

SUPPORTING INFORMATION

Multicomponent Synthesis of α -Branched Amides

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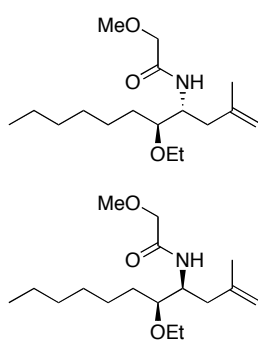
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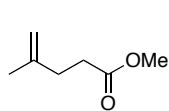
General Experimental Proton (^1H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at 300 MHz and 75 MHz or at 500 MHz and 125 MHz if specified. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^1H NMR: $\text{CDCl}_3 = 7.27$ ppm, $\text{CD}_3\text{OD} = 3.31$, for ^{13}C NMR: $\text{CDCl}_3 = 77.23$, $\text{CD}_3\text{OD} = 49.00$. Data are reported as follows: (s = singlet; d = doublet; t = triplet; q = quartet; sept = septet; sext = sextet; dd = doublet of doublets; ddd = doublet of doublet of doublets; dt = doublet of triplets; td = triplet of doublets; dtd = doublet of triplet of doublets; br = broad). High resolution and low resolution mass spectra were recorded on a VG 7070 spectrometer. Samples for IR were prepared as a thin film on a NaCl plate by dissolving the compound in CH_2Cl_2 and then evaporating the CH_2Cl_2 . Optical rotations were measured at ambient temperature. Tetrahydrofuran and diethyl ether were distilled from sodium and benzophenone. Methylene chloride and benzene was distilled under N_2 from CaH_2 . All acid chlorides were freshly distilled prior to use. Analytical TLC was performed on pre-coated (25 mm) silica gel 60F-254 plates. Visualization was done under UV (254 nm). Flash chromatography was done using 60 Å silica gel. Reagent grade ethyl acetate, diethyl ether and hexanes (commercial mixture) were used as is for chromatography. All reactions were performed in oven or flame-dried glassware under argon with magnetic stirring unless otherwise noted. All the reactions related to Schwartz reagent ($\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$) were performed under argon unless otherwise specified. The Schwartz reagent was prepared according to Buchwald's procedure.¹



N-anti-5-(Ethoxy-2-methylundec-1-en-4-yl)-2-methoxyacetamide (10)
and *N-syn-5-(ethoxy-2-methylundec-1-en-4-yl)-2-methoxyacetamide (11)*

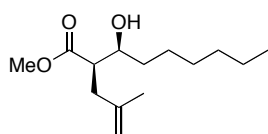
To a solution of **8**² (117 mg, 0.690 mmol) and CH_2Cl_2 (6.9 mL) was added $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ (213 mg, 0.828 mmol) and stirred for 15 minutes. The reaction was cooled to 0 °C and methoxyacetyl chloride (70 μL , 0.83 mmol) was added dropwise. The reaction was stirred for 15 minutes at 0 °C and ZnBr_2 (180 mg, 0.690 mmol) was added and stirred for 5 minutes. The reaction was removed from the ice bath and methylallyltrimethylsilane (266 mg, 2.07 mmol) was added dropwise. The reaction was stirred overnight at room temperature. The reaction was quenched with saturated NaHCO_3 (15 mL), washed with 1N HCl (10 mL) and brine (15 mL). The mixture was extracted with CH_2Cl_2 (3 x 15 mL) and the combined extracts were dried (MgSO_4), concentrated under reduced pressure and purified by column chromatography (5% - 35% EtOAc in hexanes) to give **11** (113 mg, 55%) as a colorless oil. When $\text{Sc}(\text{OTf})_3$ was used as the Lewis acid a 60% yield of a 1:1 mixture of **10** and **11** was isolated. For faster eluding *anti*-product **10**: ^1H NMR (300 MHz, CDCl_3) δ 6.59 (d, $J = 9.2$ Hz, 1H), 4.80 (s, 1H), 4.73 (s, 1H), 4.21 (ddt, $J = 1.7, 7.7, 9.4$ Hz, 1H), 3.88 (s, 2H), 3.62 (ddd, $J = 7.0, 9.3, 16.2$ Hz, 1H), 3.48 (ddd, $J = 2.2, 7.0, 14.0$ Hz, 1H), 3.41 (s, 3H), 3.35-3.25 (m, 1H), 2.32 (dd, $J = 7.1, 13.8$ Hz, 1H), 2.24 (dd, $J = 8.0, 13.7$ Hz, 1H), 1.77 (s, 3H), 1.57-1.23 (m, 10H), 1.19 (t, $J = 7.0$ Hz, 3H), 0.88 (t, $J = 6.8$, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 169.2, 142.6, 113.0, 79.4, 72.1, 66.0, 59.2, 48.5, 40.7, 31.7, 31.3, 29.4, 25.8, 22.6, 22.1, 15.7, 14.0; IR (neat) 3420, 2928, 2857, 1680, 1597, 1517, 1450, 1377, 1113 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{33}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 322.2338, found 322.2358. For slower eluding *syn*-product **11**: ^1H NMR (300 MHz, CDCl_3) δ 6.50 (d, $J = 9.1$ Hz, 1H), 4.77 (s, 1H), 4.72 (s, 1H), 4.33-4.18 (m, 1H), 3.86 (d, $J = 3.9$ Hz, 2H) 3.5 (ddd, $J = 2.2, 7.1, 9.2$ Hz, 2H), 3.48-3.32 (m, 6H), 2.27 (dd, $J = 4.2, 14.3$ Hz, 1H), 2.19 (dd, $J = 6.5, 14.2$ Hz, 1H), 1.74 (s, 3H), 1.57-1.15 (m, 8H), 0.88 (t, $J = 6.36$ Hz,

3H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.9, 142.4, 112.9, 81.3, 72.0, 66.1, 59.2, 48.5, 37.4, 31.7, 31.1, 29.4, 25.8, 22.6, 22.0, 15.6, 14.0; IR (neat) 3418, 2928, 2857, 1677, 1523, 1455, 1375, 1114 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{33}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 322.2338, found 322.2358.



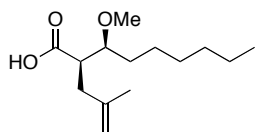
Methyl 4-methylpent-4-enoate (**12**)³

To a solution of 2-methylprop-2-en-1-ol (3.02 g, 41.9 mmol) and trimethyl orthoacetate (2.01 g, 16.8 mmol) was added propionic acid (154 mg, 2.09 mmol) at room temperature. The reaction was heated to 140 °C for 1 hour. After 1 hour, the reaction flask was cooled to 110 °C and fitted with a short path distillation head and the volatile side products were collected for 1 hour. The mixture was then heated to 160 °C until no more waste was collected. The mixture was cooled to room temperature, then extracted with Et_2O (3 x 15 mL), and washed with water (2 x 10 mL) and brine (1 x 10 mL). The combined organic extracts were dried (MgSO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (2%-5% Et_2O in pentane) to give the desired product (1.98 g, 88%): ^1H NMR (300 MHz, CDCl_3) δ 4.77 (s, 1H), 4.71 (s, 1H), 3.67 (s, 3H), 2.42 (m, 2H), 2.33 (m, 2H), 1.73 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 174.3, 144.7, 110.9, 52.2, 33.2, 33.0, 23.1.



syn-Methyl 3-hydroxy-2-(2-methylallyl)nonanoate (**13**)

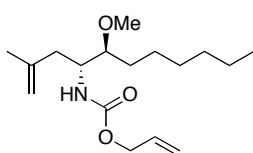
To a solution of **12** (1.87 g, 14.6 mmol) in CH_2Cl_2 (117 mL) was added $i\text{Pr}_2\text{NEt}$ (2.83 g, 21.89 mmol) dropwise at -78 °C. Immediately after, Bu_2BOTf (1M solution in CH_2Cl_2 , 18.8 mL, 18.8 mmol) was added dropwise. The reaction was stirred for 2 hours at -78 °C. After 2 hours, *n*-heptanal (2.17 g, 19.0 mmol) was added dropwise at -78 °C and stirred for 1 hour. The reaction was warmed to 0 °C and stirred for 1.5 hours then cooled to -78 °C and quenched with 150 mL of a buffered peroxide solution (pH 7 phosphate buffer (53 mL), 30% hydrogen peroxide (26 mL), and MeOH (513 mL)). The mixture was stirred for 4 hours at 0 °C then was concentrated to ~30 mL, extracted with EtOAc (4 x 20 mL), and washed with brine (1 x 20 mL). The combined organic extracts were dried (MgSO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (10%-25% Et_2O in pentane) to give desired product (1.61 g, 45%): ^1H NMR (300 MHz, CDCl_3) δ 4.75 (s, 1H), 4.70 (s, 1H), 3.79 (m, 1H), 3.68 (s, 3H), 2.70 (m, 1H), 2.40 (m, 2H), 1.75 (s, 3H), 1.45 (m, 3H), 1.33 (m, 8H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 175.4, 143.1, 112.1, 72.1, 51.6, 49.5, 35.5, 34.2, 31.75, 29.7, 29.2, 25.8, 22.6, 22.3, 14.1; IR (neat) 3456, 2930, 2857, 1738, 1650, 1439, 1375, 1262, 1199, 1164, 1037, 892 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{24}\text{O}_2$ $[\text{M}-\text{H}_2\text{O}]^+$ 224.1882, found 224.1876.



syn-3-Methoxy-2-(2-methylallyl)nonanoic acid (**14**)

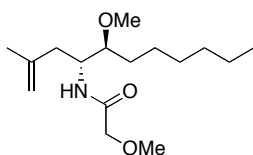
To a solution of **13** (200 mg, 0.825 mmol) in CH_2Cl_2 (1.6 mL) at 0 °C were sequentially added 2,6-di-*tert*-butylpyridine (237 mg, 1.24 mmol) and methyl triflate (820 mg, 5 eq). After 10 minutes the reaction was warmed to room temperature and stirred for 2 days. The mixture was quenched with water (10 mL), then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried (MgSO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (2%-10% EtOAc in hexanes) to give desired product (216 mg, 89%): ^1H NMR (300 MHz, CDCl_3) δ 4.72 (s, 1H), 4.68 (s, 1H), 3.66 (s, 3H), 3.38 (s, 3H), 3.33 (m, 2H), 2.82 (ddd, J = 5.1, 6.9, 9.9 Hz, 1H), 2.36 (m, 2H), 1.74 (s, 3H), 1.48-1.26 (m, 6H), 1.21 (t, J = 7.0 Hz, 3H), 0.89 (t, J = 6.9, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 174.3, 143.3, 111.6, 81.9, 57.8, 51.5, 48.0, 36.7, 31.8, 31.7,

29.7, 29.4, 25.2, 22.6, 22.4, 15.3, 14.1; IR (neat) 2926, 2856, 1724, 1618, 1418, 1325, 1194, 1091 cm^{-1} . To a solution of the methyl ester (40 mg, 0.16 mmol) in *p*-dioxane/ H_2O (2:1, 3 mL) was added lithium hydroxide monohydrate (59 mg, 1.4 mmol). After 10 minutes the reaction was fitted with a condenser, heated to 40 $^\circ\text{C}$, and stirred overnight. The reaction was cooled to room temperature and acidified to pH 1 with 0.5N HCl. The mixture was extracted with Et_2O (5 x 10 mL), then the combined organic extracts were dried (MgSO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (12%-40% EtOAc in hexanes) to give desired product (39 mg, 94%): ^1H NMR (300 MHz, CDCl_3) δ 4.80 (s, 1H), 4.76 (s, 1H), 3.42 (s, 3H), 3.38-3.35 (m, 1H), 2.86 (td, $J = 9.6, 5.6$ Hz, 1H), 1.76 (s, 3H), 1.54-1.29 (m, 10H) 0.89 (t, $J = 6.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 178.6, 142.7, 111.9, 81.7, 57.7, 46.9, 35.8, 31.7, 31.3, 30.3, 29.2, 25.3, 22.5, 22.3, 13.99; IR (neat) 3077, 2930, 2858, 1709, 1651, 1445, 1376, 1287, 1159, 1100, 892 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{26}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$ 265.1780, found 265.1769.



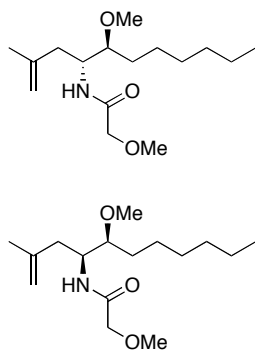
Allyl *anti*-5-methoxy-2-methylundec-1-en-4-ylcarbamate (15)

To a solution of **14** (21 mg, 0.087 mmol) in dry *p*-dioxane (1 mL), was added diphenylphosphoryl azide (24 mg, 0.087 mmol), allyl alcohol (50 mg, 0.87 mmol) and triethylamine (8.9 mg, 0.087 mmol) at room temperature. The reaction was fitted with a condenser, heated to 110 $^\circ\text{C}$, and stirred overnight. The mixture was then cooled to room temperature, quenched with water (10 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic extracts were dried with (MgSO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (5%-7% EtOAc in hexanes) to give the desired product (5.6 mg, 23%): ^1H NMR (300 MHz, CDCl_3) δ 6.02-5.84 (m, 1H), 5.29 (d, $J = 17.2$ Hz, 1H), 5.20 (d, $J = 10.4$ Hz, 1H), 4.81 (s, 1H), 4.75 (s, 1H), 4.58 (d, $J = 5.4$ Hz, 2H), 4.03-3.95 (m, 1H), 3.40 (s, 3H), 3.27 (br s, 1H), 2.23 (dd, $J = 4.0, 14.3$ Hz, 1H), 2.11 (dd, $J = 10.6, 14.2$ Hz, 1H), 1.75 (s, 3H), 1.57-1.23 (m, 8H), 0.90 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 161.2, 147.6, 138.3, 134.8, 122.6, 118.4, 88.6, 70.61, 63.7, 56.1, 42.8, 36.9, 35.6, 34.7, 31.0, 27.8, 27.2, 19.3; IR (neat) 3336, 2928, 2856, 1702, 1650, 1509, 1457, 1376, 1319, 1243, 1152, 1097 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{31}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 320.2202, found 320.2213.



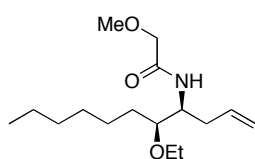
2-Methoxy-*N-anti*-5-methoxy-2-methylundec-1-en-4-yl)acetamide (16)

To a solution of **15** (6.4 mg, 0.022 mmol) and CH_2Cl_2 (0.40 mL) was added methoxyacetyl chloride (2.5 mg, 0.023 mmol) at room temperature. A solution of $\text{Pd}(\text{PPh}_3)_4$ (0.02 M, 0.24 mL, 5 μmol) was added followed by Bu_3SnH (7.0 mg, 0.024 mmol). The mixture was stirred for 4 hours. The reaction was quenched with water (12 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organics were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (8%-30% EtOAc in hexanes) to give the desired product (5.2 mg, 81%): ^1H NMR (300 MHz, CDCl_3) δ 6.56 (d, $J = 9.1$ Hz, 1H), 4.78 (s, 1H), 4.72 (s, 1H), 4.33-4.24 (m, 1H), 3.89 (app d, $J = 15.4$, 2H) 3.5-3.42 (m, 2H), 3.39 (s, 6H), 3.31-3.22 (m, 1H), 2.25 (dd, $J = 3.9, 14.2$ Hz, 1H), 2.15 (dd, $J = 10.7, 14.2$ Hz, 1H), 1.74 (s, 3H), 1.65-1.15 (m, 8H), 0.88 (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 169.3, 142.2, 113.0, 83.2, 69.4, 59.3, 59.2, 58.4, 37.2, 31.7, 30.5, 29.4, 25.8, 22.6, 21.9, 14.0; IR (neat) 3418, 2929, 2856, 2827, 1680, 1523, 1456, 1196, 1111 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{31}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 308.2202, found 308.2202.



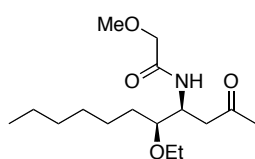
2-Methoxy-*N*-anti-5-methoxy-2-methylundec-1-en-4-yl)acetamide (16)
and 2-Methoxy-*N*-syn-5-methoxy-2-methylundec-1-en-4-yl)acetamide (18)

To a solution of methoxy nitrile **17** (80 mg, 0.52 mmol) in CH₂Cl₂ (5.0 mL) was added Cp₂Zr(H)Cl (159 mg, 0.618 mmol). The reaction was stirred for 15 min, then cooled to 0 °C and methoxyacetyl chloride (66 μL, 0.72 mmol) was added. The cold bath was removed and the mixture was stirred for 15 min. the flask was cooled to 0 °C and Sc(OTf)₃ (253 mg, 0.515 mmol) was added. The mixture was stirred at 0 °C for 10 min, and then cooled to -78 °C. Methallyltrimethylsilane (0.27 mL, 1.5 mmol) was added dropwise. After 5 min, the cold bath was removed and the reaction was stirred overnight. After that time, the reaction was quenched with saturated NaHCO₃ solution (2 mL) and water (15 mL), and extracted with EtOAc (3 x 25 mL). The combined organic extracts were dried (Na₂SO₄), filtered and concentrated. The residue was purified by column chromatography (15% - 25% EtOAc in hexanes) to give amides **16** and **18** (79 mg, 54%) as a 1:1 mixture.



***N*-syn-5-ethoxyundec-1-en-4-yl)-2-methoxyacetamide (19)**

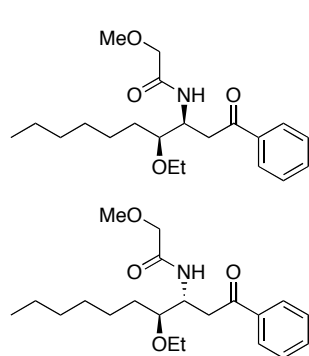
To a solution of **8** (117 mg, 0.690 mmol) and CH₂Cl₂ (6.9 mL) was added Cp₂Zr(H)Cl (213 mg, 0.828 mmol). The mixture was stirred for 15 minutes then was cooled to 0 °C and methoxyacetyl chloride (70 μL, 0.83 mmol) was added dropwise. The reaction was stirred for 15 minutes at 0 °C and ZnBr₂ (180 mg, 0.690 mmol) was added and stirred for 5 minutes. The reaction was removed from the ice bath and allyltrimethylsilane (394 mg, 3.45 mmol) was added dropwise and the reaction was stirred for 72 hours. The reaction was quenched with saturated NaHCO₃ (15 mL), washed with 1N HCl (10 mL) and brine (15 mL). The mixture was extracted with CH₂Cl₂ (3 x 15 mL) and the combined extracts were dried (MgSO₄), concentrated under reduced pressure and purified by column chromatography (5% - 40% EtOAc in hexanes) to give desired product (37 mg, 19%) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 6.62 (d, *J* = 9.3 Hz, 1H), 5.78 (tdd, *J* = 7.0, 10.1, 17.1 Hz, 1H), 5.13-5.0 (m, 2H), 4.08 (ddt, *J* = 2.2, 7.3, 9.4 Hz, 1H), 3.89 (s, 2H), 3.64 (ddd, *J* = 7.0, 9.2, 16.2 Hz, 1H), 3.55-3.44 (m, 1H), 3.41 (s, 3H), 3.33-3.27 (m, 1H), 2.44-2.27 (m, 2H), 1.56-1.21 (m, 5H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.2, 135.1, 117.3, 79.4, 72.1, 65.9, 59.2, 50.2, 37.0, 31.7, 31.3, 29.4, 25.7, 22.6, 15.6, 14.0; IR (neat) 3420, 2929, 2857, 1684, 1518, 1456, 1197, 1112, 914 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₆H₃₁NNaO₃ [M+Na]⁺ 308.2202, found 308.2209.



***N*-syn-5-ethoxy-2-oxoundecan-4-yl)-2-methoxyacetamide (20)**

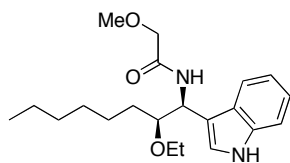
To a solution of **8** (111 mg, 0.654 mmol) in CH₂Cl₂ (6.5 mL) was added Cp₂Zr(H)Cl (210 mg, 0.818 mmol). The reaction was stirred for 15 minutes then was cooled to 0 °C and methoxyacetyl chloride (84 μL, 0.92 mmol) was added dropwise. The reaction was stirred for 15 minutes at 0 °C followed by the addition of ZnBr₂ (171 mg, 0.654 mmol). The mixture was stirred for 10 minutes the was cooled to -78 °C and 2-trimethylsilyloxypropene (170 mg, 1.31 mmol) was added dropwise. After 5 minutes the mixture was warmed to room temperature and stirred overnight. The reaction was quenched with saturated NaHCO₃ (15 mL), then was washed with

1N HCl (10 mL) and brine (15 mL). The mixture was extracted into CH₂Cl₂ (3 x 15 mL) and the combined extracts were dried (MgSO₄), concentrated under reduced pressure and purified by column chromatography (30% - 50% EtOAc in hexanes) to give the desired product (110 mg, 56% yield) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 6.79 (d, *J* = 8.9 Hz, 1H), 4.47 (ddt, *J* = 2.1, 6.0, 8.1 Hz, 1H), 3.86 (s, 2H), 3.63 (ddd, *J* = 7.0, 9.4, 16.3), 3.5-3.33 (m, 6H), 2.77 (dd, *J* = 7.5, 16.2 Hz, 1H), 2.64 (dd, *J* = 6.2, 16.3 Hz, 1H), 2.17 (s, 3H), 1.67-1.23 (m, 10H), 1.18 (t, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 6.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 207.5, 169.8, 80.0, 72.6, 66.5, 59.8, 47.7, 46.4, 32.3, 31.7, 30.8, 29.9, 26.2, 23.1, 16.1, 14.6; IR (neat) 3418, 3336, 3062, 2929, 2858, 1683, 1597, 1580, 1519, 1450, 1371, 1284, 1198, 1113, 988 cm⁻¹; HRMS (ESI): *m/z* calcd for C₁₆H₃₁NNaO₄ [M+Na]⁺ 324.2151, found 324.2146.



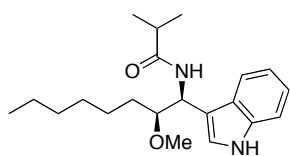
***N*-syn-4-ethoxy-1-oxo-1-phenyldecan-3-yl)-2-methoxyacetamide (21) and *N*-anti-4-ethoxy-1-oxo-1-phenyldecan-3-yl)-2-methoxyacetamide**

To a solution of **8** (104 mg, 0.612 mmol) in CH₂Cl₂ (6.1 mL) was added Cp₂Zr(H)Cl (197 mg, 0.765 mmol). The mixture was stirred for 15 minutes then was cooled to 0 °C. Methoxyacetyl chloride (93 μL, 0.86 mmol) was added dropwise, the reaction was stirred for 15 minutes at 0 °C, then ZnBr₂ (160 mg, 0.612 mmol) was added and the mixture was stirred for 10 minutes. The reaction was cooled to -78 °C and 2-trimethylsilyloxy-3-phenyl-1-propene (170 mg, 1.31 mmol) was added dropwise and stirred for 3 hours at -78 °C. The reaction was quenched with saturated NaHCO₃ (15 mL) at -78 °C and warmed to room temperature, then was washed with 1N HCl (10 mL) and brine (15 mL). The mixture was extracted with CH₂Cl₂ (3 x 15 mL) and the combined extracts were dried (MgSO₄), concentrated under reduced pressure and purified by column chromatography (10% - 30% EtOAc in hexanes) to give desired product (125 mg, 56% yield) as a colorless oil in a 5.25:1 (*anti*:*syn*) diastereomeric ratio. For the faster eluding *anti*-product: ¹H NMR (300 MHz, CDCl₃) δ 8.05-7.96 (m, 2H), 7.61-7.57 (m, 1H) 7.55-7.43 (m, 2H), 4.60 (ddt, *J* = 1.9, 5.1, 8.5 Hz, 1H), 3.89 (s, 2H), 3.63 (ddd, *J* = 7.0, 9.3, 16.4 Hz, 1H), 3.55-3.38 (m, 6H), 3.32 (dd, *J* = 8.3, 16.2 Hz, 1H) 3.21 (dd, *J* = 5.2, 16.2 Hz, 1H), 1.6-1.22 (m, H), 1.16 (t, *J* = 7.0 Hz, 3H), 0.87 (t, *J* = 6.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 198.9, 169.8, 137.4, 133.8, 129.3, 128.8, 79.6, 72.7, 66.5, 59.8, 48.5, 41.1, 32.3, 31.8, 30.0, 26.2, 23.2, 16.2, 14.6; IR (neat) 3417, 3305, 2921, 2855, 1713, 1676, 1520, 1452, 1358, 1297, 1197, 1111, 985 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₁H₃₄NO₄ [M+H]⁺ 364.2478, found 364.2488. For the slower eluding *syn*-product **21**: 8.06-7.92 (m, 2H), 7.63-7.53 (m, 1H), 7.53-7.43 (m, 1H), 7.19 (d, *J* = 8.9 Hz, 1H), 4.65-5.48 (m, 1H), 3.86 (d, *J* = 3.7 Hz, 2H), 3.68-3.39 (m, 8H), 3.39-3.13 (m, 1H), 3.09 (dd, *J* = 4.7, 16.8 Hz, 1H), 1.55-1.13 (m, 9H), 1.09 (t, *J* = 6.0 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 199.8, 169.6, 137.7, 133.8, 80.8, 72.6, 66.4, 59.8, 49.1, 38.5, 32.4, 31.9, 30.1, 25.8, 23.2, 16.1, 14.7; IR (neat) 3417, 3305, 2921, 2855, 1713, 1676, 1520, 1452, 1358, 1297, 1197, 1111, 985 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₁H₃₄NO₄ [M+H]⁺ 364.2478, found 364.2488.



