

Supporting Information

Desymmetrizing Asymmetric Ring Expansion of Cyclohexanones with α -Diazoacetates Catalyzed by Chiral Aluminum Lewis Acid

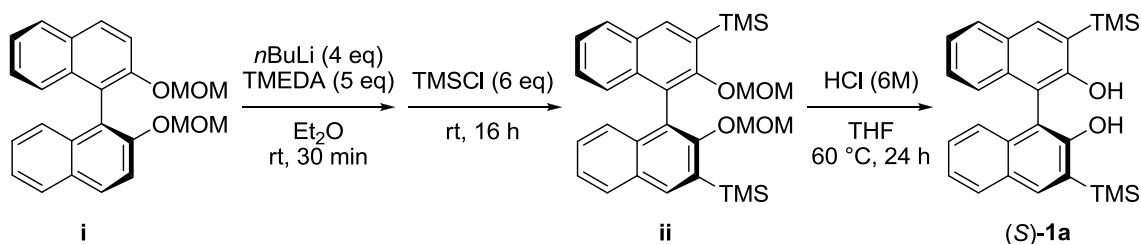
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General Information. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^1H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double-doublet, ddd = double-double-doublet, dt = double-triplet, m = multiplet, br = broad, and app = apparent), coupling constants (Hz), and assignment. ^{13}C NMR spectra were measured on a JEOL JNM-FX400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments at 210 nm using 4.6 mm x 25 cm Daicel chiral columns. High-resolution mass spectra (HRMS) were performed on Bruker microTOF. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60 (Merck, 230-400 mesh).

In experiments requiring dry solvent, toluene was purchased from Kanto Chemical Co. Inc. as “Dehydrated” and further purified by passing through neutral alumina under nitrogen atmosphere. Simple ketones were purchased and used after distillation or column chromatography on silica gel. Other cyclic ketones were synthesized according to the literature.¹

•Preparation of (*S*)-3,3'-bis(trimethylsilyl)-1,1'-binaphthyl-2,2'-diol ((*S*)-1a).^{2a}

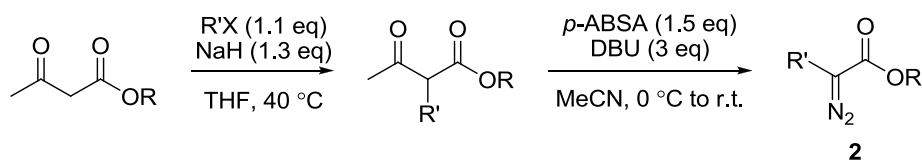


To a stirred solution of (*S*)-1,1'-binaphthyl-2,2'-diol derivative **i** (2.0 g, 5.34 mmol) in Et₂O (100 mL), TMEDA (4.0 mL, 26.7 mmol) and *n*-BuLi (1.6 M solution in hexane, 13.4 mL, 21.4 mmol) were added dropwise at room temperature under Ar atmosphere. After stirring for 30 min, TMSCl (4.0 mL, 32.0 mmol) was added dropwise to the resulting suspension at room temperature, and the mixture was stirred at the same temperature for additional 16 h. The reaction mixture was quenched with saturated aqueous NH₄Cl and extracted with ethyl acetate. The combined organic layers were dried over Na₂SO₄ and evaporated. The residue was purified by flash column chromatography (eluting with hexane/ethyl acetate = 100:1) to afford the compound **ii** in 83% yield (2.3 g, 4.43 mmol).

To a stirred solution of the compound **ii** (2.3 g, 4.43 mmol) in THF (100 mL), 6 M HCl (100 mL) was added at room temperature. The solution was kept stirring at 60 °C for 24 h. The resulting mixture was cooled down to room temperature and extracted with Et₂O. The combined organic layers were dried over Na₂SO₄ and evaporated. The residue was purified by flash column chromatography (eluting with hexane) to afford (*S*)-1a as a white solid in 64% yield (1.2 g, 2.79 mmol).

¹H NMR (400 MHz, CDCl₃) δ 8.07 (2H, s), 7.88 (2H, d, *J* = 8.0 Hz), 7.24-7.39 (4H, m), 7.09 (2H, s), 5.23 (2H, s), 0.41 (18H, s). The detailed spectral data of (*S*)-1 were reported in the literature.²

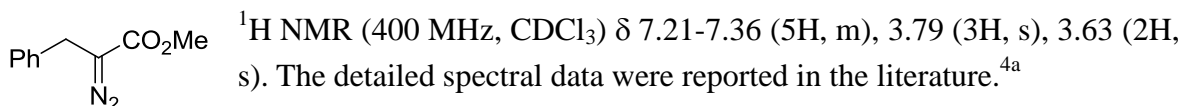
•Preparation of α-alkyldiazoacetates (**2**).^{1,3}



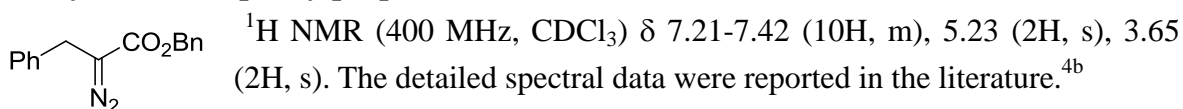
To a stirred suspension of NaH (60 % dispersion in mineral oil, 1.04 g, 26 mmol) in THF (20 mL), acetoacetate (20 mmol) was added dropwise at room temperature under Ar atmosphere. After the formation of a clear solution, the corresponding alkyl halide (22 mmol) was added dropwise, and the mixture was stirred at 40 °C for 10 h. The resulting mixture was quenched with saturated aqueous NH₄Cl and extracted with ethyl acetate. The combined organic layers were dried over Na₂SO₄ and evaporated. The residue was purified by flash column chromatography to afford the corresponding α-alkyl-β-ketoesters.

To a stirred solution of thus-formed α -alkyl- β -ketoester (5 mmol) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (1.92 g, 7.5 mmol) in MeCN (10 mL) was added DBU (2.2 ml, 15 mmol) at 0 °C. The reaction mixture was then allowed to warm to room temperature. After stirring for 12 h, the resulting mixture was quenched with 1N HCl, and extracted with hexane. The combined organic layers were washed with saturated aqueous NaHCO₃ and brine, and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and purified by flash column chromatography to give the corresponding α -alkyldiazoacetates **2**.

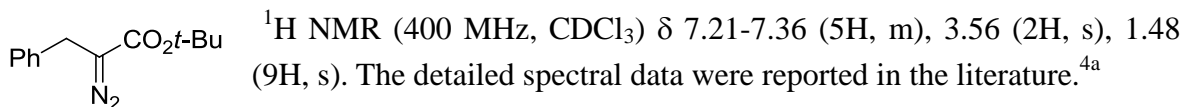
Methyl 2-diazo-3-phenylpropanoate (2a).



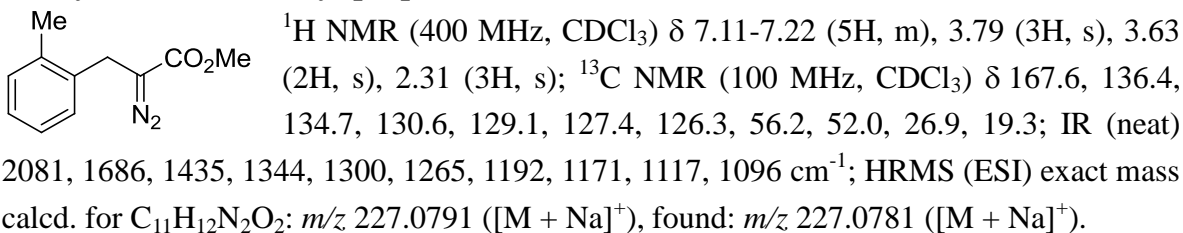
Benzyl 2-diazo-3-phenylpropanoate (2b).



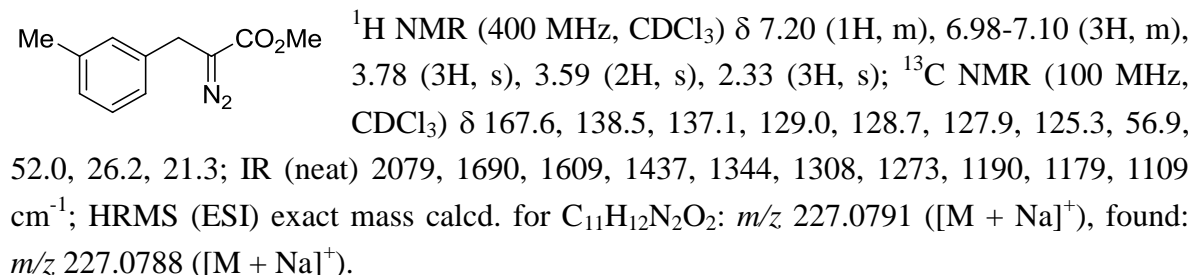
***tert*-Butyl 2-diazo-3-phenylpropanoate (2c).**



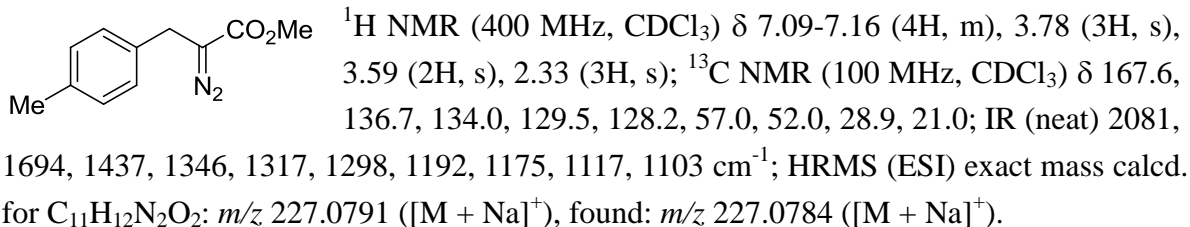
Methyl 2-diazo-3-(*o*-tolyl)propanoate (2d).



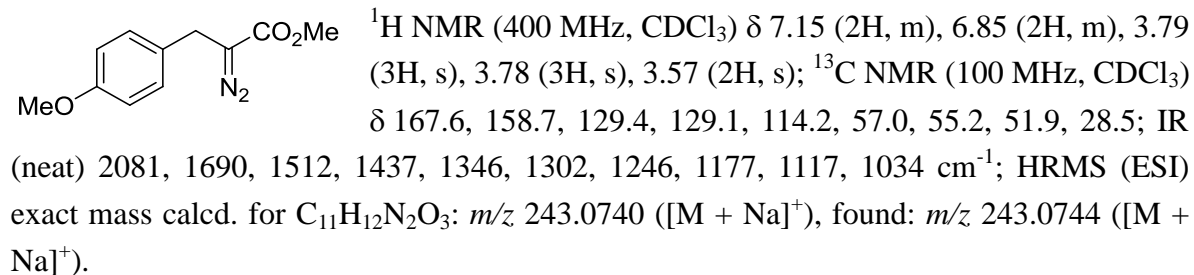
Methyl 2-diazo-3-(*m*-tolyl)propanoate (2e).



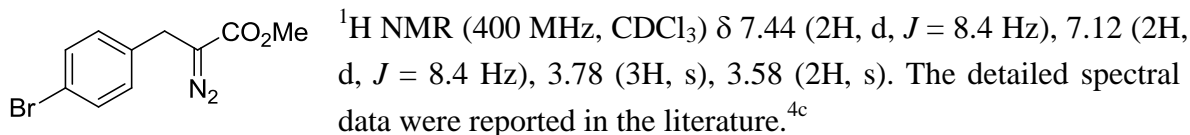
Methyl 2-diazo-3-(*p*-tolyl)propanoate (2f).



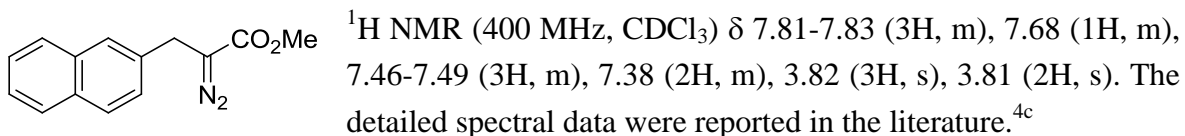
Methyl 2-diazo-3-(4-methoxyphenyl)propanoate (2g).



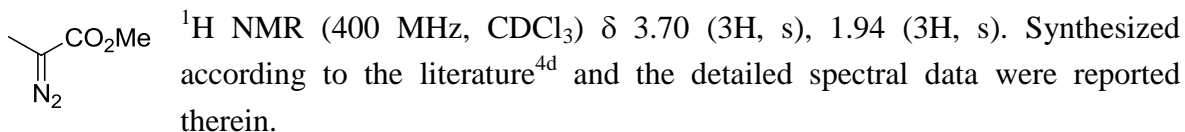
Methyl 3-(4-bromophenyl)-2-diazopropanoate (2h).



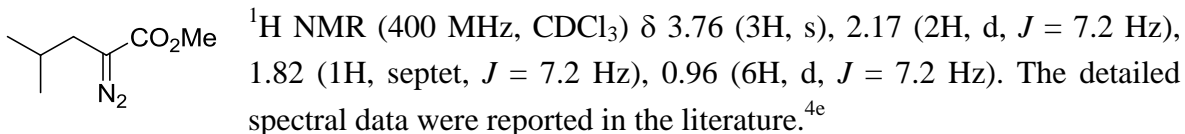
Methyl 2-diazo-3-(2-naphthalenyl)propanoate (2i).



Methyl 2-diazopropanoate (2j).

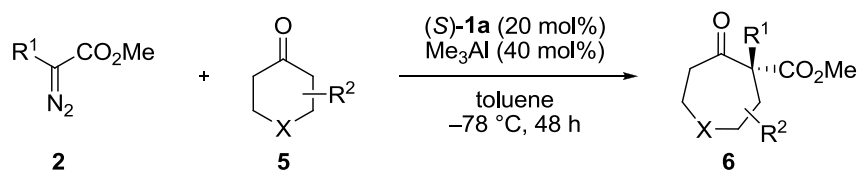


Methyl 2-diazo-4-methylpentanoate (2k).



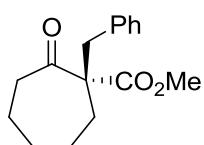
•General procedure for the chiral aluminum Lewis acid catalyzed desymmetrizing asymmetric ring expansion of substituted cyclohexanones 5 with

α -alkyl- α -diazooacetates **2**.



To a solution of (S)-**1a** (17.2 mg, 0.040 mmol) in degassed toluene (2 mL) was added dropwise a 0.5 M toluene solution of trimethylaluminum (160 μL , 0.080 mmol) at room temperature under Ar and stirred for 60 min. Cyclohexanone **5** (0.20 mmol) was then added to the resulting solution at the same temperature, and the solution was cooled to $-78\text{ }^\circ\text{C}$. Methyl α -alkyldiazoacetate **2** (0.22 mmol) was added to this solution, and the stirring was maintained at the same temperature for 48 h. The mixture was quenched with 1N HCl, extracted with ethyl acetate and dried over Na_2SO_4 . After concentration under reduced pressure, the residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 40/1) to give the desired product **6**.

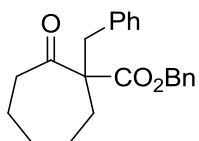
Methyl (S)-1-benzyl-2-oxocycloheptanecarboxylate (**4a**).



^1H NMR (400 MHz, CDCl_3) δ 7.18-7.30 (3H, m), 7.05-7.11 (2H, m), 3.69 (3H, s), 3.36 (1H, d, $J = 14.0$ Hz), 2.97 (1H, d, $J = 14.0$ Hz), 2.61 (1H, ddd, $J = 12.8, 9.6, 3.2$ Hz), 2.30 (1H, ddd, $J = 12.8, 10.0, 3.6$ Hz), 2.05 (1H, ddd, $J = 14.8, 8.8, 1.2$ Hz), 1.81 (1H, ddd, $J = 15.2, 10.8, 1.6$ Hz), 1.38-1.75 (6H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 209.3, 172.3, 136.7, 130.3, 128.2, 126.8, 64.3, 52.2, 42.3, 40.8, 31.5, 29.8, 25.4, 24.4; IR (neat) 2934, 2359, 1734, 1711, 1454, 1445, 1234, 1200, 1173, 1146 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_3$: m/z 283.1305 ($[\text{M} + \text{Na}]^+$), found: m/z 283.1297 ($[\text{M} + \text{Na}]^+$); $[\alpha]_D^{25} = -43.8$ ($c = 1.0, \text{CHCl}_3$; 90% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OJ-H, hexane/isopropanol = 97/3, flow rate = 0.5 mL/min, retention time; 28.3 min (major) and 33.1 min (minor)). The absolute configuration of this product was established to be *S* by comparison with the literature.⁵

Benzyl 1-benzyl-2-oxocycloheptanecarboxylate (**4b**).

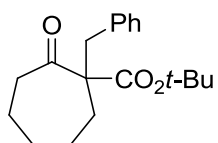


^1H NMR (400 MHz, CDCl_3) δ 7.16-7.41 (8H, m), 6.99-7.05 (2H, m), 5.14 (1H, d, $J = 12.0$ Hz), 5.09 (1H, d, $J = 12.0$ Hz), 3.37 (1H, d, $J = 14.0$ Hz), 2.98 (1H, d, $J = 14.0$ Hz), 2.56 (1H, ddd, $J = 12.8, 9.2, 3.6$ Hz), 2.30 (1H, ddd, $J = 12.0, 8.8, 3.2$ Hz), 2.05 (1H, ddd, $J = 14.8, 8.8, 1.6$ Hz), 1.80 (1H, ddd, $J = 15.2, 10.4, 1.2$ Hz), 1.34-1.74 (6H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 209.1, 171.6, 136.7, 130.4, 128.5, 128.4, 128.3, 128.1, 126.7, 67.0, 64.3, 42.3, 40.7, 31.5, 29.7, 25.3, 24.4; IR (neat) 2932, 2859, 1732, 1709, 1497, 1454, 1231, 1213, 1194, 1167, 1144

cm⁻¹; HRMS (ESI) exact mass calcd. for C₂₂H₂₄O₃: *m/z* 359.1618 ([M + Na]⁺), found: *m/z* 359.1621 ([M + Na]⁺).

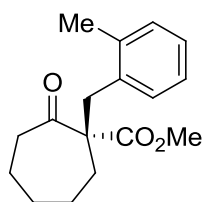
The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min, retention time; 17.0 min and 21.9 min).

***tert*-Butyl 1-benzyl-2-oxocycloheptanecarboxylate (4c).**



¹H NMR (400 MHz, CDCl₃) δ 7.12-7.27 (5H, m), 3.29 (1H, d, *J* = 14.0 Hz), 2.98 (1H, d, *J* = 14.0 Hz), 2.62 (1H, ddd, *J* = 12.8, 8.4, 3.2 Hz), 2.30 (1H, ddd, *J* = 12.8, 10.0, 3.6 Hz), 2.00 (1H, ddd, *J* = 14.4, 8.8, 0.8 Hz), 1.18-1.82 (7H, m), 1.42 (9H, s). The detailed spectral data has been reported in the literature.^{2b} The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/isopropanol = 99/1, flow rate = 0.5 mL/min, retention time; 15.3 min and 17.9 min).

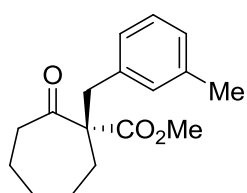
Methyl (*S*)-1-(2-methylbenzyl)-2-oxocycloheptanecarboxylate (4d).



¹H NMR (400 MHz, CDCl₃) δ 7.05-7.16 (3H, m), 6.94 (1H, m), 3.69 (3H, s), 3.38 (1H, d, *J* = 14.8 Hz), 3.09 (1H, d, *J* = 14.8 Hz), 2.60 (1H, ddd, *J* = 12.4, 10.4, 3.6 Hz), 2.37 (1H, ddd, *J* = 12.4, 8.8, 3.2 Hz), 2.26 (3H, s), 2.04 (1H, dd, *J* = 15.2, 9.6 Hz), 1.83 (1H, ddd, *J* = 15.2, 10.4, 1.2 Hz), 1.33-1.79 (6H, m); ¹³C NMR (100 MHz, CDCl₃) δ 209.3, 172.7, 137.3, 135.2, 130.5, 130.4, 126.7, 125.6, 64.2, 52.2, 42.1, 36.1, 30.8, 30.0, 25.9, 24.6, 19.9; IR (neat) 2947, 2932, 2860, 1732, 1713, 1495, 1456, 1202, 1173, 1146 cm⁻¹; HRMS (ESI) exact mass calcd. for C₁₇H₂₂O₃: *m/z* 297.1461 ([M + Na]⁺), found: *m/z* 297.1463 ([M + Na]⁺); [α]_D²⁵ = -48.9 (*c* = 0.5, CHCl₃; 71% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK IC, hexane/isopropanol = 30/1, flow rate = 0.5 mL/min, retention time; 23.6 min (major) and 27.8 min (minor)).

Methyl (*S*)-1-(3-methylbenzyl)-2-oxocycloheptanecarboxylate (4e).

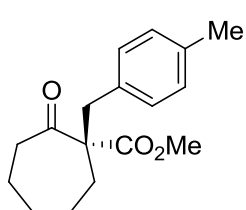


¹H NMR (400 MHz, CDCl₃) δ 7.13 (1H, m), 7.02 (1H, m), 6.83-6.91 (2H, m), 3.69 (3H, s), 3.32 (1H, d, *J* = 13.6 Hz), 2.93 (1H, d, *J* = 13.6 Hz), 2.60 (1H, ddd, *J* = 12.4, 9.2, 3.6 Hz), 2.33 (1H, ddd, *J* = 12.0, 8.8, 3.2 Hz), 2.30 (3H, s), 2.04 (1H, ddd, *J* = 15.2, 9.2, 1.2 Hz), 1.81 (1H, ddd, *J* = 15.2, 10.4, 1.6 Hz), 1.37-1.76 (6H, m); ¹³C NMR (100 MHz, CDCl₃) δ 209.3, 172.4, 137.6, 136.6, 131.1, 128.0, 127.5, 127.3, 64.3, 52.1, 42.3, 40.7, 31.4, 29.8, 25.4, 24.4, 21.4; IR (neat) 2930, 2860, 1732, 1711, 1454, 1443, 1233, 1200, 1171, 1146 cm⁻¹; HRMS (ESI) exact mass calcd. for C₁₇H₂₂O₃: *m/z* 297.1461 ([M + Na]⁺), found:

m/z 297.1467 ($[M + Na]^+$); $[\alpha]_D^{23} = -39.7$ ($c = 1.0$, $CHCl_3$; 81% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OD-H, hexane/isopropanol = 99/1, flow rate = 0.5 mL/min, retention time; 20.3 min (major) and 26.1 min (minor)).

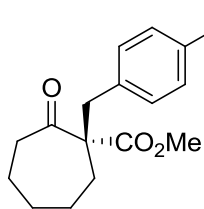
Methyl (S)-1-(4-methylbenzyl)-2-oxocycloheptanecarboxylate (4f).



1H NMR (400 MHz, $CDCl_3$) δ 7.05 (2H, d, $J = 8.0$ Hz), 6.96 (2H, d, $J = 8.0$ Hz), 3.70 (3H, s), 3.31 (1H, d, $J = 14.0$ Hz), 2.93 (1H, d, $J = 14.0$ Hz), 2.60 (1H, ddd, $J = 12.8, 9.6, 3.6$ Hz), 2.33 (1H, ddd, $J = 12.0, 8.8, 3.2$ Hz), 2.30 (3H, s), 2.04 (1H, ddd, $J = 14.8, 9.2, 1.2$ Hz), 1.81 (1H, ddd, $J = 15.2, 10.4, 1.6$ Hz), 1.38-1.75 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4, 172.4, 136.3, 133.5, 130.2, 128.9, 64.3, 52.1, 42.4, 40.3, 31.4, 29.8, 25.4, 24.4, 21.0; IR (neat) 2930, 1734, 1711, 1514, 1443, 1233, 1198, 1171, 1146, 1117 cm^{-1} ; HRMS (ESI) exact mass calcd. for $C_{17}H_{22}O_3$: m/z 297.1461 ($[M + Na]^+$), found: m/z 297.1465 ($[M + Na]^+$); $[\alpha]_D^{27} = -37.9$ ($c = 1.0$, $CHCl_3$; 84% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/isopropanol = 99/1, flow rate = 0.5 mL/min, retention time; 24.0 min (major) and 25.7 min (minor)).

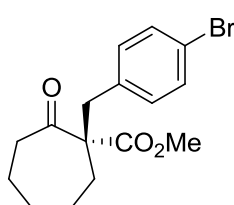
Methyl (S)-1-(4-methoxybenzyl)-2-oxocycloheptanecarboxylate (4g).



1H NMR (400 MHz, $CDCl_3$) δ 7.00 (2H, m), 6.78 (2H, m), 3.77 (3H, s), 3.69 (3H, s), 3.29 (1H, d, $J = 14.4$ Hz), 2.93 (1H, d, $J = 14.4$ Hz), 2.59 (1H, ddd, $J = 12.8, 9.2, 3.2$ Hz), 2.32 (1H, ddd, $J = 12.0, 8.8, 3.2$ Hz), 2.04 (1H, ddd, $J = 15.2, 8.8, 1.2$ Hz), 1.81 (1H, ddd, $J = 15.2, 10.4, 1.6$ Hz), 1.37-1.75 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 172.4, 158.4, 131.3, 128.6, 113.6, 64.4, 55.1, 52.1, 42.5, 40.0, 31.6, 29.8, 25.4, 24.5; IR (neat) 2932, 1732, 1709, 1512, 1456, 1443, 1248, 1200, 1179, 1034 cm^{-1} ; HRMS (ESI) exact mass calcd. for $C_{17}H_{22}O_4$: m/z 313.1410 ($[M + Na]^+$), found: m/z 313.1408 ($[M + Na]^+$); $[\alpha]_D^{27} = -29.6$ ($c = 1.0$, $CHCl_3$; 84% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OD-H, hexane/isopropanol = 97/3, flow rate = 0.5 mL/min, retention time; 19.6 min (major) and 22.2 min (minor)).

Methyl (S)-1-(4-bromobenzyl)-2-oxocycloheptanecarboxylate (4h).

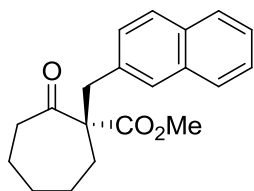


1H NMR (400 MHz, $CDCl_3$) δ 7.37 (2H, m), 6.97 (2H, m), 3.68 (3H, s), 3.30 (1H, d, $J = 13.6$ Hz), 2.92 (1H, d, $J = 13.6$ Hz), 2.62 (1H, ddd, $J = 12.8, 9.2, 3.6$ Hz), 2.35 (1H, ddd, $J = 12.0, 8.8, 3.2$ Hz), 2.05 (1H, m), 1.34-1.82 (7H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 172.1, 135.8,

132.1, 131.2, 120.8, 64.1, 52.2, 42.4, 40.2, 31.8, 29.7, 25.3, 24.5; IR (neat) 2932, 1732, 1709, 1487, 1443, 1233, 1200, 1171, 1146, 1013 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{16}\text{H}_{19}\text{BrO}_3$: m/z 361.0410 ($[\text{M} + \text{Na}]^+$), found: m/z 361.0410 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{22} = -25.8$ ($c = 1.0$, CHCl_3 ; 89% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AS-H, hexane/isopropanol = 97/3, flow rate = 0.5 mL/min, retention time; 14.2 min (minor) and 16.1 min (major)).

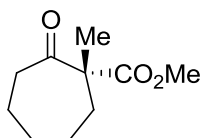
Methyl (S)-1-(naphthalen-2-ylmethyl)-2-oxocycloheptanecarboxylate (4i).



^1H NMR (400 MHz, CDCl_3) δ 7.69-7.84 (3H, m), 7.55 (1H, s), 7.39-7.49 (2H, m), 7.20 (1H, dd, $J = 8.4, 1.6$ Hz), 3.69 (3H, s), 3.52 (1H, d, $J = 13.6$ Hz), 3.16 (1H, d, $J = 13.6$ Hz), 2.62 (1H, ddd, $J = 13.2, 9.6, 4.0$ Hz), 2.34 (1H, ddd, $J = 12.0, 8.8, 3.2$ Hz), 2.09 (1H, ddd, $J = 14.8, 8.4, 1.2$ Hz), 1.86 (1H, ddd, $J = 15.2, 10.8, 1.6$ Hz), 1.39-1.76 (6H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 209.3, 172.4, 134.3, 133.3, 132.3, 129.1, 128.5, 127.6, 127.5, 125.9, 125.6, 64.4, 52.2, 42.5, 41.0, 31.7, 29.8, 25.3, 24.5; IR (neat) 2932, 2859, 1732, 1709, 1454, 1443, 1217, 1198, 1171, 1148 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_3$: m/z 333.1461 ($[\text{M} + \text{Na}]^+$), found: m/z 333.1461 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{21} = -31.4$ ($c = 1.0$, CHCl_3 ; 80% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min, retention time; 18.9 min (minor) and 20.0 min (major)).

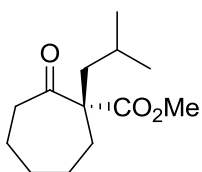
Methyl (R)-1-methyl-2-oxocycloheptanecarboxylate (4j).



^1H NMR (400 MHz, CDCl_3) δ 3.71 (3H, s), 2.73 (1H, ddd, $J = 12.4, 10.4, 2.8$ Hz), 2.51 (1H, ddd, $J = 12.8, 8.8, 2.8$ Hz), 2.16 (1H, dd, $J = 13.2, 9.2$ Hz), 1.49-1.87 (6H, m), 1.41 (1H, m), 1.35 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 210.3, 174.0, 58.8, 52.3, 42.0, 35.4, 30.1, 25.8, 24.7, 21.5; IR (neat) 2936, 1740, 1728, 1705, 1447, 1261, 1234, 1192, 1153, 1105 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{10}\text{H}_{16}\text{O}_3$: m/z 207.0992 ($[\text{M} + \text{Na}]^+$), found: m/z 207.0993 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{26} = 10.5$ ($c = 1.0$, CHCl_3 ; 14% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK IC, hexane/isopropanol = 50/1, flow rate = 0.5 mL/min, retention time; 35.4 min (major) and 41.8 min (minor)).

Methyl (S)-1-isobutyl-2-oxocycloheptanecarboxylate (4k).

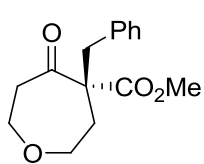


^1H NMR (400 MHz, CDCl_3) δ 3.71 (3H, s), 2.61 (1H, m), 2.49 (1H, m), 2.20 (1H, dd, $J = 14.8, 9.6$ Hz), 1.97 (1H, dd, $J = 14.4, 7.2$ Hz), 1.41-1.80

(9H, m), 0.89 (3H, d, $J = 6.4$ Hz), 0.83 (3H, d, $J = 6.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 209.5, 173.4, 62.8, 52.0, 43.5, 41.6, 32.7, 29.8, 25.8, 24.7, 24.6, 24.5, 23.3; IR (neat) 2953, 2868, 1732, 1711, 1454, 1223, 1150 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{13}\text{H}_{22}\text{O}_3$: m/z 249.1461 ($[\text{M} + \text{Na}]^+$), found: m/z 249.1468 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{24} = -14.9$ ($c = 1.0$, CHCl_3 ; 43% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OD-H (triple), hexane/isopropanol = 50/1, flow rate = 0.3 mL/min, retention time; 49.6 min (minor) and 51.5 min (major)).

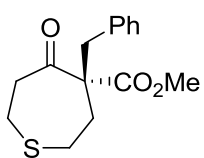
Methyl (*R*)-4-benzyl-5-oxooxepane-4-carboxylate (**4l**).



^1H NMR (400 MHz, CDCl_3) δ 7.19-7.31 (3H, m), 7.03-7.14 (2H, m), 3.80 (1H, ddd, $J = 12.8, 6.4, 4.4$ Hz), 3.73-3.78 (2H, m), 3.72 (3H, s), 3.62 (1H, ddd, $J = 12.4, 8.4, 3.6$ Hz), 3.31 (1H, d, $J = 14.0$ Hz), 3.08 (1H, d, $J = 14.0$ Hz), 2.82 (1H, ddd, $J = 14.8, 6.8, 3.6$ Hz), 2.63 (1H, ddd, $J = 14.8, 8.8, 4.4$ Hz), 2.13 (1H, ddd, $J = 15.6, 3.6, 2.8$ Hz), 1.89 (1H, ddd, $J = 15.6, 7.2, 6.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 206.0, 171.9, 136.0, 130.4, 128.3, 127.0, 68.2, 65.8, 63.5, 52.3, 45.7, 41.6, 34.0; IR (neat) 2953, 1707, 1441, 1287, 1256, 1198, 1180, 1148, 1132, 1103 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_4$: m/z 285.1097 ($[\text{M} + \text{Na}]^+$), found: m/z 285.1099 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{25} = -29.2$ ($c = 1.0$, CHCl_3 ; 80% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK IA, hexane/ethanol = 99/1, flow rate = 0.5 mL/min, retention time; 51.6 min (major) and 61.2 min (minor)).

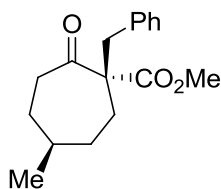
Methyl (*R*)-4-benzyl-5-oxothiepane-4-carboxylate (**4m**).



^1H NMR (400 MHz, CDCl_3) δ 7.19-7.30 (3H, m), 7.02-7.08 (2H, m), 3.69 (3H, s), 3.37 (1H, d, $J = 14.0$ Hz), 3.11 (1H, ddd, $J = 13.6, 6.4, 3.2$ Hz), 2.99 (1H, d, $J = 14.0$ Hz), 2.89 (1H, ddd, $J = 15.6, 11.2, 2.0$ Hz), 2.74-2.86 (2H, m), 2.54-2.66 (2H, m), 2.45 (1H, ddd, $J = 14.8, 6.0, 2.4$ Hz), 1.87 (1H, ddd, $J = 14.8, 11.6, 2.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 205.7, 171.9, 136.1, 130.1, 128.2, 127.0, 64.3, 52.1, 44.7, 41.9, 36.0, 28.8, 26.0; IR (neat) 2949, 2926, 1711, 1495, 1267, 1240, 1200, 1175, 1082 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_3\text{S}$: m/z 301.0869 ($[\text{M} + \text{Na}]^+$), found: m/z 301.0870 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{28} = -71.9$ ($c = 1.0$, CHCl_3 ; 77% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK IA, hexane/ethanol = 99/1, flow rate = 0.5 mL/min, retention time; 28.0 min (minor) and 30.4 min (major)).

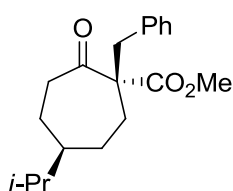
Methyl (*1S,5R*)-1-benzyl-5-methyl-2-oxocycloheptanecarboxylate (**6a**).



^1H NMR (400 MHz, CDCl_3) δ 7.18-7.30 (3H, m), 7.02-7.11 (2H, m), 3.68 (3H, s), 3.51 (1H, d, $J = 14.4$ Hz), 2.81 (1H, d, $J = 14.4$ Hz), 2.68 (1H, ddd, $J = 12.8, 11.2, 2.4$ Hz), 2.39 (1H, ddd, $J = 11.6, 7.2, 2.8$ Hz), 1.97-2.14 (2H, m), 1.90 (1H, m), 1.59-1.75 (2H, m), 1.21 (1H, m), 0.95 (1H, m), 0.90 (3H, d, $J = 6.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 208.5, 171.6, 137.1, 130.2, 128.2, 126.7, 64.8, 52.4, 40.1, 38.5, 36.6, 35.0, 31.7, 28.4, 22.5; IR (neat) 2951, 2928, 1730, 1711, 1454, 1238, 1196, 1173, 1148, 1020 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_3$: m/z 297.1461 ($[\text{M} + \text{Na}]^+$), found: m/z 297.1465 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{20} = -79.8$ ($c = 1.0$, CHCl_3 ; 86% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/isopropanol = 99/1, flow rate = 0.5 mL/min, retention time; 22.0 min (major) and 24.9 min (minor)).

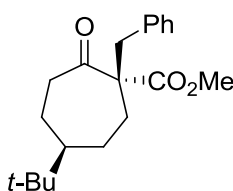
Methyl (1S,5R)-1-benzyl-5-isopropyl-2-oxocycloheptanecarboxylate (6b).



^1H NMR (400 MHz, CDCl_3) δ 7.17-7.32 (3H, m), 7.03-7.12 (2H, m), 3.67 (3H, s), 3.50 (1H, d, $J = 14.4$ Hz), 2.81 (1H, d, $J = 14.4$ Hz), 2.65 (1H, m), 2.44 (1H, ddd, $J = 11.6, 7.6, 2.4$ Hz), 2.02-2.11 (2H, m), 1.83 (1H, m), 1.69 (1H, m), 1.54 (1H, m), 1.25-1.42 (2H, m), 0.89 (1H, m), 0.82 (6H, d, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 208.7, 171.6, 137.1, 130.2, 128.2, 126.7, 64.6, 52.4, 47.8, 40.1, 38.5, 32.6, 29.6, 28.7, 26.3, 19.5, 19.3; IR (neat) 2955, 2934, 1728, 1711, 1454, 1443, 1252, 1236, 1196, 1173 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{19}\text{H}_{26}\text{O}_3$: m/z 325.1774 ($[\text{M} + \text{Na}]^+$), found: m/z 325.1771 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{29} = -82.2$ ($c = 1.0$, CHCl_3 ; 93% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OD-H, hexane/isopropanol = 99/1, flow rate = 0.5 mL/min, retention time; 16.9 min (major) and 18.8 min (minor)).

Methyl (1S,5R)-1-benzyl-5-tert-butyl-2-oxocycloheptanecarboxylate (6c).

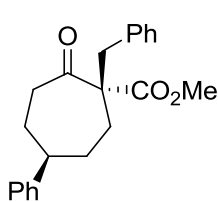


^1H NMR (400 MHz, CDCl_3) δ 7.18-7.30 (3H, m), 7.02-7.12 (2H, m), 3.67 (3H, s), 3.51 (1H, d, $J = 14.2$ Hz), 2.80 (1H, d, $J = 14.2$ Hz), 2.64 (1H, ddd, $J = 12.4, 11.2, 2.4$ Hz), 2.43 (1H, ddd, $J = 10.8, 6.0, 1.6$ Hz), 1.94-2.16 (3H, m), 1.87 (1H, m), 1.16-1.37 (2H, m), 0.84 (9H, s), 0.72 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 208.7, 171.6, 137.1, 130.2, 128.2, 126.7, 64.6, 52.4, 40.1, 38.2, 33.2, 28.83, 28.80, 28.6, 27.6, 24.3; IR (neat) 2955, 1732, 1711, 1454, 1441, 1240, 1229, 1196, 1175 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{20}\text{H}_{28}\text{O}_3$: m/z 339.1931 ($[\text{M} + \text{Na}]^+$), found: m/z 339.1921 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{23} = -80.1$ ($c = 1.0$, CHCl_3 ; 90% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel

CHIRALPAK AD-H, hexane/ethanol = 97/3, flow rate = 0.5 mL/min, retention time; 14.2 min (major) and 15.8 min (minor)).

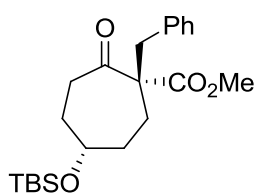
Methyl (*1S,5R*)-1-benzyl-2-oxo-5-phenylcycloheptanecarboxylate (6d).



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.15-7.34 (6H, m), 7.03-7.15 (4H, m), 3.71 (3H, s), 3.57 (1H, d, $J = 14.4$ Hz), 2.87 (1H, d, $J = 14.4$ Hz), 2.83 (1H, ddd, $J = 13.6, 11.2, 2.4$ Hz), 2.73 (1H, app ddt, $J = 12.4, 4.8, 2.4$ Hz), 2.52 (1H, ddd, $J = 11.2, 6.8, 2.4$ Hz), 2.04-2.31 (3H, m), 1.92 (1H, m), 1.70 (1H, m), 1.38 (1H, m); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 208.2, 171.4, 146.3, 137.0, 130.2, 128.5, 128.3, 126.8, 126.6, 126.4, 64.8, 52.5, 48.9, 40.4, 38.2, 35.0, 31.0, 28.9; IR (neat) 2949, 1728, 1709, 1493, 1452, 1234, 1196, 1173 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{22}\text{H}_{24}\text{O}_3$: m/z 359.1618 ($[\text{M} + \text{Na}]^+$), found: m/z 359.1618 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{25} = -15.0$ ($c = 1.0$, CHCl_3 ; 91% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/ethanol = 99/1, flow rate = 0.5 mL/min, retention time; 42.1 min (minor) and 43.9 min (major)).

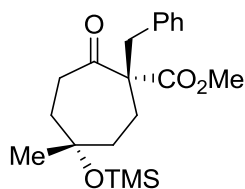
Methyl (*1S,5R*)-1-benzyl-5-(*tert*-butyldimethylsilyloxy)-2-oxocycloheptanecarboxylate (6e).



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.18-7.30 (3H, m), 7.04-7.13 (2H, m), 3.83 (1H, br), 3.70 (3H, s), 3.36 (1H, d, $J = 14.0$ Hz), 2.98 (1H, d, $J = 14.0$ Hz), 2.83 (1H, ddd, $J = 12.4, 10.8, 2.4$ Hz), 2.48 (1H, dd, $J = 15.2, 10.0$ Hz), 2.18 (1H, ddd, $J = 11.6, 8.8, 2.4$ Hz), 1.58-1.83 (4H, m), 1.42 (1H, ddd, $J = 14.4, 10.0, 1.6$ Hz), 0.87 (9H, s), 0.02 (6H, s); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 209.2, 172.0, 136.8, 130.3, 128.2, 126.8, 69.4, 64.1, 52.3, 40.0, 36.8, 34.6, 32.1, 25.8, 23.7, 18.0, -4.8, -4.9; IR (neat) 2951, 2928, 2857, 1736, 1711, 1441, 1252, 1206, 1080, 1043 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{22}\text{H}_{34}\text{O}_4\text{Si}$: m/z 413.2119 ($[\text{M} + \text{Na}]^+$), found: m/z 413.2128 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{25} = -31.4$ ($c = 1.0$, CHCl_3 ; 88% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OD-H, hexane/ethanol = 99/1, flow rate = 0.5 mL/min, retention time; 13.6 min (major) and 17.1 min (minor)).

Methyl (*1S,5S*)-1-benzyl-5-methyl-2-oxo-5-(trimethylsilyloxy)cycloheptanecarboxylate (6f).

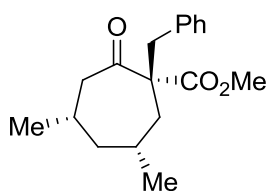


$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.20-7.28 (3H, m), 7.05-7.09 (2H, m), 3.68 (3H, s), 3.48 (1H, d, $J = 14.0$ Hz), 2.95 (1H, ddd, $J = 12.4, 12.0, 2.4$ Hz), 2.84 (1H, d, $J = 14.0$ Hz), 2.62 (1H, m), 2.18 (1H, ddd, $J =$

12.0, 7.6, 2.4 Hz), 1.86 (1H, ddt, $J = 14.8, 7.6, 2.4$ Hz), 1.63-1.79 (2H, m), 1.49 (1H, ddd, $J = 14.4, 12.4, 2.0$ Hz), 1.23 (3H, s), 1.19 (1H, m), 0.11 (9H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 209.1, 171.6, 137.1, 130.2, 128.2, 126.7, 73.7, 64.7, 52.4, 41.1, 38.7, 37.2, 36.7, 30.9, 23.1, 2.4; IR (neat) 2955, 1732, 1713, 1443, 1250, 1196, 1134, 1082, 1045, 1005 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{20}\text{H}_{30}\text{O}_4\text{Si}$: m/z 385.1806 ($[\text{M} + \text{Na}]^+$), found: m/z 385.1798 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{27} = -39.3$ ($c = 1.0, \text{CHCl}_3$; 60% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/isopropanol = 99/1, flow rate = 0.5 mL/min, retention time; 14.9 min (minor) and 16.3 min (major)).

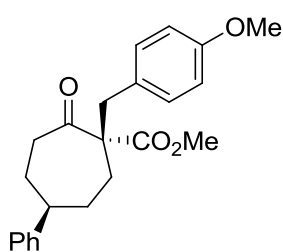
Methyl (*1S,4S,6R*)-1-benzyl-4,6-dimethyl-2-oxocycloheptanecarboxylate (**6g**).



^1H NMR (400 MHz, CDCl_3) δ 7.17-7.32 (3H, m), 7.02-7.12 (2H, m), 3.68 (3H, s), 3.48 (1H, d, $J = 14.0$ Hz), 2.84 (1H, d, $J = 14.0$ Hz), 2.51 (1H, dd, $J = 11.6, 10.8$ Hz), 2.32 (1H, m), 1.99 (1H, dd, $J = 15.2, 9.6$ Hz), 1.64-1.88 (3H, m), 1.26 (1H, m), 1.01 (3H, d, $J = 6.8$ Hz), 0.97 (1H, m), 0.93 (3H, d, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 206.7, 171.6, 137.1, 130.3, 128.2, 126.7, 64.1, 52.4, 48.8, 48.6, 38.3, 37.2, 35.1, 29.1, 24.9, 23.6; IR (neat) 2953, 2928, 1711, 1454, 1263, 1200, 1184, 1169, 1150, 1045 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{18}\text{H}_{24}\text{O}_3$: m/z 311.1618 ($[\text{M} + \text{Na}]^+$), found: m/z 311.1617 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{30} = -65.5$ ($c = 1.0, \text{CHCl}_3$; 58% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/ethanol = 99/1, flow rate = 0.5 mL/min, retention time; 18.6 min (major) and 19.8 min (minor)).

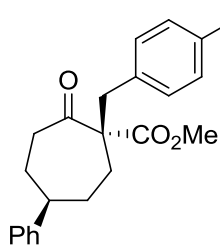
Methyl (*1S,5R*)-1-(4-methoxybenzyl)-2-oxo-5-phenylcycloheptanecarboxylate (**6h**).



^1H NMR (400 MHz, CDCl_3) δ 7.23-7.33 (2H, m), 7.19 (1H, m), 7.08-7.14 (2H, m), 6.99 (2H, m), 6.79 (2H, m), 3.76 (3H, s), 3.71 (3H, s), 3.51 (1H, d, $J = 14.4$ Hz), 2.84 (1H, d, $J = 14.4$ Hz), 2.82 (1H, ddd, $J = 14.0, 11.6, 2.8$ Hz), 2.73 (1H, ddt, $J = 12.0, 4.4, 2.0$ Hz), 2.51 (1H, ddd, $J = 11.2, 6.4, 2.4$ Hz), 2.03-2.30 (3H, m), 1.91 (1H, m), 1.69 (1H, m), 1.38 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 208.3, 171.5, 158.5, 146.4, 131.1, 128.8, 128.5, 126.6, 126.4, 113.7, 64.8, 55.2, 52.5, 48.9, 40.4, 37.4, 35.0, 31.1, 29.0; IR (neat) 2951, 1709, 1512, 1452, 1441, 1248, 1196, 1179, 1113, 1034 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{23}\text{H}_{26}\text{O}_4$: m/z 389.1723 ($[\text{M} + \text{Na}]^+$), found: m/z 389.1727 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{25} = -3.0$ ($c = 1.0, \text{CHCl}_3$; 91% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/ethanol = 95/5, flow rate = 0.5 mL/min, retention time; 31.9 min (minor) and 34.9 min (major)).

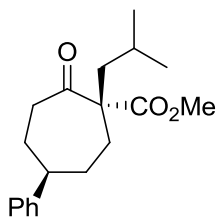
Methyl (*1S,5R*)-1-(4-bromobenzyl)-2-oxo-5-phenylcycloheptanecarboxylate (6i).



^1H NMR (400 MHz, CDCl_3) δ 7.37 (2H, m), 7.15-7.32 (3H, m), 7.07-7.13 (2H, m), 6.96 (2H, m), 3.70 (3H, s), 3.51 (1H, d, $J = 14.0$ Hz), 2.84 (1H, d, $J = 14.0$ Hz), 2.82 (1H, ddd, $J = 14.0, 11.6, 2.4$ Hz), 2.73 (1H, ddt, $J = 12.0, 4.0, 2.0$ Hz), 2.53 (1H, ddd, $J = 11.2, 6.4, 2.0$ Hz), 2.28 (1H, dd, $J = 15.6, 10.8$ Hz), 2.05-2.17 (2H, m), 1.91 (1H, m), 1.69 (1H, m), 1.36 (1H, dt, $J = 14.8, 11.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 207.9, 171.3, 146.2, 136.0, 131.9, 131.4, 128.6, 126.6, 126.5, 120.9, 64.6, 52.6, 48.9, 40.4, 37.8, 35.0, 31.1, 29.3; IR (neat) 2949, 1730, 1709, 1489, 1450, 1250, 1196, 1173, 1111, 1013 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{22}\text{H}_{23}\text{BrO}_3$: m/z 437.0723 ($[\text{M} + \text{Na}]^+$), found: m/z 437.0719 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{26} = 3.2$ ($c = 1.0$, CHCl_3 ; 90% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/ethanol = 95/5, flow rate = 0.5 mL/min, retention time; 21.3 min (minor) and 25.0 min (major)).

