Supporting Information For

Design of Modified Amine Transfer Reagents Allows the Synthesis of α-Chiral Secondary Amines via CuH-Catalyzed Hydroamination

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General Information

Flash column chromatography was performed using Silicycle SiliaFlash P60 (230–400 mesh) silica gel. Anhydrous tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purified by passing through two packed columns of neutral alumina and copper (II) oxide under a positive pressure of argon. $Cu(OAc)_2$ was purchased from Sigma Aldrich Chemical Co. and used as received. DTBM-SEGPHOS was purchased from Takasago International Co. or Strem and used as received. Styrenes were purchased from Alfa Aesar, Sigma Aldrich, Combi-Blocks or prepared according to known literature procedures. 4-(Dimethylamino)benzoic acid was purchased from Sigma Aldrich and used as received. $HSiMe(OEt)_2$ (moisture-sensitive) was purchased from TCI and was stored in a nitrogen-filled glovebox at −20 °C. *m*-CPBA (<= 77%) was purchased from Sigma Aldrich and used as received. GC yields were determined by using dodecane as an internal standard. All reported yields of the copper-catalyzed hydroamination reactions stated are isolated yields and the average of at least two experiments unless otherwise stated. The screw-top reaction tubes, caps and septa used in the copper-catalyzed hydroamination reactions are shown as below:

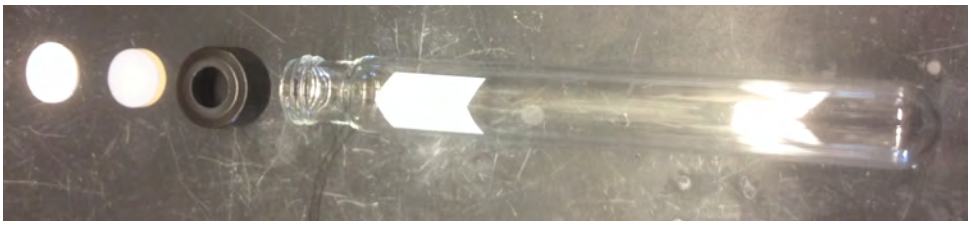
Small tubes:

Fisher 13 x 100 mm tubes (Cat. No. 1495925A)

Caps: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No. 03378316)

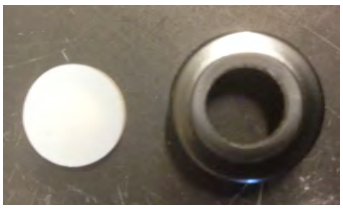
Medium tubes:

Fisher16 x 125 mm tubes (Cat. No. 1495925C)



Caps: Closure OT S/T 15-425TH 14 (Cat. No. 033407E)

Gray septa: Thermo Scientific SPTA PTFE/SIL F/15-425 10 (Cat. No. 03394A)



Large tubes:

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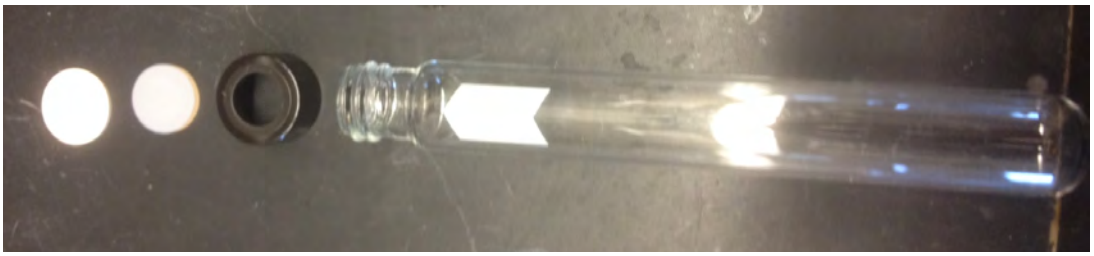


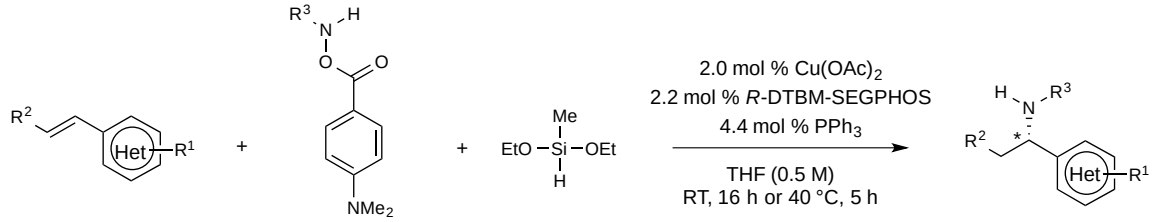
Caps: CLOSURE OT S/T 18-400TH 14 (Cat. No. 033407G)

Gray septa: Thermo Scientific SPTA SPTA PTFE/SIL F/18-400 10 (Cat. No. 03394B)

General Analytical Information

All new compounds were characterized by NMR spectroscopy, IR spectroscopy, elemental analysis (or high-resolution mass spectroscopy), and melting point (if solids). NMR spectra were recorded on a Bruker AMX 400 spectrometer or Varian Inova-500 NMR spectrometer and were calibrated using residual deuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR; CD_3OD: 3.31 ppm for ^1H NMR and 49.20 ppm for ^{13}C NMR). All IR spectra were taken on a Thermo Scientific Nicolet iS5 spectrometer (iD5 ATR, diamond). Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. HRMS spectra were recorded on a Bruker Daltonics APEXIV 4.7 Tesla Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS). Melting points (M.p.) were obtained on a Mel-Temp capillary melting point apparatus. GC analyses were performed on an Agilent 6890 gas chromatograph with an FID detector using a J & W DB-1 column (10 m, 0.1 mm I.D.). The enantiomeric excesses (ee) of the products were determined by high-performance liquid chromatography (HPLC) analysis performed on Agilent 1200 Series chromatographs using a chiral column (25 cm) as noted for each compound unless noted otherwise. Optical rotations were measured on a Jasco P-1010 polarimeter with $[\alpha]_D$ values reported in degrees; concentration (c) is in g/100 mL.

Synthesis of Chiral Secondary Amines via Copper-Catalyzed Direct



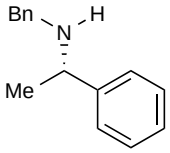
styrene 1 **electrophilic amine 2** **hydrosilane 3** **secondary amine 4**

General Procedure I

For hydroamination reactions a stock solution of LCuH was prepared for immediate use in multiple reactions. The stock solution was prepared in a nitrogen-filled glovebox, using an oven-dried, screw-cap reaction tube (20 mm x 150 mm) equipped with a magnetic stir bar. The reaction tube was charged with $Cu(OAc)_2$ (18 mg, 0.1 mmol), PPh_3 (58 mg, 0.22 mmol) and *R*-DTBM-SEGPHOS (130 mg, 0.22 mmol). Anhydrous THF (8.4 mL) was added, and the reaction tube was closed with a PTFE screw cap equipped with a septum. The reaction mixture was vigorously stirred at room temperature for 10 min until it was homogeneous. Then $HSiMe(OEt)_2$ (1.6 mL, 10.0 mmol) was added via syringe. The resulting reaction mixture was stirred at room temperature for 15 min and the color of the solution changed from blue to orange. For 1 mmol of alkene substrate, 2 mL of this LCuH stock solution was used.

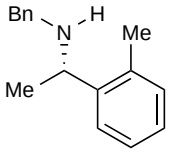
A second oven-dried, screw-cap reaction tube (13 mm x 100 mm) was charged with an amine electrophile (1.2 mmol, 1.2 equiv), loosely capped with a PTFE screw cap equipped with a septum, and taken into the glovebox. The alkene (1.0 mmol, 1.0 equiv) was added, and then 2 mL of the 'LCuH' stock solution was added via syringe. The reaction tube was tightly closed and removed from the glovebox and stirred (at rt or 40 °C) for 5-16 h as indicated for each substrate. After the reaction was complete, the reaction mixture was allowed to cool to room temperature and then diluted with Et_2O (50 mL) and extracted with 6 M HCl (aq) (15-20 mL x 3). The combined aqueous layers were washed with hexanes (2 x 50 mL) and then carefully basified to ca. pH 11 by slow addition of saturated aqueous K_2CO_3 [CAUTION: GAS EVOLUTION!]. The aqueous layer was extracted with CH_2Cl_2 (45 mL x 3) and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield the secondary amine product.

Products in Figure 3d



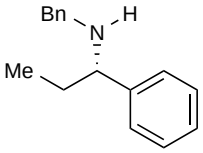
11a

***(S)*-*N*-Benzyl-1-phenylethan-1-amine (11a)**[1] was prepared following **General Procedure I** from styrene (104 mg, 1.0 mmol, 1.0 equiv) and *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (324 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h. The product was isolated as a beige oil (1st run: 194 mg, 92%; 2nd run: 198 mg, 94%). **IR (thin film, cm^{-1})** 3024, 1492, 1451, 1270, 1116, 1027, 760, 695; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.40 - 7.23 (m, 10H), 3.83 (q, *J* = 6.6 Hz, 1H), 3.68 (d, *J* = 13.2 Hz, 1H), 3.61 (d, *J* = 13.2 Hz, 1H), 1.68 (s, 1H), and 1.39 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 145.7, 140.8, 128.6, 128.5, 128.3, 127.1, 127.0, 126.9, 57.7, 51.8, and 24.7; **HPLC analysis** (OD, Hexanes:*i*PrOH:Et_2NH = 90:5:0.1, 0.7 mL/min) indicated 97% ee: t_R (major) = 7.30 min, t_R (minor) = 6.83 min; **$[\alpha]_D^{23}$** = –45.1 (c = 1.0, $CHCl_3$).



11b

(*S*)-*N*-benzyl-1-(o-tolyl)ethan-1-amine (11b)[2] was prepared following **General Procedure I** from 1-methyl-2-vinylbenzene (118 mg, 1.0 mmol, 1.0 equiv) and *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (324 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h. The product was isolated as a beige oil (1st run: 189 mg, 84%; 2nd run: 190 mg, 84%). **IR (thin film, cm^{-1})** 3024, 2962, 2922, 1603, 1487, 1452, 1114, 1028, 758, 726, and 696; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.57 (d, *J* = 7.7 Hz, 1H), 7.37-7.23 (m, 6H), 7.20-7.15 (m, 2H), 4.11 (q, *J* = 6.6 Hz, 1H), 3.71 (d, *J* = 13.1 Hz, 1H), 3.63 (d, *J* = 13.1 Hz, 1H), 2.30 (s, 3H), 1.62 (br s, 1H), and 1.35 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 143.5, 140.8, 135.5, 130.5, 128.5, 128.3, 127.0, 126.54, 126.53, 125.4, 52.8, 51.8, 23.4, and 19.2; **Anal. Calcd. for $C_{16}H_{19}N$**: C, 85.28; H, 8.50. Found: C, 85.28; H, 8.47; **HPLC analysis** (OD, Hexanes:*i*PrOH:Et_2NH = 90:5:0.1, 0.7 mL/min) indicated 94% ee: t_R (major) = 7.0 min, t_R (minor) = 6.4 min; **$[\alpha]_D^{23}$** = –43.2 (c = 1.0, $CHCl_3$).

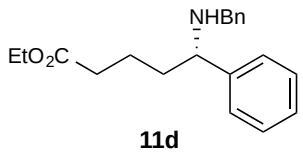


11c

(*S*)-*N*-benzyl-1-phenylpropan-1-amine (11c)[3] was prepared using the following procedure: In a nitrogen-filled glovebox, an oven-dried, screw-cap reaction tube (16 mm x 125 mm, labeled as Tube A) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (3.6 mg, 0.02 mmol, 2 mol%),

PPh_3 (11 mg, 0.044 mmol, 4.4 mol%) and *R*-DTBM-SEGPHOS (26 mg, 0.022 mmol, 2.2 mol %). After addition of THF (0.8 mL), the reaction tube was closed with a PTFE screw cap equipped with a septum and vigorously stirred at room temperature for 10 min until it was homogeneous. $HSiMe(OEt)_2$ (0.32 mL, 2.0 mmol, 2.0 equiv) was added via syringe and the resulting reaction mixture was stirred at room temperature for 15 min and the color of solution changed from blue to orange. Then (*E*)-prop-1-en-1-ylbenzene (118 mg, 1.0 mmol, 1.0 equiv) was added via syringe.

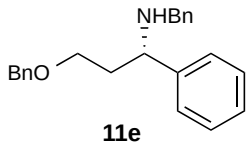
A second oven-dried, screw-cap reaction tube (13 mm x 100 mm, labeled as Tube B) equipped with a magnetic stir bar was charged with *O*-(4-dimethylaminobenzoyl)-N-benzylhydroxylamine (324 mg, 1.2 mmol, 1.2 equiv), loosely capped with a PTFE screw cap equipped with a septum and taken into the glovebox. $HSiMe(OEt)_2$ (0.16 mL, 1.0 mmol, 1.0 equiv) and THF (0.8 mL) were added and the reaction tube was tightly closed. Both reaction tubes were removed from the glovebox. The solution in tube B was loaded into a syringe (3 mL NORM-JECT® plastic syringe) and 0.2 mL was added to tube A. Tube A was then placed in an oil bath preheated to 40 °C, and the remaining contents in tube B were slowly added to tube A over 1.5 h via syringe pump. After the addition was complete, the resulting reaction mixture was stirred at 40 °C for an additional 3.5 h. The reaction mixture was allowed to cool to room temperature and then diluted with Et_2O (50 mL) and extracted with 6 M HCl (aq) (15–20 mL x 3). The combined aqueous layers were washed with hexanes (2 x 50 mL) and then carefully basified to ca. pH 11 by slow addition of saturated aqueous K_2CO_3 [CAUTION: GAS EVOLUTION]. The aqueous layer was extracted with CH_2Cl_2 (45 mL x 3) and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield the product **9c** as a beige oil (1st run: 202 mg, 90%; 2nd run: 197 mg, 88%). **IR (thin film, cm^{-1})** 3061, 3024, 2960, 1602, 1492, 1452, 1065, 1027 and 748; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.41-7.24 (m, 10H), 3.69 (d, *J* = 13.2 Hz, 1H), 3.58 (d, *J* = 13.1 Hz, 1H), 3.57 (dd, *J* = 7.7, 6.3 Hz, 1H), 1.85-1.63 (m, 2H), 1.62 (br s, 1H), and 0.85 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 144.2, 140.9, 128.46, 128.44, 128.3, 127.6, 127.1, 126.9, 64.4, 51.7, 31.3, and 10.9; **Anal. Calcd. For $C_{16}H_{19}N$**: C, 85.28; H, 8.50. Found: C, 85.08; H, 8.41. **HPLC analysis** (OD, Hexanes:*i*PrOH:Et_2NH = 90:5:0.1, 0.7 mL/min) indicated 96% ee: t_R (major) = 6.3 min, t_R (minor) = 6.0 min; **$[\alpha]_D^{23}$** = –53.0 (c = 1.0, $CHCl_3$).



11d

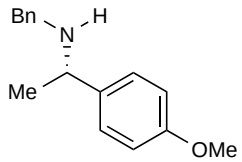
(*S*)-Ethyl (*S*)-5-(benzylamino)-5-phenylpentanoate (11d) was prepared following **General Procedure I** from ethyl (*E*)-5-phenylpent-4-enoate[4] (204 mg, 1.0 mmol, 1.0 equiv) and *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (324 mg, 1.2 mmol,

1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h. The product was isolated as a light yellow oil (1st run: 224 mg, 72%; 2nd run: 230 mg, 74%). **IR (thin film, cm^{-1})** 3024, 2932, 1732, 1600, 1493, 1452, 749, and 697; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.38-7.22 (m, 10H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.65 (d, *J* = 13.1 Hz, 1H), 3.63 (t, *J* = 6.9 Hz, 1H), 3.54 (d, *J* = 13.1 Hz, 1H), 2.25 (t, *J* = 6.8 Hz, 2H), 1.80-1.60 (m, 4H), 1.56-1.45 (m, 1H), and 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 173.6, 144.0, 140.8, 128.6, 128.5, 128.3, 127.4, 127.2, 127.0, 62.4, 60.3, 51.6, 37.8, 34.3, 21.9, and 14.4; **Anal. Calcd. for $C_{20}H_{25}NO_2$**: C, 77.14; H, 8.09. Found: C, 77.02; H, 7.96; **HPLC analysis** (OD, Hexanes:*i*PrOH:Et_2NH = 90:5:0.1, 0.7 mL/min) indicated 95% ee: t_R (major) = 9.7 min, t_R (minor) = 8.5 min; **$[\alpha]_D^{23}$** = -22.2 (c = 1.0, $CHCl_3$).



11e

(*S*)-N-benzyl-3-(benzyloxy)-1-phenylpropan-1-amine (11e) was prepared following **General Procedure I** from (*E*)-(3-(benzyloxy)prop-1-en-1-yl)benzene[5] (224 mg, 1.0 mmol, 1.0 equiv) and *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (324 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h. After the described extractive workup, the product was isolated as a colorless oil (1st run: 291 mg, 88%; 2nd run: 288 mg, 87%). **IR (thin film, cm^{-1})** 3025, 2858, 1493, 1452, 1359, 1098, 733, and 694; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.50-7.30 (m, 15H), 4.55 (d, *J* = 11.8 Hz, 1H), 4.52 (d, *J* = 11.9 Hz, 1H), 3.96 (t, *J* = 6.7 Hz, 1H), 3.74 (d, *J* = 13.1 Hz, 1H), 3.63 (d, *J* = 13.1 Hz, 1H), 3.64-3.58 (m, 1H), 3.53-3.47 (m, 1H), 2.25-2.15 (m, 1H), 2.09 (br s, 1H), and 2.03-1.95 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 144.0, 140.7, 138.5, 128.5, 128.4, 128.3, 128.2, 127.7, 127.6, 127.4, 127.1, 126.8, 73.1, 68.1, 60.4, 51.6, and 38.3; **HPLC analysis** (IA, Hexanes:*i*PrOH:Et_2NH = 90:5:0.1, 1.0 mL/min) indicated 96% ee: t_R (major) = 6.0 min, t_R (minor) = 4.9 min; **Anal. Calcd.** for $C_{23}H_{25}NO$: C, 83.34; H, 7.60. Found: C, 83.25; H, 7.73; **$[\alpha]_D^{23}$** = -16.3 (c = 1.0, $CHCl_3$).



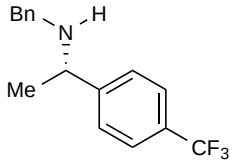
11f

(*S*)-*N*-Benzyl-1-(4-methoxyphenyl)ethan-1-amine (11f)[1] was prepared following the procedure described for **11c**, from 4-vinylanisole (134 mg, 1.0 mmol, 1.0 equiv), *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (324 mg, 1.2 mmol, 1.2 equiv). The product was isolated as a colorless oil (1st run: 212 mg, 88%; 2nd run: 198 mg, 82%). **IR (thin film, cm^{-1})** 3300, 3026, 2958, 2833, 1610, 1584, 1510, 1452, 1242, 1035, 830, and 697; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.34-7.22 (m, 7H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 3.78 (q, *J* = 6.6 Hz, 1H), 3.66

(d, *J* = 13.1 Hz, 1H), 3.59 (d, *J* = 13.2 Hz, 1H), 1.58 (br s, 1H), and 1.35 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 158.7, 140.8, 137.8, 128.5, 128.3, 127.9, 126.9, 113.9, 56.9, 55.4, 51.7, and 24.7; **HRMS (DART-TOF)** calculated for $C_{16}H_{20}NO$ $[M+H]^+$ m/z 242.1539, found 242.1539; **HPLC analysis** (OD, Hexanes:*i*PrOH:Et_2NH = 90:5:0.1, 0.7 mL/min) indicated 92% ee: t_R (major) = 5.7 min, t_R (minor) = 4.8 min; **$[\alpha]_D^{23}$** = –54.5 (c = 1.0, $CHCl_3$).

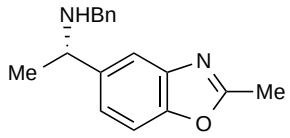
For 5 mmol scale reaction:

An oven-dried screw-top reaction tube (20 mm x 150 mm, labeled as Tube A) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (18 mg, 0.1 mmol, 2 mol%), PPh_3 (55 mg, 0.22 mmol, 4.4 mol%), and *R*-DTBM-SEGPHOS (*R*-**L**: 130 mg, 0.11 mmol, 2.2 mol%). The tube was closed with a PTFE screw cap equipped with a septum and then evacuated and backfilled with argon (this process was repeated a total of 3 times). Anhydrous THF (3.4 mL) was added and the resulting mixture was stirred vigorously at room temperature (for 10 min) until it was homogeneous. $HSiMe(OEt)_2$ (1.6 mL, 10.0 mmol, 2.0 equiv) was then added via a syringe. The resulting solution was stirred at room temperature (for ca. 10 min) until the color of the mixture changed from blue to orange. 4-Vinyl anisole (670 μL, 670 mg, 5 mmol) was added to the tube via a syringe. A second oven-dried screw-top reaction tube (20 mm x 150 mm, labeled as Tube B) was charged with *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (1.62 g, 6 mmol, 1.2 equiv). The tube was closed with a PTFE screw cap equipped with a septum and then evacuated and backfilled with argon (this process was repeated a total of 3 times). $HSiMe(OEt)_2$ (0.8 mL, 5.0 mmol, 1.0 equiv) and THF (4.2 mL) are added sequentially via syringes. The solution in tube B was loaded into a 10 mL NORM-JECT® plastic syringe and 1 mL was added to Tube A. Tube A was then placed in an oil bath preheated to 40 °C, and the remaining contents in tube B were slowly added to tube A over 1.5 h via a syringe pump. After addition, the resulting solution was stirred at 40 °C for an additional 3.5 hours. The reaction mixture was allowed to cool to room temperature and then diluted with Et_2O (200 mL). The organic phase was then extracted with 6 M aqueous HCl (30-40 mL x 3). The combined aqueous layers were washed with hexanes (50 mL x 2), and then carefully basified to ca. pH 11 by slow addition of saturated aqueous K_2CO_3. The aqueous layer was extracted with CH_2Cl_2 (40-50 mL x 3). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated *in vacuo* to give **11f** as a brown oil (1.05 g, .4.35 mmol, 87% yield).



11g

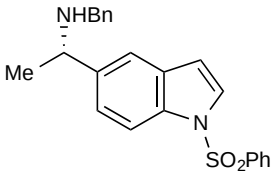
(*S*)-*N*-Benzyl-1-(4-trifluoromethylphenyl)ethan-1-amine (11g)[2] was prepared following **General Procedure I** from 1-trifluoromethyl-4-vinylbenzene (172 mg, 1.0 mmol, 1.0 equiv) and *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (324 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h. After the described extractive workup, the product was isolated as a pale yellow oil (1st run: 262 mg, 0.94 mmol, 94%; 2nd run: 246 mg, 88%). **IR (thin film, cm^{-1})** 3028, 2969, 1618, 1495, 1322, 1117, 1066, 1016, and 840; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.61 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.35-7.23 (m, 5H), 3.89 (q, *J* = 6.6 Hz, 1H), 3.65 (d, *J* = 13.2 Hz, 1H), 3.59 (d, *J* = 13.2 Hz, 1H), 1.62 (br s, 1H), and 1.37 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 149.9, 140.4, 129.35 (q, *J* = 32.2 Hz), 128.6, 128.2, 127.2, 127.1, 125.6 (q, *J* = 3.7 Hz), 123.1, 57.3, 51.8, and 24.7; **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -67.3; **Anal. Calcd. for $C_{16}H_{16}F_3N$**: C, 68.80; H, 5.77. Found: C, 68.64; H, 5.92; **HPLC analysis** (OD, Hexanes:*i*PrOH:Et_2NH = 90:5:0.1, 0.7 mL/min) indicated 92% ee: t_R (major) = 8.7 min, t_R (minor) = 7.2 min; **$[\alpha]_D^{23}$** = –42.8 (c = 1.0, $CHCl_3$).



11h

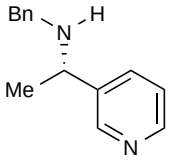
(*S*)-*N*-benzyl-1-(2-methylbenzo[d]oxazol-5-yl)ethan-1-amine (11h) was prepared following **General Procedure I** with a modified workup procedure from 2-methyl-5-vinylbenzo[*d*]oxazole[6] (159 mg, 1.0 mmol, 1.0 equiv) and *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (324 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h. The reaction mixture was diluted with 60 mL of Et_2O, to which 3 mL of 1M HCl in Et_2O and 15 mL of water was added and separated. Addition of HCl and H_2O was repeated for a total of three times. The combined aqueous layers were washed with hexanes (20 mL x 2), and then carefully basified to pH 11 by addition of sat. K_2CO_3 solution, and the resulting mixture was extracted with CH_2Cl_2 (25 mL x 3). The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated *in vacuo* to give the title product as a light brown oil (1st run: 199 mg, 74%; 2nd run: 195 mg, 73%). **IR (thin film, cm^{-1})** 3305, 3026, 2963, 1604, 1578, 1495, 1435, 1264, 1180, 1118, and 919; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.65 (s, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.35-7.21 (m, 6H), 3.92 (q, *J* = 6.5 Hz, 1H), 3.65 (d, *J* = 13.1 Hz, 1H), 3.58 (d, *J* = 13.1 Hz, 1H), 2.64 (s, 3H), 1.59 (br s, 1H), and 1.39 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 164.2, 150.2, 142.2, 141.9, 140.1, 128.5, 128.3, 127.0, 123.3, 117.6, 110.1, 57.6, 51.8, 25.2, and 14.7; **HRMS (DART-TOF)** calculated for $C_{17}H_{18}N_2O$ $[M+H]^+$ m/z 267.1492,

found 267.1496; **HPLC analysis** (IA, Hexanes:*i*PrOH:Et_2NH = 90:5:0.1, 0.6 mL/min) indicated 99% ee: t_R (major) = 13.9 min, t_R (minor) = 13.3 min; **$[\alpha]_D^{23}$** = –46.7 (c = 1.0, $CHCl_3$).



11i

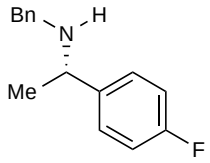
(*S*)-N-benzyl-1-(1-(phenylsulfonyl)-1H-indol-5-yl)ethan-1-amine (11i) was prepared following **General Procedure I** from 1-(phenylsulfonyl)-5-vinyl-1H-indole (283 mg, 1.0 mmol, 1.0 equiv) and *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (324 mg, 1.2 mmol, 1.2 equiv). After the reaction is complete, the reaction mixture was allowed to cool to room temperature and then diluted with ether (200 mL). Aqueous HCl (2 M, 50 mL) was added. The mixture was vigorously shaken and most of the product precipitated as the HCl salt. The solid was filtered and combined with the aqueous layer, which was then carefully basified to ca. pH 11 by slow addition of saturated aqueous K_2CO_3. The mixture was extracted with CH_2Cl_2 (20 mL x 3). The combined organic layer were washed with brine, dried (Na_2SO_4), filtered and concentrated *in vacuo* to yield product as a light yellow oil (1st run: 310 mg, 80%; 2nd run: 330 mg, 84%). **IR (thin film, cm^{-1})** 3061, 2962, 1447, 1368, 1173, 1126, 994, and 593; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.96 (d, *J* = 8.5 Hz, 1H), 7.90 (br d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 3.6 Hz, 1H), 7.52 (tt, *J* = 7.4, 1.2 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.35-7.20 (m, 6H), 6.64 (d, *J* = 3.6 Hz, 1H), 3.87 (q, *J* = 6.6 Hz, 1H), 3.62 (d, *J* = 13.2 Hz, 1H), 3.57 (d, *J* = 13.2 Hz, 1H), and 1.36 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 141.0, 140.7, 138.5, 134.1, 133.9, 131.0, 129.4, 128.5, 128.2, 127.0, 126.9, 126.6, 123.8, 119.5, 113.6, 109.3, 57.4, 51.8, and 24.9; **$[\alpha]_D^{23}$** = –40.9 (c = 0.5, $CHCl_3$). **Anal. Calcd. for $C_{23}H_{23}ClN_2O_2S$** (HCl salt): C, 64.70; H, 5.43. Found: C, 64.53; H, 5.42; **HPLC analysis** (IA, Hexanes:*i*PrOH:Et_2NH = 90:5:0.1, 1.0 mL/min) indicated 97% ee: t_R (major) = 15.2 min, t_R (minor) = 16.6 min.



11j

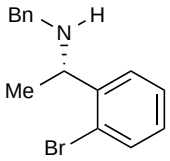
(*S*)-*N*-benzyl-1-(pyridin-3-yl)ethan-1-amine (11j) was prepared following **General Procedure I** from 3-vinylpyridine (105 mg, 1.0 mmol, 1.0 equiv) and *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (324 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h. The product was isolated as a yellow oil (1st run: 170 mg, 80%; 2nd run: 183 mg, 86%). **IR (thin film, cm^{-1})** 3284, 3027, 2966, 1576, 1494, 1452, 1423, 1025, 737, 716, and 698; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 8.57 (d, *J* = 2.0 Hz, 1H), 8.50 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.72 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.36-7.23 (m, 6H), 3.85 (q, *J* = 6.6 Hz, 1H), 3.64 (d, *J* = 13.2 Hz, 1H), 3.59 (d, *J* = 13.2 Hz, 1H), and 1.37 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (101**

MHz, $CDCl_3$) δ: 149.2, 148.7, 140.3, 134.3, 128.6, 128.2, 127.2, 55.3, 51.8, and 24.5; **HRMS (DART-TOF)** calculated for $C_{14}H_{16}N_2$ $[M+H]^+$ m/z 213.1386, found 213.1374; **HPLC analysis** ee was determined after benzylation, (OD-H, Hexanes:*i*PrOH = 95:5, 0.8 mL/min) indicated 99% ee: t_R (major) = 14.0 min, t_R (minor) = 17.2 min; **$[\alpha]_D^{23}$** = –53.4 (c = 1.0, $CHCl_3$).



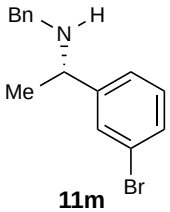
11k

(*S*)-*N*-Benzyl-1-(4-fluorophenyl)ethan-1-amine (11k)[1] An oven-dried screw-top reaction tube (13 mm x 100 mm, labeled as Tube A) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (3.6 mg, 0.02 mmol, 2 mol %), PPh_3 (11 mg, 0.044 mmol, 4.4 mol%), and *R*-DTBM-SEGPHOS (*R*-L: 26 mg, 0.022 mmol, 2.2 mol %). The reaction tube was closed with a PTFE screw cap equipped with a septum. The tube was evacuated and backfilled with argon (this process was repeated a total of 3 times). Anhydrous THF (1.7 mL) was added, and vigorously stirred at room temperature for 10 min until it was homogeneous. Then $HSiMe(OEt)_2$ (0.32 mL, 2.0 mmol, 2.0 equiv) was added via syringe. The resulting reaction mixture was stirred at room temperature for 15 min and the color of solution changed from blue to orange. A second oven-dried, screw-cap reaction tube (13 mm x 100 mm, labeled as Tube B) equipped with a magnetic stir bar was charged with *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (324 mg, 1.2 mmol, 1.2 equiv) and 1-fluoro-4-vinylbenzene (122 mg, 1.0 mmol, 1.0 equiv). Then the 'LCuH' solution in Tube A was added via syringe to Tube B, and the reaction mixture was stirred at 40 °C for 5 h. The reaction mixture was allowed to cool to room temperature and then diluted with Et_2O (50 mL) and extracted with 6 M HCl (aq) (15-20 mL x 3). The combined aqueous layers were washed with hexanes (50 mL x 3) and then carefully basified to ca. pH 11 by slow addition of saturated aqueous K_2CO_3. The aqueous layer was extracted with CH_2Cl_2 (45 mL x 3) and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield the product as a beige oil (1st run: 205 mg, 90%; 2nd run: 215 mg, 94%). **IR (thin film, cm^{-1})** 2964, 1601, 1508, 1453, 1220, 1153, 1123, 834, 734, and 698; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.35-7.21 (m, 7H), 7.02 (dd, *J* = 8.7, 8.7 Hz, 2H), 3.80 (q, *J* = 6.6 Hz, 1H), 3.64 (d, *J* = 13.2 Hz, 1H), 3.57 (d, *J* = 13.2 Hz, 1H), 1.53 (br s, 1H), and 1.33 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 161.9 (d, *J* = 244 Hz), 141.4 (d, *J* = 2.9 Hz), 140.7, 128.4 (d, *J* = 31.5 Hz), 127.0, 141.4 (d, *J* = 2.9 Hz), 115.4, 115.2, 56.9, 51.8, and 24.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -116 ppm; **HPLC analysis** (OD, Hexanes:*i*PrOH:Et_2NH = 90:5:0.1, 0.7 mL/min) indicated 95% ee: t_R (major) = 7.51 min, t_R (minor) = 6.83 min; **$[\alpha]_D^{23}$** = –40.8 (c = 1.0, $CHCl_3$).



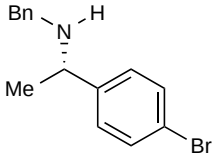
11l

(*S*)-*N*-Benzyl-1-(2-bromophenyl)ethan-1-amine (11l) was prepared following **General Procedure I** from 1-bromo-2-vinylbenzene (182 mg, 1.0 mmol, 1.0 equiv) and *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (324 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h. The product was isolated as a light yellow oil (1st run: 270 mg, 93%; 2nd run: 251 mg, 87%). **IR (thin film, cm^{-1})** 3334, 3062, 2963, 1494, 1460, 1369, 1021, and 750; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.64 (d, *J* = 7.7, 1.6 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.38-7.29 (m, 5H), 7.28-7.22 (m, 1H), 7.12 (ddd, *J* = 7.8, 7.8, 1.7 Hz, 1H), 4.32 (q, *J* = 6.6 Hz, 1H), 3.66 (d, *J* = 13.0 Hz, 1H), 3.61 (d, *J* = 13.0 Hz, 1H), 1.85 (br s, 1H), and 1.36 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 144.1, 140.5, 133.0, 128.5, 128.39, 128.36, 128.0, 127.8, 127.1, 123.9, 56.5, 51.9, and 23.0; **Anal. Calcd. for $C_{15}H_{16}BrN$**: C, 62.08; H, 5.56. Found: C, 62.33; H, 5.54; **HPLC analysis** (OD, Hexanes:*i*PrOH:Et_2NH = 90:5:0.1, 0.7 mL/min) indicated 92% ee: t_R (major) = 7.7 min, t_R (minor) = 6.7 min; **$[\alpha]_D^{23}$** = –4.1 (c = 1.0, $CHCl_3$).



11m

(*S*)-*N*-Benzyl-1-(2-bromophenyl)ethan-1-amine (11m)[7] was prepared following **General Procedure I** from 1-bromo-3-vinylbenzene (182 mg, 1.0 mmol, 1.0 equiv) and *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (324 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h. The product was isolated as a light yellow oil (1st run: 250 mg, 87%; 2nd run: 259 mg, 90%). **IR (thin film, cm^{-1})** 3027, 2963, 1592, 1567, 1493, 1452, 1118, 782, 748, and 694; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.58 (dd, *J* = 1.8, 1.8 Hz, 1H), 7.41 (ddd, *J* = 7.9, 1.6, 1.6 Hz, 1H), 7.22 (dd, *J* = 7.7, 7.7 Hz 1H), 3.80 (q, *J* = 6.6 Hz, 1H), 3.69 (d, *J* = 13.2 Hz, 1H), 3.61 (d, *J* = 13.2 Hz, 1H), 1.63 (br s, 1H), and 1.37 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 148.2, 140.4, 130.1, 130.0, 129.8, 128.4, 128.1, 126.9, 125.4, 122.7, 57.1, 51.7, and 24.5; **Anal. Calcd. for $C_{15}H_{16}BrN$**: C, 62.08; H, 5.56. Found: C, 61.98; H, 5.39; **HPLC analysis** (OD, Hexanes:*i*PrOH:Et_2NH = 90:5:0.1, 0.7 mL/min) indicated 94% ee: t_R (major) = 5.31 min, t_R (minor) = 4.77 min; **$[\alpha]_D^{23}$** = –48.9 (c = 1.0, $CHCl_3$).

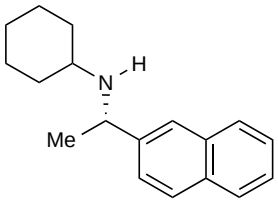


11n

(*S*)-*N*-Benzyl-1-(4-bromophenyl)ethan-1-amine (11n)[1] was prepared following **General Procedure I** from 1-bromo-4-vinylbenzene (182 mg, 1.0 mmol, 1.0 equiv) and *O*-4-dimethylaminobenzoyl-*N*-benzylhydroxylamine (324 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock

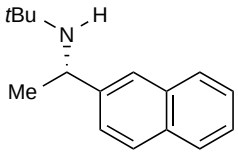
extractive workup, the product was isolated as a pale yellow oil (1st run: 270 mg, 93%; 2nd run: 263 mg, 91%). **IR (thin film, cm^{-1})** 3026, 2965, 2821, 1642, 1488, 1451, 1403, 1068, 1009, and 694; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.46 (d, *J* = 8.4 Hz, 2H), 7.33-7.23 (m, 7H), 3.78 (q, *J* = 6.6 Hz, 1H), 3.63 (d, *J* = 13.1 Hz, 1H), 3.56 (d, *J* = 13.2 Hz, 1H), 1.55 (br s, 1H), and 1.33 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 144.8, 140.5, 131.7, 128.64, 128.61, 128.5, 128.2, 127.1, 120.6, 57.1, 51.7, and 24.7; **Anal. Calcd. for $C_{15}H_{16}BrN$**: C, 62.08; H, 5.56. Found: C, 62.30; H, 5.57; **HPLC analysis** (OD, Hexanes:*i*PrOH:Et_2NH = 90:5:0.1, 0.7 mL/min) indicated 96% ee: t_R (major) = 8.3 min, t_R (minor) = 7.2 min; **$[\alpha]_D^{23}$** = –37.6 (c = 1.0, $CHCl_3$).

Products in Table 1



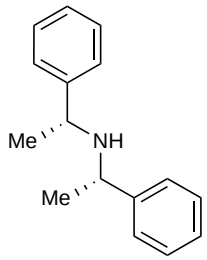
17a

(*S*)-*N*-(1-(naphthalen-2-yl)ethyl)cyclohexanamine (17a) was prepared following **General Procedure I** from 2-vinylnaphthalene (154 mg, 1.0 mmol, 1.0 equiv), *O*-4-dimethylaminobenzoyl-*N*-cylclohexylamine (314 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h. The product was isolated as a colorless oil (1st run: 226 mg, 90% 2nd run: 230 mg, 0.91 mmol, 91%). **IR (thin film, cm^{-1})** 3050, 2921, 2851, 1600, 1506, 1446, 1365, 1127, 854, and 744; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.87–7.83 (m, 3H), 7.72 (d, *J* = 1.2 Hz, 1H), 7.50–7.42 (m, 3H), 4.14 (q, *J* = 6.6 Hz, 1H), 2.35-2.25 (m, 1H), 2.07-2.01 (m, 1H), 1.75-1.50 (m, 4H), 1.41 (d, *J* = 6.6 Hz, 3H), 1.18-1.00 (m, 5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 144.0, 133.6, 132.8, 128.3, 127.9, 127.8, 126.0, 125.5, 125.1, 125.0, 54.8, 53.8, 34.8, 33.4, 26.3, 25.3, 25.2, and 25.1; **Anal. Calcd. for $C_{18}H_{23}N$**: C, 85.32; H, 9.15. Found: C, 85.04; H, 9.22; **HPLC analysis** (IA, Hexanes:*i*PrOH:Et_2NH = 98:2:0.08, 0.7 mL/min) indicated 96% ee: t_R (major) = 6.1 min, t_R (minor) = 6.5 min; **$[\alpha]_D^{23}$** = –56.5 (c = 1.0, $CHCl_3$).



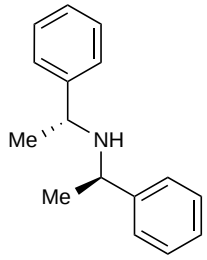
17b

(*S*)-*N*-(1-(naphthalen-2-yl)ethyl)cyclohexanamine (17b) was prepared following **General Procedure I** from 2-vinylnaphthalene (154 mg, 1.0 mmol, 1.0 equiv) and 4-(((tert-butylamino)oxy)carbonyl)-*N*,*N*-dimethylaniline (283 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h, then stirred at 40 °C for 5 h to ensure the excess amine electrophile is fully consumed. The product was isolated as a light yellow oil (1st run: 204 mg, 90%; 2nd run: 211 mg, 93%). **IR (thin film, cm^{-1})** 3054, 2957, 2923, 1599, 1507, 1446, 1359, 1287, 854, 817, and 744; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.84-7.80 (m, 4H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.48-7.42 (m, 2H), 4.16 (q, *J* = 6.6 Hz, 1H), 1.41 (d, *J* = 6.6 Hz, 3H), 1.29 (br s, 1H), and 1.07 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 146.6, 133.7, 132.7, 128.0, 127.8, 127.7, 125.9, 125.4, 125.3, 124.7, 52.8, 51.6, 30.3, and 27.4; **HRMS (DART-TOF)** calculated for $C_{16}H_{21}NO$ $[M+H]^+$ m/z 228.1747, found 228.1749; **HPLC analysis** (OJ-H, Hexanes:*i*PrOH:Et_2NH = 99:1:0.04, 1.0 mL/min) indicated 93% ee: t_R (major) = 9.1 min, t_R (minor) = 10.2 min; **$[\alpha]_D^{23}$** = -40.1 (c = 1.0, $CHCl_3$).



17c

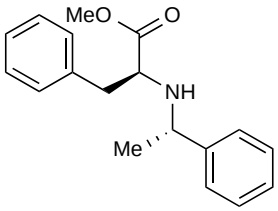
(*S*)-1-phenyl-N-((*R*)-1-phenylethyl)ethan-1-amine (17c)[8] was prepared following **General Procedure I** from styrene (104 mg, 1.0 mmol, 1.0 equiv) and (*R*)-*N*,*N*-dimethyl-4-((((1-phenylethyl)amino)oxy)carbonyl)aniline (340 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h, then stirred at 40 °C for 5 h to ensure the excess amine electrophile is fully consumed. The product was isolated as a colorless oil (1st run: 209 mg, 93%; 2nd run: 205 mg, 91%). **IR (thin film, cm^{-1})** 3061, 3023, 2969, 1601, 1491, 1450, 1369, 1217, 758, and 696; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.42-7.26 (m, 10H), 3.84 (q, *J* = 6.5 Hz, 2H), 1.65 (br s, 1H), 1.42 (d, *J* = 6.5 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 146.0, 128.5, 126.9, 126.6, 54.9, and 23.3.



17d

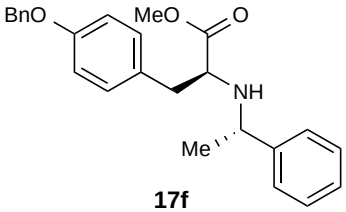
(*R*)-Bis((R)-1-phenylethyl)amine (17d)[9] was prepared following **General Procedure I** from styrene (104 mg, 1.0 mmol, 1.0 equiv) and (*R*)-*N*,*N*-dimethyl-4-((((1-phenylethyl)amino)oxy)carbonyl)aniline (340 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h, then stirred at 40 °C for 5 h to ensure the excess amine electrophile is fully consumed. The product was isolated as a colorless oil (1st run: 190 mg, 84%; 2nd run: 206 mg, 92%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.39-7.23 (m, 10H), 3.54 (q, *J* = 6.7 Hz, 2H), 1.70 (br s, 1H), 1.31 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 145.9, 128.5, 126.9, 126.8, 55.2, and 25.1. **$[\alpha]_D^{23}$** = 150.8 (c = 1.0, $CHCl_3$).

Following the above procedure except using either (±)-DTBM-SEGPHOS or (±)-*N*,*N*-dimethyl-4-((((1-phenylethyl)amino)oxy)carbonyl)aniline. The reaction mixture was stirred at RT for 10 min, and quenched by the addition of CH_2Cl_2 and aqueous Na_2CO_3. The samples were then analyzed by GC/MS to show ca. 1:1 mixture of diastereomers were formed in both cases.



17e

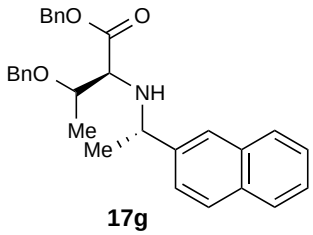
Methyl ((*S*)-1-phenylethyl)-*L*-phenylalaninate (17e) was prepared according to **General Procedure I** with a modified workup procedure from styrene (52 mg, 0.5 mmol, 1.0 equiv) and methyl ((4-(dimethylamino)benzoyl)oxy)-*L*-phenylalaninate (222 mg, 0.65 mmol, 1.3 equiv) using 'LCuH' solution prepared from $Cu(OAc)_2$ (3.6 mg, 0.02 mmol, 4 mol%), PPh_3 (11 mg, 0.044 mmol, 8.8 mol%), *R*-DTBM-SEGPHOS (26 mg, 0.022 mmol, 4.4 mol%), diethoxymethylsilane (0.16 mL, 1 mmol, 2.0 equiv), and THF (0.8 mL). The reaction mixture was stirred at RT for 16 h. The resulting solution was separated between CH_2Cl_2 (10 mL) and pH 10.5 solution (15 mL), and the aqueous layer was washed with CH_2Cl_2 (10 mL x 2). The combined organic layers were washed with brine (15 mL) and concentrated *in vacuo*. The residue was purified by flash column chromatography [SiO_2 (10g), Hexane:EtOAc = 1:0 then 20:1, permanganate stain]. The product was isolated as a colorless oil (1st run: 95 mg, 67%; 2nd run: 92 mg, 65%). **IR (thin film, cm^{-1})** 3026, 2969, 1732, 1602, 1494, 1451, 1365, 1274, 1200, 1170, 762, and 698; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.28-7.16 (m, 6H), 7.11-7.06 (m, 4H), 3.69 (q, *J* = 6.5 Hz, 1H), 3.65 (s, 3H), 3.28 (dd, *J* = 7.7, 6.2 Hz, 1H), 2.90 (dd, *J* = 13.5, 6.2 Hz, 1H), 2.83 (dd, *J* = 13.4, 7.7 Hz, 1H), 1.78 (br s, 1H), and 1.28 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 175.8, 144.9, 137.5, 129.4, 128.44, 128.37, 127.0, 126.9, 126.7, 60.4, 56.7, 51.7, 40.3, and 25.4; **HRMS (DART-TOF)** calculated for $C_{18}H_{21}NO_2$ $[M+H]^+$ m/z 284.1645, found 284.1630; **$[\alpha]_D^{23}$** = –57.1 (c = 1.0, $CHCl_3$).



17f

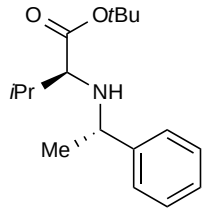
Methyl *O*-Benzyl ((*S*)-1-phenylethyl)-*L*-tyrosinate (17f) was prepared according to **General Procedure I** with a modified workup procedure from styrene (52 mg, 0.5 mmol, 1.0 equiv) and methyl (*S*)-3-(4-(benzyloxy)phenyl)-2-(((4-(dimethylamino)benzoyl)oxy)amino)propanoate (280 mg, 0.65 mmol, 1.3 equiv) using 'LCuH' solution prepared from $Cu(OAc)_2$ (3.6 mg, 0.02 mmol, 4 mol%), PPh_3 (11 mg, 0.044 mmol, 8.8 mol%), *R*-DTBM-SEGPHOS (26 mg, 0.022 mmol, 4.4 mol%), diethoxymethylsilane (0.16 mL, 1 mmol, 2.0 equiv), and THF (0.8 mL). The reaction mixture was stirred at RT for 16 h. The resulting solution was separated between CH_2Cl_2 (10 mL) and pH 10.5 solution (15 mL), and the aqueous layer was washed with CH_2Cl_2 (10 mL x 2). The combined organic layers were washed with brine (15 mL) and concentrated *in vacuo*. The residue was purified by flash column chromatography [SiO_2 (10g), Hexane:EtOAc = 1:0 then 20:1, permanganate stain]. The product was isolated as a colorless oil (1st run: 111 mg, 58%; 2nd run:

117 mg, 60%). **IR (thin film, cm^{-1})** 3028, 2970, 1735, 1610, 1583, 1510, 1369, 1365, 1229, 1217, 1173, 1125, 1008, 762, and 696; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.44 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.24-7.17 (m, 3H), 7.10 (br d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.1 Hz, 2H), 5.06 (s, 2H), 3.69 (q, *J* = 6.5 Hz, 1H), 3.64 (s, 3H), 3.24 (dd, *J* = 7.6, 6.2 Hz, 1H), 2.84 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.78 (dd, *J* = 13.6, 7.6 Hz, 1H), 1.75 (br s, 1H), and 1.29 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 175.8, 157.7, 144.9, 137.2, 130.4, 129.8, 128.7, 128.4, 128.0, 127.6, 127.0, 126.9, 114.8, 70.1, 60.5, 56.7, 51.7, 39.4, and 25.4. **HRMS (DART-TOF)** calculated for $C_{25}H_{27}NO_3$ $[M+H]^+$ m/z 390.2064, found 390.2059; **$[\alpha]_D^{23}$** = –12.5 (c = 1.0, $CHCl_3$).



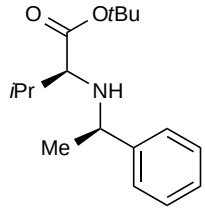
17g

Benzyl *O*-benzyl-*N*-((*S*)-1-(naphthalen-2-yl)ethyl)-*L*-allothreoninate (17g) was prepared using the following procedure. In a nitrogen-filled glove box, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol, 4 mol%) and *R*-DTBM-SEGPHOS (26 mg, 0.022 mmol, 4.4 mol%) were weighed into an oven-dried screw-top reaction tube (130 mm x 10 mm) containing a stir bar. Toluene (1 mL) was added, and the resulting mixture was vigorously stirred for 15 min, after which diethoxymethylsilane (0.16 mL, 1.0 mmol, 2.0 equiv) is added, and the mixture is stirred for another 15 min. The mixture remained hetereogeneous. 2-Vinylnaphthalene (77 mg, 0.5 mmol, 1.0 equiv) and benzyl *O*-benzyl-*N*-(pivaloyloxy)-*L*-allothreoninate (250 mg, 0.625 mmol, 1.25 equiv) was added to the tube sequentially. The tube was tightly sealed and removed from the glove box. The reaction mixture is vigorously stirred at RT for 16 h. The resulting solution was directly purified by column chromatography (Hexanes:EtOAc = 1:0 then 20:1). The product was isolated as a colorless oil (1st run: 144 mg, 64%; 2nd run: 150 mg, 66%). **IR (thin film, cm^{-1})** 3345, 3031, 2969, 1735, 1600, 1507, 1497, 1371, 1150, 1098, 746, and 695; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.86-7.81 (m, 2H), 7.81-7.78 (m, 1H), 7.71 (s, 1H), 7.57 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.51-7.45 (m, 2H), 7.36–7.23 (m, 10H), 5.19 (d, *J* = 12.2 Hz, 1H), 5.13 (d, *J* = 12.2 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 4.31 (d, *J* = 11.9 Hz, 1H), 4.00 (q, *J* = 6.5 Hz, 1H), 3.87 (qd, *J* = 6.2, 3.0 Hz, 1H), 3.10 (d, *J* = 3.0 Hz, 1H), 2.47 (br s, 1H), 1.48 (d, *J* = 6.6 Hz, 3H) and 1.28 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 173.8, 142.7, 138.5, 135.9, 133.5, 133.0, 128.6, 128.3, 128.2, 127.8, 127.71, 127.66, 127.5, 126.0, 125.9, 125.5, 125.3, 75.8, 70.9, 66.5, 63.3, 56.9, 25.4, and 16.6; **Anal. Calcd. for $C_{30}H_{31}NO_3$**: C, 79.44; H, 6.89. Found: C, 79.18; H, 6.78; **$[\alpha]_D^{23}$** = –95.4 (c = 1.0, $CHCl_3$).



17h

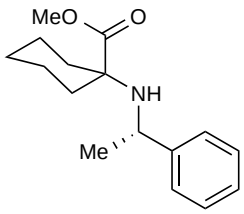
***tert*-Butyl ((*S*)-1-phenylethyl)-*L*-valinate (17h)** was prepared following the **General Procedure I** with a modified workup procedure from styrene (52 mg, 0.5 mmol, 1.0 equiv) and *tert*-butyl ((4-(dimethylamino)benzoyl)oxy)-*L*-valinate (215 mg, 0.65 mmol, 1.3 equiv) using 'LCuH' solution made from $Cu(OAc)_2$ (2.7 mg, 0.015 mmol, 3 mol%), *R*-DTBM-SEGPHOS (20 mg, 0.0165 mmol, 3.3 mol%), PPh_3 (8.6 mg, 6.6 mol%), diethoxymethylsilane (0.16 mL, 1.0 mmol, 2.0 equiv), and THF (0.8 mL). The reaction mixture was stirred at 40 °C for 16 h. The resulting solution was allowed to cool to room temperature and then directly purified by column chromatography [SiO_2 (10g), Hexane:EtOAc = 1:0 then 20:1, permanganate stain]. **[**If the product contained silane after chromatography, then the mixture was dissolved in a saturated MeOH solution of NH_4F (5 mL), concentrated, and partitioned between H_2O (10 mL) and CH_2Cl_2 (10 mL). The aqueous layer was washed with CH_2Cl_2 (10 mL x 2). The combined organic layers were washed with brine (10 mL), dried with Na_2SO_4, filtered and concentrated *in vacuo*.] The product was isolated as a colorless oil (1st run: 107 mg, 78%; 2nd run: 113 mg, 81%). **IR (thin film, cm^{-1})** 2969, 2931, 1723, 1602, 1493, 1366, 1146, 759, and 699; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.36-7.28 (m, 4H), 7.25-7.20 (m, 1H), 3.67 (q, *J* = 6.5 Hz, 1H), 2.63 (d, *J* = 6.1 Hz, 1H), 1.81 (d of heptet, *J* = 6.5, 6.5 Hz, 1H), 1.77 (br s, 1H), 1.48 (s, 9H), 1.33 (d, *J* = 6.5 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 175.3, 145.6, 128.3, 127.2, 127.0, 80.8, 65.3, 56.9, 31.8, 28.4, 25.8, 19.6, and 18.6; **Anal. Calcd. for $C_{17}H_{27}NO_2$**: C, 73.61; H, 9.81. Found: C, 73.81; H, 9.90; **$[\alpha]_D^{23}$** = –96.6 (c = 1.0, $CHCl_3$).



17i

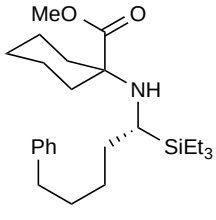
***tert*-butyl ((*R*)-1-phenylethyl)-*L*-valinate (17i)** was prepared following the **General Procedure I** with a modified workup procedure from styrene (52 mg, 0.5 mmol, 1.0 equiv) and *tert*-butyl ((4-(dimethylamino)benzoyl)oxy)-*L*-valinate (215 mg, 0.65 mmol, 1.3 equiv) using 'LCuH' solution made from $Cu(OAc)_2$ (2.7 mg, 0.015 mmol, 3 mol%), *S*-DTBM-SEGPHOS (20 mg, 0.0165 mmol, 3.3 mol%), PPh_3 (8.6 mg, 6.6 mol%), diethoxymethylsilane (0.16 mL, 1.0 mmol, 2.0 equiv), and THF (0.8 mL). The reaction mixture was stirred at 40 °C for 16 h. The resulting solution was allowed to cool to room temperature and then directly purified by column chromatography [SiO_2 (10g), Hexane:EtOAc = 1:0 then 20:1, permanganate stain]. **[**If the product contained silane after chromatography, then the mixture was dissolved in a saturated MeOH solution of NH_4F (5 mL), concentrated, and partitioned between H_2O (10 mL) and CH_2Cl_2 (10 mL). The aqueous layer was washed with CH_2Cl_2 (10 mL x 2). The combined organic layers were washed with brine (10 mL), dried with Na_2SO_4 filtered and concentrated *in vacuo*.] The product

was isolated as a colorless oil (1st run: 97 mg, 70%; 2nd run: 102 mg, 73%). **IR (thin film, cm^{-1})** 2969, 2930, 1722, 1603, 1494, 1365, 1147, 763, and 700; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.35-7.27 (m, 4H), 7.25-7.20 (m, 1H), 3.70 (q, *J* = 6.5 Hz, 1H), 2.96 (d, *J* = 5.9 Hz, 1H), 1.87 (d of heptet, *J* = 6.5, 6.5 Hz, 1H), 1.85 (br s, 1H), 1.42 (s, 9H), 1.32 (d, *J* = 6.5 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H), and 0.94 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 174.7, 146.4, 128.5, 127.1, 126.9, 80.8, 65.4, 56.9, 32.0, 28.3, 22.6, 19.3, and 18.8; **Anal. Calcd. for $C_{17}H_{27}NO_2$**: C, 73.61; H, 9.81. Found: C, 73.81; H, 9.90; **$[\alpha]_D^{23}$** = 14.1 (c = 1.0, $CHCl_3$).



17j

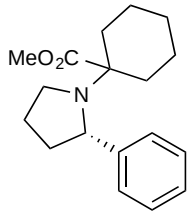
Methyl (*S*)-1-((1-phenylethyl)amino)cyclohexane-1-carboxylate (17j) was prepared following the **General Procedure I** with a modified workup procedure using from styrene (62 mg, 0.6 mmol, 1.2 equiv) and methyl 1-(((4-(dimethylamino)benzoyl)oxy)amino)cyclohexane-1-carboxylate (160 mg, 0.5 mmol, 1.0 equiv) using 1 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h. The resulting solution was separated between CH_2Cl_2 (15 mL) and pH 10.5 solution (15 mL), and the aqueous layer was washed with CH_2Cl_2 (10 mL X 2). The combined organic layers were washed with brine (15 mL) and concentrated. The residue was purified by column chromatography [SiO_2 (10g), Hexane:EtOAc = 1:0 then 20:1, permanganate stain]. The product was isolated as a colorless oil (1st run: 113 mg, 87%; 2nd run: 127 mg, 97%). **IR (thin film, cm^{-1})** 2930, 2854, 1724, 1449, 1203, 1135, 762, and 700; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.32-7.25 (m, 4H), 7.21-7.15 (m, 1H), 3.73 (q, *J* = 6.7 Hz, 1H), 3.49 (s, 3H), 1.95-2.88 (m, 1H), 1.78-1.53 (m, 4H), 1.55-1.10 (m, 5H), and 1.29 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 176.9, 147.4, 128.2, 126.7, 126.6, 62.3, 53.6, 51.4, 34.9, 33.6, 26.6, 25.7, 22.3, and 22.1; **Anal. Calcd. for $C_{16}H_{23}NO_2$:** C, 73.53; H, 8.87. Found: C, 73.82; H, 8.91; **HPLC analysis** (OJ-H, Hexanes:IPr = 97:3, 0.8 mL/min) indicated 95% ee. t_R (major) = 7.1 min, t_R (minor) = 7.8 min; **$[\alpha]_D^{23}$** = –44.7 (c = 1.0, $CHCl_3$).



17k

Methyl (*R*)-1-((5-phenyl-1-(triethylsilyl)pentyl)amino)cyclohexane-1-carboxylate (17k) was prepared following the **General Procedure I** from (*E*)-triethyl(5-phenylpent-1-en-1-yl)silane (130 mg, 0.5 mmol, 1.0 equiv) and methyl 1-(((4-(dimethylamino)benzoyl)oxy)amino)cyclohexane-1-carboxylate (192 mg, 0.6 mmol, 1.2 equiv), using 1 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h.

Without extractive workup, the reaction mixture was directly purified by column chromatography (Hexane:EtOAc = 1:0 then 20:1, permanganate stain). The product was isolated as a colorless oil (1st run: 165 mg, 79%; 2nd run: 167 mg, 80%). **IR (thin film, cm^{-1})** 2933, 2873, 1725, 1453, 1200, 1131, 722, and 697; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.28-7.24 (m, 2H), 7.18-7.14 (m, 3H), 3.61 (s, 3H), 2.63-2.54 (m, 2H), 2.38 (dd, *J* = 7.1, 3.0 Hz, 1H), 2.00-1.93 (m, 1H), 1.87-1.80 (m, 1H), 1.74-1.62 (m, 1H), 1.60-1.12 (m, 13H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.54 (q, *J* = 7.8 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 178.1, 142.8, 128.5, 128.3, 125.7, 61.0, 51.5, 39.9, 36.7, 36.1, 32.7, 32.4, 32.0, 27.1, 25.8, 22.5, 22.4, 7.9, and 2.8; **Anal. Calcd. for $C_{23}H_{29}N$**: C, 71.89; H, 10.38. Found: C, 71.99; H, 10.41; **HPLC analysis** (OD-H, Pentane:*i*PrOH = 99.8:0.2, 0.4 mL/min) indicated 99% ee: t_R (major) = 17.38 min, t_R (minor) = 18.43 min; **$[\alpha]_D^{23}$** = 21.8 (c = 1.0, $CHCl_3$).

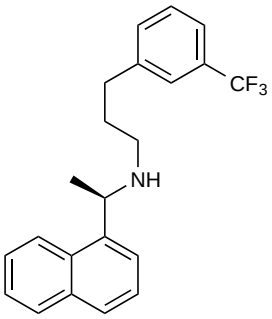


17l

Methyl (*S*)-1-(2-phenylpyrrolidin-1-yl)cyclohexane-1-carboxylate (17l) was prepared using the following procedure. In a nitrogen-filled glovebox, $Cu(OAc)_2$ (4.5 mg, 0.025 mmol, 5 mol%) and *R*-DTBM-SEGPHOS (33 mg, 0.0275 mmol, 5.5 mol%) were weighed into an oven dried tube (13 mm x 100 mm, labeled as Tube A), and THF (2.2 mL) was added. The mixture was stirred vigorously until it was homogeneous. Diethoxymethylsilane (0.32 mL, 2.0 mmol, 4.0 equiv) was added, and the resulting solution is stirred for 10 min, during which time the color of the solution turns from blue to bright orange. A 1.5 dram flat bottom vial (13 mm x 50 mm, labeled as Tube B) containing a 8 mm long stir bar was charged with (*E*)-(4-chlorobut-1-en-1-yl)benzene (83 mg, 0.5 mmol, 1.0 equiv) and methyl 1-(((4-(dimethylamino)benzoyl)oxy)amino)cyclohexane-1-carboxylate (192 mg, 0.6 mmol, 1.2 equiv), loosely capped with a PTFE screw cap equipped with a septum, and taken into the glovebox. The solution in Tube A is then transferred to Tube B, followed by addition of LiOMe (100 mg, 2.5 mmol, 5 equiv). The reaction tube was tightly closed, removed from the glovebox and the resulting mixture was vigorously stirred at 45 °C for 40 h. The resulting solution was allowed to cool to room temperature and then purified by flash column chromatography (permanganate stain, Hexane:EtOAc = 1:0 then 20:1). The product was isolated as a colorless oil (1st run: 77 mg, 54%; 2nd run: 79 mg, 55%). **IR (thin film, cm^{-1})** 2935, 2858, 1718, 1601, 1490, 1450, 1365, 1199, 1147, 1129, and 701; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.36 (d, *J* = 7.8 Hz, 2H), 7.29-7.24 (m, 2H), 7.19-7.14 (m, 1H), 4.37 (dd, *J* = 9.0, 1.7 Hz, 1H), 3.71 (s, 3H), 3.23 (br t, *J* = 8.7 Hz, 1H), 2.92-2.85 (m, 1H), 2.18-2.10 (m, 1H), 2.07-1.97 (m, 1H), 1.87-1.75 (m, 2H), 1.72-1.52 (m, 4H), 1.41-1.15 (m, 5H), and 1.07-0.96 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 174.1, 149.8, 127.9,

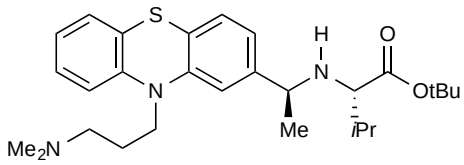
126.7, 125.9, 65.9, 61.4, 51.0, 48.8, 36.2, 34.6, 34.3, 25.6, 23.7, 22.9, and 22.7; **Anal. Calcd. for $C_{23}H_{29}N$**: C, 75.22; H, 8.77. Found: C, 75.23; H, 8.81; **Enantiomeric excess** is determined to be 97% by ^{1}H NMR [A 1:1 mole ratio of product (17 mg) and *R*- or *S*-mandelic acid (9.1 mg) is dissolved in 1 mL of C_6D_6. The ^{1}H NMR spectra obtained are compared with the one obtained from a 1:1 mixture of racemic product (17 mg) to *R*-mandelic acid (9.1 mg).]; $\mathbf{[\alpha]_D^{23}}$ = –146.3 (c = 1.0, $CHCl_3$).

Products in Scheme 1



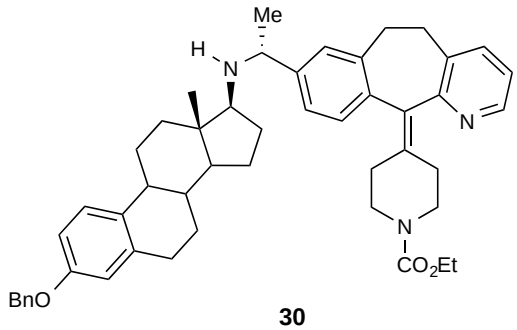
21

(*R*)-*N*-(1-(naphthalen-1-yl)ethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine (21)[10] was made following the **General Procedure I** with a modified workup procedure from 1-vinylnaphthalene (154 mg, 1.0 mmol, 1.0 equiv) and *N*,*N*-dimethyl-4-((((3-(3-(trifluoromethyl)phenyl)propyl)amino)oxy)carbonyl)aniline (439 mg, 1.2 mmol, 1.2 equiv) using 2 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h. The resulting solution is then diluted with CH_2Cl_2 (40 mL) and washed with 3 M aqueous K_2CO_3 (30 mL x 3). The organic layer was concentrated and purified by flash column chromatography (Hexanes:EtOAc = 3:1 then 1:1 then 1:2). The product was isolated as a light yellow oil (1st run: 292 mg, 82%; 2nd run: 290 mg, 0.81 mmol, 81%). **IR (thin film, cm^{-1})** 2927, 1596, 1446, 1326, 1160, 1119, 1072, 798, 771, and 754; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 8.20 (d, *J* = 8.2 Hz, 1H), 7.88 (br d, *J* = 7.4 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.55-7.46 (m, 3H), 7.45-7.42 (m, 2H), 7.38–7.29 (m, 2H), 4.64 (q, *J* = 6.6 Hz, 1H), 2.80-2.55 (m, 4H), 1.85 (tt, *J* = 7.5, 7.5 Hz, 2H), and 1.51 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 143.2, 141.3, 134.1,131.91, 131.89, 131.4, 130.7 (q, *J* = 32.1 Hz), 129.1, 128.8, 127.3, 125.9, 125.8, 125.5, 125.2 (q, *J* = 4.0 Hz), 123.0, 122.8, 122.7 (q, *J* = 3.8 Hz), 53.9, 47.4, 33.6, 32.0, and 23.8; **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -67.5; **Anal. Calcd. for $C_{22}H_{22}F_3N$**: C, 73.93; H, 6.20. Found: C, 73.72; H, 6.19; **HPLC analysis** (IA, Hexanes:*i*PrOH:Et_2NH = 98:2:0.08, 1.0 mL/min) indicated 89% ee: t_R (major) = 5.1 min, t_R (minor) = 4.6 min; **$[\alpha]_D^{23}$** = 17.8 (c = 1.0, $CHCl_3$). {Lit[10] **$[\alpha]_D$** = 10 (c = 0.1, $CHCl_3$).}



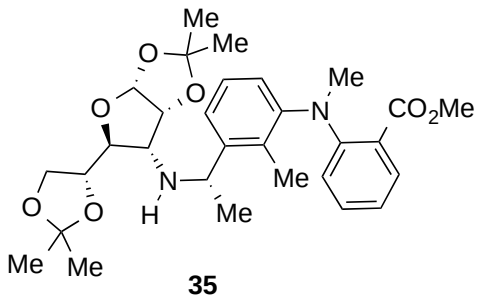
25

***tert*-Butyl ((*S*)-1-(10-(3-(dimethylamino)propyl)-10*H*-phenothiazin-2-yl)ethyl)-*L*-valinate (25)** was prepared following the **General Procedure I** from *N,N*-dimethyl-3-(2-vinyl-10*H*-phenothiazin-10-yl)propan-1-amine (155 mg, 0.5 mmol, 1.0 equiv) and *tert*-butyl ((4-(dimethylamino)benzoyl)oxy)-*L*-valinate (201 mg, 0.6 mmol, 1.2 equiv) using 'LCuH' solution made from $Cu(OAc)_2$ (2.7 mg, 0.015 mmol, 3 mol%), *R*-DTBM-SEGPHOS (19.5 mg, 0.0165 mmol, 3.3 mol%), PPh_3 (8.6 mg, 0.033 mmol, 6.6 mol%), diethoxymethylsilane (0.24 mL, 1.5 mmol, 3.0 equiv), and THF (1.25 mL). The reaction mixture was stirred at RT for 16 h. Without extractive workup, the resulting solution was directly purified by flash column chromatography [SiO_2 (10 g), 100% hexanes, then hexanes:EtOAc:Et_3N = 10:10:1] to give the product as a light brown oil (1st run: 197 mg, 81%; 2nd run: 199 mg, 0.41 mmol, 82%). **IR (thin film, cm^{-1})** 2970, 2816, 1723, 1458, 1365, 1217, 1148, and 747; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.17-7.13 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 1.5 Hz, 1H), 6.92-6.88 (m, 2H), 6.85 (dd, *J* = 7.8, 1.6 Hz, 1H), 3.93 (t, *J* = 6.9 Hz, 2H), 3.60 (q, *J* = 6.5 Hz, 1H), 2.62 (d, *J* = 6.1 Hz, 1H), 2.47 (t, *J* = 6.6 Hz, 2H), 2.24 (s, 6H), 1.99 (pentet, *J* = 6.7 Hz, 2H), 1.80 (d of heptet, *J* = 6.5 Hz, 1H), 1.46 (s, 9H), 1.28 (d, *J* = 6.5 Hz, 2H), 0.91 (d, *J* = 6.8 Hz, 2H), and 0.89 (d, *J* = 6.8 Hz, 3H); (The ^{1}H NMR spectrum of the diastereomer made using *S*-DTBM-SEGPHOS is provided for comparison.) **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 175.1, 145.6, 145.4, 145.2, 127.5, 127.2, 125.4, 123.2, 122.4, 121.5, 115.6, 114.0, 80.8, 65.2, 57.3, 56.7, 45.7, 45.5, 31.8, 28.3, 25.9, 25.4, 19.6, and 18.6; **Anal. Calcd. for $C_{28}H_{41}N_3O_2S$**: C, 69.53; H, 8.54. Found: C, 68.63; H, 8.61; **$[\alpha]_D^{23}$** = –101.3 (c = 1.0, $CHCl_3$).



