An entry to non-racemic β-tertiary-β-amino alcohols, building blocks for the synthesis of aziridine, piperazine, and morpholine scaffolds

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Electronic supplementary materials

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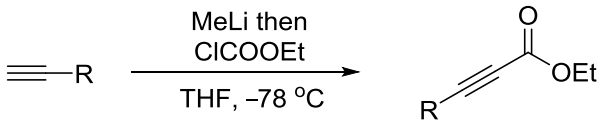
1. General info

NMR Spectra (^{1}H, ^{13}C) were performed at 298 K. ^{1}H NMR spectra were referenced to residual non-deuterated 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 HPLC, ^{1}H NMR, and/or by TLC on silica gel plates (TLC Silica gel 60 F254, Aluminium sheets). TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using UV light, and $KMnO_4$ of 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 system (Reveleris X2, with ELSD and UV (235 and 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.

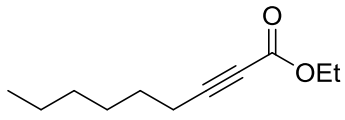
Ethyl 2-butynoate [4341-76-8] was purchased from Fluorochem, phenyl carbamate [622-46-8] was purchased from Alfa Aesar, and dibutyltin maleate [78-04-6] was purchased from TCI.

2. The synthesis of alkynes 4b and 4c

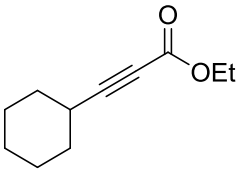


General procedure: A solution of alkyne (1.0 equiv., 18.1 mmol) in THF (24 mL) was cooled to −78 °C, and MeLi (1.06 equiv., 19.0 mmol, 11.9 mL, 1.6 M in Et_2O) was added dropwise. After 30 min ethyl chloroformate (2.2 g, 1.9 mL, 20.0 mmol,

1.1 equiv.) was added and after 5 min. a cooling bath was removed and the reaction mixture was allowed to warm to rt. Next, reaction was quenched by addition of sat. aq. NH_4Cl. The aqueous layer was separated and extracted with Et_2O. The combined organic phases were dried over anhydr. Na_2SO_4. After the removal of the solvents, the residue was purified by a column chromatography on silica gel (0-10% AcOEt in hexanes).

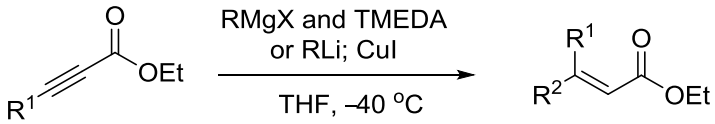


Ethyl non-2-ynoate (4b): Yield: 3.2 g (98%) starting from 2.0 g of oct-1-yne; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (q, *J* = 7.0 Hz, 2H), 2.29 (t, *J* = 7.1 Hz, 2H), 1.60 – 1.48 (m, 2H), 1.42 – 1.32 (m, 2H), 1.32 – 1.19 (m, 7H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 89.3, 73.1, 61.6, 31.1, 28.5, 27.5, 22.4, 18.6, 14.0, 13.9; Elem. Anal Found: C, 72.53; H, 10.01; N, 7.59%, $C_{11}H_{18}O_2$ requires C, 72.49; H, 9.95%.



Ethyl 3-cyclohexylpropiolate (4c): Yield: 2.8 g (85%) starting from 2.0 g of ethynylcyclohexane; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (q, *J* = 7.1 Hz, 2H), 2.57 – 2.40 (m, 1H), 1.88 – 1.75 (m, 2H), 1.74 – 1.61 (m, 2H), 1.57 – 1.40 (m, 3H), 1.37 – 1.19 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 92.7, 73.1, 61.6, 31.4, 28.8, 25.6, 24.6, 14.0; Elem. Anal Found: C, 73.28; H, 8.94%, $C_{11}H_{16}O_2$ requires C, 73.30; H, 8.95%.

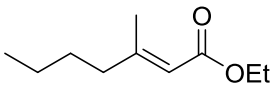
3. The Cu(I)-mediated 1,4-addtion to alkynoates 5



Method A, general procedure:[1] A suspension of CuI (11.0 mmol, 2.1 g) in THF (30 mL) was cooled to −40 °C, and RLi (10.6 mmol) was added. The resulting mixture was stirred at −40 °C for 30 min and then cooled to −78 °C. A solution of ethyl alkynoate (10.0 mmol) in THF (1 mL) was added portionwise and the resulting mixture was stirred for 2 h at −78 °C. The progress of the reaction was followed by TLC. Next, the reaction was quenched by an addition of aq. NH_4Cl at −78 °C, after that the cooling bath was removed and the mixture was left to adjust to rt. The reaction mixture was filtrated through a short pad of Celite. The collected solids were rinsed with Et_2O. After that, the aqueous phase was separated and extracted with Et_2O. The combined organic layers were dried over anhydr. Na_2SO_4. After the removal of solvents, the crude residue was purified by a column chromatography on silica gel (1-10% Et_2O in pentanes).

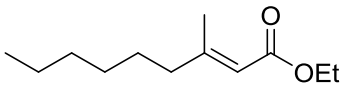
Method B, general procedure:[1] A suspension of CuI (15.0 mmol, 2.9 g) in THF (90 mL) was cooled to −40 °C, and RMgX (12 mmol) and TMEDA (45.0 mmol, 5.1 g, 6.8 mL) were added. The mixture was stirred at −40 °C for 30 min and then cooled to −78 °C. A solution of ethyl alkynoate (12.0 mmol) in THF (2 mL) was added portionwise and the resulting suspension was stirred for 4 h at −78 °C. The progress of the reaction was followed by TLC. The reaction was quenched by addition of aq. NH_4Cl. The cooling bath was removed and mixture was left to adjust to rt. The reaction mixture was filtrated through a short pad of Celite. The collected solids were rinsed with Et_2O. After that, the aqueous phase was separated and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4. After the removal of solvents, the crude residue was purified by a column chromatography on silica gel (1-10% Et_2O in pentanes).

Ethyl (*E*)-3-methylhept-2-enoate (5a):



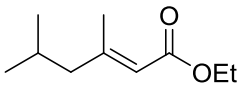
Method A. *n*-BuLi (2.5 M solution in hexane) was used. Yield: 1.5 g (90%; *E/Z* ratio >95:5, acc. ^{1}H NMR) starting from 1.1 g (9.8 mmol) of ethyl but-2-ynoate; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 – 5.56 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.20 – 2.01 (m, 5H), 1.51 – 1.37 (m, 2H), 1.35 – 1.18 (m, 5H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 160.2, 115.4, 59.4, 40.6, 29.5, 22.3, 18.7, 14.3, 13.8; Elem. Anal Found: C, 70.52; H, 10.69%, $C_{11}H_{18}O_2$ requires C, 70.55; H, 10.66%.

Ethyl (*E*)-3-methylnon-2-enoate (5b):



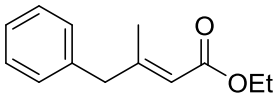
Method A. *n*-HexLi (2.3 M solution in hexane) was used. Yield: 2.4 g (99%; *E/Z* ratio >95:5, ^{1}H NMR) starting from 1.3 g (11.6 mmol) of ethyl but-2-ynoate; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (q, *J* = 1.2 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.17 – 2.06 (m, 5H), 1.51 – 1.39 (m, 2H), 1.35 – 1.20 (m, 9H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 160.2, 115.4, 59.4, 40.9, 31.6, 28.8, 27.3, 22.5, 18.7, 14.3, 14.0; Elem. Anal Found: C, 72.71; H, 11.22; %, $C_{12}H_{22}O_2$ requires C, 72.68; H, 11.18%.

Ethyl (*E*)-3,5-dimethylhex-2-enoate (5c):



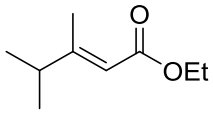
Method B. *i*-BuMgBr (2 M solution in Et_2O) was used. Yield: 1.9 g (96%; *E/Z* ratio >95:5, acc. ^{1}H NMR) starting from 1.3 g (11.6 mmol) of ethyl but-2-ynoate; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 – 5.53 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.11 (d, *J* = 1.3 Hz, 3H), 2.02 – 1.93 (m, 2H), 1.91 – 1.77 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 159.1, 116.7, 59.4, 50.5, 26.2, 22.4, 18.6, 14.3; Elem. Anal Found: C, 72.53; H, 10.01%, $C_{10}H_{18}O_2$ requires C, 70.55; H, 10.66%.

Ethyl (*E*)-3-methyl-4-phenylbut-2-enoate (5f):



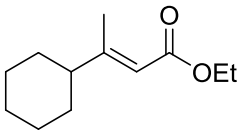
Method B. BnMgCl (1 M solution in Et_2O) was used. Yield: 2.5 g (96%; *E/Z* ratio >95:5, acc. ^1H NMR) starting from 1.3 g (11.6 mmol) of ethyl but-2-ynoate; yellowish oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.07 (m, 5H), 5.79 – 5.60 (m, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.52 – 3.31 (m, 2H), 2.12 (d, *J* = 1.3 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 158.2, 137.8, 129.1, 128.5, 126.7, 117.3, 59.6, 47.1, 18.6, 14.3 Elem. Anal Found: C, 76.48; H, 7.95%, $C_{13}H_{16}O_2$ requires C, 76.44; H, 7.90%.

Ethyl (*E*)-3,4-dimethylpent-2-enoate (5d):



Method B. *i*-PrMgCl (2 M solution in THF) was used. Yield: 938 mg (overall 75%; *E/Z* ratio >95:5, acc. ^1H NMR) starting from 897 mg (8.0 mmol) of ethyl but-2-ynoate; yellowish liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 5.73 – 5.54 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.41 – 2.27 (m, 1H), 2.10 (d, *J* = 1.3 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 165.3, 113.6, 59.4, 38.1, 20.8, 16.3, 14.3; Elem. Anal Found: C, 69.14; H, 10.30; %, $C_9H_{16}O_2$ requires C, 69.19; H, 10.32%.

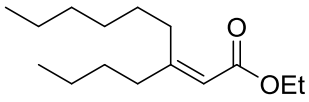
Ethyl (*E*)-3-cyclohexylbut-2-enoate (5e):



Method B. CyMgCl (1.3 M solution in THF/toluene) was used. Yield: 2.0 g (85%; *E/Z* ratio >95:5, acc. ^1H NMR) starting from 1.3 g (11.6 mmol) of ethyl but-2-ynoate; yellowish liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 5.73 – 5.52 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.13 (d, *J* = 1.3 Hz, 3H), 2.01 – 1.90 (m, 1H), 1.84 – 1.63 (m, 5H), 1.35 – 1.07 (m,

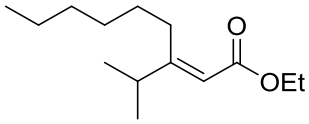
8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 164.8, 113.9, 59.4, 48.7, 31.4, 26.4, 26.1, 17.3, 14.3 Elem. Anal Found: C, 73.40; H, 10.24; %, $C_{12}H_{20}O_2$ requires C, 73.43; H, 10.27%.

Ethyl (*Z*)-3-butylnon-2-enoate (5g):



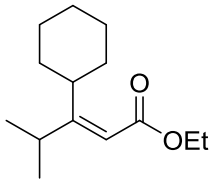
Method A. *n*-BuLi (2.5 M solution in hexane) was used. Yield: 1.25 g (overall 95%; *Z/E* ratio 95:5, ^{1}H NMR) starting from 1.0 g (5.5 mmol) of ethyl non-2-ynoate (**4b**); yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 (s, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.64 – 2.46 (m, 2H), 2.20 – 2.01 (m, 2H), 1.51 – 1.38 (m, 4H), 1.37 – 1.20 (m, 10H), 0.95 – 0.79 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 164.8, 115.1, 59.3, 38.1, 32.1, 31.7, 29.8, 29.6, 28.6, 22.6, 22.4, 14.3, 14.0, 13.9; Elem. Anal Found: C, 74.91; H, 11.69%, $C_{15}H_{28}O_2$ requires C, 74.95; H, 11.74%.

Ethyl (*E*)-3-isopropylnon-2-enoate (5h):



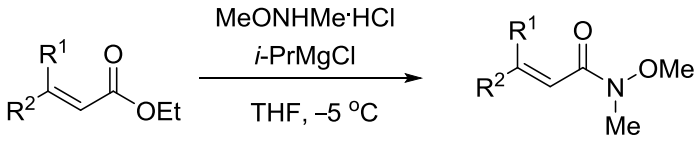
Method B. *i*-PrMgCl (2 M solution in THF) was used. Yield: 1.2 g (94%; *E/Z* ratio 95:5, acc. ^{1}H NMR) starting from 1.0 g (5.5 mmol) of ethyl non-2-ynoate (**4b**); yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.61 – 2.48 (m, 2H), 2.41 – 2.29 (m, 1H), 1.49 – 1.17 (m, 11H), 1.06 (d, *J* = 6.8 Hz, 6H), 0.91 – 0.79 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 166.9, 113.0, 59.4, 36.1, 31.8, 31.7, 29.8, 29.3, 22.6, 21.6, 14.3, 14.0; Elem. Anal Found: C, 74.33; H, 11.62%, $C_{14}H_{26}O_2$ requires C, 74.29; H, 11.58%.

Ethyl (*Z*)-3-cyclohexyl-4-methylpent-2-enoate (5i):



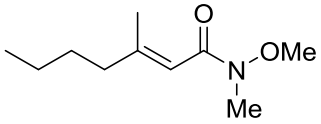
Method B. CyMgCl (1.3 M solution in THF/toluene) was used. Yield: 1.5 g (89%; *Z/E* ratio 95:5, ^{1}H NMR) starting from 1.4 g (7.8 mmol) of ethyl 3-cyclohexylpropiolate (**4c**); yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.79 – 3.59 (m, 1H), 2.64 – 2.48 (m, 1H), 1.83 – 1.63 (m, 3H), 1.62 – 1.50 (m, 2H), 1.42 – 1.31 (m, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.24 – 1.07 (m, 1H), 1.04 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 167.2, 112.8, 59.4, 40.9, 30.3, 30.0, 26.3, 26.1, 23.9, 14.3; Elem. Anal Found: C, 75.02; H, 10.82; %, $C_{14}H_{24}O_2$ requires C, 74.95; H, 10.78%.

4. The synthesis of Weinreb amides S1



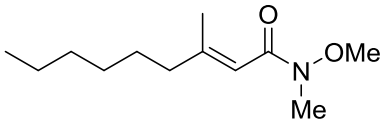
General procedure: A suspension of α,β-unsaturated ester **5** (1 equiv) and MeNHOMe·HCl (2 equiv) in dry THF (*c* 0.2-0.3 M) was cooled to −5 °C under argon atmosphere, and 2M soln. of *i*-PrMgCl in THF (4 equiv.) was added dropwise. The progress of the reaction was followed by TLC. After stirring at −5 °C for 30-60 min, the reaction was quenched by an addition of sat. NH_4Cl. The aqueous phase was separated and extracted with AcOEt. The combined organic phases were washed with brine, and dried over anhydr. Na_2SO_4. After the removal of the solvents, the crude pruduct was purified by a column chromatography on silica gel to provide pure *E* or *Z* isomer (10-30% AcOEt in hexanes).

(*E*)-*N*-Methoxy-*N*,3-dimethylhept-2-enamide (S1a):



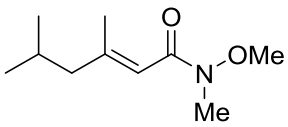
Yield: 1.4 g (92%) starting from 1.4 g (8.2 mmol) of ester **5a**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, 1H), 3.65 (s, 3H), 3.18 (s, 3H), 2.19 – 1.97 (m, 5H), 1.51 – 1.37 (m, 2H), 1.38 – 1.22 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 156.8, 113.8, 61.3, 40.8, 32.2, 29.7, 22.3, 18.6, 13.8; Elem. Anal Found: C, 64.87; H, 10.38; N, 7.59%, $C_{10}H_{19}NO_2$ requires C, 64.83; H, 10.34; N, 7.56%.

(*E*)-*N*-Methoxy-*N*,3-dimethylnon-2-enamide (S1b):



Yield: 2.3 g (92%) starting from 2.3 g (8.2 mmol) of ester **5b**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 1H), 3.64 (s, 3H), 3.17 (s, 3H), 2.23 – 1.92 (m, 5H), 1.56 – 1.36 (m, 2H), 1.36 – 1.12 (m, 6H), 0.95 – 0.73 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 156.7, 113.8, 61.3, 41.1, 32.3, 31.6, 28.9, 27.5, 22.6, 18.6, 14.0; Elem. Anal Found: C, 67.60; H, 10.86; N, 6.61 %, $C_{12}H_{23}NO_2$ requires C, 67.57; H, 10.87; N, 6.57%.

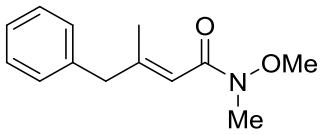
(*E*)-*N*-Methoxy-*N*,3,5-trimethylhex-2-enamide (S1c)



Yield: 1.8 g (90%) starting from 1.9 g (11.2 mmol) of ester **5c**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (s, 1H), 3.64 (s, 3H), 3.17 (s, 3H), 2.07 (d, *J* = 1.4 Hz, 3H), 1.99 (dd, *J* = 7.6, 0.8 Hz, 2H), 1.92 – 1.76 (m, 1H), 0.87 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 155.6, 115.0, 61.3, 50.8, 32.2, 26.2, 22.4, 18.5; Elem.

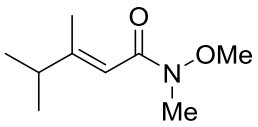
Anal Found: C, 64.85; H, 10.31; N, 7.59 %, $C_{10}H_{19}NO_2$ requires C, 64.83; H, 10.34; N, 7.56%.

(*E*)-*N*-Methoxy-*N*,3-dimethyl-4-phenylbut-2-enamide (S1f):



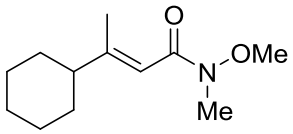
Yield: 1.4 g (87%) starting from 1.5 g (7.3 mmol) of ester **5f**; yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.12 (m, 5H), 6.10 (s, 1H), 3.61 (s, 3H), 3.44 (d, *J* = 1.3 Hz, 2H), 3.18 (s, 3H), 2.08 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 154.7, 138.3, 129.1, 128.4, 126.5, 115.9, 61.4, 47.2, 32.3, 18.6; Elem. Anal Found: C, 71.25; H, 7.83; N, 6.41 %, $C_{13}H_{17}NO_2$ requires C, 71.21; H, 7.81; N, 6.39%.

(*E*)-*N*-Methoxy-*N*,3,4-trimethylpent-2-enamide (S1d)



Yield: 1.3 g (85%) starting from 1.4 g (9.0 mmol) of ester **5d**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 1H), 3.62 (s, 3H), 3.16 (s, 3H), 2.41 – 2.25 (m, 1H), 2.04 (d, *J* = 1.4 Hz, 3H), 1.03 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 161.5, 112.1, 61.2, 38.1, 32.3, 21.0, 16.0; Elem. Anal Found: C, 63.15; H, 9.98; N, 8.21 %, $C_9H_{17}NO_2$ requires C, 63.13; H, 10.01; N, 8.18%.

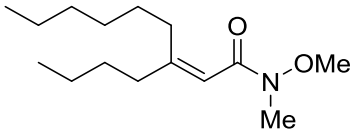
(*E*)-3-Cyclohexyl-*N*-methoxy-*N*-methylbut-2-enamide (S1e):



Yield: 1.4 g (90%) starting from 1.4 g (7.1 mmol) of ester **5e**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (s, 1H), 3.64 (s, 3H), 3.17 (s, 3H), 2.06 (d, *J* = 1.4 Hz, 3H), 2.00 – 1.90 (m, 1H), 1.84 – 1.62 (m, 4H), 1.37 – 1.05 (m, 6H); ^{13}C NMR (101 MHz,

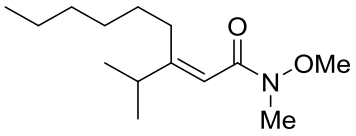
$CDCl_3$) δ 168.6, 160.9, 112.4, 61.3, 48.7, 32.3, 31.5, 26.5, 26.1, 17.1; Elem. Anal Found: C, 68.41; H, 9.97; N, 6.58 %, $C_{12}H_{21}NO_2$ requires C, 68.21; H, 10.02; N: 6.63%.

(*Z*)-3-Butyl-*N*-methoxy-*N*-methylnon-2-enamide (S1g)



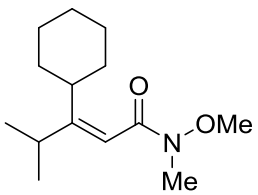
Yield: 1.2 g (92%) starting from 1.2 g (5.0 mmol) of ester **5g**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (s, 1H), 3.65 (s, 3H), 3.17 (s, 3H), 2.62 – 2.40 (m, 2H), 2.19 – 2.06 (m, 2H), 1.50 – 1.19 (m, 12H), 0.95 – 0.75 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 161.0, 113.5, 61.3, 38.0, 32.3, 32.0, 31.7, 30.0, 29.6, 28.7, 22.6, 22.4, 14.0, 13.9; Elem. Anal Found: C, 70.49; H, 11.48; N, 5.50 %, $C_{15}H_{29}NO_2$ requires C, 70.54; H, 11.45; N, 5.48%.

(*E*)-3-Isopropyl-*N*-methoxy-*N*-methylnon-2-enamide (S1h):



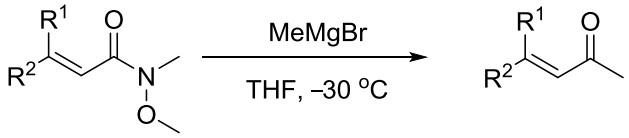
Yield: 1.1 g (92%) starting from 1.3 g (5.7 mmol) of ester **5h**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (br s, 1H), 3.65 (s, 3H), 3.18 (s, 3H), 2.57 – 2.46 (m, 2H), 2.43 – 2.30 (m, 1H), 1.51 – 1.38 (m, 2H), 1.38 – 1.21 (m, 6H), 1.07 (d, *J* = 6.8 Hz, 6H), 0.92 – 0.78 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 166.6, 111.5, 61.2, 35.7, 32.5, 31.7, 31.7, 29.9, 29.4, 22.6, 21.9, 14.0; Elem. Anal Found: C, 69.70; H, 11.31; N, 5.78 %, $C_{14}H_{27}NO_2$ requires C, 69.67; H, 11.28; N, 5.80%.

(*Z*)-3-Cyclohexyl-*N*-methoxy-*N*,4-dimethylpent-2-enamide (S1i):

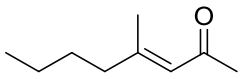


Yield: 1.4 g (92%) starting from 1.4 g (6.2 mmol) of ester **5i**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (s, 1H), 3.63 (s, 3H), 3.50 – 3.30 (m, 1H), 3.18 (s, 3H), 2.60 – 2.43 (m, 1H), 1.84 – 1.50 (m, 5H), 1.44 – 1.08 (m, 5H), 1.04 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 168.7, 112.0, 61.2, 41.4, 32.6, 30.5, 29.7, 26.2, 26.1, 24.2; Elem. Anal Found: C, 70.28; H, 11.55; N, 5.83 %, $C_{14}H_{25}NO_2$ requires C, 70.25; H, 10.53; N, 5.85%.

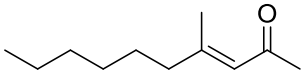
5. The synthesis of enones 6



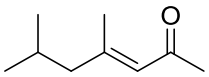
General procedure: A 3 M soln. of MeMgBr in THF (1.3 equiv) was slowly added to a pre-cooled (−30 °C) solution of Weinreb amide **S1** (1 equiv) in THF (*c* 0.2-0.3 M). Next, the mixture was slowly warmed to −5 °C and stirred for 30-60 min. The progress of the reaction was followed by TLC. Next, sat. NH_4Cl was added and the resulting mixture was extracted with Et_2O. The combined organic layers were washed with brine, and dried over Na_2SO_4. After the removal of the solvents, the residue was purified by a column chromatography on silica gel (1-10% Et_2O in pentanes).



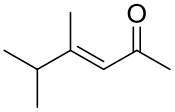
(*E*)-4-Methyloct-3-en-2-one (6a): Yield: 1.7 g (86%) starting from 2.6 g (14.0 mmol) of amide **S1a**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (q, *J* = 1.3 Hz, 1H), 2.15 (s, 3H), 2.12 – 2.06 (m, 5H), 1.50 – 1.38 (m, 2H), 1.36 – 1.26 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 158.9, 123.4, 40.9, 31.7, 29.6, 22.3, 19.2, 13.8; Elem. Anal Found: C, 77.11; H, 11.53%, $C_9H_{16}O$ requires C, 77.09; H, 11.50%.



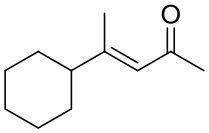
(*E*)-4-Methyldec-3-en-2-one (6b): Yield: 1.7 g (96%) starting from 2.3 g (10.8 mmol) of amide **S1b**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (q, *J* = 1.3 Hz, 1H), 2.14 (s, 3H), 2.11 – 2.05 (m, 5H), 1.51 – 1.38 (m, 2H), 1.35 – 1.21 (m, 6H), 0.93 – 0.80 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 158.9, 123.4, 41.2, 31.7, 31.6, 28.9, 27.4, 22.5, 19.2, 14.0; Elem. Anal Found: C, 78.56; H, 12.03%, $C_{11}H_{20}O$ requires C, 78.51; H, 11.98%.



(*E*)-4,6-Dimethylhept-3-en-2-one (6c): Yield: 717 mg (82%) starting from 1.2 g (6.5 mmol) of amide **S1c**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (q, *J* = 1.3 Hz, 1H), 2.16 (s, 3H), 2.09 (d, *J* = 1.3 Hz, 3H), 2.00 – 1.93 (m, 2H), 1.91 – 1.78 (m, 1H), 0.87 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 157.7, 124.7, 50.8, 31.7, 26.3, 22.4, 19.1; Elem. Anal Found: C, 77.12; H, 11.52%, $C_9H_{16}O$ requires C, 77.09; H, 11.50%.

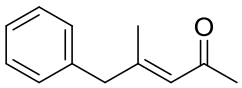


(*E*)-4,5-Dimethylhex-3-en-2-one (6d): Yield: 691 mg (78%) starting from 1.2 g (7.0 mmol) of amide **S1d**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 – 5.82 (m, 1H), 2.37 – 2.25 (m, 1H), 2.15 (s, 3H), 2.07 (d, *J* = 1.3 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 163.9, 121.4, 38.2, 31.8, 20.9, 16.7; Elem. Anal Found: C, 76.18; H, 11.22%, $C_8H_{14}O$ requires C, 76.14; H, 11.18%.

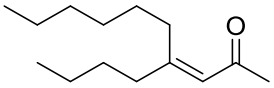


(*E*)-4-Cyclohexylpent-3-en-2-one (6e): Yield: 983 mg (86%) starting from 1.4 g (6.6 mmol) of amide **S1e**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 – 5.81 (m, 1H), 2.15 (s, 3H), 2.09 (d, *J* = 1.3 Hz, 3H), 2.01 – 1.87 (m,

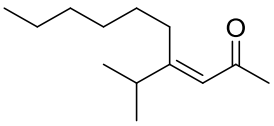
1H), 1.83 – 1.74 (m, 2H), 1.75 – 1.62 (m, 3H), 1.34 – 1.08 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 163.3, 121.8, 48.9, 31.8, 31.4, 26.4, 26.1, 17.7; Elem. Anal Found: C, 79.50; H, 10.95%, $C_{11}H_{18}O$ requires C, 79.46; H, 10.91%.



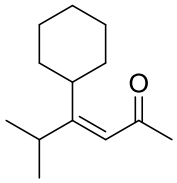
(*E*)-4-Methyl-5-phenylpent-3-en-2-one (6f): Yield: 1.0 g (94%) starting from 1.4 g (6.4 mmol) of amide **S1f**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.08 (m, 5H), 6.15 – 5.94 (m, 1H), 3.41 (s, 2H), 2.17 (s, 3H), 2.09 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 156.6, 137.8, 129.1, 128.6, 126.7, 125.0, 47.2, 31.8, 19.1; Elem. Anal Found: C, 82.68; H, 8.06%, $C_{12}H_{14}O$ requires C, 82.72; H, 8.10%.



(*Z*)-4-Butyldec-3-en-2-one (6g): Yield: 820 mg (89%) starting from 1.1 g (4.3 mmol) of amide **S1g**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (s, 1H), 2.60 – 2.47 (m, 2H), 2.21 – 2.02 (m, 5H), 1.51 – 1.23 (m, 12H), 0.89 (dt, *J* = 15.6, 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 163.7, 123.0, 38.4, 32.4, 31.8, 31.6, 29.9, 29.6, 28.6, 22.6, 22.5, 14.0, 13.9; Elem. Anal Found: C, 79.90; H, 12.41; %, $C_{14}H_{26}O$ requires C, 79.94; H, 12.46%.

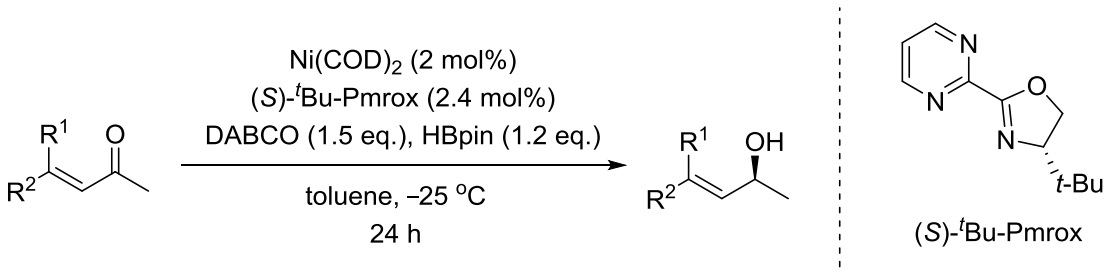


(*E*)-4-Isopropyldec-3-en-2-one (6h): Yield: 705 mg (95%) starting from 921 mg (3.8 mmol) of amide **S1h**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (s, 1H), 2.56 – 2.45 (m, 2H), 2.40 – 2.29 (m, 1H), 2.16 (s, 3H), 1.46 – 1.22 (m, 8H), 1.06 (d, *J* = 6.8 Hz, 6H), 0.91 – 0.79 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 169.3, 120.6, 36.3, 32.0, 31.9, 31.6, 29.8, 29.2, 22.6, 21.6, 14.0, 14.0; Elem. Anal Found: C, 79.49; H, 12.27%, $C_{13}H_{24}O$ requires C, 79.53; H, 12.32%.



(*Z*)-4-Cyclohexyl-5-methylhex-3-en-2-one (6i): Yield: 1.0 g (91%) starting from 1.4 g (5.8 mmol) of amide **S1i**; yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (s, 1H), 3.69 – 3.46 (m, 1H), 2.65 – 2.47 (m, 1H), 2.16 (s, 3H), 1.82 – 1.61 (m, 3H), 1.59 – 1.45 (m, 2H), 1.42 – 1.25 (m, 4H), 1.23 – 1.07 (m, 1H), 1.03 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 173.6, 120.8, 40.9, 32.1, 30.3, 29.8, 26.2, 26.1, 23.9; Elem. Anal Found: C, 80.31; H, 11.37%, $C_{13}H_{22}O$ requires C, 80.35; H, 11.41%.

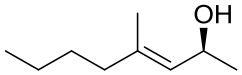
6. NiH-catalyzed 1,2-reduction of α,β-unsaturated ketones 6



General procedure:[2] A flask was charged with $Ni(COD)_2$ (4 µmol, 2.0 mol %, 1.1 mg), (*S*)-^{t}Bu-Pmrox (4.8 µmol, 2.4 mol%, 1.0 mg) and DABCO (1.5 equiv, 0.3 mmol, 33.6 mg) under an Ar atmosphere. Toluene (0.8 mL) was added and the mixture was stirred for 10 min before pinBH (1.2 equiv, 0.24 mmol, 30.7 mg, 35 µL) was added. Next, the reaction mixture was cooled to –25 °C and a solution of enone **6** (1.0 equiv, 0.2 mmol) in 0.2 mL toluene was added by syringe. The reaction mixture was left to stir at this temperature. The progress of the reaction was followed by TLC. When the reaction was completed, a saturated solution of NH_4F in MeOH (1 mL) was added and cooling bath was removed. The mixture was stirred at rt for 30 min followed by an addition of H_2O (2 mL) and Et_2O (3 mL). The aqueous phase was separated and extracted with Et_2O (2x) and dried over anhydr. Na_2SO_4. After the removal of the solvents, the crude residue was purified by a

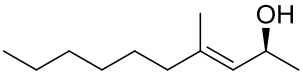
column chromatography on silica gel (0-20% Et_2O in pentanes). The enantiomeric excess of product (% *ee*) was determined by HPLC analysis for the corresponding *p*-nitrobenzoate ester derivatives.

(*S*,*E*)-4-Methyloct-3-en-2-ol (3a)



The reaction mixture was stirred for 24 h. Yield: 498 mg (90%) starting from 544 mg of ketone **6a**; yellowish oil; $[\alpha]_D^{21}$ –24.5 (*c* 1.02, $CHCl_3$, *ee* 94%; HPLC of *p*-nitrobenzoate ester: R_t 6.1 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (dq, *J* = 8.4, 1.3 Hz, 1H), 4.55 (dq, *J* = 8.4, 6.3 Hz, 1H), 1.96 (td, *J* = 7.5, 1.2 Hz, 2H), 1.65 (d, *J* = 1.3 Hz, 3H), 1.45 (br s, 1H), 1.41 – 1.32 (m, 2H), 1.31 – 1.23 (m, 2H), 1.21 (d, *J* = 6.3 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 128.9, 64.7, 39.1, 29.8, 23.6, 22.3, 16.3, 13.9; FTIR (film) *v*: 3347, 2960, 2928, 1670, 1456, 1380, 1099, 1058, 866 cm^{-1}; HRMS (EI) m/z calcd for $C_9H_{18}O$ [M] 142.1358; found 142.1364; HPLC (for *p*-nitrobenzoate ester, racemate) column: Chiralpak AS-H, 5% *i*-PrOH in hexanes, flow 1 mL min^{-1}, det. 254 nm; 6.0 min (*R*-enantiomer) and R_t 7.5 min (*S*-enantiomer).

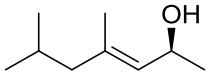
(*S*,*E*)-4-Methyldec-3-en-2-ol (3b):



The reaction mixture was stirred for 24 h. Yield: 605 mg (85%) starting from 700 mg of ketone **6b**; yellowish oil; $[\alpha]_D^{21}$ –21.2 (*c* 1.13, $CHCl_3$), *ee* 94%; HPLC of *p*-nitrobenzoate ester: R_t 30.4 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (dq, *J* = 8.4, 1.3 Hz, 1H), 4.56 (dq, *J* = 8.4, 6.2 Hz, 1H), 2.03 – 1.87 (m, 2H), 1.65 (d, *J* = 1.3 Hz, 3H), 1.49 – 1.33 (m, 3H), 1.33 – 1.12 (m, 9H), 0.95 – 0.77 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 128.9, 64.8, 39.4, 31.7, 28.9, 27.6, 23.6, 22.6, 16.3, 14.0; FTIR (film) *v*: 3340, 2960, 2928, 2857, 1670, 1456, 1379, 1104, 1059, 866 cm^{-1}; HRMS (EI) m/z

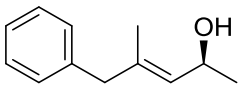
calcd for $C_{11}H_{22}O$ [M] 170.1671; found 170.1676; HPLC (for *p*-nitrobenzoate ester, racemate) column: Chiralcel OD-H, 100% hexanes, flow 1 mL min^{-1}, det. 254 nm; R_t 27.3 min (*S*-enantiomer) and 30.9 min (*R*-enantiomer).

(*S*,*E*)-4,6-Dimethylhept-3-en-2-ol (3c):



The reaction mixture was stirred for 24 h. Yield: 444 mg (87%) starting from 438 mg of ketone **6c**; yellowish oil; $[\alpha]_D^{22}$ –20.3 (*c* 0.99, $CHCl_3$), *ee* 92%; HPLC of *p*-nitrobenzoate ester: R_t 24.7 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18 (dq, *J* = 8.4, 1.3 Hz, 1H), 4.56 (dq, *J* = 8.4, 6.2 Hz, 1H), 1.90 – 1.68 (m, 3H), 1.63 (d, *J* = 1.3 Hz, 3H), 1.40 (s, 1H), 1.21 (d, *J* = 6.2 Hz, 3H), 0.88 – 0.78 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 130.5, 64.8, 49.2, 25.9, 23.6, 22.5, 22.1, 16.2; FTIR (film) *v*: 3342, 2954, 2925, 2869, 1669, 1464, 1383, 1367, 1102, 1057, 864 cm^{-1}; HRMS (EI) m/z calcd for $C_9H_{18}O$ [M] 142.1358; found 142.1363; HPLC (for *p*-nitrobenzoate ester, racemate) column: Chiralcel OD-H, 100% hexanes, flow 1 mL min^{-1}, det. 254 nm; R_t 22.1 min (*S*-enantiomer) and 26.2 min (*R*-enantiomer).

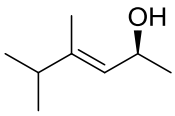
(*S*,*E*)-4-methyl-5-phenylpent-3-en-2-ol (3d):



The reaction mixture was stirred for 24 h. Yield: 701 mg (99%) starting from 700 mg of ketone **6f**; yellowish oil; $[\alpha]_D^{22}$ –25.1 (*c* 0.98, $CHCl_3$), *ee* 98%; HPLC for free alcohol R_t 39.1 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 2H), 7.25 – 7.12 (m, 3H), 5.33 (dq, *J* = 8.4, 1.4 Hz, 1H), 4.59 (dq, *J* = 8.4, 6.3 Hz, 1H), 3.29 (s, 2H), 1.62 (d, *J* = 1.4 Hz, 3H), 1.50 (br s, 1H), 1.27 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 136.7, 131.1, 128.9, 128.3, 126.2, 64.8, 46.0, 23.6, 16.2; FTIR (film) *v*: 3346, 2969, 2923, 1669, 1602, 1494, 1452, 1381, 1058, 742, 699 cm^{-1}; HRMS (EI) m/z calcd for $C_{12}H_{16}O$ [M] 176.1201; found 176.1200; HPLC (racemate) column: Chiralcel OD-

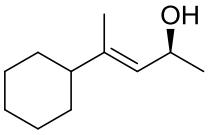
H, 1% *i*-Pr in hexanes, flow 1 mL min^{-1}, det. 210 nm; R_t 40.1 min (*S*-enantiomer) and 47.6 min (*R*-enantiomer).

(*S*,*E*)-4,5-dimethylhex-3-en-2-ol (3e):



The reaction mixture was stirred for 48 h. Yield: 328 mg (70%) starting from 461 mg of ketone **6d**; yellowish oil; $[\alpha]_D^{22}$ –23.9 (*c* 0.92, $CHCl_3$), *ee* 88%; HPLC of *p*-nitrobenzoate ester: R_t 28.7 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (dq, *J* = 8.3, 1.3 Hz, 1H), 4.57 (dq, *J* = 8.3, 6.3 Hz, 1H), 2.32 – 2.10 (m, 1H), 1.63 (d, *J* = 1.3 Hz, 3H), 1.39 (s, 1H), 1.22 (d, *J* = 6.3 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 126.8, 64.7, 36.5, 23.6, 21.2, 13.8; FTIR (film) *v*: 3347, 2963, 2928, 1666, 1463, 1379, 1053, 857 cm^{-1}; HRMS (EI) m/z calcd for $C_6H_{16}O$ [M] 128.1201; found 128.1200; HPLC (for *p*-nitrobenzoate ester, racemate) column: Chiralcel OD-H, 100% hexanes, flow 1 mL min^{-1}, det. 254 nm; R_t 26.3 min (*S*-enantiomer) and 30.6 min (*R*-enantiomer).

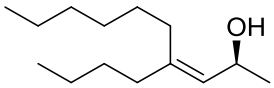
(*S*,*E*)-4-cyclohexylpent-3-en-2-ol (3f):



The reaction mixture was stirred for 48 h. Yield: 602 mg (85%) starting from 700 mg of ketone **6e**; yellowish oil; $[\alpha]_D^{22}$ –23.5 (*c* 1.09, $CHCl_3$), *ee* 88%; HPLC of *p*-nitrobenzoate ester: R_t 35.5 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18 (dq, *J* = 8.3, 1.3 Hz, 1H), 4.57 (dq, *J* = 8.3, 6.3 Hz, 1H), 1.87 – 1.58 (m, 9H), 1.40 (br s, 1H), 1.33 – 1.04 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 127.2, 64.7, 47.0, 31.7, 31.7, 26.6, 26.3, 23.6, 14.7; FTIR (film) *v*: 3335, 2925, 2852, 1448, 1058 cm^{-1}; HRMS (EI) m/z calcd for $C_{11}H_{20}O$ [M] 168.1514; found 168.1517; HPLC (for *p*-nitrobenzoate ester,

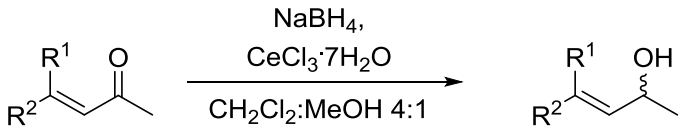
racemate) column: Chiralcel OD-H, 100% hexanes, flow 1 mL min^{-1}, det. 254 nm; R_t 33.9 min (*S*-enantiomer) and 37.7 min (*R*-enantiomer).

(*S*,*Z*)-4-butyldec-3-en-2-ol (3g):



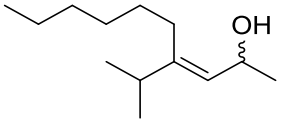
The reaction mixture was stirred for 48 h. Yield: 495 mg (98%) starting from 500 mg of ketone **6g**; yellowish oil; $[\alpha]_D^{22}$ –9.0 (*c* 0.92, $CHCl_3$, *ee* 82%; determined by HPLC of *p*-nitrobenzoate ester: R_t 15.5 min); ^1H NMR (400 MHz, $CDCl_3$) δ 5.17 (d, *J* = 8.7 Hz, 1H), 4.58 (dq, *J* = 8.7, 6.2 Hz, 1H), 2.14 – 1.89 (m, 4iH), 1.47 – 1.14 (m, 16H), 0.97 – 0.77 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 128.9, 64.4, 36.3, 31.7, 30.6, 30.2, 29.4, 28.9, 23.9, 22.6, 22.5, 14.0, 14.0; FTIR (film) *v*: 3334, 2958, 2927, 2858, 1464, 1055 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{28}O$ [M] 212.2140; found 212.2136; HPLC (for *p*-nitrobenzoate ester, racemate) column: Chiralpak AS-H, 100% hexanes, flow 1 mL min^{-1}, det. 254 nm; 10.5 min (*R*-enantiomer) and R_t 14.8 min (*S*-enantiomer).

7. The synthesis of racemic allylic alcohols (*rac*-3)



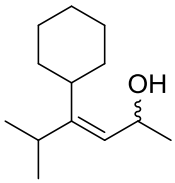
General procedure: To a suspension of enone **6** (3 mmol) and $CeCl_3 \cdot 7H_2O$ (3.6 mmol) in CH_2Cl_2/MeOH (4:1 v/v, 50 mL), $NaBH_4$ (3.6 mmol) was added portionwise. After 2 h at ambient temperature, the reaction mixture was partitioned between CH_2Cl_2 and H_2O. The organic layer was separated, and the aqueous one was extracted with CH_2Cl_2. The combined organic solutions were dried over anhydr. Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel (5-20% AcOEt in hexanes) to afford alcohol ***rac*-3**.

(*E*)-4-isopropyldec-3-en-2-ol (*rac*-3h)



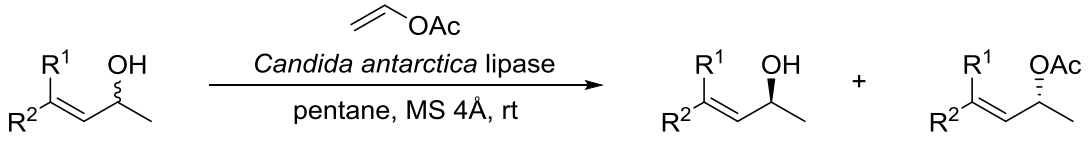
Yield: 379 mg (94%) starting from 400 mg of ketone **6h**; yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (d, *J* = 8.8 Hz, 1H), 4.57 (dq, *J* = 8.8, 6.2 Hz, 1H), 2.29 – 2.14 (m, 1H), 2.14 – 1.95 (m, 2H), 1.47 – 1.15 (m, 12H), 1.05 – 0.95 (m, 6H), 0.92 – 0.78 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 126.5, 64.6, 33.9, 31.7, 30.1, 30.1, 29.7, 23.8, 22.6, 22.0, 22.0, 14.0; FTIR (film) *v*: 3333, 2960, 2928, 2860, 1465, 1057 cm^{-1}; HRMS (EI) m/z calcd for $C_{13}H_{26}O$ [M] 198.1984; found 198.1989; HPLC (for *p*-nitrobenzoate ester, racemate) column: Chiralcel OD-H, 100% hexanes, flow 1 mL min^{-1}, det. 254 nm; 21.1 min (*S*-enantiomer) and 23.1 min (*R*-enantiomer).

(*Z*)-4-Cyclohexyl-5-methylhex-3-en-2-ol (*rac*-3i):



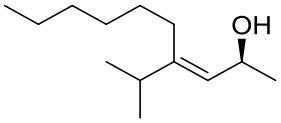
Yield: 330 mg (99%) starting from 330 mg of ketone **6i**; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (d, *J* = 8.7 Hz, 1H), 4.72 (dq, *J* = 8.7, 6.2 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.29 (hept, *J* = 6.9 Hz, 1H), 1.83 – 1.09 (m, 14H), 1.05 – 0.92 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 126.3, 64.0, 41.3, 31.6, 29.9, 26.7, 26.6, 26.1, 24.1, 24.1, 24.0; FTIR (film) *v*: 3332, 2961, 2926, 2853, 1448, 1047 cm^{-1}; HRMS (EI) m/z calcd for $C_{13}H_{24}O$ [M] 196.1827; found 196.1829; HPLC (for *p*-nitrobenzoate ester, racemate) column: Chiralcel OD-H, 100% hexanes, flow 1 mL min^{-1}, det. 254 nm; 25.6 min (*S*-enantiomer) and 36.5 min (*R*-enantiomer).

8. Enzymatic kinetic resolution of racemic allyl alcohols (*rac*-3)



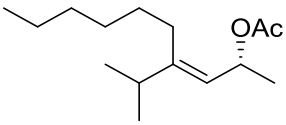
General procedure: A suspension of racemic alcohol ***rac-3*** (2.5 mmol), Novozyme 435 (18 mg), 4 Å molecular sieves (100 mg), and vinyl acetate (25 mmol, 2.2 g, 2.3 mL) in pentane (7 mL) was stirred in room temperature. The progress of the reaction was followed by ^{1}H NMR. The reaction mixture was filtered through Celite, and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel (0-20% Et_2O in pentanes).

(*S*,*E*)-4-Isopropyldec-3-en-2-ol (3h):



The reaction mixture was stirred for 11 days. Yield: 172 mg (46%) starting from 374 mg of racemic alcohol ***rac*-3h**; yellowish oil; $[\alpha]_D^{22}$ –12.7 (*c* 0.88, $CHCl_3$), *ee* 95%; HPLC of *p*-nitrobenzoate ester: R_t 21.9 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (d, *J* = 8.8 Hz, 1H), 4.57 (dq, *J* = 8.8, 6.2 Hz, 1H), 2.29 – 2.14 (m, 1H), 2.14 – 1.95 (m, 2H), 1.47 – 1.15 (m, 12H), 1.05 – 0.95 (m, 6H), 0.92 – 0.78 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 126.5, 64.6, 33.9, 31.7, 30.1, 30.1, 29.7, 23.8, 22.6, 22.0, 22.0, 14.0; FTIR (film) *v*: 3333, 2960, 2928, 2860, 1465, 1057 cm^{-1}; HRMS (EI) m/z calcd for $C_{13}H_{26}O$ [M] 198.1984; found 198.1989; HPLC (for *p*-nitrobenzoate ester, racemate) column: Chiralcel OD-H, 100% hexanes, flow 1 mL min^{-1}, det. 254 nm; R_t 21.1 min (*S*-enantiomer) and 23.1 min (*R*-enantiomer).

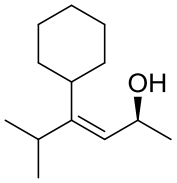
(*R*,*E*)-4-Isopropyldec-3-en-2-yl acetate (8):



The reaction mixture was stirred for 11 days. Yield: 196 mg (43%) starting from 374 mg of racemic alcohol ***rac*-3h**; yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (dq, *J* = 9.1, 6.3 Hz, 1H), 5.11 (d, *J* = 9.1 Hz, 1H), 2.30 – 2.07 (m, 2H), 2.05 – 1.90 (m, 4H), 1.42 – 1.17 (m, 11H), 1.04 – 0.93 (m, 6H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101

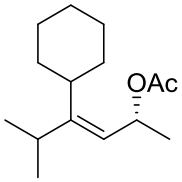
MHz, $CDCl_3$) δ 170.2, 150.0, 122.1, 68.0, 33.9, 31.7, 30.2, 29.7, 29.6, 22.6, 22.0, 21.9, 21.4, 21.3, 14.0; Elem. Anal Found: C, 74.99; H, 11.77%, $C_{15}H_{28}O_2$ requires C, 74.95; H, 11.74%.

(*S*,*Z*)-4-cyclohexyl-5-methylhex-3-en-2-ol (3i):



The reaction mixture was stirred for 40 days; after each 7 days the fresh portion of enzyme was added. Yield: 159 mg (47%) starting from 341 mg of racemic alcohol ***rac*-3i**; yellow oil; $[\alpha]_D^{24}$ –12.2 (*c* 0.62, $CHCl_3$, *ee* 79%), HPLC of *p*-nitrobenzoate ester: R_t 21.6 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (d, *J* = 8.7 Hz, 1H), 4.72 (dq, *J* = 8.7, 6.2 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.29 (hept, *J* = 6.9 Hz, 1H), 1.83 – 1.09 (m, 14H), 1.05 – 0.92 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 126.3, 64.0, 41.3, 31.6, 29.9, 26.7, 26.6, 26.1, 24.1, 24.1, 24.0; FTIR (film) *v*: 3332, 2961, 2926, 2853, 1448, 1047 cm^{-1}; HRMS (EI) m/z calcd for $C_{13}H_{24}O$ [M] 196.1827; found 196.1829; HPLC (for *p*-nitrobenzoate ester, racemate) column: Chiralcel OD-H, 100% hexanes, flow 1 mL min^{-1}, det. 254 nm; R_t 25.6 min (*S*-enantiomer) and 36.5 min (*R*-enantiomer).

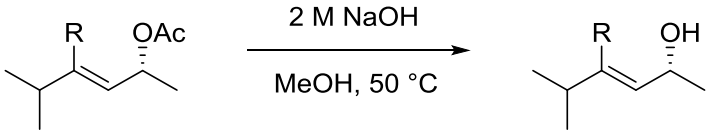
(*R*,*Z*)-4-Cyclohexyl-5-methylhex-3-en-2-yl acetate (9):



The reaction mixture was stirred for 40 days; after each 7 days the fresh portion of enzyme was added. Yield: 207 mg (50%) starting from 341 mg of racemic alcohol ***rac*-3i**; yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (dq, *J* = 8.9, 6.3 Hz, 1H), 5.11 (d, *J* = 8.9 Hz, 1H), 2.50 – 2.36 (m, 1H), 2.29 (hept, *J* = 6.7 Hz, 1H), 1.98 (s, 3H), 1.79 – 1.60 (m, 3H), 1.56 – 1.47 (m, 1H), 1.46 – 1.08 (m, 9H), 1.02 – 0.90 (m, 6H); ^{13}C NMR

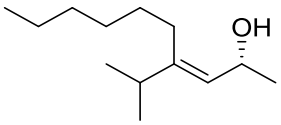
(101 MHz, $CDCl_3$) δ 170.3, 155.0, 121.7, 67.6, 41.5, 31.1, 31.1, 29.3, 26.5, 26.5, 26.1, 24.4, 24.0, 21.5, 21.4; Elem. Anal Found: C, 75.62; H, 11.02; %, $C_{15}H_{26}O_2$ requires C, 75.58; H, 10.99%.

9. The hydrolysis of acetates 8 and 9



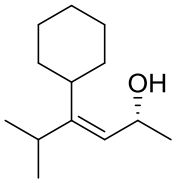
General procedure: A mixture of allyl acetate (1.0 mmol), MeOH (5 mL) and 2 M aq. NaOH (2 mL) was stirred for 24 h at 50 ºC. When the reaction was complete, water was added to the mixture. The aqueous phase was extracted with CH_2Cl_2 and the combined organic phase was dried over sodium sulfate. After the removal of the solvent, the crude product was used without a purification.

(*R*,*E*)-4-Isopropyldec-3-en-2-ol (*ent*-3h):



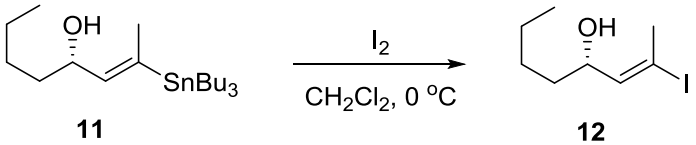
Yield: 180 mg (99%) starting from 196 mg of acetate **8**; yellow oil; $[\alpha]_D^{24}$ +12.5 (*c* 0.61, $CHCl_3$, *ee* 99%; determined by HPLC of *p*-nitrobenzoate ester: R_t 19.8 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (d, *J* = 8.8 Hz, 1H), 4.57 (dq, *J* = 8.8, 6.2 Hz, 1H), 2.29 – 2.14 (m, 1H), 2.14 – 1.95 (m, 2H), 1.47 – 1.15 (m, 12H), 1.05 – 0.95 (m, 6H), 0.92 – 0.78 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 126.5, 64.6, 33.9, 31.7, 30.1, 30.1, 29.7, 23.8, 22.6, 22.0, 22.0, 14.0; FTIR (film) *v*: 3333, 2960, 2928, 2860, 1465, 1057 cm^{-1}; HRMS (EI) m/z calcd for $C_{13}H_{26}O$ [M] 198.1984; found 198.1989; HPLC (for *p*-nitrobenzoate ester, racemate) column: Chiralcel OD-H, 100% hexanes, flow: 1 mL min^{-1}, det. 254 nm; 21.1 min (*S*-enantiomer) and R_t 23.1 min (*R*-enantiomer).

(*R*,*Z*)-4-Cyclohexyl-5-methylhex-3-en-2-ol (*ent*-3i):



Yield: 169 mg (99%) starting from 207 mg of acetate **9**; yellow oil; $[\alpha]_D^{24}$ +15.7 (*c* 1.20, $CHCl_3$), *ee* 90%; determined by HPLC of *p*-nitrobenzoate ester: R_t 26.8 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (d, *J* = 8.7 Hz, 1H), 4.72 (dq, *J* = 8.7, 6.2 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.29 (hept, *J* = 6.9 Hz, 1H), 1.83 – 1.09 (m, 14H), 1.05 – 0.92 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 126.3, 64.0, 41.3, 31.6, 29.9, 26.7, 26.6, 26.1, 24.1, 24.1, 24.0; FTIR (film) *v*: 3332, 2961, 2926, 2853, 1448, 1047 cm^{-1}; HRMS (EI) m/z calcd for $C_{13}H_{24}O$ [M] 196.1827; found 196.1829; HPLC (for *p*-nitrobenzoate ester, racemate) column: Chiralcel OD-H, 100% hexanes, flow 1 mL min^{-1}, det. 254 nm; 25.6 min (*S*-enantiomer) and R_t 36.5 min (*R*-enantiomer).

10. The synthesis of (*S*,*E*)-2-iodooct-2-en-4-ol

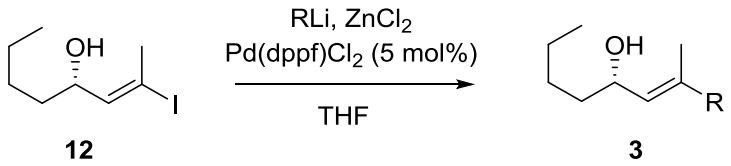


11 **12** 95%

In a darkness, β-vinyltributylstannane **11**[3] (4.8 mmol, 2.0 g) was dissolved in dry CH_2Cl_2 (0.1 M, 48 mL) and cooled to 0 °C, and next, I_2 (1.2 equiv., 5.8 mmol, 730 mg) was added portionwise. The progress of the reaction was followed by a TLC. After 1 h at 0 °C, the resulting mixture was washed with sat. aq. KF, followed by an addition of sat. aq. $Na_2S_2O_3$. The organic phase was dried over anhydr. Na_2SO_4. After the removal of the solvents, the crude residue was purified by a column chromatography on a silica gel deactivated with Et_3N (0-10% AcOEt in hexanes) to provide β-vinyliodine **12** (1.2 g, 95%) as yellowish oil; $[\alpha]_D^{23}$ +8.1 (*c* 1.19, $CHCl_3$, 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (dq, *J* = 8.7, 1.5 Hz, 1H), 4.40 – 4.21 (m, 1H), 2.44 (d, *J* = 1.5 Hz, 3H), 1.71 (br s, 1H), 1.62 – 1.51 (m, 1H), 1.50 – 1.39 (m, 1H), 1.38 – 1.18 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 97.5, 69.6,

36.7, 28.3, 27.3, 22.6, 14.0; FTIR (film) *v*: 3327, 2955, 2929, 2858, 1637, 1465, 1377, 1131, 1065, 1023, 646 cm^{-1}; Elem. Anal Found: C, 37.85; H, 5.63; I, 50.0%, $C_8H_{15}IO$ requires C, 37.81; H, 5.59; I, 49.94%. HRMS (EI) *m/z* calcd for $C_8H_{15}O^+$ [M-I] 127.1117; found 127.1115.

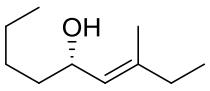
11. The synthesis of β,β-disubstituted allyl alcohols via Negishi coupling



12 **3**

A soln. of RLi (3 equiv., 2.4 mmol) was added to a 1M soln. of $ZnCl_2$ in THF (3 equiv., 2.4 mmol, 2.4 mL), pre-cooled to –30 °C. After stirring for 1 h at rt, the resulting mixture was transferred to the mixture of vinyl iodine **12** (1 equiv., 0.79 mmol, 200 mg) and Pd(dppf)Cl_2 (5 mol %, 29 mg) in dry and degassed THF pre-cooled to 0 °C. Mixture was left to stand overnight at rt. The progress of the reaction was followed by TLC. After removal of solvent, the crude residue was purified by column chromatography.

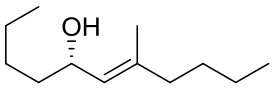
(*S*,*E*)-3-Methylnon-3-en-5-ol (3j):



Column chromatography: silica gel, 0–20% Et_2O in pentanes. Yield: 97 mg (80%) starting from 200 mg of vinyl iodide **12**; yellowish oil; $[\alpha]_D^{22}$ –16.0 (*c* 1.08, $CHCl_3$), *ee* 96%; HPLC of *p*-nitrobenzoate ester: R_t 27.8 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 (dq, *J* = 8.7, 1.4 Hz, 1H), 4.34 (dt, *J* = 8.7, 6.5 Hz, 1H), 2.08 – 1.93 (m, 2H), 1.67 (d, *J* = 1.4 Hz, 3H), 1.62 – 1.49 (m, 1H), 1.49 – 1.17 (m, 6H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 126.7, 68.6, 37.5, 32.2, 27.6, 22.7, 16.5, 14.0, 12.4; FTIR (film) *v*: 3339, 2956, 2929, 2858, 1637, 1464, 1378, 1065, 1023, 1007, 646 cm^{-1}; HRMS (EI) m/z calcd for $C_{10}H_{20}O$ [M] 156.1514; found 156.1519; HPLC (for *p*-nitrobenzoate ester, racemate) column: Chiralcel OD-H,

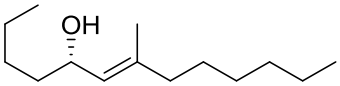
100% hexanes, flow 1 mL min^{-1}, det. 254 nm; R_t 28.6 min (*S*-enantiomer) and 33.5 min (*R*-enantiomer).

(*S*,*E*)-7-Methylundec-6-en-5-ol (3k):



Column chromatography: silica gel, 5–20% AcOEt in hexanes. Yield 126 mg (88%) starting from 200 mg of vinyl iodide **12**; yellowish oil; $[\alpha]_D^{23}$ –10.1 (*c* 1.12, $CHCl_3$), *ee* 92%; HPLC of *p*-nitrobenzoate ester: R_t 21.4 min); ^1H NMR (400 MHz, $CDCl_3$) δ 5.15 (dq, *J* = 8.7, 1.4 Hz, 1H), 4.35 (dt, *J* = 8.7, 6.5 Hz, 1H), 2.05 – 1.92 (m, 2H), 1.66 (d, *J* = 1.4 Hz, 3H), 1.63 – 1.52 (m, 1H), 1.49 – 1.18 (m, 10H), 0.90 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 127.9, 68.6, 39.2, 37.5, 29.9, 27.6, 22.7, 22.3, 16.5, 14.0, 13.9; FTIR (film) *v*: 3341, 2957, 2929, 2859, 1466, 1379, 998 cm^{-1}; HRMS (EI) m/z calcd for $C_{12}H_{24}O$ [M] 184.1827; found 184.1832; HPLC (for *p*-nitrobenzoate ester, racemate) column: Chiralcel OD-H, 100% hexanes, flow 1 mL min^{-1}, det. 254 nm; R_t 21.4 min (*S*-enantiomer) and 24.1 min (*R*-enantiomer).

(*S*,*E*)-7-Methyltridec-6-en-5-ol (3l):

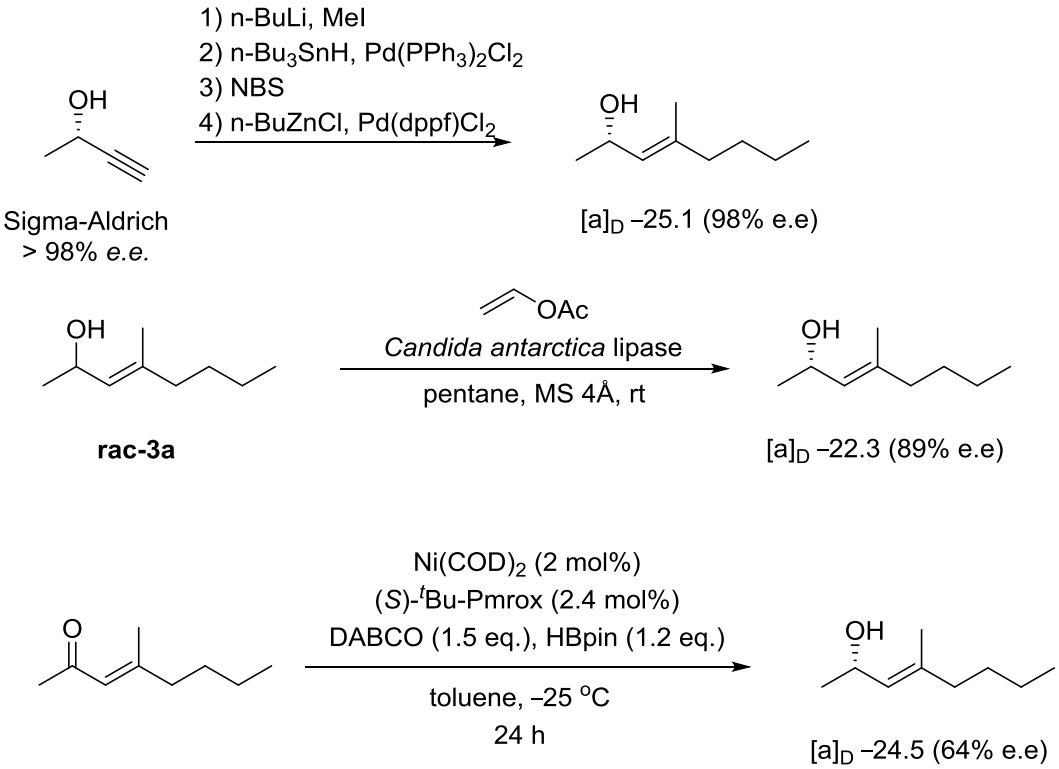


Column chromatography: silica gel, 5–20% AcOEt in hexanes. Yield 152 mg (92%) starting from 200 mg of vinyl iodide **12**; yellowish oil; $[\alpha]_D^{23}$ –9.7 (*c* 1.00, $CHCl_3$), *ee* 94%; HPLC of *p*-nitrobenzoate ester: R_t 20.7 min); ^1H NMR (400 MHz, $CDCl_3$) δ 5.14 (d, *J* = 8.7 Hz, 1H), 4.34 (dt, *J* = 8.7, 6.6 Hz, 1H), 2.17 – 1.83 (m, 2H), 1.73 – 1.50 (m, 4H), 1.50 – 1.10 (m, 15H), 1.02 – 0.73 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 127.9, 68.7, 39.6, 37.5, 31.7, 28.9, 27.6, 22.7, 22.6, 16.5, 14.0; FTIR (film) *v*: 3341, 2957, 2928, 2857, 1465, 1379, 1004 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{28}O$ [M] 212.2140; found 212.2133; HPLC (for *p*-nitrobenzoate ester, racemate) column:

Chiralcel OD-H, 100% hexanes, flow 1 mL min^{-1}, det. 254 nm; R_t 20.6 min (*S*-enantiomer) and 23.6 min (*R*-enantiomer).

12. Confirmation of absolute configuration of 3a

Independently, analytic samples of **3a** were prepared by sequential coupling starting from commercially available (*S*)-3-butyn-2-ol, enzymatic kinetic resolution of ***rac*-3a**, and enantioselective reduction of enone **6a**. Optical rotatory power ($[\alpha]_D$) values for all free samples had the same sign indicating that all of them provided (S)-enantiomer.

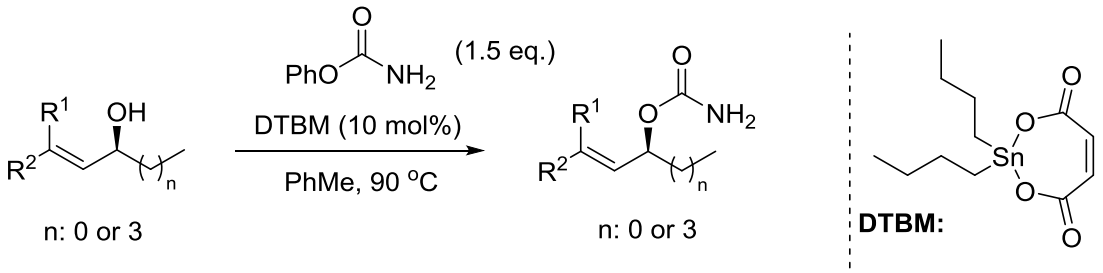


The same experiments were performed to confirmed an absolute configuration of **3g**. Again the signs of $[\alpha]_D$ values of sample obtained from (*S*)-butyn-2-ol and via reduction of **6g** were the same.

Unfortunately, we could not prepare alcohols **3h** and **3i** by sequential coupling strategy staring from (*S*)-3-butyn-2-ol. In both cases final Negishi coupling was ineffective. However, since $[\alpha]_D$ values for **3h** and **3i** are negative ($[\alpha]_D$ –12.7 and $[\alpha]_D$ –12.1, respectively) as for all other allyl alcohols of type **3**, we assume that both alcohols have (*S*)-absolute configuration. To get a hard proof for such assumption we tried to perform X-ray analysis for various derivatives of alcohols **3h** and **3i** (e.g. *p*-tosylate/nosylate, o/p-nitrobenzoate, o/p-bromobenzoate).

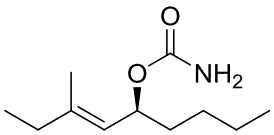
However, beside many attempts, none of the tested derivatives did not provide suitable crystals for structural analysis.

13. Transcarbamoylation of allyl alcohols 3



General procedure:[4] A solution of allyl alcohol **3** (0.52 mmol), phenyl carbamate (0.78 mmol), and dibutyltin maleate (53 µmol, 10 mol%) in toluene (*c* 0.2 M) was stirred at 90 °C. The progress of the reaction was followed by TLC. When the reaction was completed, the solution was cooled to 0 °C and diluted with 2 M aqueous NaOH. After stirring at 0 °C for 10 min, CH_2Cl_2 and H_2O were added. The organic layer was separated and washed with 2 M aqueous NaOH, H_2O, and brine, dried over Na_2SO_4. After the removal of the solvent, the crude residue was purified by a column chromatography on a silica gel deactivated with Et_3N (0–30% AcOEt in hexanes).

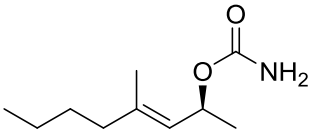
(*S*,*E*)-3-Methylnon-3-en-5-yl carbamate (13a):



The reaction mixture was stirred for 8 h. Yield: 84 mg (74%) starting from 89 mg of alcohol **3j**; waxy solid; $[\alpha]_D^{23}$ +5.9 (*c* 1.14, $CHCl_3$, *ee* 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (dt, *J* = 9.1, 6.7 Hz, 1H), 5.08 (dq, *J* = 9.1, 1.3 Hz, 1H), 4.56 (br s, 2H), 2.13 – 1.90 (m, 2H), 1.77 – 1.58 (m, 4H), 1.54 – 1.41 (m, 1H), 1.40 – 1.18 (m, 5H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 142.1, 122.4, 72.4, 34.9, 32.2, 27.2, 22.5, 16.8, 14.0, 12.4; FTIR (film) *v*: 3433, 3330, 3261,

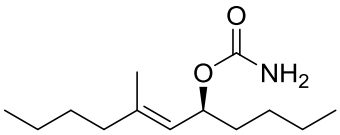
3212, 2959, 2929, 2860, 1681, 1611, 1404, 1044 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{21}NO_2Na$ [(M+Na)$^+$] 222.1470; found 222.1465.

(*S*,*E*)-4-Methyloct-3-en-2-yl carbamate (13b):



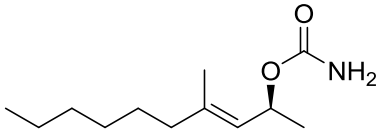
The reaction mixture was stirred for 4 h. Yield: 567 mg (89%) starting from 490 mg of alcohol **3a**; white solid; m.p. 68-70 °C; $[\alpha]_D^{20}$ –7.2 (*c* 1.20, $CHCl_3$, *ee* 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (dq, *J* = 8.7, 6.3 Hz, 1H), 5.12 (dq, *J* = 8.7, 1.4 Hz, 1H), 4.87 (br s, 2H), 2.02 – 1.89 (m, 2H), 1.66 (d, *J* = 1.4 Hz, 3H), 1.43 – 1.15 (m, 7H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 139.8, 124.5, 68.9, 39.1, 29.7, 22.3, 21.1, 16.5, 13.9; FTIR (film) *v*: 3433, 3330, 3261, 3210, 2962, 2929, 1681, 1612, 1405, 1047 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_{19}NO_2Na$ [(M+Na)$^+$] 208.1313; found 208.1307.

(*S*,*E*)-7-Methylundec-6-en-5-yl carbamate (13c):



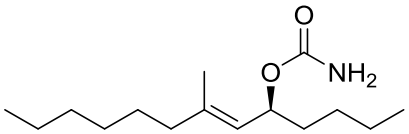
The reaction mixture was stirred for 5 h. Yield: 113 mg (80%) starting from 115 mg of alcohol **3k**; waxy solid; $[\alpha]_D^{22}$ +1.4 (*c* 1.38, $CHCl_3$, *ee* 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (dt, *J* = 9.0, 6.7 Hz, 1H), 5.09 (dq, *J* = 9.1, 1.3 Hz, 1H), 4.48 (br s, 2H), 2.12 – 1.89 (m, 2H), 1.77 – 1.60 (m, 4H), 1.53 – 1.11 (m, 9H), 0.98 – 0.75 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 140.7, 123.6, 72.4, 39.2, 34.9, 29.8, 27.2, 22.5, 22.3, 16.7, 14.0, 13.9; FTIR (film) *v*: 3346, 2957, 2930, 2861, 1711, 1383, 1310, 1039 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{25}NO_2Na$ [(M+Na)$^+$] 250.1783; found 250.1783.

(*S*,*E*)-4-Methyldec-3-en-2-yl carbamate (13d):



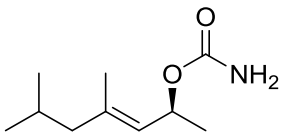
The reaction mixture was stirred for 4 h. Yield: 624 mg (85%) starting from 585 mg of alcohol **3b**; white solid; m.p. 61-62 °C; $[\alpha]_D^{22}$ –9.2 (*c* 1.44, $CHCl_3$, *ee* 94%); ^1H NMR (400 MHz, $CDCl_3$) δ 5.48 (dq, *J* = 8.7, 6.3 Hz, 1H), 5.13 (dq, *J* = 8.7, 1.3 Hz, 1H), 4.70 (br s, 2H), 2.03 – 1.90 (m, 2H), 1.68 (d, *J* = 1.3 Hz, 3H), 1.46 – 1.30 (m, 2H), 1.33 – 1.14 (m, 9H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 139.9, 124.5, 68.9, 39.4, 31.7, 28.9, 27.5, 22.6, 21.1, 16.6, 14.0; FTIR (film) *v*: 3435, 3261, 2929, 1683, 1612, 1404, 1046 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{23}NO_2Na$ $[(M+Na)^+]$ 236.1626; found 236.1620.

(*S*,*E*)-7-Methyltridec-6-en-5-yl carbamate (13e):



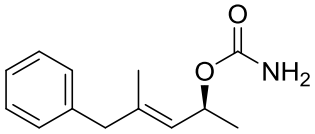
The reaction mixture was stirred for 5 h. Yield: 140 mg (83%) starting from 140 mg of alcohol **3l**; waxy solid; $[\alpha]_D^{22}$ –0.4 (*c* 1.00, $CHCl_3$, *ee* 94%); ^1H NMR (400 MHz, $CDCl_3$) δ 5.37 (dt, *J* = 9.0, 6.7 Hz, 1H), 5.08 (dq, *J* = 9.0, 1.3 Hz, 1H), 4.51 (br s, 2H), 2.05 – 1.95 (m, 2H), 1.77 – 1.54 (m, 4H), 1.53 – 1.17 (m, 13H), 0.96 – 0.76 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 140.8, 123.6, 72.5, 39.5, 34.9, 31.7, 28.8, 27.6, 27.2, 22.6, 22.6, 16.7, 14.0, 14.0; FTIR (film) *v*: 3439, 3343, 2956, 2928, 2857, 1682, 1648, 1399, 1038, 581 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{29}NO_2Na$ $[(M+Na)^+]$ 278.2096; found 278.2097.

(*S*,*E*)-4,6-Dimethylhept-3-en-2-yl carbamate (13f)



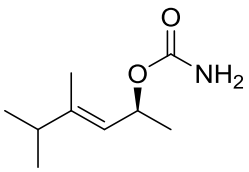
The reaction mixture was stirred for 4 h. Yield: 349 mg (83%) starting from 322 mg of alcohol **3c**; white solid; m.p. 85-87 °C; $[\alpha]_D^{22}$ –5.3 (*c* 0.94, $CHCl_3$, *ee* 92%); ^1H NMR (400 MHz, $CDCl_3$) δ 5.48 (dq, *J* = 8.7, 6.4 Hz, 1H), 5.12 (dq, *J* = 8.7, 1.4 Hz, 1H), 4.69 (br s, 2H), 1.91 – 1.68 (m, 3H), 1.66 (d, *J* = 1.4 Hz, 3H), 1.26 (d, *J* = 6.4 Hz, 3H), 0.91 – 0.73 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 138.6, 126.1, 68.9, 49.2, 25.9, 22.5, 22.1, 21.1, 16.5; FTIR (film) *v*: 3433, 3331, 3262, 3208, 2952, 2925, 1681, 1611, 1404, 1046 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_{19}NO_2Na$ $[(M+Na)^+]$ 208.1313; found 208.1311.

(*S*,*E*)-4-Methyl-5-phenylpent-3-en-2-yl carbamate (13g):



The reaction mixture was stirred for 4 h. Yield: 702 mg (83%) starting from 678 mg of alcohol **3d**; white solid; m.p. 105-107 °C; $[\alpha]_D^{20}$ –30.5 (*c* 1.27, $CHCl_3$, *ee* 98%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.10 (m, 5H), 5.51 (dq, *J* = 8.6, 6.4 Hz, 1H), 5.27 (dq, *J* = 8.6, 1.4 Hz, 1H), 4.83 (br s, 2H), 3.30 (d, *J* = 3.2 Hz, 2H), 1.66 (d, *J* = 1.4 Hz, 3H), 1.30 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 139.3, 138.5, 128.9, 128.3, 126.9, 126.2, 68.9, 45.9, 21.1, 16.5; FTIR (film) *v*: 3426, 3330, 3263, 3205, 2976, 1681, 1614, 1409, 1044, 695 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{17}NO_2Na$ $[(M+Na)^+]$ 242.1157; found 242.1156.

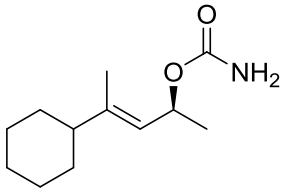
(*S*,*E*)-4,5-Dimethylhex-3-en-2-yl carbamate (13h):



The reaction mixture was stirred for 3 h. Yield: 322 mg (74%) starting from 326 mg of alcohol **3e**; waxy solid; $[\alpha]_D^{21}$ –3.7 (*c* 1.27, $CHCl_3$, *ee* 88%); ^1H NMR (400 MHz, $CDCl_3$) δ 5.47 (dq, *J* = 8.6, 6.4 Hz, 1H), 5.13 (dq, *J* = 8.6, 1.4 Hz, 1H), 4.84 (br s, 1H), 2.19 (hept, *J* = 6.9 Hz, 1H), 1.64 (d, *J* = 1.4 Hz, 3H), 1.24 (d, *J* = 6.4 Hz, 3H), 0.97 (d, *J* =

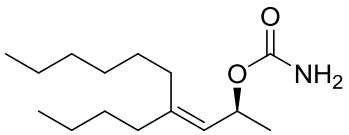
6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 145.1, 122.5, 68.9, 36.4, 21.2, 21.1, 14.1; FTIR (film) *v*: 3443, 3332, 3195, 2963, 1720, 1385, 1315, 1041, 1011 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_9H_{17}NO_2Na$ [$(M+Na)^+$] 194.1157; found 194.1154.

(*S*,*E*)-4-Cyclohexylpent-3-en-2-yl carbamate (13i):



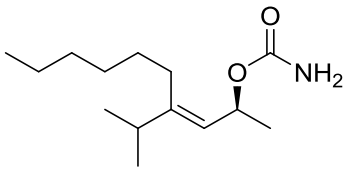
The reaction mixture was stirred for 4 h. Yield: 561 mg (86%) starting from 518 mg of alcohol **3f**; white solid; 88-100 °C; $[\alpha]_D^{21}$ –15.0 (*c* 1.07, $CHCl_3$, *ee* 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 (dq, *J* = 8.6, 6.3 Hz, 1H), 5.12 (dq, *J* = 8.6, 1.3 Hz, 1H), 4.83 (br s, 2H), 1.89 – 1.56 (m, 9H), 1.34 – 1.01 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 144.6, 122.9, 68.9, 47.0, 31.7, 31.6, 26.6, 26.6, 26.3, 21.2, 15.0; FTIR (film) *v*: 3440, 3331, 3258, 2926, 2854, 1683, 1612, 1404, 1044 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{21}NO_2Na$ [$(M+Na)^+$] 234.1470; found 234.1463.

(*S*,*Z*)-4-Butyldec-3-en-2-yl carbamate (13j):



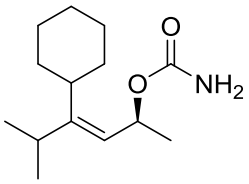
The reaction mixture was stirred for 5 h. Yield: 427 mg (91%) starting from 391 mg of alcohol **3g**; waxy solid; $[\alpha]_D^{22}$ +12.5 (*c* 0.90, $CHCl_3$, *ee* 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (dq, *J* = 9.0, 6.3 Hz, 1H), 5.11 (d, *J* = 9.0 Hz, 1H), 4.75 (br s, 2H), 2.23 – 2.08 (m, 1H), 2.07 – 1.88 (m, 3H), 1.49 – 1.14 (m, 15H), 0.96 – 0.75 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 144.3, 124.4, 68.6, 36.2, 31.7, 30.8, 30.0, 29.4, 28.6, 22.6, 22.4, 21.5, 14.0, 13.9; FTIR (film) *v*: 3339, 2956, 2929, 2859, 1713, 1373, 1317, 1043 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{29}NO_2Na$ [$(M+Na)^+$] 278.2096; found 278.2097.

(*S*,*E*)-4-Isopropyldec-3-en-2-yl carbamate (13k):



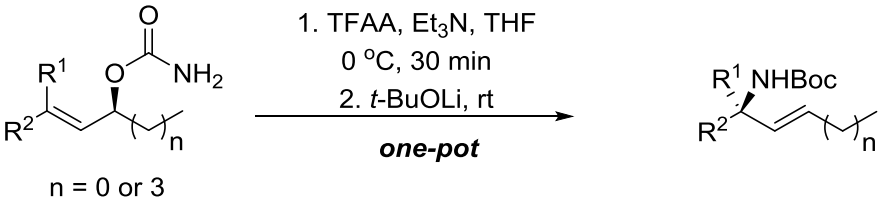
The reaction mixture was stirred for 4 h. Yield: 162 mg (84%) starting from 159 mg of alcohol **3h**; waxy solid; $[\alpha]_D^{24}$ +8.4 (*c* 1.70, $CHCl_3$, *ee* 95%); ^1H NMR (400 MHz, $CDCl_3$) δ 5.49 (dq, *J* = 9.0, 6.3 Hz, 1H), 5.11 (dd, *J* = 9.0, 1.0 Hz, 1H), 4.78 (br s, 2H), 2.28 – 2.08 (m, 2H), 2.07 – 1.93 (m, 1H), 1.43 – 1.19 (m, 11H), 1.04 – 0.94 (m, 6H), 0.91 – 0.80 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 150.1, 122.2, 68.8, 33.8, 31.7, 30.2, 29.7, 29.6, 22.6, 22.0, 21.9, 21.6, 14.0; FTIR (film) *v*: 3336, 2959, 2930, 2871, 1711, 1601, 1466, 1374, 1315, 1037 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{27}NO_2Na$ $[(M+Na)^+]$ 264.1939; found 264.1931.

(*S*,*Z*)-4-Cyclohexyl-5-methylhex-3-en-2-yl carbamate (13l)



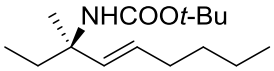
The reaction mixture was stirred for 6 h. Yield: 138 mg (90%) starting from 125 mg of alcohol **3i**; waxy solid; $[\alpha]_D^{24}$ –2.5 (*c* 0.68, $CHCl_3$, *ee* 79%); ^1H NMR (400 MHz, $CDCl_3$) δ 5.70 – 5.50 (m, 1H), 5.11 (d, *J* = 8.7 Hz, 1H), 4.79 (br s, 2H), 2.53 – 2.37 (m, 1H), 2.30 (hept, *J* = 6.5 Hz, 1H), 1.80 – 1.05 (m, 13H), 1.05 – 0.88 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 155.0, 121.8, 68.4, 41.4, 31.2, 29.3, 26.5, 26.4, 26.1, 24.4, 24.1, 21.8; FTIR (film) *v*: 3343, 2927, 2853, 1713, 1378, 1040 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{25}NO_2Na$ $[(M+Na)^+]$ 262.1783; found 262.1776.

14. [3,3]-Sigmatropic rearrangement of allyl carbamates 13



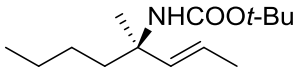
General procedure: A solution of carbamate **13** (0.5 mmol) and Et_3N (3 mmol, 304 mg, 418 µL) in dry THF (10 mL) was cooled to 0 °C, and TFAA (1 mmol, 210 mg, 139 µL) was added. The resulting mixture was warmed slowly to room temperature and stirred for 0.5–1 h. After that, the *t*-BuOLi (3 mmol, 240 mg) was added portionwise to the generated allyl isocyanate. The progress of the reaction was followed by TLC. After 1 h, volatiles were removed under reduced pressure. The residue was purified by a flash chromatography on a silica gel (2–20% AcOEt in hexanes).

***tert*-Butyl (*R*,*E*)-(3-methylnon-4-en-3-yl)carbamate (14a):**



Yield 91 mg (89%) starting from 81 mg of carbamate **13a**; colourless oil; $[\alpha]_D^{25}$ –6.7 (*c* 1.08, $CHCl_3$, *ee* 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 – 5.28 (m, 2H), 4.46 (br s, 1H), 2.12 – 1.91 (m, 2H), 1.79 – 1.53 (m, 2H), 1.42 (s, 9H), 1.38 – 1.18 (m, 7H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 135.2, 128.2, 78.6, 55.8, 32.6, 32.0, 31.6, 28.4, 24.7, 22.1, 13.8, 8.1; FTIR (film) *v*: 3362, 2966, 2928, 1725, 1699, 1492, 1366, 1247, 1171, 1079 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{29}NO_2Na$ [$(M+Na)^+$] 278.2096; found 278.2083.

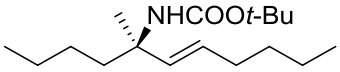
***tert*-Butyl (*R*,*E*)-(4-methyloct-2-en-4-yl)carbamate (14b):**



Yield 617 mg (86%) starting from 552 mg of carbamate **13b**; yellowish oil; $[\alpha]_D^{23}$ –9.0 (*c* 1.12, $CHCl_3$, *ee* 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 – 5.36 (m, 2H), 4.46 (br

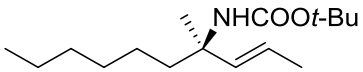
s, 1H), 1.72 – 1.56 (m, 5H), 1.39 (s, 9H), 1.34 – 1.09 (m, 7H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 136.8, 122.3, 78.5, 55.5, 39.8, 28.3, 26.0, 25.0, 22.9, 17.7, 14.0; FTIR (film) *v*: 3359, 2961, 2931, 1725, 1698, 1492, 1365, 1249, 1172, 1083 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{27}NO_2Na$ [(M+Na)$^+$] 264.1939; found 264.1931.

tert-Butyl (*R*,*E*)-(5-methylundec-6-en-5-yl)carbamate (14c):



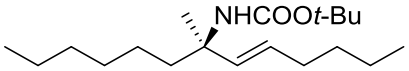
Yield 98 mg (75%) starting from 105 mg of carbamate **13c**; colourless oil; $[\alpha]_D^{25}$ – 5.6 (*c* 1.08, $CHCl_3$, *ee* 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 – 5.33 (m, 2H), 4.46 (br s, 1H), 2.12 – 1.89 (m, 2H), 1.75 – 1.53 (m, 2H), 1.41 (s, 9H), 1.37 – 1.09 (m, 11H), 0.88 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 135.6, 128.0, 78.6, 55.6, 39.9, 32.0, 31.6, 28.4, 26.1, 25.2, 23.0, 22.1, 14.0, 13.8; FTIR (film) *v*: 3364, 2958, 2929, 2861, 1727, 1697, 1490, 1365, 1172 1082, 1046, 969 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{33}NO_2Na$ [(M+Na)$^+$] 306.2409; found 306.2406.

tert-Butyl (*R*,*E*)-(4-methyldec-2-en-4-yl)carbamate (14d):



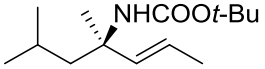
Yield 640 mg (84%) starting from 600 mg of carbamate **13d**; yellowish oil; $[\alpha]_D^{23}$ – 8.3 (*c* 1.16, $CHCl_3$, *ee* 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 – 5.35 (m, 2H), 4.46 (br s, 1H), 1.68 – 1.51 (m, 5H), 1.37 (s, 9H), 1.31 – 1.08 (m, 11H), 0.89 – 0.76 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 136.8, 122.4, 78.5, 55.6, 40.1, 31.7, 29.5, 28.4, 25.0, 23.7, 22.5, 17.7, 14.0; FTIR (film) *v*: 3361, 2960, 2929, 2858, 1725, 1698, 1491, 1453, 1365, 1248, 1172 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{31}NO_2Na$ [(M+Na)$^+$] 292.2252; found 292.2245.

tert-Butyl (*R*,*E*)-(7-methyltridec-5-en-7-yl)carbamate (14e):



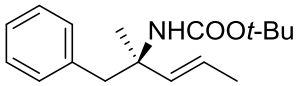
Yield 132 mg (80%) starting from 135 mg of carbamate **13e**; colourless oil; $[\alpha]_D^{25}$ – 5.9 (*c* 1.09, $CHCl_3$, *ee* 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 – 5.30 (m, 2H), 4.46 (br s, 1H), 2.12 – 1.91 (m, 2H), 1.71 – 1.53 (m, 2H), 1.41 (s, 9H), 1.38 – 1.10 (m, 15H), 0.96 – 0.76 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 135.6, 128.0, 78.6, 55.6, 40.2, 32.0, 31.8, 31.6, 29.5, 28.4, 25.2, 23.8, 22.6, 22.1, 14.0, 13.9; FTIR (film) *v*: 3362, 2957, 2927, 2857, 1725, 1698, 1490, 1366, 1247, 1170, 1052 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{37}NO_2Na$ $[(M+Na)^+]$ 334.2722; found 334.2710.

tert-Butyl (*R*,*E*)-(4,6-dimethylhept-2-en-4-yl)carbamate (14f):



Yield 356 mg (83%) starting from 328 mg of carbamate **13f**; yellowish oil; $[\alpha]_D^{24}$ – 10.4 (*c* 0.95, $CHCl_3$, *ee* 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61 – 5.33 (m, 2H), 4.48 (br s, 1H), 1.75 – 1.47 (m, 6H), 1.38 (s, 9H), 1.33 – 1.15 (m, 3H), 0.87 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 137.4, 122.0, 78.6, 55.9, 48.3, 28.4, 25.8, 24.6, 24.5, 24.1, 17.7; FTIR (film) *v*: 3364, 2957, 2930, 1725, 1698, 1492, 1366, 1243, 1168, 1083 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{27}NO_2Na$ $[(M+Na)^+]$ 264.1939; found 264.1934.

