Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Enantioselective Synthesis of Piperidines through the Formation of Chiral Mixed Phosphoric Acid Acetals: Experimental and Theoretical Studies**

Zhankui Sun, Grace A. Winschel, Paul M. Zimmerman, and Pavel Nagorny**

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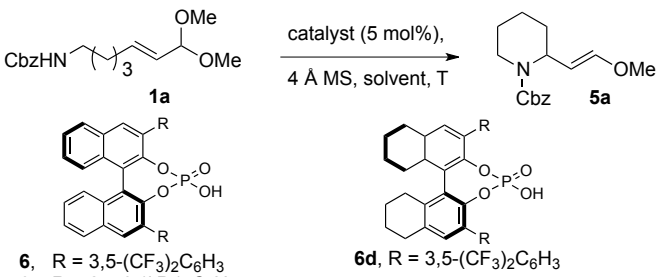
Table SI - I. Complete list of evaluated solvents and catalysts for Table 1 provided in the manuscript



entry	catalyst	solvent	T	time, h	yield, %	ee, %
1	(*S*)-**6a**	CH_3CN	rt	14	78	0
2	(*S*)-**6a**	THF	rt	14	20	5
3	(*S*)-**6a**	DCM	rt	14	93	0
4	(*S*)-**6a**	Et_2O	rt	14	15	3
5	(*S*)-**6a**	EtOAc	rt	14	20	13
6	(*S*)-**6a**	Toluene	rt	14	91	17
7	(*S*)-**6a**	CCl_4	rt	14	95	24
8	(*S*)-**6a**	Hexanes	rt	14	86	27
9	(*S*)-**6**	Hexanes	rt	14	96	55
10	(*S*)-**6b**	Hexanes	rt	14	78	28
11	(*S*)-**6c**	Hexanes	rt	14	83	9
12	(*S*)-**6d**	Hexanes	rt	14	95	51
13	(*S*)-**6**	Toluene	rt	14	88	50
14	(*S*)-**6**	Benzene	rt	14	91	56
15	(*S*)-**6**	CCl_4	rt	14	89	57
16	(*S*)-**6**	CCl_4	-20 ˚C	14	86	71
17[b]	(*S*)-**6**	CCl_4	-20 ˚C	14	88	75
18[b,c]	(*S*)-**6**	CCl_4	-20 ˚C	14	83	63
18[b,d]	(*S*)-**6**	CCl_4	-20 ˚C	24	81	84
19[b,d]	(*S*)-**6**	CCl_4	-20 ˚C	30	75	87
20[d,e]	(*S*)-**6**	CCl_4	-20 ˚C	24	74	88
21[d,e]	(*S*)-**6**	CCl_4	-20 ˚C	30	71	90
22[d,e]	(*S*)-**6**	CCl_4	-20 ˚C	48	62	95

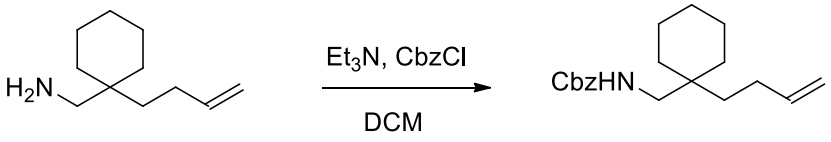
[a] All reactions were performed on 0.1 mmol scale (0.02 M solution) with E/Z> 20:1 starting material, 5% catalyst and 200 mg 4 Å molecue sieves.[b] 10% catalyst was used. [c] E/Z= 10:1 starting material was used. [d] 100 mg 4 Å molecue sieves. [e] 15% catalyst was used

II. General Methods

All reagents and solvents were purchased from Sigma-Aldrich or Fisher Scientific and were used as received without further purification unless specified. All reactions were carried out under a positive pressure of nitrogen in flame- or oven-dried glassware with magnetic stirring. Reactions were cooled using external cooling baths: ice water (0 °C) or dry ice/acetone (-78 °C). Heating was achieved by use of a silicone bath with heating controlled by electronic contact thermometer. Deionized water was used in the preparation of all aqueous solutions and for all aqueous extractions. Solvents used for extraction and chromatography were ACS or HPLC grade. Purification of reactions mixtures was performed by flash chromatography using SiliCycle SiliaFlash P60 (230-400 mesh).

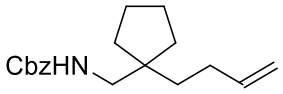
^{1}H NMR spectra were recorded on Varian vnmrs 700 (700 MHz), Varian vnmrs 500 (500 MHz), Varian INOVA 500 (500 MHz) or Varian MR400 (400 MHz) spectrometers and chemical shifts (δ) are reported in parts per million (ppm) with solvent resonance as the internal standard ($CDCl_3$ at δ 7.26). Data are reported as (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz; integration). Proton-decoupled ^{13}C NMR spectra were recorded on Varian vnmrs 700 (700 MHz), Varian vnmrs 500 (500 MHz), Varian INOVA 500 (500 MHz) or Varian MR400 (400 MHz) spectrometers and chemical shifts (δ) are reported in ppm with solvent resonance as the internal standard ($CDCl_3$ at δ 77.0, C_6D_6 at δ 127.683). High resolution mass spectra (HRMS) were recorded on Micromass AutoSpec Ultima or VG (Micromass) 70-250-S Magnetic sector mass spectrometers in the University of Michigan mass spectrometry laboratory. Infrared (IR) spectra were recorded as thin films on NaCl plates on a Perkin Elmer Spectrum BX FT-IR spectrometer. Absorption peaks were reported in wavenumbers (cm^{-1}). The 4 Å molecules sieves were purchased from Sigma-Aldrich. The catalog number is 688363-500g. The molecules sieves were flame-dried under high vacuum for 10 min before use.

III. Synthesis of the Alkenes



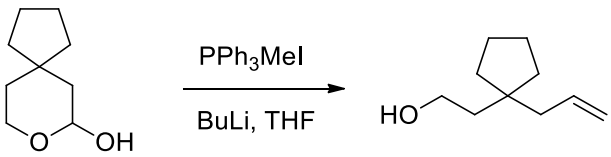
S1 **S2**

Benzyl-((1-(but-3-en-1-yl)cyclohexyl)methyl)carbamate (S2).
The amine **S1** (1.0 mmol, 167 mg) was dissolved in DCM (5 mL). Et_3N (1.2 mmol, 0.17 mL) was added followed by CbzCl (1.2 mmol, 0.17 mL). The mixture was stirred at room temperature for 6 hours. Saturated NH_4Cl (10 mL) solution was added. The resultant mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The obtained residue was purified by column chromatography (10% EtOAc/hexanes) to provide the product **S2** (242 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.29 (m, 5H), 5.80-5.75 (m, 1H), 5.09 (s, 2H), 4.99 (d, *J* =16.8 Hz, 1H), 4.92 (d, *J* =10.0 Hz, 1H), 4.77 (br, 1H), 3.11 (d, *J* =6.4 Hz, 2H), 2.02-1.94 (m, 2H), 1.45-1.26 (m, 12H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 156.7, 139.2, 136.7, 128.5, 128.2, 128.1, 114.2, 66.6, 47.1, 36.2, 34.7, 33.4, 27.3, 26.2, 21.4. HRMS (ES) *m/z* calcd for $C_{19}H_{27}NNaO_2^+$ $[M+Na]^+$ 324.1934, found 324.1936. IR (thin film, cm^{-1}) 3344, 2926, 1710, 1453, 1223.



S3

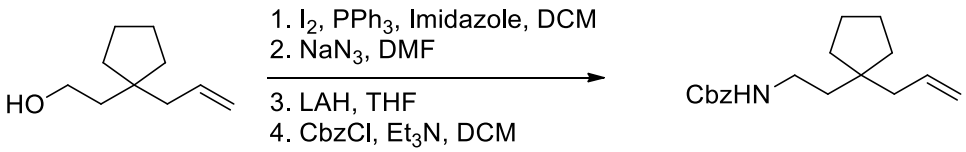
Benzyl-((1-(but-3-en-1-yl)cyclopentyl)methyl)carbamate (S3).
S3 was synthesized employing a procedure similar to that used to synthesize **S2.** ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.35-7.25(m, 5H), 5.81-5.77 (m, 1H), 5.09 (s, 2H), 4.99 (d, *J* =16.8 Hz, 1H), 4.92 (d, *J* =9.8 Hz, 1H), 4.75 (br, 1H), 3.11 (d, *J* =6.3 Hz, 2H), 2.02-1.99 (m, 2H), 1.61-1.58 (m, 4H) 1.42-1.36 (m, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 156.7, 139.0, 136.6, 128.5, 128.2, 128.1, 114.2, 66.7, 47.4, 45.9, 36.9, 35.5, 29.1, 24.9. HRMS (ES) *m/z* calcd for $C_{18}H_{25}NNaO_2^+$ $[M+Na]^+$ 310.1778, found 310.1780. IR (thin film, cm^{-1}) 3341, 2935, 1713, 1451.



S4 **S5**

2-(1-Allylcyclopentyl)ethanol (S5).
n-BuLi (16 mmol) was added drop-wise to a solution of PPh_3MeI (16 mmol, 6.52 g) in THF (30 mL) at room temperature. The solution was stirred at room temperature for 30 minutes before hemiacetal **S4** (11 mmol, 1.72 g) in THF (10 mL) was added. When the reaction was deemed complete following TLC analysis, saturated NH_4Cl (20 mL) solution was added. The resultant mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The obtained residue was purified by column chromatography (10% EtOAc/hexanes) to provide the product (1.44 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85-5.78 (m, 1H), 5.06-5.02 (m, 2H), 3.73-3.69 (m, 2H), 2.06-2.04 (m, 2H),

1.65-1.59 (m, 7H) 1.50-1.39 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 116.6, 59.3, 43.7, 42.9, 41.5, 37.3, 24.4. HRMS (ES) *m/z* calcd for $C_{10}H_{18}NaO^+$ $[M+Na]^+$ 177.1250, found 177.1252. IR (thin film, cm^{-1}) 3352, 2950, 1638, 1451, 1041.

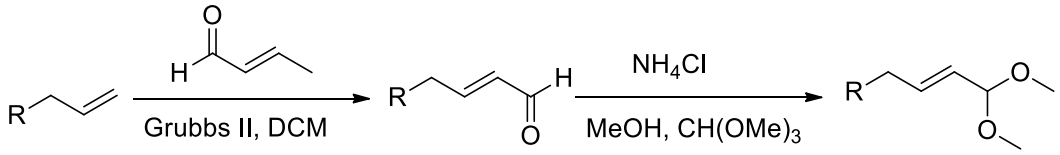


S5 **S6**

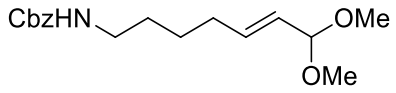
Benzyl-(2-(1-allylcyclopentyl)ethyl)carbamate (S6).

2-(1-allylcyclopentyl)ethanol (**S5)** (9.4 mmol, 1.44 g) was dissolved in DCM (50 mL). Imidazole (12 mmol, 820 mg) and PPh_3 (12 mmol, 3.14 g) were added. I_2 (12 mmol, 3.1 g) was added slowly. The mixture was stirred at room temperature for 2 hours. When the reaction was deemed complete following TLC analysis, saturated $Na_2S_2O_3$ (20 mL) solution was added. The resultant mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give the crude iodide product. The iodide was then dissolved in DMF (15 mL). NaN_3 (15 mmol, 1.04 g) was added. The mixture was stirred at room temperature for 30 hours. When the reaction was deemed complete following TLC analysis, saturated brine (30 mL) solution was added. The resultant mixture was extracted with Et_2O. The combined organic layers were washed twice with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give the crude azide. The azide was then dissolved in THF (50 mL). LAH (15 mmol, 600 mg) was added slowly. The mixture was stirred for 3 hours before it was slowly quenched with water (2 mL). $MgSO_4$ was added. The mixture was filtered through Celite. The solid was washed twice with Et_2O. The filtrate was concentrated *in vacuo* to give the crude amine. The amine was dissolved in DCM (30 mL). Et_3N (15 mmol, 2.1 mL) was added followed by CbzCl (15 mmol, 2.1 mL). The mixture was stirred at room temperature for 6 hours. Saturated NH_4Cl (10 mL) solution was added. The resultant mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The obtained residue was purified by column chromatography (10% EtOAc/hexanes) to provide the product **S6** (1.42 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 5H), 5.80-5.75 (m, 1H), 5.08 (s, 2H), 5.05-5.02 (m, 2H), 4.77 (br, 1H), 3.21-3.16 (m, 2H), 2.02 (d, J =6.8 Hz, 2H), 1.59-1.57 (m, 4H) 1.51-1.31 (m, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 156.3, 136.7, 135.7, 128.5, 128.1, 128.0, 117.0, 66.5, 44.0, 42.7, 38.9, 37.7, 37.3, 24.5. HRMS (ES) *m/z* calcd for $C_{18}H_{25}NNaO_2^+$ $[M+Na]^+$ 310.1778, found 310.1777. IR (thin film, cm^{-1}) 3346, 2922, 1714, 1451, 1220.

IV. Synthesis of the Acetals

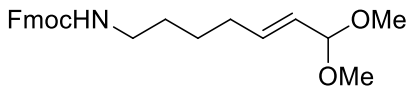


The alkene (1.0 mmol) was dissolved in DCM (2 mL). Crotonaldehyde (5.0 mmol, 350 mg) was added. Grubbs II catalyst (0.02 mmol, 16 mg) or Hoveyda-Grubbs II catalyst (0.02 mmol, 12 mg) was added. The mixture was stirred overnight at room temperature. TLC showed complete conversion. The mixture was concentrated *in vacuo*. The remaining mixture was purified by column chromatography (20% acetone/hexanes) to give the product. The aldehyde was dissolved in a mixture of MeOH (2 mL) and $CH(OMe)_3$ (2.0 mL) . Solid NH_4Cl (2.0 mmol, 108 mg) was added. The mixture was stirred overnight at room temperature. TLC showed complete conversion. Saturated $NaHCO_3$ (40 mL) solution was added. The resultant mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The obtained residue was purified by column chromatography (1% triethylamine, 16% EtOAc/hexanes) to provide the desired acetal.



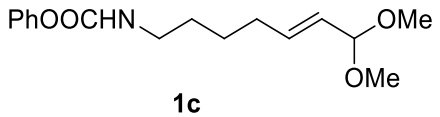
1a

(*E*)-Benzyl (7,7-dimethoxyhept-5-en-1-yl)carbamate (1a).
Following the general procedure provided above, **1a** (0.64 mmol, 196 mg) was obtained in 64% (two steps). ^{1}H NMR (400 MHz, C_6D_6) δ 7.22-7.20 (m, 2H), 7.08-7.05 (m, 2H), 7.04-7.00 (m, 1H), 5.71-5.64 (m, 1H), 5.46 (dd, J = 4.4 Hz, 15.2 Hz, 1H), 5.04 (s, 2H), 4.71 (d, J =4.4 Hz, 1H), 4.01 (br, 1H), 3.14 (s, 6H), 2.85-2.80 (m, 2H), 1.74-1.69 (m, 2H), 1.05-0.98 (m, 4H); ^{13}C NMR (175 MHz, C_6D_6) δ 155.9, 137.3, 134.2, 128.3, 128.1, 127.8., 127.7, 127.5, 127.4, 102.7, 66.1, 51.7, 40.6, 31.5, 29.3, 25.8. HRMS (ES) *m/z* calcd for $C_{17}H_{25}NNaO_4^+$ $[M+Na]^+$ 330.1676, found 330.1679. IR (thin film, cm^{-1}) 3359, 2931, 1677, 1536, 1426.



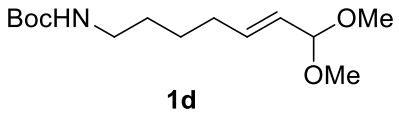
1b

(*E*)-(9H-Fluoren-9-yl)methyl (7,7-dimethoxyhept-5-en-1-yl)carbamate (1b).
Following the general procedure provided above, **1b** (0.53 mmol, 209 mg) was obtained in 53% (two steps). ^{1}H NMR (500 MHz, C_6D_6) δ 7.55 (d, J =7.0 Hz, 2H), 7.41 (d, J =7.0 Hz, 2H), 7.20-7.17 (m, 2H), 7.14-7.11 (m, 2H), 5.70-5.67 (m, 1H), 5.47-5.44 (m, 1H), 4.71-4.70 (m, 1H), 4.44-4.42 (m, 2H), 4.02 (br, 1H), 3.97-3.95 (m, 1H), 3.14 (s, 6H), 2.81-2.78 (m, 2H), 1.75-1.71 (m, 2H), 1.02-1.00 (m, 4H); ^{13}C NMR (125 MHz, C_6D_6) δ 155.9, 144.3, 141.5, 134.3, 127.9, 127.8, 127.7, 127.5, 127.4, 126.9, 124.9, 119.8, 102.7, 65.5, 51.7, 47.5, 40.5, 31.5, 29.2, 25.8. HRMS (ES) *m/z* calcd for $C_{24}H_{29}NNaO_4^+$ $[M+Na]^+$ 418.1989, found 418.1989. IR (thin film, cm^{-1}) 3339, 2933, 1712, 1449, 1223, 1049.



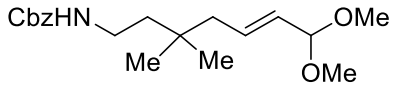
1c

(*E*)-Phenyl (7,7-dimethoxyhept-5-en-1-yl)carbamate (1c).
Following the general procedure provided above, **1c** (0.55 mmol, 161 mg) was obtained in 55% (two steps). ^{1}H NMR (700 MHz, C_6D_6) δ 7.17-7.16 (m, 2H), 7.05-7.03 (m, 2H), 6.88-6.85 (m, 1H), 5.70-5.68 (m, 1H), 5.49-5.46 (m, 1H), 4.71 (d, *J* =4.9 Hz, 1H), 4.44 (br, 1H), 3.14 (s, 6H), 2.86-2.83 (m, 2H), 1.75-1.74 (m, 2H), 1.10-1.00 (m, 4H); ^{13}C NMR (175 MHz, C_6D_6) δ 154.0, 151.7, 134.2, 129.0, 127.4, 124.7, 121.6, 102.7, 51.8, 40.7, 31.5, 29.1, 25.8; HRMS (ES) *m/z* calcd for $C_{16}H_{23}NNaO_4^+$ $[M+Na]^+$ 316.1519, found 316.1519. IR (thin film, cm^{-1}) 3583, 2932, 1717, 1363.



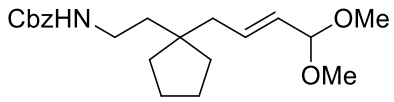
1d

(*E*)-*tert*-Butyl(7,7-dimethoxyhept-5-en-1-yl)carbamate (1d).
Following the general procedure provided above, **1d** (0.54 mmol, 147 mg) was obtained in 54% (two steps). ^{1}H NMR (700 MHz, C_6D_6) δ 5.69-5.66 (m, 1H), 5.45-5.43 (m, 1H), 4.69 (d, *J* =4.2 Hz, 1H), 4.12 (br, 1H), 3.13 (s, 6H), 2.89-2.86 (m, 2H), 1.75-1.74 (m, 2H), 1.40 (s, 9H), 1.15-1.03 (m, 4H); ^{13}C NMR (175 MHz, C_6D_6) δ 155.4, 134.3, 127.4, 102.7, 77.9, 51.7, 40.1, 31.5, 29.4, 28.1, 25.9. HRMS (ES) *m/z* calcd for $C_{14}H_{27}NNaO_4^+$ $[M+Na]^+$ 296.1832, found 296.1834. IR (thin film, cm^{-1}) 3363, 2930, 1713, 1364, 1222, 1055.



1e

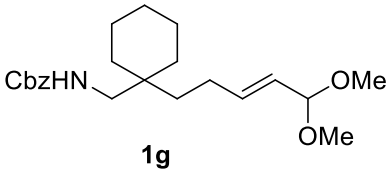
(*E*)-Benzyl(7,7-dimethoxy-3,3-dimethylhept-5-en-1-yl)carbamate (1e).
Following the general procedure provided above, **1e** (0.66 mmol, 221 mg) was obtained in 66% (two steps). ^{1}H NMR (700 MHz, C_6D_6) δ 7.22 (d, *J* =7.7 Hz, 2H), 7.08 (t, *J* =7.7 Hz, 2H), 7.01 (t, *J* =7.7 Hz, 1H), 5.80-5.78 (m, 1H), 5.46 (dd, *J* =4.2, 15.4 Hz, 1H), 5.06 (s, 2H), 4.73 (d, *J* =4.2 Hz, 1H), 4.04 (br, 1H), 3.14 (s, 6H), 2.94-2.91 (m, 2H), 1.70 (d, *J* =7.7 Hz, 2H), 1.07-1.04 (m, 2H), 0.64 (s, 6H); ^{13}C NMR (175 MHz, C_6D_6) δ 155.8, 137.4, 130.9, 130.0, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 102.4, 66.1, 51.7, 44.6, 41.2, 37.0, 32.2, 26.5. HRMS (ES) *m/z* calcd for $C_{19}H_{29}NNaO_4^+$ $[M+Na]^+$ 358.1989, found 358.1985. IR (thin film, cm^{-1}) 3413, 2956, 1708, 1365, 1222, 1096.



1f

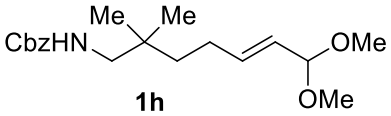
(*E*)-Benzyl(2-(1-(4,4-dimethoxybut-2-en-1-yl)cyclopentyl)ethyl)carbamate (1f).
Following the general procedure provided above, **1f** (0.62 mmol, 224 mg) was obtained in 62% (two steps). ^{1}H NMR (400 MHz, C_6D_6) δ 7.21-7.19 (m, 2H), 7.10-7.05 (m, 2H), 7.02-7.00 (m, 1H), 5.81-5.76 (m, 1H), 5.47 (dd, *J* =4.8, 15.6 Hz, 1H), 5.03 (s, 2H), 4.72 (m, 2H), 3.13 (s, 6H),

3.03-2.98 (m, 2H), 1.81 (d, J =7.2 Hz, 2H), 1.38-1.35 (m, 4H), 1.29-1.14 (m, 6H); ^{13}C NMR (175 MHz, C_6D_6) δ 156.0, 137.4, 131.6, 129.7, 128.2, 128.0, 127.9, 127.6, 127.4, 102.4, 66.0, 51.7, 43.9, 40.7, 38.9, 37.5, 37.0, 24.4; HRMS (ES) *m/z* calcd for $C_{21}H_{31}NNaO_4^+$ $[M+Na]^+$ 384.2145, found 384.2143. IR (thin film, cm^{-1}) 3582, 2947, 1715, 1362, 1222.



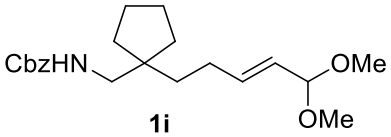
1g

(*E*)-Benzyl((1-(5,5-dimethoxypent-3-en-1-yl)cyclohexyl)methyl)carbamate (1g).
Following the general procedure provided above, **1g** (0.68 mmol, 255 mg) was obtained in 68% (two steps). ^{1}H NMR (500 MHz, C_6D_6) δ 7.24-7.23 (m, 2H), 7.13-7.10 (m, 2H), 7.06-7.03 (m, 1H), 5.80-5.77 (m, 1H), 5.58-5.54 (m, 1H), 5.08 (s, 2H), 4.75 (d, J =5.0 Hz, 1H), 4.49 (br, 1H), 3.17 (s, 6H), 2.96 (d, J =6.5 Hz, 2H), 1.88-1.83 (m, 2H), 1.28-1.11 (m, 8H), 0.99-0.98 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 156.5, 137.3, 135.4, 128.2, 128.1, 127.9, 127.7, 127.6, 127.4, 126.8, 102.9, 66.3, 51.7, 46.9, 36.1, 34.5, 33.1, 26.1, 25.6, 21.3. HRMS (ES) *m/z* calcd for $C_{22}H_{33}NNaO_4^+$ $[M+Na]^+$ 398.2302, found 398.2300. IR (thin film, cm^{-1}) 3345, 2926, 1712, 1363, 1222, 1131.



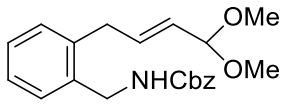
1h

(*E*)-Benzyl(7,7-dimethoxy-2,2-dimethylhept-5-en-1-yl)carbamate (1h).
Following the general procedure provided above, **1h** (0.58 mmol, 194 mg) was obtained in 58% (two steps). ^{1}H NMR (700 MHz, C_6D_6) δ 7.21 (d, J =7.7 Hz, 2H), 7.08 (t, J =7.7 Hz, 2H), 7.01 (t, J =7.7 Hz, 1H), 5.73-5.70 (m, 1H), 5.48 (dd, J =4.9, 16.1 Hz, 1H), 5.04 (s, 2H), 4.75 (t, J =5.6 Hz, 1H), 4.69 (d, J =4.2 Hz, 1H), 3.14 (s, 6H), 2.84 (d, J =6.3 Hz, 2H), 1.83-1.79 (m, 2H), 1.05-1.03 (m, 2H), 0.59 (s, 6H); ^{13}C NMR (175 MHz, C_6D_6) δ 156.5, 137.3, 135.1, 128.3, 128.1, 127.8, 127.7, 127.6, 127.5, 126.9, 102.8, 66.3, 51.7, 50.6, 38.6, 34.1, 26.6, 24.3. HRMS (ES) *m/z* calcd for $C_{19}H_{29}NNaO_4^+$ $[M+Na]^+$ 358.1989, found 358.1989. IR (thin film, cm^{-1}) 3582, 2920, 1713, 1364, 1223.



1i

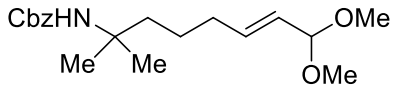
(*E*)-Benzyl((1-(5,5-dimethoxypent-3-en-1-yl)cyclopentyl)methyl)carbamate (1i).
Following the general procedure provided above, **1i** (0.60 mmol, 217 mg) was obtained in 60% (two steps). ^{1}H NMR (700 MHz, C_6D_6) δ 7.22-7.21 (m, 2H), 7.09-7.07 (m, 2H), 7.02-7.00 (m, 1H), 5.77-5.73 (m, 1H), 5.52 (dd, J =4.2, 16.1 Hz, 1H), 5.06 (s, 2H), 4.72 (d, J =4.2 Hz, 1H), 4.38 (br, 1H), 3.15 (s, 6H), 2.92 (d, J =6.3 Hz, 2H), 1.85-1.81 (m, 2H), 1.41-1.31 (m, 4H), 1.13-1.05 (m, 4H), 1.03-0.98 (m, 2H); ^{13}C NMR (175 MHz, C_6D_6) δ 156.4, 137.2, 135.1, 128.3, 128.2, 127.9, 1278, 127.7, 127.5, 126.9, 102.9, 66.3, 51.8, 47.2, 45.9, 36.8, 35.0, 27.3, 24.8. HRMS (ES) *m/z* calcd for $C_{21}H_{31}NNaO_4^+$ $[M+Na]^+$ 384.2145, found 384.2145. IR (thin film, cm^{-1}) 3348, 2949, 1710, 1452, 1241, 1131.



1j

(*E*)-Benzyl-2-(4,4-dimethoxybut-2-en-1-yl)benzylcarbamate (1j).

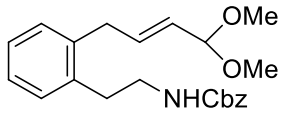
Following the general procedure provided above, **1j** (0.57 mmol, 202 mg) was obtained in 57% (two steps). ^{1}H NMR (500 MHz, C_6D_6) δ 7.21-6.93 (m, 9H), 5.88-5.83 (m, 1H), 5.44-5.41 (m, 1H), 5.05 (s, 2H), 4.81 (br, 1H), 4.64 (d, *J* =4.5 Hz, 1H), 4.19 (d, *J* =5.5 Hz, 2H), 3.13 (d, *J* =6.0 Hz, 2H), 3.10 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 155.9, 137.6, 137.2, 136.7, 133.2, 129.8, 128.9, 128.5, 128.3, 128.1,128.0, 127.8, 127.7, 127.6, 127.5, 126.6, 102.4, 66.4, 51.8, 42.4, 35.2. HRMS (ES) *m/z* calcd for $C_{21}H_{25}NNaO_4^+$ $[M+Na]^+$ 378.1676, found 378.1675. IR (thin film, cm^{-1}) 3582, 1711, 1640, 1364.



1k

(*E*)-Benzyl(8,8-dimethoxy-2-methyloct-6-en-2-yl)carbamate (1k).

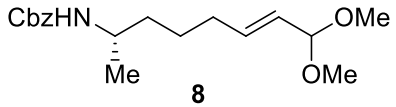
Following the general procedure provided above, **1k** (0.70 mmol, 235 mg) was obtained in 70% (two steps). ^{1}H NMR (700 MHz, C_6D_6) δ 7.20 (d, *J* =7.7 Hz, 2H), 7.08 (t, *J* =7.7 Hz, 2H), 7.01 (t, *J* =7.7 Hz, 1H), 5.76-5.72 (m, 1H), 5.50-5.47 (m, 1H), 5.01 (s, 2H), 4.72 (d, *J* =4.9 Hz, 1H), 4.29 (br, 1H), 3.15 (s, 6H), 1.80 (q, *J* =7.0 Hz, 2H), 1.47-1.44 (m, 2H), 1.12-1.08 (m, 2H), 1.03 (s, 6H); ^{13}C NMR (175 MHz, C_6D_6) δ 154.2, 137.4, 134.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 102.8, 65.7, 52.1, 51.7, 39.7, 32.2, 26.6, 23.4. HRMS (ES) *m/z* calcd for $C_{19}H_{29}NNaO_4^+$ $[M+Na]^+$ 358.1989, found 358.1986. IR (thin film, cm^{-1}) 3348, 2935, 1712, 1365, 1222.



1l

(E)-benzyl 2-(4,4-dimethoxybut-2-en-1-yl)phenethylcarbamate (1l).

Following the general procedure provided above, **1l** (188 mg, 0.51 mmol) was obtained in 51% (two steps). ^{1}H NMR (700 MHz, C_6D_6) δ 7.21-6.78 (m, 9H), 5.88-5.80 (m, 1H), 5.48-5.44 (m, 1H), 5.03 (s, 2H), 4.65 (d, *J* =4.9 Hz, 1H), 4.35 (br, 1H), 3.18 (d, *J* =6.3 Hz, 2H), 3.10-3.08 (m, 8H), 2.54 (t, *J* =7.0 Hz, 2H); ^{13}C NMR (125 MHz, C_6D_6) δ 155.9, 137.8, 137.2, 137.0, 133.5, 129.9, 129.8, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 126.6, 102.5, 66.1, 51.8, 41.8, 35.4, 32.9. HRMS (ES) *m/z* calcd for $C_{22}H_{27}NNaO_4^+$ $[M+Na]^+$ 392.1832, found 392.1830. IR (thin film, cm^{-1}) 3339, 2934, 1716, 1537, 1454, 1252.



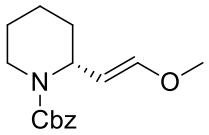
8

(*S*,*E*)-Benzyl(8,8-dimethoxyoct-6-en-2-yl)carbamate (6).

Following the general procedure provided above, **6** (0.68 mmol, 218 mg) was obtained in 68% (two steps). $[\alpha]^{24}_{D}$ = 10.2 (*c* 1.2, acetone). ^{1}H NMR (500 MHz, C_6D_6) δ 7.21 (d, *J* =7.5 Hz, 2H), 7.08 (t, *J* =7.5 Hz, 2H), 7.02 (t, *J* =7.5 Hz, 1H), 5.72-5.68 (m, 1H), 5.46 (dd, *J* =4.5, 15.5 Hz, 1H), 5.05 (s, 2H), 4.69 (d, *J* =4.5 Hz, 1H), 4.64 (d, *J* =8.0 Hz, 1H), 3.70-3.67 (m, 1H), 3.13 (s, 6H), 1.84-1.79 (m, 2H), 1.17-1.06 (m, 4H), 0.84 (d, *J* =6.5 Hz, 3H); ^{13}C NMR (175 MHz, C_6D_6) δ 155.6, 137.3, 134.4, 128.2, 128.0, 127.8, 127.7, 127.5, 127.4, 102.7, 66.0, 51.7, 46.6, 36.3, 31.8, 25.3, 20.8. HRMS (ES) *m/z* calcd for $C_{18}H_{27}NNaO_4^+$ $[M+Na]^+$ 344.1832, found 344.1833. IR (thin film, cm^{-1}) 3330, 2935, 1709, 1531, 1243, 1074.

V. Enantioselective Micheal-Aza Addition

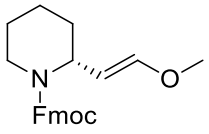
General procedure: The starting material (0.1 mmol) was added to a round bottom flask. Molecules sieves (100 mg) were added. The catalyst (0.015 mmol, 11.7 mg) was added. The mixture was protected under nitrogen and cooled to -78 °C. After 1 minute, CCl_4 (5 mL) was added. The mixture was then warmed up to -20 °C and stirred for a certain time. Triethylamine (0.2 mL) was added to quench the reaction. The mixture was loaded on the column directly and purified (10% EtOAc /hexanes) to give the desired product.



5a

(*E*)-Benzyl-2-(2-methoxyvinyl)piperidine-1-carboxylate (5a).

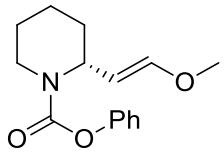
Following the general procedure provided above, after 24 hours, **5a** (0.074 mmol, 20.4 mg) was obtained in 74%, ee = 88%; after 30 hours, **5a** (0.071 mmol, 19.4 mg) was obtained 71% , ee = 90%. $[\alpha]^{24}_D$ = +55.1 (*c* 0.55, $CHCl_3$ for 91% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (m, 5H), 6.42 (d, *J* =12.8 Hz, 1H), 5.10 (dd, *J* =12.4, 20.8 Hz, 2H), 4.93 (dd, *J* =8.0, 12.8 Hz, 1H), 4.82-4.80 (m, 1H), 4.01-3.98 (m, 1H), 3.50 (s, 3H), 2.93-2.87 (m, 1H), 1.72-1.55 (m, 5H), 1.47-1.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 149.8, 136.9, 128.4, 127.9, 127.8, 100.2, 66.9, 56.1, 49.6, 39.7, 30.4, 25.5, 19.2; HRMS (ES) *m/z* calcd for $C_{16}H_{22}NO_3^+$ $[M+H]^+$ 276.1594, found 276.1594. HPLC DAICEL CHIRALPAK AD-H, hexane/2-proponal =98/2, flow rate: 1 mL/minute, t(major) = 15.0 minutes, t(minor) = 17.5 minutes. After 24 hours, ee = 88%. After 30 hours, ee = 91%. IR (thin film, cm^{-1}) 2935, 1695, 1419, 1260, 1179, 1090.



5b

(*E*)-(9H-Fluoren-9-yl)methyl-2-(2-methoxyvinyl)piperidine-1-carboxylate (5b).

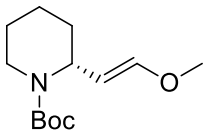
Following the general procedure provided above, after 24 hours, **5b** (0.076 mmol, 27.6 mg) was obtained in 76% , ee = 88%; after 30 hours, **5b** (0.070 mmol, 25.4 mg) was obtained 70% , ee = 90%. $[\alpha]^{24}_D$ = +35.2 (*c* 1.05, $CHCl_3$ for 90% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* =7.5 Hz, 2H), 7.58 (d, *J* =7.0 Hz, 2H), 7.40 (t, *J* =7.5 Hz, 2H), 7.31 (t, *J* =7.5 Hz, 2H), 6.32 (br, 1H), 4.92 (dd, *J* =7.5, 12.5 Hz, 1H), 4.74 (br, 1H), 4.46-4.40 (m, 2H), 4.25 (t, *J* =6.5 Hz, 1H), 3.98 (d, *J* =12.5 Hz, 1H), 3.52 (s, 3H), 2.92 (t, *J* =13.0 Hz, 1H), 1.72-1.55 (m, 4H), 1.49-1.40 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 149.8, 144.2, 144.1, 141.3, 127.6, 127.0, 125.0, 120.0, 119.9, 100.2, 67.0, 56.1, 49.6, 47.4, 39.7, 30.5, 25.5, 19.2. HRMS (ES) *m/z* calcd for $C_{23}H_{26}NO_3^+$ $[M+H]^+$ 364.1907, found 364.1908. HPLC DAICEL CHIRALPAK AD-H, hexane/2-proponal =90/10, flow rate: 1 mL/minute, t(major) = 10.1 minutes, t(minor) = 13.5 minutes. After 24 hours, ee = 88%. After 30 hours, ee = 90%. IR (thin film, cm^{-1}) 3434, 2927, 1713, 1642, 1449.



5c

(*E*)-Phenyl-2-(2-methoxyvinyl)piperidine-1-carboxylate (5c).

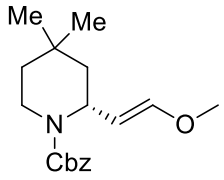
Following the general procedure provided above, after 24 hours, **5c** (0.079 mmol, 20.6 mg) was obtained in 79% , ee = 78%; after 48 hours, **5c** (0.064 mmol, 16.7 mg) was obtained 64%, ee = 89%. $[\alpha]^{24}_{D}$ = +66.0 (*c* 2.0, $CHCl_3$ for 89% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2H), 7.18-7.14 (m, 1H), 7.09-7.07 (m, 2H), 6.55 (d, *J* =12.8 Hz, 1H), 5.04 (dd, *J* =8.4, 12.8 Hz, 1H), 4.92-4.89 (m, 1H), 4.11-4.07 (m, 1H), 3.55 (s, 3H), 3.06-2.99 (m, 1H), 1.85-1.80 (m, 1H), 1.72-1.64 (m, 4H), 1.51-1.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 151.5, 150.1, 129.2, 125.1, 121.8, 100.1, 56.2, 50.2, 40.2, 30.5, 25.5, 19.2. HRMS (ES) *m/z* calcd for $C_{15}H_{20}NO_3^+$ $[M+H]^+$ 262.1438, found 262.1437. HPLC DAICEL CHIRALPAK AD-H, hexane/2-proponal =98/2, flow rate: 1 mL/minute, t(major) = 13.3 minutes, t(minor) = 16.7 minutes. After 24 hours, ee = 78%. After 48 hours, ee = 89%. IR (thin film, cm^{-1}) 3582, 2928, 1713, 1365, 1205.



5d

(*E*)-*tert*-Butyl-2-(2-methoxyvinyl)piperidine-1-carboxylate (5d).

Following the general procedure provided above, after 24 hours, **5d** (0.079 mmol, 19.0 mg) was obtained in 79% , ee = 79%; after 48 hours, **5d** (0.065 mmol, 15.7 mg) was obtained 65%, ee = 82%. $[\alpha]^{24}_{D}$ = +37.2 (*c* 0.43, $CHCl_3$, for 82% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.41 (d, *J* =12.8 Hz, 1H), 4.90 (dd, *J* =7.6, 12.4 Hz, 1H), 4.72-4.70 (m, 1H), 3.90-3.86 (m, 1H), 3.50 (s, 3H), 2.83-2.76 (m, 1H), 1.69-1.33 (m, 15H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.0, 149.4, 100.6, 79.2, 56.0, 49.3, 39.4, 30.5, 28.5, 25.5, 19.3. HRMS (ES) *m/z* calcd for $C_{13}H_{24}NO_3^+$ $[M+H]^+$ 242.1751, found 242.1753. HPLC DAICEL CHIRALPAK AD-H, hexane/2-proponal =99.5/0.5, flow rate: 1 mL/minute, t(major) = 10.0 minutes, t(minor) = 11.4 minutes. After 24 hours, ee = 79%. After 48 hours, ee = 82%. IR (thin film, cm^{-1}) 2933, 1684, 1419, 1158.

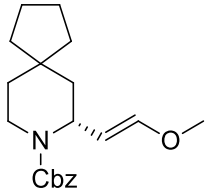


5e

(*E*)-Benzyl-2-(2-methoxyvinyl)-4,4-dimethylpiperidine-1-carboxylate (5e).

Following the general procedure provided above, after 14 hours, **5e** (0.073 mmol, 22.1 mg) was obtained in 73% , ee = 95%; after 24 hours, **5e** (0.066 mmol, 20.1 mg) was obtained 66%, ee = 99%. $[\alpha]^{24}_{D}$ = +20.2 (*c* 0.9, $CHCl_3$ for 99% ee). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.34-7.28 (m, 5H), 6.29 (d, *J* =12.6 Hz, 1H), 5.12 (dd, *J* =12.6, 27.3 Hz, 2H), 4.85 (dd, *J* =7.0, 12.6 Hz, 1H), 4.75-4.74 (m, 1H), 3.95-3.93 (m, 1H), 3.48 (s, 3H), 3.08-3.04 (m, 1H), 1.60-1.57 (m, 2H), 1.43-1.31 (m, 2H), 1.04 (s, 3H) , 0.90 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.5, 148.4, 137.0,

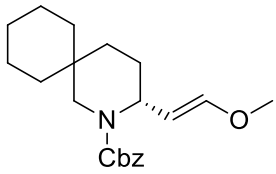
128.4, 127.8, 127.8, 103.2, 67.0, 56.2, 49.3, 43.0, 37.9, 36.7, 33.0, 28.9, 26.9. HRMS (ES) *m/z* calcd for $C_{18}H_{26}NO_3^+$ $[M+H]^+$ 304.1907, found 304.1907. HPLC DAICEL CHIRALPAK AD-H, hexane/2-proponal =97/3, flow rate: 1 mL/minute, t(major) = 12.5 minutes, t(minor) = 14.8 minutes. After 14 hours, ee = 95%. After 24 hours, ee = 99%. IR (thin film, cm^{-1}) 2927, 1692, 1423, 1220.



5f

(*E*)-Benzyl-7-(2-methoxyvinyl)-8-azaspiro[4.5]decane-8-carboxylate (5f).

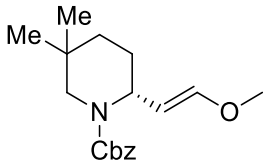
Following the general procedure provided above, after 8 hours, **5f** (0.077 mmol, 25.3 mg) was obtained in 77%, ee = 93%; after 12 hours, **5f** (0.071 mmol, 23.2 mg) was obtained 71%, ee = 95%. $[\alpha]^{24}_D$ = +19.4 (*c* 0.55, $CHCl_3$ for 95% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (m, 5H), 6.32 (d, *J* =12.0 Hz, 1H), 5.11 (dd, *J* =12.4, 20.0 Hz, 2H), 4.91 (dd, *J* =8.0, 12.4 Hz, 1H), 4.75-4.72 (m, 1H), 3.97-3.93 (m, 1H), 3.48 (s, 3H), 3.00 (dt, *J* =2.8, 13.2 Hz ,1H), 1.84-1.79 (m, 1H), 1.69-1.29 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 148.7, 137.0, 128.4, 127.8, 127.8, 102.6, 66.9, 56.1, 50.0, 42.6, 42.4, 40.5, 37.4, 35.9, 35.7, 24.9, 22.7. HRMS (ES) *m/z* calcd for $C_{20}H_{28}NO_3^+$ $[M+H]^+$ 330.2064, found 330.2066. HPLC DAICEL CHIRALPAK AD-H, hexane/2-proponal = 95/5, flow rate: 1 mL/minute, t(minor) = 13.3 minutes, t(major) = 15.6 minutes. After 8 hours, ee = 93%. After 12 hours, ee = 95%. IR (thin film, cm^{-1}) 3426, 2927, 1702, 1421, 1215.



5g

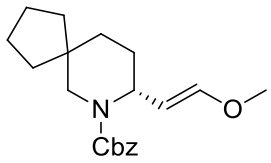
(*E*)-Benzyl-3-(2-methoxyvinyl)-2-azaspiro[5.5]undecane-2-carboxylate (5g).

Following the general procedure provided above, after 24 hours, **5g** (0.074 mmol, 25.3 mg) was obtained in 74%, ee = 95%; after 30 hours, **5g** (24.3 mg, 0.071 mmol) was obtained 71%, ee = 96%. $[\alpha]^{24}_D$ = +20.5 (*c* 0.72, $CHCl_3$ for 95% ee). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.30 (m, 5H), 6.45 (d, *J* =11.0 Hz, 1H), 5.19 (d, *J* =12.5Hz, 1H), 5.09 (d, *J* =12.5Hz, 1H), 4.93 (dd, *J* =7.5, 12.5 Hz, 1H), 4.84 (br, 1H), 3.96 (d, *J* =12.5 Hz, 1H), 3.52 (s, 3H), 2.60 (d, *J*=13.0 Hz ,1H), 1.97-1.91 (m, 1H), 1.46-1.36 (m, 10H), 1.28-1.22 (m, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.7, 149.8, 137.1, 128.4, 127.8, 127.8, 100.4, 66.9, 56.1, 49.5, 47.7, 38.0, 33.0, 31.0, 26.6, 25.5, 21.6, 21.5. HRMS (ES) *m/z* calcd for $C_{21}H_{30}NO_3^+$ $[M+H]^+$ 344.2220, found 344.2225. HPLC DAICEL CHIRALPAK OD-H, hexane/2-proponal =99/1, flow rate: 1 mL/minute, t(major) = 8.8 minutes, t(minor) = 10.7 minutes. After 24 hours, ee = 95%. After 30 hours, ee = 96%. IR (thin film, cm^{-1}) 3582, 2927, 1702, 1421, 1205, 1144.



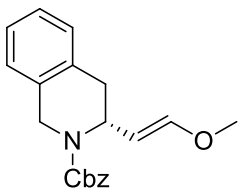
5h

(*E*)-Benzyl-2-(2-methoxyvinyl)-5,5-dimethylpiperidine-1-carboxylate (5h).
Following the general procedure provided above, after 24 hours, **5h** (0.076 mmol, 23.1 mg) was obtained in 76%, ee = 92%; after 30 hours, **5h** (22.4 mg, 0.074 mmol) was obtained 74%, ee = 93%. $[\alpha]^{24}_{D}$ = +26.5 (*c* 1.00, $CHCl_3$ for 93% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 5H), 6.42 (d, *J* =12.4 Hz, 1H), 5.11 (dd, *J* =12.4, 32 Hz, 2H), 4.91-4.82 (m, 2H), 3.58 (d, *J* =13.6 Hz, 1H), 3.50 (s, 3H), 2.68 (d, *J* =13.2 Hz, 1H), 1.93-1.91 (m, 1H), 1.49-1.42 (m, 2H), 1.28-1.24 (m, 1H), 0.90 (s, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.7, 149.9, 137.1, 128.4, 127.8, 127.7, 100.2, 66.9, 56.1, 50.3, 48.9, 32.9, 30.6, 28.9, 26.3, 23.0; HRMS (ES) *m/z* calcd for $C_{18}H_{26}NO_3^+$ $[M+H]^+$ 304.1907, found 304.1910. HPLC DAICEL CHIRALPAK AD-H and OD-H column connected together, hexane/2-proponal =99/1, flow rate: 1 mL/minute, t(major) = 29.0 minutes, t(minor) = 31.1 minutes. After 24 hours, ee = 92%. After 30 hours, ee = 93%. IR (thin film, cm^{-1}) 3582, 3004, 1712, 1364, 1222, 1092.



5i

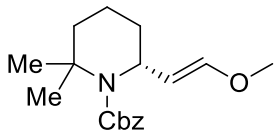
(*E*)-Benzyl-8-(2-methoxyvinyl)-7-azaspiro[4.5]decane-7-carboxylate (5i).
Following the general procedure provided above, after 24 hours, **5i** (0.078 mmol, 25.7 mg) was obtained in 78%, ee = 92%; after 30 hours, **5i** (0.073 mmol, 23.8 mg) was obtained 73%, ee = 93%. $[\alpha]^{24}_{D}$ = +20.4 (*c* 0.70, $CHCl_3$ for 93% ee). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.35-7.28 (m, 5H), 6.44 (br, 1H), 5.17 (d, *J* =12.6Hz, 1H), 5.07 (d, *J* =12.6Hz, 1H), 4.92 (dd, *J* =7.7, 12.6 Hz, 1H), 4.83 (br, 1H), 3.68 (d, *J* =12.6 Hz, 1H), 3.50 (s, 3H), 2.70 (d, *J*=13.3 Hz ,1H), 1.85-1.84 (m, 1H), 1.66-1.56 (m, 5H), 1.51-1.49 (m, 1H), 1.36-1.31 (m, 3H), 1.21-1.20 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.7, 149.8, 137.0, 128.4, 127.8, 127.7, 100.2, 66.9, 56.1, 49.0, 48.4, 42.7, 38.5, 33.7, 32.1, 27.7, 24.9, 24.2. HRMS (ES) *m/z* calcd for $C_{20}H_{28}NO_3^+$ $[M+H]^+$ 330.2064, found 330.2063. HPLC DAICEL CHIRALPAK OD-H, hexane/2-proponal =99/1, flow rate: 1 mL/minute, t(major) = 9.0 minutes, t(minor) = 10.2 minutes. After 24 hours, ee = 92%. After 30 hours, ee = 93%. IR (thin film, cm^{-1}) 2936, 1692, 1425, 1271, 1208.



5j

(*E*)-Benzyl-3-(2-methoxyvinyl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (5j).

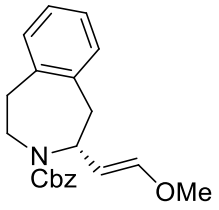
Following the general procedure provided above, after 6 hours, **5j** (0.088 mmol, 28.4 mg) was obtained in 88%, ee = 81%; after 24 hours, **5j** (0.073 mmol, 23.6 mg) was obtained 73%, ee = 93%. $[\alpha]^{24}_{D}$ = -21.4 (*c* 0.61, $CHCl_3$ for 93% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H), 7.18-7.16 (m, 2H), 7.12-7.10 (m, 2H), 6.50 (br, 1H), 5.17 (dd, *J* =12.8, 20.8 Hz, 2H), 5.04 (br, 1H), 4.82 (d, *J* =16.8 Hz, 1H), 4.60 (dd, *J* =8.4, 12.8 Hz, 1H), 4.36 (d, *J* =16.8 Hz, 1H), 3.37 (s, 3H), 3.17 (dd, *J* =5.2, 16.0 Hz, 1H), 2.69 (d, *J* =15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 150.3, 136.7, 132.7, 129.1, 128.5, 128.0, 127.9, 126.7, 126.3, 126.1, 100.9, 67.2, 56.0, 48.8, 43.0, 34.7. HRMS (ES) *m/z* calcd for $C_{20}H_{22}NO_3^+$ $[M+H]^+$ 324.1594, found 324.1591. HPLC DAICEL CHIRALPAK OD-H, hexane/2-proponal =97/3, flow rate: 1 mL/minute, t(major) = 11.3 minutes, t(minor) = 17.6 minutes. After 6 hours, ee = 81%. After 24 hours, ee = 93%. IR (thin film, cm^{-1}) 3411, 1712, 1414, 1364, 1221, 1121.



5k

(*E*)-Benzyl-6-(2-methoxyvinyl)-2,2-dimethylpiperidine-1-carboxylate (5k).

Following the general procedure provided above, after 18 hours, **5k** (0.022 mmol, 6.7 mg) was obtained in 22%, ee = 83%; after 72 hours, **5k** (0.054 mmol, 16.4 mg) was obtained 54%, ee = 56%. $[\alpha]^{24}_{D}$ = -28.2 (*c* 0.42, acetone for 82% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 5H), 6.34 (d, *J* =12.8 Hz, 1H), 5.09 (dd, *J* =12.4, 18.4 Hz, 2H), 4.92 (dd, *J* =7.6, 12.4 Hz, 1H), 4.74-4.70 (m, 1H), 3.45 (s, 3H), 1.86-1.57 (m, 6H), 1.45 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 156.0, 149.0, 137.0, 128.4, 128.1, 127.8, 105.5, 66.6, 56.1, 54.6, 50.8, 38.1, 28.6, 28.3, 27.8, 14.8. HRMS (ES) *m/z* calcd for $C_{18}H_{26}NO_3^+$ $[M+H]^+$ 304.1907, found 304.1909. HPLC DAICEL CHIRALPAK AD-H, hexane/2-proponal =99/1, flow rate: 1 mL/minute, t(minor) = 10.1 minutes, t(major) = 11.1 minutes. After 18 hours, ee = 83%. After 72 hours, ee = 56%. IR (thin film, cm^{-1}) 2934, 1698, 1384, 1280, 1207.



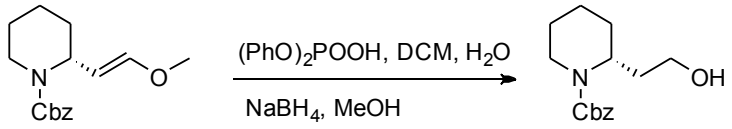
5l

(R,E)-benzyl 2-(2-methoxyvinyl)-4,5-dihydro-1H-benzo[d]azepine-3(2H)-carboxylate.

Following the general procedure provided above, the reaction was done in 0 °C and with *R*-CF_3-CPA. After 24 hs, **5l** (24.0 mg, 0.072 mmol) was obtained in 72% , ee = 73%; after 48 hs, (21.1 mg, 0.062 mmol) was obtained 73% , ee = 80%. $[\alpha]^{24}_{D}$ = -46.6 (*c* 0.81, $CHCl_3$ for 80% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.09(m, 9H), 6.50 (br, 1H), 5.17 (dd, *J* =12.8, 20.8 Hz, 2H), 5.04 (br, 1H), 4.62 (m, 1H), 4.19 (br, 1H), 3.50 (m, 1H), 3.42 (s, 3H), 3.18-3.02 (m, 2H), 2.94-2.82 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 150.3, 136.9, 130.7, 129.5, 128.5, 128.0, 127.9, 127.7, 126.8, 126.5, 100.1, 67.0, 56.1, 52.5, 41.7, 41.0, 36.1. HRMS (ES) *m/z* calcd for $C_{21}H_{24}NO_3^+$ $[M+H]^+$ 338.1751, found 338.1755. HPLC DAICEL CHIRALPAK OD-H,

hexane/2-proponal =97/3, flow rate: 1mL/min, t(minor) = 15.2 min, t(major) = 17.0 min. After 24 hs, ee = 73%. After 48 hs, ee = 80%. IR (thin film, cm^{-1}) 2931, 1692, 1549, 1421, 1208.

VI. Determination of Absolute Stereochemistry

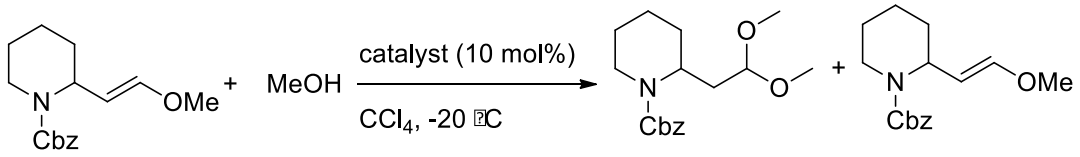


5a

The starting material (0.1 mmol, 27.5 mg,) was dissolved in DCM (5 mL). $(PhO)_2POOH$ (0.04 mmol, 10 mg) and H_2O (1 mmol, 18 mg) were added. The mixture was stirred overnight. DCM (20 mL) was added. The mixture was dried over $MgSO_4$ and concentrated *in vacuo*.