30

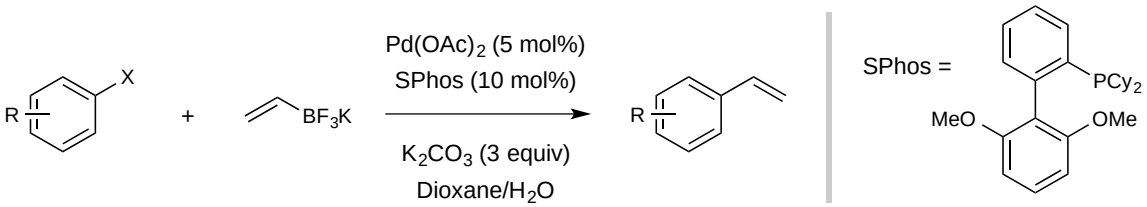
Ethyl 4-(8-((1*R*)-1-(((13*S*,17*S*)-3-(benzyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)amino)ethyl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (30) was prepared following the **General procedure I** with a modified workup procedure from ethyl 4-(8-vinyl-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (187 mg, 0.5 mmol, 1.0 equiv) and 4-(((((13*S*,17*S*)-3-(benzyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)amino)oxy)carbonyl)-*N*,*N*-dimethylaniline (262 mg, 0.5 mmol, 1.0 equiv) using 'LCuH' solution made from $Cu(OAc)_2$ (3.6 mg, 0.02 mmol, 4 mol%), *S*-DTBM-SEGPHOS (26 mg, 0.04 mmol, 4.4 mol%), PPh_3 (11 mg, 0.044 mmol, 8.8 mol%), diethoxymethylsilane (0.16 mL, 1.0 mmol, 2.0 equiv), and THF (2.3 mL). The reaction mixture was vigorously stirred at RT for 16 h. The resulting solution is then diluted with CH_2Cl_2 (40 mL) and washed with 3 M aqueous K_2CO_3 (30 mL). The organic layer was concentrated and purified by flash column chromatography [SiO_2 (25 g), 100% hexanes, then hexanes:EtOAc:Et_3N=10:10:1]. The product was isolated as a colorless foam (1st run: 320 mg, 87%; 2nd run: 302 mg, 82%). **IR (thin film, cm^{-1})** 2927, 1737, 1695, 1436, 1371, 1227, 1112, 1043, and 730; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 8.40 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.47-7.40 (m, 3H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22-7.05 (m, 5H), 6.77 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.70 (d, *J* = 2.2 Hz, 1H), 5.02 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.84 (q, *J* = 6.5 Hz, 1H), 3.9-3.75 (m, 2H), 3.48-3.32 (m, 2H), 3.24-3.08 (m, 2H), 2.90-2.74 (m, 4H), 2.55-2.38 (m, 4H), 2.37-2.20 (m, 2H), 2.17-2.02 (m, 2H), 2.02-1.92 (m, 1H), 1.87-1.80 (m, 1H), 1.65 (q, *J* = 7.4 Hz, 1H), 1.55-1.05 (m, 12H), 1.25 (t, *J* = 7.1 Hz, 3H), and 0.76 (s, 3H); (The ^{1}H NMR spectrum of the diastereomer made using *R*-DTBM-SEGPHOS is provided for comparison.) **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 158.5, 158.2, 156.9, 155.7, 146.6, 145.9, 145.8, 138.2, 138.1, 137.7, 137.3, 136.5, 133.4, 129.4, 128.6, 127.9, 127.53, 127.49, 127.3, 126.4, 126.3, 122.1, 115.1, 112.5, 70.2, 66.1, 61.3, 56.2, 56.0, 52.3, 52.2, 45.1, 45.0, 44.3, 43.0, 39.0, 37.6, 32.4, 32.3, 32.1, 31.9, 30.9, 30.7, 30.2, 29.9, 27.6, 26.6, 25.2, 23.7, 14.8, and 11.9; **HRMS (DART-TOF)** calculated for $C_{49}H_{57}N_3O_3$ $[M+H]^+$ m/z 736.4473, found 736.4471; **$[a]_D^{23}$** = 37.5 (c = 1.0, $CHCl_3$).



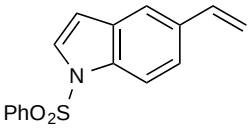
35

Methyl 2-((3-((*S*)-1-(((3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)amino)ethyl)-2-methylphenyl)(methyl)amino)benzoate (35) was prepared following the **General Procedure I** with a modified workup procedure from methyl 2-(methyl(2-methyl-3-vinylphenyl)amino)benzoate (140 mg, 0.5 mmol, 1.0 equiv) and 4-(((((3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)amino)oxy)carbonyl)-*N*,*N*-dimethylaniline (232 mg, 0.55 mmol, 1.1 equiv) using 1 mL of the prepared 'LCuH' stock solution. The reaction mixture was stirred at RT for 16 h. The resulting solution is then diluted with CH_2Cl_2 (40 mL) and washed with 3 M aqueous K_2CO_3 (30 mL). The organic layer was concentrated and purified by column chromatography [SiO_2 (25 g), 100% hexanes, then hexanes:EtOAc:Et_3N=10:10:1]. The product was isolated as a colorless foam (1st run: 193 mg, 71%; 2nd run: 201 mg, 74%). **IR (thin film, cm^{-1})** 2986, 1717, 1598, 1489, 1475, 1446, 1381, 1371, 1237, 1214, 1097, 1050, 1015, 810, and 726; **^{1}H NMR (400 MHz, $CDCl_3$)** for major isomer δ: 7.42 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.37-7.31 (m, 2H), 7.12 (t, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 6.6 Hz, 1H), 5.71 (d, *J* = 3.8 Hz, 1H), 4.39 (t, *J* = 4.1 Hz, 1H), 4.36 (dd, *J* = 7.0, 3.4 Hz, 1H), 4.29 (q, *J* = 6.3 Hz, 1H), 4.27 (t, *J* = 7.4 Hz, 1H), 3.97 (t, *J* = 7.2 Hz, 1H), 3.82 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.39 (s, 3H), 3.16 (s, 3H), 3.08 (dd, *J* = 9.4, 4.6 Hz, 1H), 2.24 (s, 3H), 1.91 (br s, 1H), 1.50 (s, 3H), 1.49 (s, 3H), 1.39 (s, 3H), 1.31 (d, *J* = 6.4 Hz, 3H), and 1.30 (s, 3H); for minor isomer δ: 7.42 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.39-7.33 (m, 2H), 7.15 (t, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.89-6.84 (m, 2H), 5.73 (d, *J* = 3.8 Hz, 1H), 4.50 (t, *J* = 4.1 Hz, 1H), 4.32 (dt, *J* = 7.1, 3.3 Hz, 1H), 4.22 (q, *J* = 6.4 Hz, 1H), 4.27 (t, *J* = 7.4 Hz, 1H), 3.94 (t, *J* = 7.7 Hz, 1H), 3.88 (dd, *J* = 9.8, 3.2 Hz, 1H), 3.79 (t, *J* = 7.0 Hz, 1H), 3.39 (s, 3H), 3.18 (s, 3H), 2.65 (dd, *J* = 9.8, 4.5 Hz, 1H), 2.19 (s, 3H), 1.56 (s, 3H), 1.36 (s, 9H), and 1.30 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 169.1, 149.18, 149.15, 146.2, 132.3, 131.8, 130.7, 126.7, 124.1, 122.8, 119.2, 117.6, 111.9, 109.5, 104.1, 79.6, 78.7, 75.6, 65.3, 59.7, 52.4, 51.5, 41.9, 26.8, 26.6, 26.5, 25.4, 22.6, and 13.5; **HRMS (DART-TOF)** calculated for $C_{30}H_{40}N_2O_7$ $[M+H]^+$ m/z 541.2908, found 541.2922; **$[\alpha]_D^{23}$** = 51.3 (c = 1.0, $CHCl_3$).

General Procedure II for the Preparation of Styrene Substrates



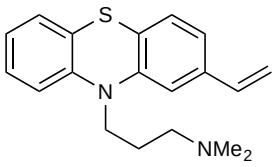
Aryl chloride (1.0 equiv), $Pd(OAc)_2$ (5 mol%), SPhos (10 mol%), potassium vinyl trifluoroborate (2.0 equiv), K_2CO_3 (3.0 equiv) are weighed into an oven dried Schlenk flask charged with a stir bar. The reaction flask was then evacuated and backfilled with argon (this process was repeated for a total of three times). A 6:1 volume ratio of dioxane/H_2O {[Aryl halide] = 0.2 M} was added via syringe. The reaction mixture was stirred at 90 °C overnight. The reaction mixture was allowed to cool to room temperature and then passed through a pad of Celite, and rinsed with EtOAc. The filtrate was partitioned between EtOAc and H_2O. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried (Na_2SO_4), filtered and concentrated. The residue was purified by flash chromatography (Hexanes:EtOAc) to give the desired substituted styrenes.



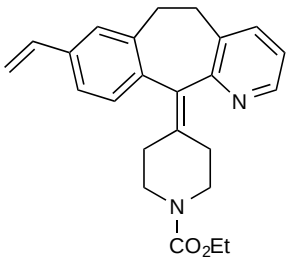
5-Bromo-1-(phenylsulfonyl)-1*H*-indole.

Commercial 5-bromo-1-(phenylsulfonyl)-1H-indole (1.67 g, 5 mmol, 1.0 equiv), $Pd(dppf)Cl_2$ (204 mg, 0.25 mmol, 5 mol%), and potassium vinyl trifluoroborate (1 g, 7.5 mmol, 1.5 equiv) are weighed into an oven dried Schlenk flask equipped with a stir bar. The reaction flask was then evacuated and backfilled with argon (this process was repeated for a total of 3 times). Isopropanol (15 mL) and Et_3N (1.5 g, 15 mmol, 3.0 equiv) were added sequentially via syringe. The reaction mixture was stirred at 80 °C overnight. The reaction mixture was allowed to cool to room temperature and then passed through a pad of Celite, and rinsed with EtOAc. The filtrate was partitioned between EtOAc and H_2O. The aqueous layer was extracted with EtOAc (40 mL x 2). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered and concentrated. The residue was purified by flash column chromatography (Hexanes:EtOAc = 1:0 then 3:1) to give the title compound as a light yellow oil (1.15 g, 4.1 mmol, 82%). **IR (thin film, cm^{-1})**: 3138, 1457, 1447, 1367, 1268, 1170, 1123, 989, 903, 882, 820, 752, 724, and 685; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.95 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 3.7 Hz, 1H), 7.51 (d, *J* = 9.4 Hz, 2H), 7.43 (m, 3H), 6.76 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.64 (d, *J* = 3.6 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 138.3, 136.8, 134.6, 134.0, 133.4, 131.2, 129.4, 127.0, 126.8, 123.0, 119.4,

113.7, 113.4, and 109.6. **HRMS (DART-TOF)** calculated for $C_{16}H_{13}NO_2S$ $[M+H]^+$ m/z 284.0740, found 284.0745.

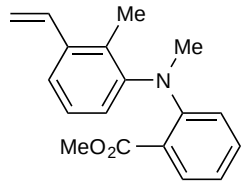


***N*,*N*-dimethyl-3-(2-vinyl-10*H*-phenothiazin-10-yl)propan-1-amine.** Following **General Procedure II**, the title compound was prepared from chlorpromazine hydrochloride (3.55 g, 10 mmol, 1.0 equiv), potassium vinyl trifluoroborate (1.5 g, 1.2 equiv), K_2CO_3 (4.14 g, 30 mmol, 3.0 equiv), $Pd(OAc)_2$ (112 mg, 0.5 mmol, 5 mol%), SPhos (410 mg, 1 mmol, 10 mol%), and dioxane/H_2O (50 mL) and stirred at 90 °C. After 2 h, an additional amount of potassium vinyl trifluoroborate (1.0 g, 0.8 equiv), K_2CO_3 (1.4 g, 10 mmol, 1.0 equiv), $Pd(OAc)_2$ (56 mg, 0.25 mmol, 2.5 mol%), SPhos (205 mg, 5 mol%) were added to the reaction mixture. The reaction was stirred at 90 °C overnight. The crude residue was purified by flash chromatography (EtOAc:Et_3N = 10:1) and isolated as a brown oil (2.5 g, 8.1 mmol, 81%). **IR (thin film, cm^{-1})** 3058, 2937, 2762, 1456, 1442, 1416, 1253, 1221, 1038, and 745; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.17-7.11 (m, 2H), 7.07 (d, *J* = 7.9 Hz, 1 H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.92-6.87 (m, 3H), 6.64 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.69 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 3.93 (t, *J* = 7.0 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 2.21 (s, 6H), and 1.96 (pentet, *J* = 7.0 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 145.6, 145.2, 137.0, 136.7, 127.5, 127.4, 127.3, 125.1, 124.9, 122.5, 120.5, 115.7, 113.7, 113.4, 57.4, 45.7, 45.6, and 25.4. **HRMS (DART-TOF)** calculated for $C_{19}H_{22}N_2S$ $[M+H]^+$ m/z 311.1576, found 311.1564.



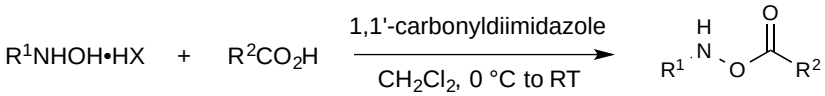
Ethyl 4-(8-vinyl-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate. Following **General Procedure II**, the title compound was prepared from loratadine (1.53 g, 4 mmol, 1.0 equiv), potassium vinyl trifluoroborate (0.8 g, 6 mmol, 1.5 equiv), K_2CO_3 (1.6 g, 12 mmol, 3.0 equiv), $Pd(OAc)_2$ (45 mg, 0.2 mmol, 5 mol%), SPhos (164 mg, 0.4 mmol, 10 mol%), and dioxane/H_2O (20 mL) and stirred at 90 °C. After 2 h, an additional amount of potassium vinyl trifluoroborate (0.6 g, 4.5 mmol, 1.1 equiv) and K_2CO_3 (1.0 g, 7.2 mmol, 1.8 equiv) were added to the reaction mixture. The reaction was stirred at 90 °C overnight. The crude residue was purified by flash column chromatography (Hexanes:EtOAc:Et_3N = 10:10:1) and isolated as a light yellow oil (1.36 g, 3.6 mmol, 91%). **IR (thin film, cm^{-1})** 2979, 2907, 1690, 1434, 1224, 1111, 995, 906, and 727; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 8.38 (d, *J* = 4.8 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.21 (m, 2H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 7.7, 4.8 Hz, 1H),

6.64 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.70 (d, *J* = 17.6 Hz, 1H), 5.19 (d, *J* = 10.9 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.81 (br t, *J* = 7 Hz, 2H), 3.45-3.30 (m, 2H), 3.17-3.07 (m, 2H), 2.48 (ddd, *J* = 14.2, 9.6, 4.6 Hz, 1H), 2.37 (t, *J* = 6.0 Hz, 2H), 2.31 (ddd, *J* = 14.2, 4.6, 4.6 Hz, 1H), and 1.24 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 157.5, 155.6, 146.6, 138.8, 137.9, 137.5, 137.0, 136.8, 136.5, 135.1, 133.7, 129.6, 127.0, 123.9, 122.2, 113.8, 61.3, 45.0, 44.9, 32.0, 31.8, 30.8, 30.6, and 14.8. **HRMS (DART-TOF)** calculated for $C_{24}H_{26}N_2O_2$ $[M+H]^+$ m/z 375.2067, found 375.2069.

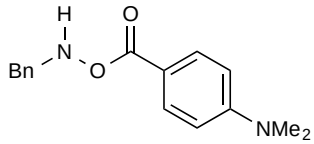


Methyl 2-(methyl(2-methyl-3-vinylphenyl)amino)benzoate. Following **General Procedure II**, the title compound was prepared from methyl 2-((3-chloro-2-methylphenyl)(methyl)amino)benzoate (1.16 g, 4 mmol, 1.0 equiv), potassium vinyl trifluoroborate (1.06 g, 8 mmol, 2.0 equiv), K_2CO_3 (1.68 g, 12 mmol, 3.0 equiv), $Pd(OAc)_2$ (45 mg, 0.2 mmol, 5 mol%), SPhos (164 mg, 0.4 mmol, 10 mol%), and dioxane/H_2O (20 mL) and stirred at 90 °C overnight. The crude residue was purified by flash column chromatography (Hexanes:EtOAc = 10:1) and isolated as a beige oil (0.9 g, 3.2 mmol, 79%). **IR (thin film, cm^{-1})** 3064, 2991, 2946, 1716, 1597, 1472, 1235, 1101, and 755; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.44 (d, *J* = 7.6 Hz, 1H), 7.36 (dd, *J* = 8.7, 8.4 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.10 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.02-6.93 (m, 2H), 6.91-6.86 (m, 2H), 5.62 (d, *J* = 17.4 Hz, 1H), 5.31 (d, *J* = 11.0 Hz, 1H), 3.40 (s, 3H), 3.16 (s, 3H), and 2.27 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 169.3, 149.4, 149.0, 139.1, 135.5, 132.8, 131.9, 130.7, 126.7, 124.9, 122.9, 122.8, 119.3, 117.7, 115.8, 51.6, 41.7, and 14.6. **HRMS (DART-TOF)** calculated for $C_{18}H_{19}NO_2$ $[M+H]^+$ m/z 282.1489, found 282.1476.

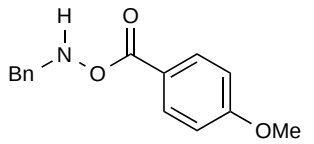
General Procedure III for the Preparation of Amine Electrophiles



The amine electrophiles were prepared according to the above general Scheme following reported protocols.[11] An oven-dried round bottom flask was charged with a carboxylic acid (1.0-1.2 equiv) and CH_2Cl_2 (0.3 M). The flask was placed in an ice-bath, and 1,1'-carbonyldiimidazole (1.0-1.2 equiv) was added. The mixture was stirred at this temperature for 30 min, at which time *N*-alkyl hydroxylamine hydrochloride/oxalate (1.0 equiv) was added. The ice-bath was removed, and the reaction mixture was allowed to stir at room temperature for 1-2 h. The resulting mixture was passed through a pad of Celite, and rinsed with CH_2Cl_2. The filtrate was concentrated and purified by flash chromatography to give the corresponding amine electrophile.

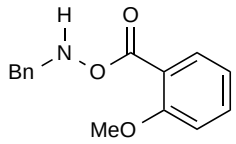


4-(((benzylamino)oxy)carbonyl)-*N*,*N*-dimethylaniline. Following **General Procedure III**, 4-(((benzylamino)oxy)carbonyl)-*N*,*N*-dimethylaniline was prepared from *N*-benzyl hydroxylamine hydrochloride (3.2 g, 20 mmol, 1.0 equiv), 4-(dimethylamino)benzoic acid (3.63 g, 22 mmol, 1.1 equiv), 1,1'-carbonyldiimidazole (3.56 g, 22 mmol, 1.1 equiv), and CH_2Cl_2 (60 mL). The crude residue was purified by flash column chromatography (Hexanes:EtOAc = 3:1) and was obtained as a colorless solid (4.05 g, 15 mmol, 75%). **IR (thin film, cm^{-1})** 3222, 2870, 1694, 1602, 1532, 1454, 1370, 1271, 1183, 1061, 855, 823, 822, 762, and 701; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 8.00 (br s, 1H), 7.86 (d, *J* = 9.2 Hz, 2H), 7.43-7.27 (m, 5H), 6.64 (d, *J* = 9.2 Hz, 2H), 4.23 (d, *J* = 6.4 Hz, 2H), 3.04 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ: 167.4, 153.6, 136.2, 131.2, 129.1, 128.6, 127.9, 114.7, 110.8, 56.9, and 40.1. **HRMS (DART-TOF)** calculated for $C_{16}H_{18}N_2O_2$ $[M+H]^+$ m/z 271.1441, found 271.1438. **Mp**: 96–97 °C.

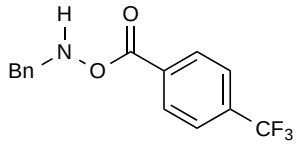


***N*-benzyl-*O*-(4-methoxybenzoyl)hydroxylamine.** Following **General Procedure III**, *N*-benzyl-*O*-(4-methoxybenzoyl)hydroxylamine was prepared from *N*-benzyl hydroxylamine hydrochloride (0.8 g, 5 mmol, 1.0 equiv), 4-(methoxy)benzoic acid (0.9 g, 5.5 mmol, 1.1 equiv), 1,1'-carbonyldiimidazole (0.89 g, 5.5 mmol, 1.1 equiv), and CH_2Cl_2 (15 mL). The crude residue was purified by flash column chromatography (Hexanes:EtOAc = 3:1) and obtained as a colorless oil (1.02 g, 3.9 mmol, 78%). **IR (thin film, cm^{-1})** 3231, 2936, 1711, 1604, 1510, 1454, 1420, 1253, 1167, 1089, 1026, 845, 762, 748, and 696; **^{1}H NMR (400 MHz, $CDCl_3$)**

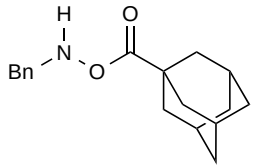
δ: 8.00 (t, *J* = 6.5 Hz, 1H), 7.94 (d, *J* = 8.9 Hz, 2H), 7.45-7.28 (m, 5H), 6.91 (d, *J* = 8.1 Hz, 2H), 4.25 (d, *J* = 6.4 Hz, 2H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 166.8, 163.8, 136.1, 131.6, 129.1, 128.8, 128.0, 120.7, 114.0, 57.0, and 55.6. **HRMS (DART-TOF)** calculated for $C_{15}H_{15}NO_3$ $[M+H]^+$ m/z 258.1125, found 258.1121.



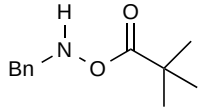
***N*-benzyl-*O*-(2-methoxybenzoyl)hydroxylamine.** Following **General Procedure III**, *N*-benzyl-*O*-(2-methoxybenzoyl)hydroxylamine was prepared from *N*-benzyl hydroxylamine hydrochloride (0.8 g, 5 mmol, 1.0 equiv), 2-(methoxy)benzoic acid (0.9 g, 5.5 mmol, 1.1 equiv), 1,1'-carbonyldiimidazole (0.89 g, 5.5 mmol, 1.1 equiv), and CH_2Cl_2 (15 mL). The crude residue was purified by flash column chromatography (Hexanes:EtOAc = 3:1) and obtained as a colorless oil (0.82 g, 3.2 mmol, 64%). **IR (thin film, cm^{-1})** 3233, 3030, 1726, 1599, 1582, 1490, 1454, 1436, 1297, 1249, 1124, 1045, 1022, 751, and 698; **^{1}H NMR (400 MHz, CD_3OD)** δ: 8.06 (t, *J* = 6.5 Hz, 1H), 7.70 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.51-7.41 (m, 3H), 7.39-7.29 (m, 3H), 6.99-6.64 (m, 1H), 4.26 (d, *J* = 6.4 Hz, 2H), 3.87 (s, 3H); **^{13}C NMR (101 MHz, CD_3OD)** δ: 166.8, 159.3, 136.2, 134.1, 131.6, 129.1, 128.7, 128.0, 120.3, 118.2, 112.1, 56.9, and 56.1. **HRMS (DART-TOF)** calculated for $C_{15}H_{15}NO_3$ $[M+H]^+$ m/z 258.1125, found 258.1132.



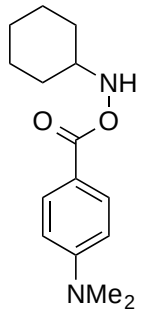
***N*-benzyl-*O*-(4-(trifluoromethyl)benzoyl)hydroxylamine.** Following **General Procedure III**, *N*-benzyl-*O*-(4-(trifluoromethyl)benzoyl)hydroxylamine was prepared from *N*-benzyl hydroxylamine hydrochloride (0.8 g, 5 mmol, 1.0 equiv), 4-(trifluoromethyl)benzoic acid (0.95 g, 5 mmol, 1.0 equiv), 1,1'-carbonyldiimidazole (0.81 g, 5 mmol, 1.0 equiv), and CH_2Cl_2 (15 mL). The crude residue was purified by flash column chromatography (Hexanes:EtOAc = 3:1) and obtained as a colorless solid (1.06 g, 3.6 mmol, 72%). **IR (thin film, cm^{-1})** 3243, 1723, 1446, 1411, 1323, 1170, 1125, 770, 860, 750, and 700; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 8.08 (d, *J* = 8.1 Hz, 2H), 8.02 (t, *J* = 6.3 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.43-7.30 (m, 5H), and 4.31 (d, *J* = 6.3 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 165.6, 135.7, 134.9 (q, *J* = 32.9 Hz), 131.7, 129.9, 129.1, 128.8, 128.2, 125.7 (q, *J* = 4.1 Hz), 123.6 (q, *J* = 272 Hz), and 56.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -63.2. **HRMS (DART-TOF)** calculated for $C_{15}H_{12}F_3NO_2$ $[M+H]^+$ m/z 296.0893, found 296.0890. **Mp**: 66–67 °C.



***O*-(adamantane-1-carbonyl)-*N*-benzylhydroxylamine.** Following **General Procedure III**, *O*-(adamantane-1-carbonyl)-*N*-benzylhydroxylamine was prepared from *N*-benzyl hydroxylamine hydrochloride (0.8 g, 5 mmol, 1.0 equiv), adamantane-1-carboxylic acid (0.9 g, 5 mmol, 1.0 equiv), 1,1'-carbonyldiimidazole (0.81 g, 5 mmol, 1.0 equiv), and CH_2Cl_2 (15 mL). The crude residue was purified by flash column chromatography (Hexanes:EtOAc = 3:1) and obtained as a colorless solid (0.87 g, 3.1 mmol, 61%). **IR (thin film, cm^{-1})** 3231, 2905, 2850, 1721, 1496, 1453, 1217, 1181, 1061, and 697; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.37-7.27 (m, 5H), 4.11 (s, 2H), 3.86 (s, 3H), 2.02-1.92 (m, 3H), 1.84 (d, *J* = 2.8 Hz, 6H), 1.75-1.63 (m, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 177.7, 136.1, 129.1, 128.6, 128.0, 56.8, 40.5, 38.7, 36.5, and 27.9. **HRMS (DART-TOF)** calculated for $C_{18}H_{23}NO_2$ $[M+H]^+$ m/z 286.1802, found 286.1818. **Mp**: 57–58 °C.

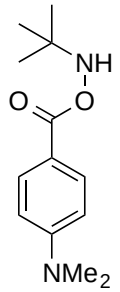


***N*-benzyl-*O*-pivaloylhydroxylamine.** Following **General Procedure III**, *N*-benzyl-*O*-pivaloylhydroxylamine was prepared from *N*-benzyl hydroxylamine hydrochloride (0.8 g, 5 mmol, 1.0 equiv), pivalic acid (0.51 g, 5 mmol, 1.0 equiv), 1,1'-carbonyldiimidazole (0.81 g, 5 mmol, 1.0 equiv), and CH_2Cl_2 (15 mL). The title compound was purified by flash column chromatography (Hexanes:EtOAc = 3:1) and obtained as a colorless oil (0.84 g, 4.1 mmol, 61%). **IR (thin film, cm^{-1})** 3231, 3030, 2972, 2872, 1723, 1497, 1479, 1454, 1132, 909, 730, and 697; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.85 (t, *J* = 5.6 Hz, 1H), 7.37-7.27 (m, 5H), 4.12 (d, *J* = 5.3 Hz, 2H), and 1.16 (s, 9H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ: 178.4, 136.0, 129.0, 128.5, 127.9, 56.7, 38.3, and 27.0. **HRMS (DART-TOF)** calculated for $C_{12}H_{17}NO_2$ $[M+H]^+$ m/z 208.1332, found 208.1329.

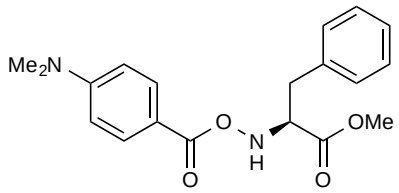


4-(((Cyclohexylamino)oxy)carbonyl)-*N*,*N*-dimethylaniline. Following **General Procedure III**, 4-(((Cyclohexylamino)oxy)carbonyl)-*N*,*N*-dimethylaniline was prepared from *N*-cyclohexyl hydroxylamine hydrochloride (0.630 g, 4.2 mmol, 1.05 equiv), 4-(dimethylamino)benzoic acid (0.66 g, 4 mmol, 1.0 equiv), 1,1'-carbonyldiimidazole (0.65 g, 4 mmol, 1.0 equiv), and CH_2Cl_2 (12 mL). The title compound was purified by flash column chromatography (Hexanes:EtOAc = 3:1) and obtained as a colorless solid (0.78 g, 3.0 mmol, 75%). **IR (thin film, cm^{-1})** 3233, 2937, 2848, 1694, 1605, 1470, 1380, 1309, 1274, 1181, 1076, 1053, 831, 762, and 696; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.88 (d, *J* = 8.9 Hz, 2H), 7.73 (br s, 1H), 6.62 (d, *J* = 9.0 Hz, 2H),

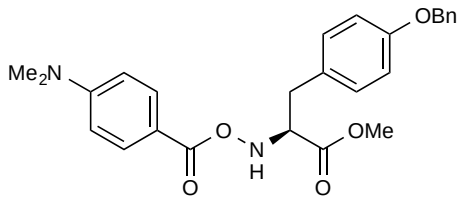
3.01 (s, 6H), 3.05-2.95 (m, 1H), 2.02-1.92 (m, 2H), 1.82-1.72 (m, 2H), 1.65-1.58 (m, 1H), and 1.34-1.12 (m, 5H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ: 167.6, 153.6, 131.1, 115.0, 110.8, 59.9, 40.1, 30.5, 26.0, and 24.6 **HRMS (DART-TOF)** calculated for $C_{15}H_{22}N_2O_2$ $[M+H]^+$ m/z 263.1754, found 263.1746. **Mp**: 125–126 °C.



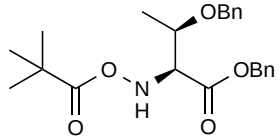
4-(((*tert*-Butylamino)oxy)carbonyl)-*N*,*N*-dimethylaniline. Following **General Procedure III**, 4-(((*tert*-Butylamino)oxy)carbonyl)-*N*,*N*-dimethylaniline was prepared from *N*-*tert*-butyl hydroxylamine acetate (1.49 g, 10 mmol, 1.0 equiv), 4-(dimethylamino)benzoic acid (1.65 g, 10 mmol, 1.0 equiv),, 1,1'-carbonyldiimidazole (1.62 g, 10 mmol, 1.0 equiv), and CH_2Cl_2 (15 mL). The title compound was purified by flash column chromatography (Hexanes:EtOAc = 3:1) and obtained as a colorless oil (2.0 g, 8.5 mmol, 85%). **IR (thin film, cm^{-1})** 3203, 2971, 1689, 1604, 1531, 1431, 1368, 1279, 1183, 1073, 995, 822, 760, and 696; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.88 (d, *J* = 9.1 Hz, 2H), 7.63 (br s, 1H), 6.65 (d, *J* = 8.6 Hz, 2H), 3.02 (s, 6H), and 1.20 (s, 9H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ: 167.4, 153.6, 131.1, 115.0, 110.9, 56.0, 40.1, and 26.7. **HRMS (DART-TOF)** calculated for $C_{13}H_{20}N_2O_2$ $[M+H]^+$ m/z 237.1598, found 237.1589.



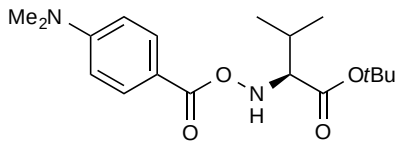
Methyl ((4-(dimethylamino)benzoyl)oxy)-*L*-phenylalaninate. Following **General Procedure III**, the title compound was prepared from methyl hydroxy-*L*-phenylalaninate (1.14 g, 4 mmol, 1.0 equiv), 4-(dimethylamino)benzoic acid (0.83 g, 5 mmol, 1.25 equiv), 1,1'-carbonyldiimidazole (0.81 g, 5 mmol, 1.25 equiv), and CH_2Cl_2 (12 mL). The title compound was purified by flash column chromatography (Hexanes:EtOAc = 5:1) and obtained as a colorless oil (1.01 g, 2.9 mmol, 73%). **IR (thin film, cm^{-1})** 3217, 2950, 1731, 1702, 1600, 1533, 1427, 1372, 1275, 1184, 821, 760, and 698; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.96 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 9.2 Hz, 2H), 7.34-7.23 (m, 5H), 6.62 (d, *J* = 9.1 Hz, 2H), 4.14 (dt, *J* = 8.0 Hz, 1H), 3.67 (s, 3H), 3.11 (d, *J* = 7.5 Hz, 2H), and 3.03 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 172.3, 166.3, 153.7, 136.4, 131.2, 129.3, 128.8, 127.2, 114.5, 110.8, 65.0, 52.3, 40.1, and 36.0; **HRMS (DART-TOF)** calculated for $C_{12}H_{17}NO_2$ $[M+H]^+$ m/z 343.1652, found 343.1652. **$[\alpha]_D^{23}$** = -0.8 (c = 0.5, $CHCl_3$).



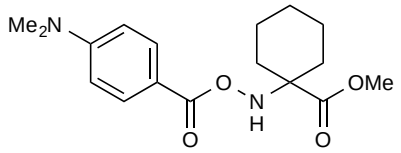
Methyl (*S*)-3-(4-(benzyloxy)phenyl)-2-(((4-(dimethylamino)benzoyl)oxy)amino)propanoate. Following **General Procedure III**, the title compound was prepared from methyl (*S*)-3-(4-(benzyloxy)phenyl)-2-(hydroxyamino)propanoate oxalate (0.8 g, 2 mmol, 1.0 equiv), 4-(dimethylamino)benzoic acid (0.4 g, 2.4 mmol, 1.2 equiv), 1,1'-carbonyldiimidazole (0.4 g, 2.4 mmol, 1.2 equiv), and CH_2Cl_2 (6 mL). The title compound was purified by flash column chromatography (Hexanes:EtOAc =5:1) and obtained as a colorless solid (0.6 g, 1.34 mmol, 67%). **IR (thin film, cm^{-1})** 3229, 3011, 1729, 1705, 1611, 1238, and 695; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.95 (br s, 1H), 7.81 (d, *J* = 9.1 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.29 (tt, *J* = 7.1, 2.6 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 9.1 Hz, 2H), 5.04 (s, 2H), 4.11 (t, *J* = 7.0 Hz, 1H), 3.66 (s, 3H), 3.05 (d, *J* = 7.1 Hz, 2H), and 3.03 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 172.4, 166.3, 158.0, 153.7, 137.2, 131.3, 130.4, 128.7, 128.6, 128.1, 127.6, 115.2, 114.6, 110.9, 70.2, 65.1, 52.3, 40.2, and 35.2; **HRMS (DART-TOF)** calculated for $C_{26}H_{28}N_2O_5$ $[M+H]^+$ m/z 449.2071, found 449.2075. **$[\alpha]_D^{23}$** = +7.6 (c = 0.5, $CHCl_3$). **Mp**: 68–70 °C.



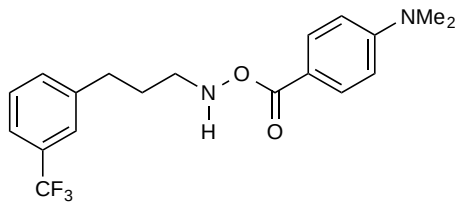
Benzyl *O*-benzyl-*N*-(pivaloyloxy)-*L*-threoninate. Following **General Procedure III**, the title compound was prepared from benzyl *O*-benzyl-*N*-hydroxy-*L*-threoninate oxalate (1.8 g, 4.5 mmol, 1.0 equiv), pivalic acid (456 mg, 4.5 mmol, 1.0 equiv), 1,1'-carbonyldiimidazole (735 g, 4.5 mmol, 1.0 equiv), and CH_2Cl_2 (15 mL). The title compound was purified by flash column chromatography (Hexanes:EtOAc = 10:1) and obtained as a colorless oil (1.47 g, 3.7 mmol, 82%). **IR (thin film, cm^{-1})** 3032, 2974, 1733, 1276, 1130, 908, and 728; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 8.16 (d, *J* = 9.1 Hz, 1H), 7.35-7.20 (m, 10H), 5.17 (d, *J* = 12.1 Hz, 1H), 5.09 (d, *J* = 12.1 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 1H), 4.36 (d, *J* = 11.7 Hz, 1H), 3.97 (qd, *J* = 6.3, 5.0 Hz, 1H), 3.86 (dd, *J* = 9.1, 4.9 Hz, 1H), 1.30 (d, *J* = 6.3 Hz, 3H), and 1.13 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 176.9, 170.2, 137.7, 135.3, 128.5, 128.43, 128.38, 128.31, 127.64, 127.60, 73.4, 71.0, 67.7, 66.9, 38.2, 26.9, and 16.6; **HRMS (DART-TOF)** calculated for $C_{23}H_{29}NO_5$ $[M+H]^+$ m/z 400.2115, found 400.2118. **$[\alpha]_D^{23}$** = -4.6 (c = 1.0, $CHCl_3$).



***tert*-Butyl ((4-(dimethylamino)benzoyl)oxy)-*L*-valinate.** Following **General Procedure III**, the title compound was prepared from *tert*-butyl hydroxy-*L*-valinate oxalate (1.67 g, 6 mmol, 1.0 equiv), 4-(dimethylamino)benzoic acid (1.19 g, 7.2 mmol, 1.2 equiv), 1,1'-carbonyldiimidazole (1.16 g, 7.2 mmol, 1.2 equiv), and CH_2Cl_2 (18 mL). The title compound was purified by flash column chromatography (Hexanes:EtOAc = 10:1) and obtained as a colorless oil (1.43 g, 4.26 mmol, 71%). **IR (thin film, cm^{-1})** 3219, 2970, 1731, 1702, 1603, 1532, 1367, 1281, 1187, 1146, 1083, 830, 761, and 697; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 8.06 (d, *J* = 10.6 Hz, 1H), 7.81 (d, *J* = 9.1 Hz, 2H), 6.60 (d, *J* = 9.0 Hz, 2H), 3.58 (dd, *J* = 9.8, 7.2 Hz, 1H), 3.01 (s, 6H), 2.03 (d of heptet, *J* = 6.9 Hz, 1H), 1.40 (s, 9H), 1.08 (d, *J* = 6.8 Hz, 3H), and 1.03 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 171.5, 166.2, 153.5, 131.0, 114.9, 110.8, 81.7, 70.1, 40.1, 29.3, 28.1, 19.5, and 19.4; **HRMS (DART-TOF)** calculated for $C_{18}H_{28}N_2O_4$ $[M+H]^+$ m/z 337.2109, found 337.2122. **$[\alpha]_D^{23}$** = -4.3 (c = 0.5, $CHCl_3$).



Methyl 1-(((4-(dimethylamino)benzoyl)oxy)amino)cyclohexane-1-carboxylate. Following **General Procedure III**, the title compound was prepared from methyl 1-(hydroxyamino)cyclohexane-1-carboxylate oxalate (1.58 g, 6 mmol, 1.0 equiv), 4-(dimethylamino)benzoic acid (1.19 g, 7.2 mmol, 1.2 equiv), 1,1'-carbonyldiimidazole (1.16 g, 7.2 mmol, 1.2 equiv), and CH_2Cl_2 (18 mL). The title compound was purified by flash column chromatography (Hexanes:EtOAc = 10:1) and obtained as a colorless solid (1.44 g, 4.5 mmol, 75%). **IR (thin film, cm^{-1})** 3220, 2937, 1738, 1699, 1608, 1531, 1453, 1423, 1365, 1274, 1230, 1182, 818, and 751; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.92 (br s, 1H), 7.80 (d, *J* = 9.0 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 2H), 3.66 (s, 3H), 3.02 (s, 6H), 2.06-1.97 (m, 2H), 1.82-1.70 (m, 4H), and 1.55-1.42 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 174.7, 166.2, 153.6, 131.1, 114.8, 110.8, 65.4, 52.3, 40.1, 31.1, 25.6, and 21.8. **HRMS (DART-TOF)** calculated for $C_{17}H_{24}N_2O_4$ $[M+H]^+$ m/z 321.1809, found 321.1822. **Mp**: 107–108 °C.



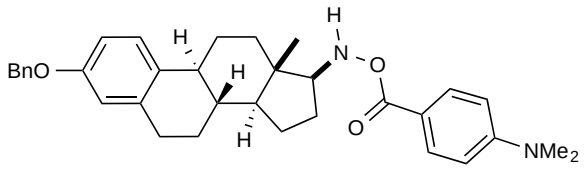
***N*,*N*-dimethyl-4-((((3-(3-(trifluoromethyl)phenyl)propyl)amino)oxy)carbonyl) aniline.**

The *N*-alkylhydroxylamine [*N*-(3-(3-(trifluoromethyl)phenyl)propyl)hydroxylamine] used in this reaction was prepared by the following procedure.[12] A 100 mL round bottom flask equipped with a magnetic stir bar and nitrogen gas inlet was charged with 3-(3-(trifluoromethyl)phenyl)propanal (2.0 g, 10 mmol), hydroxylamine hydrochloride (1.4 g, 20 mmol), and pyridine (50 mL). The reaction mixture was stirred at 50 °C for 2 h. The resulting solution was allowed to cool to room temperature, and partitioned between H_2O (50 mL) and EtOAc (50 mL). The aqueous layer was extracted with EtOAc (25 mL x 2). The combined organic layers were washed sequentially with H_2O (30 mL), 1 M HCl (20 mL), saturated aqueous $NaHCO_3$ (30 mL), and brine (30 mL), and then dried (Na_2SO_4), filtered, and concentrated *in vacuo* to give the oxime, which was used in the next step without further purification.

A 250 mL round bottom flask equipped with a stir bar was charged with the crude oxime, methyl orange indicator (3 mg), THF (50 mL), and MeOH (50 mL). A solution of $NaBH_3CN$ (1.5 g, 25 mmol) in MeOH (50 mL) was slowly added over 1 h via an addition funnel. During this course of addition, 2 M HCl in Et_2O was added occasionally to ensure the color of the reaction solution remained red (indicating pH < 3). After completion of the addition, the reaction mixture was stirred for an additional 1 h, and quenched by the addition of aqueous NaOH (2 M, 50 mL). The resulting mixture was partitioned between H_2O (50 mL) and CH_2Cl_2 (100 mL), and the aqueous layer was extracted with CH_2Cl_2 (50 mL x 2). The combined organic layers were washed with brine (50 mL), dried (Na_2SO_4), filtered, and concentrated to give the crude *N*-alkylhydroxylamine, which was used in the next step without further purification.

Following **General Procedure III**, the title compound was prepared from the crude *N*-alkylhydroxylamine, 4-(dimethylamino)benzoic acid (1.65 g, 10 mmol, 1.0 equiv), 1,1'-carbonyldiimidazole (1.62 g, 10 mmol, 1.0 equiv), and CH_2Cl_2 (30 mL). The title compound was purified by flash column chromatography (Hexanes:EtOAc = 10:1) and obtained as a colorless solid (1.9 g, 5.2 mmol, 52% overall). **IR (thin film, cm^{-1})** 3239, 2871, 1702, 1606, 1522, 1365, 1279, 1154, 1107, 827, 708, 762, 706, and 696; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.94 (br t, *J* = 5.7 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 2H), 7.48-7.38 (m, 4H), 6.65 (d, *J* = 9.2 Hz, 2H), 3.12 (td, *J* = 7.2, 6.0 Hz, 2H), 3.05 (s, 6H), 2.82 (t, *J* = 7.7 Hz, 2H), and 1.97 (tt, *J* = 7.7, 7.7 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 167.6, 153.7, 142.7, 132.0, 131.2, 131.8 (q, *J* = 31.7 Hz), 129.0, 125.7, 125.2 (q, *J* = 3.6 Hz), 123.0 (q, *J* = 3.6 Hz), 114.8, 110.9, 52.0, 40.2, 33.2, and 29.0. **^{19}F NMR**

(376 MHz, $CDCl_3$) δ: -62.6. **HRMS (DART-TOF)** calculated for $C_{19}H_{21}F_3N_2O_2$ $[M+H]^+$ m/z 367.1628, found 367.1637. **Mp**: 88–89 °C.



4-(((((8*R*,9*S*,13*S*,14*S*,17*S*)-3-(benzyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)amino)oxy)carbonyl)-*N*,*N*-dimethylaniline.

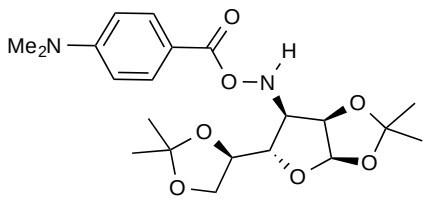
The *N*-alkylhydroxylamine [*N*-((13*S*,17*S*)-3-(benzyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)hydroxylamine] used in this reaction was prepared by the following procedure.[12]

A 100 mL round bottom flask equipped with a stir bar was charged with *O*-benzyl estrone (1.8 g, 5 mmol), hydroxylamine hydrochloride (0.7 g, 10 mmol), and pyridine (30 mL). The reaction was stirred at 50 °C for 4 h. The resulting solution was allowed to cool to room temperature, and partitioned between H_2O (50 mL) and EtOAc (50 mL). The aqueous layer was extracted with EtOAc (25 mL x 2). The combined organic layers were washed sequentially with H_2O (20 mL), 1 M HCl (20 mL), saturated aqueous $NaHCO_3$ (20 mL), and brine (20 mL), and then dried (Na_2SO_4), filtered, and concentrated *in vacuo* to give the oxime, which was used in the next step without further purification.

A 250 mL round bottom flask equipped with a stir bar was charged with the crude oxime, methyl orange indicator (3 mg), THF (30 mL), and MeOH (30 mL). A solution of $NaBH_3CN$ (0.8 g, 13 mmol) in MeOH (25 mL) was then added dropwise over 2 h via an addition funnel. During the course of addition, 2 M HCl in Et_2O was added occasionally to ensure the color of the solution remained red (indicating pH < 3). After completion of the addition, the reaction mixture was stirred for an additional 1 h, and quenched by the addition of aqueous NaOH (2 M, 25 mL). The resulting mixture was partitioned between H_2O (40 mL) and CH_2Cl_2 (40 mL), and the aqueous layer was extracted with CH_2Cl_2 (40 mL x 2). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4) filtered, and concentrated to give the crude *N*-alkylhydroxylamine, which was used in the next step without further purification.

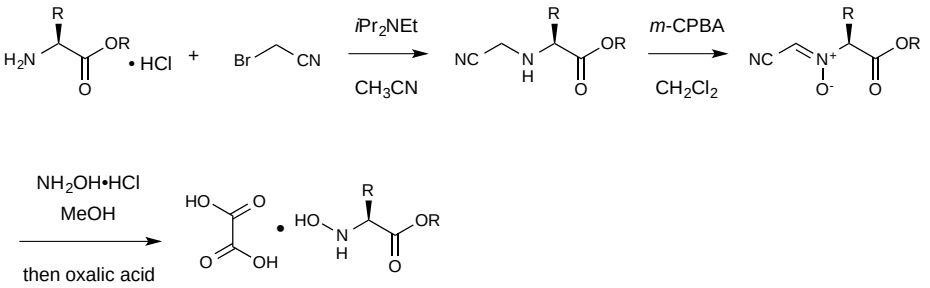
Following the **General Procedure III**, the title compound was prepared from the crude *N*-alkylhydroxylamine obtained from the previous step (1.88 g, 5 mmol, 1.0 equiv), 4-(dimethylamino)benzoic acid (1.0 g, 6 mmol, 1.2 equiv), 1,1'-carbonyldiimidazole (1.0, 6 mmol, 1.2 equiv), and CH_2Cl_2 (15 mL). The title compound was purified by flash column chromatography (Hexanes:EtOAc = 5:1) and obtained as a colorless solid (1.4 g, 2.67 mmol, 53%

overall). **IR (thin film, cm^{-1})** 3228, 2923, 2866, 1699, 1603, 1530, 1497, 1368, 1275, 906, and 727; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.92 (d, *J* = 9.0 Hz, 2H), 7.48-7.30 (m, 5H), 7.20 (d, *J* = 8.5 Hz, 1H), 6.79 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.73 (d, *J* = 2.5 Hz, 1H), 6.69 (d, *J* = 9.0 Hz, 2H), 5.05 (s, 2H), 3.26 (t, *J* = 8.9 Hz, 1H), 3.06 (s, 6H), 2.95-2.78 (m, 2H), 2.35-2.12 (m, 3H), 2.08-1.95 (m, 1H), 1.95-1.85 (m, 1H), 1.85-1.75 (m, 1H), 1.60-1.30 (m, 6H), and 0.92 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 167.2, 156.8, 153.5, 138.1, 137.4, 133.0, 131.2, 128.6, 127.9, 127.5, 126.4, 115.2, 114.9, 112.4, 111.0, 71.0, 70.0, 52.6, 44.0, 43.5, 40.2, 38.7, 38.5, 29.9, 27.6, 26.6, 25.4, 23.7, and 12.1; **HRMS (DART-TOF)** calculated for $C_{34}H_{40}N_2O_3$ $[M+H]^+$ m/z 525.3112, found 525.3118. **$[\alpha]_D^{23}$** = -64.2 (c = 0.5, $CHCl_3$). **Mp**: 167–169 °C.



4-(((((3a*R*,5*S*,6*R*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)amino)oxy)carbonyl)-*N*,*N*-dimethylaniline. Following **General Procedure III**, the title compound was prepared from the known *N*-alkylhydroxylamine [*N*-((3a*R*,5*S*,6*R*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)hydroxylamine[12c]] (1.3 g, 4.7 mmol, 1.0 equiv), 4-(dimethylamino)benzoic acid (1.0 g, 6 mmol, 1.2 equiv), 1,1'-carbonyldiimidazole (1.0, 6 mmol, 1.2 equiv), and CH_2Cl_2 (20 mL). The title compound was purified by flash column chromatography (Hexanes:EtOAc = 4:1) and obtained as a yellow sticky oil (1.3 g, 3.1 mmol, 66% overall). **IR (thin film, cm^{-1})** 3233, 2987, 2937, 1705, 1604, 1531, 1483, 1370, 1275, 1183, 1062, and 1016; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 8.39 (br s, 1H), 7.88 (d, *J* = 8.9 Hz, 2H), 6.69-6.62 (m, 2H), 5.83 (dd, *J* = 3.5, 1.9 Hz, 1H), 4,75 (dd, *J* = 4.3, 4.3 Hz, 1H), 4.26 (ddd, *J* = 5.9, 5.9, 5.9 Hz, 1H), 4.09 (dd, *J* = 6.2, 2.0 Hz, 1H), 3.97 (dd, *J* = 9.4, 5.8 Hz, 1H), 3.63 (dd, *J* = 9.3, 4.3 Hz, 1H), 3.05 (s, 6H), 1.60 (s, 3H), 1.48 (s, 3H), and 1.37 (overlapping s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ: 166.5, 153.6, 131.2, 114.7, 113.2, 110.8, 110.1, 104.7, 79.3, 76.5, 66.5, 65.6, 40.1, 27.0, 26.7, 26.5, and 25.4; **HRMS (DART-TOF)** calculated for $C_{21}H_{30}N_2O_7$ $[M+H]^+$ m/z 423.2126, found 423.2115. **$[\alpha]_D^{23}$** = +107.8 (c = 0.5, $CHCl_3$).

Preparation of *N*-hydroxyamino Esters.



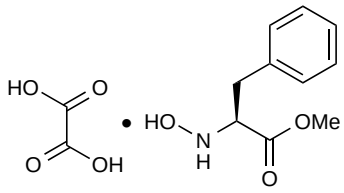
The *N*-hydroxyamino esters were prepared according to a protocol published in *Organic Synthesis*.[13] All of these *N*-hydroxyamino esters were isolated as their oxalic acid salts and stored at 0 °C before use.

An oven-dried round bottom flask was charged with an amino ester hydrochloride salt (1.0 equiv), CH_3CN (0.5 M), and *i*Pr_2NEt (3.0 equiv). After 5 min, bromoacetonitrile (2.0 equiv) was added. The resulting solution was stirred at room temperature for 24 h, and then concentrated *in vacuo*. The crude residue was partitioned between CH_2Cl_2 and saturated aqueous $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by passing through a short column of silica gel (pure hexanes, then hexanes:EtOAc = 3:1).

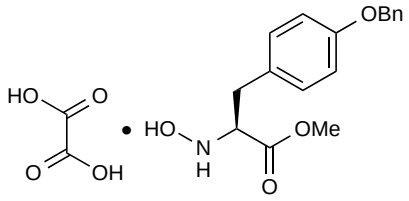
A 1-L round bottom flask was charged with the *N*-alkylated amino ester obtained from the previous step, CH_2Cl_2 (0.3 M), and a large stir bar. The reaction flask was then cooled in an ice batch and vigorously stirred. *m*-CPBA (2.5 equiv) was added to the reaction flask in 20 portions over the course of 30 min. After complete addition, the flask was removed from the ice-bath, and stirred at room temperature for 45 min. The reaction flask was then cooled in an ice-bath again, and aqueous $Na_2S_2O_3$ (2 equiv) and saturated $NaHCO_3$ (60 mL) were added. The resulting mixture was vigorously stirred until the white solid was completely dissolved. The two-phase solution was separated. The aqueous layer was extracted with CH_2Cl_2 (100 mL x 2). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo* to give the nitrone, which was used immediately.

A 1-L round-bottomed flask equipped with a reflux condenser, magnetic stirrer bar, and nitrogen gas inlet was charged with the crude nitrone and MeOH (0.5 M). After addition of hydroxylamine hydrochloride (5 equiv) at ambient temperature, the mixture was warmed to 60 °C and stirred at that temperature for 2 h. The reaction mixture was allowed to cool to room temperature and diluted with CH_2Cl_2. After stirring for 5 min, the resulting precipitate was collected by filtration and the filter cake was washed with CH_2Cl_2. The filtrate was neutralized with saturated $NaHCO_3$ and partitioned. The aqueous phase was extracted with CH_2Cl_2. The

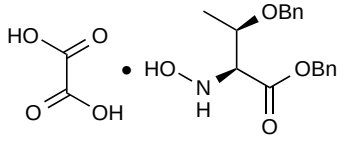
organic phase was washed with brine, dried (Na_2SO_4), filtered, and concentrated to a minimum volume (ca. 10 mL) at a temperature below 25 °C under reduced pressure. To the residue was added a MeOH solution of oxalic acid (5 M, 2 equiv) and Et_2O (50 mL). White crystals precipitated during this process and they were collected by filtration and dried under high vacuum.



Methyl hydroxy-*L*-phenylalaninate oxalate. The title compound were prepared from methyl *L*-phenylalaninate hydrochloride salt (4.3 g, 20 mmol) with an overall yield of 58%. **IR (thin film, cm^{-1})** 3001, 2970, 1750, 1485, 1365, 1217, 1069, 755, 715, and 698; **^{1}H NMR (400 MHz, CD_3OD)** δ: 7.33-7.20 (m, 5H), 4.09 (dd, *J* = 7.8, 6.4 Hz, 1H), 3.68 (s, 3H), 3.10 (dd, *J* = 13.8, 6.4 Hz, 1H), and 3.03 (dd, *J* = 13.8, 7.9 Hz, 1H); **^{13}C NMR (101 MHz, CD_3OD)** δ: 172.4, 164.1, 137.0, 130.5, 129.9, 128.4, 67.4, 53.0, and 35.5; **HRMS (DART-TOF)** calculated for $C_{10}H_{13}NO_3$ $[M+H]^+$ m/z 196.0968, found 196.0965. **$[\alpha]_D^{23}$** = 24.3 (c = 1.0, CH_3OH). **Mp**: 147–148 °C.

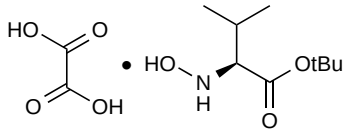


Methyl (*S*)-3-(4-(benzyloxy)phenyl)-2-(hydroxyamino)propanoate oxalate. The title compound were prepared from (*S*)-2-amino-3-(4-(benzyloxy)phenyl)propanoate hydrochloride salt (6.4 g, 20 mmol) with an overall yield of 55%. **IR (thin film, cm^{-1})** 2970, 1752, 1513, 1365, 1252, 1229, 1217, 841, 769, and 734; **^{1}H NMR (400 MHz, CD_3OD)** δ: 7.42 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.1 Hz, 2H), 7.29 (tt, *J* = 7.2, 1.5 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 5.05 (s, 2H), 3.94 (dd, *J* = 7.5, 6.6 Hz, 1H), 3.66 (s, 3H), 2.97 (dd, *J* = 13.9, 6.5 Hz, 1H), and 2.91 (dd, *J* = 13.9, 7.5 Hz, 1H); **^{13}C NMR (101 MHz, CD_3OD)** δ: 173.5, 164.9, 159.5, 138.9, 131.5, 129.7, 129.6, 129.0, 128.7, 116.3, 71.2, 67.9, 52.8, and 35.1; **HRMS (DART-TOF)** calculated for $C_{17}H_{19}NO_4$ $[M+H]^+$ m/z 302.1387, found 302.1380. **$[\alpha]_D^{23}$** = 24.1 (c = 1.0, CH_3OH). **Mp**: 142–144 °C.

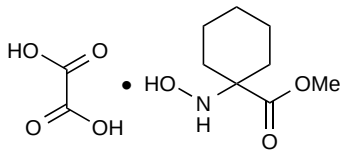


Benzyl *O*-benzyl-*N*-hydroxy-*L*-threoninate oxalate. The title compound was prepared from benzyl *O*-benzyl-*L*-threoninate hydrochloride salt (6.7 g, 20 mmol) with an overall yield of 68%. **IR (thin film, cm^{-1})** 2970, 1742, 1575, 1365, 1217, 742, and 696; **^{1}H NMR (400 MHz, CD_3OD)**

δ: 7.38-7.23 (m, 10H), 5.21 (s, 2H), 4.55 (d, *J* = 11.7 Hz, 1H), 4.40 (d, *J* = 11.7 Hz, 1H), 4.00-3.93 (m, 2H), and 1.28 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR (101 MHz, CD_3OD)** δ: 170.8, 164.1, 139.3, 136.9, 129.82, 129.78, 129.71, 129.6, 129.3, 129.0, 74.2, 72.3, 70.9, 68.6, and 17.1; **HRMS (DART-TOF)** calculated for $C_{18}H_{21}NO_4$ $[M+H]^+$ m/z 316.1543, found 316.1531. **$[\alpha]_D^{23}$** = -32.7 (c = 1.0, CH_3OH). **Mp**: 86–90 °C.

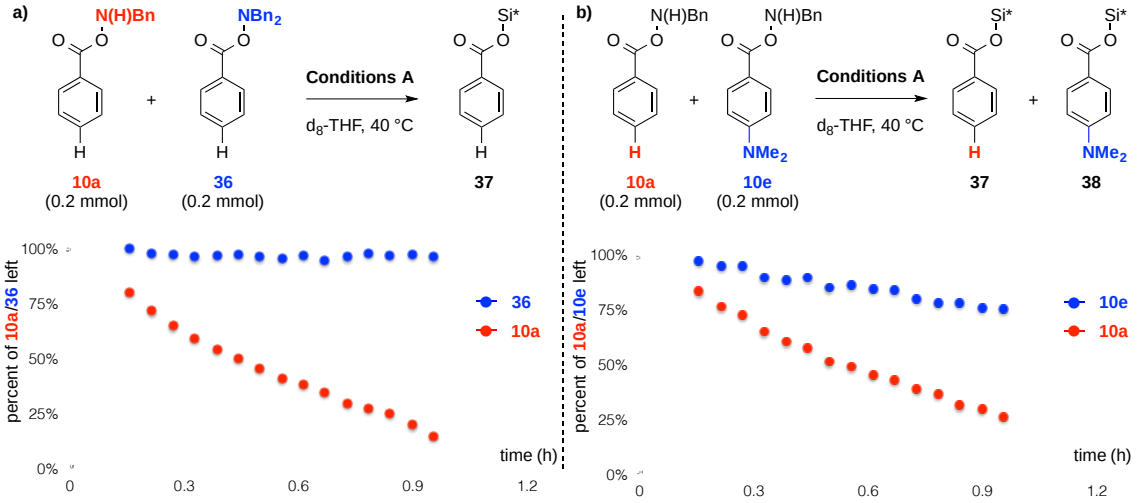


***tert*-Butyl hydroxy-*L*-valinate oxalic acid.** The title compound was prepared from benzyl *tert*-butyl *L*-valinate hydrochloride salt (4.2 g, 20 mmol) in an overall yield of 62%. **IR (thin film, cm^{-1})** 2970, 1736, 1585, 1368, 1217, 1158, 842, and 709; **^{1}H NMR (400 MHz, CD_3OD)** δ: 3.71 (d, *J* = 5.4 Hz, 1H), 2.23 (d of heptet, *J* = 6.9, 5.4 Hz, 1H), 1.53 (s, 9H), 1.11 (d, *J* = 7.0 Hz, 3H), and 1.03 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (101 MHz, CD_3OD)** δ: 169.3, 165.6, 85.0, 71.8, 29.1, 28.5, 20.1, and 18.4; **HRMS (DART-TOF)** calculated for $C_9H_{19}NO_3$ $[M+H]^+$ m/z 190.1438, found 190.1451. **$[\alpha]_D^{23}$** = 11.1 (c = 1.0, CH_3OH). **Mp**: 81–86 °C.



Methyl 1-(hydroxyamino)cyclohexane-1-carboxylate. The title compound was prepared methyl 1-aminocyclohexane-1-carboxylate (3.14 g, 20 mmol) with an overall yield of 73%. **IR (thin film, cm^{-1})** 2970, 1744, 1634, 1557, 1365, 1217, and 764; **^{1}H NMR (400 MHz, CD_3OD)** δ: 3.77 (s, 3H), 2.06-1.98 (m, 2H), 1.75-1.60 (m, 4H), and 1.57-1.35 (m, 4H); **^{13}C NMR (101 MHz, CD_3OD)** δ: 174.7, 165.9, 68.0, 53.1, 31.0, 26.4, and 22.9. **HRMS (DART-TOF)** calculated for $C_8H_{15}NO_3$ $[M+H]^+$ m/z 174.1125, found 174.1122. **Mp**: 138–140 °C.

Mechanistic Experiments (Figure 4)



These experiments were performed according to the following procedure.

In a nitrogen-filled glovebox, an oven-dried, screw-cap reaction tube (13 mm x 100 mm) equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (3.6 mg, 0.02 mmol,), PPh_3 (11 mg, 0.044 mmol, 4.4 mol%) and *R*-DTBM-SEGPHOS (26 mg, 0.022 mmol, 2.2 mol %). D_8-THF (1.0 mL) was added, the reaction tube was closed with a PTFE screw cap equipped with a septum and vigorously stirred at room temperature for 10 min until it was homogeneous. Then $HSiMe(OEt)_2$ (0.32 mL, 2.0 mmol, 2.0 equiv) was added via syringe. The resulting reaction mixture was stirred at room temperature for 15 min and the color of solution changed from blue to orange. A 0.6 mL of this freshly prepared 'LCuH' solution was transferred to a vial containing 1,3,5-trimethoxybenzene (internal standard) and the indicated substrates. [For **experiment a**, **10a** (45.4 mg, 0.2 mmol) and **36** (63.4 mg, 0.2 mmol) were used. For **experiment b**, **10a** (45.4 mg, 0.2 mmol) and **10e** (54.0 mg, 0.2 mmol) were used.] The resulting solution was transferred to a NMR tube, which was then capped and sealed with electrical tape. The NMR tube was taken outside of the glovebox. The reaction progress was directly monitored by ^{1}H NMR spectroscopy. The coil temperature of the NMR instrument were set to be 40 °C for experiment **a** and **b**.

Representative NMR spectra for each experiment with peak assignments are given in the next page. The conversion of amine transfer reagents can be deduced from the integration of the corresponding peaks.