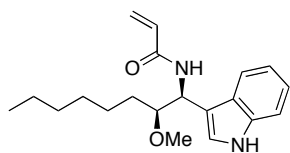
***N*-syn-2-ethoxy-1-(1H-indol-3-yl)octyl-2-methoxyacetamide (22)**

To a solution of **8** (113 mg, 0.666 mmol) in CH₂Cl₂ (6.7 mL) was added Cp₂Zr(H)Cl (206 mg, 0.799 mmol). The mixture was stirred for 15 minutes then was cooled to 0 °C. Methoxyacetyl chloride (94 μL, 0.93 mmol) was added dropwise, the reaction was stirred for 15 minutes at 0 °C, then ZnBr₂ (173 mg, 0.666 mmol) was added and stirred for 10 minutes. The reaction was cooled to -78 °C and indole (234 mg, 2.00 mmol) was added. The reaction was stirred for 3 hours at -78 °C, then was quenched with saturated NaHCO₃ (15 mL). The organic layer was washed with 1N HCl (10 mL) and brine (15 mL). The aqueous phases were extracted with CH₂Cl₂ (3 x 15 mL) and the combined extracts were dried (MgSO₄), concentrated under reduced pressure and purified by column chromatography (10% - 30% EtOAc in hexanes) to give the desired product (134 mg, 56% yield) as a light brown oil. ¹H NMR (300 MHz, CDCl₃) δ 8.09 (br s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.25 (br, 1H), 7.24-7.1 (m, 3H), 5.47 (dd, *J* = 2.2, 9.2 Hz, 1H), 3.97 (d, *J* = 15.0 Hz, 1H) 3.91 (d, *J* = 15.0 Hz, 1H), 3.72 (td, *J* = 2.5, 3.8, 6.3 Hz, 1H), 3.57-3.47 (m, 1H), 3.43 (s, 3H), 3.34-3.24 (m, 1H), 1.7-1.17 (m, 10H), 1.10 (t, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.3, 136.6, 126.4, 122.5, 122.1, 119.9, 119.8, 116.9, 111.5, 81.9, 72.5, 66.3, 65.0, 59.6, 48.3, 32.4, 32.1, 29.8, 26.3, 22.9, 15.9, 14.4; IR (neat) 3414, 3298, 2928, 2856, 1664, 1525, 1457, 1113, 741 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₁H₃₂N₂NaO₃ [M+Na]⁺ 383.2311, found 383.2310.



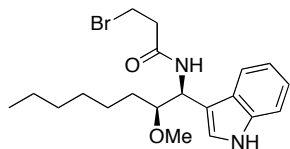
***N*-syn-(1-(1H-indol-3-yl)-2-methoxyoctyl)isobutyramide (23)**

To a solution of **17** (100 mg, 0.64 mmol) in CH₂Cl₂ (6.5 mL) at room temperature was added Cp₂Zr(H)Cl (200 mg, 0.77 mmol). After 10 minutes, the reaction mixture was cooled to 0 °C and isobutyl chloride (96 μL, 0.90 mmol) was added dropwise. After 10 minutes, the reaction mixture was cooled to -78 °C, ZnBr₂ (170 mg, 0.64 mmol) was added, and the solution was stirred for an additional 10 minutes. Afterwards, indole (150 mg 1.29 mmol) was added and the reaction was stirred at -78 °C. After 3 hours satd. NaHCO₃ (aq) (10 mL) was added, and the reaction was warmed to room temperature. The reaction mixture was extracted with CH₂Cl₂ (3 x 4 mL), and the combined organic layers were washed with 1M HCl (4 mL) and brine (4 mL). The organic layer was dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The crude residue was purified via flash chromatography (40% EtOAc in hexane) to afford the desired product as a mixture of inseparable diastereomers (dr: 4.2: 1.0, 104 mg, 47%): ¹H NMR (300 MHz, CDCl₃) δ 8.55 (br s, 1 H), 7.72-7.68 (m, 1 H), 7.35-7.32 (m, 1 H), 7.22-7.00 (m, 3 H) 6.25 (d, *J* = 9 Hz, 0.81 H), 6.11 (d, *J* = 8.4 Hz, 0.19 H), 5.50-5.44 (m, 1 H), 3.67-3.62 (m, 1H), 3.52 (s, 0.58 H), 3.28 (s, 2.42 H), 2.49-2.31 (m, 1 H), 1.69-1.28 (m, 10 H), 1.21 (d, *J* = 6.9 Hz, 3 H), 1.18-1.11 (m, 3 H), 0.92-0.82 (m, 3 H); ¹³C NMR (75 MHz, CDCl₃) δ 176.4, 175.9, 136.4, 135.9, 127.0, 126.0, 123.7, 122.0, 121.9, 119.6, 119.4, 119.4, 116.4, 112.7, 111.3, 111.1, 84.0, 83.3, 58.8, 58.0, 48.4, 47.9, 35.8, 35.7, 31.7, 31.1, 29.4, 26.0, 25.7, 22.6, 22.5, 19.8, 19.7, 19.6, 19.4, 14.1; IR (neat): 3307, 2929, 2857, 2360, 2339, 1649, 1512, 1459, 1097 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₂₁H₃₂N₂O₂Na [M + Na]⁺ 367.2361 found 367.2330.



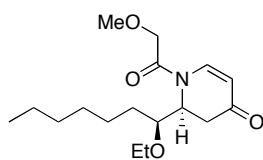
***N*-syn-(1-(1H-indol-3-yl)-2-methoxyoctyl)acrylamide (24)**

To a solution of **17** (100 mg, 0.65 mmol) in CH₂Cl₂ (6.5 mL) at room temperature was added Cp₂Zr(H)Cl (200 mg, 0.77 mmol). After 15 minutes, the reaction mixture was cooled to 0 °C and acryloyl chloride (73 μL, 0.90 mmol) was added dropwise. After 15 minutes the reaction mixture was cooled to -78 °C, ZnBr₂ was added (170 mg, 0.65 mmol), and the solution was stirred for an additional 10 minutes. Afterwards, indole (151 mg 1.29 mmol) was added and the reaction was stirred at -78 °C. After 22 hours satd. NaHCO₃ (aq) (10 mL) was added, and the reaction was warmed to room temperature. The reaction mixture was extracted with CH₂Cl₂ (3 x 4 mL), and the combined organic layers were washed with 1M HCl (4 mL) and brine (4 mL). The organic layer was dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The crude residue was purified via flash chromatography (40% EtOAc in hexane) to afford the desired product as a mixture of inseparable diastereomers (dr: 4.9: 1.0; 90 mg, 42%): ¹H NMR (300 MHz, CDCl₃) δ 8.31 (br s, 1 H), 7.61-7.71 (m, 1 H), 7.37-7.34 (m, 0.84 H), 7.29-7.28 (m, 0.16 H), 7.22-7.08 (m, 3 H), 6.38-6.28 (m, 2 H), 6.20-6.09 (m, 1 H), 5.66-5.61 (m, 1 H), 5.60-5.52 (m, 1 H), 3.70-3.65 (m, 1 H), 3.52 (s, 0.51 H), 3.30 (s, 2.49 H), 1.71-1.21 (m, 10 H), 0.92-0.81 (m, 3 H); ¹³C NMR (75 MHz, CDCl₃) δ 165.0, 136.3, 135.9, 132.3 131.0, 127.0, 126.4, 126.1, 123.8, 122.1, 122.0, 119.8, 119.6, 119.5, 119.4, 116.4, 112.7, 111.2, 11.1, 84.0, 83.3, 77.2, 58.6, 58.0, 48.4, 48.2, 31.8, 31.7, 31.2, 31.0, 29.4, 29.4, 29.2, 26.0, 25.8, 22.6, 22.5, 14.1, 14.0; IR (neat): 3288, 2929, 2857, 1657, 1623, 1514, 1407, 1097 cm⁻¹ HRMS (ESI) *m/z* calcd. for C₂₀H₂₈N₂O₂Na [M + Na] 351.2048 found 351.2039.



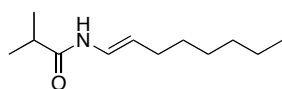
***N*-syn-(1-(1H-indol-3-yl)-2-methoxyoctyl)-3-bromopropanamide (25)**

To a solution of **17** (50 mg, 0.32 mmol) in CH₂Cl₂ (3.2 mL) at room temperature was added Cp₂Zr(H)Cl (100 mg, 0.39 mmol). After 15 minutes, the reaction mixture was cooled to 0 °C and 3-bromopropionyl chloride (46 μL, 0.45 mmol) was added dropwise. After 15 minutes the reaction mixture was cooled to -78 °C, ZnBr₂ (0.084 g, 0.48 mmol) was added, and the solution was stirred for an additional 10 minutes. Afterwards, indole (75 mg, 0.64 mmol) was added and the reaction was stirred at -78 °C. After 12 hours, satd. NaHCO₃ (aq) (10 mL) was added, and the reaction was warmed to room temperature. The reaction mixture was extracted with CH₂Cl₂ (3 x 4 mL), and the combined organic layers were washed with 1M HCl (4 mL) and brine (4 mL). The organic layer was dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The crude residue was purified via flash chromatography (40% EtOAc in hexane) to afford the desired product as a mixture of inseparable diastereomers (dr: 4.5:1.0; 74 mg, 46%) (underlined values denote the distinguishable major isomer): ¹H NMR (300 MHz, (DMSO-*d*₆) δ 10.94 (br s, 0.21 H), 10.91 (br s, 0.79 H), 8.25 (d, *J* = 9.3 Hz, 1 H), 7.59 (d, *J* = 8.1 Hz, 1 H) 7.35 (d, *J* = 8.1 Hz, 1 H), 7.29 (d, *J* = 1.8 Hz, 0.18 H) 7.26 (d, *J* = 2.1 Hz, 0.82 H), 7.07 (app t, *J* = 8.1 Hz, 1 H), 6.97 (app t *J* = 7.2 Hz, 1 H), 5.44 (dd, *J* = 4.2 Hz, 8.4 Hz, 0.18 H), 5.38 (dd, *J* = 4.2 Hz, 9.3 Hz, 0.82 H), 3.80 (ddd, *J* = 1.8, 5.7, 7.8 Hz, 1 H), 3.66 (ddd, *J* = 1.8, 6.3, 8.7 Hz, 1 H), 3.54 (dd, *J* = 5.7, 9.9 Hz, 1 H), 3.32 (s, 0.54 H), 3.23 (s, 2.46 H), 2.77-2.63 (m, 2 H), 1.45-1.18 (m, 10 H), 0.86-0.79 (m, 3 H); ¹³C NMR (75 MHz, (DMSO-*d*₆) δ 168.5, 168.3, 136.0, 126.2, 123.0, 121.0, 118.8, 118.4, 114.4, 111.4, 82.6, 57.3, 47.3, 41.3, 38.3, 38.1, 31.2, 30.4, 29.9, 28.9, 25.2, 22.1, 14.0; IR (neat): 3465, 3424, 3314, 3053, 2930, 2858, 1667, 1582, 1458, 1422, 1265, 1096 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₂₀H₂₉N₂O₂NaBr [M + Na] 431.1310, found 431.1311.



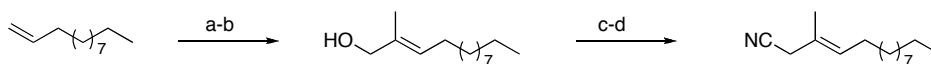
(1-Ethoxyheptyl)-1-(2-methoxyacetyl)-2,3-dihydropyridin-4(1H)-one (28)

To a solution of **8** (196 mg, 1.15 mmol) in CH₂Cl₂ (11.2 mL) was added Cp₂Zr(H)Cl (384 mg, 1.49 mmol). The mixture was stirred for 15 minutes then was cooled to 0 °C and methoxyacetyl chloride (117 μL, 1.72 mmol) was added dropwise. The reaction was stirred for 15 minutes at 0 °C, then ZnBr₂ (160 mg, .612 mmol) was added and the mixture stirred for 10 minutes. The reaction was cooled to -78 °C and the Danishefsky diene (**26**, 296 mg, 1.72 mmol) was added dropwise and stirred for 3 hours at -78 °C. The reaction was quenched with saturated NaHCO₃ (15 mL) at -78 °C, warmed to room temperature, and washed with brine (15 mL). The mixture was extracted with CH₂Cl₂ (3 x 15 mL) and the combined extracts were dried (MgSO₄), concentrated under reduced pressure and partially purified by column chromatography (20% - 60% EtOAc in hexanes, 5% intervals) to give intermediate **27** (115 mg, 28% yield) as a light brown oil. The crude product (110 mg, 0.308 mmol) was dissolved in toluene (3.1 mL). Au(PPh₃)Cl (46 mg, 0.092 mmol) and AgSbF₆ (53 mg, 0.15 mmol) were added to the solution at room temperature. The reaction was fitted with condenser and heated to 50 °C for 18 hours. The mixture was cooled to room temperature and concentrated under reduced pressure leaving ~1 mL of solvent. The crude product was purified by column chromatography (10% - 55% EtOAc in hexanes) to give the desired product (47 mg, 49% based on the assumption of pure **26**). Note: NMR spectra were recorded at high temperatures to coalesce signals that broadened due to amide rotamers. ¹H NMR (300 MHz, DMSO-d₆, 106.9 °C) δ 7.86 (dd, *J* = 1.3, 8.3 Hz, 1H), 5.27 (dd, *J* = 1.2, 8.3 Hz, 1H), 4.6 (t, *J* = 7.3 Hz, 1H), 4.44 (d, *J* = 14.8 Hz, 1H), 4.34 (d, *J* = 14.8 Hz, 1H) 3.54-3.31 (m, 5H), 2.83 (dd, *J* = 6.8, 17.1 Hz, 1H), 2.40 (td, *J* = 17.1, 1.4 Hz, 1H), 1.55-1.23 (m, 11H), 1.04 (t, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (75 MHz, DMSO-d₆, 106.9 °C) δ 191.2, 168.2, 107.0, 76.7, 65.2, 58.0, 53.8, 36.6, 30.4, 30.2, 28.0, 23.9, 21.2; IR (neat) 3340, 2927, 2857, 1672, 1602, 1457, 1415, 1308, 1193, 1127, 780 cm⁻¹; HRMS (EI): *m/z* calcd for C₁₇H₂₉NO₄ [M⁺] 311.2096, found 311.2095.



***N*-((*E*)-Non-1-enyl)isobutyramide (30)**

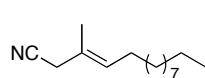
To a stirred solution of octyl cyanide (**29**, 84 mg, 0.60 mmol) in THF (6.0 mL) was added Cp₂Zr(H)Cl (171 mg, 0.663 mmol). The reaction was stirred for 20 min, then cooled to 0 °C and a solution of isobutyryl chloride (60 μL, 0.57 mmol) and Et₃N (0.25 mL, 1.8 mmol) in THF (4.0 mL) was added dropwise. The flask formerly containing the isobutyryl chloride and Et₃N was rinsed with THF (2 x 1 mL). The reaction was stirred for 10 min at 0 °C and BF₃•OEt₂ (98 μL, 0.78 mmol) was added dropwise. The cold bath was removed and the mixture was stirred overnight. After that time, the reaction was quenched with water (30 mL) and extracted with EtOAc (4 x 30 mL). The combined organic extracts were washed with water (30 mL), dried (Na₂SO₄) and concentrated in vacuo. The residue was purified by column chromatography (10% - 20% EtOAc in hexanes) to gave the title product (73 mg, 57%): ¹H NMR (300 MHz, CDCl₃) 7.24 (d, *J* = 9.6 Hz, 1H), 6.74 (app dd, *J* = 14.2, 10.5 Hz, 1H), 5.15 (td, *J* = 14.2, 7.1 Hz), 2.37 (sept, *J* = 6.9 Hz, 1H), 2.00 (q, *J* = 6.6 Hz, 2H), 1.36-1.22 (m, 10H), 1.17 (d, *J* = 6.9 Hz, 6H), 0.87 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) 174.2, 122.7, 113.3, 35.7, 32.0, 30.1, 29.9, 29.3, 29.2, 22.8, 19.6, 14.3; IR (neat) 3283, 2967, 2921, 2851, 1680, 1647, 1526, 1467, 1238, 950, 723; HRMS (EI): *m/z* calcd for C₁₃H₂₅NO [M⁺] 211.1936, found 211.1938.



Reagents and conditions

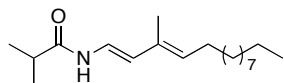
a) Methacrolein, Grubbs 2nd generation metathesis catalyst, CH_2Cl_2 , reflux. b) NaBH_4 , MeOH .
c) MsCl , Et_3N , CH_2Cl_2 , $-42\text{ }^\circ\text{C}$, then LiBr , THF . d) CuCN , DMF

Scheme 1. Synthesis of nitrile 31.



(E)-3-Methyltetradec-3-enenitrile (31)

^1H NMR (300 MHz, CDCl_3) 5.49 (sext of t, $J = 7.2, 1.4$ Hz, 1H), 3.03 (s, 2H), 2.04 (q, $J = 7.0$ Hz, 2H), 1.73 (s, 3H), 1.38-1.27 (m, 16H), 0.89 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) 130.2, 124.0, 118.0, 32.0, 29.8, 29.6, 29.5, 29.4, 29.3, 28.2, 27.4, 22.8, 16.1, 14.2; IR (neat) 2925, 2854, 2249, 1464, 1412, 1114, 721; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{27}\text{N}$ $[\text{M}]^+$ 221.2144, found 221.2152.

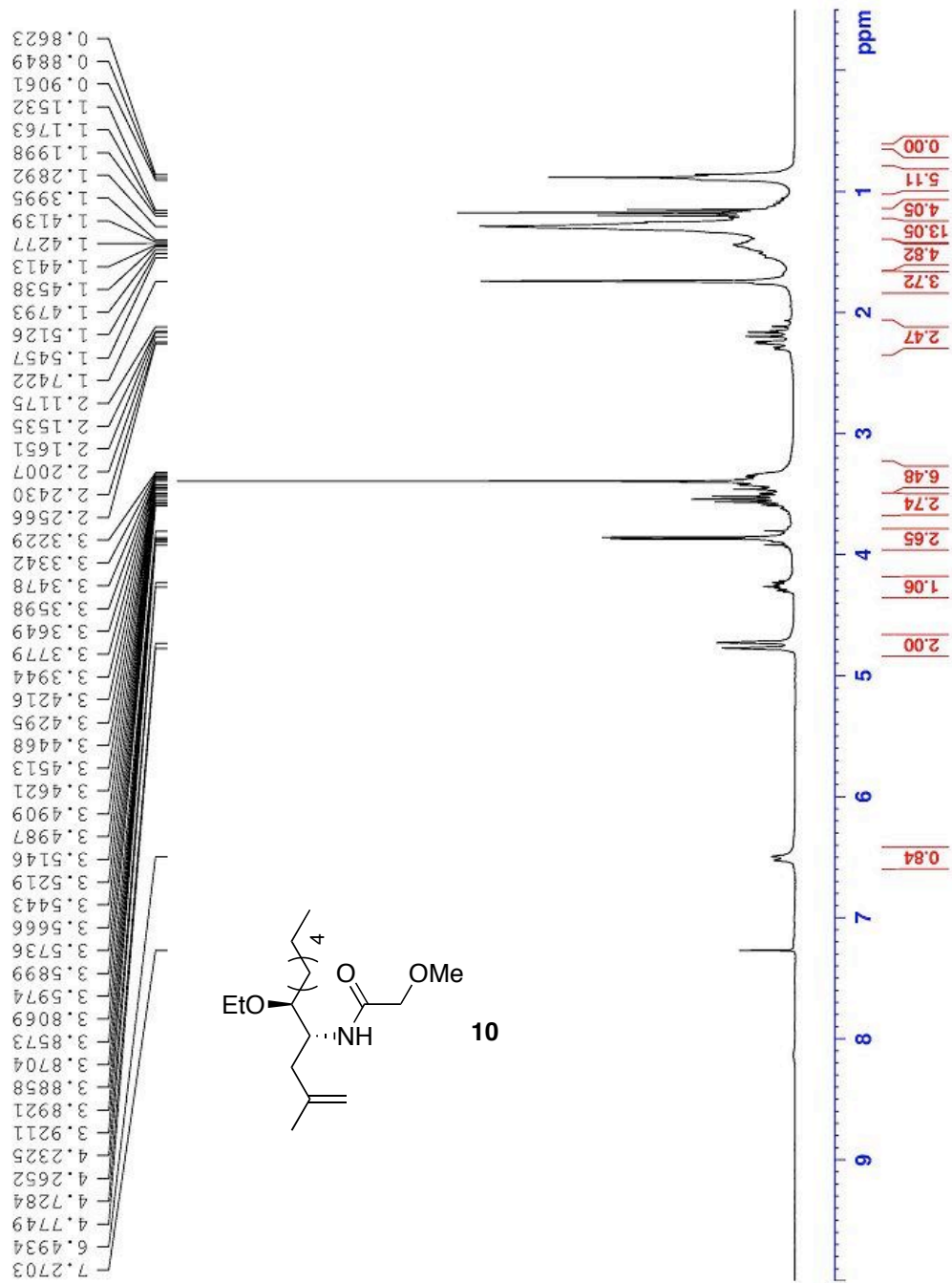


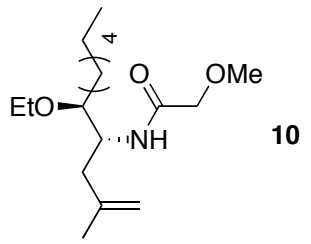
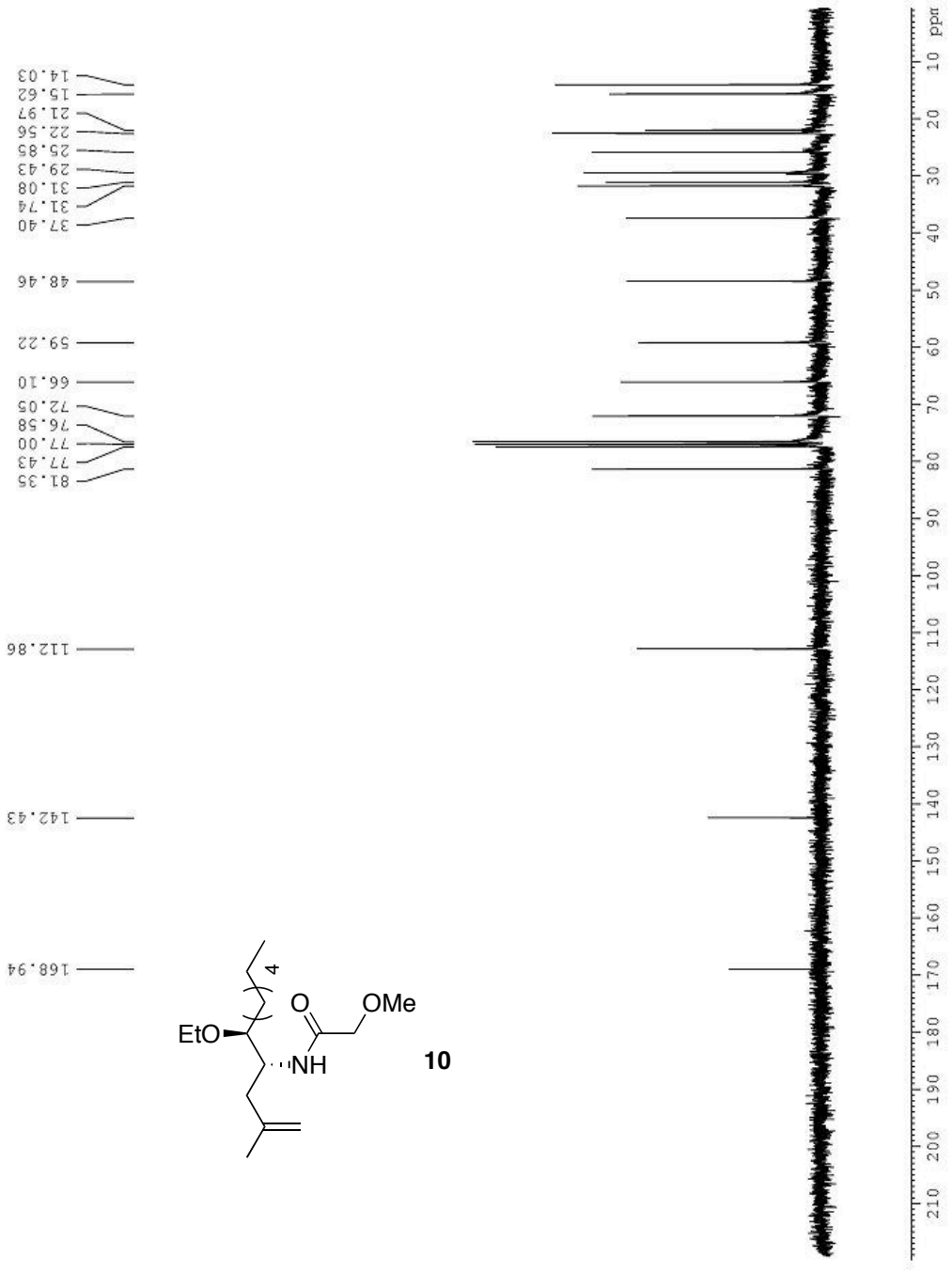
N-((1E,3E)-3-Methyltetradeca-1,3-dienyl)isobutyramide (32)