The crude product was dissolved in MeOH (5 mL). $NaBH_4$ (0.5 mmol, 20 mg) was added. The mixture was stirred at room temperature for 30 minutes. H_2O (5 mL) was added. The resultant mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The obtained residue was purified by column chromatography (20% EtOAc/hexanes) to provide the product (0.068 mmol, 18 mg). The optical rotation $[\alpha]^{24}_D = 15.0$ (*c* 0.9, $CHCl_3$) matches the literature[1,2] and also confirms that the absolute configuration is *R*.

VII. Chiral Resolution Study

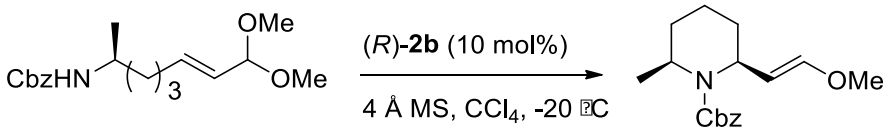


7 50%, 41% ee

5a 41%, 53% ee

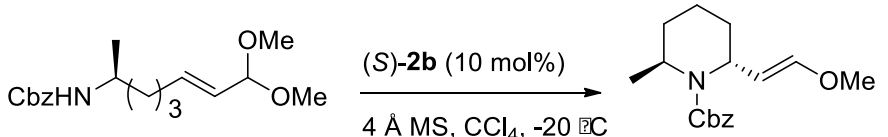
Benzyl-2-(2,2-dimethoxyethyl)piperidine-1-carboxylate (7).
The starting material (0.1 mmol, 27.5 mg) was added to a round bottom flask. The catalyst (0.01 mmol, 7.8 mg) was added. The mixture was protected under nitrogen and cooled to -78 °C. After 1 minute, MeOH (0.05 mmol, 1.6 mg) in CCl_4 (5 mL) was added. The mixture was then warmed up to -20 °C and stirred for 24 hours. Triethylamine (0.2 mL) was added to quench the reaction. The mixture was loaded on the column directly and purified (10% EtOAc/hexanes) to give the acetal product (0.05 mmol, 15.1 mg), 50% yield. $[\alpha]^{24}_D$ = 9.2 (*c* 1.2, acetone for 41% ee). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5H), 5.14-5.10 (m, 2H), 4.47 (br, 1H), 4.43 (br, 1H), 4.07 (br, 1H), 3.23 (br, 6H), 2.86 (br, 1H), 2.02-1.98 (m, 1H), 1.72-1.68 (m, 1H), 1.66-1.50 (m, 5H), 1.44-1.34 (m, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.4, 136.9, 128.4, 127.9, 127.8, 102.7, 67.0, 53.6, 52.2, 47.7, 44.5, 39.3, 33.1, 29.0, 25.5, 19.0. HRMS (ES) *m/z* calcd for $C_{17}H_{26}NO_4^+$ $[M+H]^+$ 308.1856, found 308.1859. HPLC DAICEL CHIRALPAK AD-H, hexane/2-proponal =95/5, flow rate: 1 mL/minute, t(major) = 10.0 minutes, t(minor) = 16.8 minutes. ee = 41%. IR (thin film, cm^{-1}) 3412, 3003, 2927, 1712, 1361, 1222.

VIII. Diastereoselective Cyclization Studies.



8 **8a**

(*2S,6S*)-Benzyl-2-((*E*)-2-methoxyvinyl)-6-methylpiperidine-1-carboxylate (7a).
The starting material (0.1 mmol, 32.1 mg) was added to a round bottom flask. Molecules sieves (200 mg) were added. The catalyst (0.01 mmol, 7.8 mg) was added. The mixture was protected under nitrogen and cooled to -78 °C. After 1 minute, CCl_4 (5 mL) was added. The mixture was then warmed up to -20 °C and stirred for 4 hours. Triethylamine (0.2 mL) was added to quench the reaction. The mixture was loaded on the column directly and purified (10% EtOAc/hexanes) to give the desired product. 26.0 mg product isolated, 90% yield, syn:trans=4.5:1. $[\alpha]^{24}_D$ = -40.0 (*c* 0.46, acetone). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.28 (m, 5H), 6.48 (d, *J* =12.5 Hz, 1H), 5.14 (dd, *J* =12.0, 22.0 Hz, 2H), 5.00 (dd, *J* =8.5, 12.5 Hz, 1H), 4.73-4.71 (m, 1H), 4.42-4.40 (m, 1H), 3.50 (s, 3H), 1.80-1.45 (m, 6H), 1.23 (d, *J* =7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.6, 149.4, 137.1, 128.4, 127.8, 127.8, 104.5, 66.9, 56.1, 48.7, 46.3, 30.2, 30.0, 20.8, 14.2. HRMS (ES) *m/z* calcd for $C_{17}H_{24}NO_3^+$ $[M+H]^+$ 290.1751, found 290.1749. IR (thin film, cm^{-1}) 2933, 1690, 1406, 1303, 1208.



8 **8b**

(*2R,6S*)-Benzyl-2-((*E*)-2-methoxyvinyl)-6-methylpiperidine-1-carboxylate (7b).
The starting material (0.1 mmol, 32.1 mg) was added to a round bottom flask. Molecules sieves (200 mg) were added. The catalyst (0.01 mmol, 7.8 mg) was added. The mixture was protected under nitrogen and cooled to -78 °C. After 1 minute, CCl_4 (5 mL) was added. The mixture was then warmed up to -20 °C and stirred for 4 hours. Triethylamine (0.2 mL) was added to quench the reaction. The mixture was loaded on the column directly and purified (10% EtOAc/hexanes) to give the desired product. 25.4 mg product isolated, 88% yield, syn:trans=1:4.2. $[\alpha]^{24}_D$ = 49.4 (*c* 3.8, acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 5H), 6.41 (d, *J* =12.8 Hz, 1H), 5.14 (d, *J* =12.4 Hz, 1H), 5.07 (dd, *J* =12.4, 31.2 Hz, 1H), 4.86 (dd, *J* =8.0, 12.8 Hz, 1H), 4.46-4.43 (m, 1H), 4.06-4.04 (m, 1H), 3.46 (s, 3H), 1.98-1.92 (m, 2H), 1.71-0.85 (m, 7H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.6, 149.1, 137.1, 128.4, 127.9, 127.8, 104.3, 66.6, 56.1, 50.0, 47.4, 26.5, 26.5, 20.7, 13.6. HRMS (ES) *m/z* calcd for $C_{17}H_{24}NO_3^+$ $[M+H]^+$ 290.1751, found 290.1752. IR (thin film, cm^{-1}) 2932, 1695, 1652, 1404, 1208.

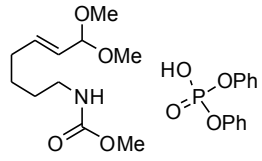
IX. Computational Studies.

With the exception of solvent computations, all density functional calculations were performed using Q-Chem 4.0.[3] Optimized geometries were evaluated using the B3LYP density functional using double-ζ-quality basis sets with polarization functions, designated 6-31G**[4-7]. Images of intermediates were generated in VMD.[8] A double-ended growing string method was used to probe the potential energy profile of the reactions.[9]

To create the reaction profiles and locate the transition states, 11-15 nodes, including the two fixed end points, were used in the growing string method. The growing string computations proceeded through the addition of new nodes after the perpendicular gradient magnitude on the most recent, frontier node was computed to be less than the 0.15 hartree/Å threshold. An initial maximum optimization step size of 0.1 was used. Following the convergence of the additive sum of the perpendicular gradient magnitudes over all nodes, F, to $F < 0.3$, the climbing image search was initiated. When $F < 0.1$, or when highest energy node had a RMS gradient below double the nodal convergence criteria and $F < 0.2$, the exact transition state search was initiated. A root mean squared (RMS) gradient criterion of <0.0005 hartree/Å was applied to the transition state node to identify complete convergence of a reaction path.

In all cases, the Gibbs free energies were first computed through single point energies obtained using a ωB97X-D exchange functional with a 6-311+G** basis set for all reported starting geometries, intermediates, transition states and final geometries.[10,11] Frequency computations were performed using the B3LYP density exchange functional with a 6-31G** basis set to account for enthalpic contributions from rotational, translational and vibrational energies as well as entropic energies at 298 K. Solvent corrections for carbon tetrachloride were performed using the SMD solvent model in GAMESS using a ωB97X-D exchange functional with a 6-311+G** basis set.[12,13] The corresponding results are collected in Table S – II.

Preliminary Computational Studies with a Model System:



Scheme SI – I. Model system for preliminary investigation.

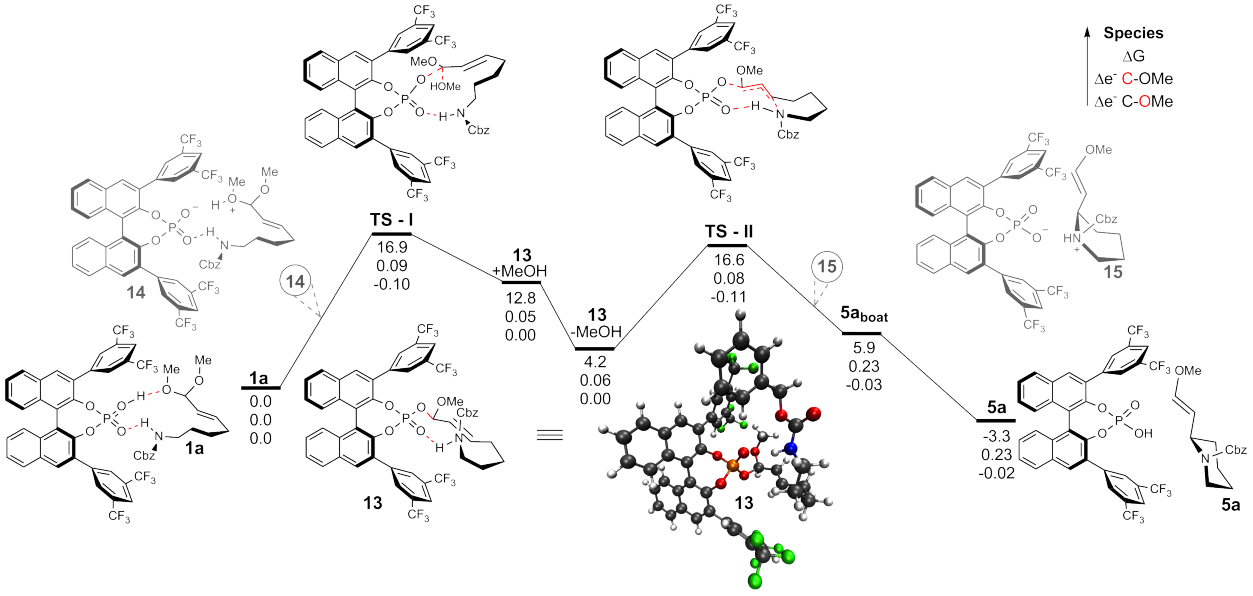
A model system of diphenylphosphoric acid and a truncated variation of the **1a** substrate were used to search for plausible reaction paths. This model substrate consisted of **1a** without the Cbz protecting group as shown in Scheme SI - I. The Zimmerman[14] methodology was used to identify potential low energy pathways through which the aza-Michael reaction could be operating. A concerted, ionic mechanism proceeding asynchronously from the starting geometry through an oxocarbenium-like transition state to the cyclized product, as well as a mechanism invoking the intermediacy of a covalently bound chiral phosphate acetal were deemed to have reasonable barriers and these pathways were to be investigated further. Details on the full system investigation are given below.

Computational Studies on the Full Reactive System:

The (*S*)-enantiomer of the 3,5-$(CH_3)_2C_6H_3$ BINOL-based phosphoric acid with full substrate **1a** was used to probe the reaction path in quantitative detail. After identification of the S_N2'-like pathway using the model studies, computations involving the full system proceeding through phosphate intermediate **13** were performed, Scheme SI - II. An investigation of the reaction pathway depicted in Scheme SI – II below revealed the mechanism to proceed via protonation of the methoxy group closest to the acidic phosphate proton to yield **14** as a transient

species. Following protonation, methanol departs from the substrate as the phosphate binds in **TS - I**. Following formation of phosphate intermediate **13**, with a PO-C bond distance of 1.50 Å methanol diffuses away from the catalyst/substrate complex in a free-energy favorable step. The second elementary step begins first with the departure of the phosphate to form species **TS - II** which undergoes a nitrogen-carbon bond forming event before immediate deprotonation of **15** to reform the chiral phosphoric acid. As the substrate becomes disengaged from the catalytic pocket, it relaxes without significant barrier from **5a$_{boat}$** into the lower-energy chair conformation **5a**. It is worth noting that the full systems are rather flexible. Four different conformations of the catalyst/substrate complex were investigated (e.g. directionality of the CBz group, orientation of the fluorinated phenyl rings of the catalyst, orientation and placement of the substrate in the catalytic pocket, cyclization directly through the chair conformation). In addition to conformational changes, the regiochemistry of protonation and departure of either methanol group and addition of either phosphate oxygen into the substrate were investigated. The data presented is for the lowest energy pathway located, as all other geometries and atom combinations gave higher barriers.

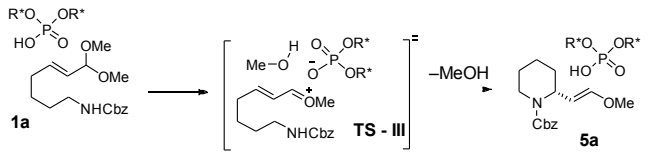
While endothermic, the reaction is overall free energy spontaneous. The slight-downhill nature of the reaction is consistant with the observation of chiral resolution. Also of note is the change in electron density of the oxygen in the methoxy group of the substrate. Over the course of the reaction, there is no significant positive charge buildup, with the largest Δe^- observed in **TS – II** at -0.11 e^-. The carbon to which the methoxy group is attached also does not display significant electron donation from the methoxy oxygen; the largest increase in electron density in a transition state is observed in **TS – I**, with an increase of 0.09 e^-. These numbers are consistent with non-ionic transition states.



Scheme SI – II. Reaction energy diagram for SN2'-like pathway to form the major piperidine stereoisomer.

Note, PO-C bond distances for the mechanisms proceeding through an **11**-like species and a **12**-like species are different. The oxocarbenium pathway through **11** should show no bond formation between the phosphate oxygen and the oxocarbenium carbon. In addition to the SN2'-like pathway, growing string was run for the pathway proceeding directly through an **11**-like ionic transition state **TS - III**, Scheme SI - III. Indeed, the PO-C distance in the transition state remains quite far at 4.29 Å. The barrier for this mechanism was computed to be too high to be a

reasonable pathway, at 31.5 kcals/mol. An investigation of the nodes along the string showed the reaction to be concerted, yet asynchronous, proceeding through three chemical changes in one



elementary step. First, protonation of the methoxy leaving group occurs, which prompts the departure of a unit of methanol, leading to transition state **TS - III**, which consists of an oxocarbenium ion pair with the chiral phosphate. In this transition state, the nitrogen is poised for cyclization, and following ring closure, the chiral phosphate deprotonates the nitrogen, yielding the pipiridene product and regenerating the catalyst.

Scheme SI – III. Depiction of alternative, concerted, ionic pathway.

A summary of calculated values including solvent and free-energy corrections is provided in Table SI - II.

Table SI - II. Calculated values for geometries of starting materials, transition states, intermediates and products for the pathways investigated at the GAMESS(SMD solvent = carbontetrachloride)/ωB97X-D/6-311+G**//B3LYP/6-31G** level.

	E(hartrees)	H (kcal/mol)	S (kcal/mol at 298 K)	ΔG
1a	-4241.100054	587.0	109.6	-
TS - I	-4241.072205	586.1	109.3	16.9
13 + MeOH	-4241.081148	587.0	108.7	11.9
13 - MeOH	-4241.071593	586.2	122.5	4.2
TS - II	-4241.052486	584.5	120.4	16.6
TS - III	-4241.054968	582.7	102.2	31.5
$5a_{boat}$	-4241.077123	584.8	115.9	5.9
5a	-4241.052750	582.9	131.8	-3.3

Cartesian coordinates for the starting geometry, transition states, intermediate and cyclized product are provided below.

1a
117

C 2.276631 -5.348571 -0.398886
C 1.376932 -6.357220 -0.651562
C 1.851870 -4.119916 0.175330
C 0.475585 -3.945476 0.531523
C -0.429706 -5.000036 0.232362
C 0.008797 -6.169842 -0.346808
H -0.705430 -6.954507 -0.577027

H 1.709947 -7.289576 -1.096959
H 3.327603 -5.469113 -0.647568
H -1.483180 -4.870737 0.447741
C 2.762647 -3.051758 0.370026
C 2.350192 -1.818848 0.829430
C 0.983246 -1.671919 1.193027
C 0.064350 -2.706387 1.139788
H 3.806134 -3.197820 0.104975
C -1.312006 -2.533604 1.691301
C -1.842095 -3.447930 2.670001
C -2.120360 -1.491045 1.266536
C -3.508962 -1.403042 1.581209
C -4.030214 -2.351781 2.437839
C -3.224162 -3.352550 3.032012
C -4.406738 -0.386118 0.966737
H -5.083823 -2.308206 2.698501
C -1.045556 -4.423570 3.328947
C -1.592404 -5.272291 4.265674
C -2.966179 -5.199154 4.593156
C -3.761771 -4.254394 3.989397
H -3.384843 -5.878999 5.328694
H -4.815016 -4.173194 4.243871
H 0.010586 -4.486907 3.098103
H -0.959457 -6.001559 4.762116
C 3.327764 -0.699209 0.958314
O 0.584295 -0.443134 1.720847
O -1.600051 -0.532364 0.398638
P -0.433047 0.494927 0.868311
O -1.045374 1.362478 2.035379
O 0.127945 1.204468 -0.301782
C -5.599276 -0.801019 0.355106
C -4.119025 0.982509 1.000054
C -6.473401 0.128840 -0.206973
C -6.173881 1.491489 -0.182529
C -4.992522 1.906900 0.426378
C 3.251860 0.425651 0.127034
C 4.210059 1.437009 0.233015
C 5.248771 1.343831 1.158467
C 5.326966 0.220809 1.981299
C 4.375501 -0.794888 1.882291
H 2.461356 0.505328 -0.611128
C 4.096535 2.654309 -0.647655
H 5.989235 2.130803 1.234229
H 4.440843 -1.659587 2.533471
C 6.484162 0.075120 2.933583
H -5.834091 -1.857841 0.297458
H -3.216262 1.328821 1.484737
C -4.607029 3.361357 0.456565
C -7.781301 -0.334824 -0.793551
H -6.845973 2.211987 -0.631496
F -7.693851 -1.584564 -1.296949
F -8.202092 0.479387 -1.784213
F -8.757320 -0.354820 0.143762
F -5.601208 4.168827 0.041937
F -3.533714 3.604606 -0.337521
F -4.256283 3.754097 1.705182
F 3.699741 2.334984 -1.895611
F 5.269121 3.316385 -0.746346
F 3.186307 3.539319 -0.162683
F 6.906659 1.272852 3.392840
F 7.544589 -0.515500 2.336247
F 6.162956 -0.683486 4.004205
H -0.902183 2.360816 2.041852
O -1.048789 3.890686 2.547824
C -1.826402 3.855249 3.754816
C 0.003218 4.871976 2.588368
O 1.015836 4.520022 3.492253
C 1.804511 3.380186 3.142133
C 0.487052 5.153426 1.191265
C -0.225225 4.997906 0.072532
C 0.255626 5.418198 -1.290767
C -0.907739 3.583066 -2.698839
C -0.720224 2.465111 -3.735051
N 0.161509 1.412186 -3.255056
C 1.268272 1.036113 -3.937377
O 1.999382 0.152069 -3.183684
O 1.591980 1.404770 -5.057281
H 1.221292 5.926801 -1.188252
H -0.449486 6.161095 -1.694105
H -1.609211 4.318061 -3.117318
H -1.393212 3.165501 -1.809503
H -1.700247 2.043071 -3.997111
H -0.276766 2.854259 -4.655376
H 0.087584 1.122062 -2.284593
C 3.183733 -0.376843 -3.820462
H -1.220265 4.564203 0.140122
H 1.474868 5.609396 1.153670
H -2.515883 3.016551 3.665234
H -1.180129 3.719017 4.626239
H -2.398713 4.783620 3.856945
H 2.598537 3.322828 3.888722
H 1.217219 2.455734 3.180246

H 2.248666 3.480943 2.146964
H -0.426504 5.782046 3.030596
C 0.404532 4.271096 -2.311164
H 0.872788 4.677662 -3.217391
H 1.100455 3.530570 -1.907396
C 2.892729 -1.649455 -4.579643
C 2.547623 -1.609774 -5.937023
C 2.263193 -2.787768 -6.628018
C 2.314474 -4.018503 -5.970606
C 2.650047 -4.066629 -4.616451
C 2.938727 -2.888090 -3.928965
H 3.876159 -0.564612 -2.996564
H 3.600242 0.388695 -4.477159
H 3.195849 -2.927076 -2.873261
H 2.093167 -4.935073 -6.510304
H 2.685268 -5.018973 -4.094763
H 2.485546 -0.647770 -6.435719
H 1.999325 -2.744209 -7.680977

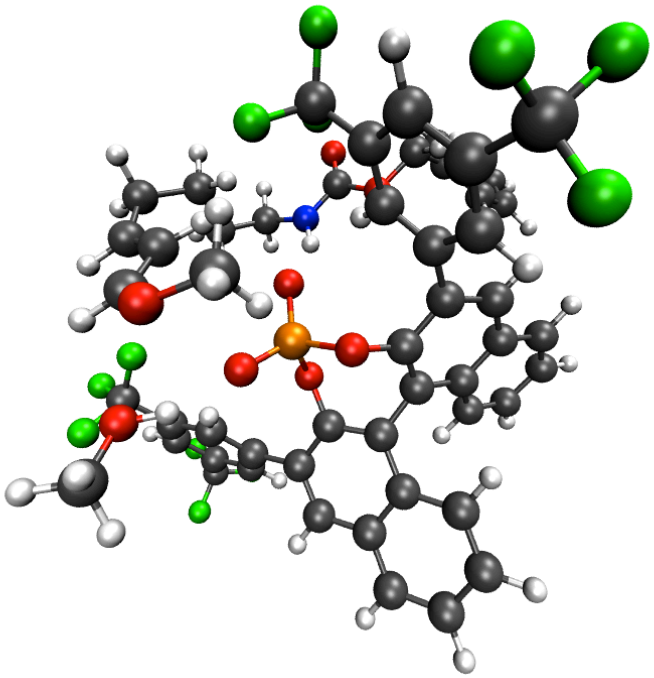


Figure SI - I: Transition state geometry for full system prior to chiral phosphate formation, **TS - I**.

TS - I
117

C 1.987502 -5.332580 -0.575068
C 1.034178 -6.303077 -0.774836
C 1.646019 -4.082686 0.009273
C 0.296850 -3.846979 0.428964
C -0.666685 -4.862465 0.181935
C -0.308723 -6.054782 -0.406492
H -1.066743 -6.809796 -0.592533
H 1.304743 -7.252737 -1.226090
H 3.019429 -5.502614 -0.871164
H -1.700196 -4.683099 0.451735
C 2.610828 -3.055649 0.170257
C 2.265411 -1.811669 0.651794
C 0.922744 -1.592796 1.073513
C -0.033328 -2.596533 1.058086
H 3.637337 -3.247244 -0.131056
C -1.361065 -2.379659 1.699446
C -1.842222 -3.278877 2.713924
C -2.155783 -1.304415 1.328520
C -3.509659 -1.171128 1.763086

C -3.997495 -2.106226 2.656010
C -3.189073 -3.144749 3.178598
C -4.427122 -0.124288 1.230275
H -5.024326 -2.023736 3.001069
C -1.027365 -4.281562 3.308069
C -1.529246 -5.128085 4.271101
C -2.876335 -5.025148 4.691213
C -3.684291 -4.048600 4.157776
H -3.262920 -5.706939 5.442604
H -4.714563 -3.943077 4.487108
H 0.008571 -4.367307 3.004169
H -0.881978 -5.878848 4.714764
C 3.285011 -0.730445 0.771331
O 0.613094 -0.368027 1.621589
O -1.668038 -0.386421 0.421072
P -0.459102 0.657207 0.860956
O -0.898156 1.576624 1.971694
O 0.117545 1.201032 -0.412687
C -5.673163 -0.520946 0.723180
C -4.113819 1.242327 1.248030
C -6.587278 0.421723 0.254544
C -6.275779 1.780222 0.281434
C -5.036857 2.180867 0.778601
C 3.228804 0.402506 -0.050407
C 4.209976 1.391262 0.056732
C 5.244727 1.278085 0.986126
C 5.296417 0.152332 1.806947
C 4.329159 -0.848076 1.696343
H 2.424347 0.504036 -0.767964
C 4.121598 2.621893 -0.800883
H 5.999821 2.051076 1.066966
H 4.373175 -1.714733 2.346233
C 6.433050 0.003276 2.782562
H -5.917502 -1.575814 0.670165
H -3.156069 1.572360 1.629832
C -4.710741 3.651086 0.850770
C -7.936201 -0.020670 -0.245091
H -6.978953 2.512104 -0.095629
F -7.900732 -1.268693 -0.760972
F -8.410987 0.804702 -1.203773
F -8.854870 -0.033964 0.750246
F -5.503473 4.383471 0.031791
F -3.429364 3.903834 0.477909
F -4.869920 4.148901 2.092002
F 3.587427 2.378058 -2.010623
F 5.321220 3.205776 -0.987135
F 3.323150 3.578458 -0.217981
F 6.778349 1.193949 3.324955
F 7.540873 -0.492043 2.187104
F 6.121107 -0.830494 3.797382
H -1.798977 2.647876 3.067300
O -2.320260 3.436019 3.321960
C -2.402728 3.545774 4.731009
C -0.045245 4.362254 2.056046
O 0.670113 3.937659 3.036717
C 1.795658 3.031432 2.844990
C 0.236042 4.261273 0.676790
C -0.511154 5.046596 -0.149272
C -0.229016 5.332069 -1.587695
C -0.867910 3.237961 -2.914643
C -0.433358 2.142235 -3.895792
N 0.514254 1.206930 -3.316369
C 1.630653 0.816272 -3.977121
O 2.317659 -0.102745 -3.227182
O 2.000039 1.211390 -5.073697
H 0.547248 6.116697 -1.563427
H -1.106543 5.811229 -2.035363
H -1.651074 3.827871 -3.409463
H -1.318807 2.776387 -2.028762
H -1.330614 1.607874 -4.239071
H 0.042895 2.575447 -4.779991
H 0.358630 0.885373 -2.362951
C 3.594609 -0.521972 -3.757783
H -1.350536 5.581199 0.295585
H 1.046137 3.648470 0.305951
H -2.937886 2.704608 5.192923
H -1.413953 3.623569 5.208224
H -2.963295 4.458702 4.954060
H 2.297635 3.010462 3.809898
H 1.381966 2.055242 2.593565
H 2.462292 3.405023 2.068060
H -0.918597 4.908424 2.400244
C 0.265653 4.178080 -2.485169
H 0.719147 4.629508 -3.375818
H 1.061490 3.614438 -1.991285
C 3.501515 -1.734651 -4.655604
C 3.577779 -1.600183 -6.047041
C 3.542096 -2.726480 -6.870619
C 3.413142 -3.999273 -6.312150
C 3.314607 -4.141573 -4.926647
C 3.363612 -3.015701 -4.105476
H 4.186540 -0.753018 -2.867922

H 4.050862 0.315150 -4.289126
H 3.287568 -3.128048 -3.026780
H 3.388580 -4.876370 -6.953064
H 3.205845 -5.129073 -4.486832
H 3.654214 -0.605937 -6.475872
H 3.614893 -2.610835 -7.948456

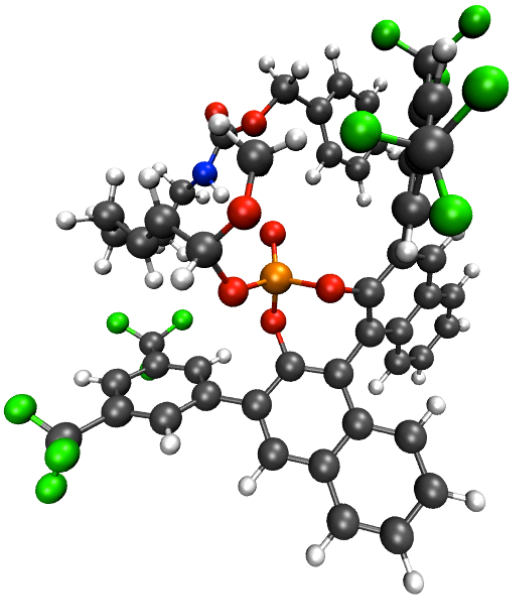


Figure SI - II: Geometry of chiral phosphate acetal intermediate **13**.

13
111

C 2.042857 -5.203119 -1.954301
C 1.134053 -6.031143 -2.570351
C 1.615011 -4.207315 -1.035370
C 0.220638 -4.087057 -0.728977
C -0.692122 -4.949299 -1.394525
C -0.246007 -5.893319 -2.292762
H -0.961761 -6.535194 -2.797451
H 1.470552 -6.783755 -3.276681
H 3.104464 -5.289481 -2.168827
H -1.753367 -4.847659 -1.200490
C 2.545216 -3.341657 -0.408345
C 2.147935 -2.324700 0.437862
C 0.750042 -2.181016 0.668320
C -0.198125 -3.072104 0.197075
H 3.604343 -3.496580 -0.591393
C -1.612669 -2.946462 0.658384
C -2.264865 -4.015238 1.367721
C -2.304883 -1.762522 0.474789
C -3.669393 -1.590238 0.839212
C -4.304876 -2.643020 1.464471
C -3.632765 -3.853323 1.762143
C -4.413228 -0.337246 0.543211
H -5.352345 -2.546228 1.734973
C -1.600045 -5.215341 1.740773
C -2.260589 -6.206788 2.431859
C -3.621865 -6.058815 2.785861
C -4.290189 -4.902944 2.458452
H -4.130373 -6.852271 3.324640
H -5.331023 -4.766661 2.738744
H -0.555129 -5.342550 1.486440
H -1.727962 -7.110437 2.712525
C 3.156752 -1.485739 1.135726
O 0.312411 -1.093411 1.430414

O -1.664905 -0.682289 -0.130039
P -0.444905 0.098393 0.608570
O -1.160350 0.898469 1.773575
O 0.373539 0.837510 -0.377123
C -4.477473 0.175787 -0.760398
C -5.111796 0.321611 1.562375
C -5.238741 1.310960 -1.033040
C -5.933786 1.964804 -0.014328
C -5.862789 1.464811 1.284252
C 4.283761 -1.005837 0.452152
C 5.284943 -0.317555 1.137410
C 5.184028 -0.095198 2.510768
C 4.057935 -0.557608 3.190237
C 3.050134 -1.242030 2.512463
H 4.371231 -1.153151 -0.617801
C 6.477215 0.234416 0.400424
H 5.973849 0.422175 3.043098
H 2.189502 -1.600473 3.062730
C 3.904619 -0.262988 4.659197
H -3.934025 -0.312546 -1.560373
H -5.048959 -0.045793 2.580359
C -6.639823 2.143402 2.382322
C -5.369343 1.809745 -2.448179
H -6.504964 2.860359 -0.229083
F -4.322237 1.441753 -3.216004
F -5.452411 3.161243 -2.493236
F -6.486139 1.331775 -3.039883
F -7.913786 1.692493 2.437495
F -6.702264 3.478824 2.193662
F -6.089367 1.924982 3.595441
F 6.368585 1.575226 0.216170
F 6.634217 -0.324790 -0.812279
F 7.619446 0.037571 1.097248
F 5.097318 -0.264037 5.294257
F 3.112300 -1.166235 5.273259
F 3.353387 0.956062 4.864926
C -0.562443 2.070092 2.496205
O 0.732460 1.813883 2.894446
C 1.835192 2.362275 2.143021
C -0.762486 3.327356 1.696674
C -1.735014 3.546520 0.810532
C -1.889467 4.832552 0.040088
C -1.973233 3.652467 -2.310620
C -0.558899 3.936025 -2.826975
N 0.468806 3.560858 -1.857370
C 1.772416 3.805748 -2.160152
O 2.590449 3.165801 -1.257820
O 2.177255 4.504082 -3.071734
H -0.905525 5.297929 -0.077609
H -2.495835 5.533134 0.633343
H -2.635753 3.609391 -3.181784
H -1.998408 2.641643 -1.881393
H -0.402805 3.388932 -3.767669
H -0.435329 4.997459 -3.066229
H 0.301611 2.739485 -1.281710
C 3.961497 3.045316 -1.655035
H -2.460590 2.757476 0.616679
H -0.052740 4.120992 1.917415
H 2.713029 1.841705 2.520317
H 1.730024 2.197057 1.070184
H 1.951262 3.431647 2.347159
H -1.171246 2.053166 3.405075
C -2.576684 4.670714 -1.328114
H -3.623219 4.388409 -1.162610
H -2.605169 5.654736 -1.813308
C 4.200600 1.846521 -2.551685
C 3.314457 0.762614 -2.578569
C 3.583789 -0.346180 -3.385539
C 4.743341 -0.391424 -4.161008
C 5.630822 0.685977 -4.134483
C 5.356626 1.797942 -3.339331
H 4.518110 2.931065 -0.720665
H 4.281068 3.965389 -2.151002
H 6.046520 2.638654 -3.334080
H 4.950607 -1.254533 -4.787313
H 6.532223 0.665102 -4.740503
H 2.412787 0.788045 -1.974320
H 2.881254 -1.175227 -3.407256

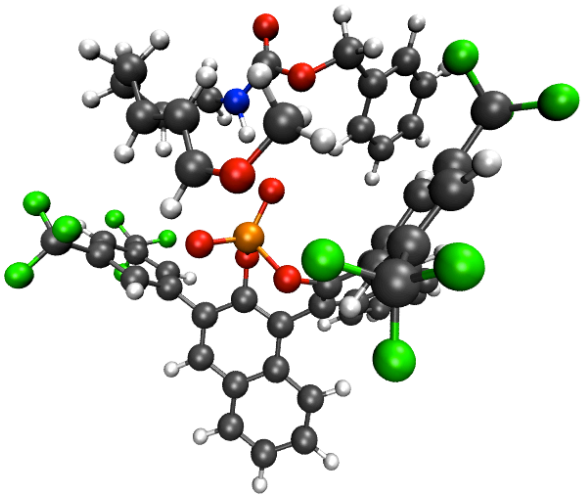


Figure SI - III: Transition state geometry **TS – II,** the full system prior to cyclization.

TS - II
111

C 2.486382 -4.900710 -1.859633
C 1.733156 -5.752689 -2.631865
C 1.867909 -4.038594 -0.917605
C 0.446979 -4.063610 -0.736512
C -0.298593 -4.962793 -1.551682
C 0.327562 -5.774683 -2.473499
H -0.265560 -6.436892 -3.097168
H 2.211997 -6.394187 -3.365950
H 3.566899 -4.851528 -1.969307
H -1.378346 -4.987975 -1.460114
C 2.647185 -3.133991 -0.167394
C 2.078902 -2.198876 0.670436
C 0.656704 -2.182711 0.794668
C -0.155605 -3.142519 0.192838
H 3.727523 -3.177531 -0.265214
C -1.625948 -3.122966 0.488152
C -2.332525 -4.221376 1.104626
C -2.315939 -1.937657 0.270268
C -3.683411 -1.765587 0.617117
C -4.339134 -2.794093 1.250754
C -3.704200 -4.035719 1.489789
C -4.434046 -0.527574 0.262324
H -5.383240 -2.675820 1.529991
C -1.749277 -5.490636 1.378535
C -2.483889 -6.508464 1.952511
C -3.841680 -6.320579 2.304086
C -4.430925 -5.100487 2.083814
H -4.411651 -7.132535 2.745823
H -5.471964 -4.928925 2.348060
H -0.711698 -5.663608 1.121496
H -2.016500 -7.470815 2.137328

C 2.998037 -1.305546 1.421316
O 0.089905 -1.166557 1.535493
O -1.656183 -0.863171 -0.282893
P -0.660697 0.065283 0.676092
O -1.438276 0.866038 1.684023
O 0.304689 0.725479 -0.265421
C -5.133074 -0.483825 -0.947270
C -4.527500 0.553246 1.143135
C -5.965150 0.595910 -1.245263
C -6.053254 1.678771 -0.372761
C -5.305633 1.662291 0.805408
C 4.125338 -0.784144 0.760139
C 5.132278 -0.134338 1.466739
C 5.037371 0.026061 2.850182
C 3.897536 -0.440780 3.503365
C 2.877620 -1.089208 2.801135
H 4.210922 -0.892330 -0.314440
C 6.322537 0.438551 0.745794
H 5.836919 0.500335 3.407548
H 2.011782 -1.463584 3.333031
C 3.740194 -0.205012 4.980594
H -5.060069 -1.316639 -1.638118
H -3.939404 0.548006 2.052605
C -5.347775 2.840890 1.738269
C -6.842775 0.524293 -2.465160
H -6.681392 2.526081 -0.616244
F -6.225794 -0.099556 -3.491625
F -7.219125 1.748435 -2.894993
F -7.976407 -0.170493 -2.211441
F -6.237436 2.675253 2.740477
F -5.681836 3.983313 1.095087
F -4.141159 3.058505 2.327520
F 6.206657 1.788382 0.599837
F 6.476793 -0.077433 -0.485566
F 7.467496 0.229023 1.430521
F 4.917322 0.075673 5.578054
F 3.197725 -1.264913 5.612299
F 2.919992 0.854974 5.219336
C 0.289261 2.849463 2.558261
O 1.362141 2.350935 3.067373
C 2.670400 2.753788 2.561197
C 0.269722 3.904736 1.625081
C -0.909372 4.362505 1.124643
C -0.984361 5.518439 0.192439
C -2.049417 4.057871 -1.692821
C -0.762852 3.682646 -2.440785
N 0.331684 3.262351 -1.567531
C 1.599604 3.662149 -1.858020
O 2.512199 2.961198 -1.092092
O 1.923197 4.537518 -2.643035
H 0.008230 5.722439 -0.219836
H -1.247516 6.392446 0.813512
H -2.852498 4.115514 -2.437564
H -2.327391 3.236205 -1.019528
H -0.998827 2.865691 -3.135492
H -0.396585 4.521127 -3.038562
H 0.250430 2.351121 -1.092571
C 3.802656 2.801898 -1.710869
H -1.835337 3.872936 1.431514
H 1.199027 4.332057 1.268452
H 3.377725 2.186036 3.154054
H 2.728455 2.500144 1.500880
H 2.814136 3.823967 2.724146
H -0.620327 2.366992 2.907222
C -2.039606 5.390670 -0.927953
H -3.035550 5.558823 -0.500477
H -1.860471 6.213138 -1.630706
C 3.852761 1.591303 -2.625831
C 2.923303 0.546294 -2.524457
C 3.016903 -0.557980 -3.377449
C 4.033918 -0.634992 -4.329774
C 4.964510 0.402388 -4.428923
C 4.871575 1.506378 -3.583482
H 4.517777 2.703631 -0.889247
H 4.043350 3.711329 -2.267495
H 5.589787 2.317273 -3.679515
H 4.097712 -1.491795 -4.994978
H 5.755343 0.357038 -5.172530
H 2.125035 0.592664 -1.788889
H 2.285766 -1.357829 -3.295032

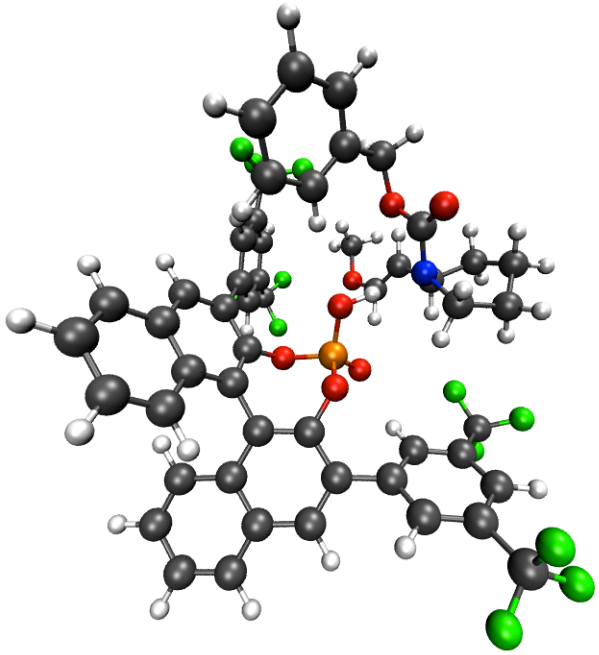


Figure SI - IV: Geometry of full system **5a$_{boat}$** following cyclization.

5a$_{boat}$
111

C 2.338451 -5.155210 -1.800683
C 1.547532 -5.965505 -2.580573
C 1.760257 -4.235514 -0.884272
C 0.334714 -4.178770 -0.747880
C -0.451477 -5.017253 -1.584091
C 0.139482 -5.883310 -2.477109
H -0.482933 -6.506343 -3.112294
H 1.998784 -6.658627 -3.283855
H 3.421293 -5.194443 -1.882260
H -1.531402 -4.960164 -1.524569
C 2.572108 -3.363655 -0.116859
C 2.031023 -2.412910 0.725450
C 0.611793 -2.363399 0.829519
C -0.236882 -3.248323 0.188488
H 3.651910 -3.447216 -0.201483
C -1.704817 -3.192500 0.452859
C -2.423681 -4.344773 0.924914
C -2.402008 -2.008229 0.265667
C -3.820384 -1.918717 0.368060
C -4.509887 -3.059806 0.726453
C -3.848779 -4.271221 1.042830
C -4.570474 -0.667411 0.067813
H -5.591616 -3.017441 0.815790
C -1.781785 -5.550232 1.321915
C -2.511677 -6.626233 1.775825
C -3.922312 -6.561714 1.856148
C -4.573783 -5.404327 1.500747
H -4.484175 -7.420316 2.210800
H -5.655267 -5.331298 1.576900
H -0.701258 -5.614811 1.280190
H -1.997343 -7.531892 2.083040
C 2.904469 -1.478339 1.482390
O 0.059070 -1.370276 1.637112
O -1.703652 -0.871490 -0.131446
P -0.699264 -0.122633 0.923008
O -1.365704 0.749493 1.914475
O 0.364537 0.517484 -0.043679
C -5.615790 -0.702764 -0.863904
C -4.298202 0.538211 0.730933
C -6.374646 0.438563 -1.129074
C -6.104323 1.634941 -0.468903
C -5.062576 1.673360 0.458643
C 3.968807 -0.838114 0.831671
C 4.808548 0.027006 1.531571
C 4.618549 0.253348 2.893741
C 3.554141 -0.369579 3.541838
C 2.701049 -1.225263 2.846544

H 4.116579 -0.983901 -0.231836
C 5.853475 0.820532 0.797301
H 5.276092 0.920780 3.436524
H 1.870618 -1.686741 3.366225
C 3.342327 -0.150281 5.017293
H -5.832240 -1.625155 -1.391758
H -3.494596 0.595768 1.457277
C -4.796661 2.942689 1.225054
C -7.446232 0.386577 -2.185433
H -6.693367 2.520422 -0.673801
F -6.937213 0.593208 -3.421324
F -8.396001 1.325219 -1.986433
F -8.061196 -0.816890 -2.212119
F -5.467309 2.977645 2.396168
F -5.173545 4.038421 0.522683
F -3.483934 3.087132 1.517979
F 5.364422 2.038868 0.426899
F 6.273150 0.209216 -0.325623
F 6.936809 1.065253 1.565618
F 3.867858 1.026831 5.430230
F 3.937922 -1.121405 5.750061
F 2.037105 -0.154876 5.343145
C 1.025860 3.027005 2.472969
O 1.974084 2.849932 3.423721
C 3.225483 3.496669 3.222788
C 1.146374 3.708534 1.323352
C -0.014234 3.902632 0.393298
C -0.193435 5.384284 -0.012272
C -2.078054 4.424641 -1.411781
C -1.382059 3.042971 -1.479088
N -0.017521 3.043649 -0.869736
C 1.020269 3.198892 -1.821216
O 2.228687 3.150559 -1.221324
O 0.862360 3.285064 -3.020659
H 0.793208 5.838693 -0.162156
H -0.647765 5.905525 0.837955
H -2.690127 4.558402 -2.309632
H -2.763553 4.457348 -0.559656
H -1.972904 2.294851 -0.942618
H -1.264820 2.713697 -2.509903
H 0.221437 1.498699 -0.291502
C 3.370448 3.160936 -2.105796
H -0.918160 3.558203 0.903649
H 2.079229 4.184115 1.048217
H 3.826683 3.262516 4.100779
H 3.725707 3.123684 2.321204
H 3.096740 4.582942 3.138618
H 0.108600 2.515114 2.751505
C -1.049089 5.554023 -1.286768
H -1.550806 6.527004 -1.274952
H -0.406133 5.548597 -2.173766
C 3.582072 1.855532 -2.842279
C 3.071713 0.643668 -2.365746
C 3.327385 -0.545629 -3.051486
C 4.107793 -0.539551 -4.207942
C 4.621708 0.667065 -4.684909
C 4.354236 1.856978 -4.008951
H 4.207807 3.361225 -1.432382
H 3.271591 3.986875 -2.815205
H 4.744374 2.795281 -4.396196
H 4.307103 -1.465793 -4.738844
H 5.222074 0.684634 -5.589945
H 2.460325 0.625930 -1.469901
H 2.910829 -1.477091 -2.677969

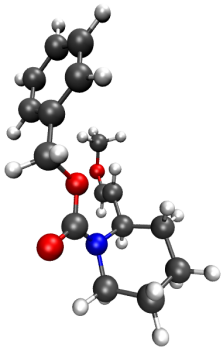


Figure SI - V: Geometry of full system **5a** following conformational change.

5a
41

C 0.51218112 -2.72807115 1.08401933
O -0.61224315 -3.46612078 1.25905002
C -1.74175391 -3.12069304 0.46632264
C 0.71137320 -1.69957787 0.24975053
C 2.06213486 -1.04717043 0.15247428
C 2.62117713 -1.00670287 -1.28680479
C 4.26940121 0.78301398 -0.52182755
C 3.62138047 0.70954303 0.86856266
N 2.20884878 0.31198055 0.75416943
C 1.31702372 1.35139436 0.65444380
O 0.09240432 0.96608490 0.20015872
O 1.56877319 2.50996227 0.95455196
H 1.99310958 -0.33375254 -1.88549386
H 2.54329599 -2.00437087 -1.73387044
H 3.80624750 1.61173674 -1.07216397
H 5.33502523 1.02289105 -0.42299505
H 4.13100272 -0.03735990 1.49071793
H 3.66199409 1.66931017 1.38172685
C -0.89118533 2.02759124 0.15712160
H 2.75153133 -1.66305677 0.74670152
H -0.07452474 -1.33762936 -0.39854499
H -2.53419203 -3.81700623 0.74452808
H -2.06735508 -2.09237863 0.66189448
H -1.52156076 -3.22574790 -0.60376283
H 1.29509440 -3.09029326 1.74647433
C 4.08454196 -0.53285415 -1.29189377
H 4.70632856 -1.31091924 -0.82622638
H 4.44552762 -0.42561407 -2.32133836
C -2.22307734 1.40941693 -0.17506348
C -2.99932573 0.82054788 0.83207683
C -4.22752876 0.23246683 0.53107717
C -4.69609642 0.22839099 -0.78519998
C -3.93206044 0.81468194 -1.79485819
C -2.70275378 1.40095420 -1.48944424
H -0.58950047 2.76356077 -0.59429979
H -0.90783948 2.53267042 1.12622240
H -2.11018417 1.85861545 -2.27748718
H -5.65503145 -0.22395671 -1.02078282
H -4.29388903 0.81910327 -2.81901800
H -2.63526648 0.82624379 1.85620182
H -4.82215779 -0.21431820 1.32267392

METHANOL BY-PRODUCT:
6

C 0.65522106 -0.03468975 -0.00000169
O -0.75303706 0.12803117 0.00000291
H 1.02396375 -0.56388940 -0.89185815
H 1.02396589 -0.56392086 0.89183518
H 1.09112801 0.96770665 0.00001535
H -1.15059349 -0.75134818 -0.00001133

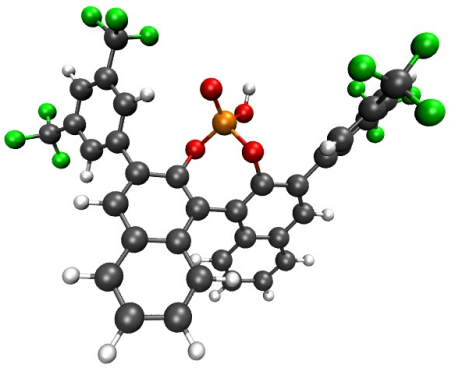


Figure SI - VI: Geometry of free catalyst system **6** following regeneration of the catalyst after the reaction.

Free Catalyst
70

C 2.37529637 -4.24112142 -2.96797790
C 1.42035282 -5.15069750 -3.35599971
C 2.08199697 -3.24545281 -1.99761116
C 0.78435861 -3.21179370 -1.39052545
C -0.18510418 -4.15262301 -1.83372779
C 0.12506196 -5.09254992 -2.79144824
H -0.63571194 -5.79437380 -3.11974936
H 1.65194398 -5.90322394 -4.10336016
H 3.36826531 -4.25852573 -3.40873436
H -1.18590595 -4.11808477 -1.42140699
C 3.04660801 -2.27155708 -1.64165045
C 2.76737233 -1.25485807 -0.75078150
C 1.47289339 -1.24237121 -0.16049397
C 0.50720769 -2.20334843 -0.40196727
H 4.03401029 -2.32776506 -2.09077105
C -0.80380624 -2.13588739 0.30866754
C -1.30333064 -3.24028138 1.08148694
C -1.57170543 -0.98487928 0.23505452
C -2.90240544 -0.89842967 0.73496545
C -3.40534584 -2.00307100 1.39349421
C -2.62815411 -3.16497915 1.61964108
C -3.76888347 0.29235165 0.51029815
H -4.41683348 -1.96702902 1.78780369
C -0.52517513 -4.39341434 1.37418350
C -1.03957770 -5.42104942 2.13303518
C -2.36026940 -5.35783711 2.63566141
C -3.13437635 -4.24949686 2.38555477
H -2.75400211 -6.17893553 3.22665159
H -4.14387007 -4.17859030 2.78106489
H 0.49267706 -4.45306257 1.00760500
H -0.42251464 -6.28729105 2.35201128
C 3.78688051 -0.21707413 -0.44459908
O 1.17898835 -0.20116581 0.72462421
O -1.05486293 0.12730218 -0.43931108
P 0.14376381 0.96112584 0.26717834
O -0.18687284 1.86857890 1.38029909
O 0.76803677 1.64673595 -1.04234179
C -5.02957728 0.11022335 -0.07541328
C -3.38231294 1.58558318 0.88581105
C -5.88223960 1.19445007 -0.28222028
C -5.49088154 2.48151721 0.08306658
C -4.23873005 2.66577373 0.66613098
C 4.50336675 0.38201076 -1.49096650
C 5.49415735 1.32652429 -1.22617121
C 5.79410670 1.69110206 0.08620738
C 5.08396299 1.10067542 1.12959536
C 4.08634218 0.15978011 0.87189271
H 4.27545841 0.11827039 -2.51772177
C 6.19465222 2.00741381 -2.37298431
H 6.56684021 2.42116411 0.29158821
H 3.54365428 -0.28189334 1.69918638
C 5.41184932 1.42907183 2.56397205
H -5.33732354 -0.88053686 -0.39210738
H -2.42072823 1.75628797 1.35800729
C -3.76193114 4.04755015 1.03425705
C -7.24984793 0.95587592 -0.86503759
H -6.14788122 3.32485788 -0.08756287
F -7.22639804 -0.00668282 -1.81398384
F -7.76150877 2.07083744 -1.42723517
F -8.12812708 0.54895214 0.08086640
F -4.75893358 4.95803280 0.98383477
F -2.79126870 4.47103480 0.19205583
F -3.24430061 4.07843267 2.27912170
F 6.35361747 1.17509372 -3.42572879
F 7.41633187 2.45721485 -2.01830972
F 5.49155711 3.07418965 -2.81833914
F 6.21686365 2.50705633 2.66756419
F 6.04137165 0.39603661 3.16907050
F 4.29519754 1.67886415 3.27896850
H 0.98511517 2.57333639 -0.86235293

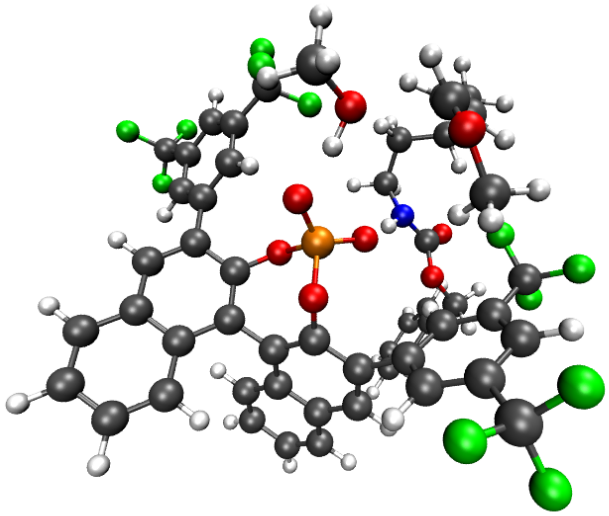


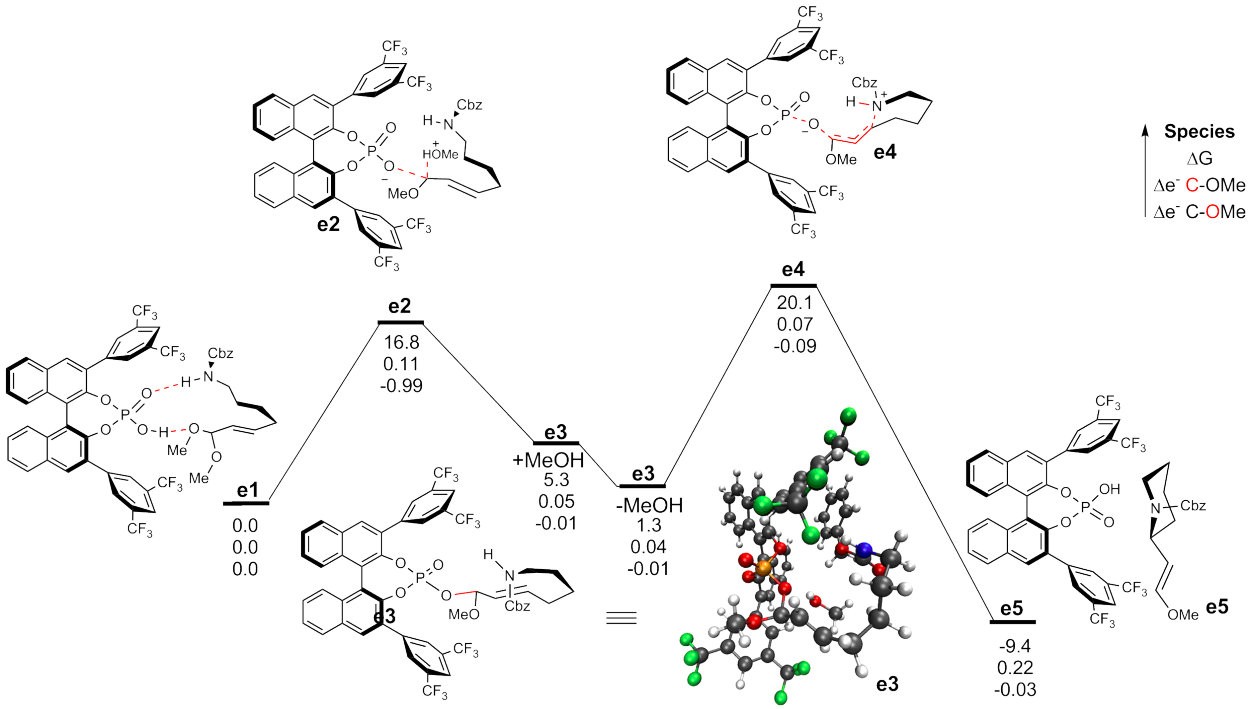
Figure SI - VII: Transition state geometry **TS – III,** the full system prior to concerted cyclization.