Figure 4a

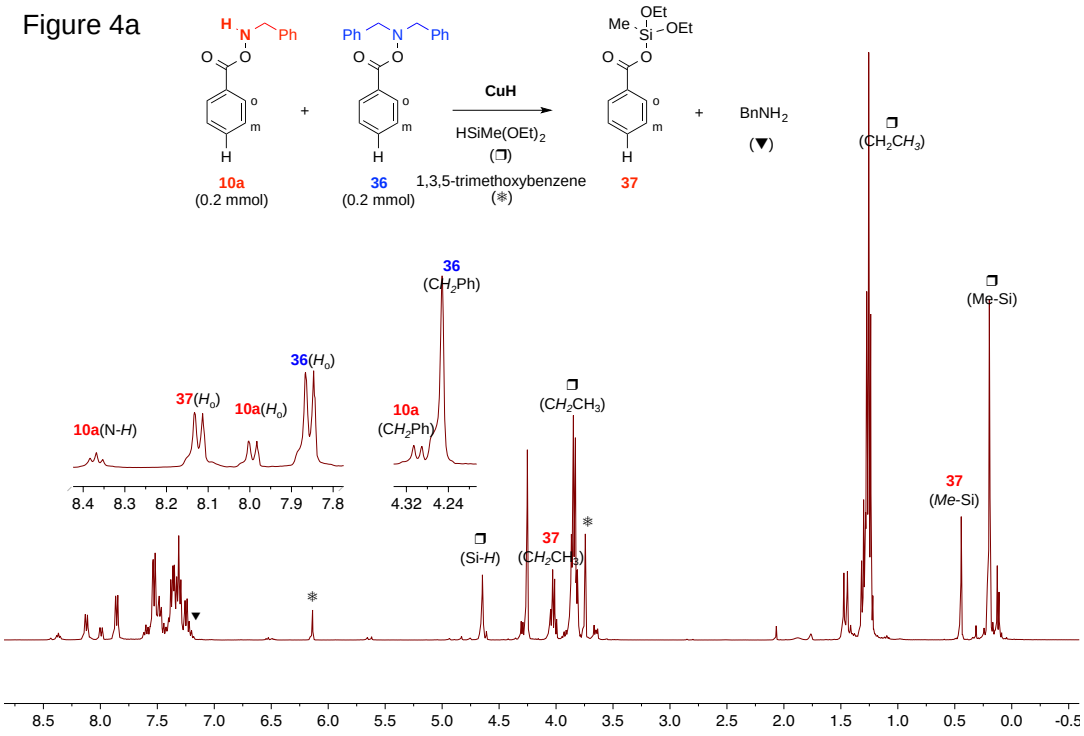
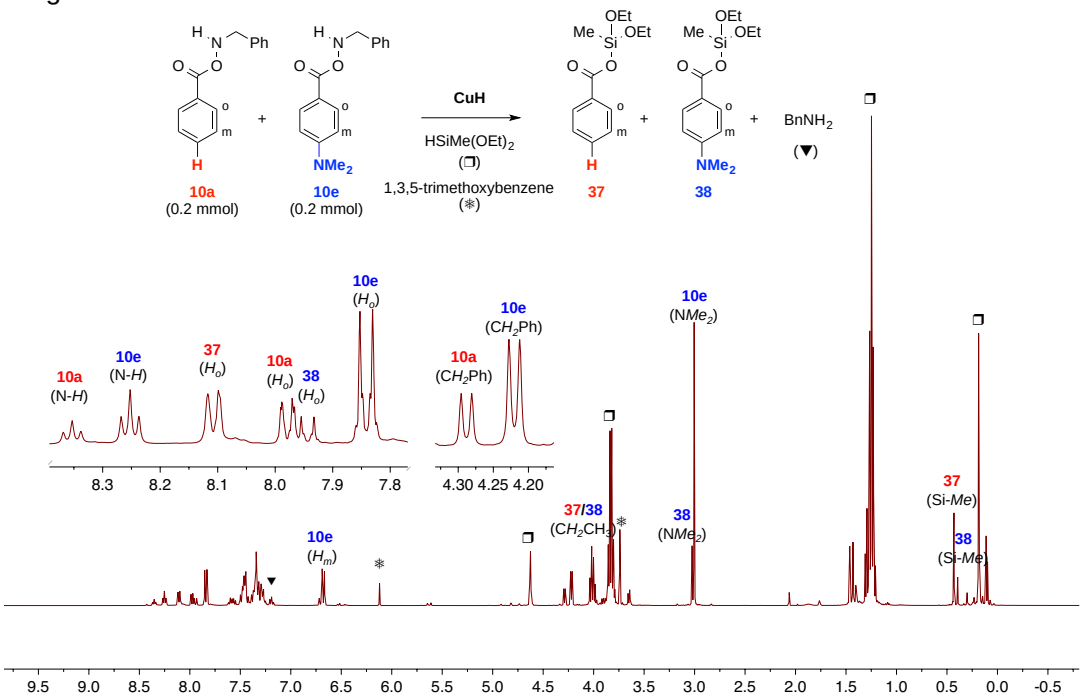


Figure 4b



References

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Analysis Method : C:\CHEM32\2\METHODS\TL-0IPA-100HEX-08MLMIN-15MIN.M
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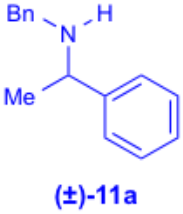
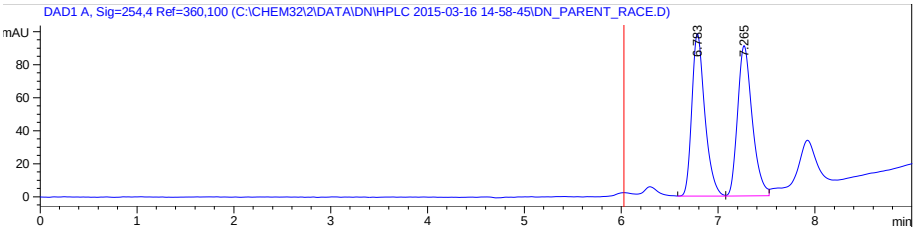


(±)-11a



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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1	6.783	VV	0.1409	919.23590	98.43860	48.9925
2	7.265	VV	0.1586	957.04163	91.04726	51.0075

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==========================================================================
Acq. Operator   : DN                                 Seq. Line :   2
Acq. Instrument : Instrument 2                      Location : Vial 73
Injection Date  : 3/16/2015 3:16:20 PM                   Inj :   1
                                                  Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2015-03-16 14-58-45\DAWENSOLD.M
Last changed    : 3/1/2015 4:36:18 PM by DN
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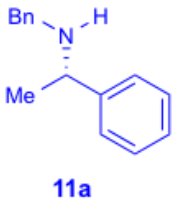
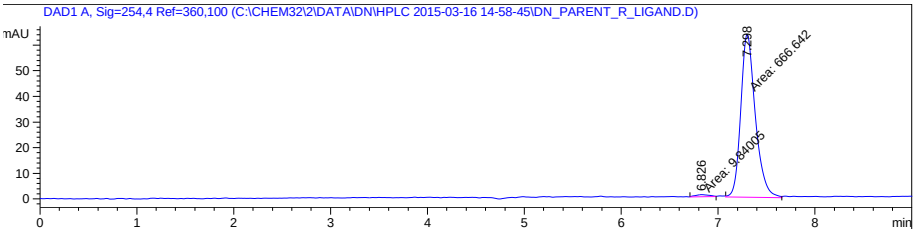


11a



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.826	MM	0.1779	9.84005	9.22016e-1	1.4546
2	7.298	MM	0.1745	666.64233	63.68275	98.5454

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Acq. Instrument : Instrument 2                  Location : Vial 31
Injection Date  : 7/3/2014 4:47:14 PM                Inj :   1
                                              Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
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Last changed    : 2/11/2015 1:00:17 PM by TL
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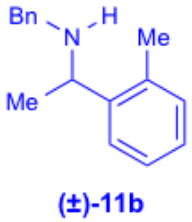
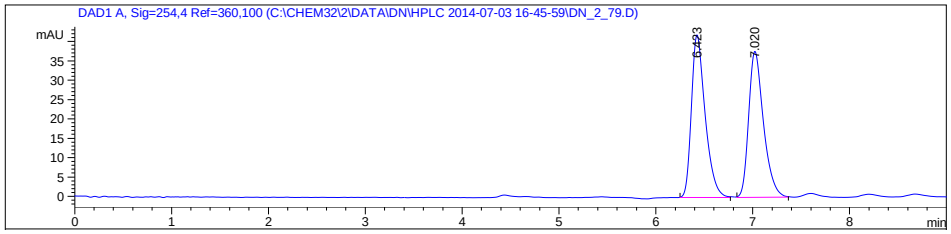


(±)-11b



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Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.423	BB	0.1470	413.79691	41.97137	50.7746
2	7.020	BB	0.1601	401.17093	37.71676	49.2254

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                                              Inj Volume : 5 µl
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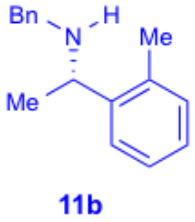
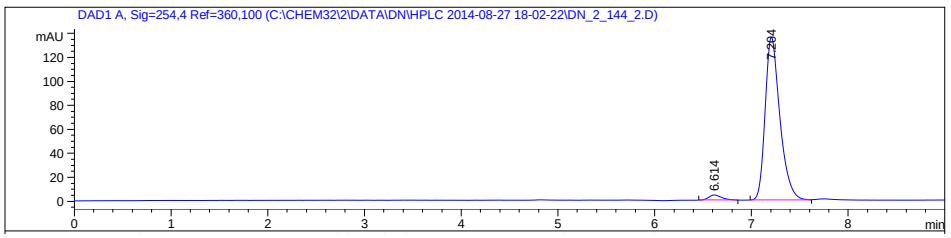


11b



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.614	BB	0.1406	41.05008	4.32862	2.7738
2	7.204	BB	0.1594	1438.86963	136.00056	97.2262

```
Acq. Operator   : DN                              Seq. Line :   1
Acq. Instrument : Instrument 2                     Location : Vial 51
Injection Date  : 8/27/2014 1:50:59 PM                  Inj :   1
                                                  Inj Volume : 5 µl
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Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
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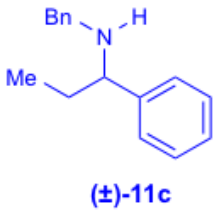
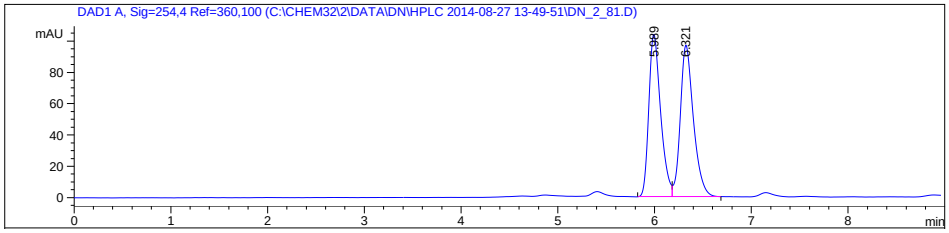


(±)-11c



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.989	BV	0.1291	881.09485	103.71407	49.1512
2	6.321	VB	0.1419	911.52771	96.77612	50.8488

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Acq. Operator   : DN                              Seq. Line :   2
Acq. Instrument : Instrument 2                     Location : Vial 52
Injection Date  : 8/27/2014 2:03:14 PM                  Inj :   1
                                                  Inj Volume : 5 µl
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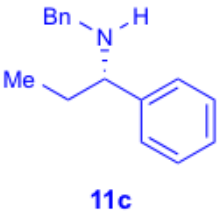
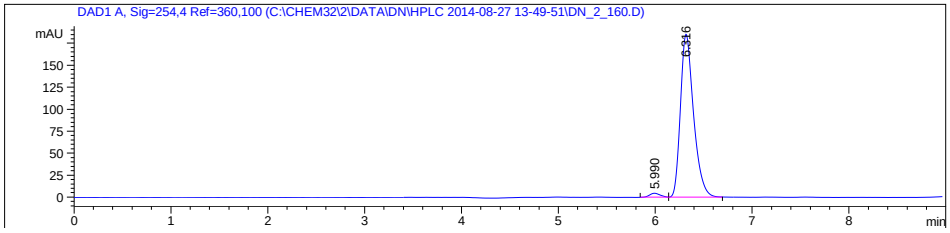


11c



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1	5.990	BV	0.1199	35.68318	4.62854	2.0061
2	6.316	VB	0.1418	1743.02661	185.25781	97.9939

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Acq. Instrument : Instrument 2                  Location : Vial 43
Injection Date  : 7/5/2014 2:12:38 PM                Inj :   1
                                                Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2014-07-05 14-11-27\DAWENOD.M
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Last changed    : 2/11/2015 1:00:17 PM by TL
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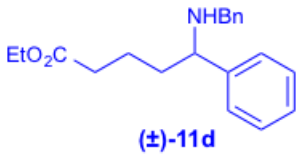

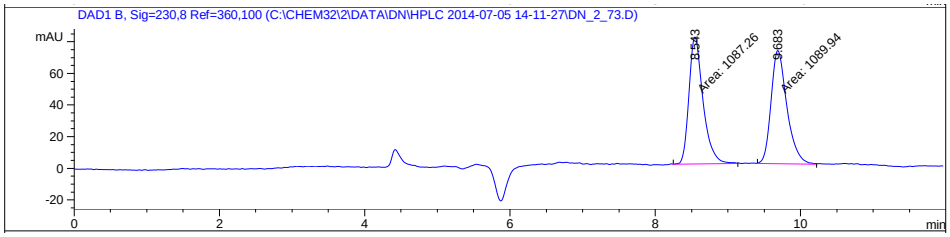

Signal 2: DAD1 B, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.543	BB	0.2017	206.84312	15.50019	49.8440
2	9.685	BB	0.2262	208.13789	13.78047	50.1560

```
Acq. Operator   : DN                           Seq. Line :   1
Acq. Instrument : Instrument 2                  Location : Vial 34
Injection Date  : 8/27/2014 6:58:26 PM               Inj :   1
                                                Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 15 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2014-08-27 18-57-10\DAWENOD.M
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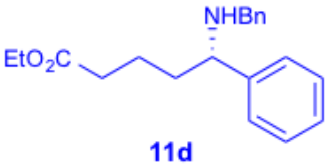

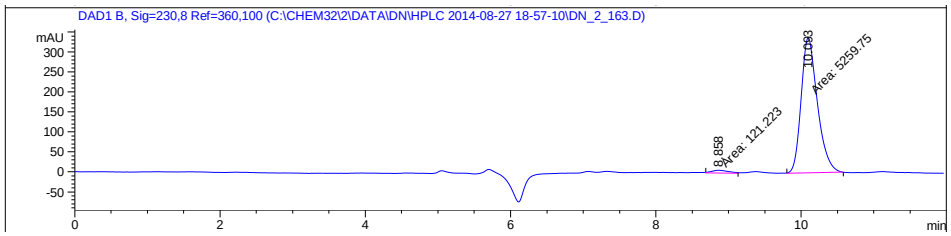

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Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.858	MM	0.2780	121.22332	7.26886	2.2528
2	10.093	MM	0.2592	5259.74951	338.18640	97.7472

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Acq. Instrument : Instrument 2                     Location : Vial 5
Injection Date  : 2/27/2015 5:48:37 PM                  Inj :   1
                                                  Inj Volume : 5 µl
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Last changed    : 2/27/2015 9:12:01 AM by TL
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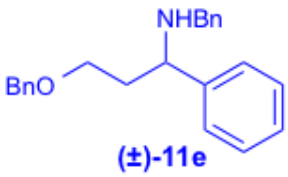

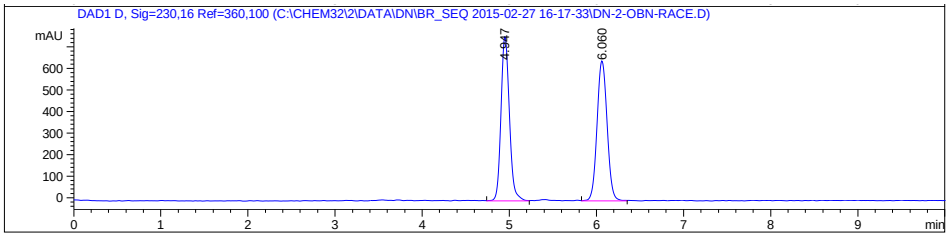

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.947	VV	0.1065	5135.20850	763.53723	49.4928
2	6.060	VV	0.1260	5240.46924	650.17651	50.5072

```
Acq. Operator   : DN                              Seq. Line :   1
Acq. Instrument : Instrument 2                     Location : Vial 6
Injection Date  : 2/27/2015 6:22:34 PM                  Inj :   1
                                                  Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\BR_SEQ 2015-02-27 18-13-31\DAWENSOLD.M
Last changed    : 2/27/2015 6:13:29 PM by DN
Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
Last changed    : 2/27/2015 9:12:01 AM by TL
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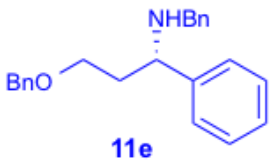

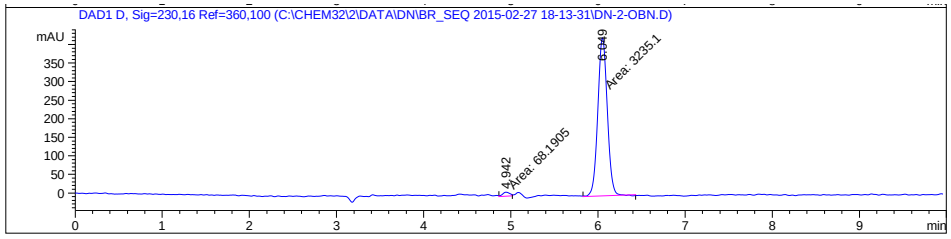

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.944	MM	0.1058	62.81025	9.89650	1.8657
2	6.049	MM	0.1283	3303.83081	429.14206	98.1343

```
Acq. Operator   : SSL                          Seq. Line :   1
Acq. Instrument : Instrument 2                  Location : Vial 33
Injection Date  : 7/3/2014 5:21:07 PM                Inj :   1
                                                Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2014-07-03 17-19-55\DAWENOD.M
Last changed    : 7/3/2014 4:20:08 PM by SSL
Analysis Method : C:\CHEM32\2\METHODS\TL-10IPA-90HEX-12MLMIN-60MIN.M
Last changed    : 2/11/2015 1:00:17 PM by TL
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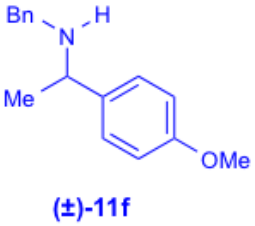
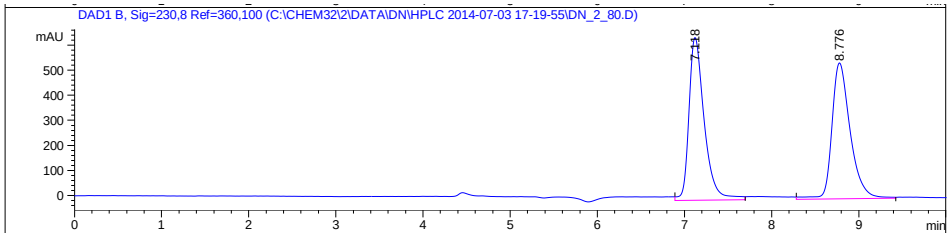


(±)-11f



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.119	BB	0.1600	439.89423	40.74548	49.8578
2	8.776	BB	0.2019	442.40430	33.10107	50.1422

```
Acq. Operator   : SSL                          Seq. Line :   1
Acq. Instrument : Instrument 2                  Location : Vial 34
Injection Date  : 7/3/2014 5:42:47 PM                Inj :   1
                                                Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2014-07-03 17-41-33\DAWENOD.M
Last changed    : 7/3/2014 4:20:08 PM by SSL
Analysis Method : C:\CHEM32\2\METHODS\TL-10IPA-90HEX-12MLMIN-60MIN.M
Last changed    : 2/11/2015 1:00:17 PM by TL
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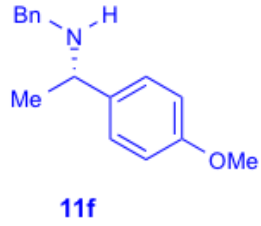
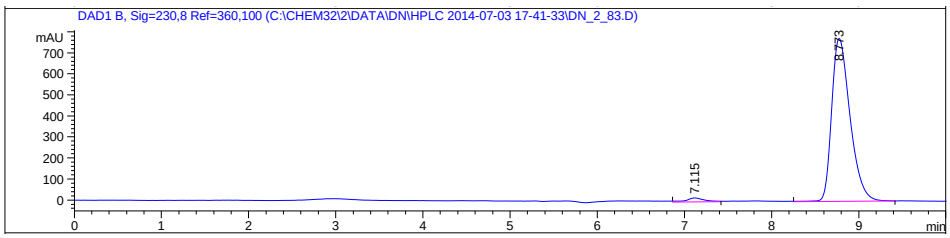


11f



Signal 2: DAD1 B, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.115	BV	0.2208	322.76465	20.16282	2.7552
2	8.773	VB	0.2254	1.13922e4	775.50659	97.2448

```
Acq. Operator   : DN                              Seq. Line :   3
Acq. Instrument : Instrument 2                     Location : Vial 41
Injection Date  : 4/23/2015 1:50:55 PM                 Inj :   1
                                                  Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2015-04-23 13-23-58\DAWENSOLD.M
Last changed    : 4/23/2015 1:38:04 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\MTP-02IPA-08ML-MIN-30MIN.M
Last changed    : 4/22/2015 7:05:24 PM by TL
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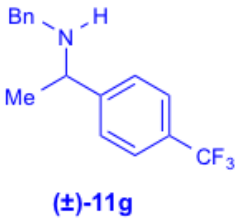
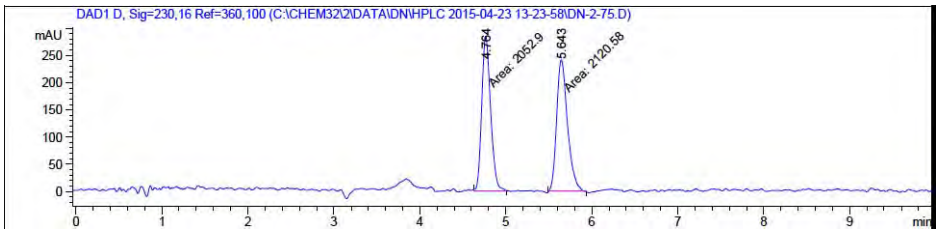


(±)-11g



Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.764	MM	0.1199	2052.90039	285.44147	49.1892
2	5.643	MM	0.1461	2120.58154	241.87518	50.8108

```
Acq. Operator   : DN                              Seq. Line :   2
Acq. Instrument : Instrument 2                     Location : Vial 42
Injection Date  : 4/23/2015 1:39:36 PM                 Inj :   1
                                                  Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2015-04-23 13-23-58\DAWENSOLD.M
Last changed    : 4/23/2015 1:38:04 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\MTP-02IPA-08ML-MIN-30MIN.M
Last changed    : 4/22/2015 7:05:24 PM by TL
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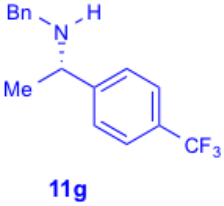
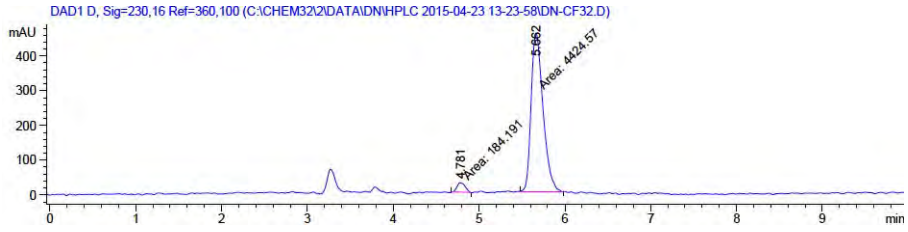


11g



Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.781	MM	0.1127	184.19069	27.24119	3.9965
2	5.662	MM	0.1614	4424.57422	457.01447	96.0035

```
Acq. Operator   : DN                          Seq. Line :   2
Acq. Instrument : Instrument 2                 Location : Vial 1
Injection Date  : 3/1/2015 4:53:57 PM               Inj :   1
                                              Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\BR_SEQ 2015-03-01 16-36-32\DAWENSOLD.M
Last changed    : 3/1/2015 4:53:08 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
Last changed    : 2/27/2015 9:12:01 AM by TL
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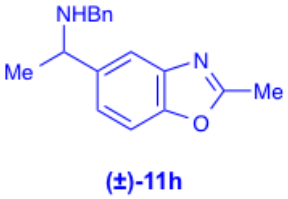
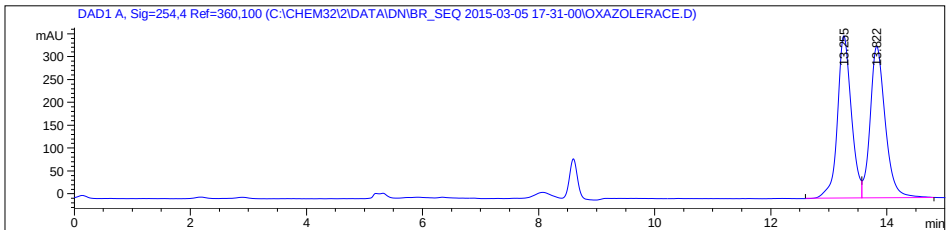


(±)-11h



Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.980	BV	0.2375	3049.63916	193.88722	49.1351
2	13.554	VB	0.2587	3157.00488	183.47958	50.8649

```
Acq. Operator   : DN                          Seq. Line :   1
Acq. Instrument : Instrument 2                 Location : Vial 65
Injection Date  : 3/5/2015 5:33:27 PM               Inj :   1
                                              Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\BR_SEQ 2015-03-05 17-31-00\DAWENSOLD.M
Last changed    : 3/5/2015 6:03:55 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
Last changed    : 2/27/2015 9:12:01 AM by TL
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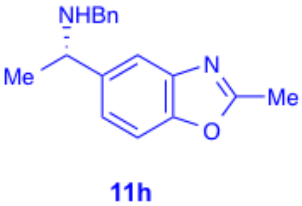
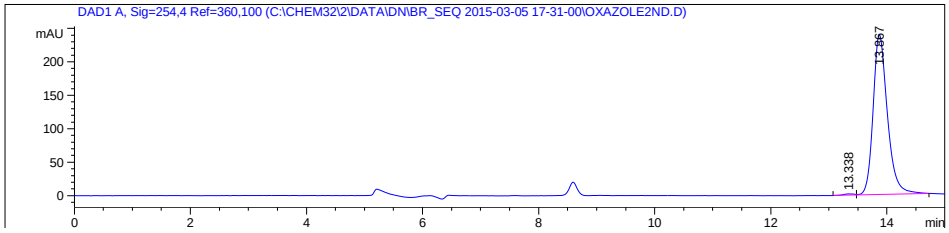


11h



Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.343	BV	0.1758	41.86881	3.13467	0.7178
2	13.867	VB	0.2627	5790.82324	333.22842	99.2822

```
Acq. Operator   : DN                              Seq. Line :   4
Acq. Instrument : Instrument 2                     Location : Vial 67
Injection Date  : 3/5/2015 6:34:06 PM                   Inj :   1
                                                 Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\BR_SEQ 2015-03-05 17-31-00\DAWENSOLD.M
Last changed    : 3/5/2015 6:33:53 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
Last changed    : 2/27/2015 9:12:01 AM by TL
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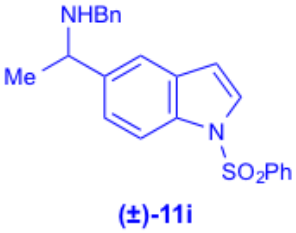
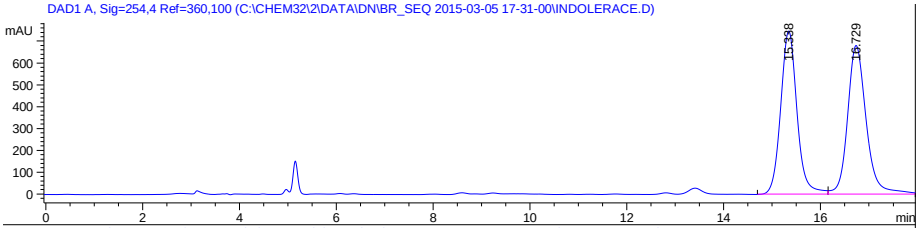


(±)-11i



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.338	BV	0.3605	1.75876e4	747.62280	49.0614
2	16.729	VBA	0.4085	1.82605e4	681.64337	50.9386

```
Acq. Operator   : DN                              Seq. Line :   5
Acq. Instrument : Instrument 2                     Location : Vial 68
Injection Date  : 3/5/2015 6:53:27 PM                   Inj :   1
                                                 Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\BR_SEQ 2015-03-05 17-31-00\DAWENSOLD.M
Last changed    : 3/5/2015 6:33:53 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
Last changed    : 2/27/2015 9:12:01 AM by TL
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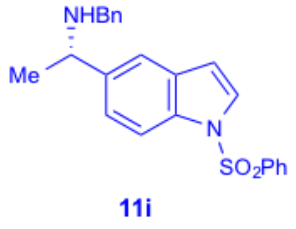
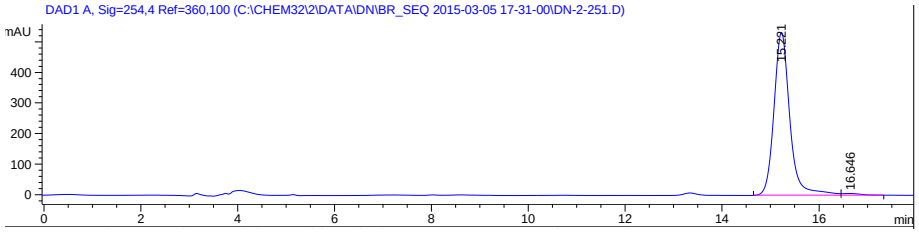


11i



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.221	BV	0.3461	1.21669e4	533.46332	98.6055
2	16.646	VB	0.3400	172.07022	6.11989	1.3945

```
Acq. Operator   : DN                              Seq. Line :   3
Acq. Instrument : Instrument 2                     Location : Vial 63
Injection Date  : 3/5/2015 3:59:54 PM                   Inj :   1
                                                  Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 4 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\BR_SEQ 2015-03-05 15-12-53\5IPA30.M
Last changed    : 3/5/2015 3:14:04 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
Last changed    : 2/27/2015 9:12:01 AM by TL
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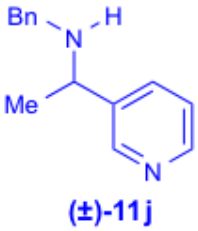
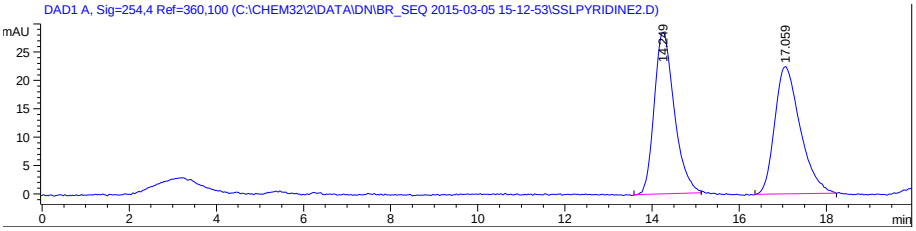


(±)-11j



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.249	BB	0.4737	914.80493	28.55936	49.9806
2	17.059	BB	0.4932	915.51410	22.47780	50.0194

```
Acq. Operator   : DN                              Seq. Line :   2
Acq. Instrument : Instrument 2                     Location : Vial 64
Injection Date  : 3/5/2015 3:37:57 PM                   Inj :   1
                                                  Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\BR_SEQ 2015-03-05 15-12-53\5IPA30.M
Last changed    : 3/5/2015 3:14:04 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
Last changed    : 2/27/2015 9:12:01 AM by TL
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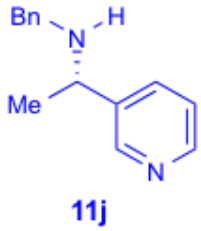
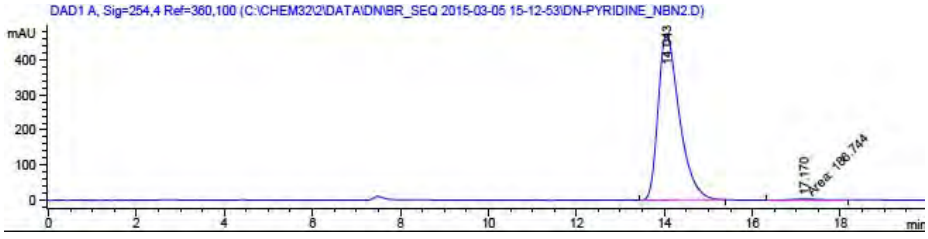


11j



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.043	VB	0.5041	1.58726e4	474.65018	98.8372
2	17.170	MM	0.8361	186.74406	3.72264	1.1628

```
Acq. Operator   : DN                          Seq. Line :   3
Acq. Instrument : Instrument 2                 Location : Vial 75
Injection Date  : 3/16/2015 6:31:37 PM              Inj :   1
                                             Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2015-03-16 18-07-33\DAWENSOLD.M
Last changed    : 3/16/2015 6:18:52 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\80A20C.M
Last changed    : 3/19/2015 4:44:13 PM by TL
Method Info     : 8020
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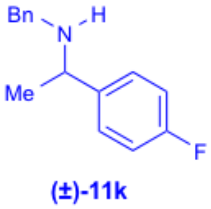
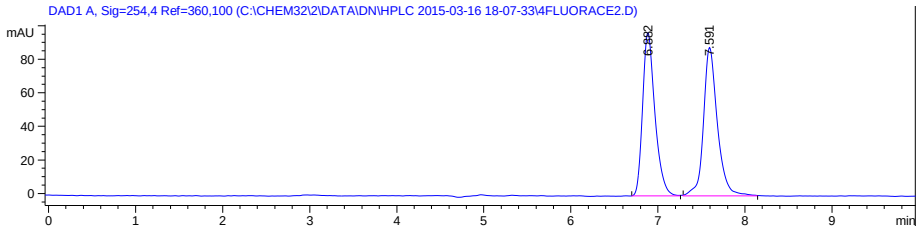


(±)-11k



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.882	BB	0.1490	959.87958	97.39813	49.3366
2	7.591	BB	0.1639	985.69366	88.50294	50.6634

```
Acq. Operator   : DN                          Seq. Line :   2
Acq. Instrument : Instrument 2                 Location : Vial 76
Injection Date  : 3/16/2015 6:20:14 PM              Inj :   1
                                             Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2015-03-16 18-07-33\DAWENSOLD.M
Last changed    : 3/16/2015 6:18:52 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\80A20C.M
Last changed    : 3/19/2015 4:44:13 PM by TL
Method Info     : 8020
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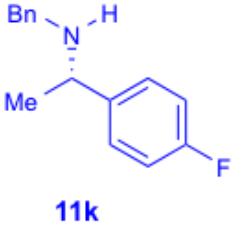
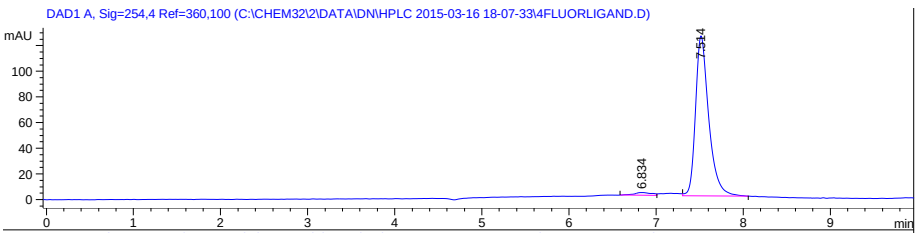


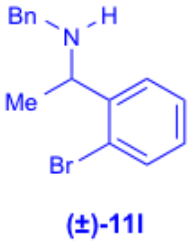
11k



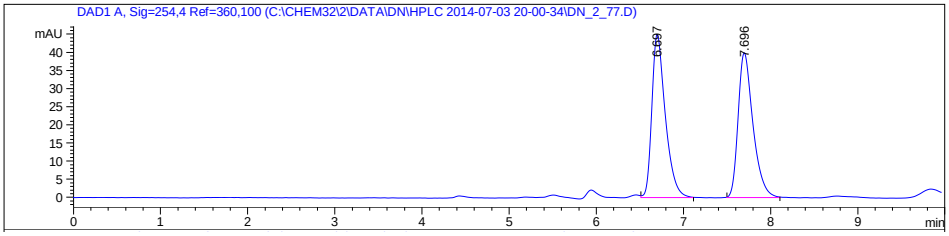
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.834	BV	0.2072	32.70732	2.20277	2.4168
2	7.514	VB	0.1576	1320.61694	124.67675	97.5832

```
Acq. Operator   : SSL                          Seq. Line :   1
Acq. Instrument : Instrument 2                  Location : Vial 38
Injection Date  : 7/3/2014 8:01:45 PM                Inj :   1
                                                Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2014-07-03 20-00-34\DAWENOD.M
Last changed    : 7/3/2014 8:11:17 PM by SSL
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\TL-10IPA-90HEX-12MLMIN-60MIN.M
Last changed    : 2/11/2015 1:00:17 PM by TL
```



(±)-11l



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.697	VB	0.1593	484.11246	45.06394	50.5784
2	7.696	BB	0.1782	473.04083	39.94307	49.4216

```
Acq. Operator   : SSL                          Seq. Line :   1
Acq. Instrument : Instrument 2                  Location : Vial 39
Injection Date  : 7/3/2014 8:14:08 PM                Inj :   1
                                                Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2014-07-03 20-12-58\DAWENOD.M
Last changed    : 7/3/2014 8:12:56 PM by SSL
Analysis Method : C:\CHEM32\2\METHODS\TL-10IPA-90HEX-12MLMIN-60MIN.M
Last changed    : 2/11/2015 1:00:17 PM by TL
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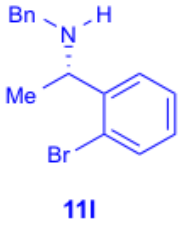
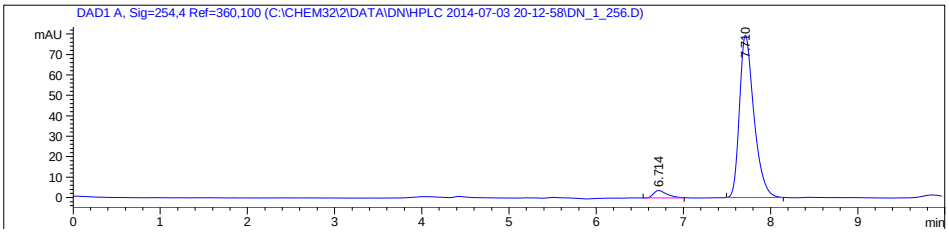


11l



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.714	BB	0.1628	40.41227	3.65965	4.2140
2	7.710	BB	0.1727	918.57794	79.56304	95.7860

```
Acq. Operator   : DN                              Seq. Line :   2
Acq. Instrument : Instrument 2                     Location : Vial 2
Injection Date  : 12/22/2014 4:36:26 PM                 Inj :   1
                                                  Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 8 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2014-12-22 16-07-22\DAWENOD.M
Last changed    : 12/22/2014 4:34:19 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\TL-10IPA-90HEX-12MLMIN-60MIN.M
Last changed    : 2/11/2015 1:00:17 PM by TL
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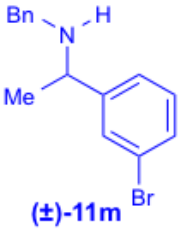

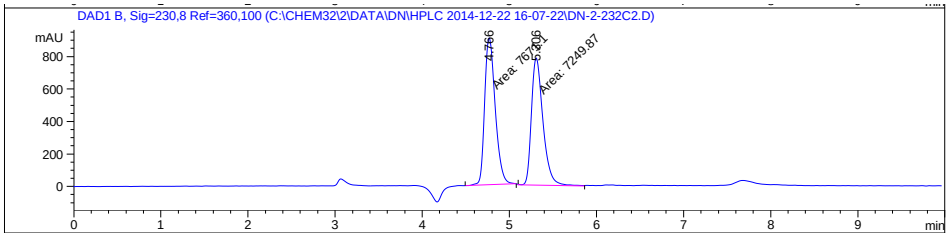

Signal 2: DAD1 B, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.766	MM	0.1422	7735.05371	906.78662	51.8910
2	5.306	MM	0.1527	7171.29346	782.87598	48.1090

```
Acq. Operator   : DN                              Seq. Line :   1
Acq. Instrument : Instrument 2                     Location : Vial 1
Injection Date  : 12/27/2014 6:01:54 PM                 Inj :   1
                                                  Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\DEF_LC 2014-12-27 18-00-03\DAWENOD.M
Last changed    : 12/27/2014 6:00:21 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
Last changed    : 2/27/2015 9:12:01 AM by TL
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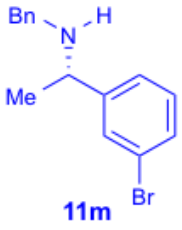
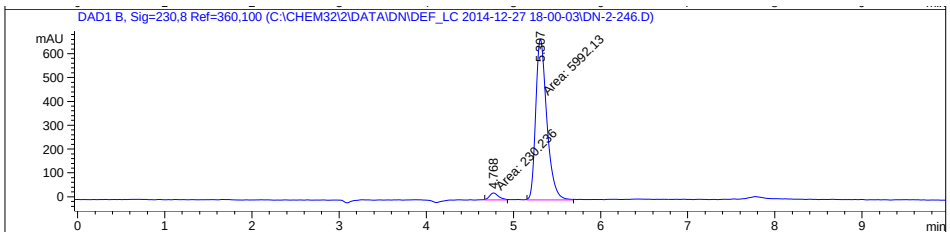


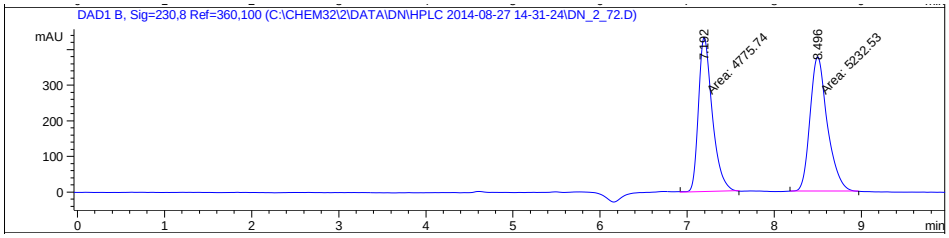


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.769	BB	0.1051	19.12051	2.75019	2.9391
2	5.307	BB	0.1256	631.44208	75.47887	97.0609

```
Acq. Operator   : DN                              Seq. Line :   1
Acq. Instrument : Instrument 2                     Location : Vial 54
Injection Date  : 8/27/2014 2:32:35 PM                  Inj :   1
                                                  Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2014-08-27 14-31-24\DAWENOD.M
Last changed    : 8/27/2014 2:41:27 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
Last changed    : 2/27/2015 9:12:01 AM by TL
```

(±)-11n

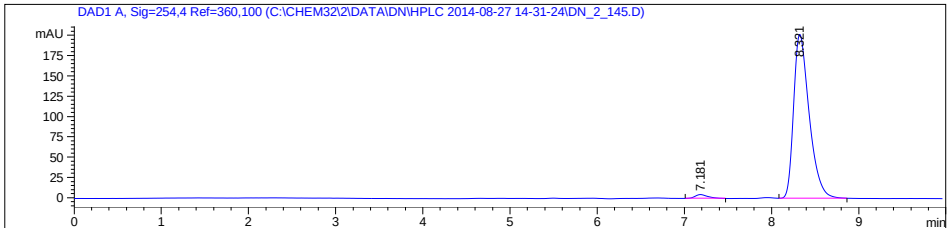


Signal 2: DAD1 B, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.192	MM	0.1838	4775.74268	433.07269	47.7180
2	8.496	MM	0.2310	5232.52539	377.47882	52.2820

```
Acq. Operator   : DN                              Seq. Line :   2
Acq. Instrument : Instrument 2                     Location : Vial 55
Injection Date  : 8/27/2014 2:43:54 PM                  Inj :   1
                                                  Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2014-08-27 14-31-24\DAWENOD.M
Last changed    : 8/27/2014 2:41:27 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\TL-10IPA-90HEX-12MLMIN-60MIN.M
Last changed    : 2/11/2015 1:00:17 PM by TL
```

11n



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.181	BB	0.1538	48.89185	4.75964	1.9097
2	8.321	VB	0.1890	2511.35059	202.01109	98.0903

```
Acq. Operator   : NDW                          Seq. Line :   1
Acq. Instrument : Instrument 2                  Location : Vial 2
Injection Date  : 12/10/2014 2:06:27 PM              Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2014-12-10 14-04-02\DAWENOD.M
Last changed    : 12/10/2014 2:04:20 PM by NDW
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
Last changed    : 2/27/2015 9:12:01 AM by TL
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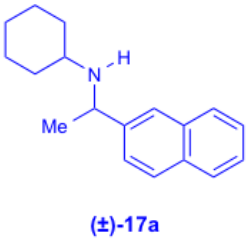
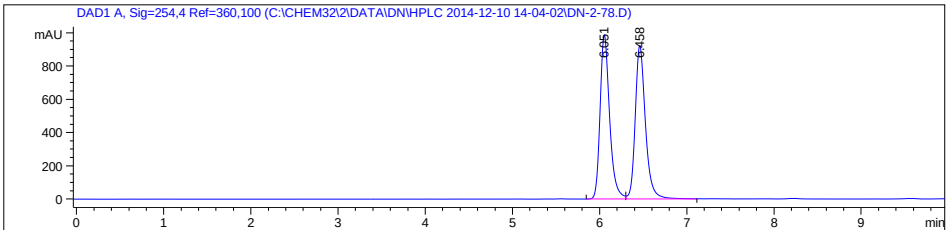


(±)-17a



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.051	BV	0.1163	7479.64551	988.20490	49.9271
2	6.458	VB	0.1228	7501.49805	922.78912	50.0729

```
Acq. Operator   : NDW                          Seq. Line :   2
Acq. Instrument : Instrument 2                  Location : Vial 4
Injection Date  : 12/10/2014 2:17:47 PM              Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2014-12-10 14-04-02\DAWENOD.M
Last changed    : 12/10/2014 2:04:20 PM by NDW
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\TL-10IPA-90HEX-12MLMIN-60MIN.M
Last changed    : 2/11/2015 1:00:17 PM by TL
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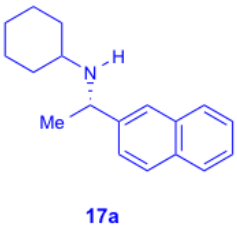
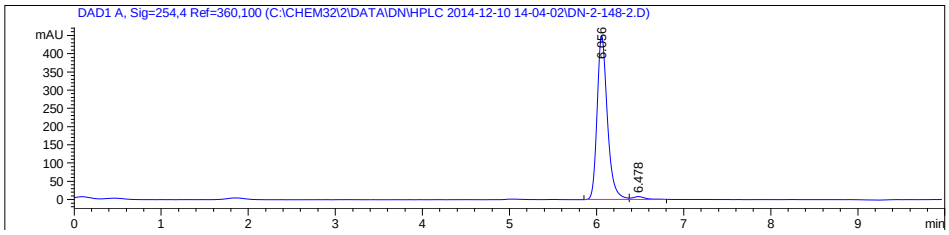


17a



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.056	BV	0.1255	3679.76294	449.67105	97.7161
2	6.478	VB	0.1543	86.00663	8.20296	2.2839

```
Acq. Operator   : DN                              Seq. Line :   1
Acq. Instrument : Instrument 2                     Location : Vial 61
Injection Date  : 3/5/2015 2:19:00 PM                   Inj :   1
                                                  Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\BR_SEQ 2015-03-05 14-16-34\DAWENSOLD.M
Last changed    : 3/1/2015 4:36:18 PM by DN
Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
Last changed    : 2/27/2015 9:12:01 AM by TL
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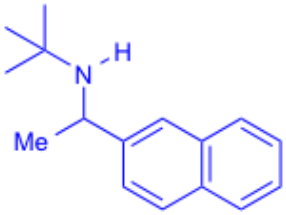
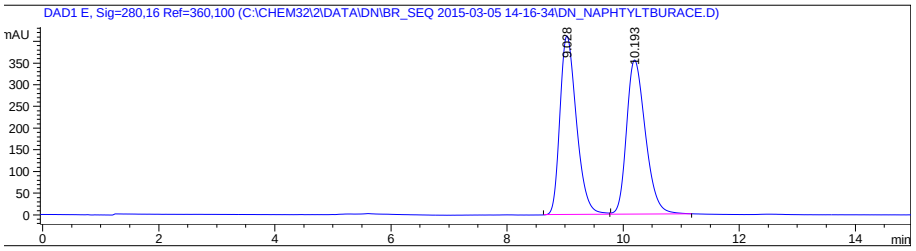


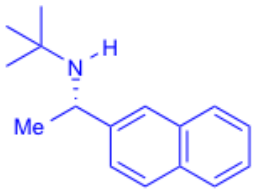
(±)-17b



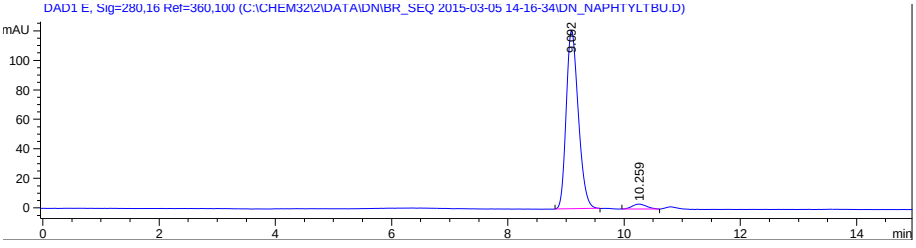
Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.028	BB	0.3053	8165.65137	411.93262	50.3805
2	10.193	BB	0.3479	8042.32031	355.56635	49.6195

```
Acq. Operator   : DN                              Seq. Line :   2
Acq. Instrument : Instrument 2                     Location : Vial 62
Injection Date  : 3/5/2015 2:35:16 PM                   Inj :   1
                                                  Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\BR_SEQ 2015-03-05 14-16-34\DAWENSOLD.M
Last changed    : 3/1/2015 4:36:18 PM by DN
Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
Last changed    : 2/27/2015 9:12:01 AM by TL
```

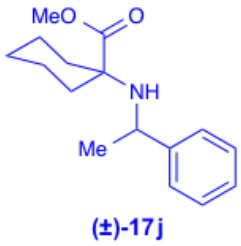


17b



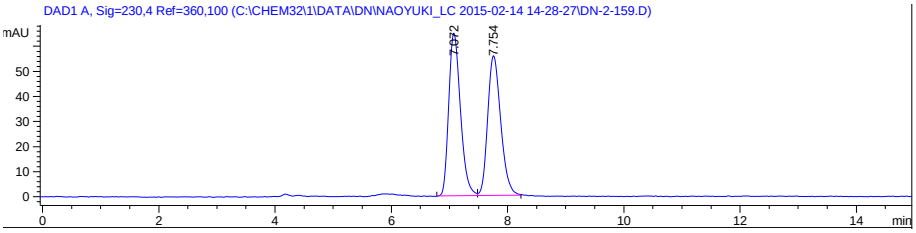
Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.092	BB	0.2246	1743.94104	120.65137	96.7023
2	10.259	BV	0.2399	59.47155	3.36951	3.2977



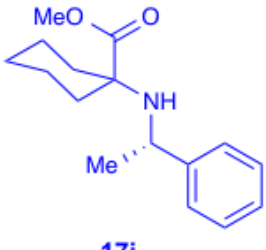
(±)-17j

```
Acq. Operator   : DN                          Seq. Line :   2
Acq. Instrument : Instrument 1                 Location : Vial 41
Injection Date  : 2/14/2015 2:48:05 PM              Inj :   1
                                              Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\1\DATA\DN\NAOYUKI_LC 2015-02-14 14-28-27\NN-3IPA-08ML-MIN-15MIN.M
Last changed    : 2/2/2015 1:38:20 PM by JEFF
Analysis Method : C:\CHEM32\1\METHODS\1IPA30 MIN.M
Last changed    : 2/19/2015 11:33:52 AM by SANDRA
Sample Info     : \
```



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.072	BV	0.2201	914.64307	65.01470	51.1410
2	7.754	VB	0.2405	873.82898	55.85737	48.8590



17j

```
Acq. Operator   : DN                          Seq. Line :   1
Acq. Instrument : Instrument 1                 Location : Vial 49
Injection Date  : 2/14/2015 2:31:16 PM              Inj :   1
                                              Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\1\DATA\DN\NAOYUKI_LC 2015-02-14 14-28-27\NN-3IPA-08ML-MIN-15MIN.M
Last changed    : 2/2/2015 1:38:20 PM by JEFF
Analysis Method : C:\CHEM32\1\METHODS\1IPA30 MIN.M
Last changed    : 2/19/2015 11:33:52 AM by SANDRA
Sample Info     : \
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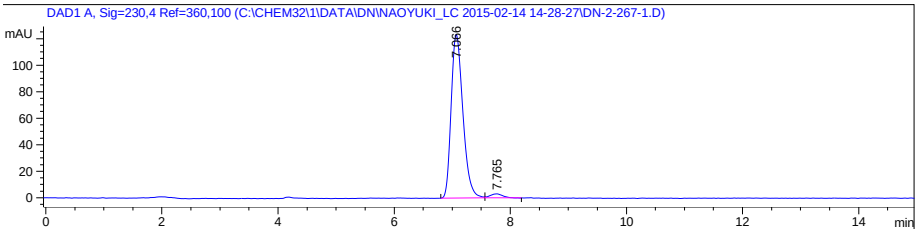

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.066	BB	0.2181	1734.39441	123.28972	97.3475
2	7.765	BB	0.1988	47.25754	3.11872	2.6525

```
Acq. Operator   : DN                              Seq. Line :   4
Acq. Instrument : Instrument 1                     Location : Vial 1
Injection Date  : 3/2/2015 4:59:49 PM                   Inj :   1
                                                 Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\CHEM32\1\DATA\DN\NAOYUKI_LC 2015-03-02 15-09-34\DAWENSOLB.M
Last changed    : 3/2/2015 4:58:01 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\1IPA30 MIN.M
Last changed    : 2/19/2015 11:33:52 AM by SANDRA
Sample Info     : \
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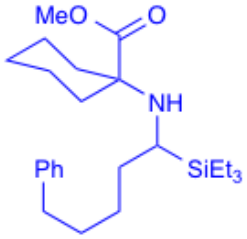
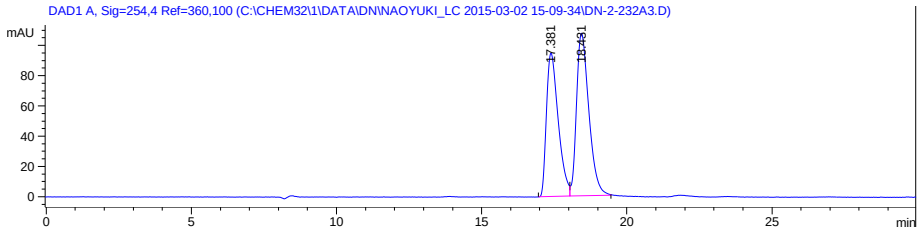


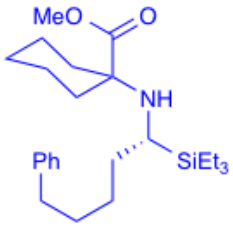
(±)-17k



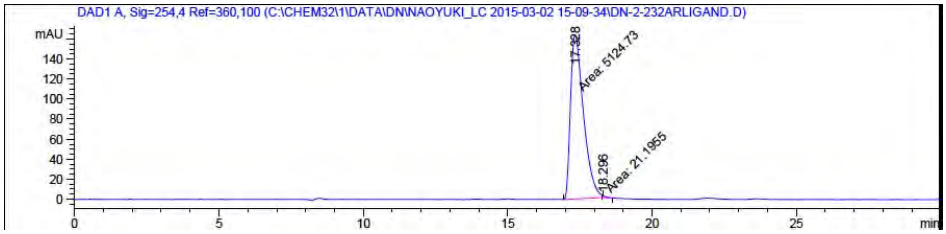
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.381	BV	0.4217	2680.56372	94.84821	45.7241
2	18.431	VB	0.4492	3181.91431	107.53085	54.2759

```
Acq. Operator   : DN                              Seq. Line :   5
Acq. Instrument : Instrument 1                     Location : Vial 2
Injection Date  : 3/2/2015 5:30:55 PM                   Inj :   1
                                                 Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\CHEM32\1\DATA\DN\NAOYUKI_LC 2015-03-02 15-09-34\DAWENSOLB.M
Last changed    : 3/2/2015 4:58:01 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\80A20C.M
Last changed    : 3/19/2015 4:44:13 PM by TL
Method Info     : 8020
```

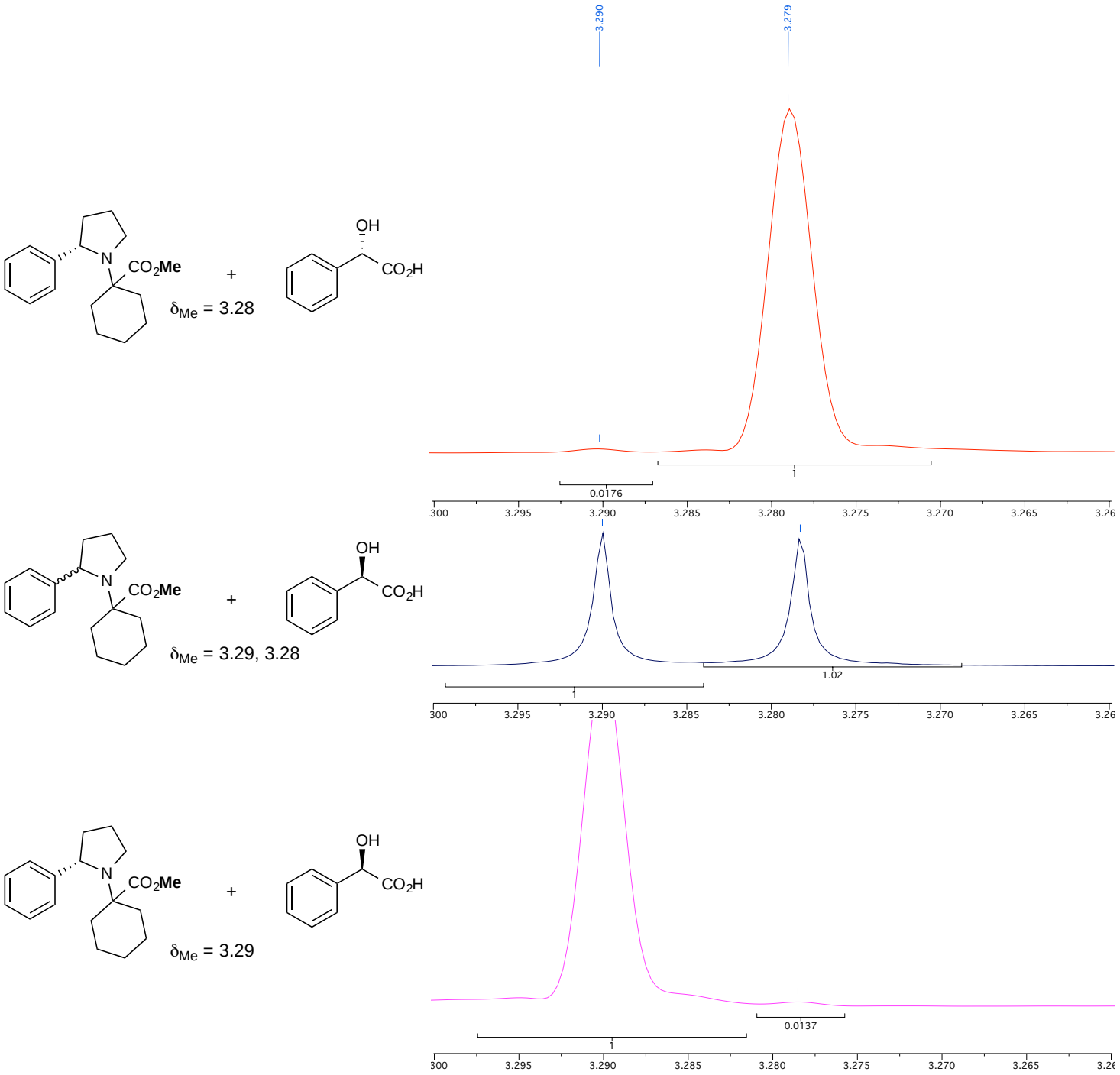


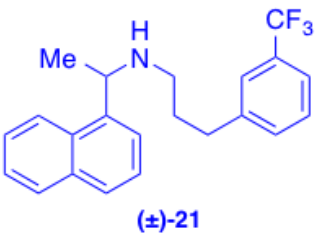
17k



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

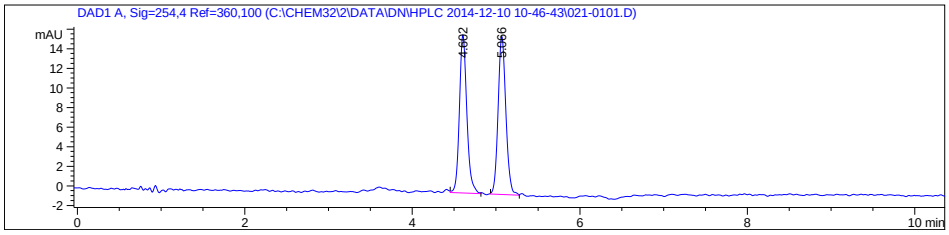
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.328	MM	0.5204	5124.72754	164.11389	99.5881
2	18.296	MM	0.1659	21.19547	2.12917	0.4119


3.290
3.279
OH
N
CO2Me
CO2H
+
δMe = 3.28
0.0176
1
3.300
3.295
3.290
3.285
3.280
3.275
3.270
3.265
OH
N
CO2Me
CO2H
+
δMe = 3.29, 3.28
1.02
1
OH
N
CO2Me
CO2H
+
δMe = 3.29
0.0137
1



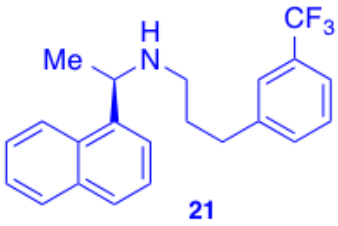
(±)-21

```
======================================================================
Acq. Operator   : NDW                          Seq. Line :   1
Acq. Instrument : Instrument 2                  Location : Vial 21
Injection Date  : 12/10/2014 10:49:08 AM             Inj :   1
                                                Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2014-12-10 10-46-43\DAWENOD.M
Last changed    : 12/10/2014 10:59:17 AM by NDW
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\90C10D.M
```



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.602	VB	0.0941	100.08929	16.20280	48.9801
2	5.066	BB	0.0991	104.25755	16.20070	51.0199



21

```
======================================================================
Acq. Operator   : DN                           Seq. Line :   3
Acq. Instrument : Instrument 2                  Location : Vial 1
Injection Date  : 1/30/2015 3:11:43 PM               Inj :   1
                                                Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\2\DATA\DN\HPLC 2015-01-30 14-44-59\DAWENOD.M
Last changed    : 1/30/2015 2:59:44 PM by DN
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\TL-10IPA-90HEX-12MLMIN-60MIN.M
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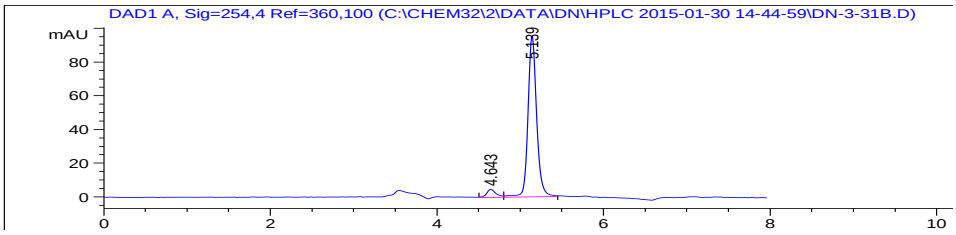
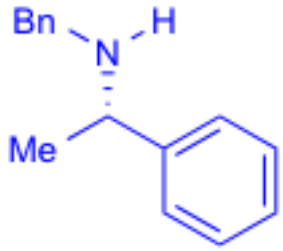


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.643	BV	0.1195	40.32051	4.92598	5.5050
2	5.139	VB	0.1104	692.11328	95.72420	94.4950

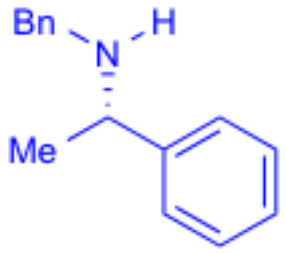
in $CDCl_3$



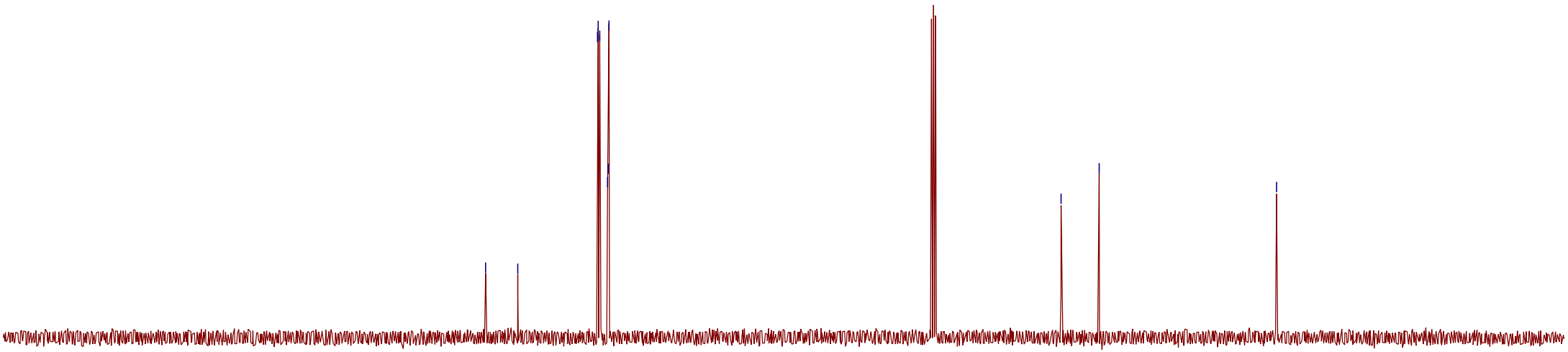
11a

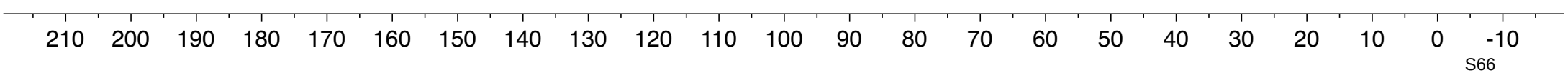
145.72
140.80
128.59
128.49
128.25
127.05
126.96
126.83
57.63
51.80
24.65

in $CDCl_3$

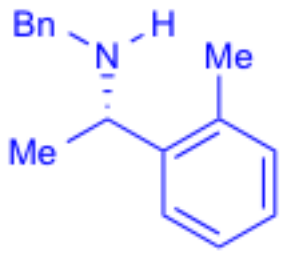


11a



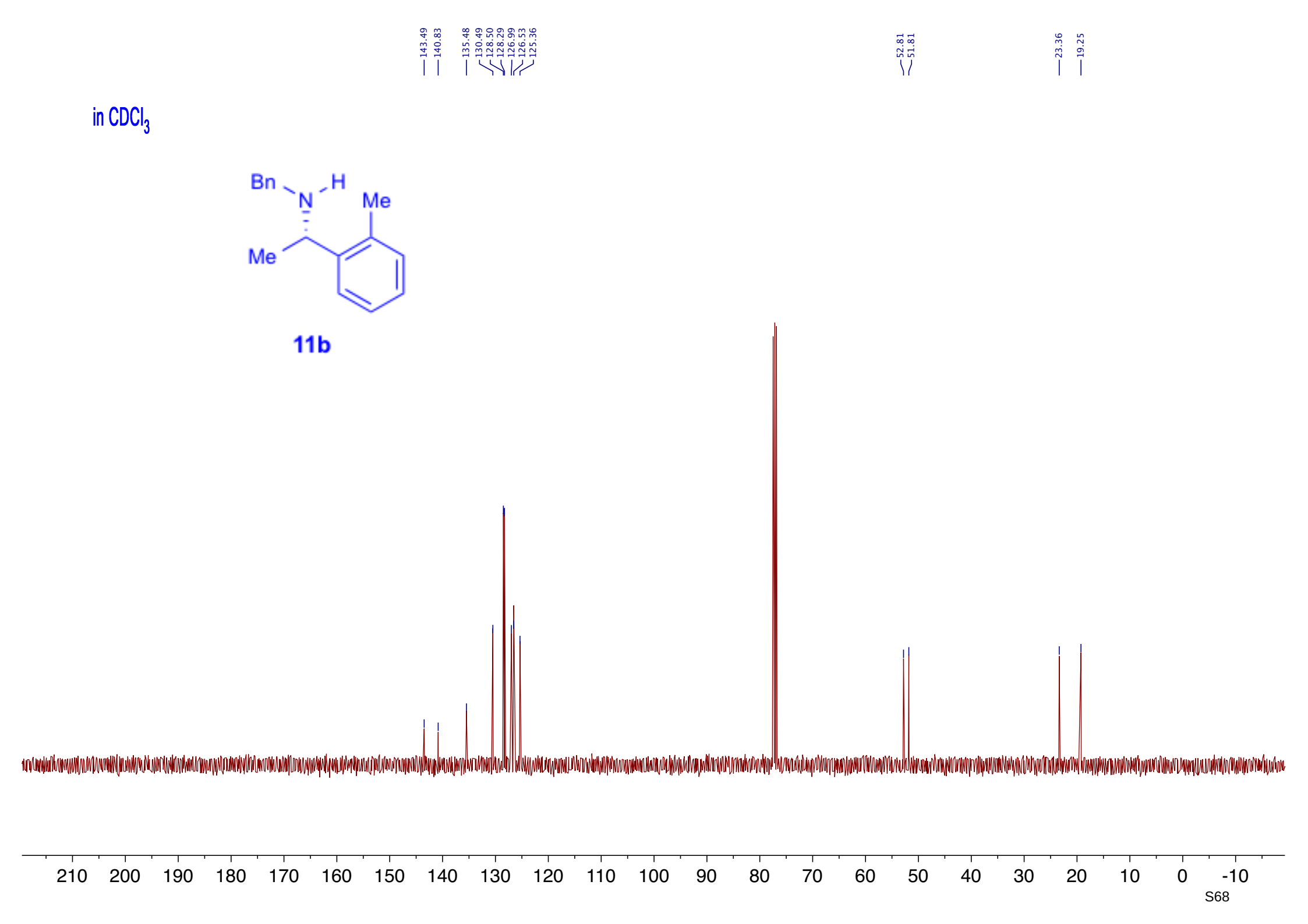


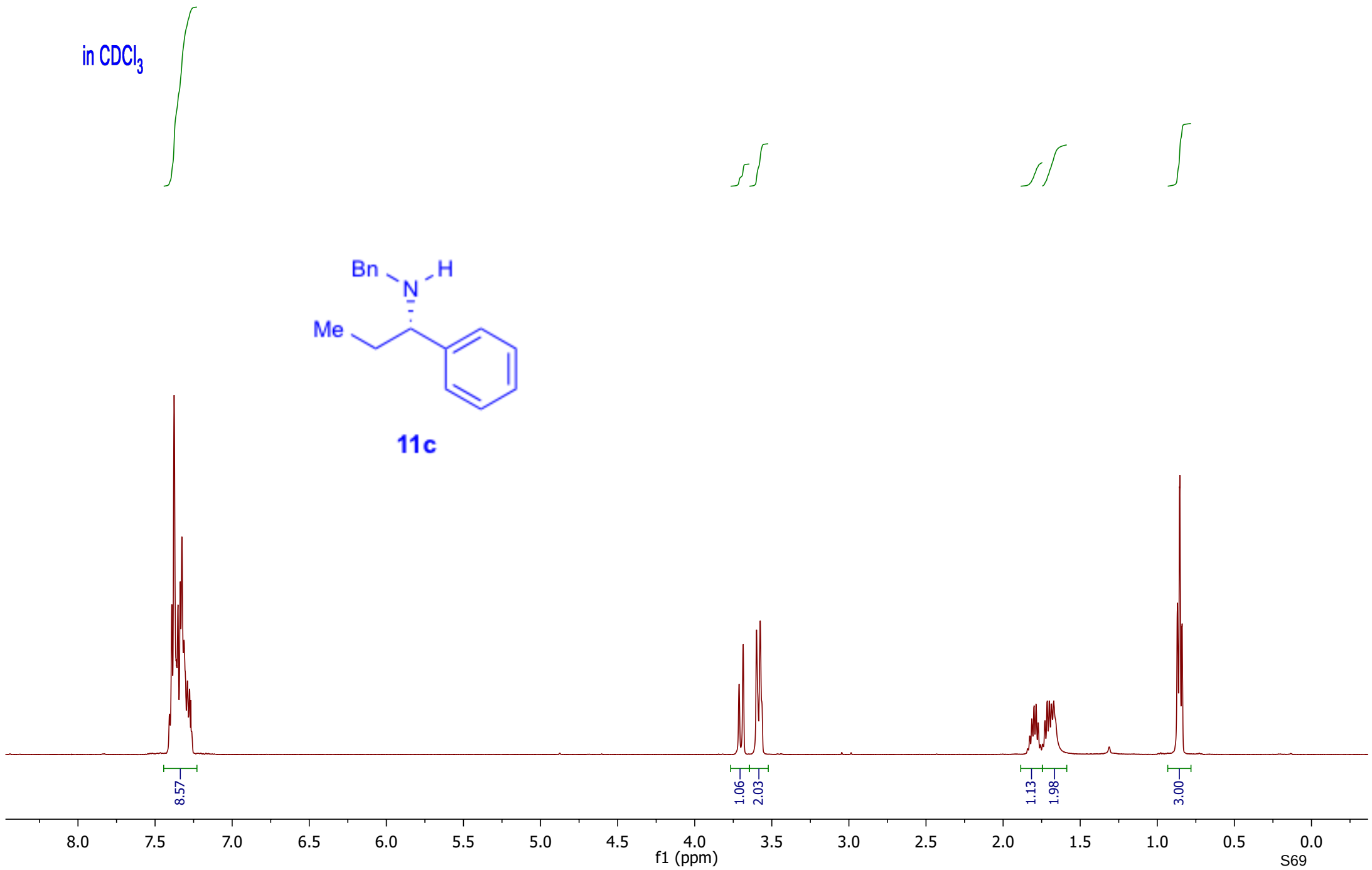
in $CDCl_3$

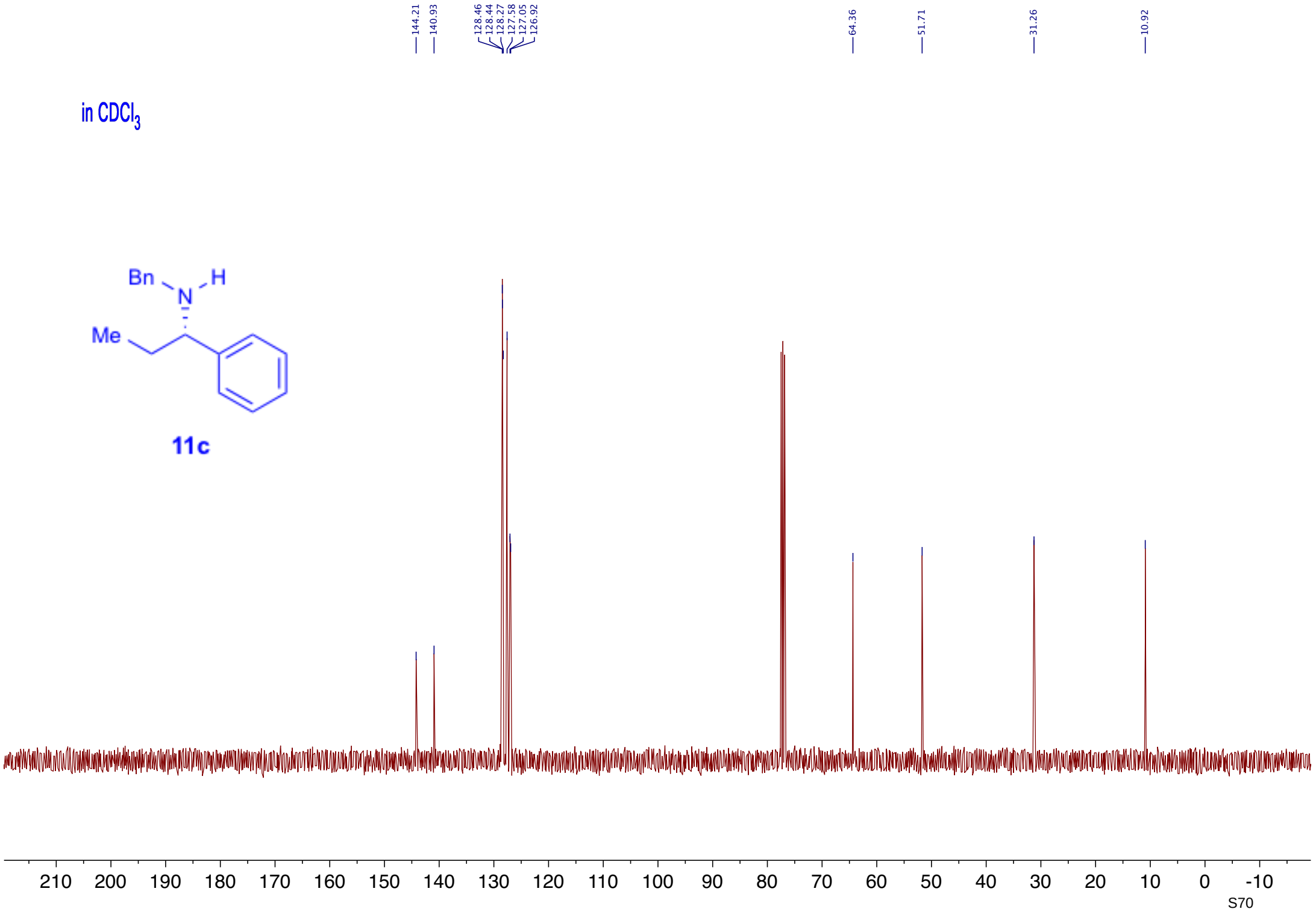

Bn
N
H
Me
Me

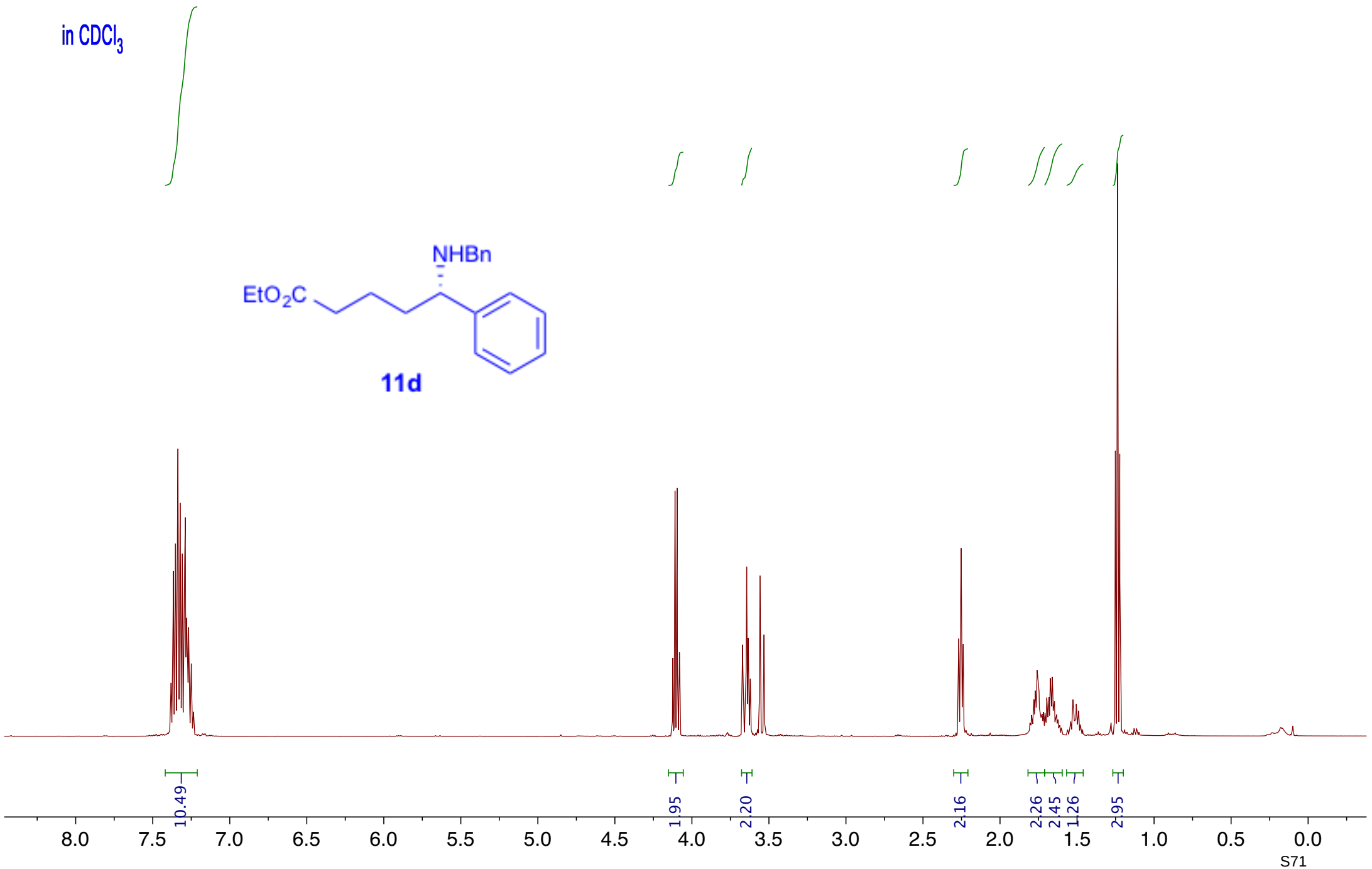
11b

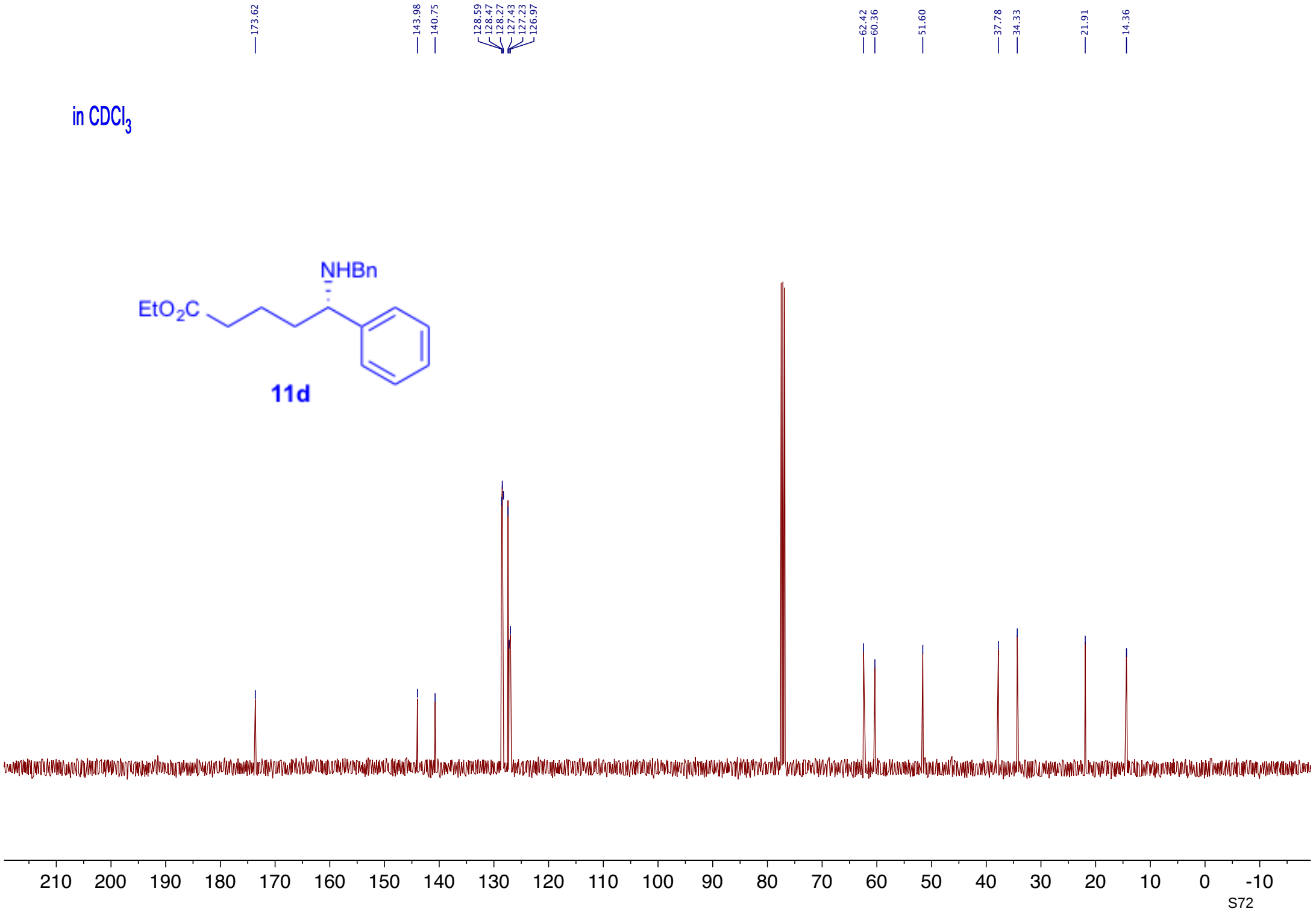
1.00
6.33
1.97
1.03
1.02
1.03
2.97
1.11
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

