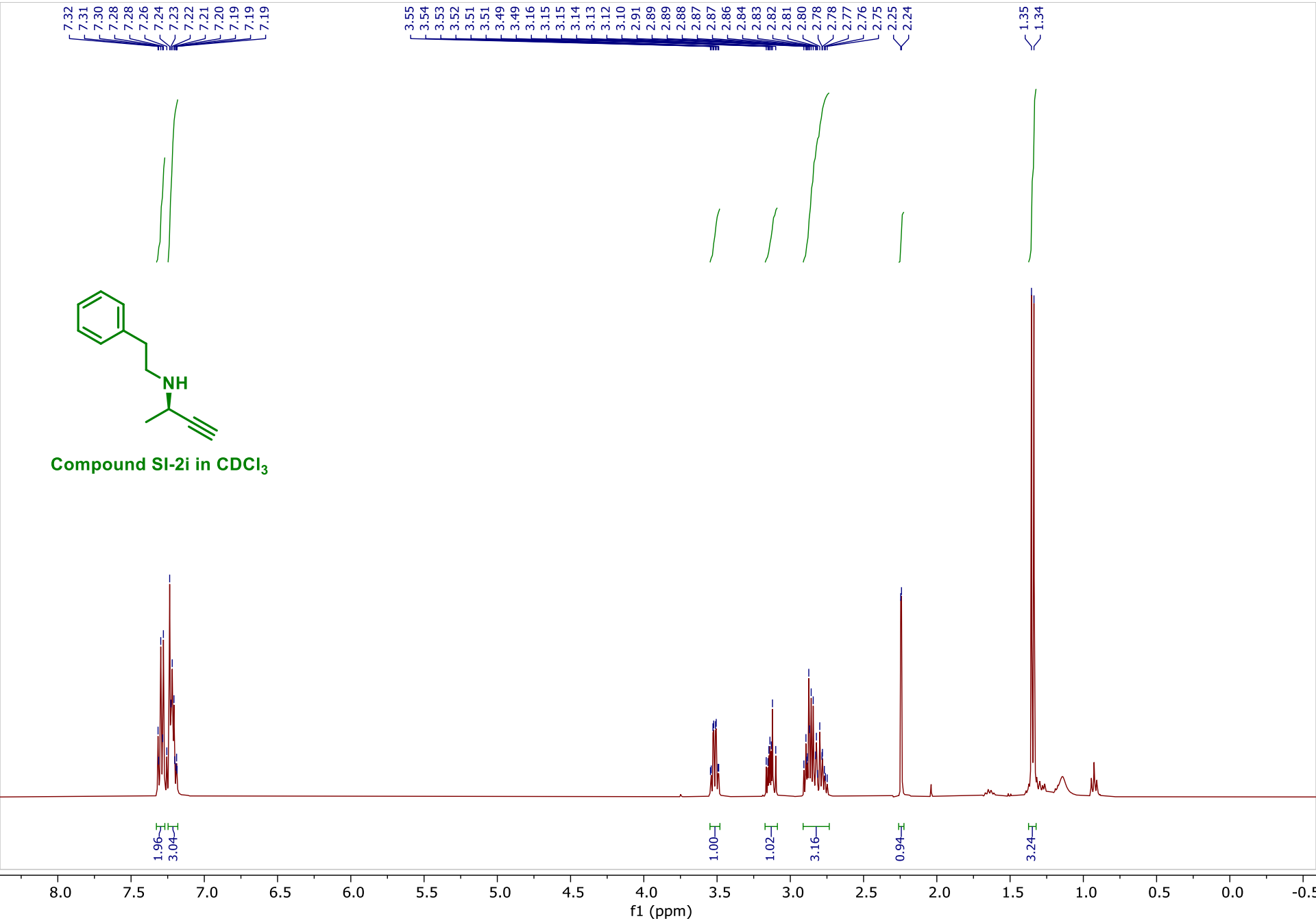

7.51
7.49
7.38
7.37
7.36
7.34
7.32
7.31
7.30
7.29
7.28
7.26
5.66
5.08
2.49
2.48
1.46
NHBoc
Compound SI-2g in CDCl3
1.96
2.99
0.87
0.88
0.92
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


154.68
138.80
128.68
128.11
126.84
82.19
80.29
72.93
46.21
28.35
NHBoc
Compound SI-2g in CDCl3
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)

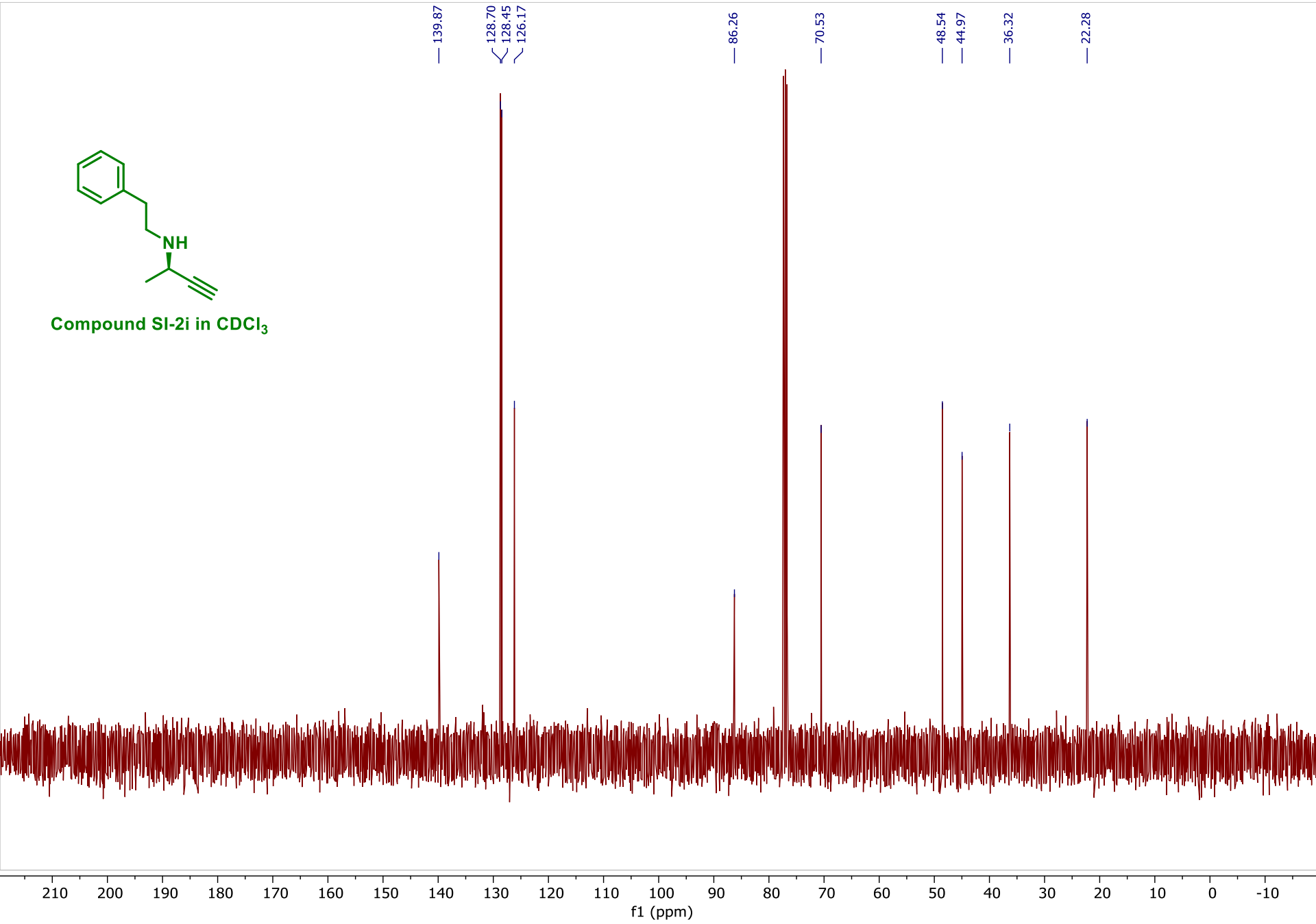


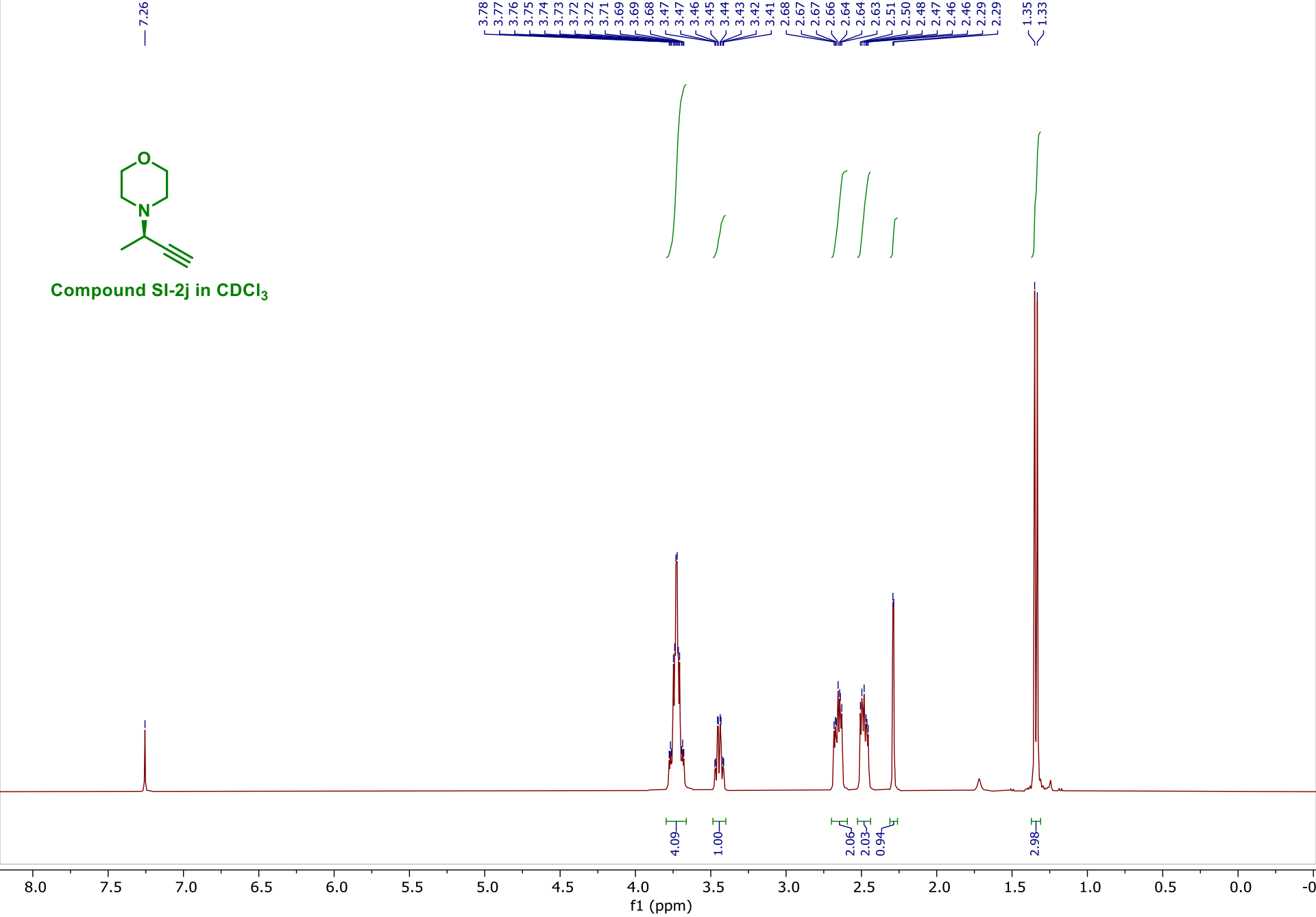
Compound SI-2h in $CDCl_3$


154.54
144.79
135.31
135.09
131.09
129.79
126.79
124.86
124.70
123.15
119.69
117.53
113.67
82.68
80.20
72.22
53.41
31.39
28.31
21.52
TsN
NHBoc
Compound SI-2h in CDCl3
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)

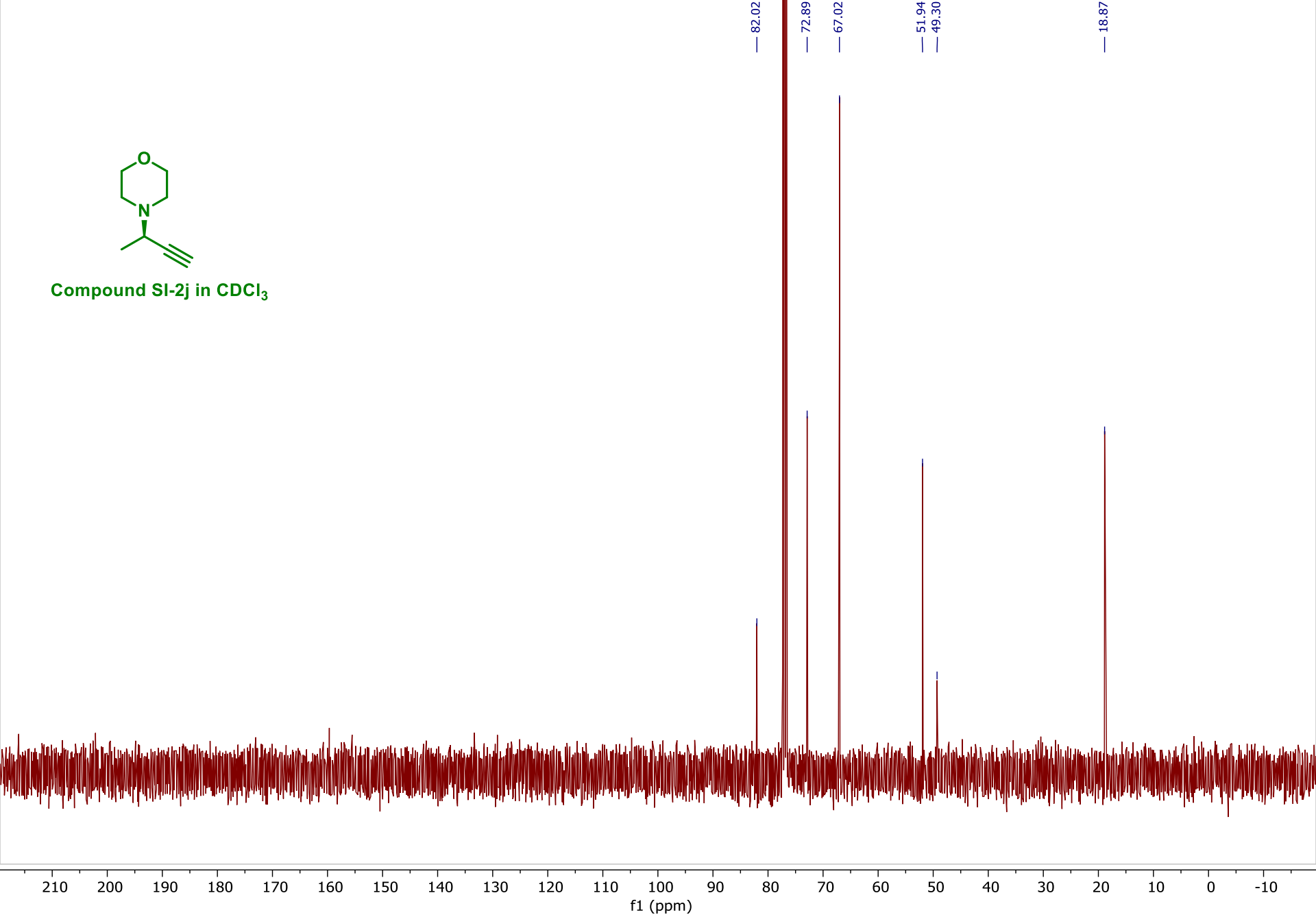


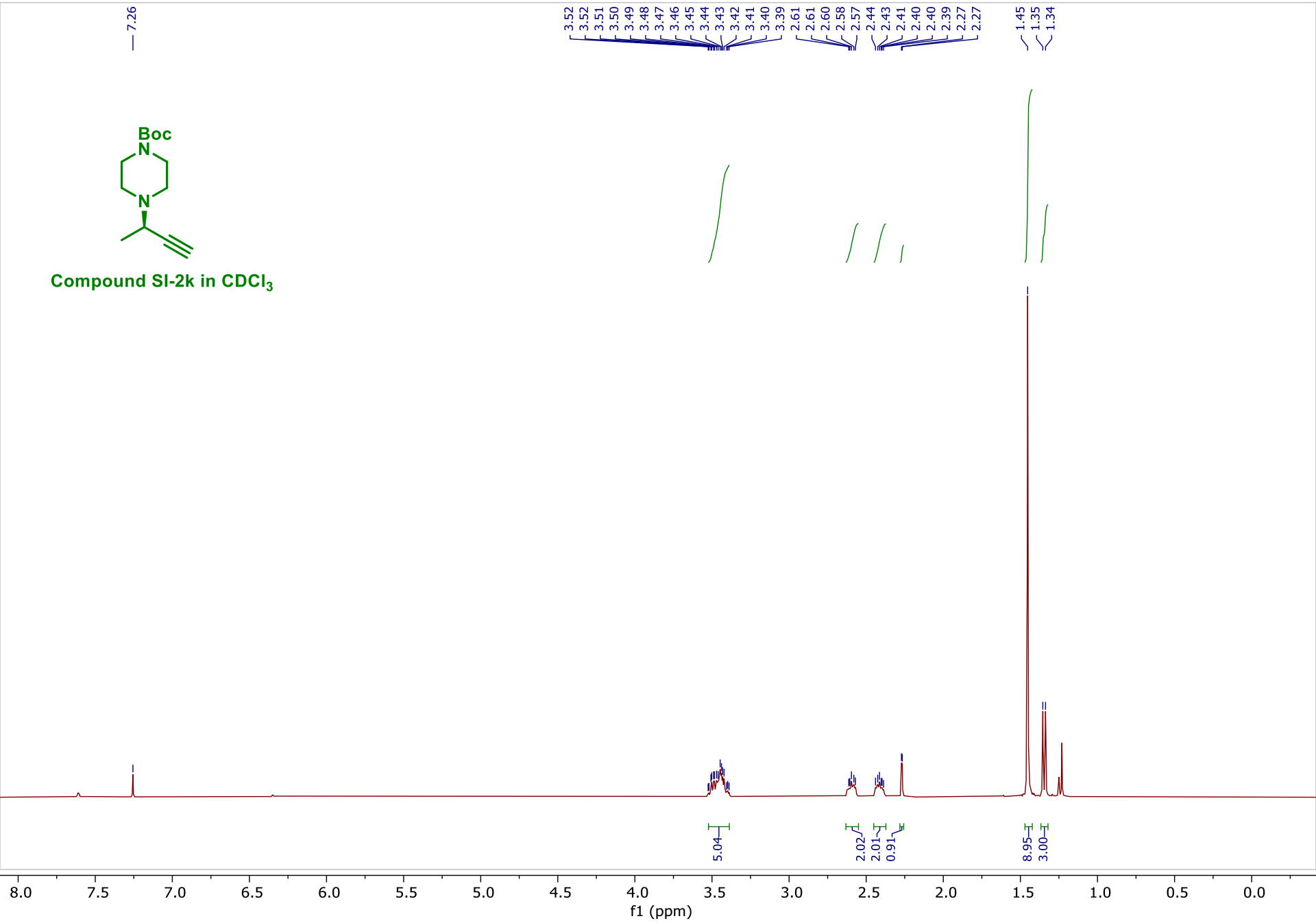
Compound SI-2i in $CDCl_3$

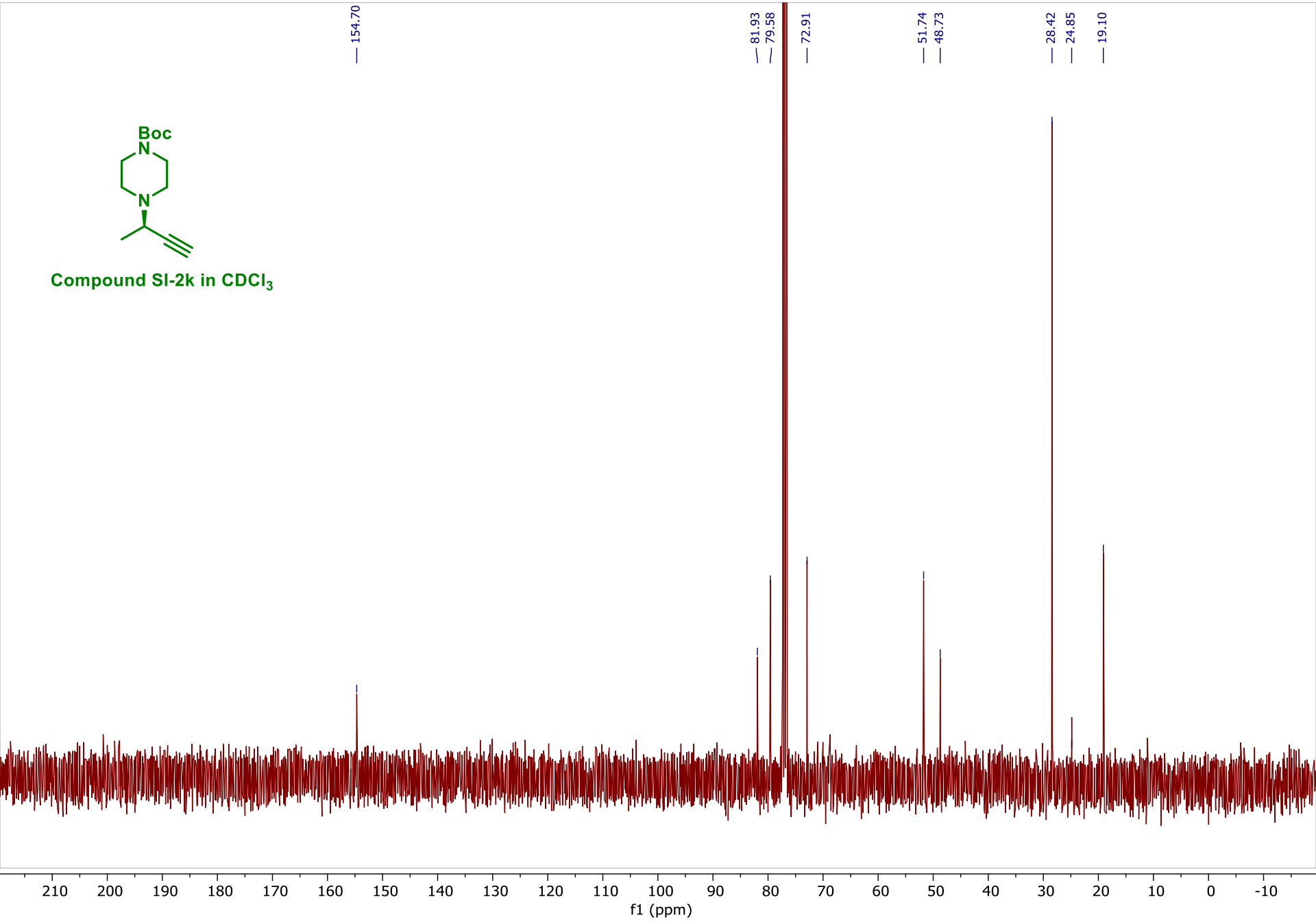

139.87
128.70
128.45
126.17
86.26
70.53
48.54
44.97
36.32
22.28
NH
Compound SI-2i in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

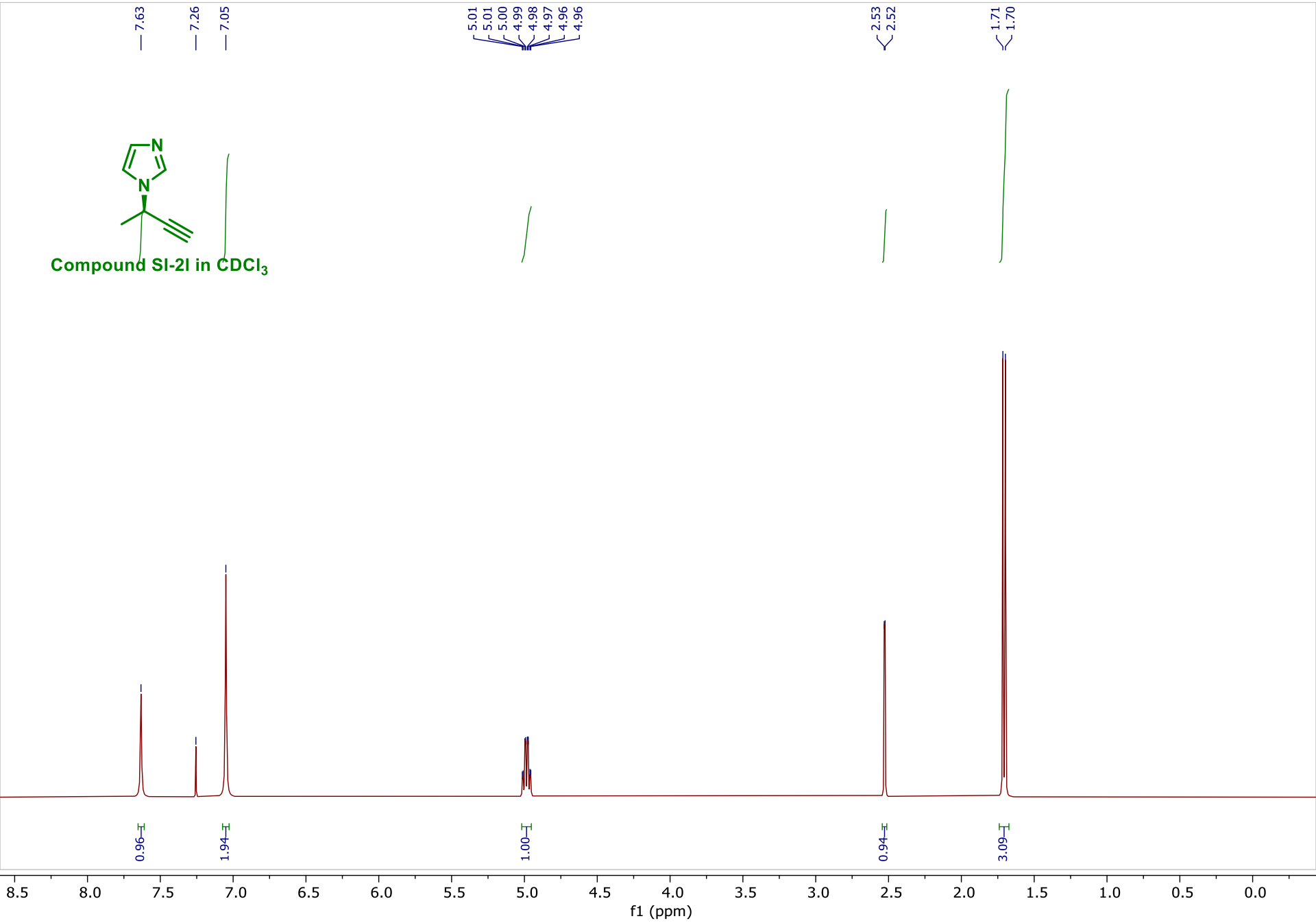


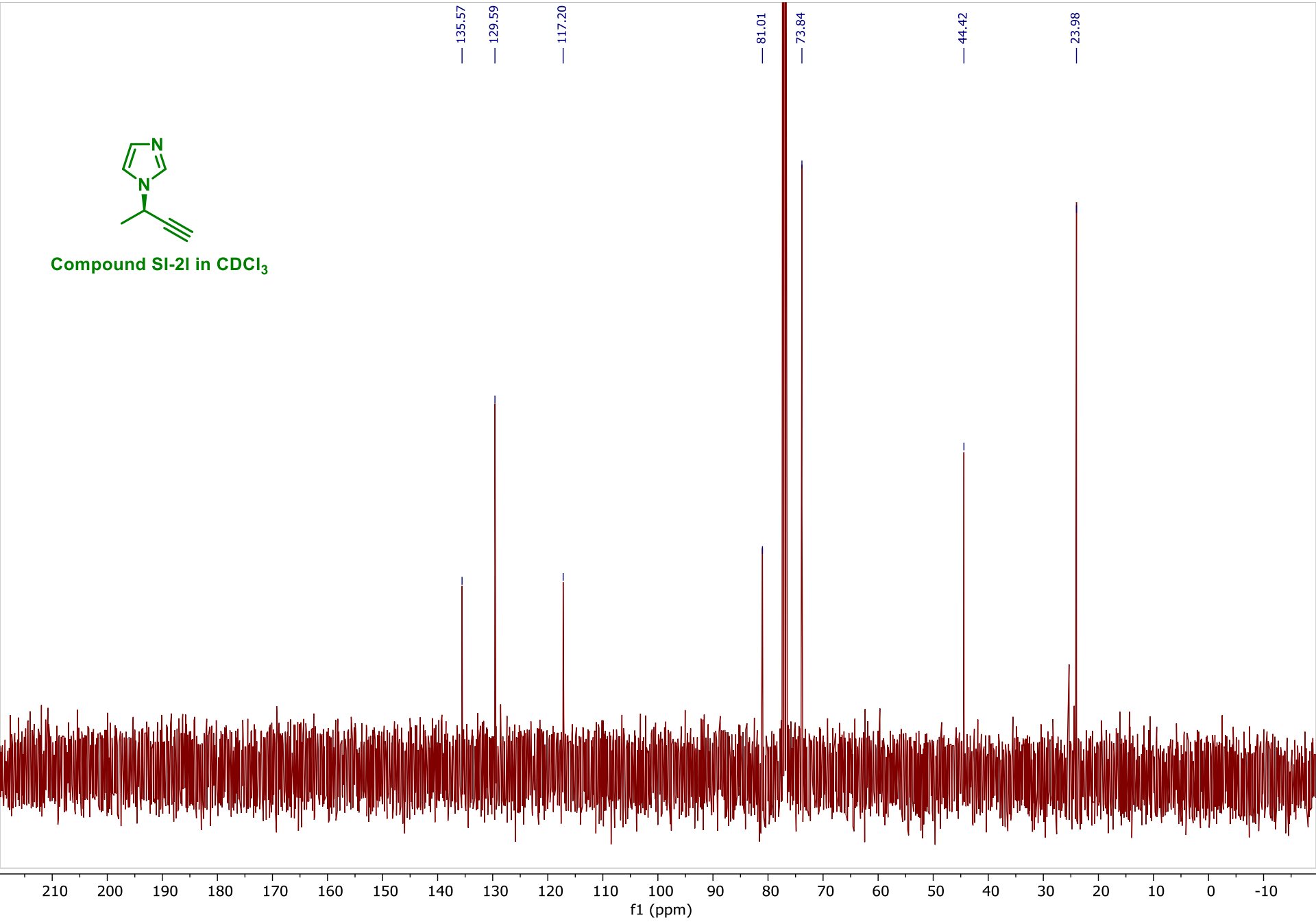
Compound SI-2j in $CDCl_3$

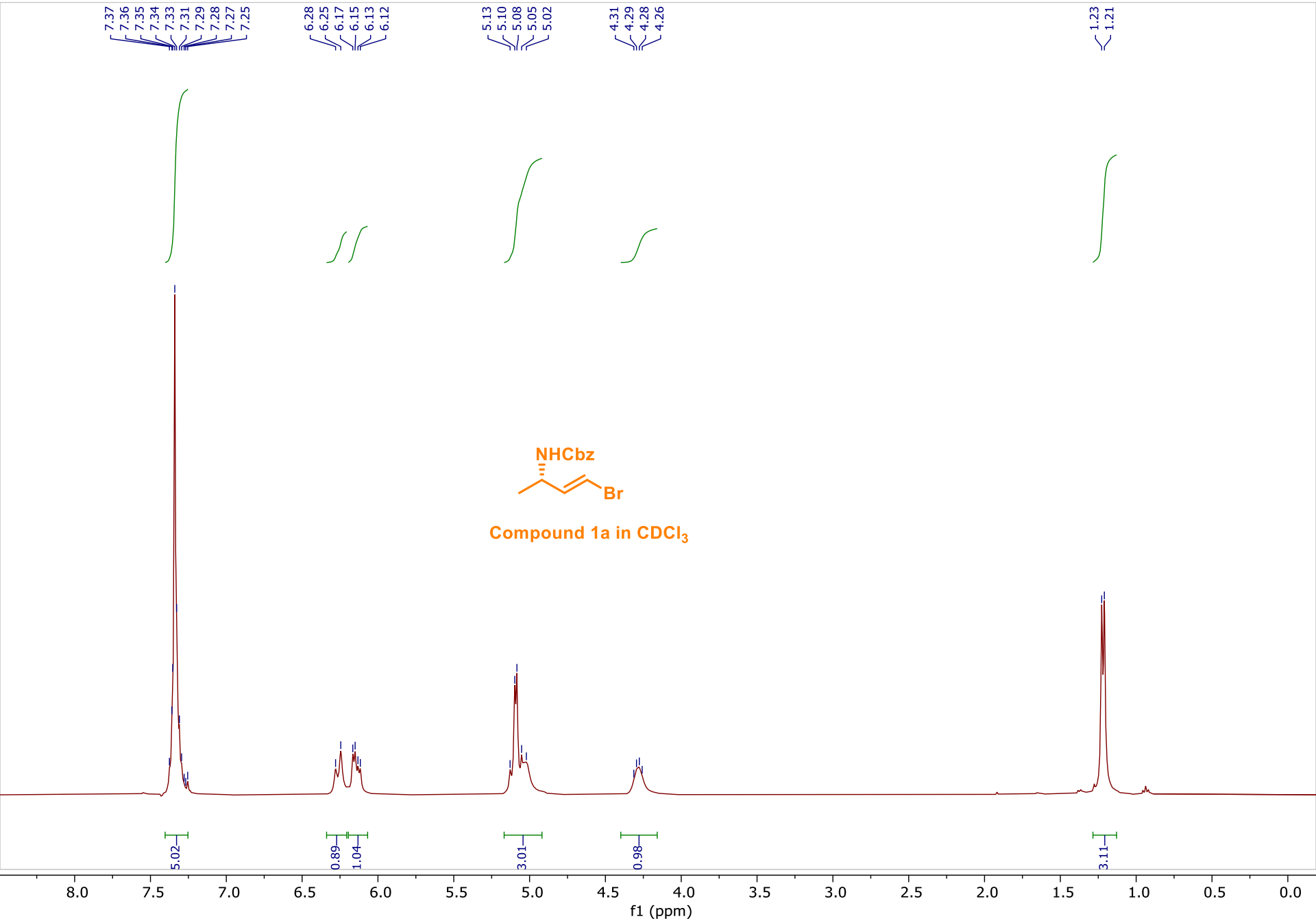

82.02
72.89
67.02
51.94
49.30
18.87
O
N
Compound SI-2j in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

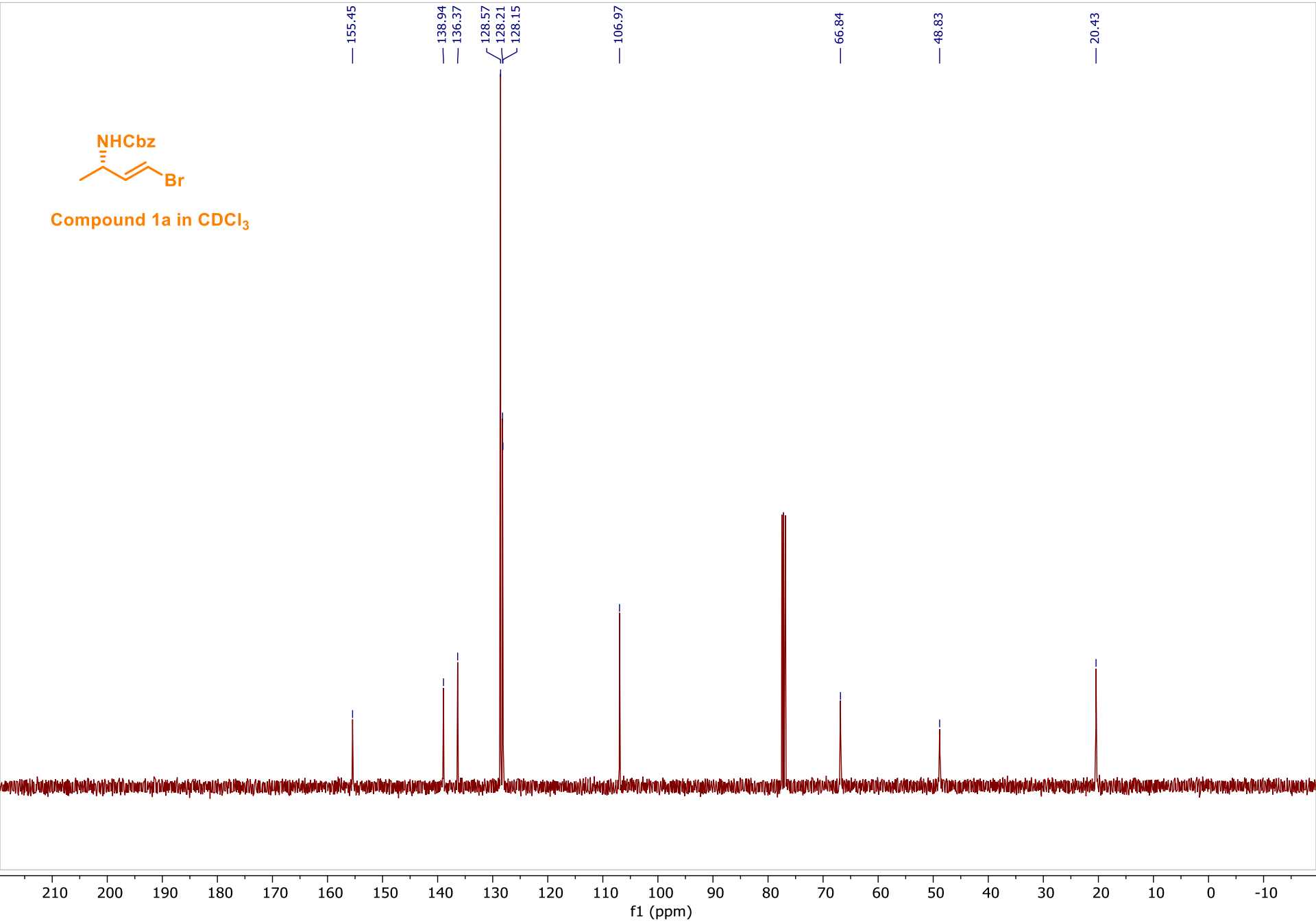

7.26
3.52
3.52
3.51
3.50
3.49
3.48
3.47
3.46
3.45
3.44
3.43
3.42
3.41
3.40
3.39
2.61
2.61
2.60
2.58
2.57
2.44
2.43
2.41
2.40
2.40
2.39
2.27
2.27
1.45
1.35
1.34
Boc
N
N
Compound SI-2k in CDCl3
5.04
2.02
2.01
0.91
8.95
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

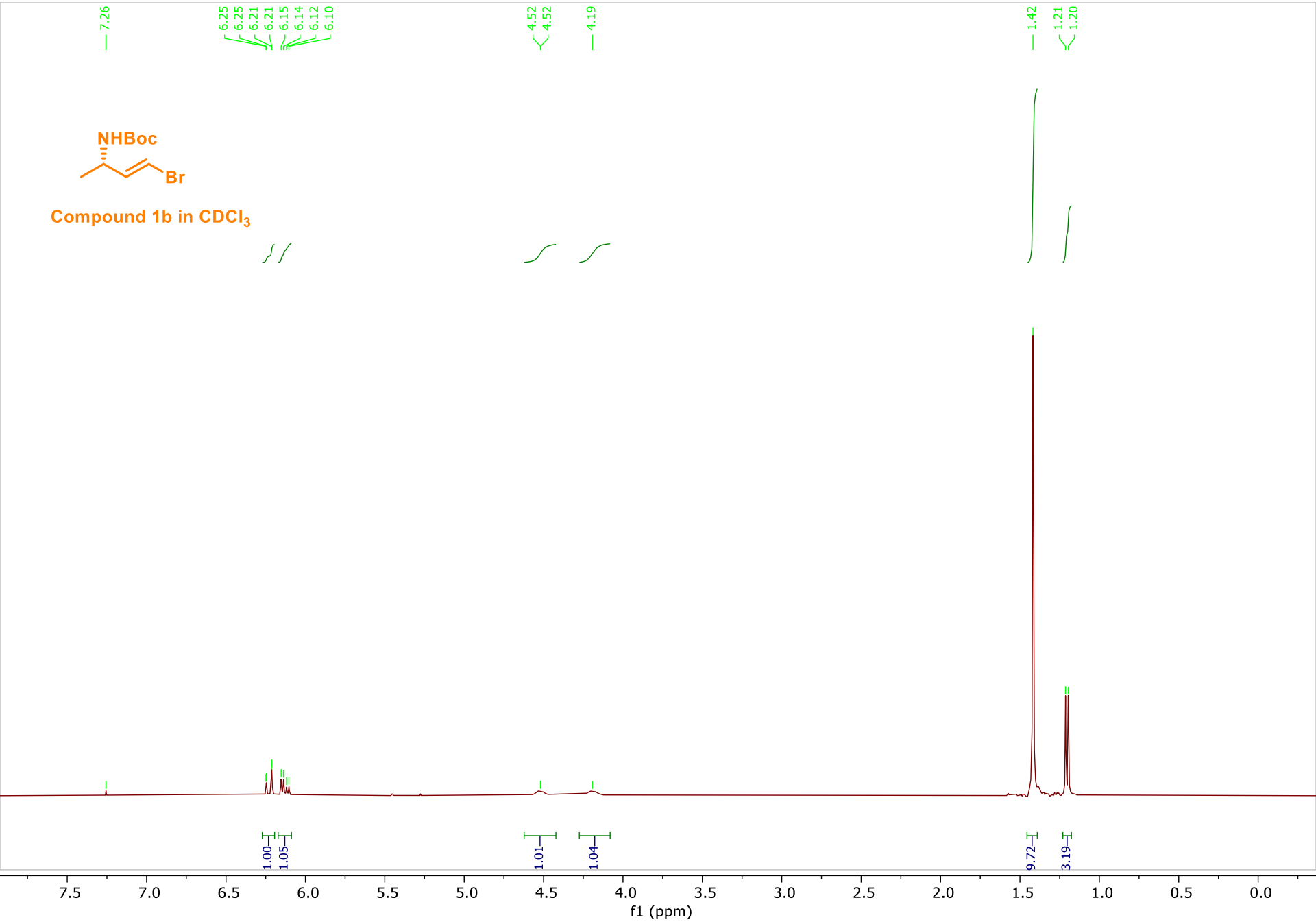

154.70
81.93
79.58
72.91
51.74
48.73
28.42
24.85
19.10
Boc
N
N
Compound SI-2k in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

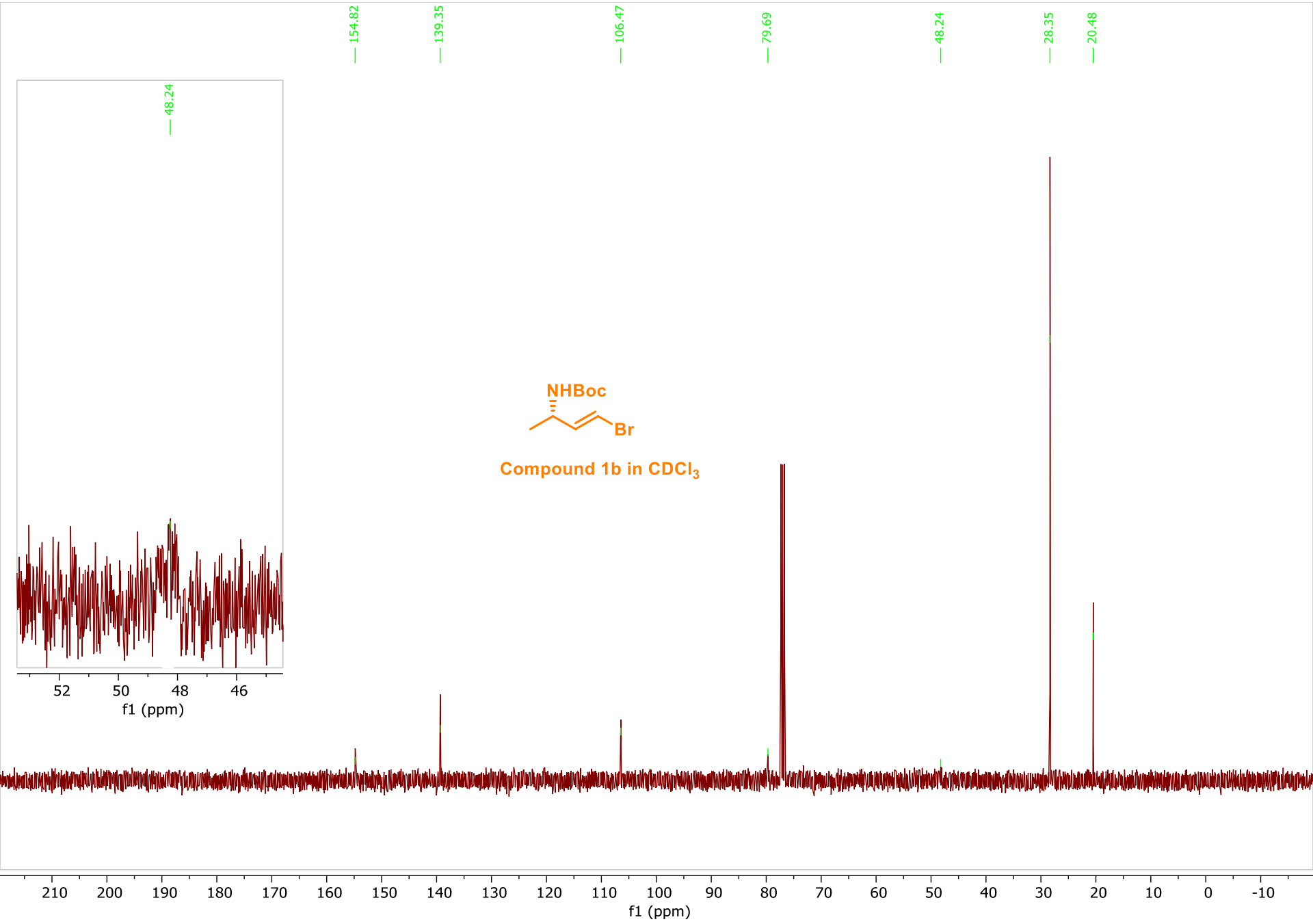

7.63
7.26
7.05
5.01
5.01
5.00
4.99
4.98
4.97
4.96
4.96
2.53
2.52
1.71
1.70
N
N
Compound SI-2l in CDCl3
0.96
1.94
1.00
0.94
3.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

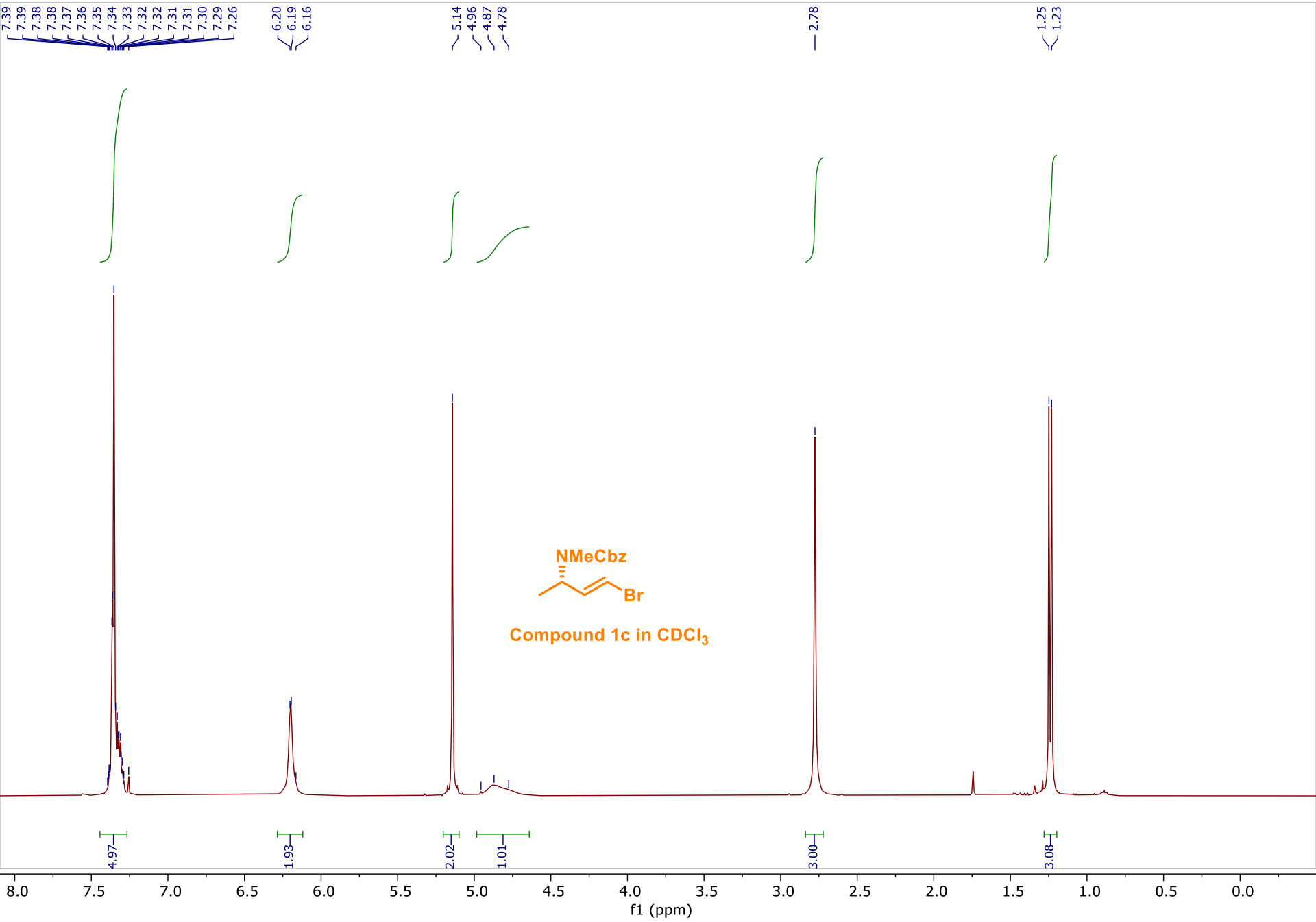

135.57
129.59
117.20
81.01
73.84
44.42
23.98
N
N
Compound SI-2l in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

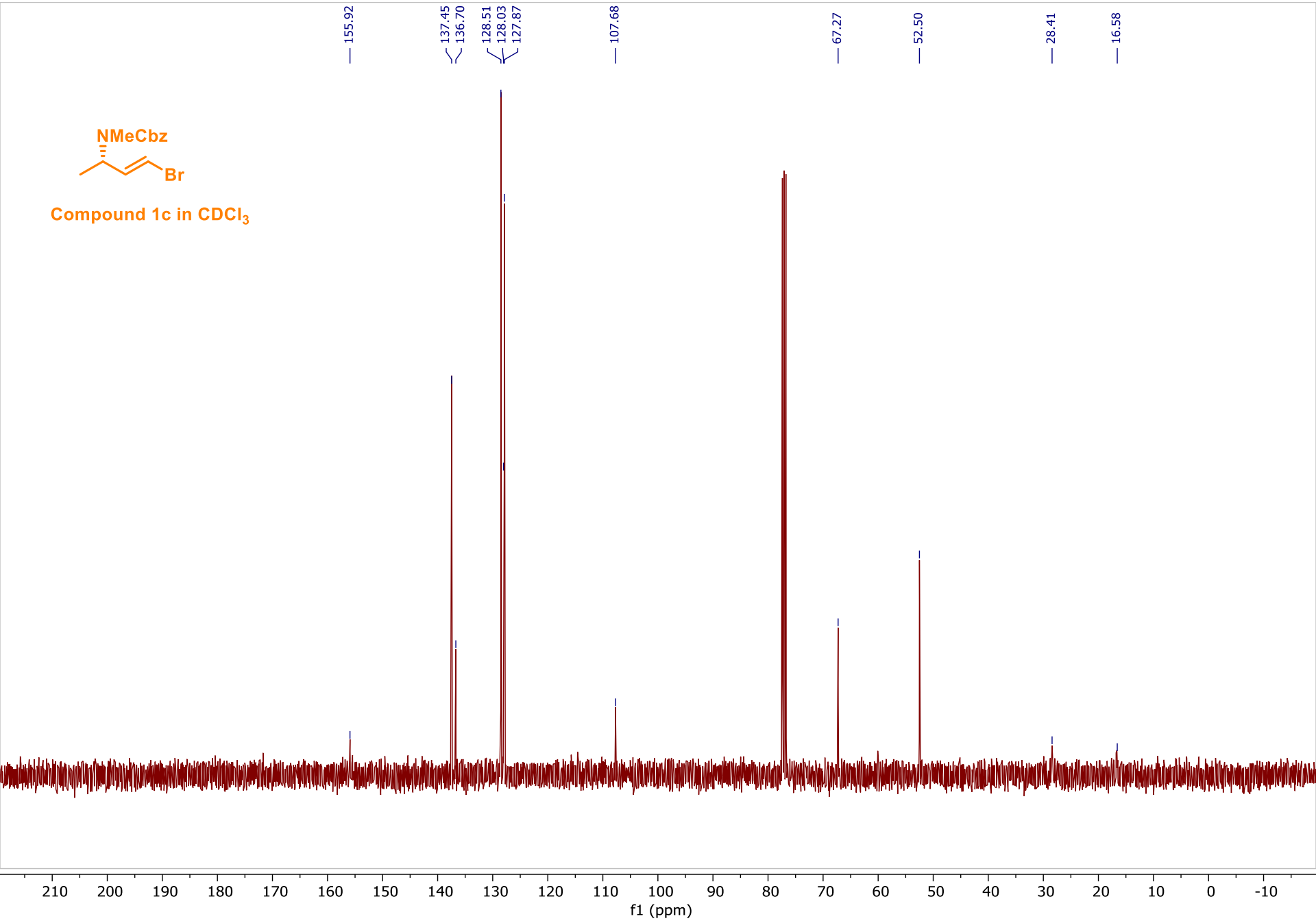

7.37
7.36
7.35
7.34
7.33
7.31
7.29
7.28
7.27
7.25
6.28
6.25
6.17
6.15
6.13
6.12
5.13
5.10
5.08
5.05
5.02
4.31
4.29
4.28
4.26
1.23
1.21
NHCbz
Br
Compound 1a in CDCl3
5.02
0.89
1.04
3.01
0.98
3.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

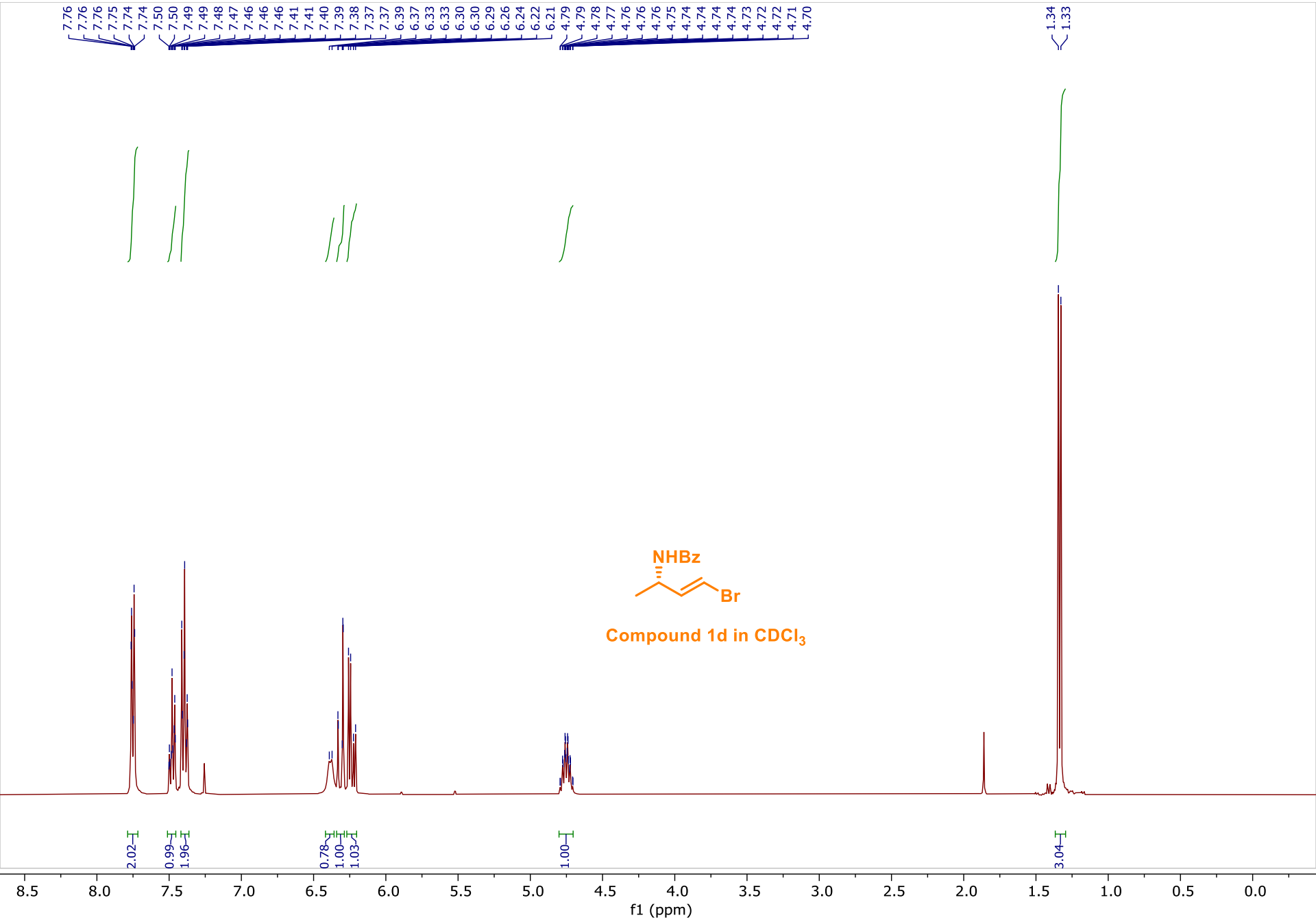

155.45
138.94
136.37
128.57
128.21
128.15
106.97
66.84
48.83
20.43
NHCbz
Br
Compound 1a in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

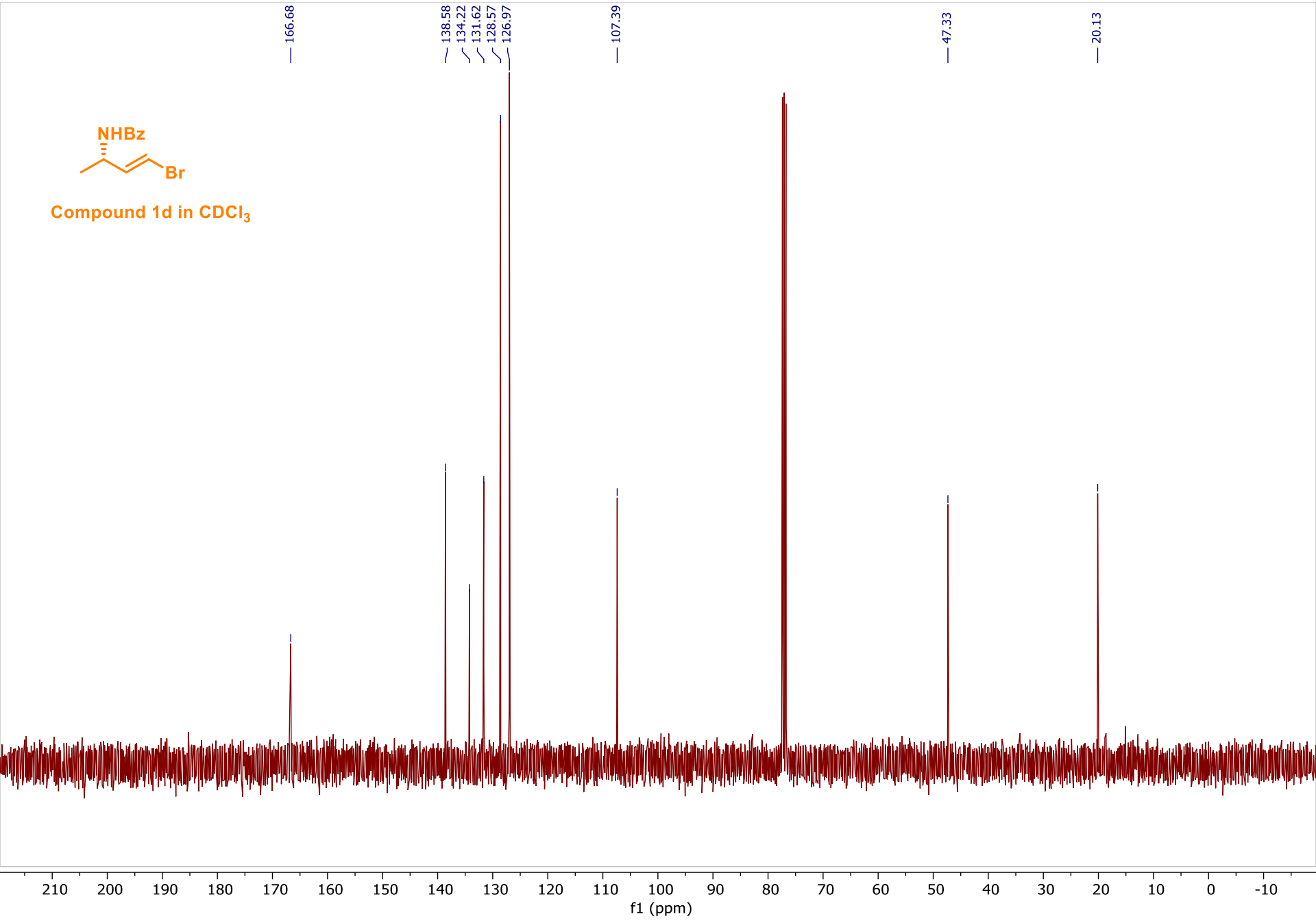

7.26
6.25
6.25
6.21
6.21
6.15
6.14
6.12
6.10
4.52
4.52
4.19
1.42
1.21
1.20
NHBoc
Br
Compound 1b in CDCl3
1.00
1.05
1.01
1.04
9.72
3.19
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

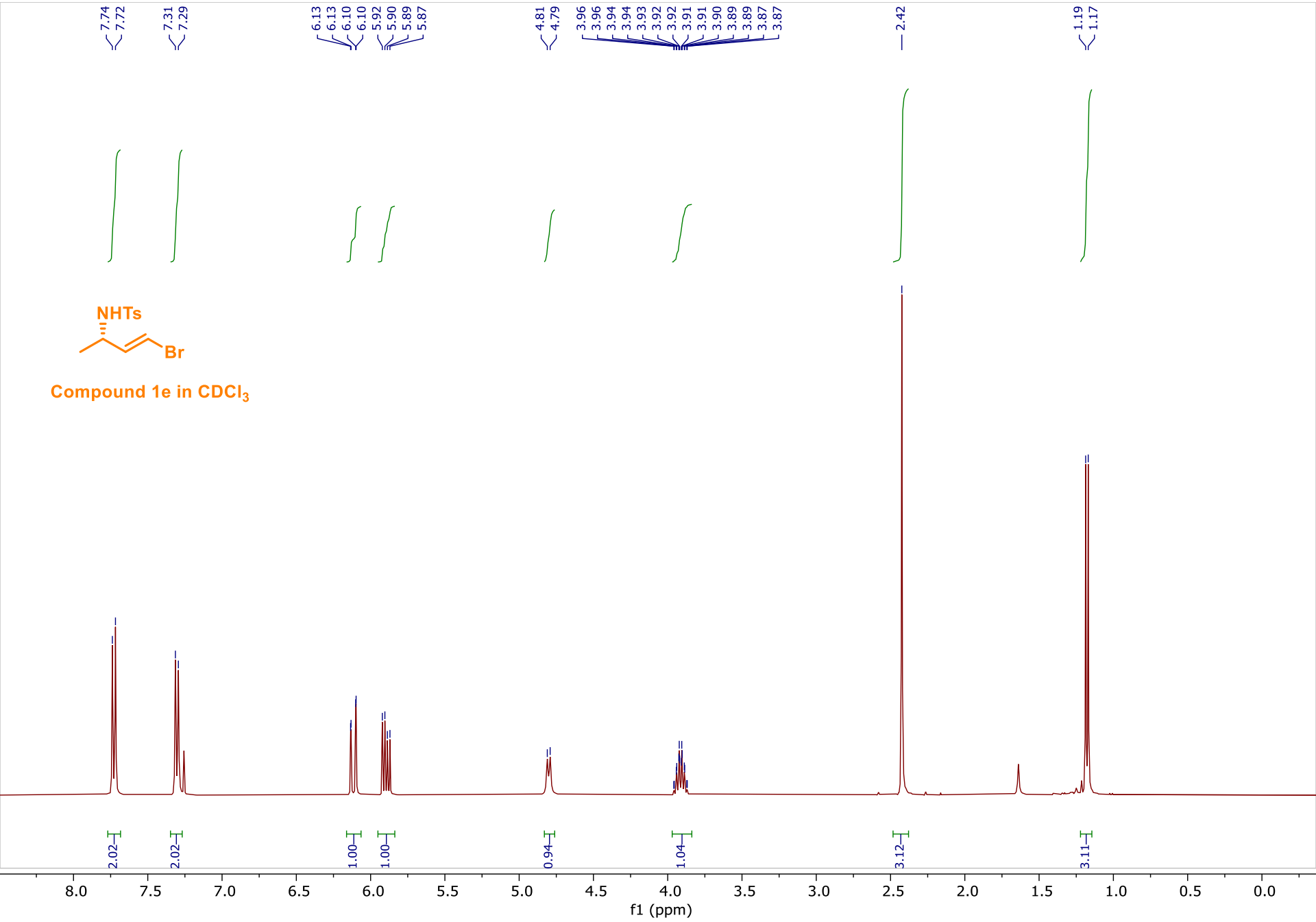

154.82
139.35
106.47
79.69
48.24
28.35
20.48
48.24
NHBoc
Br
Compound 1b in CDCl3
52
50
48
46
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

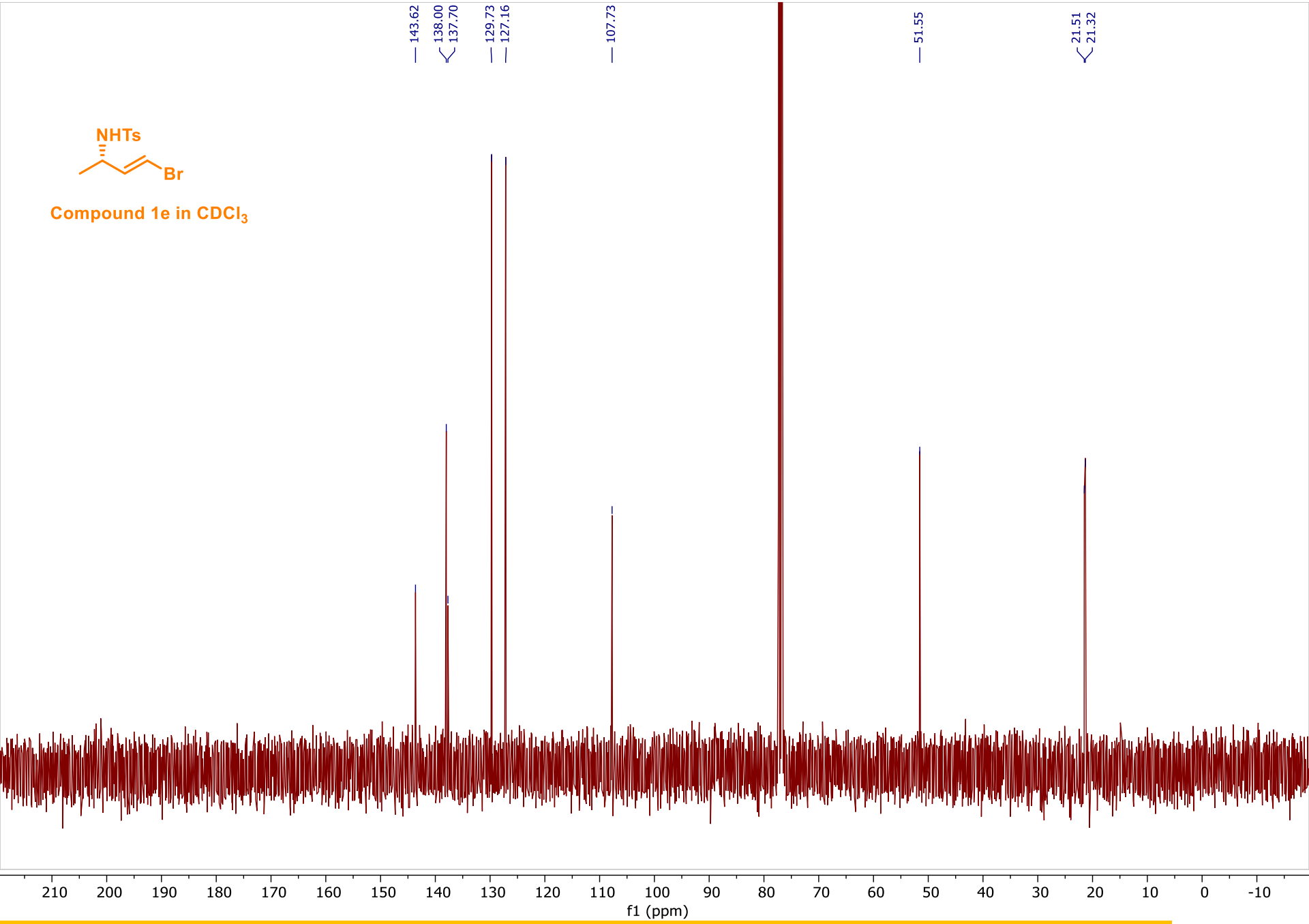

7.39
7.39
7.38
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.26
6.20
6.19
6.16
5.14
4.96
4.87
4.78
2.78
1.25
1.23
NMeCbz
Br
Compound 1c in CDCl3
4.97
1.93
2.02
1.01
3.00
3.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