TS - III
117

C 2.304891 -5.408511 -0.484394
C 1.432171 -6.432494 -0.768436
C 1.864806 -4.240713 0.195389
C 0.499599 -4.143212 0.620134
C -0.380517 -5.209268 0.282463
C 0.072987 -6.320487 -0.392131
H -0.621812 -7.116395 -0.642125
H 1.778521 -7.320091 -1.289648
H 3.348218 -5.472172 -0.783373
H -1.426881 -5.134866 0.550994
C 2.748327 -3.157887 0.437485
C 2.316869 -1.997306 1.040319
C 0.962923 -1.915222 1.468758
C 0.068962 -2.965771 1.324644
H 3.783752 -3.244861 0.118350
C -1.321516 -2.825217 1.844671
C -1.882144 -3.767072 2.774726
C -2.100309 -1.755169 1.420933
C -3.499422 -1.677846 1.703364
C -4.050960 -2.644411 2.521694
C -3.270871 -3.668793 3.108824
C -4.379812 -0.647034 1.091551
H -5.109939 -2.596161 2.760063
C -1.110848 -4.773235 3.419155
C -1.686125 -5.642773 4.318772
C -3.065450 -5.561415 4.622434
C -3.837607 -4.590705 4.028901
H -3.506766 -6.255430 5.331403
H -4.895090 -4.503667 4.264298
H -0.050494 -4.840509 3.206310
H -1.072614 -6.395271 4.805666
C 3.258551 -0.855525 1.250730
O 0.545052 -0.759543 2.096218
O -1.540801 -0.788361 0.612151
P -0.420959 0.276800 1.230161
O -1.077269 1.165995 2.259432
O 0.317070 0.858558 0.068820
C -5.583813 -1.045154 0.490482
C -4.063579 0.716945 1.109686
C -6.448687 -0.106946 -0.072042
C -6.125168 1.250556 -0.062937

C -4.931348 1.647311 0.533283
C 3.436357 0.118801 0.260819
C 4.351945 1.158194 0.460625
C 5.100333 1.234253 1.634463
C 4.917722 0.265514 2.621560
C 4.002580 -0.770051 2.433038
H 2.858930 0.069165 -0.656137
C 4.493490 2.232496 -0.586292
H 5.814173 2.034261 1.782054
H 3.859381 -1.511610 3.211412
C 5.761503 0.302429 3.867130
H -5.833528 -2.098750 0.439028
H -3.146909 1.051342 1.584417
C -4.503592 3.087957 0.528001
C -7.765908 -0.554394 -0.645301
H -6.787685 1.979645 -0.512321
F -7.706208 -1.812063 -1.134121
F -8.180165 0.253724 -1.645993
F -8.741290 -0.545298 0.294517
F -5.479401 3.929439 0.126856
F -3.448998 3.276672 -0.306568
F -4.105729 3.494910 1.755724
F 4.893925 1.752119 -1.778215
F 5.388532 3.183356 -0.216401
F 3.316077 2.879891 -0.800517
F 6.146049 1.565118 4.172249
F 6.889000 -0.428598 3.726727
F 5.101284 -0.189671 4.935954
H -0.951338 2.720140 2.240090
O -1.040713 3.728289 2.236105
C -1.698952 4.088637 3.443689
C 0.919783 4.955493 1.947797
O 1.777306 4.489027 2.793976
C 2.844423 3.614184 2.326011
C 1.125652 5.047557 0.534733
C 0.100128 5.262358 -0.325997
C 0.260930 5.698540 -1.745795
C -1.234578 3.767414 -2.716045
C -0.985463 2.291227 -3.107089
N 0.243681 1.711951 -2.594432
C 1.227101 1.346876 -3.453809
O 2.123891 0.514001 -2.838410
O 1.333292 1.707681 -4.619581
H 1.268215 6.105616 -1.885818
H -0.445482 6.532472 -1.874686
H -2.042559 4.121363 -3.367930
H -1.633508 3.820488 -1.699807
H -1.833961 1.691376 -2.758083
H -0.940675 2.210016 -4.196067
H 0.262689 1.307779 -1.653237
C 3.177893 -0.002512 -3.688903
H -0.905140 5.121036 0.069295
H 2.147031 4.984816 0.167195
H -2.438467 3.330402 3.716014
H -0.995415 4.195115 4.283474
H -2.222176 5.039400 3.296114
H 3.254877 3.161395 3.225016
H 2.424886 2.858930 1.662325
H 3.607895 4.203919 1.815420
H 0.136713 5.516802 2.430124
C 0.017289 4.647072 -2.863096
H -0.001170 5.200913 -3.807068
H 0.897200 3.999285 -2.901887
C 2.747125 -1.230019 -4.453014
C 2.264931 -1.125626 -5.763689
C 1.870684 -2.266208 -6.464049
C 1.945629 -3.521941 -5.859421
C 2.416279 -3.634356 -4.549775
C 2.817588 -2.493758 -3.854367
H 3.983418 -0.245067 -2.994071
H 3.509533 0.789060 -4.363312
H 3.178105 -2.583558 -2.832400
H 1.636954 -4.408981 -6.405055
H 2.467851 -4.606268 -4.067240
H 2.183227 -0.142712 -6.215722
H 1.500080 -2.173021 -7.481073

The stereoisomeric pathway forming the minor enantiomer of the reaction was evaluated using the same methods, as shown in Scheme SI – III, below. In addition to this pathway, three other conformers (e.g. rotated CBz group, ring-flipped chair and repositioned CBz) leading to the minor enantiomer were investigated, though none provided pathways lower in energy than the one reported below.



Scheme SI – III. Reaction energy diagram for SN2'-like pathway to form the minor piperidine stereoisomer.

A summary of calculated values including solvent and free-energy corrections is provided in Table SI - III.

Table SI - II. Calculated values for geometries of starting materials, transition states, intermediates and products for the pathways investigated at the GAMESS(SMD solvent = carbontetrachloride)/ωB97X-D/6-311+G**//B3LYP/6-31G** level.

	E(hartrees)	H (kcal/mol)	S (kcal/mol at 298 K)	ΔG
E1	-4241.093595	586.2	105.9	-
E2	-4241.065994	586.3	106.5	16.83
E3 + MeOH	-4241.078288	589.4	113.4	5.35
E3	-4241.071371	583.7	116.1	1.25
E4	-4241.043858	582.7	113.5	20.08
E5	-4241.081485	586.5	123.3	-9.45

Cartesian coordinates for the starting geometry, transition states, intermediate and cyclized product are provided below.

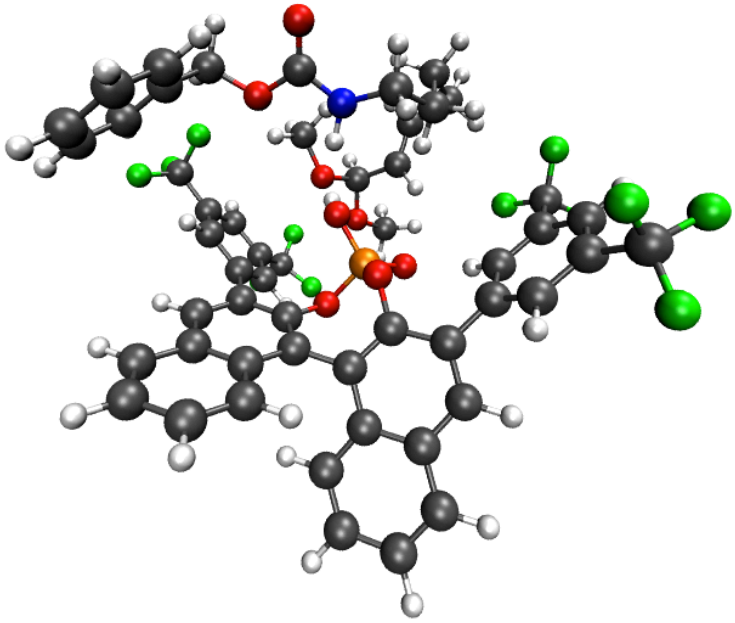


Figure SI - VIII: Geometry for full system prior to reaction forming minor enantiomer, **e1**.

e1
117

C -1.697483 -0.590661 5.766138
C -0.795709 -1.177732 6.621269
C -1.659809 -0.857835 4.370795
C -0.695470 -1.782911 3.855302
C 0.238753 -2.349519 4.764844
C 0.190018 -2.052989 6.108785
H 0.920329 -2.492612 6.781442
H -0.826639 -0.960000 7.684388
H -2.444274 0.103851 6.140869
H 1.006464 -3.014575 4.389653
C -2.534423 -0.192038 3.479658
C -2.479295 -0.383549 2.112745
C -1.543405 -1.340785 1.626637
C -0.691305 -2.062737 2.444331
H -3.258585 0.505141 3.890346
C 0.251685 -3.053068 1.846961
C 0.280868 -4.424020 2.277313
C 1.133103 -2.652777 0.853077
C 2.181567 -3.484559 0.365928
C 2.260491 -4.770209 0.864215
C 1.312520 -5.283498 1.781599
C 3.214065 -3.012360 -0.599428
H 3.047471 -5.427161 0.505031
C -0.696170 -4.981701 3.146679
C -0.636606 -6.305155 3.522487
C 0.403847 -7.143182 3.057293
C 1.355522 -6.640342 2.201842
H 0.440002 -8.183206 3.366609
H 2.149731 -7.276432 1.820429
H -1.505942 -4.356710 3.503615
H -1.400746 -6.711344 4.178434
C -3.329871 0.434322 1.209261
O -1.498714 -1.570485 0.252706
O 1.042419 -1.349997 0.357418
P -0.230561 -1.017571 -0.607979
O -0.212780 -1.622135 -1.954895
O -0.215803 0.560105 -0.481756
C 4.564542 -3.156082 -0.261808
C 2.885082 -2.488800 -1.860681
C 5.570407 -2.785419 -1.157943
C 5.244142 -2.269491 -2.407197
C 3.896315 -2.129440 -2.748983
C -3.476847 1.802505 1.474984

C -4.285553 2.603495 0.667439
C -4.946755 2.060670 -0.431439
C -4.791594 0.701981 -0.709951
C -4.001279 -0.108204 0.100862
H -2.935966 2.248636 2.302199
C -4.368637 4.079584 0.943364
H -5.561226 2.686841 -1.067311
H -3.896211 -1.158240 -0.137437
C -5.533565 0.115710 -1.882677
H 4.834909 -3.555535 0.709876
H 1.847070 -2.372493 -2.152156
C 3.558458 -1.629107 -4.128260
C 7.008547 -2.903478 -0.728490
H 6.023786 -1.983253 -3.103251
F 7.229485 -4.057459 -0.058783
F 7.362184 -1.896876 0.102951
F 7.856290 -2.871910 -1.778031
F 3.846862 -2.547223 -5.076572
F 4.275540 -0.517176 -4.438706
F 2.253246 -1.312198 -4.258887
F -4.347311 4.347230 2.270713
F -5.485940 4.632180 0.432836
F -3.316407 4.753230 0.402778
F -5.494449 0.936277 -2.955408
F -6.842996 -0.072464 -1.587476
F -5.038303 -1.080551 -2.259720
C -1.748234 1.478771 -3.413159
O -2.512127 0.316496 -3.305698
C -2.708924 -0.379959 -4.529118
C -0.336623 1.267147 -3.894334
C 1.838608 2.231002 -4.770601
C 2.604170 2.883111 -3.583031
C 3.086429 2.563107 -1.063300
N 1.812881 2.967933 -0.479980
C 0.354720 2.230307 -4.514406
C 1.646258 4.139170 0.188351
O 0.383087 4.180117 0.720125
O 2.465320 5.038971 0.285351
H 2.026900 3.738283 -3.210656
H 3.556098 3.290607 -3.943935
H 3.706976 3.459978 -1.135634
H 3.600074 1.864545 -0.388531
H 1.129193 2.241108 -0.303642
C 0.046764 5.350758 1.504782
H -3.378295 -1.207710 -4.296959
H -3.182025 0.265742 -5.283000
H -1.768272 -0.772288 -4.932431
H -2.262669 2.245896 -4.020850
C 2.881241 1.900159 -2.433003
H 2.054355 1.185757 -2.340017
H 3.765314 1.301992 -2.677632
C 0.101882 5.046450 2.981334
C -1.076061 4.880389 3.717917
C -1.024388 4.586309 5.082149
C 0.208629 4.449688 5.719496
C 1.389256 4.612078 4.989904
C 1.337425 4.912128 3.629876
H -0.968538 5.617389 1.203995
H 0.736468 6.152296 1.232763
H 2.251901 5.044232 3.058389
H 0.251983 4.220804 6.780509
H 2.351210 4.509722 5.484174
H -2.037577 4.984858 3.222100
H -1.946171 4.465766 5.644489
H 2.049413 2.789432 -5.689784
H 2.207497 1.212002 -4.920277
H -0.169091 3.150733 -4.782753
H 0.128416 0.327378 -3.602956
C -1.509904 3.354409 -1.895677
H -0.552961 3.653621 -2.333641
H -2.327690 3.914004 -2.364249
H -1.489012 3.555505 -0.827314
O -1.733573 1.948353 -2.046343
H -0.837273 1.048511 -1.121875

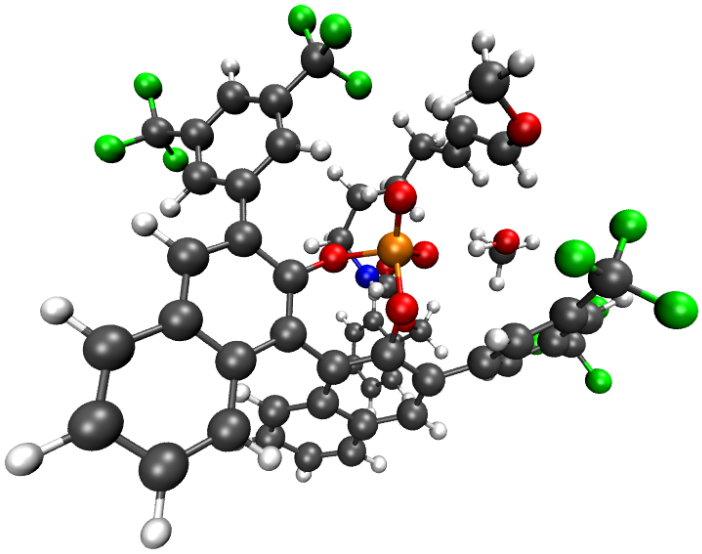


Figure SI - IX: Transition state geometry for full system prior to reaction forming minor enantiomer phosphate intermediate, **e2**.

e2
117

C 1.098613 4.704489 2.418726
C -0.060572 5.338761 2.793135
C 1.147018 3.900210 1.249136
C -0.024351 3.782946 0.431782
C -1.205869 4.451403 0.849941
C -1.224822 5.201477 2.002429
H -2.146559 5.682625 2.315464
H -0.091647 5.929427 3.703614
H 1.991671 4.782015 3.033166
H -2.109386 4.341978 0.262723
C 2.310443 3.165747 0.913513
C 2.347771 2.280696 -0.147769
C 1.165764 2.177653 -0.949013
C 0.024821 2.926638 -0.718856
H 3.187521 3.285075 1.543073
C -1.168257 2.686418 -1.583198
C -1.796344 3.720607 -2.356678
C -1.680470 1.394978 -1.644251
C -2.915269 1.104529 -2.293039
C -3.541276 2.113597 -2.994040
C -2.990740 3.412428 -3.087601
C -3.609074 -0.199696 -2.141319
H -4.474286 1.901869 -3.509051
C -1.270039 5.035773 -2.474267
C -1.890783 5.980857 -3.261774
C -3.073197 5.670776 -3.975355
C -3.608945 4.409575 -3.886493
H -3.549113 6.424598 -4.595066
H -4.512484 4.148118 -4.431878
H -0.357298 5.288570 -1.946910
H -1.464458 6.976026 -3.343762
C 3.512625 1.389175 -0.384465
O 1.117753 1.250414 -1.980612
O -1.035634 0.368392 -0.984875
P 0.424069 -0.207076 -1.590904
O 0.199843 -0.967096 -2.854195
O 1.121182 -0.811978 -0.400018
C -4.937776 -0.176701 -1.692900
C -3.024779 -1.432854 -2.458986
C -5.676308 -1.351400 -1.570270
C -5.104311 -2.576954 -1.905124
C -3.782381 -2.602763 -2.349972
C 4.269508 0.898900 0.690036

C 5.280712 -0.041231 0.482781
C 5.525489 -0.553022 -0.788840
C 4.789171 -0.058244 -1.862504
C 3.829888 0.931304 -1.673884
H 4.021766 1.192154 1.703943
C 6.104805 -0.536902 1.639437
H 6.243161 -1.351474 -0.930974
H 3.271233 1.289037 -2.524164
C 4.994745 -0.645195 -3.231933
H -5.391226 0.772612 -1.430770
H -1.993972 -1.462929 -2.802683
C -3.148615 -3.913184 -2.709950
C -7.071262 -1.280290 -1.012249
H -5.676047 -3.492070 -1.821946
F -7.716867 -0.169924 -1.434348
F -7.060932 -1.236226 0.339772
F -7.815635 -2.348755 -1.369619
F -2.540176 -3.879026 -3.917039
F -4.026021 -4.932875 -2.721231
F -2.172881 -4.255800 -1.814107
F 5.422203 -0.493550 2.811966
F 7.222192 0.203663 1.819127
F 6.507868 -1.817440 1.461082
F 5.120063 -1.997117 -3.164525
F 6.114297 -0.181680 -3.831193
F 3.961581 -0.384866 -4.059053
C 2.084204 -3.561284 -2.190501
O 2.291246 -3.316418 -3.433783
C 1.199449 -3.414972 -4.399090
C 0.897263 -4.047108 -1.609209
C -0.204510 -4.634908 0.617991
C -0.570289 -3.453133 1.576099
C -1.643244 -1.124904 1.758003
N -0.430990 -0.412036 2.127526
C 0.921237 -4.243382 -0.257621
C 0.177850 -0.683527 3.304399
O 1.183611 0.191249 3.570279
O -0.146419 -1.596026 4.059317
H 0.347945 -2.979669 1.930621
H -1.054210 -3.863829 2.466622
H -2.148624 -1.376797 2.692245
H -2.276439 -0.428280 1.202729
H 0.074010 0.101786 1.413694
C 1.823314 0.005176 4.858732
H 1.666439 -3.228218 -5.362397
H 0.770697 -4.419167 -4.366331
H 0.476815 -2.637771 -4.144500
H 2.954111 -3.366070 -1.562274
C -1.451911 -2.393797 0.911723
H -1.024640 -2.115367 -0.052861
H -2.450276 -2.802482 0.713957
C 1.052875 0.599380 6.019835
C 1.460073 1.814410 6.594814
C 0.790962 2.345130 7.699680
C -0.297209 1.667074 8.250539
C -0.711158 0.454619 7.687257
C -0.052671 -0.071542 6.576972
H 2.790295 0.500273 4.746143
H 1.982337 -1.064894 5.011831
H -0.378148 -1.003179 6.129379
H -0.818905 2.074028 9.112362
H -1.558252 -0.081772 8.106924
H 2.309824 2.352130 6.183598
H 1.123667 3.283873 8.133076
H 0.132227 -5.474922 1.240879
H -1.077497 -4.953673 0.047625
H 1.860957 -4.013117 0.238950
H -0.001659 -4.191459 -2.191090
C 3.358813 -2.720768 1.842261
H 2.463603 -3.184798 2.278124
H 4.190627 -3.424503 1.933762
H 3.597788 -1.836573 2.437741
O 3.207284 -2.421424 0.462134
H 2.439002 -1.828642 0.308619

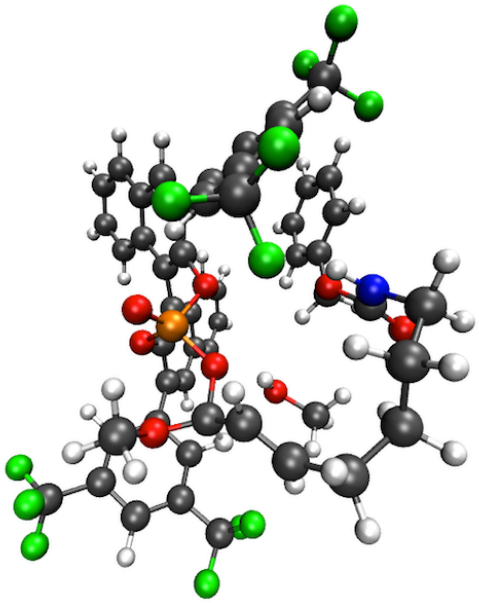


Figure SI - X: Geometry for **e3**, the chiral phosphate acetal intermediate full system prior to cyclizing to form the minor enantiomer.

e3
117

C 1.961478 -4.949329 -2.840029
C 0.881094 -5.720769 -3.195980
C 1.883836 -4.044518 -1.747307
C 0.673521 -3.955466 -0.985587
C -0.433310 -4.746162 -1.402028
C -0.329900 -5.604179 -2.474803
H -1.190992 -6.195248 -2.772380
H 0.948194 -6.404886 -4.036222
H 2.891353 -5.006547 -3.399059
H -1.375621 -4.657812 -0.877163
C 2.974162 -3.201995 -1.423617
C 2.903087 -2.278019 -0.403626
C 1.700403 -2.213695 0.352043
C 0.615729 -3.044076 0.127642
H 3.884579 -3.273841 -2.011469
C -0.609145 -2.922582 0.969451
C -1.172479 -4.049984 1.660275
C -1.246848 -1.697468 1.078603
C -2.527914 -1.540479 1.681061
C -3.108985 -2.656211 2.248921
C -2.447095 -3.907029 2.296570
C -3.268474 -0.250454 1.647547
H -4.086565 -2.564749 2.713650
C -0.500921 -5.297265 1.776361
C -1.072404 -6.348835 2.457662
C -2.347704 -6.215315 3.055037
C -3.016779 -5.016693 2.976996
H -2.788347 -7.055083 3.583530
H -3.988528 -4.893556 3.447361
H 0.481753 -5.412802 1.334244
H -0.535144 -7.288712 2.542121
C 4.031721 -1.341372 -0.153860
O 1.639057 -1.274019 1.383360
O -0.648022 -0.571351 0.503851
P 0.663856 0.022980 1.268331
O 0.434631 0.632796 2.594201
O 1.181865 0.965767 0.088466
C -4.566207 -0.223761 1.116763
C -2.719754 0.935945 2.145865
C -5.297961 0.962299 1.086443
C -4.745062 2.149096 1.569100
C -3.454593 2.122473 2.093646
C 4.447509 -0.492059 -1.183847
C 5.499880 0.404413 -0.974630
C 6.159291 0.453796 0.249315
C 5.744651 -0.397407 1.276528
C 4.687813 -1.282562 1.083566
H 3.898855 -0.491095 -2.120642
C 5.849210 1.366253 -2.076167

H 6.977999 1.146043 0.403441
H 4.374952 -1.929801 1.894260
C 6.414064 -0.297689 2.620858
H -4.993667 -1.129070 0.702532
H -1.726020 0.939706 2.581484
C -2.785131 3.390827 2.542499
C -6.663661 0.989493 0.455015
H -5.310921 3.072440 1.542401
F -7.247993 -0.227803 0.458052
F -6.607133 1.394340 -0.839420
F -7.493108 1.844529 1.091482
F -2.133048 3.246277 3.708294
F -3.648714 4.417638 2.672571
F -1.847749 3.781246 1.621640
F 4.860109 2.293074 -2.247706
F 5.994191 0.744125 -3.263765
F 6.983392 2.048738 -1.827176
F 5.942406 0.754676 3.336449
F 7.747268 -0.112627 2.499821
F 6.219894 -1.402177 3.369405
C 2.292611 1.978869 0.264085
O 3.065153 1.662140 1.363168
C 2.961354 2.446318 2.565300
C 1.689920 3.345163 0.202495
C 1.467593 5.555005 -1.043135
C 0.201043 5.514814 -1.947534
C -2.300834 4.897657 -1.787563
N -2.251529 3.455230 -1.601575
C 2.010774 4.173991 -0.796771
C -1.963684 2.576409 -2.596658
O -2.004524 1.305211 -2.104191
O -1.712826 2.871366 -3.756473
H 0.200947 4.587350 -2.530060
H 0.240552 6.329467 -2.679243
H -2.340872 5.078400 -2.864626
H -3.237421 5.270460 -1.355205
H -2.343377 3.082546 -0.667706
C -1.859893 0.227867 -3.052268
H 3.731221 2.040274 3.220824
H 3.175688 3.499916 2.360853
H 1.980397 2.330146 3.029926
H 2.896849 1.781476 -0.621316
C -1.108769 5.620486 -1.143932
H -0.973592 5.207928 -0.138417
H -1.365602 6.678132 -1.001429
C -2.975771 -0.774559 -2.876536
C -2.723550 -2.135034 -3.086558
C -3.754357 -3.071420 -2.991510
C -5.048615 -2.660013 -2.670363
C -5.305281 -1.305452 -2.447070
C -4.276413 -0.369263 -2.553477
H -0.882220 -0.235284 -2.889726
H -1.869694 0.659502 -4.057836
H -4.480692 0.679268 -2.365840
H -5.850571 -3.388600 -2.592021
H -6.304757 -0.972537 -2.184379
H -1.714997 -2.465466 -3.321147
H -3.542608 -4.123373 -3.161356
H 2.249329 6.156075 -1.519698
H 1.227658 6.048440 -0.094211
H 2.708823 3.807113 -1.550735
H 0.985085 3.623188 0.982646
C 1.698121 1.218232 -3.760323
H 0.757439 1.769012 -3.884259
H 2.499850 1.925672 -3.505565
H 1.952411 0.756080 -4.717892
O 1.594029 0.163150 -2.805599
H 1.247958 0.525929 -1.976068

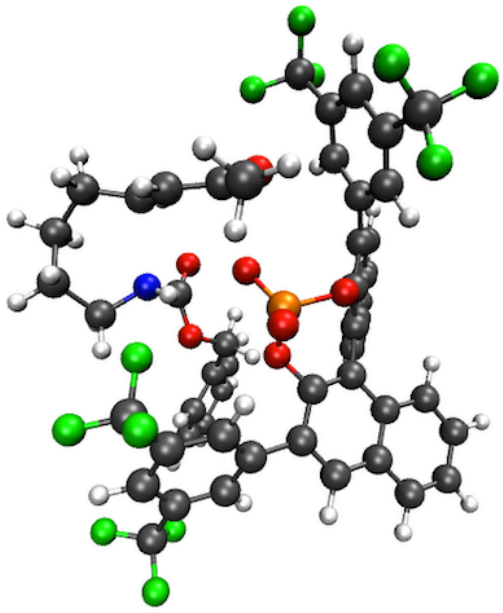


Figure SI - XI: Transition state geometry **e4** following methanol departure for full system prior to cyclization to form the minor enantiomer.

e4
111

C 2.628513 -4.399851 -2.487097
C 1.685813 -4.975833 -3.304484
C 2.244238 -3.685824 -1.321030
C 0.860395 -3.600559 -0.956954
C -0.086760 -4.195213 -1.837377
C 0.314865 -4.855539 -2.978884
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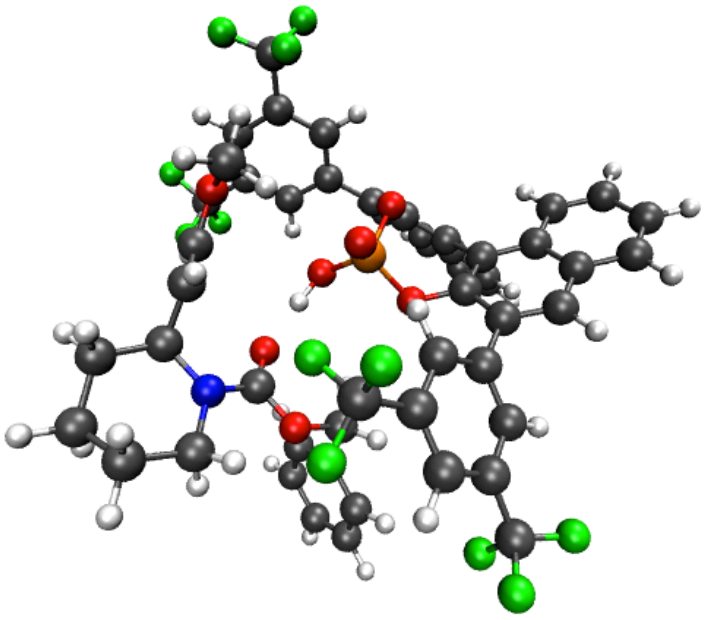

Figure SI - XII: Geometry for the minor enantiomer product, **e5**.

e5
111

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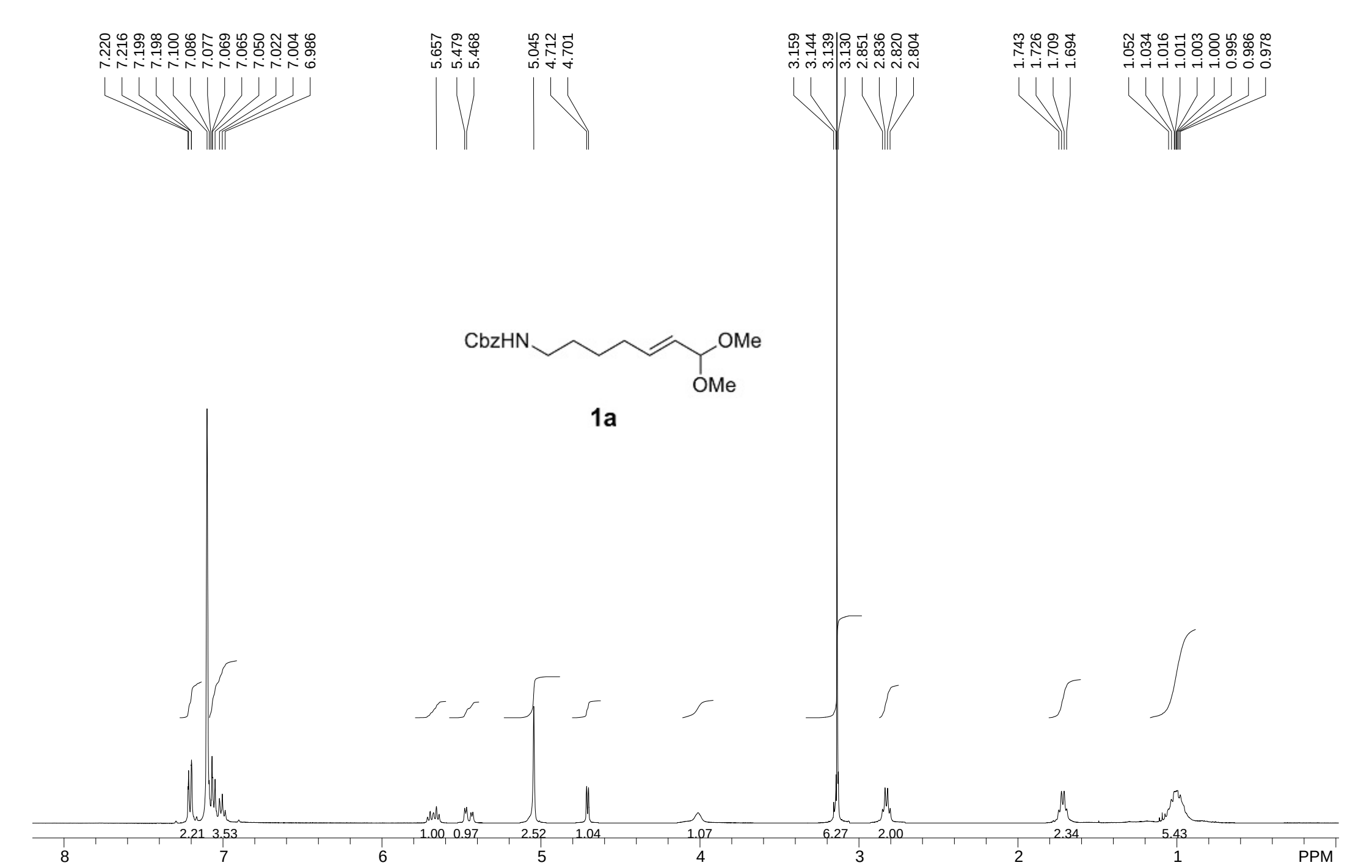
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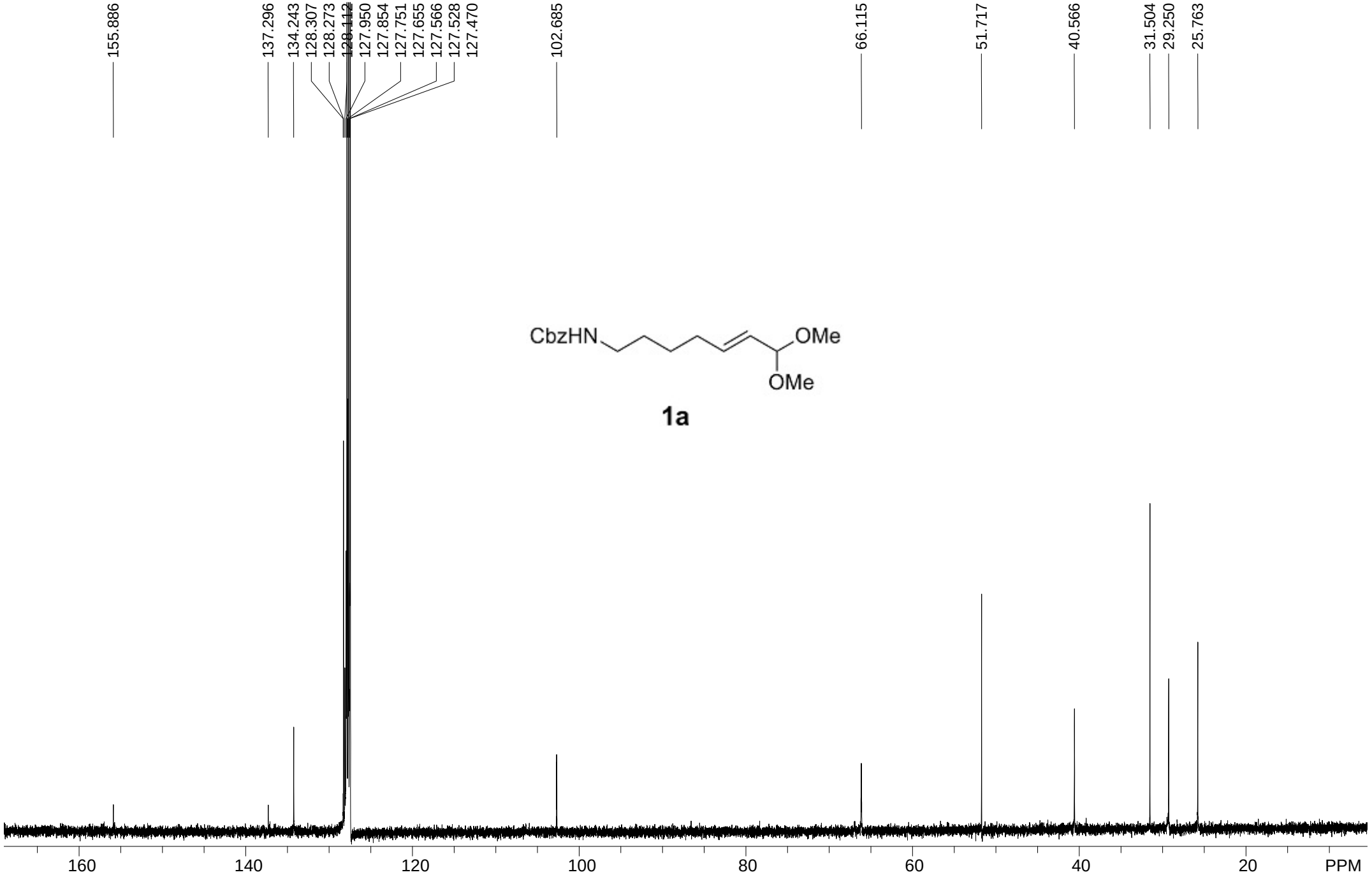
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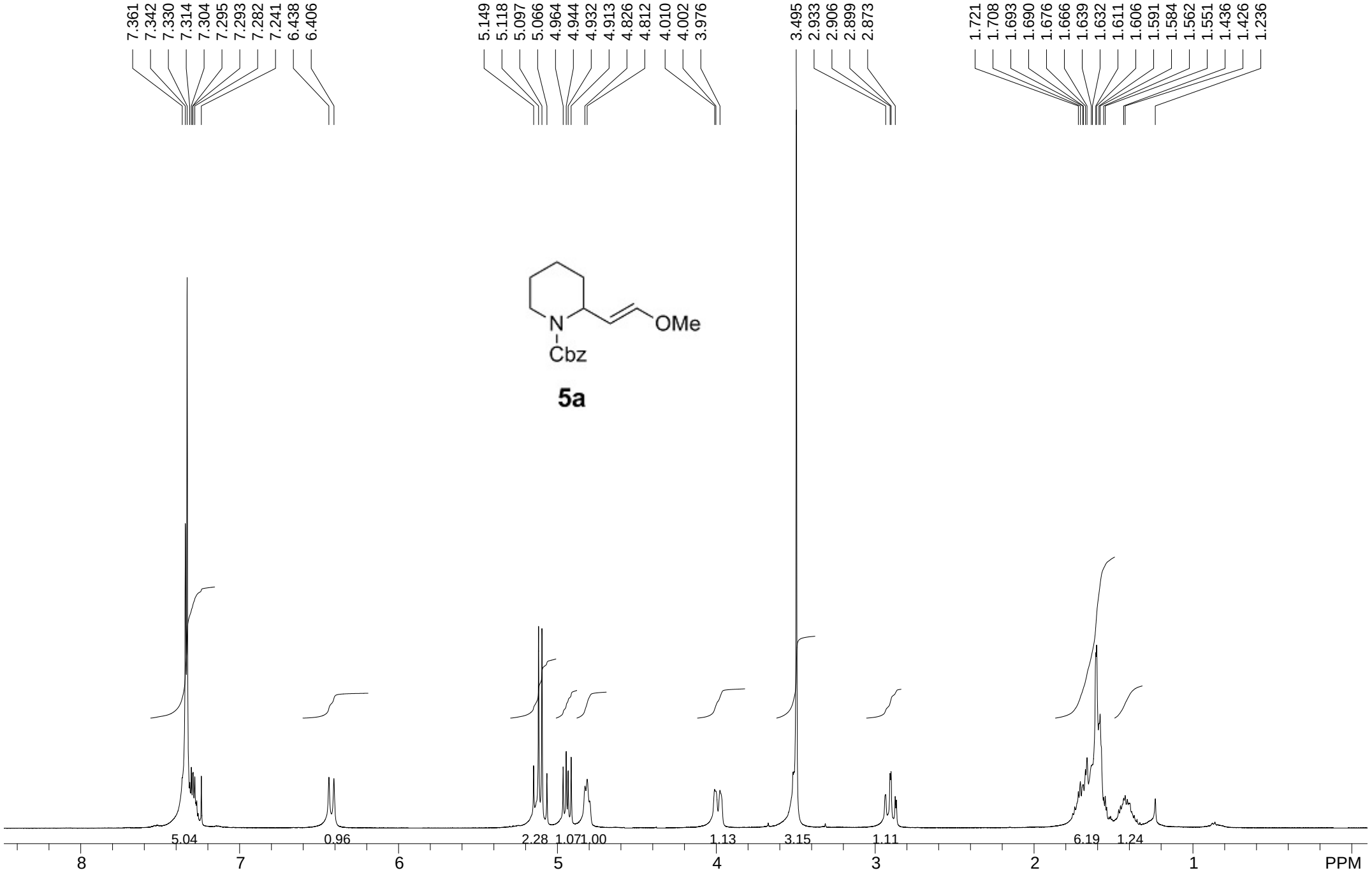
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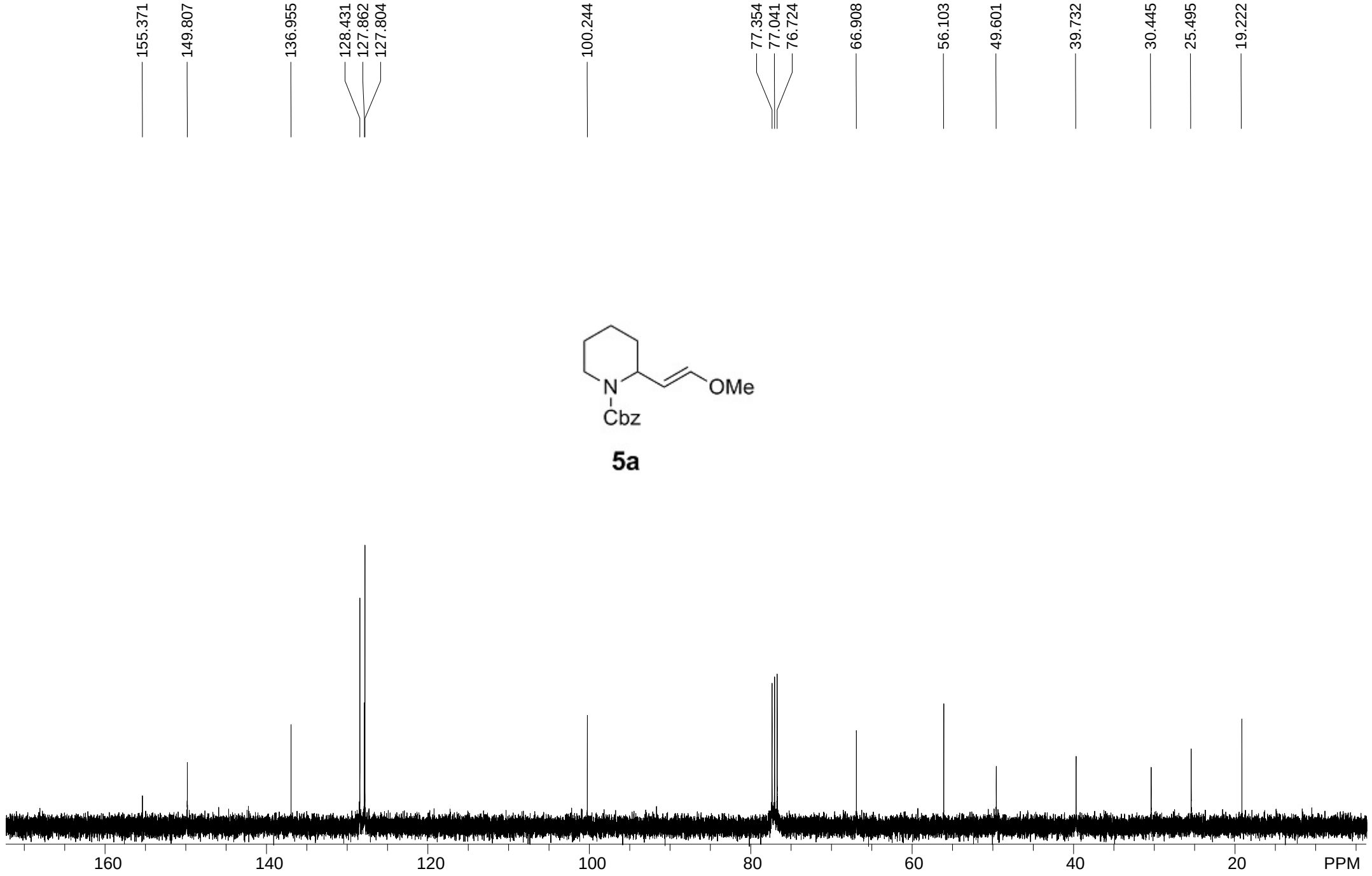
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80
60
40
20
PPM

5a

SAMPLE INFORMATION

Sample Name:	2_84_1_r	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	2_84_1_r
Vial:	89	Acq. Method Set:	adh 98% none gradient
Injection #:	1	Processing Method	NEW
Injection Volume:	10.00 ul	Channel Name:	215.0nm
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	PDA 215.0 nm
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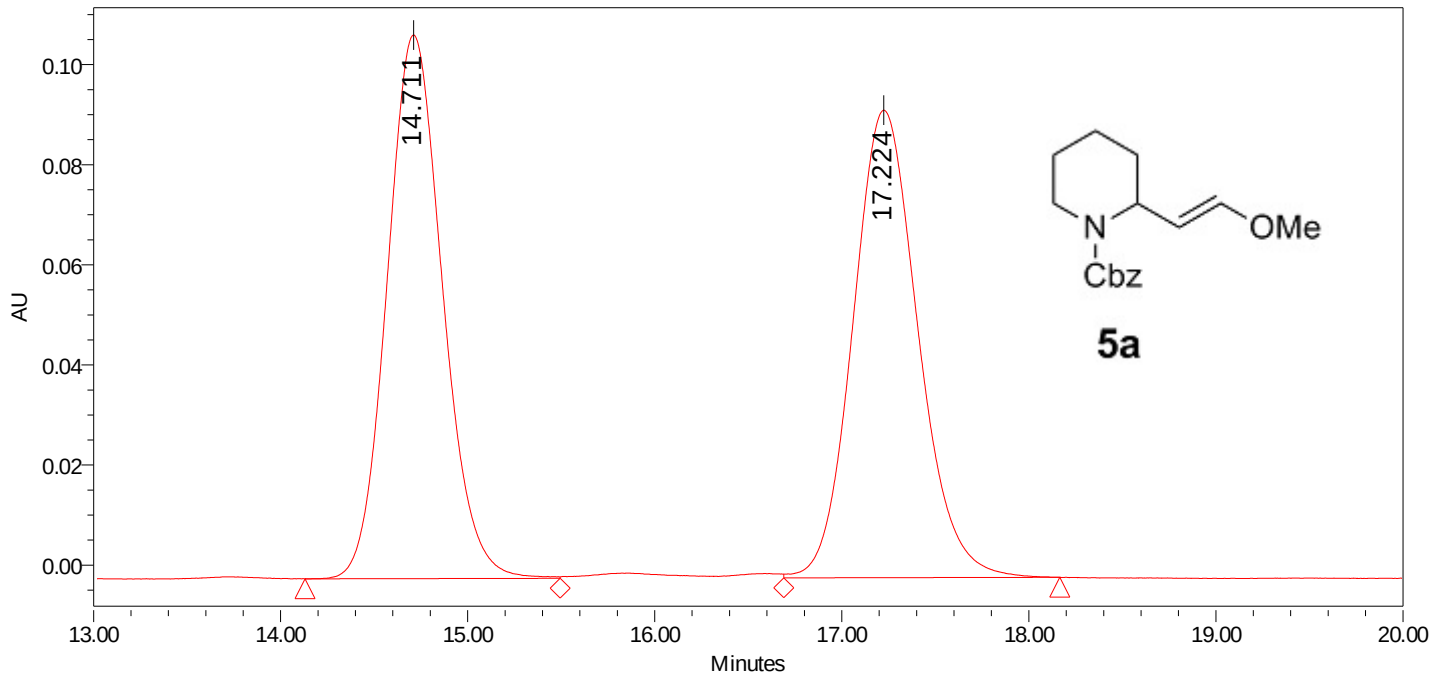
Date Processed:	9/12/2013 6:24:42 PM EDT		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	% Area
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2		17.224	2249728	93401	50.16

SAMPLE INFORMATION

Sample Name:	4_54_30h	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	4_54_30h
Vial:	59	Acq. Method Set:	adh 98%
Injection #:	1	Processing Method	NEW
Injection Volume:	10.00 ul	Channel Name:	210.3nm@3
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
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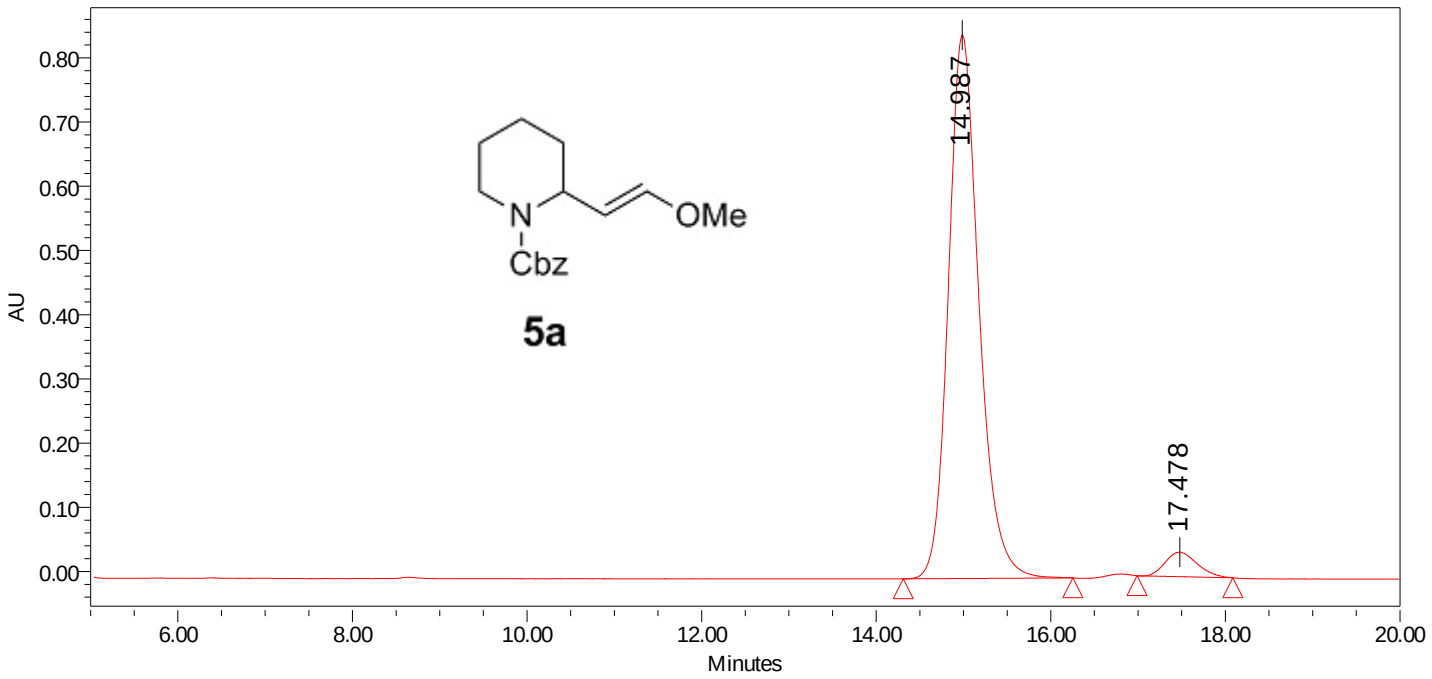
Auto-Scaled Chromatogram