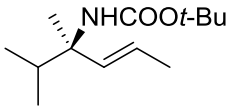
tert-Butyl (*R*,*E*)-(2-methyl-1-phenylpent-3-en-2-yl)carbamate (14g):



Yield 558 mg (89%) starting from 500 mg of carbamate **13g**; yellowish oil; $[\alpha]_D^{24}$ +19.6 (*c* 0.95, $CHCl_3$, *ee* 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 3H), 7.19 – 7.09 (m, 2H), 5.65 (dq, *J* = 15.6, 1.6 Hz, 1H), 5.46 (dq, *J* = 15.6, 6.4 Hz, 1H), 4.41 (br s, 1H), 3.15 (d, *J* = 13.2 Hz, 1H), 2.95 (d, *J* = 13.2 Hz, 1H), 1.71 (dd, *J* = 6.4, 1.6 Hz, 3H), 1.48 (s, 9H), 1.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 137.6, 136.5, 130.8, 127.8, 126.3, 123.0, 78.9, 55.9, 44.8, 28.5, 25.7, 17.8; FTIR (film) *v*: 3362, 2976, 2930,

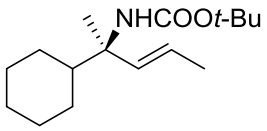
1719, 1495, 1365, 1249, 1168, 702 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{25}NO_2Na$ [$(M+Na)^+$] 298.1783; found 298.1772.

***tert*-Butyl (*R*,*E*)-(2,3-dimethylhex-4-en-3-yl)carbamate (14h):**



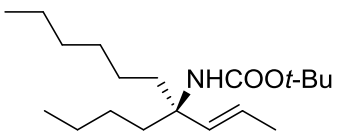
Yield 314 mg (79%) starting from 300 mg of carbamate **13h**; yellowish oil; $[\alpha]_D^{24}$ -12.4 (*c* 0.90, $CHCl_3$, *ee* 88%); ^1H NMR (400 MHz, $CDCl_3$) δ 5.63 – 5.38 (m, 2H), 4.48 (br s, 1H), 2.10 (s, 1H), 1.70 (d, *J* = 4.8 Hz, 3H), 1.41 (s, 9H), 1.31 (s, 3H), 0.88 – 0.80 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 134.5, 123.5, 78.5, 58.6, 35.2, 28.4, 21.0, 17.8, 17.2, 17.1; FTIR (film) *v*: 3360, 2969, 2931, 1725, 1696, 1493, 1452, 1389, 1367, 1250, 1170 1081, 975 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{25}NO_2Na$ [$(M+Na)^+$] 250.1783; found 250.1778.

***tert*-Butyl (*R*,*E*)-(2-cyclohexylpent-3-en-2-yl)carbamate (14i):**



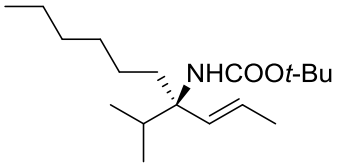
Yield 416 mg (82%) starting from 400 mg of carbamate **13i**; yellowish oil; $[\alpha]_D^{24}$ -14.0 (*c* 0.97, $CHCl_3$, *ee* 88%); ^1H NMR (400 MHz, $CDCl_3$) δ 5.58 – 5.34 (m, 2H), 4.46 (br s, 1H), 1.80 – 1.56 (m, 9H), 1.39 (s, 9H), 1.29 (s, 3H), 1.28 – 0.80 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 135.1, 123.2, 78.6, 58.5, 45.8, 28.4, 27.4, 27.3, 26.7, 26.5, 21.5, 17.8; FTIR (film) *v*: 3359, 2975, 2928, 2854,1724, 1694, 1491, 1450, 1366, 1240, 1171 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{29}NO_2Na$ [$(M+Na)^+$] 290.2096; found 290.2092.

***tert*-Butyl (*S*,*E*)-(5-(prop-1-en-1-yl)undecan-5-yl)carbamate (14j):**



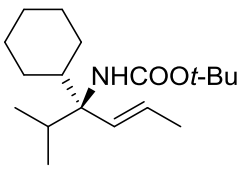
Yield 287 mg (79%) starting from 300 mg of carbamate **13j**; yellowish oil; $[\alpha]_D^{23}$ +2.5 (*c* 1.13, $CHCl_3$, *ee* 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.4 (dq, *J* = 15.9, 6.0 Hz, 1H), 5.3 (d, *J* = 15.9 Hz, 1H), 4.4 (br s, 1H), 1.9 – 1.7 (m, 2H), 1.7 (dd, *J* = 6.0, 1.3 Hz, 3H), 1.6 – 1.4 (m, 2H), 1.4 (s, 9H), 1.3 – 1.1 (m, 12H), 0.9 – 0.8 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 136.0, 122.6, 78.4, 58.5, 37.4, 37.2, 31.8, 29.5, 28.3, 25.6, 23.3, 22.9, 22.5, 17.8, 14.0, 14.0; FTIR (film) *v*: 3363, 2957, 2928, 2860, 1727, 1696, 1490, 1365, 1246, 1172, 1090, 969 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{37}NO_2Na$ $[(M+Na)^+]$ 334.2722; found 334.2719.

tert-Butyl (_R_,_E_)-(4-isopropyldec-2-en-4-yl)carbamate (14k):



Yield 131 mg (79%) starting from 135 mg of carbamate **13k**; colourless oil; $[\alpha]_D^{25}$ +14.9 (*c* 0.50, $CHCl_3$, *ee* 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 – 5.08 (m, 2H), 4.44 (br s, 1H), 2.26 (s, 1H), 1.96 (s, 1H), 1.71 (d, *J* = 6.1 Hz, 3H), 1.67 – 1.54 (m, 1H), 1.40 (s, 9H), 1.31 – 1.09 (m, 8H), 0.85 (t, *J* = 6.5 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 132.3, 123.9, 78.4, 61.7, 34.3, 34.0, 31.8, 29.6, 28.4, 23.6, 22.6, 18.0, 17.3, 17.2, 14.0; FTIR (film) *v*: 2961, 2928, 2860, 1726, 1696, 1491, 1366, 1245, 1170, 1090 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{35}NO_2Na$ $[(M+Na)^+]$ 320.2565; found 320.2561.

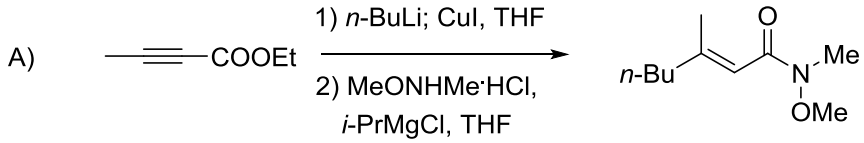
tert-Butyl (_S_,_E_)-(3-cyclohexyl-2-methylhex-4-en-3-yl)carbamate (14l):



Yield 100 mg (68%) starting from 121 mg of carbamate **13l**; colourless oil; $[\alpha]_D^{25}$ +8.9 (*c* 0.71, $CHCl_3$, *ee* 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 – 5.10 (m, 2H), 4.24

(br s, 1H), 2.50 (br s, 1H), 2.08 – 1.89 (m, 1H), 1.84 – 1.55 (m, 8H), 1.40 (s, 9H), 1.32 – 0.88 (m, 5H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 133.7, 123.7, 78.0, 65.0, 43.2, 31.3, 28.4, 28.0, 27.5, 27.0, 26.8, 17.9, 17.5, 17.2; FTIR (film) *v*: 2971, 2928, 2854, 1731, 1689, 1494, 1365, 1237, 1168 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{33}NO_2Na$ [(M+Na)$^+$] 318.2409; found 318.2400.

15. A large scale synthesis of allylamine 14b

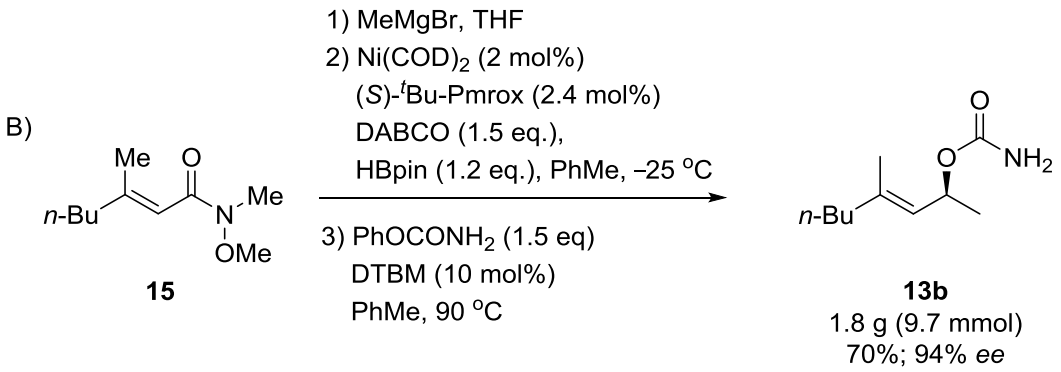


4a
2.24 g
(20 mmol)

15
2.6 g (14 mmol)
70%

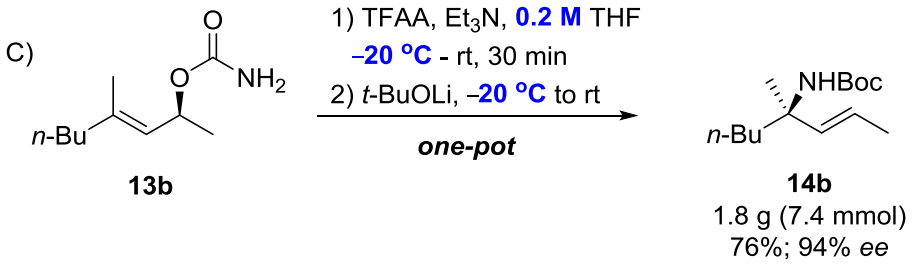
A block: A suspension of CuI (22.0 mmol, 4.2 g) in THF (60 mL) was cooled to −40 °C, and 2.5 M solution of BuLi in hexane (21.2 mmol, 8.5 mL) was added. The resulting mixture was stirred at −40 °C for 30 min and then cooled to −78 °C. A solution of ethyl but-2-ynoate (**4a**) (20.0 mmol, 2.2 g, 2.3 mL) in THF (2 mL) was added portionwise and the resulting mixture was stirred for 2 h at −78 °C. The progress of the reaction was followed by TLC. Next, the reaction was quenched by an addition of aq. NH_4Cl at −78 °C, after that the cooling bath was removed and the mixture was left to adjust to rt. The reaction mixture was filtrated through a short pad of Celite. The collected solids were rinsed with Et_2O. After that, the aqueous phase was separated and extracted with Et_2O. The combined organic layers were dried over anhydr. Na_2SO_4. After the removal of the solvent, the crude product was used in the next step without further purification. A suspension of crude α,β-unsaturated ester **5a** and MeNHOMe·HCl (2 equiv., 40 mmol, 3.9 g) in dry THF (0.3 M, 67 mL) was cooled to −5 °C under argon atmosphere, and 2M soln. of *i*-PrMgCl in THF (4 equiv., 80 mmol, 40 mL) was added dropwise. The progress of the reaction was followed by TLC. After stirring at −5 °C for 60 min, the reaction

was quenched by an addition of sat. NH_4Cl. The aqueous phase was separated and extracted with AcOEt. The combined organic phases were washed with brine, and dried over anhydr. Na_2SO_4. After the removal of the solvents, the crude pruduct was purified by a column chromatography on silica gel (10-30% AcOEt in hexanes) to provide pure *E* isomer of **15** (70%; after 2 steps, 14 mmol, 2.6 g).



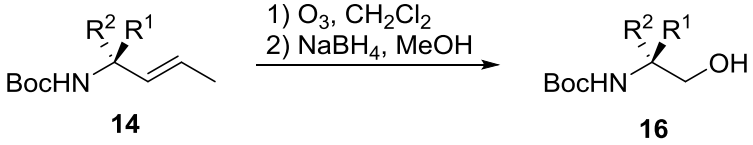
B block: A 3 M soln. of MeMgBr in THF (1.3 equiv., 18.2 mmol, 6.1 mL) was slowly added to a pre-cooled (−30 °C) solution of Weinreb amide **13b** (1 equiv., 14 mmol. 2.6 g) in THF (0.3 M, 47 mL). Next, the mixture was slowly warmed to −5 °C and stirred for 60 min. The progress of the reaction was followed by TLC. Next, sat. NH_4Cl was added and the resulting mixture was extracted with Et_2O. The combined organic layers were washed with brine, and dried over Na_2SO_4. After the removal of the solvent, the crude product was used in the next step without further purification. Next, a flask was charged with $Ni(COD)_2$ (280 µmol, 2.0 mol %, 77 mg), (*S*)-^{t}Bu-Pmrox (336 µmol, 2.4 mol%, 70.0 mg) and DABCO (1.5 equiv, 21 mmol, 2.4 g) under an Ar atmosphere. Toluene (56 mL) was added and the mixture was stirred for 10 min before pinBH (1.2 equiv, 16.8 mmol, 2.1 g, 2.5 mL) was added. Next, the reaction mixture was cooled to –25 °C and a solution of crude enone **6** in 14 mL toluene was added by syringe. The reaction mixture was left to stir at this temperature for 24 h. The progress of the reaction was followed by TLC. When the reaction was completed, a saturated solution of NH_4F in MeOH was added and cooling bath was removed. The mixture was stirred at rt for 30

min followed by an addition of H_2O and Et_2O. The aqueous phase was separated and extracted with Et_2O (2x) and dried over anhydr. Na_2SO_4. After the removal of the solvent, the crude product was used in the next step without further purification. Next, a solution of crude allyl alcohol **3a**, phenyl carbamate (1.5 equiv., 21 mmol, 2.9 g), and dibutyltin maleate (1.4 mmol, 10 mol%, 486 mg) in toluene (0.2 M, 70 mL) was stirred at 90 °C for 6 h. The progress of the reaction was followed by TLC. When the reaction was completed, the solution was cooled to 0 °C and diluted with 2 M aqueous NaOH. After stirring at 0 °C for 10 min, CH_2Cl_2 and H_2O were added. The organic layer was separated and washed with 2 M aqueous NaOH, H_2O, and brine, dried over Na_2SO_4. After the removal of the solvent, the crude residue was purified by a column chromatography on a silica gel deactivated with Et_3N (0–30% AcOEt in hexanes) to provide carbamate **13b** (70%; after 3 steps, 94% *ee*, 9.7 mmol, 1.8 g).



C block: A solution of carbamate **13b** (9.7 mmol, 1.8 g) and Et_3N (58.2 mmol, 5.9 g, 8.1 mL) in dry THF (0.2 M, 49 mL) was cooled to –20 °C, and TFAA (19.4 mmol, 4.1 g, 2.7 mL) was added. The resulting mixture was warmed slowly to room temperature and stirred for 1 h. After that, the mixture was recooled to –20 ° and the *t*-BuOLi (19.4 mmol, 4.7 g) was added portionwise to the generated allyl isocyanate. The resulting mixture was warmed slowly to room temperature and stirred for 1 h. The progress of the reaction was followed by TLC. After that, the volatiles were removed under reduced pressure. The residue was purified by a flash chromatography on a silica gel (2–20% AcOEt in hexanes) to provide carbamate **14b** (76%; after 1 step, 94% *ee*, 7.4 mmol, 1.8 g).

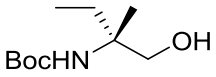
16. The synthesis of 1,2-amino alcohols 16



14 **16**

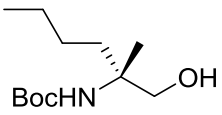
General procedure: Ozone was passed through a solution of carbamate **14** (0.5 mmol) in dry CH_2Cl_2 (20 mL) at −78 °C until the solution turned blue. Then, excess of ozone was removed by bubbling oxygen through the mixture. After that, MeOH (5 mL) and $NaBH_4$ (2.5 mmol, 95 mg) was added portiowise and the resulting mixture was slowly warmed to room temperature and stirred for 2 h. When the reaction was complete, the solvent was removed under reduced pressure and the crude product was purified by a flash column chromatography (5–30% AcOEt in hexanes).

N-Boc (*R*)-2-amino-2-methylbutan-1-ol (16a):



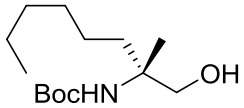
Yield 51 mg (74%) starting from 88 mg of carbamate **14b**; waxy solid; $[\alpha]_D^{23}$ +6.2 (*c* 1.07, $CHCl_3$, *ee* 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.60 (br s, 1H), 3.74 – 3.50 (m, 2H), 1.82 – 1.63 (m, 1H), 1.61 – 1.48 (m, 1H), 1.41 (s, 9H), 1.13 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 79.7, 69.4, 57.0, 29.1, 28.3, 22.0, 7.8; FTIR (film) *v*: 3412, 3314, 2973, 2927, 2881, 2855, 1685, 1502, 1458, 1366, 1251, 1169, 1082 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_{21}NO_3Na$ [$(M+Na)^+$] 226.1242; found 226.1247.

N-Boc (*R*)-2-amino-2-methylhexan-1-ol (16b):



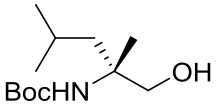
Yield 147 mg (77%) starting from 200 mg of carbamate **14b**; waxy solid; $[\alpha]_D^{23}$ +6.2 (*c* 1.07, $CHCl_3$, *ee* 94%); ^1H NMR (400 MHz, $CDCl_3$) δ 4.65 (br s, 1H), 3.73 – 3.39 (m, 2H), 1.74 – 1.43 (m, 2H), 1.40 (s, 9H), 1.34 – 1.08 (m, 9H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 79.7, 69.6, 56.8, 36.3, 28.3, 25.6, 23.1, 22.4, 14.0; FTIR (film) *v*: 3415, 3333, 2941, 2920, 2857, 1728, 1681, 1512, 1463, 1369, 1241, 1180, 1062 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{25}NO_3Na$ [$(M+Na)^+$] 254.1732; found 254.1729.

_N_-Boc (_R_)-2-amino-2-methyloctan-1-ol (16c):



Yield 238 mg (83%) starting from 300 mg of carbamate **14d**; waxy solid; $[\alpha]_D^{23}$ +12.7 (*c* 0.43, $CHCl_3$, *ee* 94%); ^1H NMR (400 MHz, $CDCl_3$) δ 4.60 (br s, 1H), 3.69 – 3.51 (m, 2H), 1.77 – 1.61 (m, 1H), 1.55 – 1.43 (m, 1H), 1.42 (s, 9H), 1.34 – 1.22 (m, 8H), 1.15 (s, 3H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 79.7, 69.6, 56.8, 36.6, 31.7, 29.6, 28.3, 23.4, 22.5, 22.4, 14.0; FTIR (film) *v*: 3410, 3334, 2956, 2928, 2858, 1720, 1683, 1502, 1466, 1366, 1252, 1172, 1067 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{29}NO_3Na$ [$(M+Na)^+$] 282.2045; found 282.2039.

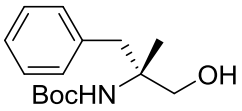
_N_-Boc (_R_)-2-amino-2,4-dimethylpentan-1-ol (16d):



Yield 123 mg (81%) starting from 160 mg of carbamate **14f**; waxy solid; $[\alpha]_D^{24}$ +2.8 (*c* 1.00, $CHCl_3$, *ee* 92%); ^1H NMR (400 MHz, $CDCl_3$) δ 4.56 (br s, 1H), 3.66 (d, *J* = 11.4 Hz, 1H), 3.55 (d, *J* = 11.4 Hz, 1H), 1.82 – 1.67 (m, 2H), 1.42 (s, 9H), 1.25 (s, 1H), 1.18 (s, 3H), 0.96 (t, *J* = 6.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 79.6, 70.3, 57.1, 44.3, 28.3, 25.0, 24.4, 23.7, 23.1; FTIR (film) *v*: 3406, 3347, 2956, 2929, 2871, 1688,

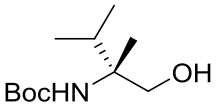
1502, 1366, 1250, 1170, 1066, 1045 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{25}NO_3Na$ [$(M+Na)^+$] 254.1732; found 254.1728.

_N_-Boc (_R_)-2-amino-2-methyl-3-phenylpropan-1-ol (16e):



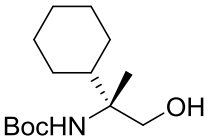
Yield 243 mg (84%) starting from 300 mg of carbamate **14g**; waxy solid; $[\alpha]_D^{24}$ +84.9 (*c* 1.08, $CHCl_3$, *ee* 98%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.11 (m, 5H), 4.50 (br s, 1H), 3.68 (s, 2H), 3.17 (d, *J* = 13.5 Hz, 1H), 2.81 (d, *J* = 13.5 Hz, 1H), 1.46 (s, 9H), 1.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 137.1, 130.6, 128.1, 126.5, 79.8, 69.5, 57.2, 41.0, 28.4, 22.9; FTIR (film) *v*: 3275, 3071, 2979, 2929, 1678, 1557, 1288, 1174, 1069, 699 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{23}NO_3Na$ [$(M+Na)^+$] 288.1398; found 288.1380.

_N_-Boc (_R_)-2-amino-2,3-dimethylbutan-1-ol (16f):



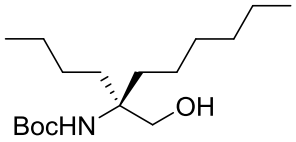
Yield 120 mg (70%) starting from 180 mg of carbamate **14h**; waxy solid; $[\alpha]_D^{24}$ +1.1 (*c* 0.94, $CHCl_3$, *ee* 88%); ^1H NMR (400 MHz, $CDCl_3$) δ 4.61 (br s, 1H), 3.72 (d, *J* = 11.8 Hz, 1H), 3.62 (d, *J* = 11.8 Hz, 1H), 2.31 (hept, *J* = 6.9 Hz, 1H), 1.42 (s, 9H), 0.99 (s, 3H), 0.95 – 0.85 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 79.8, 68.7, 59.9, 31.0, 28.3, 18.4, 17.2, 16.7; FTIR (film) *v*: 3286, 2980, 2929, 1679, 1556, 1450, 1366, 1288, 1253, 1173, 1088, 1064 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{23}NO_3Na$ [$(M+Na)^+$] 240.1576; found 240.1567.

***tert*-Butyl (_R_)-(2-cyclohexyl-1-hydroxypropan-2-yl)carbamate (16g):**



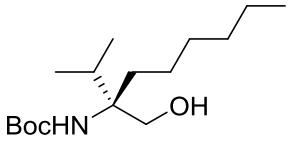
Yield 125 mg (65%) starting from 200 mg of carbamate **14i**; waxy solid; $[\alpha]_D^{25}$ +10.5 (*c* 2.81, $CHCl_3$, *ee* 88%); ^1H NMR (400 MHz, $CDCl_3$) δ 4.59 (br s, 1H), 3.72 (d, *J* = 11.8 Hz, 1H), 3.61 (d, *J* = 11.8 Hz, 1H), 2.00 – 1.85 (m, 1H), 1.84 – 1.60 (m, 4H), 1.42 (s, 9H), 1.34 – 1.18 (m, 3H), 1.17 – 0.81 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 79.8, 68.6, 59.8, 41.5, 28.3, 27.5, 26.8, 26.7, 26.6, 26.6, 19.5; FTIR (film) *v*: 3275, 2924, 2852, 1679, 1561, 1446, 1289, 1177, 1066, 737, 703 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{27}NO_3Na$ $[(M+Na)^+]$ 280.1889; found 280.1883.

_N_-Boc (_S_)-2-amino-2-butyloctan-1-ol (16h)



Yield 96 mg (71%) starting from 140 mg of carbamate **14j**; waxy solid; $[\alpha]_D^{25}$ –1.9 (*c* 0.95, $CHCl_3$, *ee* 82%); ^1H NMR (400 MHz, $CDCl_3$) δ 4.51 (br s, 1H), 3.74 – 3.54 (m, 2H), 1.62 – 1.43 (m, 4H), 1.43 (s, 9H), 1.36 – 1.12 (m, 12H), 0.95 – 0.79 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 79.6, 67.9, 59.3, 34.2, 34.0, 31.7, 29.7, 28.3, 25.3, 23.1, 23.0, 22.5, 14.0, 14.0; FTIR (film) *v*: 3410, 3332, 2956, 2930, 2862, 1685, 1501, 1366, 1251, 1172, 1070, 1054 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{35}NO_3Na$ $[(M+Na)^+]$ 324.2515; found 324.2513.

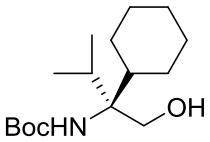
_N_-Boc (_R_)-2-amino-2-isopropyloctan-1-ol (16i):



Yield 74 mg (70%) starting from 110 mg of carbamate **14k**; waxy solid; $[\alpha]_D^{25}$ –6.9 (*c* 0.99, $CHCl_3$, *ee* 95%); ^1H NMR (400 MHz, $CDCl_3$) δ 4.58 (br s, 1H), 3.75 (d, *J* = 12.1 Hz, 1H), 3.67 (d, *J* = 12.1 Hz, 1H), 2.22 – 2.07 (m, 1H), 1.67 – 1.36 (m, 11H), 1.34 – 1.10 (m, 8H), 0.98 – 0.74 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 79.8, 66.9, 61.5, 32.2, 31.7, 31.4, 30.0, 28.3, 22.7, 22.6, 17.0, 16.6, 14.0; FTIR (film) *v*: 3265, 2927,

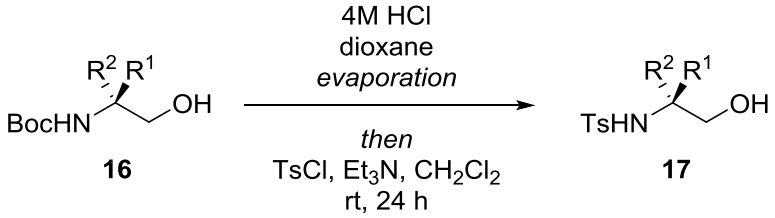
2857, 1679, 1555, 1463, 1366, 1287, 1253, 1175, 1069, 721 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{33}NO_3Na$ [$(M+Na)^+$] 310.2358; found 310.2350.

_N_-Ts (_S_)-2-amino-2-cyclohexyl-3-methylbutan-1-ol (16j):



Yield 69 mg (85%) starting from 84 mg of carbamate **14l**; waxy solid; $[\alpha]_D^{24}$ –4.6 (*c* 1.30, $CHCl_3$, *ee* 79%); ^1H NMR (400 MHz, $CDCl_3$) δ 4.49 (br s, 1H), 3.96 – 3.73 (m, 2H), 2.11 – 1.92 (m, 1H), 1.89 – 1.53 (m, 6H), 1.42 (s, 9H), 1.32 – 1.07 (m, 5H), 1.03 – 0.83 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 79.5, 65.2, 63.4, 44.4, 32.7, 28.4, 27.9, 27.7, 27.4, 27.1, 26.6, 18.1, 17.7; FTIR (film) *v*: 3277, 2925, 2853, 1681, 1554, 1284, 1176, 1069, 1001, 718, 698 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{31}NO_3Na$ [$(M+Na)^+$] 308.2202; found 308.2196.

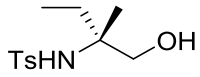
17. Synthesis of 1,2-amino alcohols 17



Method A, general procedure: *N*-Boc protected amino alcohol **16** (0.5 mmol) was dissolved in 4 M HCl/dioxane (1 mL) under an argon atmosphere. The progress of the reaction was followed by TLC. After 1 h, solvent was evaporated and crude residue was dissolved in CH_2Cl_2 (0.2 M). Next, Et_3N (2 mmol, 202 mg, 279 µL) was added and reaction mixture was stirred for 10 min. After that, TsCl (0.5 mmol, 95 mg) was added portionwise and reaction was left to stand overnight. Next, volatiles were removed under reduced pressure. The residue was purified by a flash chromatography on a silica gel (5–30% AcOEt in hexanes).

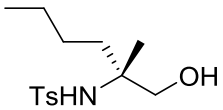
Method B, general procedure: *N*-Boc protected amino alcohol **16** (0.5 mmol) was dissolved in 4 M HCl/dioxane (1 mL) under an argon atmosphere. The progress of the reaction was followed by TLC. After 1 h, solvent was evaporated and crude residue was dissolved in MeCN (0.15 M). Next, TMEDA (3.5 mmol, 407 mg, 528 µL) was added and reaction mixture was stirred for 10 min. After that, TsCl (0.5 mmol, 95 mg) was added portionwise and reaction was left to stir for 3 days. Next, volatiles were removed under reduced pressure. The residue was purified by a flash chromatography on a silica gel (5–30% AcOEt in hexanes).

***N*-Ts (*R*)-2-amino-2-methylbutan-1-ol (17a):**



Method A. Yield 41 mg (75%) starting from 43 mg of *N*-Boc amino alcohol **16a**; colourless oil; $[\alpha]_D^{25}$ –0.7 (*c* 1.22, $CHCl_3$, *ee* 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.69 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.77 (br s, 1H), 3.59 – 3.41 (m, 2H), 2.42 (s, 3H), 1.57 – 1.45 (m, 2H), 1.04 (s, 3H), 0.79 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 139.8, 129.6, 127.0, 68.0, 61.1, 30.3, 21.5, 20.6, 7.6; FTIR (film) *v*: 3490, 3287, 2951, 2939, 1476, 1321, 1321, 1154, 1101, 1051, 664 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{19}NO_3SNa$ [$(M+Na)^+$] 280.0983; found 280.0989.

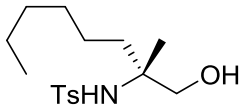
***N*-Ts (*R*)-2-amino-2-methylhexan-1-ol (17b)**



Method A. Yield 88 mg (90%) starting from 80 mg of *N*-Boc amino alcohol **16b**; colourless oil; $[\alpha]_D^{25}$ –0.1 (*c* 1.30, $CHCl_3$, *ee* 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.06 (br s, 1H), 3.68 – 3.33 (m, 2H), 2.41 (s, 3H), 1.50 – 0.99 (m, 9H), 0.78 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 139.9, 129.6, 127.0, 68.4, 60.9, 37.3, 25.4, 22.9, 21.5, 21.3, 13.9; FTIR (film) *v*: 3496,

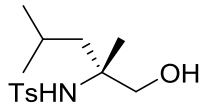
3279, 2955, 2931, 1466, 1322, 1304, 1151, 1094, 1048, 815, 663, 551 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{23}NO_3SNa$ [$(M+Na)^+$] 308.1296; found 308.1293.

_N_-Ts (_R_)-2-amino-2-methyloctan-1-ol (17c):



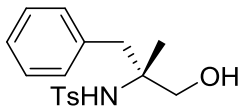
Method A. Yield 145 mg (80%) starting from 150 mg of *N*-Boc amino alcohol **16c**; colourless oil; $[\alpha]_D^{25}$ –5.2 (*c* 2.21, $CHCl_3$, *ee* 94%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 2H), 7.33 – 7.26 (m, 2H), 4.89 (br s, 1H), 3.54 (d, *J* = 11.6 Hz, 1H), 3.46 (d, *J* = 11.6 Hz, 1H), 2.41 (s, 3H), 1.47 – 1.05 (m, 10H), 1.05 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 139.8, 129.6, 127.1, 68.4, 61.0, 37.5, 31.7, 29.5, 23.2, 22.5, 21.5, 21.4, 14.0; FTIR (film) *v*: 3498, 3278, 2928, 2858, 1322, 1304, 1153, 1094, 1055, 815, 663, 551 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{27}NO_3SNa$ [$(M+Na)^+$] 336.1609; found 336.1605.

_N_-Ts (_R_)-2-amino-2,4-dimethylpentan-1-ol (17d):



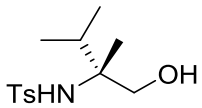
Method A. Yield 89 mg (72%) starting from 100 mg of *N*-Boc amino alcohol **16d**; colourless oil; $[\alpha]_D^{22}$ +1.2 (*c* 4.40, $CHCl_3$, *ee* 92%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.04 (br s, 1H), 3.47 (s, 2H), 2.65 – 2.44 (m, 1H), 2.40 (s, 3H), 1.79 – 1.51 (m, 1H), 1.49 – 1.21 (m, 2H), 1.08 (s, 3H), 0.97 – 0.71 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 140.0, 129.6, 127.0, 68.7, 61.4, 46.7, 24.8, 24.7, 23.6, 21.5, 21.1; FTIR (film) *v*: 3490, 3273, 2945, 2934, 1469, 1320, 1314, 1150, 1089, 1043, 811, 666, 554 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{23}NO_3SNa$ [$(M+Na)^+$] 308.1296; found 308.1288.

_N_-Ts (_R_)-2-amino-2-methyl-3-phenylpropan-1-ol (17e):



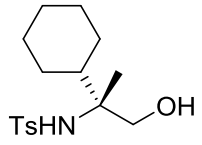
Method A. Yield 127 mg (81%) starting from 130 mg of *N*-Boc amino alcohol **16e**; waxy solid; $[\alpha]_D^{25}$ +1.7 (*c* 0.81, $CHCl_3$, *ee* 98%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 2H), 7.34 – 7.12 (m, 7H), 4.79 (br s, 1H), 3.64 – 3.37 (m, 2H), 2.85 (d, *J* = 3.9 Hz, 2H), 2.41 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 139.9, 136.0, 130.7, 129.6, 128.3, 126.9, 126.8, 67.3, 60.8, 43.9, 21.5, 20.7; FTIR (film) *v*: 3505, 3276, 2925, 1454, 1304, 1153, 1093, 1052, 988, 664 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{21}NO_3SNa$ $[(M+Na)^+]$ 342.1140; found 342.1133.

_N_-Ts (_R_)-2-amino-2,3-dimethylbutan-1-ol (17f):



Method A. Yield 76 mg (60%) starting from 102 mg of *N*-Boc aminoalcohol **16f**; colourless oil; $[\alpha]_D^{25}$ +1.4 (*c* 1.00, $CHCl_3$, *ee* 88%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 4.90 (br s, 1H), 3.58 (s, 2H), 2.41 (s, 3H), 1.99 – 1.80 (m, 1H), 0.94 (s, 3H), 0.81 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 139.8, 129.6, 127.0, 66.9, 63.9, 33.3, 21.5, 17.0, 16.7, 16.0; FTIR (film) *v*: 3479, 3271, 2929, 2849, 1327, 1311, 1155, 1097, 1051, 816, 664 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{21}NO_3SNa$ $[(M+Na)^+]$ 294.1140; found 294.1145.

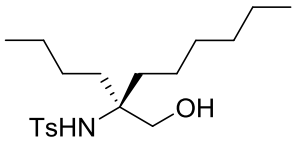
_N_-Ts (_R_)-2-amino-2-cyclohexylpropan-1-ol (17g):



Method A. Yield 84 mg (69%) starting from 106 mg of *N*-Boc aminoalcohol **16g**; waxy solid; $[\alpha]_D^{24}$ –2.6 (*c* 1.86, $CHCl_3$, *ee* 88%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.85 (br s, 1H), 3.71 – 3.44 (m, 2H), 2.41 (s, 3H), 1.81 – 1.41 (m, 5H), 1.35 – 0.70 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 139.9,

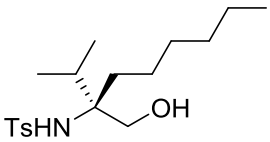
129.6, 127.1, 66.7, 63.8, 43.5, 27.2, 26.8, 26.5, 26.4, 26.3, 21.5, 17.5; FTIR (film) *v*: 3501, 3280, 2926, 2854, 1449, 1305, 1153, 1093, 663, 553 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{25}NO_3SNa$ [$(M+Na)^+$] 334.1453; found 334.1444.

_N_-Ts (S)-2-amino-2-butyloctan-1-ol (17h)



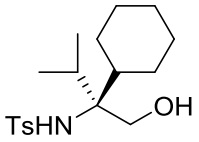
Method A. Yield 73 mg (78%) starting from 82 mg of *N*-Boc aminoalcohol **16h**; waxy solid; $[\alpha]_D^{24}$ +3.2 (*c* 1.40, $CHCl_3$, *ee* 82%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.77 (s, 1H), 3.56 (s, 2H), 2.63 (br s, 1H), 2.41 (s, 3H), 1.47 – 0.92 (m, 16H), 0.83 (t, *J* = 7.2 Hz, 3H), 0.77 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 139.7, 129.6, 127.1, 65.9, 64.2, 33.7, 33.5, 31.6, 29.4, 24.9, 22.8, 22.7, 22.6, 21.4, 14.0, 13.8; FTIR (film) *v*: 3357, 3310, 2922, 2852, 1659, 1632, 1467, 1154 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{33}NO_3SNa$ [$(M+Na)^+$] 378.2079; found 378.2078.

_N_-Ts (_R_)-2-amino-2-isopropyloctan-1-ol (17i):



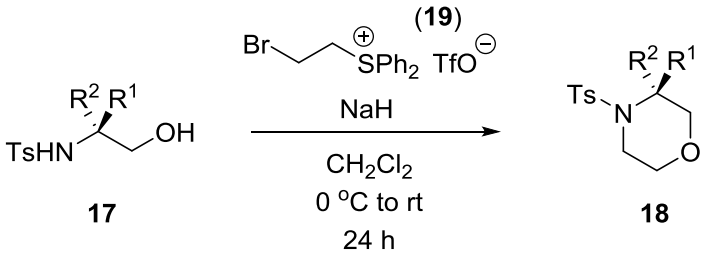
Method B. Yield 90 mg (76%) starting from 100 mg of *N*-Boc aminoalcohol **16i**; waxy solid; $[\alpha]_D^{25}$ +10.0 (*c* 0.66, $CHCl_3$, *ee* 95%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.79 (br s, 1H), 3.86 – 3.52 (m, 2H), 3.03 (br s, 1H), 2.41 (s, 3H), 1.98 – 1.77 (m, 1H), 1.51 – 0.62 (m, 19H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 139.8, 129.5, 127.0, 66.6, 65.8, 32.9, 32.6, 31.6, 29.7, 22.8, 22.6, 21.5, 17.1, 16.6, 14.0; FTIR (film) *v*: 3359, 3312, 2932, 2858, 1665, 1636, 1462, 1151 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{31}NO_3SNa$ [$(M+Na)^+$] 364.1922; found 364.1929.

***N*-Ts (*S*)-2-amino-2-cyclohexyl-3-methylbutan-1-ol (17j):**



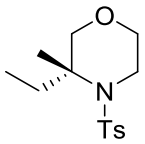
Method B. Yield 56 mg (47%) starting from 100 mg of *N*-Boc aminoalcohol **16j**; waxy solid; $[\alpha]_D^{26}$ -3.0 (*c* 0.79, $CHCl_3$, *ee* 79%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 4.42 (s, 1H), 3.82 (d, *J* = 12.6 Hz, 1H), 3.74 (d, *J* = 12.6 Hz, 1H), 2.82 (br s, 1H), 2.35 (s, 3H), 1.89 (hept, *J* = 6.9 Hz, 1H), 1.78 – 1.40 (m, 6H), 1.28 – 0.93 (m, 5H), 0.88 (d, *J* = 6.9 Hz, 3H), 0.73 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 139.9, 129.5, 126.9, 69.6, 63.6, 44.6, 33.2, 28.3, 27.9, 27.2, 26.9, 26.4, 21.5, 18.4, 17.9; FTIR (film) *v*: 3500, 3275, 2927, 2861, 1451, 1315, 1155, 1092, 549 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{29}NO_3SNa$ [$(M+Na)^+$] 362.1766; found 362.1761.

18. The synthesis of morpholines 18



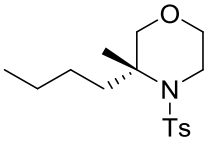
General procedure:[5, 6] NaH (3.5 equiv., 0.56 mmol, 60% in mineral oil, 22 mg) and then bromoethylsulfonium triflate **19** (1.2 equiv, 0.19 mmol, 85 mg) were slowly added to a stirred solution of **17** (1 equiv, 0.16 mmol) in CH_2Cl_2 (0.02 M) at 0 °C. The reaction was stirred at 0 °C for 2 h, then warmed to room temperature and stirred overnight. The mixture was quenched by addition of water and then extracted with CH_2Cl_2. The combined organic phases were dried over anhydr. Na_2SO_4. After the removal of the solvents, the residue was purified by a column chromatography on silica gel (5-20% AcOEt in hexanes).

***N*-Ts (*R*)-3-ethyl-3-methyl-morpholine (18a):**



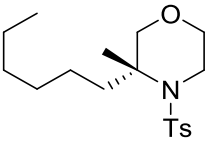
Yield 29 mg (72%) starting from 36 mg of **17a**; yellow oil; $[\alpha]_D^{24}$ –10.1 (*c* 0.70, $CHCl_3$, *ee* 96%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.86 – 3.74 (m, 1H), 3.67 – 3.47 (m, 3H), 3.46 – 3.35 (m, 1H), 3.18 (d, *J* = 11.7 Hz, 1H), 2.42 (s, 3H), 1.99 – 1.71 (m, 2H), 1.25 (s, 3H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 139.8, 129.5, 127.0, 74.3, 67.2, 61.0, 42.9, 26.6, 21.5, 20.5, 8.5; FTIR (film) *v*: 2962, 2923, 2853, 1459, 1330, 1159, 1123, 955, 814, 680, 551 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{21}NO_3SNa$ $[(M+Na)^+]$ 306.1140; found 306.1129.

***N*-Ts (*R*)-3-butyl-3-methyl-morpholine (18b):**



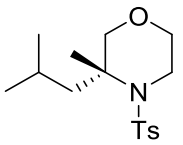
Yield 31 mg (71%) starting from 41 mg of **17b**; yellowish oil; $[\alpha]_D^{24}$ –30.1 (*c* 0.73, $CHCl_3$, *ee* 94%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 3.91 – 3.70 (m, 1H), 3.67 – 3.35 (m, 4H), 3.16 (d, *J* = 11.6 Hz, 1H), 2.41 (s, 3H), 1.92 – 1.66 (m, 2H), 1.46 – 1.11 (m, 7H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 139.8, 129.5, 127.0, 74.8, 67.3, 60.7, 43.0, 33.8, 26.2, 23.1, 21.4, 21.1, 13.9; FTIR (film) *v*: 2956, 2927, 2859, 1459, 1333, 1160, 1124, 957, 814, 684, 549 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{25}NO_3SNa$ $[(M+Na)^+]$ 334.1453; found 334.1447.

***N*-Ts (*R*)-3-hexyl-3-methyl-morpholine (18c):**



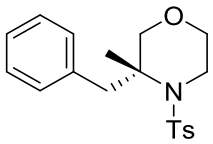
Yield 40 mg (74%) starting from 50 mg of **17c**; yellowish oil; $[\alpha]_D^{24}$ –31.9 (*c* 1.20, $CHCl_3$, *ee* 94%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.86 – 3.73 (m, 1H), 3.64 – 3.34 (m, 4H), 3.16 (d, *J* = 11.6 Hz, 1H), 2.41 (s, 3H), 1.93 – 1.65 (m, 2H), 1.34 – 1.12 (m, 11H), 0.6 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 139.8, 129.5, 127.0, 74.7, 67.3, 60.7, 43.0, 34.0, 31.7, 29.7, 24.0, 22.6, 21.4, 21.1, 14.0; FTIR (film) *v*: 2954, 2926, 2856, 1460, 1333, 1161, 1124, 956, 684, 549 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{29}NO_3SNa$ $[(M+Na)^+]$ 362.1766; found 362.1760.

_N_-Ts (_R_)-3-isobutyl-3-methyl-4-tosylmorpholine (18d):



Yield 33 mg (70%) starting from 43 mg of **17d**; waxy solid; $[\alpha]_D^{24}$ –29.3 (*c* 0.84, $CHCl_3$, *ee* 92%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 3.89 – 3.74 (m, 1H), 3.65 – 3.45 (m, 3H), 3.45 – 3.30 (m, 1H), 3.14 (d, *J* = 11.7 Hz, 1H), 2.41 (s, 3H), 1.78 – 1.71 (m, 2H), 1.69 – 1.59 (m, 1H), 1.33 (s, 3H), 0.92 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 140.0, 129.5, 127.0, 75.1, 67.2, 61.1, 43.0, 42.2, 25.0, 24.8, 24.0, 21.8, 21.4; FTIR (film) *v*: 2956, 2927, 2869, 1329, 1162, 1125, 957, 686, 549 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{25}NO_3SNa$ $[(M+Na)^+]$ 334.1453; found 334.1444.

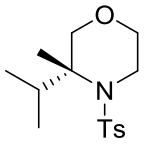
_N_-Ts (_R_)-3-benzyl-3-methyl-morpholine (18e):



Yield 55 mg (99%) starting from 50 mg of **17e**; waxy solid; $[\alpha]_D^{24}$ +26.5 (*c* 1.27, $CHCl_3$, *ee* 98%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.06 (m, 7H), 4.00 (d, *J* = 8.8 Hz, 1H), 3.85 – 3.51 (m, 3H), 3.50 – 3.30 (m, 2H), 3.06 – 2.78 (m,

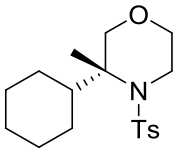
2H), 2.42 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 139.8, 136.9, 130.8, 129.6, 128.1, 127.0, 126.5, 73.2, 67.5, 60.7, 43.0, 38.7, 21.5, 21.2; FTIR (film) *v*: 2925, 2854, 1457, 1326, 1161, 1122, 956, 708, 686, 555 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{23}NO_3SNa$ [(M+Na)$^+$] 368.1296; found 368.1283.

_N_-Ts (_R_)-3-isopropyl-3-methyl-morpholine (18f)



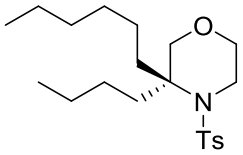
Yield 40 mg (75%) starting from 48 mg of **17e**; yellow oil; $[\alpha]_D^{24}$ –37.1 (*c* 1.22, $CHCl_3$, *ee* 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.90 – 3.58 (m, 3H), 3.55 – 3.35 (m, 2H), 3.07 (d, *J* = 11.8 Hz, 1H), 2.70 (hept, *J* = 7.2 Hz, 1H), 2.41 (s, 3H), 1.21 (s, 3H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 140.9, 129.5, 126.7, 73.1, 66.8, 64.3, 42.8, 28.4, 21.4, 17.6, 17.1, 16.2; FTIR (film) *v*: 2966, 2926, 1331, 1157, 1124, 957, 677, 553 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{23}NO_3SNa$ [(M+Na)$^+$] 320.1296; found 320.1289.

_N_-Ts (_R_)-3-cyclohexyl-3-methyl-morpholine (18g):



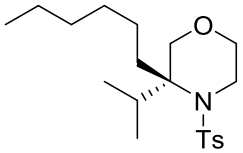
Yield 39 mg (72%) starting from 50 mg of **17g**; waxy solid; $[\alpha]_D^{25}$ –59.9 (*c* 1.24, $CHCl_3$, *ee* 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 3.89 – 3.57 (m, 2H), 3.52 – 3.33 (m, 2H), 3.02 (d, *J* = 11.8 Hz, 1H), 2.41 (s, 3H), 2.33 – 2.17 (m, 1H), 1.95 – 1.81 (m, 2H), 1.81 – 1.55 (m, 3H), 1.40 – 0.98 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 141.1, 129.5, 126.6, 72.8, 66.8, 64.3, 42.9, 38.5, 28.0, 27.0, 26.9, 26.8, 26.4, 21.4, 17.5; FTIR (film) *v*: 2927, 2852, 1452, 1334, 1293, 1157, 1120, 958, 689, 545 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{21}NO_3SNa$ [(M+Na)$^+$] 360.1609; found 360.1599.

***N*-Ts (*S*)-3-butyl-3-hexyl-morpholine (18h)**



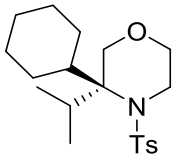
Yield 29 mg (68%) starting from 40 mg of **17h**; colourless oil; $[\alpha]_D^{25}$ –0.7 (*c* 0.60, $CHCl_3$, *ee* 82%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 3.73 – 3.55 (m, 2H), 3.48 (s, 2H), 3.41 – 3.26 (m, 2H), 2.41 (s, 3H), 2.05 – 1.83 (m, 2H), 1.83 – 1.63 (m, 2H), 1.49 – 1.05 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 139.0, 129.4, 127.4, 72.7, 66.8, 64.5, 43.4, 33.9, 33.6, 31.7, 29.9, 26.2, 24.0, 23.3, 22.6, 21.4, 14.1, 14.0; FTIR (film) *v*: 2955, 2928, 2860, 1461, 1330, 1160, 1127, 1095, 684 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{35}NO_3SNa$ $[(M+Na)^+]$ 404.2235; found 404.2225.

***N*-Ts (*R*)-3-hexyl-3-isopropyl-morpholine (18i)**



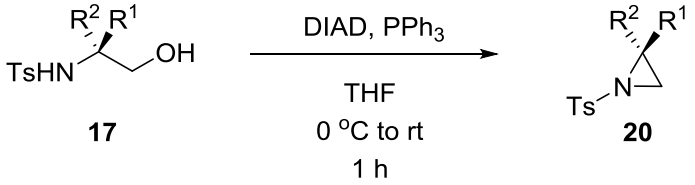
Yield 46 mg (72%) starting from 60 mg of **17i**; colourless oil; $[\alpha]_D^{25}$ –9.0 (*c* 0.84, $CHCl_3$, *ee* 95%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.80 – 3.65 (m, 2H), 3.65 – 3.55 (m, 1H), 3.51 (d, *J* = 12.1 Hz, 1H), 3.43 – 3.25 (m, 2H), 2.88 – 2.71 (m, 1H), 2.41 (s, 3H), 2.19 – 2.02 (m, 1H), 1.66 – 1.51 (m, 1H), 1.50 – 1.09 (m, 8H), 1.07 – 0.93 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 138.7, 129.4, 127.3, 70.4, 67.9, 66.2, 43.7, 33.6, 32.3, 31.8, 30.1, 24.4, 22.7, 21.4, 19.1, 17.9, 14.1; FTIR (film) *v*: 2956, 2926, 1464, 1329, 1160, 1095, 950, 677, 552 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{33}NO_3SNa$ $[(M+Na)^+]$ 390.2079; found 390.2073.

***N*-Ts (*S*)-3-cyclohexyl-3-isopropyl-morpholine (18j):**



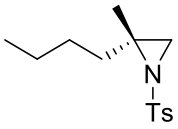
Yield 38 mg (77%) starting from 46 mg of **17j**; waxy solid; $[\alpha]_D^{25}$ –7.3 (*c* 0.95, $CHCl_3$, *ee* 79%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.81 (d, *J* = 12.4 Hz, 1H), 3.71 (d, *J* = 12.4 Hz, 1H), 3.67 – 3.49 (m, 2H), 3.39 – 3.11 (m, 2H), 2.97 – 2.75 (m, 1H), 2.53 – 2.27 (m, 4H), 2.22 – 1.96 (m, 2H), 1.88 – 1.62 (m, 3H), 1.44 – 0.98 (m, 11H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 138.3, 129.5, 127.6, 71.4, 68.6, 65.7, 43.7, 43.6, 31.9, 30.0, 29.2, 27.4, 27.3, 26.7, 21.4, 20.2, 18.9; FTIR (film) *v*: 2925, 2858, 1442, 1337, 1290, 1150, 1121, 942, 667 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{31}NO_3SNa$ [(M+Na)$^+$] 388.1922; found 388.1928.

19. The synthesis of aziridines 20



General procedure: DIAD (1.1 equiv, 0.19 mmol, 38 mg, 37 µL) was added dropwise to a stirred solution of 1,2-amino alcohol **17** (1 equiv, 0.175 mmol) and Ph_3P (0.19 mmol, 50 mg) in THF (0.1 M) at 0 °C. After that, the reaction was slowly warmed to room temperature and stirred for 1 h. Next, volatiles were removed under reduced pressure. The residue was purified by a flash chromatography on a silica gel (2–20% AcOEt in hexanes).

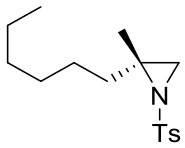
N-Ts (*R*)-2-butyl-2-methyl-aziridine (20a):



Yield 41 mg (88%) starting from 50 mg of **17b**; colourless oil; $[\alpha]_D^{26}$ –12.5 (*c* 0.91, $CHCl_3$, *ee* 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.9

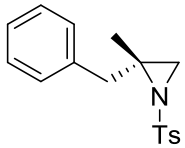
Hz, 2H), 2.53 (s, 1H), 2.41 (s, 3H), 2.27 (s, 1H), 1.73 – 1.51 (m, 5H), 1.47 – 1.19 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 138.2, 129.4, 127.3, 51.1, 41.4, 37.5, 27.9, 22.5, 21.5, 18.6, 13.9; FTIR (film) *v*: 2955, 2933, 2862, 1451, 1331, 1168, 949, 711, 569 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{21}NO_2SNa$ [$(M+Na)^+$] 290.1191; found 290.1195.

_N_-Ts (_R_)-2-hexyl-2-methyl-1-tosylaziridine (20b):



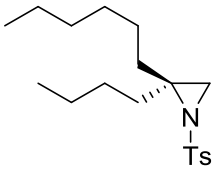
Yield 42 mg (88%) starting from 50 mg of **17c**; colourless oil; $[\alpha]_D^{27}$ –16.8 (*c* 0.97, $CHCl_3$, *ee* 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.53 (s, 1H), 2.42 (s, 3H), 2.27 (s, 1H), 1.81 – 1.10 (m, 13H), 0.87 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 138.2, 129.4, 127.3, 51.1, 41.4, 37.8, 31.6, 29.0, 25.7, 22.5, 21.5, 18.6, 14.0; FTIR (film) *v*: 2954, 2930, 2858, 1457, 1321, 1160, 947, 831, 710, 574 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{25}NO_2SNa$ [$(M+Na)^+$] 318.1504; found 318.1496.

_N_-Ts (_R_)-2-benzyl-2-methyl-aziridine (20c):



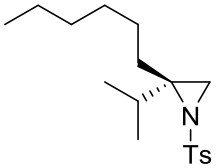
Yield 47 mg (99%) starting from 50 mg of **17e**; yellowish oil; $[\alpha]_D^{29}$ –41.5 (*c* 0.95, $CHCl_3$, *ee* 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.73 (m, 2H), 7.38 – 7.11 (m, 7H), 2.94 (s, 2H), 2.60 (s, 1H), 2.43 (s, 3H), 2.41 (s, 1H), 1.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 137.9, 136.9, 129.5, 129.5, 128.4, 127.4, 126.8, 50.8, 44.0, 40.3, 21.6, 18.4; FTIR (film) *v*: 3062, 3029, 2980, 2928, 1732, 1453, 1319, 1158, 821, 708, 570 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{19}NO_2SNa$ [$(M+Na)^+$] 324.1034; found 324.1027.

***N*-Ts (*S*)-2-butyl-2-hexyl-aziridine (20d)**



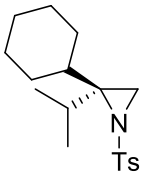
Yield 45 mg (89%) starting from 53 mg of **17h**; yellowish oil; $[\alpha]_D^{24}$ +0.1 (*c* 1.00, $CHCl_3$, *ee* 82%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 2.39 (s, 2H), 1.91 – 1.78 (m, 2H), 1.78 – 1.64 (m, 2H), 1.53 – 1.15 (m, 11H), 1.00 – 0.73 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 138.4, 129.4, 127.3, 54.9, 41.0, 32.8, 32.5, 31.7, 29.1, 28.1, 25.9, 22.6, 21.5, 14.0, 14.0; FTIR (film) *v*: 2956, 2943, 2859, 1450, 1311, 1164, 942, 710, 544 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{31}NO_2SNa$ [$(M+Na)^+$] 360.1973; found 360.1977.

***N*-Ts (*R*)-2-hexyl-2-isopropyl-aziridine (20e)**



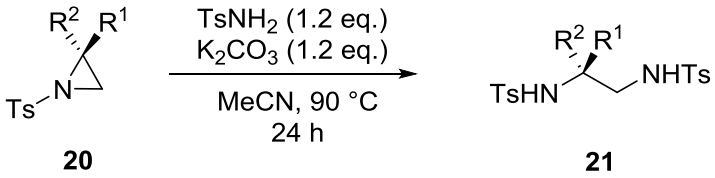
Yield 35 mg (93%) starting from 40 mg of **17i**; colourless oil; $[\alpha]_D^{25}$ –7.3 (*c* 0.94, $CHCl_3$, *ee* 95%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 1H), 2.36 (s, 3H), 2.26 (s, 1H), 2.07 – 1.82 (m, 2H), 1.45 – 1.11 (m, 5H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.87 – 0.70 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 141.4, 132.2, 130.1, 61.5, 41.7, 34.6, 33.6, 32.8, 32.2, 29.6, 25.4, 24.4, 22.1, 20.7, 16.9; FTIR (film) *v*: 2957, 2940, 2865, 1452, 1310, 1174, 949, 699, 544 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{29}NO_2SNa$ [$(M+Na)^+$] 346.1817; found 346.1820.

***N*-Ts (*S*)-2-cyclohexyl-2-isopropyl-aziridine (20f):**



Yield 38 mg (98%) starting from 42 mg of **17j**; waxy solid; *ee* 79%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.43 (s, 3H), 2.39 (s, 2H), 2.30 (hept, *J* = 7.0 Hz, 1H), 1.96 – 1.83 (m, 1H), 1.83 – 1.68 (m, 4H), 1.65 (d, *J* = 13.2 Hz, 1H), 1.47 – 1.16 (m, 5H), 1.15 – 0.92 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 138.7, 129.3, 127.3, 63.7, 39.4, 38.9, 31.6, 30.5, 30.4, 26.6, 26.4, 26.1, 21.5, 21.2, 19.6; FTIR (film) *v*: 2951, 2943, 2867, 1443, 1315, 1161, 974, 713, 546 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{27}NO_2SNa$ [$(M+Na)^+$] 344.1660; found 344.1663.

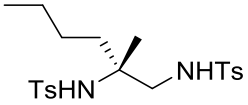
20. The synthesis of 1,2 diamines 21



20 **21**

General procedure:[7] A suspension of aziridine **20** (1 equiv, 0.2 mmol), p-toluenesulfonamide (1.2 equiv, 0.24 mmol, 41 mg) and potassium carbonate (1.2 equiv, 0.24 mmol, 33 mg) in acetonitrile (0.1 M, 2 mL) was heated at 90 °C for 24-72 h. The progress of the reaction was followed by TLC. After the complete consumption of a stating material, the reaction mixture was cooled to rt. After that, the volatiles were removed under reduced pressure. The residue was purified by a flash chromatography on a silica gel (5–40% AcOEt in hexanes).

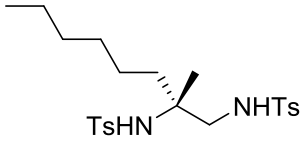
N,*N*'-diTs (*R*)-2-methylhexane-1,2-diamine (21a)



The reaction was kept at 90 °C for 24 h. Yield 60 mg (84%) starting from 43 mg of aziridine **20a**; colourless oil; $[\alpha]_D^{28}$ –3.9 (*c* 0.58, $CHCl_3$, *ee* 94%); ^{1}H NMR (500 MHz,

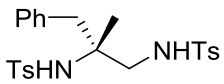
$CDCl_3$) δ 7.79 – 7.64 (m, 4H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 2H), 5.22 (t, *J* = 7.1 Hz, 1H), 4.74 (s, 1H), 3.08 – 2.89 (m, 2H), 2.43 (s, 3H), 2.42 (s, 3H), 1.50 – 0.94 (m, 9H), 0.76 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 143.3, 139.7, 137.1, 129.7, 129.6, 126.9, 126.9, 59.5, 50.8, 37.9, 25.1, 22.6, 22.5, 21.4, 21.4, 13.7; FTIR (film) *v*: 3282, 2955, 2932, 2871, 1454, 1426, 1326, 1159, 1092, 815, 664, 553 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{30}N_2O_4S_2Na$ [$(M+Na)^+$] 461.1545; found 461.1537.

_N_,_N_'-diTs (_R_)-2-methyloctane-1,2-diamine (21b):



The reaction was kept at 90 °C for 24 h. Yield 43 mg (75%) starting from 36 mg of aziridine **20b**; colourless oil; $[\alpha]_D^{28}$ –5.6 (*c* 0.48, $CHCl_3$, *ee* 94%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.50 (m, 4H), 7.34 – 7.00 (m, 4H), 5.36 (t, *J* = 7.0 Hz, 1H), 5.00 (s, 1H), 2.96 (dd, *J* = 13.2, 7.0 Hz, 1H), 2.88 (dd, *J* = 13.2, 7.0 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H), 1.47 – 0.80 (m, 13H), 0.75 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 143.3, 139.6, 137.2, 129.7, 129.6, 126.9, 126.9, 59.5, 50.9, 38.1, 31.6, 29.2, 23.0, 22.5, 22.5, 21.5, 21.4, 14.0; FTIR (film) *v*: 3289, 2961, 2931, 2861, 1459, 1423, 1320, 1165, 1096, 819, 666, 552 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{34}N_2O_4S_2Na$ [$(M+Na)^+$] 489.1858; found 489.1851.

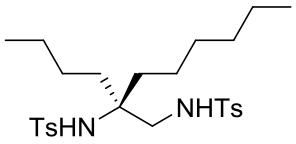
_N_,_N_'-diTs (_R_)-2-methyl-3-phenylpropane-1,2-diamine (21c):



The reaction was kept at 90 °C for 24 h. Yield 49 mg (70%) starting from 45 mg of aziridine **20c**; waxy solid; $[\alpha]_D^{26}$ +26.0 (*c* 0.78, $CHCl_3$, *ee* 98%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.6 (d, *J* = 7.9 Hz, 2H), 7.5 (d, *J* = 8.0 Hz, 2H), 7.3 – 7.0 (m, 9H), 5.2 (t, *J* = 7.0 Hz, 1H), 4.9 (s, 1H), 2.9 (d, *J* = 7.0 Hz, 2H), 2.8 (d, *J* = 13.5 Hz, 1H), 2.7 (d, *J* = 13.5 Hz,

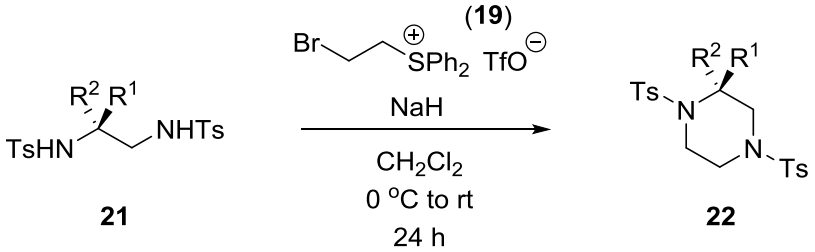
1H), 2.3 (s, 3H), 2.3 (s, 3H), 0.9 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 143.4, 139.5, 136.7, 135.2, 130.7, 129.7, 129.6, 128.4, 127.1, 127.0, 126.4, 59.2, 50.7, 44.8, 22.2, 21.5, 21.4; FTIR (film) *v*: 3275, 2925, 2855, 1454, 1329, 1160, 1092, 814, 664, 552 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{24}H_{28}N_2O_4S_2Na$ [(M+Na)$^+$] 495.1388; found 495.1382.

***N,N'*-diTs (*S*)-2-butyloctane-1,2-diamine (21d):**



The reaction was kept at 90 °C for 72 h. Yield 43 mg (71%) starting from 40 mg of aziridine **20d**; colourless oil; $[\alpha]_D^{31}$ +4.4 (*c* 0.64, $CHCl_3$, *ee* 82%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 5.30 (t, *J* = 7.1 Hz, 1H), 4.70 (s, 1H), 2.95 (d, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 2.33 (s, 3H), 1.44 – 0.78 (m, 16H), 0.76 (t, *J* = 7.3 Hz, 3H), 0.68 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 143.2, 139.5, 137.2, 129.7, 129.6, 127.0, 62.6, 48.2, 34.1, 33.8, 31.6, 29.2, 24.6, 22.6, 22.6, 22.5, 21.5, 21.4, 14.0, 13.8; FTIR (film) *v*: 3293, 2965, 2928, 2865, 1451, 1427, 1321, 1091, 828, 667, 551 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{26}H_{40}N_2O_4S_2Na$ [(M+Na)$^+$] 531.2327; found 531.2321.

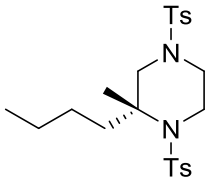
21. The synthesis of piperazines 22



General procedure:[5, 6] NaH (3.5 equiv., 0.56 mmol, 60% in mineral oil, 22 mg) and then bromoethylsulfonium triflate **19** (1.2 equiv, 0.19 mmol, 85 mg) were slowly added to a stirred solution of the diamine **21** (1 equiv, 0.16 mmol) in CH_2Cl_2 (0.02

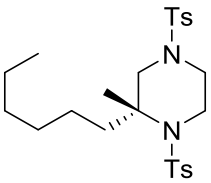
M) at 0 °C. The reaction was stirred at 0 °C for 2 h, then warmed to room temperature and stirred overnight. The mixture was quenched by addition of water and then extracted with CH_2Cl_2. The combined organic phases were dried over anhydr. Na_2SO_4. After the removal of the solvents, the residue was purified by a column chromatography on silica gel (5-30% AcOEt in hexanes).

***N*,*N'*-diTs (*R*)-2-butyl-2-methyl-piperazine (22a):**



Yield 36 mg (81%) starting from 42 mg of diamine **21a**; colourless oil; $[\alpha]_D^{25}$ +10.8 (*c* 0.98, $CHCl_3$, *ee* 94%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.39 (m, 4H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.85 – 3.71 (m, 1H), 3.50 – 3.31 (m, 2H), 3.14 (d, *J* = 11.8 Hz, 1H), 2.57 – 2.45 (m, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 2.25 (d, *J* = 11.7 Hz, 1H), 1.75 – 1.55 (m, 2H), 1.25 (s, 3H), 1.22 – 0.94 (m, 4H), 0.77 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 143.2, 139.5, 132.7, 129.8, 129.5, 127.6, 127.0, 61.0, 54.7, 46.1, 42.6, 34.2, 25.8, 22.9, 22.7, 21.5, 21.4, 13.8; FTIR (film) *v*: 2956 , 2929, 1345, 1165, 1096, 960, 660, 604, 551 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{32}N_2O_4S_2Na$ $[(M+Na)^+]$ 487.1701; found 487.1688.

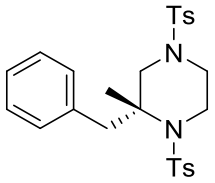
***N*,*N'*-diTs (*R*)-2-hexyl-2-methyl-piperazine (22b):**



Yield 36 mg (91%) starting from 38 mg of diamine **21b**; waxy solid; $[\alpha]_D^{25}$ +9.5 (*c* 0.87, $CHCl_3$, *ee* 94%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.45 (m, 4H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.86 – 3.72 (m, 1H), 3.48 – 3.31 (m, 2H), 3.14 (d, *J* = 11.7 Hz, 1H), 2.58 – 2.47 (m, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 2.25 (d, *J* = 11.8 Hz, 1H),

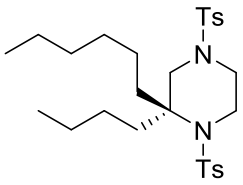
1.65 (t, *J* = 7.8 Hz, 2H), 1.25 (s, 3H), 1.23 – 0.95 (m, 8H), 0.80 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 143.2, 139.6, 132.7, 129.8, 129.5, 127.6, 127.0, 61.1, 54.7, 46.1, 42.6, 34.5, 31.6, 29.5, 23.6, 22.8, 22.5, 21.5, 21.4, 14.0; FTIR (film) *v*: 2962 , 2937, 1355, 1162, 1091, 662, 603 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{25}H_{36}N_2O_4S_2Na$ [$(M+Na)^+$] 515.2014; found 515.2019.

_N_,_N_'-diTs (_R_)-2-benzyl-2-methyl-piperazine (22c):



Yield 40 mg (82%) starting from 46 mg of diamine **21c**; waxy solid; $[\alpha]_D^{24}$ +102.3 (*c* 1.82, $CHCl_3$, *ee* 98%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.11 (m, 7H), 4.01 – 3.88 (m, 1H), 3.70 – 3.59 (m, 1H), 3.58 – 3.46 (m, 1H), 3.38 – 3.19 (m, 2H), 2.64 (d, *J* = 13.0 Hz, 1H), 2.46 – 2.35 (m, 4H), 2.32 (s, 3H), 1.94 (d, *J* = 11.7 Hz, 1H), 1.13 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.2, 143.5, 139.4, 136.1, 131.9, 131.0, 129.8, 129.7, 128.2, 127.9, 127.0, 126.8, 61.1, 53.9, 46.7, 42.6, 38.8, 23.5, 21.5, 21.5; FTIR (film) *v*: 2922, 1596, 1454, 1342, 1159, 687, 597, 548 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{26}H_{30}N_2O_4S_2Na$ [$(M+Na)^+$] 521.1545; found 521.1536.

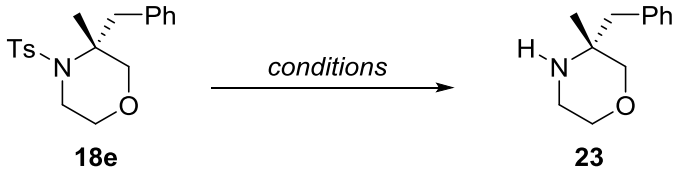
_N_,_N_'-diTs (_S_)-2-butyl-2-hexyl-piperazine (22d):



Yield 34 mg (91%) starting from 36 mg of diamine **21d**; yellow oil; $[\alpha]_D^{24}$ +0.1 (*c* 1.21, $CHCl_3$, *ee* 82%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.50 (t, *J* = 5.3 Hz, 2H), 2.93 (t, *J* = 5.3 Hz, 2H), 2.84 (s, 2H), 2.37 (s, 3H), 2.32 (s, 3H), 1.87 – 1.62 (m, 4H), 1.36

– 0.95 (m, 12H), 0.90 – 0.61 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 143.3, 139.3, 132.8, 129.8, 129.4, 127.6, 127.3, 65.2, 52.2, 45.8, 42.8, 33.9, 33.6, 31.6, 29.6, 25.8, 23.6, 23.0, 22.6, 21.5, 21.4, 14.0, 13.9; FTIR (film) *v*: 2971 , 2923, 1341, 1181, 1101, 966, 607, 559 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{28}H_{42}N_2O_4S_2Na$ [$(M+Na)^+$] 557.2484; found 557.2481.

22. Deprotection of morpholine 18e



18e **23**

Method 1: Mg, MeOH, rt, 16 h 55%
Method 2: Na, naphtalene, –78 ^{o}C, 3 h, 62%
Method 3: PhOH, 37% HBr/AcOH, rt, 12 h 75%

Method 1: Dry MeOH was added to morpholine **18e** (35 mg, 0.1 mmol) and Mg (30 mg, 15 mmol). The resulting mixture was stirred at rt for 16 h. After removal of solvent, the residue was poured to 2M aq NaOH and extracted with Et_2O. After removal of solvent the residue was chromatographed on silica gel (100% CH_2Cl_2 than 15% MeOH in CH_2Cl_2). Yield 11 mg (55%) as colorless oil.

Method 2: A flame-dried flask under nitrogen was charged with naphthalene (78 mg, 0.6 mmol) and anhydrous DME (6 mL) at rt. Next, sodium metal (15 mg, 0.62 mmol) was then added to this solution at rt under nitrogen. After 10 min the solution had become dark green in color, at this point the reaction was allowed to stir for a further 2 h. A second flame-dried flask under nitrogen was charged with morpholine **18e** (35 mg, 0.1 mmol) and anhydr. DME (3 mL, 0.1 M) at rt before cooling to –78 °C. Once cooled to –78 °C the flask was removed from the cooling bath and a solution of sodium/naphthalide (2 mL, ca. 3 equiv) was added dropwise over 5 min, whilst allowing the flask to warm gradually. After the addition of sodium/naphthalide, a dark brown-red color persisted and the reaction mixture

was allowed to warm to rt (ca. 10 min). The reaction was then quenched at rt with sat. $NaHCO_3$ (10 mL) and diluted with H_2O (10 mL). The reaction mixture was then extracted with Et_2O (5 × 15 mL), the organic phases combined, dried over Na_2SO_4 and filtered. After removal of solvent the residue was chromatographed on silica gel (100% CH_2Cl_2 than 15% MeOH in CH_2Cl_2). Yield 13 mg (62%) as colorless oil.

Method 3: Morpholine **18e** (35 mg, 0.1 mmol) and PhOH (30 mg, 0.3 mmol) were dissolved in 2 mL of 37% soln. HBr in AcOH. After stirring for 16 h, reaction mixture was poured into 2M aq NaOH and extracted with Et_2O. The combined organic layers were dried over anhydr. Na_2SO_4. After removal of solvent the residue was chromatographed on silica gel (100% CH_2Cl_2 than 15% MeOH in CH_2Cl_2). Yield 15 mg (75%) as colorless oil.

(*R*)-3-Benzyl-3-methylmorpholine (23): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.17 (m, 5H), 3.77 – 3.71 (m, 1H), 3.70 – 3.64 (m, 1H), 3.54 (d, *J* = 11.1 Hz, 1H), 3.39 (d, *J* = 11.1 Hz, 1H), 3.16 – 3.09 (m, 1H), 2.95 (d, *J* = 13.2 Hz, 1H), 2.89 (ddd, *J* = 12.6, 5.5, 3.3 Hz, 1H), 2.75 (d, *J* = 13.2 Hz, 1H), 1.01 (s, 3H); HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{17}NONa$ [$(M+Na)^+$] 214.2638; found 214.2635.