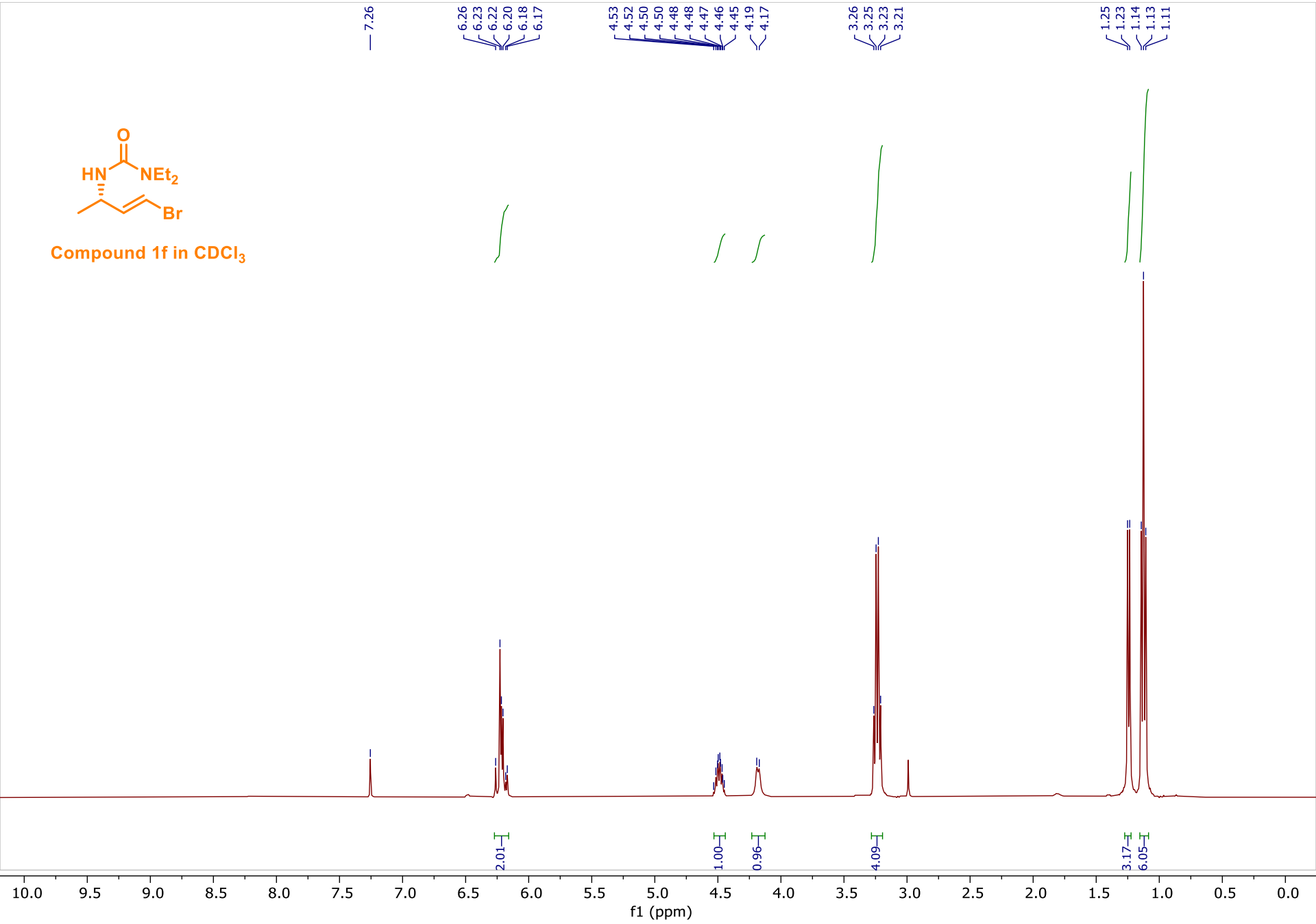

155.92
137.45
136.70
128.51
128.03
127.87
107.68
67.27
52.50
28.41
16.58
NMeCbz
Br
Compound 1c in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

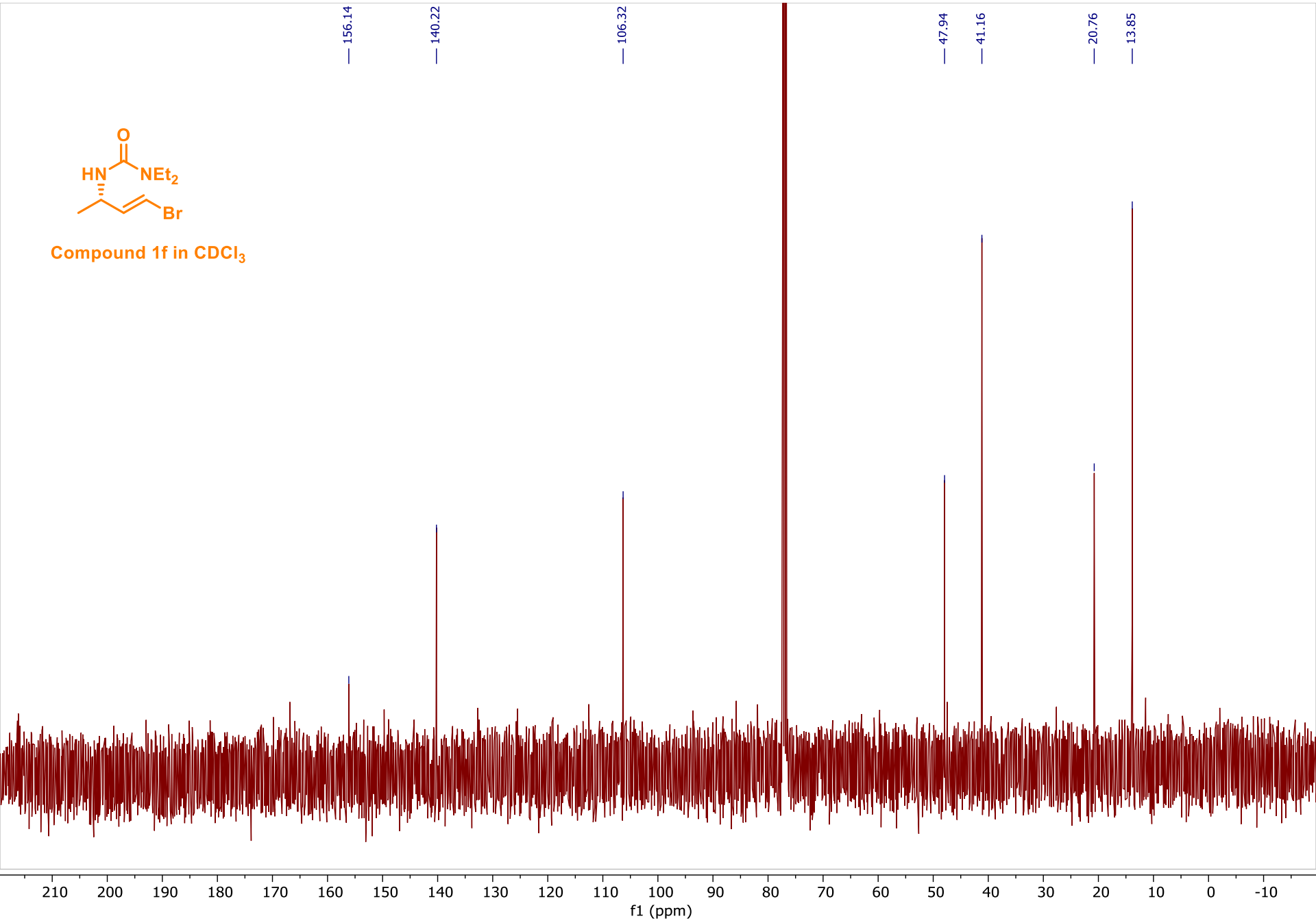

7.76 7.76 7.76 7.75 7.74 7.74 7.50 7.50 7.49 7.49 7.48 7.47 7.46 7.46 7.46 7.41 7.41 7.40 7.39 7.38 7.37 7.37 6.39 6.37 6.33 6.33 6.30 6.30 6.29 6.26 6.24 6.22 6.21
4.79 4.79 4.78 4.77 4.76 4.76 4.76 4.75 4.74 4.74 4.74 4.74 4.73 4.72 4.72 4.71 4.70
1.34 1.33
NHBz
Br
Compound 1d in $CDCl_3$
2.02 0.99 1.96 0.78 1.00 1.03 1.00 3.04
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)

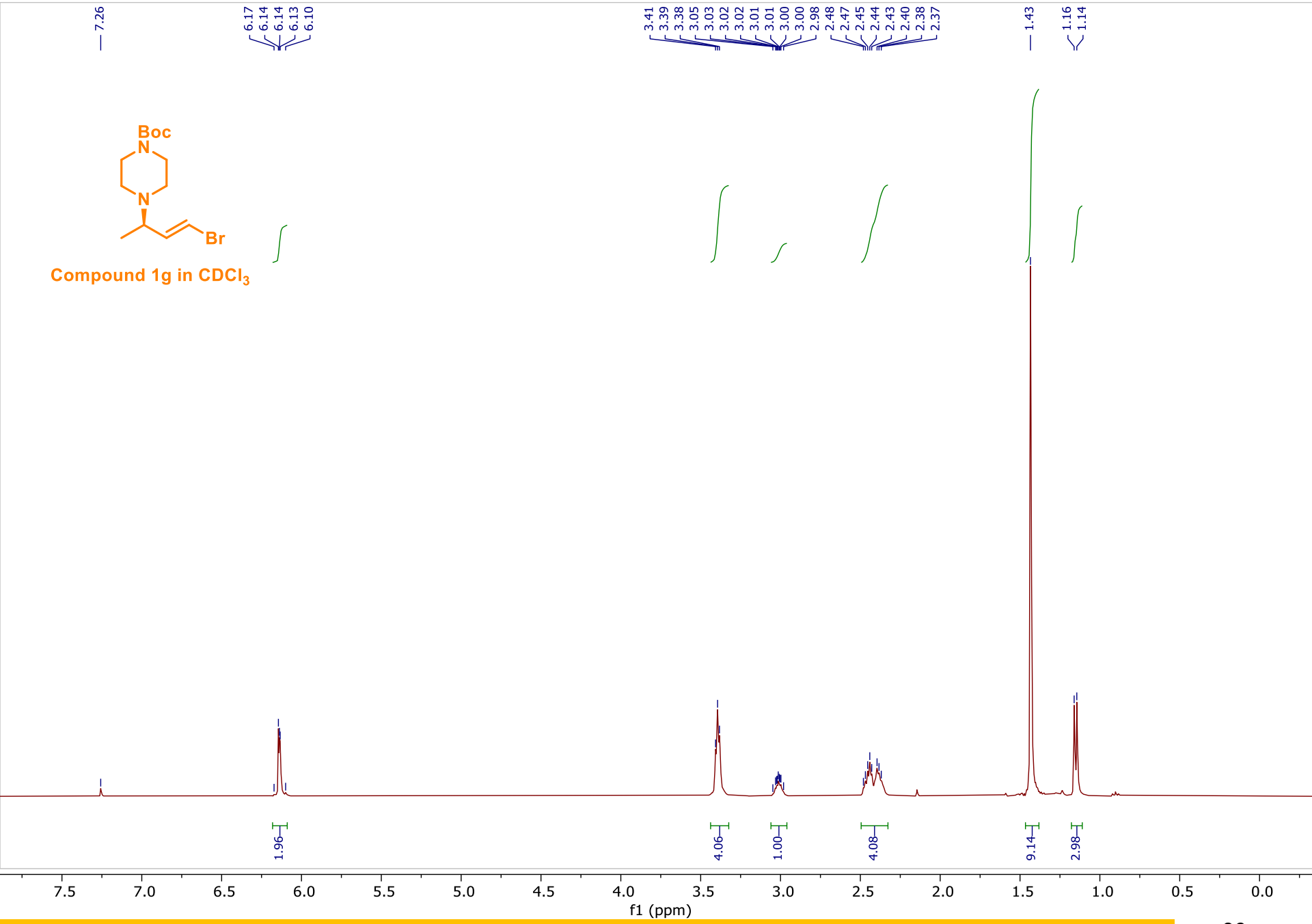

166.68
138.58
134.22
131.62
128.57
126.97
107.39
47.33
20.13
NHBz
Br
Compound 1d in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

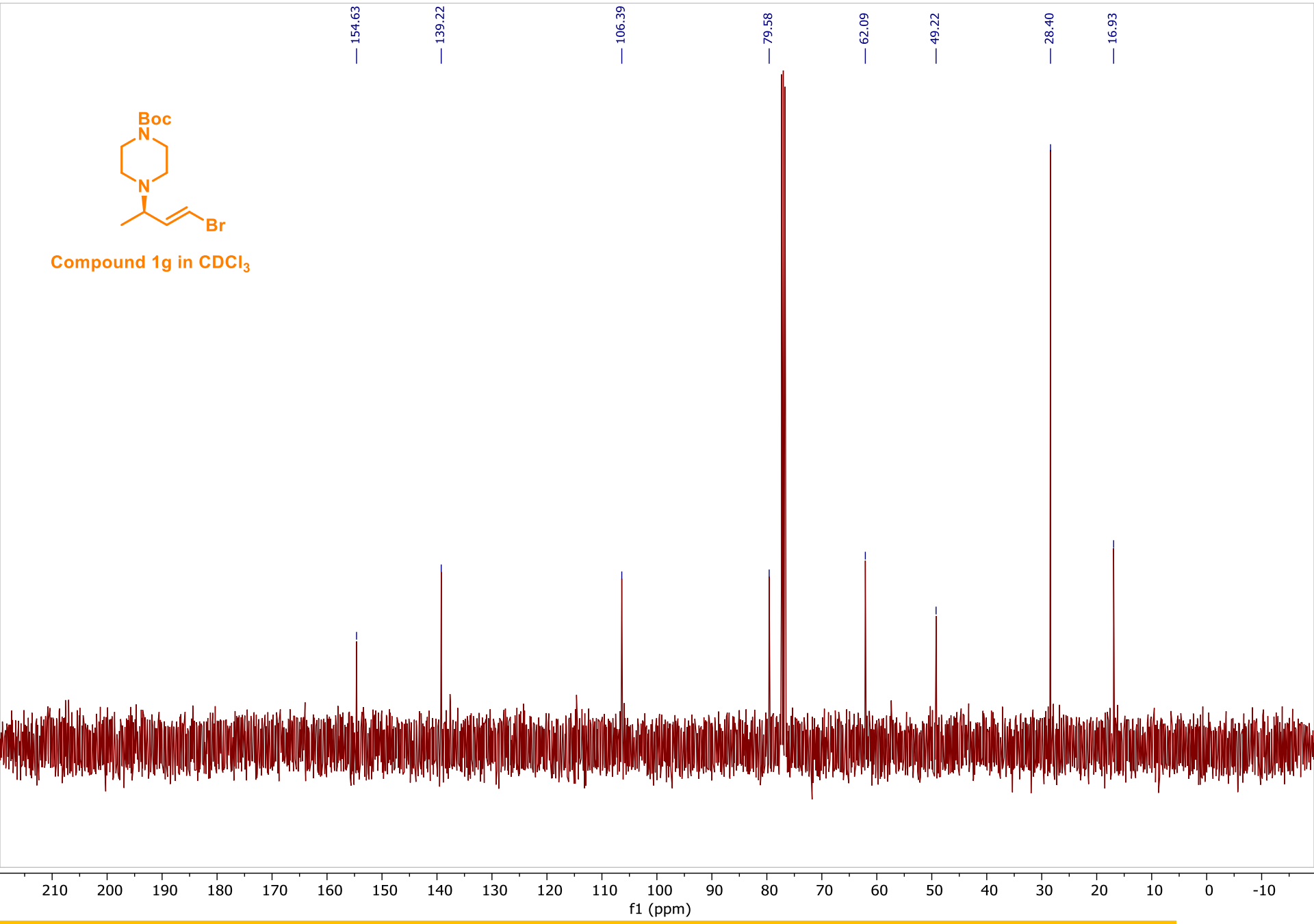

7.74
7.72
7.31
7.29
6.13
6.13
6.10
6.10
5.92
5.90
5.89
5.87
4.81
4.79
3.96
3.96
3.94
3.94
3.93
3.92
3.92
3.91
3.91
3.90
3.89
3.89
3.87
3.87
2.42
1.19
1.17
NHTs
Br
Compound 1e in CDCl3
2.02
2.02
1.00
1.00
0.94
1.04
3.12
3.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

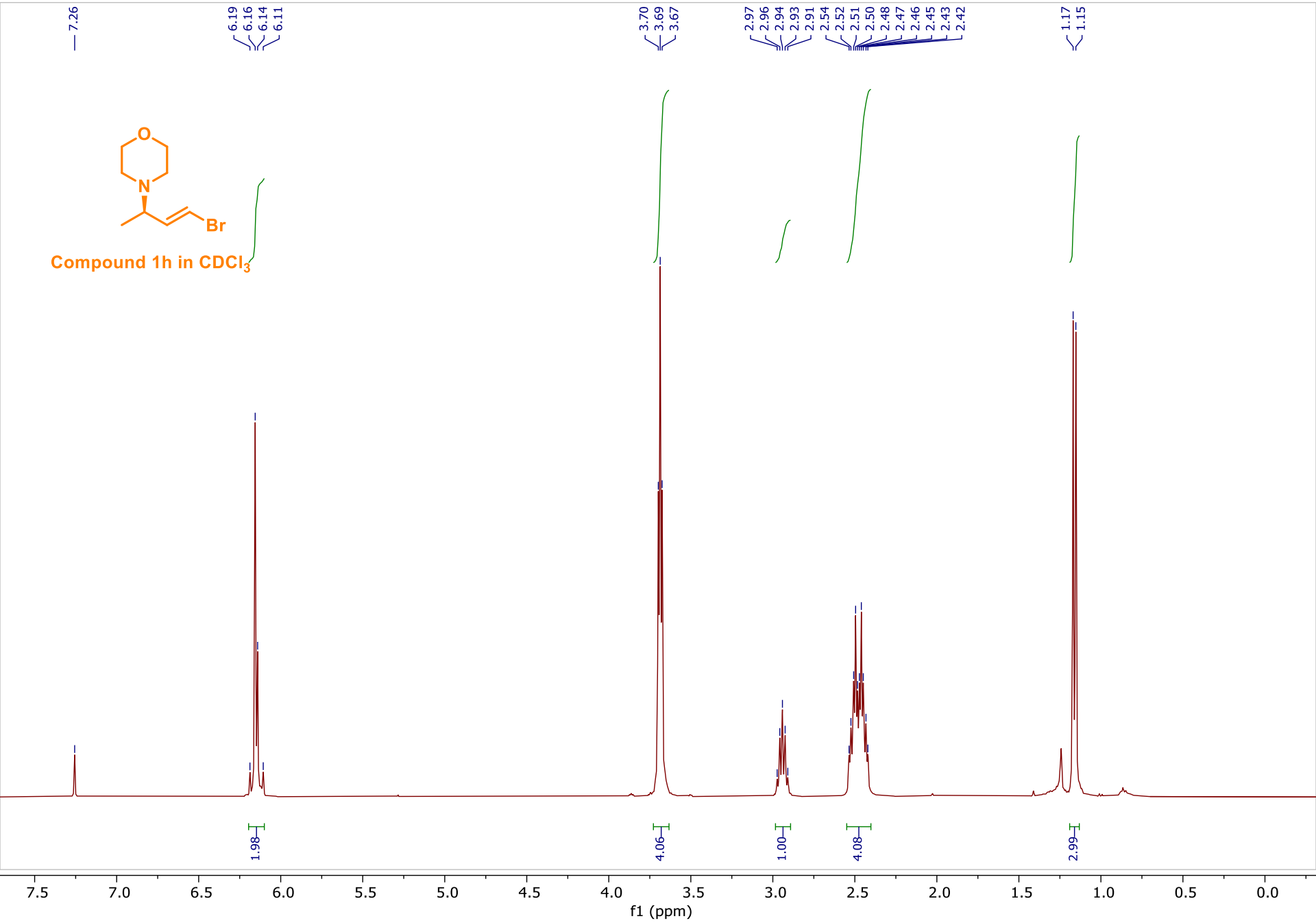

143.62
138.00
137.70
129.73
127.16
107.73
51.55
21.51
21.32
NHTs
Br
Compound 1e in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

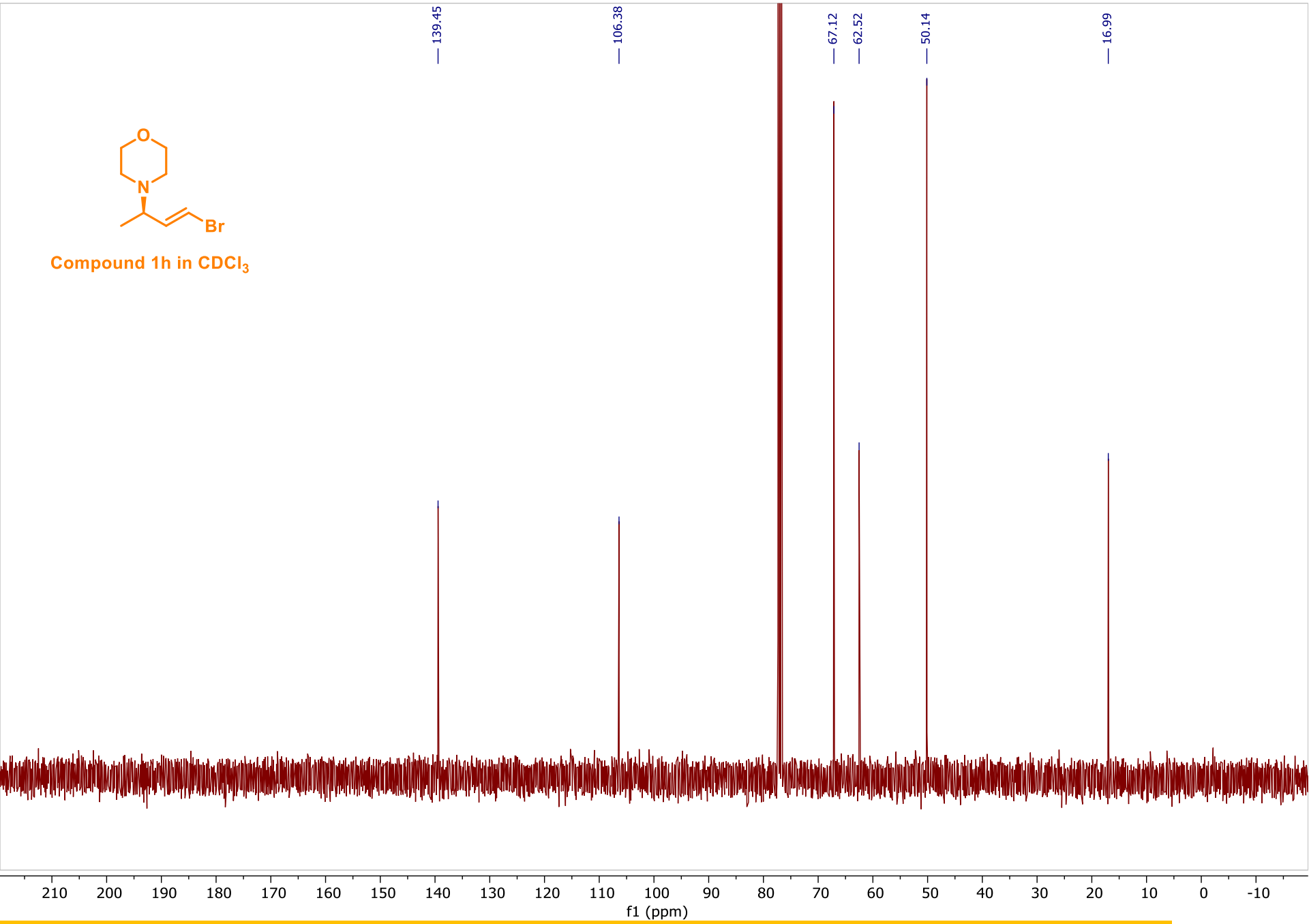

7.26
6.26
6.23
6.22
6.20
6.18
6.17
4.53
4.52
4.50
4.50
4.48
4.48
4.47
4.46
4.45
4.19
4.17
3.26
3.25
3.23
3.21
1.25
1.23
1.14
1.13
1.11
HN
NEt2
Br
Compound 1f in CDCl3
2.01
1.00
0.96
4.09
3.17
6.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

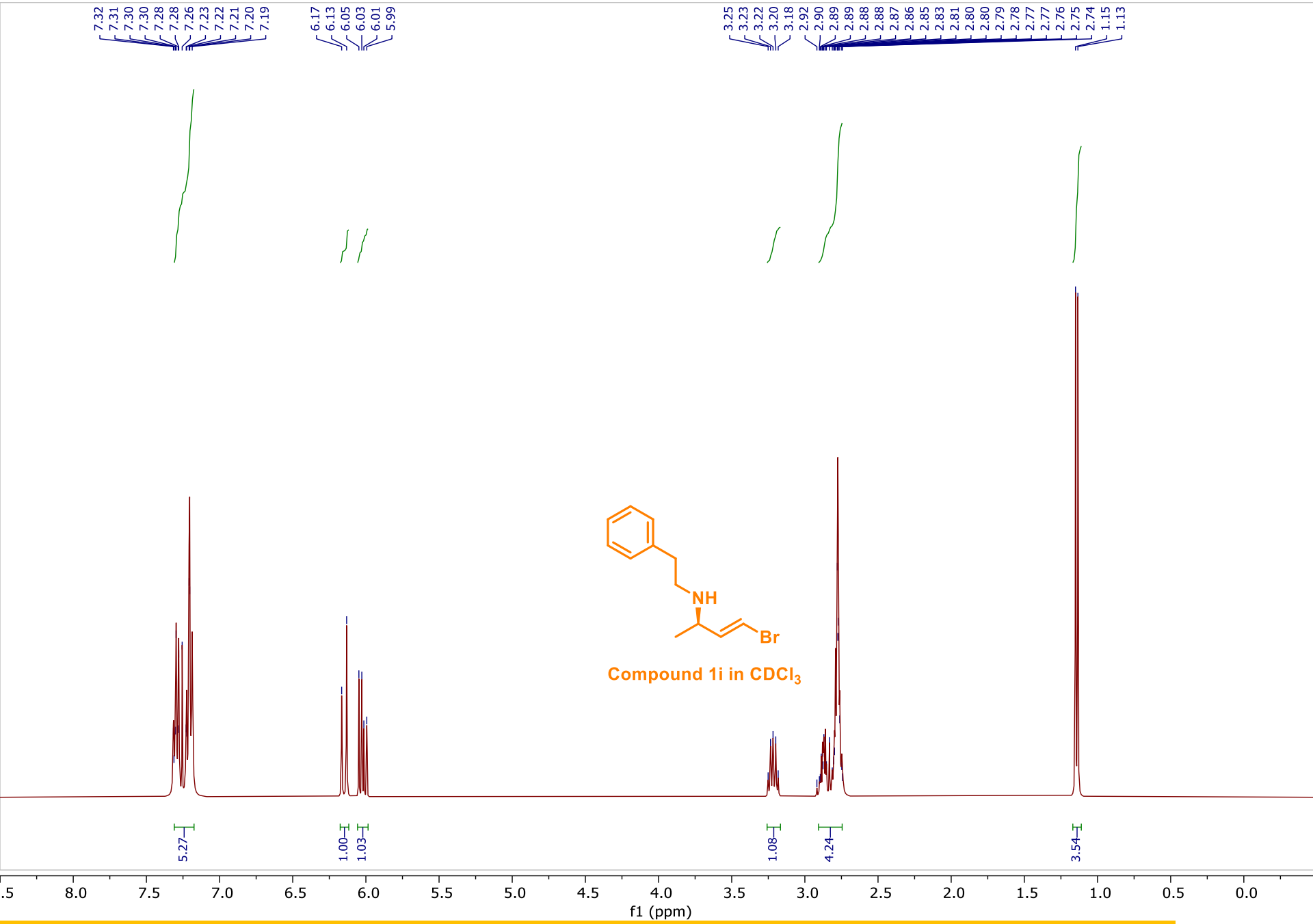

156.14
140.22
106.32
47.94
41.16
20.76
13.85
HN
NEt2
O
Br
Compound 1f in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

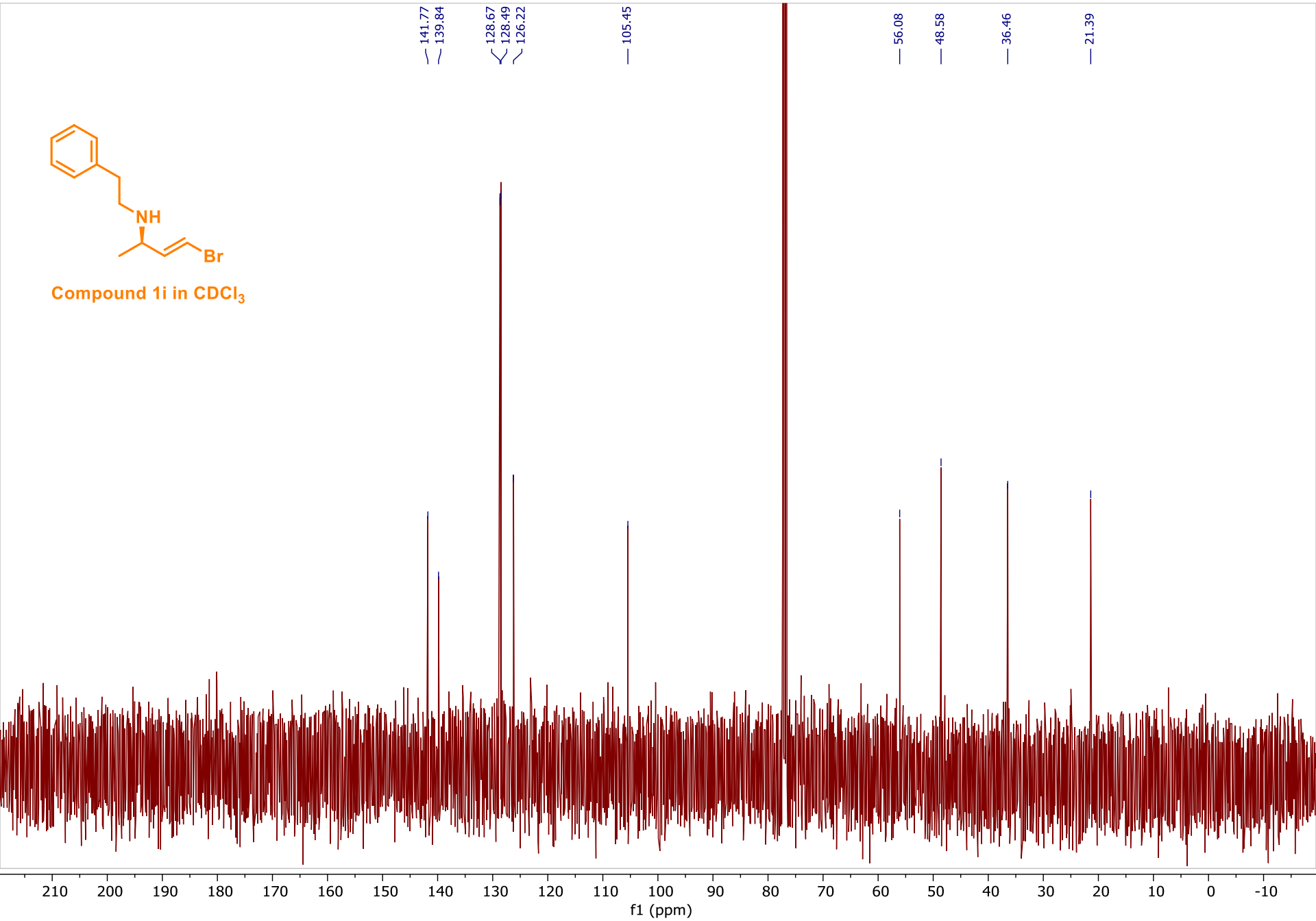

7.26
6.17
6.14
6.14
6.13
6.10
3.41
3.39
3.38
3.05
3.03
3.02
3.02
3.01
3.01
3.00
3.00
2.98
2.48
2.47
2.45
2.44
2.43
2.40
2.38
2.37
1.43
1.16
1.14
Boc
N
N
Br
Compound 1g in CDCl3
1.96
4.06
1.00
4.08
9.14
2.98
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

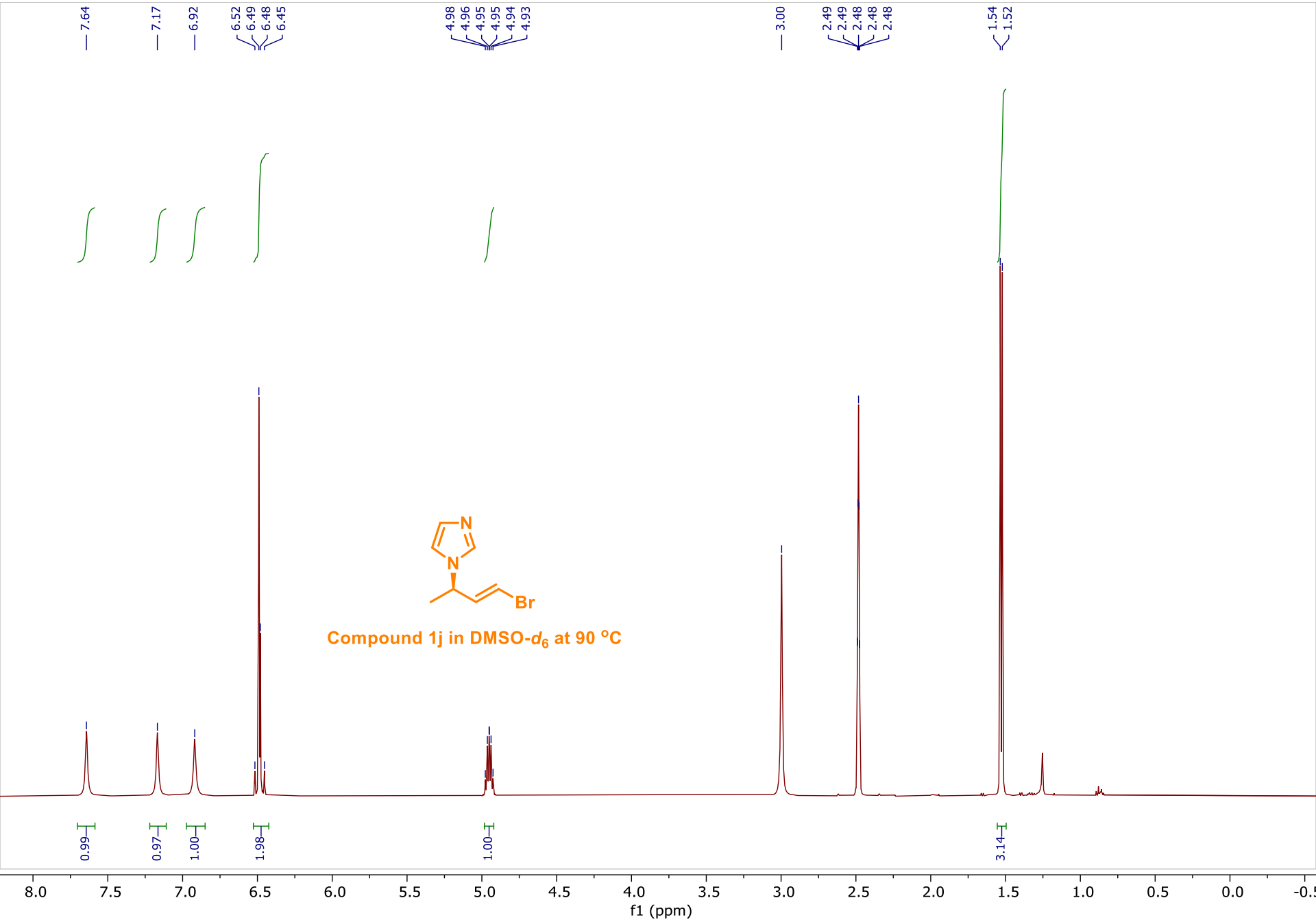

154.63
139.22
106.39
79.58
62.09
49.22
28.40
16.93
Boc
N
N
Br
Compound 1g in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

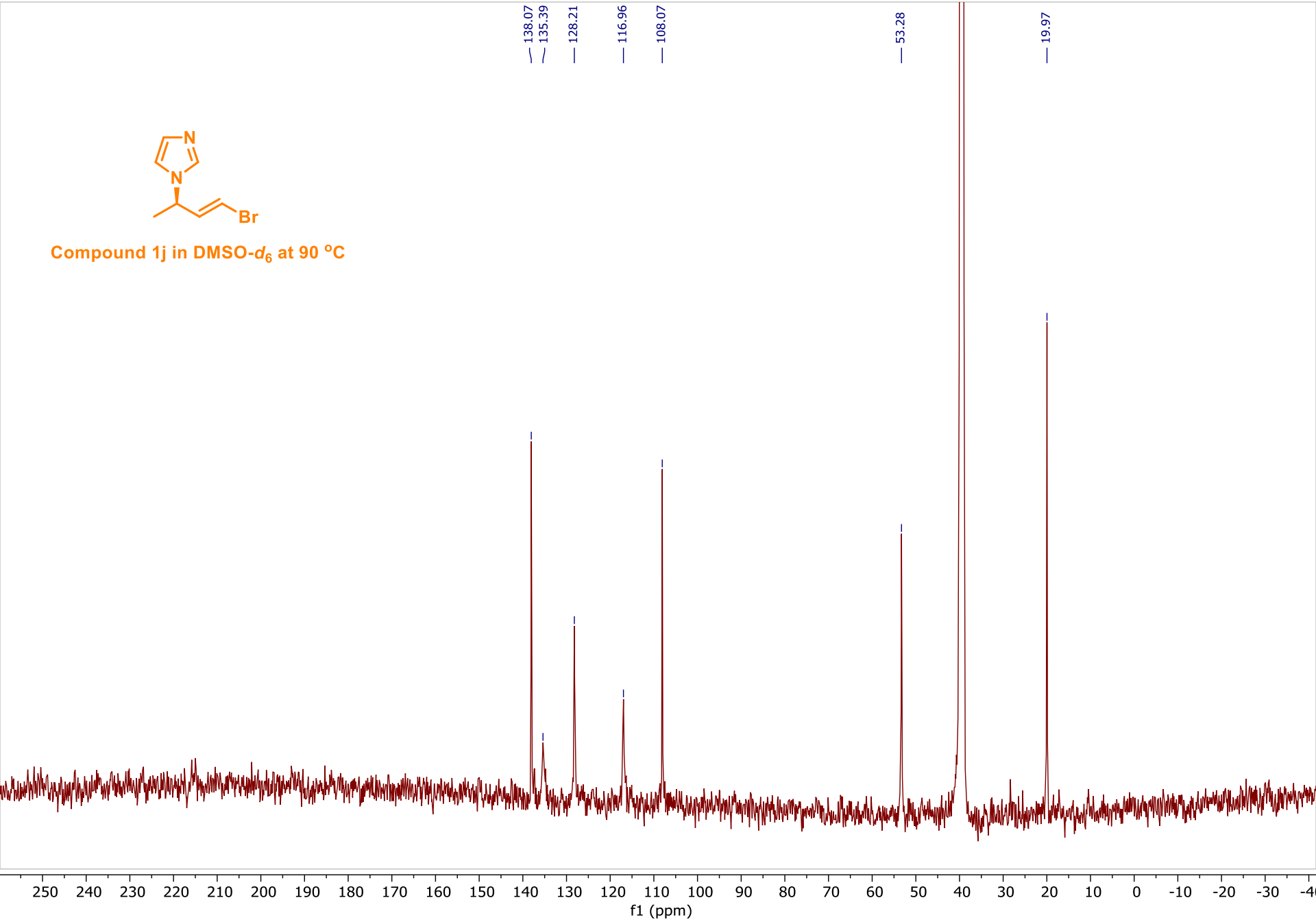

7.26
6.19
6.16
6.14
6.11
3.70
3.69
3.67
2.97
2.96
2.94
2.93
2.91
2.54
2.52
2.51
2.50
2.48
2.47
2.46
2.45
2.43
2.42
1.17
1.15
O
N
Br
Compound 1h in CDCl3
1.98
4.06
1.00
4.08
2.99
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

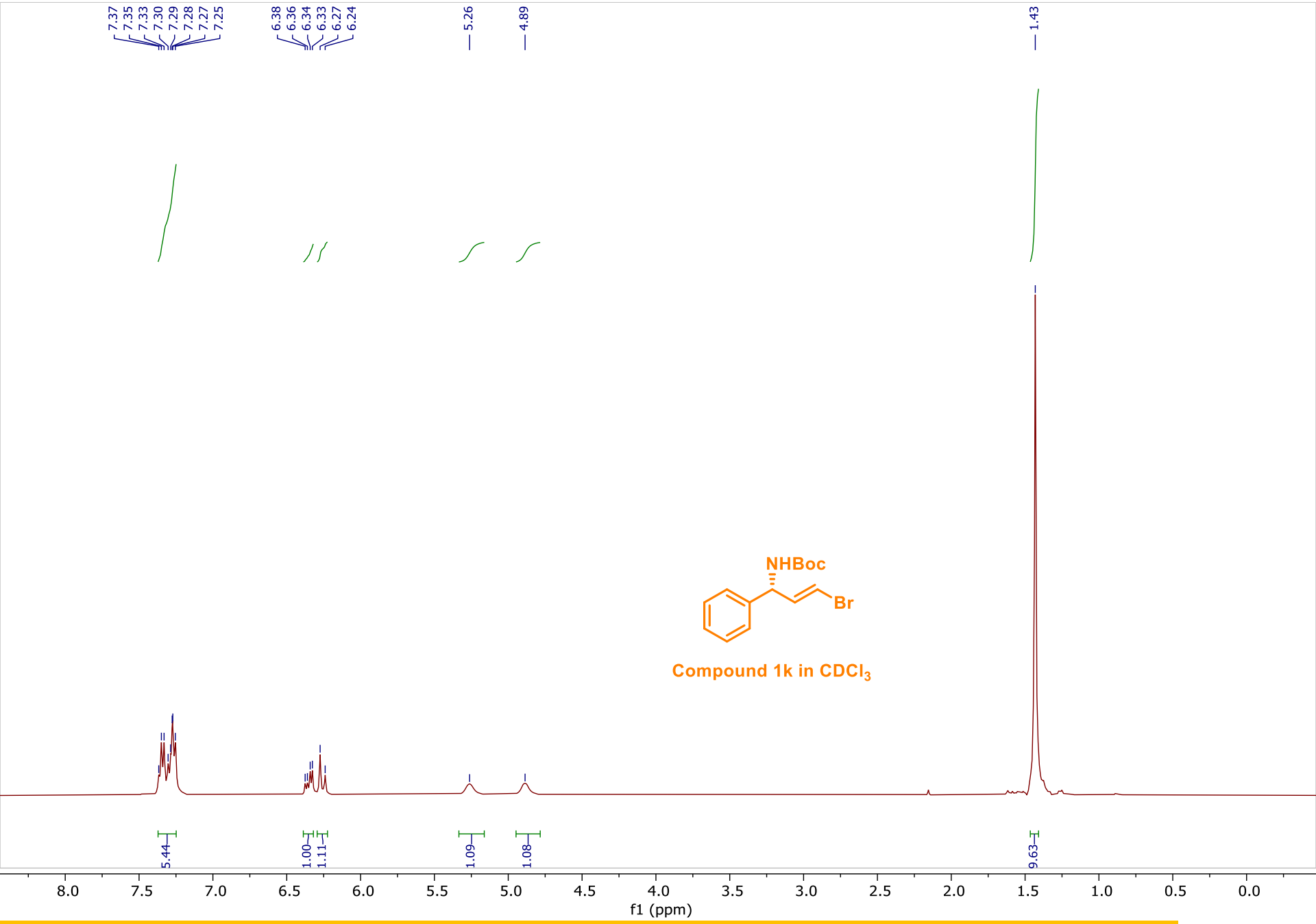

139.45
106.38
67.12
62.52
50.14
16.99
O
N
Br
Compound 1h in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

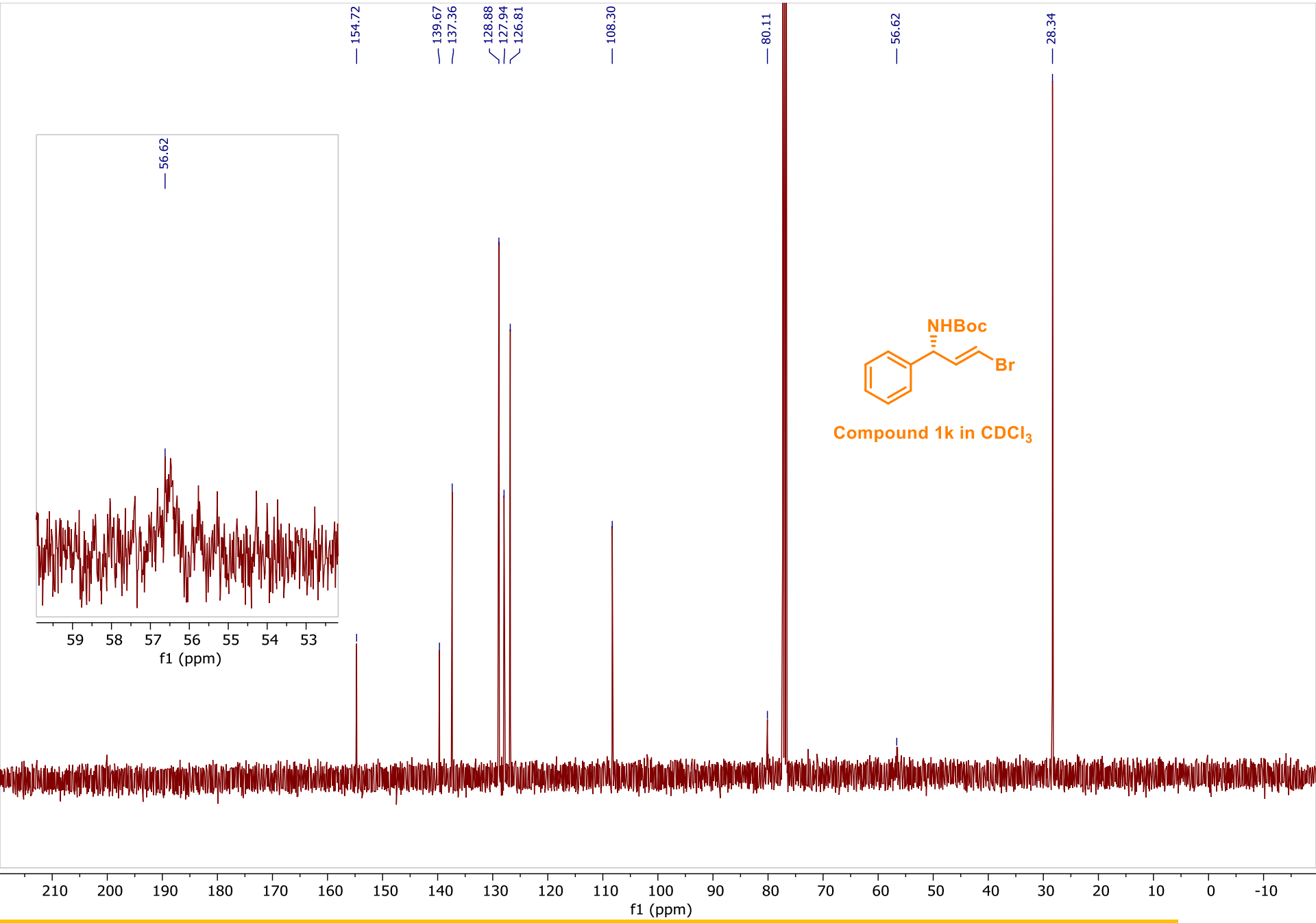

7.32
7.31
7.30
7.30
7.28
7.28
7.26
7.23
7.22
7.21
7.20
7.19
6.17
6.13
6.05
6.03
6.01
5.99
3.25
3.23
3.22
3.20
3.18
2.92
2.90
2.89
2.89
2.88
2.88
2.87
2.86
2.85
2.83
2.81
2.80
2.80
2.79
2.78
2.77
2.77
2.76
2.75
2.74
1.15
1.13
NH
Br
Compound 1i in CDCl3
5.27
1.00
1.03
1.08
4.24
3.54
8.0
7.5
7.0
6.5
6.0
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)

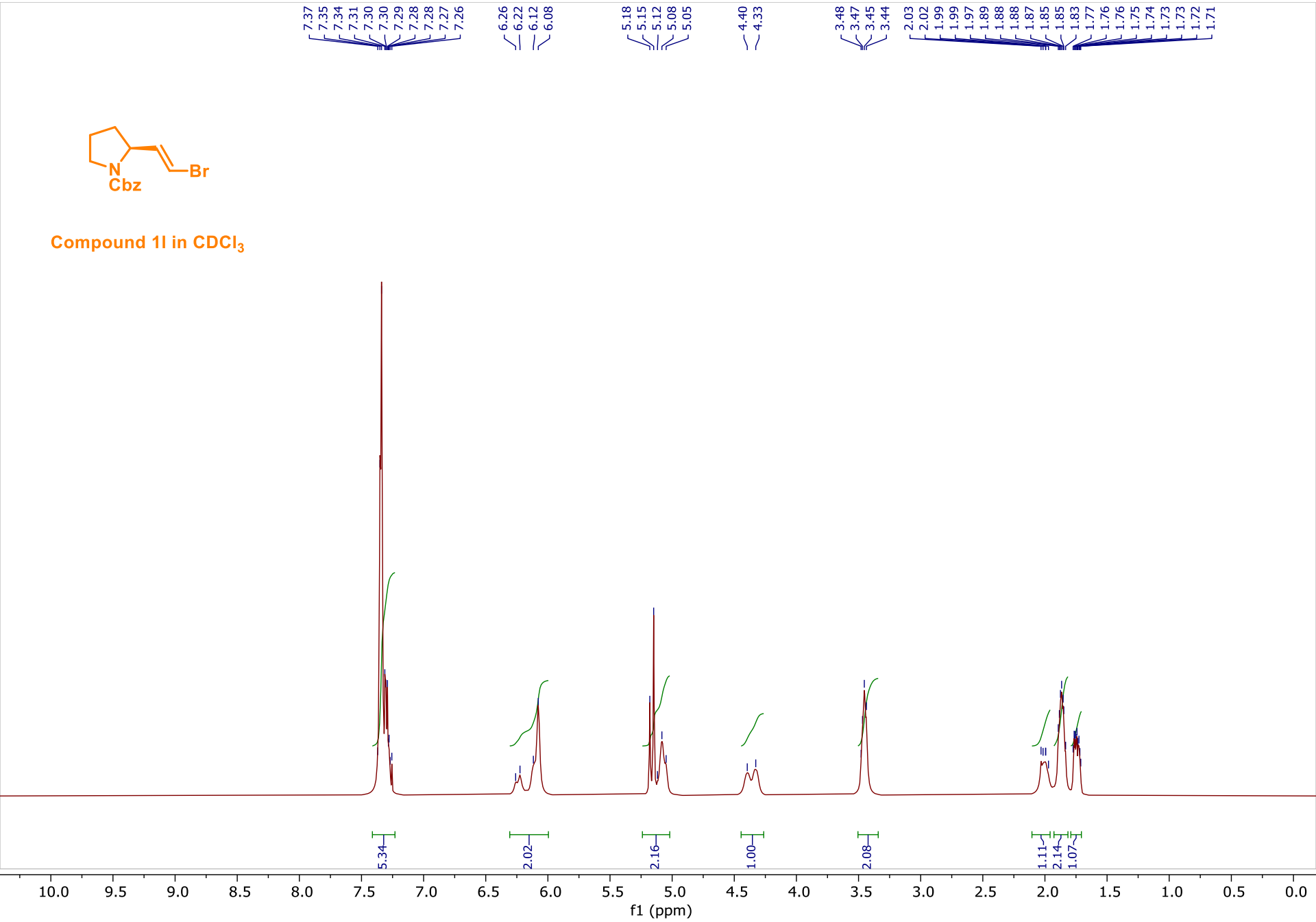

141.77
139.84
128.67
128.49
126.22
105.45
56.08
48.58
36.46
21.39
NH
Br
Compound 1i in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

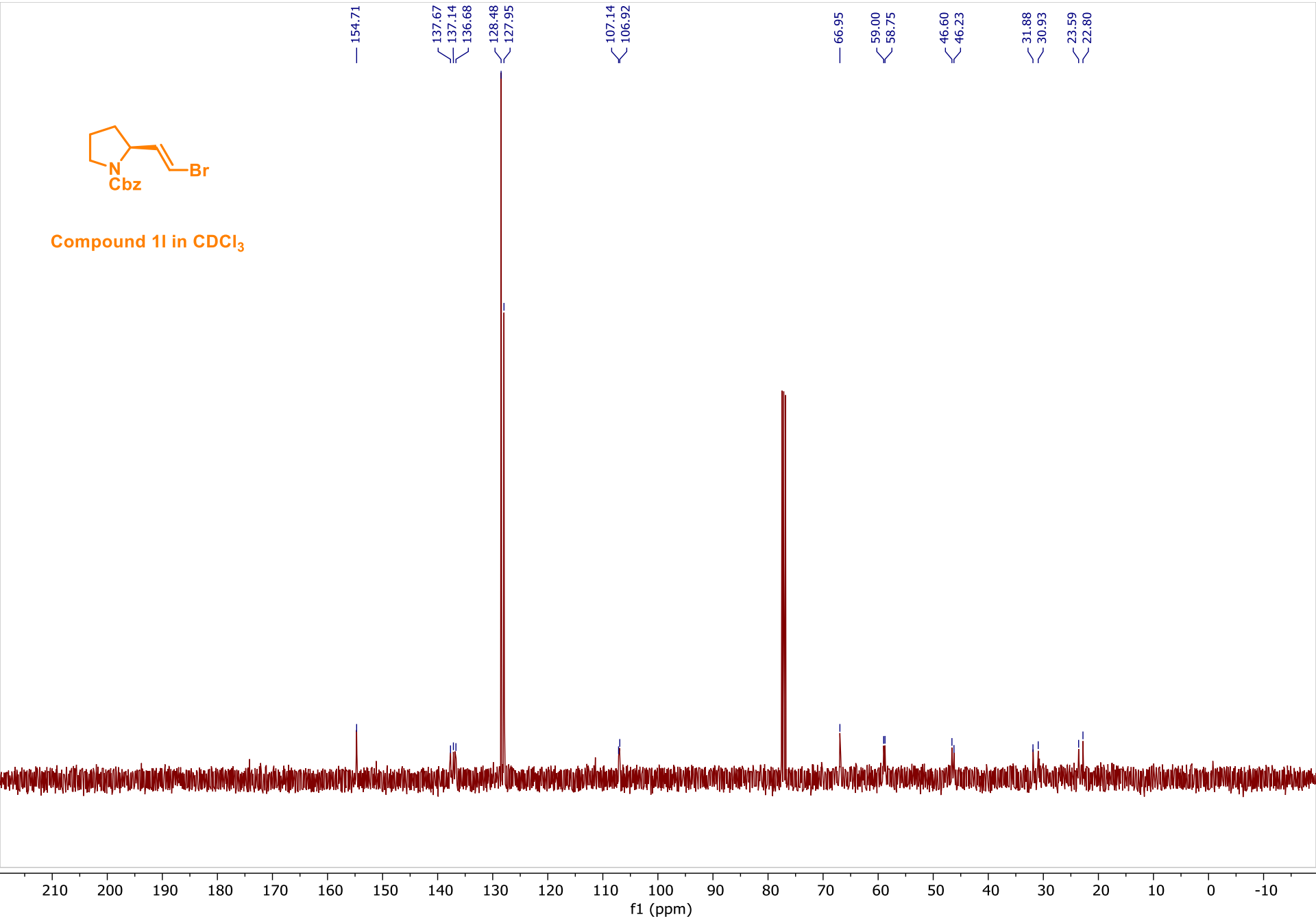

7.64
7.17
6.92
6.52
6.49
6.48
6.45
4.98
4.96
4.95
4.95
4.94
4.93
3.00
2.49
2.49
2.48
2.48
2.48
1.54
1.52
N
N
Br
Compound 1j in DMSO-d_6 at 90 °C
0.99
0.97
1.00
1.98
1.00
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

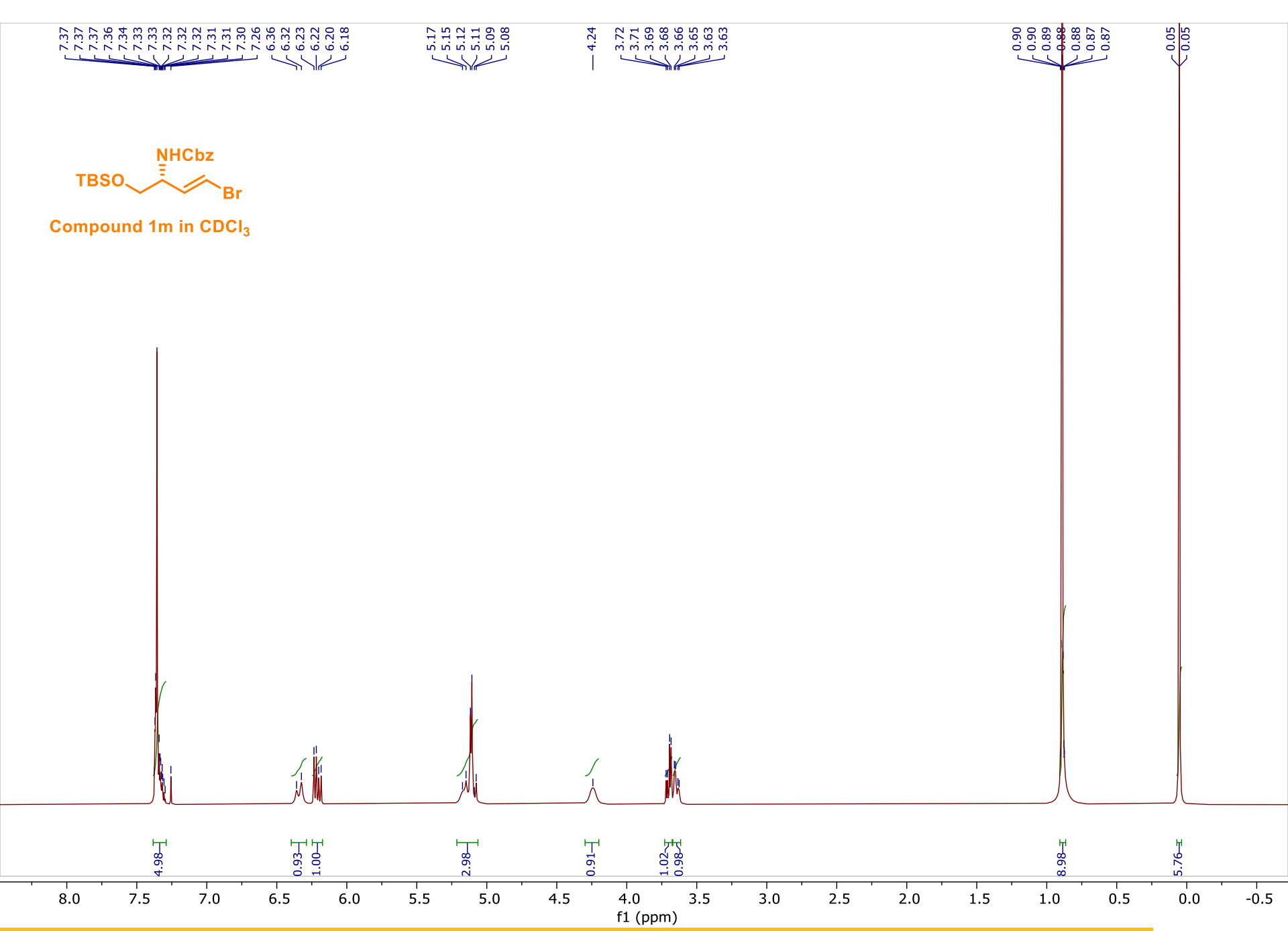

138.07
135.39
128.21
116.96
108.07
53.28
19.97
N
N
Br
Compound 1j in DMSO-d_6 at 90 °C
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

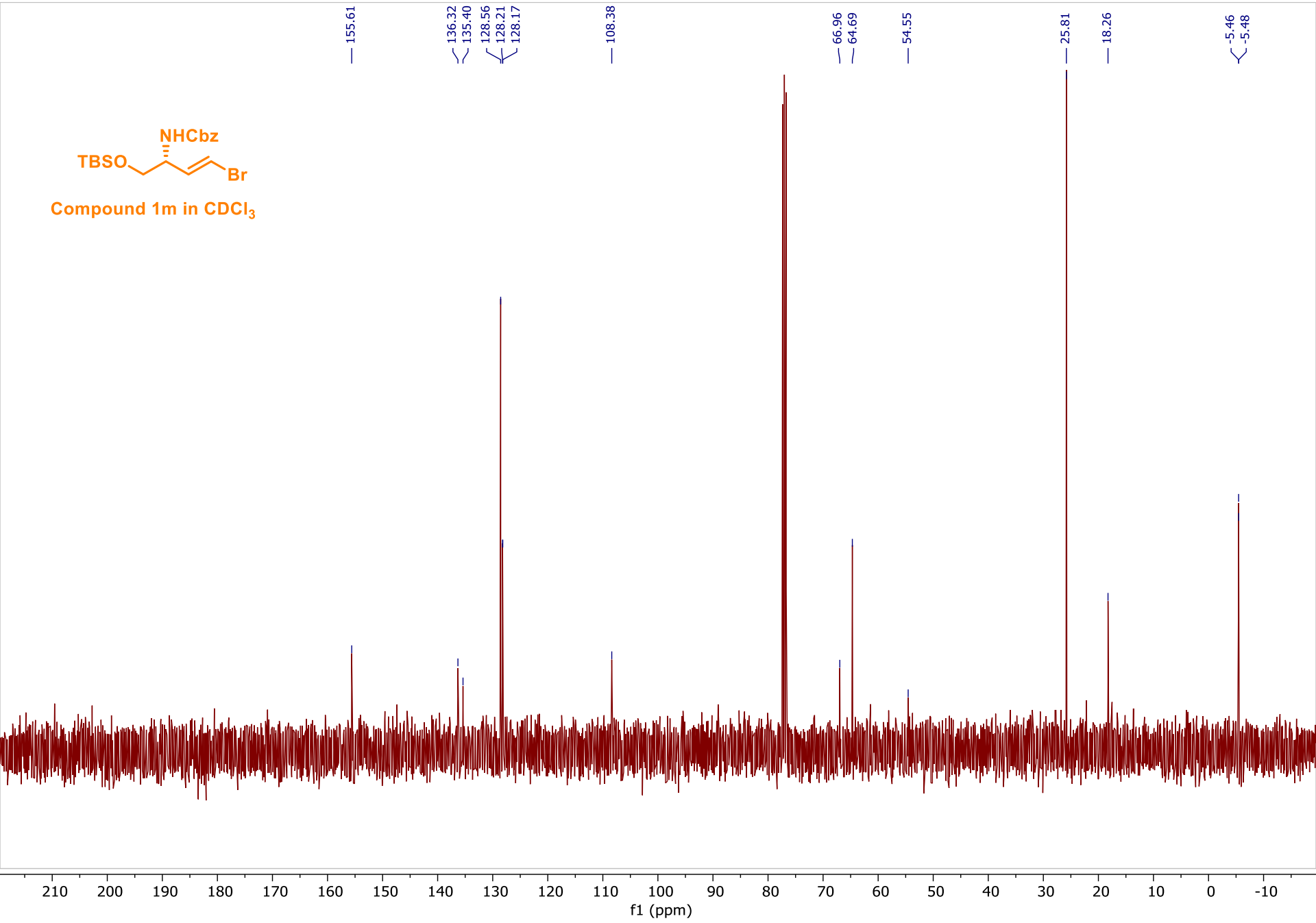

7.37
7.35
7.33
7.30
7.29
7.28
7.27
7.25
6.38
6.36
6.34
6.33
6.27
6.24
5.26
4.89
1.43
NHBoc
Br
Compound 1k in CDCl3
5.44
1.00
1.11
1.09
1.08
9.63
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

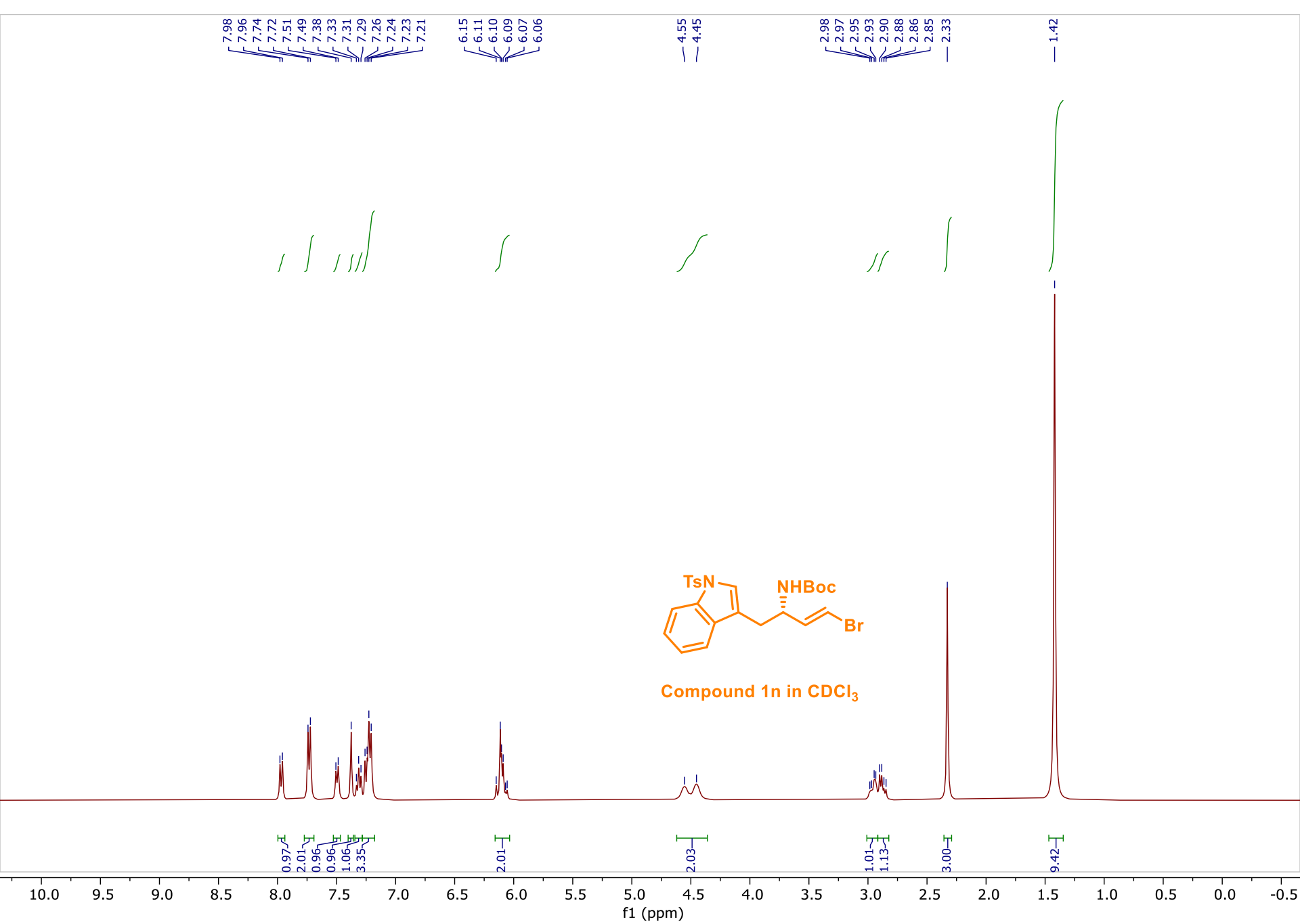

154.72
139.67
137.36
128.88
127.94
126.81
108.30
80.11
56.62
28.34
56.62
59 58 57 56 55 54 53
f1 (ppm)
NHBoc
Br
Compound 1k in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

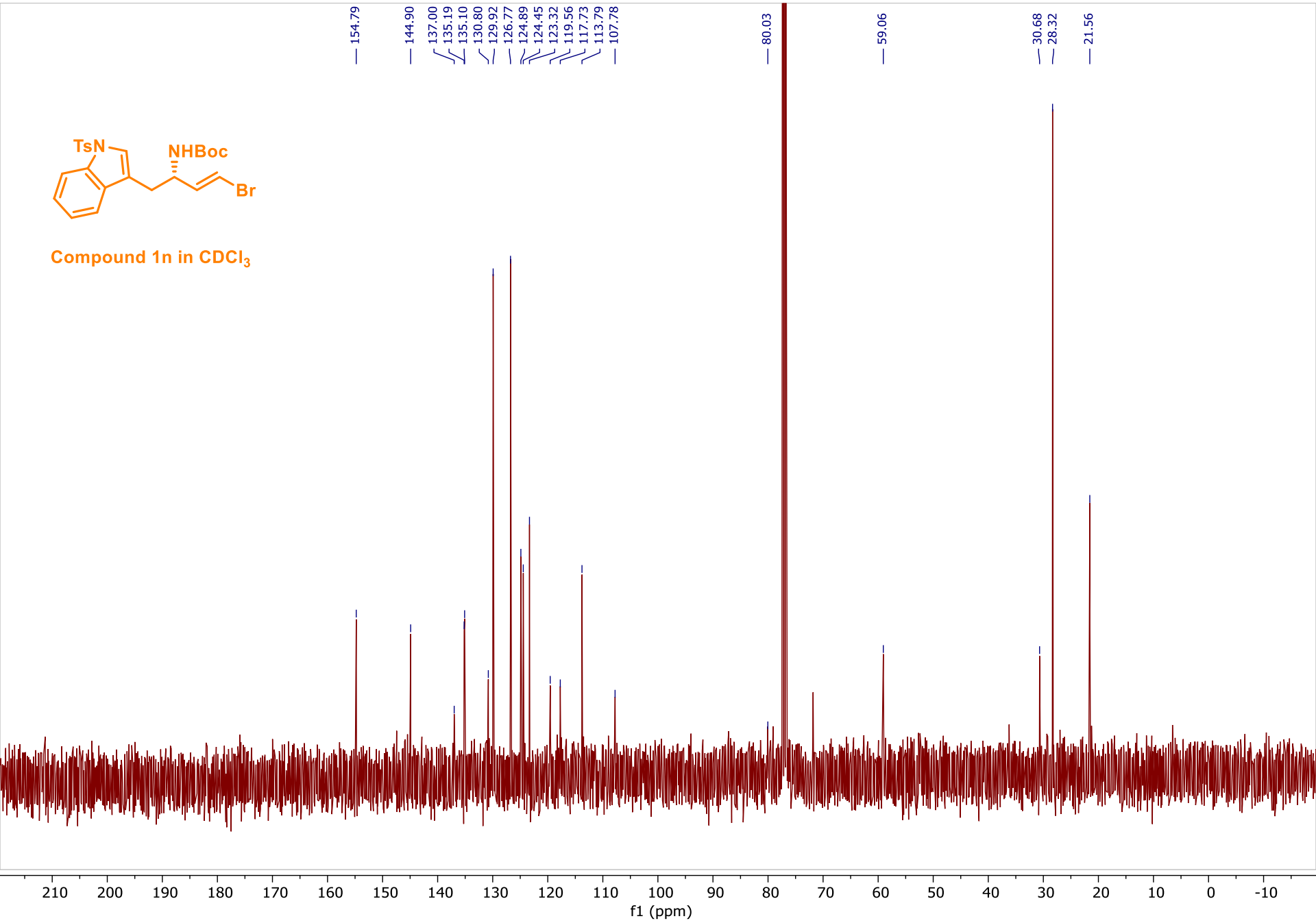

7.37 7.35 7.34 7.31 7.30 7.30 7.29 7.28 7.28 7.27 7.26
6.26 6.22 6.12 6.08
5.18 5.15 5.12 5.08 5.05
4.40 4.33
3.48 3.47 3.45 3.44
2.03 2.02 1.99 1.99 1.97 1.89 1.88 1.88 1.87 1.85 1.85 1.83 1.77 1.76 1.76 1.75 1.74 1.73 1.73 1.72 1.71
N
Cbz
Br
Compound 1l in CDCl3
5.34
2.02
2.16
1.00
2.08
1.11
2.14
1.07
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
f1 (ppm)