Peak Results

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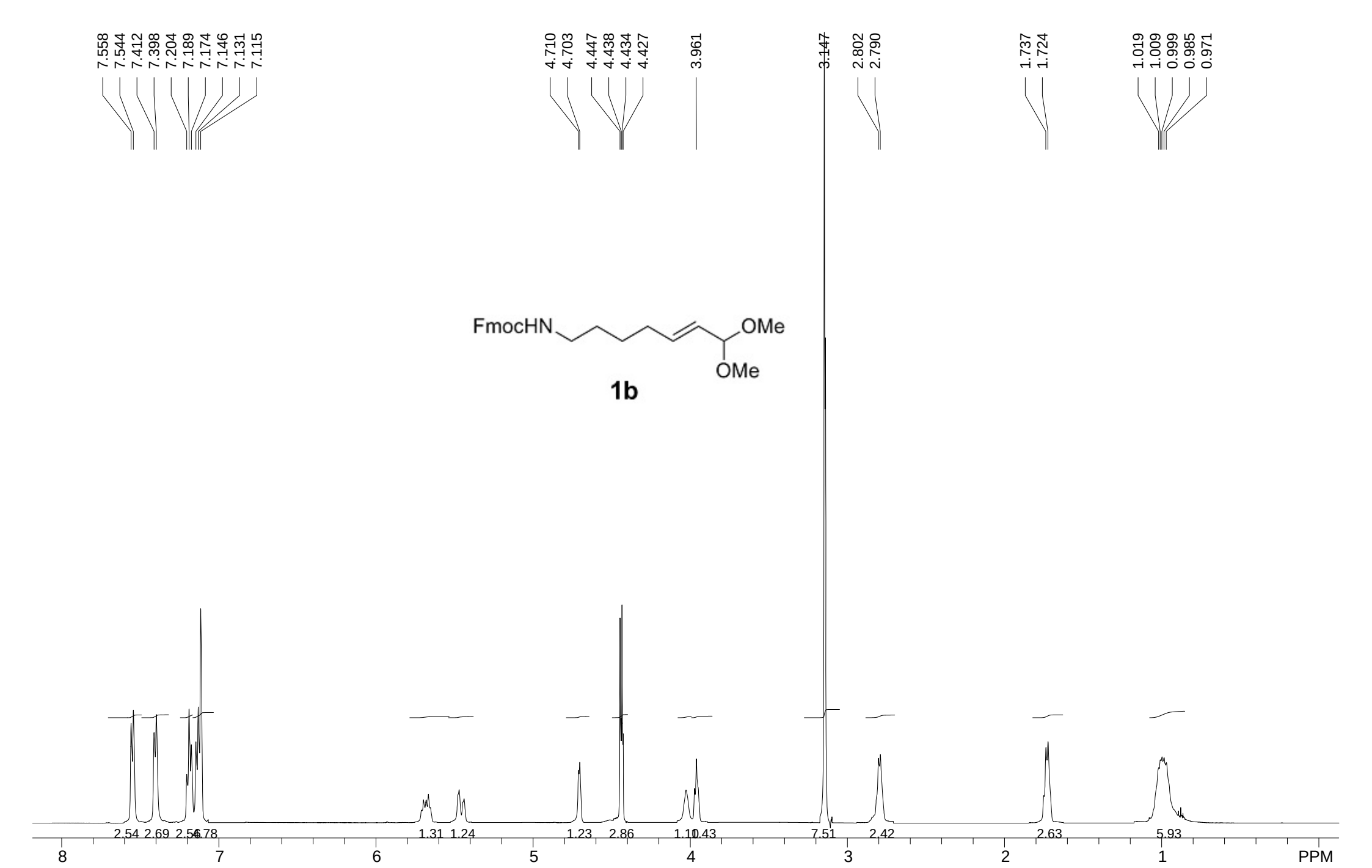
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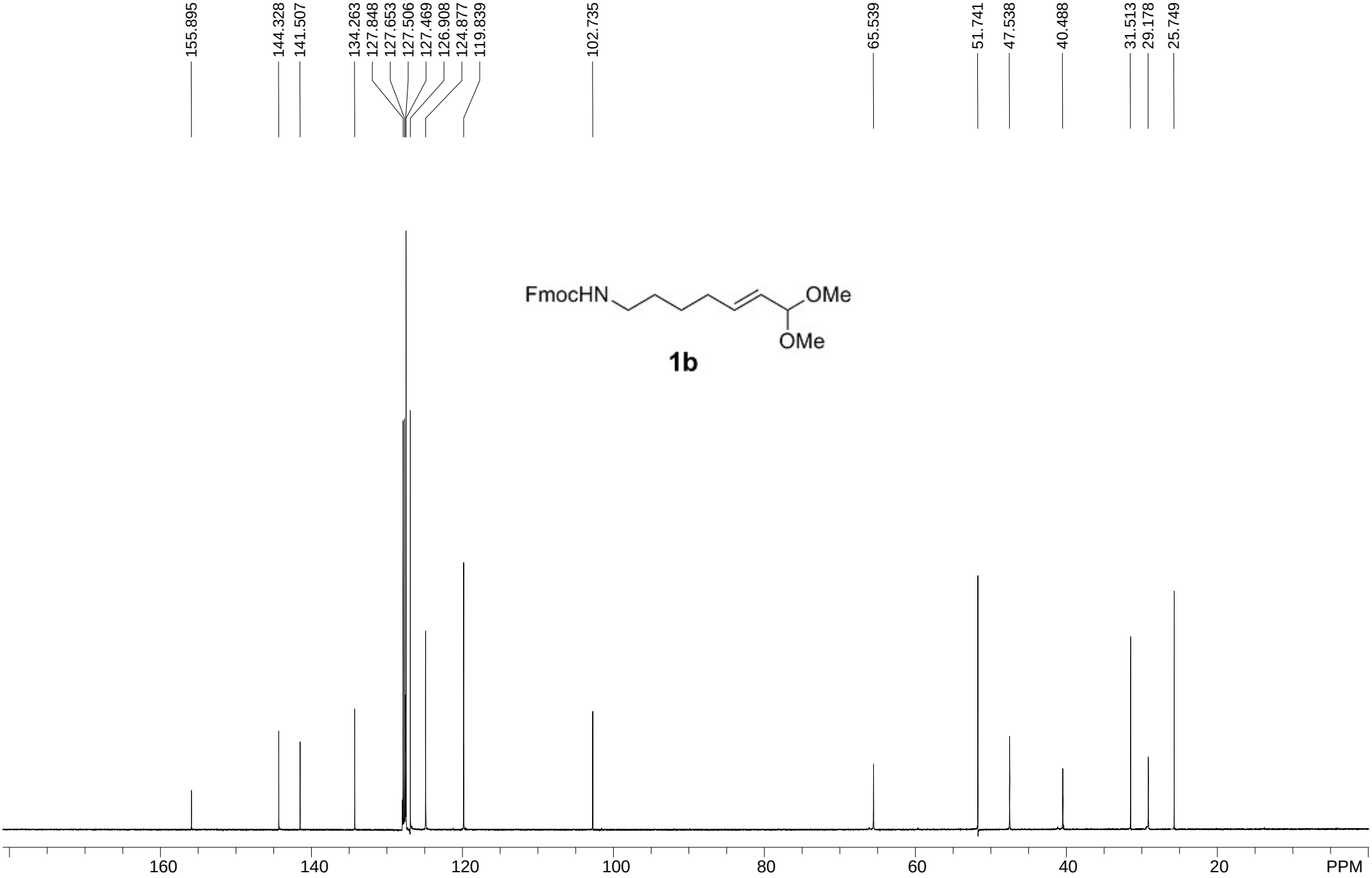
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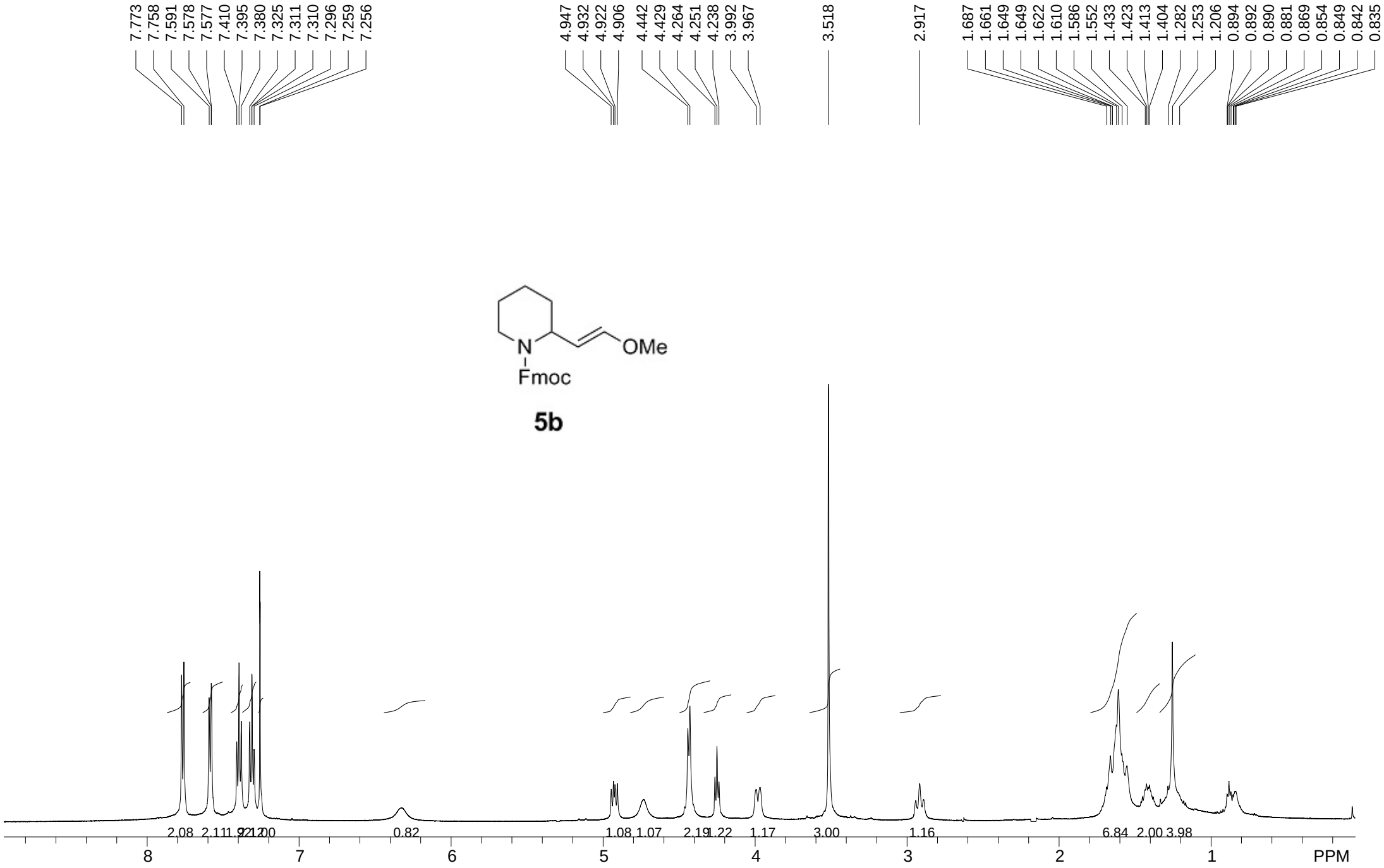
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7.259
7.256
4.947
4.932
4.922
4.906
4.442
4.429
4.264
4.251
4.238
3.992
3.967
3.518
2.917
1.687
1.661
1.649
1.649
1.622
1.610
1.586
1.552
1.433
1.423
1.413
1.404
1.282
1.253
1.206
0.894
0.892
0.890
0.881
0.869
0.854
0.849
0.842
0.835
N
Fmoc
OMe
5b
2.08
2.11
1.92
2.12
2.00
0.82
1.08
1.07
2.19
1.22
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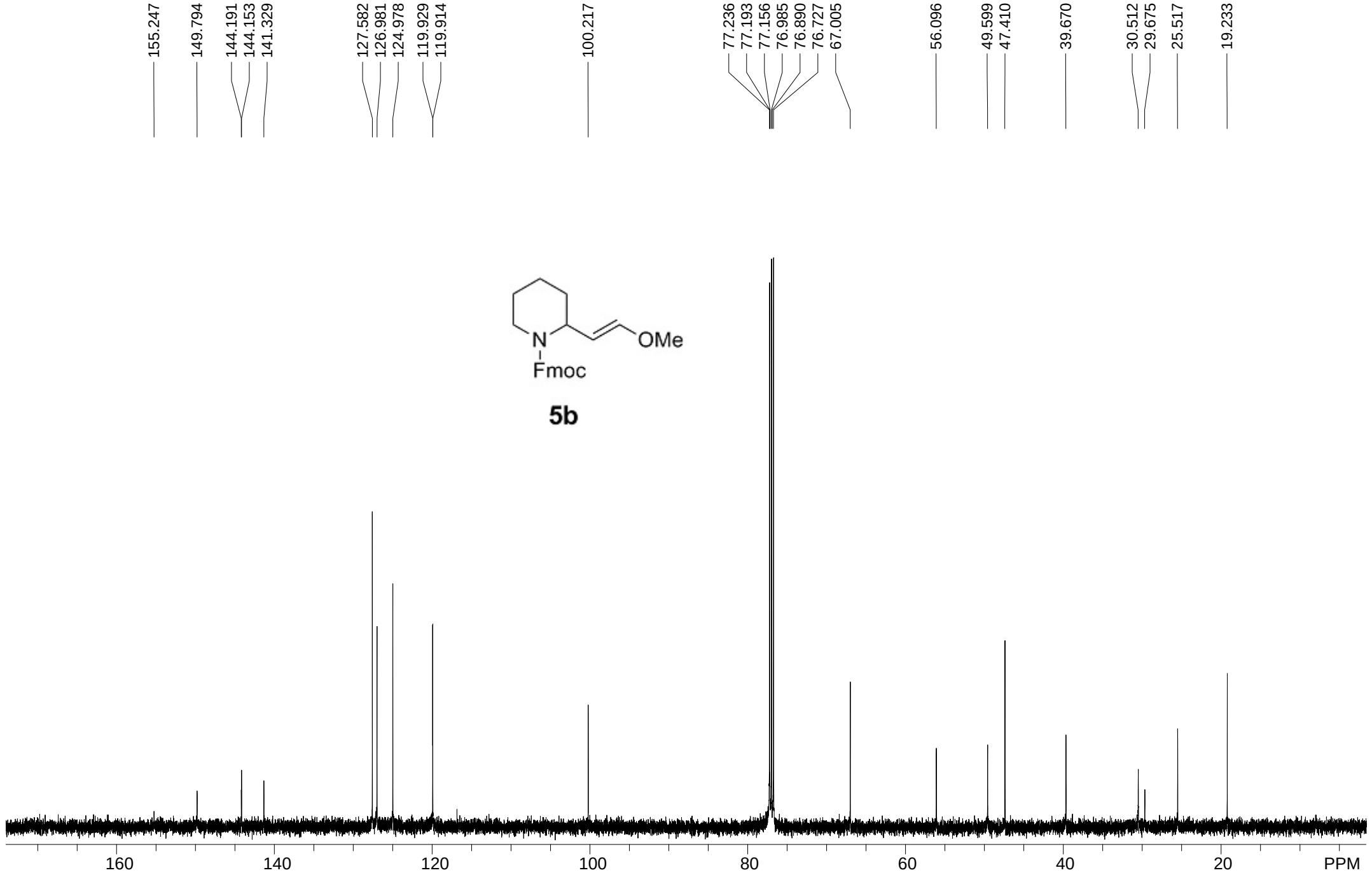
1.16
6.84
2.00
3.98
8
7
6
5
4
3
2
1
PPM

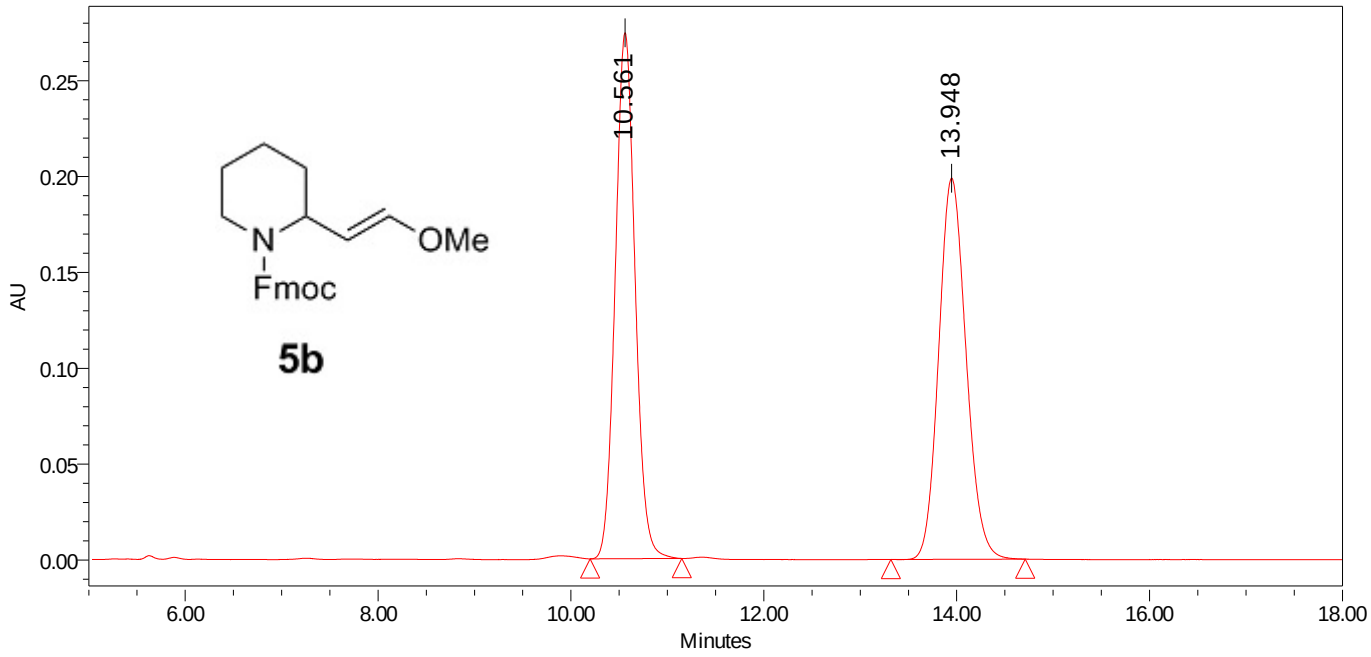

155.247
149.794
144.191
144.153
141.329
127.582
126.981
124.978
119.929
119.914
100.217
77.236
77.193
77.156
76.985
76.890
76.727
67.005
56.096
49.599
47.410
39.670
30.512
29.675
25.517
19.233
N
Fmoc
OMe
160
140
120
100
80
60
40
20
PPM

5b

SAMPLE INFORMATION

Sample Name:	2_139_1_r	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	2_139_1_r
Vial:	80	Acq. Method Set:	ADH 90%
Injection #:	1	Processing Method	NEW
Injection Volume:	10.00 ul	Channel Name:	284.5nm
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	PDA 284.5 nm
Date Acquired:	6/13/2012 7:31:23 PM EDT		
Date Processed:	9/12/2013 1:30:06 PM EDT		

Auto-Scaled Chromatogram



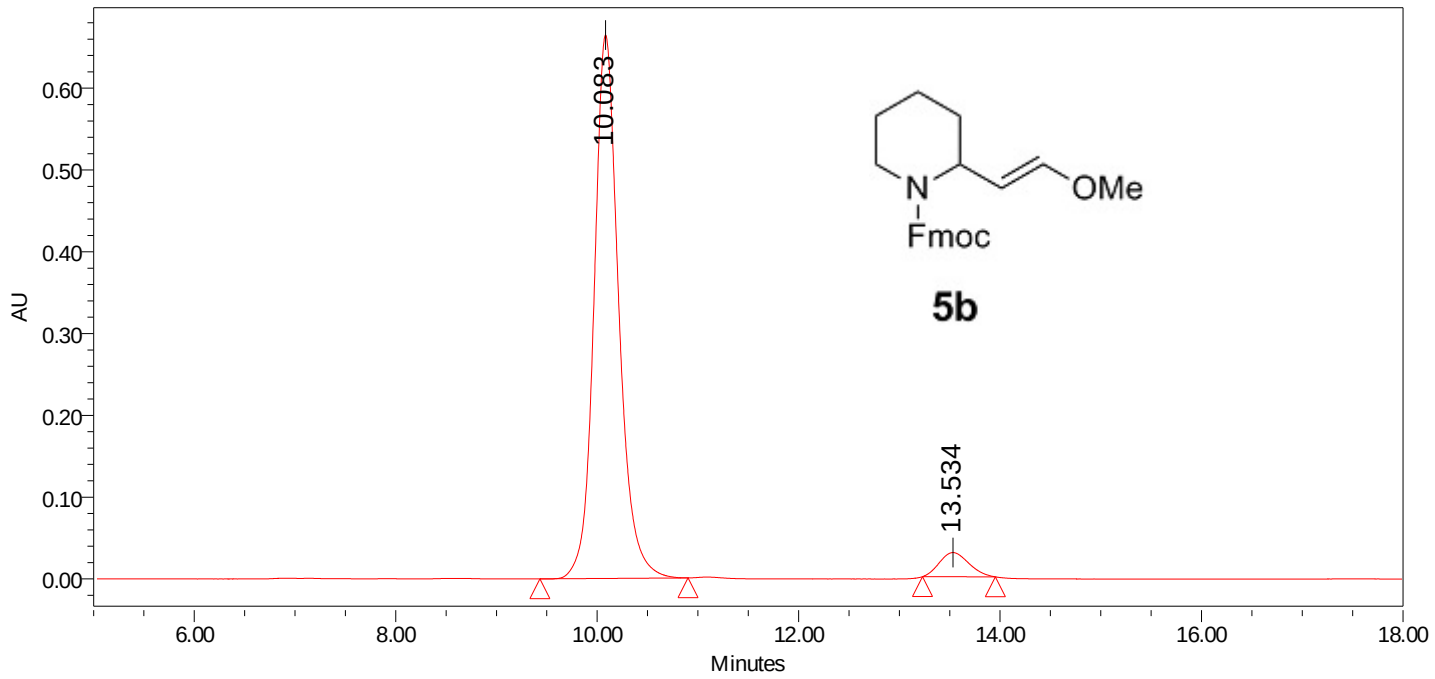
Peak Results

	Name	RT	Area	Height	% Area
1		10.561	3903848	274279	49.95
2		13.948	3911965	198783	50.05

SAMPLE INFORMATION

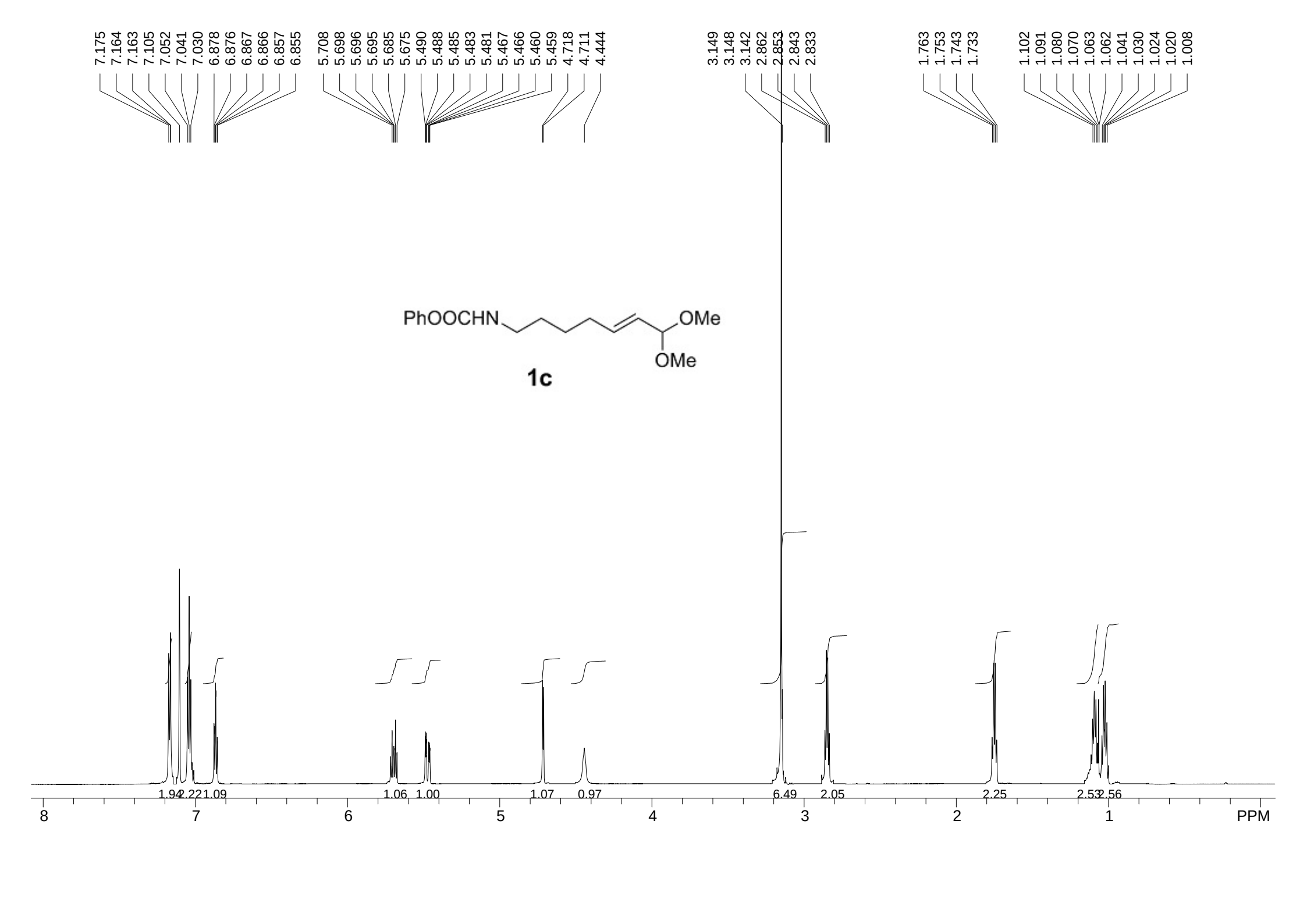
Sample Name:	3-270-1-30h	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	3_270_1_30h
Vial:	96	Acq. Method Set:	ADH 90%
Injection #:	1	Processing Method	NEW
Injection Volume:	5.00 ul	Channel Name:	220.0nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 220.0 nm
Date Acquired:	6/8/2013 12:53:26 PM EDT		
Date Processed:	9/12/2013 1:36:15 PM EDT		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	% Area
1		10.083	11278393	664451	94.95
2		13.534	599328	29568	5.05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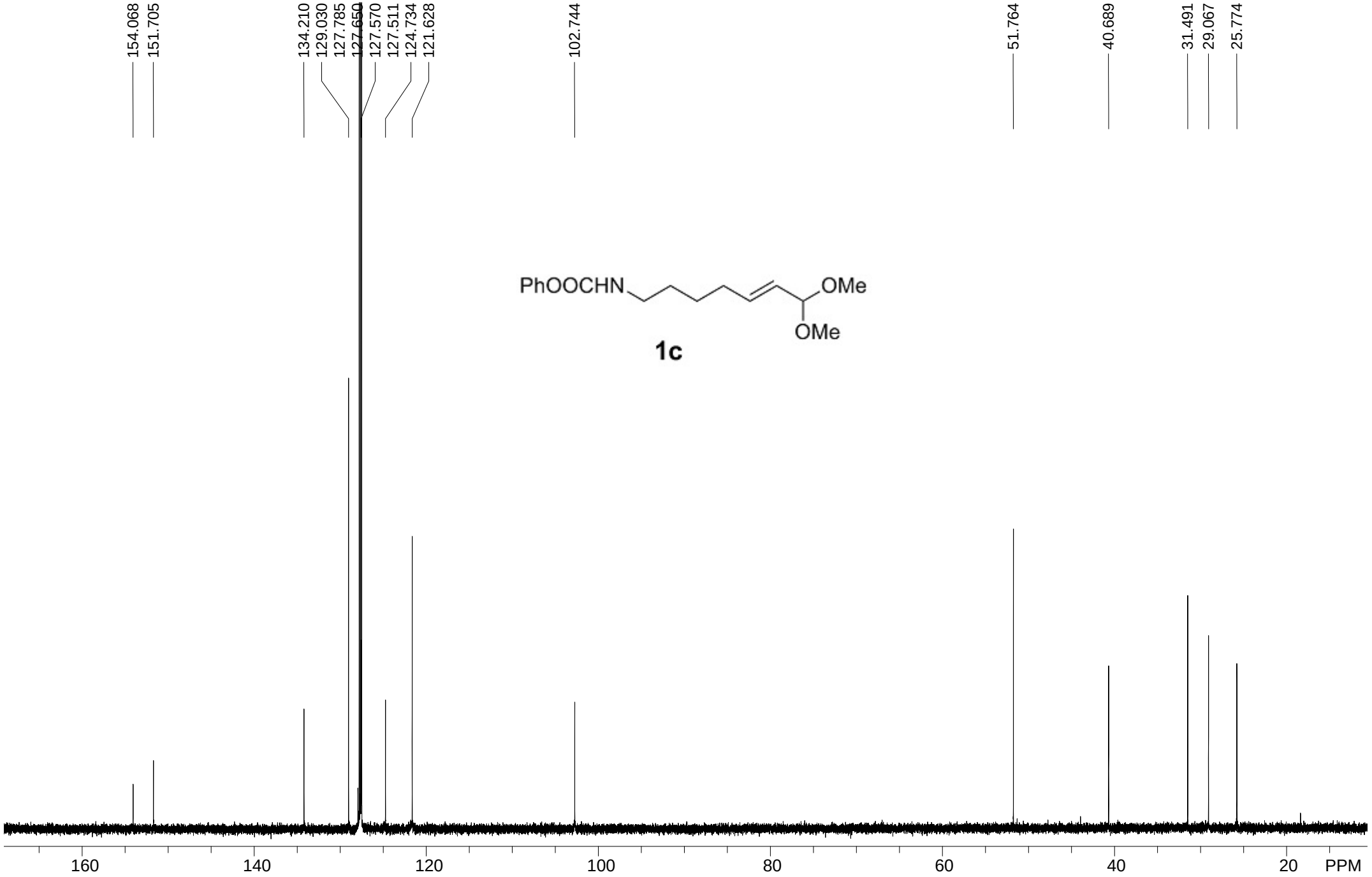
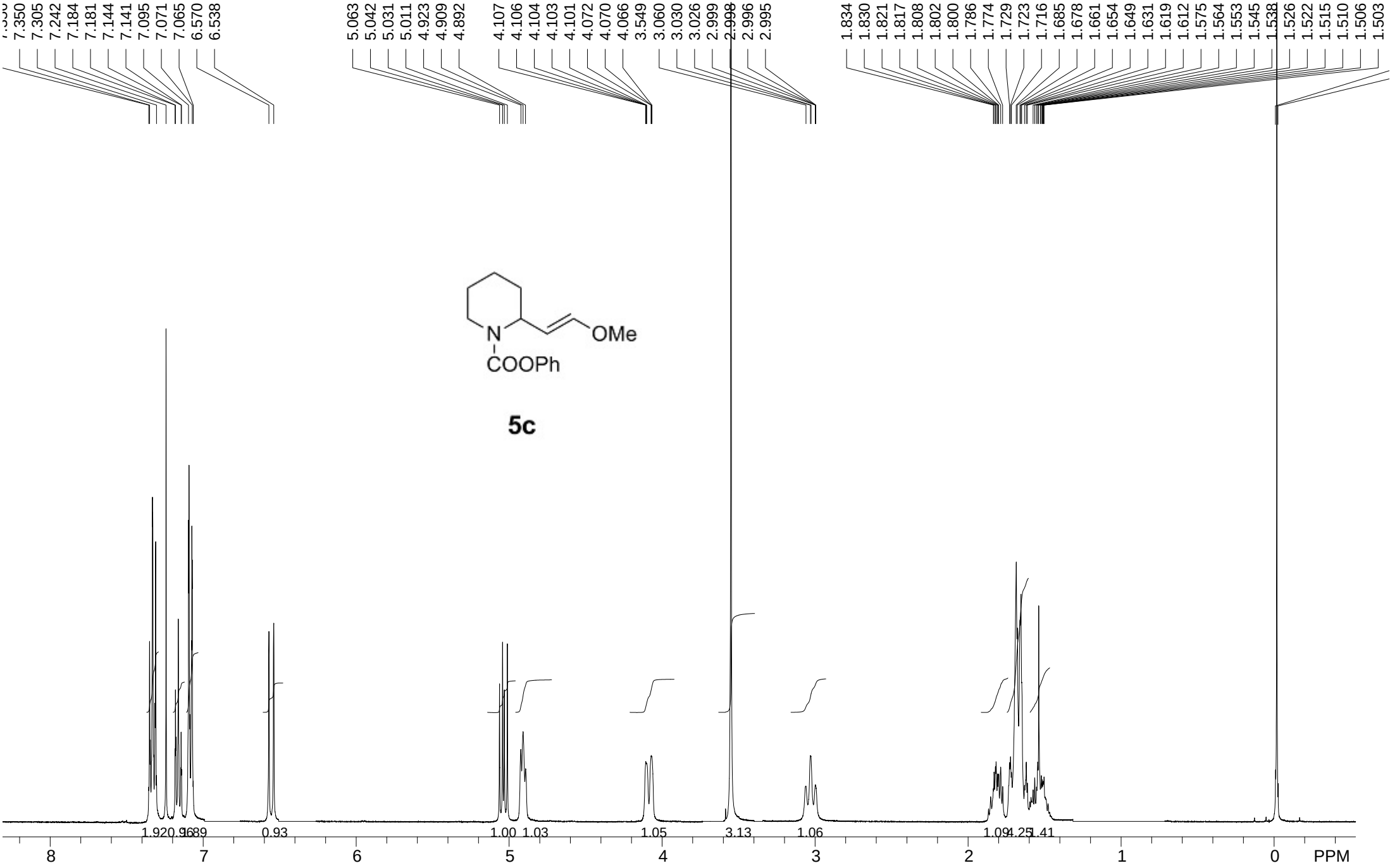
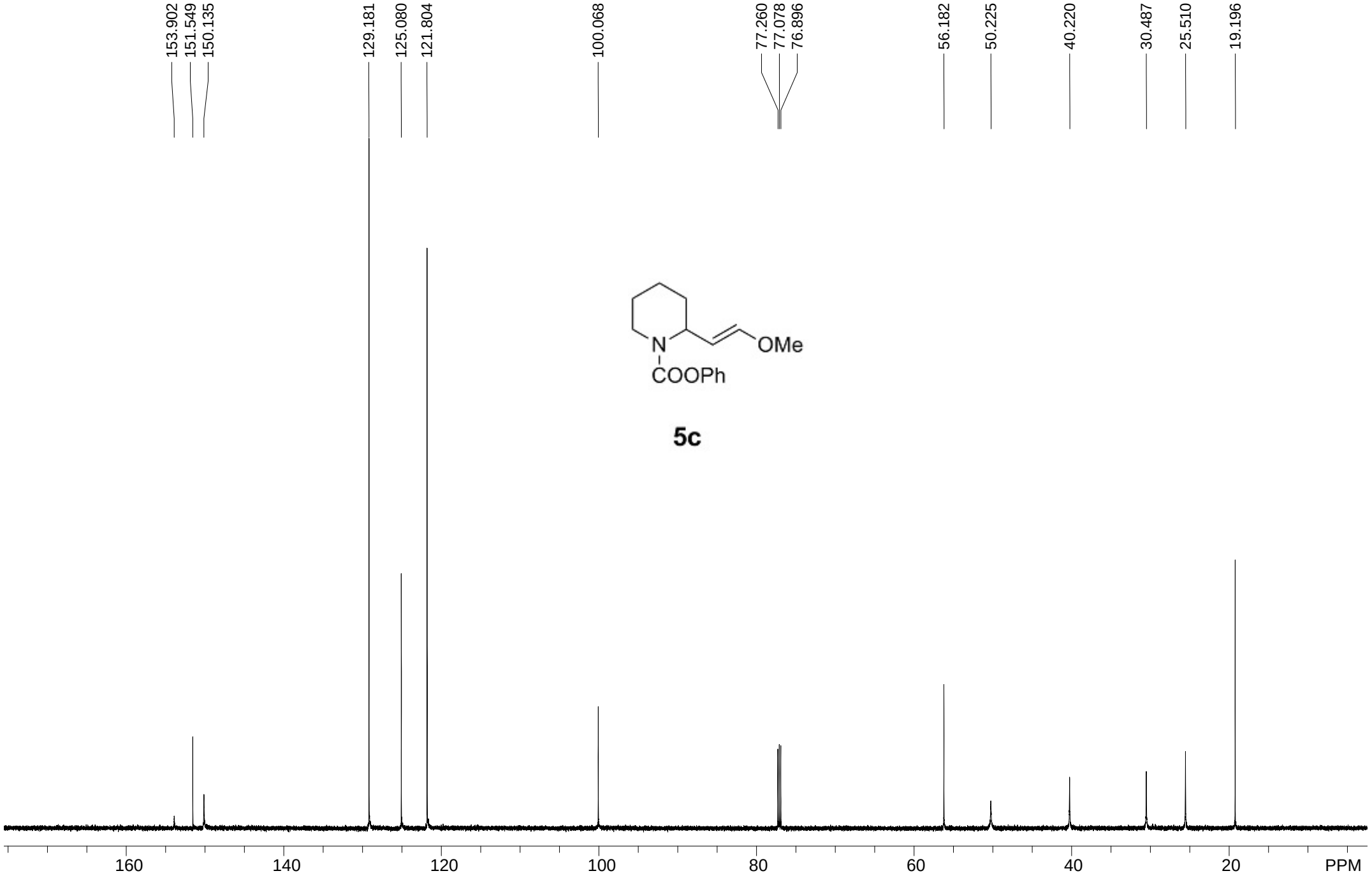
7.163
7.105
7.052
7.041
7.030
6.878
6.876
6.867
6.866
6.857
6.855
5.708
5.698
5.696
5.695
5.685
5.675
5.490
5.488
5.485
5.483
5.481
5.467
5.466
5.460
5.459
4.718
4.711
4.444
3.149
3.148
3.142
2.862
2.853
2.843
2.833
1.763
1.753
1.743
1.733
1.102
1.091
1.080
1.070
1.063
1.062
1.041
1.030
1.024
1.020
1.008
PhOOCHN
OMe
OMe
1c
1.94
2.22
1.09
1.06
1.00
1.07
0.97
6.49
2.05
2.25
2.53
2.56
8
7
6
5
4
3
2
1
PPM


154.068
151.705
134.210
129.030
127.785
127.650
127.570
127.511
124.734
121.628
102.744
51.764
40.689
31.491
29.067
25.774
PhOOCHN
OMe
OMe
1c
160
140
120
100
80
60
40
20
PPM


7.350
7.305
7.242
7.184
7.181
7.144
7.141
7.095
7.071
7.065
6.570
6.538
5.063
5.042
5.031
5.011
4.923
4.909
4.892
4.107
4.106
4.104
4.103
4.101
4.072
4.070
4.066
3.549
3.060
3.030
3.026
2.999
2.998
2.996
2.995
1.834
1.830
1.821
1.817
1.808
1.802
1.800
1.786
1.774
1.729
1.723
1.716
1.685
1.678
1.661
1.654
1.649
1.631
1.619
1.612
1.575
1.564
1.553
1.545
1.538
1.526
1.522
1.515
1.510
1.506
1.503
N
OMe
COOPh
5c
1.92
0.96
0.89
0.93
1.00
1.03
1.05
3.13
1.06
1.09
4.25
1.41
8
7
6
5
4
3
2
1
0
PPM

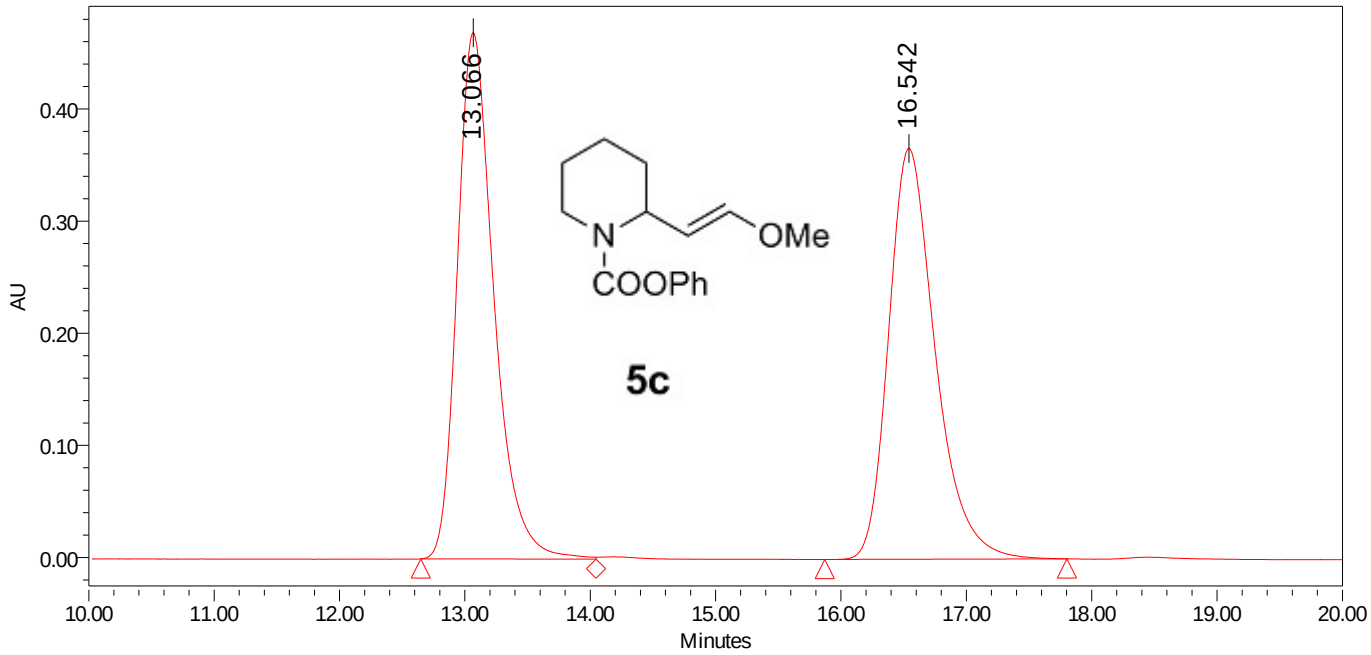

153.902
151.549
150.135
129.181
125.080
121.804
100.068
77.260
77.078
76.896
56.182
50.225
40.220
30.487
25.510
19.196
N
COOPh
OMe
160
140
120
100
80
60
40
20
PPM

5c

SAMPLE INFORMATION

Sample Name:	3-135-1-r	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	3_135_1_R
Vial:	29	Acq. Method Set:	adh 98%
Injection #:	1	Processing Method	NEW
Injection Volume:	20.00 ul	Channel Name:	210.3nm@5
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	2/21/2013 5:07:17 PM EST		
Date Processed:	9/12/2013 6:30:22 PM EDT		

Auto-Scaled Chromatogram



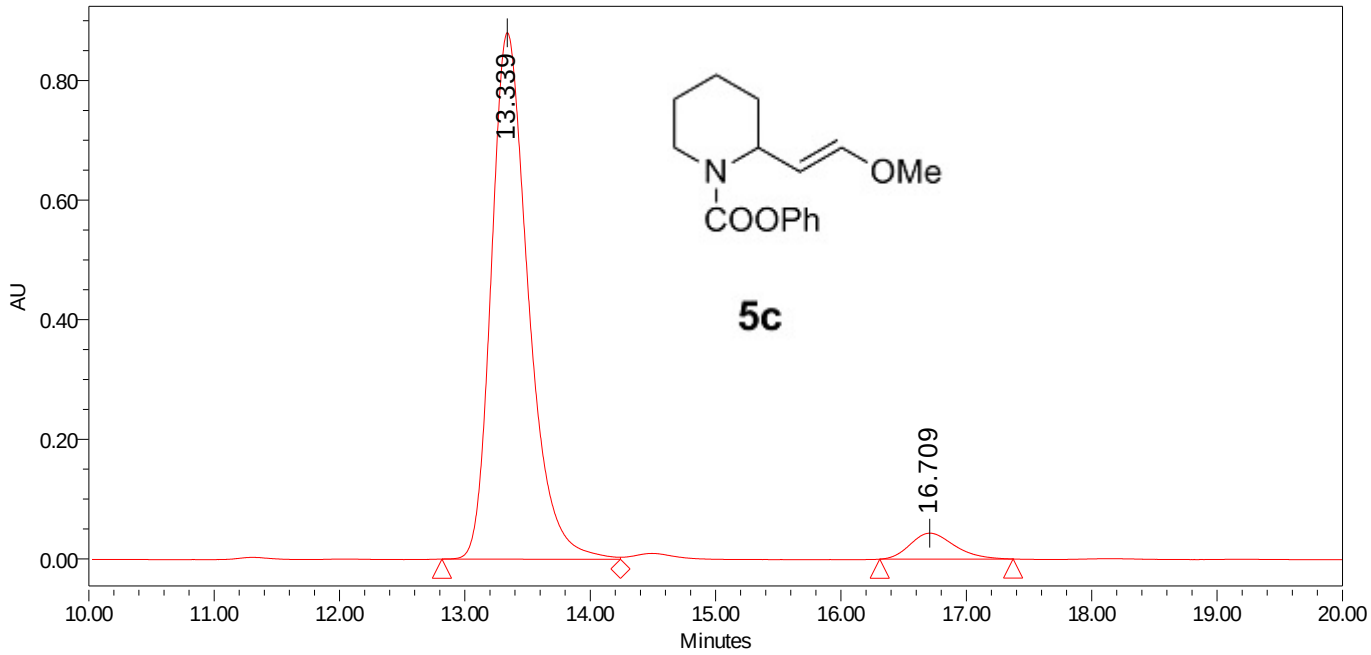
Peak Results

	Name	RT	Area	Height	% Area
1		13.066	9516541	469227	50.15
2		16.542	9458875	366382	49.85

SAMPLE INFORMATION

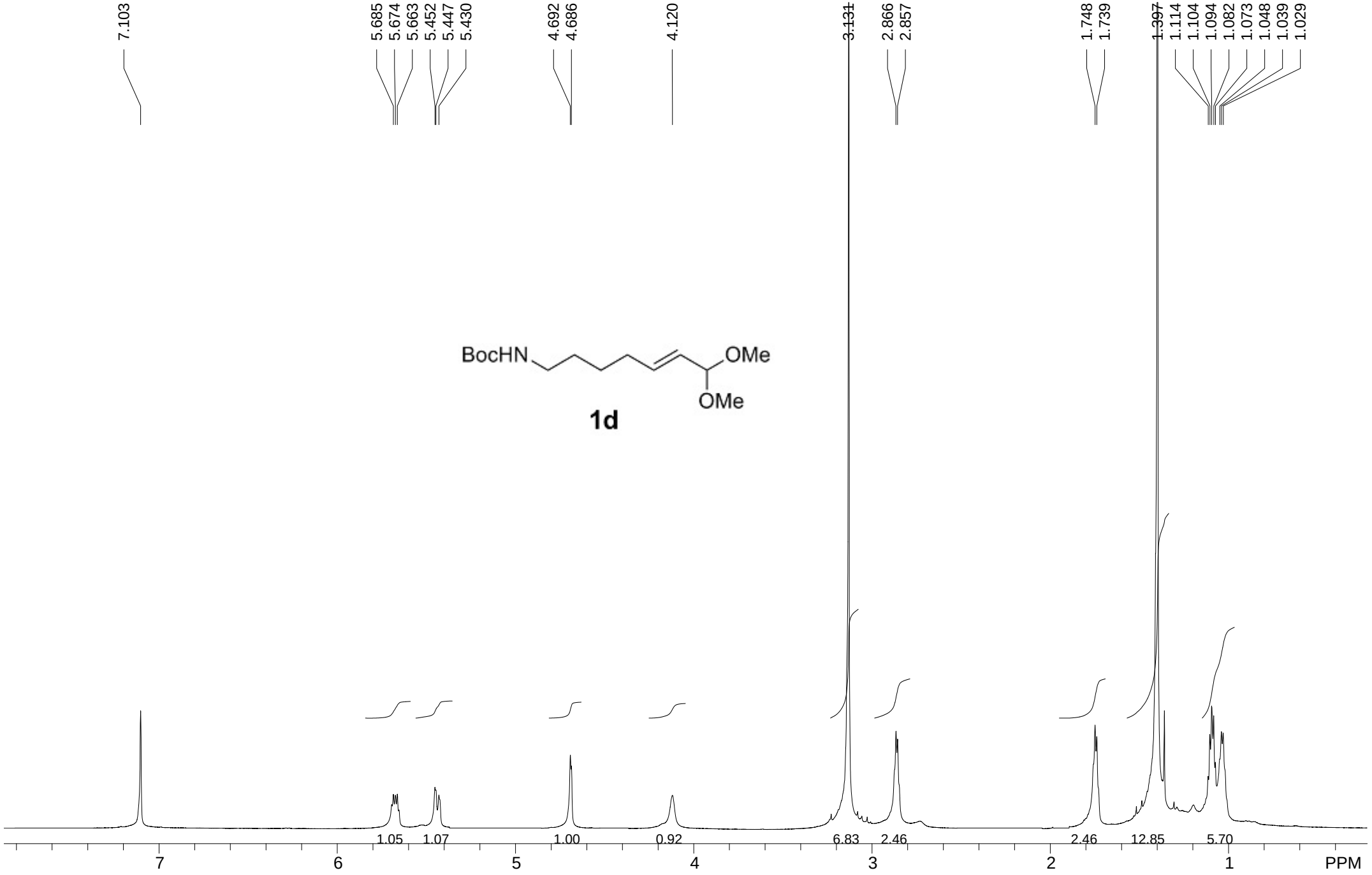
Sample Name:	3-276-1-48h	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	3_276_48h
Vial:	44	Acq. Method Set:	adh 98%
Injection #:	1	Processing Method	NEW
Injection Volume:	10.00 ul	Channel Name:	210.3nm@4
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	6/13/2013 8:30:13 PM EDT		
Date Processed:	9/12/2013 6:27:01 PM EDT		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	% Area
1		13.339	18041520	880443	94.45
2		16.709	1059463	43380	5.55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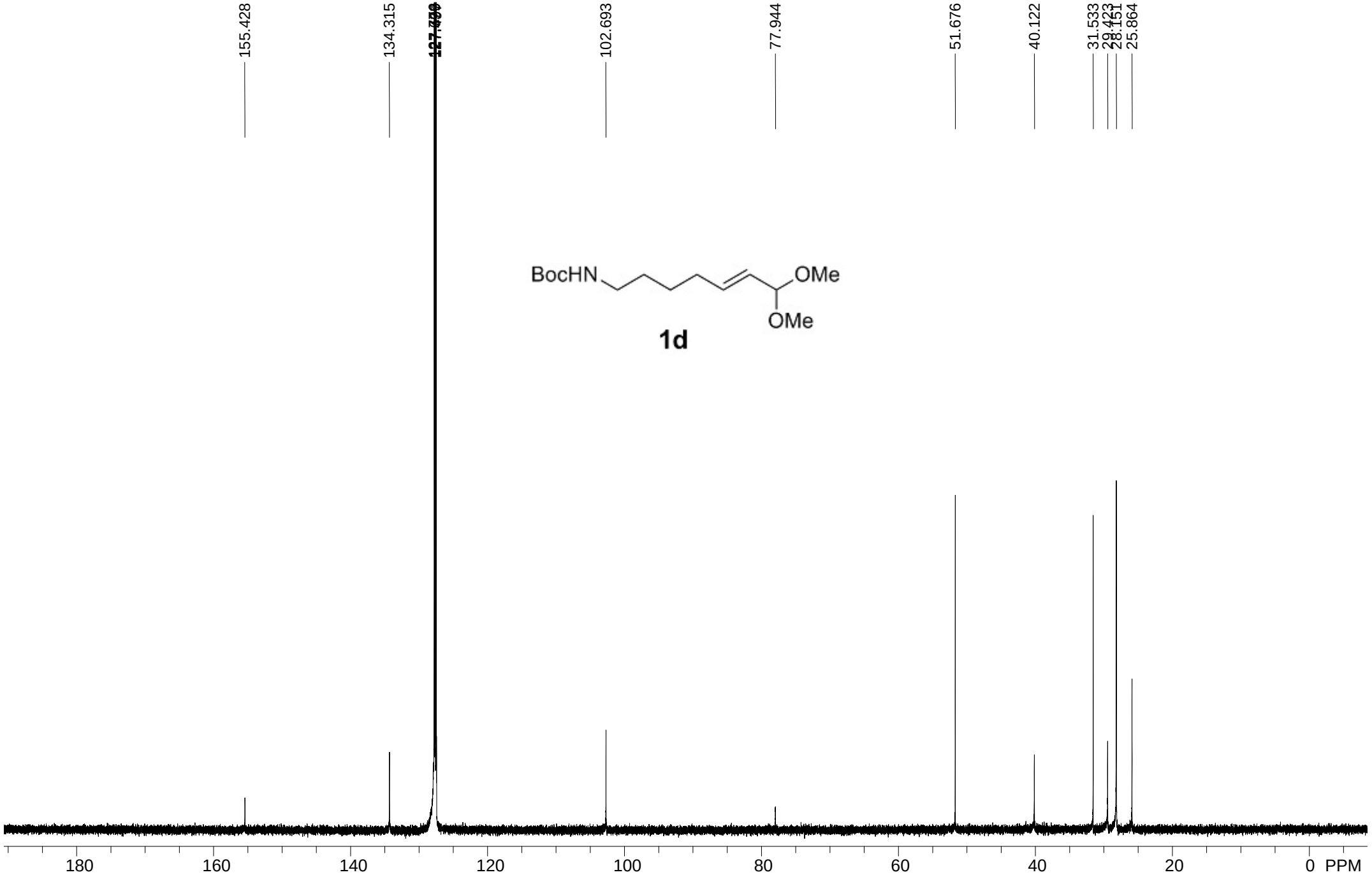
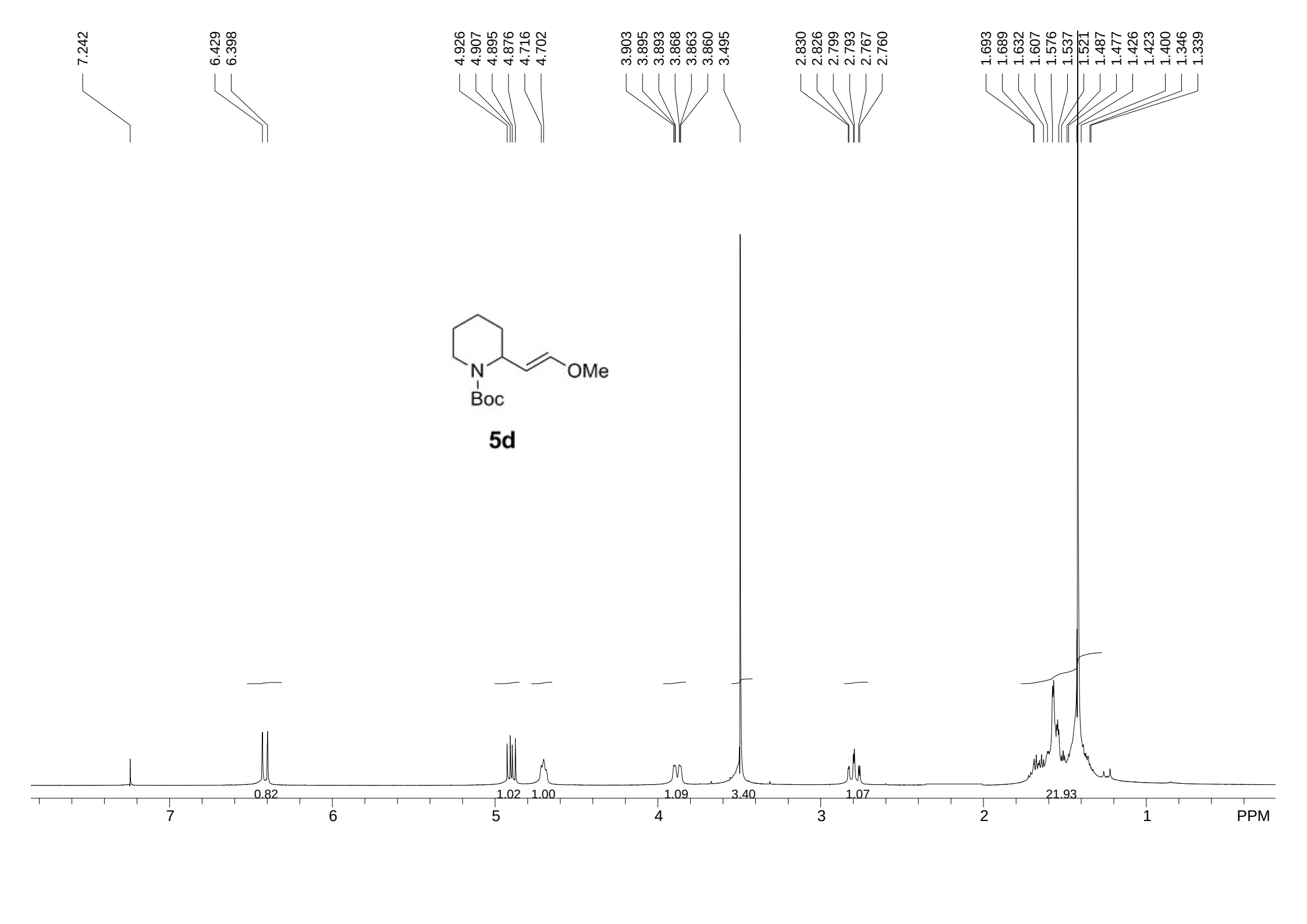
5.674
5.663
5.452
5.447
5.430
4.692
4.686
4.120
3.131
2.866
2.857
1.748
1.739
1.397
1.114
1.104
1.094
1.082
1.073
1.048
1.039
1.029
BocHN
OMe
OMe
1d
1.05
1.07
1.00
0.92
6.83
2.46
2.46
12.85
5.70
7
6
5
4
3
2
1
PPM


155.428
134.315
102.693
77.944
51.676
40.122
31.533
29.423
28.151
25.864
BocHN
OMe
OMe
1d
180
160
140
120
100
80
60
40
20
0
PPM


