The regioselective Wacker oxidation of internal allylamines: synthesis of functionalized and challenging β-amino ketones

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Electronic supplementary information

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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.

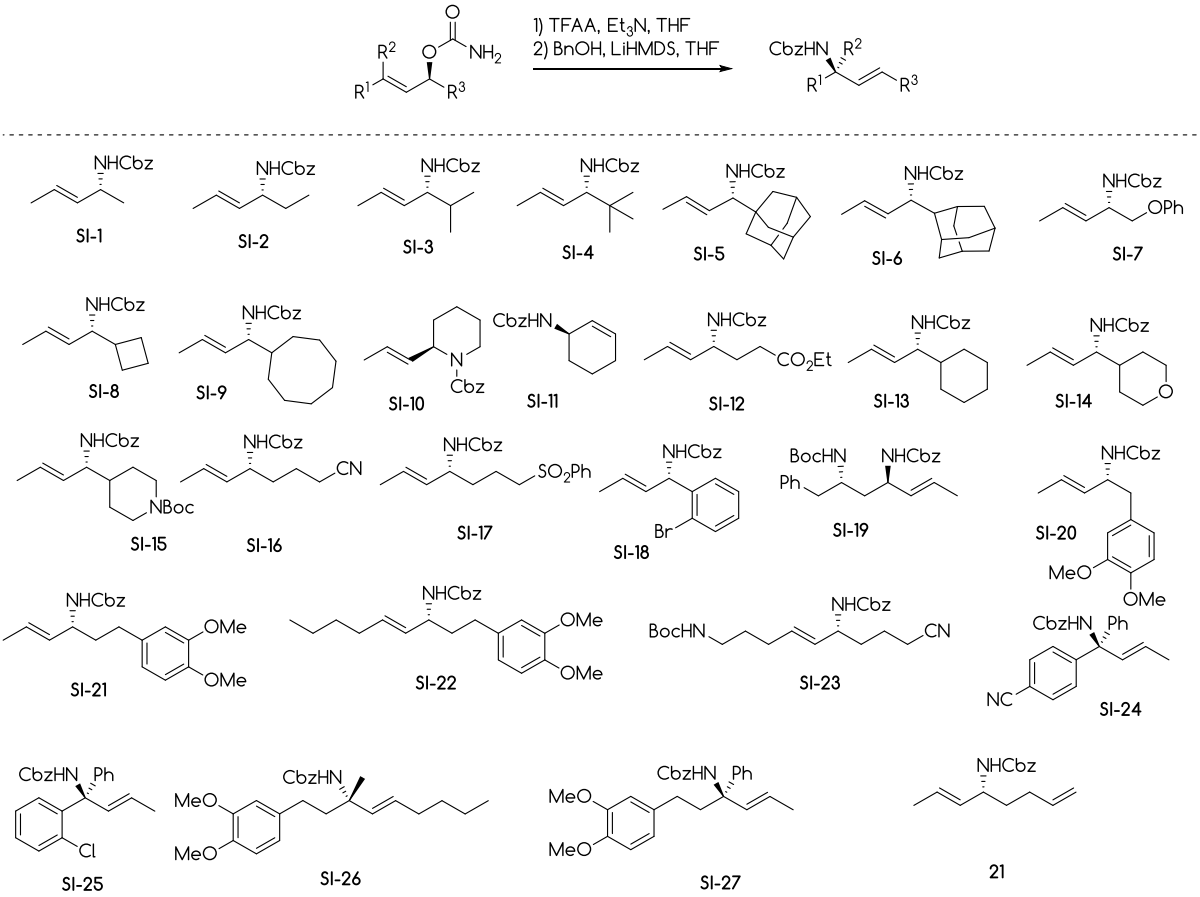
Reactions were monitored by TLC on silica gel plates (TLC Silica gel 60 F254, Aluminium sheets) and HPLC, ^{1}H NMR. TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using UV light, and $KMnO_4$ or cerium/molybdenium stains. Column chromatography was performed by using silica gel from Merck (Silica gel 60, 40-63 μm). Flash chromatography was accomplished using an automated system (Reveleris X2, with ELSD and UV detector) with silica cartridges (Merck, Silica gel 60, 40-63 μm). Solvents were purified by use of drying cartridges through a solvent delivery system.

Melting points (°C) are uncorrected. Optical rotation was recorded on Jasco P-2000 polarimeter. Microwave heating was performed by using CEM SP Discover reactor.

2. Synthesis of enantioenriched allylamines

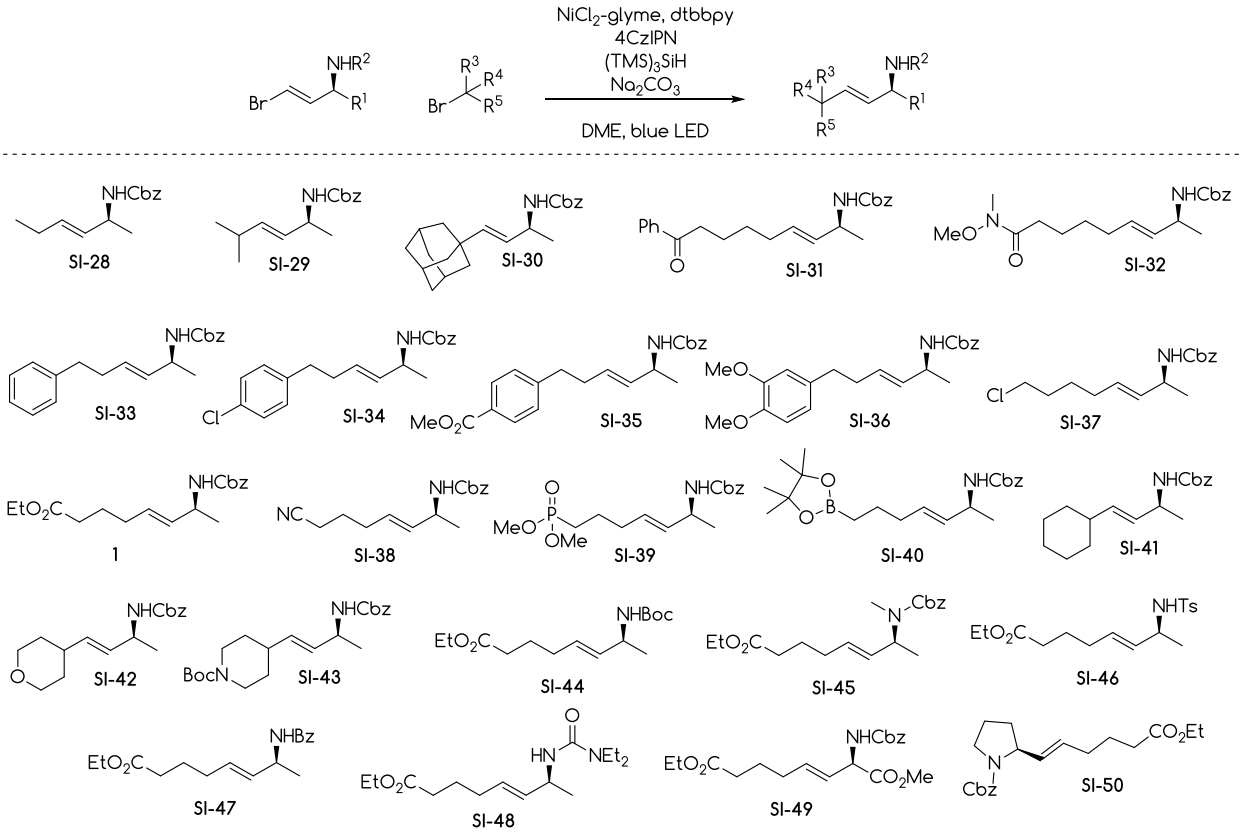
2.1. Synthesis of SI-1–SI-27 and 21 (Ichikawa rearrangement)

The allylamines **SI-1**–**SI-27** and **21** were synthesized via Ichikawa rearrangement of allyl carbamates prepared from (*S*)-butyn-2-ol according to our previous protocols.[1]



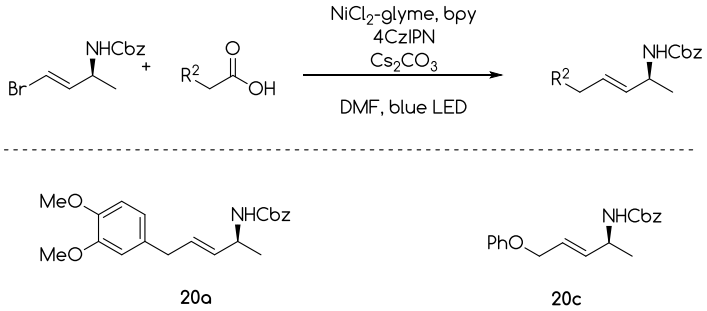
2.2. Synthesis of SI-28–SI-50 and 1 (dual photoredox/Ni-catalyzed cross-coupling with alkyl bromides)

The allylamines **SI-28** – **SI-50** and **1** were synthesized via metallaphotoredox cross-coupling strategy of vinyl bromides with alkyl bromides according to protocol developed by our group.[1e] Vinyl bromides were derived from the corresponding α-amino acids.

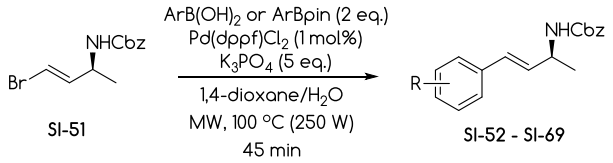


2.3. Synthesis of 20a and 20c (dual photoredox/Ni-catalyzed decarboxylative cross-coupling with alkyl carboxylic acids)

The allylamines **20a** and **20c** were synthesized via metallaphotoredox cross-coupling strategy of vinyl bromides with alkyl carboxylic acids according to protocol developed by our group.[1e] Vinyl bromides were derived from the corresponding α-amino acids.

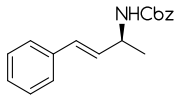


2.4. Synthesis of SI-52–SI-69 (Suzuki coupling)



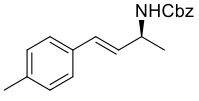
General Procedure: $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1 mol%, 2.0 mg, 2.5 μmol), phenylboronic acid or its pinacol ester (0.50 mmol, 2 eq.), vinyl bromide **SI-51** (0.25 mmol), K_3PO_4 (5 eq., 382.1 mg, 1.25 mmol) were placed in the microwave vessel. The resulting mixture was degassed and backfilled with argon three times. Degassed dioxane (2 mL) and degassed water (200 μL) were added sequentially and then the mixture was heated a microwave apparatus (100 °C, 250 W) for 45 min. Next, the reaction mixture was concentrated and the crude mixture was purified by a column chromatography on silica gel.

Benzyl (*S*,*E*)-(4-phenylbut-3-en-2-yl)carbamate (SI-52)



Yield: 60.1 mg (85%) starting from 71.0 mg (0.25 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-10% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 89.1–90.8 °C [lit.[2] 89–91 °C]; $[\alpha]_D^{25}$ -43.7 (*c* 0.42, $CHCl_3$ [lit. for (*R*) enanationer: +48.8, *c* 1.00, CH_2Cl_2]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 9H), 7.27 – 7.21 (m, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 5.8 Hz, 1H), 5.14 (s, 2H), 4.85 (s, 1H), 4.55 – 4.44 (m, 1H), 1.34 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 136.7, 136.6, 131.2, 129.6, 128.56, 128.53, 128.1 (x2), 127.6, 126.4, 66.7, 48.5, 21.1; Spectral data matches literature data.[2,3]

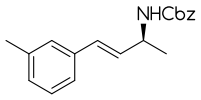
Benzyl (*S*,*E*)-(4-(*p*-tolyl)but-3-en-2-yl)carbamate (SI-53)



Yield: 69.2 mg (89%) starting from 75.1 mg (0.26 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-10% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 95.3–97.7 °C; $[\alpha]_D^{25}$ -39.8 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30

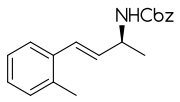
(m, 5H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.12 (dd, *J* = 15.9, 5.2 Hz, 1H), 5.14 (s, 2H), 4.84 (s, 1H), 4.48 (s, 1H), 2.34 (s, 3H), 1.34 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 137.4, 136.6, 133.9, 130.2, 129.5, 129.3, 128.5, 128.13, 128.10, 126.3, 66.7, 48.5, 21.2(×2); Spectral data matches literature data.[3]

Benzyl (*S*,*E*)-(4-(*m*-tolyl)but-3-en-2-yl)carbamate (SI-54)



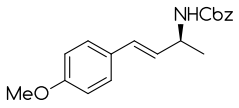
Yield: 78.5 mg (87%) starting from 87.2 mg (0.31 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-10% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 58.7–60.2 °C; $[\alpha]_D^{25}$ -38.5 (*c* 0.67, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 5H), 7.23 – 7.15 (m, 3H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.16 (dd, *J* = 15.9, 5.6 Hz, 1H), 5.14 (s, 2H), 4.86 (s, 1H), 4.49 (s, 1H), 2.35 (s, 3H), 1.35 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 138.1, 136.6, 131.0, 129.7, 128.54, 128.46, 128.41(×2), 128.14, 128.11, 127.2, 123.6, 66.7, 48.5, 21.4, 21.1; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{21}NO_2Na$ [(M+Na)$^+$] 318.1470; found: 318.1461; FTIR (film) ν: 3322, 3032, 2972, 1698, 1604, 1526, 1453, 1244, 1049 cm^{-1}.

Benzyl (*S*,*E*)-(4-(*o*-tolyl)but-3-en-2-yl)carbamate (SI-55)



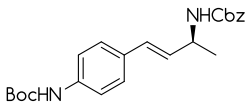
Yield: 64.4 mg (85%) starting from 73.3 mg (0.26 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-10% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 58.7–60.2 °C; $[\alpha]_D^{25}$ -38.5 (*c* 0.67, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.29 (m, 5H), 7.19 – 7.08 (m, 4H), 6.74 (d, *J* = 15.8 Hz, 1H), 6.03 (dd, *J* = 15.8, 5.8 Hz, 1H), 5.15 (s, 2H), 4.86 (s, 1H), 4.51 (s, 1H), 2.32 (s, 3H), 1.36 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 136.6, 135.8, 135.5, 132.6, 130.3, 128.5, 128.1 (×2), 127.6, 127.5, 126.1, 125.7, 66.7, 48.8, 21.2, 19.8; Spectral data matches literature data.[3]

Benzyl (*S*,*E*)-(4-(4-methoxyphenyl)but-3-en-2-yl)carbamate (SI-56)



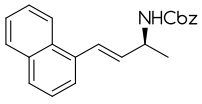
Yield: 66.8 mg (86%) starting from 70.7 mg (0.25 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0–15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 93.9–95.2 °C; $[\alpha]_D^{25}$ -42.4 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 7H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.02 (dd, *J* = 15.9, 5.8 Hz, 1H), 5.13 (s, 2H), 4.82 (s, 1H), 4.45 (s, 1H), 3.80 (s, 3H), 1.33 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 155.6, 136.6, 129.4, 129.1, 129.0, 128.5, 128.12, 128.09, 127.6, 114.0, 66.7, 55.3, 48.6, 21.2; Spectral data matches literature data.[3]

Benzyl (*S*,*E*)-(4-(4-((*t*-butoxycarbonyl)amino)phenyl)but-3-en-2-yl)carbamate (SI-57)



Yield: 78.5 mg (87%) starting from 87.2 mg (0.31 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0–15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 192.6–195.5 °C; $[\alpha]_D^{25}$ -38.3 (*c* 0.72, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.22 (m, 9H), 6.57 (s, 1H), 6.43 (d, *J* = 15.7 Hz, 1H), 6.05 (dd, *J* = 15.7, 5.1 Hz, 1H), 5.12 (s, 2H), 4.81 (s, 1H), 4.45 (s, 1H), 1.51 (s, 9H), 1.32 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 152.7, 137.8, 136.6, 131.5, 129.7, 129.0, 128.5, 128.1 (×2), 127.0, 118.5, 80.6, 66.7, 48.5, 28.3, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{28}N_2O_4Na$ [$(M+Na)^+$] 419.1947; found: 419.1951; FTIR (film) ν: 3327, 3274, 3032, 2973, 1685, 1598, 1532, 1451, 1323, 1248, 1157, 1048 cm^{-1}.

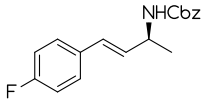
Benzyl (*S*,*E*)-(4-(naphthalen-1-yl)but-3-en-2-yl)carbamate (SI-58)



Yield: 72.4 mg (86%) starting from 72.1 mg (0.25 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0–10% AcOEt in hexanes, flow 15 mL/min, 30 min); white waxy solid; $[\alpha]_D^{25}$ -20.9 (*c* 0.64, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.87 – 7.82

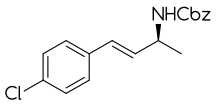
(m, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.24 (m, 10H), 6.18 (dd, *J* = 15.6, 5.7 Hz, 1H), 5.18 (s, 2H), 4.93 (s, 1H), 4.61 (s, 1H), 1.43 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 136.6, 134.5, 133.6, 131.2, 128.56, 128.51(×2), 128.1 (×2), 128.0, 127.0, 126.1, 125.8, 125.6, 123.9, 123.8, 66.8, 48.8, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{21}NO_2Na$ [(M+Na)$^+$] 354.1470; found: 354.1480; FTIR (film) ν: 3321, 3034, 2971, 1697, 1590, 1527, 1454, 1250, 1049 cm^{-1}.

Benzyl (*S*,*E*)-(4-(4-fluorophenyl)but-3-en-2-yl)carbamate (SI-59)



Yield: 66.9 mg (88%) starting from 72.5 mg (0.26 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-10% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 107.8–109.9 °C; $[\alpha]_D^{25}$ -33.9 (*c* 0.88, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 7H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.07 (dd, *J* = 15.9, 5.7 Hz, 1H), 5.12 (s, 2H), 4.84 (s, 1H), 4.46 (s, 1H), 1.33 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 and 161.1 (d, *J* = 246.5 Hz), 155.59, 136.55, 132.86 and 132.83 (d, *J* = 3.1 Hz), 131.0, 128.53, 128.45, 128.1 (×2), 127.95 and 127.87 (d, *J* = 8.2 Hz), 115.54 and 115.33 (d, *J* = 21.7 Hz), 66.75, 48.49, 21.08; ^{19}F NMR (376 MHz, $CDCl_3$) δ –114.5; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{18}NO_2FNa$ [(M+Na)$^+$] 322.1219; found: 322.1222; FTIR (film) ν: 3314, 3035, 2969, 1685, 1599, 1539, 1452, 1267, 1228 cm^{-1}.

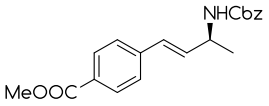
Benzyl (*S*,*E*)-(4-(4-chlorophenyl)but-3-en-2-yl)carbamate (SI-60)



Yield: 66.2 mg (84%) starting from 71.0 mg (0.25 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-10% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 105.6–108.0 °C; $[\alpha]_D^{25}$ -41.5 (*c* 0.59, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 7.29 – 7.21 (m, 4H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.13 (dd, *J* = 16.0, 5.7 Hz, 1H), 5.12 (s, 2H), 4.83 (s, 1H), 4.46 (s, 1H), 1.33 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 136.5, 135.2, 133.2, 132.0, 128.7, 128.5, 128.4, 128.1(×2), 127.6, 66.8, 48.5, 21.0; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{18}NO_2NaCl$ [(M+Na)$^+$]

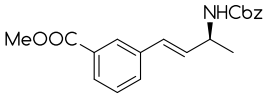
338.0924; found: 338.0927; FTIR (film) ν: 3306, 3033, 2966, 1688, 1589, 1537, 1452, 1253, 1102 cm^{-1}.

Methyl (*S*,*E*)-4-(3-(((benzyloxy)carbonyl)amino)but-1-en-1-yl)benzoate (SI-61)



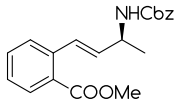
Yield: 88.5 mg (86%) starting from 86.5 mg (0.30 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 102.9–105.4 °C; $[\alpha]_D^{25}$ -39.5 (*c* 0.78, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.29 (m, 7H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.27 (dd, *J* = 15.9, 5.7 Hz, 1H), 5.12 (s, 2H), 4.83 (s, 1H), 4.48 (s, 1H), 3.90 (s, 3H), 1.35 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 155.6, 141.2, 136.5, 134.0, 129.9, 129.1, 128.7, 128.5, 128.2 (×2), 126.3, 66.8, 52.0, 48.5, 21.0; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{21}NO_4Na$ [(M+Na)$^+$] 362.1368; found: 362.1380; FTIR (film) ν: 3323, 3033, 2952, 1718, 1607, 1527, 1452, 1282, 1239, 1111, 1050 cm^{-1}.

Methyl (*S*,*E*)-3-(3-(((benzyloxy)carbonyl)amino)but-1-en-1-yl)benzoate (SI-62)



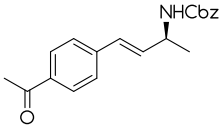
Yield: 80.7 mg (83%) starting from 81.7 mg (0.29 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white waxy solid; $[\alpha]_D^{25}$ -34.0 (*c* 0.59, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.28 (m, 6H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J* = 15.9, 5.4 Hz, 1H), 5.11 (s, 2H), 4.95 (s, 1H), 4.48 (s, 1H), 3.91 (s, 3H), 1.33 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 155.6, 137.0, 136.5, 132.6, 130.9, 130.5, 128.6, 128.56, 128.54(×2), 128.1(×2), 127.4, 66.8, 52.2, 48.4, 21.0; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{21}NO_4Na$ [(M+Na)$^+$] 362.1368; found: 362.1374; FTIR (film) ν: 3328, 3033, 2952, 1717, 1607, 1522, 1454, 1282, 1240, 1111, 1050 cm^{-1}.

Methyl (*S*,*E*)-2-(3-(((benzyloxy)carbonyl)amino)but-1-en-1-yl)benzoate (SI-63)



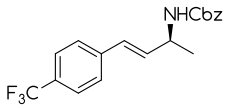
Yield: 65.6 mg (77%) starting from 71.1 mg (0.25 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 71.2–72.4 °C; $[\alpha]_D^{25}$ -34.6 (*c* 0.46, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.25 (m, 7H), 6.07 (dd, *J* = 15.9, 5.1 Hz, 1H), 5.13 (s, 2H), 4.90 (s, 1H), 4.51 (s, 1H), 3.87 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 155.6, 138.7, 136.6, 133.9, 132.1, 130.5, 128.53, 128.51, 128.49, 128.1 (×2), 127.5, 127.2, 66.7, 52.0, 48.4, 20.8; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{21}NO_4Na$ [(M+Na)$^+$] 362.1368; found: 362.1373; FTIR (film) ν: 3326, 3033, 2956, 1718, 1605, 1527, 1454, 1277, 1239, 1111, 1050 cm^{-1}.

Benzyl (*S*,*E*)-(4-(4-acetylphenyl)but-3-en-2-yl)carbamate (SI-64)



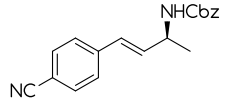
Yield: 66.5 mg (78%) starting from 74.6 mg (0.26 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 99.8–101.1 °C; $[\alpha]_D^{25}$ -41.6 (*c* 0.78, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.29 (m, 5H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.28 (dd, *J* = 15.9, 5.6 Hz, 1H), 5.12 (s, 2H), 4.92 (s, 1H), 4.49 (s, 1H), 2.57 (s, 3H), 1.34 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 155.6, 141.4, 136.5, 136.1, 134.3, 128.7, 128.5(×2), 128.2(×2), 126.5, 66.8, 48.5, 26.5, 20.9; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{21}NO_3Na$ [(M+Na)$^+$] 346.1419; found: 346.1424; FTIR (film) ν: 3330, 3033, 2973, 1703, 1680, 1603, 1525, 1454, 1360, 1270, 1239, 1049 cm^{-1}.

Benzyl (*S*,*E*)-(4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl)carbamate (SI-65)



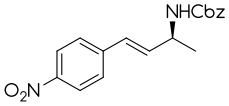
Yield: 64.1 mg (73%) starting from 71.9 mg (0.25 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-10% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 111.5–113.5 °C; $[\alpha]_D^{25}$ -29.5 (*c* 0.82, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.28 (m, 5H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 15.9, 5.5 Hz, 1H), 5.13 (s, 2H), 4.84 (s, 1H), 4.49 (s, 1H), 1.35 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 140.2, 136.5, 134.0, 129.4 (q, J_{C-F} = 33.4 Hz), 128.5, 128.3, 128.2 (×2), 126.6, 125.5 (q, J_{C-F} = 3.7 Hz), 124.2 (q, J_{C-F} = 271.5 Hz), 66.8, 48.4, 20.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.5; Spectral data matches literature data.[3]

Benzyl (*S*,*E*)-(4-(4-cyanophenyl)but-3-en-2-yl)carbamate (SI-66)



Yield: 63.9 mg (76%) starting from 78.2 mg (0.28 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 119.5–122.0 °C; $[\alpha]_D^{25}$ -41.4 (*c* 0.62, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.29 (m, 7H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.28 (dd, *J* = 15.9, 5.3 Hz, 1H), 5.11 (s, 2H), 4.87 (s, 1H), 4.48 (s, 1H), 1.34 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 141.2, 136.4, 135.4, 132.4, 128.5, 128.2, 128.1, 128.0, 126.9, 118.9, 110.8, 66.8, 48.4, 20.9; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{18}N_2O_2Na$ $[(M+Na)^+]$ 329.1266; found: 329.1271; FTIR (film) ν: 3329, 3034, 2974, 2225, 1703, 1604, 1523, 1453, 1237, 1049 cm^{-1}.

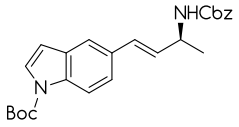
Benzyl (*S*,*E*)-(4-(4-nitrophenyl)but-3-en-2-yl)carbamate (SI-67)



Yield: 73.4 mg (72%) starting from 88.7 mg (0.31 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p.

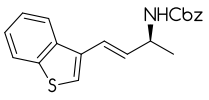
98.0–99.7 °C; $[\alpha]_D^{25}$ -46.1 (*c* 0.63, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.40 – 7.29 (m, 5H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.33 (dd, *J* = 15.8, 5.5 Hz, 1H), 5.12 (s, 2H), 4.89 (s, 1H), 4.50 (s, 1H), 1.36 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 147.0, 143.2, 136.4, 136.3, 128.6, 128.21, 128.15, 127.6, 126.9, 123.9, 66.9, 48.5, 20.8; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{18}N_2O_4Na$ [(M+Na)$^+$] 349.1164; found: 349.1172; FTIR (film) ν: 3303, 3034, 2972, 1697, 1596, 1515, 1453, 1343, 1237, 1048 cm^{-1}.

t-Butyl (*S*,*E*)-5-(3-(((benzyloxy)carbonyl)amino)but-1-en-1-yl)-1*H*-indole-1-carboxylate (SI-68)



Yield: 75.1 mg (69%) starting from 73.8 mg (0.26 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 98.0–99.7 °C; $[\alpha]_D^{25}$ -32.0 (*c* 0.49, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 3.5 Hz, 1H), 7.51 (s, 1H), 7.40 – 7.30 (m, 6H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.53 (d, *J* = 3.5 Hz, 1H), 6.16 (dd, *J* = 15.8, 5.6 Hz, 1H), 5.13 (s, 2H), 4.86 (s, 1H), 4.50 (s, 1H), 1.67 (s, 9H), 1.36 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 149.7, 136.6, 134.8, 131.4, 130.9, 129.93, 129.88, 128.5, 128.2, 128.1, 126.4, 122.7, 119.0, 115.2, 107.4, 83.7, 66.7, 48.5, 28.2, 21.2; HRMS (ESI-TOF) *m/z* calcd for $C_{25}H_{28}N_2O_4Na$ [(M+Na)$^+$] 443.1947; found: 443.1938; FTIR (film) ν: 3331, 3032, 2978, 1728, 1711, 1609, 1528, 1452, 1329, 1246, 1159, 1090, 1049 cm^{-1}.

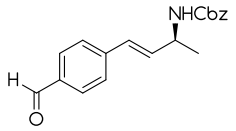
Benzyl (*S*,*E*)-(4-(benzo[*b*]thiophen-3-yl)but-3-en-2-yl)carbamate (SI-69)



Yield: 79.5 mg (92%) starting from 72.8 mg (0.26 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-10% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 88.5–90.2 °C; $[\alpha]_D^{25}$ -33.2 (*c* 0.92, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.43 – 7.31 (m, 8H), 6.79 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 15.9, 5.5 Hz, 1H),

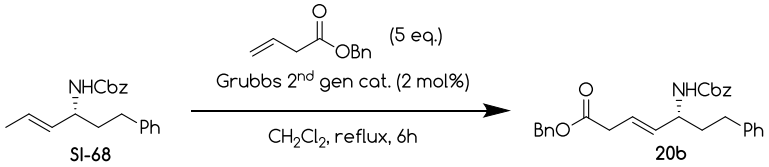
5.16 (s, 2H), 4.94 (s, 1H), 4.55 (s, 1H), 1.39 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 140.5, 137.7, 136.6, 133.3, 133.0, 128.6, 128.2 (×2), 124.5, 124.3, 122.9, 122.1, 122.0, 121.9, 66.8, 48.7, 21.1; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{19}NO_2NaS$ [$(M+Na)^+$] 360.1034; found: 360.1035; FTIR (film) ν: 3321, 3032, 2970, 1694, 1530, 1450, 1329, 1246, 1051, 731 cm^{-1}.

Benzyl (*S*,*E*)-(4-(4-formylphenyl)but-3-en-2-yl)carbamate (SI-70)



Yield: 70 mg (75%) starting from 85 mg (0.3 mmol) of allylamine **SI-51**; purification: flash column chromatography on silica gel (12 g column cartridge, 0–15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 96–98 °C; $[\alpha]_D^{25}$ −42 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.24 (m, 7H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 15.9, 5.6 Hz, 1H), 5.13 – 5.04 (m, 2H), 4.94 – 4.82 (m, 1H), 4.52 – 4.40 (m, 1H), 1.31 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 155.4, 141.2, 136.3, 135.9, 134.1, 128.5, 128.3, 127.9, 126.3, 66.6, 48.2, 20.7.; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{23}NO_4Na$ [$(M+MeOH+Na)^+$] 364.1525; found: 364.1520; FTIR (film) ν: 3332, 3031, 2975, 1701, 1682, 1607, 1525, 1456, 1362, 1271, 1241, 1052 cm^{-1}.

2.5. Synthesis of compound 20b (cross-metathesis)

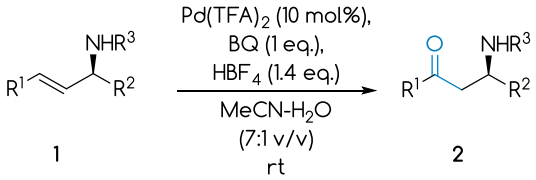


A Young's flask was charged with allylamine **SI-68** (91.4 mg, 0.30 mmol), benzyl but-3-enoate (260 mg, 1.48 mmol) and anhydr. CH_2Cl_2 (1 mL). In a separate flask, Grubbs 2nd generation metathesis catalyst (5.0 mg, 5.9 µmol) was dissolved in 0.5 mL of anhydr. CH_2Cl_2 and transferred to the reaction mixture, which was degassed by flushing with argon stream for 5 min. Next, the Young's flask was sealed and the reaction mixture was stirred at 40 °C for 6h. Solvent was removed and the crude residue was purified using column chromatography (10% AcOEt in hexanes) to give 78.2 mg (0.18 mmol, 60% yield) of **20b** as a colourless oil. $[\alpha]_D^{25}$ +1.1 (*c* 0.60, $CHCl_3$); ^{1}H NMR (400 MHz,

$CDCl_3$) 7.38 – 7.12 (m, 15H), 5.76 (dt, *J* = 15.3, 6.8 Hz, 1H), 5.54 (dd, *J* = 15.3, 5.7 Hz, 1H), 5.16 – 5.06 (m, 4H), 4.72 (s, 1H), 4.26- 4.17 (m, 1H), 3.12 (d, *J* = 6.8 Hz, 2H), 2.65 (t, *J* = 7.9 Hz, 2H), 1.91 – 1.79 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 155.7, 141.3, 136.5, 135.8, 134.4, 128.58, 128.53, 128.44, 128.37, 128.30, 128.24, 128.11, 128.09, 126.0, 123.0, 66.8, 66.5, 52.4, 37.6, 36.9, 32.1; HRMS (ESI-TOF) *m/z* calcd for $C_{28}H_{29}NO_4Na$ [(M+Na)$^+$] 466.1994; found: 466.1992; FTIR (film) ν: 3334, 3033, 2938, 1730, 1527, 1455, 1236, 1178, 1045 cm^{-1}.

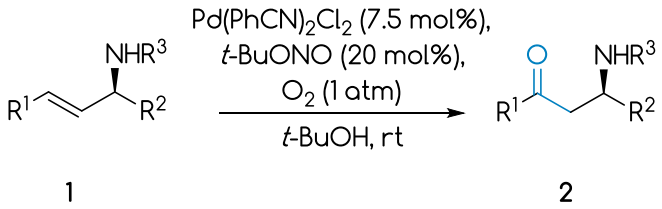
3. Wacker oxidation of internal allylamine derivatives

General Procedure A (GPA):



A round-bottom flask was charged with allylamine (0.20 mmol), $Pd(TFA)_2$ (6.6 mg, 0.02 mmol) and benzoquinone (21.6 mg, 0.20 mmol), followed by addition of MeCN (1 mL), H_2O (0.14 mL, 7:1 *v*/*v*) and HBF_4 (48% solution in water, 0.28 mmol, 36 µL). The reaction was stirred at rt until TLC analysis indicated complete conversion of allylamine. Next, $CHCl_3$ and sat. aqueous NaCl were added and layers were separated. Aqueous layer was washed with $CHCl_3$ (***Note***: An use of $CHCl_3$ allowed to remove ~90% of hydroquinone formed within reaction due to its low solubility in this solvent. This is important since hydroquinone was difficult or impossible to separate from β-amino ketones chromatographically in numerous cases). The combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The crude residue was purified chromatographically to provide amino ketones.

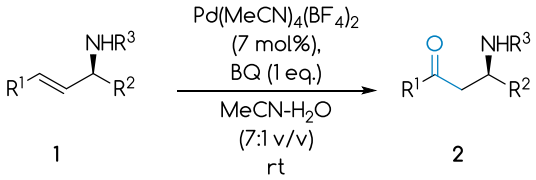
General procedure B (GPB):



$Pd(PhCN)_2Cl_2$ (14.4 mg, 0.0375 mmol, 7.5 mol%) was weighed directly into a dry Schlenk tube and dried under vacuum for 15 min. Next, under an

atmosphere of oxygen (1 atm, balloon), *t*-BuOH (2 mL) and *t*-BuONO (10.2 mg, 0.1 mmol , 20 mol%) were added followed by the addition of allylamine (0.5 mmol). The reaction mixture was stirred at 25 °C and monitored by TLC. After completion, the reaction was quenched by addition of water (5 mL) and extracted three times with CH_2Cl_2. The combined organic layers were subsequently washed with brine and dried over Na_2SO_4. The organic solvent was removed under reduced pressure and the crude product was purified by flash column chromatography on silica gel.

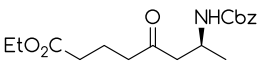
General Procedure C (GPC):



1 2

A round-bottom flask was charged with allylamine (0.20 mmol), $Pd(MeCN)_4(BF_4)_2$ (6.2 mg, 0.014 mmol) and benzoquinone (21.6 mg, 0.20 mmol), followed by addition of MeCN (1 mL), H_2O (0.14 mL, 7:1 *v*/*v*). The reaction was stirred at rt until TLC analysis indicated complete conversion of allylamine. The procedure for the work-up and an isolation of the product was the same as for GPA.

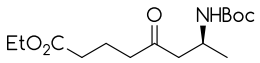
Ethyl (*S*)-7-(((benzyloxy)carbonyl)amino)-5-oxooctanoate (2)



Method A. Reaction time: 30 min. Yield: 61.3 mg (91%) starting from 64.2 mg (0.20 mmol) of allylamine **1**; Method B: Reaction time: 96 h, Yield: 53 mg (78%) starting from 64.2 mg (0.20 mmol) of allylamine **1**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ −8.5 (*c* 0.70, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 5.18 (s, 1H), 5.07 (s, 2H), 4.14 – 4.01 (m, 3H), 2.68 (dd, *J* = 16.6, 5.0 Hz, 1H), 2.55 (dd, *J* = 16.6, 6.0 Hz, 1H), 2.45 (t, *J* = 7.0 Hz, 2H), 2.29 (t, *J* = 7.2 Hz, 2H), 1.86 (p, *J* = 7.2 Hz, 2H), 1.26 – 1.17 (m, 6H); ^{13}C

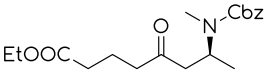
NMR (101 MHz, $CDCl_3$) δ 208.6, 173.1, 155.6, 136.6, 128.5, 128.05, 128.02, 66.6, 60.4, 48.3, 43.9, 42.2, 33.2, 20.6, 18.7, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{25}NO_5Na$ [(M+Na)$^+$] 358.1630; found: 358.1632; FTIR (film) ν: 3351, 3033, 2972, 1714, 1528, 1453, 1376, 1251, 1065 cm^{-1}.

Ethyl (*S*)-7-((*t*-butoxycarbonyl)amino)-5-oxooctanoate (4)



Method B. Reaction time: 48 h. Yield: 32.3 mg (61%) starting from 50.3 mg (0.18 mmol) of allylamine **SI-44**; Method C. Reaction time: 45 min. Yield: 45 mg (85%) starting from 50.3 mg (0.18 mmol) of allylamine **SI-44**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ -8.3 (*c* 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 4.01 (hept, *J* = 6.5 Hz, 1H), 2.65 (dd, *J* = 16.2, 5.3 Hz, 1H), 2.57 – 2.45 (m, 3H), 2.31 (t, *J* = 7.2 Hz, 2H), 1.88 (p, *J* = 7.2 Hz, 2H), 1.42 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.18 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.8, 173.1, 155.1, 79.3, 60.3, 48.7, 43.4, 42.1, 33.2, 28.4, 20.7, 18.7, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{27}NO_5Na$ [(M+Na)$^+$] 324.1787; found: 324.1791; FTIR (film) ν: 3340, 2963, 1714, 1453, 1373, 1250, 1060 cm^{-1}.

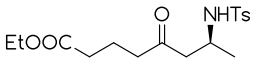
Ethyl (*S*)-7-(((benzyloxy)carbonyl)(methyl)amino)-5-oxooctanoate (5)



Method A. Reaction time: 60 min. Yield: 30.3 mg (87%) starting from 33.1 mg (0.10 mmol) of allylamine **SI-45**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –2.2 (*c* 0.72, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.10 (s, 2H), 4.56 (h, *J* = 6.9 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.80 (s, 3H), 2.75 – 2.60 (m, 1H), 2.58 – 2.37 (m, 3H), 2.30 – 2.22 (m, 2H), 1.88 – 1.76 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.19 – 1.14 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 173.1, 155.9, 136.8, 128.5, 127.9, 127.7, 66.9, 60.3, 49.0, 47.3, 41.4, 33.2, 29.5, 18.7, 18.0, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{27}NO_5Na$ [(M+Na)$^+$] 372.1787; found:

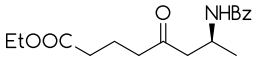
372.1788; FTIR (film) ν: 3033, 2977, 1730, 1697, 1452, 1403, 1329, 1210, 1146, 1028 cm^{-1}.

Ethyl (*S*)-7-((4-methylphenyl)sulfonamido)-5-oxooctanoate (6)



Method A. Reaction time: 30 min. Yield: 21.8 mg (45%) starting from 46.5 mg (0.14 mmol) of allylamine **SI-46**; Method B. Reaction time: 96 h. Yield: 24 mg (50%) starting from 46.5 mg (0.14 mmol) of allylamine **SI-46**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-35% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ -30.9 (*c* 0.64, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 5.10 (d, *J* = 8.2 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.69 – 3.58 (m, 1H), 2.60 (dd, *J* = 17.4, 4.7 Hz, 1H), 2.52 (dd, *J* = 17.4, 5.8 Hz, 1H), 2.42 (s, 3H), 2.40 – 2.34 (m, 2H), 2.27 (t, *J* = 7.2 Hz, 2H), 1.81 (p, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.7, 173.0, 143.4, 138.0, 129.7, 127.1, 60.4, 48.3, 46.4, 42.3, 33.1, 21.5, 21.0, 18.6, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{25}NO_5NaS$ [$(M+Na)^+$] 378.1351; found: 378.1356; FTIR (film) ν: 3279, 3063, 2979, 1729, 1713, 1599, 1410, 1377, 1332, 1161, 1093, 1025 cm^{-1}.

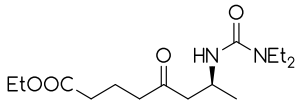
Ethyl (*S*)-7-benzamido-5-oxooctanoate (7)



Method A. Reaction time: 4 h. Yield: 33.8 mg (81%) starting from 39.8 mg (0.14 mmol) of allylamine **SI-47**; Method B. Reaction time: 4 h. Yield: 28 mg (66%) starting from 39.8 mg (0.14 mmol) of allylamine **SI-47**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-35% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 72.3–73.4 °C; $[\alpha]_D^{25}$ –17.4 (*c* 0.74, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.3 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 2H), 6.92 (d, *J* = 7.4 Hz, 1H), 4.57 – 4.43 (m, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.78 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.69 (dd, *J* = 16.8, 5.6 Hz, 1H), 2.51 (t, *J* = 7.2 Hz, 2H), 2.30 (t, *J* = 7.2 Hz, 2H), 1.88 (p, *J* = 7.2 Hz, 2H), 1.31 (d, *J* = 6.8 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.8, 173.0, 166.6, 134.6, 131.4, 128.5, 126.9, 60.4, 47.4, 42.5, 42.5, 33.2, 20.2, 18.7, 14.2; HRMS (ESI-TOF) *m/z*

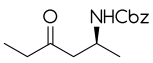
calcd for $C_{17}H_{23}NO_4Na$ [(M+Na)$^+$] 328.1525; found: 328.1534; FTIR (film) ν: 3316, 3061, 2978, 1730, 1713, 1638, 1536, 1375, 1306, 1186, 1159, 1090, 1030 cm^{-1}.

Ethyl (*S*)-7-(3,3-diethylureido)-5-oxooctanoate (8)



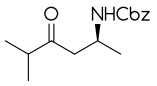
Method A. Reaction time: 30 min. Yield: 23.9 mg (59%) starting from 38.2 mg (0.13 mmol) of allylamine **SI-48**; purification: flash column chromatography on silica gel (12 g column cartridge, 15-70% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –21.7 (*c* 0.56, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.99 (d, *J* = 7.8 Hz, 1H), 4.26 – 4.17 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.22 (q, *J* = 7.1 Hz, 4H), 2.64 (t, *J* = 5.3 Hz, 2H), 2.52 – 2.45 (m, 2H), 2.30 (t, *J* = 7.3 Hz, 2H), 1.91 – 1.82 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.4, 173.1, 156.6, 60.3, 48.3, 43.3, 42.4, 41.1, 33.2, 20.9, 18.7, 14.2, 13.8; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{28}N_2O_4Na$ [(M+Na)$^+$] 323.1947; found: 323.1950; FTIR (film) ν: 3415, 3349, 2975, 1732, 1713, 1626, 1520, 1453, 1376, 1271, 1190, 1083, 1035 cm^{-1}.

Benzyl (*S*)-(4-oxohexan-2-yl)carbamate (12a)



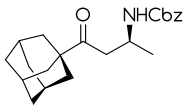
Method A. Reaction time: 30 min. Yield: 34.5 mg (85%) starting from 38.0 mg (0.16 mmol) of allylamine **SI-28**; Method B. Reaction time: 90 h. Yield: 30 mg (78%) starting from 38.0 mg (0.16 mmol) of allylamine **SI-28**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 72.0–73.2 °C; $[\alpha]_D^{25}$ -13.1 (*c* 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 5H), 5.22 (s, 1H), 5.07 (s, 2H), 4.12 – 4.01 (m, 1H), 2.69 (dd, *J* = 16.6, 4.8 Hz, 1H), 2.56 (dd, *J* = 16.6, 6.0 Hz, 1H), 2.44 – 2.35 (m, 2H), 1.21 (d, *J* = 6.8 Hz, 3H), 1.02 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.1, 155.6, 136.6, 128.5, 128.04, 128.00, 66.5, 47.8, 43.9, 36.6, 20.5, 7.6; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{19}NO_3Na$ [(M+Na)$^+$] 272.1263; found: 272.1266; FTIR (film) ν: 3330, 3033, 2974, 1712, 1681, 1535, 1455, 1250, 1086, 1059 cm^{-1}.

Benzyl (*S*)-(5-methyl-4-oxohexan-2-yl)carbamate (12b)



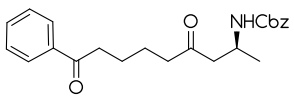
Synthesized according to General Procedure A. Reaction time: 24 h. Yield: 37.3 mg (76%) starting from 46.0 mg (0.19 mmol) of allylamine **SI-29**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 74.8–76.1 °C; $[\alpha]_D^{25}$ -13.4 (*c* 0.55, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 5H), 5.28 (s, 1H), 5.07 (s, 2H), 4.12 – 4.01 (m, 1H), 2.76 (dd, *J* = 16.9, 4.2 Hz, 1H), 2.63 – 2.51 (m, 2H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.06 (2x d, *J* = 6.9, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.4, 155.6, 136.6, 128.5, 128.02, 128.00, 66.5, 45.6, 43.9, 41.3, 20.4, 17.94, 17.90; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{21}NO_3Na$ $[(M+Na)^+]$ 286.1419; found: 286.1422; FTIR (film) ν: 3333, 3033, 2973, 1712, 1682, 1544, 1456, 1250, 1055 cm^{-1}.

Benzyl ((*S*)-4-(adamantan-1-yl)-4-oxobutan-2-yl)carbamate (12c)



Method A. Reaction time: 120 h. Yield: 29.6 mg (56%) starting from 50.8 mg (0.15 mmol) of allylamine **SI-30**; purification: flash column chromatography on silica gel (12 g column cartridge, 3-15% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ -8.0 (*c* 1,16, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 5.35 (s, 1H), 5.08 (s, 2H), 4.11 – 4.00 (m, 1H), 2.81 (d, *J* = 17.4 Hz, 1H), 2.56 (dd, *J* = 17.4, 5.9 Hz, 1H), 2.03 (s, 3H), 1.78 – 1.54 (m, 12H), 1.19 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.6, 155.6, 136.7, 128.5, 128.0 (×2), 66.4, 46.6, 43.9, 41.2, 37.9, 36.5, 27.9, 20.3; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{29}NO_3Na$ $[(M+Na)^+]$ 378.2045; found: 378.2041; FTIR (film) ν: 3332, 3033, 2970, 1701, 1535, 1452, 1250, 1060 cm^{-1}.

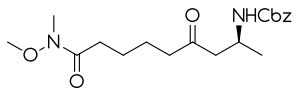
Benzyl (*S*)-(4,9-dioxo-9-phenylnonan-2-yl)carbamate (12e)



Method A. Reaction time: 30 min. Yield: 43.8 mg (86%) starting from 48.7 mg (0.13 mmol) of allylamine **SI-31**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min,

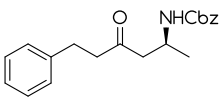
30 min); white solid, m.p. 98.0–99.5 °C; $[\alpha]_D^{25}$ -6.3 (*c* 0.80, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.28 (m, 5H), 5.21 (s, 1H), 5.07 (s, 2H), 4.15 – 4.00 (m, 1H), 2.96 (t, *J* = 6.7 Hz, 2H), 2.70 (dd, *J* = 16.5, 4.1 Hz, 1H), 2.57 (dd, *J* = 16.5, 5.4 Hz, 1H), 2.44 (t, *J* = 6.3 Hz, 2H), 1.76 – 1.59 (m, 4H), 1.21 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3, 199.8, 155.6, 137.0, 136.6, 133.0, 128.6, 128.5, 128.04, 128.0 (×2), 66.5, 48.2, 43.9, 43.2, 38.2, 23.6, 23.2, 20.6; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{27}NO_4Na$ [$(M+Na)^+$] 404.1838; found: 404.1838; FTIR (film) ν: 3331, 3032, 2931, 1715, 1687, 1597, 1523, 1451, 1239, 1141, 1059 cm^{-1}.

Benzyl (*S*)-(9-(methoxy(methyl)amino)-4,9-dioxononan-2-yl)carbamate (12f)



Method A. Reaction time: 30 min. Yield: 40.3 mg (78%) starting from 49.6 mg (0.14 mmol) of allylamine **SI-32**; purification: flash column chromatography on silica gel (12 g column cartridge, 15-65% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 56.5–58.1 °C; $[\alpha]_D^{25}$ -7.4 (*c* 0.78, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 5H), 5.22 (s, 1H), 5.07 (s, 2H), 4.11 – 3.99 (m, 1H), 3.66 (s, 3H), 3.16 (s, 3H), 2.69 (d, *J* = 16.4 Hz, 1H), 2.56 (dd, *J* = 16.4, 5.1 Hz, 1H), 2.45 – 2.31 (m, 4H), 1.64 – 1.50 (m, 4H), 1.21 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3, 174.2, 155.6, 136.6, 128.5, 128.0 (×2), 66.5, 61.2, 48.1, 43.8, 43.2, 32.2, 31.6, 24.0, 23.3, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{28}N_2O_5Na$ [$(M+Na)^+$] 387.1896; found: 387.1898; FTIR (film) ν: 3335, 3033, 2934, 1717, 1527, 1454, 1255, 1222, 1110, 1055 cm^{-1}.

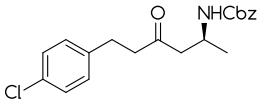
Benzyl (*S*)-(4-oxo-6-phenylhexan-2-yl)carbamate (12g)



Method A. Reaction time: 30 min. Yield: 36.0 mg (78%) starting from 43.9 mg (0.14 mmol) of allylamine **SI-33**; Method B. Reaction time: 96 h. Yield: 33.0 mg (72%) starting from 43.9 mg (0.14 mmol) of allylamine **SI-33**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20%

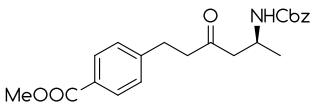
AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 97.8–99.4 °C; $[\alpha]_D^{25}$ -5.7 (*c* 1.20, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 7H), 7.21 – 7.14 (m, 3H), 5.19 – 5.06 (m, 3H), 4.12 – 4.01 (m, 1H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.75 – 2.65 (m, 3H), 2.54 (dd, *J* = 16.6, 5.9 Hz, 1H), 1.19 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.6, 155.6, 140.8 136.6, 128.5, 128.3(×2), 128.08, 128.03, 126.2, 66.6, 48.5, 44.8, 43.9, 29.6, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{23}NO_3Na$ $[(M+Na)^+]$ 348.1576; found: 348.1580; FTIR (film) ν: 3330, 3033, 2943, 1710, 1528, 1455, 1357, 1251, 1057 cm^{-1}.

Benzyl (*S*)-(6-(4-chlorophenyl)-4-oxohexan-2-yl)carbamate (12h)



Method A. Reaction time: 24 h. Yield: 43.4 mg (67%) starting from 61.7 mg (0.18 mmol) of allylamine **SI-34**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 96.4–97.8 °C; $[\alpha]_D^{25}$ -2.1 (*c* 0.68, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.17 – 5.03 (m, 3H), 4.15- 4.03 (m, 1H), 2.83 (t, *J* = 7.1 Hz, 2H), 2.73 - 2.63 (m, 3H), 2.54 (dd, *J* = 16.4, 5.5 Hz, 1H), 1.19 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.2, 155.6, 139.3, 136.5, 131.9, 129.7, 128.6, 128.5, 128.1, 128.0, 66.6, 48.6, 44.5, 43.9, 28.8, 20.6; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{22}NO_3NaCl$ $[(M+Na)^+]$ 382.1186; found: 382.1181; FTIR (film) ν: 3336, 3033, 2972, 1709, 1512, 1455, 1250, 1218, 1092, 1057 cm^{-1}.

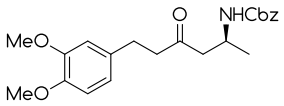
Methyl (*S*)-4-(5-(((benzyloxy)carbonyl)amino)-3-oxohexyl)benzoate (12i)



Method A. Reaction time: 30 min. Yield: 34.2 mg (77%) starting from 42.8 mg (0.12 mmol) of allylamine **SI-35**; Method B. Reaction time: 100 h min. Yield: 31.5 mg (71%) starting from 42.8 mg (0.12 mmol) of allylamine **SI-35**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p.

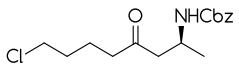
100.2–101.7 °C; $[\alpha]_D^{25}$ -2.9 (*c* 0.56, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.36 – 7.28 (m, 5H), 7.22 (d, *J* = 7.9 Hz, 2H), 5.18 – 4.97 (m, 3H), 4.12 – 4.01 (m, 1H), 3.89 (s, 3H), 2.92 (t, *J* = 7.0 Hz, 2H), 2.79 – 2.64 (m, 3H), 2.54 (dd, *J* = 16.4, 5.3 Hz, 1H), 1.19 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 167.0, 155.5, 146.3, 136.5, 129.8, 128.5, 128.4, 128.2, 128.1, 128.0, 66.6, 52.0, 48.6, 44.2, 43.9, 29.4, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{25}NO_5Na$ $[(M+Na)^+]$ 406.1630; found: 406.1624; FTIR (film) ν: 3340, 3033, 2951, 1715, 1609, 1524, 1454, 1265, 1235, 1111, 1059 cm^{-1}.

Benzyl (*S*)-(6-(3,4-dimethoxyphenyl)-4-oxohexan-2-yl)carbamate (12j)



Method A. Reaction time: 30 min. Yield: 47.4 mg (59%) starting from 77.4 mg (0.21 mmol) of allylamine **SI-36**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 99.8–101.6 °C; $[\alpha]_D^{25}$ -6.7 (*c* 0.79, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.36 – 7.28 (m, 5H), 7.22 (d, *J* = 7.9 Hz, 2H), 5.18 – 4.97 (m, 3H), 4.12 – 4.01 (m, 1H), 3.89 (s, 3H), 2.92 (t, *J* = 7.0 Hz, 2H), 2.79 – 2.64 (m, 3H), 2.54 (dd, *J* = 16.4, 5.3 Hz, 1H), 1.19 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 167.0, 155.5, 146.3, 136.5, 129.8, 128.5, 128.4, 128.2, 128.1, 128.0, 66.6, 52.0, 48.6, 44.2, 43.9, 29.4, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{27}NO_5Na$ $[(M+Na)^+]$ 408.1787; found: 408.1789; FTIR (film) ν: 3349, 3033, 2935, 1712, 1590, 1516, 1453, 1258, 1239, 1154, 1057, 1028 cm^{-1}.

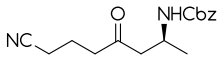
Benzyl (*S*)-(8-chloro-4-oxooctan-2-yl)carbamate (12k)



Method A. Reaction time: 30 min. Yield: 49.3 mg (85%) starting from 54.8 mg (0.19 mmol) of allylamine **SI-37**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); white waxy solid; $[\alpha]_D^{25}$ -7.9 (*c* 1.21, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.28 (m, 5H), 5.18 (s, 1H), 5.07 (s, 2H), 4.13 – 4.01 (m, 1H), 3.50 (t, *J* = 5.8 Hz, 2H), 2.69 (dd, *J* = 16.1, 5.5 Hz, 1H), 2.56 (dd, *J* = 16.1, 5.1 Hz, 1H), 2.45 – 2.39 (m, 2H),

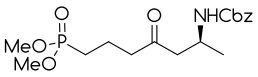
1.77 – 1.64 (m, 4H), 1.21 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.9, 155.6, 136.5, 128.5, 128.09, 128.03, 66.6, 48.3, 44.6, 43.9, 42.3, 31.8, 20.8, 20.6; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{22}NO_3NaCl$ [(M+Na)$^+$] 334.1186; found: 334.1182; FTIR (film) ν: 3335, 3033, 2957, 1708, 1513, 1455, 1250, 1217, 1068 cm^{-1}.

Benzyl (*S*)-(7-cyano-4-oxoheptan-2-yl)carbamate (12l)



Method A. Reaction time: 30 min. Yield: 34.8 mg (87%) starting from 38 mg (0.14 mmol) of allylamine **SI-38**; Method B. Reaction time: 90 h. Yield: 32 mg (81%) starting from 38 mg (0.14 mmol) of allylamine **SI-38**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 59.7 – 61.0 °C; $[\alpha]_D^{25}$ -10.5 (*c* 0.61, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 5H), 5.14 – 4.97 (m, 3H), 4.15 – 4.02 (m, 1H), 2.73 – 2.49 (m, 4H), 2.37 (t, *J* = 7.0 Hz, 2H), 1.88 (p, *J* = 7.0 Hz, 2H), 1.22 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.4, 155.6, 136.5, 128.5, 128.13, 128.06, 119.2, 66.7, 48.8, 43.9, 40.9, 20.7, 19.1, 16.4; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{20}N_2O_3Na$ [(M+Na)$^+$] 311.1372; found: 311.1374; FTIR (film) ν: 3333, 3033, 2971, 2246, 1710, 1529, 1456, 1357, 1250, 1062 cm^{-1}.

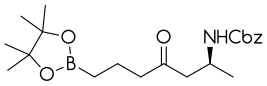
Benzyl (*S*)-(7-(dimethoxyphosphoryl)-4-oxoheptan-2-yl)carbamate (12m)



Method A. Reaction time: 24 h. Yield: 24.7 mg (38%) starting from 62.2 mg (0.18 mmol) of allylamine **SI-39**; purification: flash column chromatography on silica gel (12 g column cartridge, 0-5% MeOH in AcOEt, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ -7.9 (*c* 1.42, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 5.24 (s, 1H), 5.06 (s, 2H), 4.13 - 4.01 (m, 1H), 3.72 (d, *J* = 3.2 Hz, 3H), 3.69 (d, *J* = 3.2 Hz, 3H), 2.68 (dd, *J* = 16.5, 5.0 Hz, 1H), 2.60 – 2.47 (m, 3H), 1.90 – 1.67 (m, 4H), 1.20 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.29, 155.58, 136.54, 128.48, 128.06, 128.02, 66.55, 52.33 and 52.27 (d, *J* = 6.5 Hz) , 48.40, 43.85, 42.92 and 42.79 (d, *J* = 13.4 Hz), 24.22 and 22.82 (d, *J* = 141.1 Hz), 20.56, 16.37 and 16.32 (d, *J* = 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.91; HRMS (ESI-TOF) *m/z*

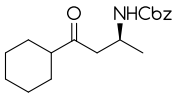
calcd for $C_{17}H_{26}NO_6NaP$ [$(M+Na)^+$] 394.1395; found: 394.1397; FTIR (film) ν: 3276, 3033, 2954, 1712, 1535, 1454, 1250, 1184, 1056, 1032, 819 cm^{-1}.

Benzyl (*S*)-(4-oxo-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-2-yl)carbamate (12n)



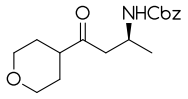
Method A. Reaction time: 30 min. Yield: 49.7 mg (77%) starting from 62.0 mg (0.17 mmol) of allylamine **SI-40**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ -8.9 (*c* 0.83, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5H), 5.25 (s, 1H), 5.07 (s, 2H), 4.11 – 3.98 (m, 1H), 2.67 (dd, *J* = 16.7, 4.7 Hz, 1H), 2.54 (dd, *J* = 16.7, 6.0 Hz, 1H), 2.38 (t, *J* = 7.6 Hz, 2H), 1.66 (p, *J* = 7.6 Hz, 2H), 1.22 (s, 12H), 1.20 (d, *J* = 6.8 Hz, 3H), 0.75 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.9, 155.6, 136.6, 128.5, 128.01, 128.00, 83.1, 66.5, 47.9, 45.7, 43.9, 24.8, 20.5, 18.3 [carbon α to boron is not visible]; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.32; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{32}NO_5NaB$ [$(M+Na)^+$] 412.2271; found: 412.2280; FTIR (film) ν: 3338, 3033, 2977, 1710, 1529, 1455, 1375, 1324, 1249, 1145, 1094, 1056 cm^{-1}.

Benzyl (*S*)-(4-cyclohexyl-4-oxobutan-2-yl)carbamate (12o)



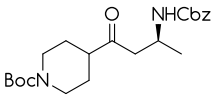
Method A. Reaction time: 24 h. Yield: 41.8 mg (78%) starting from 50.7 mg (0.18 mmol) of allylamine **SI-41**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 73.0–74.3 °C; $[\alpha]_D^{25}$ -14.2 (*c* 0.82, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 5.28 (s, 1H), 5.07 (s, 2H), 4.11 – 3.99 (m, 1H), 2.74 (dd, *J* = 16.9, 4.1 Hz, 1H), 2.57 (dd, *J* = 16.9, 5.9 Hz, 1H), 2.32 – 2.24 (m, 1H), 1.83 – 1.72 (m, 4H), 1.68 – 1.62 (m, 1H), 1.34 – 1.16 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.9, 155.6, 136.6, 128.5, 128.01, 127.99, 66.5, 51.2, 45.8, 43.9, 28.22, 28.16, 25.8, 25.6, 25.5, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{25}NO_3Na$ [$(M+Na)^+$] 326.1732; found: 326.1729; FTIR (film) ν: 3331, 3034, 2935, 1712, 1690, 1541, 1443, 1300, 1258, 1058 cm^{-1}.

Benzyl (*S*)-(4-oxo-4-(tetrahydro-2*H*-pyran-4-yl)butan-2-yl)carbamate (12p)



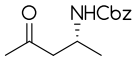
Method A. Reaction time: 24 h. Yield: 40.2 mg (80%) starting from 47.7 mg (0.17 mmol) of allylamine **SI-42**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 73.0–74.3 ºC; $[\alpha]_D^{25}$ -12.1 (*c* 0.74, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 5H), 5.23 (s, 1H), 5.06 (s, 2H), 4.11 – 4.01 (m, 1H), 4.00 – 3.91 (m, 2H), 3.42 – 3.33 (m, 2H), 2.76 (dd, *J* = 16.8, 4.1 Hz, 1H), 2.62 – 2.44 (m, 2H), 1.75 – 1.56 (m, 4H), 1.21 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.6, 155.6, 136.6, 128.5, 128.08, 128.03, 67.12, 67.11, 66.5, 47.9, 45.8, 43.8, 27.9, 27.8, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{23}NO_4Na$ [(M+Na)$^+$] 328.1525; found: 328.1523; FTIR (film) ν: 3329, 3033, 2938, 1712, 1690, 1545, 1368, 1264, 1088, 1055 cm^{-1}.

***t*-Butyl (*S*)-4-(3-(((benzyloxy)carbonyl)amino)butanoyl)piperidine-1-carboxylate (12q)**



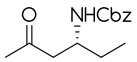
Method A. Reaction time: 24 h. Yield: 46.5 mg (74%) starting from 60.3 mg (0.16 mmol) of allylamine **SI-43**; Method B. Reaction time: 120 h. Yield: 53 mg (65%) starting from 60 mg (0.16 mmol) of allylamine **SI-43**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ -11.3 (*c* 0.74, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 5.21 (s, 1H), 5.06 (s, 2H), 4.13 – 3.99 (m, 3H), 2.80 - 2.66 (m, 3H), 2.59 (dd, *J* = 16.8, 5.9 Hz, 1H), 2.41 (t, *J* = 11.0 Hz, 1H), 1.79 - 1.68 (m, 2H), 1.52 - 1.38 (m, 11H), 1.20 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.8, 155.6, 154.6, 136.5, 128.5, 128.09, 128.03, 79.7, 66.6, 48.9, 46.1, 43.8, 43.1, 28.4, 27.3, 27.2, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{32}N_2O_5Na$ [(M+Na)$^+$] 427.2209; found: 427.2207; FTIR (film) ν: 3329, 3033, 2937, 1698, 1539, 1440, 1363, 1253, 1172, 1060 cm^{-1}.

Benzyl (*R*)-(4-oxopentan-2-yl)carbamate (13a)



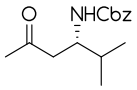
Method A. Reaction time: 30 min. Yield: 58.7 mg (89%) starting from 61.5 mg (0.28 mmol) of allylamine **SI-1**; Method B. Reaction time: 90 h. Yield: 50 mg (76%) starting from 62 mg (0.28 mmol) of allylamine **SI-1**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 56.2–57.9 °C; $[\alpha]_D^{25}$ +15.9 (*c* 0.49, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 5H), 5.21 (s, 1H), 5.07 (s, 2H), 4.07 (hept, *J* = 6.6 Hz, 1H), 2.70 (dd, *J* = 16.6, 5.2 Hz, 1H), 2.57 (dd, *J* = 16.9, 6.2 Hz, 1H), 2.12 (s, 3H), 1.21 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.3, 155.6, 136.5, 128.5, 128.1, 128.0, 66.6, 49.2, 43.8, 30.5, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{17}NO_3Na$ [$(M+Na)^+$] 258.1106; found: 258.1116; FTIR (film) ν: 3331, 3033, 2973, 1708, 1530, 1454, 1254, 1066 cm^{-1}.

Benzyl (*R*)-(5-oxohexan-3-yl)carbamate (13b)



Method A. Reaction time: 30 min. Yield: 42.7 mg (89%) starting from 45.0 mg (0.19 mmol) of allylamine **SI-2**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 86.5–88.0 °C; $[\alpha]_D^{25}$ +35.2 (*c* 0.67, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 5H), 5.19 – 5.02 (m, 3H), 3.93 – 3.80 (m, 1H), 2.73 – 2.56 (m, 2H), 2.13 (s, 3H), 1.56 (p, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.6, 156.0, 136.6, 128.45 128.04, 127.97, 66.6, 49.5, 47.4, 30.5, 27.5, 10.6; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{19}NO_3Na$ [$(M+Na)^+$] 272.1263; found: 272.1261; FTIR (film) ν: 3325, 3063, 2955, 1713, 1681, 1538, 1454, 1250, 1085 cm^{-1}.

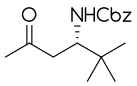
Benzyl (*S*)-(2-methyl-5-oxohexan-3-yl)carbamate (13c)



Method A. Reaction time: 30 min. Yield: 52.7 mg (84%) starting from 59.0 mg (0.24 mmol) of allylamine **SI-3**; Method B. Reaction time: 100 h. Yield: 47 mg

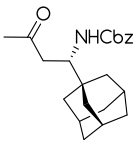
(74%) starting from 60.0 mg (0.24 mmol) of allylamine **SI-3**;purification: flash column chromatography on silica gel (12 g column cartridge, 5-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 86.2–87.6 °C; $[\alpha]_D^{25}$ +37.7 (*c* 0.52, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 5H), 5.16 – 5.02 (m, 3H), 3.85 – 3.76 (m, 1H), 2.66 – 2.53 (m, 2H), 2.14 (s, 3H), 1.93 – 1.81 (m, 1H), 0.89 (2x d, *J* = 6.6, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.7, 156.1, 136.6, 128.5, 128.03, 127.96, 66.6, 53.4, 45.7, 31.6, 30.2, 19.4, 18.5; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{21}NO_3Na$ [(M+Na)$^+$] 286.1419; found: 286.1420; FTIR (film) ν: 3323, 3063, 2959, 1712, 1682, 1540, 1456, 1253, 1037 cm^{-1}.

Benzyl (*S*)-(2,2-dimethyl-5-oxohexan-3-yl)carbamate (13d)



Method A. Reaction time: 4 h. Yield: 37.2 mg (70%) starting from 50.2 mg (0.19 mmol) of allylamine **SI-4**; purification: flash column chromatography on silica gel (12 g column cartridge, 3-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white waxy solid; $[\alpha]_D^{25}$ +52.5 (*c* 1.60, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.12 - 5.04 (m, 2H), 4.78 (d, *J* = 10.2 Hz, 1H), 4.00 (td, *J* = 10.2, 3.5 Hz, 1H), 2.68 (dd, *J* = 14.8, 3.5 Hz, 1H), 2.34 (dd, *J* = 14.8, 10.2 Hz, 1H), 2.18 (s, 3H), 0.91 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.6, 156.2, 136.5, 128.5, 128.05, 127.97, 66.8, 56.2, 45.2, 35.0, 29.6, 26.2; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{23}NO_3Na$ [(M+Na)$^+$] 300.1576; found: 300.1566; FTIR (film) ν: 3325, 3063, 2959, 1712, 1683, 1540, 1455, 1250, 1036 cm^{-1}.

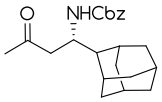
Benzyl ((*S*)-1-(adamantan-1-yl)-3-oxobutyl)carbamate (13e)



Method A. Reaction time: 8 h. Yield: 84.6 mg (77%) starting from 105.2 mg (0.31 mmol) of allylamine **SI-5**; purification: flash column chromatography on silica gel (12 g column cartridge, 3-15% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +31.5 (*c* 0.74, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 5H), 5.06 (s, 2H), 4.90 (d, *J* = 10.2 Hz, 1H), 3.82 (td, *J* = 10.2, 3.9 Hz, 1H), 2.66 (dd, *J* = 14.9, 3.9 Hz, 1H), 2.33 (dd, *J* = 15.2, 9.9 Hz, 1H), 2.15 (s, 2H), 1.98 (s,

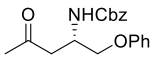
3H), 1.69 (d, *J* = 12.2 Hz, 3H), 1.59 (d, *J* = 12.3 Hz, 3H), 1.54 – 1.40 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) 208.1, 156.4, 136.6, 128.5, 128.02, 127.96, 66.7, 56.6, 43.5, 38.5, 36.8, 36.7, 29.6, 28.2; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{29}NO_3Na$ [(M+Na)$^+$] 378.2045; found: 378.2032; FTIR (film) *ν*: 3332, 3033, 2941, 1709, 1535, 1452, 1254, 1055 cm^{-1}.

Benzyl ((*S*)-1-(adamantan-2-yl)-3-oxobutyl)carbamate (13f)



Method A. Reaction time: 30 min. Yield: 70.0 mg (86%) starting from 77.9 mg (0.23 mmol) of allylamine **SI-6**; purification: flash column chromatography on silica gel (12 g column cartridge, 3-15% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +51.5 (*c* 0.51, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 5.27 (d, *J* = 8.1 Hz, 1H), 5.06 (s, 2H), 4.28 – 4.19 (m, 1H), 2.69 (d, *J* = 4.8 Hz, 2H), 2.13 (s, 3H), 2.01 (d, *J* = 13.0 Hz, 1H), 1.91 – 1.75 (m, 7H), 1.73 – 1.62 (m, 5H), 1.52 (t, *J* = 12.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) 208.4, 156.2, 136.7, 128.4, 128.0, 127.9, 66.5, 48.5, 46.9, 44.8, 38.9, 38.6, 38.0, 31.7, 31.5, 30.6, 29.8, 28.5, 27.8, 27.6; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{29}NO_3Na$ [(M+Na)$^+$] 378.2045; found: 378.2032; FTIR (film) *ν*: 3330, 3033, 2903, 2848, 1706, 1535, 1452, 1254, 1054 cm^{-1}.

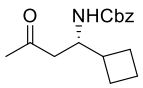
Benzyl (*S*)-(4-oxo-1-phenoxypentan-2-yl)carbamate (13g)



Method A. Reaction time: 30 min. Yield: 79.2 mg (81%) starting from 92.6 mg (0.30 mmol) of allylamine **SI-7**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 65.0–66.7 °C; $[\alpha]_D^{25}$ –17.7 (*c* 1.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.18 (m, 7H), 7.02 – 6.94 (m, 1H), 6.87 (d, *J* = 8.1 Hz, 2H), 5.56 (d, *J* = 8.8 Hz, 1H), 5.11 (s, 2H), 4.45 – 4.34 (m, 1H), 4.12 – 3.98 (m, 2H), 2.92 (dd, *J* = 17.4, 5.1 Hz, 1H), 2.84 (dd, *J* = 17.2, 6.7 Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1, 158.3, 155.8, 136.3, 129.6, 128.6, 128.2, 128.1, 121.3, 114.5, 68.3, 66.9, 47.1, 44.1, 30.5; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{21}NO_4Na$ [(M+Na)$^+$] 350.1368;

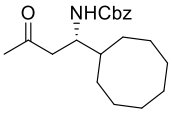
found: 350.1361; FTIR (film) ν: 3329, 3034, 2950, 1713, 1599, 1496, 1240, 1173, 1065, 1041 cm^{-1}.

Benzyl (*S*)-(1-cyclobutyl-3-oxobutyl)carbamate (13h)



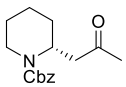
Synthesized according to General Procedure A. Reaction time: 30 min. Yield: 64.7 mg (96%) starting from 63.2 mg (0.24 mmol) of allylamine **SI-8**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 84.4–85.8 °C; $[\alpha]_D^{25}$ +34.1 (*c* 0.89, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 5H), 5.15 (d, *J* = 9.3 Hz, 1H), 5.07 (s, 2H), 3.90 (tt, *J* = 9.3, 5.5 Hz, 1H), 2.56 – 2.46 (m, 3H), 2.11 (s, 3H), 2.00 – 1.89 (m, 2H), 1.85 – 1.62 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.7, 156.2, 136.6, 128.5, 128.0, 127.9, 66.6, 52.9, 45.1, 39.0, 30.5, 25.5, 25.3, 17.3; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{21}NO_3Na$ $[(M+Na)^+]$ 298.1419; found: 298.1424; FTIR (film) ν: 3330, 3033, 2965, 1711, 1686, 1538, 1258, 1070 cm^{-1}.

Benzyl (*S*)-(1-cyclooctyl-3-oxobutyl)carbamate (13i)



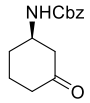
Method A. Reaction time: 30 min. Yield: 70.0 mg (84%) starting from 79.2 mg (0.25 mmol) of allylamine **SI-9**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 63.0–64.5 °C; $[\alpha]_D^{25}$ +14.2 (*c* 0.51, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 5H), 5.10 - 5.01 (s, 3H), 3.90 - 3.82 (m, 1H), 2.63 - 2.57 (m, 2H), 2.14 (s, 3H), 1.81 – 1.21 (m, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.7, 156.1, 136.6, 128.5, 128.02, 127.96, 66.6, 53.5, 45.9, 40.4, 30.2, 30.0, 28.4, 26.8, 26.48 (x2), 26.2, 25.3; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{29}NO_3Na$ $[(M+Na)^+]$ 354.2045; found: 354.2061; FTIR (film) ν: 3332, 3033, 2921, 1710, 1532, 1452, 1253, 1054 cm^{-1}.

Benzyl (*R*)-2-(2-oxopropyl)piperidine-1-carboxylate (13j)



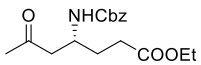
Method A. Reaction time: 30 min. Yield: 34.6 mg (77%) starting from 42.3 mg (0.16 mmol) of allylamine **SI-10**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-15% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +10.9 (*c* 1.18, $CHCl_3$) [lit.[4] $[\alpha]_D^{25}$ +10.2 (*c* 2.5, $CHCl_3$), 95% *ee*]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 5.16 – 5.06 (m, 2H), 4.84 – 4.75 (m, 1H), 4.04 (d, *J* = 12.4 Hz, 1H), 2.85 (t, *J* = 12.0 Hz, 1H), 2.73 – 2.61 (m, 2H), 2.13 (s, 3H), 1.71 – 1.38 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) 206.7, 155.3, 136.8, 128.5, 127.9, 127.8, 67.1, 47.5, 44.3, 39.8, 30.0, 28.3, 25.2, 18.8; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{21}NO_3Na$ [(M+Na)$^+$] 298.1419; found: 298.1417; FTIR (film) ν: 3033, 2939, 1696, 1421, 1356, 1261, 1167, 1051 cm^{-1}.

Benzyl (*R*)-(3-oxocyclohexyl)carbamate (13k)



Method A. Reaction time: 4 h. Yield: 27.8 mg (81%) starting from 32.3 mg (0.14 mmol) of allylamine **SI-11**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 71.0–72.8 °C; $[\alpha]_D^{25}$ +4.6 (*c* 1.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.09 (s, 2H), 4.83 (s, 1H), 4.02 – 3.91 (m, 1H), 2.74 – 2.65 (m, 1H), 2.41 – 2.31 (m, 1H), 2.32 – 2.19 (m, 2H), 2.12 - 2.04 (m, 1H), 2.03 – 1.91 (m, 1H), 1.77 – 1.61 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.5, 155.3, 136.3, 128.6, 128.22, 128.15, 66.8, 50.2, 47.9, 40.8, 31.1, 21.9; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{17}NO_3Na$ [(M+Na)$^+$] 270.1106; found: 270.1096; FTIR (film) ν: 3324, 3033, 2950, 1710, 1531, 1454, 1336, 1270, 1246, 1218, 1046 cm^{-1}.

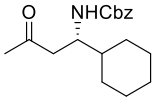
Ethyl (*R*)-4-(((benzyloxy)carbonyl)amino)-6-oxoheptanoate (13l)



Method A. Reaction time: 30 min. Yield: 60.7 mg (84%) starting from 68.7 mg (0.22 mmol) of allylamine **SI-12**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 100.2–101.3 °C; $[\alpha]_D^{25}$ +30.3 (*c* 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.27 (m, 5H), 5.32 (d, *J* = 7.0 Hz, 1H), 5.05 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.96 (dt, *J* = 14.0, 7.2 Hz, 1H), 2.76 – 2.59 (m, 2H), 2.35 (t, *J* = 7.3

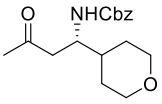
Hz, 2H), 2.11 (s, 3H), 1.93 – 1.77 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 173.2, 155.9, 136.5, 128.5, 128.1, 128.0, 66.6, 60.5, 47.8, 47.7, 31.2, 30.4, 29.3, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{23}NO_5Na$ [(M+Na)$^+$] 344.1474; found: 344.1467; FTIR (film) ν: 3309, 3068, 2958, 1720, 1692, 1546, 1453, 1377, 1267, 1191, 1065 cm^{-1}.

Benzyl (*S*)-(1-cyclohexyl-3-oxobutyl)carbamate (13m)



Method A. Reaction time: 30 min. Yield: 70.6 mg (95%) starting from 70.2 mg (0.24 mmol) of allylamine **SI-13**; Method B. Reaction time: 96 h. Yield: 65 mg (87%) starting from 70 mg (0.24 mmol) of allylamine **SI-13**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 111.0–112.4 °C; $[\alpha]_D^{25}$ +28.3 (*c* 0.57, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 5H), 5.18 (d, *J* = 8.7 Hz, 1H), 5.06 (s, 2H), 3.83 – 3.73 (m, 1H), 2.73 – 2.55 (m, 2H), 2.13 (s, 3H), 1.83 – 1.68 (m, 3H), 1.67 – 1.42 (m, 3H), 1.31 – 1.06 (m, 3H), 1.01 – 0.81 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 156.1, 136.6, 128.5, 128.01, 127.95, 66.6, 52.8, 45.4, 41.2, 30.2, 30.0, 29.1, 26.2, 26.0, 25.9; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{25}NO_3Na$ [(M+Na)$^+$] 326.1732; found: 326.1723; FTIR (film) ν: 3316, 3065, 2917, 1712, 1690, 1542, 1443, 1302, 1258, 1057 cm^{-1}.

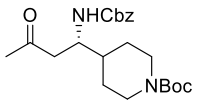
Benzyl (*S*)-(3-oxo-1-(tetrahydro-2H-pyran-4-yl)butyl)carbamate (13n)



Method A. Reaction time: 30 min. Yield: 40.3 mg (86%) starting from 44.4 mg (0.15 mmol) of allylamine **SI-14**; Method B. Reaction time: 96 h. Yield: 40 mg (84%) starting from 45 mg (0.15 mmol) of allylamine **SI-14**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 102.8–104.5 °C; $[\alpha]_D^{25}$ +25.8 (*c* 0.70, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 5H), 5.27 (d, *J* = 9.6 Hz, 1H), 5.06 (s, 2H), 3.95 (dt, *J* = 10.9, 5.0 Hz, 2H), 3.80 – 3.70 (m, 1H), 3.37 – 3.26 (m, 2H), 2.76 – 2.59 (m, 2H), 2.13 (s, 3H), 1.86 – 1.74 (m, 1H), 1.64 (d, *J* =

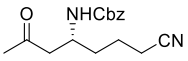
13.4 Hz, 1H), 1.44 (d, *J* = 13.0 Hz, 1H), 1.39 – 1.22 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.6, 156.1, 136.5, 128.5, 128.1, 128.0, 67.8, 67.4, 66.7, 52.3, 44.5, 38.4, 30.4, 30.0, 29.4; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{23}NO_4Na$ [(M+Na)$^+$] 328.1525; found: 328.1523; FTIR (film) ν: 3315, 3033, 2950, 1712, 1690, 1545, 1368, 1265, 1092, 1050 cm^{-1}.

t-Butyl (*S*)-4-(1-(((benzyloxy)carbonyl)amino)-3-oxobutyl)piperidine-1-carboxylate (13o)



Method A. Reaction time: 30 min. Yield: 89.6 mg (89%) starting from 96.7 mg (0.25 mmol) of allylamine **SI-14**; Method B. Reaction time: 96 h. Yield: 85 mg (89%) starting from 97 mg (0.25 mmol) of allylamine **SI-14**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +24.9 (*c* 0.66, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 5H), 5.33 – 5.23 (m, 1H), 5.05 (s, 2H), 4.13 – 4.04 (m, 2H), 3.81 – 3.70 (m, 1H), 2.73 – 2.51 (m, 4H), 2.12 (s, 3H), 1.72 – 1.65 (m, 2H), 1.54 – 1.46 (m, 1H), 1.42 (s, 9H), 1.12 (td, *J* = 12.3, 4.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 156.1, 154.6, 136.5, 128.5, 128.1, 128.0, 79.4, 66.7, 52.1, 44.8, 43.6, 39.5, 30.3, 29.1, 28.4; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{32}N_2O_5Na$ [(M+Na)$^+$] 427.2209; found: 427.2213; FTIR (film) ν: 3323, 3033, 2937, 1693, 1536, 1425, 1365, 1253, 1167, 1053 cm^{-1}.

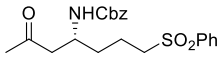
Benzyl (*R*)-(1-cyano-6-oxoheptan-4-yl)carbamate (13p)



Method A. Reaction time: 30 min. Yield: 72.1 mg (75%) starting from 90.9 mg (0.33 mmol) of allylamine **SI-16**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 54.6–56.1 °C; $[\alpha]_D^{25}$ +29.6 (*c* 0.78, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 5H), 5.35 (d, *J* = 8.4 Hz, 1H), 5.05 (s, 2H), 3.93 (m, 1H), 2.65 (m, 2H), 2.33 (t, *J* = 5.5 Hz, 2H), 2.11 (s, 3H), 1.65 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.3, 156.0, 136.4, 128.5, 128.2, 128.0, 119.4, 66.7, 47.7, 47.0, 33.4, 30.5, 22.3, 16.7;

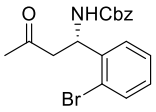
HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{20}N_2O_3Na$ [(M+Na)$^+$] 311.1372; found: 311.1381; FTIR (film) ν: 3333, 3033, 2952, 2246, 1712, 1530, 1454, 1357, 1254, 1066 cm^{-1}.

Benzyl (*R*)-(6-oxo-1-(phenylsulfonyl)heptan-4-yl)carbamate (13q)



Method A. Reaction time: 30 min. Yield: 74.9 mg (75%) starting from 95.9 mg (0.25 mmol) of allylamine **SI-17**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 76.2–77.5 °C; $[\alpha]_D^{25}$ +27.5 (*c* 0.61, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.38 – 7.25 (m, 5H), 5.40 – 5.24 (m, 1H), 5.02 (s, 2H), 3.94 – 3.82 (m, 1H), 3.19 – 2.98 (m, 2H), 2.71 – 2.56 (m, 2H), 2.08 (s, 3H), 1.87 – 1.53 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 155.9, 139.1, 136.4, 133.7, 129.3, 128.5, 128.1, 127.99, 127.96, 66.7, 55.5, 47.5, 47.1, 32.8, 30.5, 19.6; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{25}NO_5NaS$ [(M+Na)$^+$] 426.1351; found: 426.1347; FTIR (film) ν: 3348, 3063, 2952, 1712, 1529, 1447, 1358, 1300, 1247, 1146, 1086, 1060 cm^{-1}.

Benzyl (*S*)-(1-(2-bromophenyl)-3-oxobutyl)carbamate (13r)

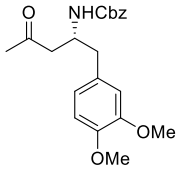


Method A. Reaction time: 8 h. Yield: 388.5 mg (79%) starting from 470.0 mg (1.31 mmol) of allylamine **SI-18**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-15% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 96.5–98.0 °C; $[\alpha]_D^{25}$ –102.3 (*c* 0.87, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.24 (m, 7H), 7.12 (td, *J* = 7.9, 1.5 Hz, 1H), 6.06 (s, 1H), 5.47 – 5.41 (m, 1H), 5.12 – 4.98 (m, 2H), 3.10 – 2.91 (m, 2H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1, 155.5, 140.0, 136.3, 133.2, 129.0, 128.5(x2), 128.11, 128.07, 127.7, 122.5, 66.9, 51.5, 47.0, 30.5; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{18}NO_3NaBr$ [(M+Na)$^+$] 398.0368; found: 398.0371; FTIR (film) ν: 3332, 3033, 2945, 1695, 1542, 1444, 1302, 1255, 1057 cm^{-1}.

Compound 13s

Method A. Reaction time: 30 min. Yield: 61.0 mg (53%) starting from 110.3 mg (0.25 mmol) of allylamine **SI-19**; Method C. Reaction time: 120 h. Yield: 88 mg (53%) starting from 111 mg (0.25 mmol) of allylamine **SI-19**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 98.4–100.8 °C; $[\alpha]_D^{25}$ +12.9 (*c* 0.89, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.10 (m, 10H), 5.37 (s, 1H), 5.05 (s, 2H), 4.54 (s, 1H), 3.95 (s, 1H), 3.79 (s, 1H), 2.88 – 2.59 (m, 4H), 2.08 (s, 3H), 1.91 – 1.77 (m, 1H), 1.52 (m, 1H), 1.38 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.4, 155.8, 155.6, 138.0, 136.6, 129.4, 128.5, 128.4, 128.02, 127.96, 126.4, 79.3, 66.5, 49.3, 47.3, 45.3, 41.4, 38.2, 30.5, 28.4; HRMS (ESI-TOF) *m/z* calcd for $C_{26}H_{34}N_2O_5Na$ [(M+Na)$^+$] 477.2365; found: 477.2364; FTIR (film) ν: 3347, 3030, 2975, 1709, 1527, 1453, 1365, 1251, 1171, 1064 cm^{-1}.

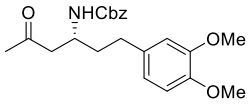
Benzyl (*R*)-(1-(3,4-dimethoxyphenyl)-4-oxopentan-2-yl)carbamate (13t)



Method A. Reaction time: 30 min. Yield: 38.0 mg (33%) starting from 108.9 mg (0.31 mmol) of allylamine **SI-20**; Method B. Reaction time: 90 h. Yield: 56 mg (50%) starting from 110 mg (0.31 mmol) of allylamine **SI-20**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 95.6–97.0 °C; $[\alpha]_D^{25}$ +25.6 (*c* 0.82, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.65 (m, 2H), 5.30 (s, 1H), 5.06 (s, 2H), 4.22 – 4.09 (m, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.89 (t, *J* = 13.5, 6.9 Hz, 1H), 2.78 (dd, *J* = 13.5, 7.9 Hz, 1H), 2.71 – 2.54 (m, 2H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 155.7, 149.0, 147.8, 136.5, 130.4, 128.49, 128.1, 128.0, 121.2, 112.3, 111.3, 66.6, 55.9, 55.8, 49.3, 45.8, 39.6, 30.5; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{25}NO_5Na$ [(M+Na)$^+$] 394.1630; found:

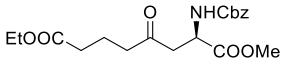
394.1617; FTIR (film) ν: 3331, 3033, 2937, 1712, 1692, 1590, 1538, 1517, 1453, 1353, 1268, 1236, 1158, 1057, 1029 cm^{-1}.

Benzyl (*R*)-(1-(3,4-dimethoxyphenyl)-5-oxohexan-3-yl)carbamate (13u)



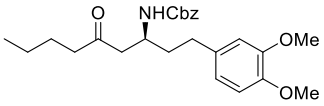
Method A. Reaction time: 30 min. Yield: 89.3 mg (89%) starting from 95.8 mg (0.26 mmol) of allylamine **SI-21**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 103.3–104.8 °C; $[\alpha]_D^{25}$ +19.8 (*c* 0.63, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 5H), 6.75 (d, *J* = 8.3 Hz, 1H), 6.71 - 6.65 (m, 2H), 5.29 (d, *J* = 7.9 Hz, 1H), 5.10 (s, 2H), 4.02 – 3.92 (m, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 2.71 – 2.50 (m, 4H), 2.08 (s, 3H), 1.94 – 1.85 (m, 1H), 1.82 – 1.70 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.6, 155.9, 148.9, 147.3, 136.6, 134.0, 128.5, 128.1, 128.0, 120.2, 111.8, 111.4, 66.6, 55.9, 55.8, 47.8(×2), 36.3, 32.2, 30.5; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{27}NO_5Na$ [(M+Na)$^+$] 408.1787; found: 408.1791; FTIR (film) ν: 3330, 3033, 2938, 1712, 1692, 1590, 1538, 1516, 1453, 1353, 1260, 1159, 1058, 1029 cm^{-1}.

8-Ethyl 1-methyl (*R*)-2-(((benzyloxy)carbonyl)amino)-4-oxooctanedioate (14a)



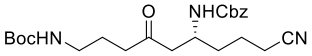
Method A. Reaction time: 120 h. Yield: 29.7 mg (52%) starting from 57.0 mg (0.15 mmol) of allylamine **SI-49**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-35% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ -9.0 (*c* 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 5.73 (d, *J* = 7.8 Hz, 1H), 5.11 (s, 2H), 4.61 – 4.51 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 3.16 (dd, *J* = 18.1, 4.0 Hz, 1H), 2.95 (dd, *J* = 18.1, 4.0 Hz, 1H), 2.54 – 2.41 (m, 2H), 2.30 (t, *J* = 7.2 Hz, 2H), 1.87 (p, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 173.0, 171.5, 156.0, 136.2, 128.5, 128.2, 128.1, 67.1, 60.4, 52.7, 49.9, 44.3, 41.5, 33.1, 18.6, 14.2; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{25}NO_7Na$ [(M+Na)$^+$] 402.1529; found: 402.1537; FTIR (film) ν: 3356, 3033, 2955, 1705, 1527, 1454, 1352, 1251, 1222, 1158, 1059 cm^{-1}.