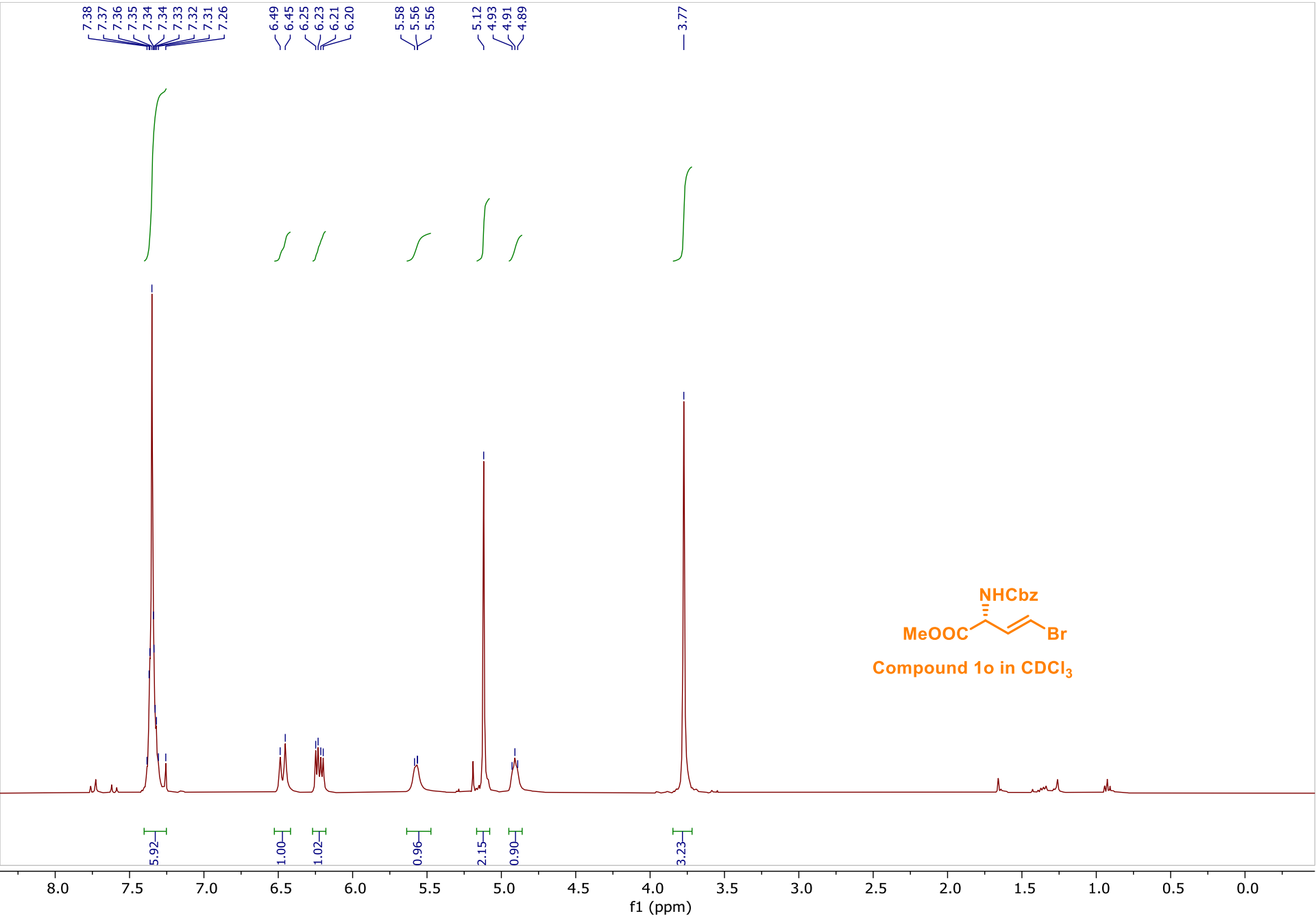

154.71
137.67
137.14
136.68
128.48
127.95
107.14
106.92
66.95
59.00
58.75
46.60
46.23
31.88
30.93
23.59
22.80
N
Cbz
Br
Compound 1l in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

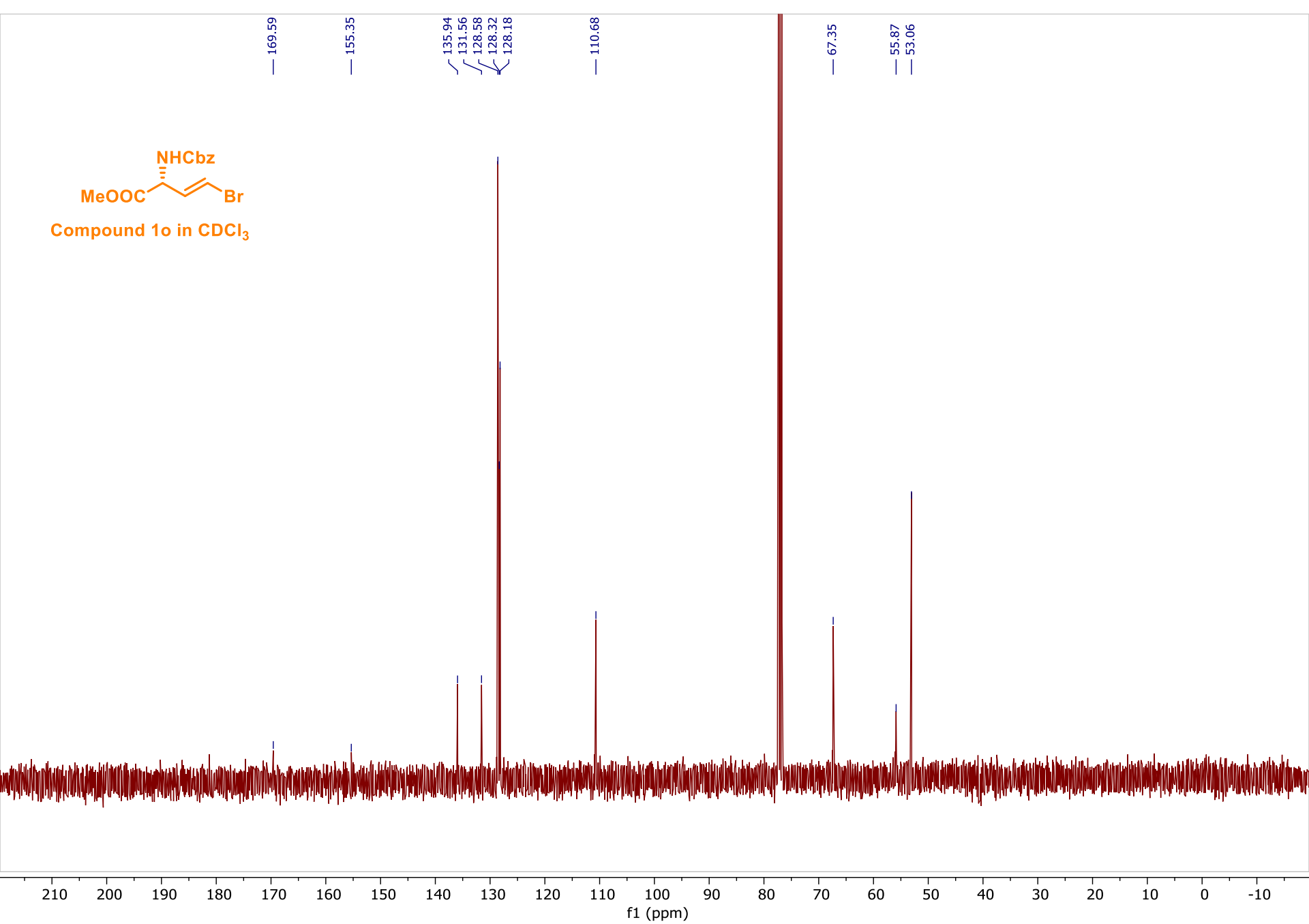

NHCbz
TBSO
Br
Compound 1m in CDCl3
7.37 7.37 7.37 7.36 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.26
6.36 6.32 6.23 6.22 6.20 6.18
5.17 5.15 5.12 5.11 5.09 5.08
4.24
3.72 3.71 3.69 3.68 3.66 3.65 3.63 3.63
0.90 0.90 0.89 0.88 0.88 0.87 0.87
0.05 0.05
4.98 0.93 1.00 2.98 0.91 1.02 0.98 8.98 5.76
8.0 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)

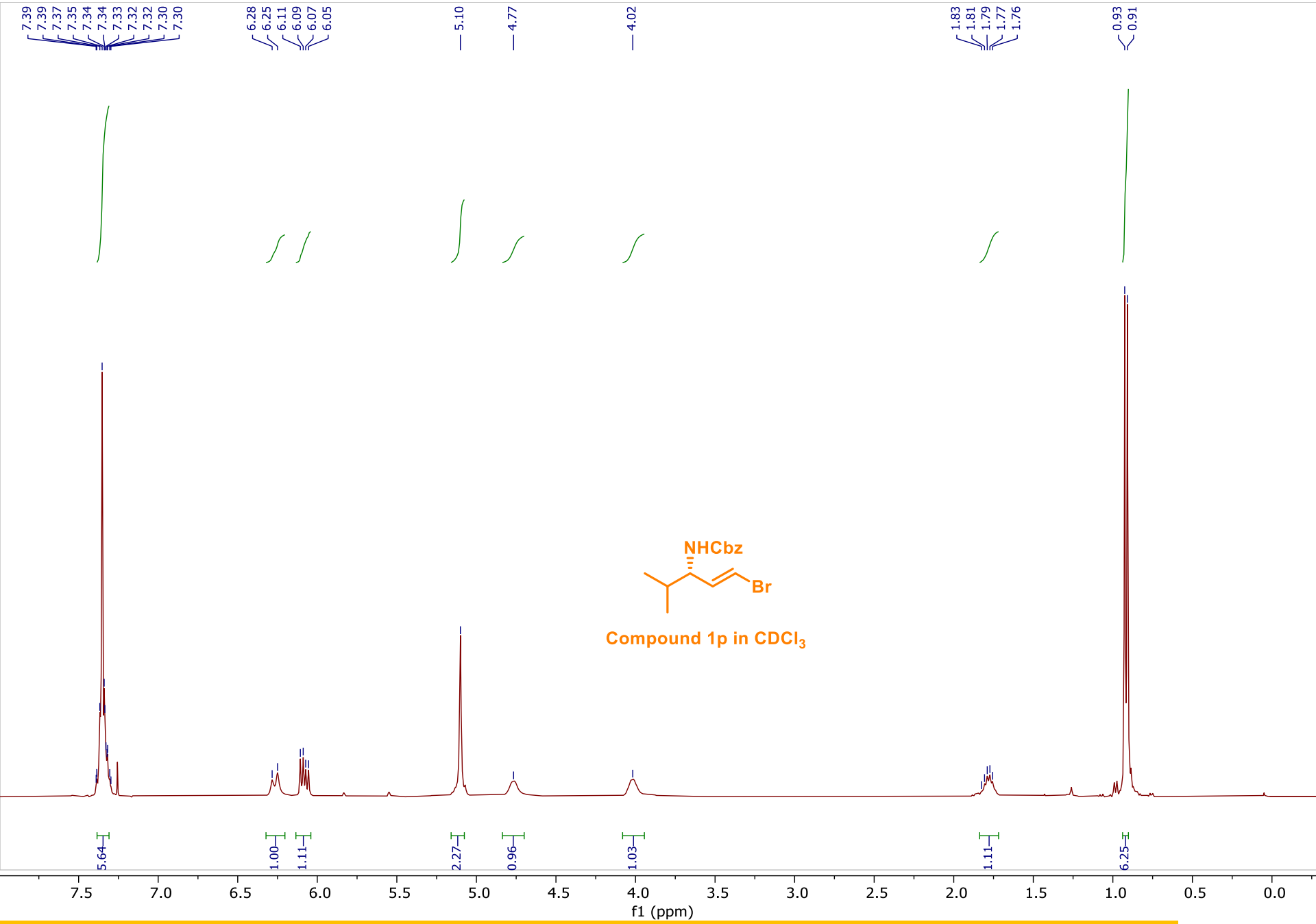

155.61
136.32
135.40
128.56
128.21
128.17
108.38
66.96
64.69
54.55
25.81
18.26
-5.46
-5.48
NHCbz
TBSO
Br
Compound 1m in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

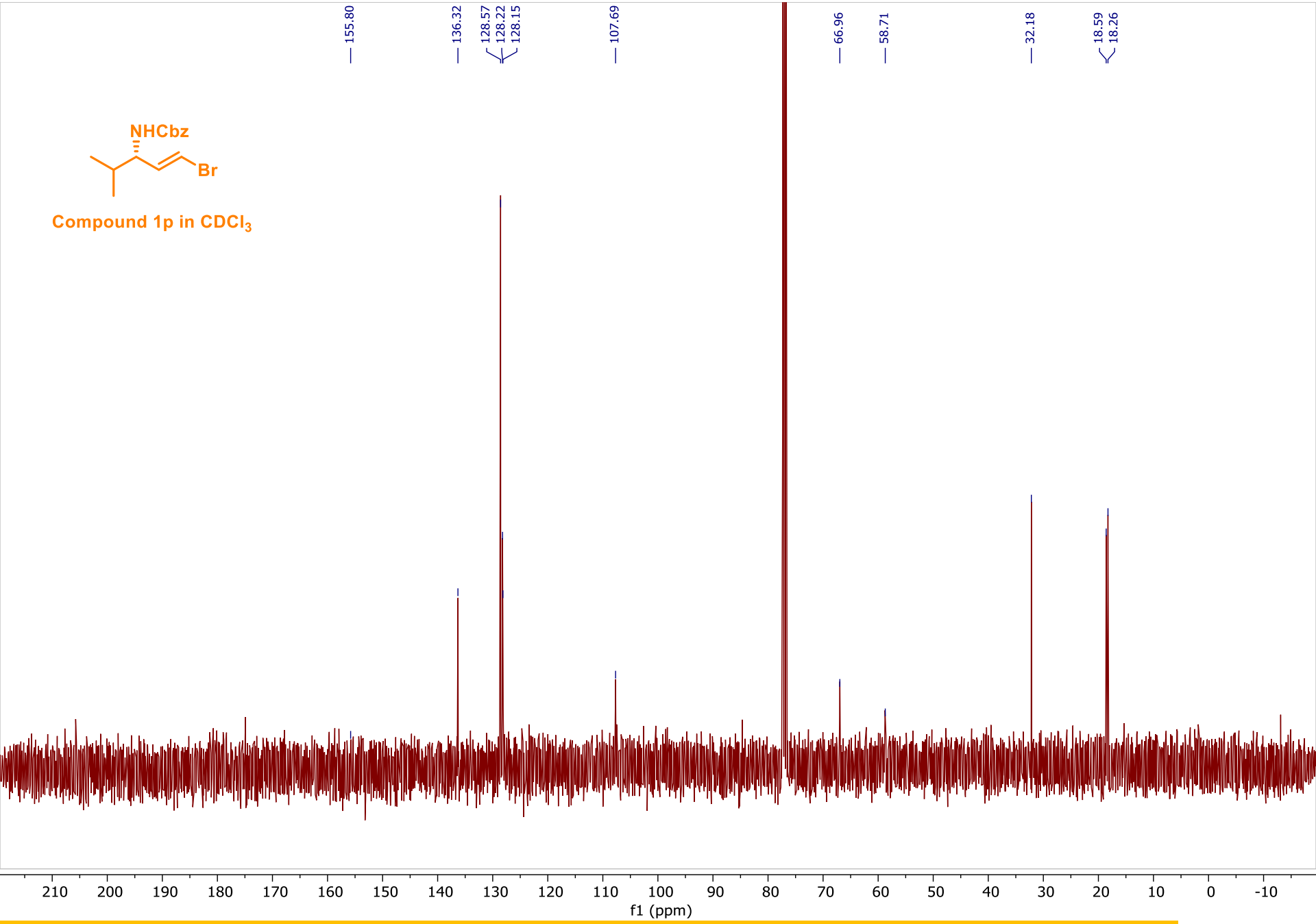

7.98
7.96
7.74
7.72
7.51
7.49
7.38
7.33
7.31
7.29
7.26
7.24
7.23
7.21
6.15
6.11
6.10
6.09
6.07
6.06
4.55
4.45
2.98
2.97
2.95
2.93
2.90
2.88
2.86
2.85
2.33
1.42
TsN
NHBoc
Br
Compound 1n in CDCl3
0.97
2.01
0.96
0.96
1.06
3.35
2.01
2.03
1.01
1.13
3.00
9.42
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

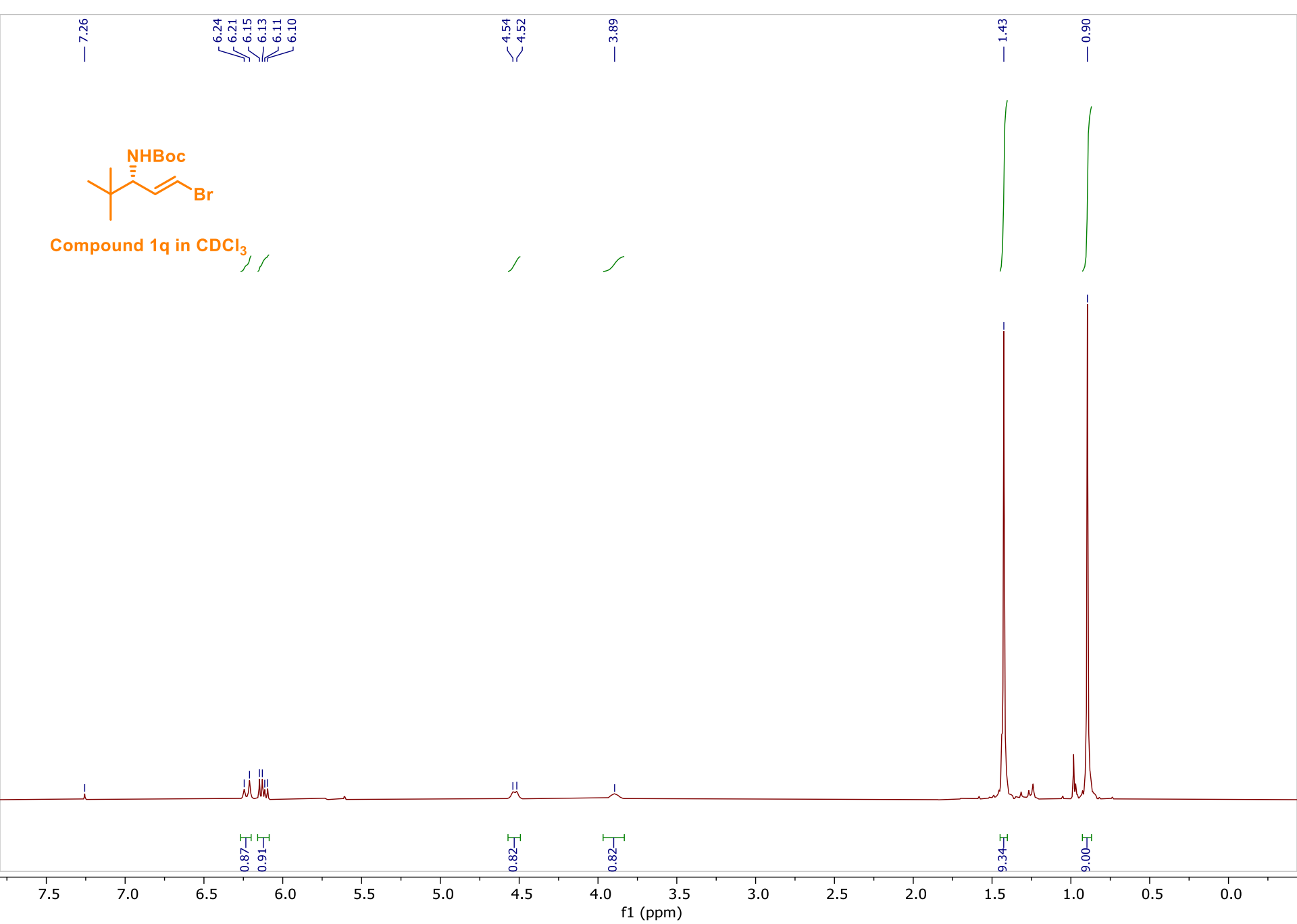

154.79
144.90
137.00
135.19
135.10
130.80
129.92
126.77
124.89
124.45
123.32
119.56
117.73
113.79
107.78
80.03
59.06
30.68
28.32
21.56
TsN
NHBoc
Br
Compound 1n in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

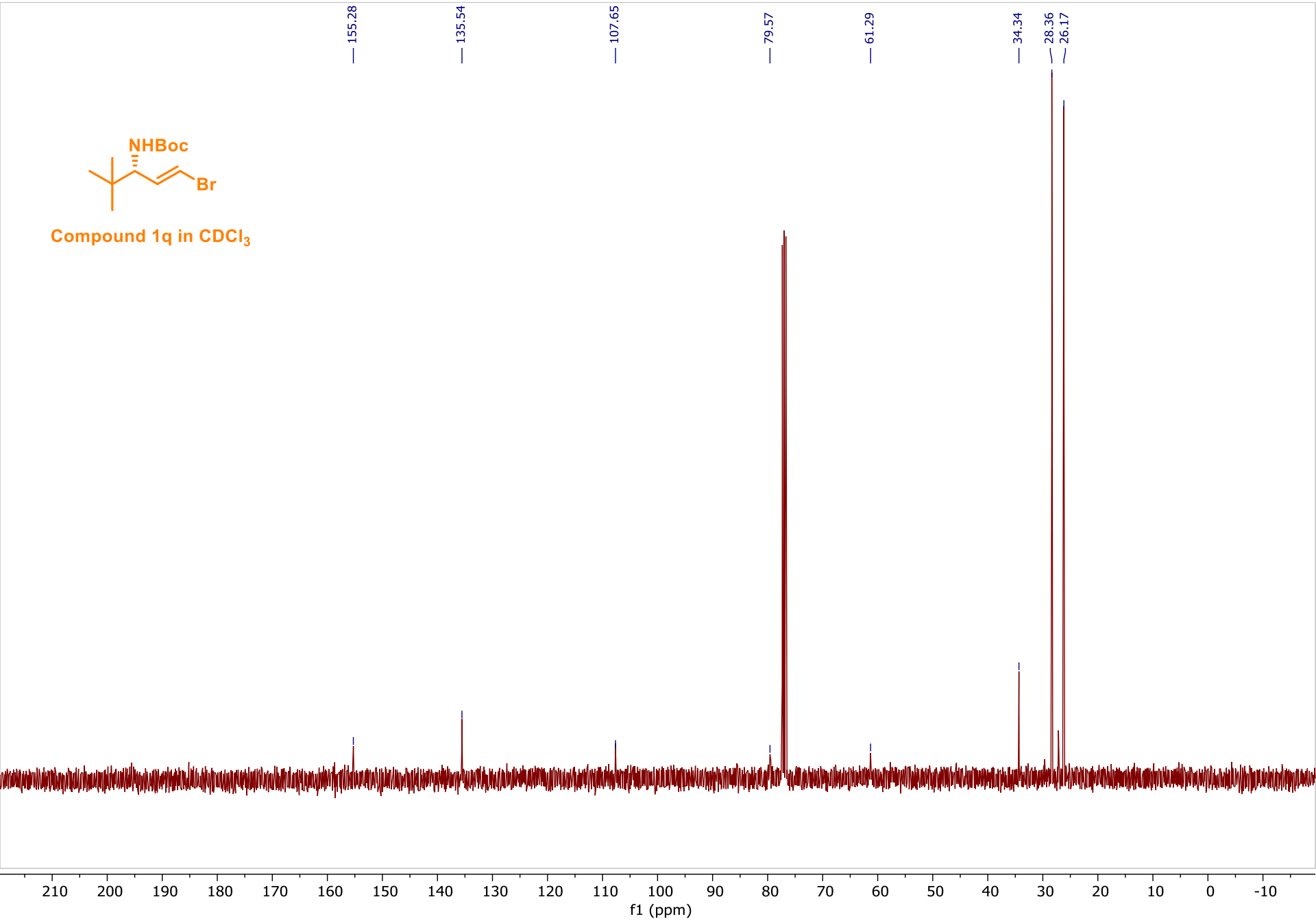

7.38
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.26
6.49
6.45
6.25
6.23
6.21
6.20
5.58
5.56
5.56
5.12
4.93
4.91
4.89
3.77
5.92
1.00
1.02
0.96
2.15
0.90
3.23
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
NHCbz
MeOOC
Br
Compound 1o in CDCl3

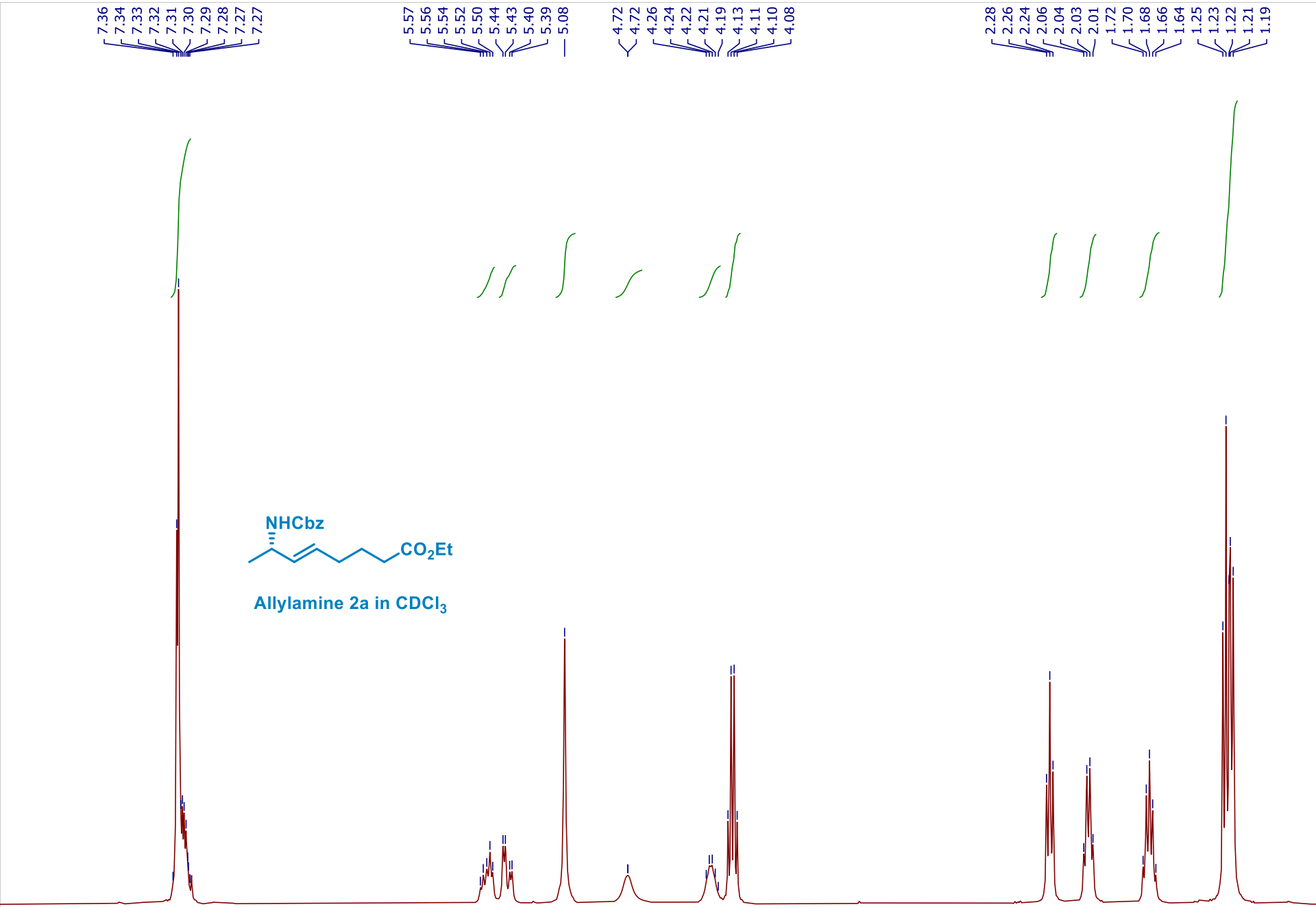

169.59
155.35
135.94
131.56
128.58
128.32
128.18
110.68
67.35
55.87
53.06
NHCbz
MeOOC
Br
Compound 1o in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

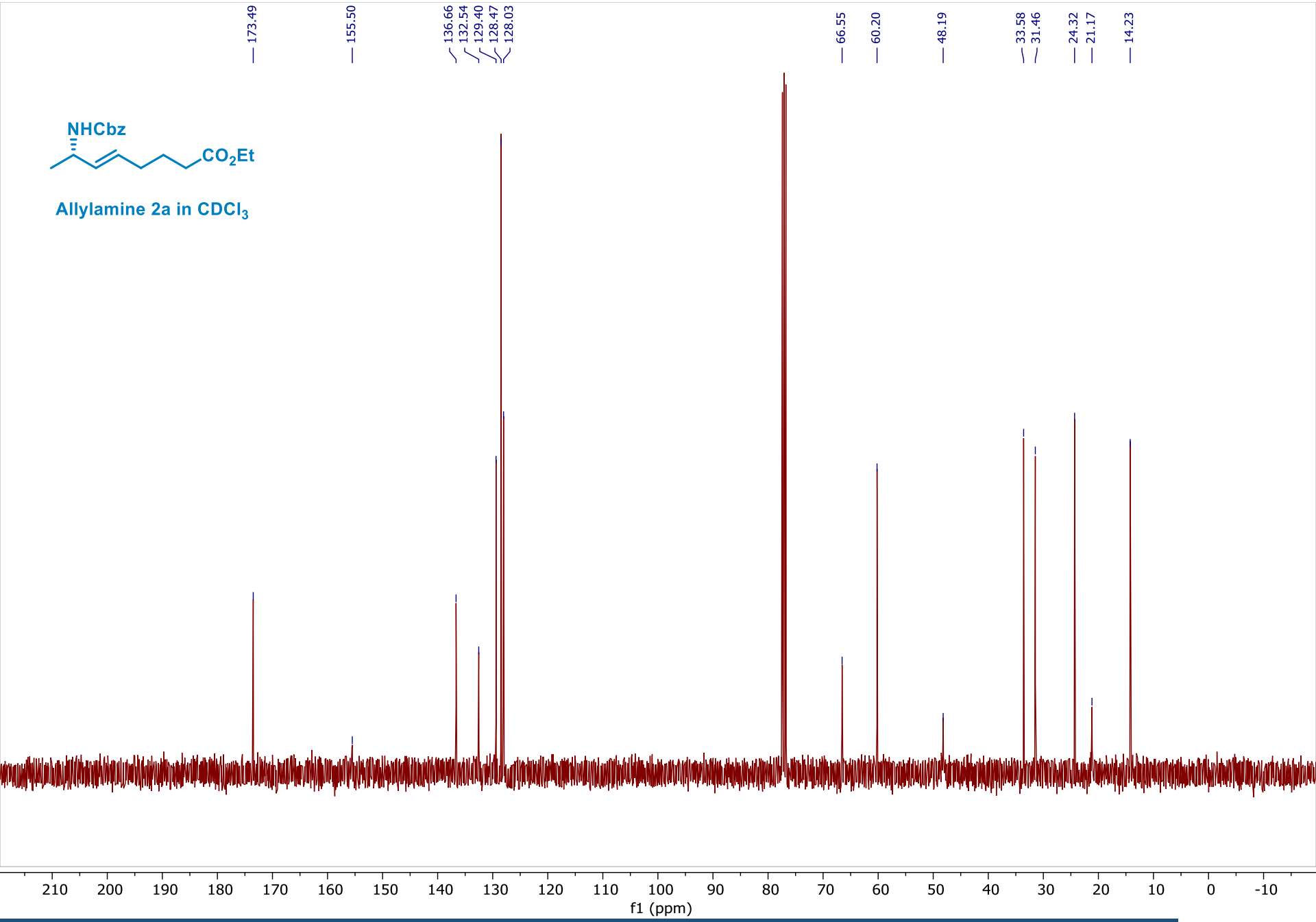

7.39
7.39
7.37
7.35
7.34
7.34
7.33
7.32
7.32
7.30
7.30
6.28
6.25
6.11
6.09
6.07
6.05
5.10
4.77
4.02
1.83
1.81
1.79
1.77
1.76
0.93
0.91
NHCbz
Br
Compound 1p in CDCl3
5.64
1.00
1.11
2.27
0.96
1.03
1.11
6.25
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

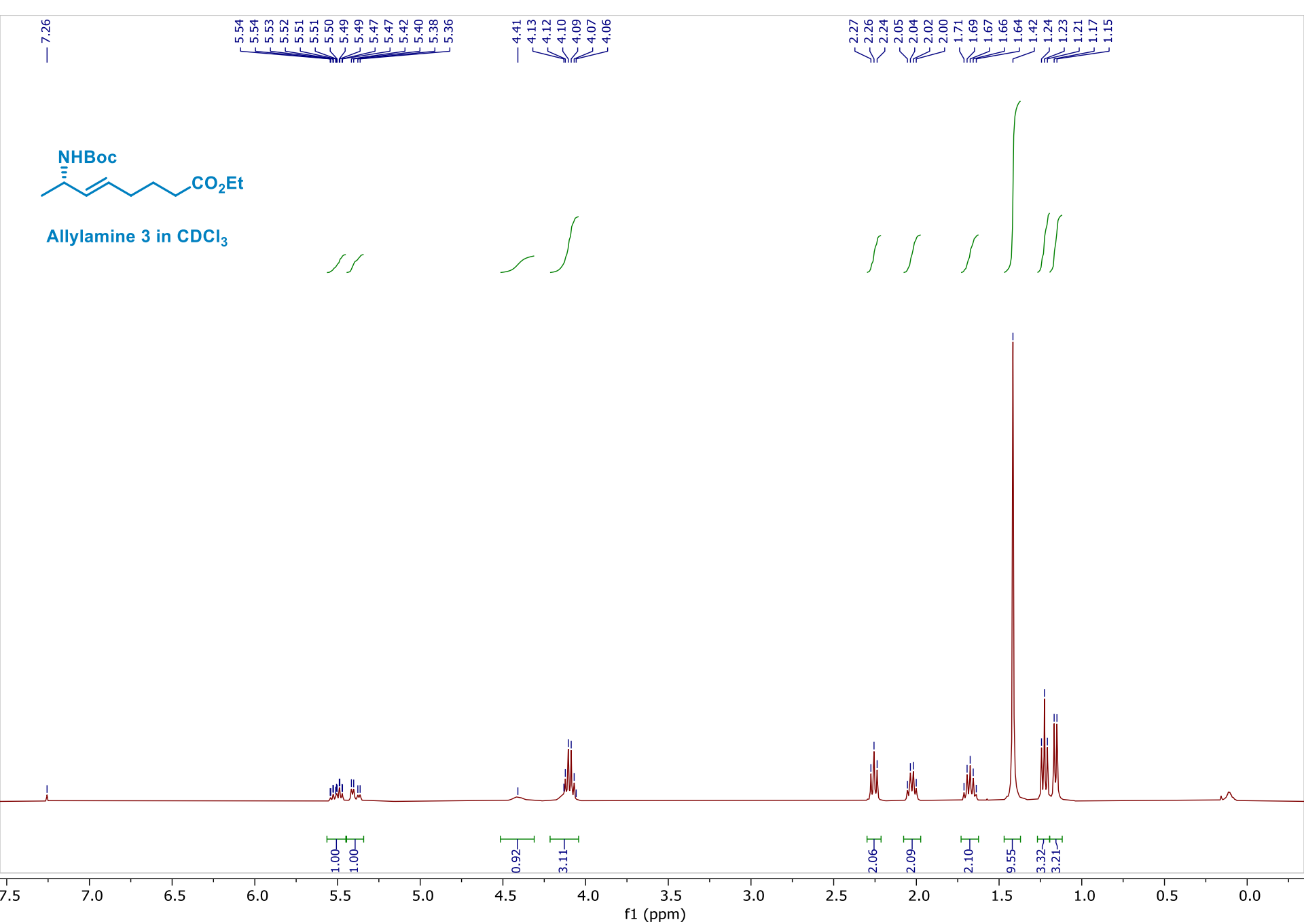

155.80
136.32
128.57
128.22
128.15
107.69
66.96
58.71
32.18
18.59
18.26
NHCbz
Br
Compound 1p in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

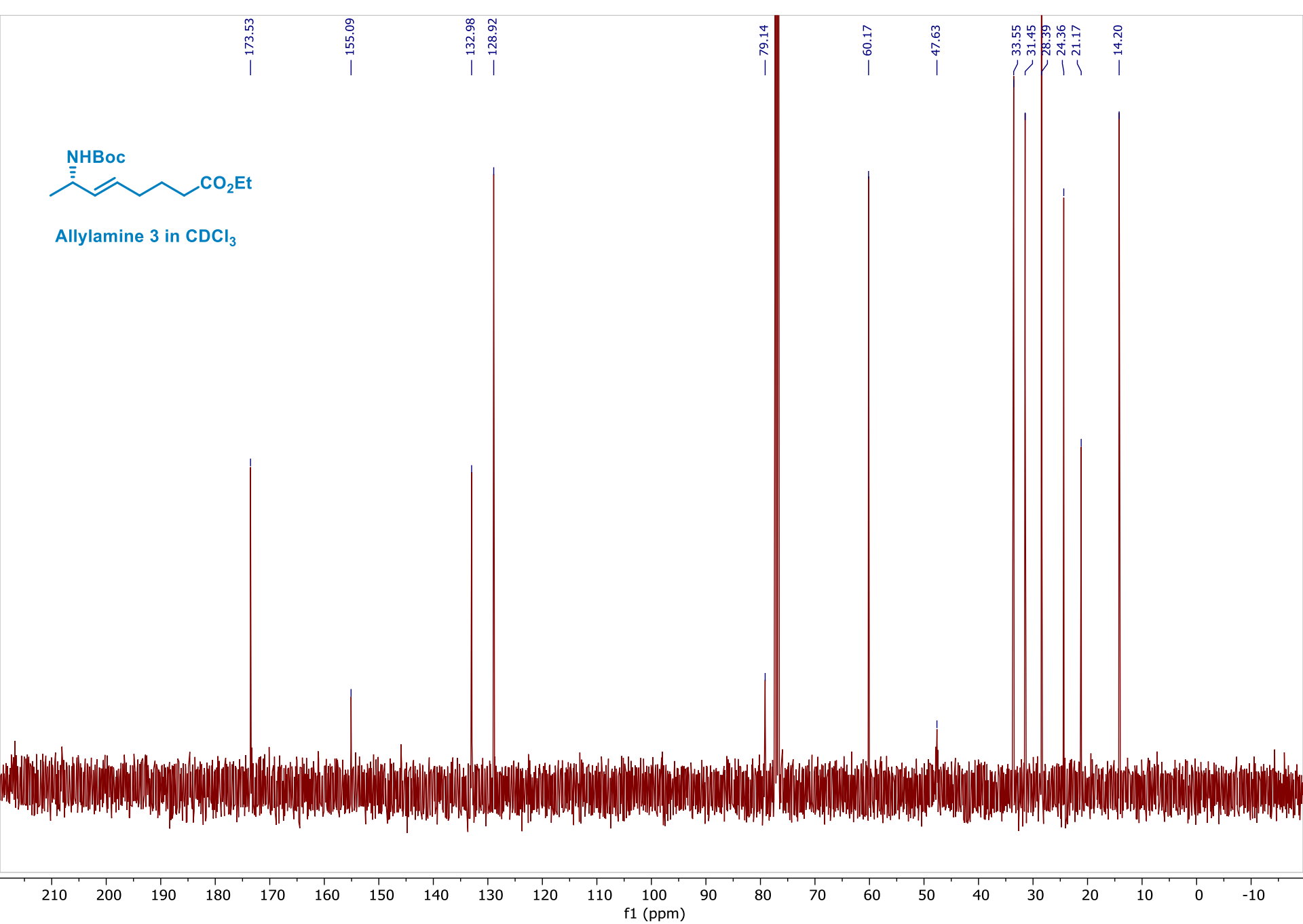

7.26
6.24
6.21
6.15
6.13
6.11
6.10
4.54
4.52
3.89
1.43
0.90
NHBoc
Br
Compound 1q in CDCl3
0.87
0.91
0.82
0.82
9.34
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.28
135.54
107.65
79.57
61.29
34.34
28.36
26.17
NHBoc
Br
Compound 1q in CDCl3
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)


7.36
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.27
5.57
5.56
5.54
5.52
5.50
5.44
5.43
5.40
5.39
5.08
4.72
4.72
4.26
4.24
4.22
4.21
4.19
4.13
4.11
4.10
4.08
2.28
2.26
2.24
2.06
2.04
2.03
2.01
1.72
1.70
1.68
1.66
1.64
1.25
1.23
1.22
1.21
1.19
NHCbz
CO2Et
Allylamine 2a in CDCl3


173.49
155.50
136.66
132.54
129.40
128.47
128.03
66.55
60.20
48.19
33.58
31.46
24.32
21.17
14.23
NHCbz
CO2Et
Allylamine 2a in CDCl3
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)


7.26
5.54 5.54 5.53 5.52 5.51 5.51 5.50 5.49 5.49 5.47 5.47 5.42 5.40 5.38 5.36
4.41 4.13 4.12 4.10 4.09 4.07 4.06
2.27 2.26 2.24 2.05 2.04 2.02 2.00 1.71 1.69 1.67 1.66 1.64 1.42 1.24 1.23 1.21 1.17 1.15
NHBoc
CO2Et
Allylamine 3 in CDCl3
1.00 1.00 0.92 3.11 2.06 2.09 2.10 9.55 3.32 3.21
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)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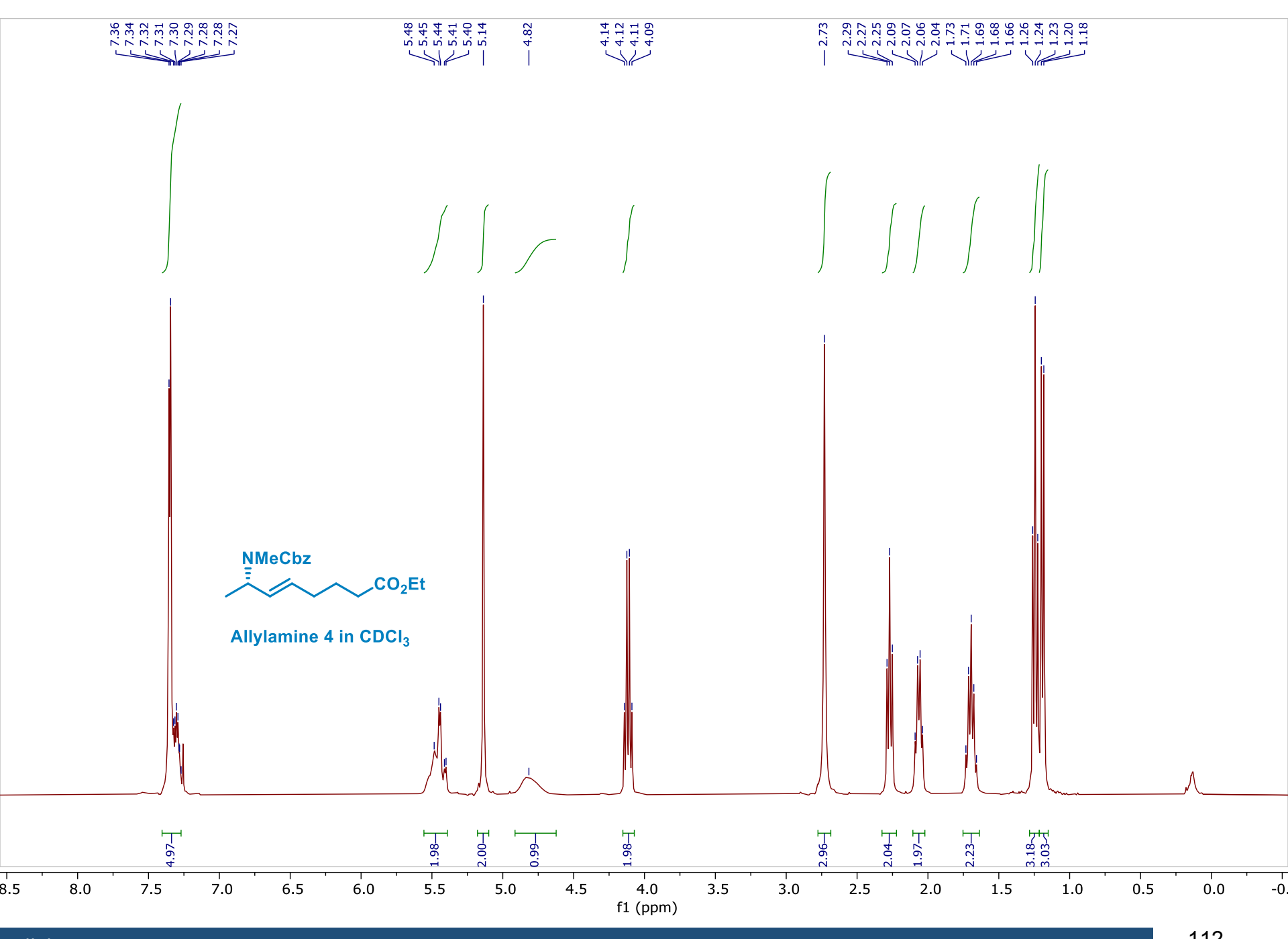
155.09
132.98
128.92
79.14
60.17
47.63
33.55
31.45
28.39
24.36
21.17
14.20
NHBoc
CO2Et
Allylamine 3 in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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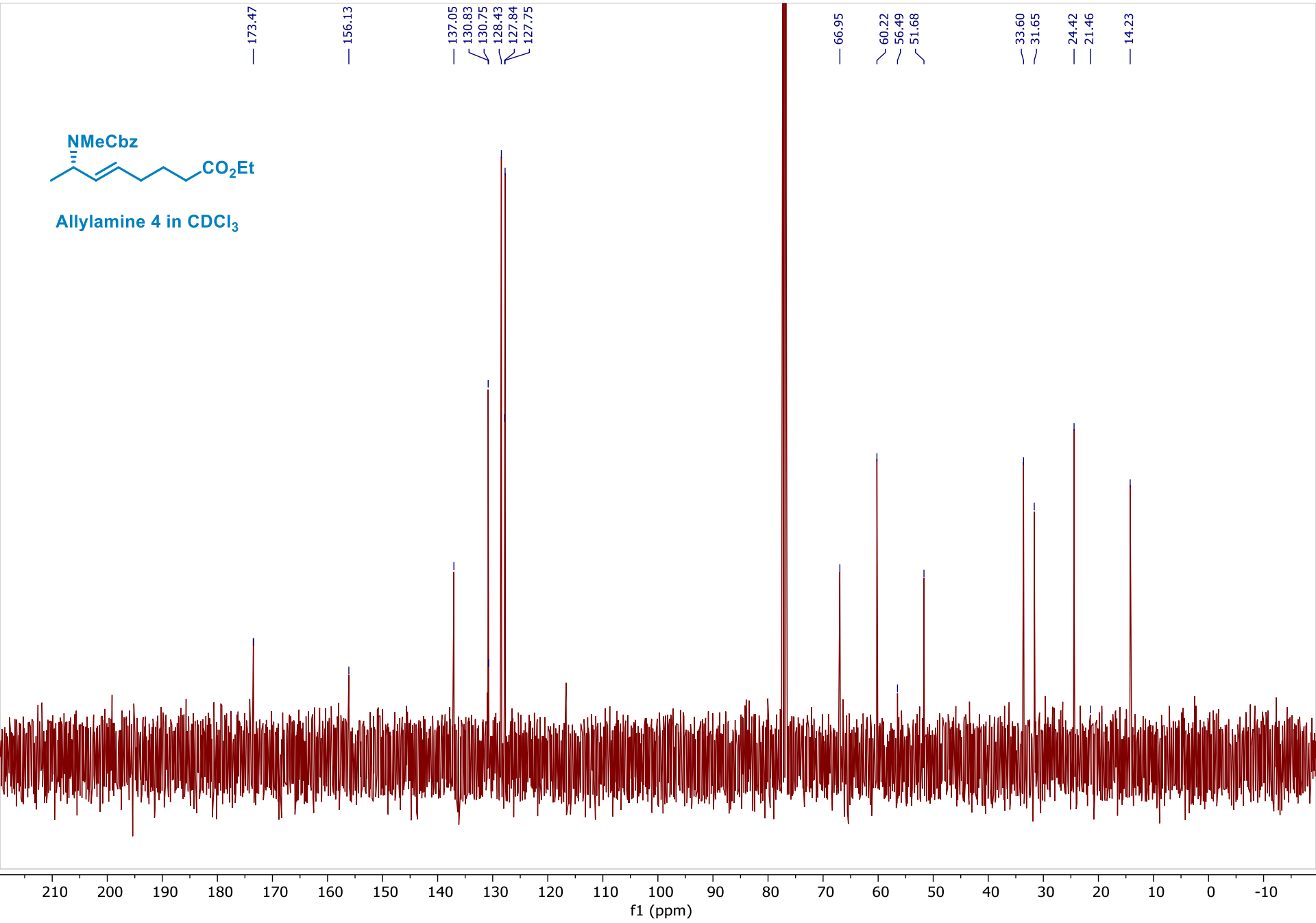
7.34
7.32
7.31
7.30
7.29
7.28
7.28
7.27
5.48
5.45
5.44
5.41
5.40
5.14
4.82
4.14
4.12
4.11
4.09
2.73
2.29
2.27
2.25
2.09
2.07
2.06
2.04
1.73
1.71
1.69
1.68
1.66
1.26
1.24
1.23
1.20
1.18
NMeCbz
CO2Et
Allylamine 4 in CDCl3
4.97
1.98
2.00
0.99
1.98
2.96
2.04
1.97
2.23
3.18
3.03
f1 (ppm)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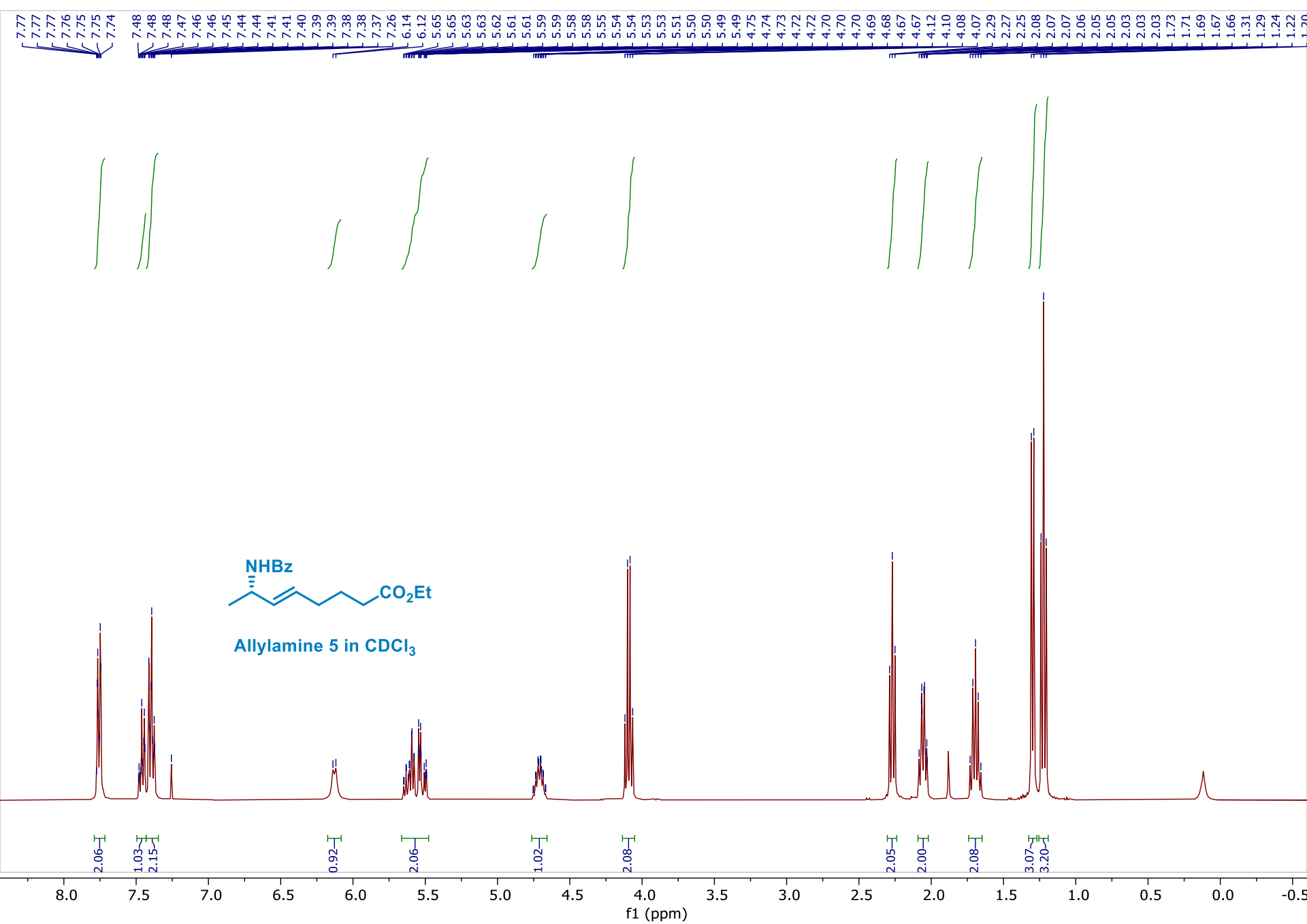
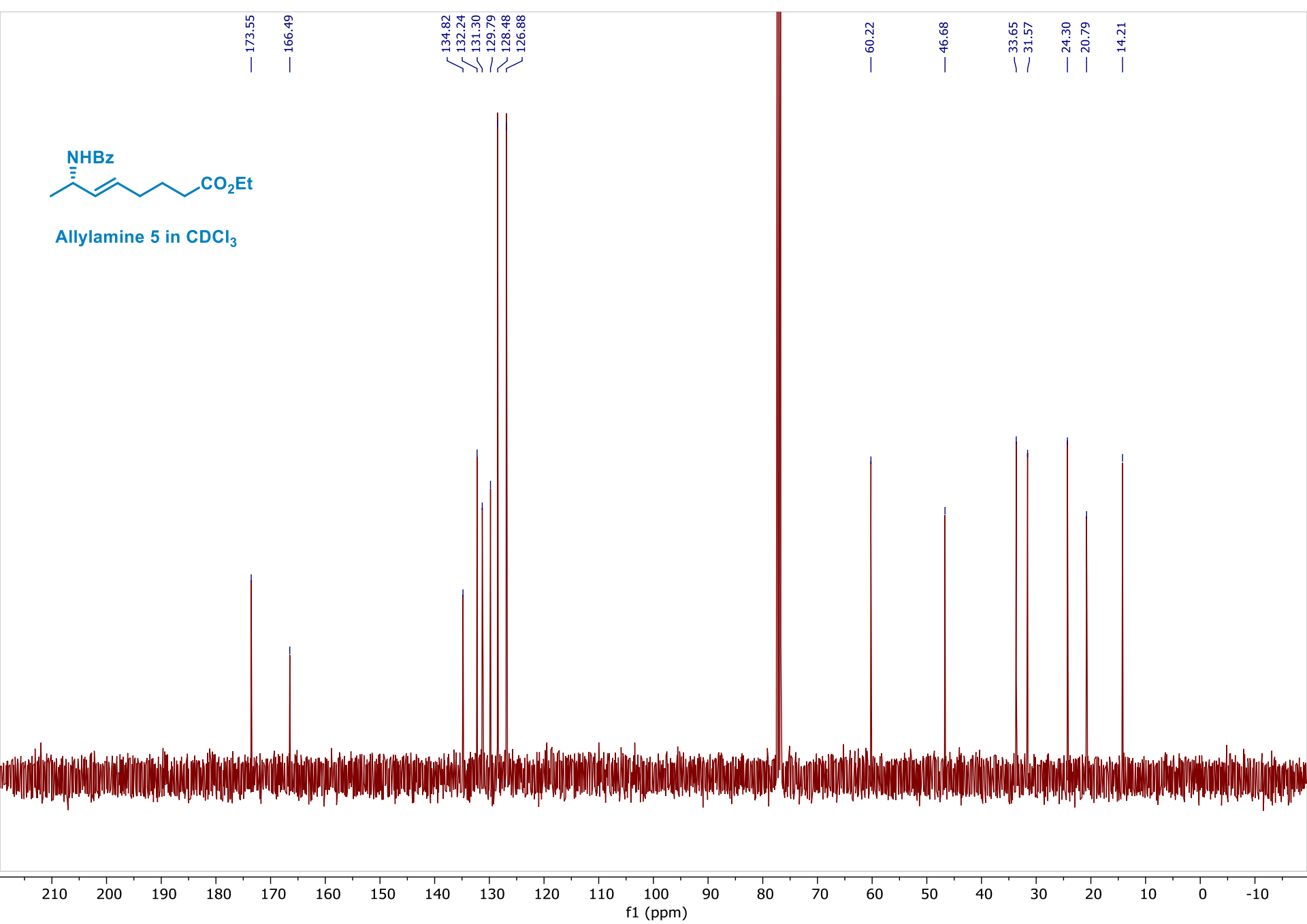
156.13
137.05
130.83
130.75
128.43
127.84
127.75
66.95
60.22
56.49
51.68
33.60
31.65
24.42
21.46
14.23
NMeCbz
CO2Et
Allylamine 4 in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NHBz
CO2Et
Allylamine 5 in CDCl3
f1 (ppm)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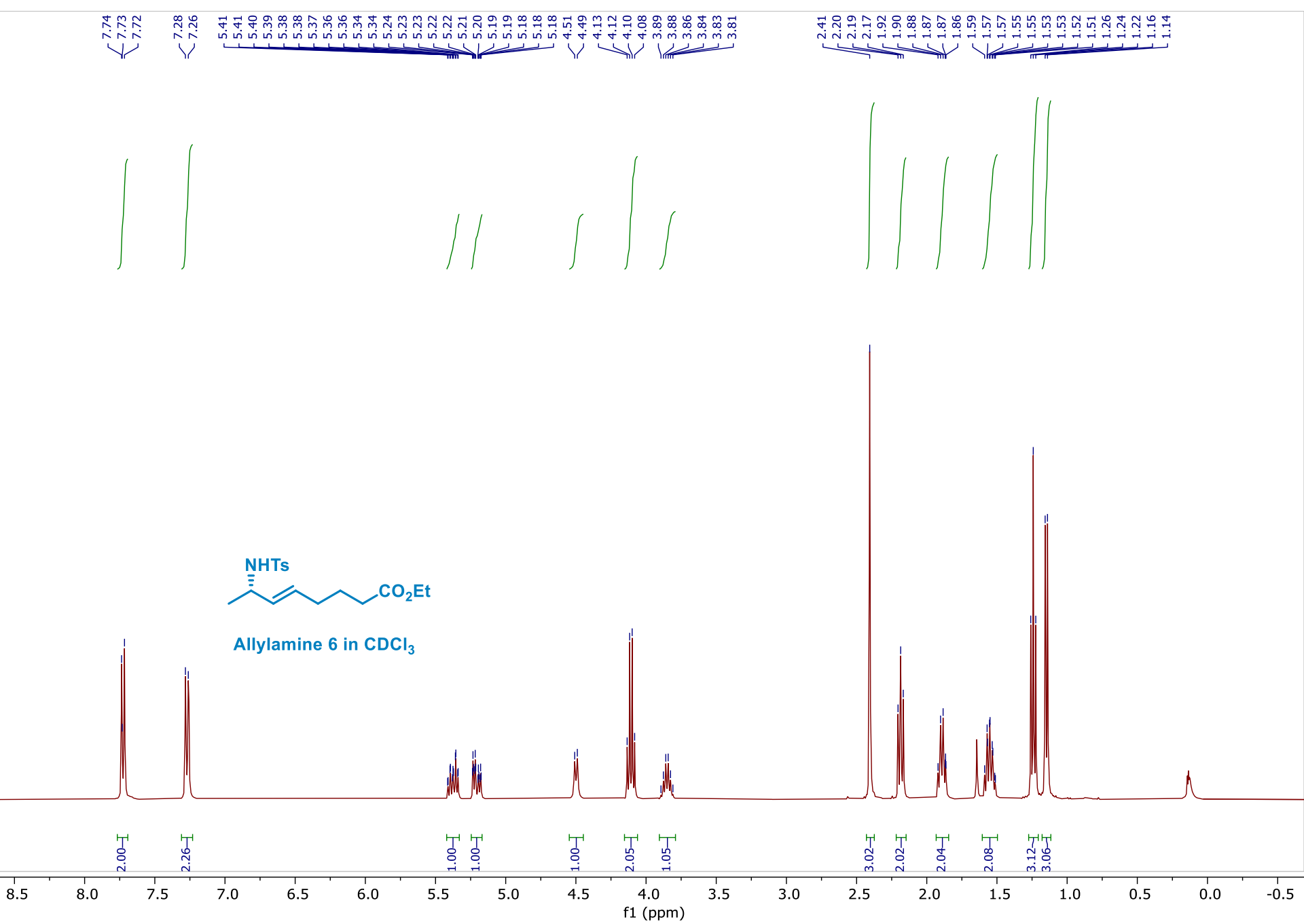
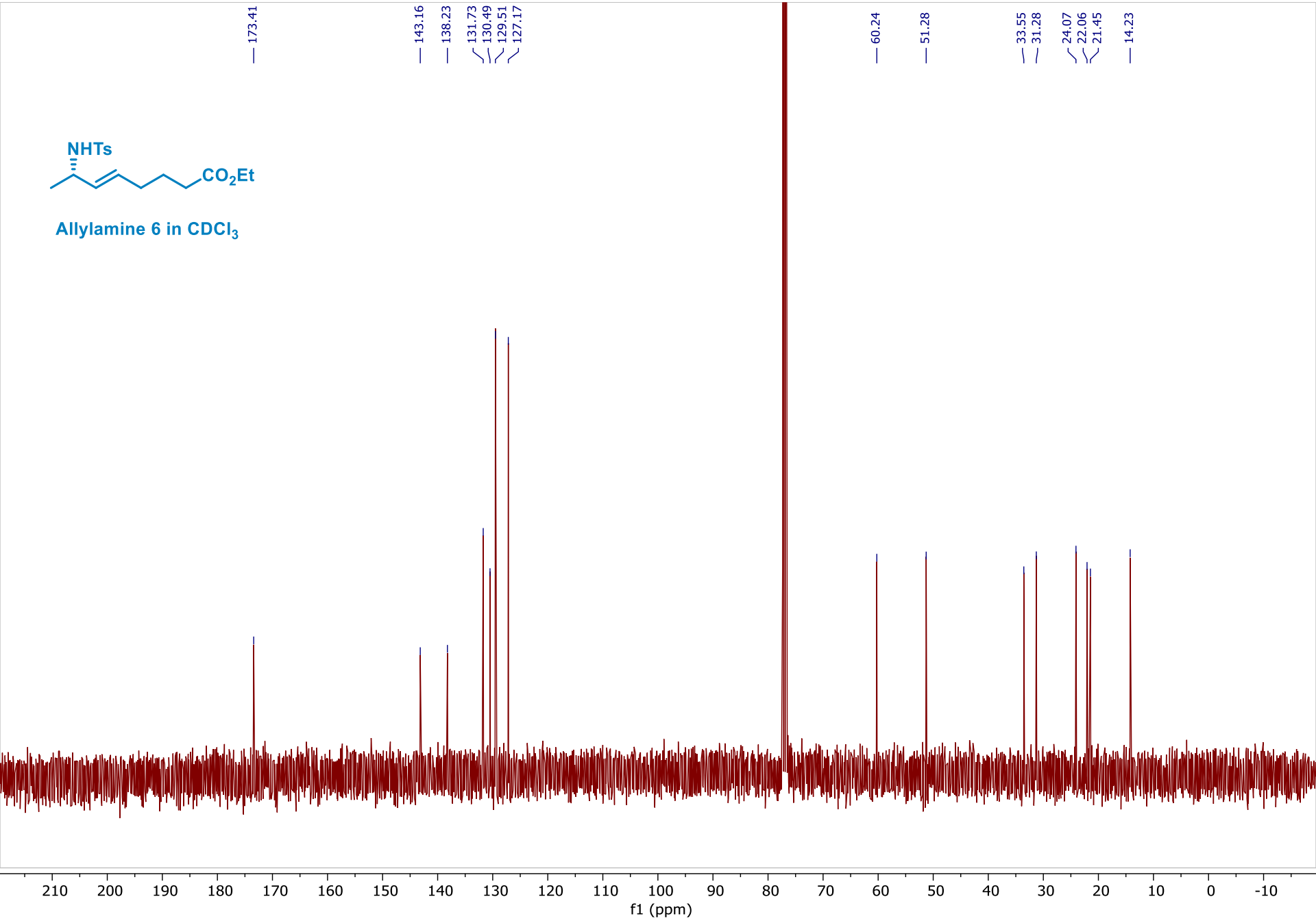
166.49
134.82
132.24
131.30
129.79
128.48
126.88
60.22
46.68
33.65
31.57
24.30
20.79
14.21
NHBz
CO2Et
Allylamine 5 in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NHTs
CO2Et
Allylamine 6 in CDCl3
f1 (ppm)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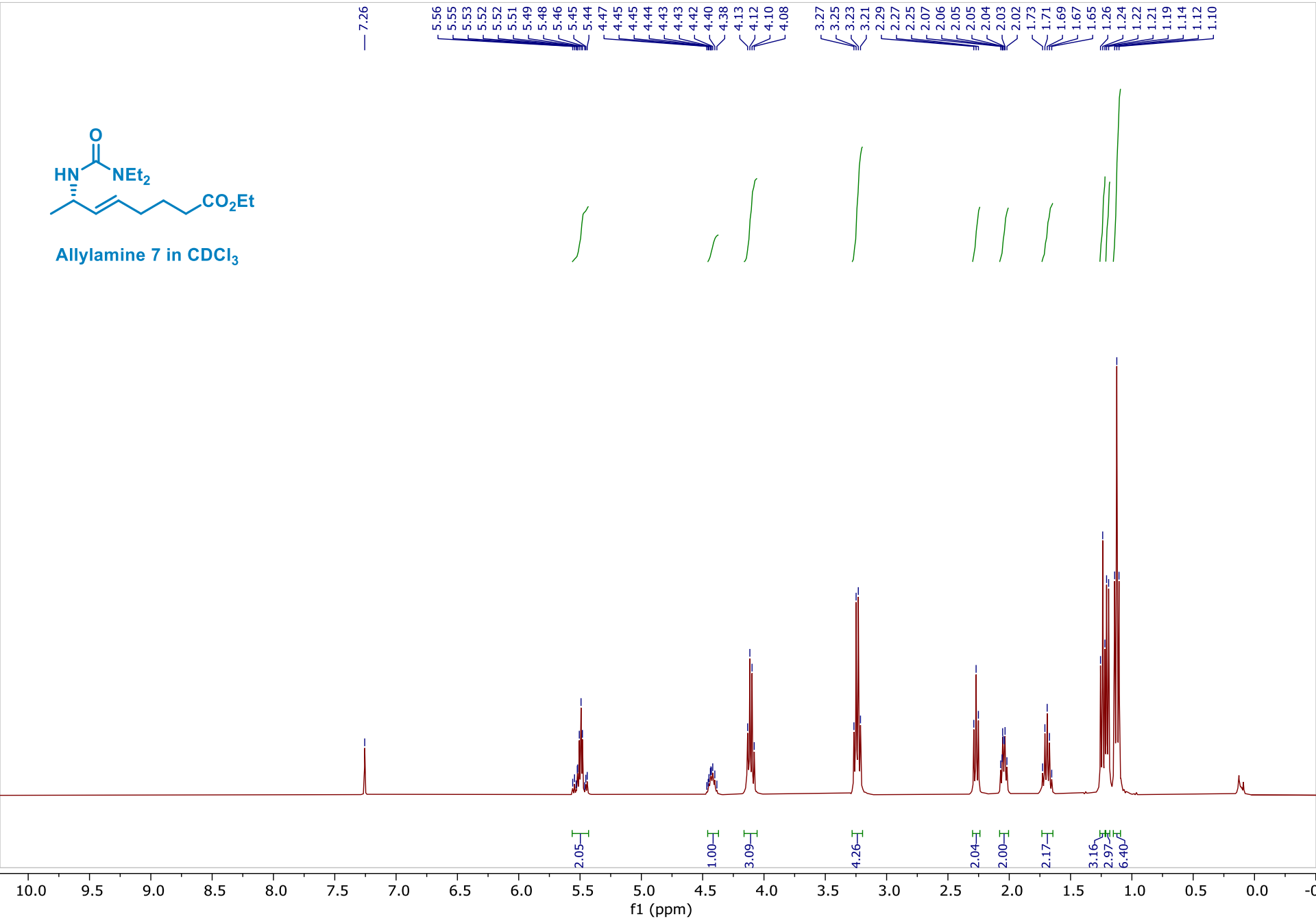
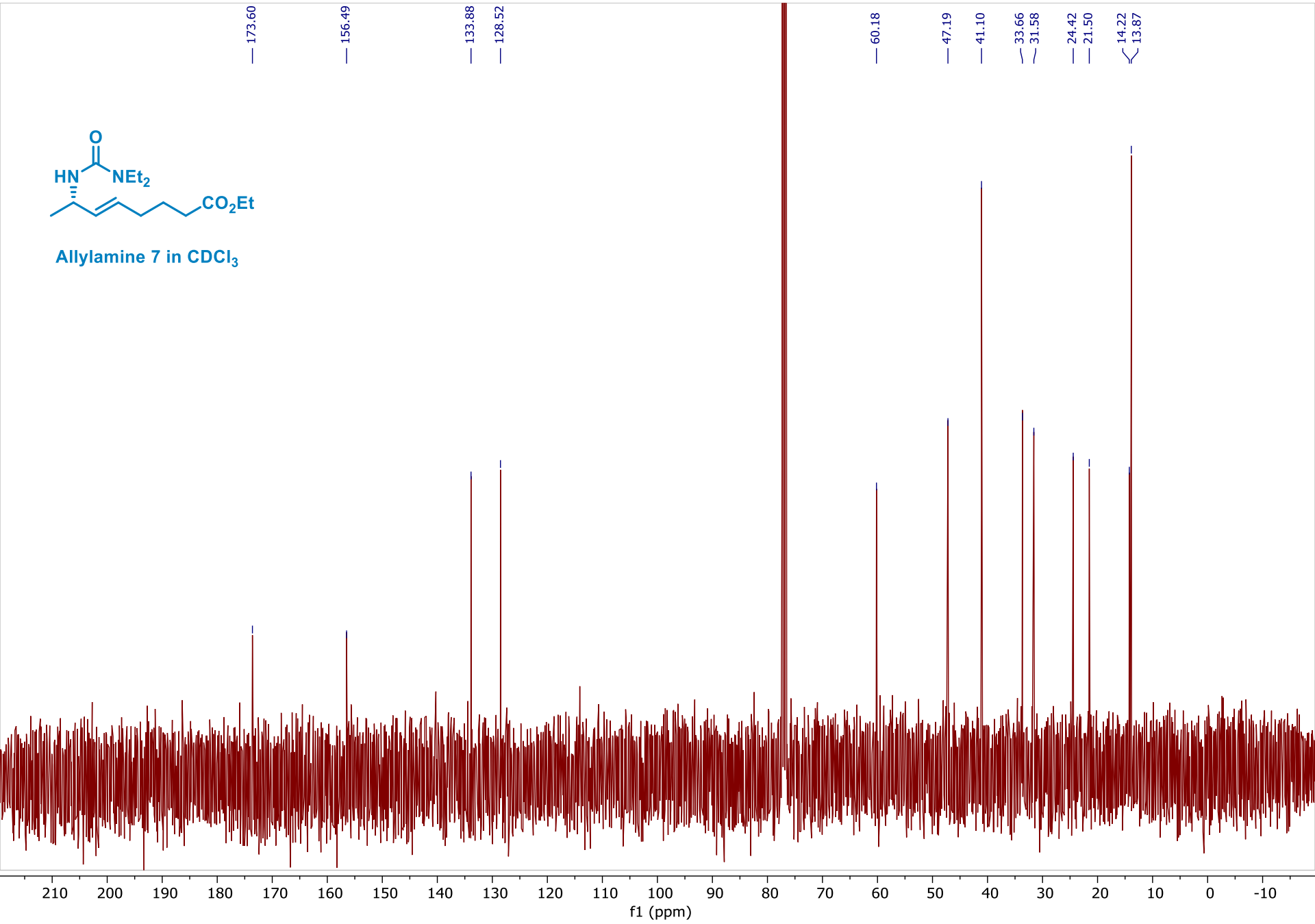
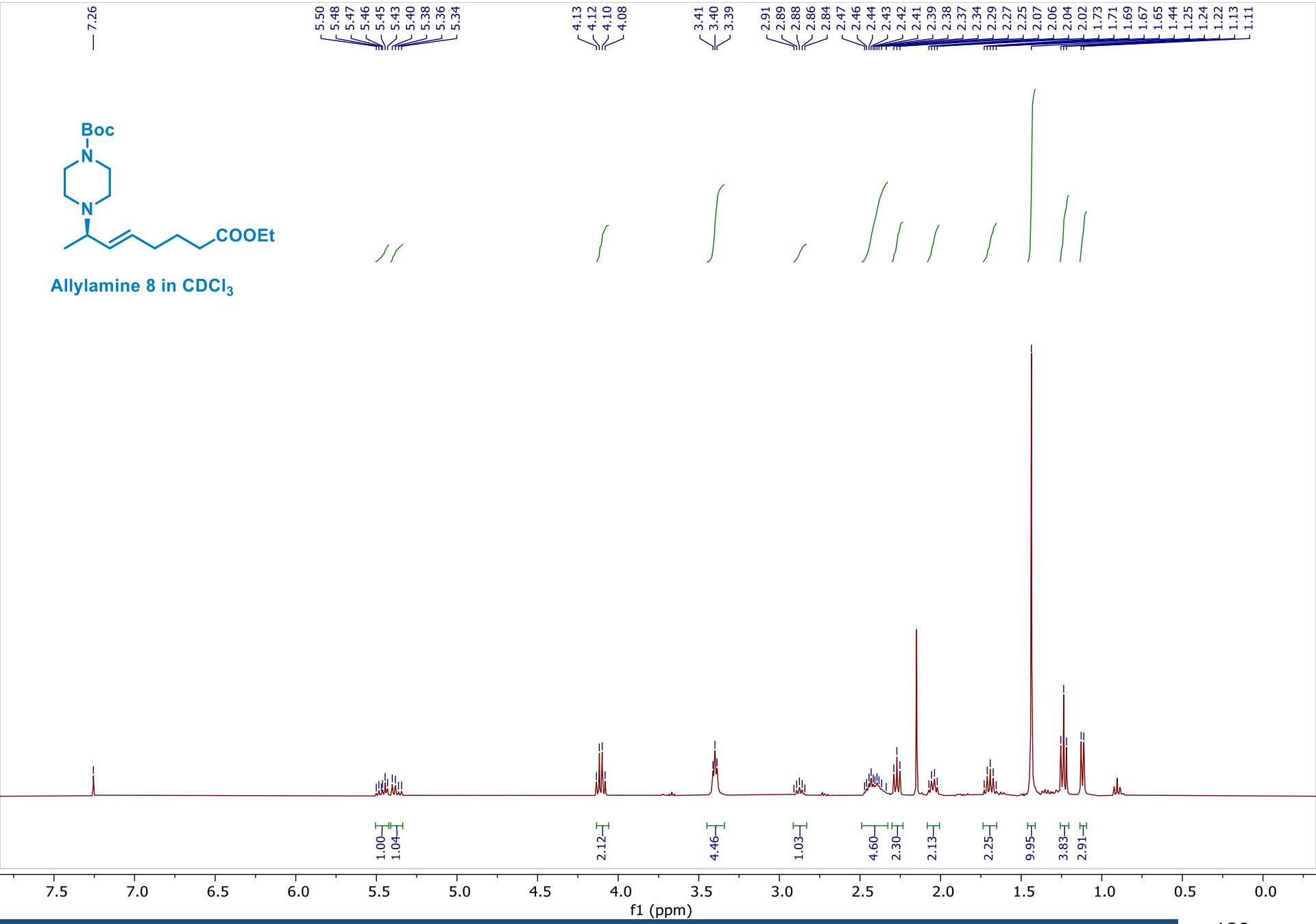
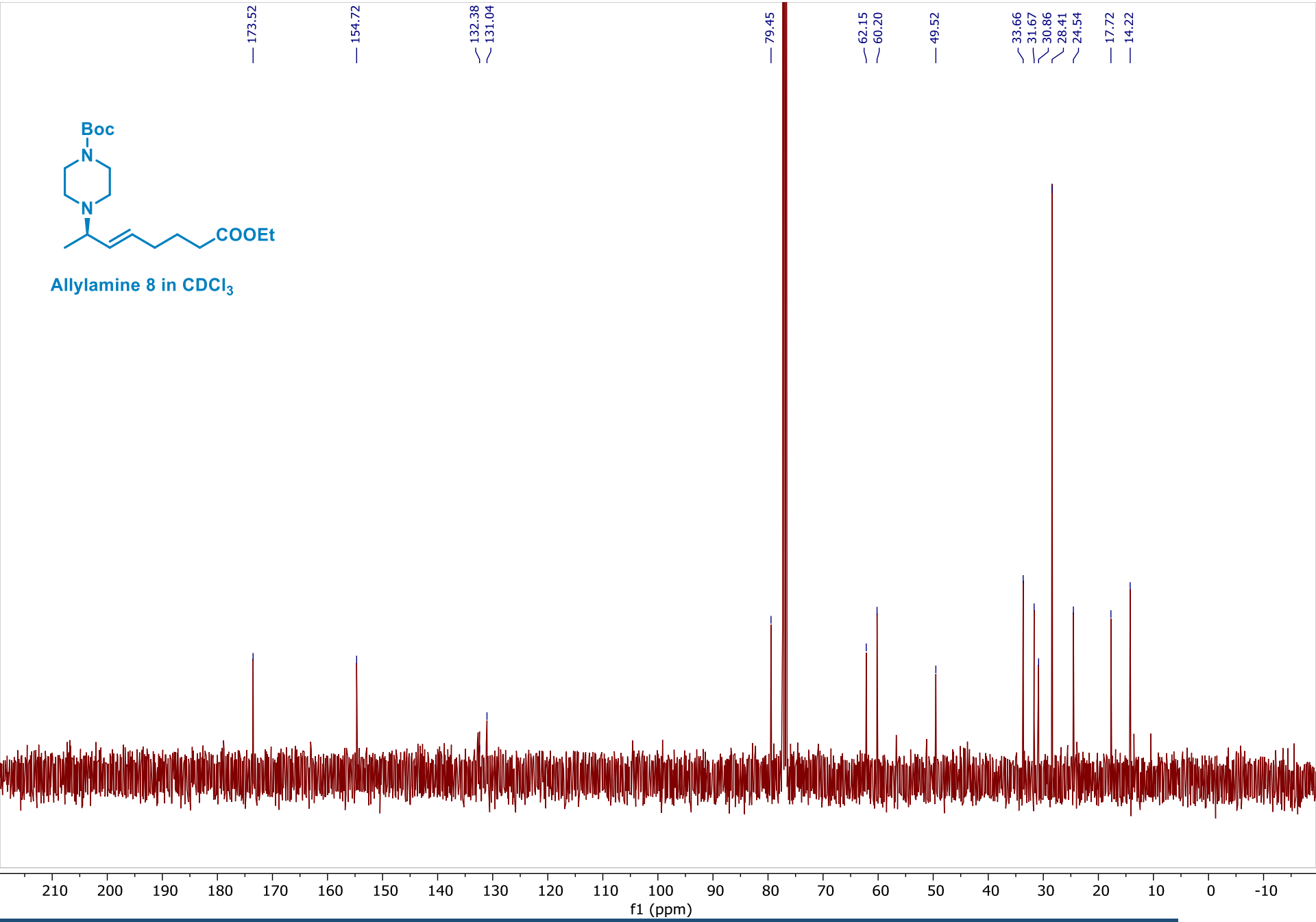
143.16
138.23
131.73
130.49
129.51
127.17
60.24
51.28
33.55
31.28
24.07
22.06
21.45
14.23
NHTs
CO2Et
Allylamine 6 in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