7.242
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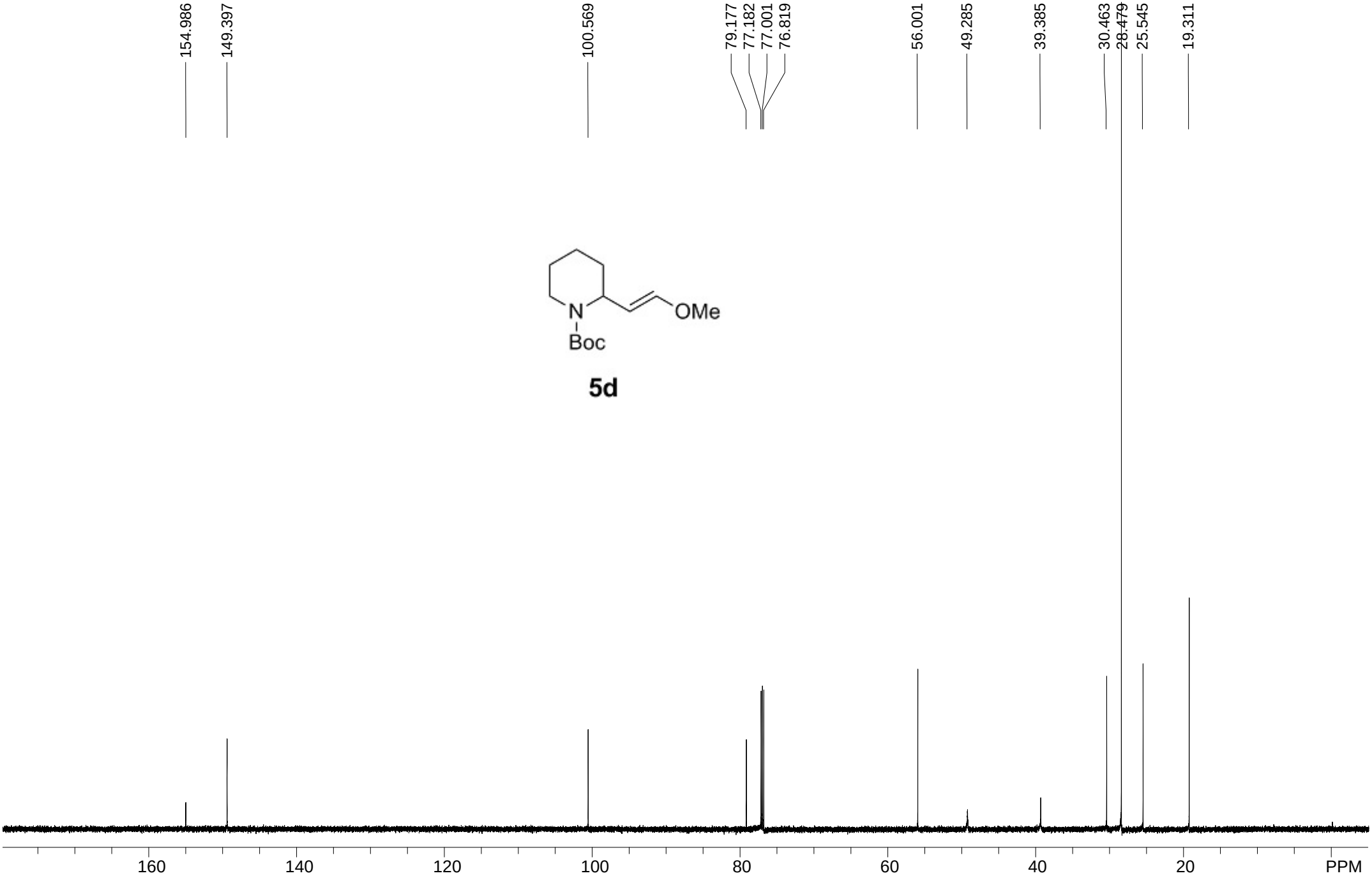
4.926
4.907
4.895
4.876
4.716
4.702
3.903
3.895
3.893
3.868
3.863
3.860
3.495
2.830
2.826
2.799
2.793
2.767
2.760
1.693
1.689
1.632
1.607
1.576
1.537
1.521
1.487
1.477
1.426
1.423
1.400
1.346
1.339
N
Boc
OMe
5d
0.82
1.02
1.00
1.09
3.40
1.07
21.93
7
6
5
4
3
2
1
PPM

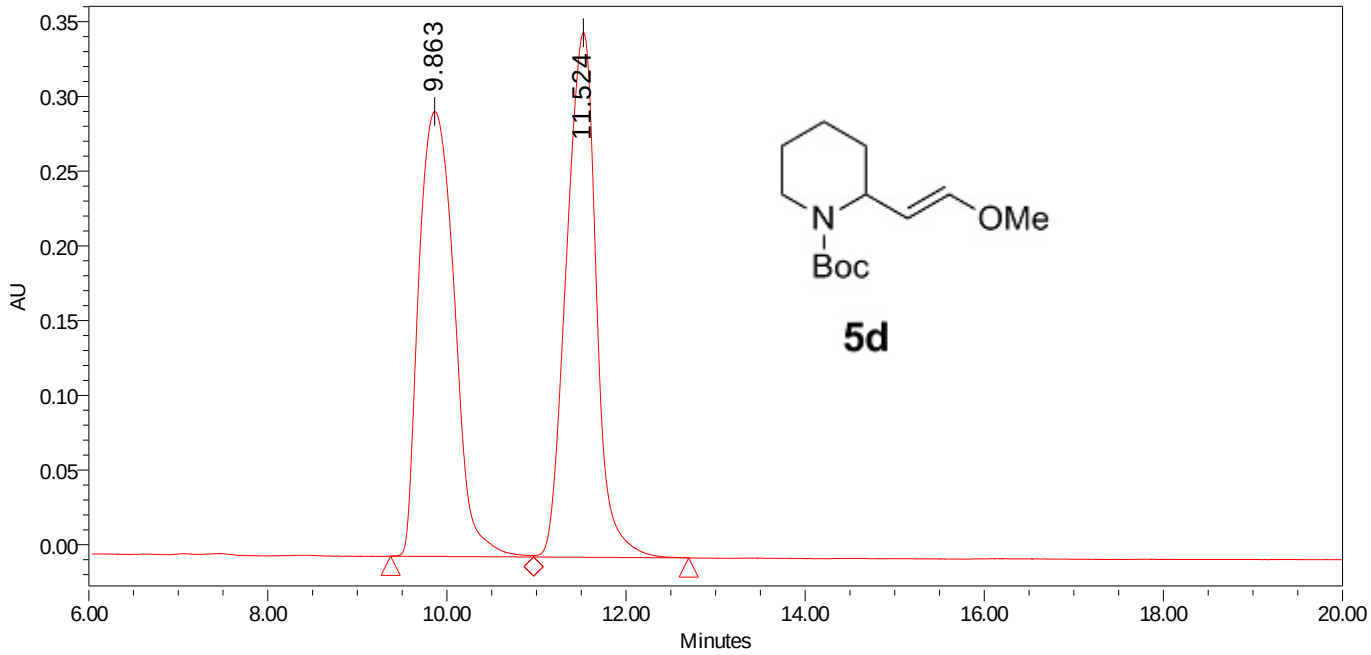

154.986
149.397
100.569
79.177
77.182
77.001
76.819
56.001
49.285
39.385
30.463
28.479
25.545
19.311
N
Boc
OMe
160
140
120
100
80
60
40
20
PPM

5d

SAMPLE INFORMATION

Sample Name:	3-139-1-R	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	3_139_1_R
Vial:	89	Acq. Method Set:	ADH 995
Injection #:	1	Processing Method	NEW
Injection Volume:	10.00 ul	Channel Name:	210.3nm
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	2/22/2013 7:56:08 PM EST		
Date Processed:	9/12/2013 6:36:03 PM EDT		

Auto-Scaled Chromatogram



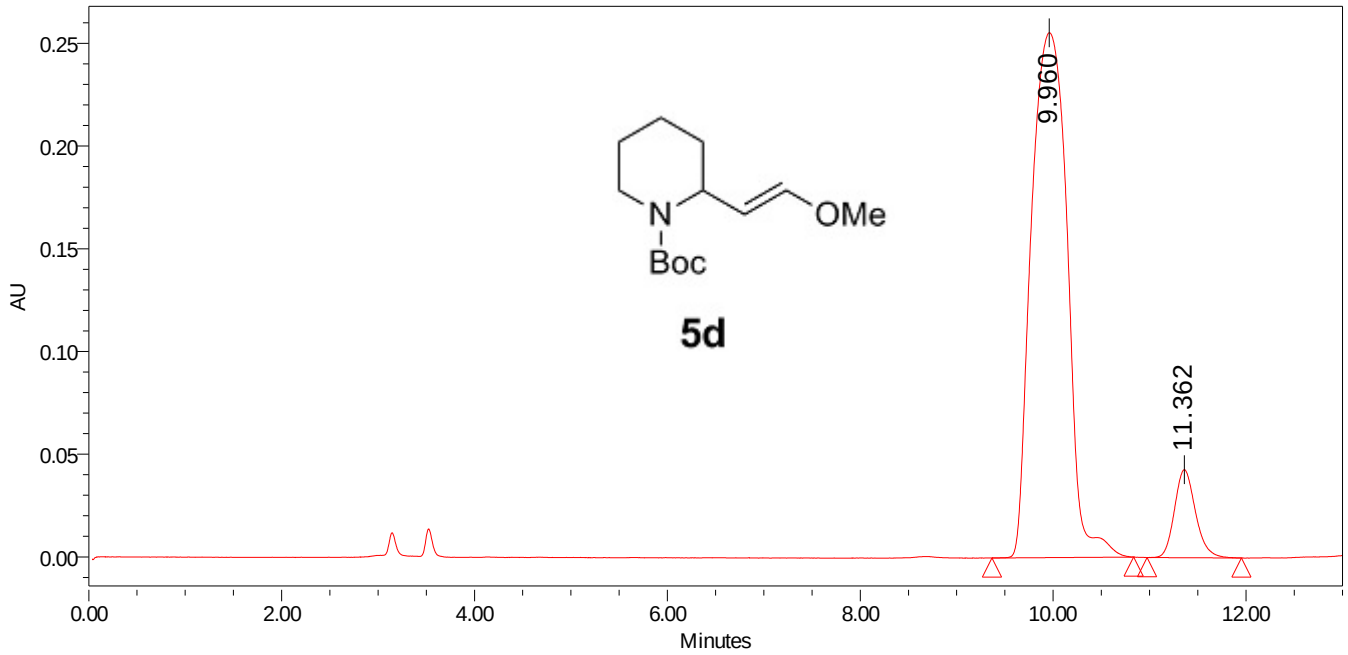
Peak Results

	Name	RT	Area	Height	% Area
1		9.863	8198523	297669	50.22
2		11.524	8126798	350938	49.78

SAMPLE INFORMATION

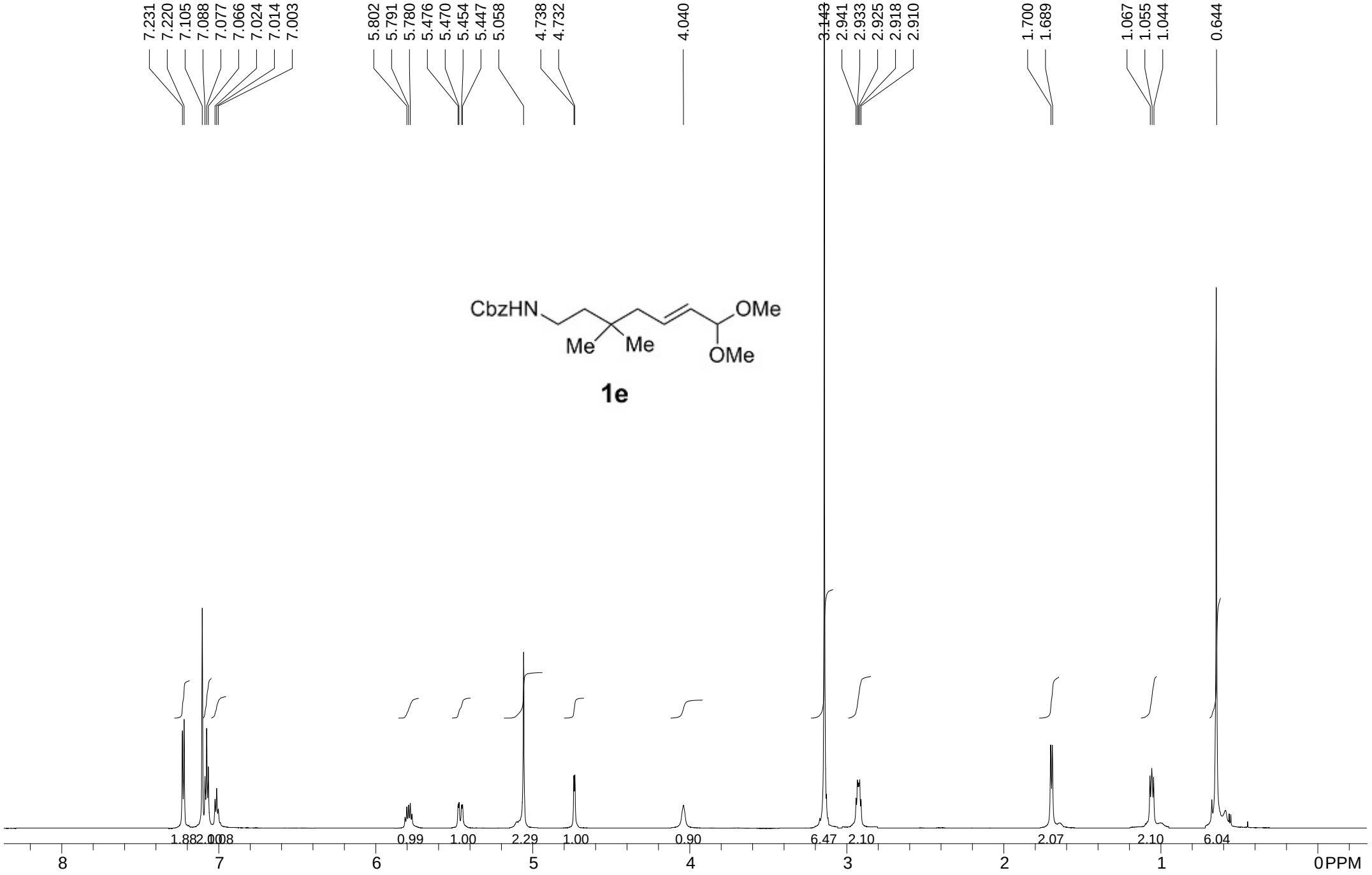
Sample Name:	3-277-48h	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	3_277_48h
Vial:	44	Acq. Method Set:	ADH 995
Injection #:	1	Processing Method	NEW
Injection Volume:	10.00 ul	Channel Name:	210.3nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	6/14/2013 11:44:47 AM EDT		
Date Processed:	9/12/2013 6:40:32 PM EDT		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	% Area
1		9.960	6610675	255527	91.08
2		11.362	647654	42876	8.92


7.231
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7.105
7.088
7.077
7.066
7.024
7.014
7.003
5.802
5.791
5.780
5.476
5.470
5.454
5.447
5.058
4.738
4.732
4.040
3.143
2.941
2.933
2.925
2.918
2.910
1.700
1.689
1.067
1.055
1.044
0.644
CbzHN
OMe
Me
Me
OMe
1e
1.88
2.00
1.08
0.99
1.00
2.29
1.00
0.90
6.47
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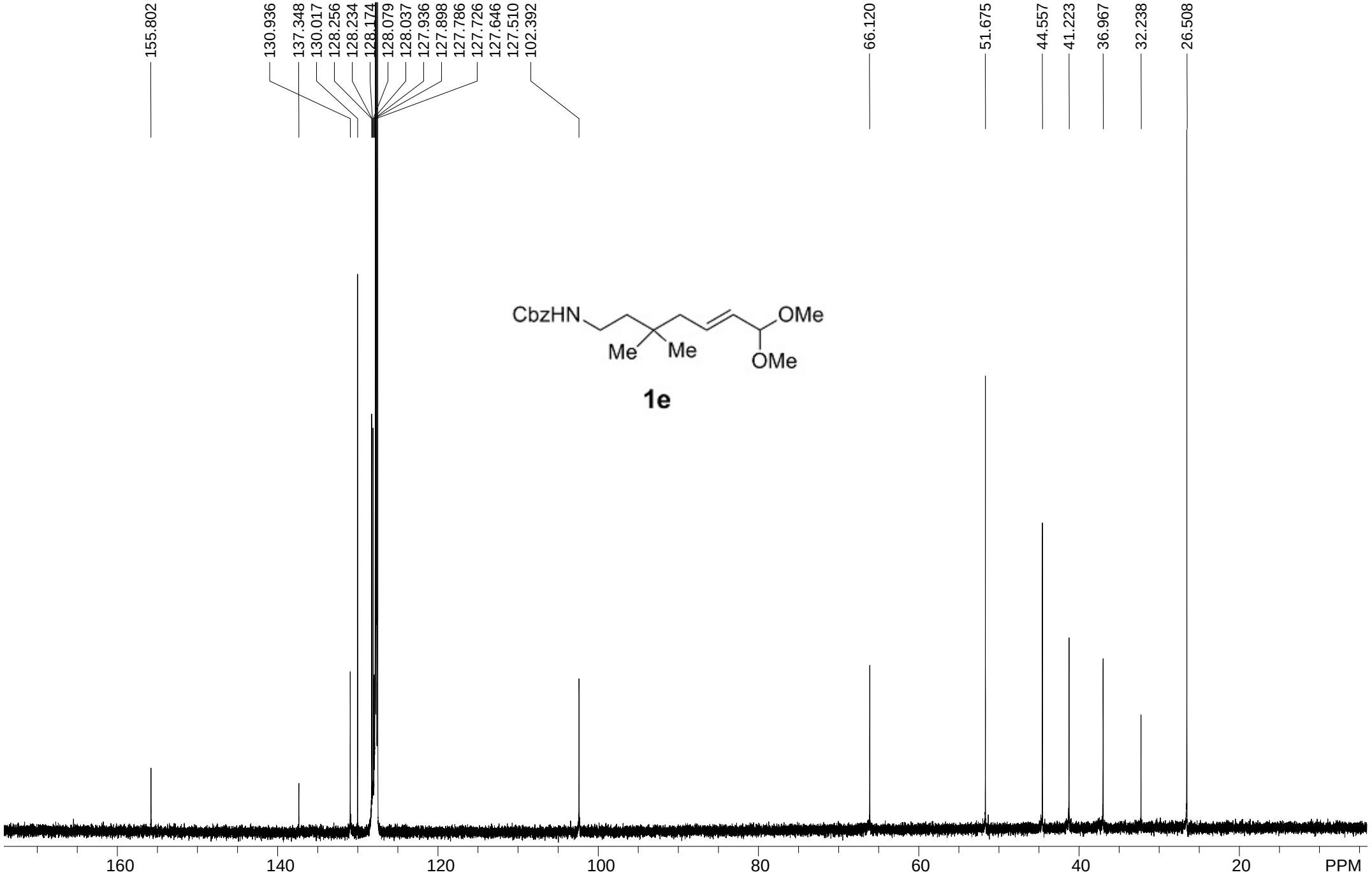
2.07
2.10
6.04
8
7
6
5
4
3
2
1
0
PPM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128.234
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128.079
128.037
127.936
127.898
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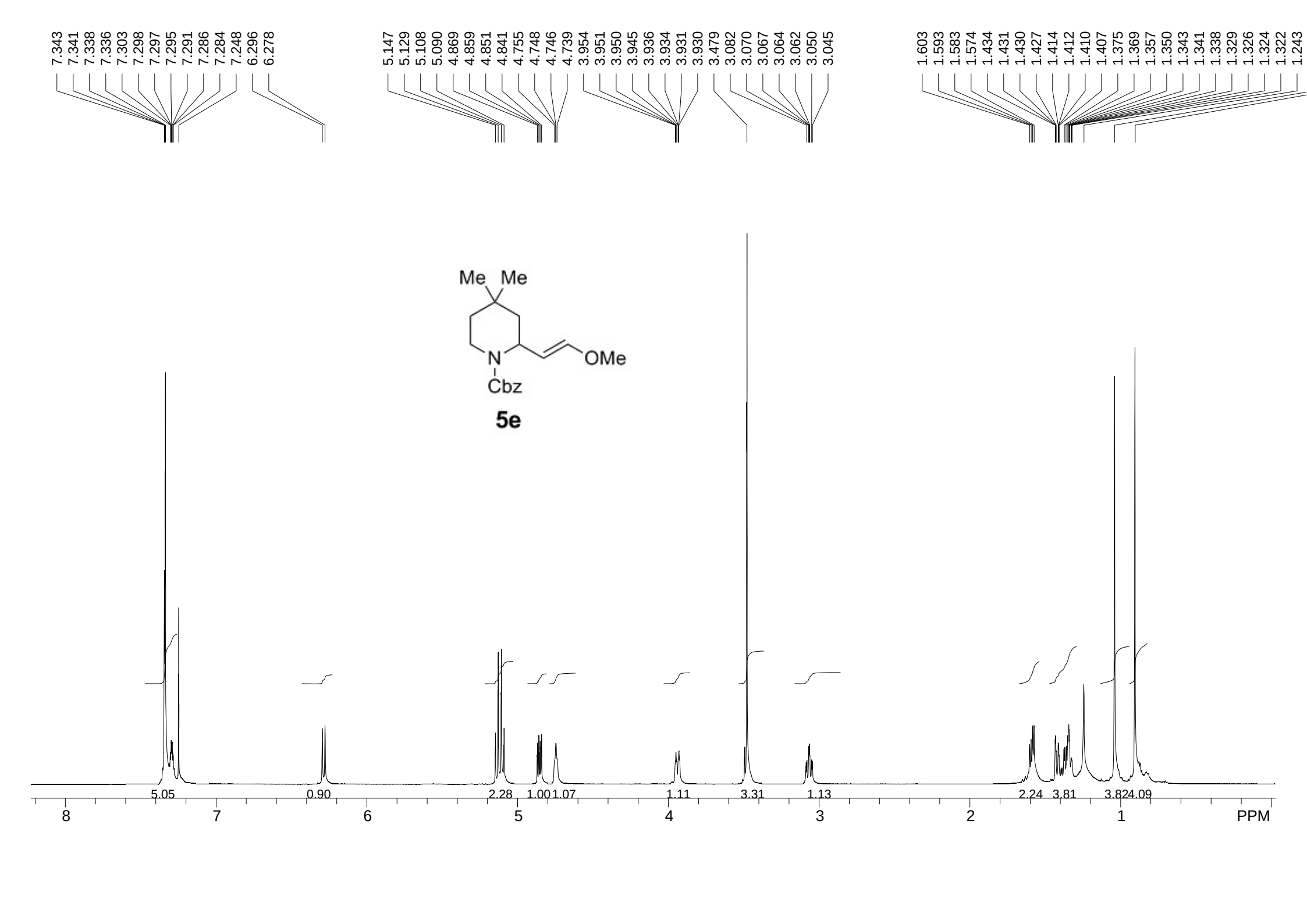
127.726
127.646
127.510
102.392
66.120
51.675
44.557
41.223
36.967
32.238
26.508
CbzHN
OMe
Me
Me
OMe
160
140
120
100
80
60
40
20
PPM

1e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7.286
7.284
7.248
6.296
6.278
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5.129
5.108
5.090
4.869
4.859
4.851
4.841
4.755
4.748
4.746
4.739
3.954
3.951
3.950
3.945
3.936
3.934
3.931
3.930
3.479
3.082
3.070
3.067
3.064
3.062
3.050
3.045
1.603
1.593
1.583
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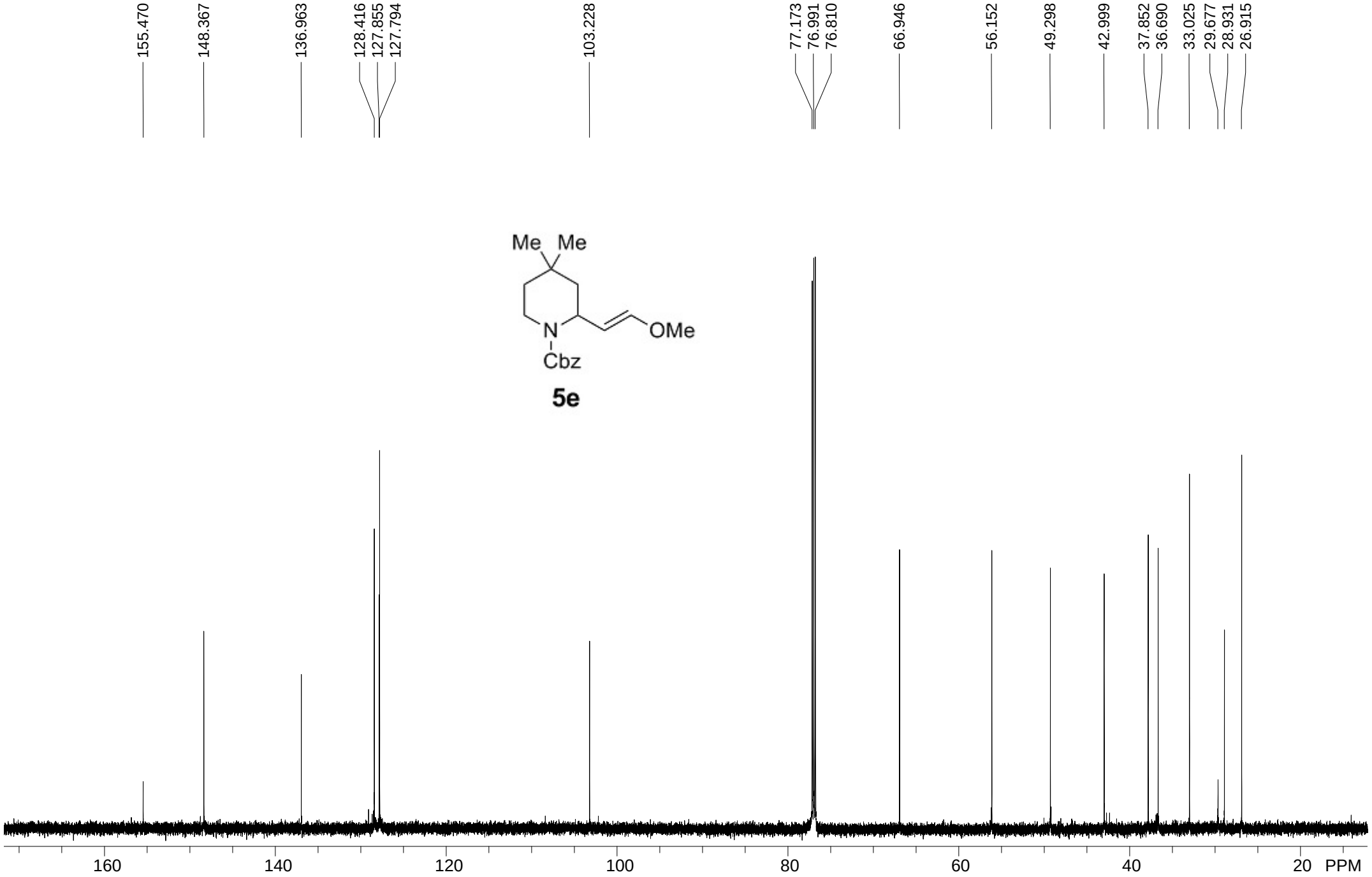
1.431
1.430
1.427
1.414
1.412
1.410
1.407
1.375
1.369
1.357
1.350
1.343
1.341
1.338
1.329
1.326
1.324
1.322
1.243
Me Me
N
Cbz
OMe
5e
5.05
0.90
2.28
1.00
1.07
1.11
3.31
1.13
2.24
3.81
3.82
4.09
8
7
6
5
4
3
2
1
PPM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77.173
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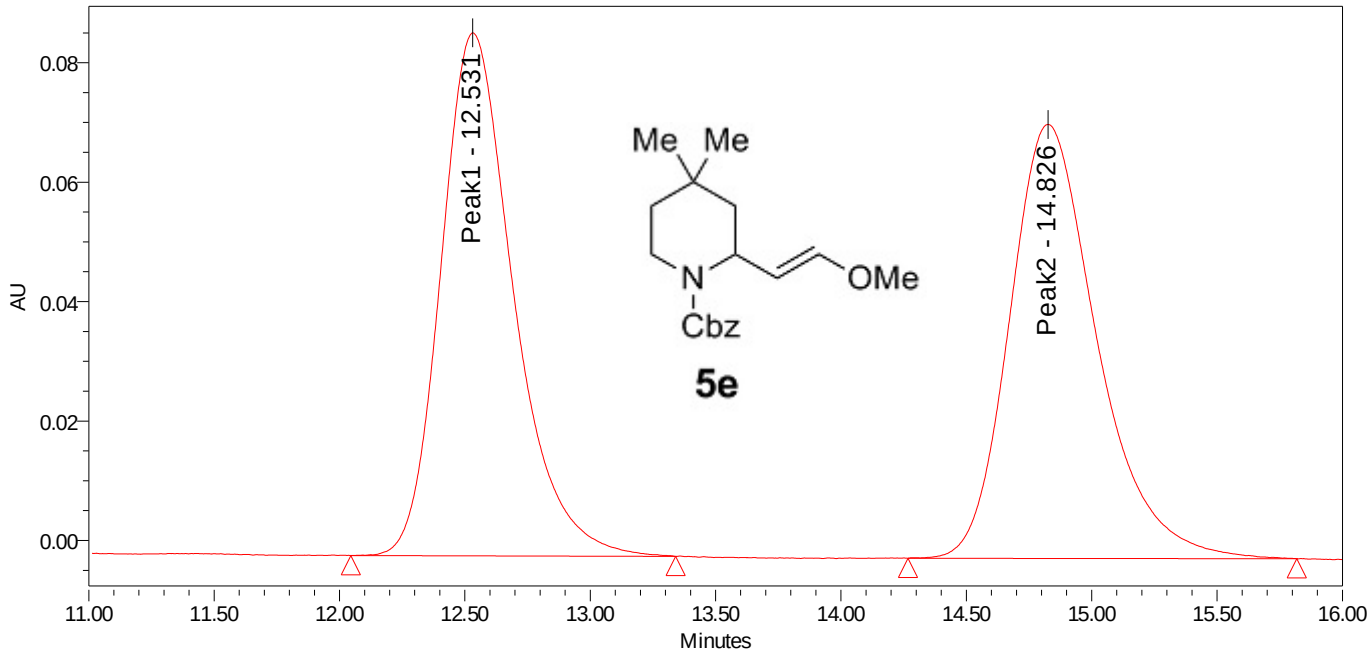
76.810
66.946
56.152
49.298
42.999
37.852
36.690
33.025
29.677
28.931
26.915
Me Me
N
Cbz
OMe
5e
160
140
120
100
80
60
40
20
PPM

SAMPLE INFORMATION

Sample Name:	3-55-1-r	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	3_55_1_R
Vial:	40	Acq. Method Set:	ADH 97
Injection #:	1	Processing Method	n
Injection Volume:	10.00 ul	Channel Name:	210.3nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	1/11/2013 10:15:30 AM EST		
Date Processed:	9/12/2013 12:21:38 PM EDT		

Auto-Scaled Chromatogram



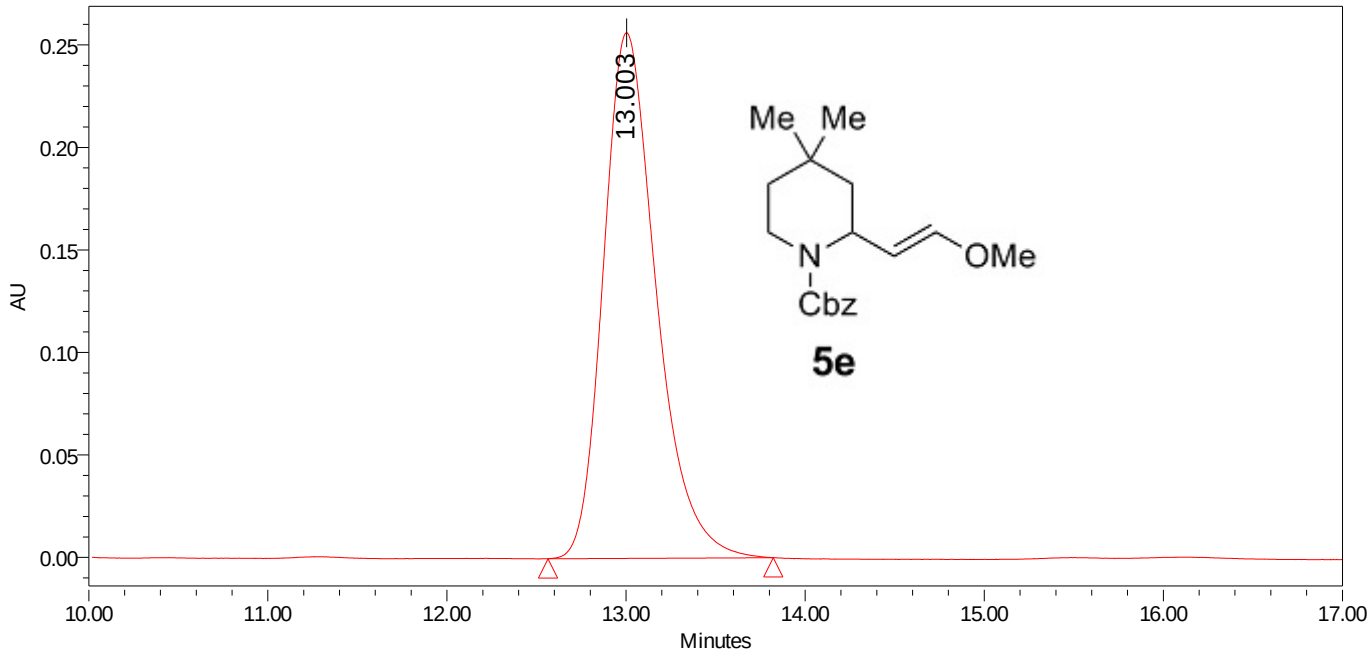
Peak Results

	Name	RT	Area	Height	Amount	Units
1	Peak1	12.531	1755686	87601		
2	Peak2	14.826	1758920	72673		

SAMPLE INFORMATION

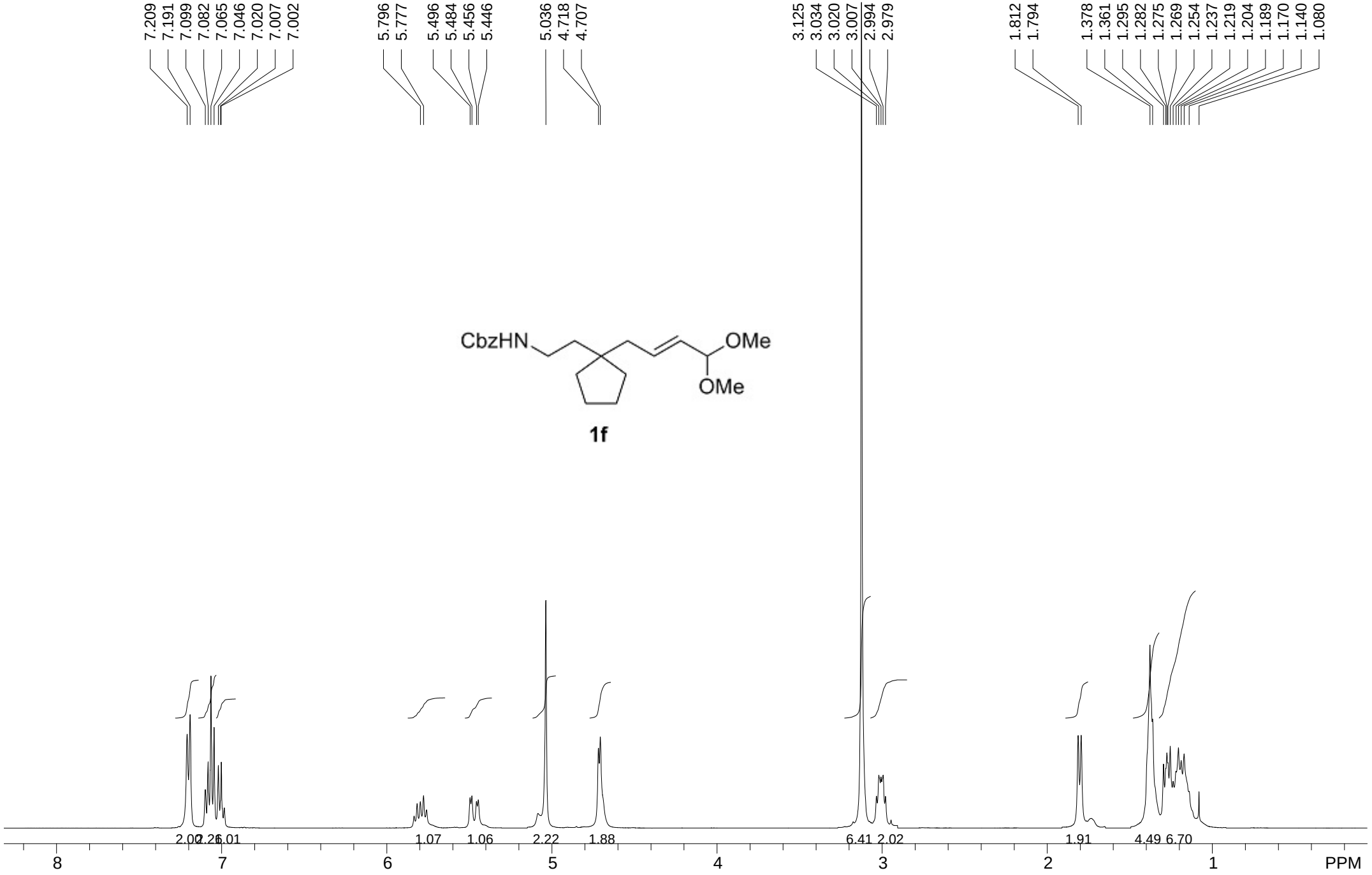
Sample Name:	3-275-24h	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	3_275_24h
Vial:	93	Acq. Method Set:	ADH 97
Injection #:	1	Processing Method	n
Injection Volume:	10.00 ul	Channel Name:	210.3nm@1
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	6/12/2013 5:14:23 PM EDT		
Date Processed:	9/12/2013 12:38:25 PM EDT		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	Amount	Units
1		13.003	5260612	256429		


7.209
7.191
7.099
7.082
7.065
7.046
7.020
7.007
7.002
5.796
5.777
5.496
5.484
5.456
5.446
5.036
4.718
4.707
3.125
3.034
3.020
3.007
2.994
2.979
1.812
1.794
1.378
1.361
1.295
1.282
1.275
1.269
1.254
1.237
1.219
1.204
1.189
1.170
1.140
1.080
CbzHN
OMe
OMe
1f
2.00
2.26
6.01
1.07
1.06
2.22
1.88
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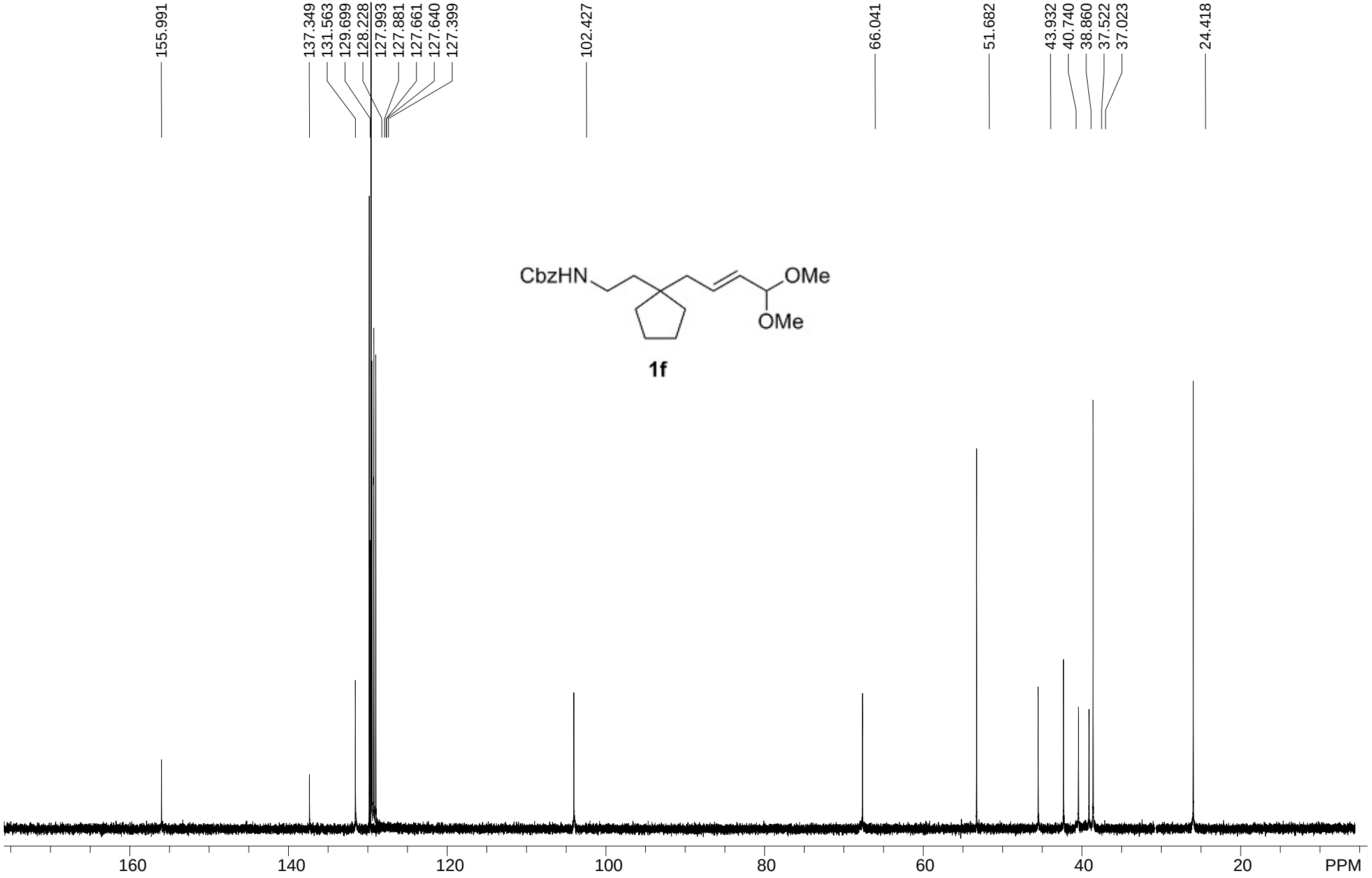
2.02
1.91
4.49
6.70
8
7
6
5
4
3
2
1
PPM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129.699
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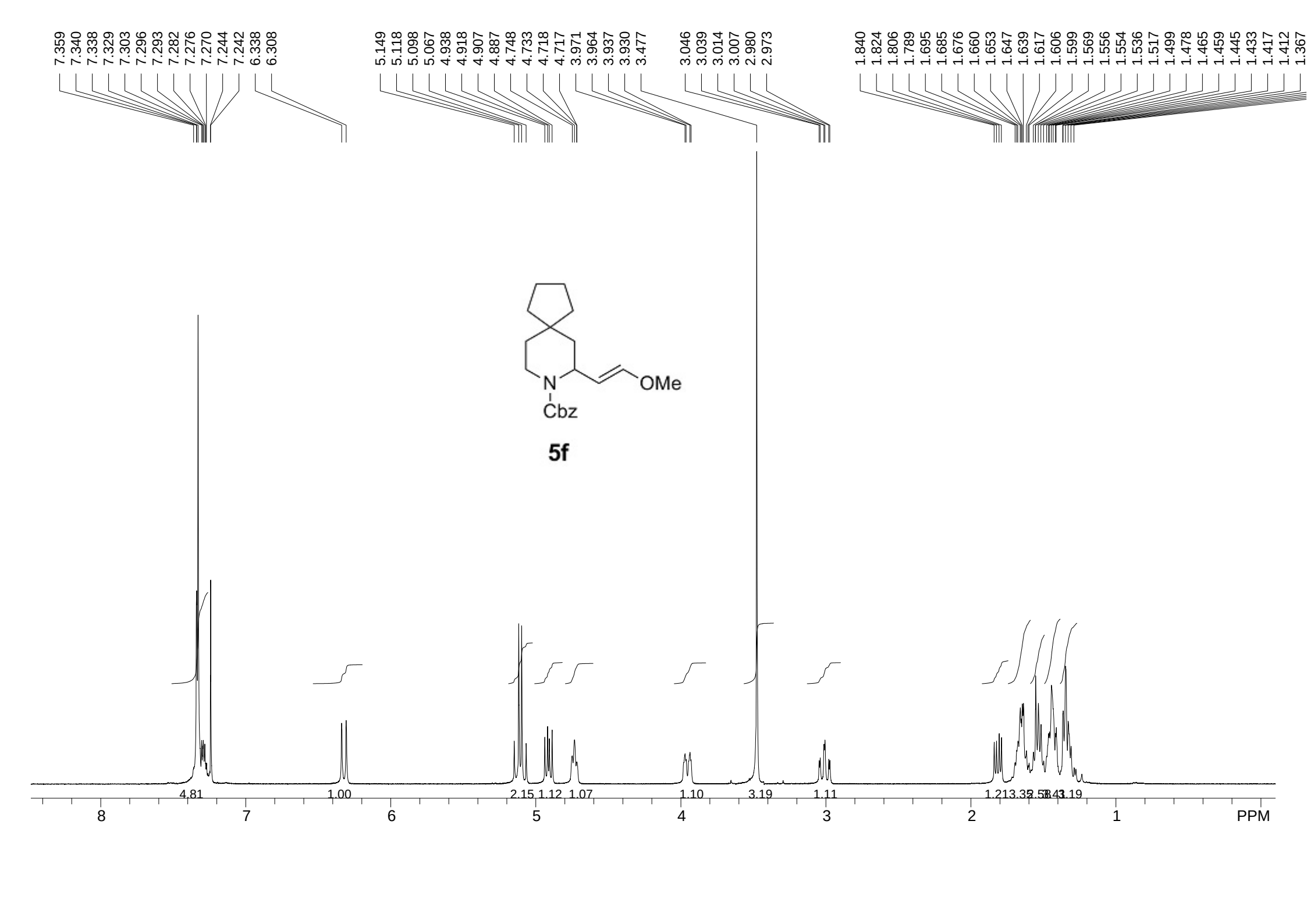
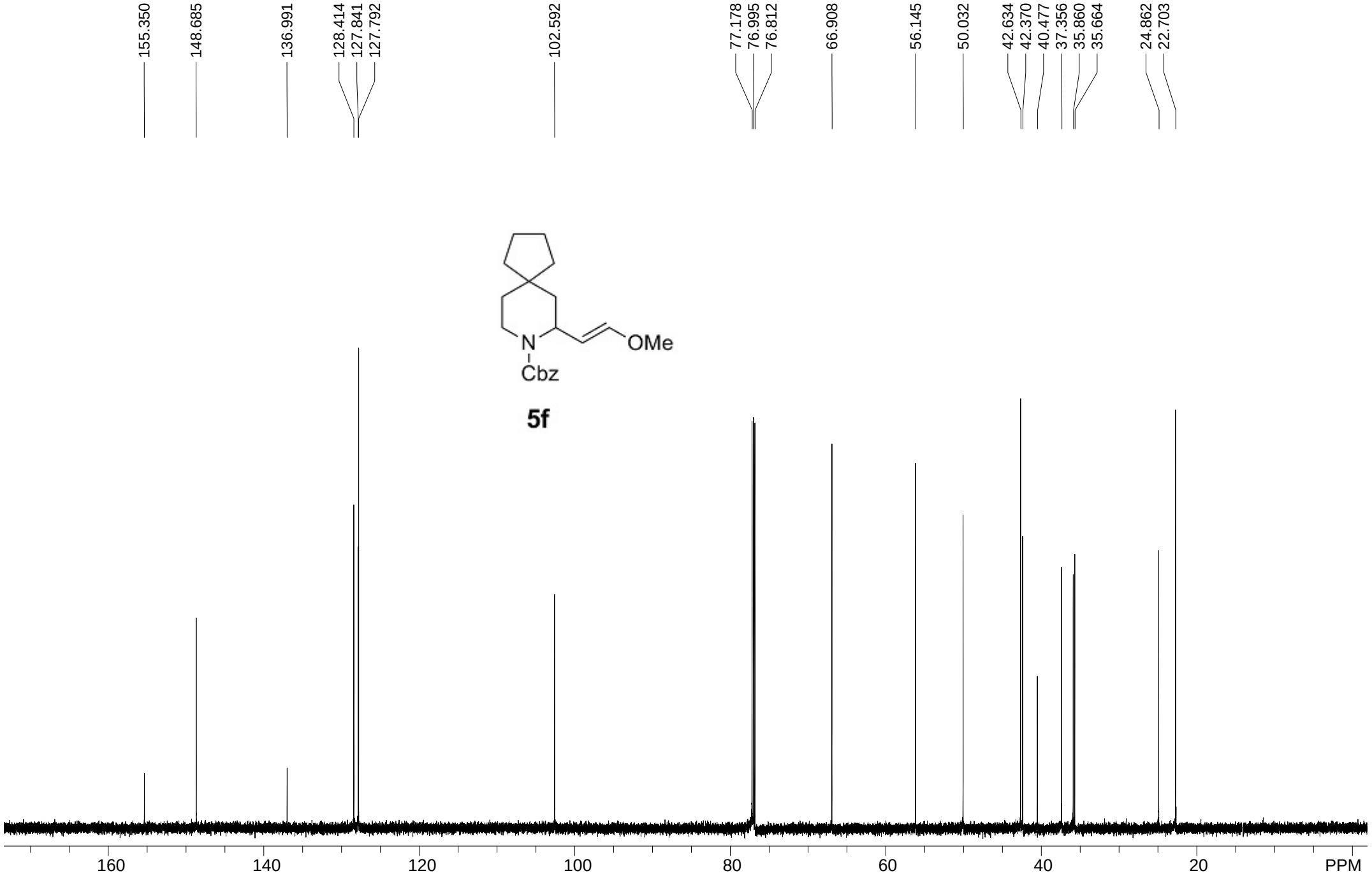
127.993
127.881
127.661
127.640
127.399
102.427
66.041
51.682
43.932
40.740
38.860
37.522
37.023
24.418
CbzHN
OMe
OMe
160
140
120
100
80
60
40
20
PPM

1f


7.359
7.340
7.338
7.329
7.303
7.296
7.293
7.282
7.276
7.270
7.244
7.242
6.338
6.308
5.149
5.118
5.098
5.067
4.938
4.918
4.907
4.887
4.748
4.733
4.718
4.717
3.971
3.964
3.937
3.930
3.477
3.046
3.039
3.014
3.007
2.980
2.973
1.840
1.824
1.806
1.789
1.695
1.685
1.676
1.660
1.653
1.647
1.639
1.617
1.606
1.599
1.569
1.556
1.554
1.536
1.517
1.499
1.478
1.465
1.459
1.445
1.433
1.417
1.412
1.367
N
Cbz
OMe
5f
4.81
1.00
2.15
1.12
1.07
1.10
3.19
1.11
1.21
3.19
8
7
6
5
4
3
2
1
PPM


155.350
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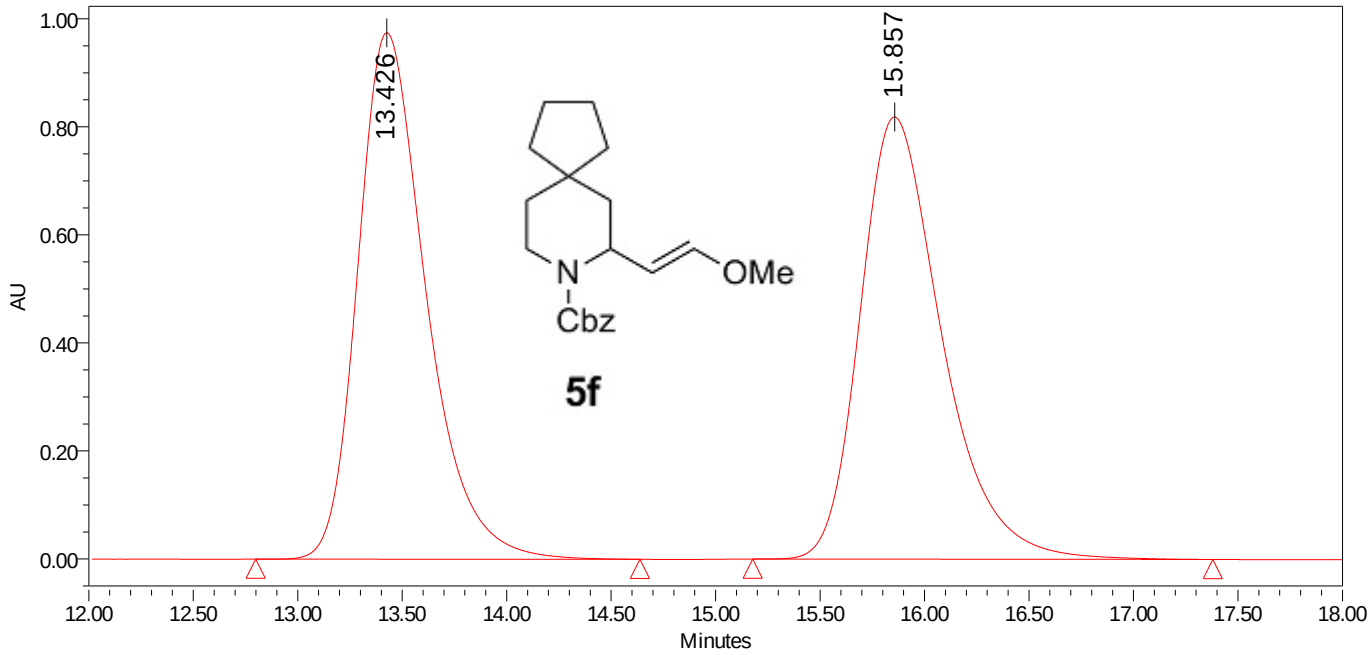
136.991
128.414
127.841
127.792
102.592
77.178
76.995
76.812
66.908
56.145
50.032
42.634
42.370
40.477
37.356
35.860
35.664
24.862
22.703
N
Cbz
OMe
5f
160
140
120
100
80
60
40
20
PPM

SAMPLE INFORMATION

Sample Name:	3-109-1-R	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	3_109_1_R
Vial:	32	Acq. Method Set:	ADH 95
Injection #:	1	Processing Method	NEW
Injection Volume:	20.00 ul	Channel Name:	210.3nm@2
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	2/1/2013 6:51:34 PM EST		
Date Processed:	9/12/2013 6:46:54 PM EDT		

Auto-Scaled Chromatogram



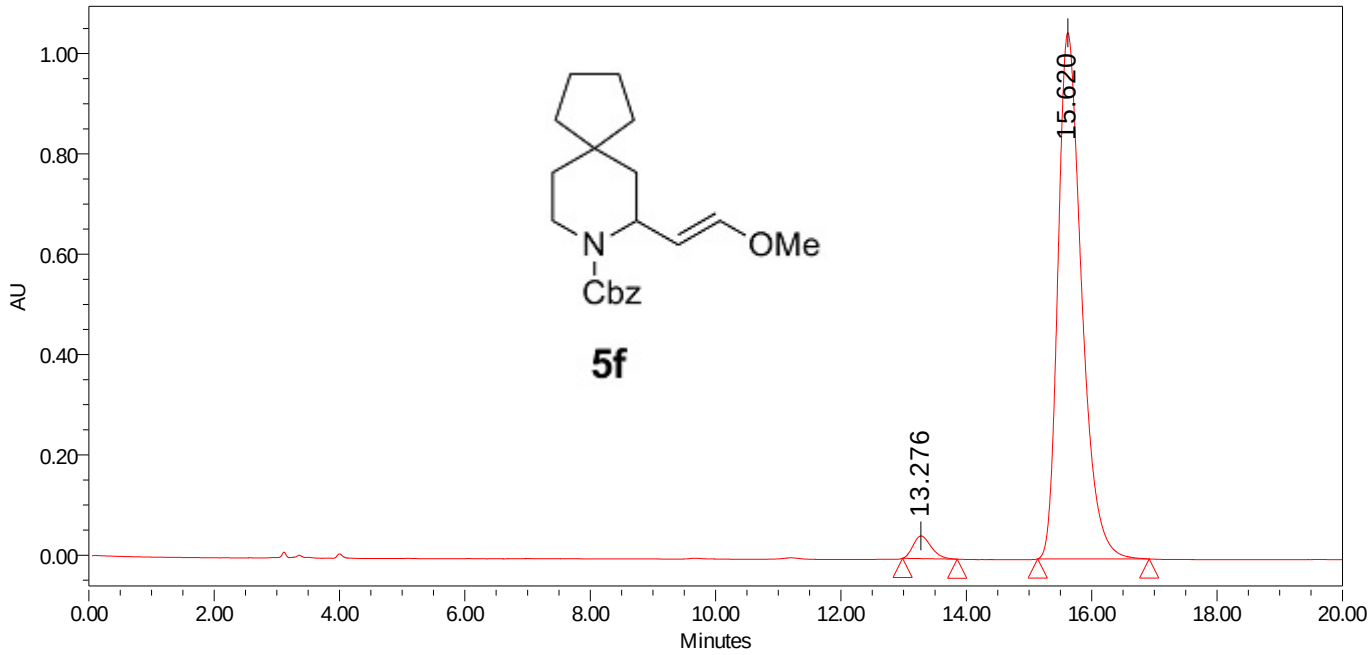
Peak Results

	Name	RT	Area	Height	% Area
1		13.426	22112516	974572	49.87
2		15.857	22226618	818530	50.13