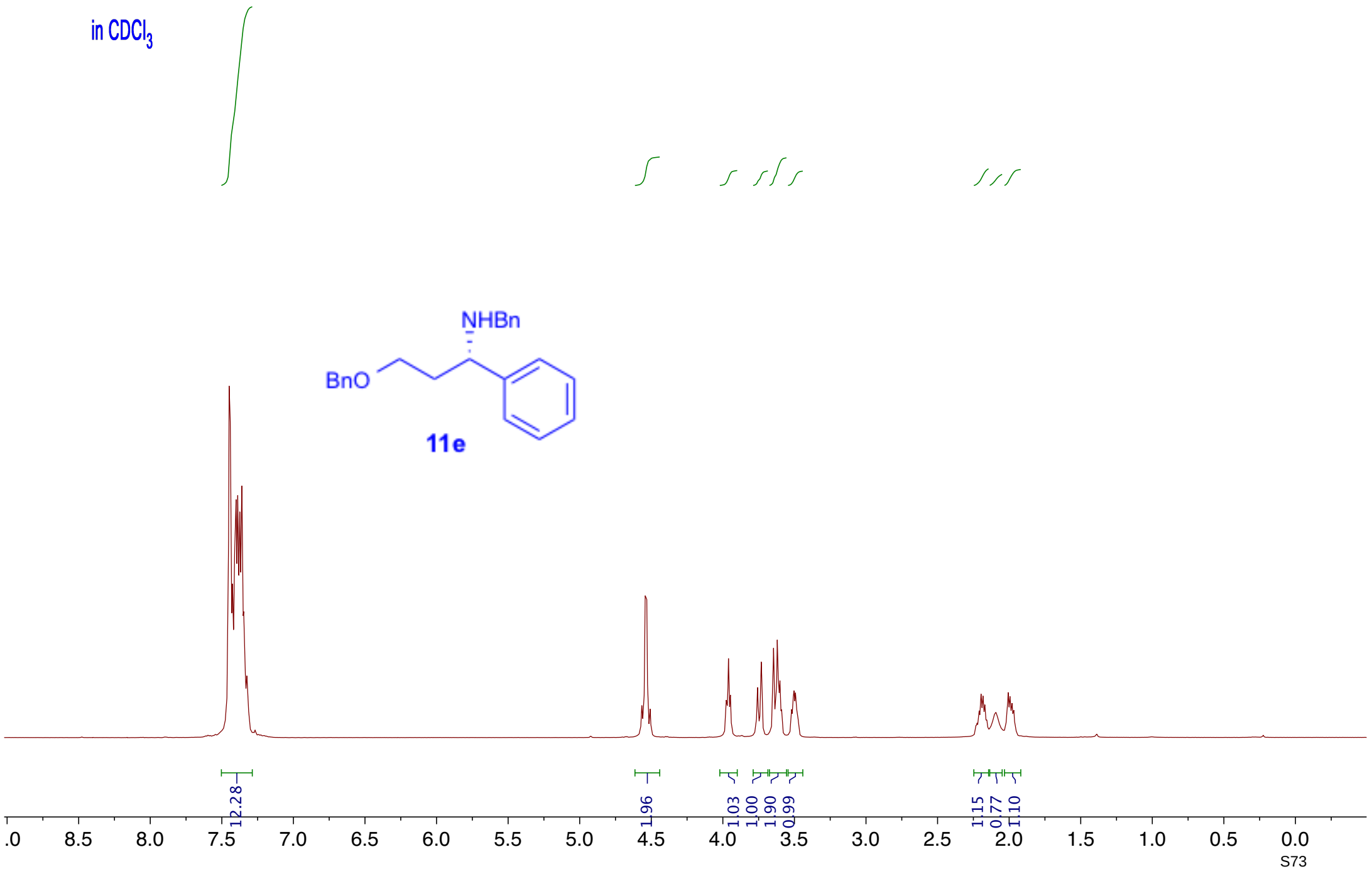

143.49
140.83
135.48
130.49
128.50
128.29
126.99
126.53
125.36
52.81
51.81
23.36
19.25
in CDCl3
Bn
N
H
Me
Me
11b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


in CDCl3
Bn
N
H
Me
11c
8.57
1.06
2.03
1.13
1.98
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

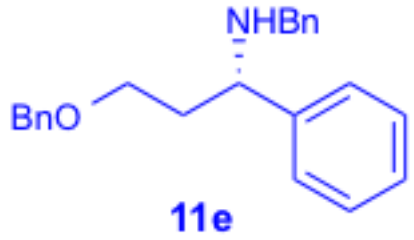

144.21
140.93
128.46
128.44
128.27
127.58
127.05
126.92
64.36
51.71
31.26
10.92
in CDCl3
Bn
N
H
Me
11c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


in CDCl3
NHBn
EtO2C
11d
10.49
1.95
2.20
2.16
2.26
2.45
1.26
2.95
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


173.62
143.98
140.75
128.59
128.47
128.27
127.43
127.23
126.97
62.42
60.36
51.60
37.78
34.33
21.91
14.36
in CDCl3
NHBn
EtO2C
11d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

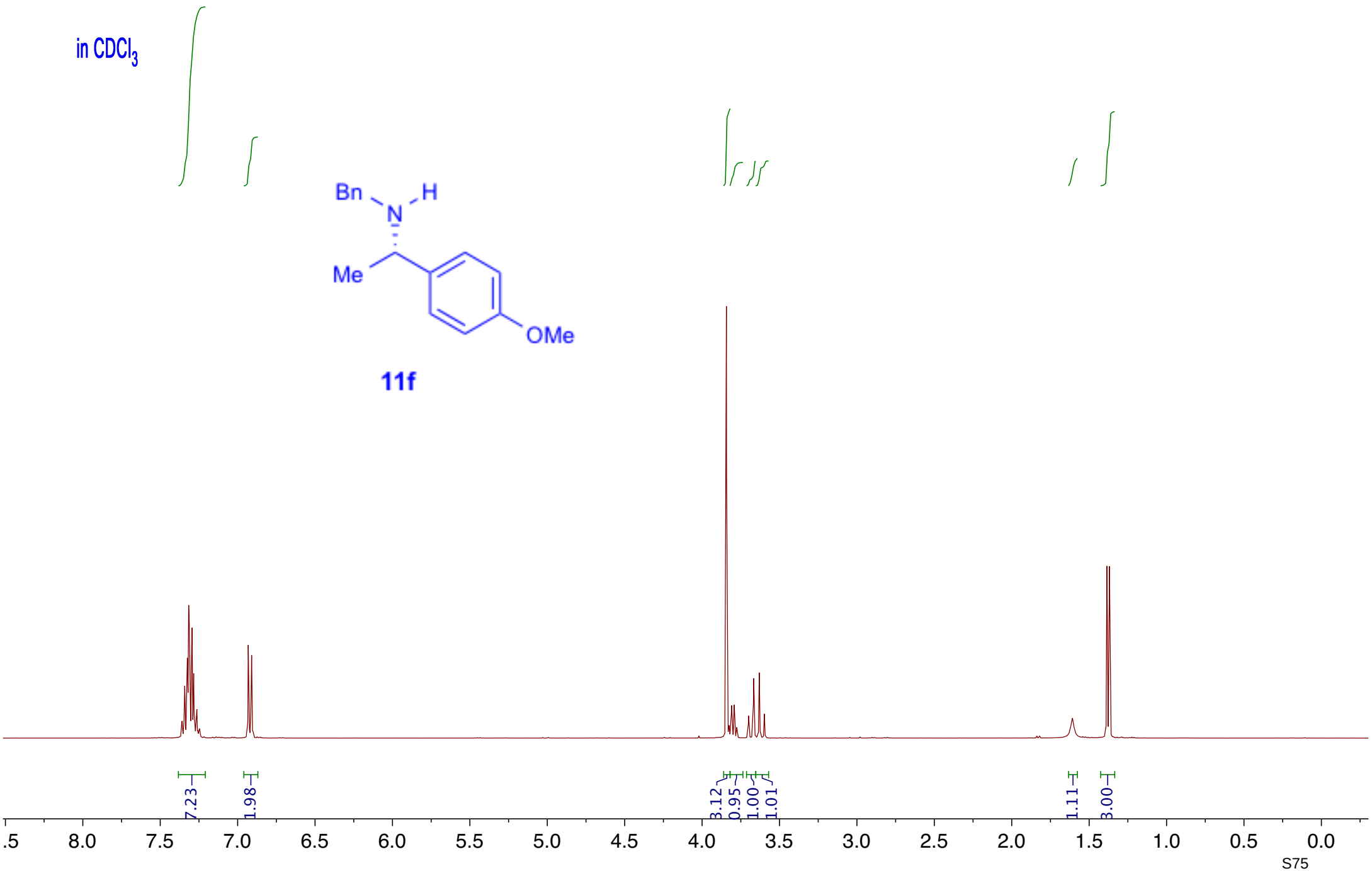

in CDCl3
NHBn
BnO
11e
12.28
1.96
1.03
1.00
1.90
0.99
1.15
0.77
1.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

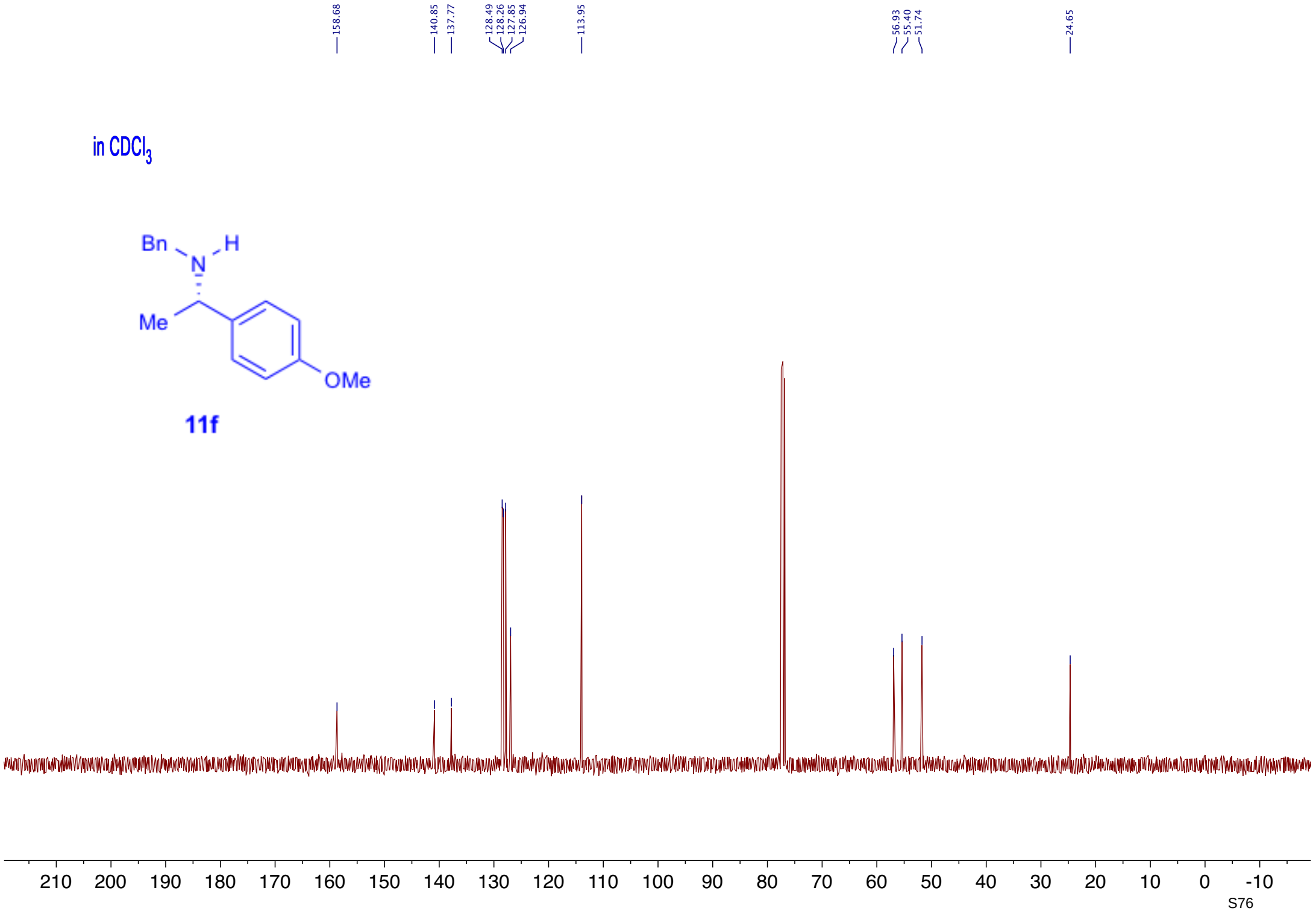
in $CDCl_3$

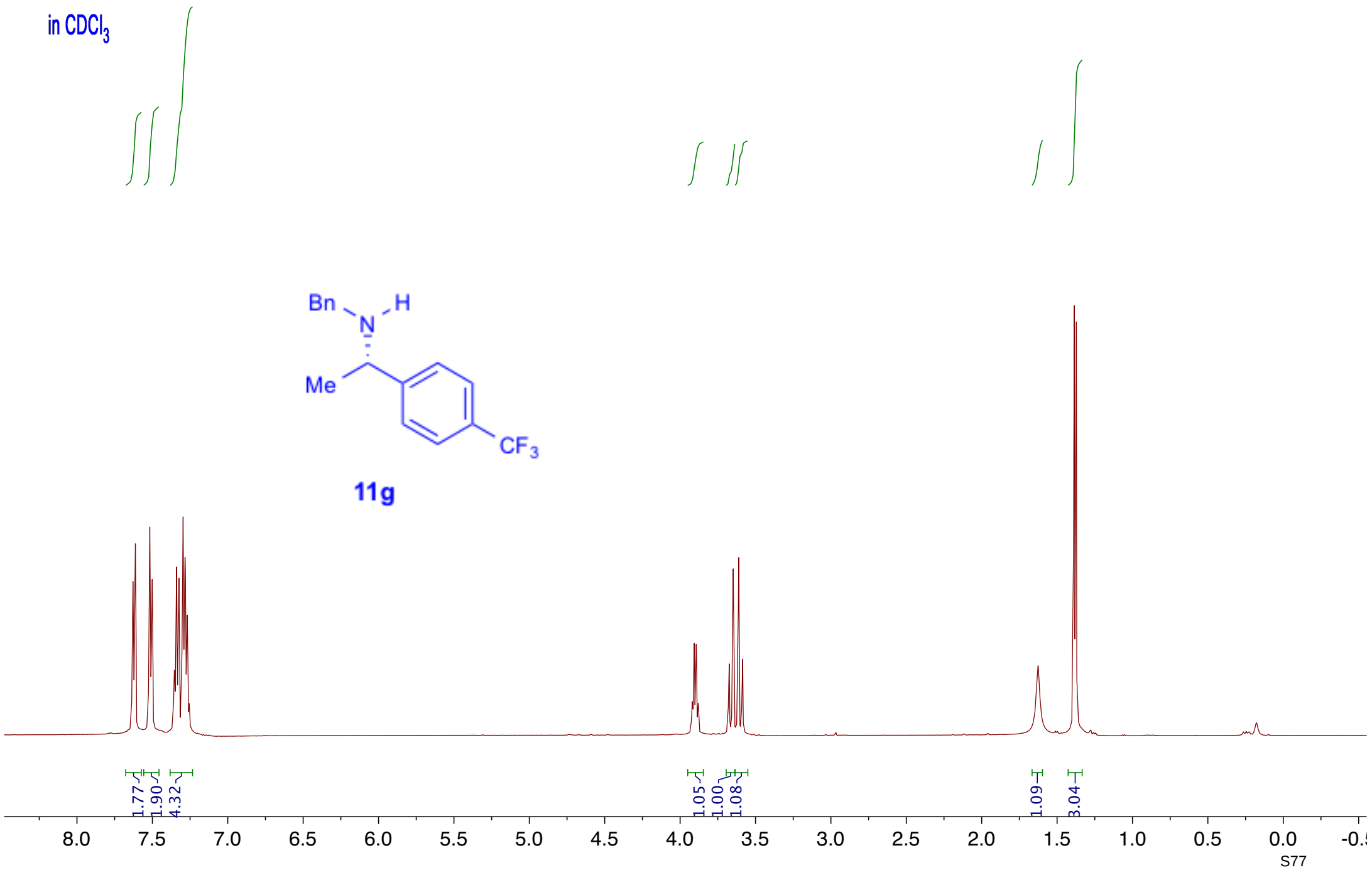

NHBn
BnO

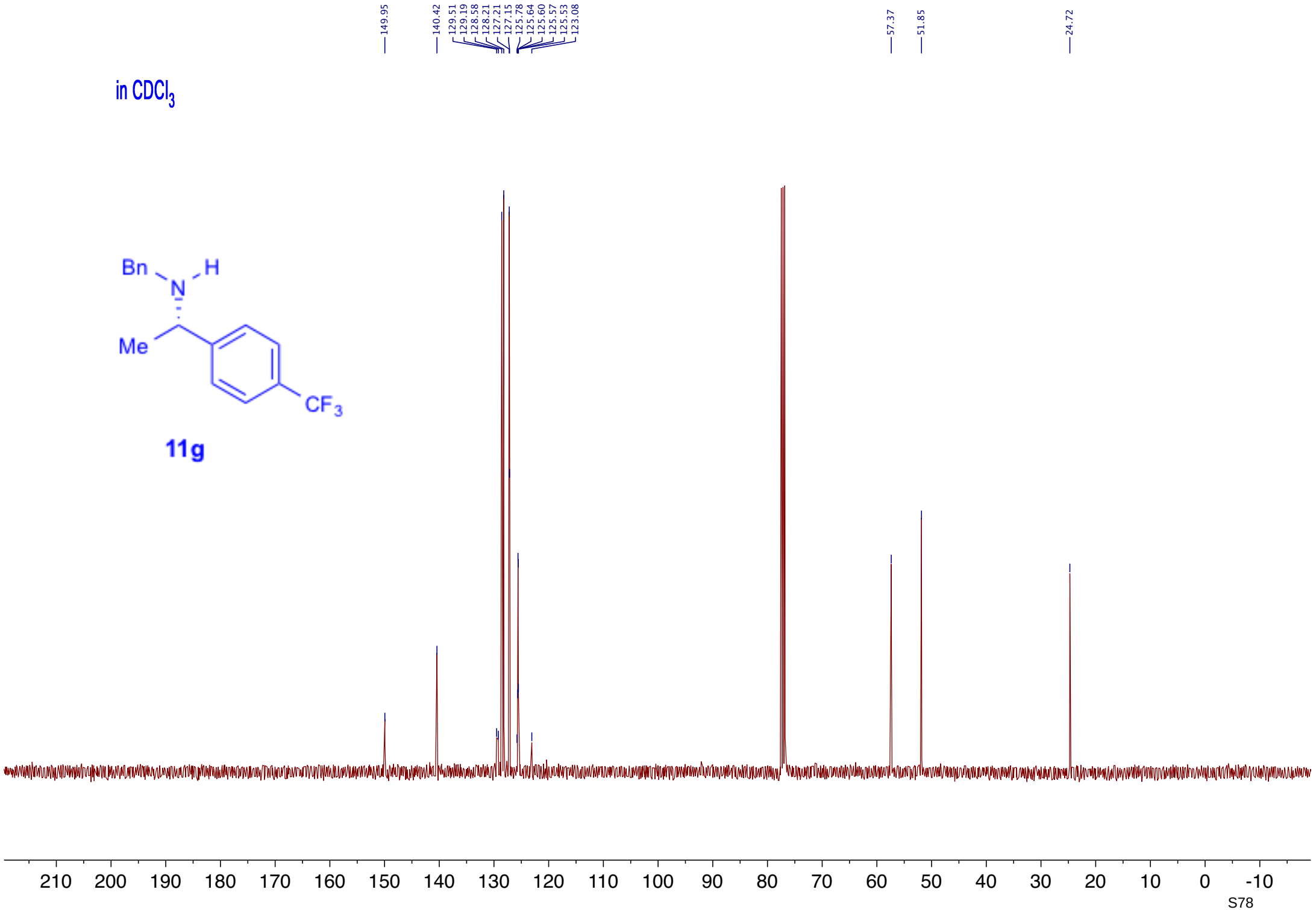
11e

144.02
140.77
138.46
128.48
128.40
128.34
128.20
127.70
127.57
127.35
127.07
126.80
73.05
68.09
60.43
51.61
38.32
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

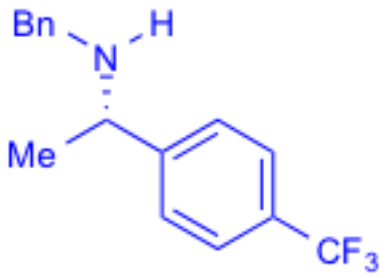

in CDCl3
Bn
N
H
Me
OMe
11f
7.23
1.98
3.12
0.95
1.00
1.01
1.11
3.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


158.68
140.85
137.77
128.49
128.26
127.85
126.94
113.95
56.93
55.40
51.74
24.65
in CDCl3
Bn
N
H
Me
OMe
11f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


in CDCl3
Bn
N
H
Me
CF3
11g
1.77
1.90
4.32
1.05
1.00
1.08
1.09
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


149.95
140.42
129.51
129.19
128.58
128.21
127.21
127.15
125.78
125.64
125.60
125.57
125.53
123.08
57.37
51.85
24.72
in CDCl3
Bn
N
H
Me
CF3
11g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

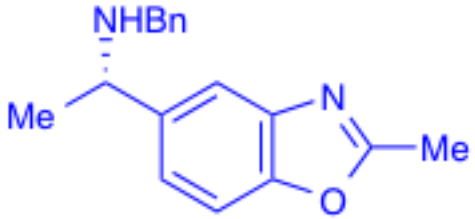
in $CDCl_3$


Bn
N
H
Me
CF_3

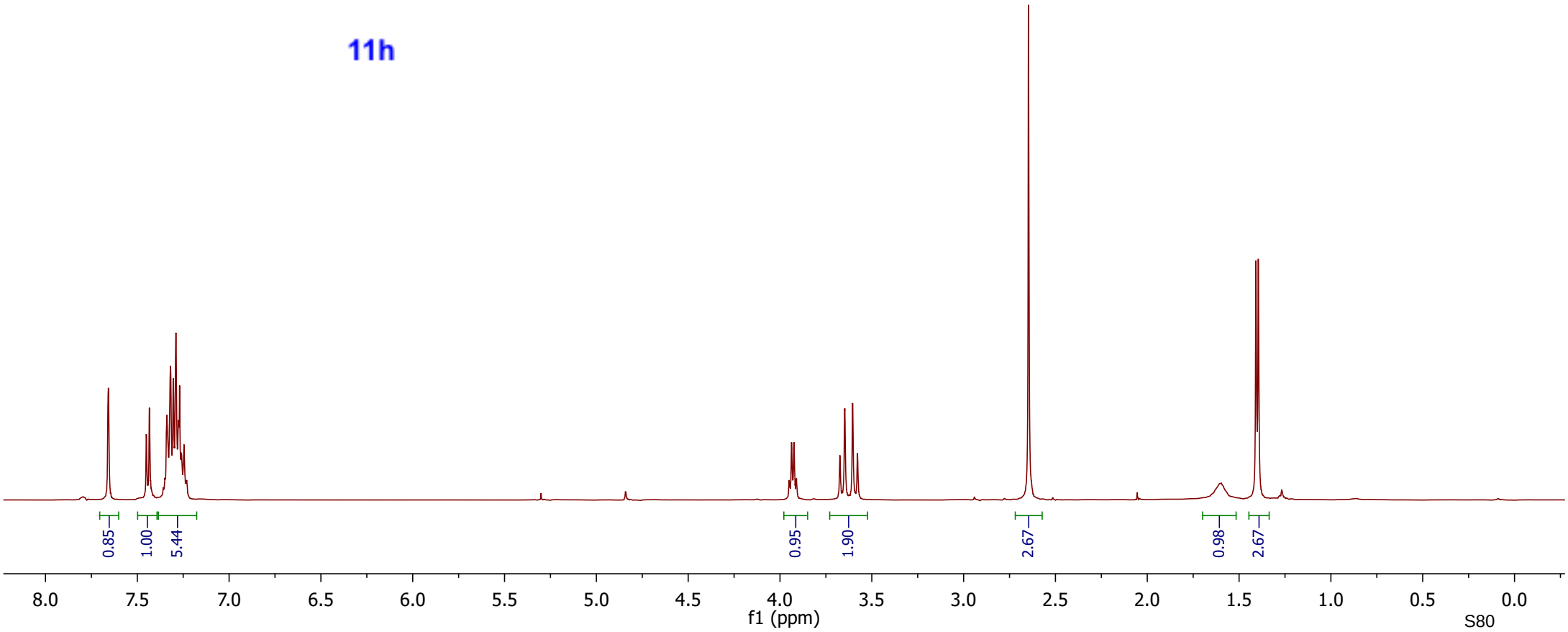
11g

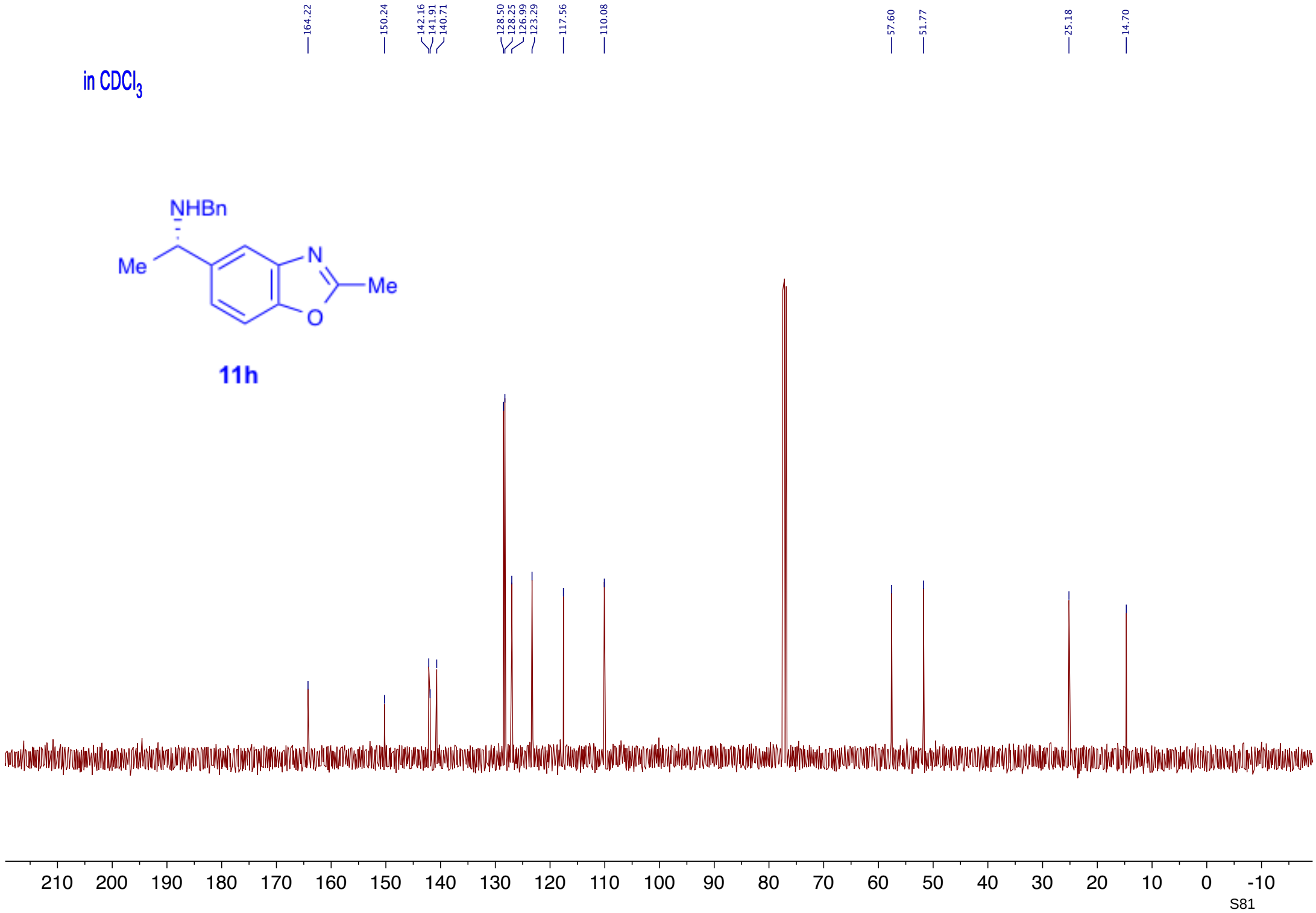
-62.33
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

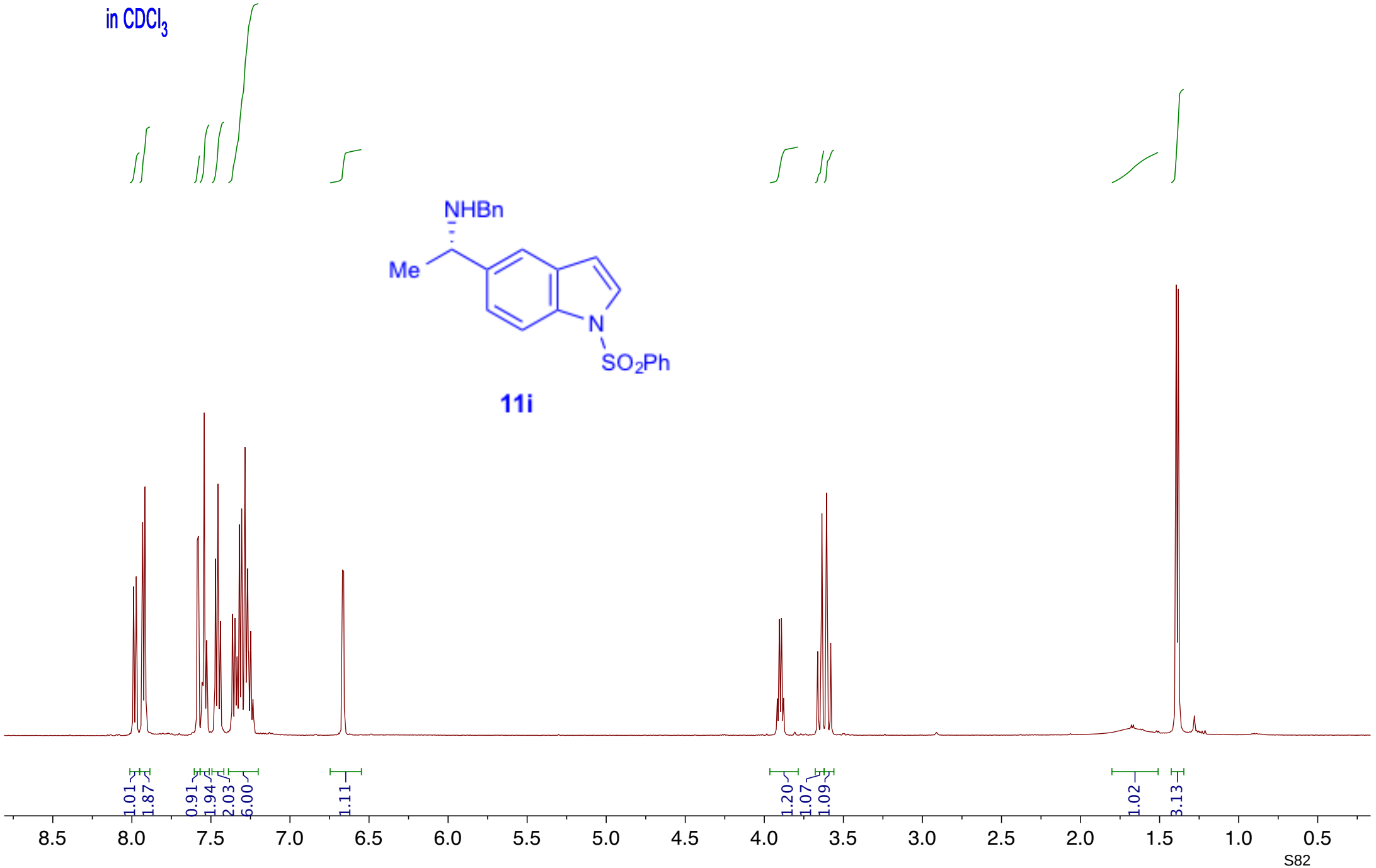
in $CDCl_3$

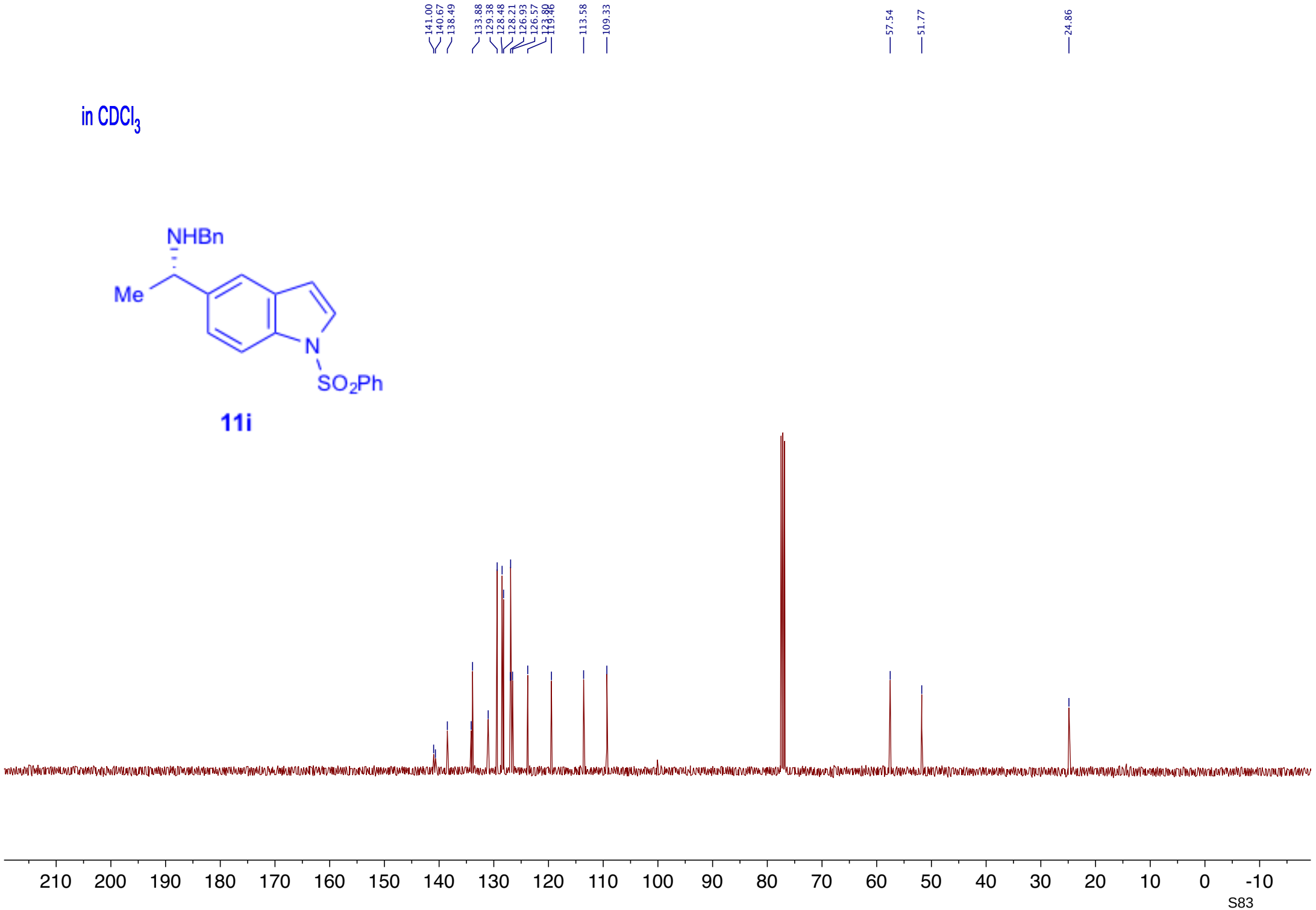

NHBn
Me
N
Me
O

11h

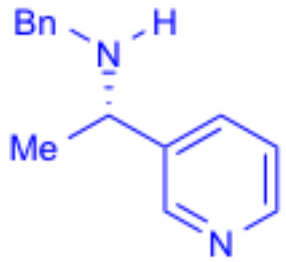

0.85
1.00
5.44
0.95
1.90
2.67
0.98
2.67
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.22
150.24
142.16
141.91
140.71
128.50
128.25
126.99
123.29
117.56
110.08
57.60
51.77
25.18
14.70
in CDCl3
NHBn
Me
N
Me
O
11h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

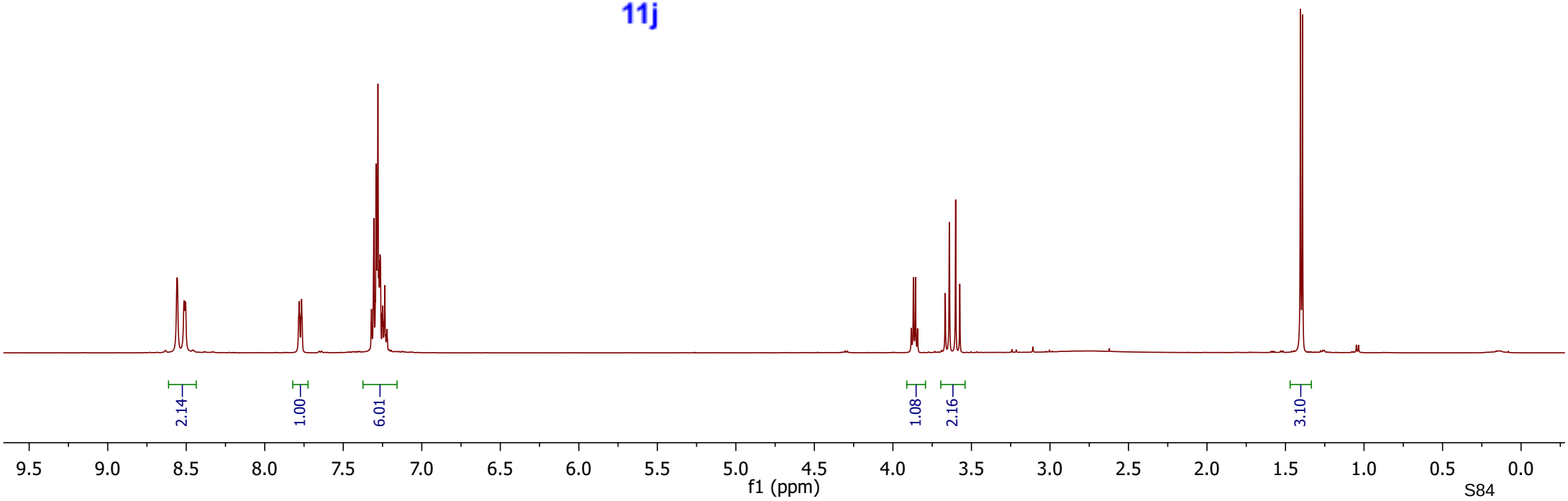

in CDCl3
NHBn
Me
N
SO2Ph
11i
1.01
1.87
0.91
1.94
2.03
6.00
1.11
1.20
1.07
1.09
1.02
3.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

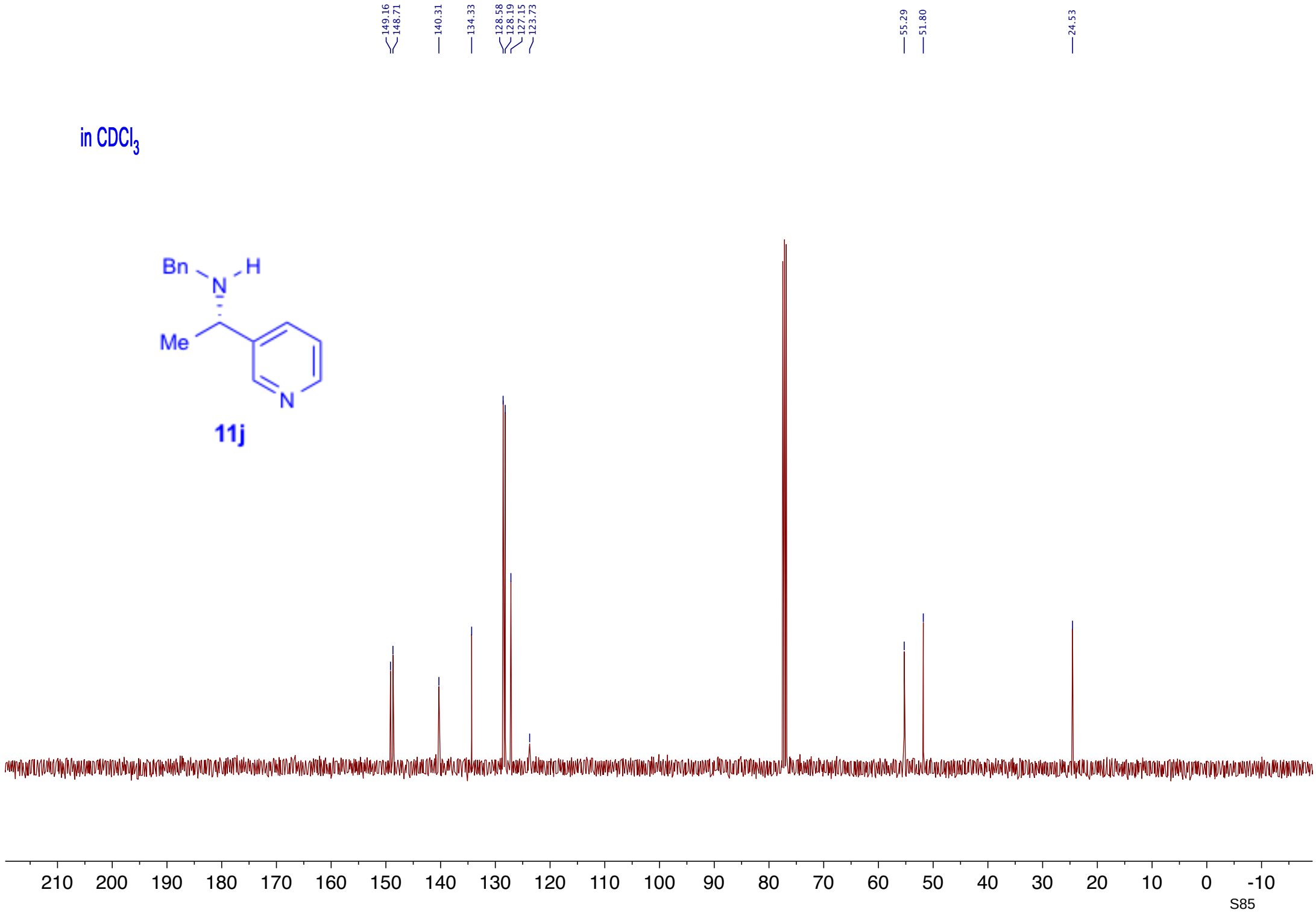

141.00
140.67
138.49
133.88
129.38
128.48
128.21
126.93
126.57
123.80
113.58
109.33
57.54
51.77
24.86
in CDCl3
NHBn
Me
N
SO2Ph
11i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

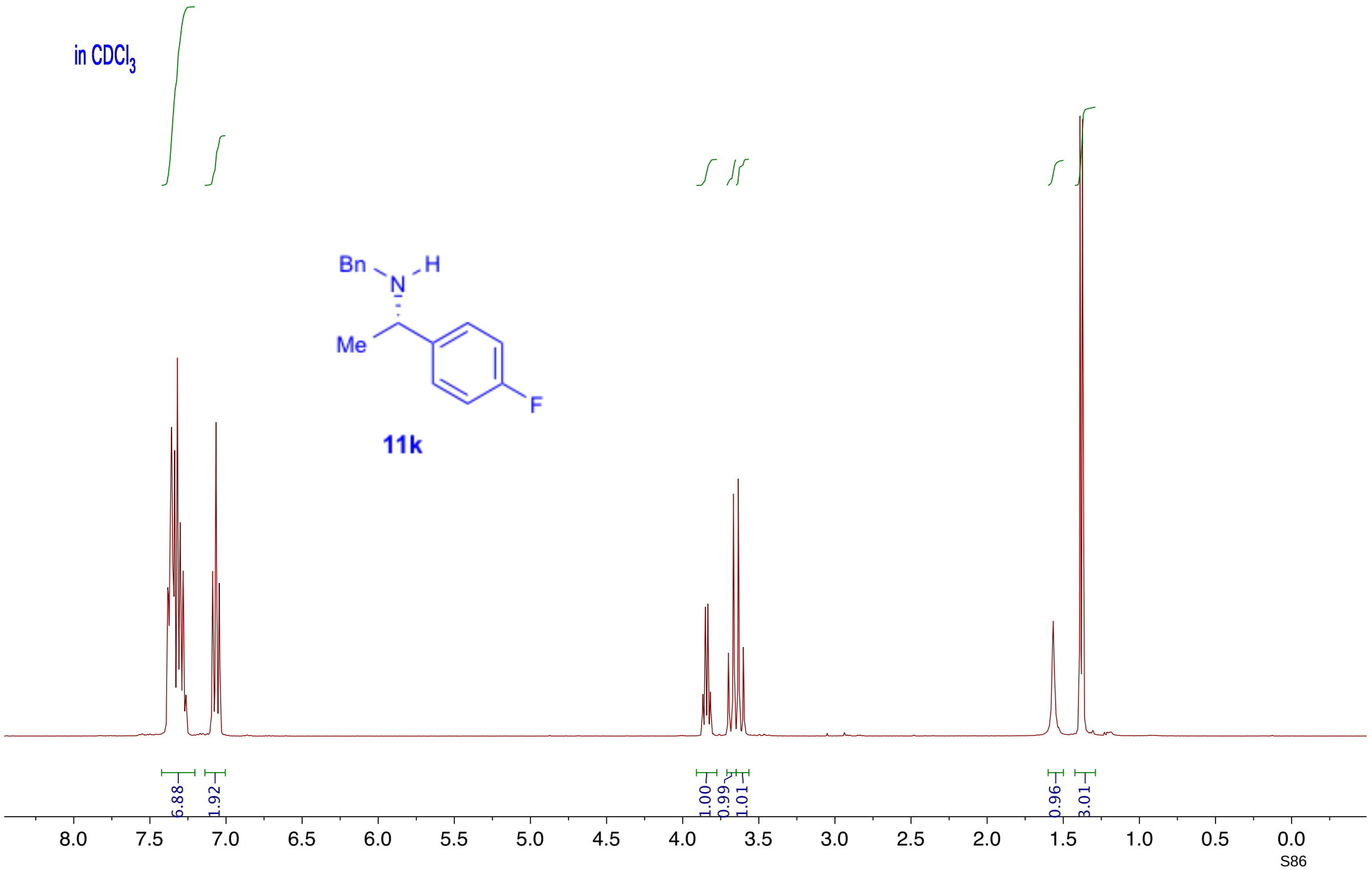
in $CDCl_3$


Bn
N
H
Me
N

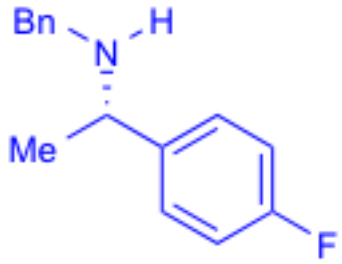
11j


2.14
1.00
6.01
1.08
2.16
3.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

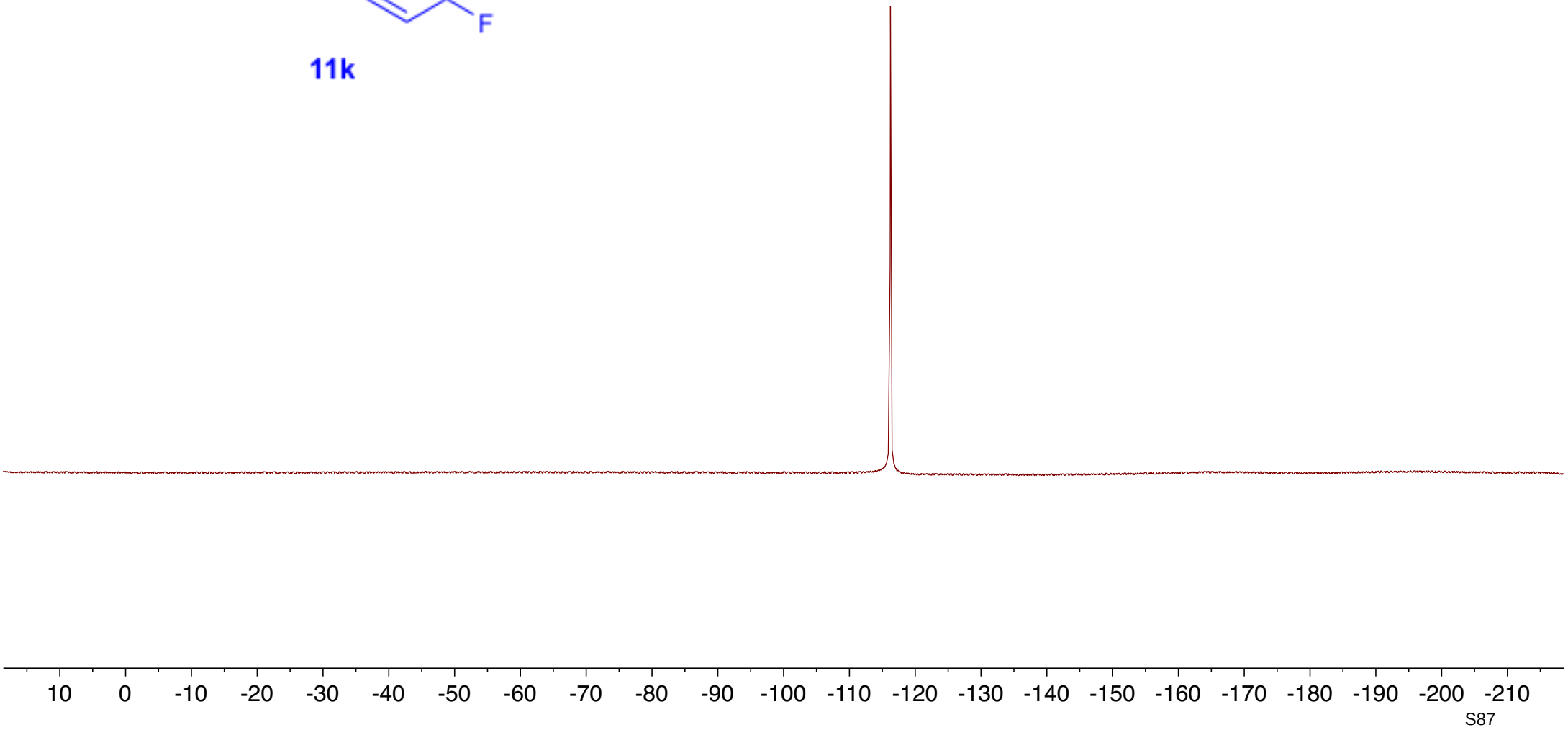

149.16
148.71
140.31
134.33
128.58
128.19
127.15
123.73
55.29
51.80
24.53
in CDCl3
Bn
N
H
Me
N
11j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

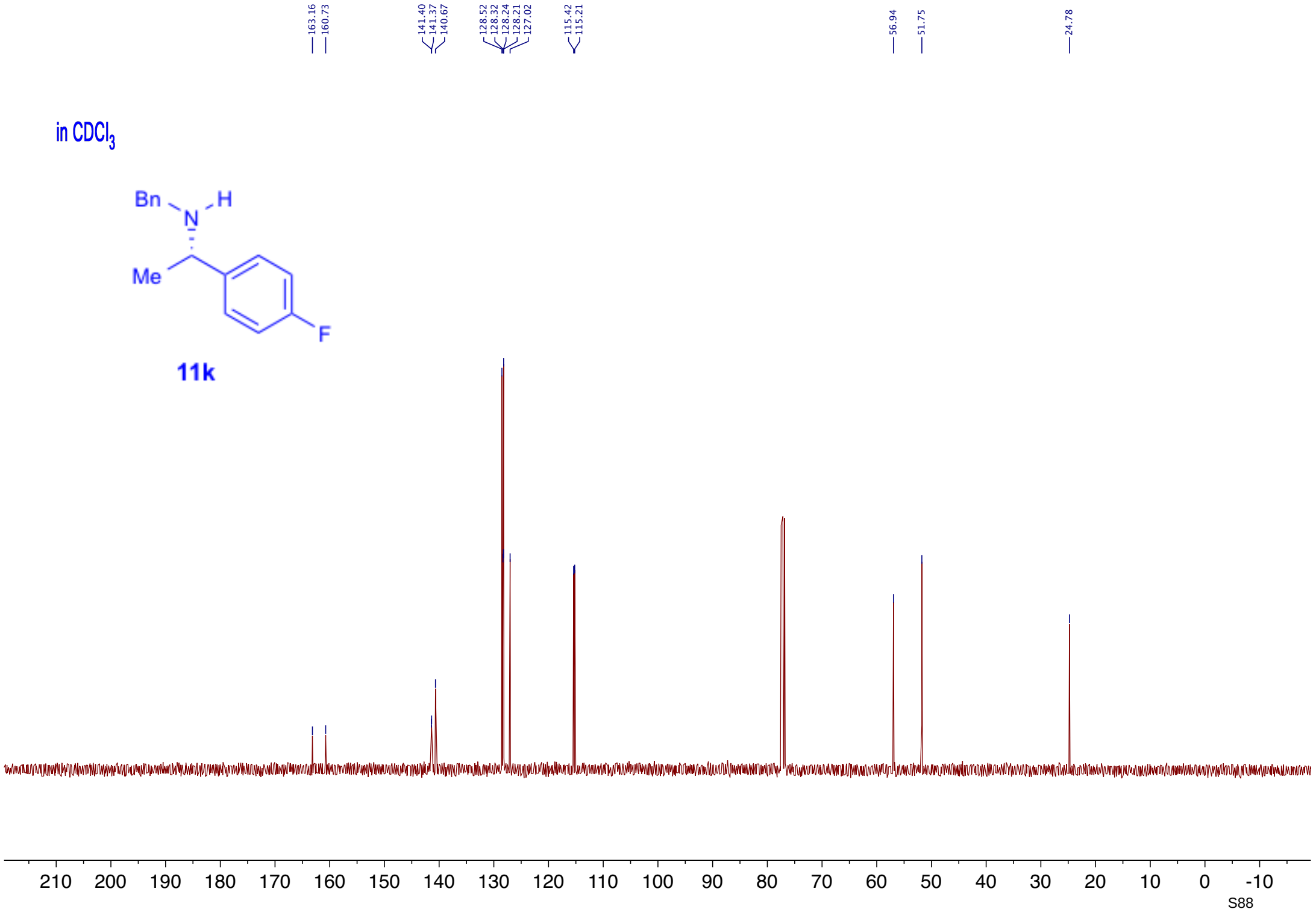

in CDCl3
Bn
N
H
Me
F
11k
6.88
1.92
1.00
0.99
1.01
0.96
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

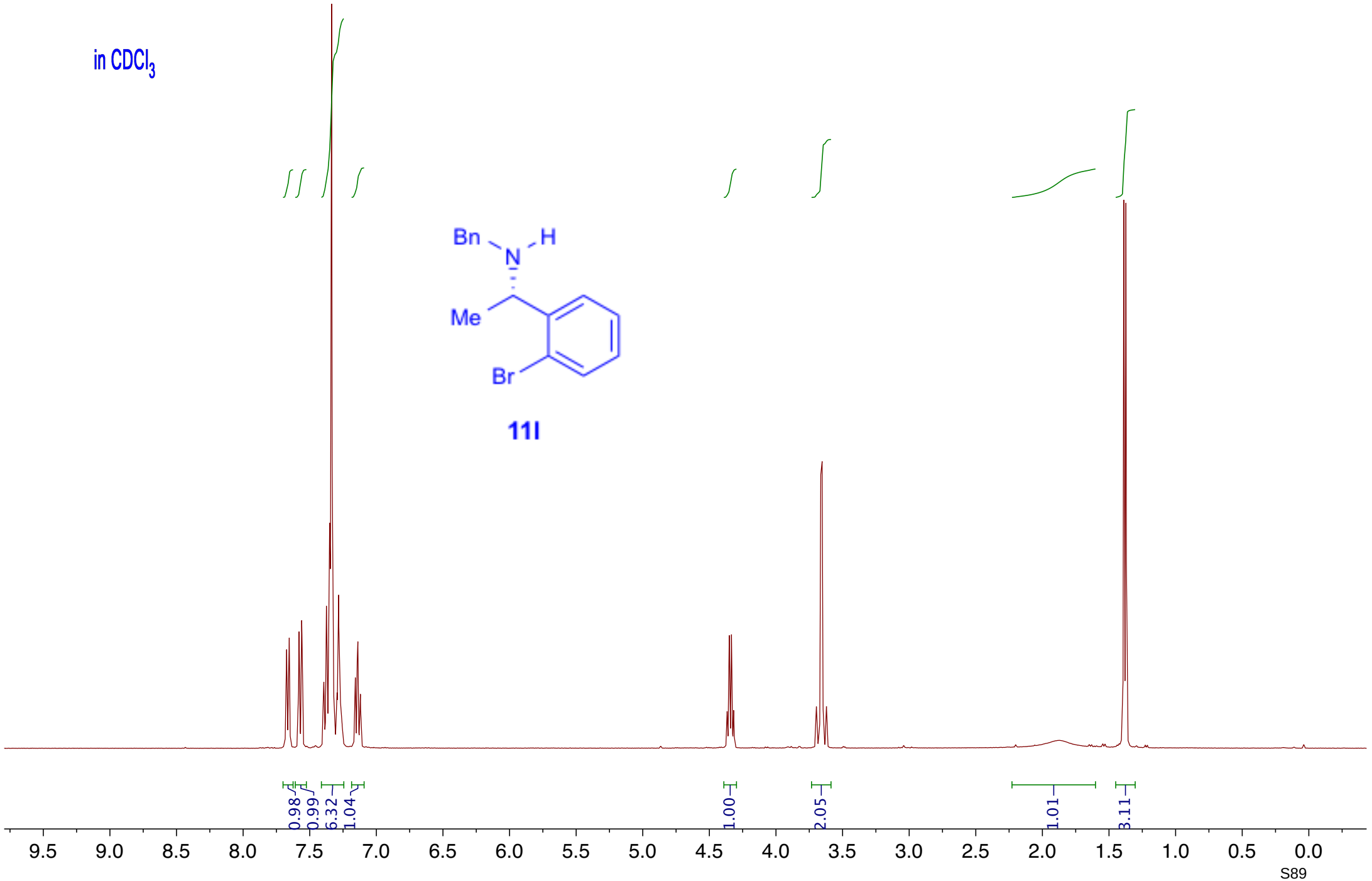
in $CDCl_3$


Bn
N
H
Me
F

11k

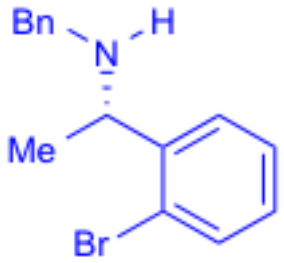

10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210


163.16
160.73
141.40
141.37
140.67
128.52
128.32
128.24
128.21
127.02
115.42
115.21
56.94
51.75
24.78
in CDCl3
Bn
N
H
Me
F
11k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

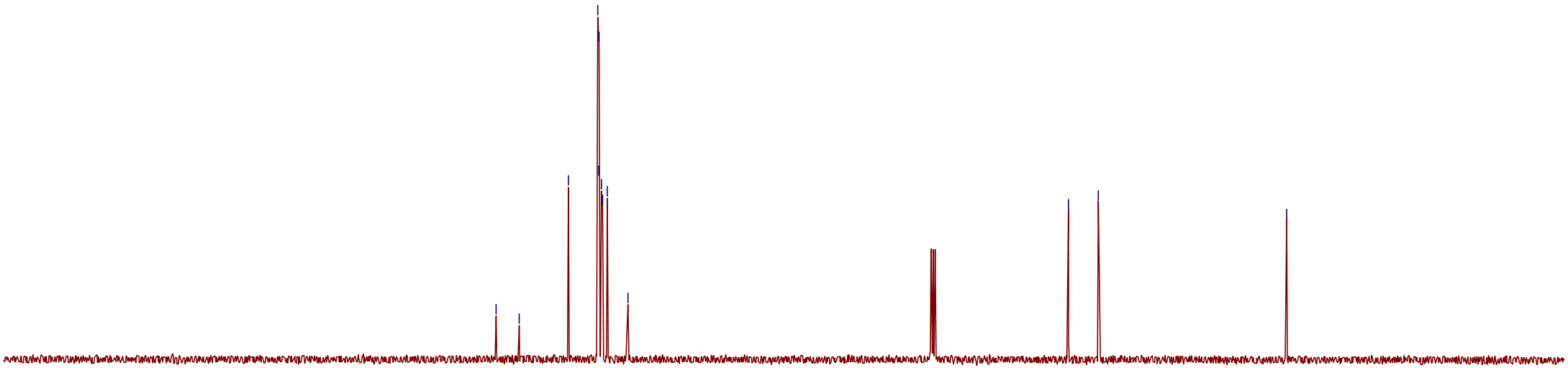

in CDCl3
Bn
N
H
Me
Br
11l
0.98
0.99
6.32
1.04
1.00
2.05
1.01
3.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