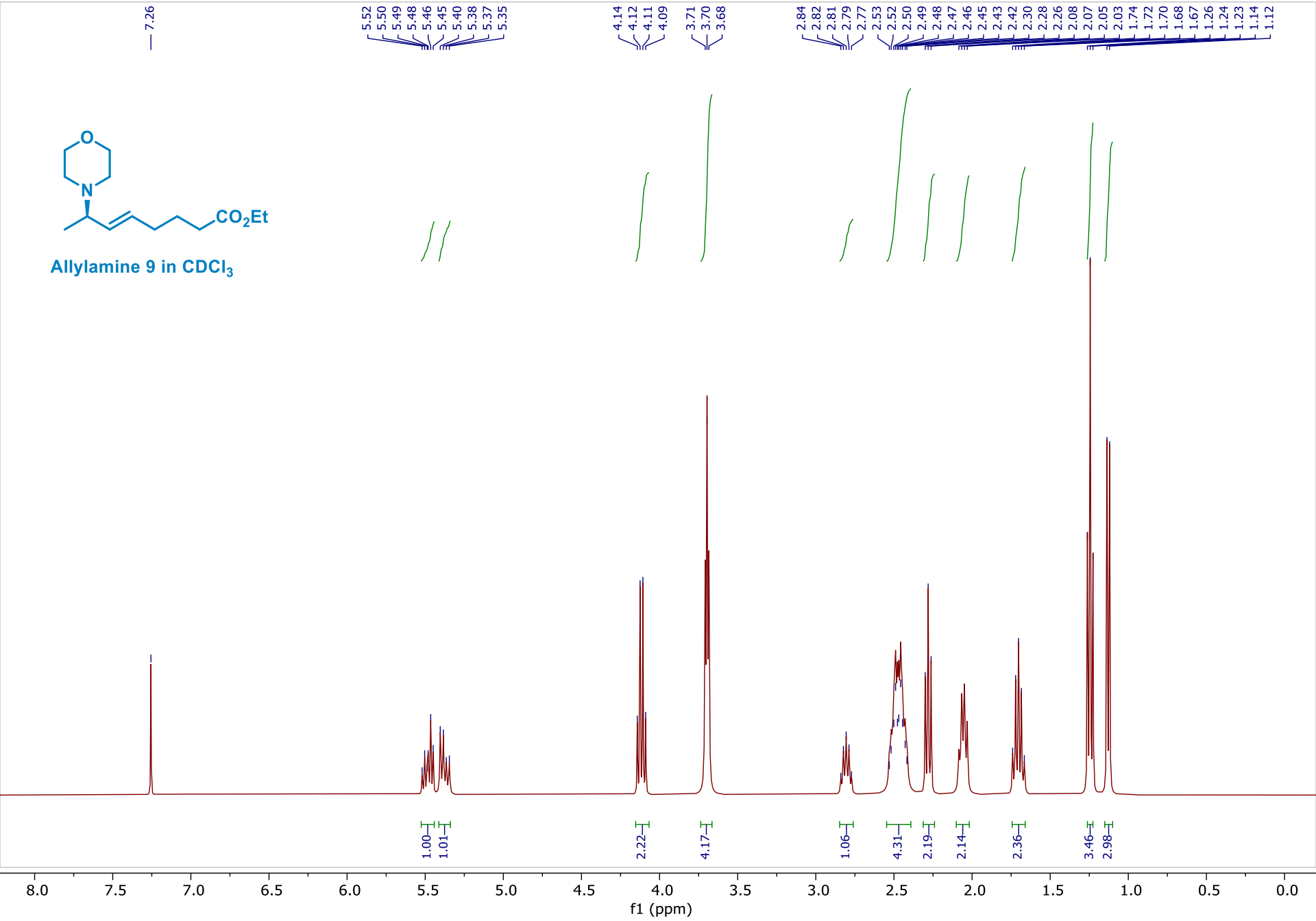

7.26
5.56 5.55 5.53 5.52 5.52 5.51 5.49 5.48 5.46 5.45 5.44
4.47 4.45 4.45 4.44 4.43 4.43 4.42 4.40 4.38
4.13 4.12 4.10 4.08
3.27 3.25 3.23 3.21
2.29 2.27 2.25 2.07 2.06 2.05 2.05 2.04 2.03 2.02
1.73 1.71 1.69 1.67 1.65
1.26 1.24 1.22 1.21 1.19 1.14 1.12 1.10
HN
NEt2
CO2Et
Allylamine 7 in CDCl3
2.05
1.00
3.09
4.26
2.04
2.00
2.17
3.16
2.97
6.40
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
f1 (ppm)

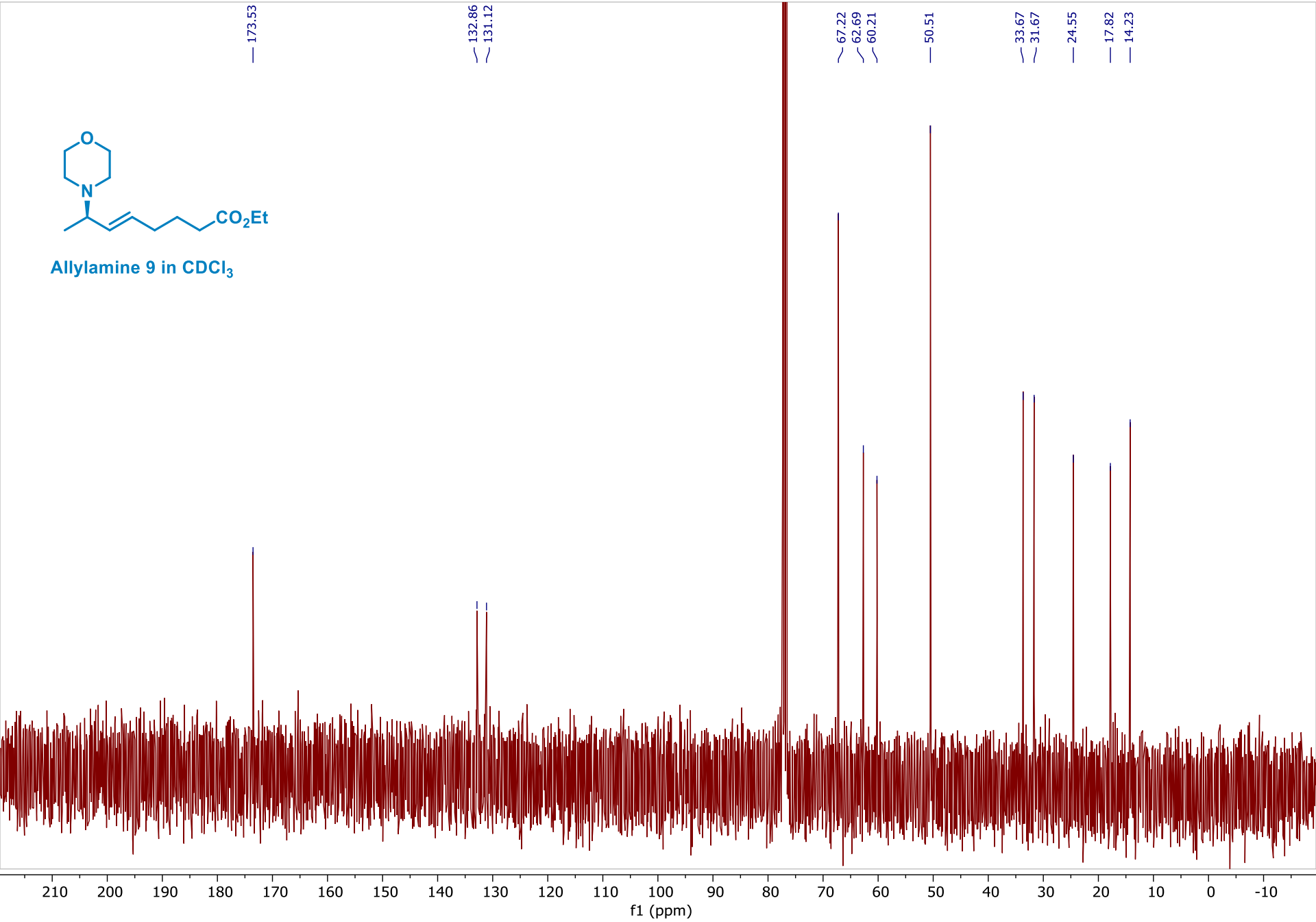

173.60
156.49
133.88
128.52
60.18
47.19
41.10
33.66
31.58
24.42
21.50
14.22
13.87
O
HN
NEt2
CO2Et
Allylamine 7 in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

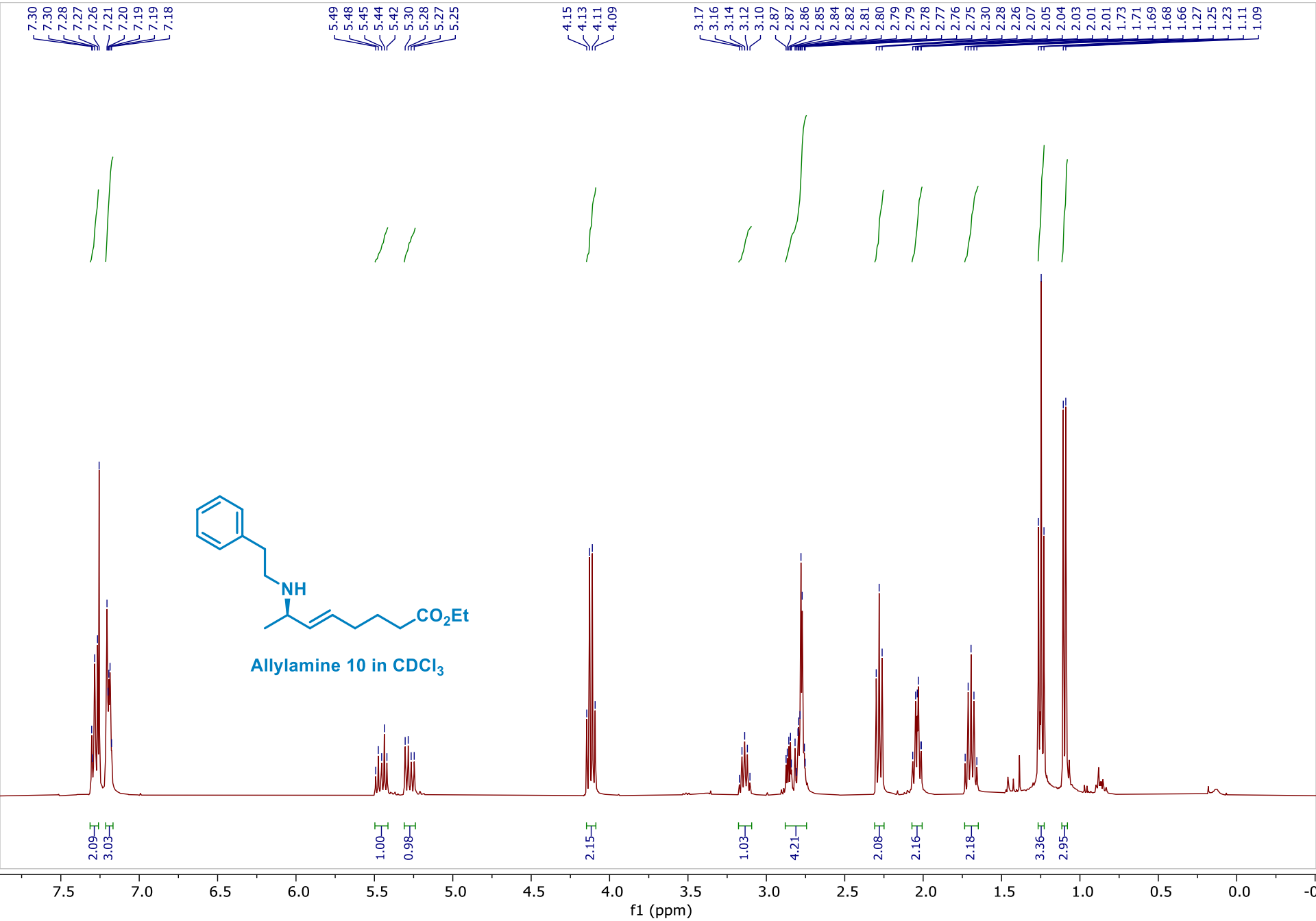


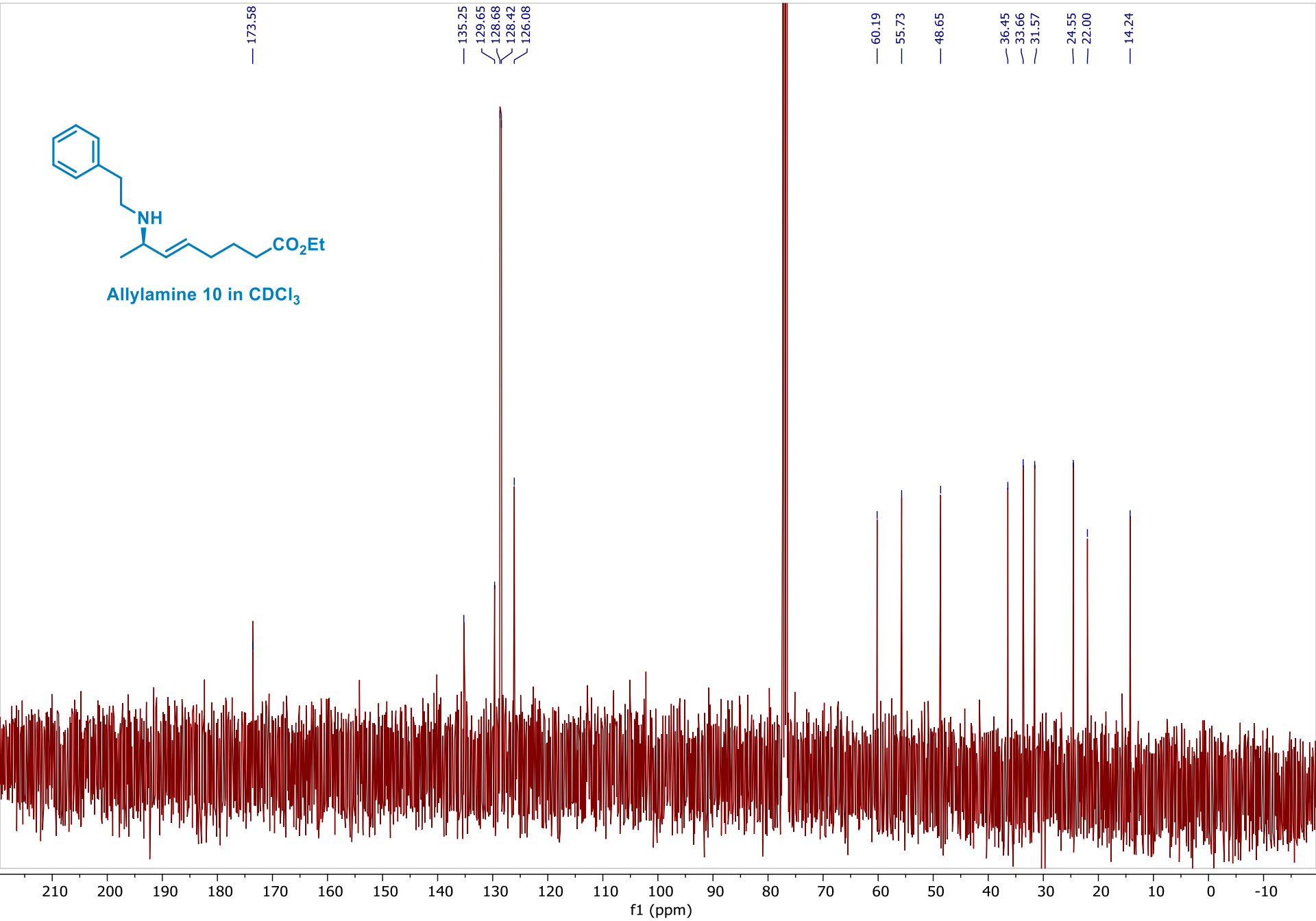
Allylamine 8 in $CDCl_3$


173.52
154.72
132.38
131.04
79.45
62.15
60.20
49.52
33.66
31.67
30.86
28.41
24.54
17.72
14.22
Boc
N
N
COOEt
Allylamine 8 in CDCl3
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)


7.26
5.52
5.50
5.49
5.48
5.46
5.45
5.40
5.38
5.37
5.35
4.14
4.12
4.11
4.09
3.71
3.70
3.68
2.84
2.82
2.81
2.79
2.77
2.53
2.52
2.50
2.49
2.48
2.47
2.46
2.45
2.43
2.42
2.30
2.28
2.26
2.08
2.07
2.05
2.03
1.74
1.72
1.70
1.68
1.67
1.26
1.24
1.23
1.14
1.12
O
N
CO2Et
Allylamine 9 in CDCl3
1.00
1.01
2.22
4.17
1.06
4.31
2.19
2.14
2.36
3.46
2.98
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)


173.53
132.86
131.12
67.22
62.69
60.21
50.51
33.67
31.67
24.55
17.82
14.23
O
N
CO2Et
Allylamine 9 in CDCl3
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)


7.30 7.30 7.28 7.27 7.26 7.21 7.20 7.19 7.19 7.18
5.49 5.48 5.45 5.44 5.42 5.30 5.28 5.27 5.25
4.15 4.13 4.11 4.09
3.17 3.16 3.14 3.12 3.10 2.87 2.86 2.85 2.84 2.82 2.81 2.80 2.79 2.79 2.78 2.77 2.76 2.75 2.30 2.28 2.26 2.07 2.05 2.04 2.03 2.01 2.01 1.73 1.71 1.69 1.68 1.66 1.27 1.25 1.23 1.11 1.09
NH
CO2Et
Allylamine 10 in CDCl3
2.09 3.03 1.00 0.98 2.15 1.03 4.21 2.08 2.16 2.18 3.36 2.95
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)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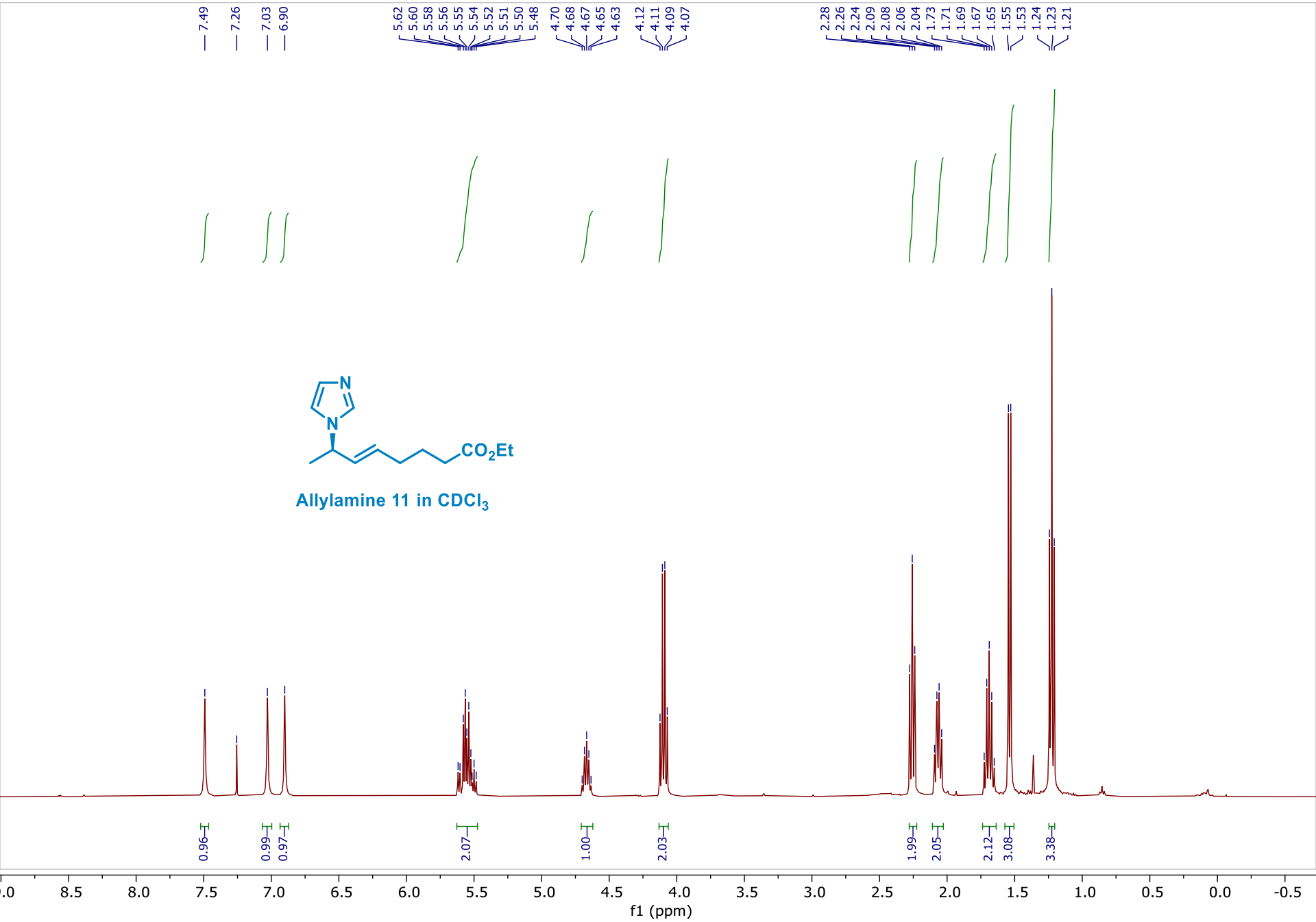
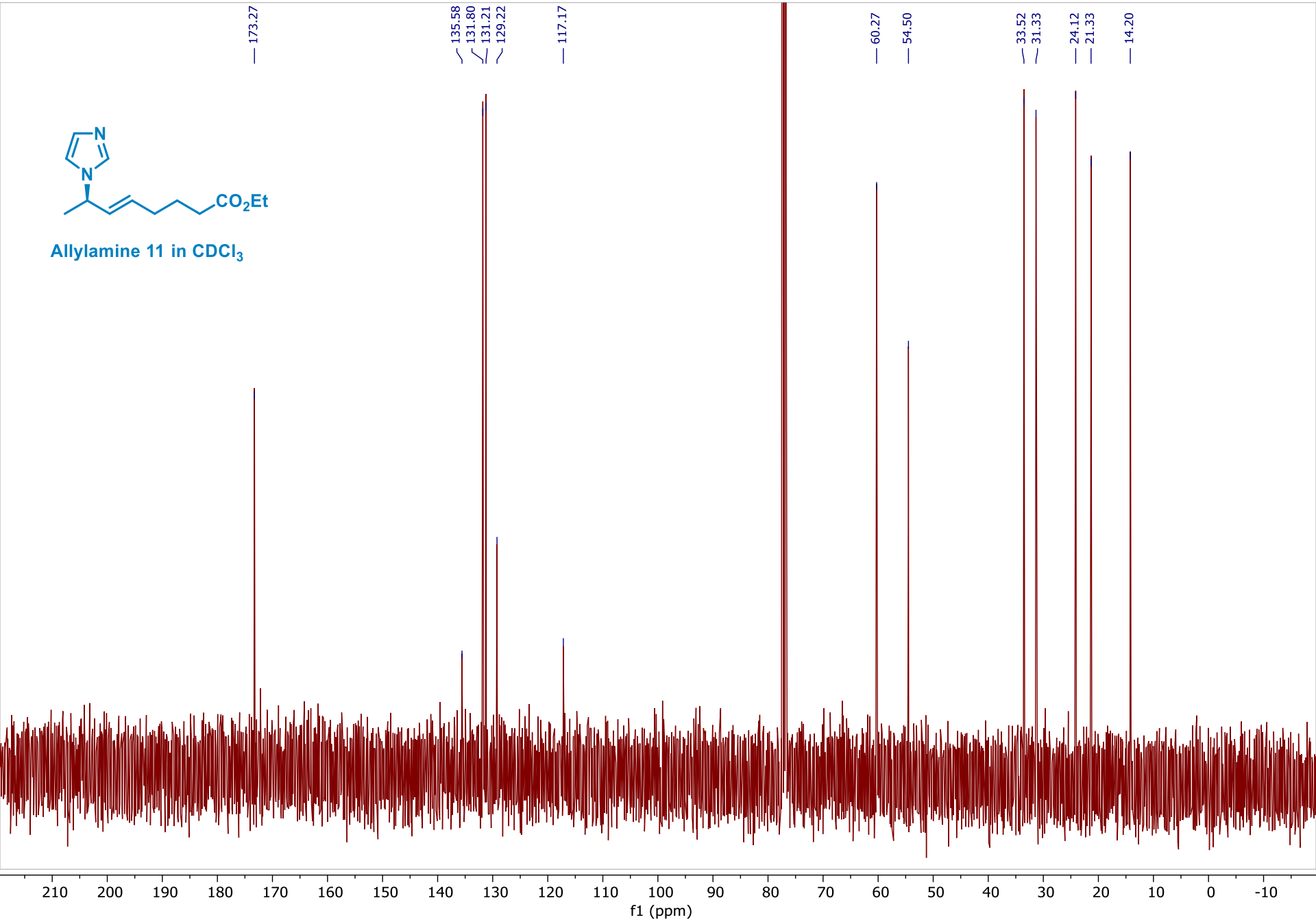
135.25
129.65
128.68
128.42
126.08
60.19
55.73
48.65
36.45
33.66
31.57
24.55
22.00
14.24
NH
CO2Et
Allylamine 10 in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.49
7.26
7.03
6.90
5.62
5.60
5.58
5.56
5.55
5.54
5.52
5.51
5.50
5.48
4.70
4.68
4.67
4.65
4.63
4.12
4.11
4.09
4.07
2.28
2.26
2.24
2.09
2.08
2.06
2.04
1.73
1.71
1.69
1.67
1.65
1.55
1.53
1.24
1.23
1.21
N
N
CO2Et
Allylamine 11 in CDCl3
0.96
0.99
0.97
2.07
1.00
2.03
1.99
2.05
2.12
3.08
3.38
f1 (ppm)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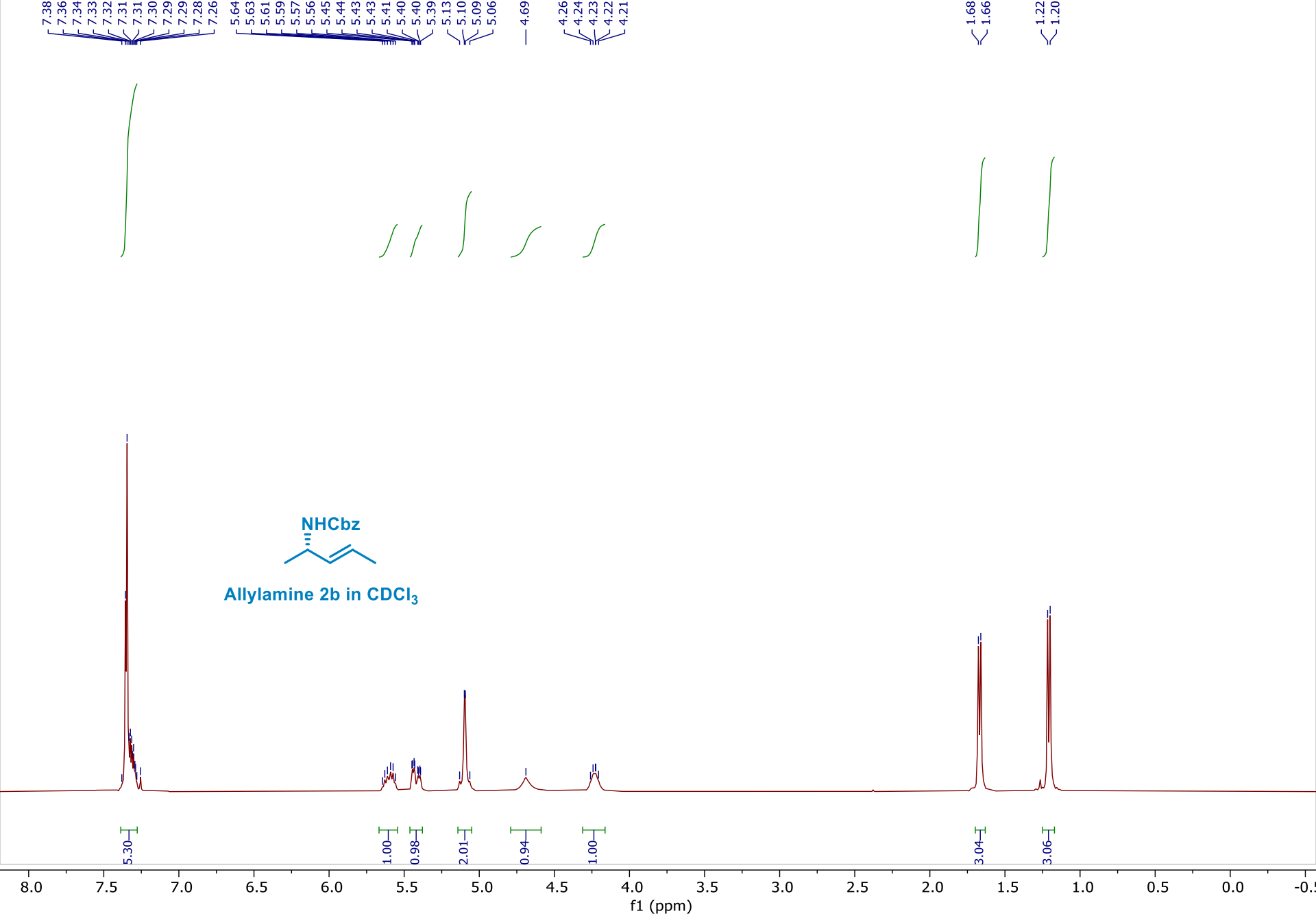
135.58
131.80
131.21
129.22
117.17
60.27
54.50
33.52
31.33
24.12
21.33
14.20
N
N
CO2Et
Allylamine 11 in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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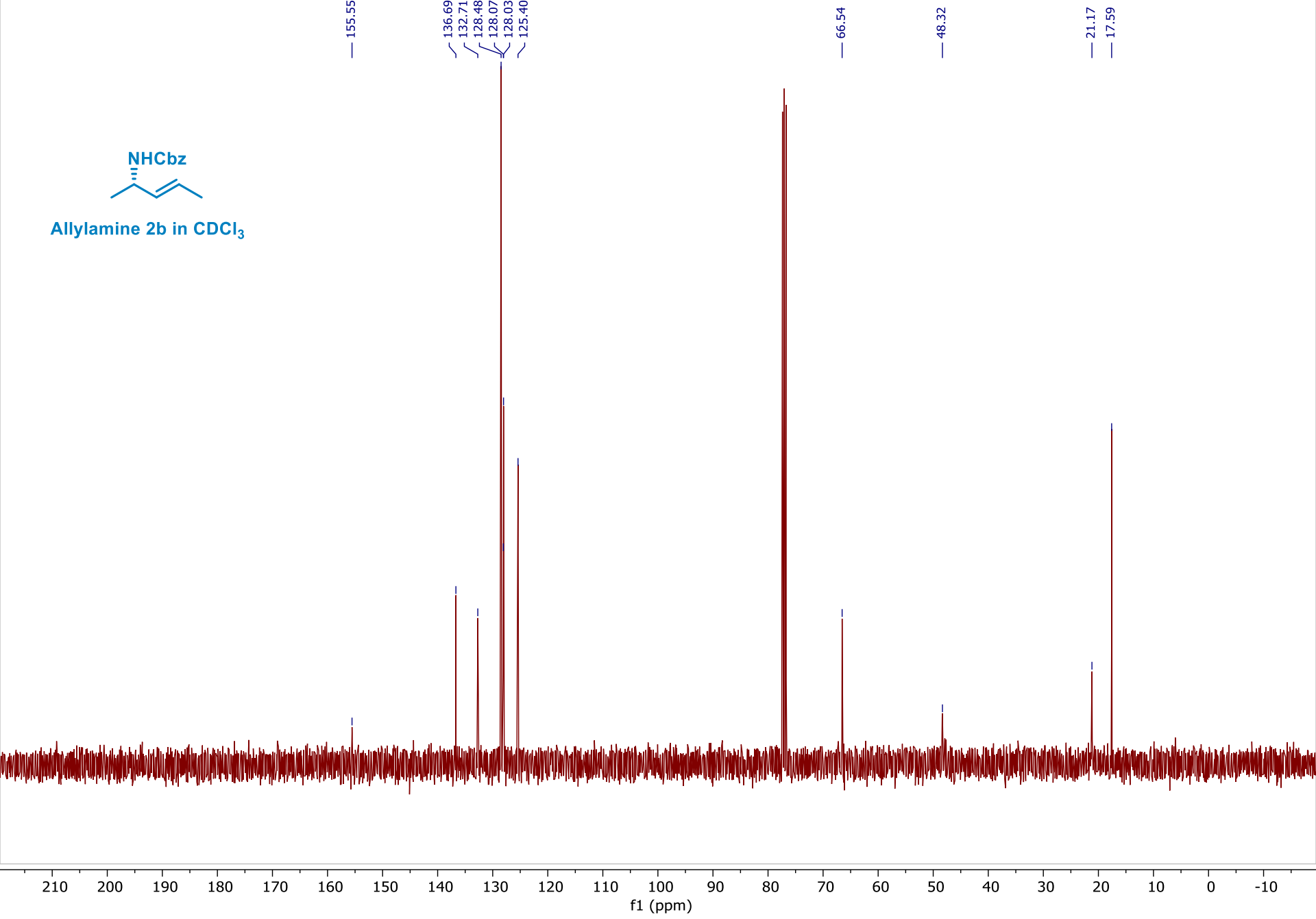
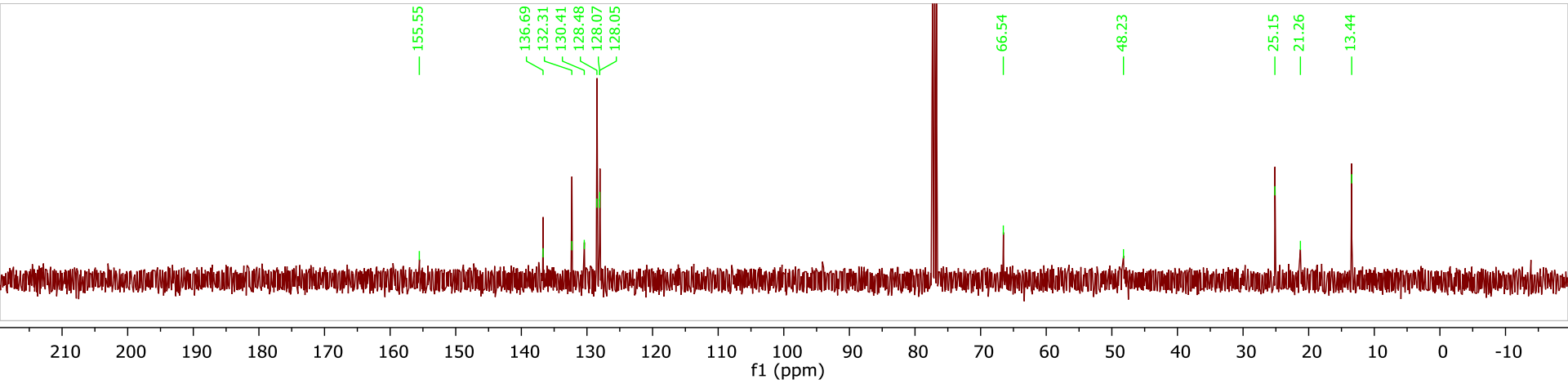
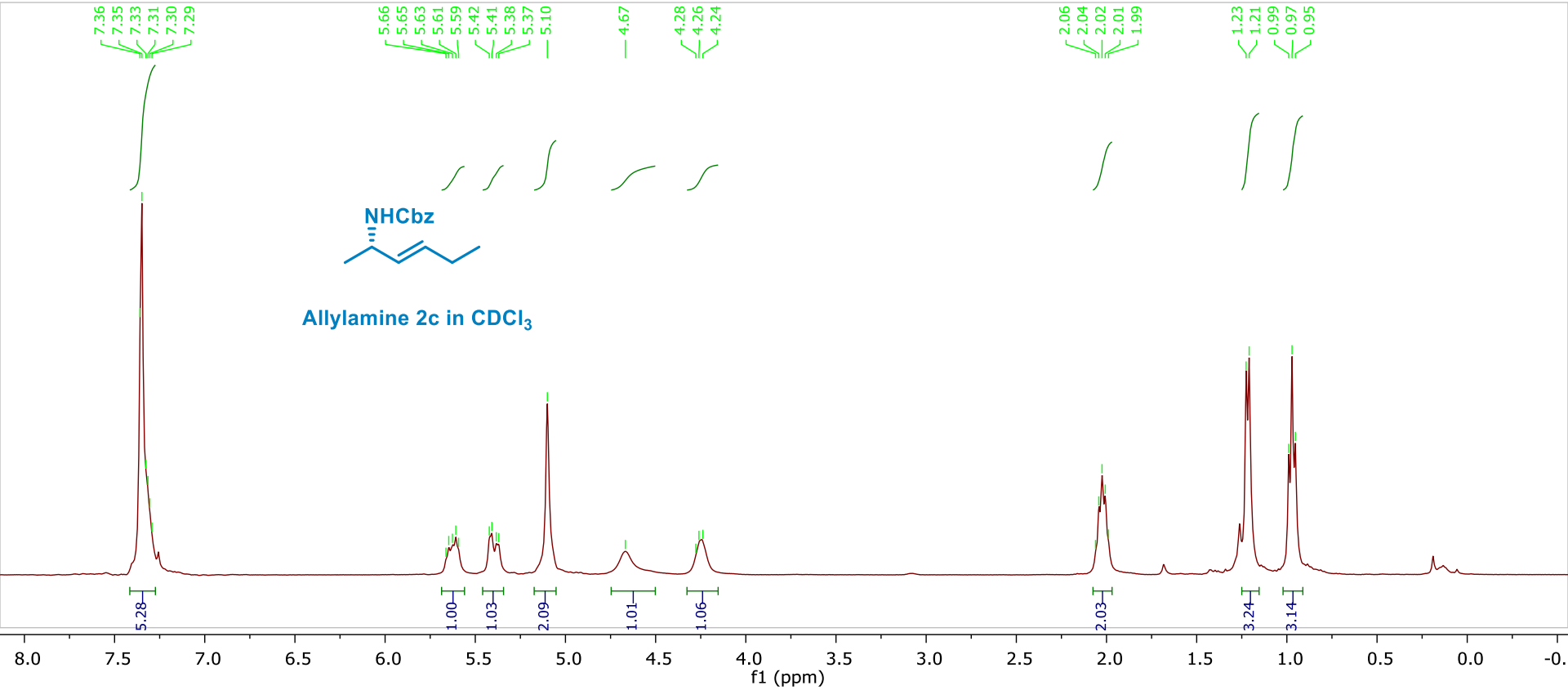
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.26
5.64
5.63
5.61
5.59
5.57
5.56
5.45
5.44
5.43
5.43
5.41
5.40
5.40
5.39
5.13
5.10
5.09
5.06
4.69
4.26
4.24
4.23
4.22
4.21
1.68
1.66
1.22
1.20
NHCbz
Allylamine 2b in CDCl3
5.30
1.00
0.98
2.01
0.94
1.00
3.04
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


155.55
136.69
132.71
128.48
128.07
128.03
125.40
66.54
48.32
21.17
17.59
NHCbz
Allylamine 2b in CDCl3
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)


155.55
136.69
132.31
130.41
128.48
128.07
128.05
66.54
48.23
25.15
21.26
13.44
f1 (ppm)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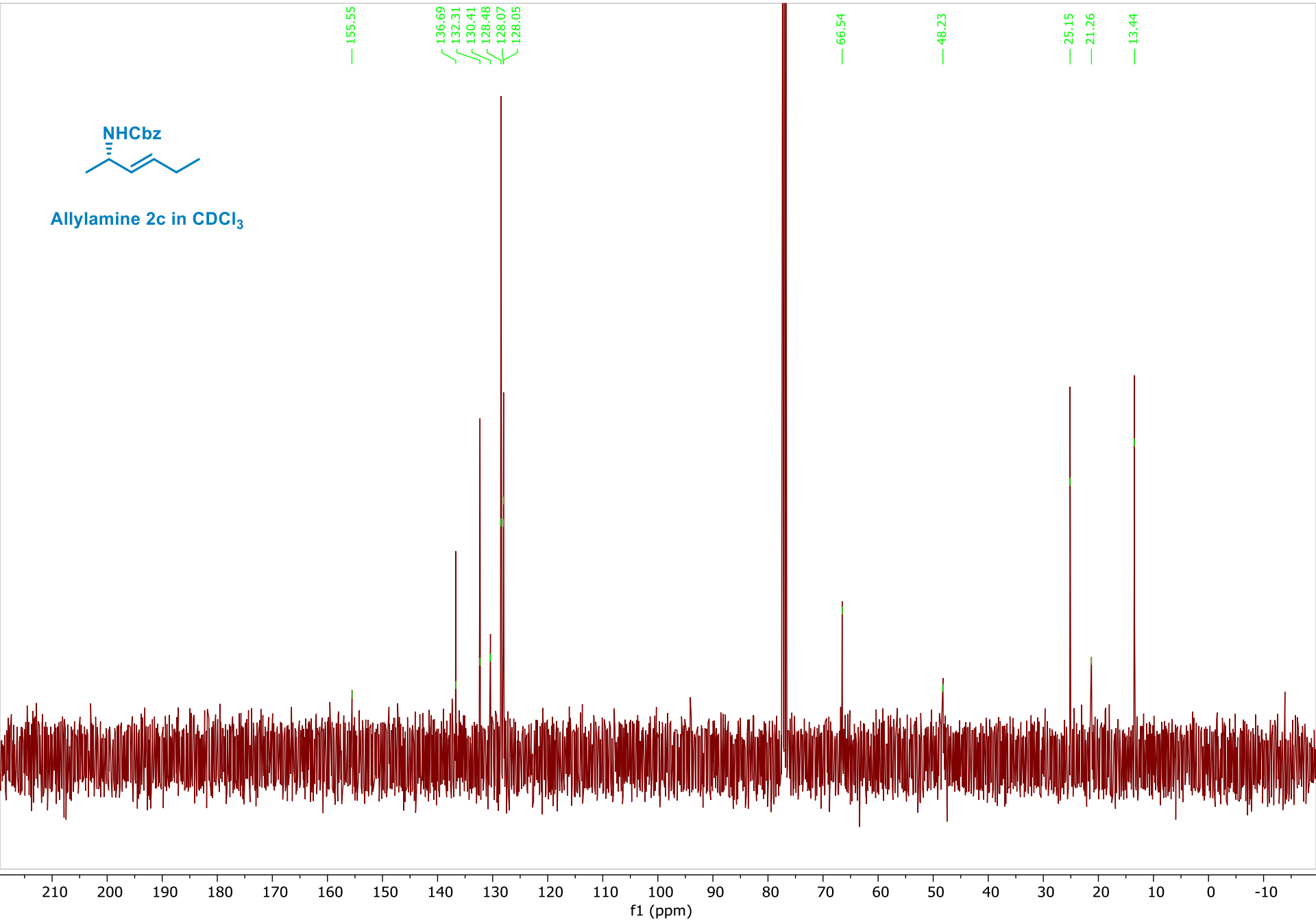
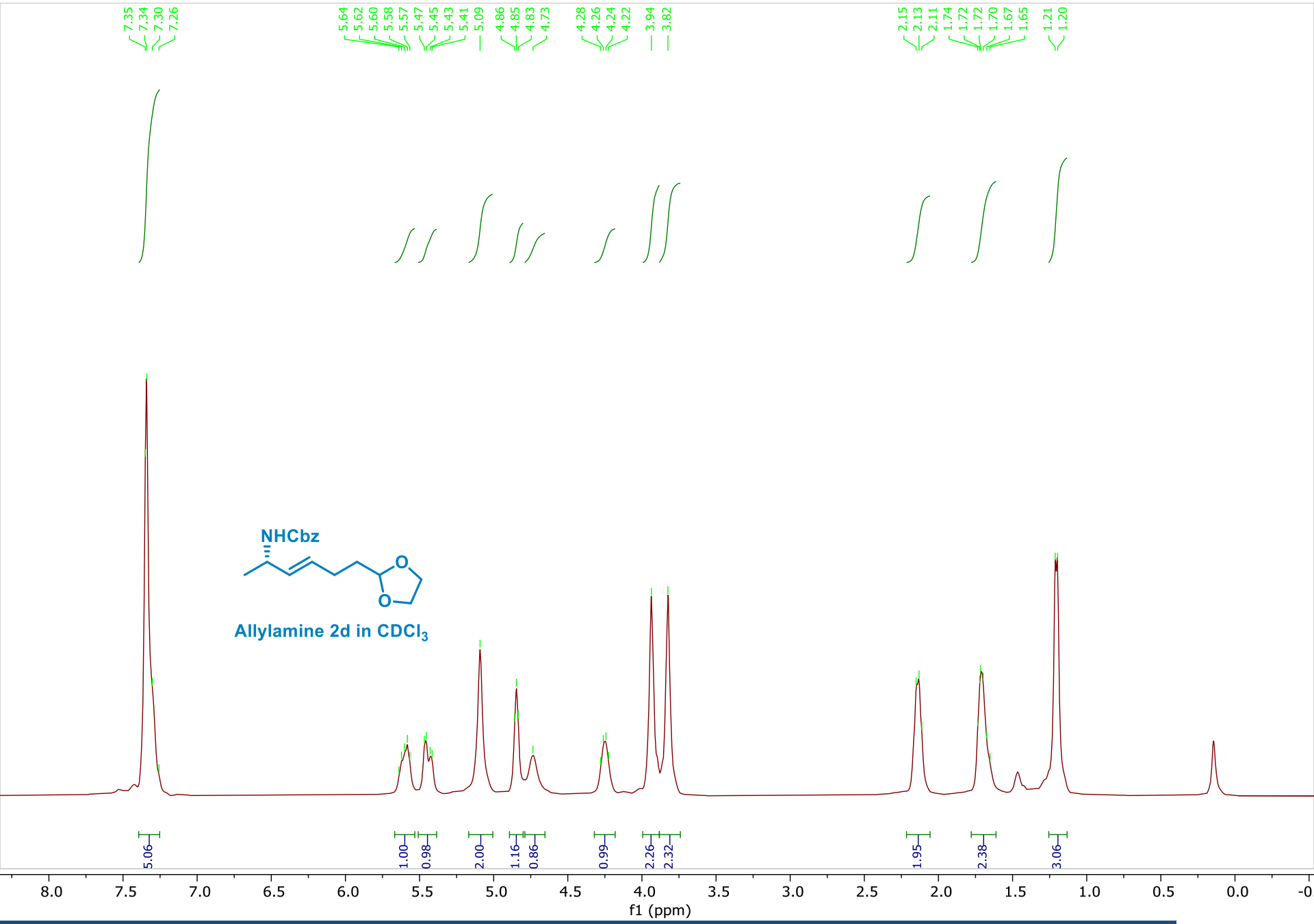
7.35
7.33
7.31
7.30
7.29
5.66
5.65
5.63
5.61
5.59
5.42
5.41
5.38
5.37
5.10
4.67
4.28
4.26
4.24
2.06
2.04
2.02
2.01
1.99
1.23
1.21
0.99
0.97
0.95
NHCbz
Allylamine 2c in CDCl3
5.28
1.00
1.03
2.09
1.01
1.06
2.03
3.24
3.14
f1 (ppm)