Benzyl (*S*)-(1-(3,4-dimethoxyphenyl)-5-oxononan-3-yl)carbamate (14b)



Synthesized according to General Procedure A. Reaction time: 30 min. Yield: 55.8 mg (79%) starting from 67.9 mg (0.17 mmol) of allylamine **SI-22**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 90.3 – 92.1 °C; $[\alpha]_D^{25}$ -13.8 (*c* 1.10, $CHCl_3$); HPLC: Chiralpak IA, hexanes/*i*-PrOH 95:5, 1 ml/min, det. 235 nm) Racemate: R_t = 25.67 min, R_t = 34.03 min, Enantioenriched: R_t (minor) = 26.07 min, R_t (major) = 33.63 min, *ee* = 97% [the *ee* of substrate was 98%[1d]]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.72 - 6.65 (m, 2H), 5.30 (d, *J* = 8.0 Hz, 1H), 5.08 (s, 2H), 4.02 – 3.92 (m, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.72 - 2.50 (m, 4H), 2.41 – 2.26 (m, 2H), 1.98 – 1.84 (m, 1H), 1.82 – 1.72 (m, 1H), 1.50 (p, *J* = 7.3 Hz, 2H), 1.27 (h, *J* = 7.3 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.1, 155.9, 148.9, 147.3, 136.6, 134.0, 128.5, 128.1, 128.0, 120.2, 111.8, 111.4, 66.6, 55.9, 55.8, 47.8, 46.7, 43.1, 36.3, 32.3, 25.7, 22.2, 13.8; HRMS (ESI-TOF) *m/z* calcd for $C_{25}H_{33}NO_5Na$ $[(M+Na)^+]$ 450.2256; found: 450.2239; FTIR (film) ν: 3324, 3002, 2932, 1704, 1692, 1589, 1518, 1453, 1281, 1250, 1234, 1141, 1069, 1029 cm^{-1}.

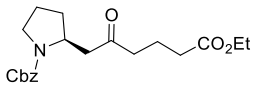
N^6-Benzyl N^6-*tert*-butyl (9-cyano-4-oxononane-1,6-diyl)(*R*)-dicarbamate (14c)



Method A. Reaction time: 30 min. Yield: 44.2 mg (84%) starting from 50.8 mg (0.12 mmol) of allylamine **SI-23**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-35% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 97.3–98.9 °C; $[\alpha]_D^{25}$ –16.7 (*c* 1.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 5.30 (s, 1H), 5.07 (s, 2H), 4.57 (s, 1H), 4.01 – 3.91 (m, 1H), 3.14 – 3.00 (m, 2H), 2.74 – 2.59 (m, 2H), 2.47 – 2.30 (m, 4H), 1.79 – 1.60 (m, 6H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.7, 156.5, 156.1, 136.4, 128.5, 128.2, 128.1, 119.3, 79.3, 66.8, 47.0, 46.8, 40.2, 39.7, 33.5, 28.4, 23.9, 22.3, 16.8; HRMS

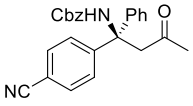
(ESI-TOF) *m/z* calcd for $C_{23}H_{33}N_3O_5Na$ [(M+Na)$^+$] 454.2318; found: 454.2297; FTIR (film) ν: 3334, 3033, 2934, 2246, 1714, 1530, 1455, 1352, 1254, 1134, 1063 cm^{-1}.

Benzyl (*S*)-2-(6-ethoxy-2,6-dioxohexyl)pyrrolidine-1-carboxylate (14d)



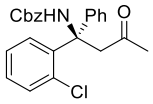
Method A. Reaction time: 30 min. Yield: 31.1 mg (82%) starting from 36.3 mg (0.11 mmol) of allylamine **SI-50**; Method B. Reaction time: 100 h. Yield: 35 mg (78%) starting from 36 mg (0.11 mmol) of allylamine **SI-50**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-35% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –15.2 (*c* 0.78, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6, 90 °C) δ 7.35 – 7.25 (m, 5H), 5.06 (s, 2H), 4.12 – 4.02 (m, 3H), 3.39 – 3.28 (m, 2H), 2.82 (dd, *J* = 15.8, 2.8 Hz, 1H), 2.54 – 2.50 (dd, *J* = 15.8, 8.9 Hz, 1H), 2.41 (t, J = 7.1 Hz, 2H), 2.23 (t, J = 7.1 Hz, 2H), 2.03 – 1.95 (m, 1H), 1.87 – 1.68 (m, 4H), 1.62 – 1.55 (m, 1H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6, 90 °C) δ 207.6, 171.8, 153.3, 136.7, 127.8, 127.1, 126.9, 65.3, 59.1, 53.1, 46.1, 45.6, 41.1, 32.4, 30.3, 22.3, 18.2, 13.5; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{27}NO_5Na$ [(M+Na)$^+$] 384.1787; found: 384.1781; FTIR (film) ν: 3033, 2965, 1710, 1455, 1352, 1261, 1132, 1062 cm^{-1}.

Benzyl (*R*)-(1-(4-cyanophenyl)-3-oxo-1-phenylbutyl)carbamate (14e)



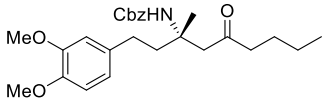
Method A. Reaction time: 8 h. Yield: 72.9 mg (75%) starting from 93.2 mg (0.24 mmol) of allylamine **SI-24**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +9.0 (*c* 0.64, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.22 (m, 10H), 6.50 (s, 1H), 5.01 (s, 2H), 3.74 (d, *J* = 16.8 Hz, 1H), 3.67 (d, *J* = 16.8 Hz, 1H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.1, 155.2, 149.5, 142.3, 136.3, 132.1, 128.8, 128.5, 128.2, 128.1, 127.7, 127.3, 126.1, 118.6, 110.9, 66.8, 62.7, 50.4, 31.7; HRMS (ESI-TOF) *m/z* calcd for $C_{25}H_{22}N_2O_3Na$ [(M+Na)$^+$] 421.1528; found: 421.1516; FTIR (film) ν: 3376, 3033, 2957, 2227, 1727, 1606, 1496, 1454, 1235, 1044 cm^{-1}.

Benzyl (*R*)-(1-(2-chlorophenyl)-3-oxo-1-phenylbutyl)carbamate (14f)



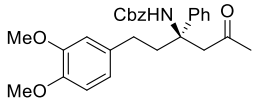
Method A. Reaction time: 24 h. Yield: 43.5 mg (56%) starting from 75.2 mg (0.19 mmol) of allylamine **SI-25**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +10.6 (*c* 1.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.36 – 7.18 (m, 13H), 6.44 (s, 1H), 5.07 (d, *J* = 12.4 Hz, 1H), 4.99 (d, *J* = 12.4 Hz, 1H), 4.14 (d, *J* = 15.5 Hz, 1H), 3.71 (d, *J* = 15.5 Hz, 1H), 1.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 154.9, 142.1, 140.1, 136.5, 132.8, 132.0, 129.7, 129.0, 128.4, 128.2, 128.0, 127.9, 127.4, 126.6, 126.5, 66.5, 63.2, 50.2, 31.9; HRMS (ESI-TOF) *m/z* calcd for $C_{24}H_{22}NO_3NaCl$ [$(M+Na)^+$] 430.1186; found: 430.1176; FTIR (film) ν: 3385, 3032, 2957, 1728, 1493, 1448, 1233, 1042 cm^{-1}.

Benzyl (*S*)-(1-(3,4-dimethoxyphenyl)-3-methyl-5-oxononan-3-yl)carbamate (14g)



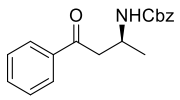
Method A. Reaction time: 8 h. Yield: 37.8 mg (78%) starting from 46.8 mg (0.11 mmol) of allylamine **SI-26**; Method A. Reaction time: 8 h. Yield: 37.8 mg (78%) starting from 46.8 mg (0.11 mmol) of allylamine **SI-26**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +15.3 (*c* 1.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 6.76 (d, *J* = 8.6 Hz, 1H), 6.71 – 6.65 (m, 2H), 5.22 (s, 1H), 5.05 (s, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 2.97 (d, *J* = 16.3 Hz, 1H), 2.75 (d, *J* = 16.3 Hz, 1H), 2.60 – 2.44 (m, 2H), 2.35 (t, *J* = 7.3 Hz, 2H), 2.14 (ddd, *J* = 13.6, 10.6, 6.3 Hz, 1H), 1.97 (ddd, *J* = 13.6, 10.5, 6.8 Hz, 1H), 1.50 (p, *J* = 7.4 Hz, 2H), 1.41 (s, 3H), 1.27 (h, *J* = 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.2, 154.9, 148.9, 147.3, 136.8, 134.5, 128.5, 128.0, 127.9, 120.2, 111.8, 111.4, 66.1, 56.0, 55.8, 54.3, 49.4, 44.4, 41.1, 29.7, 25.6, 24.8, 22.2, 13.8; HRMS (ESI-TOF) *m/z* calcd for $C_{26}H_{35}NO_5Na$ [$(M+Na)^+$] 464.2413; found: 464.2405; FTIR (film) ν: 3352, 3033, 2949, 1716, 1590, 1515, 1454, 1258, 1233, 1156, 1056, 1030 cm^{-1}.

Benzyl (*R*)-(1-(3,4-dimethoxyphenyl)-5-oxo-3-phenylhexan-3-yl)carbamate (14h)



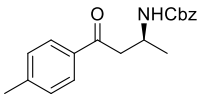
Method A. Reaction time: 8 h. Yield: 70.9 mg (84%) starting from 81.2 mg (0.18 mmol) of allylamine **SI-27**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ +16.9 (*c* 1.51, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 10H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.65 – 6.56 (m, 2H), 5.93 (s, 1H), 5.07 (s, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.36 (d, *J* = 15.7 Hz, 1H), 3.11 (d, *J* = 15.7 Hz, 1H), 2.55 – 2.46 (m, 1H), 2.43 – 2.33 (m, 3H), 1.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 154.9, 148.9, 147.3, 143.7, 136.7, 134.2, 128.6, 128.5, 128.0, 127.9, 127.1, 125.0, 120.2, 111.8, 111.3, 66.4, 59.9, 56.0, 55.8, 49.8, 41.6, 32.0, 29.7; HRMS (ESI-TOF) *m/z* calcd for $C_{28}H_{31}NO_5Na$ $[(M+Na)^+]$ 484.2100; found: 484.2110; FTIR (film) ν: 3363, 3032, 2936, 1726, 1590, 1515, 1454, 1260, 1236, 1156, 1056, 1029 cm^{-1}.

Benzyl (*S*)-(4-oxo-4-phenylbutan-2-yl)carbamate (16a)



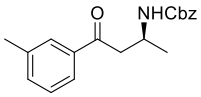
Synthesized according to General Procedure A. Reaction time: 3 h. Yield: 49.9 mg (86%) starting from 55.2 mg (0.20 mmol) of allylamine **SI-52**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 82.1–83.3 °C [lit.[5] 81–82 °C (racemate)]; $[\alpha]_D^{25}$ –2.4 (*c* 0.62, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.24 (m, 5H), 5.34 (s, 1H), 5.09 (s, 2H), 4.31 – 4.18 (m, 1H), 3.37 (dd, *J* = 16.4, 3.2 Hz, 1H), 3.05 (dd, *J* = 16.4, 6.4 Hz, 1H), 1.30 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 155.6, 136.9, 136.6, 133.3, 128.7, 128.5, 128.11, 128.05, 128.03, 66.6, 44.3, 44.2, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{19}NO_3Na$ $[(M+Na)^+]$ 320.1263; found: 320.1261; FTIR (film) ν: 3335, 3033, 2977, 1700, 1604, 1527, 1454, 1297, 1249, 1101, 1060 cm^{-1}.

Benzyl (*S*)-(4-oxo-4-(*p*-tolyl)butan-2-yl)carbamate (16b)



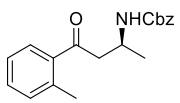
Method A. Reaction time: 3 h. Yield: 56.1 mg (84%) starting from 63.7 mg (0.22 mmol) of allylamine **SI-53**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 92.0–93.8 °C; $[\alpha]_D^{25}$ –2.2 (*c* 0.64, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 2H), 7.39 – 7.22 (m, 7H), 5.36 (s, 1H), 5.09 (s, 2H), 4.29 – 4.18 (m, 1H), 3.33 (dd, *J* = 16.3, 2.8 Hz, 1H), 3.02 (dd, *J* = 16.3, 6.4 Hz, 1H), 2.40 (s, 3H), 1.29 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 155.6, 144.2, 136.6, 134.5, 129.3, 128.5, 128.2, 128.0 (2x), 66.5, 44.5, 44.0, 21.6, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{21}NO_3Na$ $[(M+Na)^+]$ 334.1419; found: 334.1434; FTIR (film) ν: 3333, 3033, 2973, 1702, 1604, 1585, 1527, 1454, 1301, 1249, 1100, 1059 cm^{-1}.

Benzyl (*S*)-(4-oxo-4-(*m*-tolyl)butan-2-yl)carbamate (16c)



Method A. Reaction time: 3 h. Yield: 57.2 mg (86%) starting from 62.9 mg (0.21 mmol) of allylamine **SI-54**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 68.4–70.0 °C; $[\alpha]_D^{25}$ –3.4 (*c* 0.86, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.68 (m, 2H), 7.45 – 7.23 (m, 7H), 5.36 (s, 1H), 5.09 (s, 2H), 4.30 – 4.19 (m, 1H), 3.34 (dd, *J* = 16.5, 2.9 Hz, 1H), 3.05 (dd, *J* = 16.5, 6.3 Hz, 1H), 2.40 (s, 3H), 1.29 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 155.6, 138.5, 137.0, 136.6, 134.1, 128.6, 128.54, 128.49, 128.03, 128.01, 125.4, 66.5, 44.3, 44.2, 21.3, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{21}NO_3Na$ $[(M+Na)^+]$ 334.1419; found: 334.1434; FTIR (film) ν: 3333, 3033, 2973, 1695, 1604, 1585, 1527, 1454, 1300, 1249, 1103, 1059 cm^{-1}.

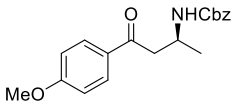
Benzyl (*S*)-(4-oxo-4-(*o*-tolyl)butan-2-yl)carbamate (16d)



Method A. Reaction time: 3 h. Yield: 51.5 mg (78%) starting from 63.0 mg (0.21 mmol) of allylamine **SI-55**; purification: flash column chromatography on

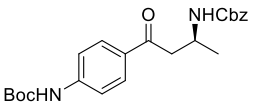
silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); white waxy solid; $[\alpha]_D^{25}$ –3.8 (*c* 0.61, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.6 Hz, 1H), 7.33 (m, 6H), 7.24 (t, *J* = 6.6 Hz, 2H), 5.32 (s, 1H), 5.09 (s, 2H), 4.26 – 4.16 (m, 1H), 3.26 (dd, *J* = 16.5, 3.5 Hz, 1H), 3.00 (dd, *J* = 16.5, 6.3 Hz, 1H), 2.48 (s, 3H), 1.29 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 155.6, 138.2, 137.7, 136.6, 132.1, 131.5, 128.6, 128.5, 128.05, 128.03, 125.8, 66.5, 47.0, 44.5, 21.3, 20.6; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{21}NO_3Na$ [(M+Na)$^+$] 334.1419; found: 334.1434; FTIR (film) ν: 3333, 3033, 2973, 1699, 1602, 1585, 1527, 1454, 1299, 1249, 1103, 1060 cm^{-1}.

Benzyl (*S*)-(4-(4-methoxyphenyl)-4-oxobutan-2-yl)carbamate (16e)



Method A. Reaction time: 3 h. Yield: 51.4 mg (82%) starting from 59.7 mg (0.19 mmol) of allylamine **SI-56**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 89.3–91.4 °C; $[\alpha]_D^{25}$ +0.8 (*c* 1.14, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.25 (m, 5H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.37 (s, 1H), 5.08 (s, 2H), 4.26 – 4.17 (m, 1H), 3.85 (s, 3H), 3.31 (d, *J* = 16.1 Hz, 1H), 2.98 (dd, *J* = 16.1, 6.6 Hz, 1H), 1.28 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 163.7, 155.7, 136.6, 130.5, 130.1, 128.5, 128.0 (×2), 113.8, 66.5, 55.5, 44.5, 43.8, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{21}NO_4Na$ [(M+Na)$^+$] 350.1368; found: 350.1364; FTIR (film) ν: 3335, 3033, 2971, 1715, 1673, 1601, 1511, 1455, 1310, 1261, 1173, 1058 cm^{-1}.

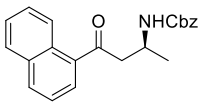
Benzyl (*S*)-(4-(4-((*t*-butoxycarbonyl)amino)phenyl)-4-oxobutan-2-yl)carbamate (16f)



Method A. Reaction time: 24 h. Yield: 65.1 mg (85%) starting from 73.5 mg (0.19 mmol) of allylamine **SI-57**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-35% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 128.1–131.6 °C; $[\alpha]_D^{25}$ –1.7 (*c* 1.87, $CHCl_3$); ^1H NMR (400 MHz,

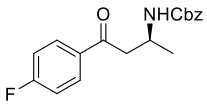
$CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.36 – 7.26 (m, 5H), 6.83 (s, 1H), 5.35 (s, 1H), 5.08 (s, 2H), 4.27 – 4.19 (m, 1H), 3.30 (d, *J* = 15.4 Hz, 1H), 3.00 (dd, *J* = 15.4, 6.5 Hz, 1H), 1.52 (s, 9H), 1.28 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 155.7, 152.1, 143.2, 136.6, 131.5, 129.6, 128.5, 128.0 (×2), 117.5, 81.3, 66.5, 44.4, 43.8, 28.3, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{28}N_2O_5Na$ [(M+Na)$^+$] 435.1896; found: 435.1898; FTIR (film) ν: 3328, 3034, 2978, 1701, 1591, 1528, 1454, 1411, 1368, 1317, 1235, 1150, 1055 cm^{-1}.

Benzyl (*S*)-(4-(naphthalen-1-yl)-4-oxobutan-2-yl)carbamate (16g)



Method A. Reaction time: 3 h. Yield: 52.8 mg (82%) starting from 61.6 mg (0.19 mmol) of allylamine **SI-58**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); white waxy solid; $[\alpha]_D^{25}$ –9.0 (*c* 0.89, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.77 (m, 2H), 7.61 – 7.45 (m, 3H), 7.37 – 7.27 (m, 5H) 5.36 (s, 1H), 5.09 (s, 2H), 4.35 – 4.24 (m, 1H), 3.44 (d, *J* = 16.3 Hz, 1H), 3.15 (dd, *J* = 16.3, 6.3 Hz, 1H), 1.34 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 155.6, 136.6, 135.6, 134.0, 133.0, 130.1, 128.51, 128.49, 128.07(×2), 128.03, 127.98, 126.5, 125.7, 124.4, 66.6, 47.6, 44.8, 20.6; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{21}NO_3Na$ [(M+Na)$^+$] 370.1419; found: 370.1422; FTIR (film) ν: 3336, 3033, 2969, 1718, 1604, 1583, 1527, 1454, 1302, 1249, 1103, 1060 cm^{-1}.

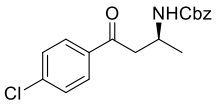
Benzyl (*S*)-(4-(4-fluorophenyl)-4-oxobutan-2-yl)carbamate (16h)



Method A. Reaction time: 3 h. Yield: 46.9 mg (82%) starting from 54.3 mg (0.18 mmol) of allylamine **SI-59**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 76.5–78.0 °C; $[\alpha]_D^{25}$ –1.5 (*c* 1.47, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.36 – 7.28 (m, 5H), 7.11 (t, *J* = 8.4 Hz, 2H), 5.28 (s, 1H), 5.08 (s, 2H), 4.28 – 4.14 (m, 1H), 3.35 (d, *J* = 16.3 Hz, 1H), 3.01 (dd, *J* = 16.3, 6.6 Hz, 1H), 1.29 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 167.1 and

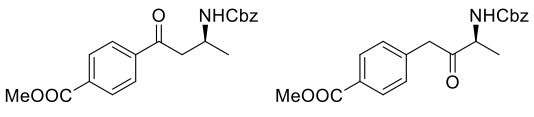
164.6 (J_{C-F} = 256.4 Hz), 155.6, 136.5, 133.35 and 133.32 (J_{C-F} = 2.9 Hz), 130.9 and 130.8 (J_{C-F} = 9.4 Hz), 128.5, 128.09, 128.04, 115.9 and 115.7 (J_{C-F} = 22.1 Hz), 66.6, 44.4, 44.2, 20.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –104.8; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{18}NO_3FNa$ [(M+Na)$^+$] 338.1168; found: 338.1163; FTIR (film) ν: 3337, 3034, 2974, 1691, 1598, 1527, 1508, 1454, 1401, 1302, 1233, 1157, 1102, 1059 cm^{-1}.

Benzyl (*S*)-(4-(4-chlorophenyl)-4-oxobutan-2-yl)carbamate (16i)



Method A. Reaction time: 24 h. Yield: 44.1 mg (72%) starting from 58.7 mg (0.19 mmol) of allylamine **SI-60**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-20% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 82.2–84.0 °C; $[\alpha]_D^{25}$ –2.1 (*c* 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.30 (m, 5H), 5.26 (s, 1H), 5.08 (s, 2H), 4.22 (hept, *J* = 6.8 Hz, 1H), 3.34 (d, *J* = 16.3 Hz, 1H), 3.01 (dd, *J* = 16.3, 6.4 Hz, 1H), 1.29 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 155.6, 139.8, 136.5, 135.2, 129.6, 129.0, 128.5, 128.10, 128.05, 66.6, 44.3(×2), 20.3; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{18}NO_3NaCl$ [(M+Na)$^+$] 354.0873; found: 354.0864; FTIR (film) ν: 3335, 3033, 2974, 1692, 1589, 1528, 1455, 1250, 1121, 1092, 1059 cm^{-1}.

Methyl (*S*)-4-(3-(((benzyloxy)carbonyl)amino)butanoyl)benzoate (β-16j) and Methyl (*S*)-4-(3-(((benzyloxy)carbonyl)amino)-2-oxobutyl)benzoate (α-16j)



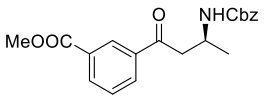
Method A (modified). Reaction time: 30 h; after 24 h additional 5% of $Pd(TFA)_2$ and 0.5 eq of BQ were added. A separable mixture of α- and β-amino ketone was obtained; Purification: flash column chromatography on silica gel (12 g column cartridge, 5-40% AcOEt in hexanes, flow 15 mL/min, 60 min);

Compound **β-16j**: Yield: 46.2 mg (74%) starting from 59.8 mg (0.18 mmol) of allylamine **SI-61**; white solid, m.p. 104.3–106.2 °C; $[\alpha]_D^{25}$ –2.5 (*c* 1.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.36 –

7.26 (m, 5H), 5.22 (s, 1H), 5.08 (s, 2H), 4.32 – 4.17 (m, 1H), 3.94 (s, 3H), 3.39 (d, *J* = 16.5 Hz, 1H), 3.09 (dd, *J* = 16.5, 6.4 Hz, 1H), 1.31 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 166.1, 155.6, 140.0, 136.5, 134.1, 129.9, 128.5, 128.10, 128.06, 128.00, 66.6, 52.4, 44.6, 44.2, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{21}NO_5Na$ [(M+Na)$^+$] 378.1317; found: 378.1311; FTIR (film) ν: 3312, 3033, 2980, 1714, 1687, 1536, 1454, 1439, 1285, 1260, 1210, 1111, 1061 cm^{-1}.

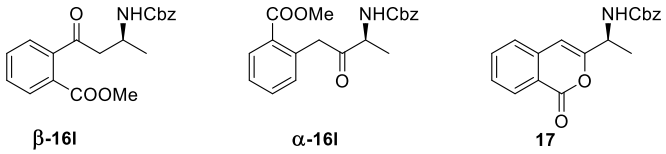
Compound **α-16j**: Yield: 4.8 mg (8%) starting from 59.8 mg (0.18 mmol) of allylamine **SI-61**; white waxy solid; $[\alpha]_D^{25}$ +2.9 (*c* 0.48, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.30 (m, 7H), 5.40 (s, 1H), 5.10 (s, 2H), 4.52 – 4.44 (m, 1H), 3.91 (s, 3H), 3.88 – 3.85 (m, 2H), 1.38 (d, *J* = 6.7 Hz, 3H); This amount of compound was insufficient to obtain a proper ^{13}C NMR spectrum. HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{21}NO_5Na$ [(M+Na)$^+$] 378.1317; found: 378.1309; FTIR (film) ν: 3330, 3033, 2971, 1720, 1599, 1536, 1454, 1285, 1261, 1111, 1058 cm^{-1}.

Methyl (*S*)-3-(3-(((benzyloxy)carbonyl)amino)butanoyl)benzoate (16k)



Method A. Reaction time: 24 h. Yield: 64.5 mg (82%) starting from 74.9 mg (0.22 mmol) of allylamine **SI-62**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white waxy solid; $[\alpha]_D^{25}$ –7.3 (*c* 1.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.22 (d, *J* = 7.7 Hz, 1H), 8.13 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.37 – 7.27 (m, 5H), 5.31 (s, 1H), 5.08 (s, 2H), 4.32 – 4.20 (m, 1H), 3.94 (s, 3H), 3.38 (d, *J* = 16.7 Hz, 1H), 3.11 (dd, *J* = 16.7, 6.4 Hz, 1H), 1.30 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 166.2, 155.6, 137.1, 136.5, 134.0, 132.2, 130.8, 129.2, 128.9, 128.5, 128.05, 128.02, 66.6, 52.4, 44.3, 44.2, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{21}NO_5Na$ [(M+Na)$^+$] 378.1317; found: 378.1319; FTIR (film) ν: 3329, 3033, 2973, 1714, 1689, 1588, 1536, 1454, 1288, 1260, 1210, 1116, 1061 cm^{-1}.

Methyl (*S*)-2-(3-(((benzyloxy)carbonyl)amino)butanoyl)benzoate (β-16l) and Methyl (*S*)-2-(3-(((benzyloxy)carbonyl)amino)-2-oxobutyl)benzoate (α-16l) and Benzyl (*S*)-(1-(1-oxo-1*H*-isochromen-3-yl)ethyl)carbamate (17)



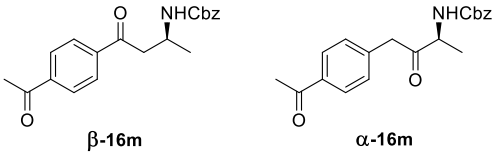
Method A (modified). Reaction time: 30 h; after 24 h an additional amount of 5% of $Pd(TFA)_2$ and 0.5 eq of BQ were added. β-amino ketone **β-16l** was obtained as a pure product, additionally α-amino ketone **α-16l** was obtained as a mixture with its cyclisation product **17** in ~10:7 ratio; Purification: flash column chromatography on silica gel (24 g column cartridge, 5-40% AcOEt in hexanes, flow 15 mL/min, 60 min);

Compound **β-16l**: Yield: 25.7 mg (40%) starting from 61.6 mg (0.18 mmol) of allylamine **SI-63**; white solid, m.p. 98.4–99.7 °C; $[\alpha]_D^{25}$ –44.6 (*c* 0.47, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.45 (m, 2H), 7.37 – 7.28 (m, 6H), 5.38 (s, 1H), 5.10 (s, 2H), 4.20 (hept, *J* = 6.5 Hz, 1H), 3.86 (s, 3H), 3.11 (dd, *J* = 17.2, 5.1 Hz, 1H), 2.98 (dd, *J* = 17.2, 5.5 Hz, 1H), 1.35 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 167.1, 155.7, 142.8, 136.7, 132.2, 123.0, 128.54, 128.48, 128.2, 128.1, 128.0, 126.4, 66.5, 52.6, 47.9, 44.0, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{21}NO_5Na$ [$(M+Na)^+$] 378.1317; found: 378.1323; FTIR (film) ν: 3312, 3033, 2980, 1714, 1687, 1536, 1454, 1439, 1285, 1260, 1210, 1111, 1061 cm^{-1}.

Compounds **α-16l** and **17**: Yield: 25.5 mg (40% in total, **α-16l** to **17** ratio is 10:7) starting from 61.6 mg (0.18 mmol) of allylamine **SI-63**; white waxy solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.9 Hz, 0.7H), 8.06 – 7.99 (d, *J* = 7.9 Hz, 1H), 7.69 (td, *J* = 7.7, 1.2 Hz, 0.7H), 7.48 (m, 1.7H), 7.40 – 7.27 (m, 9.5H), 7.19 (d, *J* = 7.3 Hz, 0.7H), 6.45 (s, 0.7H, =C-**H** of **17**), 5.64 (d, *J* = 7.2 Hz, 1H), 5.23 (d, *J* = 7.2 Hz, 0.7H), 5.16 – 5.04 (m, 3.4H), 4.70 (p, *J* = 7.2 Hz, 0.7H, HN-C**-H** of **17**), 4.59 (p, *J* = 7.3 Hz, 1H, HN-C**-H** of **α-16l**), 4.27 (d, *J* = 17.3 Hz, 1H, O=C=**CH_2**- (diastereotopic) of **α-16l**), 4.14 (d, *J* = 17.3 Hz, 1H, O=C=**CH_2**- (diastereotopic) of **α-16l**), 3.81 (s, 3H, COO**CH_3** of **α-16l**), 1.51 (d, *J* = 7.2 Hz, 2.1H), 1.47 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 207.2 (ketone **C**=O of **α-16l**), 167.5 (ester **C**=O of **α-16l**), 162.0 (ester **C**=O of **17**), 158.3 (alkene C=**C**-O of **17**), 156.0, 137.4, 137.3, 136.6, 135.8, 133.1, 132.7, 130.6, 130.2, 129.3, 128.8, 128.2, 128.2, 127.5, 126.6, 120.1 (multiple overlapping aromatic signals of **α-16l** and **17**), 102.0 (alkene **C**=C-O of **17**), 66.0, 55.8, 52.4, 48.5, 44.8, 19.0 (**C**H_3 of **17**), 16.6 (**C**H_3 of **α-16l**); HRMS for **α-16l**

(ESI-TOF) *m/z* calcd for $C_{20}H_{21}NO_5Na$ [(M+Na)$^+$] 378.1317; found: 378.1309; HRMS for **17** (ESI-TOF) *m/z* calcd for $C_{19}H_{17}NO_4Na$ [(M+Na)$^+$] 346.1055; found: 346.1060;

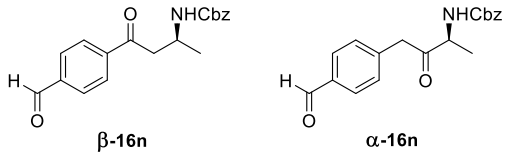
Benzyl (*S*)-(4-(4-acetylphenyl)-4-oxobutan-2-yl)carbamate (β-16m) and Benzyl (*S*)-(4-(4-acetylphenyl)-3-oxobutan-2-yl)carbamate (α-16m)



Method A (modified). Reaction time: 30 h; after 24 h an additional amount of 5% of $Pd(TFA)_2$ and 0.5 eq of BQ were added. A inseparable mixture of α- and β-amino ketone was obtained; Purification: flash column chromatography on silica gel (24 g column cartridge, 10-50% AcOEt in hexanes, flow 15 mL/min, 60 min);

Compounds **β-16m + α-16m**: Yield: 49.3 mg (81% in total, **β-16m** to **α-16m** ratio is 6:1) starting from 58.1 mg (0.18 mmol) of allylamine **SI-64**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 4H, aromatics of **β-16m**), 7.90 (d, *J* = 7.9 Hz, 0.34H), 7.37 – 7.24 (m, 6.19H), 5.48 (s, 0.17H), 5.24 (s, 1H), 5.11 – 5.04 (m, 2.34H), 4.48 (p, *J* = 7.1 Hz, 0.17H), 4.30 – 4.19 (m, 1H), 3.91 – 3.79 (m, 0.34H), 3.39 (d, *J* = 16.5 Hz, 1H), 3.07 (dd, *J* = 16.5, 6.6 Hz, 1H), 2.62 (s, 3H), 2.57 (s, 0.51H), 1.37 (d, *J* = 7.1 Hz, 0.51H), 1.30 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) for **β-16m** δ 198.1, 197.4, 155.6, 140.3, 140.0, 136.5, 129.8, 128.53, 128.51, 128.3, 128.11, 128.05, 66.6, 44.7, 44.3, 26.9, 20.3 (one extra signal in aromatic region – probably from the minor regioisomer **α-16m**); HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{21}NO_4Na$ [(M+Na)$^+$] 362.1368; found: 362.1382; FTIR (film) ν: 3349, 3033, 2974, 1714, 1685, 1606, 1526, 1454, 1263, 1211, 1109, 1058 cm^{-1}.

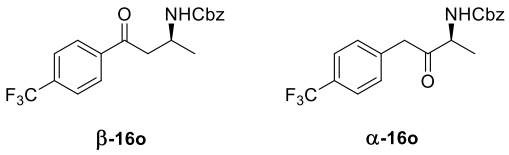
Benzyl (*S*)-(4-(4-formylphenyl)-4-oxobutan-2-yl)carbamate (β-16n) and benzyl (*S*)-(4-(4-formylphenyl)-3-oxobutan-2-yl)carbamate (α-16n):



Method A (modified). Reaction time: 30 h; after 24 h an additional amount of 5% of $Pd(TFA)_2$ and 0.5 eq of BQ were added. A inseparable mixture of α- and β-amino ketone was obtained; Purification: flash column chromatography on silica gel (24 g column cartridge, 10-50% AcOEt in hexanes, flow 15 mL/min, 60 min);

Compounds **β-16n + α-16n**: Yield: 48 mg (59% in total, **β-16n** to **α-16n** ratio is 6:1) starting from 77 mg (0.25 mmol) of allylamine **SI-64**; NMR data for major product (β-16n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H)8.05 – 7.97 (m, 2H), 7.39 – 7.26 (m, 7H), 5.32 – 5.16 (m, 1H), 5.10 – 5.05 (m, 2H), 4.33 – 4.17 (m, 2H), 3.39 (d, *J* = 14.1 Hz, 1H), 3.07 (dd, *J* = 14.1, 6.6 Hz, 1H), 1.30 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.4, 197.1, 155.3, 140.5, 136.5, 129.8, 128.5, 128.4, 128.3, 128.2, 67.3, 44.9, 20.2; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{21}NO_4Na$ [(M+MeOH+Na)$^+$] 380.1474; found: 380.1469.

Benzyl (*S*)-(4-oxo-4-(4-(trifluoromethyl)phenyl)butan-2-yl)carbamate (β-16o) and benzyl (*S*)-(3-oxo-4-(4-(trifluoromethyl)phenyl)butan-2-yl)carbamate (α-16o)



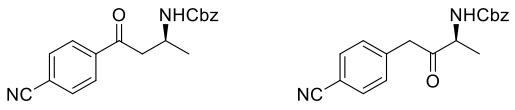
Method A (modified). Reaction time: 30 h; after 24 h an additional amount of 5% of $Pd(TFA)_2$ and 0.5 eq of BQ were added. A separable mixture of α- and β-amino ketone was obtained; Purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 60 min);

Compound **β-16o**: Yield: 37.3 mg (65%) starting from 55.1 mg (0.16 mmol) of allylamine **SI-65**; white waxy solid; $[\alpha]_D^{25}$ −0.9 (*c* 1.65, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.38 – 7.27 (m, 5H), 5.23 – 5.03 (m, 3H), 4.30 – 4.18 (m, 1H), 3.40 (d, *J* = 16.5 Hz, 1H), 3.07 (dd, *J* = 16.5, 6.6

Hz, 1H), 1.31 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 155.6, 139.4, 136.4, 134.6 (q, J_{C-F} = 32.4 Hz), 128.52, 128.46, 128.14, 128.08, 125.7 (q, J_{C-F} = 3.7 Hz), 123.6 (q, J_{C-F} = 273.1 Hz) 66.6, 44.7, 44.3, 20.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{18}NO_3F_3Na$ [(M+Na)$^+$] 388.1136; found: 388.1147; FTIR (film) ν: 3331, 3034, 2973, 1712, 1657, 1581, 1512, 1445, 1327, 1248, 1170, 1131, 1060 cm^{-1}.

Compound **α-16o**: Yield: 9.8 mg (17%) starting from 59.8 mg (0.18 mmol) of allylamine **SI-65**; white waxy solid; $[\alpha]_D^{25}$ +1.8 (*c* 0.98, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.8 Hz, 2H), 7.40 – 7.27 (m, 7H), 5.41 (s, 1H), 5.10 (s, 2H), 4.53 – 4.43 (m, 1H), 3.94 – 3.80 (m, 2H), 1.39 (d, J = 7.1 Hz, 3H); This amount of compound was insufficient to obtain a proper ^{13}C NMR spectrum. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{18}NO_3F_3Na$ [(M+Na)$^+$] 388.1136; found: 388.1147; FTIR (film) ν: 3312, 3033, 2972, 1710, 1687, 1536, 1454, 1327, 1249, 1270, 1122, 1061 cm^{-1}.

Benzyl (*S*)-(4-(4-cyanophenyl)-4-oxobutan-2-yl)carbamate (β-16p) and benzyl (*S*)-(4-(4-cyanophenyl)-3-oxobutan-2-yl)carbamate (α-16p)



β-16p α-16p

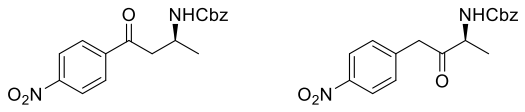
Method A (modified). Reaction time: 30 h; after 24 h an additional amount of 5% of $Pd(TFA)_2$ and 0.5 eq of BQ were added. A separable mixture of α- and β-amino ketone was obtained; Purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 60 min);

Compound **β-16p**: Yield: 30.9 mg (56%) starting from 52.7 mg (0.17 mmol) of allylamine **SI-66**; white solid, m.p. 97.2–99.8 °C; $[\alpha]_D^{25}$ +5.0 (*c* 1.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 2H), 7.74 (d, J = 7.8 Hz, 2H), 7.39 – 7.27 (m, 5H), 5.19 – 5.01 (m, 3H), 4.28 – 4.18 (m, 1H), 3.39 (d, J = 16.4 Hz, 1H), 3.05 (dd, J = 16.4, 6.7 Hz, 1H), 1.30 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 155.6, 139.7, 136.4, 132.6, 128.5, 128.18, 128.11, 128.08, 117.8, 116.6, 66.7, 44.7, 44.2, 20.3; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{18}N_2O_3Na$ [(M+Na)$^+$] 345.1215; found:

345.1212; FTIR (film) ν: 3357, 3033, 2974, 2230, 1695, 1606, 1524, 1445, 1405, 1249, 1211, 1107, 1059 cm^{-1}.

Compound **α-16p**: Yield: 15.8 mg (29%) starting from 52.7 mg (0.17 mmol) of allylamine **SI-66**; white solid, m.p. 88.3–90.3 °C; $[\alpha]_D^{25}$ +2.2 (*c* 0.96, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.8 Hz, 2H), 7.40 – 7.22 (m, 7H), 5.37 (s, 1H), 5.10 (s, 2H), 4.46 (p, *J* = 7.1 Hz, 1H), 3.92 – 3.79 (m, 2H), 1.38 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.2, 155.7, 138.7, 132.4, 130.4, 128.6, 128.3, 128.1 (x2), 118.6, 111.3, 67.1, 55.5, 45.8, 17.4; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{18}N_2O_3Na$ [(M+Na)$^+$] 345.1215; found: 345.1212; FTIR (film) ν: 3333, 3033, 2974, 2230, 1718, 1695, 1600, 1524, 1445, 1405, 1251, 1211, 1110, 1061 cm^{-1}.

Benzyl (*S*)-(4-(4-nitrophenyl)-4-oxobutan-2-yl)carbamate (β-16q) and benzyl (*S*)-(4-(4-nitrophenyl)-3-oxobutan-2-yl)carbamate (α-16q)



β-16q α-16q

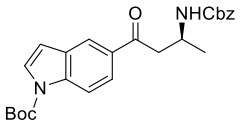
Method A (modified). Reaction time: 30 h; after 24 h an additional amount of 5% of $Pd(TFA)_2$ and 0.5 eq of BQ were added. A separable mixture of α- and β-amino ketone was obtained; Purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 60 min);

Compound **β-16q**: Yield: 28.1 mg (44%) starting from 60.5 mg (0.19 mmol) of allylamine **SI-67**; white solid, m.p. 83.1–85.3°C; $[\alpha]_D^{25}$ +2.3 (*c* 1.56, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.7 Hz, 2H), 8.10 (d, *J* = 7.7 Hz, 2H), 7.39 – 7.27 (m, 5H), 5.18 – 5.02 (m, 3H), 4.29 – 4.17 (m, 1H), 3.43 (d, *J* = 16.5 Hz, 1H), 3.09 (dd, *J* = 16.5, 6.7 Hz, 1H), 1.32 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 155.6, 150.5, 141.1, 136.3, 129.2, 128.5, 128.2, 128.1, 123.9, 66.7, 45.1, 44.3, 22.6; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{18}N_2O_5Na$ [(M+Na)$^+$] 365.1113; found: 365.1106; FTIR (film) ν: 3330, 3033, 2974, 1695, 1594, 1524, 1445, 1405, 1343, 1249, 1211, 1107, 1059 cm^{-1}.

Compound **α-16q**: Yield: 24.2 mg (38%) starting from 60.5 mg (0.19 mmol) of allylamine **SI-67**; white solid, m.p. 100.4–102.1 °C; $[\alpha]_D^{25}$ +1.6 (*c* 1.33, $CHCl_3$); ^1H

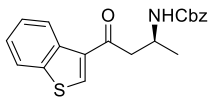
NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.29 (m, 7H), 5.37 (s, 1H), 5.11 (s, 2H), 4.52 – 4.43 (m, 1H), 3.98 – 3.89 (m, 2H), 1.40 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.1, 155.8, 147.3, 140.6, 136.0, 130.5, 128.6, 128.3, 128.1, 123.8, 67.1, 55.5, 45.4, 17.4; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{18}N_2O_5Na$ [(M+Na)$^+$] 365.1113; found: 365.1106; FTIR (film) ν: 3333, 3033, 2978, 1698, 1598, 1524, 1449, 1404, 1343, 1250, 1211, 1111, 1061 cm^{-1}.

t-Butyl (*S*)-5-(3-(((benzyloxy)carbonyl)amino)butanoyl)-1*H*-indole-1-carboxylate (18a)



Synthesized according to General Procedure A. Reaction time: 3 h. Yield: 31.2 mg (58%) starting from 52.2 mg (0.22 mmol) of allylamine **SI-68**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); colourless oil; $[\alpha]_D^{25}$ –3.1 (*c* 0.66, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.10 (m, 2H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.65 (d, *J* = 3.5 Hz, 1H), 7.38 – 7.27 (m, 5H), 6.65 (d, *J* = 3.5 Hz, 1H), 5.37 (s, 1H), 5.09 (s, 2H), 4.35 – 4.21 (m, 1H), 3.43 (d, *J* = 14.6 Hz, 1H), 3.13 (dd, *J* = 14.6, 6.4 Hz, 1H), 1.68 (s, 9H), 1.32 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 155.7 (×2), 149.3, 138.0, 136.6, 132.0, 130.4, 128.5, 128.0, 127.4, 124.3, 122.0, 115.1, 107.9, 84.5, 66.5, 44.5, 44.1, 28.1, 20.5; HRMS (ESI-TOF) *m/z* calcd for $C_{25}H_{28}N_2O_5Na$ [(M+Na)$^+$] 459.1896; found: 459.1904; FTIR (film) ν: 3339, 3032, 2976, 1738, 1676, 1607, 1531, 1454, 1369, 1335, 1254, 1231, 1159, 1084, 1057, 1024 cm^{-1}.

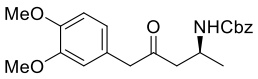
Benzyl (*S*)-(4-(benzo[*b*]thiophen-3-yl)-4-oxobutan-2-yl)carbamate (18b)



Method A. Reaction time: 3 h. Yield: 56.5 mg (77%) starting from 70.2 mg (0.21 mmol) of allylamine **SI-69**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 108.3–110.0 °C; $[\alpha]_D^{25}$ +8.6 (*c* 1.09, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 7.9 Hz, 1H), 8.44 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.52 –

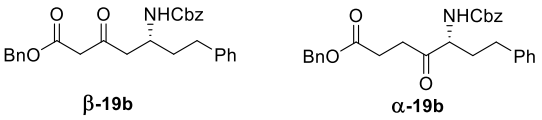
7.28 (m, 7H), 5.34 (s, 1H), 5.11 (s, 2H), 4.32 – 4.19 (m, 1H), 3.44 (d, *J* = 12.6 Hz, 1H), 2.98 (dd, *J* = 12.6, 7.0 Hz, 1H), 1.33 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 155.7, 139.9, 137.9, 136.5, 135.1, 128.5, 128.12(×2), 128.06, 125.9, 125.7, 125.5, 122.3, 66.6, 46.2, 45.0, 20.3; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{19}NO_3NaS$ [(M+Na)$^+$] 376.0983; found: 376.0984; FTIR (film) ν: 3319, 3032, 2974, 1722, 1709, 1690, 1514, 1495, 1458, 1254, 1190, 1105, 1055 cm^{-1}.

Benzyl (*S*)-(5-(3,4-dimethoxyphenyl)-4-oxopentan-2-yl)carbamate (19a)



Method A. Reaction time: 30 min. Yield: 48.7 mg (70%) starting from 66.8 mg (0.19 mmol) of allylamine **20a**; purification: flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 30 min); white solid, m.p. 104.5–106.2 °C; $[\alpha]_D^{25}$ -24.9 (*c* 0.66, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 5H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.74 – 6.66 (m, 2H), 5.17 – 5.01 (m, 3H), 4.11 – 4.00 (m, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.59 (s, 2H), 2.72 (dd, *J* = 16.8, 4.9 Hz, 1H), 2.59 (dd, *J* = 16.9, 5.9 Hz, 1H), 1.15 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 155.5, 149.2, 148.3, 136.5, 128.5, 128.1, 128.0, 126.1, 121.6, 112.5, 111.5, 66.5, 55.89, 55.88, 50.2, 47.2, 43.8, 20.4; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{25}NO_5Na$ [(M+Na)$^+$] 394.1630; found: 394.1627; FTIR (film) ν: 3314, 3032, 2938, 1711, 1688, 1516, 1450, 1261, 1238, 1157, 1140, 1061, 1028 cm^{-1}.

Benzyl (*R*)-5-(((benzyloxy)carbonyl)amino)-3-oxo-7-phenylheptanoate (β-19b) and Benzyl (*R*)-5-(((benzyloxy)carbonyl)amino)-4-oxo-7-phenylheptanoate (α-19b)

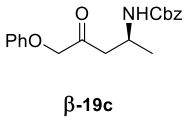


Method A. Reaction time: 24 h; A separable mixture of α- and β-amino ketone was obtained; Purification: flash column chromatography on silica gel (12 g column cartridge, 5-35% AcOEt in hexanes, flow 15 mL/min, 60 min);

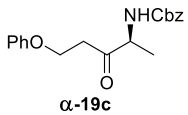
Compound **β-19b**: Yield: 34.5 mg (52%) starting from 63.5 mg (0.14 mmol) of allylamine **20b**; white solid, m.p. 88.8–90.4°C; $[\alpha]_D^{25}$ +18.7 (*c* 0.84, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, *keto*:*enol* ratio is 10:1) δ 12.06 (s, 0.1H, **O<u>H</u>** of *enol* form), 7.39 – 7.22 (m, 12H), 7.21 – 7.10 (m, 3H), 5.18 – 5.02 (m, 5.1H, 2x **C<u>H₂</u>** of OBn and NHCbz group + **N-<u>H</u>** + **=C-<u>H</u>** of *enol* form), 4.03 – 3.92 (m, 1H), 3.49 – 3.37 (m, 1.8H, **C<u>H₂</u>** of *keto* form), 2.88 – 2.54 (m, 4H), 1.94 – 1.74 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$, *keto* form) δ 201.3, 166.7, 155.8, 141.2, 136.5, 135.2, 128.6, 128.52, 128.46, 128.42, 128.35, 128.2, 128.1, 128.0, 126.0, 67.2, 66.7, 49.5, 47.7, 47.1, 35.9, 32.6 [small signal at 91.5 was also detected – resulting from **HO-C=<u>C</u>-** sp_2 carbon of *enol* form]; HRMS (ESI-TOF) *m/z* calcd for $C_{28}H_{29}NO_5Na$ [$(M+Na)^+$] 482.1943; found: 482.1948; FTIR (film) ν: 3330, 3033, 2974, 1695, 1594, 1524, 1445, 1405, 1343, 1249, 1211, 1107, 1059 cm^{-1}.

Compound **α-19b**: Yield: 18.2 mg (28%) starting from 63.5 mg (0.14 mmol) of allylamine **20b**; colourless oil; $[\alpha]_D^{25}$ -23.3 (*c* 0.66, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 12H), 7.22 – 7.13 (m, 3H), 5.45 (d, *J* = 6.8 Hz, 1H), 5.17 – 5.06 (m, 4H), 4.49 – 4.40 (m, 1H), 2.90 – 2.56 (m, 6H), 2.32 – 2.20 (m, 1H), 1.93 – 1.81 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.9, 172.2, 156.0, 140.7, 136.3, 135.7, 128.6, 128.5(×2), 128.4(×2), 128.3, 128.2, 128.1, 126.2, 67.0, 66.6, 59.3, 34.3, 33.3, 31.2, 27.7 [2 signals in aromatic region are missing – probably due to overlapping]; HRMS (ESI-TOF) *m/z* calcd for $C_{28}H_{29}NO_5Na$ [$(M+Na)^+$] 482.1943; found: 482.1951; FTIR (film) ν: 3312, 3033, 2974, 1704, 1594, 1525, 1454, 1409, 1249, 1210, 1107, 1059 cm^{-1}.

Benzyl (*S*)-(4-oxo-5-phenoxypentan-2-yl)carbamate (β-19c) and Benzyl (*S*)-(3-oxo-5-phenoxypentan-2-yl)carbamate (α-19c)



β-19c



α-19c

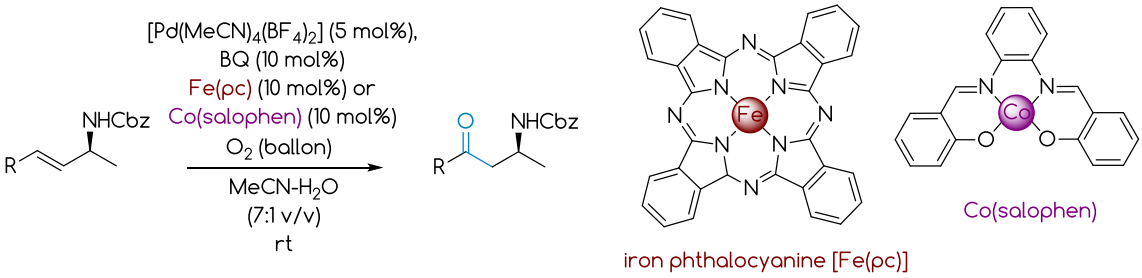
Method A. Reaction time: 24 h; A separable mixture of α- and β-amino ketone was obtained; Purification: flash column chromatography on silica gel (12 g column cartridge, 5-35% AcOEt in hexanes, flow 15 mL/min, 60 min);

Compound **β-19c**: Yield: 19.7 mg (38%) starting from 49.3 mg (0.16 mmol) of allylamine **20c**; white solid, m.p. 103.1–104.8°C; $[\alpha]_D^{25}$ -12.7 (*c* 1.11, $CHCl_3$); ^1H NMR

(400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 7H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 2H), 5.13 – 5.07 (m, 3H), 4.56 – 4.49 (m, 2H), 4.24 – 4.16 (m, 1H), 2.90 (dd, *J* = 16.8, 4.9 Hz, 1H), 2.79 (dd, *J* = 16.9, 5.5 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 157.6, 155.5, 136.5, 129.7, 128.5, 128.10, 128.05, 121.9, 114.5, 73.0, 66.6, 44.9, 43.6, 20.7; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{21}NO_4Na$ [(M+Na)$^+$] 350.1368; found: 350.1372; FTIR (film) ν: 3315, 3033, 2932, 1715, 1600, 1515, 1452, 1240, 1060 cm^{-1}.

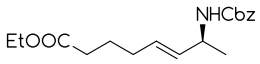
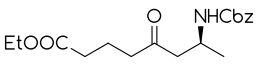
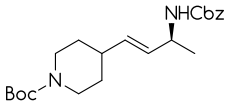
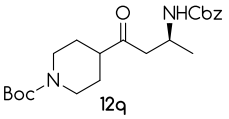
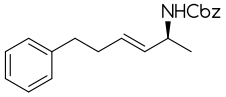
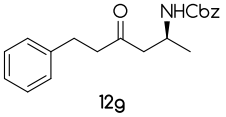
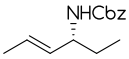
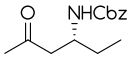
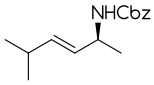
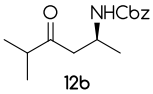
Compound **α-19c**: Yield: 19.0 mg (37%) starting from 49.3 mg (0.16 mmol) of allylamine **20c**; white solid, m.p. 94.8–97.0°C; $[\alpha]_D^{25}$ +13.0 (*c* 0.96, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 7H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 2H), 5.52 (s, 1H), 5.11 (s, 2H), 4.49 – 4.41 (m, 1H), 4.32 – 4.20 (m, 2H), 3.05 – 2.86 (m, 2H), 1.41 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.7, 158.4, 155.6, 136.3, 129.5, 128.5, 128.2, 128.1, 121.1, 114.6, 66.9, 62.7, 56.0, 38.8, 17.4; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{21}NO_4Na$ [(M+Na)$^+$] 350.1368; found: 350.1372; FTIR (film) ν: 3329, 3032, 2932, 1711, 1599, 1499, 1452, 1244, 1069, 1026 cm^{-1}.

4. Wacker oxidation of allyl amines under aerobic conditions



General procedure: $[Pd(MeCN)_4(BF_4)_2]$(11 mg, 24.5 μmol, 5 mol%), benzoquinone (5.3 mg, 49 μmol, 10 mol%) and Fe(phtalocyanin) (28 mg, 49 μmol, 10 mol%) or Co(salophene) (20 mg, 49 μmol, 10 mol%) were charged in a 20-mL vial under air. A mixture of MeCN (7 mL) and water (1 mL) was added. The mixture was then purged with oxygen for 5 min, and after the addition of the corresponding substrate (0.5 mmol), the homogenous reaction mixture was stirred at room temperature under an atmospheric pressure of oxygen (balloon). The progress of the reaction was followed by TLC analysis. Next, $CHCl_3$ and sat. aqueous NaCl were added and layers were separated. Aqueous layer was washed with $CHCl_3$. The combined organic layers were

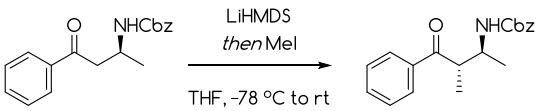
dried over anhydr. Na_2SO_4, filtered and evaporated. The crude residue was purified chromatographically to provide the corresponding amino ketone.

substrate	ETM	product	Time [h]	yield
	Fe(pc) Co(salophen)		4 5	88%(86%*) 83%
	Fe(pc) Co(salophen)	 12q	5 5	74% 72%
	Fe(pc) Co(salophen)	 12g	4 5	79% 75%
 2.3 g (10 mmol) scale of SM)	Fe(pc) Co(salophen)	 13b	20 22	89% (2.23 g of product)* 88% (2.20 g of product)
	Fe(pc) Co(salophen)	 12b	6 5	80% 78%

* active catalyst generated in situ from $Pd(TFA)_2$ (5 mol%) and HBF_4 (1.4 eq)

5. Functionalization of selected products

5.1. α-Alkylation of β-amino ketone 16a

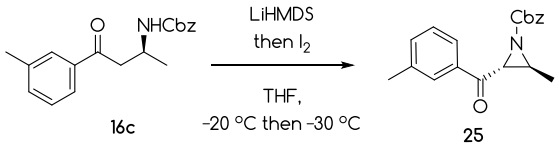


16a 24

A solution of **16a** (45 mg, 0.15 mmol) in anhydr. THF (1 mL) was treated with LiHMDS (1M solution in THF, 0.50 mmol, 0.50 mL) at -78 °C and stirred for 1 h.[6] Next, methyl iodide (38 µL, 86 mg, 0.60 mmol) was added and stirred at the same temperature for 30 min. Next the reaction mixture was slowly allowed to warm to rt. After 1 h, sat. aqueous NH_4Cl was added, followed by AcOEt. Layers were separated. Aqueous layer was washed with AcOEt. The combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The *dr* was judged to be >20:1, according to ^1H NMR spectra of crude reaction mixture. The crude residue was purified by a flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in

hexanes, flow 15 mL/min, 30 min) to give 29.3 mg (0.09 mmol, 62% yield) of **24** as a colourless oil. $[\alpha]_D^{25}$ +15.7 (*c* 0.75, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.59 – 7.23 (m, 8H), 5.68 (d, *J* = 7.4 Hz, 1H), 5.20 – 5.06 (m, 2H), 4.15 – 4.05 (m, 1H), 3.84 – 3.75 (m, 1H), 1.24 (d, *J* = 7.1 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9, 156.1, 136.6, 136.5, 133.4, 128.8, 128.5, 128.4, 128.04, 127.97, 66.6, 49.4, 44.1, 18.5, 14.0; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{21}NO_3Na$ [$(M+Na)^+$] 334.1419; found: 334.1414; FTIR (film) ν: 3324, 3033, 2973, 1697, 1602, 1585, 1527, 1453, 1298, 1249, 1100, 1060 cm^{-1}.

5.2. Aziridination of β-amino ketone 16c



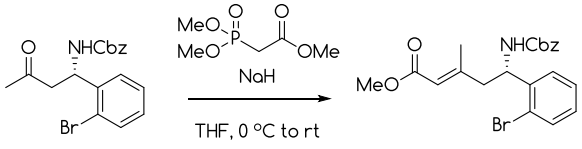
A solution of **16c** (45.4 mg, 0.15 mmol) in anhydr. THF (1 mL) was treated with LiHMDS (1M solution in THF, 0.32 mmol, 0.32 mL) at -20 °C and stirred for 45 min.[7] Next, iodine (40.7 mg, 0.16 mmol) in anhydr. THF (0.5 mL) was added at -30 °C and stirred at the same temperature for 1 h. Next, sat. aqueous $Na_2S_2O_3$ was added, followed by AcOEt. Layers were separated. Aqueous layer was washed with AcOEt. Combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The *dr* was judged to be >20:1, according to ^1H NMR spectra of crude reaction mixture. The crude residue was purified by a flash column chromatography on silica gel (12 g column cartridge, 5-25% AcOEt in hexanes, flow 15 mL/min, 30 min) to give 21.8 mg (0.11 mmol, 73% yield) of **25** as a colourless oil. $[\alpha]_D^{25}$ -5.1 (*c* 0.67, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.34 – 7.26 (m, 5H), 5.20 (d, *J* = 12.2 Hz, 1H), 5.12 (d, *J* = 12.2 Hz, 1H), 3.76 (d, *J* = 2.6 Hz, 1H), 2.95 (qd, *J* = 5.5, 2.6 Hz, 1H), 2.41 (s, 3H), 1.42 (d, *J* = 5.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 160.9, 138.7, 136.5, 135.7, 134.6, 128.9, 128.7, 128.40, 128.36, 128.2, 125.6, 68.2, 44.5, 42.0, 21.3, 16.9; HRMS (ESI-TOF) *m/z* calcd for $C_{19}H_{19}NO_3Na$ [$(M+Na)^+$] 332.1263; found: 332.1266; FTIR (film) ν: 3033, 2929, 1729, 1677, 1604, 1425, 1302, 1256, 1197, 1068 cm^{-1}.

5.3. Grignard reaction of 13r

13r 21

A solution of **13r** (40 mg, 0.11 mmol) in anhydr. Et_2O (0.5 mL) was cooled down to 0 °C, followed by addition of PhMgBr (3M solution in Et_2O, 71 µL, 0.21 mmol) and stirred at rt for 4 h. Next, sat. aqueous NH_4Cl was added, followed by AcOEt. Layers were separated. Aqueous layer was washed with AcOEt. Combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The crude residue was purified by a flash column chromatography on silica gel (12 g column cartridge, 10-35% AcOEt in hexanes, flow 15 mL/min, 30 min) to give 36.5 mg (0.11 mmol, 76% yield) of **21** as a white waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereoisomers) δ 7.52 – 7.43 (m, 3H), 7.34 – 7.18 (m, 10H), 7.10 – 7.04 (m, 1H), 5.90 (s, 1H), 5.38 – 5.29 (m, 1H), 5.04 – 4.90 (m, 2H), 2.61 (s, 1H), 2.26 – 2.06 (m, 2H), 1.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of diastereoisomers) δ 155.8, 148.4, 141.8, 136.4, 133.2, 128.6, 128.4, 128.3, 128.1, 128.0, 127.8, 127.5, 126.9, 124.3, 122.3, 74.5, 66.8, 52.8, 48.0, 29.4; HRMS (ESI-TOF) *m/z* calcd for $C_{24}H_{24}NO_3NaBr$ [$(M+Na)^+$] 476.0837; found: 476.0836; FTIR (film) ν: 3365, 3031, 2973, 1702, 1510, 1444, 1262, 1070, 1026 cm^{-1}.

5.4. Olefination of 13r



13r 22

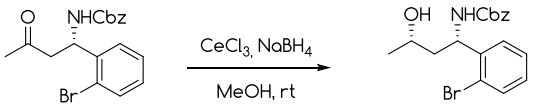
NaH (60% dispersion in mineral oil, 6.4 mg, 0.16 mmol) was suspended in anhydr. THF (0.5 mL) and cooled down to 0 °C, followed by addition of trimethyl phosphonoacetate (25 µL, 31 mg, 0.17 mmol) and stirred at rt for 30 min. Next, a solution of **13r** (40 mg, 0.11 mmol) in anhydr. THF (0.5 mL) was added and the resulting mixture was stirred at rt overnight. Next, water and AcOEt were added.

Layers were separated. Aqueous layer was washed with AcOEt. Combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The

crude residue was purified by a flash column chromatography on silica gel (12 g column cartridge, 5-30% AcOEt in hexanes, flow 15 mL/min, 30 min) to give 29.6 mg (0.07 mmol, 62% yield) of **29** as a white waxy solid. $[\alpha]_D^{25}$ +8.7 (*c* 0.76, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.25 (m, 7H), 7.18 – 7.09 (m, 1H), 5.71 (s, 1H), 5.36 – 5.28 (m, 1H), 5.19 (s, 1H), 5.06 (s, 2H), 3.69 (s, 3H), 2.73 (d, *J* = 12.0 Hz, 1H), 2.45 – 2.34 (m, 1H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 155.4, 155.0, 141.2, 136.2, 133.4, 129.1, 128.5, 128.1 (×2), 127.9, 127.2, 122.5, 118.5, 67.0, 53.0, 51.0, 46.6, 18.2; HRMS (ESI-TOF) *m/z* calcd for $C_{21}H_{22}NO_4NaBr$ $[(M+Na)^+]$ 454.0630; found: 454.0631; FTIR (film) ν: 3331, 3033, 2949, 1717, 1696, 1650, 1532, 1437, 1227, 1153, 1024 cm^{-1}.

5.5. Diastereoselective reductions of 13r

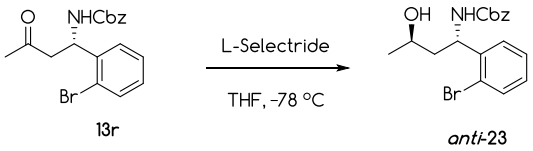
5.5.1. *Syn*-selective reduction



13r *syn*-23

To a stirred solution of **13r** (50 mg, 0.13 mmol) and $CeCl_3$ (32.8 mg, 0.13 mmol) in anhydr. MeOH (1 mL) $NaBH_4$ (10.0 mg, 0.26 mmol) was added portionwise.[8] The resulting mixture was stirred at rt for 30 min. Next, sat. aqueous $NaHCO_3$ was added and mixture was extracted with CH_2Cl_2 three times. Combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The crude residue was purified by a flash column chromatography on silica gel (12 g column cartridge, 10-40% AcOEt in hexanes, flow 15 mL/min, 30 min) to give 34.1 mg (0.09 mmol, 68% yield) of ***syn*-23** and 8.6 mg (0.02 mmol, 17% yield) of ***anti*-23**. Data for *syn* isomer: Colourless oil; $[\alpha]_D^{25}$ +4.9 (*c* 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.21 (m, 7H), 7.12 (td, *J* = 7.8, 1.6 Hz, 1H), 6.02 (d, *J* = 7.2 Hz, 1H), 5.38 – 5.30 (m, 1H), 5.14 – 5.04 (m, 2H), 3.89 - 3.79 (m, 1H), 2.85 (s, 1H), 2.01 – 1.92 (m, 1H), 1.88 – 1.76 (m, 1H), 1.20 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 140.7, 136.4, 133.4, 128.9, 128.5, 128.2 (×2), 127.8, 127.6, 123.1, 67.0, 64.6, 52.6, 42.9, 23.6; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{20}NONaBr$ $[(M+Na)^+]$ 400.0524; found: 400.0526; FTIR (film) ν: 3336, 3033, 2966, 1699, 1511, 1454, 1260, 1120, 1059 cm^{-1}.

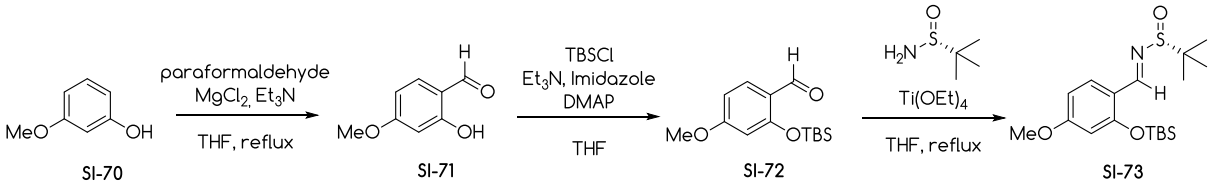
5.5.2. *Anti*-selective reduction



To a stirred solution of **13r** (150 mg, 0.40 mmol) in anhydr. THF (2 mL) L-Selectride (1M solution in THF, 1.2 mL, 1.2 mmol) was added dropwise at -78 °C.[9] The resulting mixture was stirred at the same temperature for 3 h. Next, sat. aqueous NH_4Cl was added and mixture was extracted with Et_2O three times. The combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The crude residue was purified by a flash column chromatography on silica gel (12 g column cartridge, 10-40% AcOEt in hexanes, flow 15 mL/min, 30 min) to give 91.9 mg (0.24 mmol, 61% yield) of ***anti*-23** and 47.2 mg (0.13 mmol, 31% yield) of ***syn*-23**. Data for *anti*-isomer: Colourless oil; $[\alpha]_D^{25}$ +15.1 (*c* 0.74, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.20 (m, 7H), 7.10 (td, *J* = 7.9, 1.8 Hz, 1H), 5.98 (s, 1H), 5.21 – 4.98 (m, 3H), 3.97 – 3.85 (m, 1H), 2.18 (s, 1H), 1.97 – 1.73 (m, 2H), 1.23 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 141.7, 136.4, 133.3, 128.7, 128.5, 128.1 (×2), 127.9, 127.6, 122.5, 66.82, 66.77, 54.4, 44.4, 24.2; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{20}NONaBr$ [$(M+Na)^+$] 400.0524; found: 400.0523; FTIR (film) ν: 3369, 3033, 2966, 1690, 1511, 1454, 1258, 1122, 1060 cm^{-1}.

5.6. Synthesis of 30

5.6.1. Synthesis of sulfinylimine (SI-73)



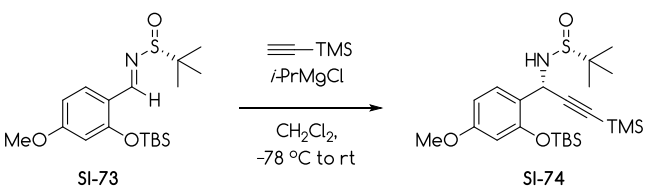
Step 1:[10] To a stirred suspension of anhydr. $MgCl_2$ (1.73 g, 18.13 mmol) and paraformaldehyde (4.35 g, 90.62 mmol) in anhydr. THF (60 mL) was added Et_3N (6.3 mL, 4.59 g, 45.31 mmol) and 3-methoxyphenol **SI-70** (1.3 mL, 1.50 g, 12.08 mmol) and the resulting mixture was stirred at reflux for 4 h. The mixture was diluted with Et_2O and treated with 1M HCl, and the layers were separated. The organic layer was washed with 1M HCl and water, dried over anhydr.

Na_2SO_4, filtered and evaporated to obtain crude **SI-71** as a yellow oil. The crude residue was used in the step without further purification.

Step 2: The crude **SI-71** (12.08 mmol), DMAP (148 mg, 1.21 mmol) were dissolved in anhydr. CH_2Cl_2 (36 mL), followed by addition of Et_3N (1.8 mL, 1.35 g, 13.29 mmol) and cooled down to 0 °C. Next, TBSCl (1.82 g, 12.08 mmol) in anhydr. CH_2Cl_2 (10 mL) was added dropwise. The resulting solution was stirred at rt overnight. Next, sat. aqueous NH_4Cl was added and layers were separated. Aqueous layer was washed with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and evaporated to give crude **SI-72** as a brown oil which was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 6.58 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.34 (d, *J* = 2.2 Hz, 1H), 3.83 (s, 3H), 1.02 (s, 9H), 0.28 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 165.7, 160.7, 130.1, 121.4, 107.8, 105.3, 55.5, 25.7, 18.3, -4.3;

Step 3: The crude **SI-72** (12.08 mmol) and (*R*)-*t*-butanesulfinamide (1.54 g, 12.68 mmol) were dissolved in anhydr. THF (120 mL), followed by addition of $Ti(OEt)_4$ (7.6 mL, 8.27 g, 36.24 mmol) and stirred at reflux for 6 h. Next, sat. aqueous NaCl (120 mL) were added and the resulting suspension was stirred for 30 min. The resulting mixture was filtered through Celite® pad and filtrate was dried over anhydr. Na_2SO_4, filtered and evaporated. The residue was purified by a column chromatography (silica gel, 10% AcOEt in hexanes) to give 3.74 g (10.12 mmol, 84% after 3 steps) of **SI-73** as a colourless oil. $[\alpha]_D^{25}$ -142.8 (*c* 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, CD_3OD) δ 8.91 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 6.59 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.37 (d, *J* = 2.4 Hz, 1H), 3.81 (s, 3H), 1.22 (s, 9H), 1.03 (s, 9H), 0.25 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 158.5, 158.2, 129.5, 119.1, 108.2, 105.3, 57.3, 55.4, 25.7, 22.5, 18.3, -4.28, -4.34; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{31}NO_3NaSSi$ [$(M+Na)^+$] 392.1692; found: 392.1685; FTIR (film) ν: 2961, 2857, 1585, 1495, 1298, 1252, 1084, 1042, 835, 776 cm^{-1}.

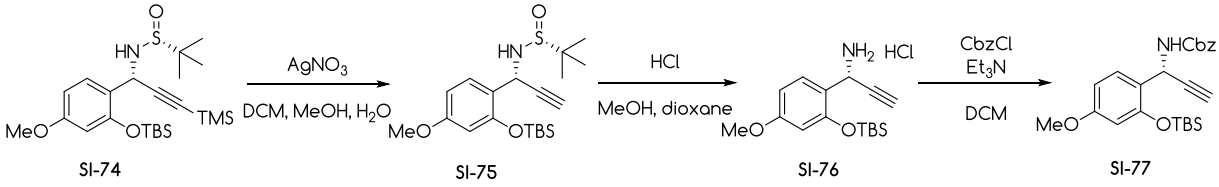
5.6.2. Alkynylation of SI-73



SI-73 SI-74

Trimethylsilylacetylene (3.6 mL, 2.48 g, 25.23 mmol) was added dropwise to a cooled (0 °C) *i*-PrMgCl solution in 2 M THF (10.1 mL, 20.18 mmol), stirred at this temperature for 30 min and 15 min at rt. Next, in a separate flask **SI-73** (3.73 g, 10.09 mmol) was dissolved in anhydr. CH_2Cl_2 (50 mL), cooled down to -78 °C followed by dropwise addition of freshly generated Grignard reagent in the first flask. The resulting solution was stirred at the same temperature for 1 h and for 6 h at rt. Next, sat. aqueous NH_4Cl was added and layers were separated. Aqueous layer was washed with CH_2Cl_2 twice. Combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The crude residue was purified by a column chromatography (silica gel, 10-20% AcOEt in hexanes) to give 4.35 g (9.30 mmol, 92% yield) of **SI-74** as a colourless oil. $[\alpha]_D^{25}$ +8.3 (*c* 0.89, $CHCl_3$); ^{1}H NMR (400 MHz, CD_3OD) δ 7.45 (d, *J* = 8.6 Hz, 1H), 6.53 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.37 (d, *J* = 2.4 Hz, 1H), 5.50 (d, *J* = 4.5 Hz, 1H), 3.77 (s, 3H), 3.64 (d, *J* = 4.5 Hz, 1H), 1.17 (s, 9H), 1.03 (s, 9H), 0.30 (s, 3H), 0.27 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 153.8, 129.3, 122.4, 106.2, 105.1, 104.5, 90.0, 55.9, 55.2, 45.7, 25.9, 22.5, 18.3, -0.2, -3.9, -4.2; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{41}NO_3NaSSi_2$ [$(M+Na)^+$] 467.2346; found: 467.2349; FTIR (film) ν: 3194, 2959, 2852, 2176, 1605, 1497, 1250, 1234, 1069, 845, 770 cm^{-1}.

5.6.3. Transformation of SI-74 to terminal *N*-Cbz propargyl amine (SI-77)



SI-74 SI-75 SI-76 SI-77

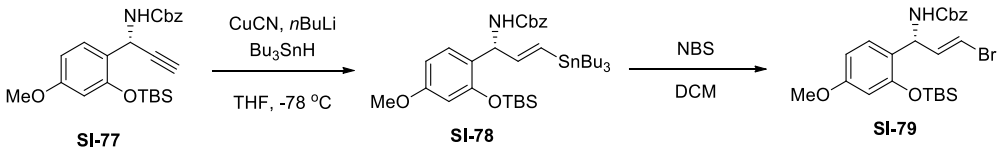
Step 1: SI-74 (4.34 g, 9.28 mmol) was dissolved in CH_2Cl_2 (112 mL), MeOH (64 mL) and water (16 mL). The flask was covered with a tinfoil, followed by addition of $AgNO_3$ (315 mg, 1.86 mmol). The resulting mixture was stirred at rt for 24 h. Next, sat. aqueous NaCl was added and layers were separated. Aqueous layer was washed with CH_2Cl_2 three times. The combined organic layers were dried over Na_2SO_4, filtered and evaporated to give the crude residue **SI-75** which was used in the next step without further purification.

Step 2: The crude **SI-75** (9.28 mmol) was dissolved in anhydr. MeOH (25 mL) and HCl (4M solution in dioxane, 4.6 mL, 18.55 mmol) was added and the

resulting mixture was stirred at rt for 2 h, followed by evaporation of volatiles to obtain crude **SI-76** that was used in the next step without further purification.

Step 3: The crude **SI-76** (9.28 mmol) was dissolved in anhydr. CH_2Cl_2 (45 mL), followed by addition of Et_3N (3.9 mL, 2.82 g, 27.83 mmol) and cooled down to 0 °C. Next, CbzCl (1.46 mL, 1.74 g, 10.20 mmol) was added dropwise and the resulting solution was stirred at rt overnight. Next, sat. aqueous NH_4Cl was added and layers were separated. The aqueous layer was washed with CH_2Cl_2 twice. The combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The residue was purified by a column chromatography (silica gel, 10% AcOEt in hexanes) to give 2.78 g (6.53 mmol, 70% after 3 steps) of **SI-77** as a white waxy solid. $[\alpha]_D^{25}$ +19.8 (*c* 1.25, $CHCl_3$); ^{1}H NMR (400 MHz, CD_3OD) δ 7.40 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.28 (m, 5H), 6.51 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 5.77 (dd, *J* = 8.0, 2.4 Hz, 1H), 5.44 (s, 1H), 5.13 (s, 2H), 3.77 (s, 3H), 2.40 (d, *J* = 2.4 Hz, 1H), 1.04 (s, 9H), 0.32 (s, 3H), 0.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 155.1, 154.0, 136.4, 129.2, 128.5, 128.0 (×2), 121.1, 105.9, 105.5, 82.9, 71.7, 66.9, 55.3, 42.7, 25.9, 18.3, -3.9, -4.1; HRMS (ESI-TOF) *m/z* calcd for $C_{24}H_{31}NO_4NaSi$ [$(M+Na)^+$] 448.1920; found: 448.1917; FTIR (film) ν: 3298, 3032, 2961, 1690, 1605, 1522, 1464, 1256, 1085, 1045, 835, 777 cm^{-1}.

5.6.4. Synthesis of vinyl bromide (SI-79)

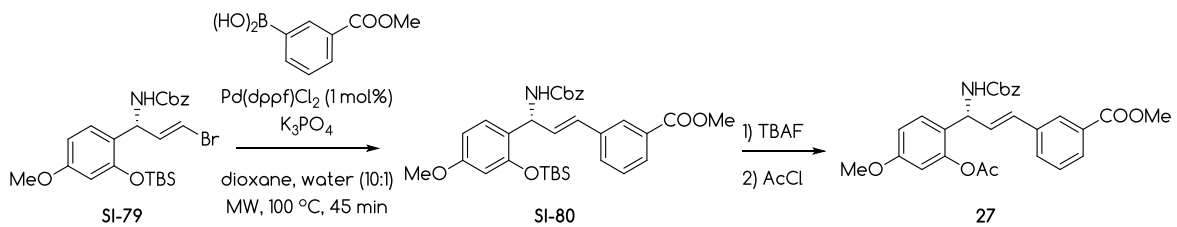


Step 1: CuCN (1.17 g, 13.0 mmol) was suspended in anhydr. THF (85 mL) and cooled down to −78 °C, followed by dropwise addition of *n*-BuLi (2.5 M solution in hexanes, 10.7 mL, 26.7 mmol) and stirred for 30 min. Next, at the same temperature, Bu_3SnH (7.96 g, 7.4 mL, 27.3 mmol) was added dropwise and stirred for 30 min, followed by dropwise addition of **SI-77** (2.77 g, 6.5 mmol) as a solution in anhydr. THF (10 mL). Reaction mixture was stirred at -78 °C for 1 h. Sat. aqueous NH_4Cl was added and mixture was allowed to warm to rt. Next, AcOEt was added and layers were separated. Organic layer was washed with water and brine, dried over anhydr. Na_2SO_4, filtered and

evaporated. The crude residue was purified by a silica gel column chromatography (1 – 2% AcOEt in hexanes) to yield 4.05 g (5.65 mmol, 87% yield) of **SI-78** as a colourless oil. $[\alpha]_D^{25}$ –8.4 (*c* 0.77, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 5H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.49 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.43 (s, 1H), 6.22 – 5.94 (m, 2H), 5.54 (d, *J* = 6.8 Hz, 1H), 5.43 (s, 1H), 5.14 – 5.08 (m, 2H), 3.77 (s, 3H), 1.52 – 1.43 (m, 6H), 1.30 (h, J = 7.2 Hz, 6H), 1.03 (s, 9H), 0.91 – 0.84 (m, 15H), 0.30 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 155.5, 154.1, 147.1, 136.8, 129.0, 128.4, 127.9 (×2), 127.2, 123.6, 105.8, 105.5, 66.5, 55.3, 55.1, 29.1, 27.3, 25.9, 18.3, 13.7, 9.5, -3.9, -4.1; HRMS (ESI-TOF) *m/z* calcd for $C_{36}H_{59}NO_4NaSiSn$ [$(M+Na)^+$] 740.3133; found: 740.3121; FTIR (film) ν: 3333, 3032, 2926, 1709, 1605, 1495, 1462, 1288, 1233, 1045, 833, 777 cm^{-1}.

Step 2: SI-78 (4.04 g, 5.64 mmol) was dissolved in CH_2Cl_2 (30 mL) and cooled down to 0 °C, followed by addition of NBS (1.0 g, 5.64 mmol) in one portion. The reaction mixture was stirred at rt for 45 min. Next, sat. aqueous $NaHCO_3$ was added and layers were separated. Aqueous layer was washed with CH_2Cl_2 twice. The combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The crude residue was purified by a silica gel column chromatography (10-15% AcOEt in hexanes) to yield 2.54 g (5.00 mmol, 89% yield) of **SI-79** as a colourless oil. $[\alpha]_D^{25}$ -9.4 (*c* 0.90, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 5H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.50 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 6.40 (dd, *J* = 13.6, 5.3 Hz, 1H), 6.13 (d, *J* = 13.6 Hz, 1H), 5.62 (s, 1H), 5.49 – 5.43 (m, 1H), 5.12 (s, 2H), 3.77 (s, 3H), 1.04 (s, 9H), 0.33 (s, 3H), 0.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 13C NMR (101 MHz, CDCl3) δ 160.3, 155.3, 154.1, 137.6, 136.5, 129.3, 128.5, 128.1, 128.0, 121.6, 107.6, 106.0, 105.7, 66.8, 55.3, 53.5, 25.9, 18.3, -3.8, -4.2; HRMS (ESI-TOF) *m/z* calcd for $C_{24}H_{32}NO_4NaSiBr$ [$(M+Na)^+$] 528.1182; found: 528.1187; FTIR (film) ν: 3318, 3032, 2957, 1707, 1605, 1497, 1464, 1288, 1234, 1043, 833, 777 cm^{-1}.

5.6.5. Suzuki coupling and phenol deprotection/protection



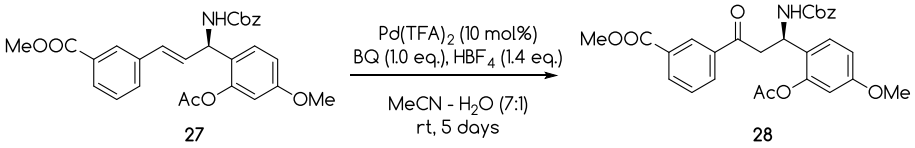
Step 1: $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (22.0 mg, 26.9 μmol), 3-(methoxycarbonyl)-phenylboronic acid (969 mg, 5.39, 2 eq.), **SI-79** (1.0 g, 2.69 mmol), K_3PO_4 (2.86 g, 13.4 mmol) were placed in the microwave vessel. The resulting mixture was degassed and backfilled with argon three times. Degassed dioxane (15 mL) and degassed water (1.5 mL) were added sequentially and then the mixture was heated at a microwave reactor at 100 °C (250 W) for 45 min. Next, the reaction mixture was concentrated and the crude mixture was purified by a column chromatography on silica gel (20% AcOEt in hexanes) to yield 1.23 g (2.19 mmol, 81% yield) of **SI-80** as a colourless oil. $[\alpha]_D^{25}$ –16.2 (*c* 0.78, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.27 (m, 6H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.51 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.47 – 6.43 (m, 3H), 5.69 – 5.58 (m, 2H), 5.14 (s, 2H), 3.91 (s, 3H), 3.78 (s, 3H), 1.01 (s, 9H), 0.31 (s, 3H), 0.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 160.1, 155.5, 154.2, 137.2, 136.7, 131.5, 130.8, 130.5, 129.4, 129.0(×2), 128.54(×2), 128.45, 128.0, 127.5, 122.9, 105.9, 105.7, 66.7, 55.3, 53.0, 52.1, 25.8, 18.3, –3.8, –4.1; HRMS (ESI-TOF) *m/z* calcd for $C_{32}H_{39}NO_6NaSi$ $[(M+Na)^+]$ 584.2444; found: 584.2449; FTIR (film) ν: 3339, 3033, 2951, 1720, 1605, 1496, 1455, 1291, 1235, 1109, 1042, 968, 835, 777 cm^{-1}.

Step 2: SI-80 (1.22 g, 2.17 mmol) was dissolved in anhydr. THF (11 mL) and cooled down to 0 °C, followed by dropwise addition of TBAF (1M solution in THF, 2.4 mL, 2.4 mmol) and stirred at rt for 2 h. Next, sat. aqueous NH_4Cl was added and layers were separated. Aqueous layer was washed with Et_2O three times. Combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The crude residue **SI-81** was used in the next step without further purification.

Step 3: Crude **SI-81** (2.17 mmol) was dissolved in anhydr. CH_2Cl_2 (22 mL), followed by addition of Et_3N (286 mg, 0.39 mL, 2.82 mmol) and cooled down to 0 °C. Next, AcCl (196 mg, 0.18 mL, 2.50 mmol) and stirred at rt overnight. Next, sat. aqueous NH_4Cl was added and layers were separated. Aqueous layer was washed with CH_2Cl_2 twice. Combined organic layers were dried over anhydr. Na_2SO_4, filtered and evaporated. The crude residue was purified by a silica gel column chromatography (25% AcOEt in hexanes) to give 965 mg (1.97 mmol, 91% yield) of **27** as a white solid, m.p. 121.1–123.1 °C; $[\alpha]_D^{25}$ –19.3 (*c* 0.58, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.90 (d, *J* = 7.7 Hz, 1H),

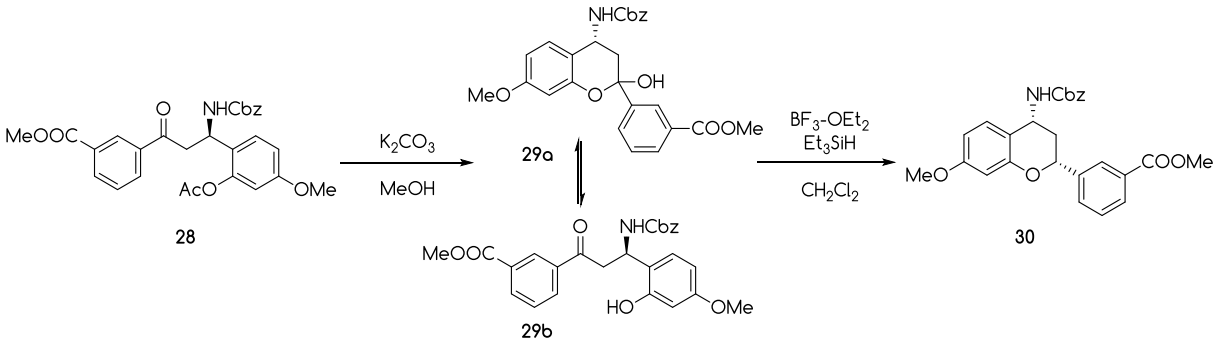
7.51 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.29 (m, 6H), 7.25-7.23 (m, 1H), 6.78 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.38 (dd, *J* = 16.0, 4.3 Hz, 1H), 5.65 (s, 1H), 5.21 – 5.09 (m, 3H), 3.91 (s, 3H), 3.79 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 166.9, 160.1, 155.5, 149.4, 136.8, 136.4, 130.8, 130.6, 130.1, 129.3, 129.2, 128.72, 128.68, 128.5, 128.2 (×2), 127.6, 124.4, 112.2, 109.2, 67.0, 55.5, 52.1, 51.7, 20.9; HRMS (ESI-TOF) *m/z* calcd for $C_{28}H_{27}NO_7Na$ [(M+Na)$^+$] 512.1685; found: 512.1682; FTIR (film) ν: 3321, 3033, 2951, 1725, 1605, 1496, 1454, 1291, 1233, 1109, 1042 cm^{-1}.

5.6.6. Wacker oxidation of allylamine 28



Compound **34** (955 mg, 1.95 mmol), benzoquinone (211 mg, 1.95 mmol) and $Pd(TFA)_2$ (65 mg, 0.19 mmol) were dissolved in MeCN (9.2 mL) and water (1.4 mL), followed by addition of HBF_4 (48% solution in water, 2.73 mmol, 0.36 mL). The resulting solution was stirred at rt for 5 days. $CHCl_3$ and sat. aqueous NaCl were added and layers were separated. Aqueous layer was washed with $CHCl_3$ three times. Combined organic layers were dried over Na_2SO_4, filtered and evaporated. The crude residue was purified by a silica gel column chromatography (30–50% AcOEt in hexanes) to give 504 mg (1.00 mmol, 51% yield) of **28** as a white solid, m.p. 143.8–145.4 °C; $[\alpha]_D^{25}$ –65.3 (*c* 0.67, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.19 (d, *J* = 7.7 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.35 – 7.25 (m, 6H), 6.73 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.62 (d, *J* = 2.3 Hz, 1H), 5.65 (d, *J* = 7.9 Hz, 1H), 5.47 – 5.41 (m, 1H), 5.05 (s, 2H), 3.92 (s, 3H), 3.74 (s, 3H), 3.65 – 3.58 (m, 1H), 3.42 (d, *J* = 11.7 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 169.4, 166.1, 159.7, 155.5, 148.8, 136.9, 136.4, 134.1, 132.3, 130.8, 129.2, 128.9(×2), 128.4(×2), 128.0, 124.9, 112.3, 108.7, 66.8, 55.5, 52.4, 46.3, 43.4, 20.9; HRMS (ESI-TOF) *m/z* calcd for $C_{28}H_{27}NO_8Na$ [(M+Na)$^+$] 528.1634; found: 528.1630; FTIR (film) ν: 3330, 3032, 2962, 1722, 1692, 1604, 1496, 1438, 1292, 1261, 1236, 1200, 1122, 1036 cm^{-1}.

5.6.7. Cyclisation and diastereoselective reduction of amino ketone 28



Step 1: Compound **28** (495 mg, 0.98 mmol) was dissolved in MeOH (10 mL), followed by addition of K_2CO_3 (271 mg, 1.96 mmol). The resulting mixture was stirred at rt for 90 min. DCM and water were added and layers were separated. Aqueous layer was washed with DCM three times. Combined organic layers were dried over Na_2SO_4, filtered and evaporated. The crude residue was purified by a silica gel column chromatography (40–70% AcOEt in hexanes) to give 391 mg (0.84 mmol, 86% yield) of mixture of **29a/b** as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, mixture of tautomers, *keto*:*hemiacetal* 2:1) δ 8.55 (s, 1H), 8.40 (s, 1H), 8.30 (s, 0.5H), 8.17 – 7.98 (m, 2.5H), 7.85 – 7.76 (m, 0.5H), 7.48 – 7.42 (m, 1.5H), 7.38 – 7.25 (m, 8H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.58 – 6.43 (m, 1.5H), 6.34 – 6.23 (m, 3H), 5.48 – 5.40 (m, 1H), 5.15 – 4.97 (m, 3.5H), 3.89 (s, 4.5H), 3.73 (s, 1.5H), 3.63 – 3.51 (m, 5H), 2.38 (d, J = 14.5 Hz, 0.5H), 2.17 (dd, J = 14.5, 5.6 Hz, 0.5H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of tautomers) δ 198.2, 166.9, 166.2, 160.5, 160.1, 156.7, 155.1, 152.1, 144.0, 136.7, 136.2, 134.1, 132.4, 130.6, 130.4, 130.0, 129.9, 129.4, 128.9, 128.5, 128.2, 128.1, 128.0, 126.7, 119.3, 109.0, 105.5, 102.4, 102.2, 97.7, 67.2, 66.8, 55.3, 55.1, 52.4, 52.3, 43.5, 40.0; HRMS (ESI-TOF) *m/z* calcd for $C_{26}H_{25}NO_7Na$ [$(M+Na)^+$] 486.1529; found: 486.1521;

Step 2: Compounds **29a/b** (365 mg, 0.79 mmol) was dissolved in anhydr. DCM (8 mL) and cooled down to –78 °C. Next, Et_3SiH (1,9 mL, 1.37 g, 11.8 mmol) was added, followed by dropwise addition of $BF_3{\cdot}Et_20$ (0.39 mL, 0.47 g, 3.15 mmol). Reaction mixture was stirred at the same temperature for 1 h, allowed to warm to –30 °C and stirred for 3 h. Volatiles were evaporated and the residue was purified by a silica gel column chromatography (15–25% AcOEt in hexanes) to give 194 mg of **30** (0.43 mmol, 55% yield) as *trans* diastereoisomer (*dr* > 20:1, by ^{1}H NMR analysis of both crude and pure sample). White solid, m.p. 102.3–103.8 °C; $[\alpha]_D^{25}$ –15.3 (*c* 0.91, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.46

(t, *J* = 7.5 Hz, 1H), 7.38 – 7.30 (m, 5H), 7.20 (d, *J* = 8.5 Hz, 1H), 6.53 (d, *J* = 8.5 Hz, 1H), 6.47 (s, 1H), 5.24 – 5.11 (m, 4H), 4.91 (d, *J* = 8.9 Hz, 1H), 3.92 (s, 3H), 3.76 (s, 3H), 2.60 (dd, *J* = 12.4, 5.2 Hz, 1H), 2.00 – 1.88 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 160.4, 156.3, 156.0, 140.9, 136.3, 130.6, 130.5, 129.4, 128.7, 128.6, 128.2, 128.1, 127.8, 127.1, 114.9, 108.5, 101.6, 76.9, 67.0, 55.4, 52.2, 46.8, 37.9; HRMS (ESI-TOF) *m/z* calcd for $C_{26}H_{25}NO_6Na$ [$(M+Na)^+$] 470.1580; found: 470.1585; FTIR (film) ν: 3333, 3033, 2972, 1702, 1605, 1452, 1292, 1235, 1200, 1122, 1039 cm^{-1}.