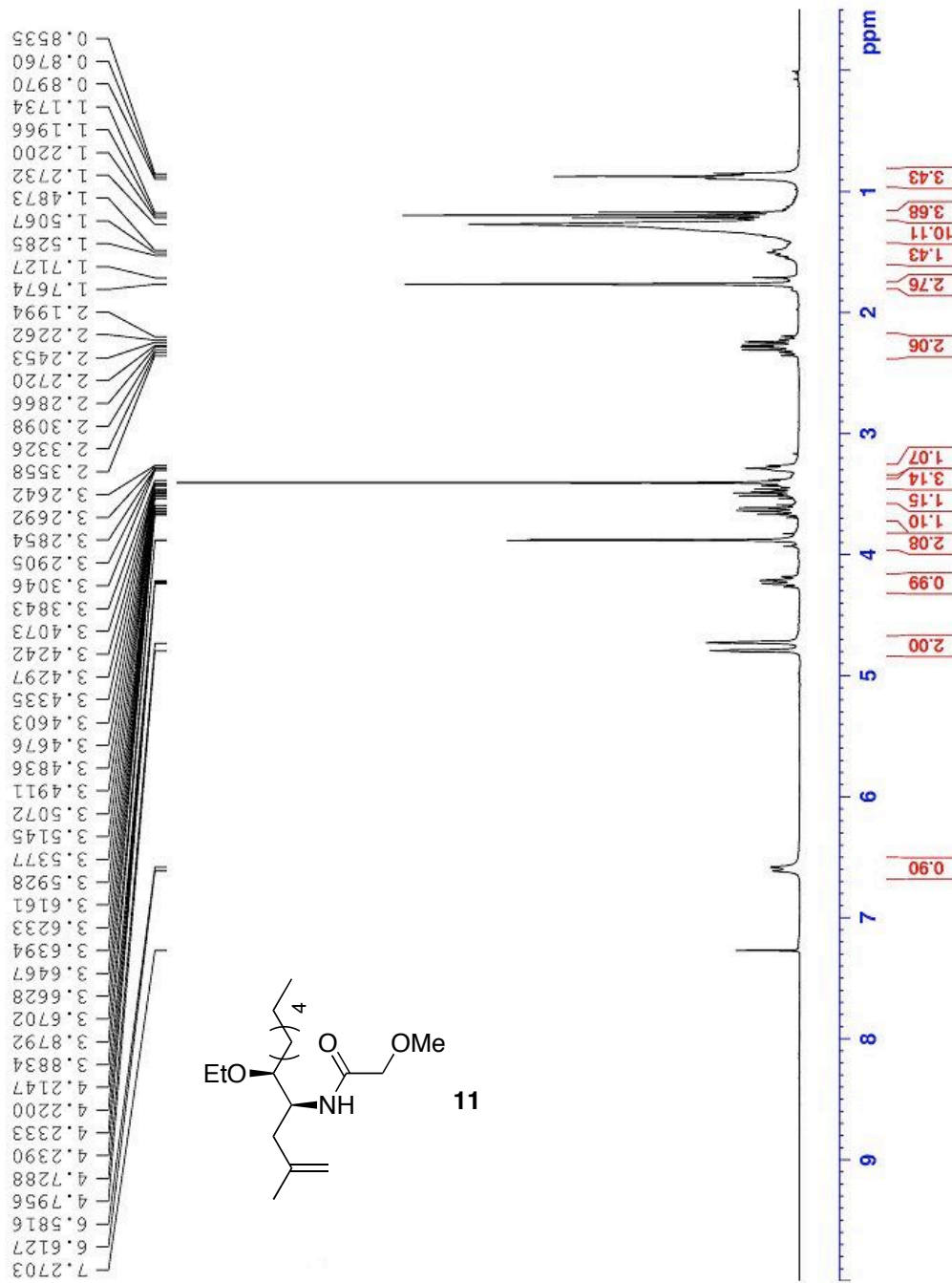
To a stirred solution of **31** (90 mg, 0.41 mmol) in THF (5.0 mL) was added $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ (157 mg, 0.609 mmol). The reaction was stirred for 30 min, then cooled to $0\text{ }^\circ\text{C}$ and a solution of isobutyryl chloride (51 μL , 0.49 mmol) and Et_3N (0.18 mL, 1.3 mmol) in THF (2.0 mL) was added dropwise. The flask formerly containing the isobutyryl chloride and Et_3N was rinsed with THF (0.5 mL). The reaction was stirred for 2 min at $0\text{ }^\circ\text{C}$ and $\text{BF}_3 \cdot \text{OEt}_2$ (76 μL , 0.61 mmol) was added dropwise. The cold bath was removed and the mixture was stirred for 2 h. After that time, the reaction was diluted with Et_2O (3 mL) and filtered through a small plug of silica gel. The residue was washed with Et_2O (30 mL) and the combined filtrate was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (5% - 17% EtOAc in hexanes containing 0.5% Et_3N) to give the title product (74 mg, 62%) as a colorless oil: ^1H NMR (300 MHz, CDCl_3) 7.10 (d, $J = 10.3$ Hz, 1H), 6.91 (dd, $J = 14.2, 10.7$ Hz, 1H), 5.83 (d, $J = 14.3$ Hz, 1H), 5.34 (t, $J = 7.2$ Hz, 1H), 2.40 (sept, $J = 6.9$ Hz, 1H), 2.10 (q, $J = 7.0$ Hz, 2H), 1.75 (s, 3H), 1.40-1.27 (m, 16H), 1.20 (d, $J = 6.9$ Hz, 6H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) 174.3, 131.8, 130.8, 120.4, 118.5, 35.9, 32.1, 30.0, 29.9, 29.8, 29.6, 28.4, 22.9, 19.7, 14.3, 12.7; IR (neat) 3276, 2924, 2854, 1644, 1531, 1467, 1253, 950; HRMS (EI): m/z calcd for $\text{C}_{19}\text{H}_{35}\text{NO}$ $[\text{M}]^+$ 293.2719, found 293.2717.

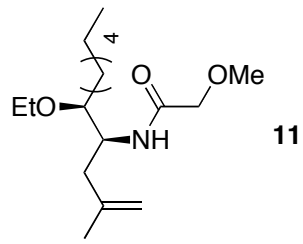
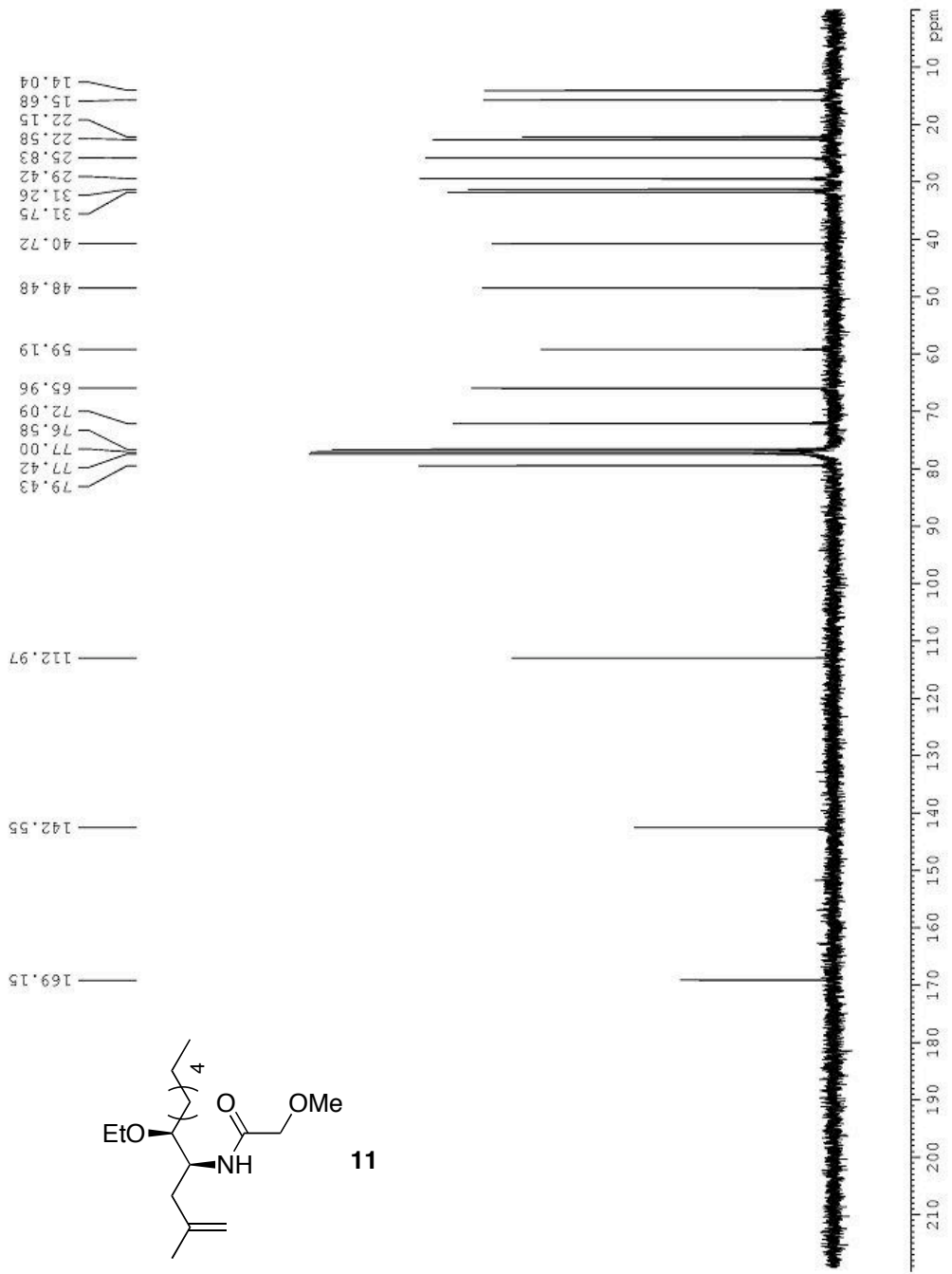
References

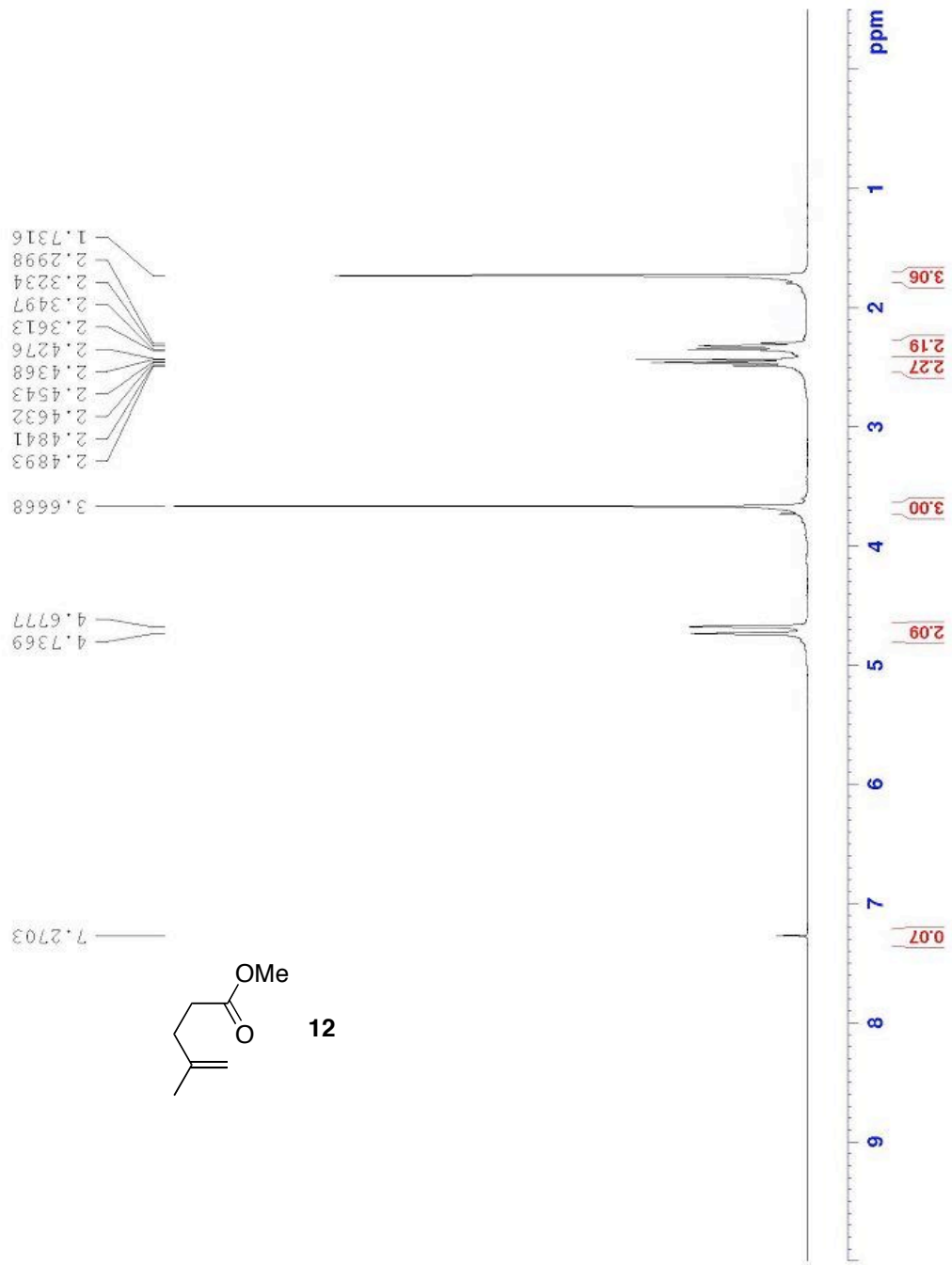
- Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Org. Synth.* **1993**, *71*, 77.
- Wan, S.; Green, M. E.; Park, J.-H.; Floreancig, P. E. *Org. Lett.* **2007**, *9*, 5385.
- Funk, R. L.; Stallman, J. B.; Wos, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 8847.