Methyl (*1S,5R*)-1-isobutyl-2-oxo-5-phenylcycloheptanecarboxylate (6j).

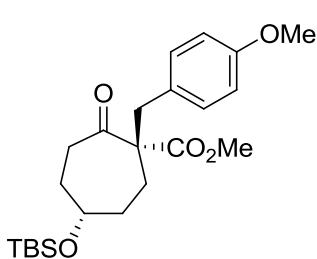


^1H NMR (400 MHz, CDCl_3) δ 7.23-7.33 (2H, m), 7.10-7.23 (3H, m), 3.72 (3H, s), 2.79 (1H, ddd, $J = 13.2, 12.0, 2.8$ Hz), 2.75 (1H, m), 2.47 (1H, ddd, $J = 11.2, 6.4, 2.4$ Hz), 2.41 (1H, dd, $J = 13.2, 11.2$ Hz), 2.11-2.27 (2H, m), 2.06 (1H, m), 1.93 (1H, dd, $J = 14.8, 8.8$ Hz), 1.61-1.75 (2H, m), 1.52 (1H, dd, $J = 14.8, 5.2$ Hz), 1.39 (1H, dt, $J = 14.8, 11.6$ Hz), 0.92 (3H, d, $J = 6.4$ Hz), 0.85 (3H, d, $J = 6.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 208.9, 172.9, 146.5, 128.5, 126.7, 126.4, 62.8, 52.4, 48.9, 41.2, 40.2, 35.0, 31.2, 30.4, 24.7, 24.4, 23.1; IR (neat) 2955, 2870, 2361, 1711, 1456, 1227, 1206, 1155, 1123 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{19}\text{H}_{26}\text{O}_3$: m/z 325.1774 ($[\text{M} + \text{Na}]^+$), found: m/z 325.1776 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{27} = -52.6$ ($c = 1.0$, CHCl_3 ; 66% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/isopropanol = 99/1, flow rate = 0.5 mL/min, retention time; 19.0 min (minor) and 23.3 min (major)).

Methyl

(*1S,5S*)-5-(*tert*-butyldimethylsilyloxy)-1-(4-methoxybenzyl)-2-oxocycloheptanecarboxylate (6k).



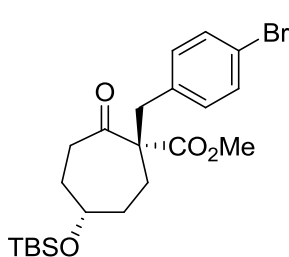
^1H NMR (400 MHz, CDCl_3) δ 6.98 (2H, m), 6.76 (2H, m), 3.79 (1H, br), 3.75 (3H, s), 3.67 (3H, br), 3.25 (1H, d, $J = 13.6$ Hz), 2.91 (1H, d, $J = 13.6$ Hz), 2.79 (1H, ddd, $J = 12.8, 10.8, 2.8$ Hz), 2.43 (1H, dd, $J = 14.8, 9.6$ Hz), 2.14 (1H, ddd, $J = 11.6, 8.8, 2.8$

Hz), 1.58-1.77 (4H, m), 1.40 (1H, m), 0.84 (9H, s), 0.01 (6H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 209.4, 172.2, 158.5, 131.3, 128.6, 113.6, 69.6, 64.2, 55.2, 52.3, 39.4, 37.0, 34.5, 32.2, 25.8, 23.9, 18.0, -4.8; IR (neat) 2951, 2930, 1736, 1711, 1512, 1250, 1206, 1179, 1076, 1036 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{23}\text{H}_{36}\text{O}_5\text{Si}$: m/z 443.2224 ($[\text{M} + \text{Na}]^+$), found: m/z 443.2216 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{27} = -23.0$ ($c = 1.0$, CHCl_3 ; 78% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK IC, hexane/isopropanol = 30/1, flow rate = 0.5 mL/min, retention time; 31.9 min (major) and 35.3 min (minor)).

Methyl

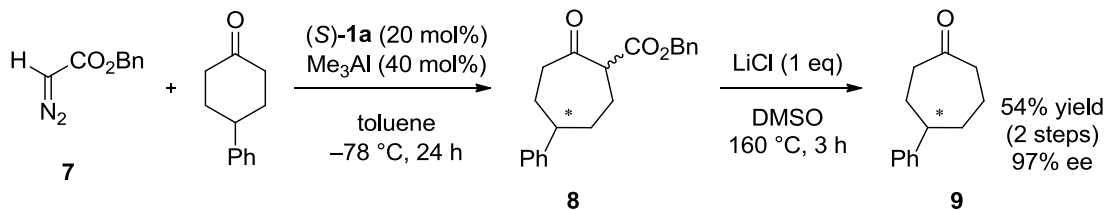
(1*S*,5*S*)-1-(4-bromobenzyl)-5-(*tert*-butyldimethylsilyloxy)-2-oxocycloheptanecarboxylate (**6l**).



^1H NMR (400 MHz, CDCl_3) δ 7.37 (2H, m), 6.98 (2H, m), 3.84 (1H, br), 3.69 (3H, s), 3.29 (1H, d, $J = 14.0$ Hz), 2.93 (1H, d, $J = 14.0$ Hz), 2.86 (1H, ddd, $J = 12.8, 11.6, 2.8$ Hz), 2.51 (1H, dd, $J = 15.6, 9.6$ Hz), 2.19 (1H, ddd, $J = 12.0, 8.4, 2.8$ Hz), 1.52-1.84 (4H, m), 1.37 (1H, m), 0.87 (9H, s), 0.03 (6H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 208.9, 171.9, 135.9, 132.1, 131.3, 120.9, 69.2, 64.0, 52.4, 39.4, 36.8, 34.6, 32.1, 25.8, 23.8, 18.0, -4.82, -4.84; IR (neat) 2951, 2930, 2857, 1736, 1711, 1489, 1254, 1207, 1074, 1013 cm^{-1} ; HRMS (ESI) exact mass calcd. for $\text{C}_{22}\text{H}_{33}\text{BrO}_4\text{Si}$: m/z 491.1224 ($[\text{M} + \text{Na}]^+$), found: m/z 491.1229 ($[\text{M} + \text{Na}]^+$); $[\alpha]_{\text{D}}^{29} = -28.3$ ($c = 1.0$, CHCl_3 ; 88% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/isopropanol = 99/1, flow rate = 0.5 mL/min, retention time; 14.6 min (minor) and 15.7 min (major)).

•Procedure for synthesis of optically active 4-phenylcycloheptanone **9** via traceless catalytic desymmetrizing asymmetric expansion.



To a solution of (*S*)-**1a** (17.2 mg, 0.040 mmol) in degassed toluene (2 mL) was added dropwise a 0.5 M toluene solution of trimethylaluminum (160 μL , 0.080 mmol) at room temperature under Ar and stirred for 60 min. 4-Phenylcyclohexanone (34.8 mg, 0.20 mmol) was then added to the resulting solution at the same temperature, and the solution was cooled to -78 $^{\circ}\text{C}$. Benzyl diazoacetate **7** (42.3 mg, 0.24 mmol) was added to this solution

and the stirring was maintained at the same temperature for 24 h. The mixture was quenched with 1N HCl, extracted with ethyl acetate and dried over Na₂SO₄. After concentration under reduced pressure, the residue was used for the next step without further purification.

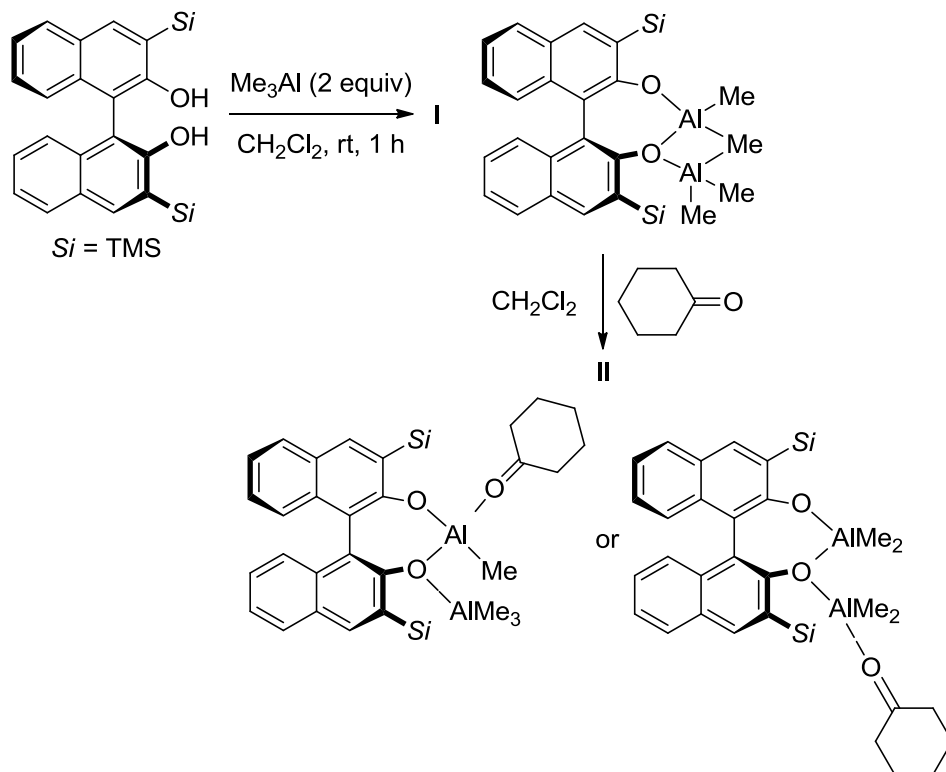
To a solution of thus-obtained ethyl 2-oxo-5-phenylcycloheptanecarboxylate **8** in DMSO (2 mL) was added lithium chloride (8.5 mg, 0.2 mmol) at room temperature. The mixture was stirred at 160 °C for 3 h. The resulting solution was poured into brine and extracted with Et₂O. The combined organic layers were dried over anhydrous Na₂SO₄ and removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 30/1) to give 4-phenylcycloheptanone **9** in 54% yield in 2 steps (20.4 mg, 0.11 mmol) with 97% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.24-7.34 (2H, m), 7.15-7.23 (3H, m), 2.65-2.75 (2H, m), 2.55-2.64 (3H, m), 2.14 (1H, m), 1.98-2.08 (2H, m), 1.71-1.94 (2H, m), 1.63 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 214.7, 147.5, 128.5, 126.5, 126.2, 48.7, 43.8, 42.9, 38.4, 31.8, 23.8; IR (neat) 2926, 2860, 1699, 1493, 1452, 1342, 1252, 1163 cm⁻¹; HRMS (ESI) exact mass calcd. for C₁₃H₁₆O: *m/z* 211.1093 ([M + Na]⁺), found: *m/z* 211.1097 ([M + Na]⁺); [α]_D²⁹ = -138.0 (*c* = 1.0, CHCl₃; 97% ee).

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/isopropanol = 97/3, flow rate = 0.5 mL/min, retention time; 17.7 min (major) and 29.9 min (minor)).

•Preliminary NMR experiments of (*S*)-1a/Me₃Al complexes using no-D NMR spectroscopy.⁶

(*S*)-1a/Me₃Al 1:2 complex (I)



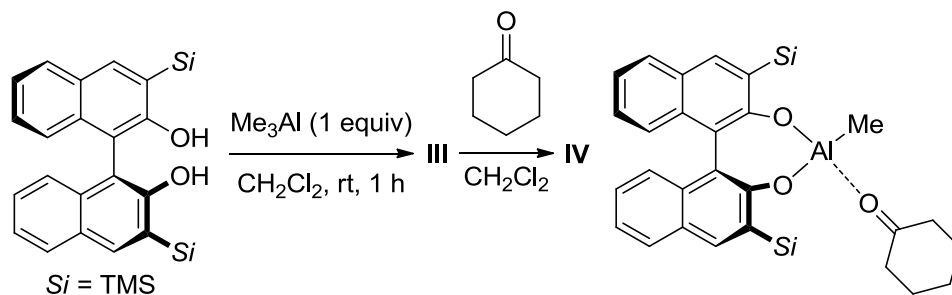
To a stirred solution of (*S*)-1a (34.4 mg, 0.080 mmol) in CH₂Cl₂ (1.0 mL) was added a 1M CH₂Cl₂ solution of Me₃Al (160 μ L, 0.16 mmol). After stirring for 1 h, the sample was taken to low pressure/vacuum (LPV) sample tube (Wilmad) and subjected to no-D ¹H and ¹³C NMR studies (JEOL JNM-FX500 (500 and 125 MHz) (see Charts 1-4). The NMR spectra at room temperature showed the peaks assigned to be a symmetrical structure having only 5 peaks at the aromatic region in accordance with Yamamoto and co-workers observation.⁷ On the other hand, the VT-NMR spectroscopy at -78 °C resulted in the appearance of the unsymmetrical structure. From these studies and the previous X-ray study by Rothwell,⁸ we assumed the formation of dinuclear aluminum complex I whose Al-Me moieties were in rapid equilibrium at room temperature.

(*S*)-1a/Me₃Al /cyclohexanone 1:2:1 complex (II)

To this solution was added cyclohexanone (8.3 μ L, 0.80 mmol) and this sample was subjected to no-D NMR studies (Chart 5-8). The symmetrical peaks of the complex I (Charts 1 and 2) varied apparently to provide new unsymmetrical peaks (Charts 5 and 6) at room temperature. Although VT NMR experiments at -78 °C led to the slight shift of some peaks and the splitting of the peaks assigned to cyclohexanone, the fundamental structure seems to be retained (Charts 7 and 8). In consideration of these facts, we propose two possibilities as below, both of which constitute Lewis acid-assisted Lewis acid as an active

species.⁹

(S)-1a/Me₃Al 1:1 complex (III)



To a stirred solution of (S)-**1a** (34.4 mg, 0.080 mmol) in CH₂Cl₂ (1.0 mL) was added a 1M CH₂Cl₂ solution of Me₃Al (80 μL, 0.080 mmol). After stirring for 1 h, the sample was taken to low pressure/vacuum (LPV) sample tube (Wilmad) and subjected to no-D ¹H and ¹³C NMR studies (JEOL JNM-FX500 (500 and 125 MHz) (see Charts 9-12). These experiments clearly showed the formation of an unsymmetrical structure which could not be superimposed with the free ligand (S)-**1a** or (S)-**1a**/Me₃Al 1:2 complex. The elucidation of this complex needs to await further investigation.

(S)-1a/Me₃Al/cyclohexanone 1:1:1 complex (IV)

To this solution was added cyclohexanone (8.3 μL, 0.80 mmol) and this sample was subjected to no-D NMR studies (Charts 13-16). Addition of cyclohexanone immediately led to the formation of new species having a C₂-symmetry and this symmetry was retained even at -78 °C. In addition, one sharp peak assignable to the Al-Me group appeared at -78 °C. Based on these observations, this complex is assumed to be a monomeric BINOL-Al complex coordinated by cyclohexanone.

Chart 1. ^1H NMR spectra of the complex **I** at rt

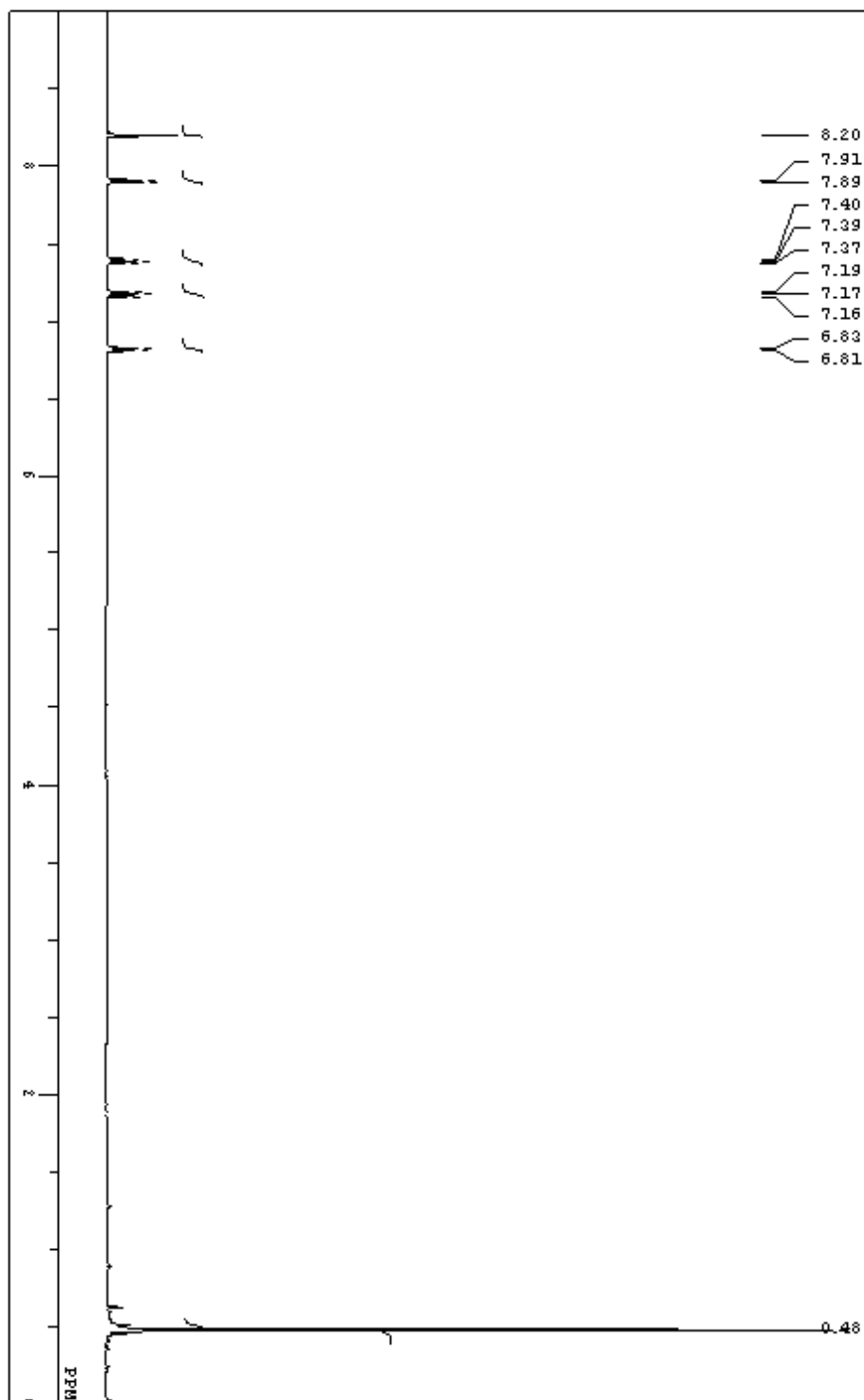


Chart 2. ^{13}C NMR spectra of the complex I at rt

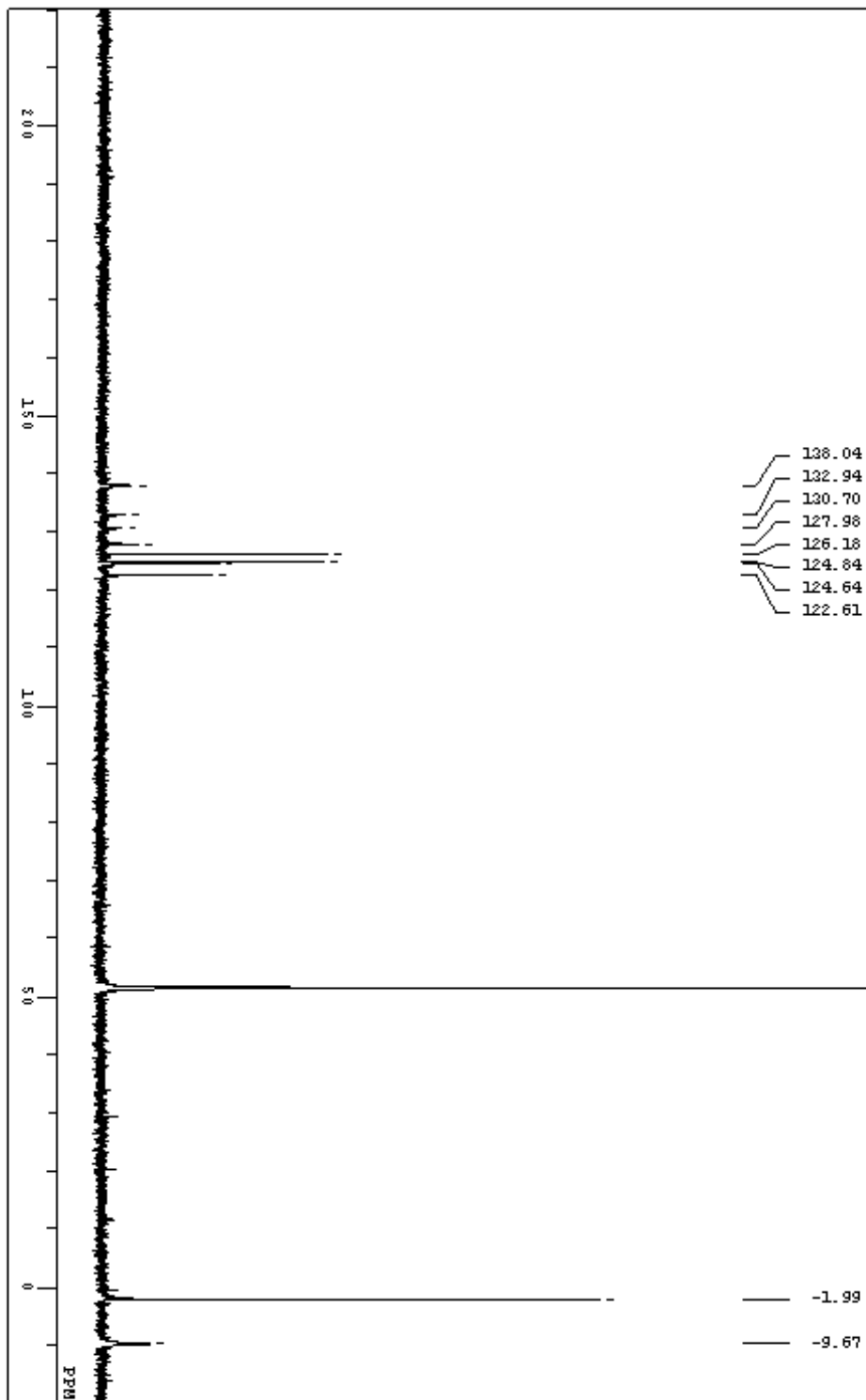


Chart 3. ^1H NMR spectra of the complex **I** at $-78\text{ }^\circ\text{C}$

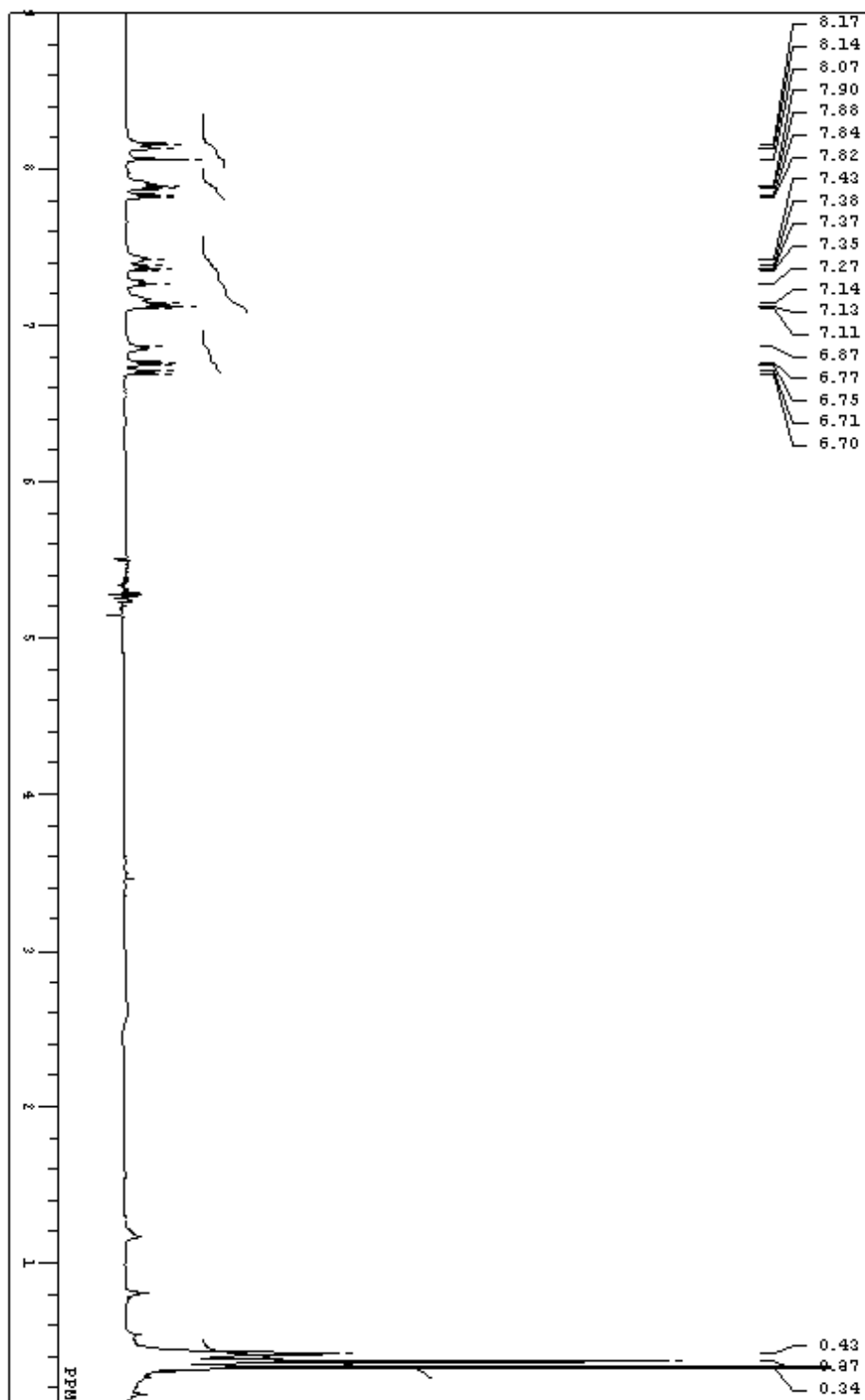


Chart 4. ^{13}C NMR spectra of the complex I at $-78\text{ }^{\circ}\text{C}$

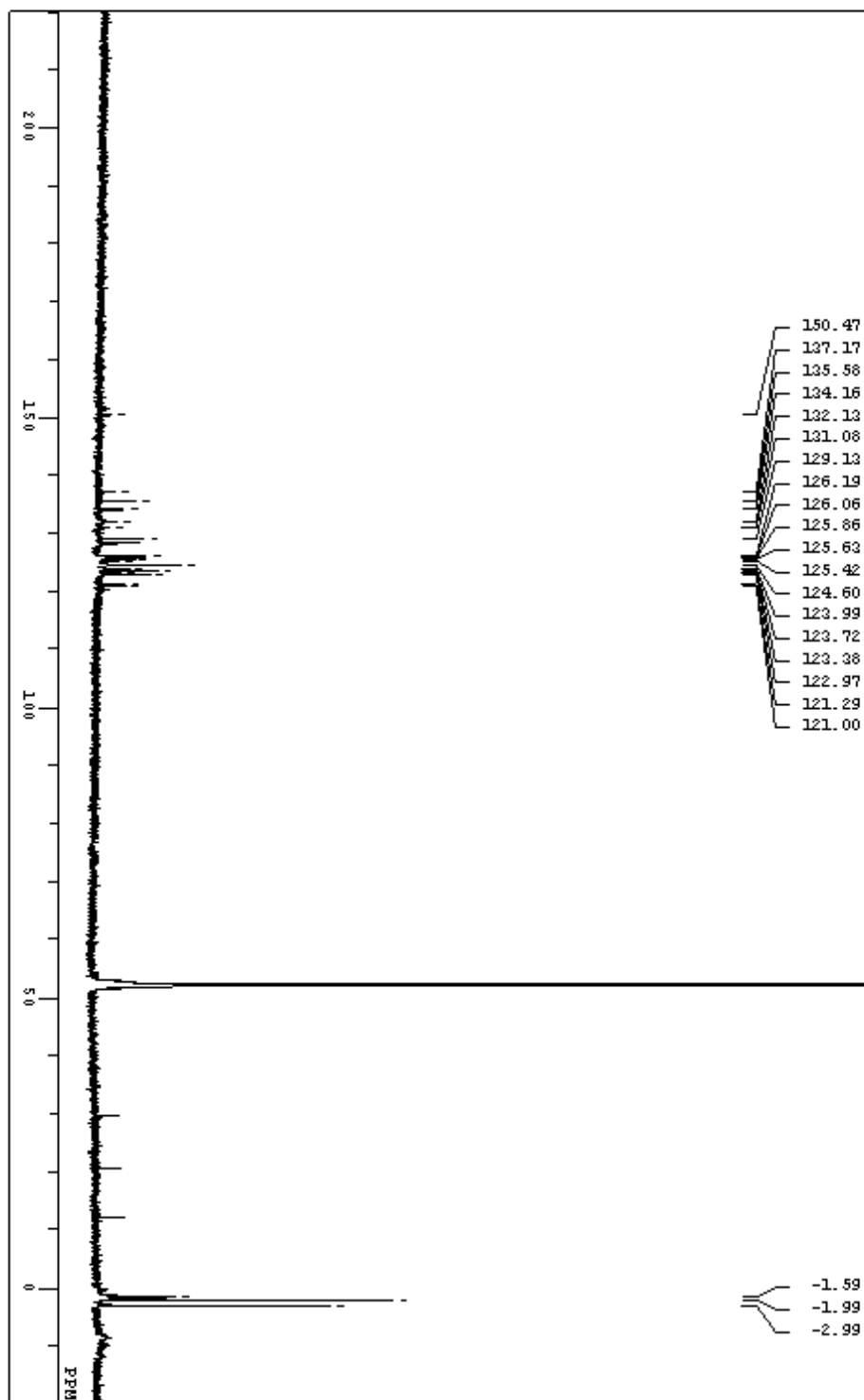


Chart 5. ^1H NMR spectra of the complex **II** at rt

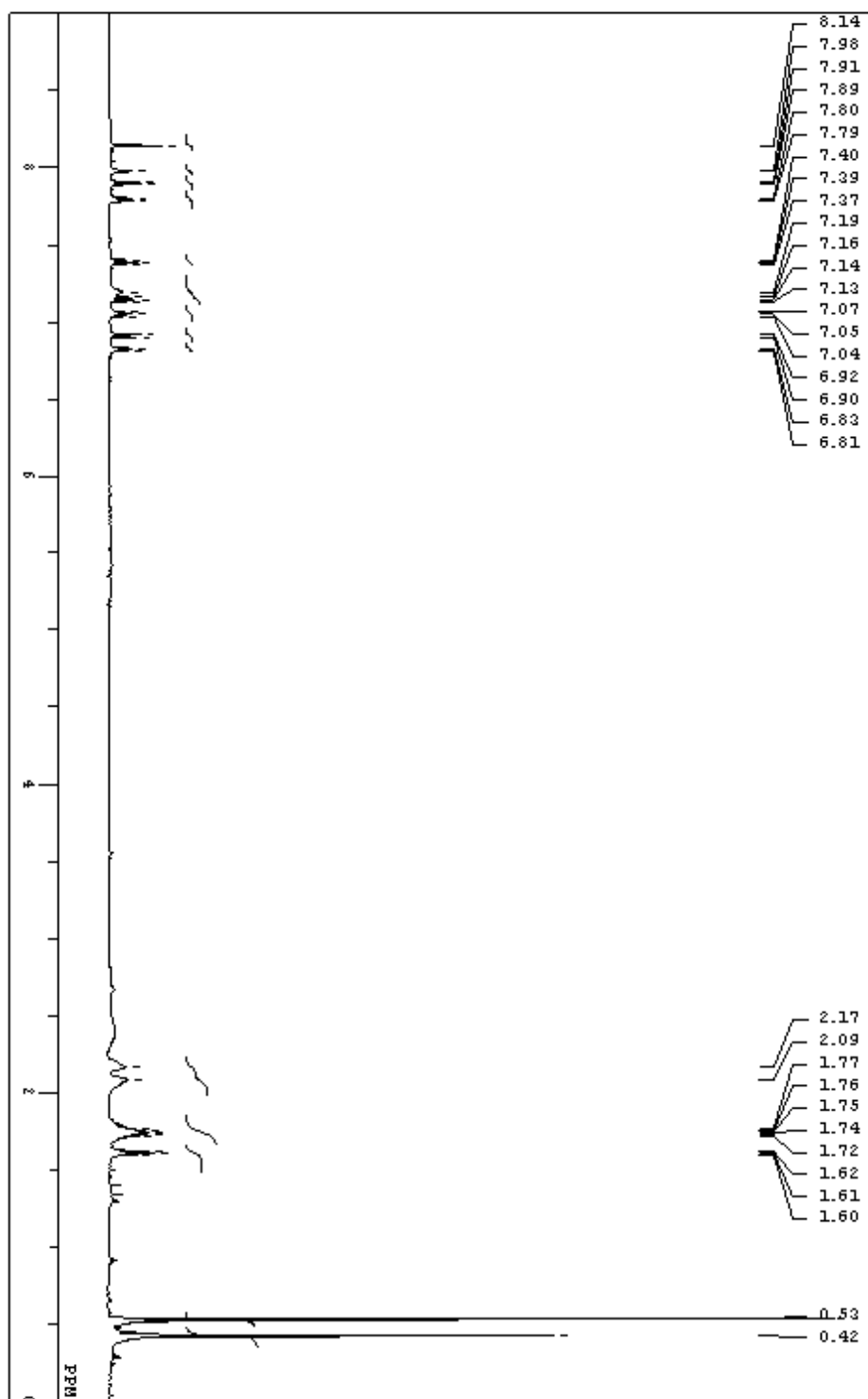


Chart 6. ^{13}C NMR spectra of the complex **II** at rt

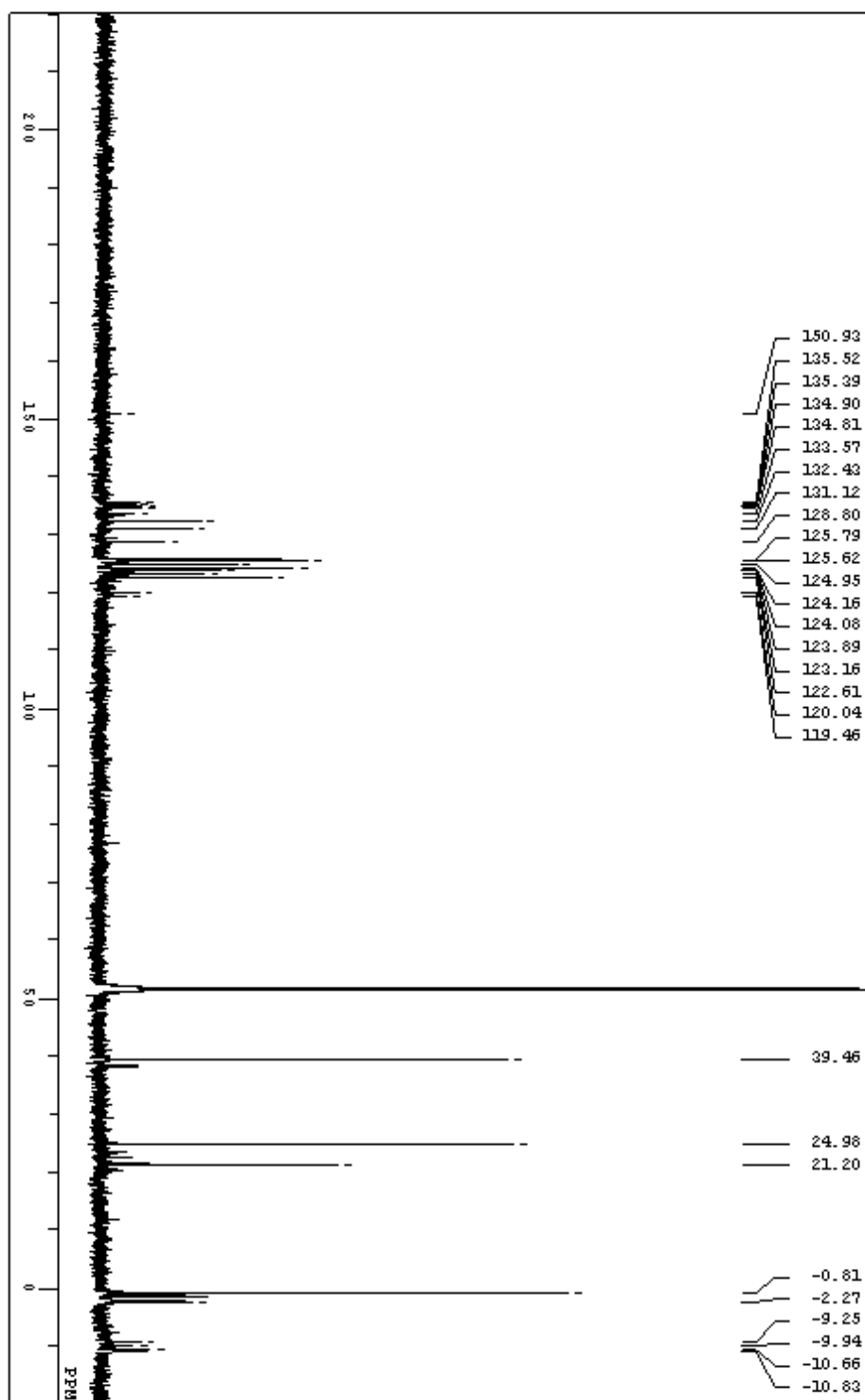


Chart 7. ^1H NMR spectra of the complex **II** at $-78\text{ }^\circ\text{C}$

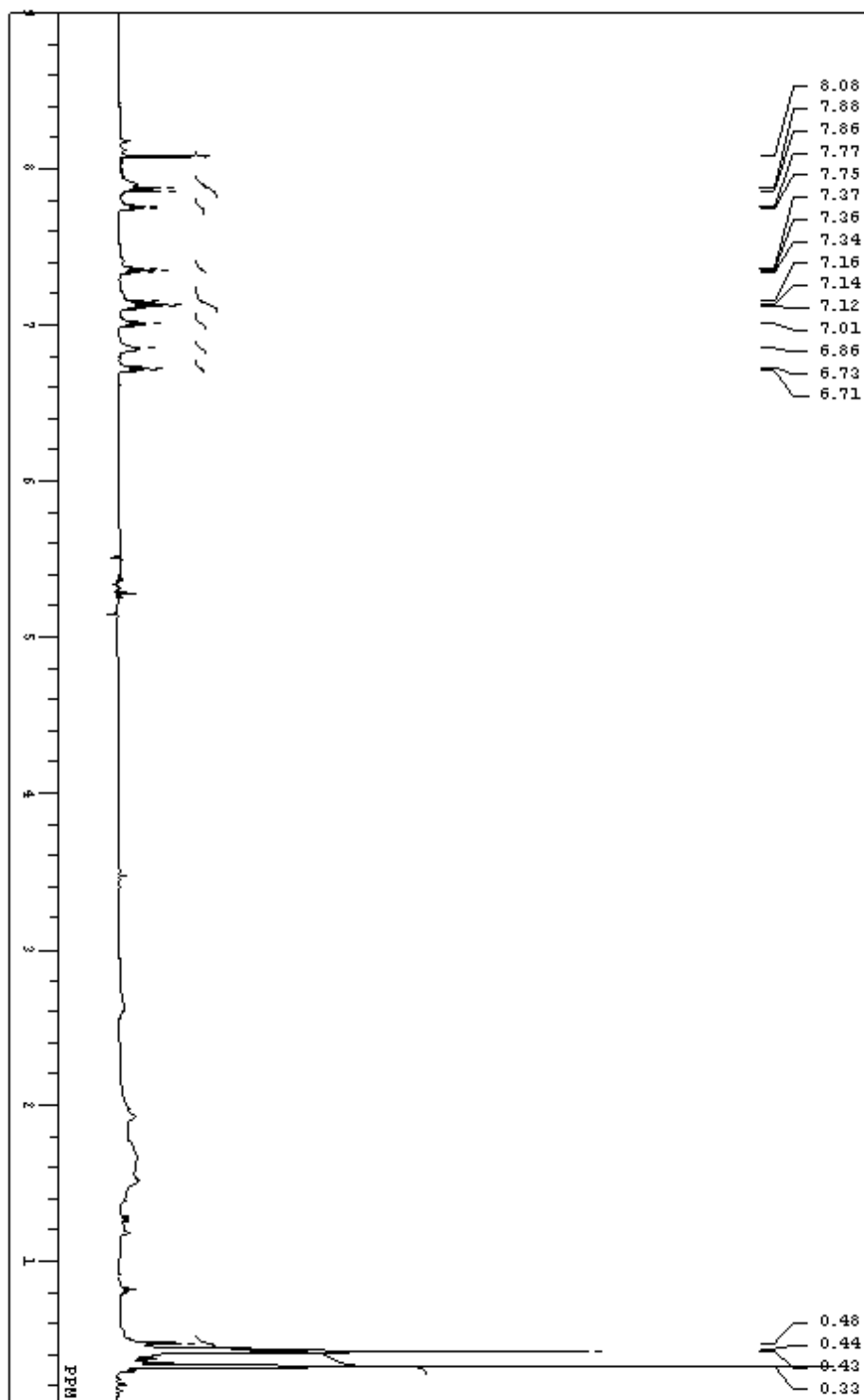


Chart 8. ^{13}C NMR spectra of the complex **II** at $-78\text{ }^{\circ}\text{C}$