23. References

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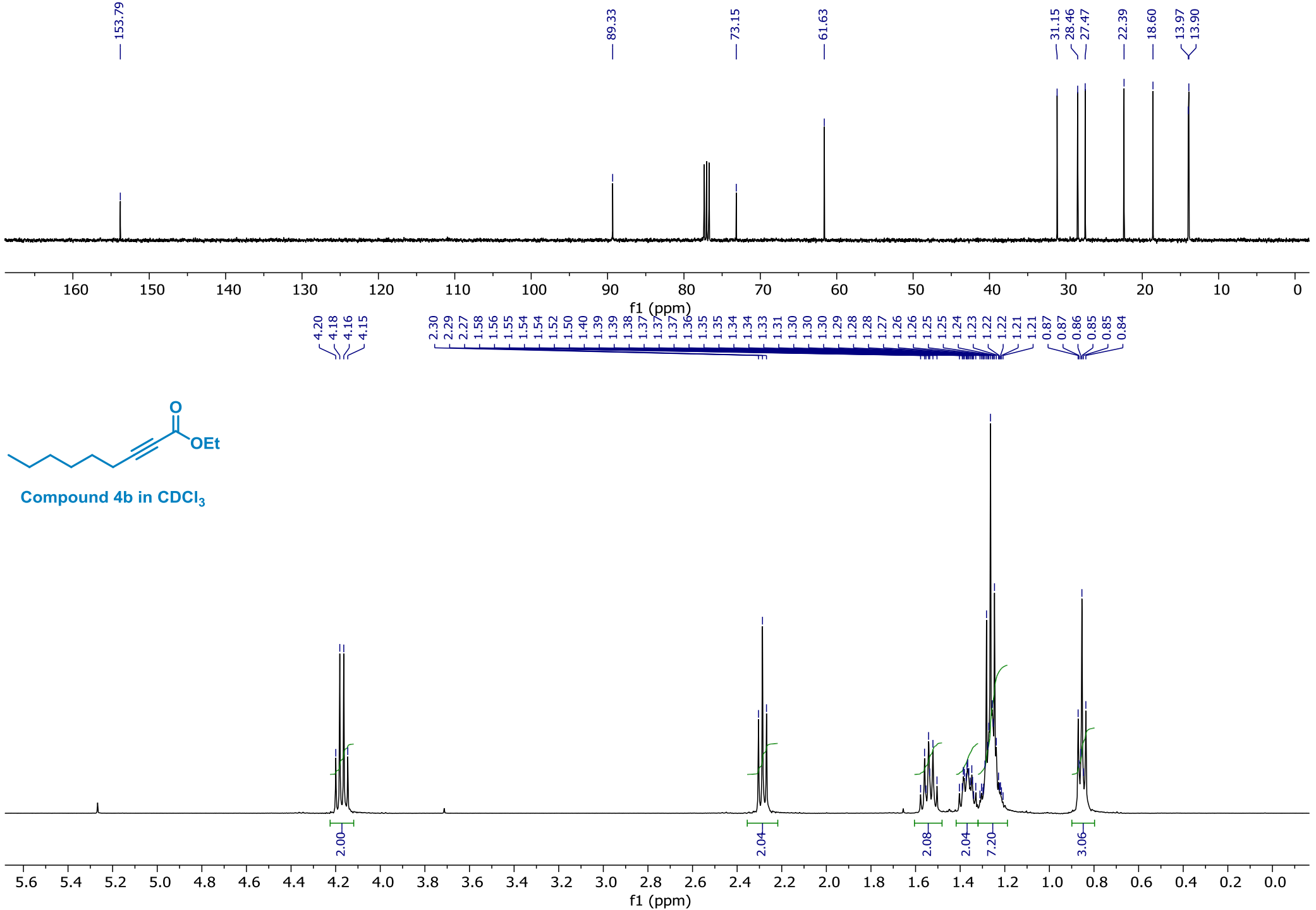
24. ^{1}H, ^{13}C NMR spectra and HPLC chromatograms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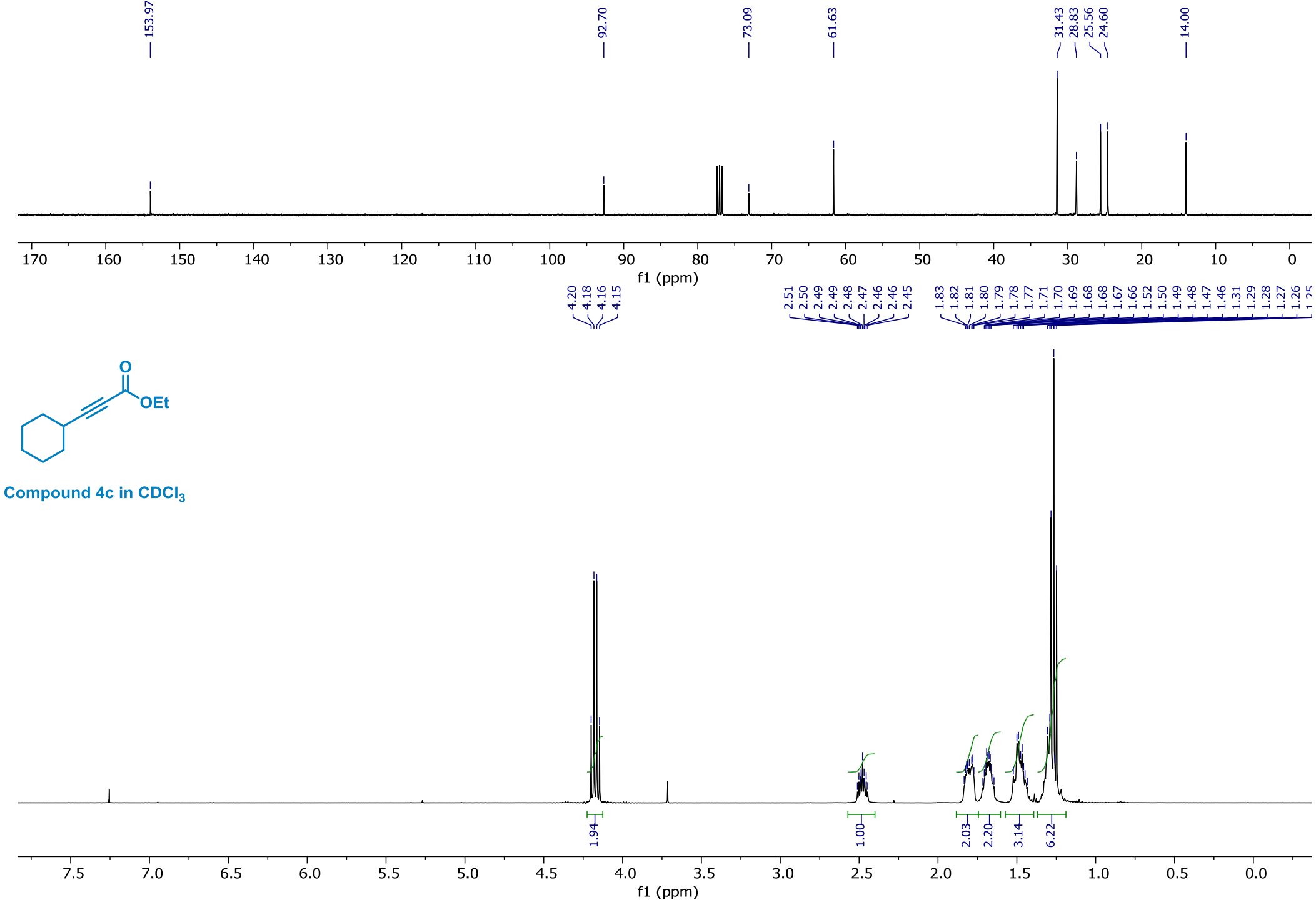
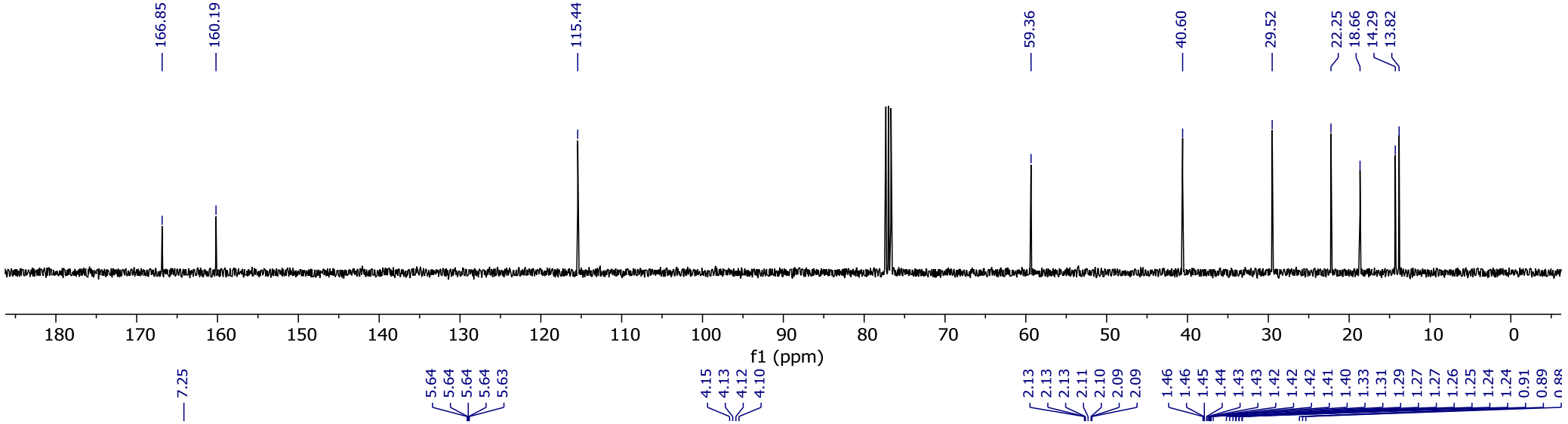
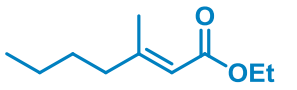
89.33
73.15
61.63
31.15
28.46
27.47
22.39
18.60
13.97
13.90
f1 (ppm)
4.20
4.18
4.16
4.15
2.30
2.29
2.27
1.58
1.56
1.55
1.54
1.54
1.52
1.50
1.40
1.39
1.39
1.38
1.37
1.37
1.37
1.36
1.35
1.35
1.34
1.34
1.33
1.31
1.30
1.30
1.30
1.29
1.28
1.28
1.27
1.26
1.26
1.25
1.25
1.24
1.23
1.22
1.22
1.21
1.21
0.87
0.87
0.86
0.85
0.85
0.84
O
OEt
Compound 4b in CDCl3
2.00
2.04
2.08
2.04
7.20
3.06
f1 (ppm)

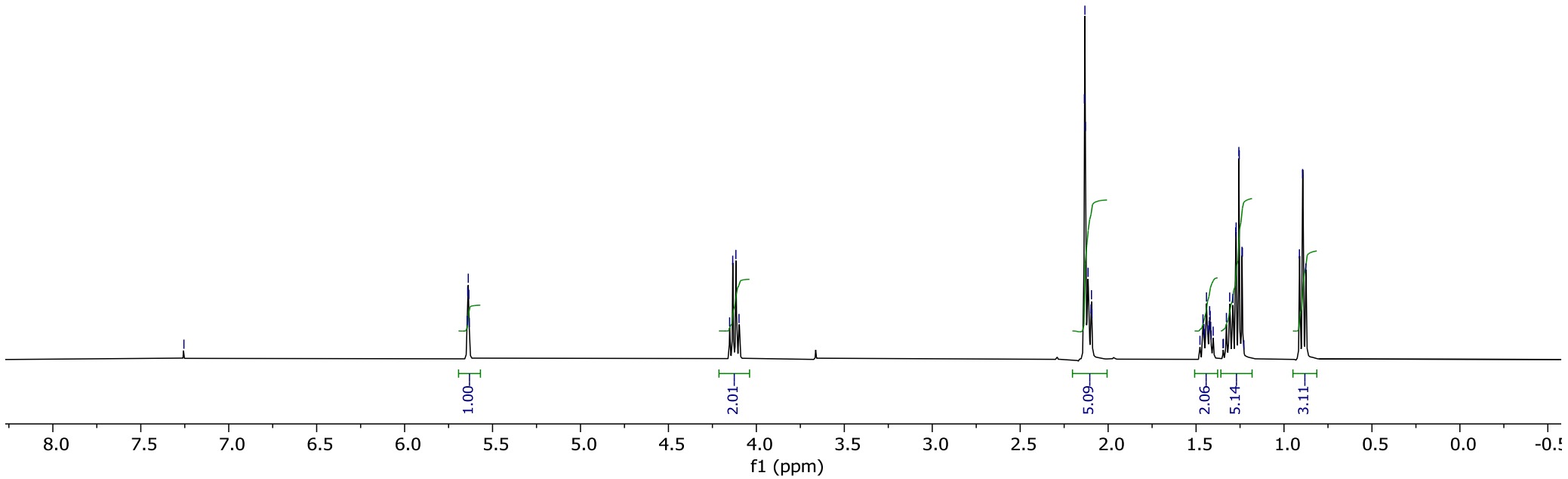


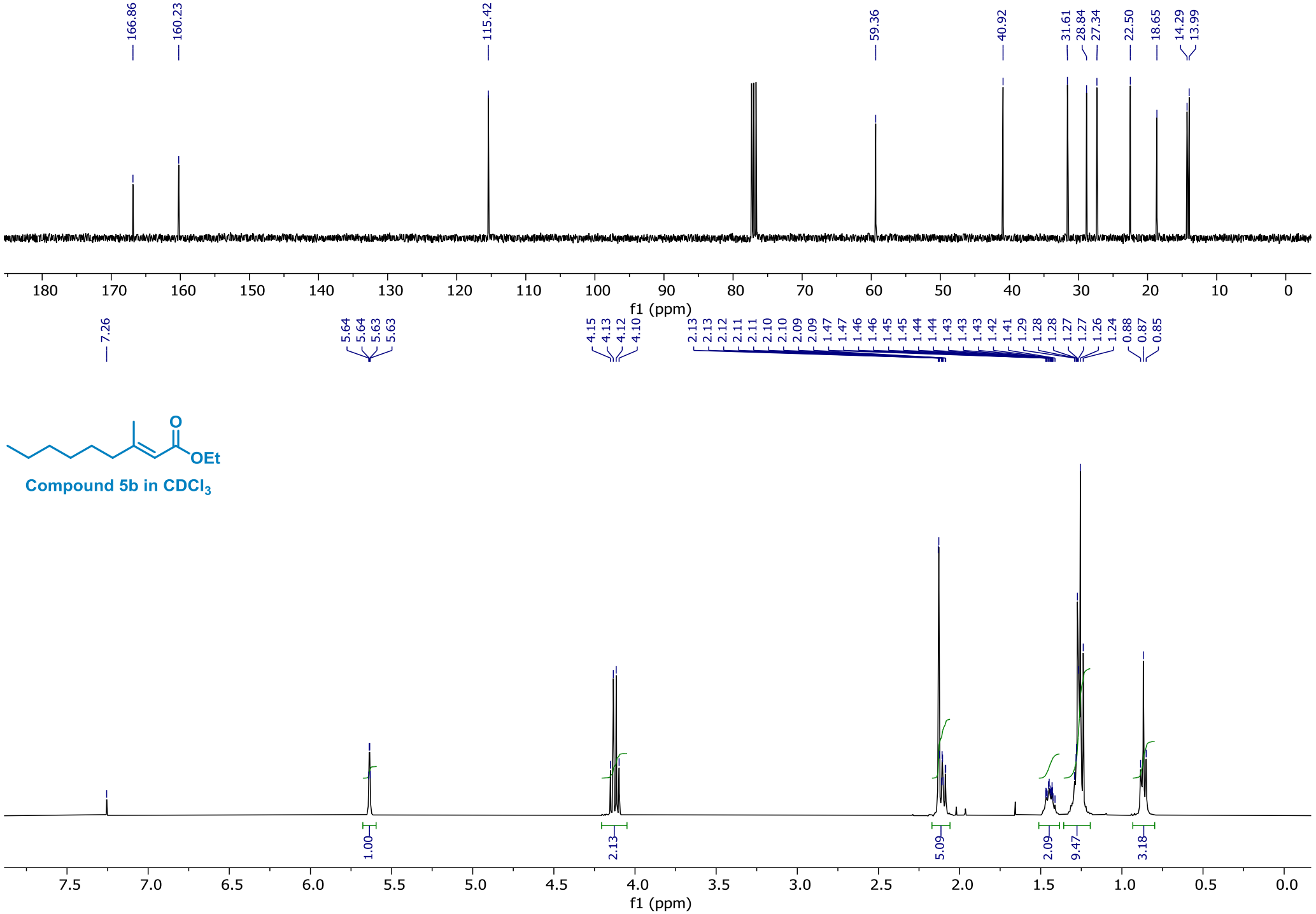
Compound 4c in $CDCl_3$





Compound 5a in $CDCl_3$

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160.23
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59.36
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31.61
28.84
27.34
22.50
18.65
14.29
13.99
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7.26
5.64
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5.63
5.63
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4.13
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2.10
2.10
2.09
2.09
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1.47
1.46
1.46
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1.44
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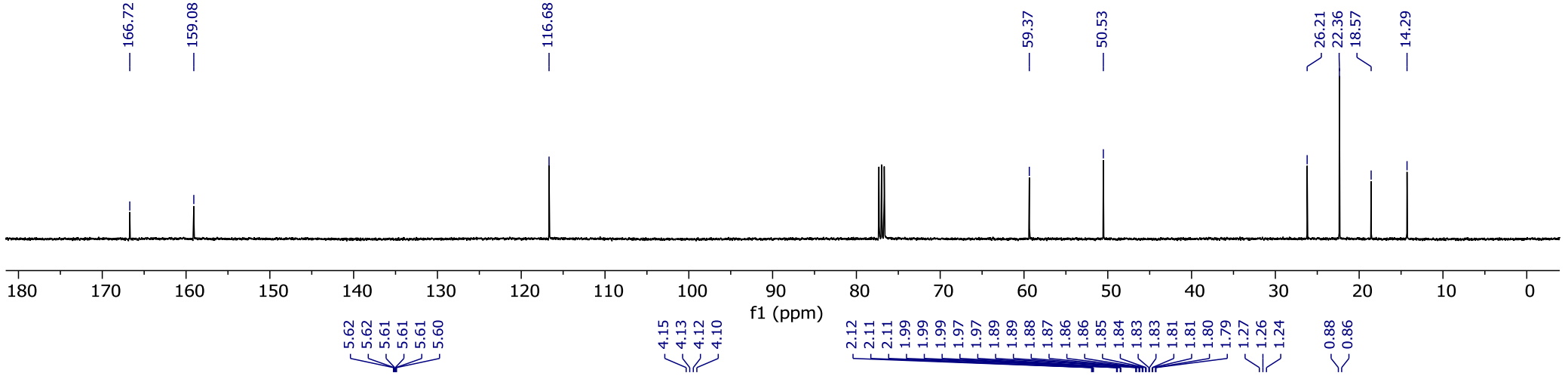
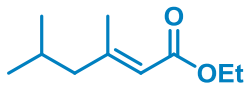
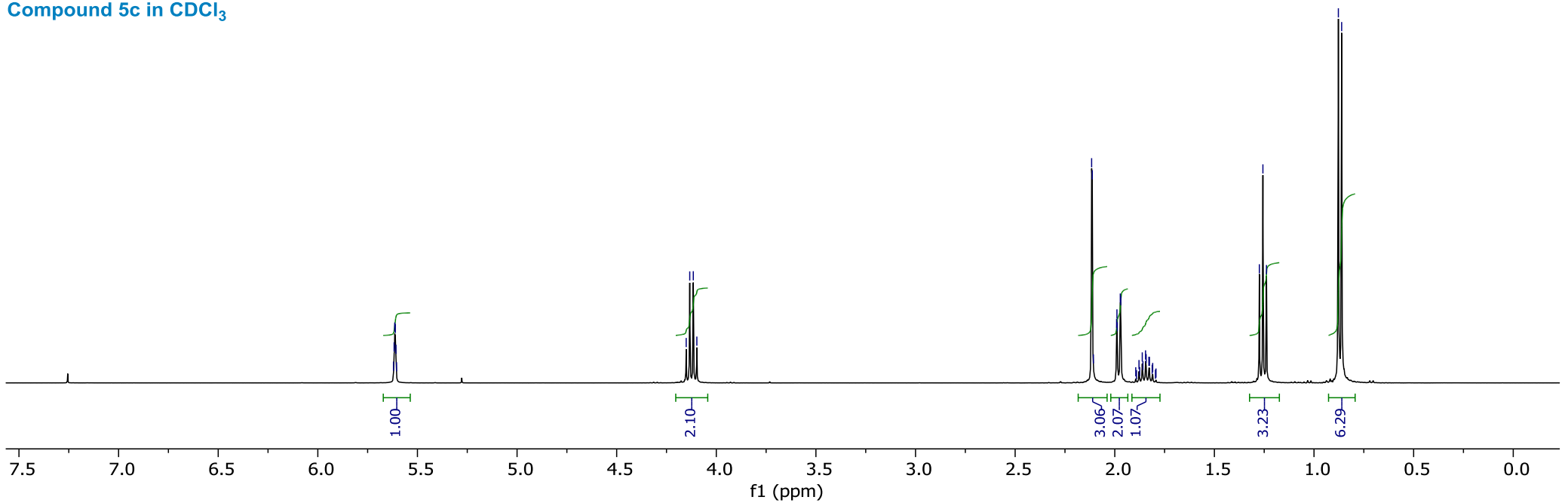
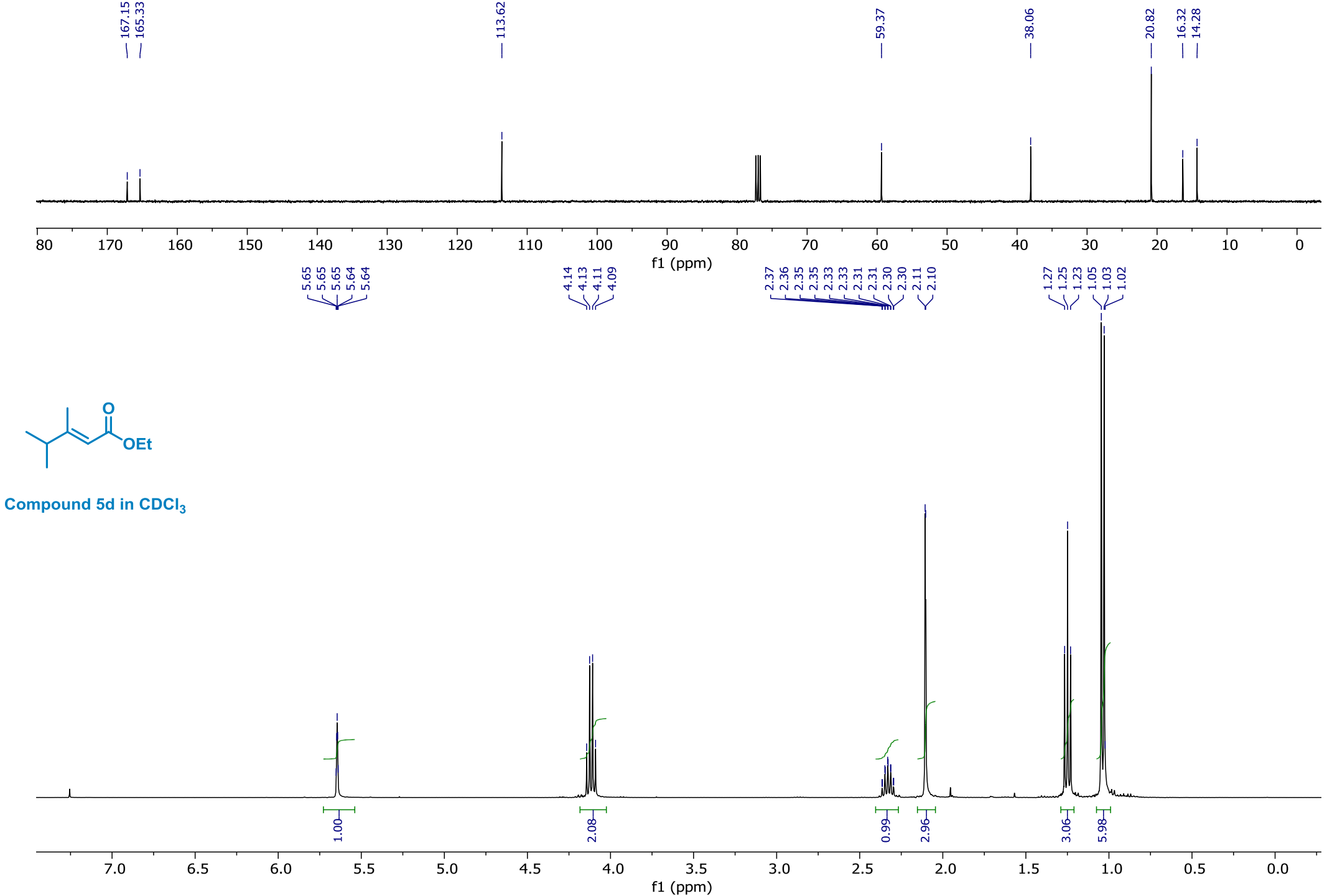
1.43
1.43
1.43
1.42
1.41
1.29
1.28
1.28
1.27
1.27
1.26
1.24
0.88
0.87
0.85
O
OEt
Compound 5b in CDCl3
1.00
2.13
5.09
2.09
9.47
3.18
f1 (ppm)



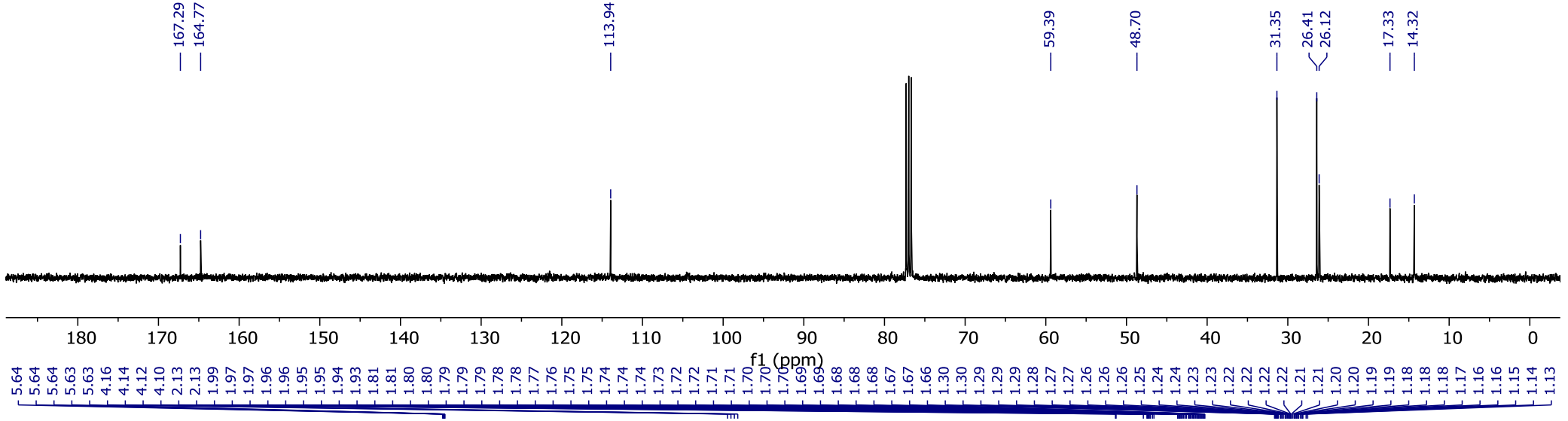


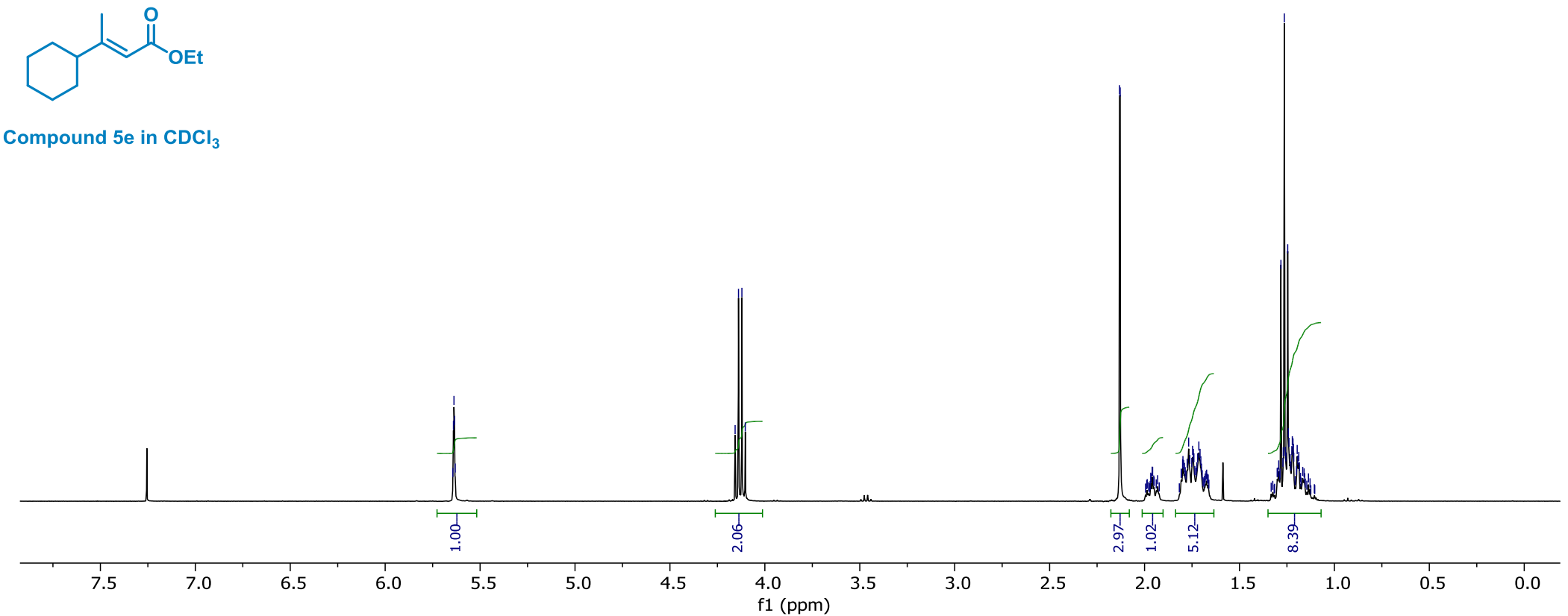
Compound 5c in $CDCl_3$



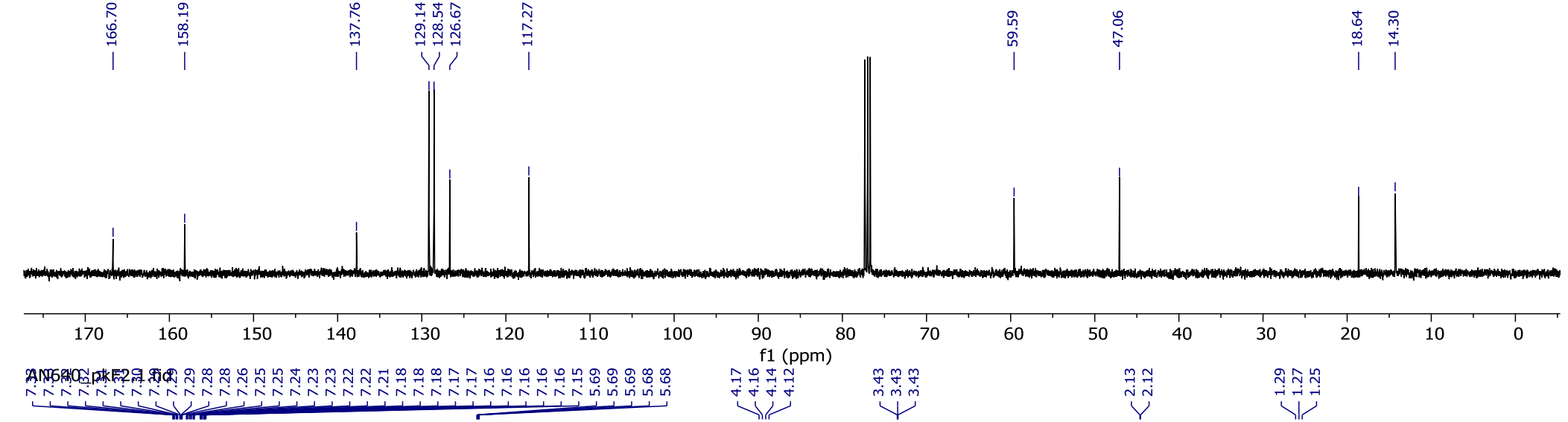


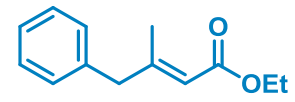
Compound 5d in $CDCl_3$



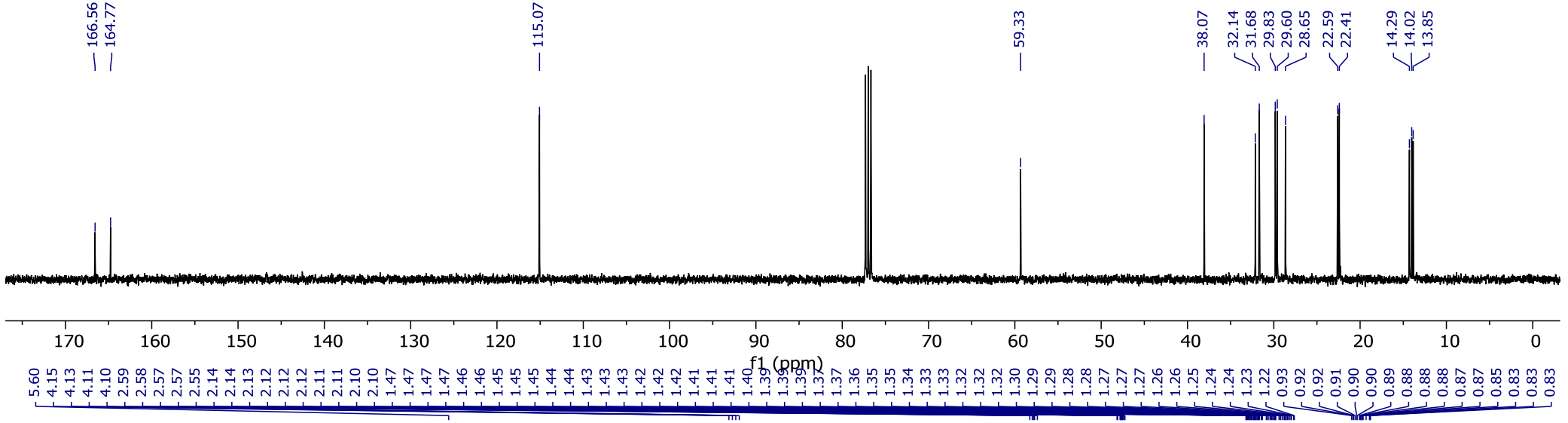


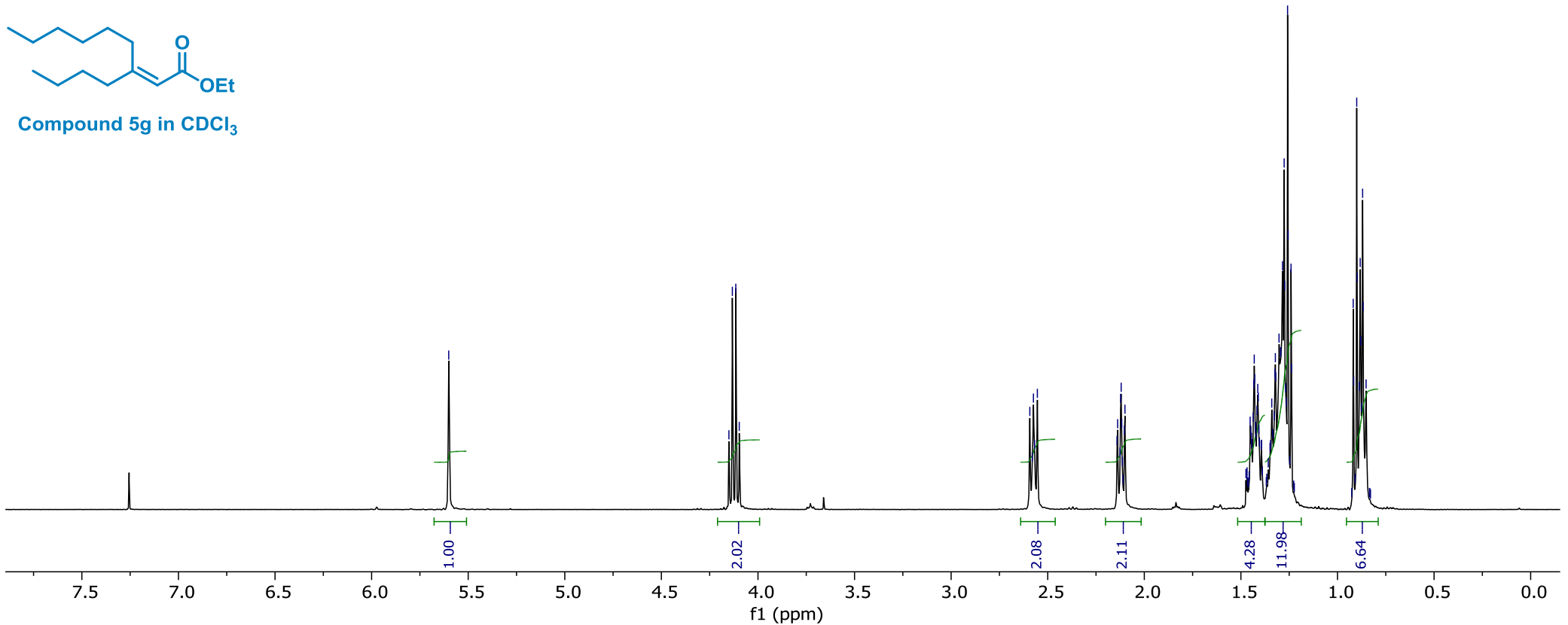
Compound 5e in $CDCl_3$



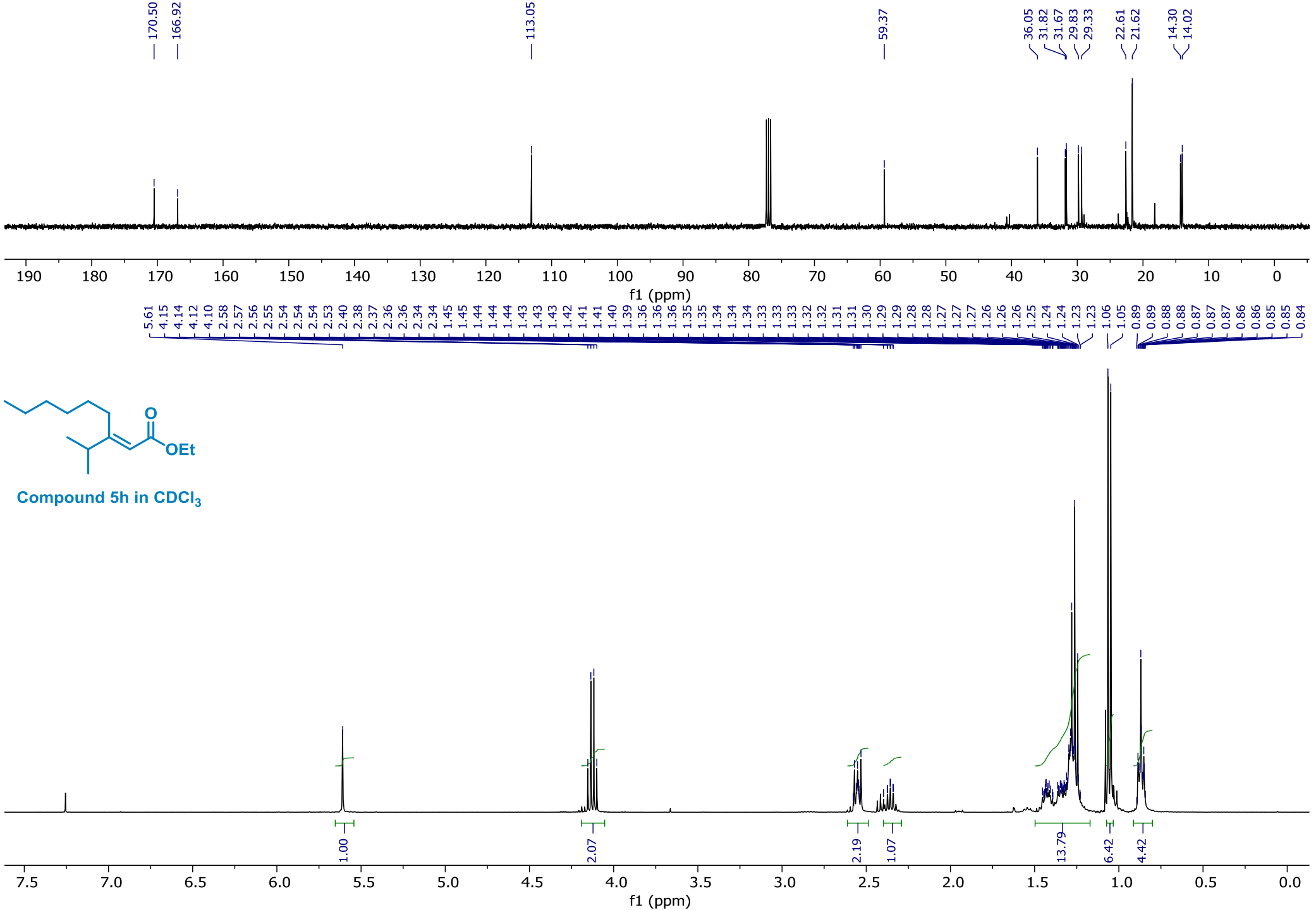


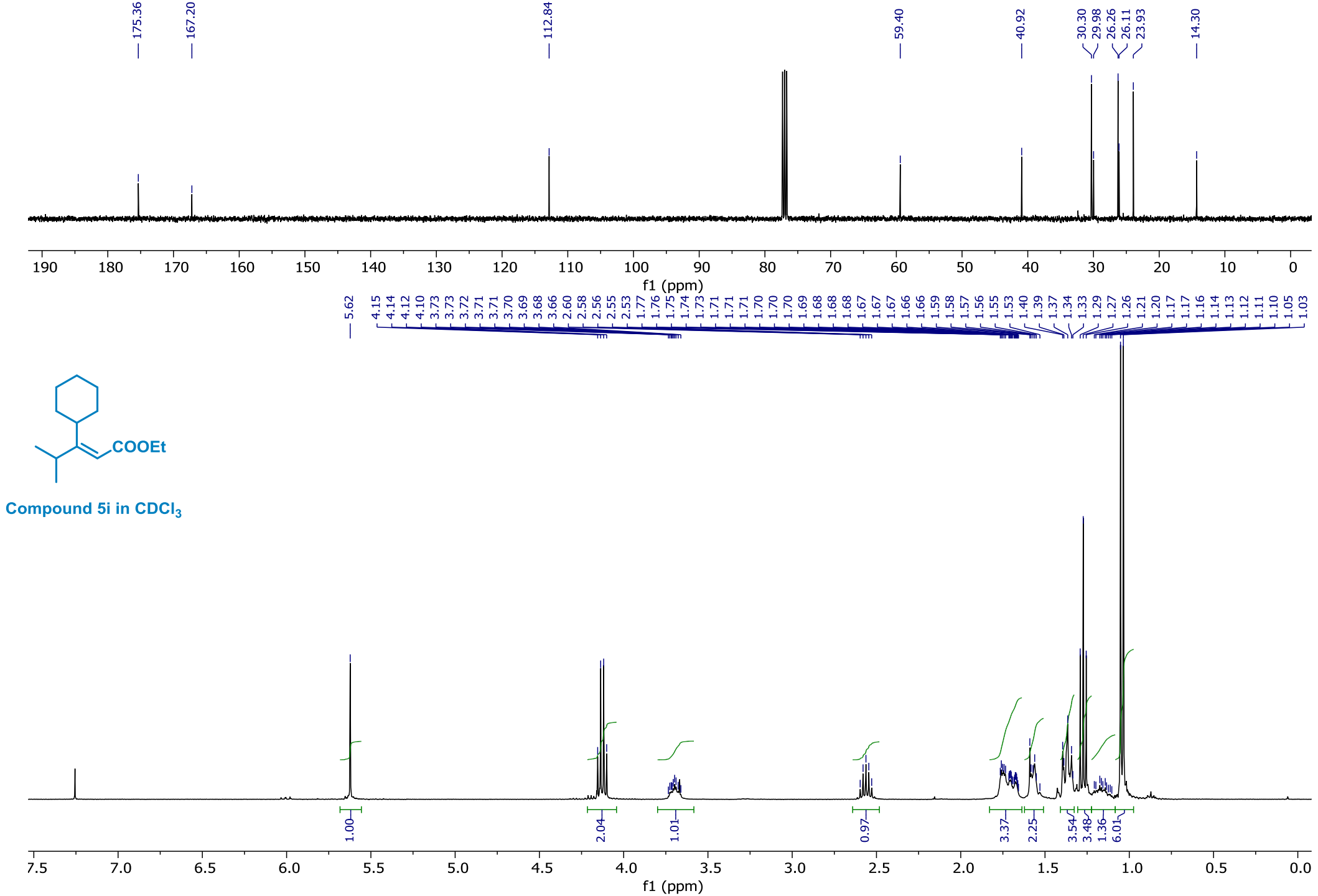
Compound 5f in $CDCl_3$



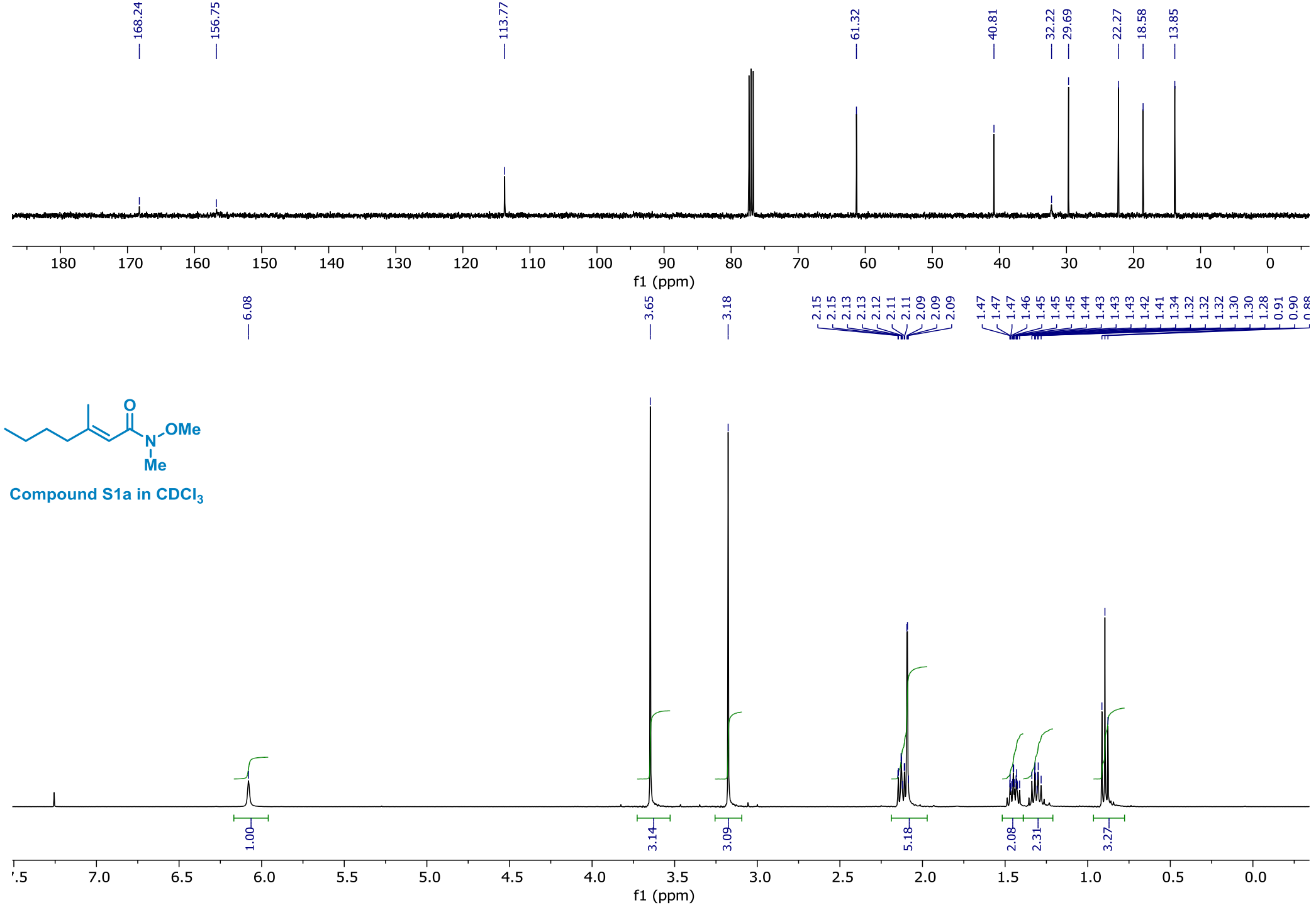


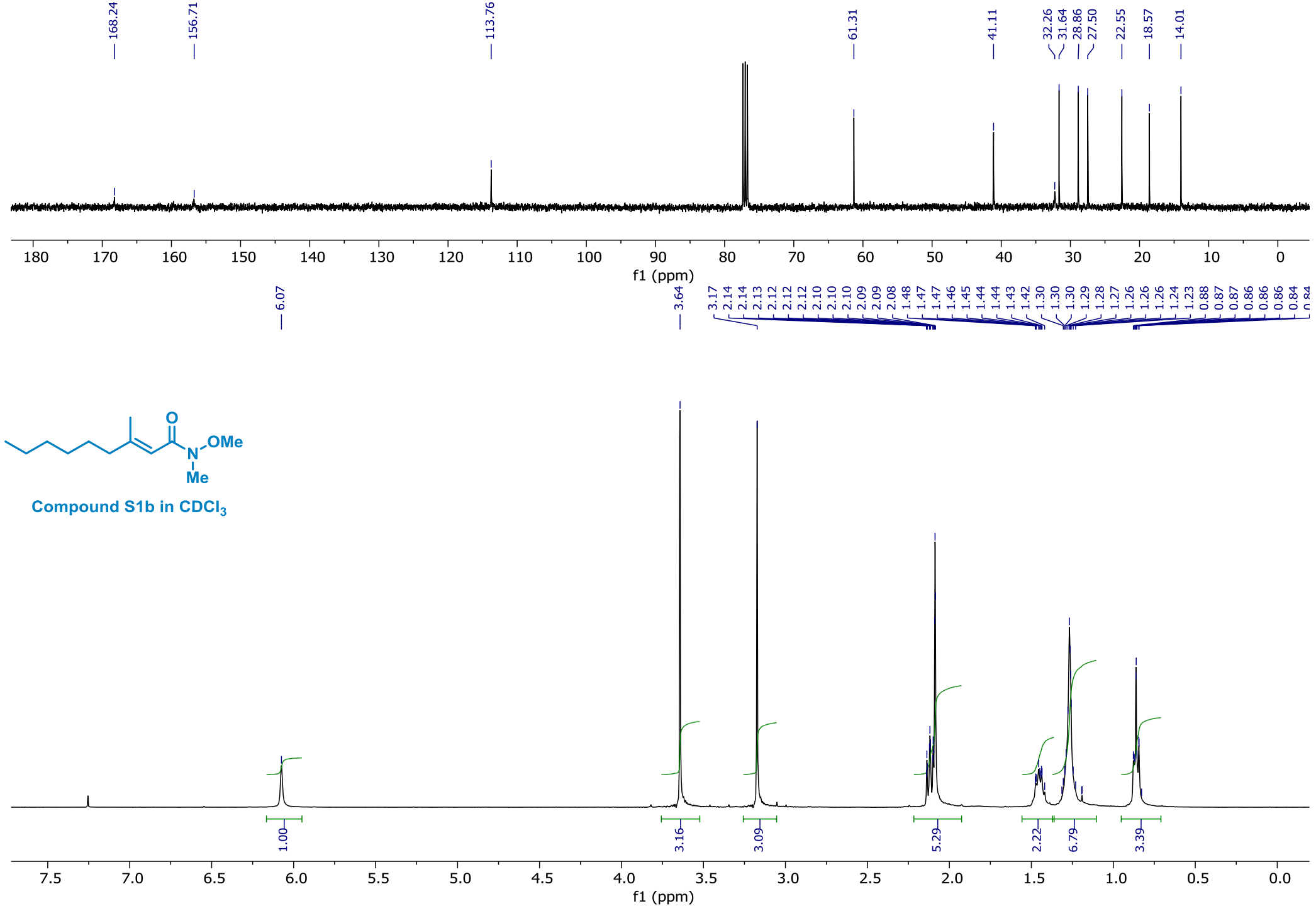
Compound 5g in $CDCl_3$


170.50
166.92
113.05
59.37
36.05
31.82
31.67
29.83
29.33
22.61
21.62
14.30
14.02
f1 (ppm)
5.61
4.15
4.14
4.12
4.10
2.58
2.57
2.56
2.55
2.54
2.54
2.54
2.53
2.40
2.38
2.37
2.36
2.36
2.34
2.34
1.45
1.45
1.44
1.44
1.44
1.43
1.43
1.43
1.42
1.41
1.41
1.40
1.39
1.36
1.36
1.36
1.35
1.35
1.34
1.34
1.34
1.33
1.33
1.33
1.32
1.32
1.31
1.31
1.30
1.29
1.29
1.28
1.28
1.27
1.27
1.27
1.26
1.26
1.25
1.24
1.24
1.23
1.23
1.06
1.05
0.89
0.89
0.88
0.88
0.87
0.87
0.87
0.86
0.86
0.85
0.85
0.84
O
OEt
Compound 5h in CDCl3
1.00
2.07
2.19
1.07
13.79
6.42
4.42
f1 (ppm)

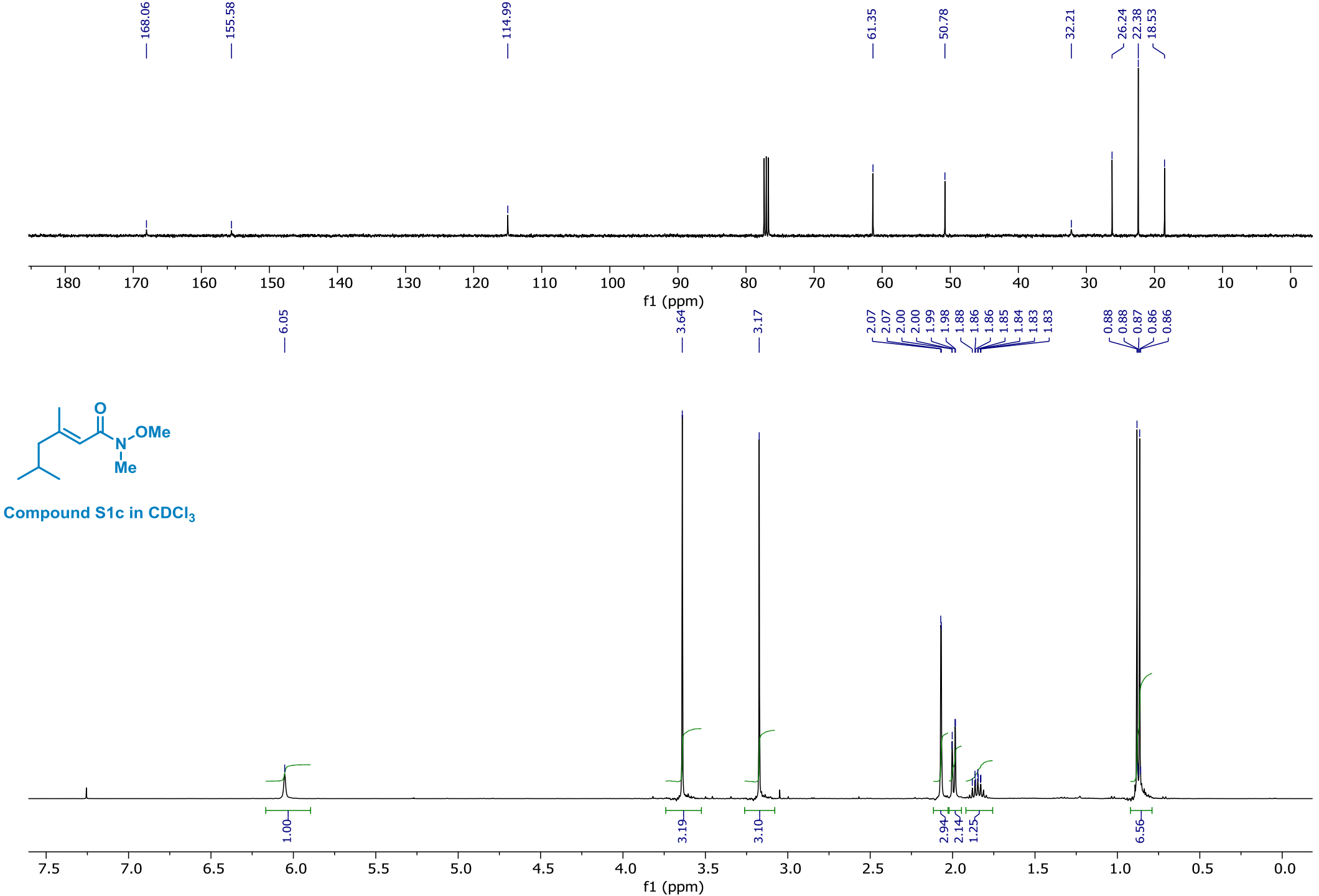


Compound 5i in $CDCl_3$

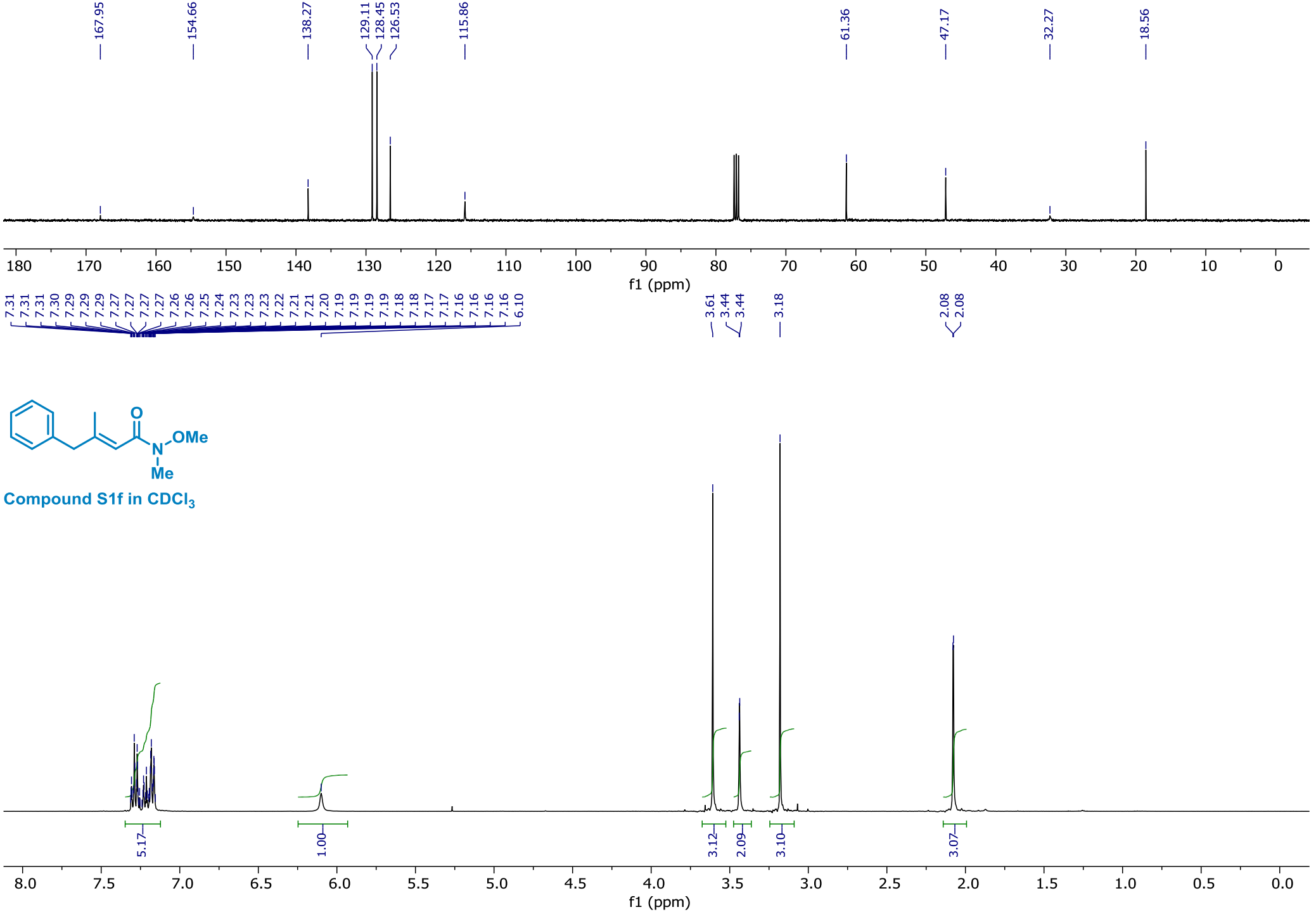

168.24
156.75
113.77
61.32
40.81
32.22
29.69
22.27
18.58
13.85
f1 (ppm)
6.08
3.65
3.18
2.15 2.15 2.13 2.13 2.12 2.11 2.11 2.09 2.09 2.09
1.47 1.47 1.47 1.46 1.45 1.45 1.44 1.43 1.43 1.43 1.42 1.41 1.34 1.32 1.32 1.32 1.30 1.30 1.28 0.91 0.90
O
N
OMe
Me
Compound S1a in CDCl3
1.00
3.14
3.09
5.18
2.08
2.31
3.27
f1 (ppm)

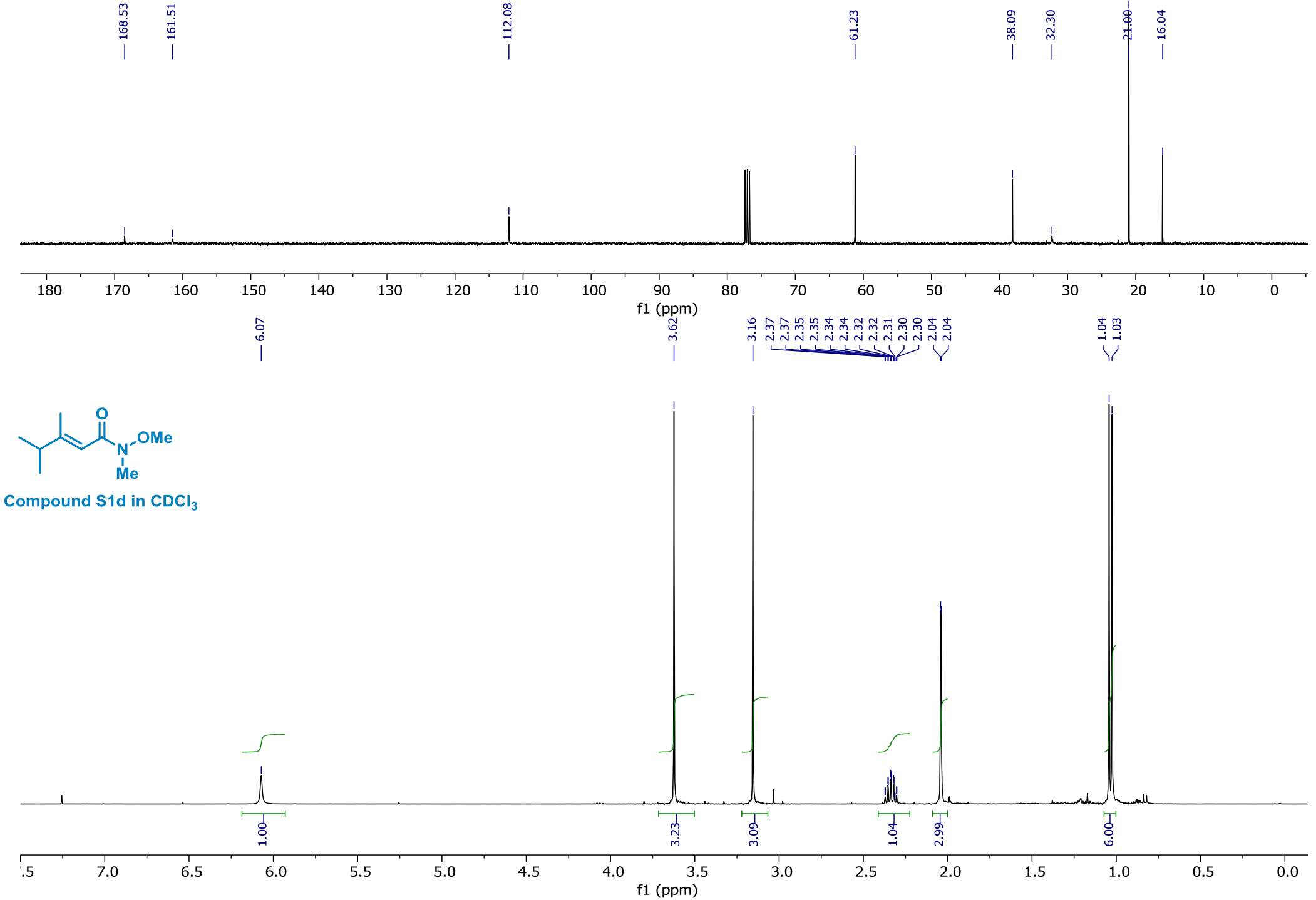


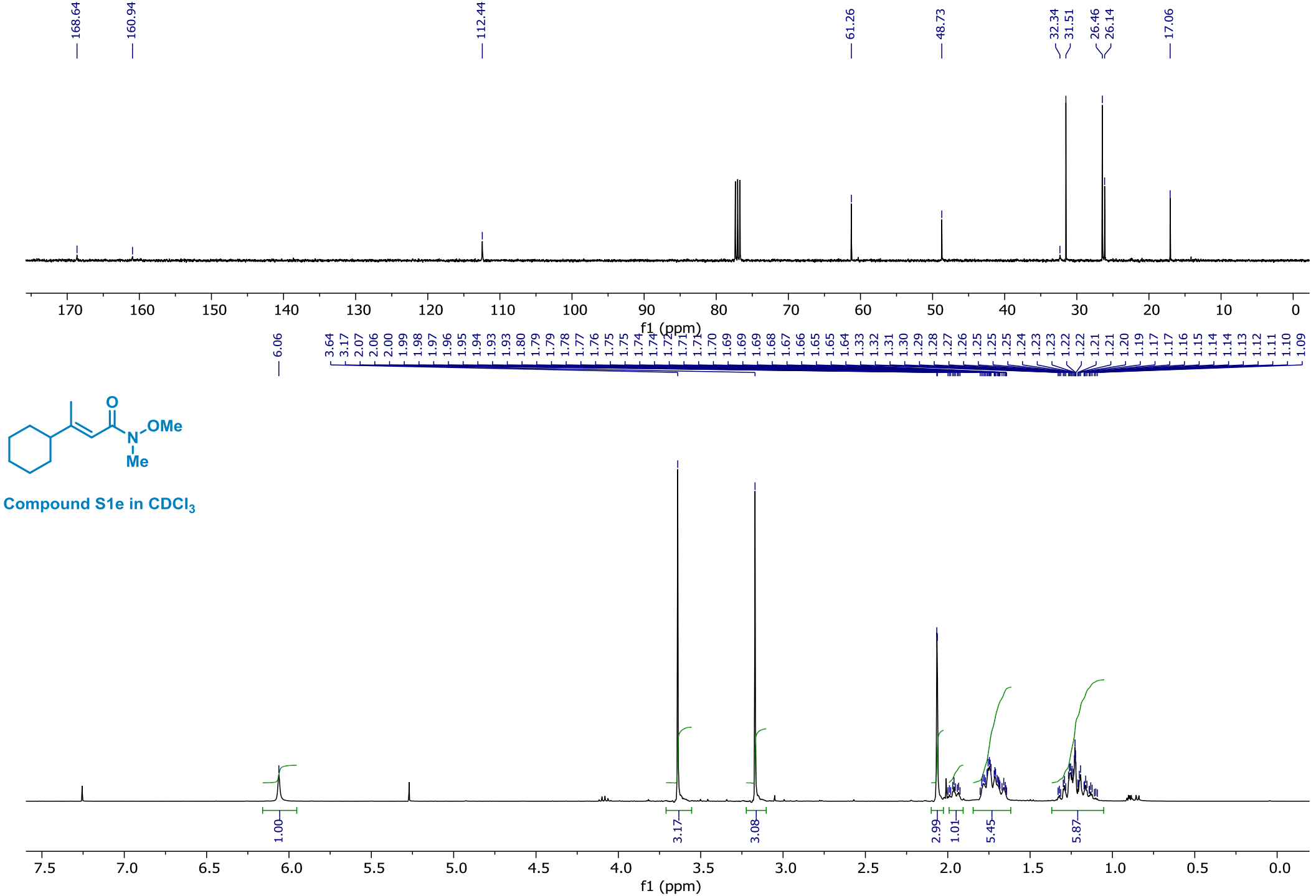
Compound S1b in $CDCl_3$



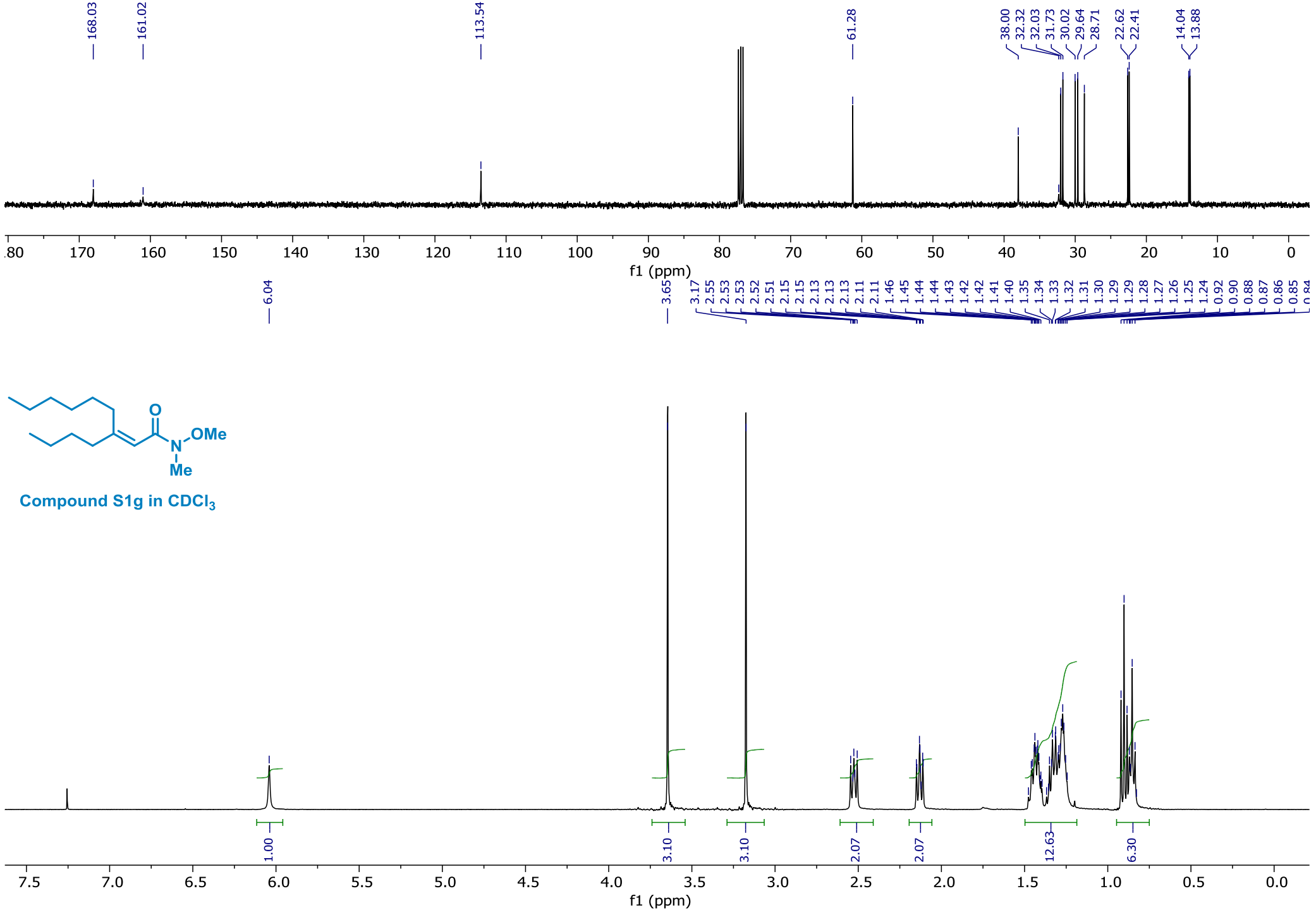
Compound S1c in $CDCl_3$

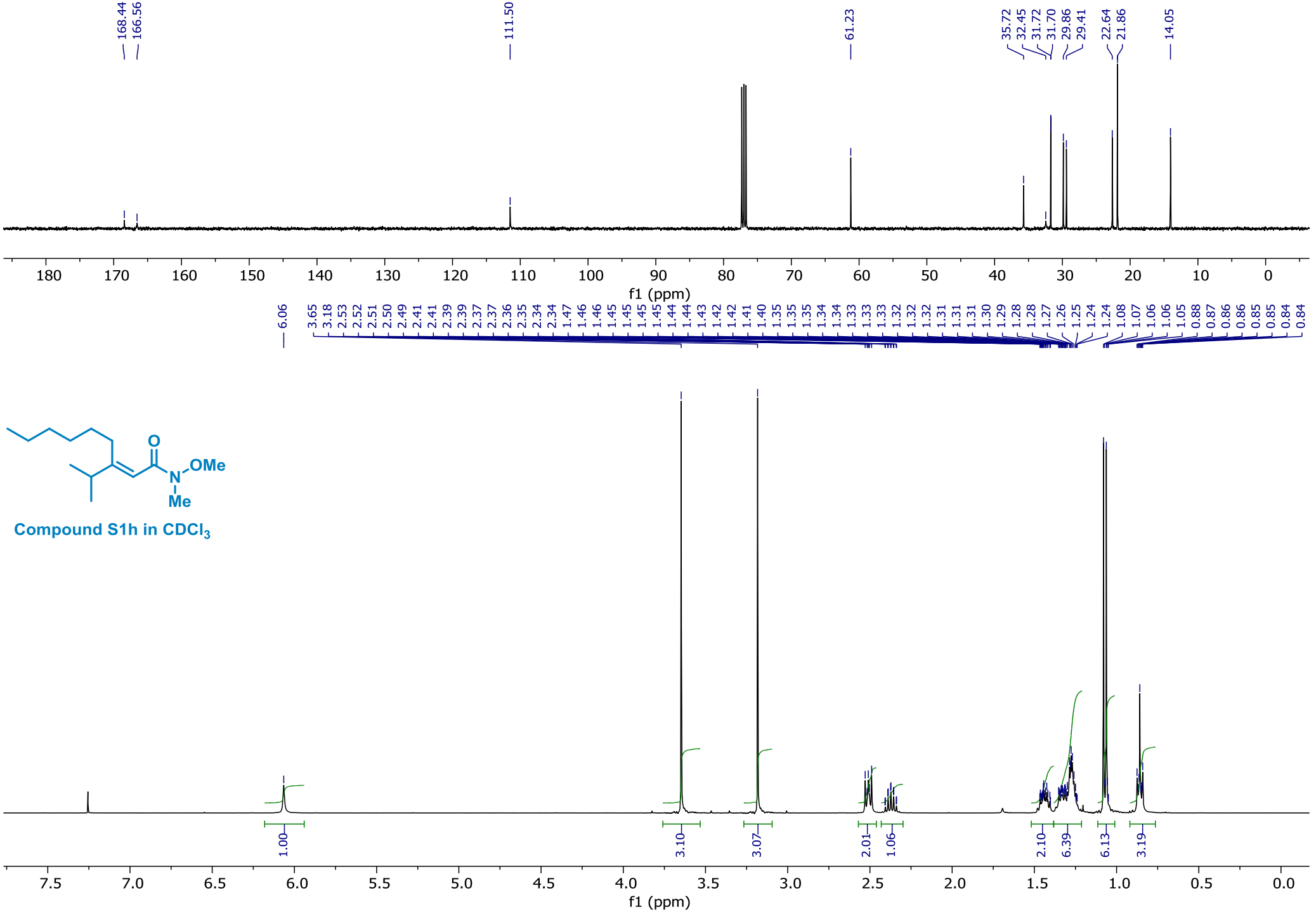

167.95
154.66
138.27
129.11
128.45
126.53
115.86
61.36
47.17
32.27
18.56
f1 (ppm)
7.31 7.31 7.31 7.30 7.29 7.29 7.29 7.27 7.27 7.27 7.27 7.26 7.26 7.25 7.24 7.23 7.23 7.23 7.22 7.21 7.21 7.20 7.19 7.19 7.19 7.19 7.18 7.17 7.17 7.16 7.16 7.16 7.16 6.10
3.61 3.44 3.44 3.18
2.08 2.08
O
N
OMe
Me
Compound S1f in CDCl3
5.17
1.00
3.12
2.09
3.10
3.07
f1 (ppm)

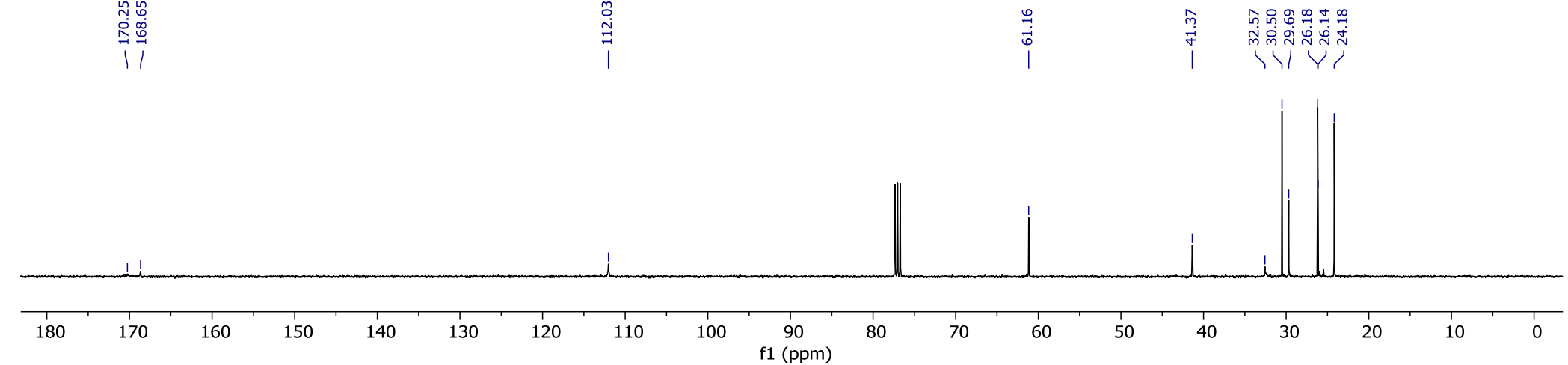

168.53
161.51
112.08
61.23
38.09
32.30
21.00
16.04
f1 (ppm)
6.07
3.62
3.16
2.37
2.37
2.35
2.35
2.34
2.34
2.32
2.32
2.31
2.30
2.30
2.04
2.04
1.04
1.03
O
OMe
N
Me
Compound S1d in CDCl3
1.00
3.23
3.09
1.04
2.99
6.00
f1 (ppm)

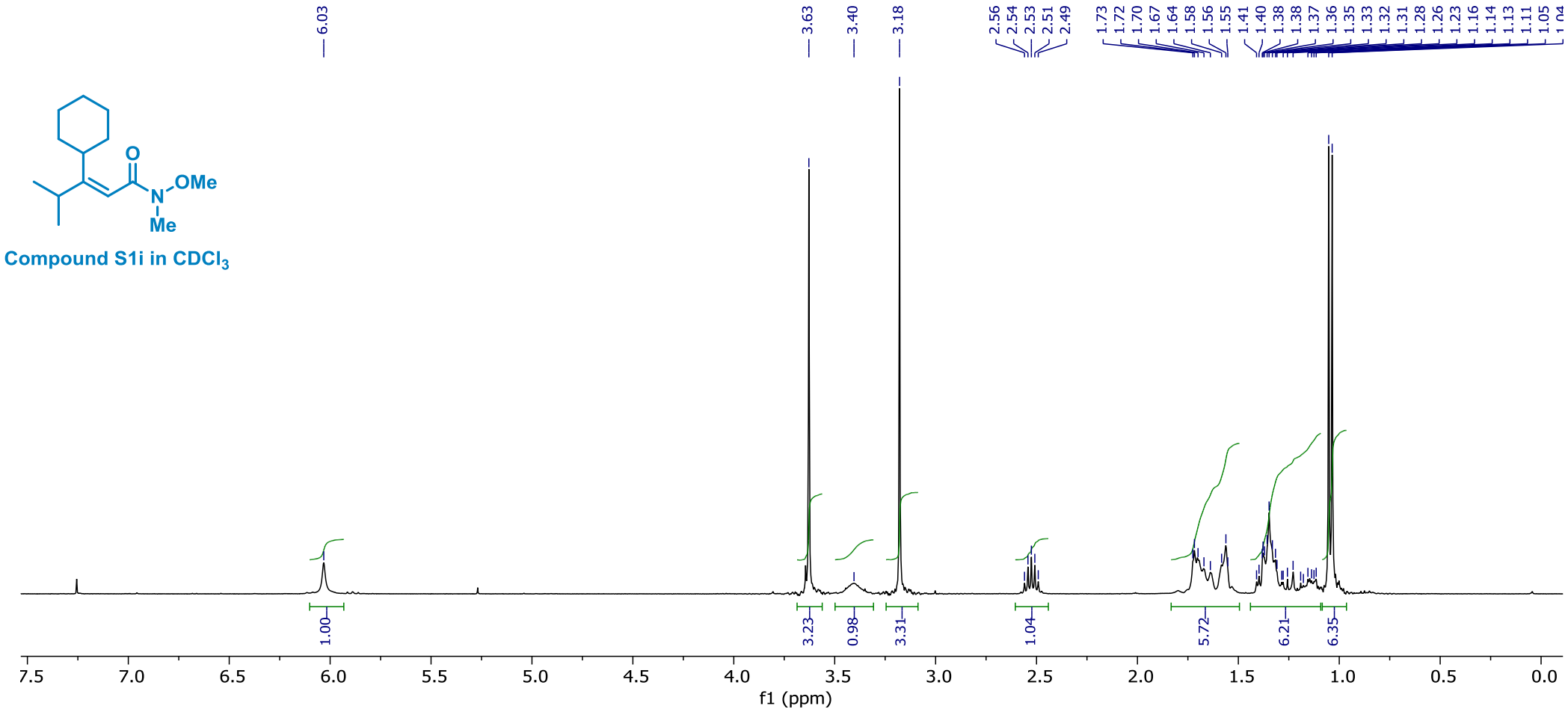


Compound S1e in $CDCl_3$

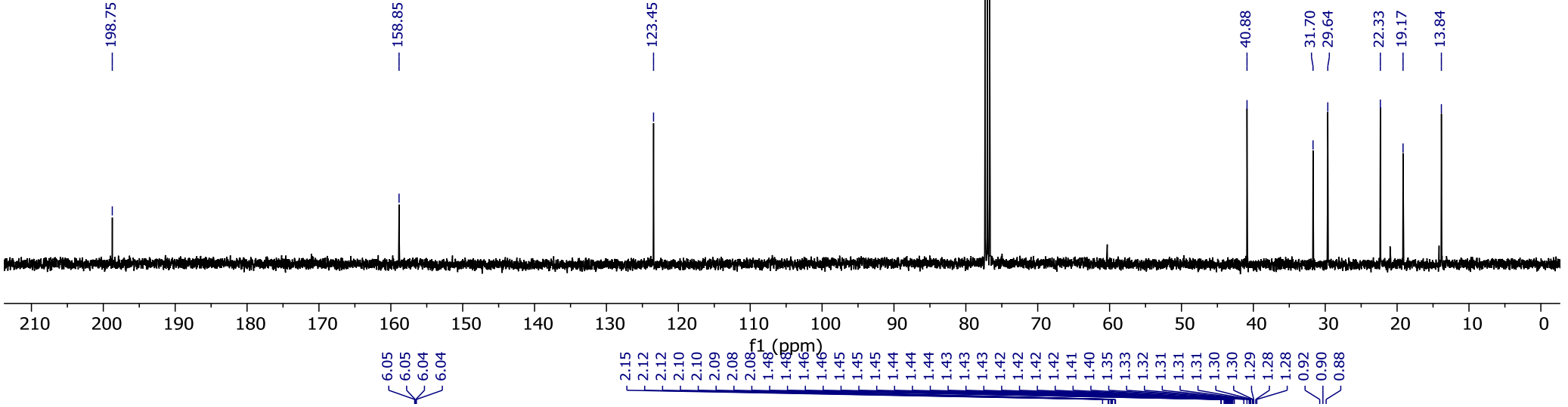

168.03
161.02
113.54
61.28
38.00
32.32
32.03
31.73
30.02
29.64
28.71
22.62
22.41
14.04
13.88
f1 (ppm)
6.04
3.65
3.17
2.55
2.53
2.53
2.52
2.51
2.15
2.15
2.13
2.13
2.13
2.11
2.11
1.46
1.45
1.44
1.44
1.43
1.42
1.42
1.41
1.40
1.35
1.34
1.33
1.32
1.31
1.30
1.29
1.29
1.28
1.27
1.26
1.25
1.24
0.92
0.90
0.88
0.87
0.86
0.85
O
N
OMe
Me
Compound S1g in CDCl3
1.00
3.10
3.10
2.07
2.07
12.63
6.30
f1 (ppm)

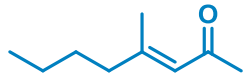

168.44
166.56
111.50
61.23
35.72
32.45
31.72
31.70
29.86
29.41
22.64
21.86
14.05
f1 (ppm)
6.06
3.65
3.18
2.53
2.52
2.51
2.50
2.49
2.41
2.41
2.39
2.39
2.37
2.37
2.36
2.35
2.34
2.34
1.47
1.46
1.46
1.45
1.45
1.45
1.45
1.44
1.44
1.43
1.42
1.42
1.41
1.40
1.35
1.35
1.35
1.34
1.34
1.33
1.33
1.33
1.32
1.32
1.31
1.31
1.31
1.30
1.29
1.28
1.28
1.27
1.26
1.25
1.24
1.24
1.08
1.07
1.06
1.06
1.05
0.88
0.87
0.86
0.86
0.85
0.85
0.84
0.84
O
N
OMe
Me
Compound S1h in CDCl3
1.00
3.10
3.07
2.01
1.06
2.10
6.39
6.13
3.19
f1 (ppm)



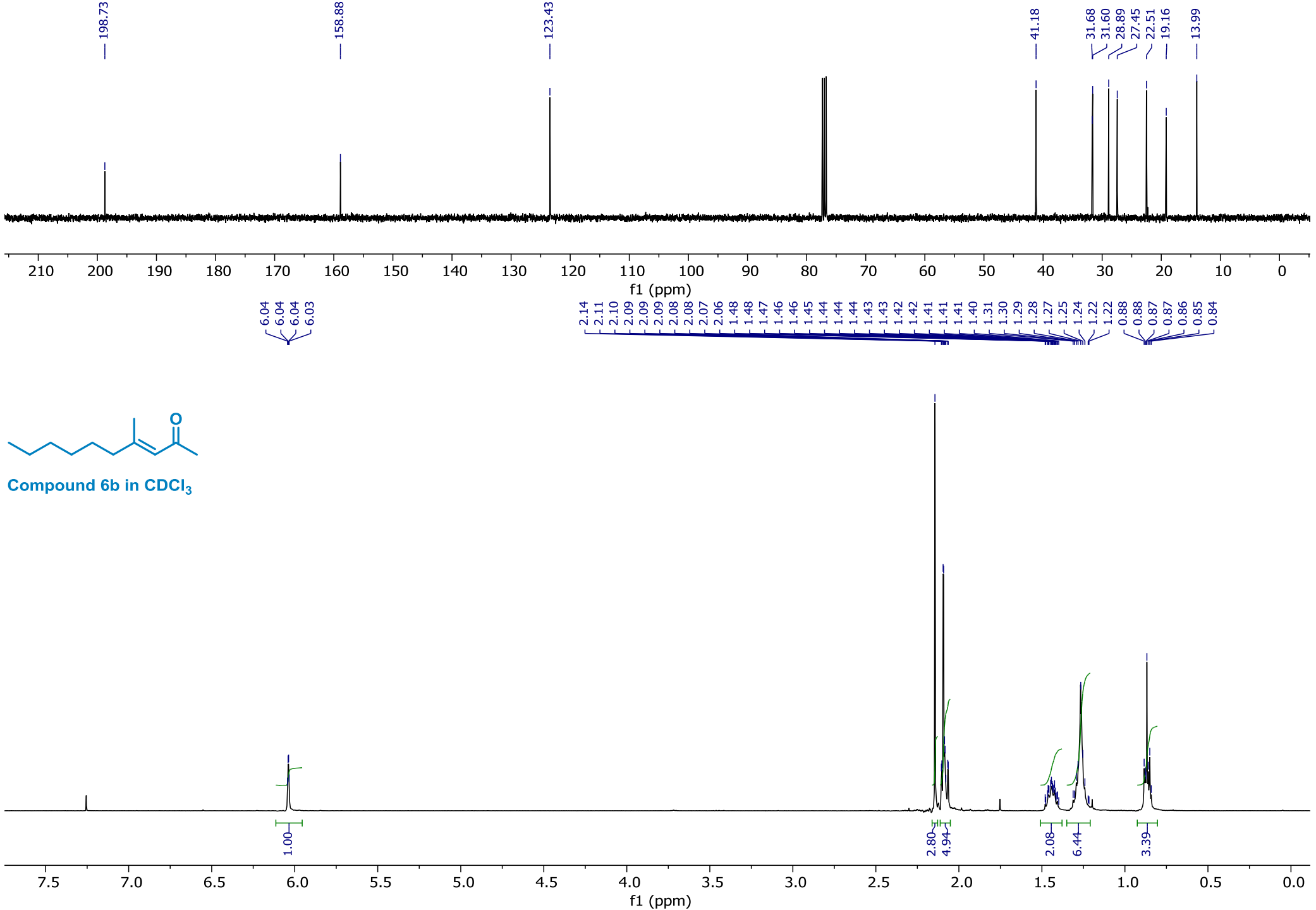


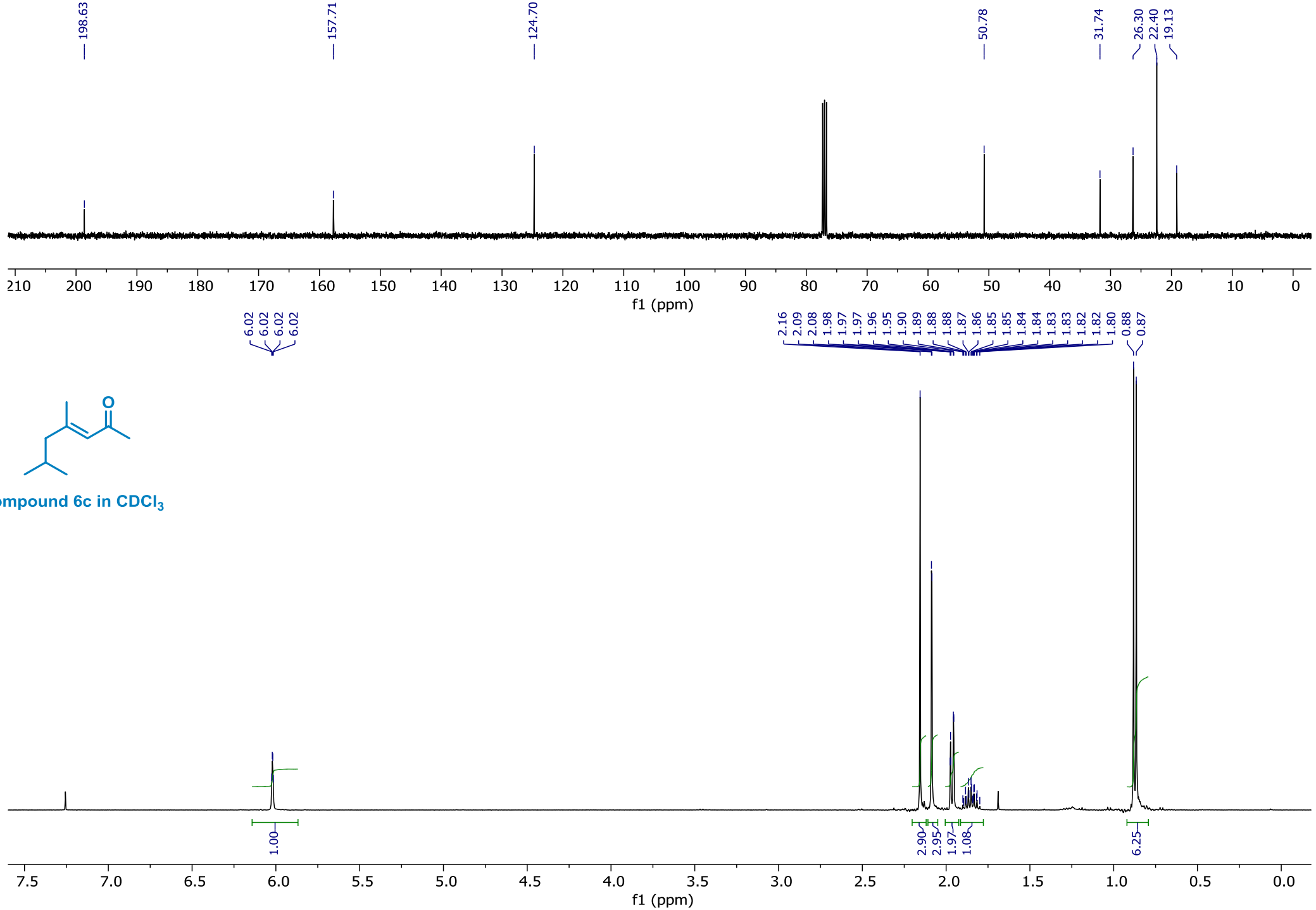
Compound S1i in $CDCl_3$



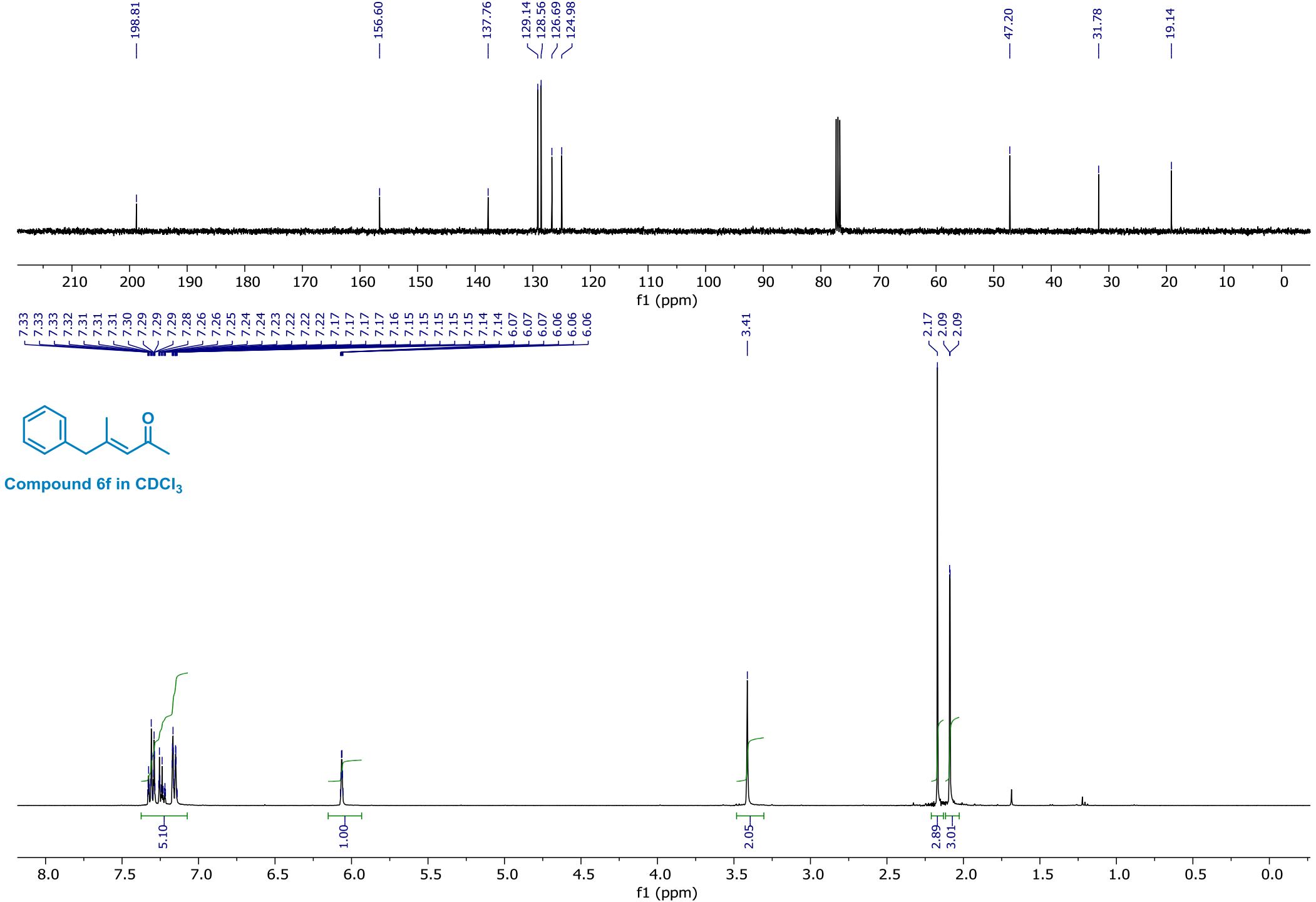


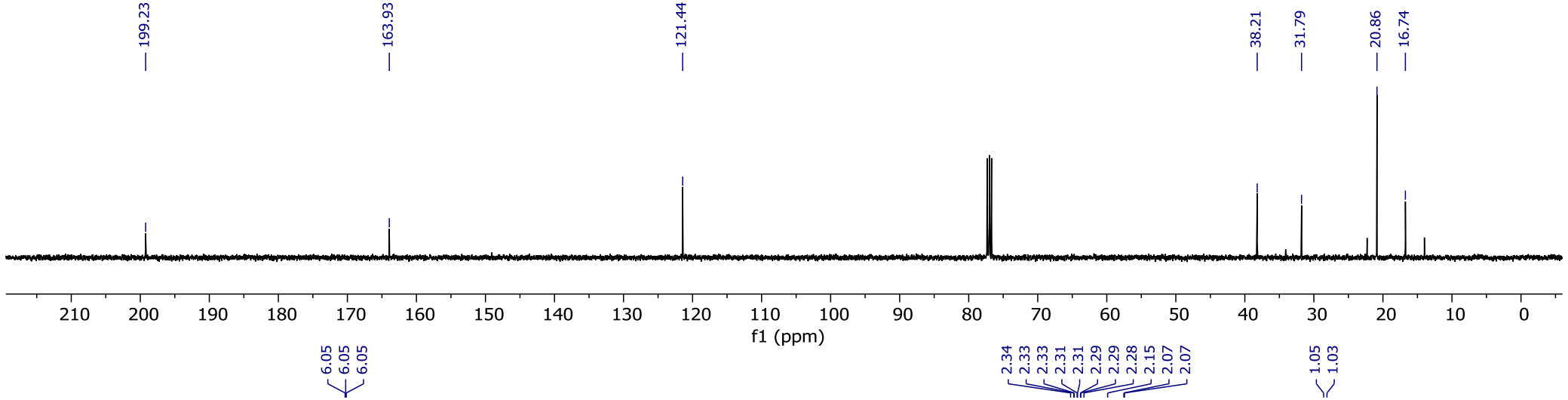
Compound 6a in $CDCl_3$

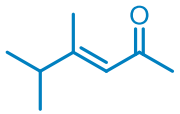

198.73
158.88
123.43
41.18
31.68
31.60
28.89
27.45
22.51
19.16
13.99
f1 (ppm)
6.04
6.04
6.04
6.03
2.14
2.11
2.10
2.09
2.09
2.09
2.08
2.08
2.07
2.06
1.48
1.48
1.47
1.46
1.46
1.45
1.44
1.44
1.44
1.43
1.43
1.42
1.42
1.41
1.41
1.41
1.40
1.31
1.30
1.29
1.28
1.27
1.25
1.24
1.22
1.22
0.88
0.88
0.87
0.87
0.86
0.85
0.84
O
Compound 6b in CDCl3
1.00
2.80
4.94
2.08
6.44
3.39
f1 (ppm)