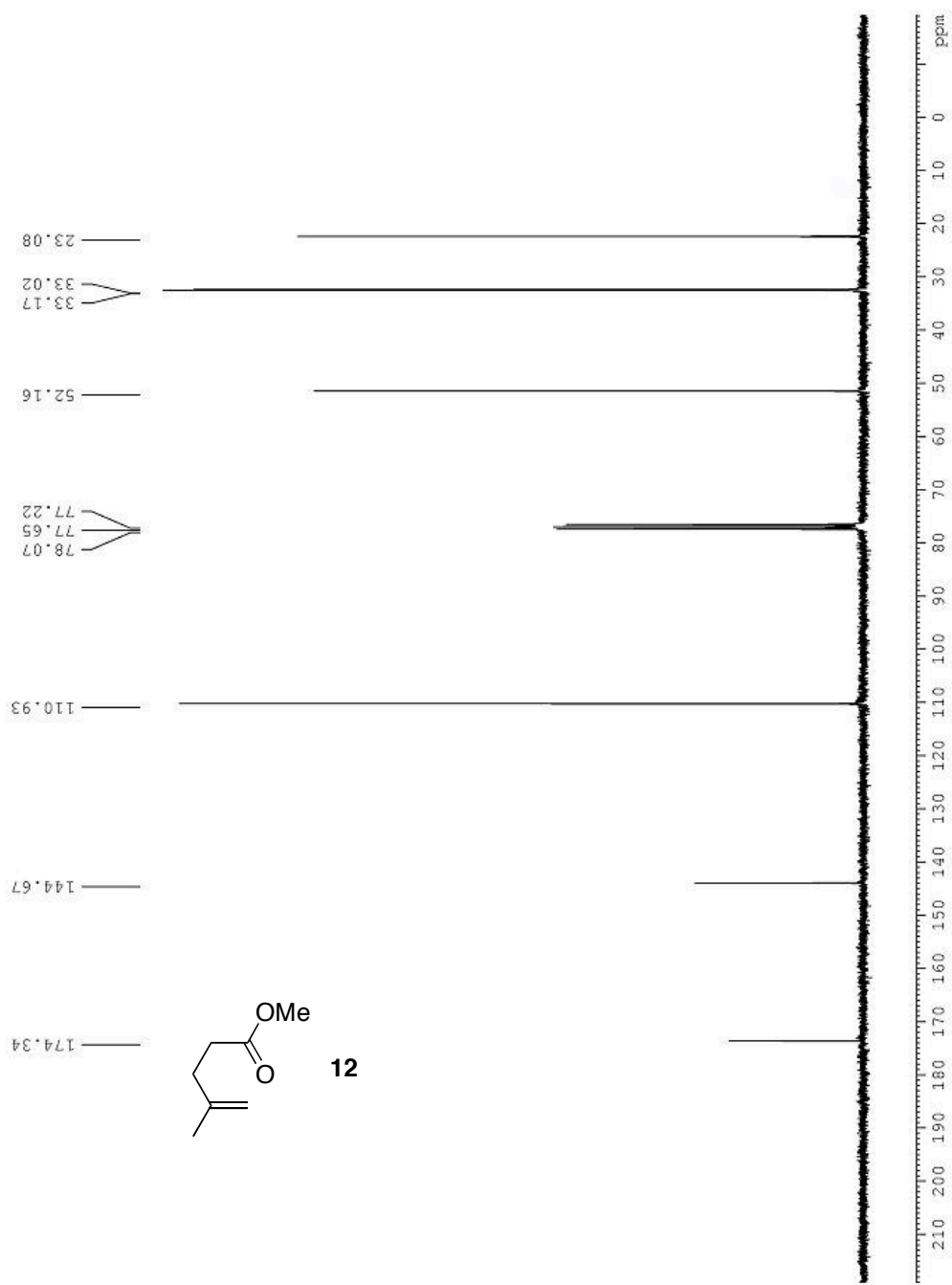


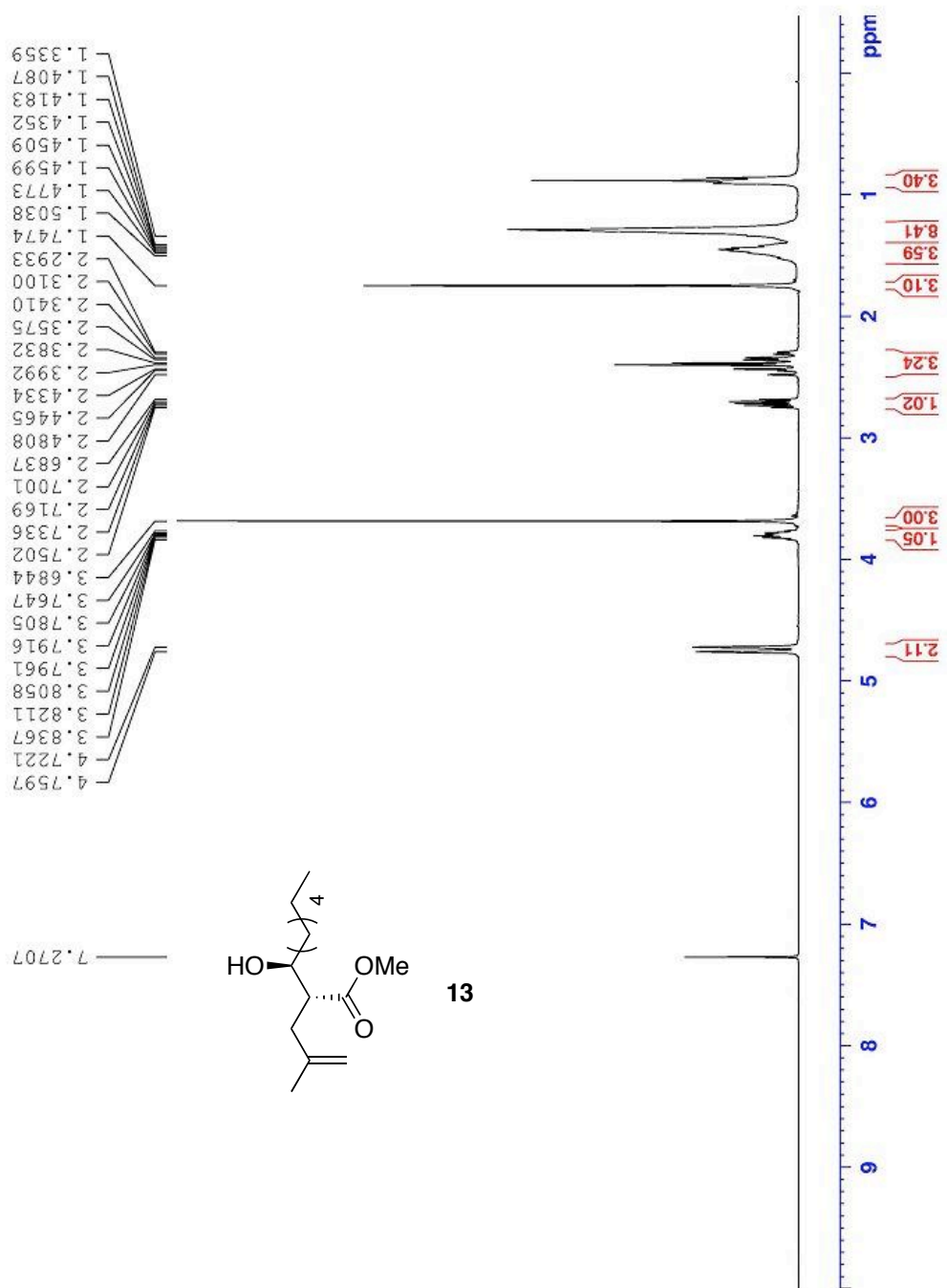


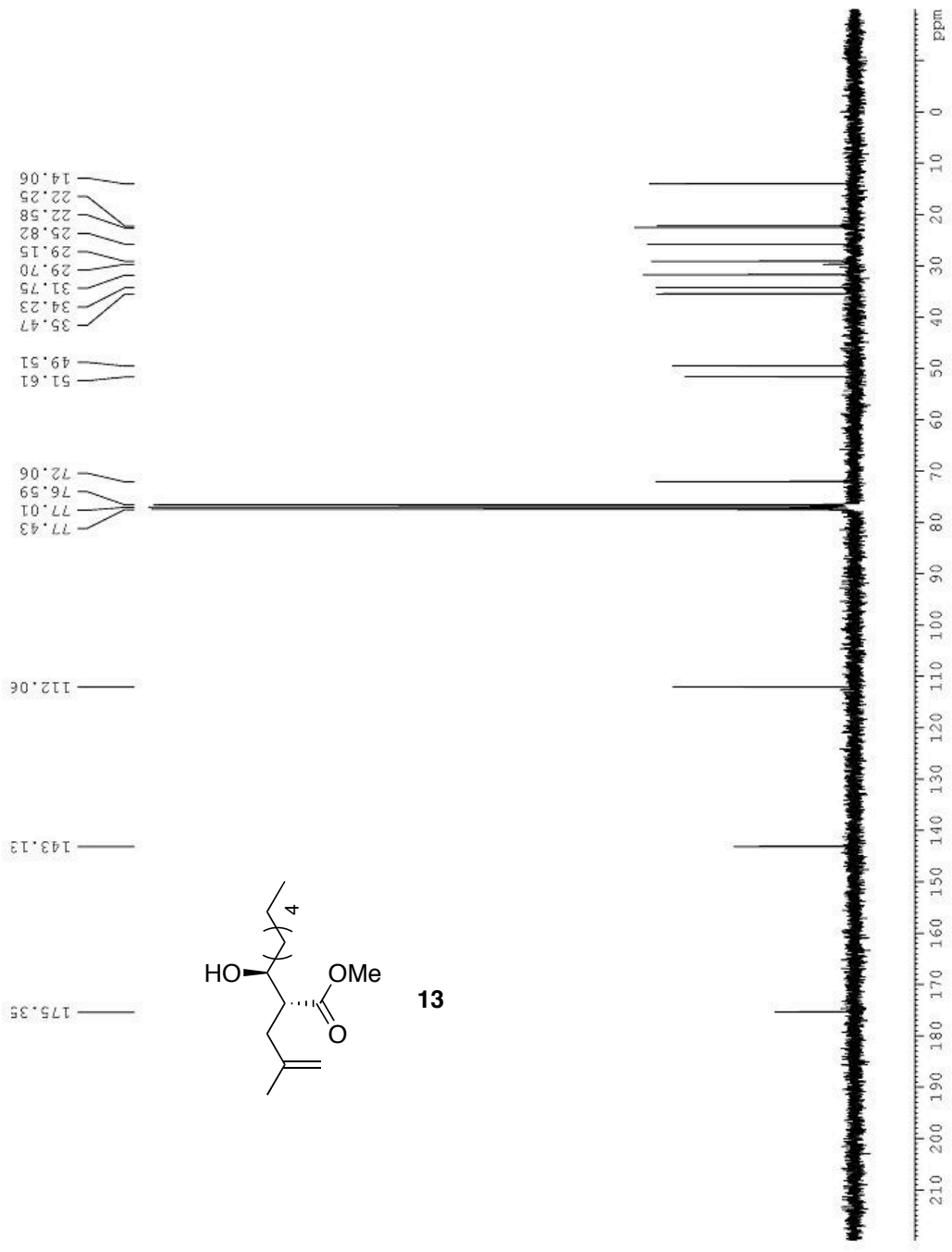


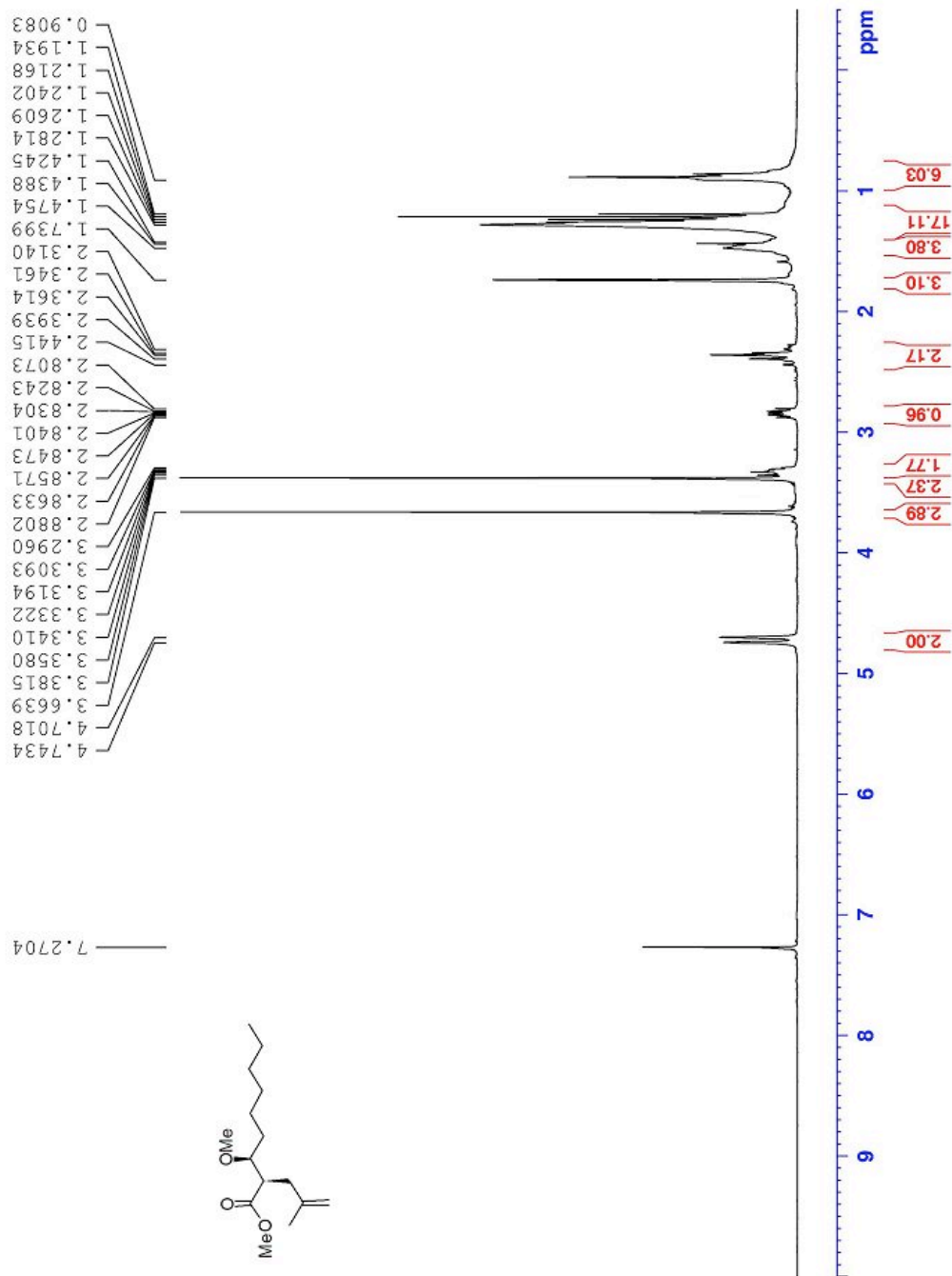


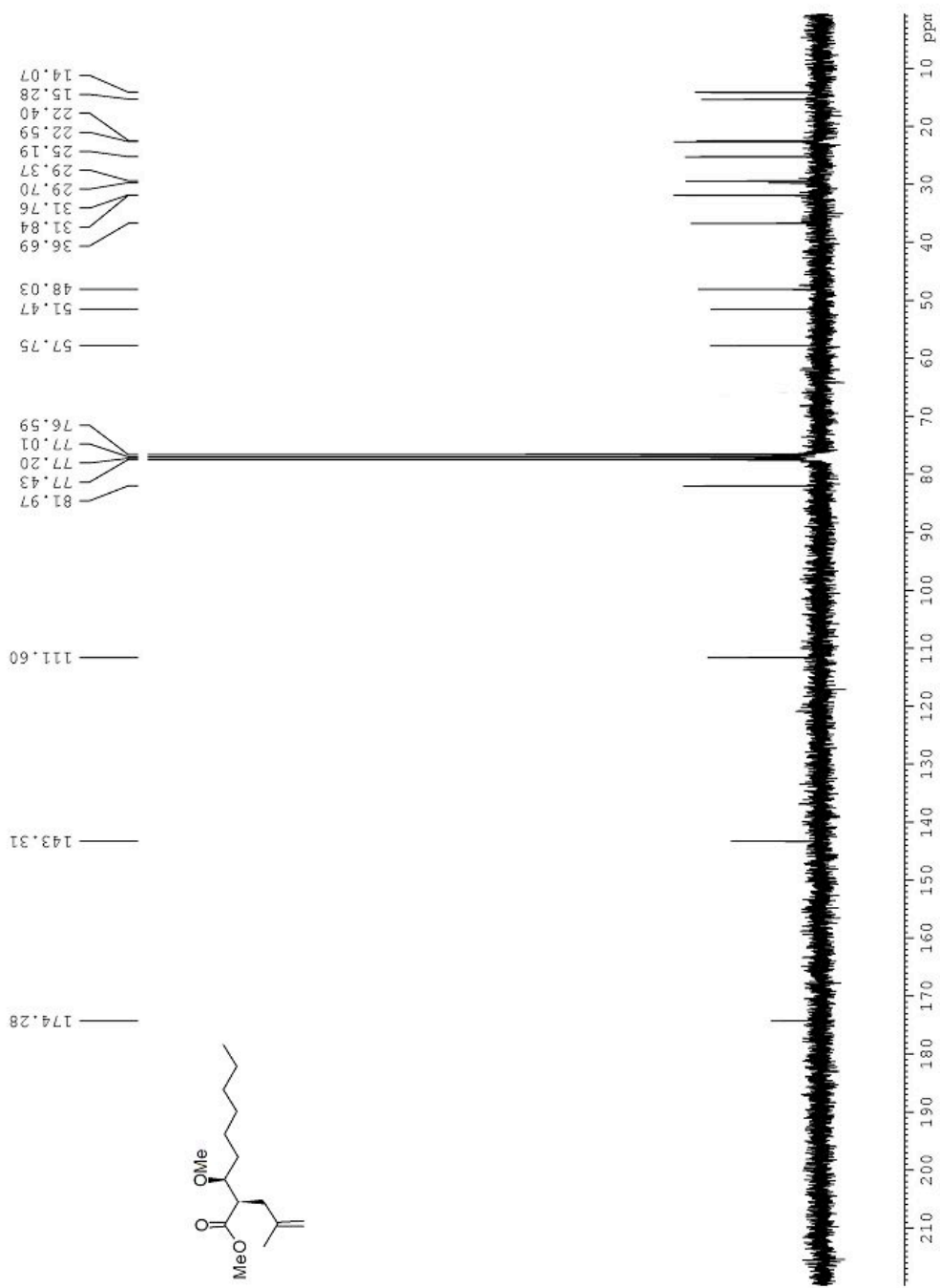


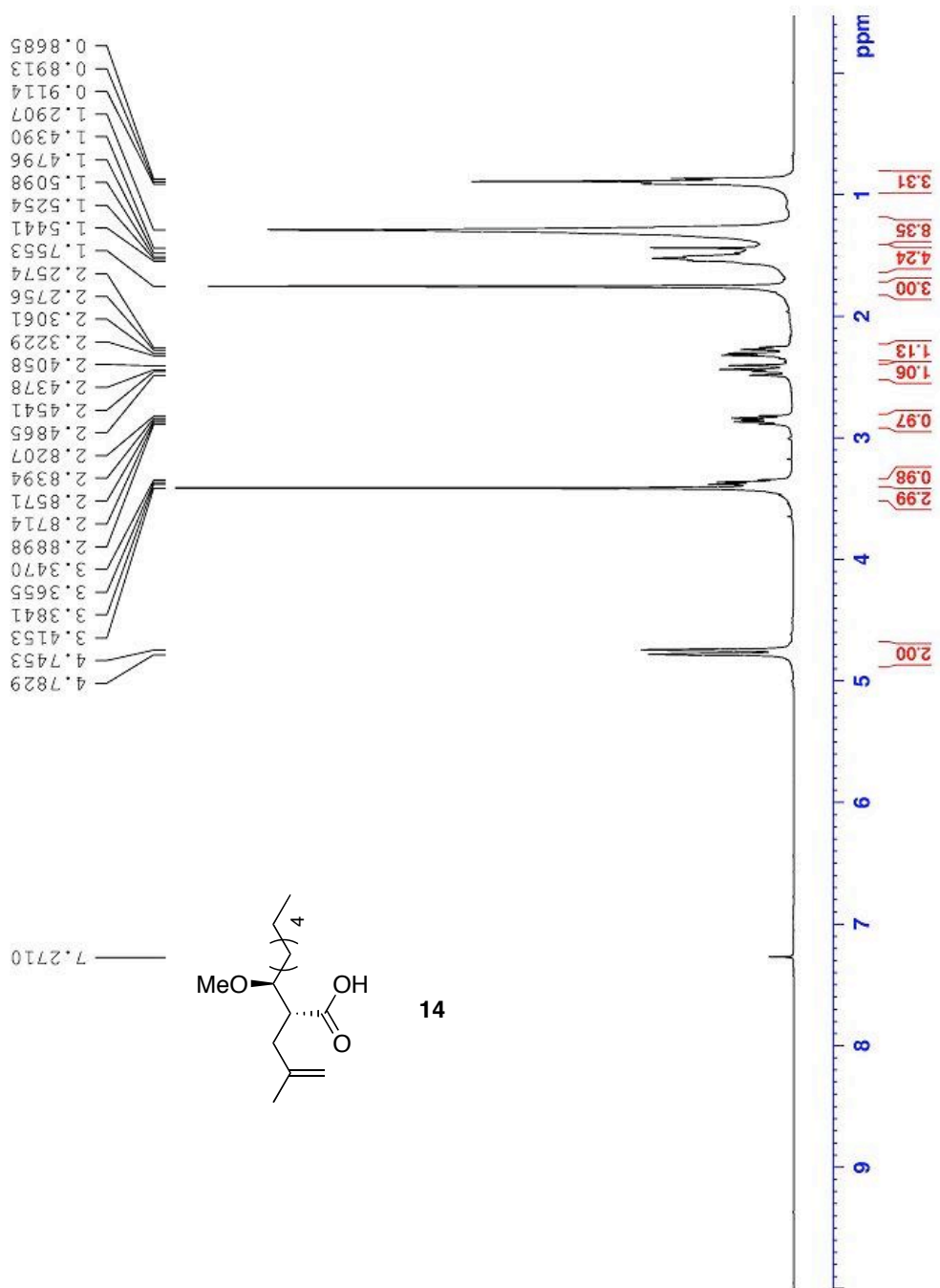


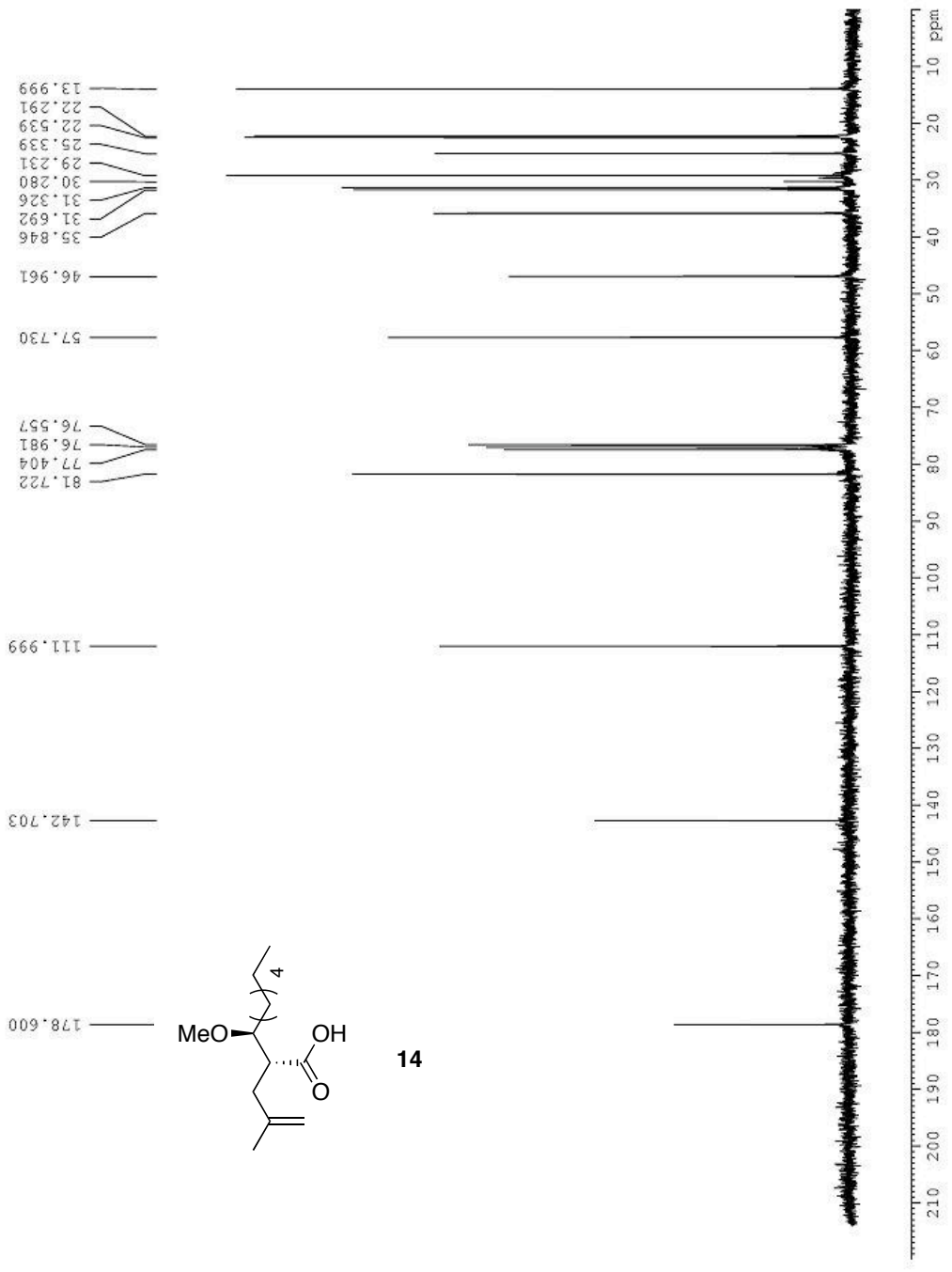


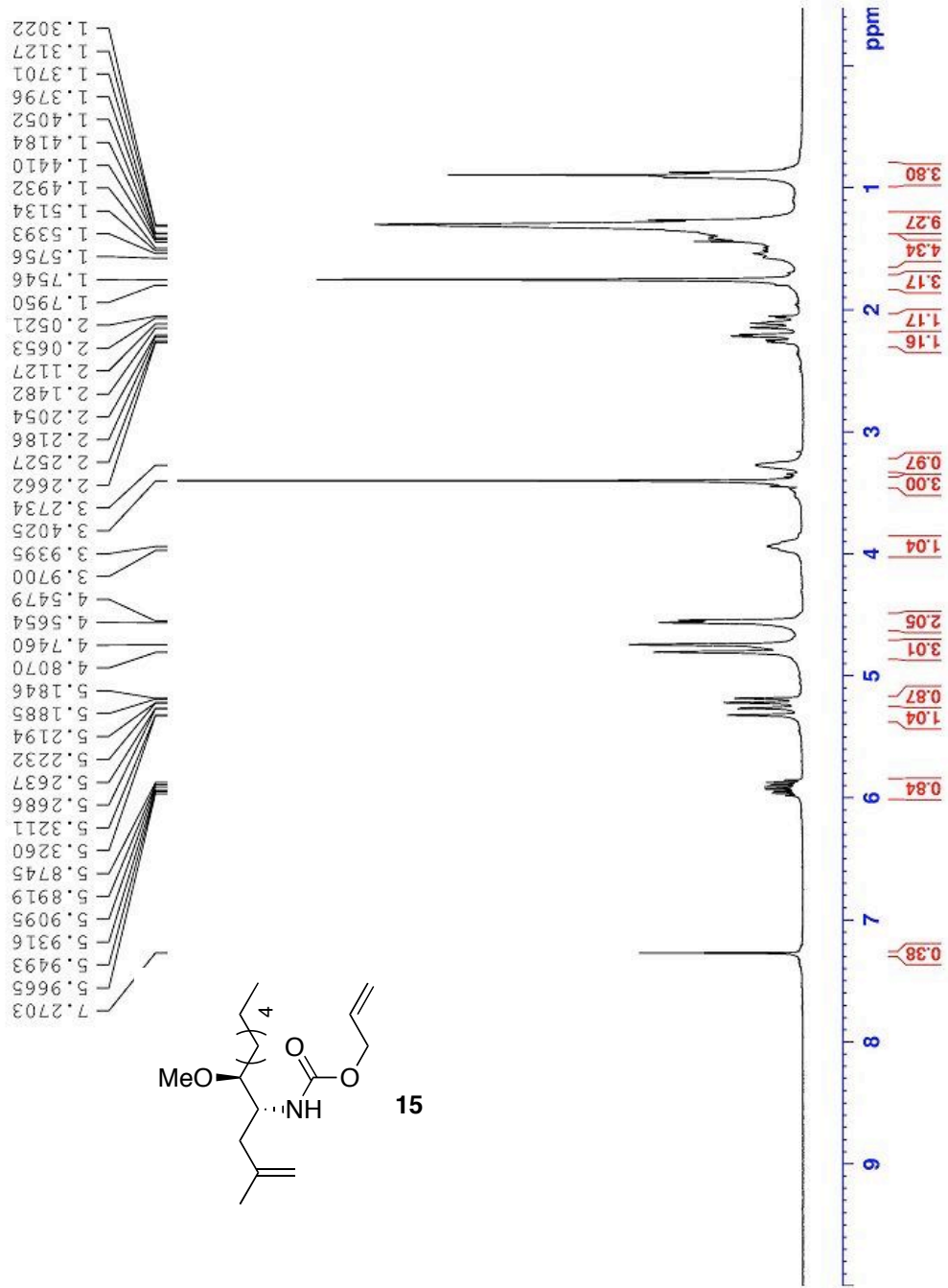


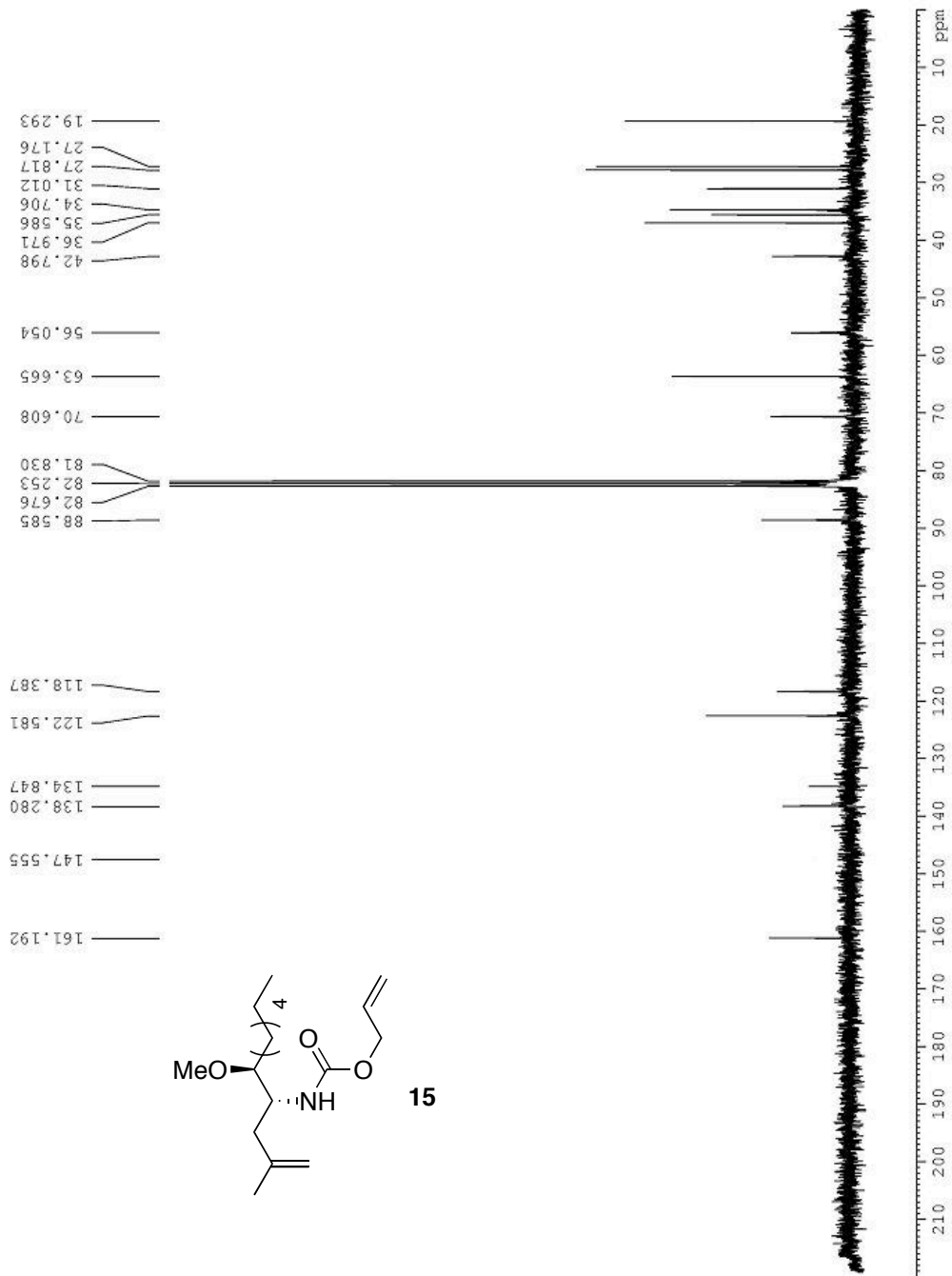


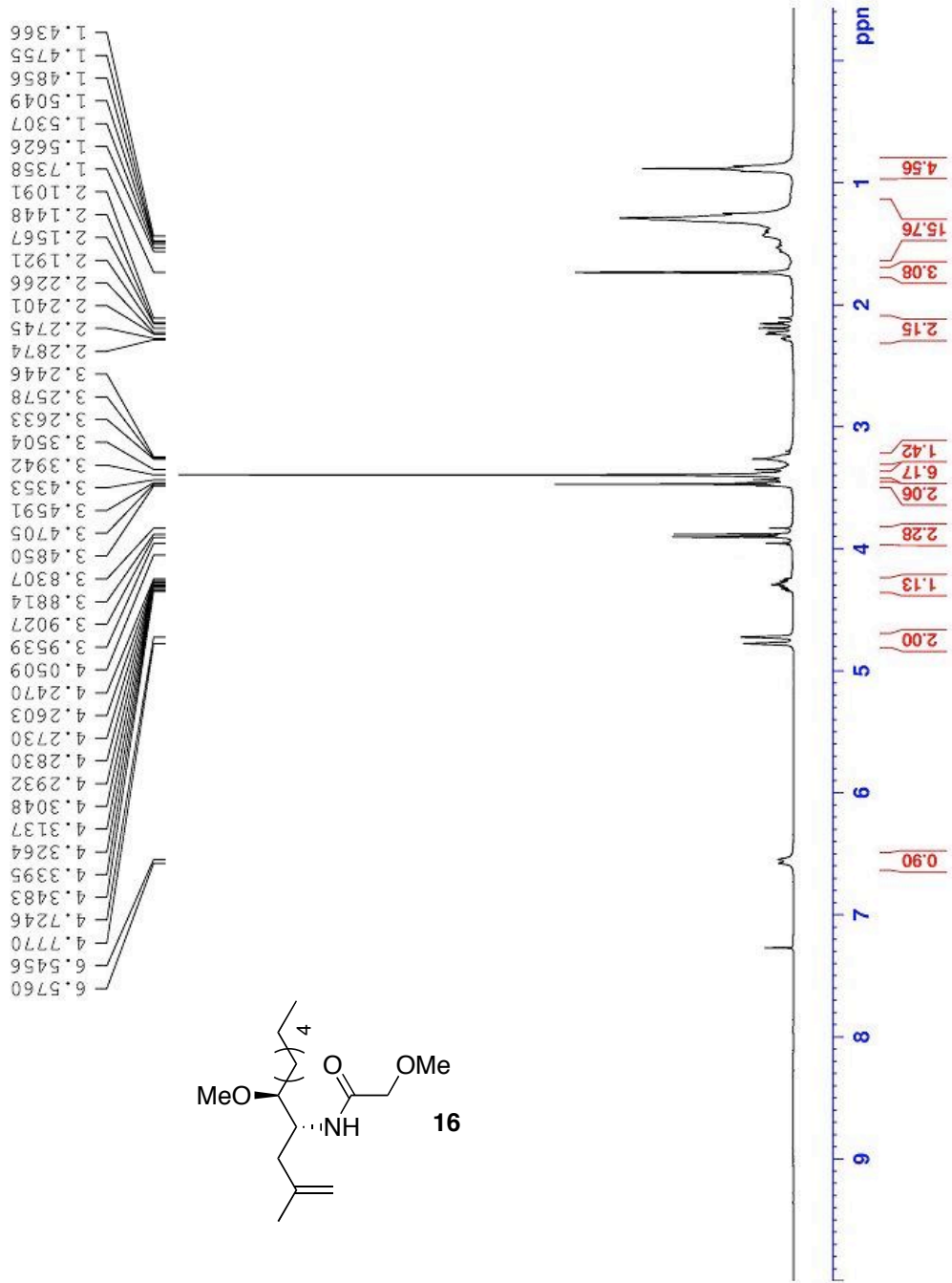


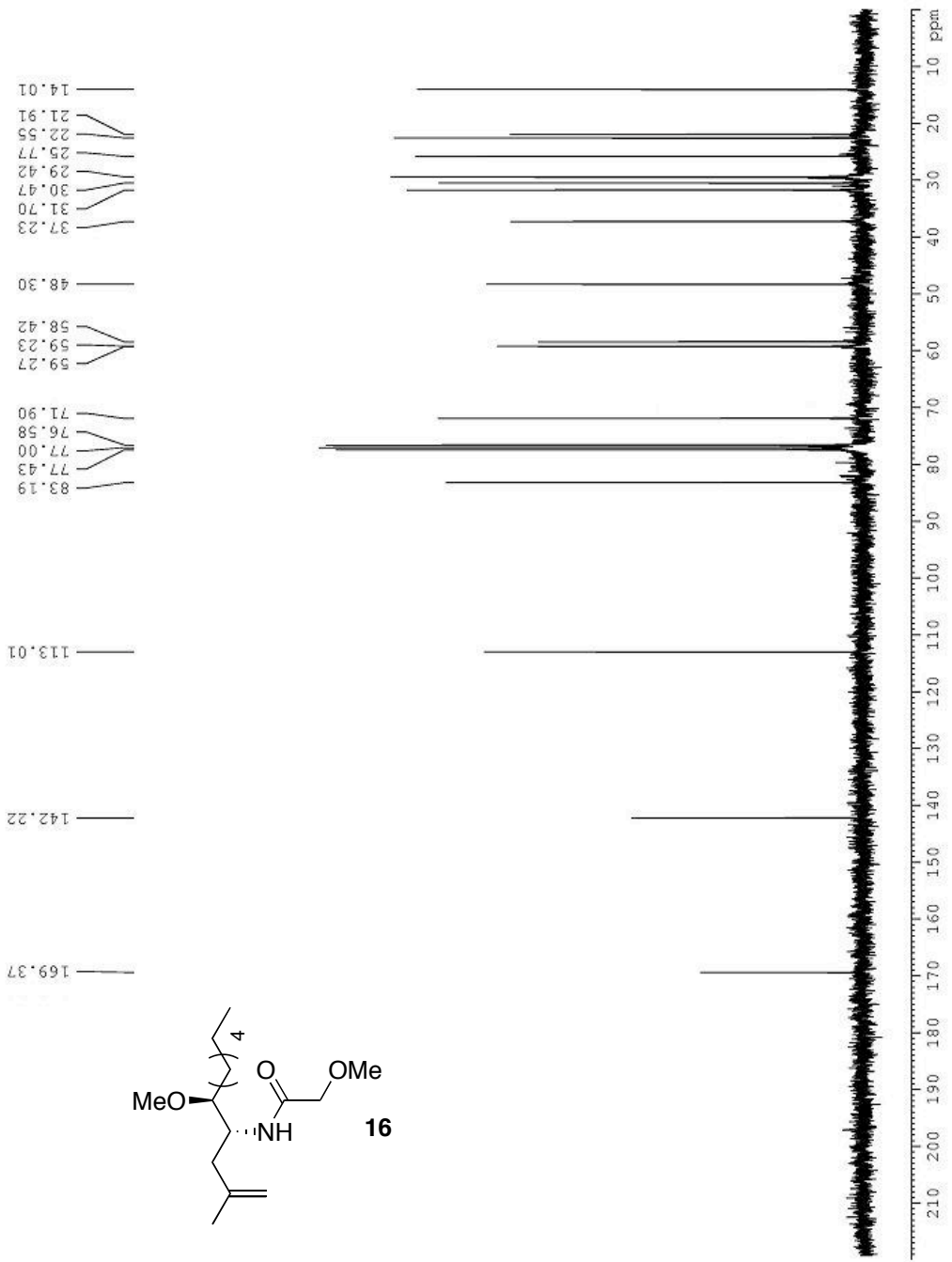


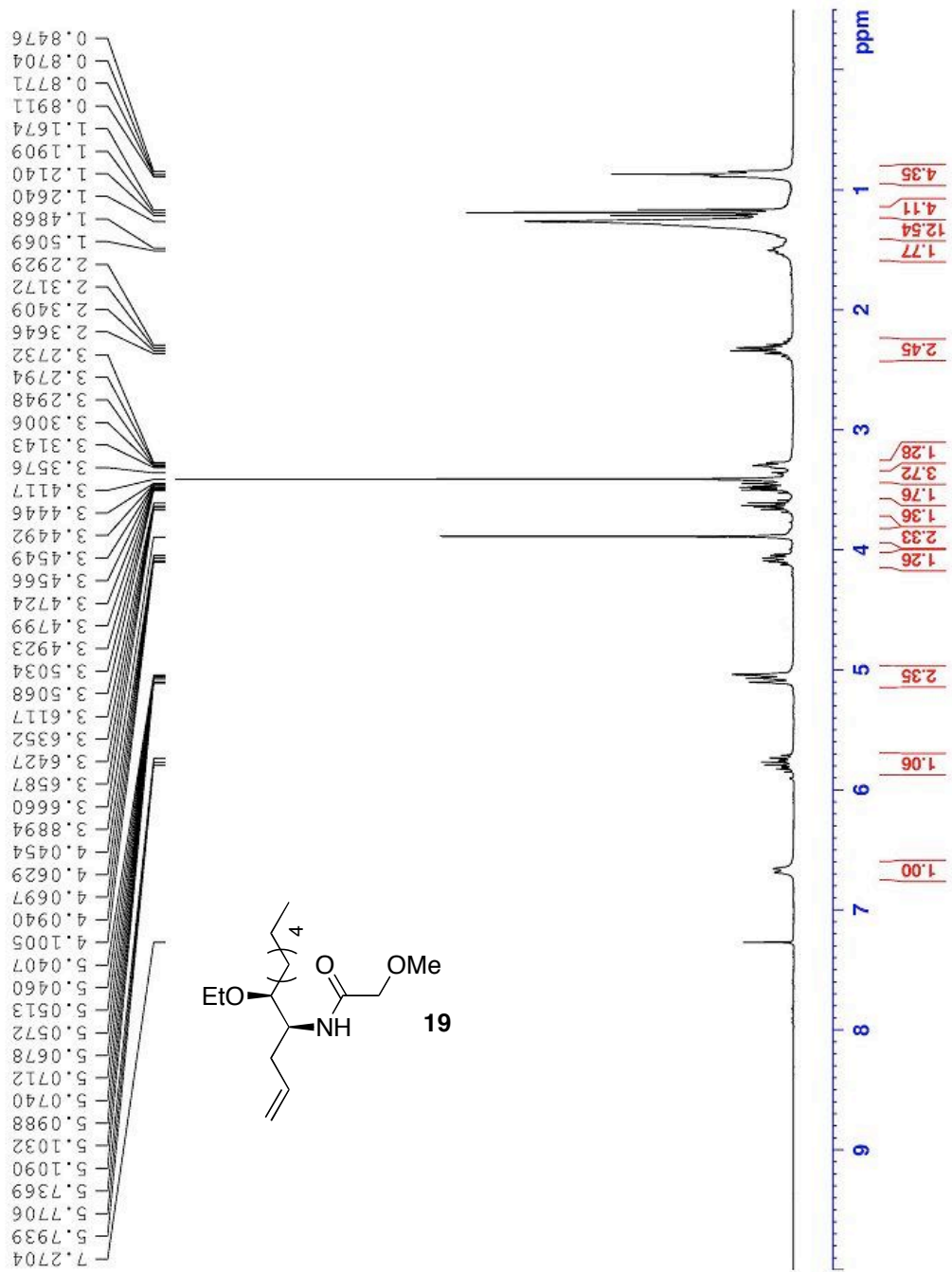


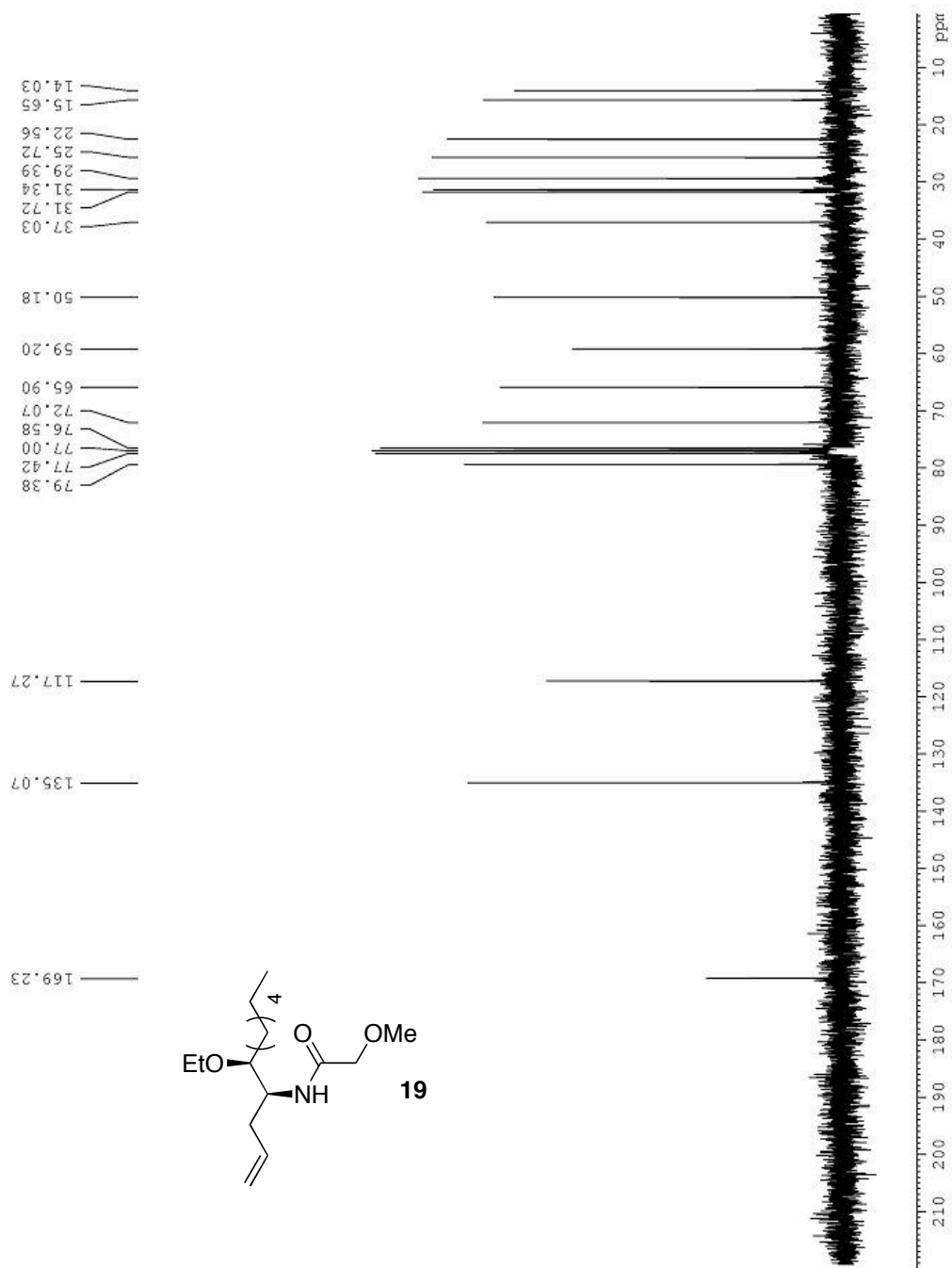


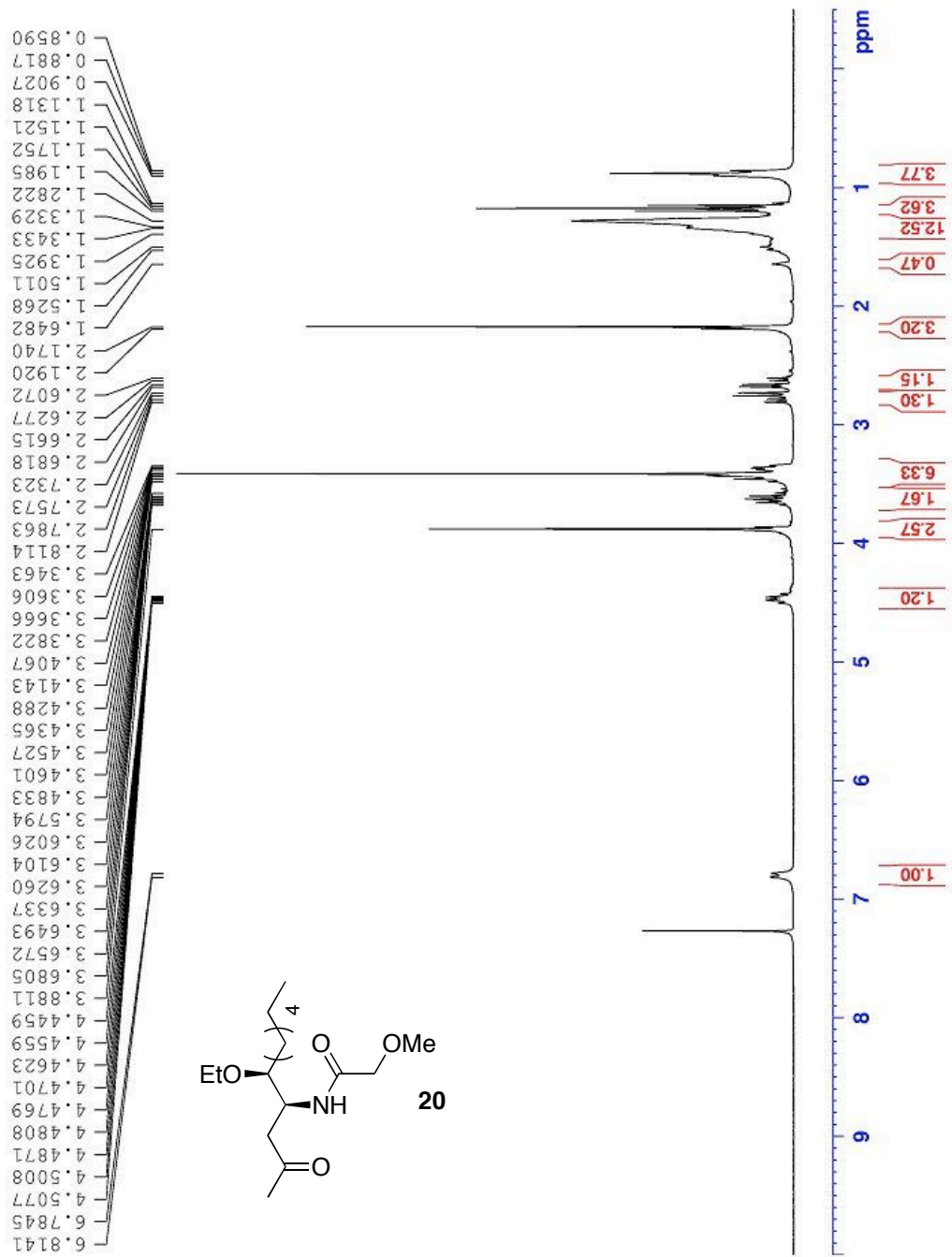


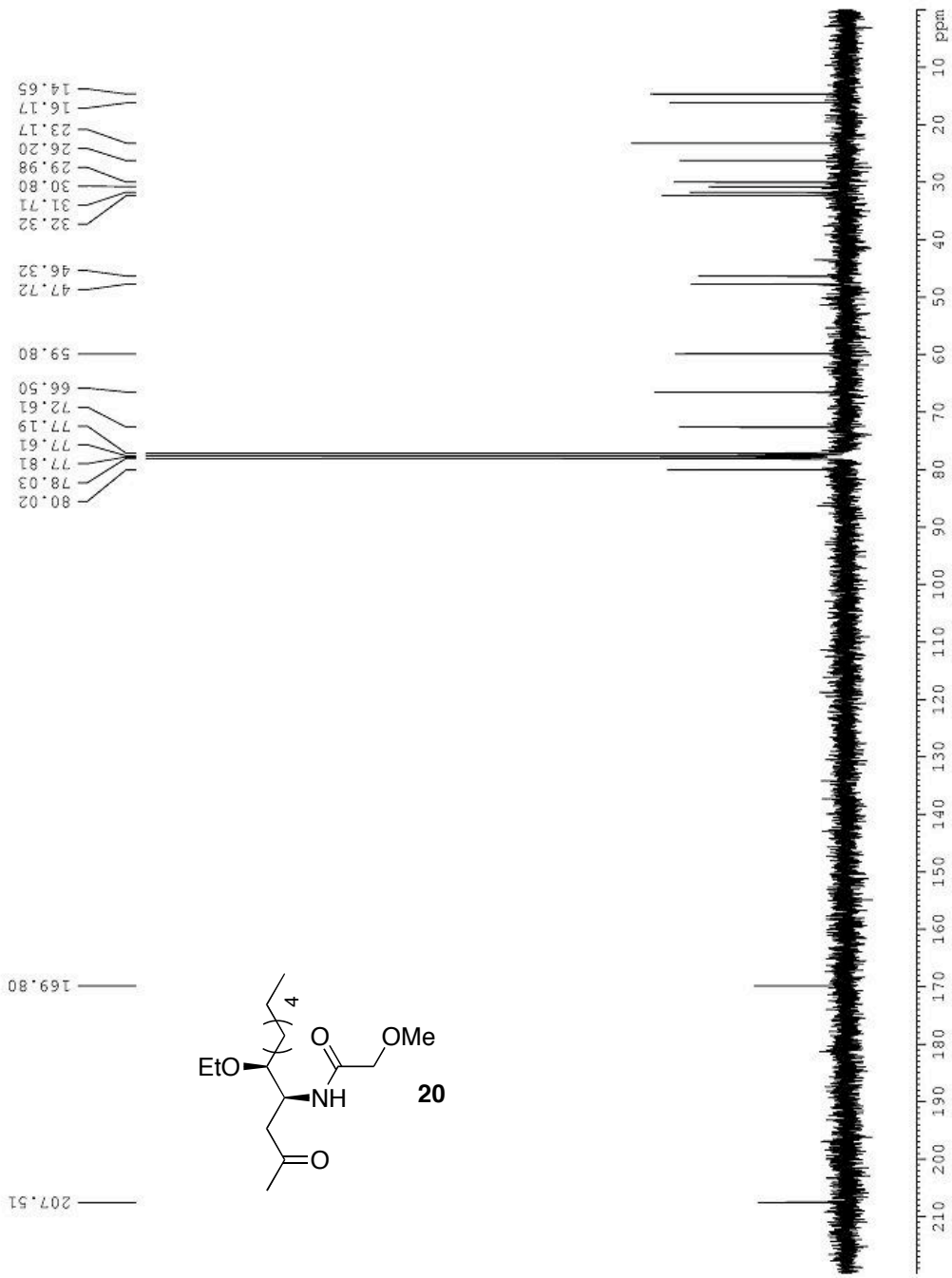


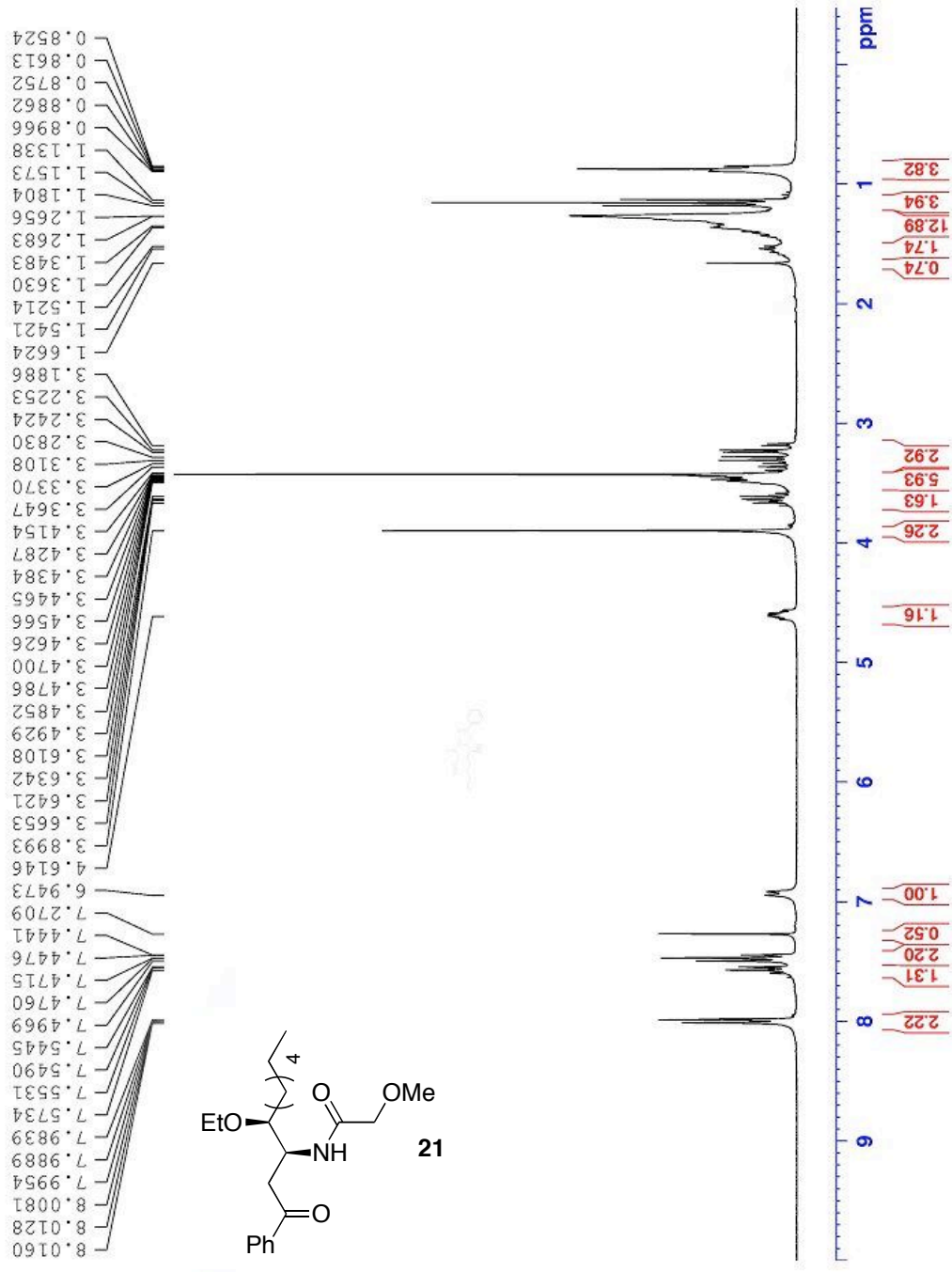


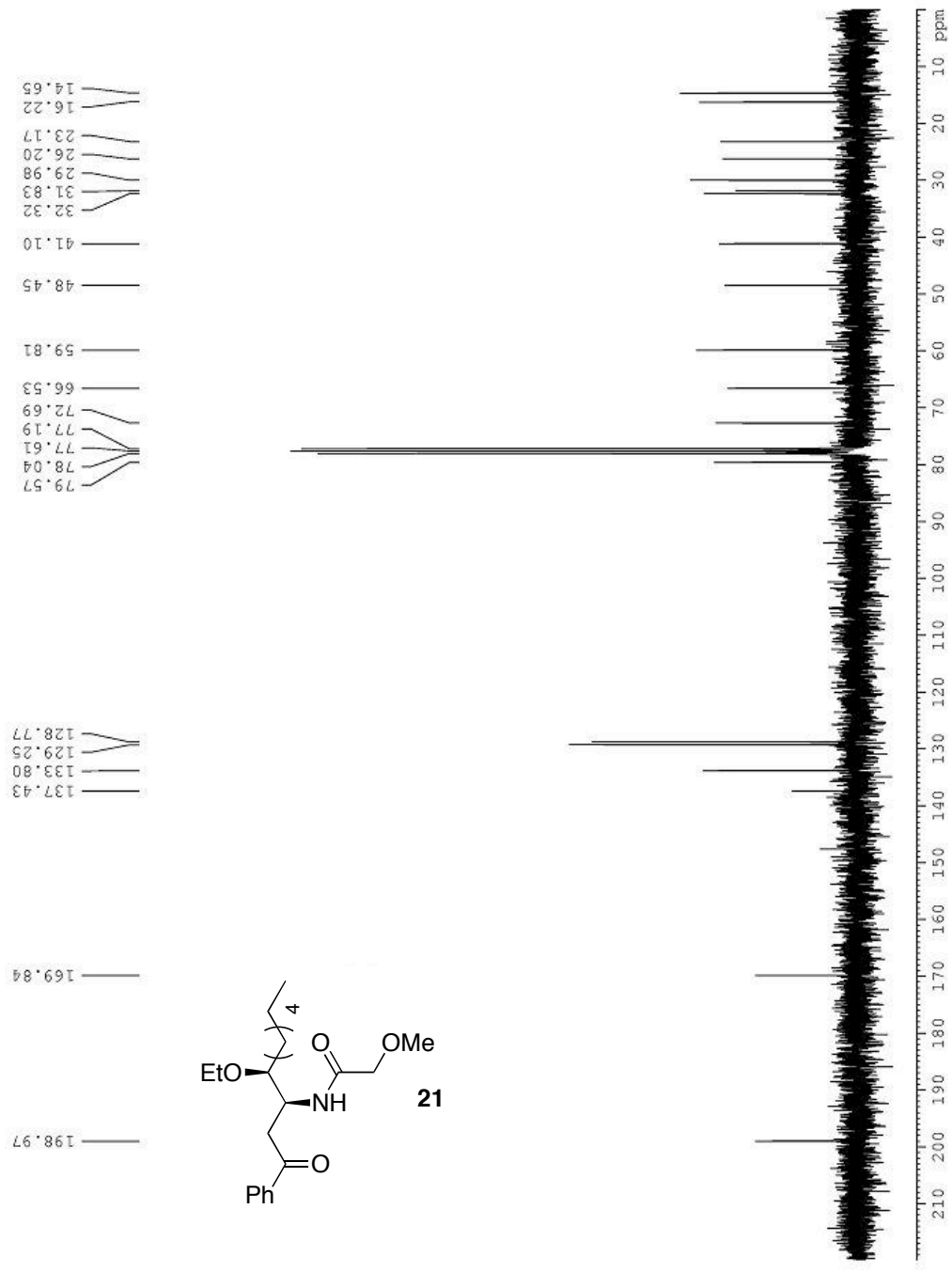


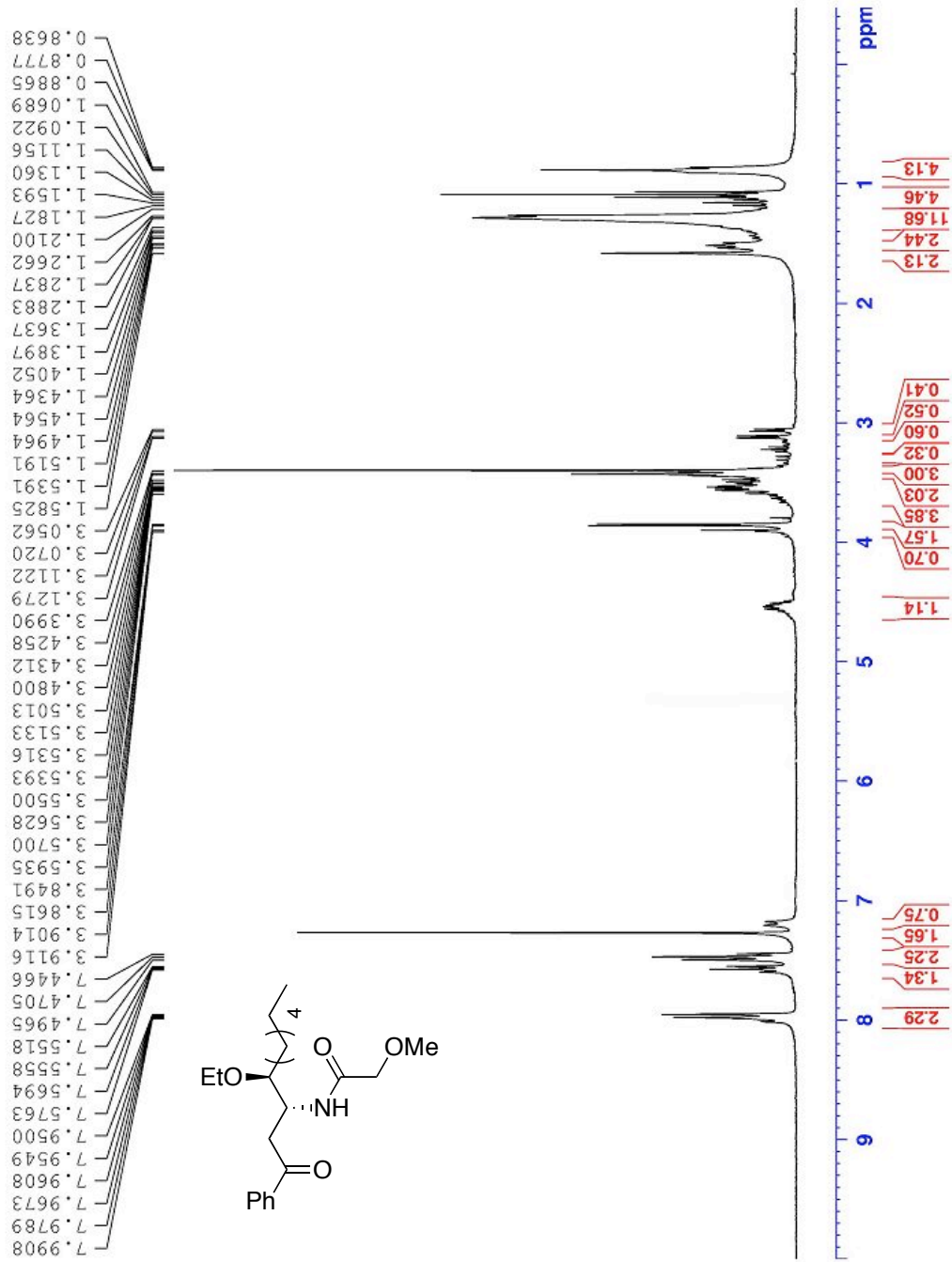


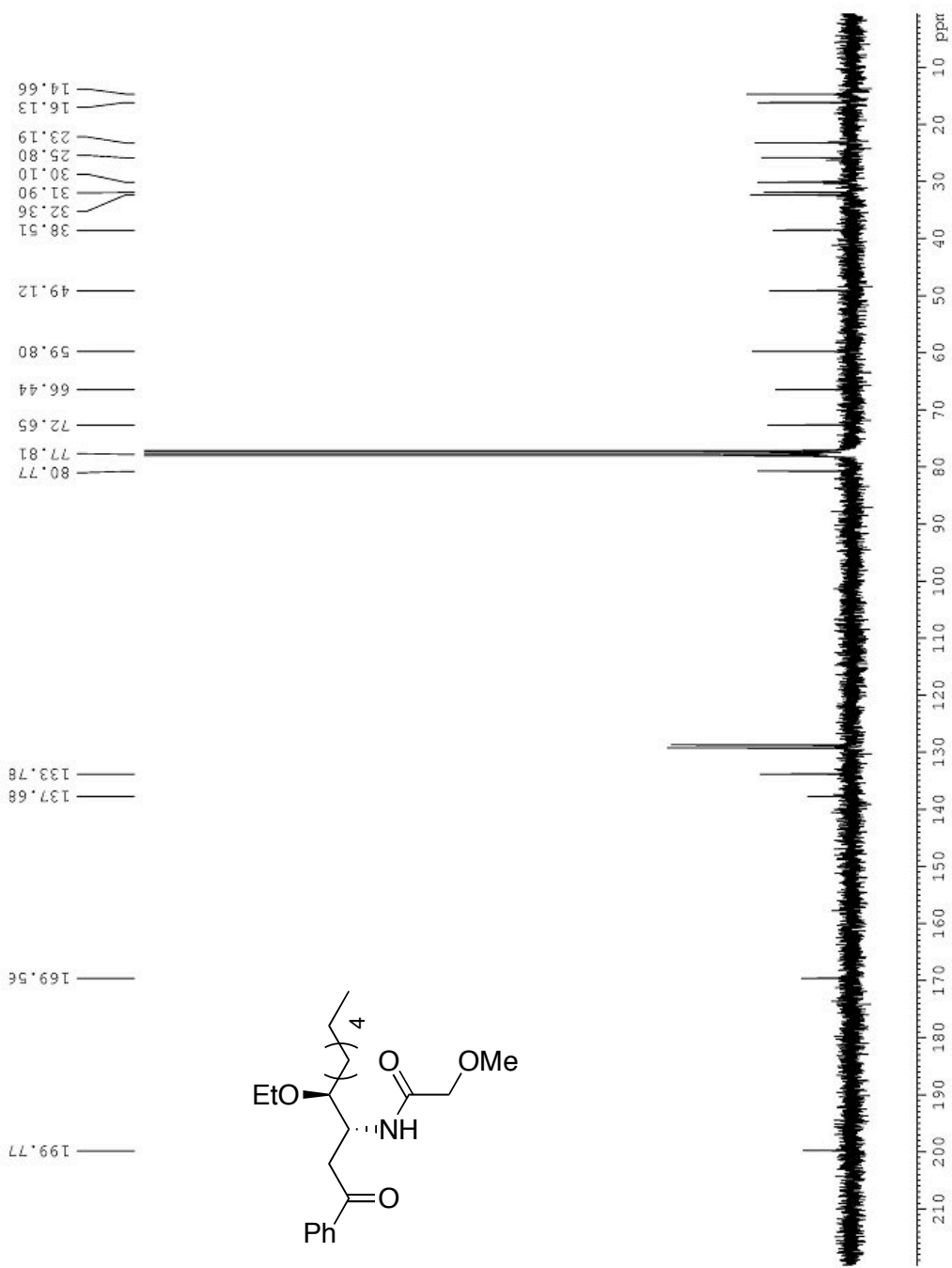


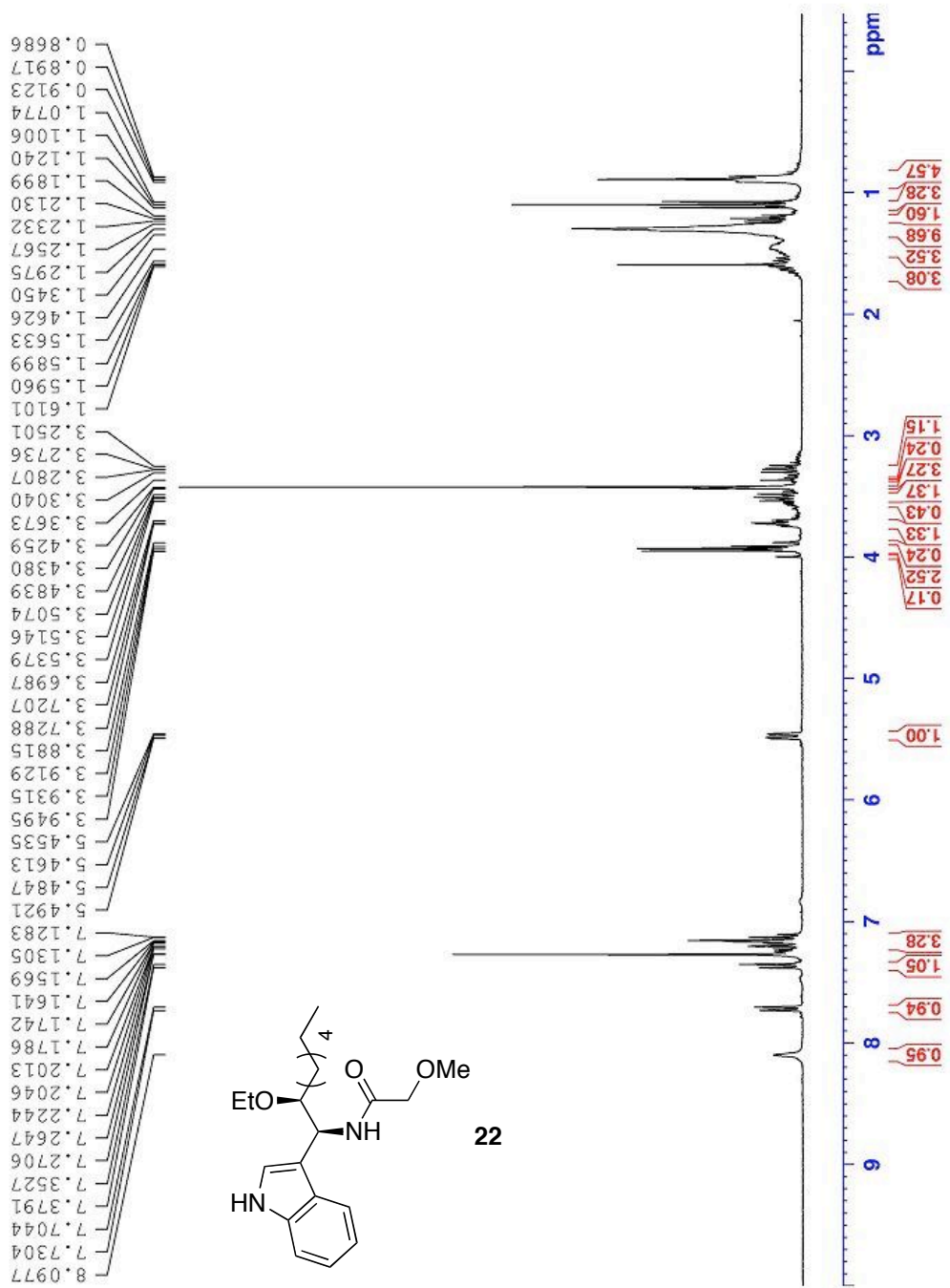


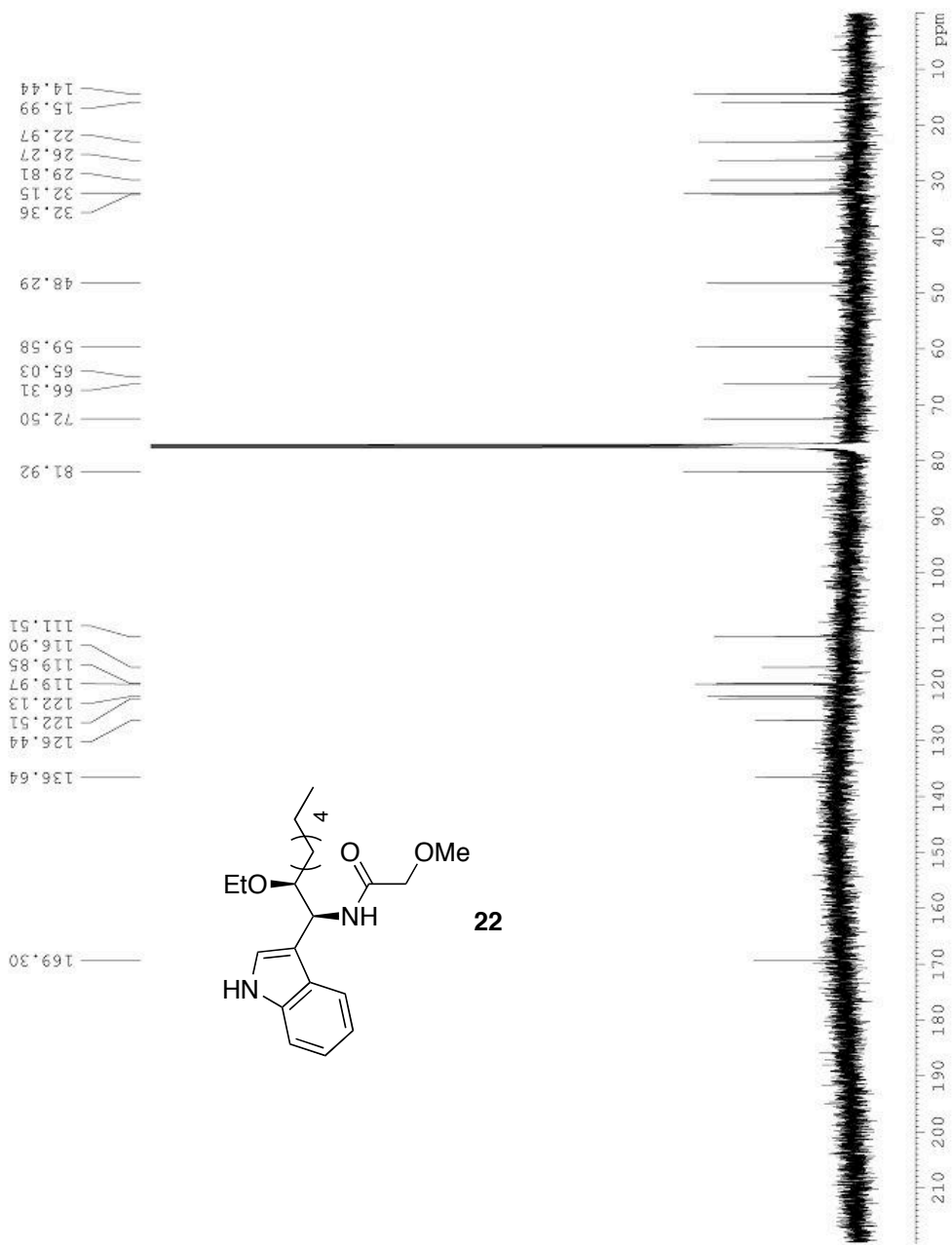


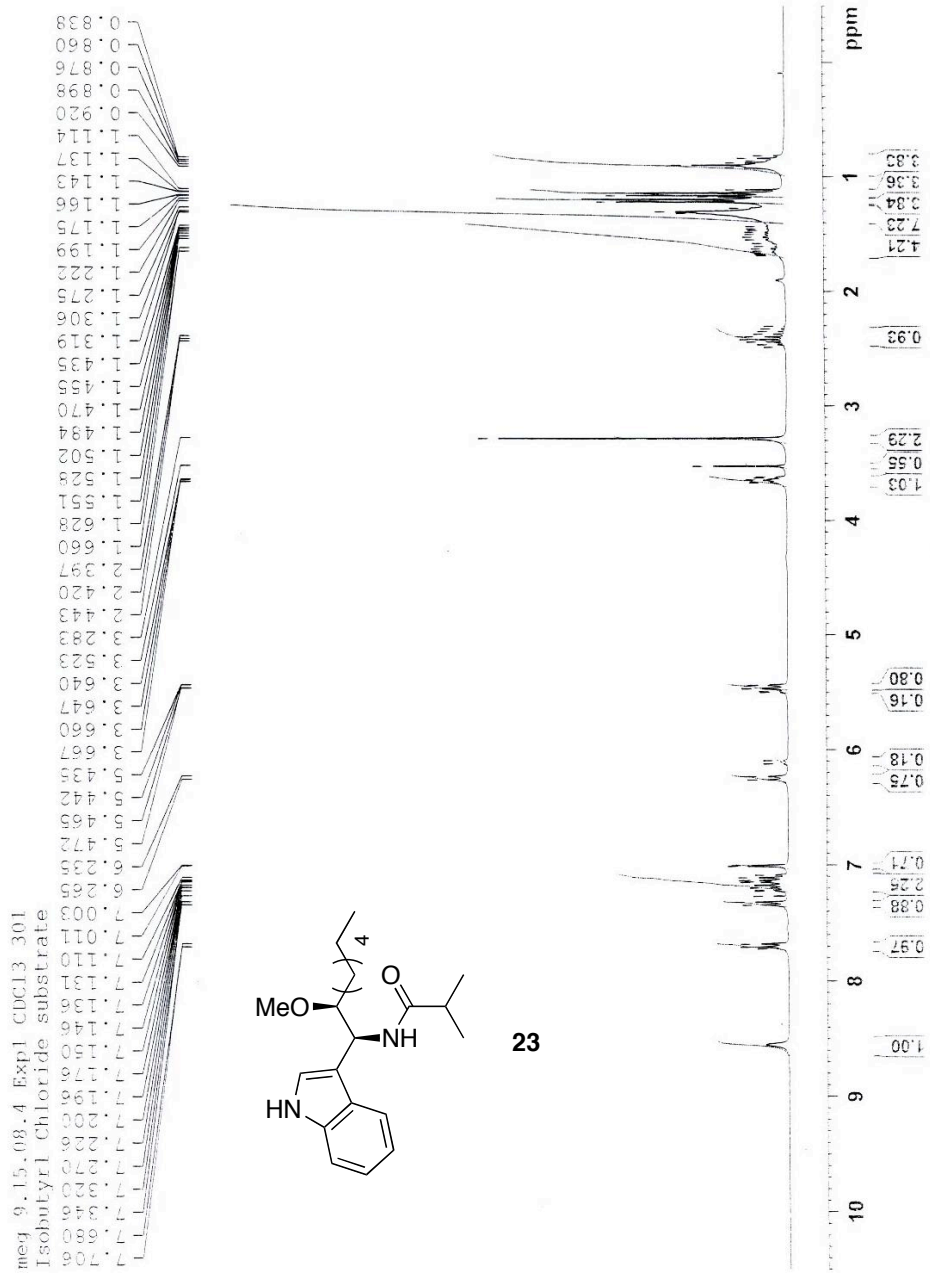




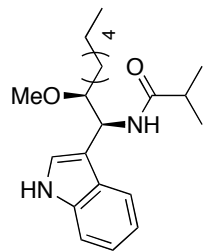




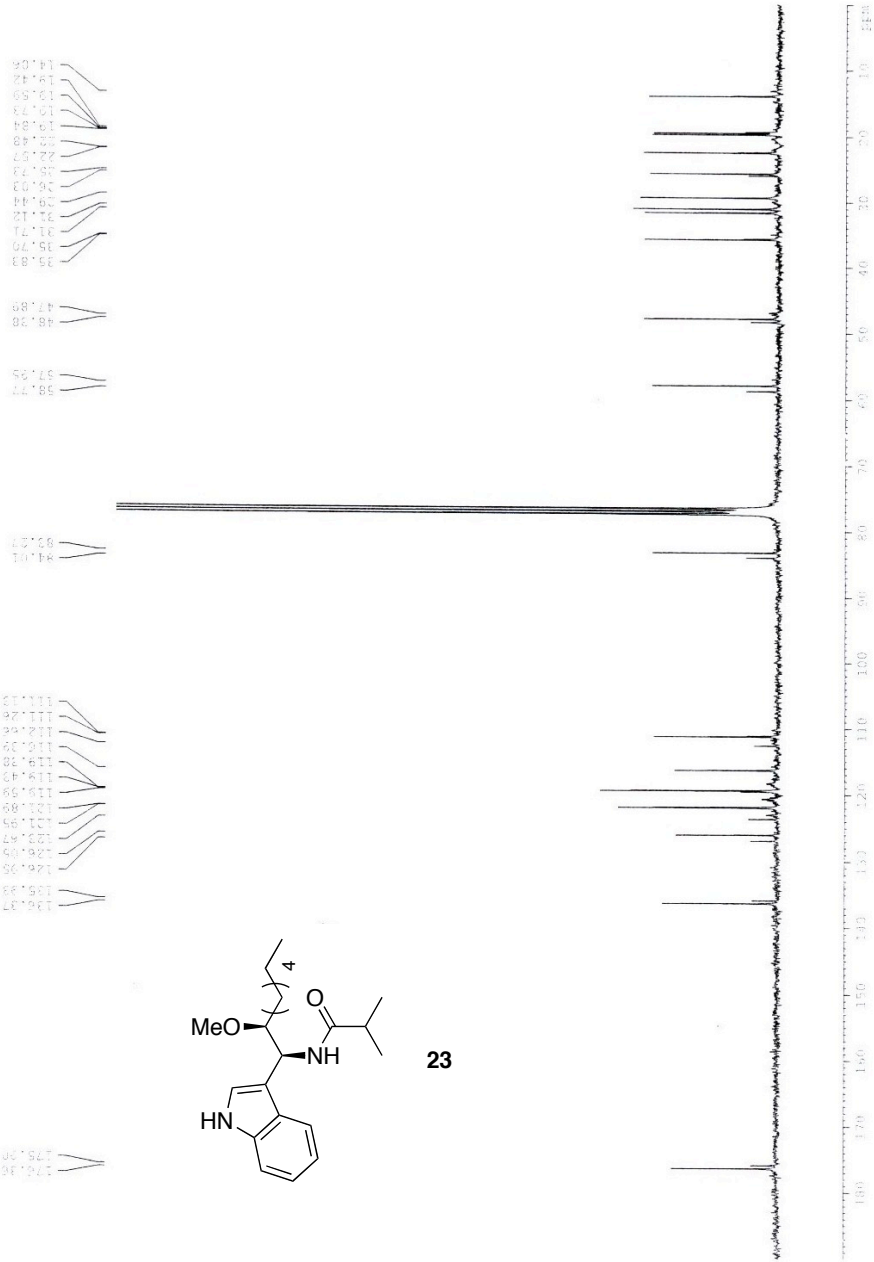


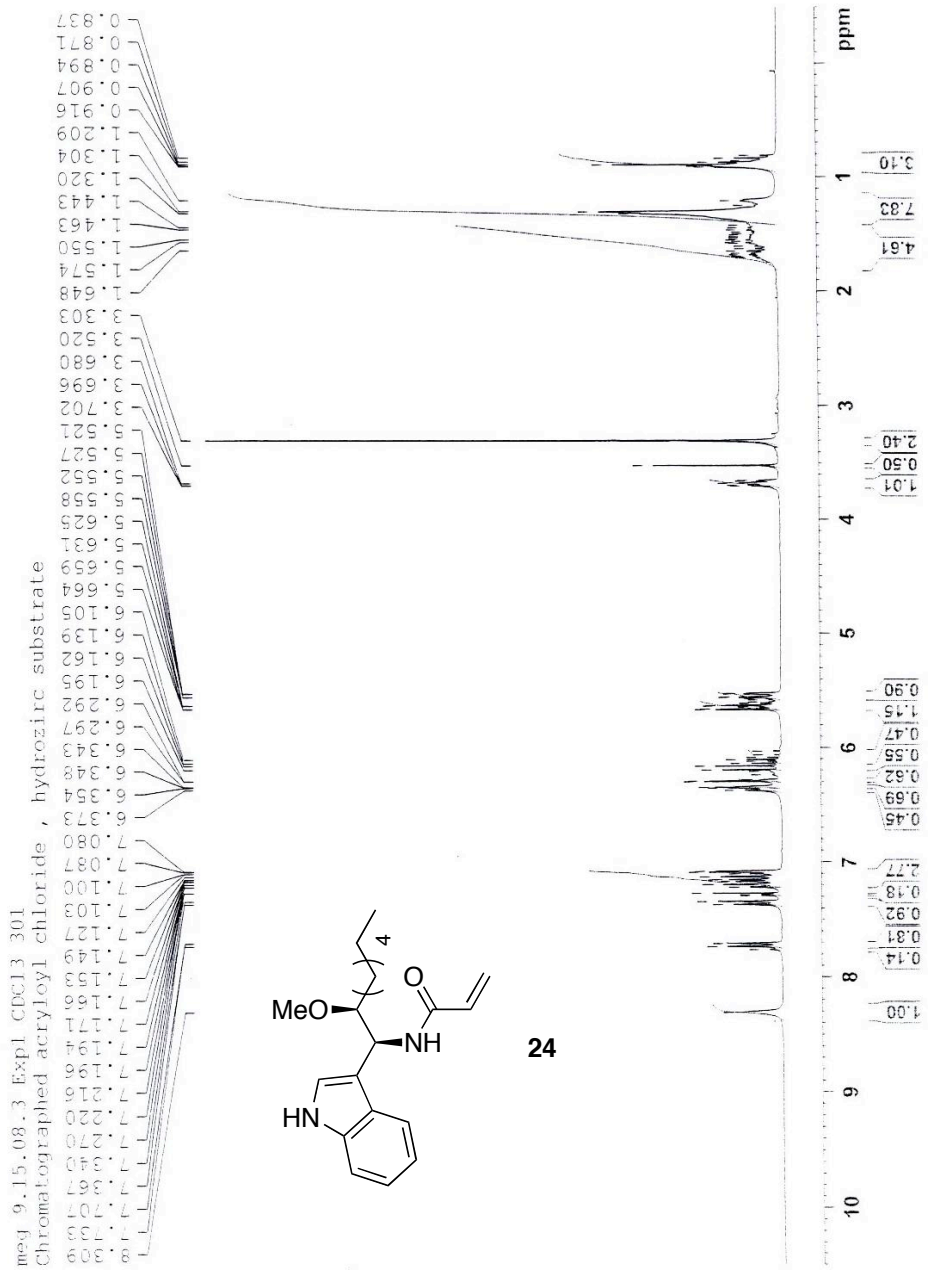


meg 9.16.08.7 Exp2 CDCl3
Isbutyrl substrate

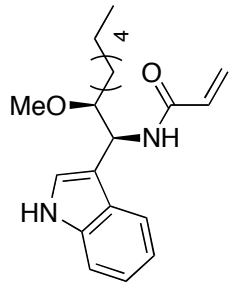


23

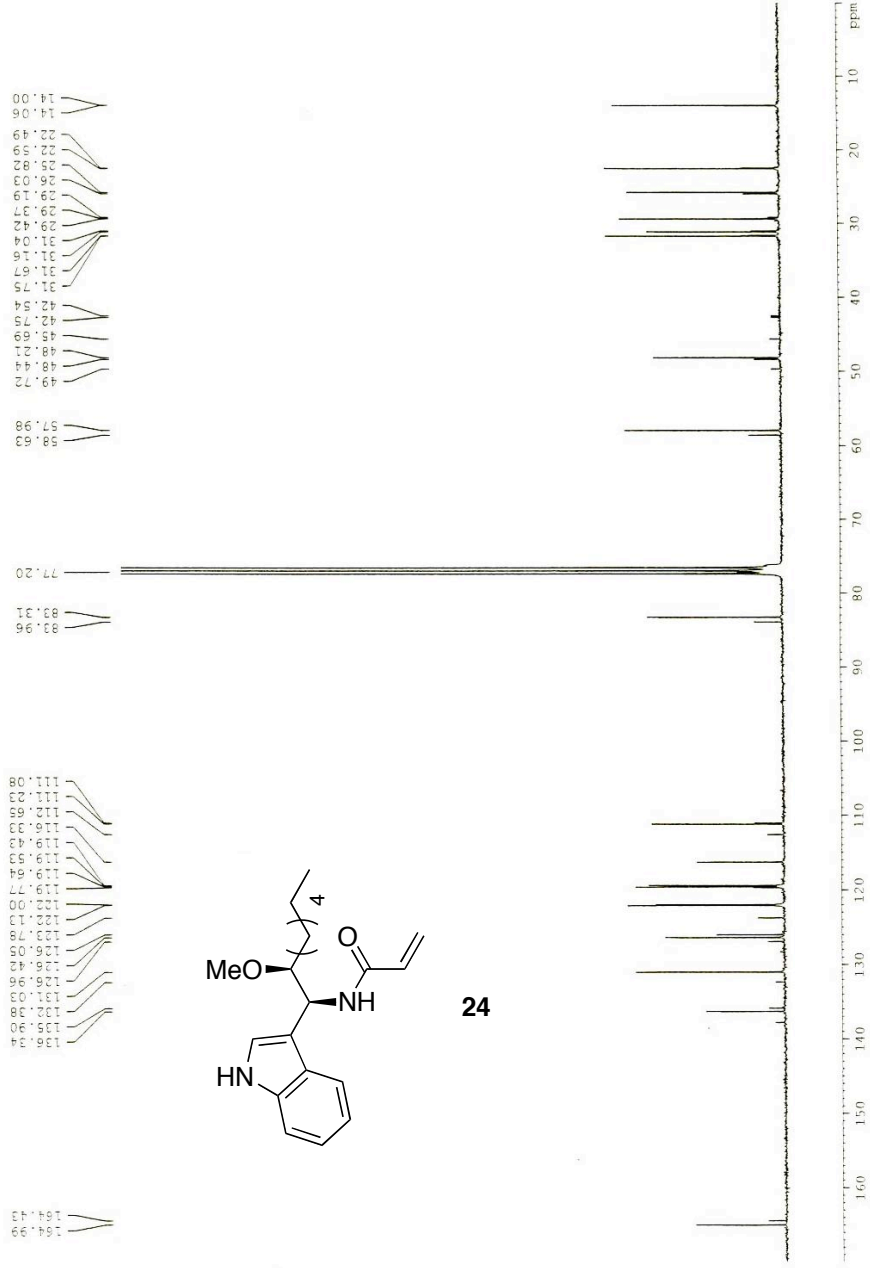


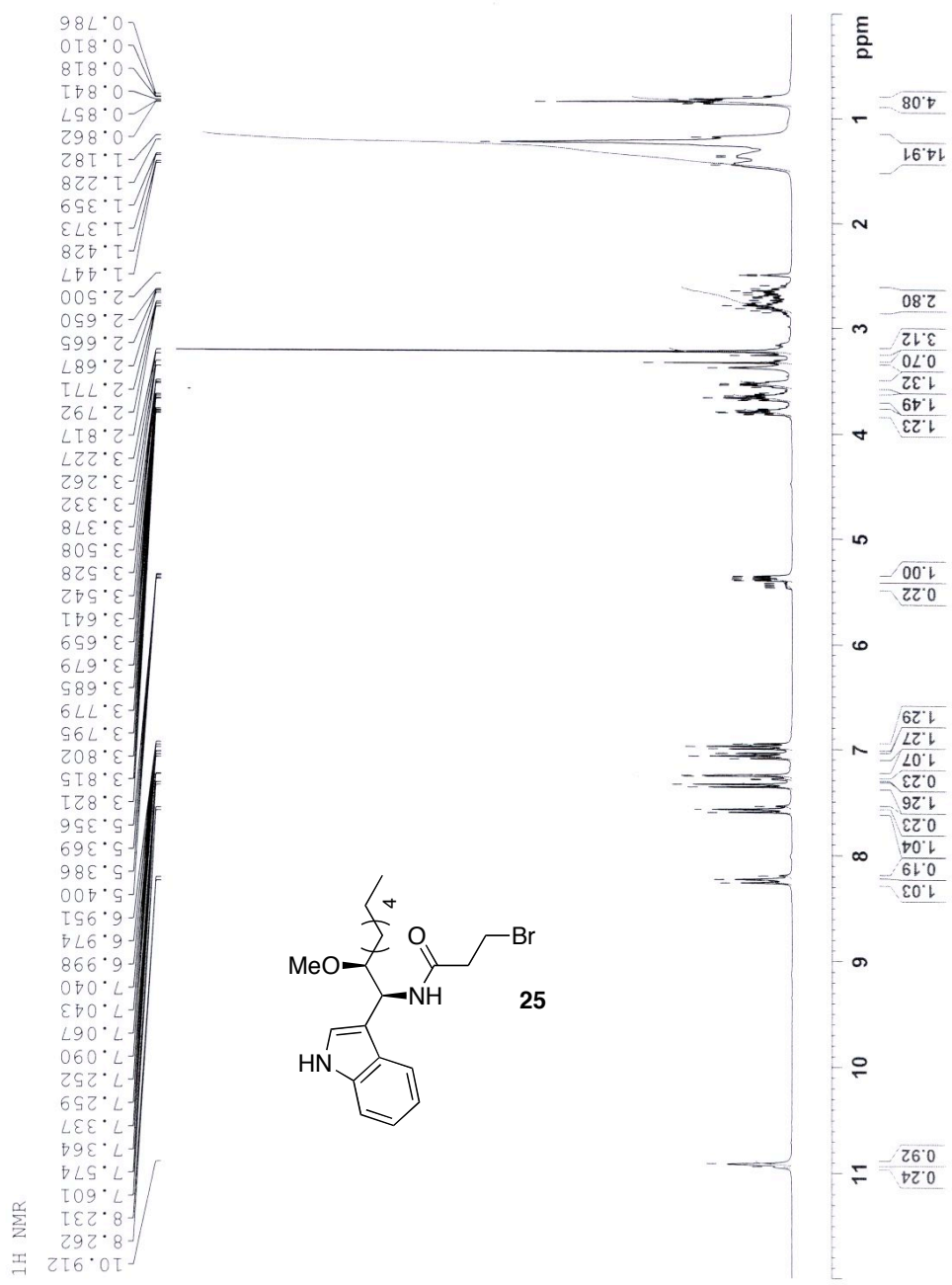


meg 9.15.08.5 Exp1 CDCl3 301a