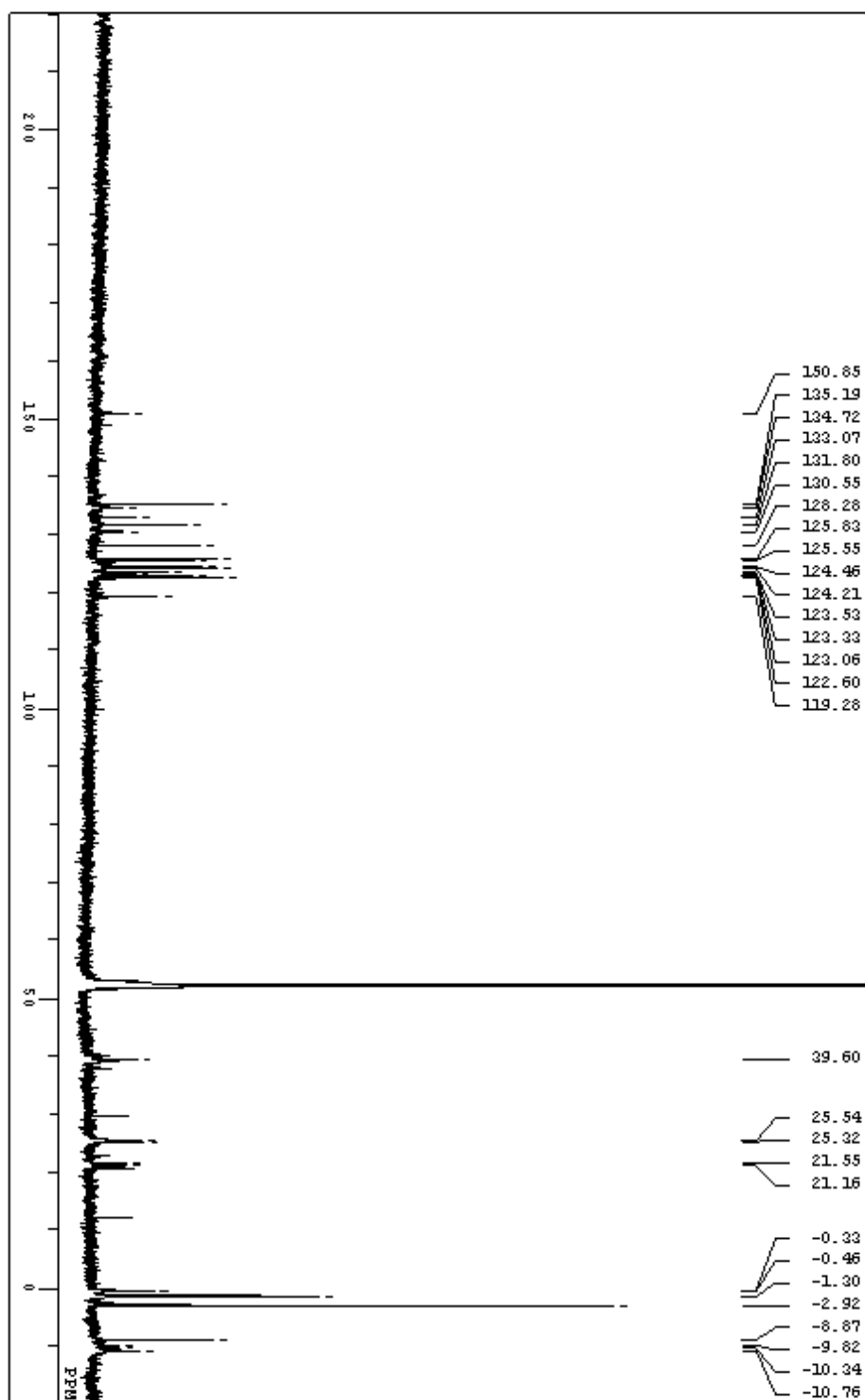


Chart 9. ^1H NMR spectra of the complex **III** at rt

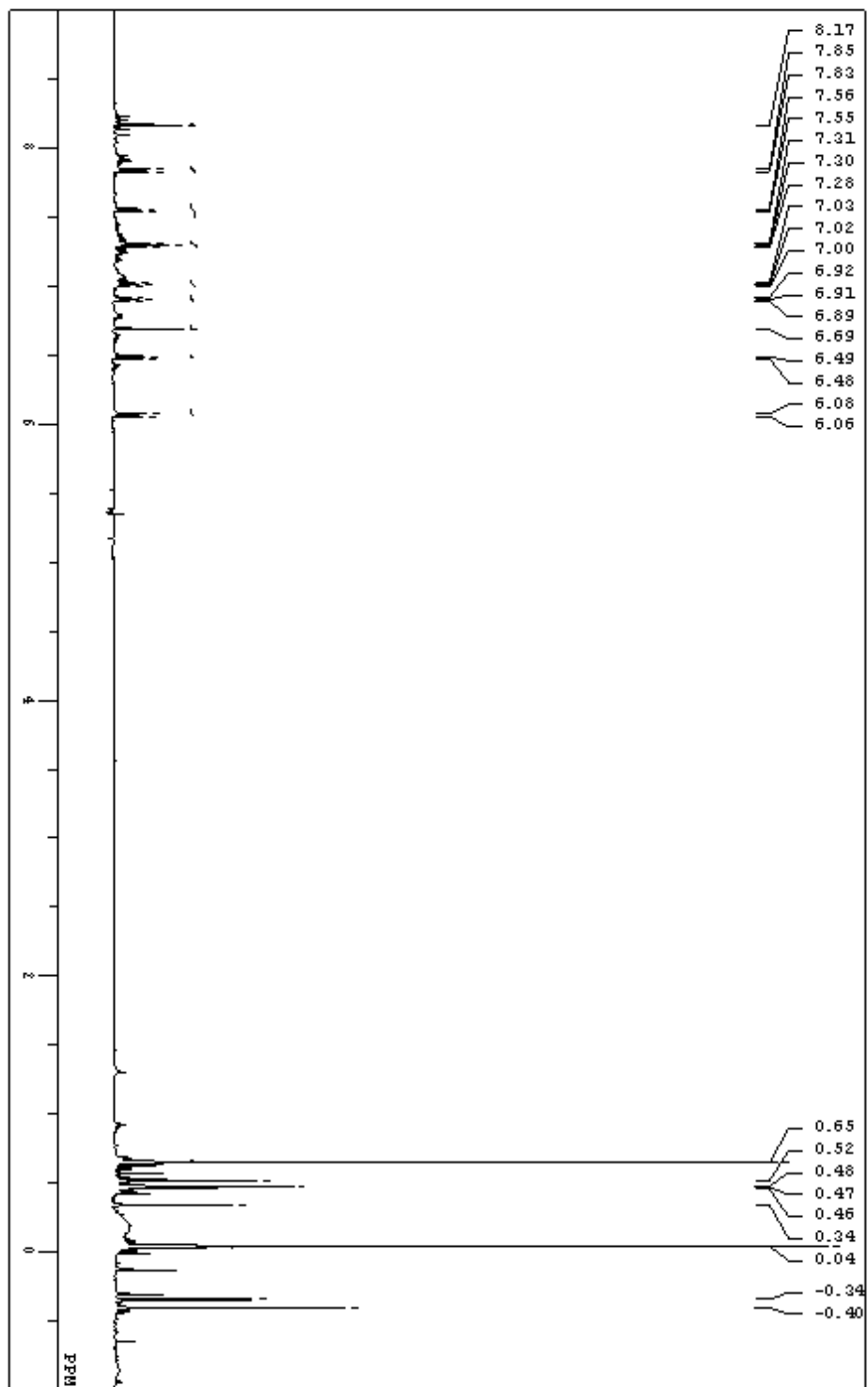


Chart 10. ^{13}C NMR spectra of the complex **III** at rt

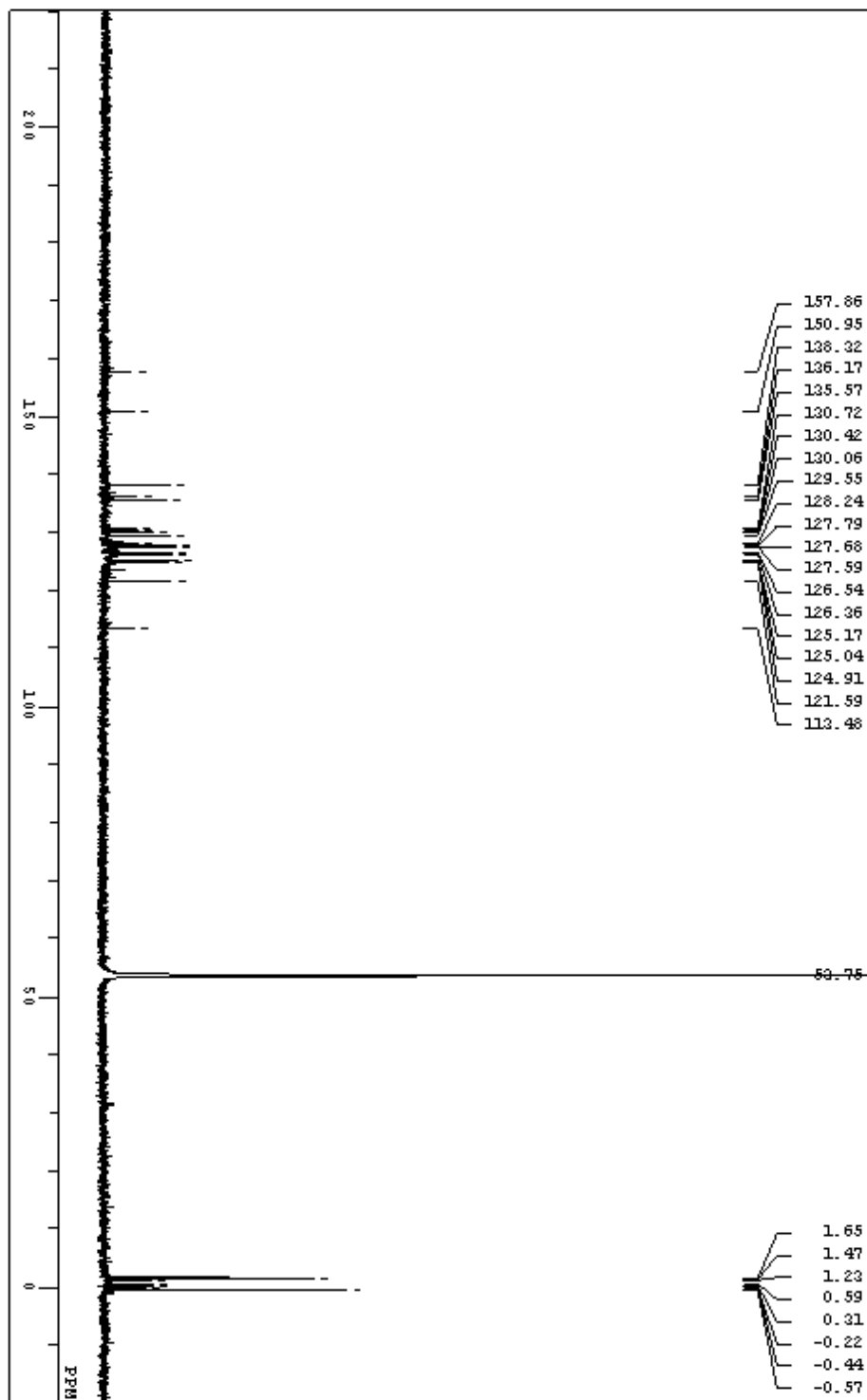


Chart 11. ^1H NMR spectra of the complex **III** at $-78\text{ }^\circ\text{C}$

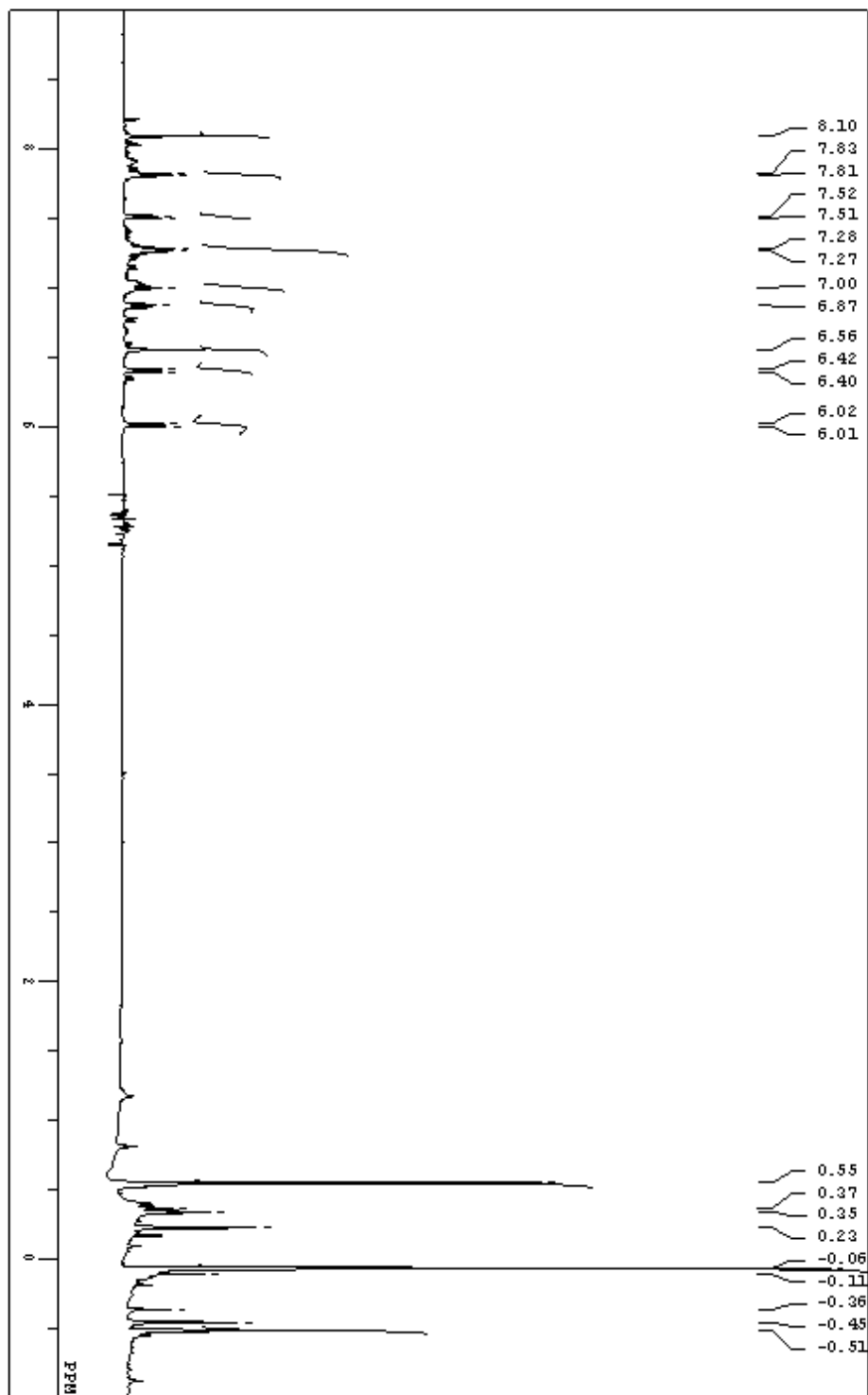


Chart 12. ^{13}C NMR spectra of the complex **III** at $-78\text{ }^{\circ}\text{C}$

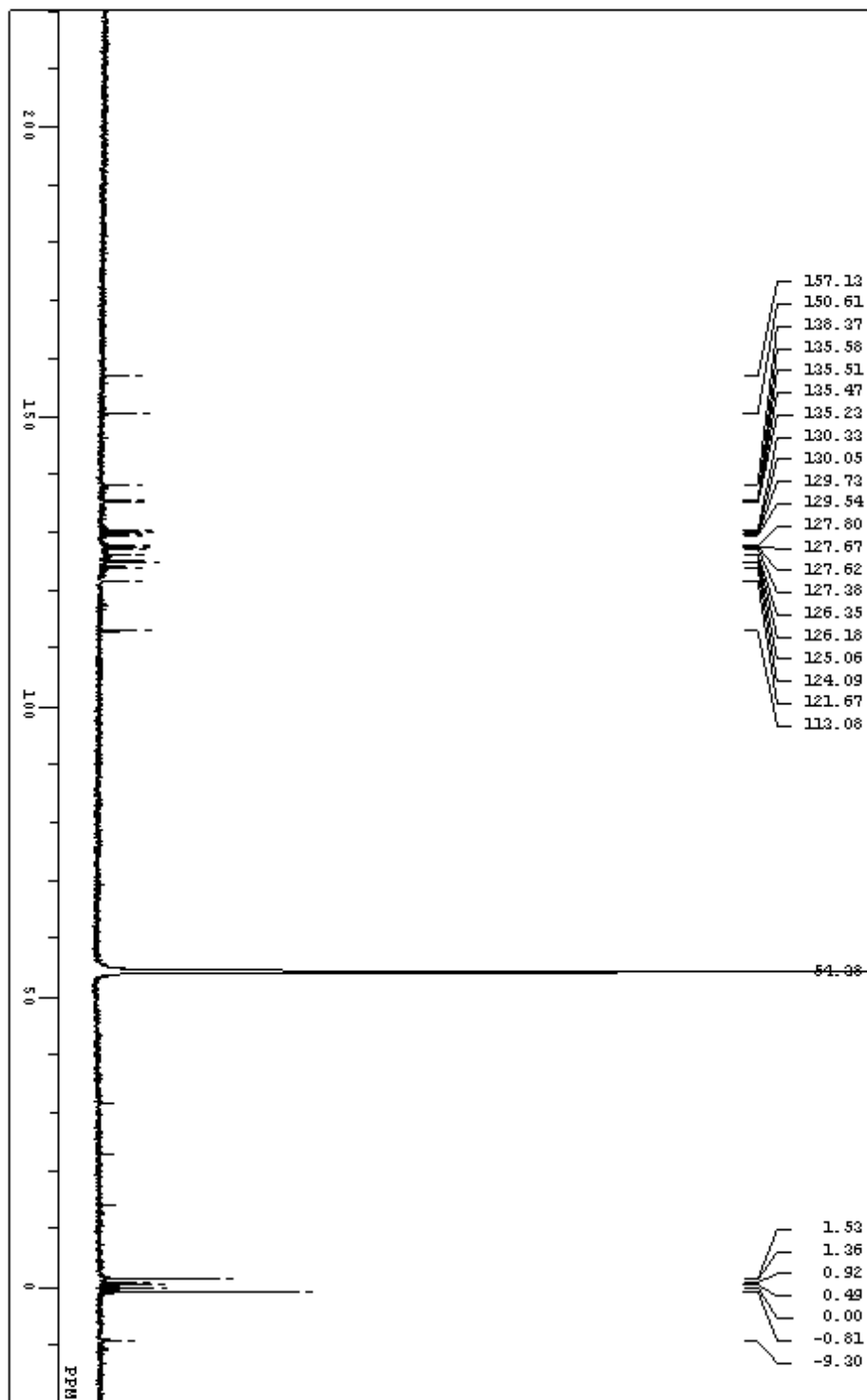


Chart 13. ^1H NMR spectra of the complex **IV** at rt

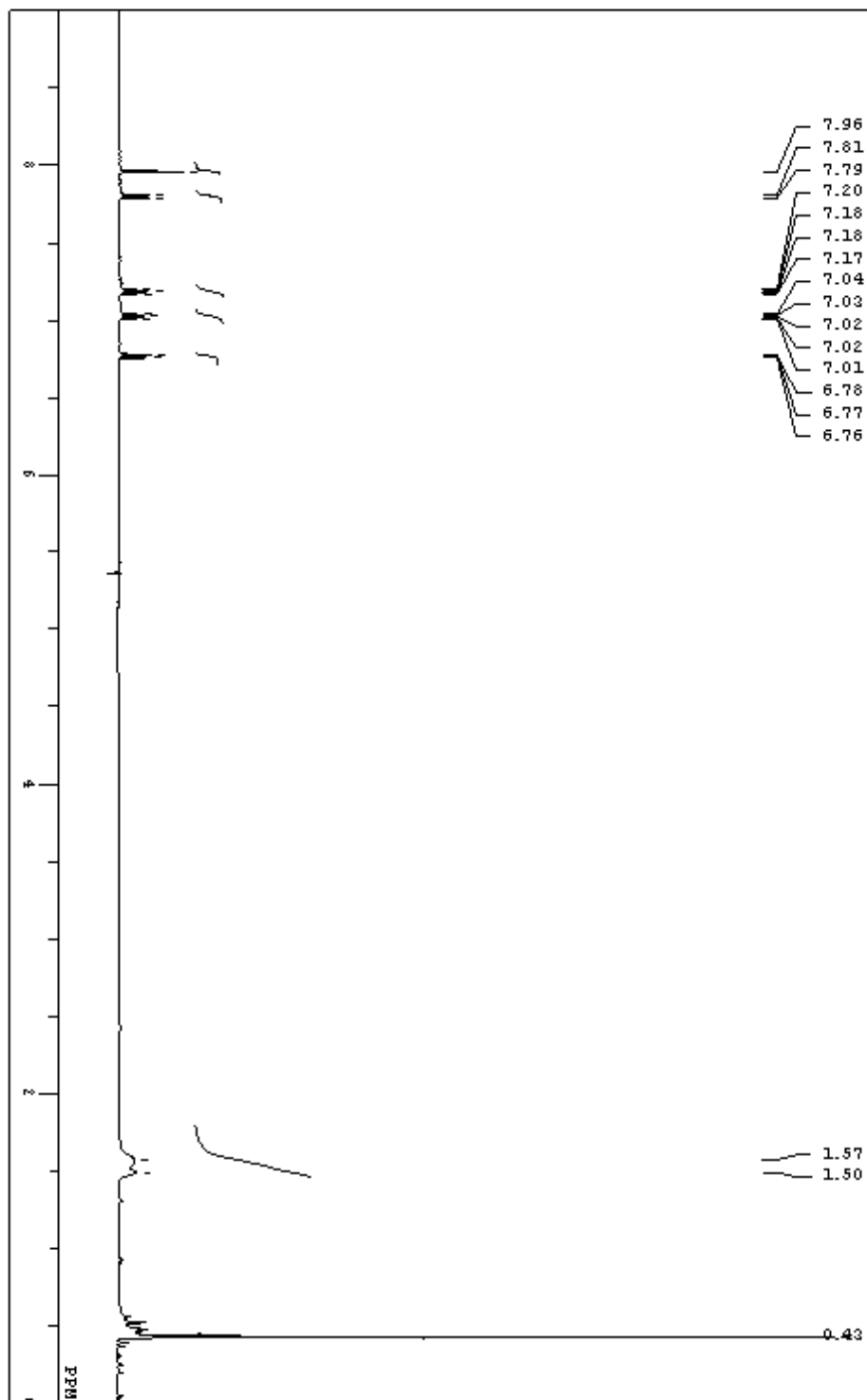


Chart 14. ^{13}C NMR spectra of the complex **IV** at rt

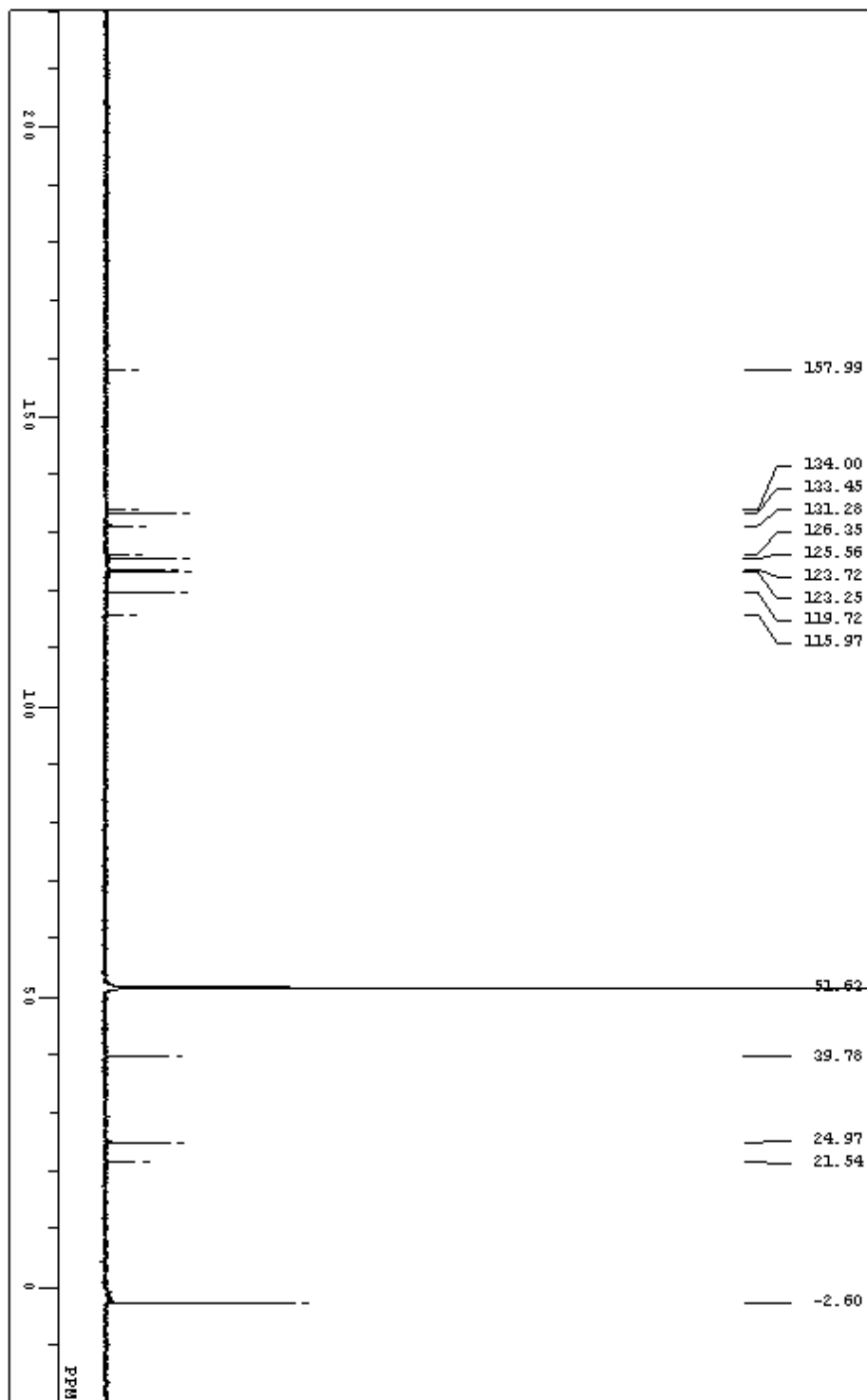


Chart 15. ^1H NMR spectra of the complex **IV** at $-78\text{ }^\circ\text{C}$

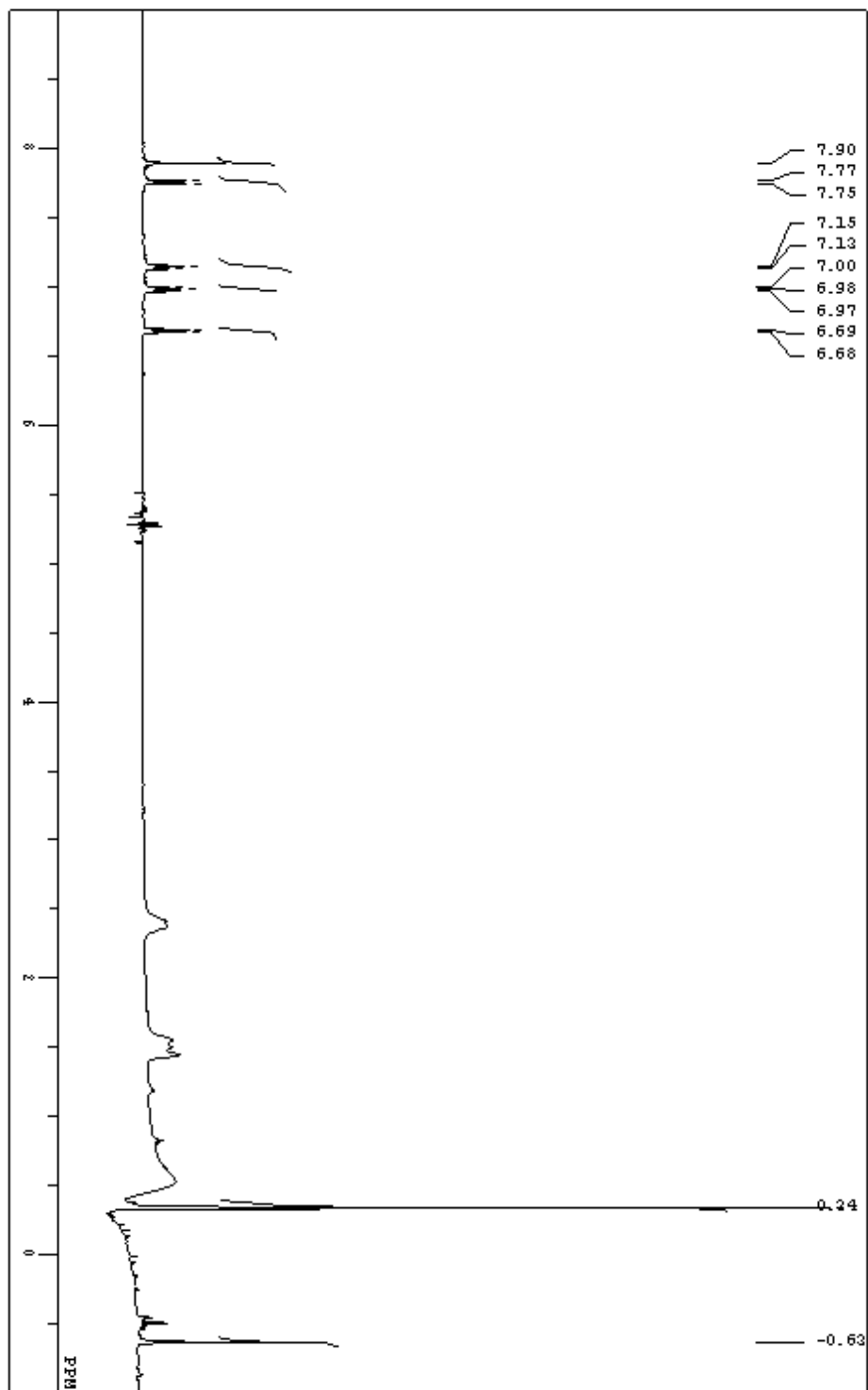
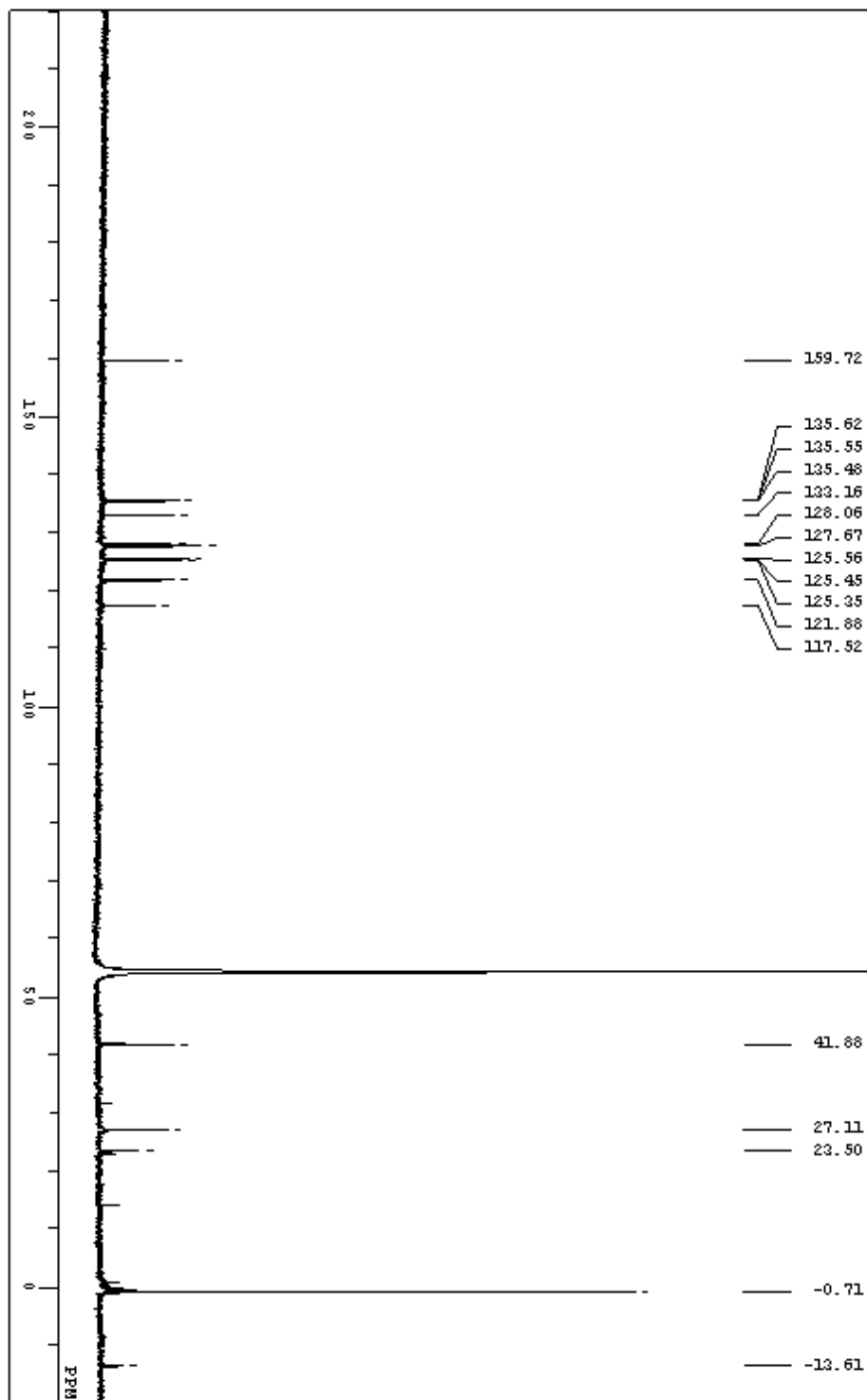
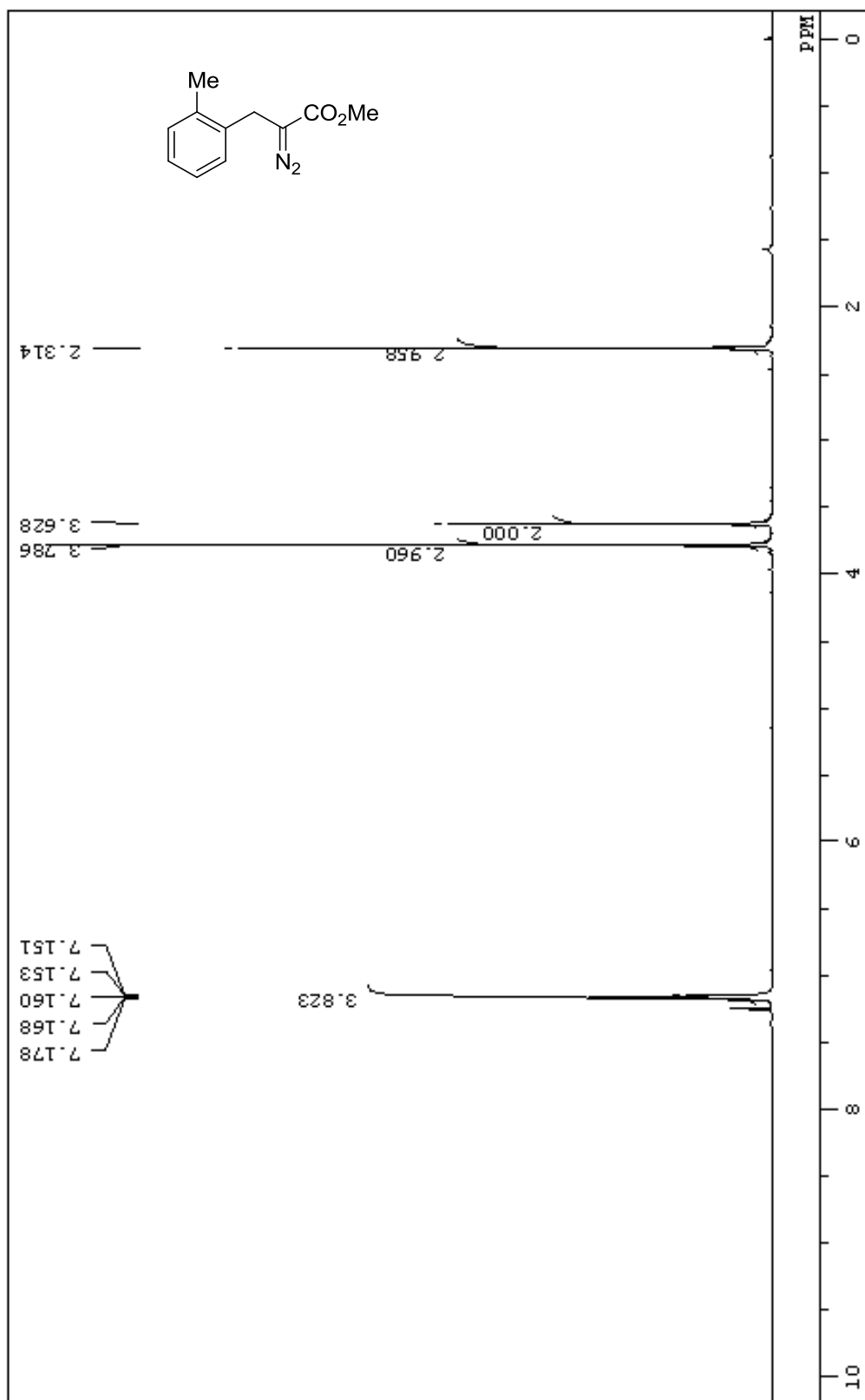


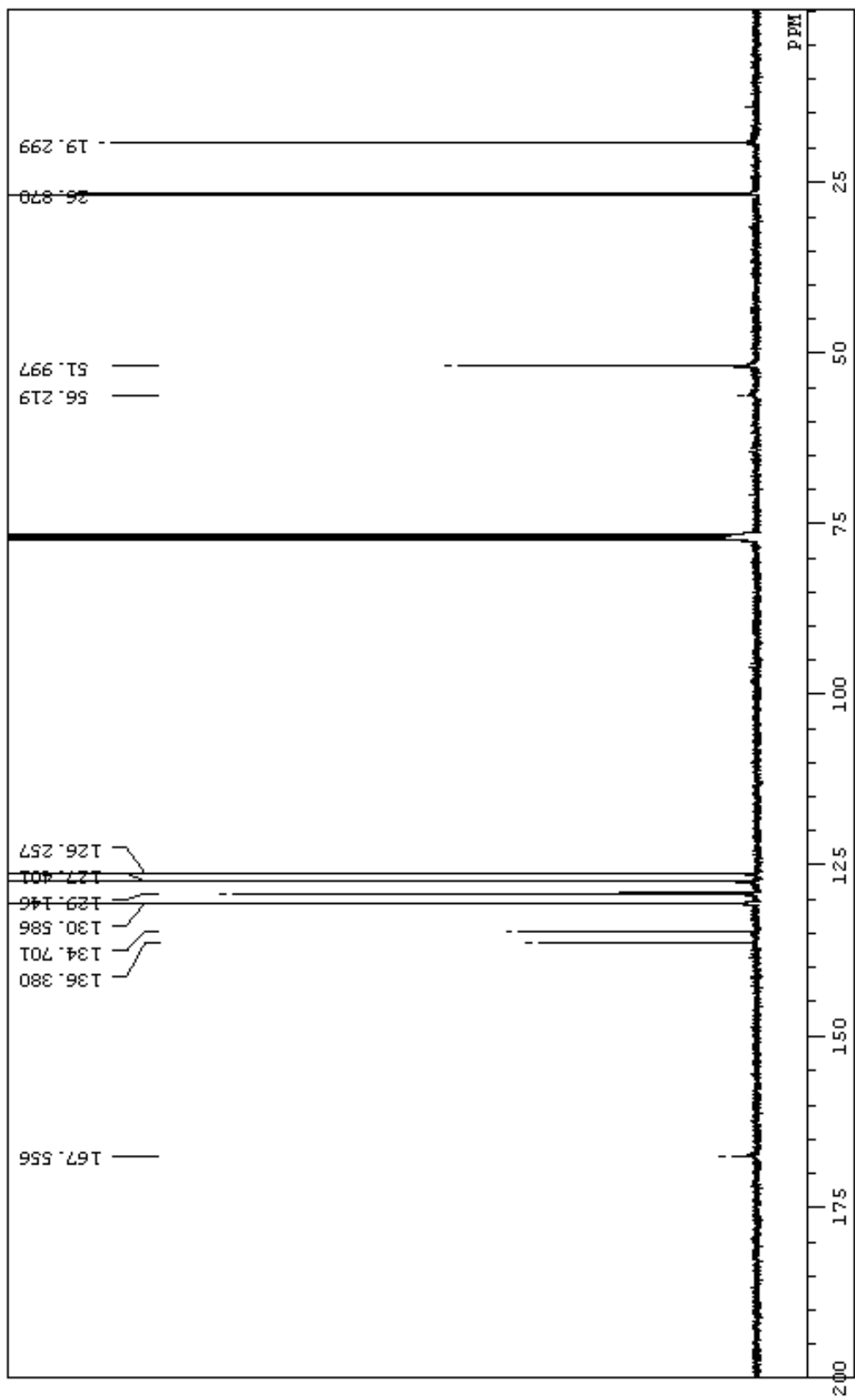
Chart 16. ^{13}C NMR spectra of the complex **IV** at $-78\text{ }^{\circ}\text{C}$

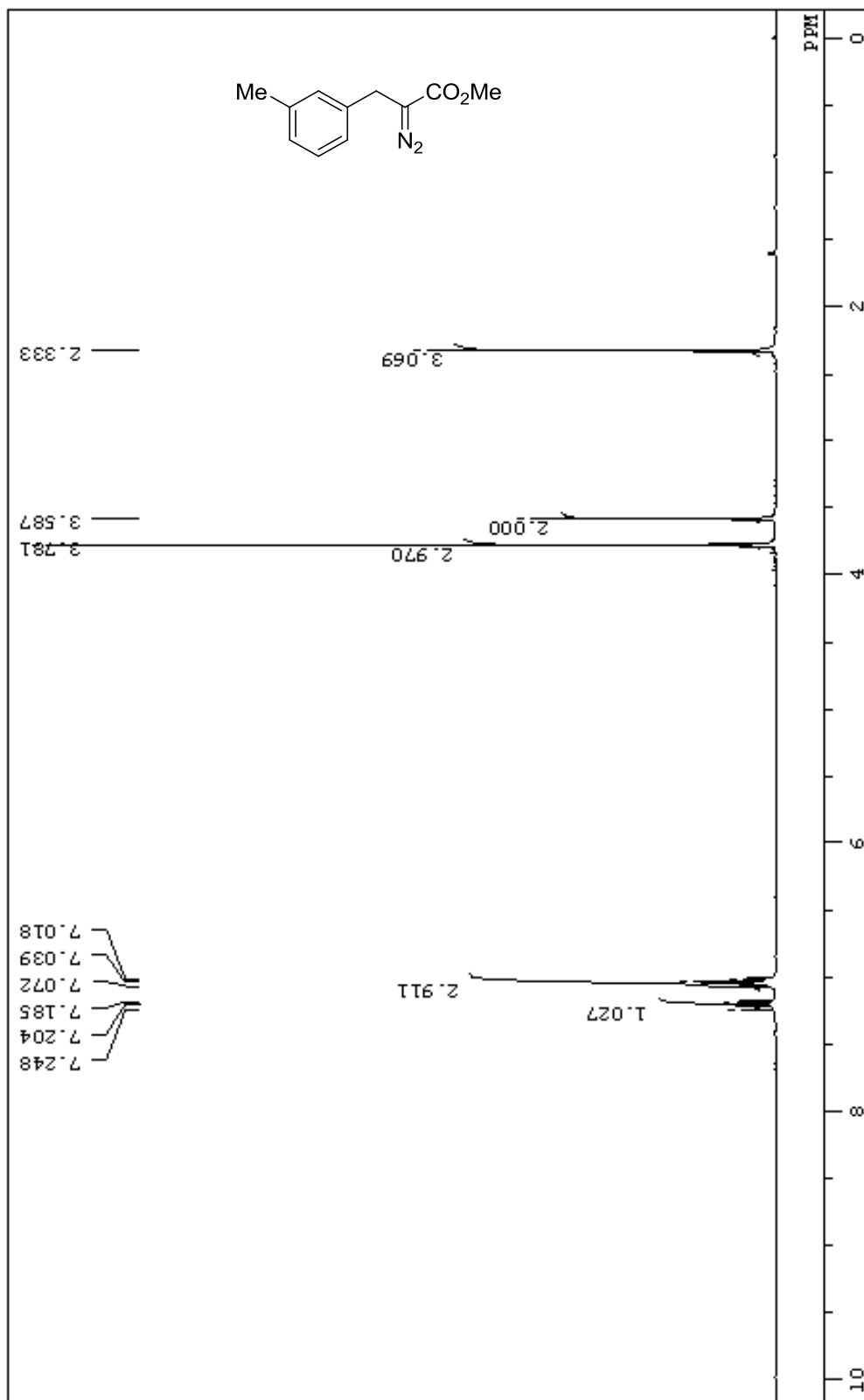


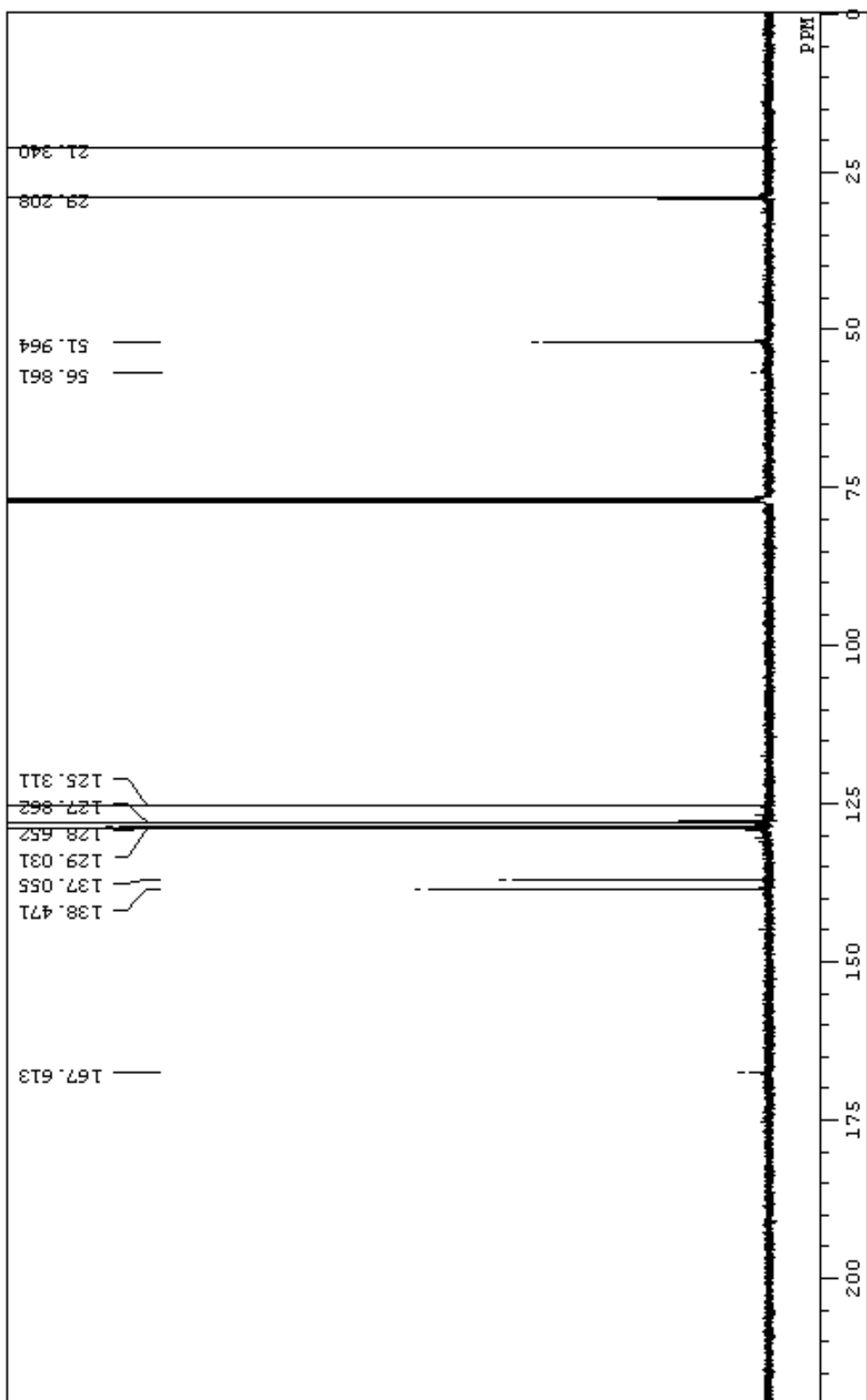
•References.