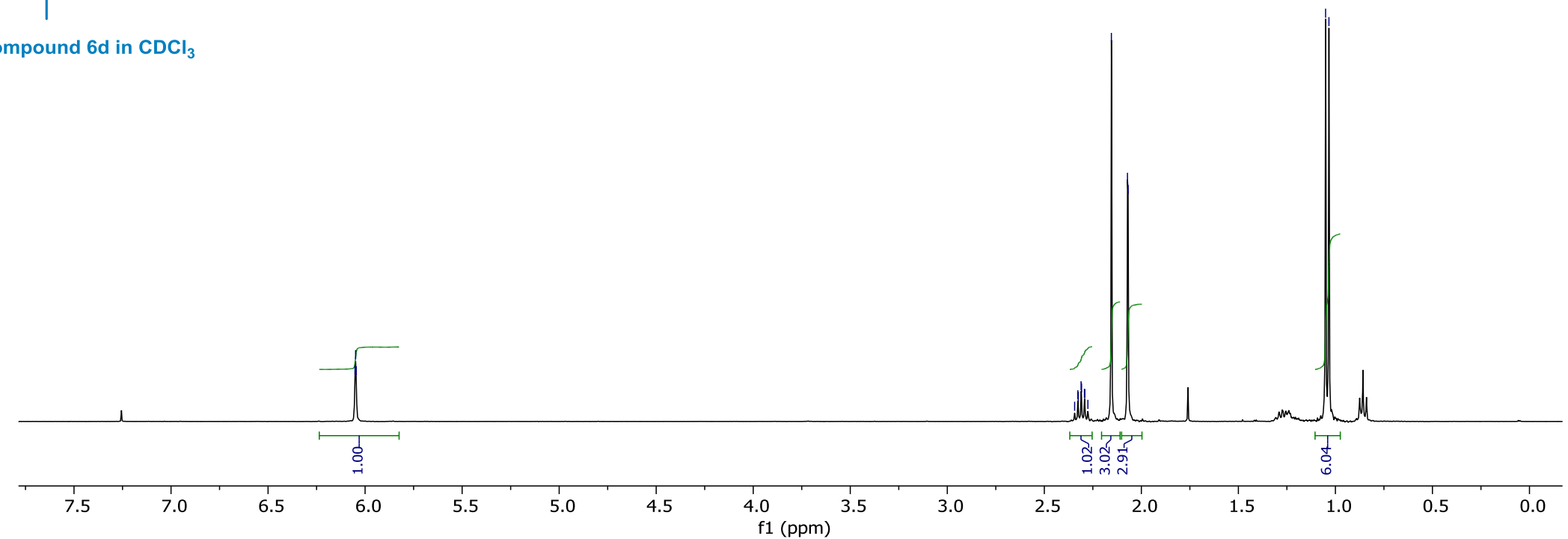
Compound 6c in $CDCl_3$

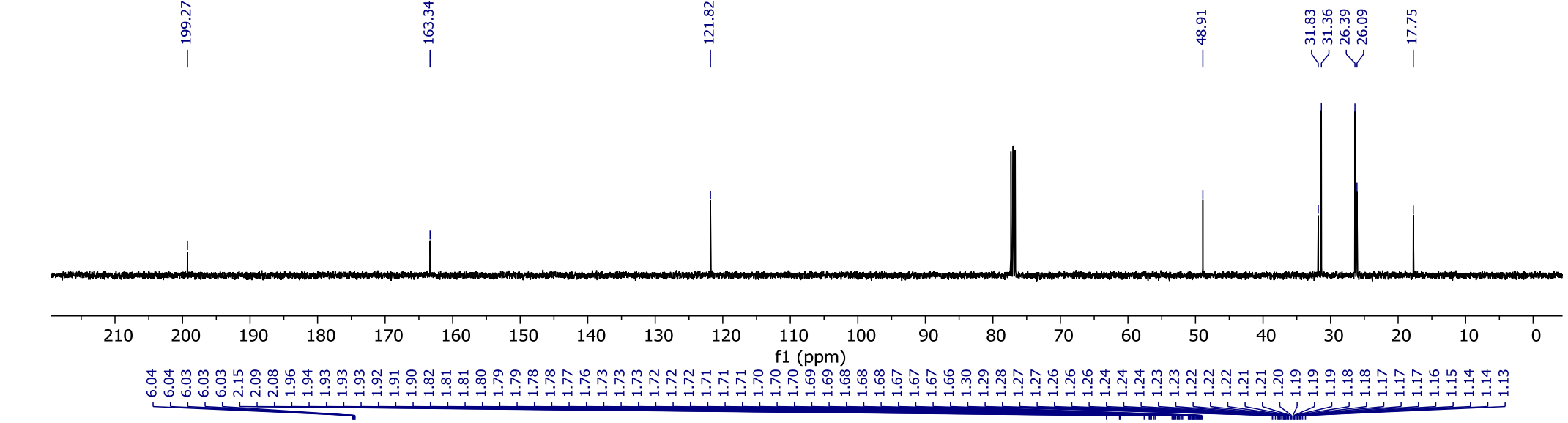

198.81
156.60
137.76
129.14
128.56
126.69
124.98
47.20
31.78
19.14
f1 (ppm)
7.33
7.33
7.33
7.32
7.31
7.31
7.31
7.30
7.29
7.29
7.29
7.28
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.22
7.17
7.17
7.17
7.17
7.16
7.15
7.15
7.15
7.15
7.14
7.14
6.07
6.07
6.06
6.06
6.06
3.41
2.17
2.09
2.09
O
Compound 6f in CDCl3
5.10
1.00
2.05
2.89
3.01
f1 (ppm)

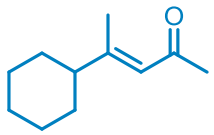




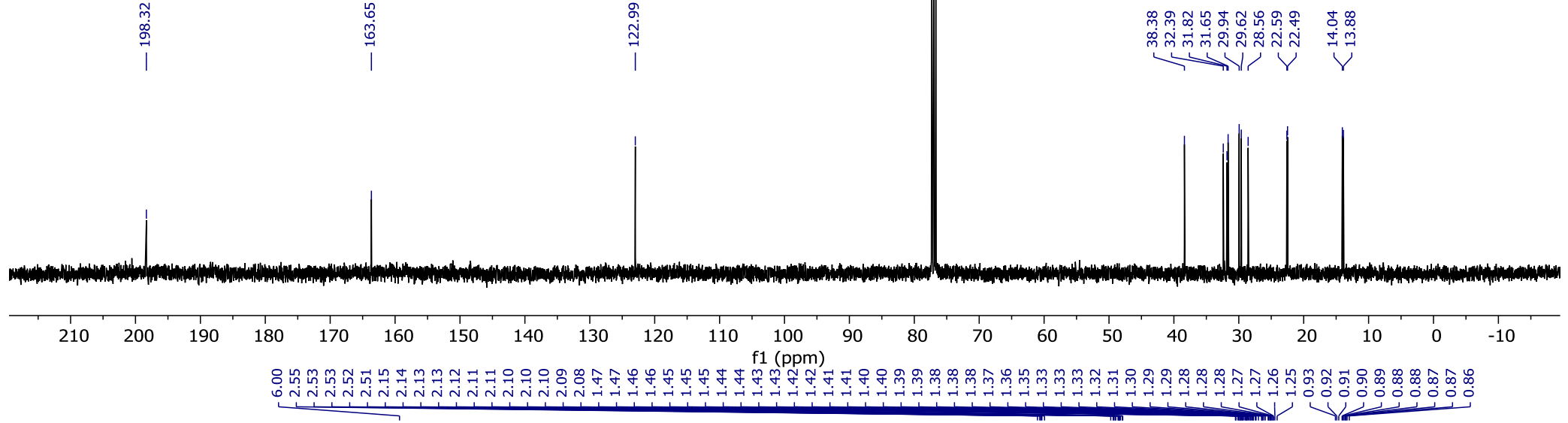
Compound 6d in $CDCl_3$

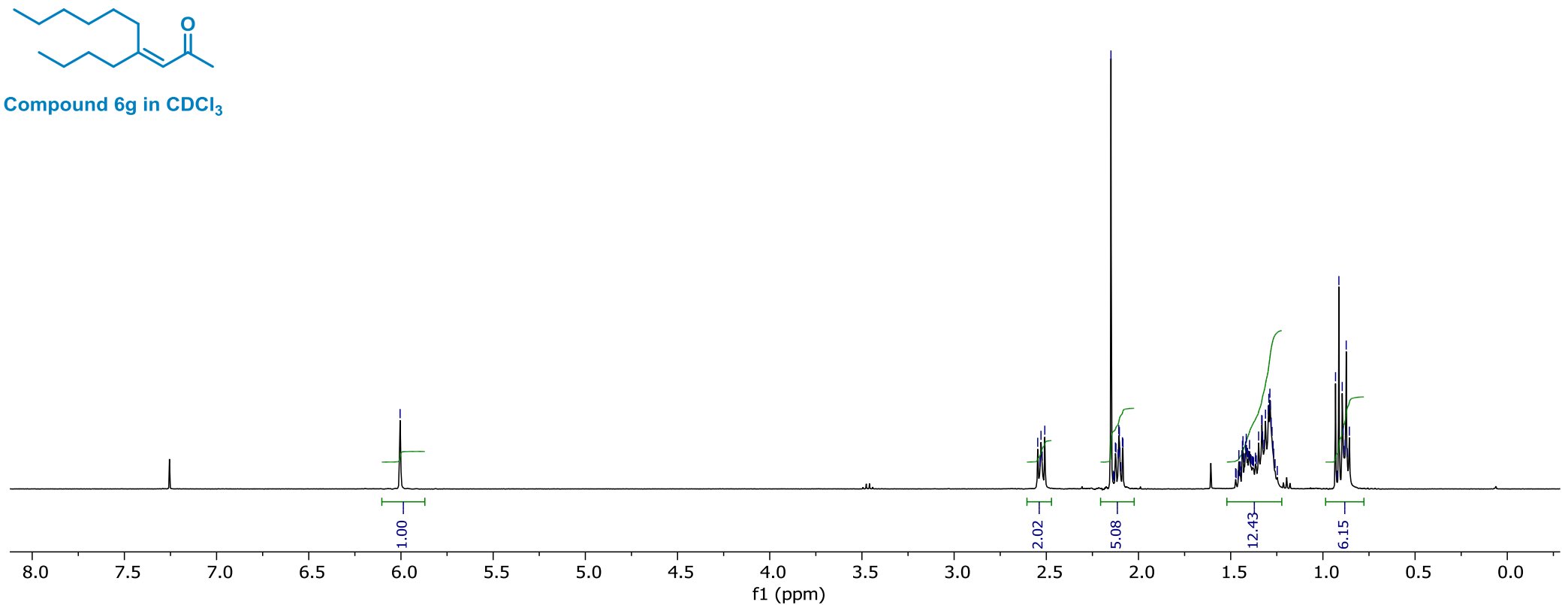




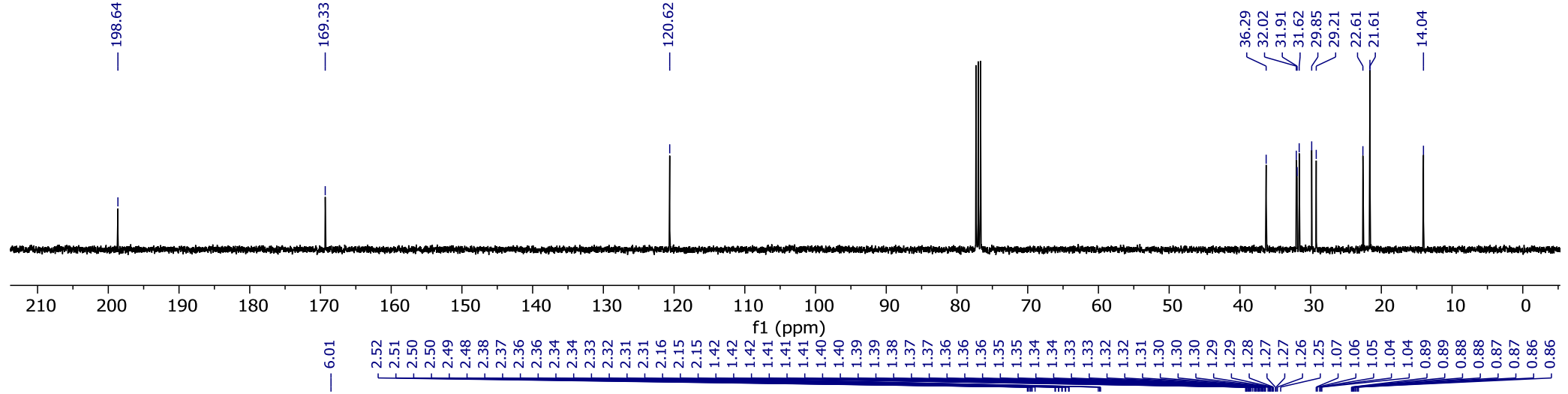


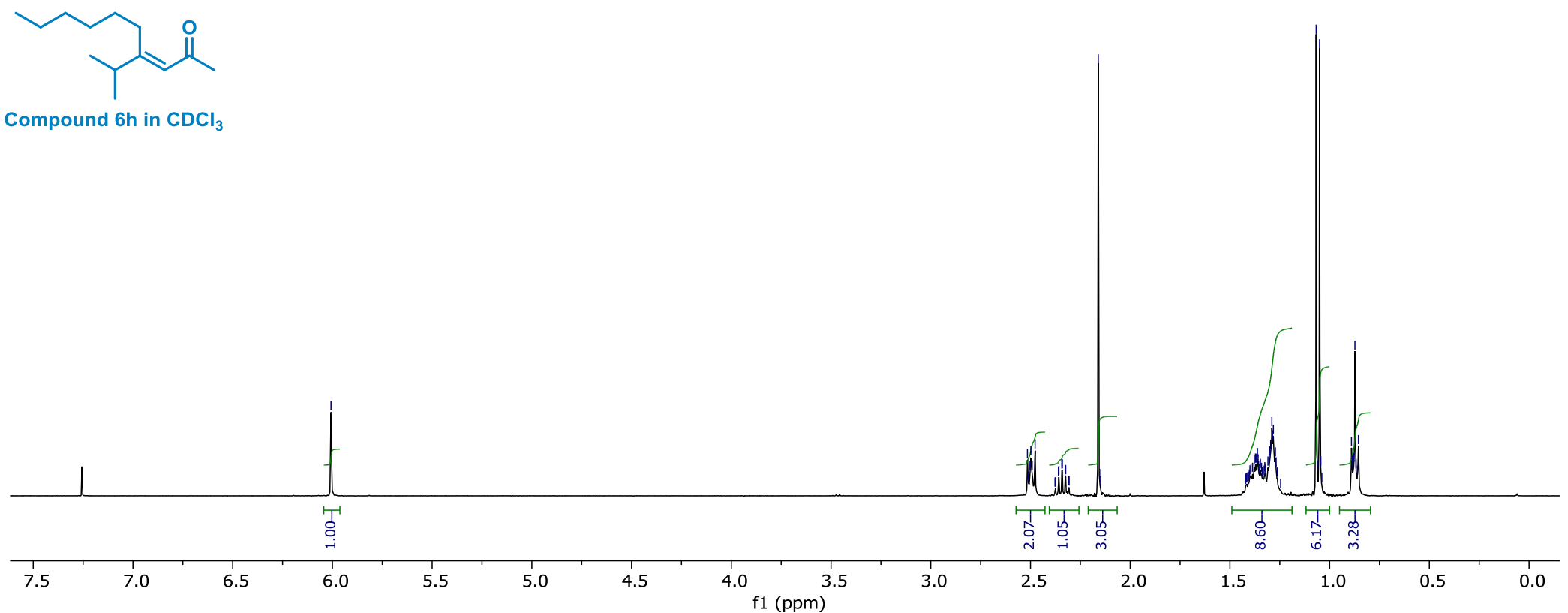
Compound 6e in $CDCl_3$



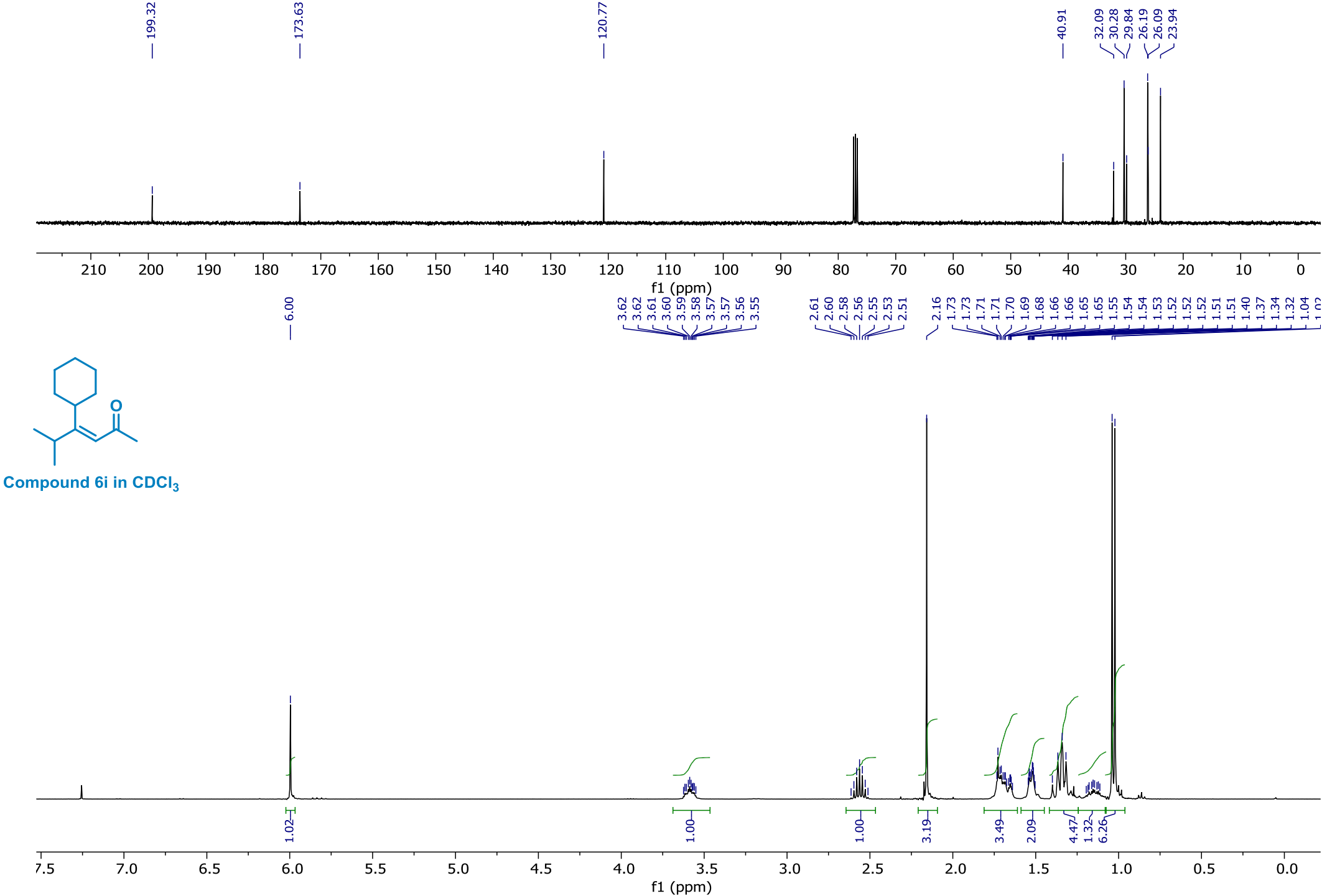


Compound 6g in $CDCl_3$

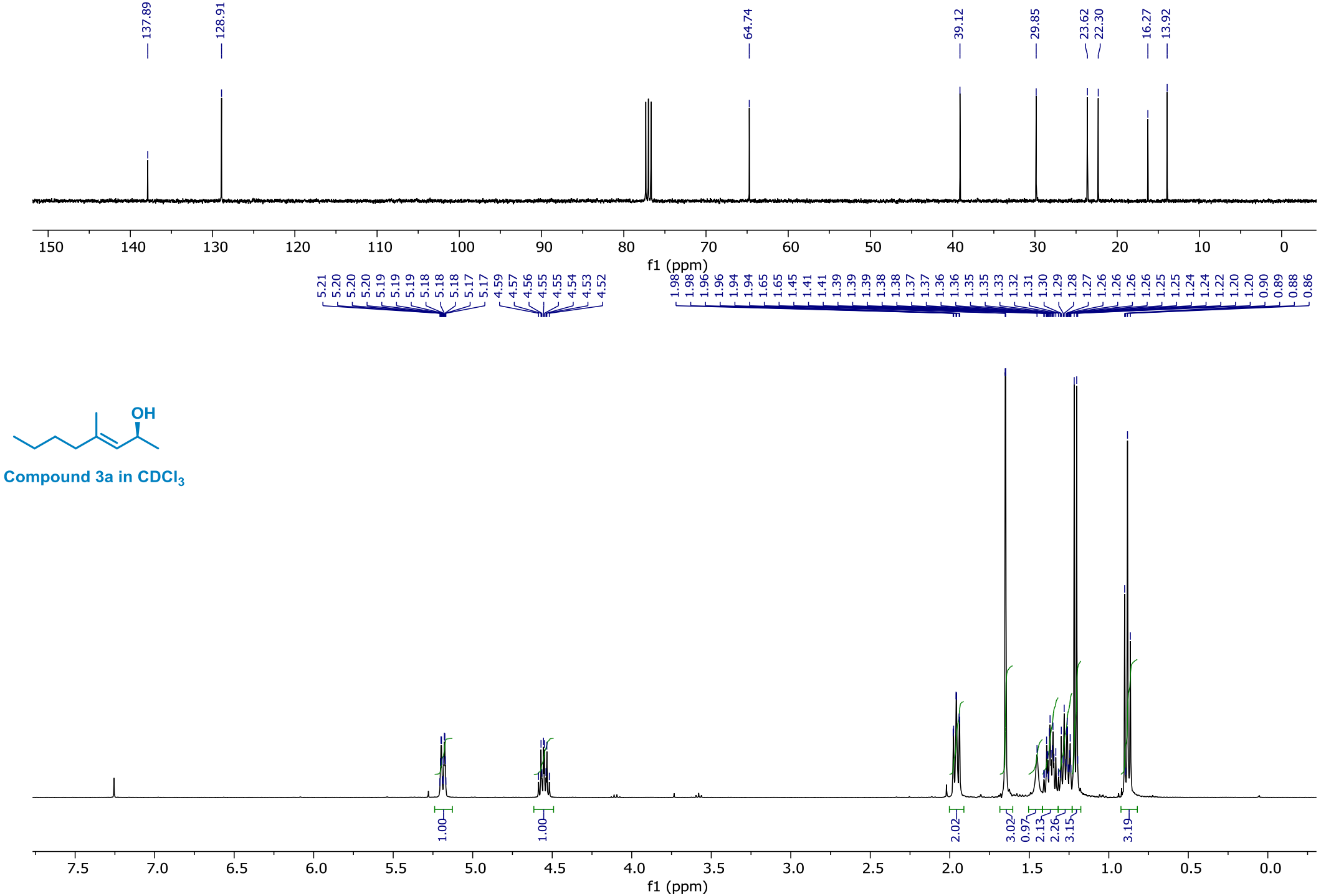




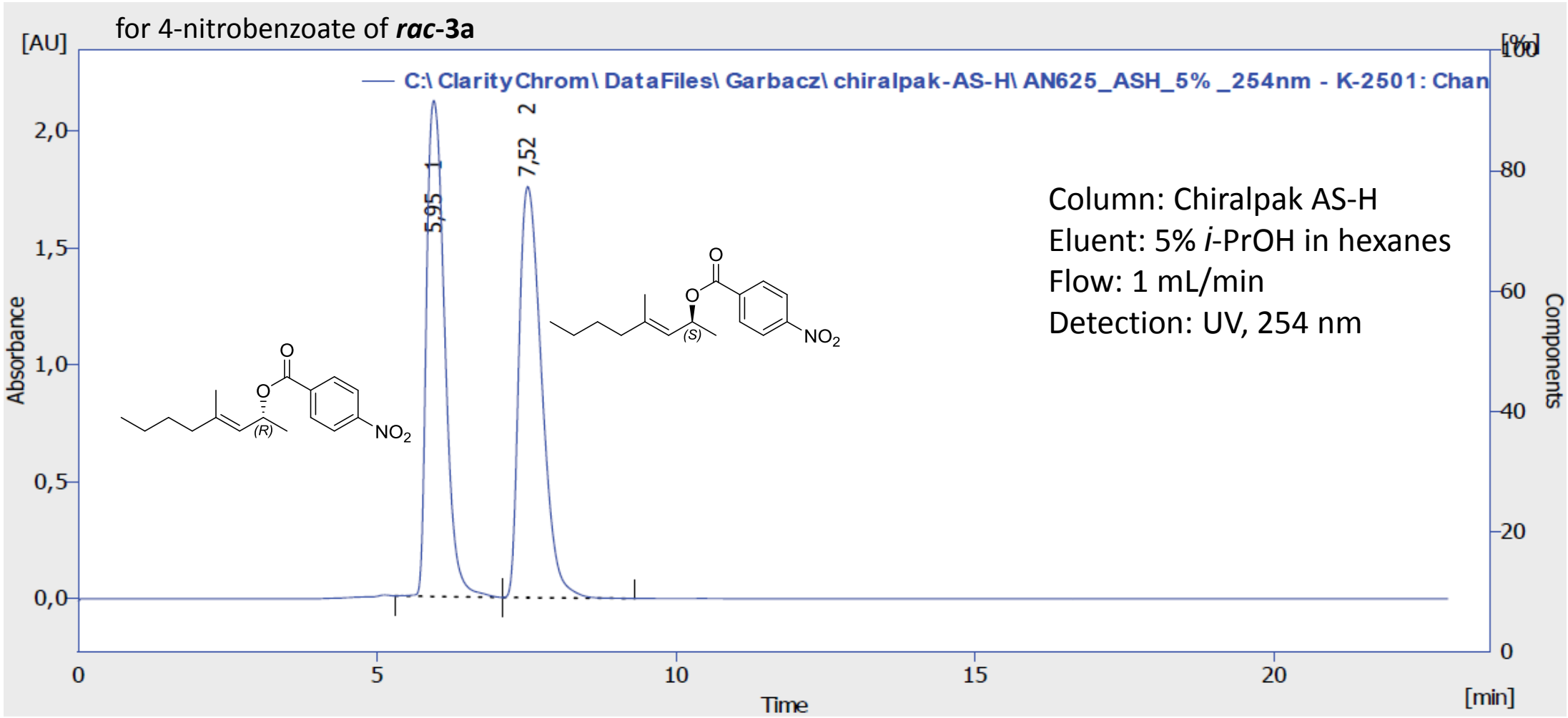
Compound 6h in $CDCl_3$



Compound 6i in $CDCl_3$


137.89
128.91
64.74
39.12
29.85
23.62
22.30
16.27
13.92
f1 (ppm)
OH
Compound 3a in CDCl3
1.00
1.00
2.02
3.02
0.97
2.13
2.26
3.15
3.19
f1 (ppm)

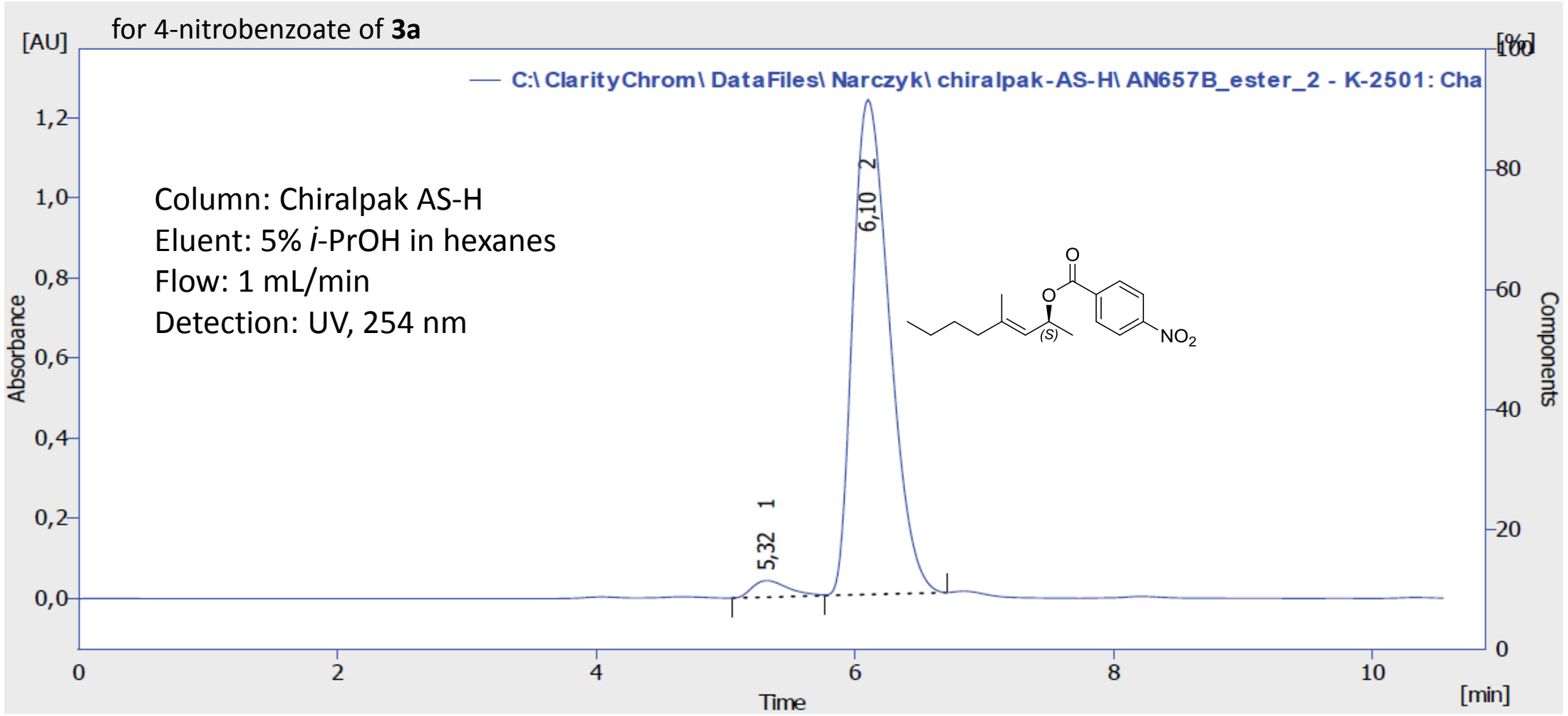
for 4-nitrobenzoate of ***rac*-3a**



Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Garbacz\|chiralpak-AS-H\|AN625_ASH_5%_254nm - K-2501: Channel 1)

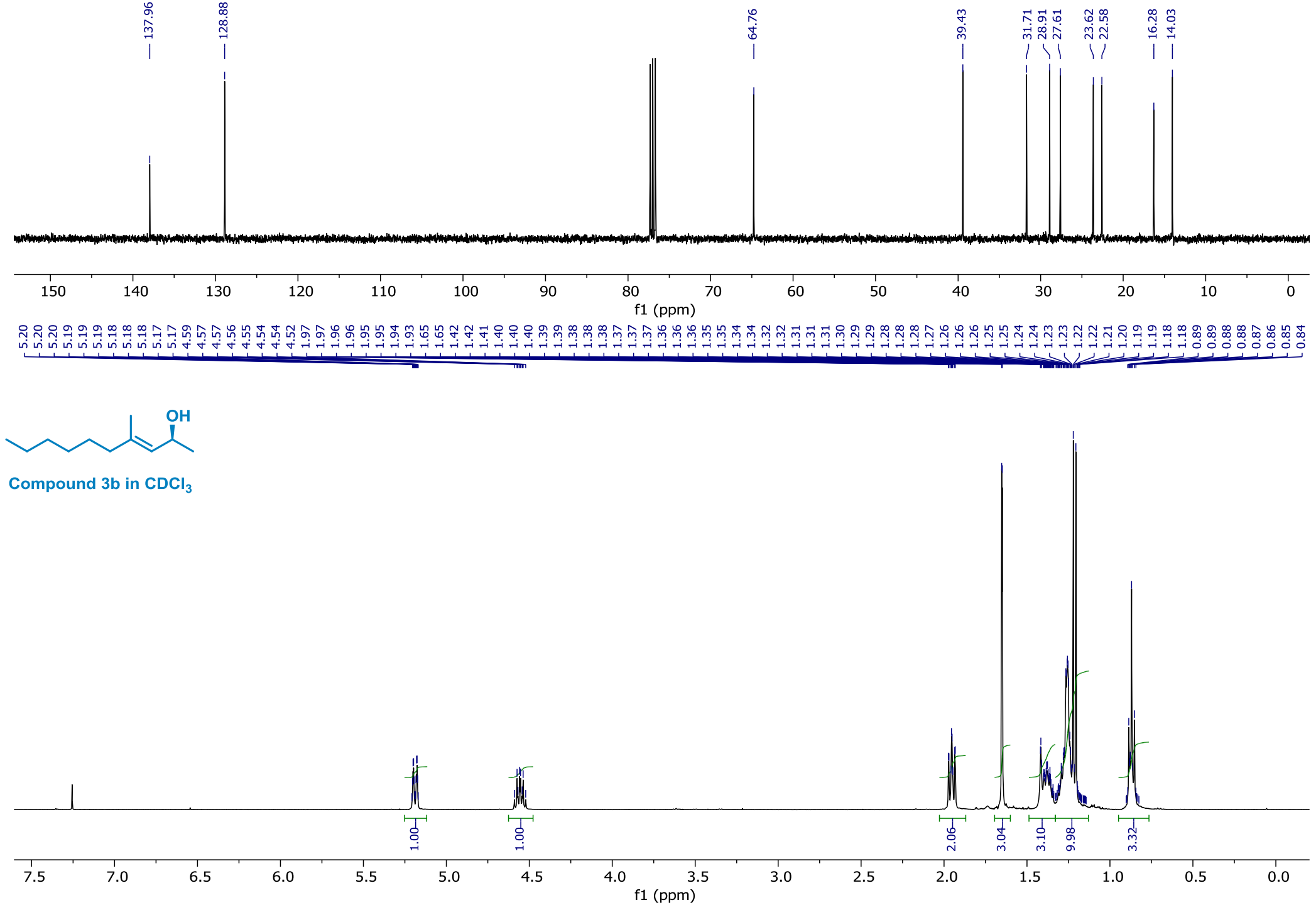
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5,950	44767,975	2121,819	49,2	54,7	0,35	
2	7,517	46262,793	1759,162	50,8	45,3	0,43	
	Total	91030,768	3880,980	100,0	100,0		

for 4-nitrobenzoate of **3a**

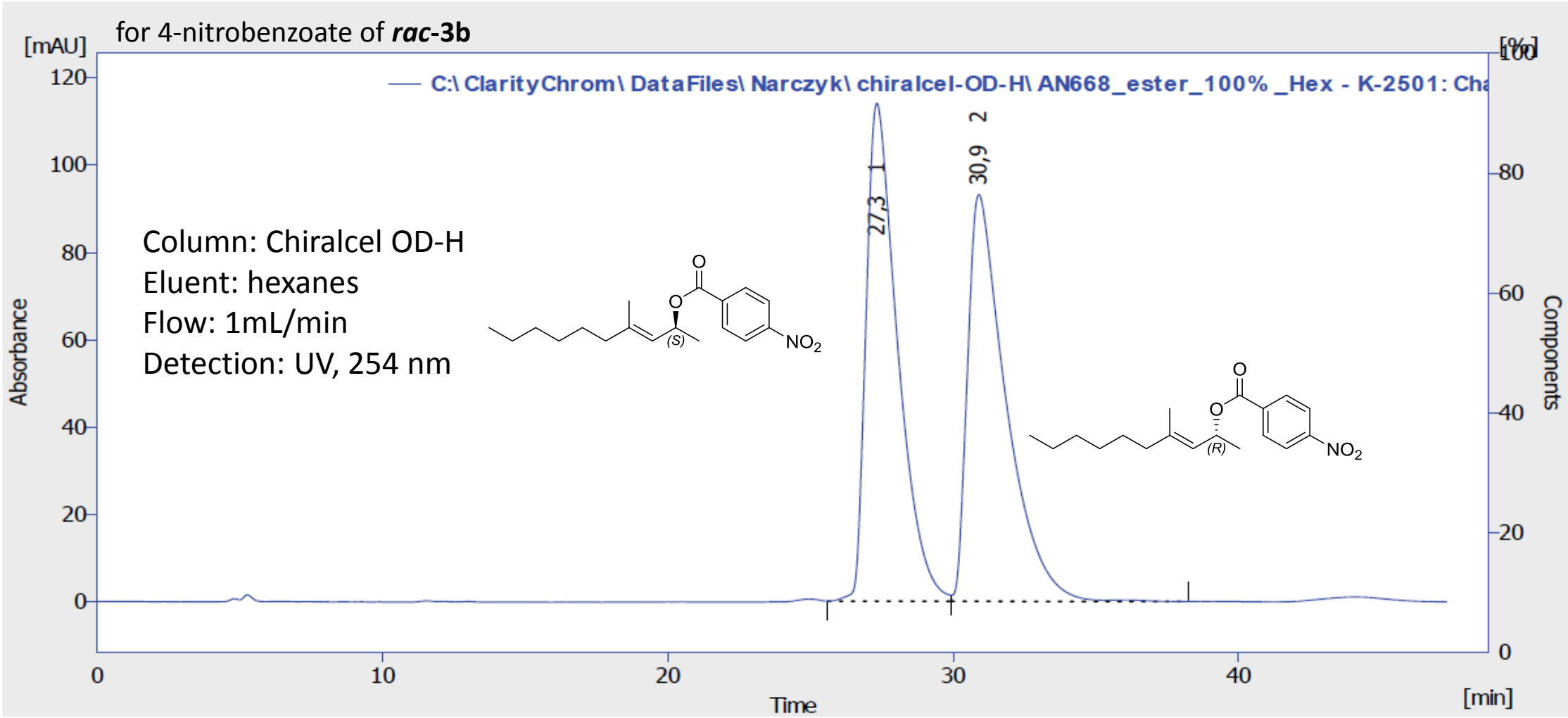


Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralpak-AS-H\|AN657B_ester_2 - K-2501: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5,317	797,080	41,276	3,2	3,2	0,33	
2	6,100	24335,231	1235,657	96,8	96,8	0,32	
	Total	25132,311	1276,934	100,0	100,0		


137.96
128.88
64.76
39.43
31.71
28.91
27.61
23.62
22.58
16.28
14.03
f1 (ppm)
OH
Compound 3b in CDCl3
1.00
1.00
2.06
3.04
3.10
9.98
3.32
f1 (ppm)

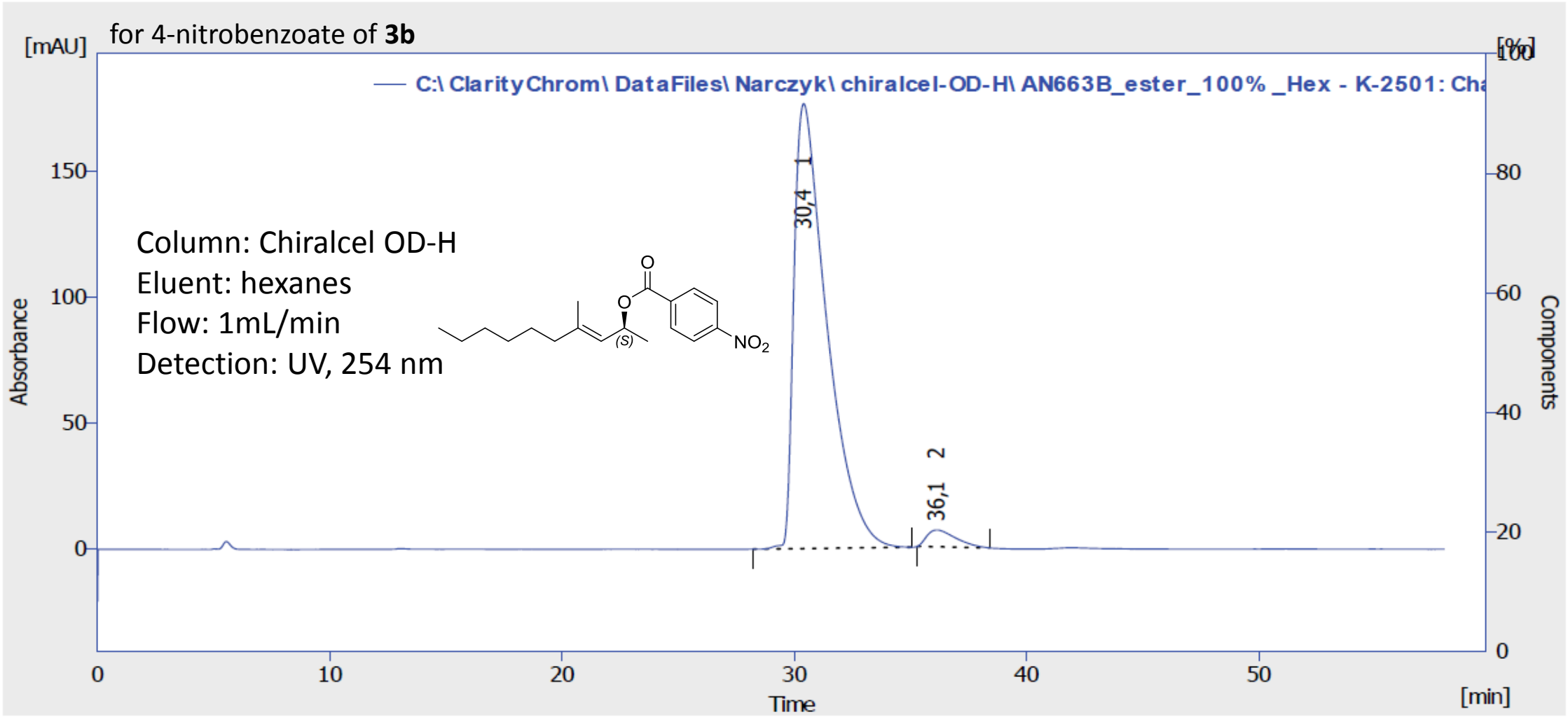
for 4-nitrobenzoate of ***rac*-3b**



Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN668_ester_100%_Hex - K-2501: Channel 1)

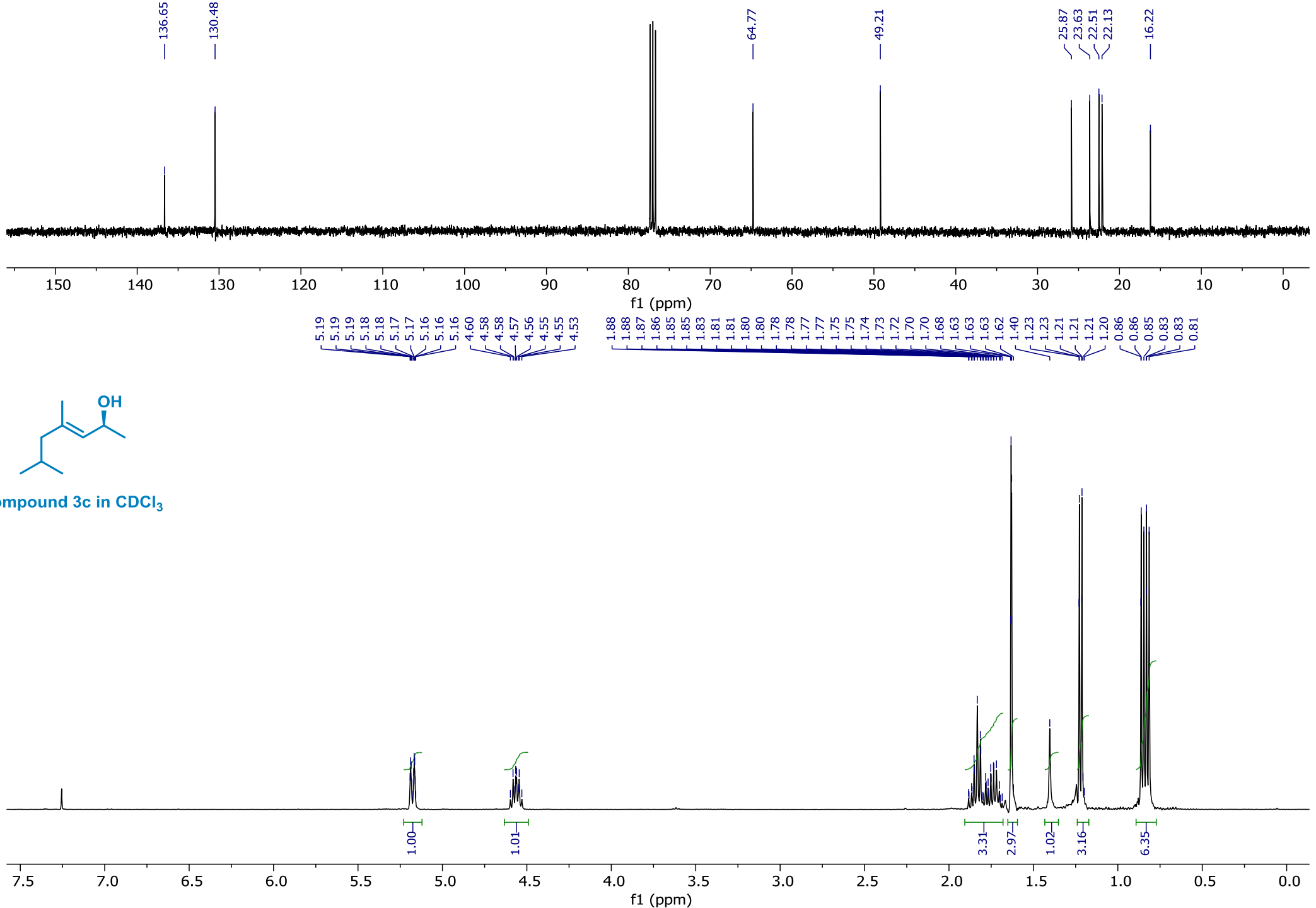
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	27,333	8775,738	114,167	50,0	55,0	1,18	
2	30,900	8768,887	93,255	50,0	45,0	1,40	
	Total	17544,625	207,422	100,0	100,0		

for 4-nitrobenzoate of **3b**

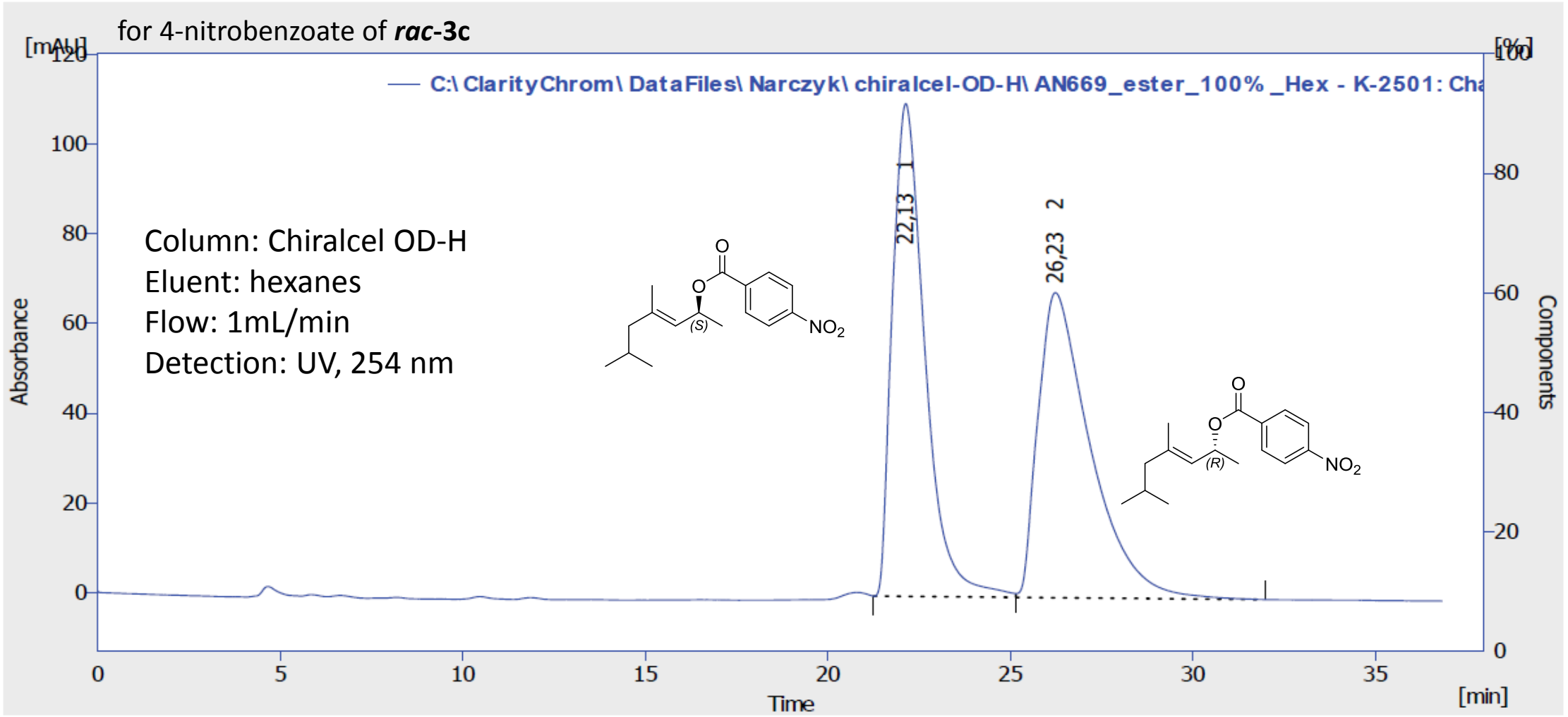


Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN663B_ester_100%_Hex - K-2501: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	30,400	17356,062	176,363	96,8	96,4	1,48	
2	36,133	576,797	6,642	3,2	3,6	1,38	
	Total	17932,859	183,005	100,0	100,0		


136.65
130.48
64.77
49.21
25.87
23.63
22.51
22.13
16.22
f1 (ppm)
OH
Compound 3c in CDCl3
1.00
1.01
3.31
2.97
1.02
3.16
6.35
f1 (ppm)

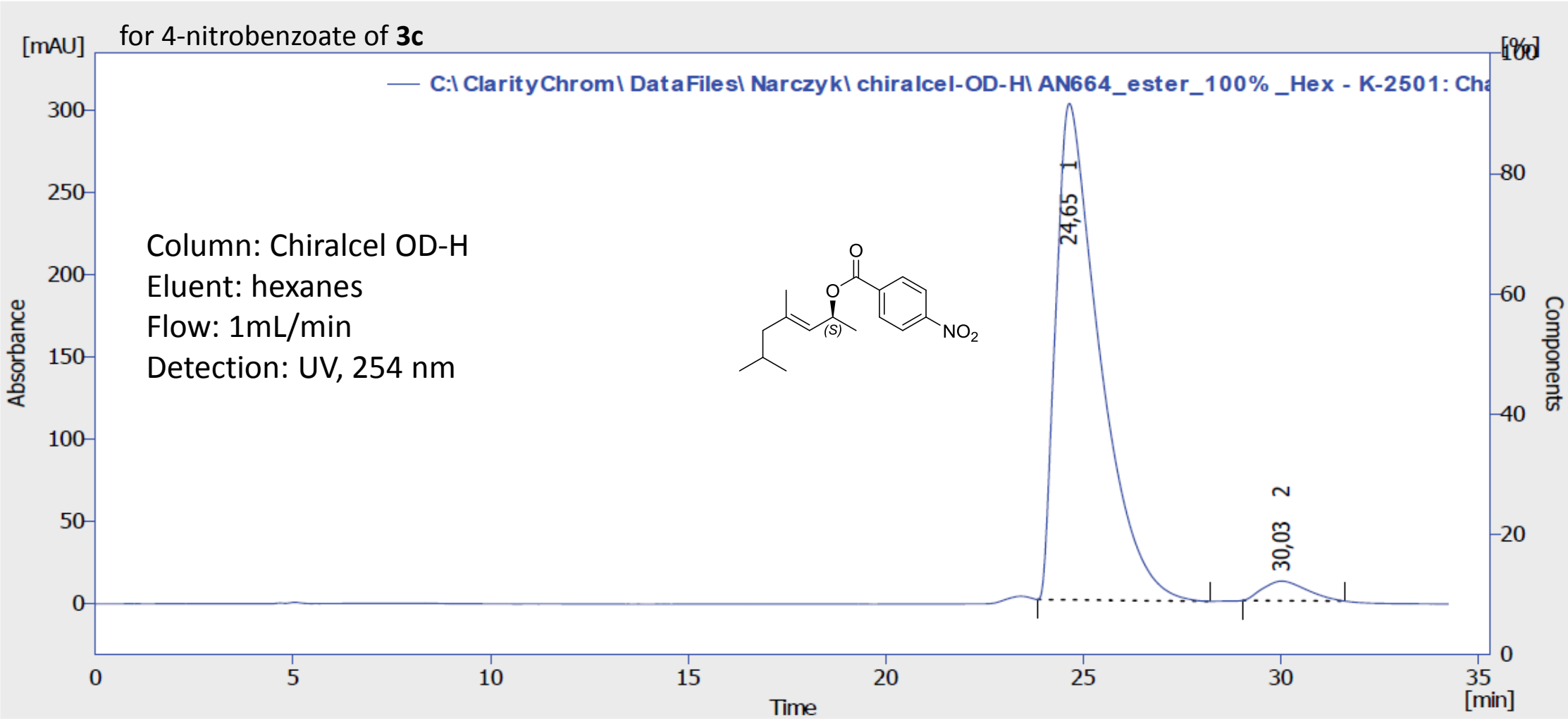
for 4-nitrobenzoate of ***rac*-3c**



Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN669_ester_100%_Hex - K-2501: Channel 1)

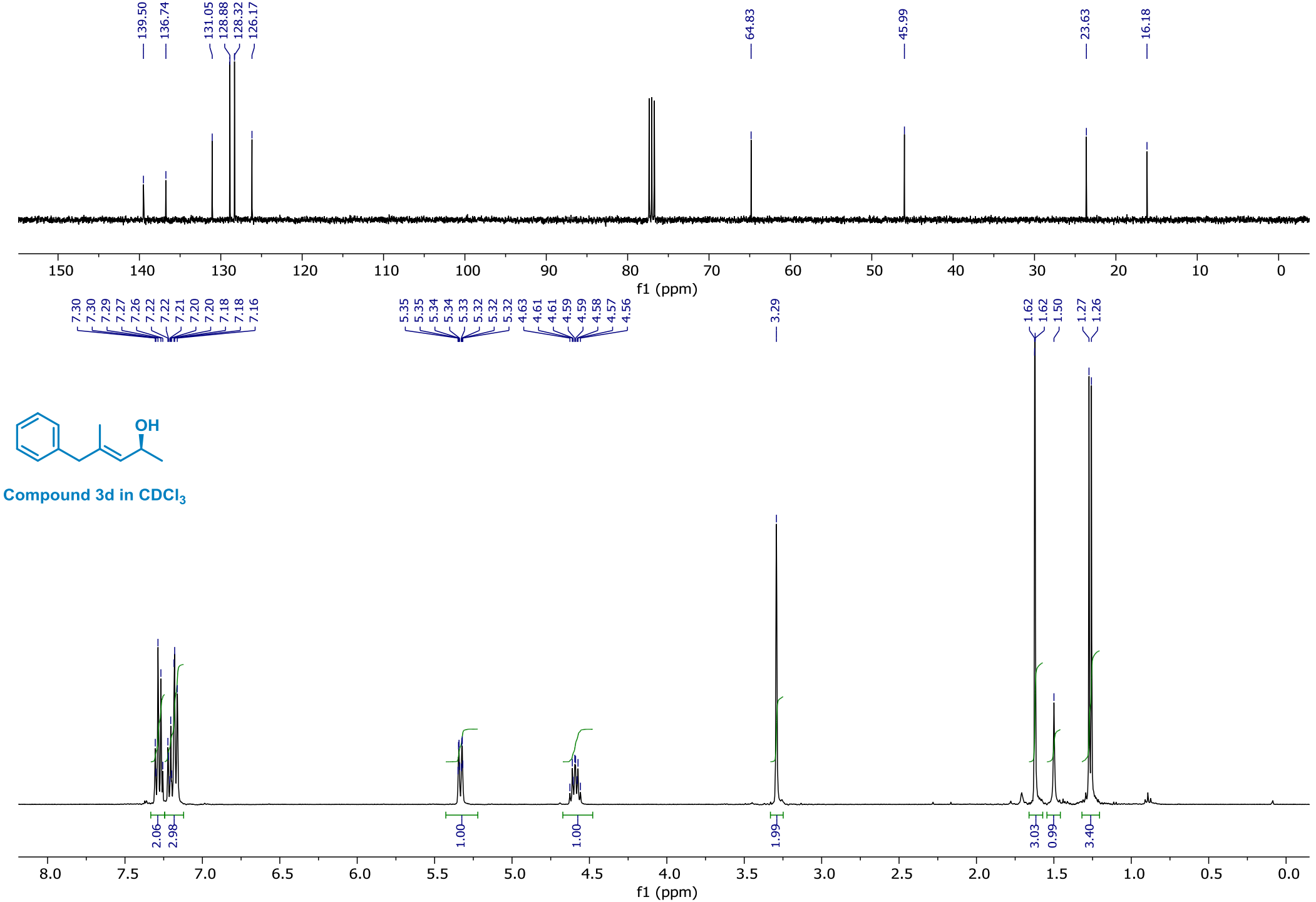
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	22,133	6795,309	109,858	50,0	61,8	0,97	
2	26,233	6792,114	68,008	50,0	38,2	1,52	
	Total	13587,424	177,866	100,0	100,0		

for 4-nitrobenzoate of **3c**

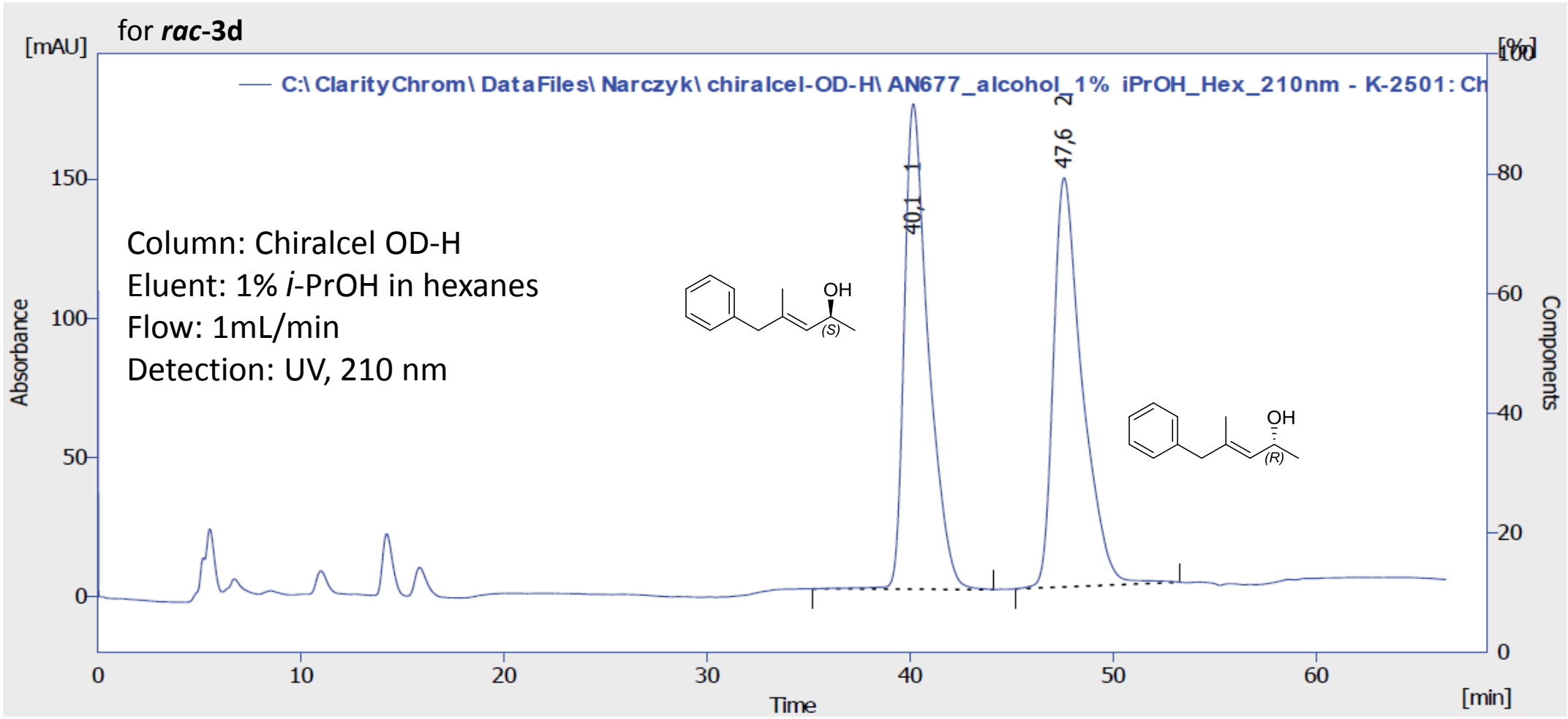


Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN664_ester_100%_Hex - K-2501: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	24,650	23134,109	301,574	96,2	96,2	1,18	
2	30,033	920,188	11,876	3,8	3,8	1,28	
	Total	24054,297	313,450	100,0	100,0		


139.50
136.74
131.05
128.88
128.32
126.17
64.83
45.99
23.63
16.18
f1 (ppm)
7.30
7.30
7.29
7.27
7.26
7.22
7.22
7.21
7.20
7.20
7.18
7.18
7.16
5.35
5.35
5.34
5.34
5.33
5.32
5.32
5.32
4.63
4.61
4.61
4.59
4.59
4.58
4.57
4.56
3.29
1.62
1.62
1.50
1.27
1.26
OH
Compound 3d in CDCl3
2.06
2.98
1.00
1.00
1.99
3.03
0.99
3.40
f1 (ppm)

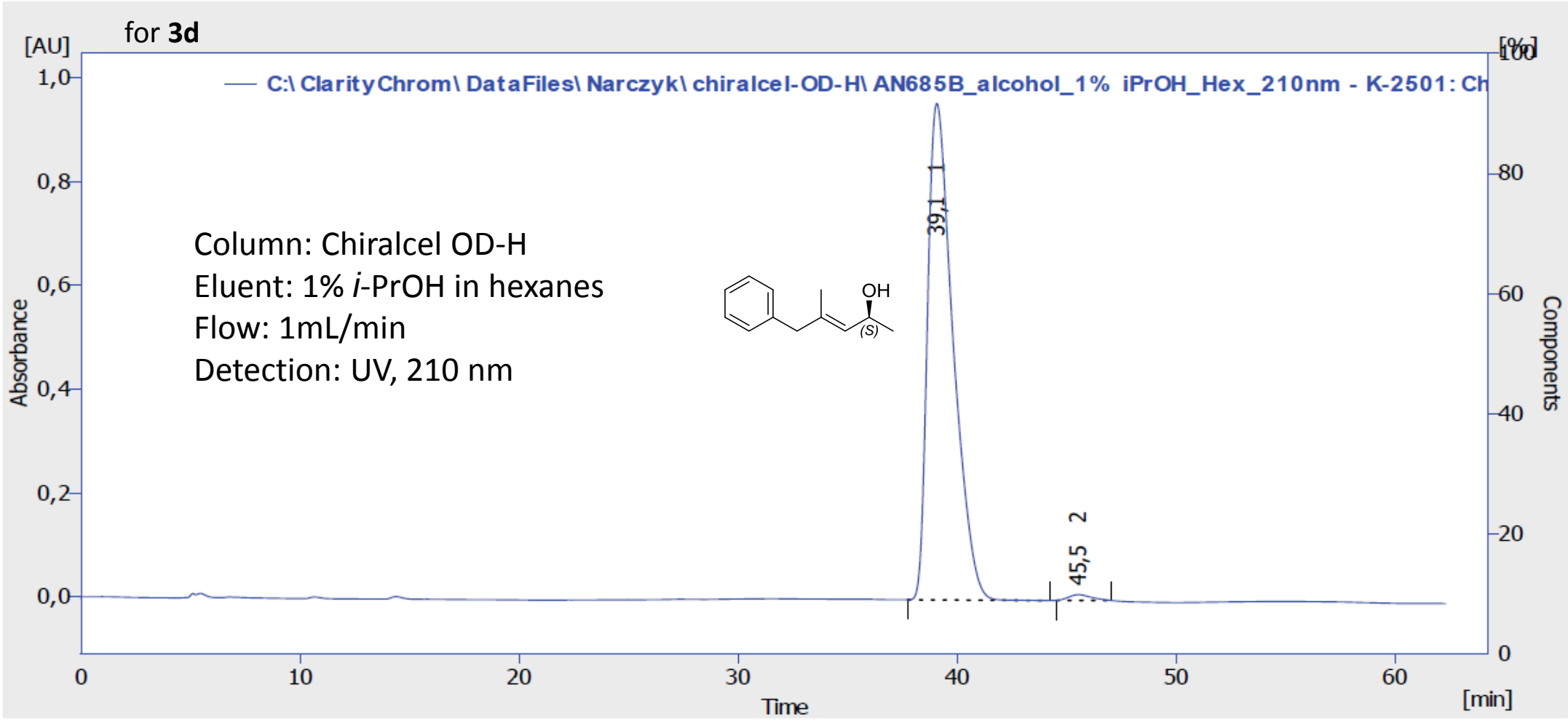
for ***rac*-3d**



Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN677_alcohol_1% iPrOH_Hex_210nm - K-2501: Channel 1)

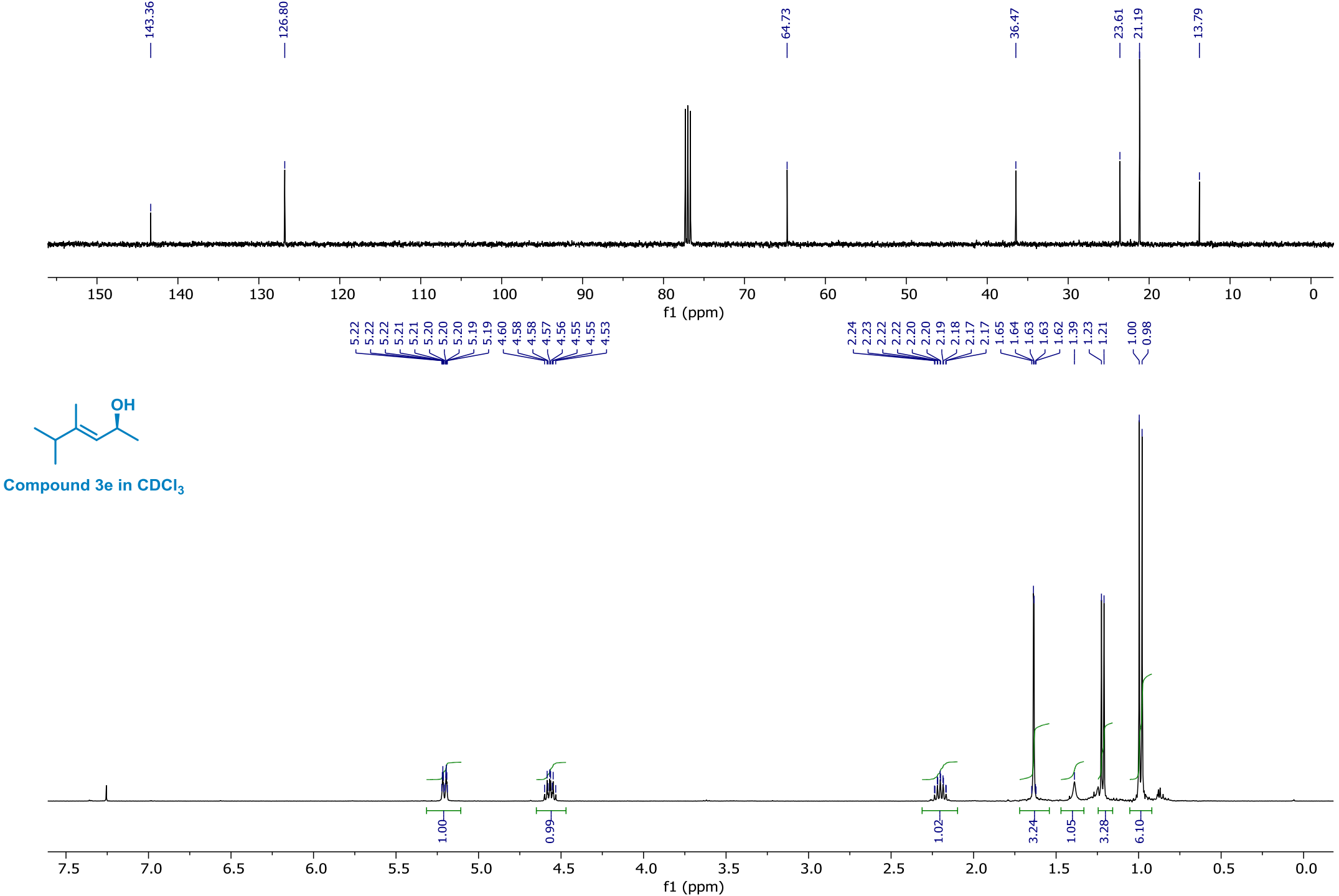
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	40,150	14400,527	174,180	49,8	54,3	1,23	
2	47,583	14512,956	146,834	50,2	45,7	1,47	
	Total	28913,482	321,014	100,0	100,0		

for **3d**

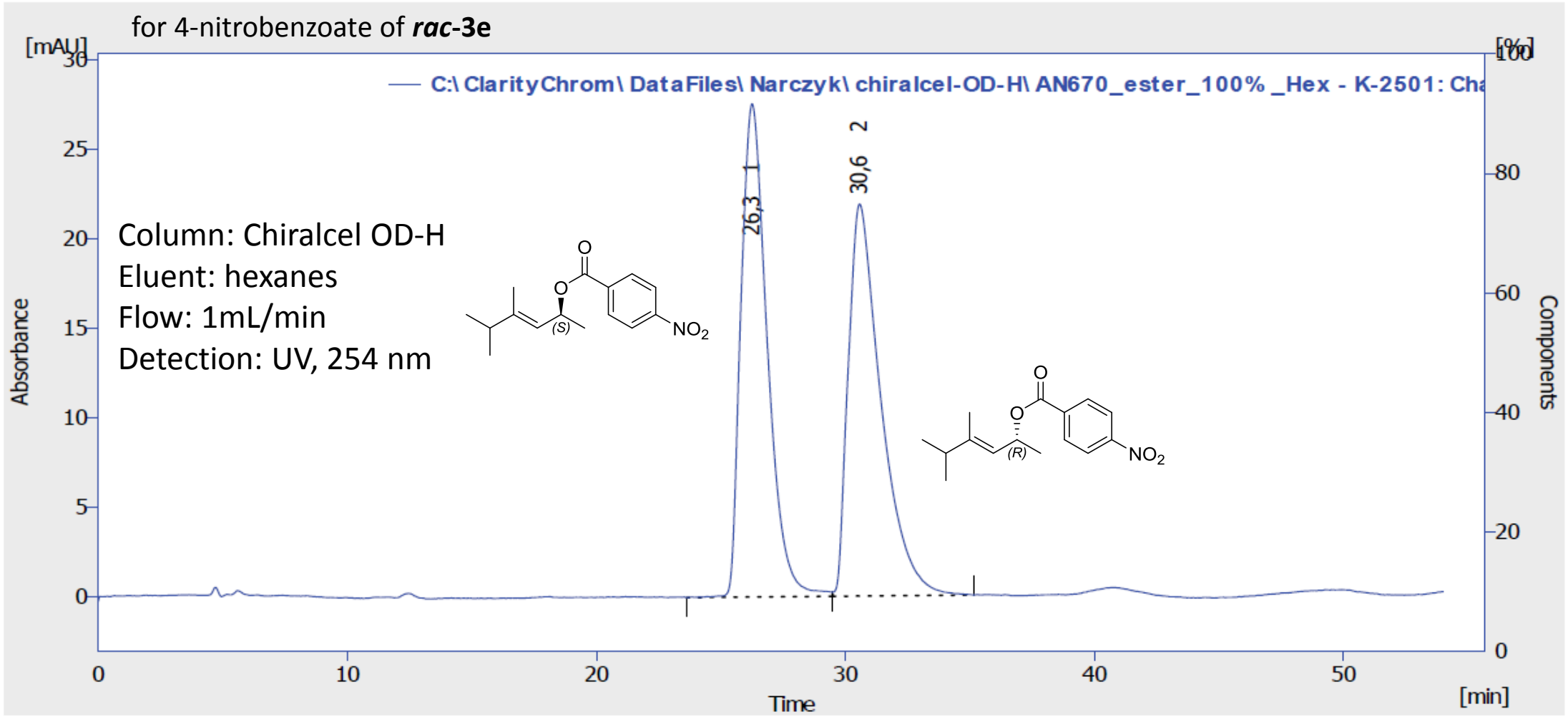


Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN685B_alcohol_1% iPrOH_Hex_210nm - K-2501: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	39,083	77222,401	957,204	99,0	98,9	1,25	
2	45,550	801,594	11,074	1,0	1,1	1,15	
	Total	78023,995	968,278	100,0	100,0		


143.36
126.80
64.73
36.47
23.61
21.19
13.79
f1 (ppm)
OH
Compound 3e in CDCl3
1.00
0.99
1.02
3.24
1.05
3.28
6.10
f1 (ppm)

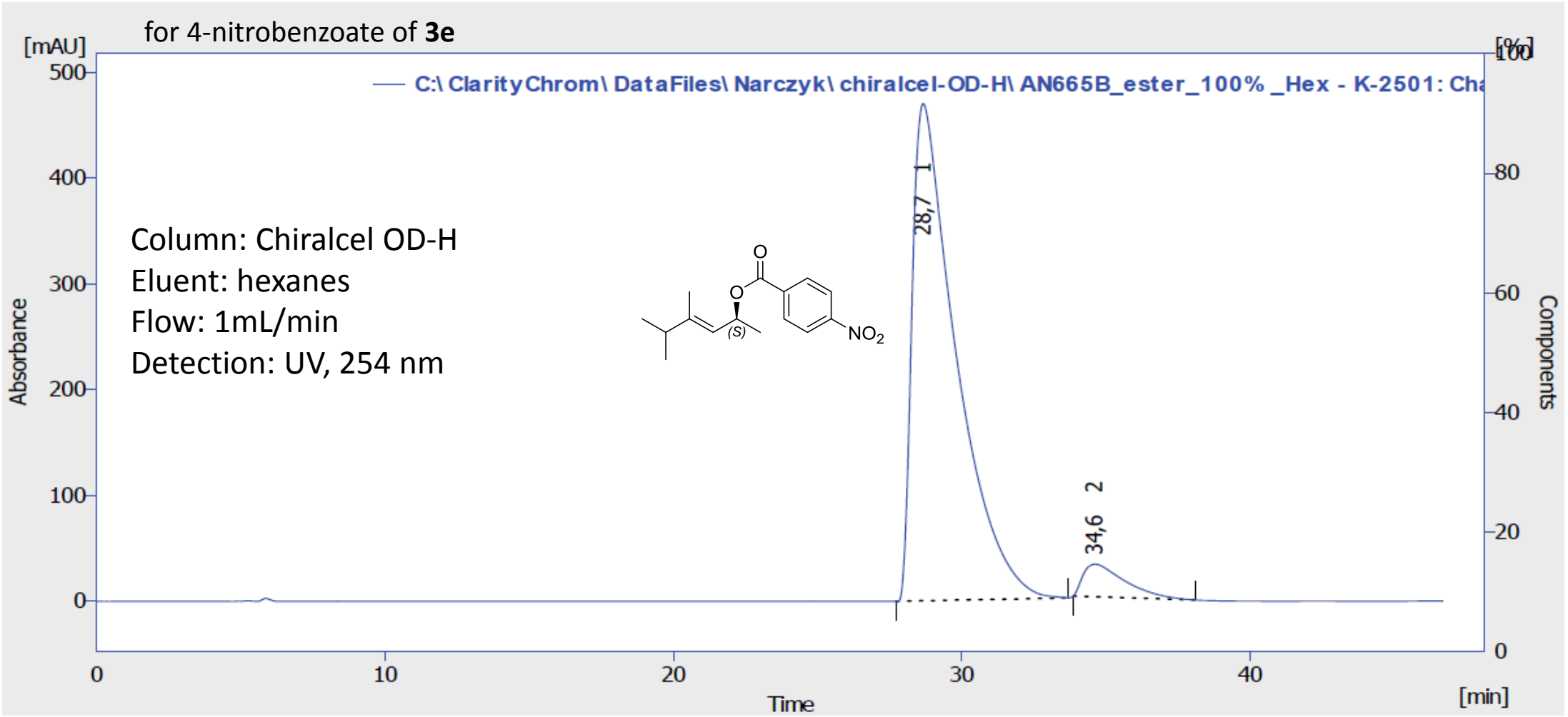
for 4-nitrobenzoate of ***rac*-3e**



Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN670_ester_100%_Hex - K-2501: Channel 1)

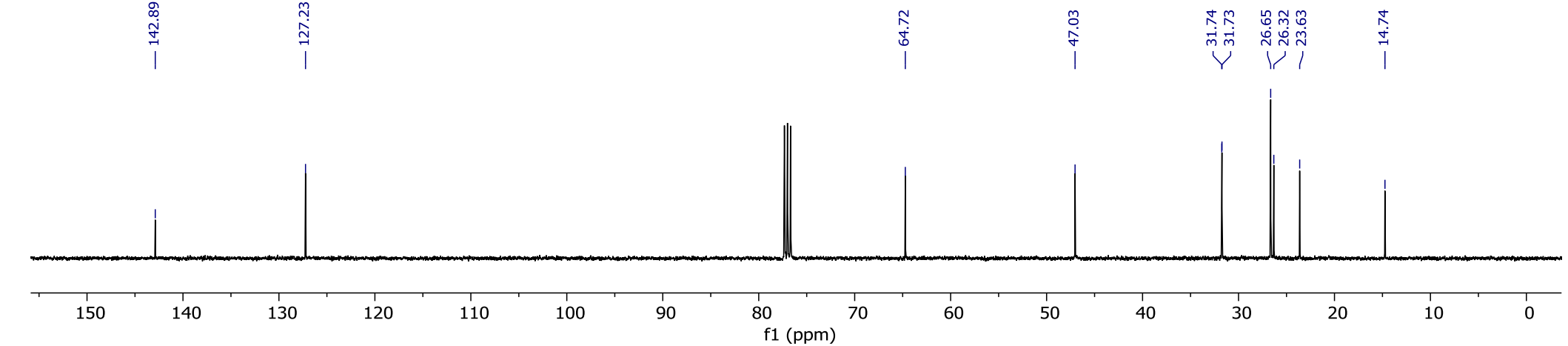
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	26,250	2033,156	27,603	50,4	55,7	1,15	
2	30,567	2004,322	21,934	49,6	44,3	1,40	
	Total	4037,477	49,537	100,0	100,0		

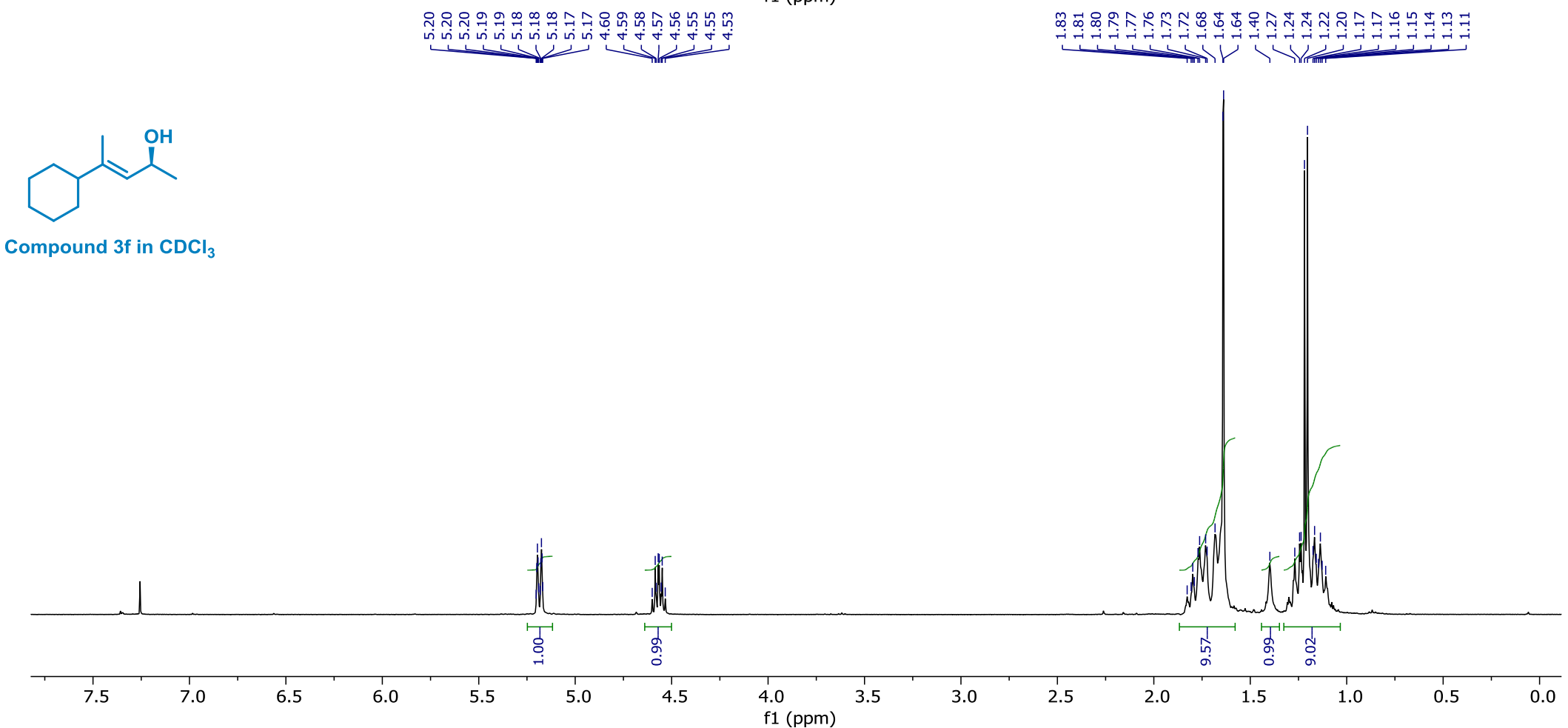
for 4-nitrobenzoate of **3e**



Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN665B_ester_100%_Hex - K-2501: Channel 1)

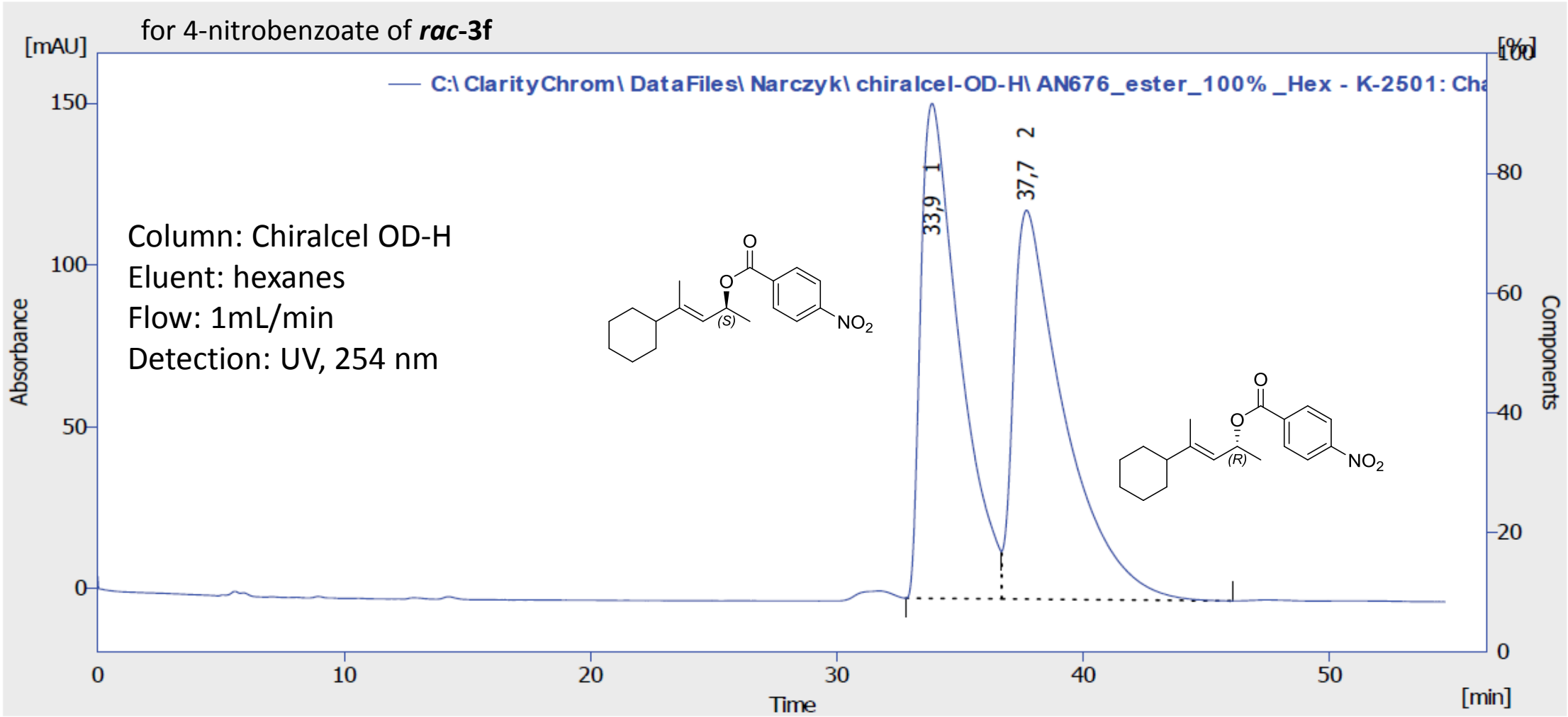
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	28,667	49732,684	469,898	94,1	93,8	1,57	
2	34,617	3114,321	30,803	5,9	6,2	1,53	
	Total	52847,005	500,701	100,0	100,0		