SAMPLE INFORMATION

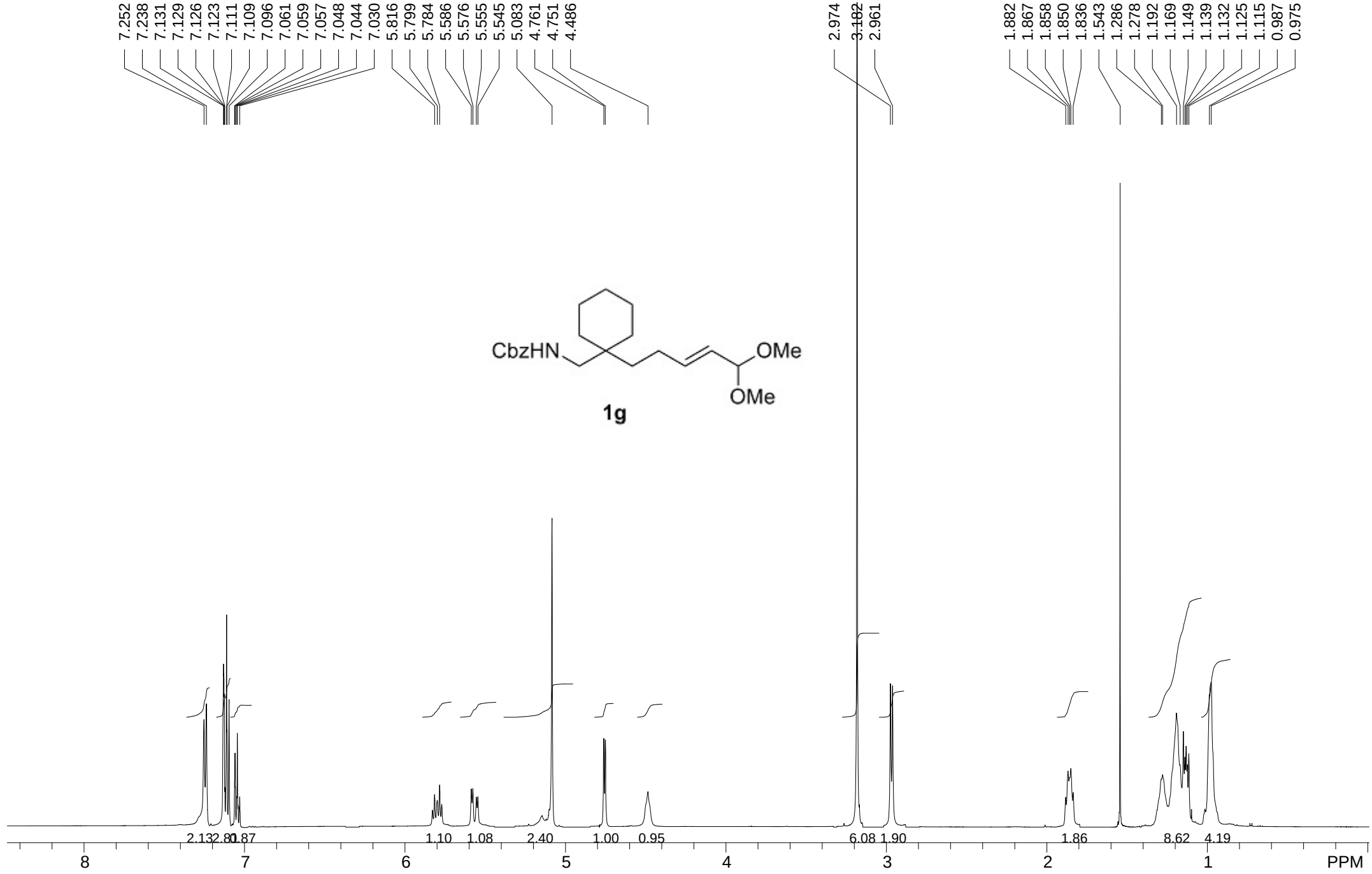
Sample Name:	3-285-8h	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	3_285_8h
Vial:	79	Acq. Method Set:	ADH 95
Injection #:	1	Processing Method	NEW
Injection Volume:	10.00 ul	Channel Name:	210.3nm@3
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	6/21/2013 10:04:50 AM EDT		
Date Processed:	9/12/2013 6:49:46 PM EDT		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	% Area
1		13.276	903426	45195	3.18
2		15.620	27469048	1048836	96.82


7.252
7.238
7.131
7.129
7.126
7.123
7.111
7.109
7.096
7.061
7.059
7.057
7.048
7.044
7.030
5.816
5.799
5.784
5.586
5.576
5.555
5.545
5.083
4.761
4.751
4.486
2.974
3.182
2.961
1.882
1.867
1.858
1.850
1.836
1.543
1.286
1.278
1.192
1.169
1.149
1.139
1.132
1.125
1.115
0.987
0.975
CbzHN
OMe
OMe
1g
2.13
2.80
0.87
1.10
1.08
2.40
1.00
0.95
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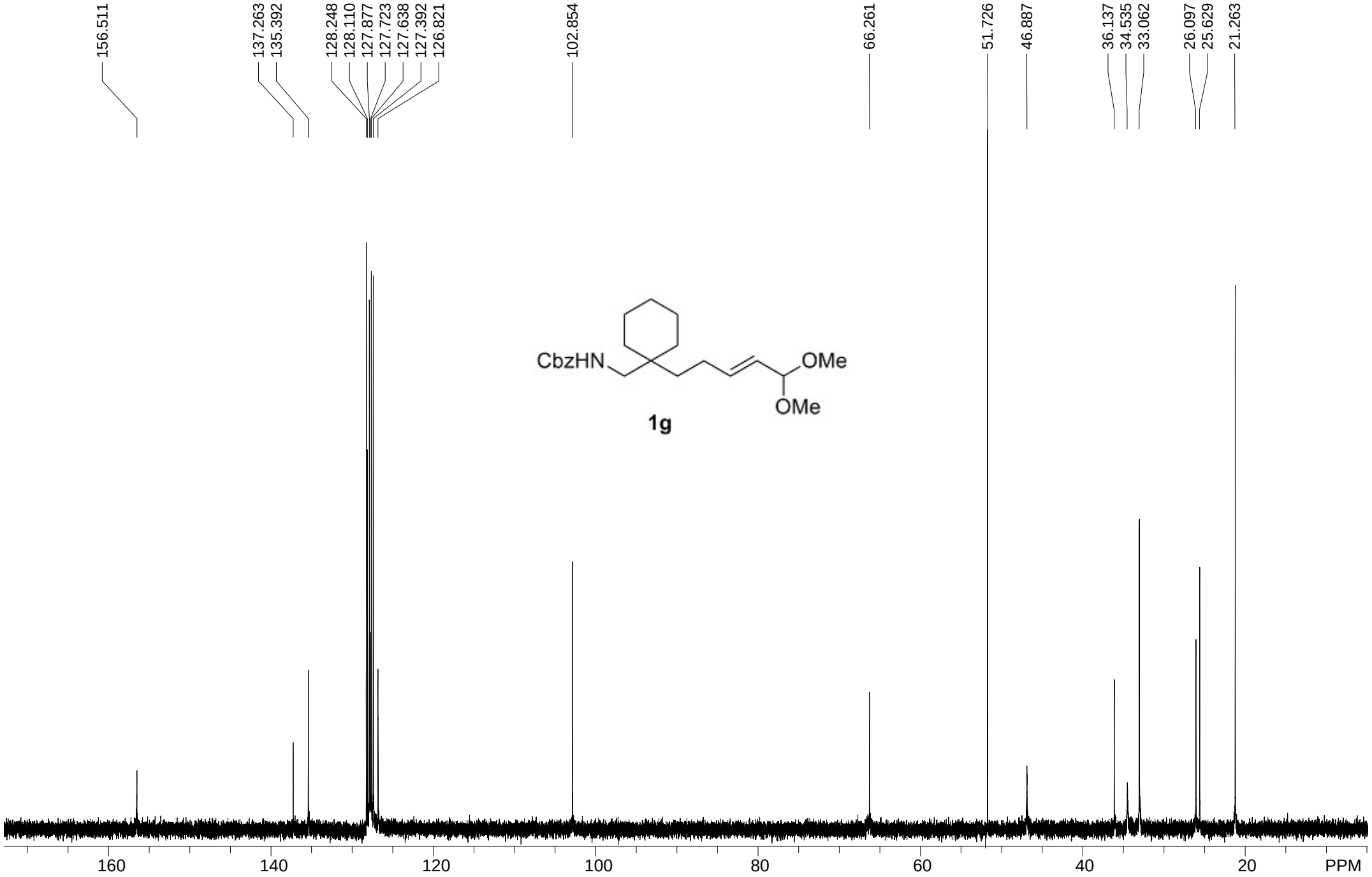
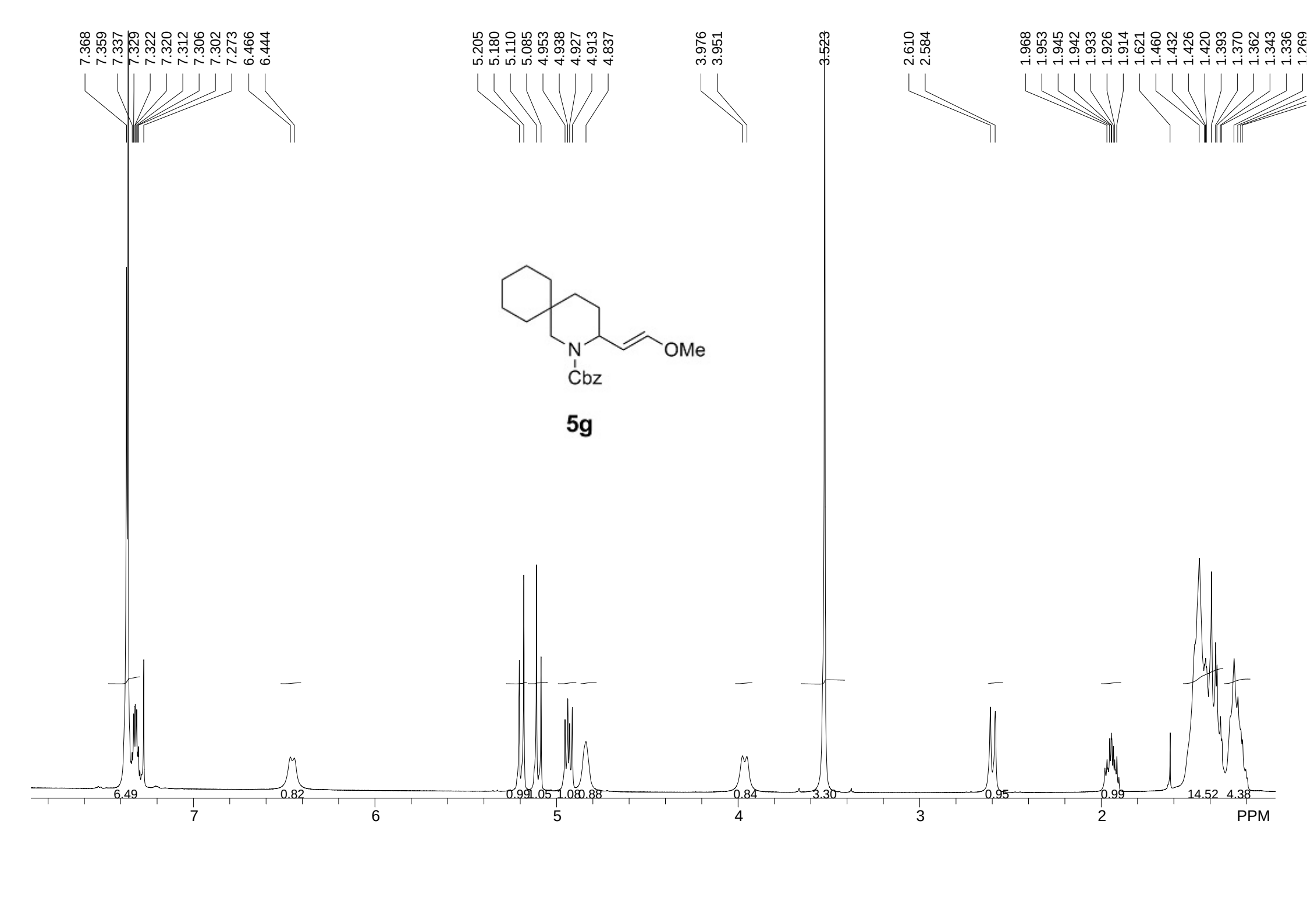
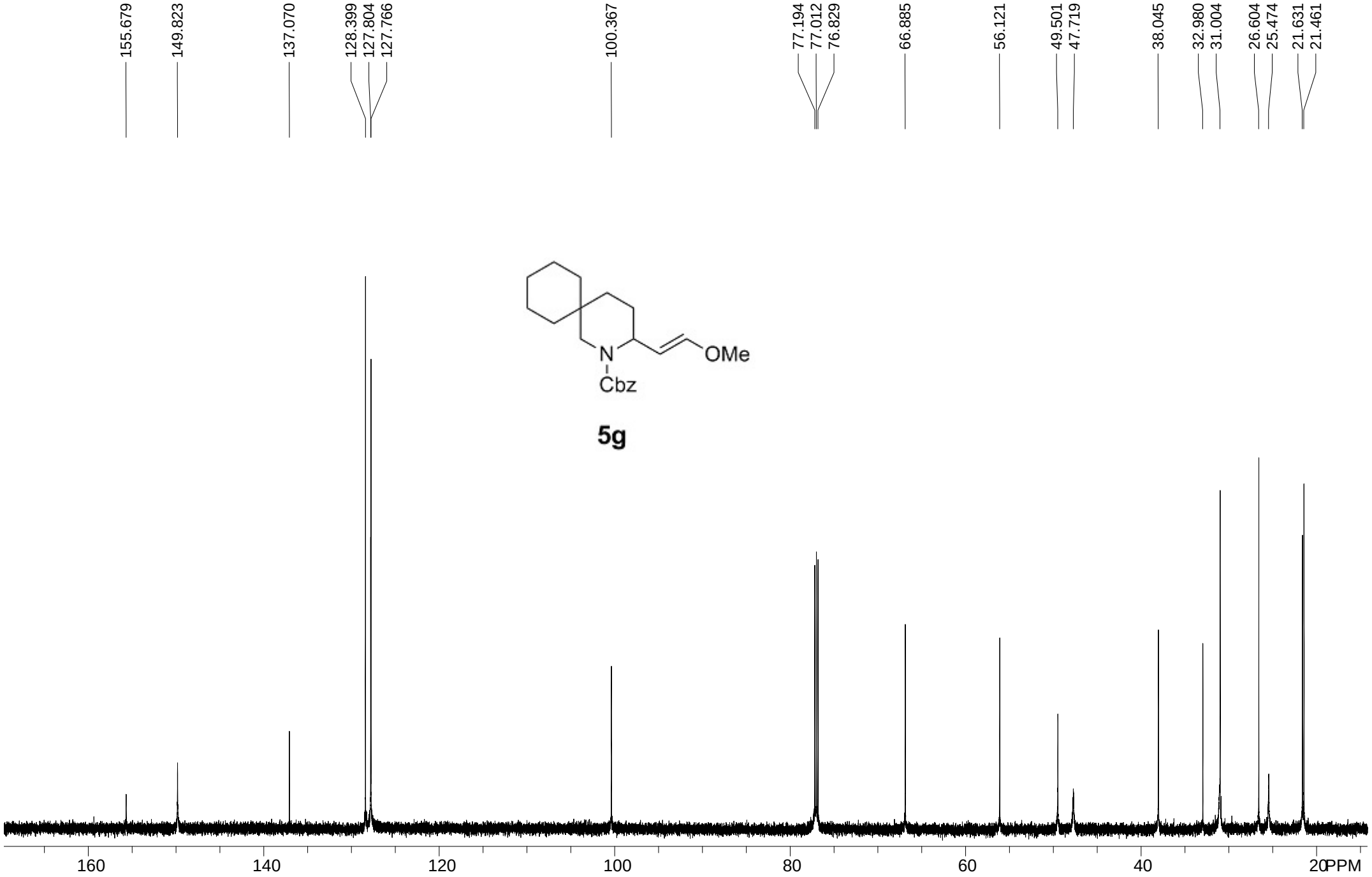
1.90
1.86
8.62
4.19
8
7
6
5
4
3
2
1
PPM


156.511
137.263
135.392
128.248
128.110
127.877
127.723
127.638
127.392
126.821
102.854
66.261
51.726
46.887
36.137
34.535
33.062
26.097
25.629
21.263
CbzHN
OMe
OMe
1g
160
140
120
100
80
60
40
20
PPM


7.368
7.359
7.337
7.329
7.322
7.320
7.312
7.306
7.302
7.273
6.466
6.444
5.205
5.180
5.110
5.085
4.953
4.938
4.927
4.913
4.837
3.976
3.951
3.523
2.610
2.584
1.968
1.953
1.945
1.942
1.933
1.926
1.914
1.621
1.460
1.432
1.426
1.420
1.393
1.370
1.362
1.343
1.336
N
Cbz
OMe
6.49
0.82
0.99
1.05
1.08
0.88
0.84
3.30
0.95
0.99
14.52
4.38
7
6
5
4
3
2
PPM

5g


155.679
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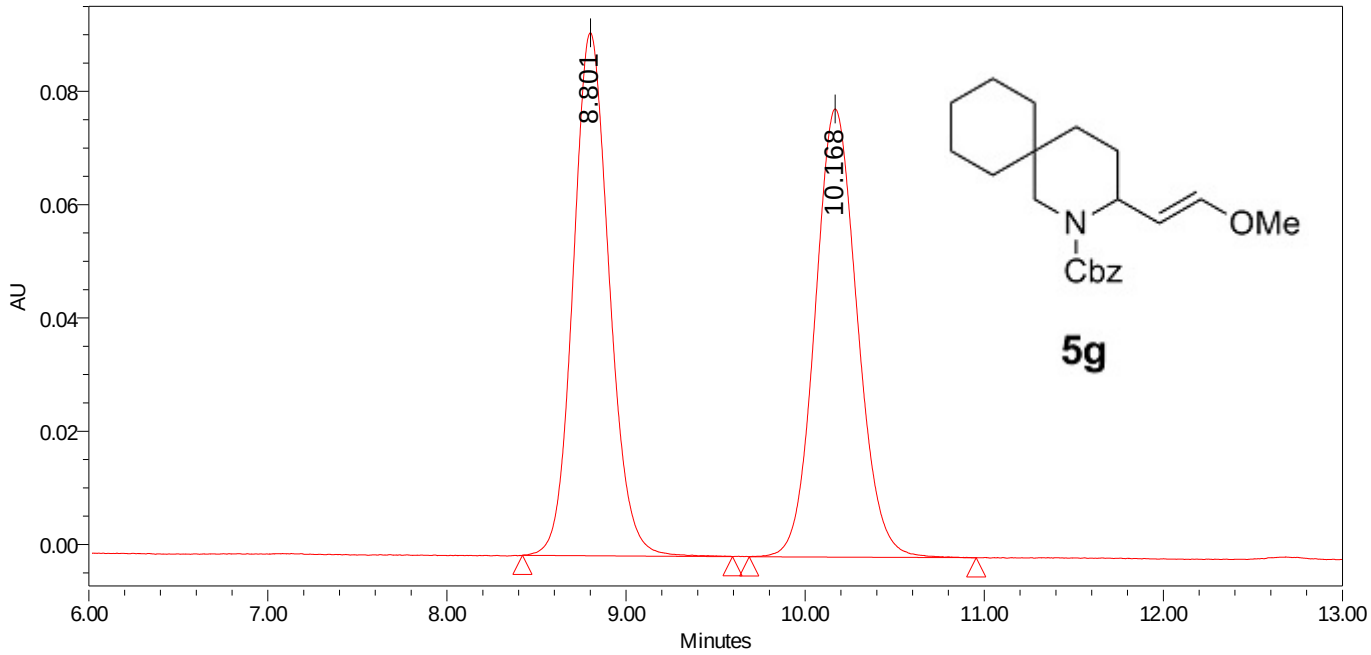
137.070
128.399
127.804
127.766
100.367
77.194
77.012
76.829
66.885
56.121
49.501
47.719
38.045
32.980
31.004
26.604
25.474
21.631
21.461
N
Cbz
OMe
160
140
120
100
80
60
40
20
PPM

5g

SAMPLE INFORMATION

Sample Name:	3-95-1-R	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	3_95_1_R
Vial:	82	Acq. Method Set:	ODH 99 HEXANE
Injection #:	1	Processing Method	s
Injection Volume:	10.00 ul	Channel Name:	210.3nm@1
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	1/23/2013 11:47:11 AM EST		
Date Processed:	9/12/2013 1:13:42 PM EDT		

Auto-Scaled Chromatogram



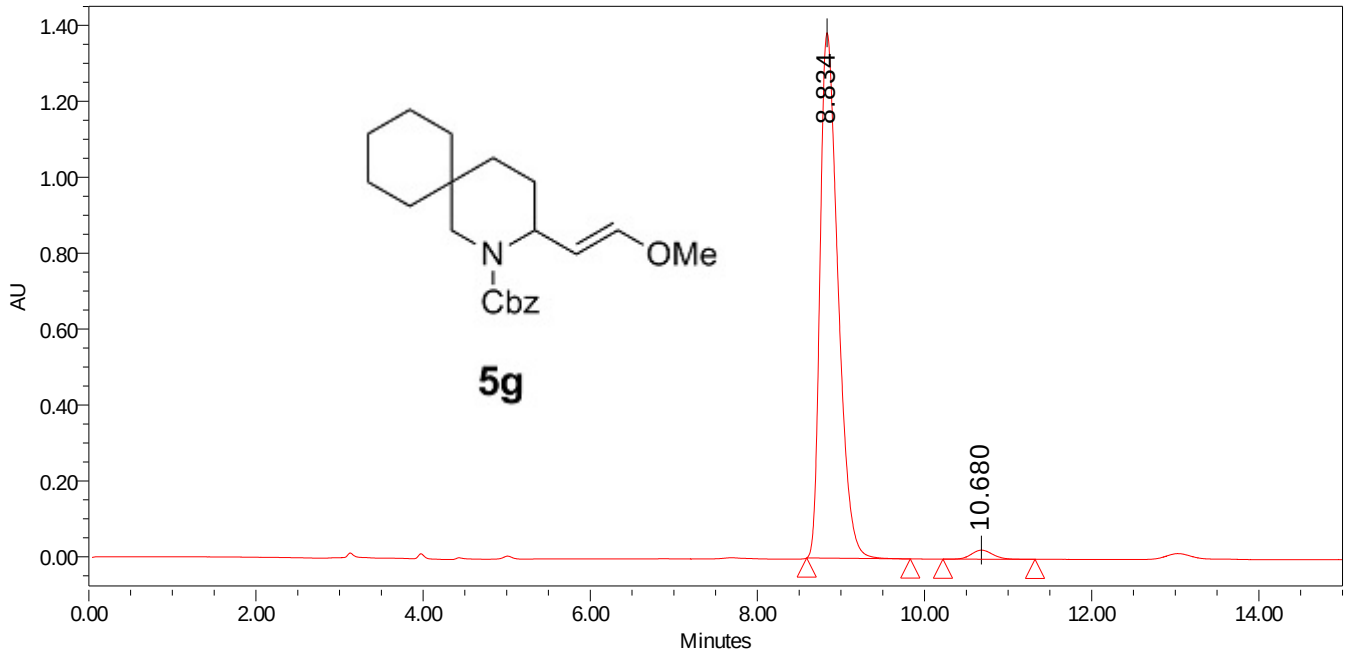
Peak Results

	Name	RT	Area	Height	% Area
1		8.801	1291236	92339	49.91
2		10.168	1296057	79124	50.09

SAMPLE INFORMATION

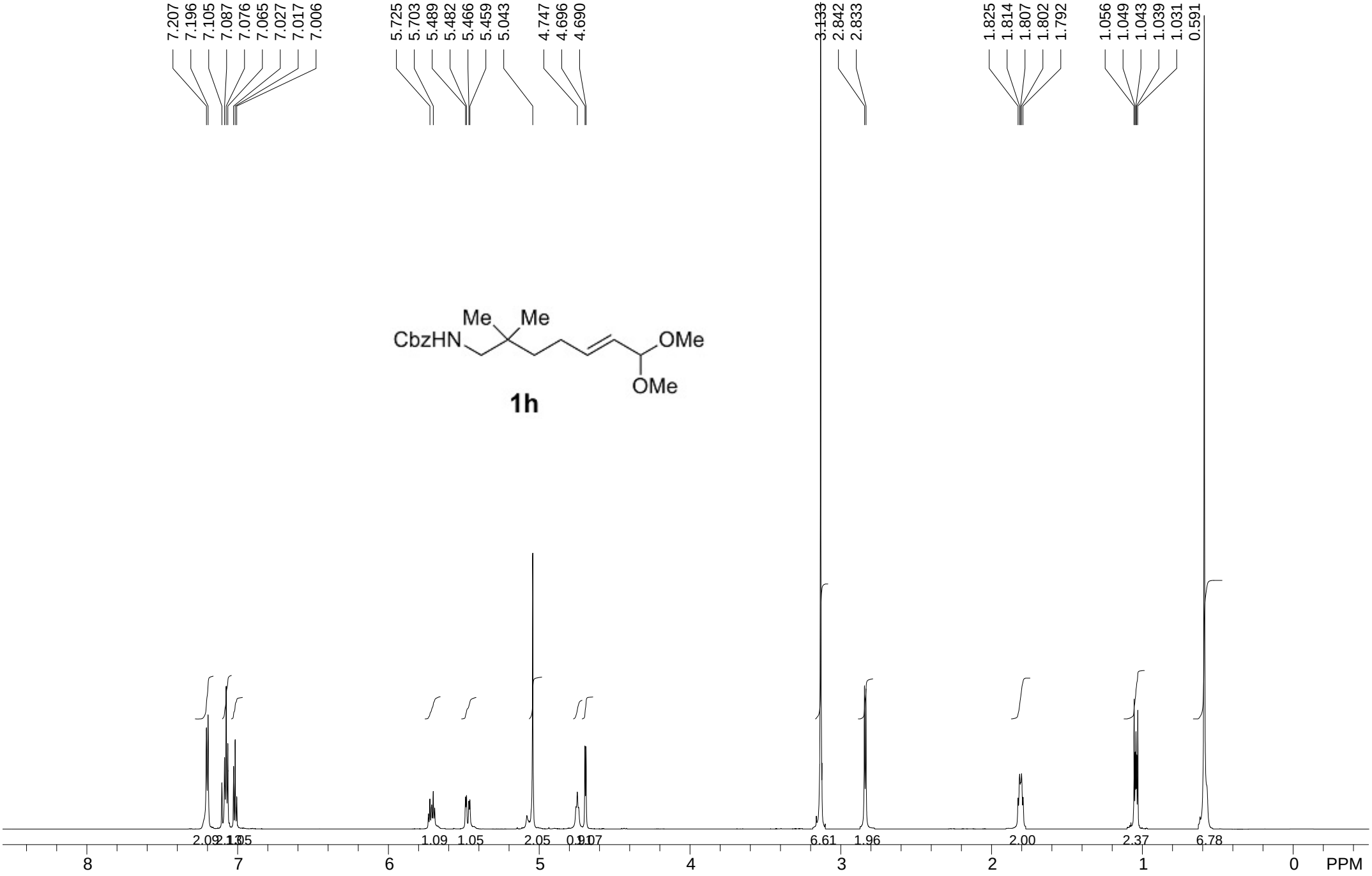
Sample Name:	3-269-1-30h	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	3_269_1_30h
Vial:	50	Acq. Method Set:	ODH 99 HEXANE
Injection #:	1	Processing Method	s
Injection Volume:	10.00 ul	Channel Name:	210.3nm
Run Time:	15.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	6/7/2013 7:35:49 PM EDT		
Date Processed:	9/12/2013 1:07:54 PM EDT		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	% Area
1		8.834	20545067	1383970	97.99
2		10.680	422216	23892	2.01


7.207
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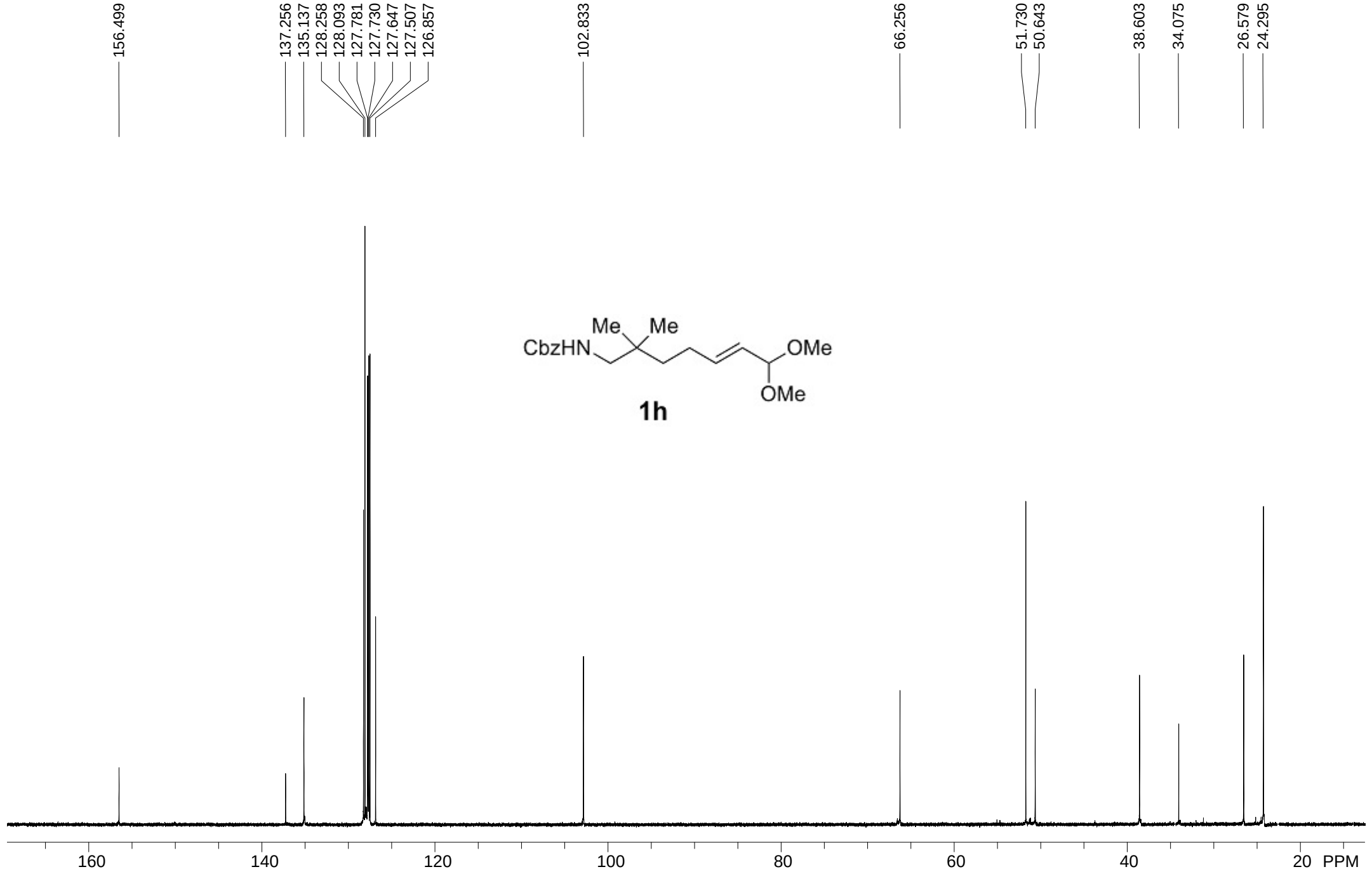
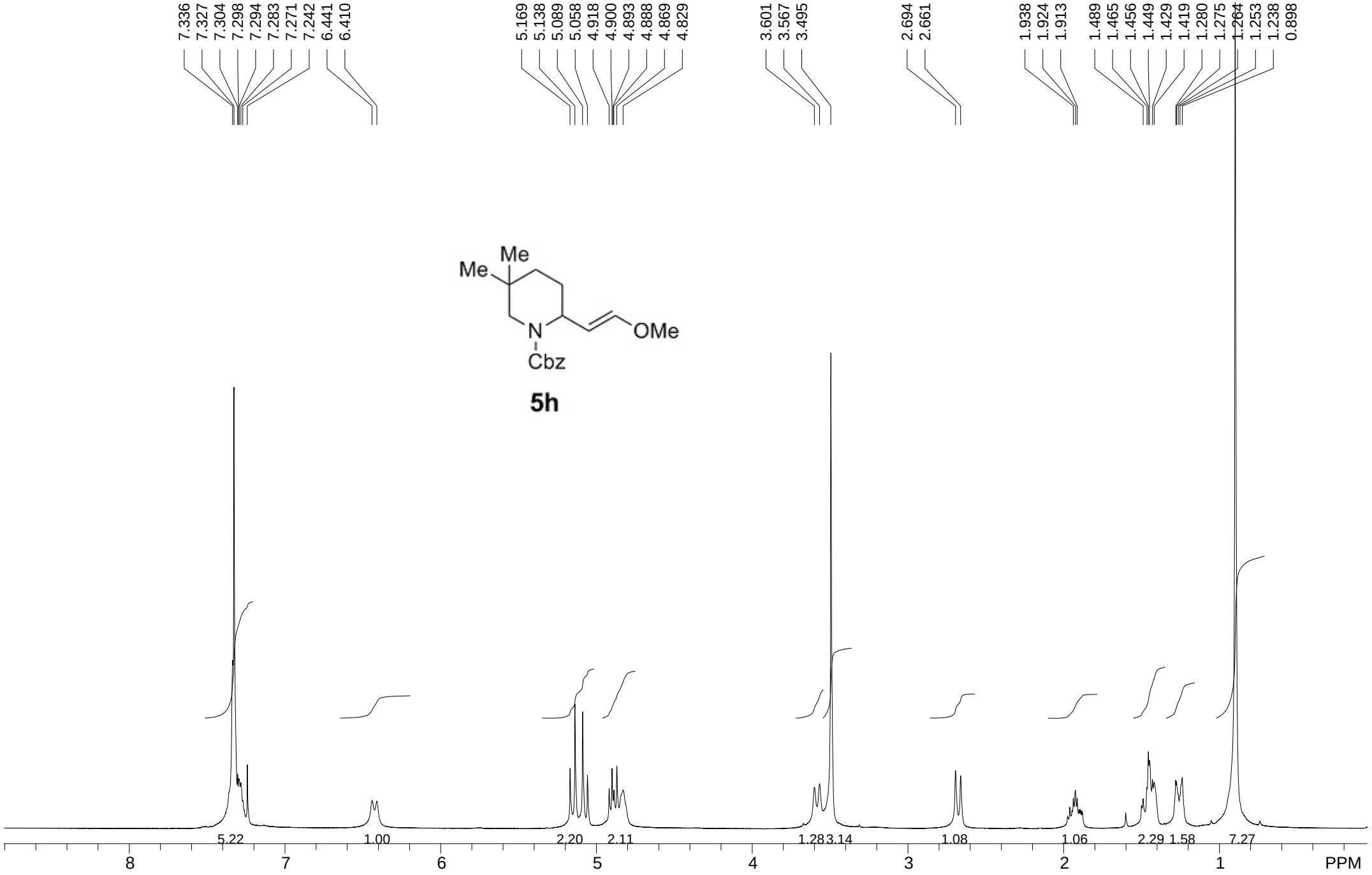
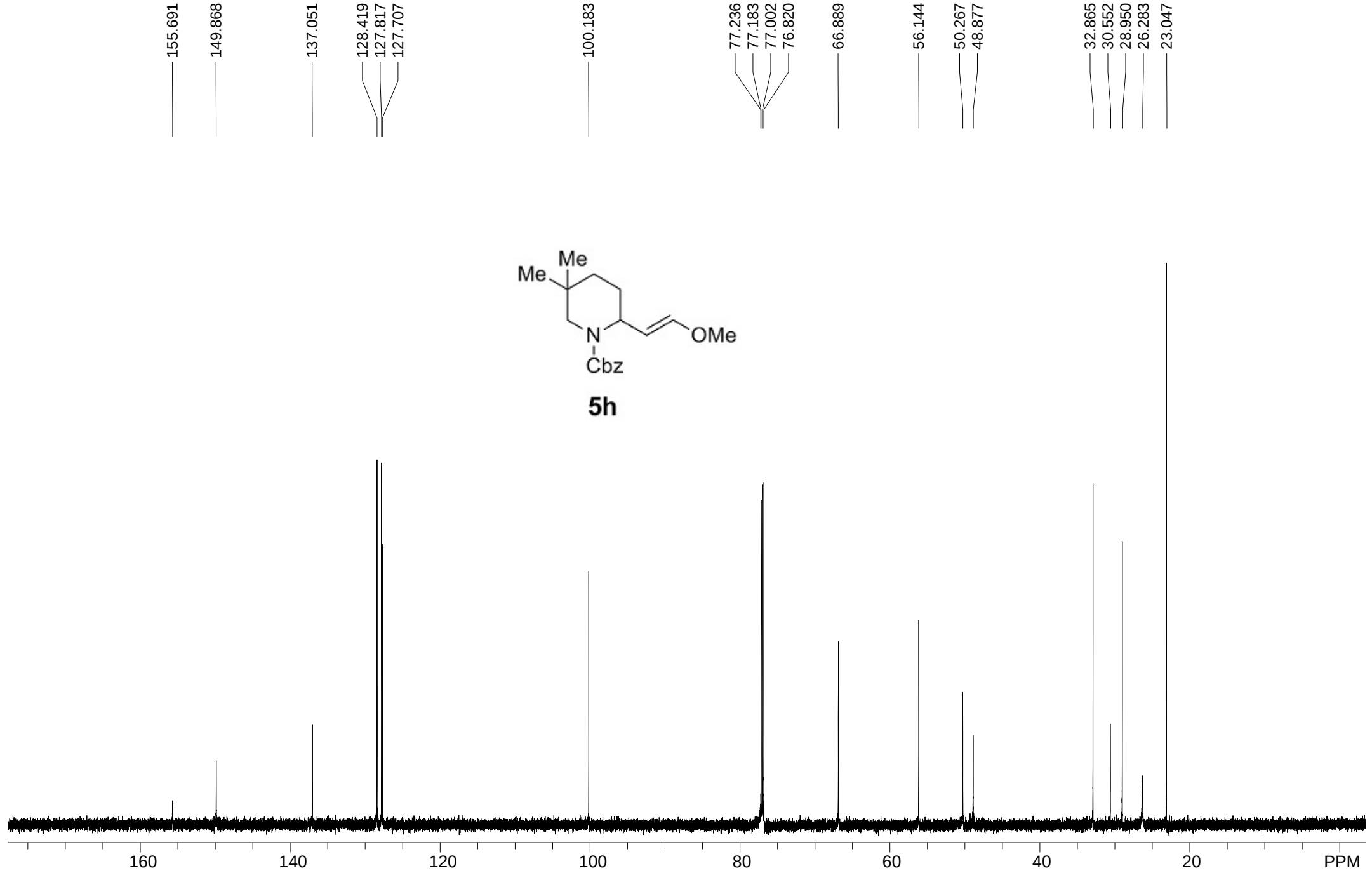
7.105
7.087
7.076
7.065
7.027
7.017
7.006
5.725
5.703
5.489
5.482
5.466
5.459
5.043
4.747
4.696
4.690
3.133
2.842
2.833
1.825
1.814
1.807
1.802
1.792
1.056
1.049
1.043
1.039
1.031
0.591
Me
Me
CbzHN
OMe
OMe
1h
2.09
2.13
2.05
1.09
1.05
2.05
0.91
0.97
6.61
1.96
2.00
2.37
6.78
8
7
6
5
4
3
2
1
0
PPM


156.499
137.256
135.137
128.258
128.093
127.781
127.730
127.647
127.507
126.857
102.833
66.256
51.730
50.643
38.603
34.075
26.579
24.295
Me
Me
CbzHN
OMe
OMe
1h
160
140
120
100
80
60
40
20
PPM


7.336
7.327
7.304
7.298
7.294
7.283
7.271
7.242
6.441
6.410
5.169
5.138
5.089
5.058
4.918
4.900
4.893
4.888
4.869
4.829
3.601
3.567
3.495
2.694
2.661
1.938
1.924
1.913
1.489
1.465
1.456
1.449
1.429
1.419
1.280
1.275
1.264
1.253
1.238
0.898
Me
Me
N
Cbz
OMe
5h
5.22
1.00
2.20
2.11
1.28
3.14
1.08
1.06
2.29
1.58
7.27
8
7
6
5
4
3
2
1
PPM


155.691
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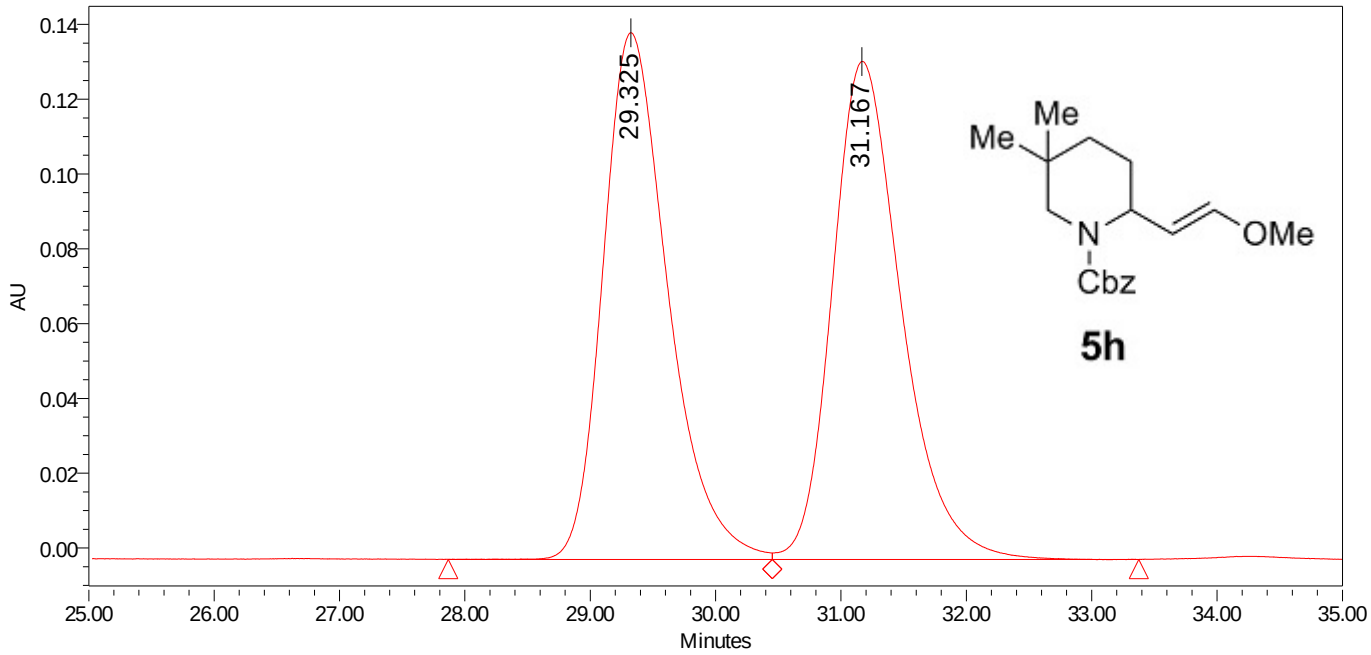
137.051
128.419
127.817
127.707
100.183
77.236
77.183
77.002
76.820
66.889
56.144
50.267
48.877
32.865
30.552
28.950
26.283
23.047
Me
Me
N
Cbz
OMe
160
140
120
100
80
60
40
20
PPM

5h

SAMPLE INFORMATION

Sample Name:	3-272-1-r	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	3_272_1_r
Vial:	43	Acq. Method Set:	adh 99% none gradient
Injection #:	1	Processing Method	n
Injection Volume:	20.00 ul	Channel Name:	210.3nm@2
Run Time:	35.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	6/10/2013 10:34:45 AM EDT		
Date Processed:	9/12/2013 1:04:58 PM EDT		

Auto-Scaled Chromatogram



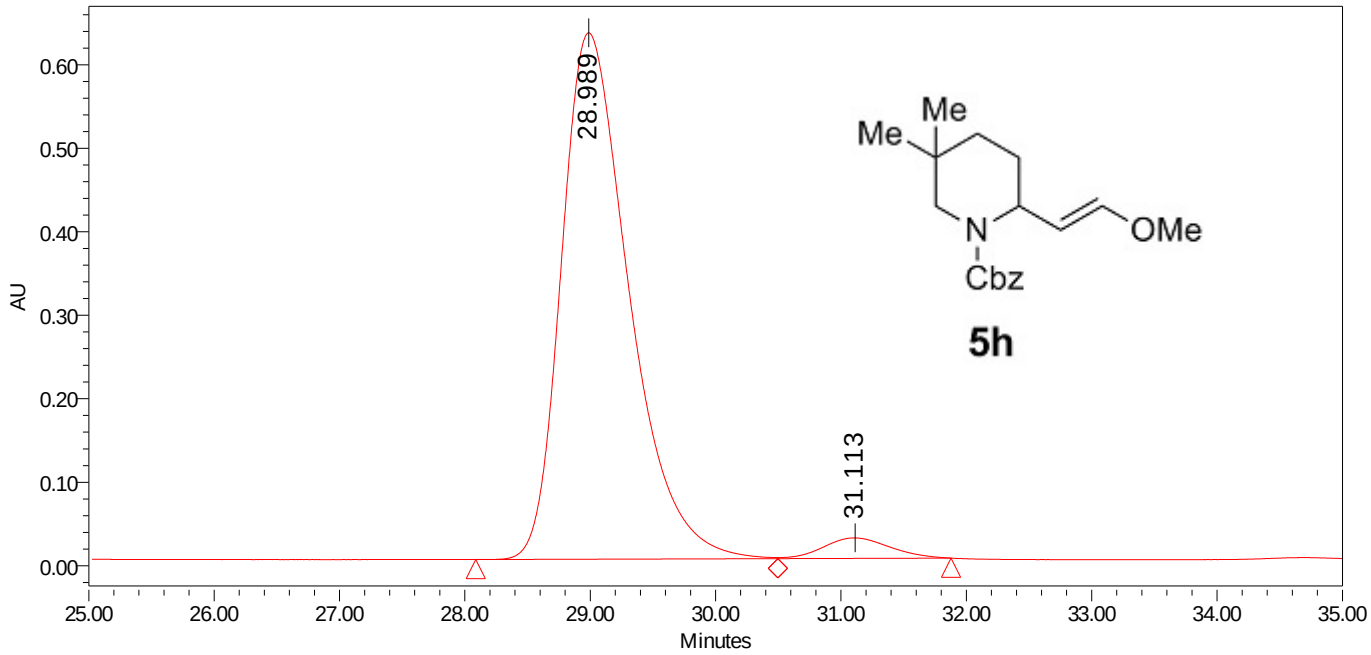
Peak Results

	Name	RT	Area	Height	% Area
1		29.325	5070488	140813	49.89
2		31.167	5093240	133113	50.11

SAMPLE INFORMATION

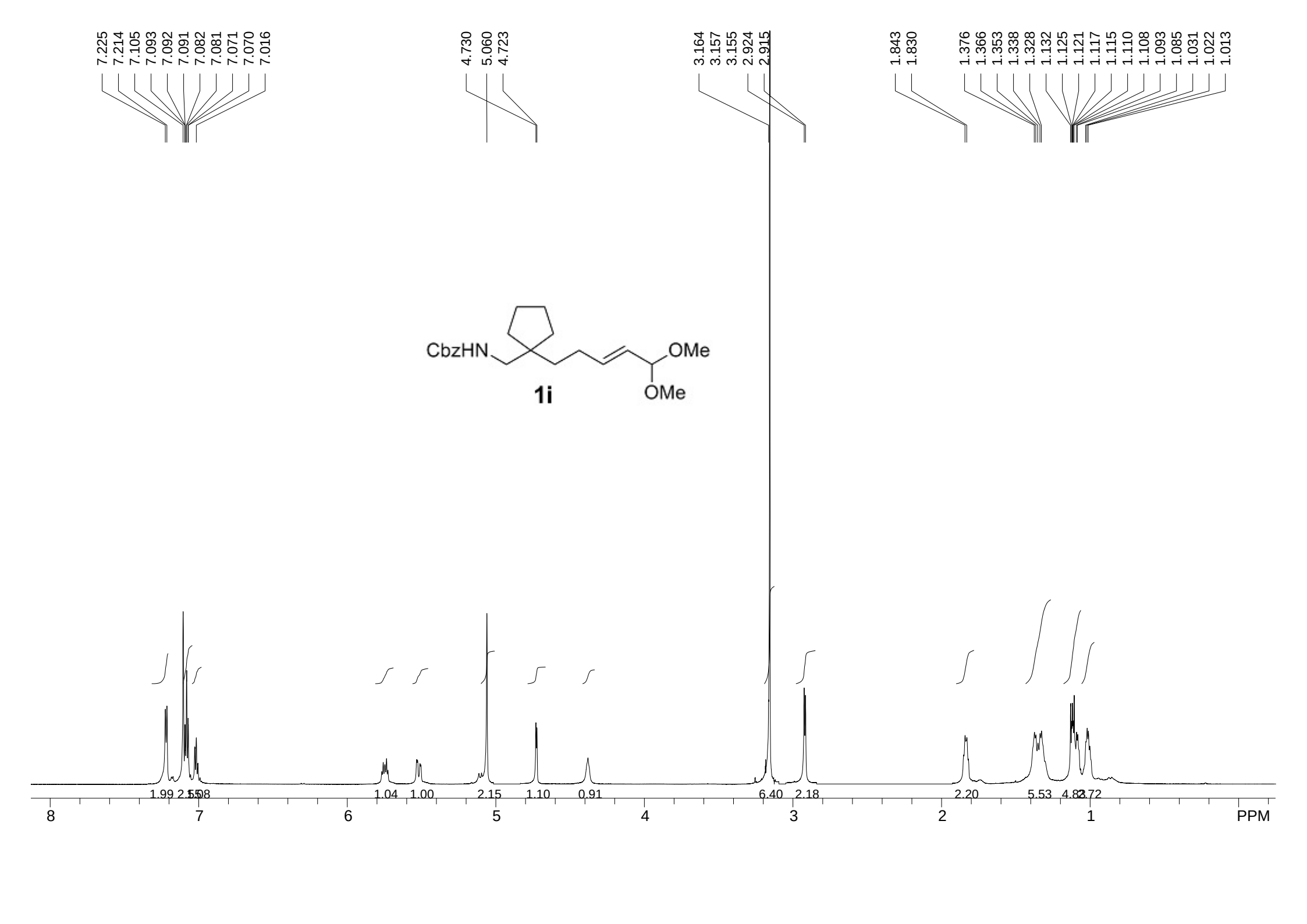
Sample Name:	3-272-1-24h	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	3_272_1_24h
Vial:	58	Acq. Method Set:	adh 99% none gradient
Injection #:	1	Processing Method	n
Injection Volume:	5.00 ul	Channel Name:	210.3nm@1
Run Time:	35.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	6/8/2013 5:00:04 PM EDT		
Date Processed:	9/12/2013 12:56:57 PM EDT		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	% Area
1		28.989	23598585	630687	96.31
2		31.113	905147	24600	3.69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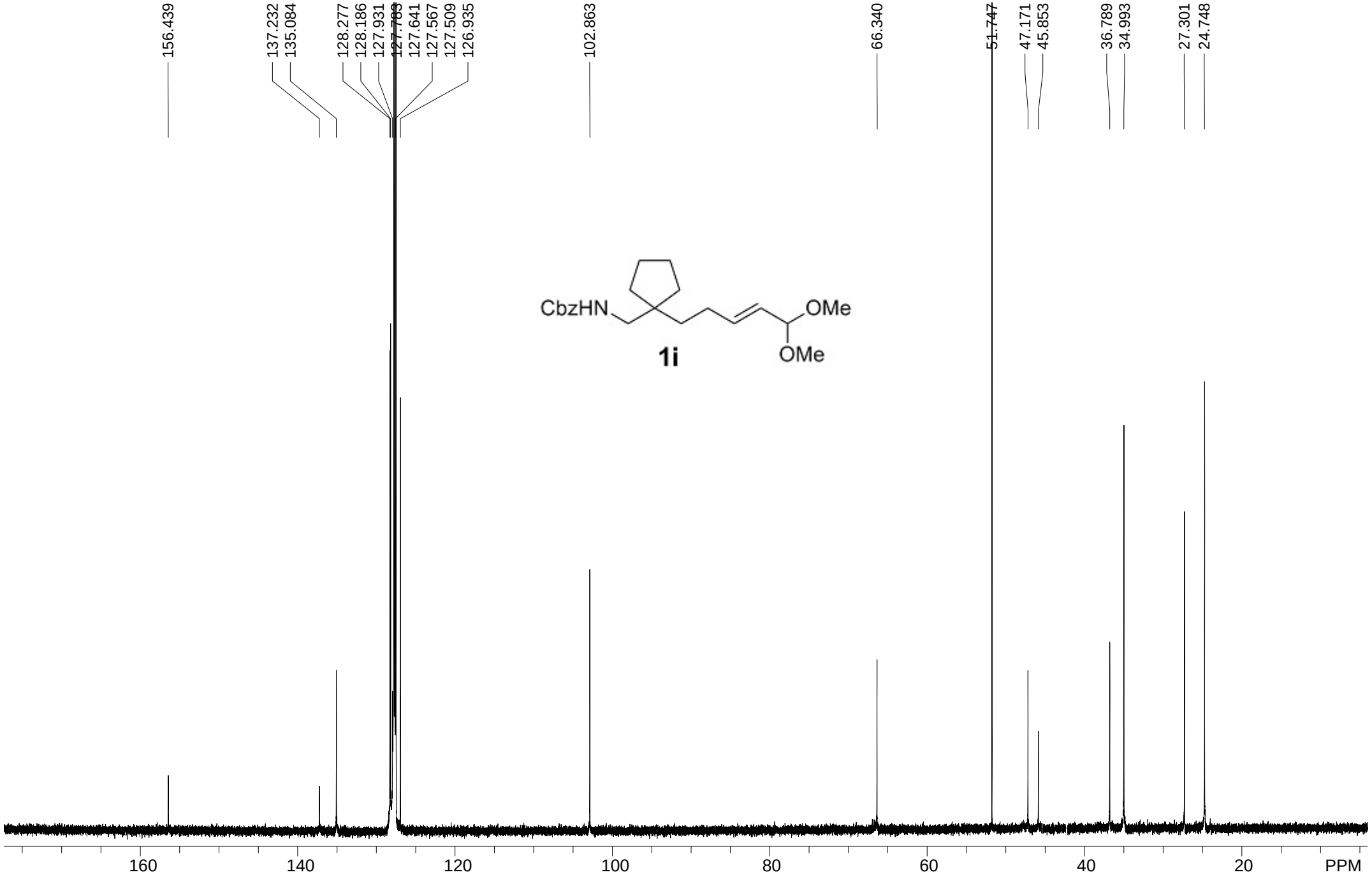
7.105
7.093
7.092
7.091
7.082
7.081
7.071
7.070
7.016
4.730
5.060
4.723
3.164
3.157
3.155
2.924
2.915
1.843
1.830
1.376
1.366
1.353
1.338
1.328
1.132
1.125
1.121
1.117
1.115
1.110
1.108
1.093
1.085
1.031
1.022
1.013
CbzHN
OMe
OMe
1i
1.99
1.04
1.00
2.15
1.10
0.91
6.40
2.18
2.20
5.53
8
7
6
5
4
3
2
1
PPM