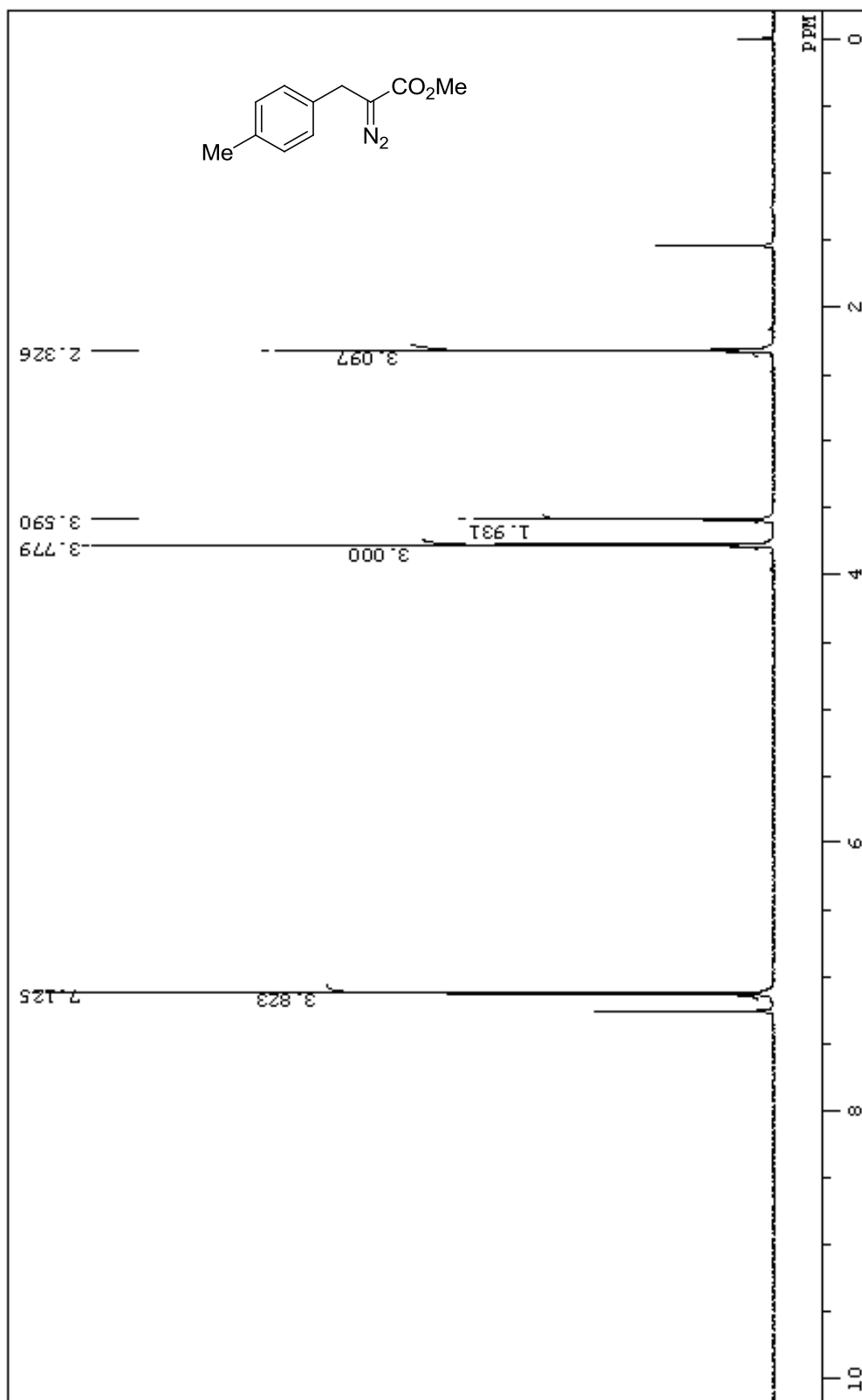
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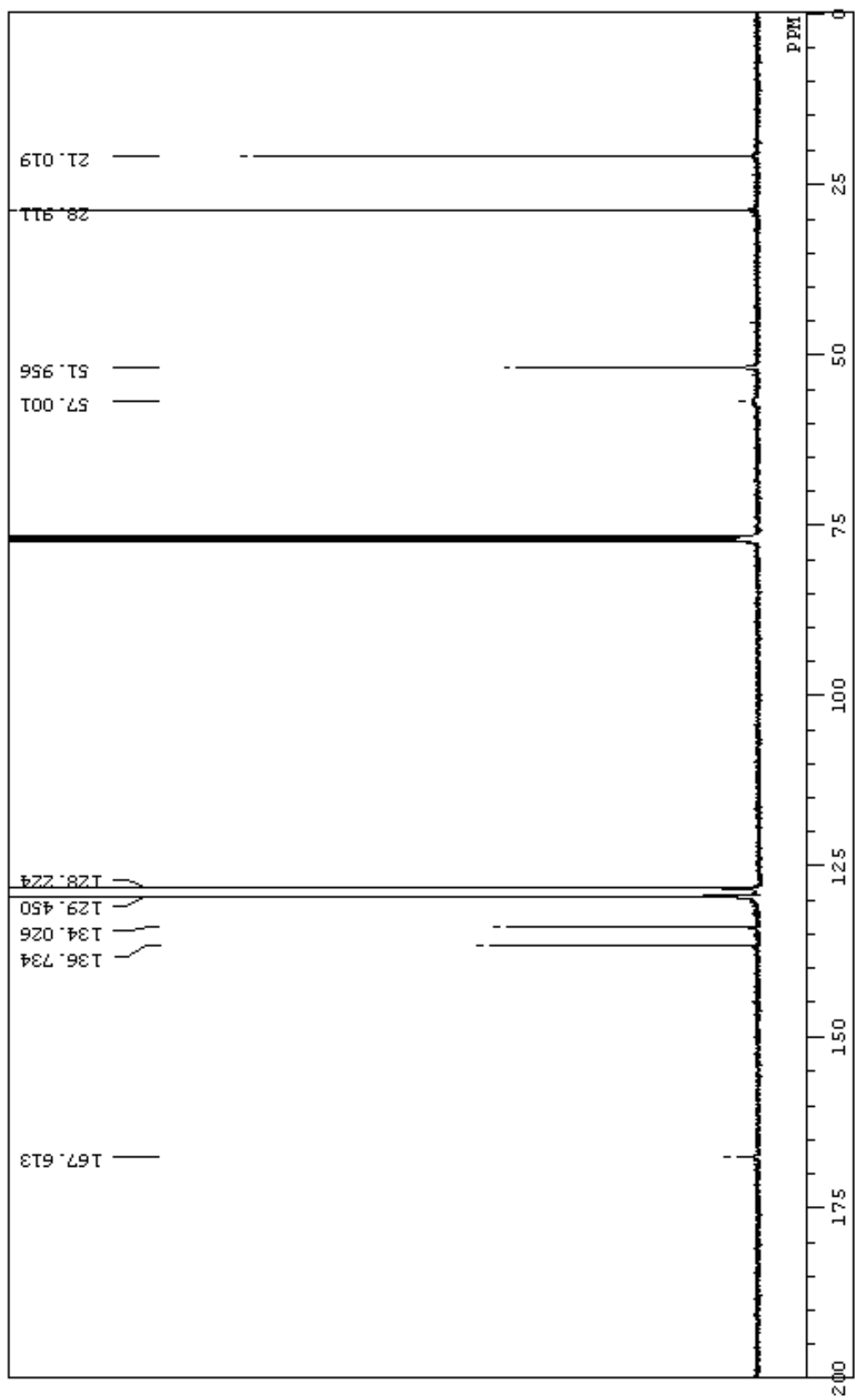