155.55
136.69
132.31
130.41
128.48
128.07
128.05
66.54
48.23
25.15
21.26
13.44
NHCbz
Allylamine 2c in CDCl3
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)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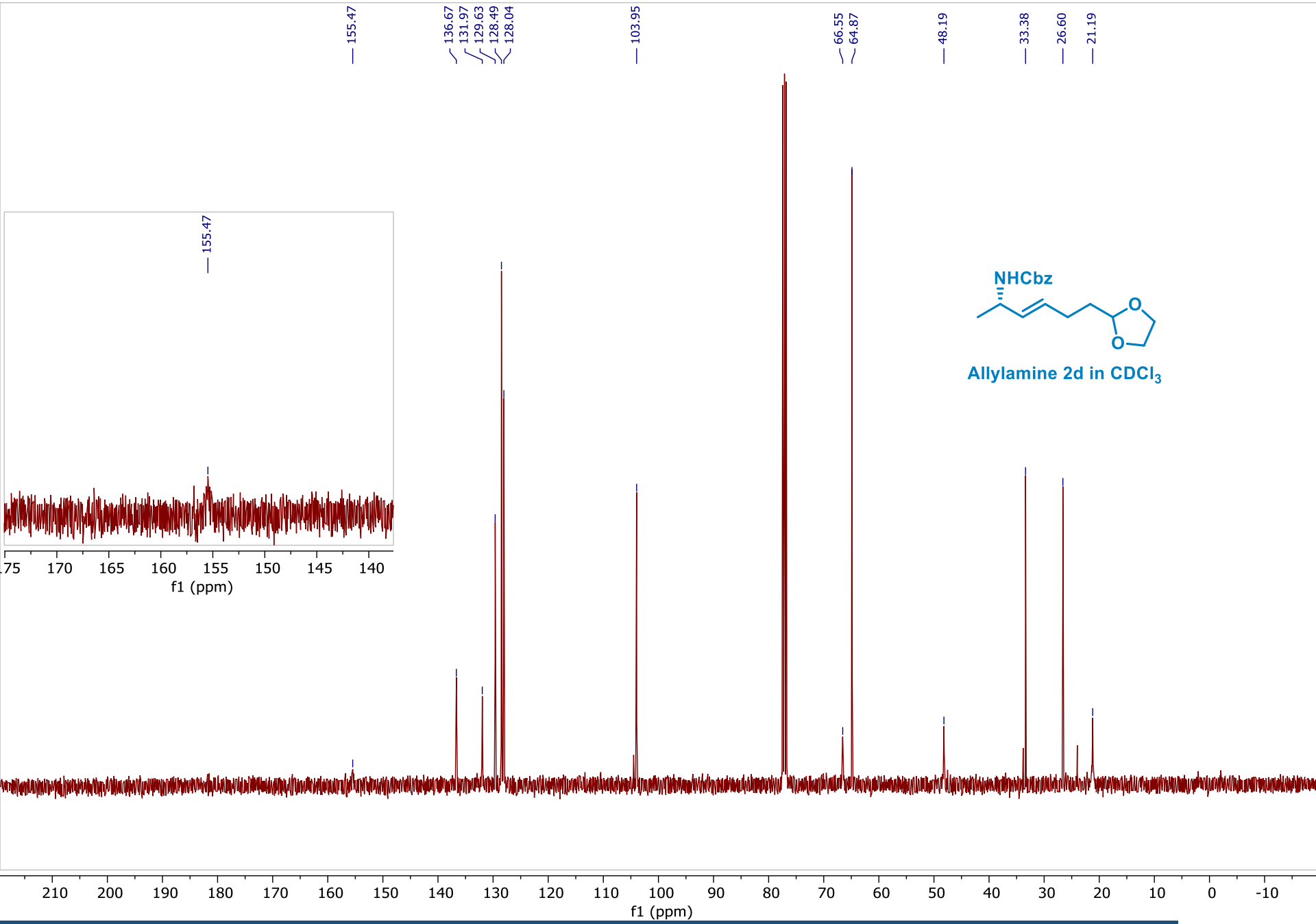
7.34
7.30
7.26
5.64
5.62
5.60
5.58
5.57
5.47
5.45
5.43
5.41
5.09
4.86
4.85
4.83
4.73
4.28
4.26
4.24
4.22
3.94
3.82
2.15
2.13
2.11
1.74
1.72
1.72
1.70
1.67
1.65
1.21
1.20
NHCbz
O
O
Allylamine 2d in CDCl3
5.06
1.00
0.98
2.00
1.16
0.86
0.99
2.26
2.32
1.95
2.38
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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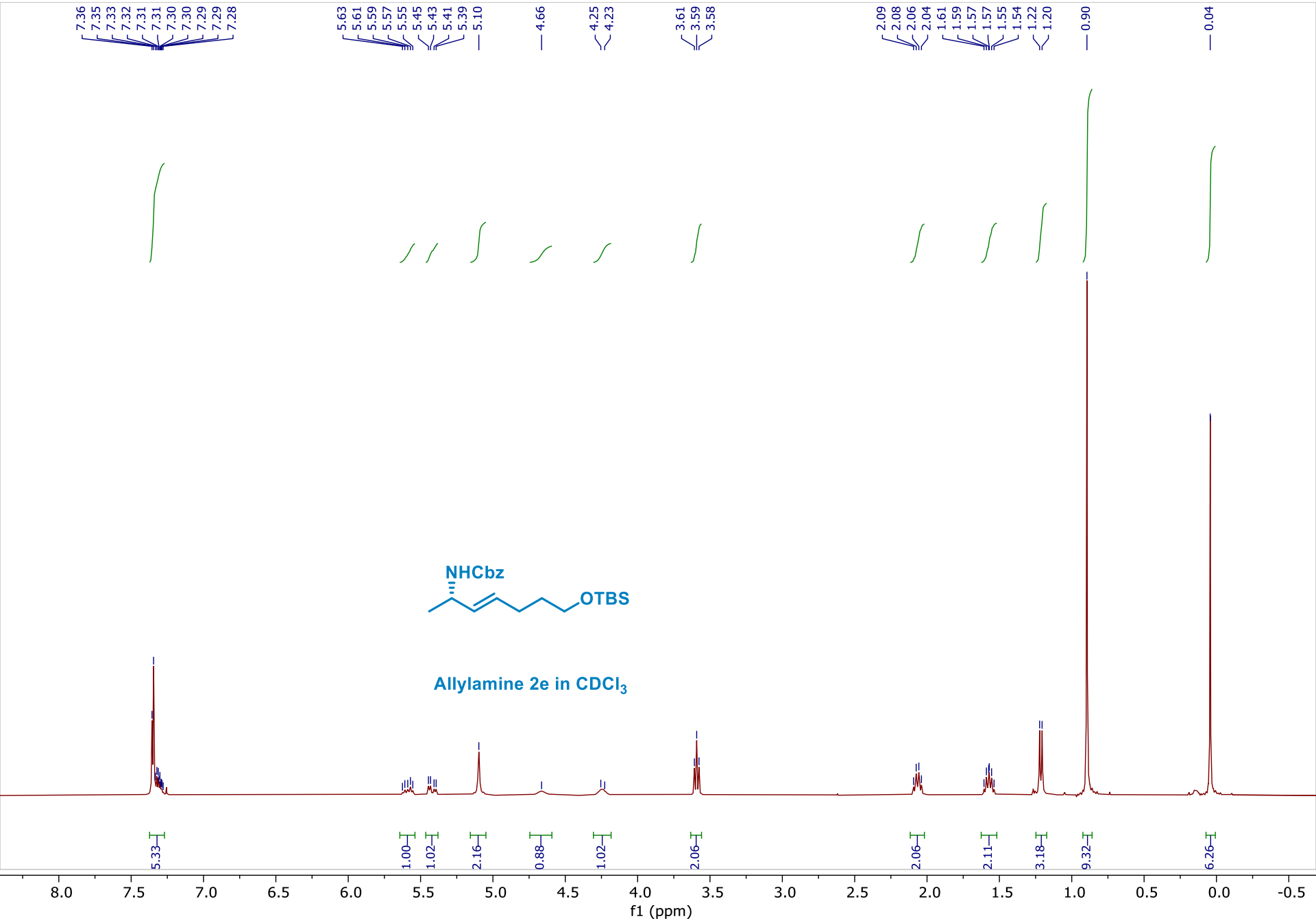
136.67
131.97
129.63
128.49
128.04
103.95
66.55
64.87
48.19
33.38
26.60
21.19
NHCbz
O
O
Allylamine 2d in CDCl3
f1 (ppm)
f1 (ppm)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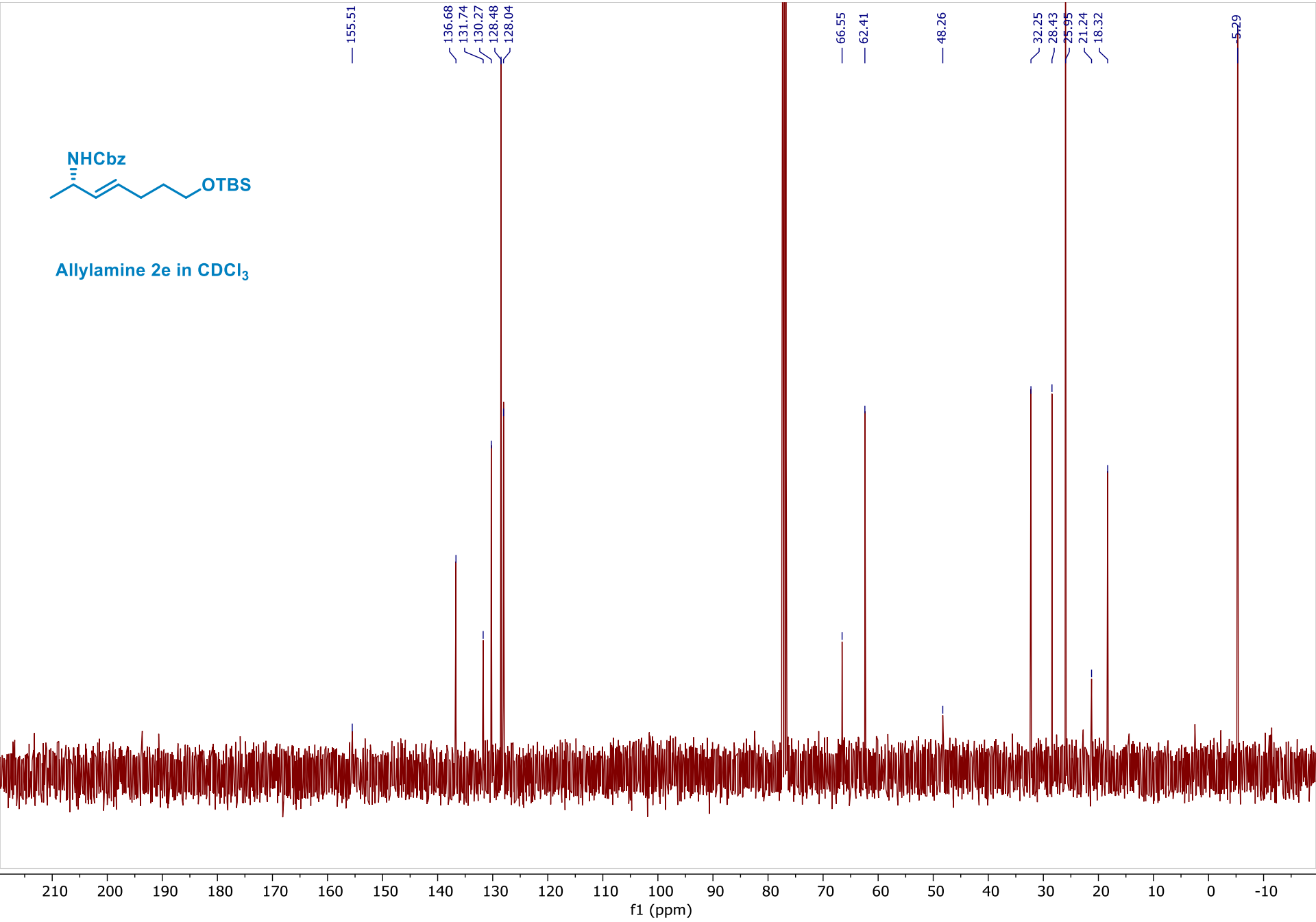
7.35
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
5.63
5.61
5.59
5.57
5.55
5.45
5.43
5.41
5.39
5.10
4.66
4.25
4.23
3.61
3.59
3.58
2.09
2.08
2.06
2.04
1.61
1.59
1.57
1.57
1.55
1.54
1.22
1.20
0.90
0.04
NHCbz
OTBS
Allylamine 2e in CDCl3
5.33
1.00
1.02
2.16
0.88
1.02
2.06
2.06
2.11
3.18
9.32
6.26
8.0
7.5
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)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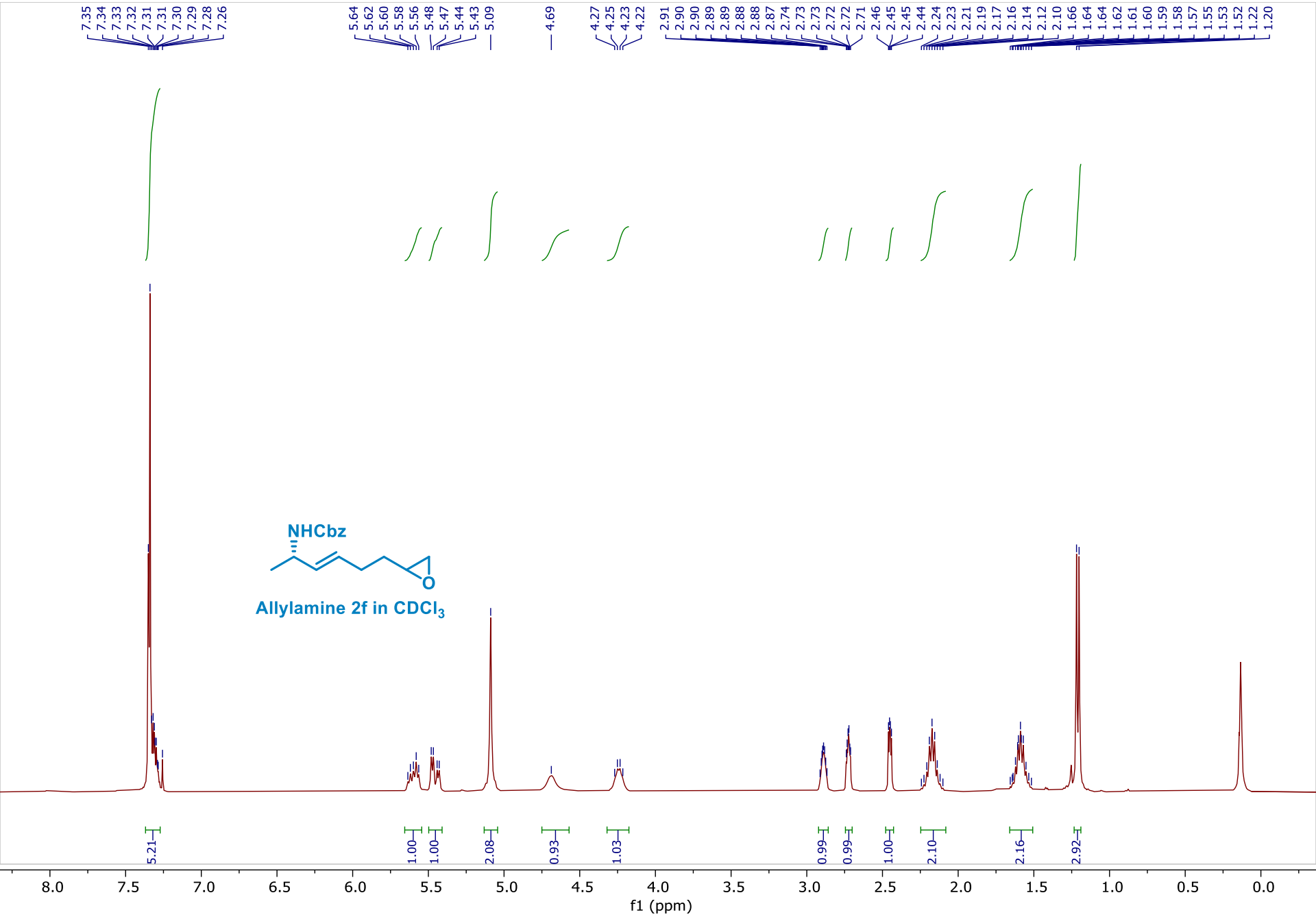
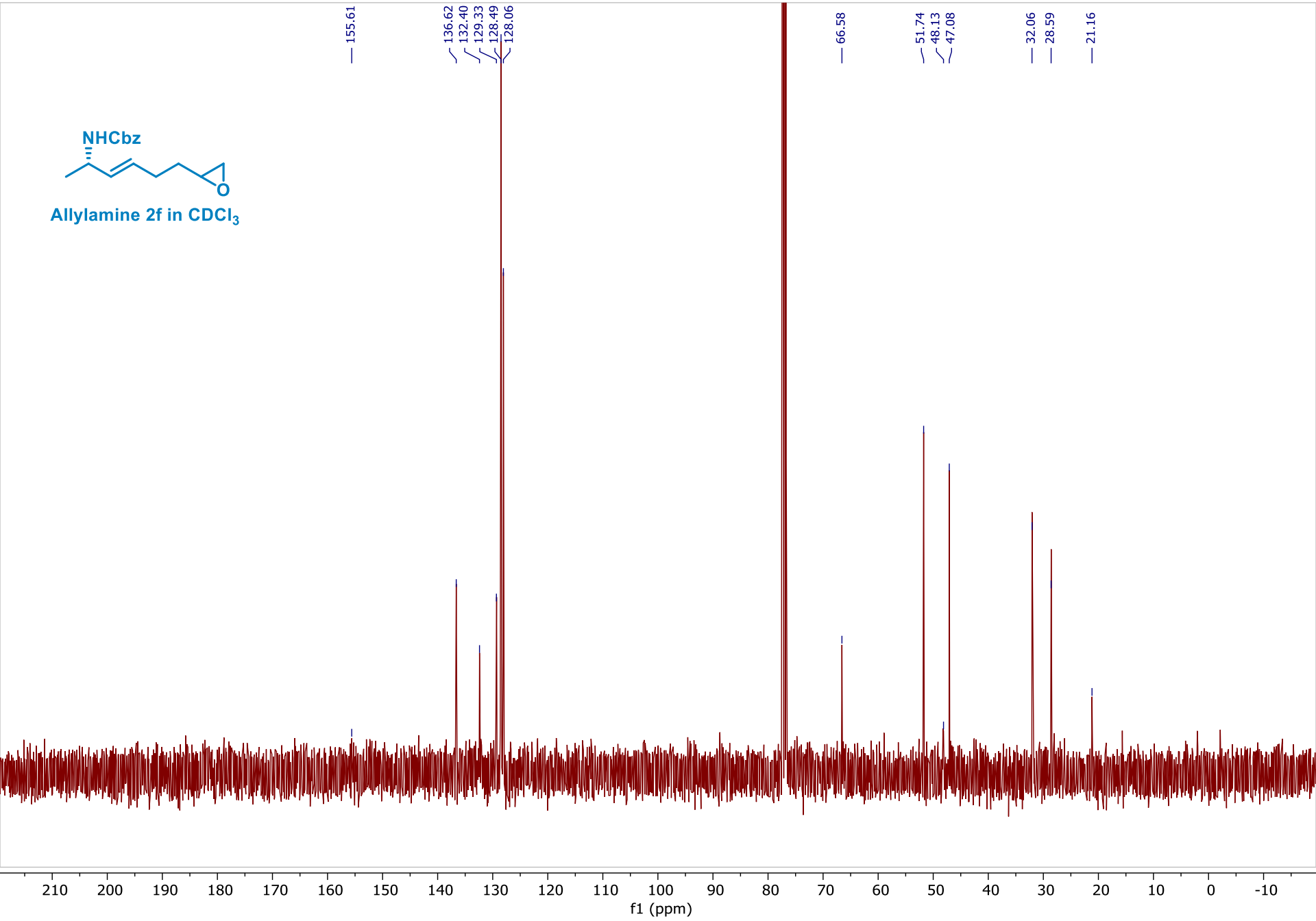
136.68
131.74
130.27
128.48
128.04
66.55
62.41
48.26
32.25
28.43
25.95
21.24
18.32
5.29
NHCbz
OTBS
Allylamine 2e in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NHCbz
O
Allylamine 2f in CDCl3
f1 (ppm)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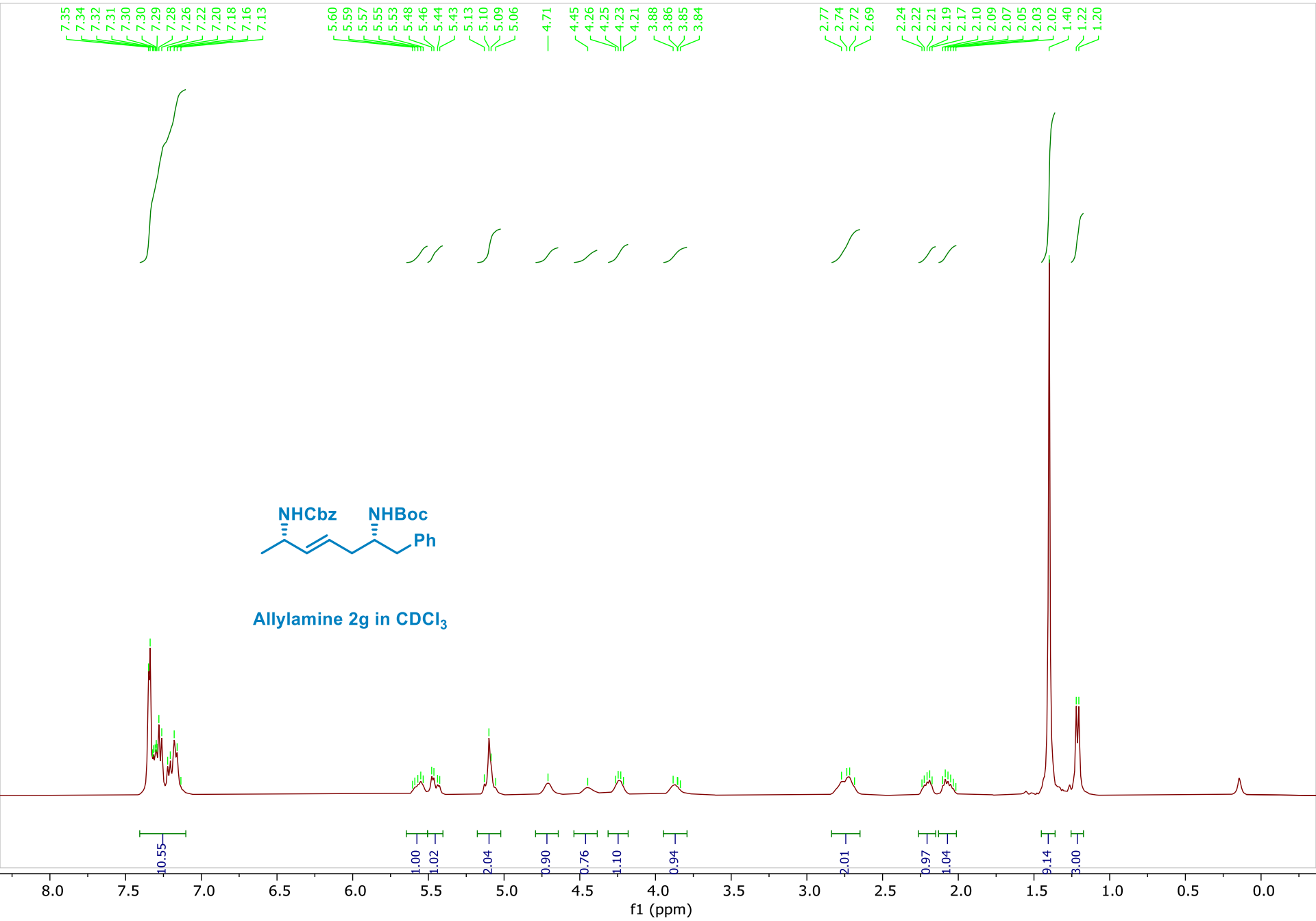
136.62
132.40
129.33
128.49
128.06
66.58
51.74
48.13
47.08
32.06
28.59
21.16
NHCbz
O
Allylamine 2f in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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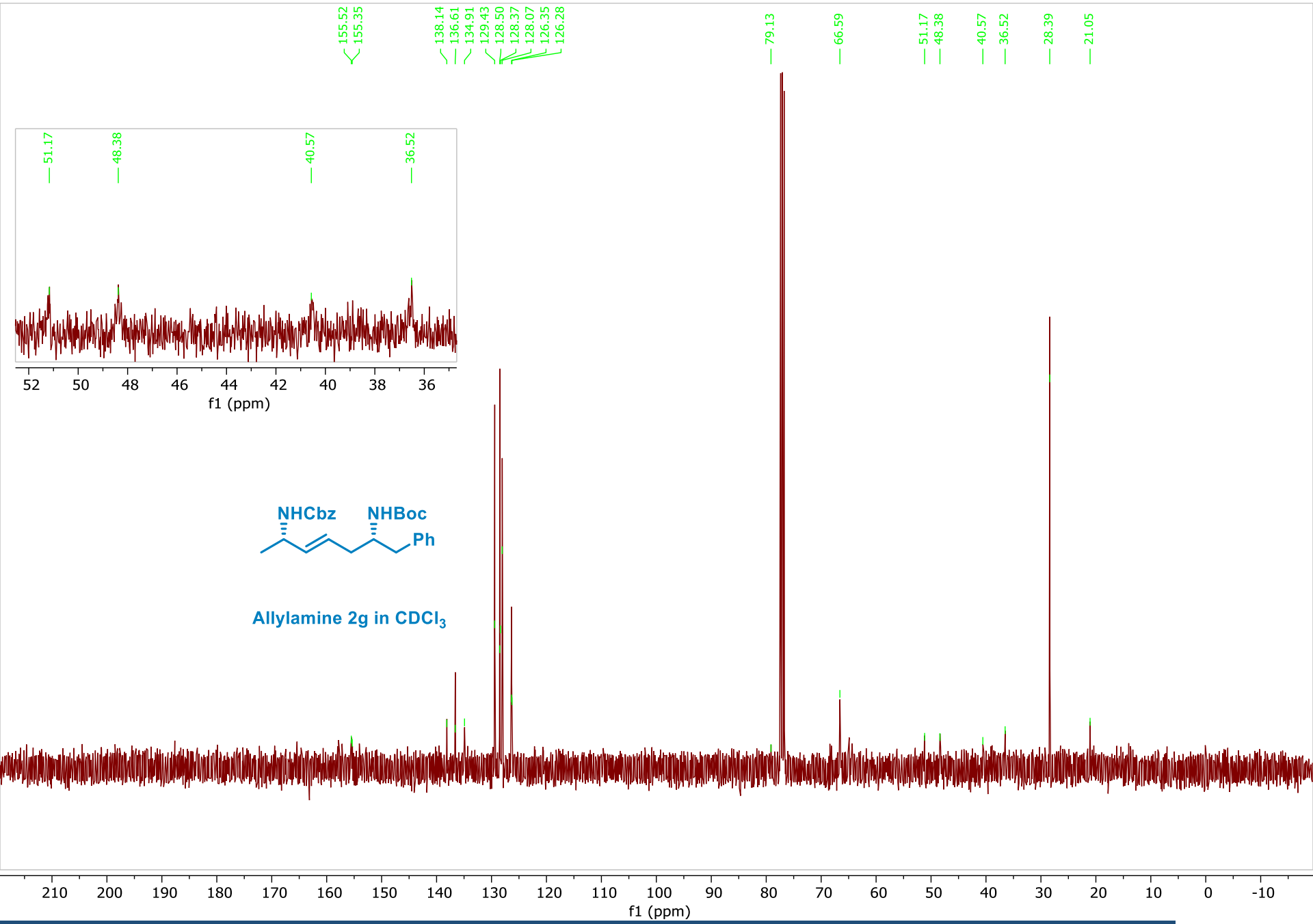
5.60 5.59 5.57 5.55 5.53 5.48 5.46 5.44 5.43 5.13 5.10 5.09 5.06
4.71
4.45 4.26 4.25 4.23 4.21
3.88 3.86 3.85 3.84
2.77 2.74 2.72 2.69
2.24 2.22 2.21 2.19 2.17 2.10 2.09 2.07 2.05 2.03 2.02
1.40 1.22 1.20
NHCbz
NHBoc
Ph
Allylamine 2g in CDCl3
10.55
1.00 1.02 2.04 0.90 0.76 1.10 0.94
2.01
0.97 1.04
9.14 3.00
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)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126.35
126.28
79.13
66.59
51.17
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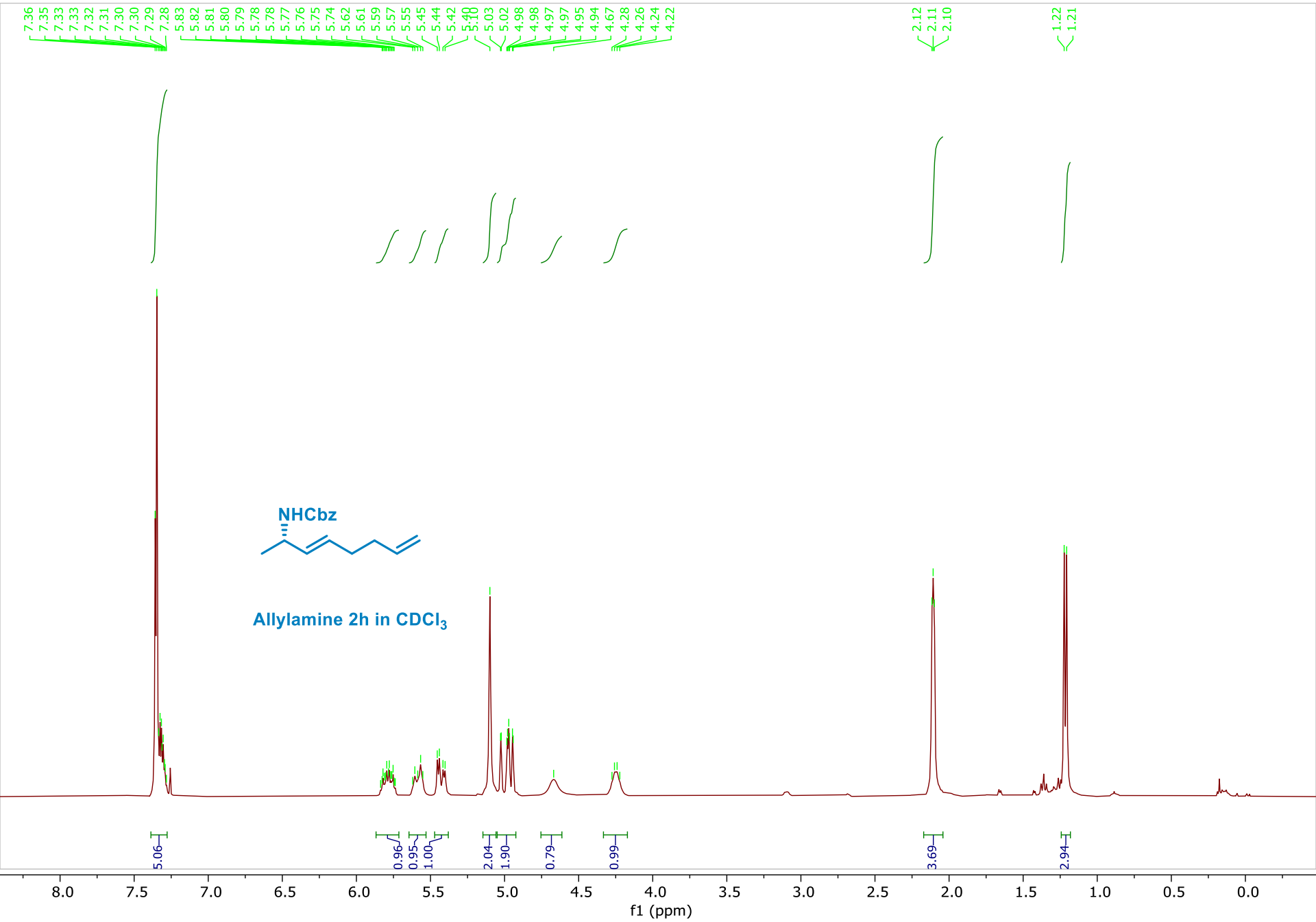
40.57
36.52
28.39
21.05
NHCbz
NHBoc
Ph
Allylamine 2g in CDCl3
f1 (ppm)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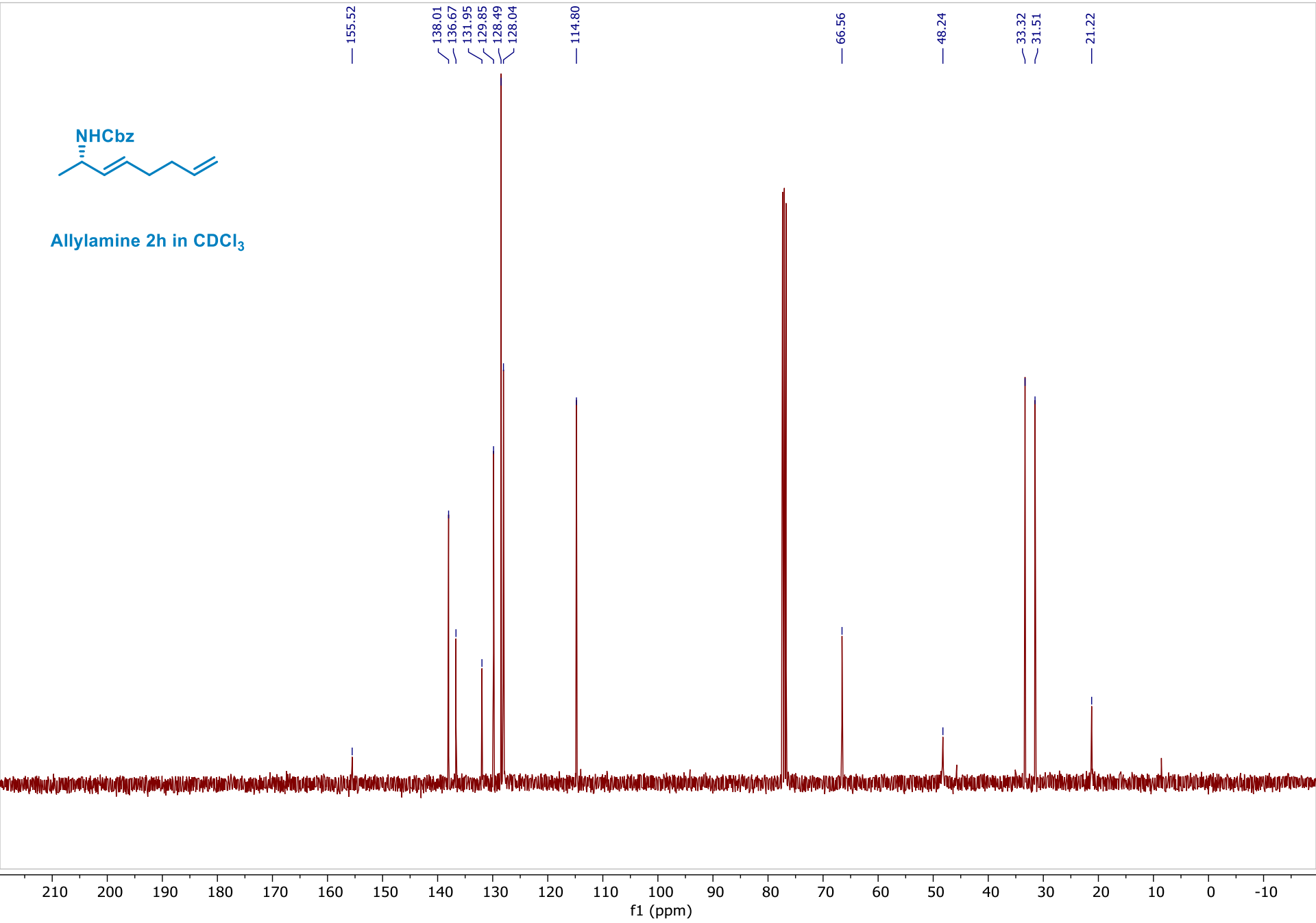
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.28
5.83
5.82
5.81
5.80
5.79
5.78
5.78
5.77
5.76
5.75
5.74
5.62
5.61
5.59
5.57
5.55
5.45
5.44
5.42
5.40
5.10
5.03
5.02
4.98
4.98
4.97
4.97
4.95
4.94
4.67
4.28
4.26
4.24
4.22
2.12
2.11
2.10
1.22
1.21
NHCbz
Allylamine 2h in CDCl3
5.06
0.96
0.95
1.00
2.04
1.90
0.79
0.99
3.69
2.94
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)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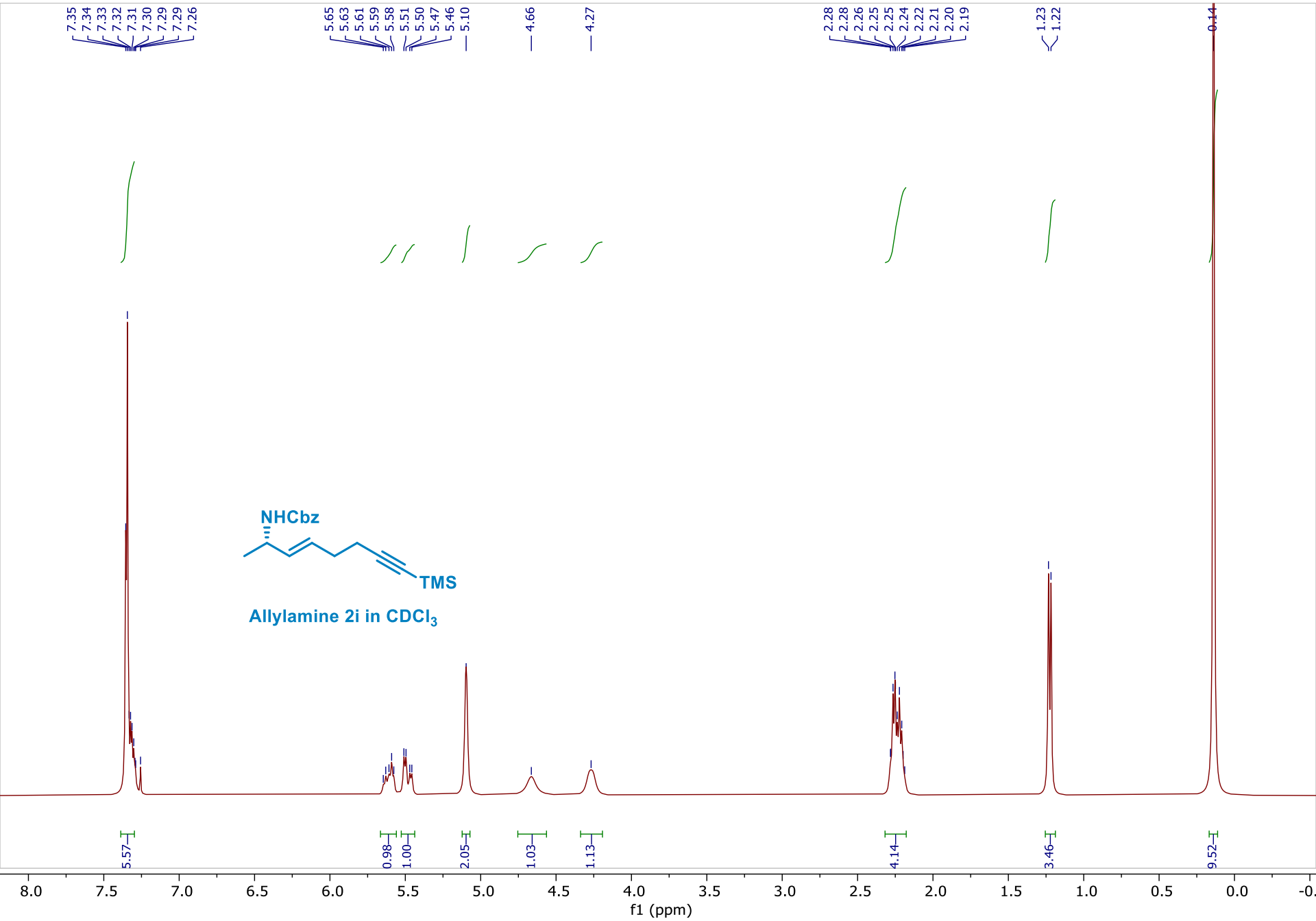
138.01
136.67
131.95
129.85
128.49
128.04
114.80
66.56
48.24
33.32
31.51
21.22
NHCbz
Allylamine 2h in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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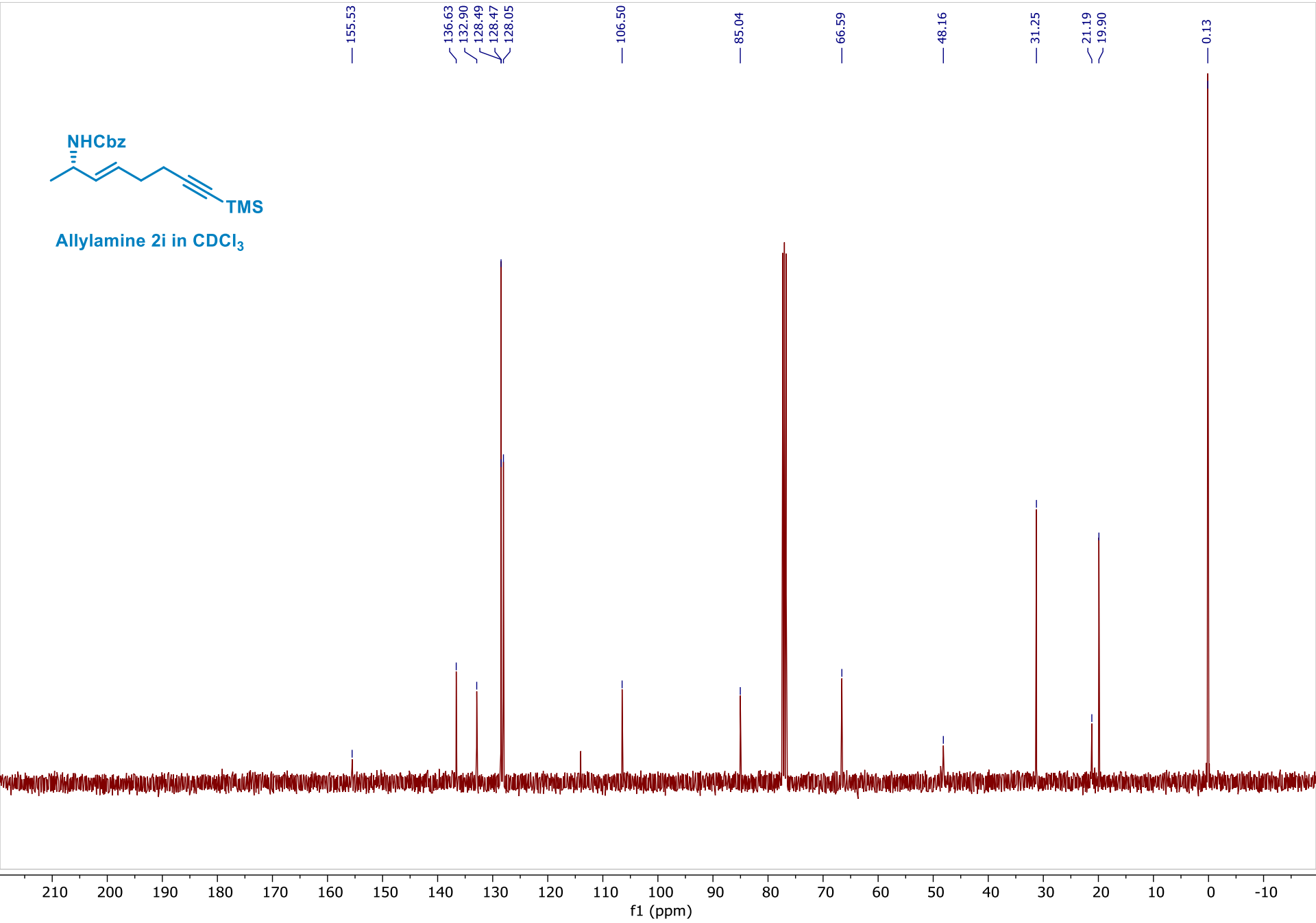
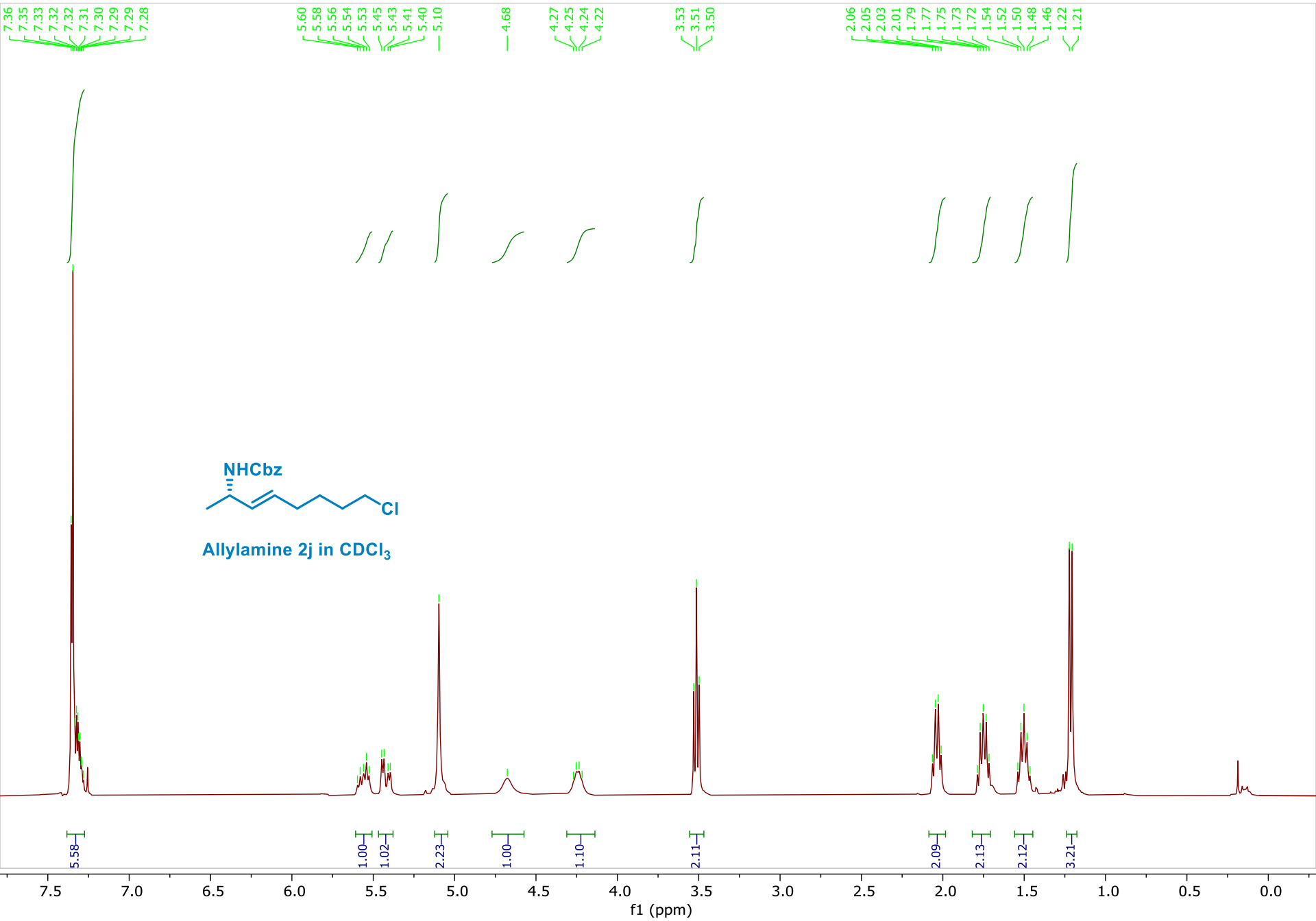
7.34
7.33
7.32
7.31
7.30
7.29
7.29
7.26
5.65
5.63
5.61
5.59
5.58
5.51
5.50
5.47
5.46
5.10
4.66
4.27
2.28
2.28
2.26
2.25
2.25
2.24
2.22
2.21
2.20
2.19
1.23
1.22
0.14
NHCbz
TMS
Allylamine 2i in CDCl3
5.57
0.98
1.00
2.05
1.03
1.13
4.14
3.46
9.52
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.53
136.63
132.90
128.49
128.47
128.05
106.50
85.04
66.59
48.16
31.25
21.19
19.90
0.13
NHCbz
TMS
Allylamine 2i in CDCl3
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)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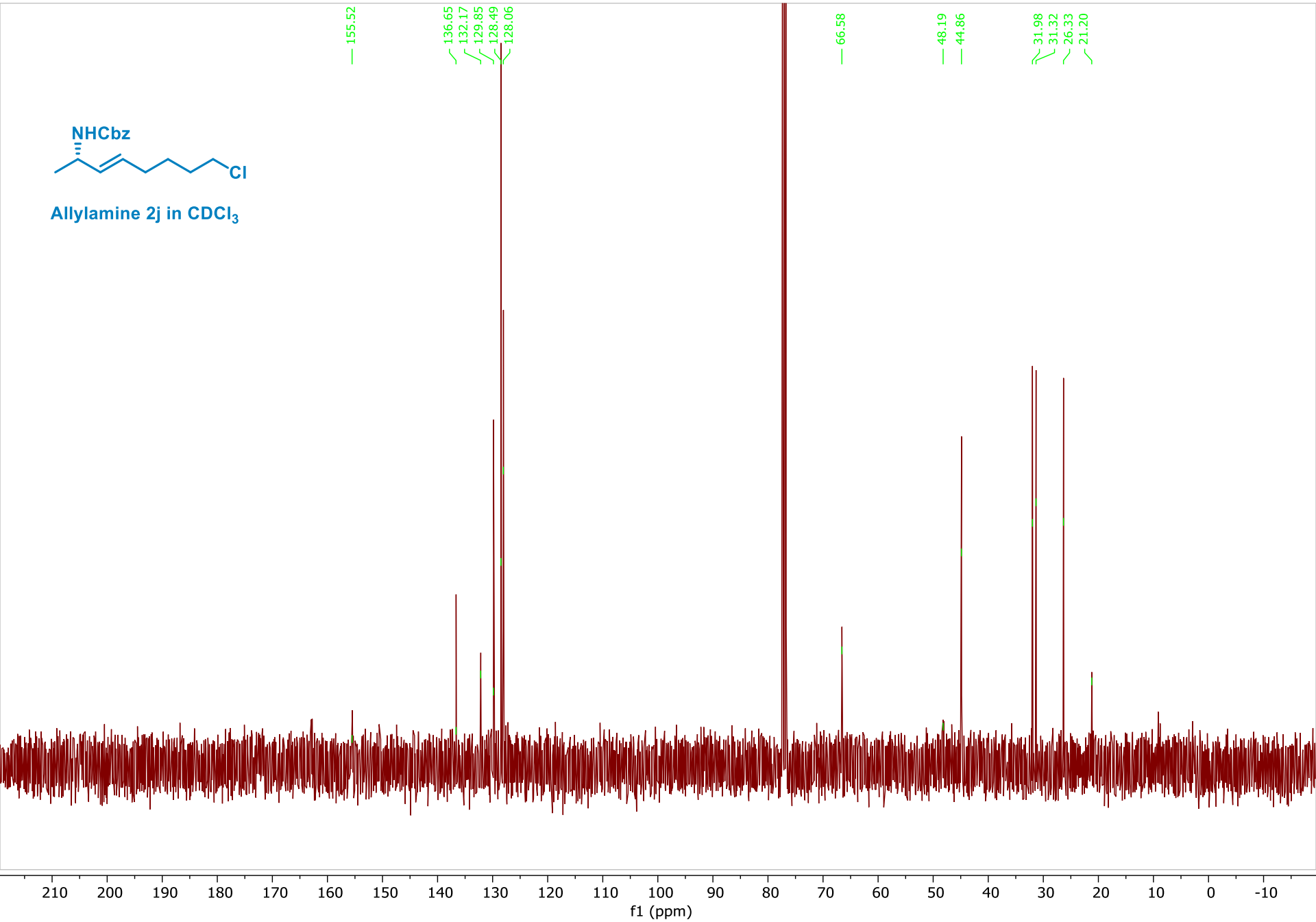
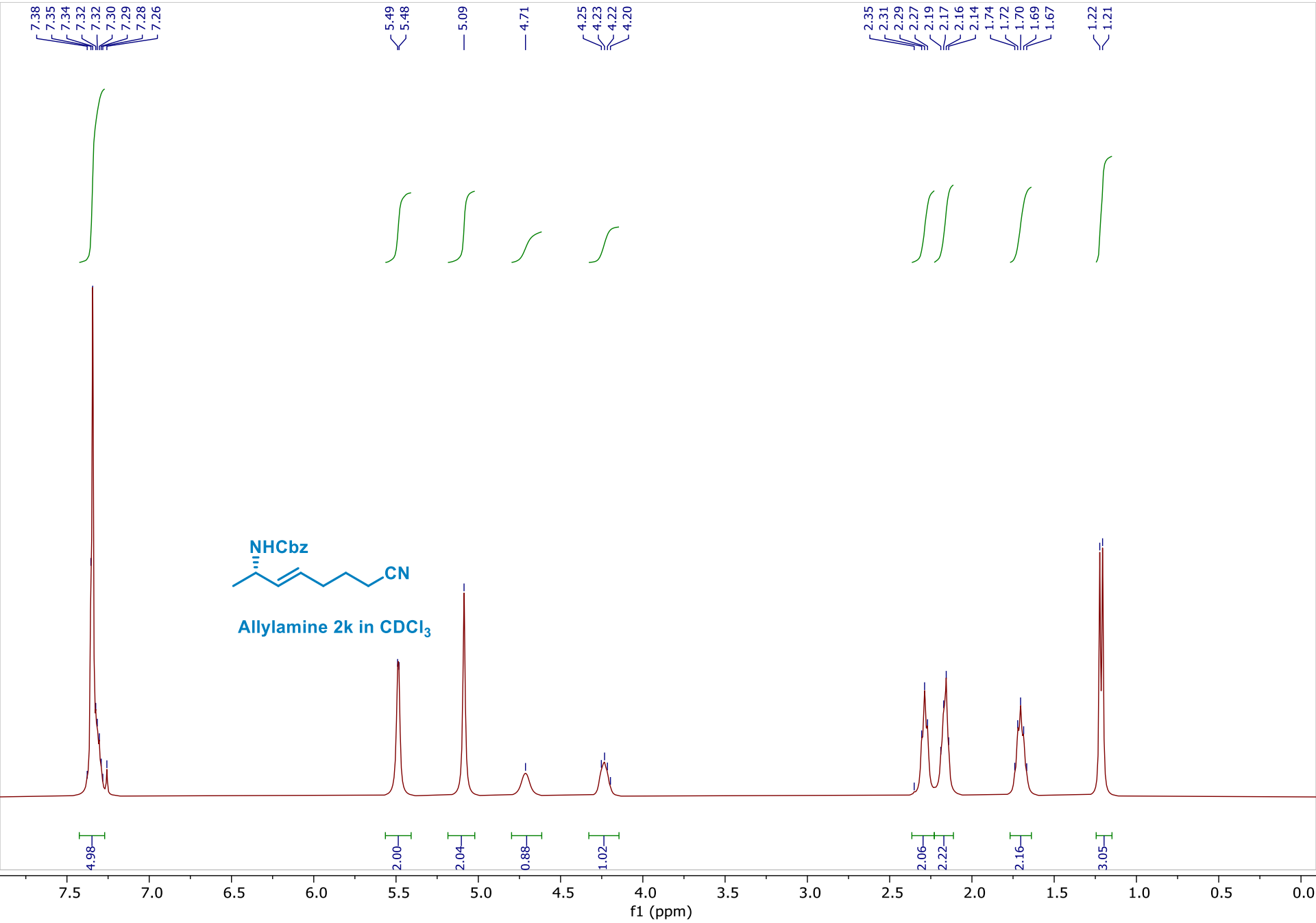
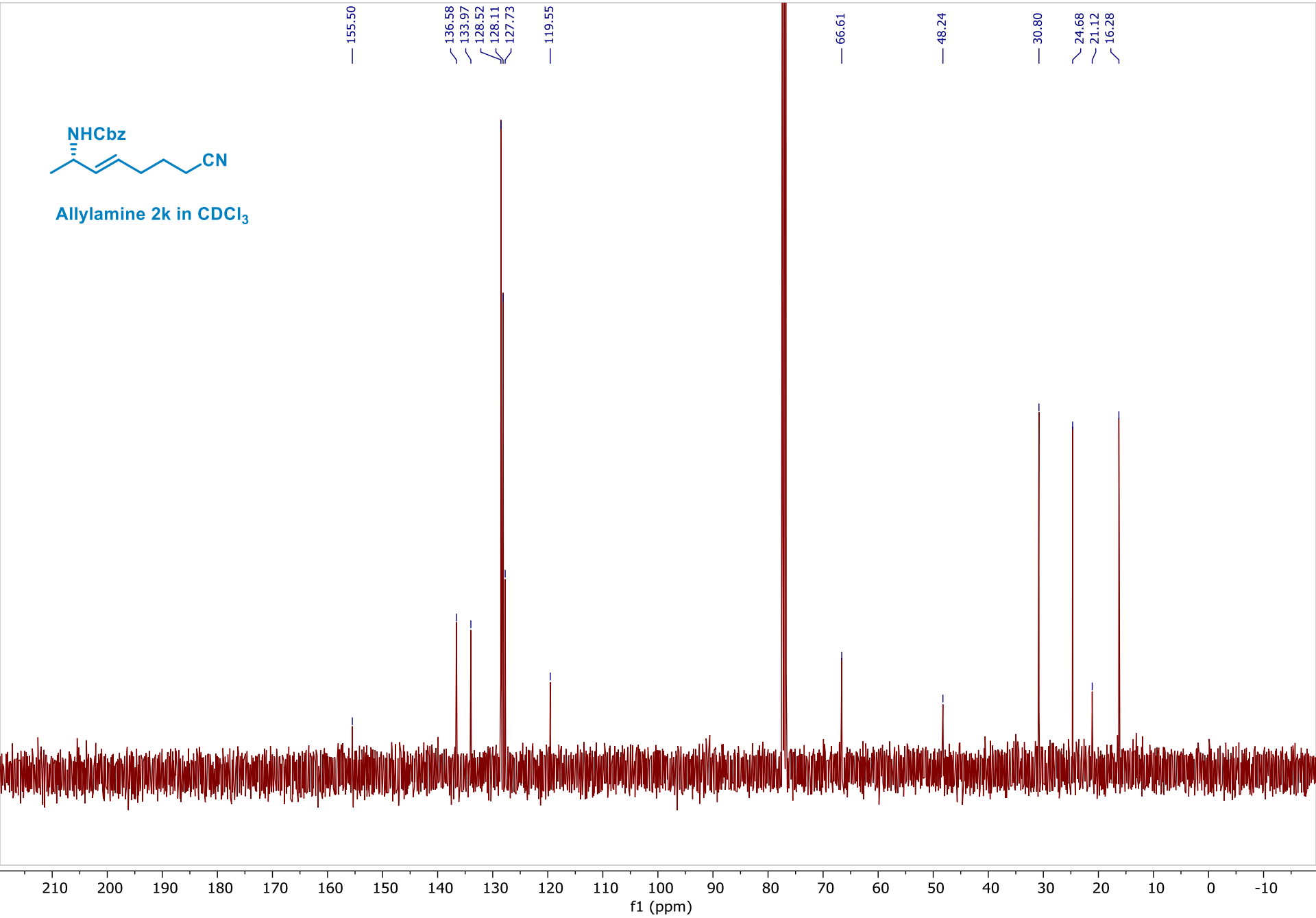
7.35
7.33
7.32
7.32
7.31
7.30
7.29
7.29
7.28
5.60
5.58
5.56
5.54
5.53
5.45
5.43
5.41
5.40
5.10
4.68
4.27
4.25
4.24
4.22
3.53
3.51
3.50
2.06
2.05
2.03
2.01
1.79
1.77
1.75
1.73
1.72
1.54
1.52
1.50
1.48
1.46
1.22
1.21
NHCbz
Cl
Allylamine 2j in CDCl3
5.58
1.00
1.02
2.23
1.00
1.10
2.11
2.09
2.13
2.12
3.21
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)


155.52
136.65
132.17
129.85
128.49
128.06
66.58
48.19
44.86
31.98
31.32
26.33
21.20
NHCbz
Cl
Allylamine 2j in CDCl3
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)


7.38
7.35
7.34
7.32
7.32
7.30
7.29
7.28
7.26
5.49
5.48
5.09
4.71
4.25
4.23
4.22
4.20
2.35
2.31
2.29
2.27
2.19
2.17
2.16
2.14
1.74
1.72
1.70
1.69
1.67
1.22
1.21
NHCbz
CN
Allylamine 2k in CDCl3
4.98
2.00
2.04
0.88
1.02
2.06
2.22
2.16
3.05
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)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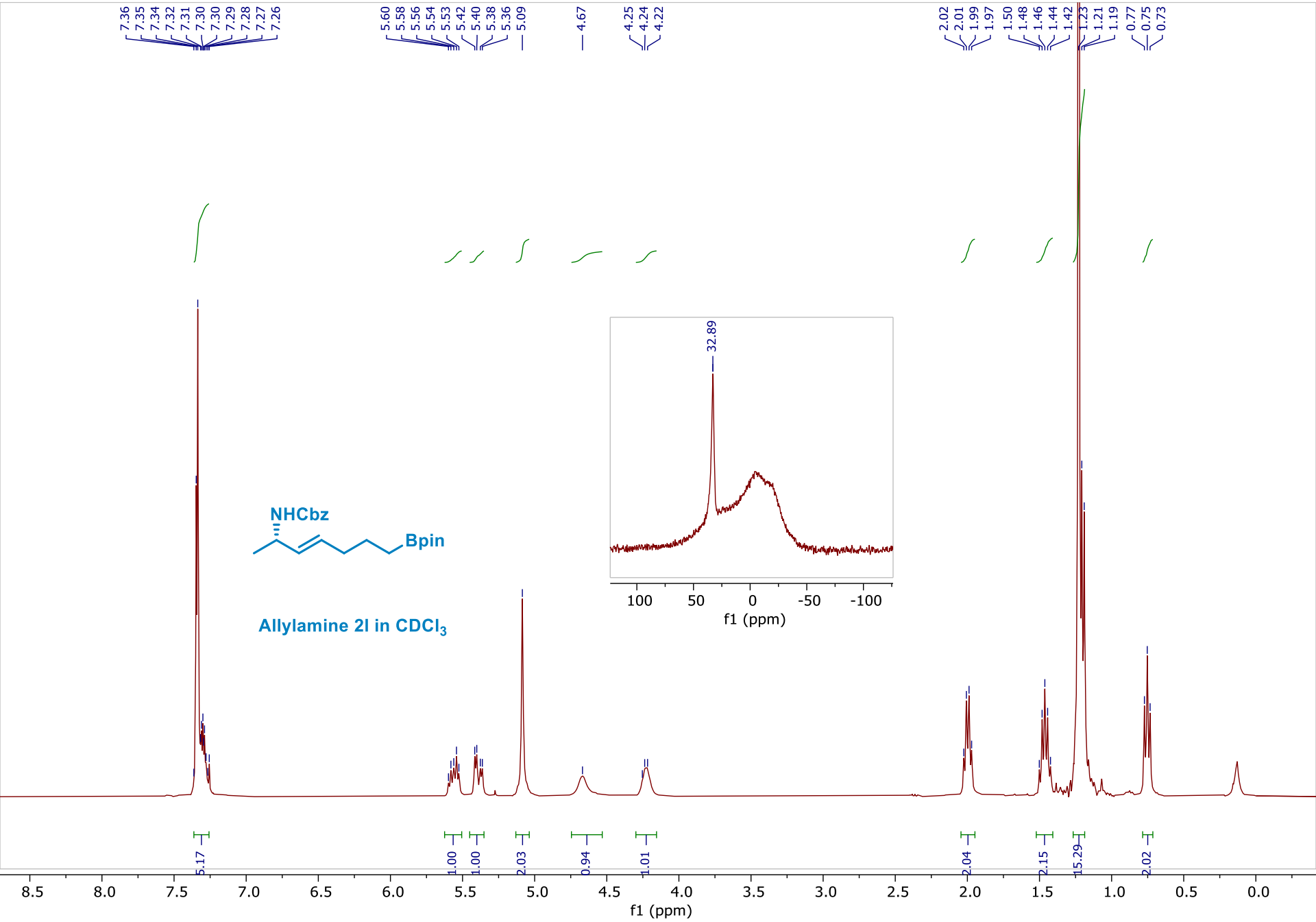
136.58
133.97
128.52
128.11
127.73
119.55
66.61
48.24
30.80
24.68
21.12
16.28
NHCbz
CN
Allylamine 2k in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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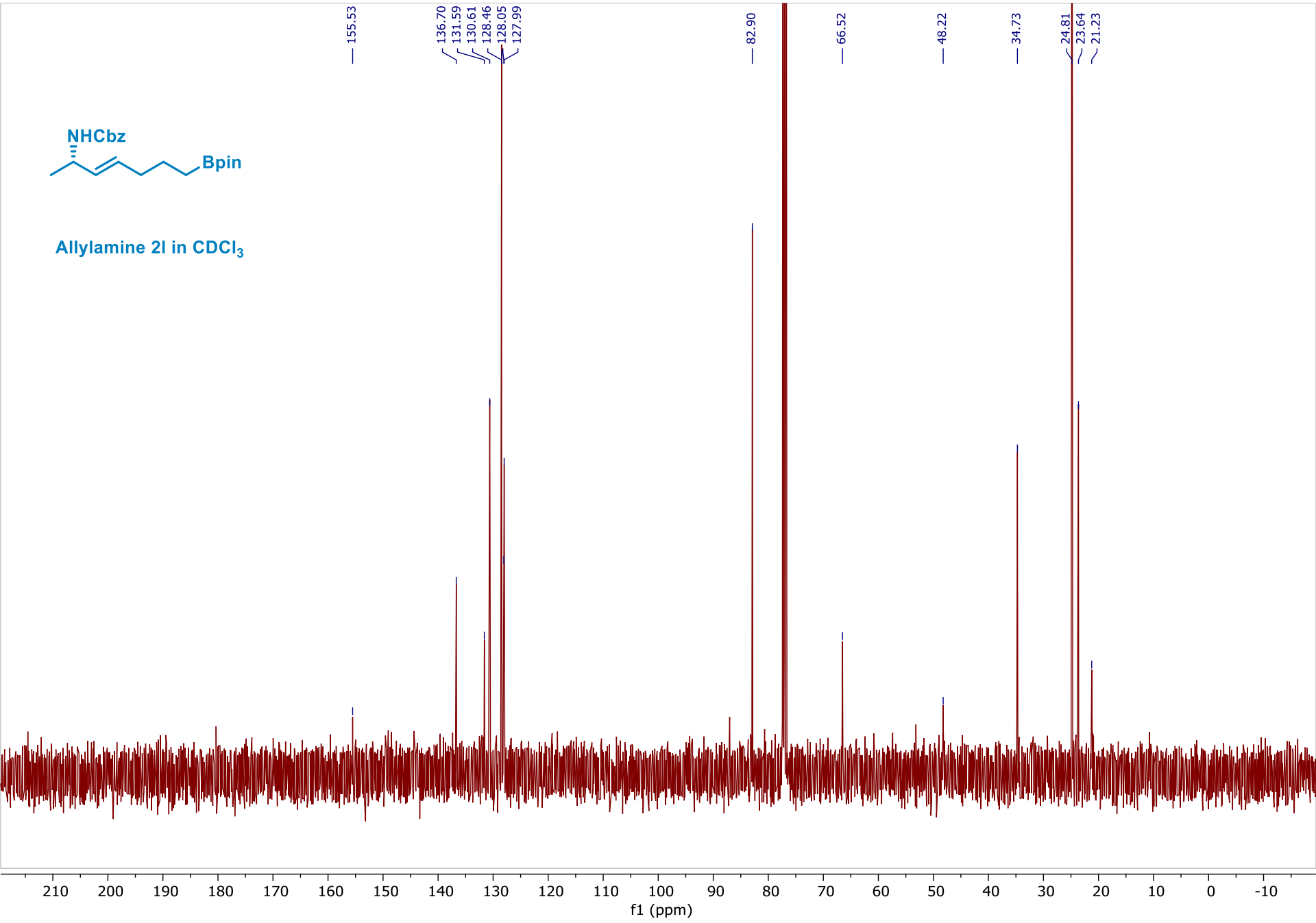
7.32
7.31
7.30
7.30
7.29
7.28
7.27
7.26
5.60
5.58
5.56
5.54
5.53
5.42
5.40
5.38
5.36
5.09
4.67
4.25
4.24
4.22
2.02
2.01
1.99
1.97
1.50
1.48
1.46
1.44
1.42
1.23
1.21
1.19
0.77
0.75
0.73
NHCbz
Bpin
Allylamine 2l in CDCl3
32.89
100
50
0
-50
-100
f1 (ppm)
5.17
1.00
1.00
2.03
0.94
1.01
2.04
2.15
15.29
2.02
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)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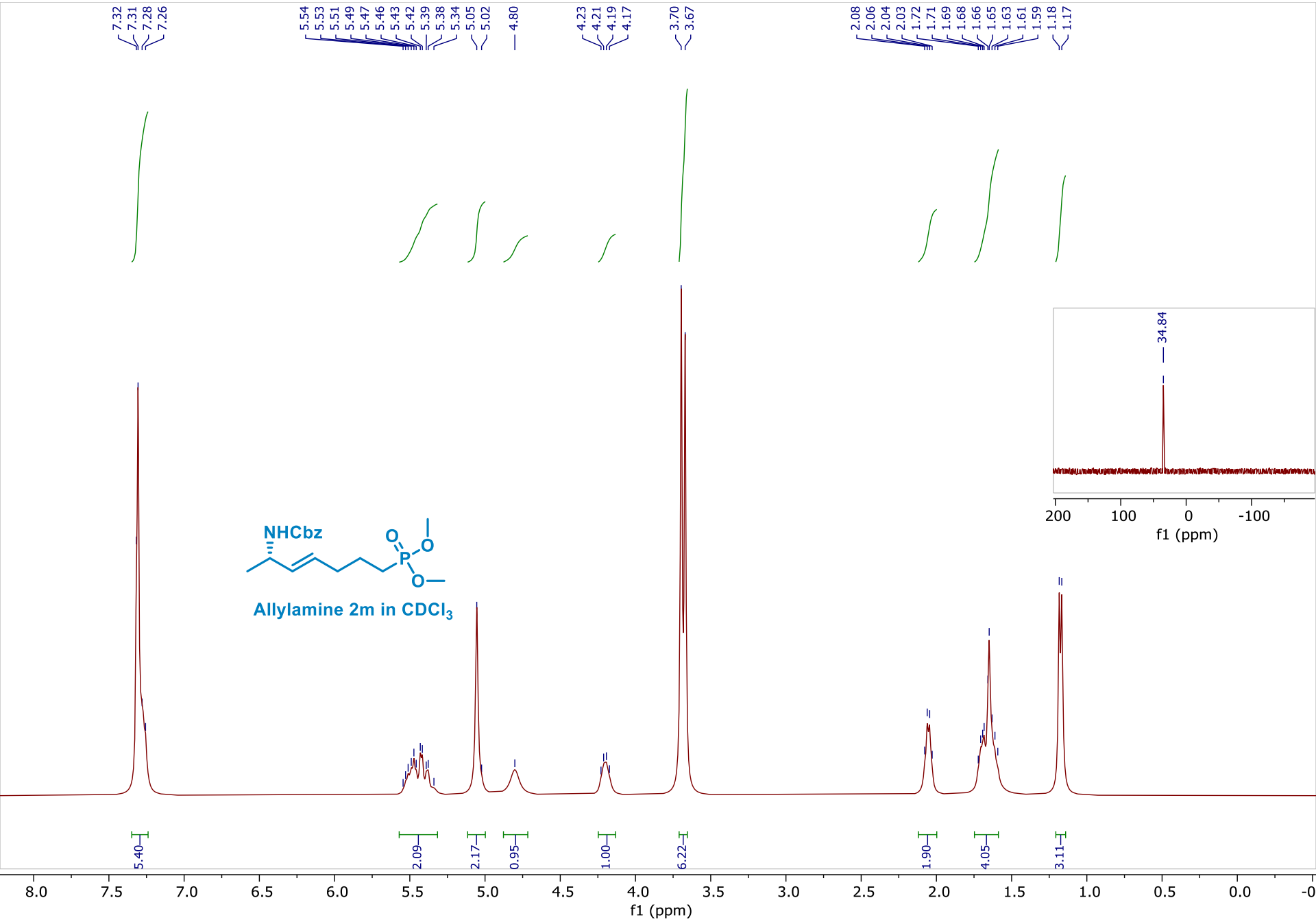
136.70
131.59
130.61
128.46
128.05
127.99
82.90
66.52
48.22
34.73
24.81
23.64
21.23
NHCbz
Bpin
Allylamine 2l in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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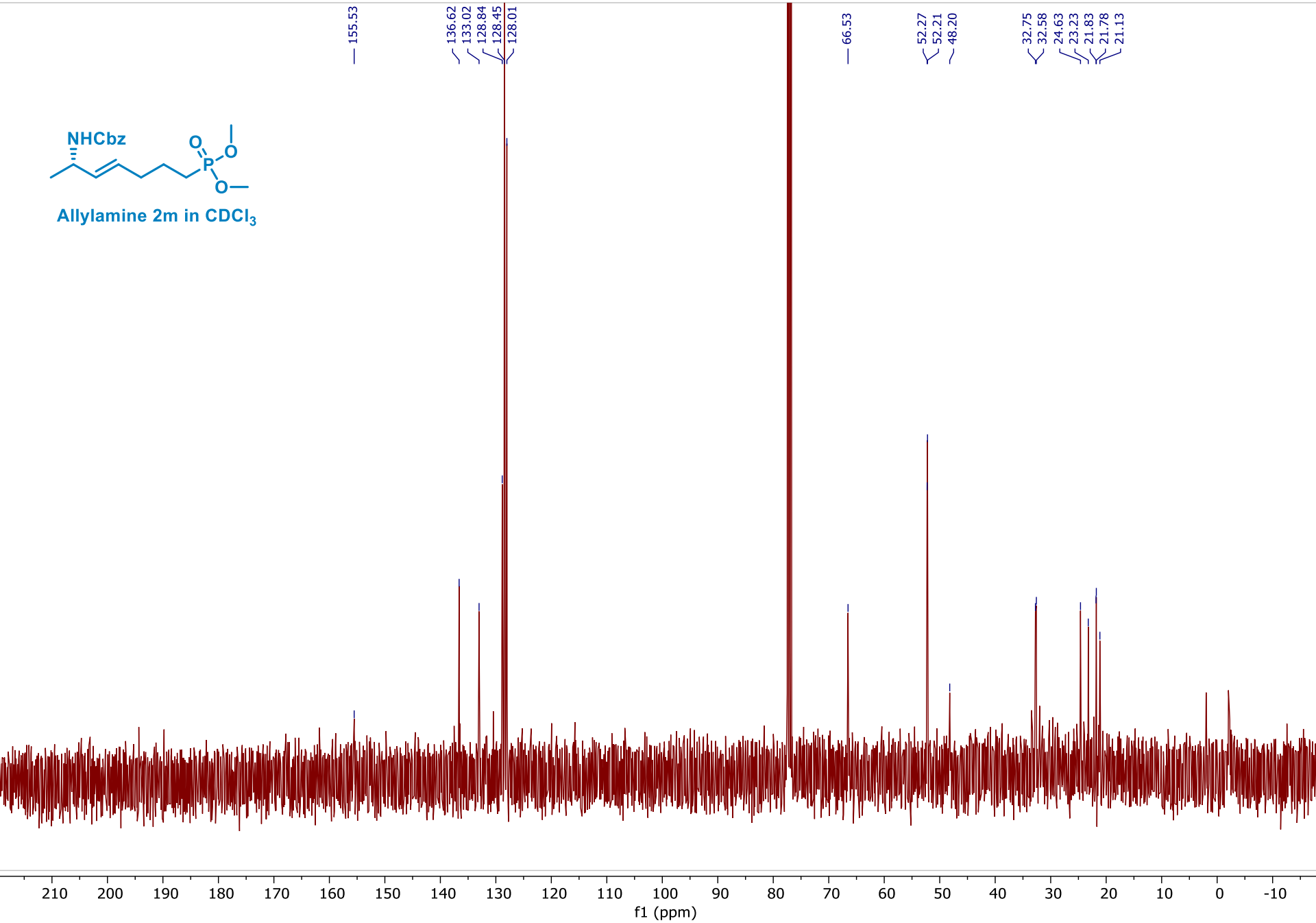
7.31
7.28
7.26
5.54
5.53
5.51
5.49
5.47
5.46
5.43
5.42
5.39
5.38
5.34
5.05
5.02
4.80
4.23
4.21
4.19
4.17
3.70
3.67
2.08
2.06
2.04
2.03
1.72
1.71
1.69
1.68
1.66
1.65
1.63
1.61
1.59
1.18
1.17
34.84
200
100
0
-100
f1 (ppm)
NHCbz
O
O
P
O
O
Allylamine 2m in CDCl3
5.40
2.09
2.17
0.95
1.00
6.22
1.90
4.05
3.11
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
f1 (ppm)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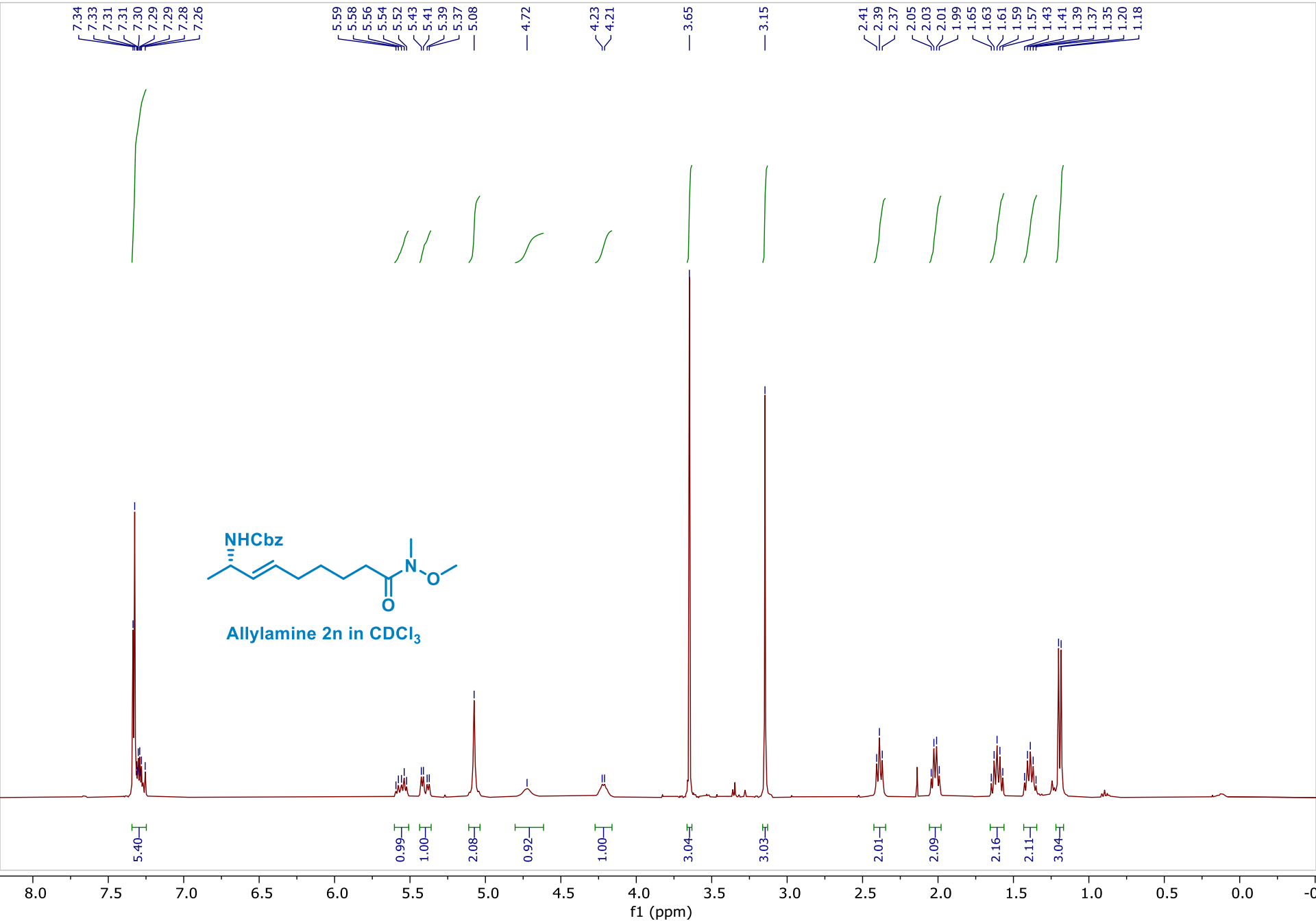
136.62
133.02
128.84
128.45
128.01
66.53
52.27
52.21
48.20
32.75
32.58
24.63
23.23
21.83
21.78
21.13
NHCbz
O
O
P
O
Allylamine 2m in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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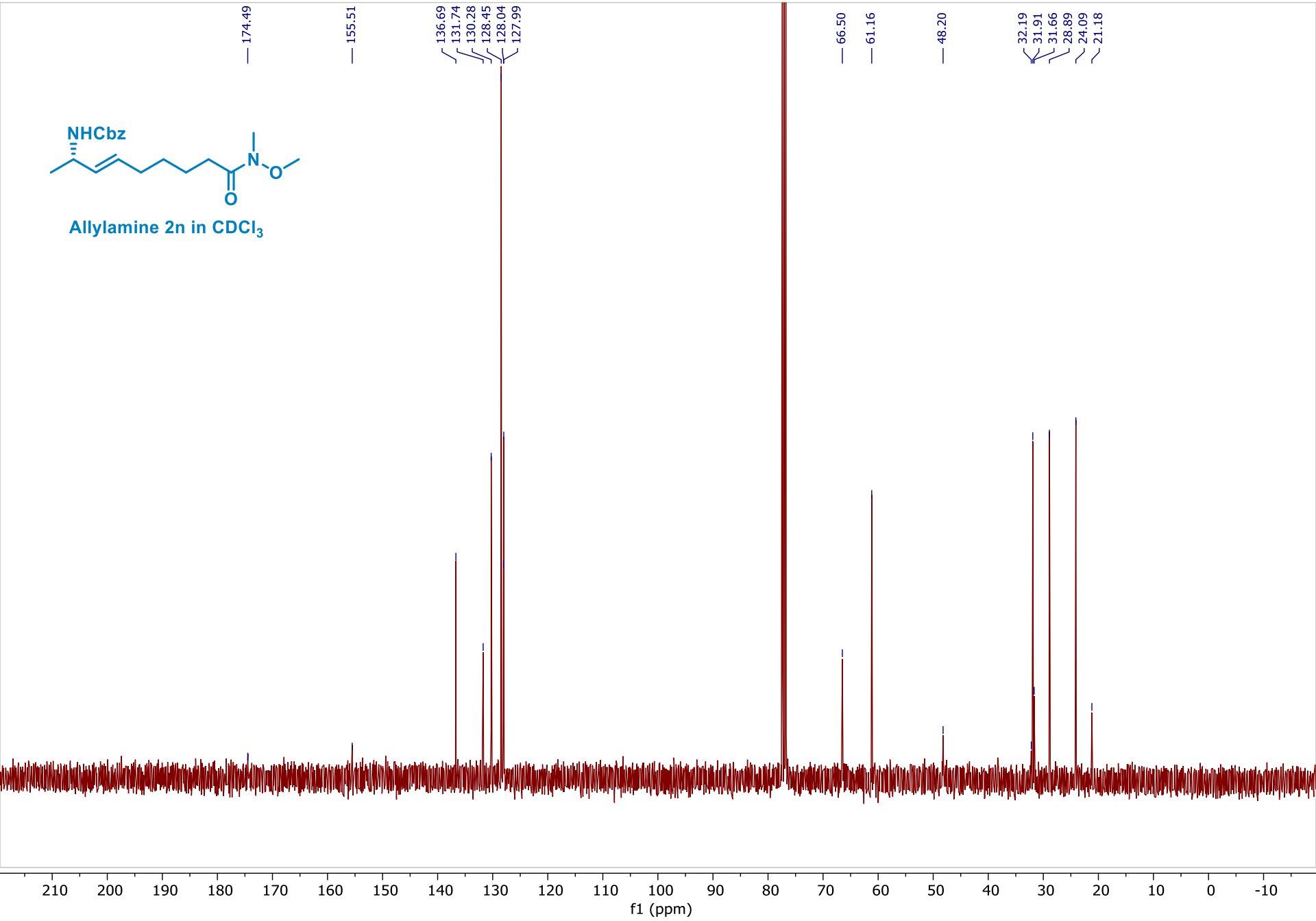
7.29
7.29
7.28
7.26
5.59
5.58
5.56
5.54
5.52
5.43
5.41
5.39
5.37
5.08
4.72
4.23
4.21
3.65
3.15
2.41
2.39
2.37
2.05
2.03
2.01
1.99
1.65
1.63
1.61
1.59
1.57
1.43
1.41
1.39
1.37
1.35
1.20
1.18
NHCbz
N
O
O
Allylamine 2n in CDCl3
5.40
0.99
1.00
2.08
0.92
1.00
3.04
3.03
2.01
2.09
2.16
2.11
3.04
8.0
7.5
7.0
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)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155.51
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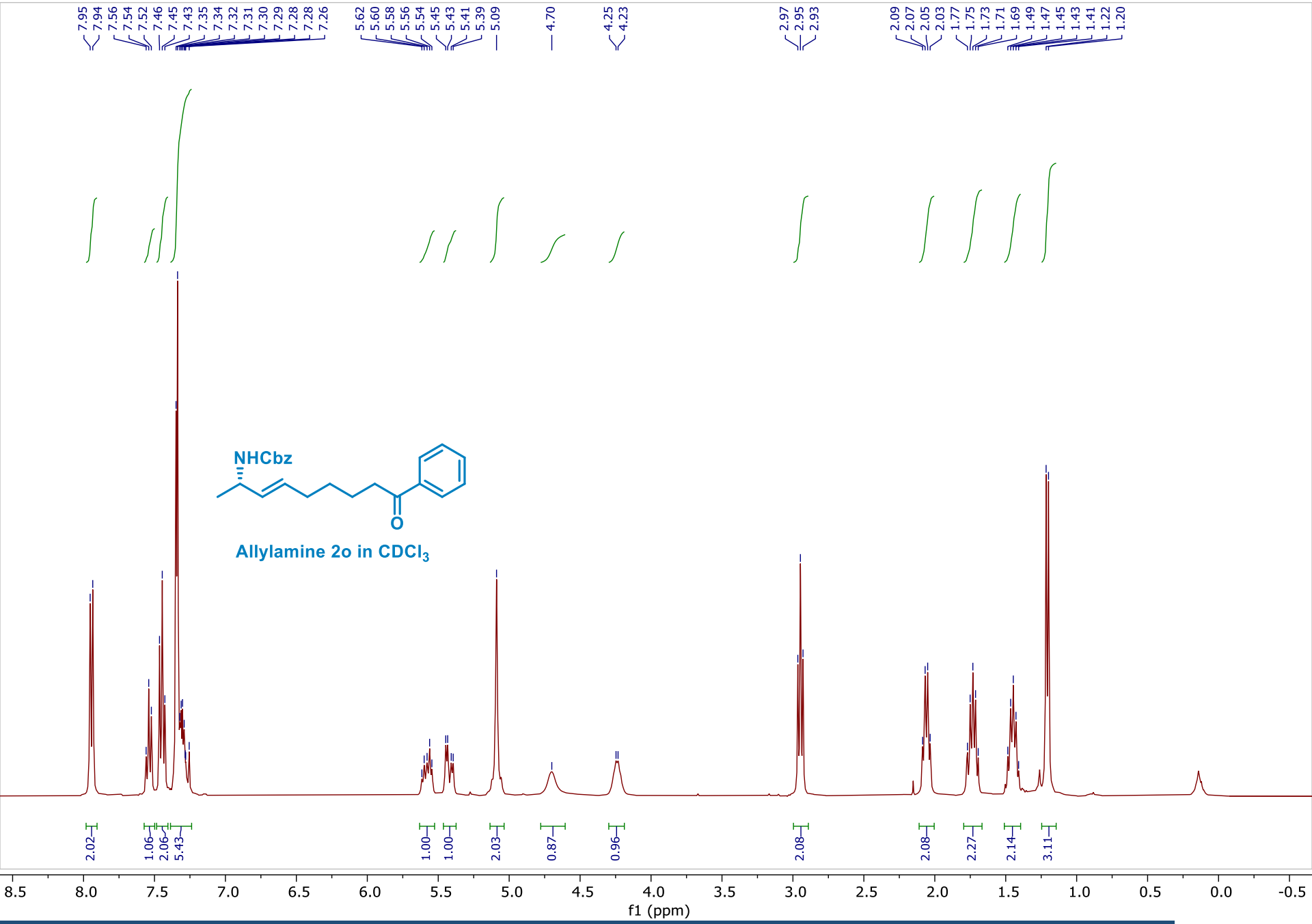
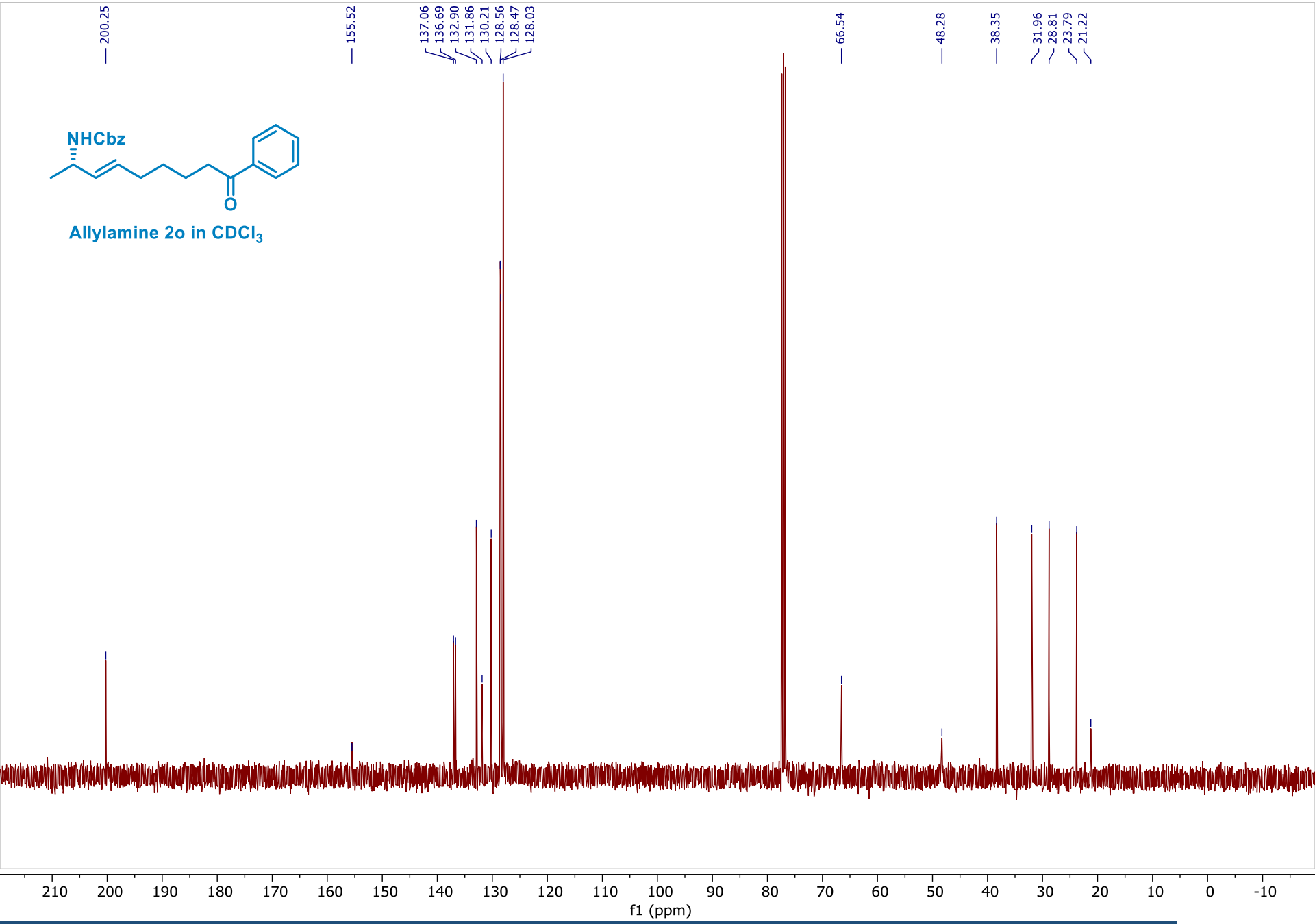
131.74
130.28
128.45
128.04
127.99
66.50
61.16
48.20
32.19
31.91
31.66
28.89
24.09
21.18
NHCbz
N
O
O
Allylamine 2n in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