156.439
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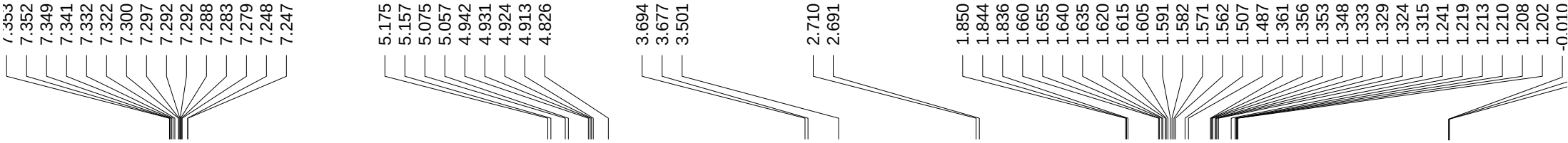
135.084
128.277
128.186
127.931
127.783
127.641
127.567
127.509
126.935
102.863
66.340
51.747
47.171
45.853
36.789
34.993
27.301
24.748
CbzHN
OMe
OMe
1i
160
140
120
100
80
60
40
20
PPM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7.341
7.332
7.322
7.300
7.297
7.292
7.292
7.288
7.283
7.279
7.248
7.247
5.175
5.157
5.075
5.057
4.942
4.931
4.924
4.913
4.826
3.694
3.677
3.501
2.710
2.691
1.850
1.844
1.836
1.660
1.655
1.640
1.635
1.620
1.615
1.605
1.591
1.582
1.571
1.562
1.507
1.487
1.361
1.356
1.353
1.348
1.333
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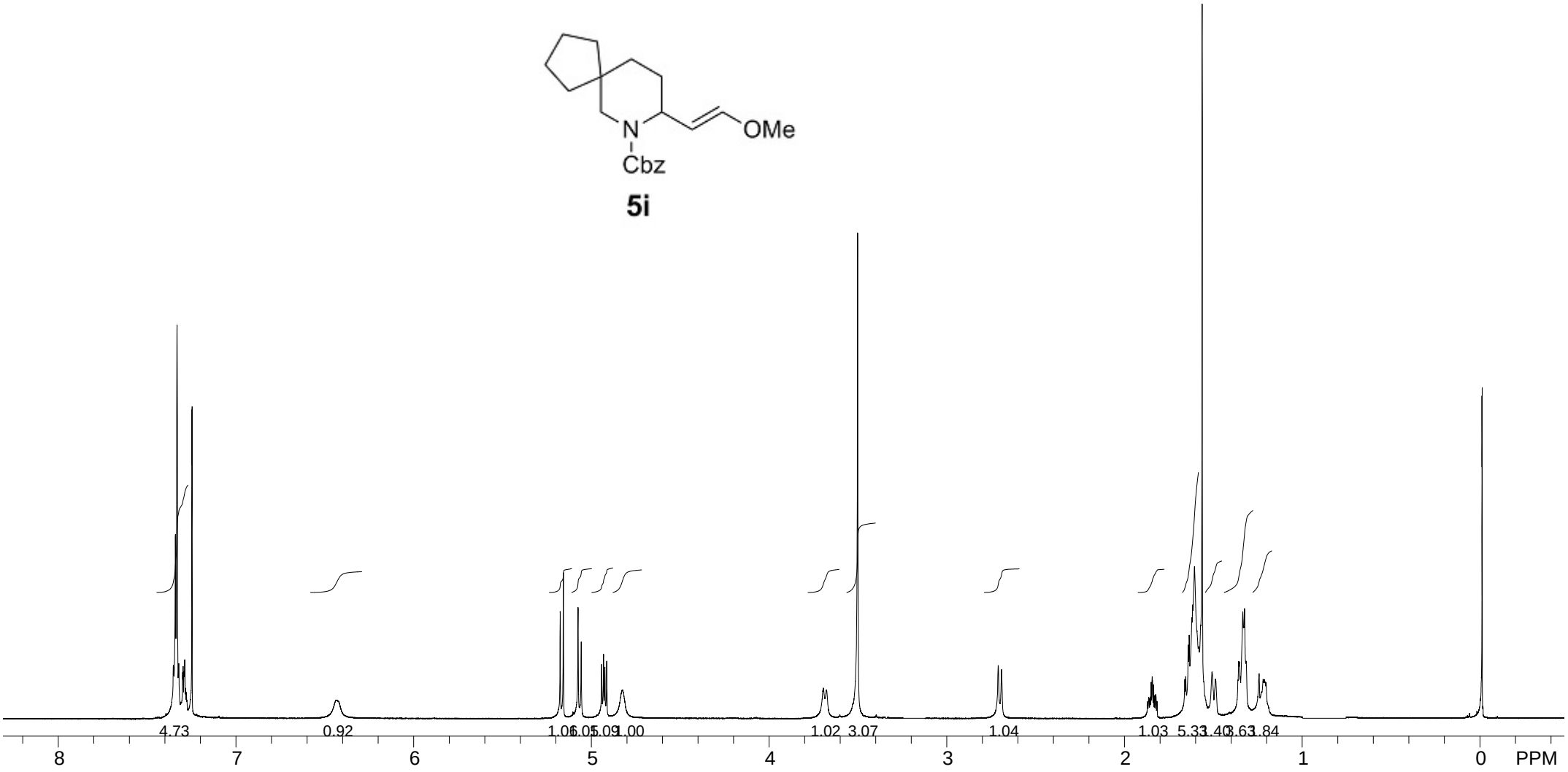
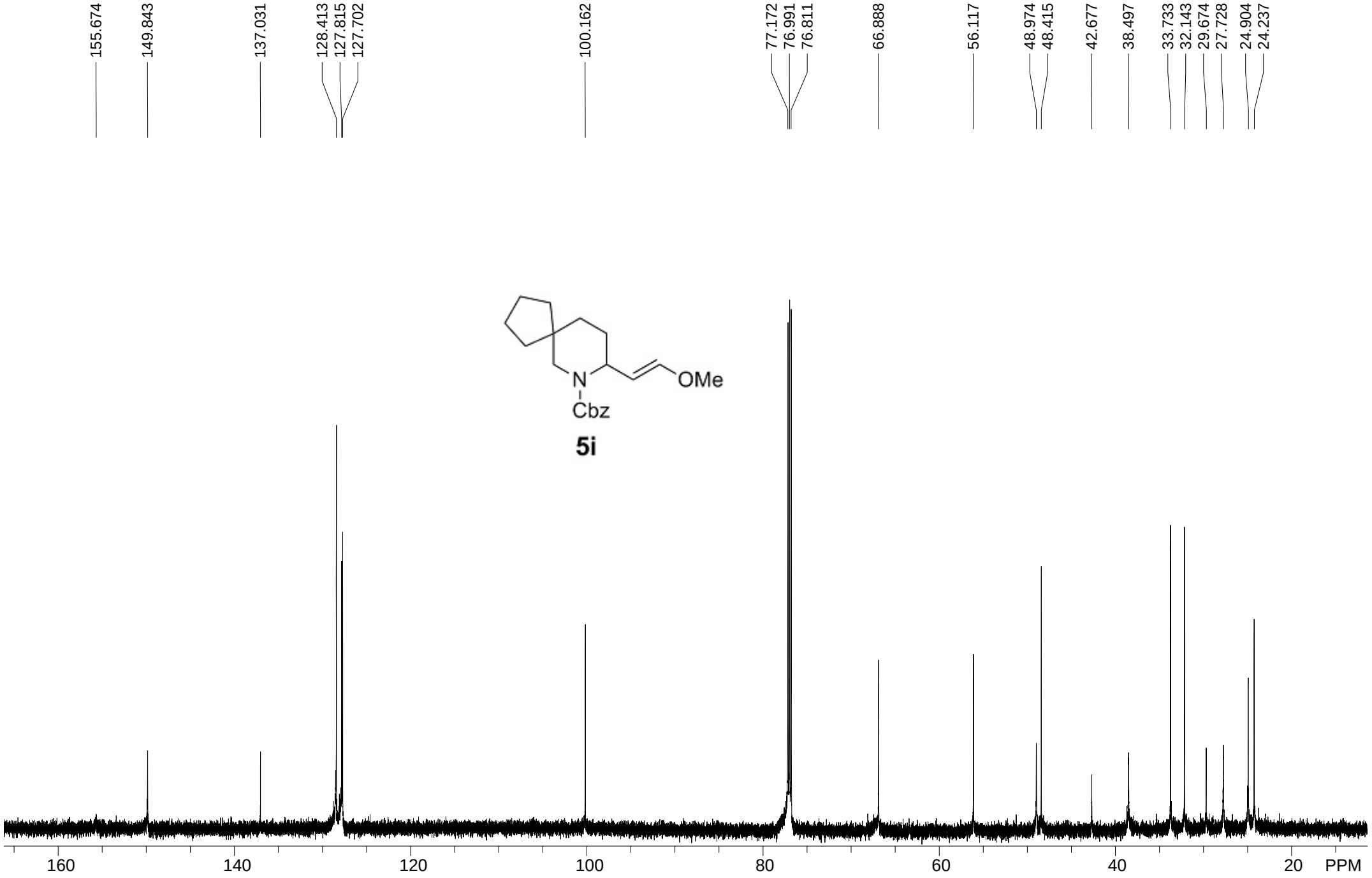
1.324
1.315
1.241
1.219
1.213
1.210
1.208
1.202

N
Cbz
OMe

5i

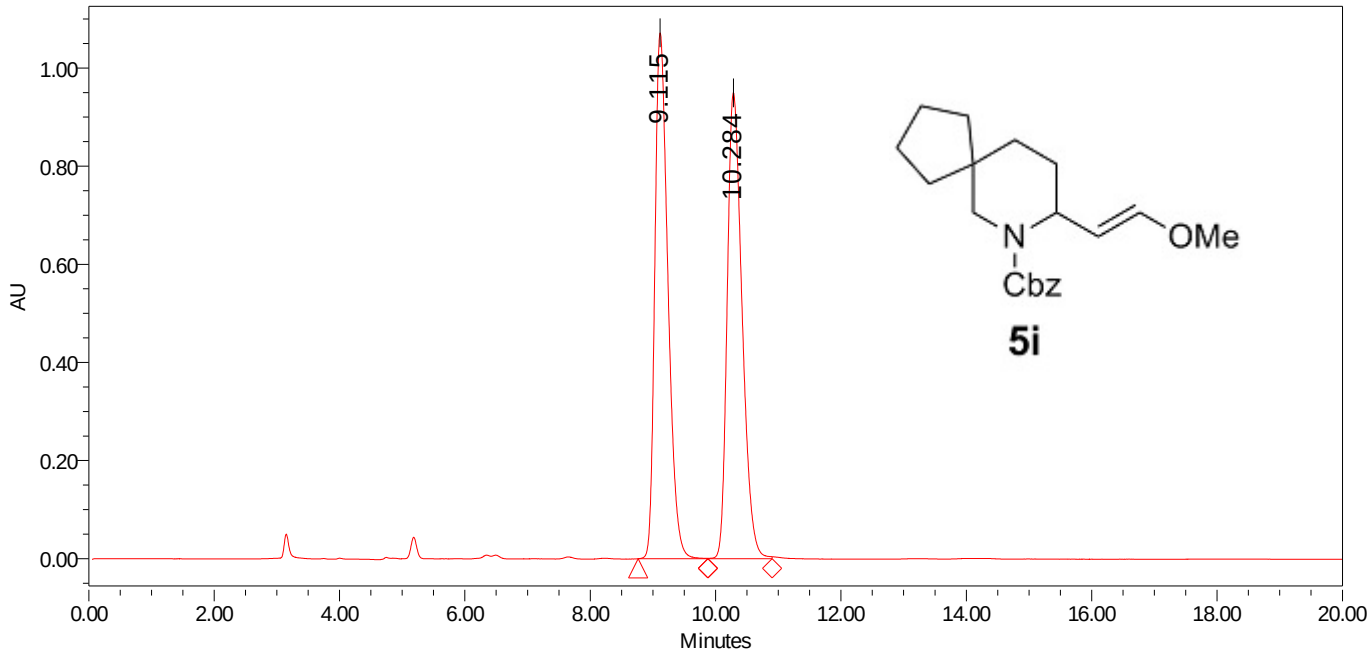

4.73
0.92
1.06
6.05
5.09
1.00
1.02
3.07
1.04
1.03
5.33
3.40
3.63
1.84
8
7
6
5
4
3
2
1
0
PPM


155.674
149.843
137.031
128.413
127.815
127.702
100.162
77.172
76.991
76.811
66.888
56.117
48.974
48.415
42.677
38.497
33.733
32.143
29.674
27.728
24.904
24.237
N
Cbz
OMe
5i
160
140
120
100
80
60
40
20
PPM

SAMPLE INFORMATION

Sample Name:	4-9-1-R	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	4_9_1_r
Vial:	64	Acq. Method Set:	ODH 99 HEXANE
Injection #:	1	Processing Method	s
Injection Volume:	40.00 ul	Channel Name:	210.3nm@3
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	7/13/2013 12:03:41 PM EDT		
Date Processed:	9/12/2013 6:51:46 PM EDT		

Auto-Scaled Chromatogram



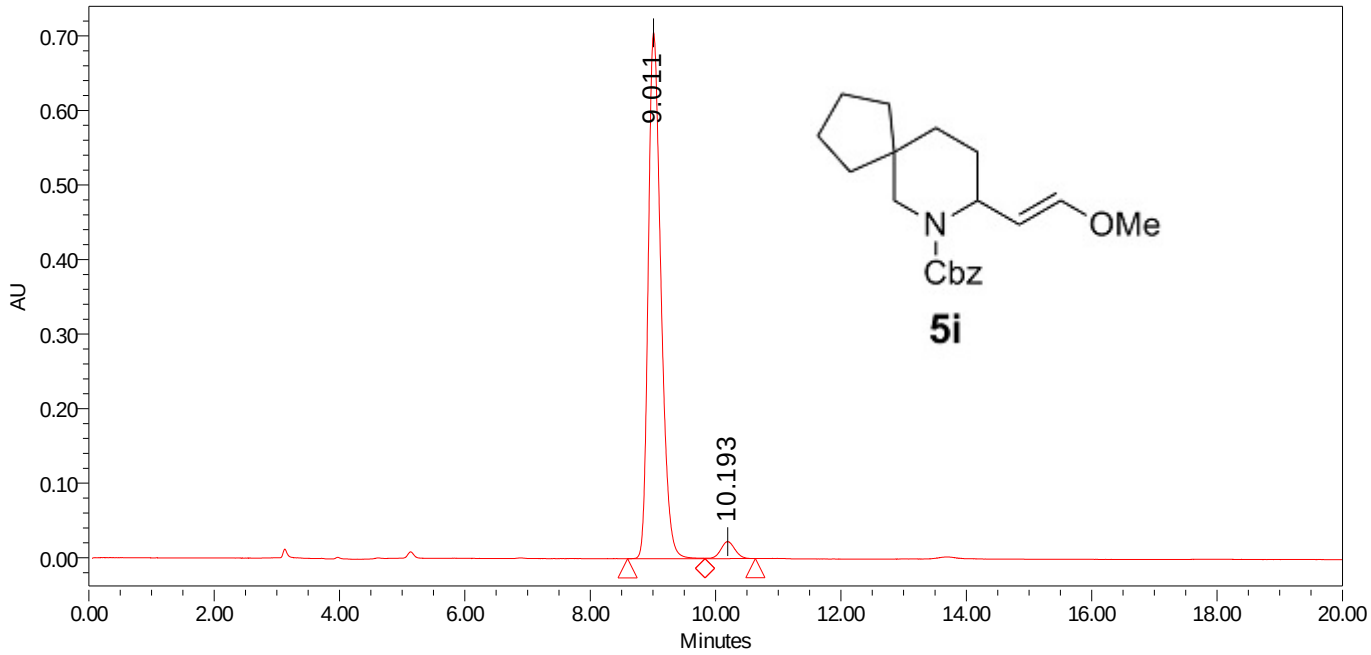
Peak Results

	Name	RT	Area	Height	% Area
1		9.115	15562311	1071989	49.88
2		10.284	15639011	949609	50.12

SAMPLE INFORMATION

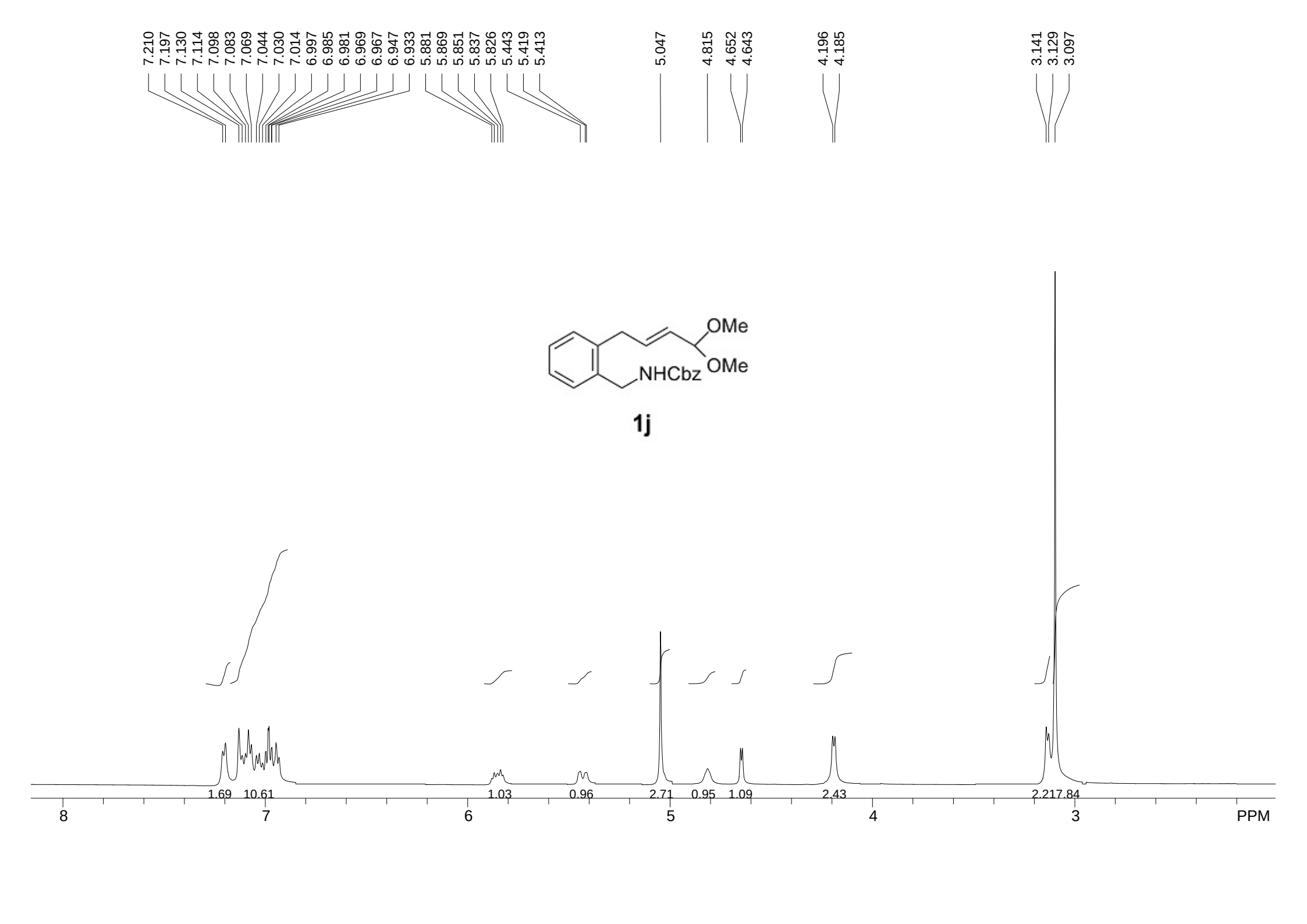
Sample Name:	4-9-1-30h	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	4_9_1_30h
Vial:	49	Acq. Method Set:	ODH 99 HEXANE
Injection #:	1	Processing Method	s
Injection Volume:	10.00 ul	Channel Name:	210.3nm@4
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	7/15/2013 10:30:31 AM EDT		
Date Processed:	9/12/2013 6:52:54 PM EDT		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	% Area
1		9.011	9909476	705469	96.51
2		10.193	358369	22822	3.49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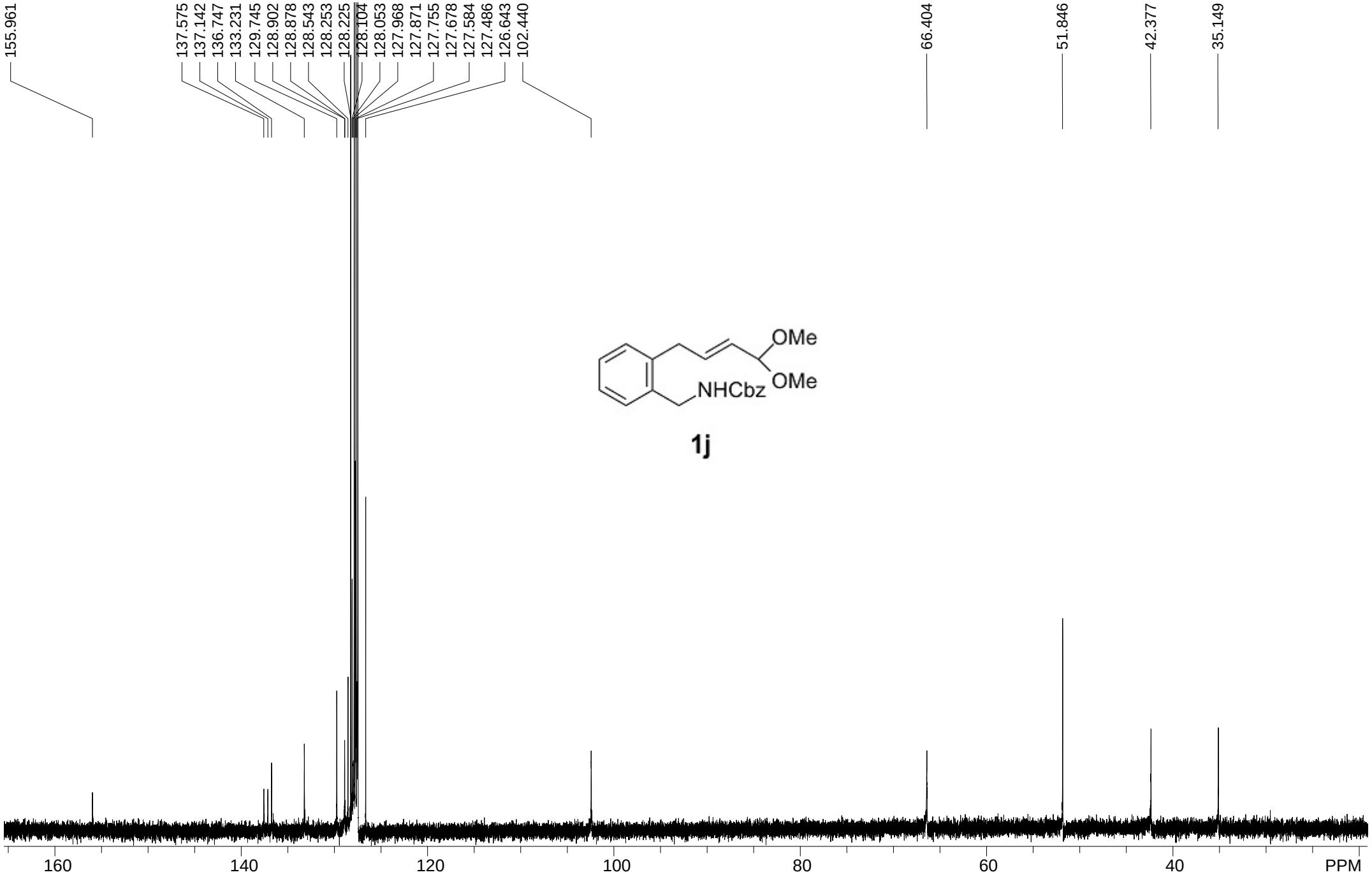
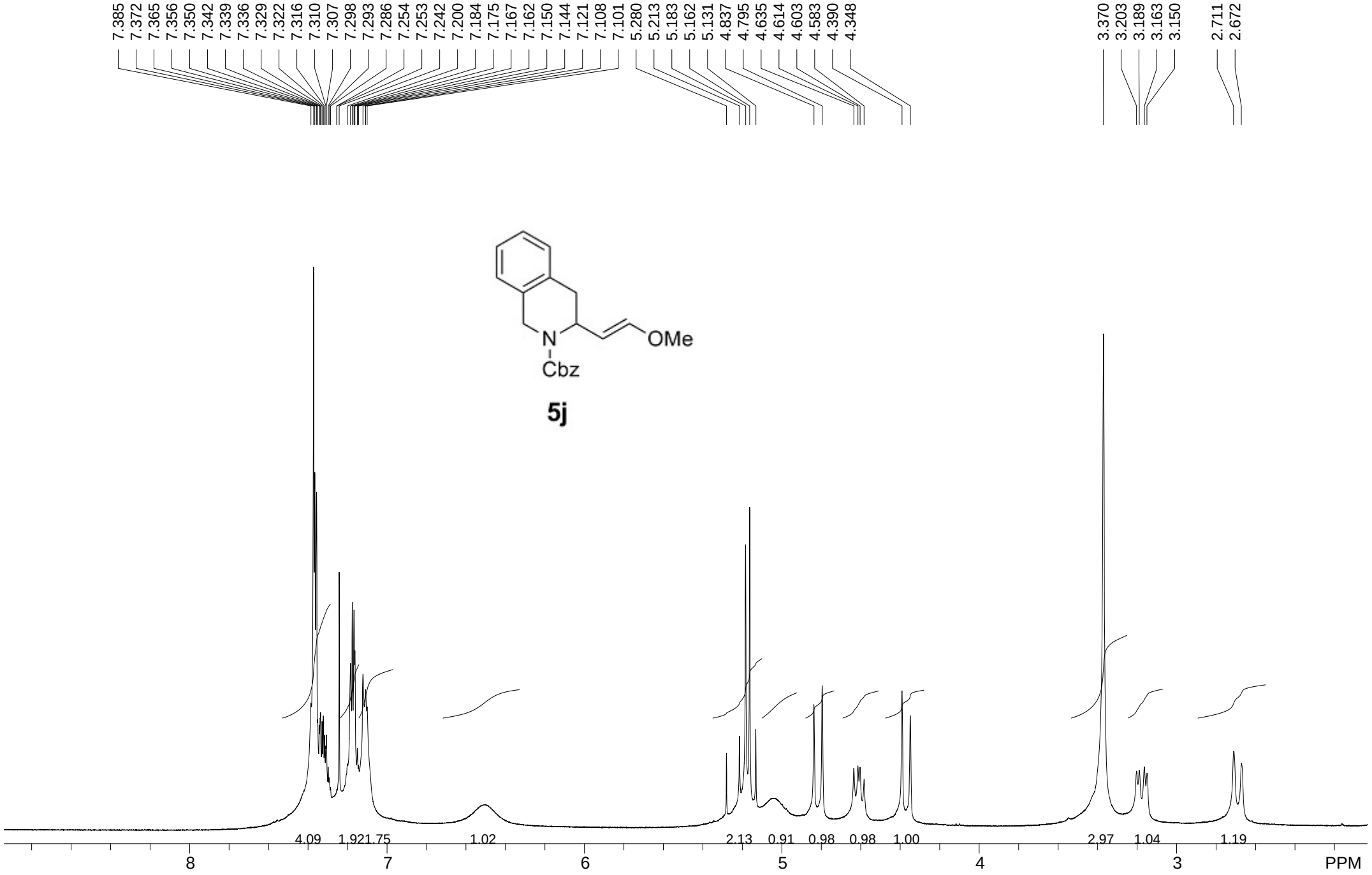
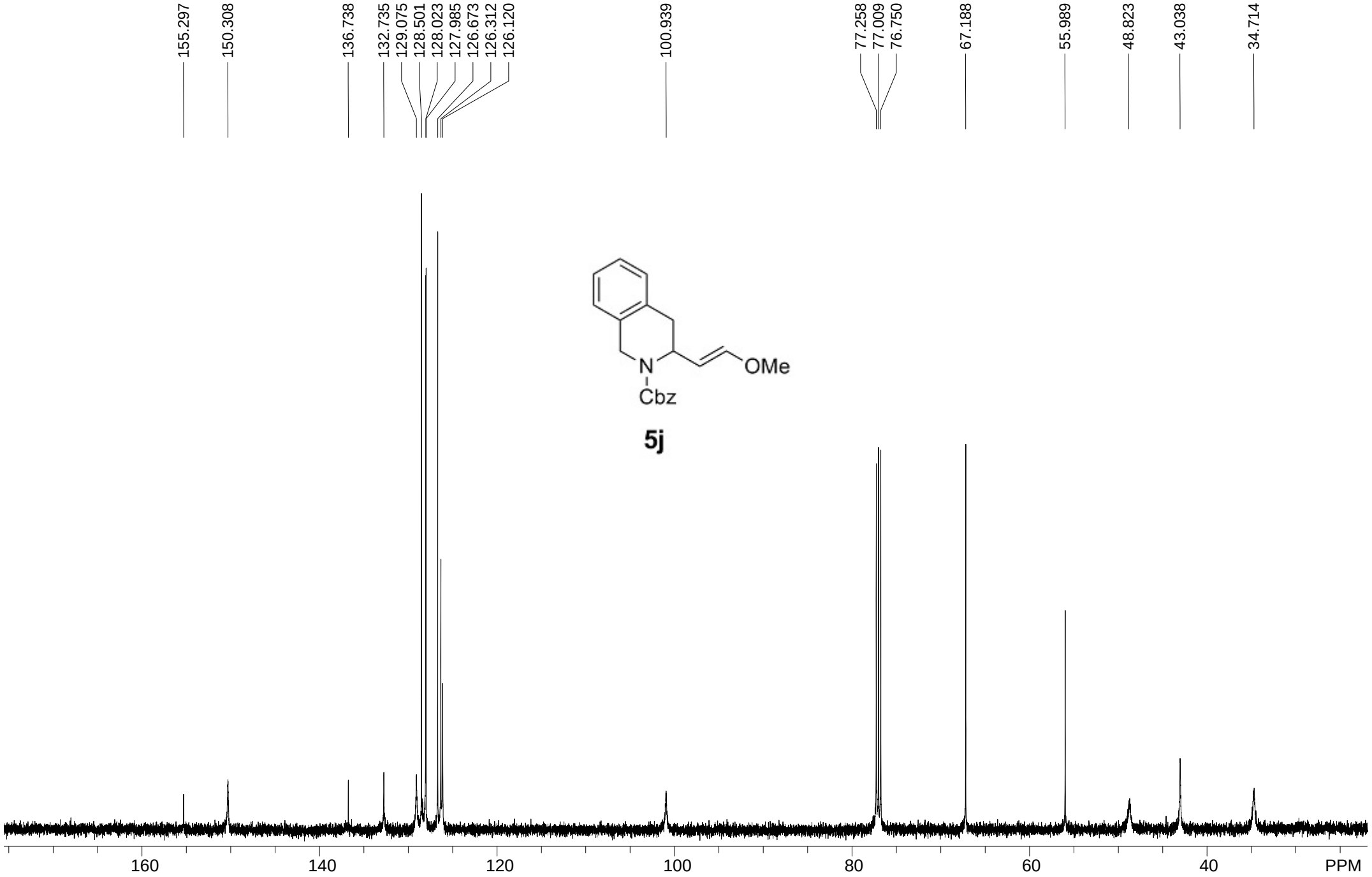
7.197
7.130
7.114
7.098
7.083
7.069
7.044
7.030
7.014
6.997
6.985
6.981
6.969
6.967
6.947
6.933
5.881
5.869
5.851
5.837
5.826
5.443
5.419
5.413
5.047
4.815
4.652
4.643
4.196
4.185
3.141
3.129
3.097
OMe
OMe
NHCbz
1j
1.69
10.61
1.03
0.96
2.71
0.95
1.09
2.43
2.21
7.84
8
7
6
5
4
3
PPM


155.961
137.575
137.142
136.747
133.231
129.745
128.902
128.878
128.543
128.253
128.225
128.104
128.053
127.968
127.871
127.755
127.678
127.584
127.486
126.643
102.440
66.404
51.846
42.377
35.149
OMe
OMe
NHCbz
160
140
120
100
80
60
40
PPM

1j


7.385
7.372
7.365
7.356
7.350
7.342
7.339
7.336
7.329
7.322
7.316
7.310
7.307
7.298
7.293
7.286
7.254
7.253
7.242
7.200
7.184
7.175
7.167
7.162
7.150
7.144
7.121
7.108
7.101
5.280
5.213
5.183
5.162
5.131
4.837
4.795
4.635
4.614
4.603
4.583
4.390
4.348
3.370
3.203
3.189
3.163
3.150
2.711
2.672
N
Cbz
OMe
5j
4.09
1.92
1.75
1.02
2.13
0.91
0.98
0.98
1.00
2.97
1.04
1.19
8
7
6
5
4
3
PPM


155.297
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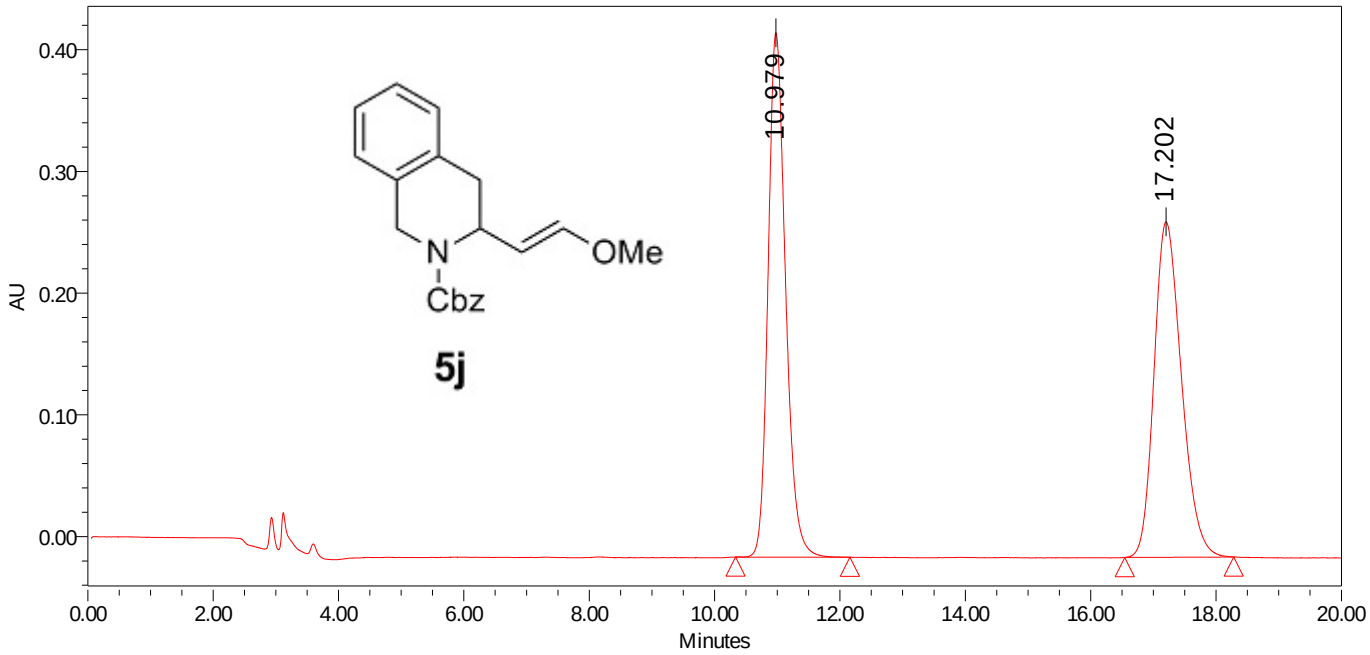
136.738
132.735
129.075
128.501
128.023
127.985
126.673
126.312
126.120
100.939
77.258
77.009
76.750
67.188
55.989
48.823
43.038
34.714
N
Cbz
OMe
5j
160
140
120
100
80
60
40
PPM

SAMPLE INFORMATION

Sample Name:	4-37-1-r	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	4_37_1_r
Vial:	59	Acq. Method Set:	odh 97%
Injection #:	1	Processing Method	1
Injection Volume:	10.00 ul	Channel Name:	210.3nm@3
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	8/19/2013 6:30:23 PM EDT		
Date Processed:	9/12/2013 6:57:32 PM EDT		

Auto-Scaled Chromatogram



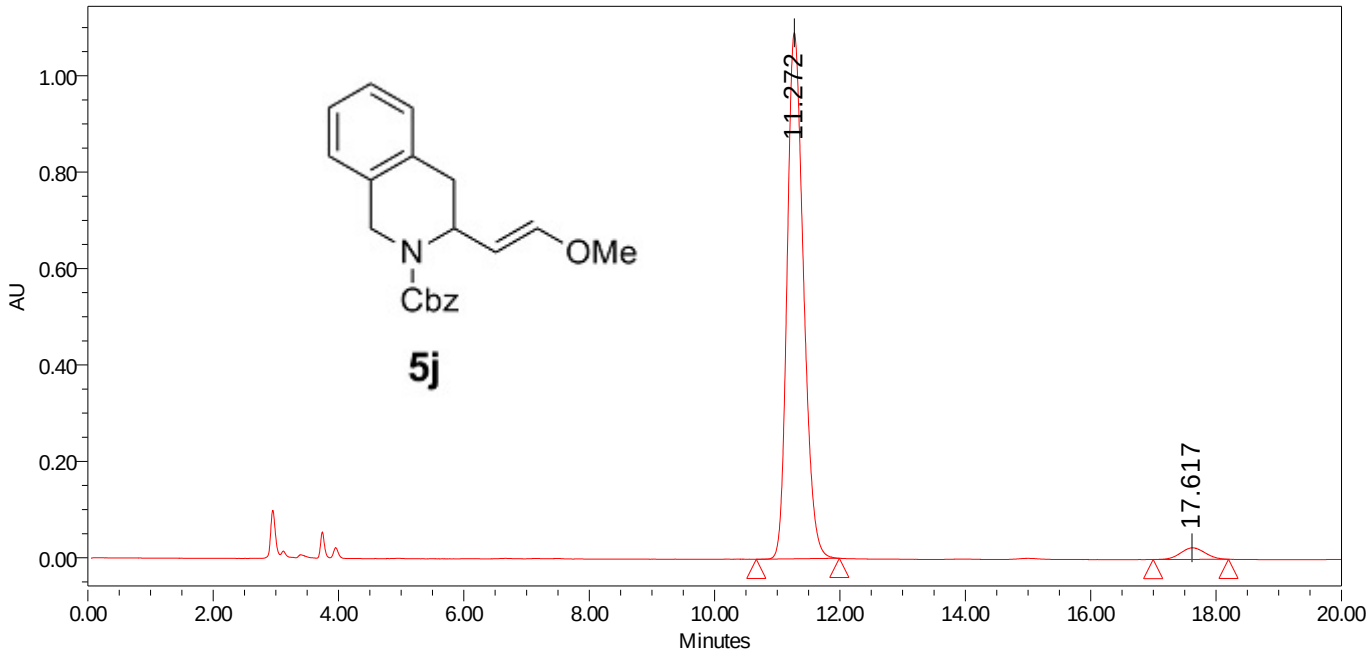
Peak Results

	Name	RT	Area	Height	% Area
1		10.979	8337201	430822	49.90
2		17.202	8371967	275676	50.10

SAMPLE INFORMATION

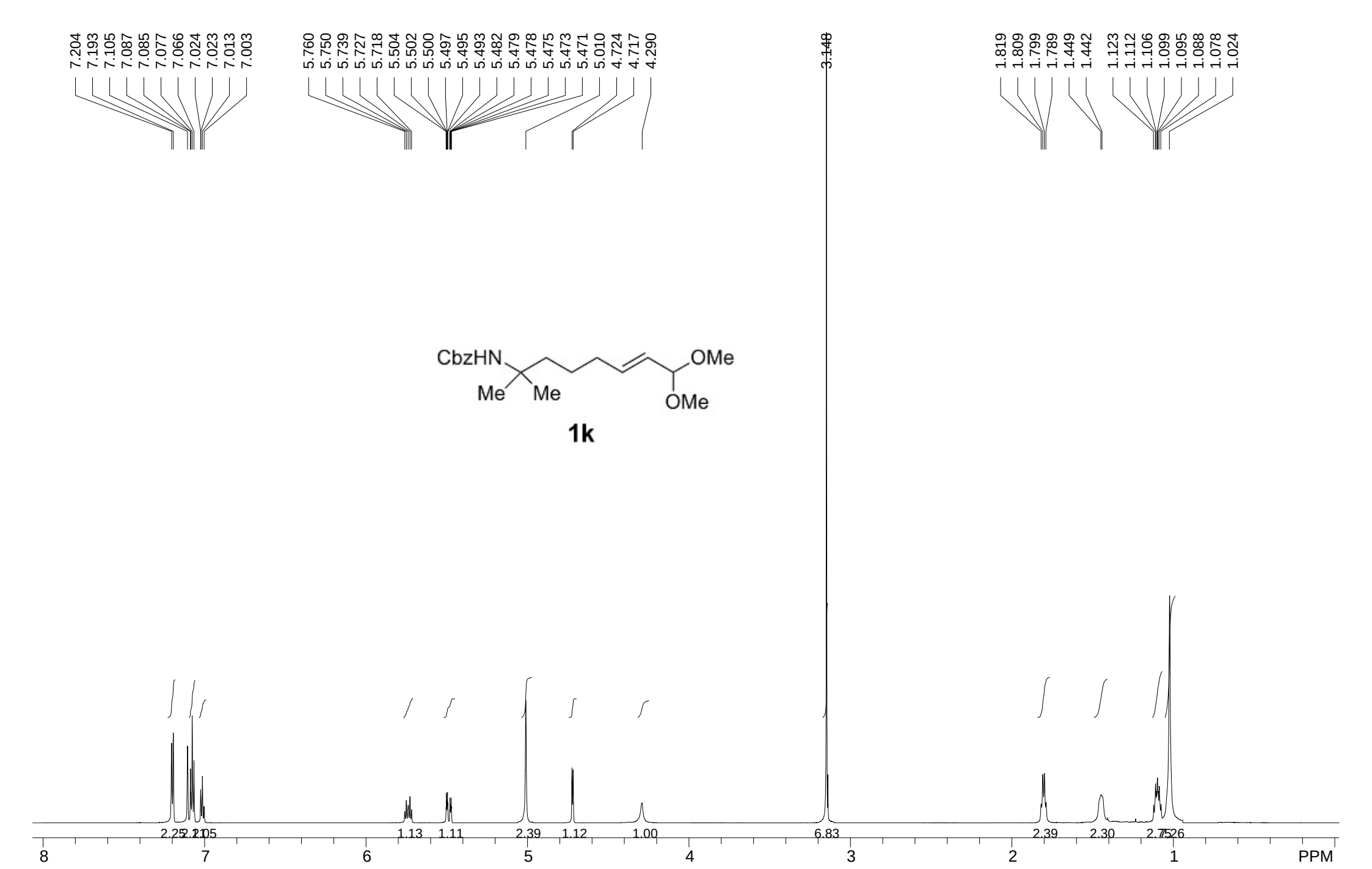
Sample Name:	4-37-24h	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	4_37_24h
Vial:	55	Acq. Method Set:	odh 97%
Injection #:	1	Processing Method	1
Injection Volume:	10.00 ul	Channel Name:	210.3nm@2
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	8/9/2013 11:02:00 AM EDT		
Date Processed:	9/12/2013 6:56:04 PM EDT		

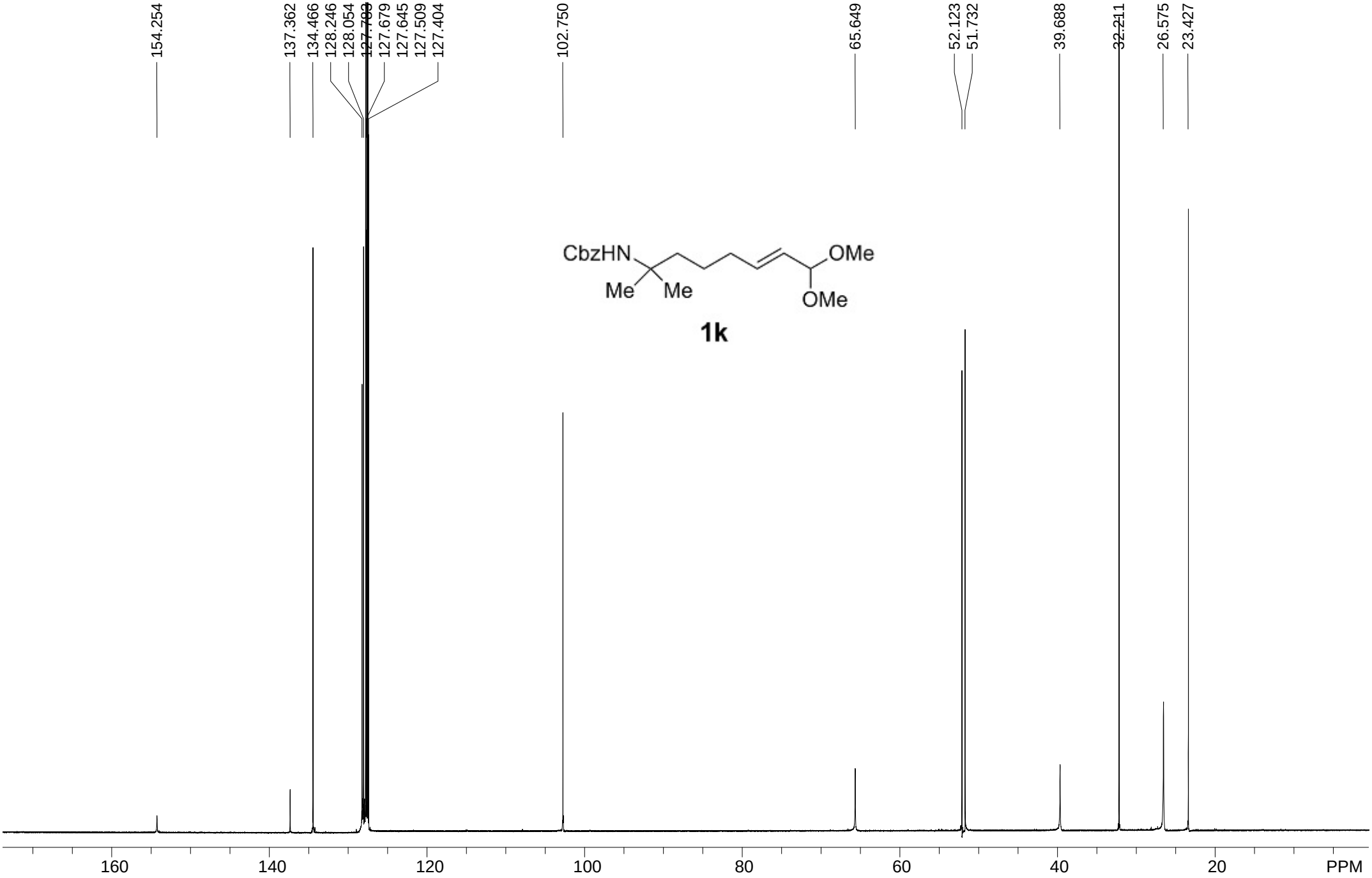
Auto-Scaled Chromatogram

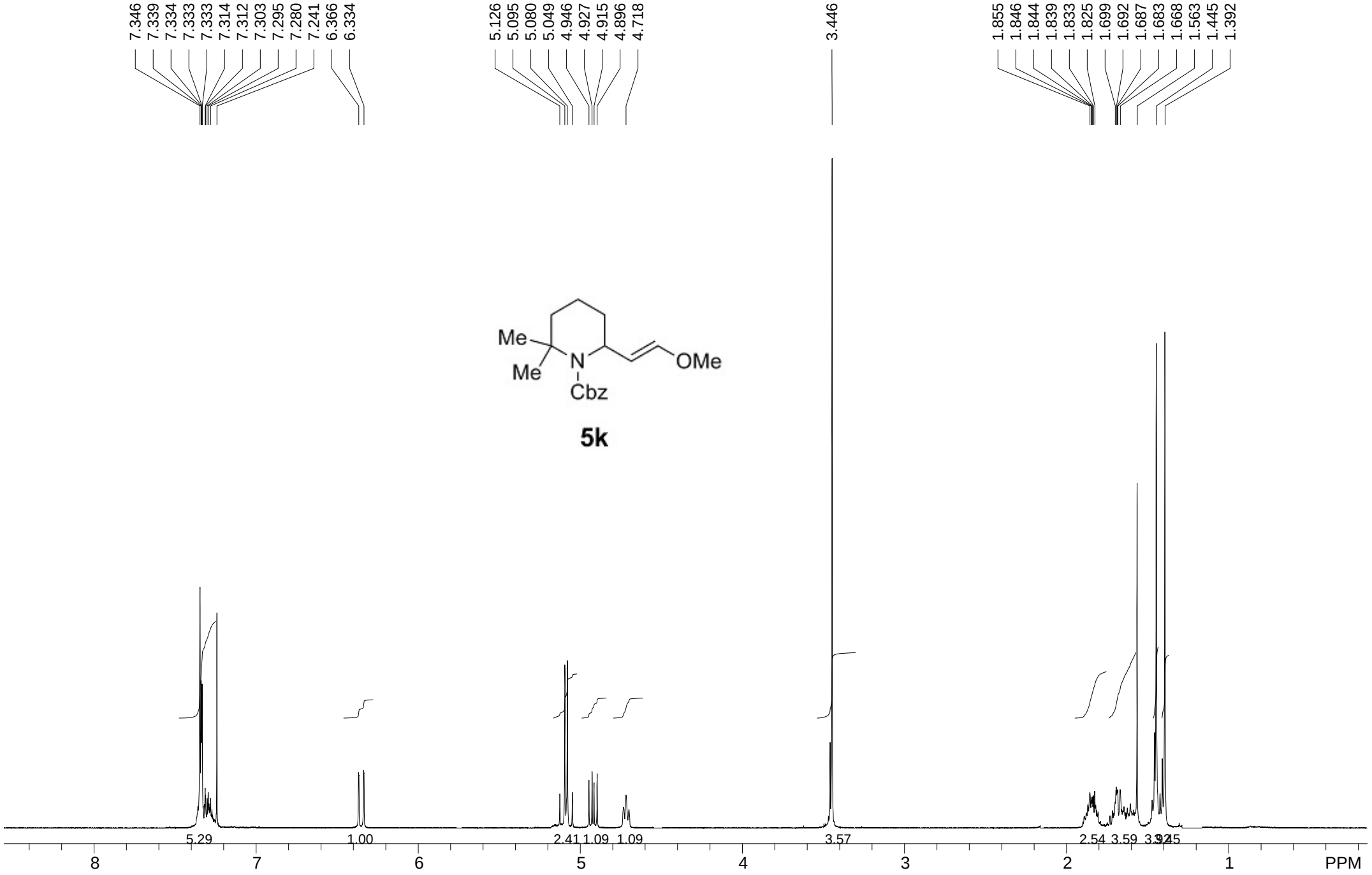


Peak Results

	Name	RT	Area	Height	% Area
1		11.272	19796624	1091378	96.80
2		17.617	654472	24017	3.20


7.204
7.193
7.105
7.087
7.085
7.077
7.066
7.024
7.023
7.013
7.003
5.760
5.750
5.739
5.727
5.718
5.504
5.502
5.500
5.497
5.495
5.493
5.482
5.479
5.478
5.475
5.473
5.471
5.010
4.724
4.717
4.290
3.148
1.819
1.809
1.799
1.789
1.449
1.442
1.123
1.112
1.106
1.099
1.095
1.088
1.078
1.024
CbzHN
Me
Me
OMe
OMe
1k
2.25
2.21
1.05
1.13
1.11
2.39
1.12
1.00
6.83
2.39
2.30
2.76
1.26
8
7
6
5
4
3
2
1
PPM