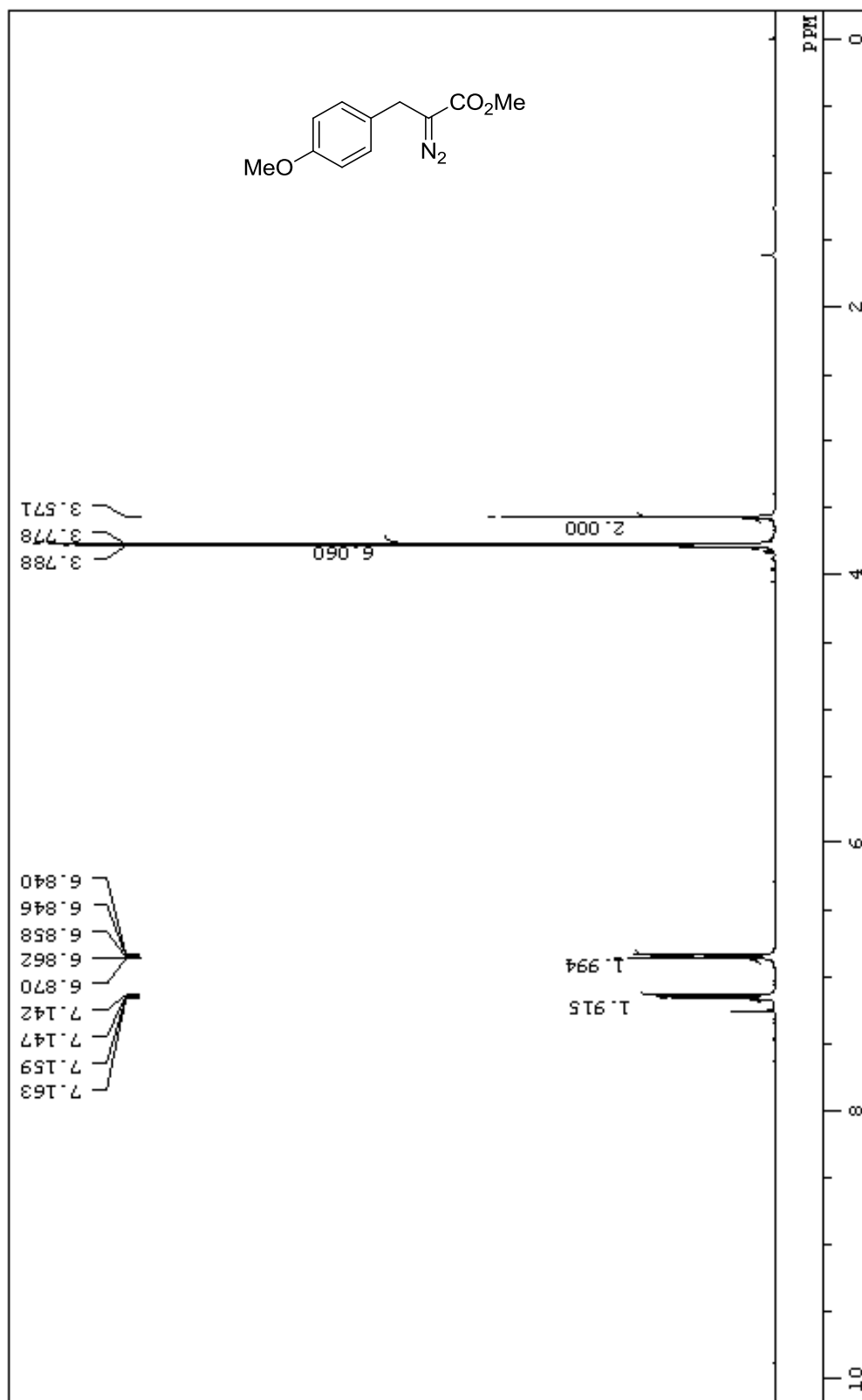


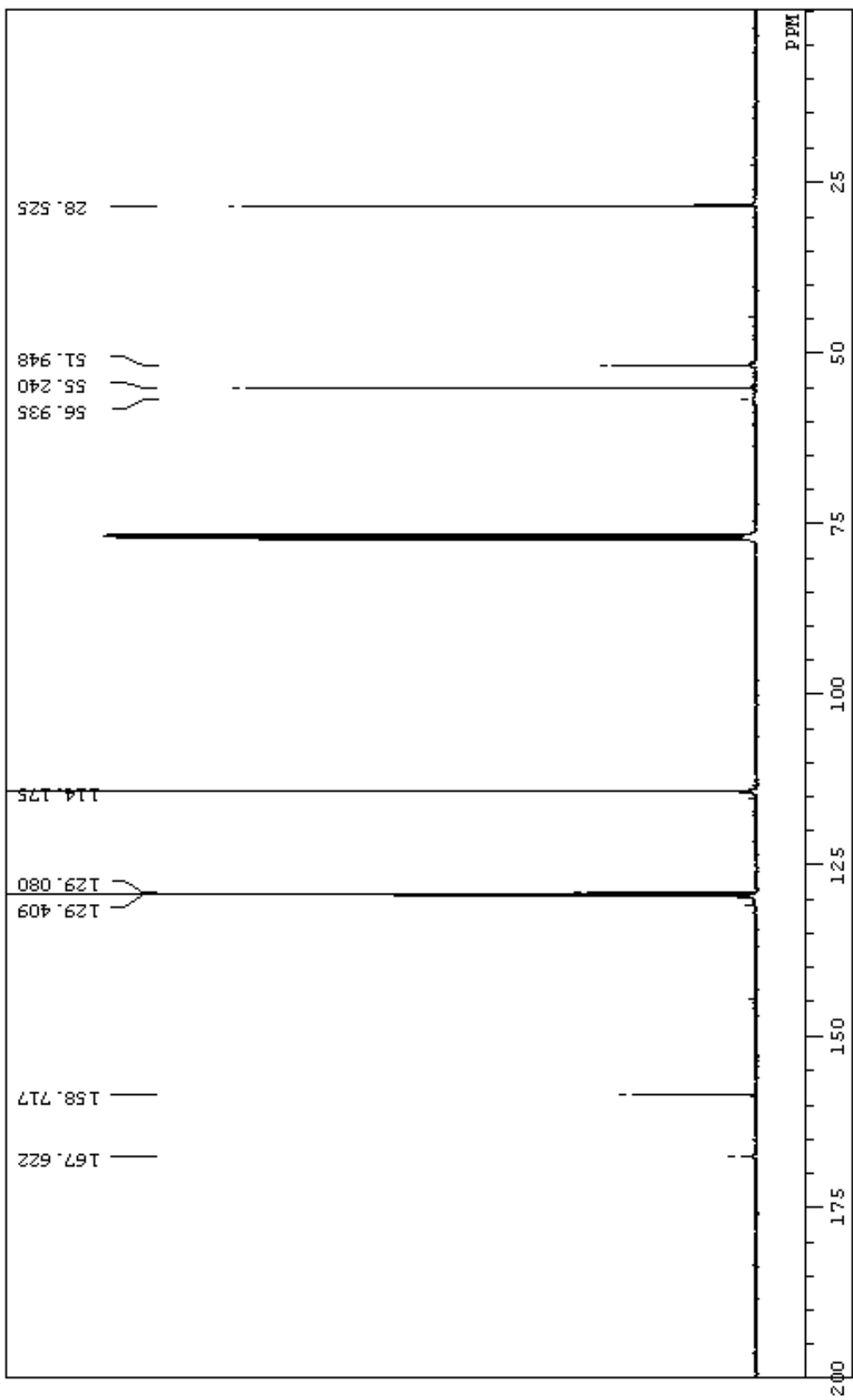


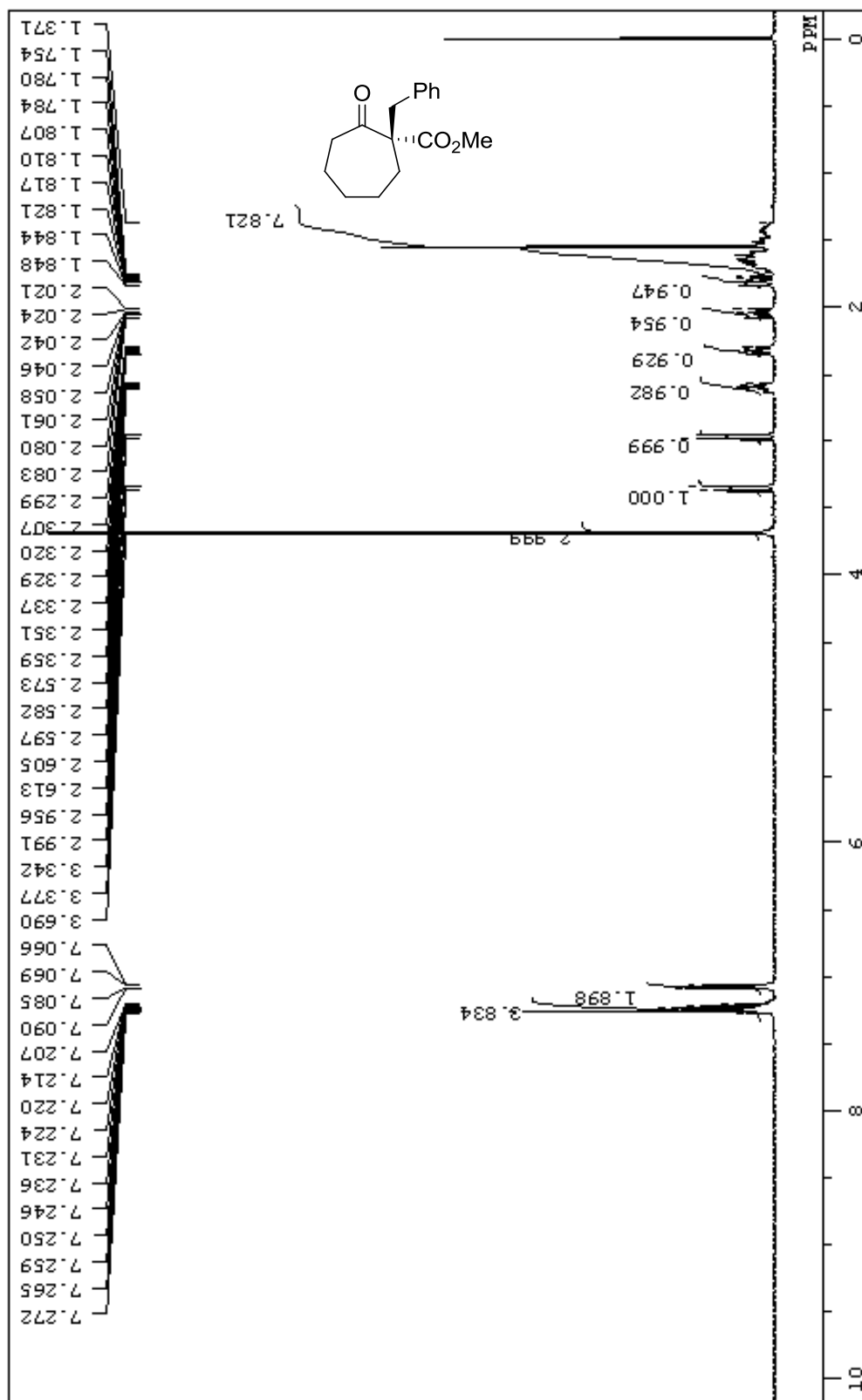


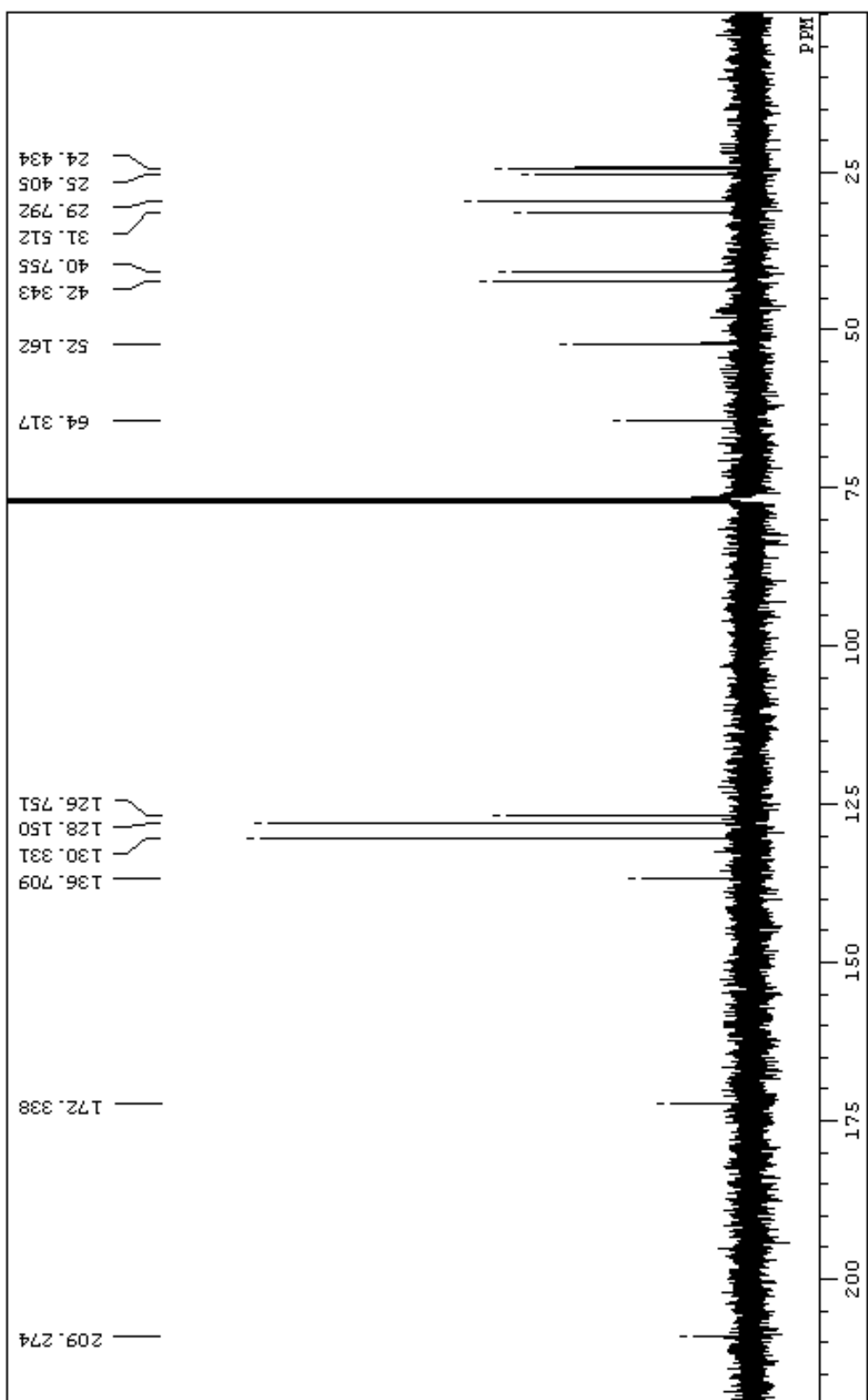


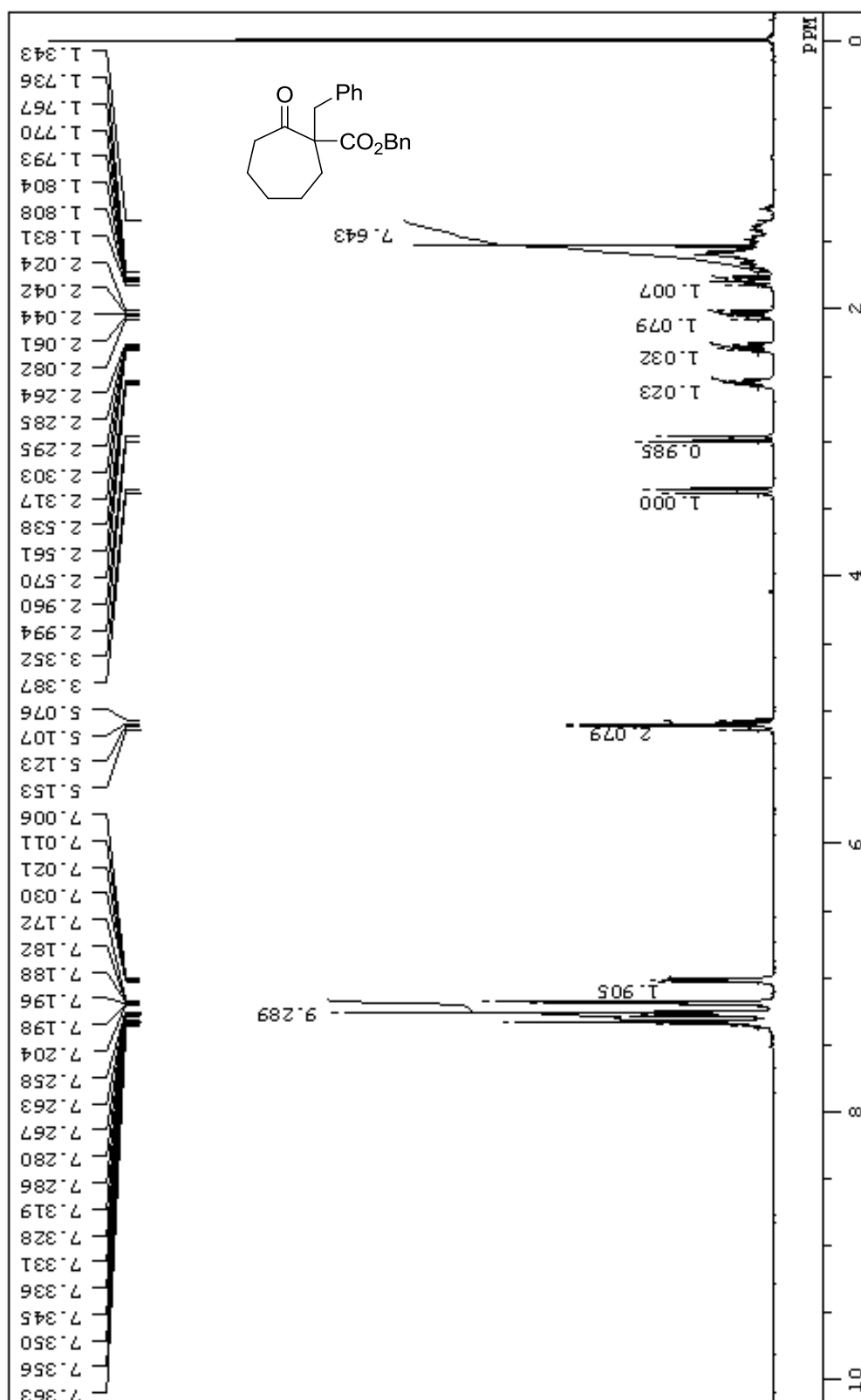


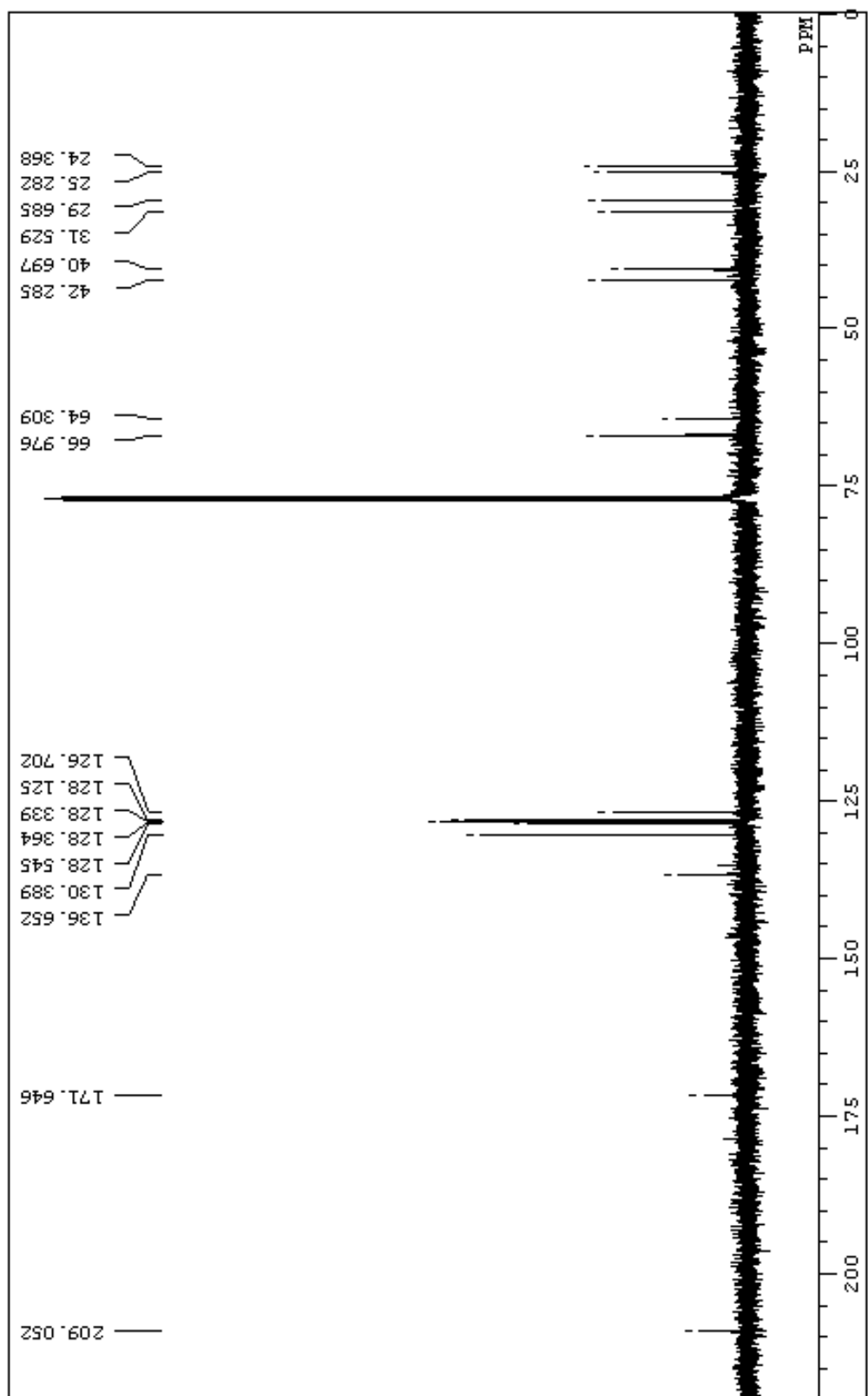


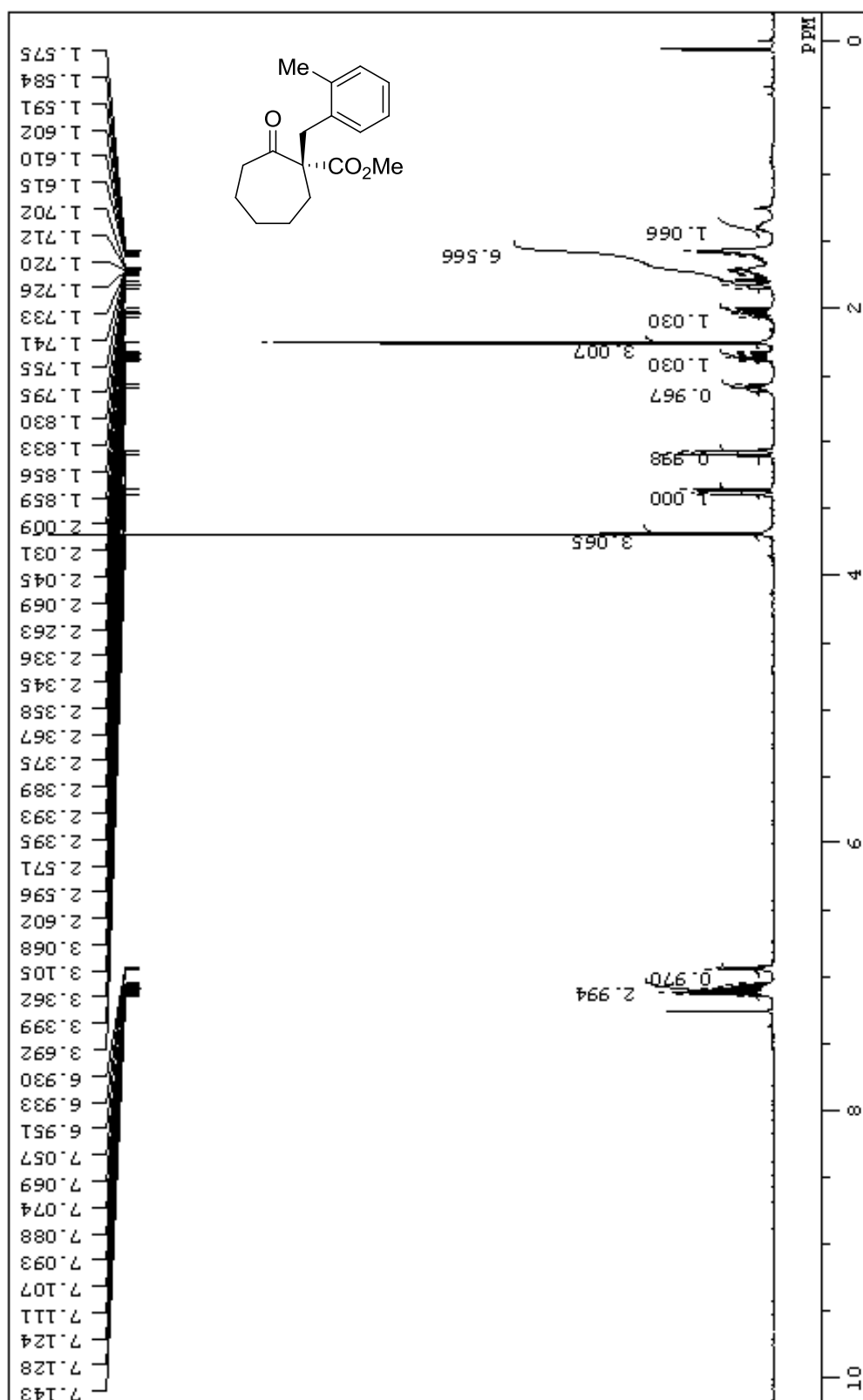


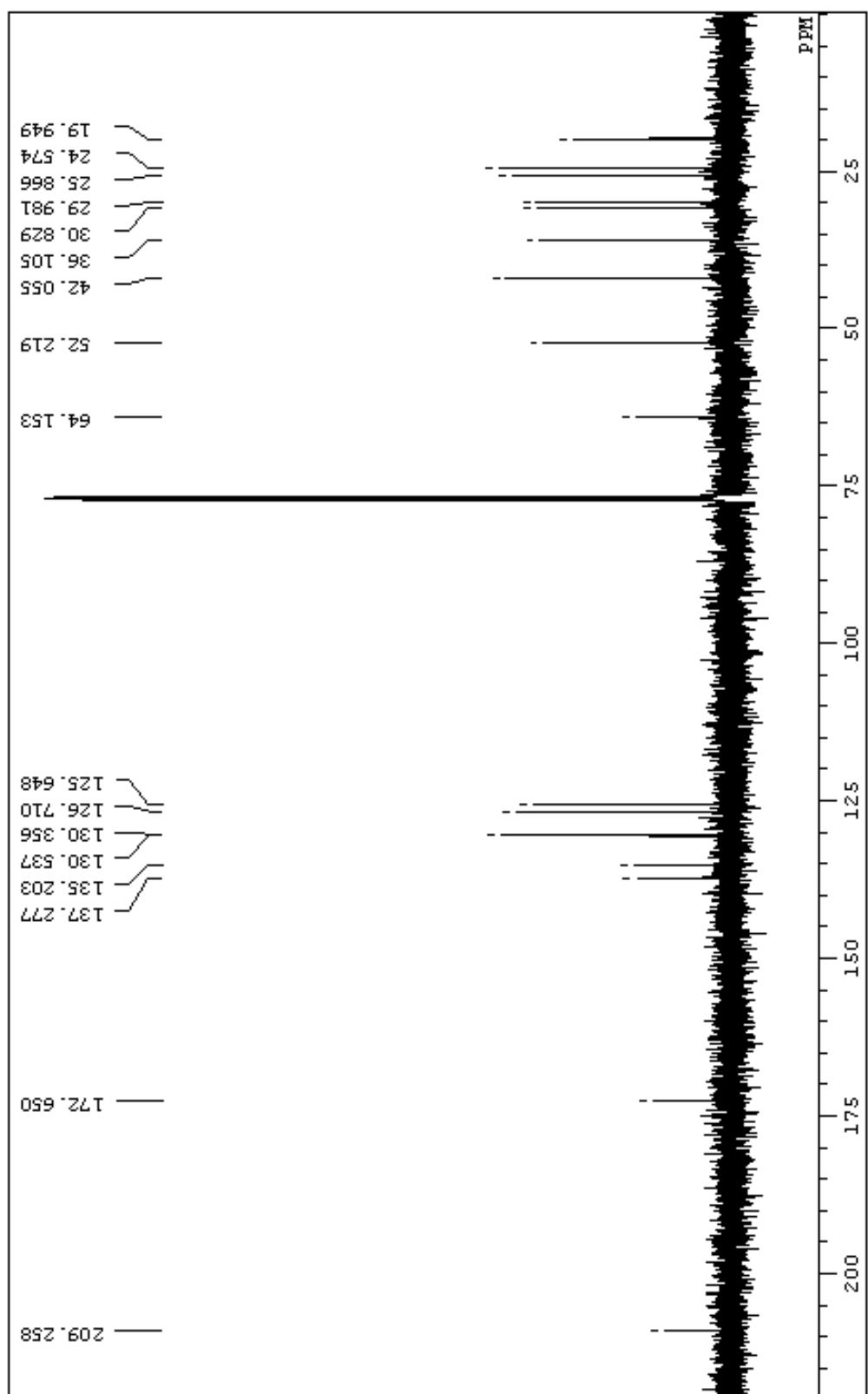


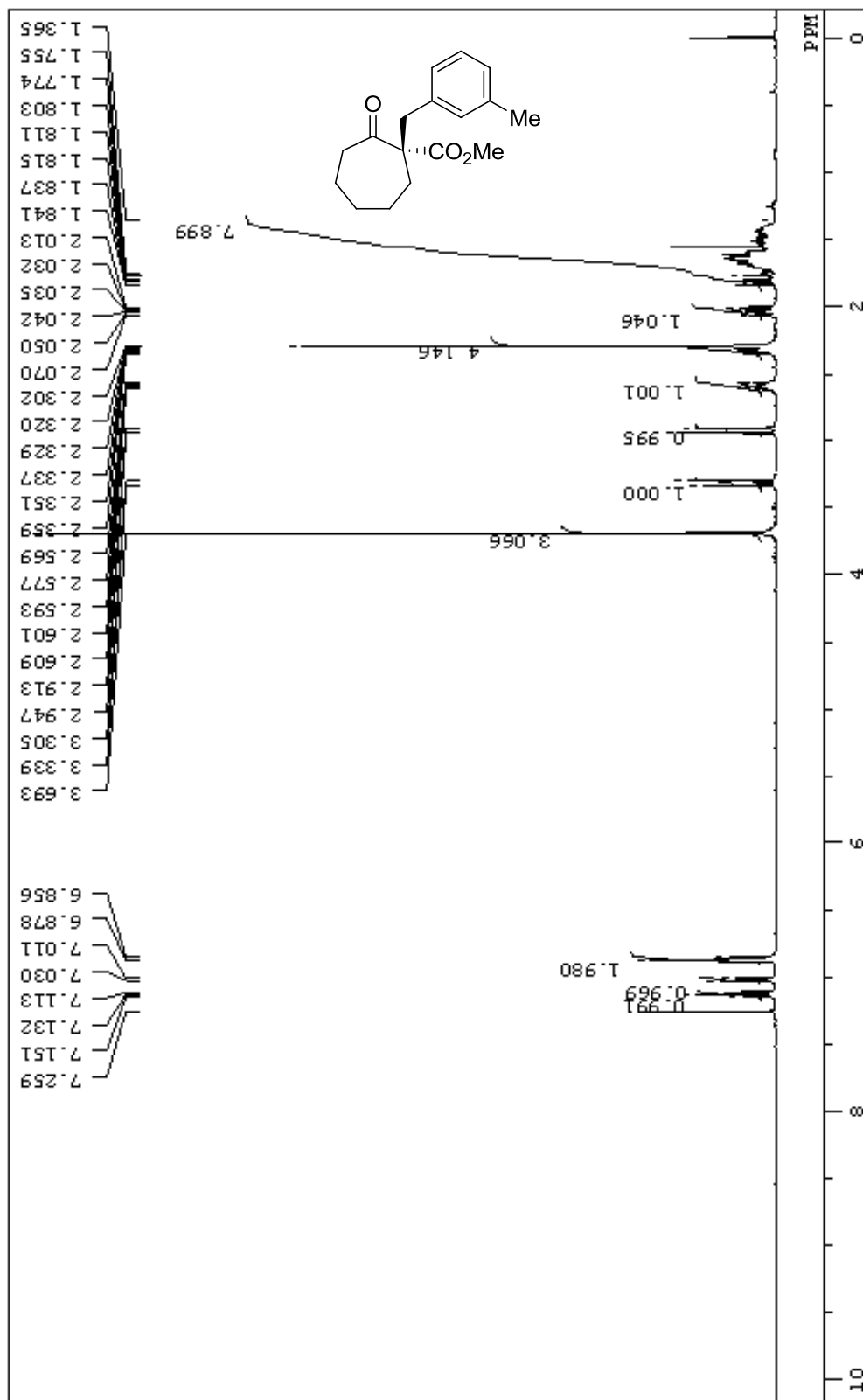


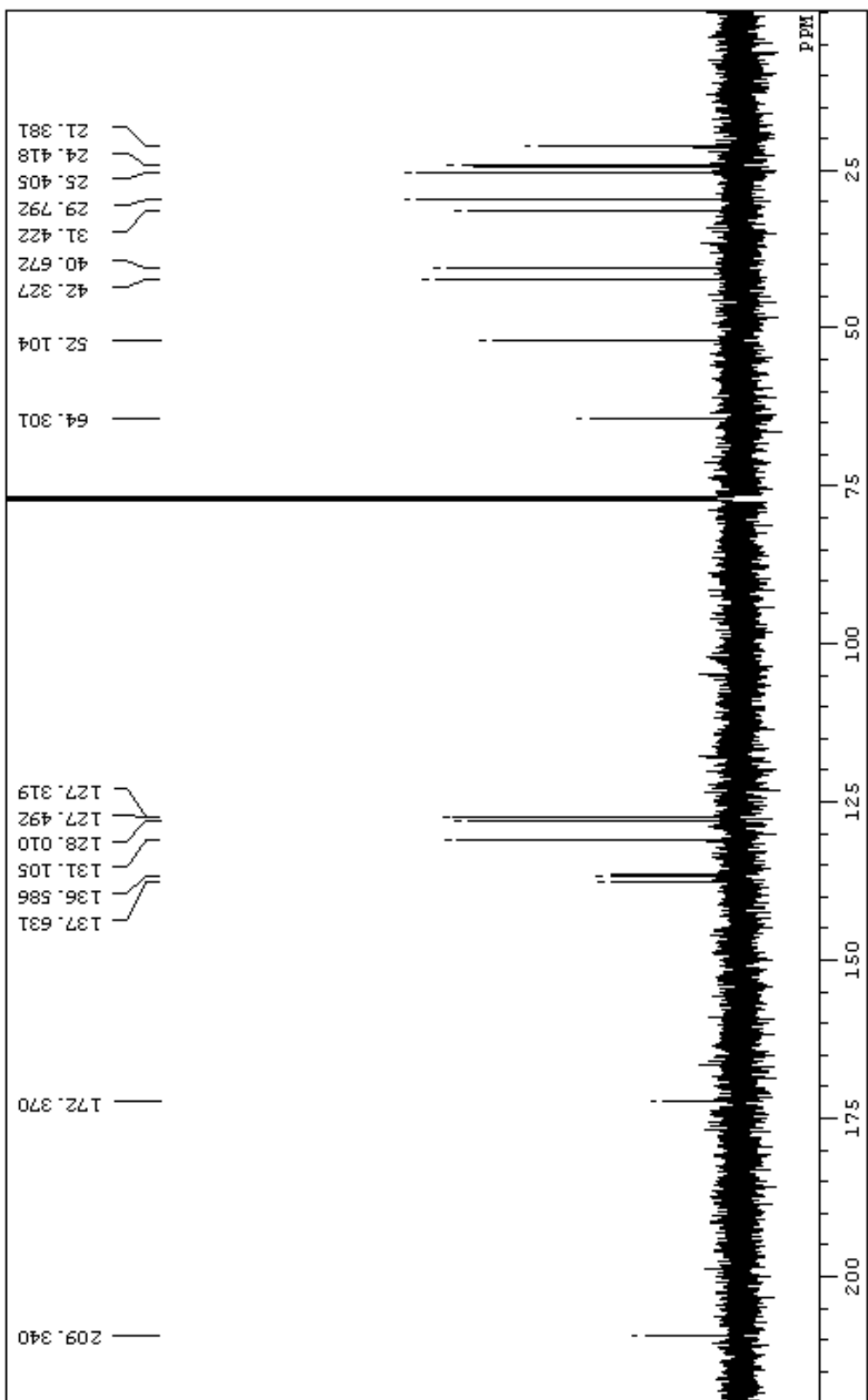


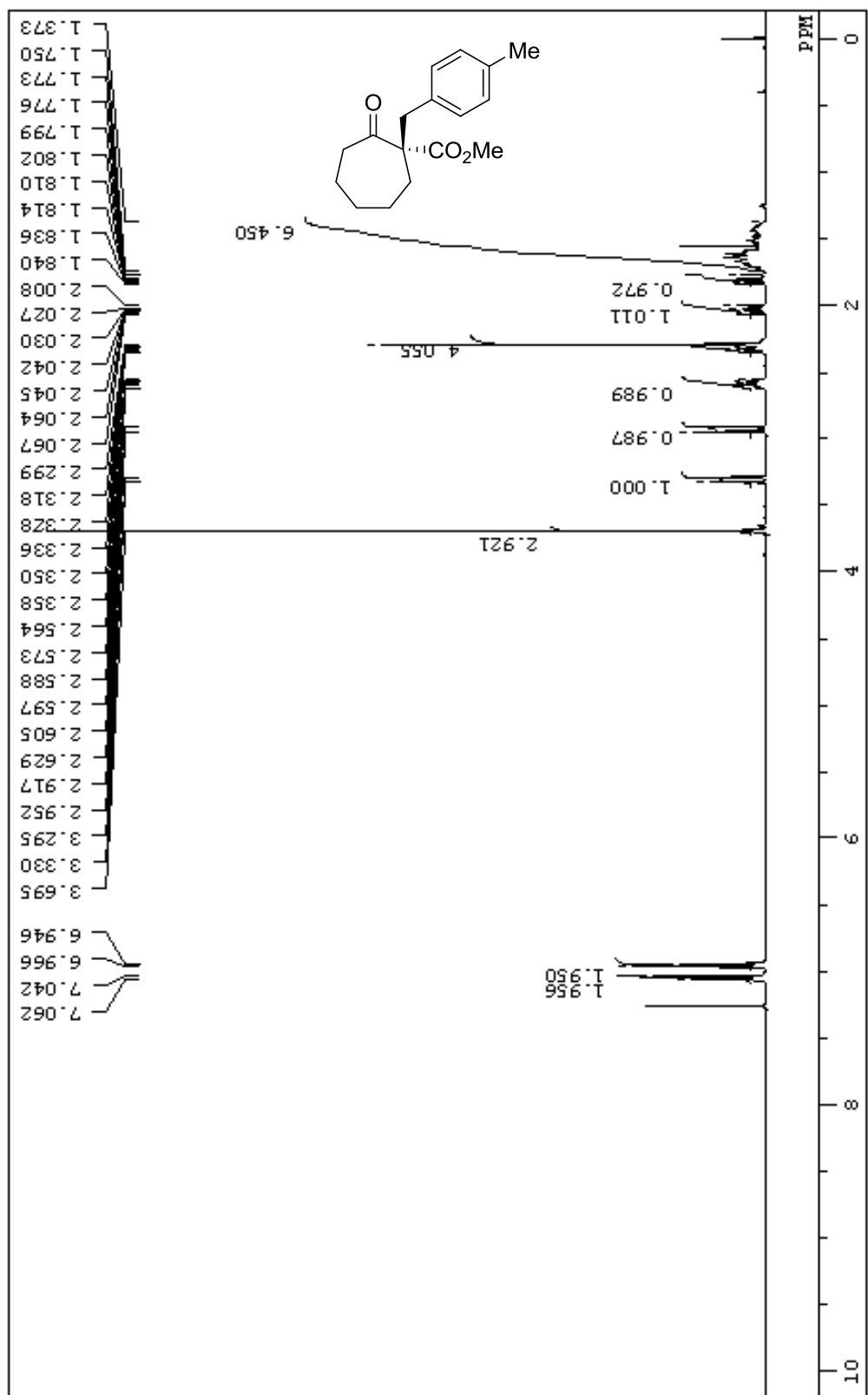


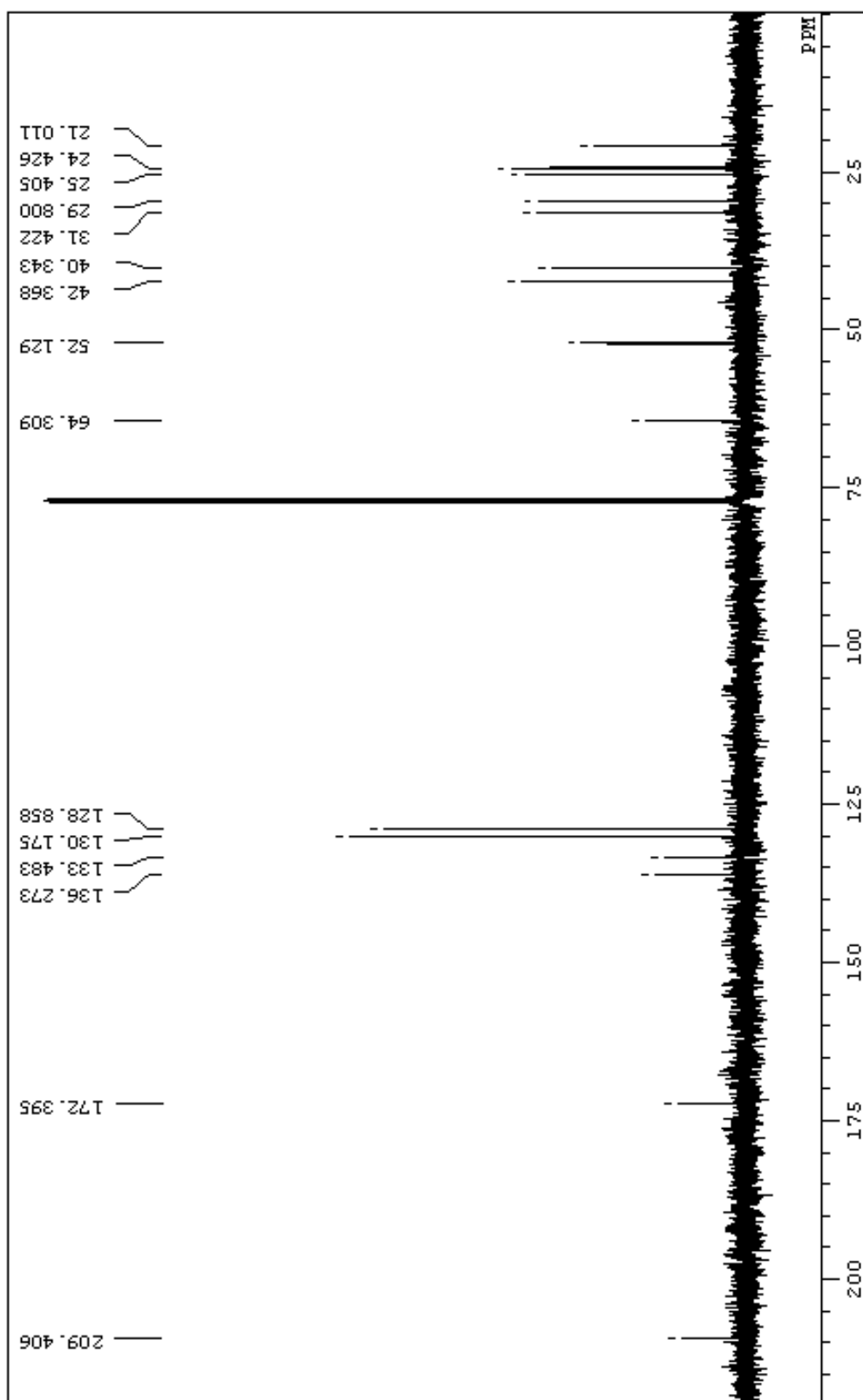


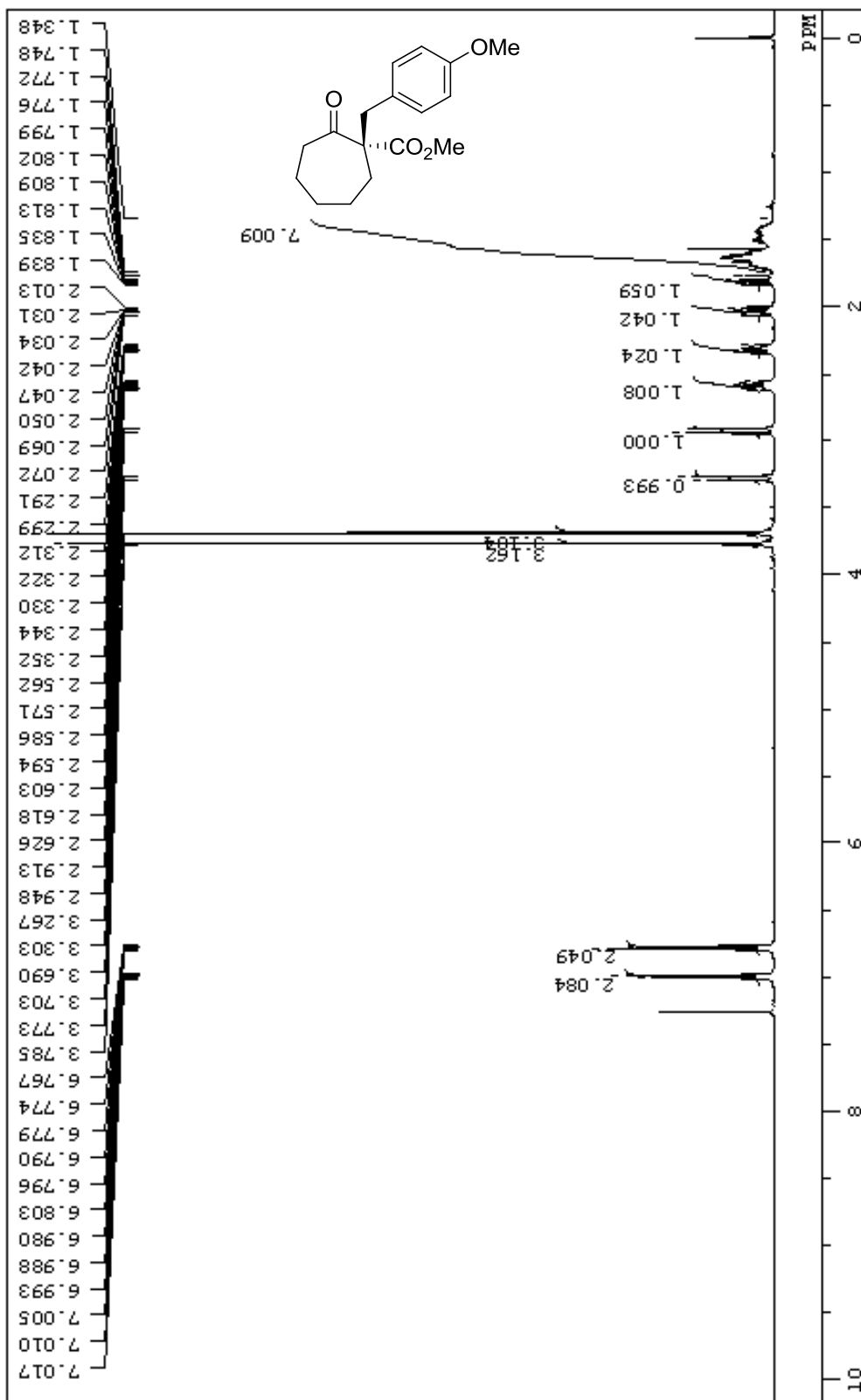


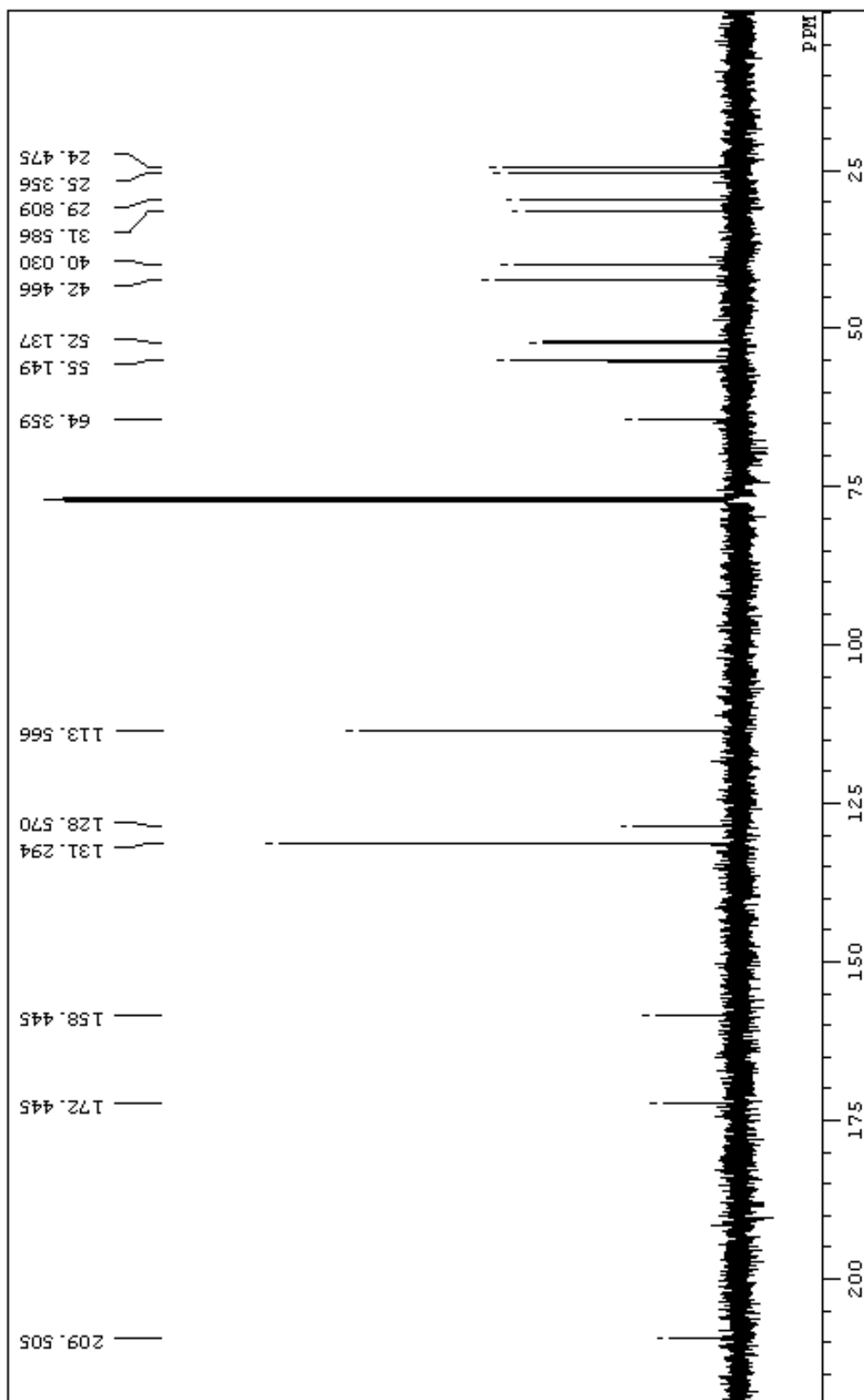


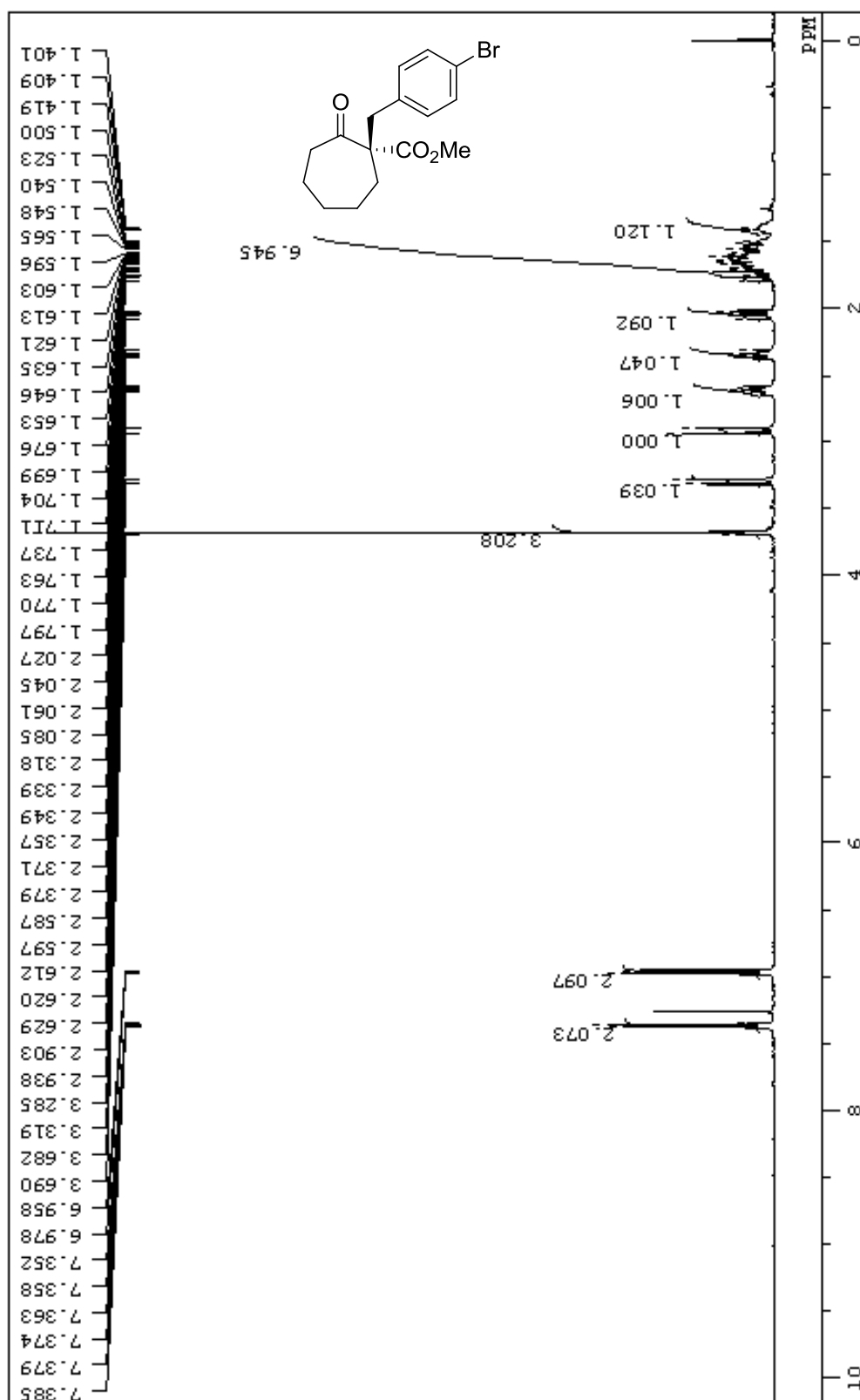


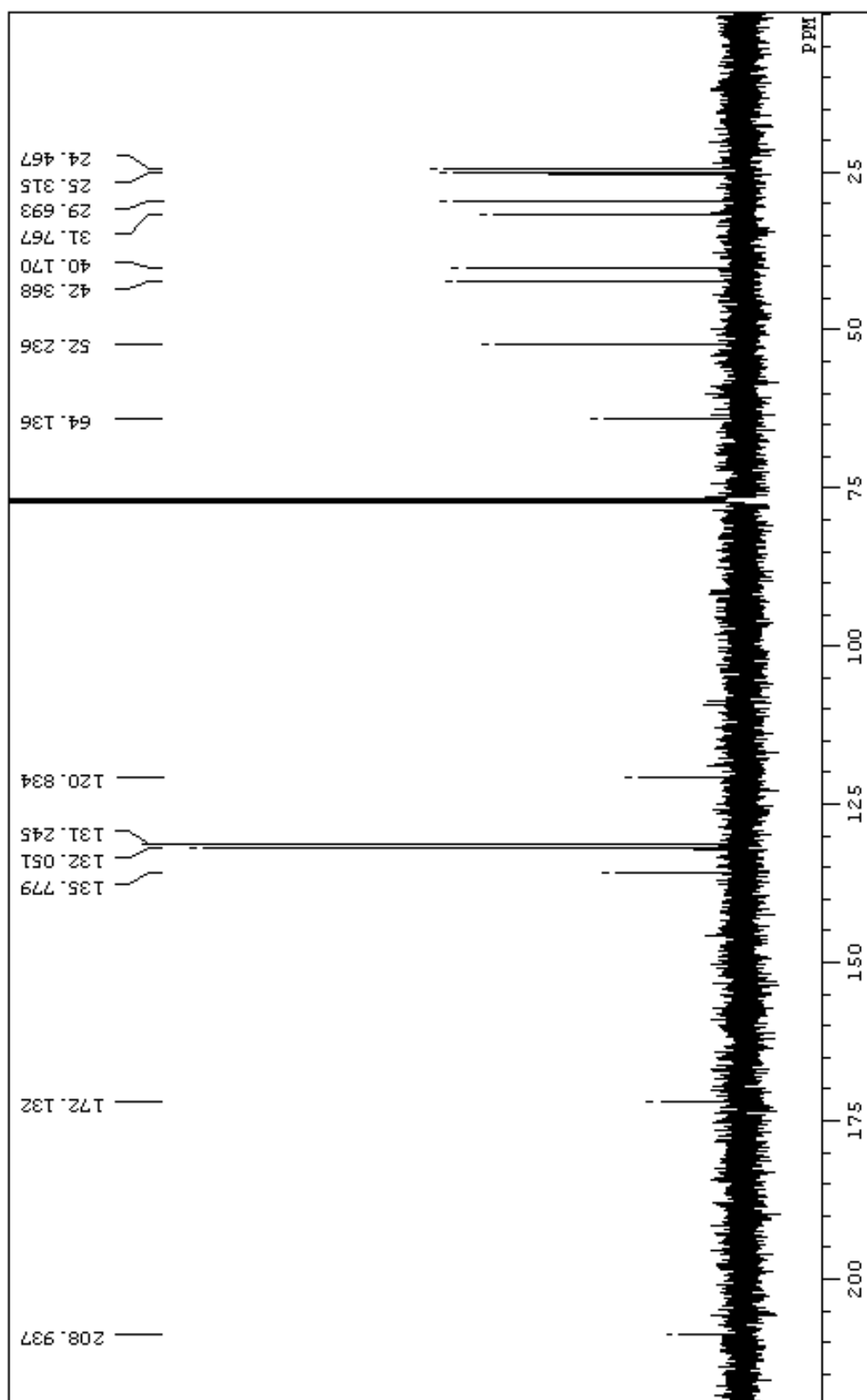


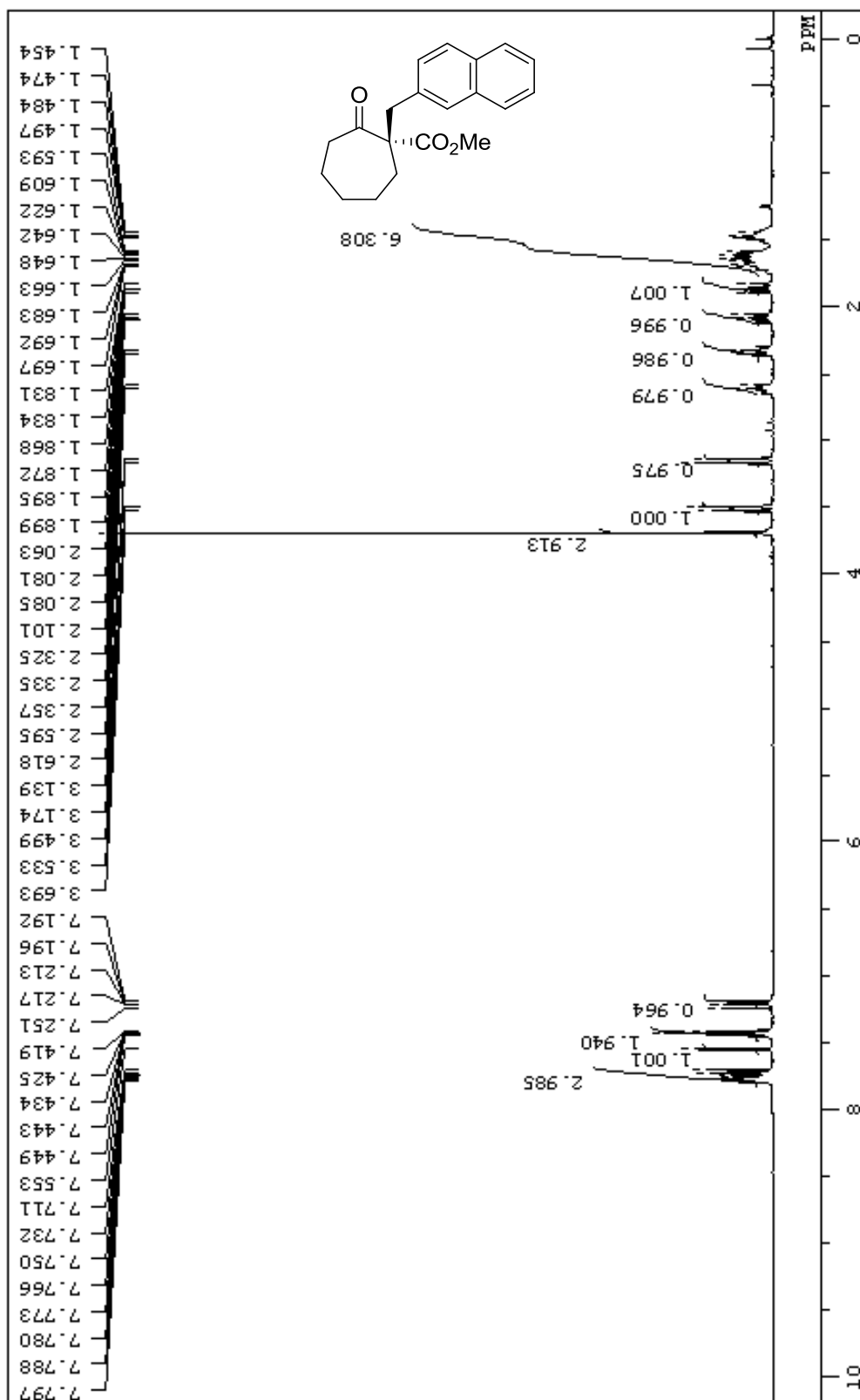


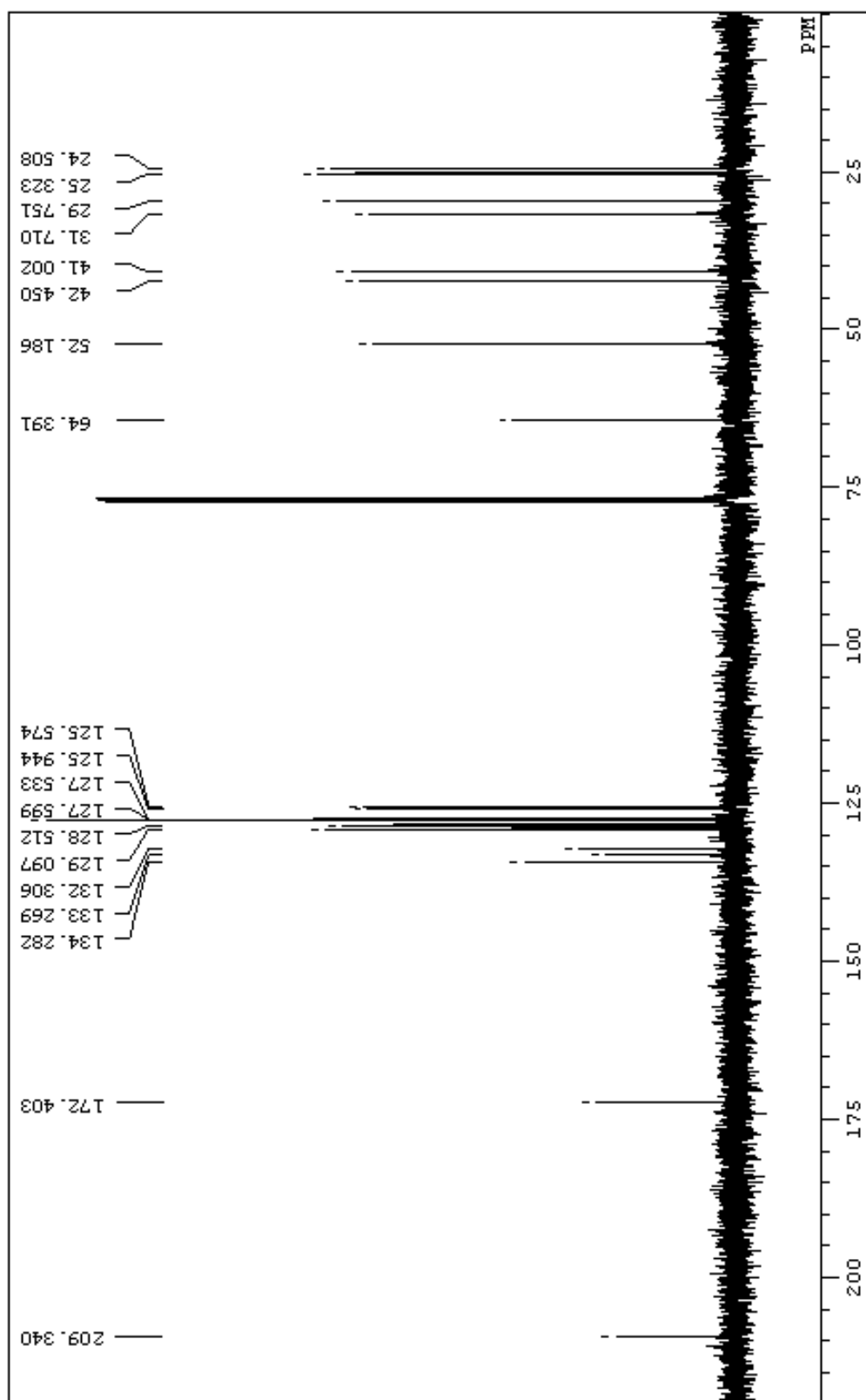


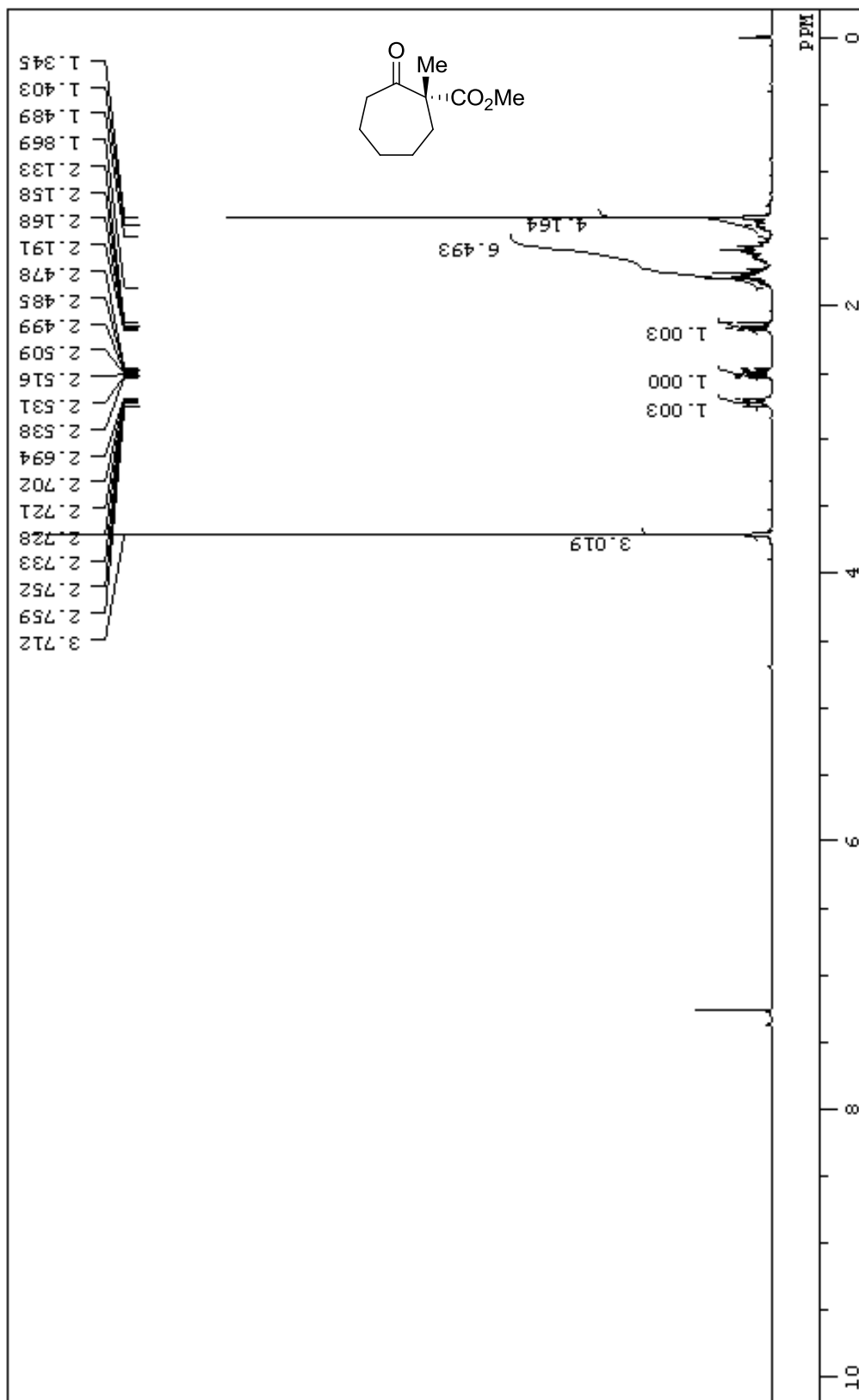


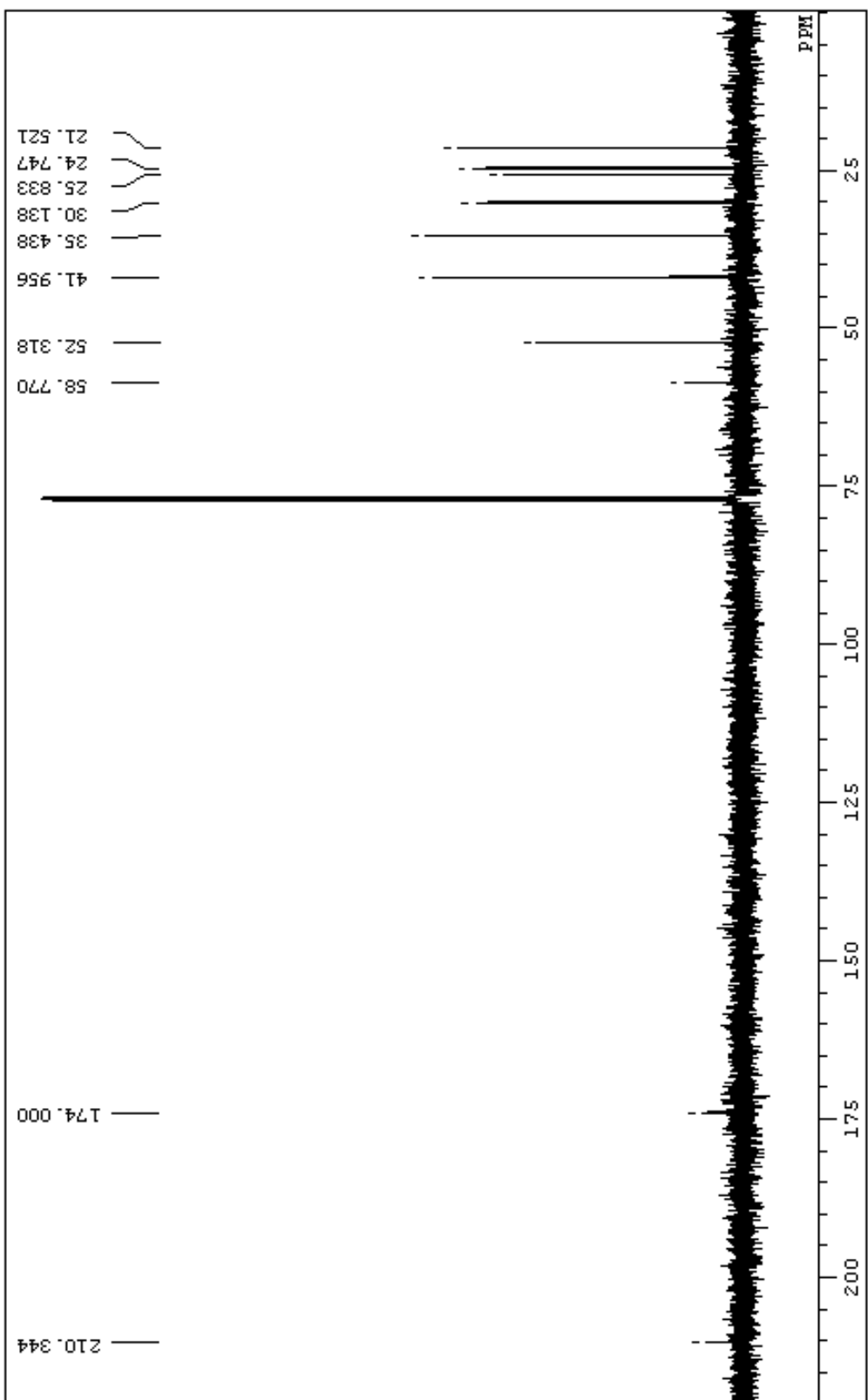


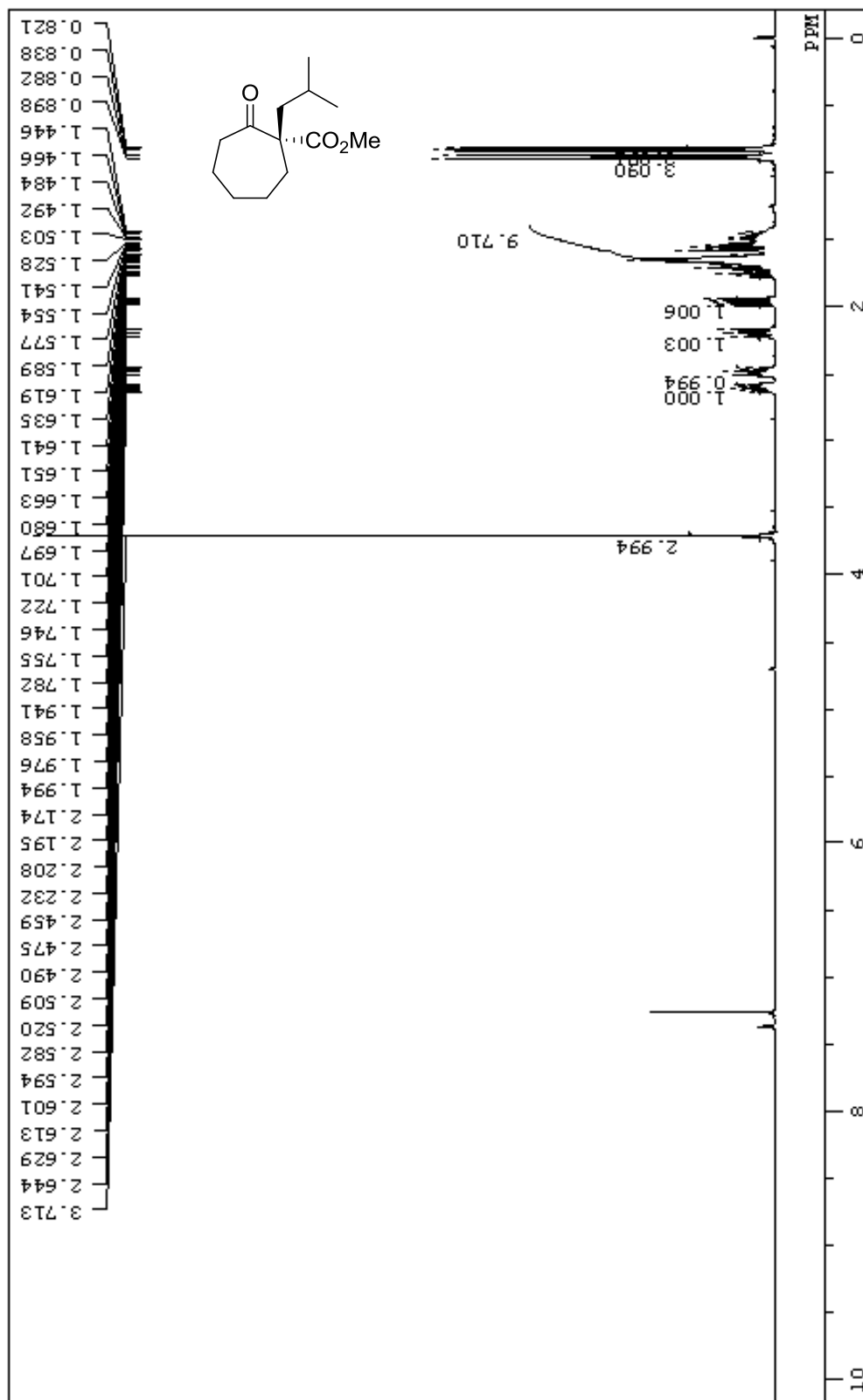


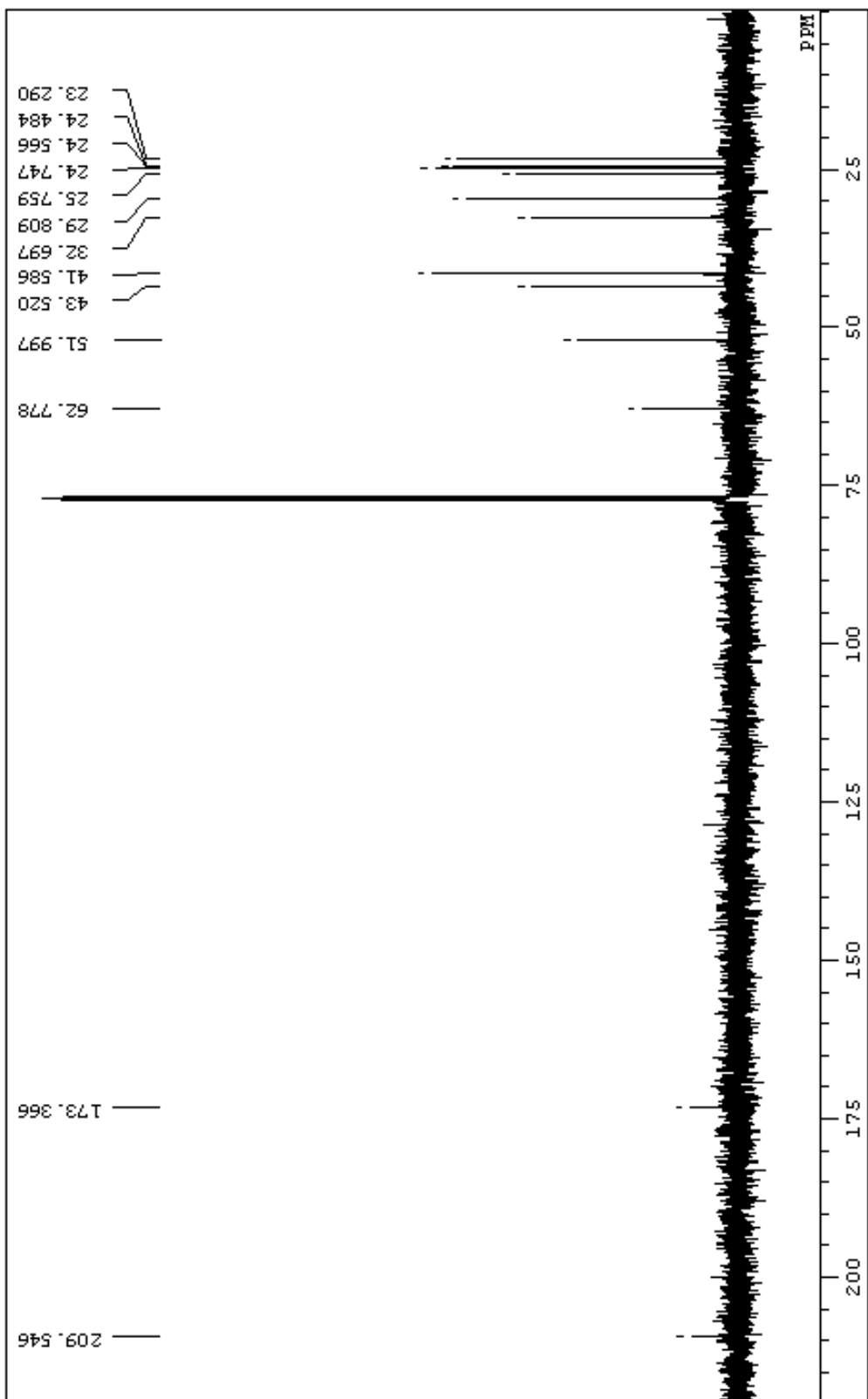


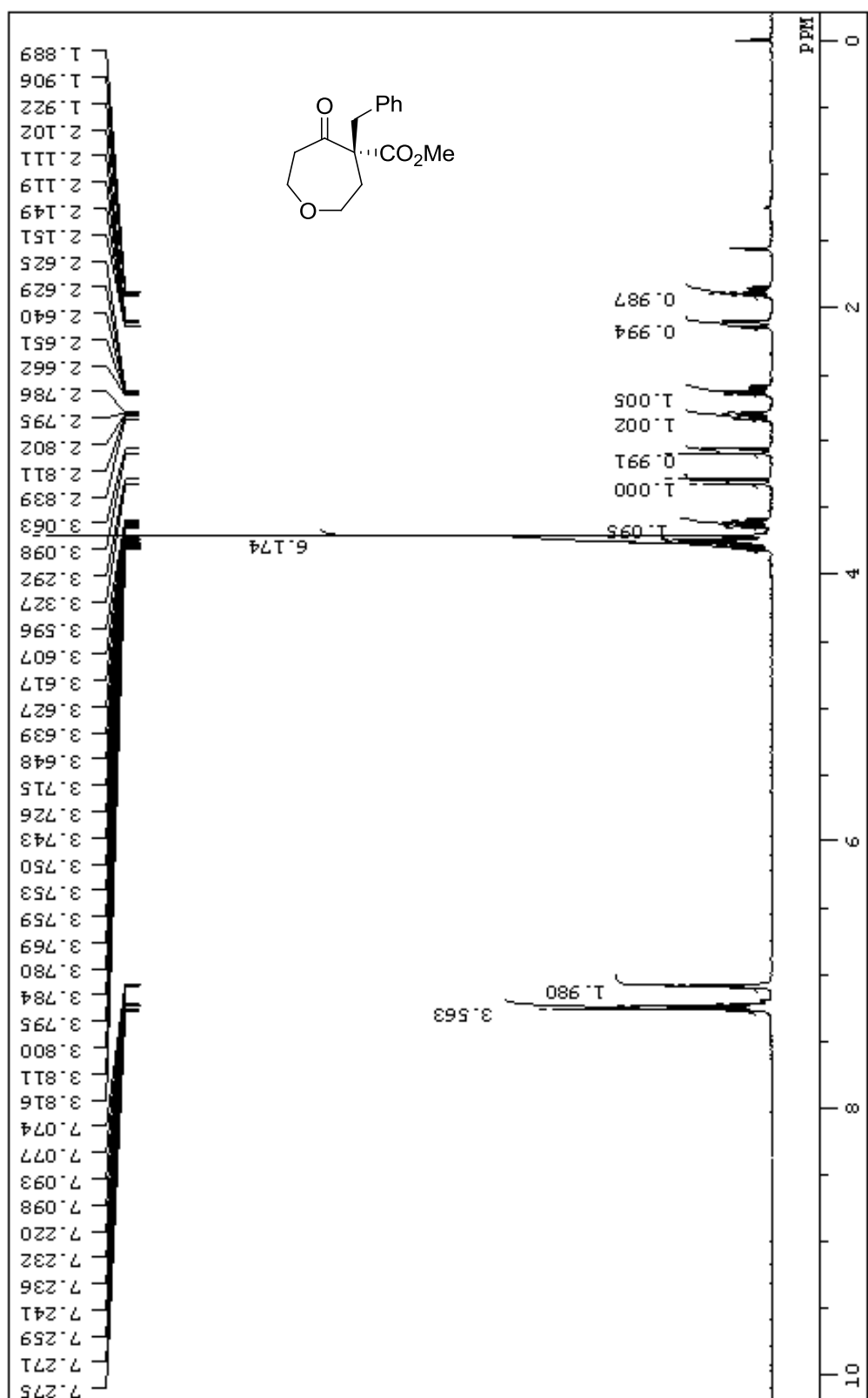


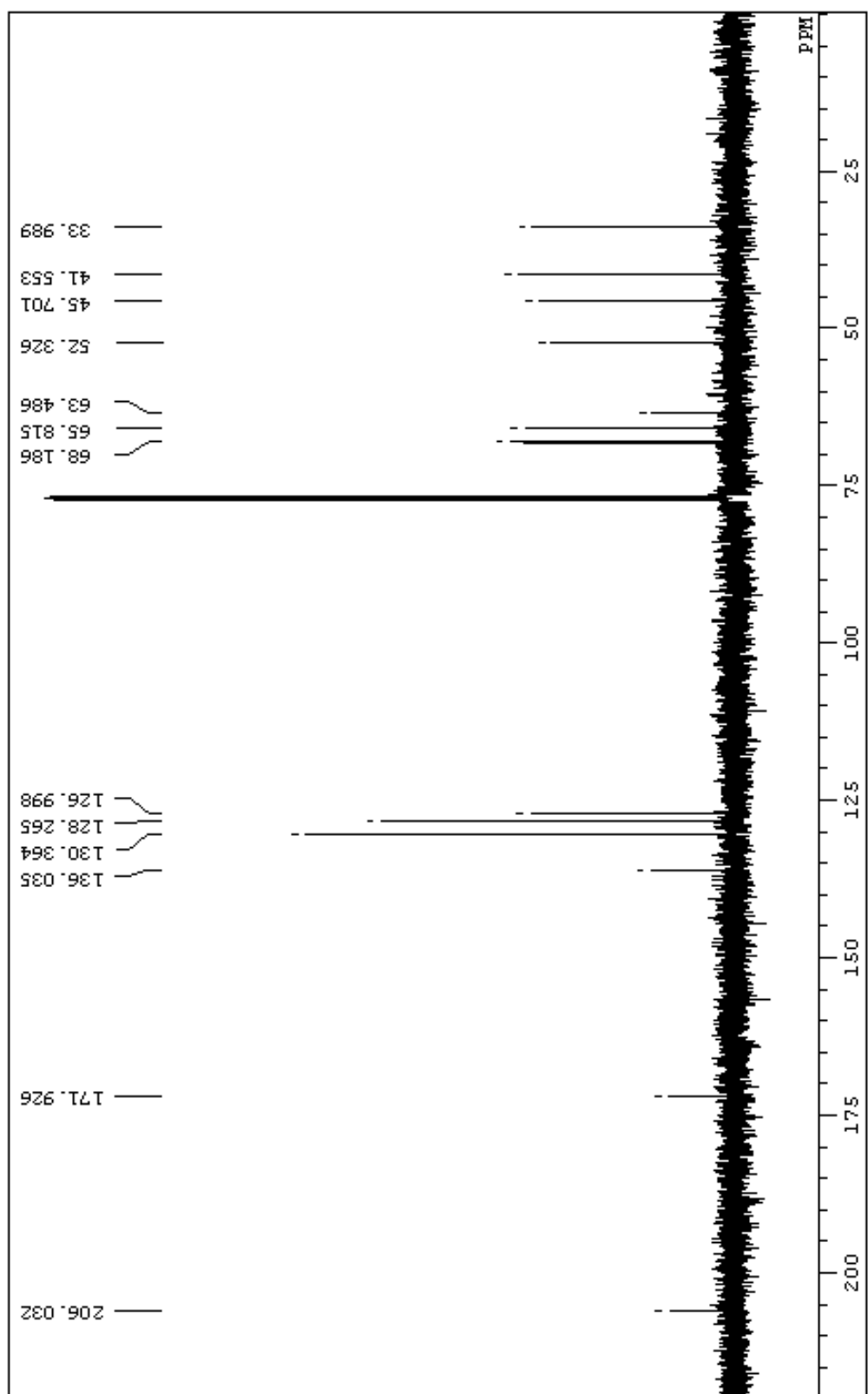


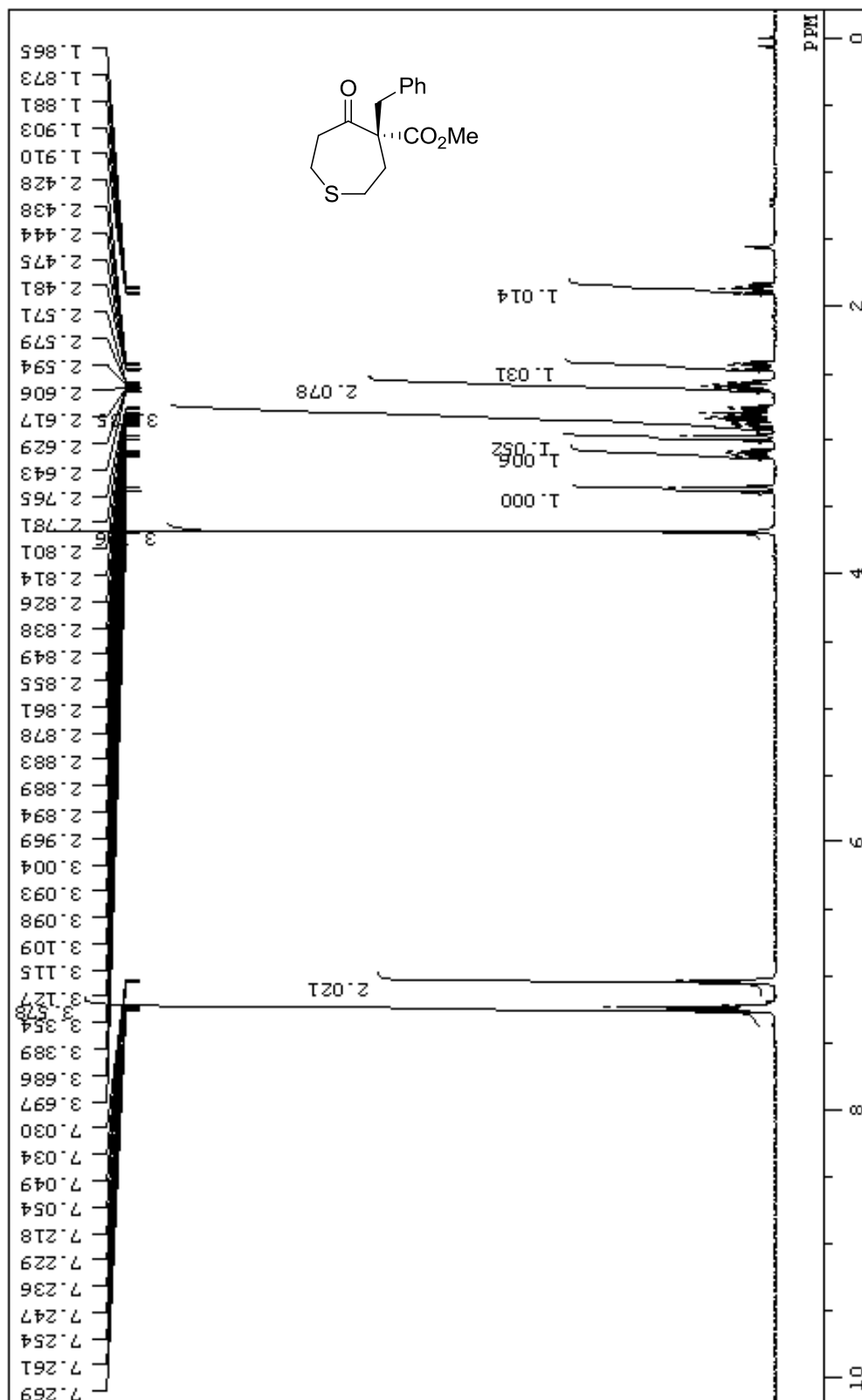


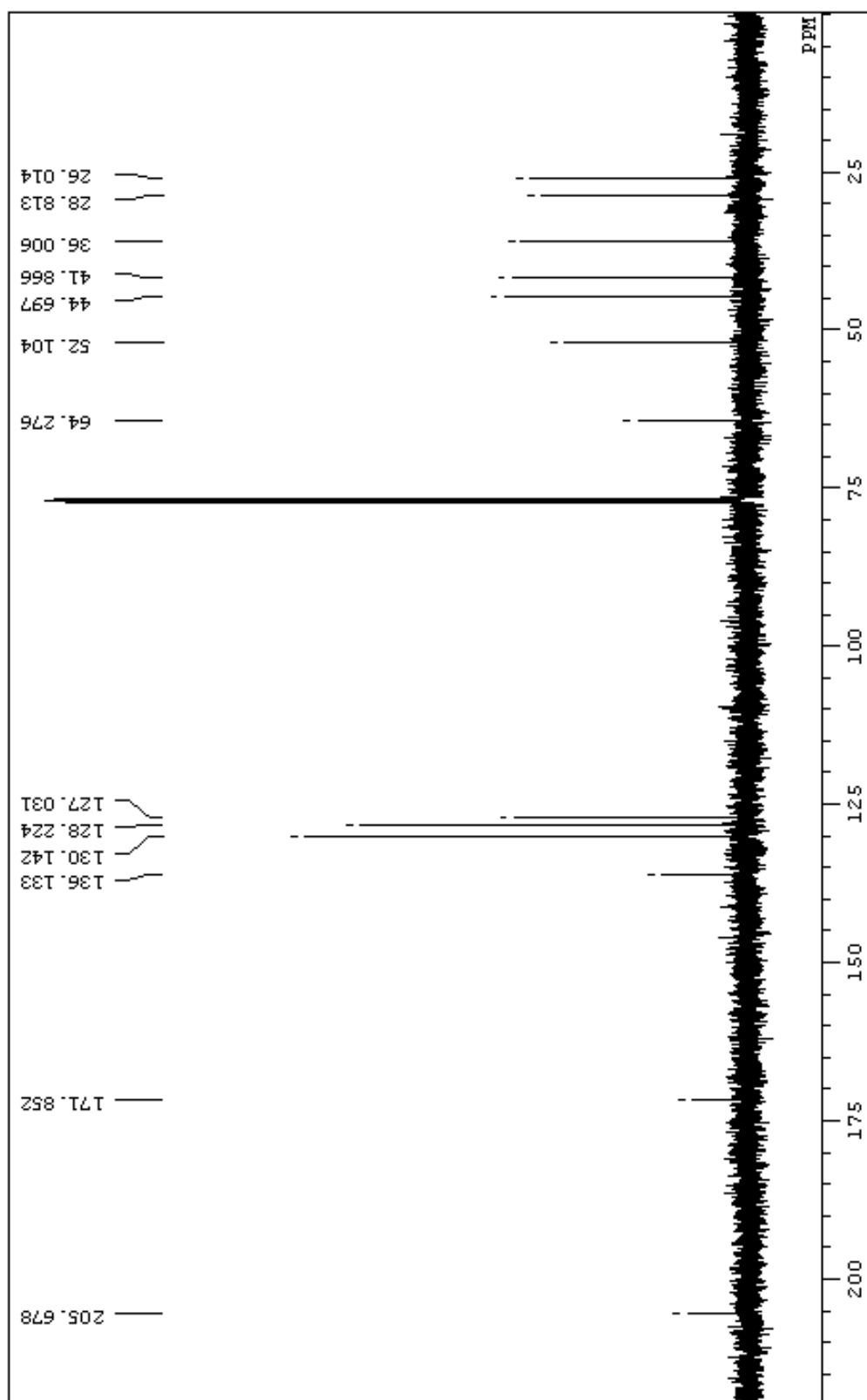


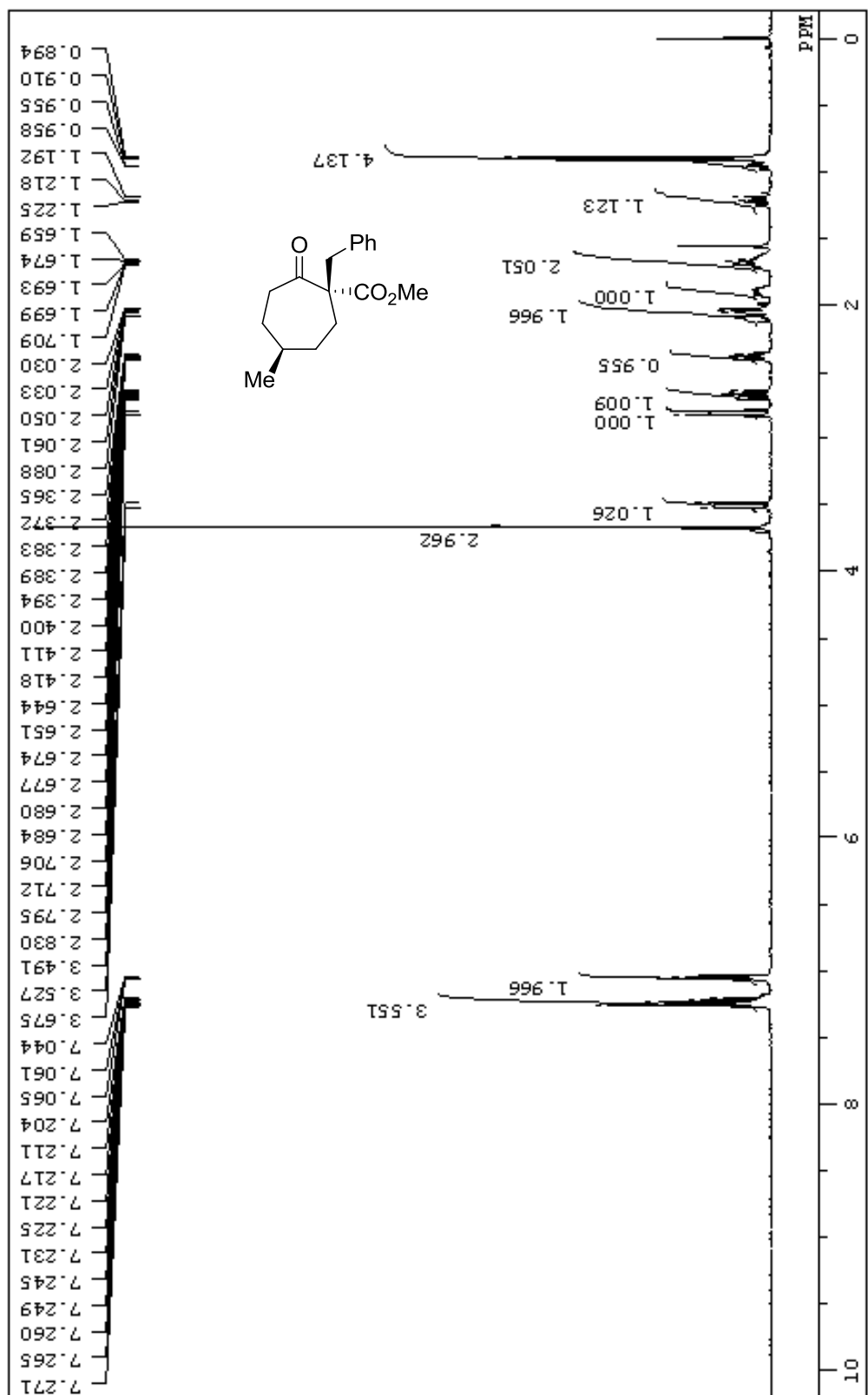