NHCbz
O
Allylamine 2o in CDCl3
f1 (ppm)


200.25
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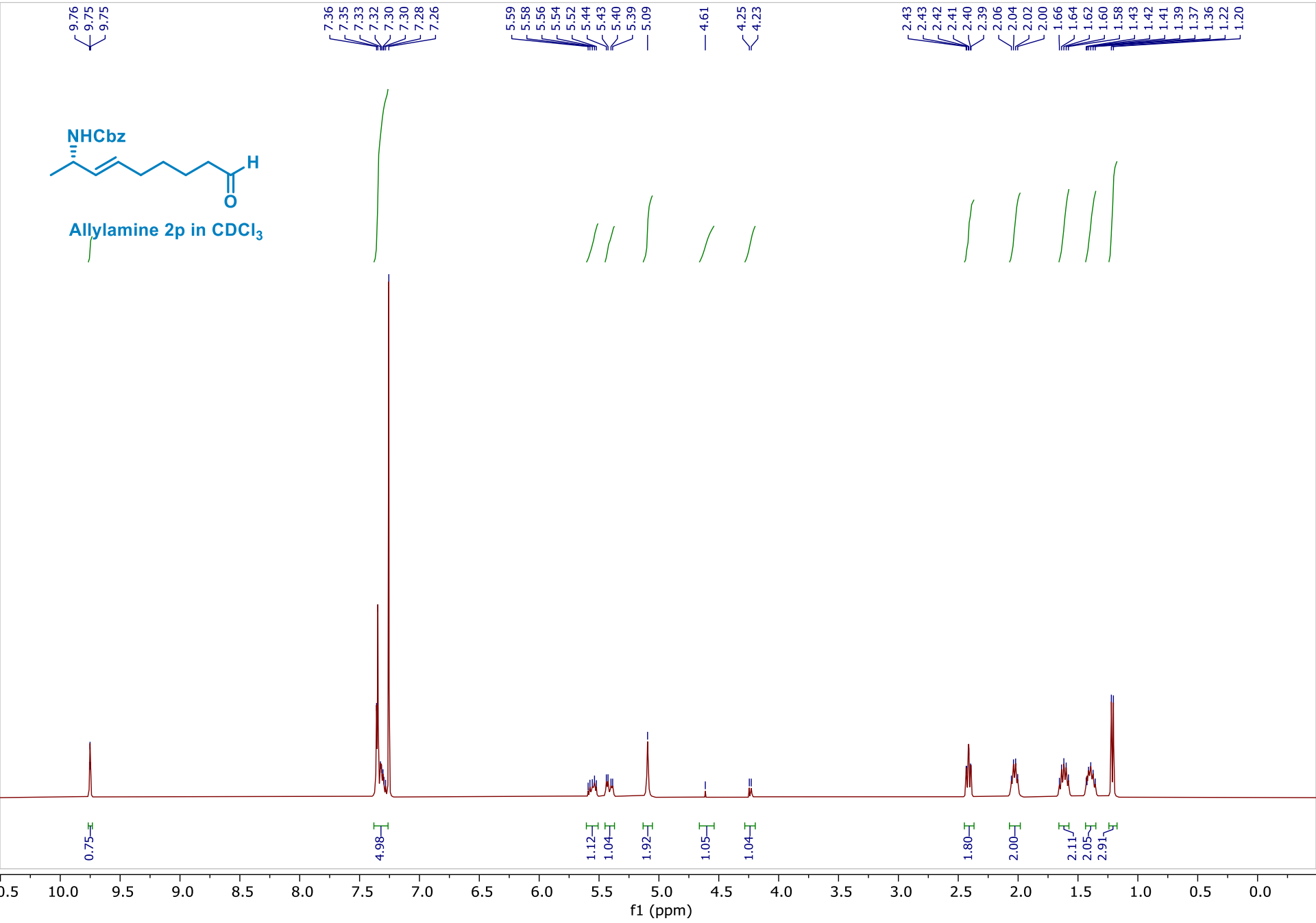
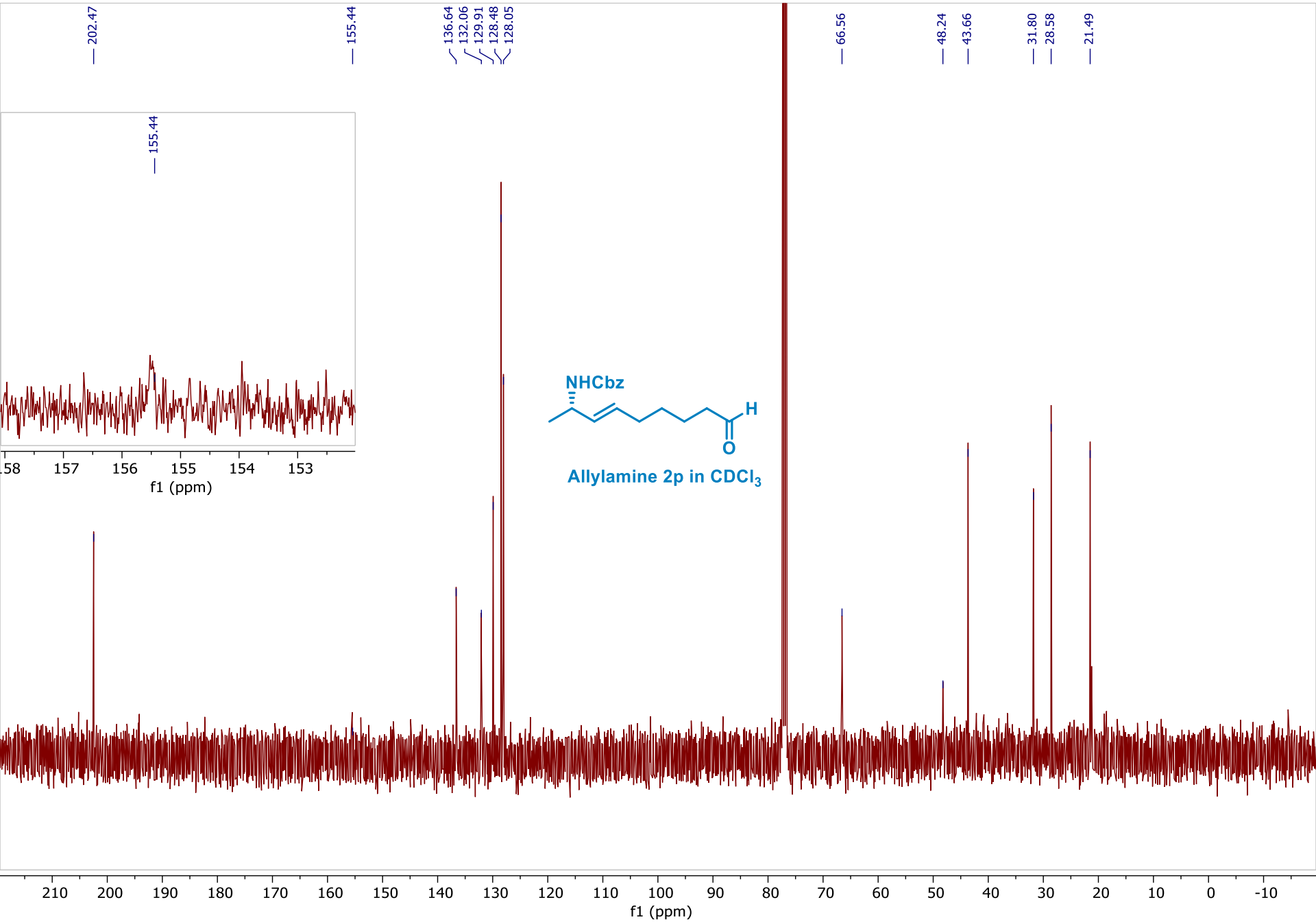
136.69
132.90
131.86
130.21
128.56
128.47
128.03
66.54
48.28
38.35
31.96
28.81
23.79
21.22
NHCbz
O
Allylamine 2o in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


NHCbz
H
O
Allylamine 2p in CDCl3
f1 (ppm)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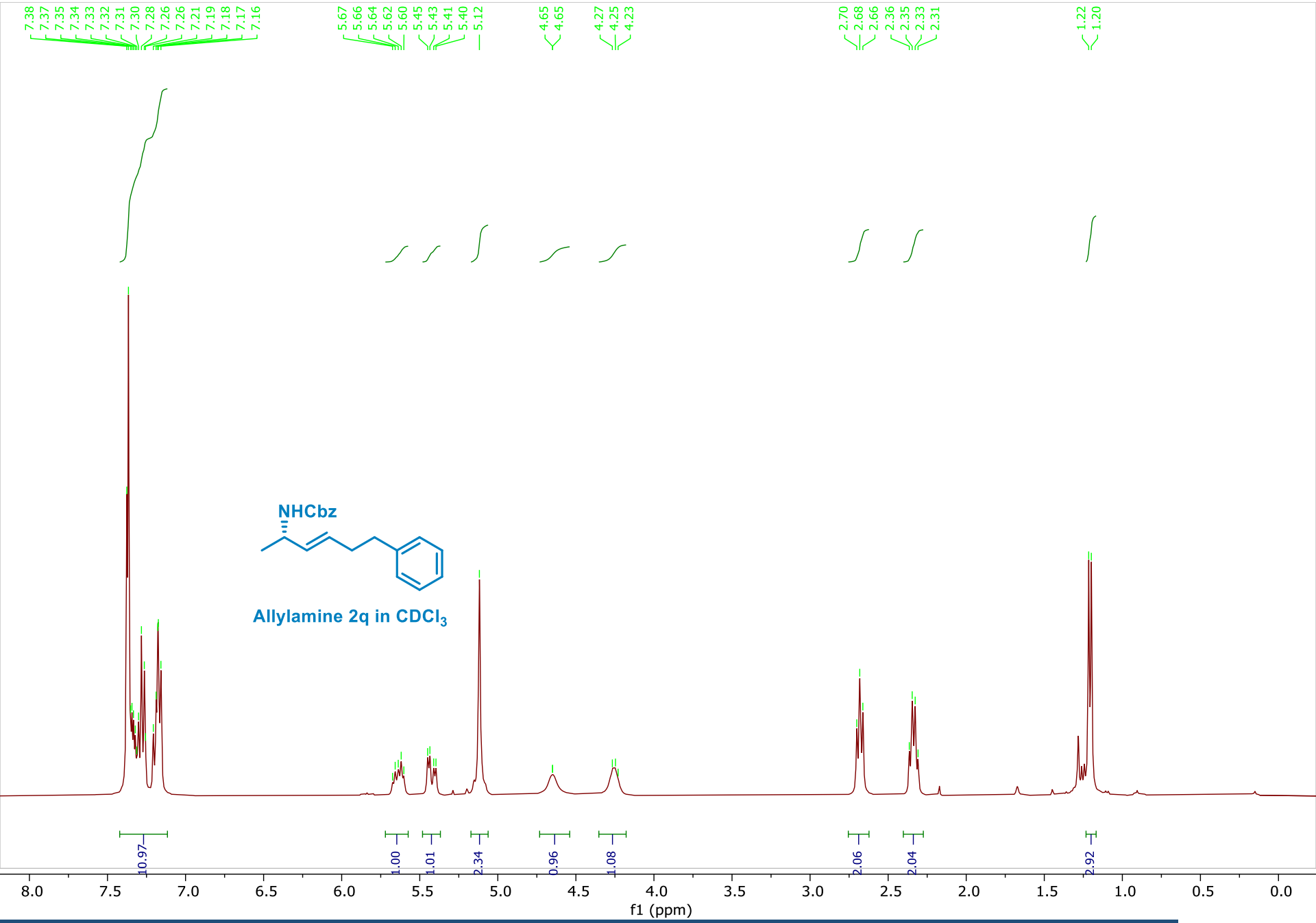
129.91
128.48
128.05
66.56
48.24
43.66
31.80
28.58
21.49
155.44
158
157
156
155
154
153
f1 (ppm)
NHCbz
H
O
Allylamine 2p in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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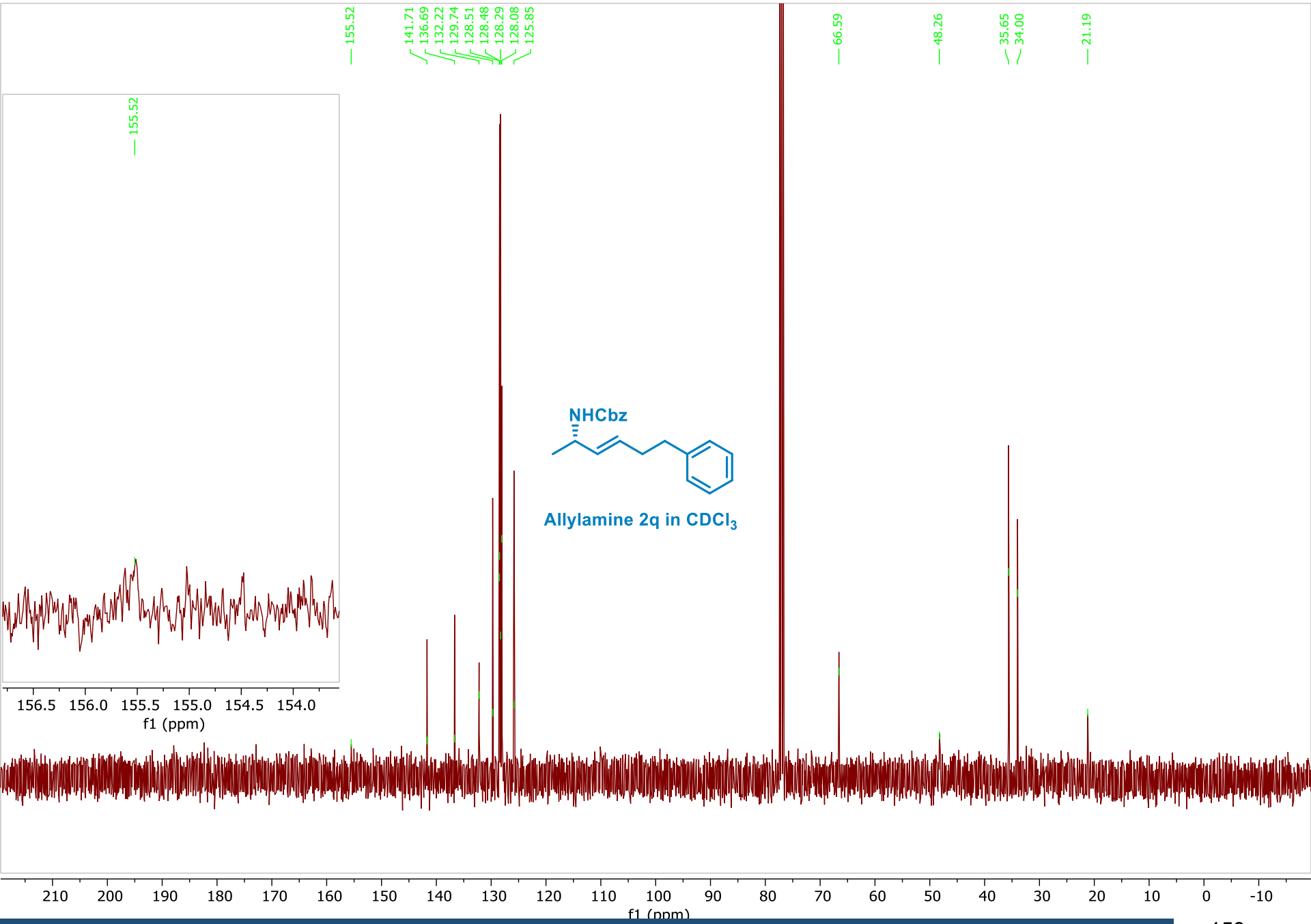
7.30
7.28
7.26
7.26
7.21
7.19
7.18
7.17
7.16
5.67
5.66
5.64
5.62
5.60
5.45
5.43
5.41
5.40
5.12
4.65
4.65
4.27
4.25
4.23
2.70
2.68
2.66
2.36
2.35
2.33
2.31
1.22
1.20
NHCbz
Allylamine 2q in CDCl3
10.97
1.00
1.01
2.34
0.96
1.08
2.06
2.04
2.92
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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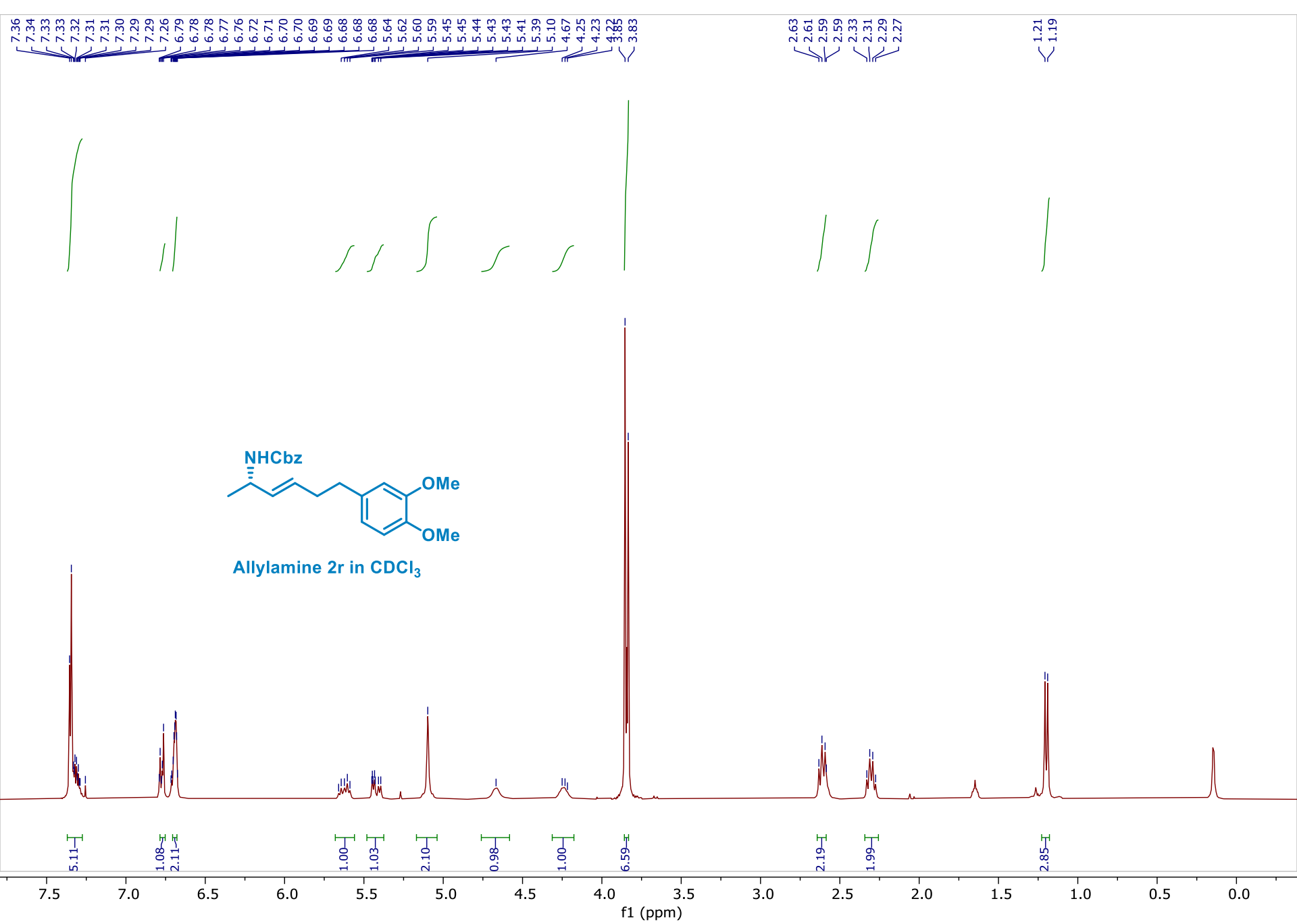
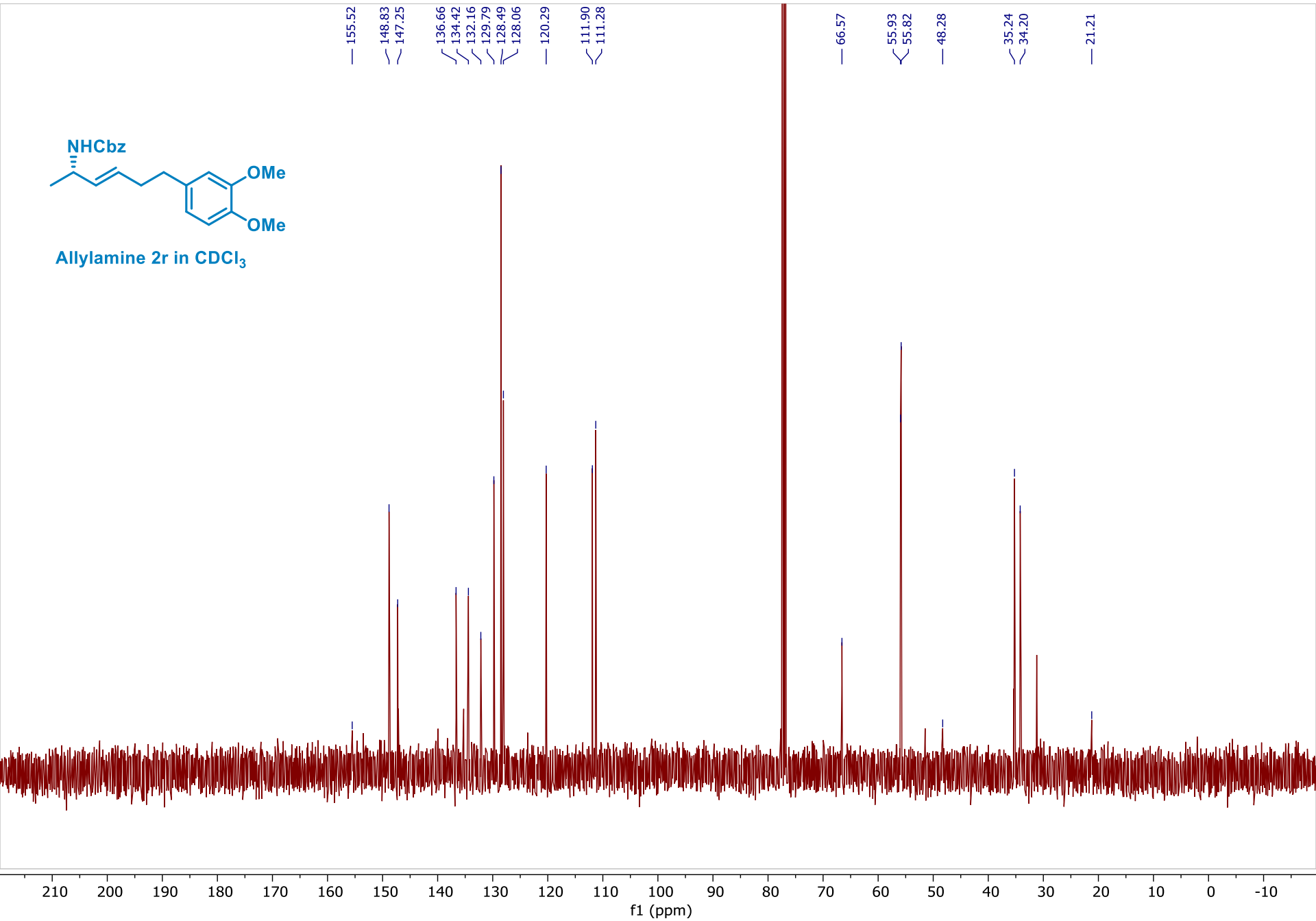
141.71
136.69
132.22
129.74
128.51
128.48
128.29
128.08
125.85
66.59
48.26
35.65
34.00
21.19
NHCbz
Allylamine 2q in CDCl3
f1 (ppm)


NHCbz
OMe
OMe
Allylamine 2r in CDCl3
f1 (ppm)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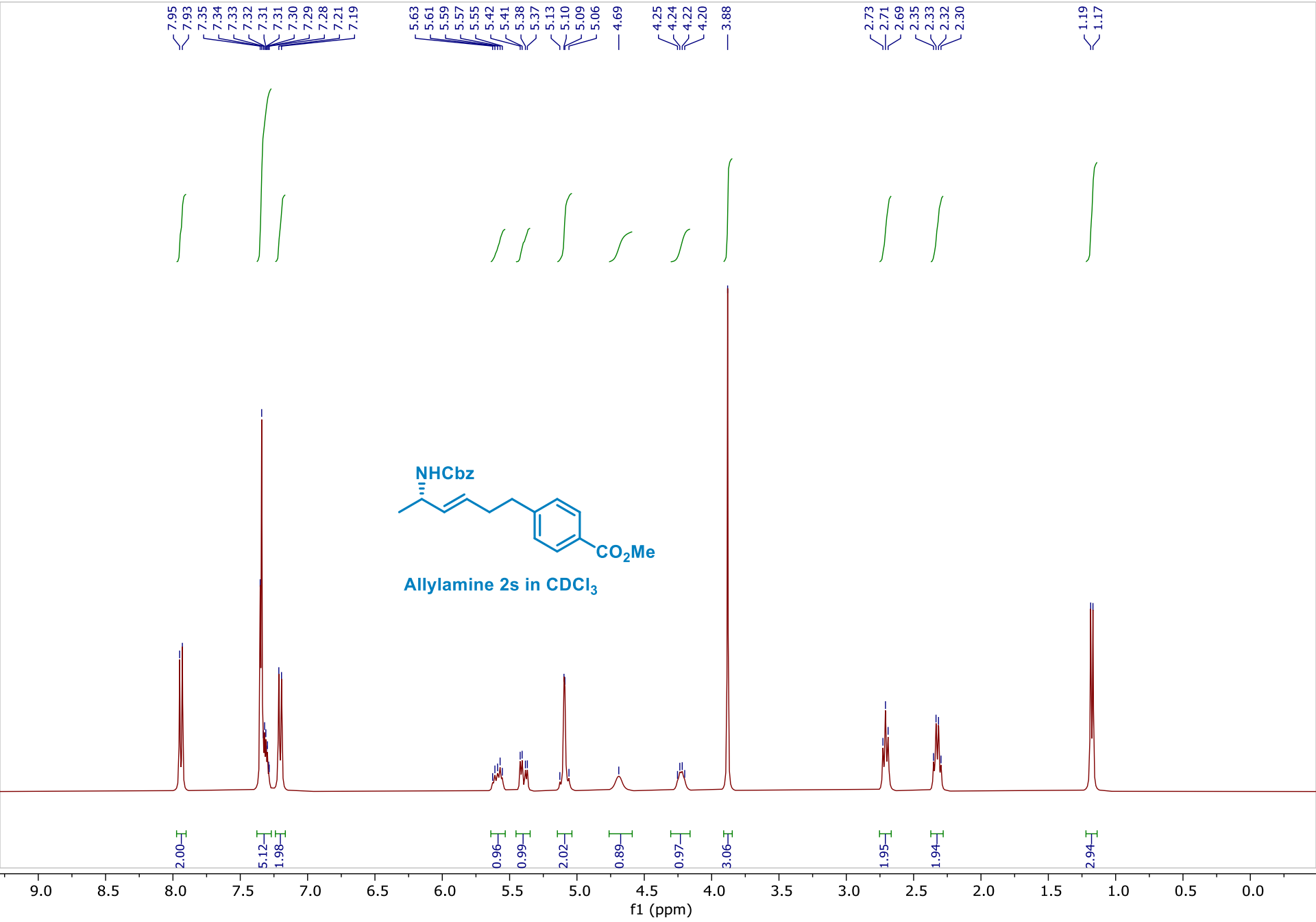
148.83
147.25
136.66
134.42
132.16
129.79
128.49
128.06
120.29
111.90
111.28
66.57
55.93
55.82
48.28
35.24
34.20
21.21
NHCbz
OMe
OMe
Allylamine 2r in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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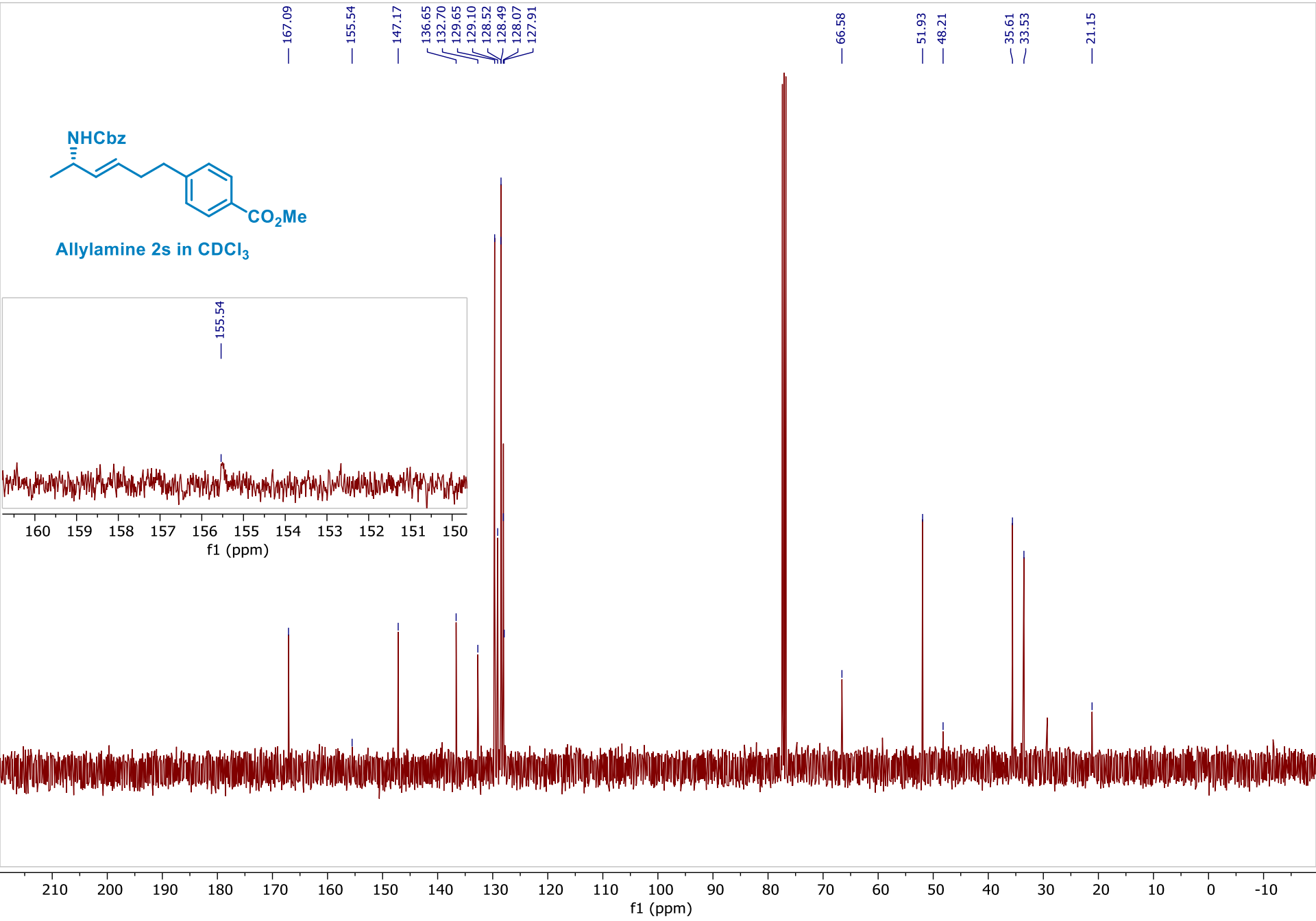
7.93
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.21
7.19
5.63
5.61
5.59
5.57
5.55
5.42
5.41
5.38
5.37
5.13
5.10
5.09
5.06
4.69
4.25
4.24
4.22
4.20
3.88
2.73
2.71
2.69
2.35
2.33
2.32
2.30
1.19
1.17
NHCbz
CO2Me
Allylamine 2s in CDCl3
2.00
5.12
1.98
0.96
0.99
2.02
0.89
0.97
3.06
1.95
1.94
2.94
9.0
8.5
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)


167.09
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147.17
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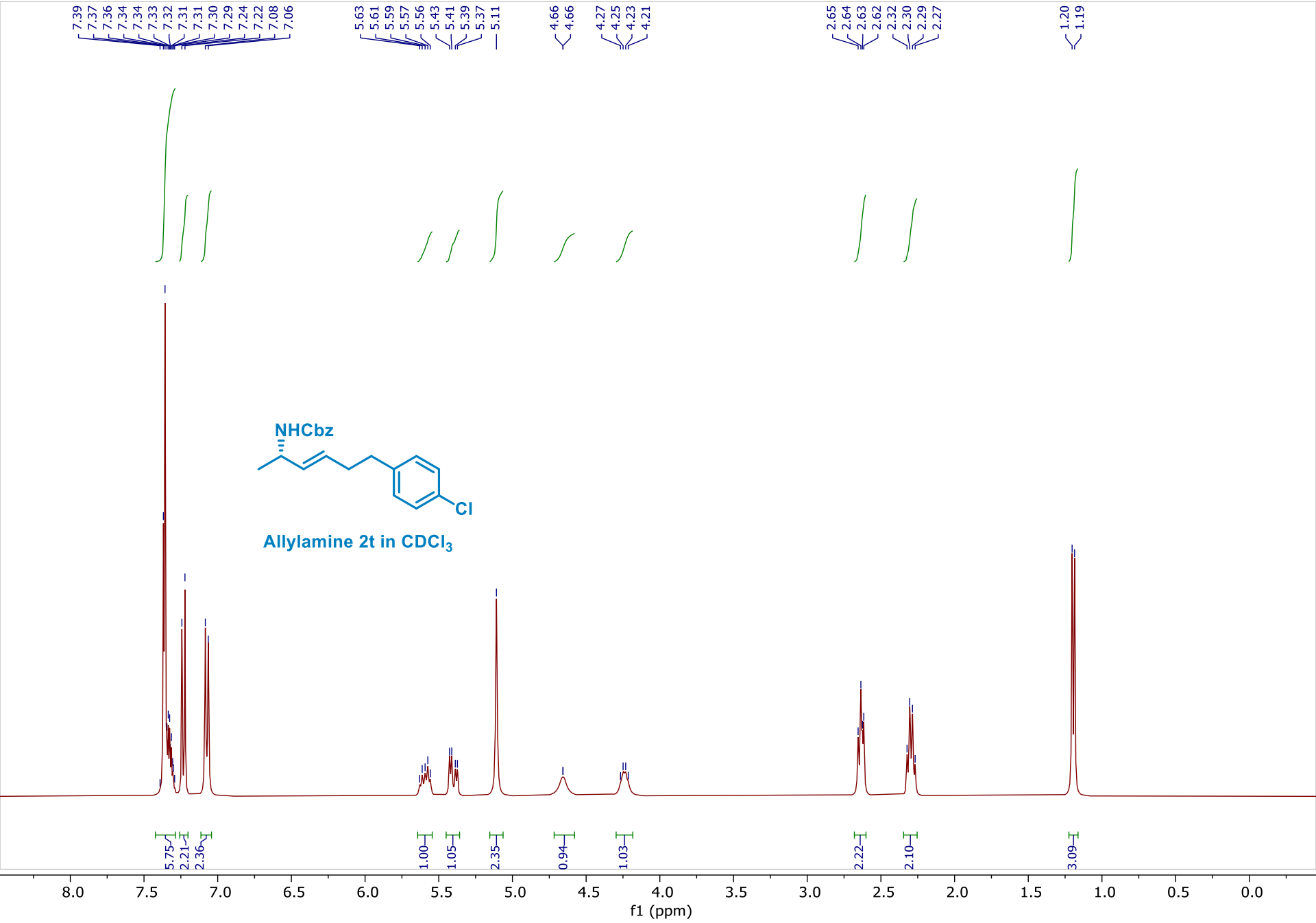
129.65
129.10
128.52
128.49
128.07
127.91
66.58
51.93
48.21
35.61
33.53
21.15
NHCbz
CO2Me
Allylamine 2s in CDCl3
155.54
160 159 158 157 156 155 154 153 152 151 150
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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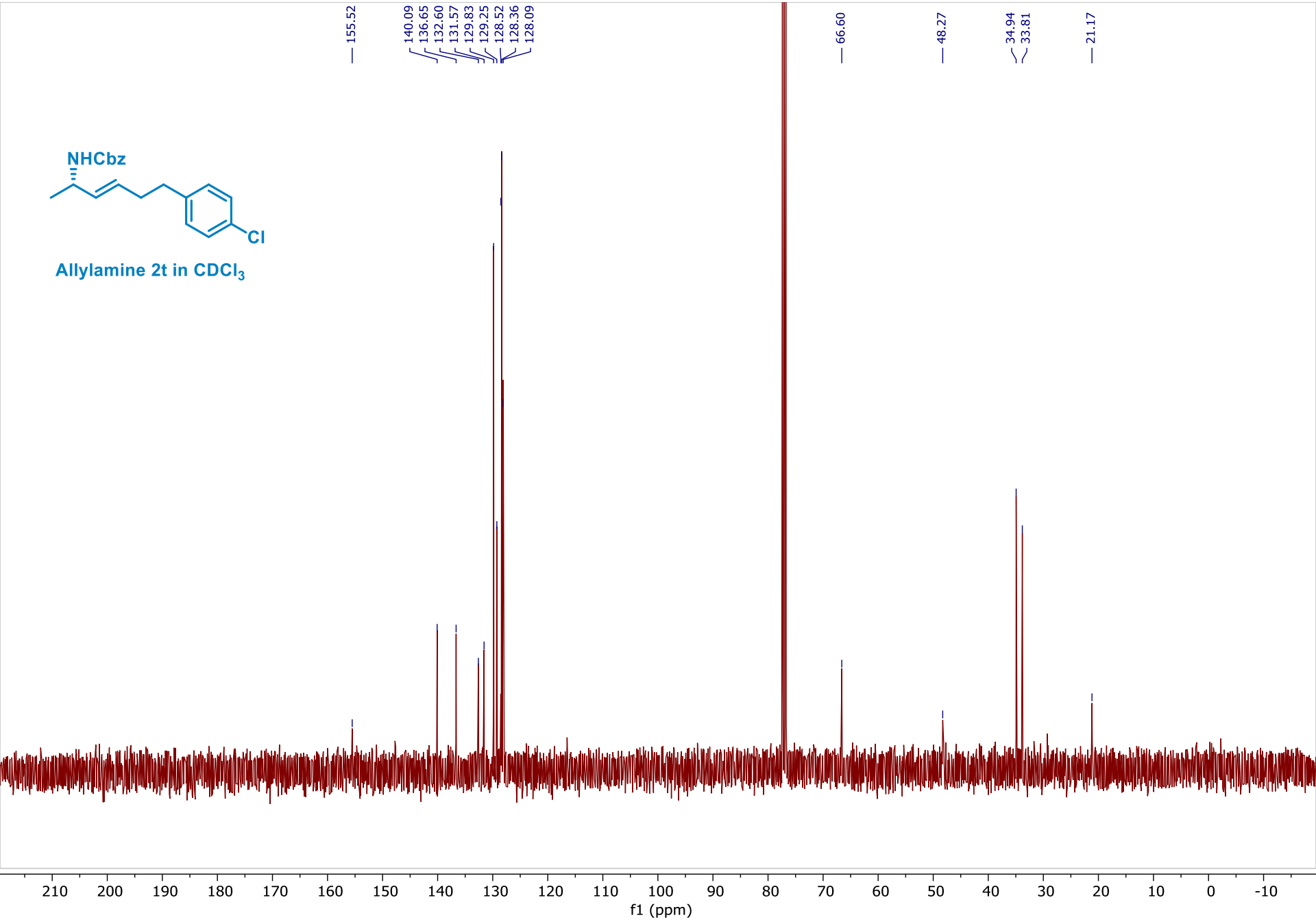
7.37
7.36
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.24
7.22
7.08
7.06
5.63
5.61
5.59
5.57
5.56
5.43
5.41
5.39
5.37
5.11
4.66
4.66
4.27
4.25
4.23
4.21
2.65
2.64
2.63
2.62
2.32
2.30
2.29
2.27
1.20
1.19
NHCbz
Cl
Allylamine 2t in CDCl3
5.75
2.21
2.36
1.00
1.05
2.35
0.94
1.03
2.22
2.10
3.09
8.0
7.5
7.0
6.5
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)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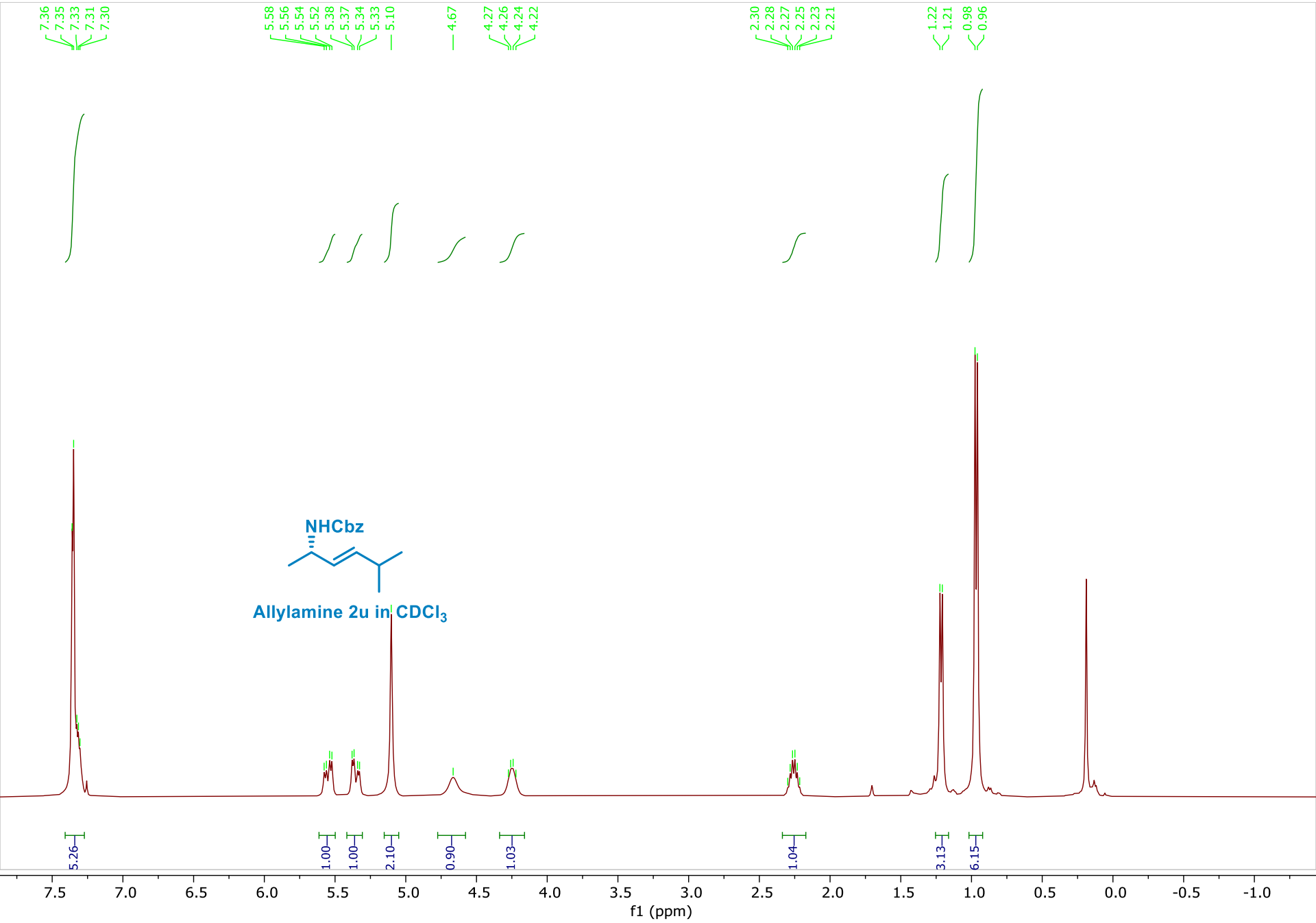
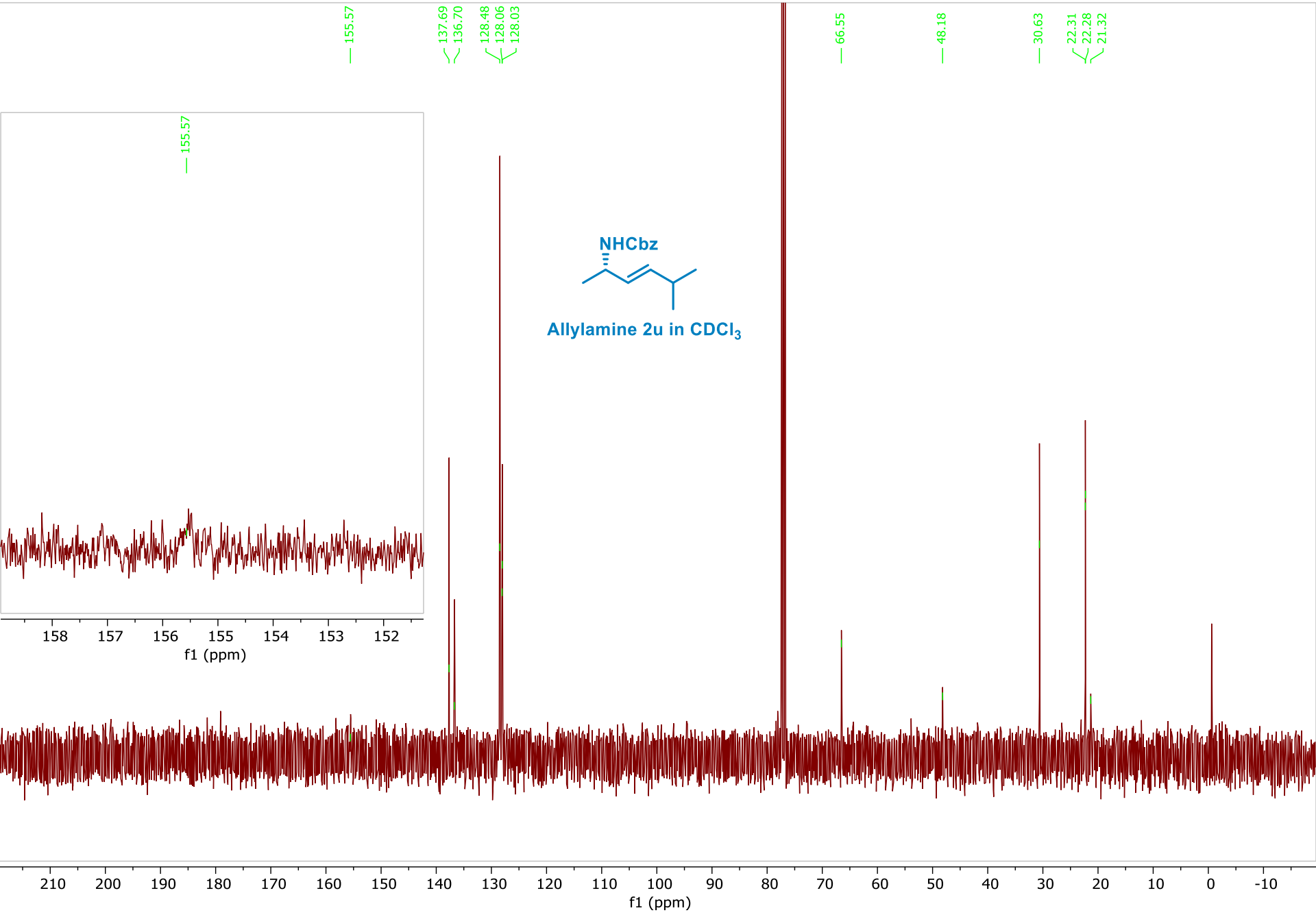
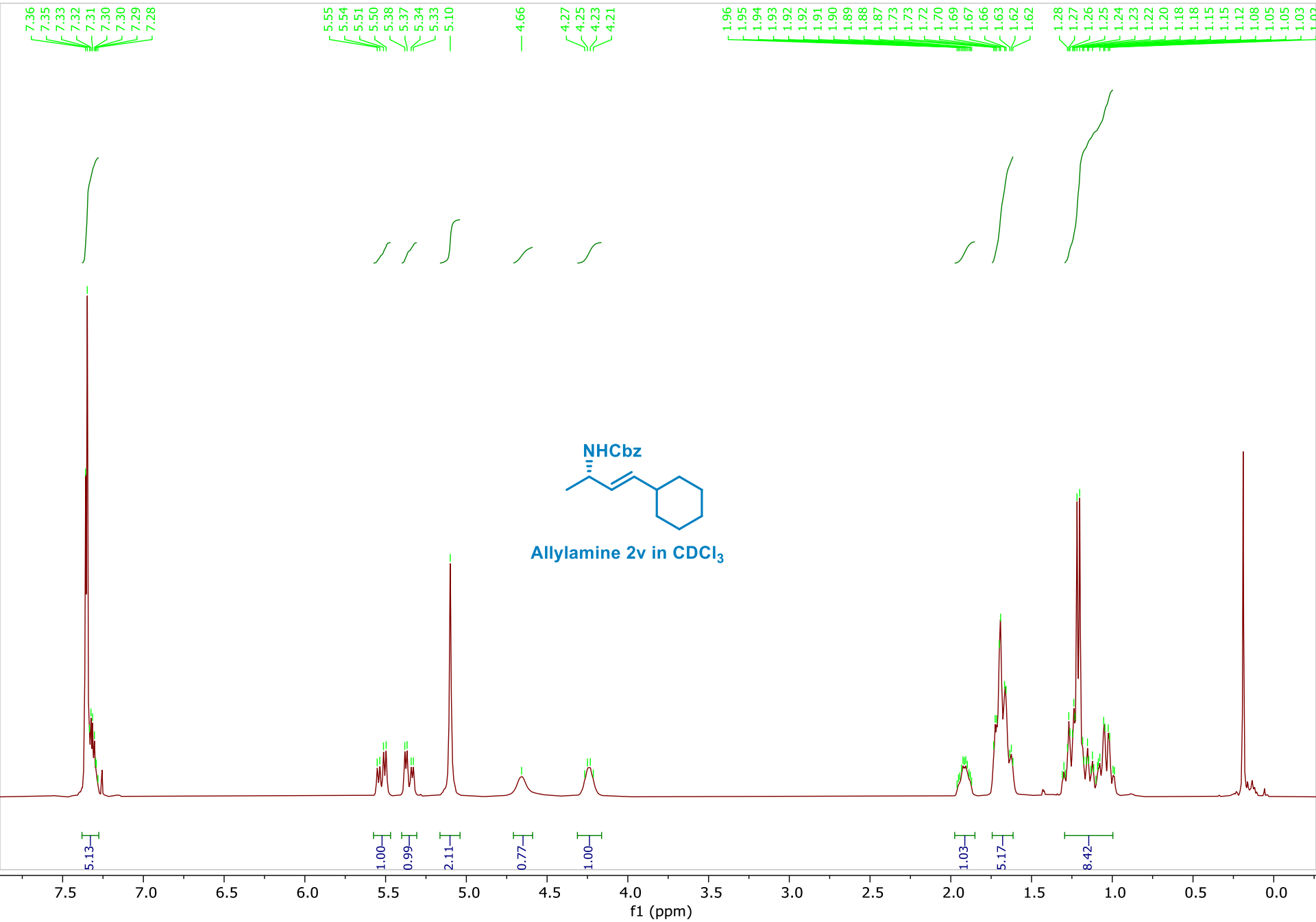
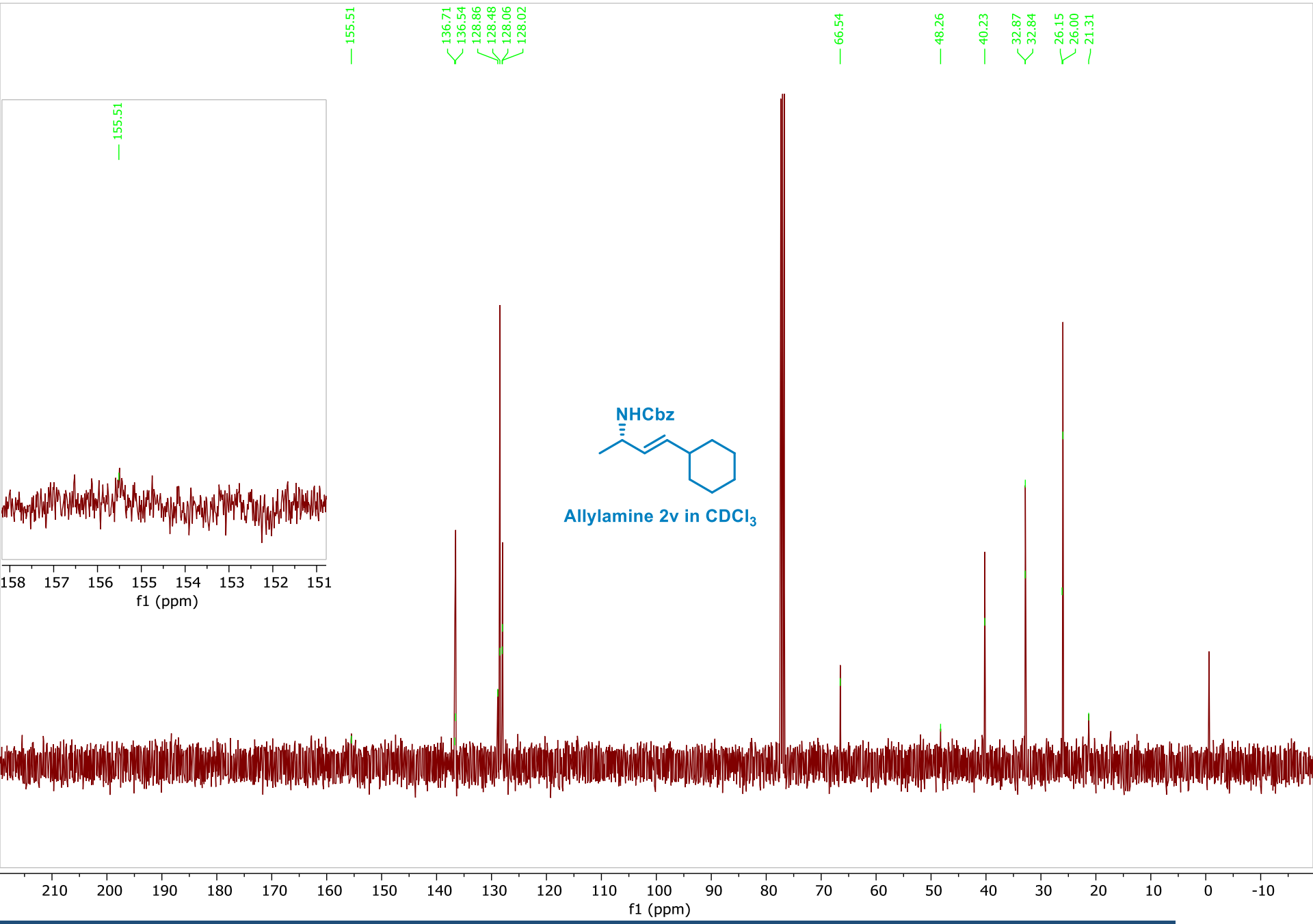
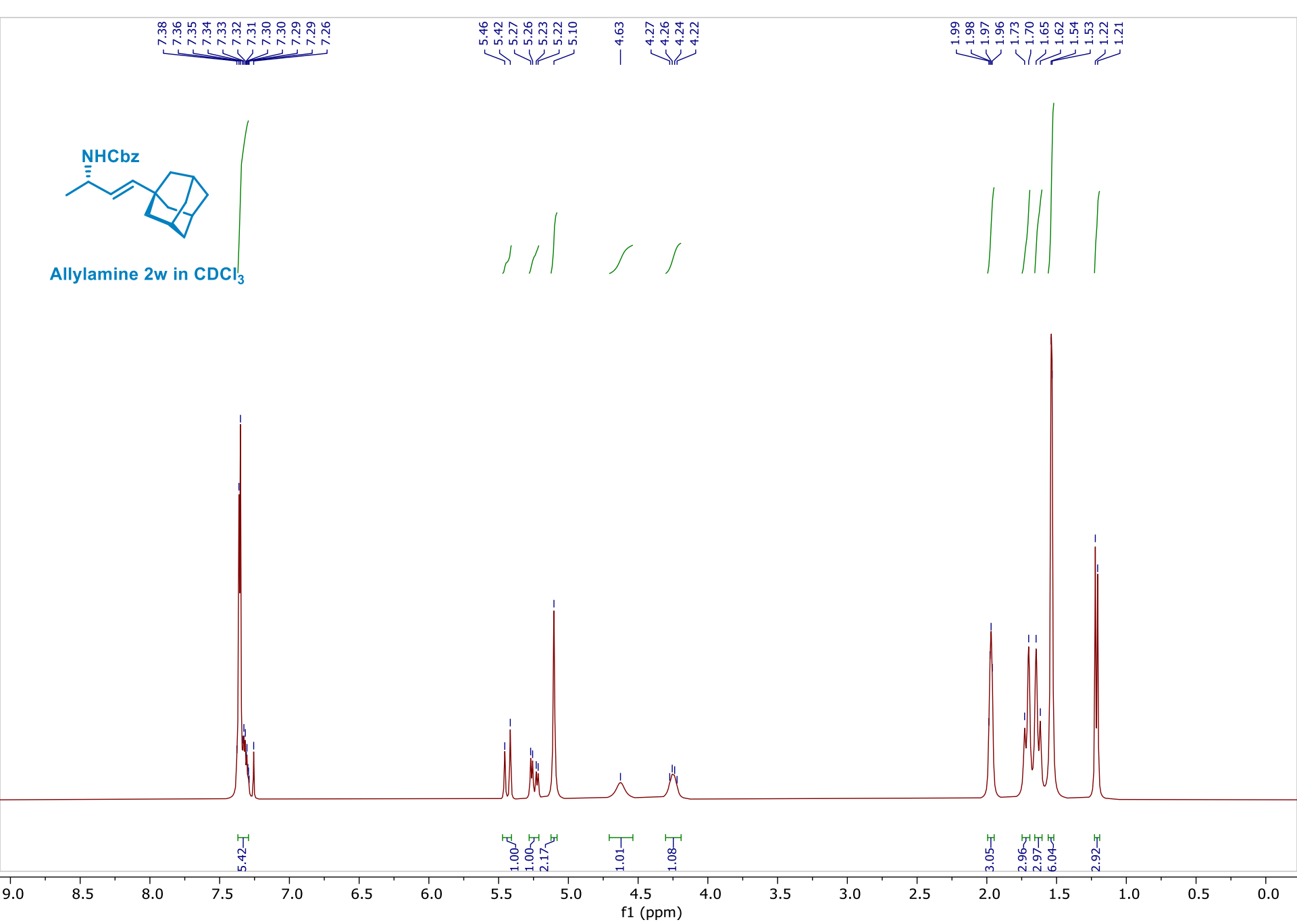
140.09
136.65
132.60
131.57
129.83
129.25
128.52
128.36
128.09
66.60
48.27
34.94
33.81
21.17
NHCbz
Cl
Allylamine 2t in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

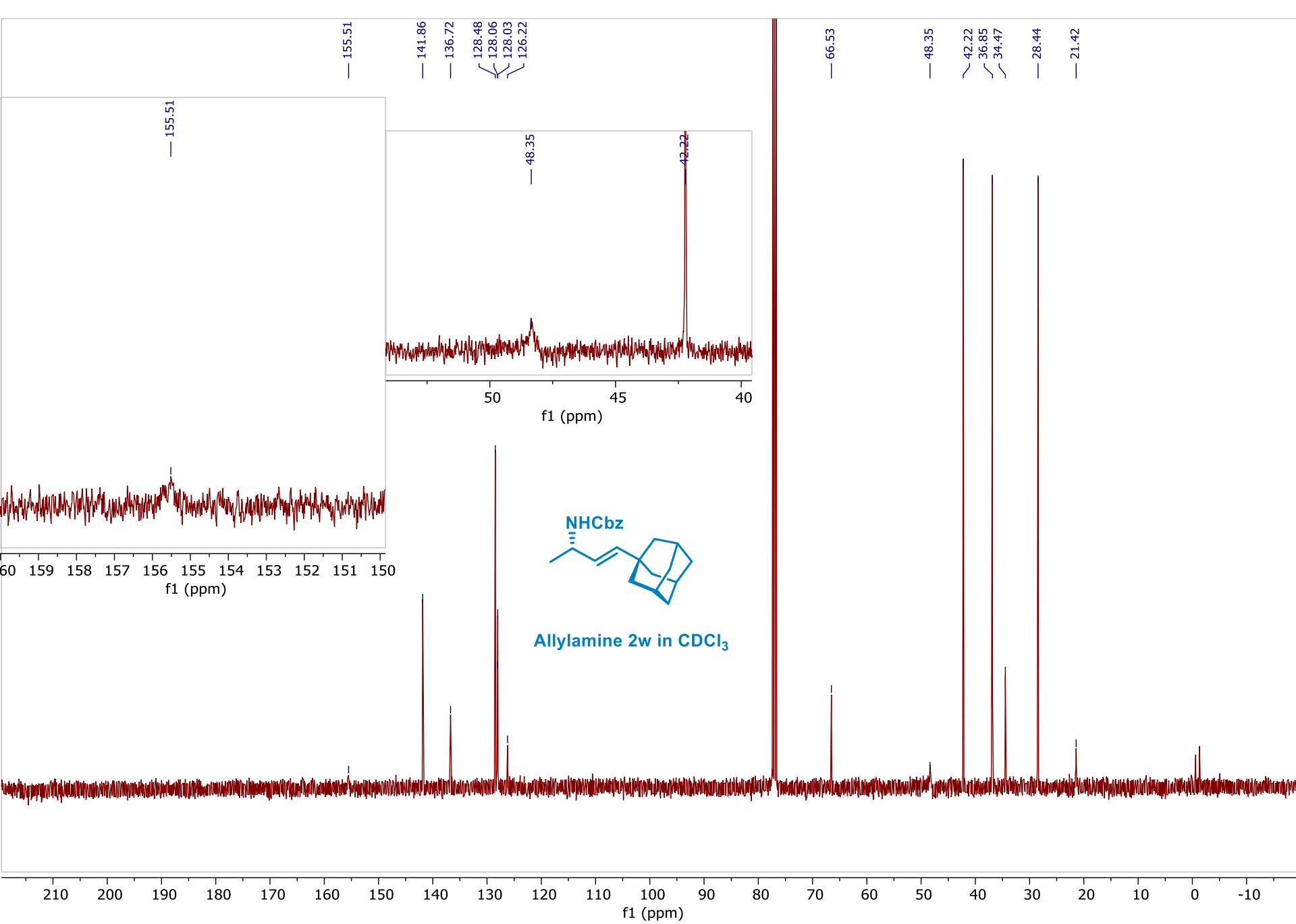

7.36
7.35
7.33
7.31
7.30
5.58
5.56
5.54
5.52
5.38
5.37
5.34
5.33
5.10
4.67
4.27
4.26
4.24
4.22
2.30
2.28
2.27
2.25
2.23
2.21
1.22
1.21
0.98
0.96
NHCbz
Allylamine 2u in CDCl3
5.26
1.00
1.00
2.10
0.90
1.03
1.04
3.13
6.15
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


155.57
137.69
136.70
128.48
128.06
128.03
66.55
48.18
30.63
22.31
22.28
21.32
NHCbz
Allylamine 2u in CDCl3
f1 (ppm)


NHCbz
Allylamine 2v in CDCl3
f1 (ppm)


155.51
136.71
136.54
128.86
128.48
128.06
128.02
66.54
48.26
40.23
32.87
32.84
26.15
26.00
21.31
NHCbz
Allylamine 2v in CDCl3
f1 (ppm)