154.254
137.362
134.466
128.246
128.054
127.703
127.679
127.645
127.509
127.404
102.750
65.649
52.123
51.732
39.688
32.211
26.575
23.427
CbzHN
Me
Me
OMe
OMe
1k
160
140
120
100
80
60
40
20
PPM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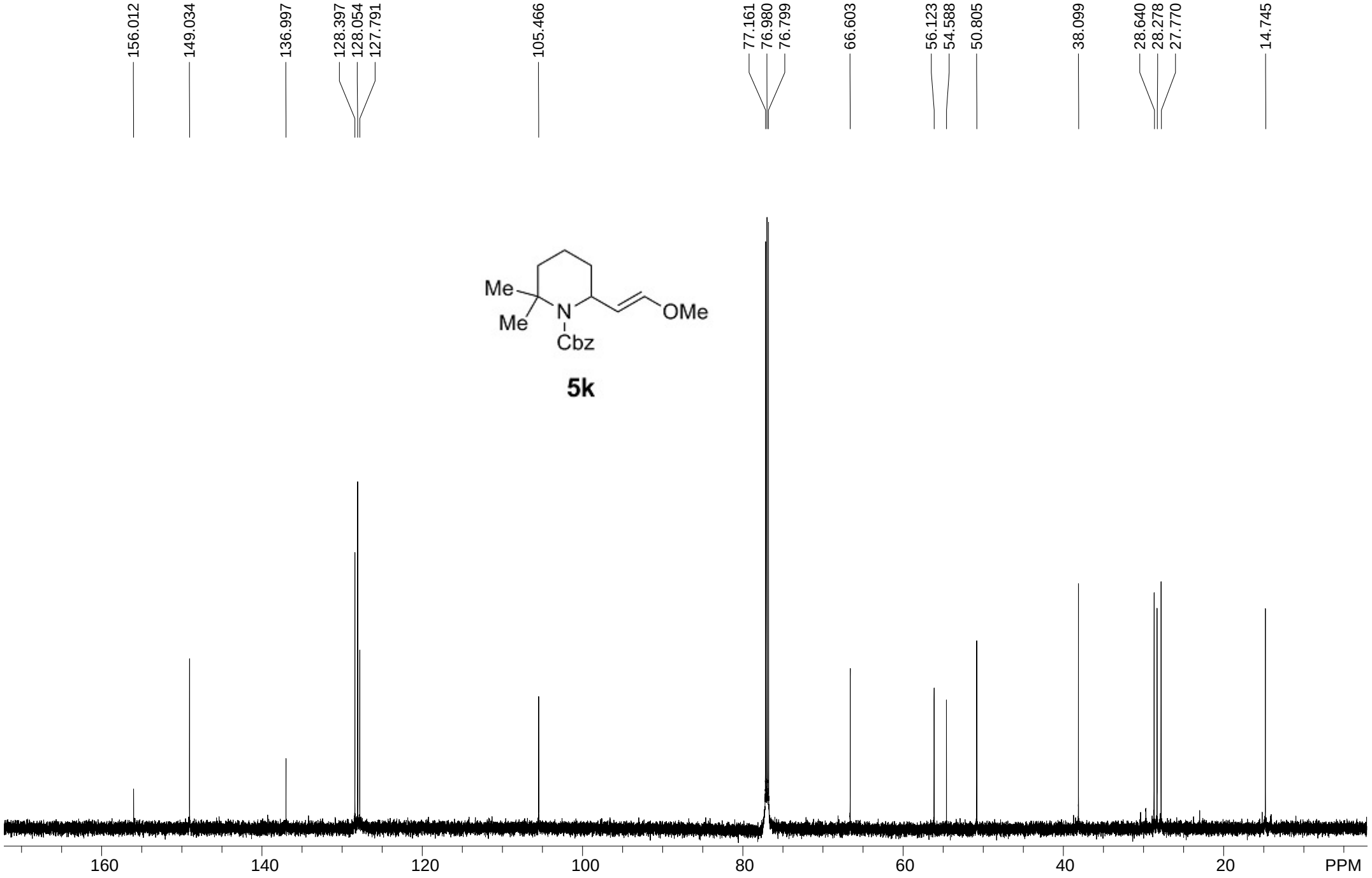
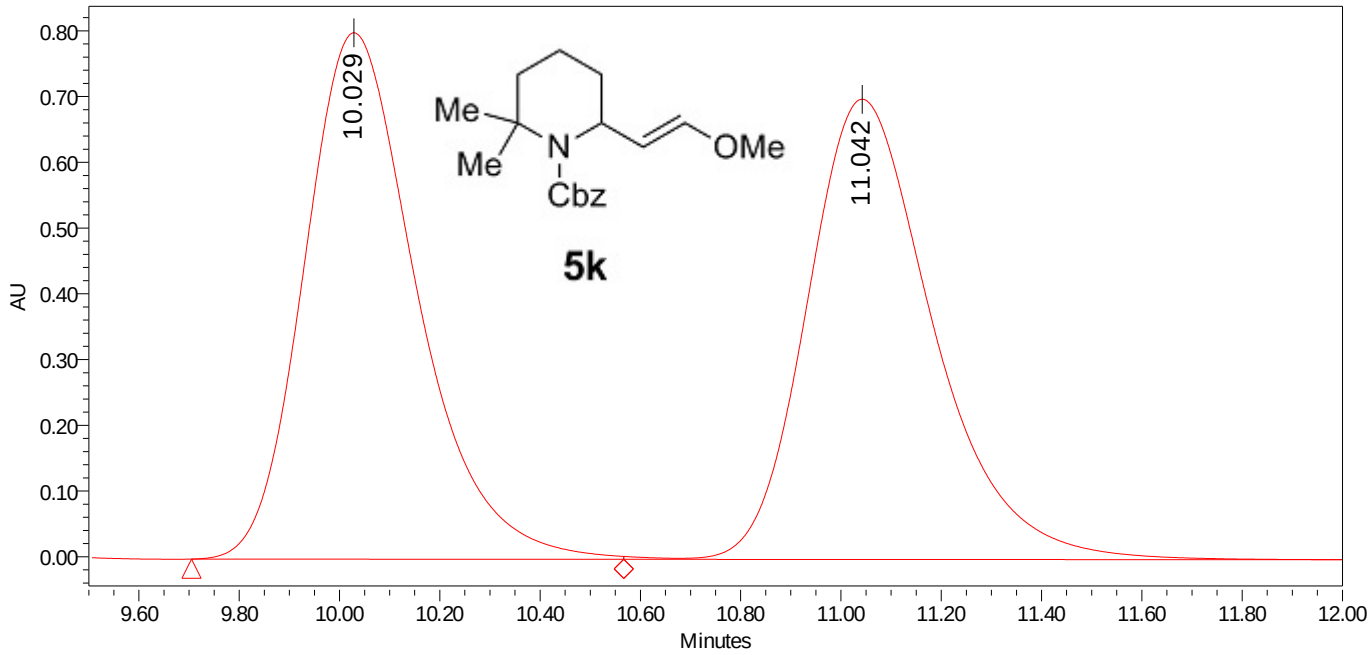
7.333
7.333
7.314
7.312
7.303
7.295
7.280
7.241
6.366
6.334
5.126
5.095
5.080
5.049
4.946
4.927
4.915
4.896
4.718
3.446
1.855
1.846
1.844
1.839
1.833
1.825
1.699
1.692
1.687
1.683
1.668
1.563
1.445
1.392
Me
Me
N
Cbz
OMe
5k
5.29
1.00
2.41
1.09
1.09
3.57
2.54
3.59
8
7
6
5
4
3
2
1
PPM


156.012
149.034
136.997
128.397
128.054
127.791
105.466
77.161
76.980
76.799
66.603
56.123
54.588
50.805
38.099
28.640
28.278
27.770
14.745
Me
Me
N
Cbz
OMe
5k
160
140
120
100
80
60
40
20
PPM

SAMPLE INFORMATION

Sample Name:	4-27-1-r	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	4_27_1_r
Vial:	48	Acq. Method Set:	ADH 99
Injection #:	1	Processing Method	NEW
Injection Volume:	10.00 ul	Channel Name:	210.3nm@1
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	9/23/2013 11:25:18 AM EDT		
Date Processed:	9/23/2013 12:10:22 PM EDT		

Auto-Scaled Chromatogram



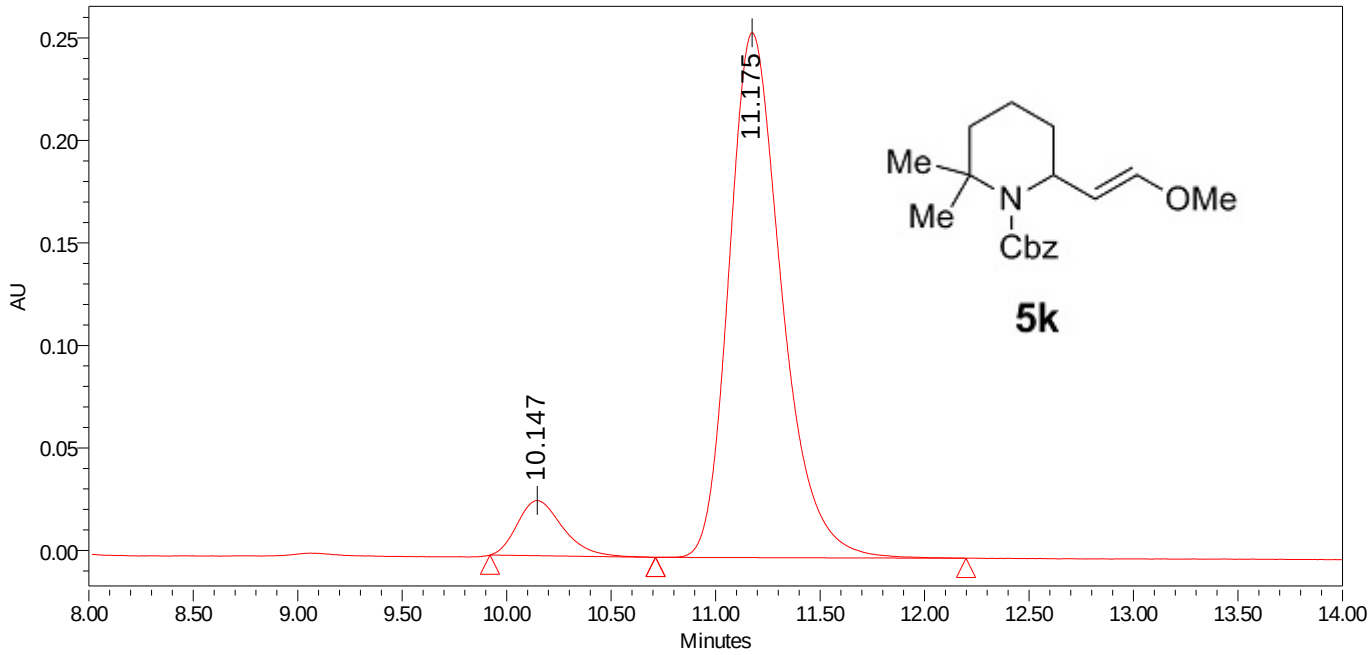
Peak Results

	Name	RT	Area	Height	% Area
1		10.029	12512696	800756	50.54
2		11.042	12243155	699882	49.46

SAMPLE INFORMATION

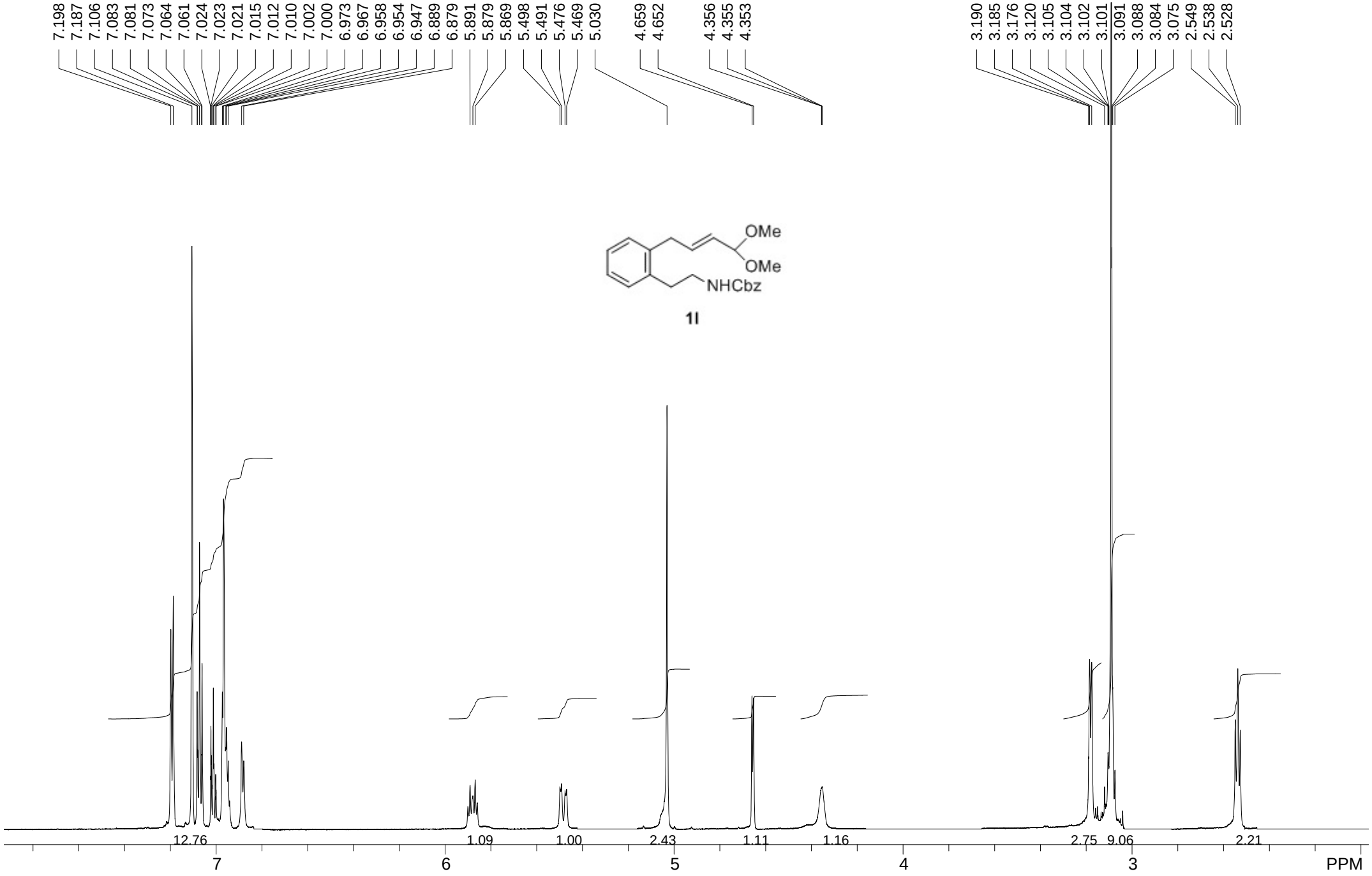
Sample Name:	4-27-18h	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	4_27_18h
Vial:	73	Acq. Method Set:	ADH 99
Injection #:	1	Processing Method	NEW
Injection Volume:	10.00 ul	Channel Name:	210.3nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.3 nm
Date Acquired:	8/2/2013 10:47:44 AM EDT		
Date Processed:	9/12/2013 6:59:21 PM EDT		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	% Area
1		10.147	406940	26936	8.32
2		11.175	4483713	256090	91.68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7.083
7.081
7.073
7.064
7.061
7.024
7.023
7.021
7.015
7.012
7.010
7.002
7.000
6.973
6.967
6.958
6.954
6.947
6.889
6.879
5.891
5.879
5.869
5.498
5.491
5.476
5.469
5.030
4.659
4.652
4.356
4.355
4.353
3.190
3.185
3.176
3.120
3.105
3.104
3.102
3.101
3.091
3.088
3.084
3.075
2.549
2.538
2.528
OMe
OMe
NHCbz
12.76
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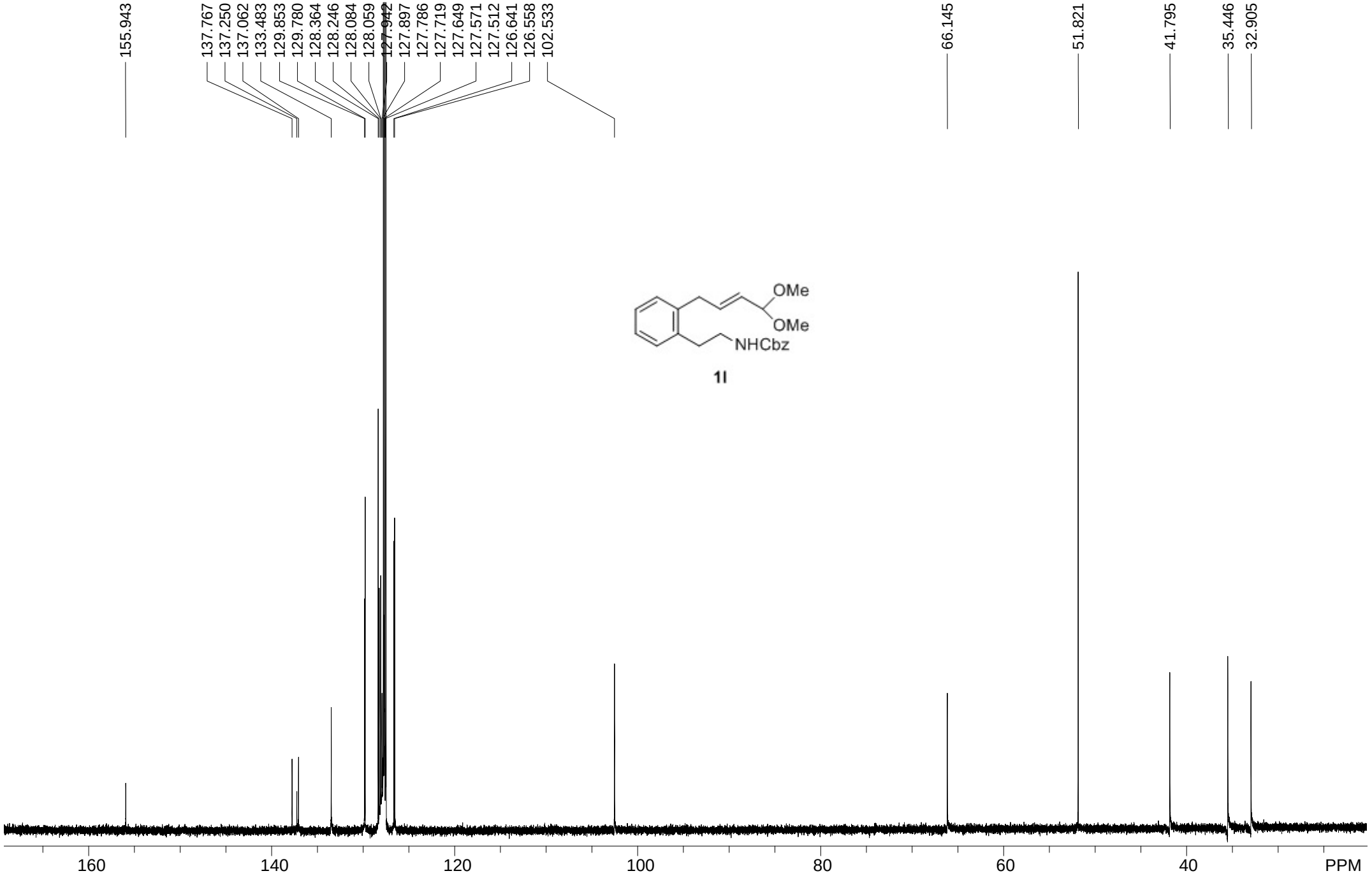
1.11
1.16
2.75
9.06
2.21
7
6
5
4
3
PPM

1l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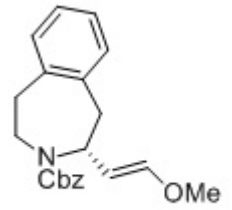
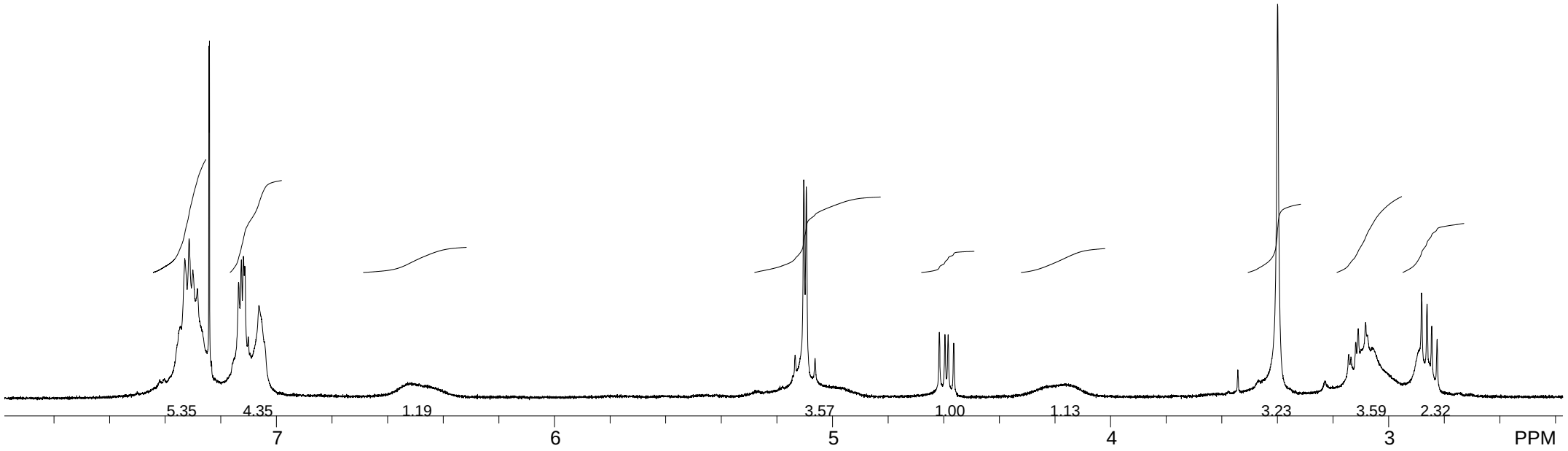
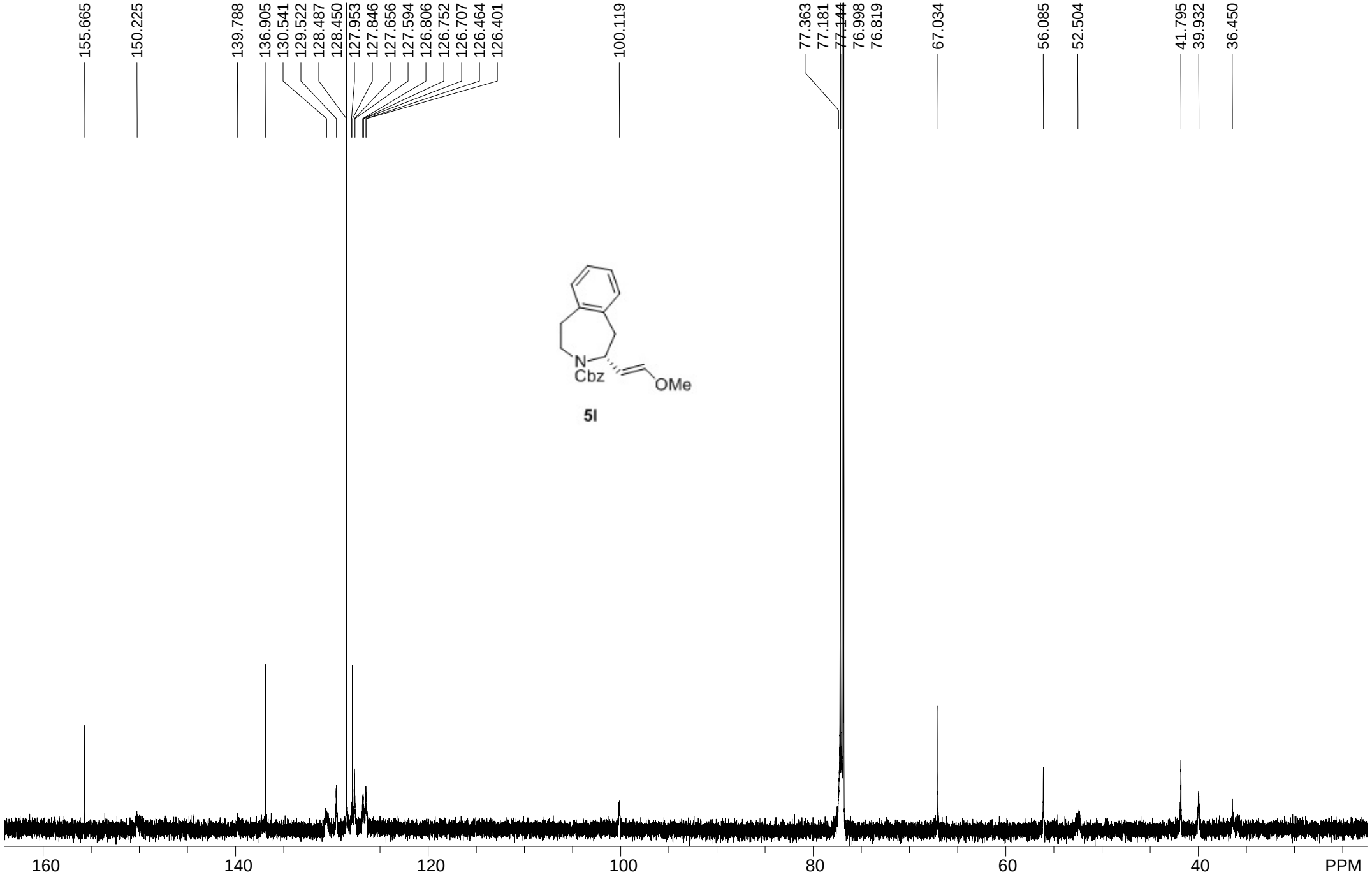
137.250
137.062
133.483
129.853
129.780
128.364
128.246
128.084
128.059
127.942
127.897
127.786
127.719
127.649
127.571
127.512
126.641
126.558
102.533
66.145
51.821
41.795
35.446
32.905
OMe
OMe
NHCbz
160
140
120
100
80
60
40
PPM

1l



5l

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128.450
127.953
127.846
127.656
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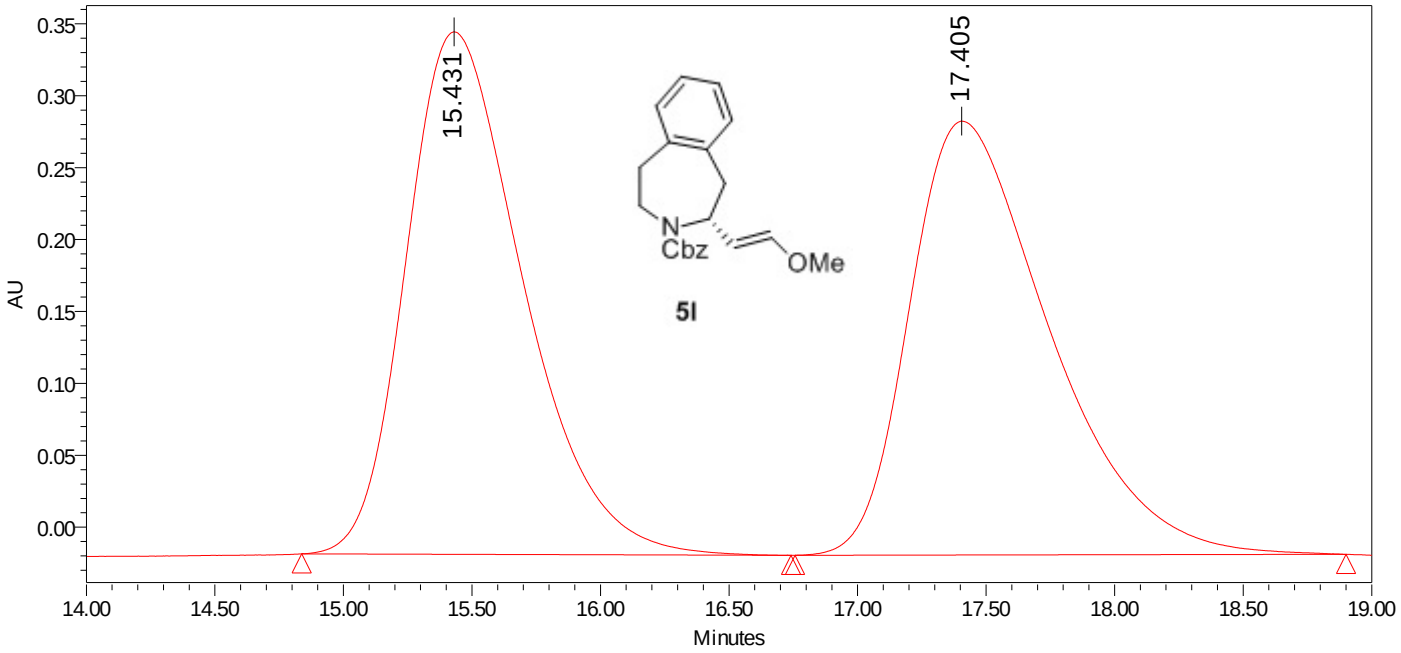
126.752
126.707
126.464
126.401
100.119
77.363
77.181
77.144
76.998
76.819
67.034
56.085
52.504
41.795
39.932
36.450
N
Cbz
OMe
160
140
120
100
80
60
40
PPM

5l

SAMPLE INFORMATION

Sample Name:	4-205-1-r	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	4_205_1_r
Vial:	45	Acq. Method Set:	odh 97%
Injection #:	1	Processing Method	n
Injection Volume:	20.00 ul	Channel Name:	210.2nm@1
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.2 nm
Date Acquired:	5/5/2014 4:30:37 PM EDT		
Date Processed:	5/7/2014 12:45:53 PM EDT		

Auto-Scaled Chromatogram



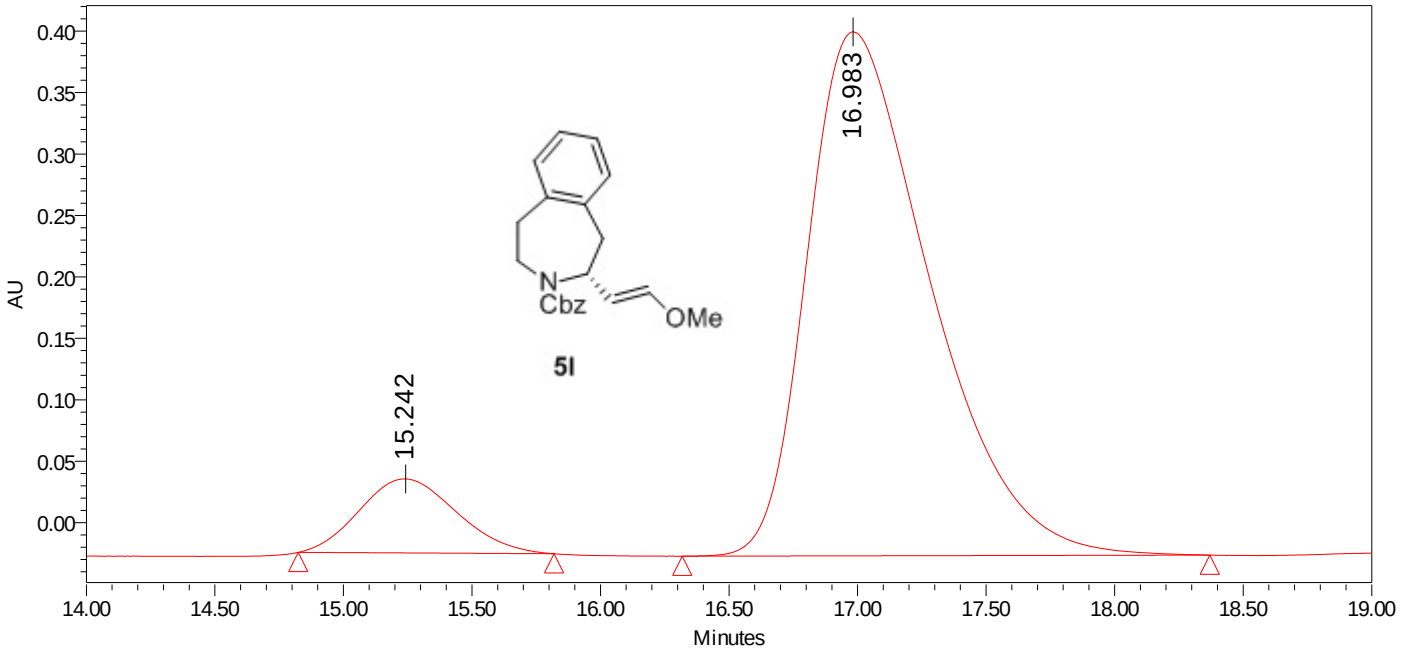
Peak Results

	Name	RT	Area	Height	Amount	Units
1		15.431	1146954	363276		
2		17.405	1140192	301702		

SAMPLE INFORMATION

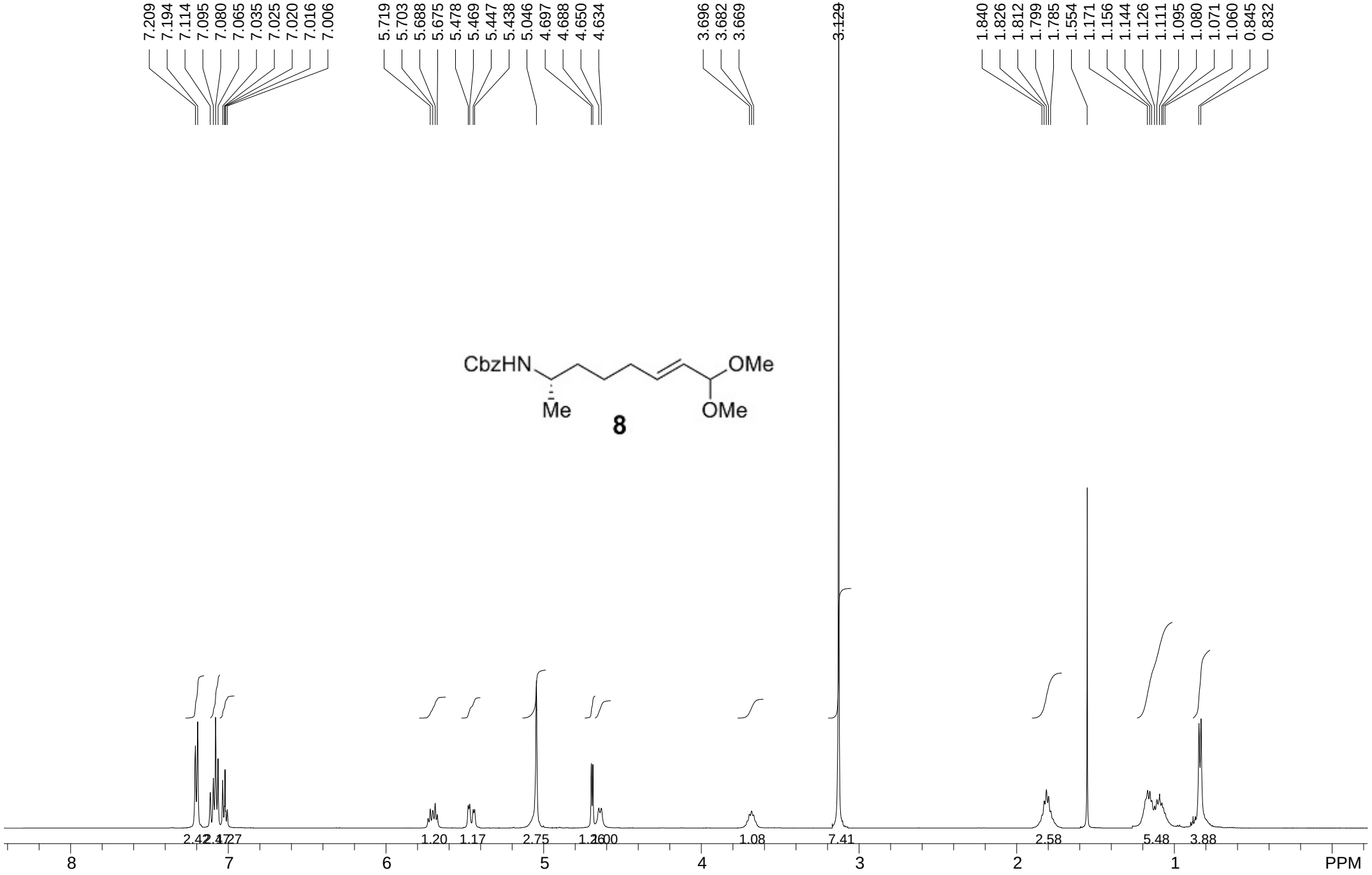
Sample Name:	4-207-0-48h	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	4_207_0_48h
Vial:	48	Acq. Method Set:	odh 97%
Injection #:	1	Processing Method	n
Injection Volume:	25.00 ul	Channel Name:	210.2nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	PDA 210.2 nm
Date Acquired:	5/6/2014 7:34:54 PM EDT		
Date Processed:	5/7/2014 12:43:33 PM EDT		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height	Amount	Units
1		15.242	1575819	60255		
2		16.983	14160191	426361		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7.194
7.114
7.095
7.080
7.065
7.035
7.025
7.020
7.016
7.006
5.719
5.703
5.688
5.675
5.478
5.469
5.447
5.438
5.046
4.697
4.688
4.650
4.634
3.696
3.682
3.669
3.129
1.840
1.826
1.812
1.799
1.785
1.554
1.171
1.156
1.144
1.126
1.111
1.095
1.080
1.071
1.060
0.845
0.832
CbzHN
OMe
Me
OMe
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2.42
2.47
2.27
1.20
1.17
2.75
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2.58
5.48
3.88
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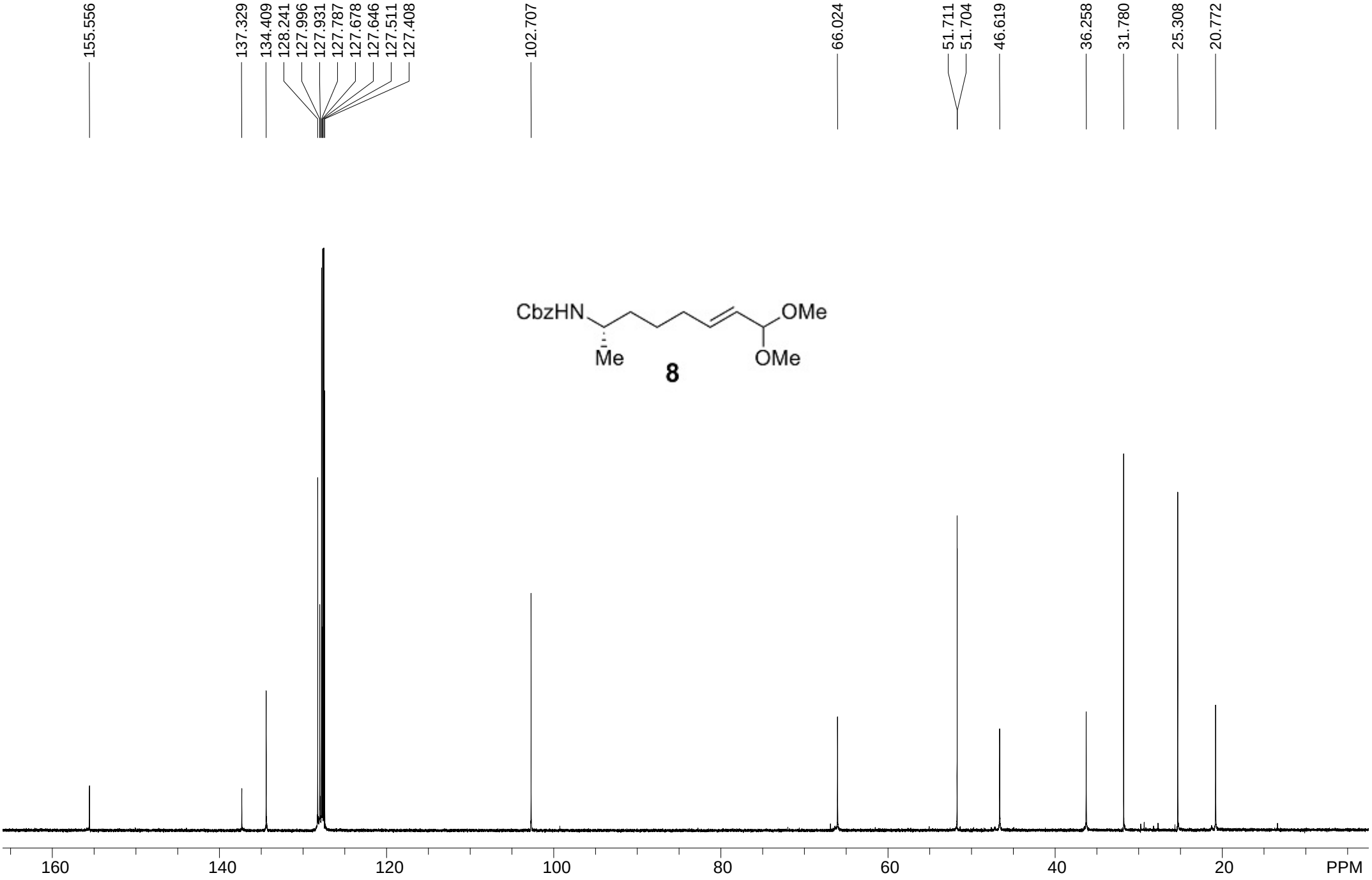
7
6
5
4
3
2
1
PPM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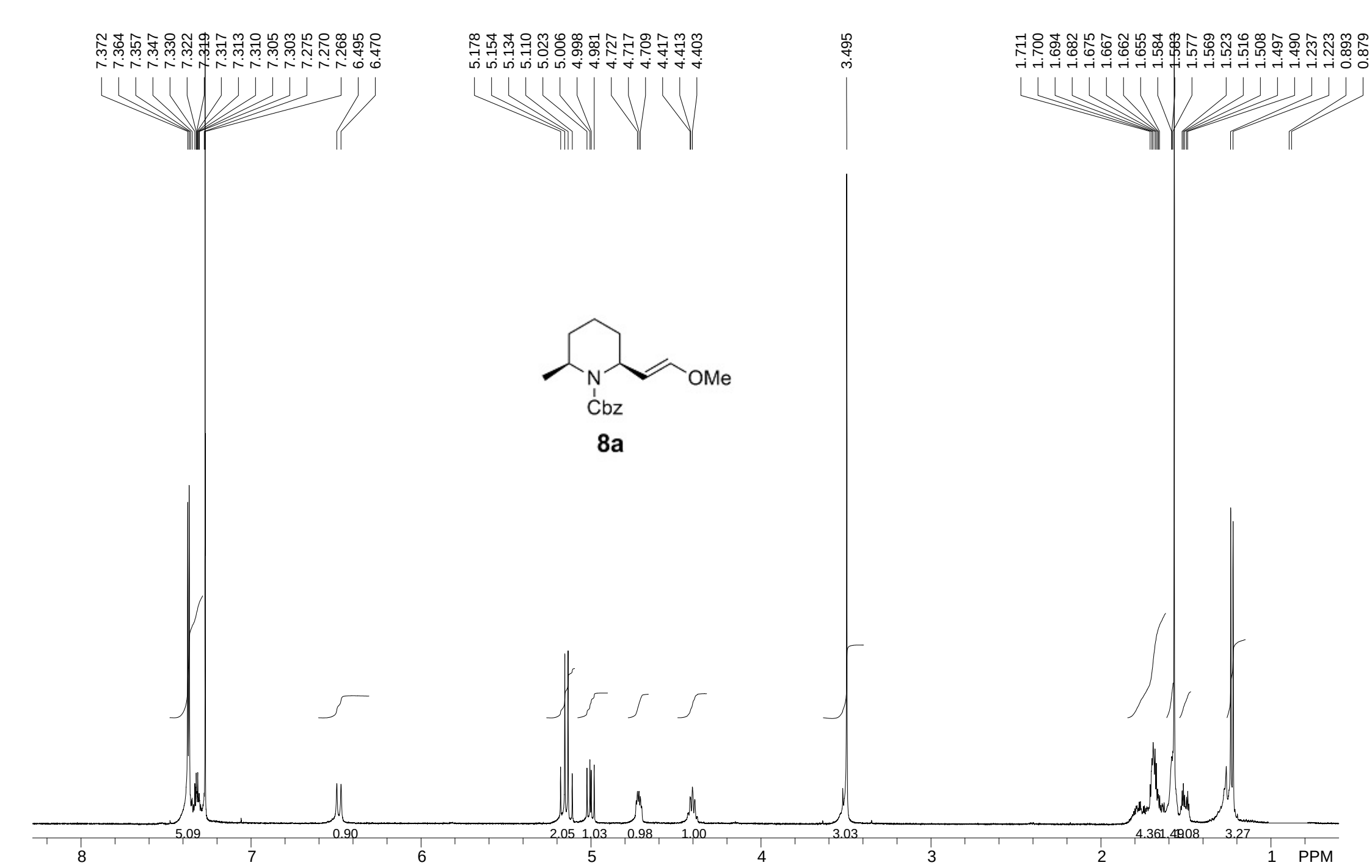
127.511
127.408
102.707
66.024
51.711
51.704
46.619
36.258
31.780
25.308
20.772
CbzHN
OMe
Me
OMe
8
160
140
120
100
80
60
40
20
PPM


7.372
7.364
7.357
7.347
7.330
7.322
7.319
7.317
7.313
7.310
7.305
7.303
7.275
7.270
7.268
6.495
6.470
5.178
5.154
5.134
5.110
5.023
5.006
4.998
4.981
4.727
4.717
4.709
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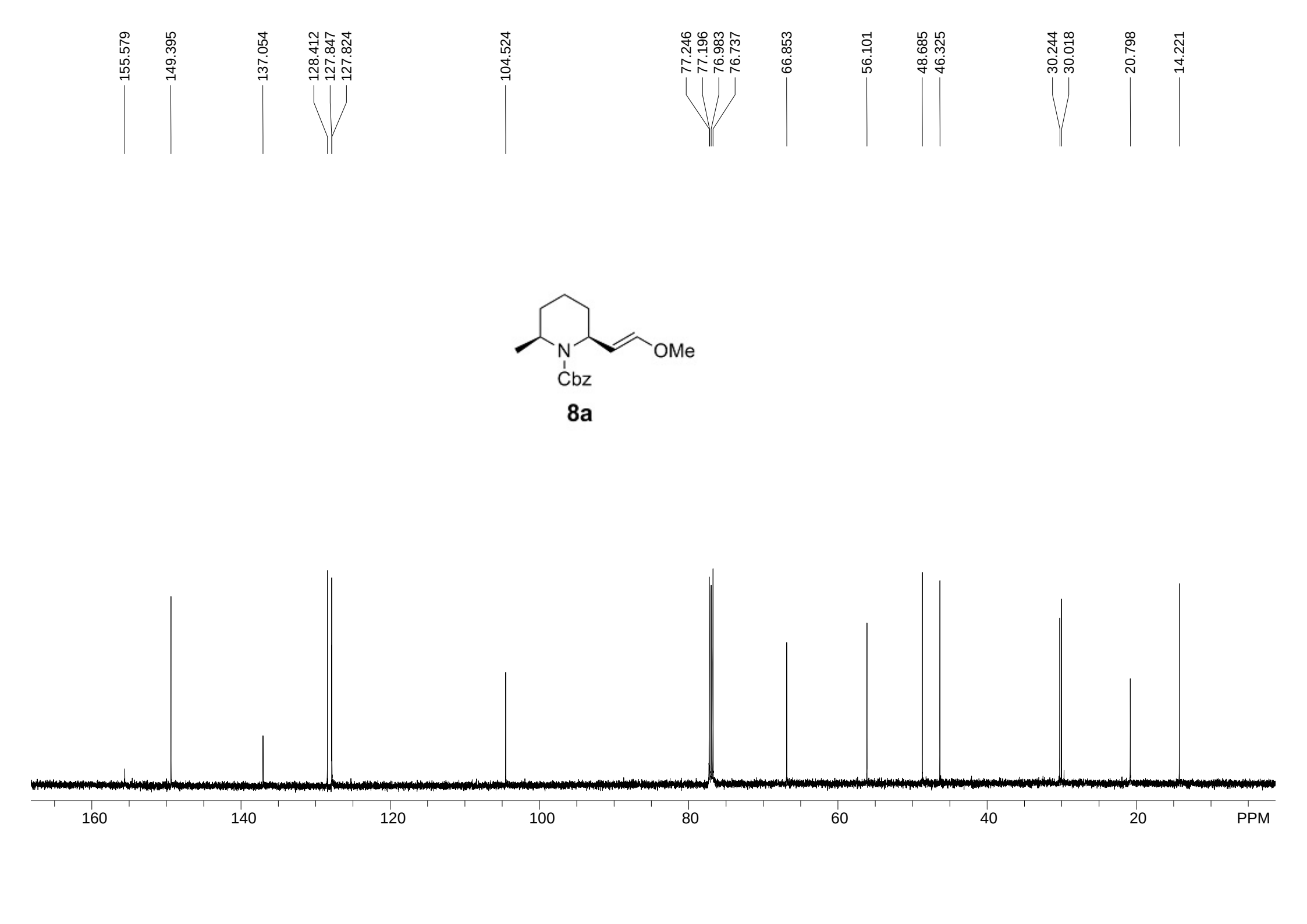
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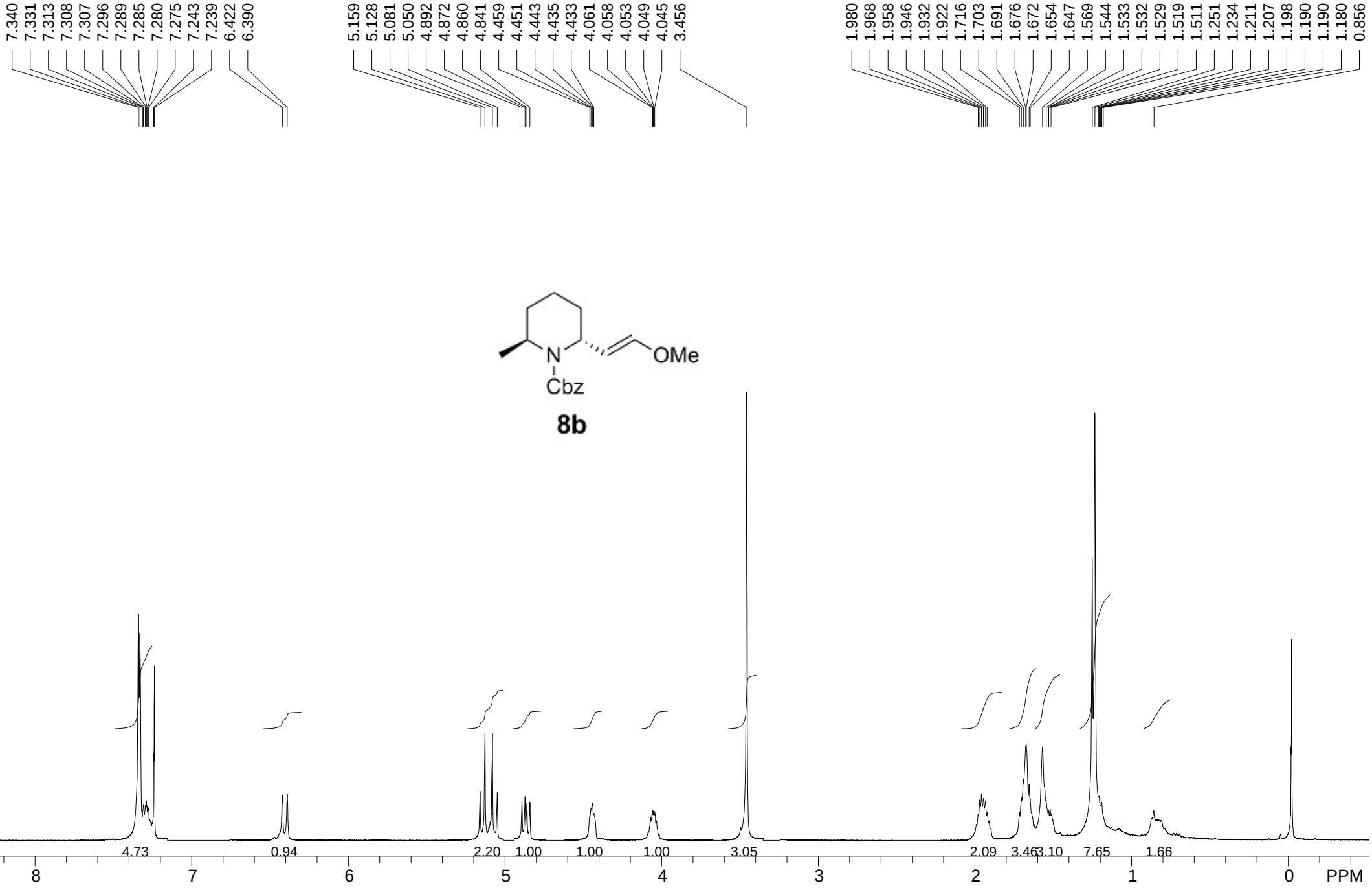
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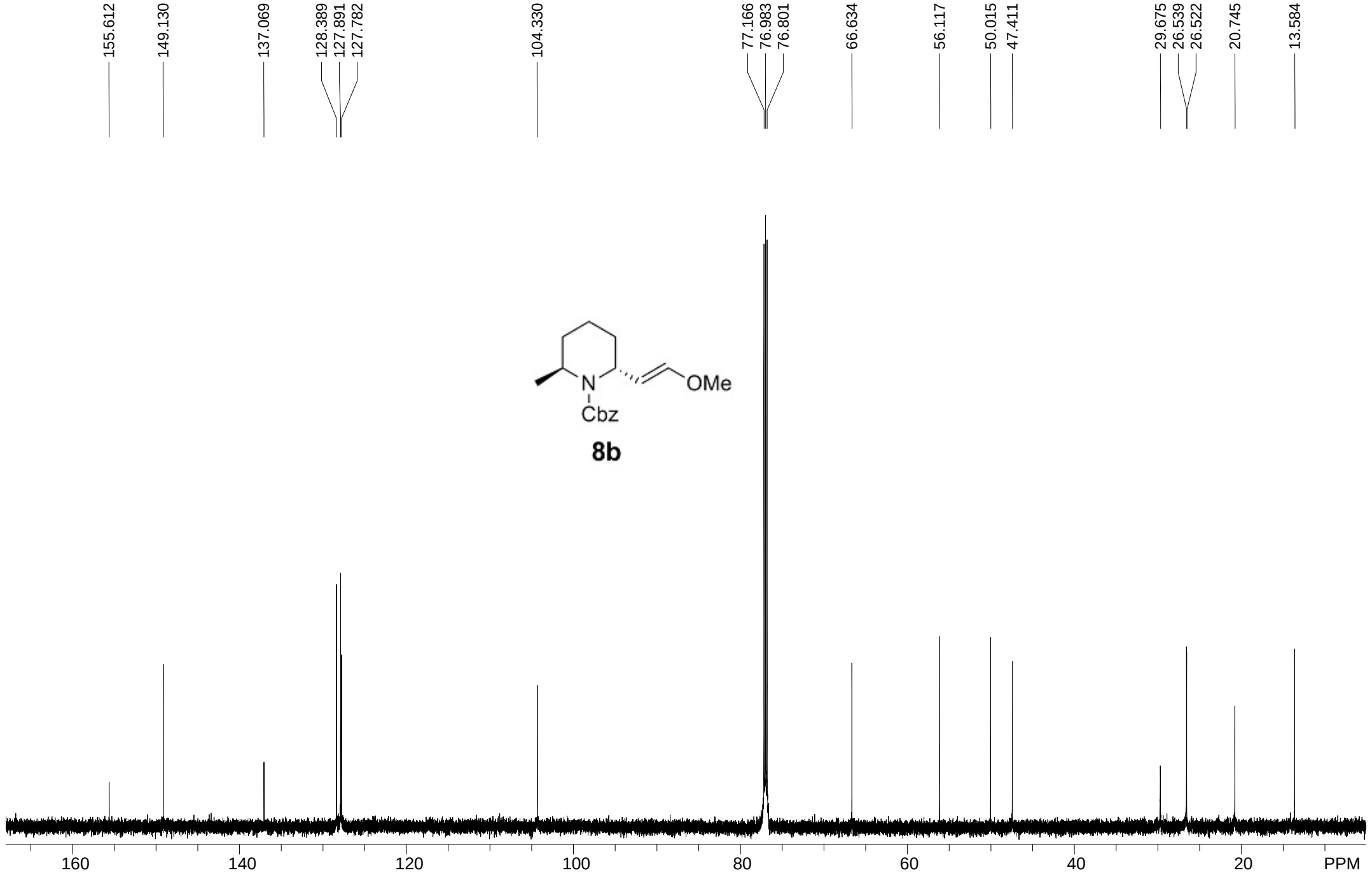
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