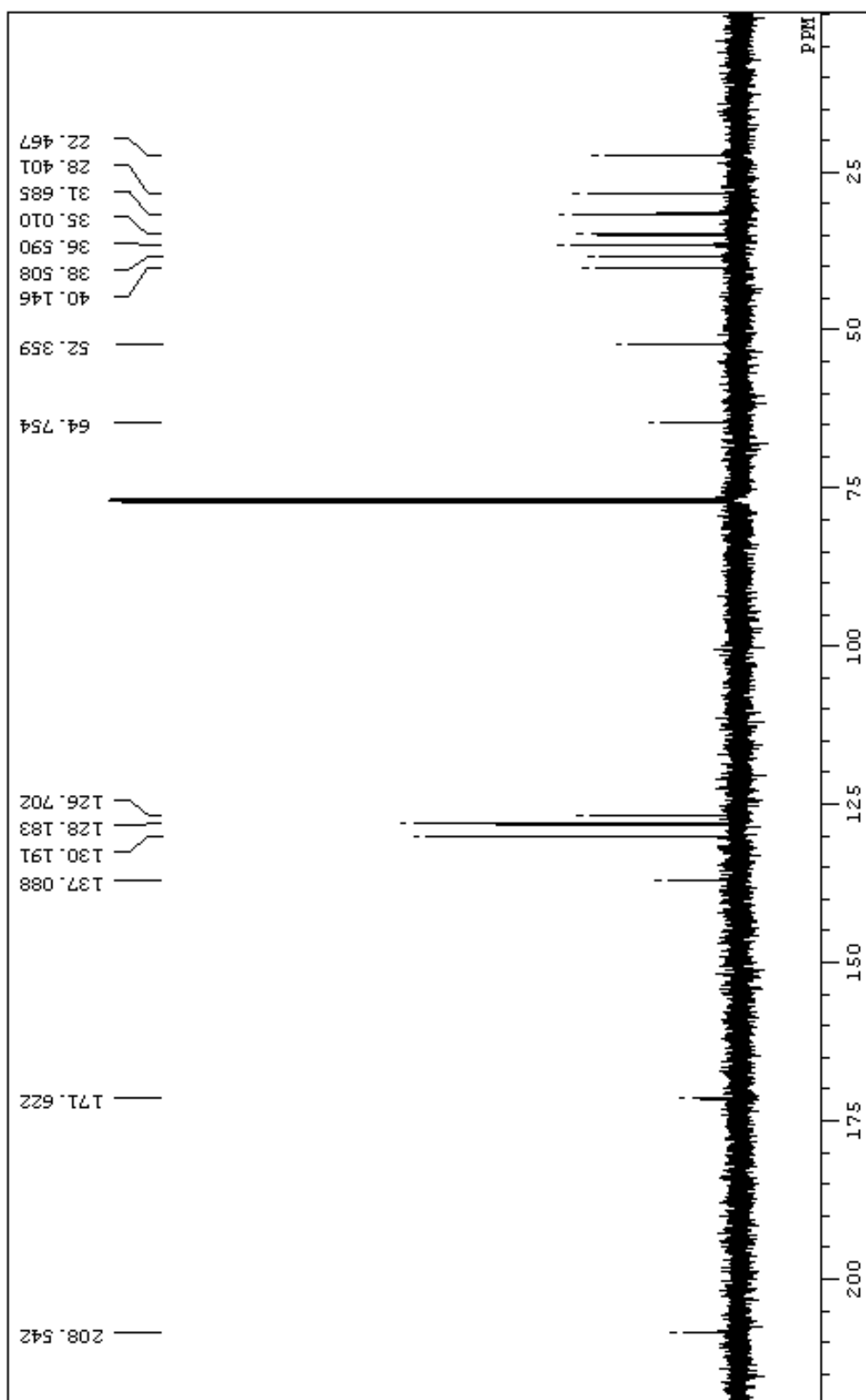


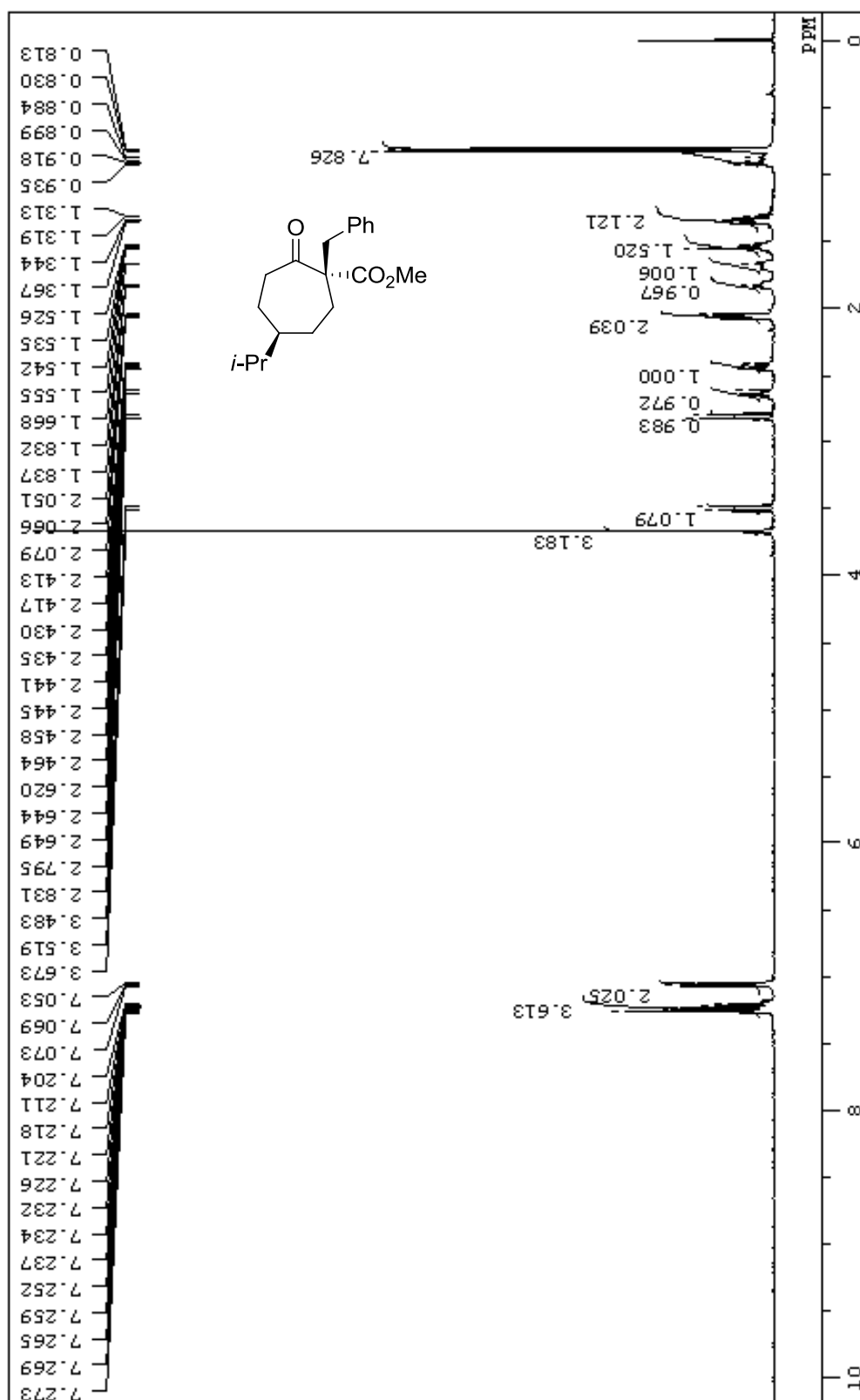


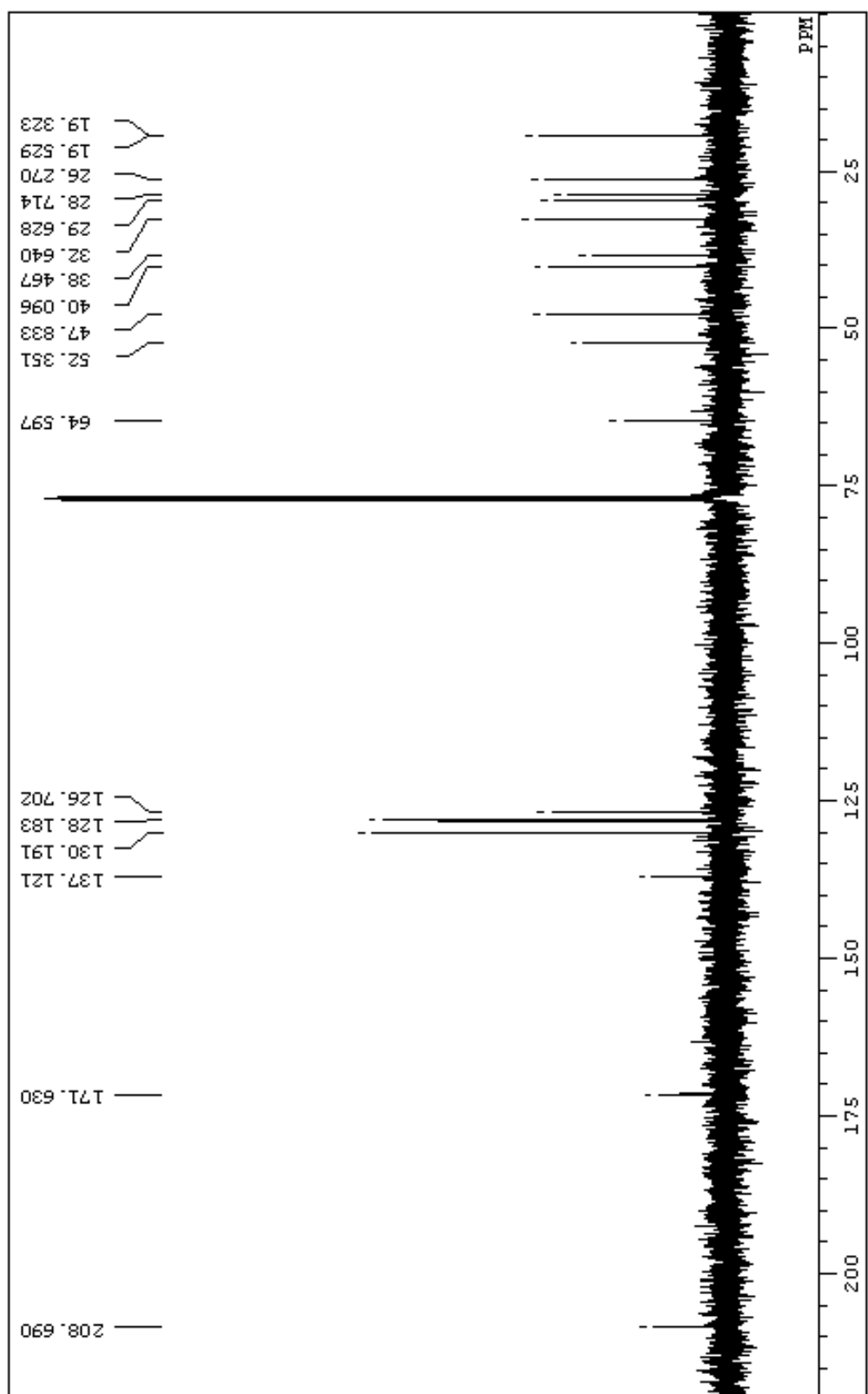


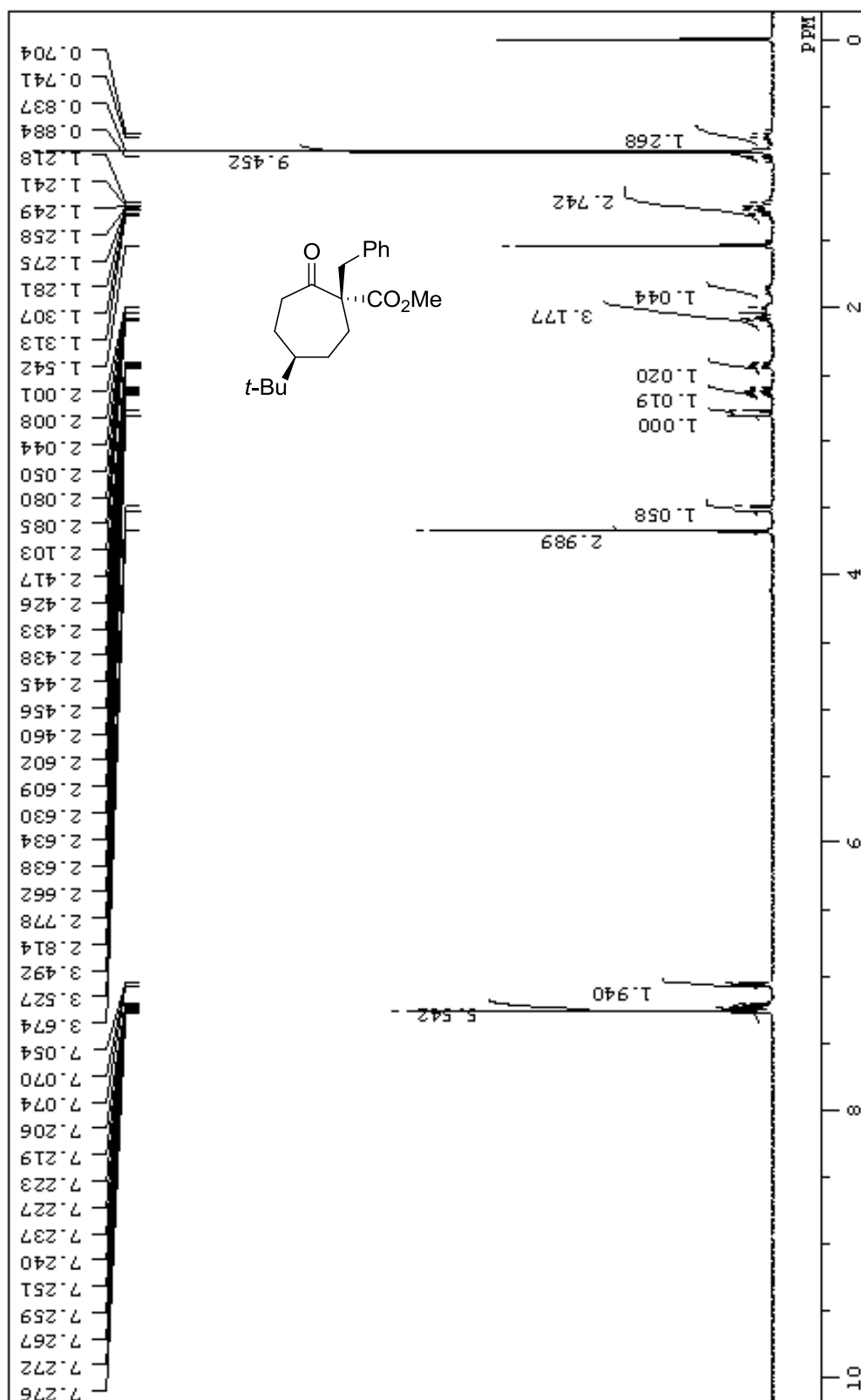


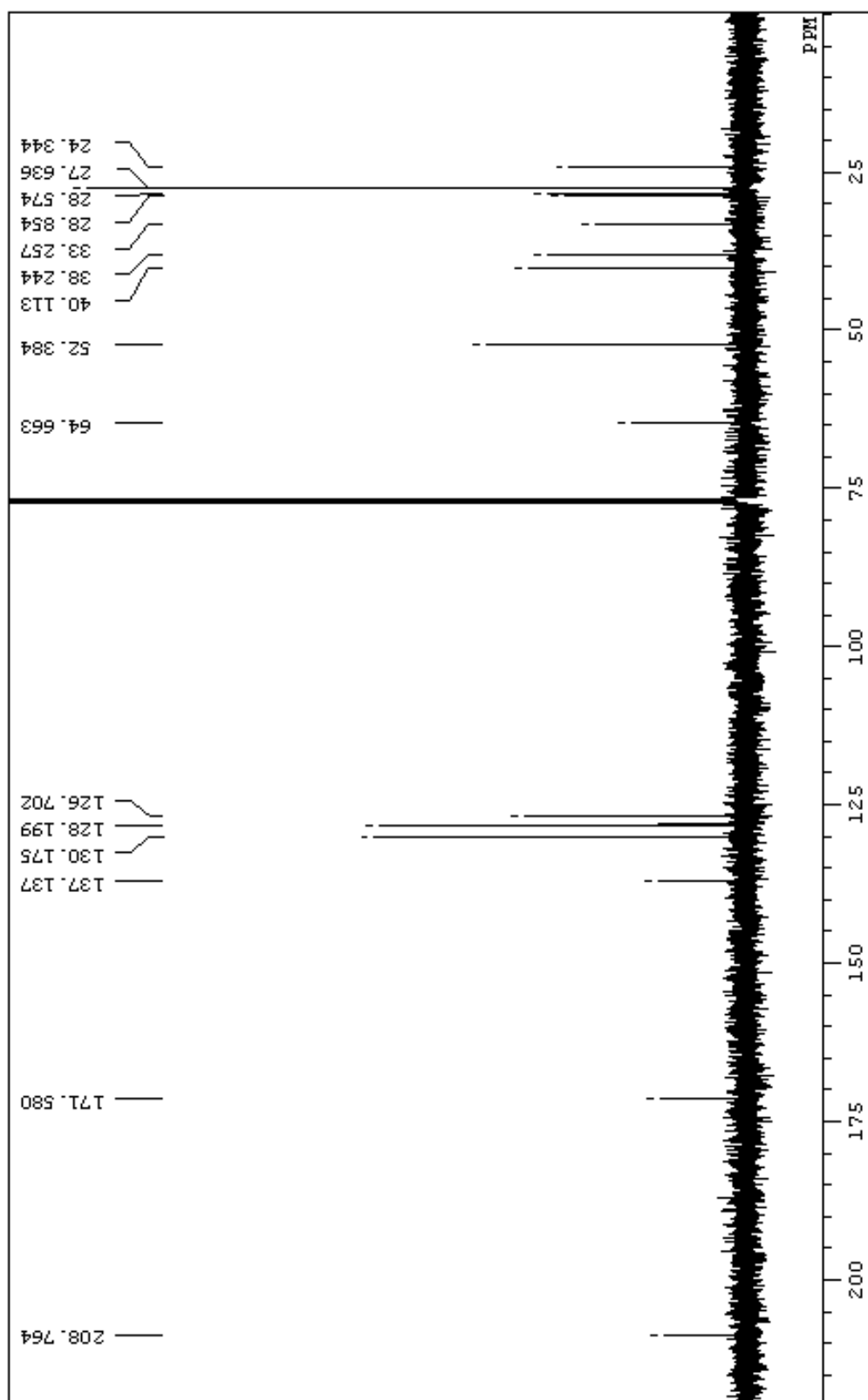


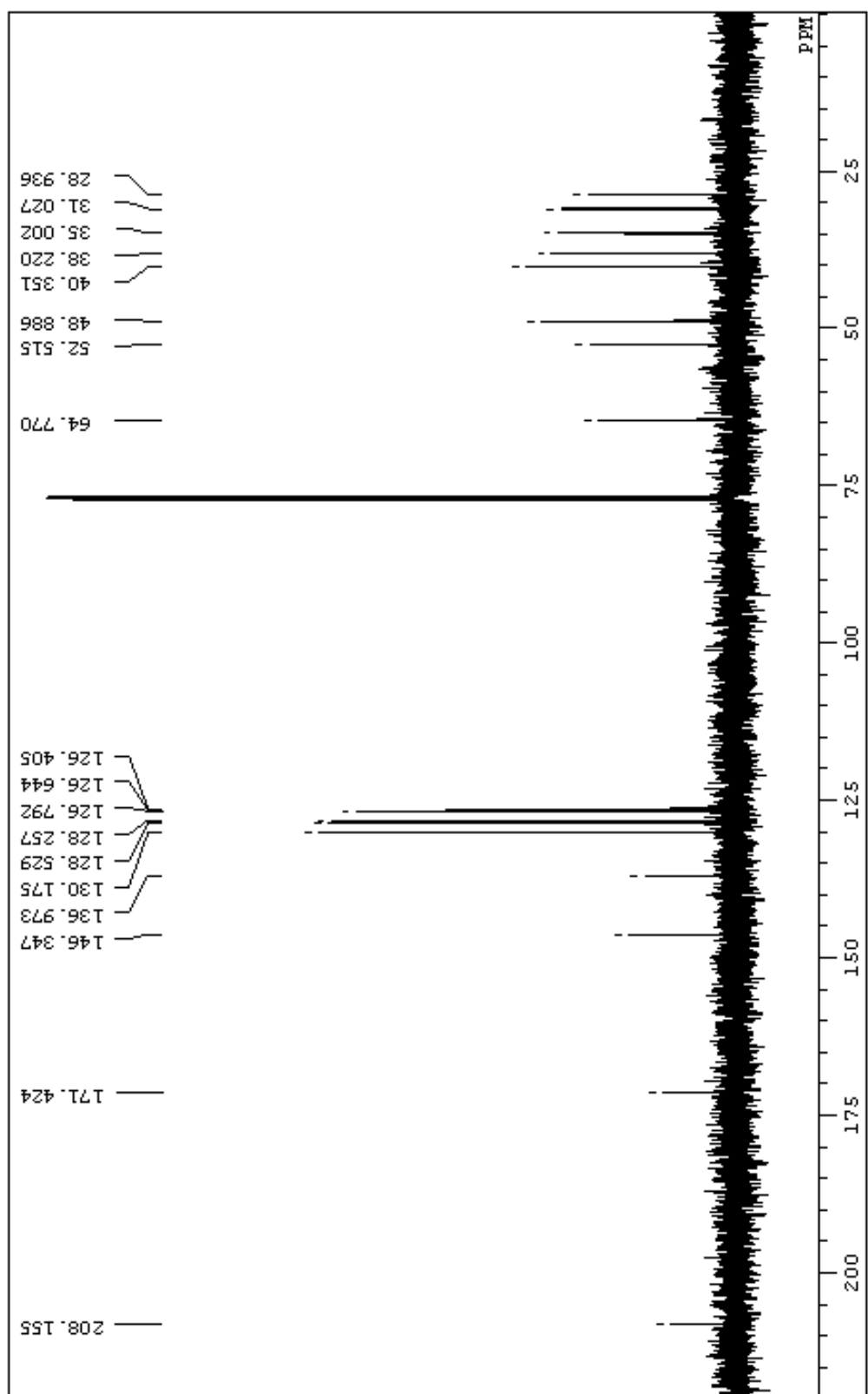


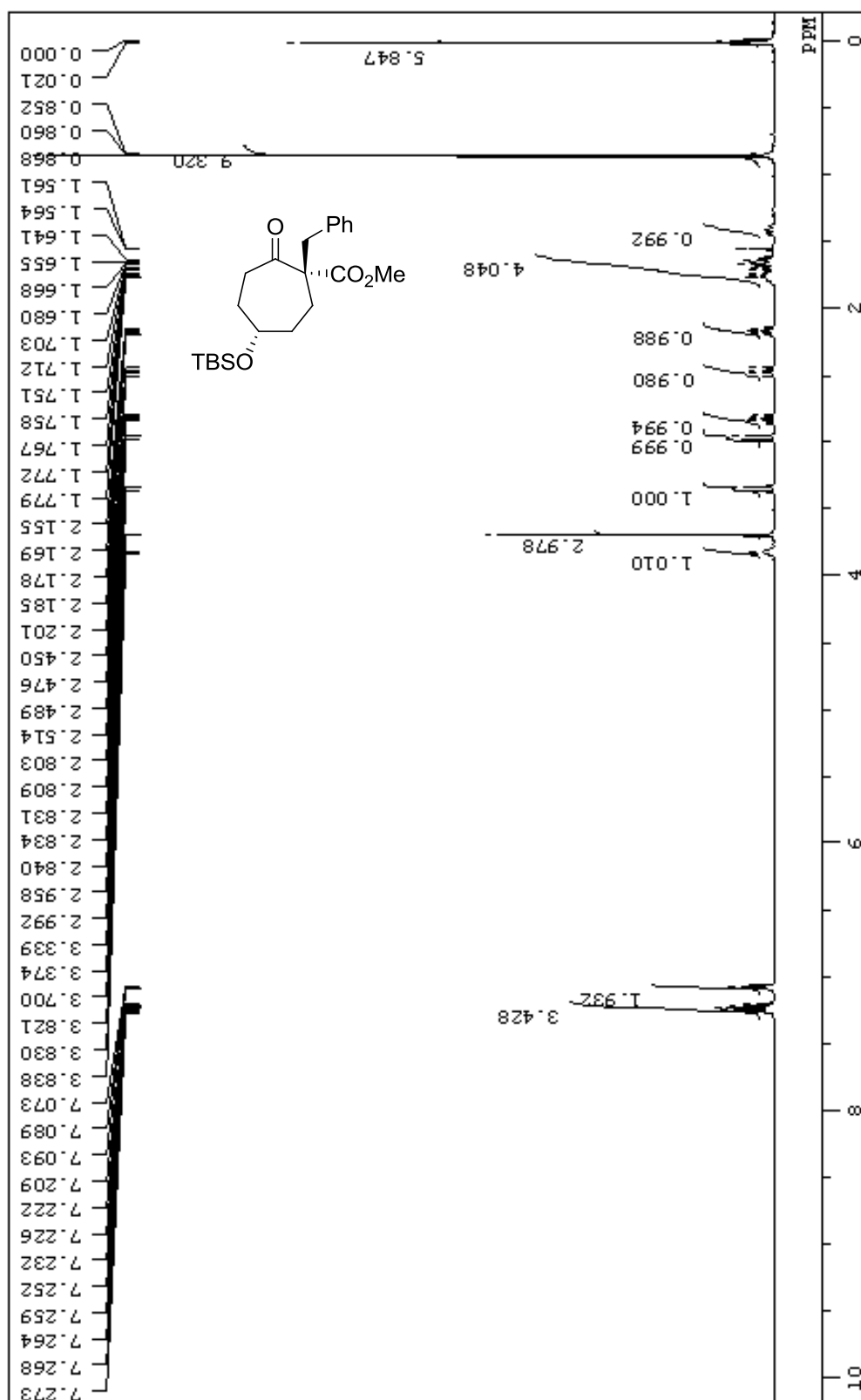


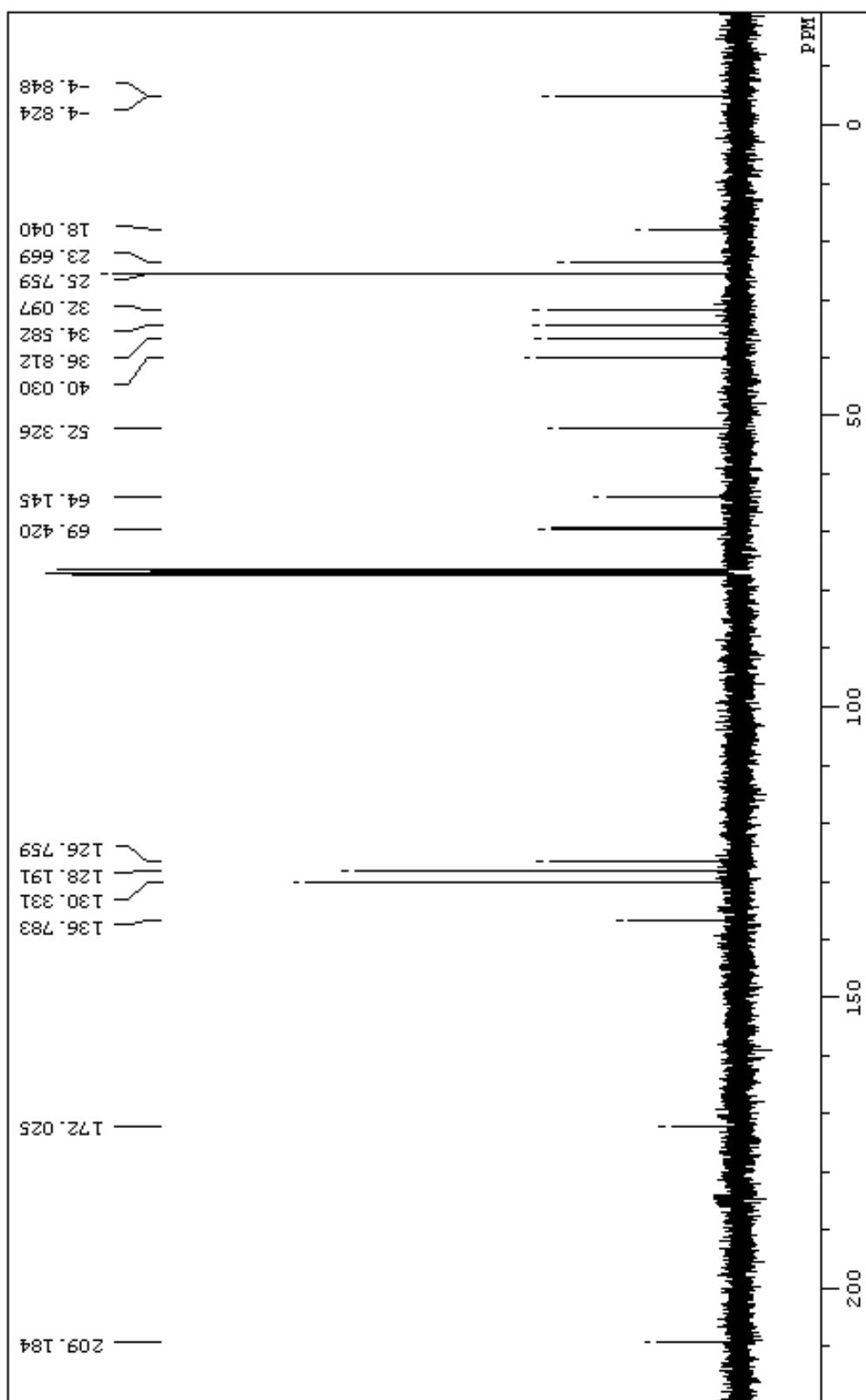


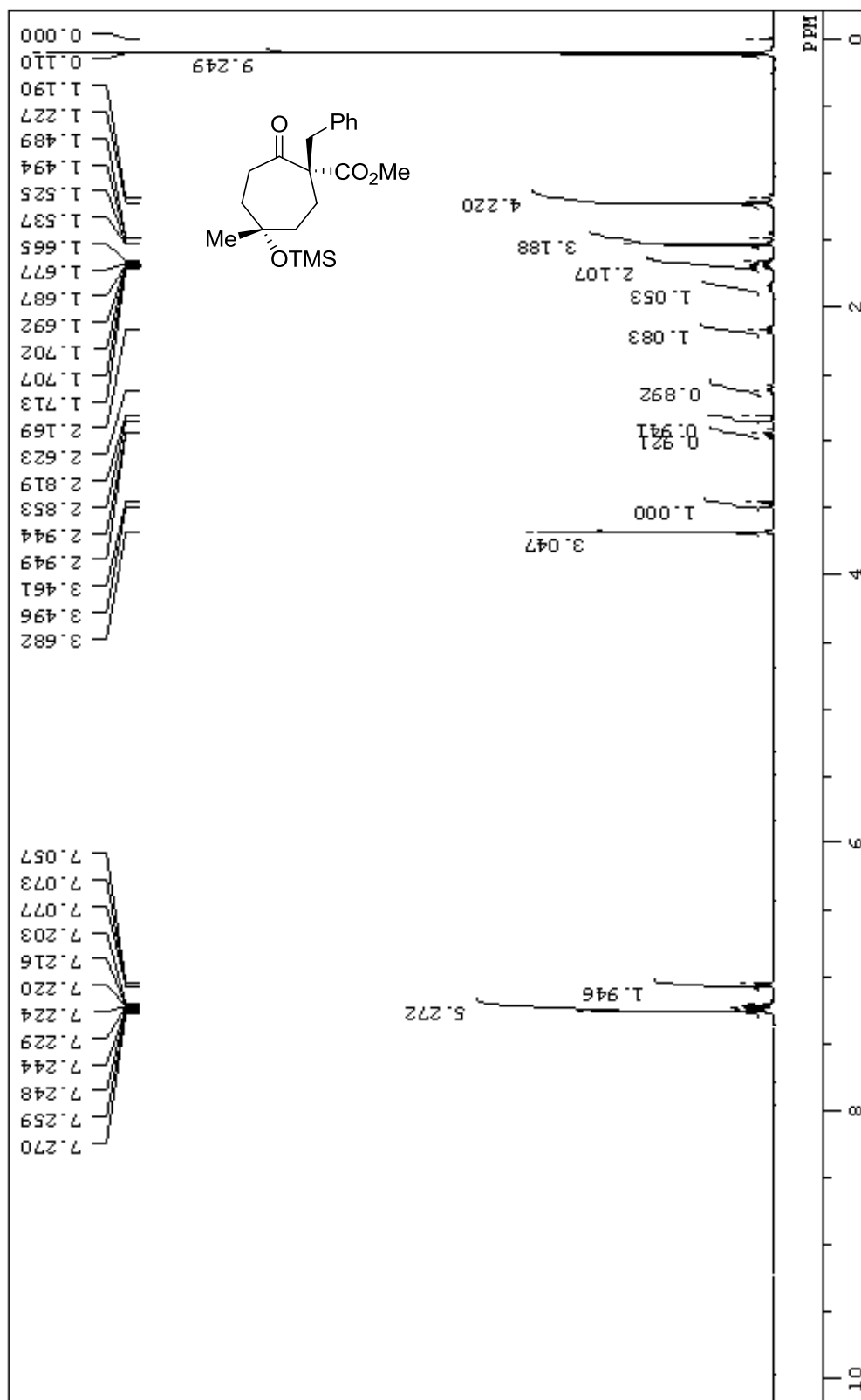


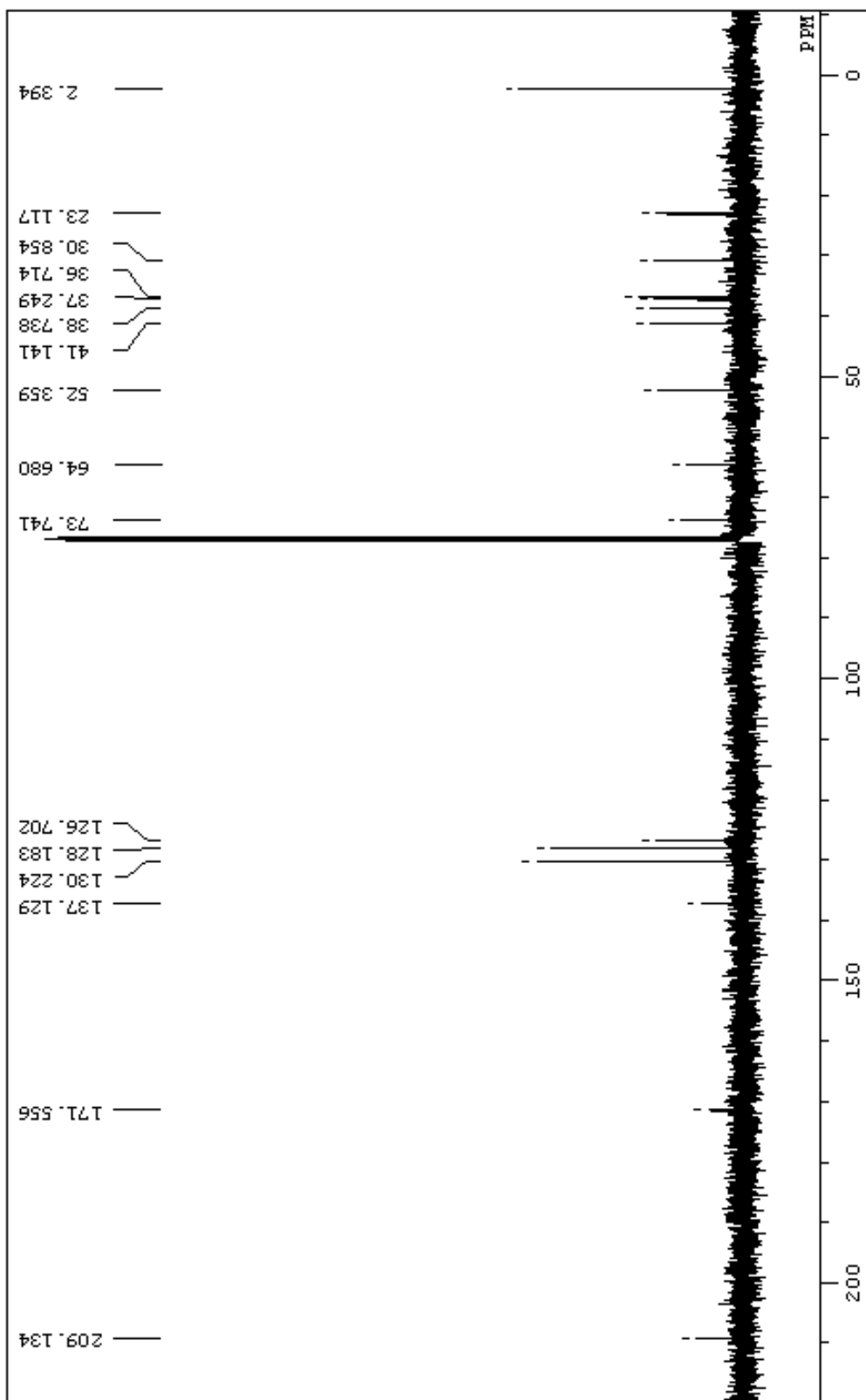


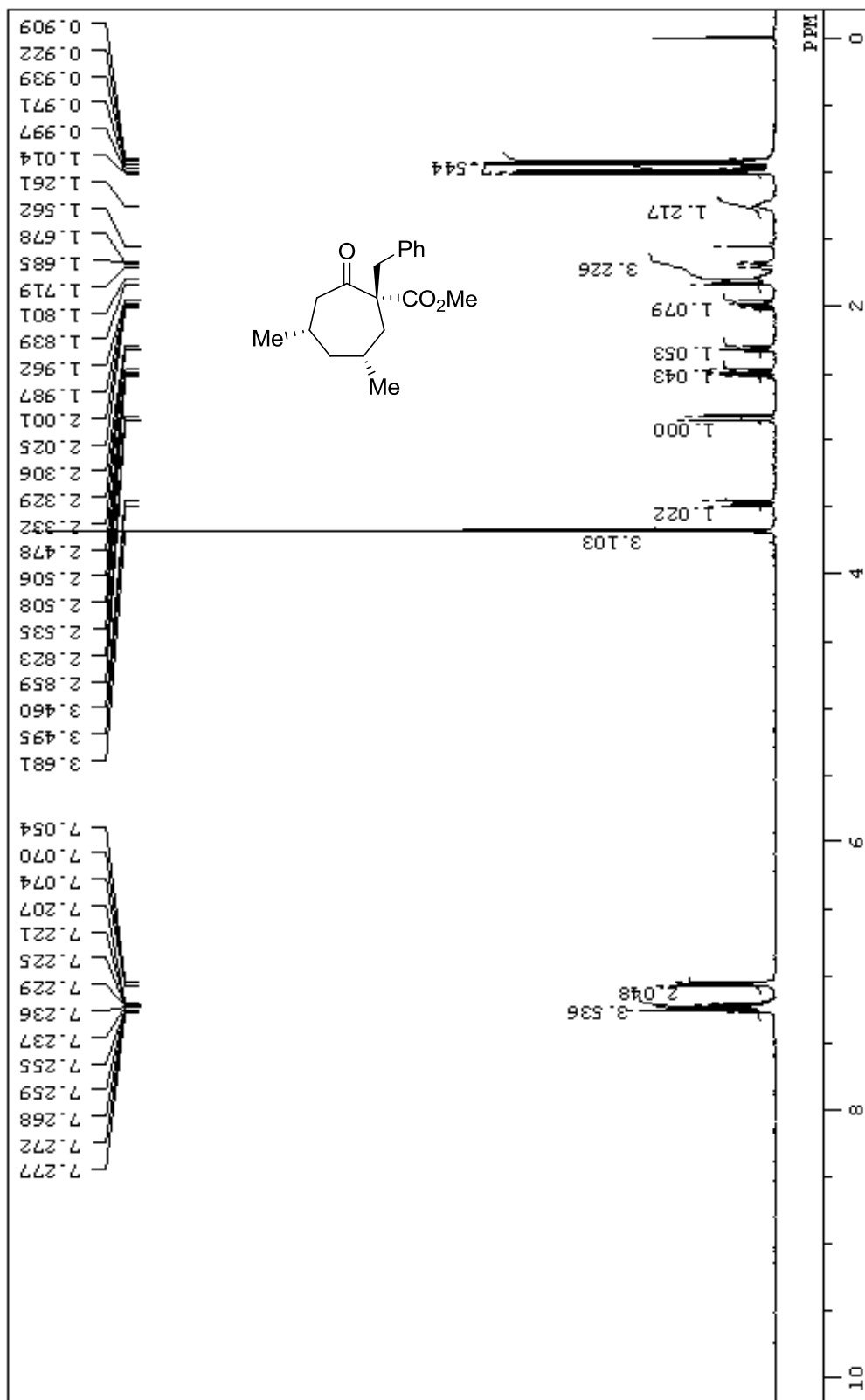


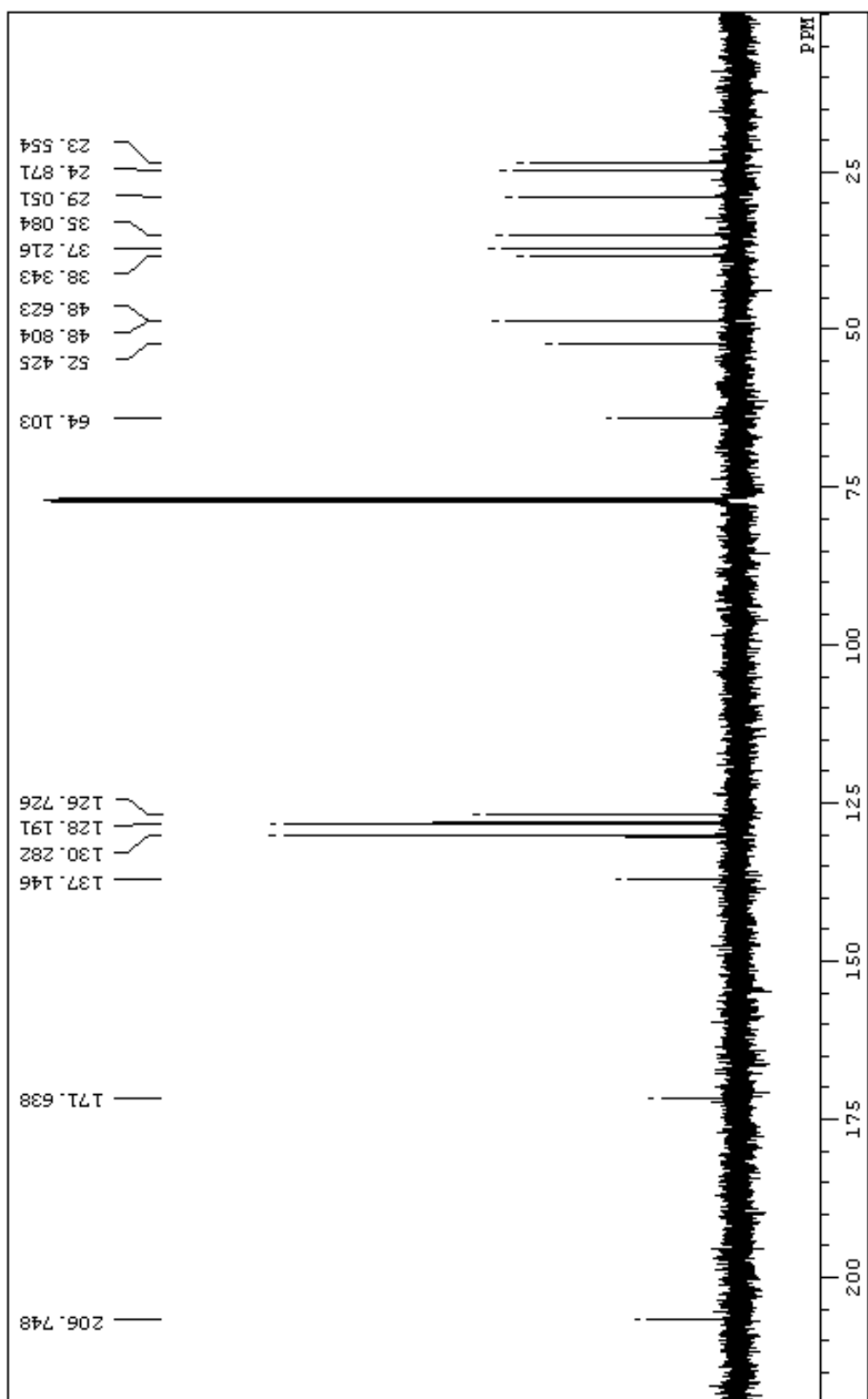


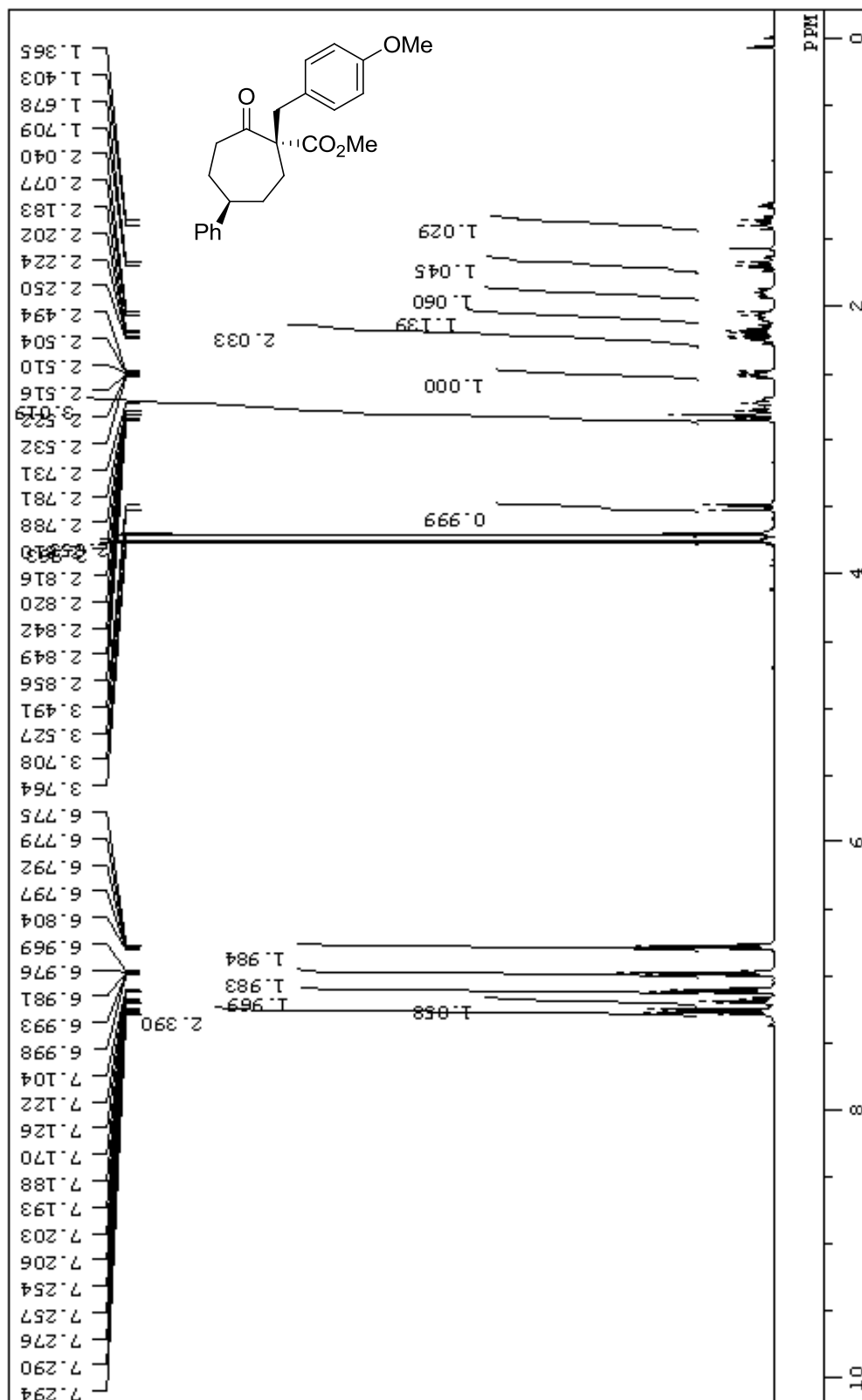


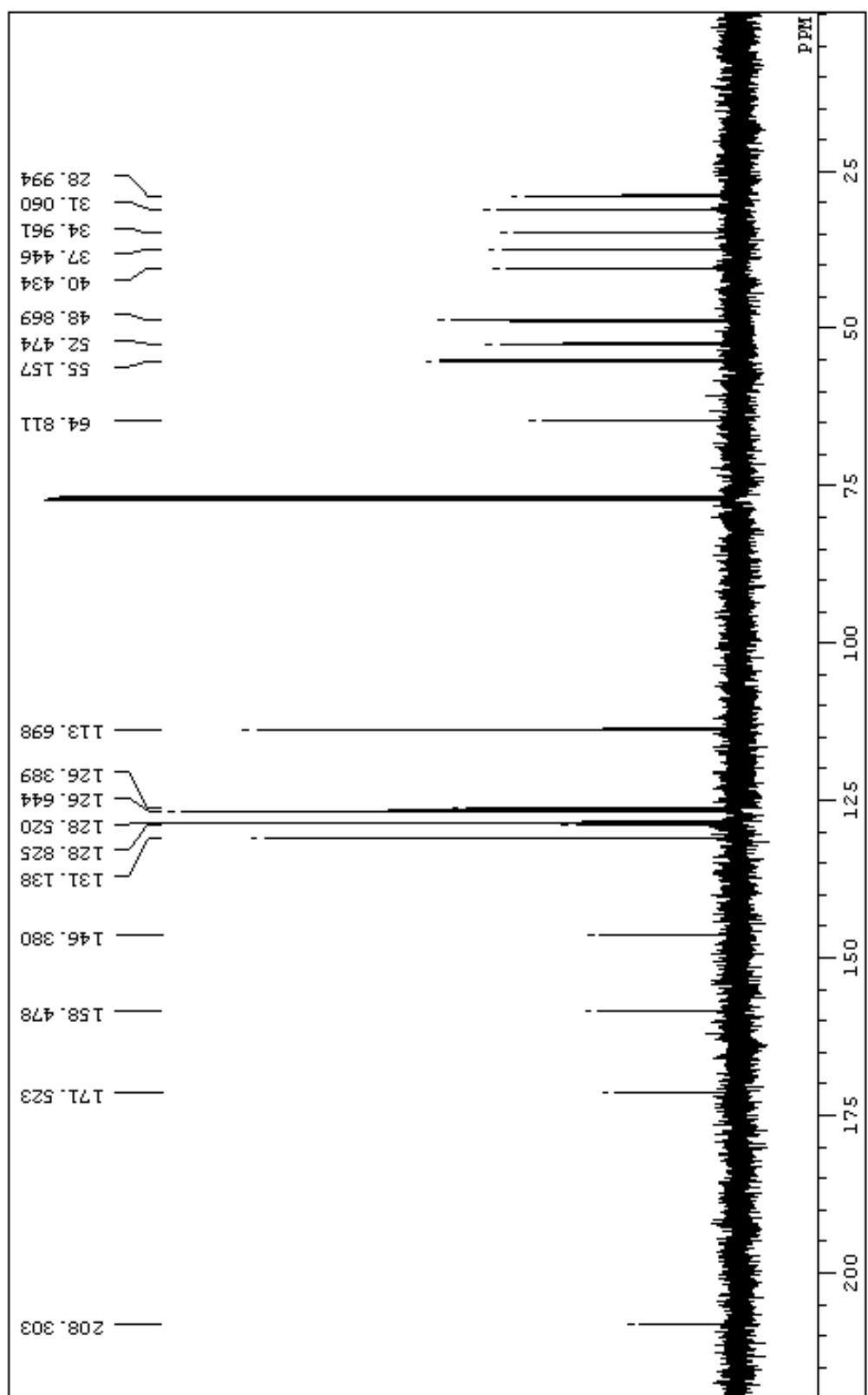


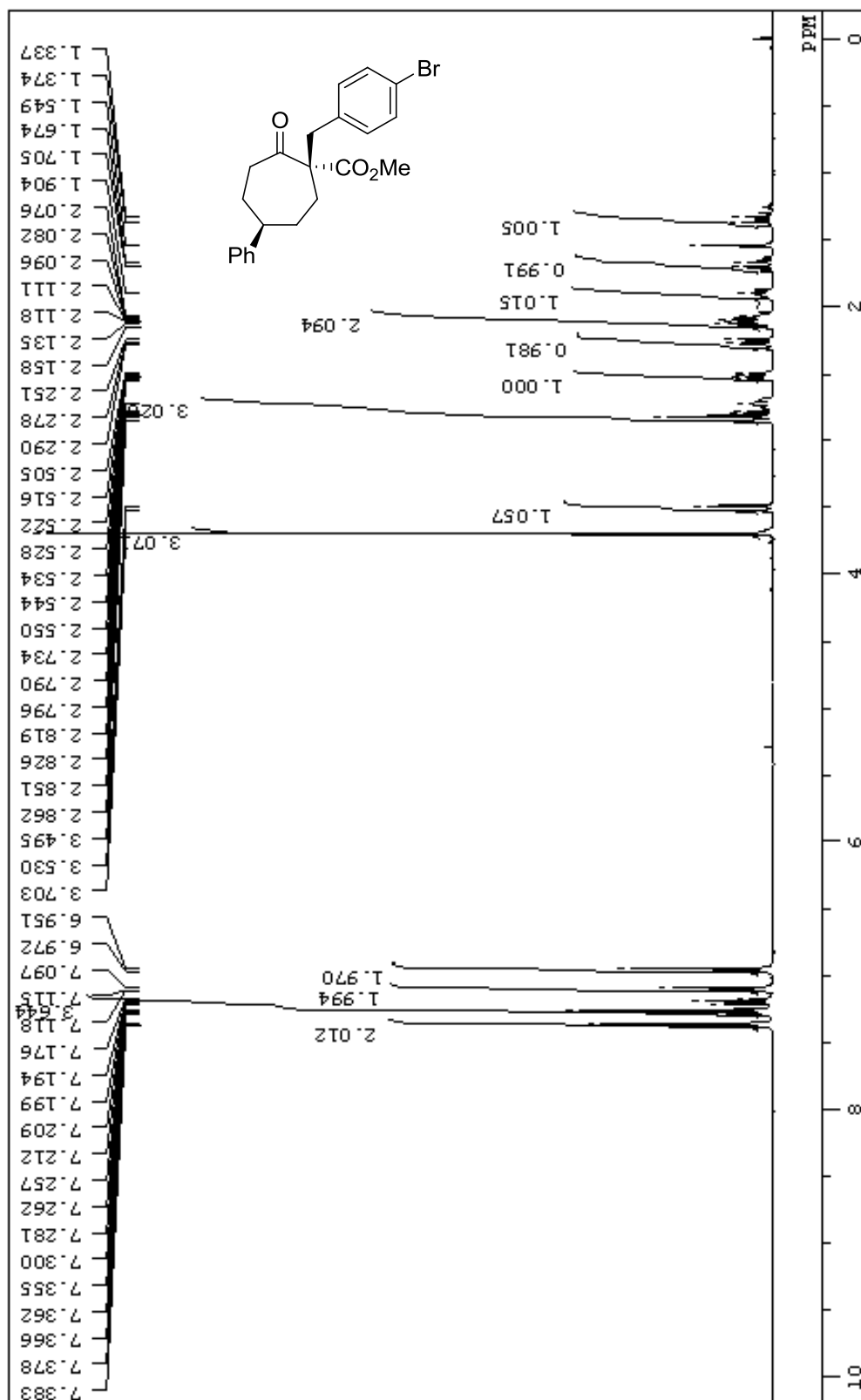


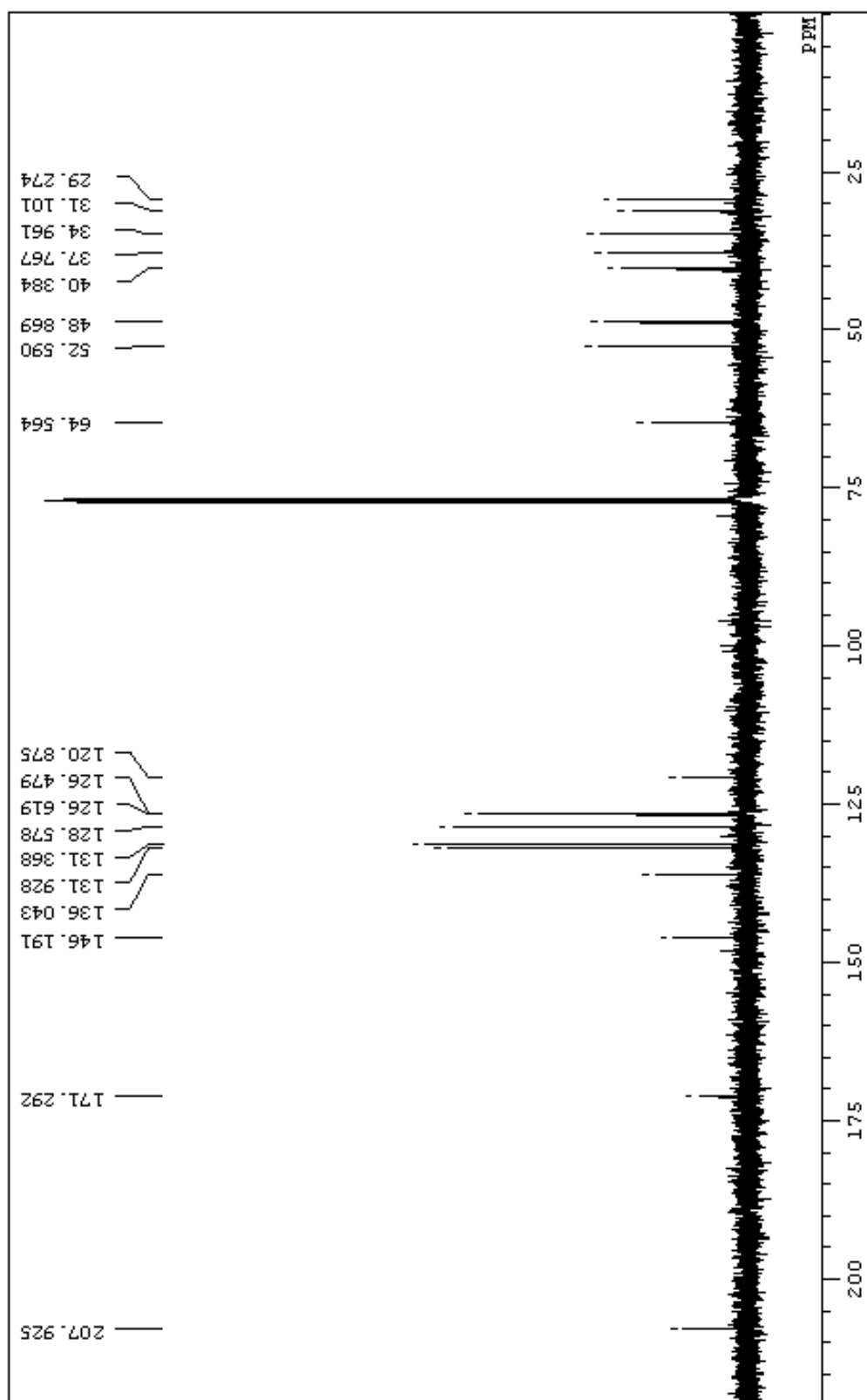


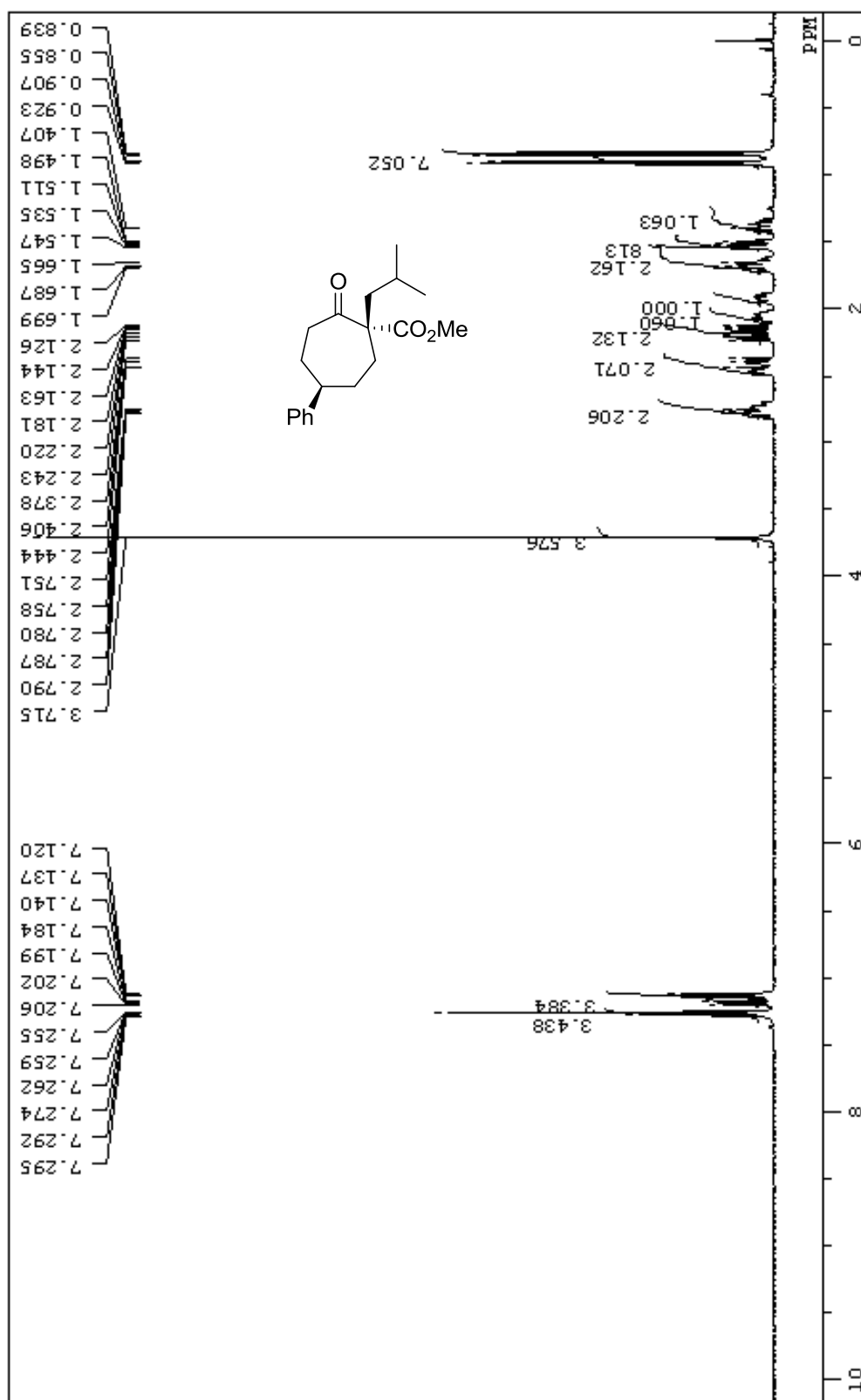


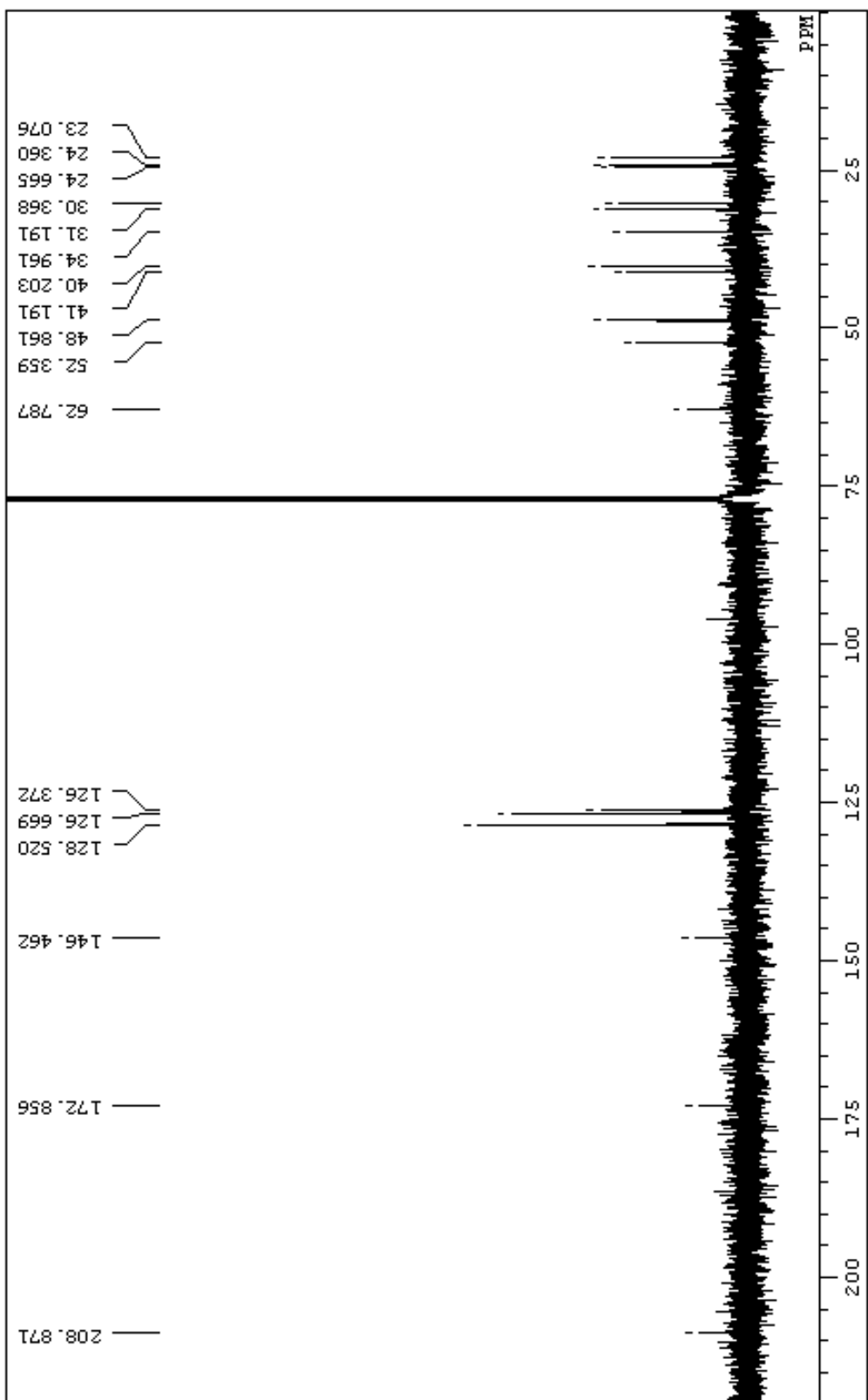


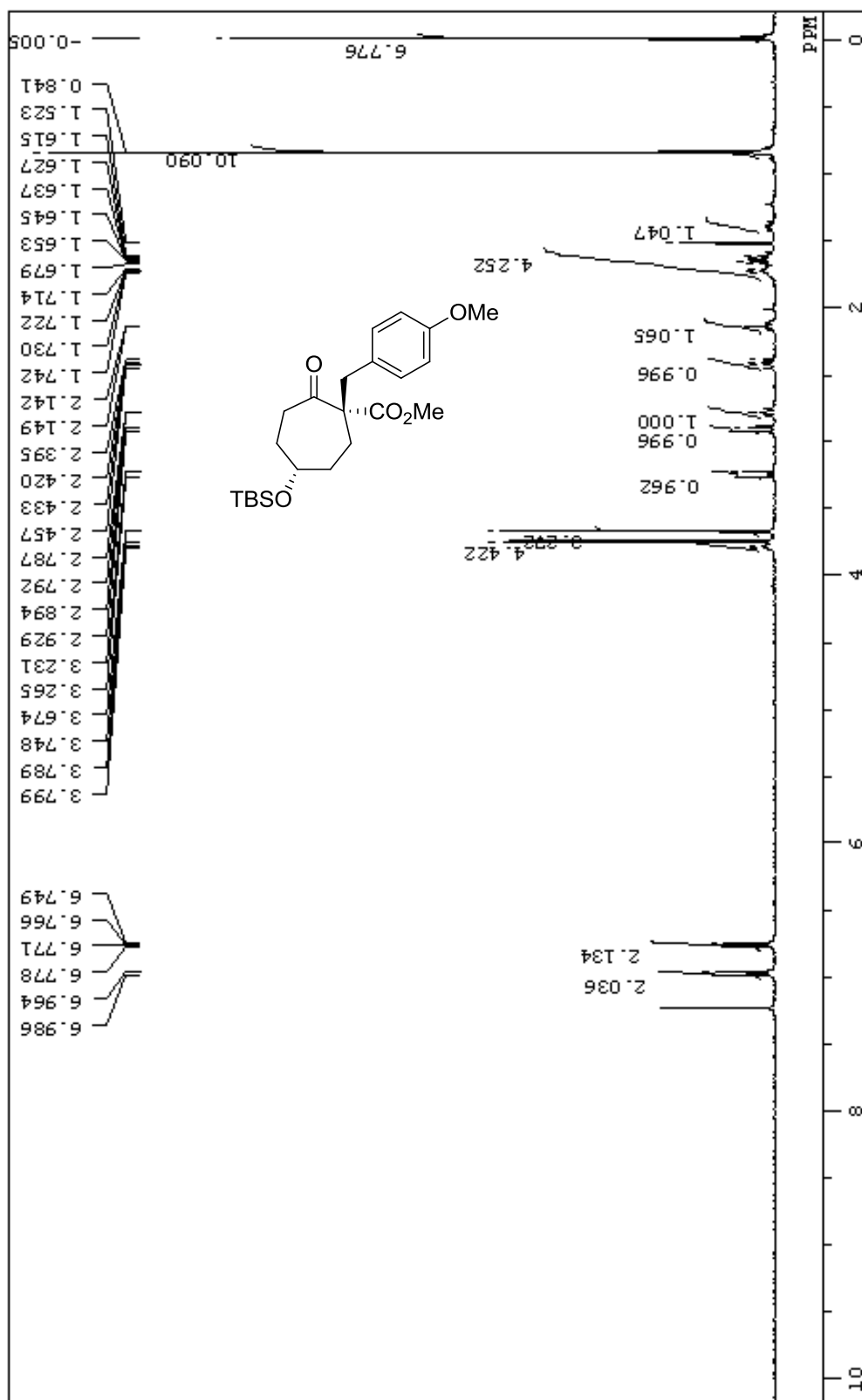


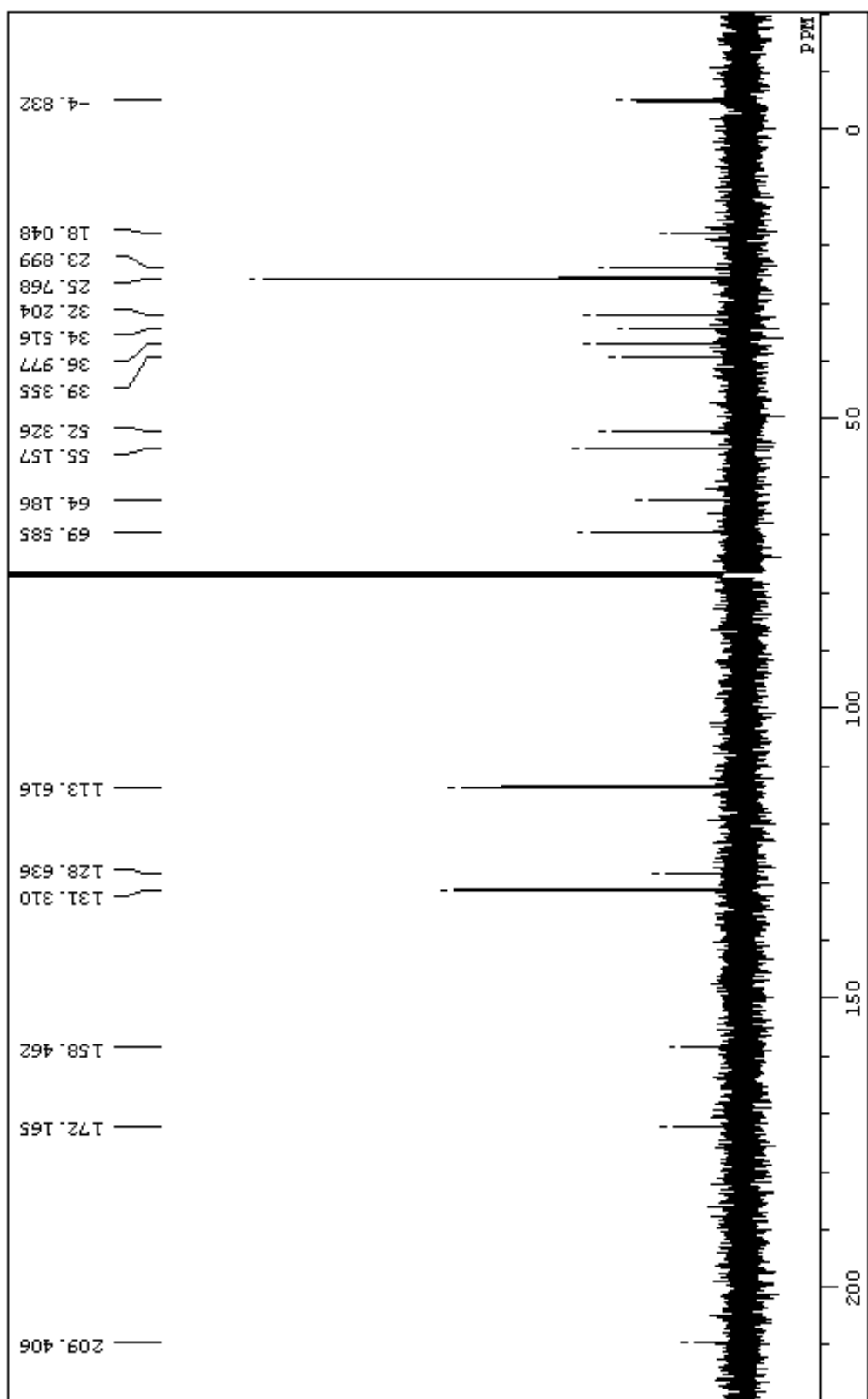


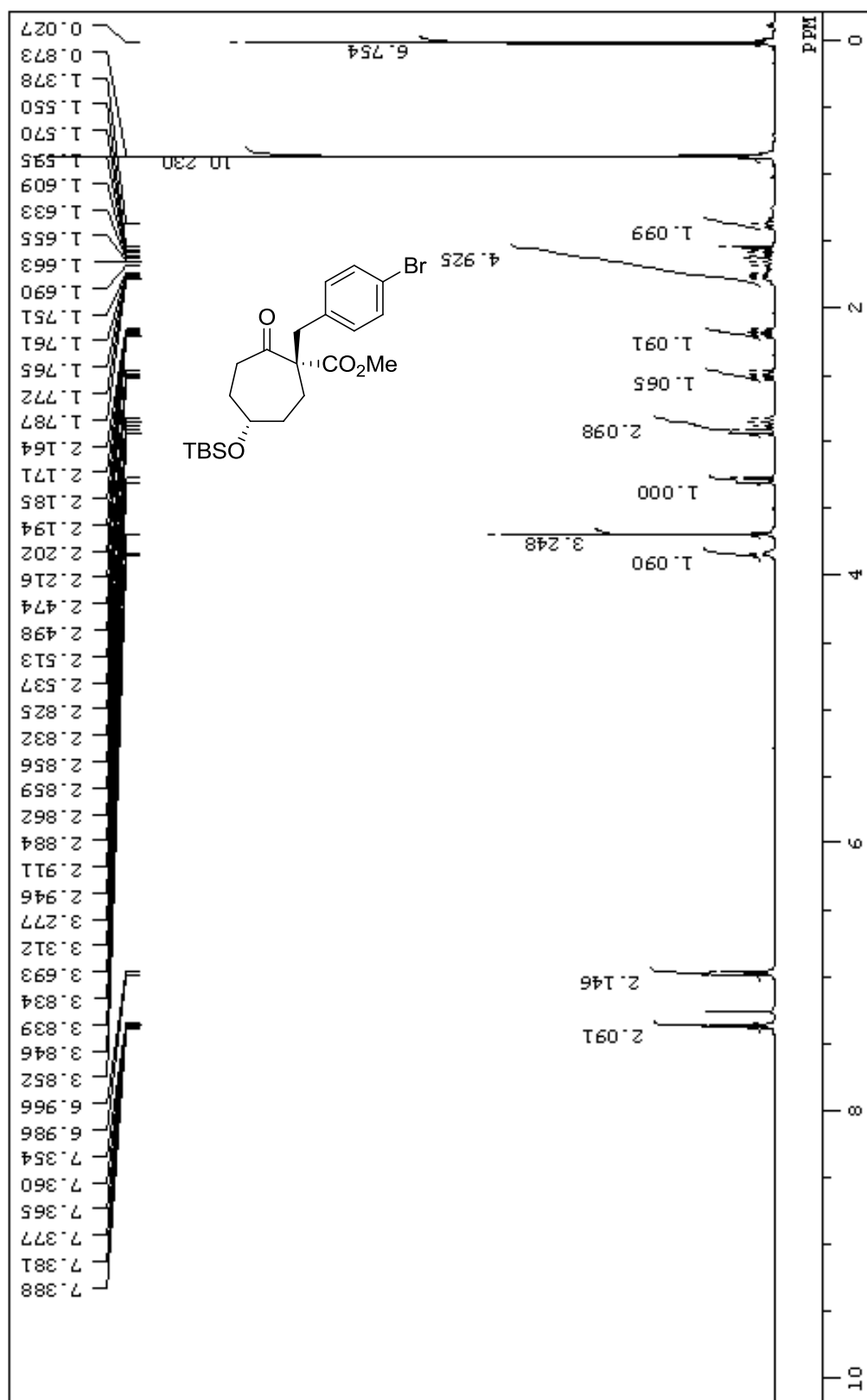


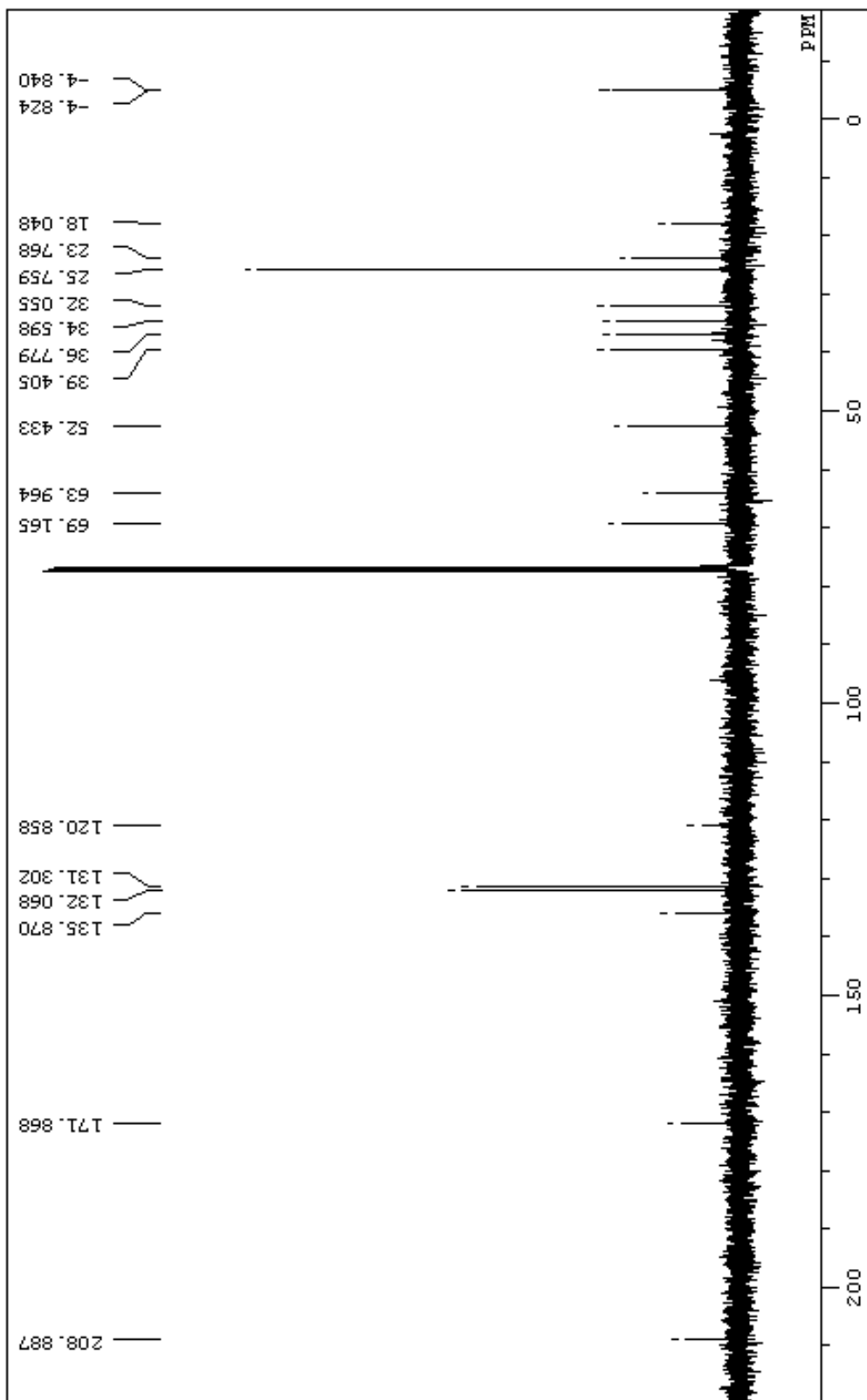


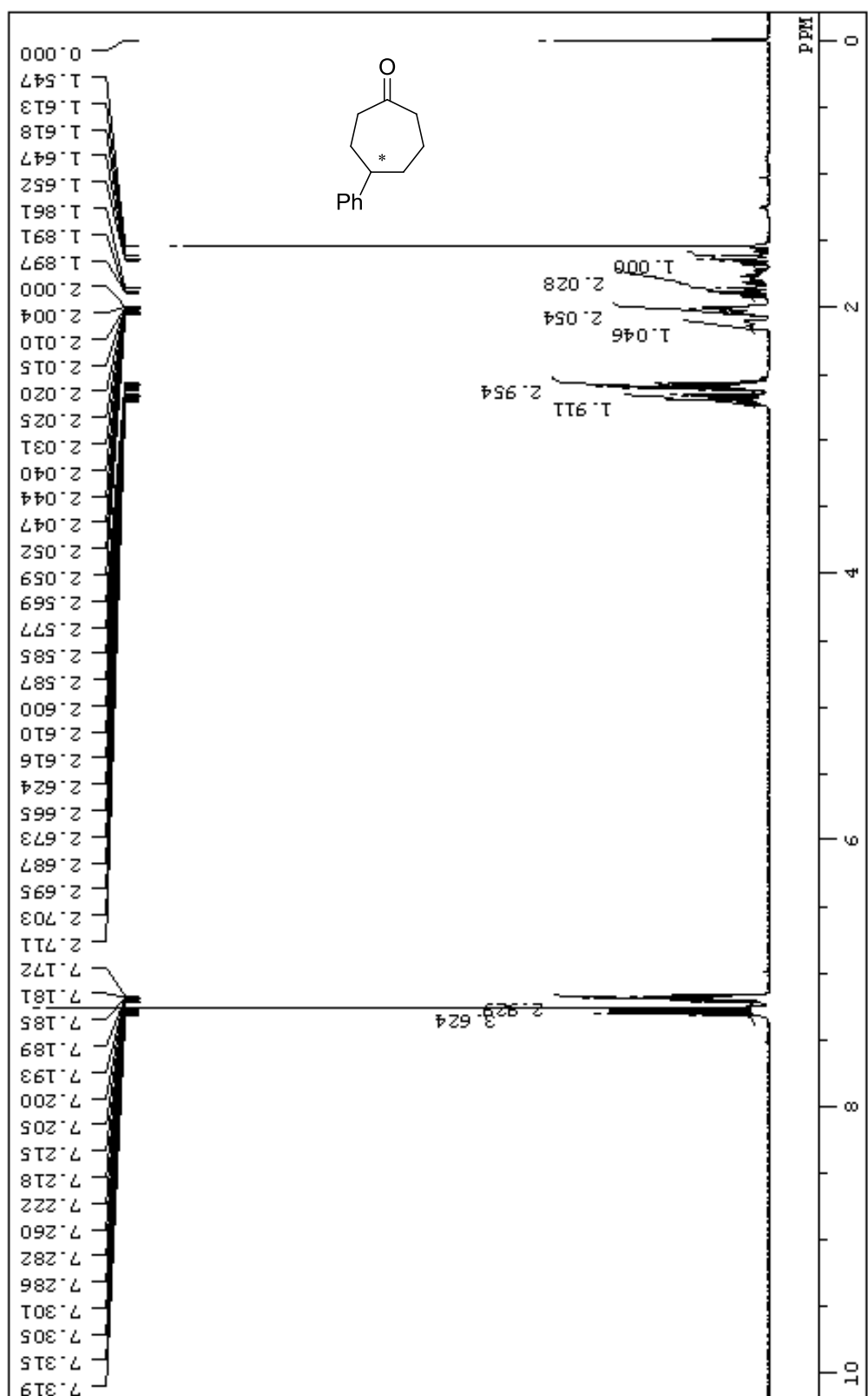


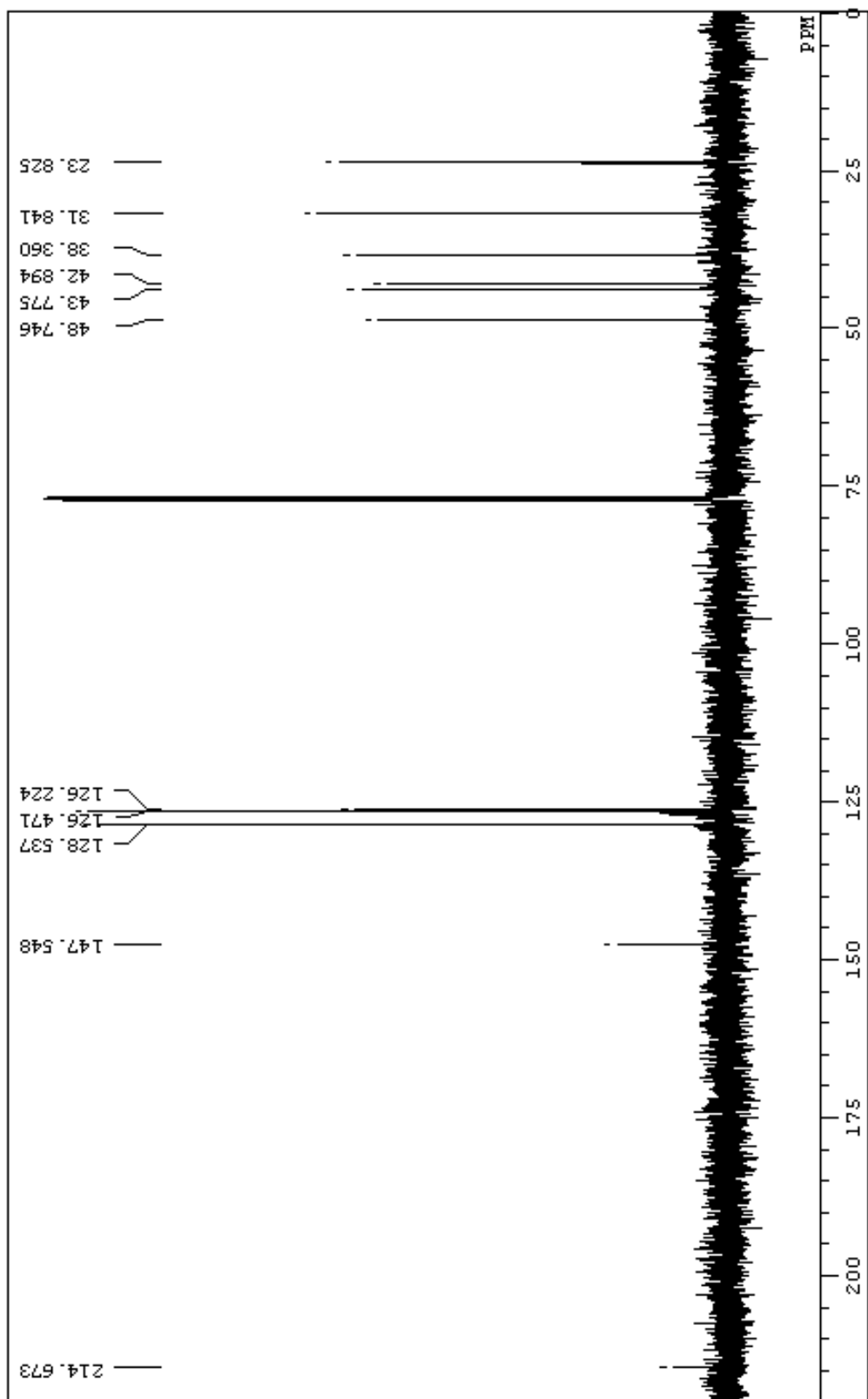










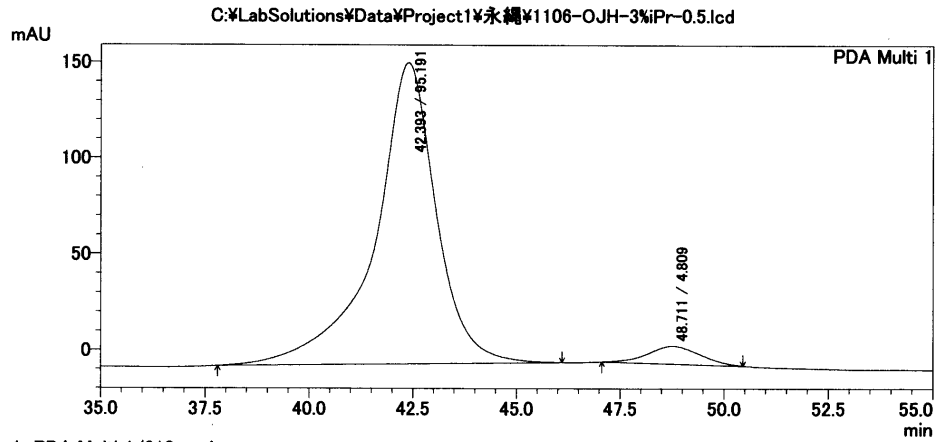


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1106-OJH-3%iPr-0.5.lcd