NHCbz
Allylamine 2w in CDCl3
7.38
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.30
7.29
7.29
7.26
5.46
5.42
5.27
5.26
5.23
5.22
5.10
4.63
4.27
4.26
4.24
4.22
1.99
1.98
1.97
1.96
1.73
1.70
1.65
1.62
1.54
1.53
1.22
1.21
5.42
1.00
1.00
2.17
1.01
1.08
3.05
2.96
2.97
6.04
2.92
f1 (ppm)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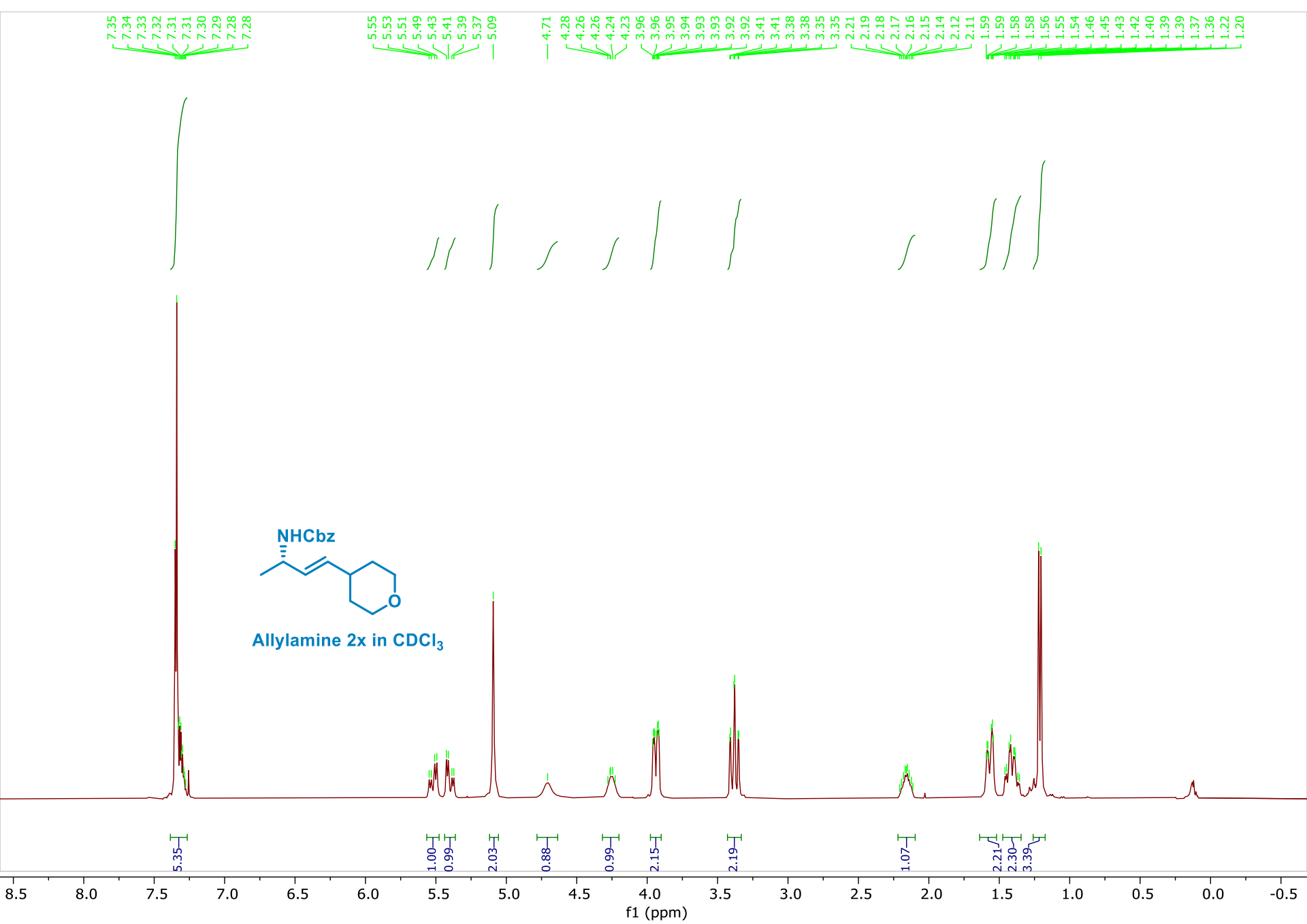
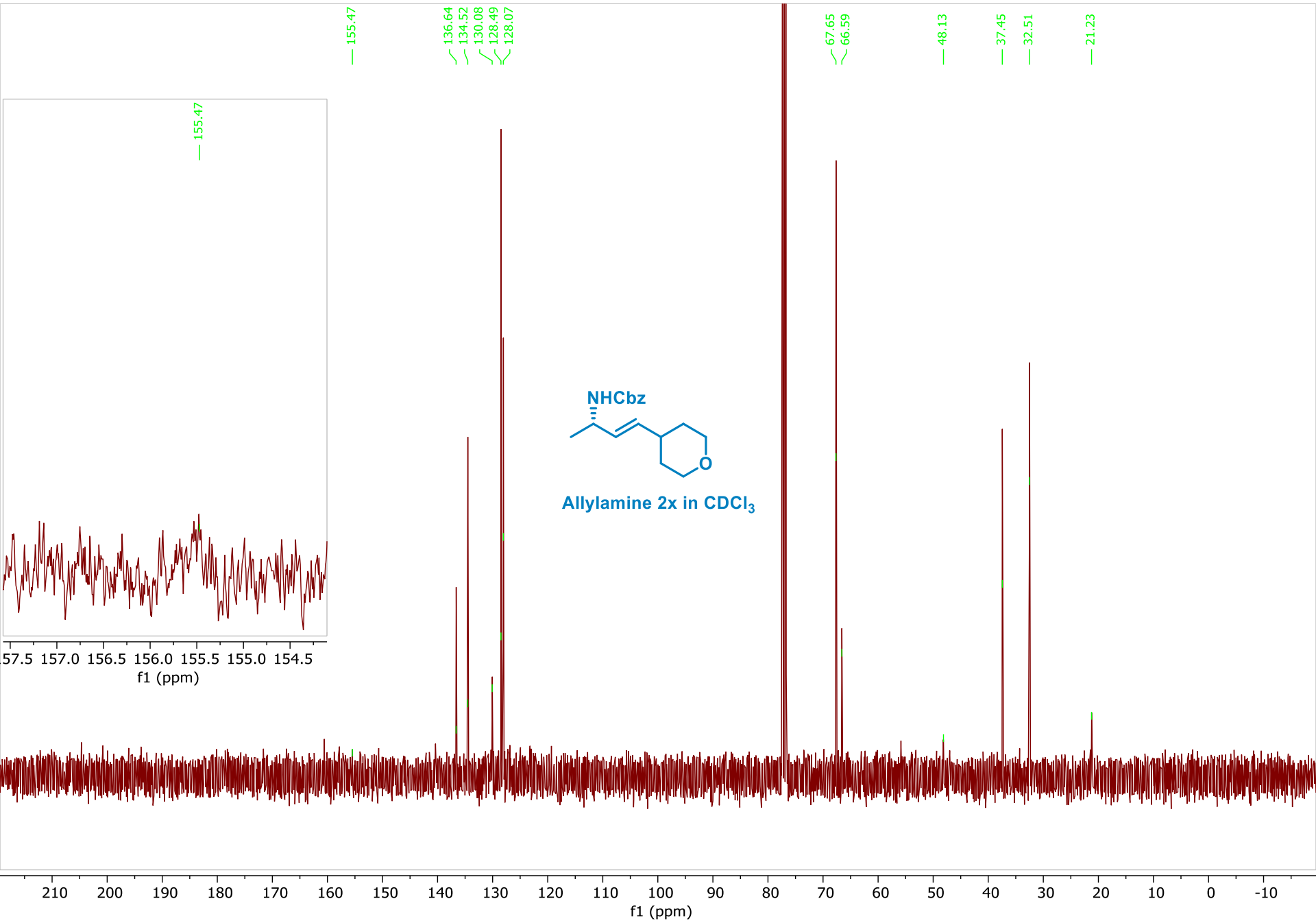
141.86
136.72
128.48
128.06
128.03
126.22
66.53
48.35
42.22
36.85
34.47
28.44
21.42
155.51
48.35
42.22
50
45
40
f1 (ppm)
60 159 158 157 156 155 154 153 152 151 150
f1 (ppm)
NHCbz
Allylamine 2w in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NHCbz
O
Allylamine 2x in CDCl3
f1 (ppm)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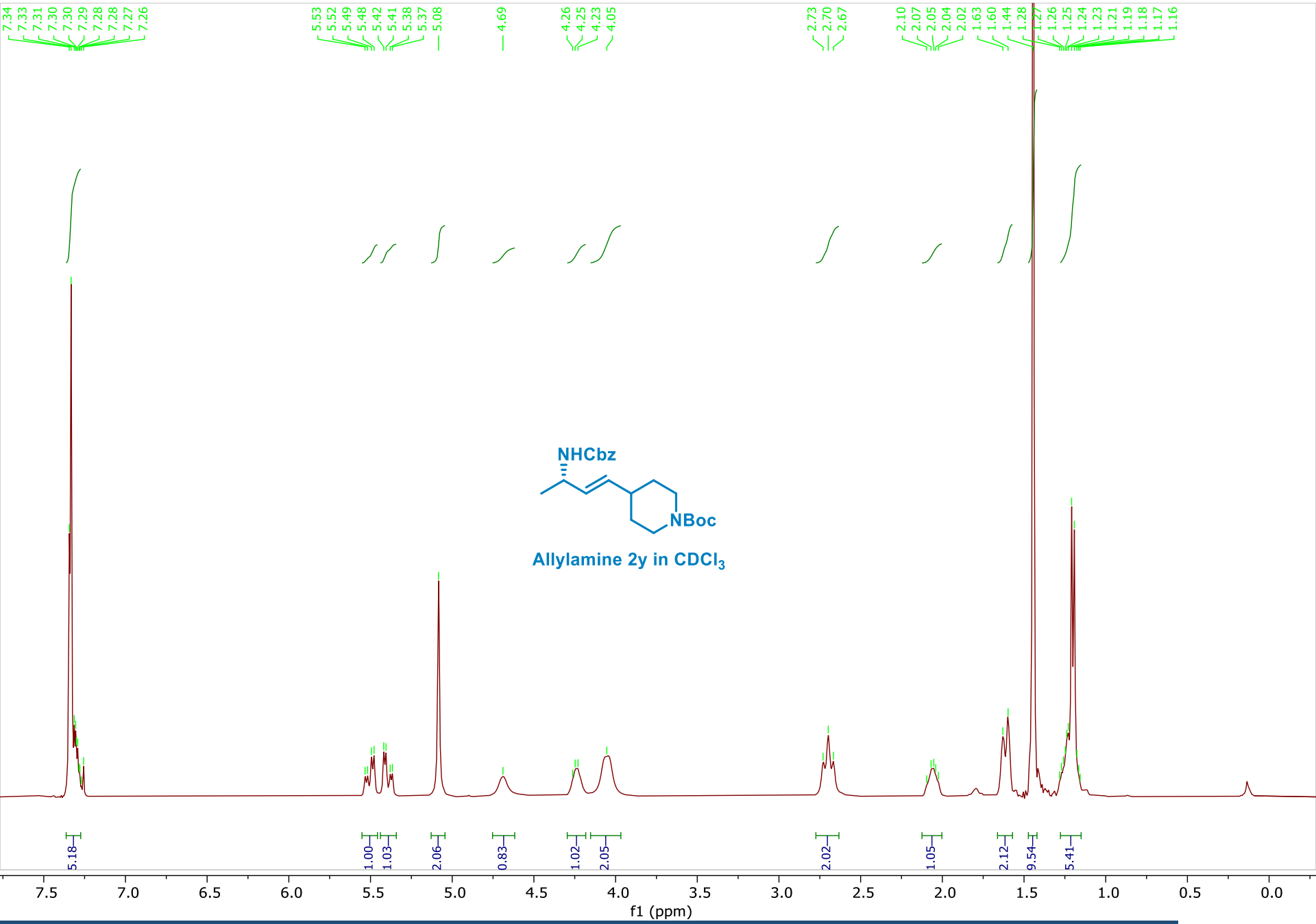
136.64
134.52
130.08
128.49
128.07
67.65
66.59
48.13
37.45
32.51
21.23
NHCbz
O
Allylamine 2x in CDCl3
f1 (ppm)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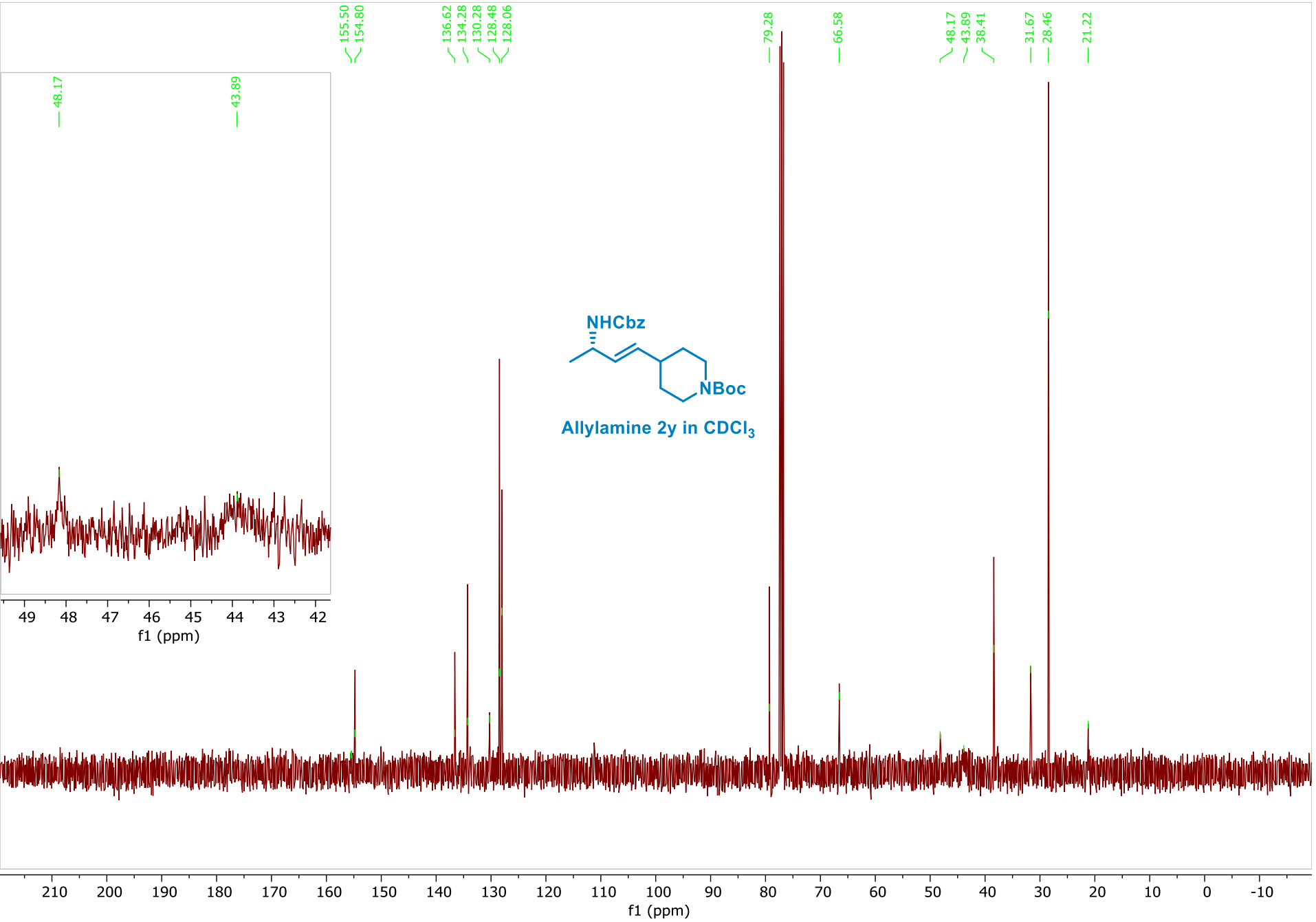
7.33
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.26
5.53
5.52
5.49
5.48
5.42
5.41
5.38
5.37
5.08
4.69
4.26
4.25
4.23
4.05
2.73
2.70
2.67
2.10
2.07
2.05
2.04
2.02
1.63
1.60
1.44
1.28
1.27
1.26
1.25
1.24
1.23
1.21
1.19
1.18
1.17
1.16
NHCbz
NBoc
Allylamine 2y in CDCl3
5.18
1.00
1.03
2.06
0.83
1.02
2.05
2.02
1.05
2.12
9.54
5.41
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)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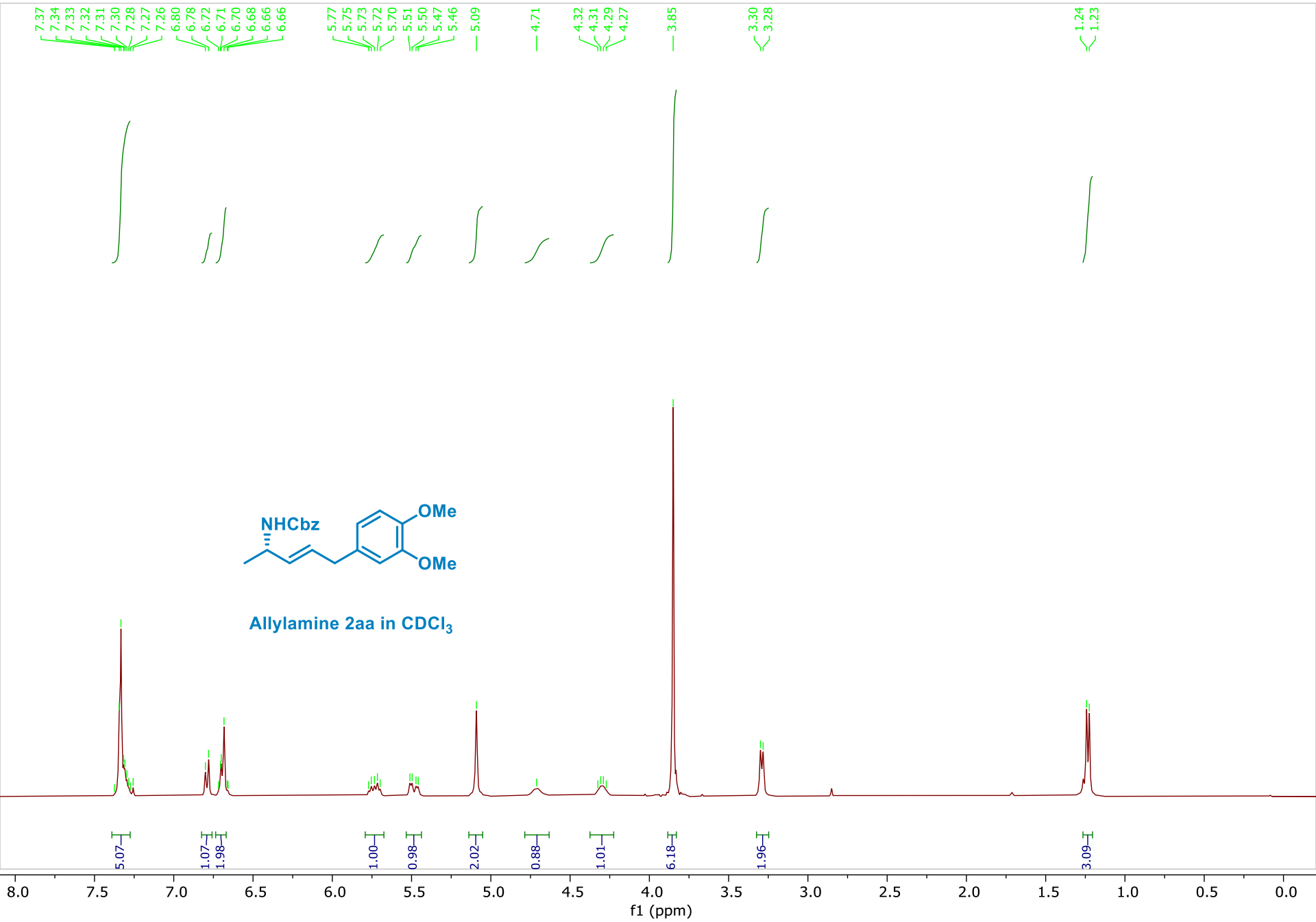
134.28
130.28
128.48
128.06
79.28
66.58
48.17
43.89
38.41
31.67
28.46
21.22
48.17
43.89
NHCbz
NBoc
Allylamine 2y in CDCl3
f1 (ppm)
f1 (ppm)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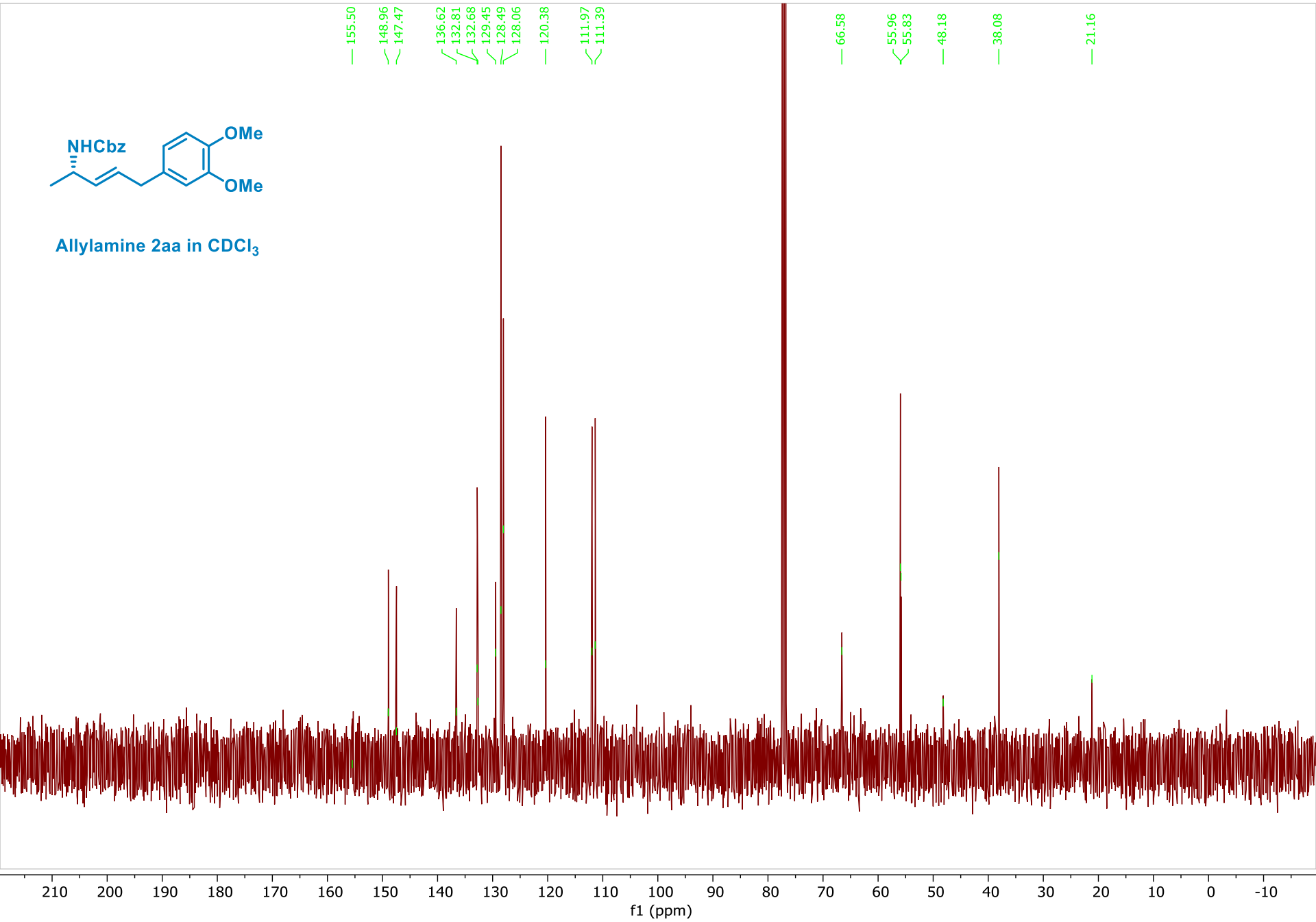
7.32
7.31
7.30
7.28
7.27
7.26
6.80
6.78
6.72
6.71
6.70
6.68
6.66
6.66
5.77
5.75
5.73
5.72
5.70
5.51
5.50
5.47
5.46
5.09
4.71
4.32
4.31
4.29
4.27
3.85
3.30
3.28
1.24
1.23
NHCbz
OMe
OMe
Allylamine 2aa in CDCl3
5.07
1.07
1.98
1.00
0.98
2.02
0.88
1.01
6.18
1.96
3.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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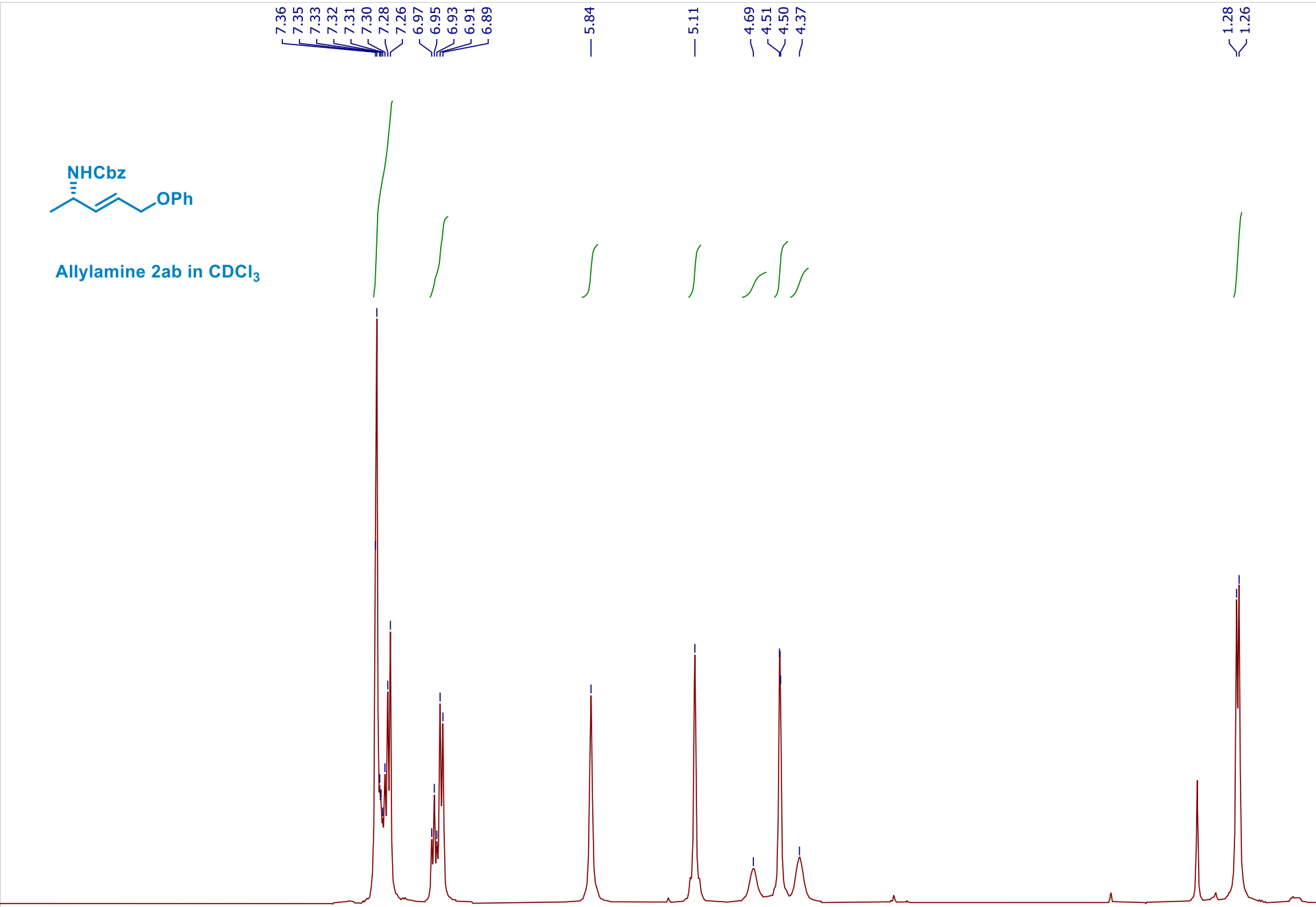
147.47
136.62
132.81
132.68
129.45
128.49
128.06
120.38
111.97
111.39
66.58
55.96
55.83
48.18
38.08
21.16
NHCbz
OMe
OMe
Allylamine 2aa in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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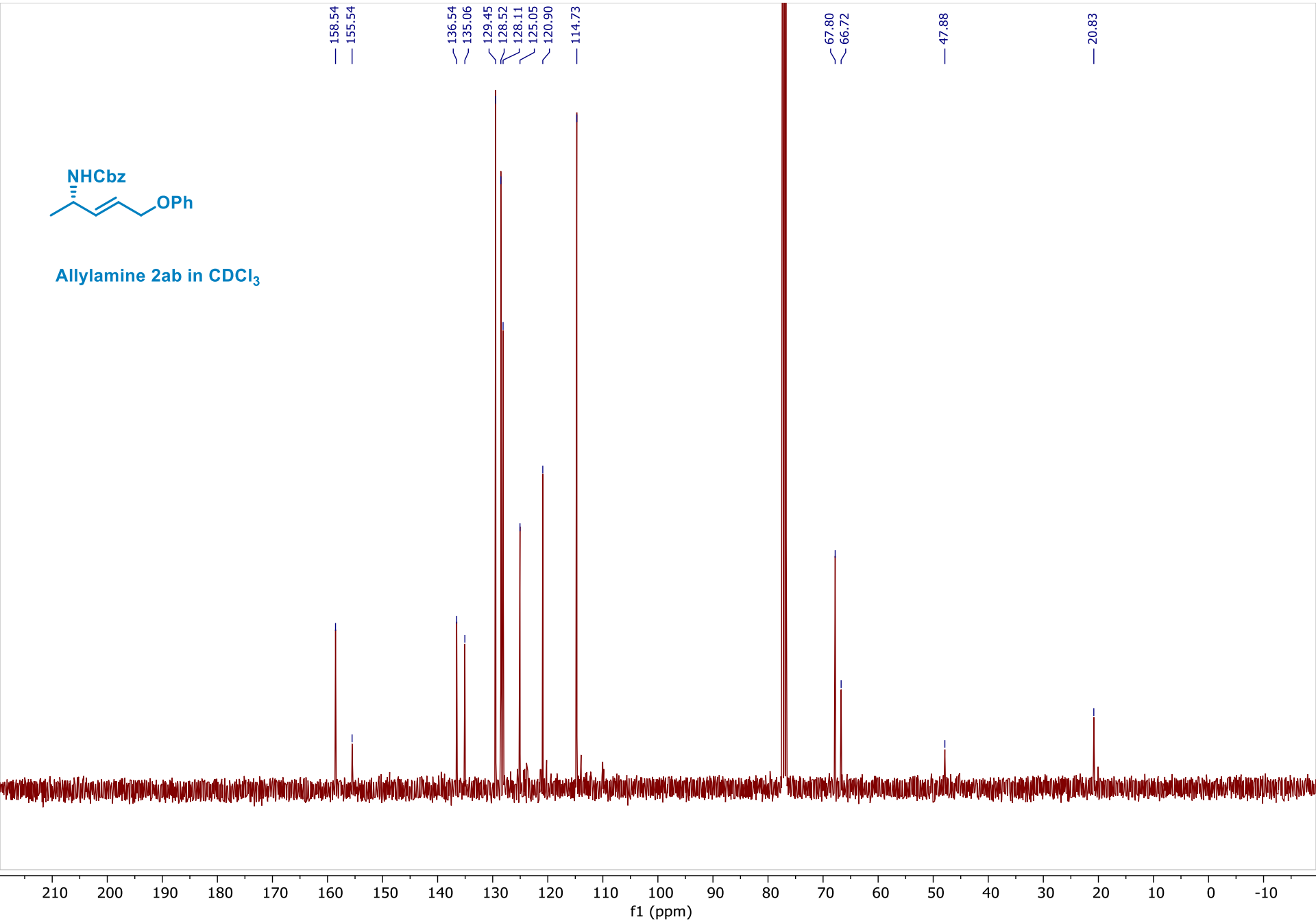
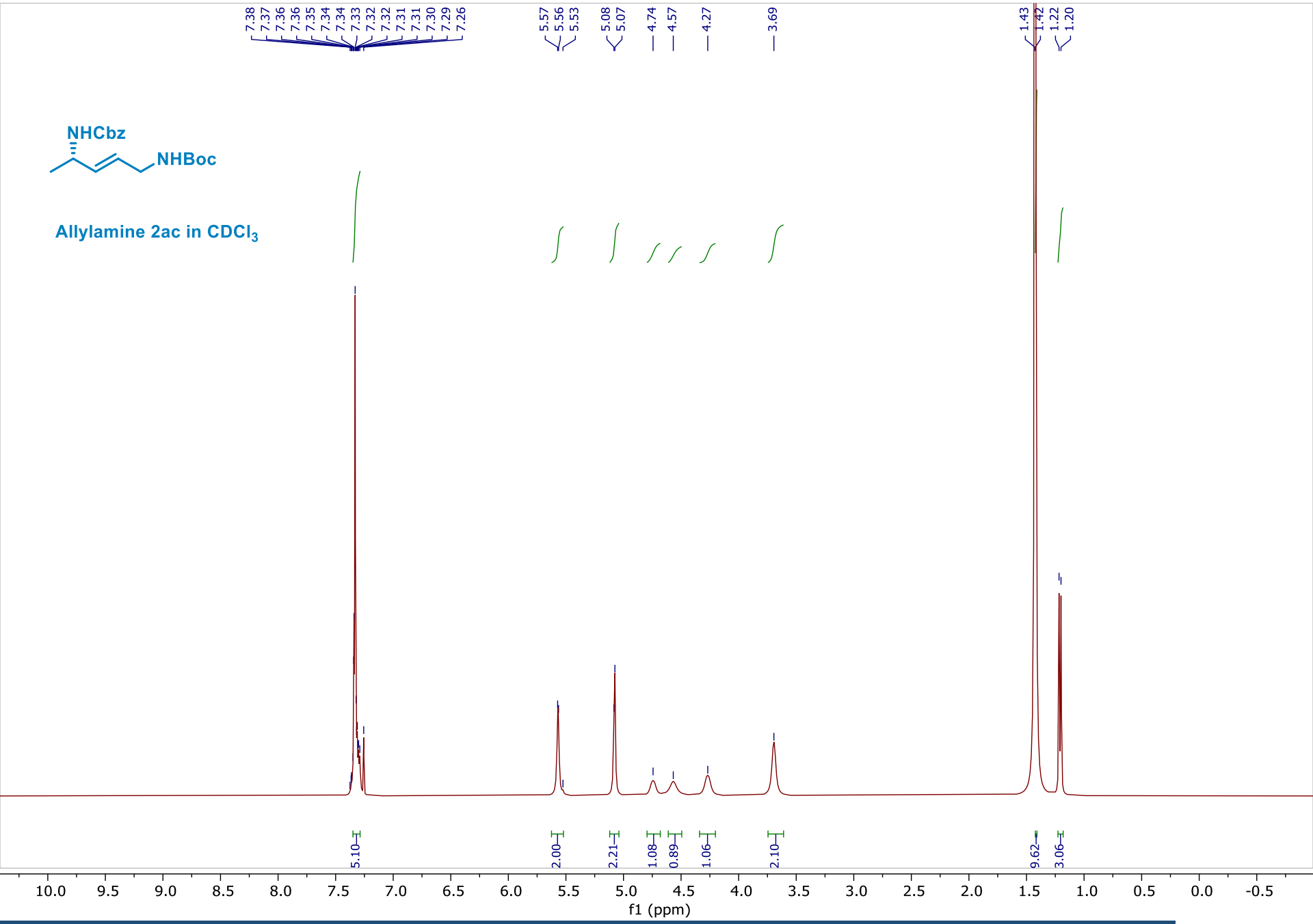
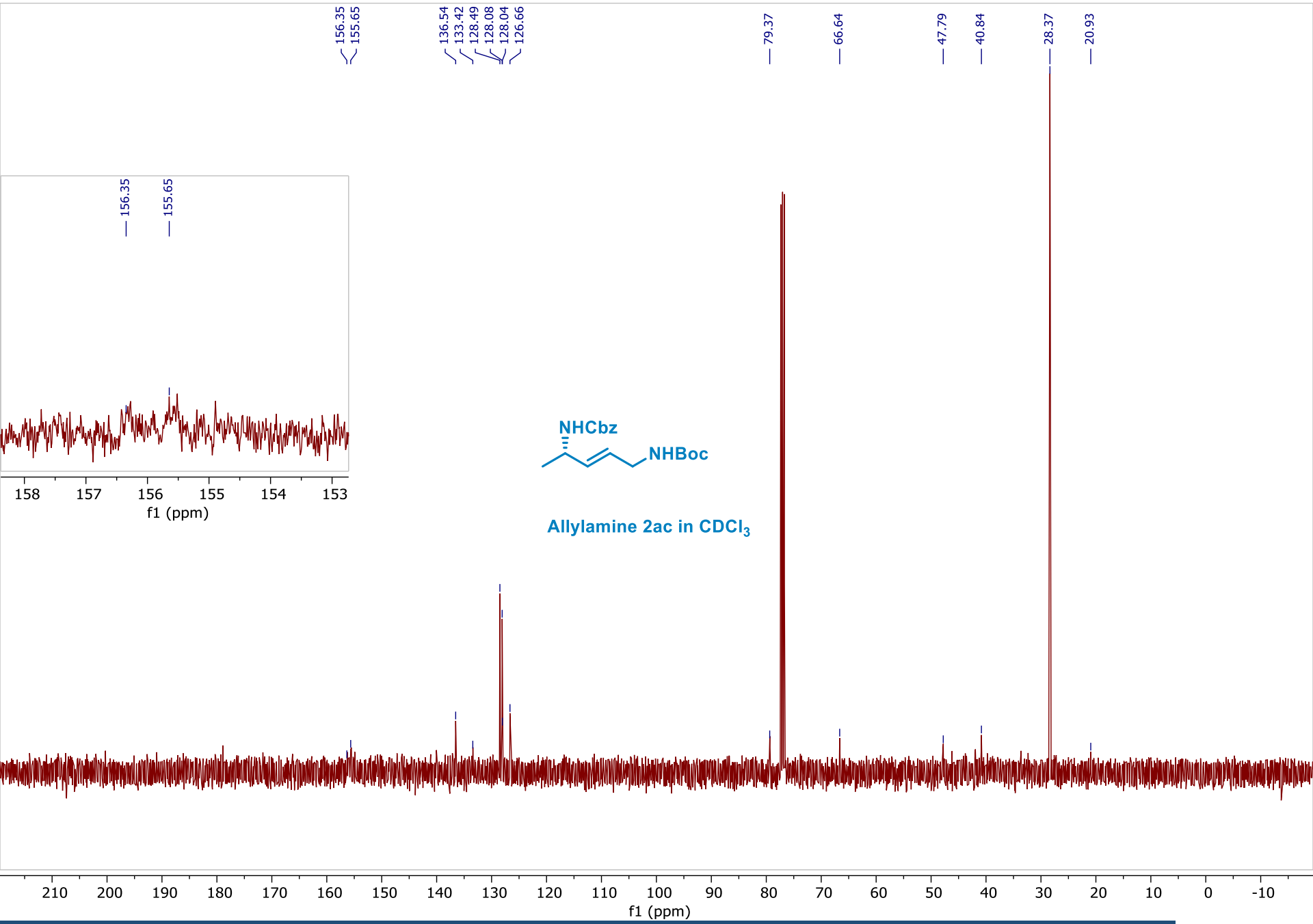
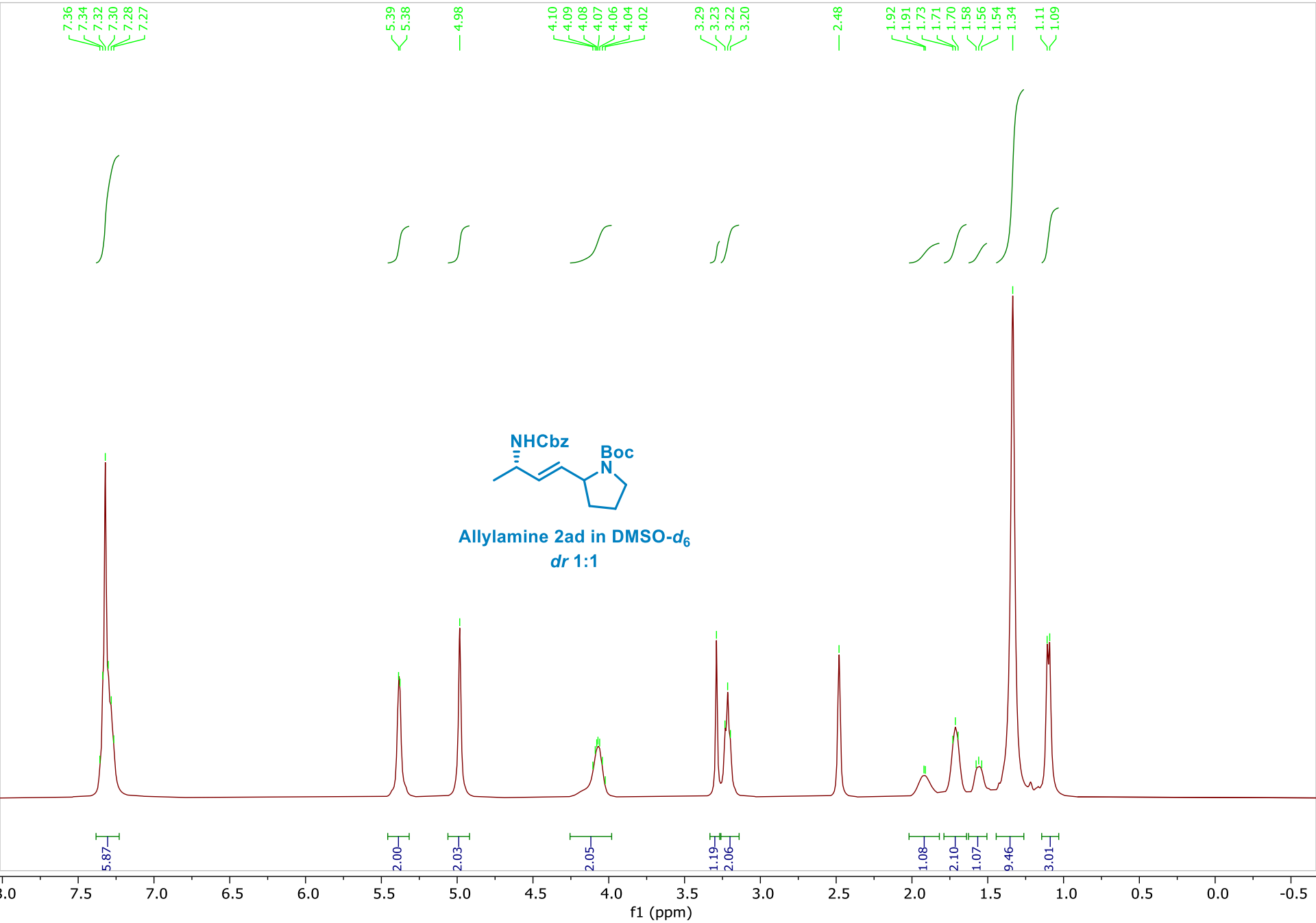
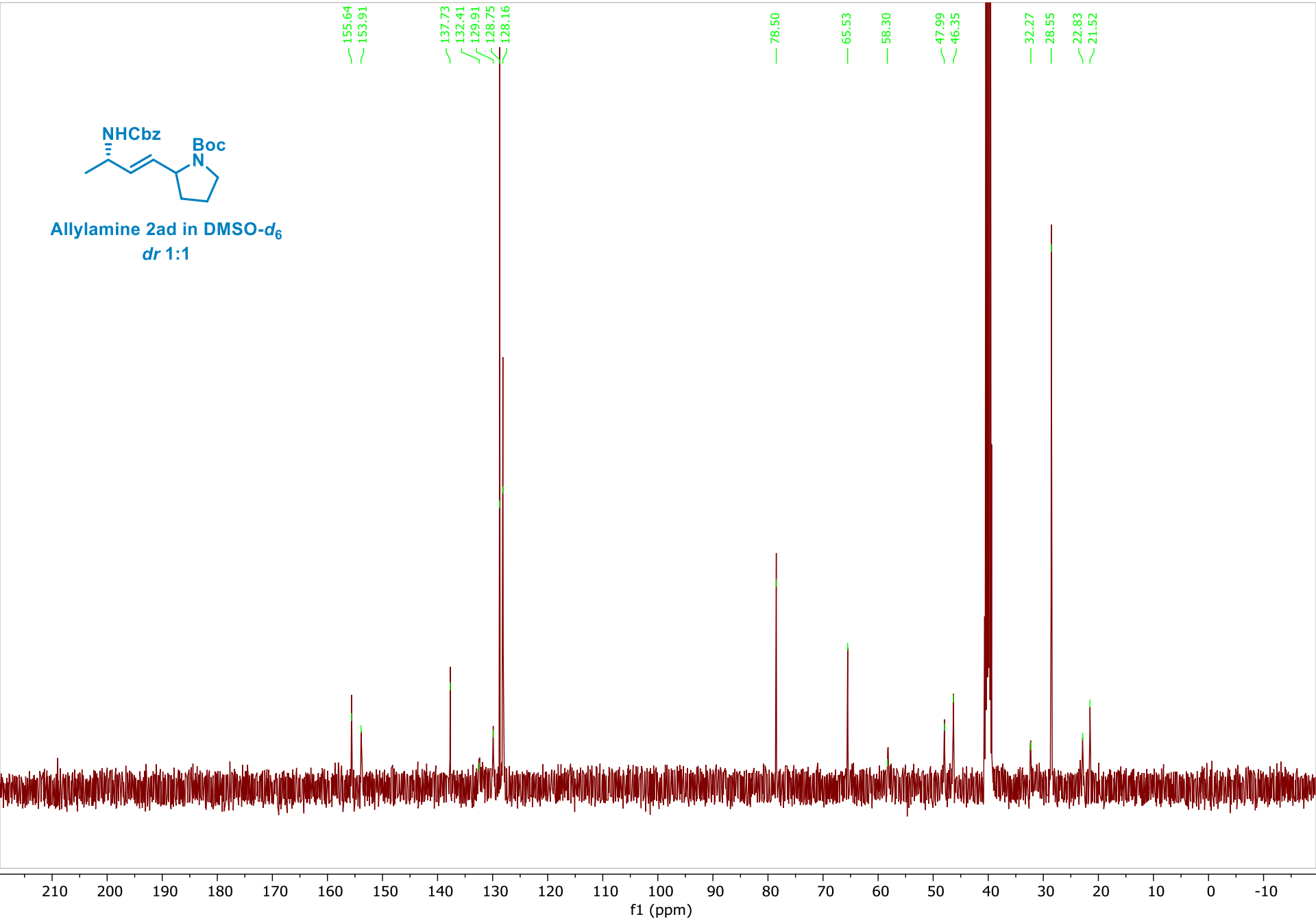
7.35
7.33
7.32
7.31
7.30
7.28
7.26
6.97
6.95
6.93
6.91
6.89
5.84
5.11
4.69
4.51
4.50
4.37
1.28
1.26
NHCbz
OPh
Allylamine 2ab in CDCl3

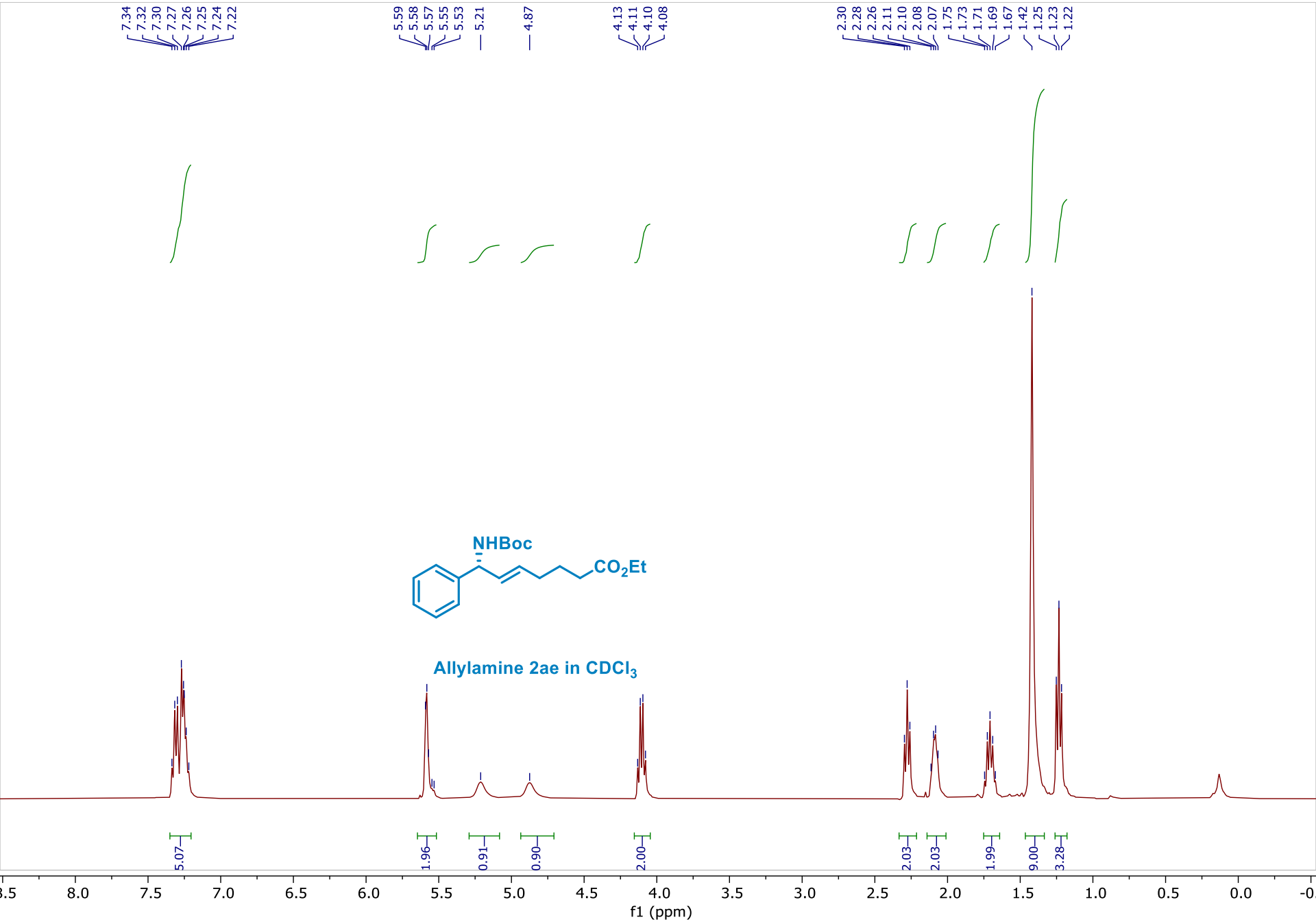

158.54
155.54
136.54
135.06
129.45
128.52
128.11
125.05
120.90
114.73
67.80
66.72
47.88
20.83
NHCbz
OPh
Allylamine 2ab in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

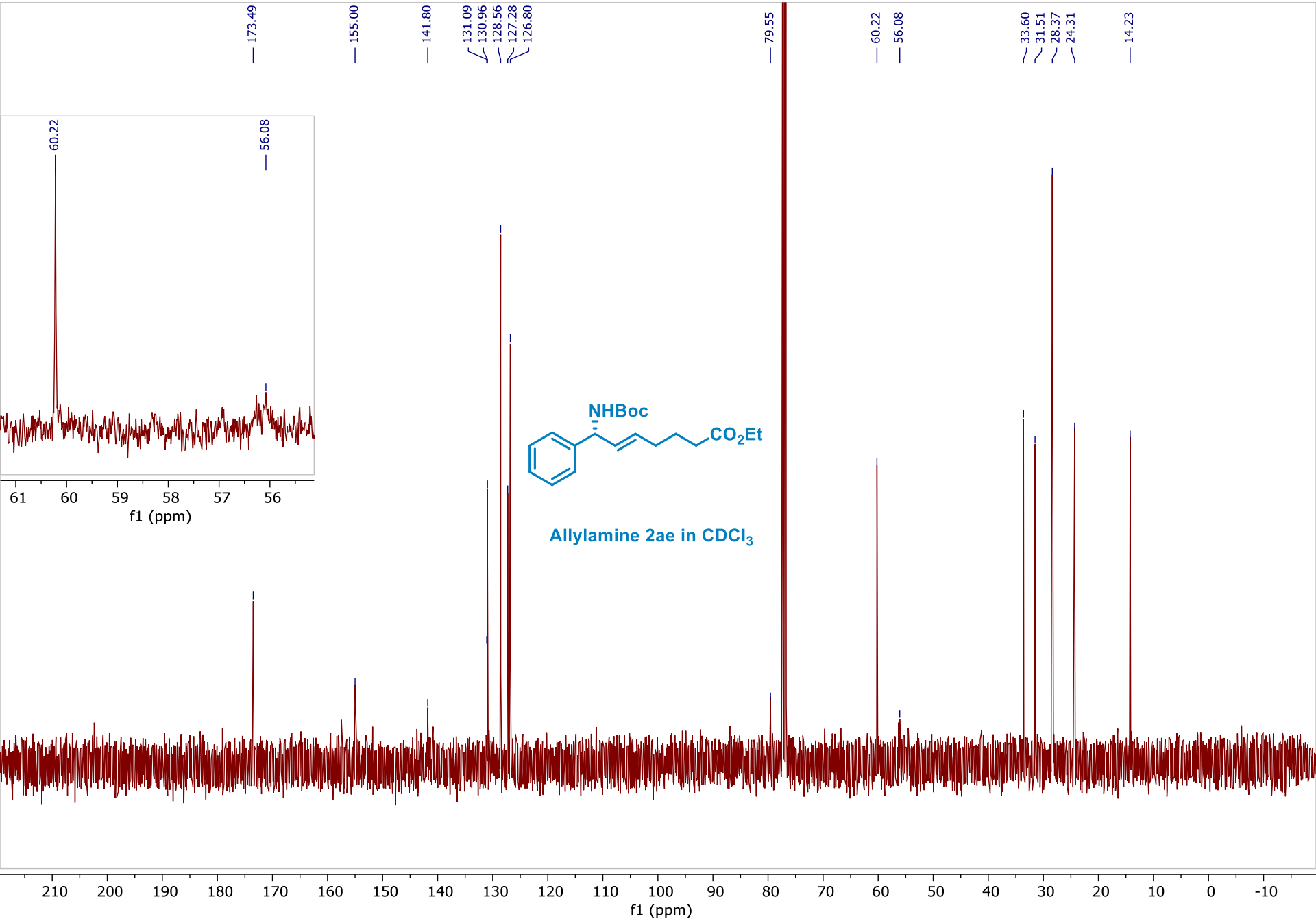

NHCbz
NHBoc
Allylamine 2ac in CDCl3
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.26
5.57
5.56
5.53
5.08
5.07
4.74
4.57
4.27
3.69
1.43
1.42
1.22
1.20
5.10
2.00
2.21
1.08
0.89
1.06
2.10
9.62
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

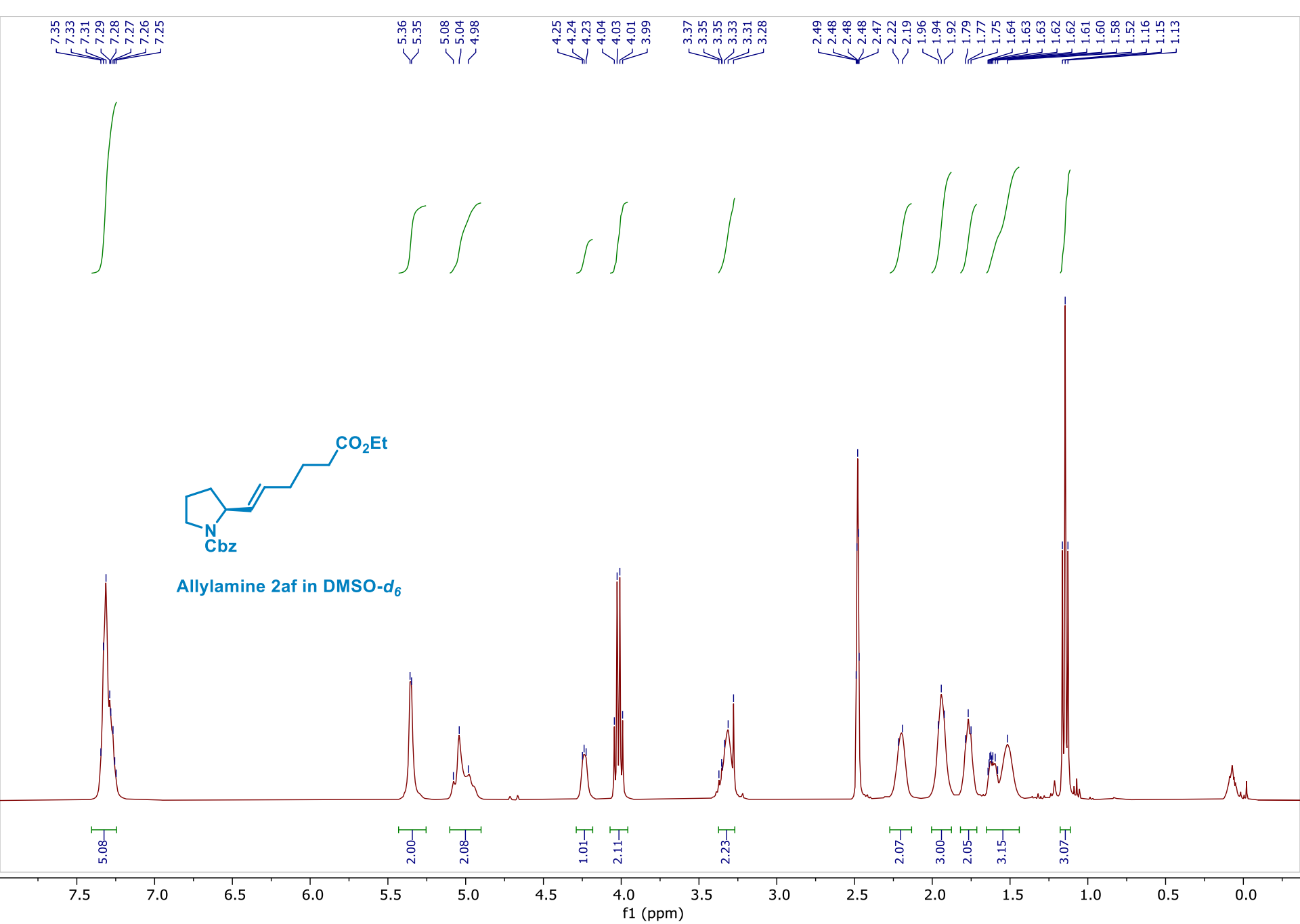

156.35
155.65
136.54
133.42
128.49
128.08
128.04
126.66
79.37
66.64
47.79
40.84
28.37
20.93
NHCbz
NHBoc
Allylamine 2ac in CDCl3
f1 (ppm)

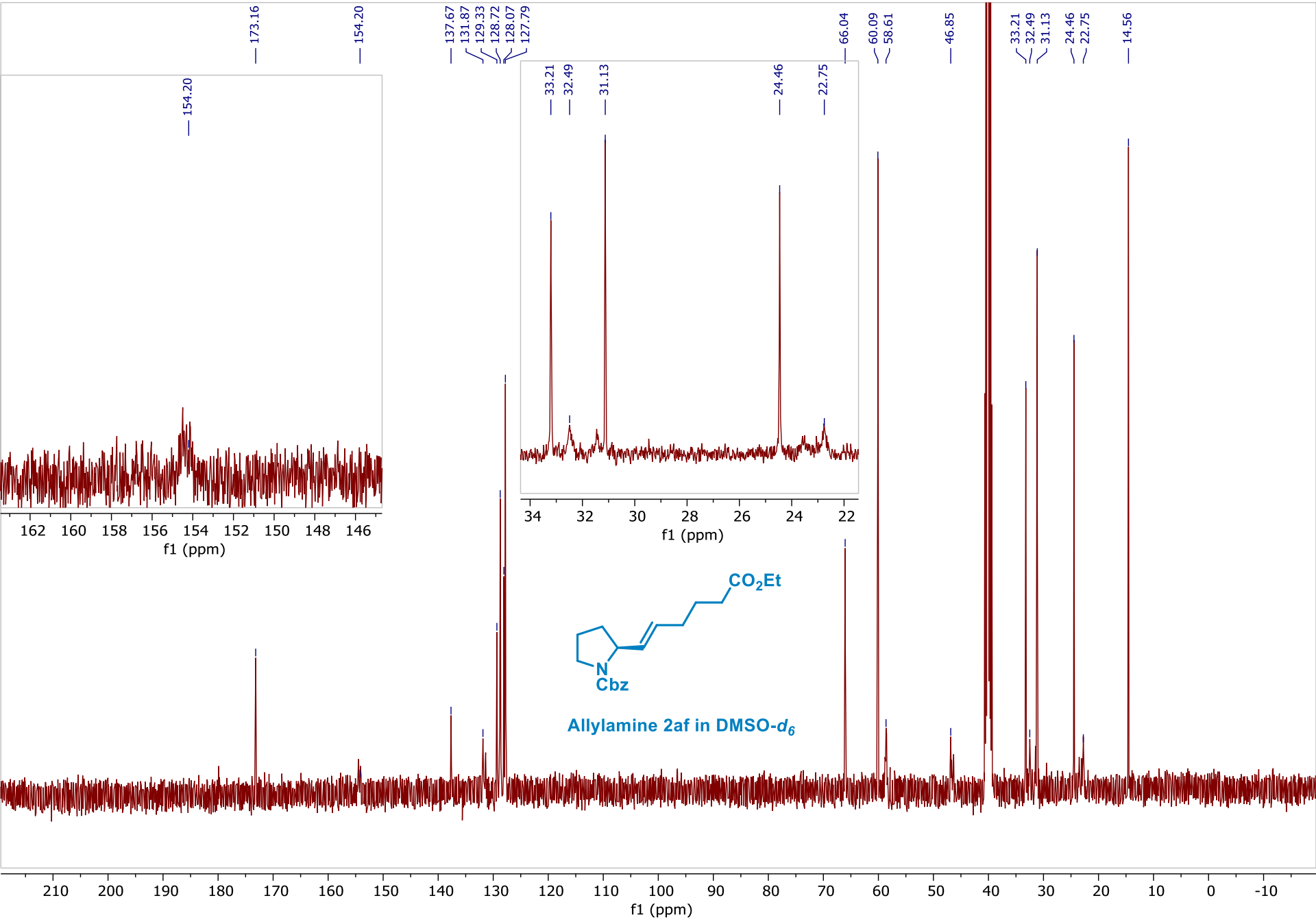

7.36
7.34
7.32
7.30
7.28
7.27
5.39
5.38
4.98
4.10
4.09
4.08
4.07
4.06
4.04
4.02
3.29
3.23
3.22
3.20
2.48
1.92
1.91
1.73
1.71
1.70
1.58
1.56
1.54
1.34
1.11
1.09
NHCbz
Boc
N
Allylamine 2ad in DMSO-d6
dr 1:1
5.87
2.00
2.03
2.05
1.19
2.06
1.08
2.10
1.07
9.46
3.01
f1 (ppm)

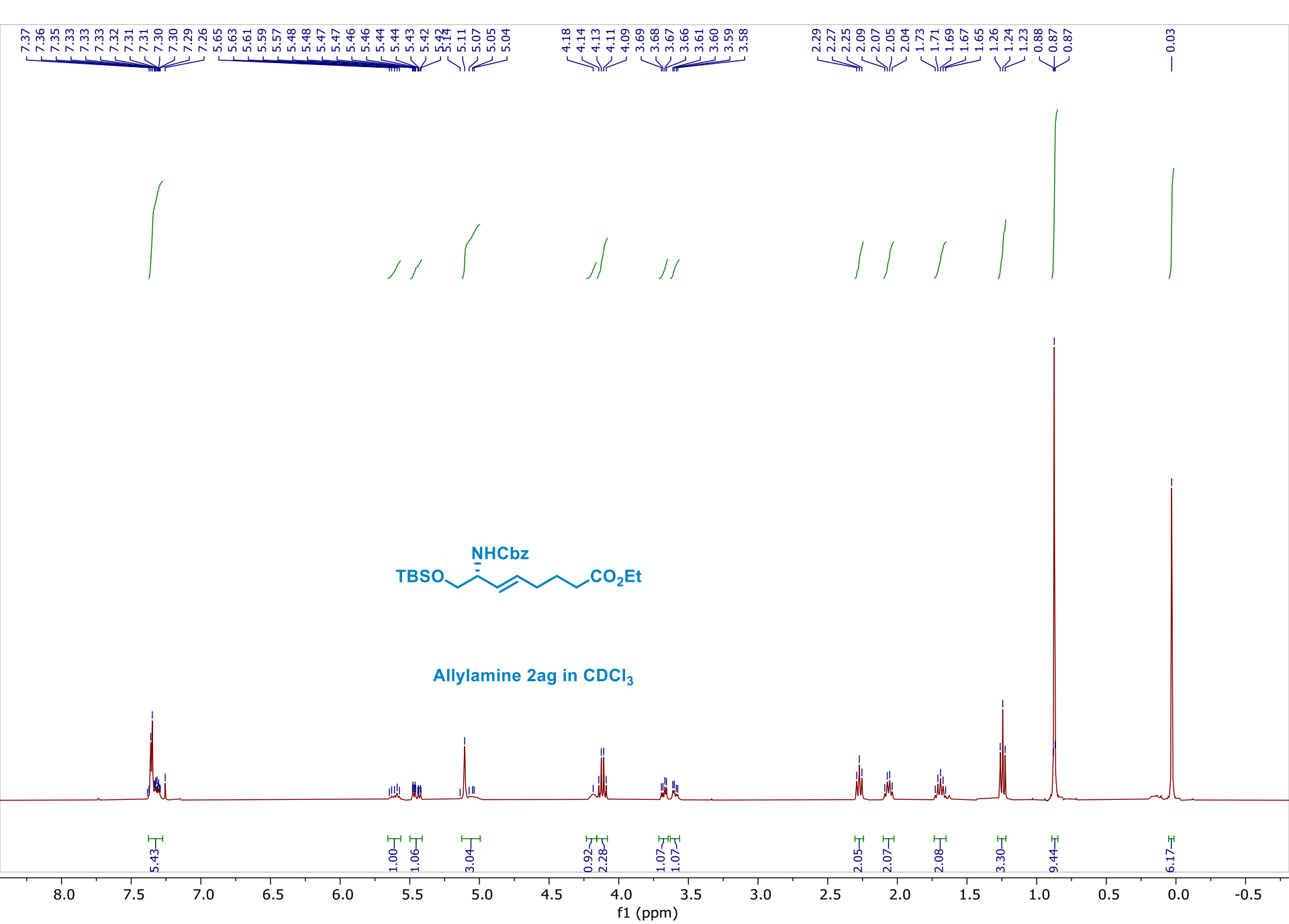

155.64
153.91
137.73
132.41
129.91
128.75
128.16
78.50
65.53
58.30
47.99
46.35
32.27
28.55
22.83
21.52
NHCbz
Boc
N
Allylamine 2ad in DMSO-d_6
dr 1:1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

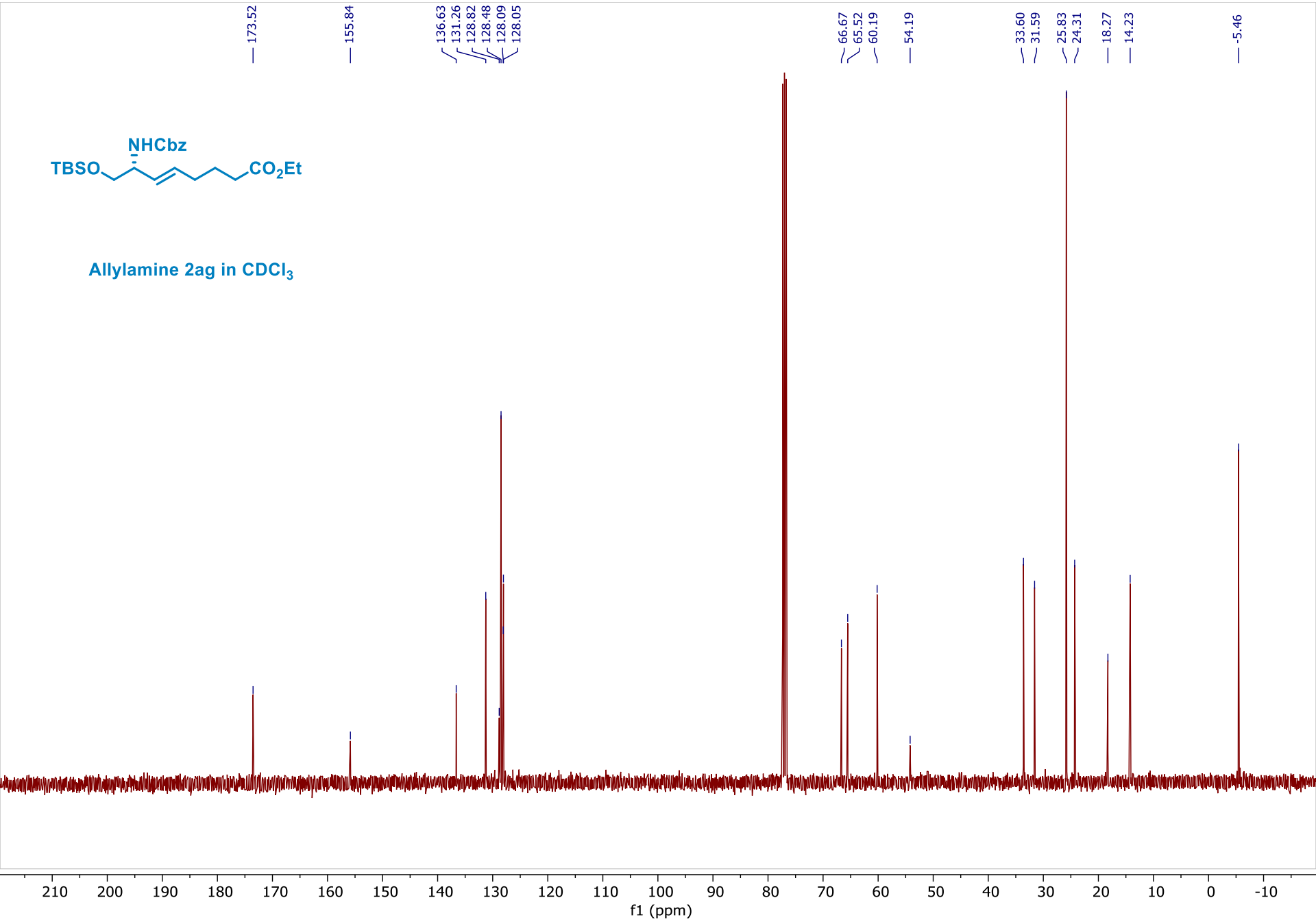

7.34
7.32
7.30
7.27
7.26
7.25
7.24
7.22
5.59
5.58
5.57
5.55
5.53
5.21
4.87
4.13
4.11
4.10
4.08
2.30
2.28
2.26
2.11
2.10
2.08
2.07
1.75
1.73
1.71
1.69
1.67
1.42
1.25
1.23
1.22
NHBoc
CO2Et
Allylamine 2ae in CDCl3
5.07
1.96
0.91
0.90
2.00
2.03
2.03
1.99
9.00
3.28
f1 (ppm)

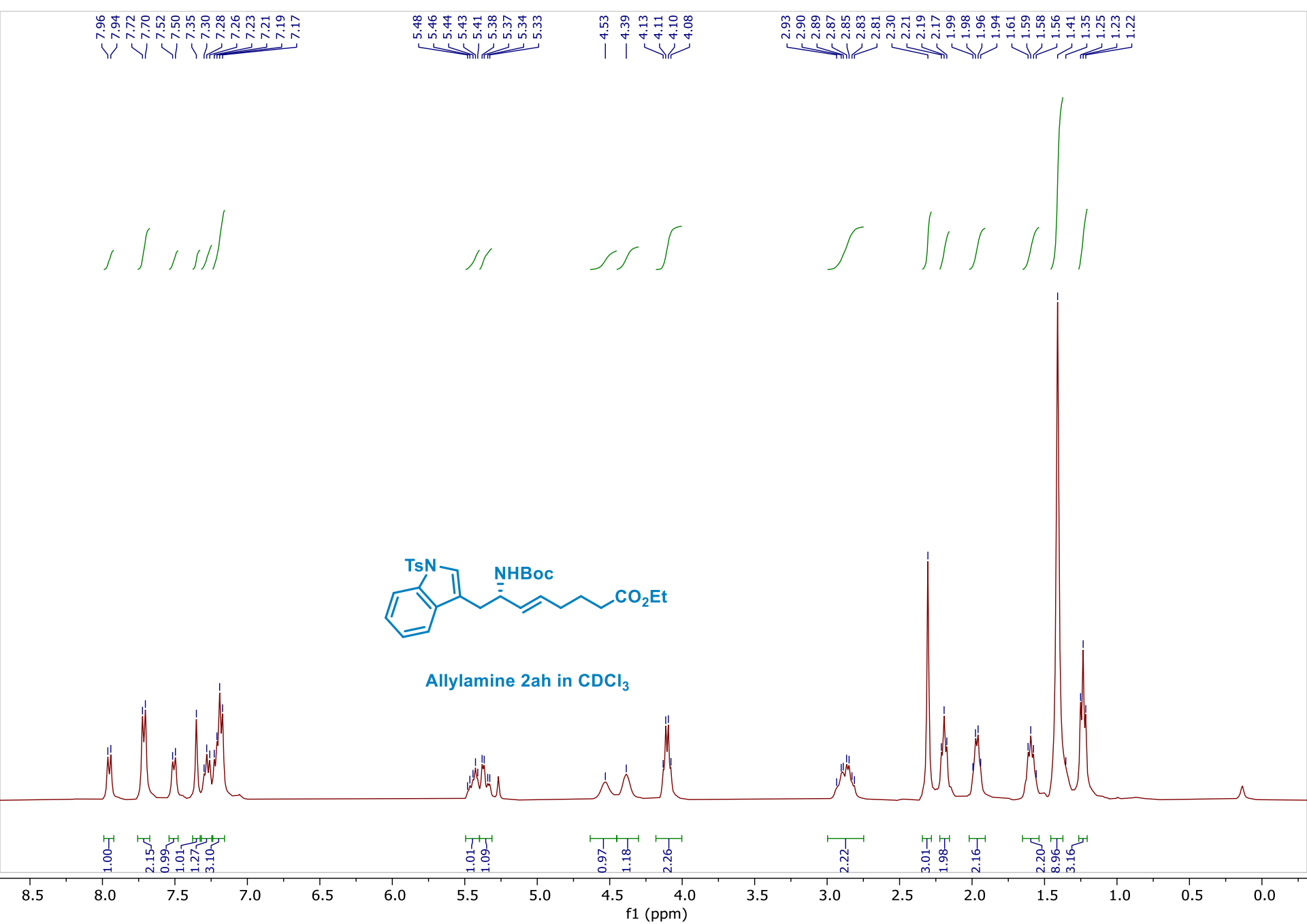

173.49
155.00
141.80
131.09
130.96
128.56
127.28
126.80
79.55
60.22
56.08
33.60
31.51
28.37
24.31
14.23
NHBoc
CO2Et
Allylamine 2ae in CDCl3
f1 (ppm)