Compound 3f in $CDCl_3$

for 4-nitrobenzoate of ***rac*-3f**

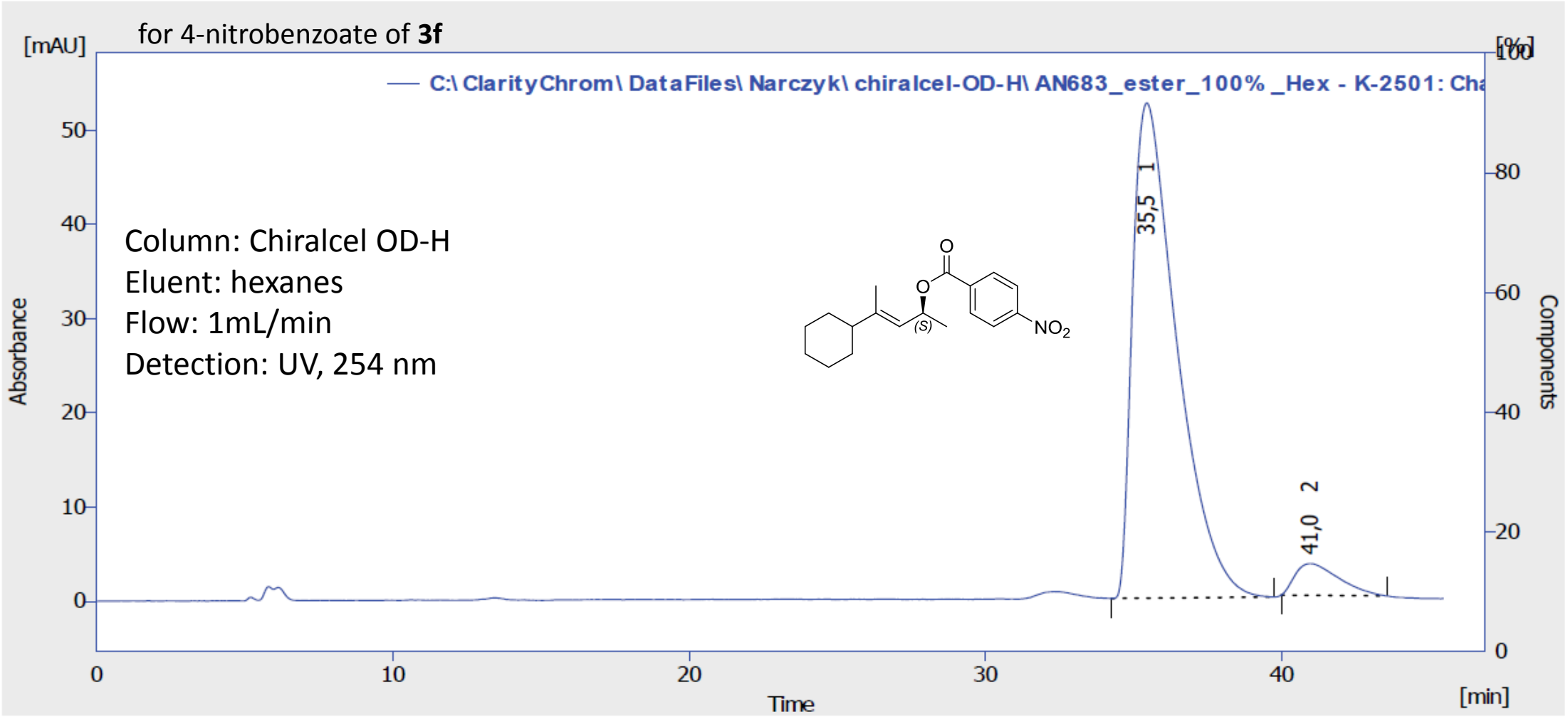


Column: Chiralcel OD-H
Eluent: hexanes
Flow: 1mL/min
Detection: UV, 254 nm

Result Table (Uncal - C:\ClarityChrom\DataFiles\Narczyk\chiralcel-OD-H\AN676_ester_100%_Hex - K-2501: Channel 1)

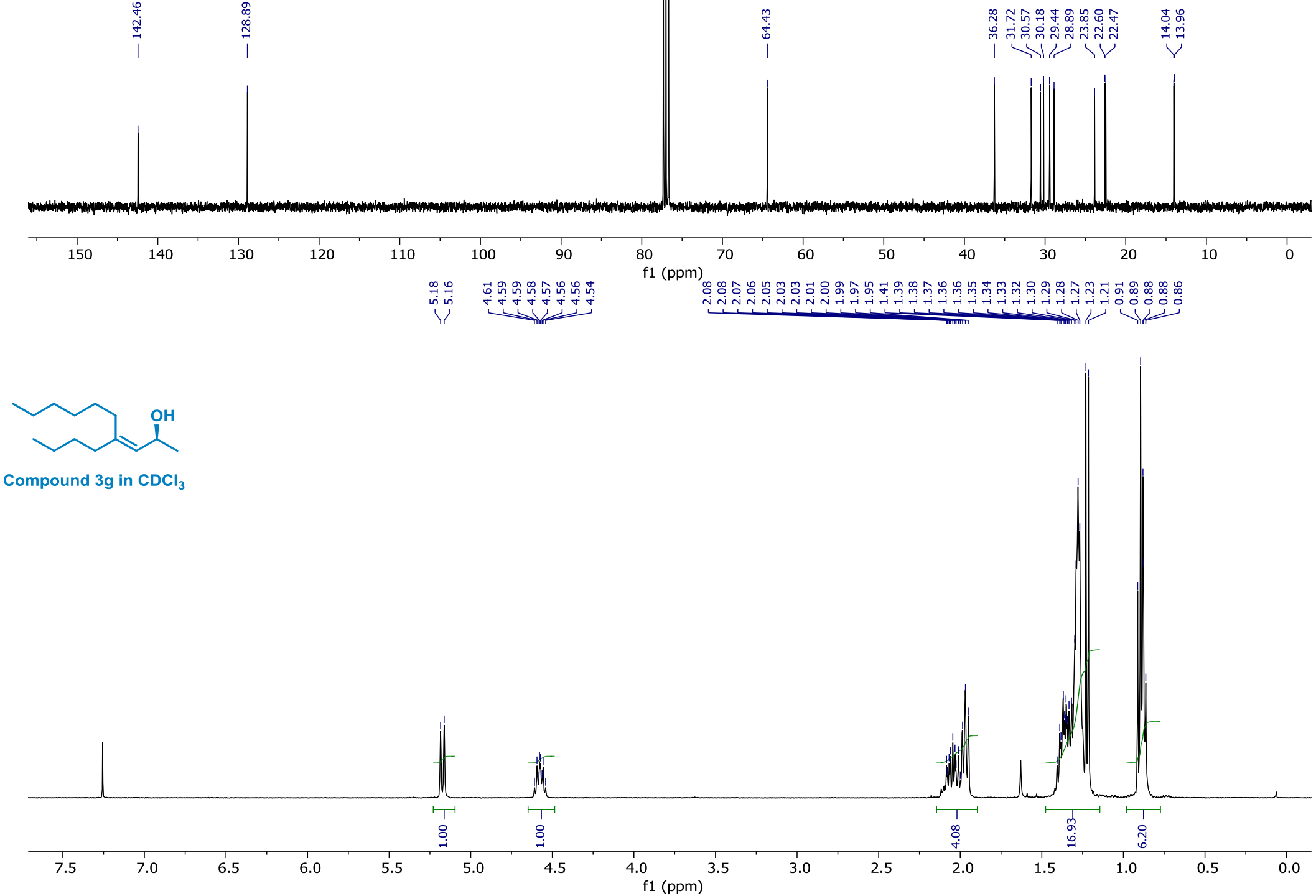
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	33,867	16671,769	152,939	49,1	56,0	1,68	
2	37,700	17309,085	120,195	50,9	44,0	2,05	
	Total	33980,854	273,134	100,0	100,0		

for 4-nitrobenzoate of **3f**

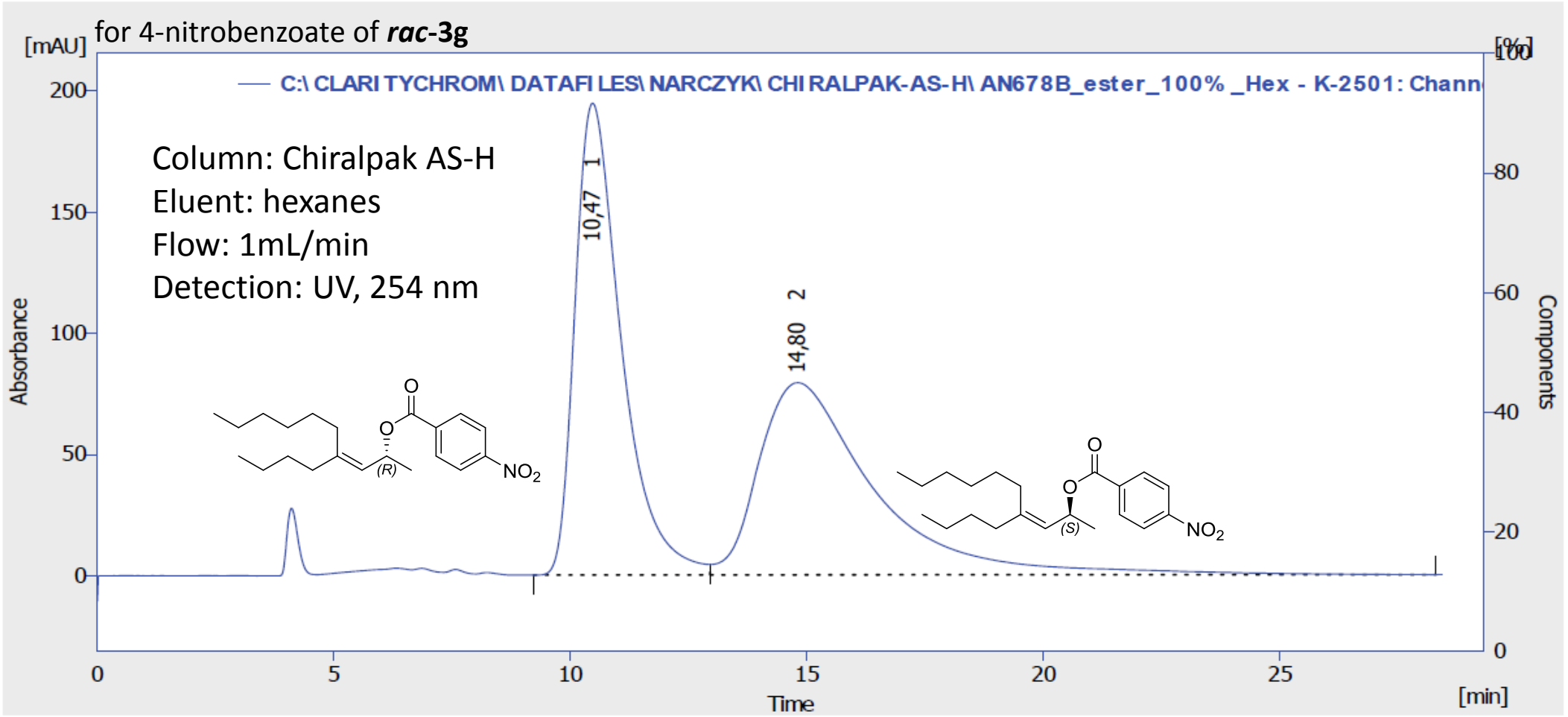


Result Table (Uncal - C:\ClarityChrom\DataFiles\Narczyk\chiralcel-OD-H\AN683_ester_100%_Hex - K-2501: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	35,450	5457,342	52,563	94,0	94,0	1,60	
2	40,967	345,734	3,363	6,0	6,0	1,67	
	Total	5803,076	55,925	100,0	100,0		


142.46
128.89
64.43
36.28
31.72
30.57
30.18
29.44
28.89
23.85
22.60
22.47
14.04
13.96
f1 (ppm)
5.18
5.16
4.61
4.59
4.59
4.58
4.57
4.56
4.56
4.54
2.08
2.08
2.07
2.06
2.05
2.03
2.03
2.01
2.00
1.99
1.97
1.95
1.41
1.39
1.38
1.37
1.36
1.36
1.35
1.34
1.33
1.32
1.30
1.29
1.28
1.27
1.23
1.21
0.91
0.89
0.88
0.88
0.86
OH
Compound 3g in CDCl3
1.00
1.00
4.08
16.93
6.20
f1 (ppm)

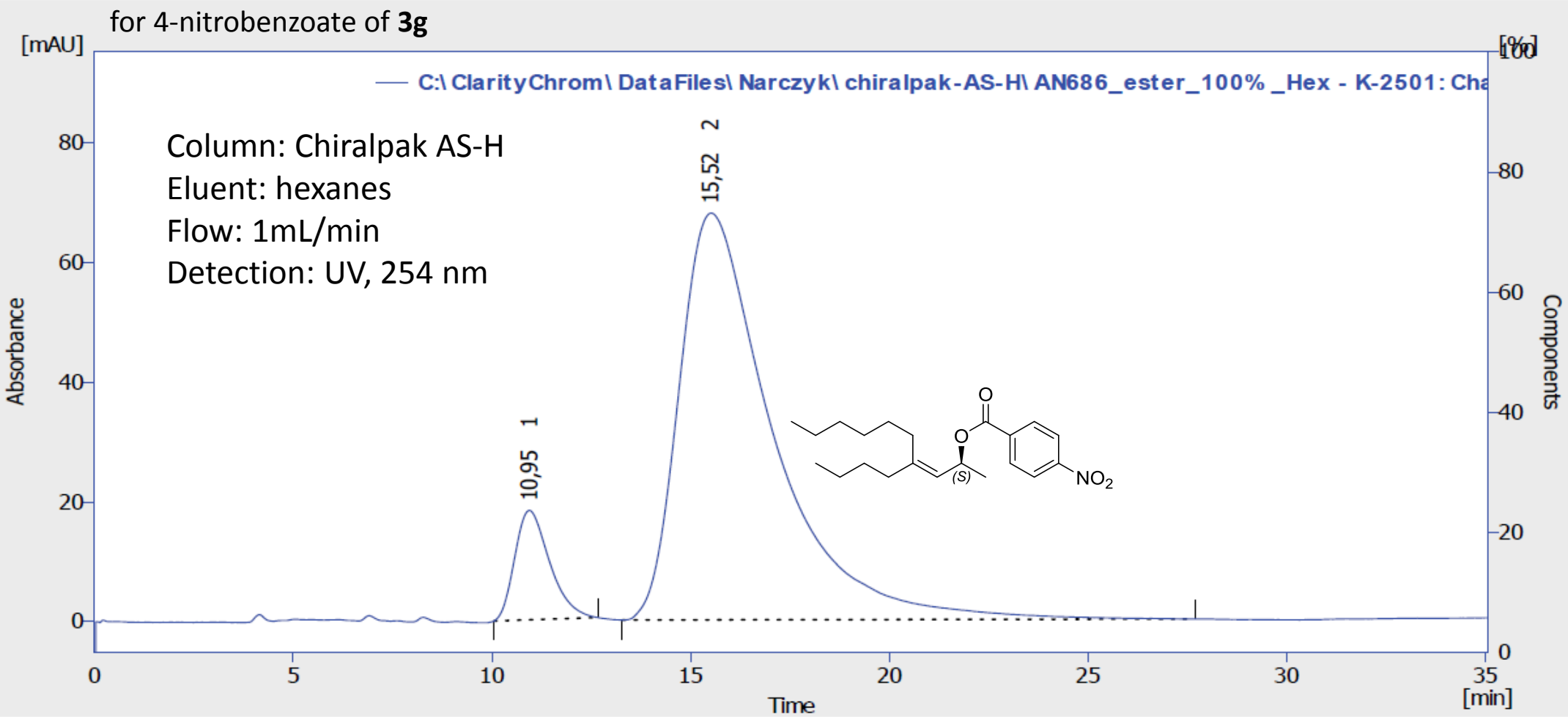
for 4-nitrobenzoate of ***rac*-3g**



Result Table (Uncal - C:\|CLARITYCHROM\|DATAFILES\|NARCZYK\|CHIRALPAK-AS-H\|AN678B_ester_100%_Hex - K-2501: Channel 1)

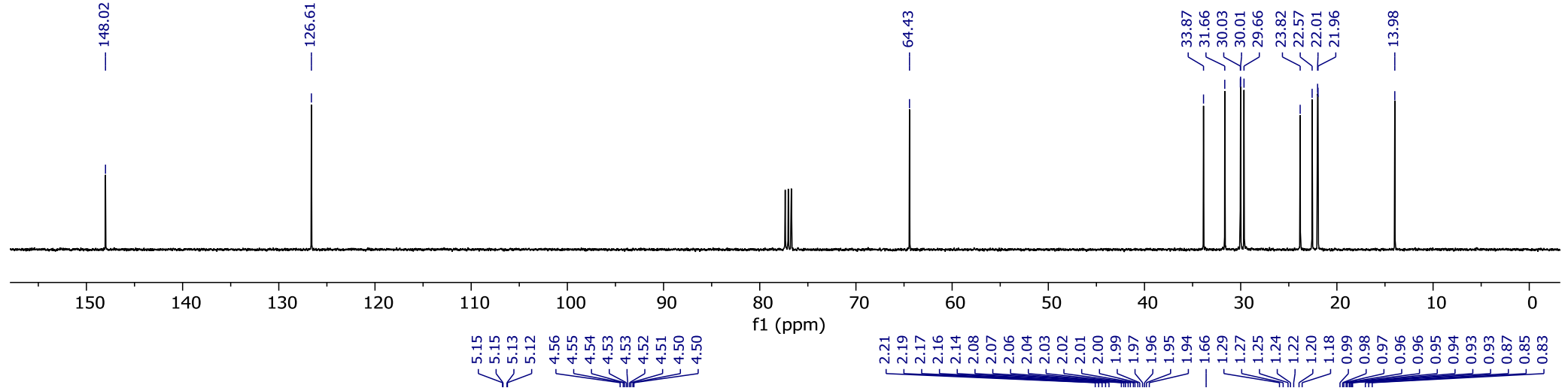
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	10,467	13281,105	194,611	49,6	71,0	1,03	
2	14,800	13492,339	79,299	50,4	29,0	2,38	
	Total	26773,443	273,910	100,0	100,0		

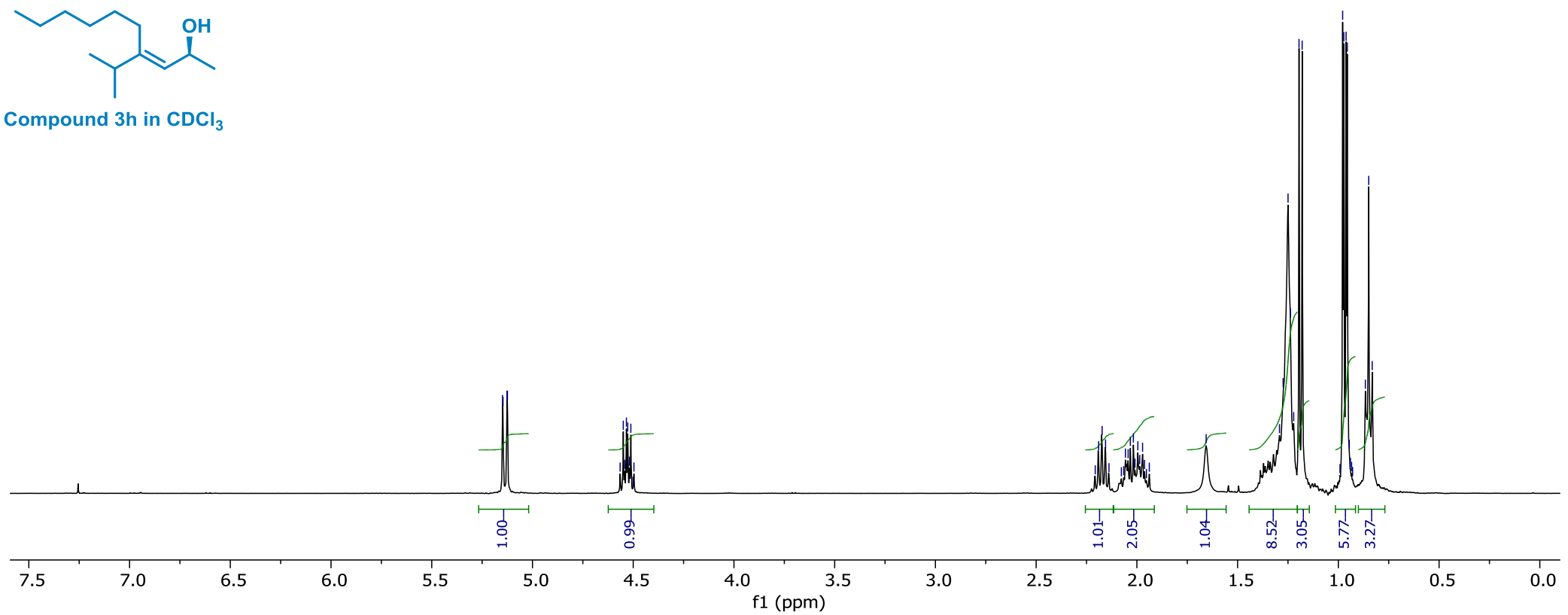
for 4-nitrobenzoate of **3g**



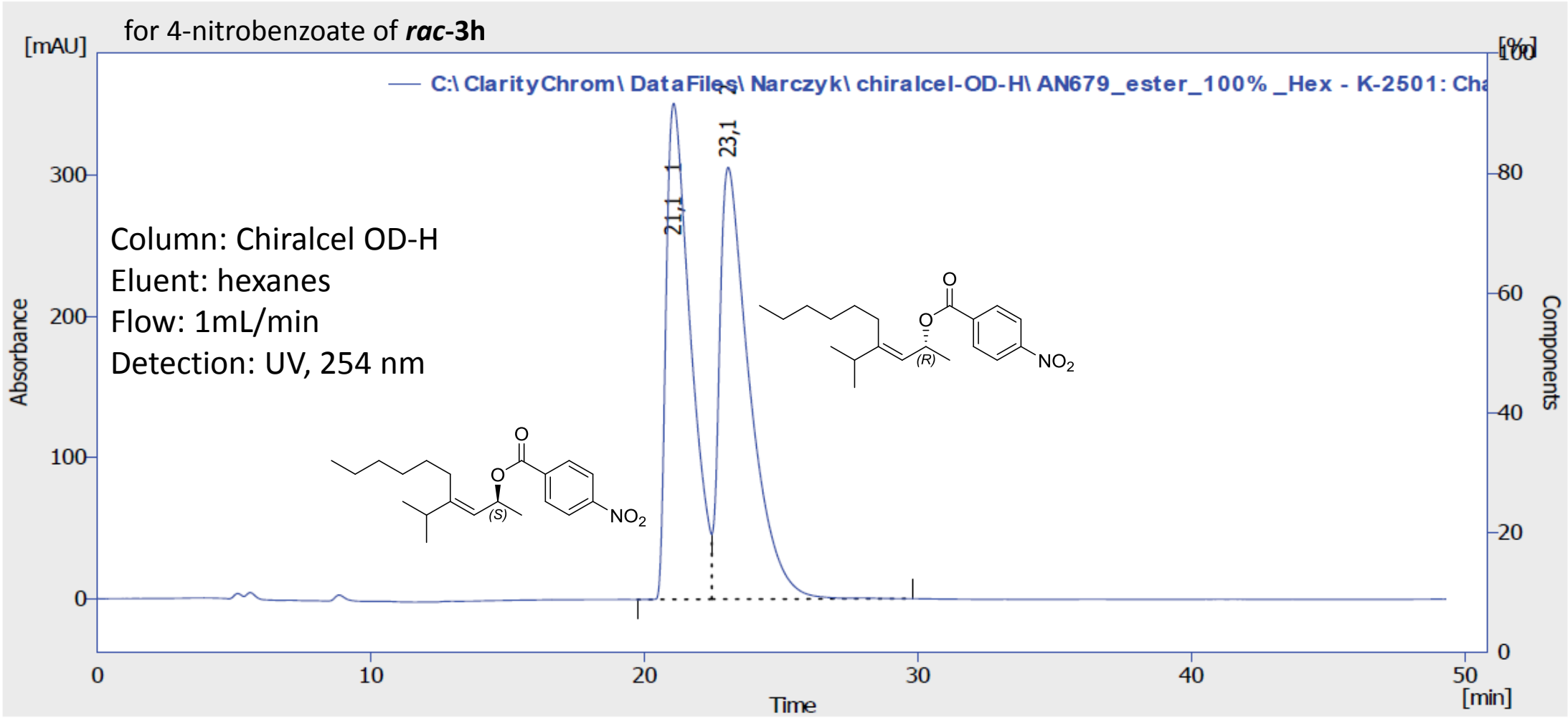
Result Table (Uncal - C:|ClarityChrom|DataFiles|Narczyk|chiralpak-AS-H|AN686_ester_100%_Hex - K-2501: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	10,950	1111,599	18,248	9,0	21,2	0,95	
2	15,517	11177,051	67,880	91,0	78,8	2,33	
	Total	12288,650	86,128	100,0	100,0		


148.02
126.61
64.43
33.87
31.66
30.03
30.01
29.66
23.82
22.57
22.01
21.96
13.98
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
5.15
5.15
5.13
5.12
4.56
4.55
4.54
4.53
4.53
4.52
4.51
4.50
4.50
2.21
2.19
2.17
2.16
2.14
2.08
2.07
2.06
2.04
2.03
2.02
2.01
2.00
1.99
1.97
1.96
1.95
1.94
1.66
1.29
1.27
1.25
1.24
1.22
1.20
1.18
0.99
0.98
0.97
0.96
0.96
0.95
0.94
0.93
0.93
0.87
0.85
0.83


OH
Compound 3h in CDCl3
1.00
0.99
1.01
2.05
1.04
8.52
3.05
5.77
3.27
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)

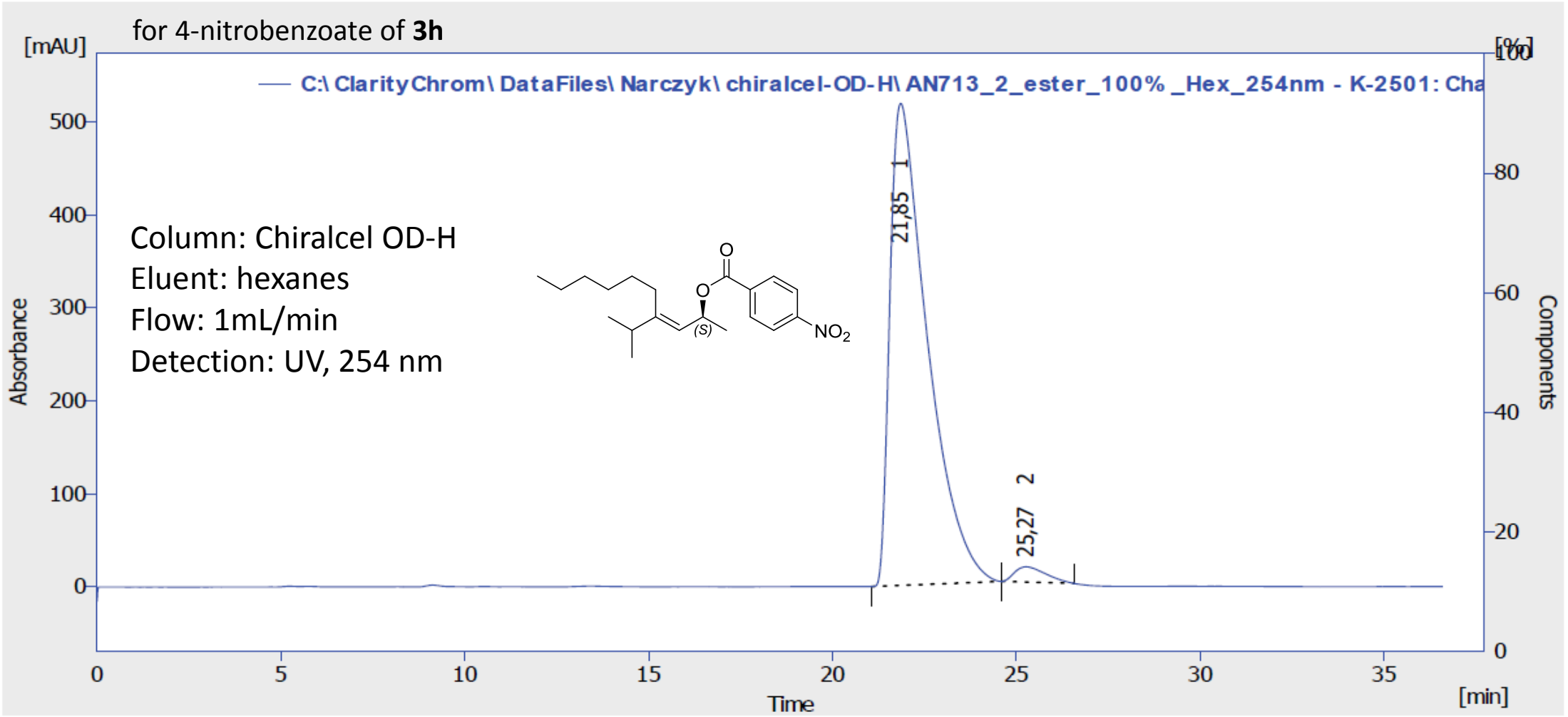
for 4-nitrobenzoate of ***rac*-3h**



Result Table (Uncal - C:\ClarityChrom\DataFiles\Narczyk\chiralcel-OD-H\AN679_ester_100%_Hex - K-2501: Channel 1)

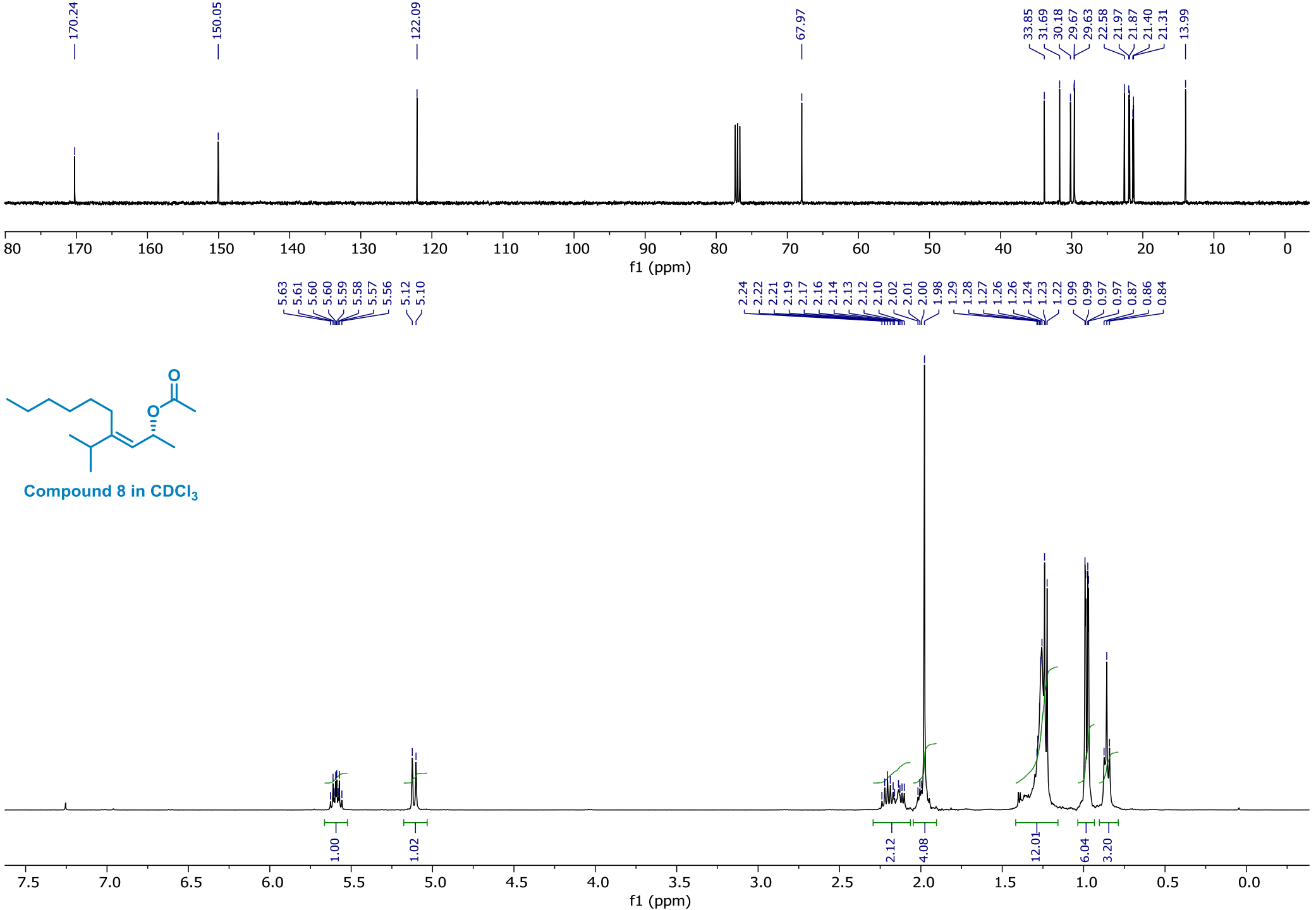
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	21,067	21685,002	351,532	47,9	53,5	0,98	
2	23,067	23598,541	305,993	52,1	46,5	1,15	
	Total	45283,544	657,525	100,0	100,0		

for 4-nitrobenzoate of **3h**

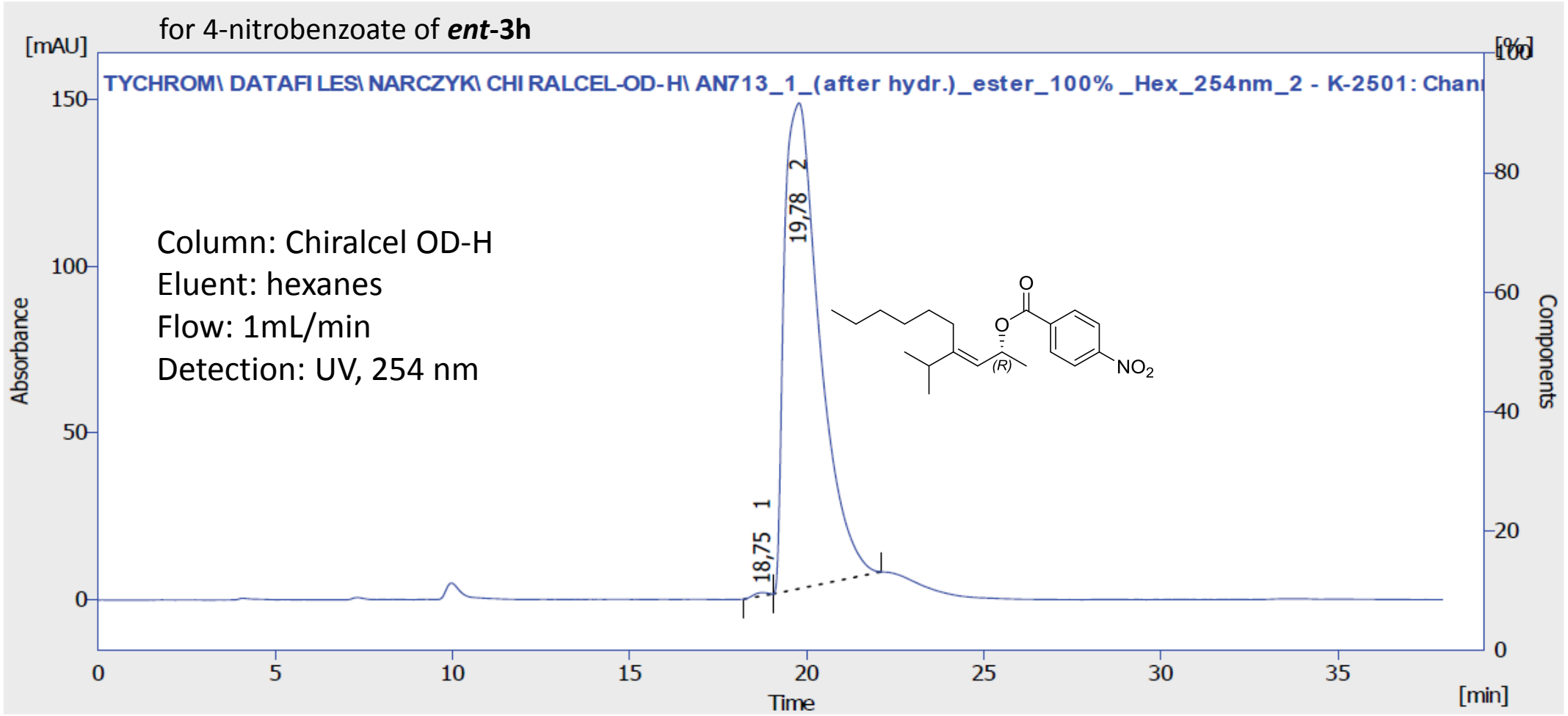


Result Table (Uncal - C:\ClarityChrom\DataFiles\Narczyk\chiralcel-OD-H\AN713_2_ester_100%_Hex_254nm - K-2501: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	21,850	36725,197	518,106	97,4	96,9	1,10	
2	25,267	970,552	16,394	2,6	3,1	0,97	
	Total	37695,749	534,501	100,0	100,0		

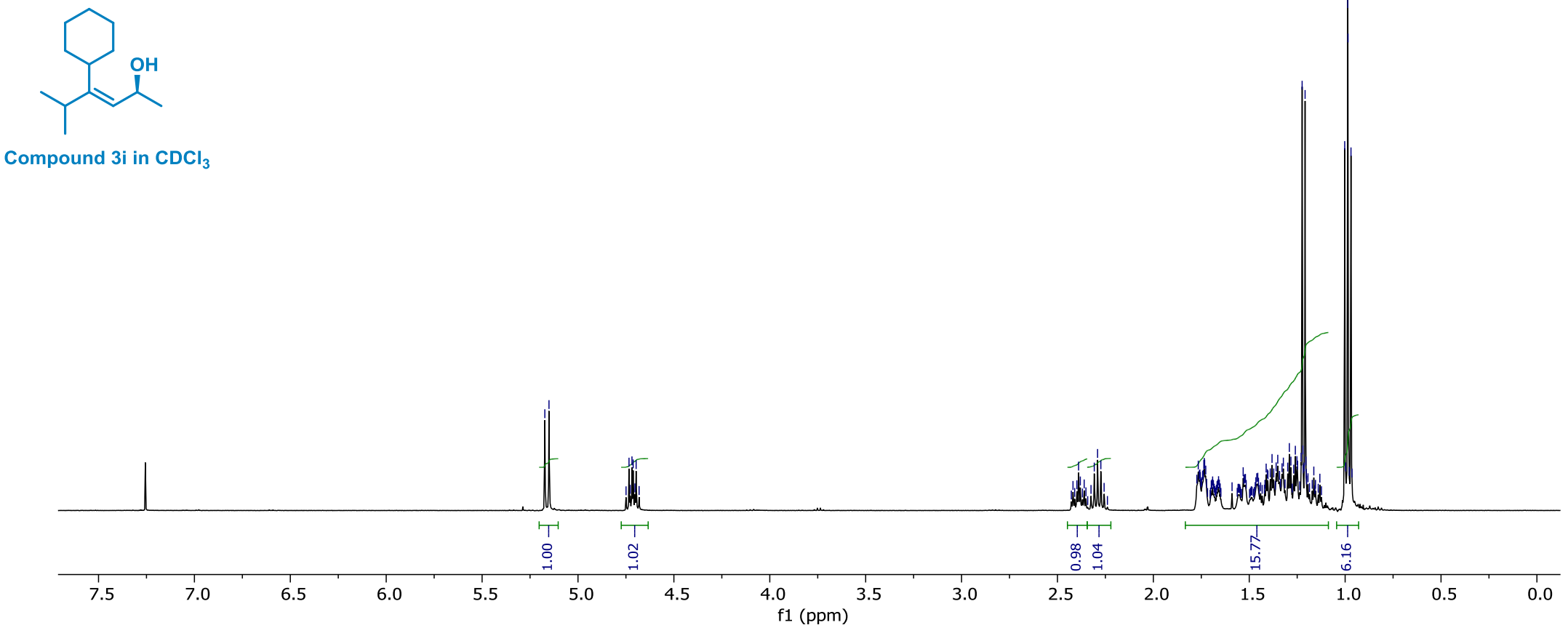

170.24
150.05
122.09
67.97
33.85
31.69
30.18
29.67
29.63
22.58
21.97
21.87
21.40
21.31
13.99
f1 (ppm)
5.63
5.61
5.60
5.60
5.59
5.58
5.57
5.56
5.12
5.10
2.24
2.22
2.21
2.19
2.17
2.16
2.14
2.13
2.12
2.10
2.02
2.01
2.00
1.98
1.29
1.28
1.27
1.26
1.26
1.24
1.23
1.22
0.99
0.99
0.97
0.97
0.87
0.86
0.84
1.00
1.02
2.12
4.08
12.01
6.04
3.20
f1 (ppm)
Compound 8 in CDCl3

for 4-nitrobenzoate of ***ent*-3h**



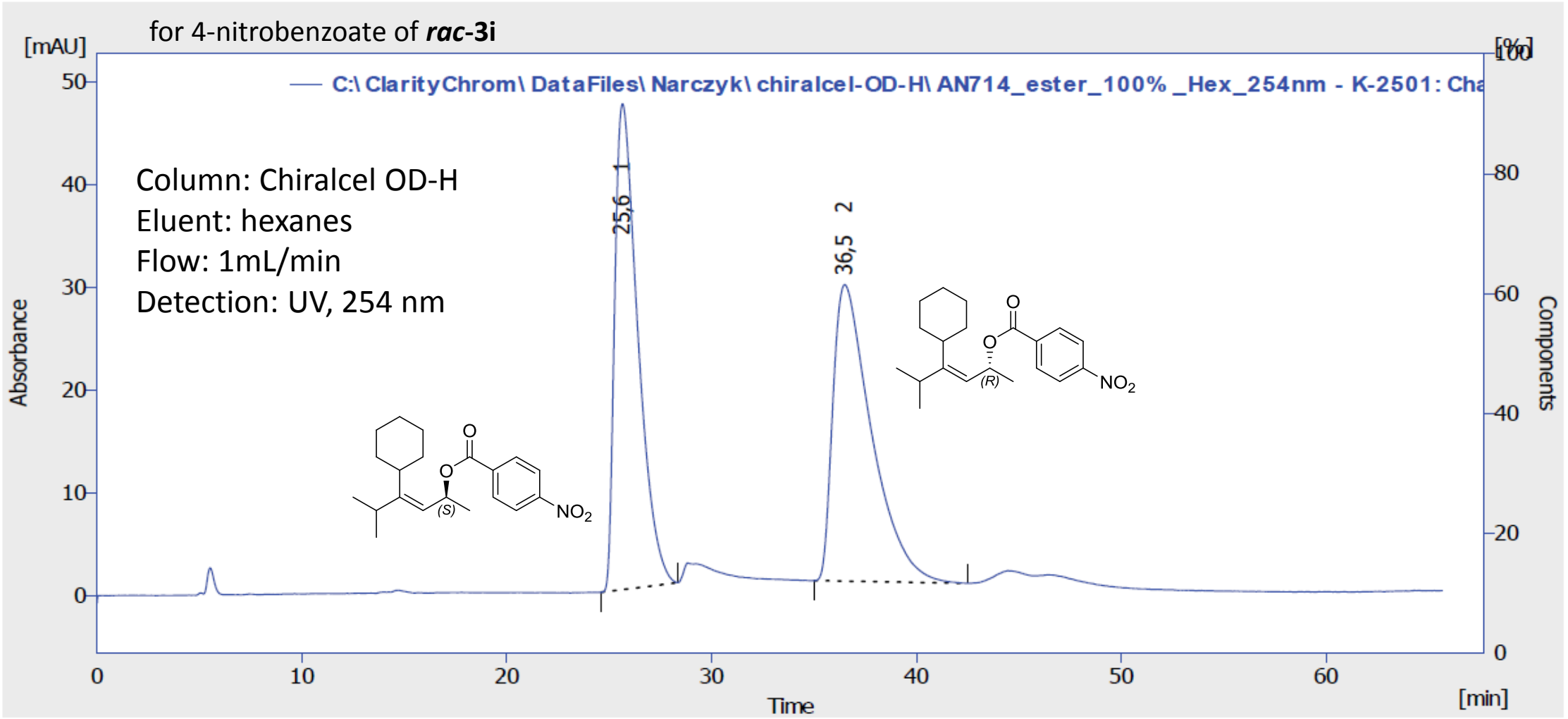
Result Table (Uncal - C:\|CLARITYCHROM\|DATAFILES\|NARCZYK\|CHIRALCEL-OD-H\|AN713_1_(after hydr.)_ester_100%_Hex_254nm_2 - K-2501: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	18,750	28,011	1,010	0,3	0,7	0,52	
2	19,783	10063,408	145,455	99,7	99,3	1,10	
	Total	10091,419	146,465	100,0	100,0		



Compound 3i in $CDCl_3$

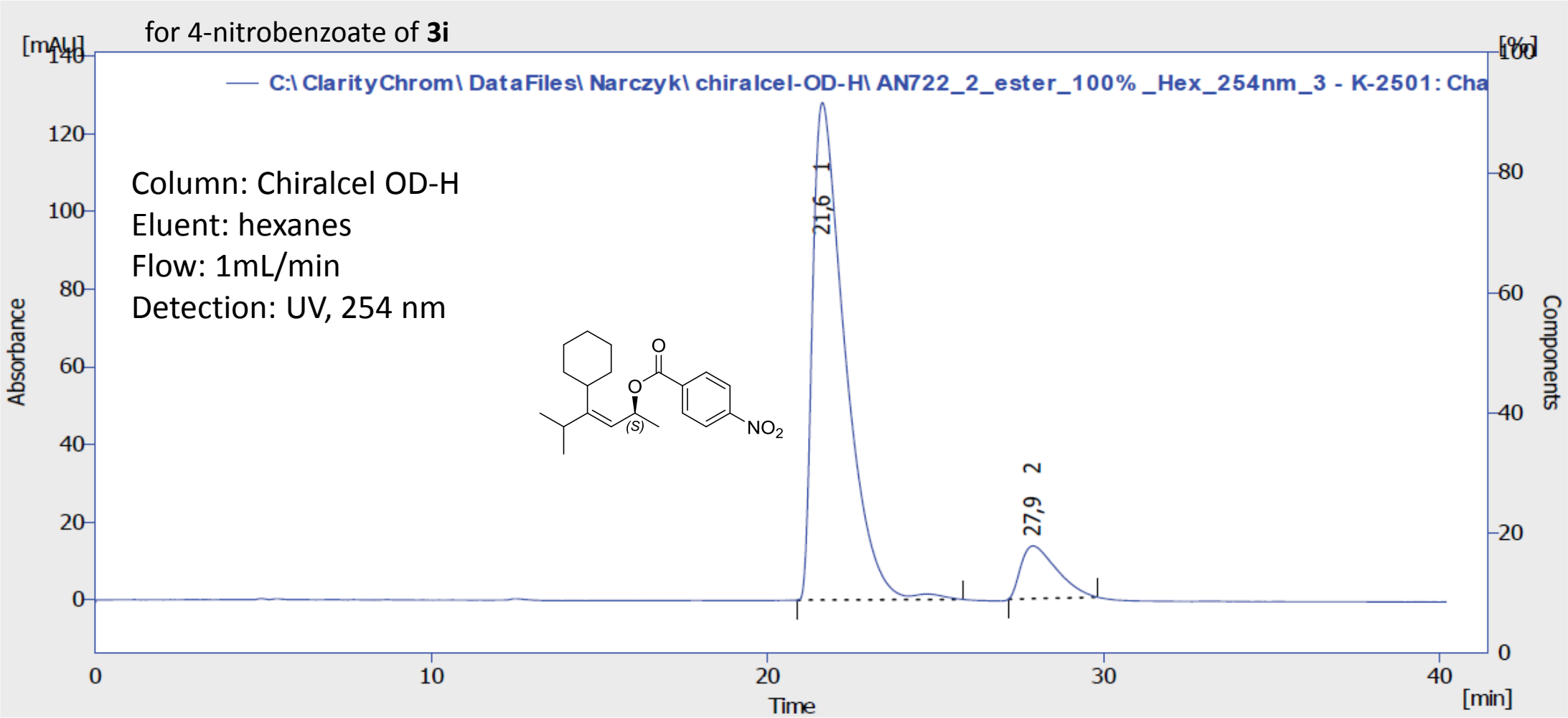
for 4-nitrobenzoate of ***rac*-3i**



Result Table (Uncal - C:\ClarityChrom\DataFiles\Narczyk\chiralcel-OD-H\AN714_ester_100%_Hex_254nm - K-2501: Channel 1)

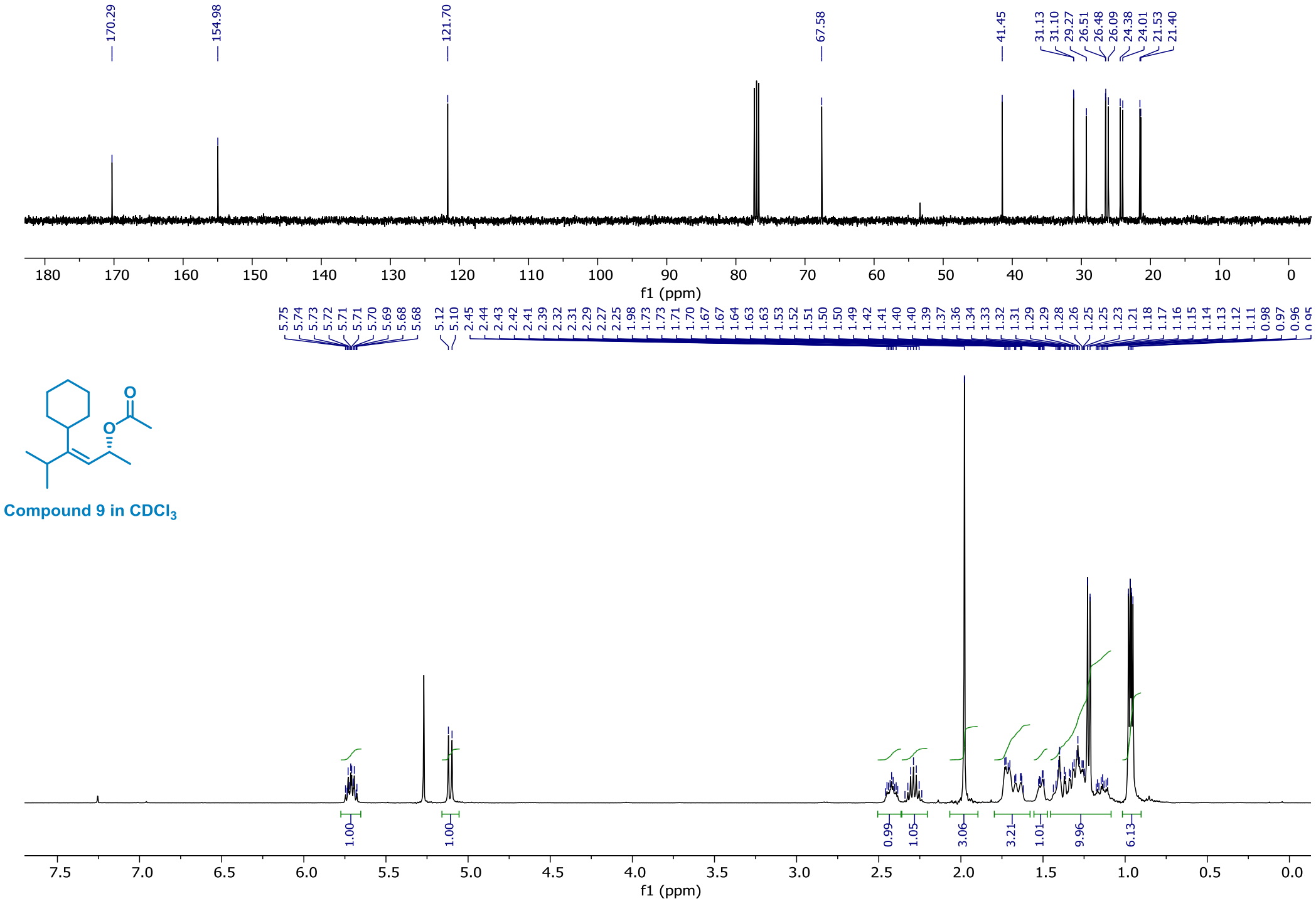
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	25,650	3715,077	47,311	49,6	62,1	1,23	
2	36,500	3782,532	28,885	50,4	37,9	1,98	
	Total	7497,610	76,196	100,0	100,0		

for 4-nitrobenzoate of **3i**



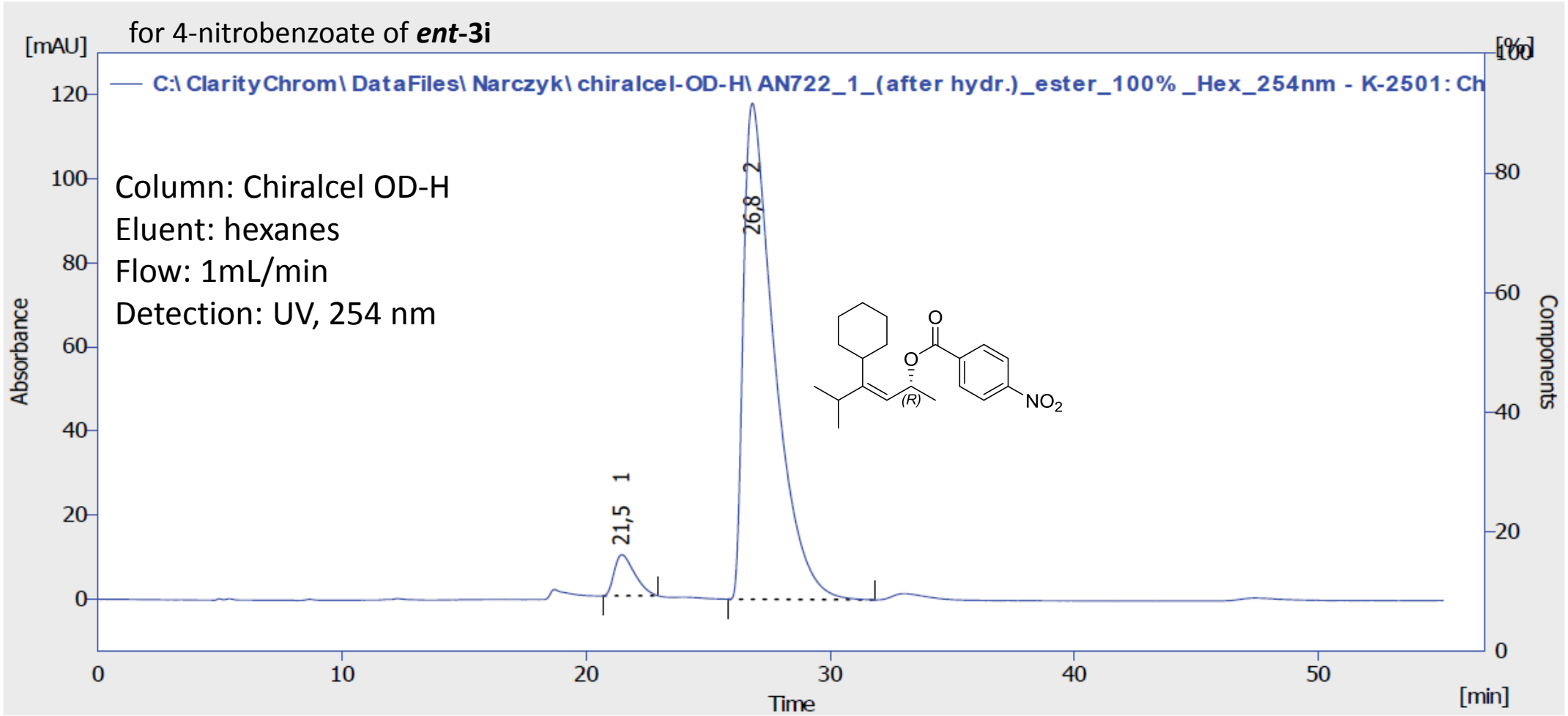
Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN722_2_ester_100%_Hex_254nm_3 - K-2501: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	21,633	8594,579	128,076	89,5	90,4	1,02	
2	27,900	1006,784	13,574	10,5	9,6	1,20	
	Total	9601,363	141,650	100,0	100,0		



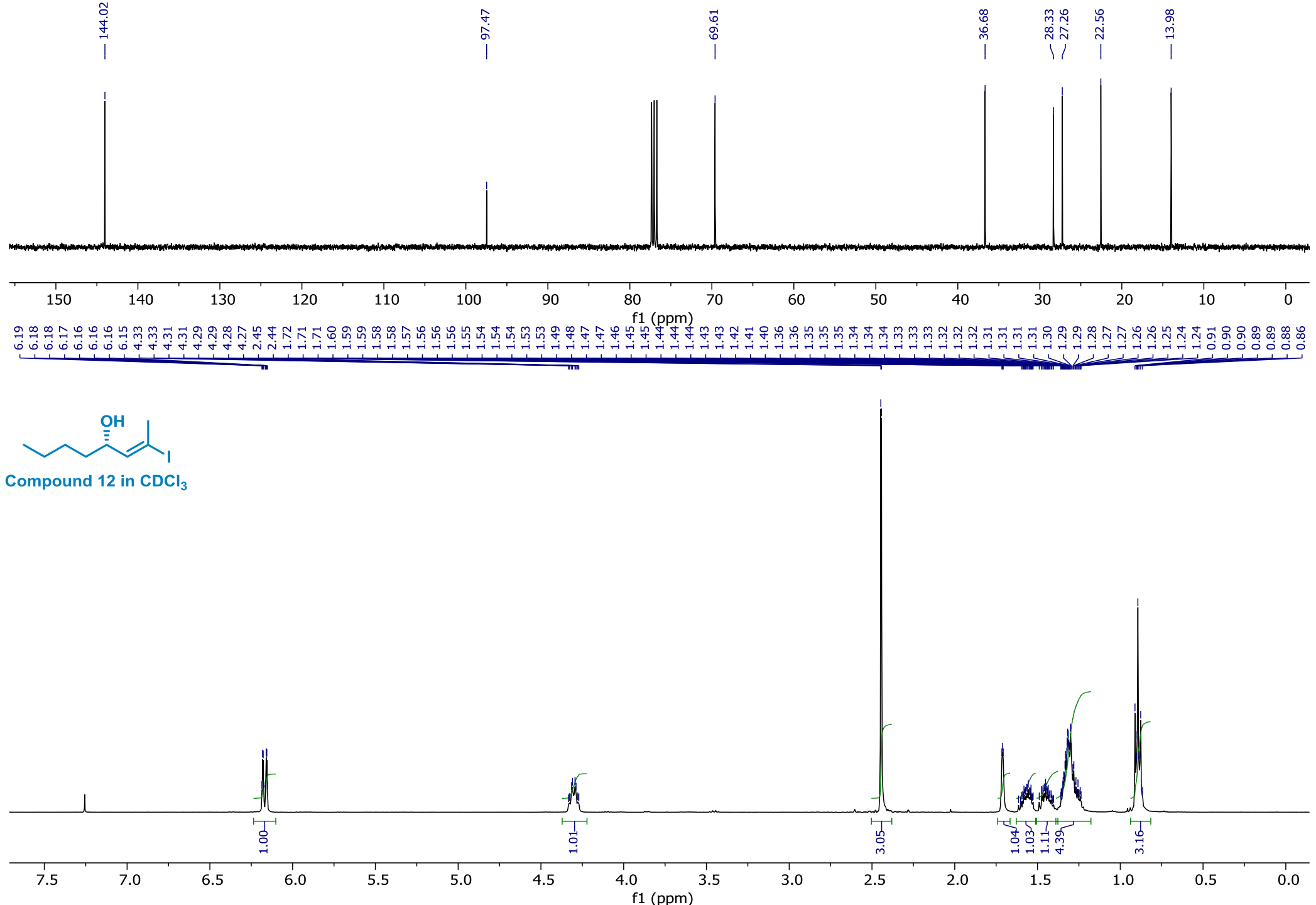
Compound 9 in $CDCl_3$

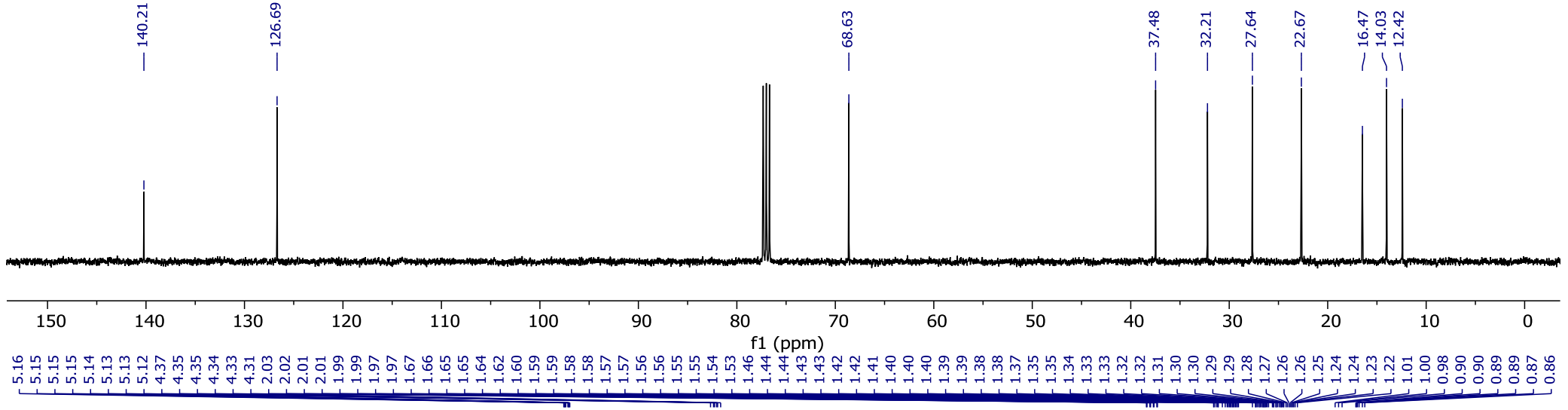
for 4-nitrobenzoate of ***ent*-3i**

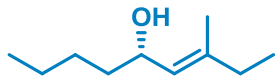


Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN722_1_(after hydr.)_ester_100%_Hex_254nm - K-2501: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	21,467	571,259	9,803	5,2	7,7	0,93	
2	26,817	10370,883	117,971	94,8	92,3	1,32	
	Total	10942,142	127,774	100,0	100,0		

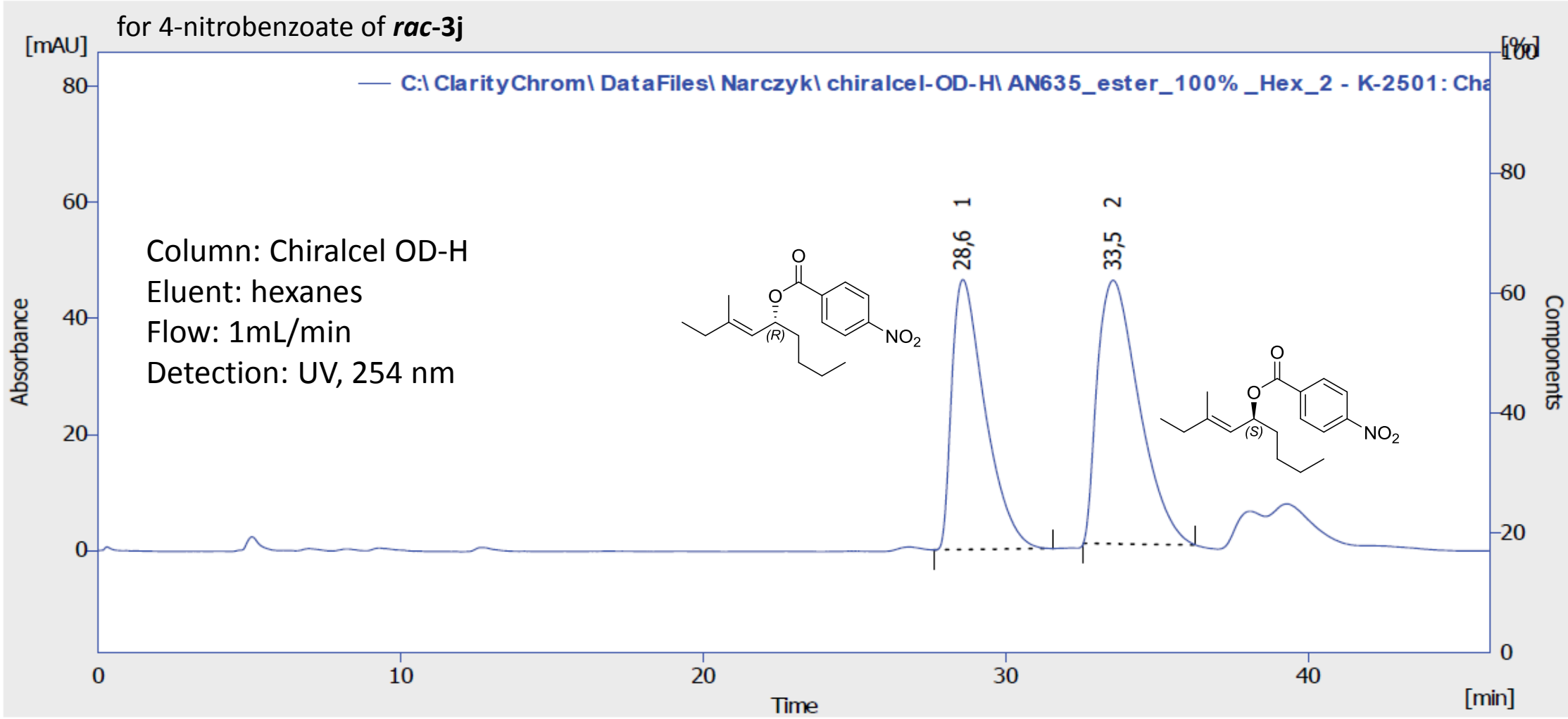

144.02
97.47
69.61
36.68
28.33
27.26
22.56
13.98
f1 (ppm)
OH
I
Compound 12 in CDCl3
1.00
1.01
3.05
1.04
1.03
1.11
4.39
3.16
f1 (ppm)





Compound 3j in $CDCl_3$

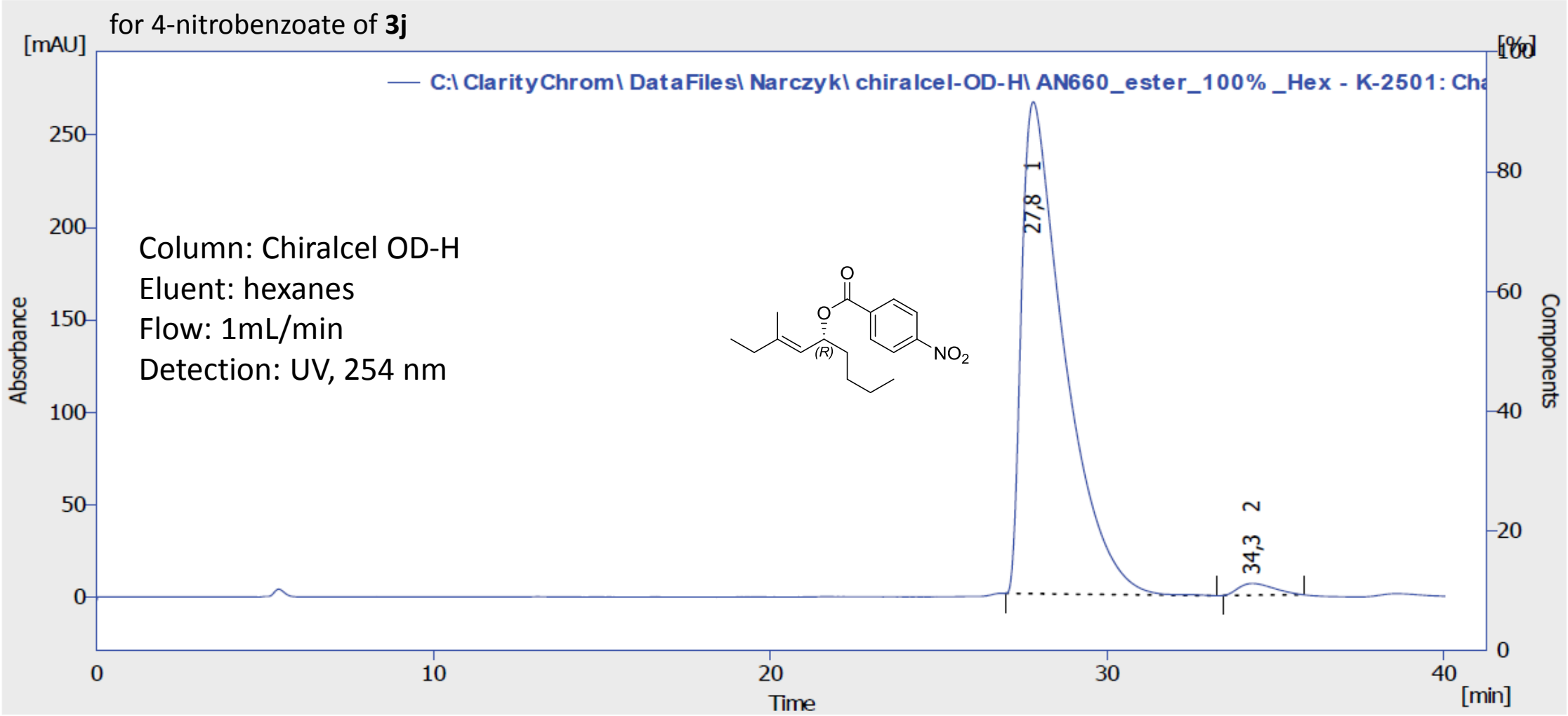
for 4-nitrobenzoate of ***rac*-3j**



Result Table (Uncal - C:\ClarityChrom\DataFiles\Narczyk\chiralcel-OD-H\AN635_ester_100%_Hex_2 - K-2501: Channel 1)

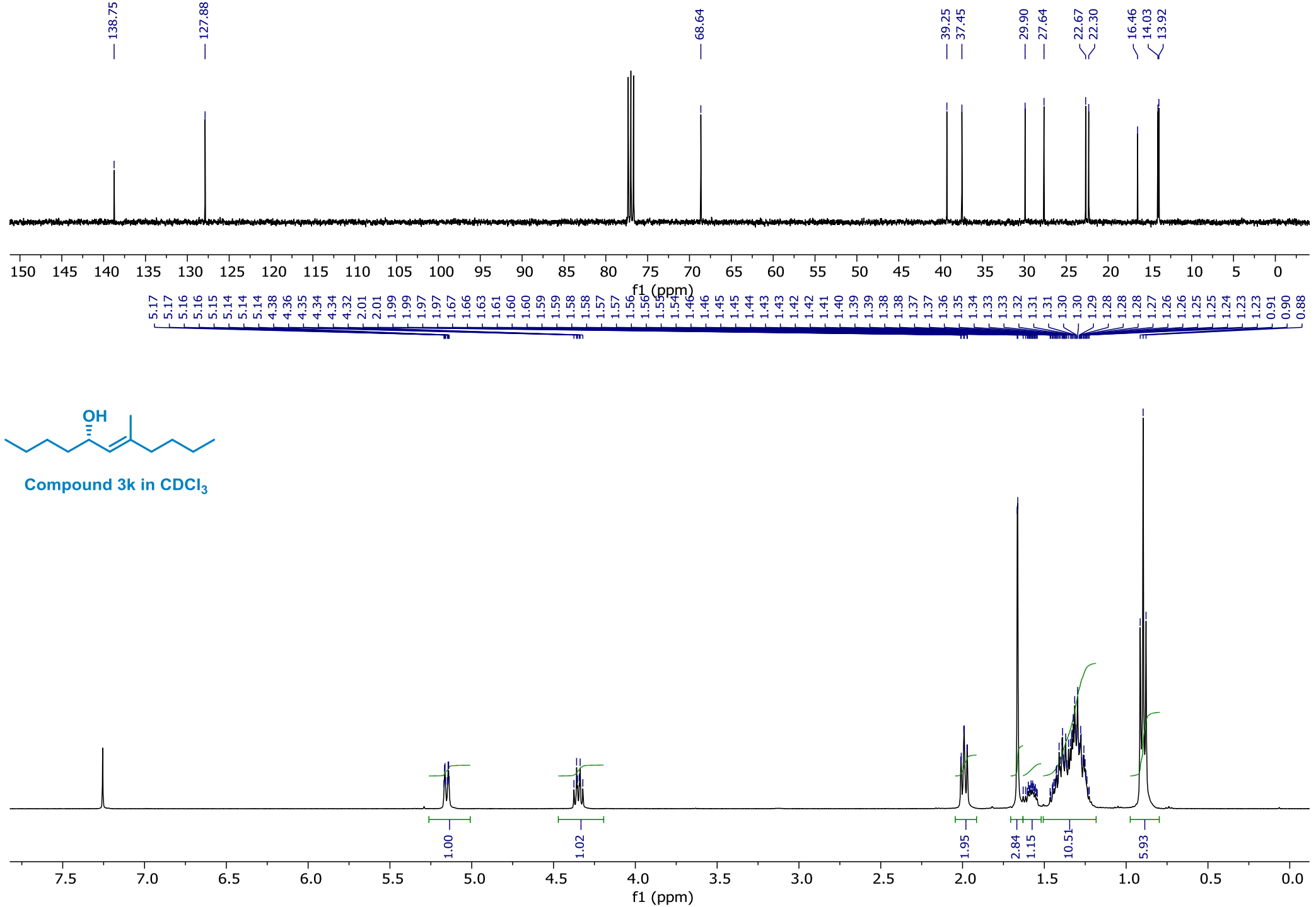
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	28,583	3557,583	46,534	45,0	50,6	1,18	
2	33,550	4348,385	45,422	55,0	49,4	1,53	
	Total	7905,969	91,957	100,0	100,0		

for 4-nitrobenzoate of **3j**

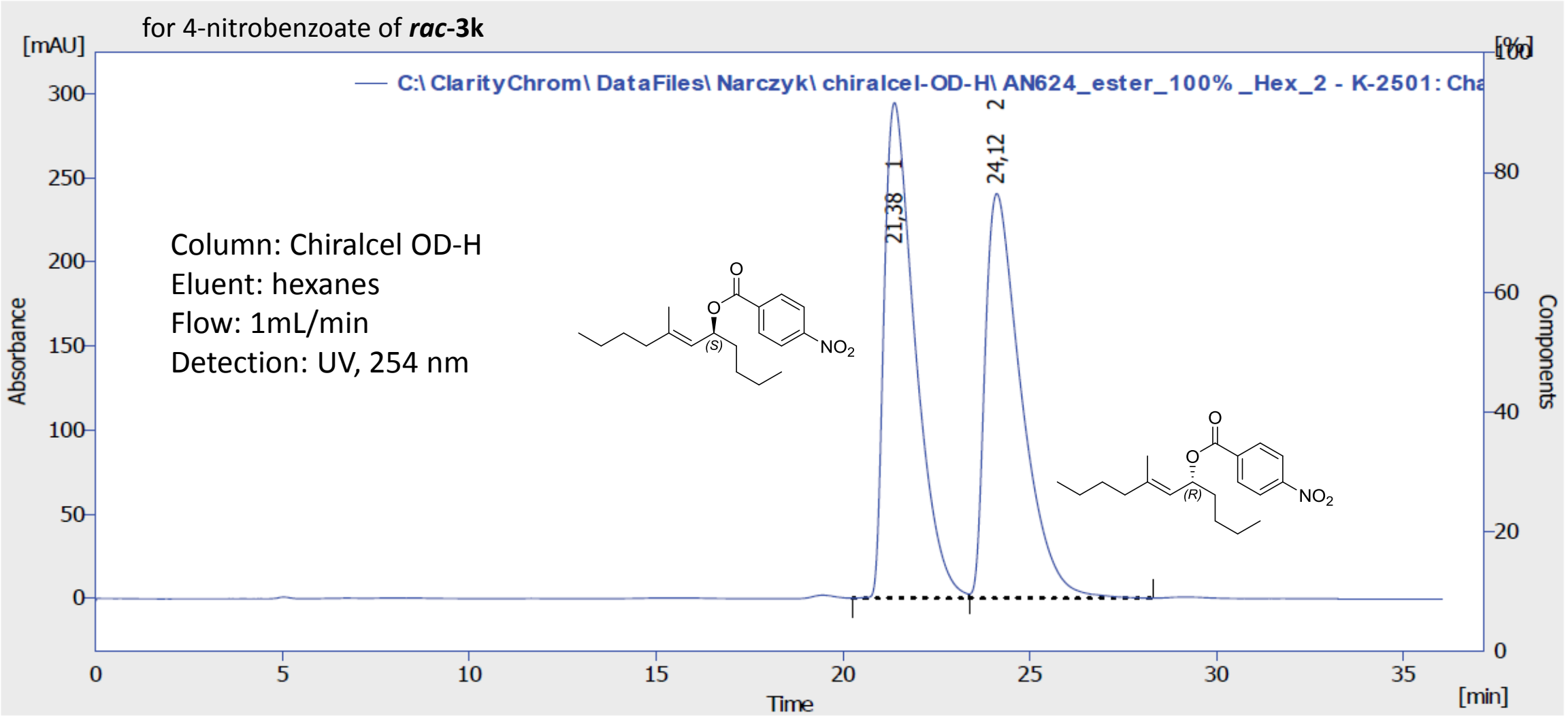


Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN660_ester_100%_Hex - K-2501: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	27,800	23492,146	266,332	98,1	97,7	1,32	
2	34,300	466,416	6,371	1,9	2,3	1,22	
	Total	23958,561	272,703	100,0	100,0		


138.75
127.88
68.64
39.25
37.45
29.90
27.64
22.67
22.30
16.46
14.03
13.92
f1 (ppm)
OH
Compound 3k in CDCl3
1.00
1.02
1.95
2.84
1.15
10.51
5.93
f1 (ppm)

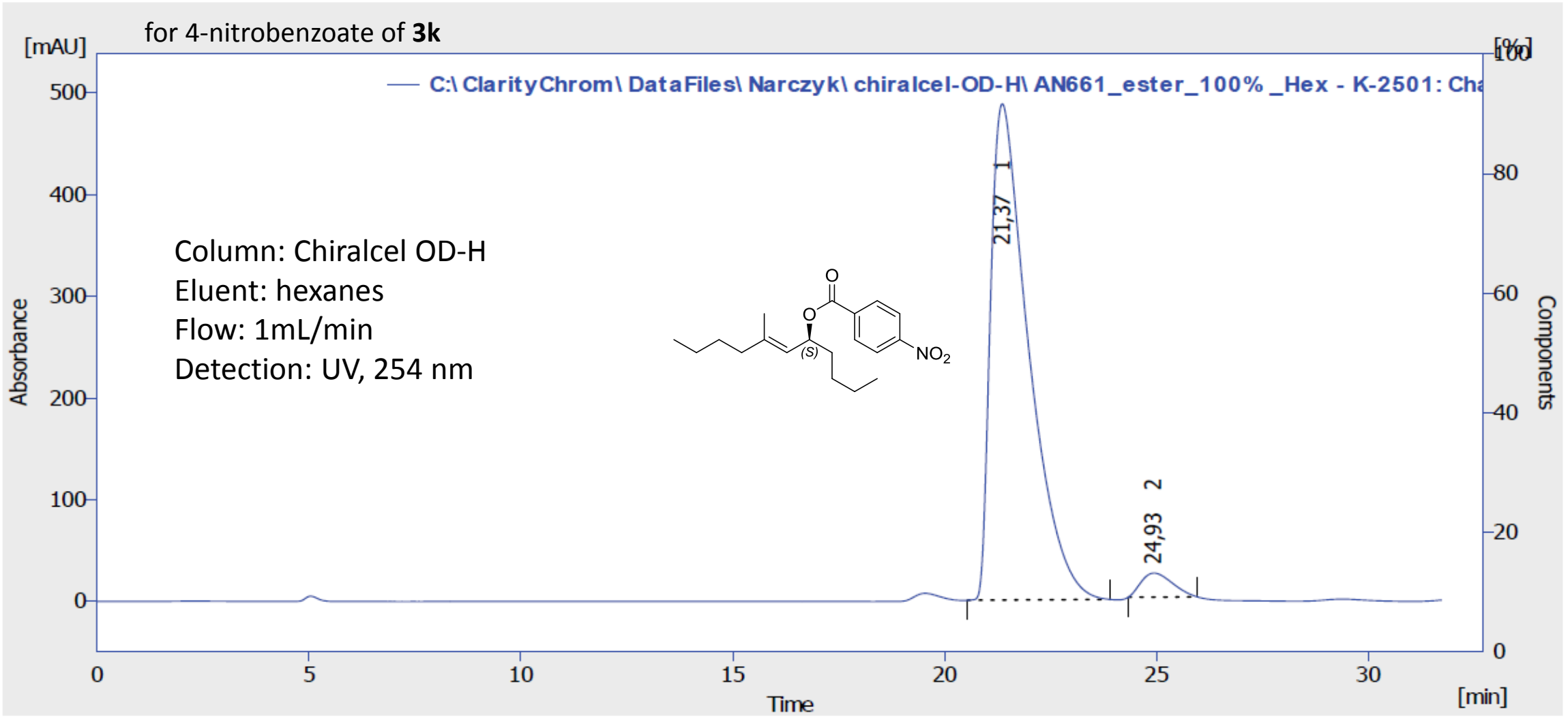
for 4-nitrobenzoate of ***rac*-3k**



Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN624_ester_100%_Hex_2 - K-2501: Channel 1)

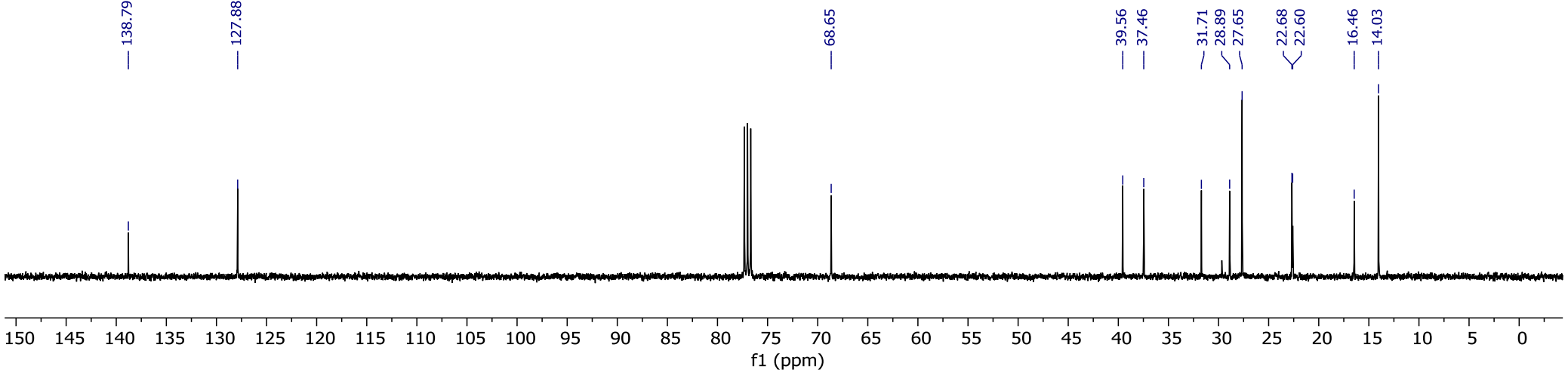
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	21,383	16896,782	294,412	51,0	55,1	0,88	
2	24,117	16210,264	240,385	49,0	44,9	1,05	
	Total	33107,046	534,797	100,0	100,0		

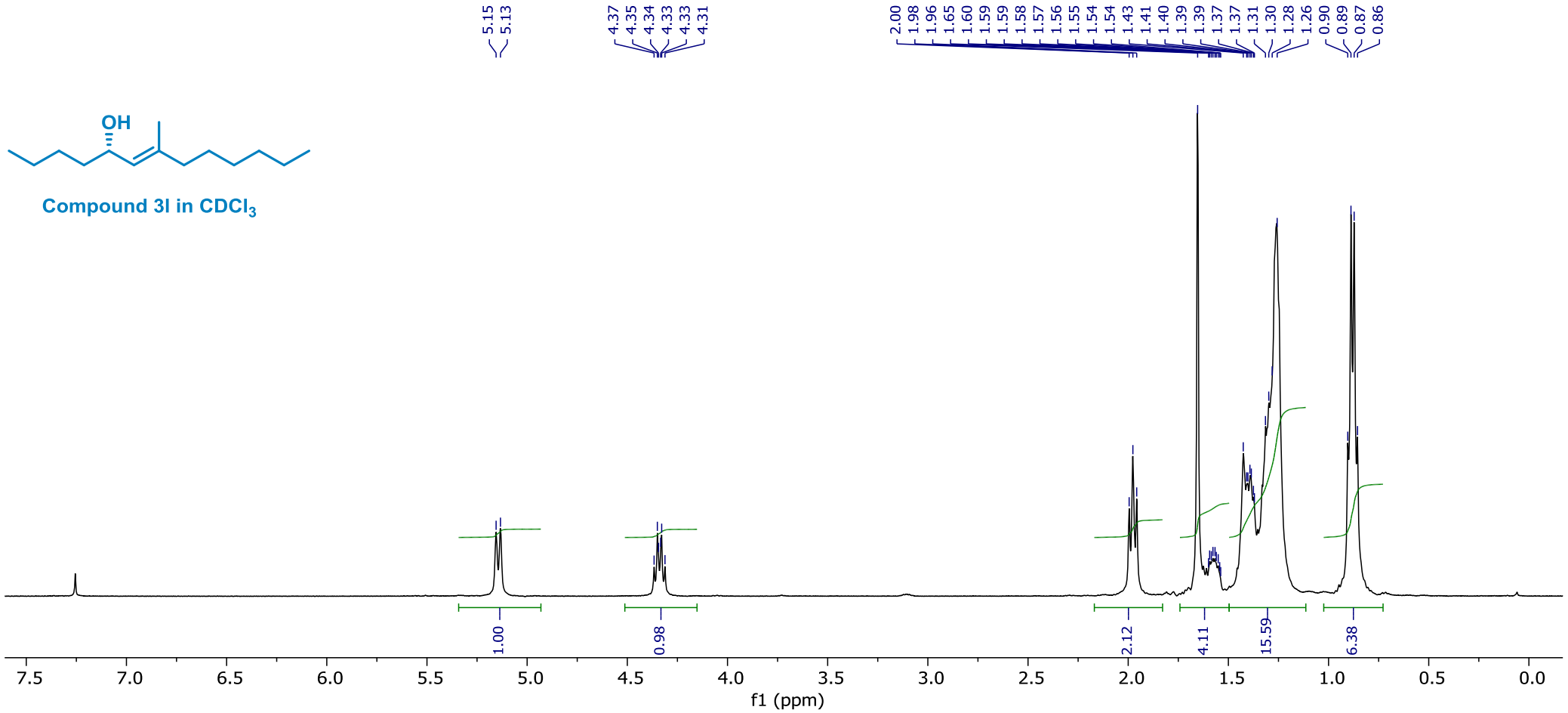
for 4-nitrobenzoate of **3k**



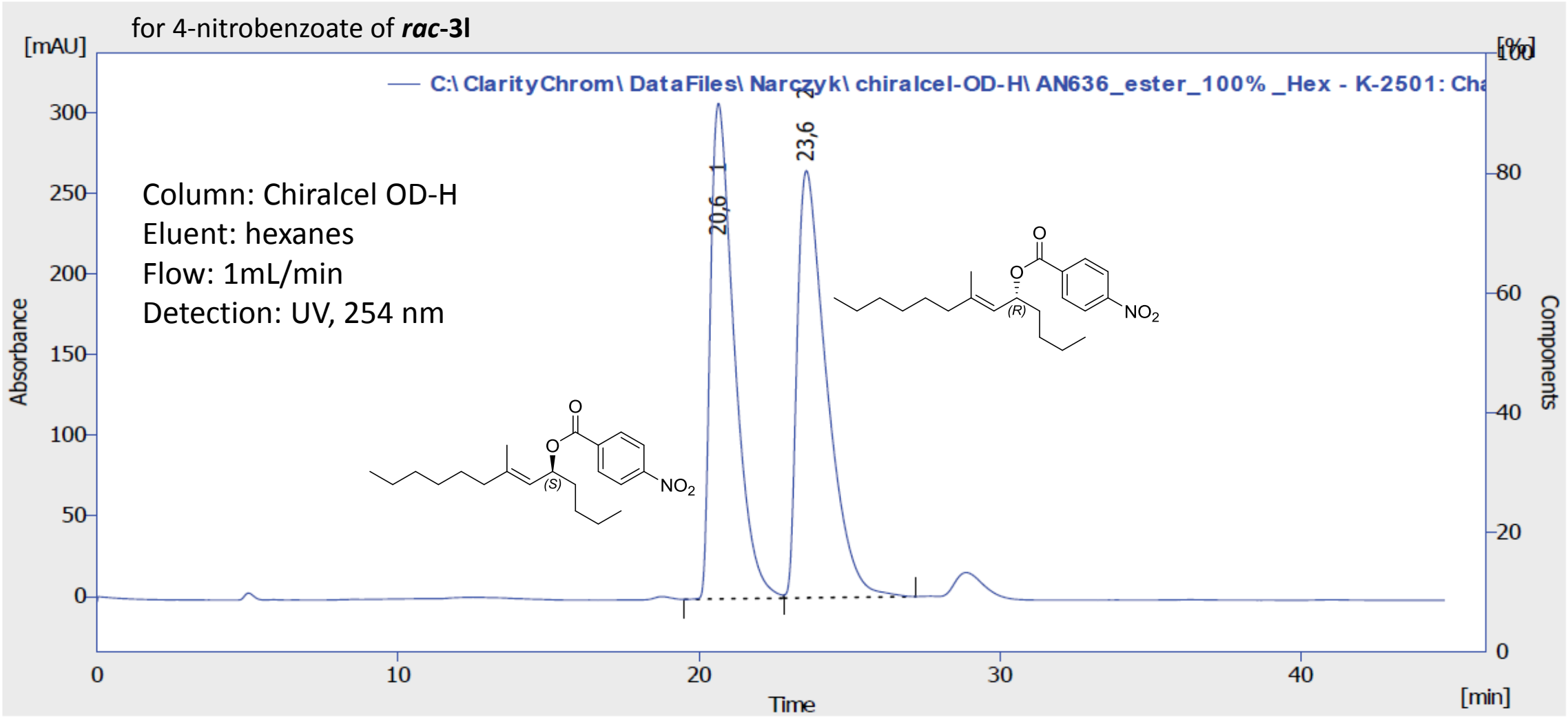
Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN661_ester_100%_Hex - K-2501: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	21,367	30320,013	487,972	96,1	95,4	0,97	
2	24,933	1221,122	23,700	3,9	4,6	0,87	
	Total	31541,135	511,672	100,0	100,0		