 サンプルID : yuki
 バイアル番号 : 69
 注入量 : 1 uL
 データファイル : 1106-OJH-3%iPr-0.5.lcd
 メソッドファイル : OJ-H iPr3% flow0.5 60min.lcm
 バッチファイル : 共用ばっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/01/08 20:01:50

No 15 ~~15~~

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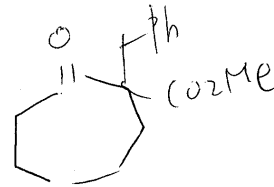
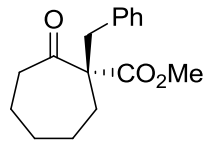


1 PDA Multi 1/210nm 4nm

<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1106-OJH-3%iPr-0.5.lcd

ピーク#	保持時間	面積	面積%	マーク
1	42.393	16208807	95.191	
2	48.711	818882	4.809	
合計		17027689	100.000	

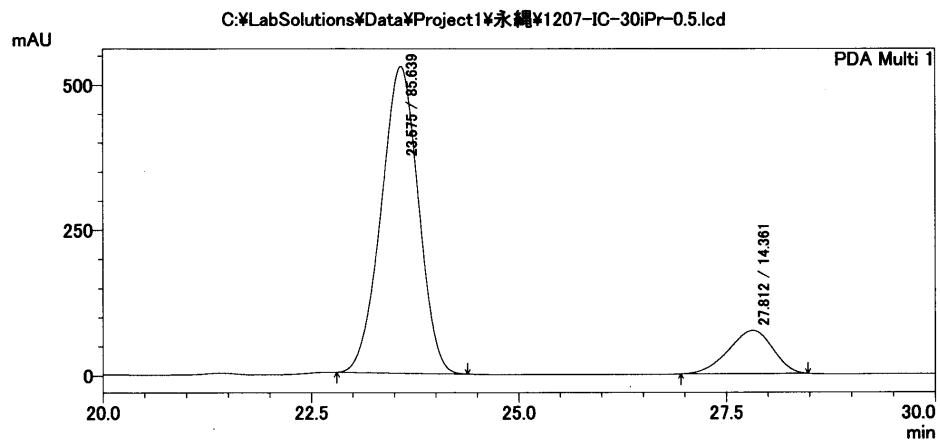


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1207-IC-30iPr-0.5.lcd
 : 1207-1
 サンプルID : 1207-1
 バイアル番号 : -1
 注入量 : 1 uL
 データファイル : 1207-IC-30iPr-0.5.lcd
 メソッドファイル : Method 120 min (190-360).lcm
 バッチファイル :
 レポートファイル : Default.lcr
 分析日時 : 2011/02/09 11:07:58

No. 183

＜クロマトグラム＞

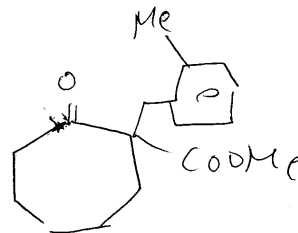
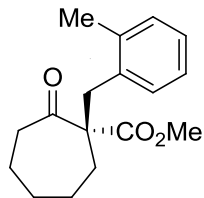


＜ピークレポート＞

C:\LabSolutions\Data\Project1\永縄\1207-IC-30iPr-0.5.lcd

SPD-M20A Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%	マーク
1	23.575	16439730	85.639	
2	27.812	2756800	14.361	
合計		19196531	100.000	