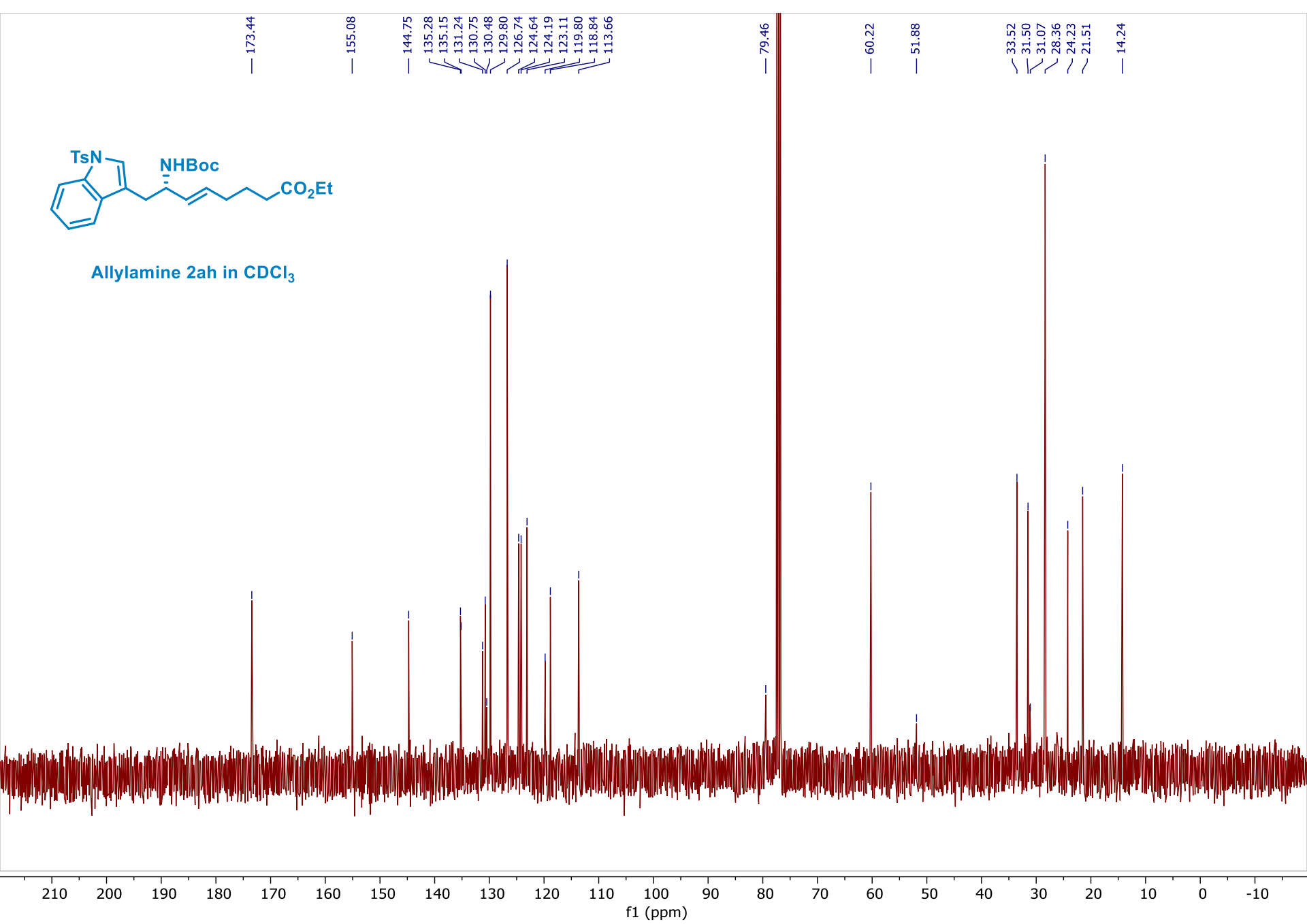

7.35
7.33
7.31
7.29
7.28
7.27
7.26
7.25
5.36
5.35
5.08
5.04
4.98
4.25
4.24
4.23
4.04
4.03
4.01
3.99
3.37
3.35
3.35
3.33
3.31
3.28
2.49
2.48
2.48
2.48
2.47
2.22
2.19
1.96
1.94
1.92
1.79
1.77
1.75
1.64
1.63
1.63
1.62
1.62
1.61
1.60
1.58
1.52
1.16
1.15
1.13
CO2Et
N
Cbz
Allylamine 2af in DMSO-d6
5.08
2.00
2.08
1.01
2.11
2.23
2.07
3.00
2.05
3.15
3.07
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)

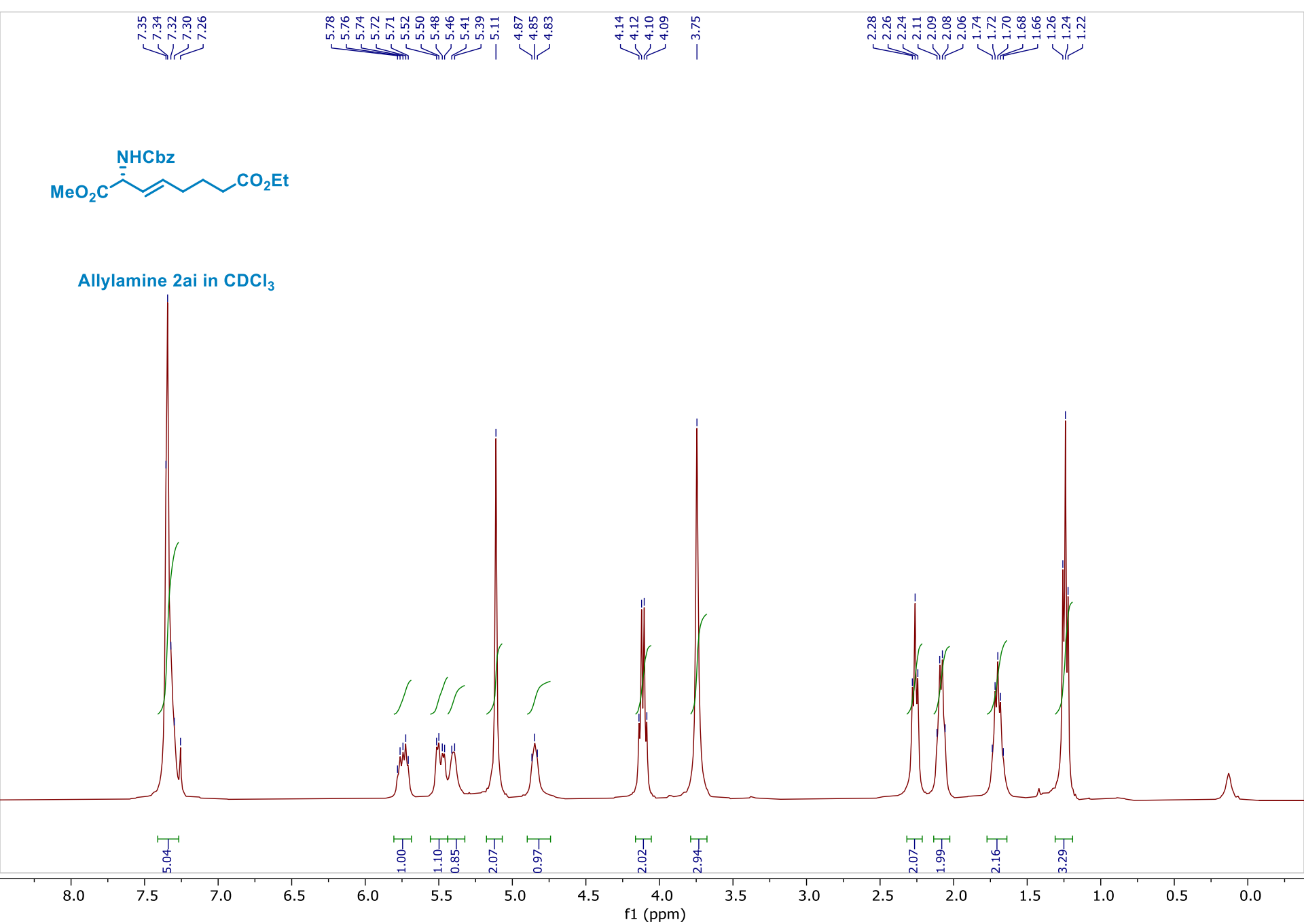

173.16
154.20
137.67
131.87
129.33
128.72
128.07
127.79
66.04
60.09
58.61
46.85
33.21
32.49
31.13
24.46
22.75
14.56
f1 (ppm)
CO2Et
N
Cbz
Allylamine 2af in DMSO-d6

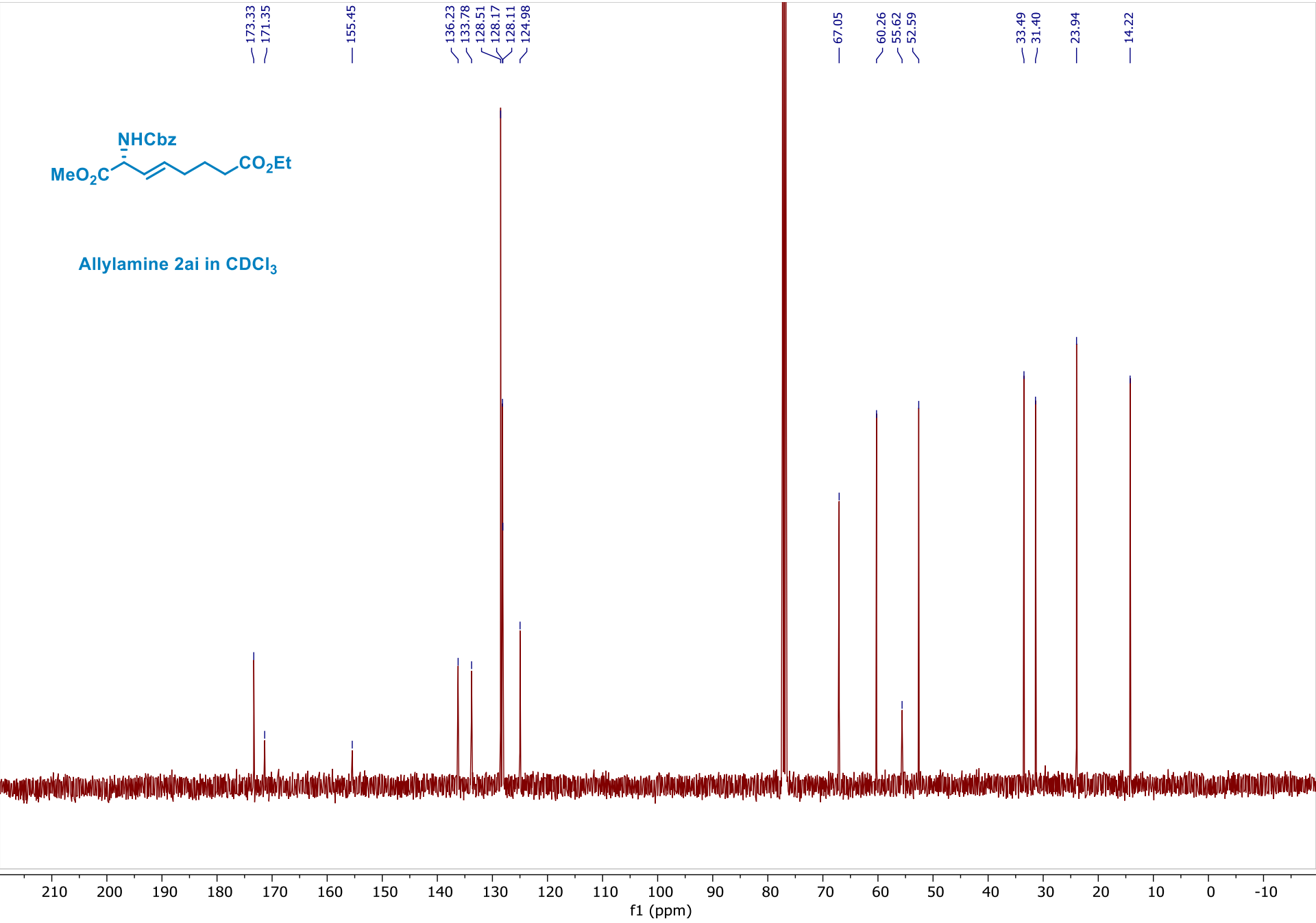

NHCbz
TBSO
CO2Et
Allylamine 2ag in CDCl3
f1 (ppm)

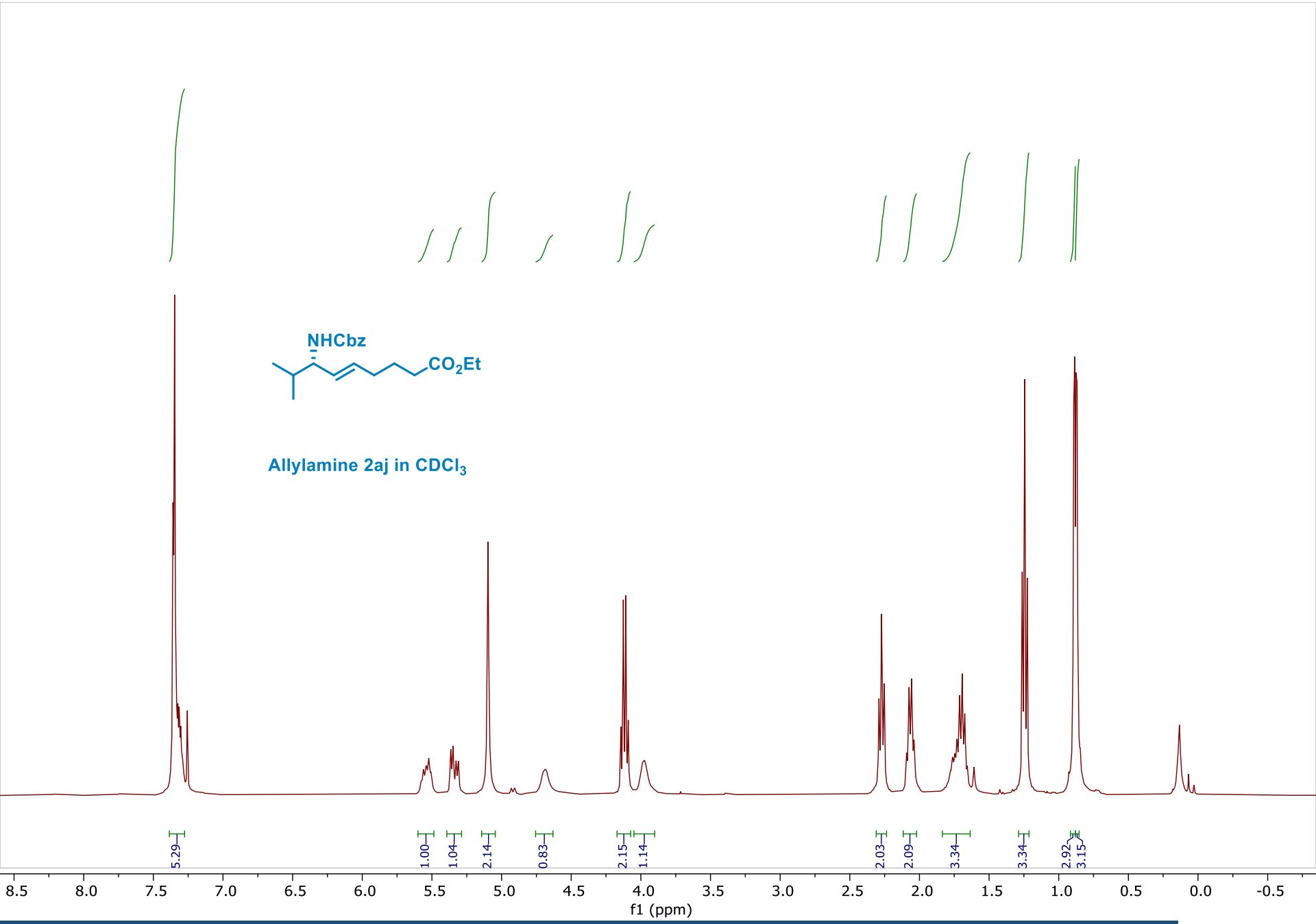

173.52
155.84
136.63
131.26
128.82
128.48
128.09
128.05
66.67
65.52
60.19
54.19
33.60
31.59
25.83
24.31
18.27
14.23
-5.46
NHCbz
TBSO
CO2Et
Allylamine 2ag in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

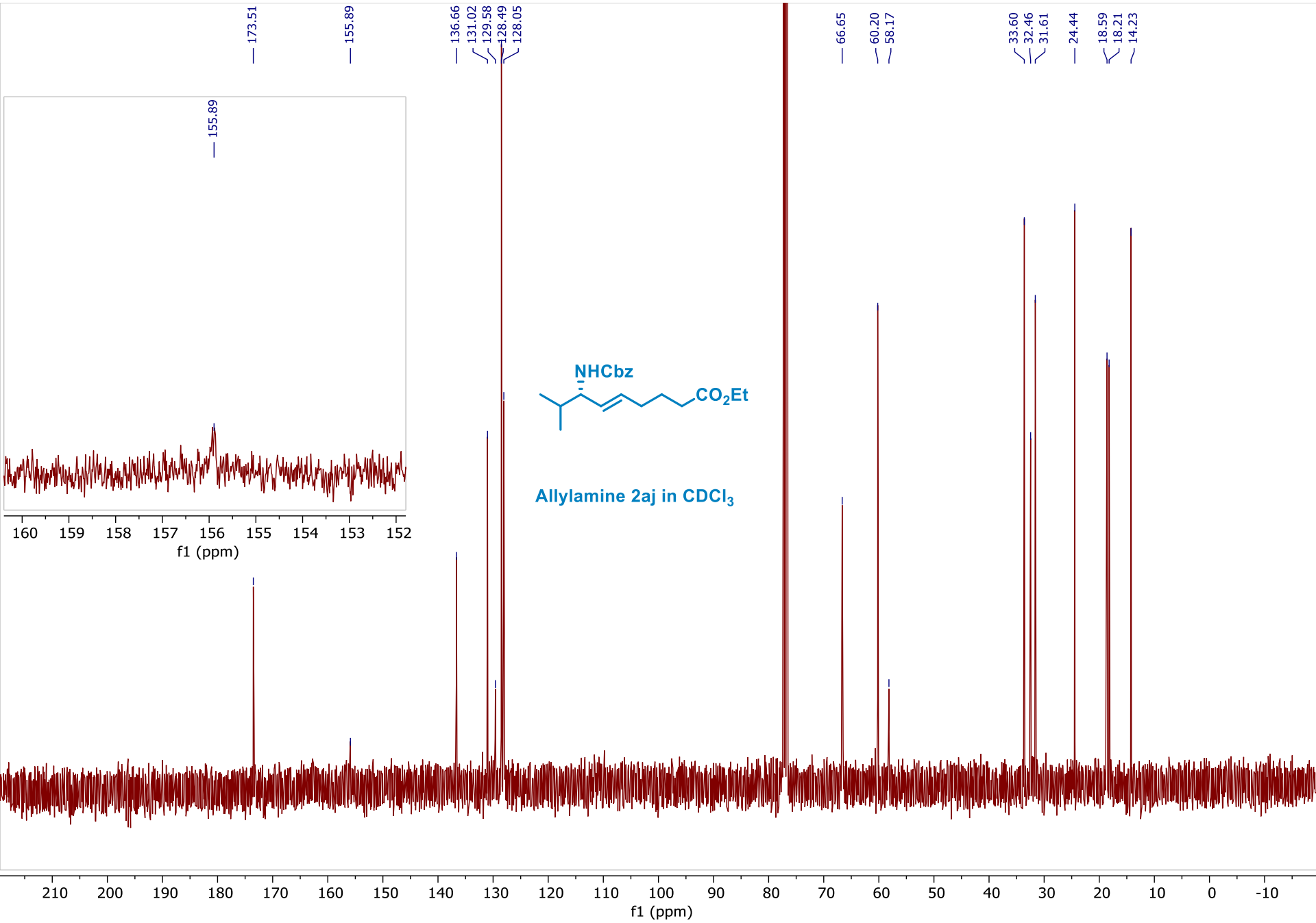

7.96
7.94
7.72
7.70
7.52
7.50
7.35
7.30
7.28
7.26
7.23
7.21
7.19
7.17
5.48
5.46
5.44
5.43
5.41
5.38
5.37
5.34
5.33
4.53
4.39
4.13
4.11
4.10
4.08
2.93
2.90
2.89
2.87
2.85
2.83
2.81
2.30
2.21
2.19
2.17
1.99
1.98
1.96
1.94
1.61
1.59
1.58
1.56
1.41
1.35
1.25
1.23
1.22
TsN
NHBoc
CO2Et
Allylamine 2ah in CDCl3
1.00
2.15
0.99
1.01
1.27
3.10
1.01
1.09
0.97
1.18
2.26
2.22
3.01
1.98
2.16
2.20
8.96
3.16
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)

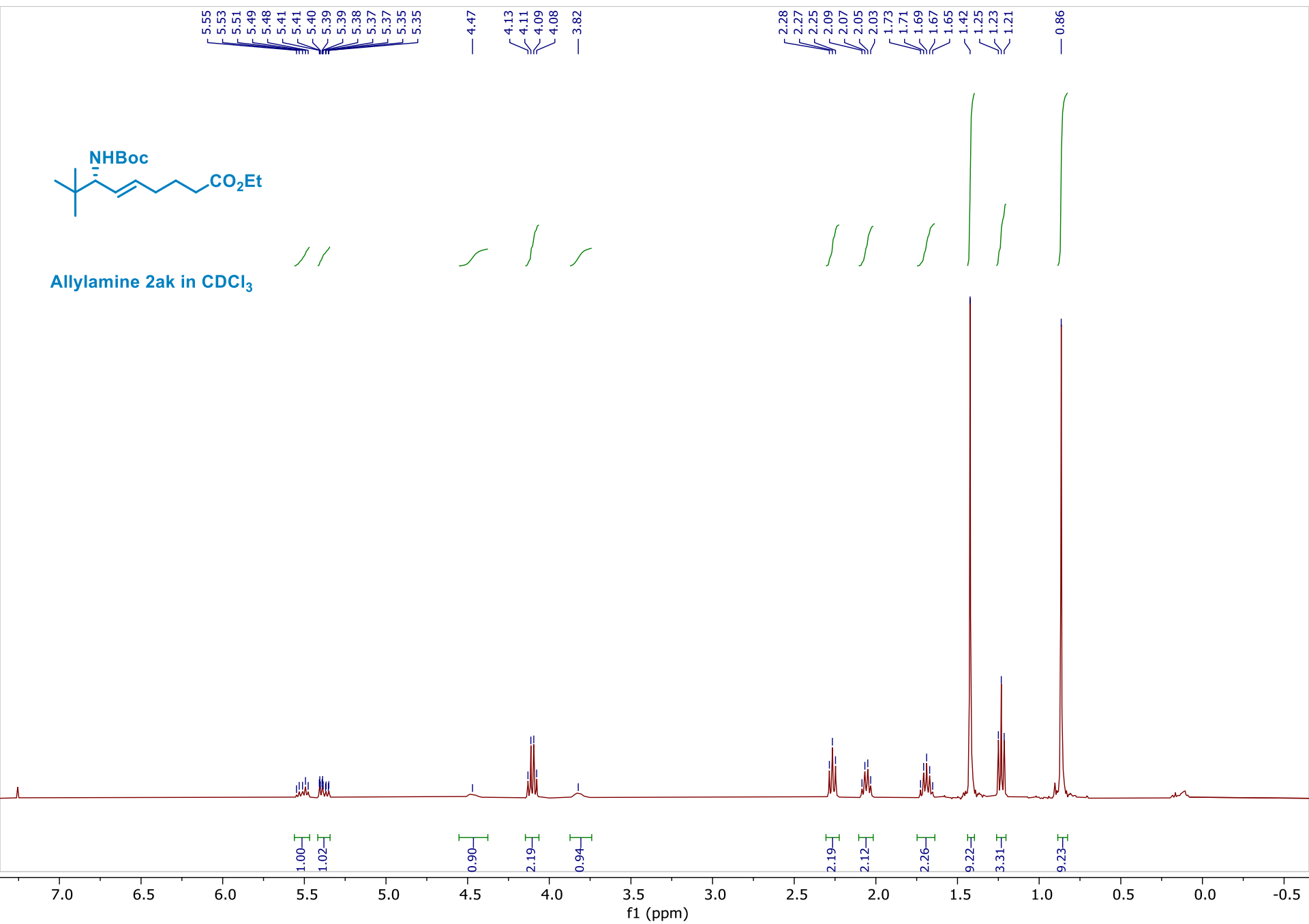

173.44
155.08
144.75
135.28
135.15
131.24
130.75
130.48
129.80
126.74
124.64
124.19
123.11
119.80
118.84
113.66
79.46
60.22
51.88
33.52
31.50
31.07
28.36
24.23
21.51
14.24
TsN
NHBoc
CO2Et
Allylamine 2ah in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

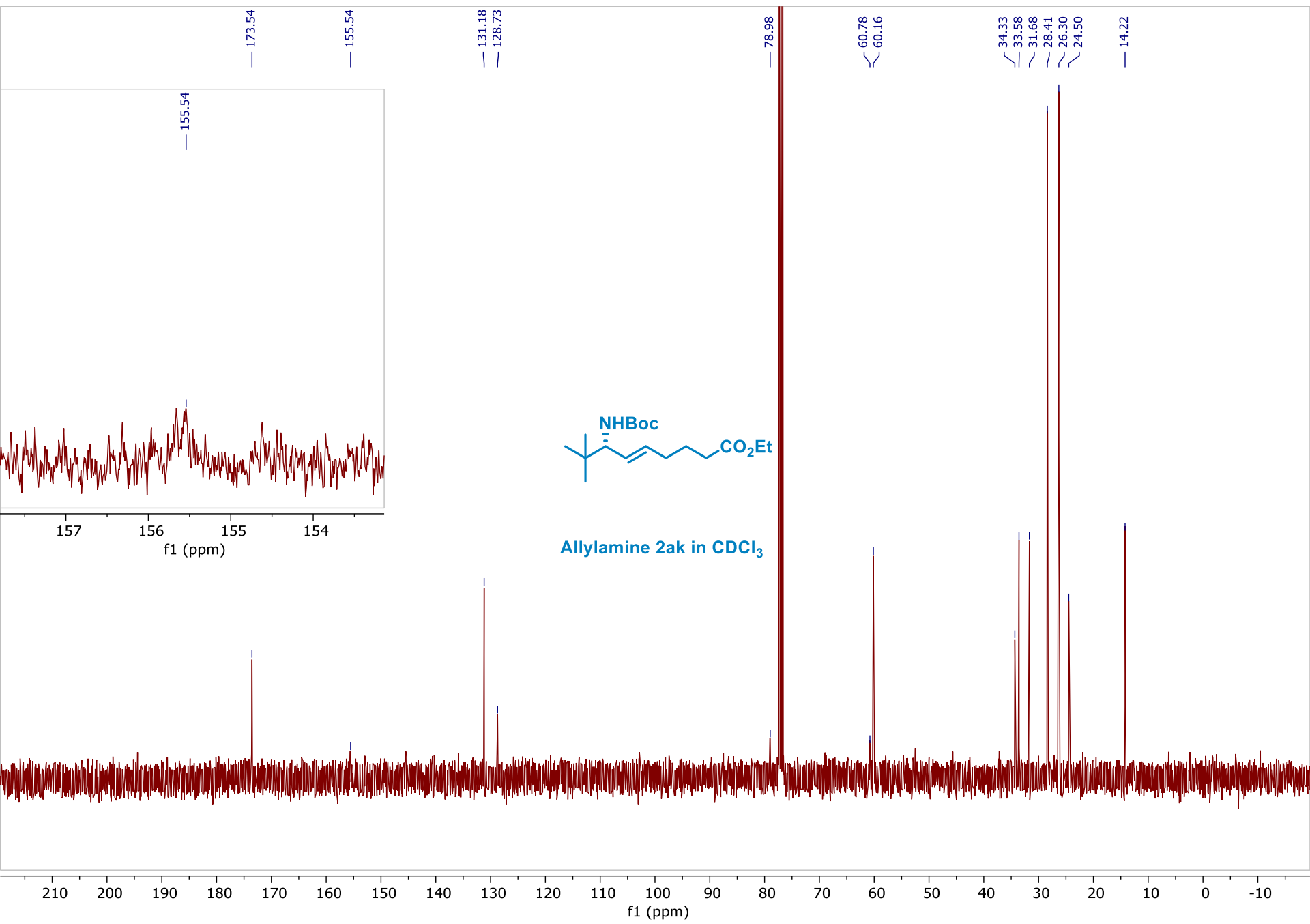

7.35
7.34
7.32
7.30
7.26
5.78
5.76
5.74
5.72
5.71
5.52
5.50
5.48
5.46
5.41
5.39
5.11
4.87
4.85
4.83
4.14
4.12
4.10
4.09
3.75
2.28
2.26
2.24
2.11
2.09
2.08
2.06
1.74
1.72
1.70
1.68
1.66
1.26
1.24
1.22
NHCbz
MeO2C
CO2Et
Allylamine 2ai in CDCl3
5.04
1.00
1.10
0.85
2.07
0.97
2.02
2.94
2.07
1.99
2.16
3.29
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)

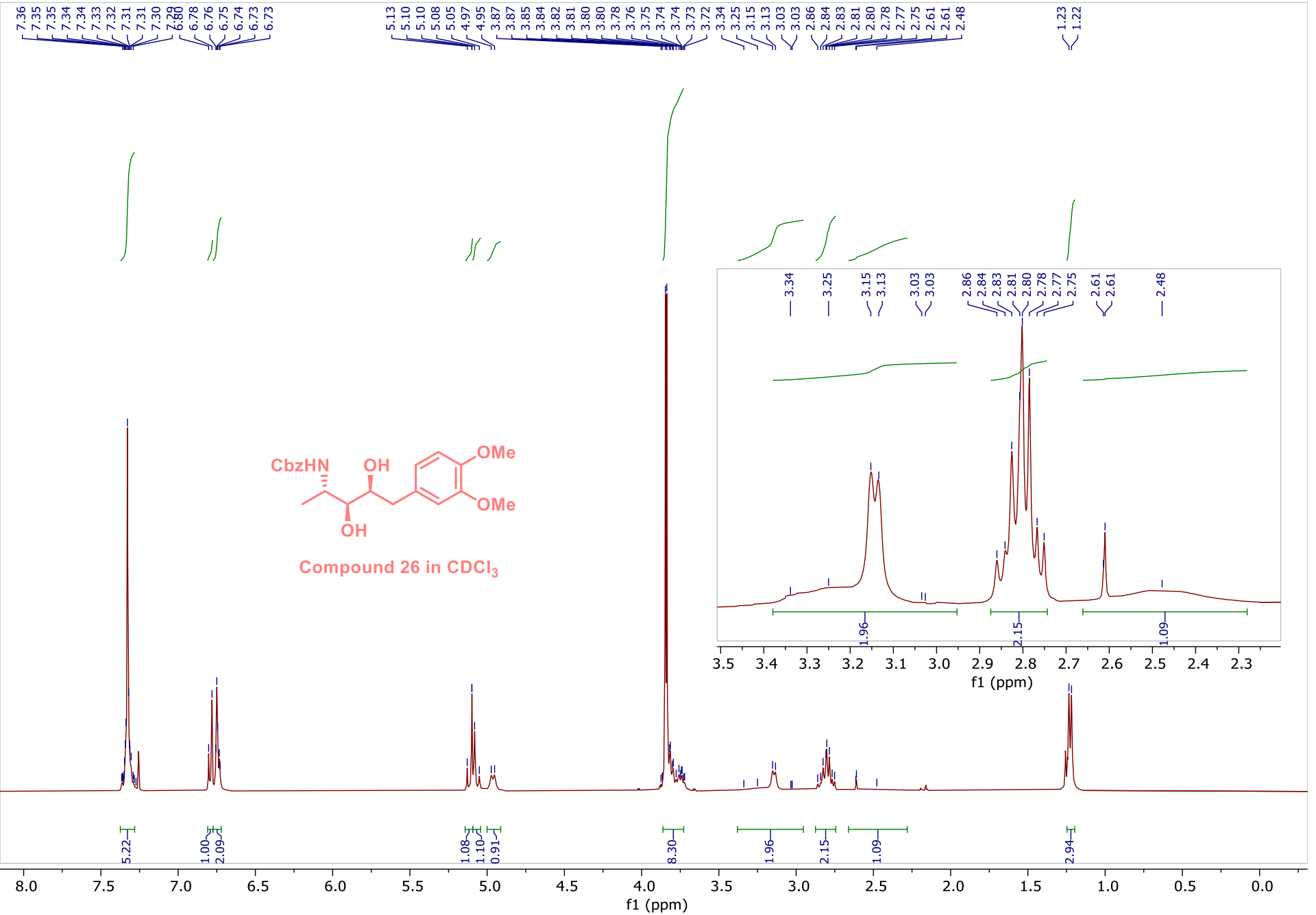

173.33
171.35
155.45
136.23
133.78
128.51
128.17
128.11
124.98
67.05
60.26
55.62
52.59
33.49
31.40
23.94
14.22
NHCbz
MeO2C
CO2Et
Allylamine 2ai in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

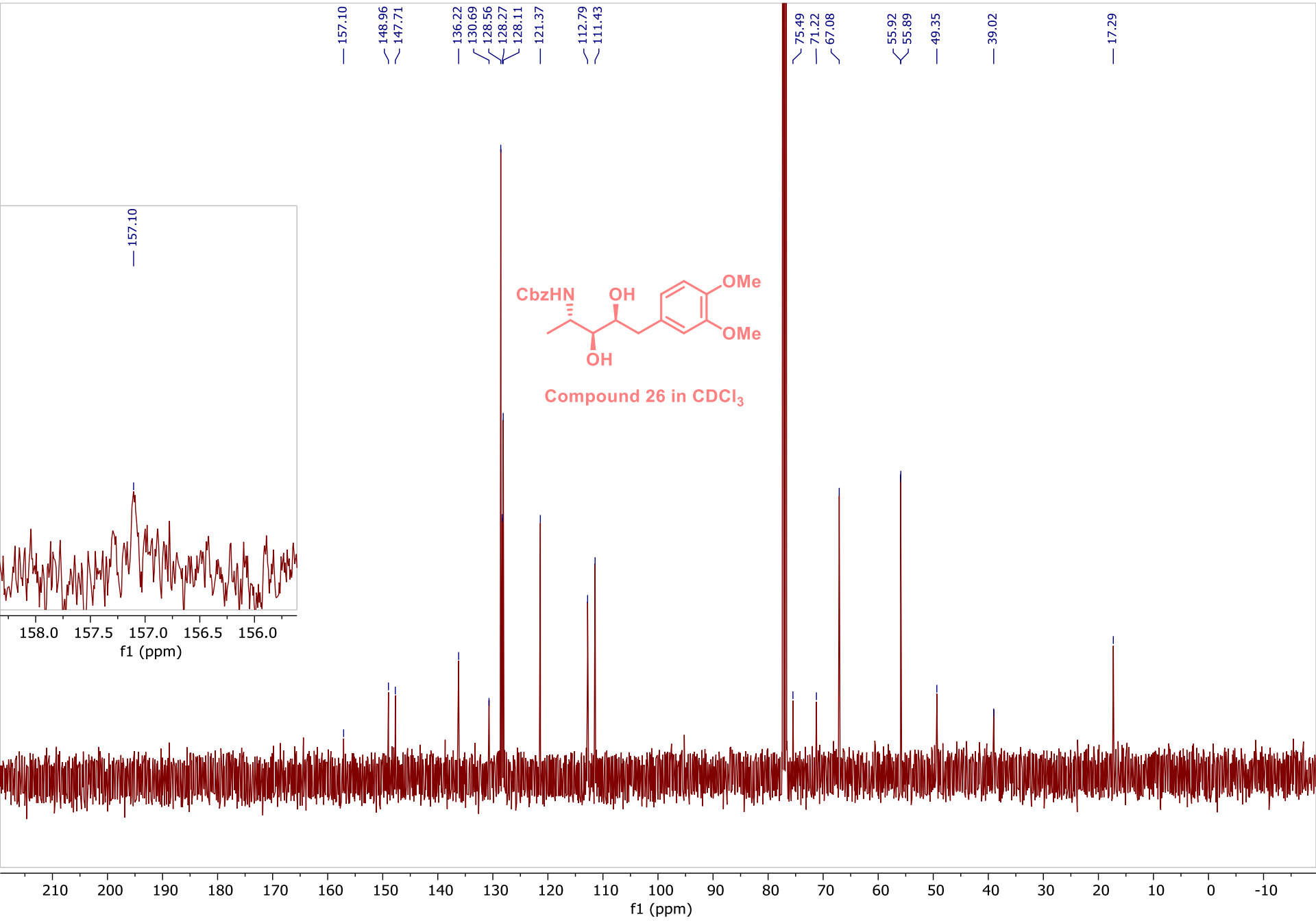

NHCbz
CO2Et
Allylamine 2aj in CDCl3
5.29
1.00
1.04
2.14
0.83
2.15
1.14
2.03
2.09
3.34
3.34
2.92
3.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

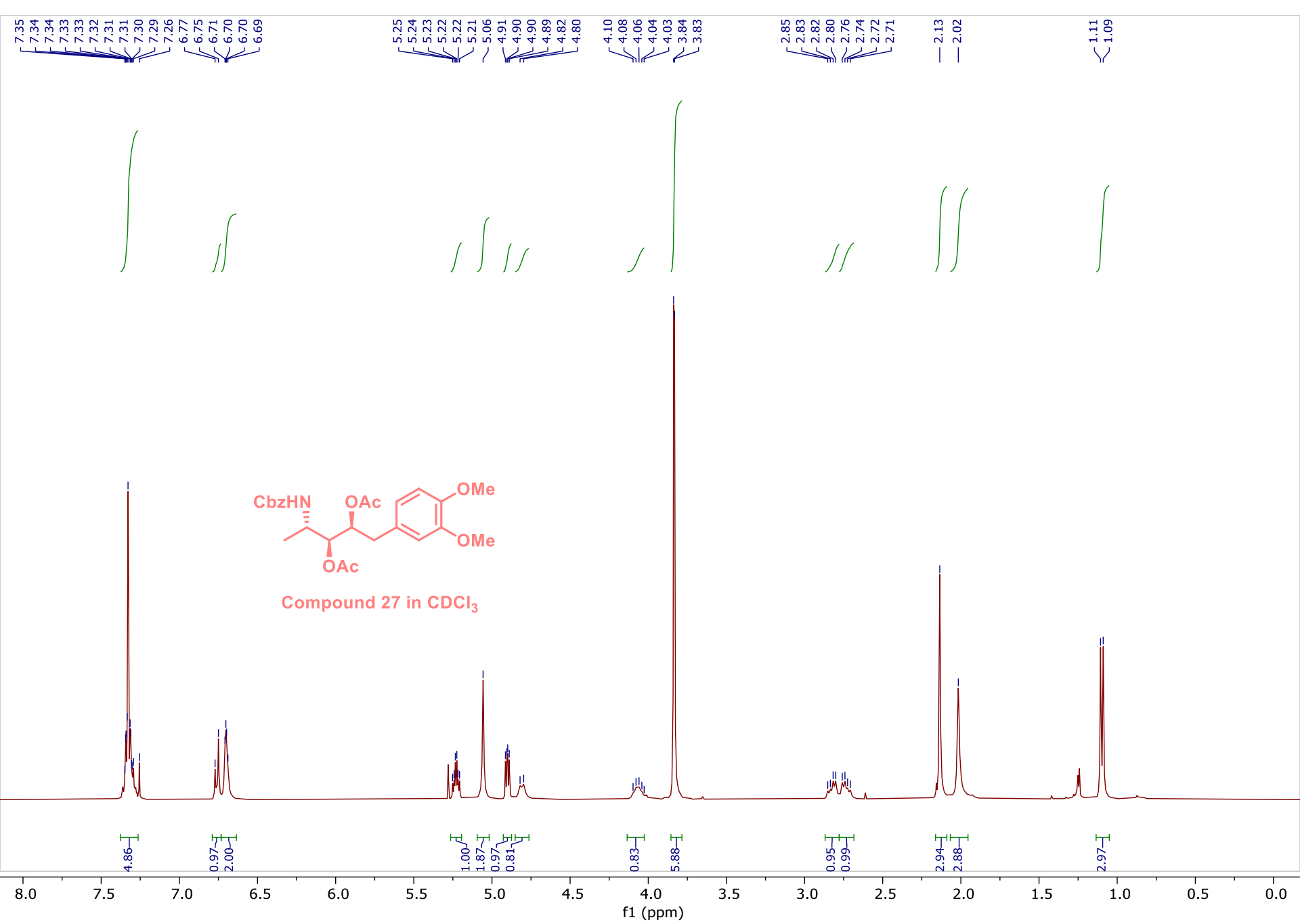

173.51
155.89
136.66
131.02
129.58
128.49
128.05
66.65
60.20
58.17
33.60
32.46
31.61
24.44
18.59
18.21
14.23
NHCbz
CO2Et
Allylamine 2aj in CDCl3
f1 (ppm)

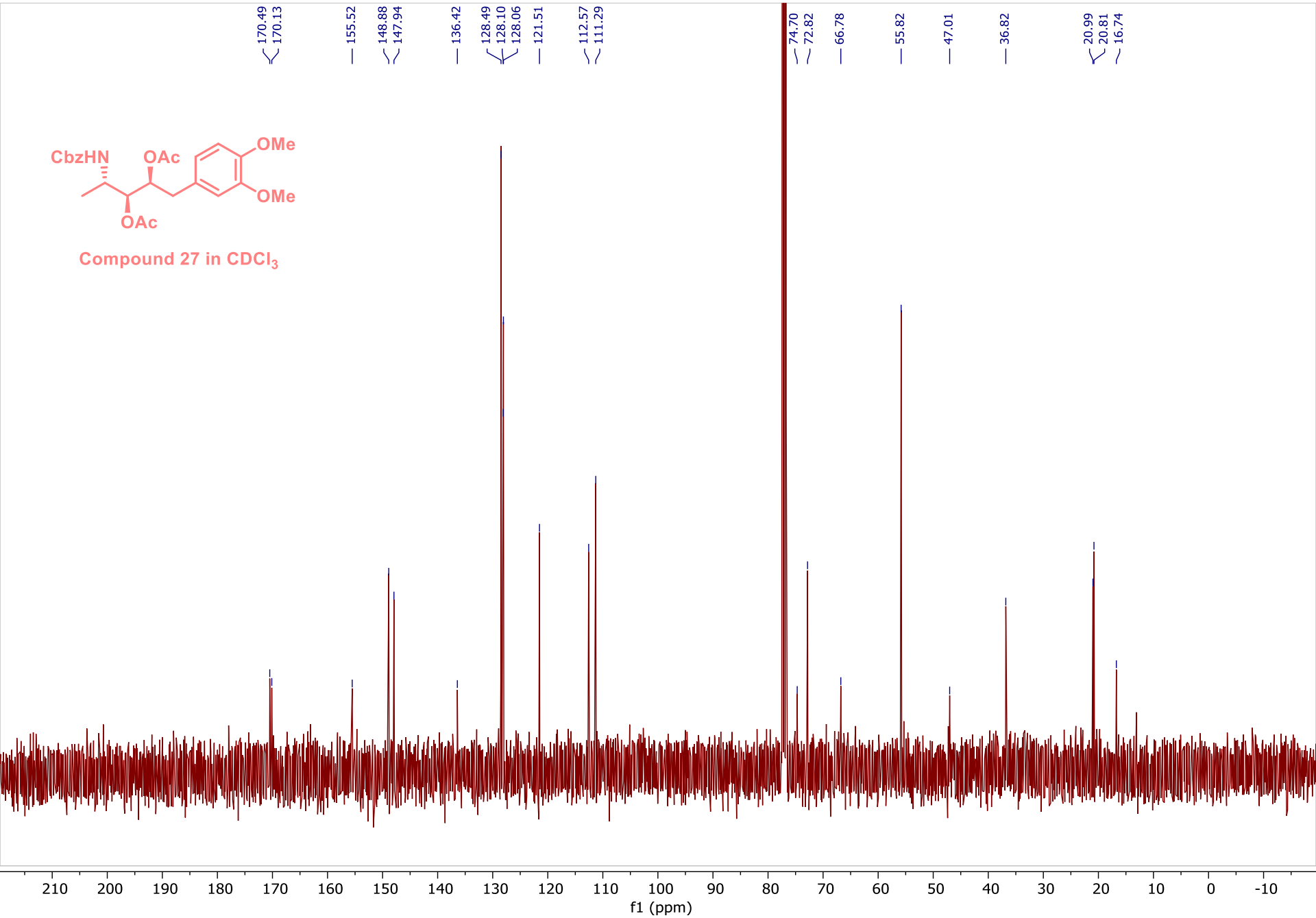

NHBoc
CO2Et
Allylamine 2ak in CDCl3
5.55 5.53 5.51 5.49 5.48 5.41 5.41 5.40 5.39 5.39 5.38 5.37 5.37 5.35 5.35
4.47
4.13 4.11 4.09 4.08
3.82
2.28 2.27 2.25 2.09 2.07 2.05 2.03
1.73 1.71 1.69 1.67 1.65
1.42
1.25 1.23 1.21
0.86
1.00 1.02 0.90 2.19 0.94 2.19 2.12 2.26 9.22 3.31 9.23
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

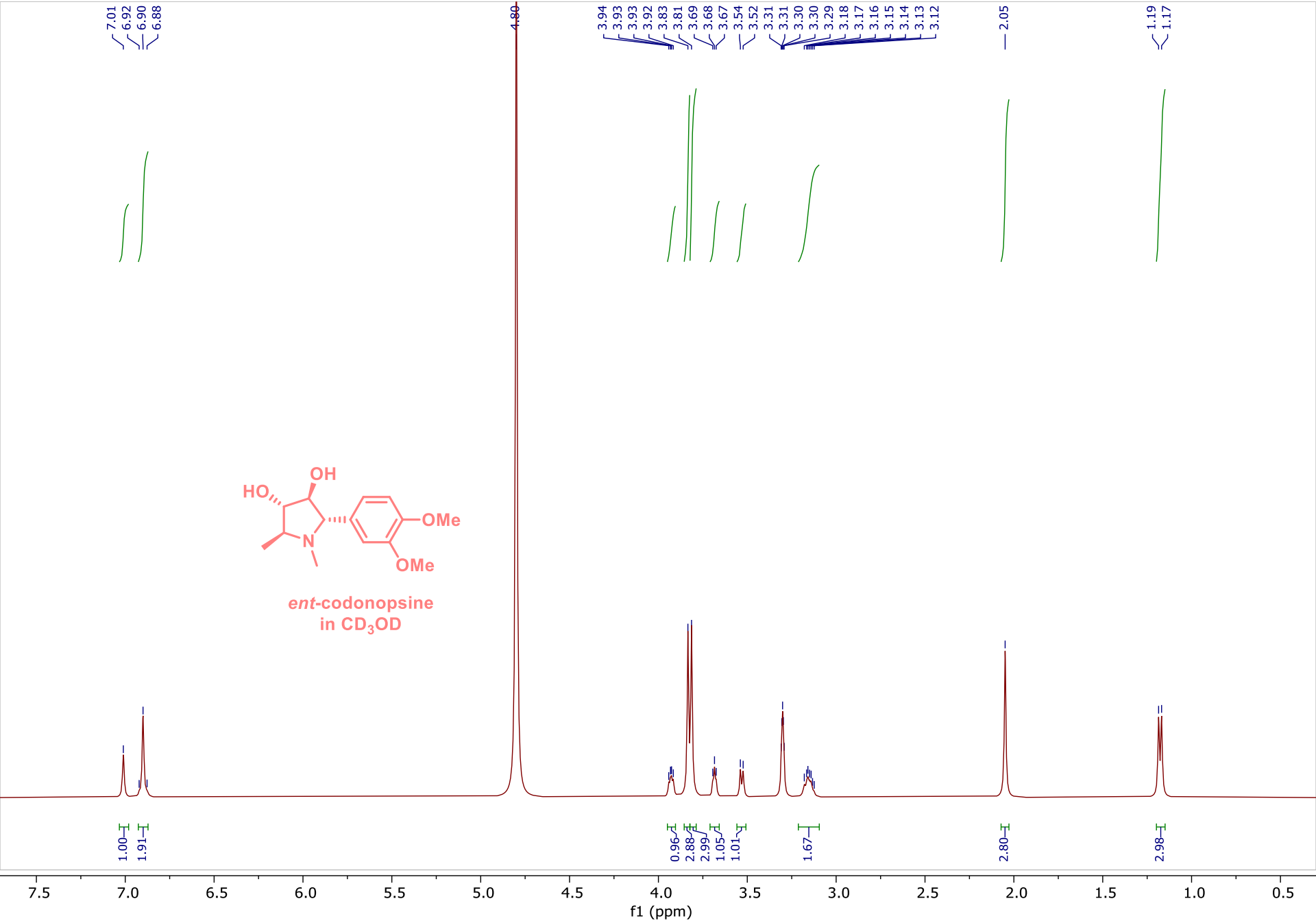

173.54
155.54
131.18
128.73
78.98
60.78
60.16
34.33
33.58
31.68
28.41
26.30
24.50
14.22
NHBoc
CO2Et
Allylamine 2ak in CDCl3
f1 (ppm)

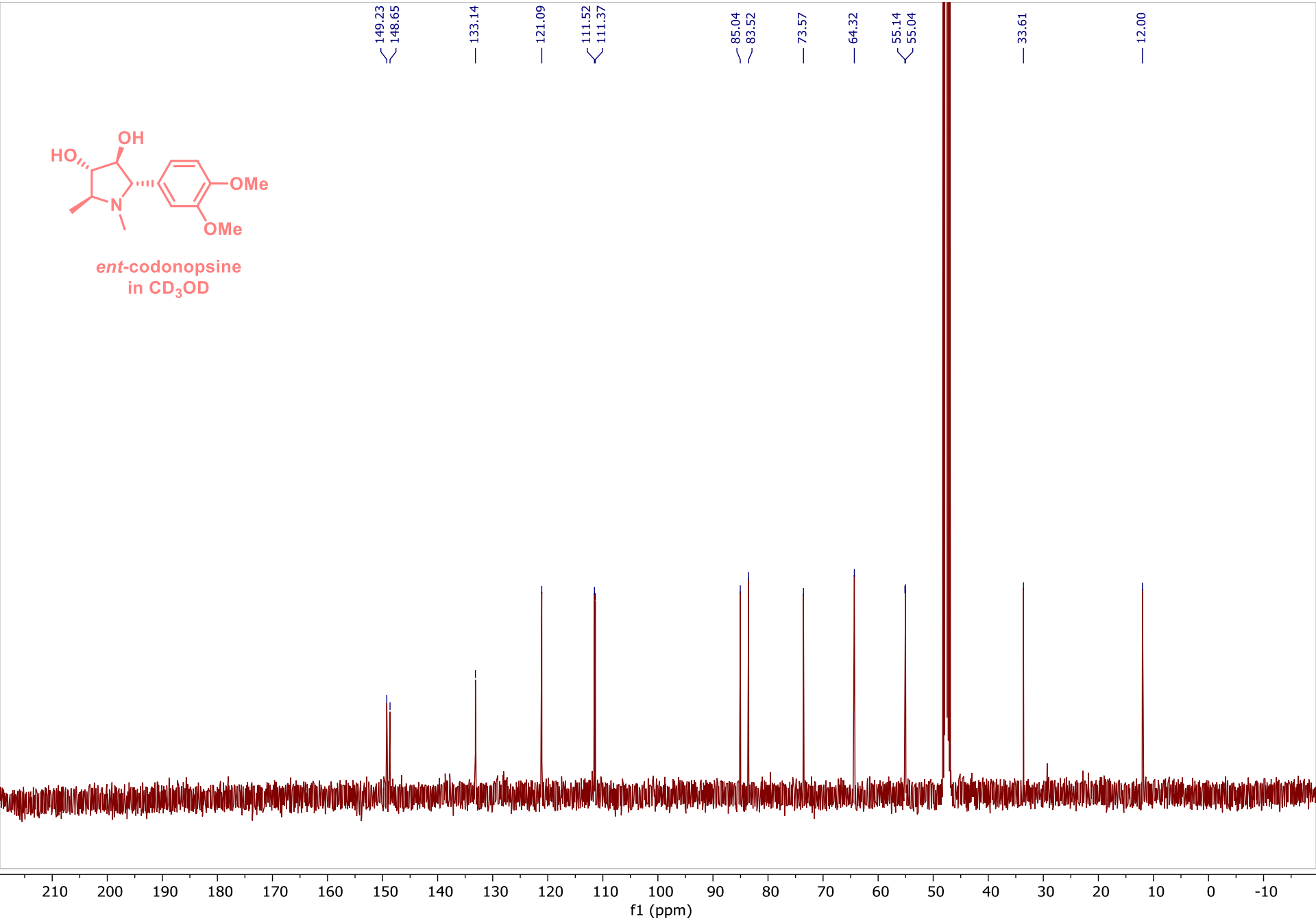

CbzHN
OH
OH
OMe
OMe
Compound 26 in CDCl3
f1 (ppm)

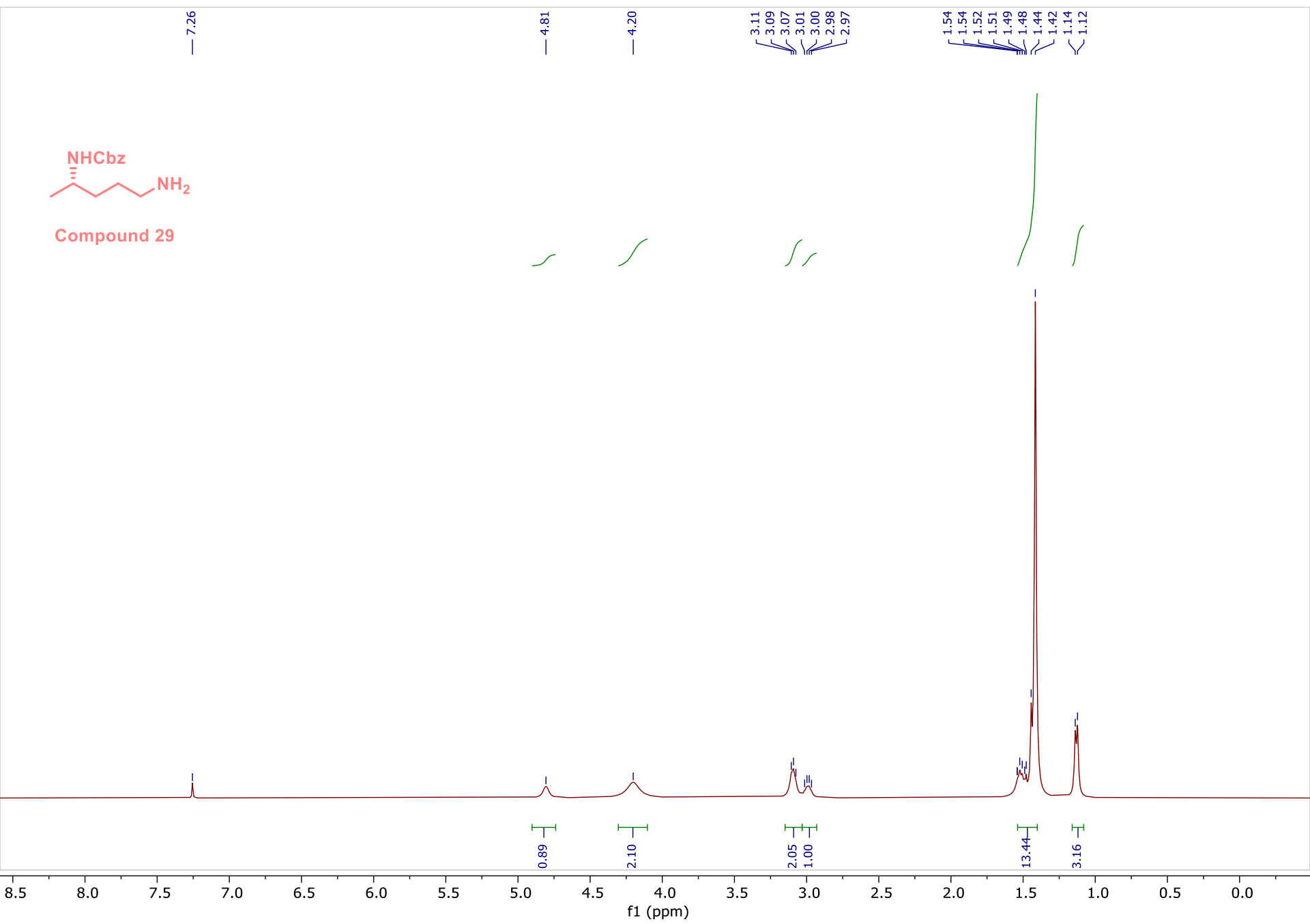

157.10
148.96
147.71
136.22
130.69
128.56
128.27
128.11
121.37
112.79
111.43
75.49
71.22
67.08
55.92
55.89
49.35
39.02
17.29
CbzHN
OH
OH
OMe
OMe
Compound 26 in CDCl3
f1 (ppm)

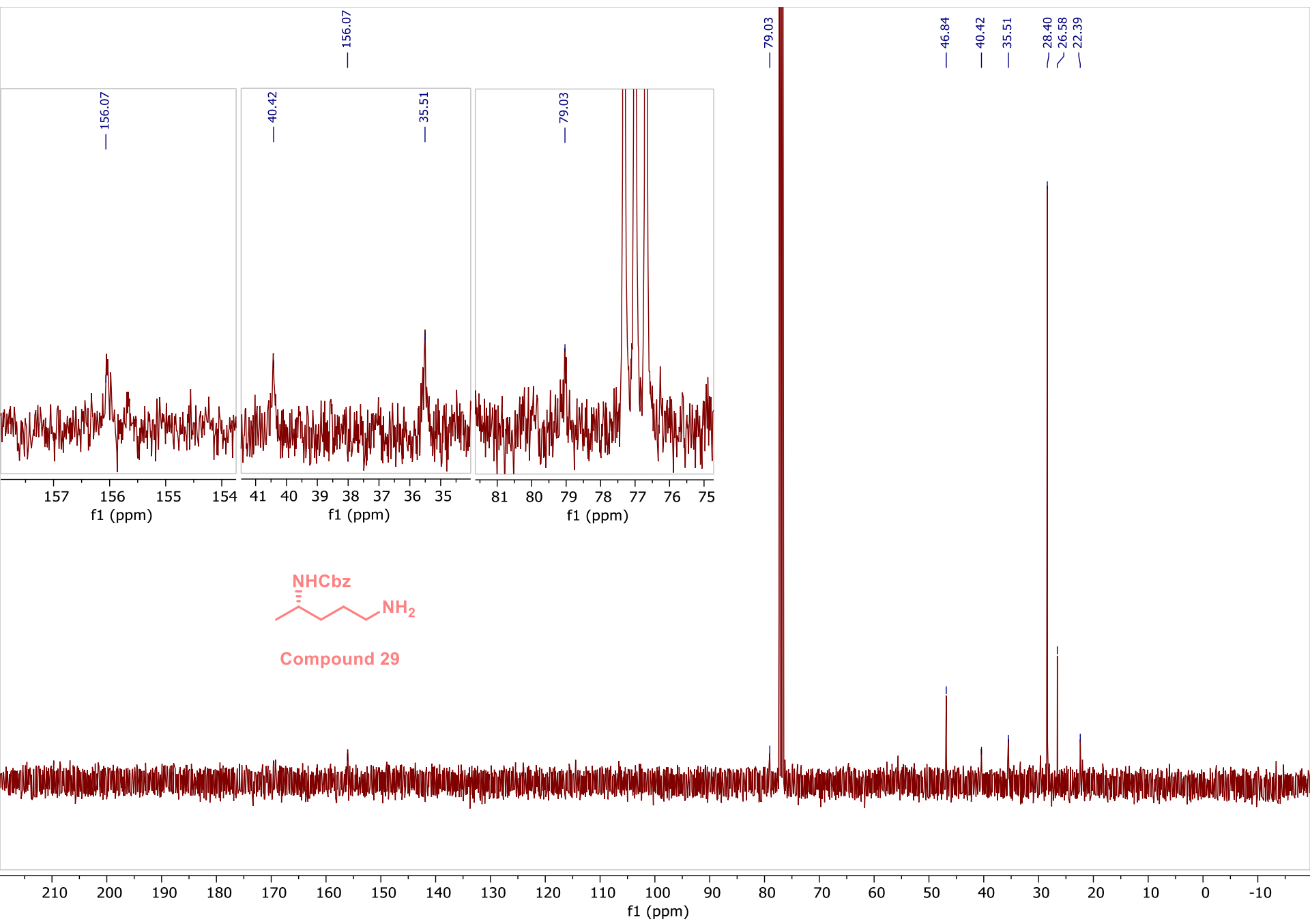

7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.29 7.26 6.77 6.75 6.71 6.70 6.70 6.69
5.25 5.24 5.23 5.22 5.22 5.21 5.06 4.91 4.90 4.90 4.89 4.82 4.80
4.10 4.08 4.06 4.04 4.03 3.84 3.83
2.85 2.83 2.82 2.80 2.76 2.74 2.72 2.71
2.13 2.02
1.11 1.09
CbzHN
OAc
OAc
OMe
OMe
Compound 27 in CDCl3
4.86 0.97 2.00 1.00 1.87 0.97 0.81 0.83 5.88 0.95 0.99 2.94 2.88 2.97
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)

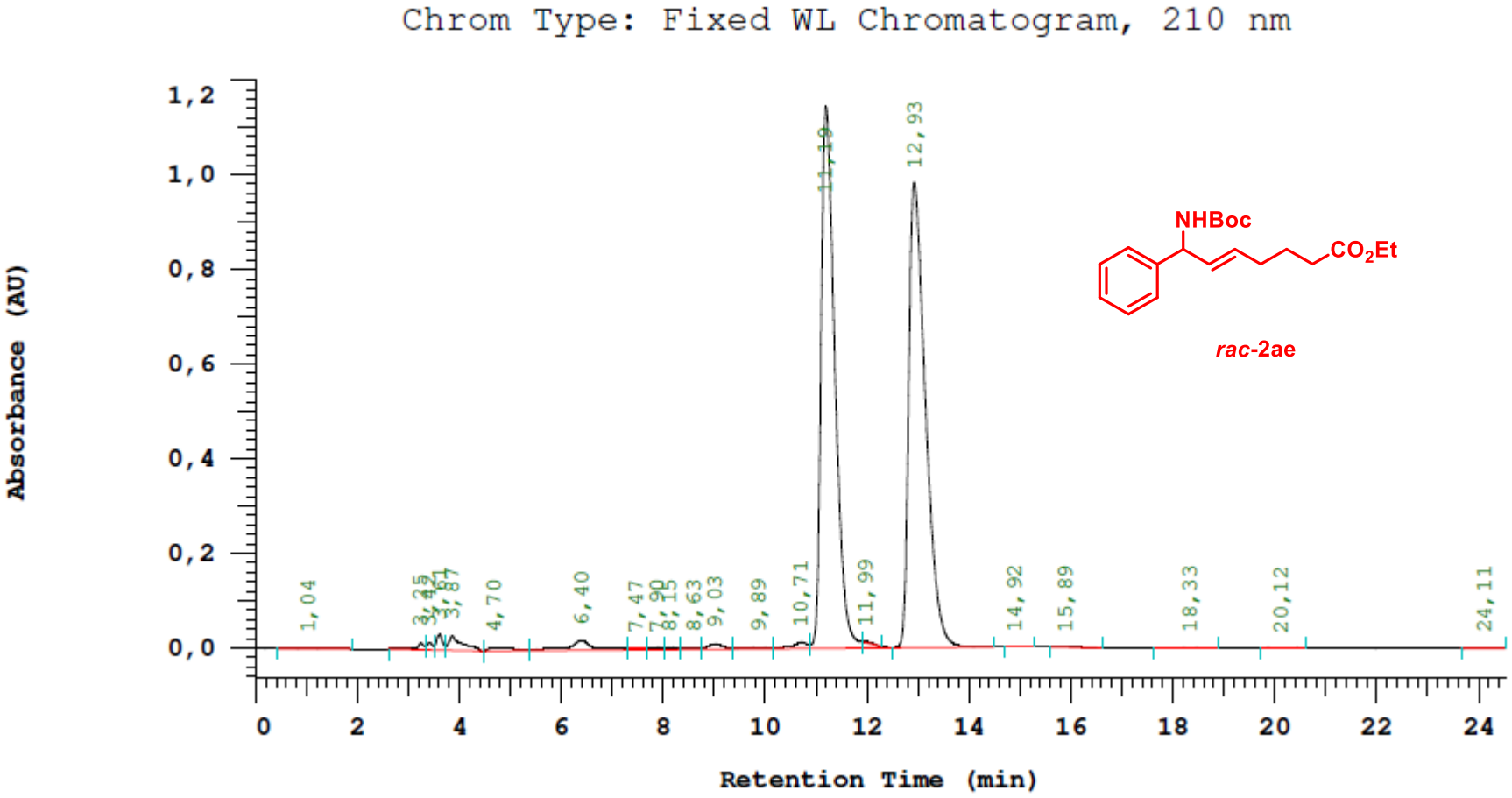

170.49
170.13
155.52
148.88
147.94
136.42
128.49
128.10
128.06
121.51
112.57
111.29
74.70
72.82
66.78
55.82
47.01
36.82
20.99
20.81
16.74
CbzHN
OAc
OAc
OMe
OMe
Compound 27 in CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.01
6.92
6.90
6.88
4.80
3.94
3.93
3.93
3.92
3.83
3.81
3.69
3.68
3.67
3.54
3.52
3.31
3.31
3.30
3.30
3.29
3.18
3.17
3.16
3.15
3.14
3.13
3.12
2.05
1.19
1.17
HO
OH
OMe
OMe
N
ent-codonopsine
in CD3OD
1.00
1.91
0.96
2.88
2.99
1.05
1.01
1.67
2.80
2.98
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
f1 (ppm)

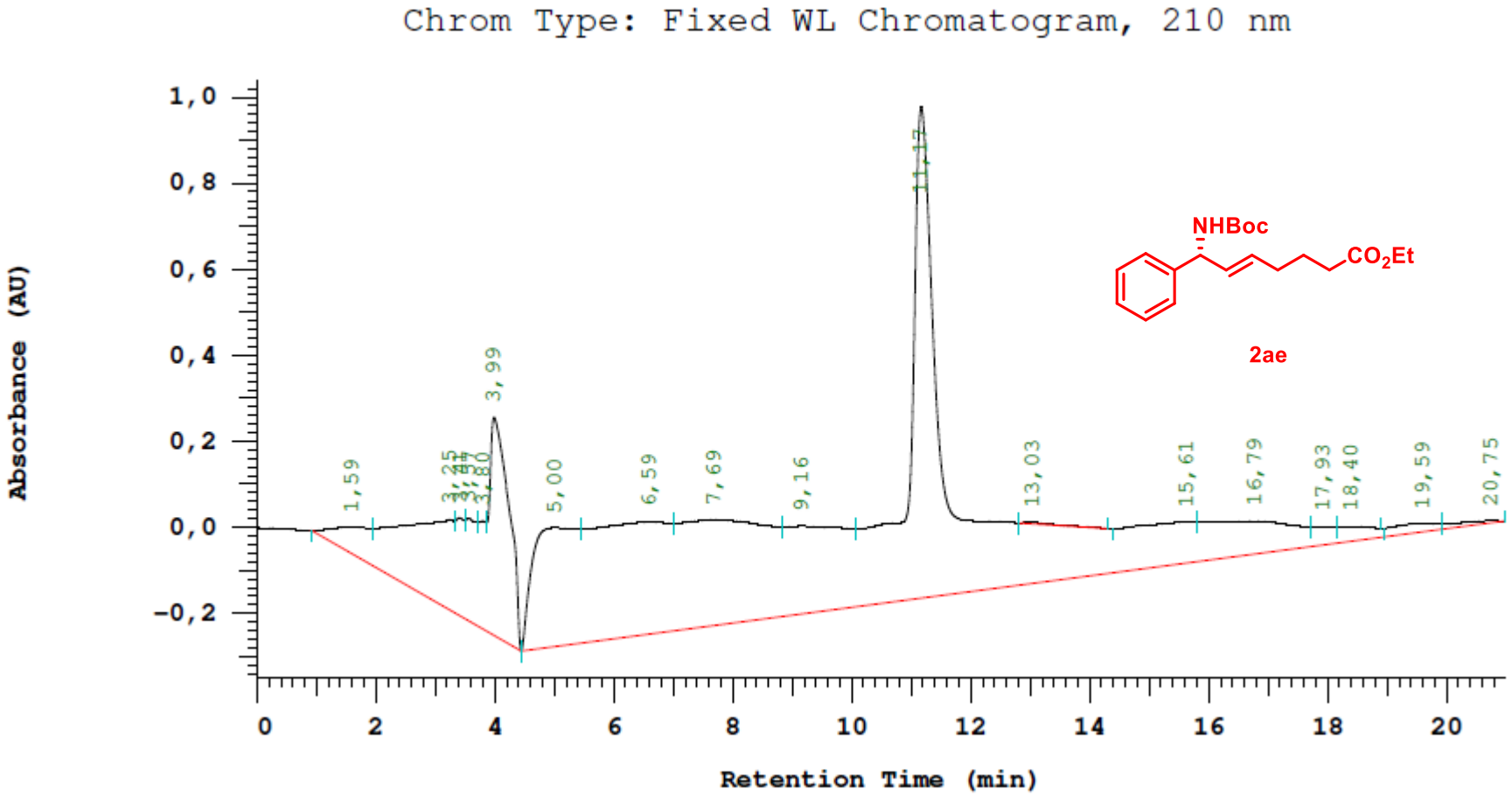

149.23
148.65
133.14
121.09
111.52
111.37
85.04
83.52
73.57
64.32
55.14
55.04
33.61
12.00
OH
HO
OMe
OMe
N
ent-codonopsine
in CD3OD
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26
4.81
4.20
3.11
3.09
3.07
3.01
3.00
2.98
2.97
1.54
1.54
1.52
1.51
1.49
1.48
1.44
1.42
1.14
1.12
NHCbz
NH2
Compound 29
0.89
2.10
2.05
1.00
13.44
3.16
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)


156.07
79.03
46.84
40.42
35.51
28.40
26.58
22.39
NHCbz
NH2
Compound 29
f1 (ppm)



13	9,89	57855	0,245	0,245	VV
14	10,71	143588	0,609	0,609	VV
15	11,19	10839482	45,952	45,952	VV
16	11,99	16560	0,070	0,070	TBB
17	12,93	11119902	47,141	47,141	VB



6	3,99	5875258	6,110	6,110	VB
7	5,00	7015533	7,296	7,296	BV
8	6,59	12256972	12,746	12,746	VV
9	7,69	12903632	13,419	13,419	VV
10	9,16	7363037	7,657	7,657	VV
11	11,17	28893378	30,047	30,047	VV
12	13,03	65037	0,068	0,068	TBB
13	15,61	4224353	4,393	4,393	VV
14	16,79	4141218	4,307	4,307	VV