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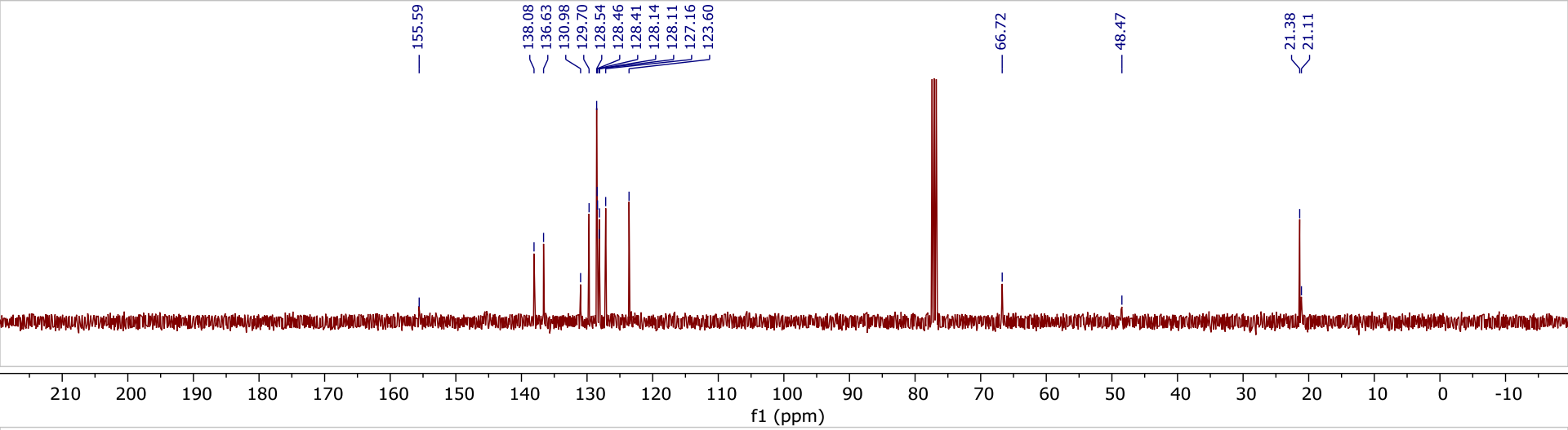
6. ^{1}H, ^{11}B, ^{13}C, ^{31}P NMR spectra and HPLC chromatograms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48.47
21.38
21.11
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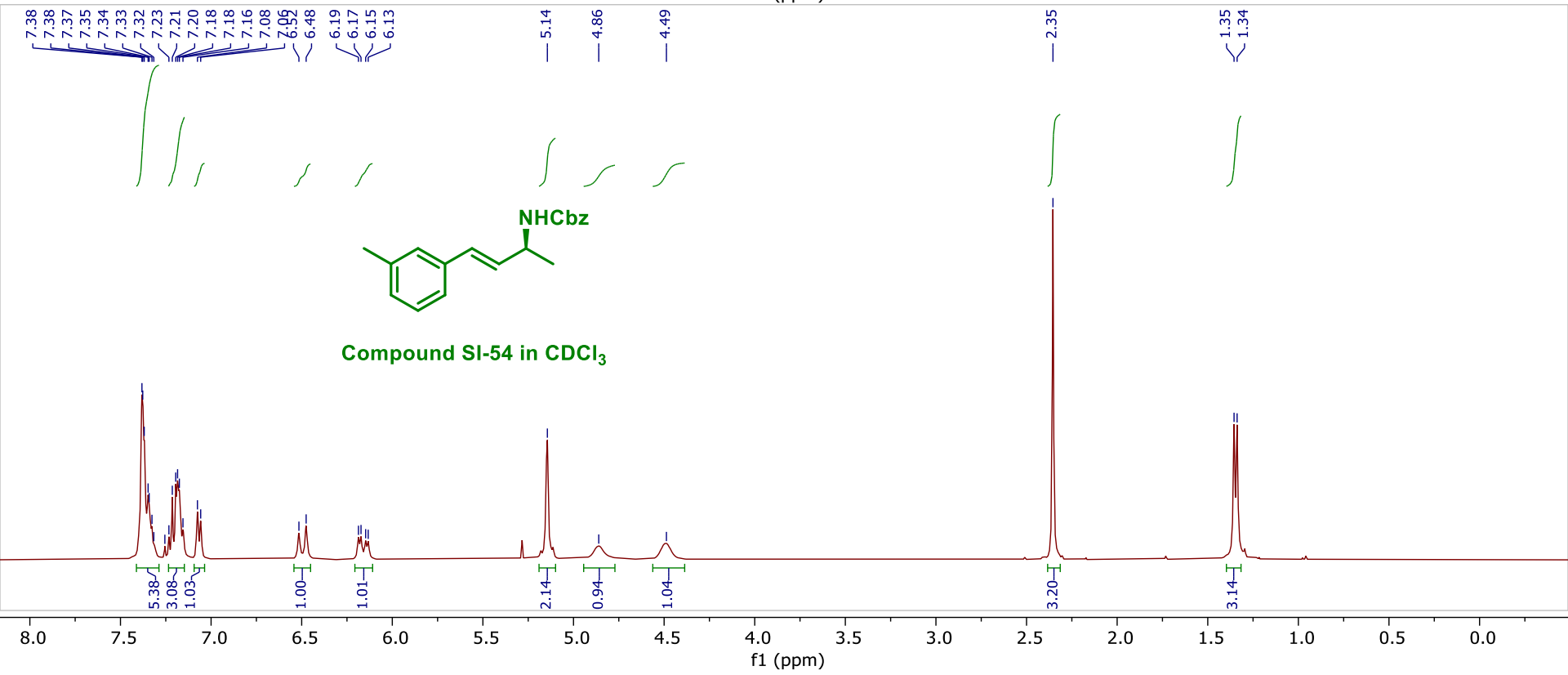
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7.34
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7.20
7.18
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7.16
7.08
7.06
6.52
6.48
6.19
6.17
6.15
6.13
5.14
4.86
4.49
2.35
1.35
1.34
NHCbz
Compound SI-54 in CDCl3
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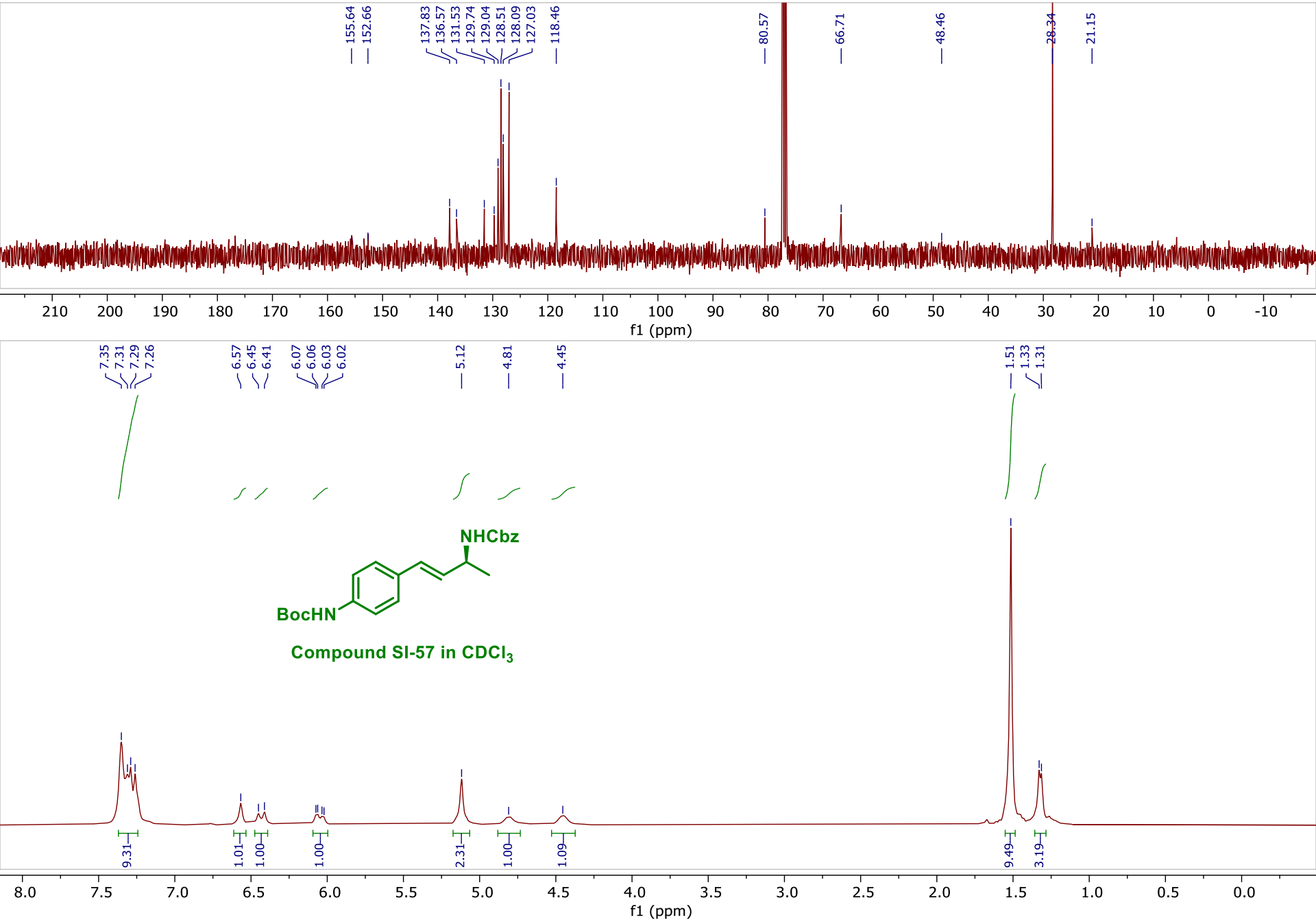
1.03
1.00
1.01
2.14
0.94
1.04
3.20
3.14
f1 (ppm)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66.71
48.46
28.34
21.15
f1 (ppm)
7.35
7.31
7.29
7.26
6.57
6.45
6.41
6.07
6.06
6.03
6.02
5.12
4.81
4.45
1.51
1.33
1.31
NHCbz
BocHN
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1.00
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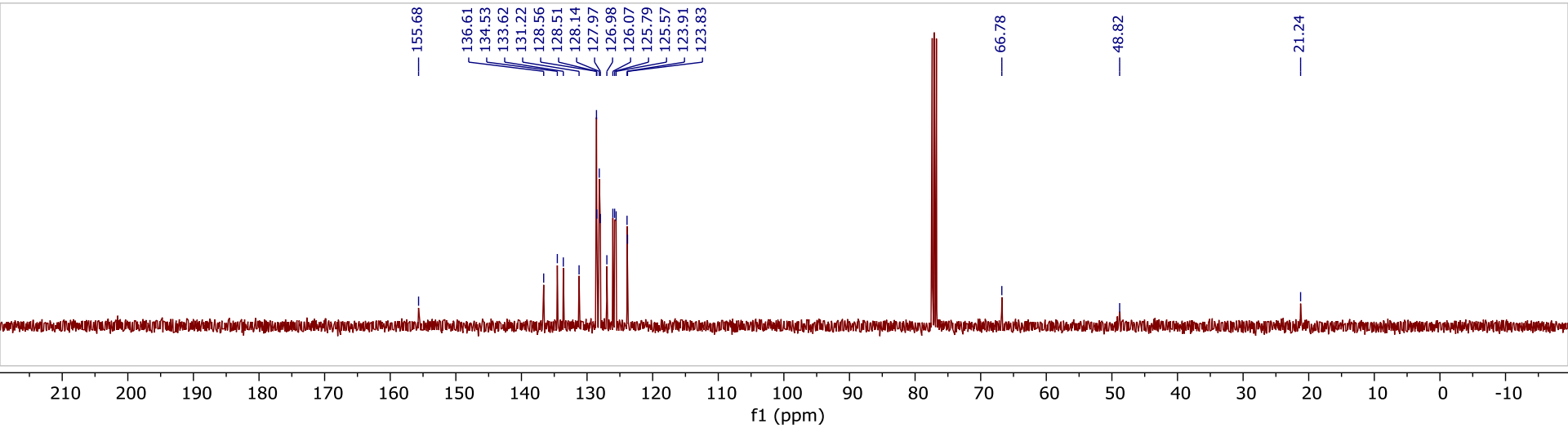
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128.14
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123.83
66.78
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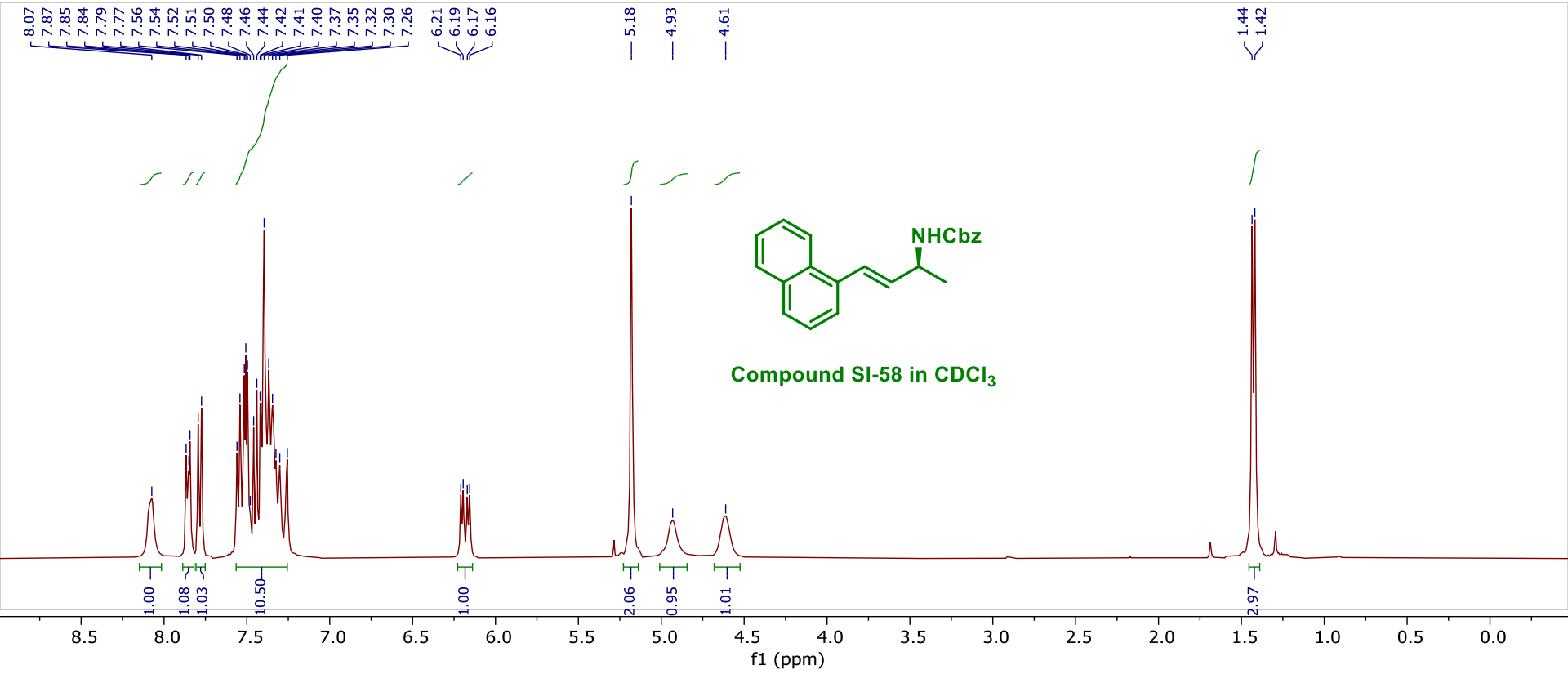
f1 (ppm)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7.44
7.42
7.41
7.40
7.37
7.35
7.32
7.30
7.26
6.21
6.19
6.17
6.16
5.18
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4.61
1.44
1.42
NHCbz
Compound SI-58 in CDCl3
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1.03
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1.00
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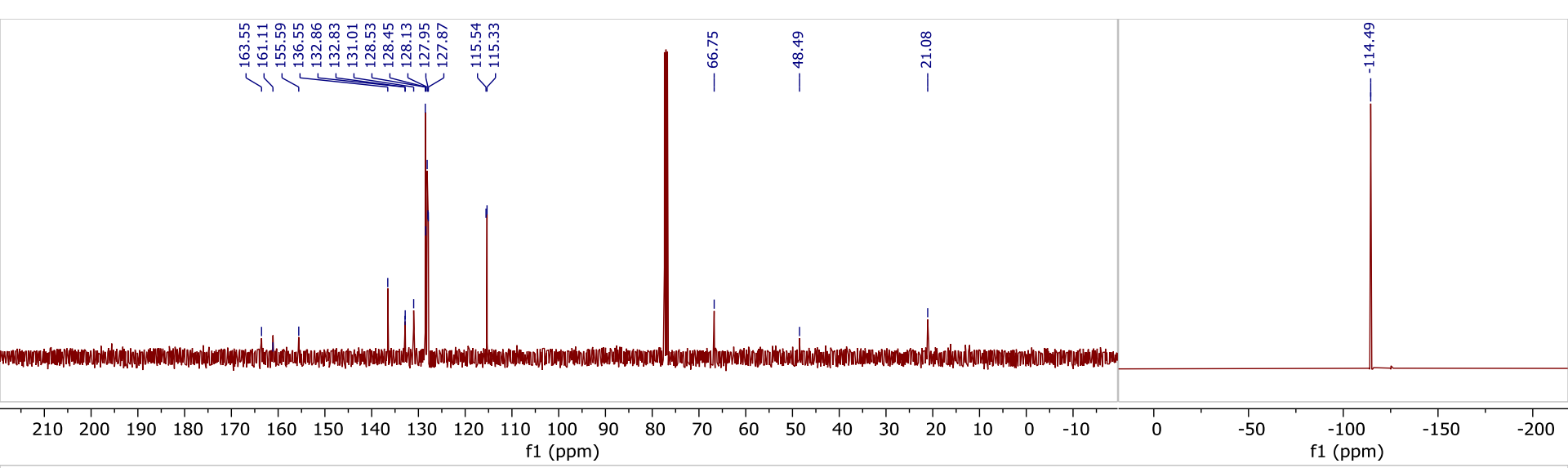
1.01
2.97
f1 (ppm)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136.55
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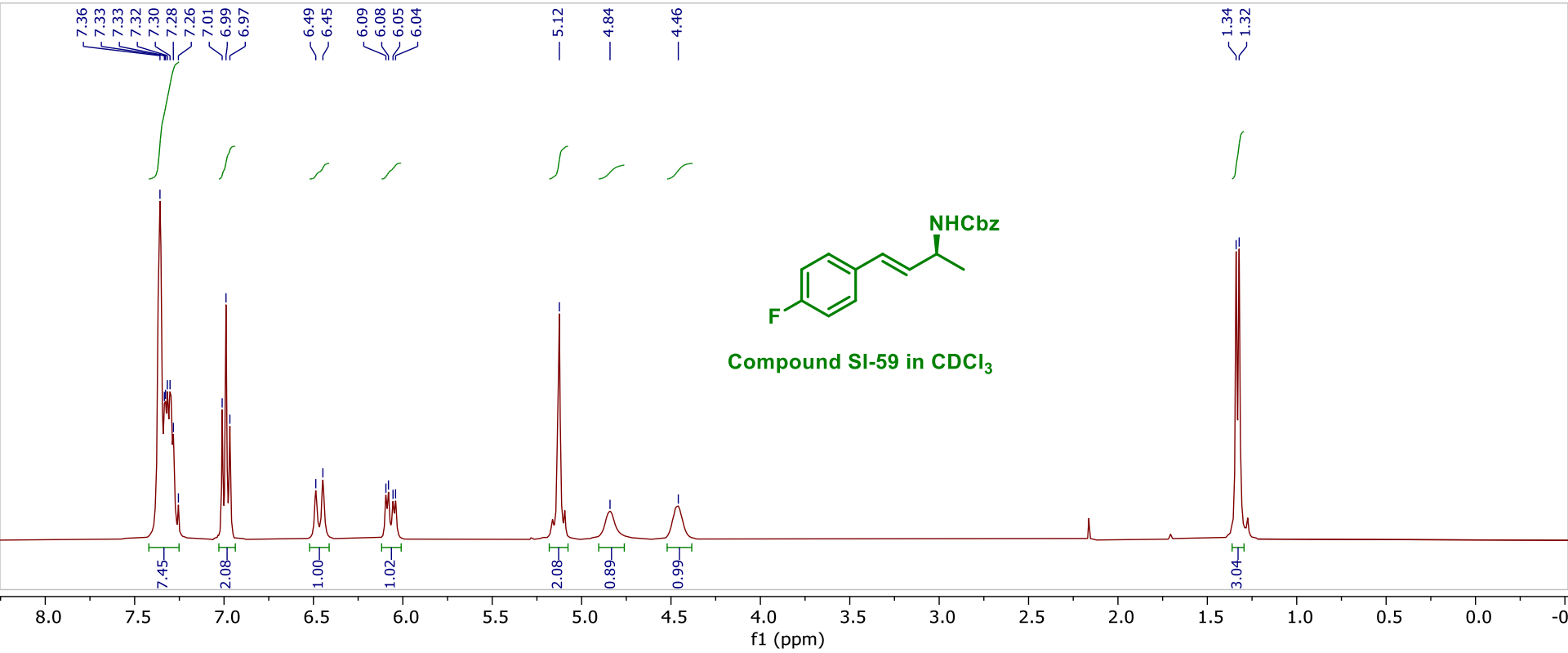
48.49
21.08
-114.49
f1 (ppm)
f1 (ppm)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6.49
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6.09
6.08
6.05
6.04
5.12
4.84
4.46
1.34
1.32
NHCbz
F
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2.08
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1.02
2.08
0.89
0.99
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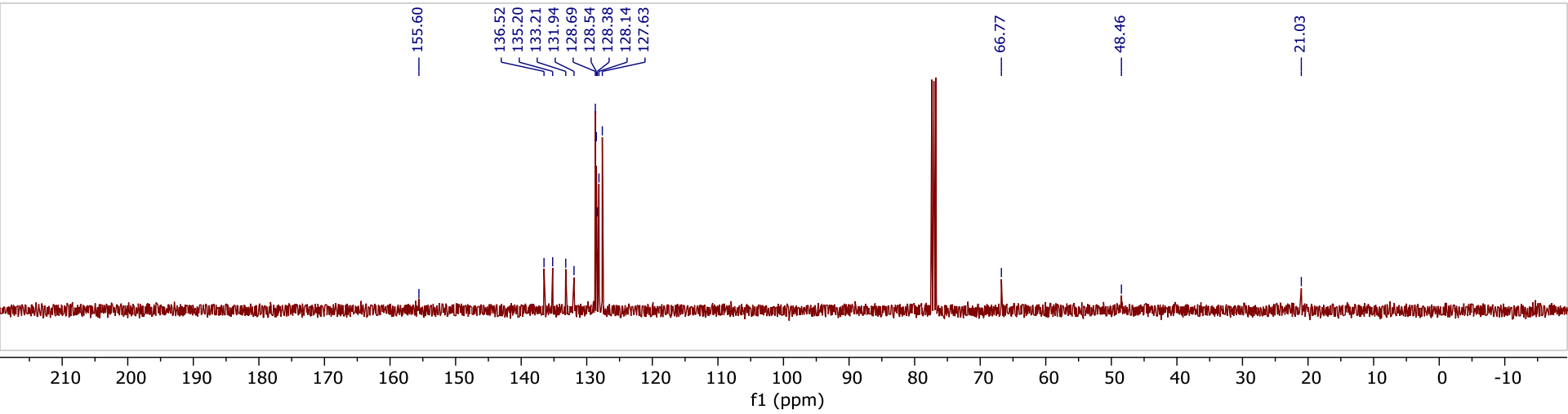
f1 (ppm)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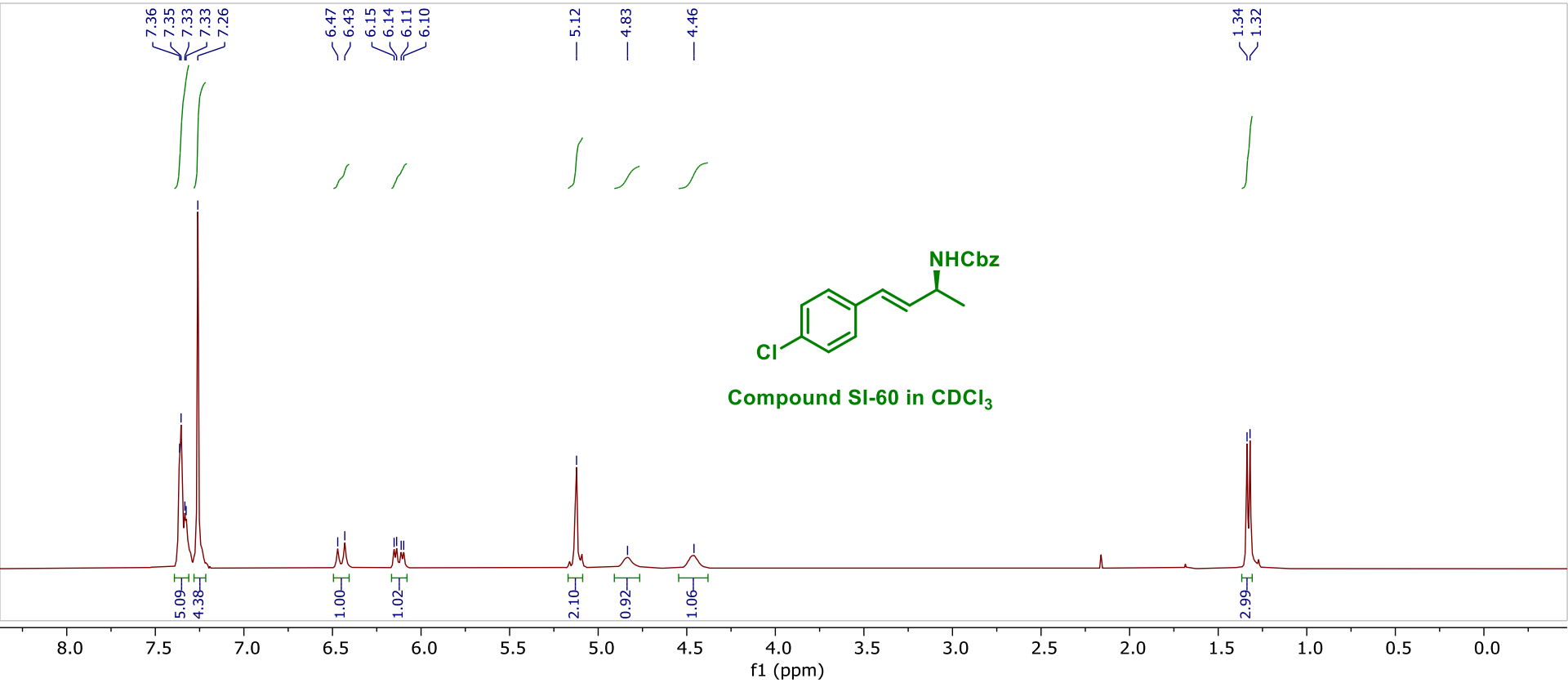
48.46
21.03
f1 (ppm)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6.47
6.43
6.15
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6.11
6.10
5.12
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4.46
1.34
1.32
NHCbz
Cl
Compound SI-60 in CDCl3
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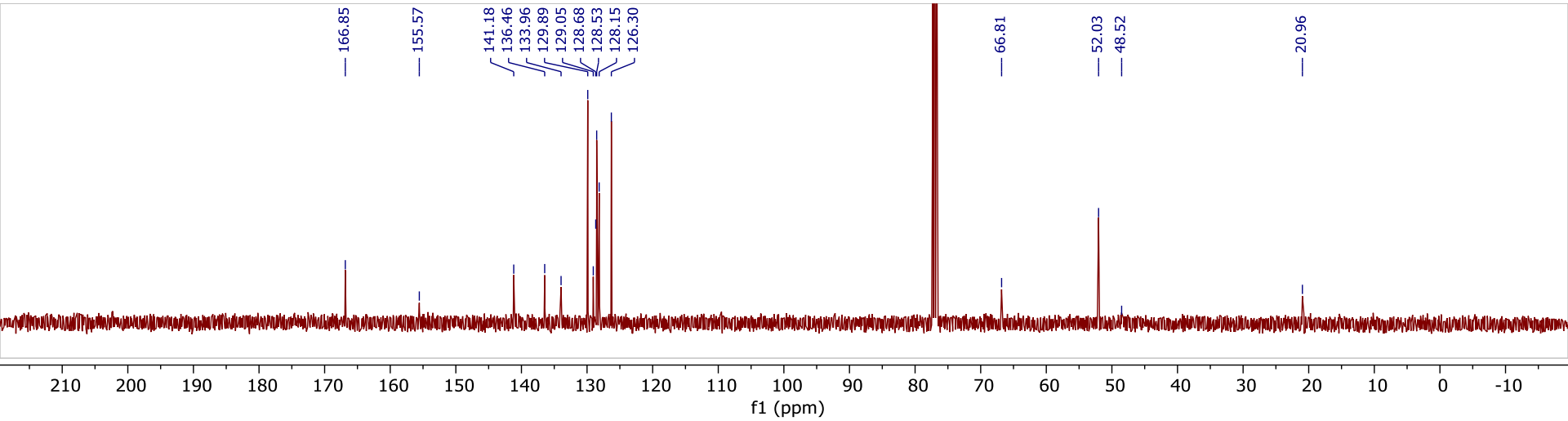
4.38
1.00
1.02
2.10
0.92
1.06
2.99
f1 (ppm)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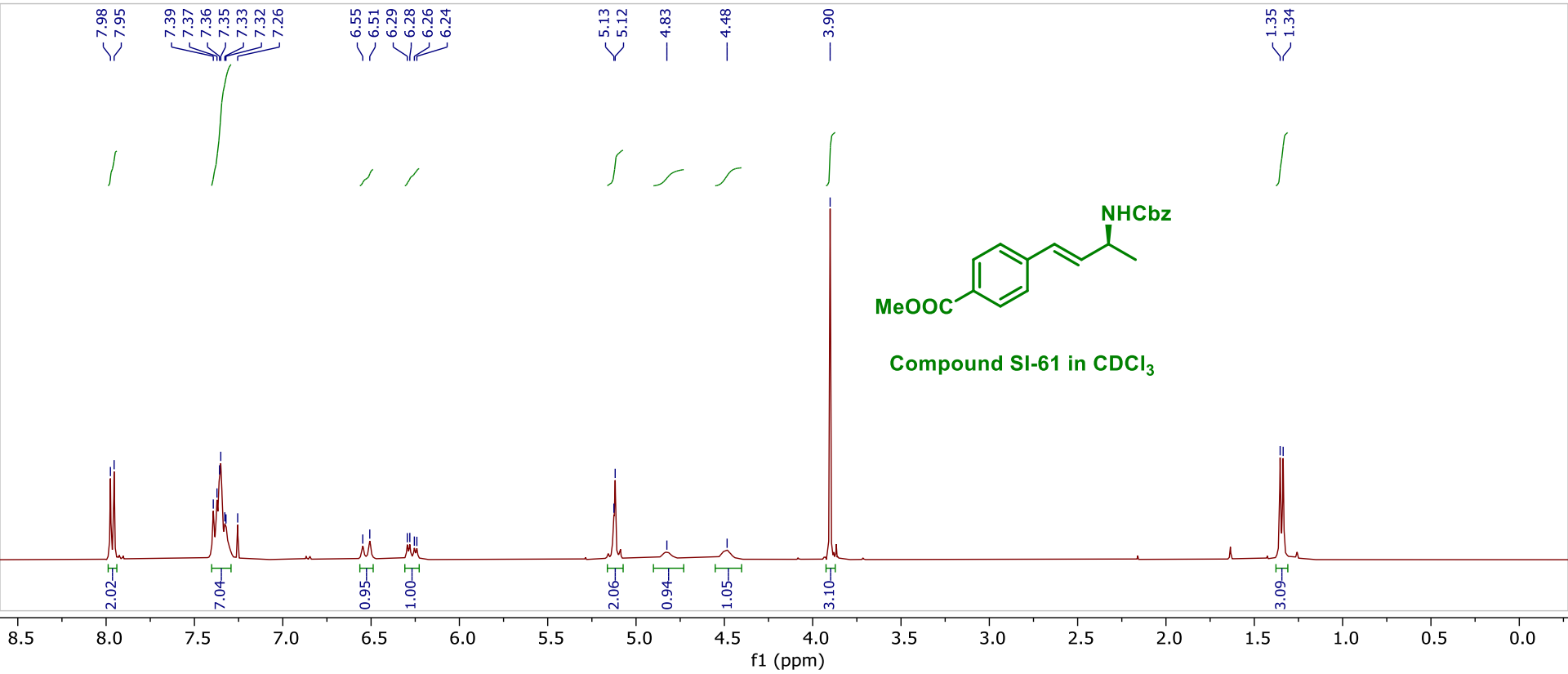
52.03
48.52
20.96
f1 (ppm)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5.12
4.83
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3.90
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MeOOC
Compound SI-61 in CDCl3
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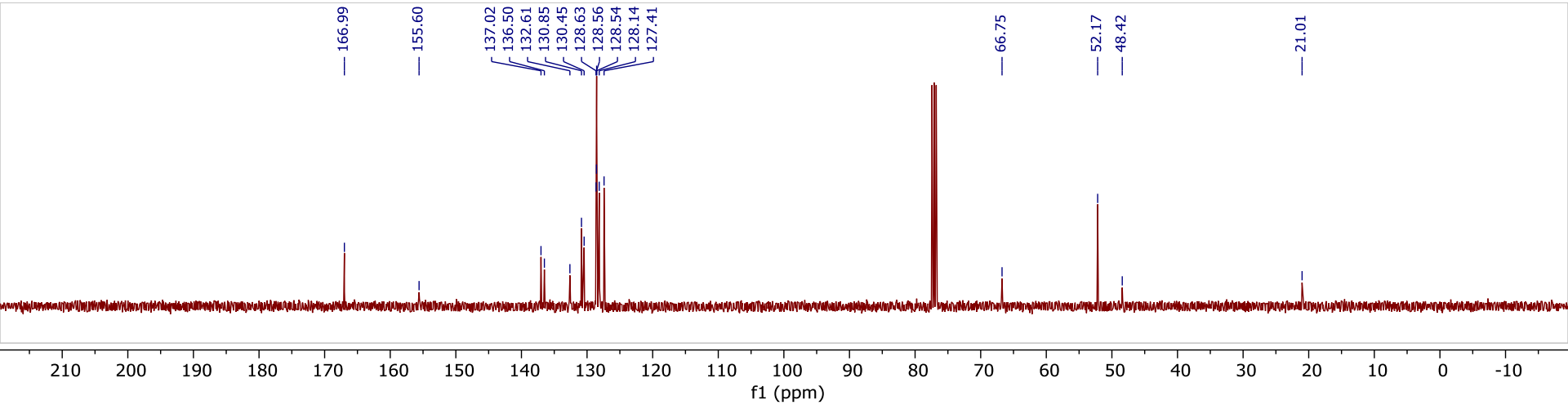
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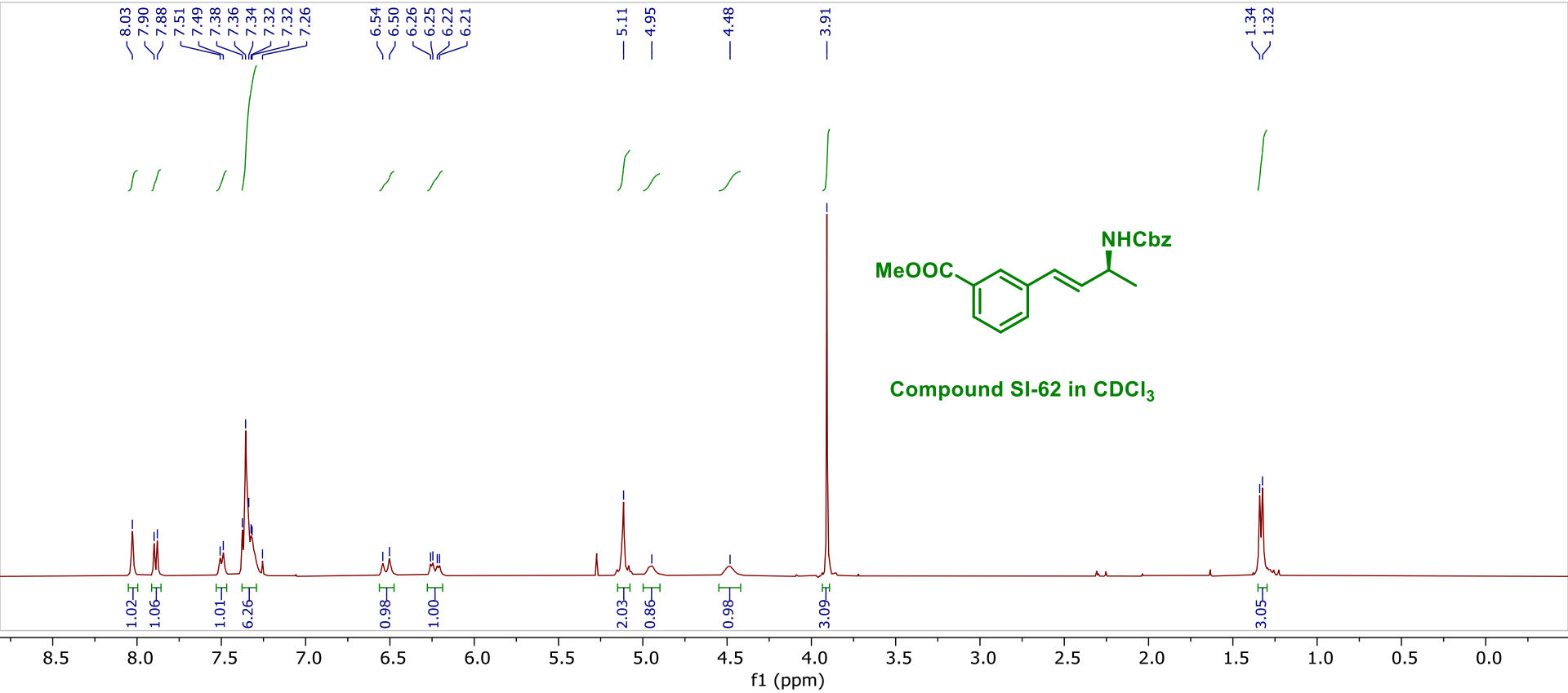
f1 (ppm)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7.34
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6.26
6.25
6.22
6.21
5.11
4.95
4.48
3.91
1.34
1.32
NHCbz
MeOOC
Compound SI-62 in CDCl3
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6.26
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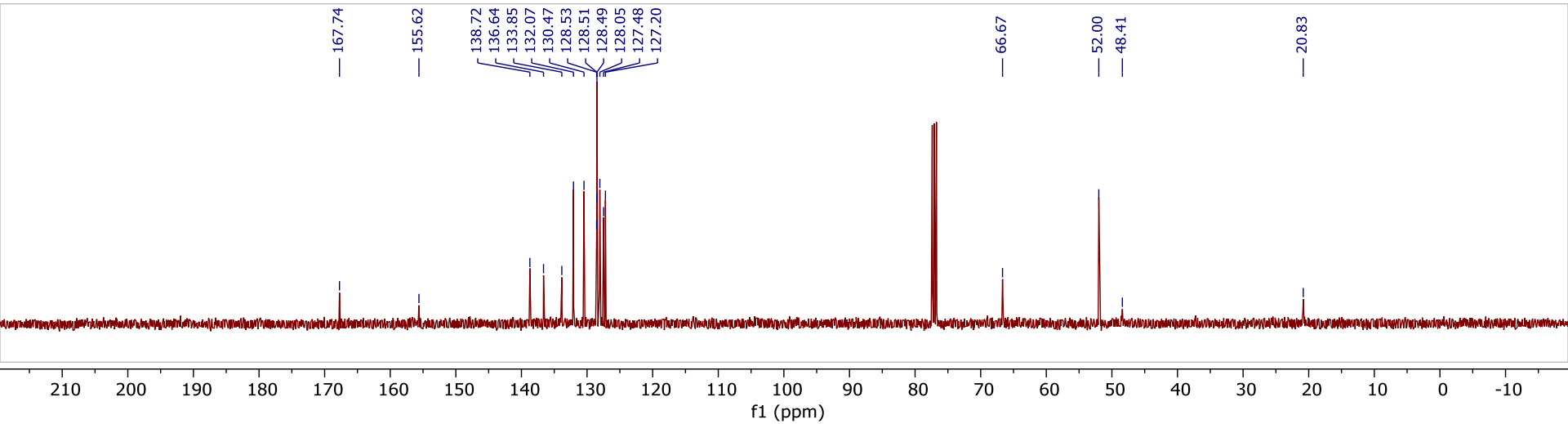
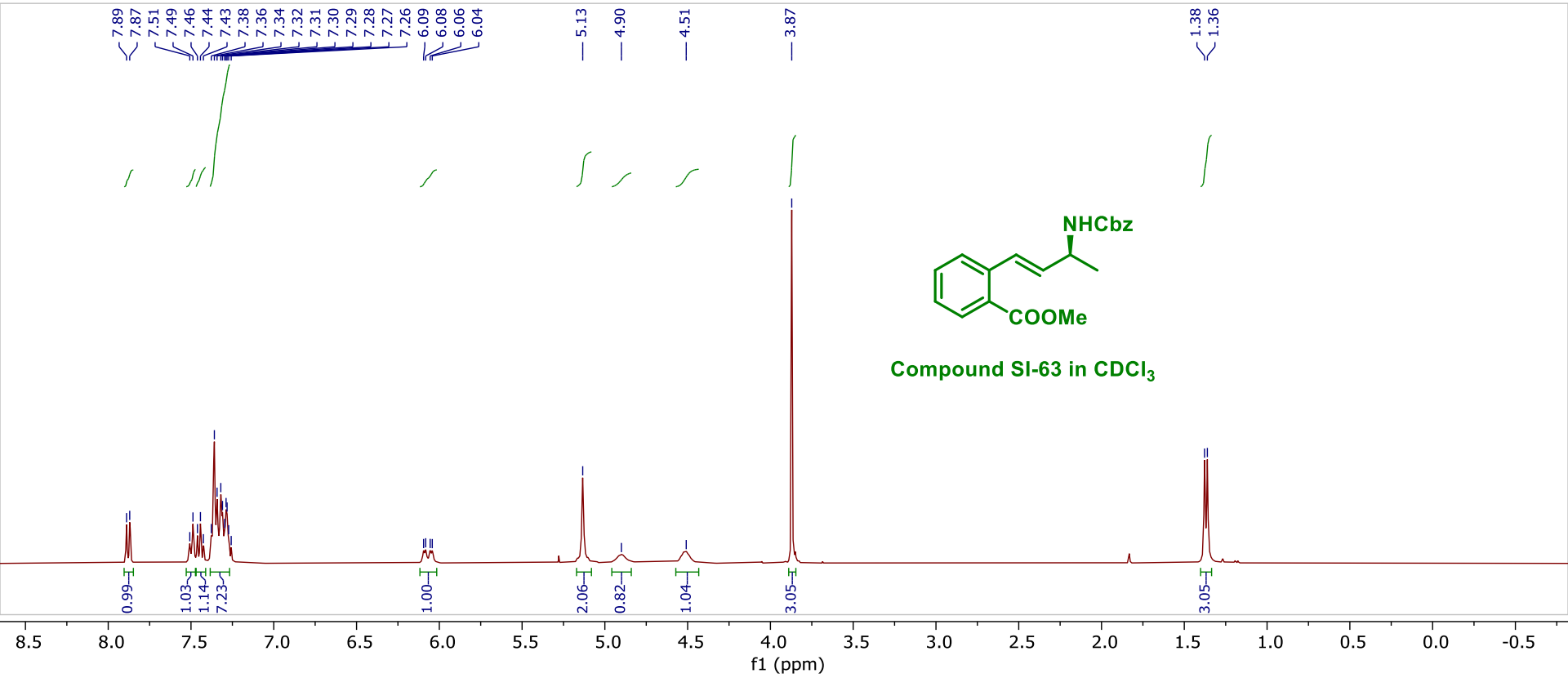
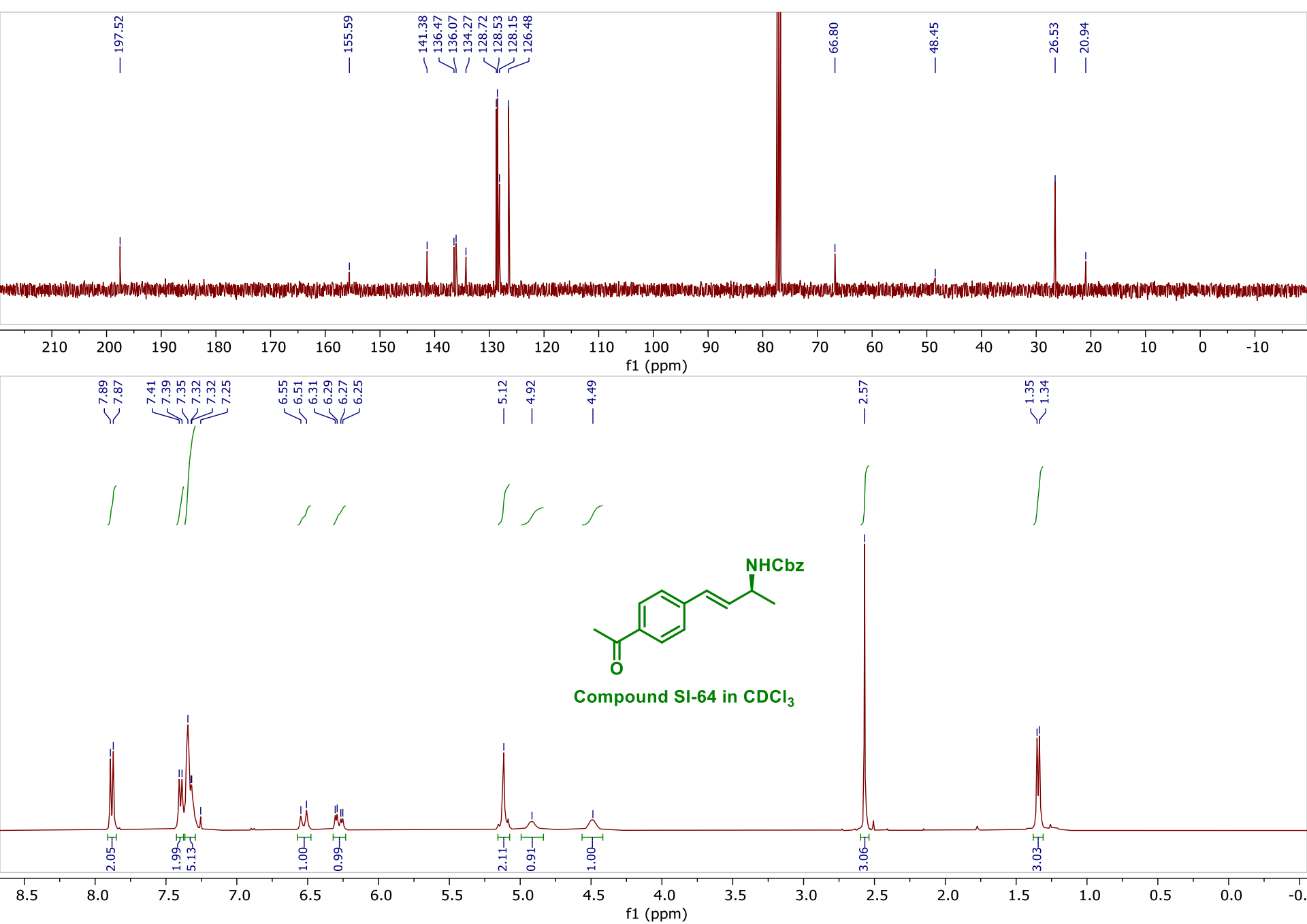




Compound SI-63 in $CDCl_3$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20.94
f1 (ppm)
7.89
7.87
7.41
7.39
7.35
7.32
7.32
7.25
6.55
6.51
6.31
6.29
6.27
6.25
5.12
4.92
4.49
2.57
1.35
1.34
NHCbz
O
Compound SI-64 in CDCl3
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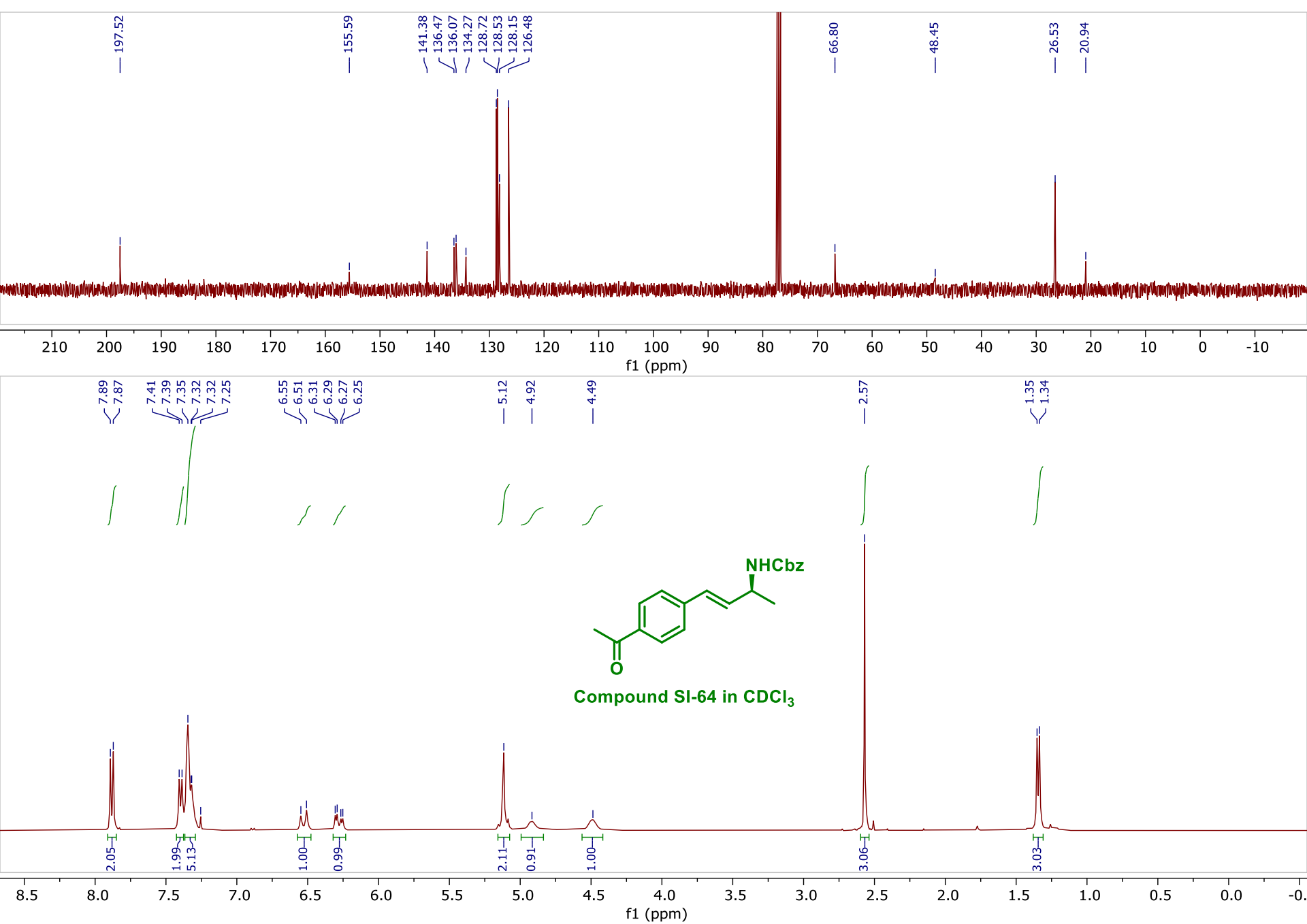
3.03
f1 (ppm)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26.53
20.94
f1 (ppm)
7.89
7.87
7.41
7.39
7.35
7.32
7.32
7.25
6.55
6.51
6.31
6.29
6.27
6.25
5.12
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4.49
2.57
1.35
1.34
NHCbz
O
Compound SI-64 in CDCl3
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2.11
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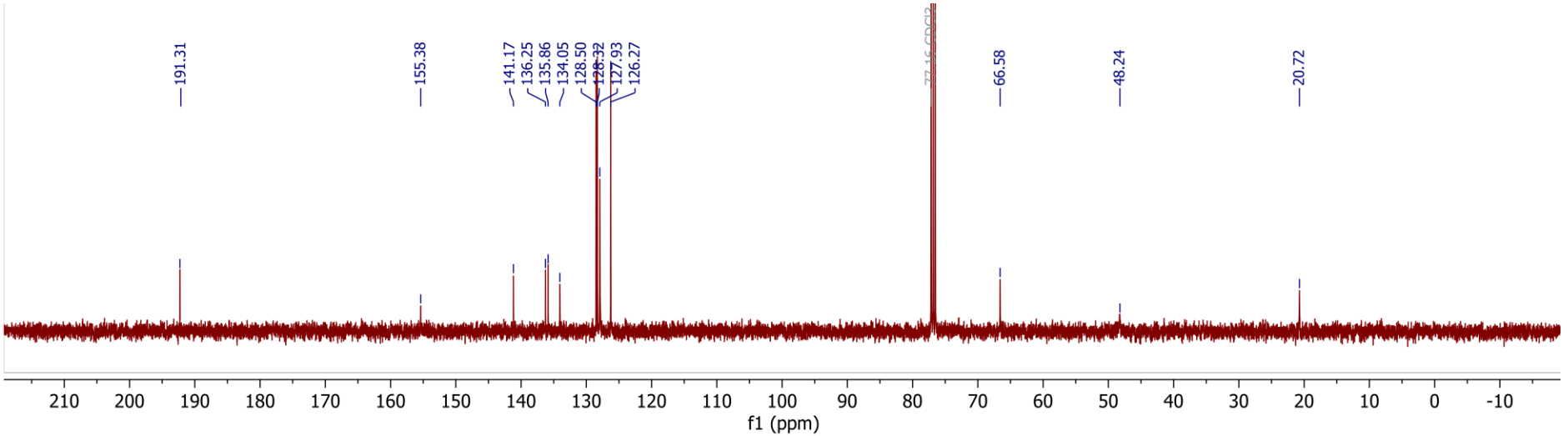
3.03
f1 (ppm)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128.32
127.93
126.27
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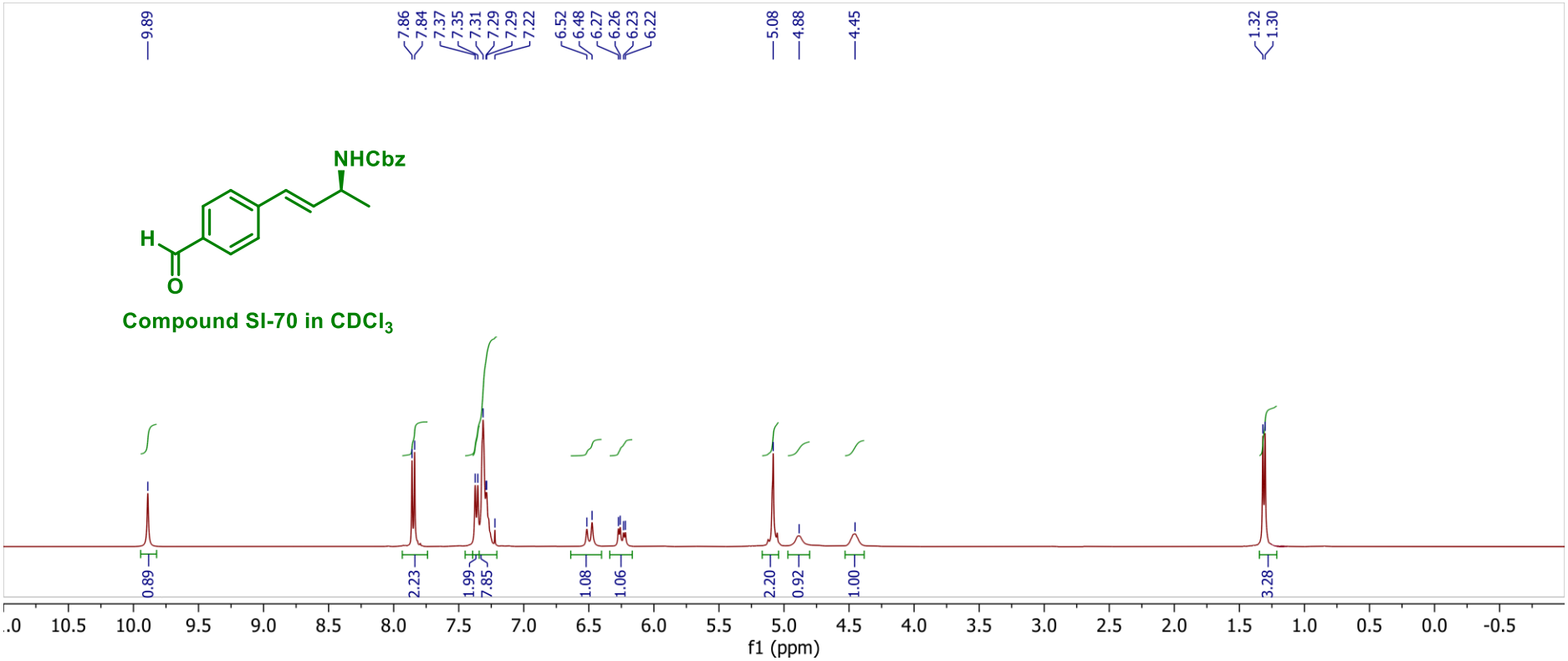
66.58
48.24
20.72
f1 (ppm)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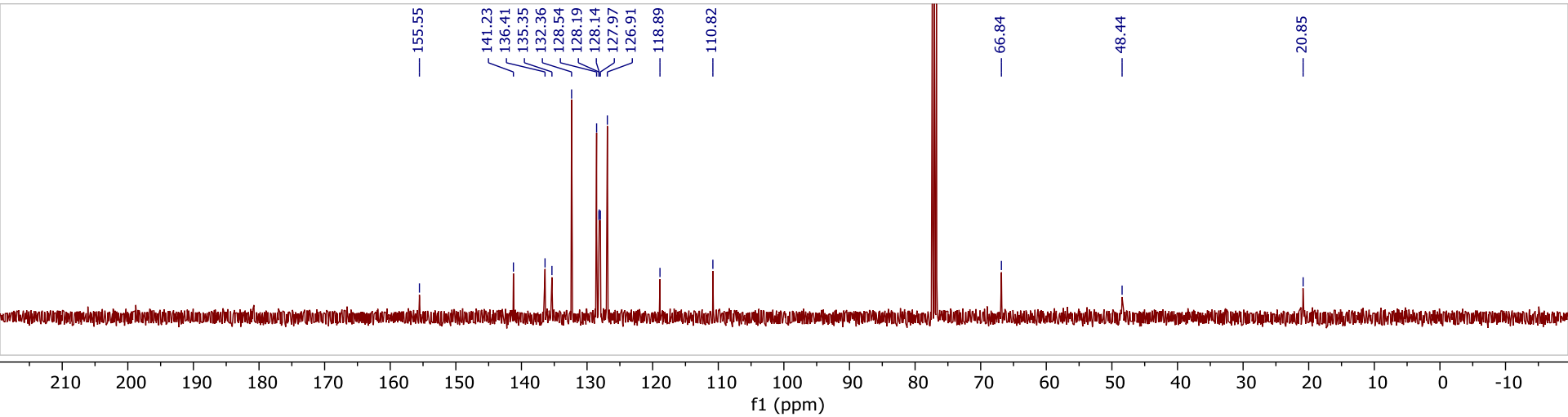
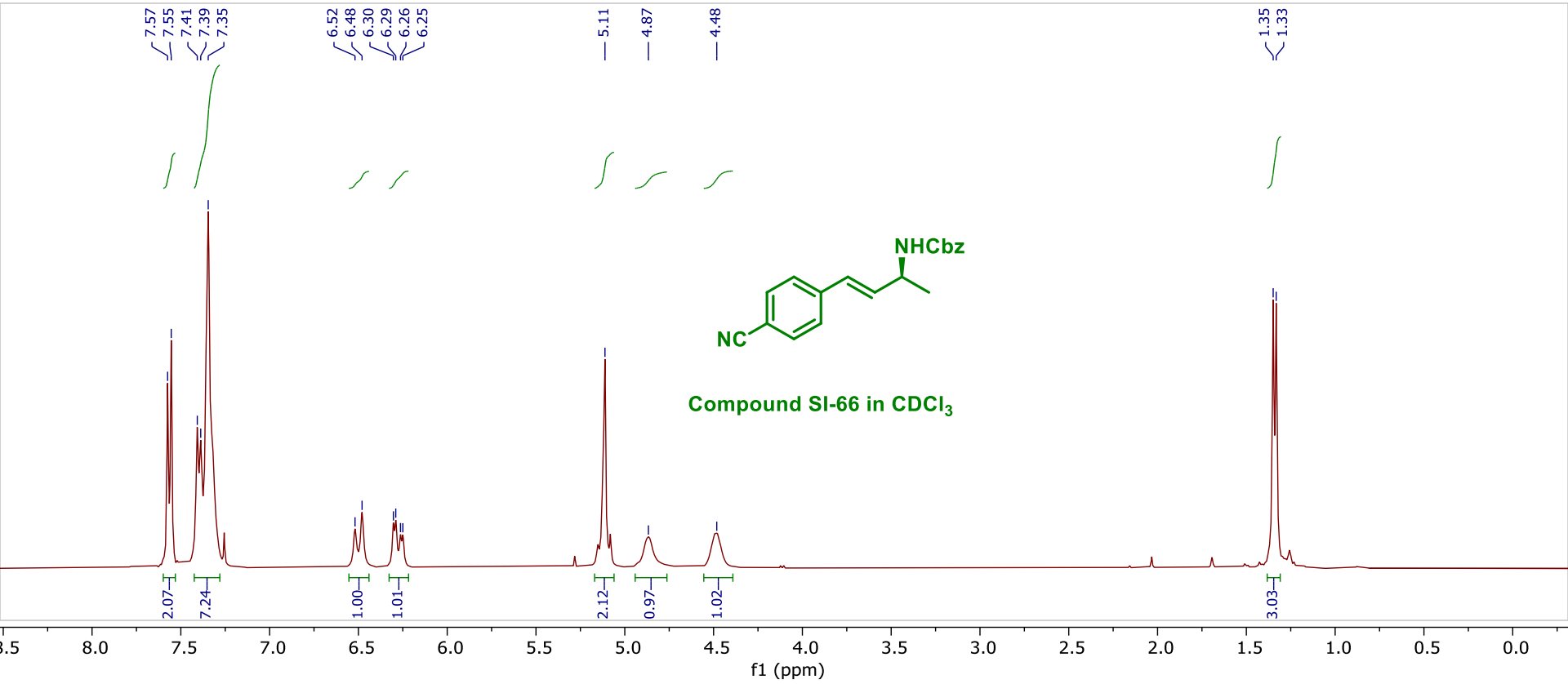
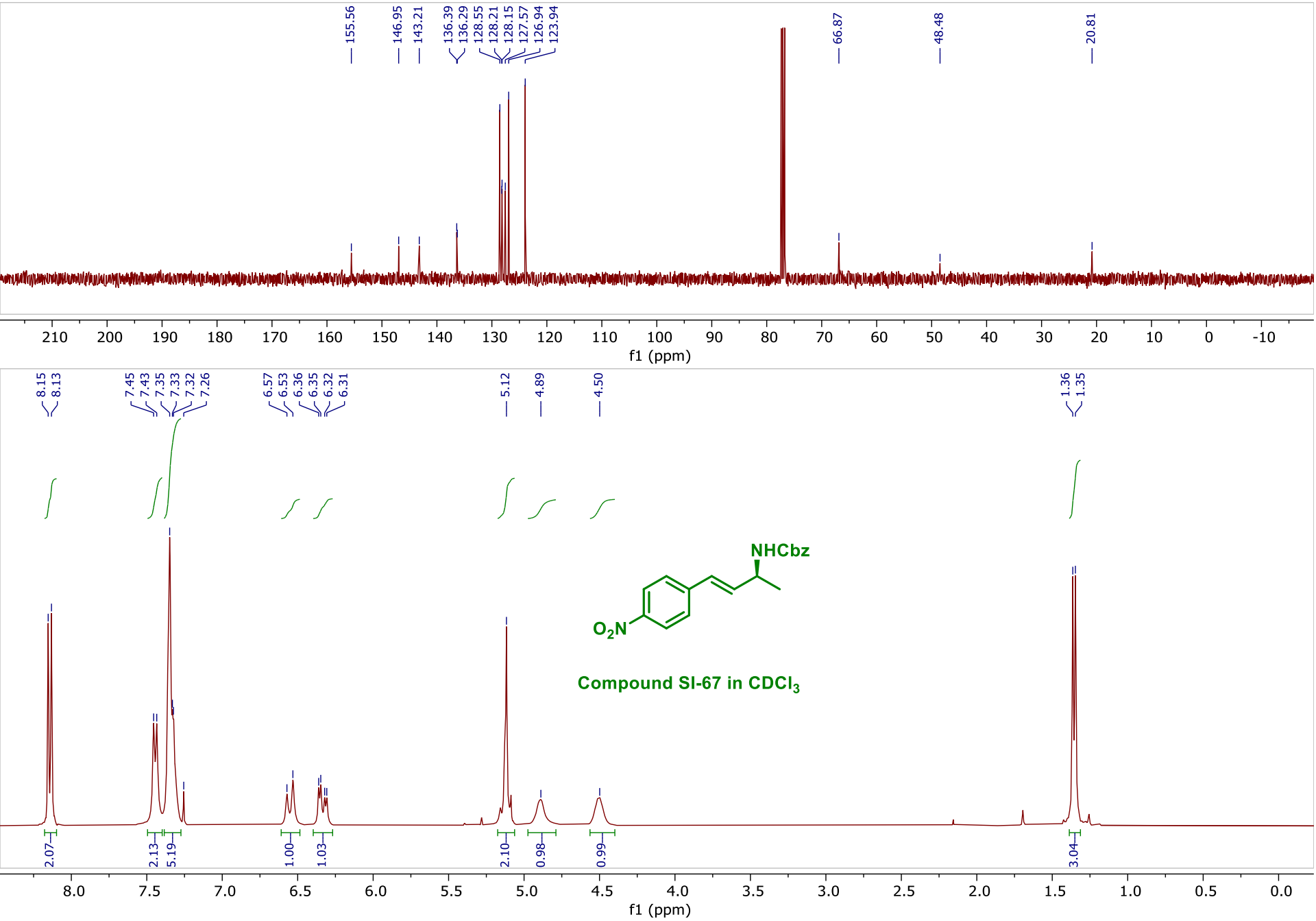
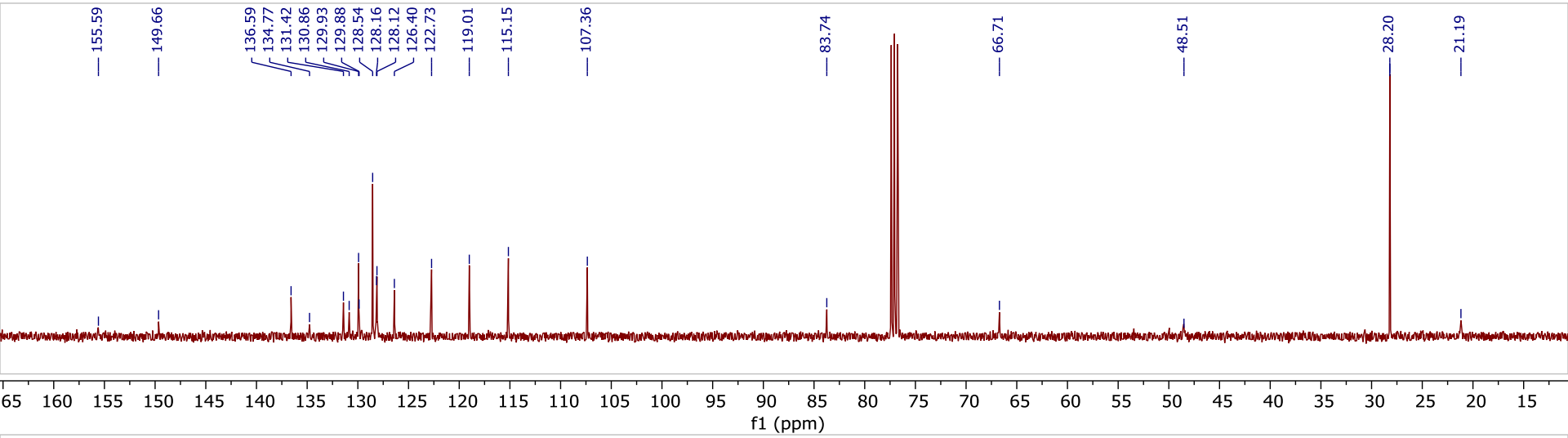
7.29
7.22
6.52
6.48
6.27
6.26
6.23
6.22
5.08
4.88
4.45
1.32
1.30
NHCbz
H
O
Compound SI-70 in CDCl3
0.89
2.23
1.99
7.85
1.08
1.06
2.20
0.92
1.00
3.28
f1 (ppm)


155.55
141.23
136.41
135.35
132.36
128.54
128.19
128.14
127.97
126.91
118.89
110.82
66.84
48.44
20.85
f1 (ppm)


7.57
7.55
7.41
7.39
7.35
6.52
6.48
6.30
6.29
6.26
6.25
5.11
4.87
4.48
1.35
1.33
NHCbz
NC
Compound SI-66 in CDCl3
2.07
7.24
1.00
1.01
2.12
0.97
1.02
3.03
f1 (ppm)


155.56
146.95
143.21
136.39
136.29
128.55
128.21
128.15
127.57
126.94
123.94
66.87
48.48
20.81
f1 (ppm)
8.15
8.13
7.45
7.43
7.35
7.33
7.32
7.26
6.57
6.53
6.36
6.35
6.32
6.31
5.12
4.89
4.50
1.36
1.35
NHCbz
O2N
Compound SI-67 in CDCl3
2.07
2.13
5.19
1.00
1.03
2.10
0.98
0.99
3.04
f1 (ppm)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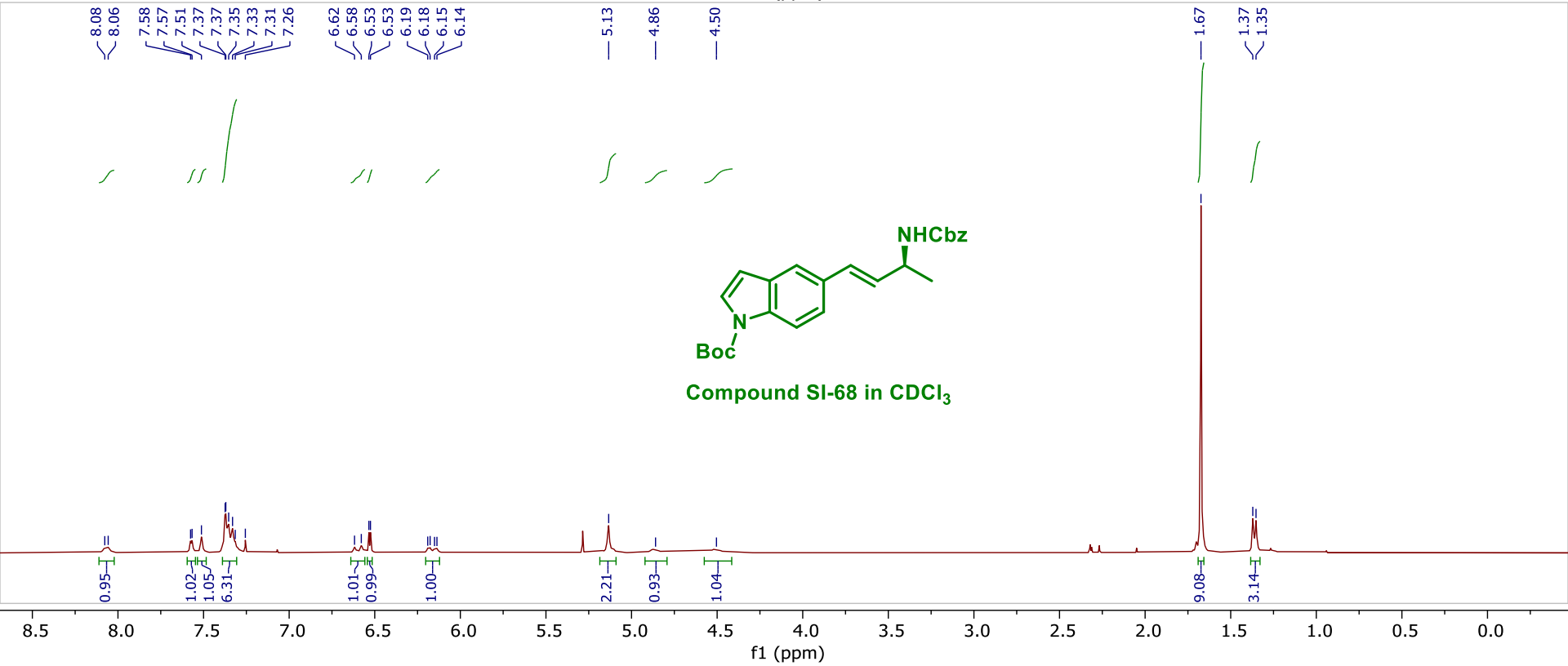
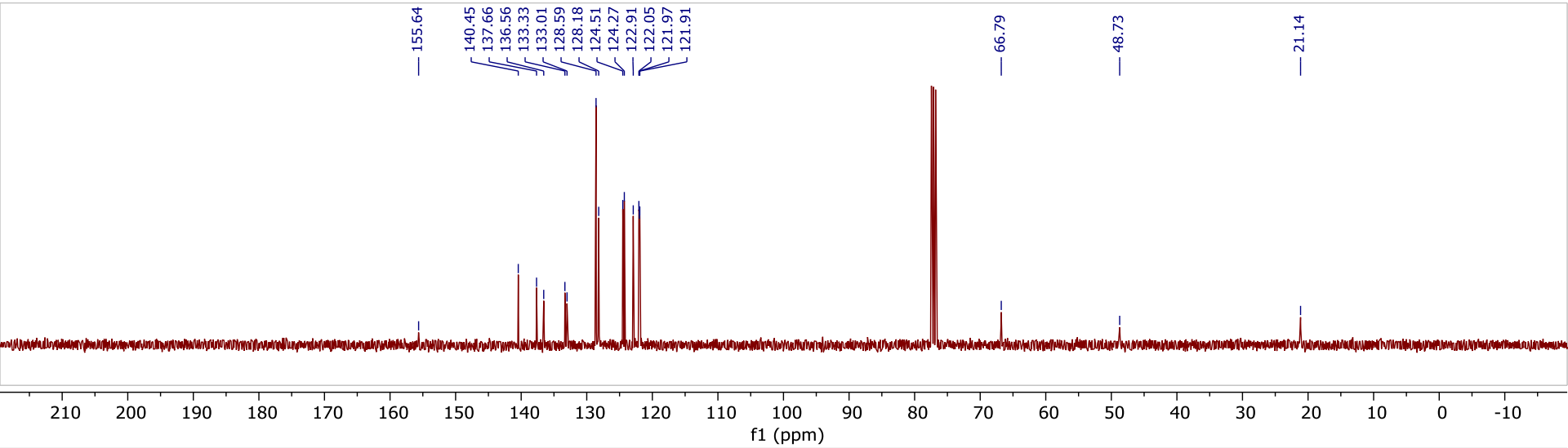
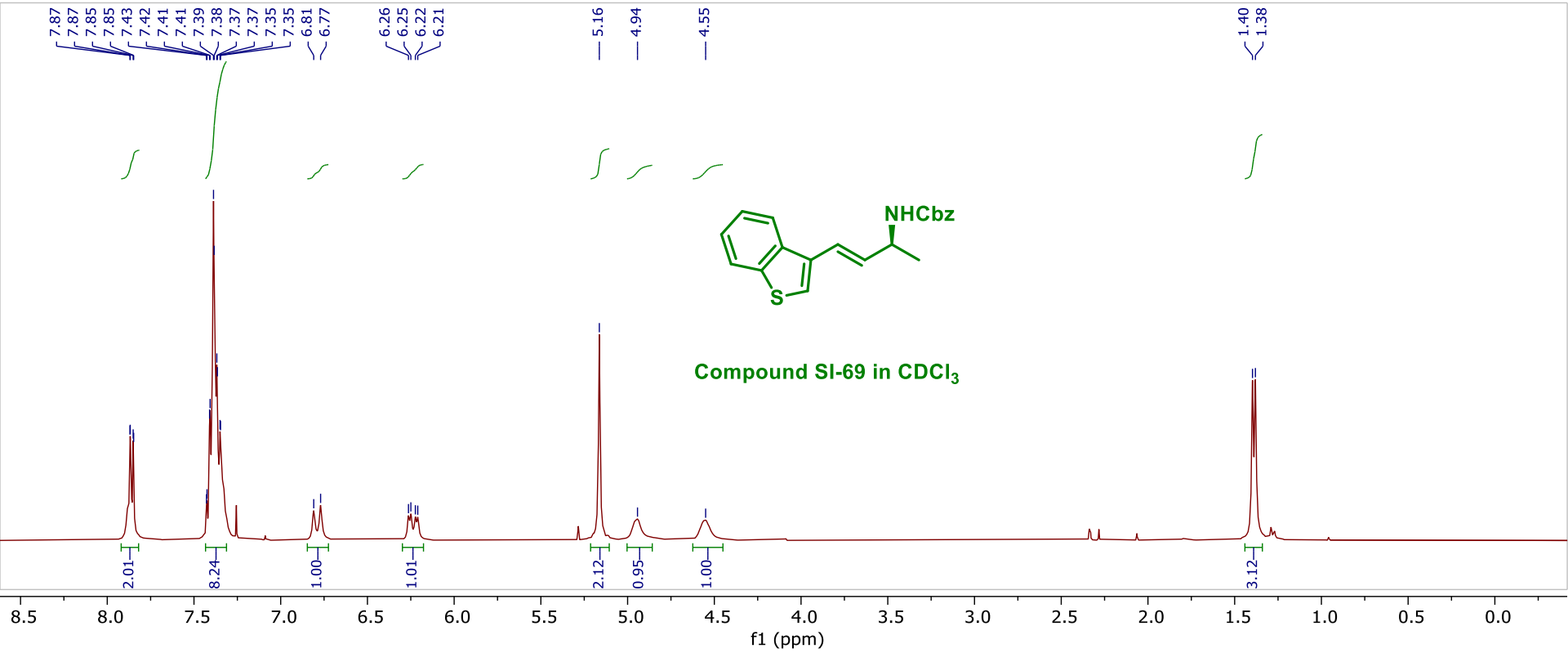
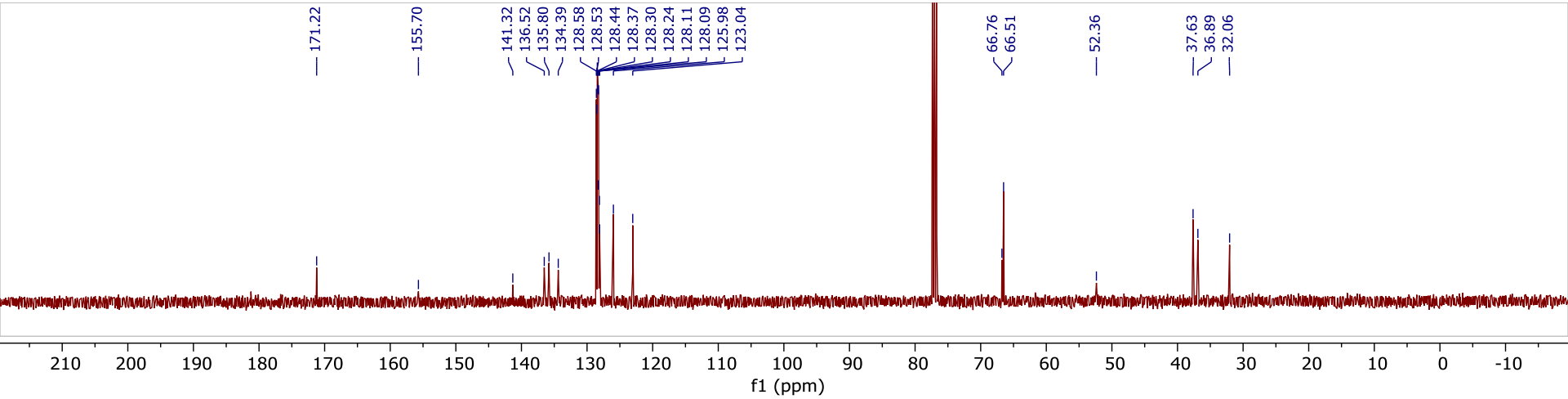
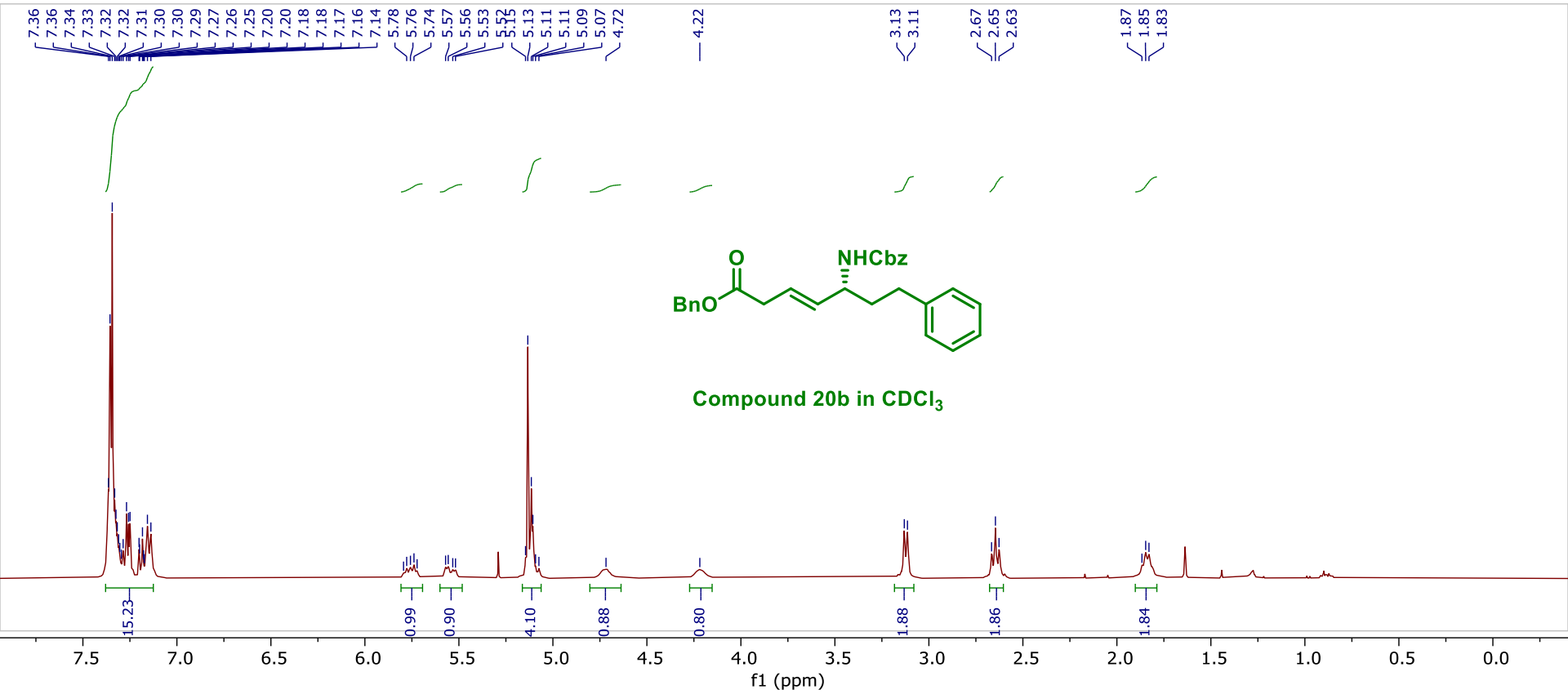
149.66
136.59
134.77
131.42
130.86
129.93
129.88
128.54
128.16
128.12
126.40
122.73
119.01
115.15
107.36
83.74
66.71
48.51
28.20
21.19
f1 (ppm)

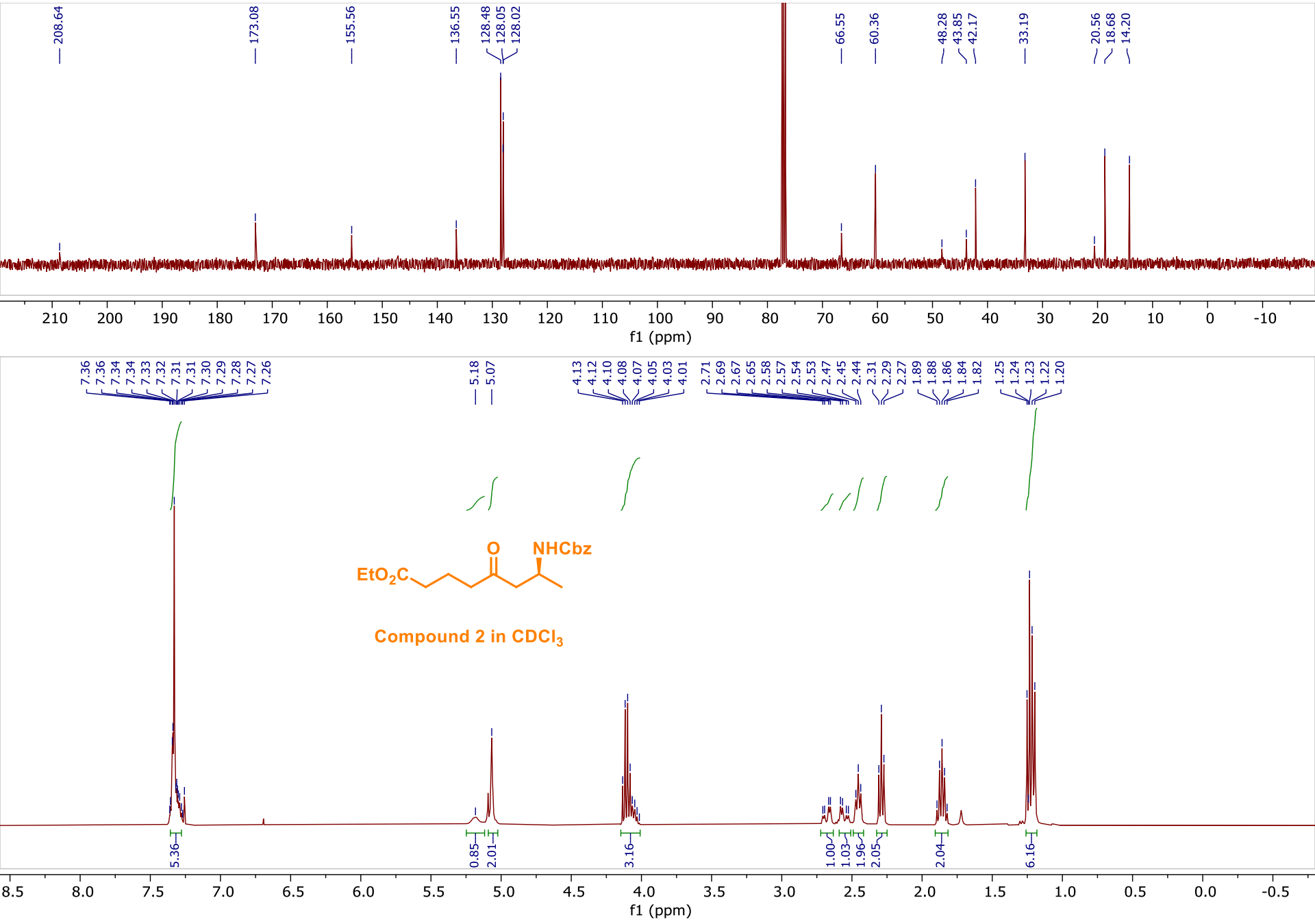

8.08
8.06
7.58
7.57
7.51
7.37
7.37
7.35
7.33
7.31
7.26
6.62
6.58
6.53
6.53
6.19
6.18
6.15
6.14
5.13
4.86
4.50
1.67
1.37
1.35
NHCbz
N
Boc
Compound SI-68 in CDCl3
0.95
1.02
1.05
6.31
1.01
0.99
1.00
2.21
0.93
1.04
9.08
3.14
f1 (ppm)