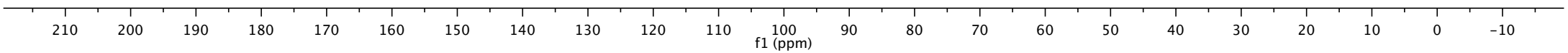
144.06
140.52
132.99
128.50
128.35
128.30
127.93
127.76
127.04
123.87
56.44
51.87
23.04

in $CDCl_3$

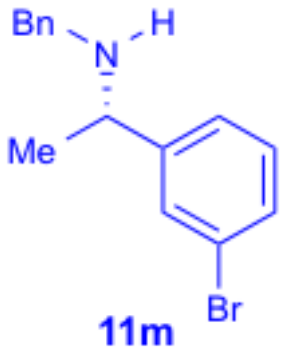


11l



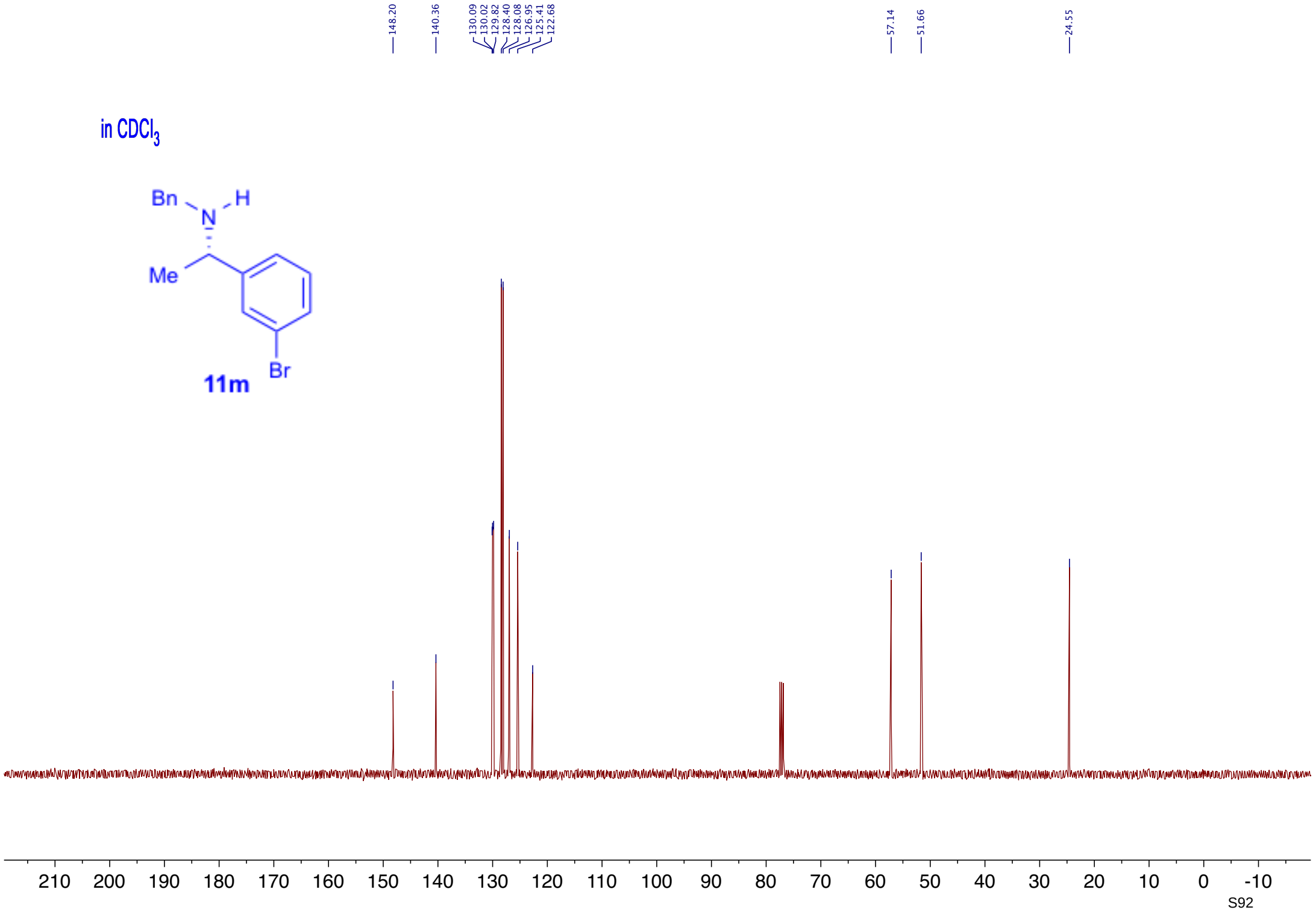


in $CDCl_3$

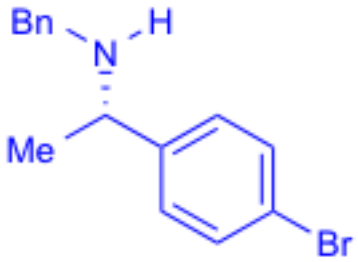

Bn
N
H
Me
Br

11m

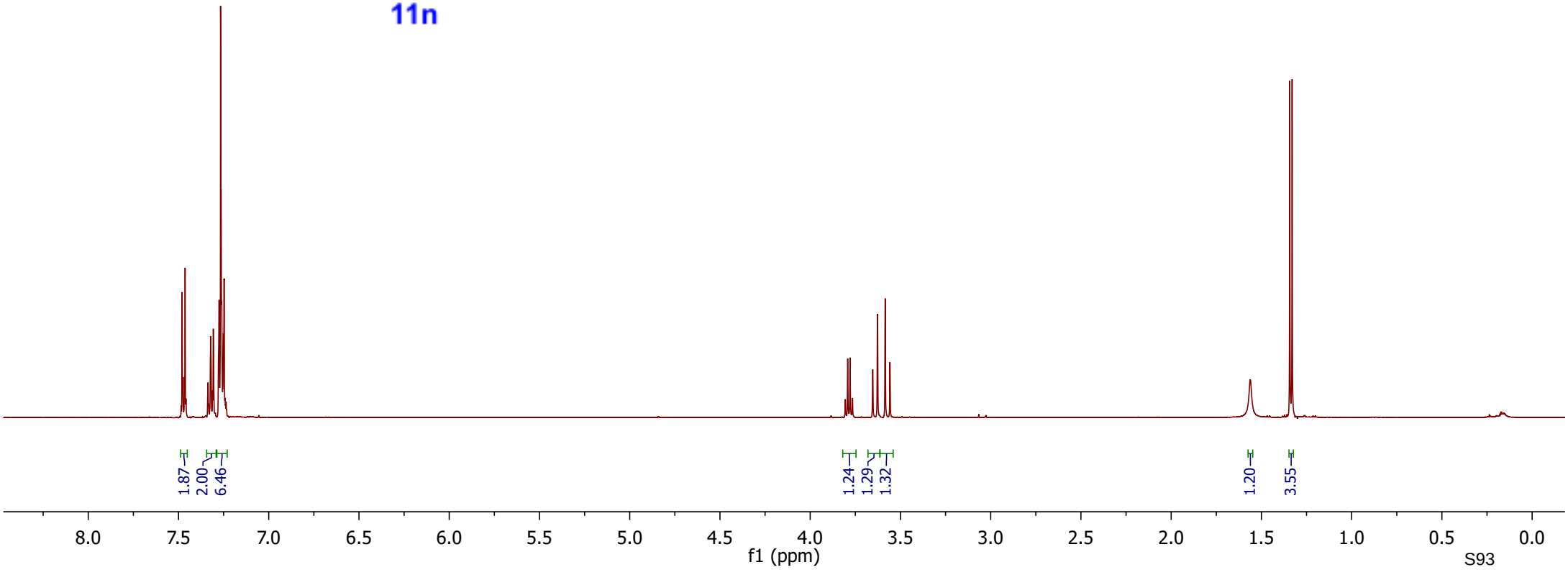
0.94
8.02
1.00
1.89
0.92
2.91
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

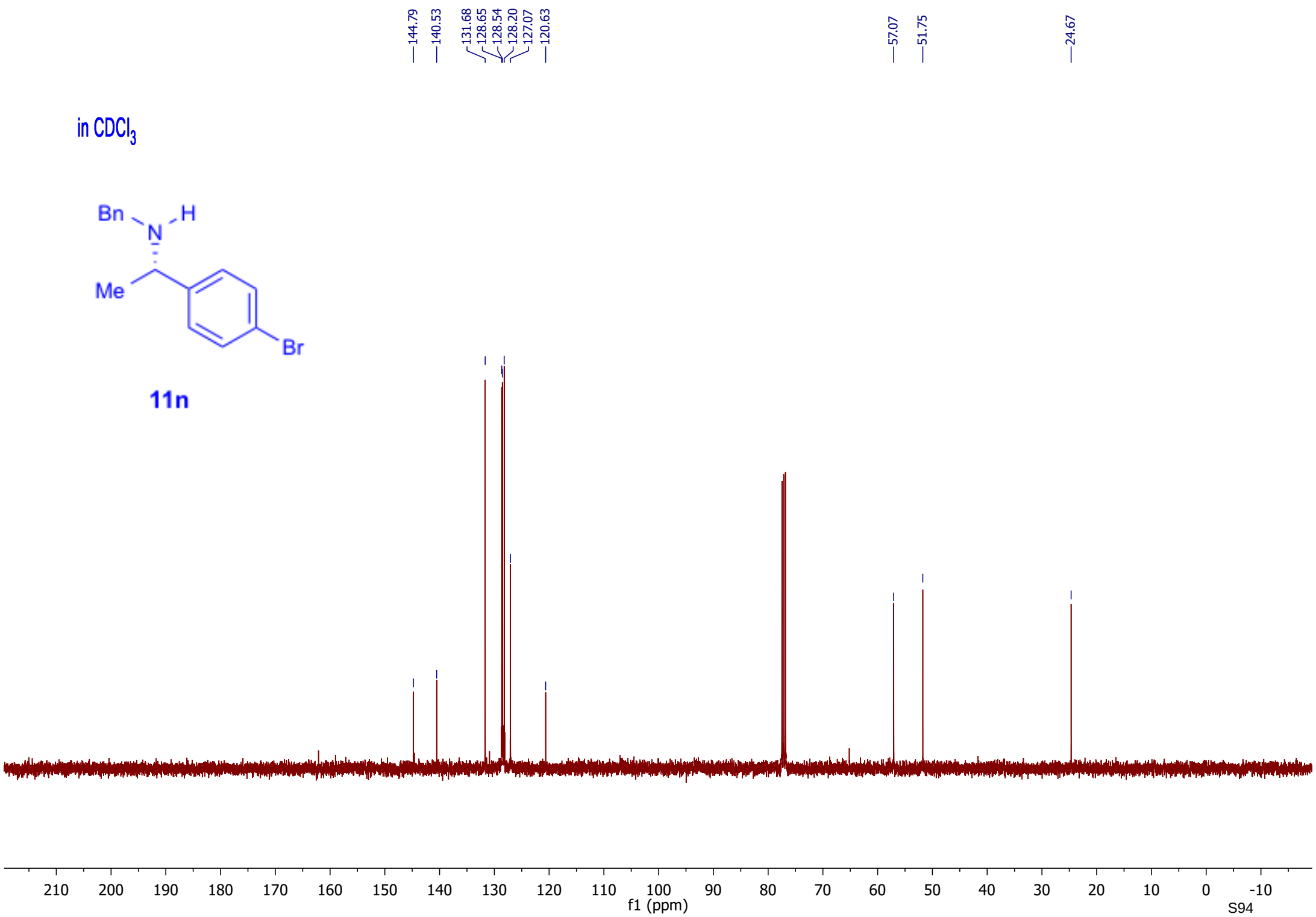

148.20
140.36
130.09
130.02
129.82
128.40
128.08
126.95
125.41
122.68
57.14
51.66
24.55
in CDCl3
Bn
N
H
Me
Br
11m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

in $CDCl_3$

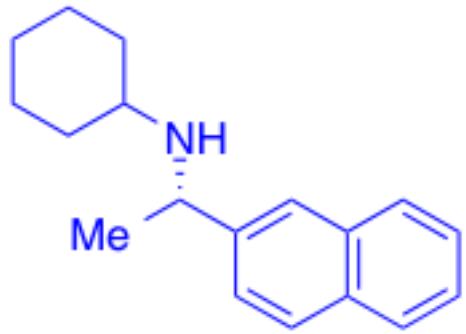

Bn
N
H
Me
Br

11n


1.87
2.00
6.46
1.24
1.29
1.32
1.20
3.55
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)


144.79
140.53
131.68
128.65
128.54
128.20
127.07
120.63
57.07
51.75
24.67
in CDCl3
Bn
N
H
Me
Br
11n
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)

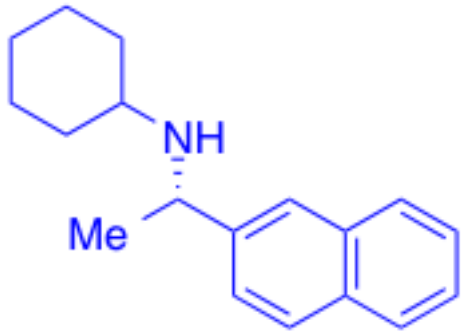
in $CDCl_3$


NH
Me

17a

3.04
1.00
3.03
1.02
1.02
1.04
3.12
1.16
3.91
5.32
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

in $CDCl_3$

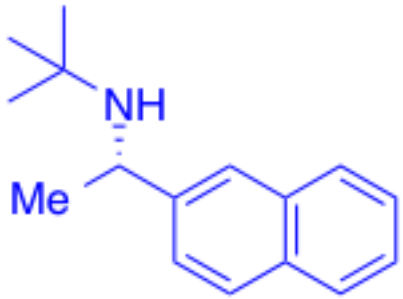


17a

143.99
133.63
132.85
128.27
127.86
127.77
126.01
125.47
125.13
124.99
54.76
53.84
34.80
33.39
26.30
25.36
25.19
25.08

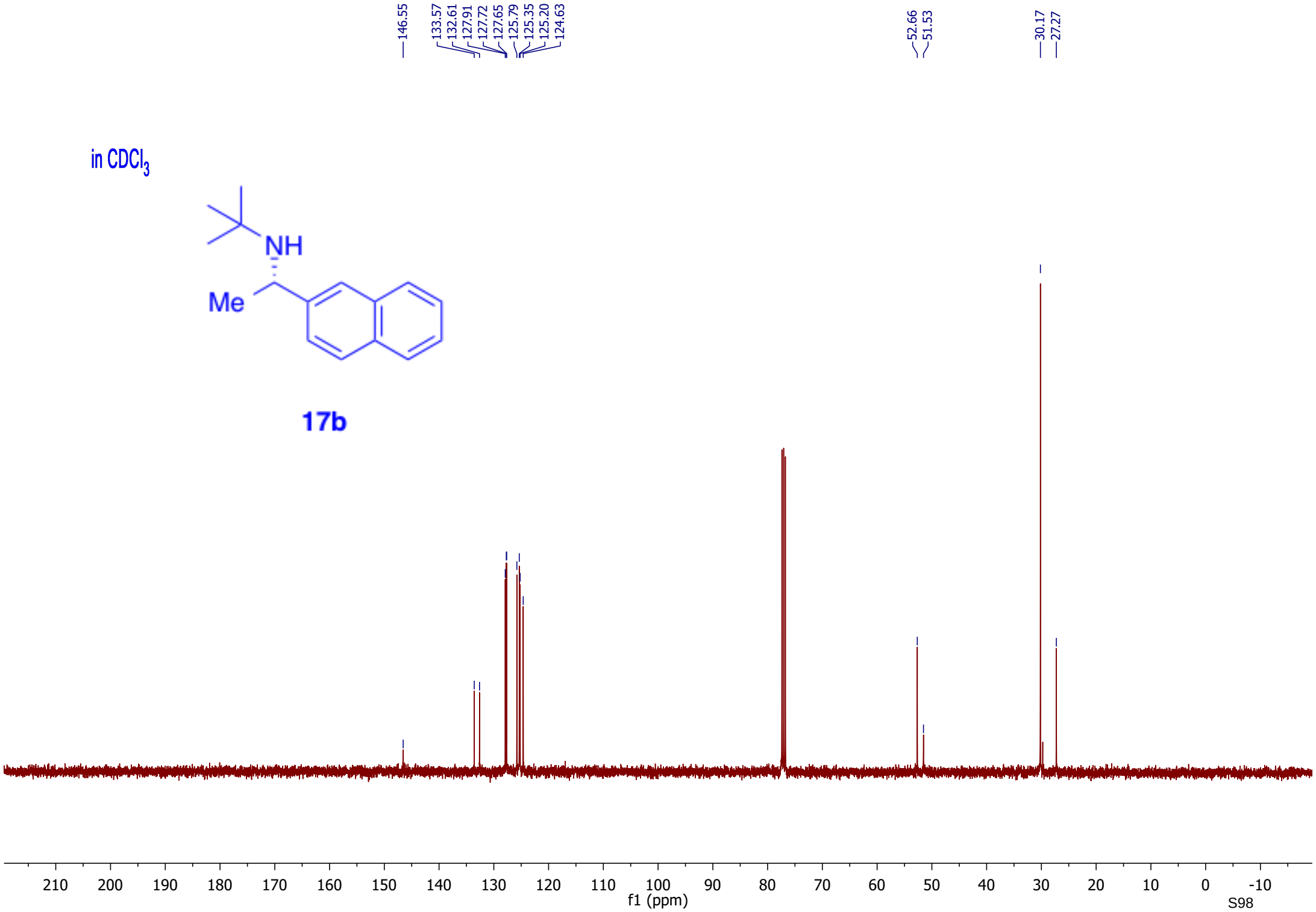
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

in $CDCl_3$

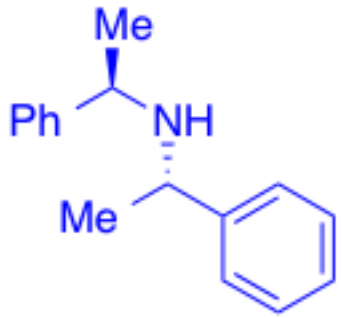

NH
Me

17b

4.02
1.02
2.04
1.00
3.25
1.01
9.37
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)

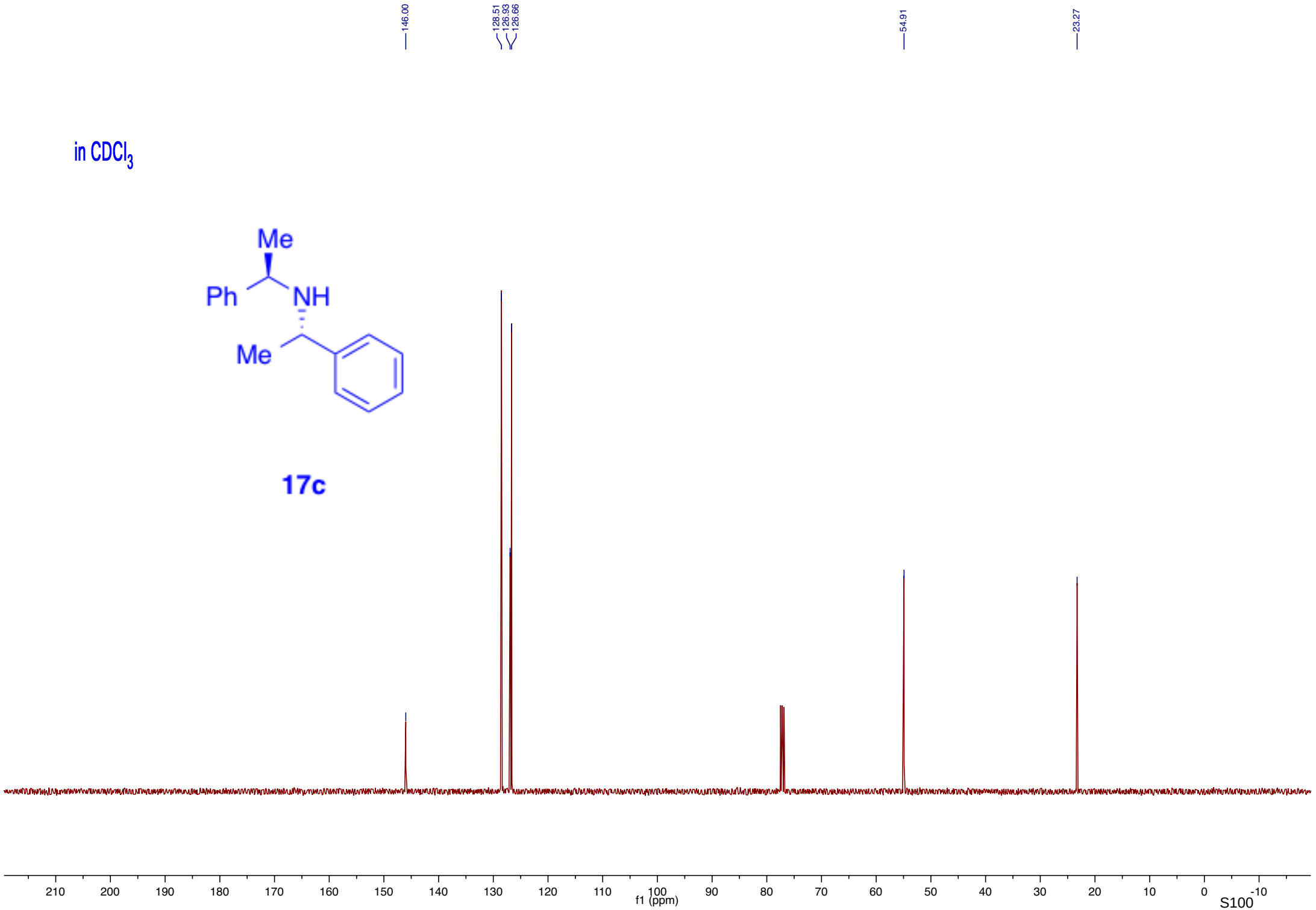

146.55
133.57
132.61
127.91
127.72
127.65
125.79
125.35
125.20
124.63
52.66
51.53
30.17
27.27
in CDCl3
NH
Me
17b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

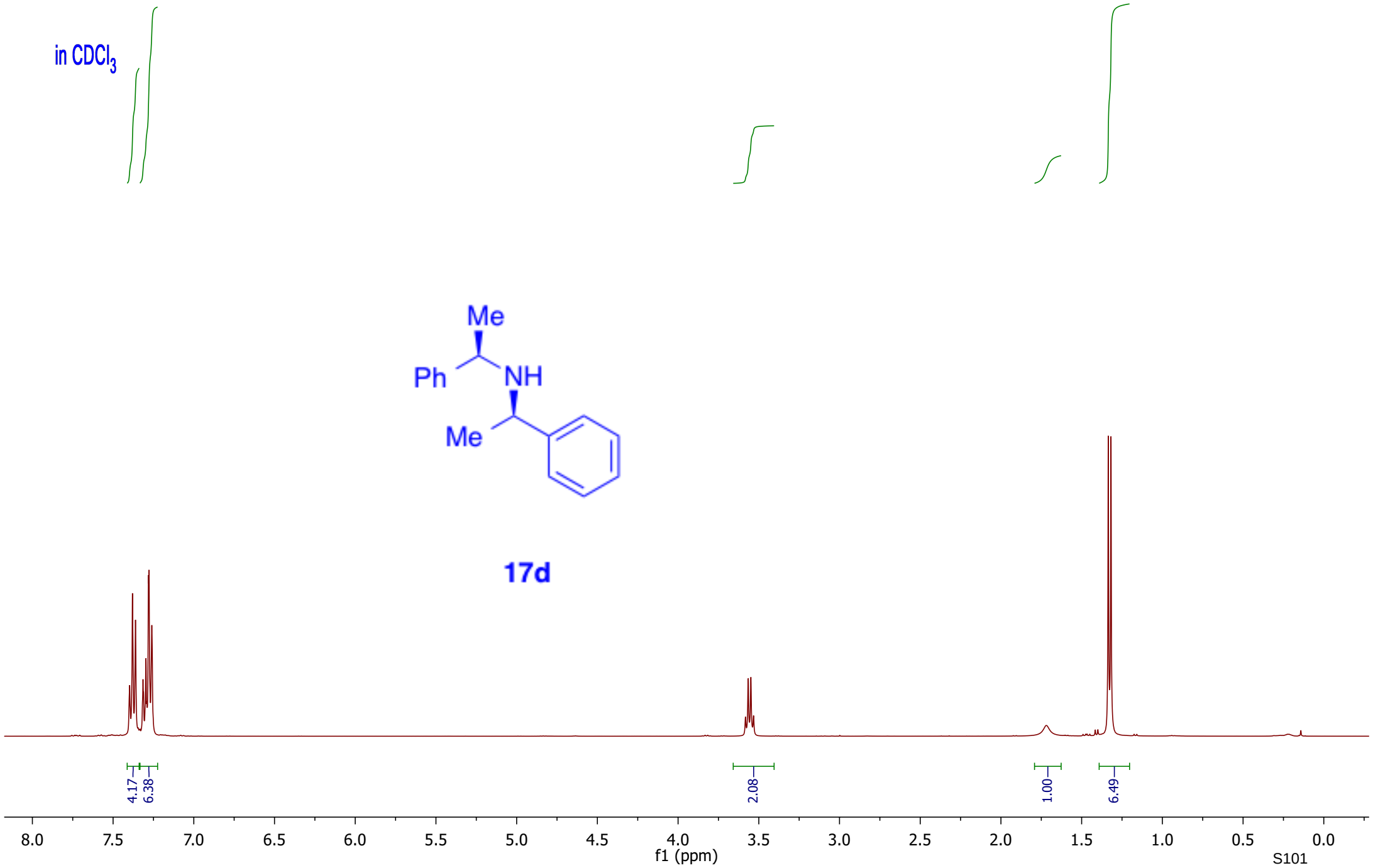
in $CDCl_3$

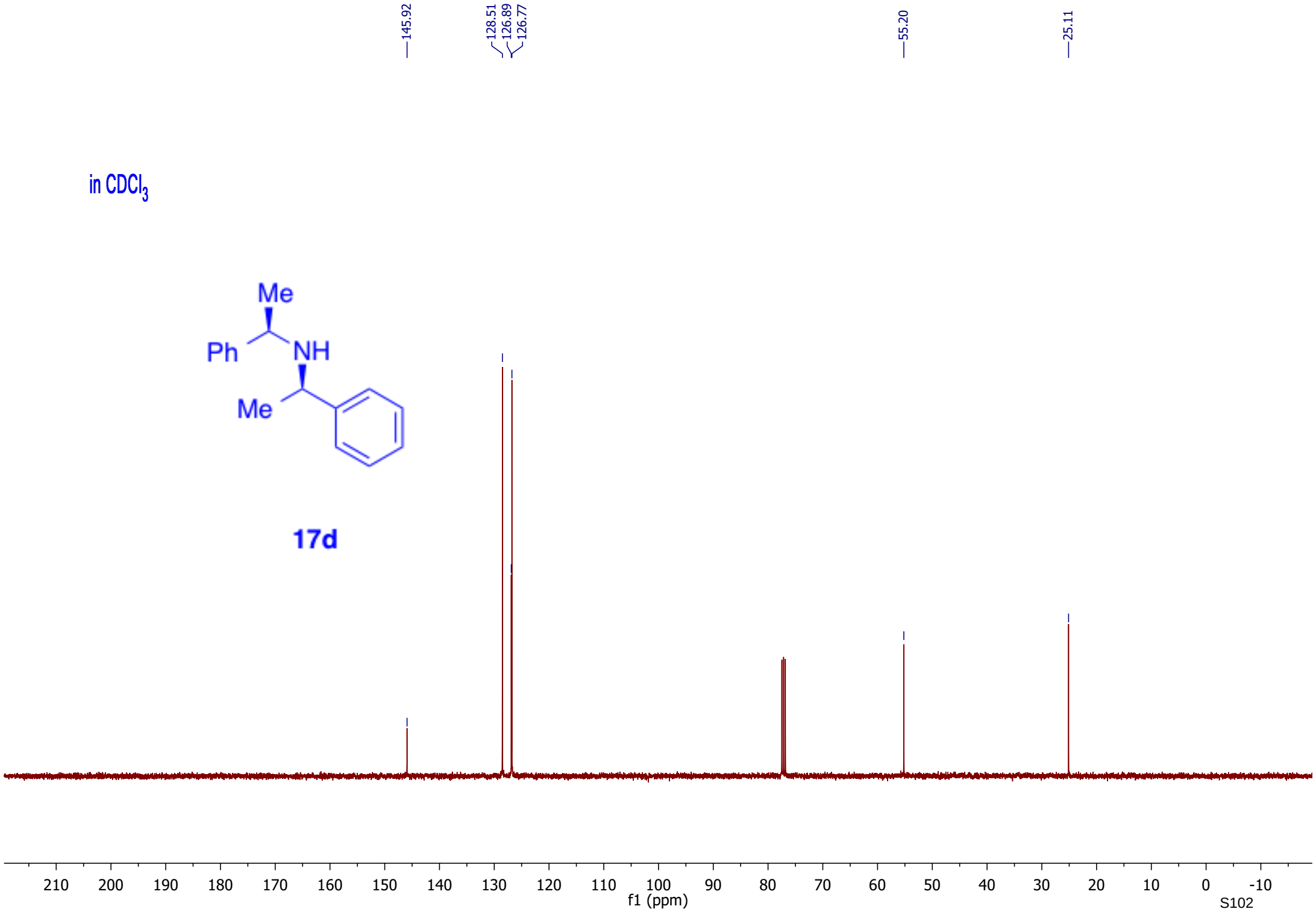

Me
Ph
NH
Me

17c

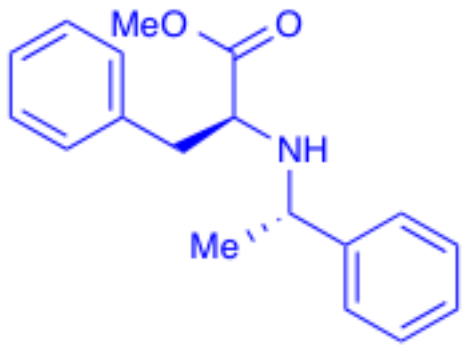
10.15
2.00
0.82
6.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.00
128.51
126.93
126.66
54.91
23.27
in CDCl3
Me
Ph
NH
Me
17c
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)


in CDCl3
Me
Ph
NH
Me
17d
4.17
6.38
2.08
1.00
6.49
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)

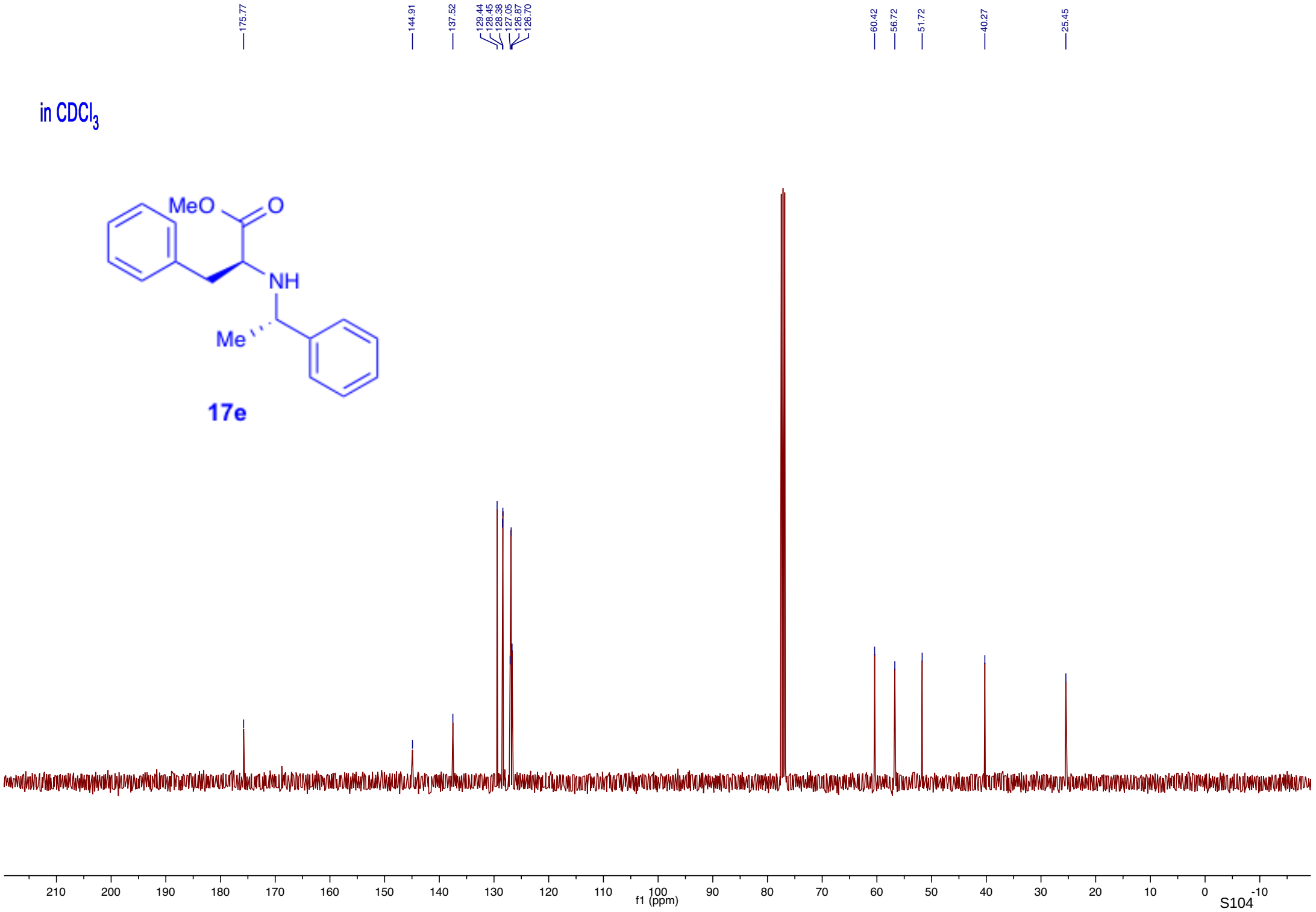

145.92
128.51
126.89
126.77
55.20
25.11
in CDCl3
Me
Ph
NH
Me
17d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

in $CDCl_3$

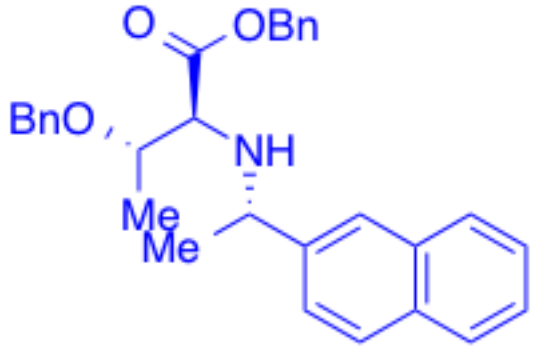

MeO
O
NH
Me

17e

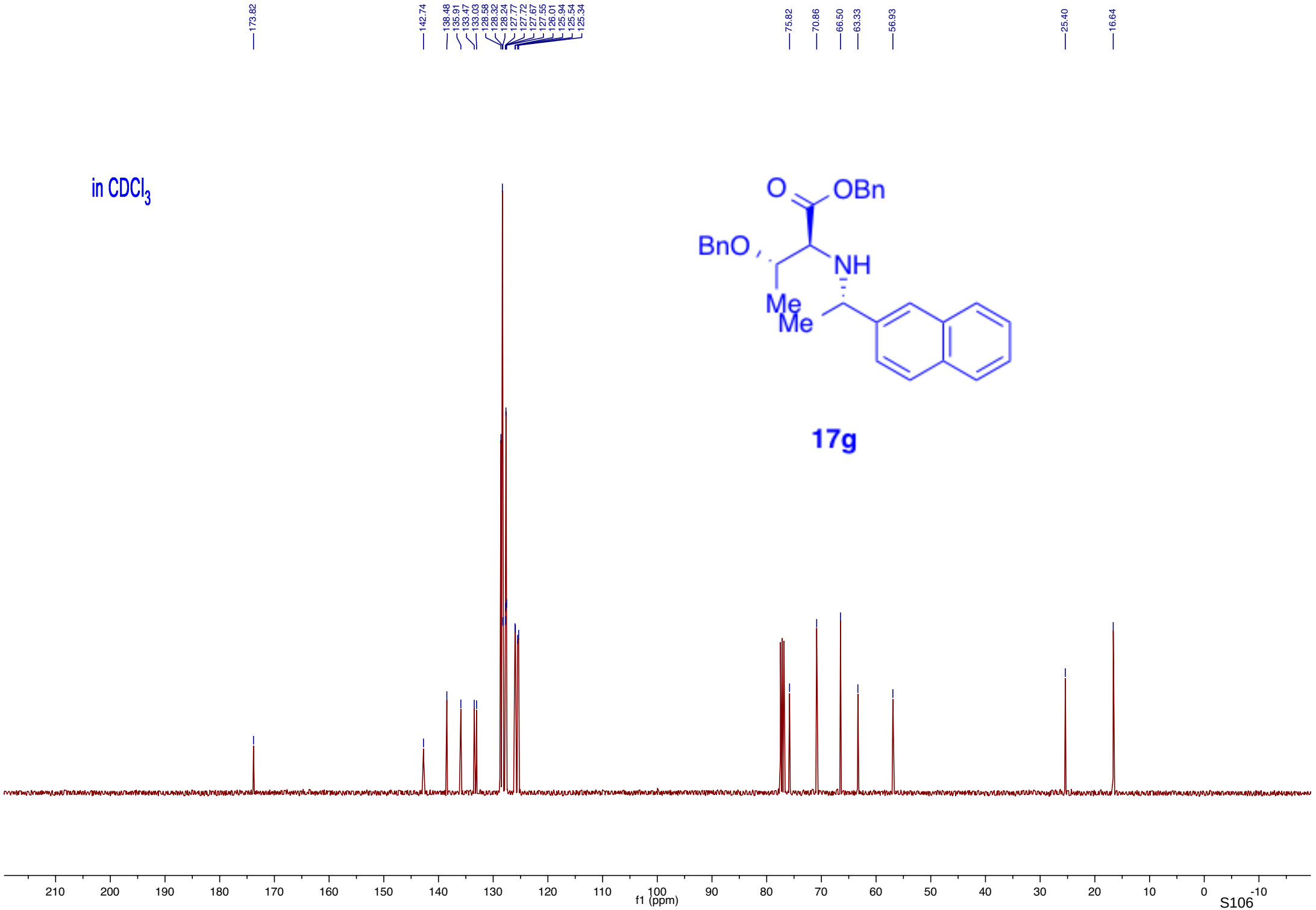
4.77
3.82
1.00
2.95
1.00
2.02
1.03
3.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

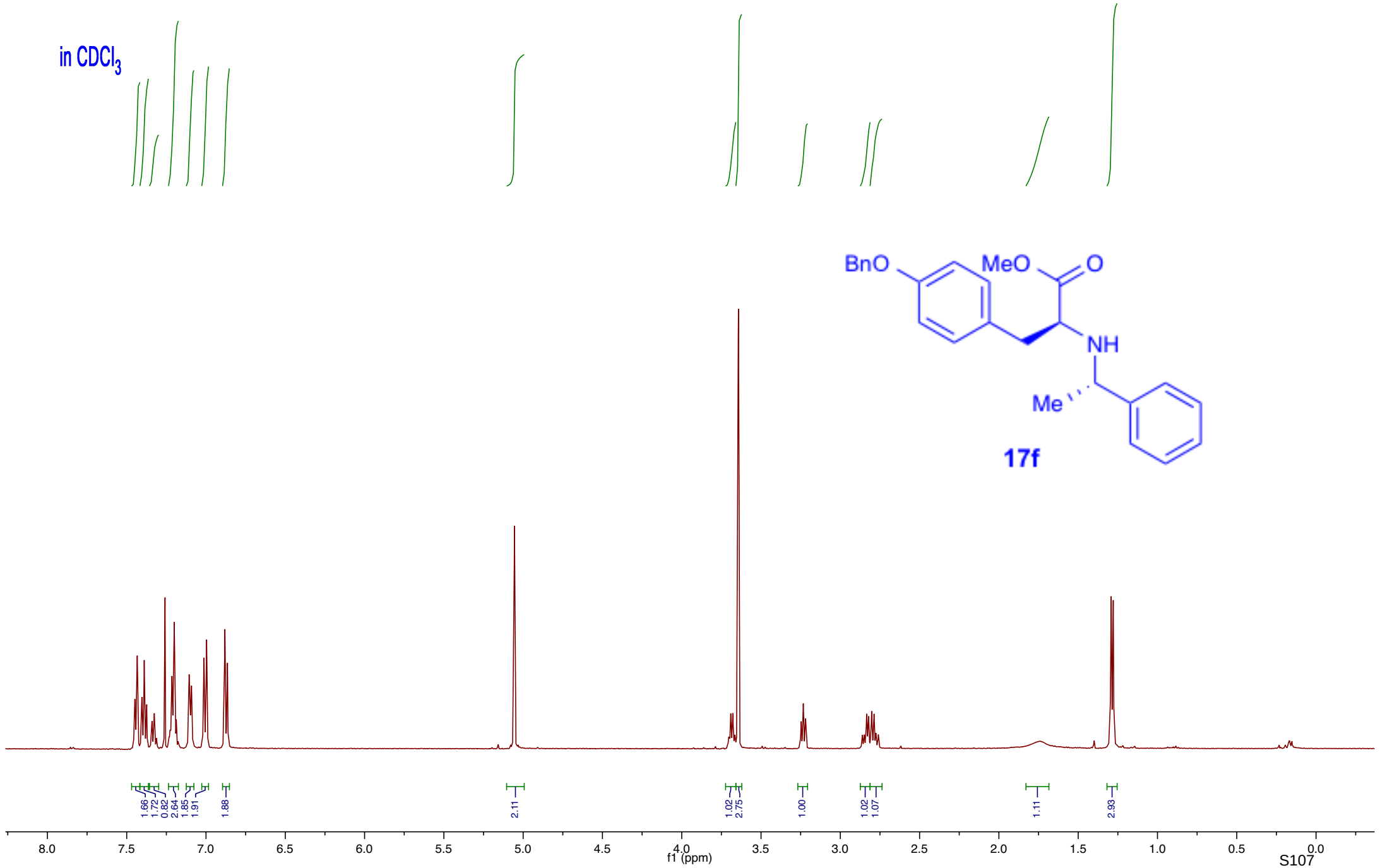

175.77
144.91
137.52
129.44
128.45
128.38
127.05
126.87
126.70
60.42
56.72
51.72
40.27
25.45
in CDCl3
MeO
O
NH
Me
17e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

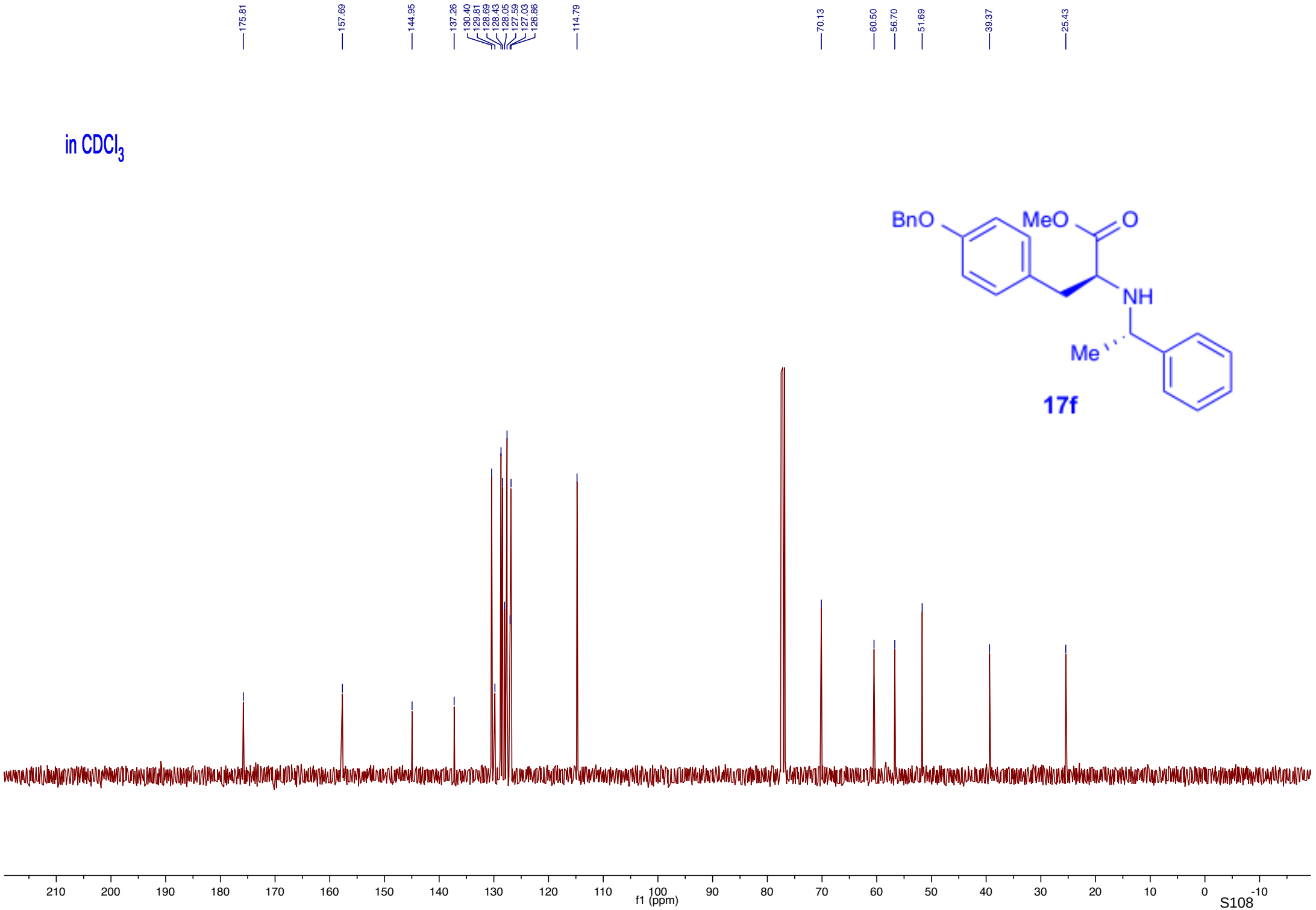
in $CDCl_3$



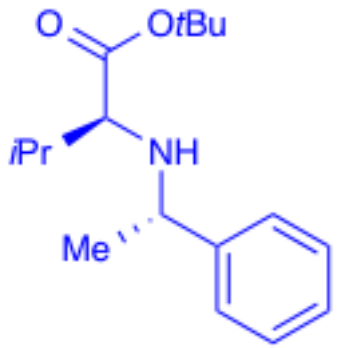
17g


173.82
142.74
138.48
135.91
133.47
133.03
128.58
128.32
128.24
127.77
127.72
127.67
127.55
126.01
125.94
125.54
125.34
75.82
70.86
66.50
63.33
56.93
25.40
16.64
in CDCl3
O
OBn
BnO
NH
Me
Me
17g
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)


in CDCl3
BnO
MeO
O
NH
Me
17f
1.66
1.72
0.82
2.64
1.85
1.91
1.88
2.11
1.02
2.75
1.00
1.02
1.07
1.11
2.93
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)

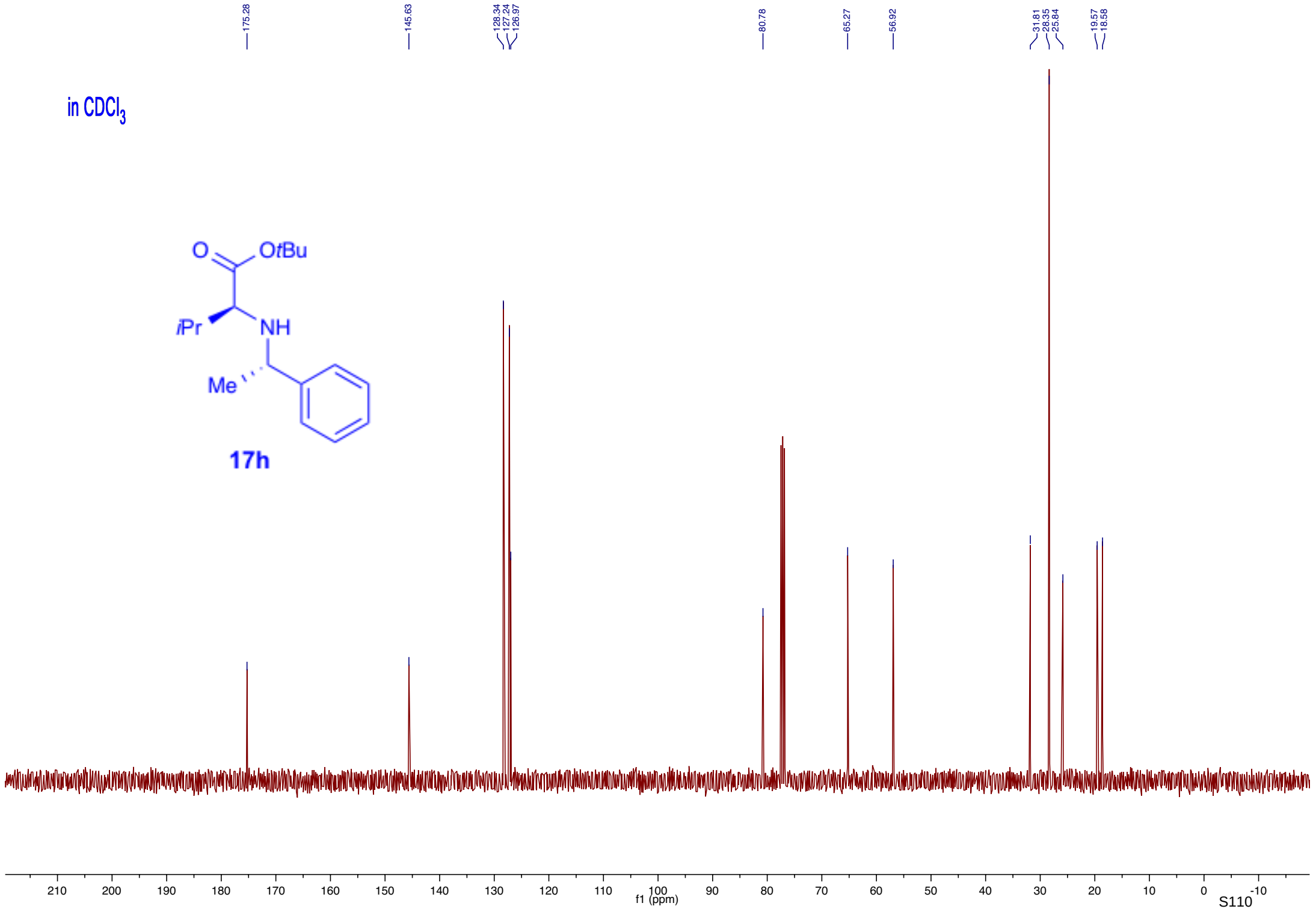

175.81
157.69
144.95
137.26
130.40
129.81
128.69
128.43
128.05
127.59
127.03
126.86
114.79
70.13
60.50
56.70
51.69
39.37
25.43
in CDCl3
BnO
MeO
O
NH
Me
17f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

in $CDCl_3$

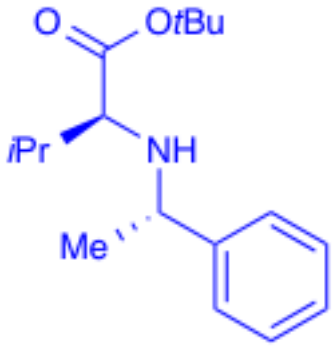

O
OtBu
iPr
NH
Me

17h

4.03
0.99
1.00
0.99
2.07
9.12
3.15
6.19
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)

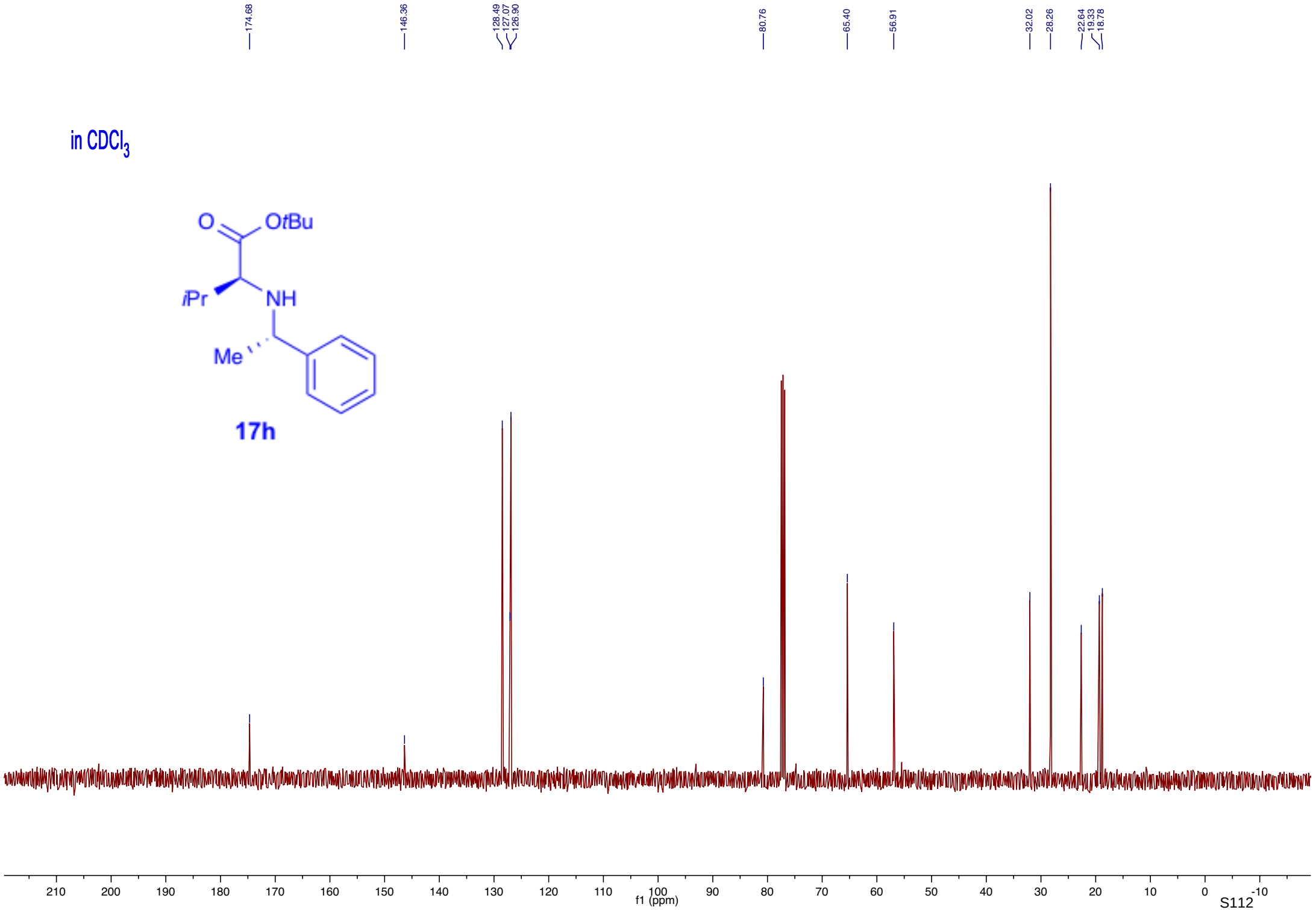

175.28
145.63
128.34
127.24
126.97
80.78
65.27
56.92
31.81
28.35
25.84
19.57
18.58
in CDCl3
O
OtBu
iPr
NH
Me
17h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

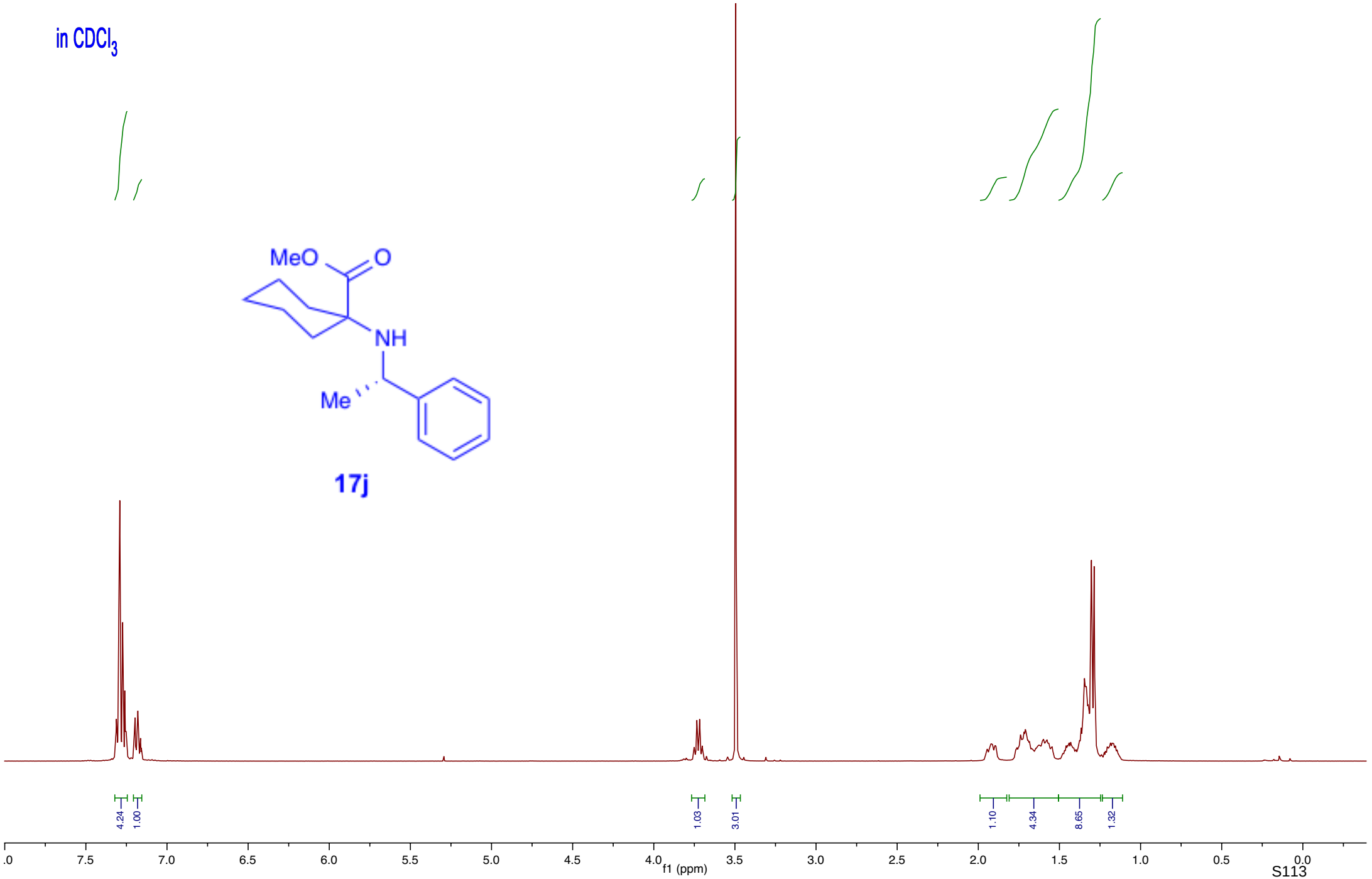
in $CDCl_3$

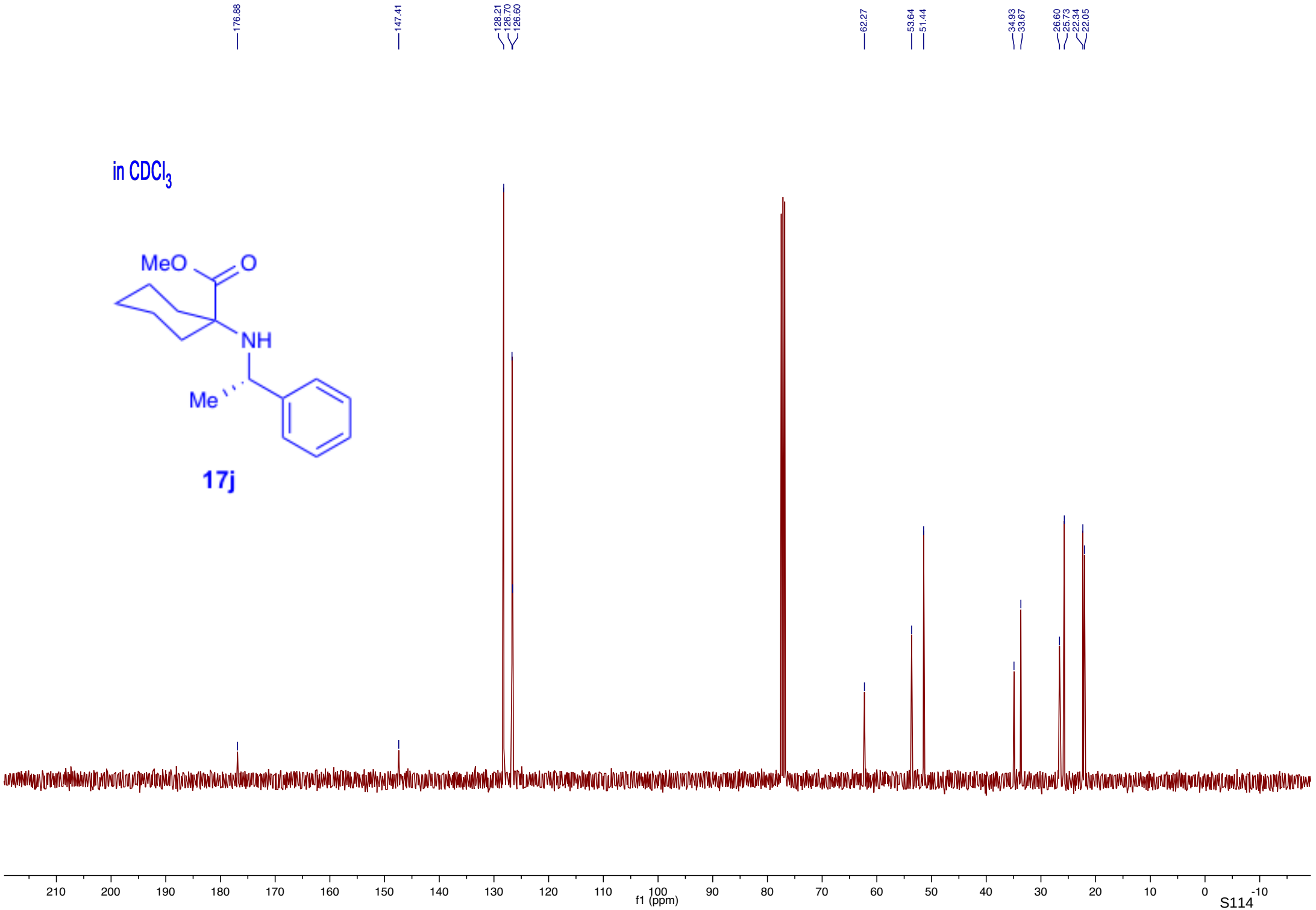

O
OtBu
iPr
NH
Me

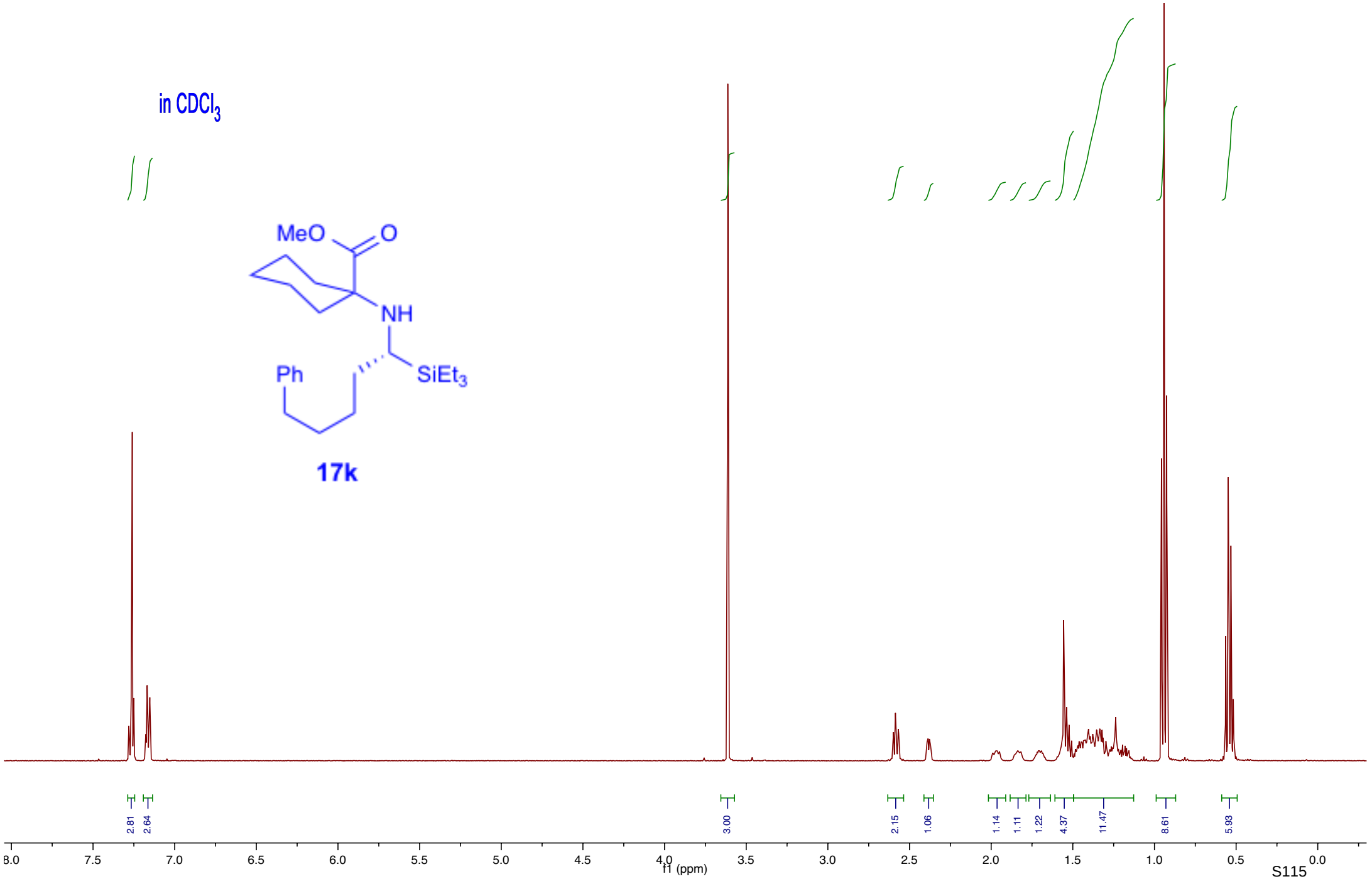
17h

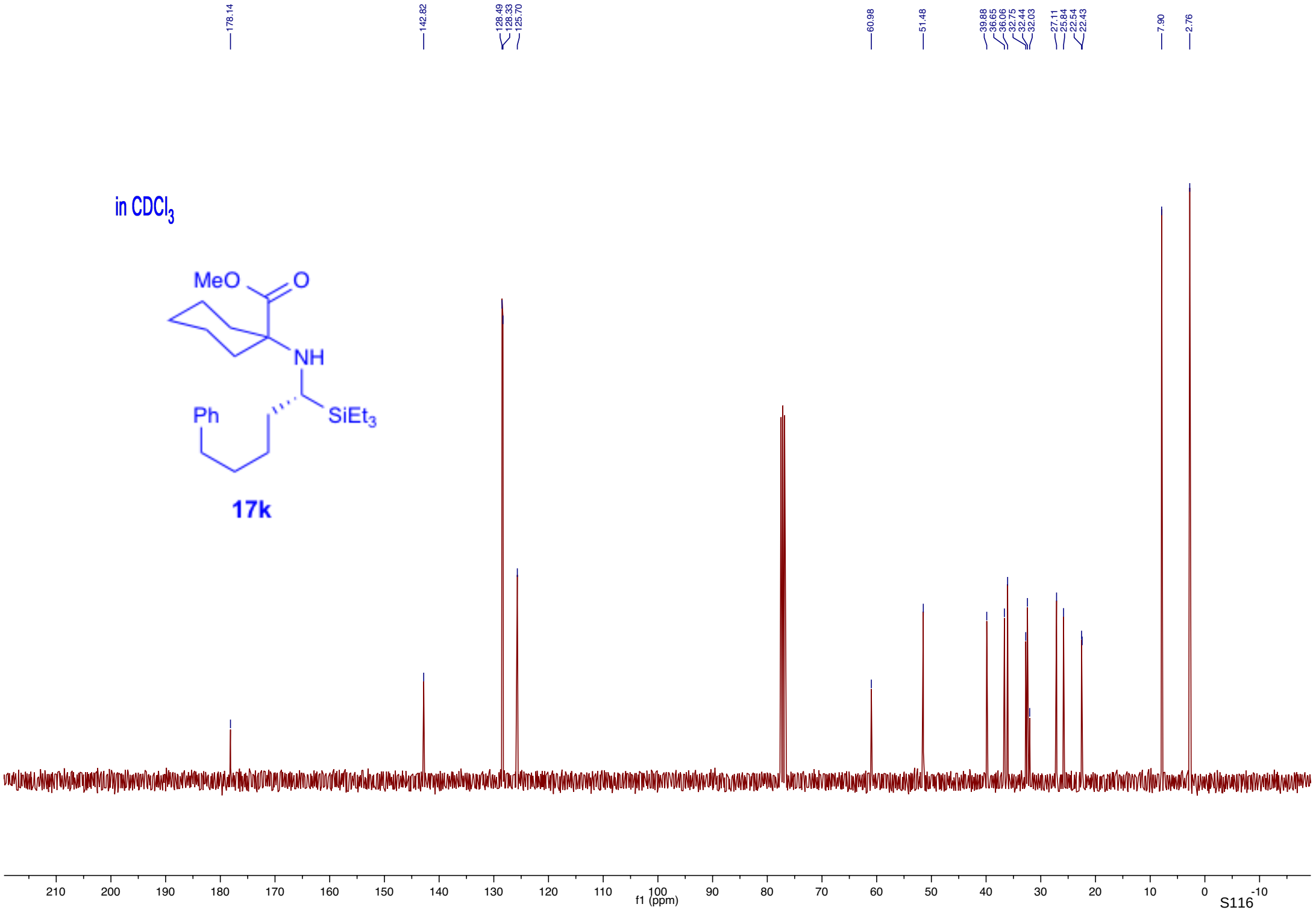
3.56
0.84
1.06
1.00
2.02
8.93
3.29
5.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


174.68
146.36
128.49
127.07
126.90
80.76
65.40
56.91
32.02
28.26
22.64
19.33
18.78
in CDCl3
O
OtBu
iPr
NH
Me
17h
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)