Chromatographed Acryloyl Chloride Substrate

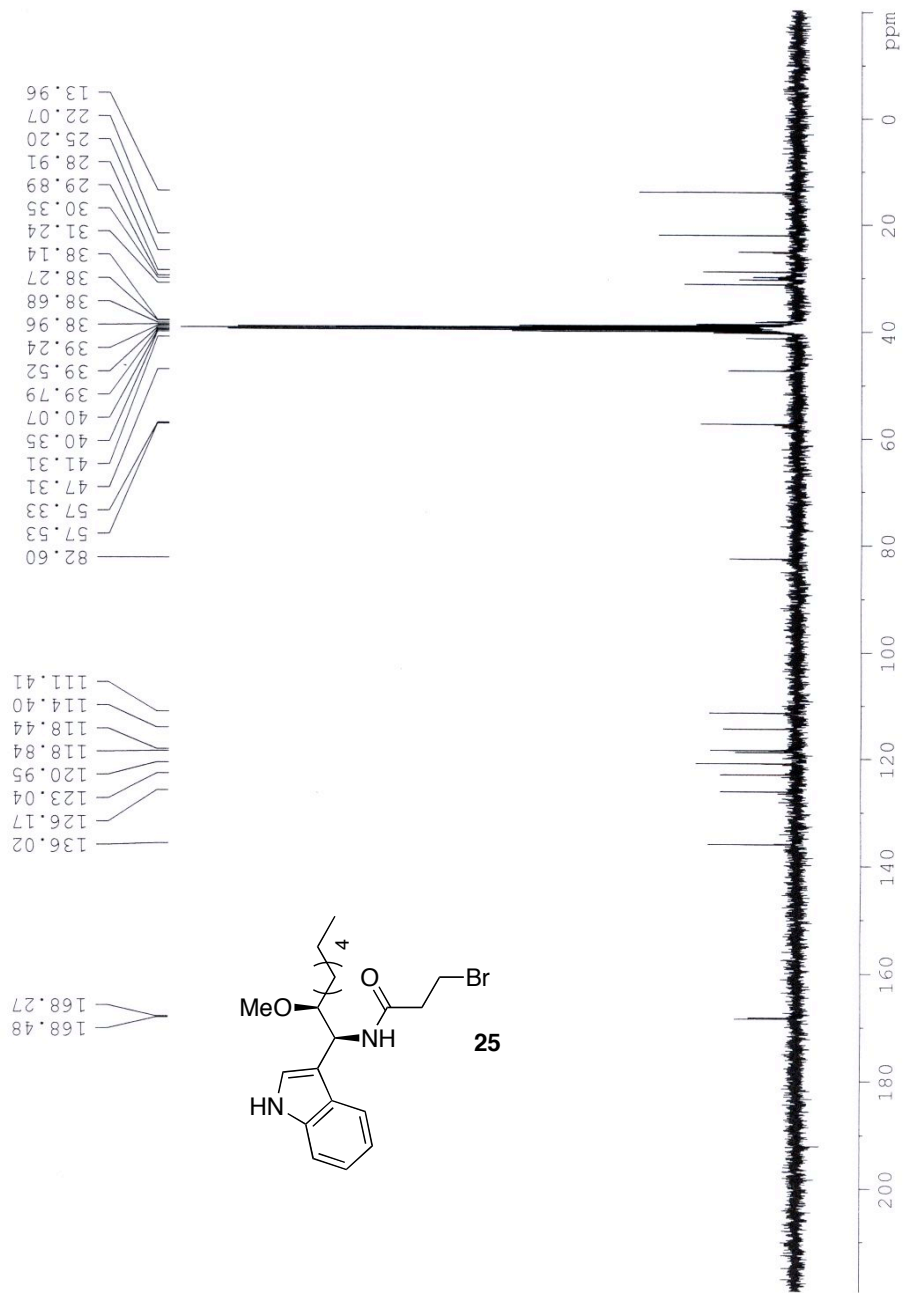


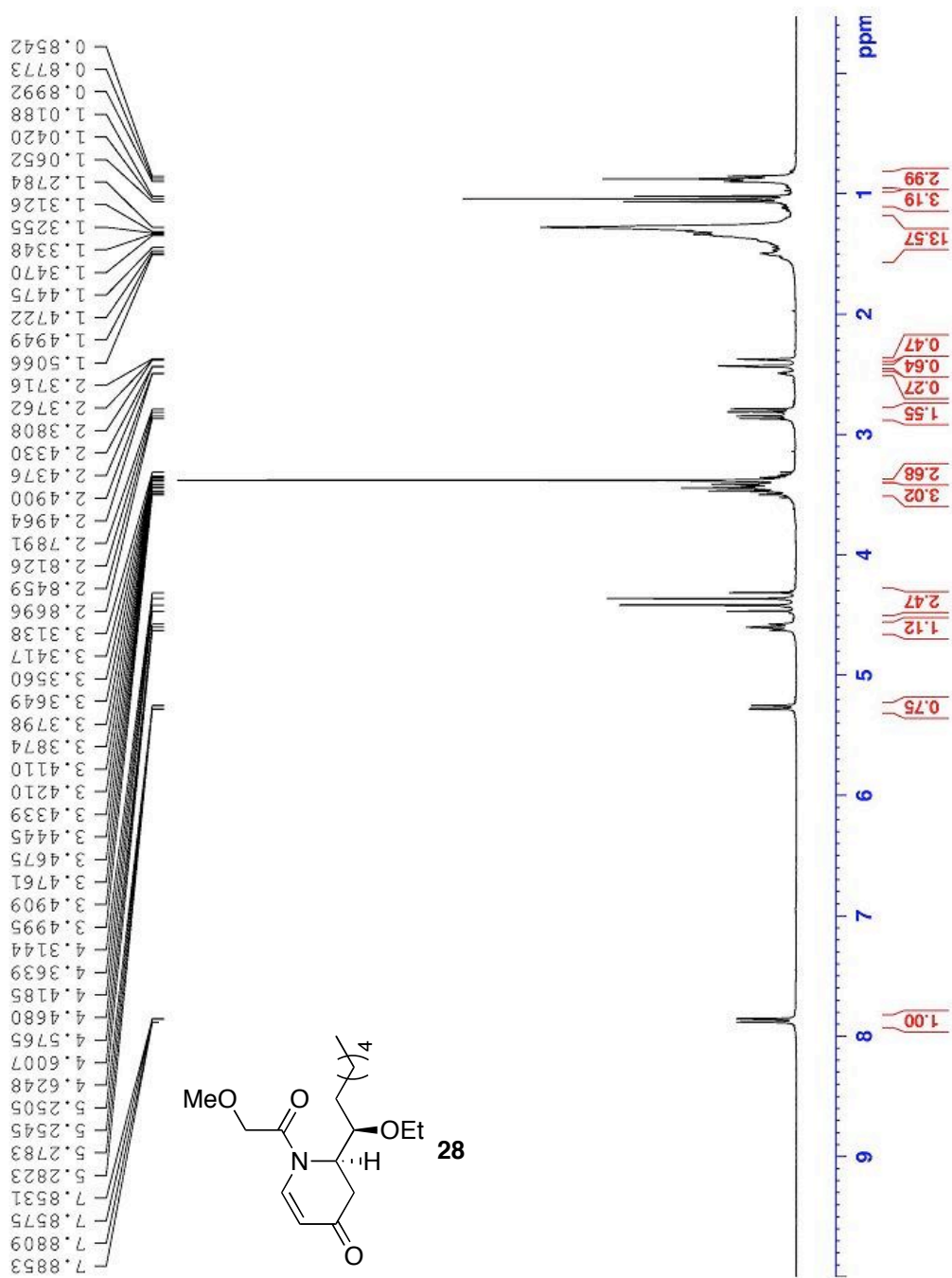
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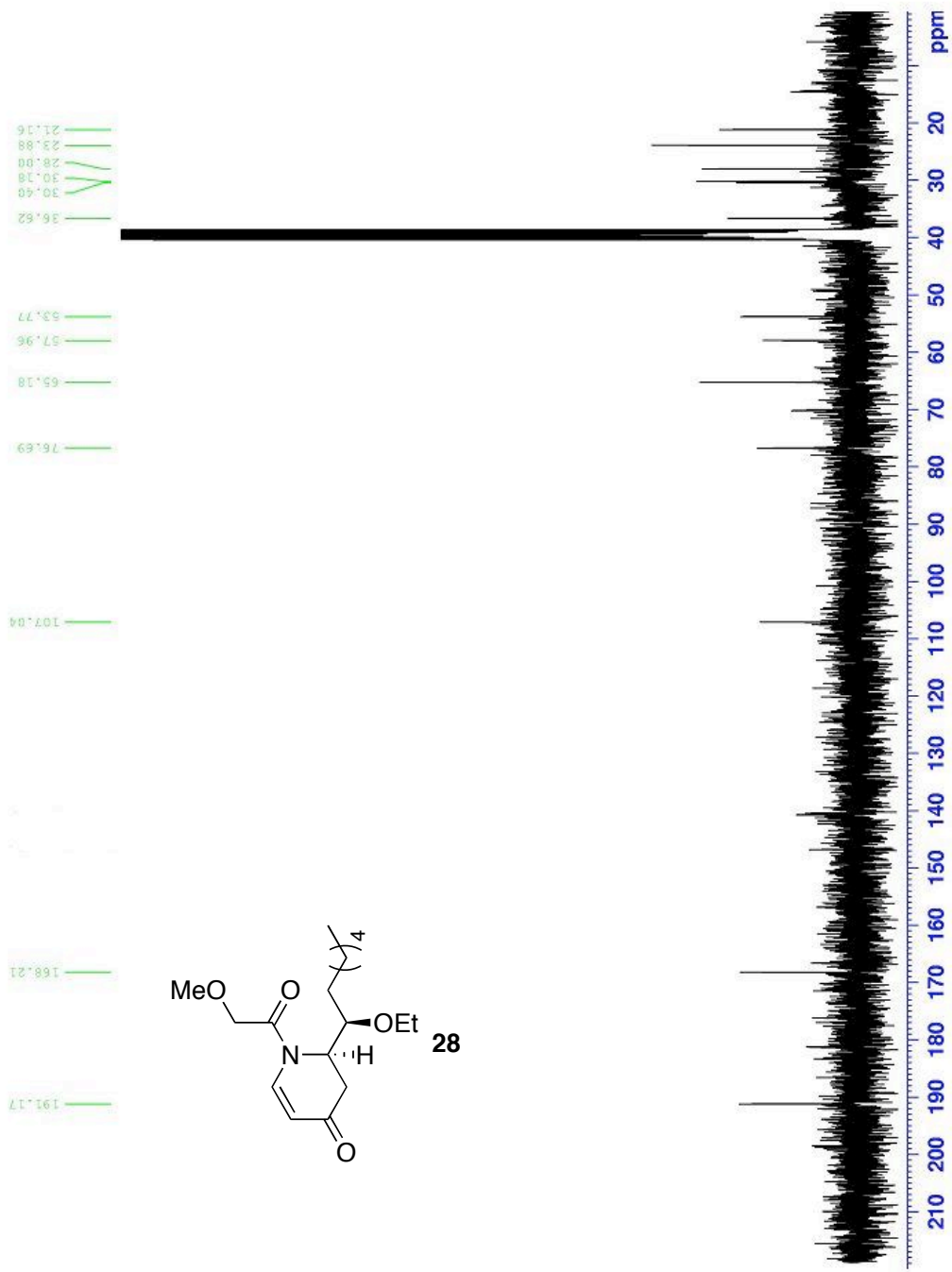




meg 9.18.08.3 Exp1 DMSO
Carbon







trans enamide



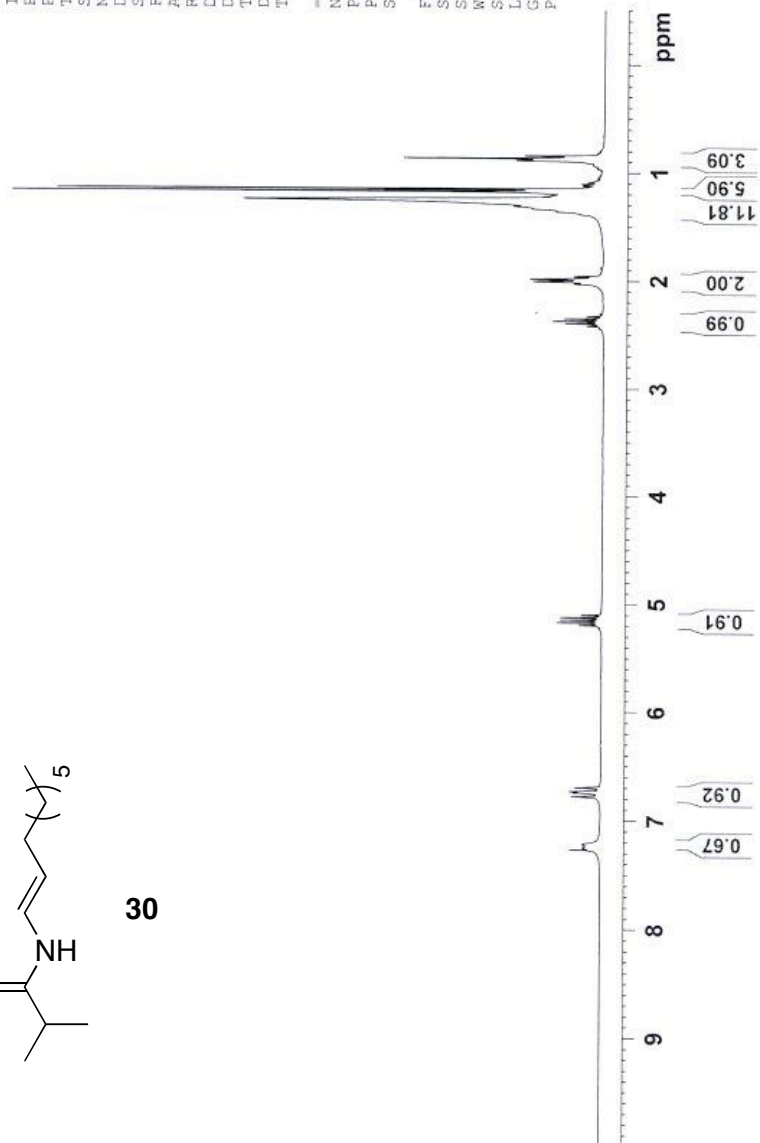
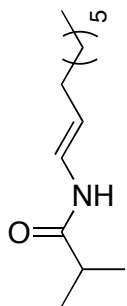
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EXPNO 1
PROCNO 1

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Date_ 20070224
Time_ 12.30
INSTRUM spect
PROBHD 5 mm DUL IH-13
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 3
DS 2
SWH 6218.905 Hz
FIDRES 0.094893 Hz
AQ 5.269145 sec
RG 45.3
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.0000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 9.00 usec
PL1 1.00 dB
SFO1 300.3818550 MHz

F2 - Processing parameters
SI 32768
SF 300.3799994 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

7.2703
7.2503
7.2184
6.7791
6.7440
6.7366
6.7317
6.6968
5.1948
5.1711
5.1474
5.1237
5.0999
2.4203
2.3975
2.3746
2.3516
2.3287
2.304
2.0085
1.9857
1.9624
1.3862
1.3585
1.3363
1.3140
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1.2220
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1.1552
1.1299
1.1145
1.1114





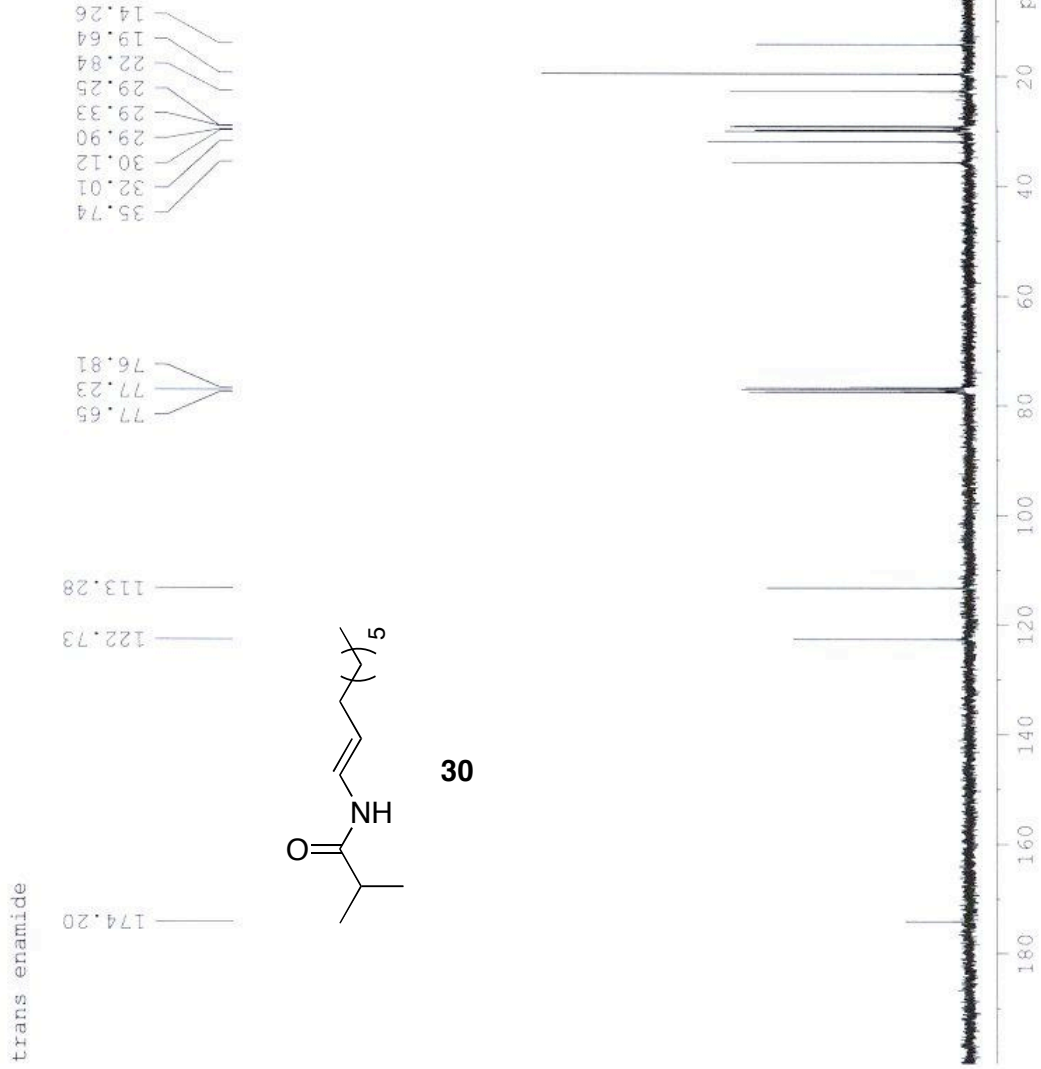