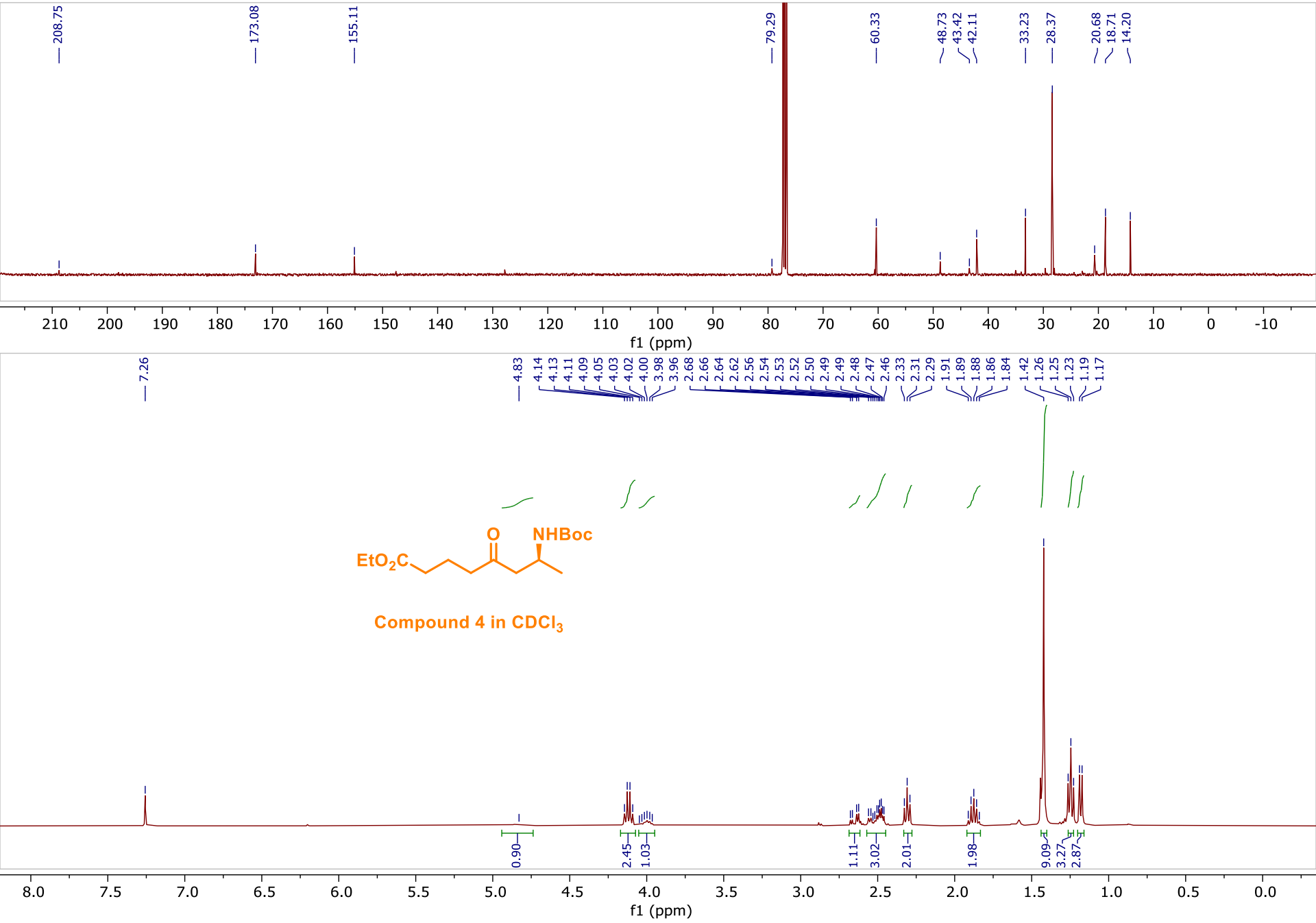

155.64
140.45
137.66
136.56
133.33
133.01
128.59
128.18
124.51
124.27
122.91
122.05
121.97
121.91
66.79
48.73
21.14
f1 (ppm)

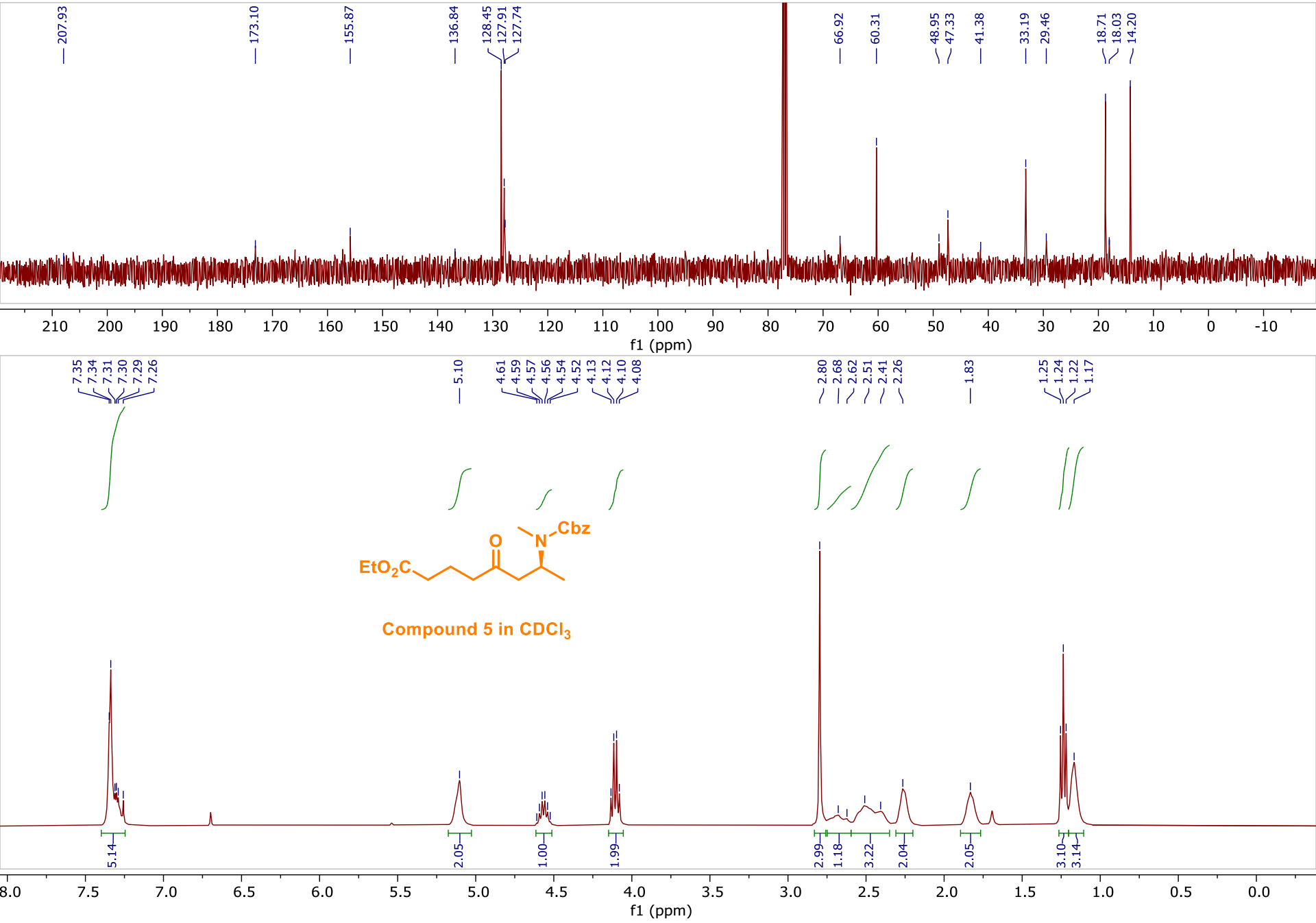

7.87
7.87
7.85
7.85
7.43
7.42
7.41
7.41
7.39
7.38
7.37
7.37
7.35
7.35
6.81
6.77
6.26
6.25
6.22
6.21
5.16
4.94
4.55
1.40
1.38
NHCbz
S
Compound SI-69 in CDCl3
2.01
8.24
1.00
1.01
2.12
0.95
1.00
3.12
f1 (ppm)

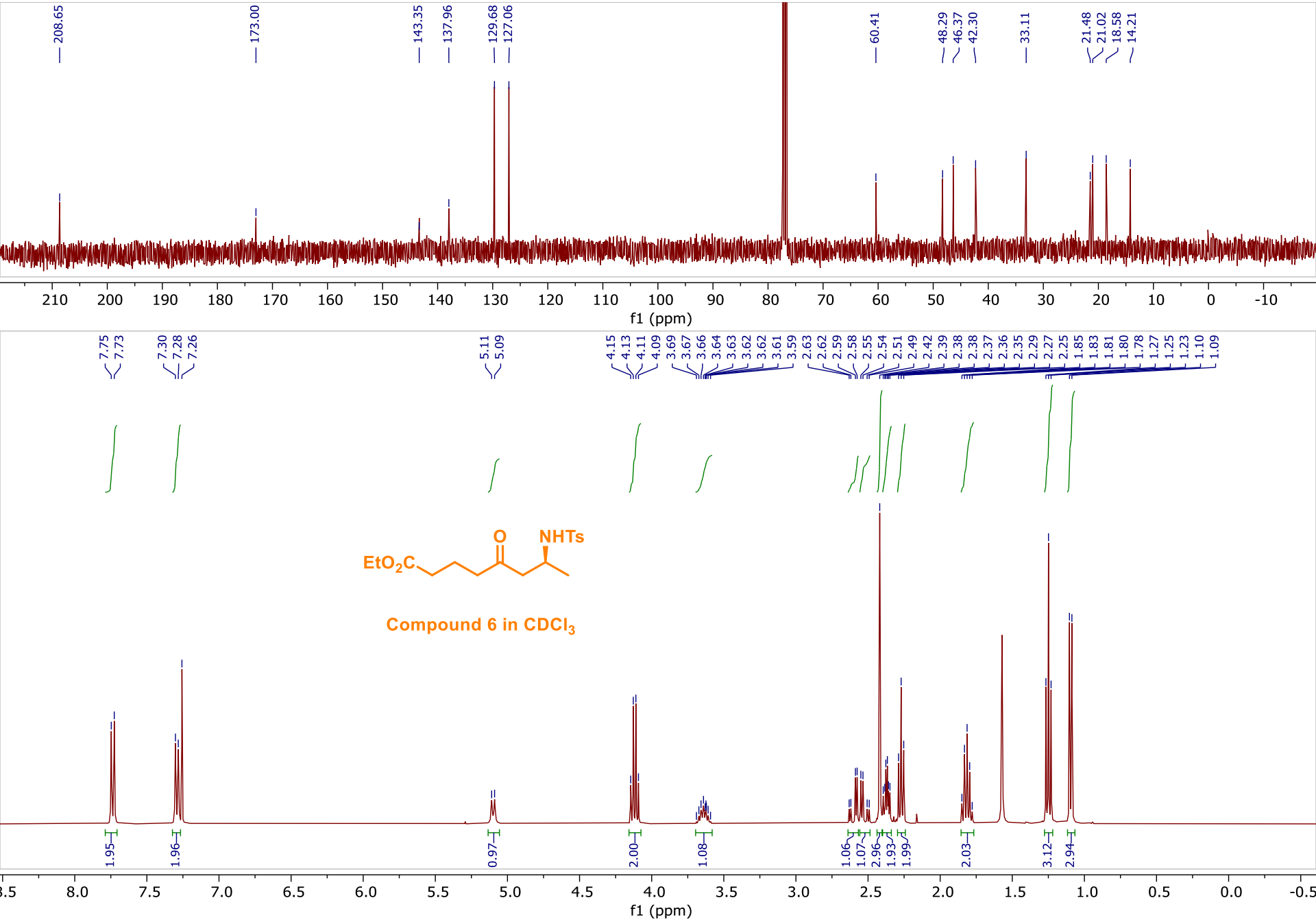

171.22
155.70
141.32
136.52
135.80
134.39
128.58
128.53
128.44
128.37
128.30
128.24
128.11
128.09
125.98
123.04
66.76
66.51
52.36
37.63
36.89
32.06
f1 (ppm)

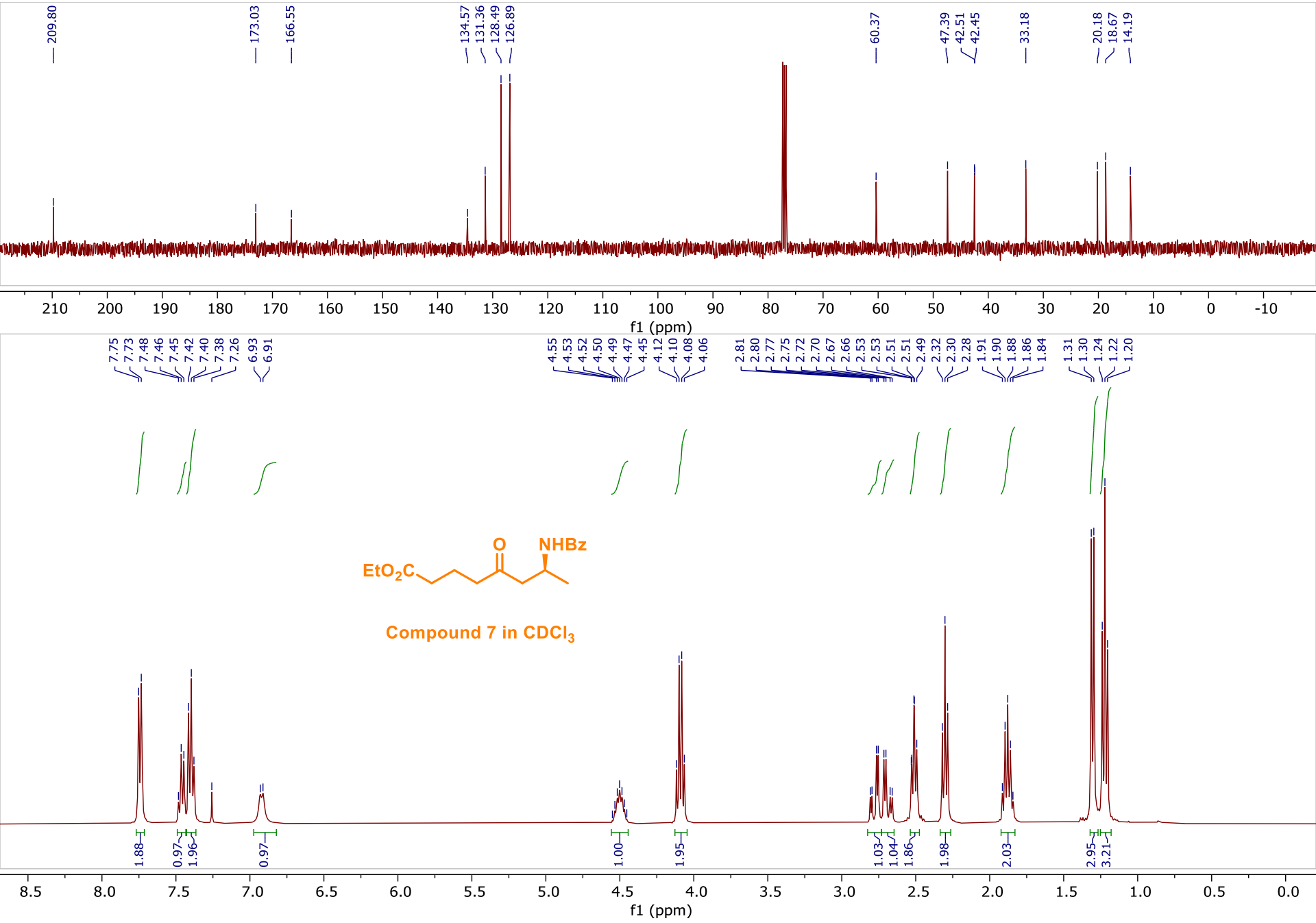

7.36
7.36
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.27
7.26
7.25
7.20
7.20
7.18
7.18
7.17
7.16
7.14
5.78
5.76
5.74
5.57
5.56
5.53
5.13
5.11
5.11
5.09
5.07
4.72
4.22
3.13
3.11
2.67
2.65
2.63
1.87
1.85
1.83
O
NHCbz
BnO
Compound 20b in CDCl3
15.23
0.99
0.90
4.10
0.88
0.80
1.88
1.86
1.84
f1 (ppm)

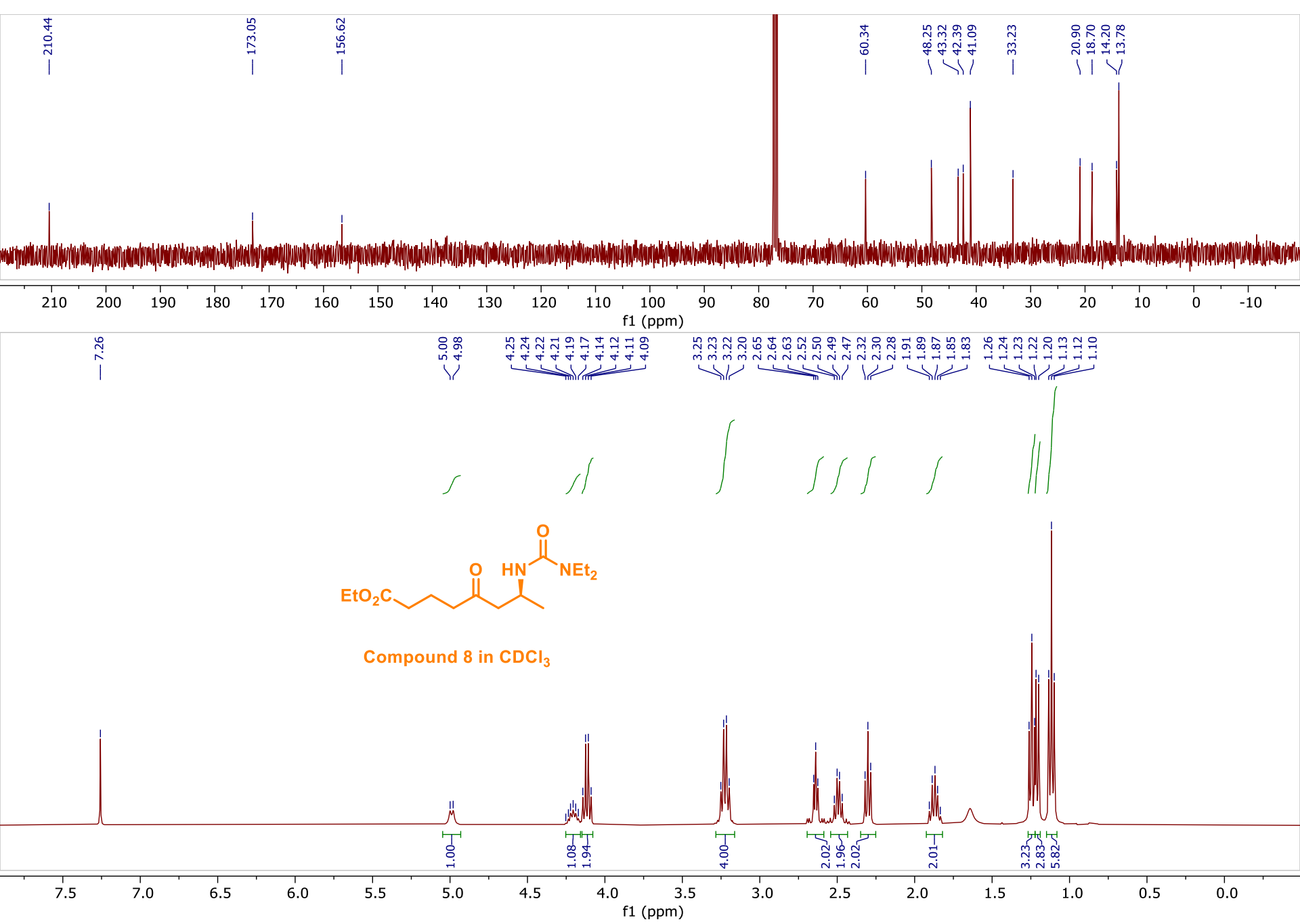

208.64
173.08
155.56
136.55
128.48
128.05
128.02
66.55
60.36
48.28
43.85
42.17
33.19
20.56
18.68
14.20
f1 (ppm)
7.36
7.36
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.26
5.18
5.07
4.13
4.12
4.10
4.08
4.07
4.05
4.03
4.01
2.71
2.69
2.67
2.65
2.58
2.57
2.54
2.53
2.47
2.45
2.44
2.31
2.29
2.27
1.89
1.88
1.86
1.84
1.82
1.25
1.24
1.23
1.22
1.20
O
NHCbz
EtO2C
Compound 2 in CDCl3
5.36
0.85
2.01
3.16
1.00
1.03
1.96
2.05
2.04
6.16
f1 (ppm)

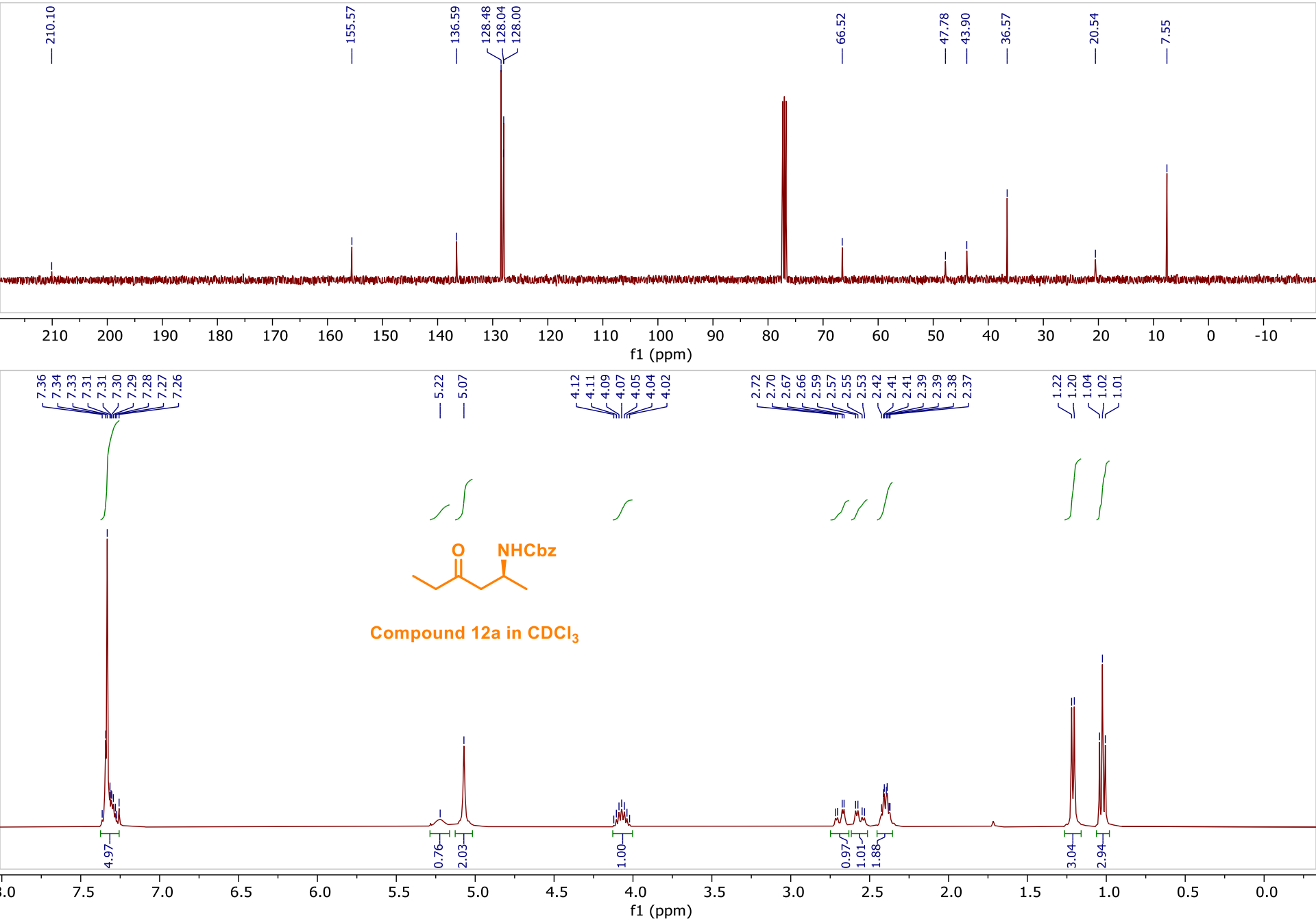

208.75
173.08
155.11
79.29
60.33
48.73
43.42
42.11
33.23
28.37
20.68
18.71
14.20
f1 (ppm)
7.26
4.83
4.14
4.13
4.11
4.09
4.05
4.03
4.02
4.00
3.98
3.96
2.68
2.66
2.64
2.62
2.56
2.54
2.53
2.52
2.50
2.49
2.49
2.48
2.47
2.46
2.33
2.31
2.29
1.91
1.89
1.88
1.86
1.84
1.42
1.26
1.25
1.23
1.19
1.17
O
NHBoc
EtO2C
Compound 4 in CDCl3
0.90
2.45
1.03
1.11
3.02
2.01
1.98
9.09
3.27
2.87
f1 (ppm)

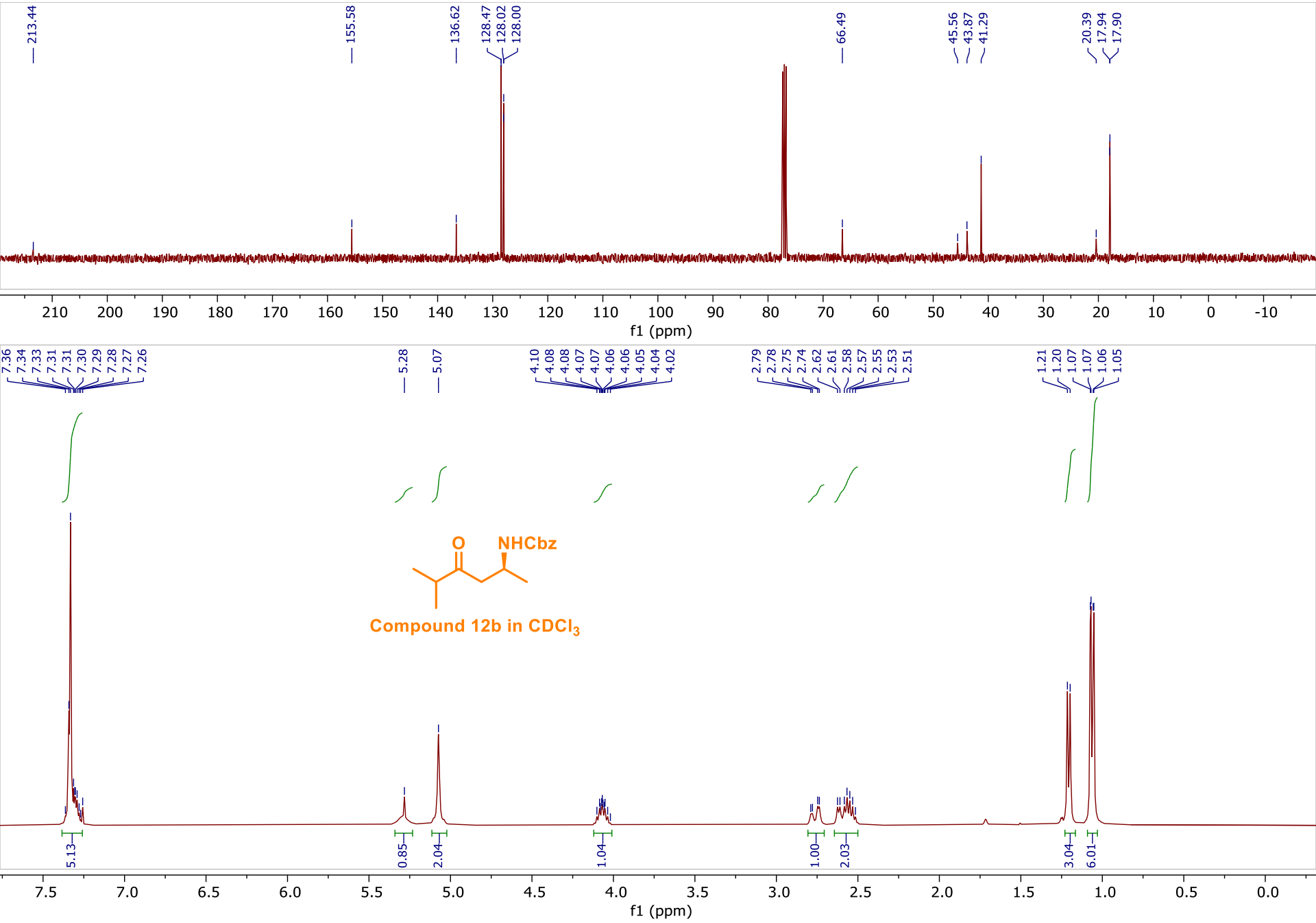

207.93
173.10
155.87
136.84
128.45
127.91
127.74
66.92
60.31
48.95
47.33
41.38
33.19
29.46
18.71
18.03
14.20
f1 (ppm)
7.35
7.34
7.31
7.30
7.29
7.26
5.10
4.61
4.59
4.57
4.56
4.54
4.52
4.13
4.12
4.10
4.08
2.80
2.68
2.62
2.51
2.41
2.26
1.83
1.25
1.24
1.22
1.17
Cbz
N
O
EtO2C
Compound 5 in CDCl3
5.14
2.05
1.00
1.99
2.99
1.18
3.22
2.04
2.05
3.10
3.14
f1 (ppm)

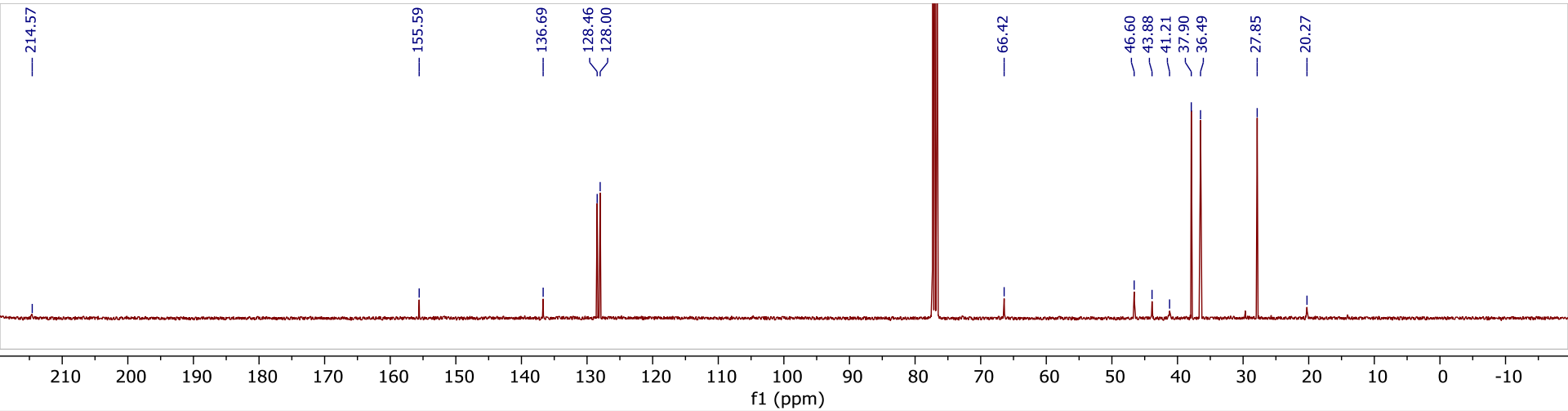

208.65
173.00
143.35
137.96
129.68
127.06
60.41
48.29
46.37
42.30
33.11
21.48
21.02
18.58
14.21
f1 (ppm)
7.75
7.73
7.30
7.28
7.26
5.11
5.09
4.15
4.13
4.11
4.09
3.69
3.67
3.66
3.64
3.63
3.62
3.62
3.61
3.59
2.63
2.62
2.59
2.58
2.55
2.54
2.51
2.49
2.42
2.39
2.38
2.38
2.37
2.36
2.35
2.29
2.27
2.25
1.85
1.83
1.81
1.80
1.78
1.27
1.25
1.23
1.10
1.09
O
NHTs
EtO2C
Compound 6 in CDCl3
1.95
1.96
0.97
2.00
1.08
1.06
1.07
2.96
1.93
1.99
2.03
3.12
2.94
f1 (ppm)

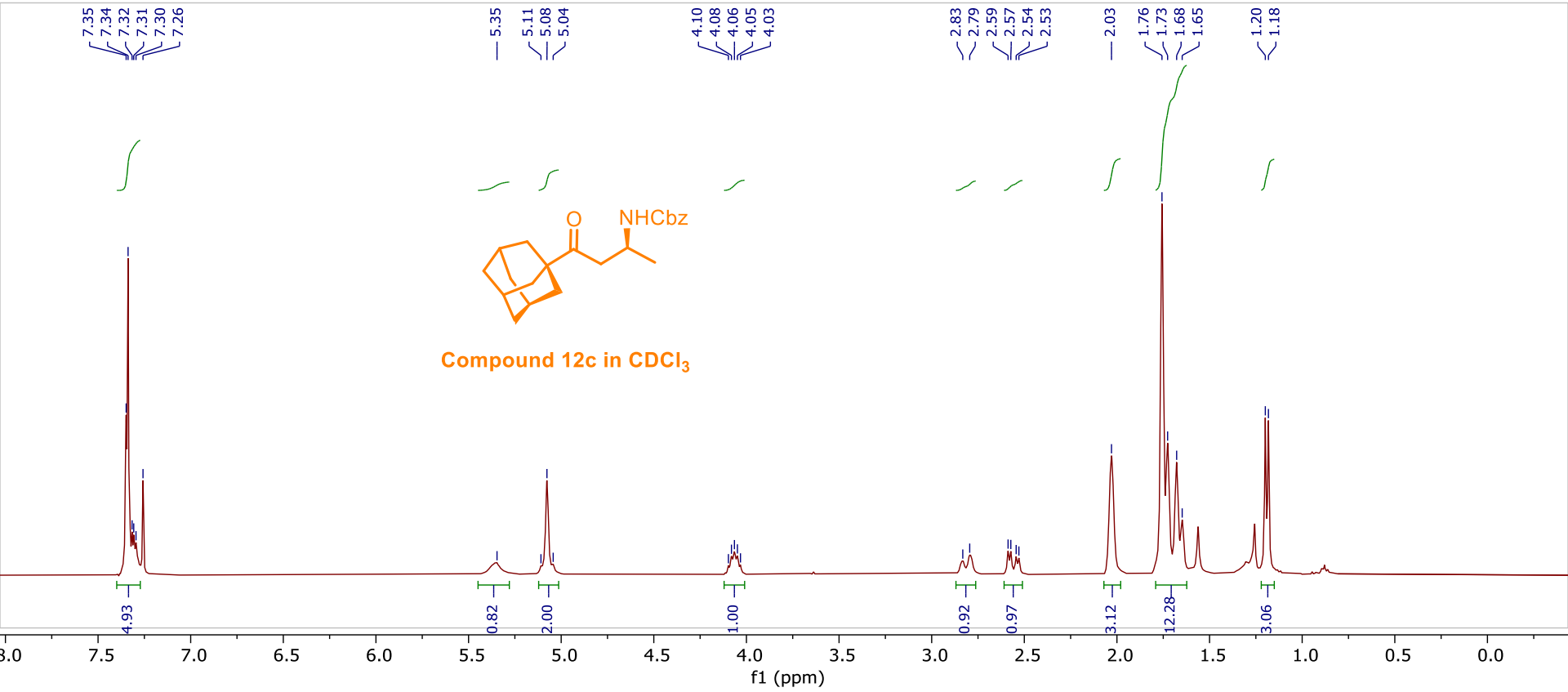

209.80
173.03
166.55
134.57
131.36
128.49
126.89
60.37
47.39
42.51
42.45
33.18
20.18
18.67
14.19
f1 (ppm)
7.75
7.73
7.48
7.46
7.45
7.42
7.40
7.38
7.26
6.93
6.91
4.55
4.53
4.52
4.50
4.49
4.47
4.45
4.12
4.10
4.08
4.06
2.81
2.80
2.77
2.75
2.72
2.70
2.67
2.66
2.53
2.53
2.51
2.51
2.49
2.32
2.30
2.28
1.91
1.90
1.88
1.86
1.84
1.31
1.30
1.24
1.22
1.20
O
NHBz
EtO2C
Compound 7 in CDCl3
1.88
0.97
1.96
0.97
1.00
1.95
1.03
1.04
1.86
1.98
2.03
2.95
3.21
f1 (ppm)

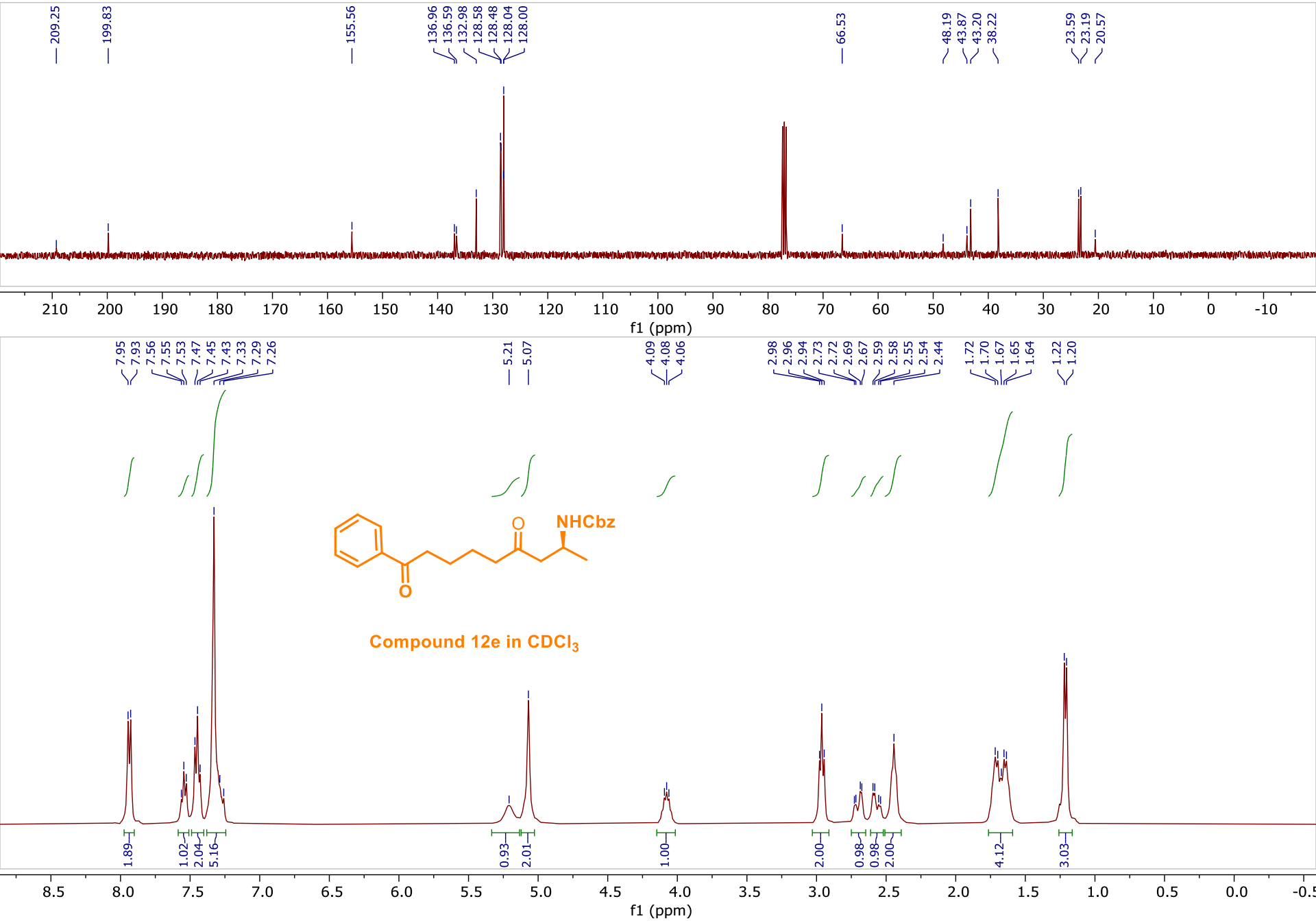

210.44
173.05
156.62
60.34
48.25
43.32
42.39
41.09
33.23
20.90
18.70
14.20
13.78
f1 (ppm)
7.26
5.00
4.98
4.25
4.24
4.22
4.21
4.19
4.17
4.14
4.12
4.11
4.09
3.25
3.23
3.22
3.20
2.65
2.64
2.63
2.52
2.50
2.49
2.47
2.32
2.30
2.28
1.91
1.89
1.87
1.85
1.83
1.26
1.24
1.23
1.22
1.20
1.13
1.12
1.10
O
HN
NEt2
EtO2C
Compound 8 in CDCl3
1.00
1.08
1.94
4.00
2.02
1.96
2.02
2.01
3.23
2.83
5.82
f1 (ppm)

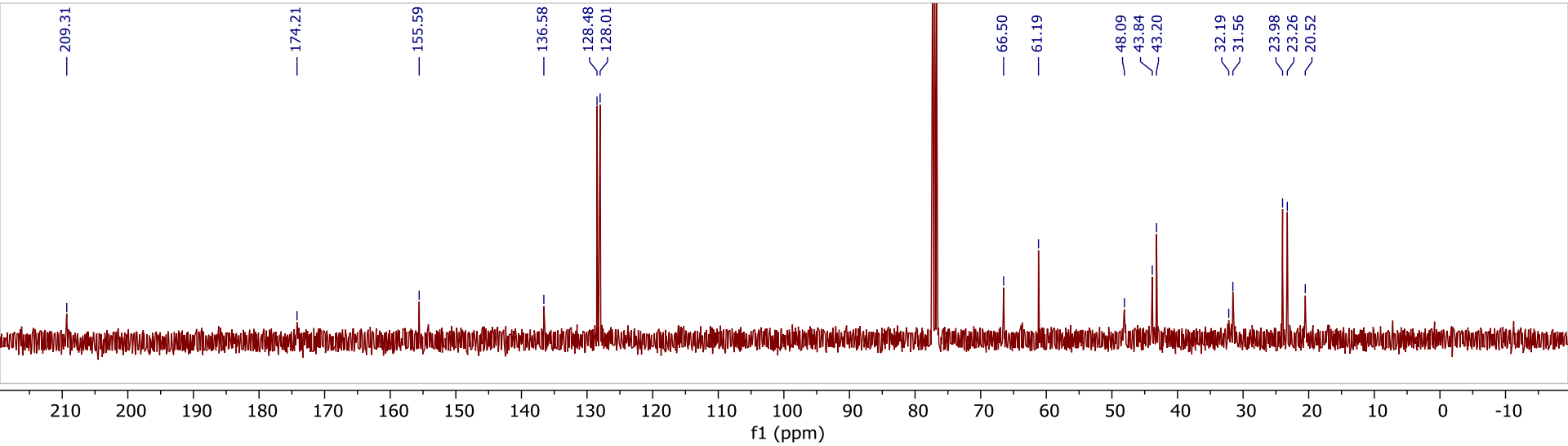

210.10
155.57
136.59
128.48
128.04
128.00
66.52
47.78
43.90
36.57
20.54
7.55
f1 (ppm)
7.36
7.34
7.33
7.31
7.31
7.30
7.29
7.28
7.27
7.26
5.22
5.07
4.12
4.11
4.09
4.07
4.05
4.04
4.02
2.72
2.70
2.67
2.66
2.59
2.57
2.55
2.53
2.42
2.41
2.41
2.39
2.39
2.38
2.37
1.22
1.20
1.04
1.02
1.01
O
NHCbz
Compound 12a in CDCl3
4.97
0.76
2.03
1.00
0.97
1.01
1.88
3.04
2.94
f1 (ppm)

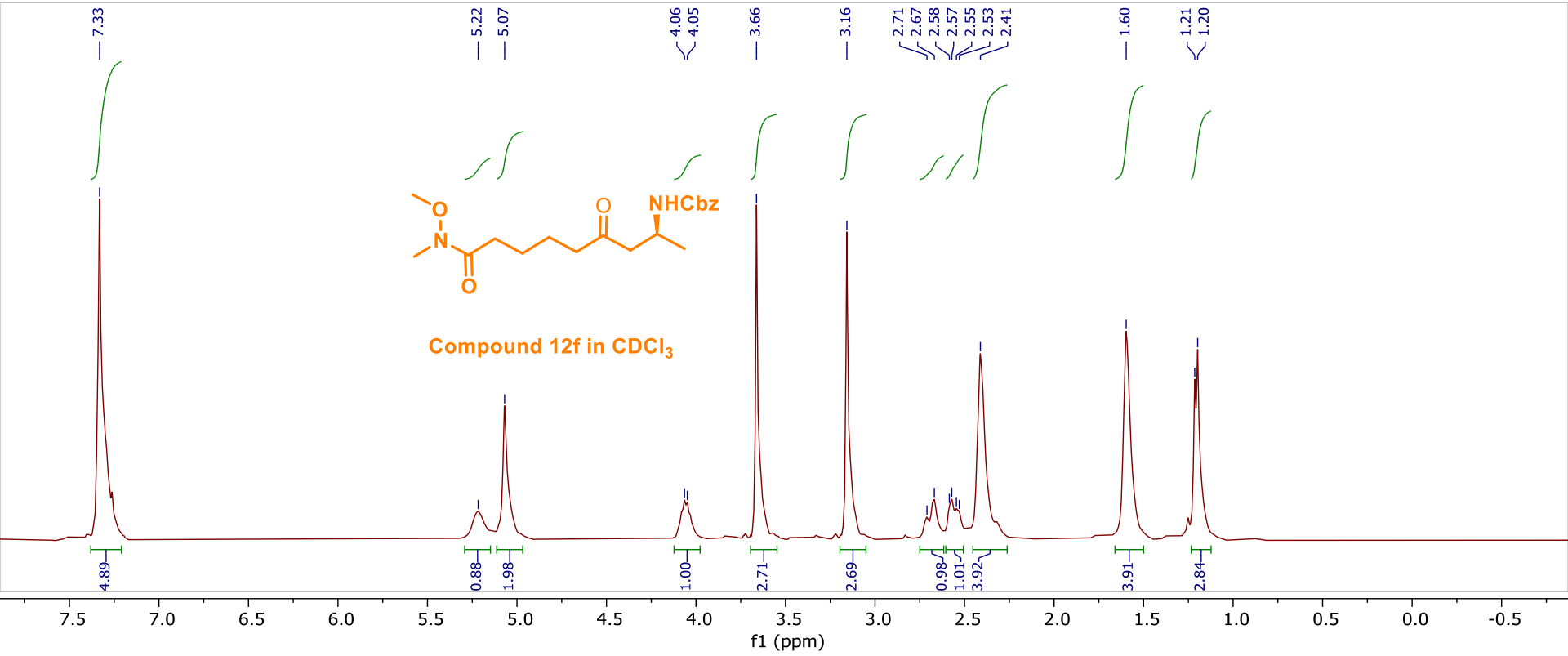

213.44
155.58
136.62
128.47
128.02
128.00
66.49
45.56
43.87
41.29
20.39
17.94
17.90
f1 (ppm)
7.36
7.34
7.33
7.31
7.31
7.30
7.29
7.28
7.27
7.26
5.28
5.07
4.10
4.08
4.08
4.07
4.07
4.06
4.06
4.05
4.04
4.02
2.79
2.78
2.75
2.74
2.62
2.61
2.58
2.57
2.55
2.53
2.51
1.21
1.20
1.07
1.07
1.06
1.05
O
NHCbz
Compound 12b in CDCl3
5.13
0.85
2.04
1.04
1.00
2.03
3.04
6.01
f1 (ppm)

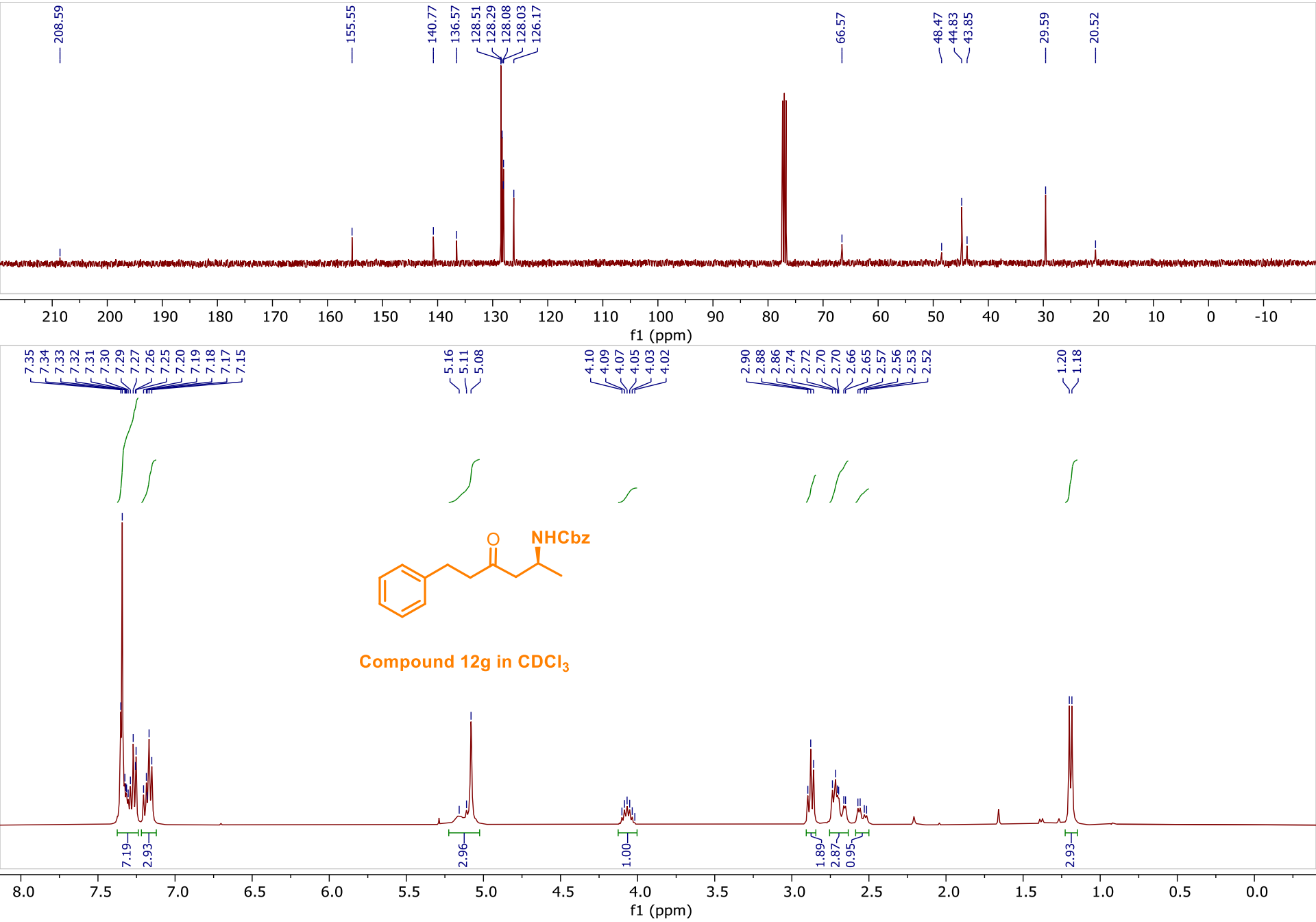

214.57
155.59
136.69
128.46
128.00
66.42
46.60
43.88
41.21
37.90
36.49
27.85
20.27
f1 (ppm)


7.35
7.34
7.32
7.31
7.30
7.26
5.35
5.11
5.08
5.04
4.10
4.08
4.06
4.05
4.03
2.83
2.79
2.59
2.57
2.54
2.53
2.03
1.76
1.73
1.68
1.65
1.20
1.18
O
NHCbz
Compound 12c in CDCl3
4.93
0.82
2.00
1.00
0.92
0.97
3.12
12.28
3.06
f1 (ppm)


209.25
199.83
155.56
136.96
136.59
132.98
128.58
128.48
128.04
128.00
66.53
48.19
43.87
43.20
38.22
23.59
23.19
20.57
f1 (ppm)
7.95
7.93
7.56
7.55
7.53
7.47
7.45
7.43
7.33
7.29
7.26
5.21
5.07
4.09
4.08
4.06
2.98
2.96
2.94
2.73
2.72
2.69
2.67
2.59
2.58
2.55
2.54
2.44
1.72
1.70
1.67
1.65
1.64
1.22
1.20
NHCbz
O
O
Compound 12e in CDCl3
1.89
1.02
2.04
5.16
0.93
2.01
1.00
2.00
0.98
0.98
2.00
4.12
3.03
f1 (ppm)


209.31
174.21
155.59
136.58
128.48
128.01
66.50
61.19
48.09
43.84
43.20
32.19
31.56
23.98
23.26
20.52
f1 (ppm)


7.33
5.22
5.07
4.06
4.05
3.66
3.16
2.71
2.67
2.58
2.57
2.55
2.53
2.41
1.60
1.21
1.20
NHCbz
Compound 12f in CDCl3
4.89
0.88
1.98
1.00
2.71
2.69
0.98
1.01
3.92
3.91
2.84
f1 (ppm)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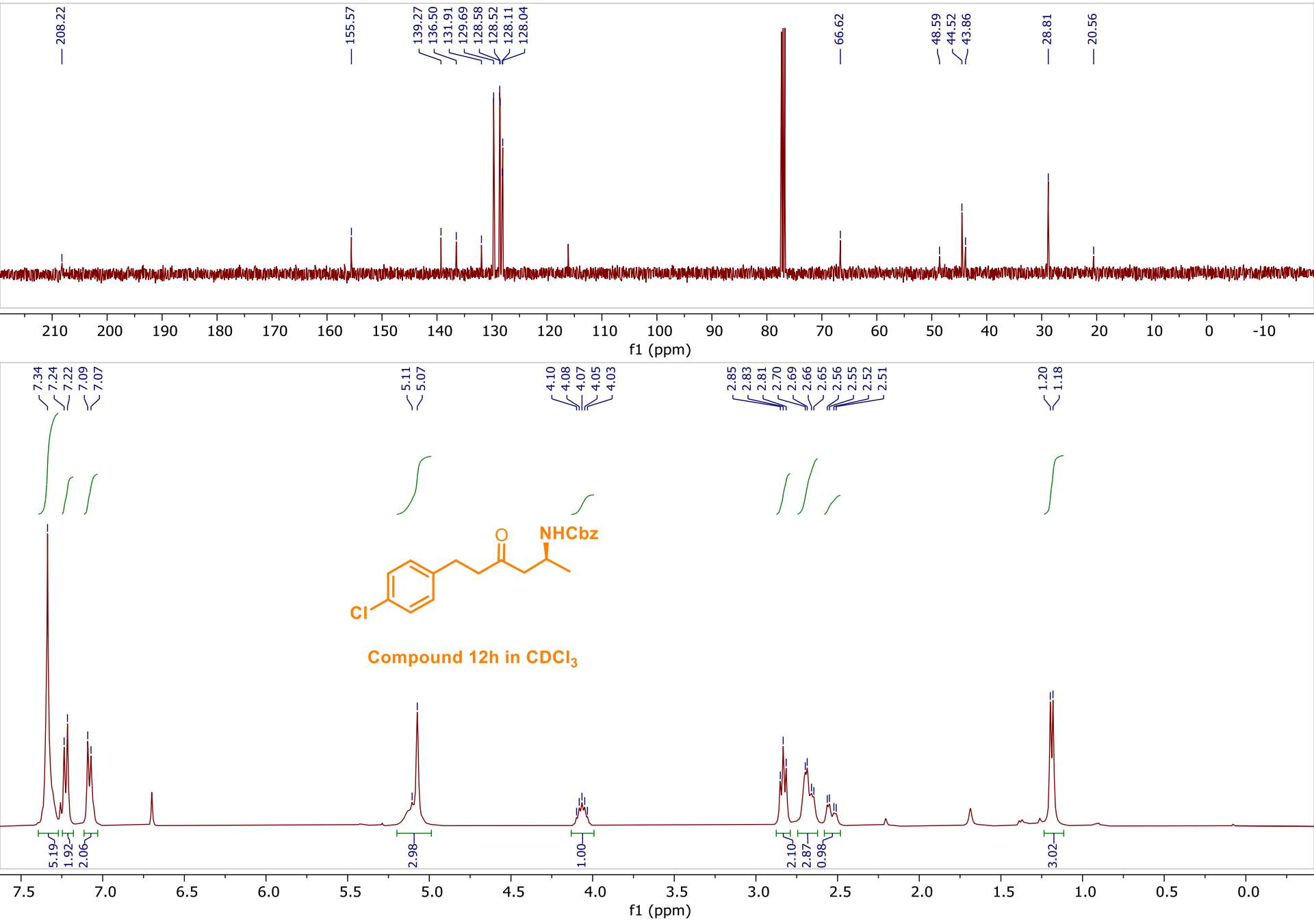
136.57
128.51
128.29
128.08
128.03
126.17
66.57
48.47
44.83
43.85
29.59
20.52
f1 (ppm)
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.27
7.26
7.25
7.20
7.19
7.18
7.17
7.15
5.16
5.11
5.08
4.10
4.09
4.07
4.05
4.03
4.02
2.90
2.88
2.86
2.74
2.72
2.70
2.70
2.66
2.65
2.57
2.56
2.53
2.52
1.20
1.18
NHCbz
Compound 12g in CDCl3
7.19
2.93
2.96
1.00
1.89
2.87
0.95
2.93
f1 (ppm)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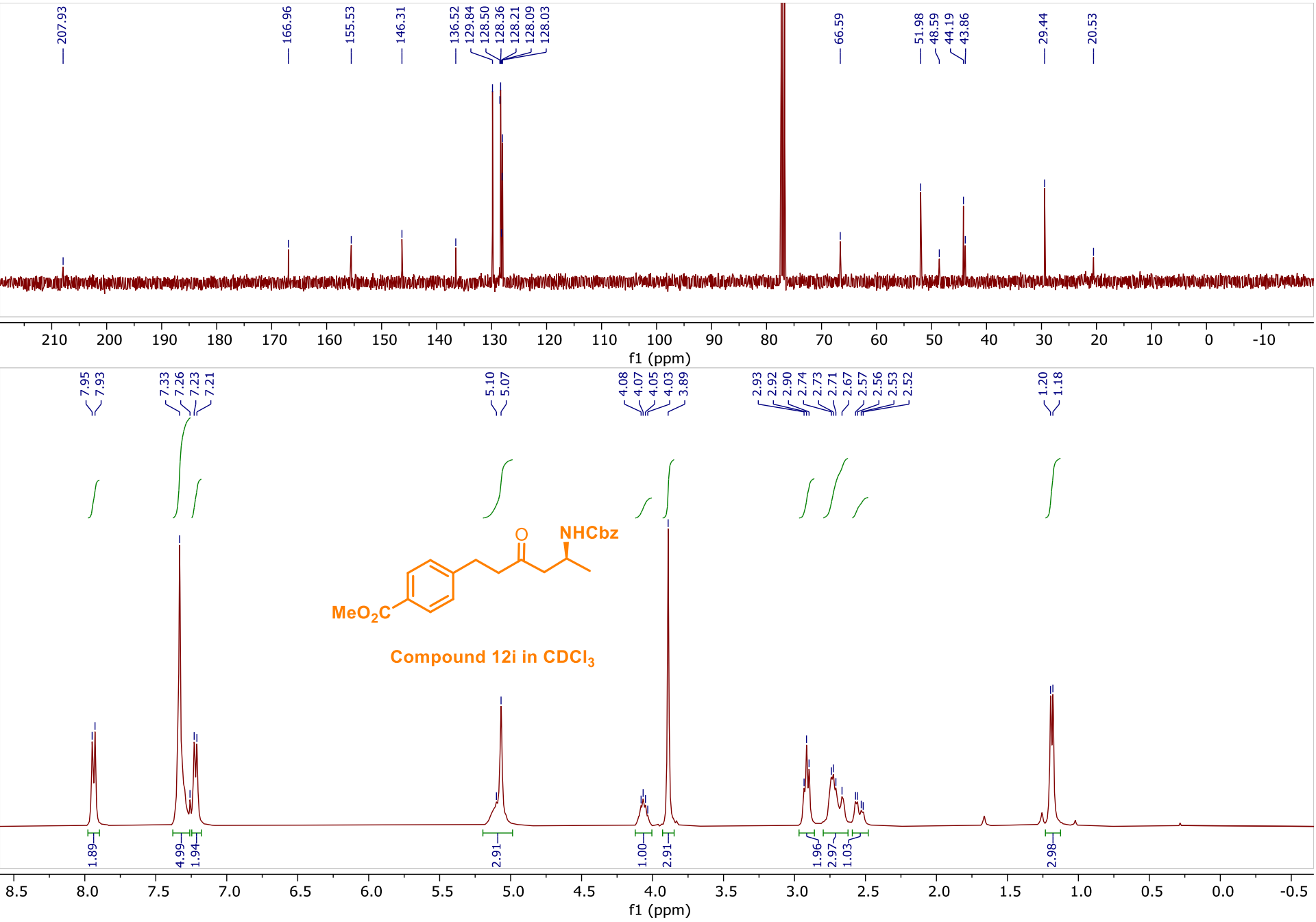
131.91
129.69
128.58
128.52
128.11
128.04
66.62
48.59
44.52
43.86
28.81
20.56
f1 (ppm)
7.34
7.24
7.22
7.09
7.07
5.11
5.07
4.10
4.08
4.07
4.05
4.03
2.85
2.83
2.81
2.70
2.69
2.66
2.65
2.56
2.55
2.52
2.51
1.20
1.18
NHCbz
Cl
Compound 12h in CDCl3
5.19
1.92
2.06
2.98
1.00
2.10
2.87
0.98
3.02
f1 (ppm)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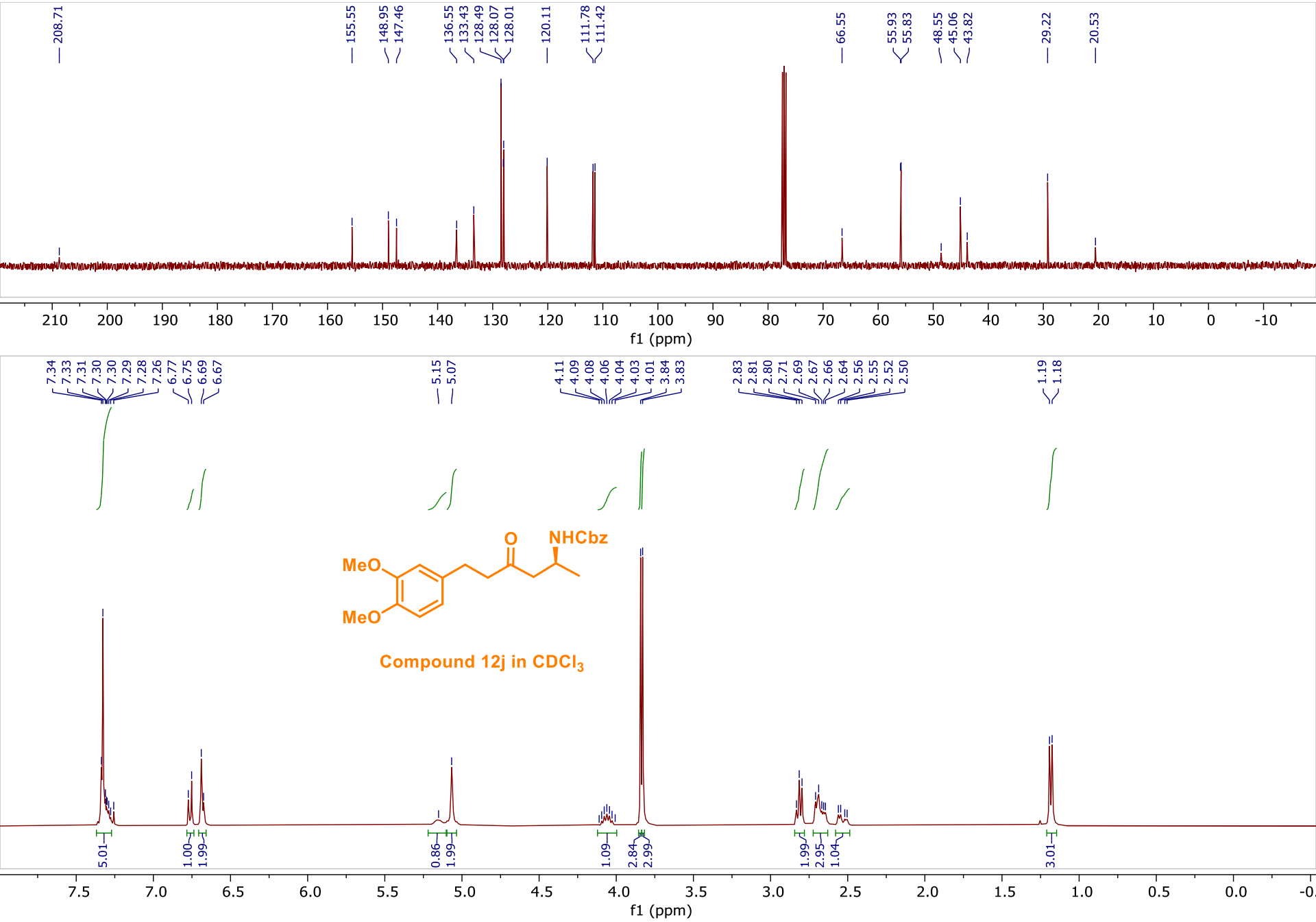
129.84
128.50
128.36
128.21
128.09
128.03
66.59
51.98
48.59
44.19
43.86
29.44
20.53
f1 (ppm)
7.95
7.93
7.33
7.26
7.23
7.21
5.10
5.07
4.08
4.07
4.05
4.03
3.89
2.93
2.92
2.90
2.74
2.73
2.71
2.67
2.57
2.56
2.53
2.52
1.20
1.18
NHCbz
MeO2C
Compound 12i in CDCl3
1.89
4.99
1.94
2.91
1.00
2.91
1.96
2.97
1.03
2.98
f1 (ppm)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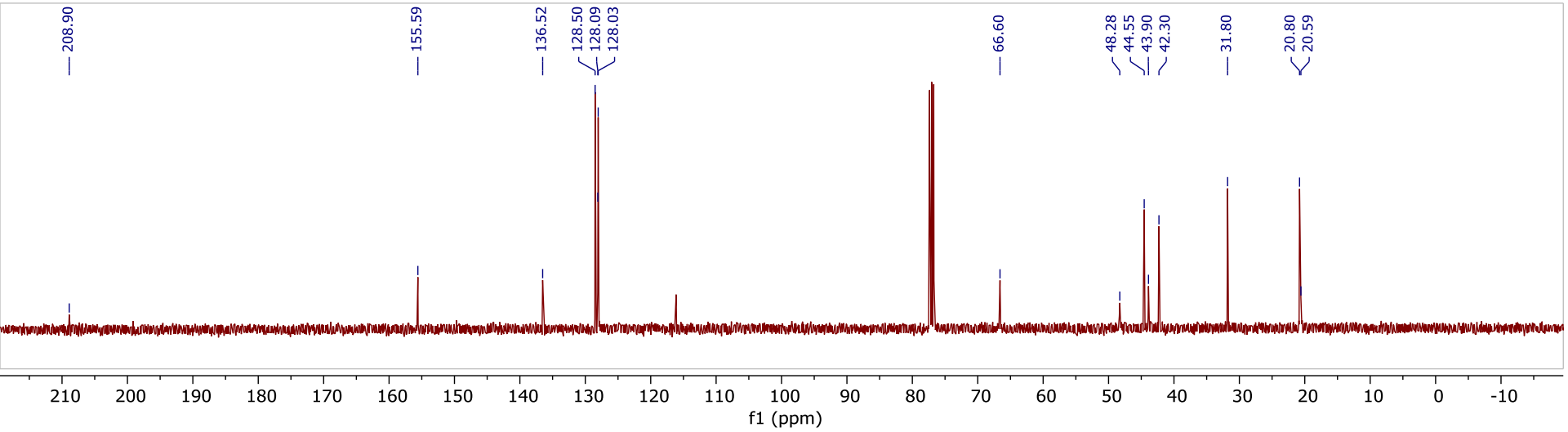
155.55
148.95
147.46
136.55
133.43
128.49
128.07
128.01
120.11
111.78
111.42
66.55
55.93
55.83
48.55
45.06
43.82
29.22
20.53
f1 (ppm)
7.34
7.33
7.31
7.30
7.30
7.29
7.28
7.26
6.77
6.75
6.69
6.67
5.15
5.07
4.11
4.09
4.08
4.06
4.04
4.03
4.01
3.84
3.83
2.83
2.81
2.80
2.71
2.69
2.67
2.66
2.64
2.56
2.55
2.52
2.50
1.19
1.18
O
NHCbz
MeO
MeO
Compound 12j in CDCl3
5.01
1.00
1.99
0.86
1.99
1.09
2.84
2.99
1.99
2.95
1.04
3.01
f1 (ppm)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155.59
136.52
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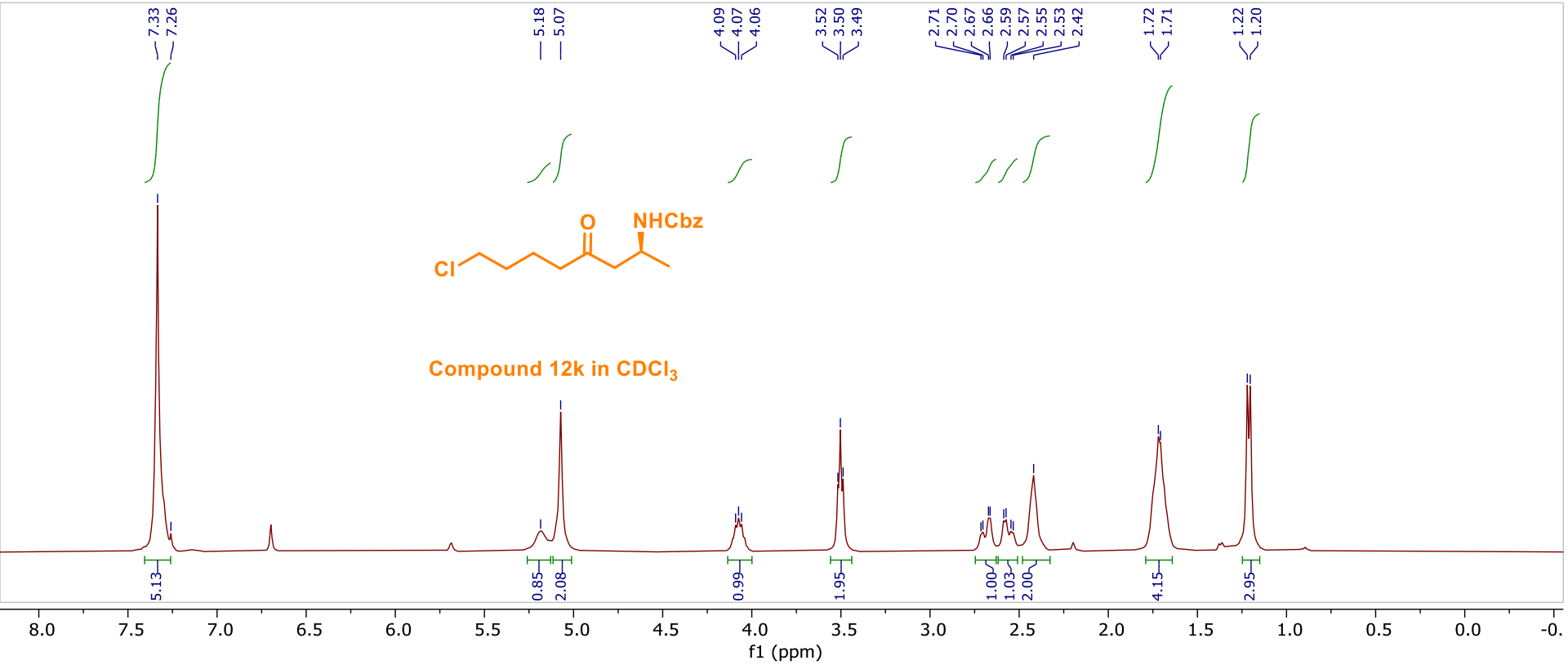
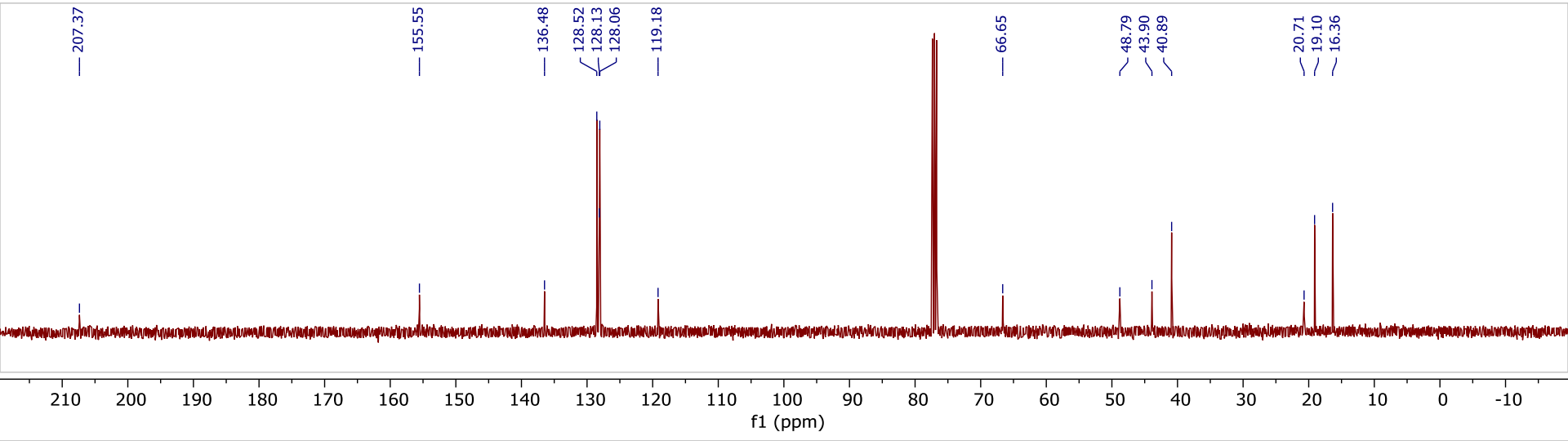
66.60
48.28
44.55
43.90
42.30
31.80
20.80
20.59
f1 (ppm)


7.33
7.26
5.18
5.07
4.09
4.07
4.06
3.52
3.50
3.49
2.71
2.70
2.67
2.66
2.59
2.57
2.55
2.53
2.42
1.72
1.71
1.22
1.20
O
NHCbz
Cl
Compound 12k in CDCl3
5.13
0.85
2.08
0.99
1.95
1.00
1.03
2.00
4.15
2.95
f1 (ppm)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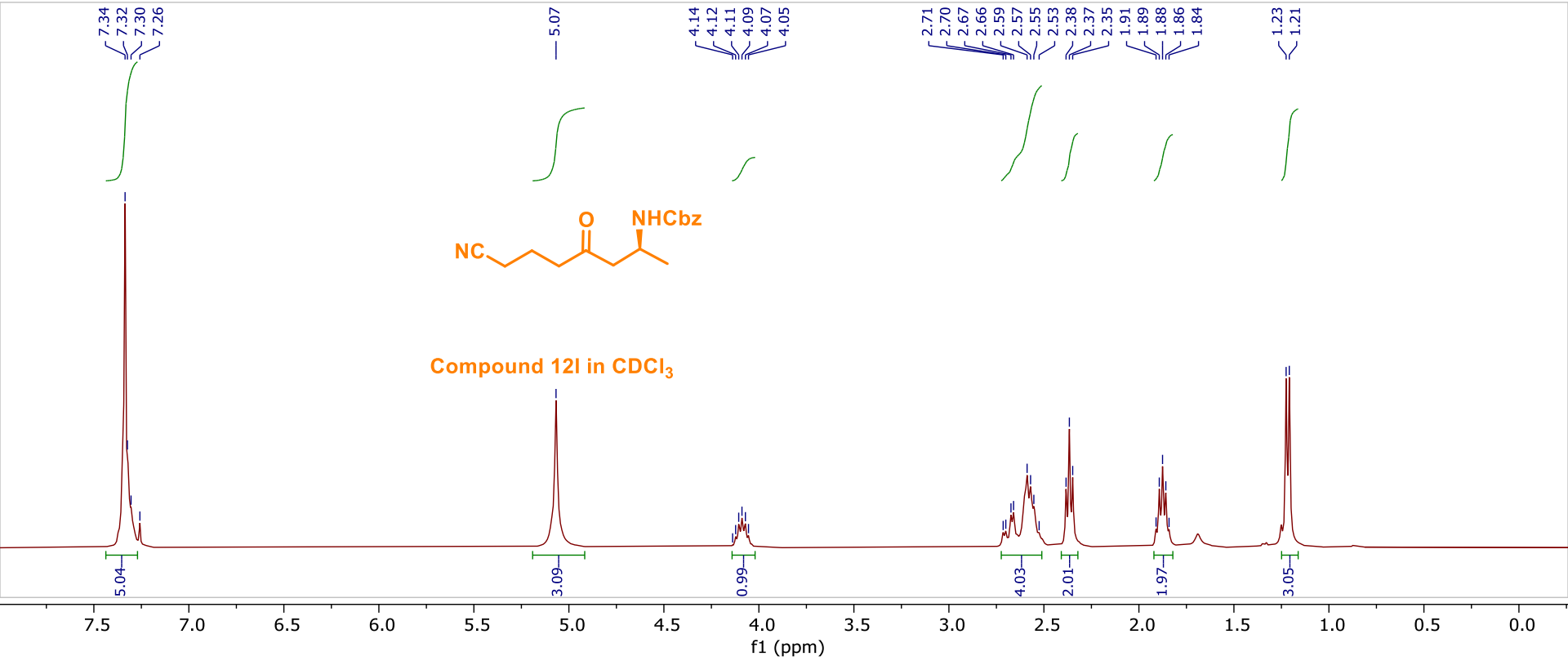
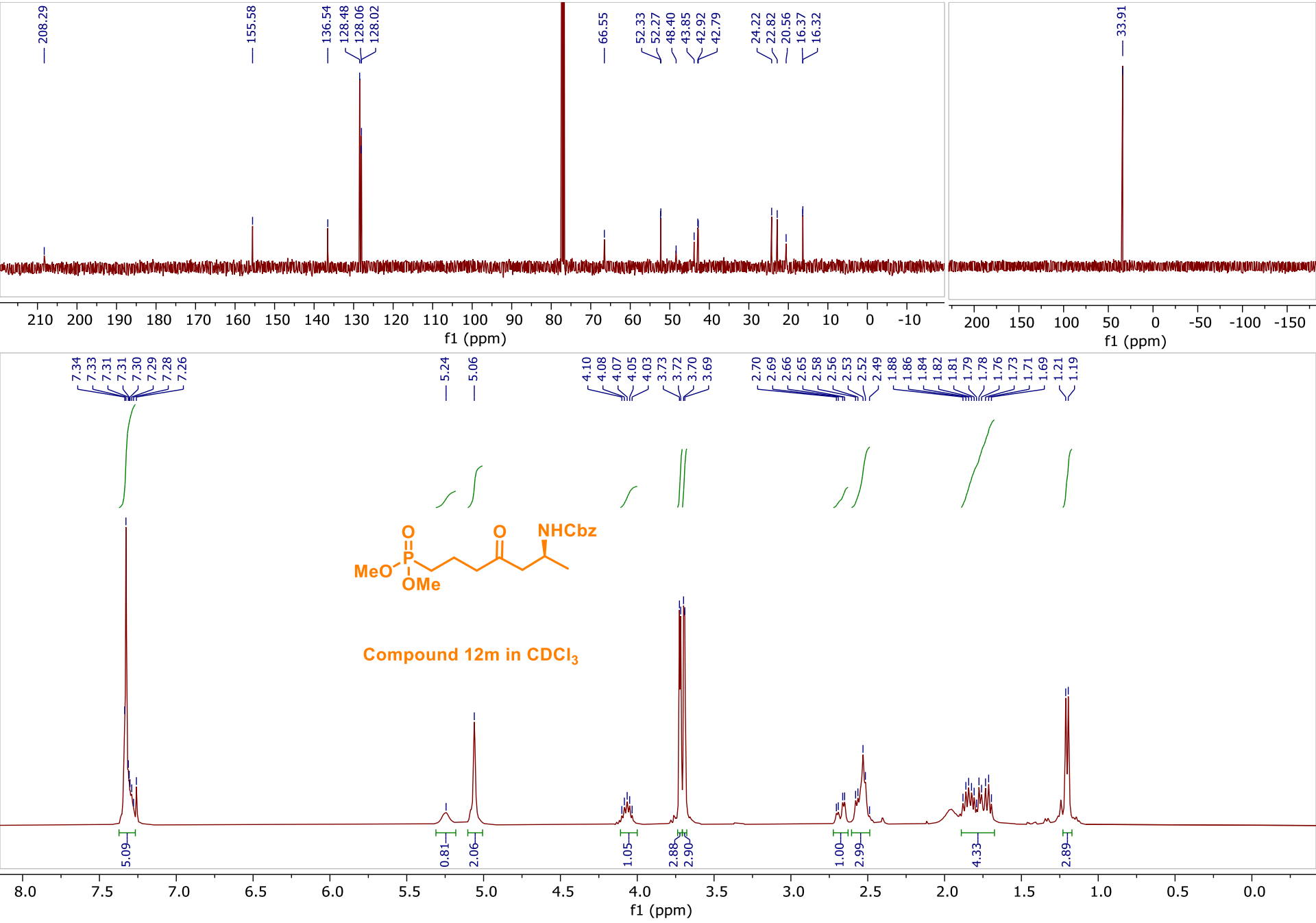
155.55
136.48
128.52
128.13
128.06
119.18
66.65
48.79
43.90
40.89
20.71
19.10
16.36
f1 (ppm)