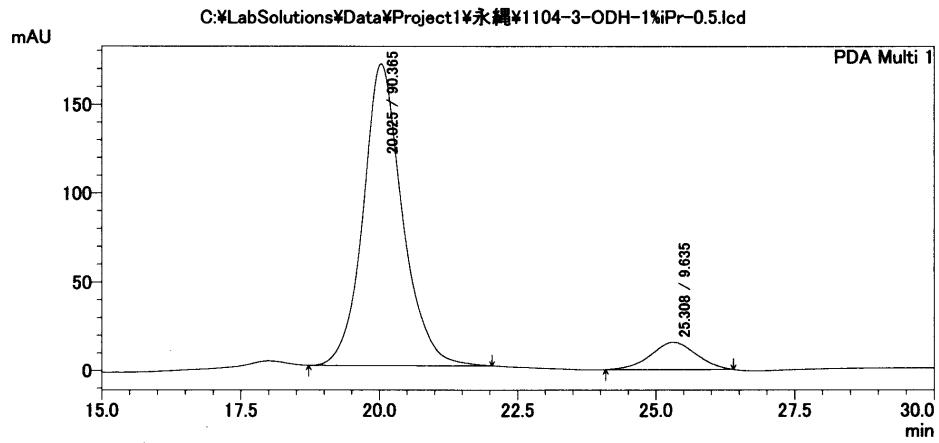


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1104-3-ODH-1%iPr-0.5.lcd
 サンプルID : yuki
 バイアル番号 : 69
 注入量 : 1 uL
 データファイル : 1104-3-ODH-1%iPr-0.5.lcd
 メソッドファイル : OD-H iPr 1% flow=0.5 60min before30min.lcm
 バッチファイル : 共用ばっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/01/07 18:33:04

No153

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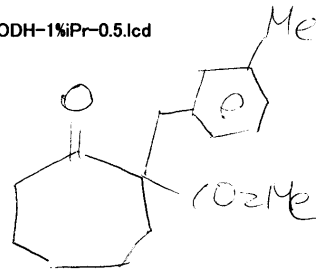
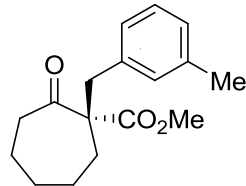


1 PDA Multi 1/210nm 4nm

<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1104-3-ODH-1%iPr-0.5.lcd

ピーク#	保持時間	面積	面積%	マーク
1	20.025	8401435	90.365	
2	25.308	895738	9.635	
合計		9297173	100.000	

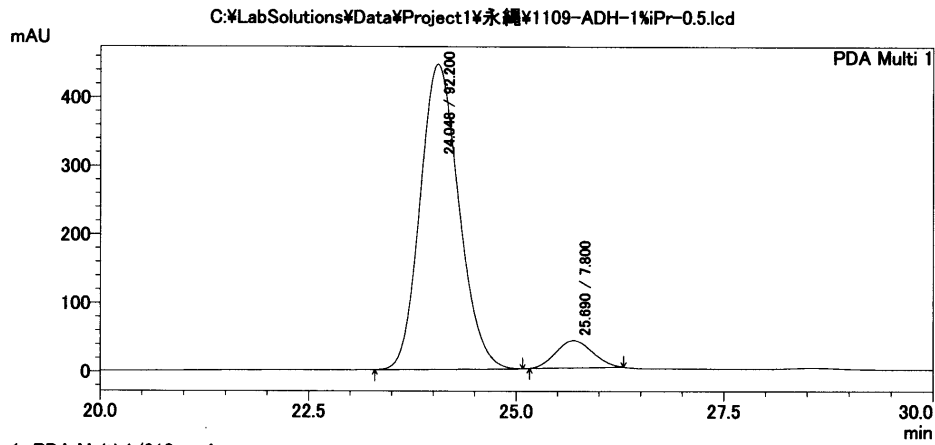


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1109-ADH-1\iPr-0.5.lcd
 サンプルID : yuki
 バイアル番号 : 69
 注入量 : 1 uL
 データファイル : 1109-ADH-1\iPr-0.5.lcd
 メソッドファイル : AD-H iPr 1% flow=0.5 60min before30min.lcm
 バッチファイル : 共用ばっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/01/12 14:38:40

No156

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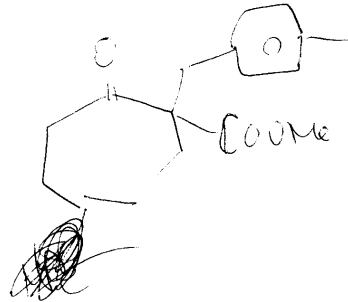
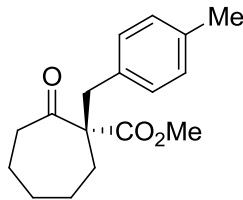


1 PDA Multi 1/210nm 4nm

<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1109-ADH-1\iPr-0.5.lcd

ピーク#	保持時間	面積	面積%	マーク
1	24.048	14486074	92.200	
2	25.690	1225579	7.800	
合計		15711652	100.000	

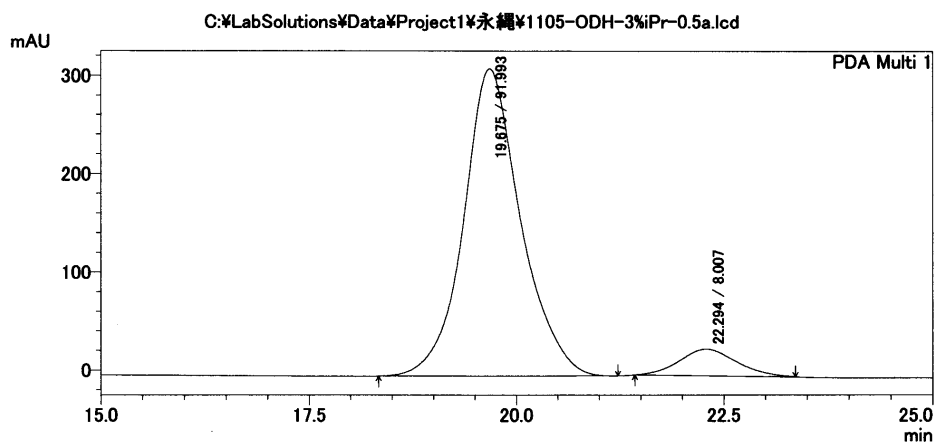


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1105-ODH-3%iPr-0.5a.lcd
 サンプルID : yuki
 バイアル番号 : 69
 注入量 : 1 uL
 データファイル : 1105-ODH-3%iPr-0.5a.lcd
 メソッドファイル : OD-H iPr 3% flow=0.5 60min before30min.lcm
 バッチファイル :
 レポートファイル :
 分析日時 : 2011/01/07 23:08:44

No154

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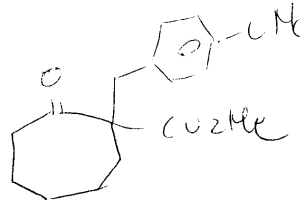
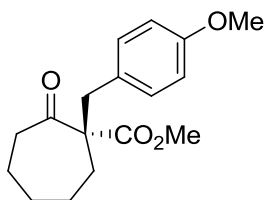


<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1105-ODH-3%iPr-0.5a.lcd

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%	マーク
1	19.675	14979542	91.993	
2	22.294	1303743	8.007	
合計		16283285	100.000	

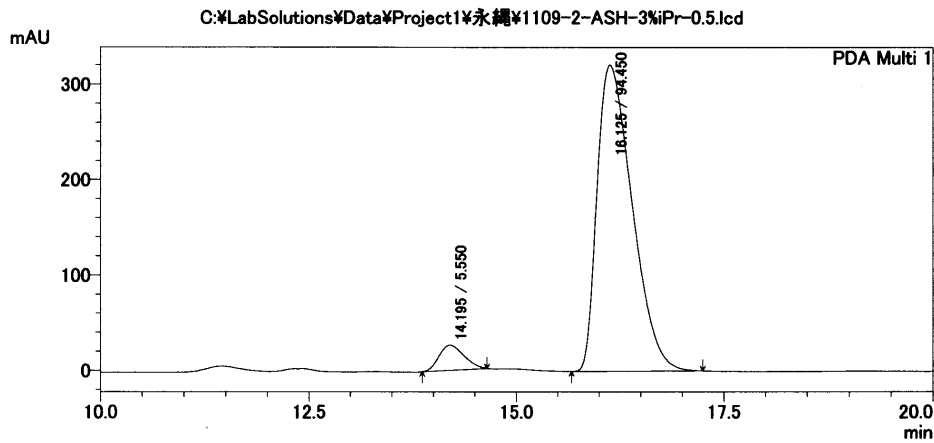


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1109-2-ASH-3\iPr-0.5.lcd
 サンプルID : yuki
 バイアル番号 : 69
 注入量 : 1 uL
 データファイル : 1109-2-ASH-3\iPr-0.5.lcd
 メソッドファイル : AS-H iPr 3% flow=0.5 60min before30min.lcm
 バッチファイル : 共用ばっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/01/12 18:50:12

No158

＜クロマトグラム＞

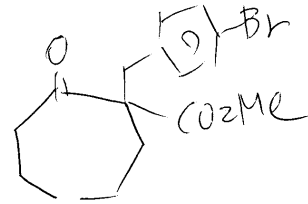
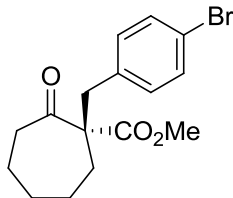


＜ピークレポート＞

C:\LabSolutions\Data\Project1\永縄\1109-2-ASH-3\iPr-0.5.lcd

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%	マーク
1	14.195	554293	5.550	
2	16.125	9433048	94.450	
合計		9987341	100.000	

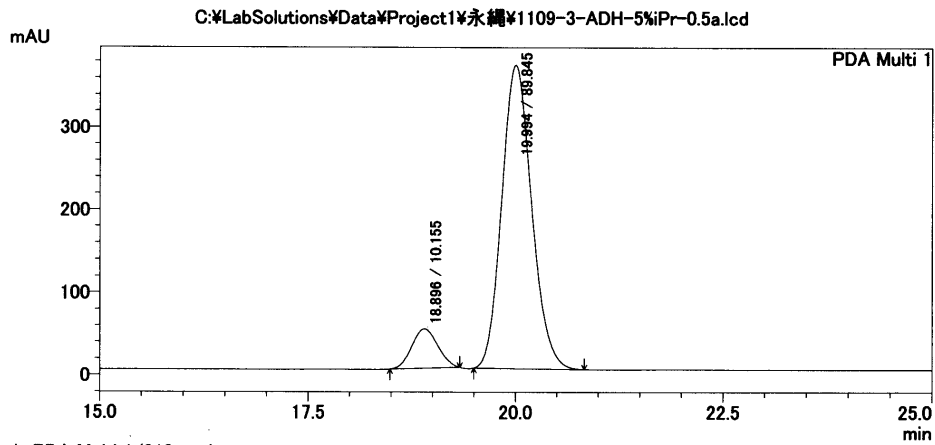


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1109-3-ADH-5%Pr-0.5a.lcd
 サンプルID : yuki
 バイアル番号 : 69
 注入量 : 1 uL
 データファイル : 1109-3-ADH-5%Pr-0.5a.lcd
 メソッドファイル : AD-H iPr 5% flow=0.5 60min before30min.lcm
 バッチファイル :
 レポートファイル :
 分析日時 : 2011/01/12 22:08:42

No159

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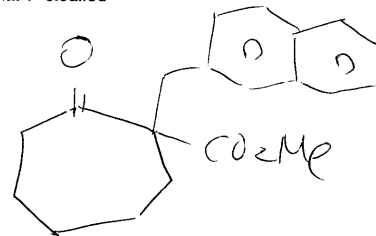
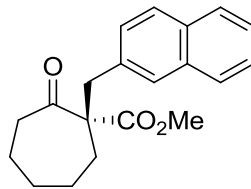


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C:\LabSolutions\Data\Project1\永縄\1109-3-ADH-5%Pr-0.5a.lcd

PDA Ch1 210nm 4nm

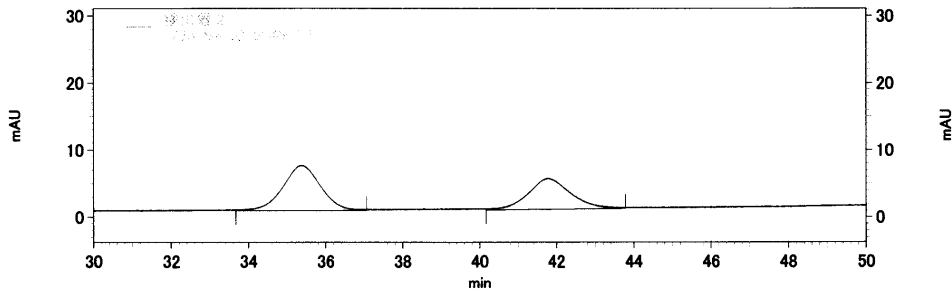
ピーク#	保持時間	面積	面積%	マーク
1	18.896	1039940	10.155	
2	19.994	9201097	89.845	
合計		10241037	100.000	



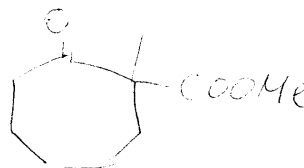
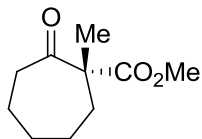
面積%レポート

データファイル名: C:\Data\Naganawa\1225-Me-IC-501Pr-0.5.dat
 メソッドファイル名: C:\Data\Shirozu\Method 120 min.met
 ユーザー名: System
 分析日時: 2011/03/02 15:51:56
 印刷日時: 2011/03/02 17:55:02

No201



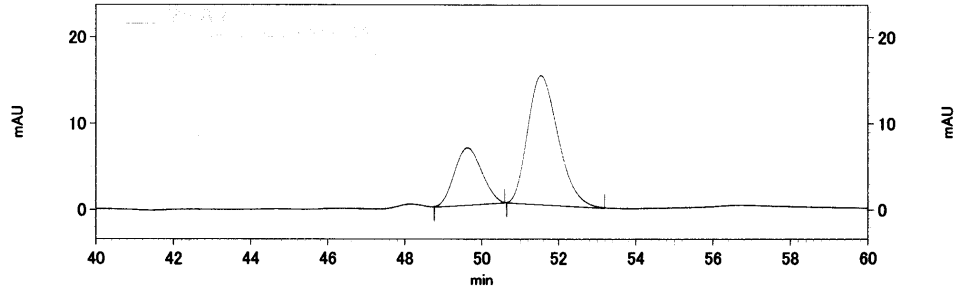
検出器 2結果 Pk #	名前	保持時間	面積	面積%	^-スライコト
1		35.35	458039	56.768	MM
2		41.80	348820	43.232	MM
トータル			806859	100.000	



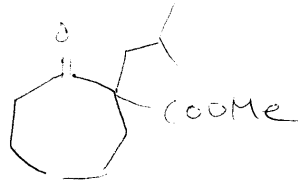
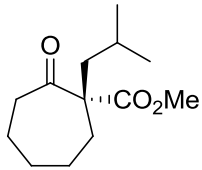
面積%レポート

データファイル名: C:\Data\Naganawa\1225-iBu-ODHtriple-50iPr-0.3.dat
 メソッドファイル名: C:\Data\Shirozu\Method 120 min.met
 ユーザー名: System
 分析日時: 2011/03/01 17:16:19
 印刷日時: 2011/03/01 19:36:04

NozOD



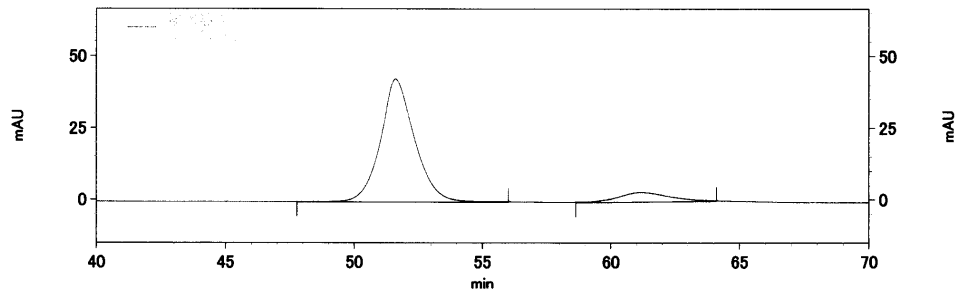
検出器	2結果	名前	保持時間	面積	面積%	ピークコメント
Pk #						
1			49.64	331705	28.534	MM
2			51.53	830794	71.466	MM
トータル				1162499	100.000	



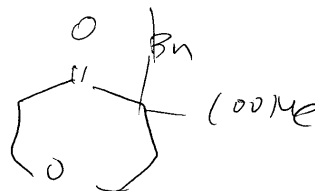
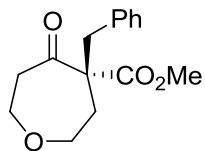
面積%レポート

データファイル名: C:\Data\Naganawa\1119-2-1A-1\Et-0.5.dat
 メソッドファイル名: C:\Data\Shirozu\Method 120 min.met
 ユーザー名: System
 分析日時: 2011/01/22 15:25:36
 印刷日時: 2011/01/22 16:46:40

No 163



検出器	2結果	名前	保持時間	面積	面積%	ピークコード
Pk #						
1			51.60	3958512	89.974	MM
2			61.24	441106	10.026	MM
トータル				4399618	100.000	

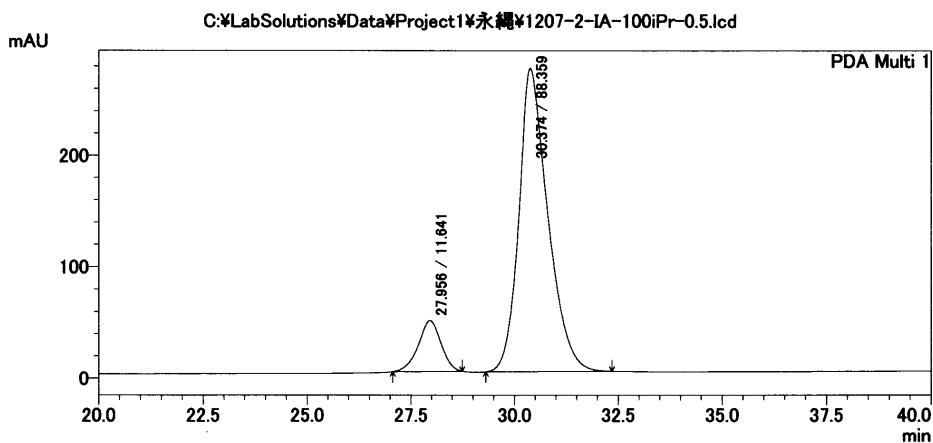


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1207-2-IA-100iPr-0.5.lcd
 サンプルID : 1207-2
 バイアル番号 : -1
 注入量 : 1 uL
 データファイル : 1207-2-IA-100iPr-0.5.lcd
 メソッドファイル : Method 120 min (190-360).lcm
 パッチファイル :
 レポートファイル : Default.lcr
 分析日時 : 2011/02/09 12:18:49

16/85

<クロマトグラム>



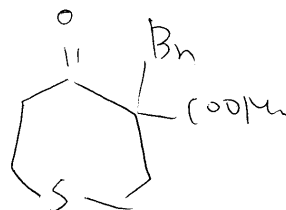
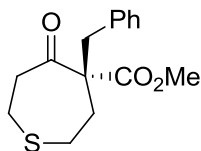
1 PDA Multi 1/210nm 4nm

<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1207-2-IA-100iPr-0.5.lcd

SPD-M20A Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%	マーク
1	27.956	1743782	11.641	
2	30.374	13235532	88.359	
合計		14979314	100.000	

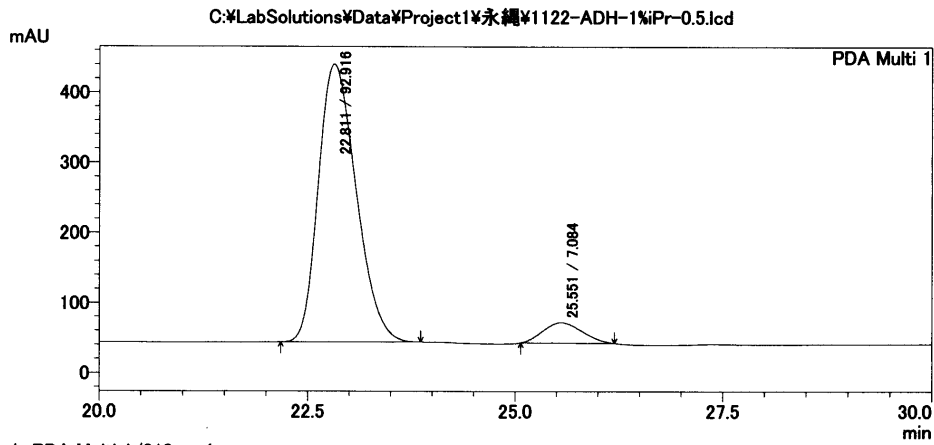


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1122-ADH-1\iPr-0.5.lcd
 サンプルID : yuki
 バイアル番号 : 69
 注入量 : 1 uL
 データファイル : 1122-ADH-1\iPr-0.5.lcd
 メソッドファイル : AD-H iPr 1% flow=0.5 60min before30min.lcm
 バッチファイル : 共用ばっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/01/25 10:28:17

N=165

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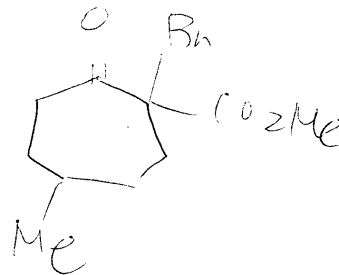
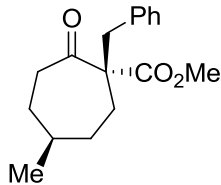


1 PDA Multi 1/210nm 4nm

<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1122-ADH-1\iPr-0.5.lcd

ピーク#	保持時間	面積	面積%	マーク
1	22.811	12550228	92.916	
2	25.551	956868	7.084	
合計		13507095	100.000	

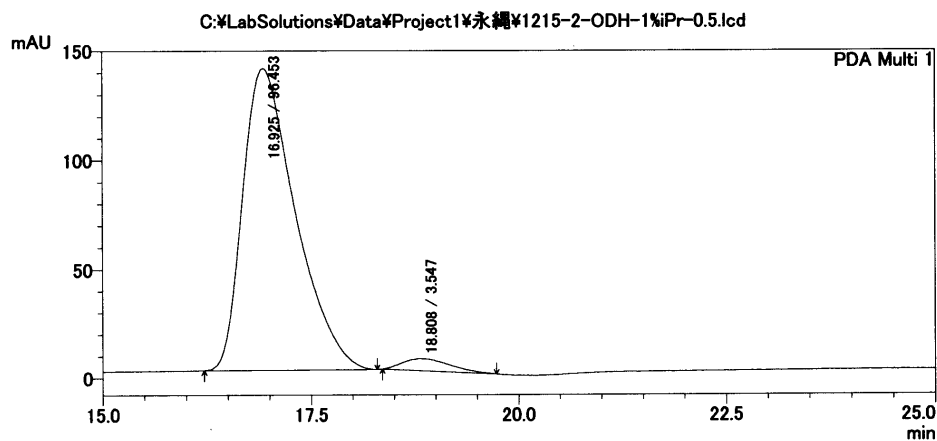


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1215-2-ODH-1%iPr-0.5.lcd
 サンプルID : yuki
 バイアル番号 : 69
 注入量 : 1 uL
 データファイル : 1215-2-ODH-1%iPr-0.5.lcd
 メソッドファイル : OD-H iPr 1% flow=0.5 60min before30min.lcm
 バッチファイル : 共用ばっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/02/18 2:13:45

No192

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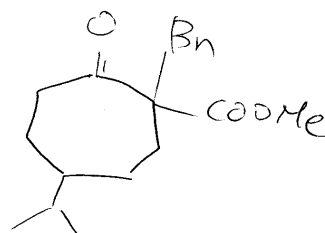
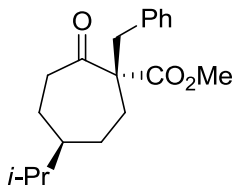


<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1215-2-ODH-1%iPr-0.5.lcd

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%	マーク
1	16.925	6099196	96.453	
2	18.808	224318	3.547	
合計		6323515	100.000	

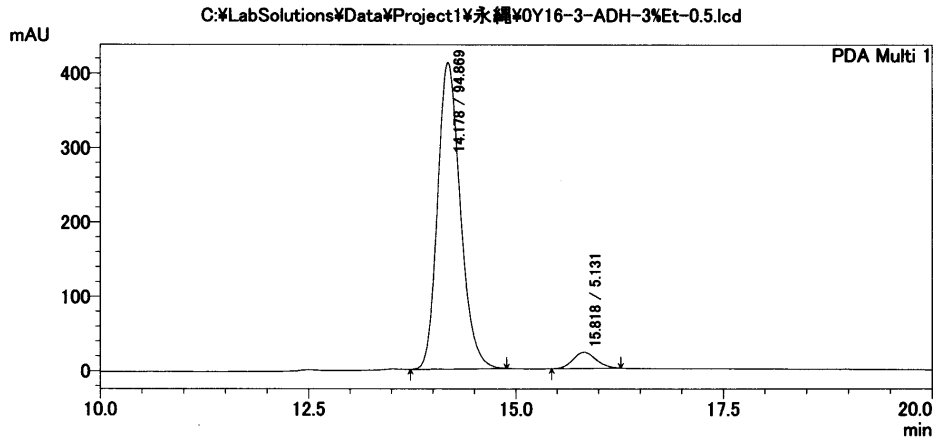


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\0Y16-3-ADH-3%Et-0.5.lcd
 サンプルID : yuki
 バイアル番号 :
 注入量 : 69
 データファイル : 1 uL
 メソッドファイル : 0Y16-3-ADH-3%Et-0.5.lcd
 バッチファイル : AD-H Et 3% flow=0.5 60min before30min.lcm
 レポートファイル : 共用ばっち.lcb
 分析日時 : Default.lcr
 : 2010/11/17 10:27:08

No 123

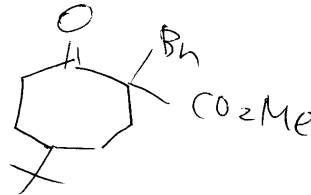
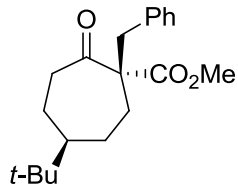
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<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\0Y16-3-ADH-3%Et-0.5.lcd

PDA Ch1 210nm 4nm				
ピーク#	保持時間	面積	面積%	マーク
1	14.178	7909674	94.869	
2	15.818	427768	5.131	
合計		8337442	100.000	

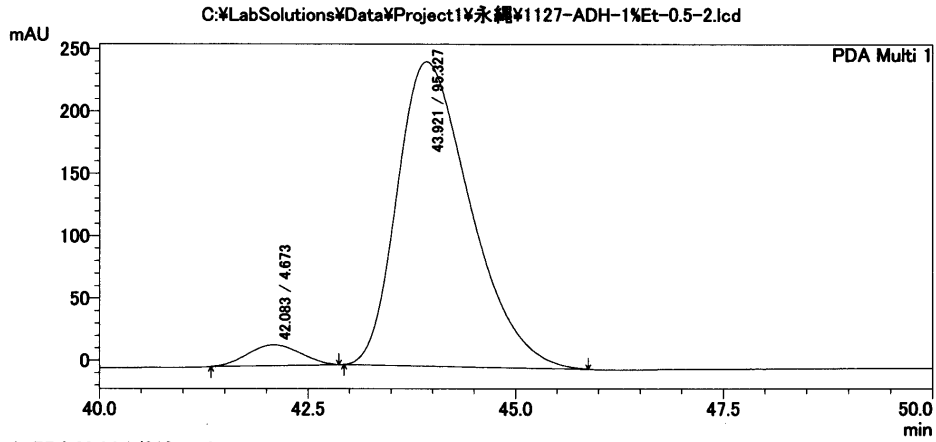


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1127-ADH-1\Et-0.5-2.lcd
 サンプルID : yuki
 バイアル番号 : 69
 注入量 : 1 uL
 データファイル : 1127-ADH-1\Et-0.5-2.lcd
 メソッドファイル : AD-H Et 1% flow=0.5 60min before30min.lcm
 バッチファイル : 共用ばっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/01/31 11:35:51

No 173

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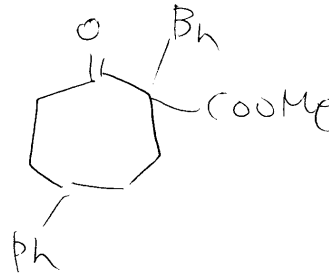
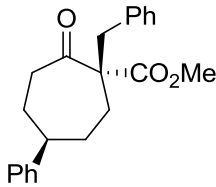


<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1127-ADH-1\Et-0.5-2.lcd

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%	マーク
1	42.083	736344	4.673	
2	43.921	15021157	95.327	
合計		15757501	100.000	



85-98 119-121

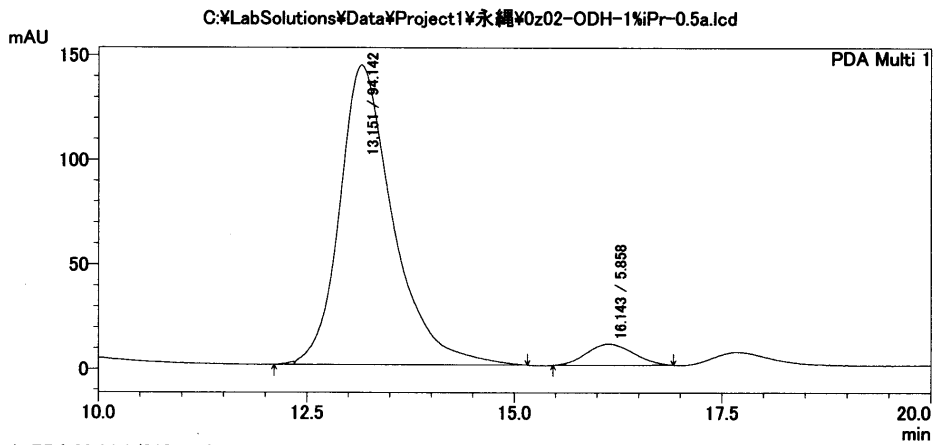
122-129 142, 143

==== Shimadzu LcSolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\0z02-ODH-1%iPr-0.5a.lcd
 サンプルID : yuki
 バイアル番号 :
 注入量 : 69
 データファイル : 1 uL
 メソッドファイル : 0z02-ODH-1%iPr-0.5a.lcd
 バッチファイル : OD-H iPr 1% flow=0.5 60min before30min.lcm
 レポートファイル :
 分析日時 : 2010/12/03 22:07:03

No135

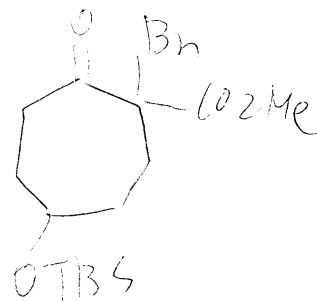
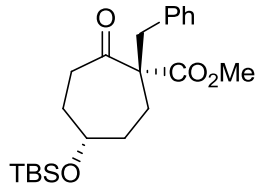
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<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\0z02-ODH-1%iPr-0.5a.lcd

ピーク#	保持時間	面積	面積%	マーク
1	13.151	6425817	94.142	
2	16.143	399820	5.858	
合計		6825638	100.000	

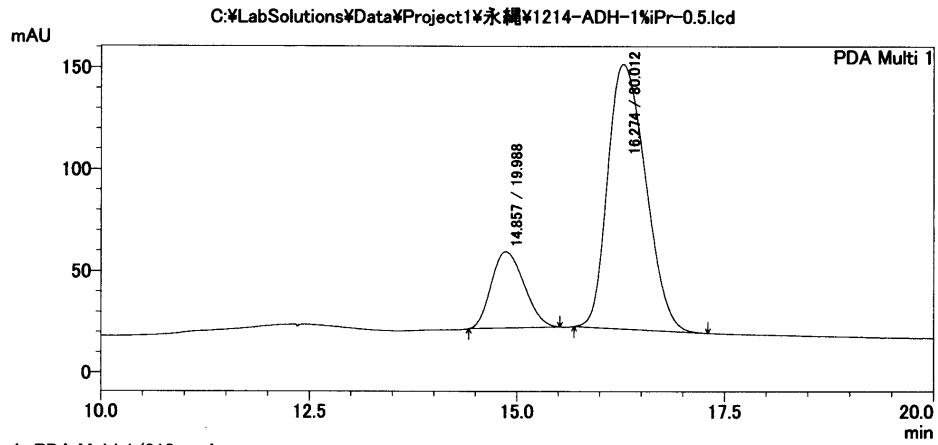


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1214-ADH-1%iPr-0.5.lcd
 サンプルID : yuki
 バイアル番号 : 69
 注入量 : 1 uL
 データファイル : 1214-ADH-1%iPr-0.5.lcd
 メソッドファイル : AD-H iPr 1% flow=0.5 60min before30min.lcm
 バッチファイル : 共用ばっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/02/16 21:03:22

No189

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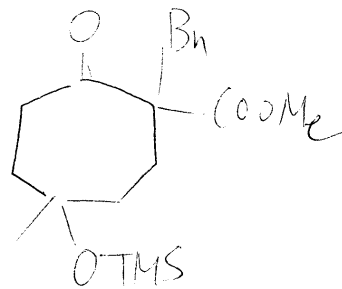
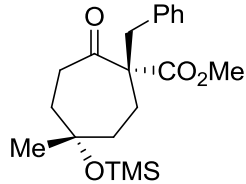
1 PDA Multi 1/210nm 4nm

<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1214-ADH-1%iPr-0.5.lcd

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%	マーク
1	14.857	1031614	19.988	
2	16.274	4129513	80.012	
合計		5161127	100.000	

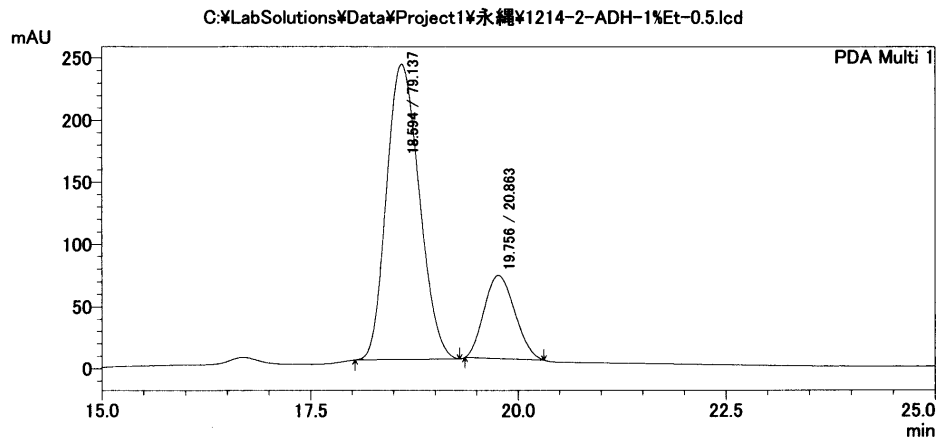


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1214-2-ADH-1\Et-0.5.lcd
 サンプルID : yuki
 バイアル番号 : 68
 注入量 : 1 uL
 データファイル : 1214-2-ADH-1\Et-0.5.lcd
 メソッドファイル : AD-H Et 1% flow=0.5 60min before30min.lcm
 バッチファイル : 共用ばっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/02/16 23:50:35

V-190

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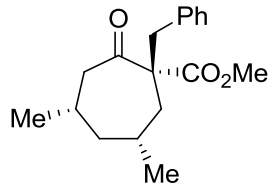


<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1214-2-ADH-1\Et-0.5.lcd

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%	マーク
1	18.594	6542924	79.137	
2	19.756	1724902	20.863	
合計		8267826	100.000	

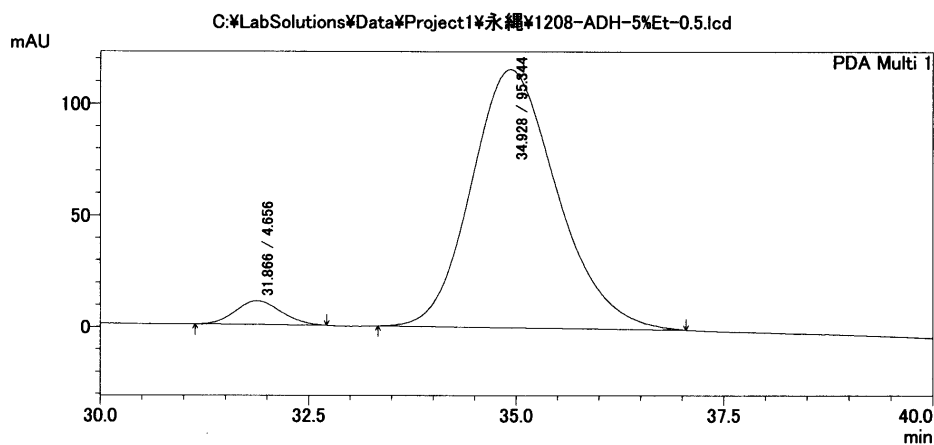


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1208-ADH-5%Et-0.5.lcd
 サンプルID : yuki
 バイアル番号 : 69
 注入量 : 1 uL
 データファイル : 1208-ADH-5%Et-0.5.lcd
 メソッドファイル : AD-H Et 5% flow=0.5 60min before30min.lcm
 バッチファイル : 共用ばっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/02/10 14:03:24

1037

<クロマトグラム>

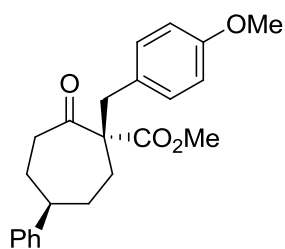


<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1208-ADH-5%Et-0.5.lcd

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%	マーク
1	31.866	407636	4.656	
2	34.928	8346752	95.344	
合計		8754388	100.000	

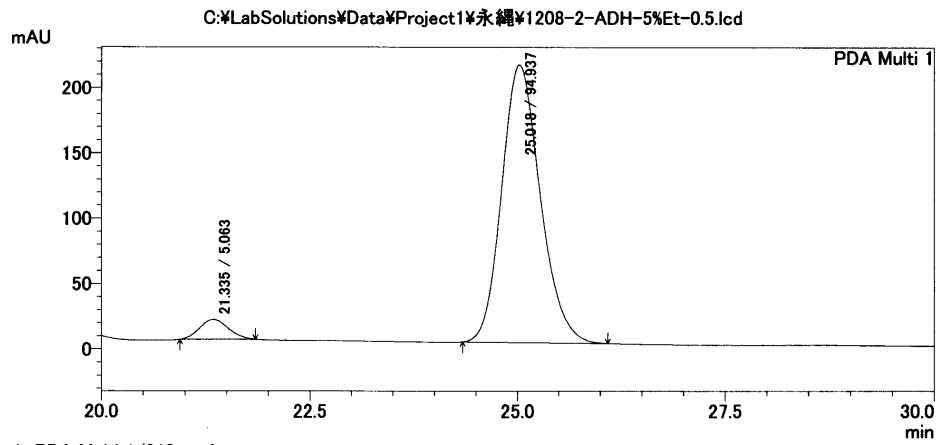


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1208-2-ADH-5%Et-0.5.lcd
 サンプルID : yuki
 バイアル番号 : 68
 注入量 : 1 uL
 データファイル : 1208-2-ADH-5%Et-0.5.lcd
 メソッドファイル : AD-H Et 5% flow=0.5 60min before30min.lcm
 バッチファイル : 共用ばっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/02/10 17:37:00

永縄

<クロマトグラム>



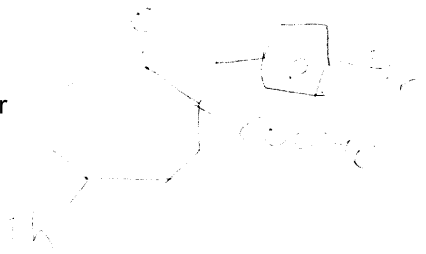
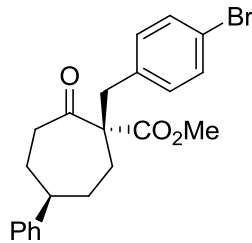
1 PDA Multi 1/210nm 4nm

<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1208-2-ADH-5%Et-0.5.lcd

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%	マーク
1	21.335	365870	5.063	
2	25.018	6860517	94.937	
合計		7226387	100.000	

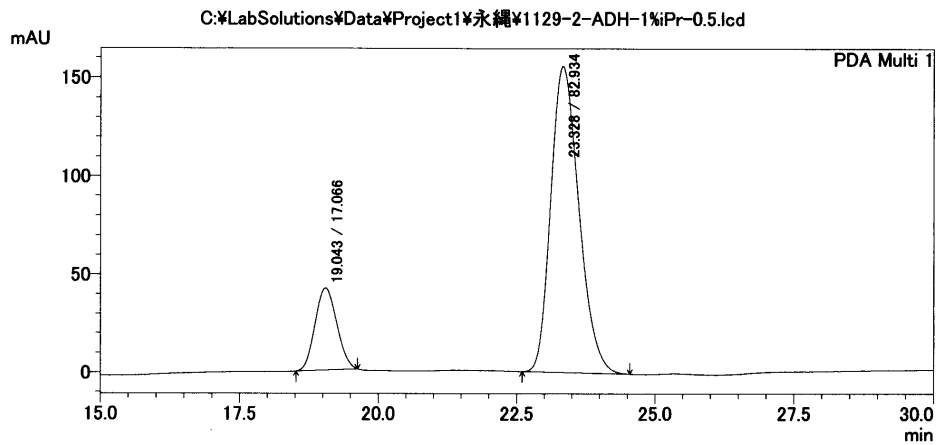


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1129-2-ADH-1%iPr-0.5.lcd
 サンプルID : yuki
 バイアル番号 : 69
 注入量 : 1 uL
 データファイル : 1129-2-ADH-1%iPr-0.5.lcd
 メソッドファイル : AD-H iPr 1% flow=0.5 60min before30min.lcm
 バッチファイル : 共用ばっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/02/01 11:53:30

No 178

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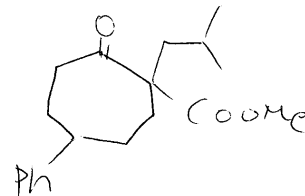
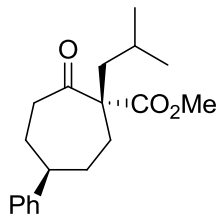


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C:\LabSolutions\Data\Project1\永縄\1129-2-ADH-1%iPr-0.5.lcd

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%	マーク
1	19.043	1140695	17.066	
2	23.328	5543486	82.934	
合計		6684181	100.000	

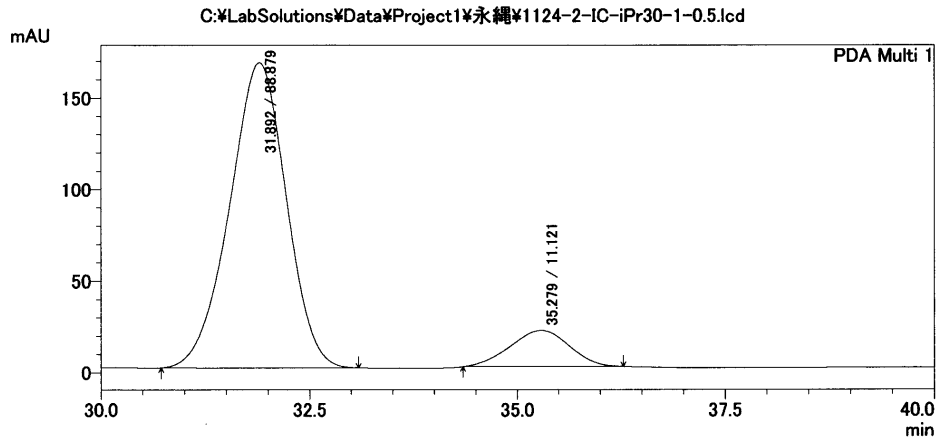


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1124-2-IC-iPr30-1-0.5.lcd
 サンプルID : yn-1124-2
 バイアル番号 : -1
 注入量 : 1 uL
 データファイル : 1124-2-IC-iPr30-1-0.5.lcd
 メソッドファイル : Method 120 min (190-360).lcm
 バッチファイル :
 レポートファイル : Default.lcr
 分析日時 : 2011/01/27 22:23:26

No169

<クロマトグラム>



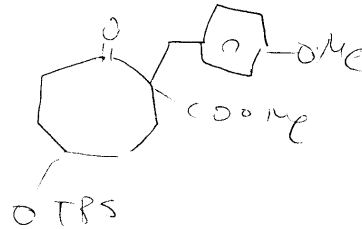
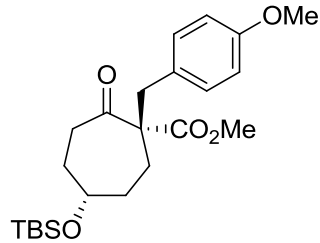
1 PDA Multi 1/210nm 4nm

<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1124-2-IC-iPr30-1-0.5.lcd

SPD-M20A Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%	マーク
1	31.892	7866651	88.879	
2	35.279	984329	11.121	
合計		8850980	100.000	

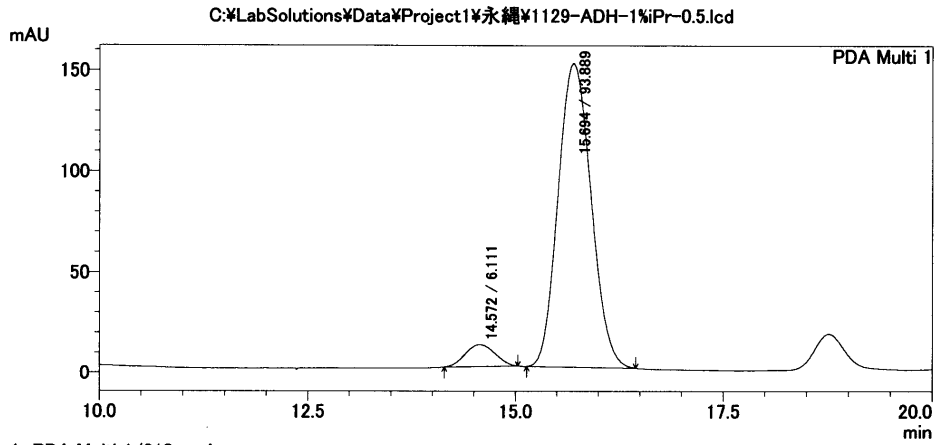


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1129-ADH-1%iPr-0.5.lcd
 サンプルID : yuki
 バイアル番号 : 68
 注入量 : 1 uL
 データファイル : 1129-ADH-1%iPr-0.5.lcd
 メソッドファイル : AD-H iPr 1% flow=0.5 60min before30min.lcm
 バッチファイル : 共用ばっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/02/01 5:06:07

No 176

<クロマトグラム>

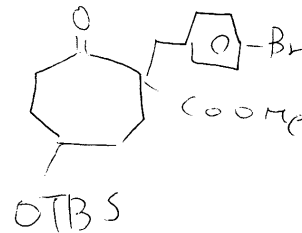
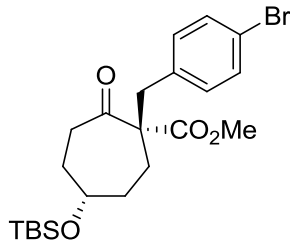


1 PDA Multi 1/210nm 4nm

<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1129-ADH-1%iPr-0.5.lcd

ピーク#	保持時間	面積	面積%	マーク
1	14.572	272544	6.111	
2	15.894	4187503	93.889	
合計		4460047	100.000	

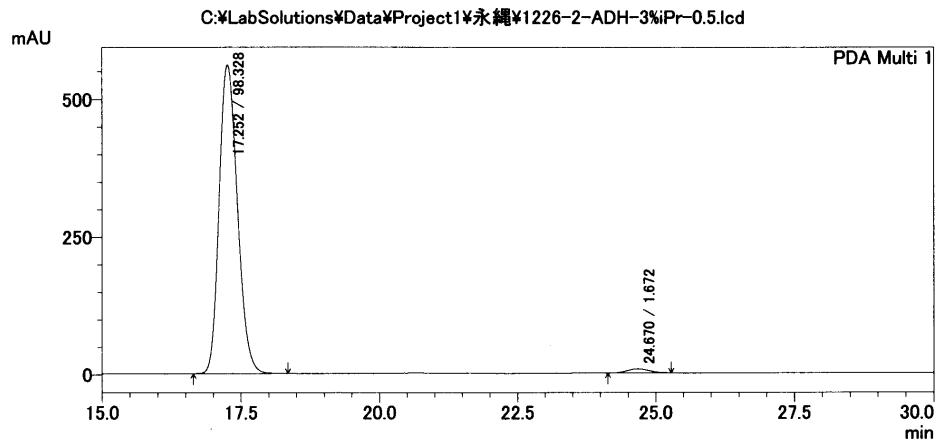


==== Shimadzu LCsolution 分析レポート ====

サンプル名 : C:\LabSolutions\Data\Project1\永縄\1226-2-ADH-3%iPr-0.5.lcd
 サンプルID : yuki
 バイアル番号 : 68
 注入量 : 1 uL
 データファイル : 1226-2-ADH-3%iPr-0.5.lcd
 メソッドファイル : AD-H iPr3% flow0.5 60min.lcm
 バッチファイル : 共用ぱっち.lcb
 レポートファイル : Default.lcr
 分析日時 : 2011/02/27 1:04:36

No199

<クロマトグラム>



<ピークレポート>

C:\LabSolutions\Data\Project1\永縄\1226-2-ADH-3%iPr-0.5.lcd

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%	マーク
1	17.252	12906232	98.328	
2	24.670	219432	1.672	
合計		13125664	100.000	