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NAME SW02240702
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070224
Time 13.17
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 38
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 13004
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 10.0000000 sec
d11 0.0300000 sec
DELTA 9.8999962 sec
TDO 1

==== CHANNEL f1 =====
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 75.4639789 MHz

==== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.24 dB
PL13 18.24 dB
SFO2 300.0862003 MHz

F2 - Processing parameters
SI 32768
SF 75.4564177 MHz
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SSB 0
GB 0
CB 0
PC 1.40





allylic nitrile

Current Data Parameters
NAME SW07110702
EXPNO 1
PROCNO 1

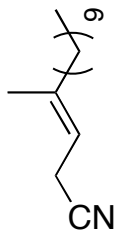
F2 - Acquisition Parameters
Date_ 20070711
Time_ 17.40
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 6
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 161.3
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 5.00 usec
PL1 0.00 dB
SFO1 300.1318530 MHz

F2 - Processing parameters
SI 16384
SF 300.1300032 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

3.0294
2.0696
2.0469
2.0236
2.0001
1.7295
1.5645
1.3786
1.3550
1.3326
1.3121
1.2719
0.9119
0.8902
0.8672

5.5171
5.5127
5.4977
5.4930
5.4884
5.4841
5.4690
5.4643

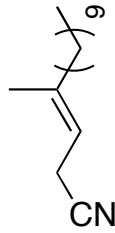


31

ppm



allylic nitrile



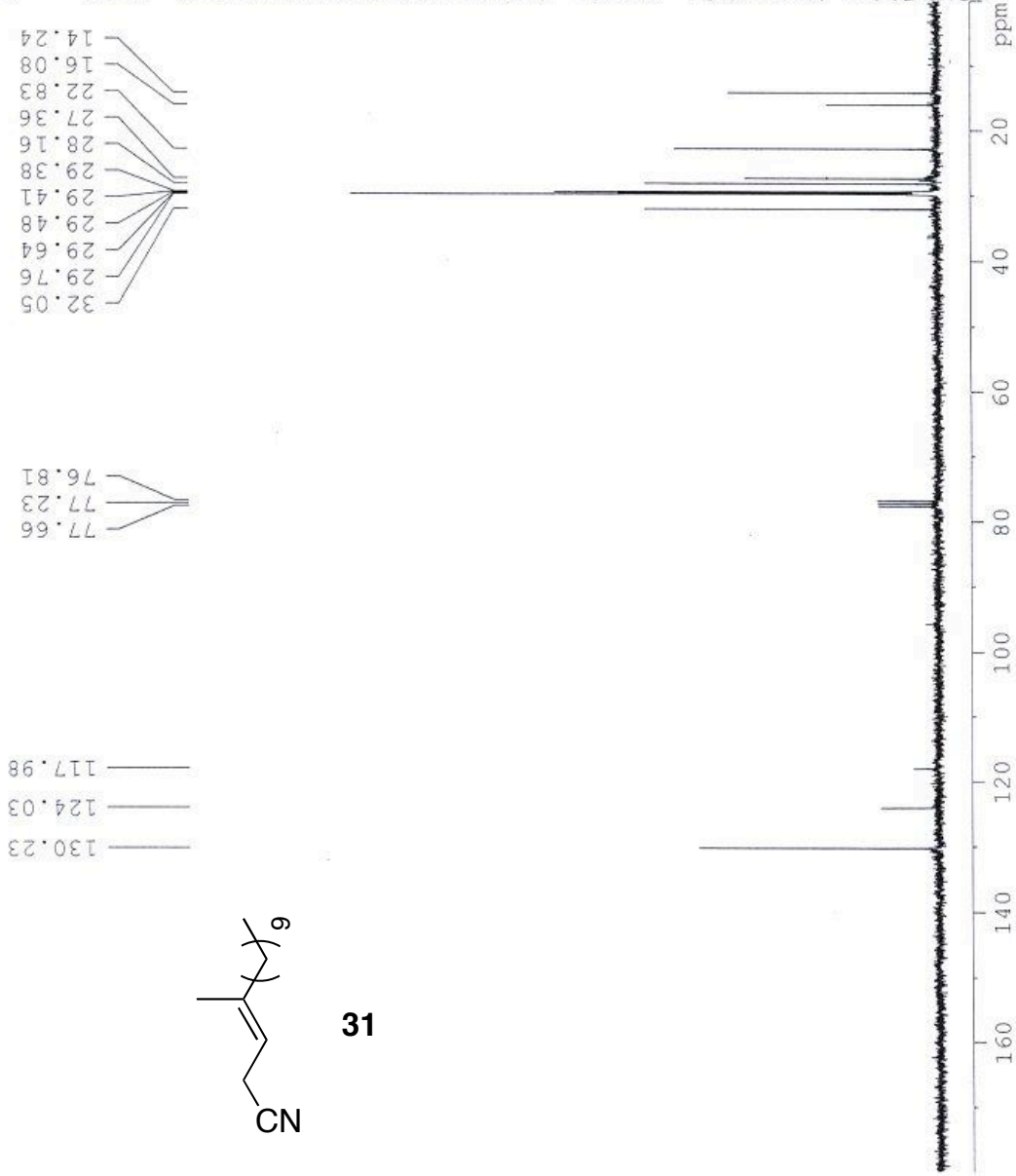
Current Data Parameters
NAME SW03230703
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070323
Time 14.01
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgpg
TD 32768
SOLVENT CDC13
NS 20
DS 2
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 1290.2
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 6.00000000 sec
d11 0.03000000 sec
DELTA 5.90000010 sec
TDO 1

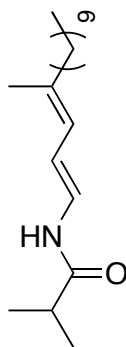
==== CHANNEL f1 =====
NUC1 13C
P1 5.00 usec
PL1 0.00 dB
SFO1 75.4752953 MHz

==== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 24.44 dB
PL13 24.44 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677371 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



trans dienamide



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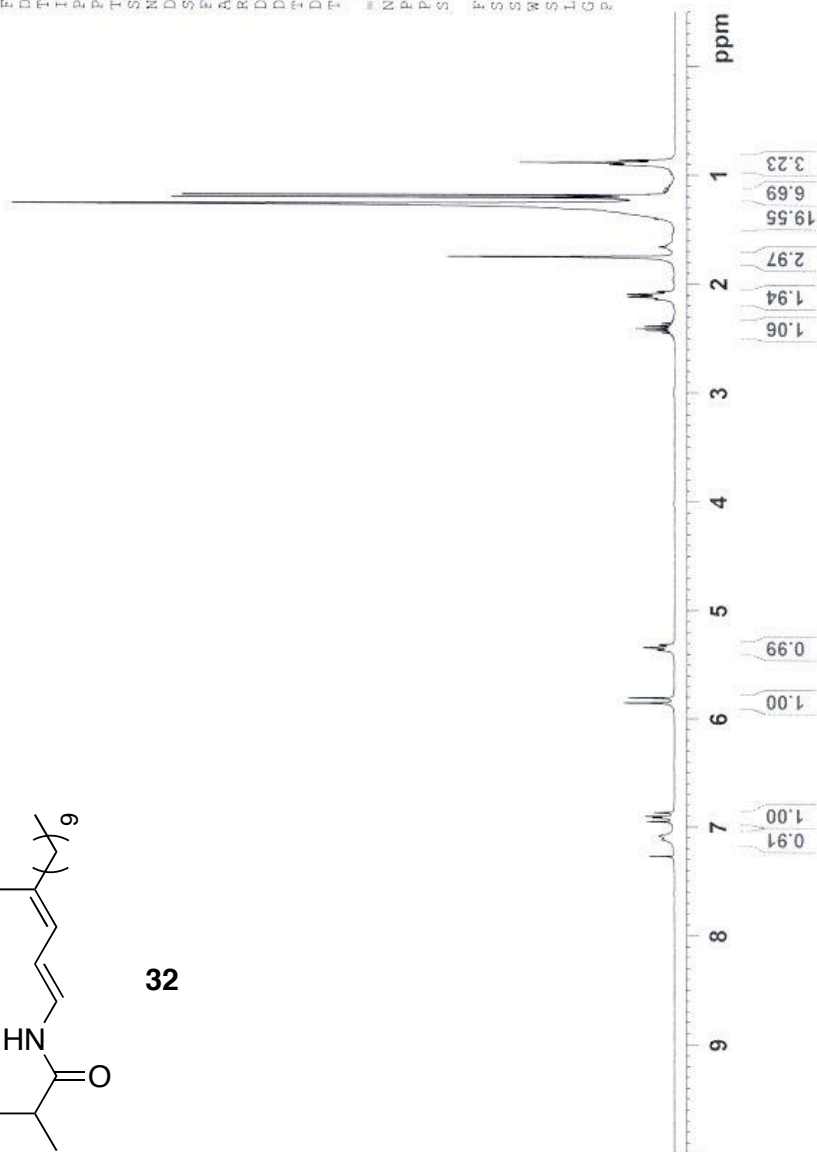
Current Data Parameters
NAME SW07120702
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070712
Time 16.36
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 4
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 101.6
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
PI 7.00 usec
PL1 0.00 dB
SFO1 300.0868531 MHz