7.34
7.32
7.30
7.26
5.07
4.14
4.12
4.11
4.09
4.07
4.05
2.71
2.70
2.67
2.66
2.59
2.57
2.55
2.53
2.38
2.37
2.35
1.91
1.89
1.88
1.86
1.84
1.23
1.21
O
NHCbz
NC
Compound 12l in CDCl3
5.04
3.09
0.99
4.03
2.01
1.97
3.05
f1 (ppm)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155.58
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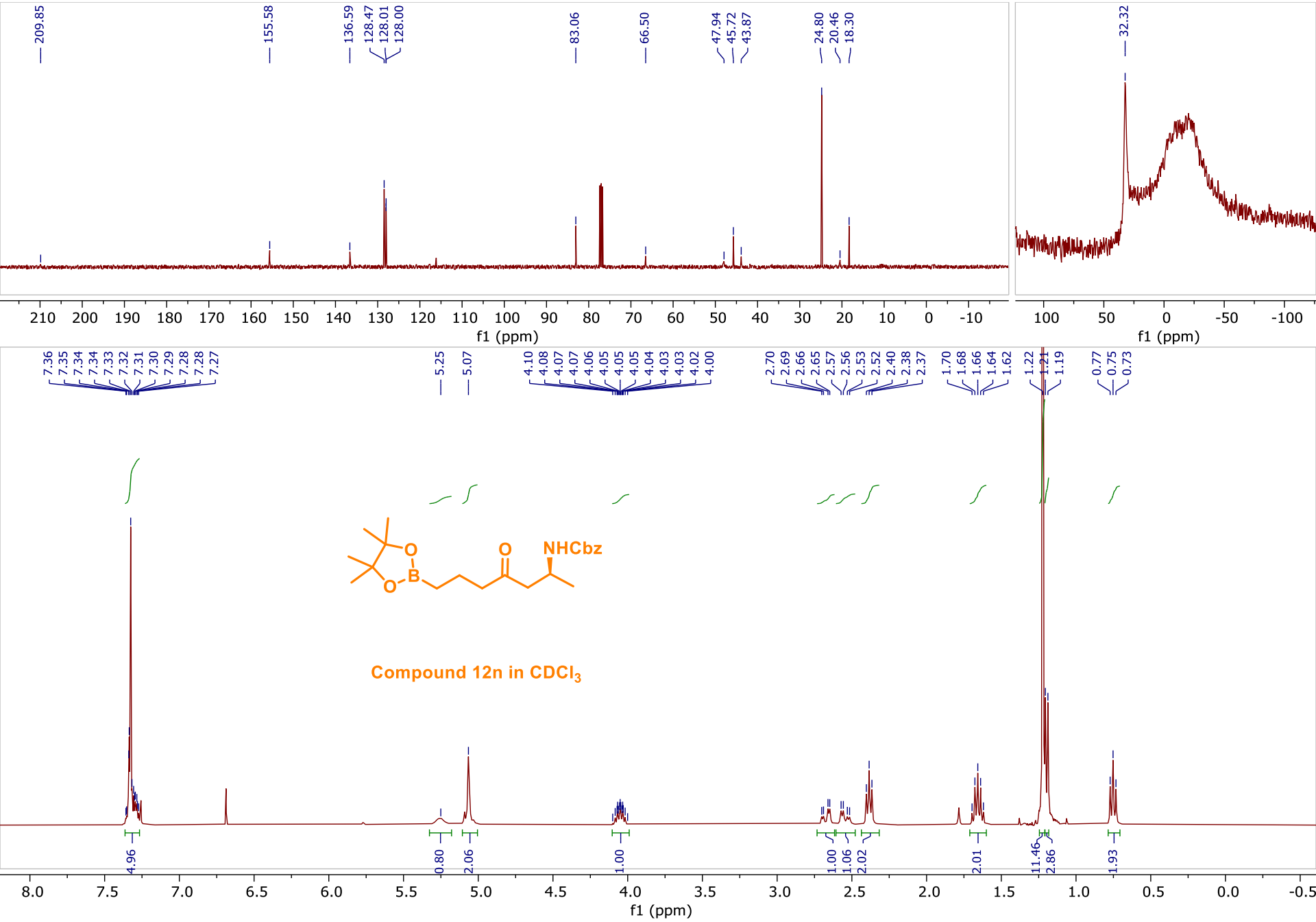
128.06
128.02
66.55
52.33
52.27
48.40
43.85
42.92
42.79
24.22
22.82
20.56
16.37
16.32
33.91
f1 (ppm)
7.34
7.33
7.31
7.31
7.30
7.29
7.28
7.26
5.24
5.06
4.10
4.08
4.07
4.05
4.03
3.73
3.72
3.70
3.69
2.70
2.69
2.66
2.65
2.58
2.56
2.53
2.52
2.49
1.88
1.86
1.84
1.82
1.81
1.79
1.78
1.76
1.73
1.71
1.69
1.21
1.19
O
O
NHCbz
MeO
P
OMe
Compound 12m in CDCl3
5.09
0.81
2.06
1.05
2.88
2.90
1.00
2.99
4.33
2.89
f1 (ppm)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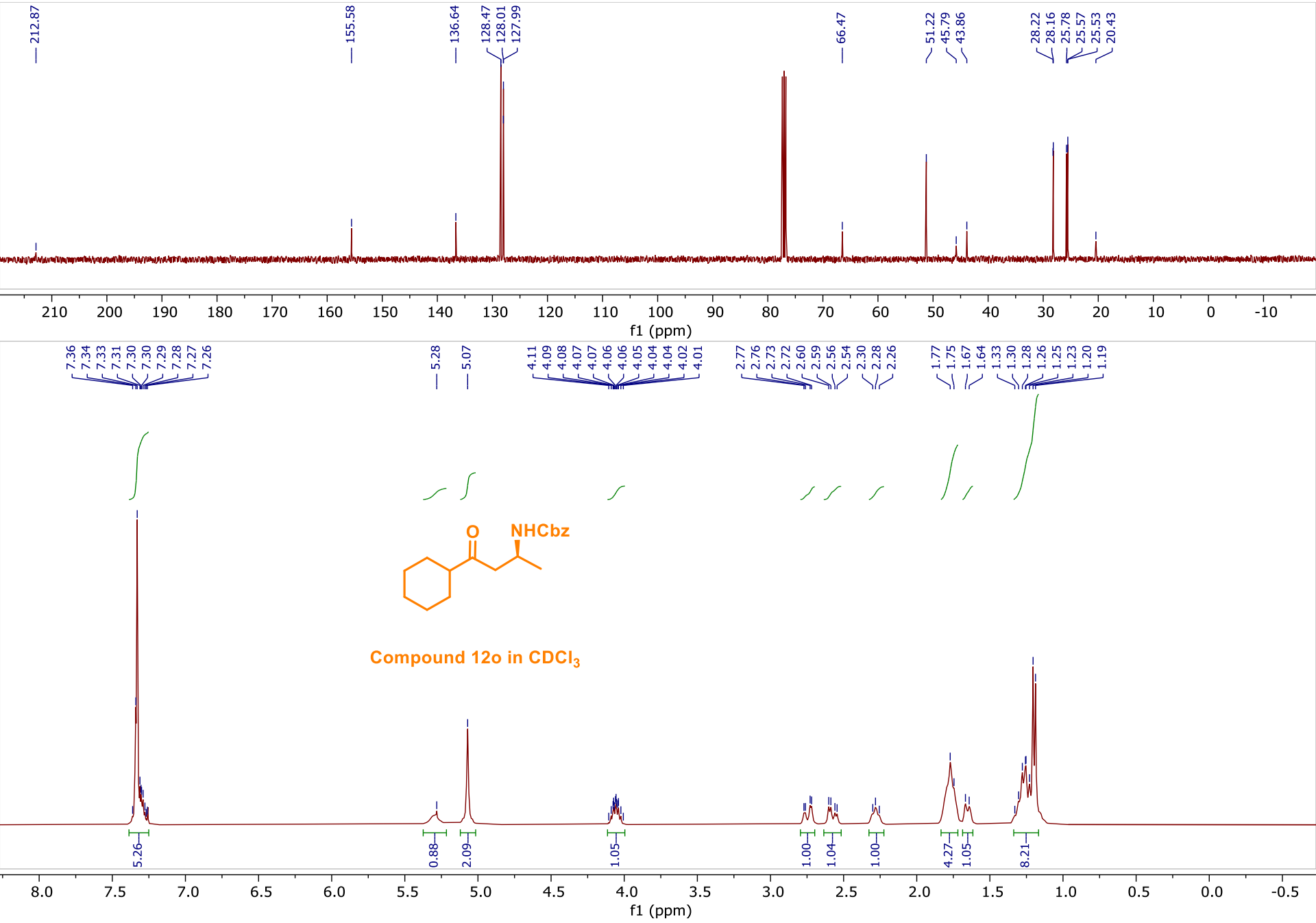
155.58
136.59
128.47
128.01
128.00
83.06
66.50
47.94
45.72
43.87
24.80
20.46
18.30
32.32
f1 (ppm)
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.28
7.27
5.25
5.07
4.10
4.08
4.07
4.07
4.06
4.05
4.05
4.05
4.04
4.03
4.03
4.02
4.00
2.70
2.69
2.66
2.65
2.57
2.56
2.53
2.52
2.40
2.38
2.37
1.70
1.68
1.66
1.64
1.62
1.22
1.21
1.19
0.77
0.75
0.73
O
O
B
O
NHCbz
Compound 12n in CDCl3
4.96
0.80
2.06
1.00
1.00
1.06
2.02
2.01
11.46
2.86
1.93
f1 (ppm)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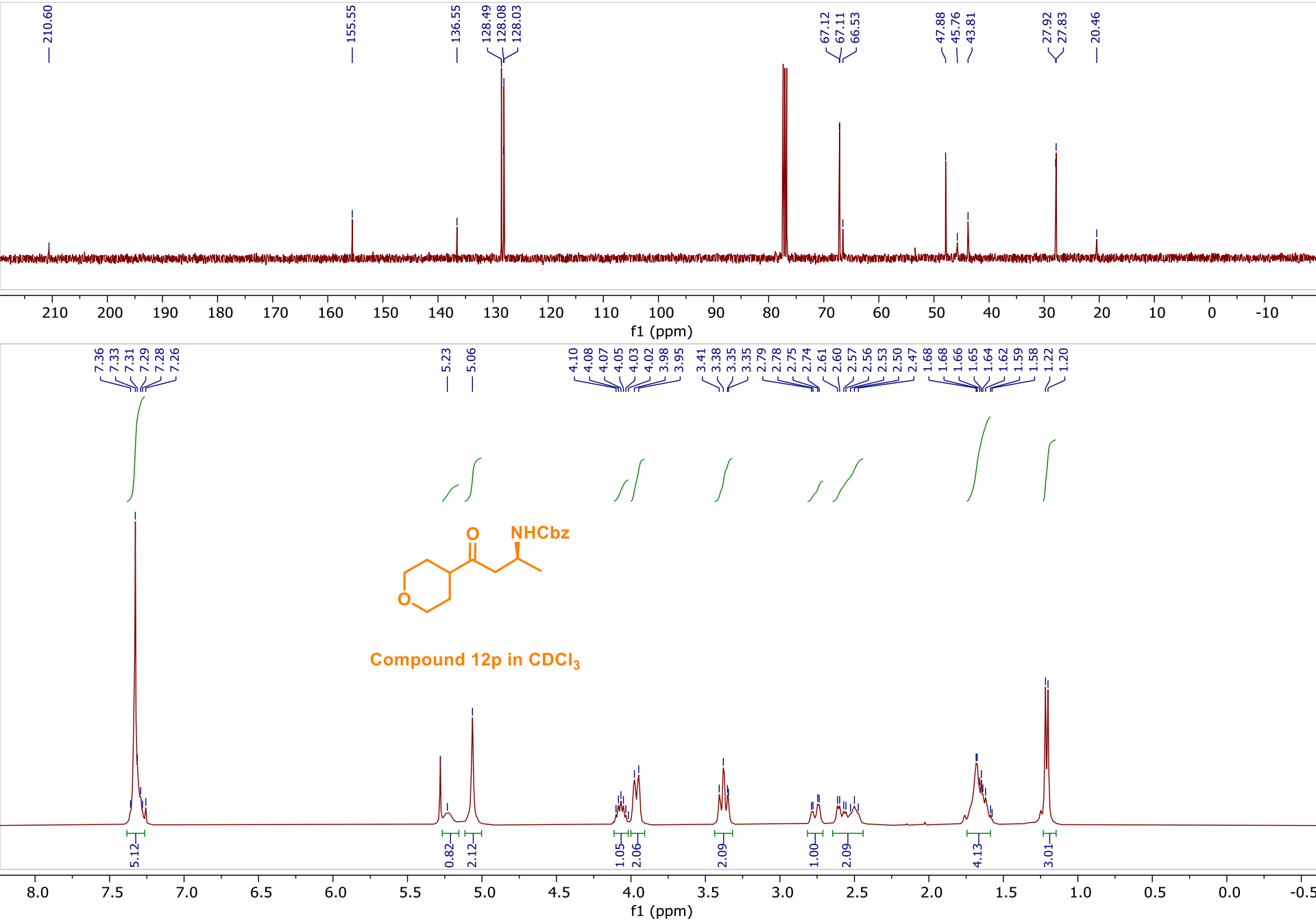
155.58
136.64
128.47
128.01
127.99
66.47
51.22
45.79
43.86
28.22
28.16
25.78
25.57
25.53
20.43
f1 (ppm)
7.36
7.34
7.33
7.31
7.30
7.30
7.29
7.28
7.27
7.26
5.28
5.07
4.11
4.09
4.08
4.07
4.07
4.06
4.06
4.05
4.04
4.04
4.02
4.01
2.77
2.76
2.73
2.72
2.60
2.59
2.56
2.54
2.30
2.28
2.26
1.77
1.75
1.67
1.64
1.33
1.30
1.28
1.26
1.25
1.23
1.20
1.19
O
NHCbz
Compound 12o in CDCl3
5.26
0.88
2.09
1.05
1.00
1.04
1.00
4.27
1.05
8.21
f1 (ppm)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128.49
128.08
128.03
67.12
67.11
66.53
47.88
45.76
43.81
27.92
27.83
20.46
f1 (ppm)
7.36
7.33
7.31
7.29
7.28
7.26
5.23
5.06
4.10
4.08
4.07
4.05
4.03
4.02
3.98
3.95
3.41
3.38
3.35
3.35
2.79
2.78
2.75
2.74
2.61
2.60
2.57
2.56
2.53
2.50
2.47
1.68
1.68
1.66
1.65
1.64
1.62
1.59
1.58
1.22
1.20
O
NHCbz
O
Compound 12p in CDCl3
5.12
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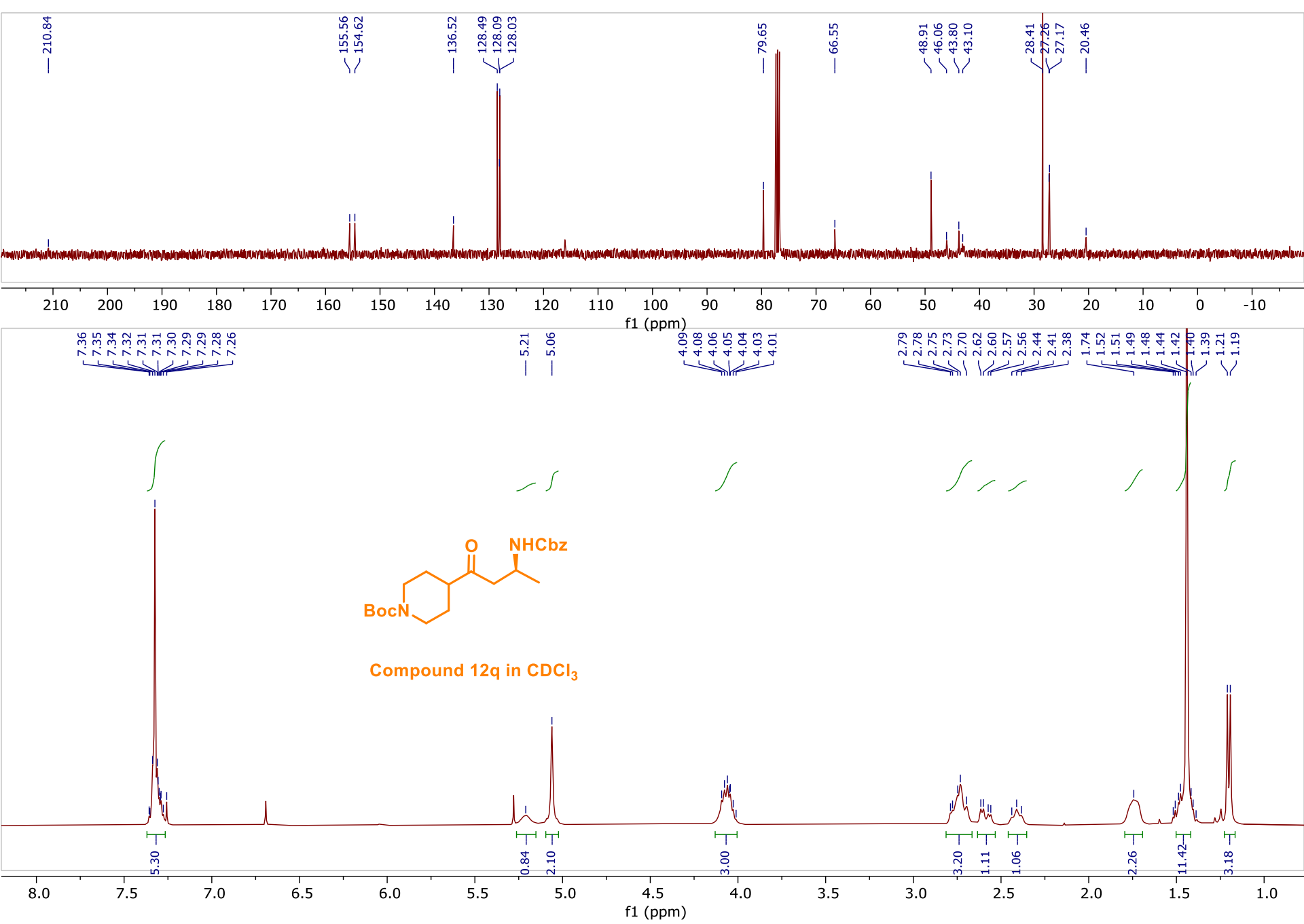
2.12
1.05
2.06
2.09
1.00
2.09
4.13
3.01
f1 (ppm)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154.62
136.52
128.49
128.09
128.03
79.65
66.55
48.91
46.06
43.80
43.10
28.41
27.26
27.17
20.46
f1 (ppm)
7.36
7.35
7.34
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.26
5.21
5.06
4.09
4.08
4.06
4.05
4.04
4.03
4.01
2.79
2.78
2.75
2.73
2.70
2.62
2.60
2.57
2.56
2.44
2.41
2.38
1.74
1.52
1.51
1.49
1.48
1.44
1.42
1.40
1.39
1.21
1.19
O
NHCbz
BocN
Compound 12q in CDCl3
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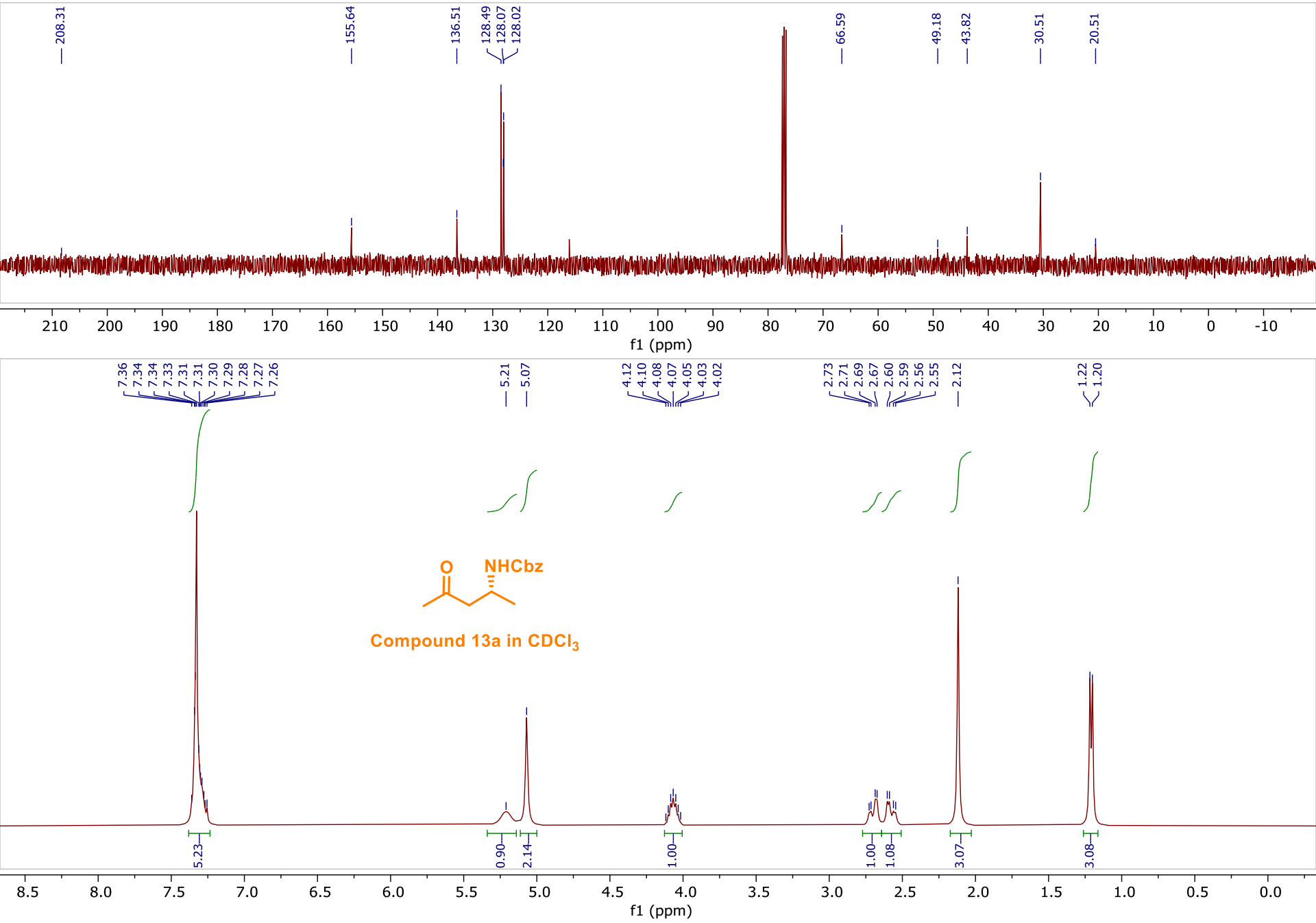
0.84
2.10
3.00
3.20
1.11
1.06
2.26
11.42
3.18
f1 (ppm)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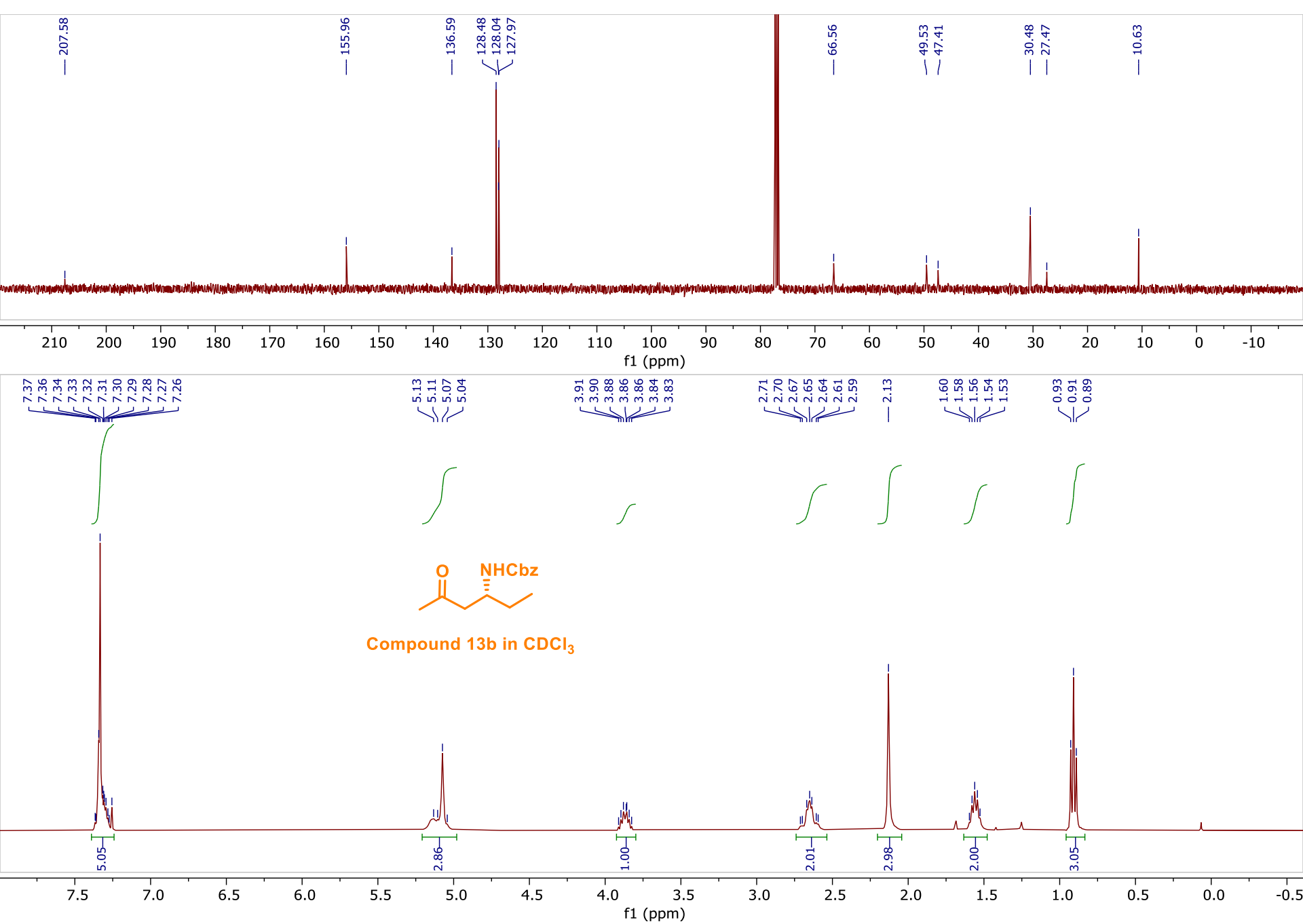
155.64
136.51
128.49
128.07
128.02
66.59
49.18
43.82
30.51
20.51
f1 (ppm)
7.36
7.34
7.34
7.33
7.31
7.31
7.30
7.29
7.28
7.27
7.26
5.21
5.07
4.12
4.10
4.08
4.07
4.05
4.03
4.02
2.73
2.71
2.69
2.67
2.60
2.59
2.56
2.55
2.12
1.22
1.20
O
NHCbz
Compound 13a in CDCl3
5.23
0.90
2.14
1.00
1.00
1.08
3.07
3.08
f1 (ppm)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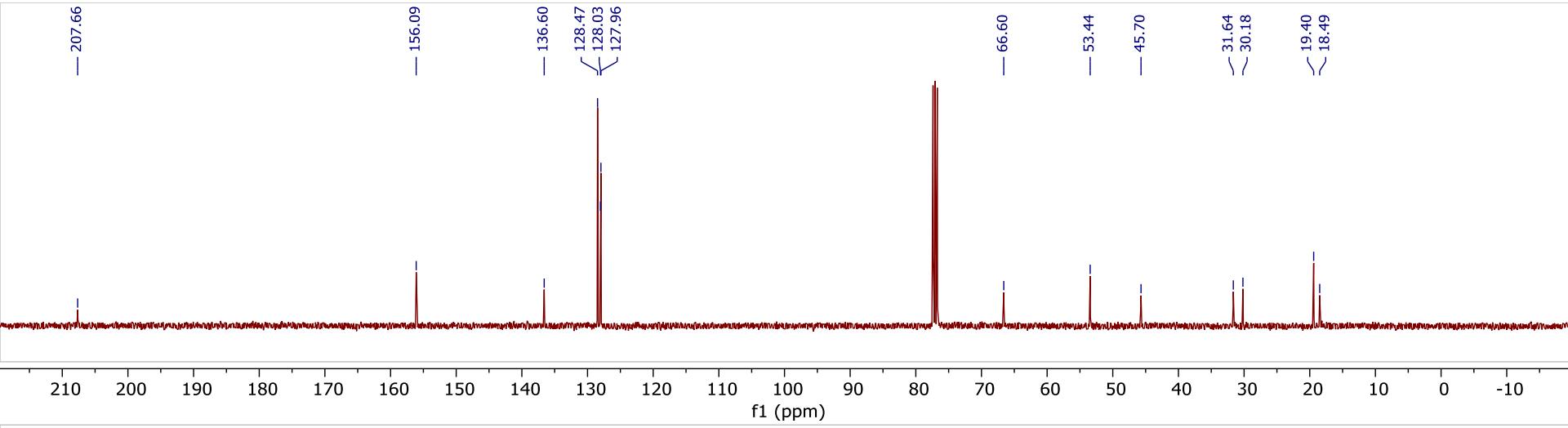
128.48
128.04
127.97
66.56
49.53
47.41
30.48
27.47
10.63
f1 (ppm)
7.37
7.36
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.26
5.13
5.11
5.07
5.04
3.91
3.90
3.88
3.86
3.86
3.84
3.83
2.71
2.70
2.67
2.65
2.64
2.61
2.59
2.13
1.60
1.58
1.56
1.54
1.53
0.93
0.91
0.89
O
NHCbz
Compound 13b in CDCl3
5.05
2.86
1.00
2.01
2.98
2.00
3.05
f1 (ppm)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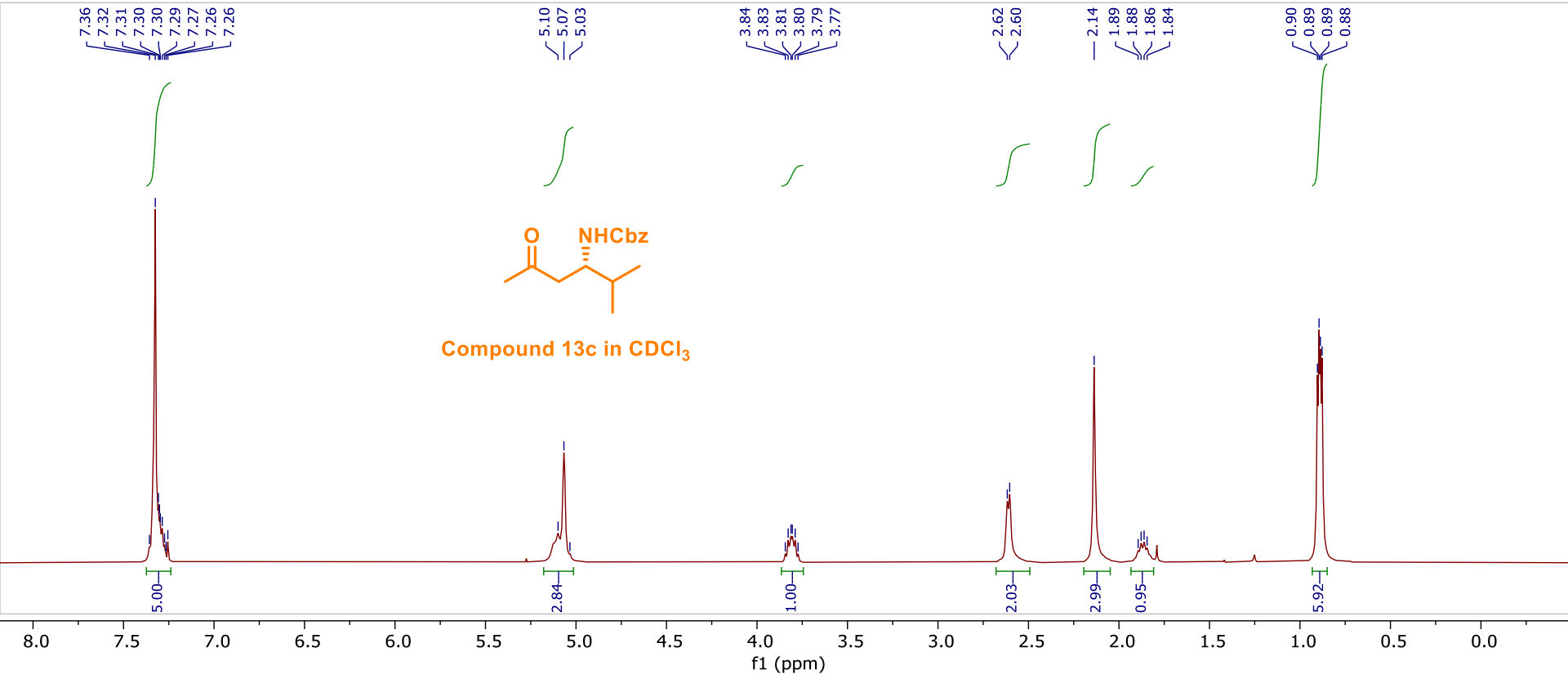
128.47
128.03
127.96
66.60
53.44
45.70
31.64
30.18
19.40
18.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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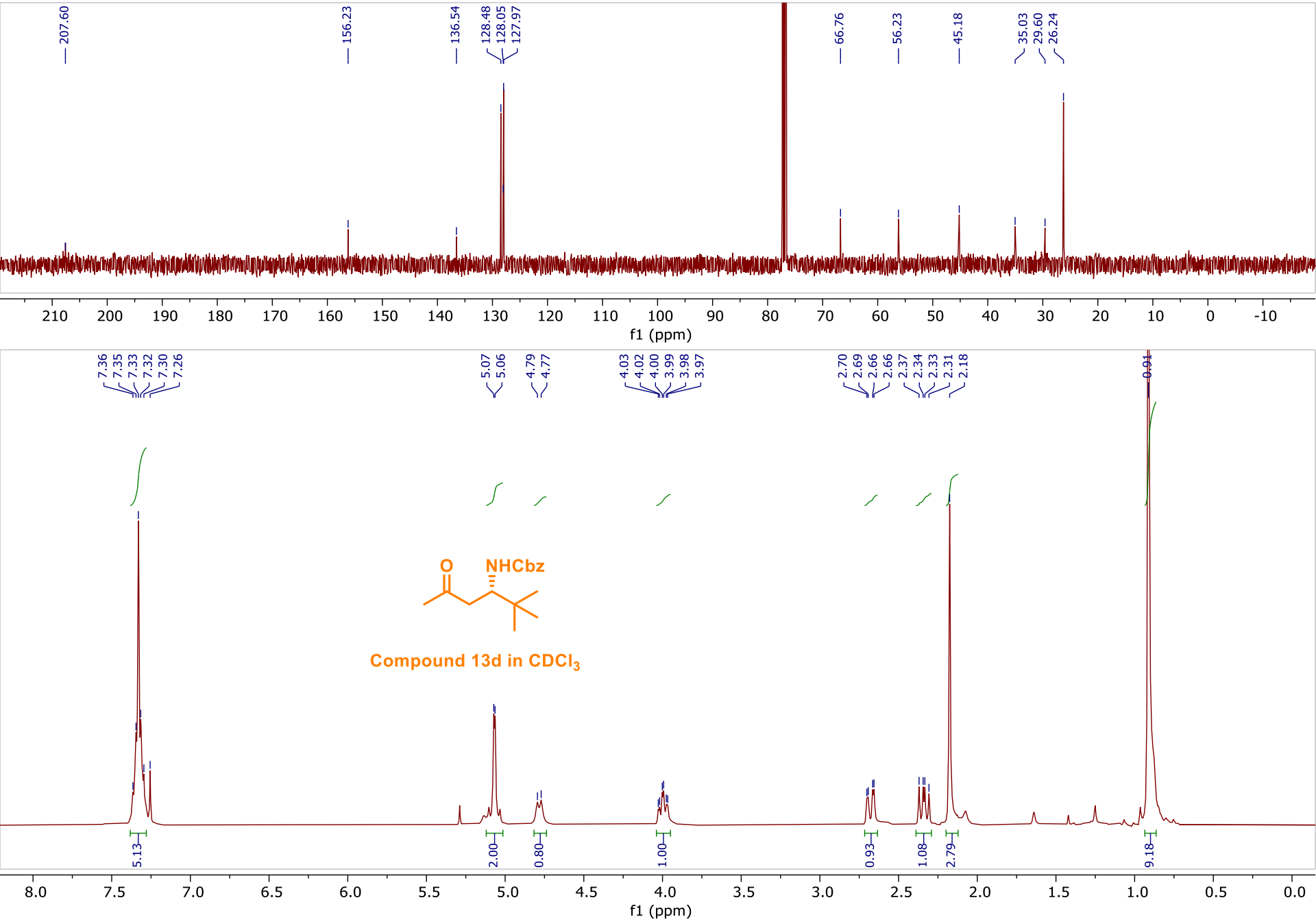
7.32
7.31
7.30
7.30
7.29
7.27
7.26
7.26
5.10
5.07
5.03
3.84
3.83
3.81
3.80
3.79
3.77
2.62
2.60
2.14
1.89
1.88
1.86
1.84
0.90
0.89
0.89
0.88
O
NHCbz
Compound 13c in CDCl3
5.00
2.84
1.00
2.03
2.99
0.95
5.92
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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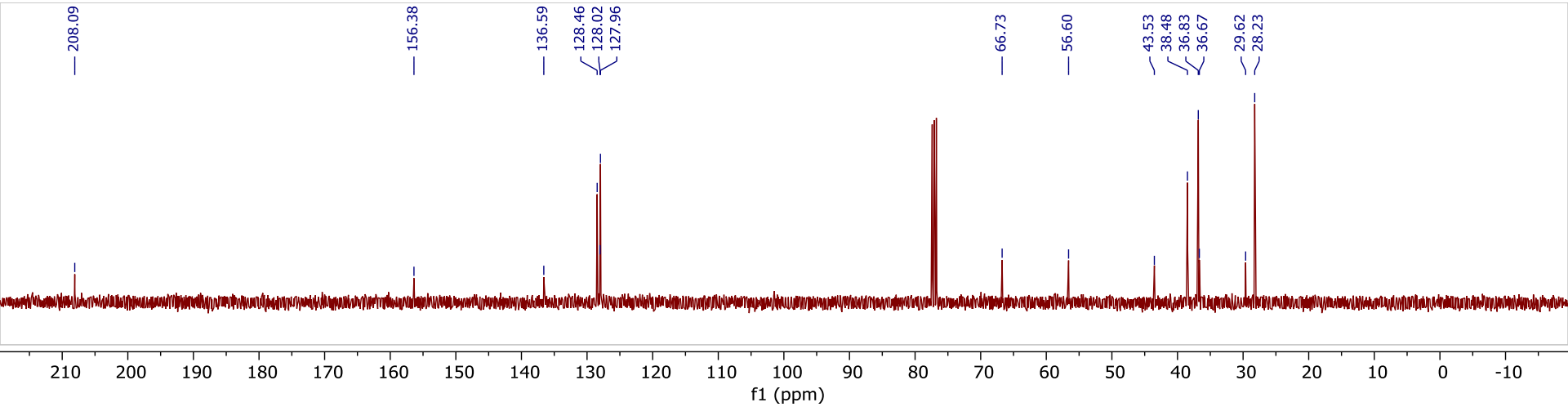
156.23
136.54
128.48
128.05
127.97
66.76
56.23
45.18
35.03
29.60
26.24
f1 (ppm)
7.36
7.35
7.33
7.32
7.30
7.26
5.07
5.06
4.79
4.77
4.03
4.02
4.00
3.99
3.98
3.97
2.70
2.69
2.66
2.66
2.37
2.34
2.33
2.31
2.18
0.91
O
NHCbz
Compound 13d in CDCl3
5.13
2.00
0.80
1.00
0.93
1.08
2.79
9.18
f1 (ppm)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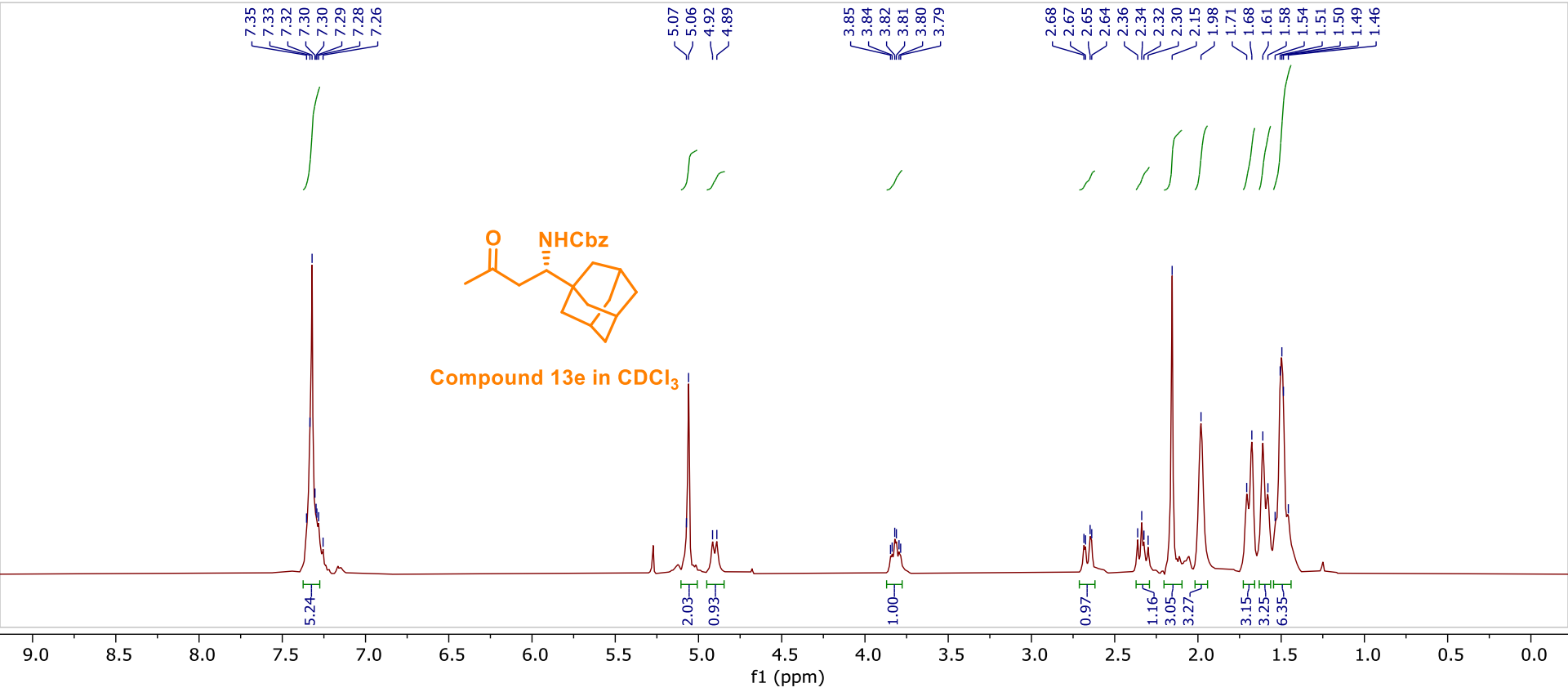
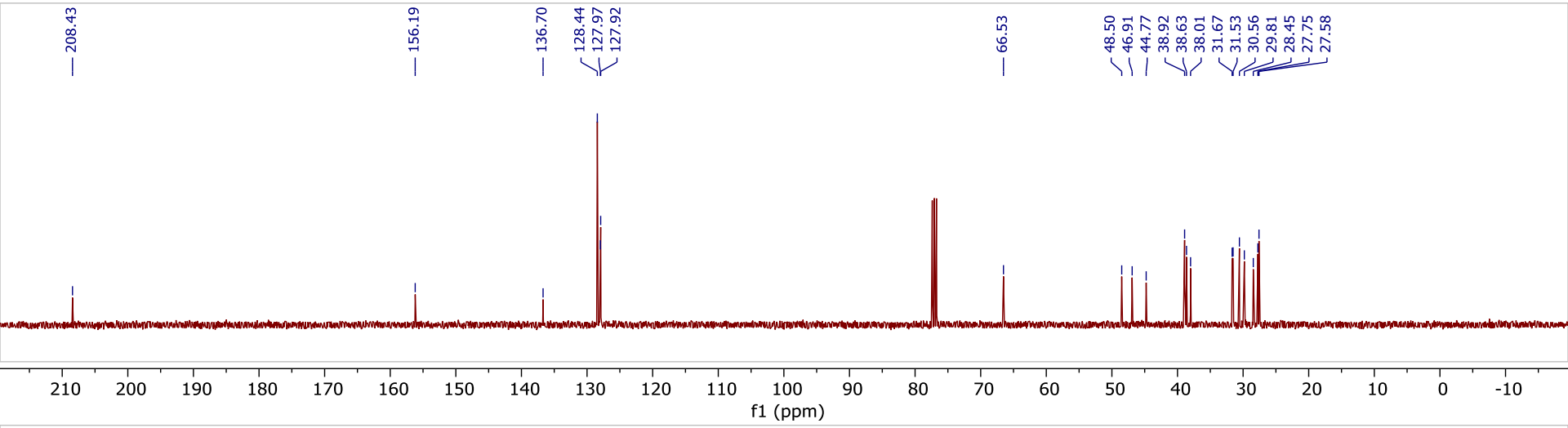
66.73
56.60
43.53
38.48
36.83
36.67
29.62
28.23
f1 (ppm)


7.35
7.33
7.32
7.30
7.30
7.29
7.28
7.26
5.07
5.06
4.92
4.89
3.85
3.84
3.82
3.81
3.80
3.79
2.68
2.67
2.65
2.64
2.36
2.34
2.32
2.30
2.15
1.98
1.71
1.68
1.61
1.58
1.54
1.51
1.50
1.49
1.46
O
NHCbz
Compound 13e in CDCl3
5.24
2.03
0.93
1.00
0.97
1.16
3.05
3.27
3.15
3.25
6.35
f1 (ppm)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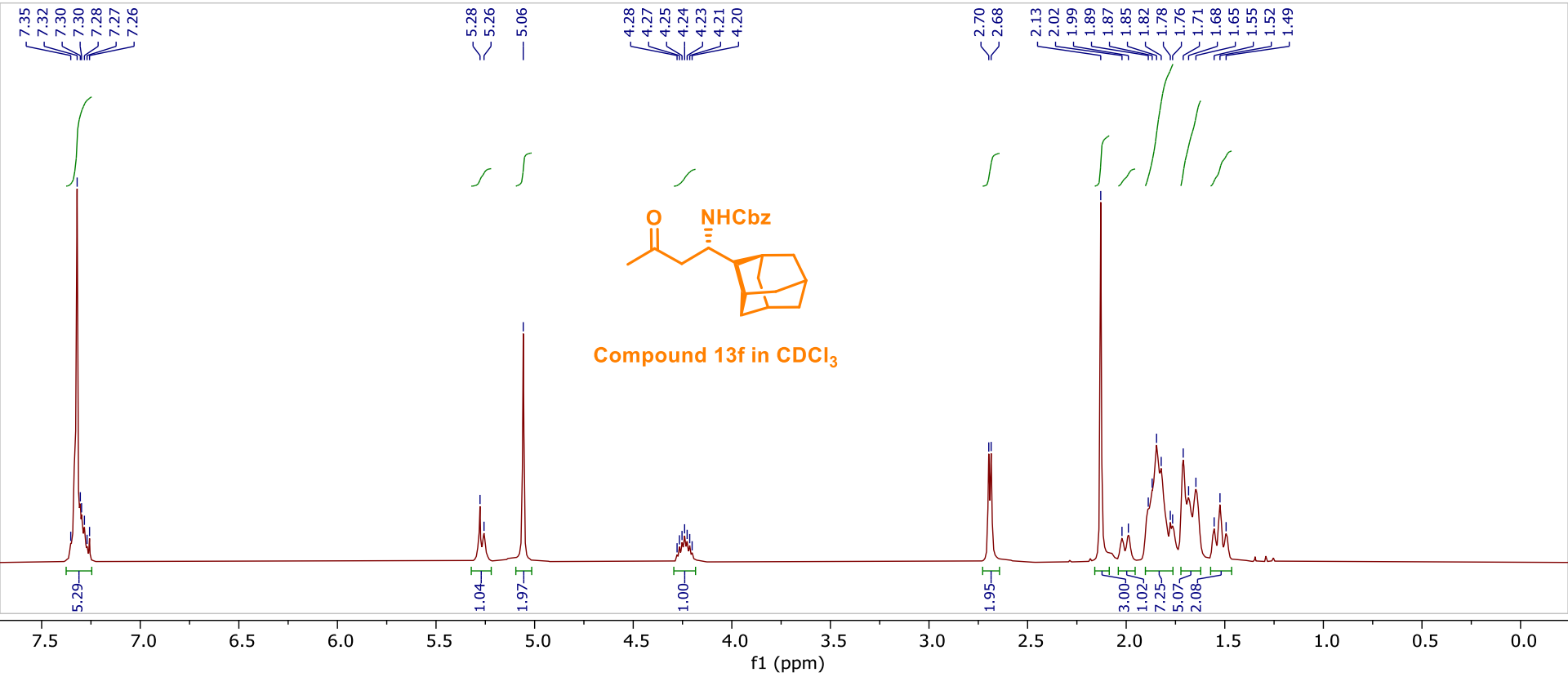
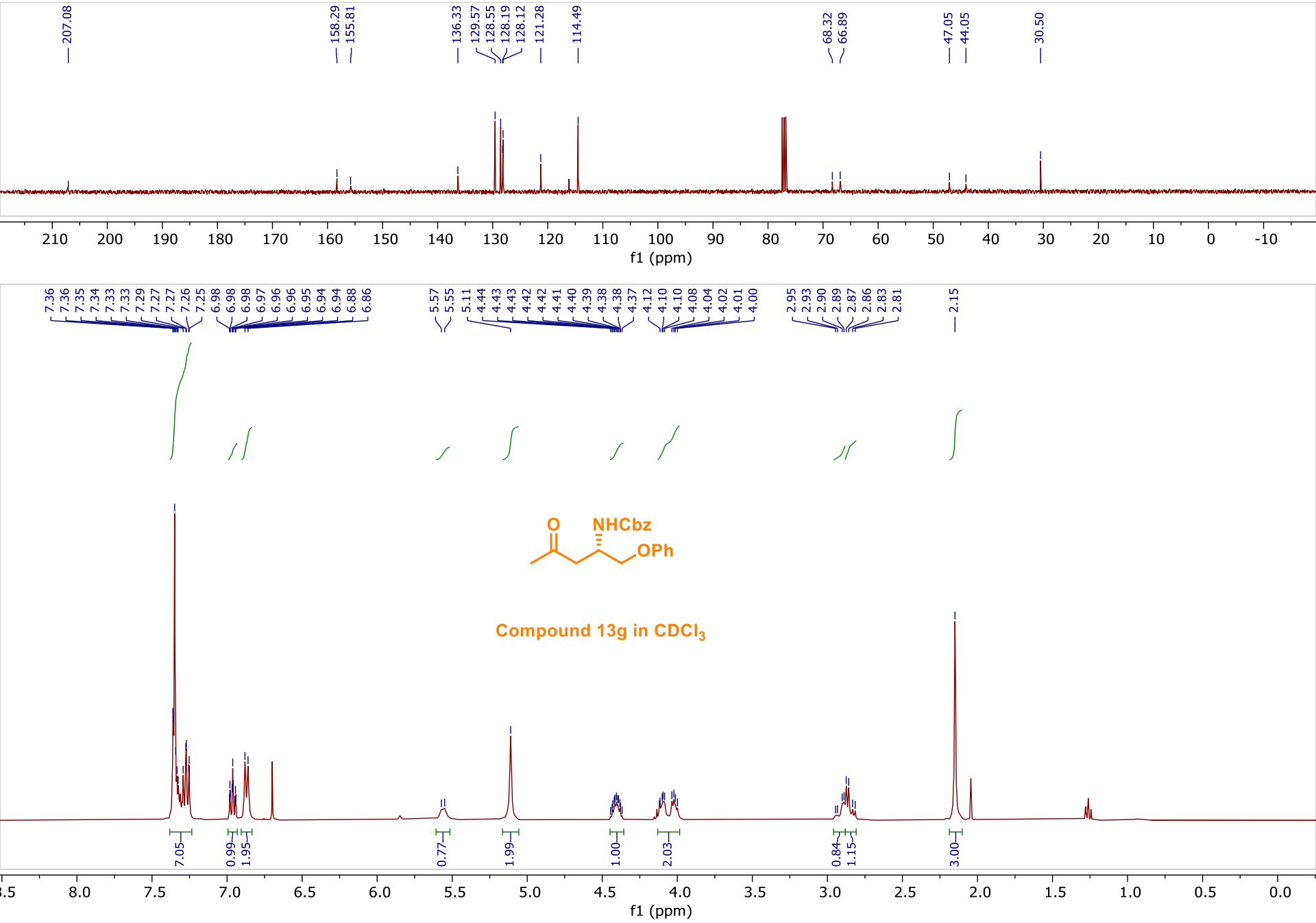
156.19
136.70
128.44
127.97
127.92
66.53
48.50
46.91
44.77
38.92
38.63
38.01
31.67
31.53
30.56
29.81
28.45
27.75
27.58
f1 (ppm)


7.35
7.32
7.30
7.30
7.28
7.27
7.26
5.28
5.26
5.06
4.28
4.27
4.25
4.24
4.23
4.21
4.20
2.70
2.68
2.13
2.02
1.99
1.89
1.87
1.85
1.82
1.78
1.76
1.71
1.68
1.65
1.55
1.52
1.49
O
NHCbz
Compound 13f in CDCl3
5.29
1.04
1.97
1.00
1.95
3.00
1.02
7.25
5.07
2.08
f1 (ppm)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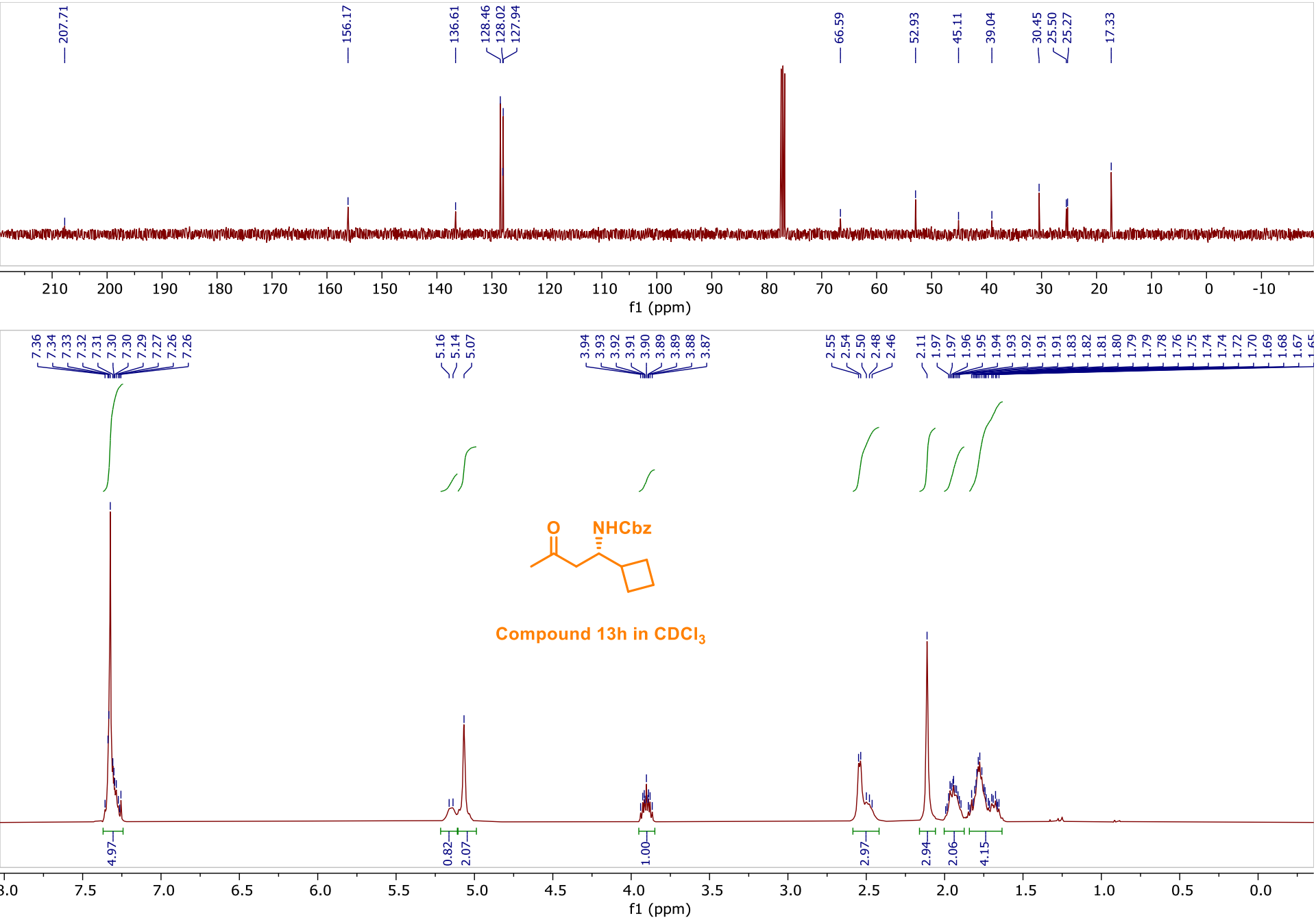
158.29
155.81
136.33
129.57
128.55
128.19
128.12
121.28
114.49
68.32
66.89
47.05
44.05
30.50
f1 (ppm)
7.36
7.36
7.35
7.34
7.33
7.33
7.29
7.27
7.27
7.26
7.25
6.98
6.98
6.98
6.97
6.96
6.96
6.95
6.94
6.94
6.88
6.86
5.57
5.55
5.11
4.44
4.43
4.43
4.42
4.42
4.41
4.40
4.39
4.38
4.38
4.37
4.12
4.10
4.10
4.08
4.04
4.02
4.01
4.00
2.95
2.93
2.90
2.89
2.87
2.86
2.83
2.81
2.15
O
NHCbz
OPh
Compound 13g in CDCl3
7.05
0.99
1.95
0.77
1.99
1.00
2.03
0.84
1.15
3.00
f1 (ppm)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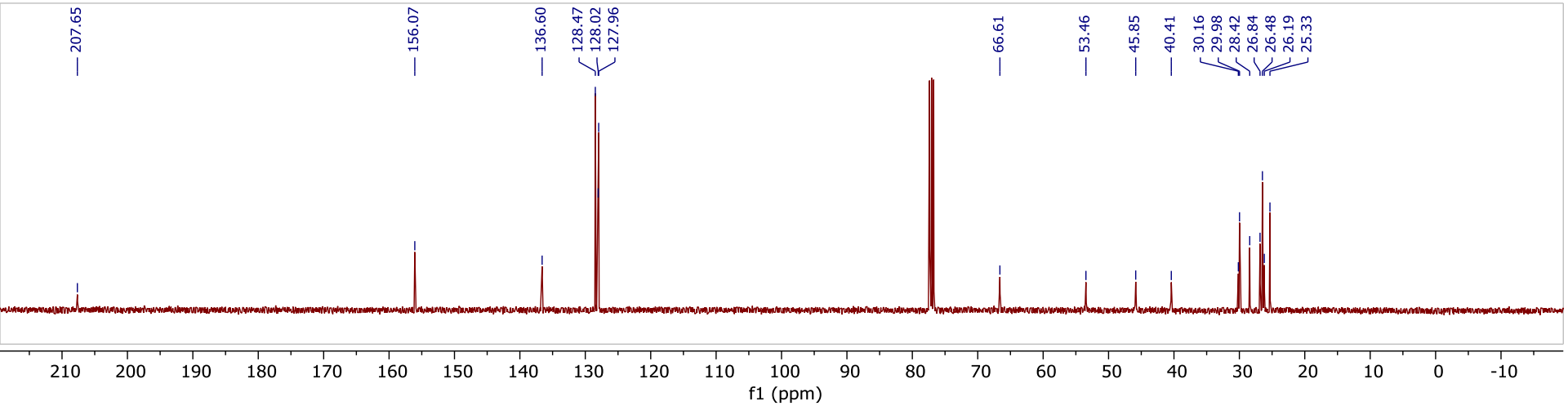
156.17
136.61
128.46
128.02
127.94
66.59
52.93
45.11
39.04
30.45
25.50
25.27
17.33
f1 (ppm)
7.36
7.34
7.33
7.32
7.31
7.30
7.30
7.29
7.27
7.26
7.26
5.16
5.14
5.07
3.94
3.93
3.92
3.91
3.90
3.89
3.89
3.88
3.87
2.55
2.54
2.50
2.48
2.46
2.11
1.97
1.97
1.96
1.95
1.94
1.93
1.92
1.91
1.91
1.83
1.82
1.81
1.80
1.79
1.79
1.78
1.76
1.75
1.74
1.74
1.72
1.70
1.69
1.68
1.67
O
NHCbz
Compound 13h in CDCl3
4.97
0.82
2.07
1.00
2.97
2.94
2.06
4.15
f1 (ppm)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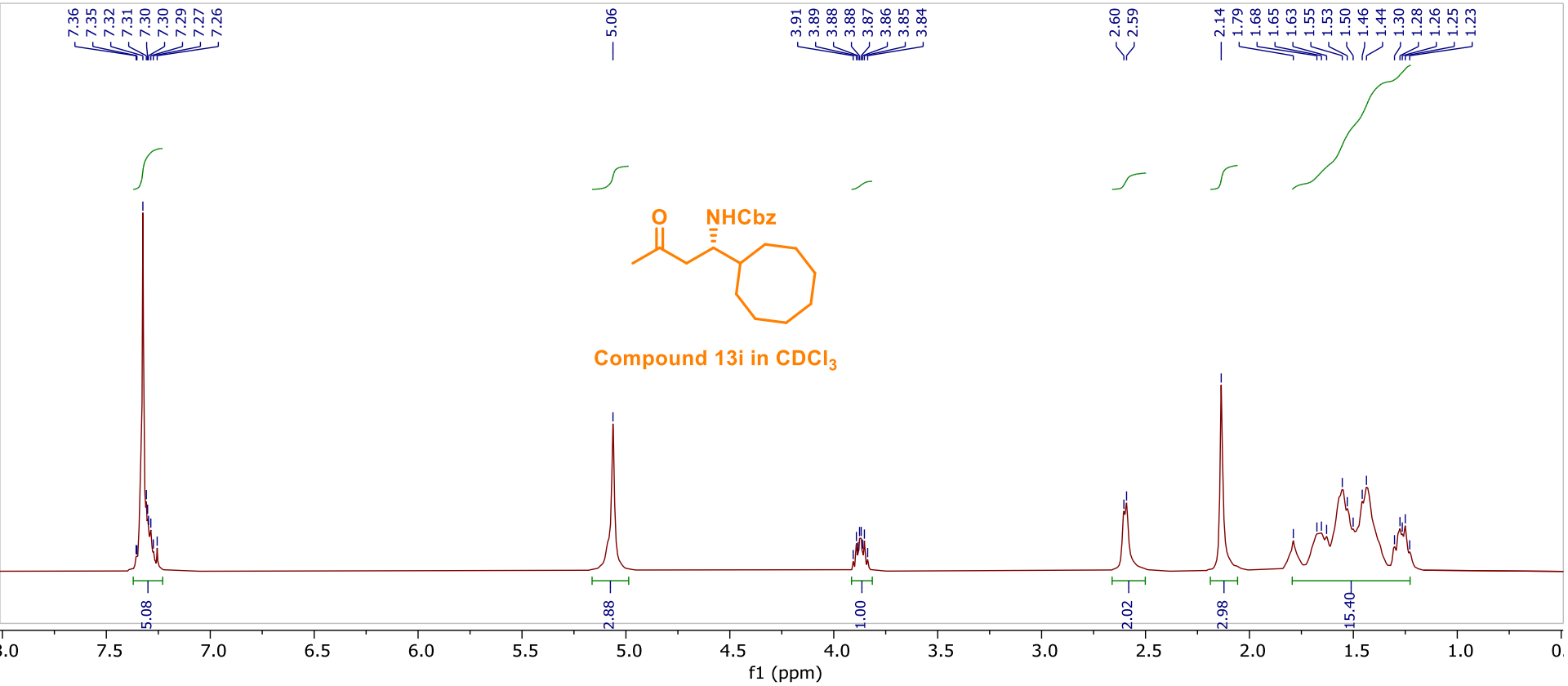
156.07
136.60
128.47
128.02
127.96
66.61
53.46
45.85
40.41
30.16
29.98
28.42
26.84
26.48
26.19
25.33
f1 (ppm)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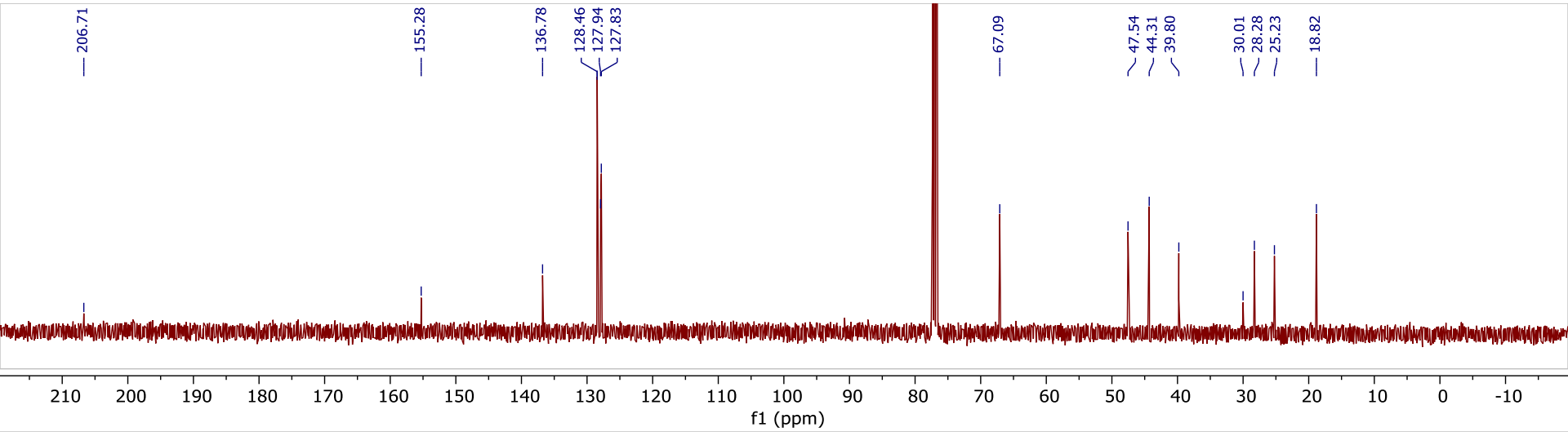
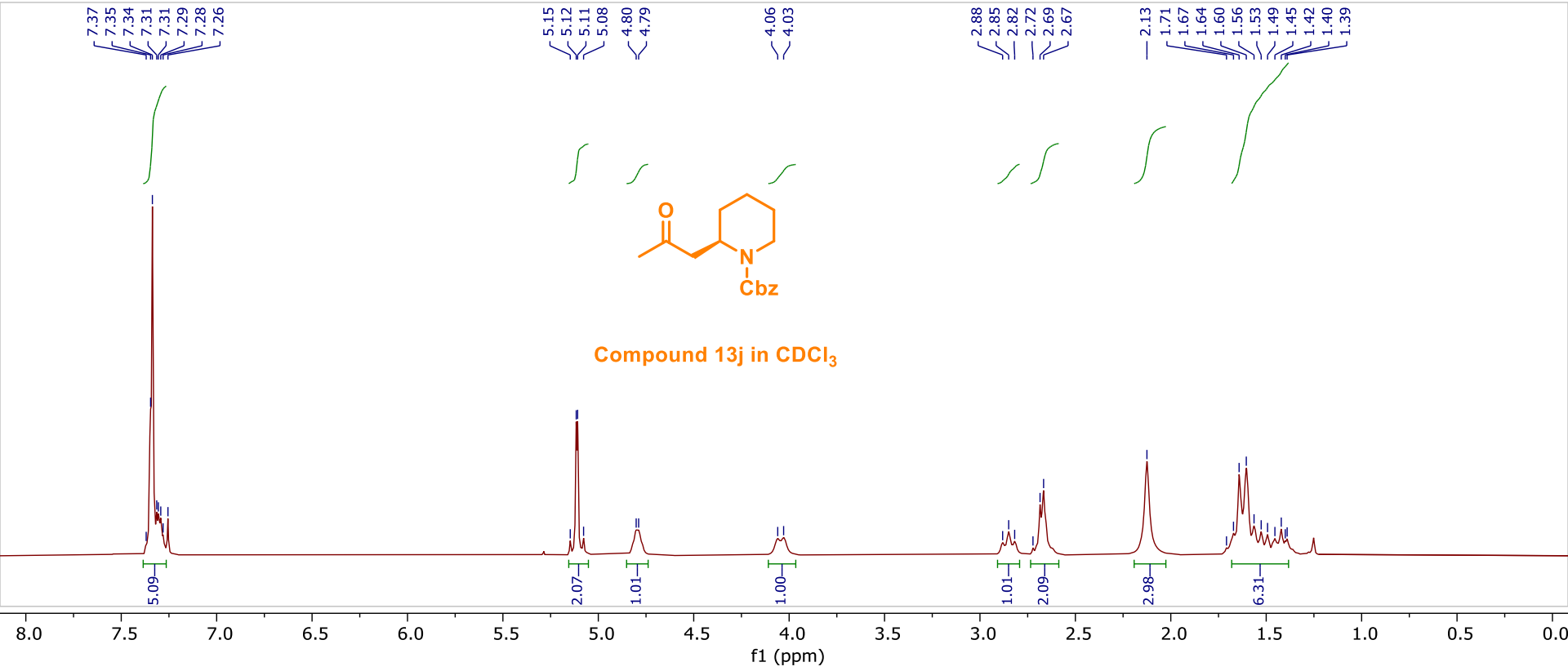
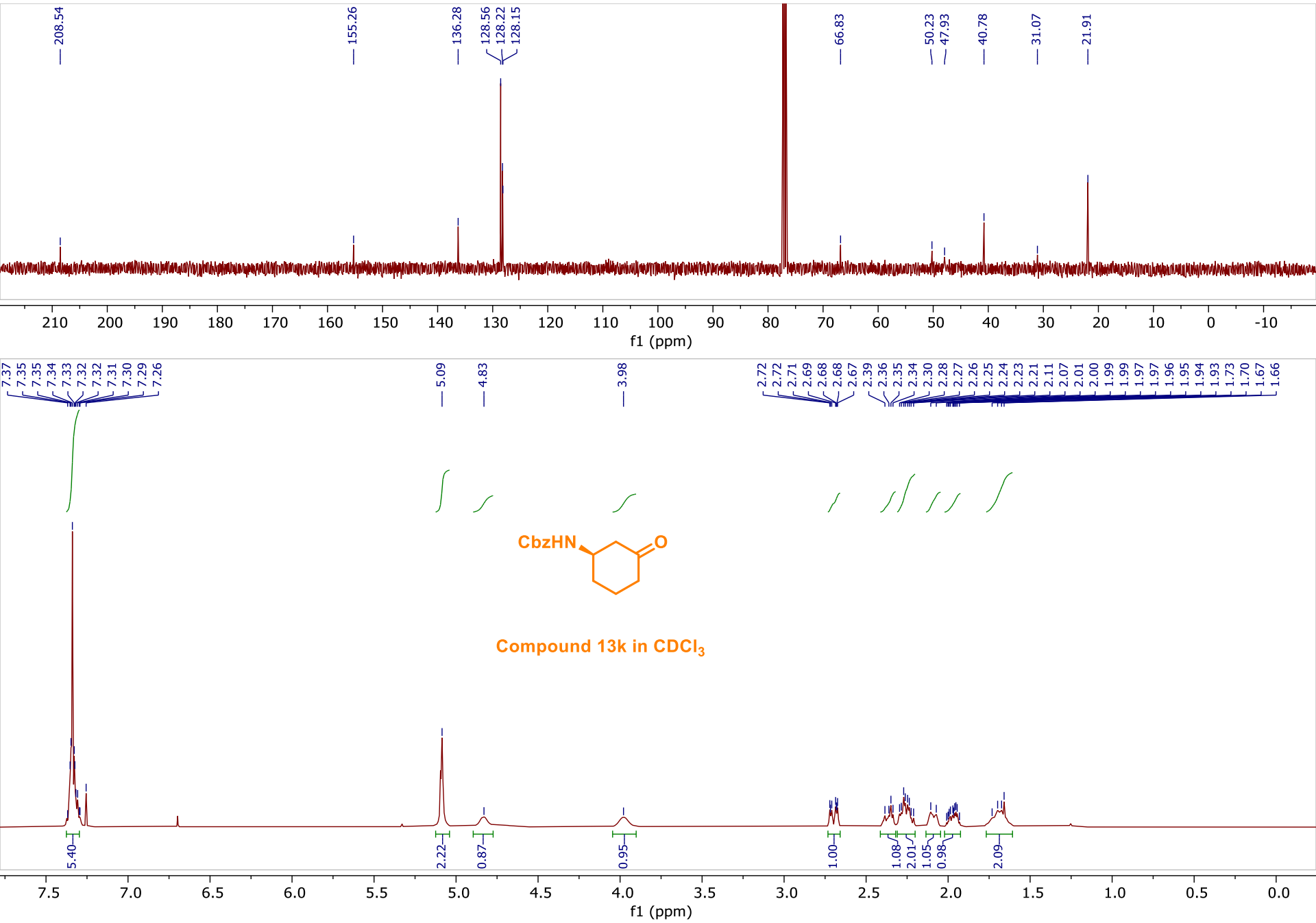
7.35
7.32
7.31
7.30
7.30
7.29
7.27
7.26
5.06
3.91
3.89
3.88
3.88
3.87
3.86
3.85
3.84
2.60
2.59
2.14
1.79
1.68
1.65
1.63
1.55
1.53
1.50
1.46
1.44
1.30
1.28
1.26
1.25
1.23
O
NHCbz
Compound 13i in CDCl3
5.08
2.88
1.00
2.02
2.98
15.40
f1 (ppm)


206.71
155.28
136.78
128.46
127.94
127.83
67.09
47.54
44.31
39.80
30.01
28.28
25.23
18.82
f1 (ppm)