138.79
127.88
68.65
39.56
37.46
31.71
28.89
27.65
22.68
22.60
16.46
14.03
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


5.15
5.13
4.37
4.35
4.34
4.33
4.33
4.31
2.00
1.98
1.96
1.65
1.60
1.59
1.59
1.58
1.57
1.56
1.55
1.54
1.54
1.43
1.41
1.40
1.39
1.39
1.37
1.37
1.31
1.30
1.28
1.26
0.90
0.89
0.87
0.86
OH
Compound 3l in CDCl3
1.00
0.98
2.12
4.11
15.59
6.38
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)

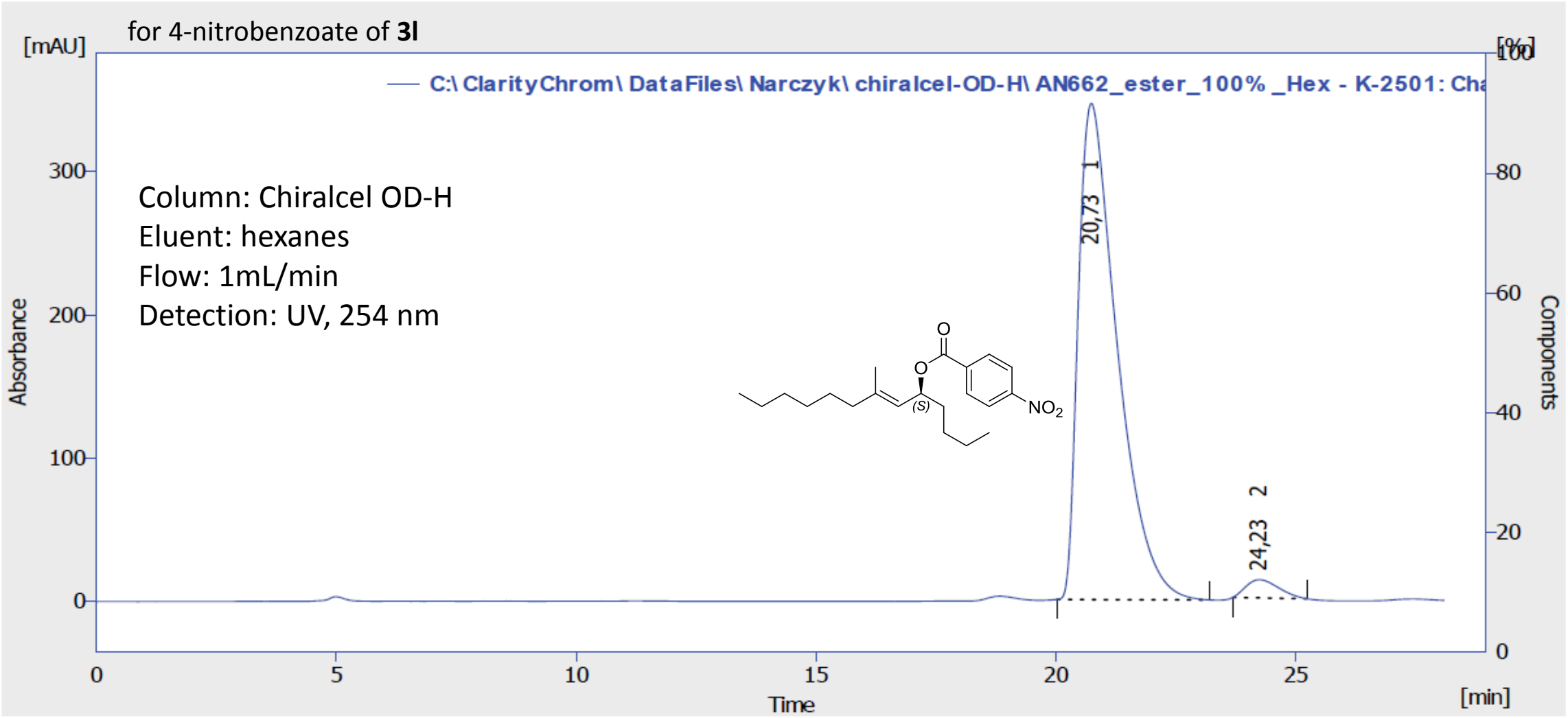
for 4-nitrobenzoate of ***rac*-3l**



Result Table (Uncal - C:\|ClarityChrom\|DataFiles\|Narczyk\|chiralcel-OD-H\|AN636_ester_100%_Hex - K-2501: Channel 1)

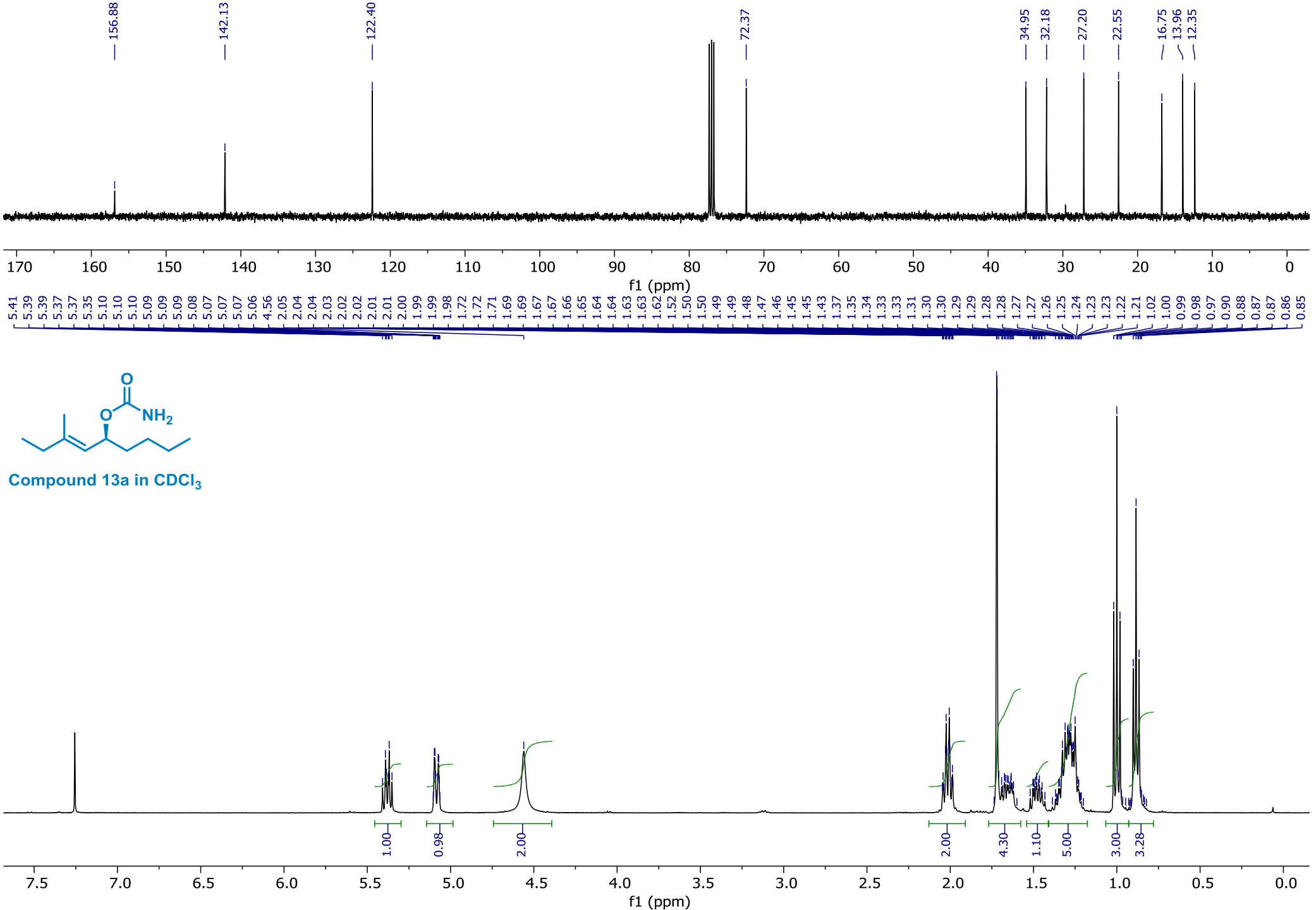
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	20,650	16973,950	307,587	48,4	53,7	0,87	
2	23,567	18085,819	265,187	51,6	46,3	1,05	
	Total	35059,769	572,774	100,0	100,0		

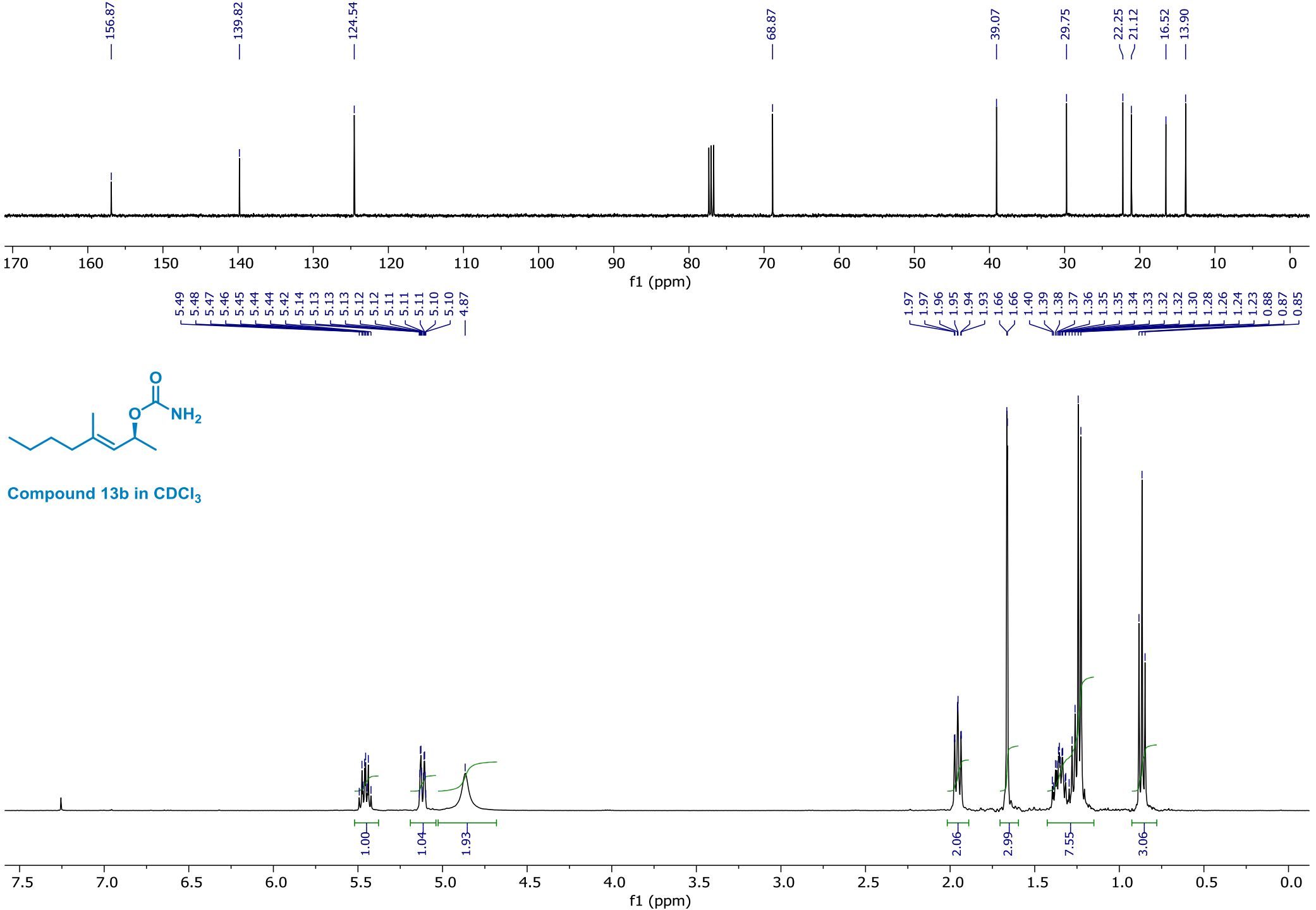
for 4-nitrobenzoate of **3l**



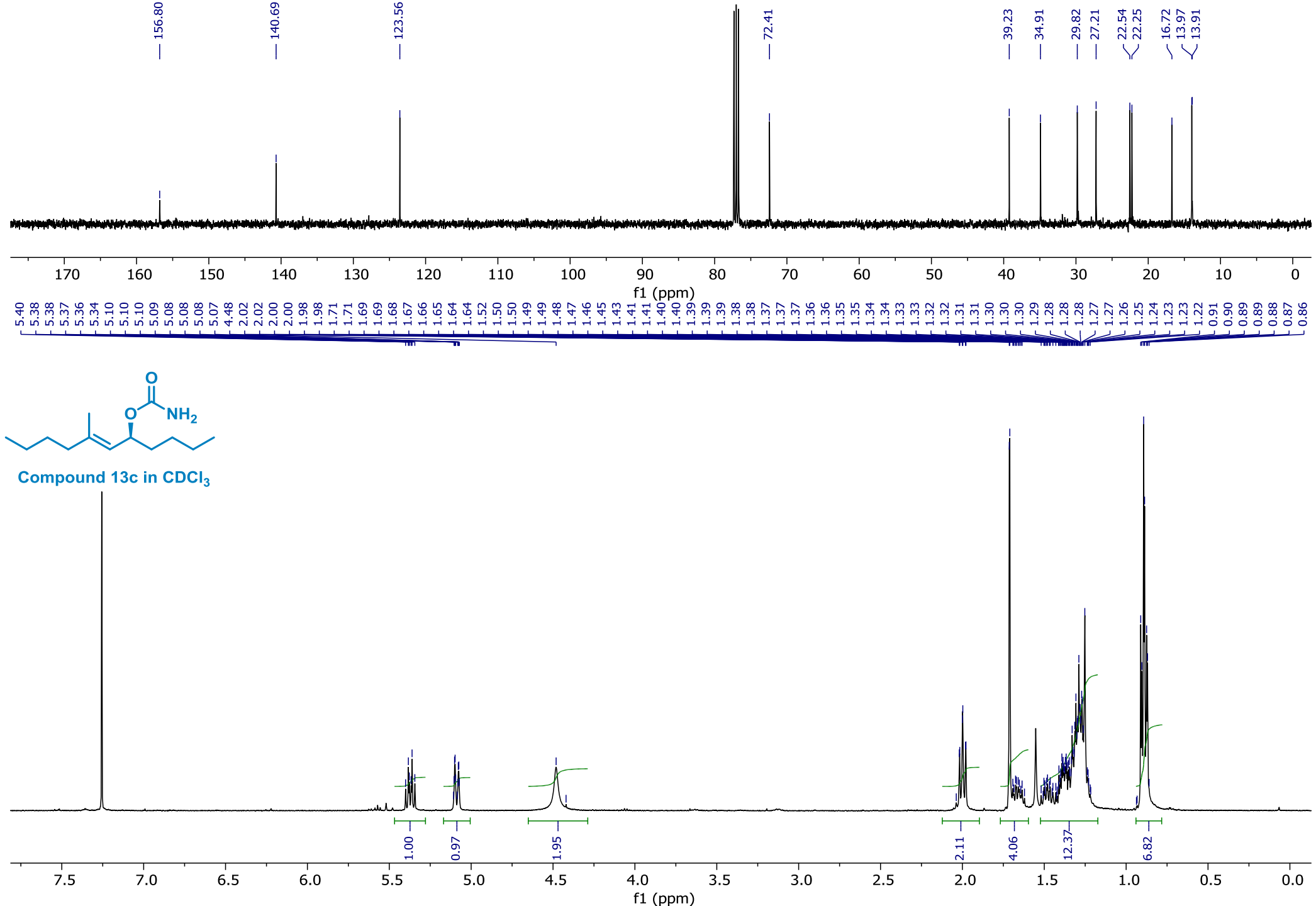
Result Table (Uncal - C:\ClarityChrom\DataFiles\Narczyk\chiralcel-OD-H\AN662_ester_100%_Hex - K-2501: Channel 1)

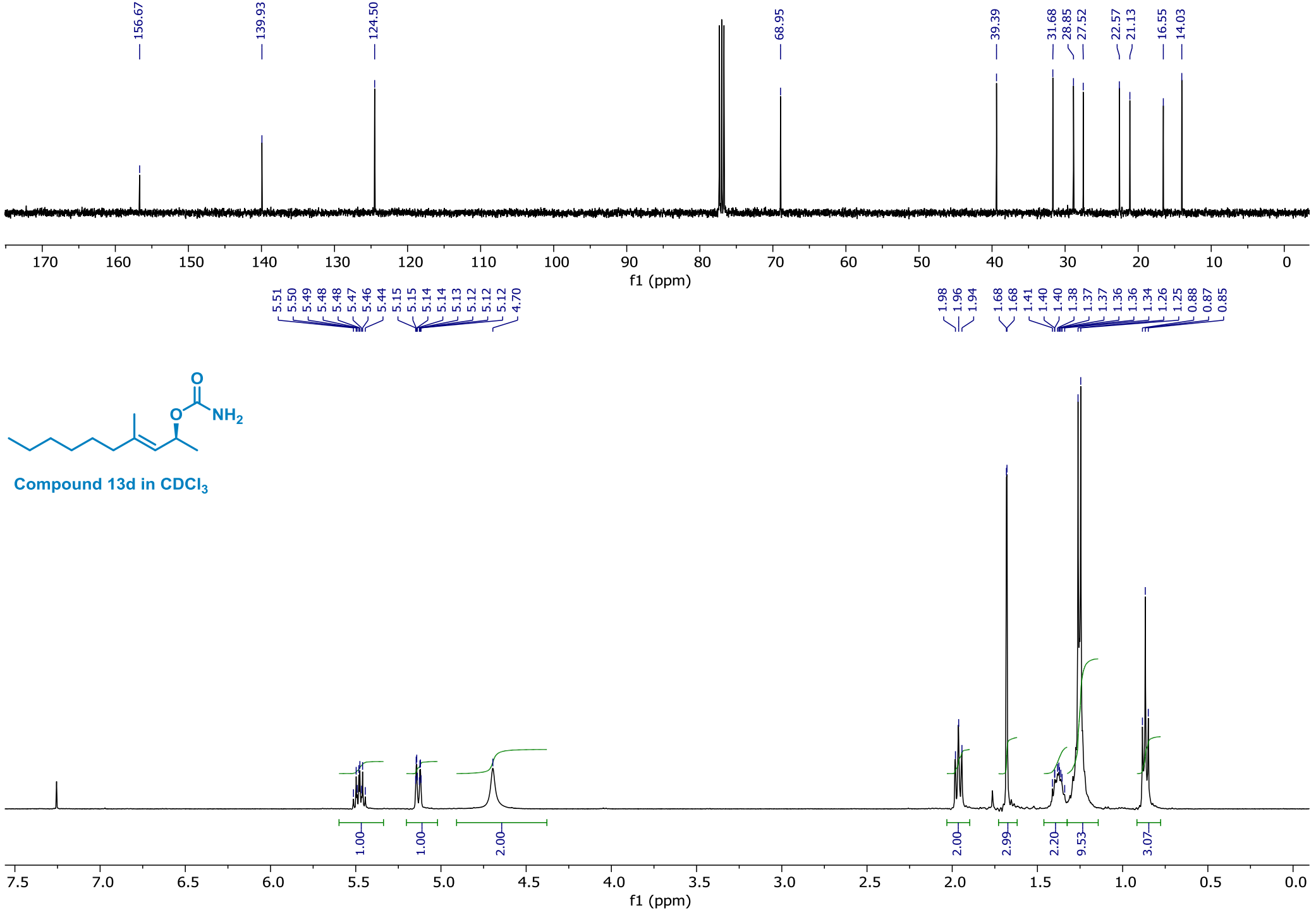
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	20,733	19508,479	346,365	97,0	96,4	0,88	
2	24,233	606,732	12,761	3,0	3,6	0,78	
	Total	20115,210	359,126	100,0	100,0		

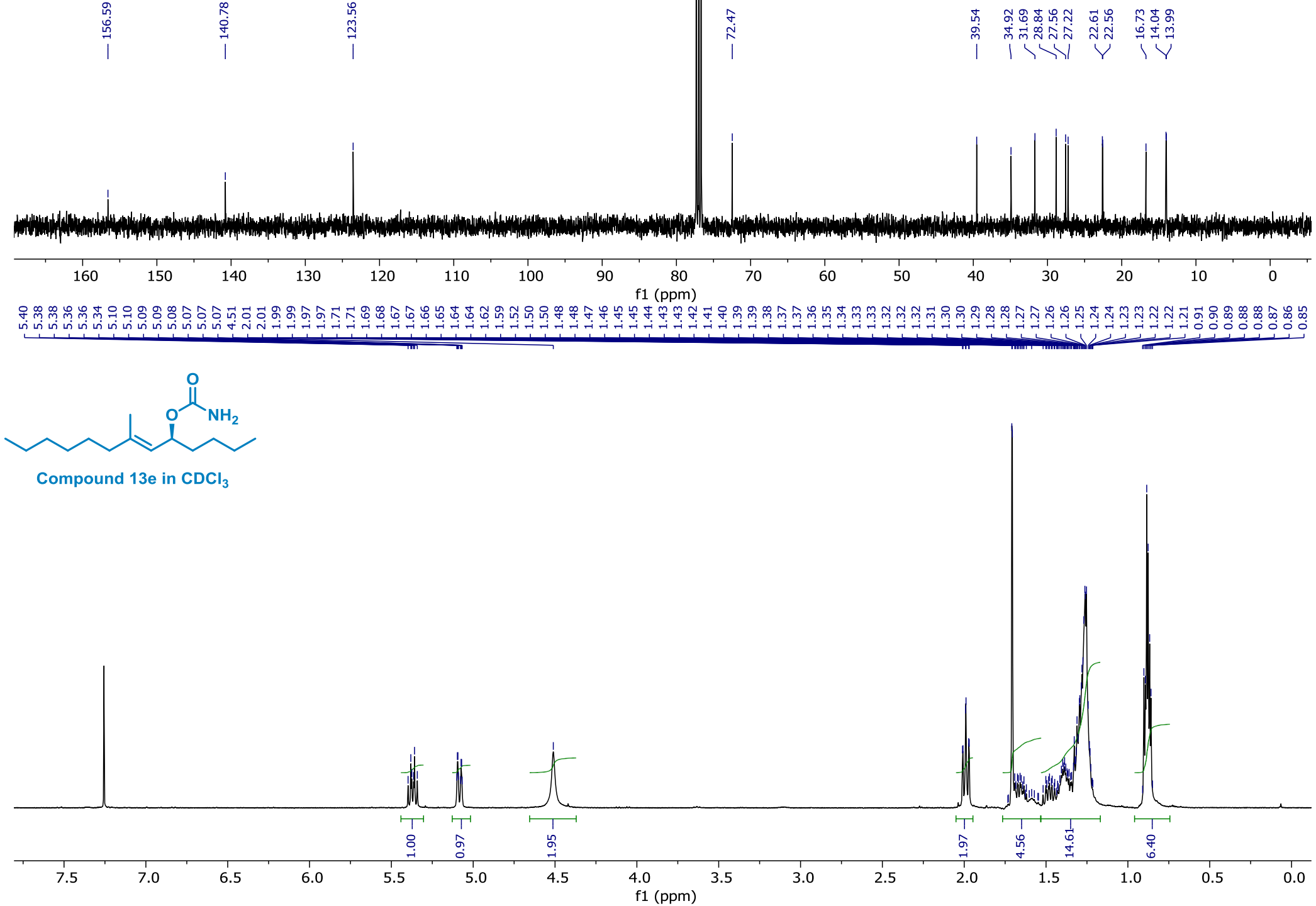

156.88
142.13
122.40
72.37
34.95
32.18
27.20
22.55
16.75
13.96
12.35
f1 (ppm)
5.41 5.39 5.39 5.37 5.37 5.35 5.10 5.10 5.09 5.09 5.09 5.08 5.07 5.07 5.06 4.56 2.05 2.04 2.04 2.03 2.02 2.02 2.01 2.01 2.00 1.99 1.99 1.98 1.72 1.72 1.71 1.69 1.69 1.67 1.67 1.66 1.65 1.64 1.64 1.63 1.63 1.62 1.52 1.50 1.50 1.49 1.49 1.48 1.47 1.46 1.45 1.45 1.43 1.37 1.35 1.34 1.33 1.33 1.31 1.30 1.30 1.29 1.29 1.28 1.28 1.27 1.27 1.26 1.25 1.24 1.23 1.23 1.22 1.21 1.02 1.00 0.99 0.98 0.97 0.90 0.88 0.87 0.87 0.86 0.85
O
O
NH2
Compound 13a in CDCl3
1.00
0.98
2.00
2.00
4.30
1.10
5.00
3.00
3.28
f1 (ppm)

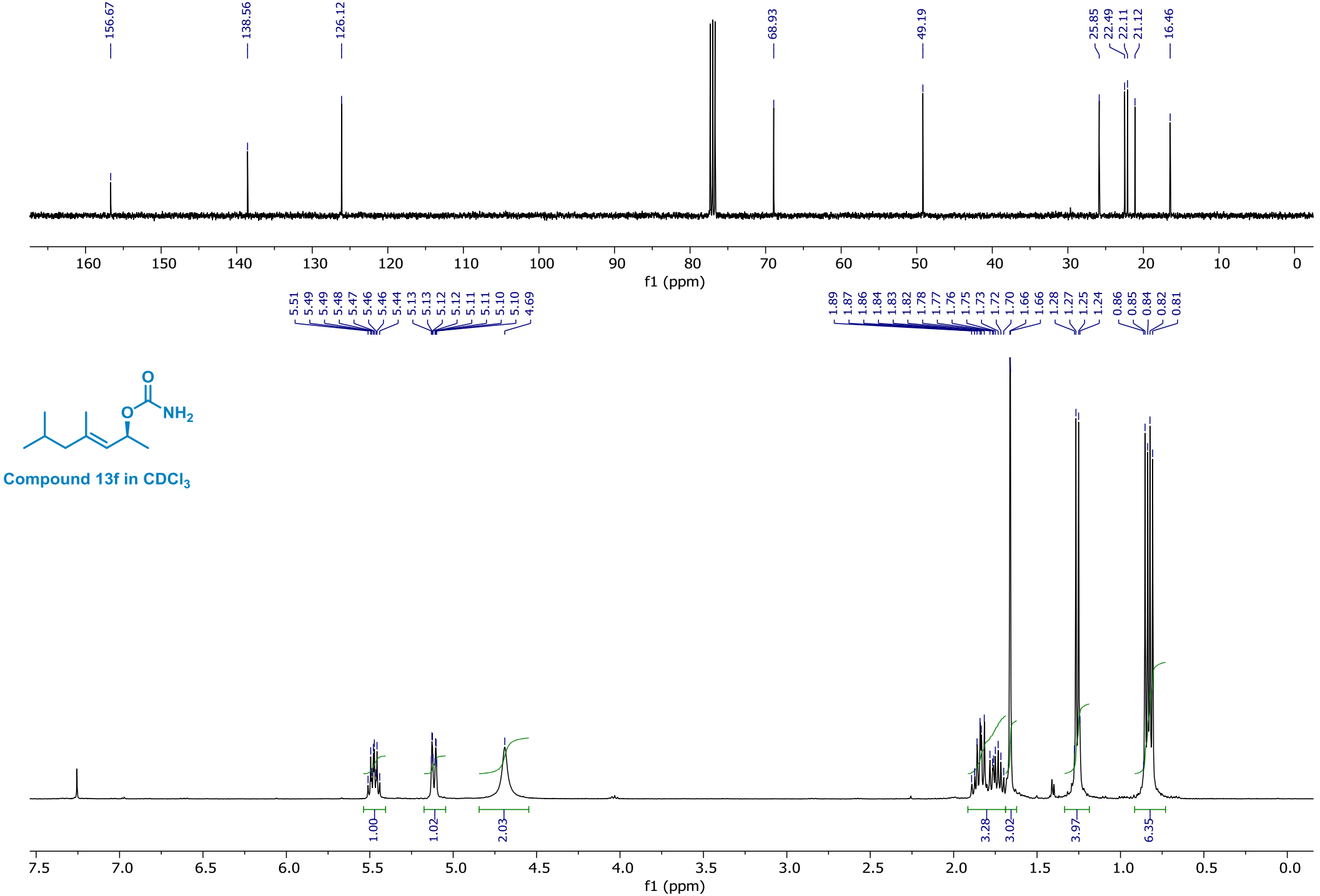


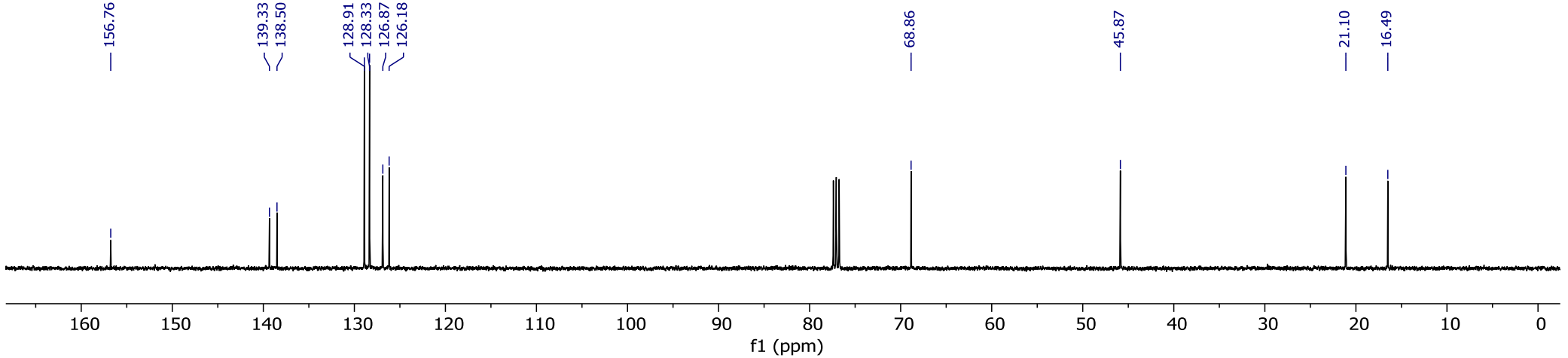
Compound 13b in $CDCl_3$

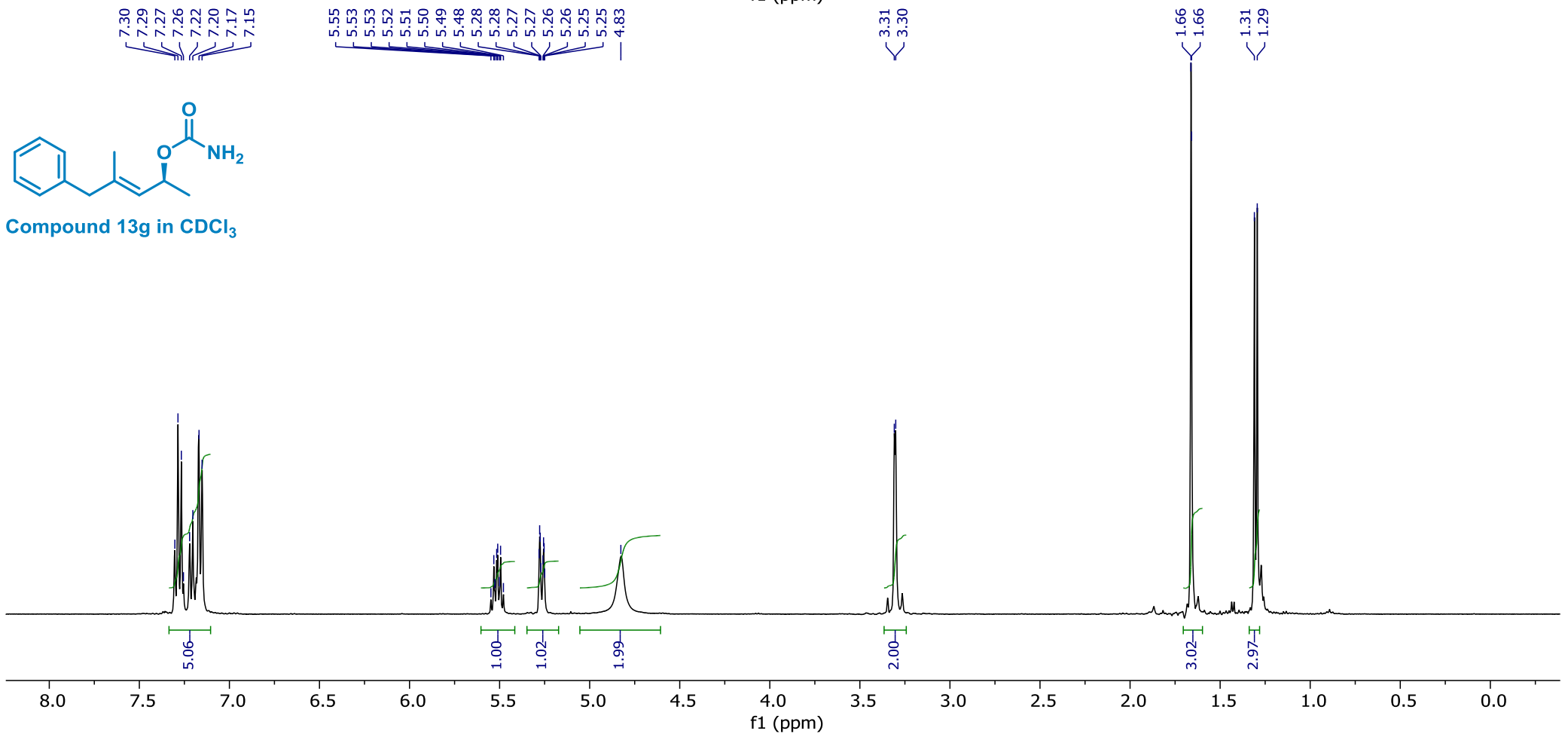

156.80
140.69
123.56
72.41
39.23
34.91
29.82
27.21
22.54
22.25
16.72
13.97
13.91
f1 (ppm)
O
O
NH2
Compound 13c in CDCl3
1.00
0.97
1.95
2.11
4.06
12.37
6.82
f1 (ppm)

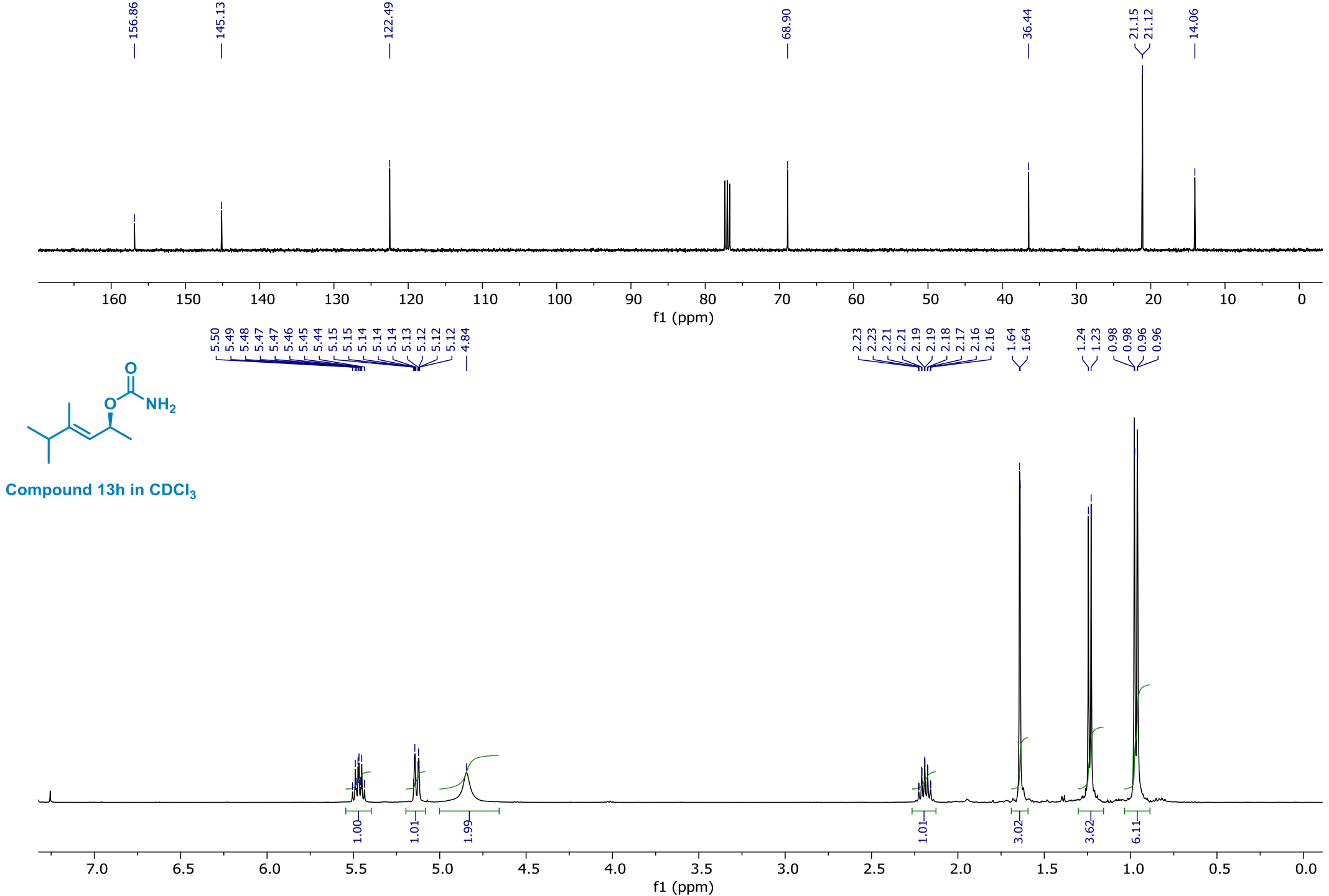

156.67
139.93
124.50
68.95
39.39
31.68
28.85
27.52
22.57
21.13
16.55
14.03
f1 (ppm)
5.51
5.50
5.49
5.48
5.48
5.47
5.46
5.44
5.15
5.15
5.14
5.14
5.13
5.12
5.12
5.12
4.70
1.98
1.96
1.94
1.68
1.68
1.41
1.40
1.40
1.38
1.37
1.37
1.36
1.36
1.34
1.26
1.25
0.88
0.87
0.85
O
O
NH2
Compound 13d in CDCl3
1.00
1.00
2.00
2.00
2.99
2.20
9.53
3.07
f1 (ppm)


156.59
140.78
123.56
72.47
39.54
34.92
31.69
28.84
27.56
27.22
22.61
22.56
16.73
14.04
13.99
f1 (ppm)
O
O
NH2
Compound 13e in CDCl3
1.00
0.97
1.95
1.97
4.56
14.61
6.40
f1 (ppm)

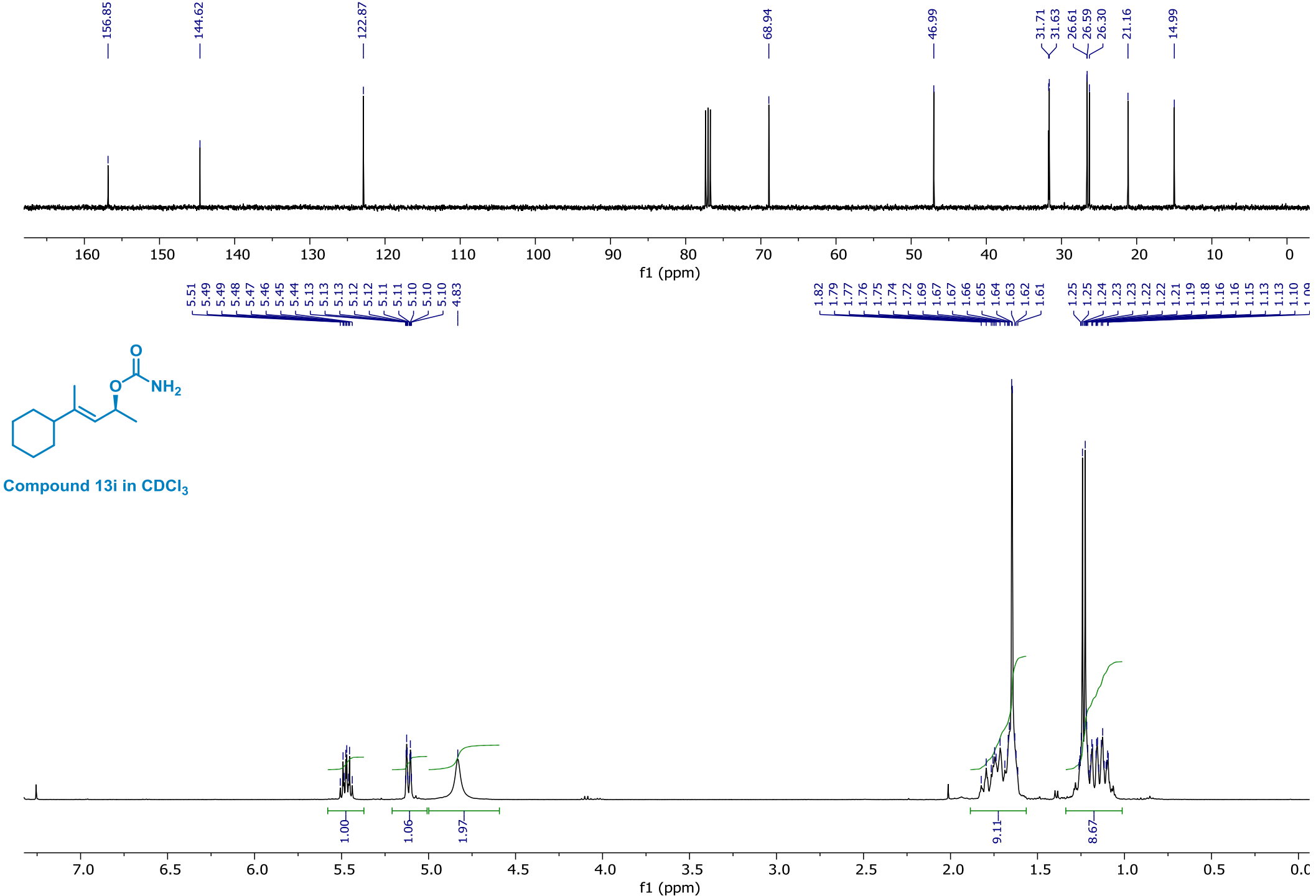

156.67
138.56
126.12
68.93
49.19
25.85
22.49
22.11
21.12
16.46
f1 (ppm)
5.51
5.49
5.49
5.48
5.47
5.46
5.46
5.44
5.13
5.13
5.12
5.12
5.11
5.11
5.10
5.10
4.69
1.89
1.87
1.86
1.84
1.83
1.82
1.78
1.77
1.76
1.75
1.73
1.72
1.70
1.66
1.66
1.28
1.27
1.25
1.24
0.86
0.85
0.84
0.82
0.81
O
O
NH2
Compound 13f in CDCl3
1.00
1.02
2.03
3.28
3.02
3.97
6.35
f1 (ppm)

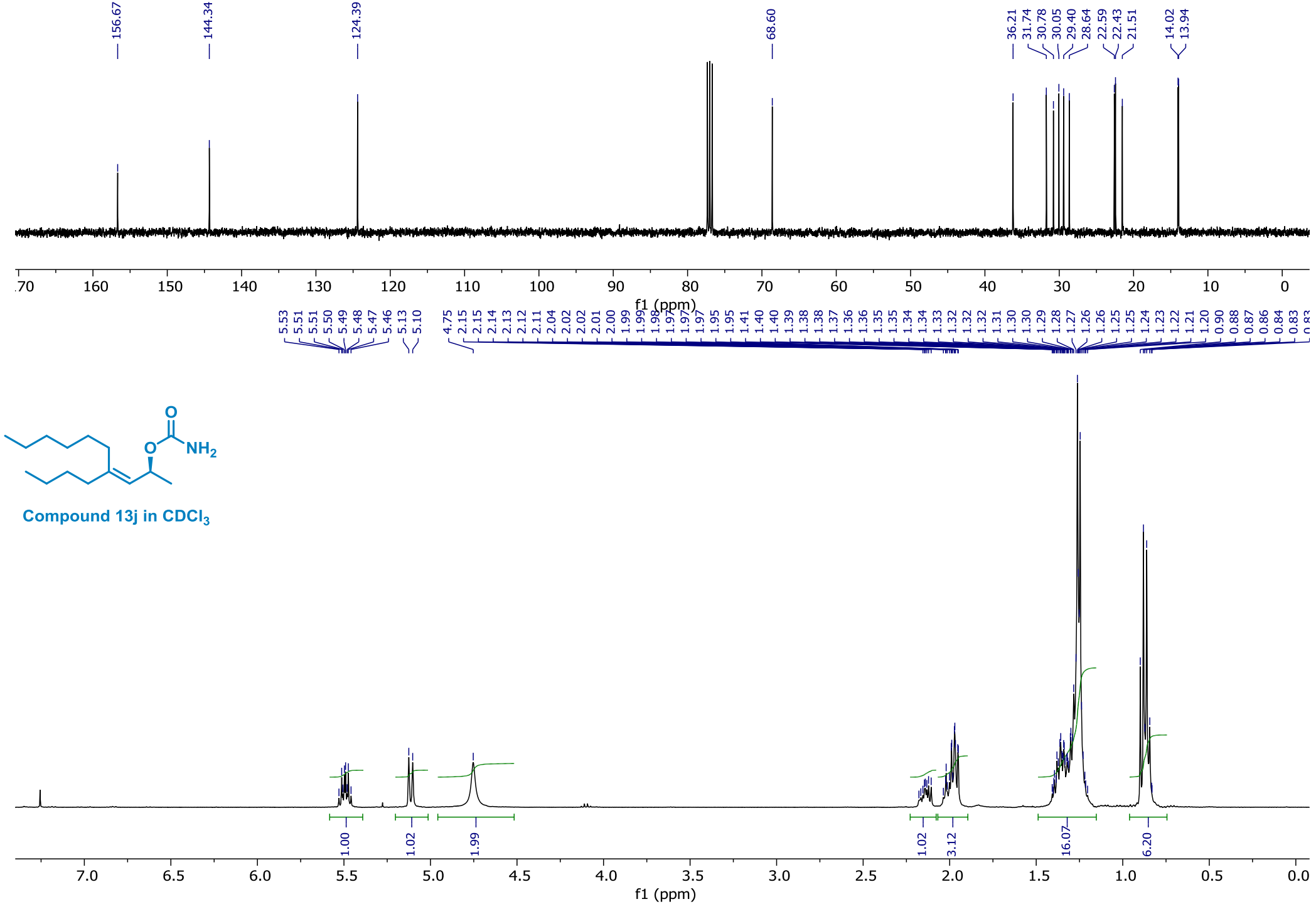

156.76
139.33
138.50
128.91
128.33
126.87
126.18
68.86
45.87
21.10
16.49
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.30
7.29
7.27
7.26
7.22
7.20
7.17
7.15
5.55
5.53
5.53
5.52
5.51
5.50
5.49
5.48
5.28
5.28
5.27
5.27
5.26
5.26
5.25
5.25
4.83
3.31
3.30
1.66
1.66
1.31
1.29
O
O
NH2
Compound 13g in CDCl3
5.06
1.00
1.02
1.99
2.00
3.02
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)

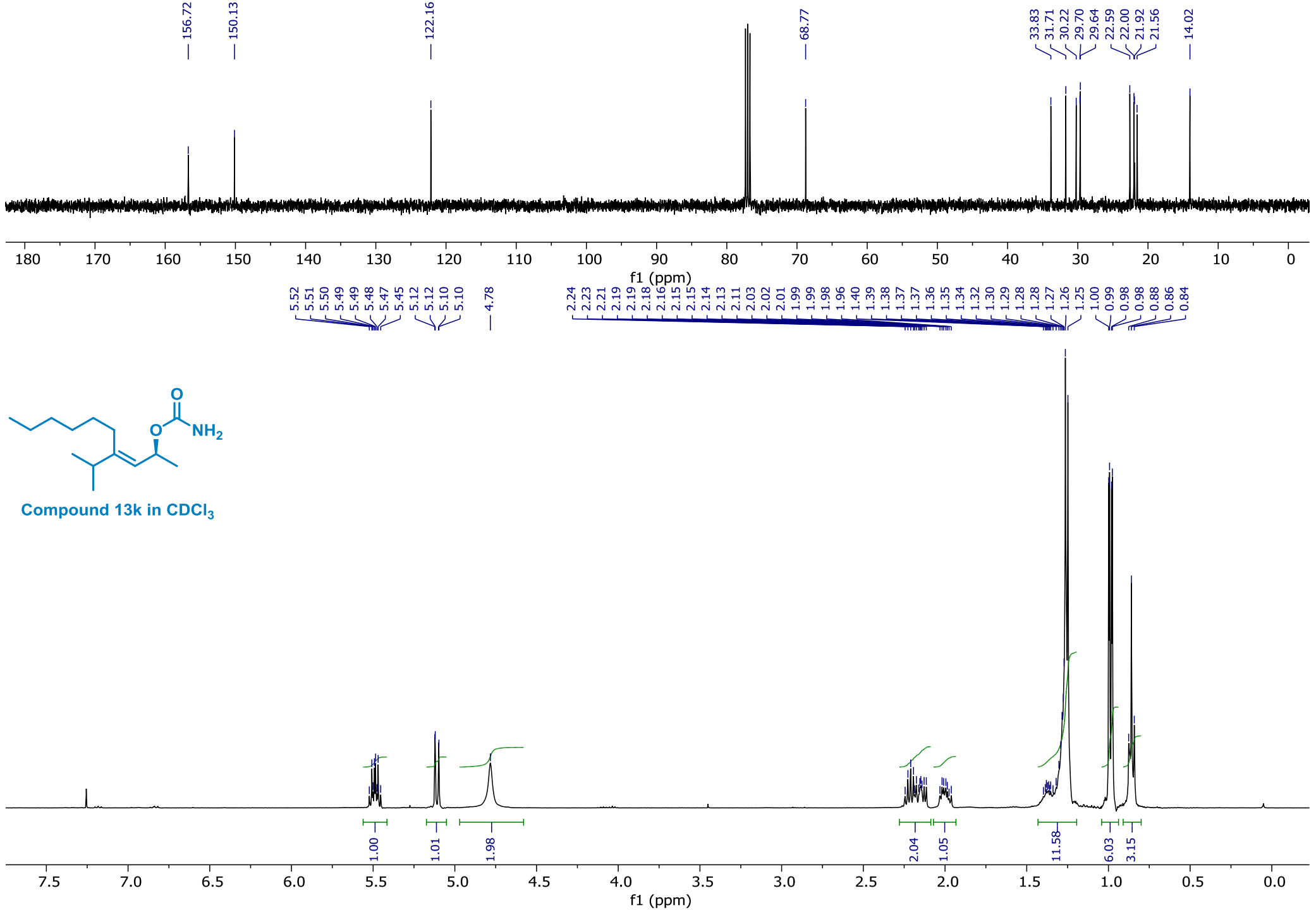


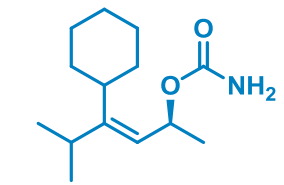
Compound 13h in $CDCl_3$


156.85
144.62
122.87
68.94
46.99
31.71
31.63
26.61
26.59
26.30
21.16
14.99
f1 (ppm)
5.51
5.49
5.49
5.48
5.47
5.46
5.45
5.44
5.13
5.13
5.13
5.12
5.12
5.11
5.11
5.10
5.10
5.10
4.83
1.82
1.79
1.77
1.76
1.75
1.74
1.72
1.69
1.67
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.25
1.25
1.24
1.23
1.23
1.22
1.22
1.21
1.19
1.18
1.16
1.16
1.15
1.13
1.13
1.10
O
O
NH2
Compound 13i in CDCl3
1.00
1.06
1.97
9.11
8.67
f1 (ppm)

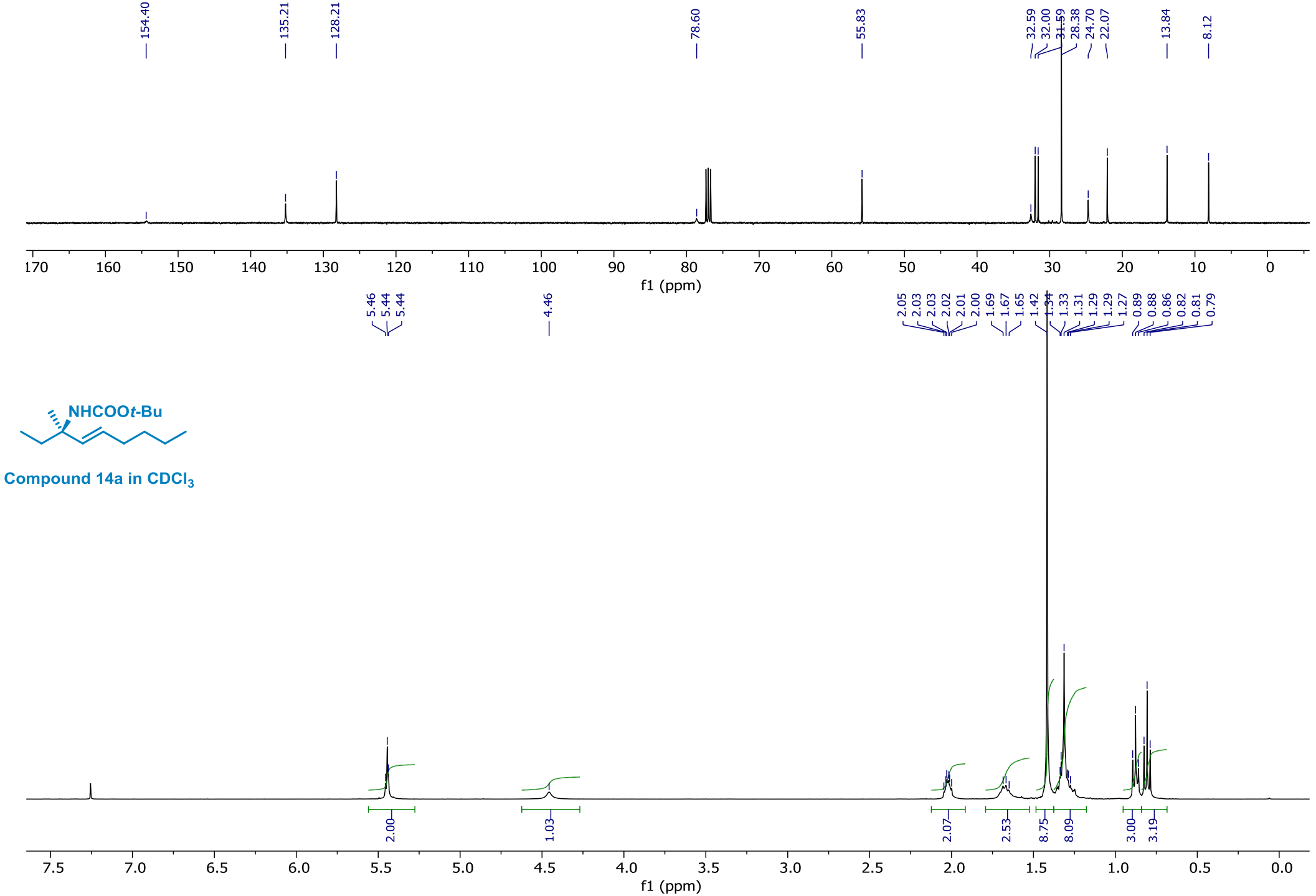


Compound 13j in $CDCl_3$


156.72
150.13
122.16
68.77
33.83
31.71
30.22
29.70
29.64
22.59
22.00
21.92
21.56
14.02
f1 (ppm)
5.52
5.51
5.50
5.49
5.49
5.48
5.47
5.45
5.12
5.12
5.10
5.10
4.78
2.24
2.23
2.21
2.19
2.19
2.18
2.16
2.15
2.15
2.14
2.13
2.11
2.03
2.02
2.01
1.99
1.99
1.98
1.96
1.40
1.39
1.38
1.37
1.37
1.36
1.35
1.34
1.32
1.30
1.29
1.28
1.28
1.27
1.26
1.25
1.00
0.99
0.98
0.98
0.88
0.86
0.84
O
O
NH2
Compound 13k in CDCl3
1.00
1.01
1.98
2.04
1.05
11.58
6.03
3.15
f1 (ppm)

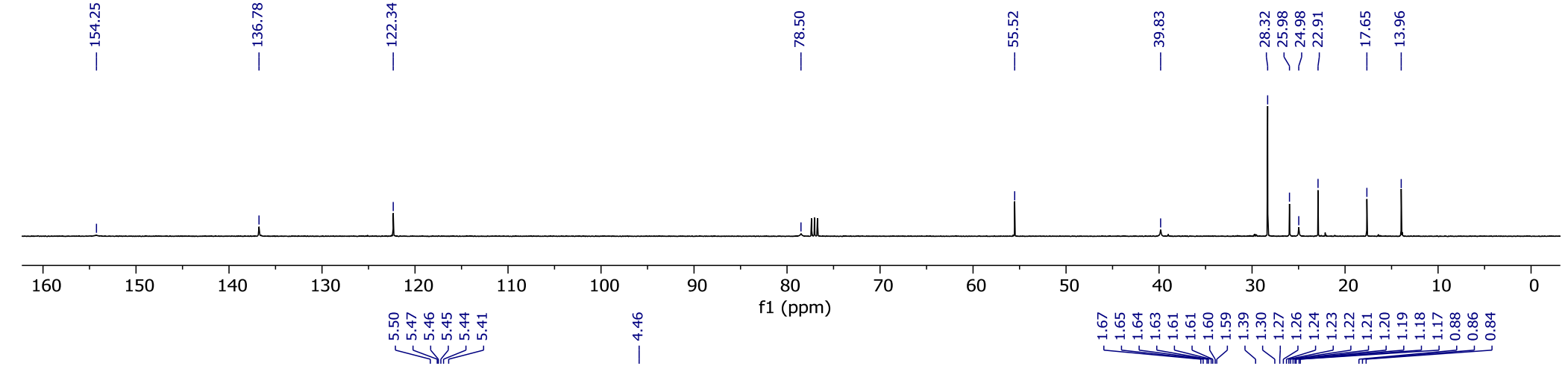


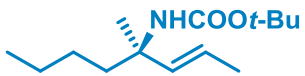
Compound 13l in $CDCl_3$



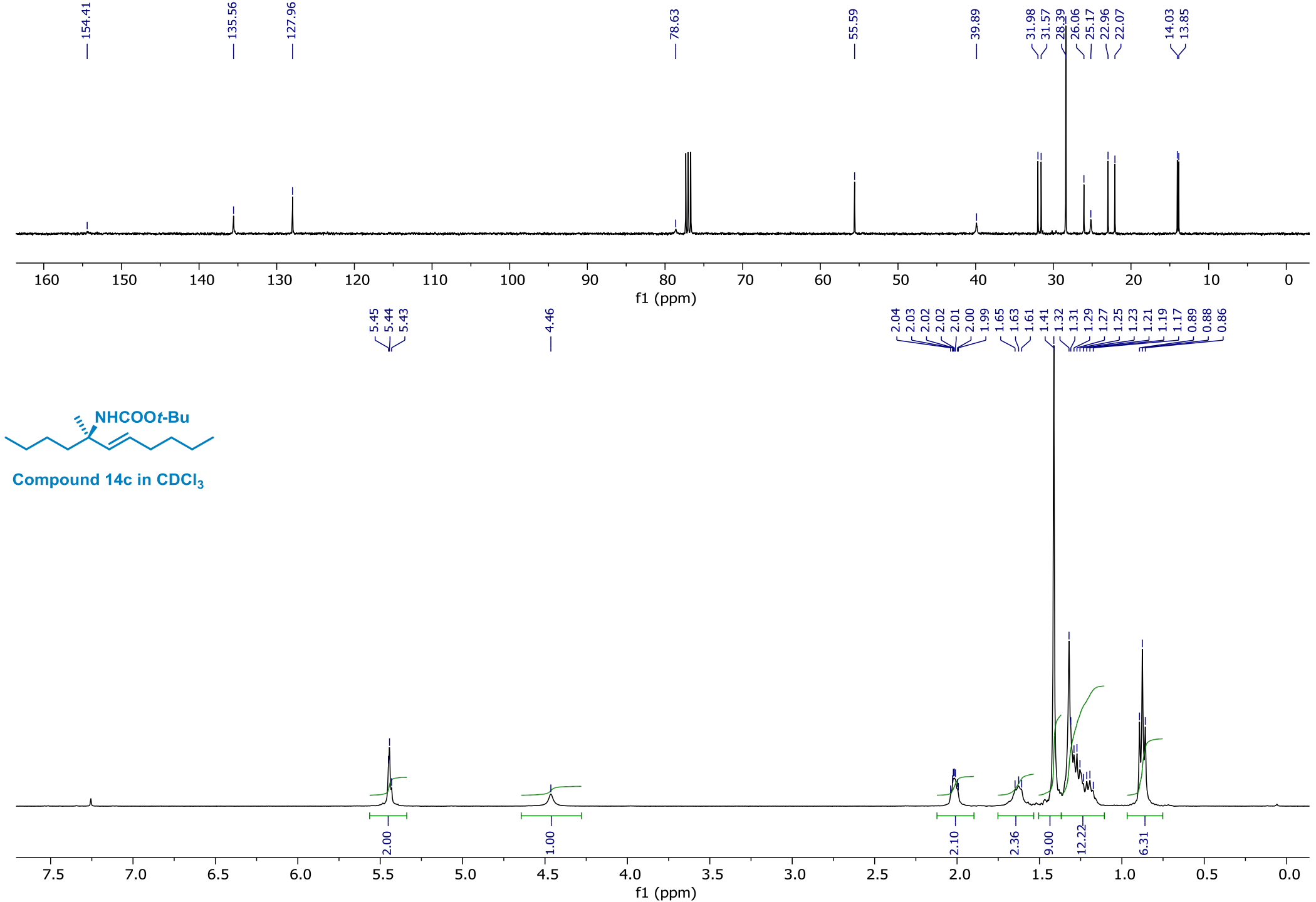
NHCOO*t*-Bu

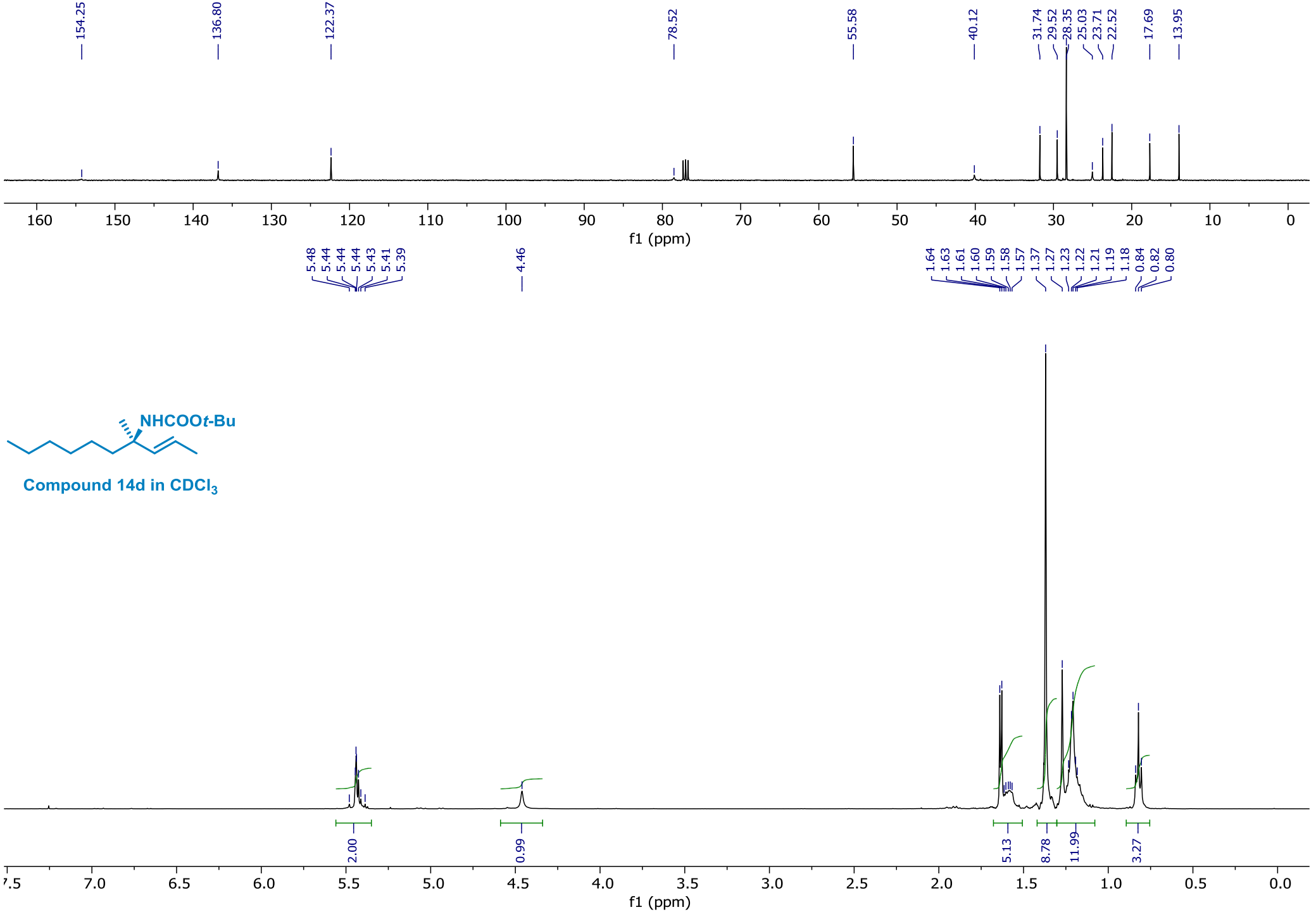
Compound 14a in $CDCl_3$

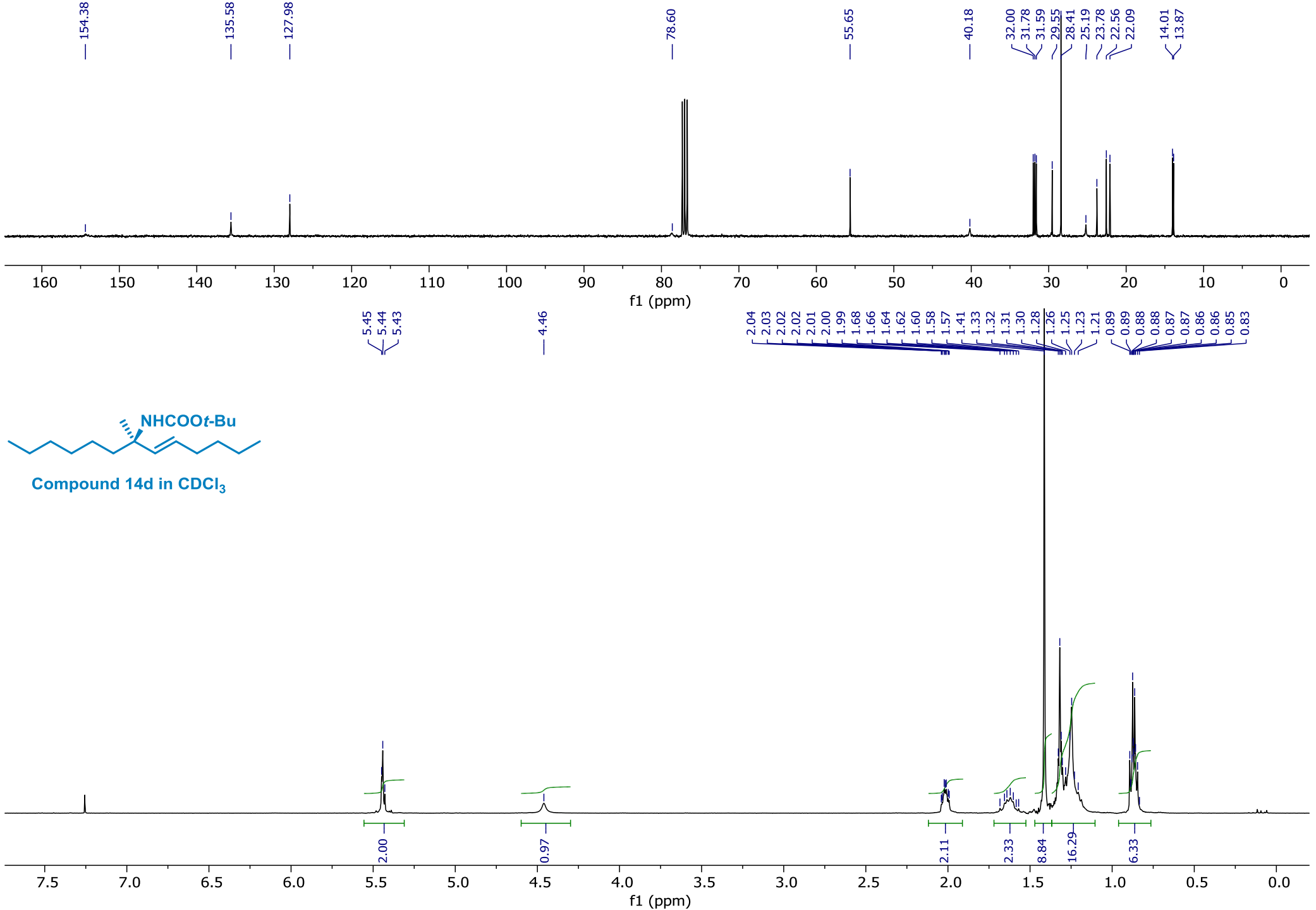


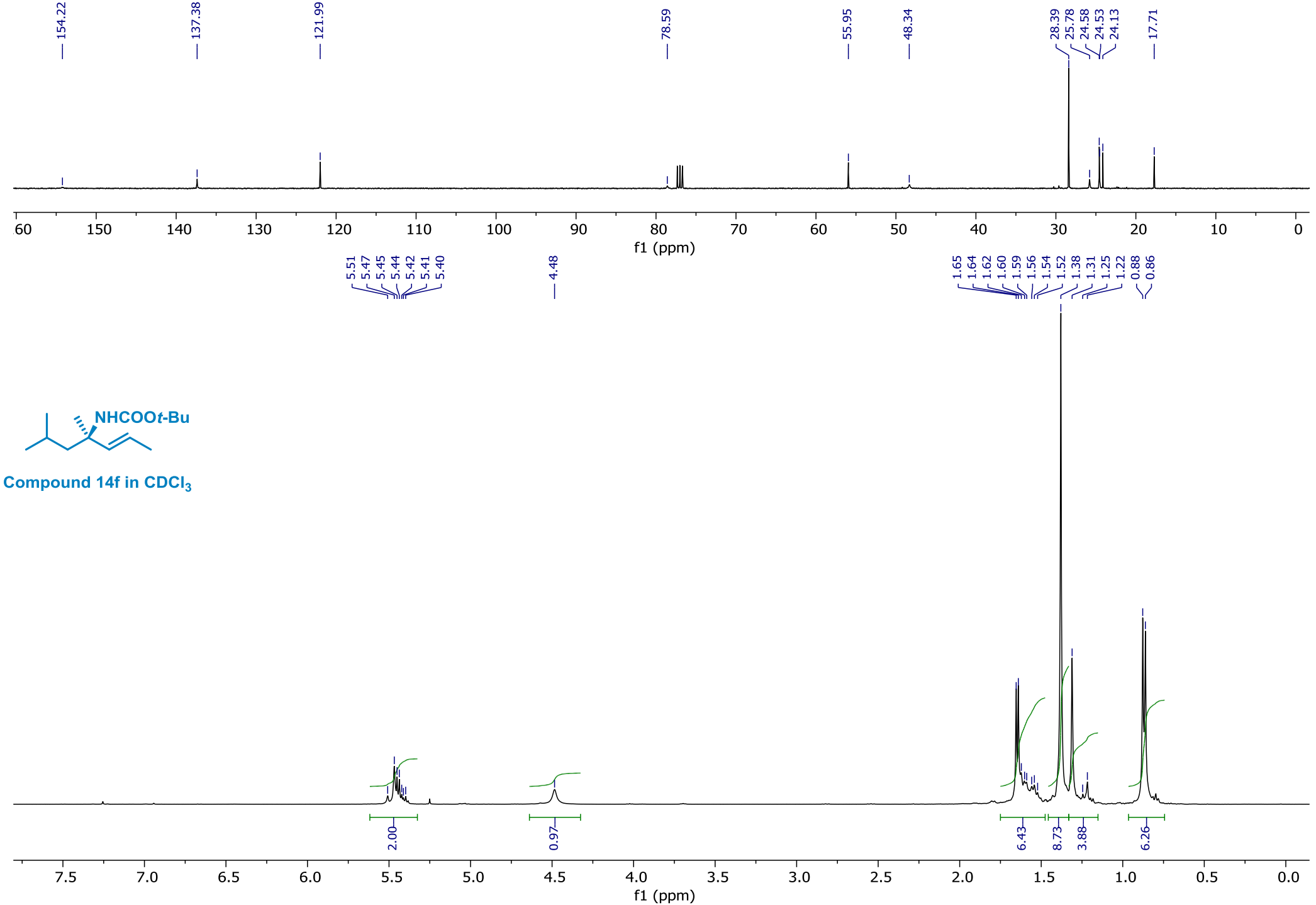


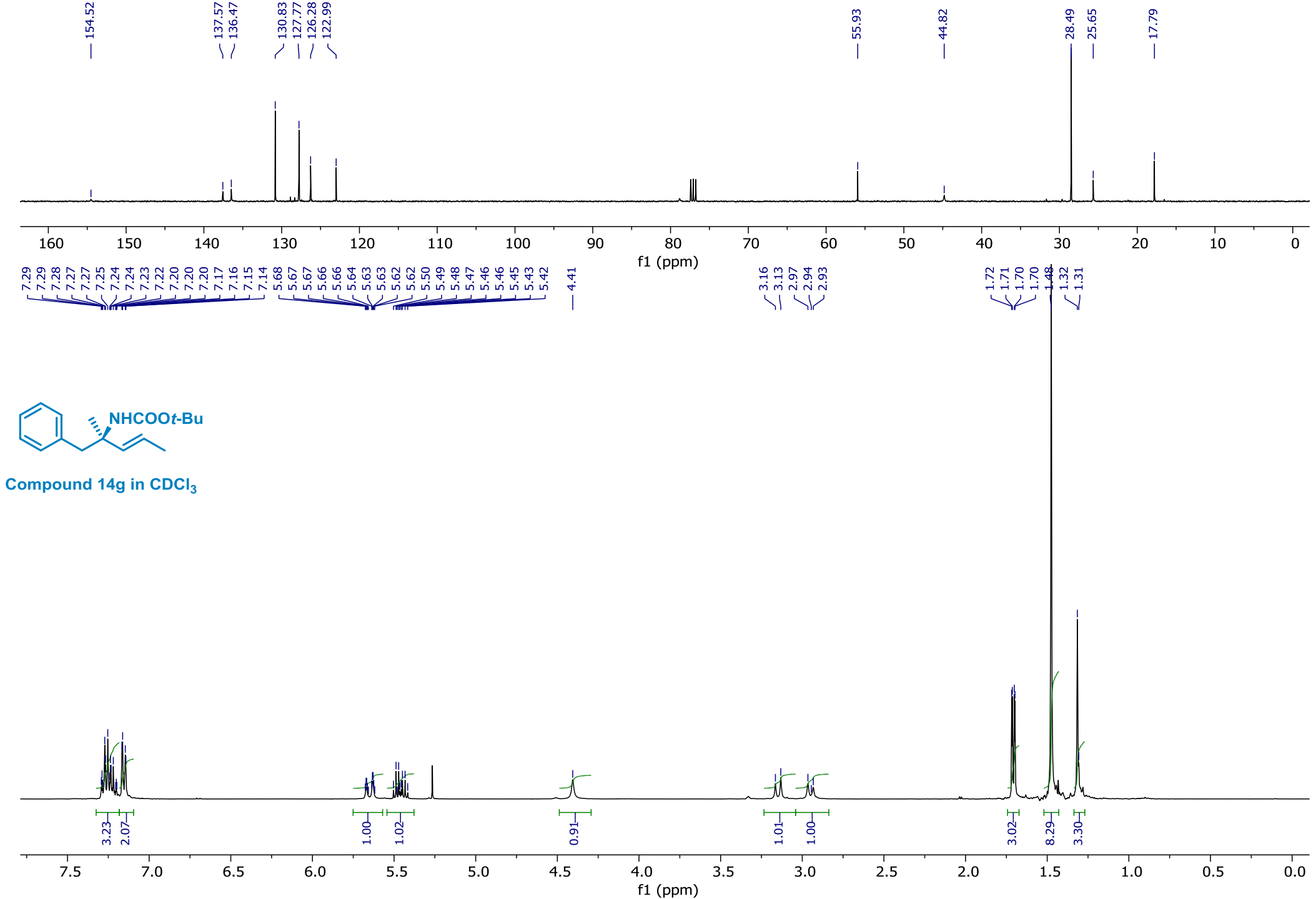
Compound 14b in $CDCl_3$

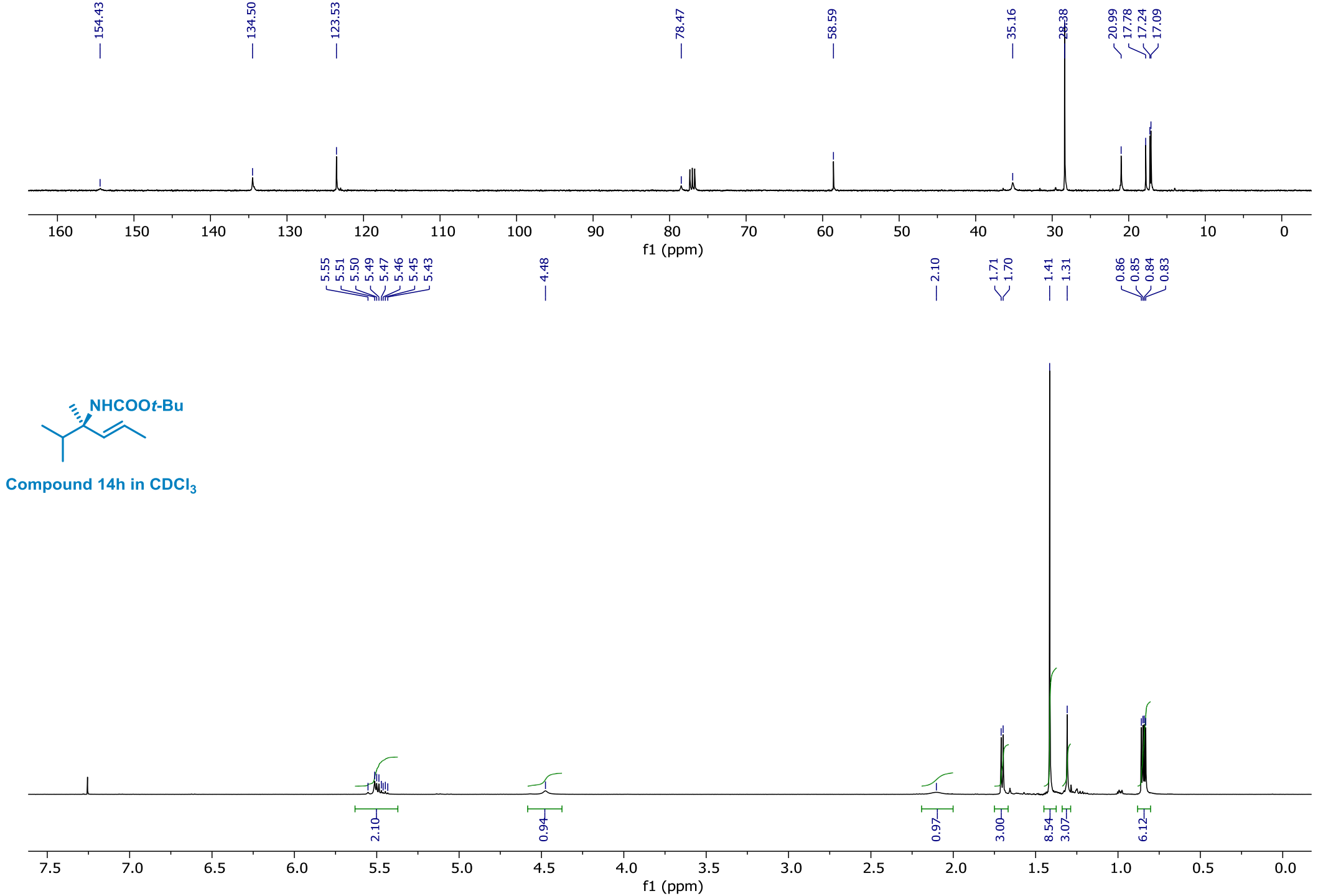

154.41
135.56
127.96
78.63
55.59
39.89
31.98
31.57
28.39
26.06
25.17
22.96
22.07
14.03
13.85
f1 (ppm)
5.45
5.44
5.43
4.46
2.04
2.03
2.02
2.02
2.01
2.00
1.99
1.65
1.63
1.61
1.41
1.32
1.31
1.29
1.27
1.25
1.23
1.21
1.19
1.17
0.89
0.88
0.86
NHCOOt-Bu
Compound 14c in CDCl3
2.00
1.00
2.10
2.36
9.00
12.22
6.31
f1 (ppm)

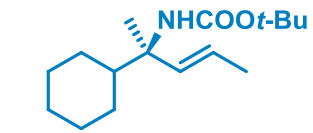

154.25
136.80
122.37
78.52
55.58
40.12
31.74
29.52
28.35
25.03
23.71
22.52
17.69
13.95
f1 (ppm)
5.48
5.44
5.44
5.44
5.43
5.41
5.39
4.46
1.64
1.63
1.61
1.60
1.59
1.58
1.57
1.37
1.27
1.23
1.22
1.21
1.19
1.18
0.84
0.82
0.80
NHCOO*t*-Bu
Compound 14d in $CDCl_3$
2.00
0.99
5.13
8.78
11.99
3.27
f1 (ppm)


154.38
135.58
127.98
78.60
55.65
40.18
32.00
31.78
31.59
29.55
28.41
25.19
23.78
22.56
22.09
14.01
13.87
f1 (ppm)
5.45
5.44
5.43
4.46
2.04
2.03
2.02
2.02
2.01
2.00
2.00
1.99
1.68
1.66
1.64
1.62
1.60
1.58
1.57
1.41
1.33
1.32
1.31
1.30
1.28
1.26
1.25
1.23
1.21
0.89
0.89
0.88
0.88
0.87
0.87
0.86
0.86
0.85
0.83
NHCOOt-Bu
Compound 14d in CDCl3
2.00
0.97
2.11
2.33
8.84
16.29
6.33
f1 (ppm)

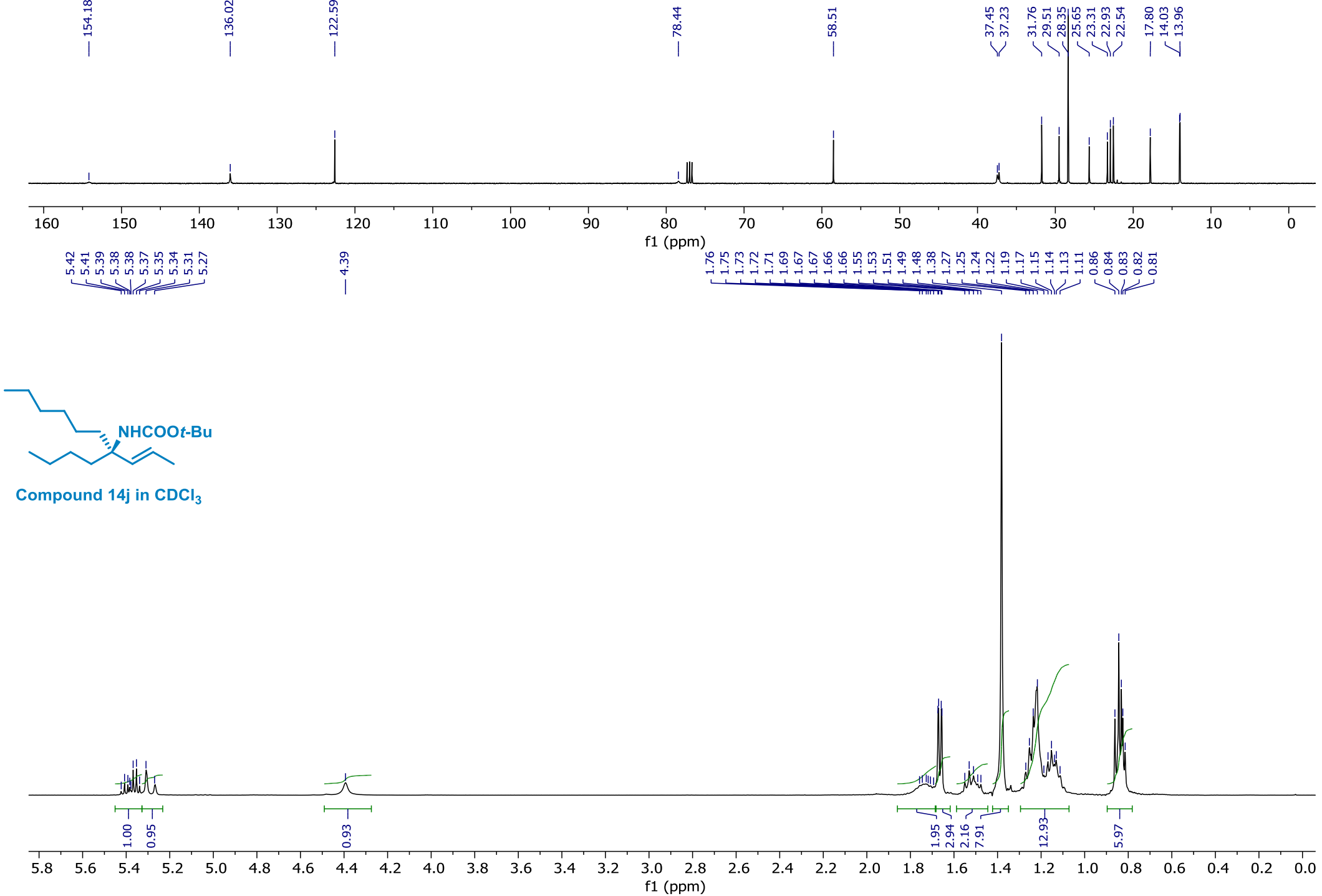

154.22
137.38
121.99
78.59
55.95
48.34
28.39
25.78
24.58
24.53
24.13
17.71
f1 (ppm)
5.51
5.47
5.45
5.44
5.42
5.41
5.40
4.48
1.65
1.64
1.62
1.60
1.59
1.56
1.54
1.52
1.38
1.31
1.25
1.22
0.88
0.86
NHCOO*t*-Bu
Compound 14f in $CDCl_3$
2.00
0.97
6.43
8.73
3.88
6.26
f1 (ppm)

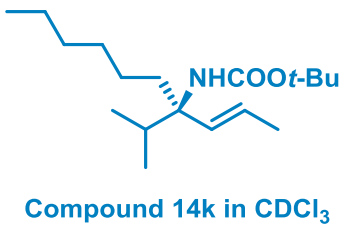

NHCOOt-Bu
Compound 14g in CDCl3
f1 (ppm)
f1 (ppm)


154.43
134.50
123.53
78.47
58.59
35.16
28.38
20.99
17.78
17.24
17.09
f1 (ppm)
5.55
5.51
5.50
5.49
5.47
5.46
5.45
5.43
4.48
2.10
1.71
1.70
1.41
1.31
0.86
0.85
0.84
0.83
NHCOOt-Bu
Compound 14h in CDCl3
2.10
0.94
0.97
3.00
8.54
3.07
6.12
f1 (ppm)