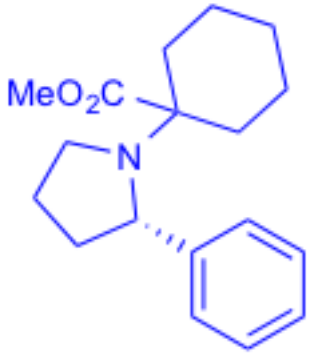

in CDCl3
MeO
O
NH
Me
17j
4.24
1.00
1.03
3.01
1.10
4.34
8.65
1.32
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
f1 (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


176.88
147.41
128.21
126.70
126.60
62.27
53.64
51.44
34.93
33.67
26.60
25.73
22.34
22.05
in CDCl3
MeO
O
NH
Me
17j
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)


in CDCl3
MeO
O
NH
Ph
SiEt3
17k
2.81
2.64
3.00
2.15
1.06
1.14
1.11
1.22
4.37
11.47
8.61
5.93
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)

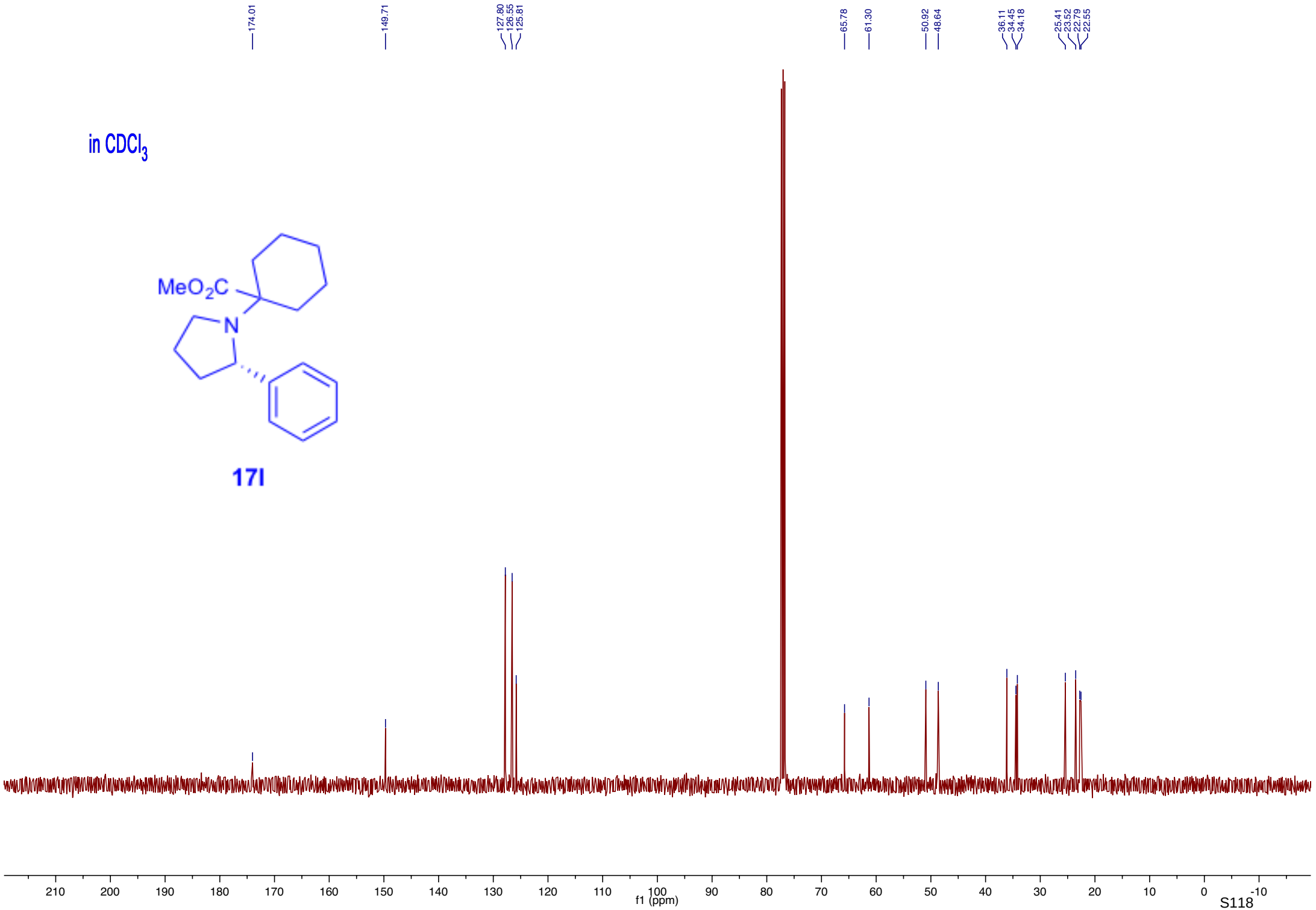

178.14
142.82
128.49
128.33
125.70
60.98
51.48
39.88
36.65
36.06
32.75
32.44
32.03
27.11
25.84
22.54
22.43
7.90
2.76
in CDCl3
MeO
O
NH
Ph
SiEt3
17k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

in $CDCl_3$

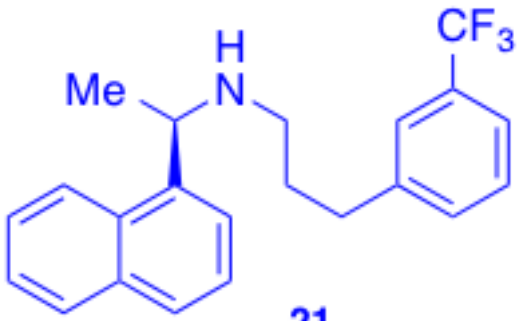

MeO2C
N

17l

2.96
2.55
1.00
1.02
3.02
1.04
1.04
1.04
1.15
2.14
4.68
6.04
1.17
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)

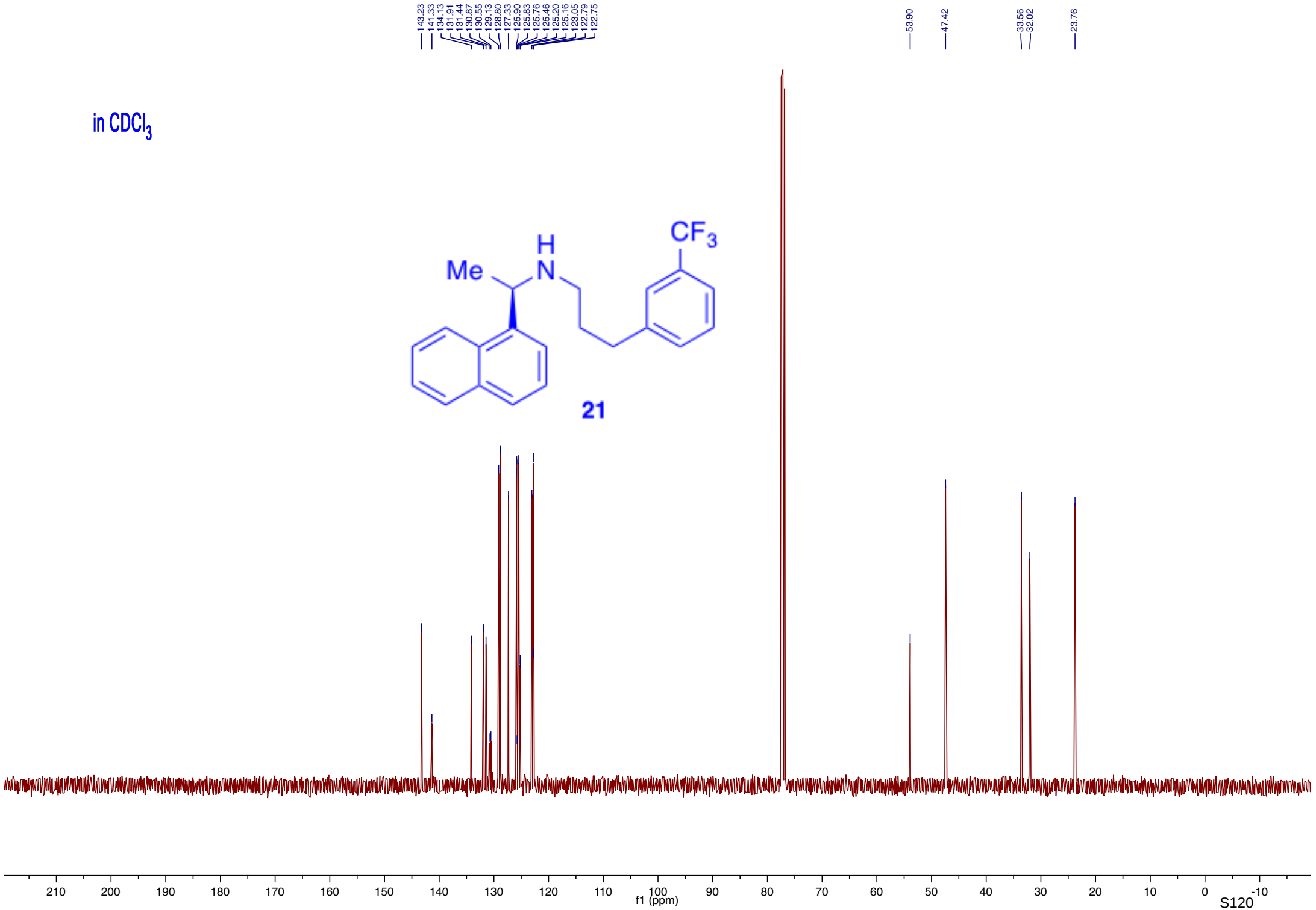

174.01
149.71
127.80
126.55
125.81
65.78
61.30
50.92
48.64
36.11
34.45
34.18
25.41
23.52
22.79
22.55
in CDCl3
MeO2C
N
17l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

in $CDCl_3$

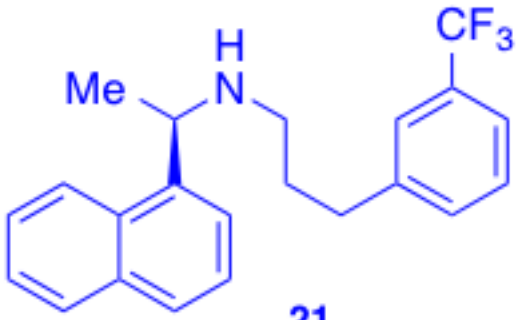

H
N
Me
CF_3

21

0.98
0.98
1.00
1.04
3.07
1.98
2.02
1.02
4.18
2.14
4.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


143.23
141.33
134.13
131.91
131.44
130.87
130.55
129.13
128.80
127.33
125.90
125.83
125.76
125.46
125.20
125.16
123.05
122.79
122.75
53.90
47.42
33.56
32.02
23.76
in CDCl3
H
N
Me
CF3
21
f1 (ppm)

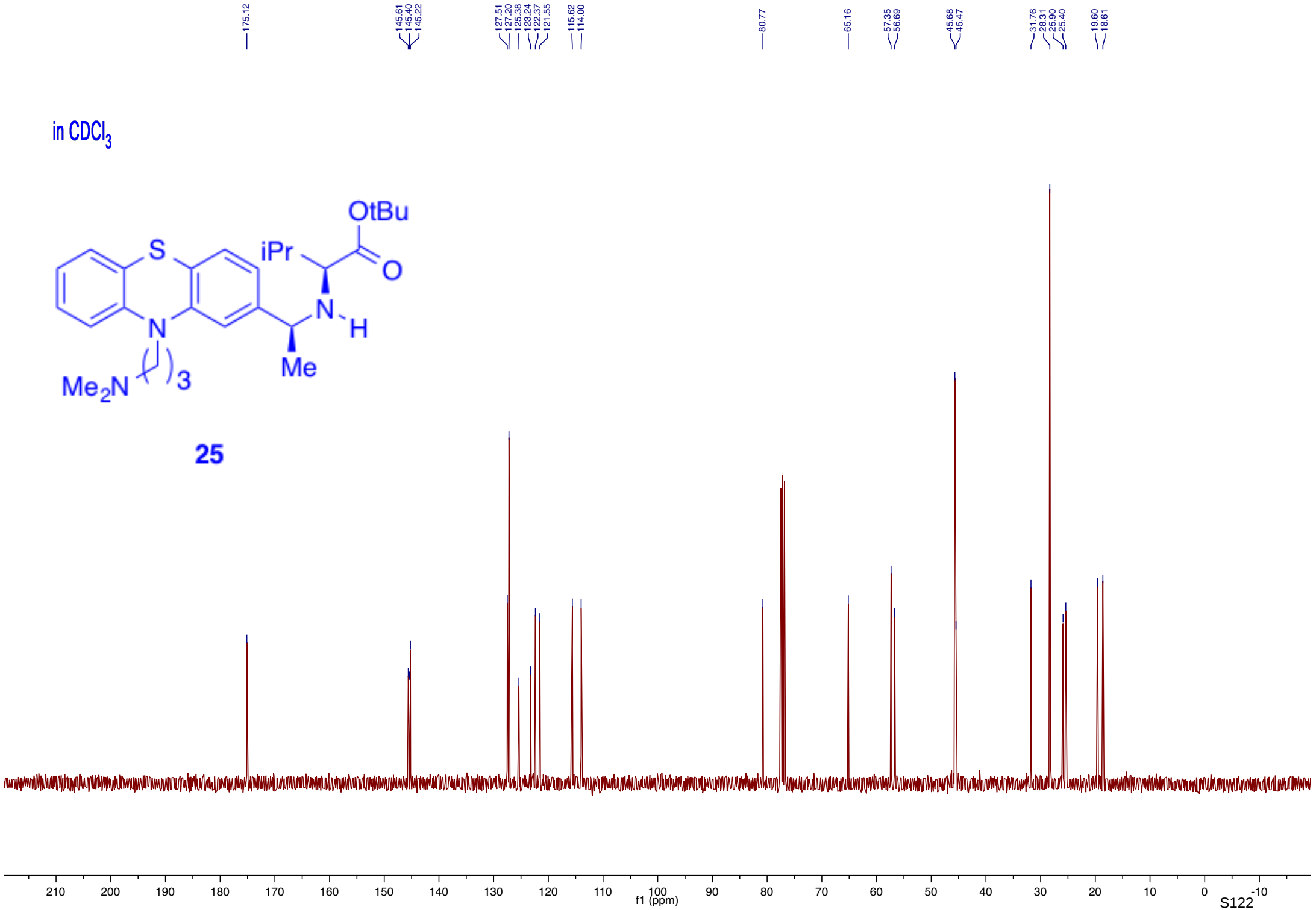
in $CDCl_3$



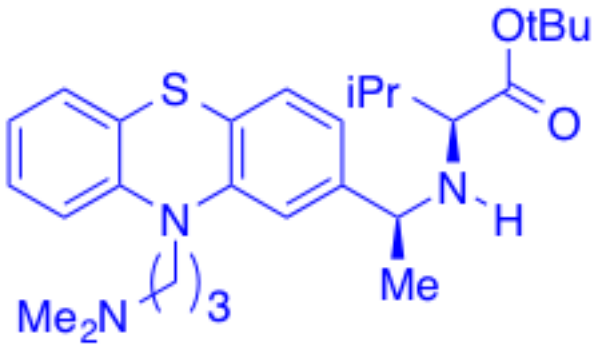
21

-62.55

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

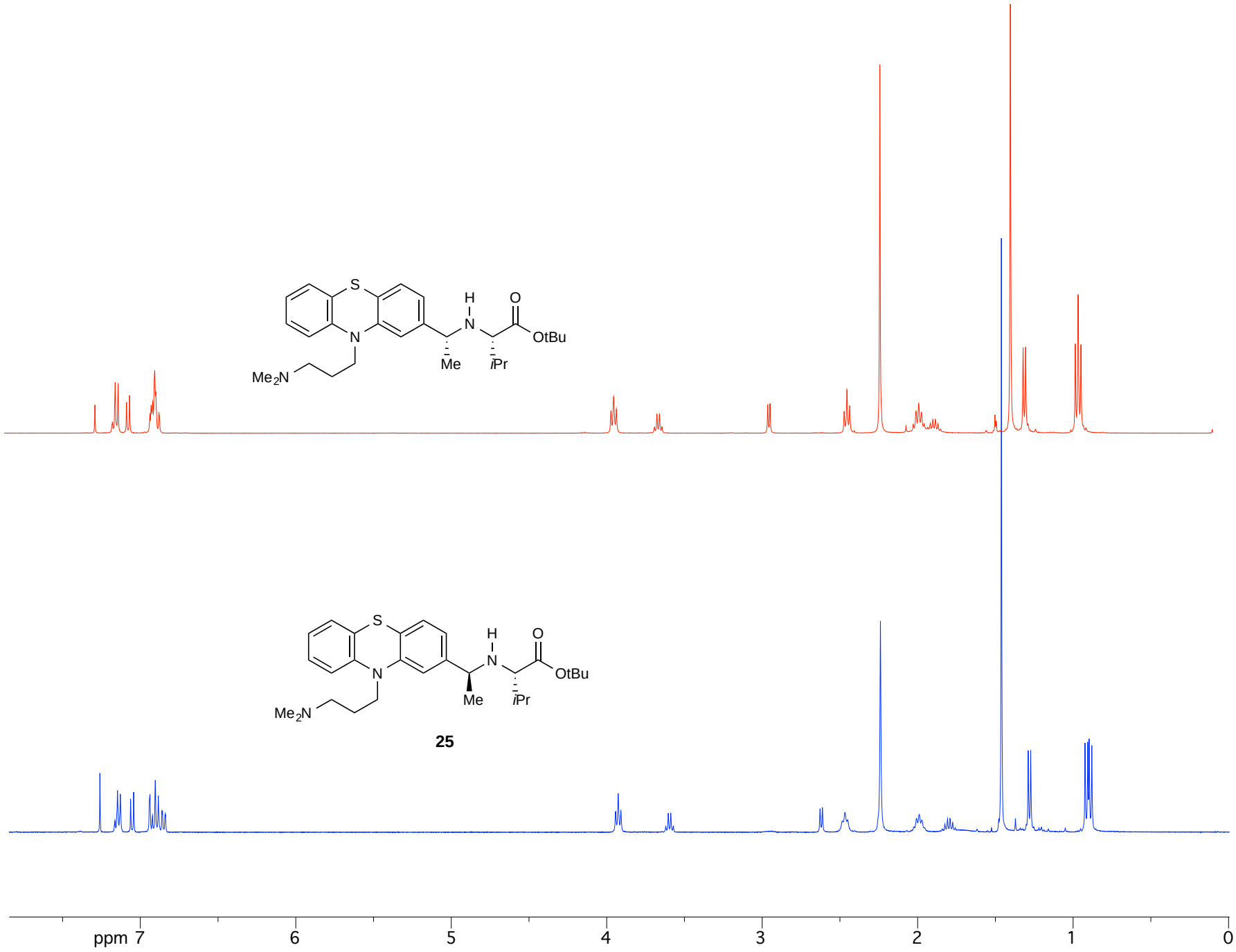

175.12
145.61
145.40
145.22
127.51
127.20
125.38
123.24
122.37
121.55
115.62
114.00
80.77
65.16
57.35
56.69
45.68
45.47
31.76
28.31
25.90
25.40
19.60
18.61
in CDCl3
OtBu
S
iPr
O
N
H
N
Me
Me2N
3
25
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

in $CDCl_3$


OtBu
S
iPr
O
N
H
N
Me
Me2N
3

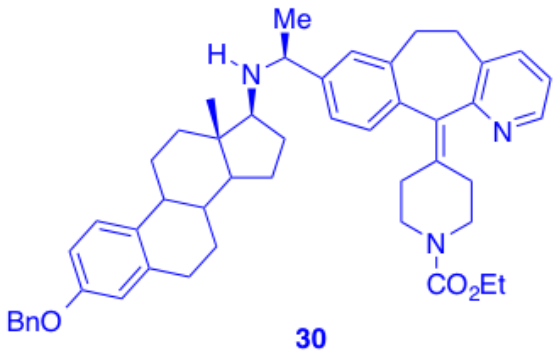
25

2.05
1.00
0.94
2.14
1.06
2.06
1.04
1.02
2.01
6.09
2.16
1.24
9.74
3.30
6.55
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)

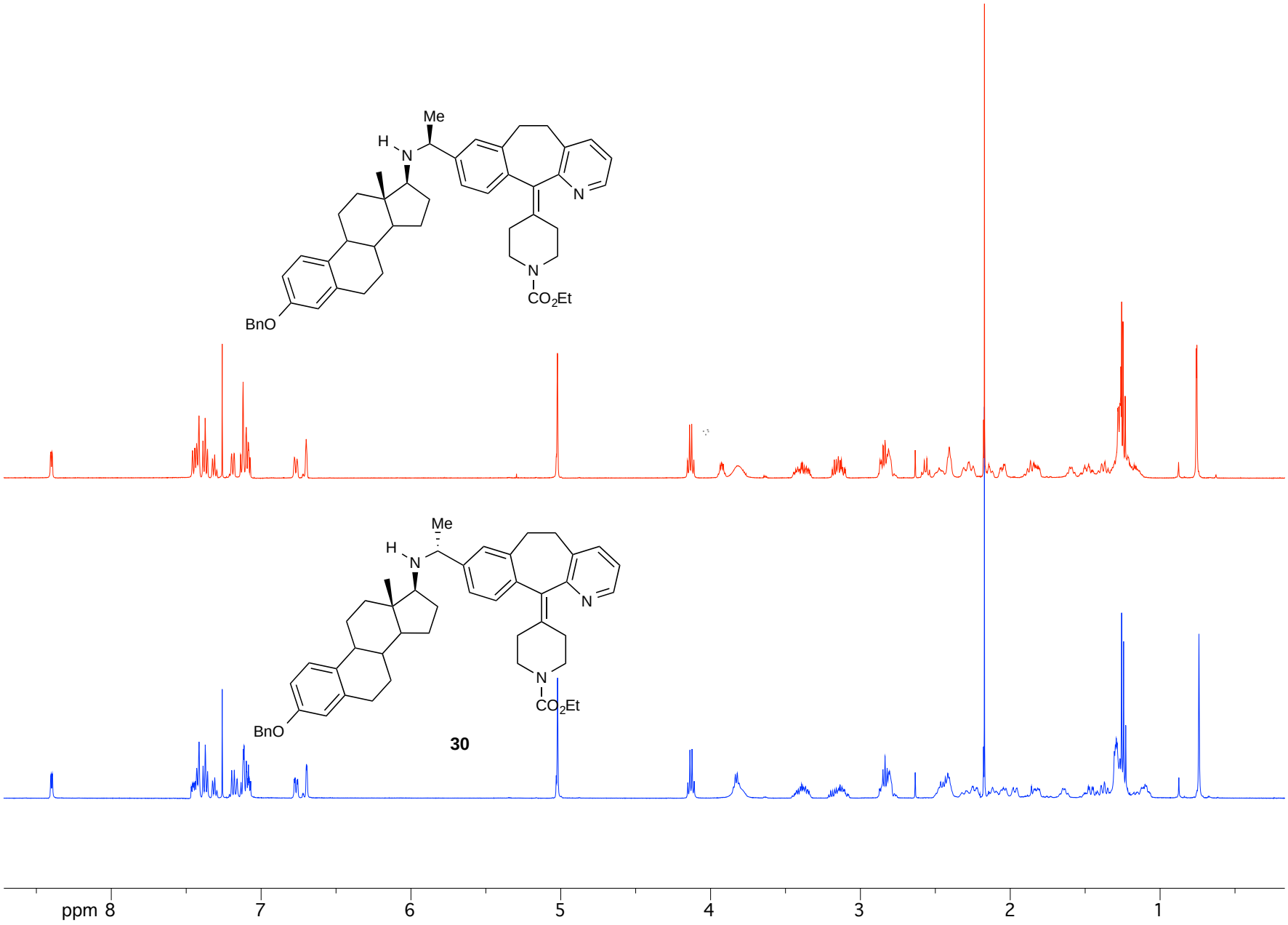


25

in $CDCl_3$

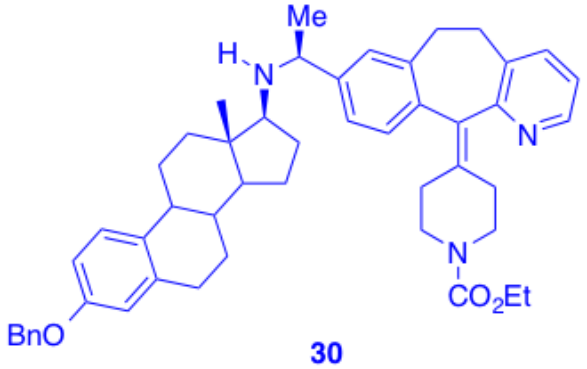


30


Me
H
N
N
N
CO2Et
BnO
Me
H
N
N
N
CO2Et
BnO
30
ppm 8
7
6
5
4
3
2
1

in $CDCl_3$

158.52
158.22
156.94
155.70
146.65
145.92
145.83
138.17
138.15
137.66
137.30
135.62
133.42
129.36
128.59
127.86
127.53
127.49
127.31
126.36
126.33
112.47
70.20
66.13
66.09
61.30
56.15
56.00
52.25
52.22
45.14
45.02
44.27
43.02
42.99
39.01
37.58
32.35
32.29
32.05
31.88
30.89
30.68
30.15
29.94
27.56
26.56
25.18
23.69
14.80
11.91

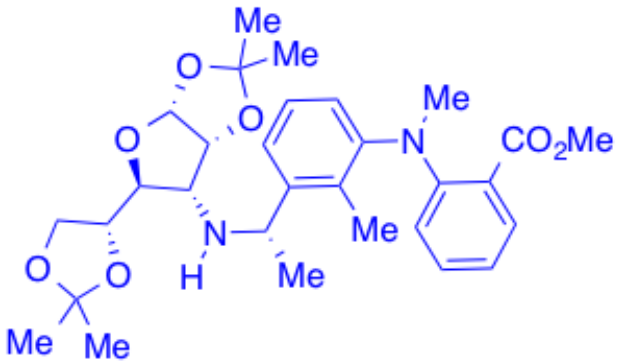


30

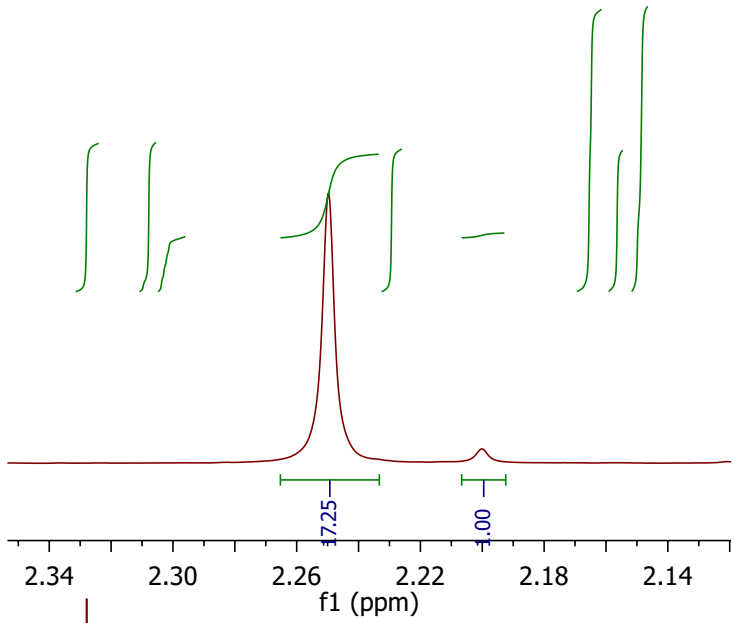
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

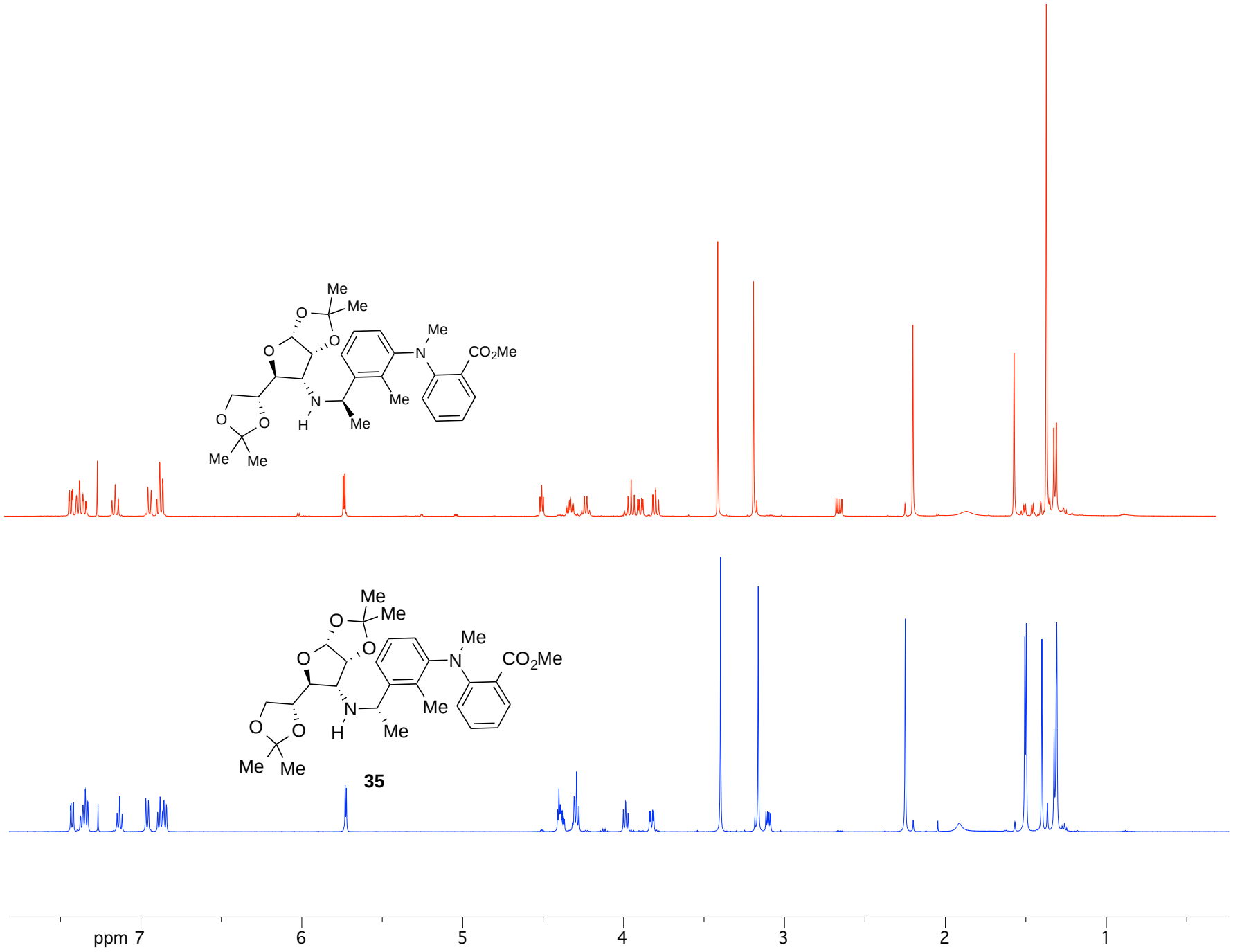
in $CDCl_3$

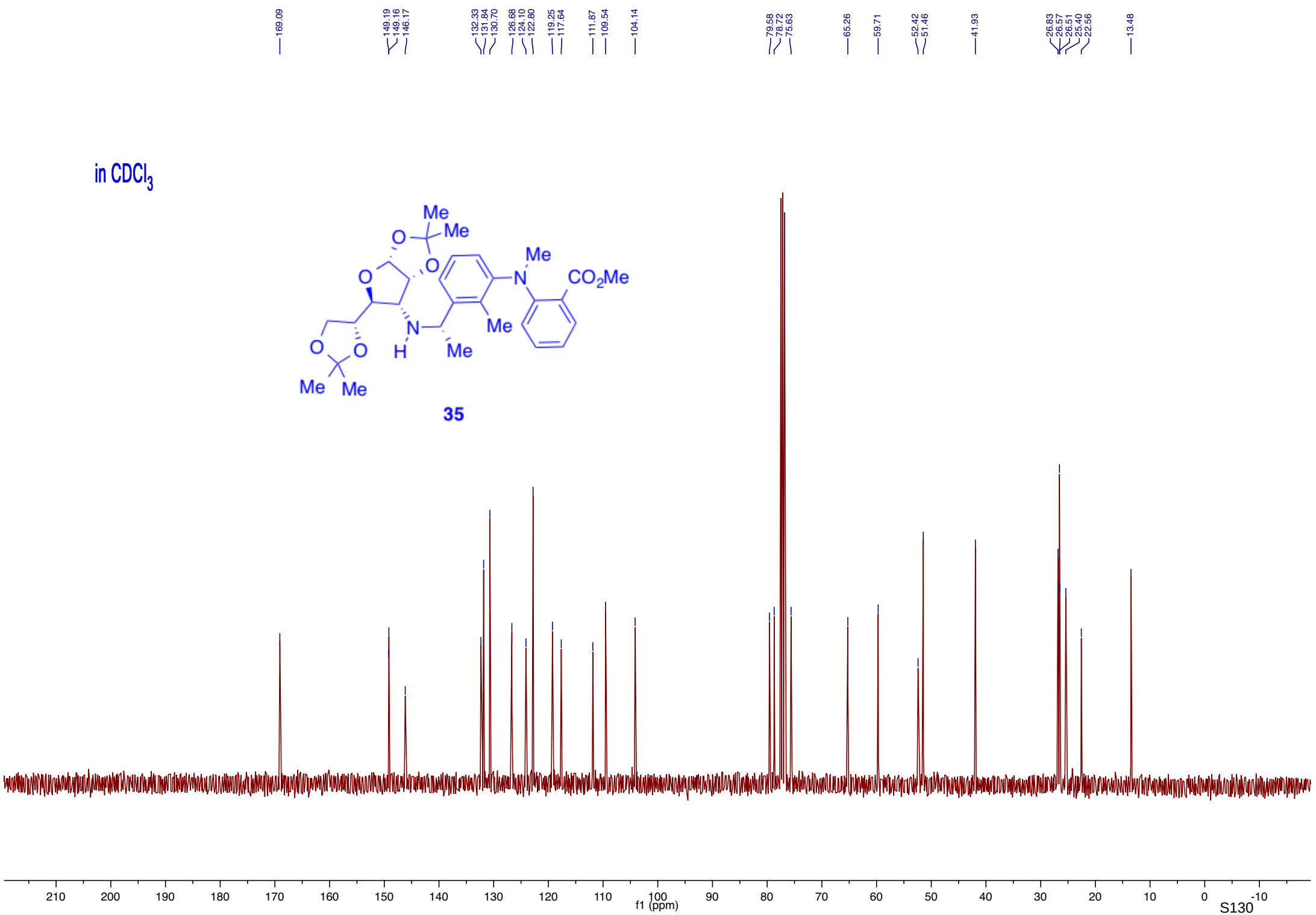

Me
Me
O
O
O
O
N
Me
CO2Me
N
H
Me
Me
O
O
Me
Me

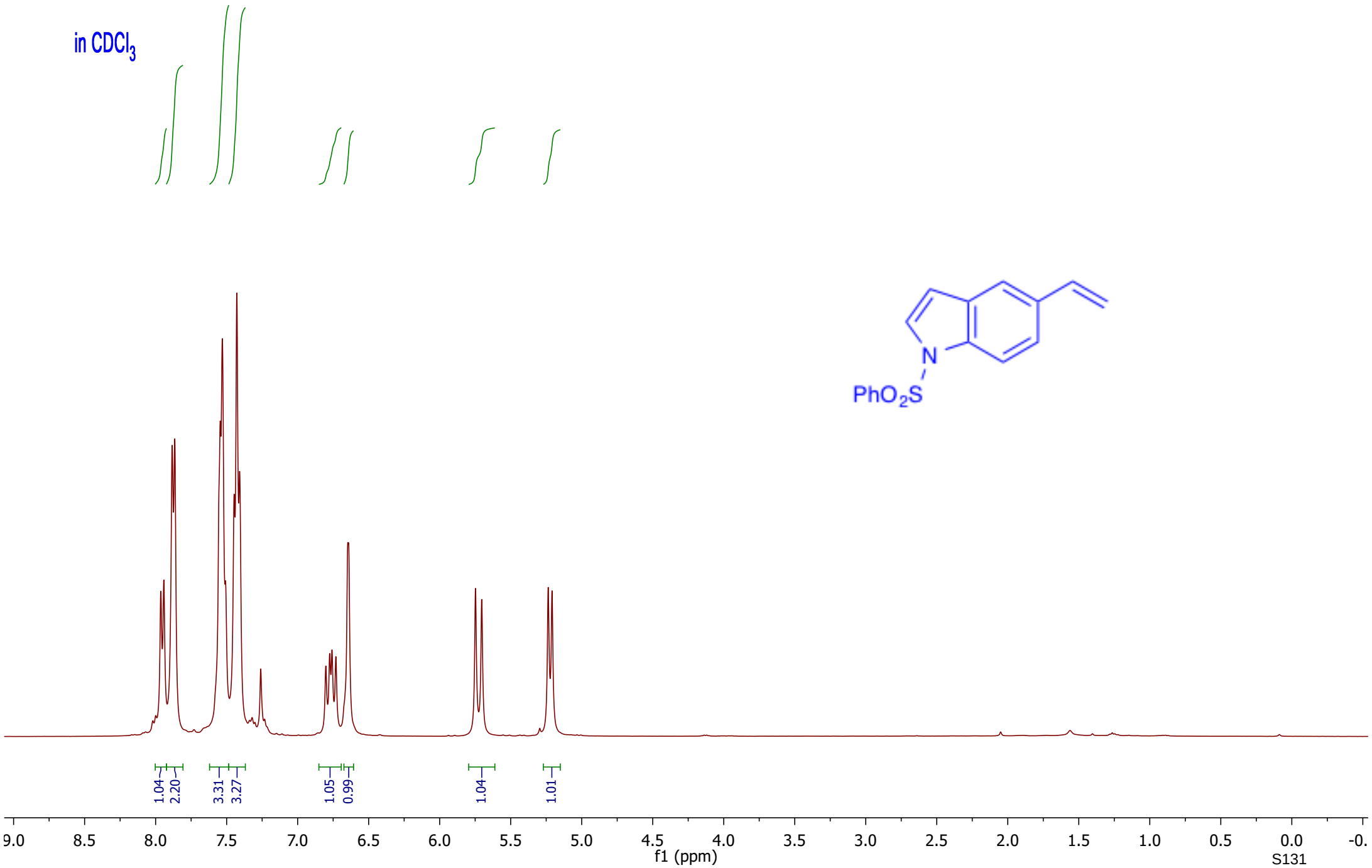
35

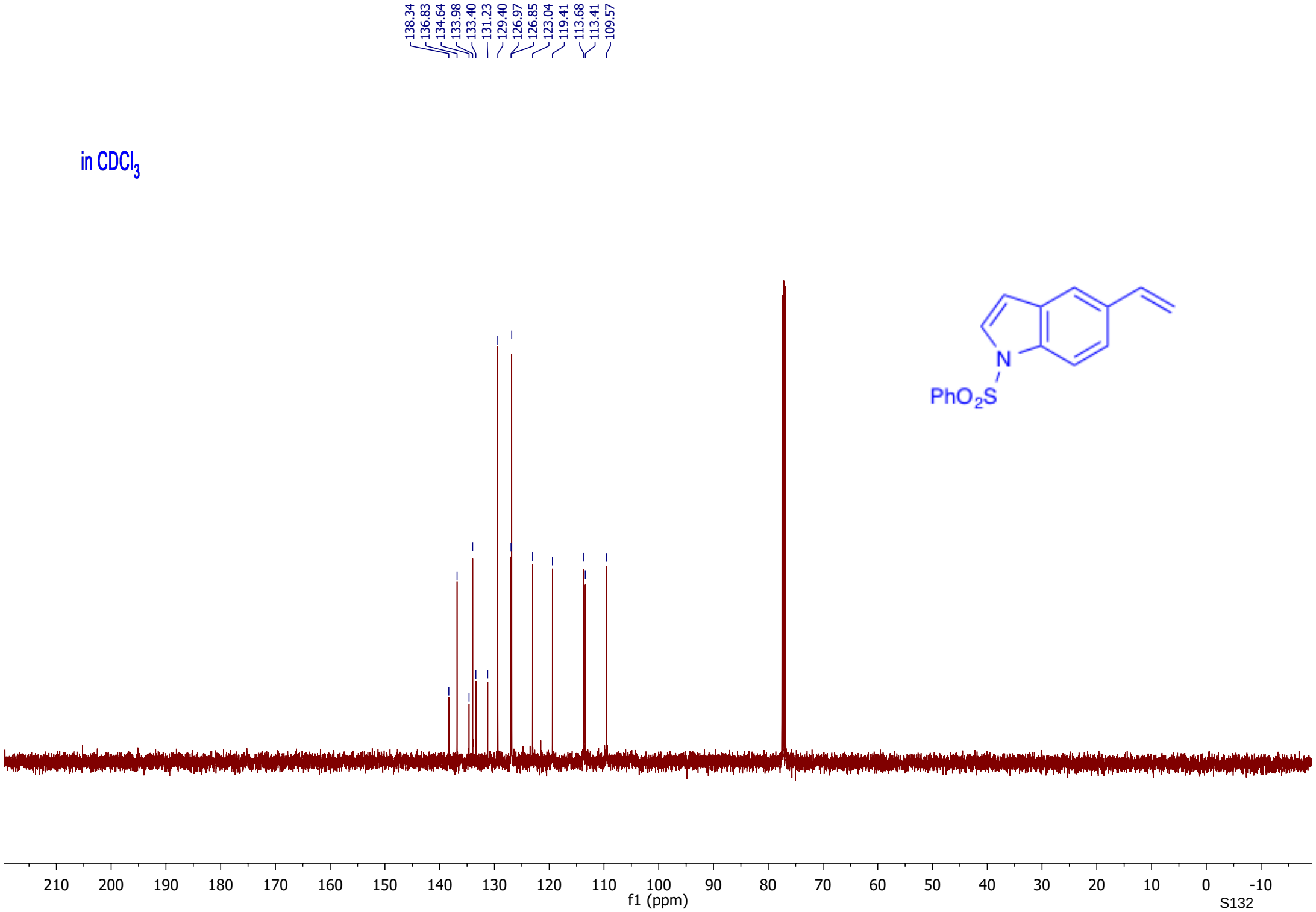

17.25
1.00
2.34
2.30
2.26
2.22
2.18
2.14
f1 (ppm)

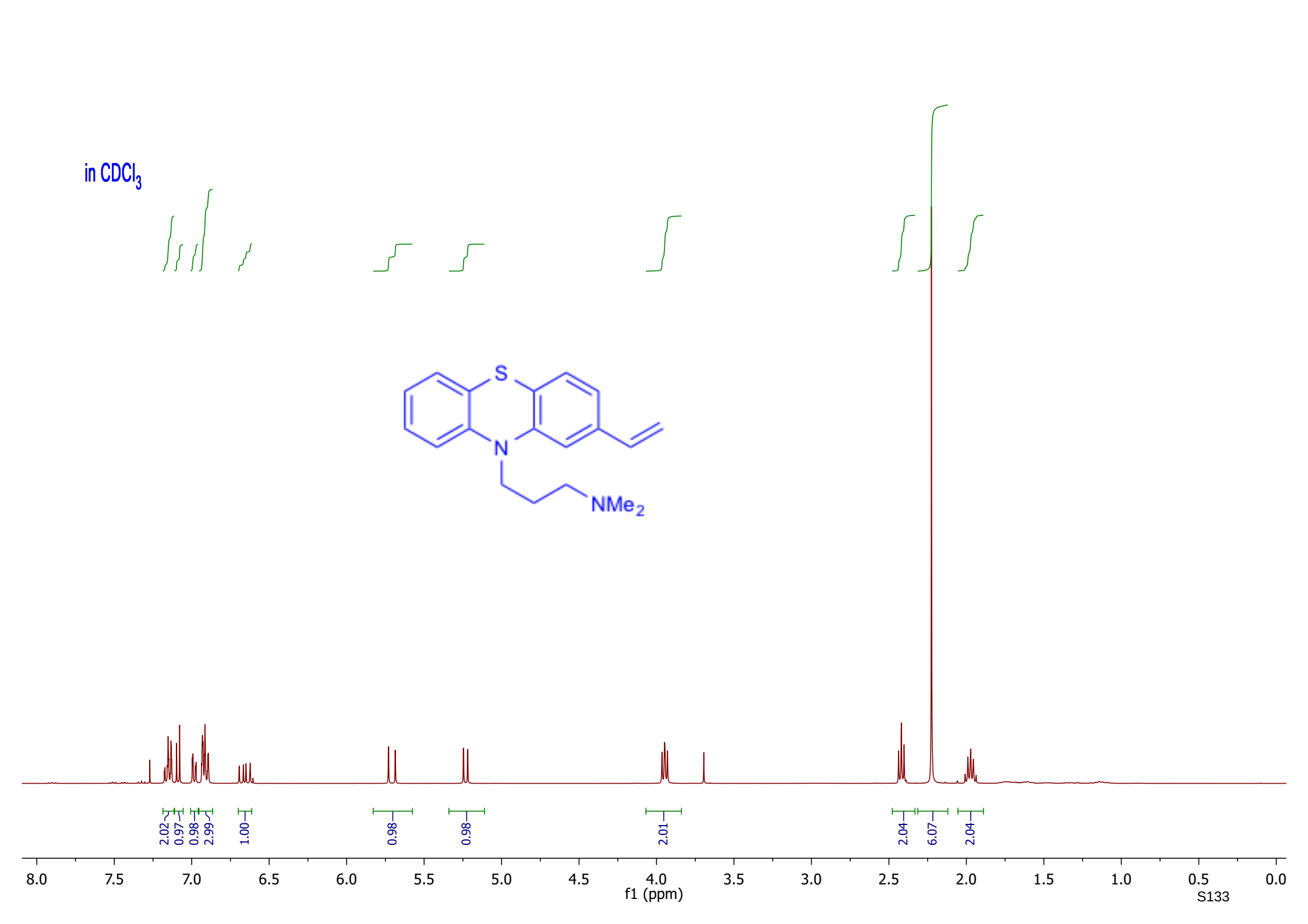
1.00
2.12
1.07
1.10
2.15
1.04
2.03
2.11
1.11
1.09
3.05
3.07
1.13
2.93
5.80
2.90
5.86
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

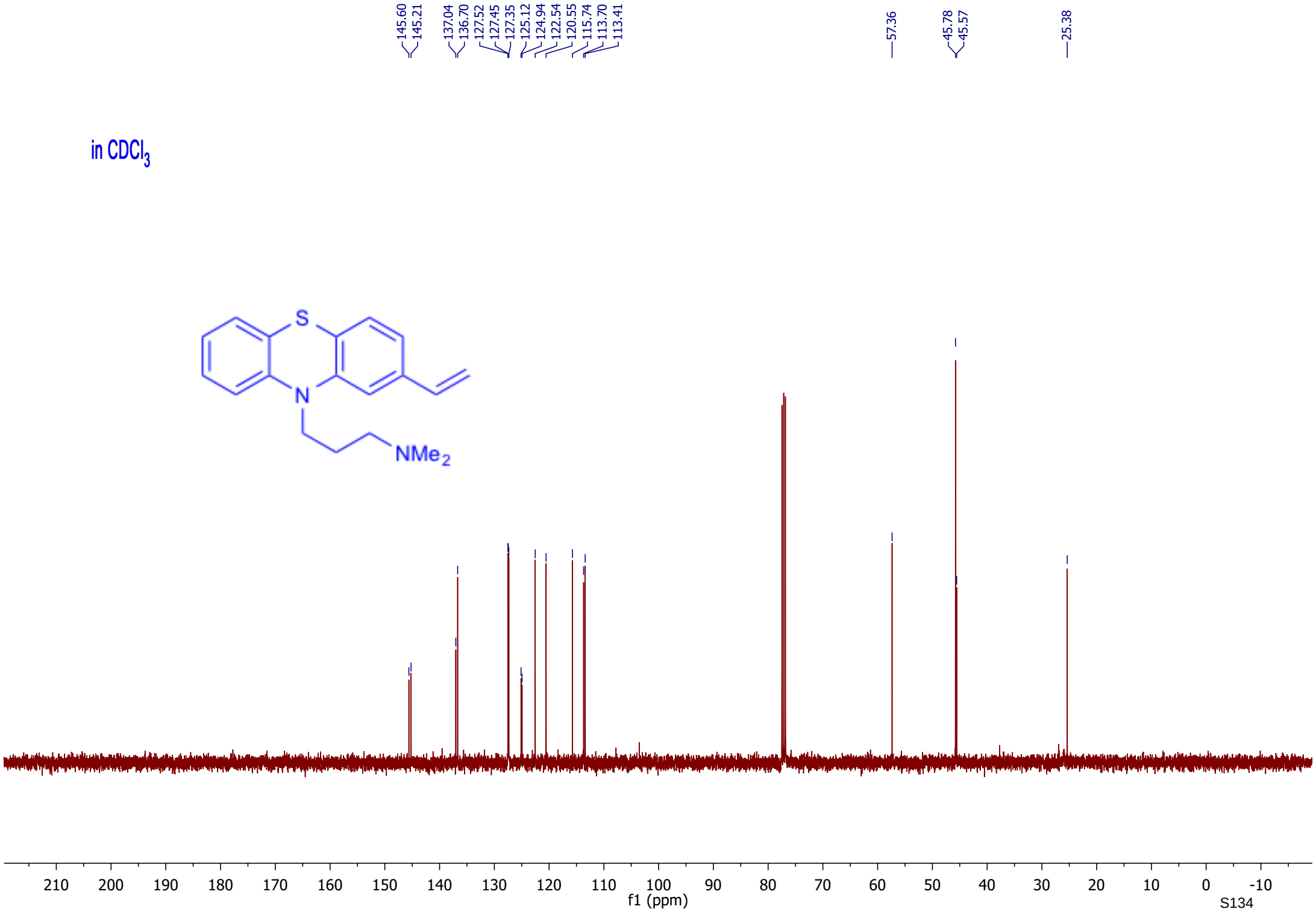

Me
Me
O
O
O
N
Me
CO2Me
Me
N
H
Me
O
O
Me
Me
Me
Me
O
Me
O
O
O
N
Me
CO2Me
Me
N
H
Me
O
O
Me
Me
35
ppm 7
6
5
4
3
2
1


169.09
149.19
149.16
146.17
132.33
131.84
130.70
126.68
124.10
122.80
119.25
117.64
111.87
109.54
104.14
79.58
78.72
75.63
65.26
59.71
52.42
51.46
41.93
26.83
26.57
26.51
25.40
22.56
13.48
in CDCl3
Me
Me
O
O
O
Me
N
CO2Me
N
H
Me
Me
O
O
Me
Me
35
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)

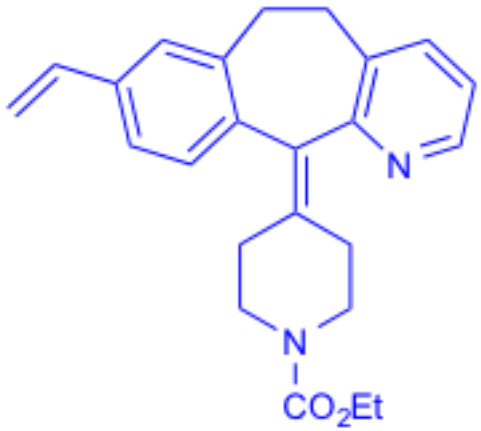

in CDCl3
N
PhO2S
1.04
2.20
3.31
3.27
1.05
0.99
1.04
1.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


138.34
136.83
134.64
133.98
133.40
131.23
129.40
126.97
126.85
123.04
119.41
113.68
113.41
109.57
in CDCl3
N
PhO2S
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)


in CDCl3
S
N
NMe2
2.02
0.97
0.98
2.99
1.00
0.98
0.98
2.01
2.04
6.07
2.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.60
145.21
137.04
136.70
127.52
127.45
127.35
125.12
124.94
122.54
120.55
115.74
113.70
113.41
57.36
45.78
45.57
25.38
in CDCl3
S
N
NMe2
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)

in $CDCl_3$

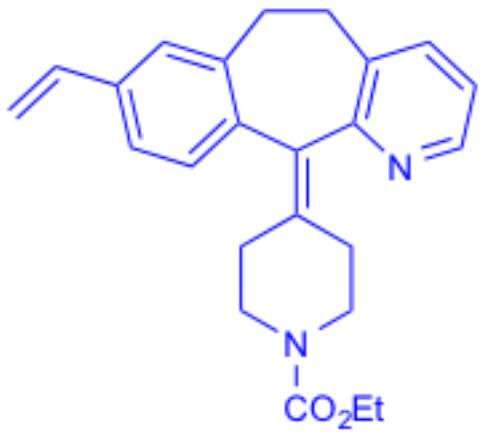


1.00 1.04 2.03 1.06 1.02 1.02 1.02 1.02 2.16 2.05 2.10 2.07 2.11 1.12 3.08 3.26

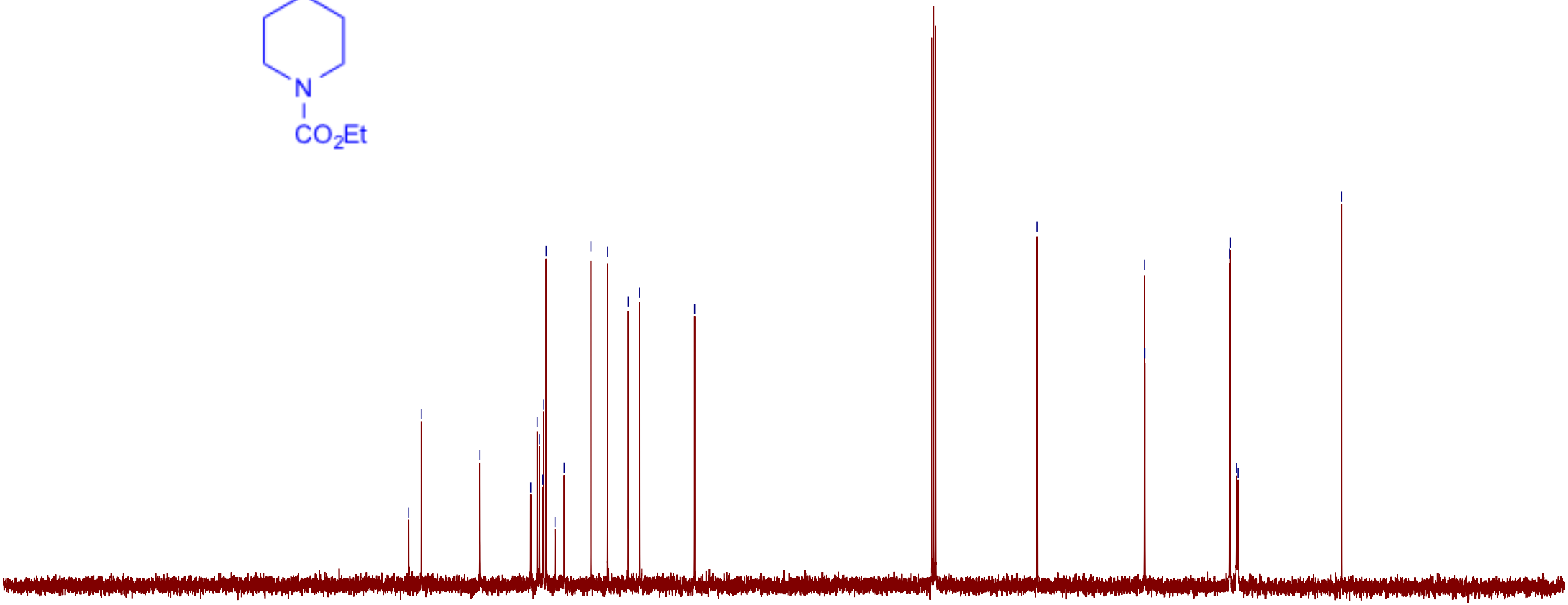
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

in $CDCl_3$



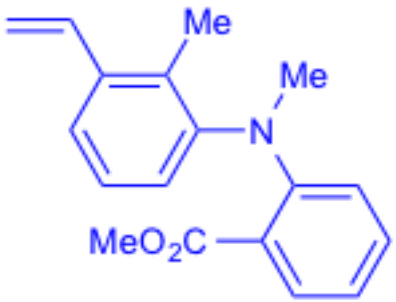
157.50
155.57
146.60
137.86
137.51
136.97
136.82
136.47
133.72
129.63
127.05
123.92
122.19
113.77
61.34
44.96
44.91
31.96
31.79
30.85
30.63
14.77



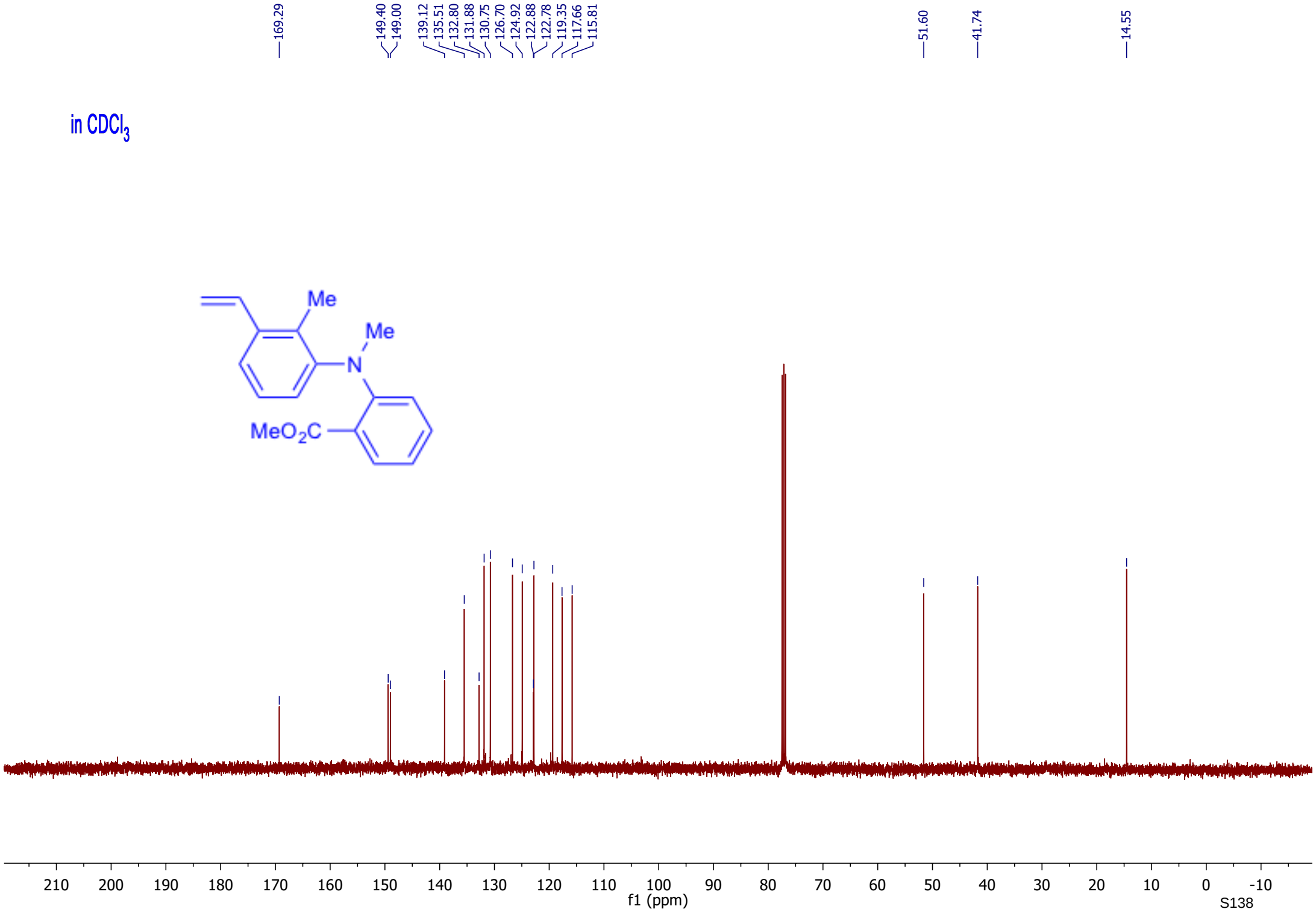
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

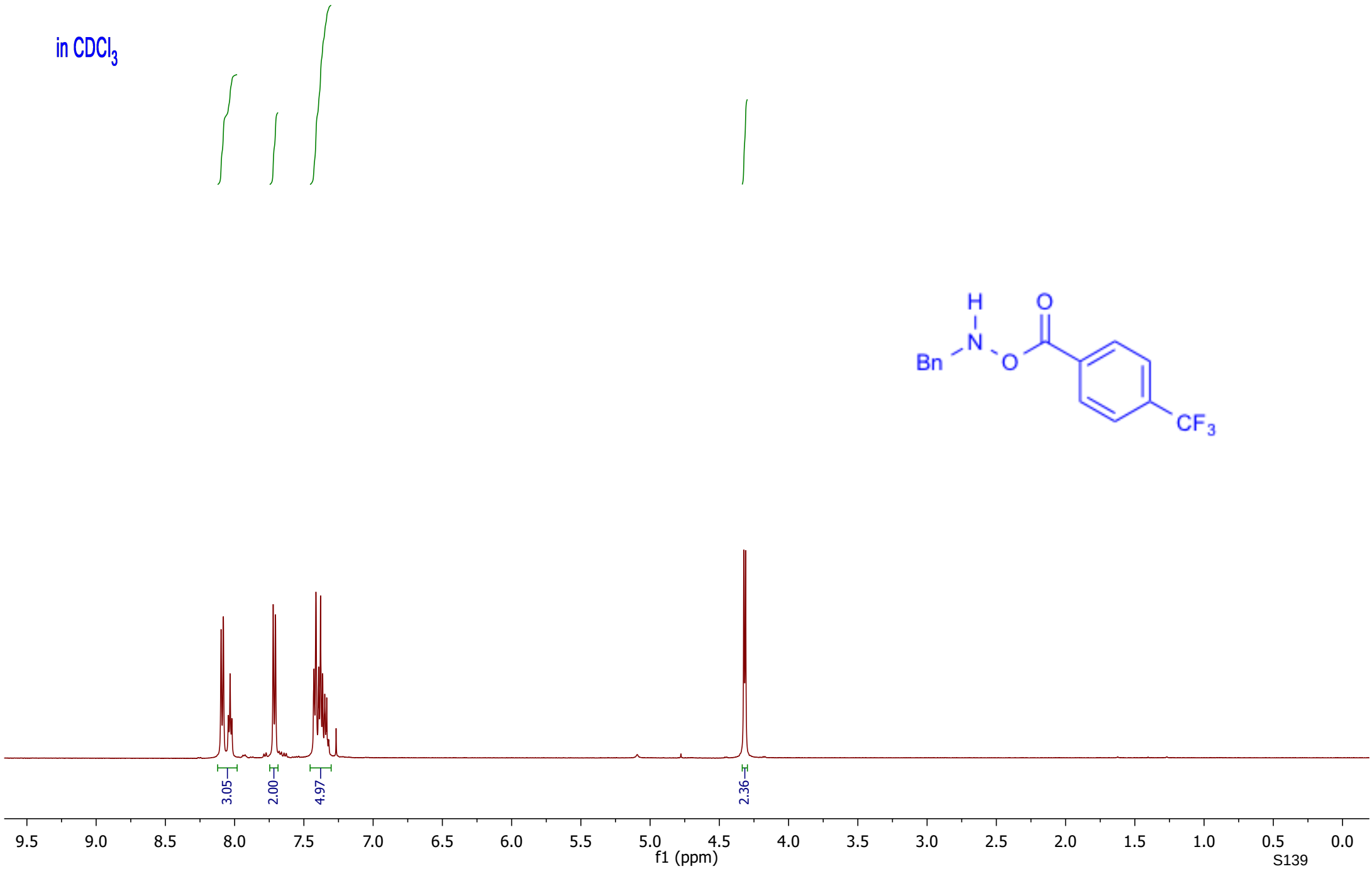
f1 (ppm)

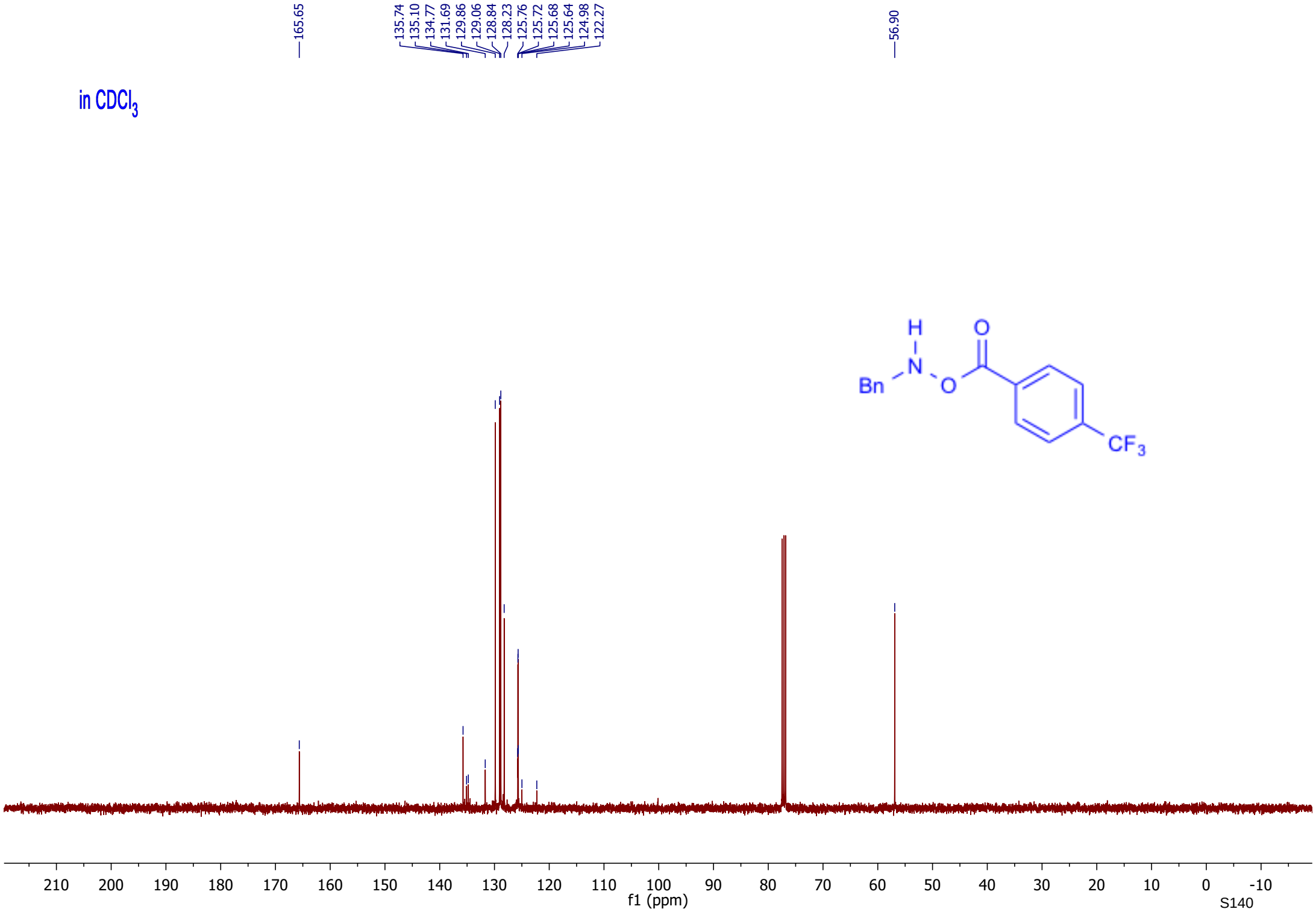
in $CDCl_3$


Me
Me
N
MeO2C

0.98
1.10
0.98
1.06
2.26
2.15
0.91
1.05
2.95
3.03
3.03
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
f1 (ppm)

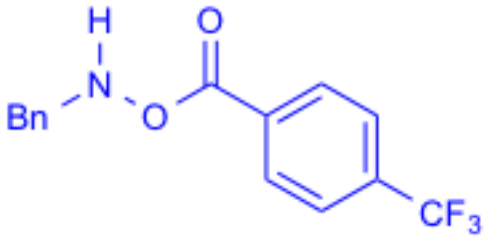

169.29
149.40
149.00
139.12
135.51
132.80
131.88
130.75
126.70
124.92
122.88
122.78
119.35
117.66
115.81
51.60
41.74
14.55
in CDCl3
Me
Me
N
MeO2C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


in CDCl3
H
N
O
O
Bn
CF3
3.05
2.00
4.97
2.36
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.65
135.74
135.10
134.77
131.69
129.86
129.06
128.84
128.23
125.76
125.72
125.68
125.64
124.98
122.27
56.90
in CDCl3
H
N
O
O
Bn
CF3
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)

-63.22

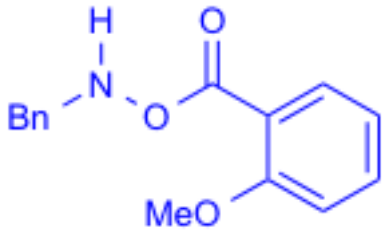
in $CDCl_3$



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

f1 (ppm)