7.37
7.35
7.34
7.31
7.31
7.29
7.28
7.26
5.15
5.12
5.11
5.08
4.80
4.79
4.06
4.03
2.88
2.85
2.82
2.72
2.69
2.67
2.13
1.71
1.67
1.64
1.60
1.56
1.53
1.49
1.45
1.42
1.40
1.39
O
N
Cbz
Compound 13j in CDCl3
5.09
2.07
1.01
1.00
1.01
2.09
2.98
6.31
f1 (ppm)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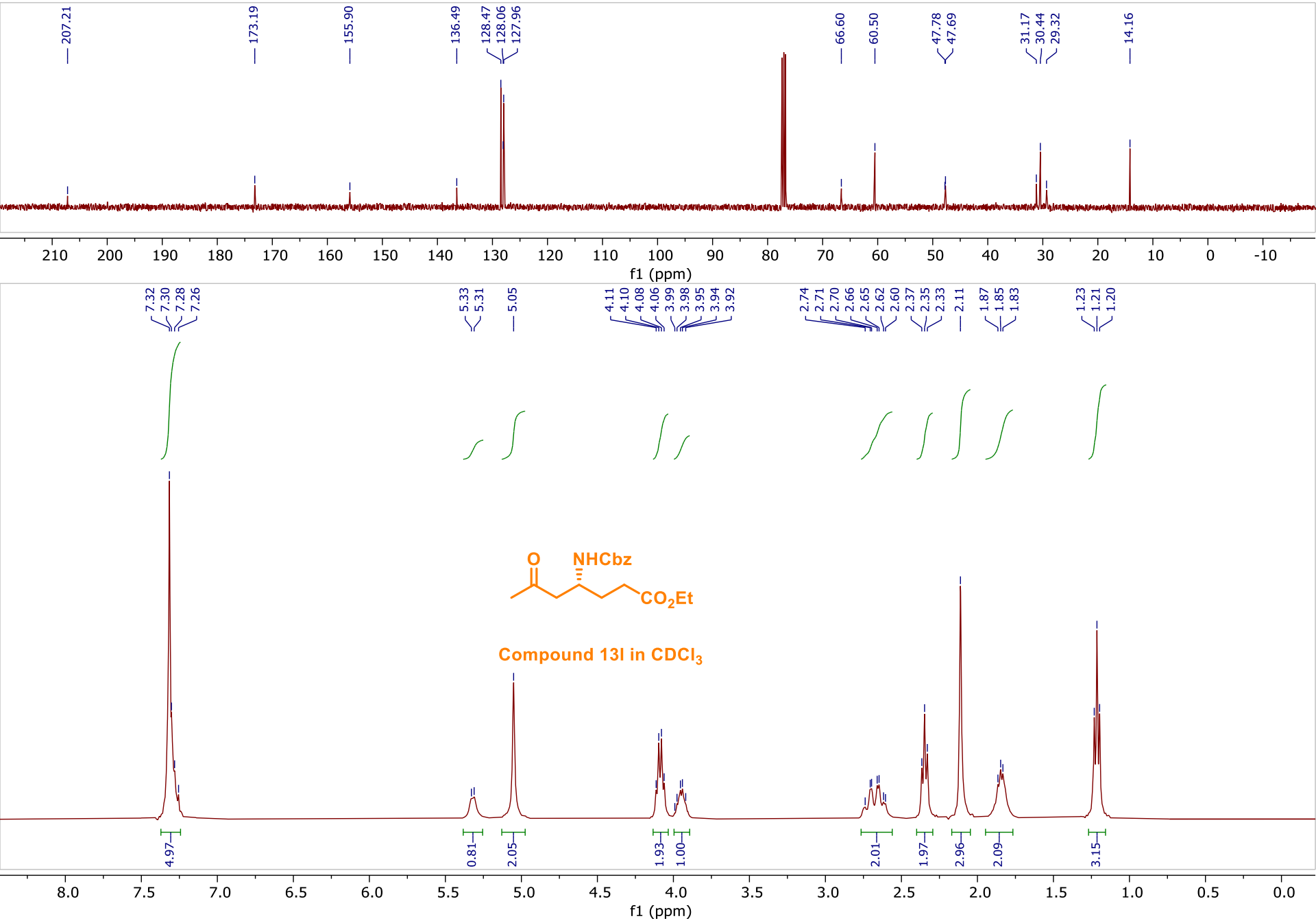
155.26
136.28
128.56
128.22
128.15
66.83
50.23
47.93
40.78
31.07
21.91
f1 (ppm)
7.37
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.30
7.29
7.26
5.09
4.83
3.98
2.72
2.72
2.71
2.69
2.68
2.68
2.67
2.39
2.36
2.35
2.34
2.30
2.28
2.27
2.26
2.25
2.24
2.23
2.21
2.11
2.07
2.01
2.00
1.99
1.99
1.97
1.97
1.96
1.95
1.94
1.93
1.73
1.70
1.67
1.66
CbzHN
O
Compound 13k in CDCl3
5.40
2.22
0.87
0.95
1.00
1.08
2.01
1.05
0.98
2.09
f1 (ppm)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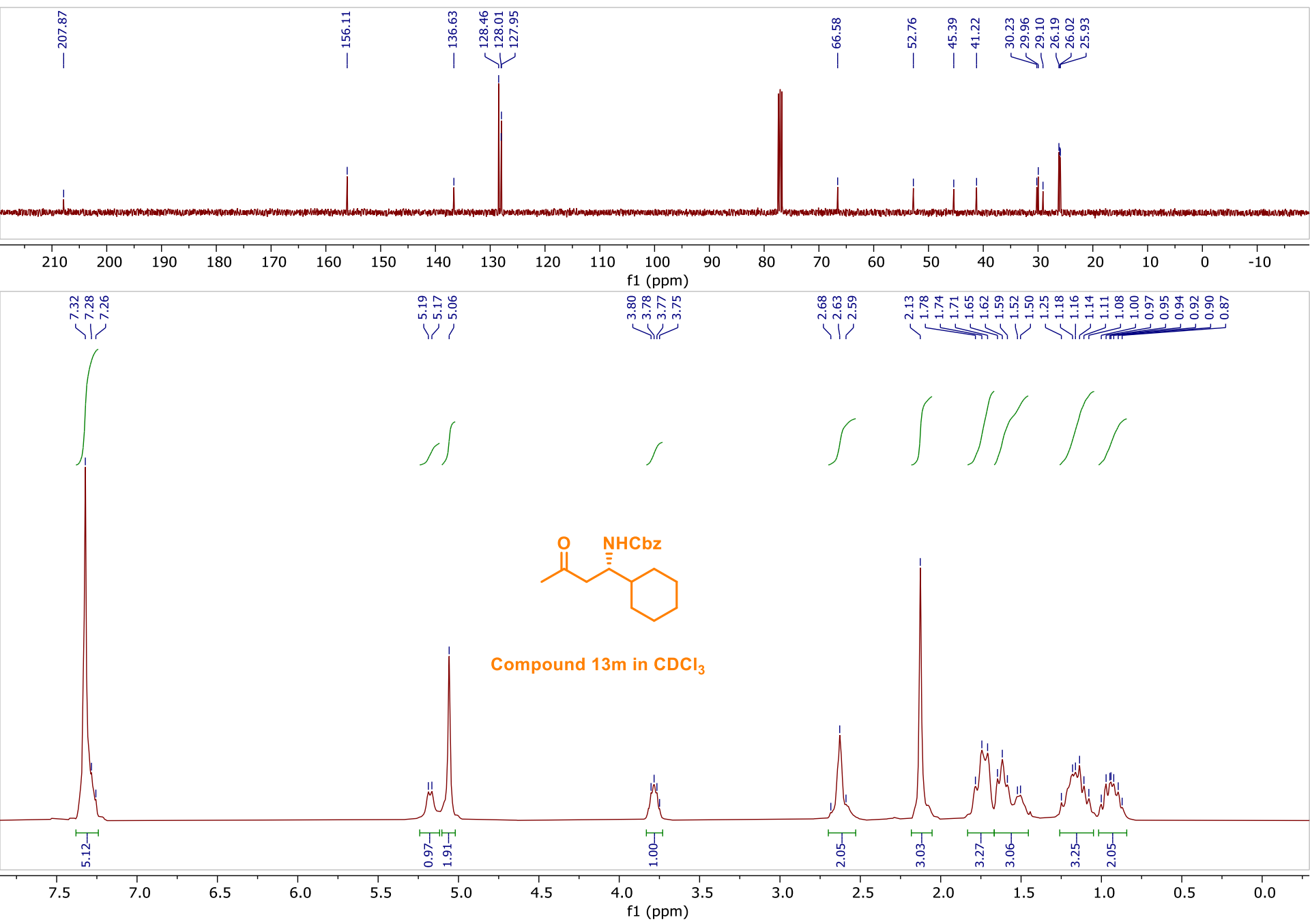
173.19
155.90
136.49
128.47
128.06
127.96
66.60
60.50
47.78
47.69
31.17
30.44
29.32
14.16
f1 (ppm)
7.32
7.30
7.28
7.26
5.33
5.31
5.05
4.11
4.10
4.08
4.06
3.99
3.98
3.95
3.94
3.92
2.74
2.71
2.70
2.66
2.65
2.62
2.60
2.37
2.35
2.33
2.11
1.87
1.85
1.83
1.23
1.21
1.20
O
NHCbz
CO2Et
Compound 13l in CDCl3
4.97
0.81
2.05
1.93
1.00
2.01
1.97
2.96
2.09
3.15
f1 (ppm)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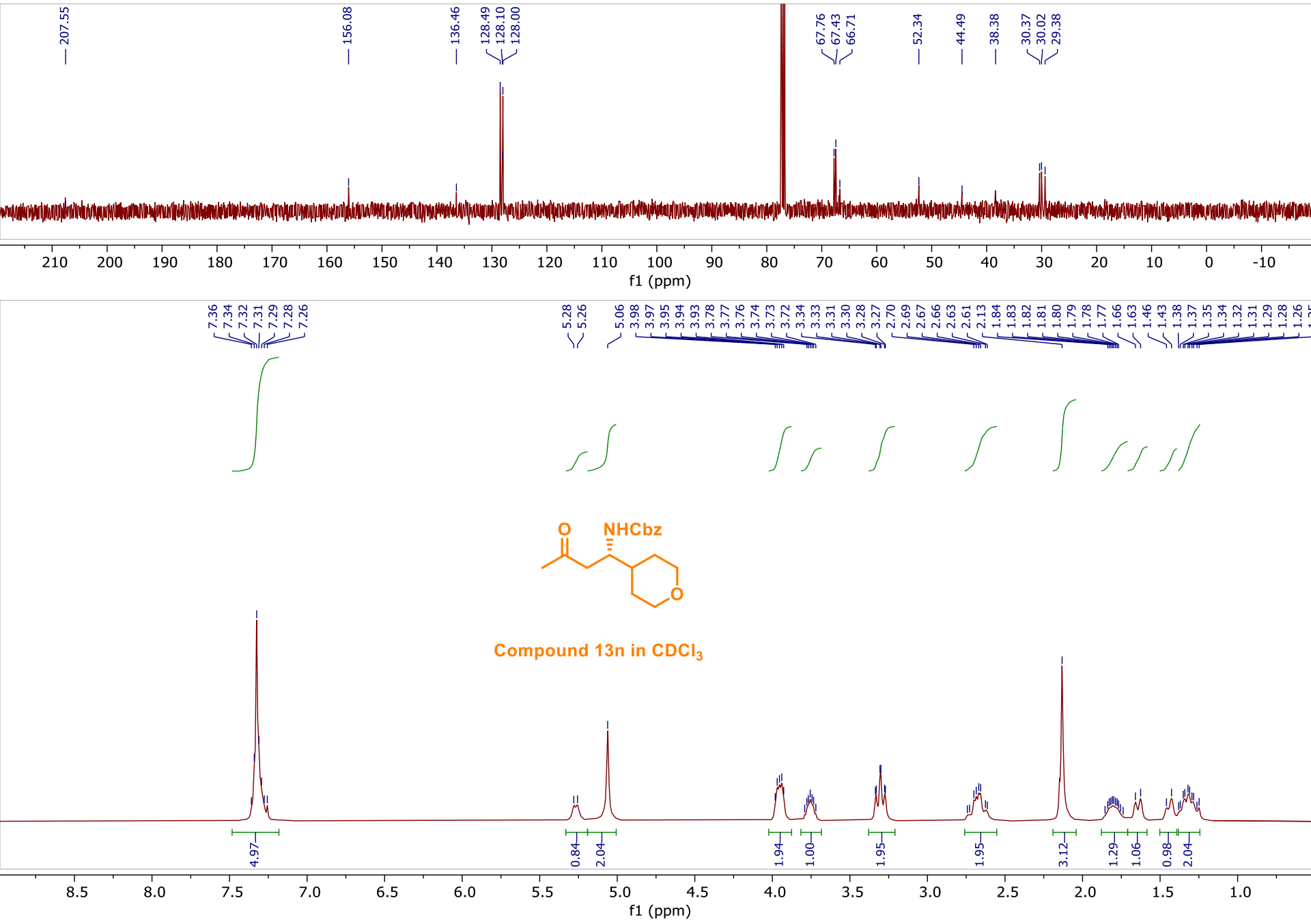
136.63
128.46
128.01
127.95
66.58
52.76
45.39
41.22
30.23
29.96
29.10
26.19
26.02
25.93
f1 (ppm)
7.32
7.28
7.26
5.19
5.17
5.06
3.80
3.78
3.77
3.75
2.68
2.63
2.59
2.13
1.78
1.74
1.71
1.65
1.62
1.59
1.52
1.50
1.25
1.18
1.16
1.14
1.11
1.08
1.00
0.97
0.95
0.94
0.92
0.90
0.87
O
NHCbz
Compound 13m in CDCl3
5.12
0.97
1.91
1.00
2.05
3.03
3.27
3.06
3.25
2.05
f1 (ppm)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156.08
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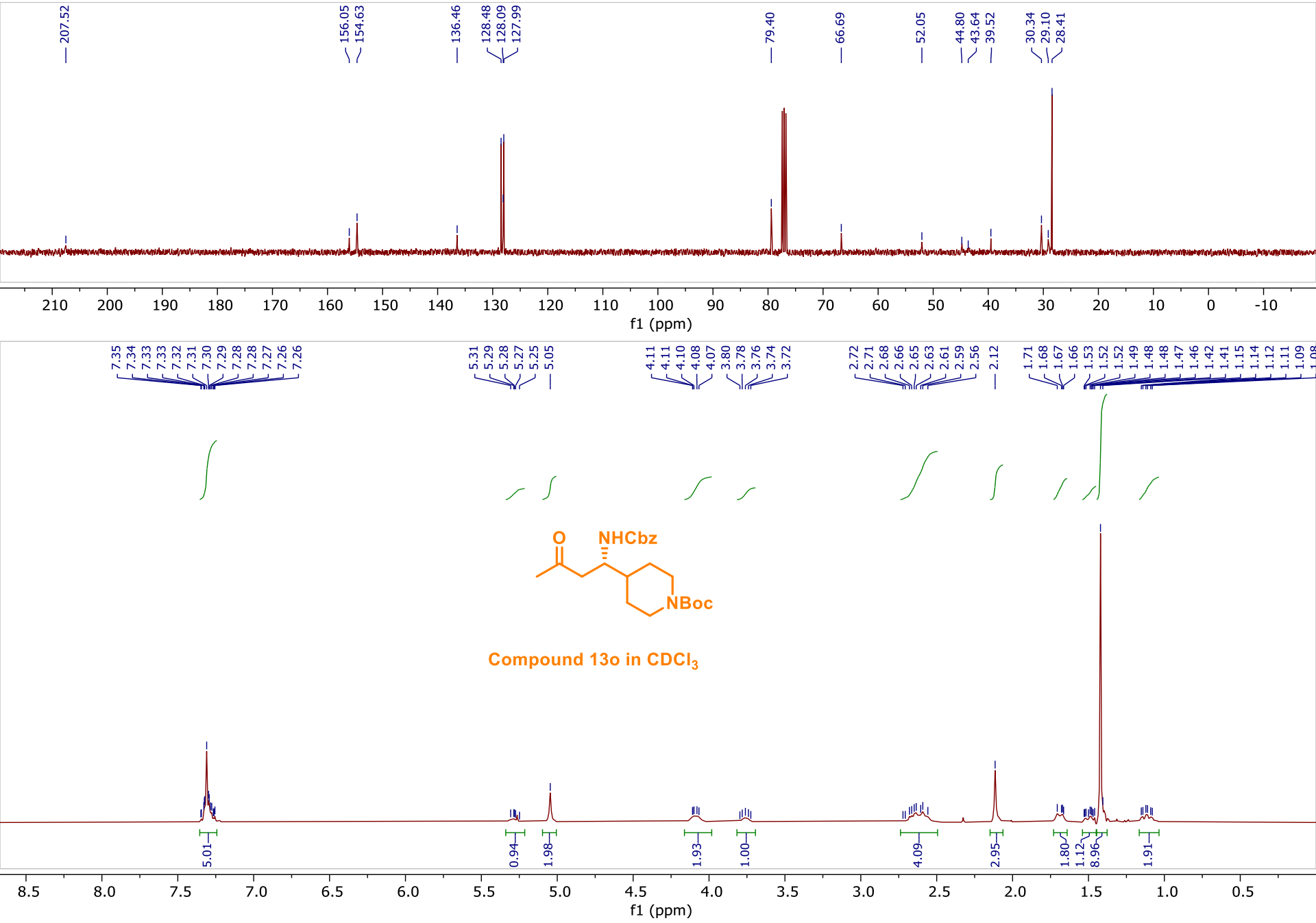
128.49
128.10
128.00
67.76
67.43
66.71
52.34
44.49
38.38
30.37
30.02
29.38
f1 (ppm)
7.36
7.34
7.32
7.31
7.29
7.28
7.26
5.28
5.26
5.06
3.98
3.97
3.95
3.94
3.93
3.78
3.77
3.76
3.74
3.73
3.72
3.34
3.33
3.31
3.30
3.28
3.27
2.70
2.69
2.67
2.66
2.63
2.61
2.13
1.84
1.83
1.82
1.81
1.80
1.79
1.78
1.77
1.66
1.63
1.46
1.43
1.38
1.37
1.35
1.34
1.32
1.31
1.29
1.28
1.26
O
NHCbz
O
Compound 13n in CDCl3
4.97
0.84
2.04
1.94
1.00
1.95
1.95
3.12
1.29
1.06
0.98
2.04
f1 (ppm)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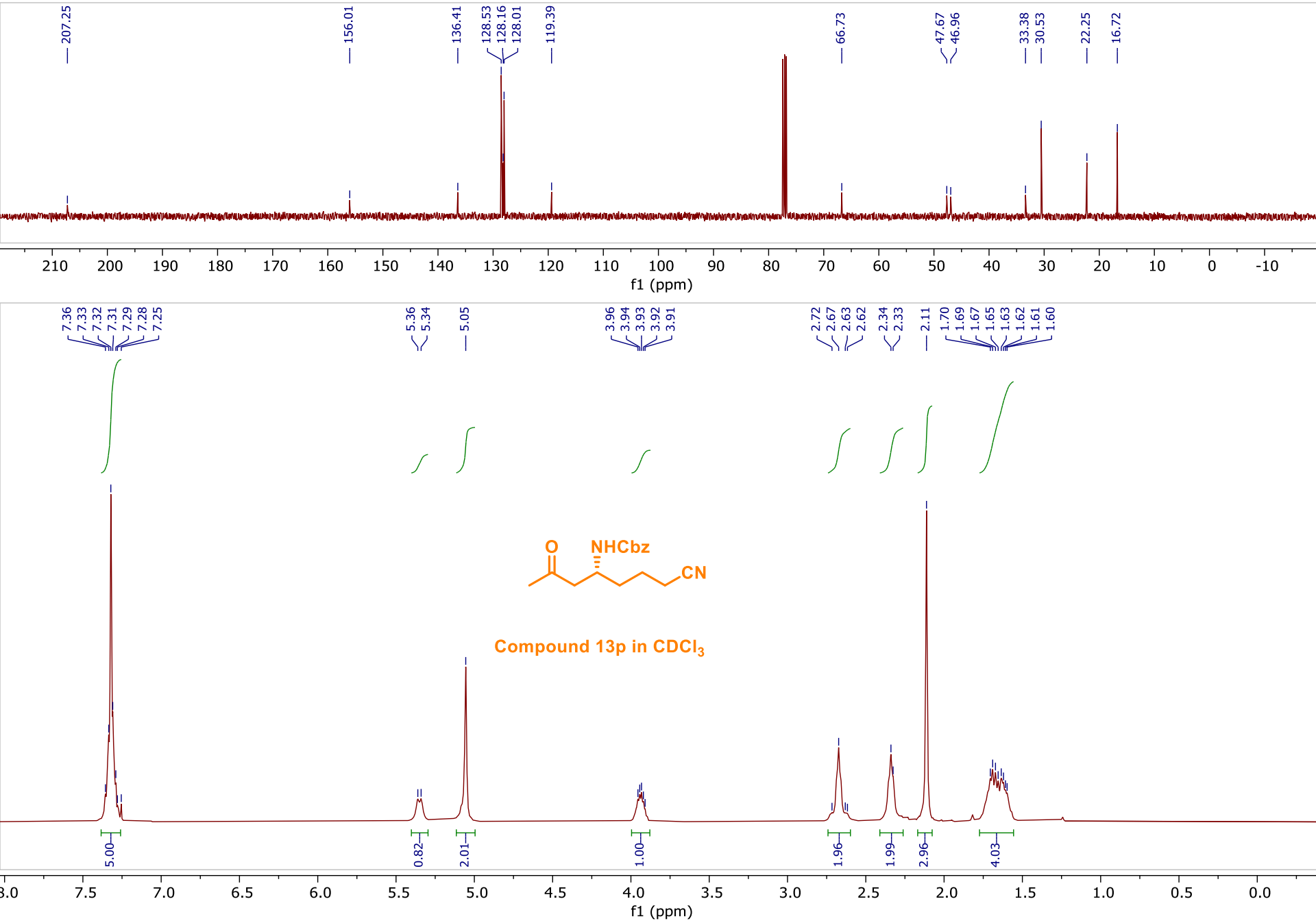
154.63
136.46
128.48
128.09
127.99
79.40
66.69
52.05
44.80
43.64
39.52
30.34
29.10
28.41
f1 (ppm)
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.28
7.28
7.27
7.26
7.26
5.31
5.29
5.28
5.27
5.25
5.05
4.11
4.11
4.10
4.08
4.07
3.80
3.78
3.76
3.74
3.72
2.72
2.71
2.68
2.66
2.65
2.63
2.61
2.59
2.56
2.12
1.71
1.68
1.67
1.66
1.53
1.52
1.52
1.49
1.48
1.48
1.47
1.46
1.42
1.41
1.15
1.14
1.12
1.11
1.09
O
NHCbz
NBoc
Compound 13o in CDCl3
5.01
0.94
1.98
1.93
1.00
4.09
2.95
1.80
1.12
8.96
1.91
f1 (ppm)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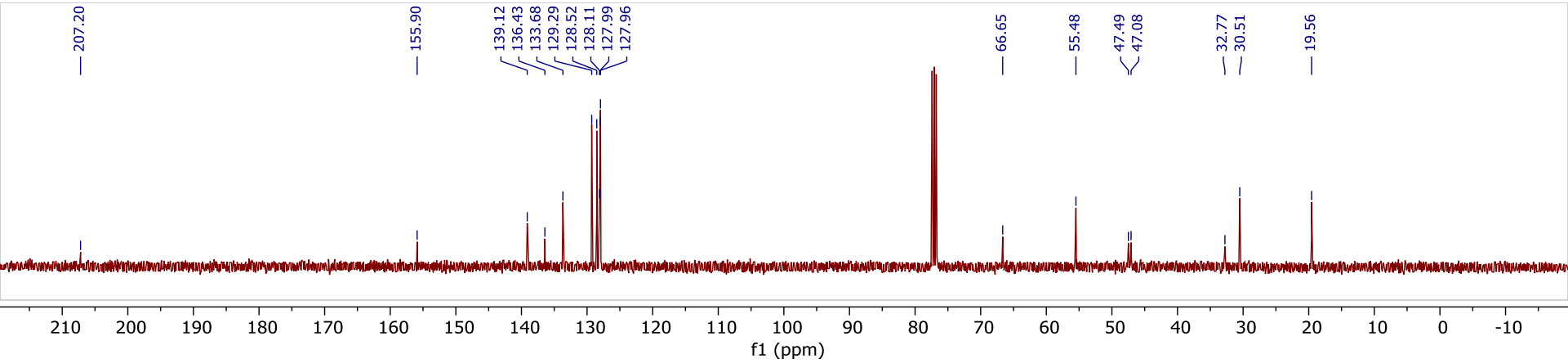
136.41
128.53
128.16
128.01
119.39
66.73
47.67
46.96
33.38
30.53
22.25
16.72
f1 (ppm)
7.36
7.33
7.32
7.31
7.29
7.28
7.25
5.36
5.34
5.05
3.96
3.94
3.93
3.92
3.91
2.72
2.67
2.63
2.62
2.34
2.33
2.11
1.70
1.69
1.67
1.65
1.63
1.62
1.61
1.60
O
NHCbz
CN
Compound 13p in CDCl3
5.00
0.82
2.01
1.00
1.96
1.99
2.96
4.03
f1 (ppm)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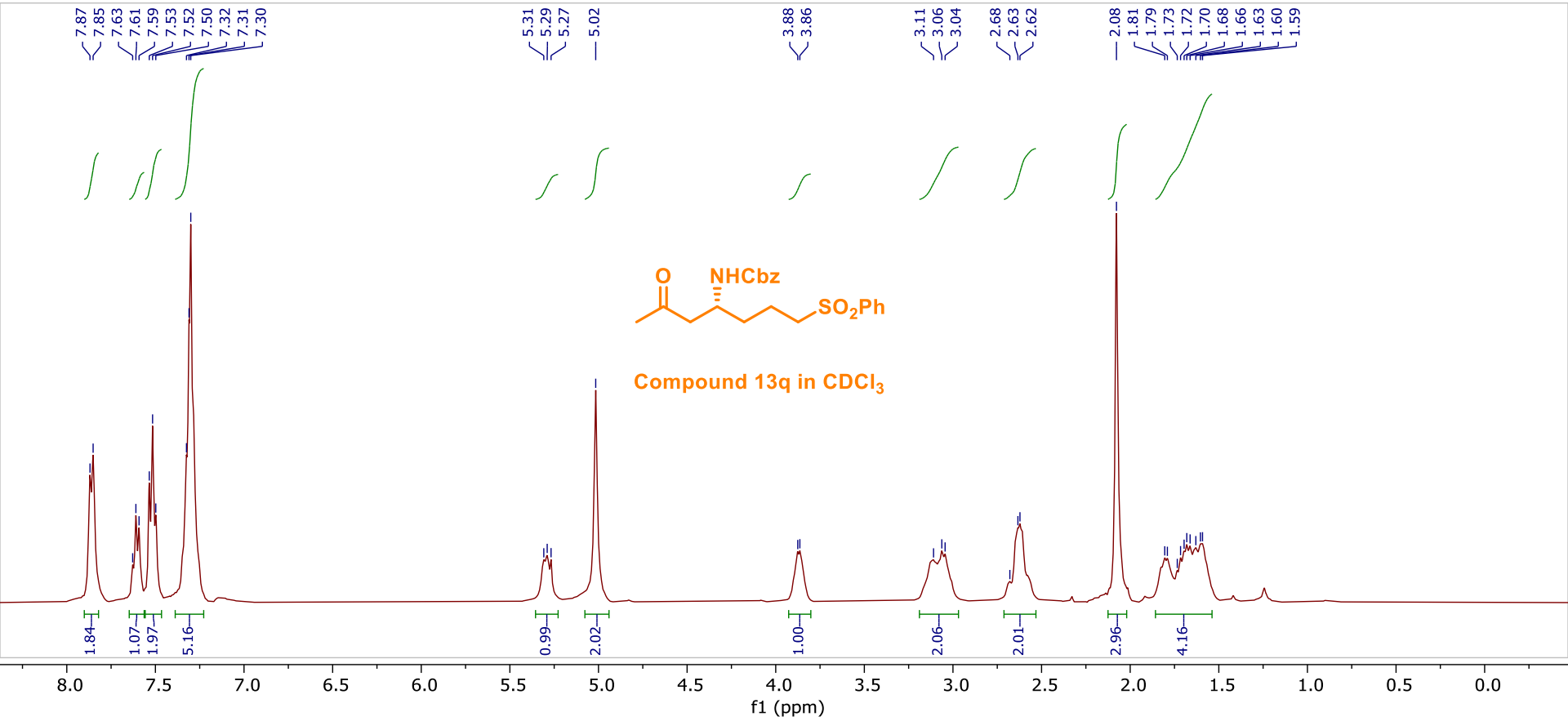
136.43
133.68
129.29
128.52
128.11
127.99
127.96
66.65
55.48
47.49
47.08
32.77
30.51
19.56
f1 (ppm)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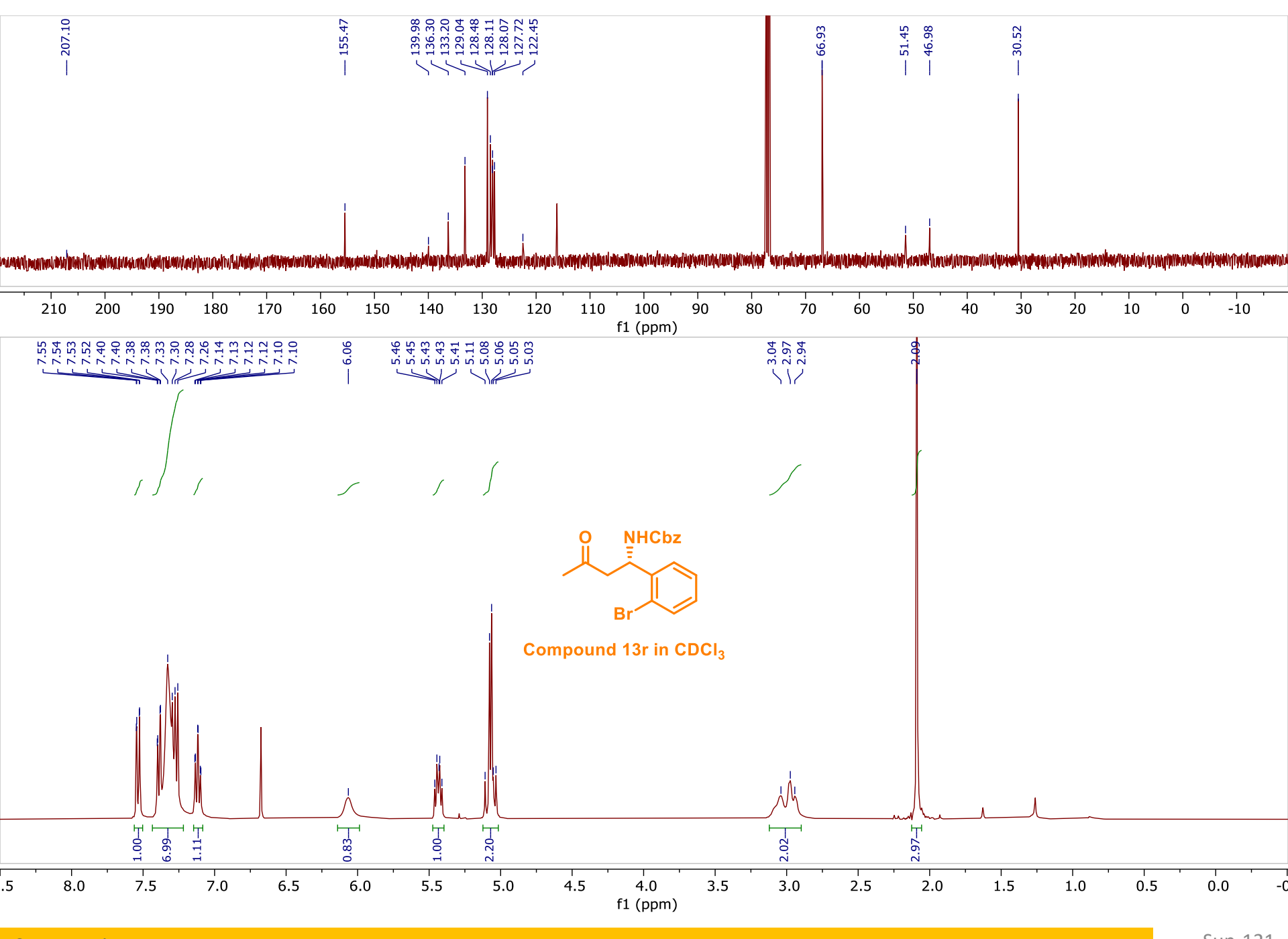
7.85
7.63
7.61
7.59
7.53
7.52
7.50
7.32
7.31
7.30
5.31
5.29
5.27
5.02
3.88
3.86
3.11
3.06
3.04
2.68
2.63
2.62
2.08
1.81
1.79
1.73
1.72
1.70
1.68
1.66
1.63
1.60
1.59
O
NHCbz
SO2Ph
Compound 13q in CDCl3
1.84
1.07
1.97
5.16
0.99
2.02
1.00
2.06
2.01
2.96
4.16
f1 (ppm)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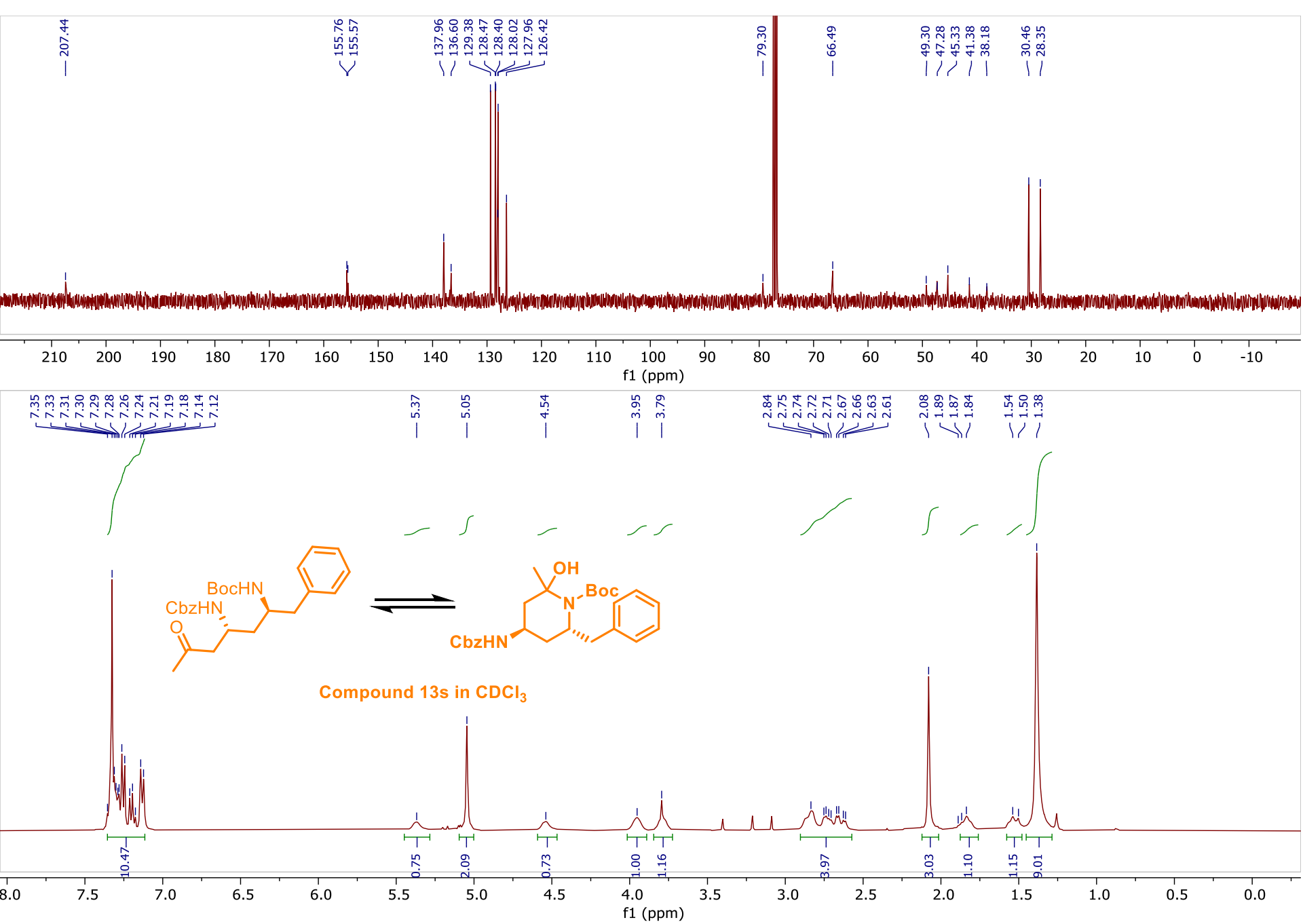
139.98
136.30
133.20
129.04
128.48
128.11
128.07
127.72
122.45
66.93
51.45
46.98
30.52
f1 (ppm)
7.55
7.54
7.53
7.52
7.40
7.40
7.38
7.38
7.33
7.30
7.28
7.26
7.14
7.13
7.12
7.12
7.10
7.10
6.06
5.46
5.45
5.43
5.43
5.41
5.11
5.08
5.06
5.05
5.03
3.04
2.97
2.94
2.09
1.00
6.99
1.11
0.83
1.00
2.20
2.02
2.97
f1 (ppm)
O
NHCbz
Br
Compound 13r in CDCl3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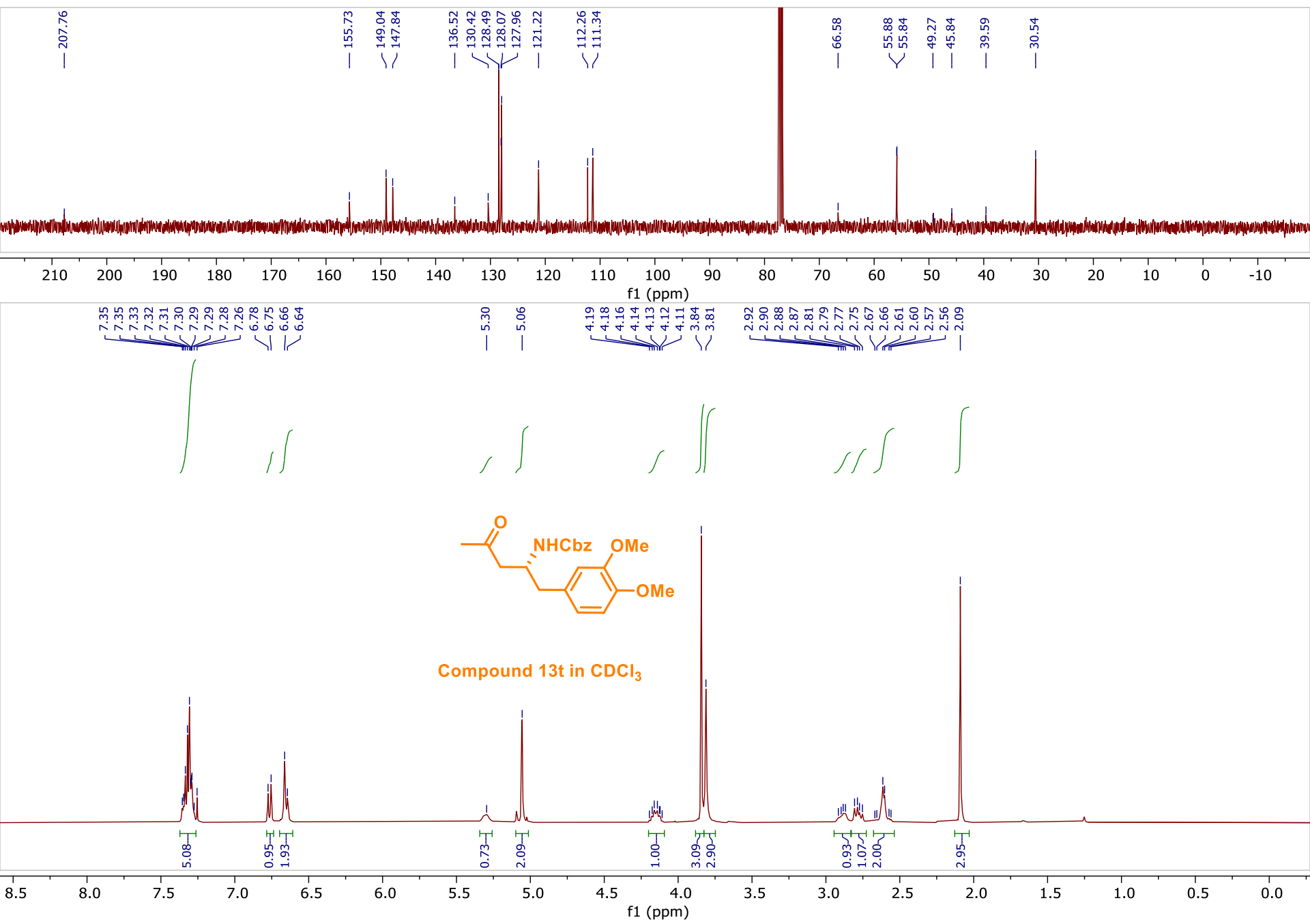
137.96
136.60
129.38
128.47
128.40
128.02
127.96
126.42
79.30
66.49
49.30
47.28
45.33
41.38
38.18
30.46
28.35
f1 (ppm)
7.35
7.33
7.31
7.30
7.29
7.28
7.26
7.24
7.21
7.19
7.18
7.14
7.12
5.37
5.05
4.54
3.95
3.79
2.84
2.75
2.74
2.72
2.71
2.67
2.66
2.63
2.61
2.08
1.89
1.87
1.84
1.54
1.50
1.38
BocHN
CbzHN
O
OH
N
Boc
CbzHN
Compound 13s in CDCl3
10.47
0.75
2.09
0.73
1.00
1.16
3.97
3.03
1.10
1.15
9.01
f1 (ppm)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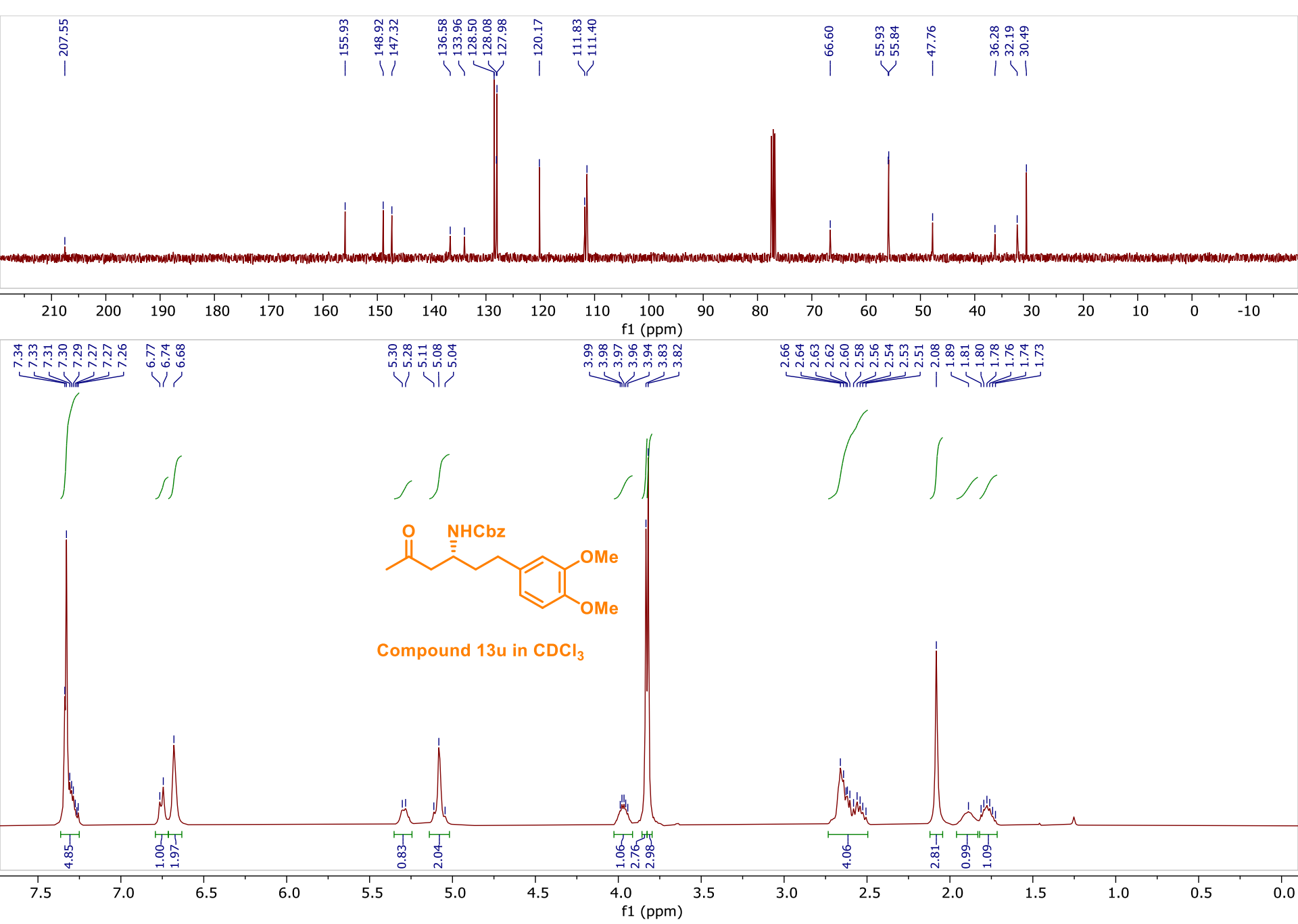
147.84
136.52
130.42
128.49
128.07
127.96
121.22
112.26
111.34
66.58
55.88
55.84
49.27
45.84
39.59
30.54
f1 (ppm)
7.35
7.35
7.33
7.32
7.31
7.30
7.29
7.29
7.28
7.26
6.78
6.75
6.66
6.64
5.30
5.06
4.19
4.18
4.16
4.14
4.13
4.12
4.11
3.84
3.81
2.92
2.90
2.88
2.87
2.81
2.79
2.77
2.75
2.67
2.66
2.61
2.60
2.57
2.56
2.09
O
NHCbz
OMe
OMe
Compound 13t in CDCl3
5.08
0.95
1.93
0.73
2.09
1.00
3.09
2.90
0.93
1.07
2.00
2.95
f1 (ppm)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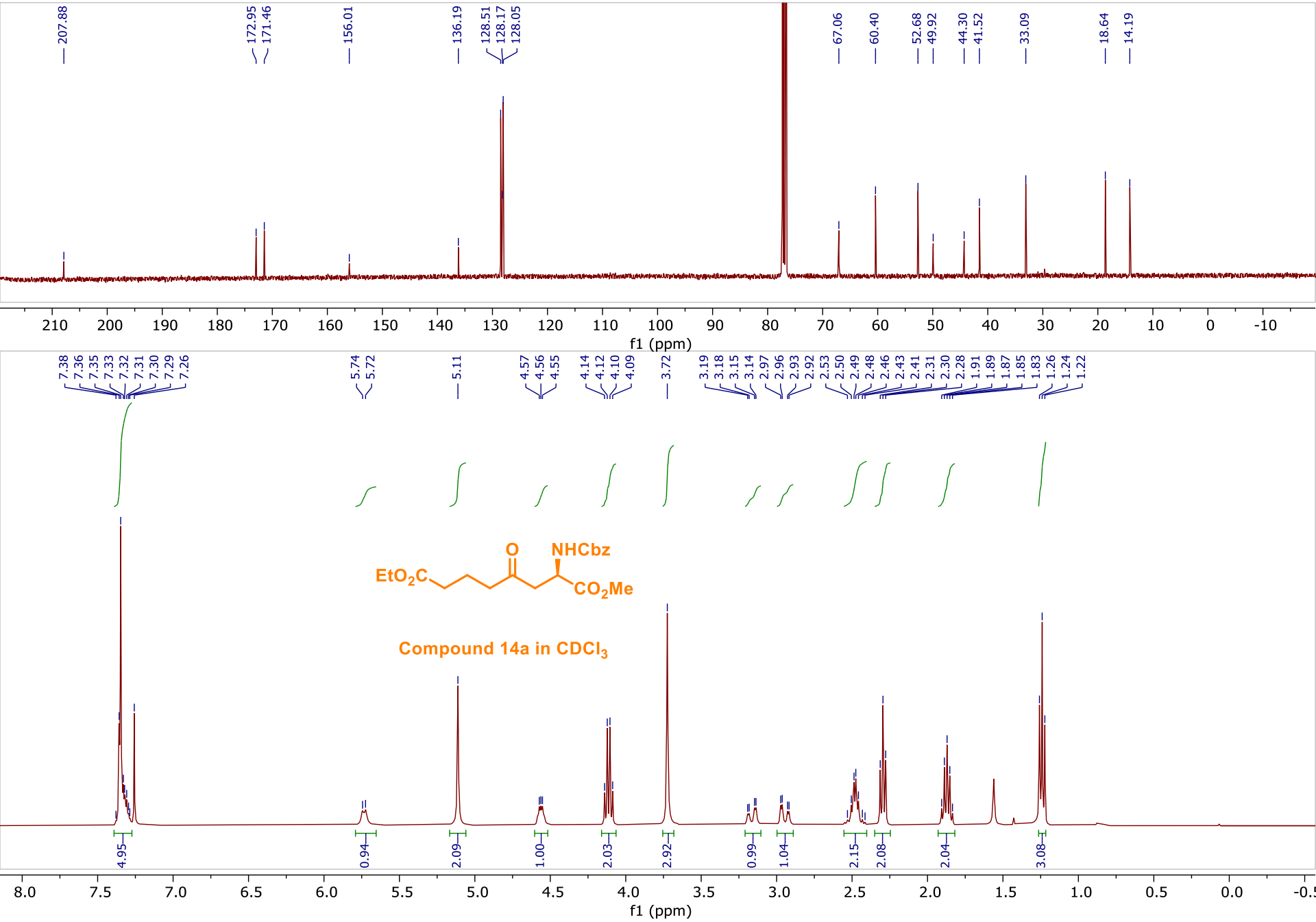
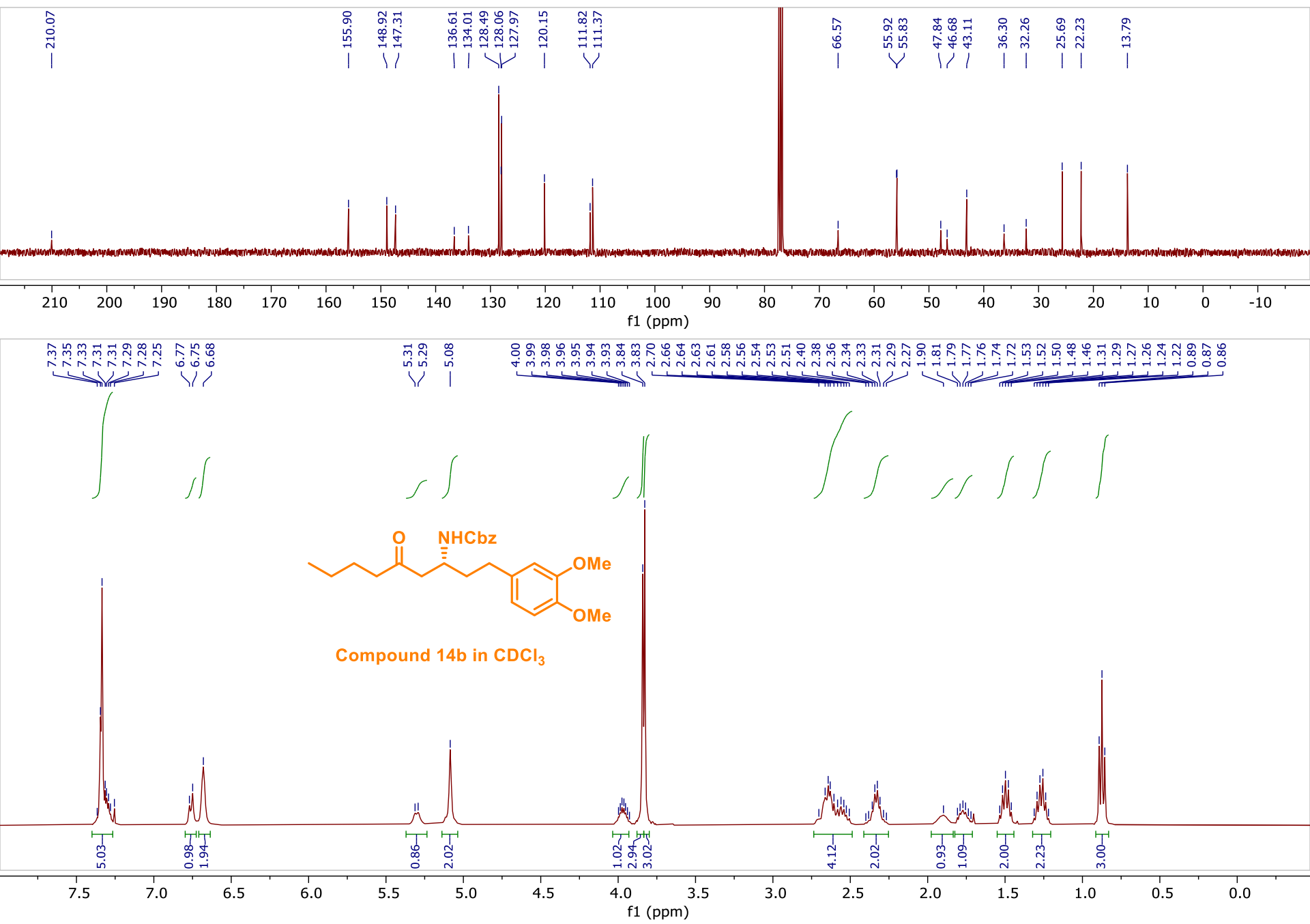
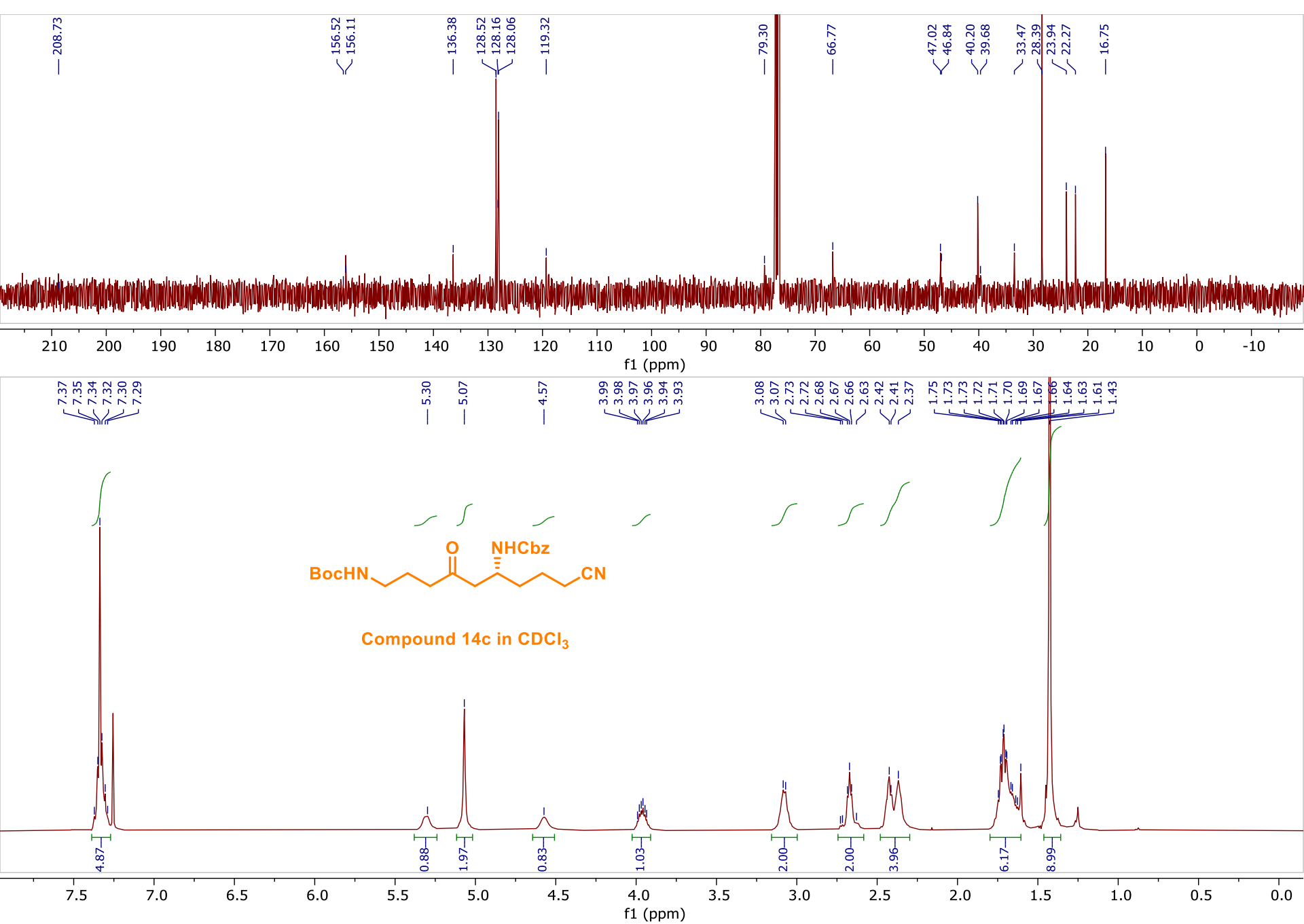
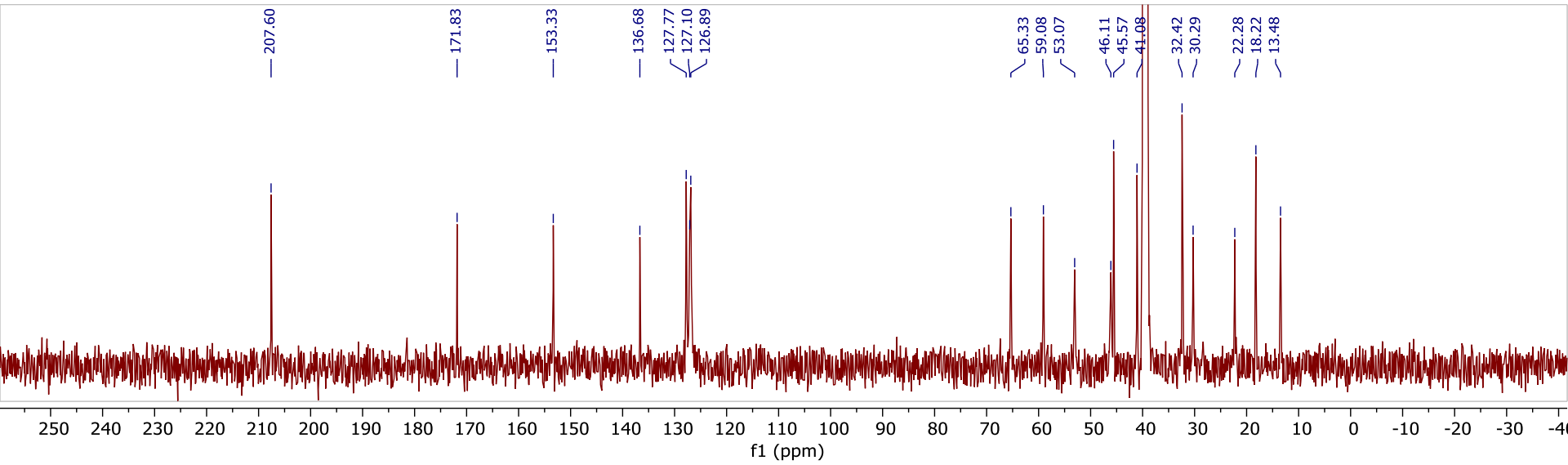
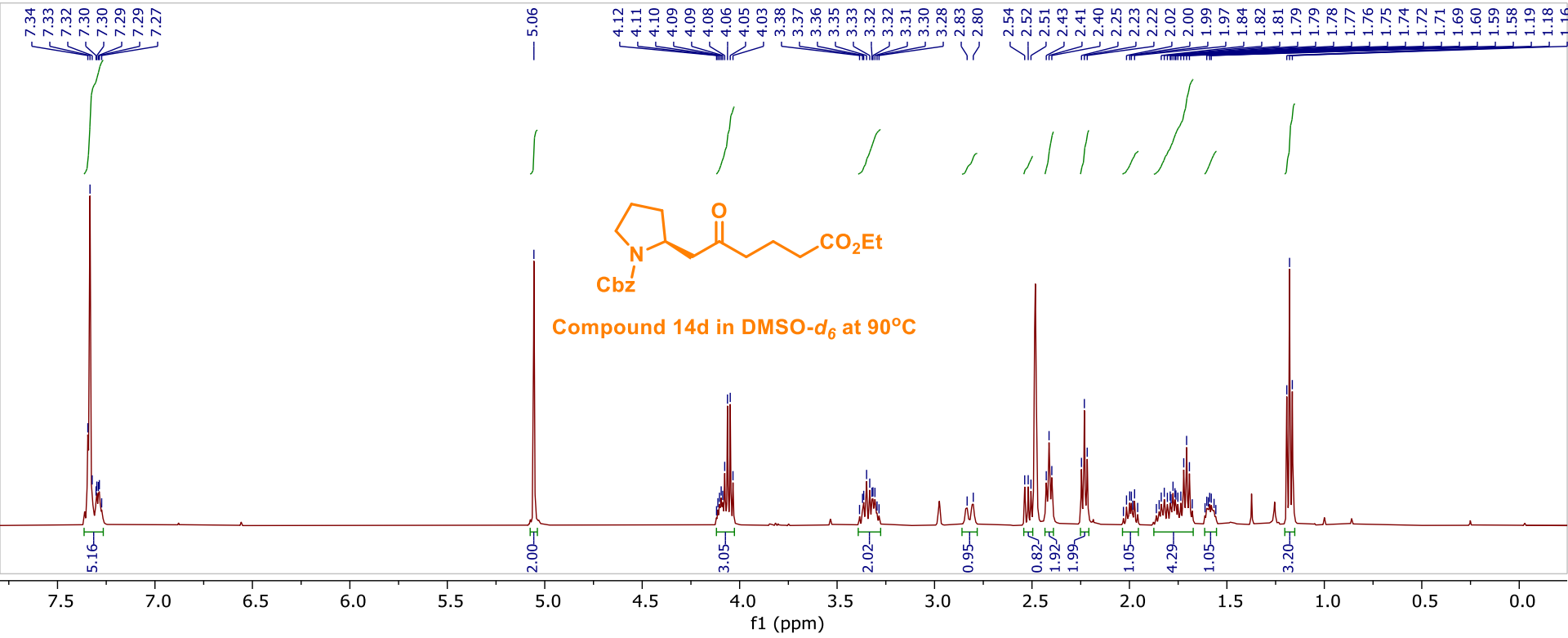
147.32
136.58
133.96
128.50
128.08
127.98
120.17
111.83
111.40
66.60
55.93
55.84
47.76
36.28
32.19
30.49
f1 (ppm)
7.34
7.33
7.31
7.30
7.29
7.27
7.27
7.26
6.77
6.74
6.68
5.30
5.28
5.11
5.08
5.04
3.99
3.98
3.97
3.96
3.94
3.83
3.82
2.66
2.64
2.63
2.62
2.60
2.58
2.56
2.54
2.53
2.51
2.08
1.89
1.81
1.80
1.78
1.76
1.74
1.73
O
NHCbz
OMe
OMe
Compound 13u in CDCl3
4.85
1.00
1.97
0.83
2.04
1.06
2.76
2.98
4.06
2.81
0.99
1.09
f1 (ppm)

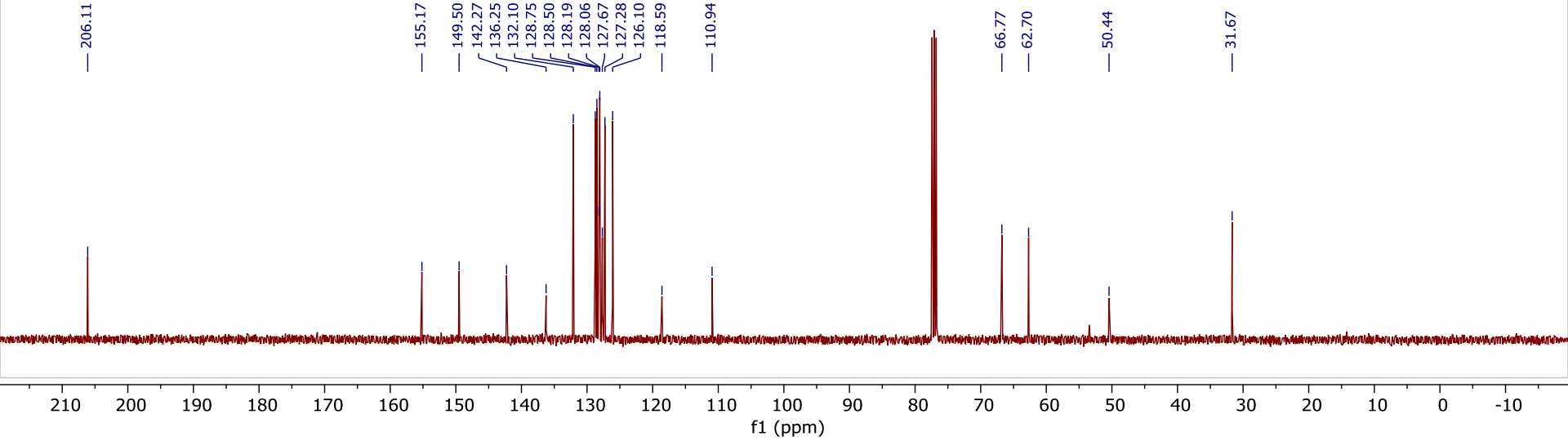

207.88
172.95
171.46
156.01
136.19
128.51
128.17
128.05
67.06
60.40
52.68
49.92
44.30
41.52
33.09
18.64
14.19
f1 (ppm)
7.38
7.36
7.35
7.33
7.32
7.31
7.30
7.29
7.26
5.74
5.72
5.11
4.57
4.56
4.55
4.14
4.12
4.10
4.09
3.72
3.19
3.18
3.15
3.14
2.97
2.96
2.93
2.92
2.53
2.50
2.49
2.48
2.46
2.43
2.41
2.31
2.30
2.28
1.91
1.89
1.87
1.85
1.83
1.26
1.24
1.22
O
NHCbz
EtO2C
CO2Me
Compound 14a in CDCl3
4.95
0.94
2.09
1.00
2.03
2.92
0.99
1.04
2.15
2.08
2.04
3.08
f1 (ppm)

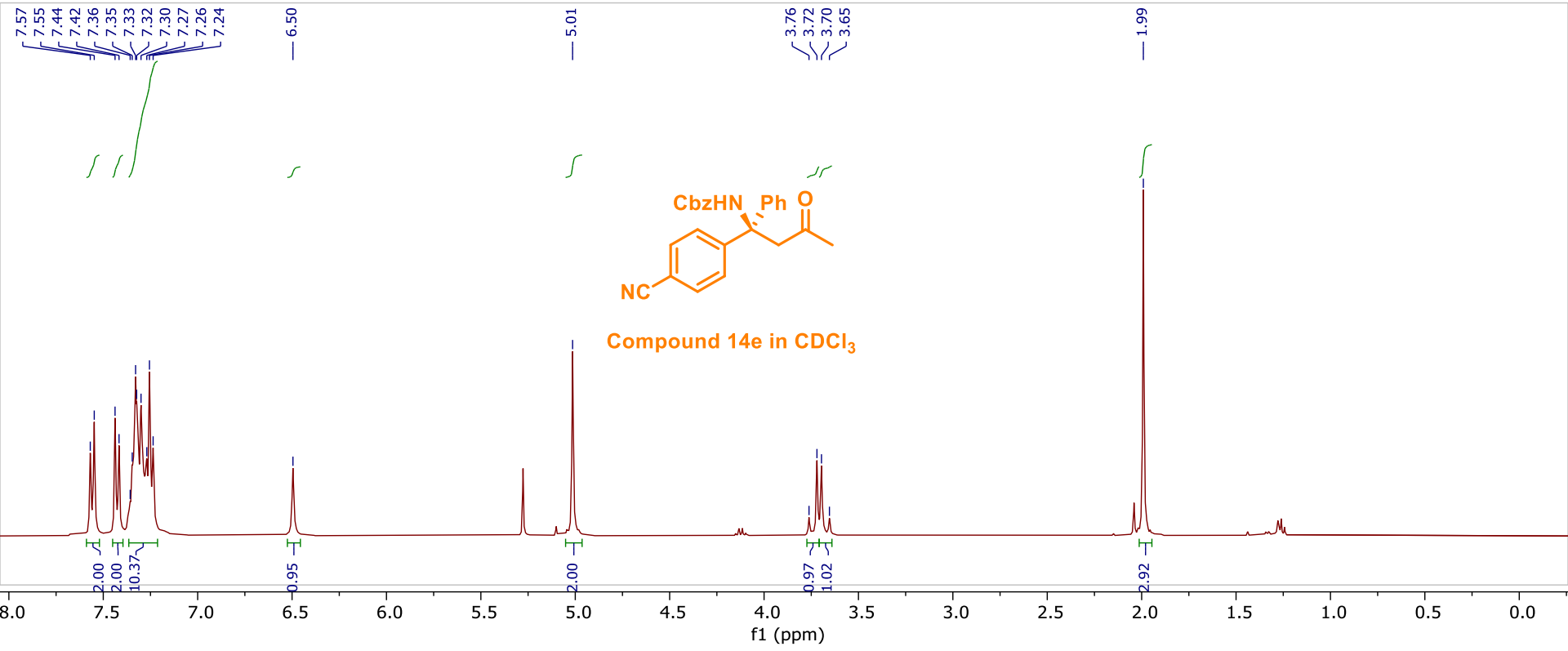

210.07
155.90
148.92
147.31
136.61
134.01
128.49
128.06
127.97
120.15
111.82
111.37
66.57
55.92
55.83
47.84
46.68
43.11
36.30
32.26
25.69
22.23
13.79
f1 (ppm)
7.37
7.35
7.33
7.31
7.31
7.29
7.28
7.25
6.77
6.75
6.68
5.31
5.29
5.08
4.00
3.99
3.98
3.96
3.95
3.94
3.93
3.84
3.83
2.70
2.66
2.64
2.63
2.61
2.58
2.56
2.54
2.53
2.51
2.40
2.38
2.36
2.34
2.33
2.31
2.29
2.27
1.90
1.81
1.79
1.77
1.76
1.74
1.72
1.53
1.52
1.50
1.48
1.46
1.31
1.29
1.27
1.26
1.24
1.22
0.89
0.87
0.86
O
NHCbz
OMe
OMe
Compound 14b in CDCl3
5.03
0.98
1.94
0.86
2.02
1.02
2.94
3.02
4.12
2.02
0.93
1.09
2.00
2.23
3.00
f1 (ppm)

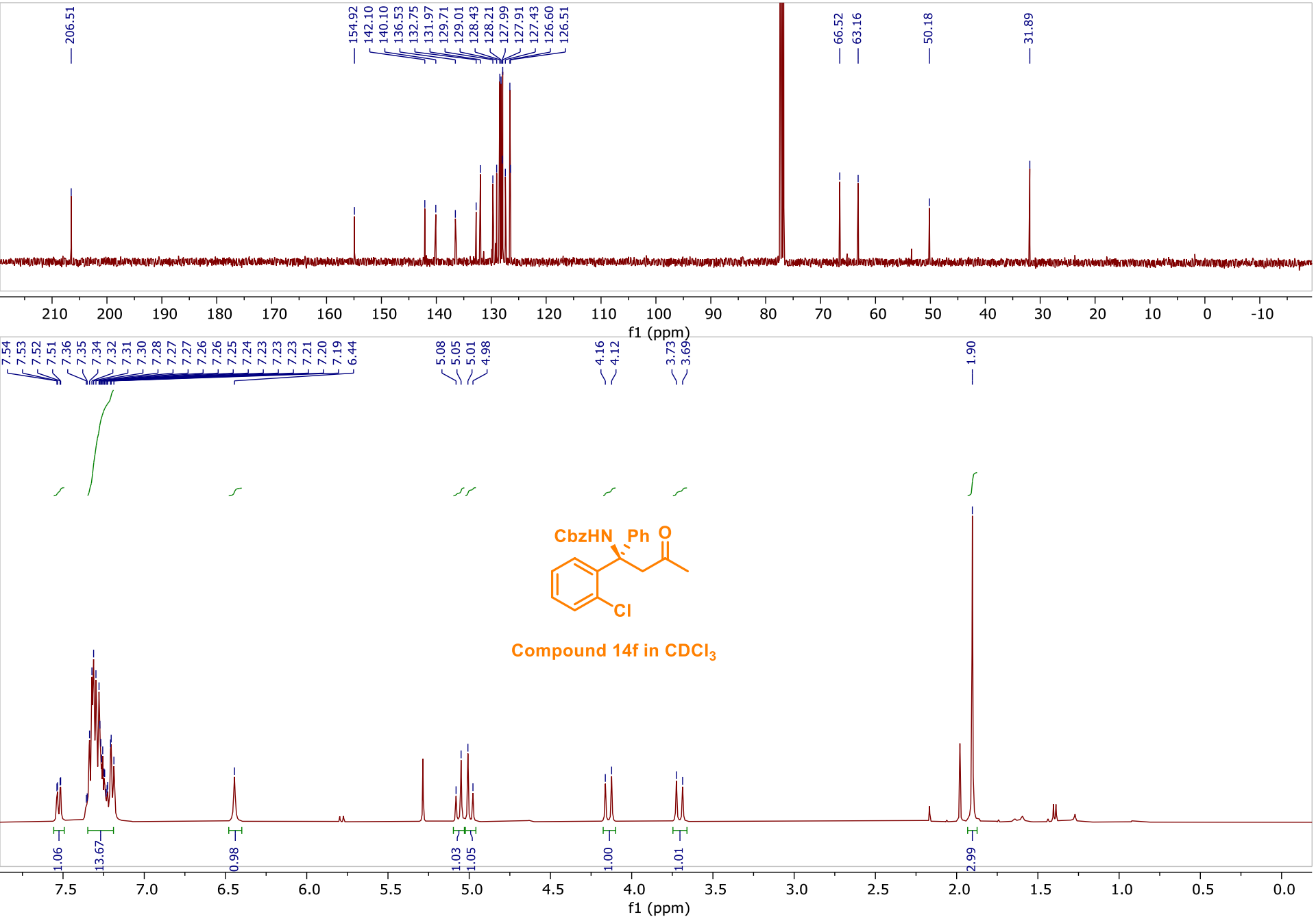

208.73
156.52
156.11
136.38
128.52
128.16
128.06
119.32
79.30
66.77
47.02
46.84
40.20
39.68
33.47
28.39
23.94
22.27
16.75
f1 (ppm)
7.37
7.35
7.34
7.32
7.30
7.29
5.30
5.07
4.57
3.99
3.98
3.97
3.96
3.94
3.93
3.08
3.07
2.73
2.72
2.68
2.67
2.66
2.63
2.42
2.41
2.37
1.75
1.73
1.73
1.72
1.71
1.70
1.69
1.67
1.66
1.64
1.63
1.61
1.43
O
NHCbz
BocHN
CN
Compound 14c in CDCl3
4.87
0.88
1.97
0.83
1.03
2.00
2.00
3.96
6.17
8.99
f1 (ppm)

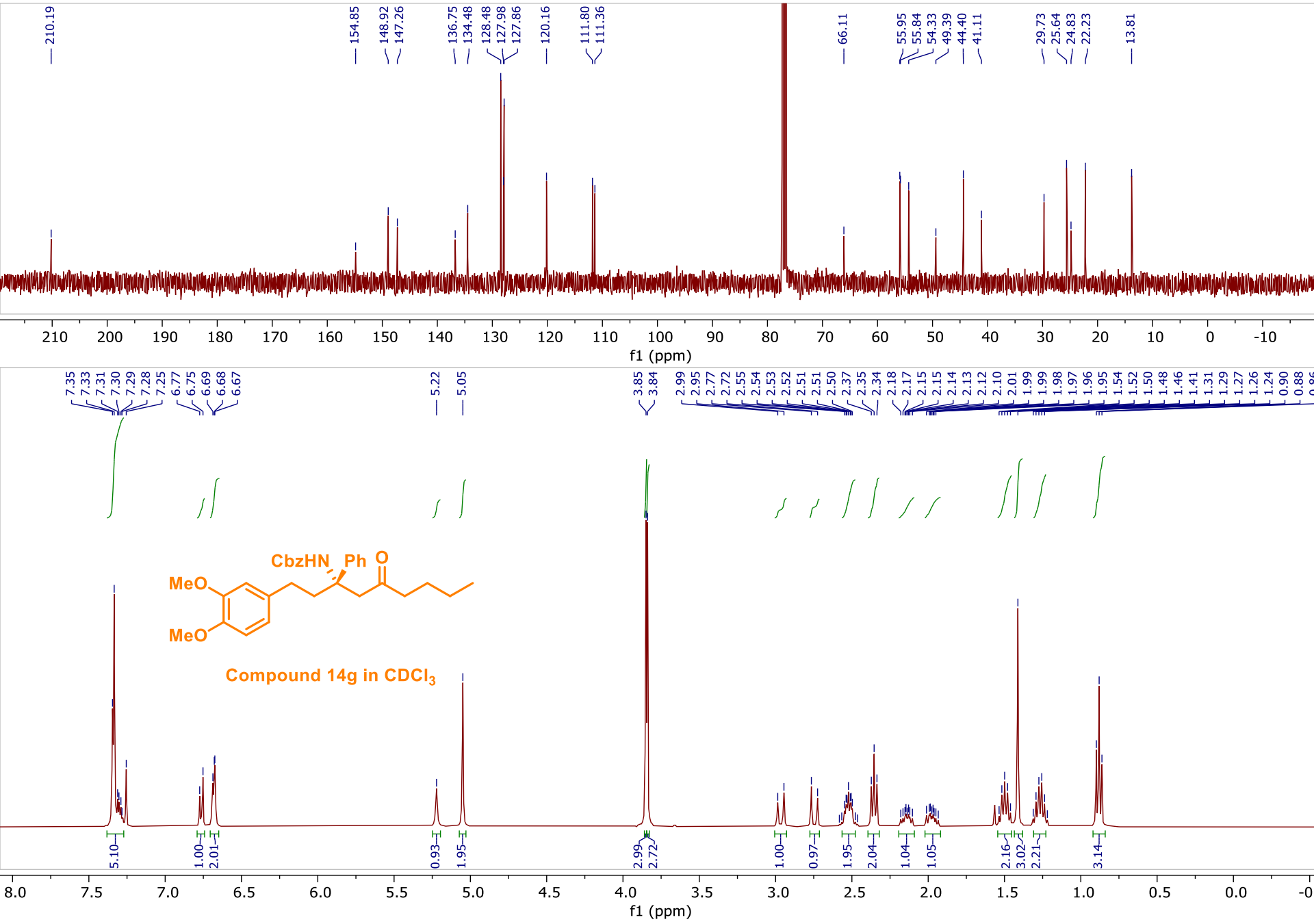

207.60
171.83
153.33
136.68
127.77
127.10
126.89
65.33
59.08
53.07
46.11
45.57
41.08
32.42
30.29
22.28
18.22
13.48
f1 (ppm)

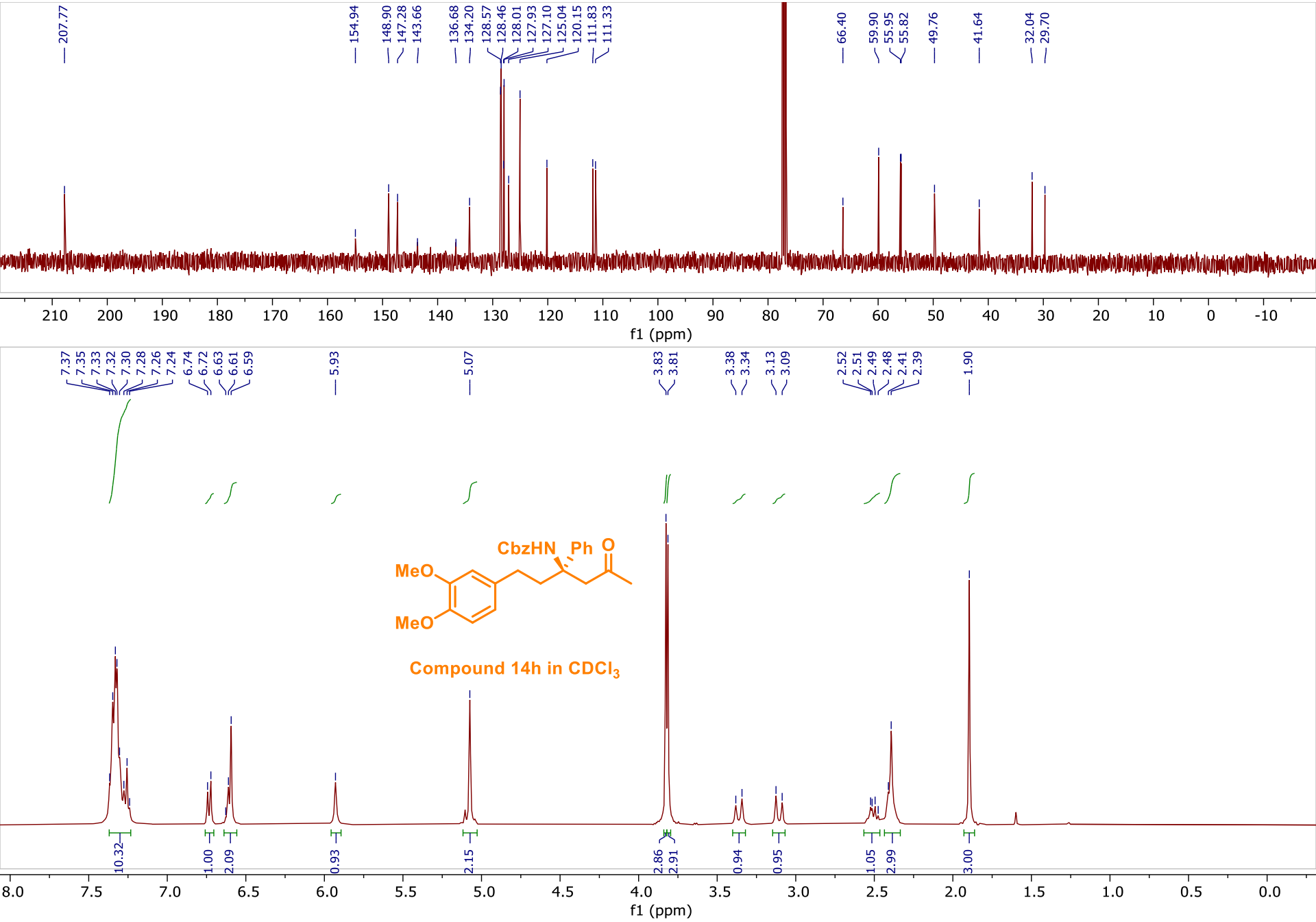

7.34
7.33
7.32
7.30
7.30
7.29
7.29
7.27
5.06
4.12
4.11
4.10
4.09
4.09
4.08
4.06
4.05
4.03
3.38
3.37
3.36
3.35
3.33
3.32
3.32
3.31
3.30
3.28
2.83
2.80
2.54
2.52
2.51
2.43
2.41
2.40
2.25
2.23
2.22
2.02
2.00
1.99
1.97
1.84
1.82
1.81
1.79
1.79
1.78
1.77
1.76
1.75
1.74
1.72
1.71
1.69
1.60
1.59
1.58
1.19
1.18
O
CO2Et
N
Cbz
Compound 14d in DMSO-d6 at 90°C
5.16
2.00
3.05
2.02
0.95
0.82
1.92
1.99
1.05
4.29
1.05
3.20
f1 (ppm)

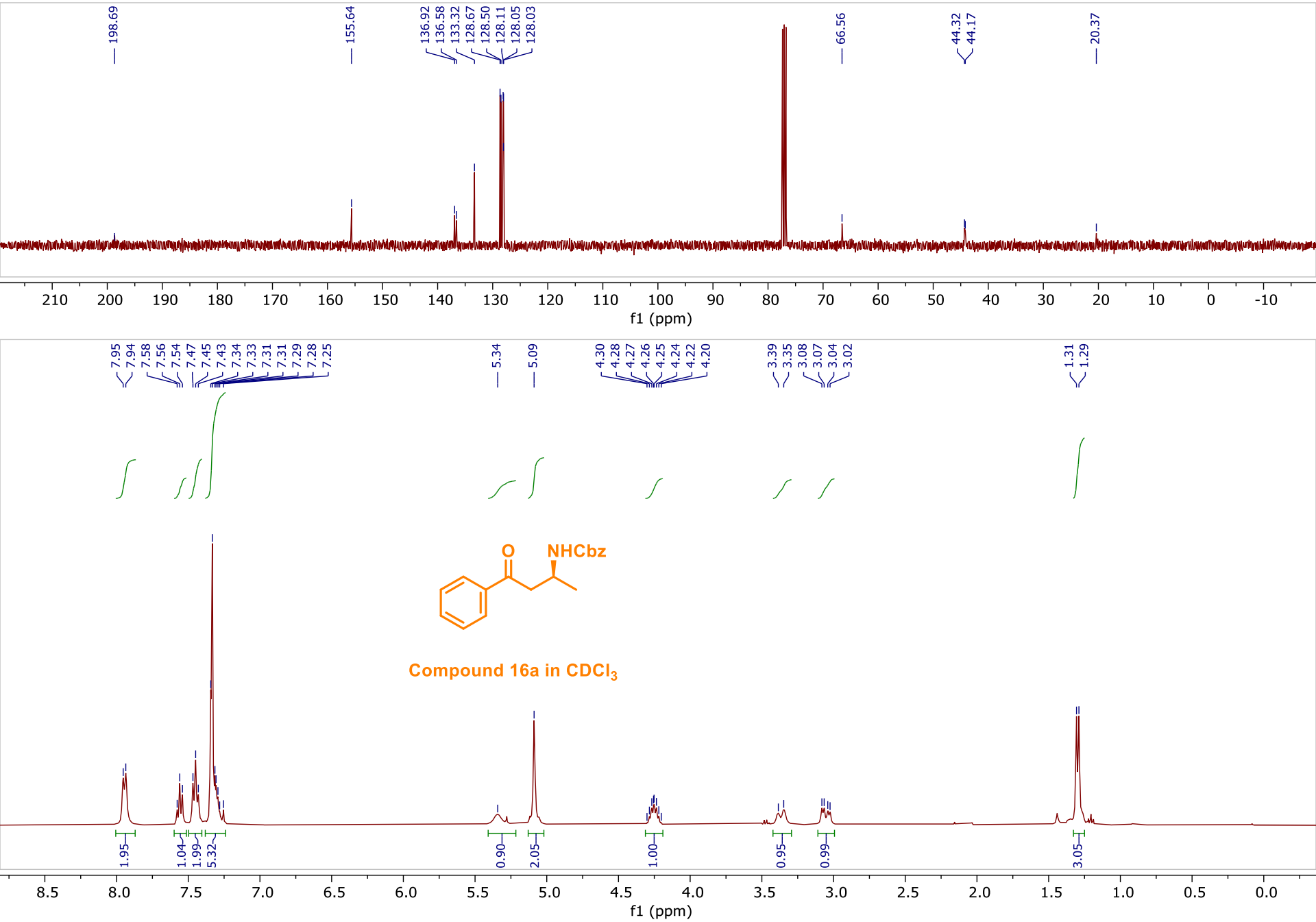

206.11
155.17
149.50
142.27
136.25
132.10
128.75
128.50
128.19
128.06
127.67
127.28
126.10
118.59
110.94
66.77
62.70
50.44
31.67
f1 (ppm)

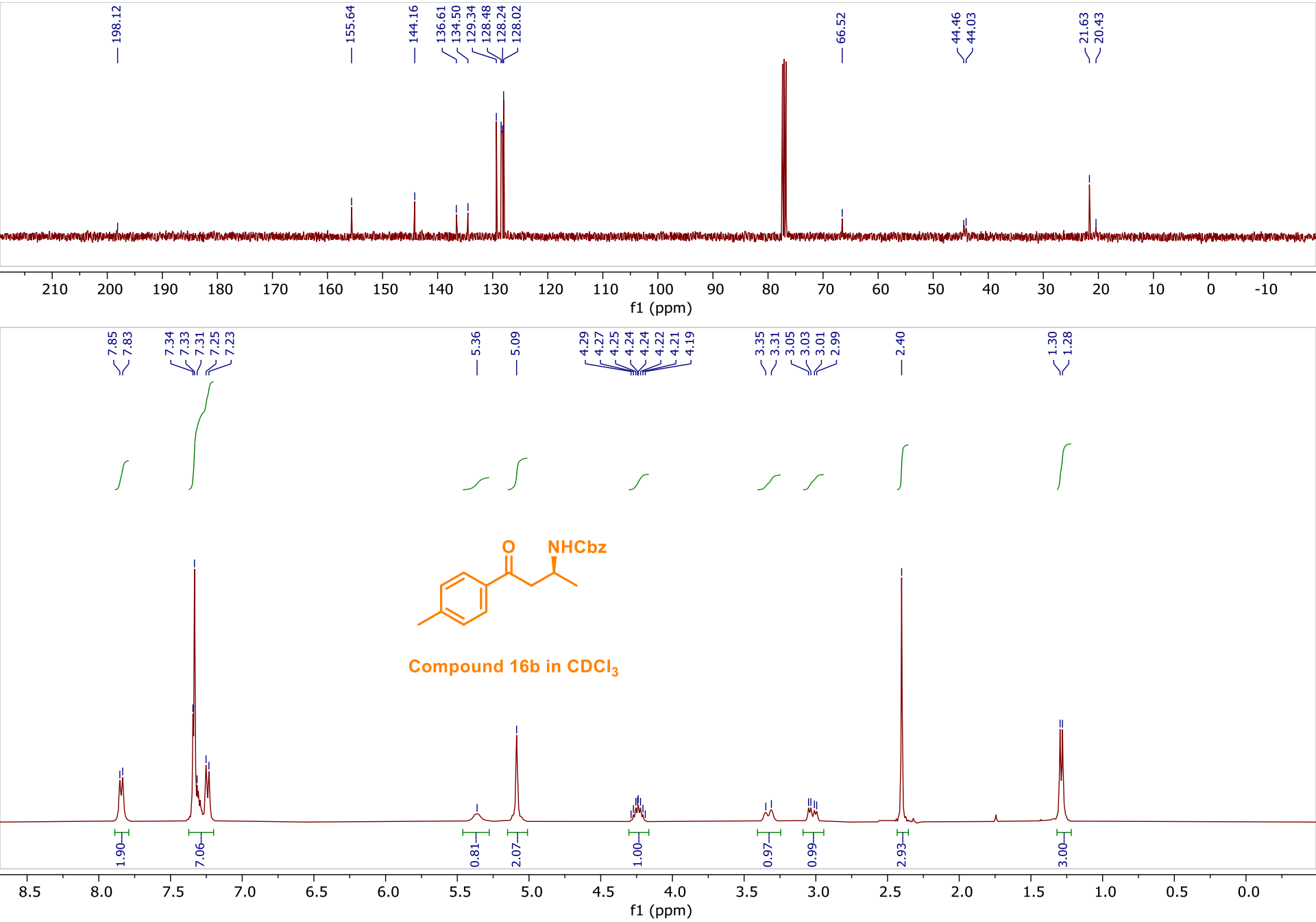

7.57
7.55
7.44
7.42
7.36
7.35
7.33
7.32
7.30
7.27
7.26
7.24
6.50
5.01
3.76
3.72
3.70
3.65
1.99
CbzHN
Ph
O
NC
Compound 14e in CDCl3
2.00
2.00
10.37
0.95
2.00
0.97
1.02
2.92
f1 (ppm)

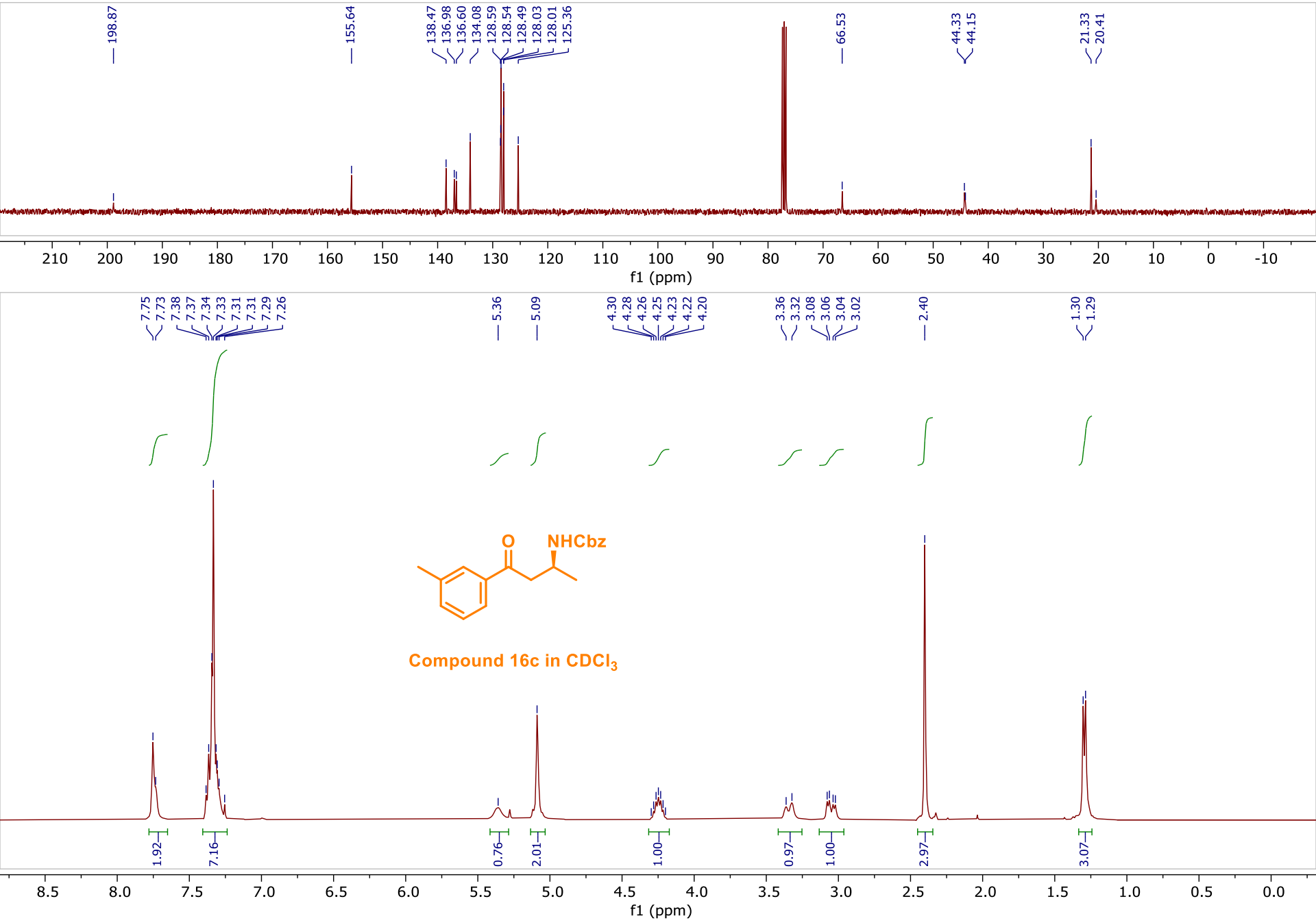

206.51
154.92
142.10
140.10
136.53
132.75
131.97
129.71
129.01
128.43
128.21
127.99
127.91
127.43
126.60
126.51
66.52
63.16
50.18
31.89
f1 (ppm)
7.54
7.53
7.52
7.51
7.36
7.35
7.34
7.32
7.31
7.30
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.23
7.23
7.23
7.21
7.20
7.19
6.44
5.08
5.05
5.01
4.98
4.16
4.12
3.73
3.69
1.90
CbzHN
Ph
O
Cl
Compound 14f in CDCl3
1.06
13.67
0.98
1.03
1.05
1.00
1.01
2.99
f1 (ppm)

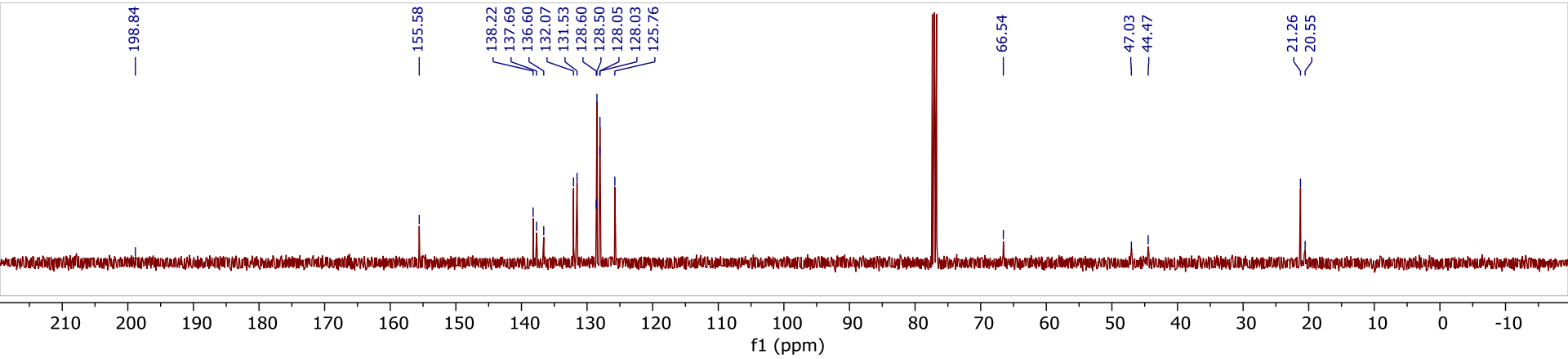

210.19
154.85
148.92
147.26
136.75
134.48
128.48
127.98
127.86
120.16
111.80
111.36
66.11
55.95
55.84
54.33
49.39
44.40
41.11
29.73
25.64
24.83
22.23
13.81
f1 (ppm)
7.35
7.33
7.31
7.30
7.29
7.28
7.25
6.77
6.75
6.69
6.68
6.67
5.22
5.05
3.85
3.84
2.99
2.95
2.77
2.72
2.55
2.54
2.53
2.52
2.51
2.51
2.50
2.37
2.35
2.34
2.18
2.17
2.15
2.15
2.14
2.13
2.12
2.10
2.01
1.99
1.99
1.98
1.97
1.96
1.95
1.54
1.52
1.50
1.48
1.46
1.41
1.31
1.29
1.27
1.26
1.24
0.90
0.88
CbzHN
Ph
O
MeO
MeO
Compound 14g in CDCl3
5.10
1.00
2.01
0.93
1.95
2.99
2.72
1.00
0.97
1.95
2.04
1.04
1.05
2.16
3.02
2.21
3.14
f1 (ppm)

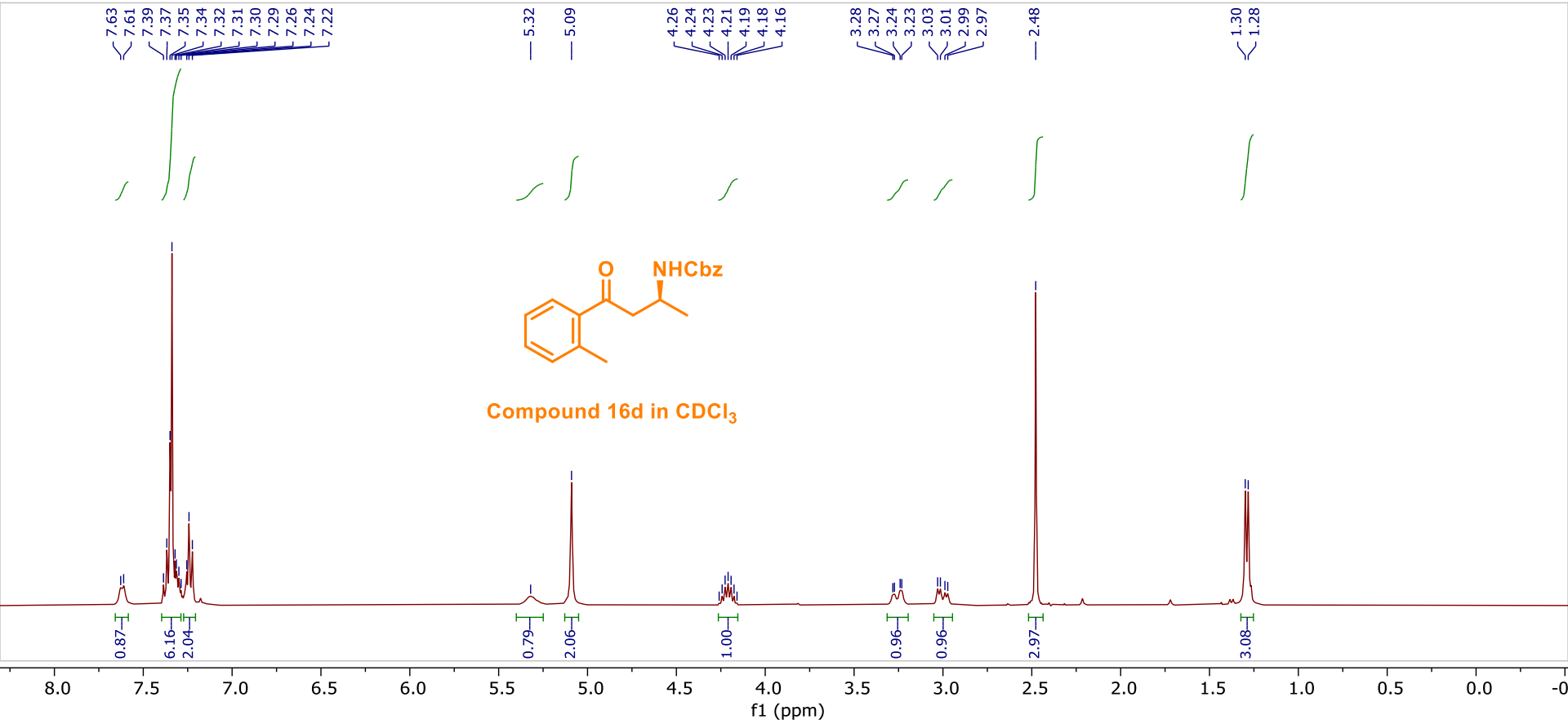

207.77
154.94
148.90
147.28
143.66
136.68
134.20
128.57
128.46
128.01
127.93
127.10
125.04
120.15
111.83
111.33
66.40
59.90
55.95
55.82
49.76
41.64
32.04
29.70
f1 (ppm)
7.37
7.35
7.33
7.32
7.30
7.28
7.26
7.24
6.74
6.72
6.63
6.61
6.59
5.93
5.07
3.83
3.81
3.38
3.34
3.13
3.09
2.52
2.51
2.49
2.48
2.41
2.39
1.90
CbzHN
Ph
O
MeO
MeO
Compound 14h in CDCl3
10.32
1.00
2.09
0.93
2.15
2.86
2.91
0.94
0.95
1.05
2.99
3.00
f1 (ppm)

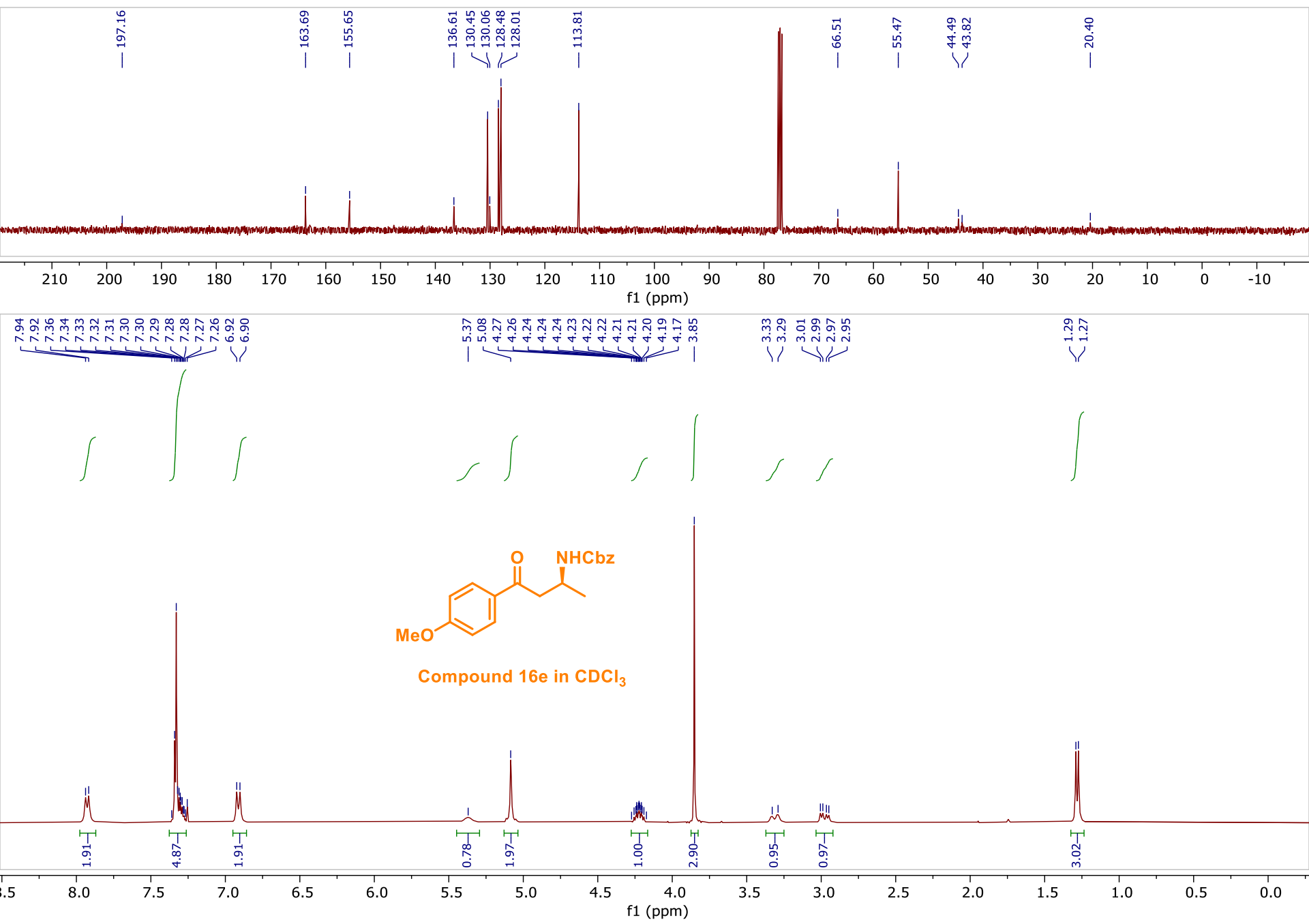

198.69
155.64
136.92
136.58
133.32
128.67
128.50
128.11
128.05
128.03
66.56
44.32
44.17
20.37
f1 (ppm)
7.95
7.94
7.58
7.56
7.54
7.47
7.45
7.43
7.34
7.33
7.31
7.31
7.29
7.28
7.25
5.34
5.09
4.30
4.28
4.27
4.26
4.25
4.24
4.22
4.20
3.39
3.35
3.08
3.07
3.04
3.02
1.31
1.29
O
NHCbz
Compound 16a in CDCl3
1.95
1.04
1.99
5.32
0.90
2.05
1.00
0.95
0.99
3.05
f1 (ppm)

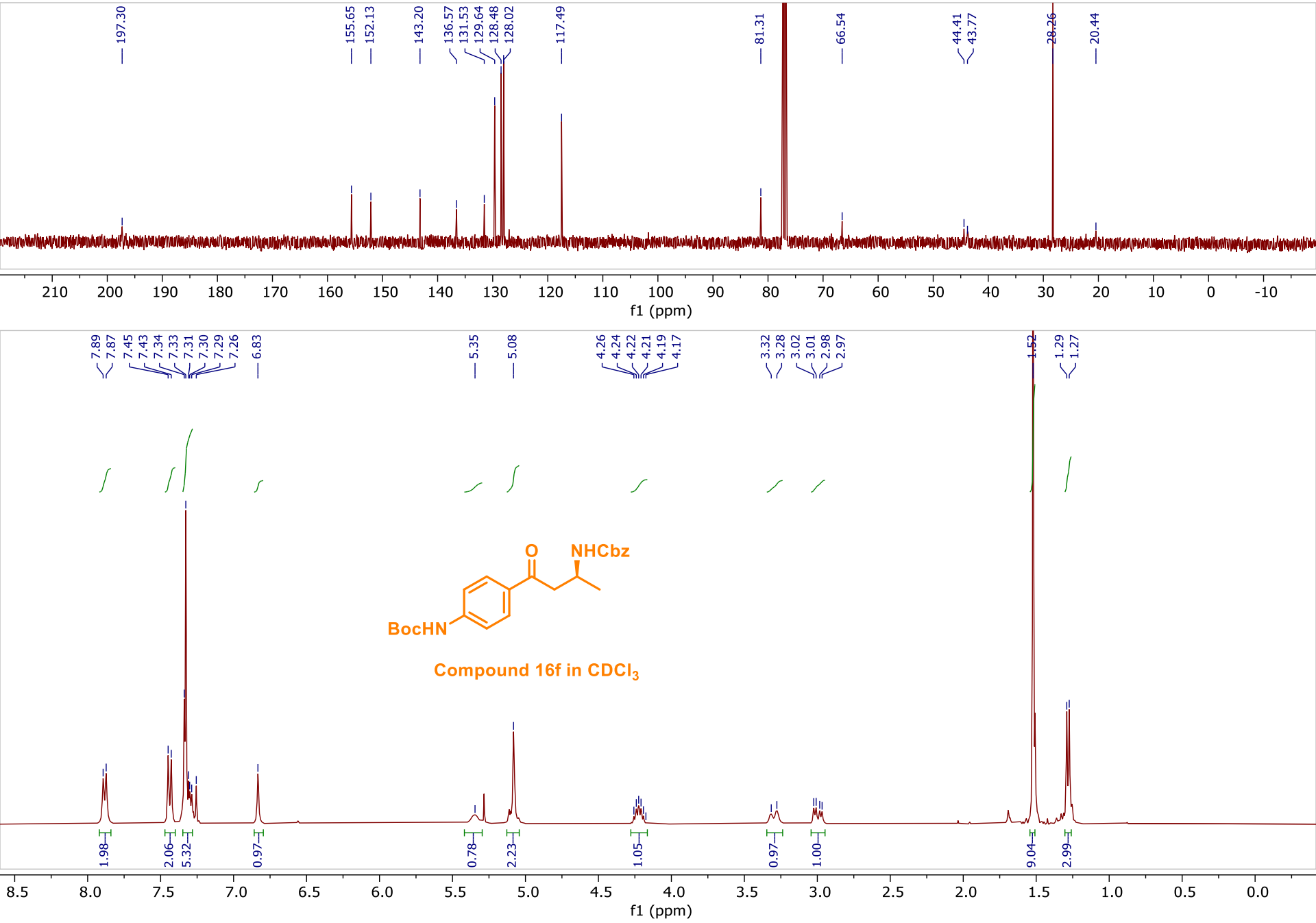

198.12
155.64
144.16
136.61
134.50
129.34
128.48
128.24
128.02
66.52
44.46
44.03
21.63
20.43
f1 (ppm)
7.85
7.83
7.34
7.33
7.31
7.25
7.23
5.36
5.09
4.29
4.27
4.25
4.24
4.24
4.22
4.21
4.19
3.35
3.31
3.05
3.03
3.01
2.99
2.40
1.30
1.28
O
NHCbz
Compound 16b in CDCl3
1.90
7.06
0.81
2.07
1.00
0.97
0.99
2.93
3.00
f1 (ppm)

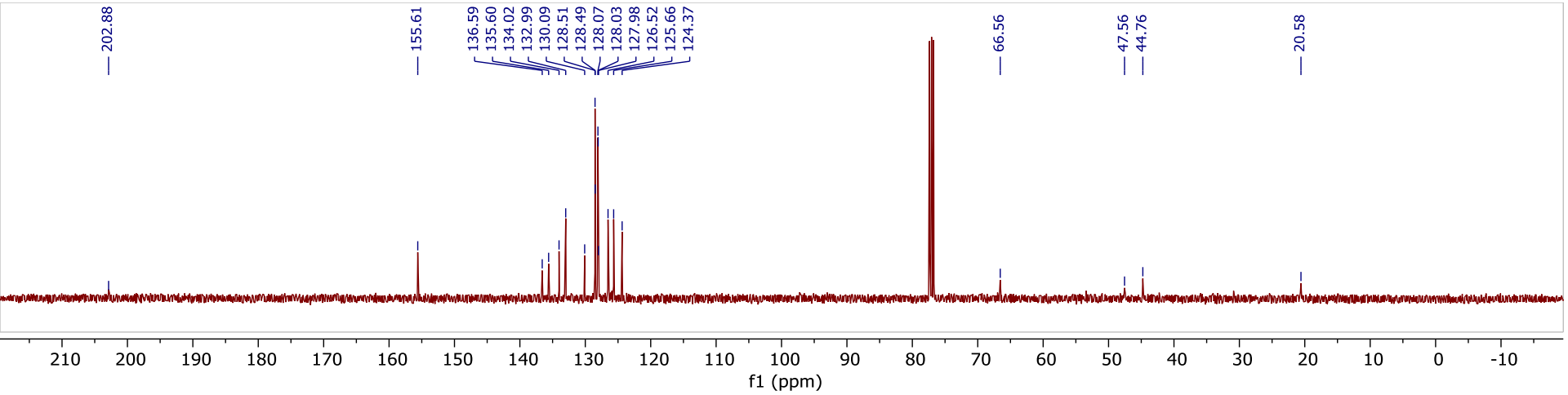

198.87
155.64
138.47
136.98
136.60
134.08
128.59
128.54
128.49
128.03
128.01
125.36
66.53
44.33
44.15
21.33
20.41
f1 (ppm)
7.75
7.73
7.38
7.37
7.34
7.33
7.31
7.31
7.29
7.26
5.36
5.09
4.30
4.28
4.26
4.25
4.23
4.22
4.20
3.36
3.32
3.08
3.06
3.04
3.02
2.40
1.30
1.29
O
NHCbz
Compound 16c in CDCl3
1.92
7.16
0.76
2.01
1.00
0.97
1.00
2.97
3.07
f1 (ppm)

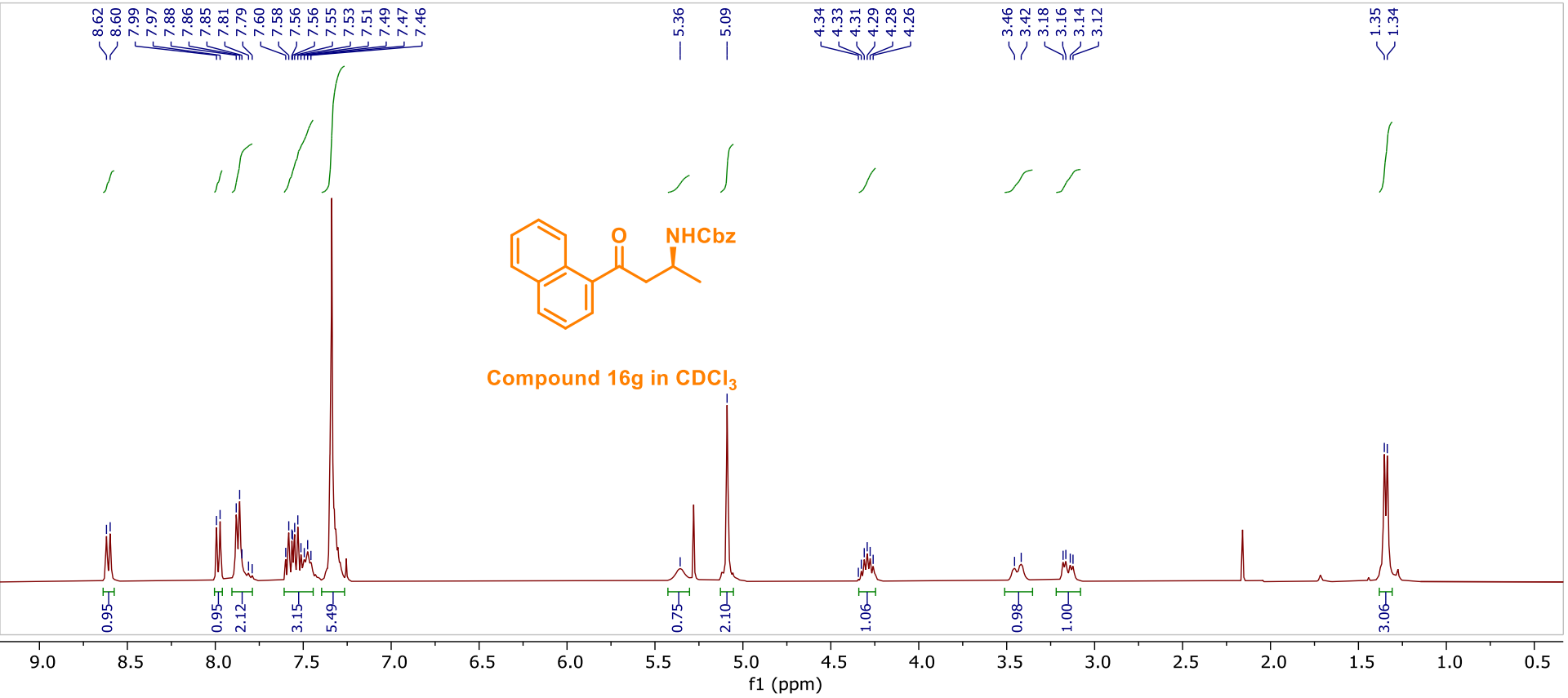

198.84
155.58
138.22
137.69
136.60
132.07
131.53
128.60
128.50
128.05
128.03
125.76
66.54
47.03
44.47
21.26
20.55
f1 (ppm)