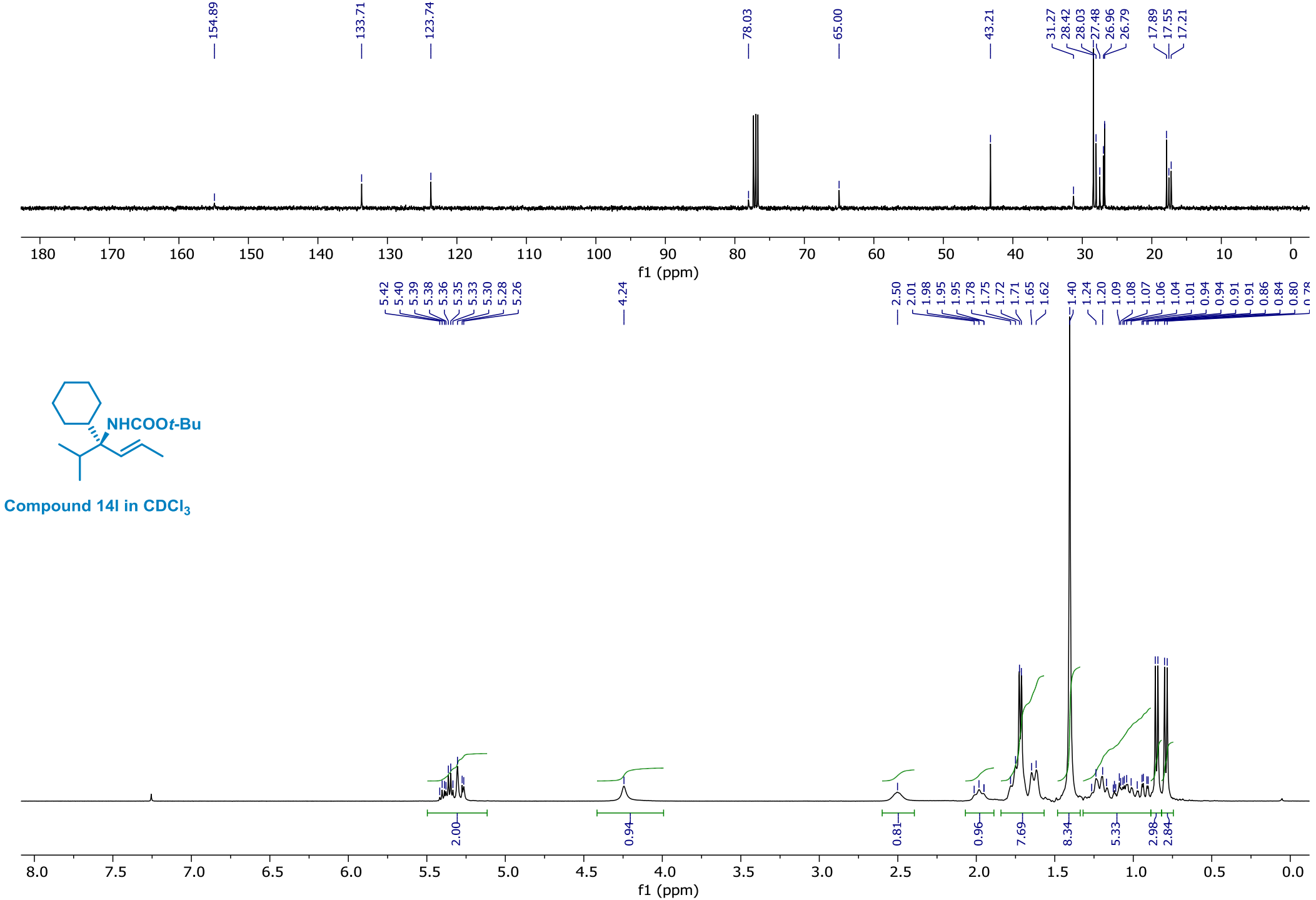


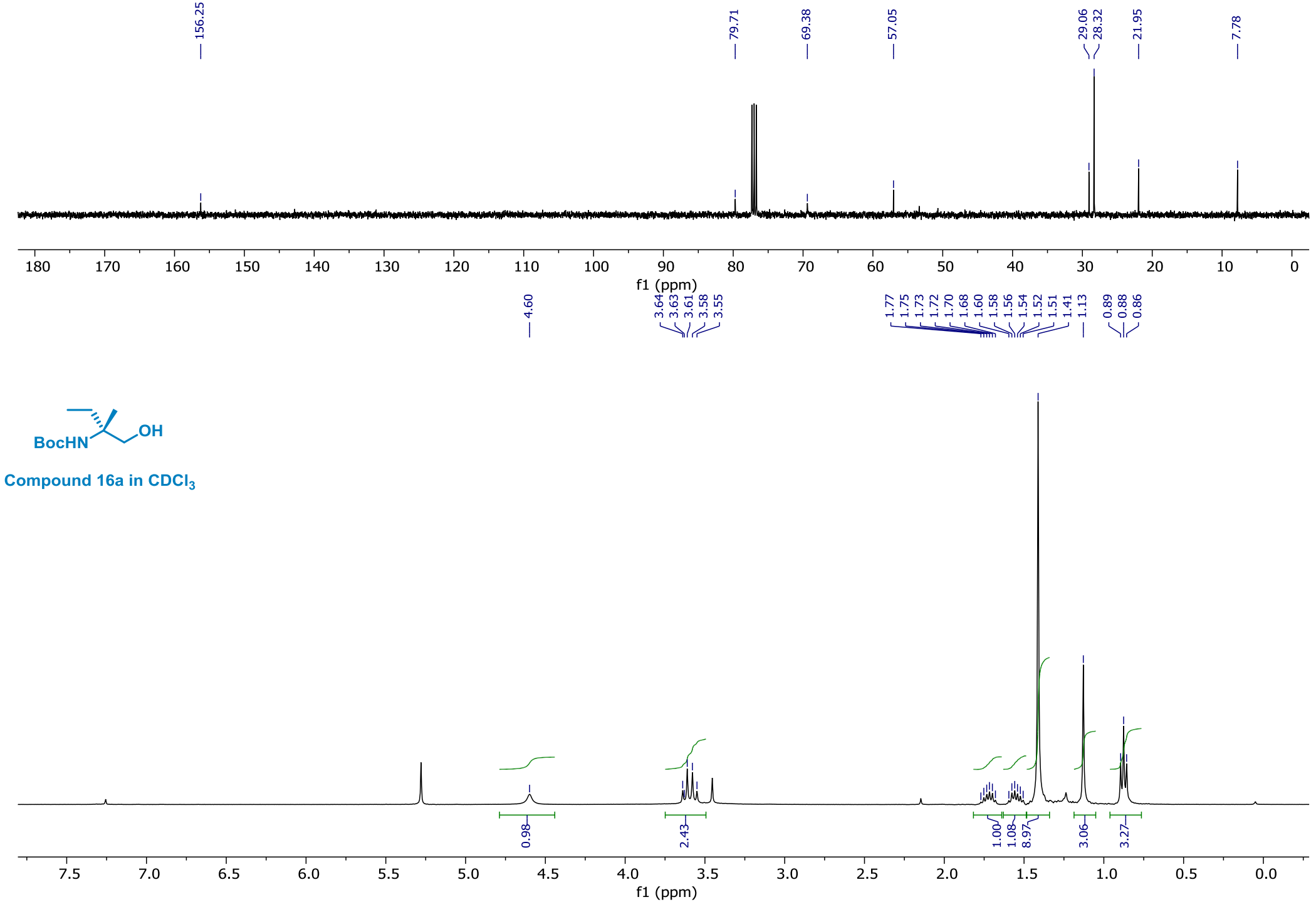
Compound 14i in $CDCl_3$

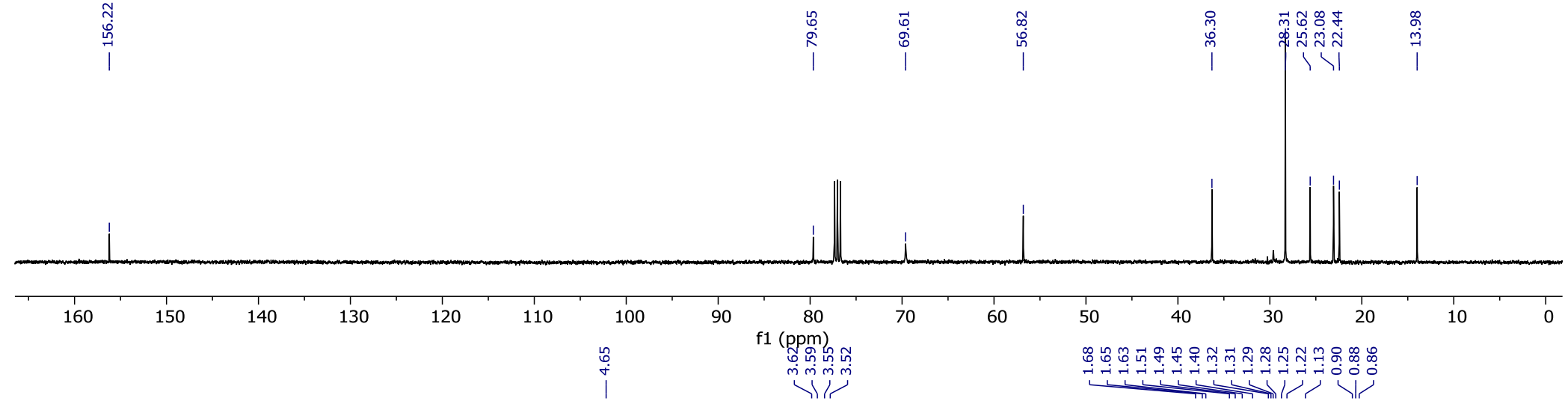

NHCOO*t*-Bu
Compound 14j in $CDCl_3$
f1 (ppm)
f1 (ppm)

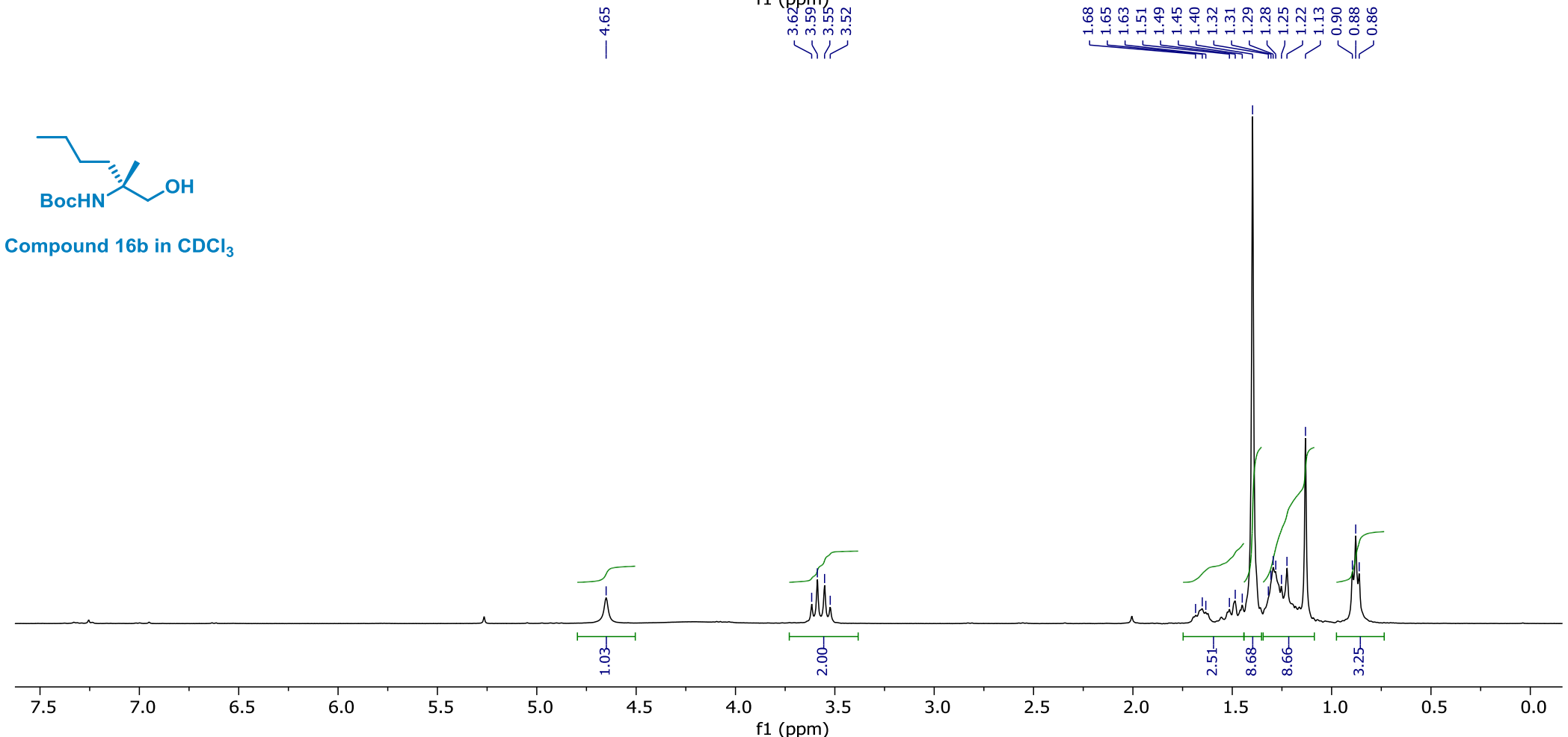


Compound 14k in $CDCl_3$

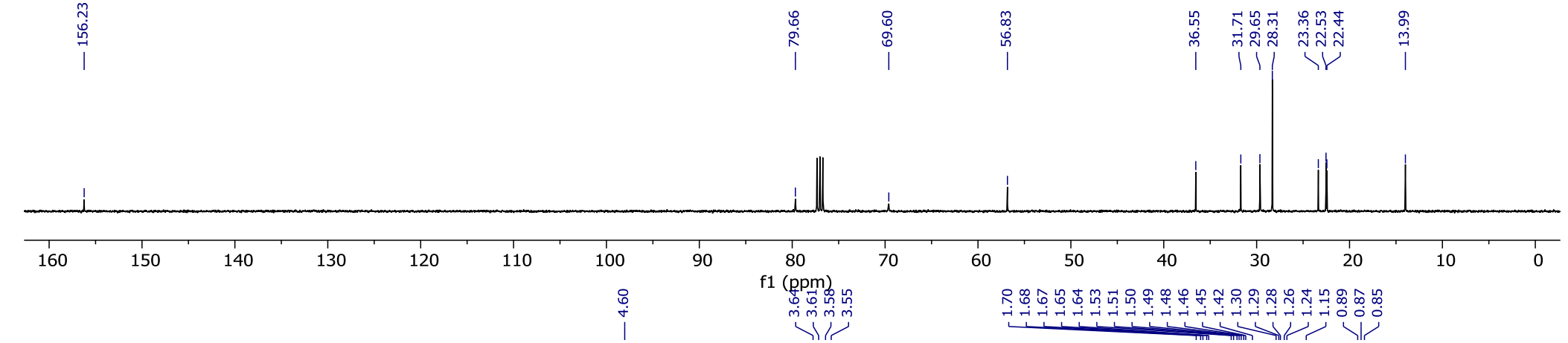

NHCOOt-Bu
Compound 14l in CDCl3
f1 (ppm)
f1 (ppm)

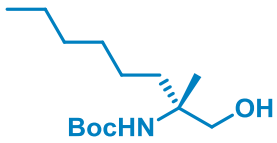

156.25
79.71
69.38
57.05
29.06
28.32
21.95
7.78
f1 (ppm)
4.60
3.64
3.63
3.61
3.58
3.55
1.77
1.75
1.73
1.72
1.70
1.68
1.60
1.58
1.56
1.54
1.52
1.51
1.41
1.13
0.89
0.88
0.86
BocHN
OH
Compound 16a in CDCl3
0.98
2.43
1.00
1.08
8.97
3.06
3.27
f1 (ppm)



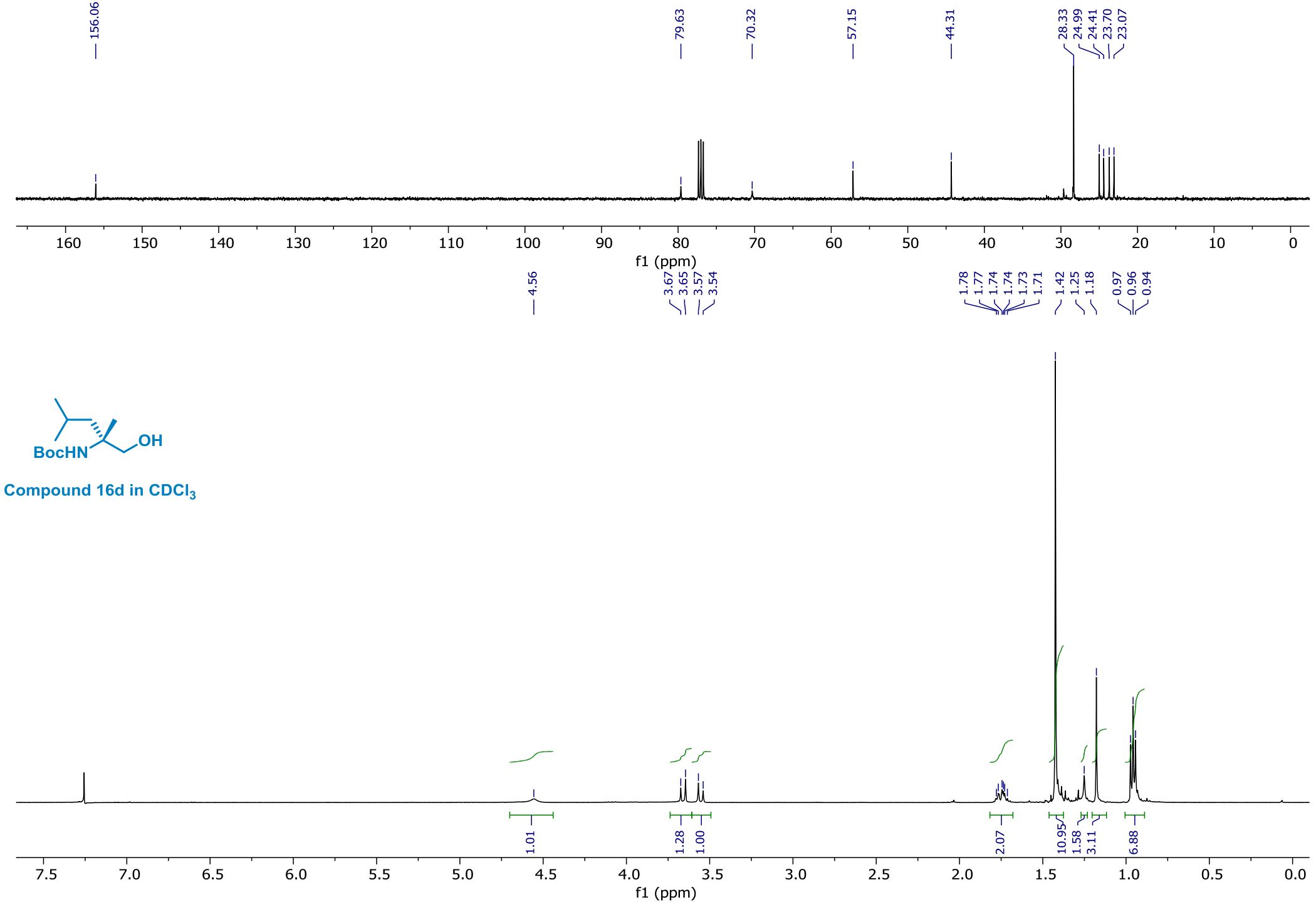


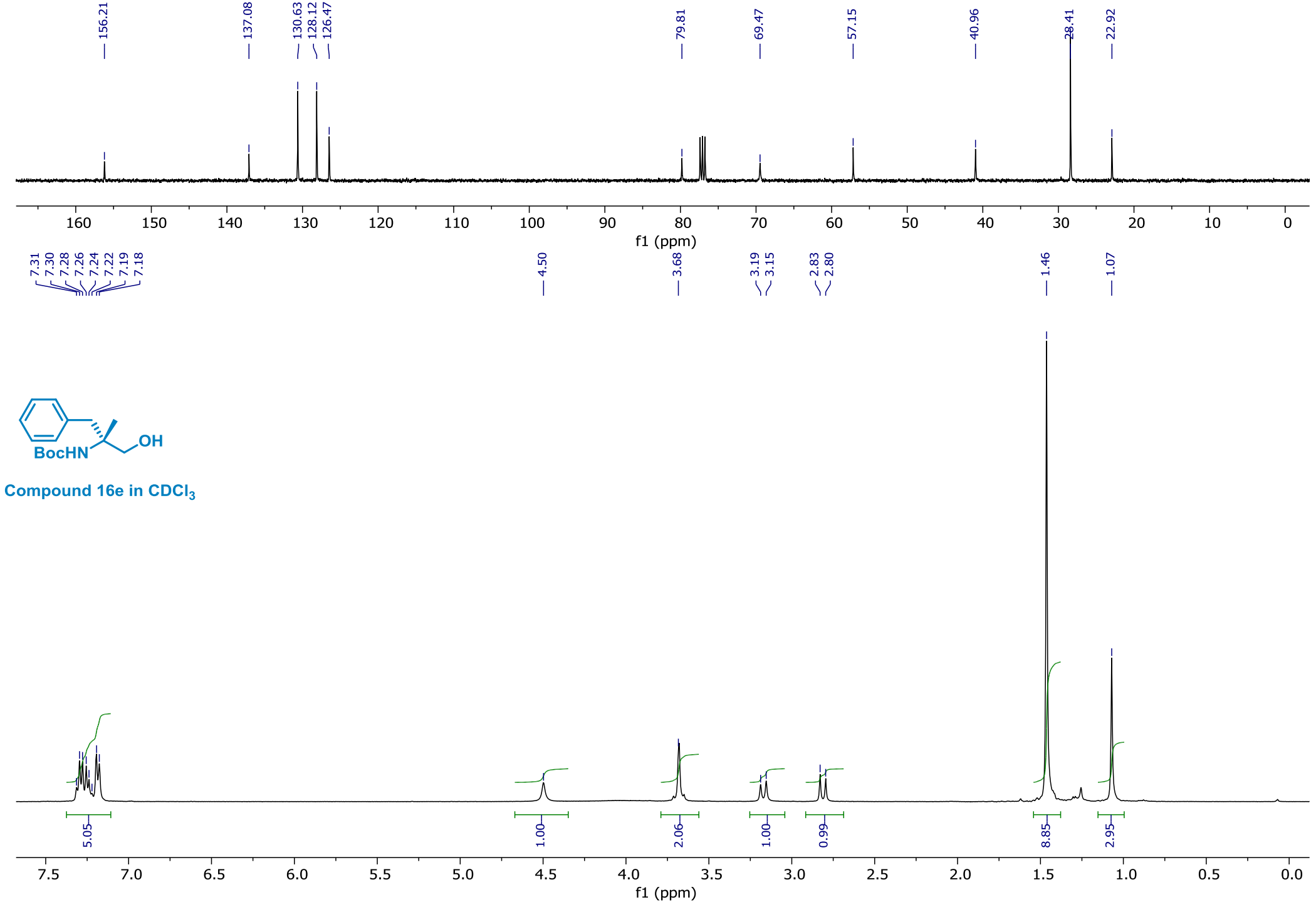
Compound 16b in $CDCl_3$

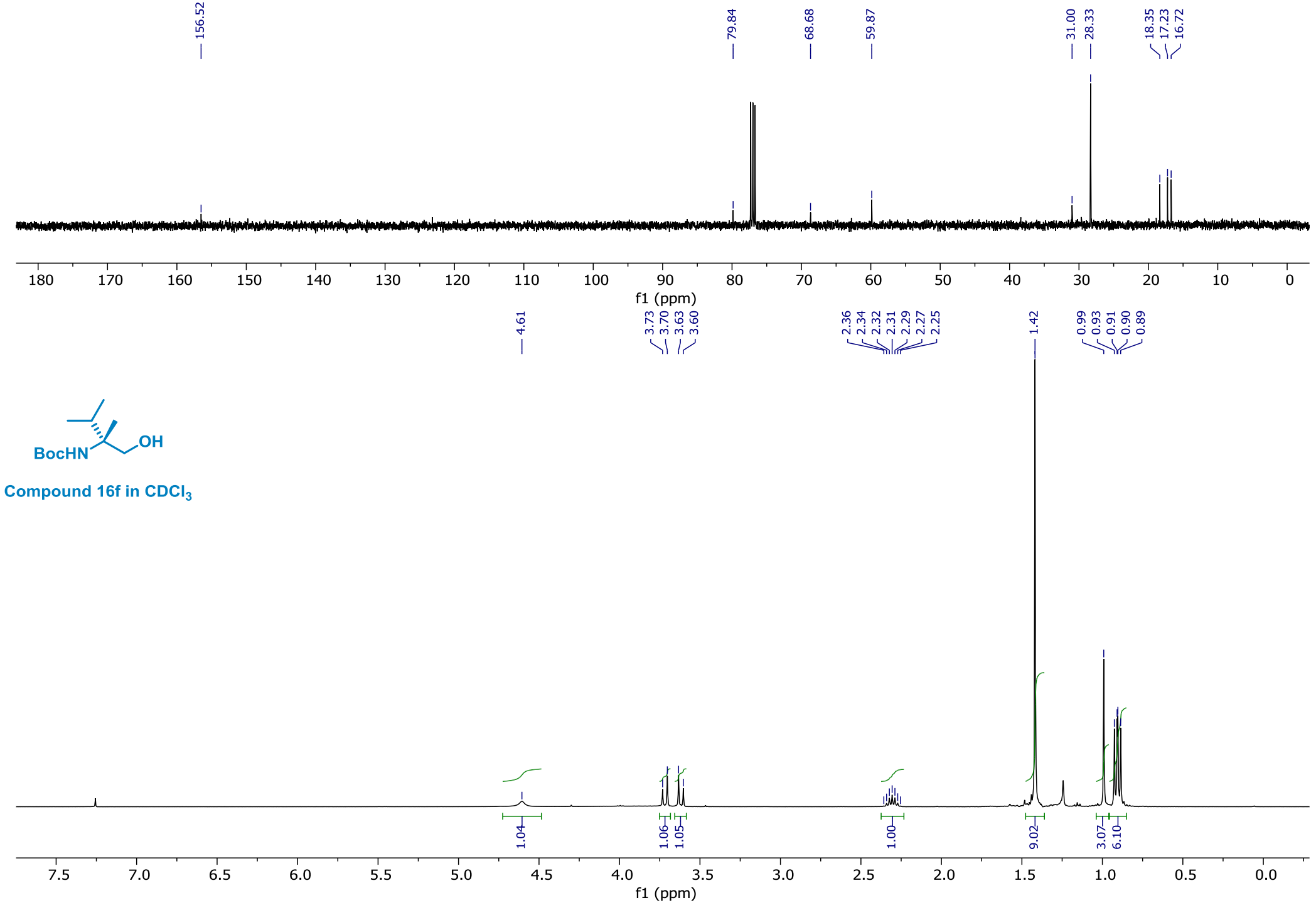


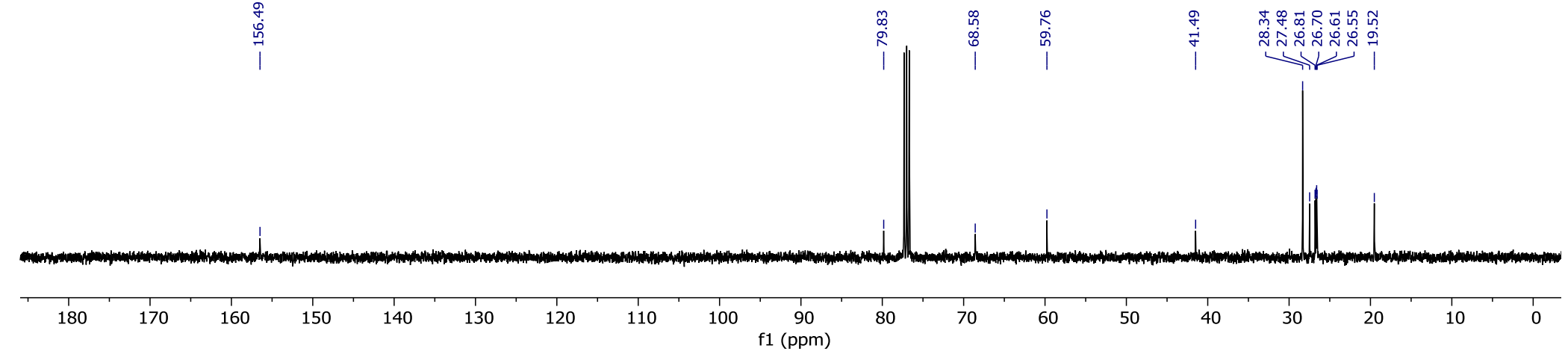


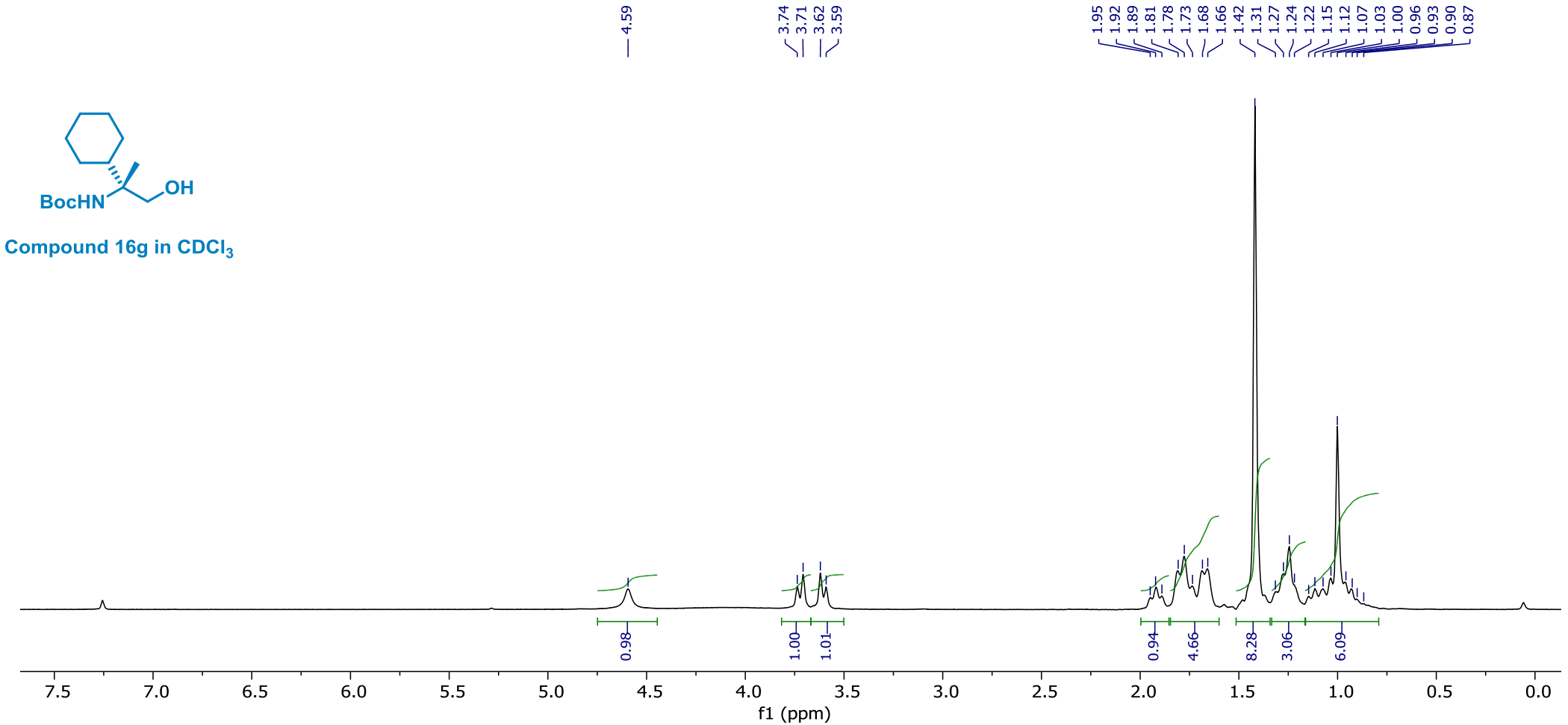
Compound 16c in $CDCl_3$


156.06
79.63
70.32
57.15
44.31
28.33
24.99
24.41
23.70
23.07
f1 (ppm)
4.56
3.67
3.65
3.57
3.54
1.78
1.77
1.74
1.74
1.73
1.71
1.42
1.25
1.18
0.97
0.96
0.94
BocHN
OH
Compound 16d in CDCl3
1.01
1.28
1.00
2.07
10.95
1.58
3.11
6.88
f1 (ppm)

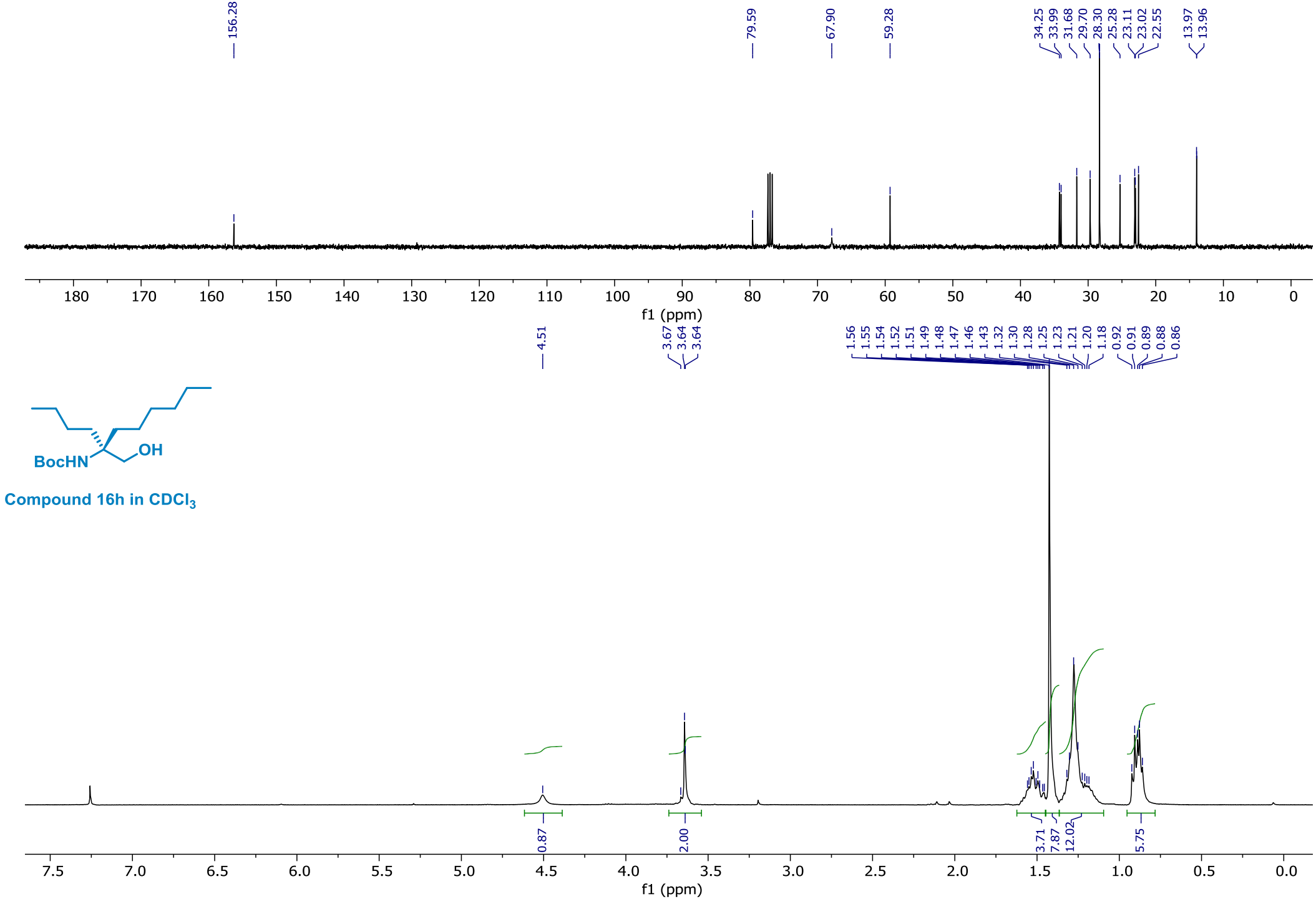

156.21
137.08
130.63
128.12
126.47
79.81
69.47
57.15
40.96
28.41
22.92
f1 (ppm)
7.31
7.30
7.28
7.26
7.24
7.22
7.19
7.18
4.50
3.68
3.19
3.15
2.83
2.80
1.46
1.07
BocHN
OH
Compound 16e in CDCl3
5.05
1.00
2.06
1.00
0.99
8.85
2.95
f1 (ppm)


156.52
79.84
68.68
59.87
31.00
28.33
18.35
17.23
16.72
f1 (ppm)
4.61
3.73
3.70
3.63
3.60
2.36
2.34
2.32
2.31
2.29
2.27
2.25
1.42
0.99
0.93
0.91
0.90
0.89
1.04
1.06
1.05
1.00
9.02
3.07
6.10
f1 (ppm)
BocHN
OH
Compound 16f in CDCl3

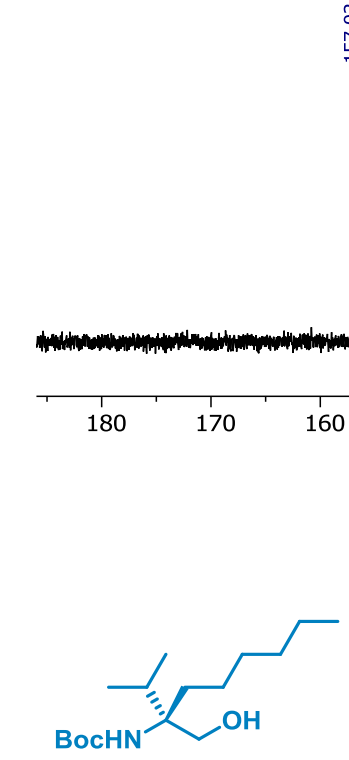




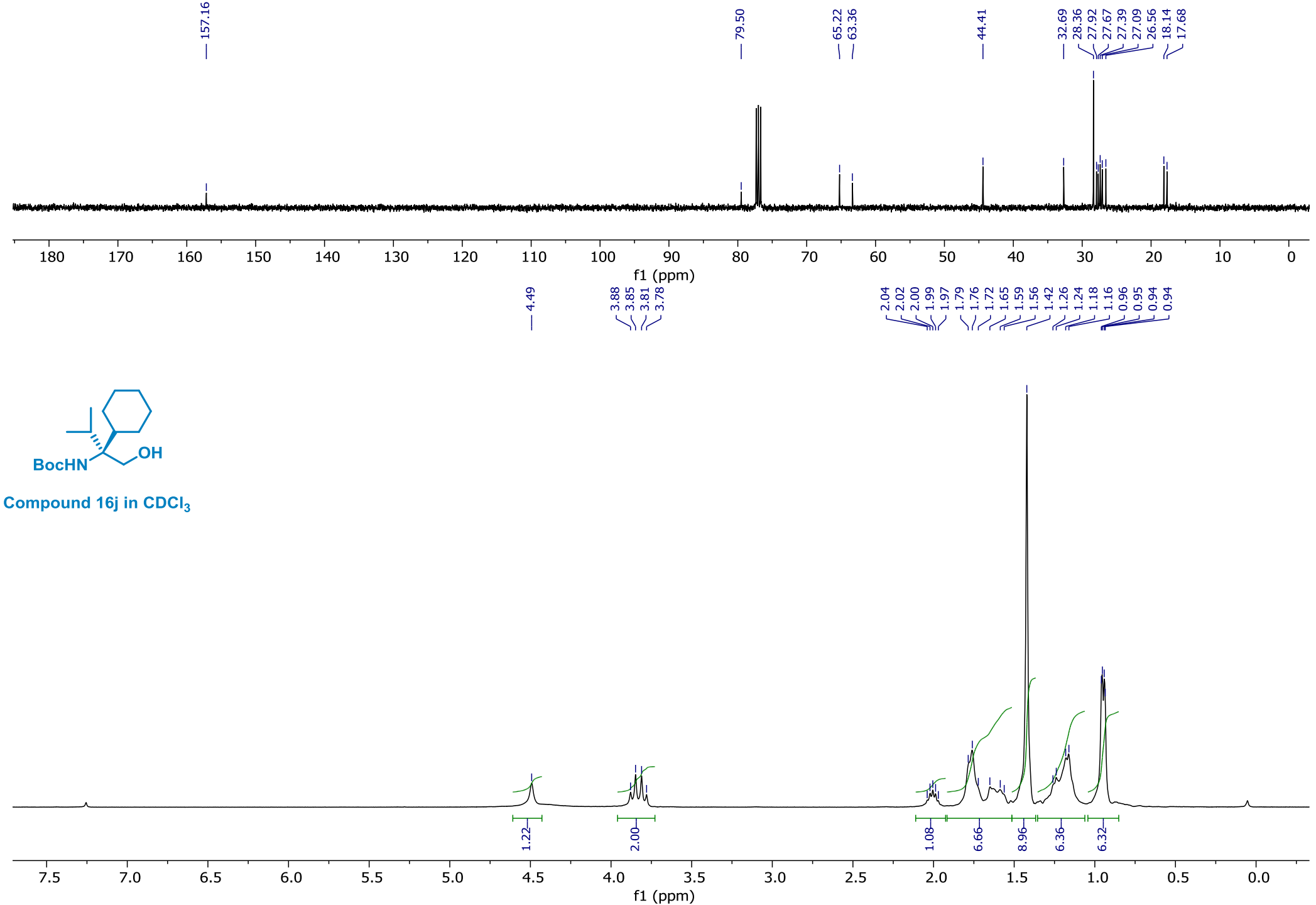
Compound 16g in $CDCl_3$

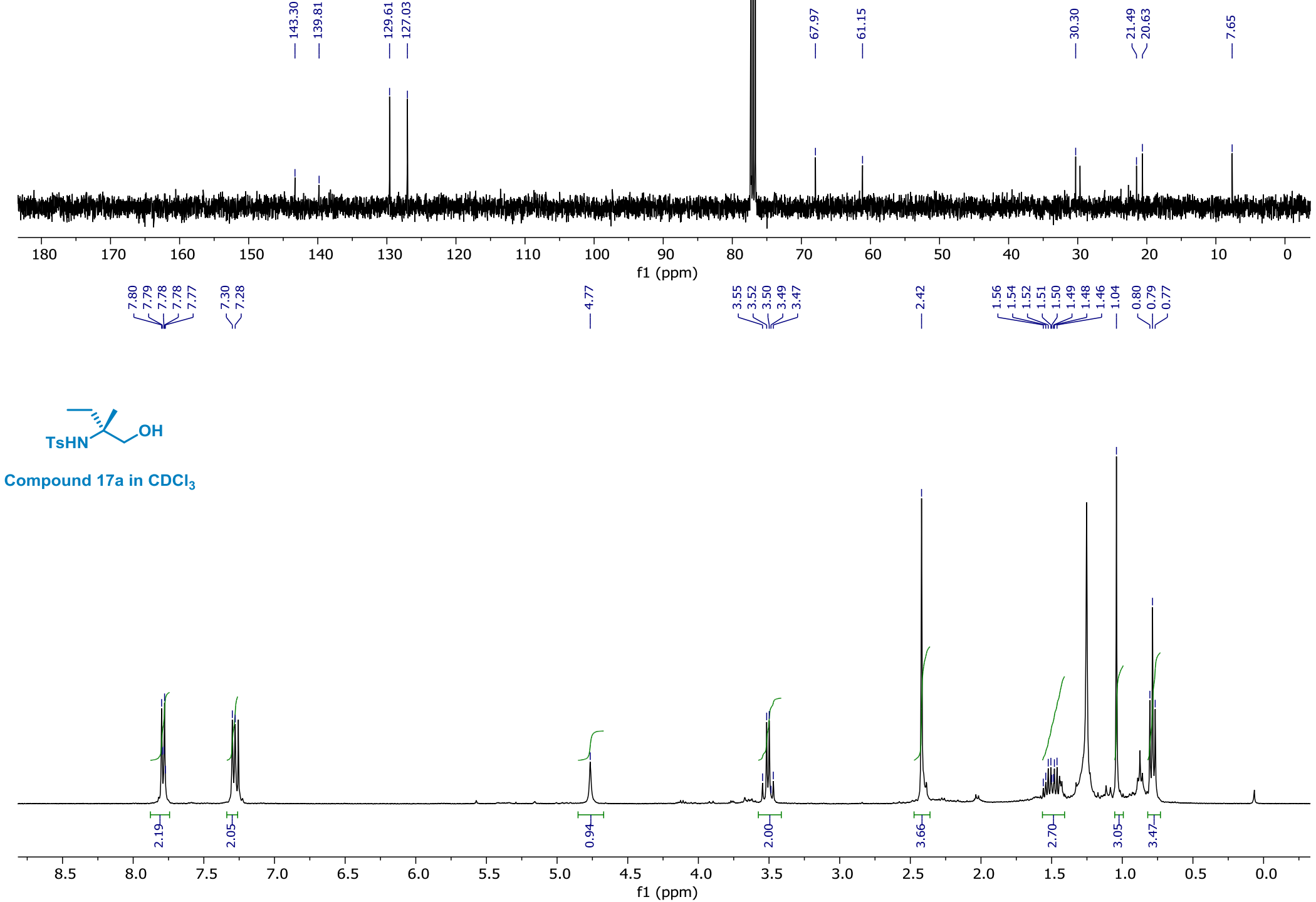


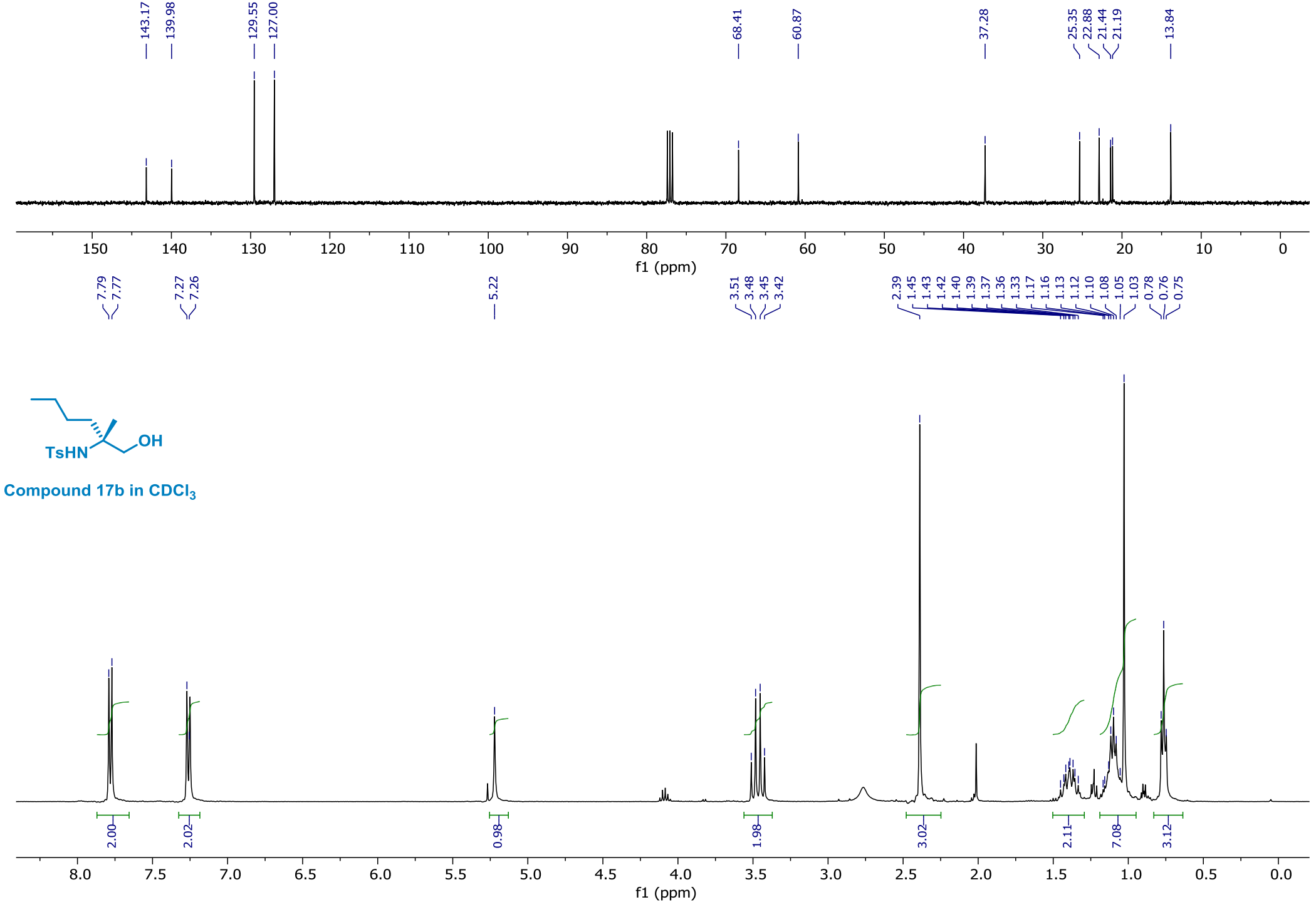
Compound 16h in $CDCl_3$

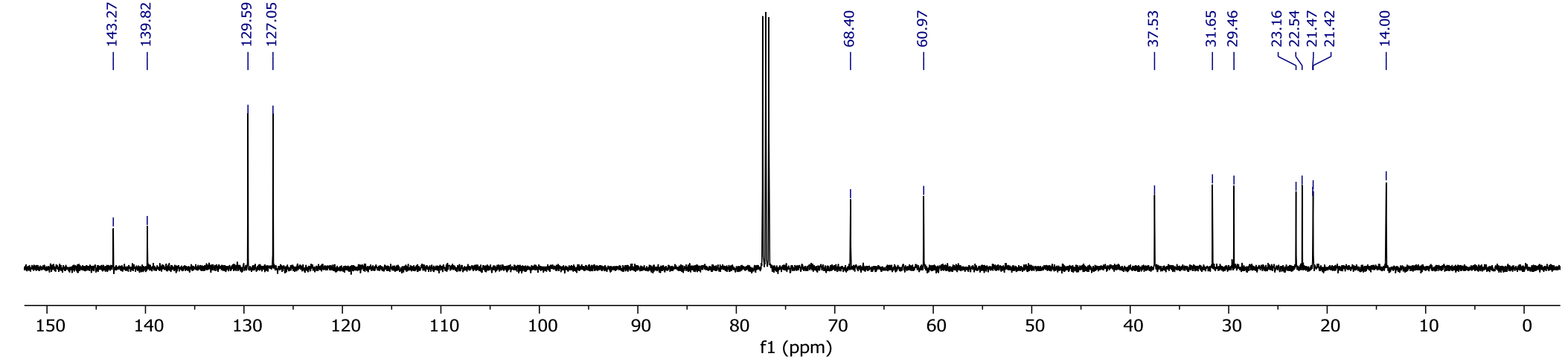


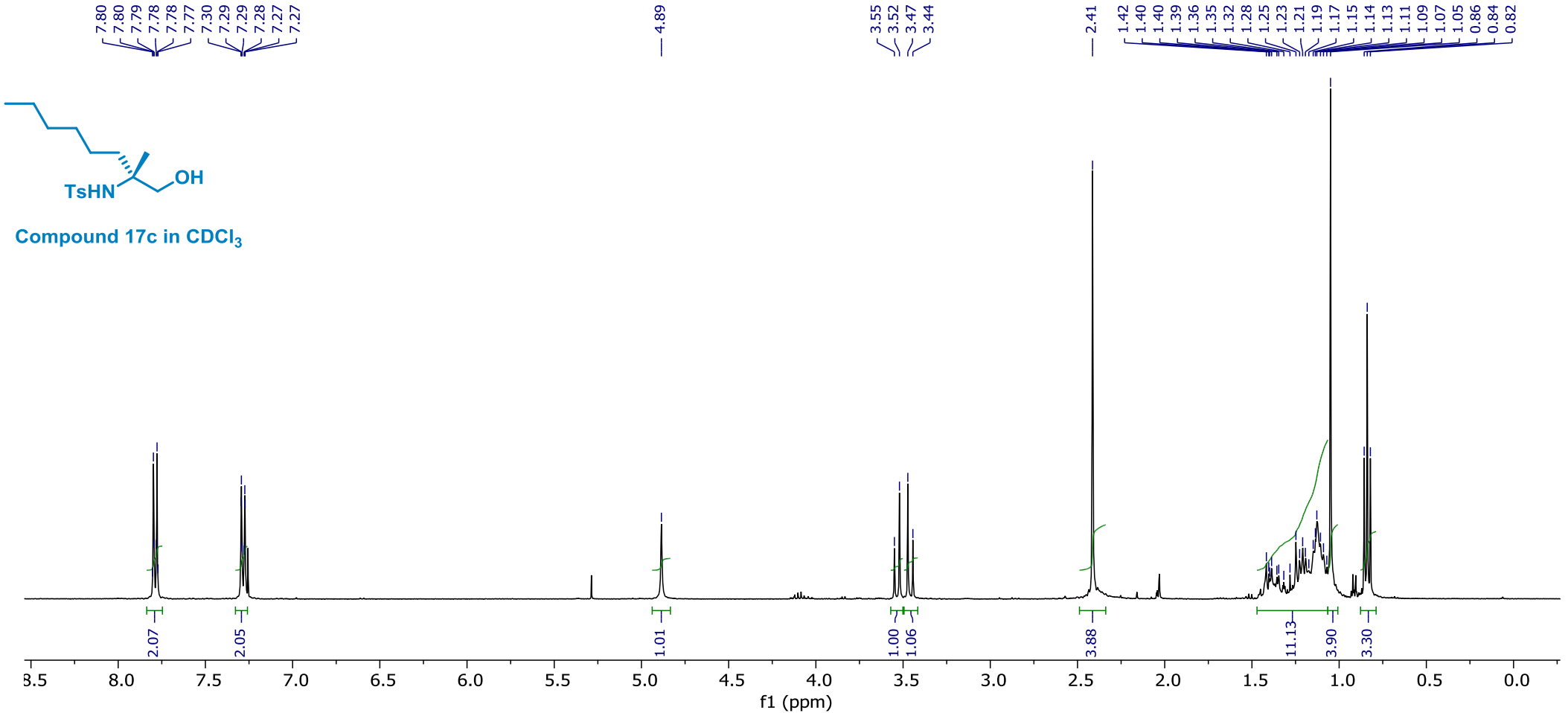
Compound 16i in $CDCl_3$


157.16
79.50
65.22
63.36
44.41
32.69
28.36
27.92
27.67
27.39
27.09
26.56
18.14
17.68
f1 (ppm)
4.49
3.88
3.85
3.81
3.78
2.04
2.02
2.00
1.99
1.97
1.79
1.76
1.72
1.65
1.59
1.56
1.42
1.26
1.24
1.18
1.16
0.96
0.95
0.94
0.94
BocHN
OH
Compound 16j in CDCl3
1.22
2.00
1.08
6.66
8.96
6.36
6.32
f1 (ppm)

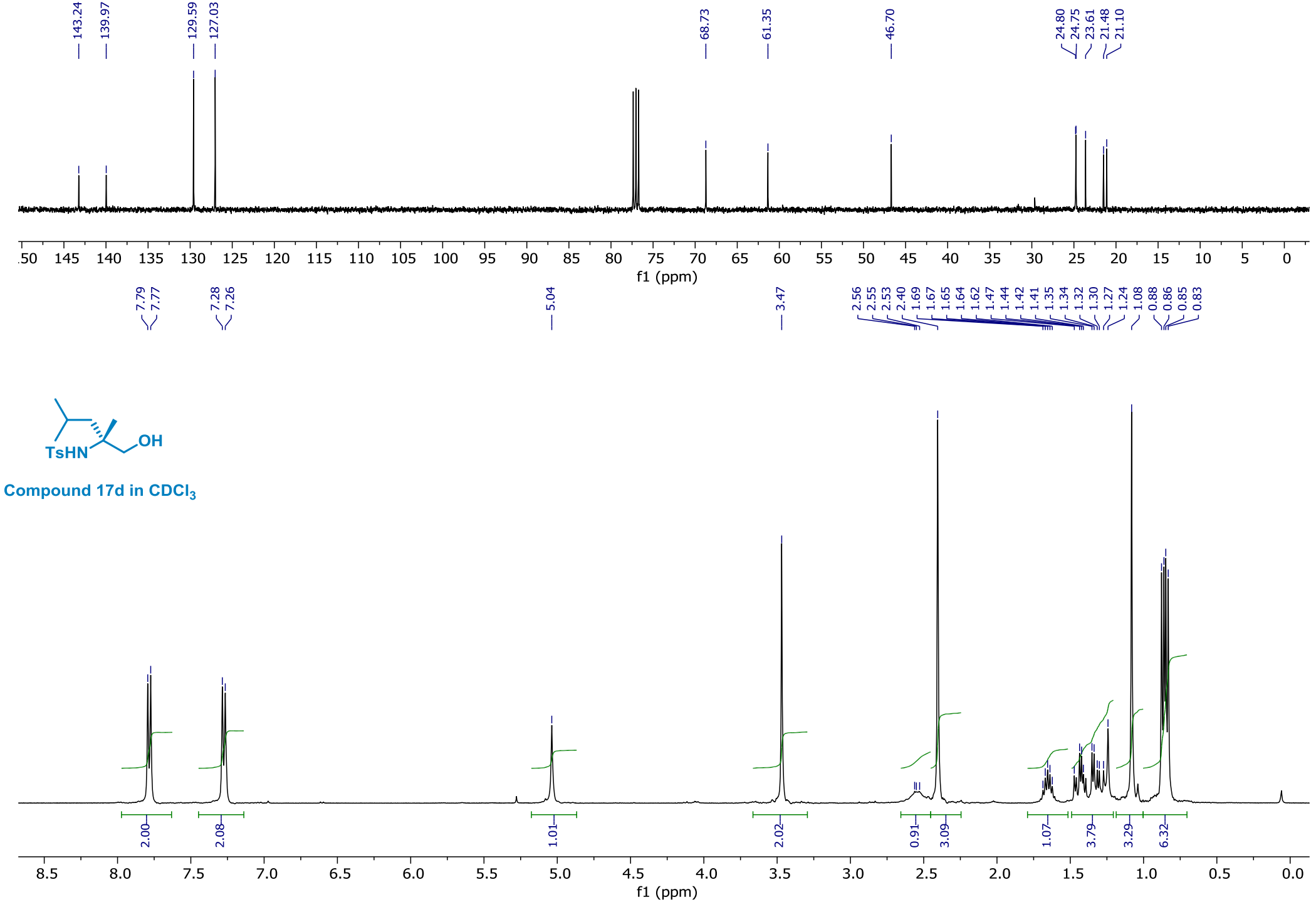

143.30
139.81
129.61
127.03
67.97
61.15
30.30
21.49
20.63
7.65
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
7.80 7.79 7.78 7.78 7.77
7.30 7.28
4.77
3.55 3.52 3.50 3.49 3.47
2.42
1.56 1.54 1.52 1.51 1.50 1.49 1.48 1.46
1.04
0.80 0.79 0.77
TsHN
OH
Compound 17a in CDCl3
2.19
2.05
0.94
2.00
3.66
2.70
3.05
3.47
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)

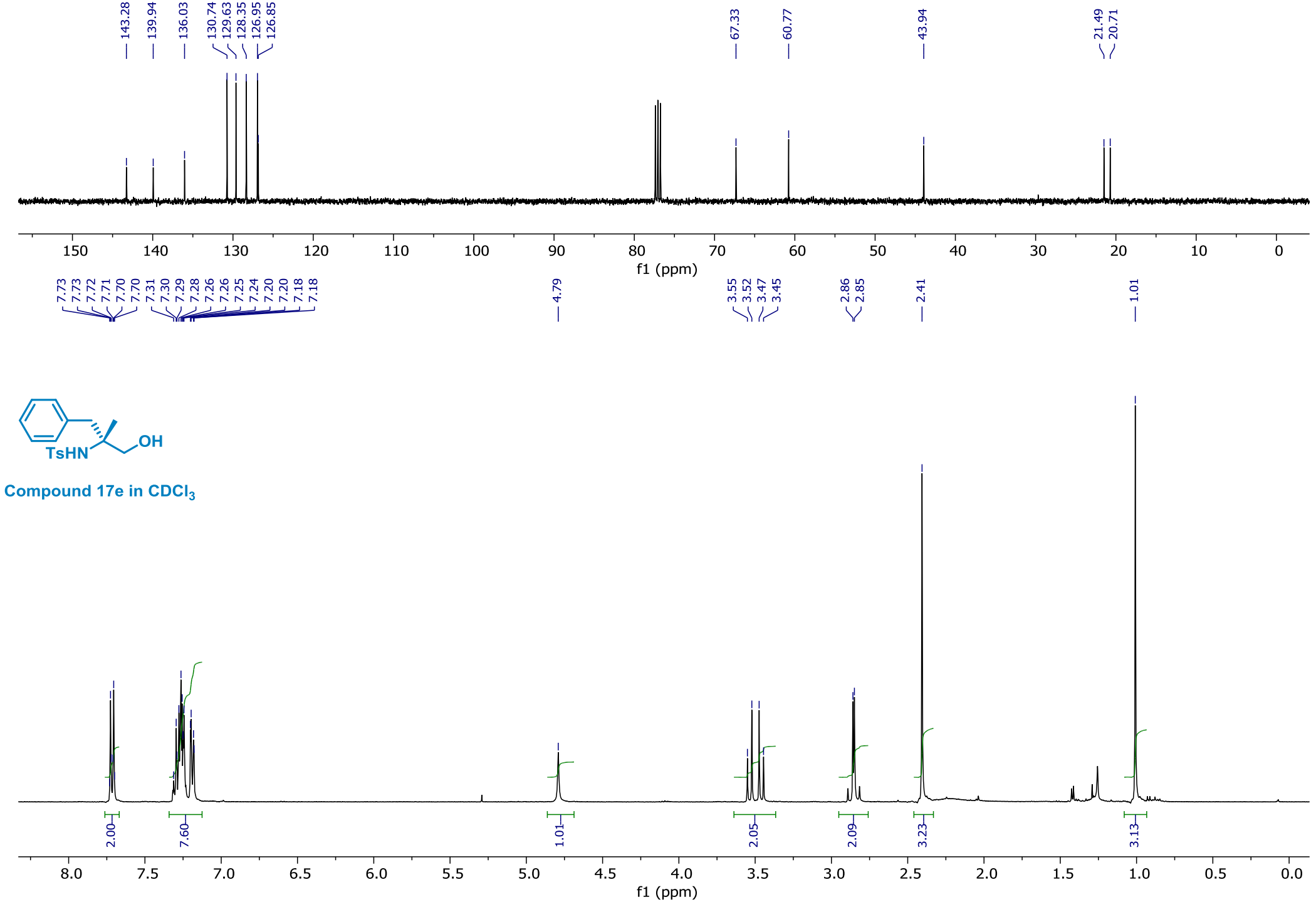

143.17
139.98
129.55
127.00
68.41
60.87
37.28
25.35
22.88
21.44
21.19
13.84
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
7.79
7.77
7.27
7.26
5.22
3.51
3.48
3.45
3.42
2.39
1.45
1.43
1.42
1.40
1.39
1.37
1.36
1.33
1.17
1.16
1.13
1.12
1.10
1.08
1.05
1.03
0.78
0.76
0.75
TsHN
OH
Compound 17b in CDCl3
2.00
2.02
0.98
1.98
3.02
2.11
7.08
3.12
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)

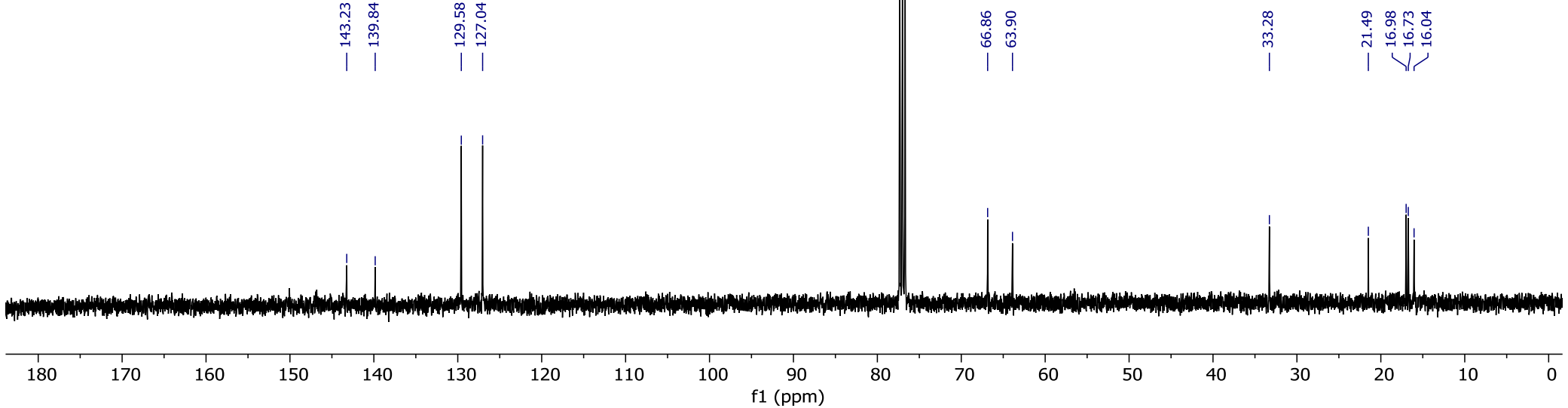


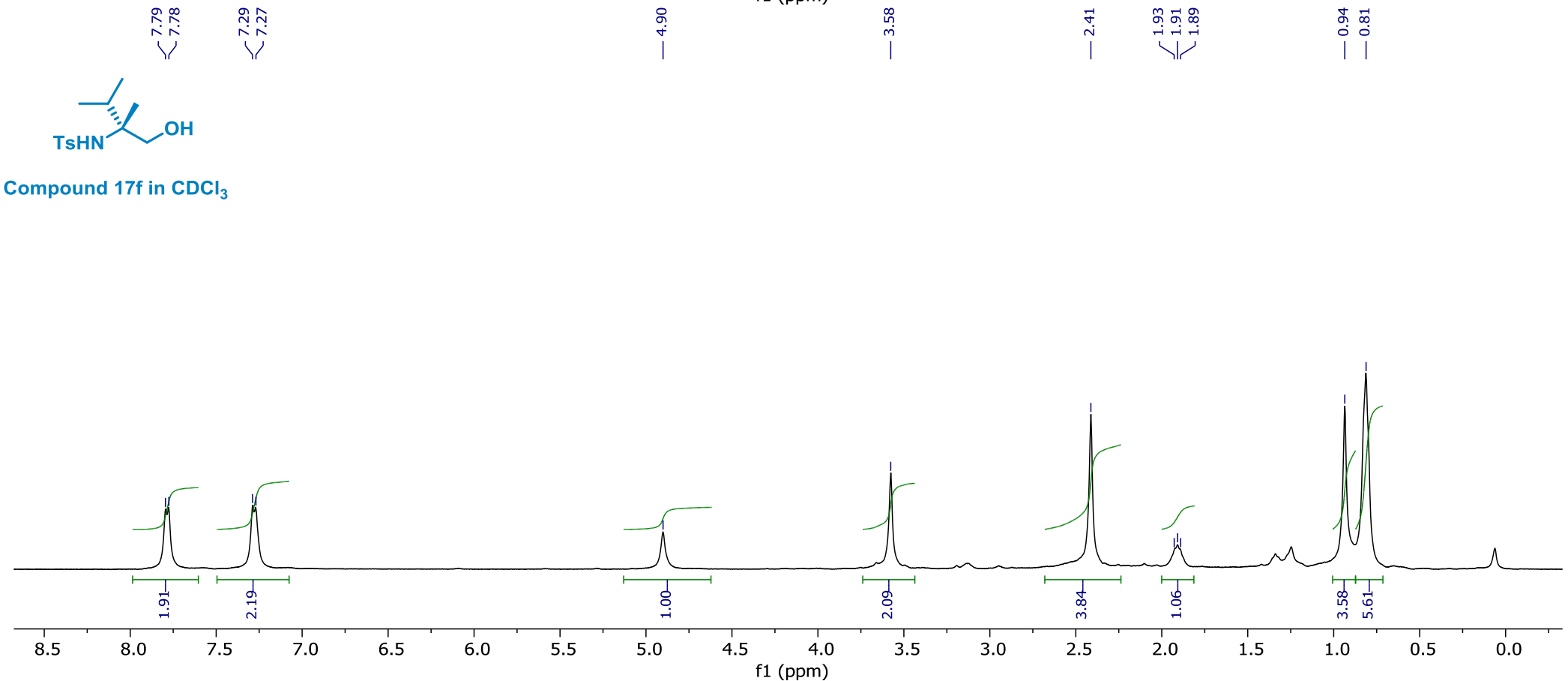


Compound 17c in $CDCl_3$

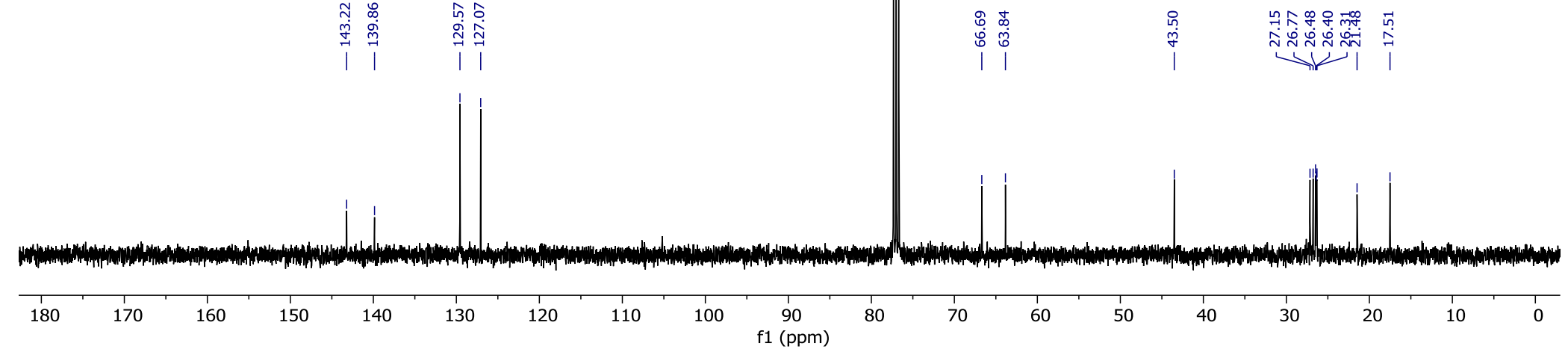

143.24
139.97
129.59
127.03
68.73
61.35
46.70
24.80
24.75
23.61
21.48
21.10
f1 (ppm)
7.79
7.77
7.28
7.26
5.04
3.47
2.56
2.55
2.53
2.40
1.69
1.67
1.65
1.64
1.62
1.47
1.44
1.42
1.41
1.35
1.34
1.32
1.30
1.27
1.24
1.08
0.88
0.86
0.85
0.83
TsHN
OH
Compound 17d in CDCl3
2.00
2.08
1.01
2.02
0.91
3.09
1.07
3.79
3.29
6.32
f1 (ppm)

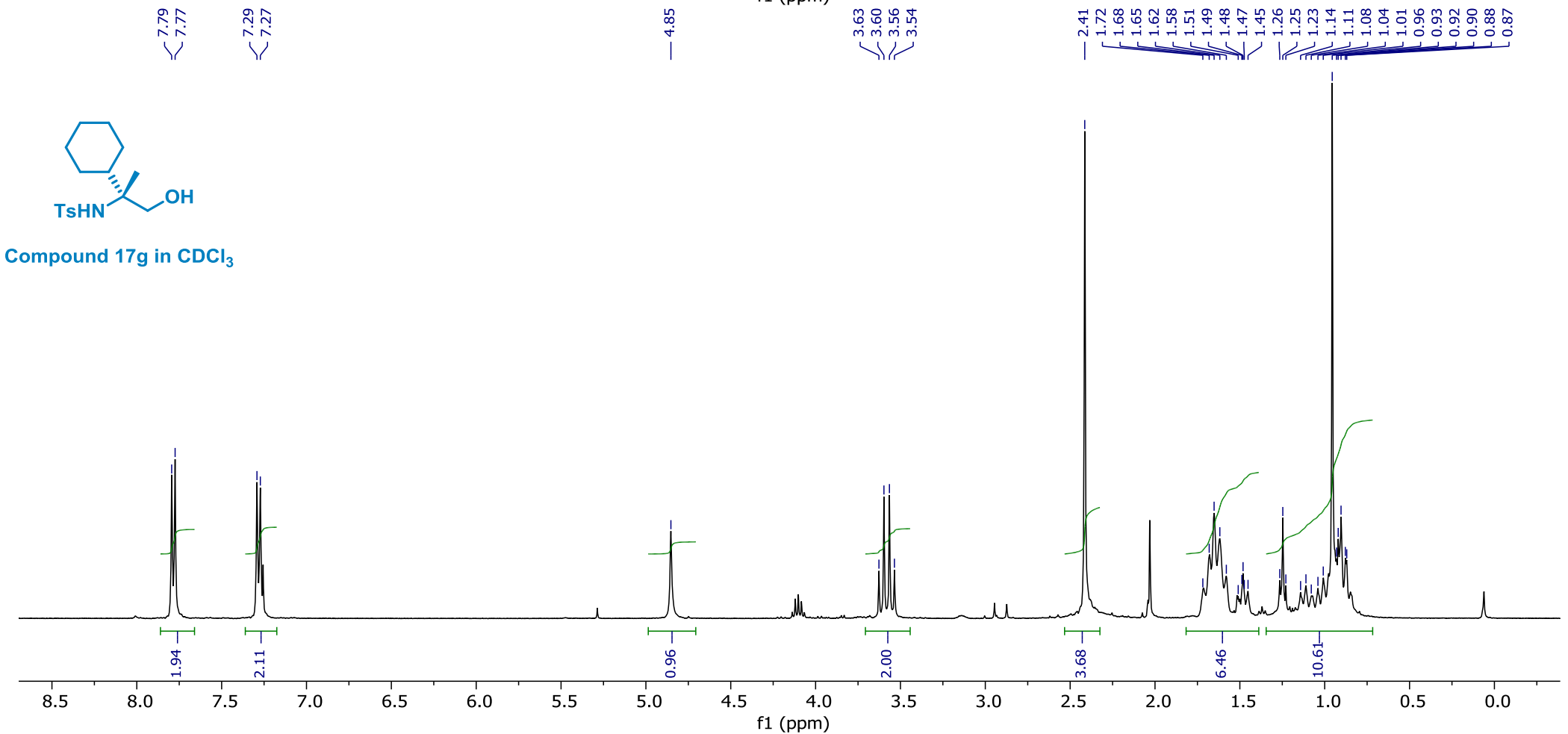

143.28
139.94
136.03
130.74
129.63
128.35
126.95
126.85
67.33
60.77
43.94
21.49
20.71
f1 (ppm)
7.73
7.73
7.72
7.71
7.70
7.70
7.31
7.30
7.29
7.28
7.26
7.26
7.25
7.24
7.20
7.20
7.18
7.18
4.79
3.55
3.52
3.47
3.45
2.86
2.85
2.41
1.01
TsHN
OH
Compound 17e in CDCl3
2.00
7.60
1.01
2.05
2.09
3.23
3.13
f1 (ppm)



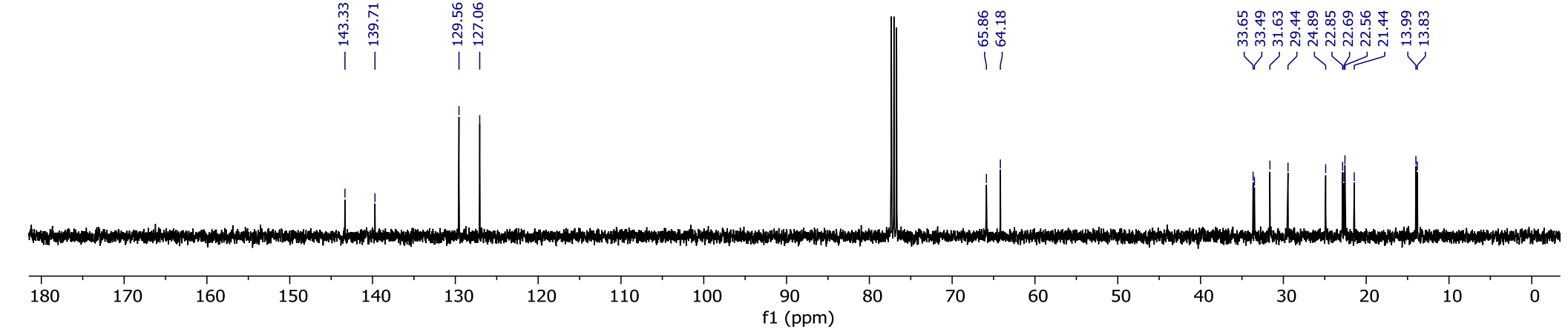


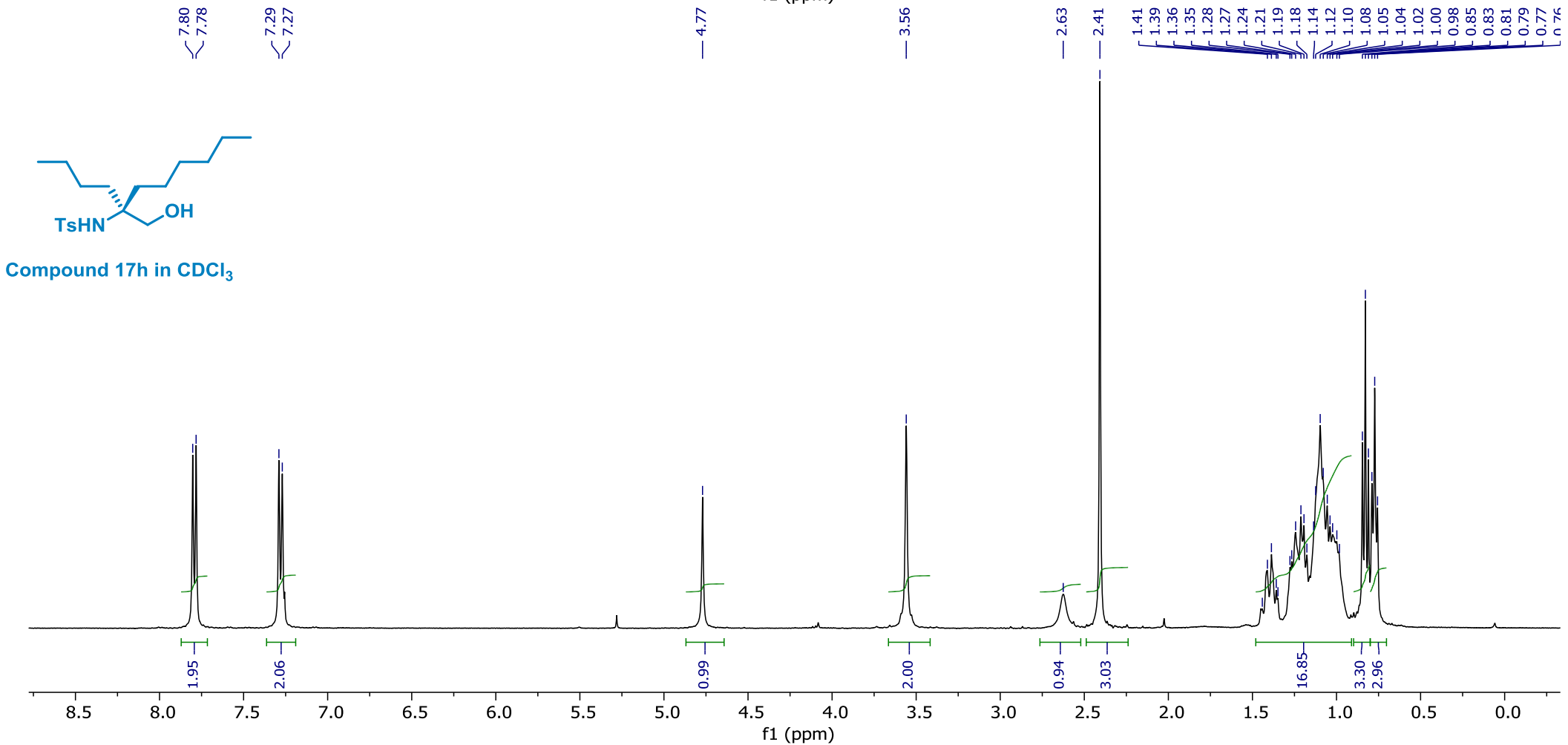
Compound 17f in $CDCl_3$



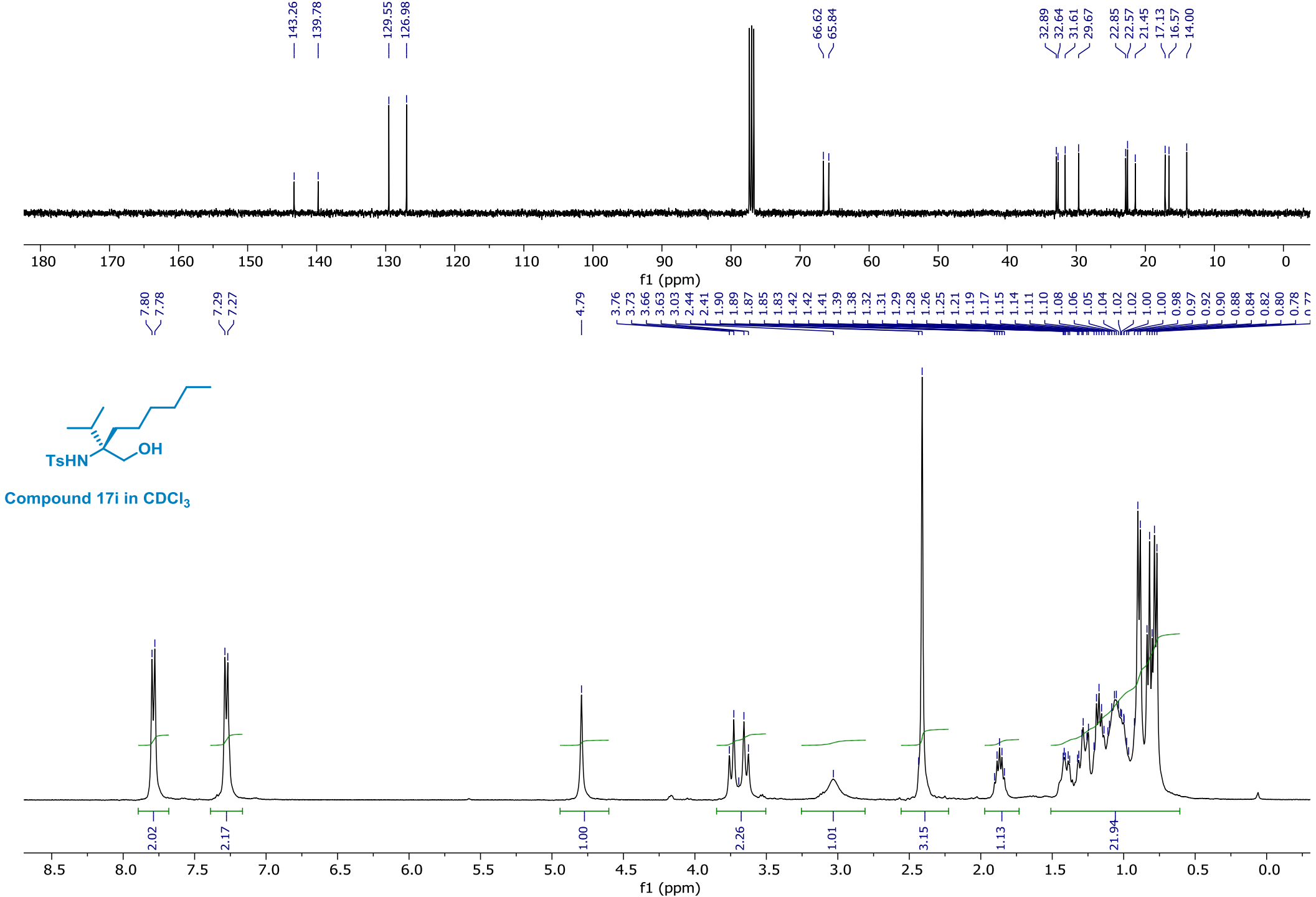


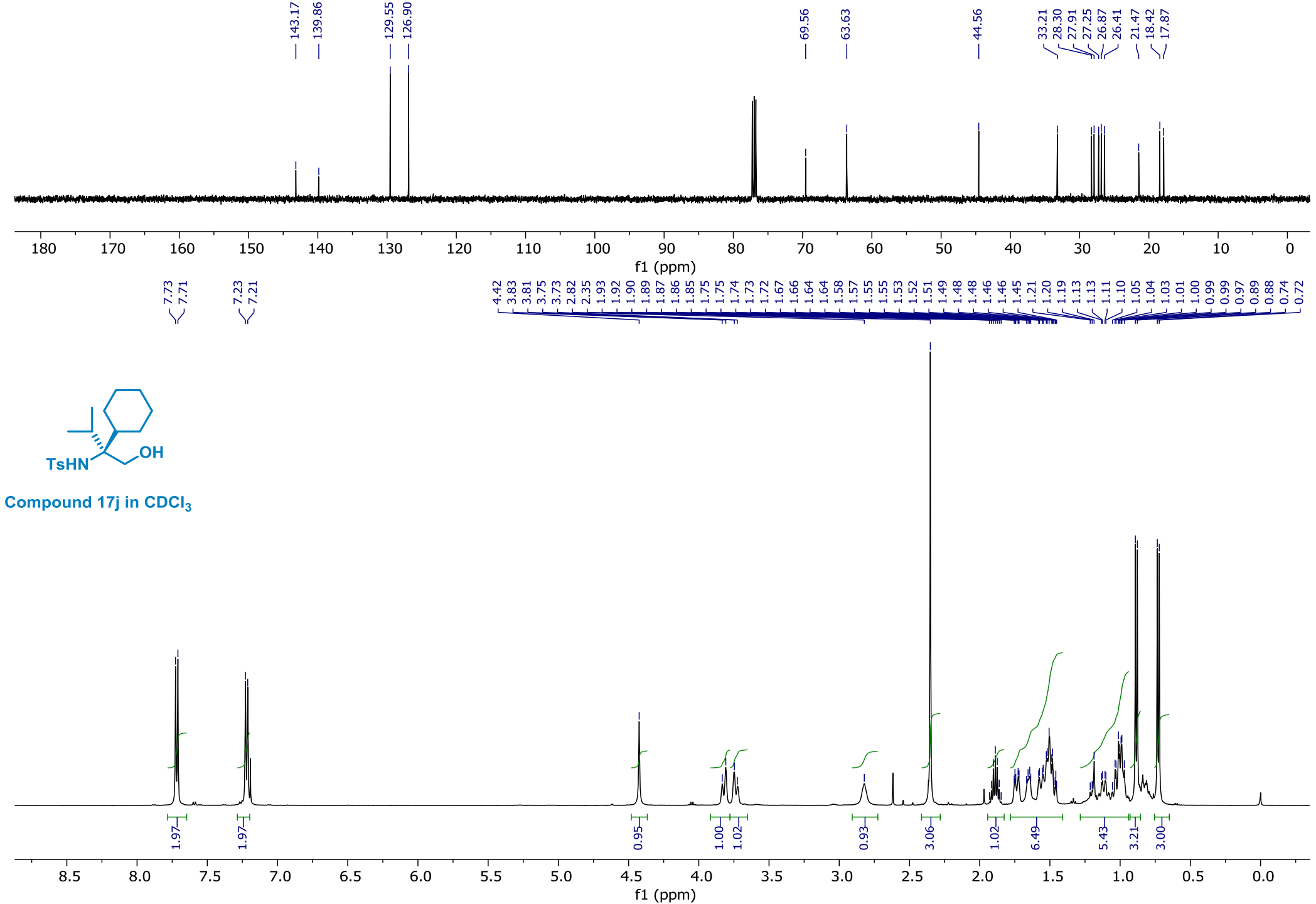
Compound 17g in $CDCl_3$

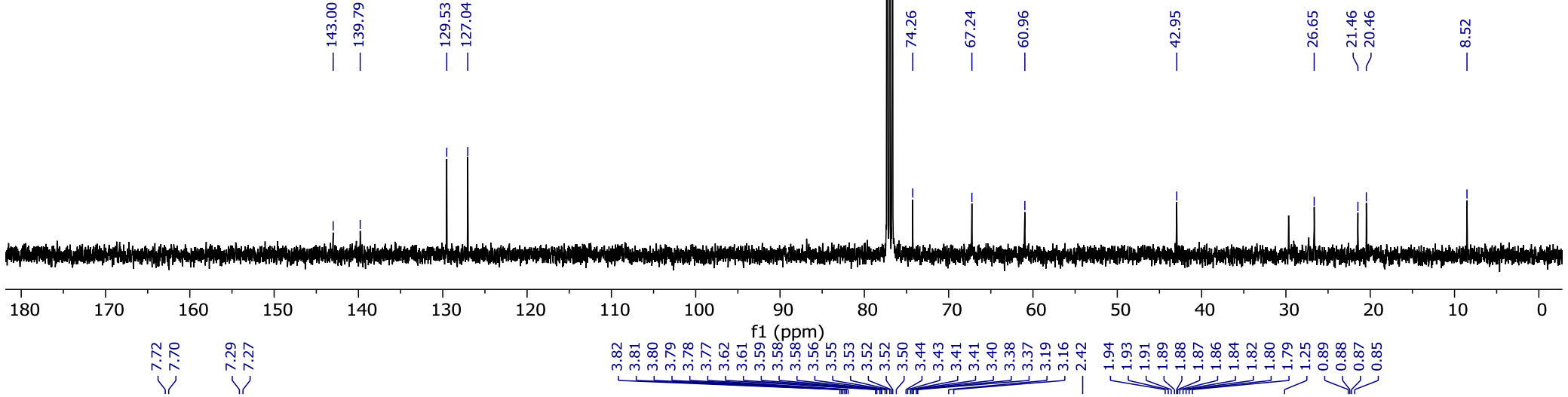


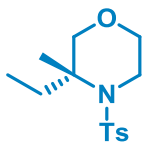


Compound 17h in $CDCl_3$

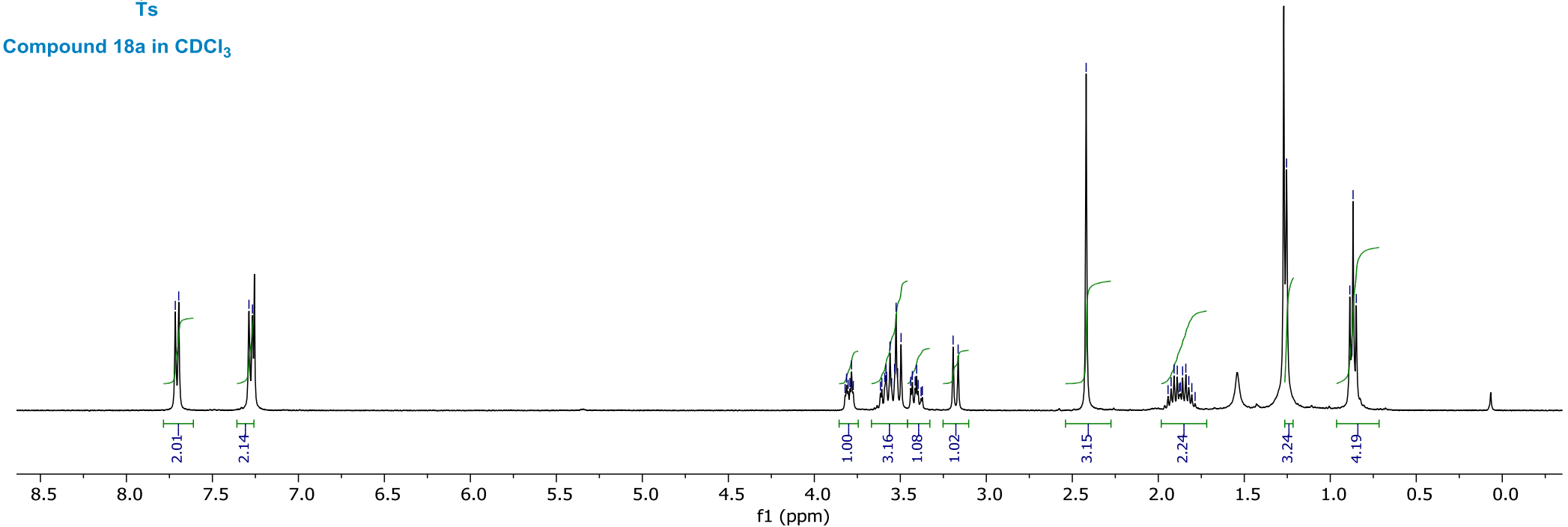

143.26
139.78
129.55
126.98
66.62
65.84
32.89
32.64
31.61
29.67
22.85
22.57
21.45
17.13
16.57
14.00
f1 (ppm)
7.80
7.78
7.29
7.27
4.79
3.76
3.73
3.66
3.63
3.03
2.44
2.41
1.90
1.89
1.87
1.85
1.83
1.42
1.42
1.41
1.39
1.38
1.32
1.31
1.29
1.28
1.26
1.25
1.21
1.19
1.17
1.15
1.14
1.11
1.10
1.08
1.06
1.05
1.04
1.02
1.02
1.00
1.00
0.98
0.97
0.92
0.90
0.88
0.84
0.82
0.80
0.78
TsHN
OH
Compound 17i in CDCl3
2.02
2.17
1.00
2.26
1.01
3.15
1.13
21.94
f1 (ppm)