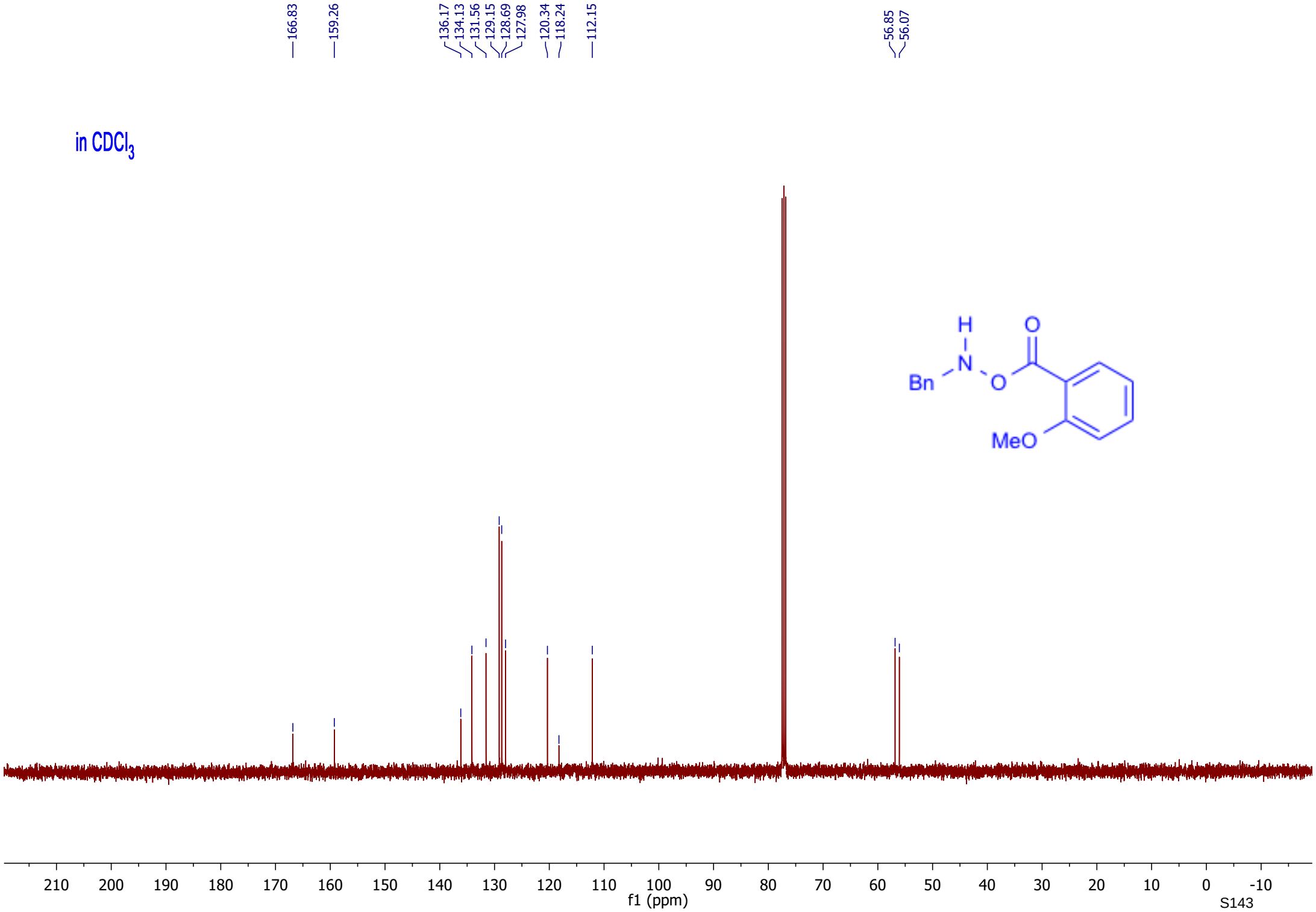
in $CDCl_3$

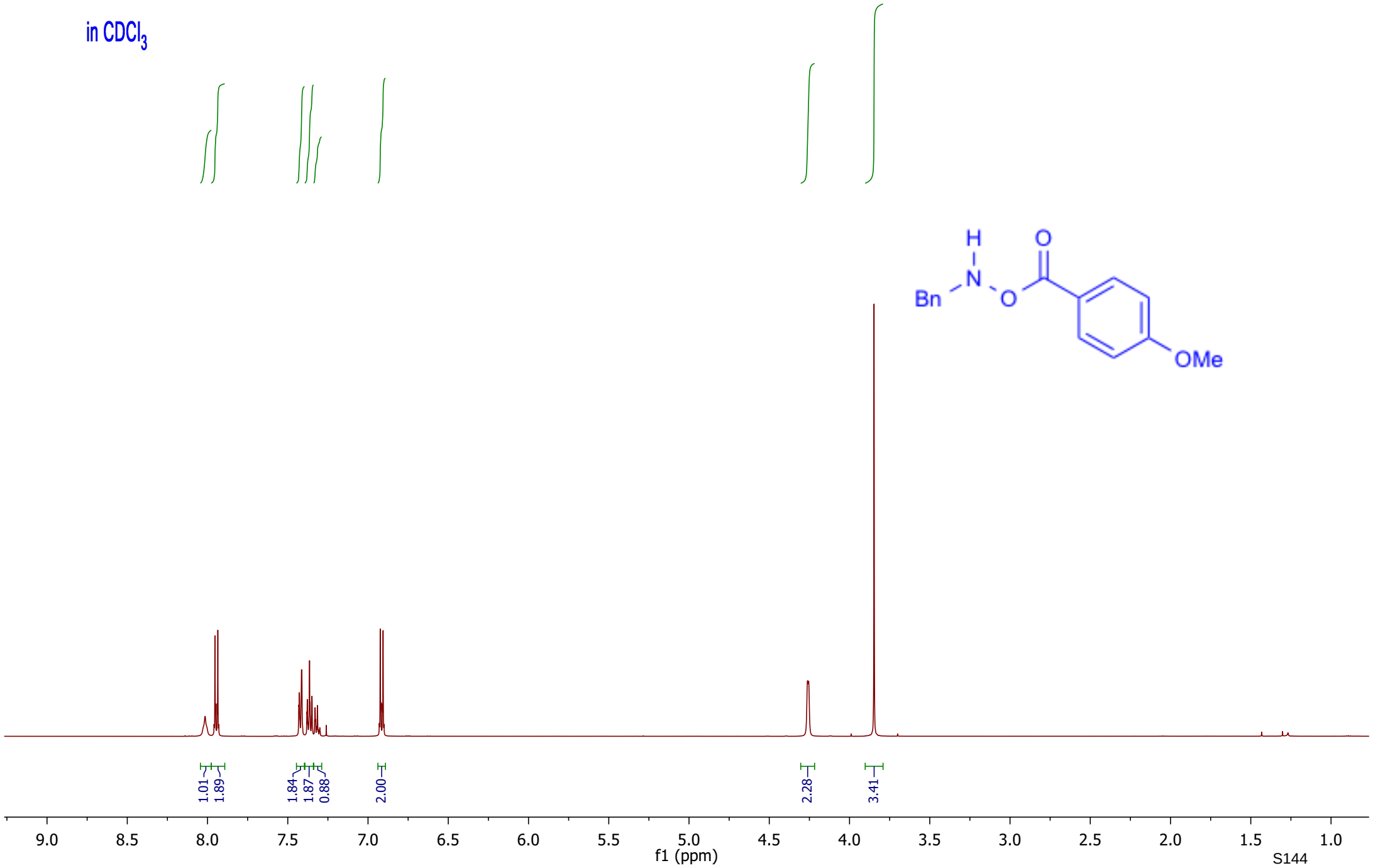


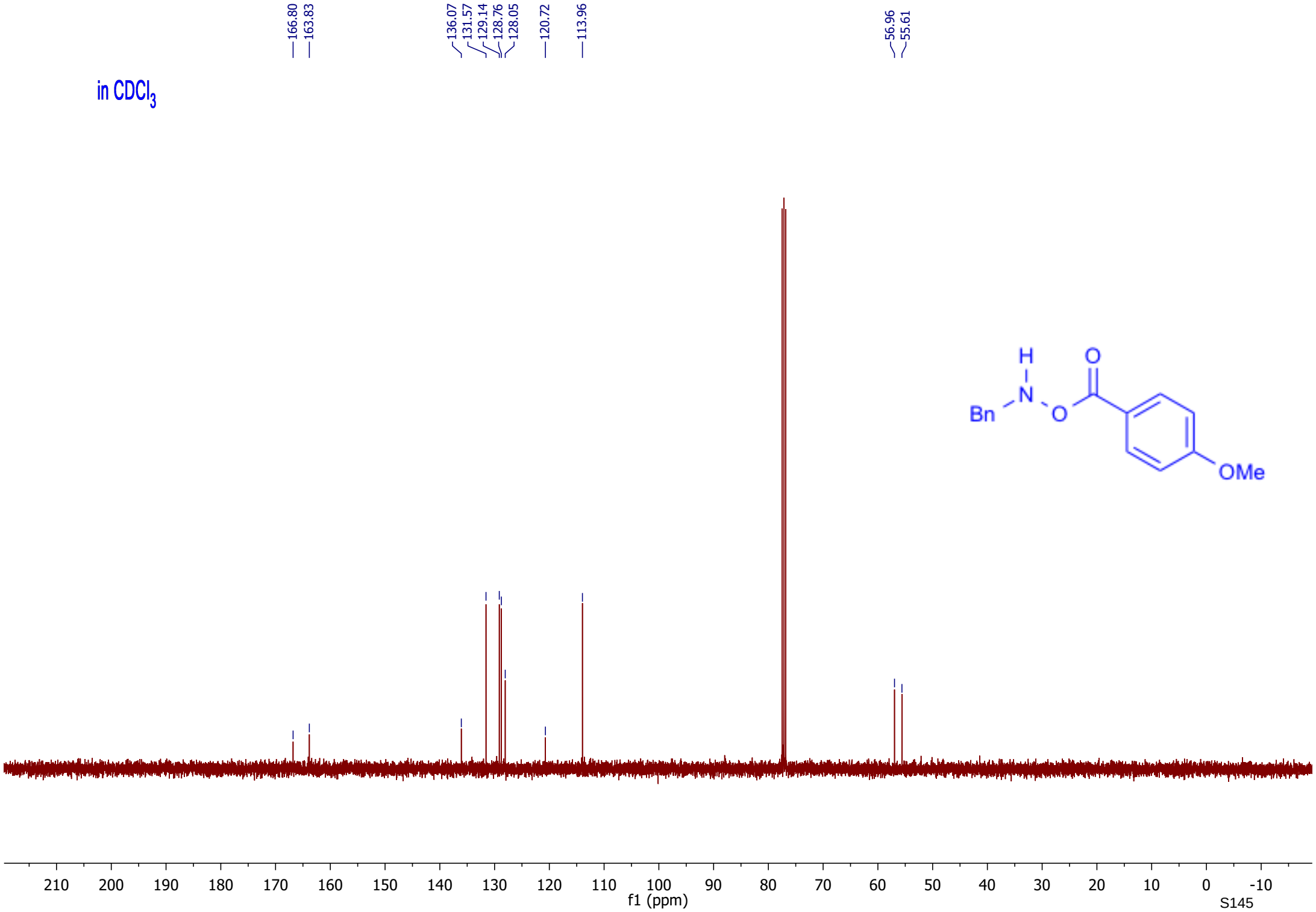
1.08 0.97 1.13 2.01 2.02 1.00 2.23 2.37 3.48

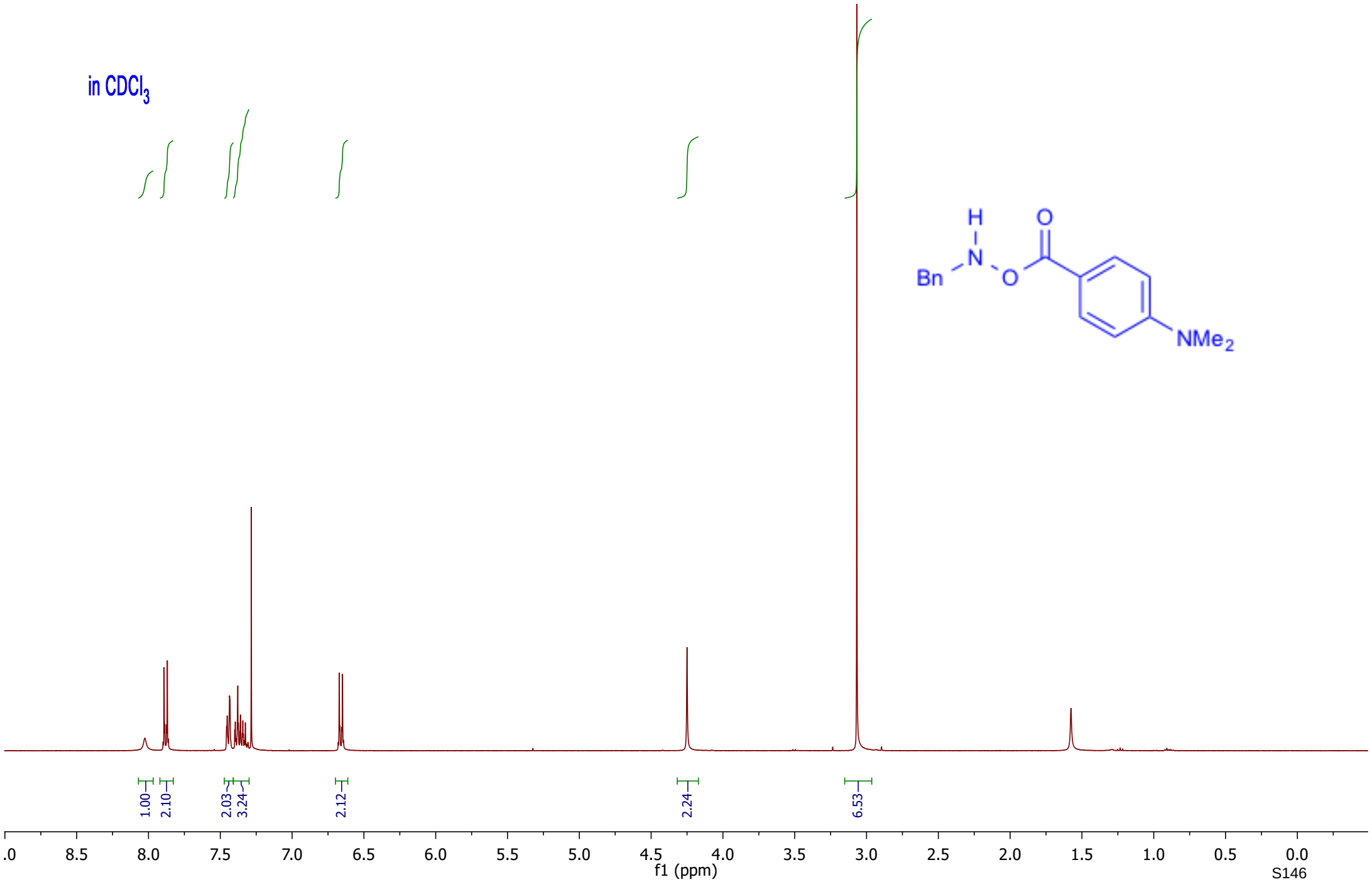
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

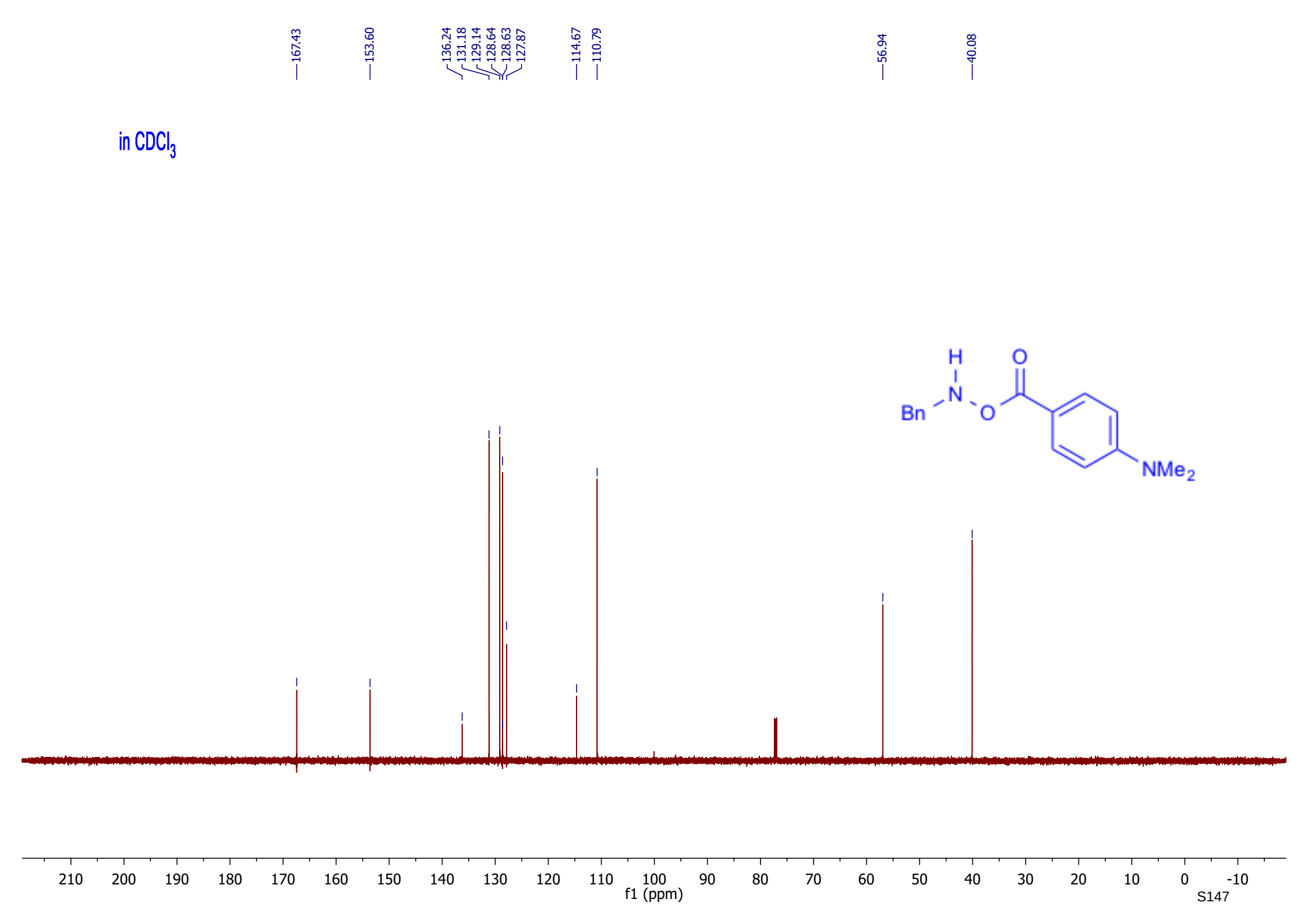
f1 (ppm)

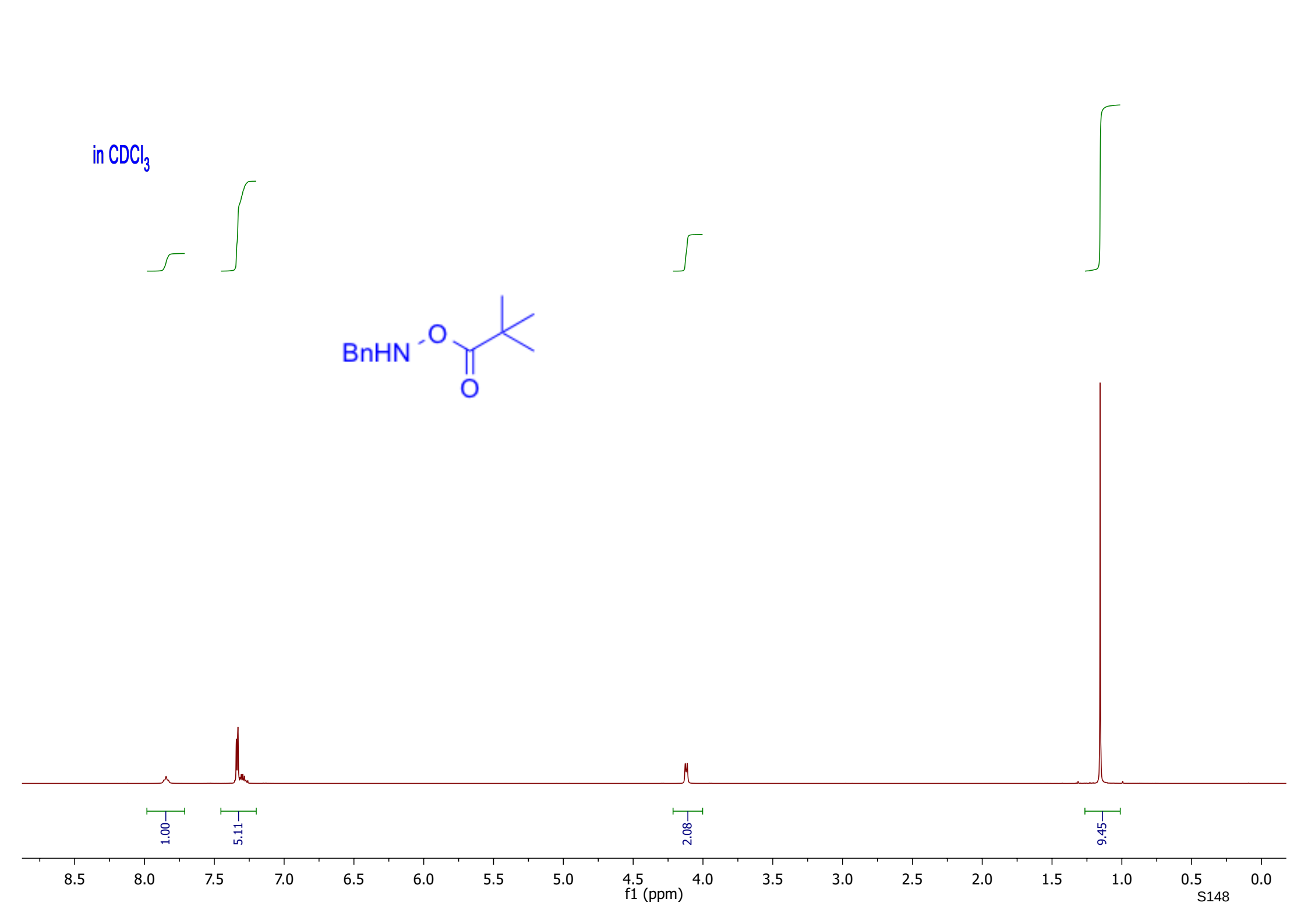

166.83
159.26
136.17
134.13
131.56
129.15
128.69
127.98
120.34
118.24
112.15
56.85
56.07
in CDCl3
H
N
O
O
Bn
MeO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

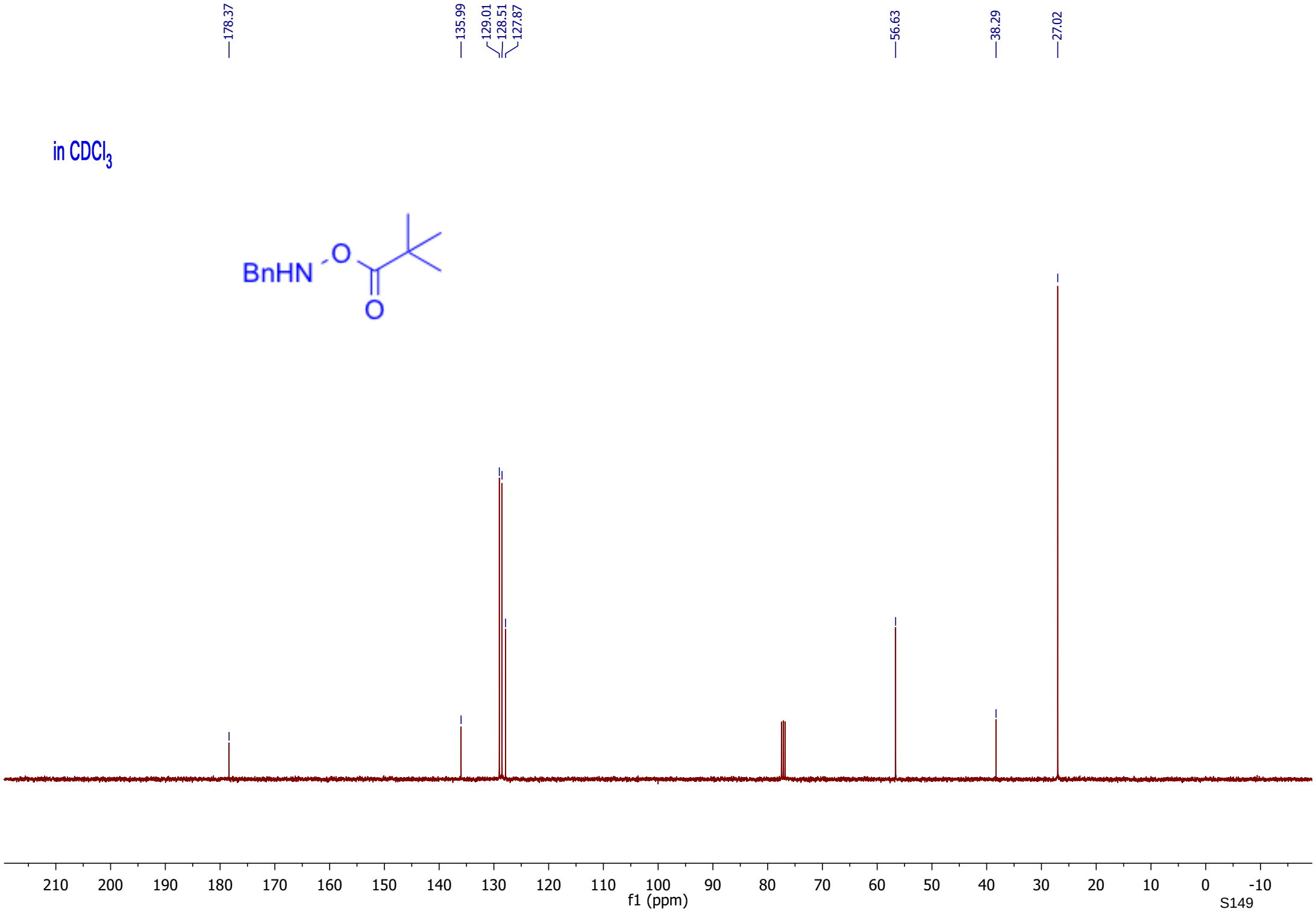

in CDCl3
H
N
O
O
Bn
OMe
1.01
1.89
1.84
1.87
0.88
2.00
2.28
3.41
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

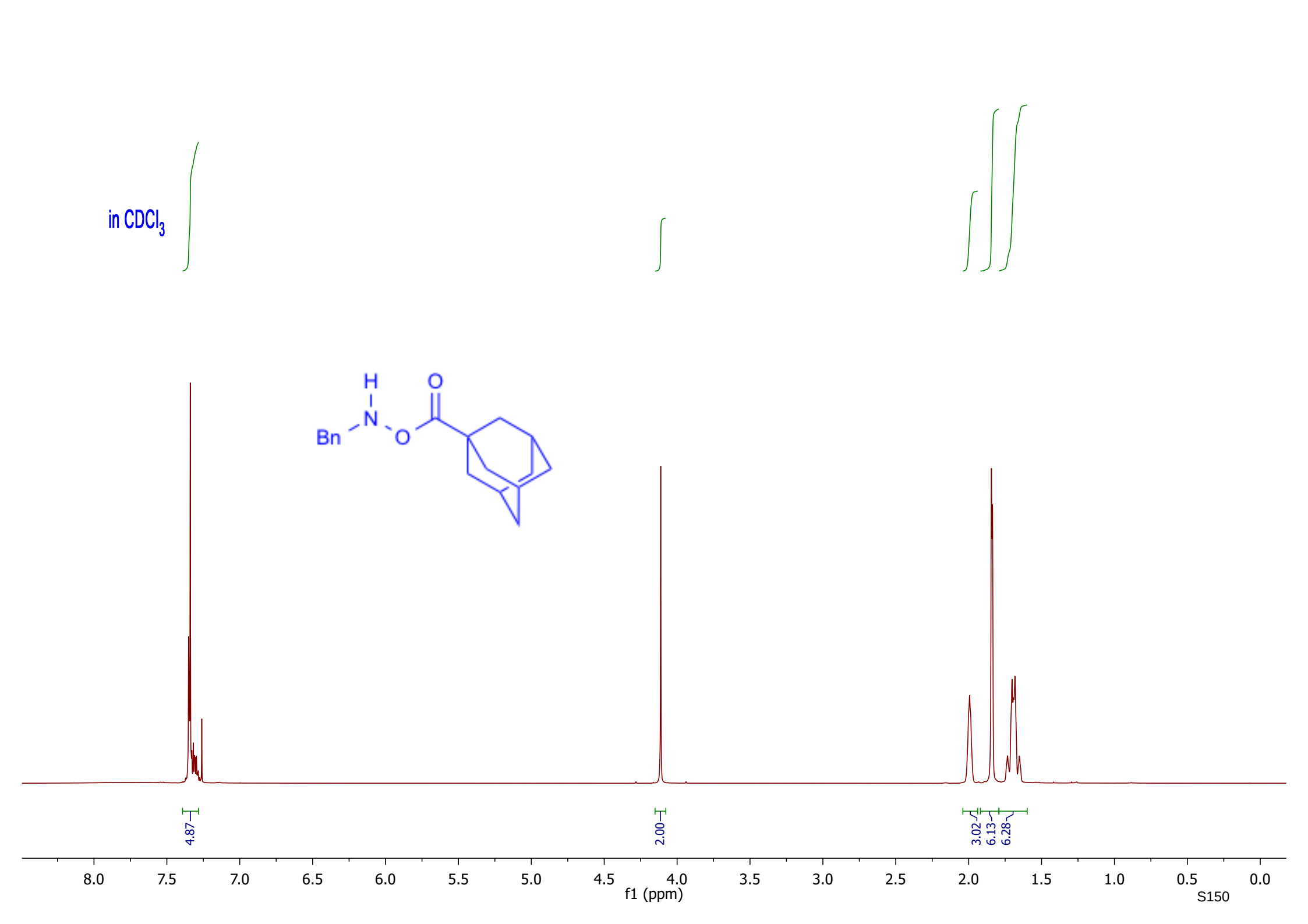

166.80
163.83
136.07
131.57
129.14
128.76
128.05
120.72
113.96
56.96
55.61
in CDCl3
H
N
O
O
Bn
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

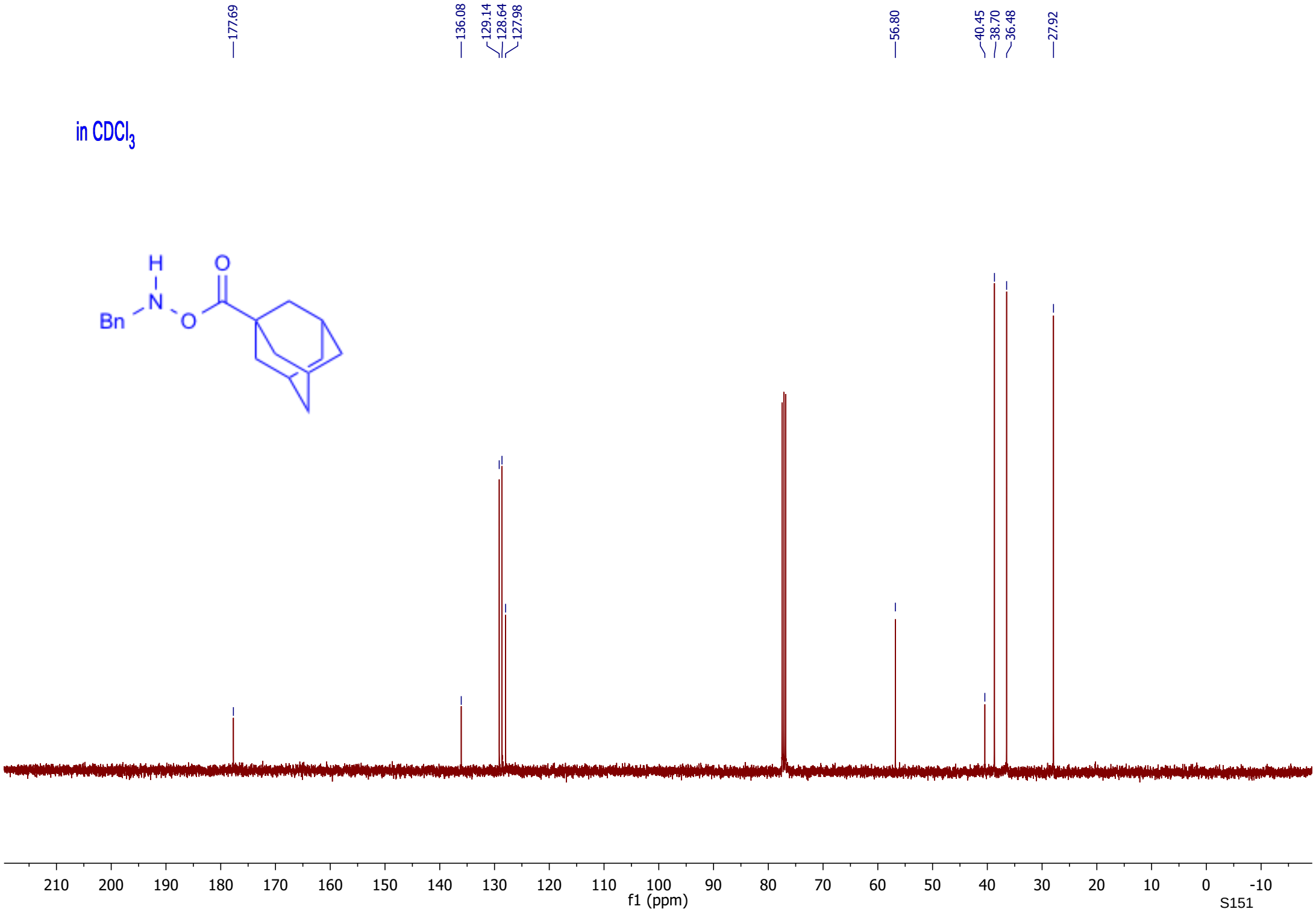

in CDCl3
H
N
O
O
Bn
NMe2
1.00
2.10
2.03
3.24
2.12
2.24
6.53
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

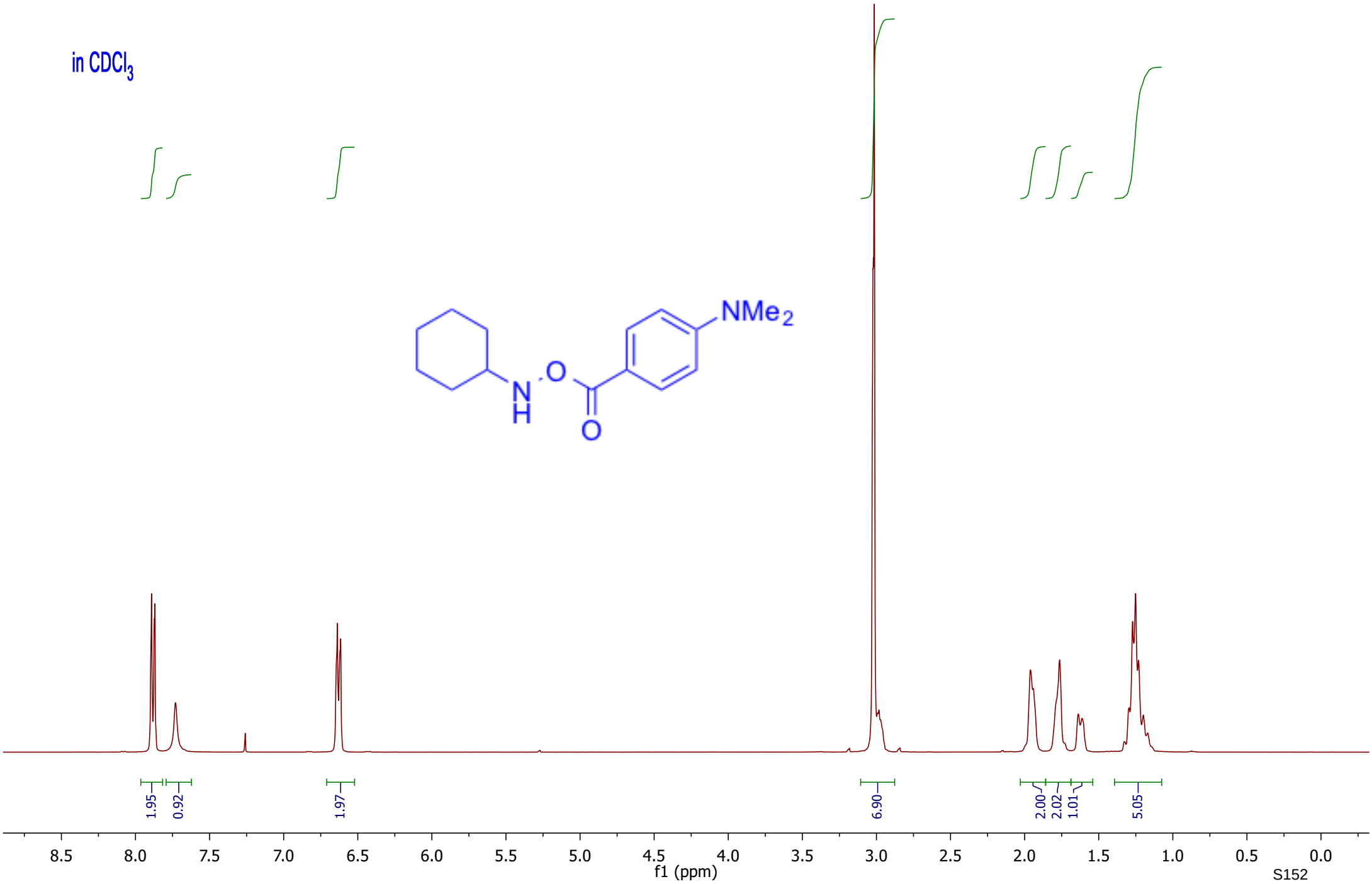

167.43
153.60
136.24
131.18
129.14
128.64
128.63
127.87
114.67
110.79
56.94
40.08
in CDCl3
H
N
O
O
Bn
NMe2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

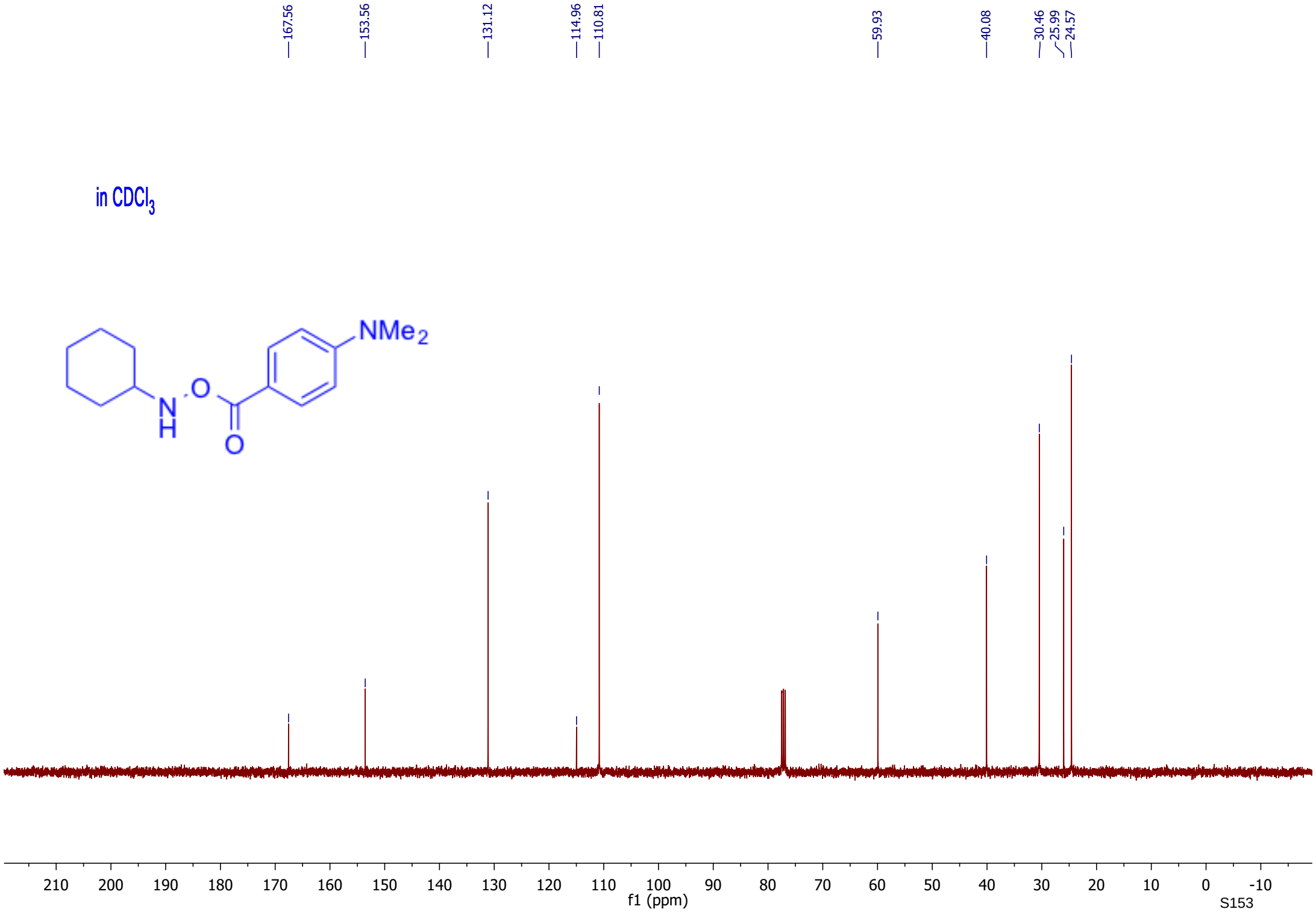

in CDCl3
BnHN
O
O
1.00
5.11
2.08
9.45
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

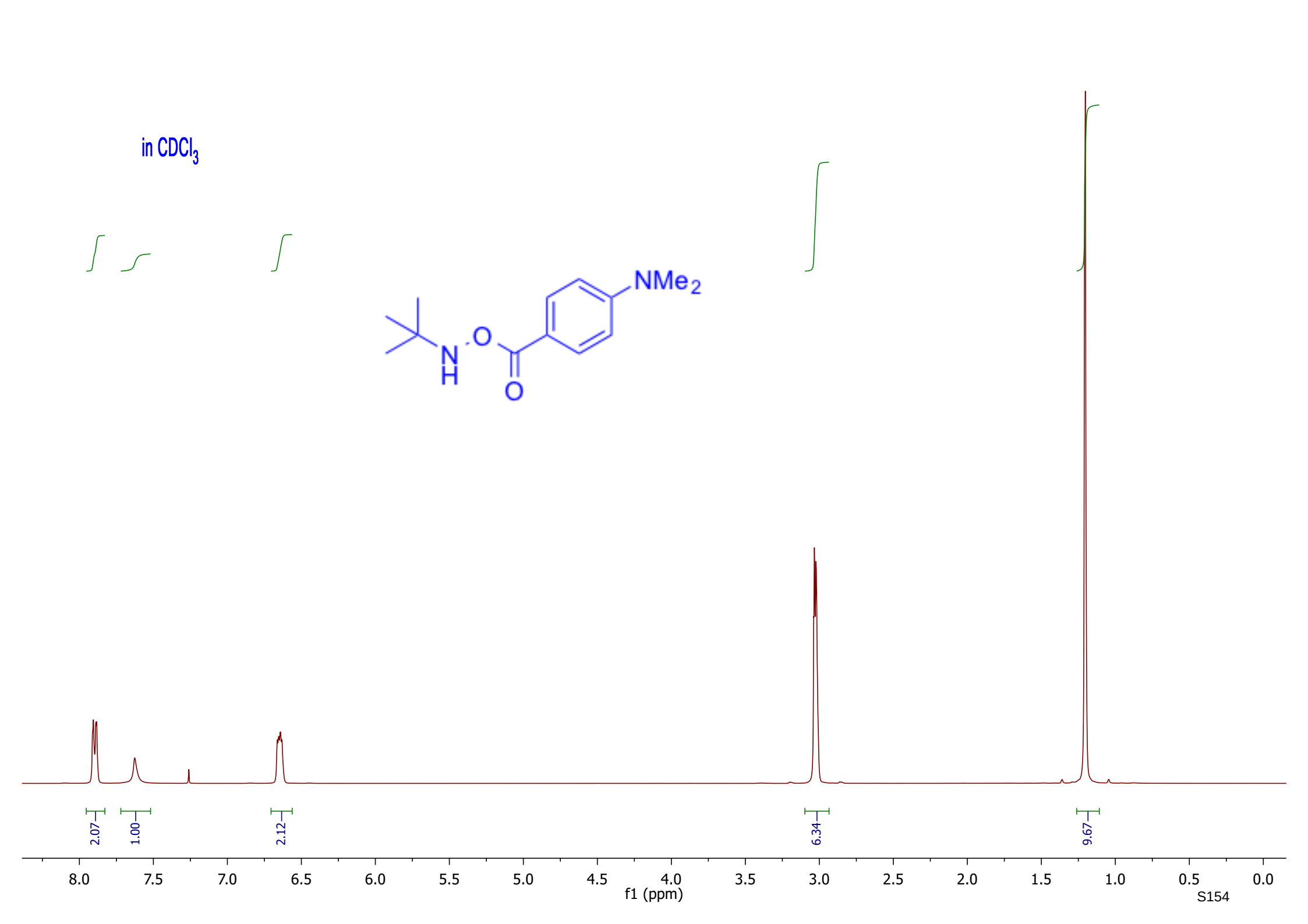

178.37
135.99
129.01
128.51
127.87
56.63
38.29
27.02
in CDCl3
BnHN
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

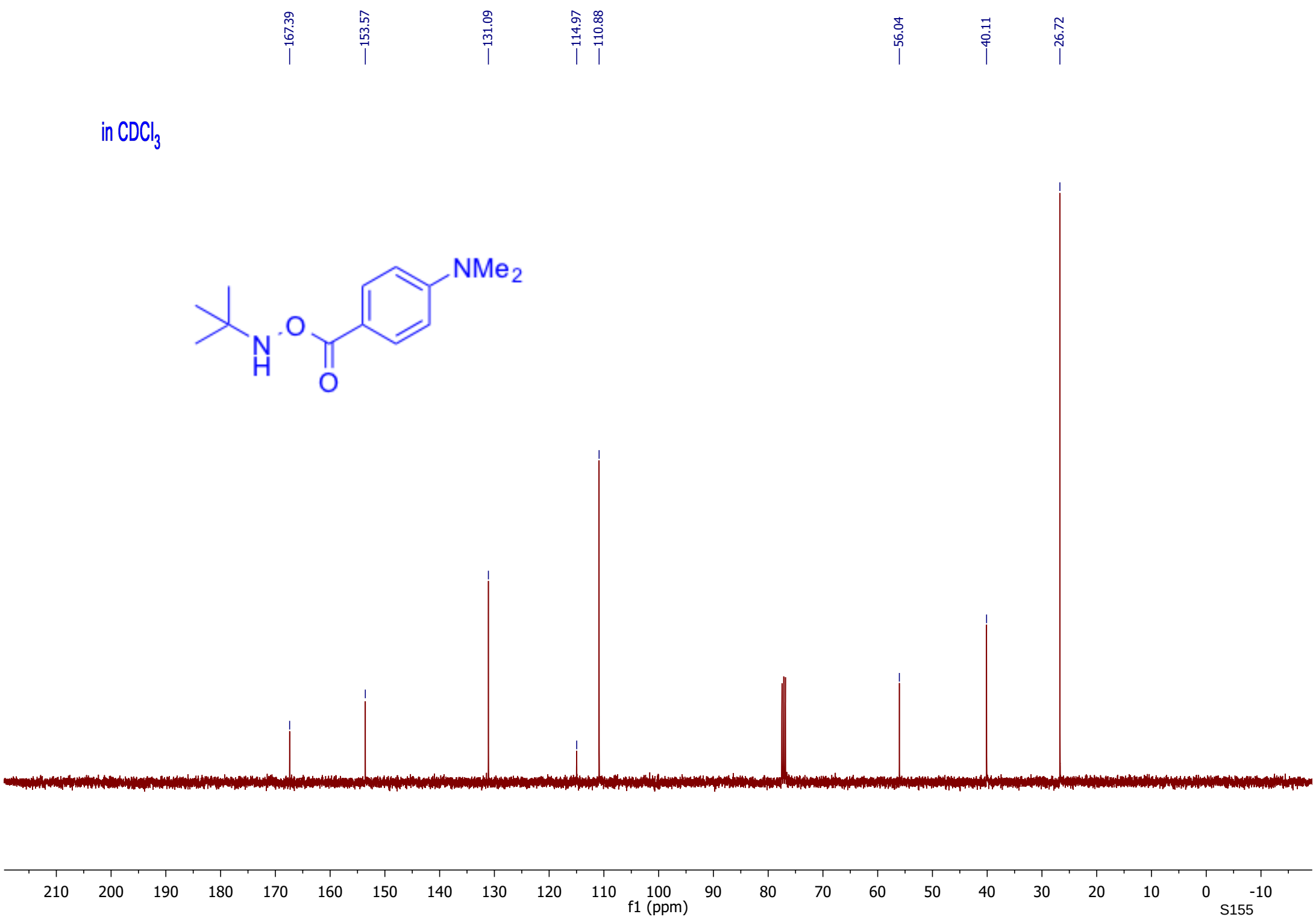

in CDCl3
H
N
O
O
Bn
4.87
2.00
3.02
6.13
6.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

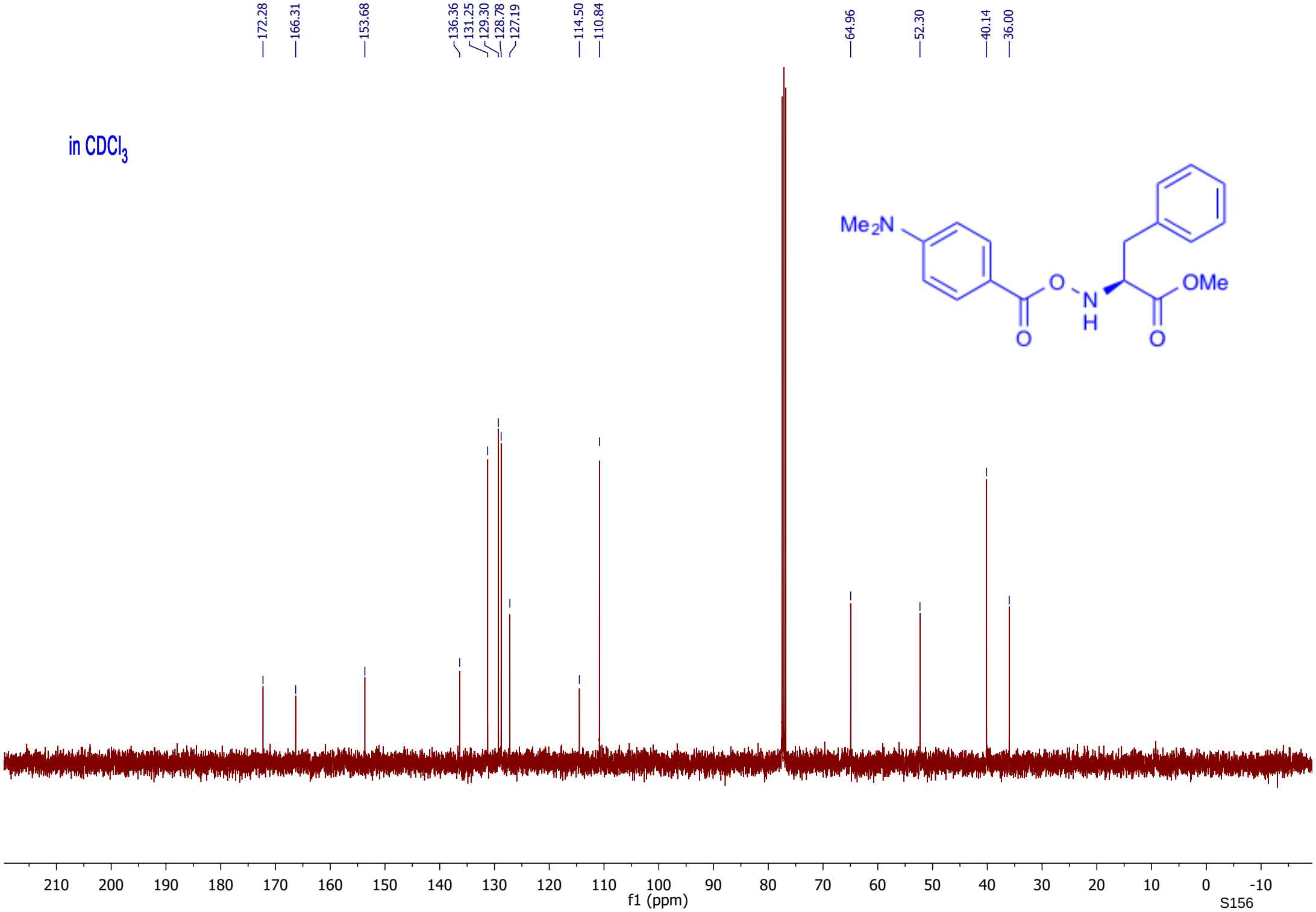

177.69
136.08
129.14
128.64
127.98
56.80
40.45
38.70
36.48
27.92
in CDCl3
H
N
O
O
Bn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
S151

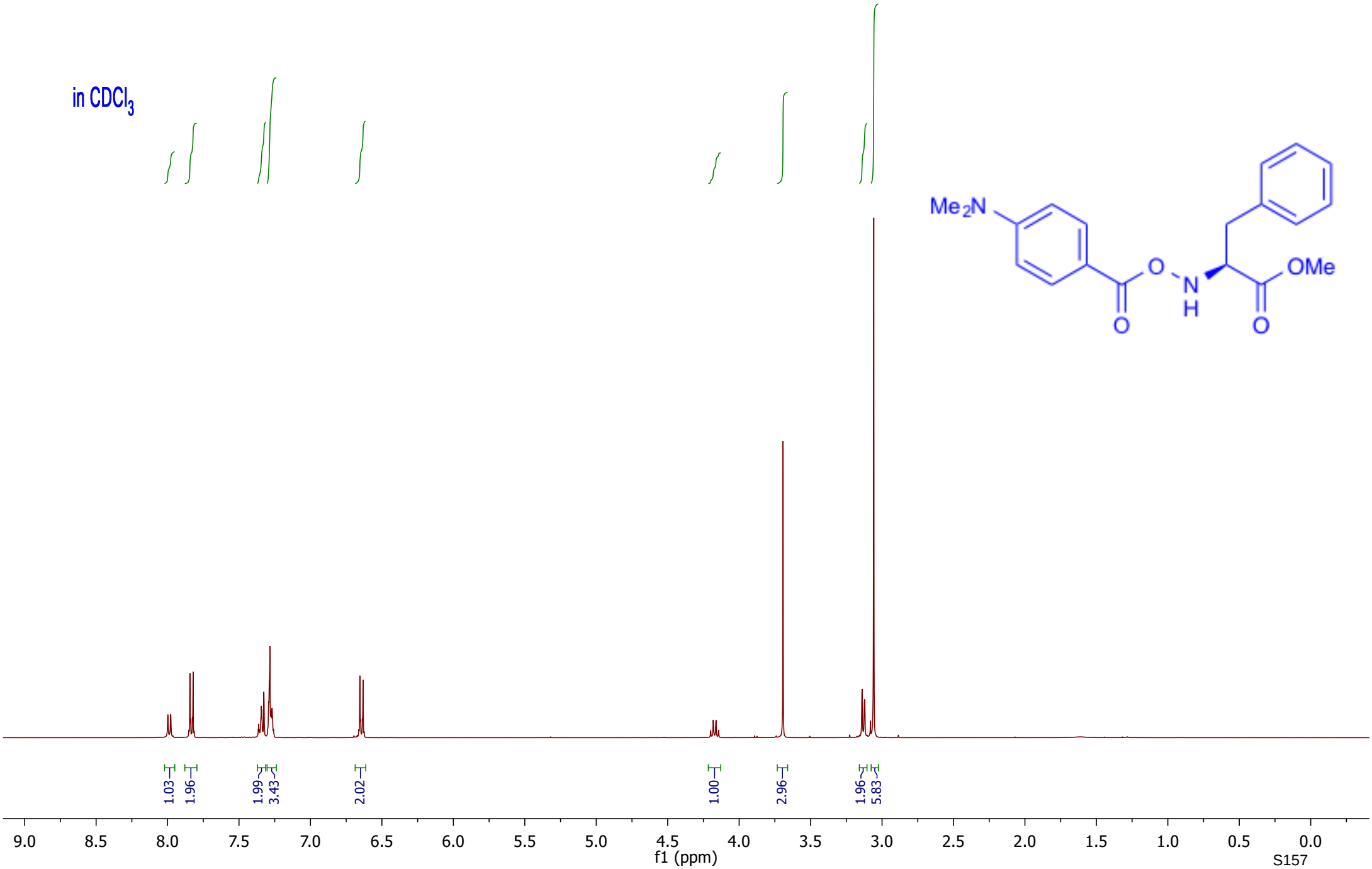

in CDCl3
NMe2
N
H
O
O
1.95
0.92
1.97
6.90
2.00
2.02
1.01
5.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

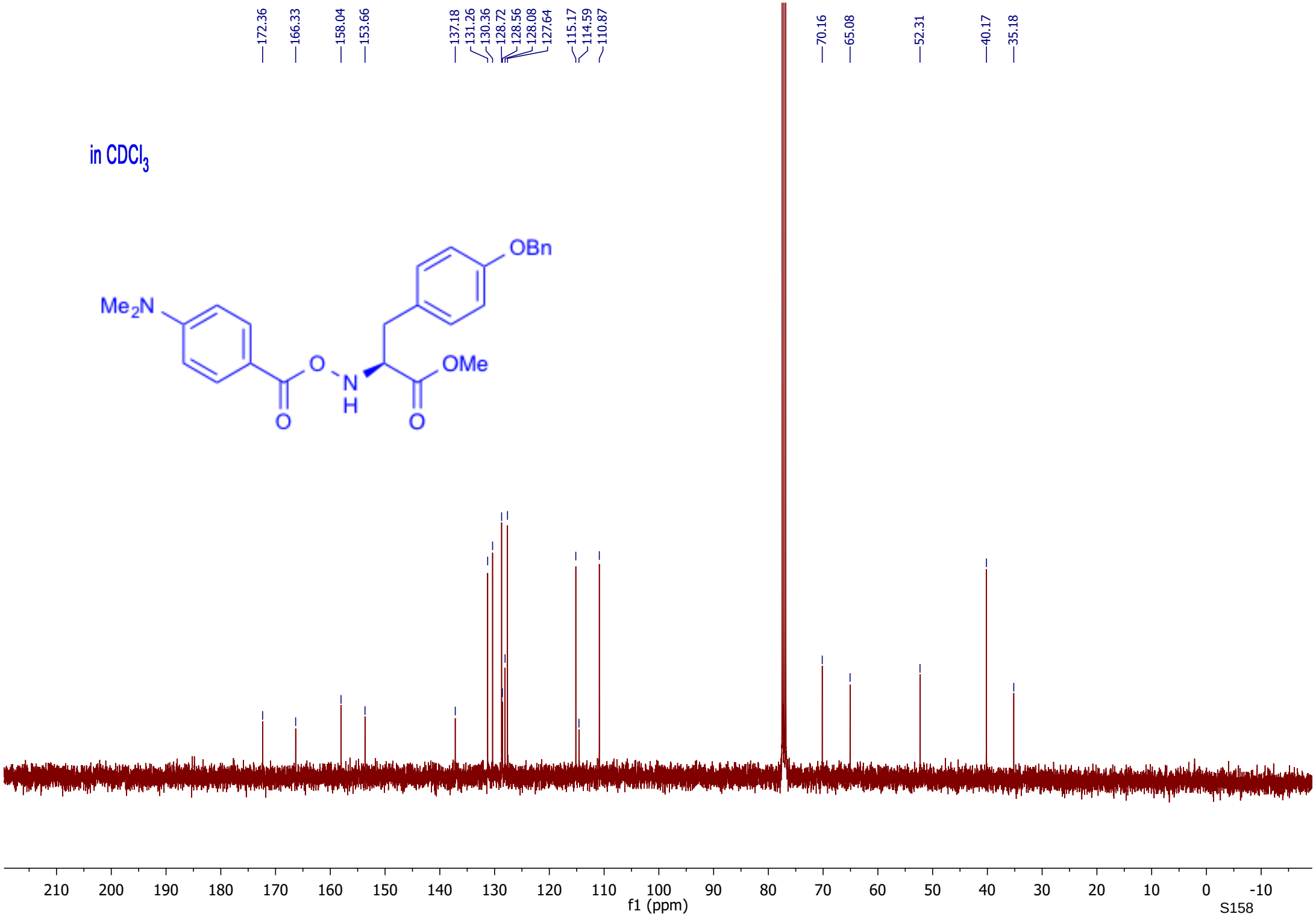

167.56
153.56
131.12
114.96
110.81
59.93
40.08
30.46
25.99
24.57
in CDCl3
NMe2
N
H
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

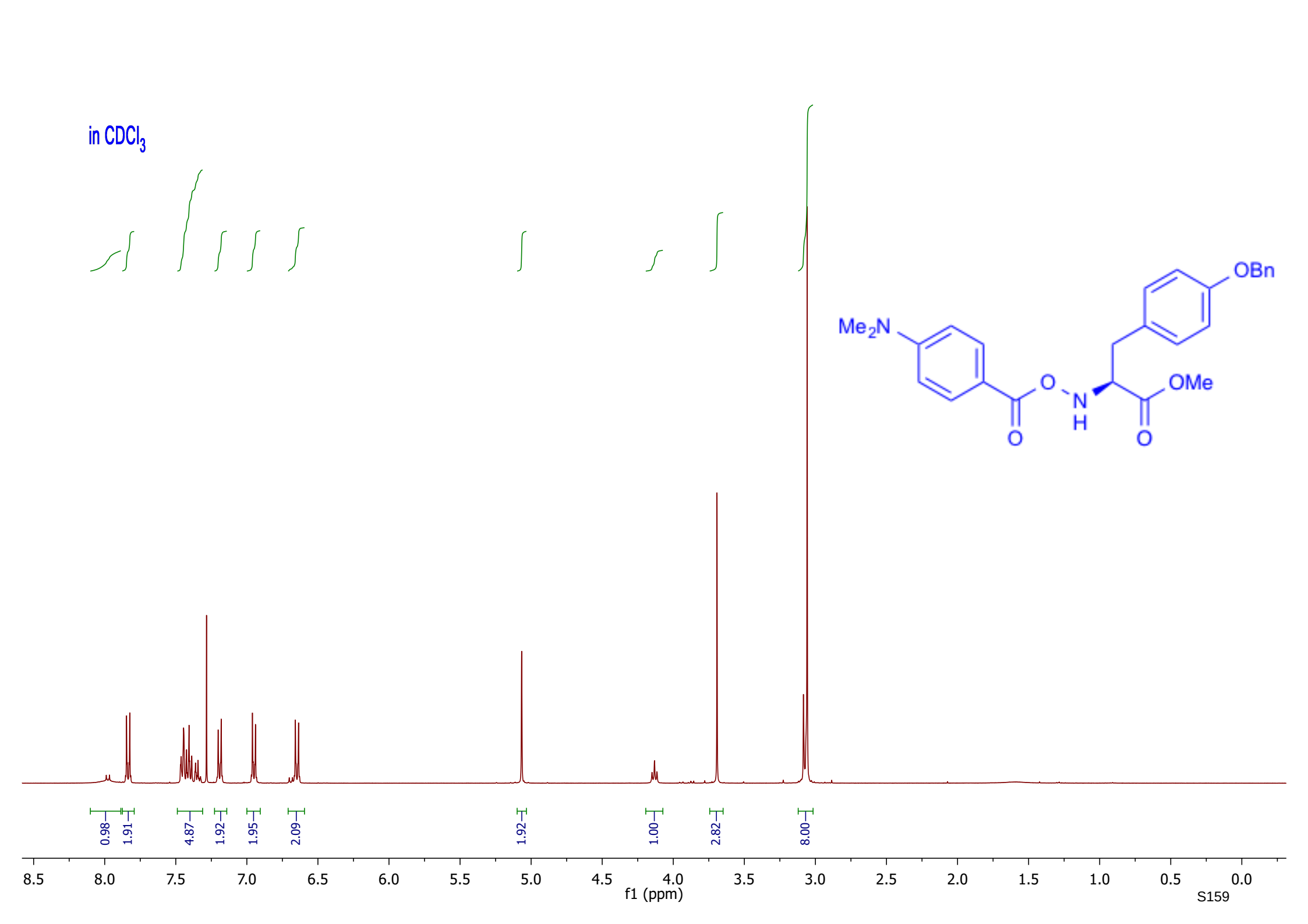

in CDCl3
NMe2
N
H
O
O
2.07
1.00
2.12
6.34
9.67
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

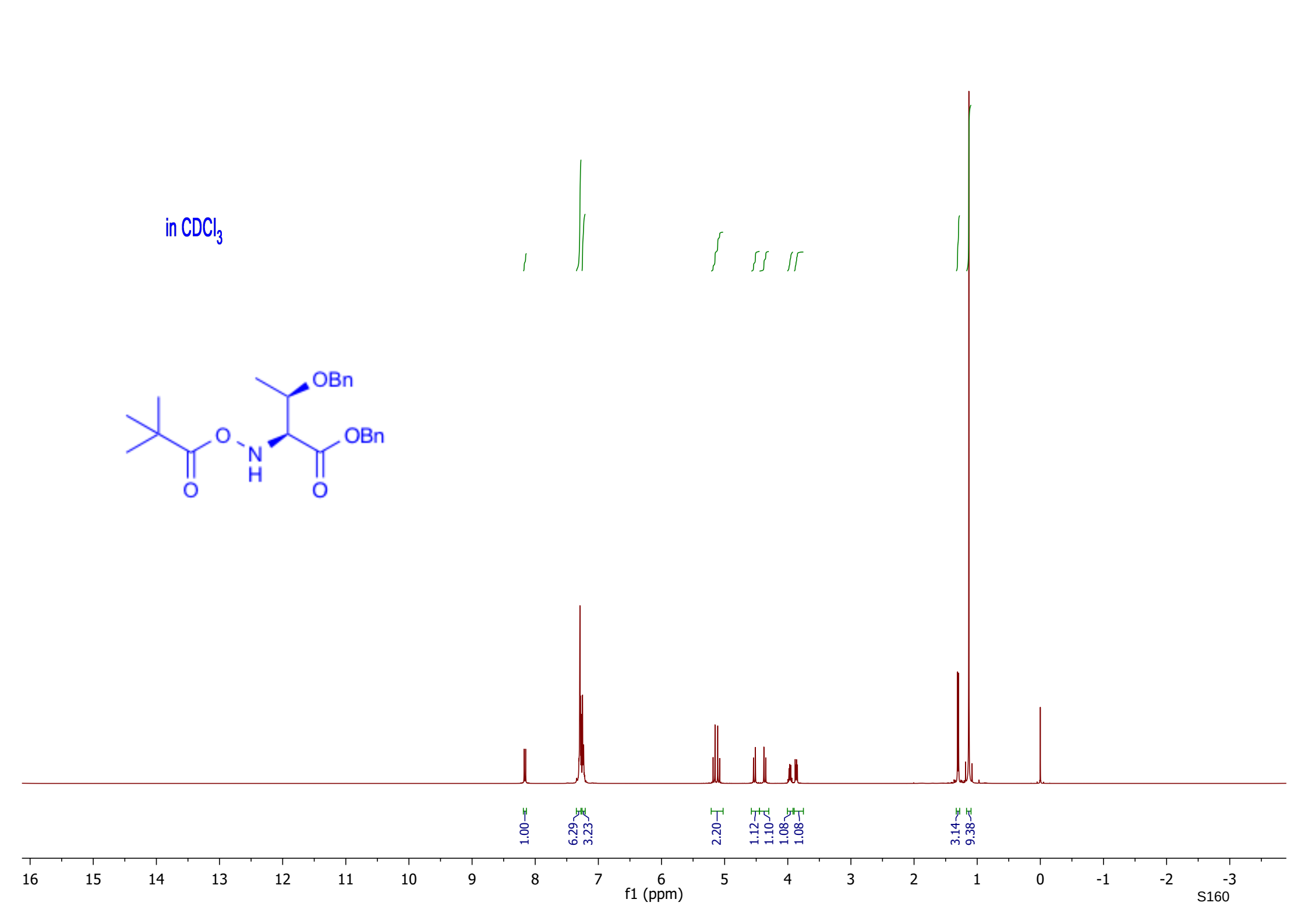

167.39
153.57
131.09
114.97
110.88
56.04
40.11
26.72
in CDCl3
NMe2
N
H
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

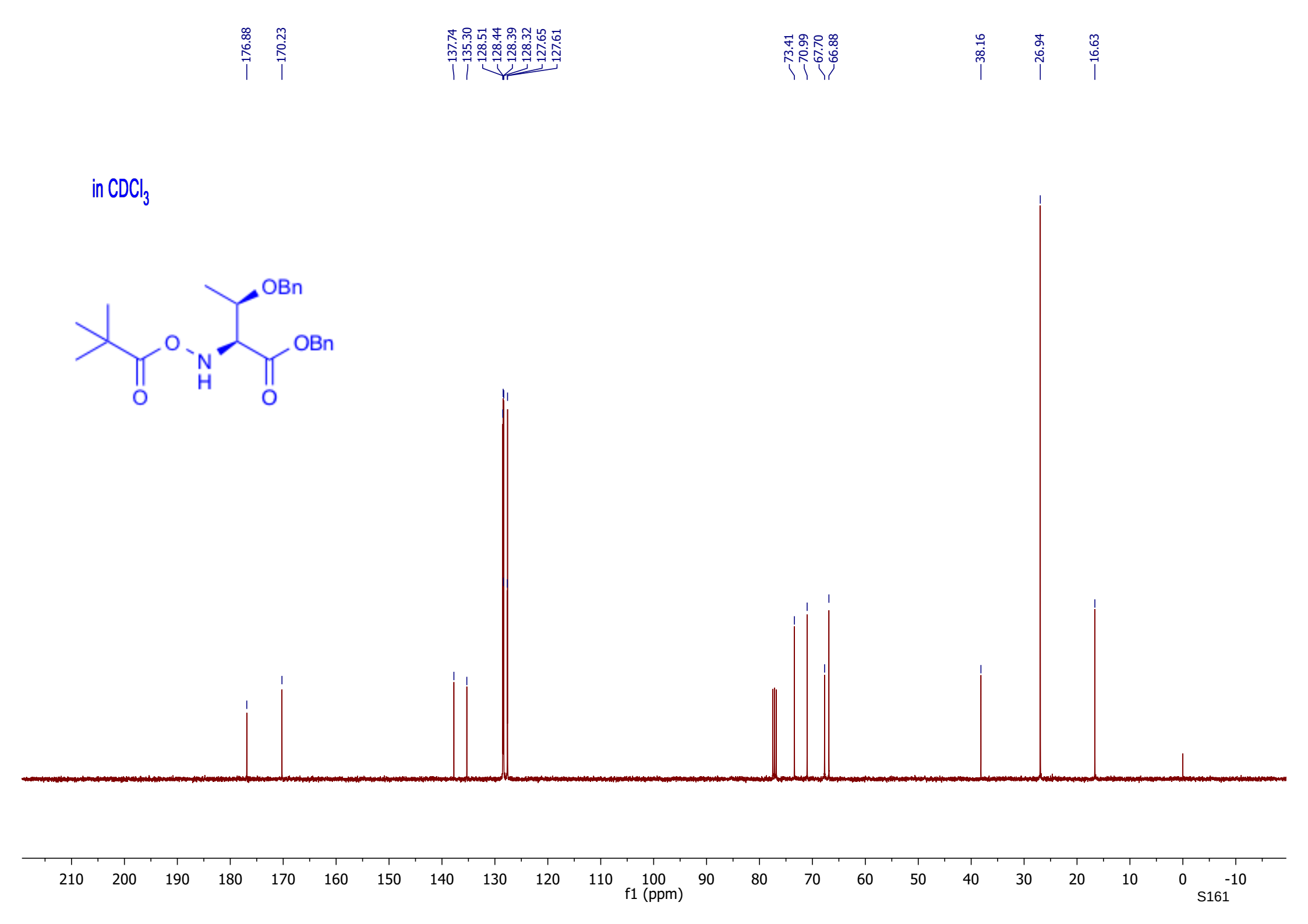

172.28
166.31
153.68
136.36
131.25
129.30
128.78
127.19
114.50
110.84
64.96
52.30
40.14
36.00
in CDCl3
Me2N
O
N
H
O
O
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