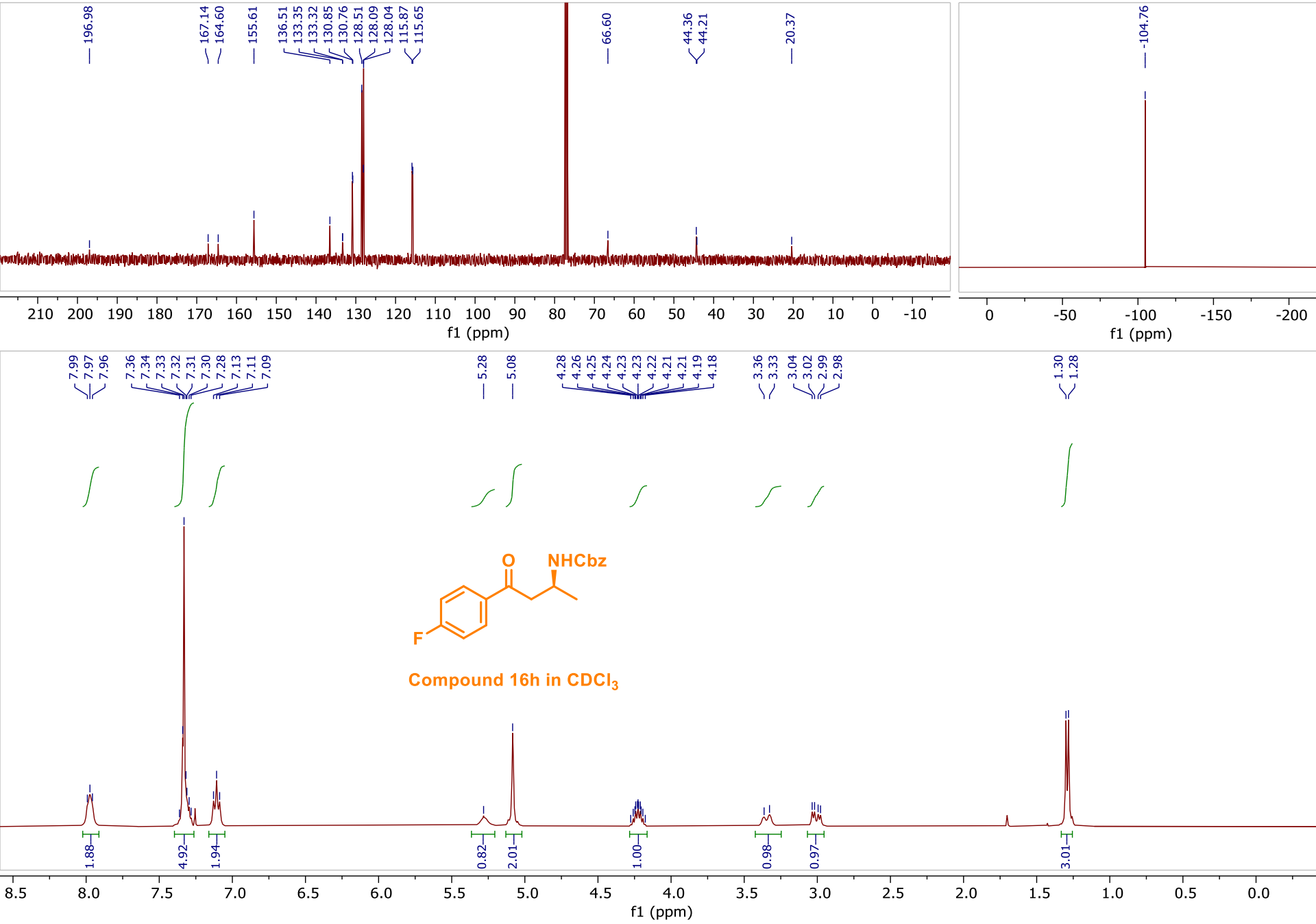

7.63
7.61
7.39
7.37
7.35
7.34
7.32
7.31
7.30
7.29
7.26
7.24
7.22
5.32
5.09
4.26
4.24
4.23
4.21
4.19
4.18
4.16
3.28
3.27
3.24
3.23
3.03
3.01
2.99
2.97
2.48
1.30
1.28
O
NHCbz
Compound 16d in CDCl3
0.87
6.16
2.04
0.79
2.06
1.00
0.96
0.96
2.97
3.08
f1 (ppm)

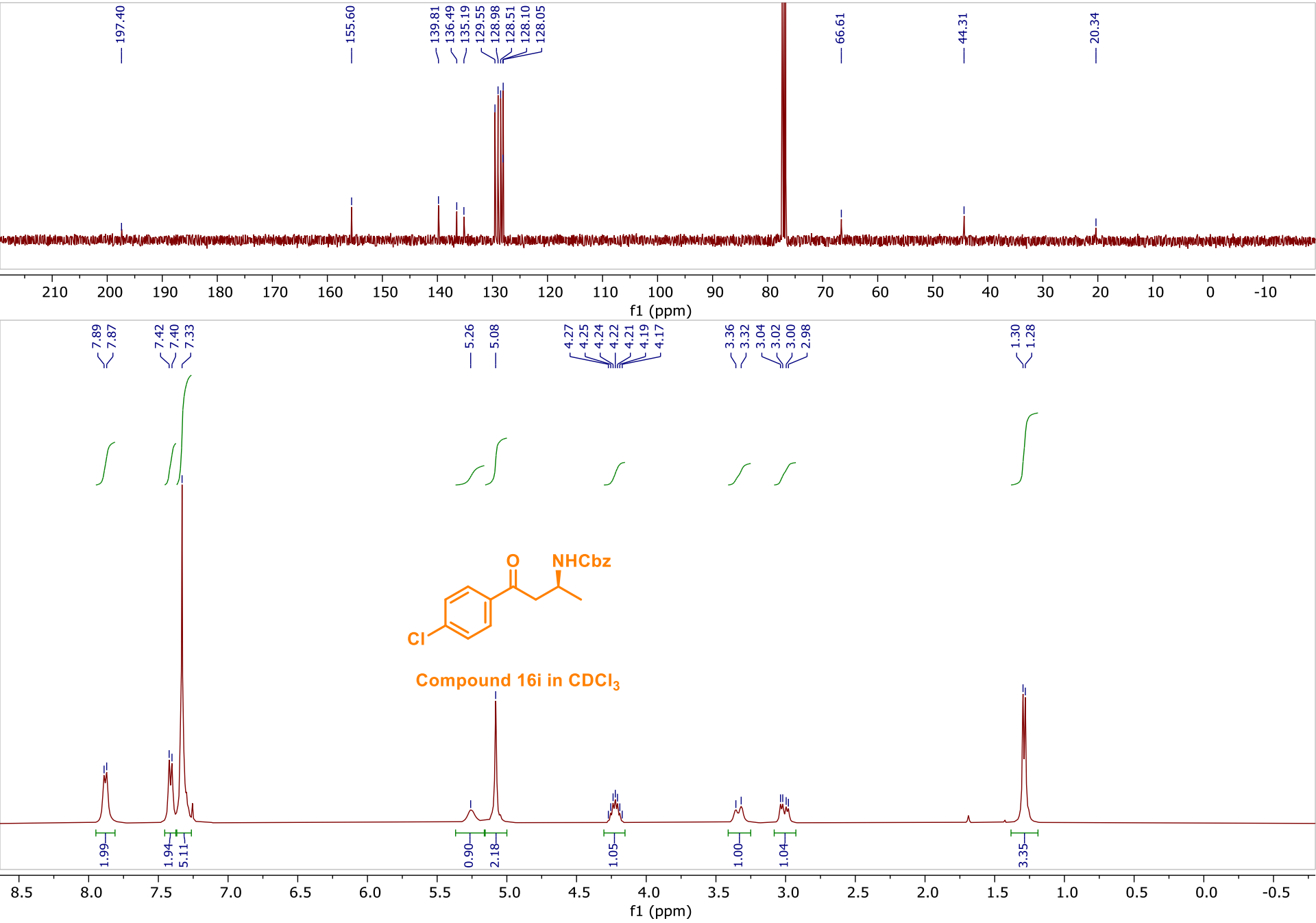

197.16
163.69
155.65
136.61
130.45
130.06
128.48
128.01
113.81
66.51
55.47
44.49
43.82
20.40
f1 (ppm)
7.94
7.92
7.36
7.34
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.26
6.92
6.90
5.37
5.08
4.27
4.26
4.24
4.24
4.24
4.23
4.22
4.22
4.21
4.21
4.20
4.19
4.17
3.85
3.33
3.29
3.01
2.99
2.97
2.95
1.29
1.27
O
NHCbz
MeO
Compound 16e in CDCl3
1.91
4.87
1.91
0.78
1.97
1.00
2.90
0.95
0.97
3.02
f1 (ppm)


197.30
155.65
152.13
143.20
136.57
131.53
129.64
128.48
128.02
117.49
81.31
66.54
44.41
43.77
28.26
20.44
f1 (ppm)
7.89
7.87
7.45
7.43
7.34
7.33
7.31
7.30
7.29
7.26
6.83
5.35
5.08
4.26
4.24
4.22
4.21
4.19
4.17
3.32
3.28
3.02
3.01
2.98
2.97
1.52
1.29
1.27
O
NHCbz
BocHN
Compound 16f in CDCl3
1.98
2.06
5.32
0.97
0.78
2.23
1.05
0.97
1.00
9.04
2.99
f1 (ppm)


202.88
155.61
136.59
135.60
134.02
132.99
130.09
128.51
128.49
128.07
128.03
127.98
126.52
125.66
124.37
66.56
47.56
44.76
20.58
f1 (ppm)


8.62
8.60
7.99
7.97
7.88
7.86
7.85
7.81
7.79
7.60
7.58
7.56
7.56
7.55
7.53
7.51
7.49
7.47
7.46
5.36
5.09
4.34
4.33
4.31
4.29
4.28
4.26
3.46
3.42
3.18
3.16
3.14
3.12
1.35
1.34
O
NHCbz
Compound 16g in CDCl3
0.95
0.95
2.12
3.15
5.49
0.75
2.10
1.06
0.98
1.00
3.06
f1 (ppm)


196.98
167.14
164.60
155.61
136.51
133.35
133.32
130.85
130.76
128.51
128.09
128.04
115.87
115.65
66.60
44.36
44.21
20.37
-104.76
f1 (ppm)
7.99
7.97
7.96
7.36
7.34
7.33
7.32
7.31
7.30
7.28
7.13
7.11
7.09
5.28
5.08
4.28
4.26
4.25
4.24
4.23
4.23
4.22
4.21
4.21
4.19
4.18
3.36
3.33
3.04
3.02
2.99
2.98
1.30
1.28
O
NHCbz
F
Compound 16h in CDCl3
1.88
4.92
1.94
0.82
2.01
1.00
0.98
0.97
3.01
f1 (ppm)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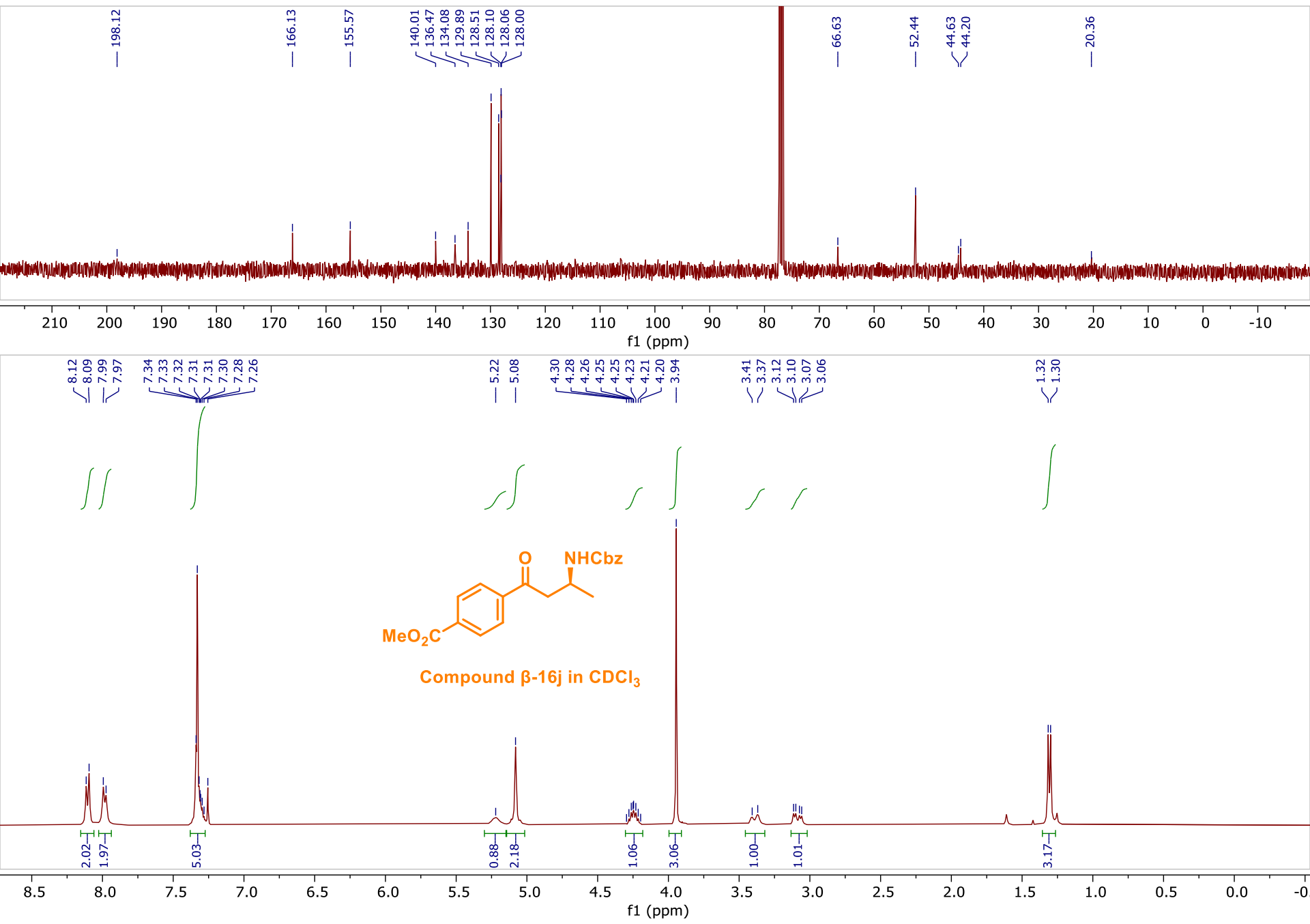
155.60
139.81
136.49
135.19
129.55
128.98
128.51
128.10
128.05
66.61
44.31
20.34
f1 (ppm)
7.89
7.87
7.42
7.40
7.33
5.26
5.08
4.27
4.25
4.24
4.22
4.21
4.19
4.17
3.36
3.32
3.04
3.02
3.00
2.98
1.30
1.28
O
NHCbz
Cl
Compound 16i in CDCl3
1.99
1.94
5.11
0.90
2.18
1.05
1.00
1.04
3.35
f1 (ppm)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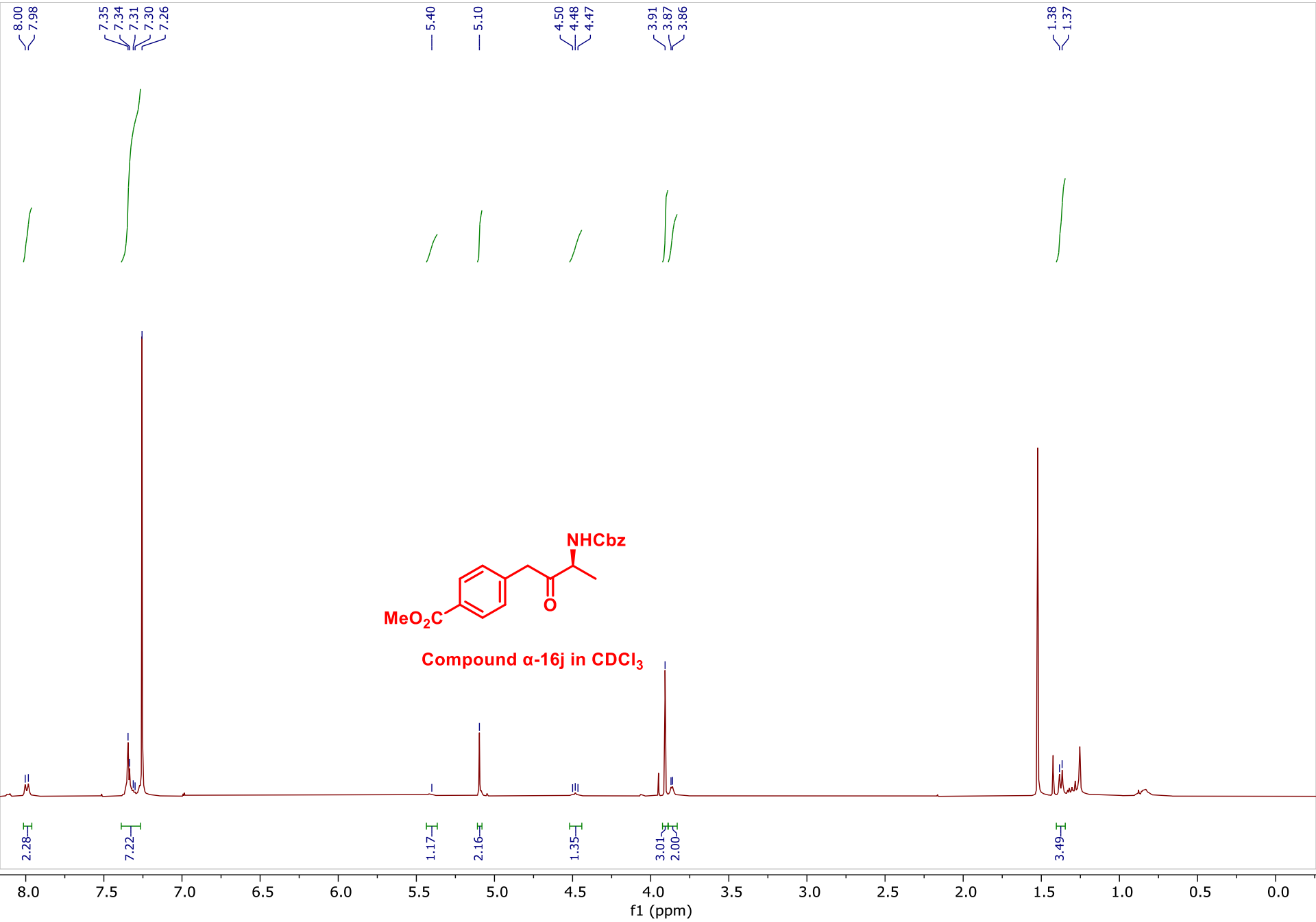
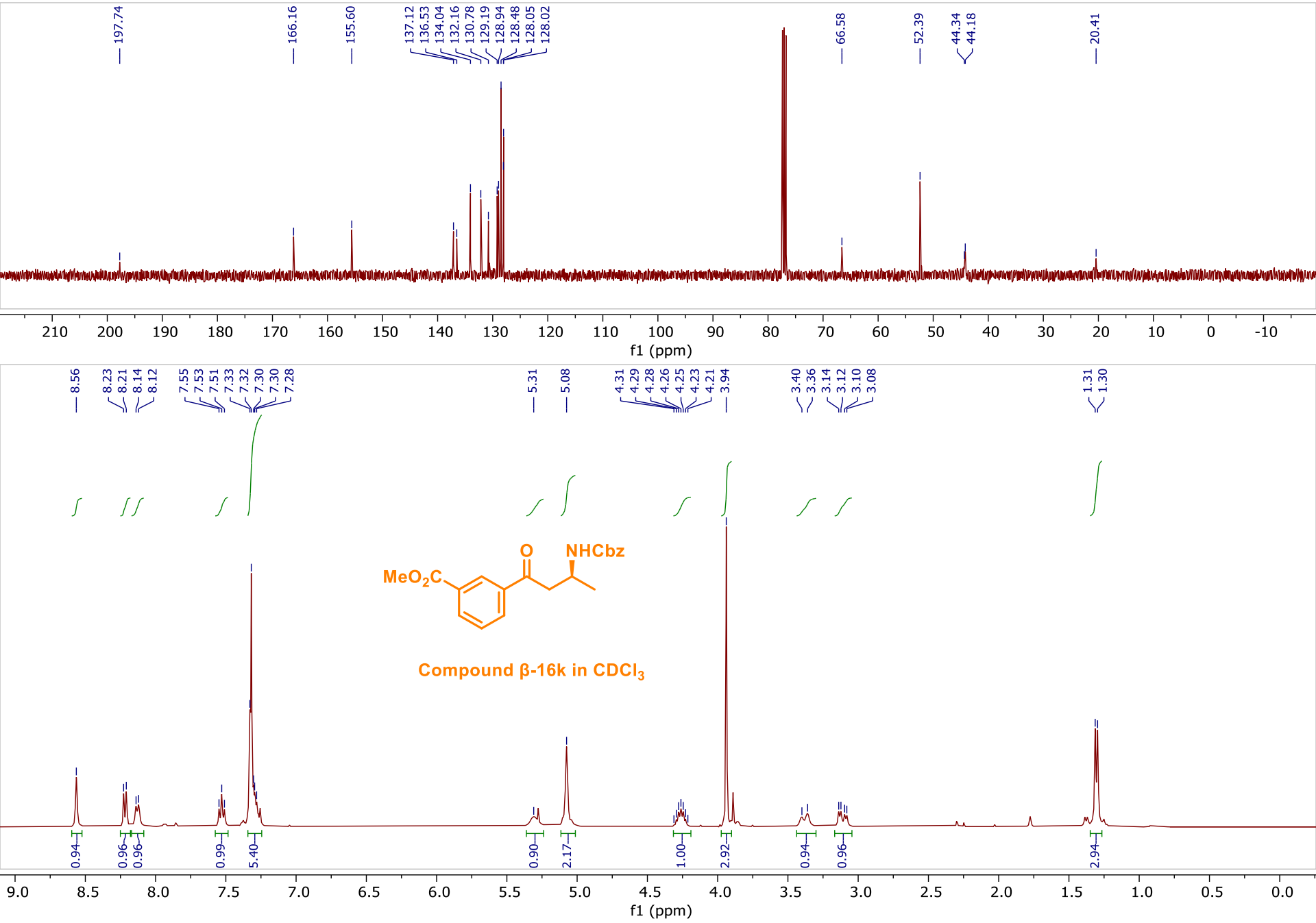
155.57
140.01
136.47
134.08
129.89
128.51
128.10
128.06
128.00
66.63
52.44
44.63
44.20
20.36
f1 (ppm)
8.12
8.09
7.99
7.97
7.34
7.33
7.32
7.31
7.31
7.30
7.28
7.26
5.22
5.08
4.30
4.28
4.26
4.25
4.25
4.23
4.21
4.20
3.94
3.41
3.37
3.12
3.10
3.07
3.06
1.32
1.30
O
NHCbz
MeO2C
Compound β-16j in CDCl3
2.02
1.97
5.03
0.88
2.18
1.06
3.06
1.00
1.01
3.17
f1 (ppm)


8.00
7.98
7.35
7.34
7.31
7.30
7.26
5.40
5.10
4.50
4.48
4.47
3.91
3.87
3.86
1.38
1.37
NHCbz
O
MeO2C
Compound α-16j in CDCl3
2.28
7.22
1.17
2.16
1.35
3.01
2.00
3.49
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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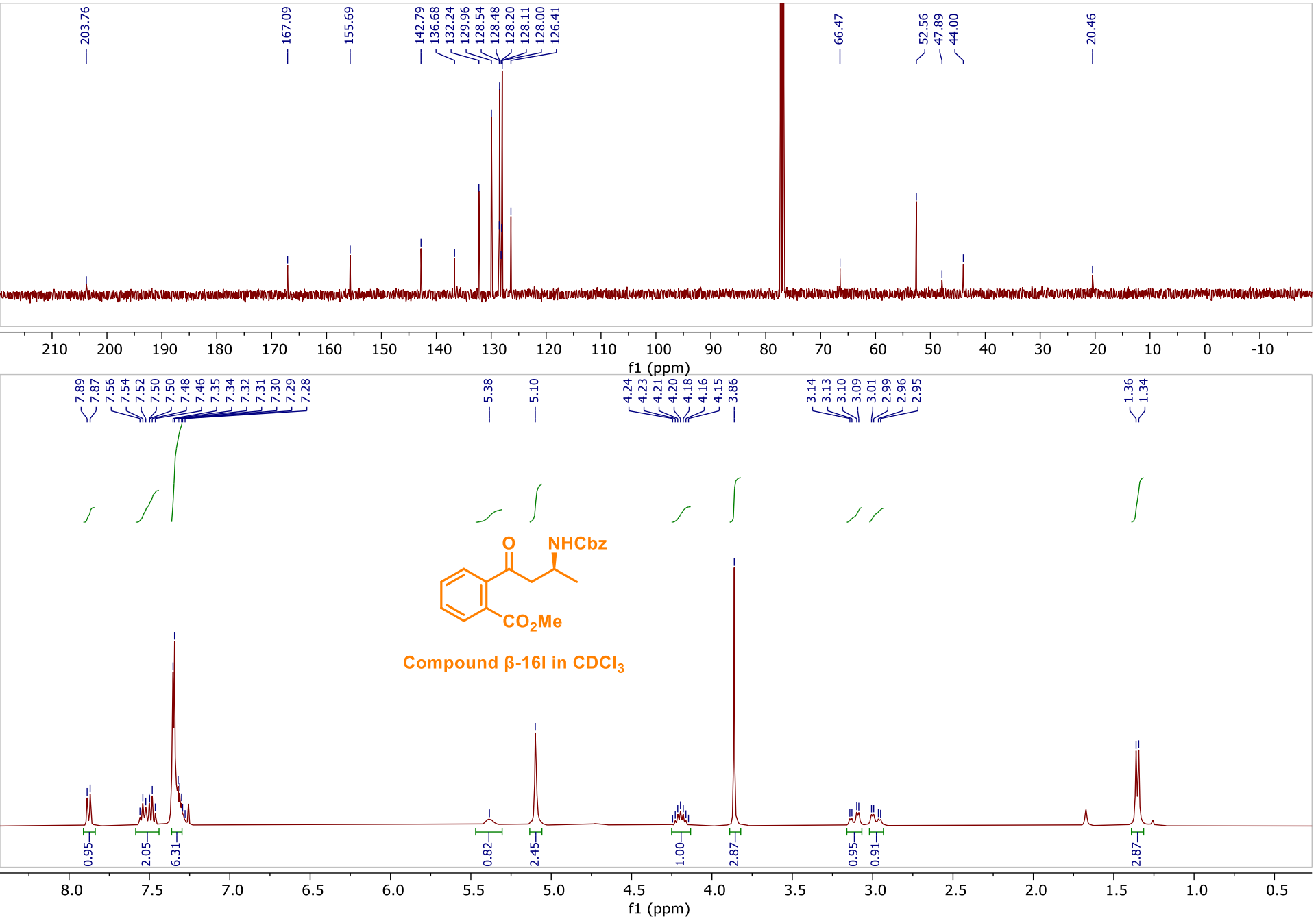
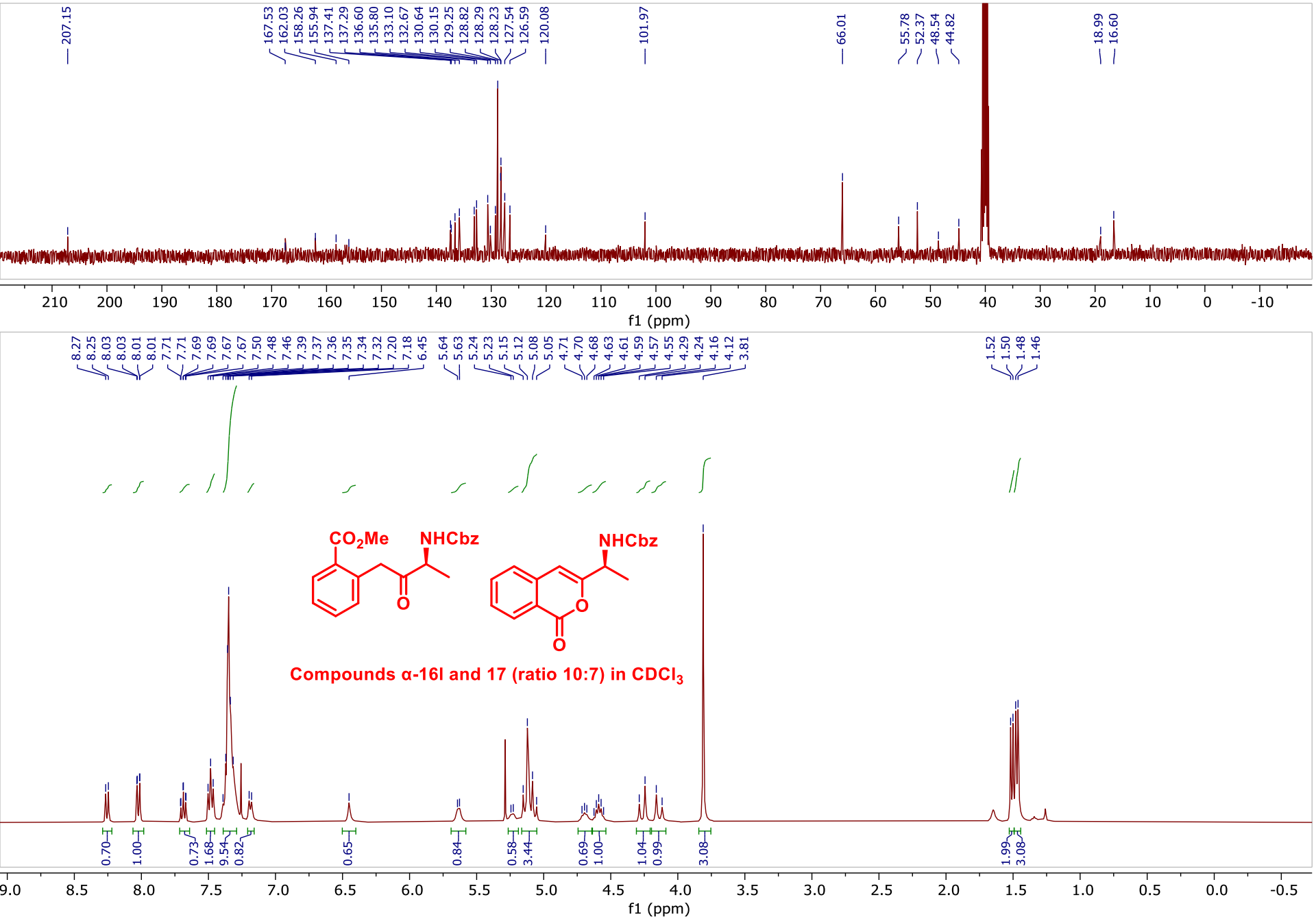
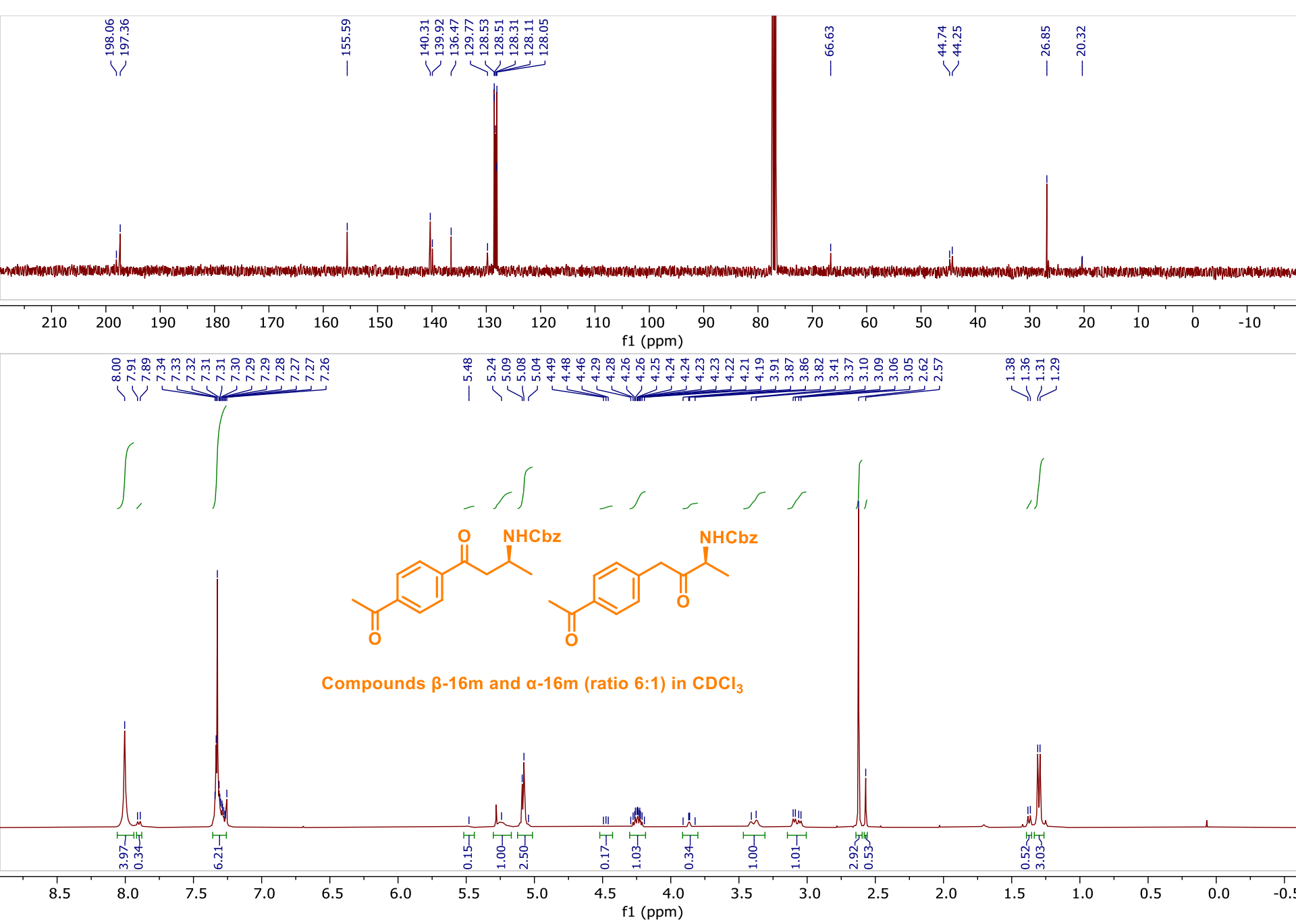
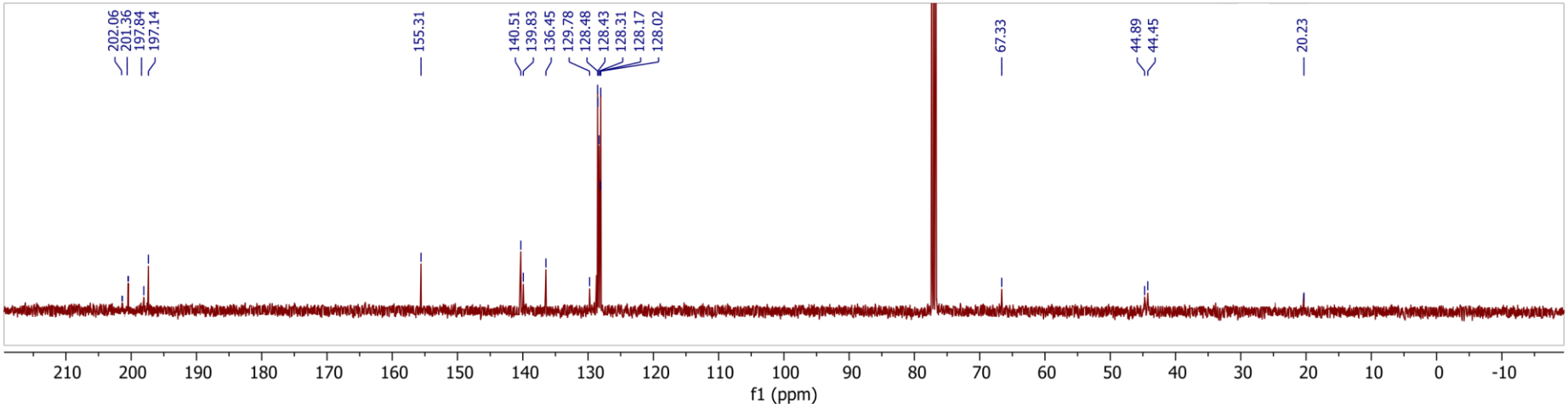
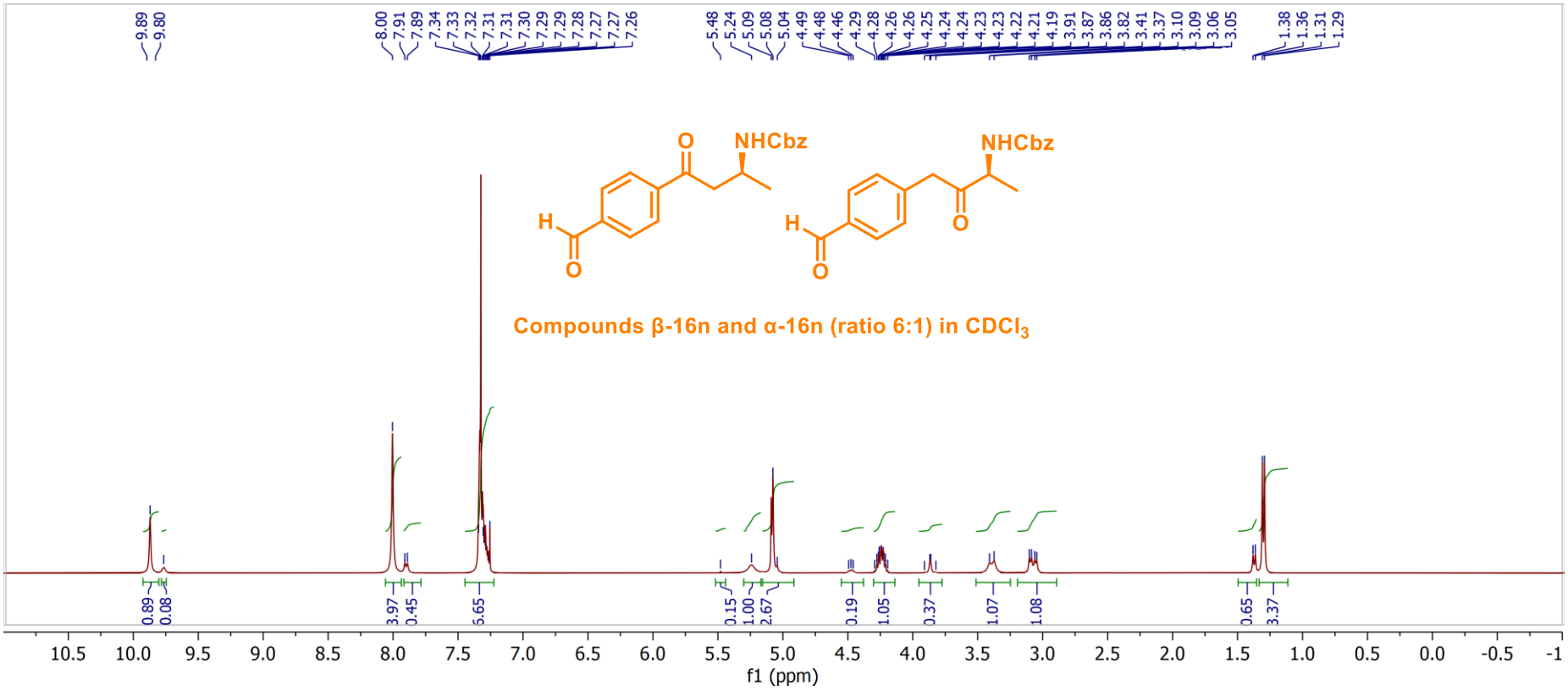
166.16
155.60
137.12
136.53
134.04
132.16
130.78
129.19
128.94
128.48
128.05
128.02
66.58
52.39
44.34
44.18
20.41
f1 (ppm)
8.56
8.23
8.21
8.14
8.12
7.55
7.53
7.51
7.33
7.32
7.30
7.30
7.28
5.31
5.08
4.31
4.29
4.28
4.26
4.25
4.23
4.21
3.94
3.40
3.36
3.14
3.12
3.10
3.08
1.31
1.30
O
NHCbz
MeO2C
Compound β-16k in CDCl3
0.94
0.96
0.96
0.99
5.40
0.90
2.17
1.00
2.92
0.94
0.96
2.94
f1 (ppm)

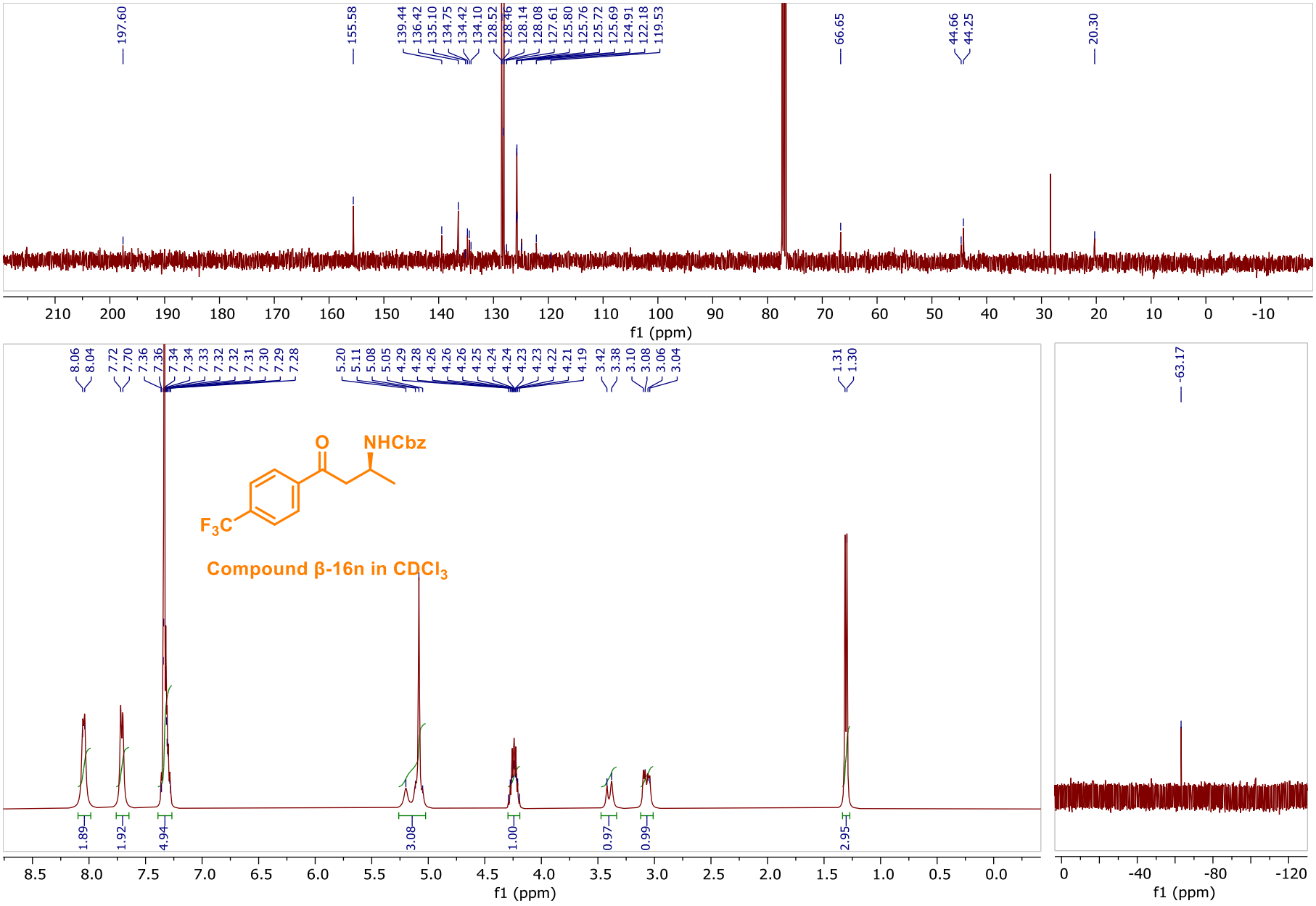

203.76
167.09
155.69
142.79
136.68
132.24
129.96
128.54
128.48
128.20
128.11
128.00
126.41
66.47
52.56
47.89
44.00
20.46
f1 (ppm)
7.89
7.87
7.56
7.54
7.52
7.50
7.50
7.48
7.46
7.35
7.34
7.32
7.31
7.30
7.29
7.28
5.38
5.10
4.24
4.23
4.21
4.20
4.18
4.16
4.15
3.86
3.14
3.13
3.10
3.09
3.01
2.99
2.96
2.95
1.36
1.34
O
NHCbz
CO2Me
Compound β-16l in CDCl3
0.95
2.05
6.31
0.82
2.45
1.00
2.87
0.95
0.91
2.87
f1 (ppm)

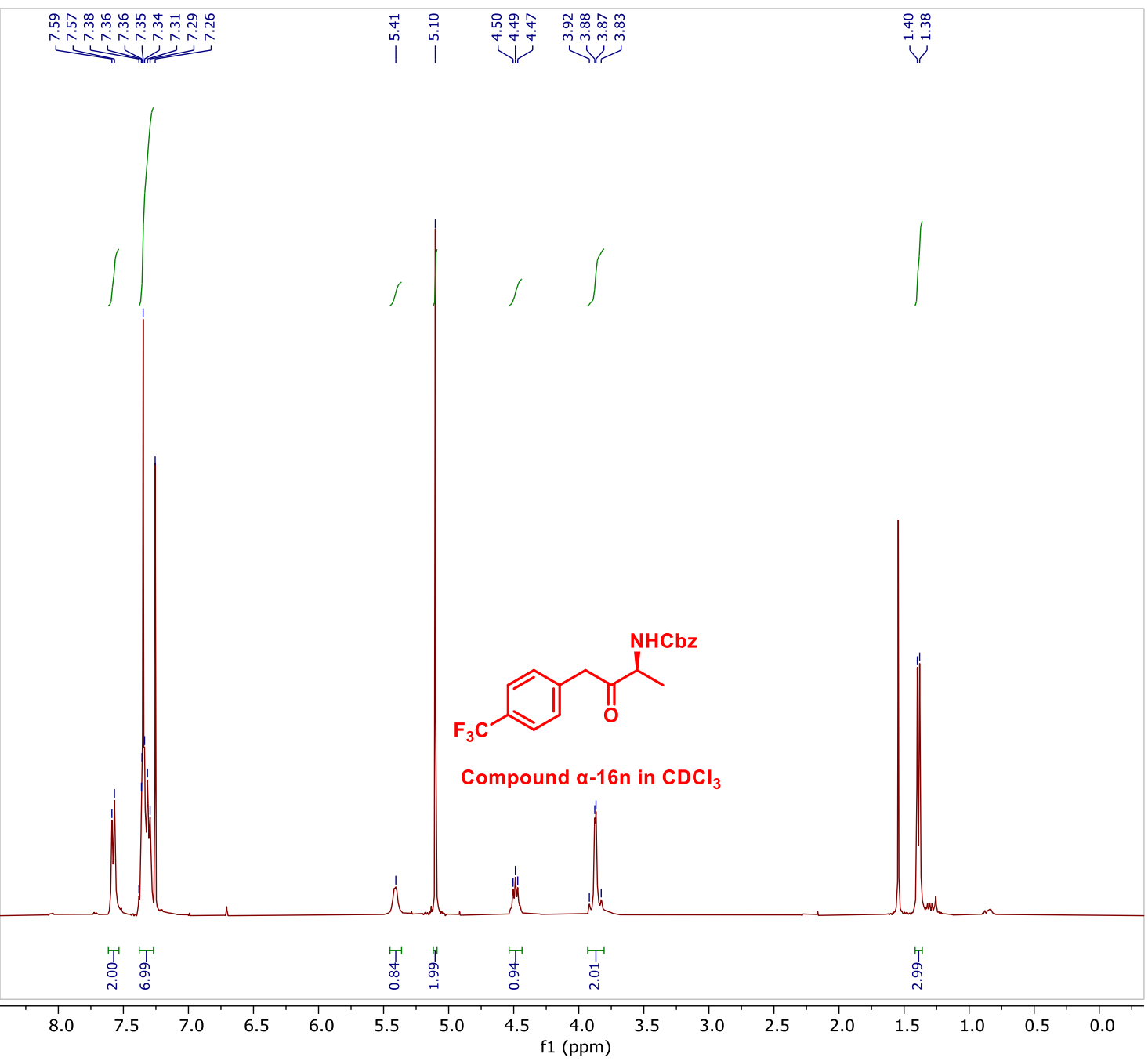

207.15
167.53
162.03
158.26
155.94
137.41
137.29
136.60
135.80
133.10
132.67
130.64
130.15
129.25
128.82
128.29
128.23
127.54
126.59
120.08
101.97
66.01
55.78
52.37
48.54
44.82
18.99
16.60
f1 (ppm)
8.27
8.25
8.03
8.03
8.01
8.01
7.71
7.71
7.69
7.69
7.67
7.67
7.50
7.48
7.46
7.39
7.37
7.36
7.35
7.34
7.32
7.20
7.18
6.45
5.64
5.63
5.24
5.23
5.15
5.12
5.08
5.05
4.71
4.70
4.68
4.63
4.61
4.59
4.57
4.55
4.29
4.24
4.16
4.12
3.81
1.52
1.50
1.48
1.46
CO2Me
NHCbz
NHCbz
O
O
O
Compounds α-16l and 17 (ratio 10:7) in CDCl3
0.70
1.00
0.73
1.68
9.54
0.82
0.65
0.84
0.58
3.44
0.69
1.00
1.04
0.99
3.08
1.99
3.08
f1 (ppm)

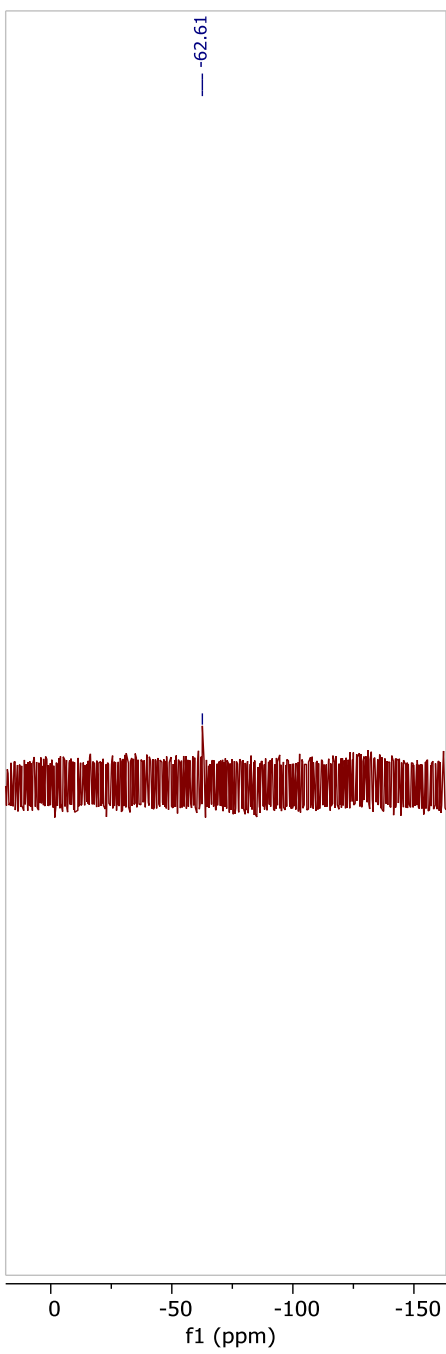

198.06
197.36
155.59
140.31
139.92
136.47
129.77
128.53
128.51
128.31
128.11
128.05
66.63
44.74
44.25
26.85
20.32
f1 (ppm)
8.00
7.91
7.89
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.26
5.48
5.24
5.09
5.08
5.04
4.49
4.48
4.46
4.29
4.28
4.26
4.26
4.25
4.24
4.24
4.23
4.23
4.22
4.21
4.19
3.91
3.87
3.86
3.82
3.41
3.37
3.10
3.09
3.06
3.05
2.62
2.57
1.38
1.36
1.31
1.29
O
NHCbz
O
NHCbz
O
O
Compounds β-16m and α-16m (ratio 6:1) in CDCl3
3.97
0.34
6.21
0.15
1.00
2.50
0.17
1.03
0.34
1.00
1.01
2.92
0.53
0.52
3.03
f1 (ppm)

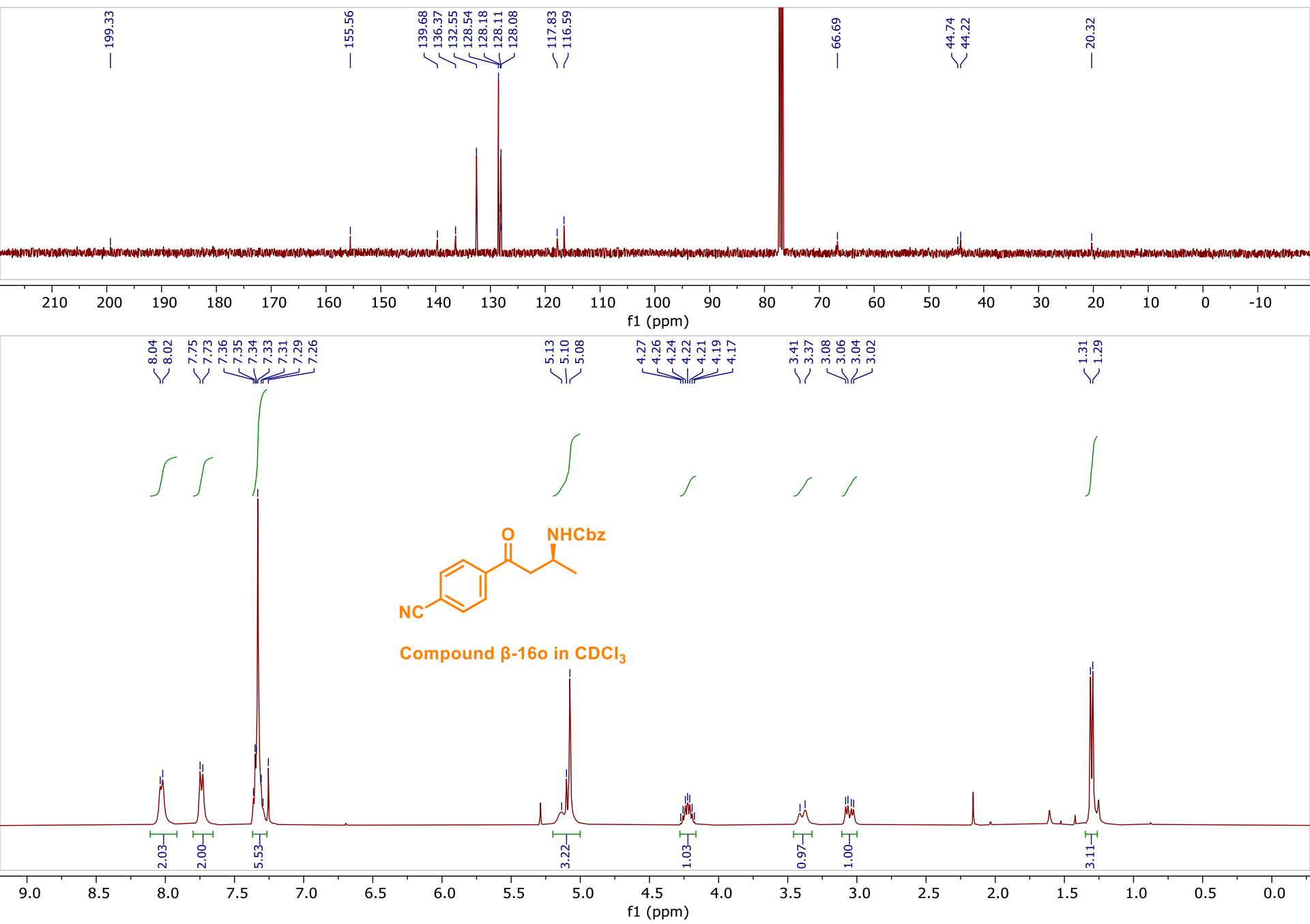

202.06
201.36
197.84
197.14
155.31
140.51
139.83
136.45
129.78
128.48
128.43
128.31
128.17
128.02
67.33
44.89
44.45
20.23
f1 (ppm)

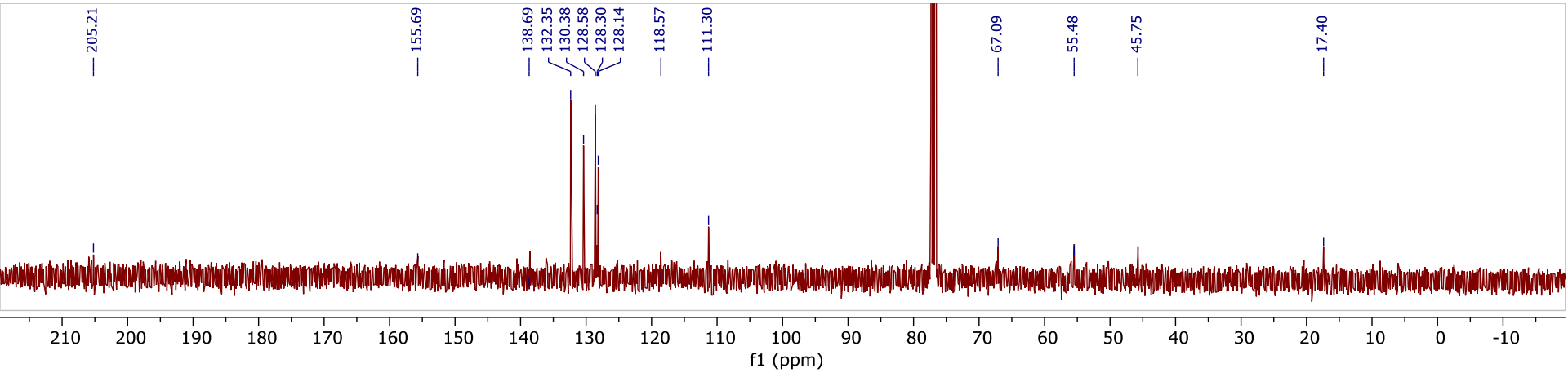

9.89
9.80
8.00
7.91
7.89
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.26
5.48
5.24
5.09
5.08
5.04
4.49
4.48
4.46
4.29
4.28
4.26
4.26
4.25
4.24
4.24
4.23
4.23
4.22
4.21
4.19
3.91
3.87
3.86
3.82
3.41
3.37
3.10
3.09
3.06
3.05
1.38
1.36
1.31
1.29
O
NHCbz
H
O
NHCbz
O
H
O
Compounds β-16n and α-16n (ratio 6:1) in CDCl3
0.89
0.08
3.97
0.45
5.65
0.15
1.00
2.67
0.19
1.05
0.37
1.07
1.08
0.65
3.37
f1 (ppm)

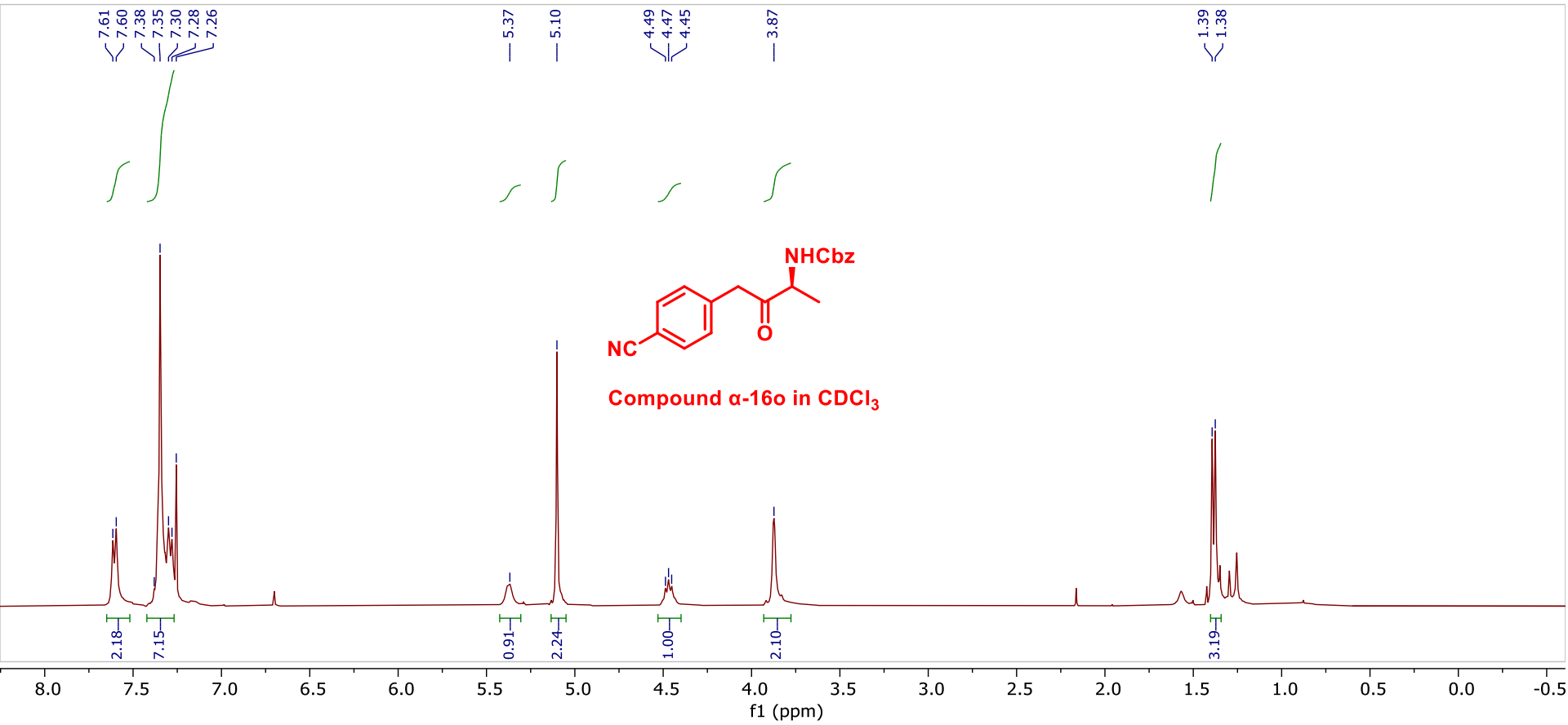

197.60
155.58
139.44
136.42
135.10
134.75
134.42
134.10
128.52
128.46
128.14
128.08
127.61
125.80
125.76
125.72
125.69
124.91
122.18
119.53
66.65
44.66
44.25
20.30
f1 (ppm)
8.06
8.04
7.72
7.70
7.36
7.36
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.29
7.28
5.20
5.11
5.08
5.05
4.29
4.28
4.26
4.26
4.26
4.25
4.24
4.24
4.23
4.23
4.22
4.21
4.19
3.42
3.38
3.10
3.08
3.06
3.04
1.31
1.30
O
NHCbz
F3C
Compound β-16n in CDCl3
1.89
1.92
4.94
3.08
1.00
0.97
0.99
2.95
f1 (ppm)
-63.17
f1 (ppm)

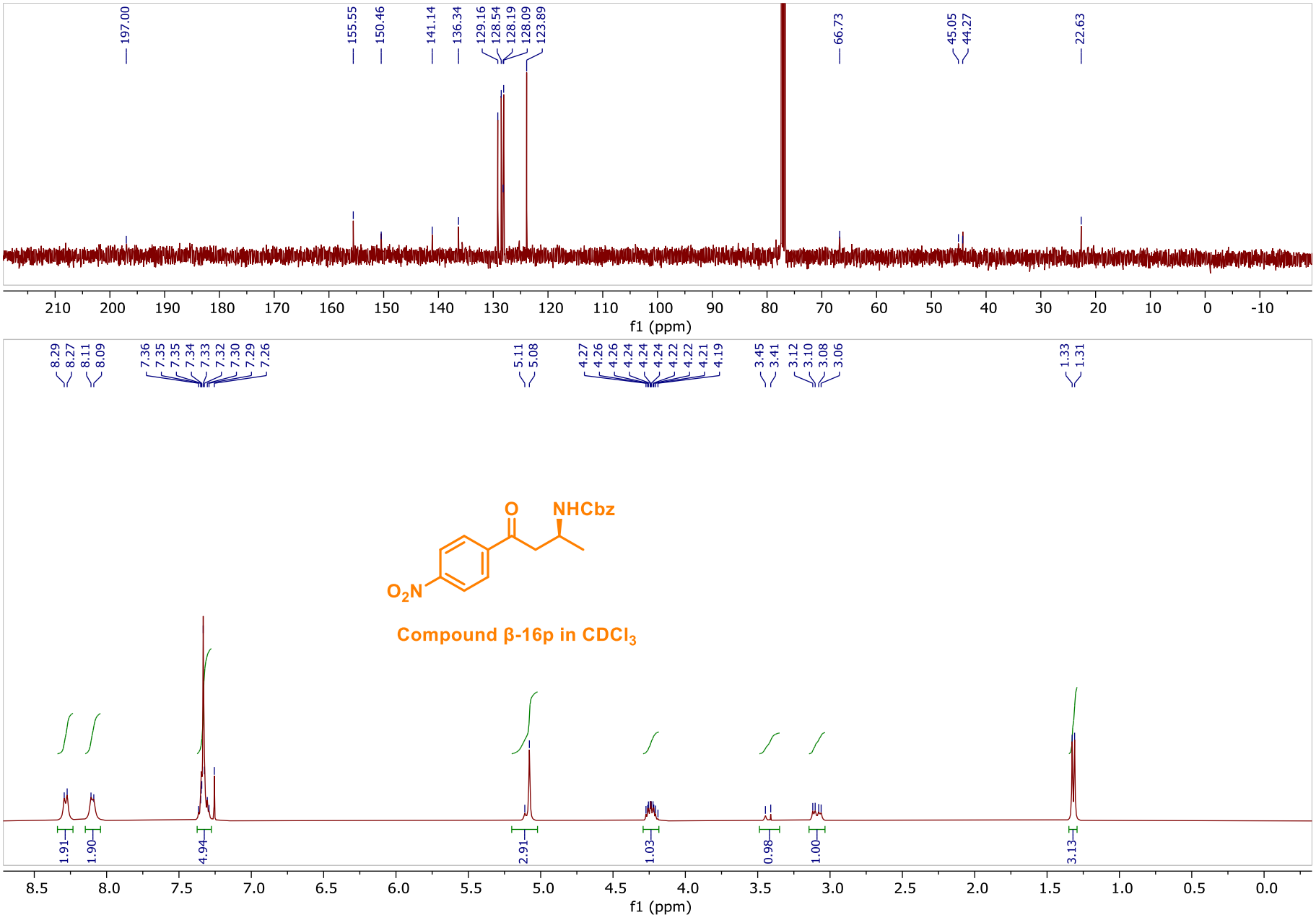

7.59
7.57
7.38
7.36
7.36
7.35
7.34
7.31
7.29
7.26
5.41
5.10
4.50
4.49
4.47
3.92
3.88
3.87
3.83
1.40
1.38
NHCbz
O
F3C
Compound α-16n in CDCl3
2.00
6.99
0.84
1.99
0.94
2.01
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

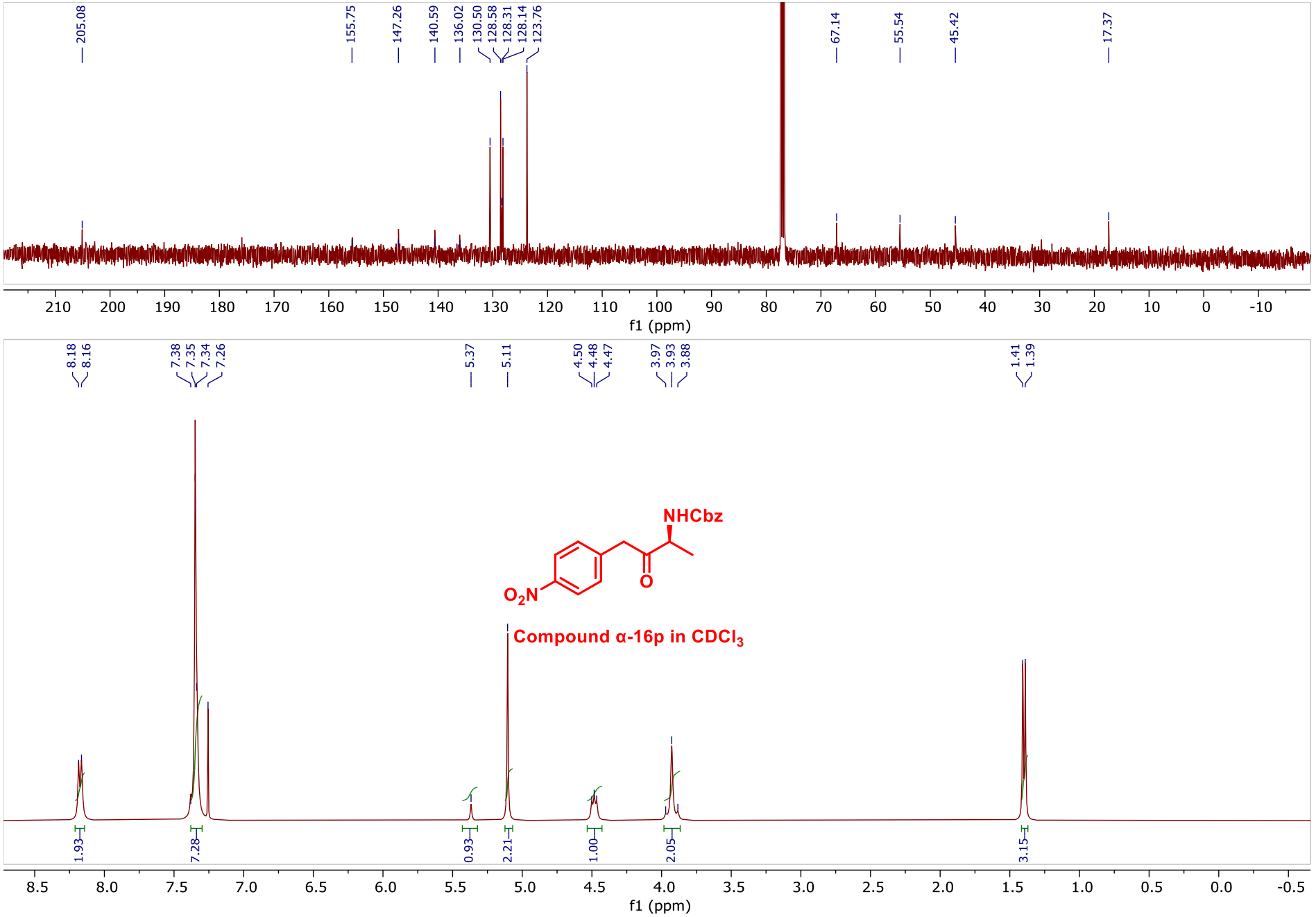

-62.61
0
-50
-100
-150
f1 (ppm)

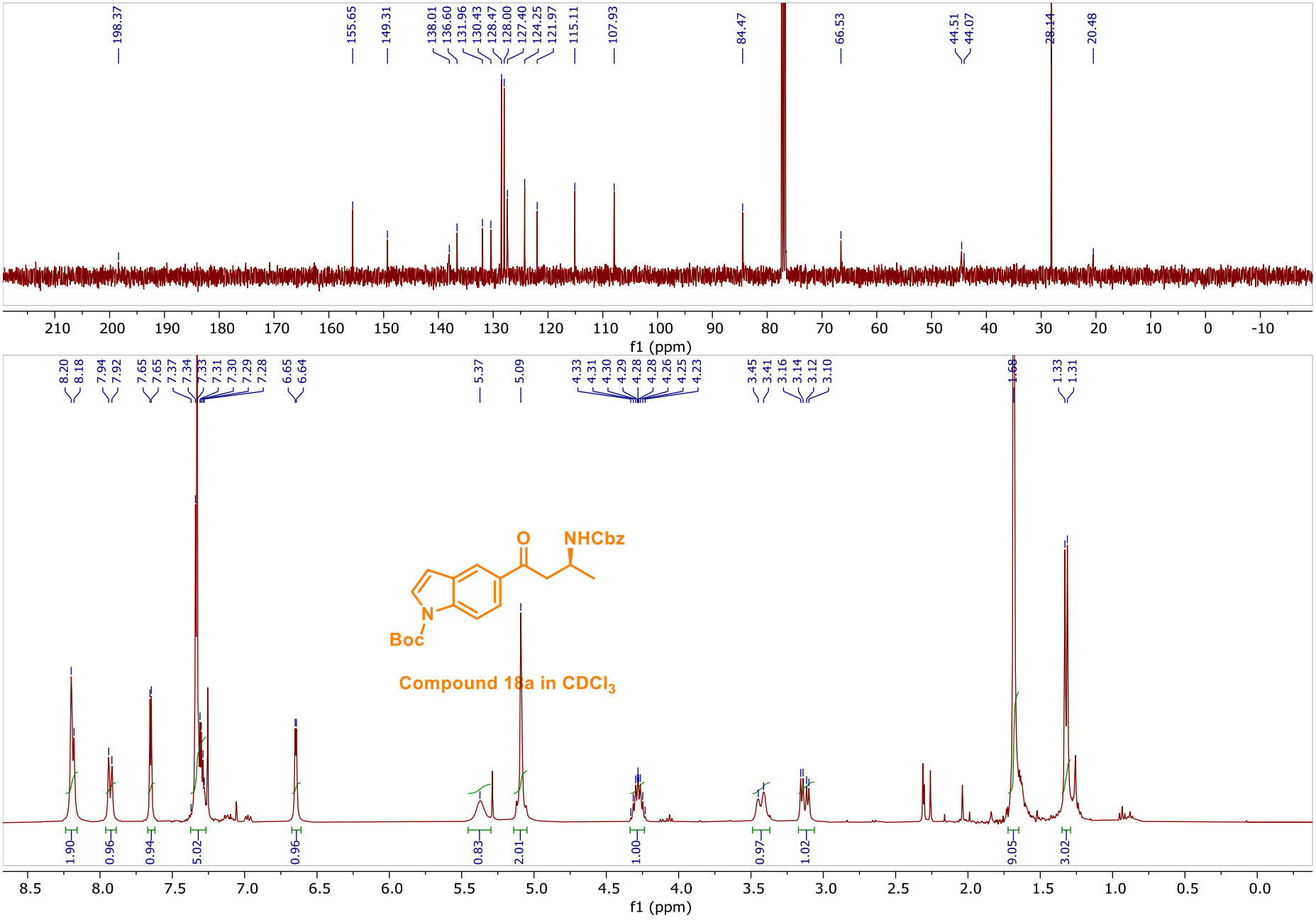

199.33
155.56
139.68
136.37
132.55
128.54
128.18
128.11
128.08
117.83
116.59
66.69
44.74
44.22
20.32
f1 (ppm)
8.04
8.02
7.75
7.73
7.36
7.35
7.34
7.33
7.31
7.29
7.26
5.13
5.10
5.08
4.27
4.26
4.24
4.22
4.21
4.19
4.17
3.41
3.37
3.08
3.06
3.04
3.02
1.31
1.29
O
NHCbz
NC
Compound β-16o in CDCl3
2.03
2.00
5.53
3.22
1.03
0.97
1.00
3.11
f1 (ppm)

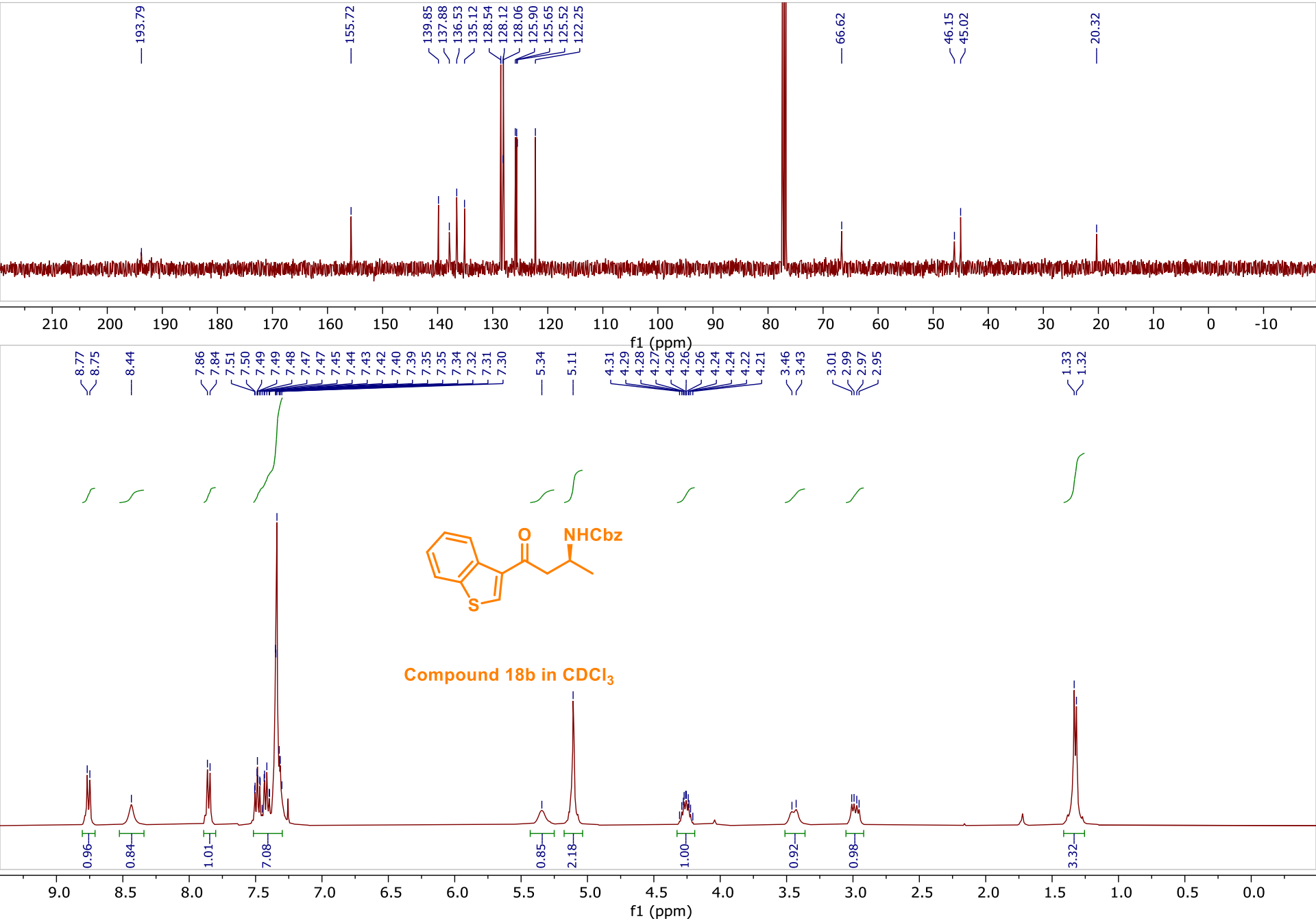

205.21
155.69
138.69
132.35
130.38
128.58
128.30
128.14
118.57
111.30
67.09
55.48
45.75
17.40
f1 (ppm)

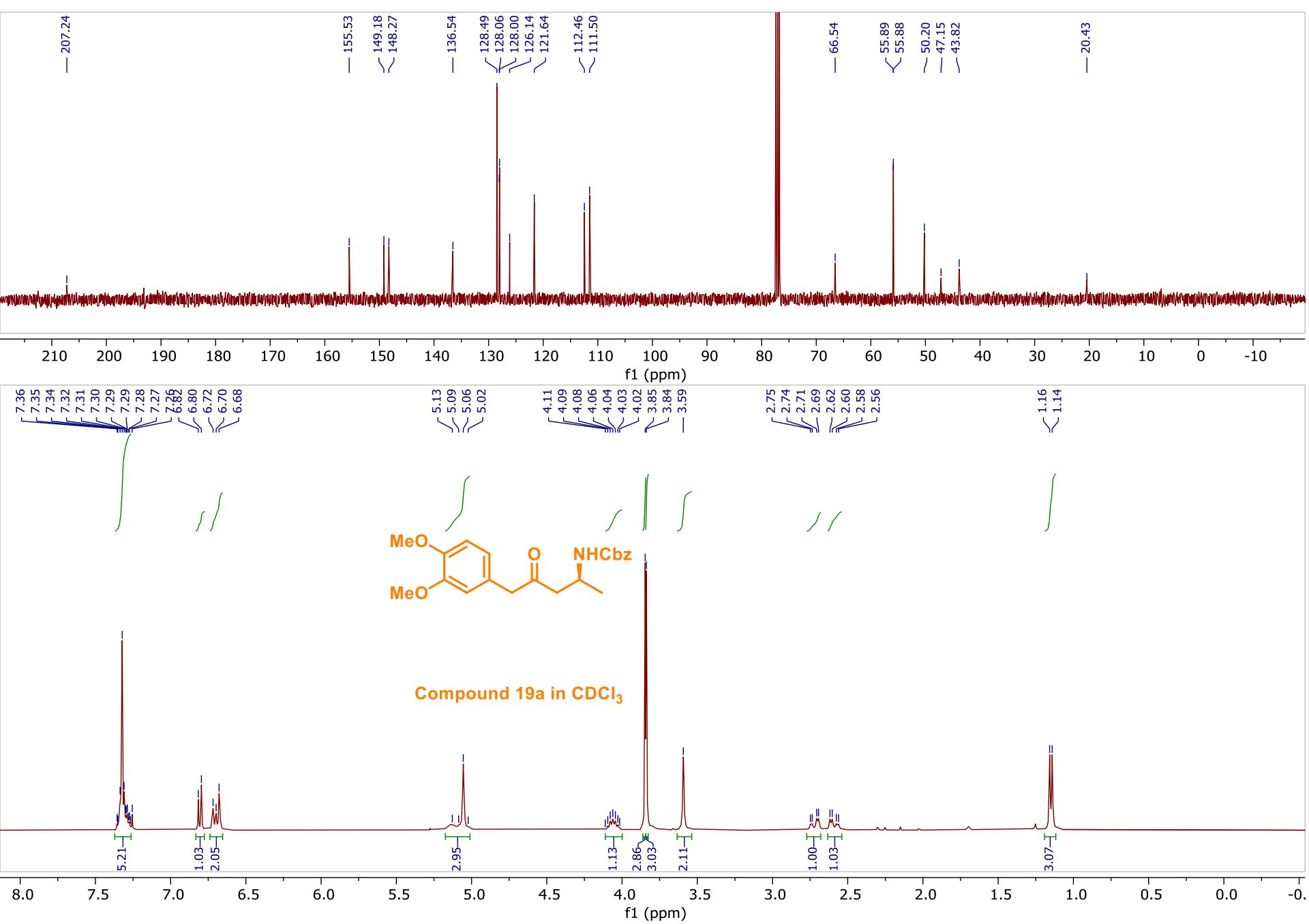

7.61
7.60
7.38
7.35
7.30
7.28
7.26
5.37
5.10
4.49
4.47
4.45
3.87
1.39
1.38
NHCbz
O
NC
Compound α-16o in CDCl3
2.18
7.15
0.91
2.24
1.00
2.10
3.19
f1 (ppm)

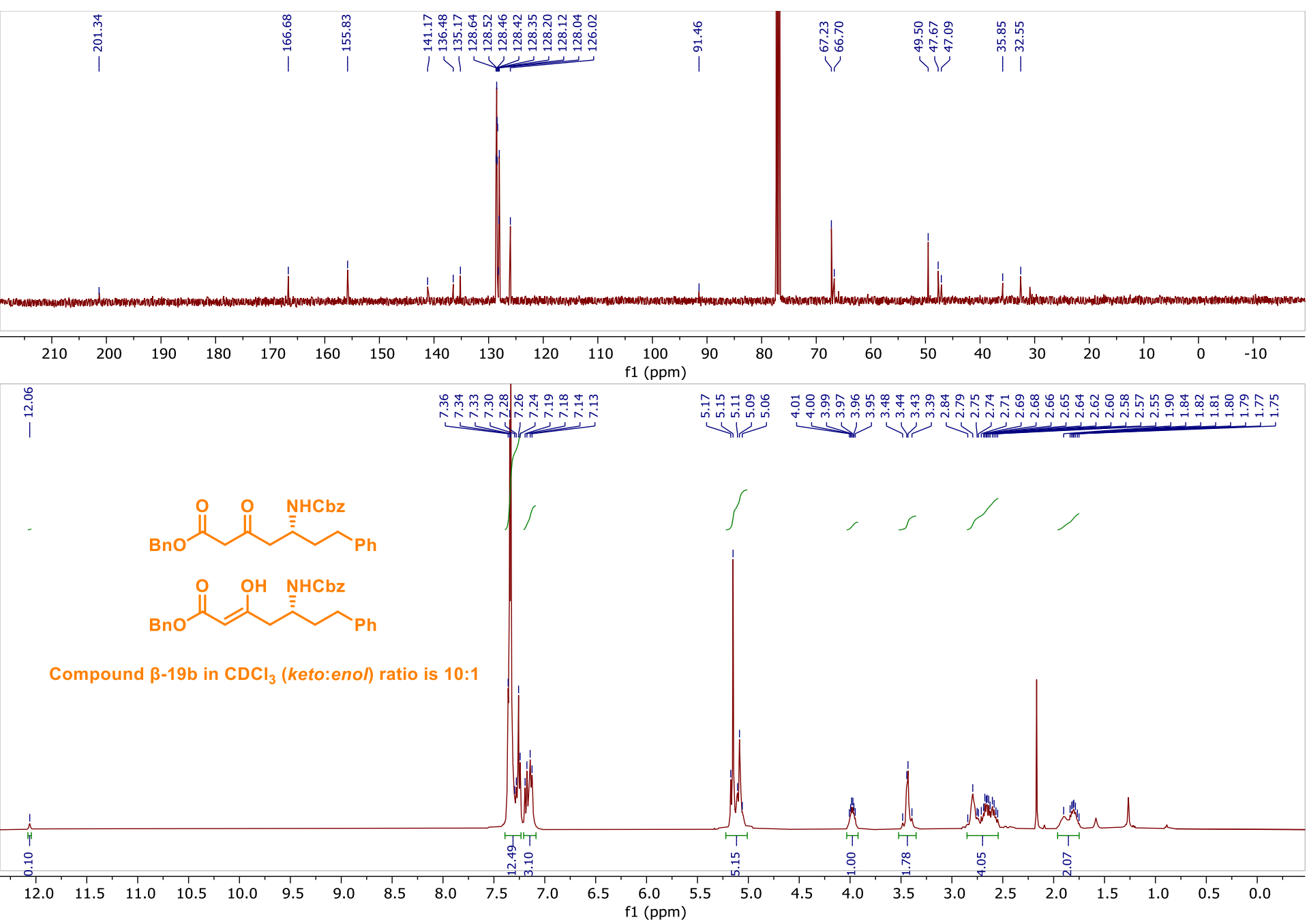

197.00
155.55
150.46
141.14
136.34
129.16
128.54
128.19
128.09
123.89
66.73
45.05
44.27
22.63
f1 (ppm)
8.29
8.27
8.11
8.09
7.36
7.35
7.35
7.34
7.33
7.32
7.30
7.29
7.26
5.11
5.08
4.27
4.26
4.26
4.24
4.24
4.24
4.22
4.22
4.21
4.19
3.45
3.41
3.12
3.10
3.08
3.06
1.33
1.31
O
NHCbz
O2N
Compound β-16p in CDCl3
1.91
1.90
4.94
2.91
1.03
0.98
1.00
3.13
f1 (ppm)

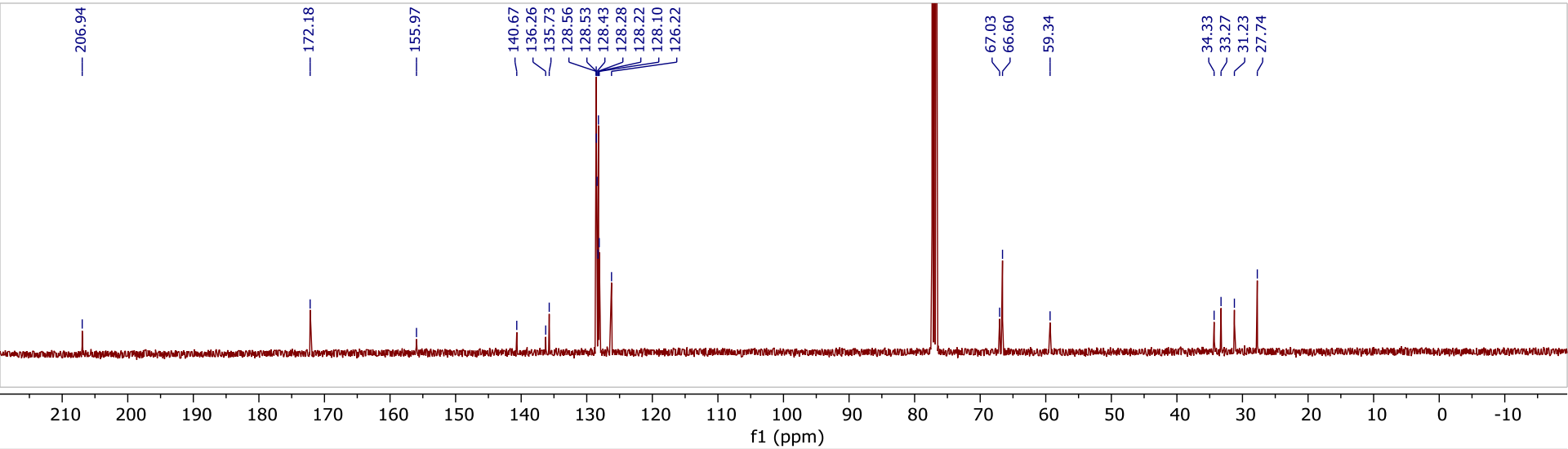

205.08
155.75
147.26
140.59
136.02
130.50
128.58
128.31
128.14
123.76
67.14
55.54
45.42
17.37
f1 (ppm)
8.18
8.16
7.38
7.35
7.34
7.26
5.37
5.11
4.50
4.48
4.47
3.97
3.93
3.88
1.41
1.39
NHCbz
O
O2N
Compound α-16p in CDCl3
1.93
7.28
0.93
2.21
1.00
2.05
3.15
f1 (ppm)

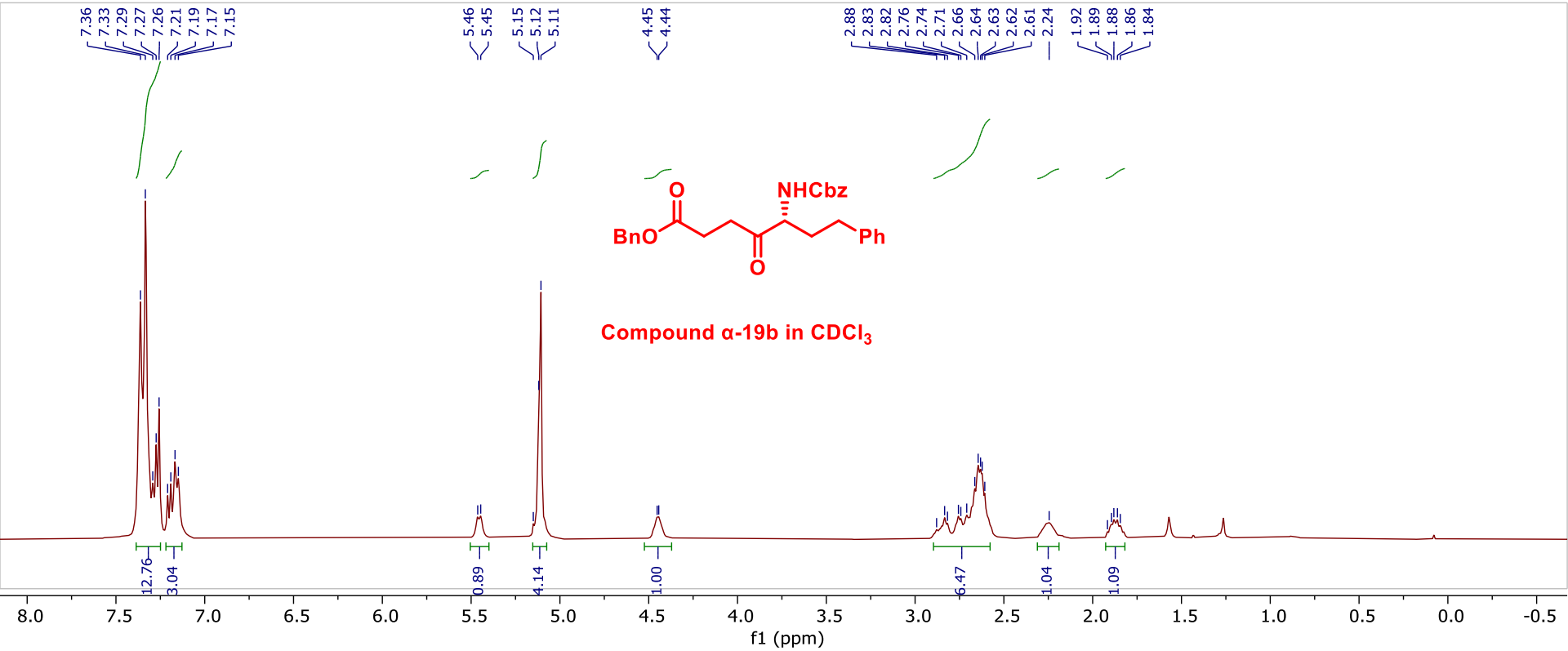

198.37
155.65
149.31
138.01
136.60
131.96
130.43
128.47
128.00
127.40
124.25
121.97
115.11
107.93
84.47
66.53
44.51
44.07
28.14
20.48
f1 (ppm)
8.20
8.18
7.94
7.92
7.65
7.65
7.37
7.34
7.33
7.31
7.30
7.29
7.28
6.65
6.64
5.37
5.09
4.33
4.31
4.30
4.29
4.28
4.28
4.26
4.25
4.23
3.45
3.41
3.16
3.14
3.12
3.10
1.68
1.33
1.31
O
NHCbz
N
Boc
Compound 18a in CDCl3
1.90
0.96
0.94
5.02
0.96
0.83
2.01
1.00
0.97
1.02
9.05
3.02
f1 (ppm)