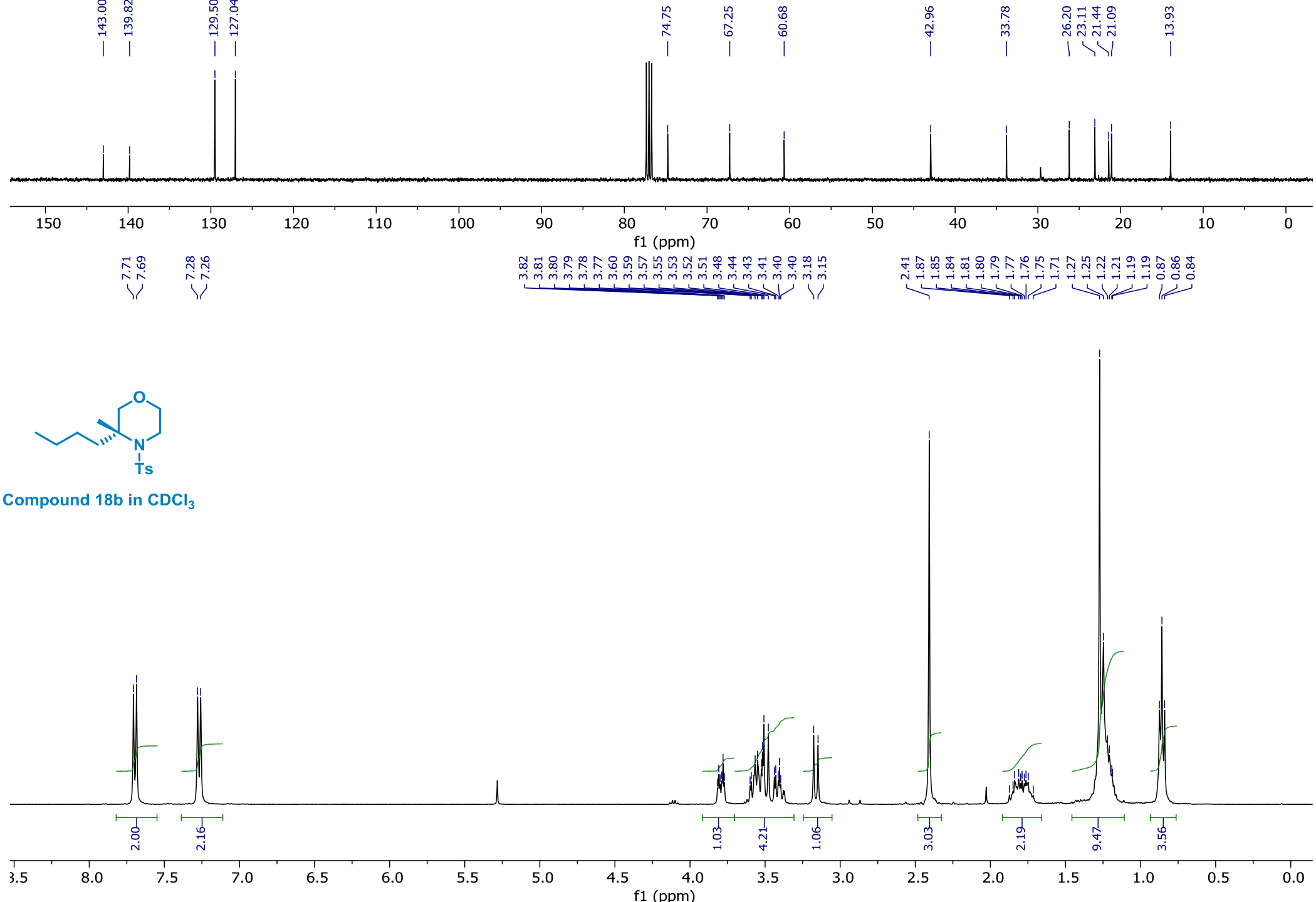

143.17
139.86
129.55
126.90
69.56
63.63
44.56
33.21
28.30
27.91
27.25
26.87
26.41
21.47
18.42
17.87
f1 (ppm)
7.73
7.71
7.23
7.21
4.42
3.83
3.81
3.75
3.73
2.82
2.35
1.93
1.92
1.90
1.89
1.87
1.86
1.85
1.75
1.75
1.74
1.73
1.72
1.67
1.66
1.64
1.64
1.58
1.57
1.55
1.55
1.53
1.52
1.51
1.49
1.48
1.48
1.46
1.46
1.45
1.21
1.20
1.19
1.13
1.13
1.11
1.10
1.05
1.04
1.03
1.01
1.00
0.99
0.99
0.97
0.89
0.88
0.74
0.72
TsHN
OH
Compound 17j in CDCl3
1.97
1.97
0.95
1.00
1.02
0.93
3.06
1.02
6.49
5.43
3.21
3.00
f1 (ppm)



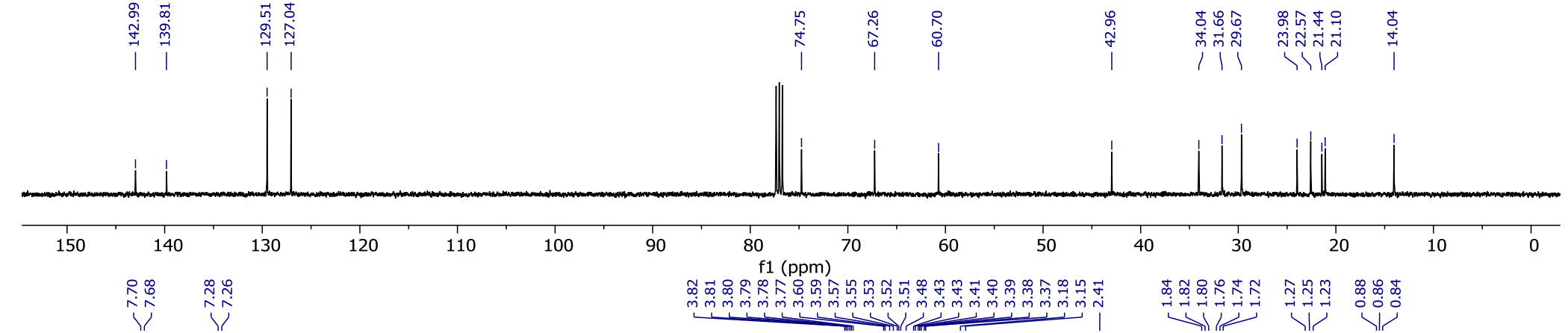


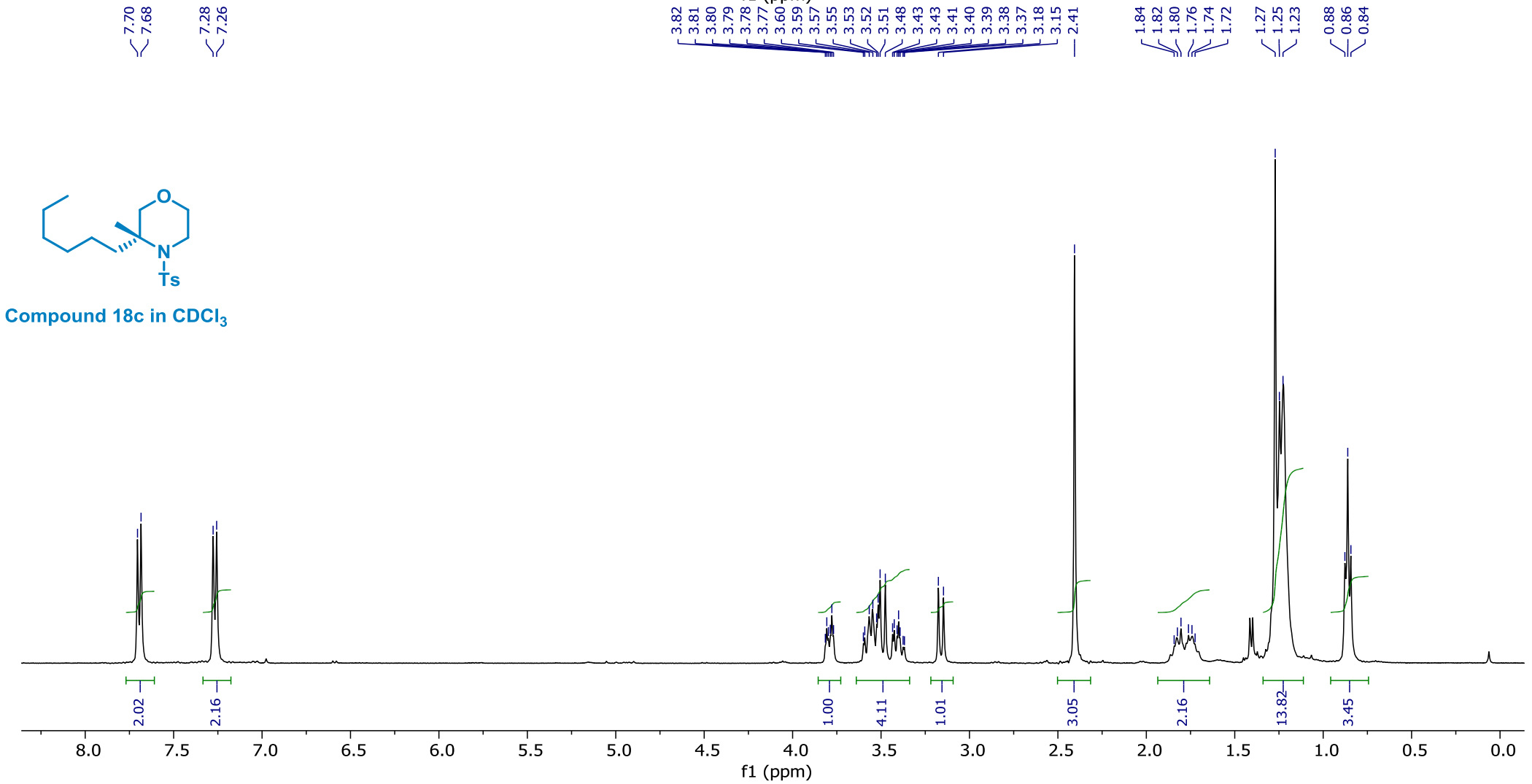
Compound 18a in $CDCl_3$



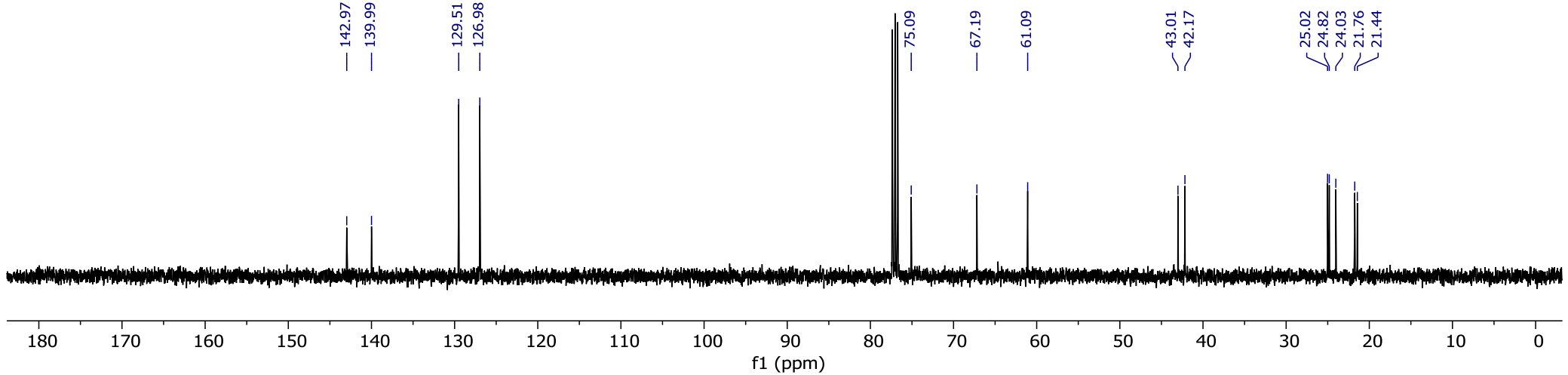


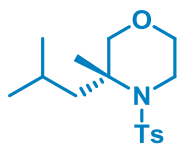
Compound 18b in $CDCl_3$



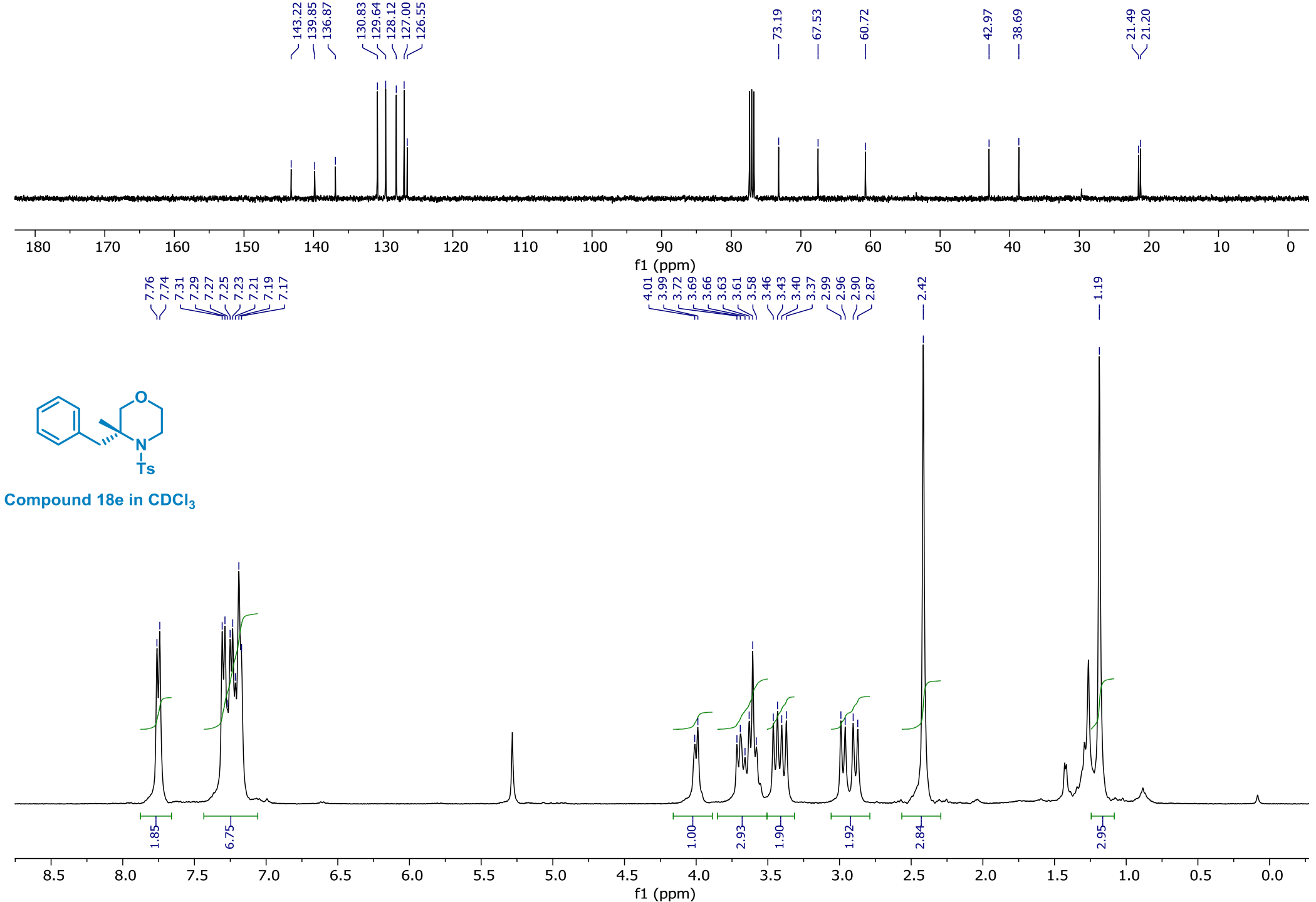


Compound 18c in $CDCl_3$

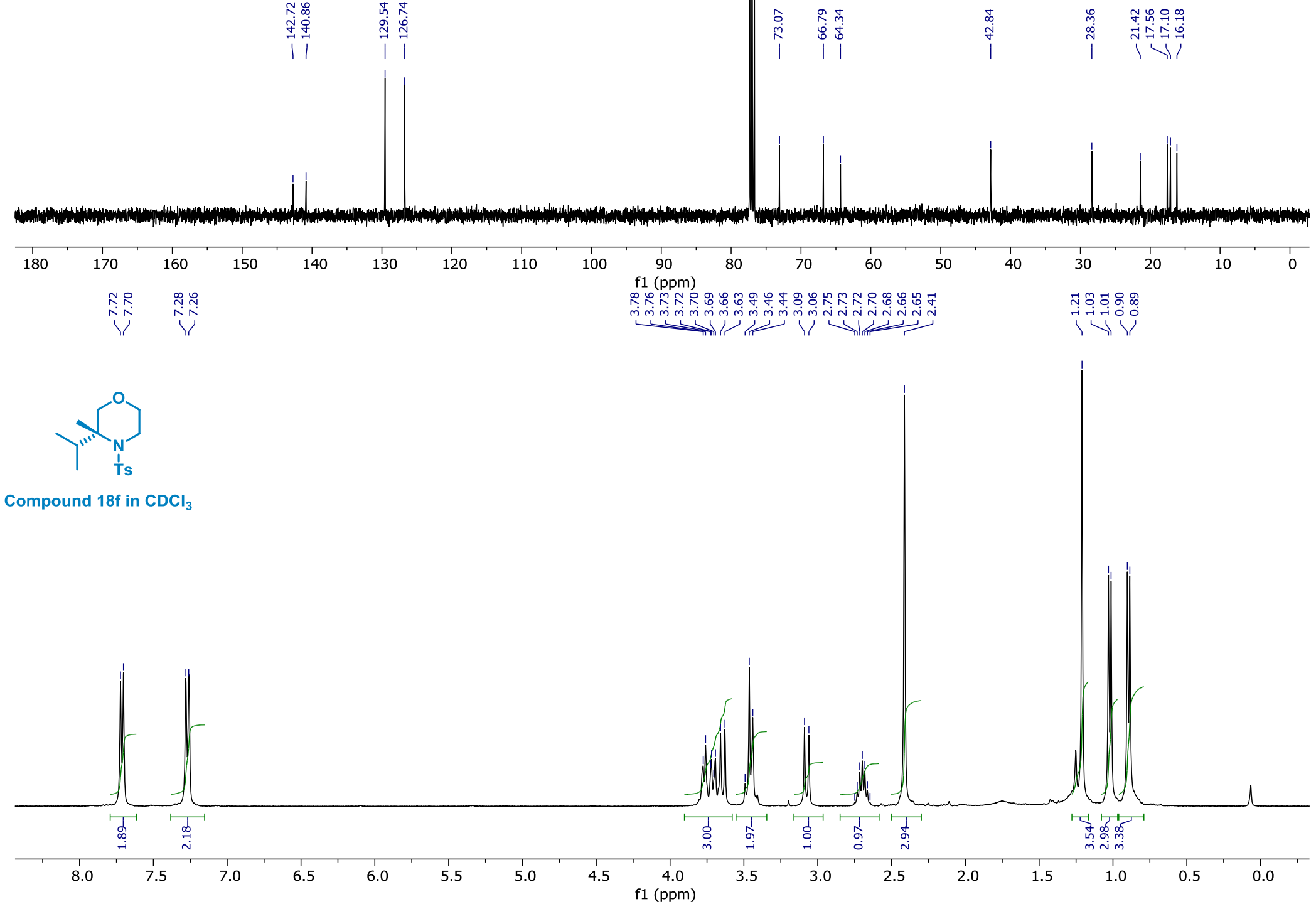




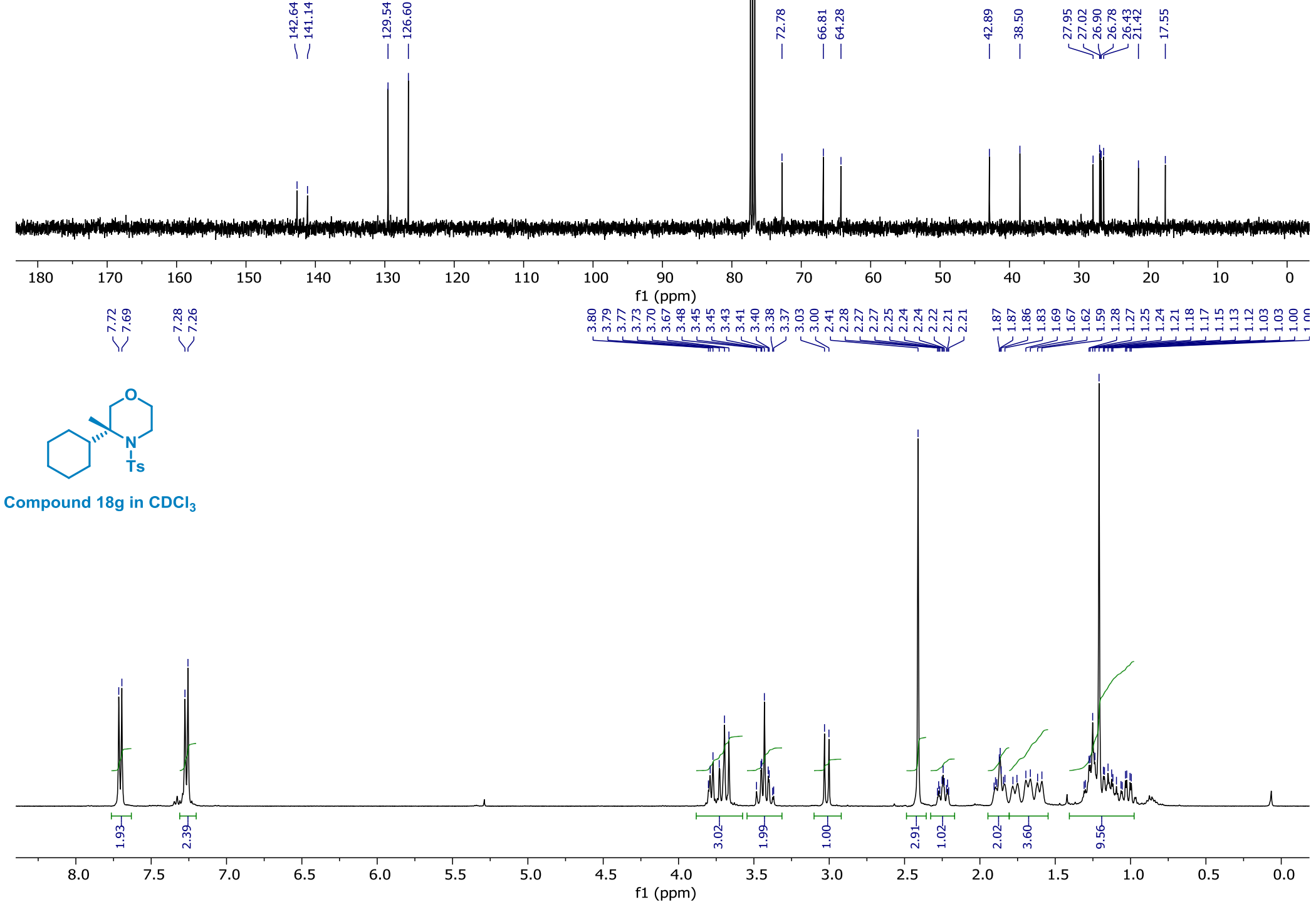
Compound 18d in $CDCl_3$



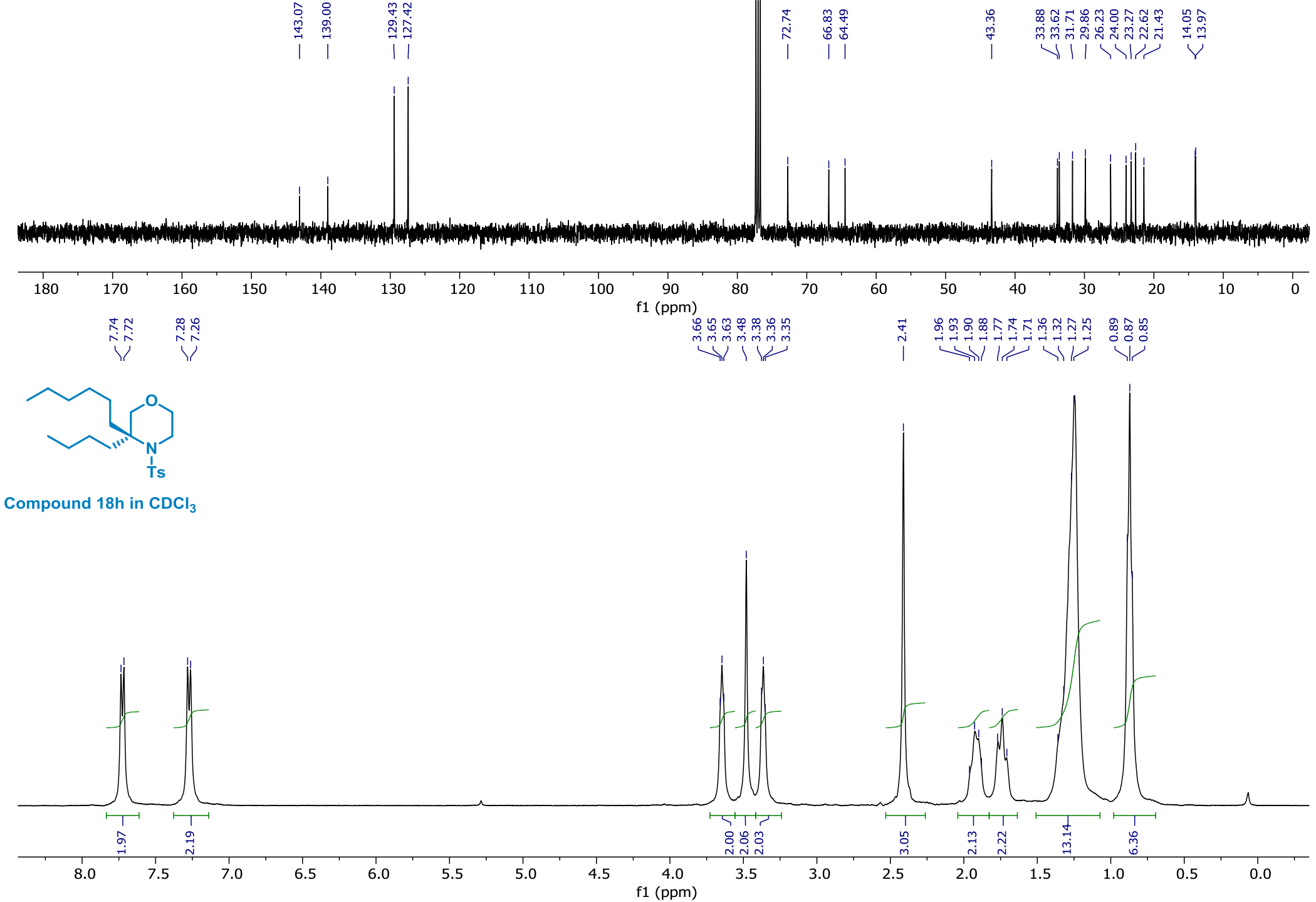
Compound 18e in $CDCl_3$

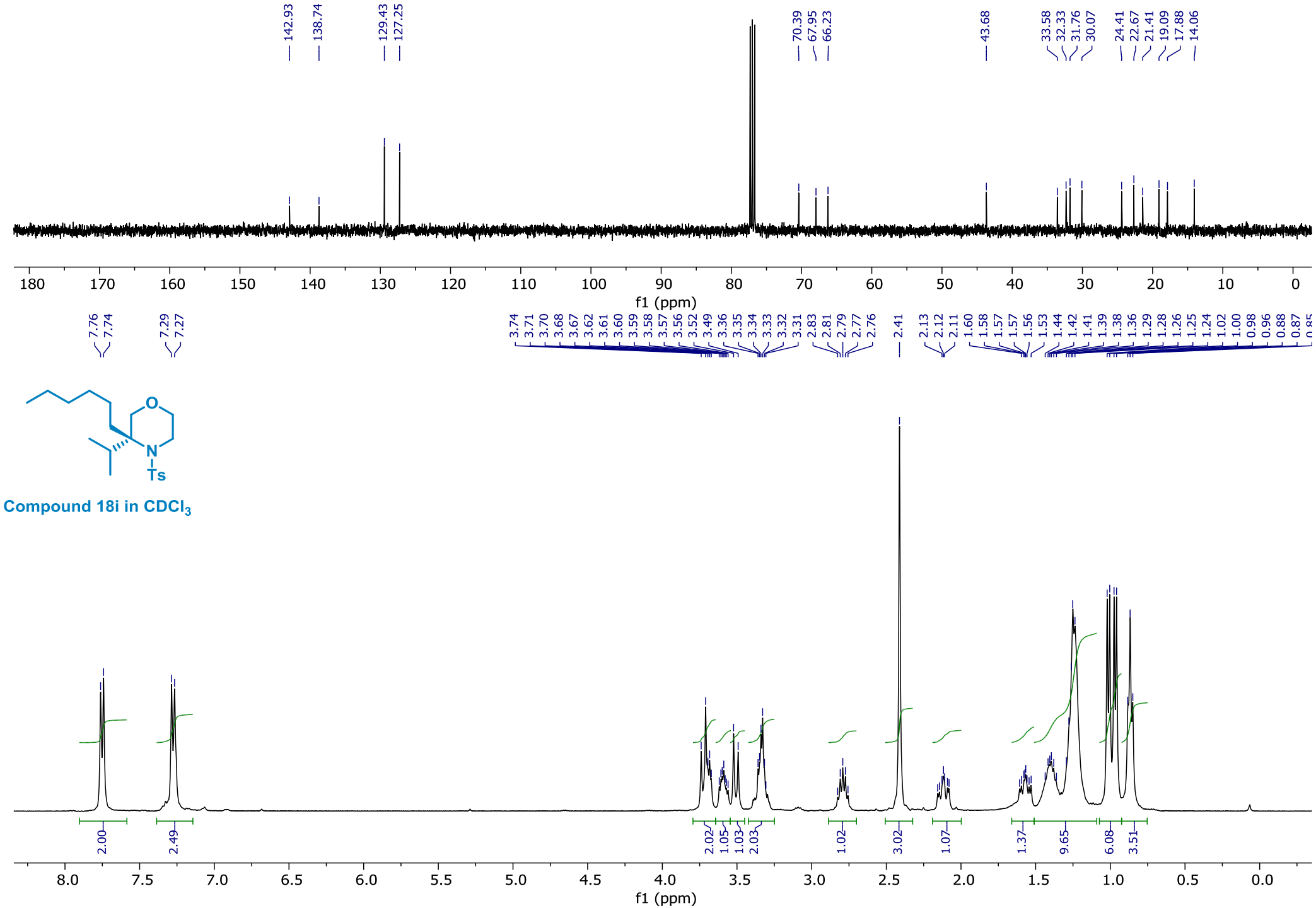


Compound 18f in $CDCl_3$

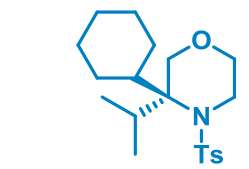


Compound 18g in $CDCl_3$

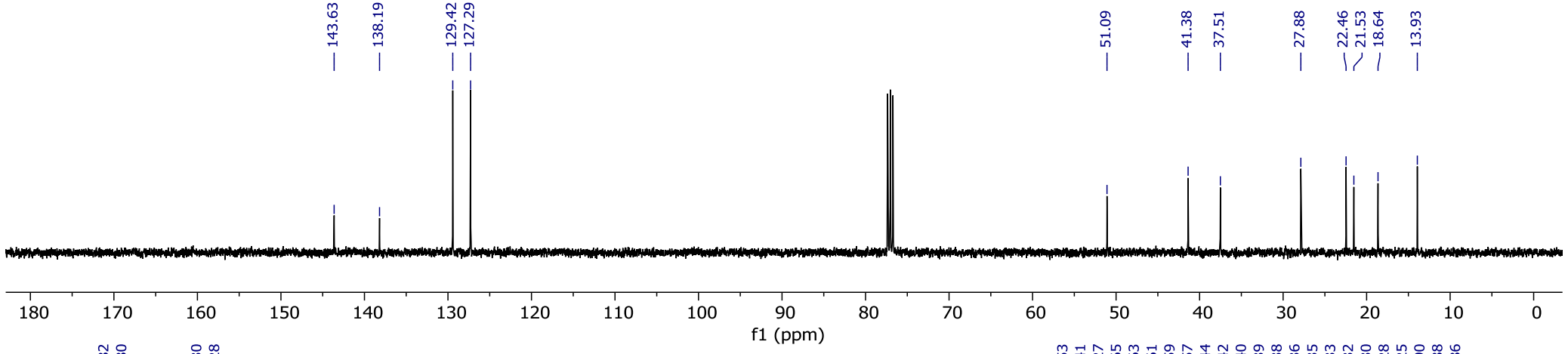

143.07
139.00
129.43
127.42
72.74
66.83
64.49
43.36
33.88
33.62
31.71
29.86
26.23
24.00
23.27
22.62
21.43
14.05
13.97
f1 (ppm)
7.74
7.72
7.28
7.26
3.66
3.65
3.63
3.48
3.38
3.36
3.35
2.41
1.96
1.93
1.90
1.88
1.77
1.74
1.71
1.36
1.32
1.27
1.25
0.89
0.87
0.85
O
N
Ts
Compound 18h in CDCl3
1.97
2.19
2.00
2.06
2.03
3.05
2.13
2.22
13.14
6.36
f1 (ppm)

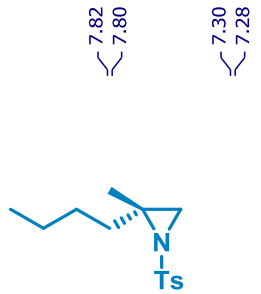


Compound 18i in $CDCl_3$

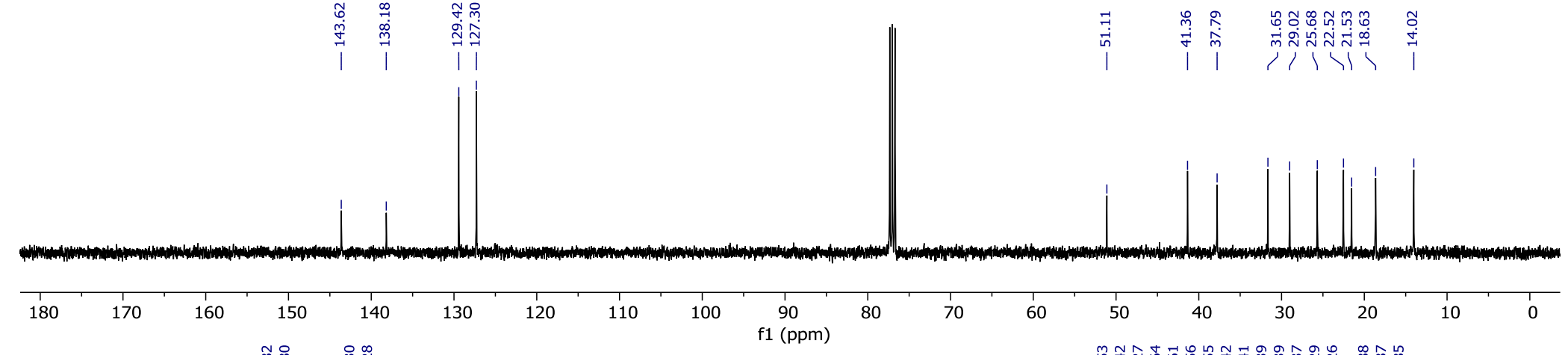


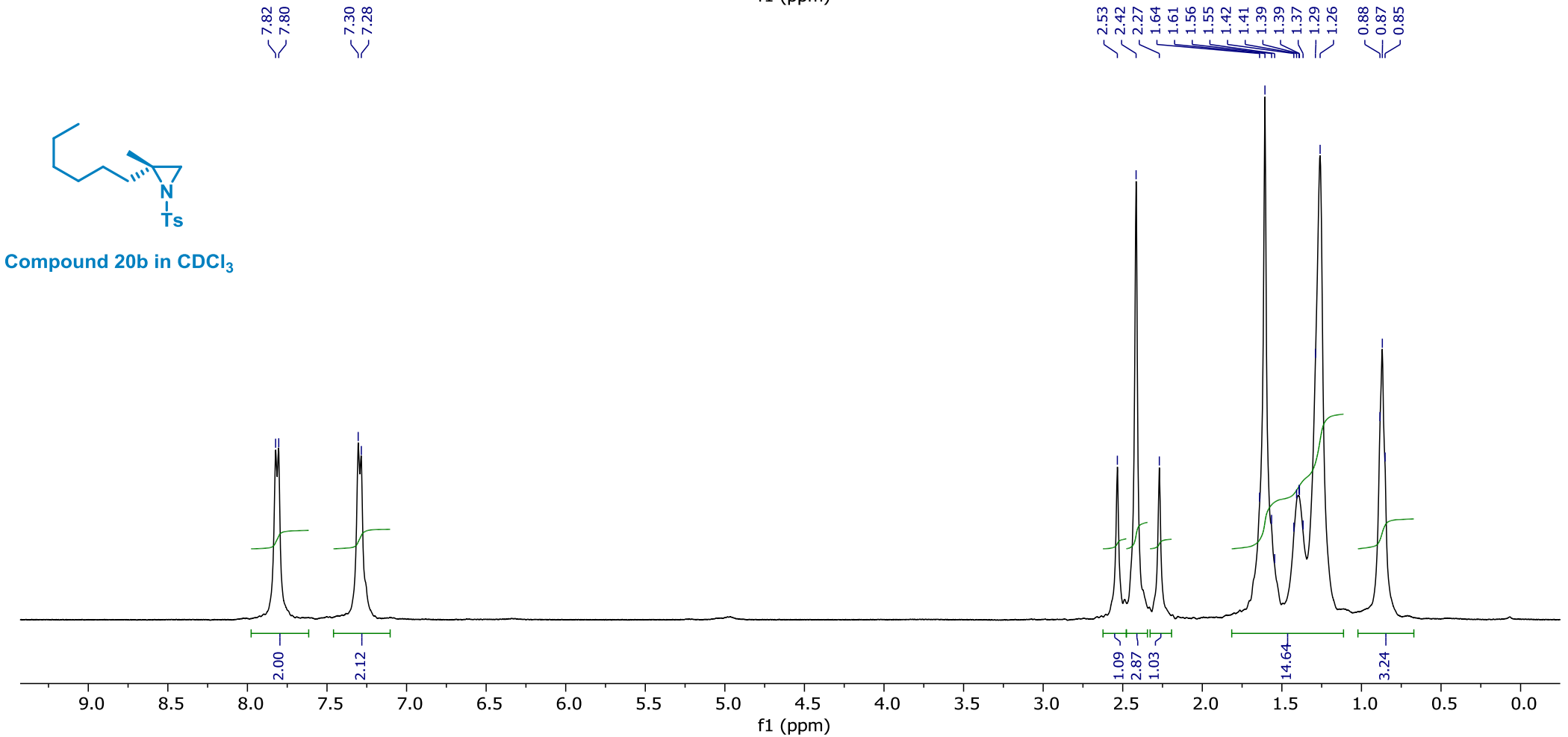
Compound 18j in $CDCl_3$



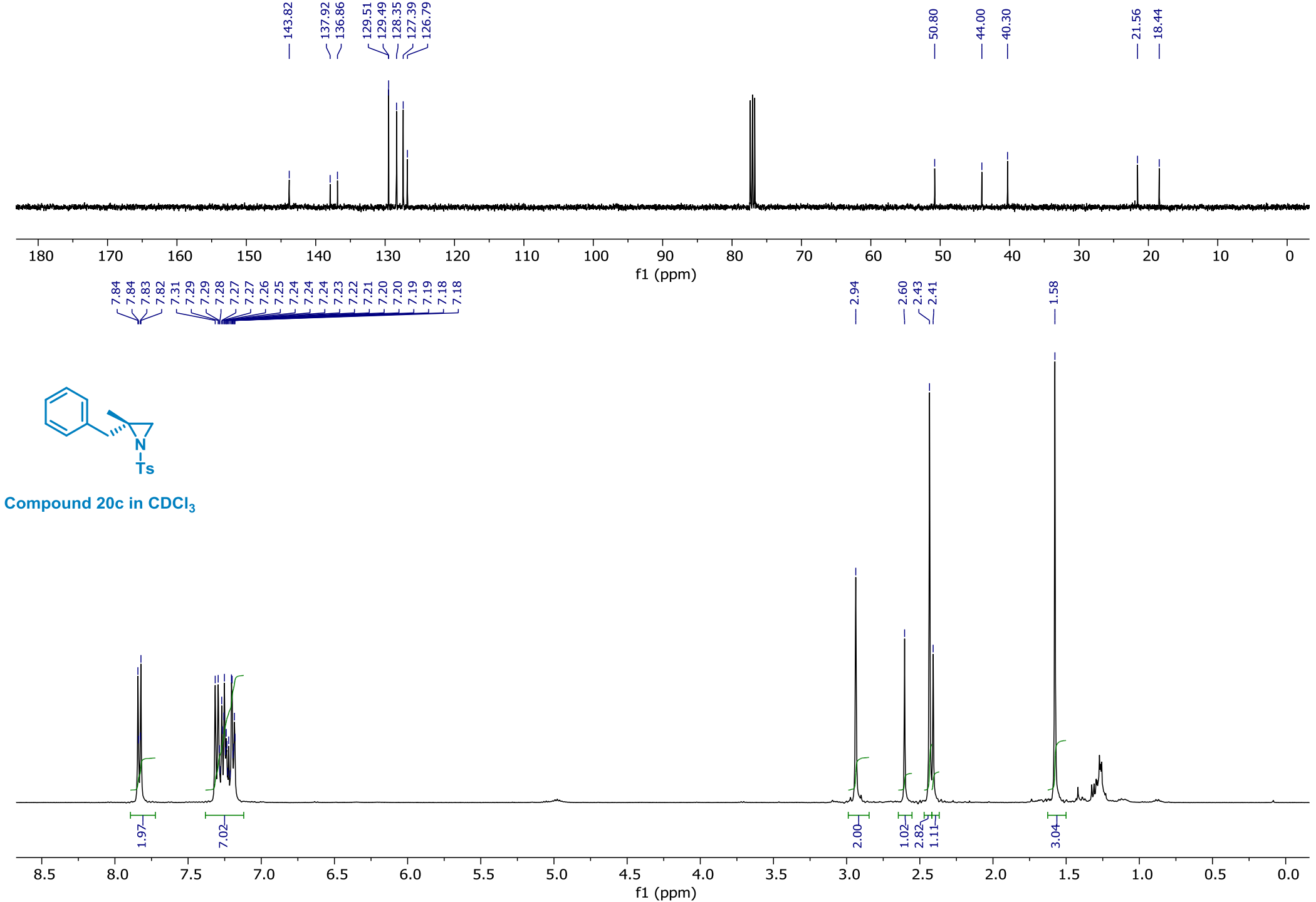


Compound 20a in $CDCl_3$

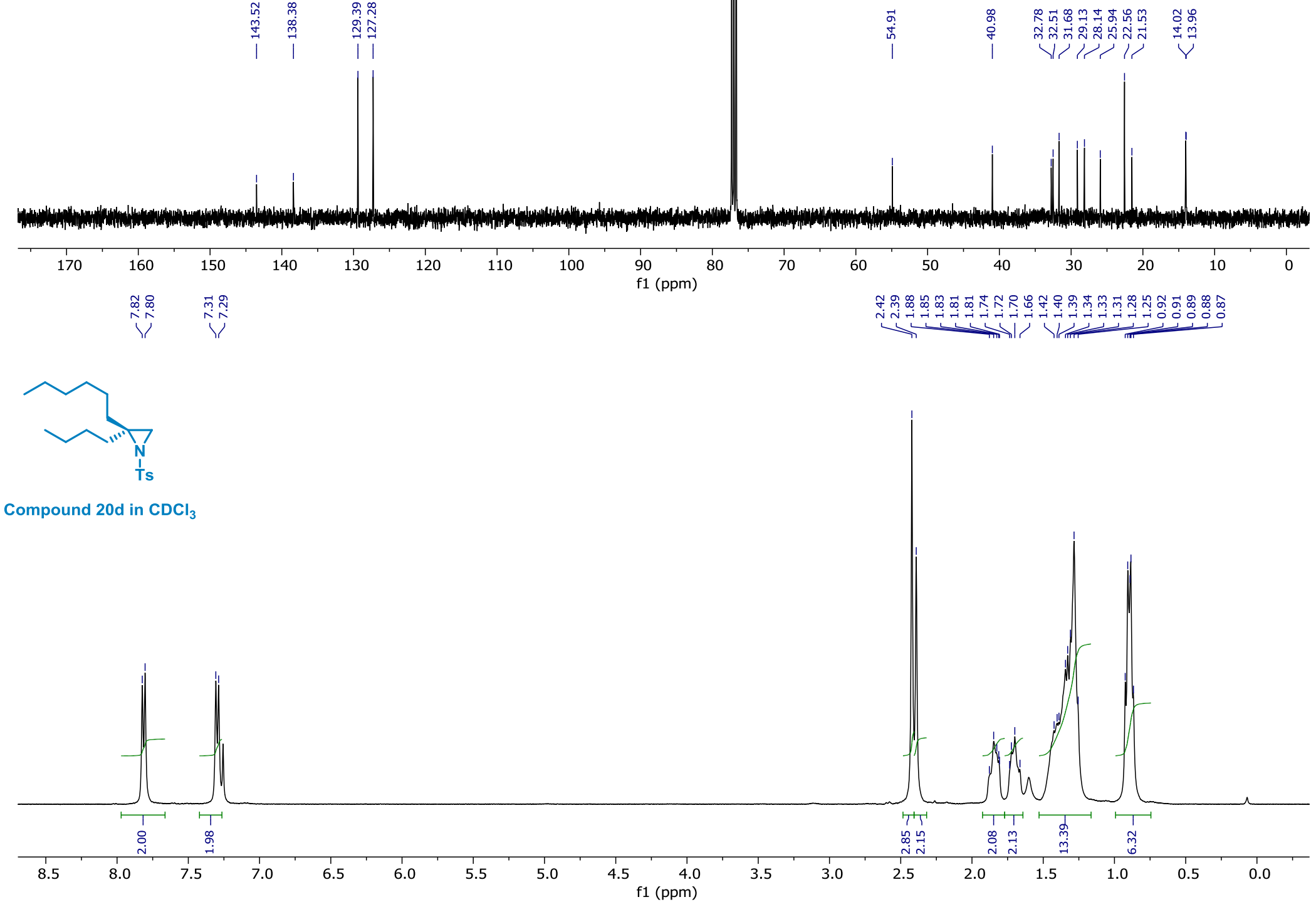


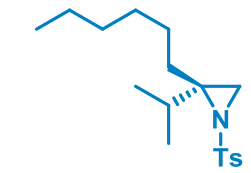


Compound 20b in $CDCl_3$

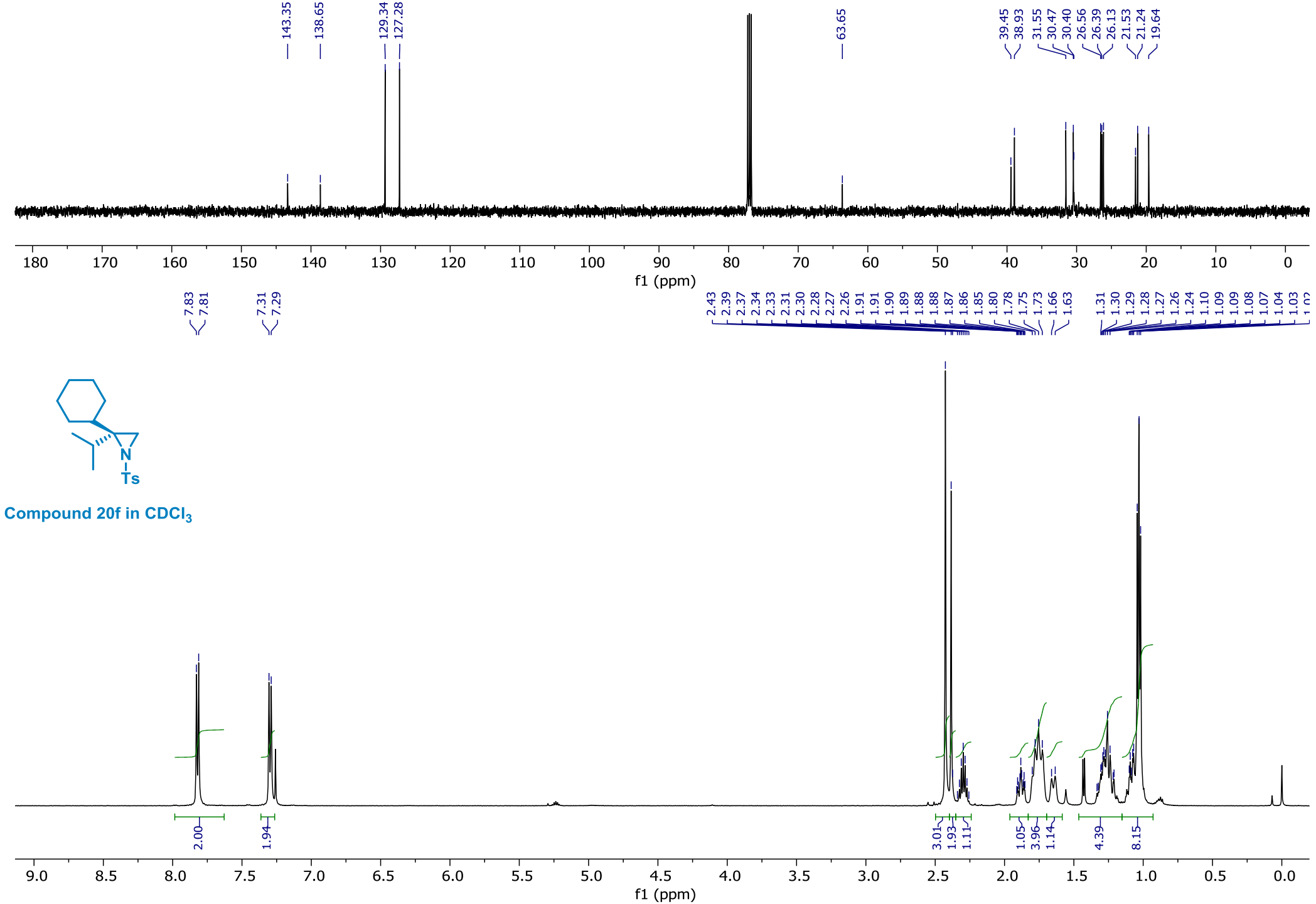


Compound 20c in $CDCl_3$

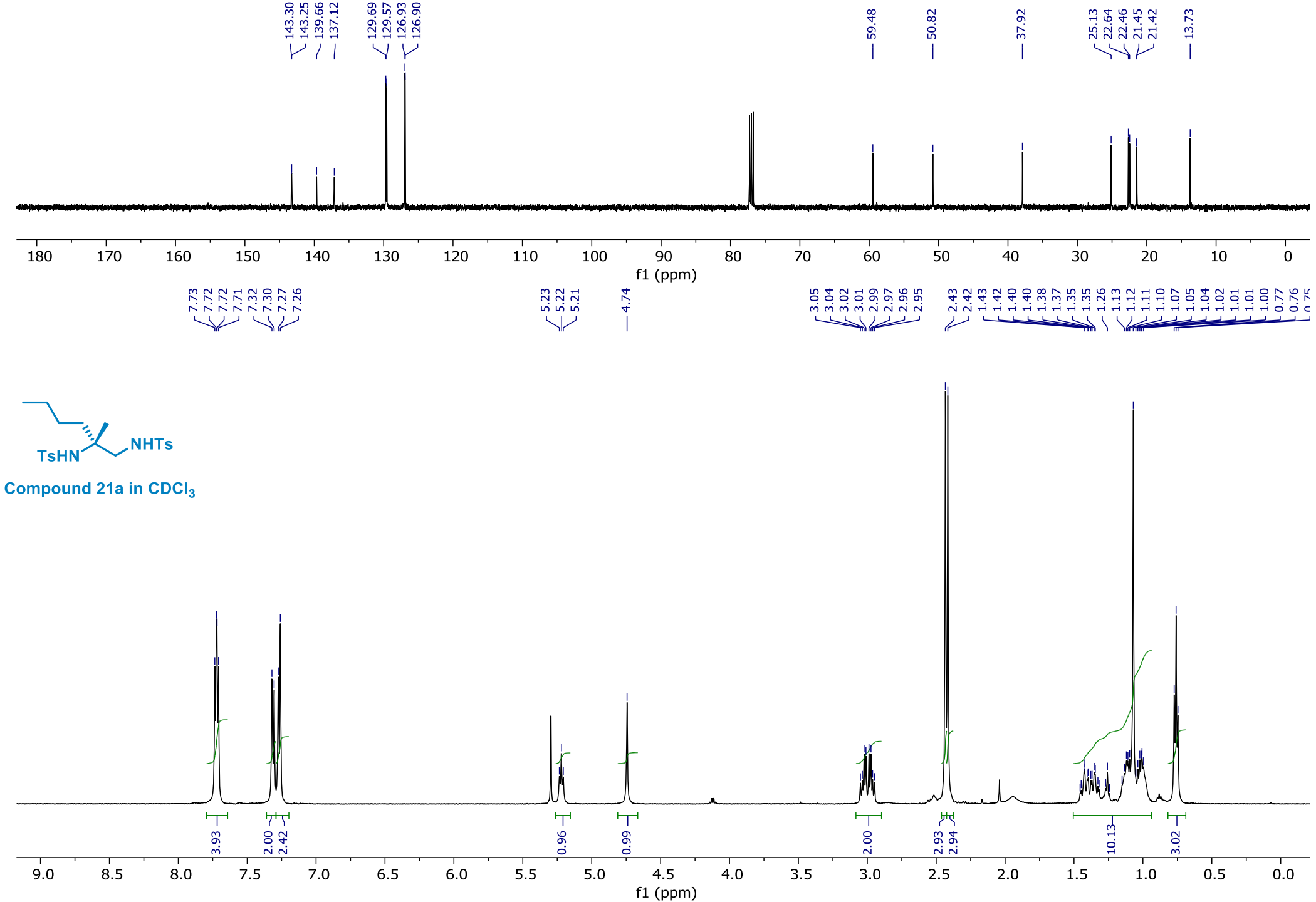

143.52
138.38
129.39
127.28
54.91
40.98
32.78
32.51
31.68
29.13
28.14
25.94
22.56
21.53
14.02
13.96
f1 (ppm)
7.82
7.80
7.31
7.29
2.42
2.39
1.88
1.85
1.83
1.81
1.81
1.74
1.72
1.70
1.66
1.42
1.40
1.39
1.34
1.33
1.31
1.28
1.25
0.92
0.91
0.89
0.88
0.87
N
Ts
Compound 20d in CDCl3
2.00
1.98
2.85
2.15
2.08
2.13
13.39
6.32
f1 (ppm)

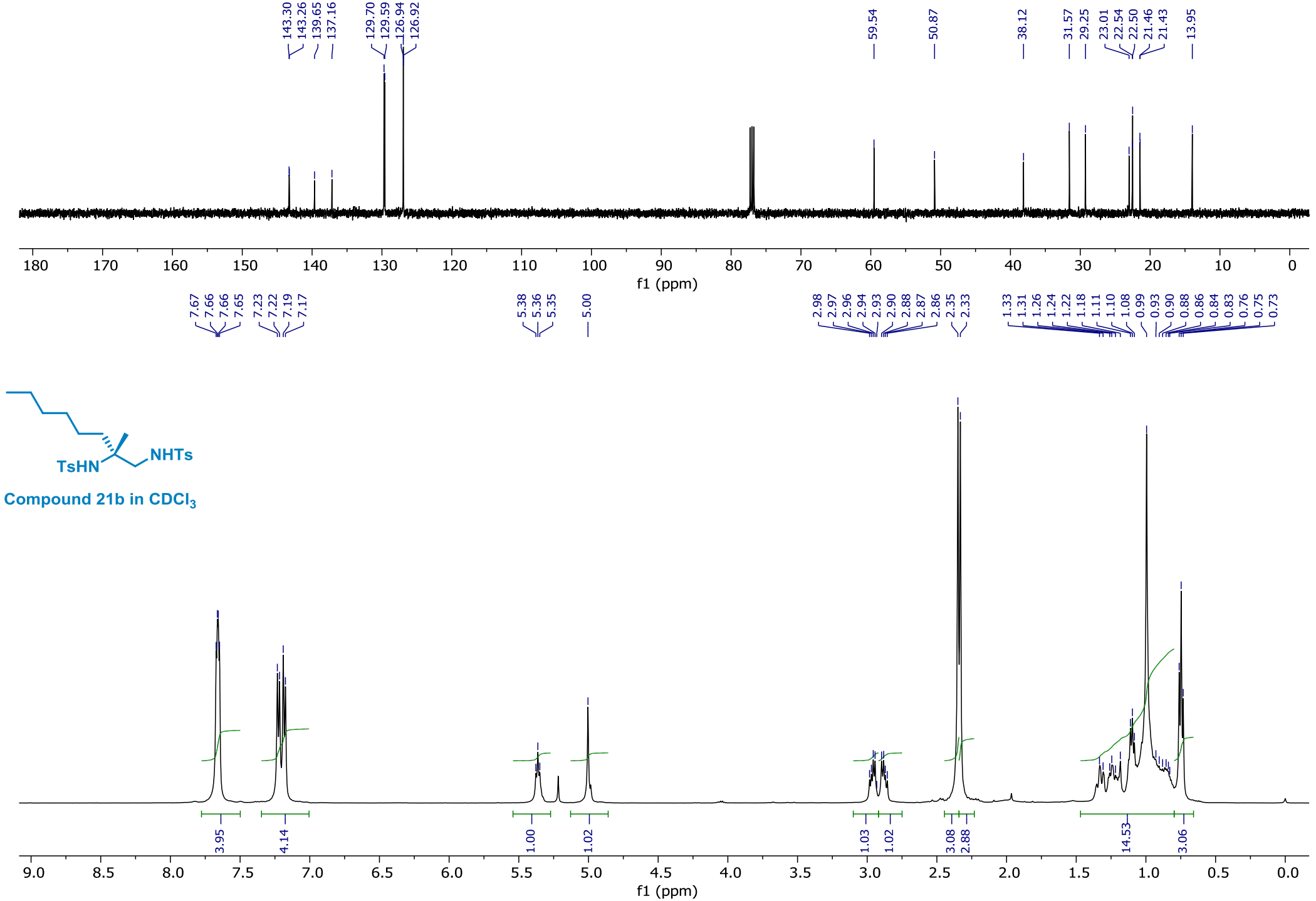


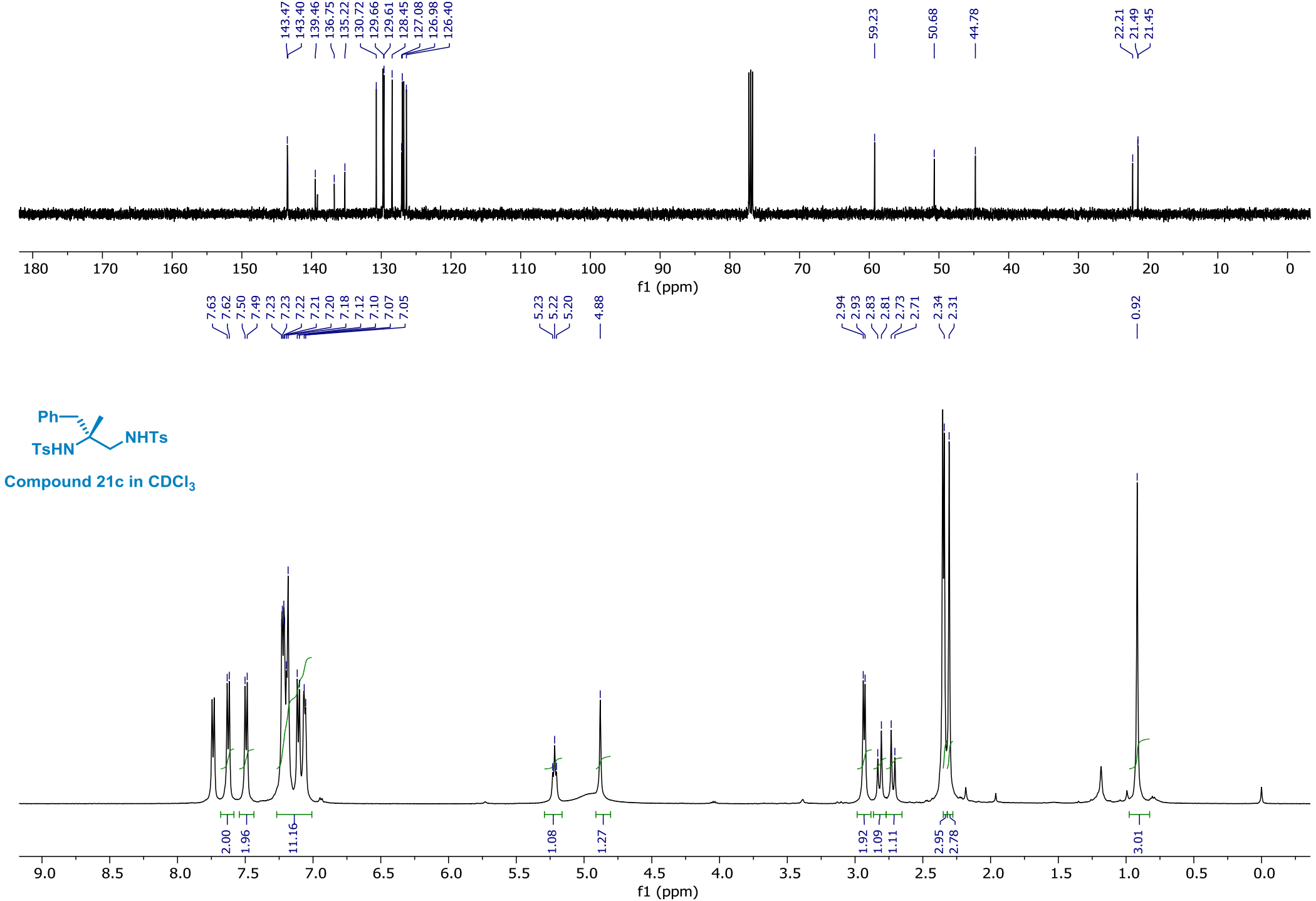
Compound 20e in $CDCl_3$

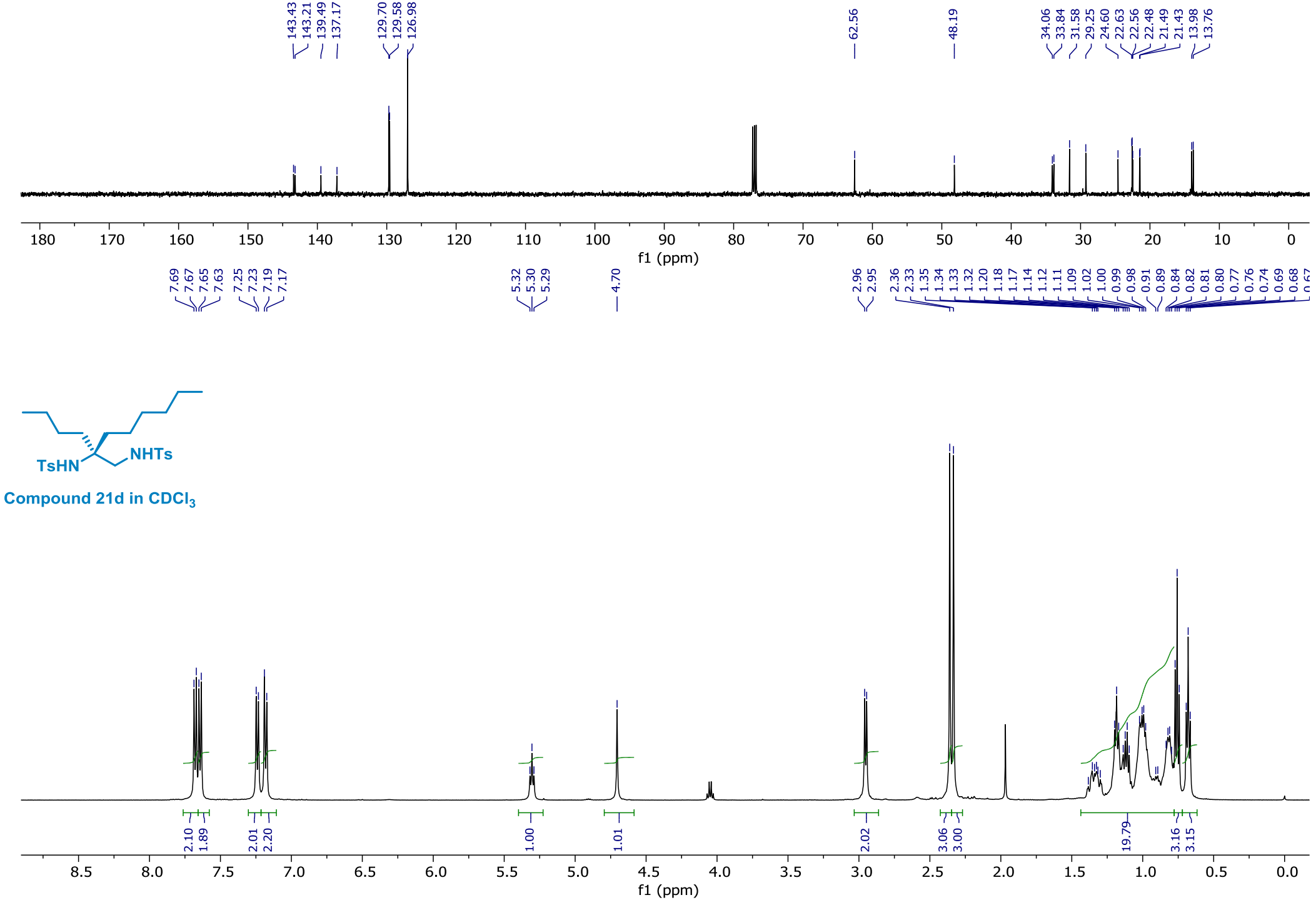


Compound 20f in $CDCl_3$

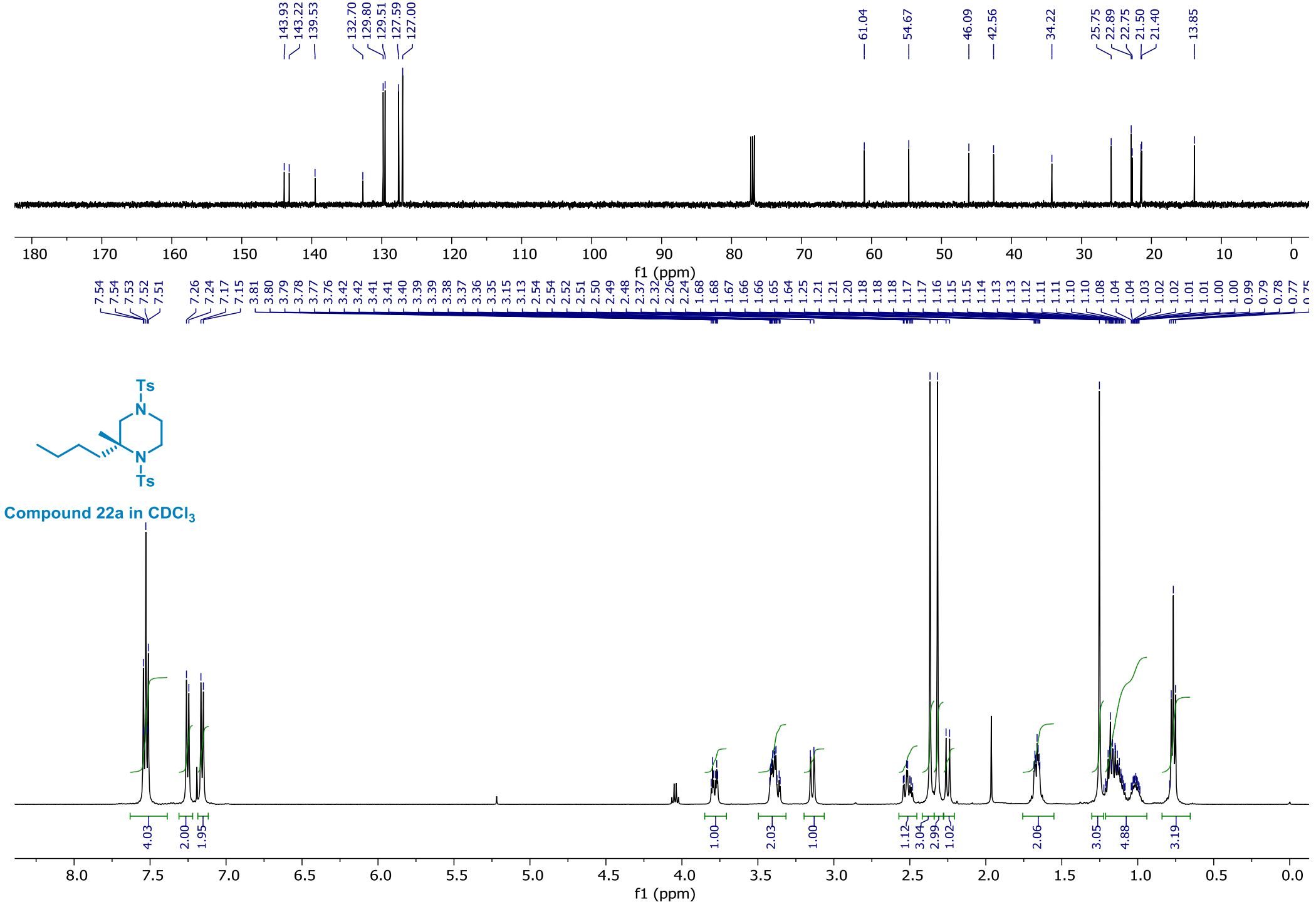

TsHN
NHTs
Compound 21a in CDCl3
f1 (ppm)
f1 (ppm)

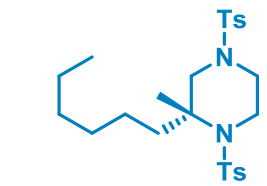

143.30
143.26
139.65
137.16
129.70
129.59
126.94
126.92
59.54
50.87
38.12
31.57
29.25
23.01
22.54
22.50
21.46
21.43
13.95
f1 (ppm)
7.67
7.66
7.66
7.65
7.23
7.22
7.19
7.17
5.38
5.36
5.35
5.00
2.98
2.97
2.96
2.94
2.93
2.90
2.88
2.87
2.86
2.35
2.33
1.33
1.31
1.26
1.24
1.22
1.18
1.11
1.10
1.08
0.99
0.93
0.90
0.88
0.86
0.84
0.83
0.76
0.75
0.73
TsHN
NHTs
Compound 21b in CDCl3
3.95
4.14
1.00
1.02
1.03
1.02
3.08
2.88
14.53
3.06
f1 (ppm)


Ph
NHTs
TsHN
Compound 21c in CDCl3
f1 (ppm)
f1 (ppm)

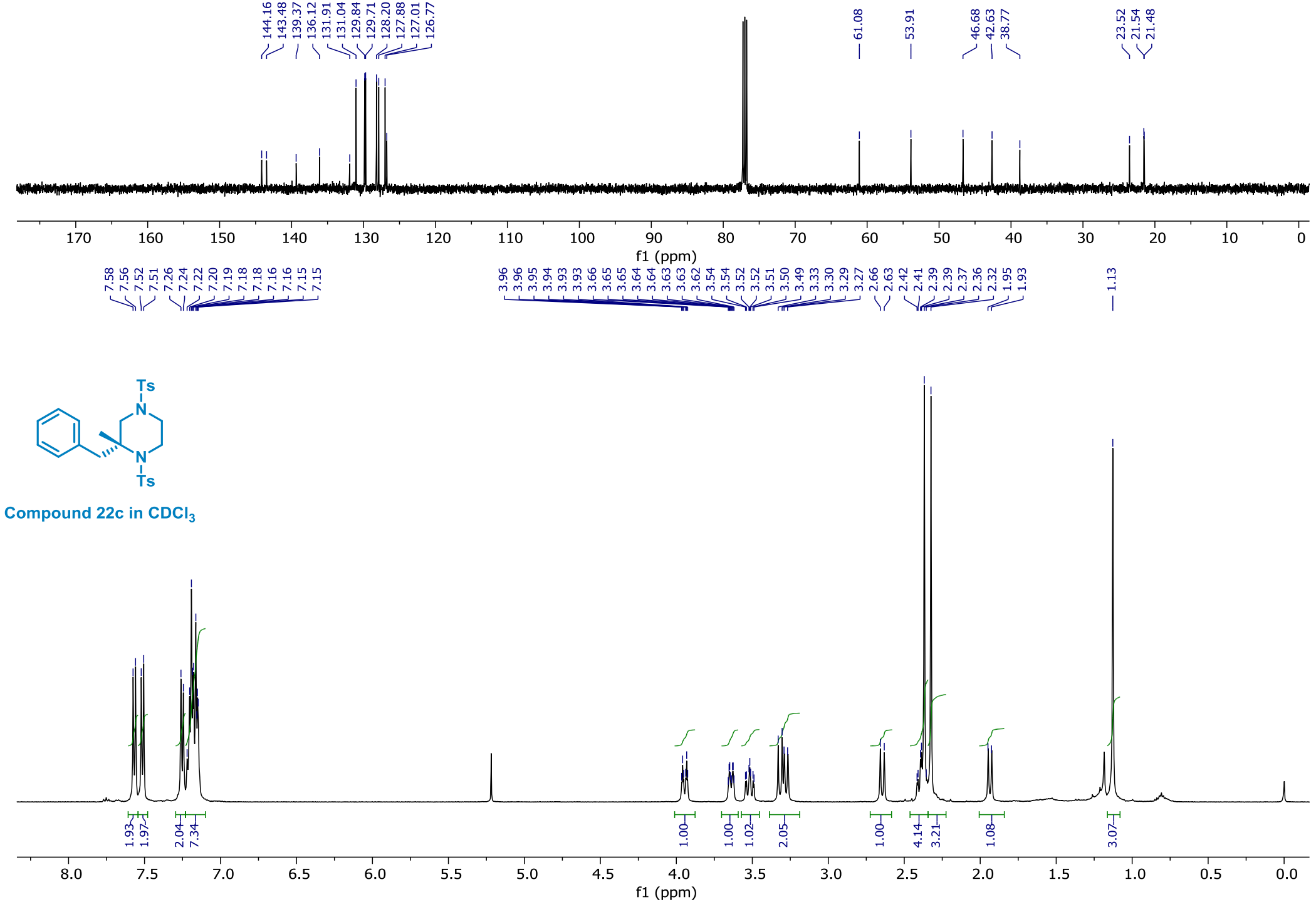


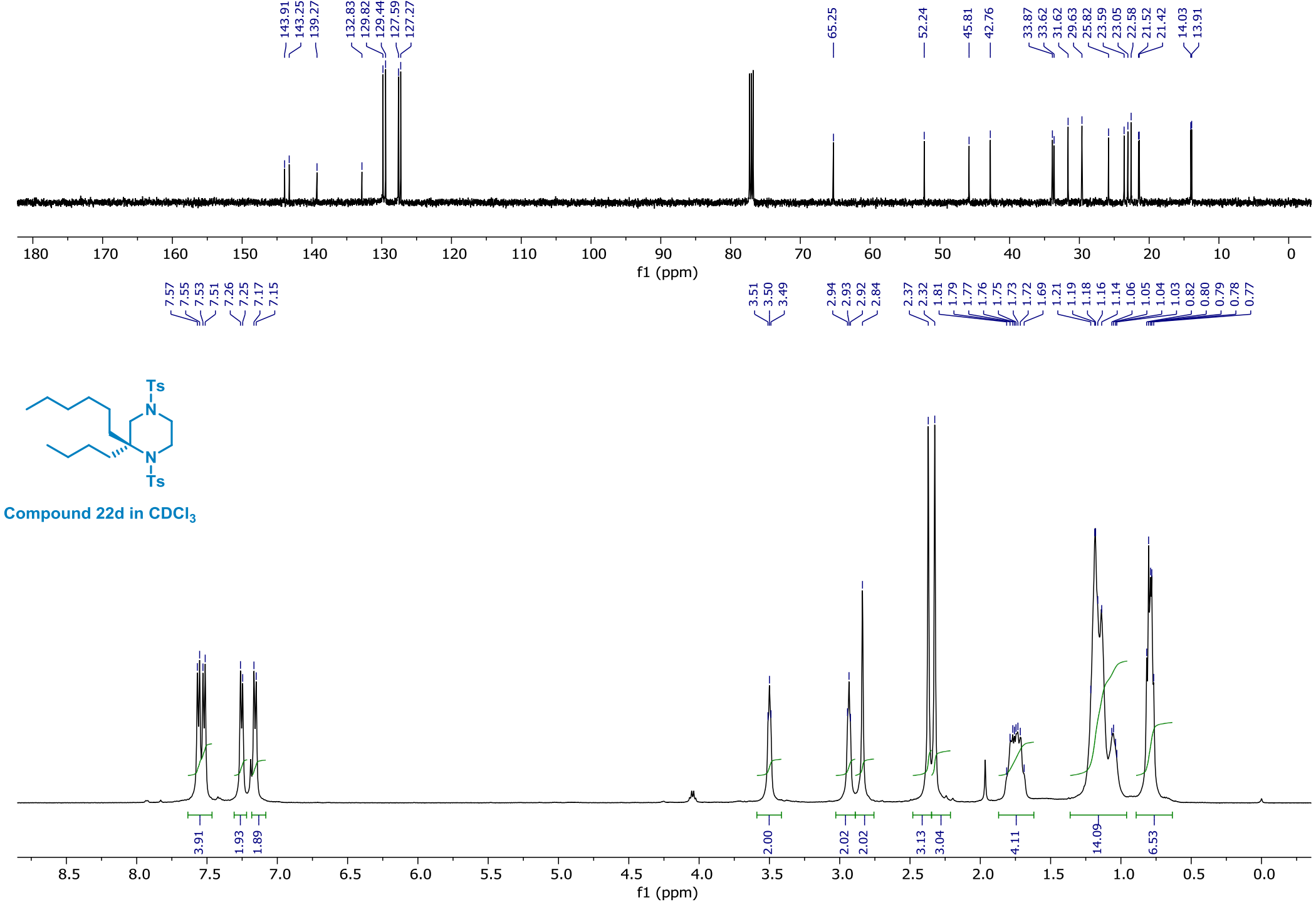
Compound 21d in $CDCl_3$


Ts
N
N
Ts
Compound 22a in CDCl3
f1 (ppm)
f1 (ppm)

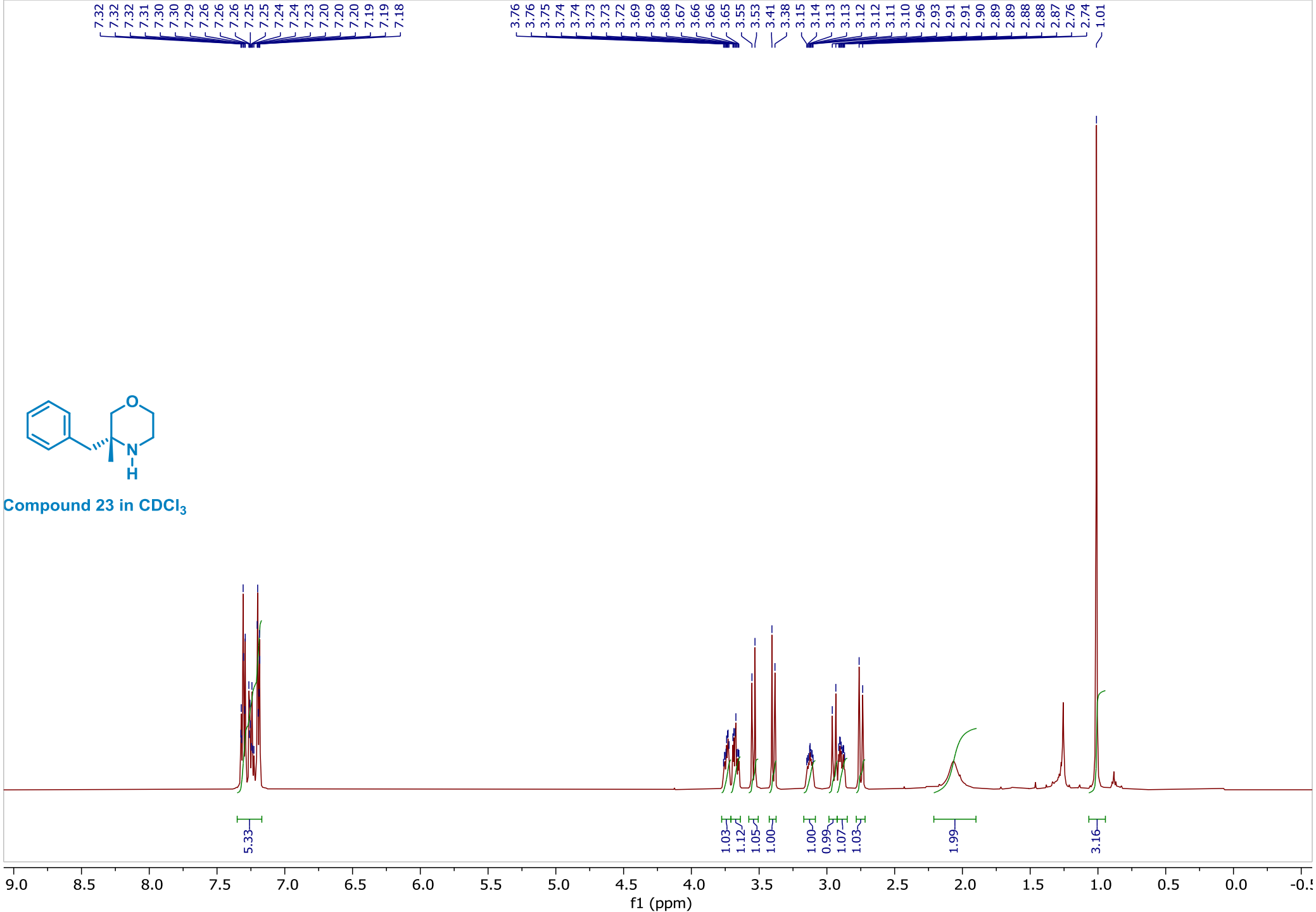


Compound 22b in $CDCl_3$


Ts
N
N
Ts
Compound 22c in CDCl3
f1 (ppm)
f1 (ppm)



Compound 22d in $CDCl_3$


Compound 23 in CDCl3
f1 (ppm)