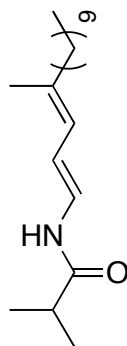
F2 - Processing parameters
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SF 300.0850017 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

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7.0833
6.9526
6.9168
6.9051
6.8694
5.8545
5.8069
5.3620
5.3380
5.3136
2.4519
2.4288
2.4059
2.3830
2.3600
2.1418
2.1192
2.0957
2.0717
1.7524
1.6581
1.6401
1.4175
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1.1601
1.1529
1.1484

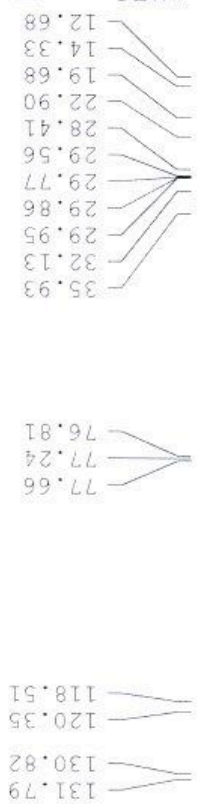




trans dienamide



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Current Data Parameters
NAME S807120703
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070712
Time 16.42
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PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 104
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 13004
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 10.00000000 sec
g11 0.03000000 sec
DELTA 9.8999962 sec
TD0 1

==== CHANNEL F1 =====
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 75.4639169 MHz

==== CHANNEL F2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 18.24 dB
PL13 18.24 dB
SFO2 300.0862003 MHz

F2 - Processing Parameters
SI 32768
SF 75.4564157 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