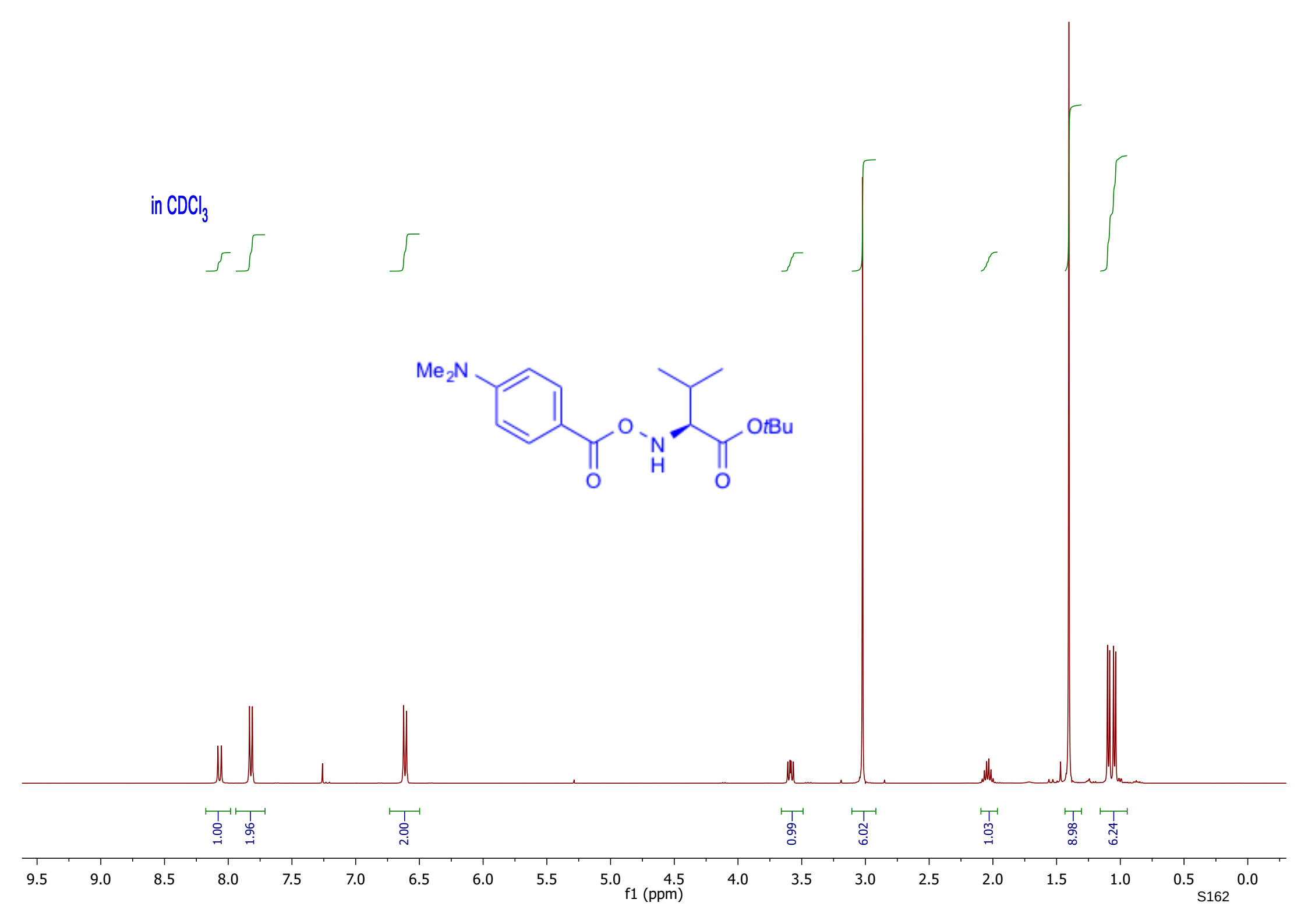

in CDCl3
Me2N
O
N
H
O
OMe
O
1.03
1.96
1.99
3.43
2.02
1.00
2.96
1.96
5.83
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

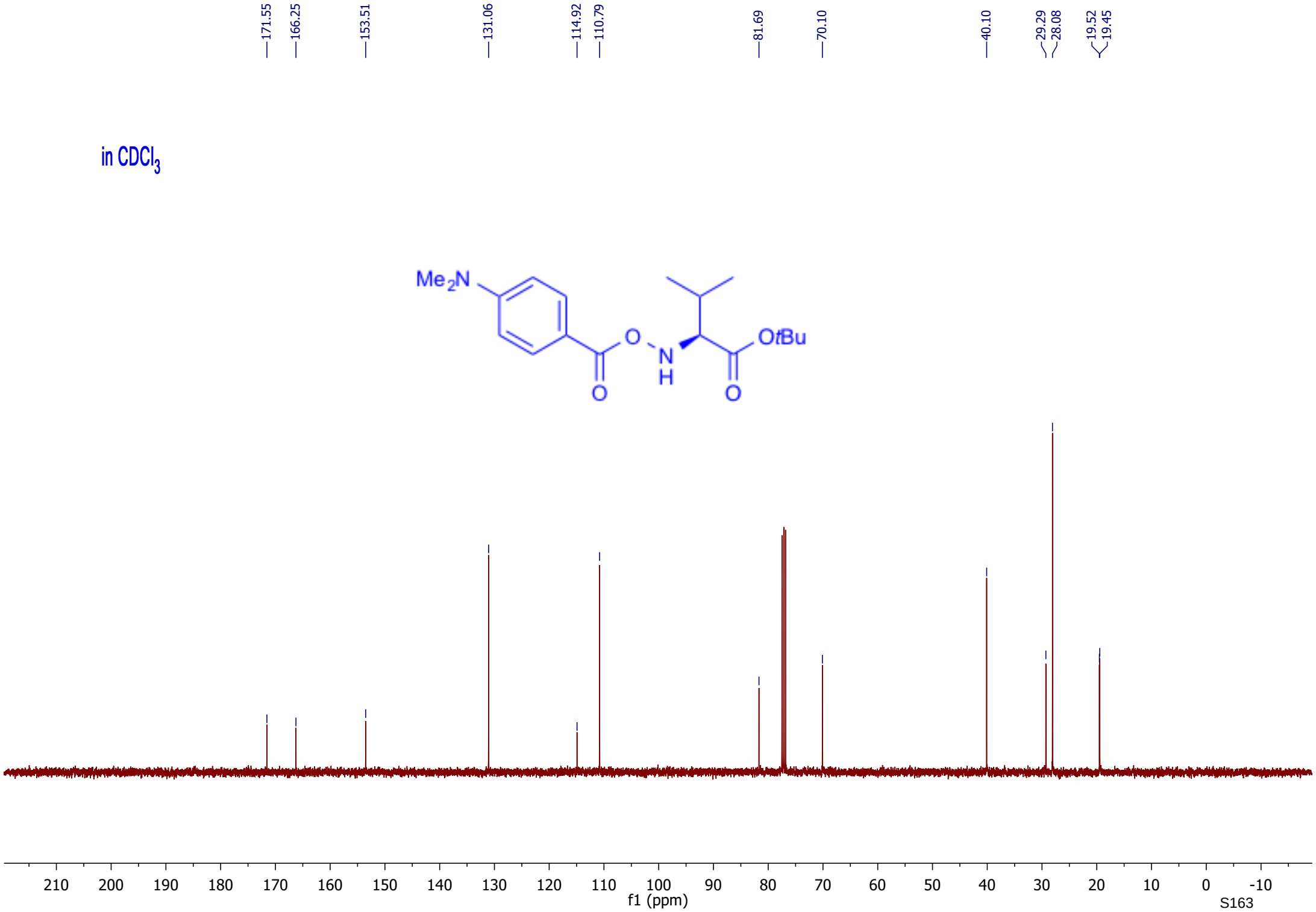

172.36
166.33
158.04
153.66
137.18
131.26
130.36
128.72
128.56
128.08
127.64
115.17
114.59
110.87
70.16
65.08
52.31
40.17
35.18
in CDCl3
Me2N
O
N
H
O
O
OMe
OBn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

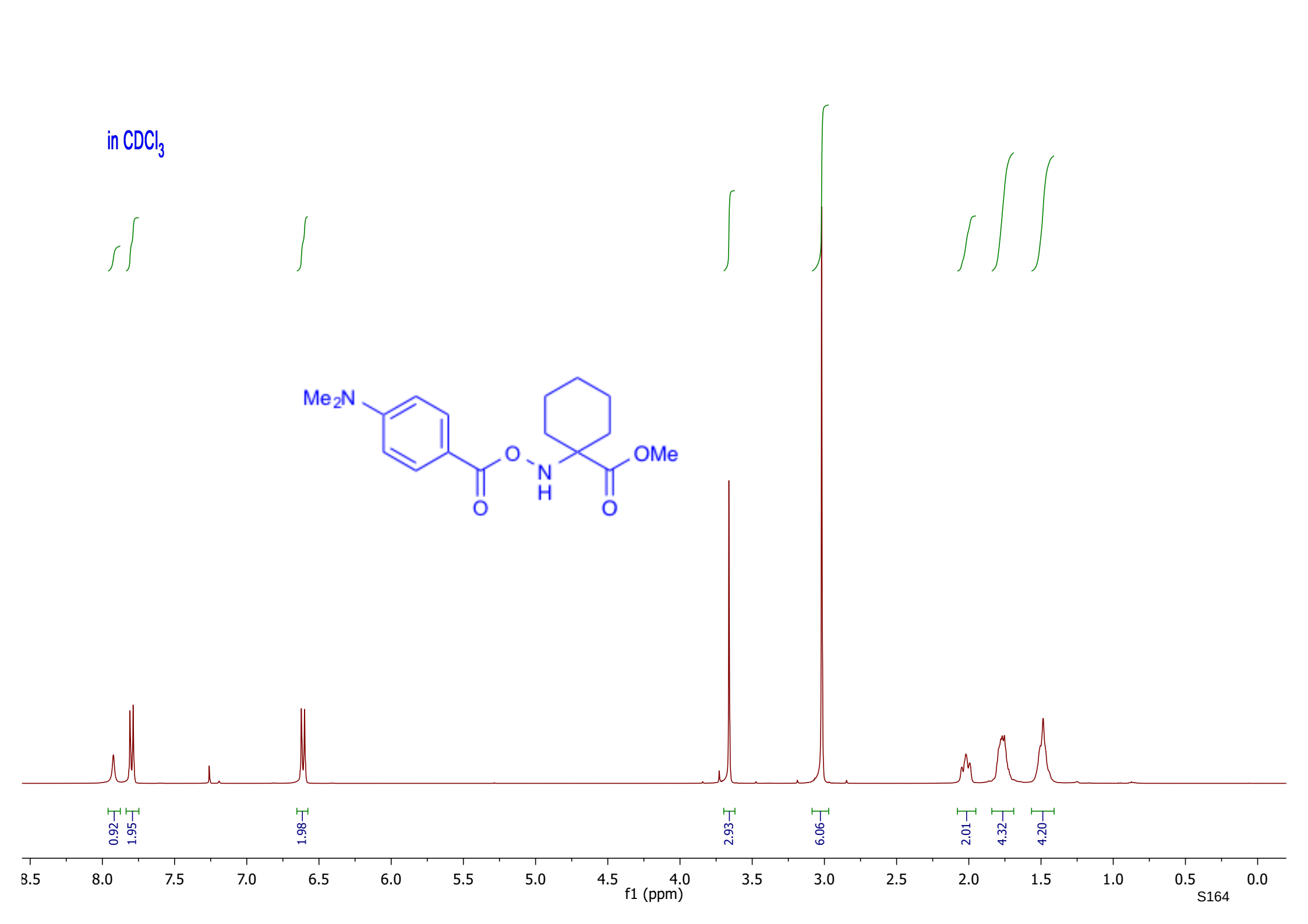

in CDCl3
Me2N
O
N
H
O
OMe
O
OBn
0.98
1.91
4.87
1.92
1.95
2.09
1.92
1.00
2.82
8.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

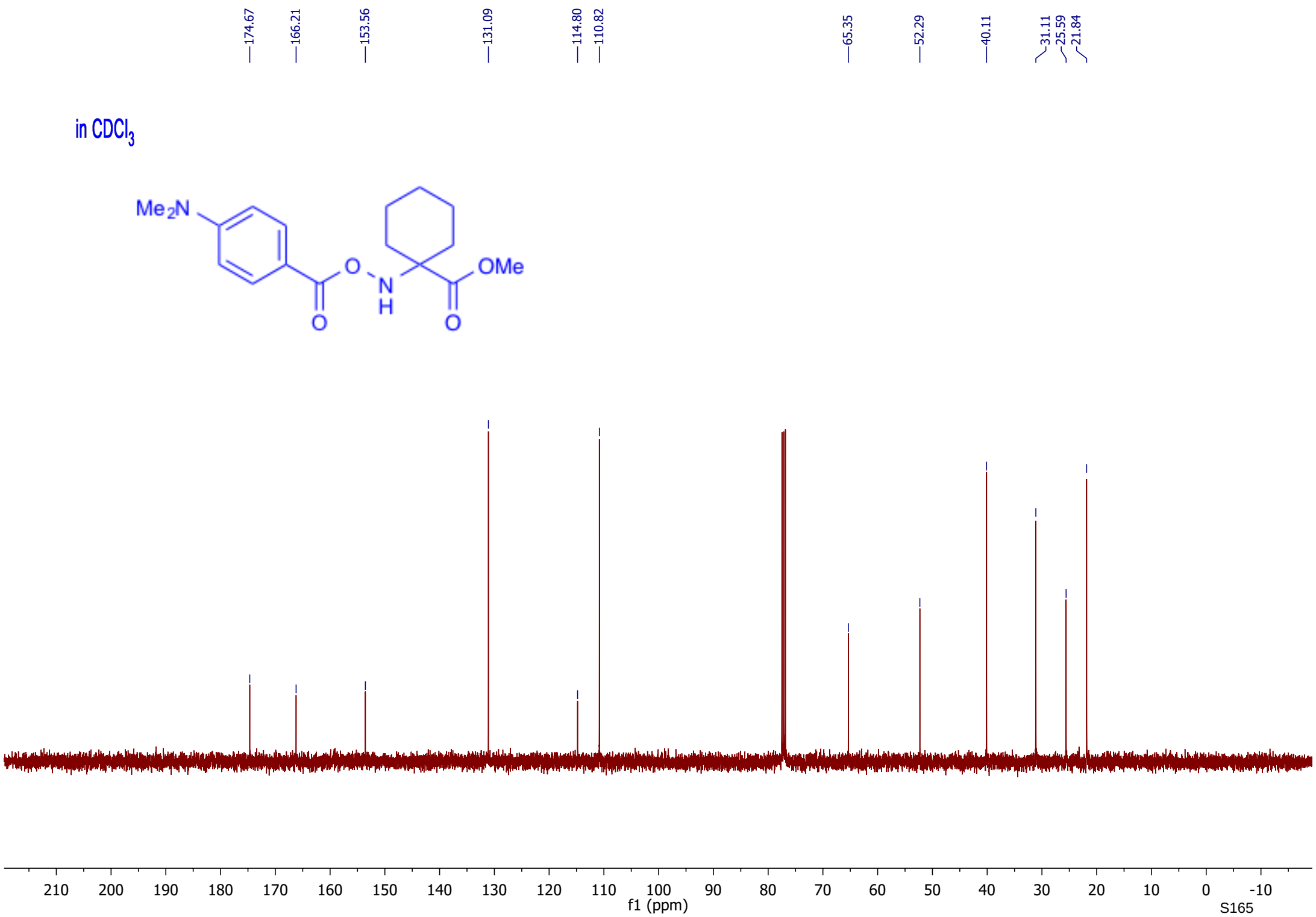

in CDCl3
OBn
OBn
O
N
H
O
O
1.00
6.29
3.23
2.20
1.12
1.10
1.08
1.08
3.14
9.38
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

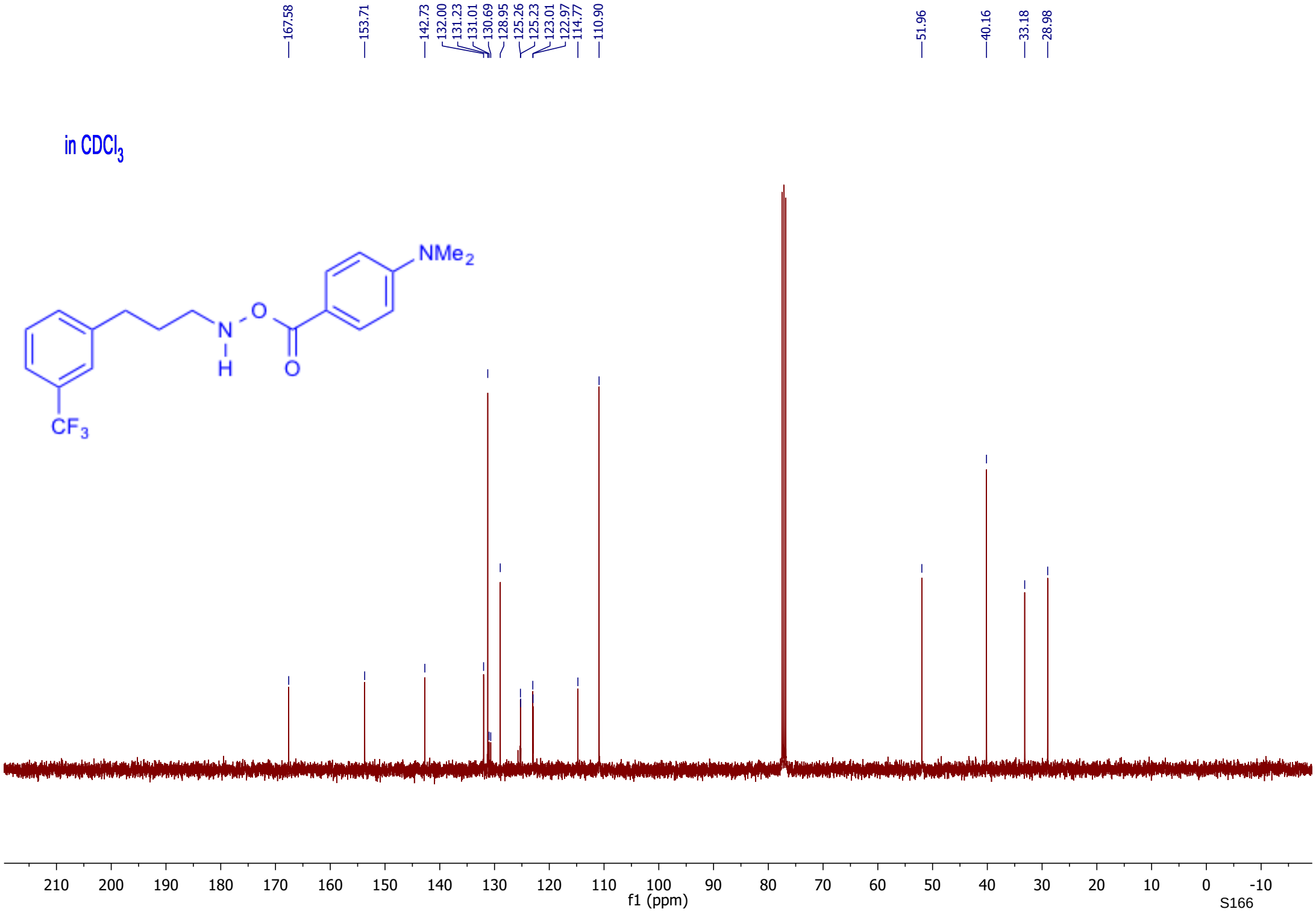

176.88
170.23
137.74
135.30
128.51
128.44
128.39
128.32
127.65
127.61
73.41
70.99
67.70
66.88
38.16
26.94
16.63
in CDCl3
OBn
OBn
O
N
H
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

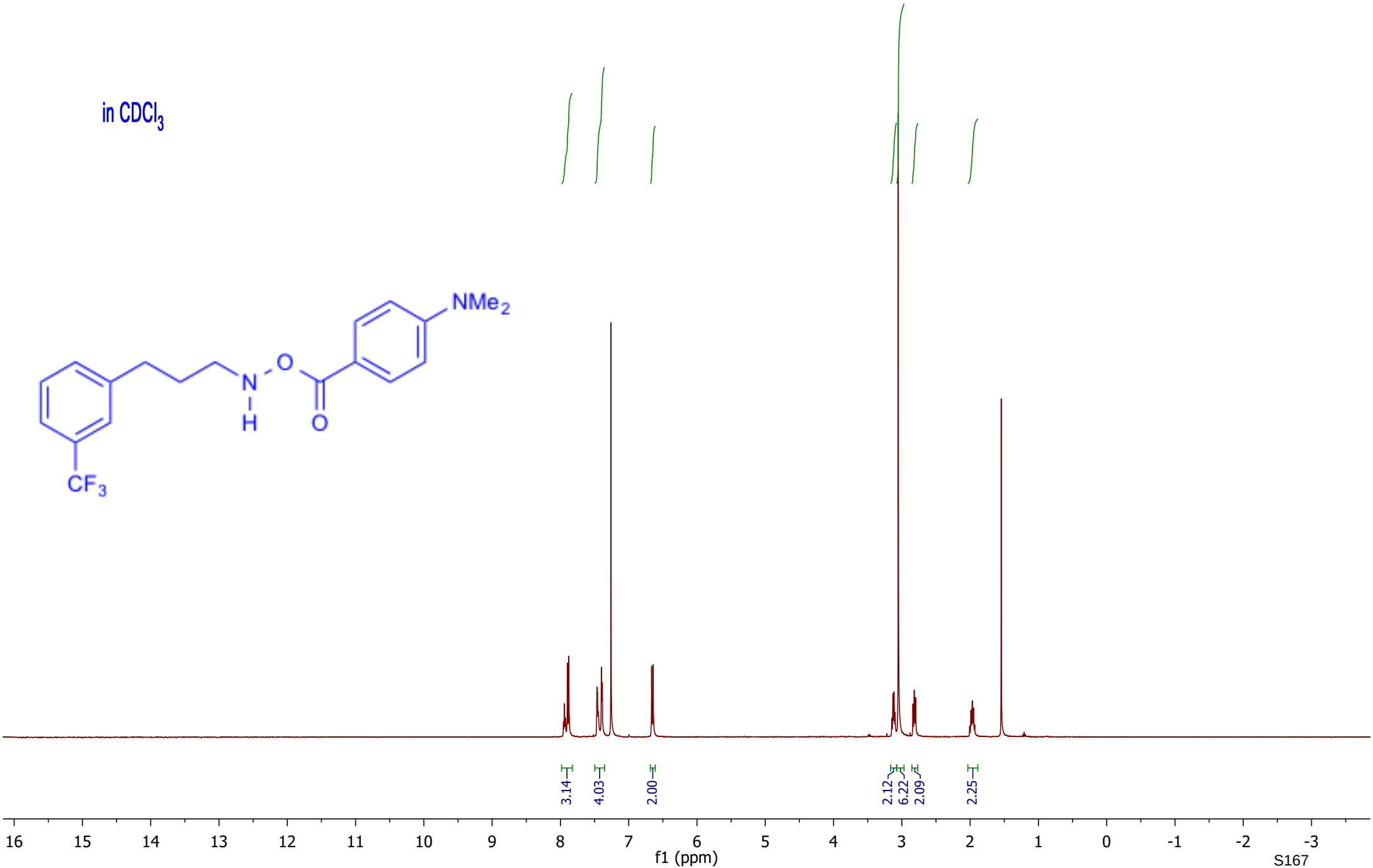

in CDCl3
Me2N
O
N
H
O
O
OtBu
1.00
1.96
2.00
0.99
6.02
1.03
8.98
6.24
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

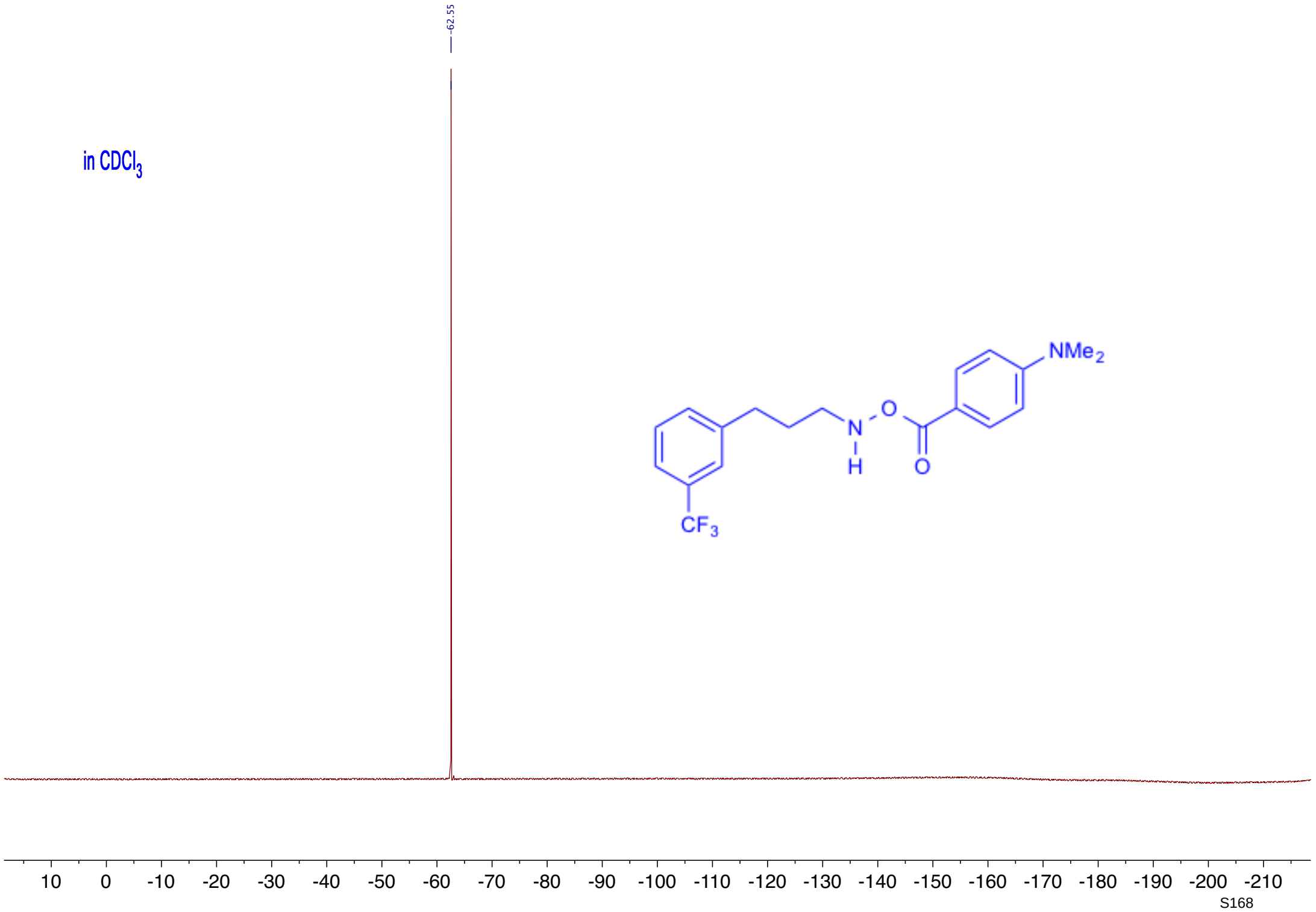

171.55
166.25
153.51
131.06
114.92
110.79
81.69
70.10
40.10
29.29
28.08
19.52
19.45
in CDCl3
Me2N
O
N
H
O
O
OtBu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


in CDCl3
Me2N
O
N
H
O
OMe
O
0.92
1.95
1.98
2.93
6.06
2.01
4.32
4.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

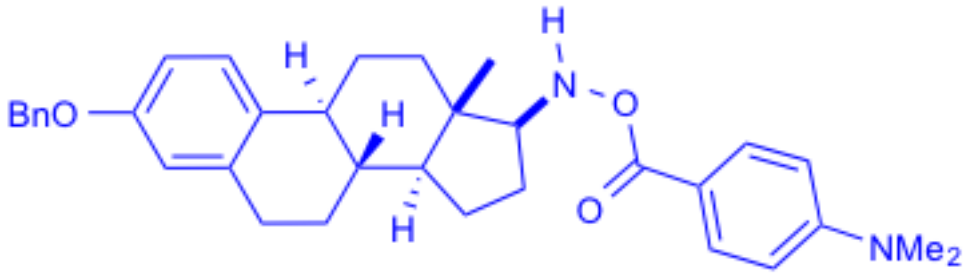

174.67
166.21
153.56
131.09
114.80
110.82
65.35
52.29
40.11
31.11
25.59
21.84
in CDCl3
Me2N
O
N
H
O
O
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


167.58
153.71
142.73
132.00
131.23
131.01
130.69
128.95
125.26
125.23
123.01
122.97
114.77
110.90
51.96
40.16
33.18
28.98
in CDCl3
NMe2
O
N
H
O
O
CF3
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)

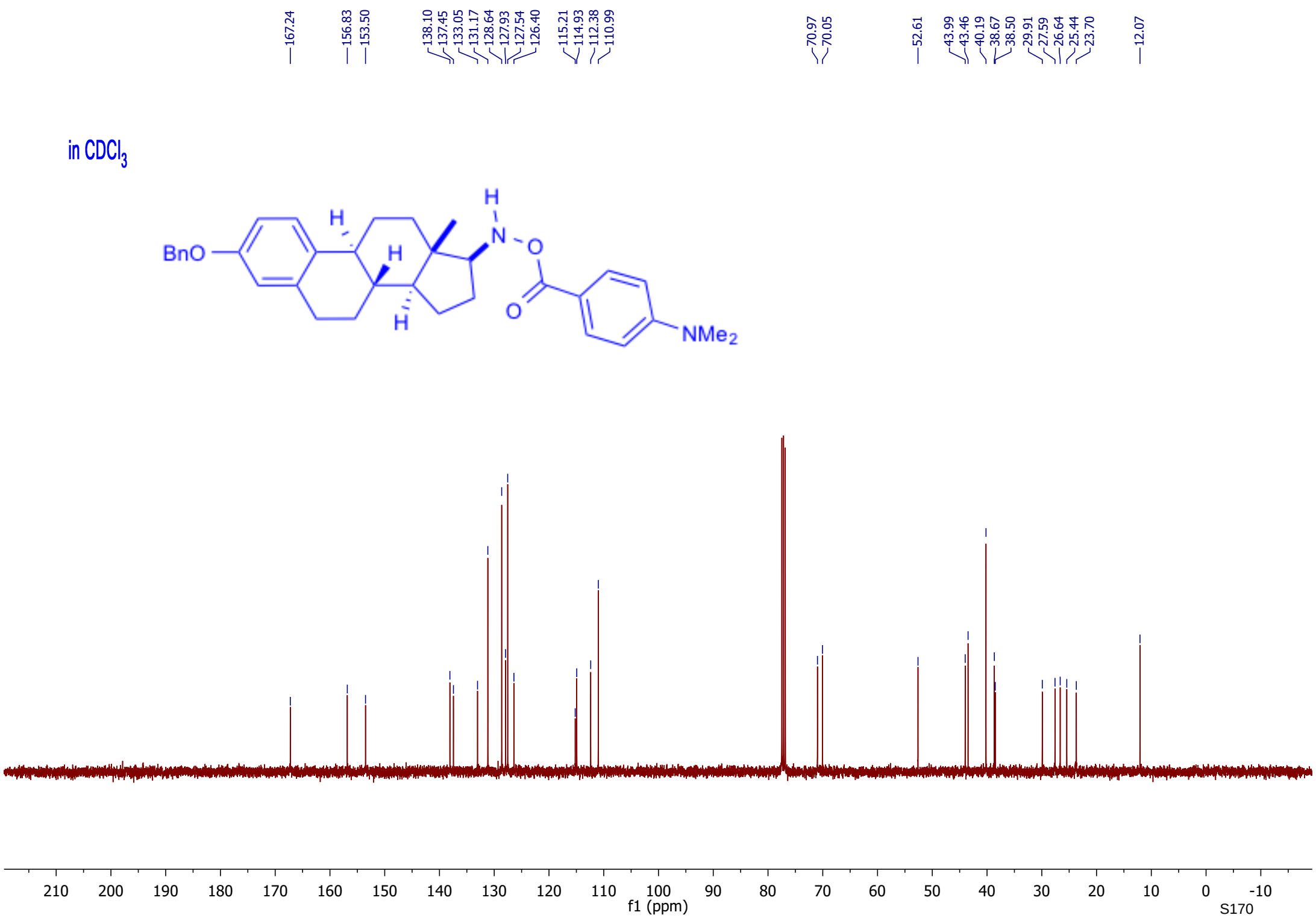

in CDCl3
NMe2
N
H
O
O
CF3
3.14
4.03
2.00
2.12
6.22
2.09
2.25
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


-62.55
in CDCl3
NMe2
O
N
H
O
O
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

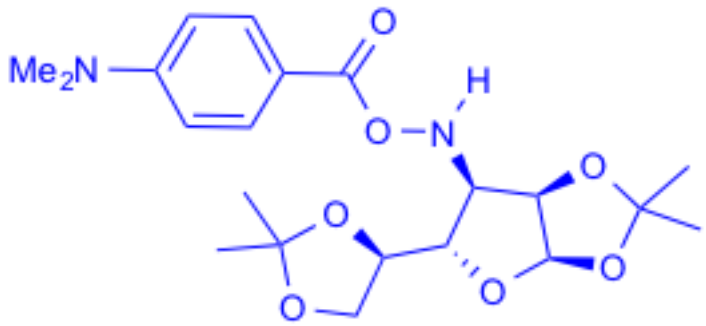
in $CDCl_3$


BnO
H
H
H
N
H
O
O
NMe2

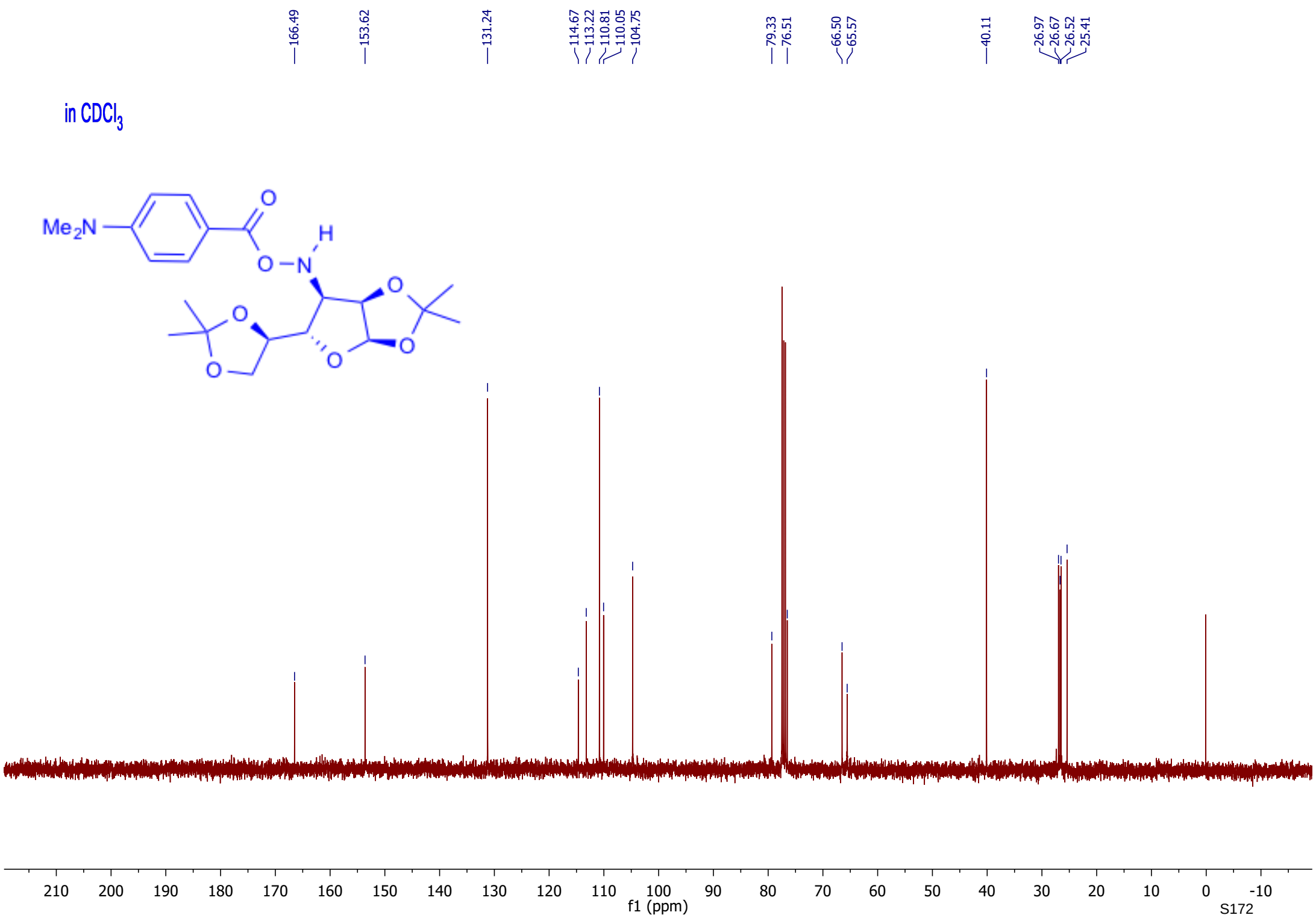
2.00
1.90
1.91
1.00
0.94
0.97
0.97
1.96
1.90
0.94
5.94
1.97
2.94
1.08
1.03
1.01
7.19
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.24
156.83
153.50
138.10
137.45
133.05
131.17
128.64
127.93
127.54
126.40
115.21
114.93
112.38
110.99
70.97
70.05
52.61
43.99
43.46
40.19
38.67
38.50
29.91
27.59
26.64
25.44
23.70
12.07
in CDCl3
BnO
H
H
H
N
O
O
NMe2
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)

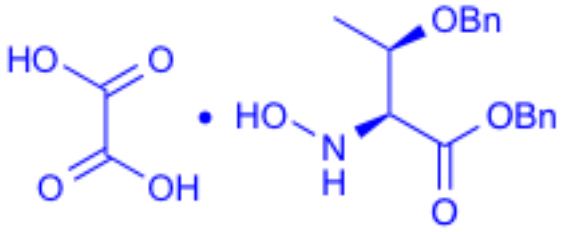
in $CDCl_3$

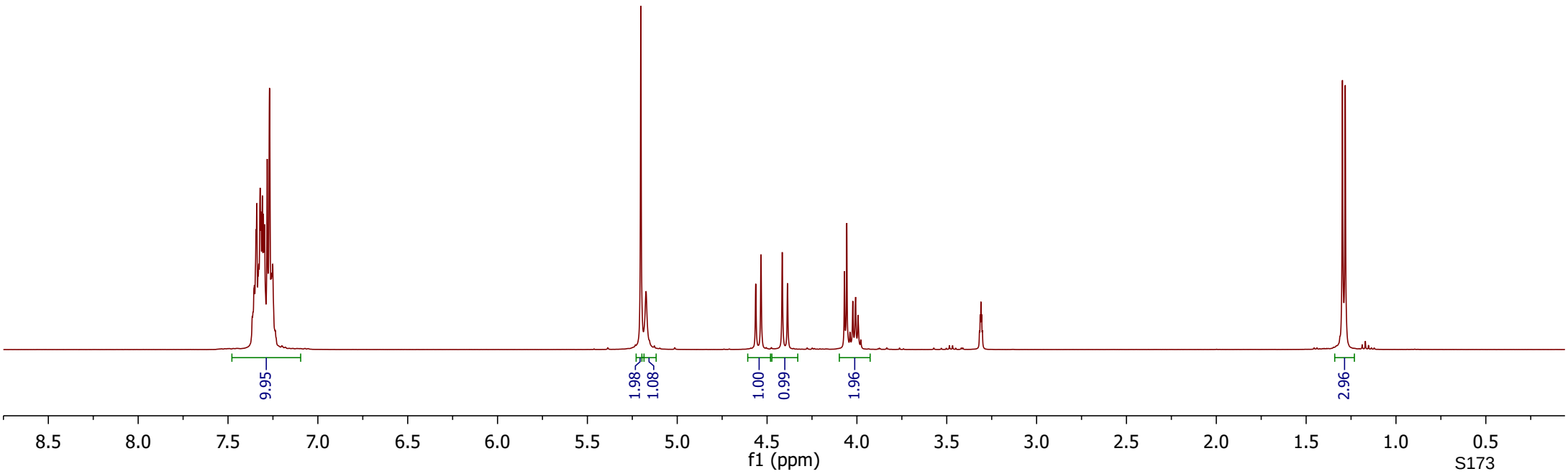

Me2N
O
O
N
H
O
O
O
O
O

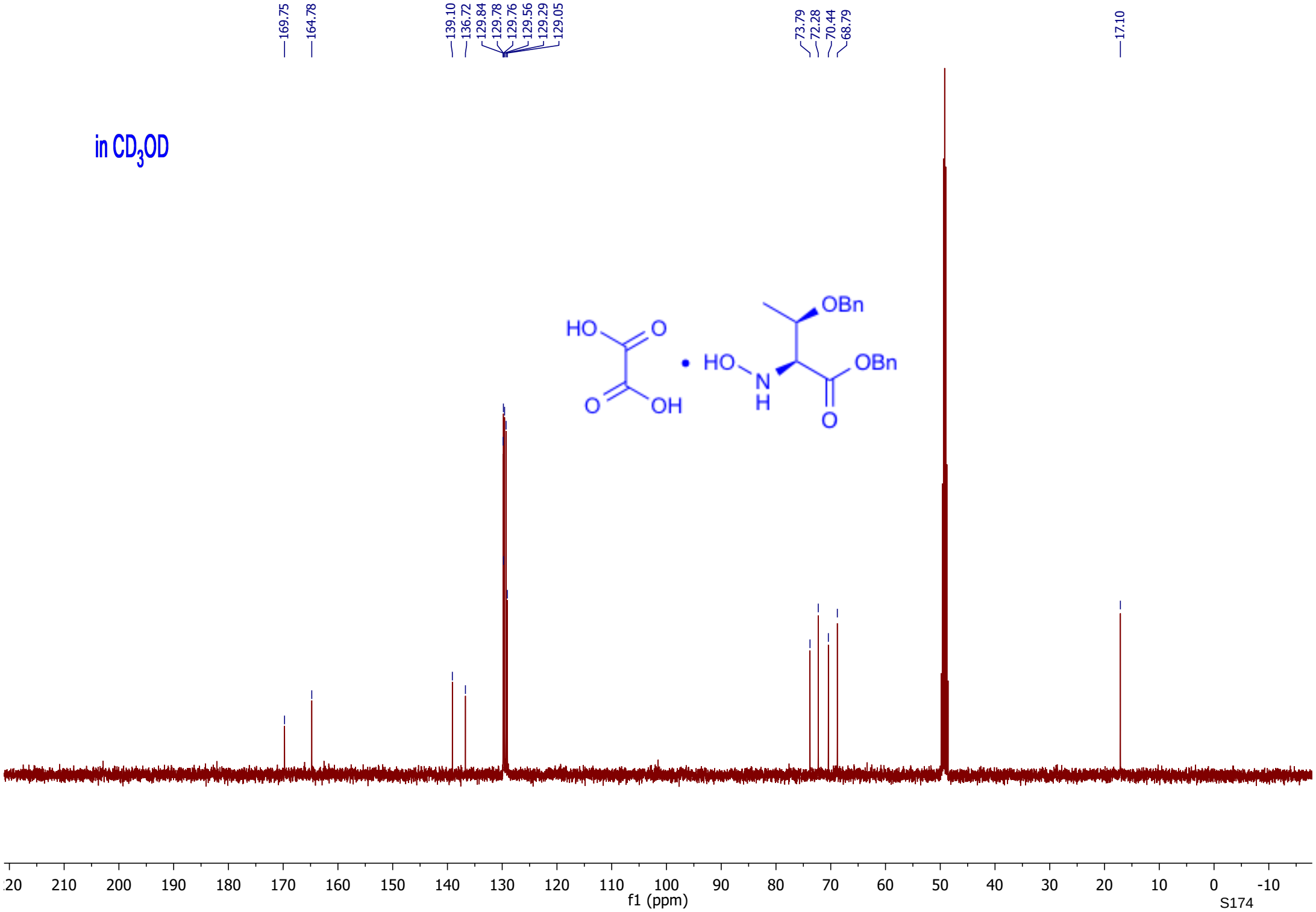
0.87
1.97
1.99
1.01
1.05
1.02
2.09
1.19
0.99
6.00
2.91
3.00
6.20
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


166.49
153.62
131.24
114.67
113.22
110.81
110.05
104.75
79.33
76.51
66.50
65.57
40.11
26.97
26.67
26.52
25.41
in CDCl3
Me2N
O
H
O
N
O
O
O
O
O
O
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)

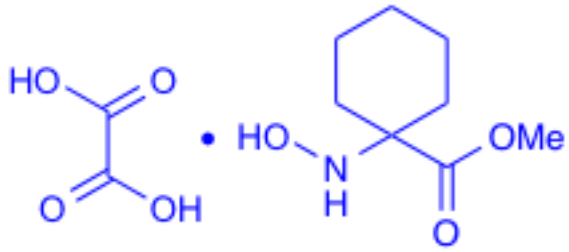
in CD_3OD


HO
O
O
OH
HO
N
H
OBn
OBn
O


9.95
1.98
1.08
1.00
0.99
1.96
2.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


169.75
164.78
139.10
136.72
129.84
129.78
129.76
129.56
129.29
129.05
73.79
72.28
70.44
68.79
17.10
in CD3OD
HO
O
O
OH
HO
N
H
OBn
OBn
O
f1 (ppm)

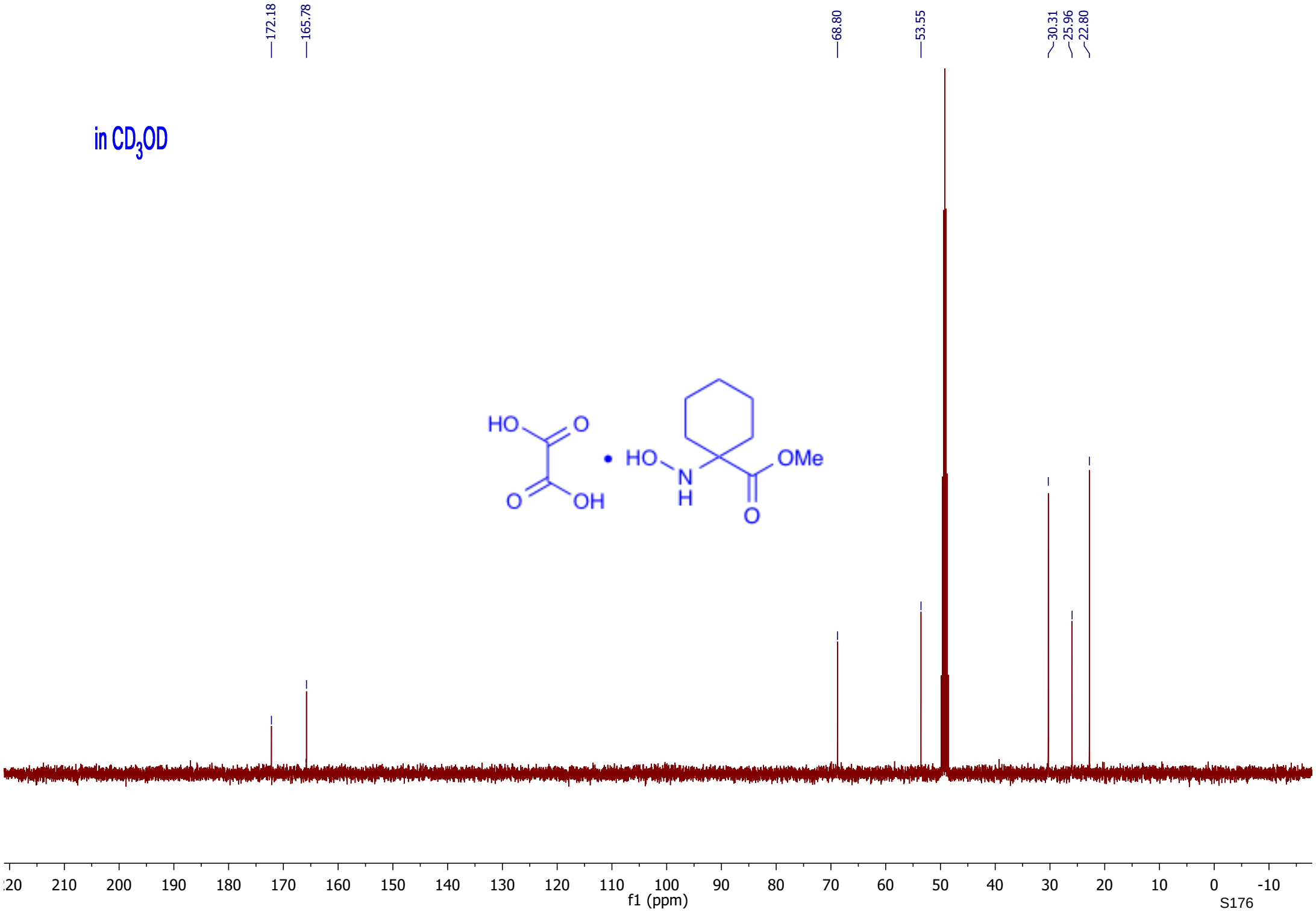
in CD_3OD

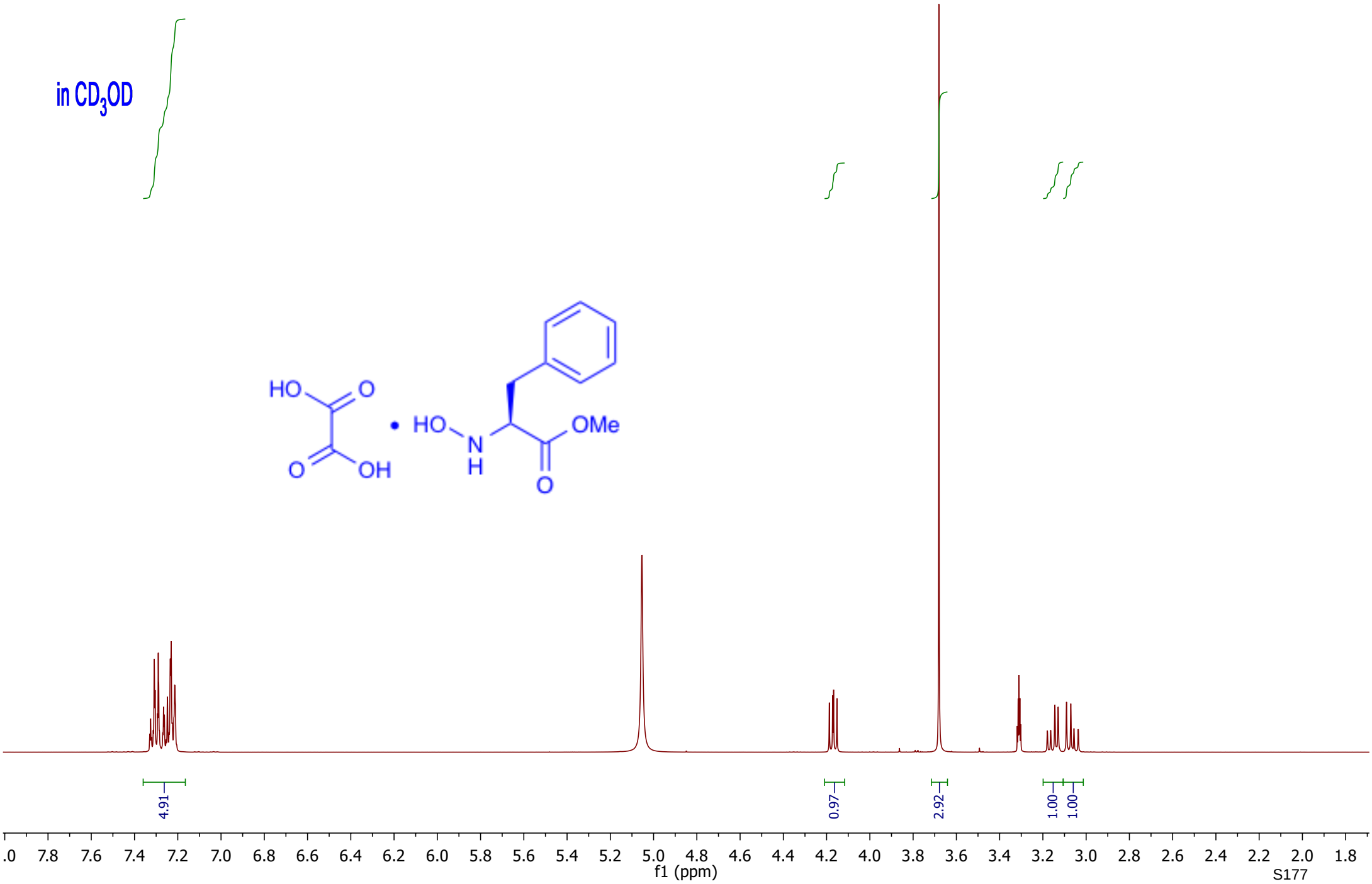


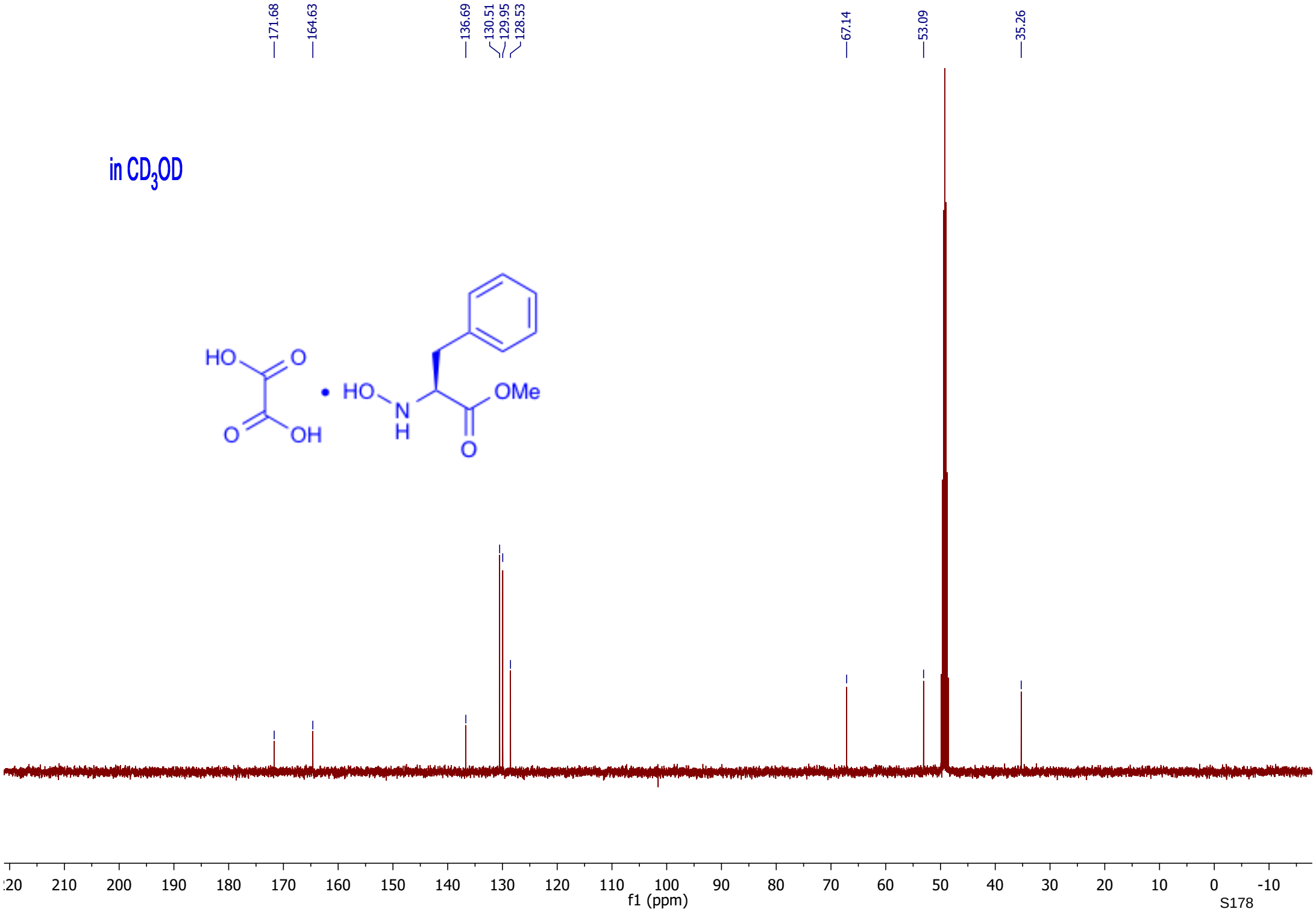
1.93 3.90 3.00 1.00

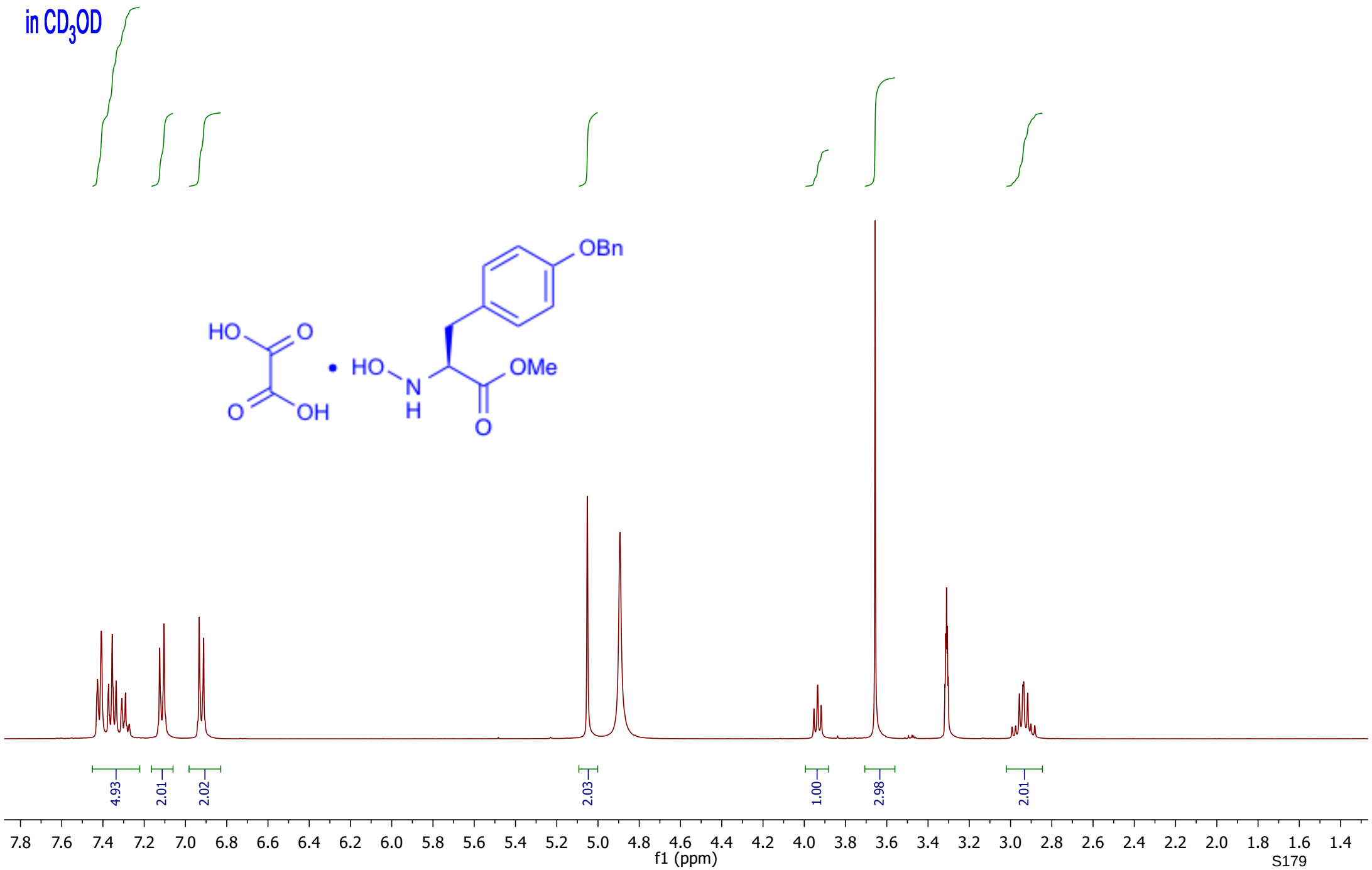
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2

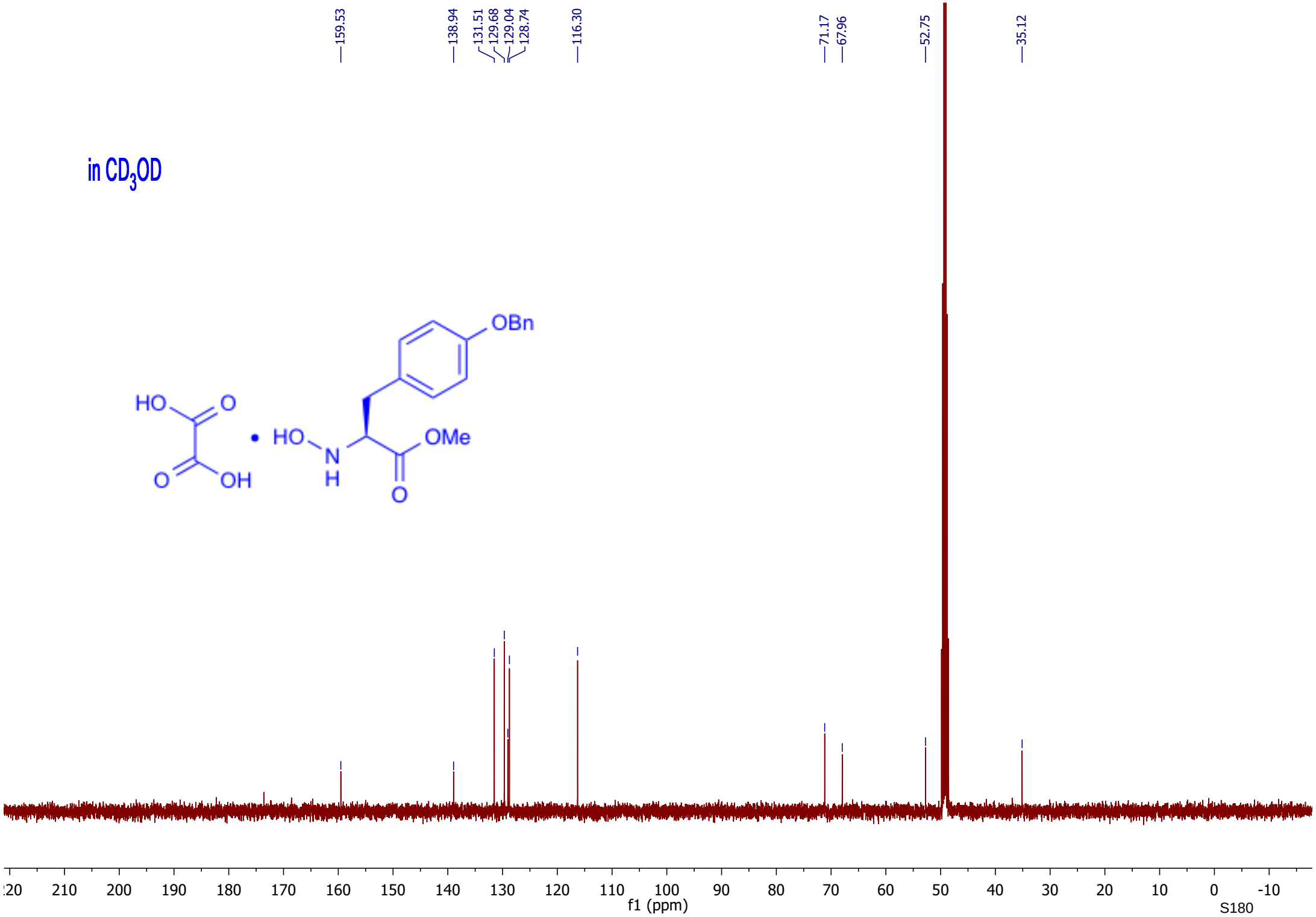
f1 (ppm)


172.18
165.78
68.80
53.55
30.31
25.96
22.80
in CD3OD
HO
O
O
OH
HO
N
H
OMe
O
f1 (ppm)

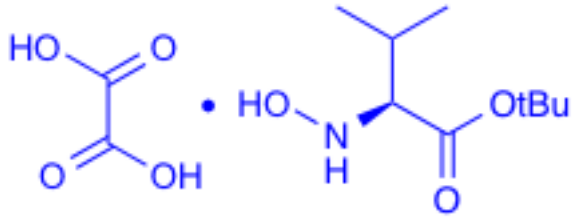

in CD3OD
HO
O
O
OH
HO
N
H
OMe
O
4.91
0.97
2.92
1.00
1.00
.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)


171.68
164.63
136.69
130.51
129.95
128.53
67.14
53.09
35.26
in CD3OD
HO
O
O
OH
HO
N
H
OMe
O
f1 (ppm)


in CD3OD
HO
O
O
OH
HO
N
H
OMe
O
OBn
4.93
2.01
2.02
2.03
1.00
2.98
2.01
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
f1 (ppm)

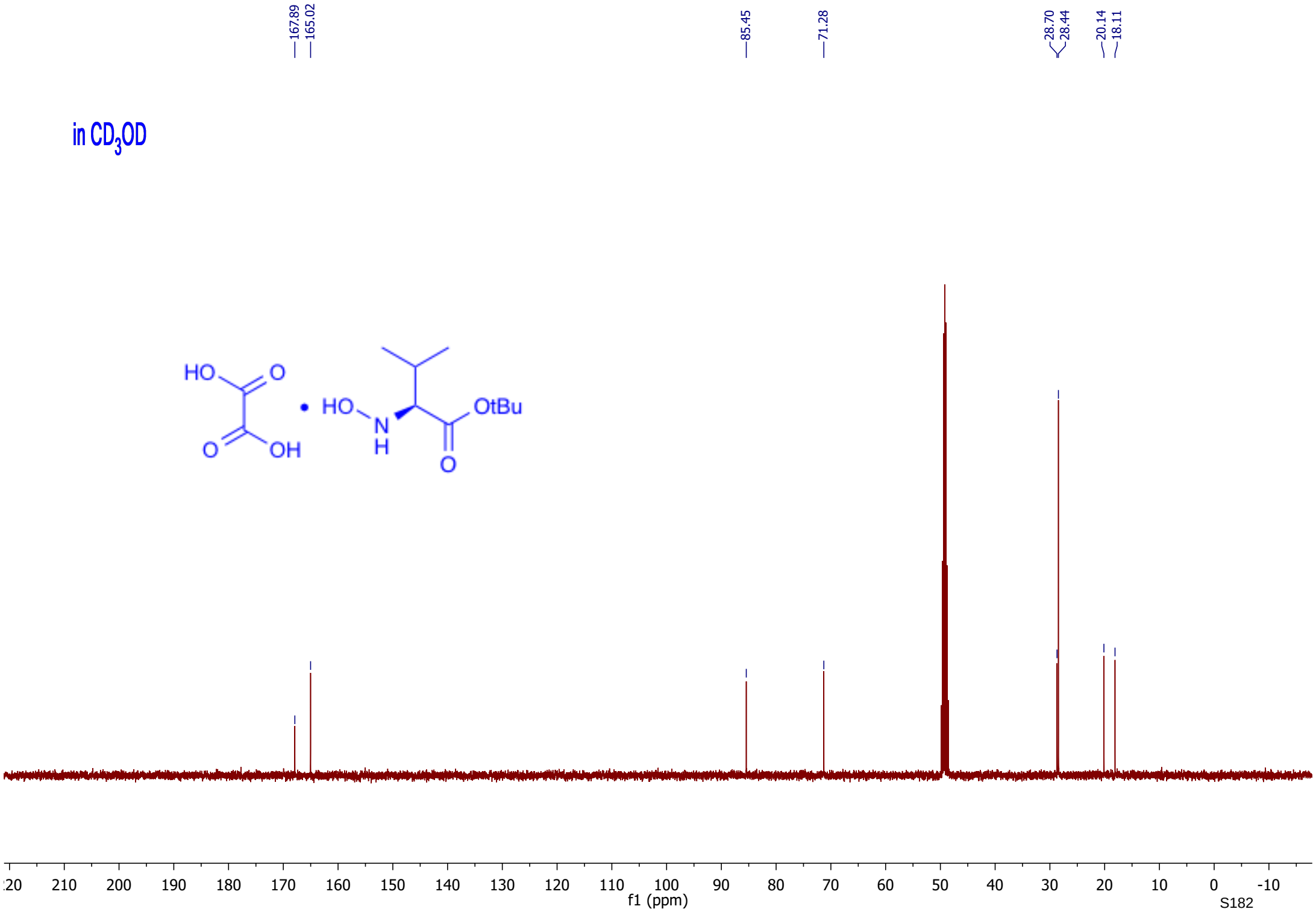

159.53
138.94
131.51
129.68
129.04
128.74
116.30
71.17
67.96
52.75
35.12
in CD3OD
HO
O
O
OH
HO
N
H
OMe
O
OBn
f1 (ppm)
S180

in CD_3OD



1.00 1.00 9.04 2.99 3.07

f1 (ppm)


167.89
165.02
85.45
71.28
28.70
28.44
20.14
18.11
in CD3OD
HO
O
O
OH
HO
N
H
OtBu
O
f1 (ppm)