193.79
155.72
139.85
137.88
136.53
135.12
128.54
128.12
128.06
125.90
125.65
125.52
122.25
66.62
46.15
45.02
20.32
f1 (ppm)
8.77
8.75
8.44
7.86
7.84
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.45
7.44
7.43
7.42
7.40
7.39
7.35
7.35
7.34
7.32
7.31
7.30
5.34
5.11
4.31
4.29
4.28
4.27
4.26
4.26
4.26
4.24
4.24
4.22
4.21
3.46
3.43
3.01
2.99
2.97
2.95
1.33
1.32
O
NHCbz
S
Compound 18b in CDCl3
0.96
0.84
1.01
7.08
0.85
2.18
1.00
0.92
0.98
3.32
f1 (ppm)

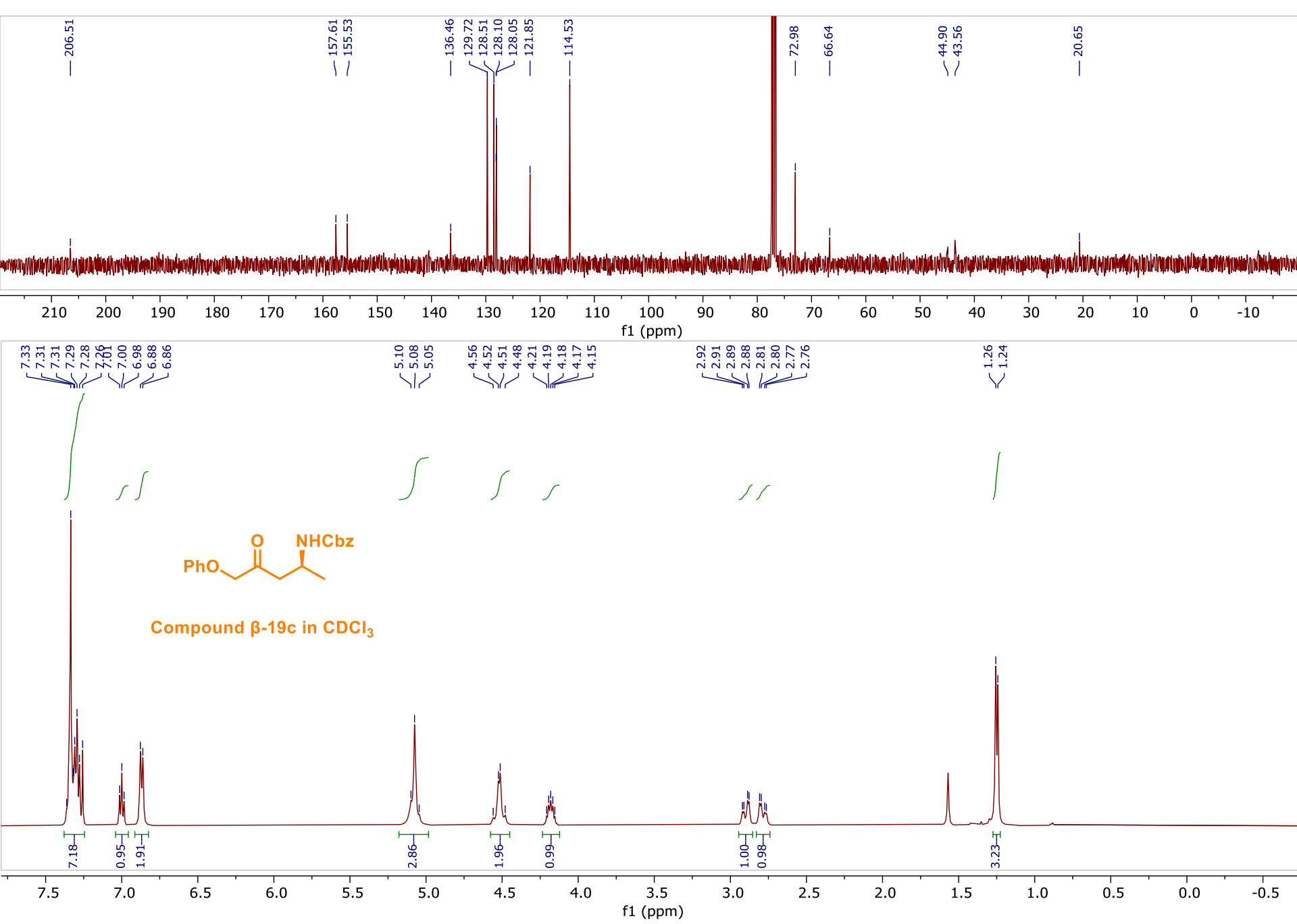

207.24
155.53
149.18
148.27
136.54
128.49
128.06
128.00
126.14
121.64
112.46
111.50
66.54
55.89
55.88
50.20
47.15
43.82
20.43
f1 (ppm)
7.36
7.35
7.34
7.32
7.31
7.30
7.29
7.29
7.28
7.27
6.80
6.72
6.70
6.68
5.13
5.09
5.06
5.02
4.11
4.09
4.08
4.06
4.04
4.03
4.02
3.85
3.84
3.59
2.75
2.74
2.71
2.69
2.62
2.60
2.58
2.56
1.16
1.14
MeO
MeO
O
NHCbz
Compound 19a in CDCl3
5.21
1.03
2.05
2.95
1.13
2.86
3.03
2.11
1.00
1.03
3.07
f1 (ppm)

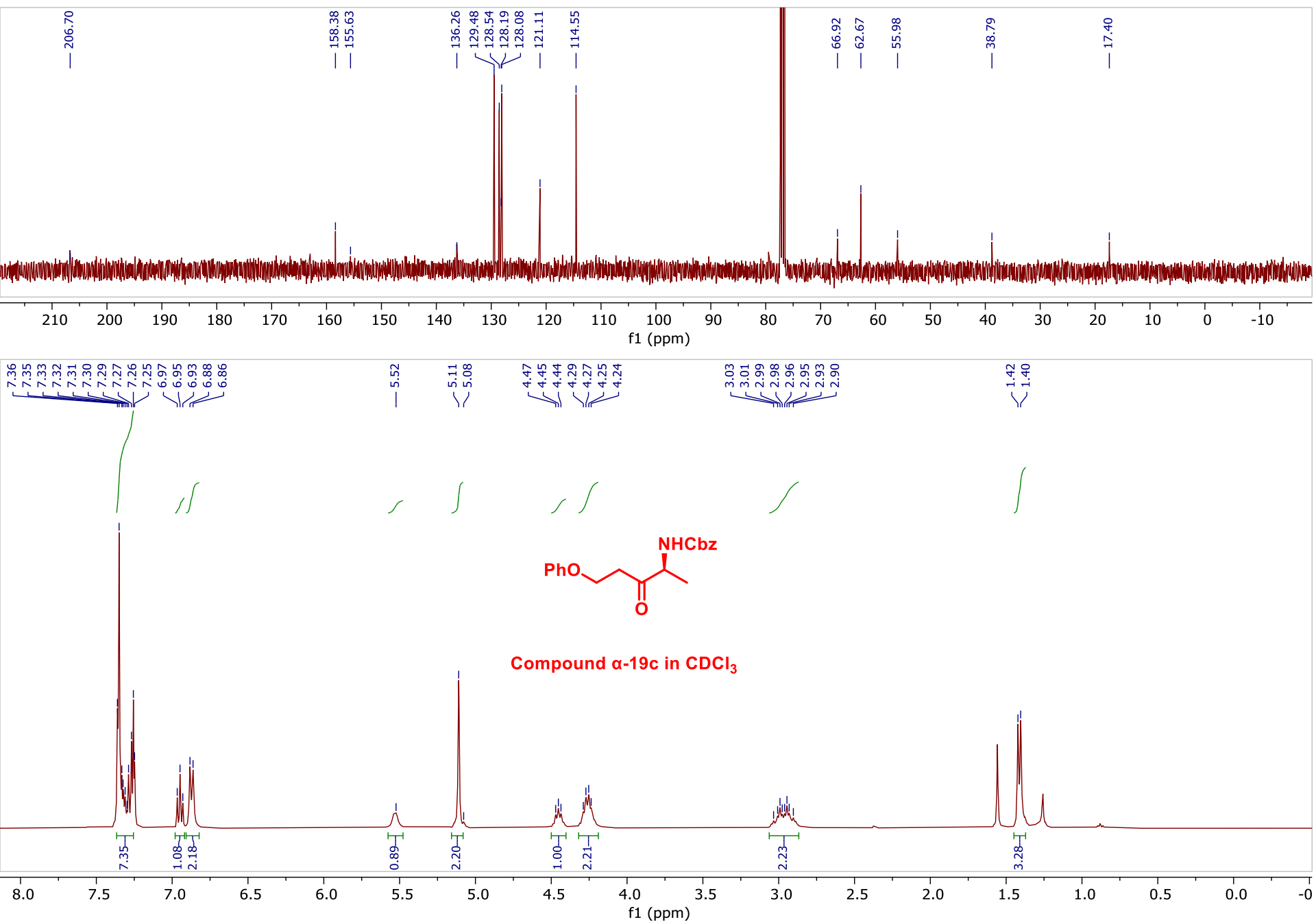

201.34
166.68
155.83
141.17
136.48
135.17
128.64
128.52
128.46
128.42
128.35
128.20
128.12
128.04
126.02
91.46
67.23
66.70
49.50
47.67
47.09
35.85
32.55
f1 (ppm)
12.06
7.36
7.34
7.33
7.30
7.28
7.26
7.24
7.19
7.18
7.14
7.13
5.17
5.15
5.11
5.09
5.06
4.01
4.00
3.99
3.97
3.96
3.95
3.48
3.44
3.43
3.39
2.84
2.79
2.75
2.74
2.71
2.69
2.68
2.66
2.65
2.64
2.62
2.60
2.58
2.57
2.55
1.90
1.84
1.82
1.81
1.80
1.79
1.77
1.75
O
O
NHCbz
BnO
Ph
O
OH
NHCbz
BnO
Ph
Compound β-19b in CDCl3 (keto:enol) ratio is 10:1
0.10
12.49
3.10
5.15
1.00
1.78
4.05
2.07
f1 (ppm)

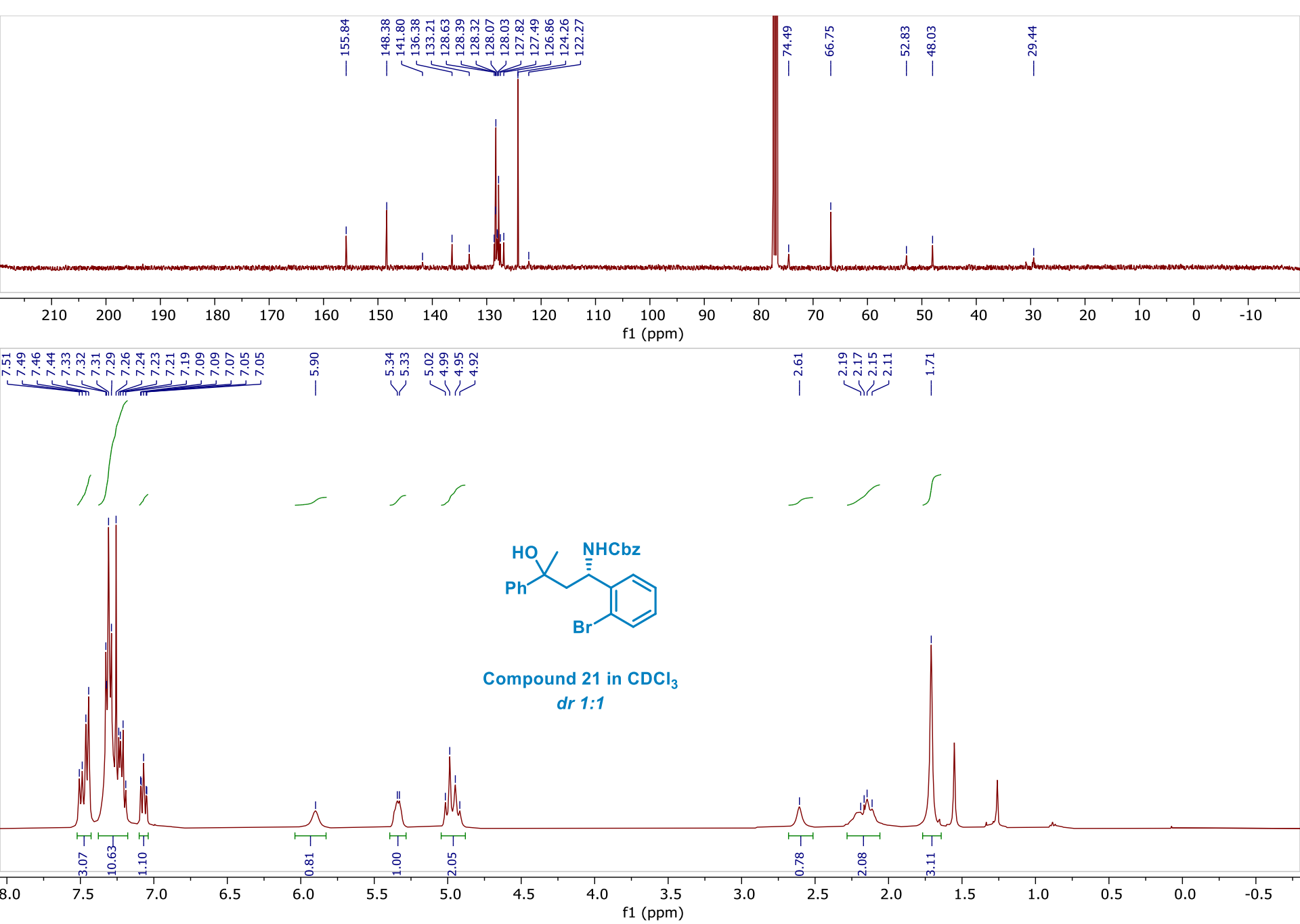


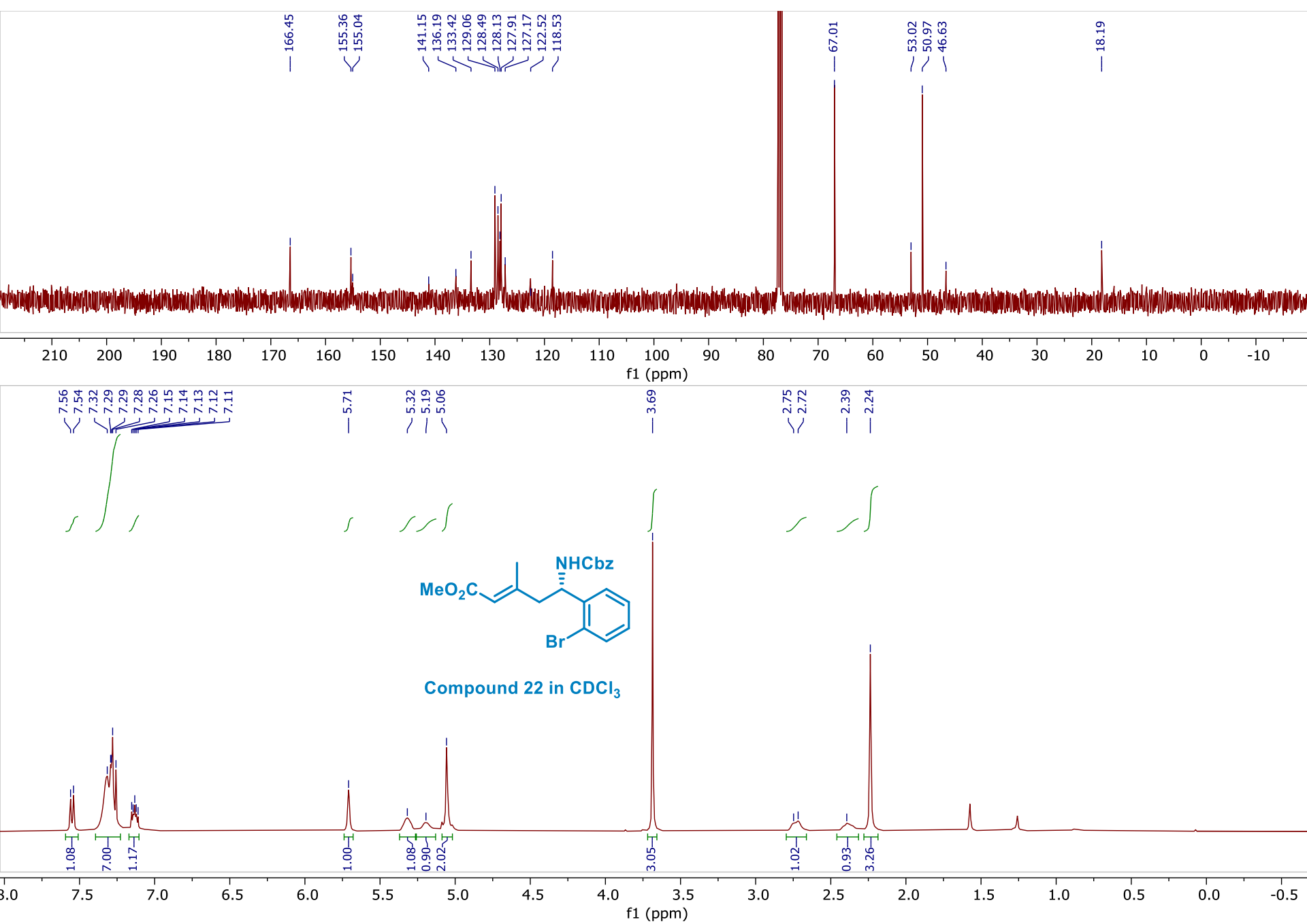


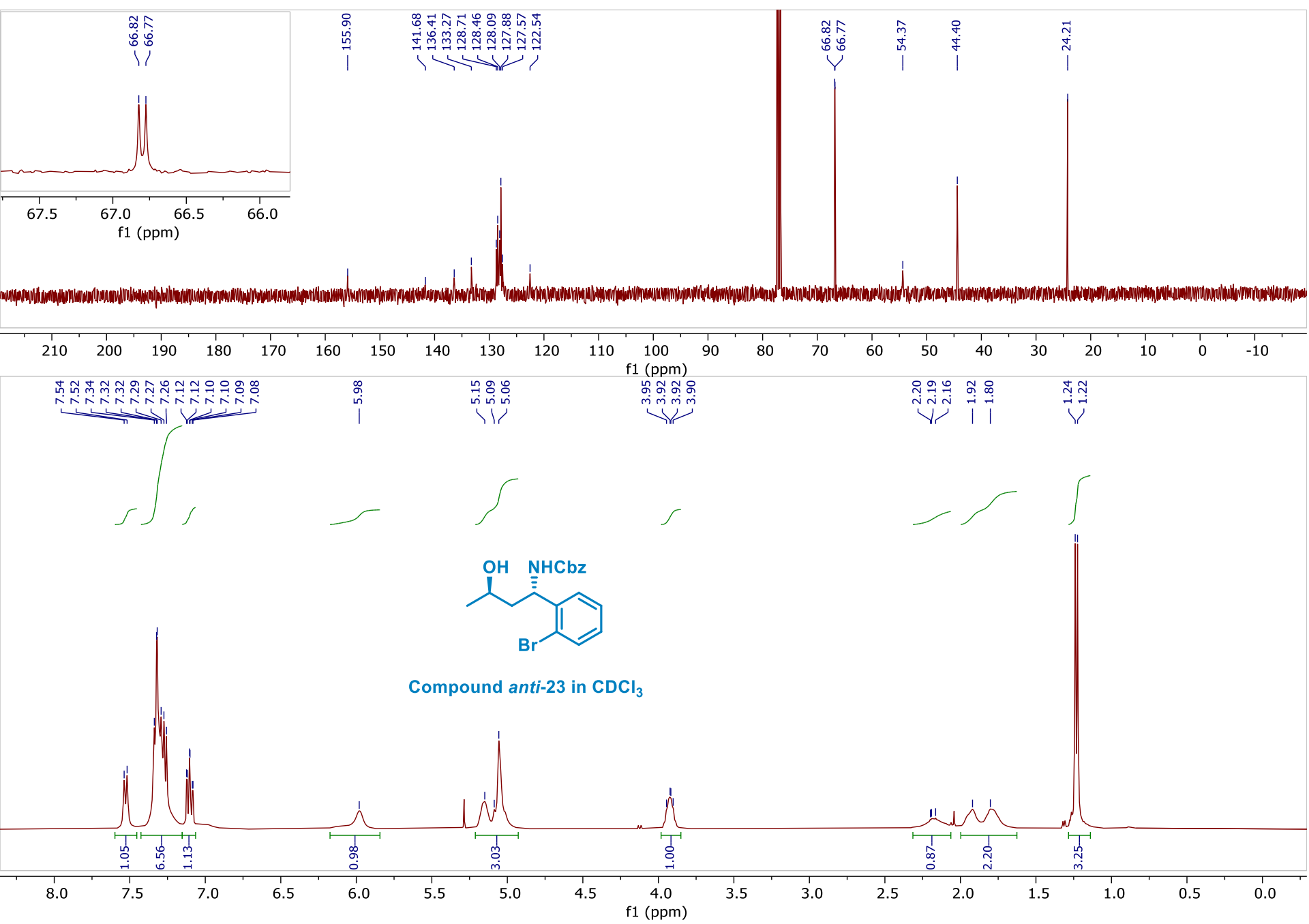
Compound α-19b in $CDCl_3$

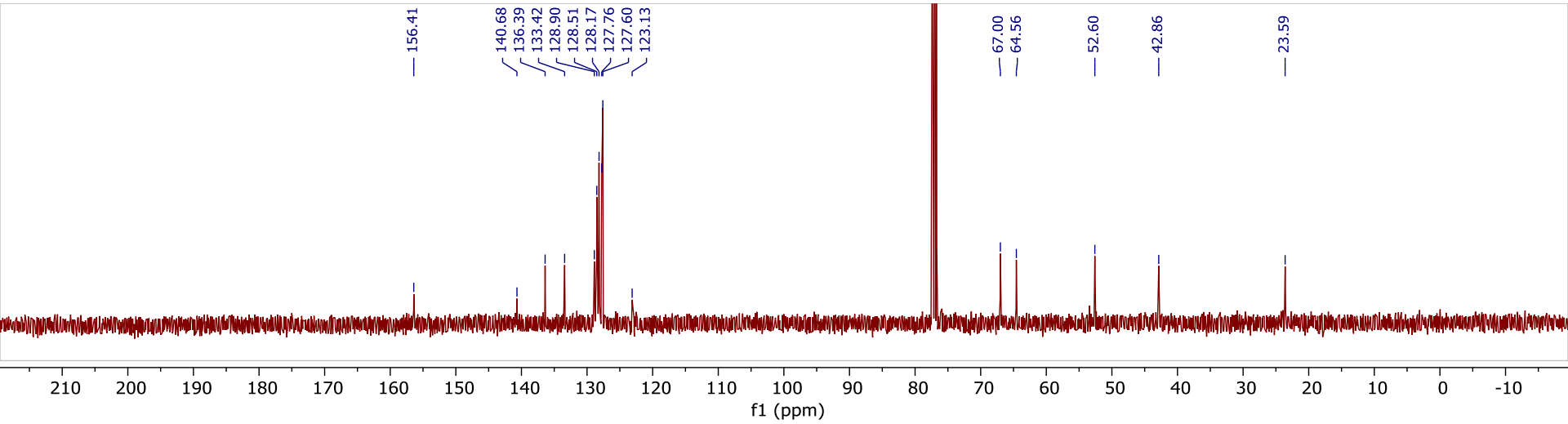

206.51
157.61
155.53
136.46
129.72
128.51
128.10
128.05
121.85
114.53
72.98
66.64
44.90
43.56
20.65
f1 (ppm)
7.33
7.31
7.31
7.29
7.28
7.26
7.01
7.00
6.98
6.88
6.86
5.10
5.08
5.05
4.56
4.52
4.51
4.48
4.21
4.19
4.18
4.17
4.15
2.92
2.91
2.89
2.88
2.81
2.80
2.77
2.76
1.26
1.24
O
NHCbz
PhO
Compound β-19c in CDCl3
7.18
0.95
1.91
2.86
1.96
0.99
1.00
0.98
3.23
f1 (ppm)

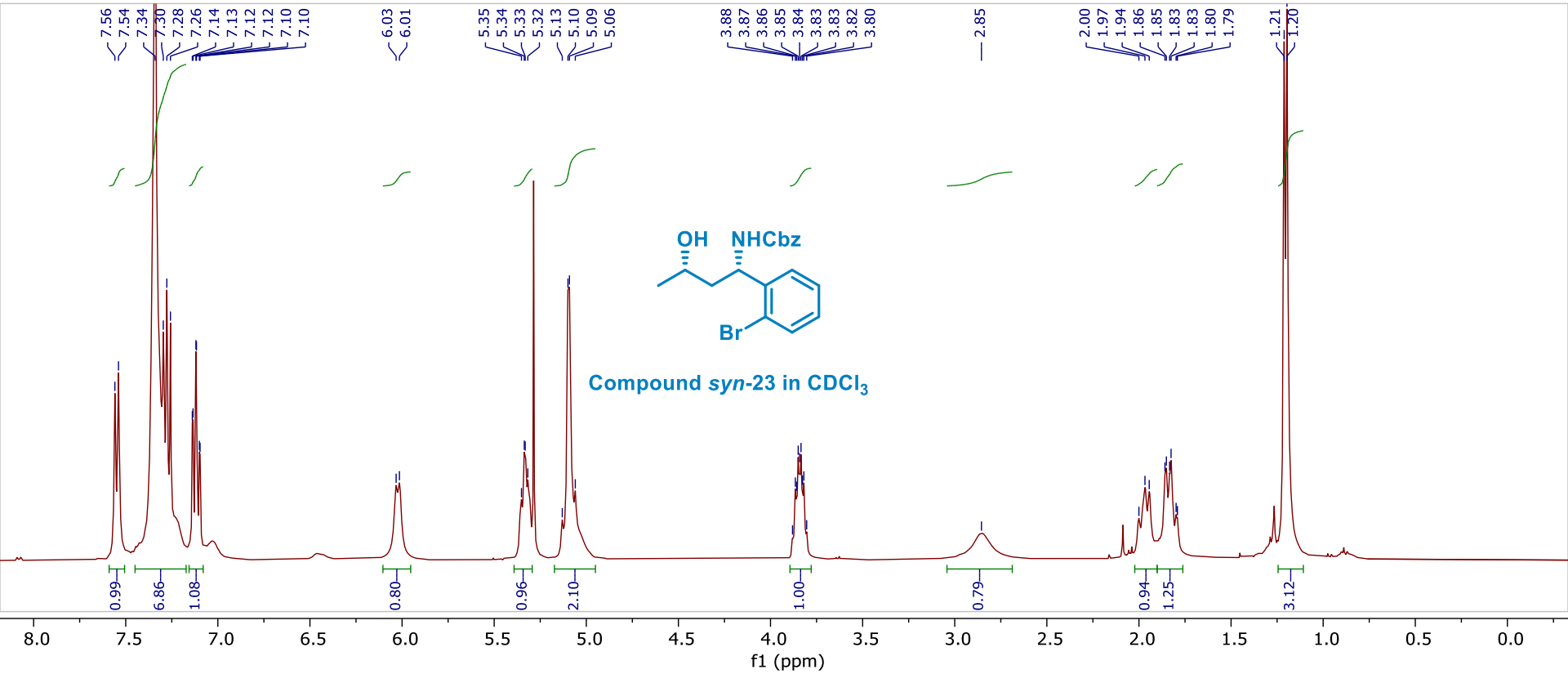

206.70
158.38
155.63
136.26
129.48
128.54
128.19
128.08
121.11
114.55
66.92
62.67
55.98
38.79
17.40
f1 (ppm)
7.36
7.35
7.33
7.32
7.31
7.30
7.29
7.27
7.26
7.25
6.97
6.95
6.93
6.88
6.86
5.52
5.11
5.08
4.47
4.45
4.44
4.29
4.27
4.25
4.24
3.03
3.01
2.99
2.98
2.96
2.95
2.93
2.90
1.42
1.40
NHCbz
PhO
O
Compound α-19c in CDCl3
7.35
1.08
2.18
0.89
2.20
1.00
2.21
2.23
3.28
f1 (ppm)

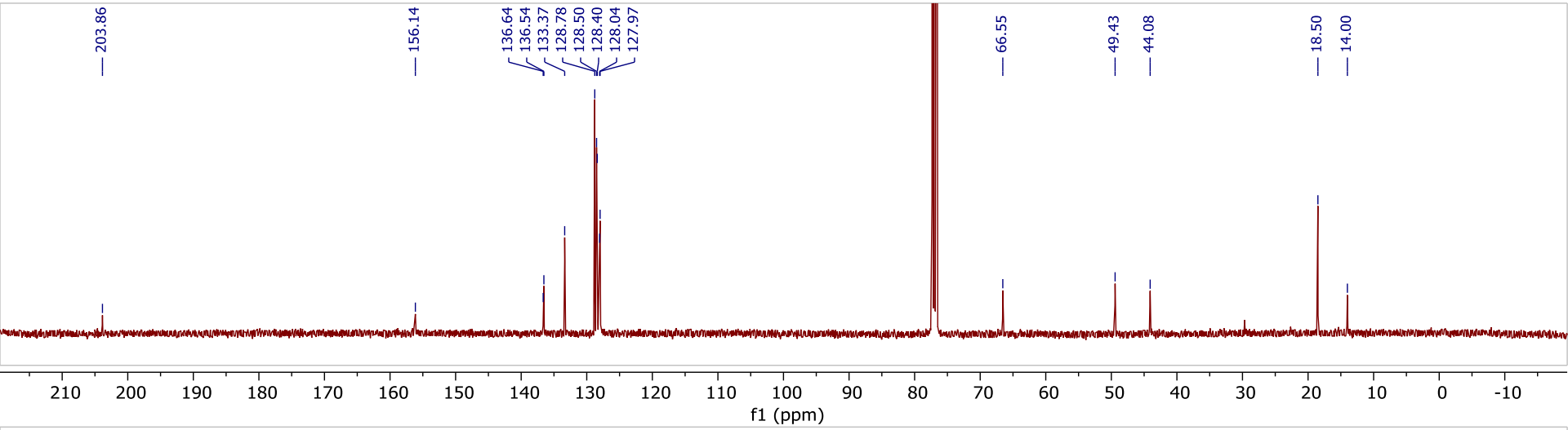

155.84
148.38
141.80
136.38
133.21
128.63
128.39
128.32
128.07
128.03
127.82
127.49
126.86
124.26
122.27
74.49
66.75
52.83
48.03
29.44
f1 (ppm)
7.51
7.49
7.46
7.44
7.33
7.32
7.31
7.29
7.26
7.24
7.23
7.21
7.19
7.09
7.09
7.07
7.05
7.05
5.90
5.34
5.33
5.02
4.99
4.95
4.92
2.61
2.19
2.17
2.15
2.11
1.71
HO
NHCbz
Ph
Br
Compound 21 in CDCl3
dr 1:1
3.07
10.63
1.10
0.81
1.00
2.05
0.78
2.08
3.11
f1 (ppm)

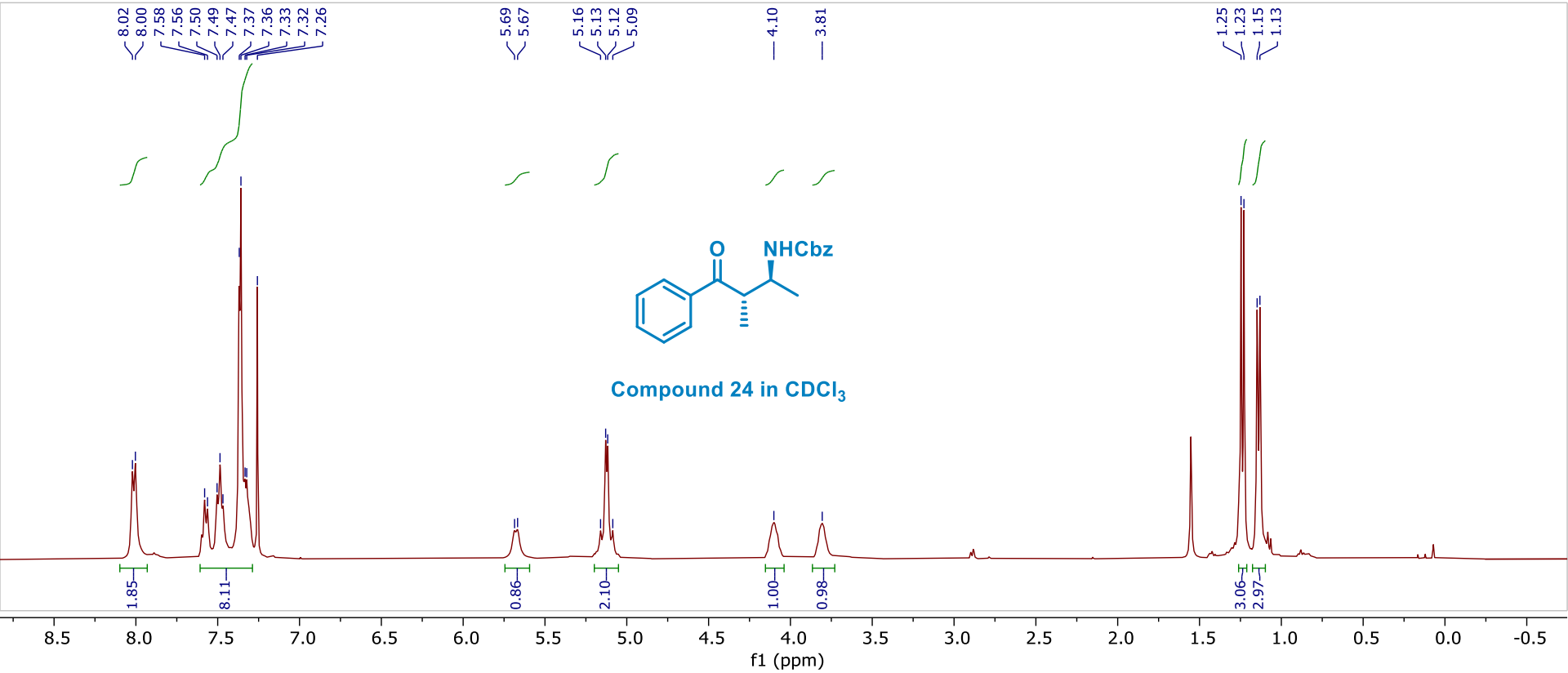

166.45
155.36
155.04
141.15
136.19
133.42
129.06
128.49
128.13
127.91
127.17
122.52
118.53
67.01
53.02
50.97
46.63
18.19
f1 (ppm)
7.56
7.54
7.32
7.29
7.29
7.28
7.26
7.15
7.14
7.13
7.12
7.11
5.71
5.32
5.19
5.06
3.69
2.75
2.72
2.39
2.24
NHCbz
MeO2C
Br
Compound 22 in CDCl3
1.08
7.00
1.17
1.00
1.08
0.90
2.02
3.05
1.02
0.93
3.26
f1 (ppm)

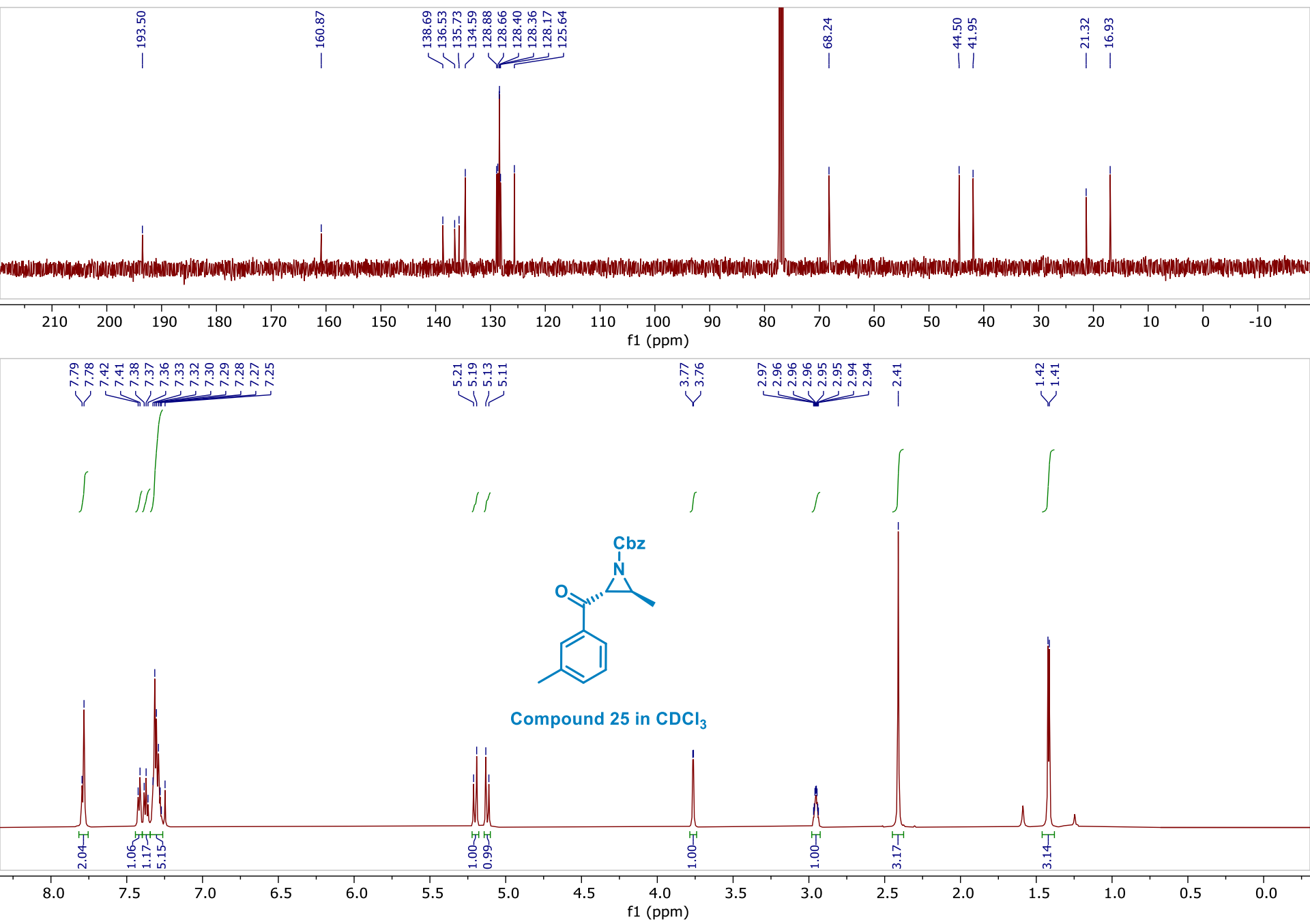

66.82
66.77
155.90
141.68
136.41
133.27
128.71
128.46
128.09
127.88
127.57
122.54
66.82
66.77
54.37
44.40
24.21
67.5
67.0
66.5
66.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
7.54
7.52
7.34
7.32
7.32
7.29
7.27
7.26
7.12
7.12
7.10
7.10
7.09
7.08
5.98
5.15
5.09
5.06
3.95
3.92
3.92
3.90
2.20
2.19
2.16
1.92
1.80
1.24
1.22
OH
NHCbz
Br
Compound anti-23 in CDCl3
1.05
6.56
1.13
0.98
3.03
1.00
0.87
2.20
3.25
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

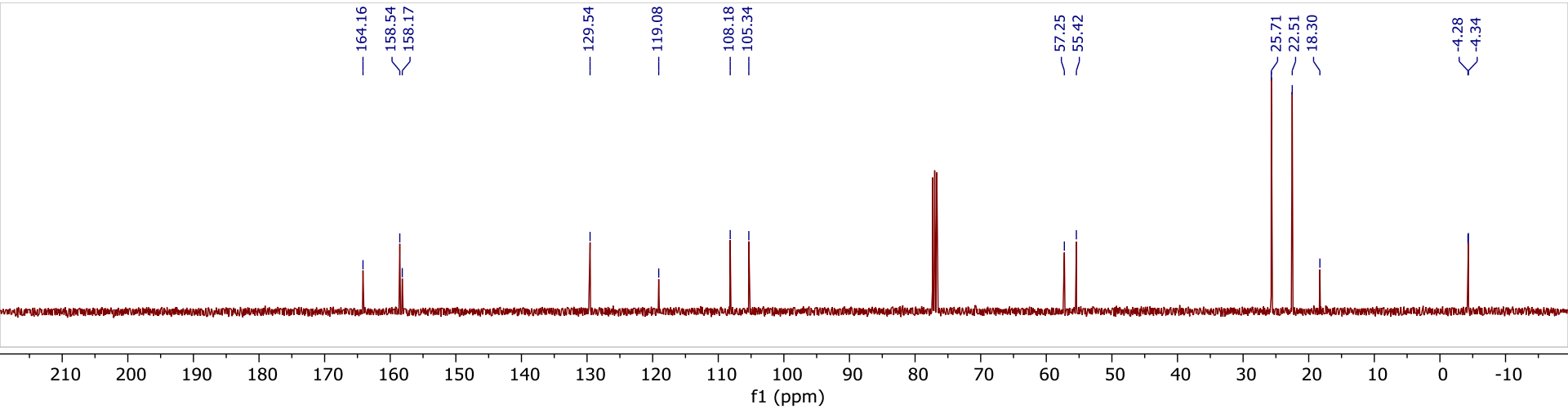

156.41
140.68
136.39
133.42
128.90
128.51
128.17
127.76
127.60
123.13
67.00
64.56
52.60
42.86
23.59
f1 (ppm)

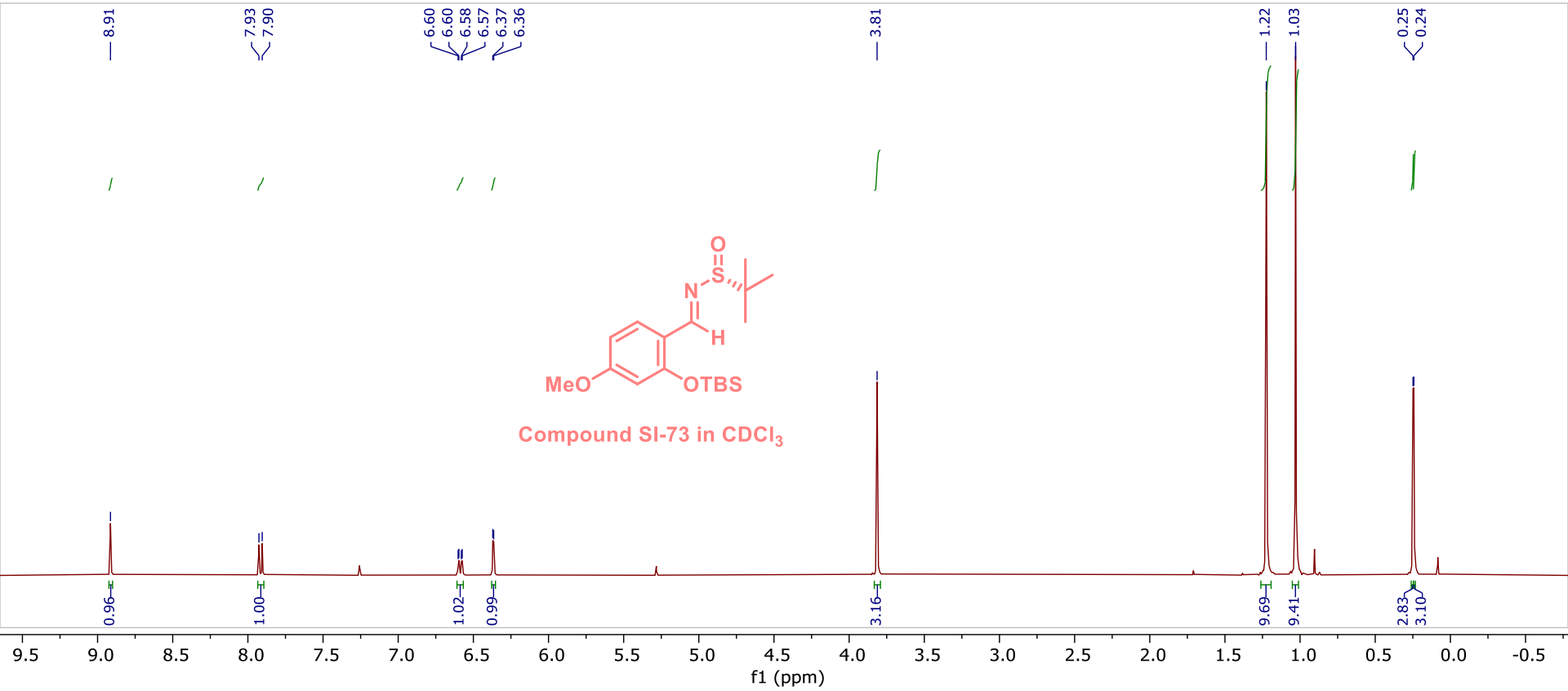

7.56
7.54
7.34
7.30
7.28
7.26
7.14
7.13
7.12
7.12
7.10
7.10
6.03
6.01
5.35
5.34
5.33
5.32
5.13
5.10
5.09
5.06
3.88
3.87
3.86
3.85
3.84
3.83
3.83
3.82
3.80
2.85
2.00
1.97
1.94
1.86
1.85
1.83
1.83
1.80
1.79
1.21
1.20
OH
NHCbz
Br
Compound syn-23 in CDCl3
0.99
6.86
1.08
0.80
0.96
2.10
1.00
0.79
0.94
1.25
3.12
f1 (ppm)

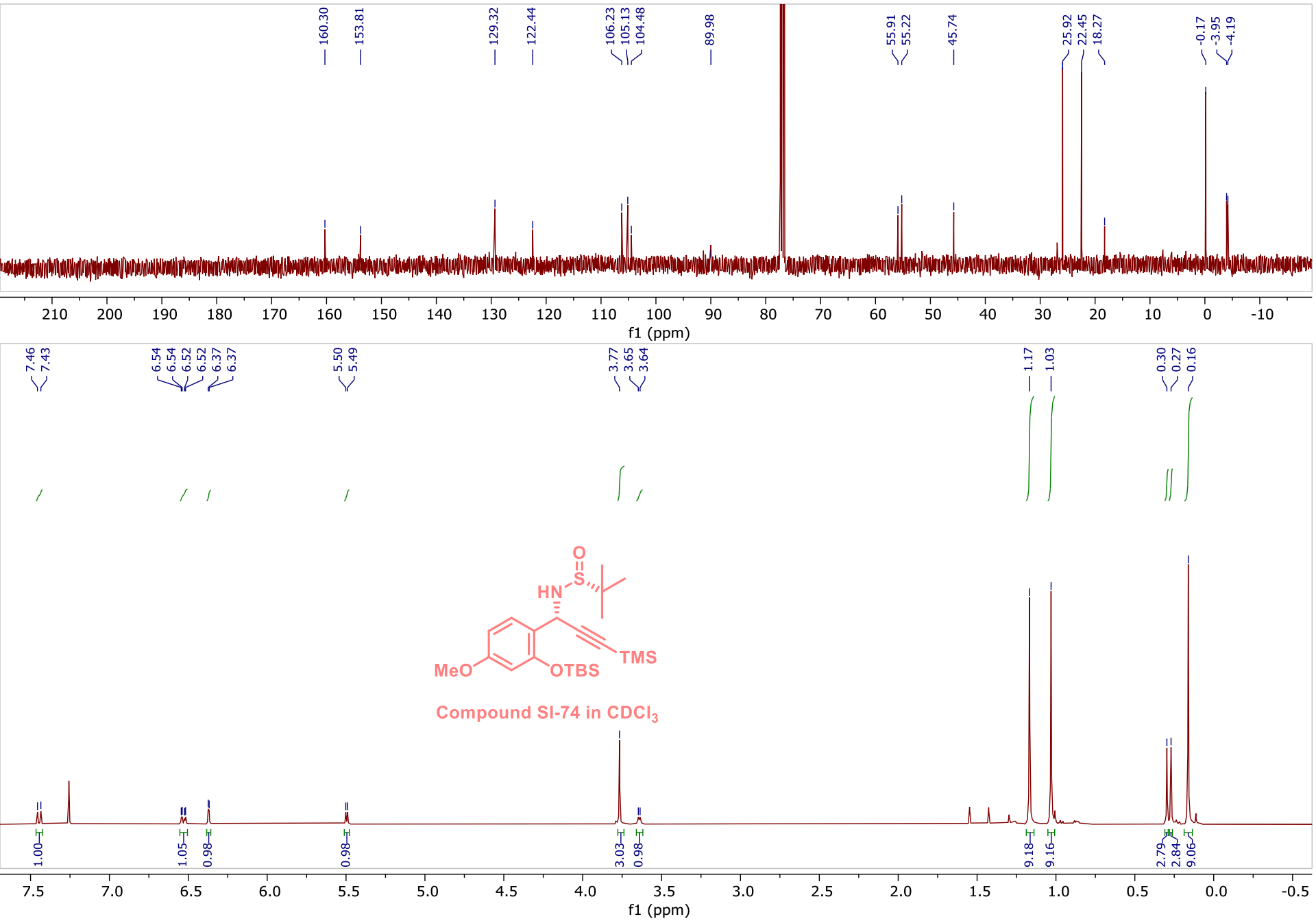

203.86
156.14
136.64
136.54
133.37
128.78
128.50
128.40
128.04
127.97
66.55
49.43
44.08
18.50
14.00
f1 (ppm)

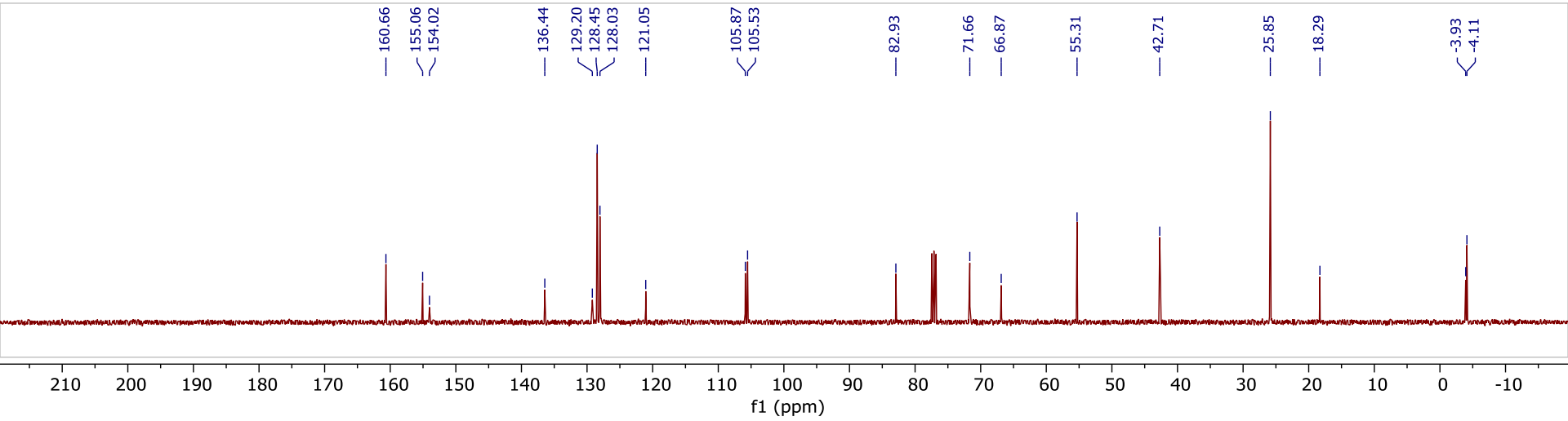

8.02
8.00
7.58
7.56
7.50
7.49
7.47
7.37
7.36
7.33
7.32
7.26
5.69
5.67
5.16
5.13
5.12
5.09
4.10
3.81
1.25
1.23
1.15
1.13
O
NHCbz
Compound 24 in CDCl3
1.85
8.11
0.86
2.10
1.00
0.98
3.06
2.97
f1 (ppm)

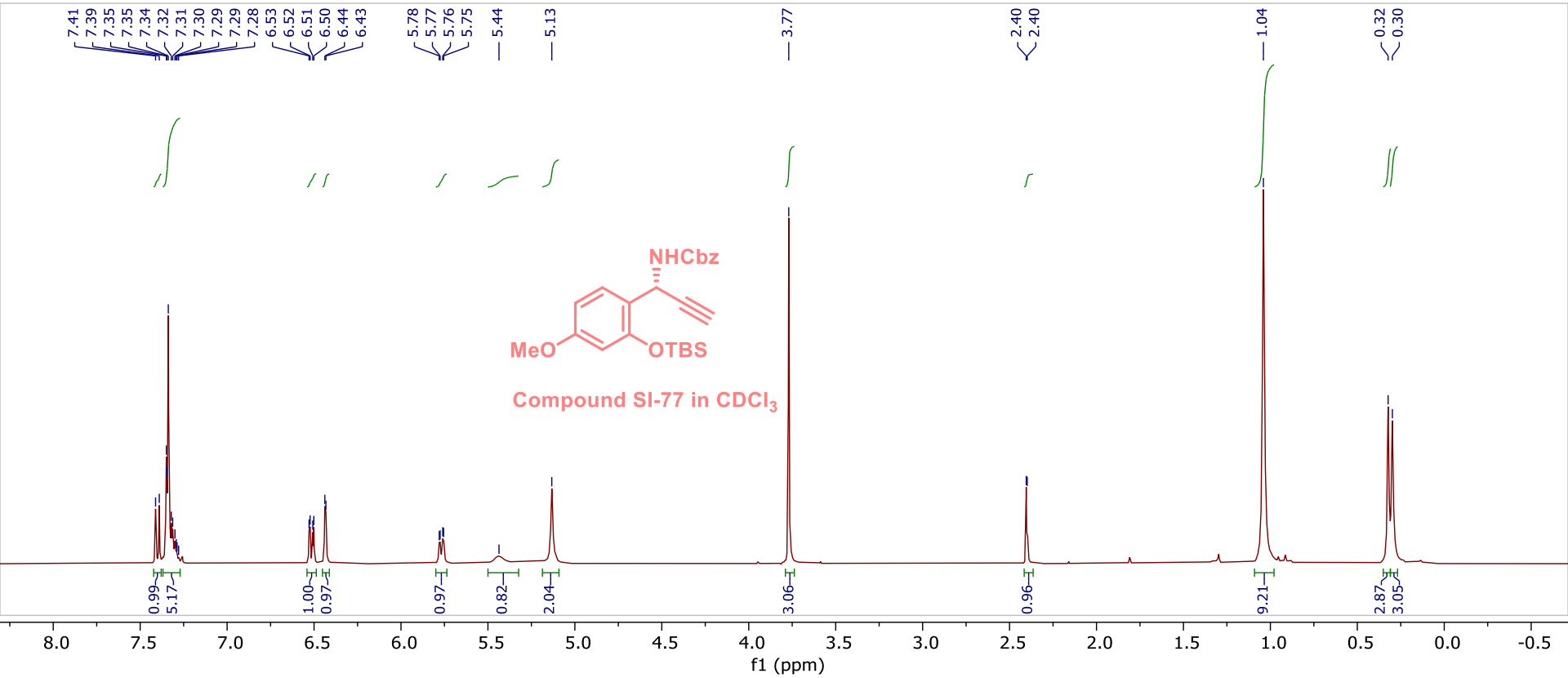

193.50
160.87
138.69
136.53
135.73
134.59
128.88
128.66
128.40
128.36
128.17
125.64
68.24
44.50
41.95
21.32
16.93
f1 (ppm)
7.79
7.78
7.42
7.41
7.38
7.37
7.36
7.33
7.32
7.30
7.29
7.28
7.27
7.25
5.21
5.19
5.13
5.11
3.77
3.76
2.97
2.96
2.96
2.96
2.95
2.95
2.94
2.94
2.41
1.42
1.41
Cbz
N
O
Compound 25 in CDCl3
2.04
1.06
1.17
5.15
1.00
0.99
1.00
1.00
3.17
3.14
f1 (ppm)

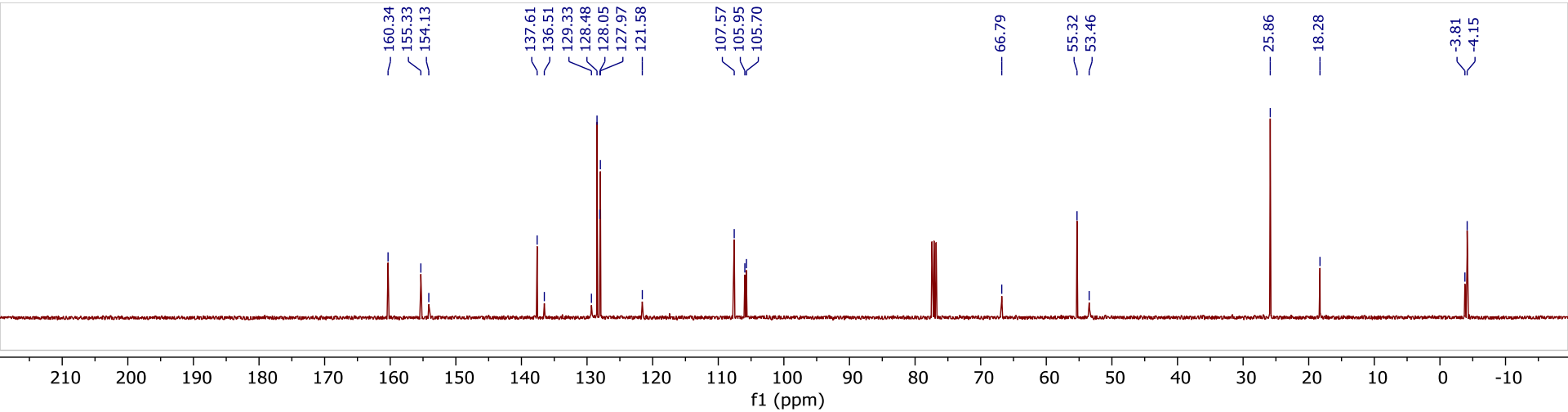

164.16
158.54
158.17
129.54
119.08
108.18
105.34
57.25
55.42
25.71
22.51
18.30
-4.28
-4.34
f1 (ppm)

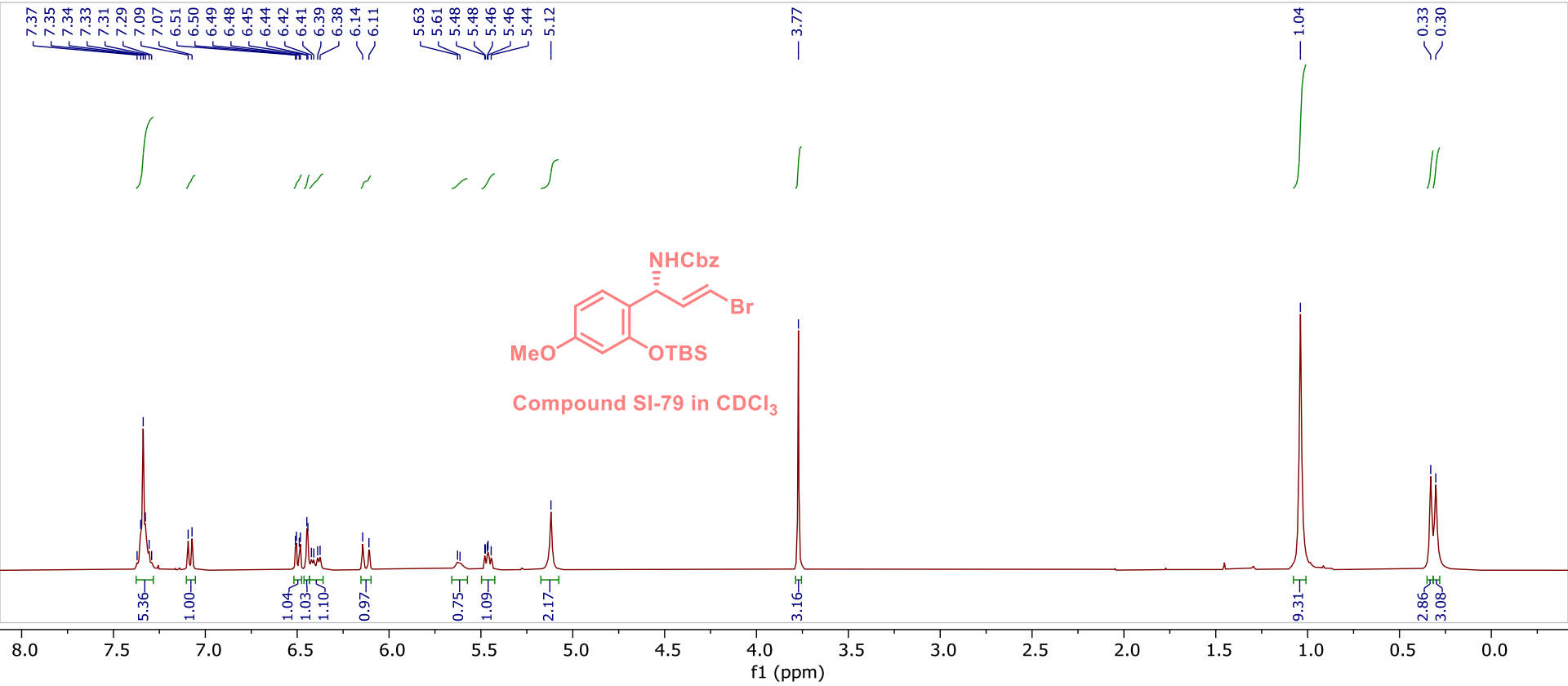

8.91
7.93
7.90
6.60
6.60
6.58
6.57
6.37
6.36
3.81
1.22
1.03
0.25
0.24
O
S
N
H
MeO
OTBS
Compound SI-73 in CDCl3
0.96
1.00
1.02
0.99
3.16
9.69
9.41
2.83
3.10
f1 (ppm)

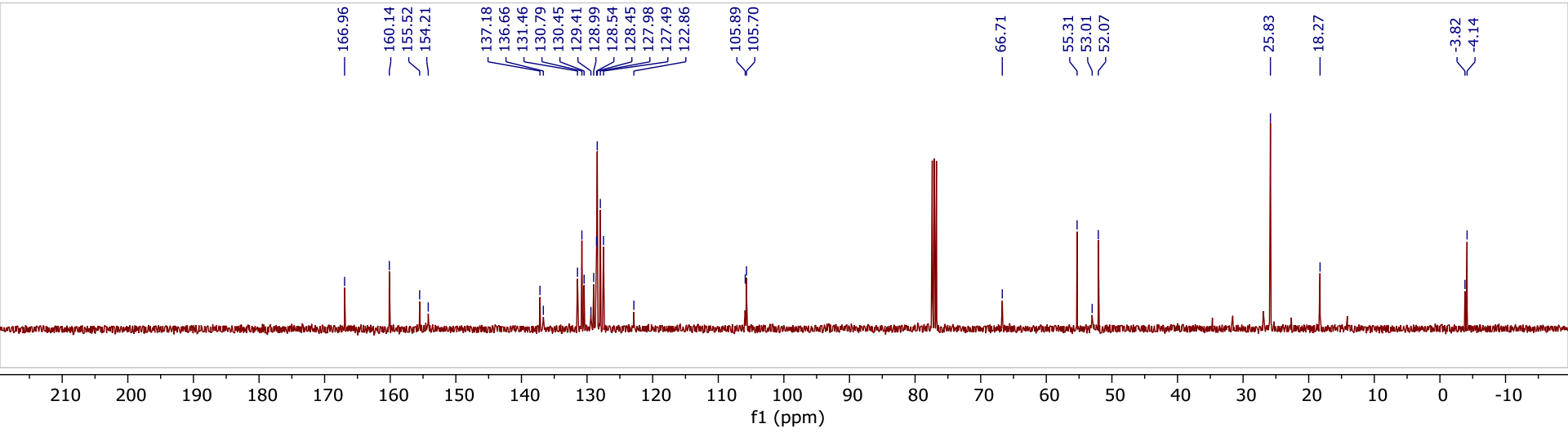

160.30
153.81
129.32
122.44
106.23
105.13
104.48
89.98
55.91
55.22
45.74
25.92
22.45
18.27
-0.17
-3.95
-4.19
f1 (ppm)
7.46
7.43
6.54
6.54
6.52
6.52
6.37
6.37
5.50
5.49
3.77
3.65
3.64
1.17
1.03
0.30
0.27
0.16
HN
O
S
MeO
OTBS
TMS
Compound SI-74 in CDCl3
1.00
1.05
0.98
0.98
3.03
0.98
9.18
9.16
2.79
2.84
9.06
f1 (ppm)

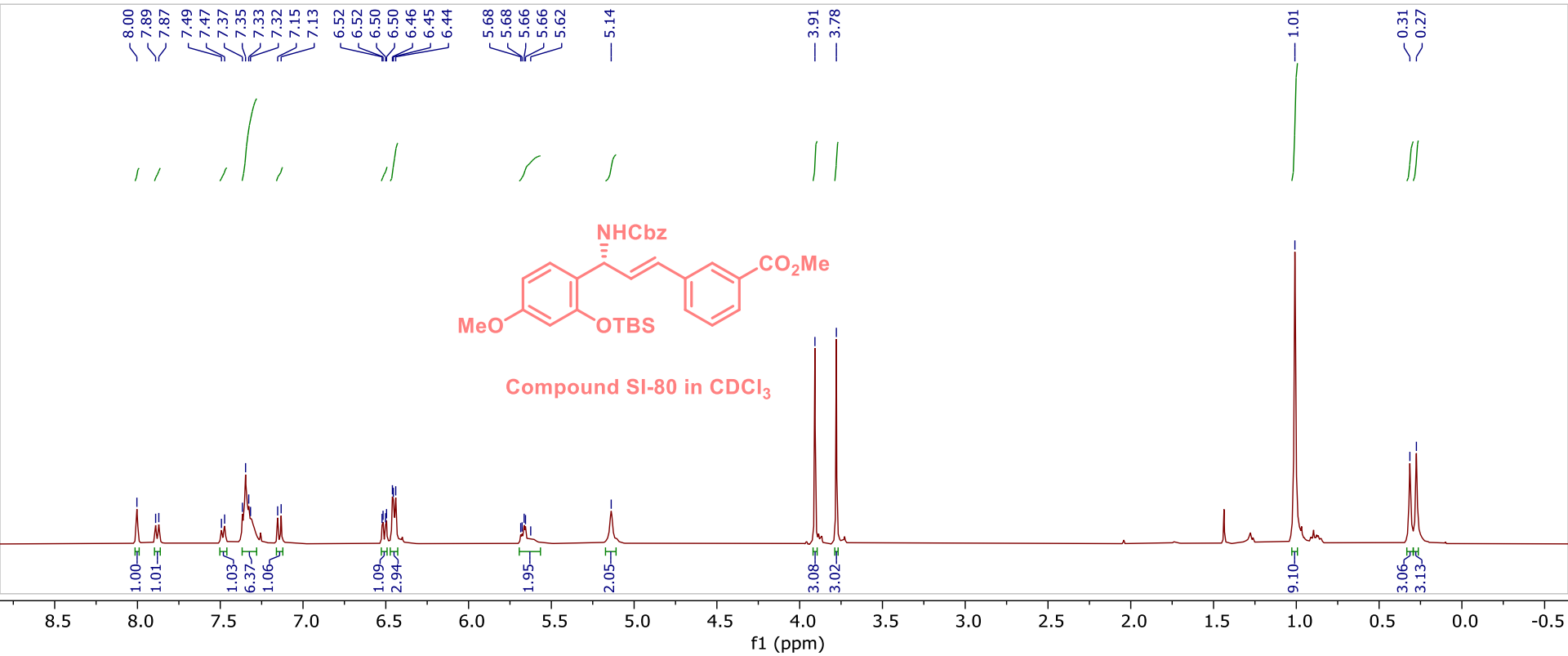

160.66
155.06
154.02
136.44
129.20
128.45
128.03
121.05
105.87
105.53
82.93
71.66
66.87
55.31
42.71
25.85
18.29
-3.93
-4.11
f1 (ppm)

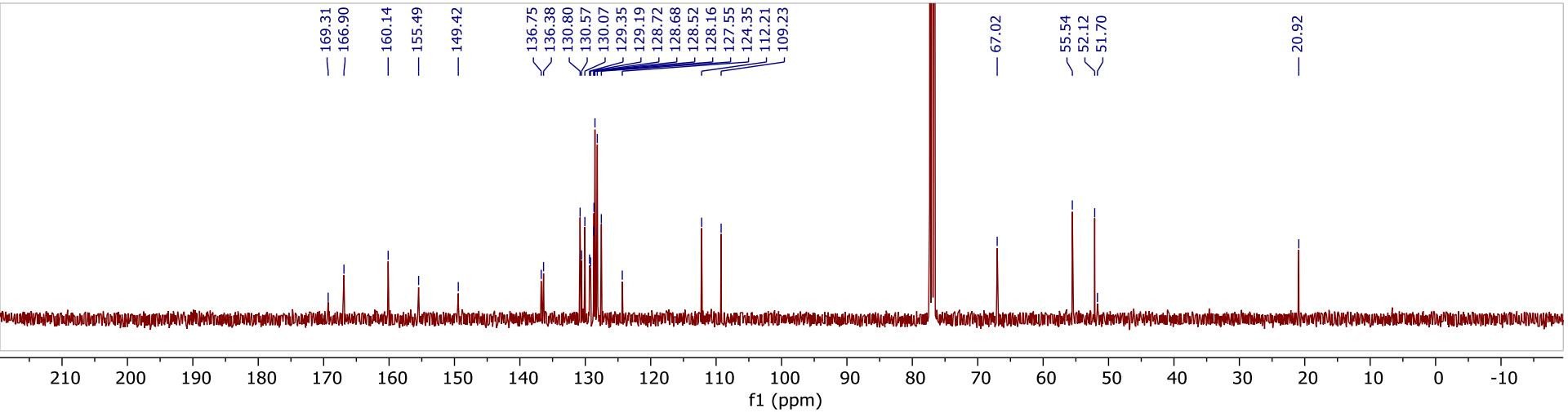

7.41
7.39
7.35
7.35
7.34
7.32
7.31
7.30
7.29
7.29
7.28
6.53
6.52
6.51
6.50
6.44
6.43
5.78
5.77
5.76
5.75
5.44
5.13
3.77
2.40
2.40
1.04
0.32
0.30
NHCbz
MeO
OTBS
Compound SI-77 in CDCl3
0.99
5.17
1.00
0.97
0.97
0.82
2.04
3.06
0.96
9.21
2.87
3.05
f1 (ppm)

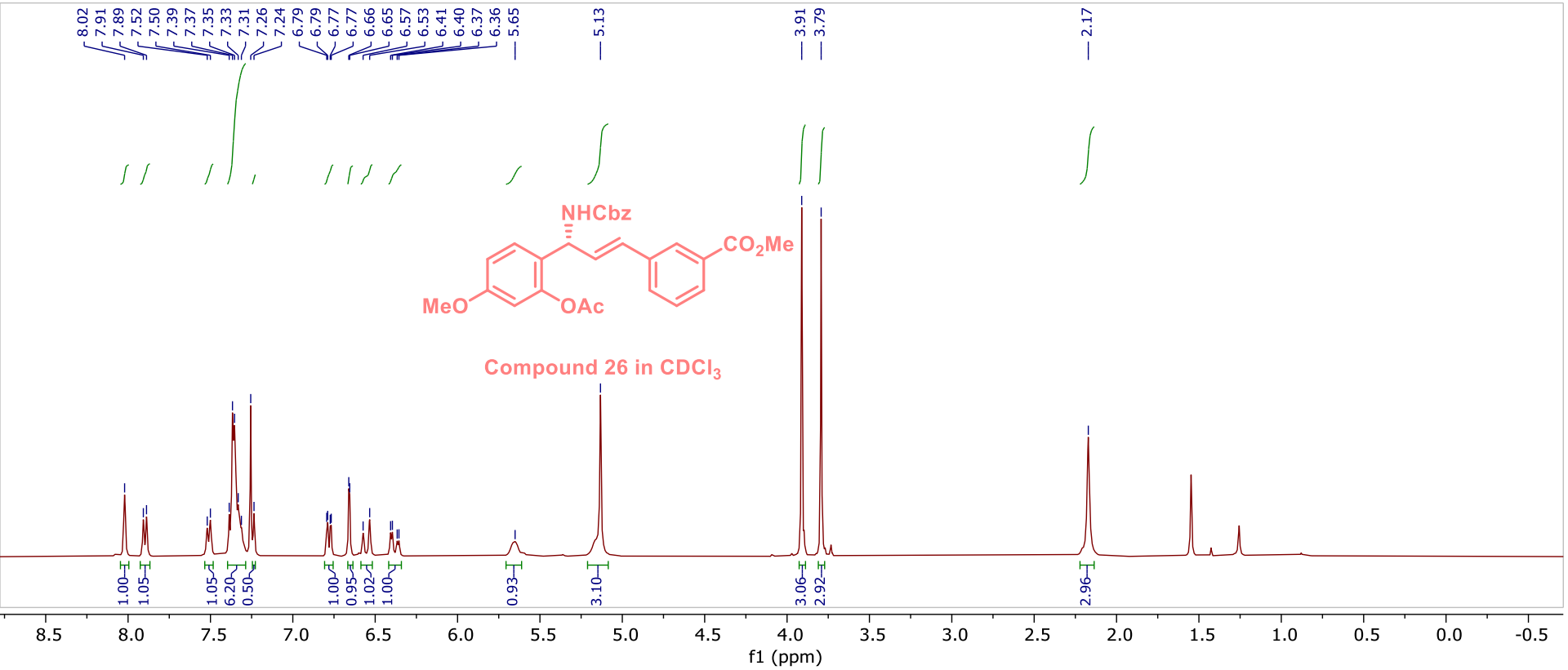

160.34
155.33
154.13
137.61
136.51
129.33
128.48
128.05
127.97
121.58
107.57
105.95
105.70
66.79
55.32
53.46
25.86
18.28
-3.81
-4.15
f1 (ppm)

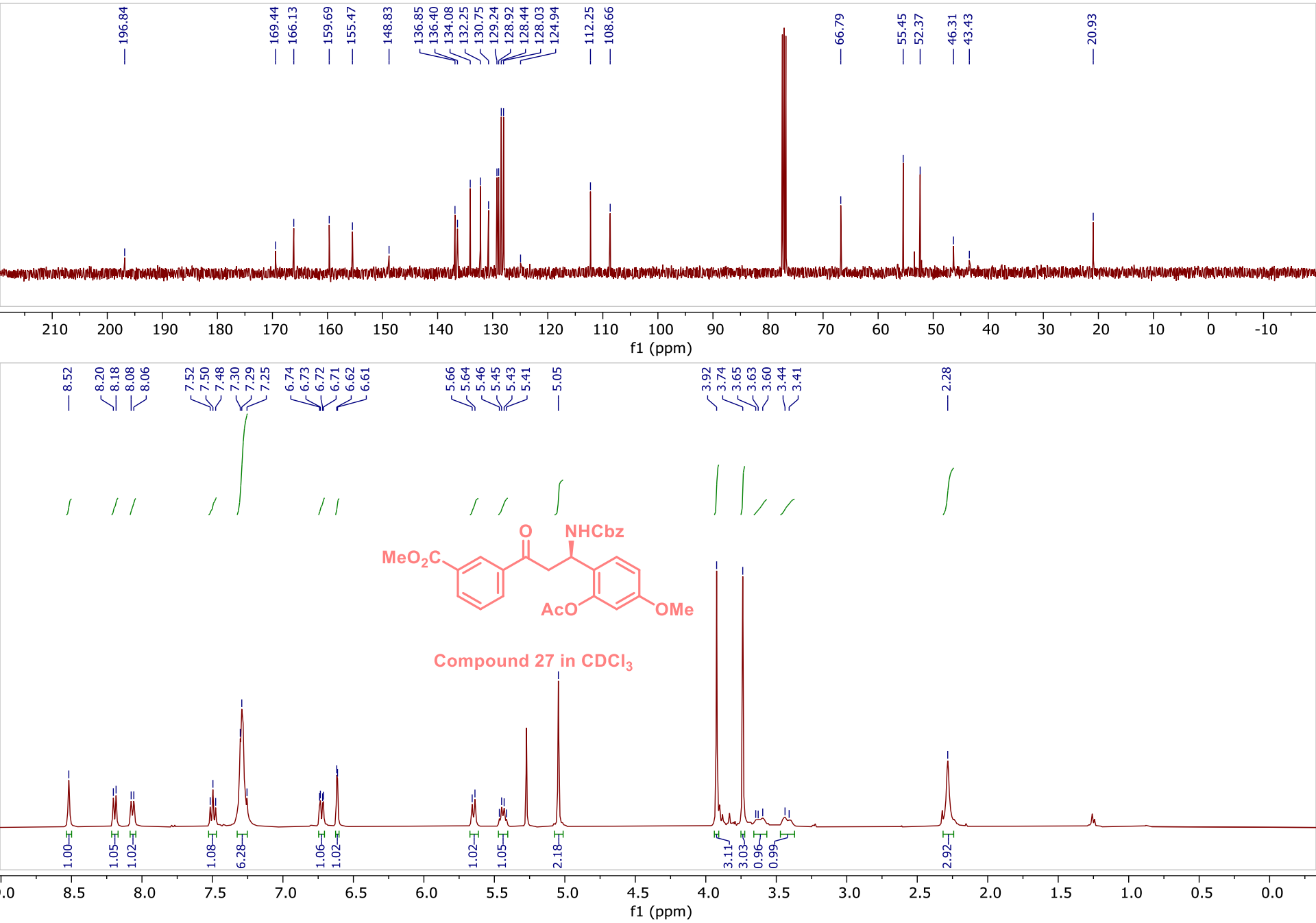

7.37
7.35
7.34
7.33
7.31
7.29
7.09
7.07
6.51
6.50
6.49
6.48
6.45
6.44
6.42
6.41
6.39
6.38
6.14
6.11
5.63
5.61
5.48
5.48
5.46
5.46
5.44
5.12
3.77
1.04
0.33
0.30
NHCbz
Br
MeO
OTBS
Compound SI-79 in CDCl3
5.36
1.00
1.04
1.03
1.10
0.97
0.75
1.09
2.17
3.16
9.31
2.86
3.08
f1 (ppm)

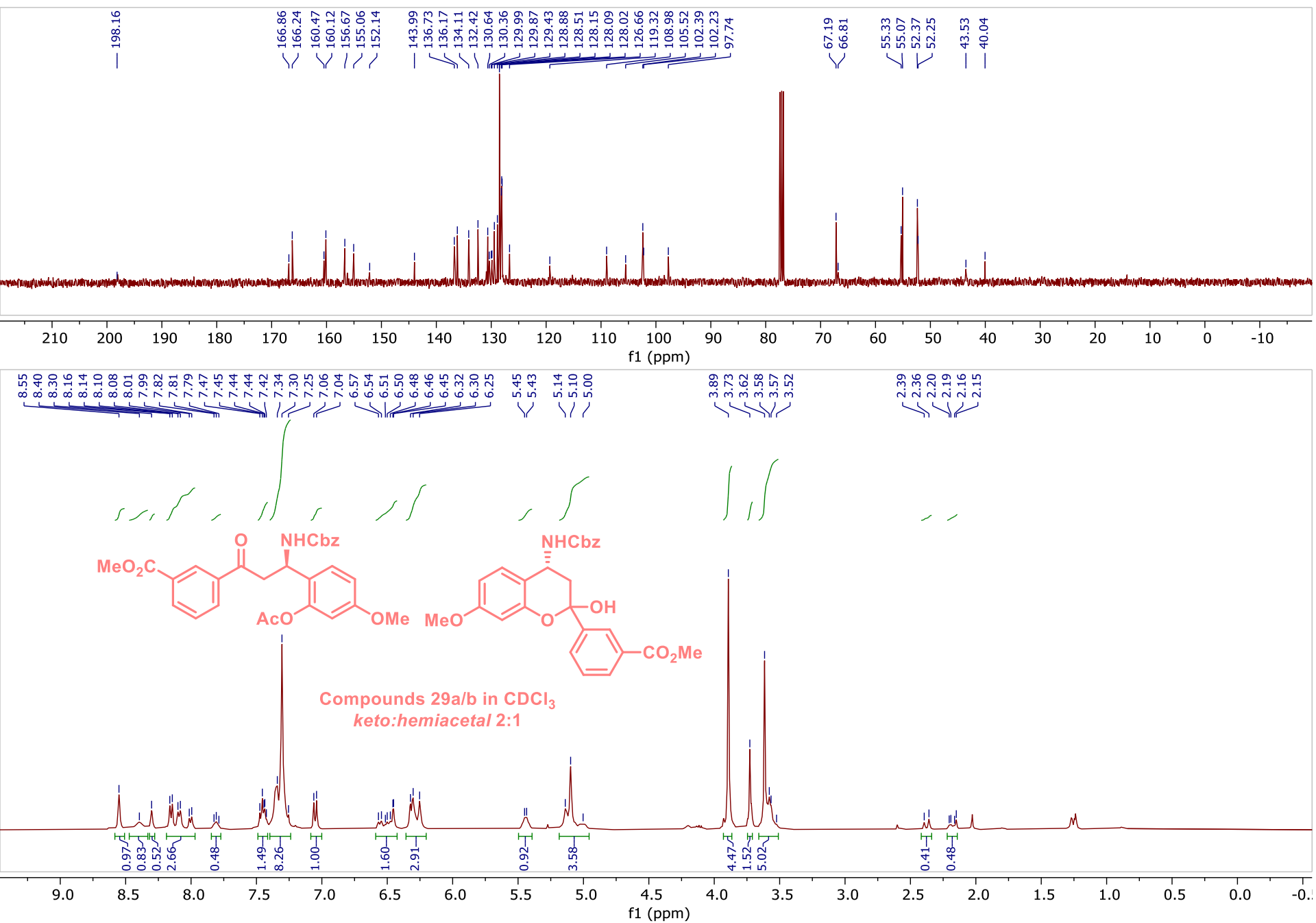

166.96
160.14
155.52
154.21
137.18
136.66
131.46
130.79
130.45
129.41
128.99
128.54
128.45
127.98
127.49
122.86
105.89
105.70
66.71
55.31
53.01
52.07
25.83
18.27
-3.82
-4.14
f1 (ppm)

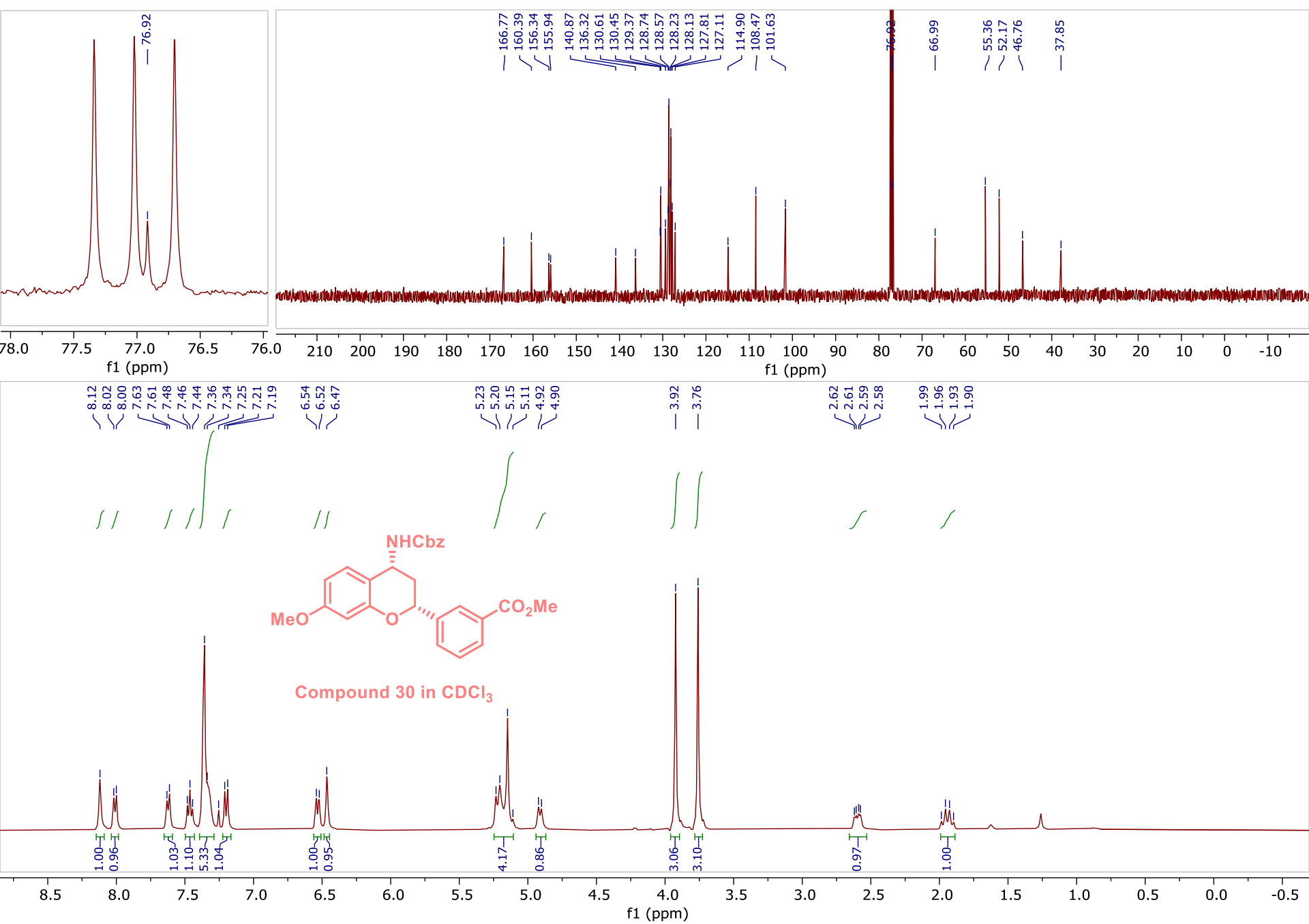

8.00
7.89
7.87
7.49
7.47
7.37
7.35
7.33
7.32
7.15
7.13
6.52
6.52
6.50
6.50
6.46
6.45
6.44
5.68
5.68
5.66
5.66
5.62
5.14
3.91
3.78
1.01
0.31
0.27
NHCbz
CO2Me
MeO
OTBS
Compound SI-80 in CDCl3
1.00
1.01
1.03
6.37
1.06
1.09
2.94
1.95
2.05
3.08
3.02
9.10
3.06
3.13
f1 (ppm)


169.31
166.90
160.14
155.49
149.42
136.75
136.38
130.80
130.57
130.07
129.35
129.19
128.72
128.68
128.52
128.16
127.55
124.35
112.21
109.23
67.02
55.54
52.12
51.70
20.92
f1 (ppm)


8.02
7.91
7.89
7.52
7.50
7.39
7.37
7.35
7.33
7.31
7.26
7.24
6.79
6.79
6.77
6.77
6.66
6.65
6.57
6.53
6.41
6.40
6.37
6.36
5.65
5.13
3.91
3.79
2.17
NHCbz
CO2Me
MeO
OAc
Compound 26 in CDCl3
1.00
1.05
1.05
6.20
0.50
1.00
0.95
1.02
1.00
0.93
3.10
3.06
2.92
2.96
f1 (ppm)


196.84
169.44
166.13
159.69
155.47
148.83
136.85
136.40
134.08
132.25
130.75
129.24
128.92
128.44
128.03
124.94
112.25
108.66
66.79
55.45
52.37
46.31
43.43
20.93
f1 (ppm)
8.52
8.20
8.18
8.08
8.06
7.52
7.50
7.48
7.30
7.29
7.25
6.74
6.73
6.72
6.71
6.62
6.61
5.66
5.64
5.46
5.45
5.43
5.41
5.05
3.92
3.74
3.65
3.63
3.60
3.44
3.41
2.28
O
NHCbz
MeO2C
AcO
OMe
Compound 27 in CDCl3
1.00
1.05
1.02
1.08
6.28
1.06
1.02
1.02
1.05
2.18
3.11
3.03
0.96
0.99
2.92
f1 (ppm)


198.16
166.86
166.24
160.47
160.12
156.67
155.06
152.14
143.99
136.73
136.17
134.11
132.42
130.64
130.36
129.99
129.87
129.43
128.88
128.51
128.15
128.09
128.02
126.66
119.32
108.98
105.52
102.39
102.23
97.74
67.19
66.81
55.33
55.07
52.37
52.25
43.53
40.04
f1 (ppm)
8.55
8.40
8.30
8.16
8.14
8.10
8.08
8.01
7.99
7.82
7.81
7.79
7.47
7.45
7.44
7.44
7.42
7.34
7.30
7.25
7.06
7.04
6.57
6.54
6.51
6.50
6.48
6.46
6.45
6.32
6.30
6.25
5.45
5.43
5.14
5.10
5.00
3.89
3.73
3.62
3.58
3.57
3.52
2.39
2.36
2.20
2.19
2.16
2.15
MeO2C
O
NHCbz
AcO
OMe
NHCbz
MeO
OH
O
CO2Me
Compounds 29a/b in CDCl3
keto:hemiacetal 2:1
0.97
0.83
0.52
2.66
0.48
1.49
8.26
1.00
1.60
2.91
0.92
3.58
4.47
1.52
5.02
0.41
0.48
f1 (ppm)


76.92
166.77
160.39
156.34
155.94
140.87
136.32
130.61
130.45
129.37
128.74
128.57
128.23
128.13
127.81
127.11
114.90
108.47
101.63
76.92
66.99
55.36
52.17
46.76
37.85
f1 (ppm)
8.12
8.02
8.00
7.63
7.61
7.48
7.46
7.44
7.36
7.34
7.25
7.21
7.19
6.54
6.52
6.47
5.23
5.20
5.15
5.11
4.92
4.90
3.92
3.76
2.62
2.61
2.59
2.58
1.99
1.96
1.93
1.90
NHCbz
MeO
O
CO2Me
Compound 30 in CDCl3
1.00
0.96
1.03
1.10
5.33
1.04
1.00
0.95
4.17
0.86
3.06
3.10
0.97
1.00
f1 (ppm)