

Synthesis of Acyclic α,β -Unsaturated Ketones *via* Pd(II)-Catalyzed Intermolecular Reaction of Alkynamides and Alkenes

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Supporting Information

Experimental Procedures

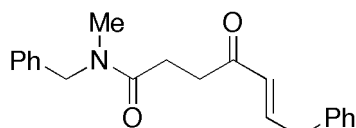
General. Reactions were carried out under an ambient atmosphere or standard grade oxygen gas in flame-dried glassware with magnetic stirring. Acetonitrile was dried through alumina. $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ was purchased from STREM Chemicals. Purification of reaction products was carried out by flash column chromatography using silica gel 60 (E. Merck 230-400 mesh), silica gel 60 silanized (E. Merck), and Florisil[®] (EM Reagent). Analytical thin layer chromatography (TLC) was performed on E. Merck precoated (0.25 mm) silica gel 60-F₂₅₄ plates. Visualization was accomplished with UV light and staining with phosphomolybdic acid solution in ethanol, followed by heating.

¹H NMR spectra were recorded on a Varian Inova-500 (500 MHz) at ambient temperature. All NMR solvents were purchased from Cambridge Isotope Laboratories. Data are reported as follows: chemical shift in ppm from a tetramethylsilane internal standard (δ), multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, coupling constants where appropriate (Hz), and assignment. ¹³C NMR was recorded on a Varian Inova-500 (125 MHz) at ambient temperature, with the resonance of deuteriochloroform at 77.0 ppm used as an internal standard. Note that amide rotamers

General Procedure for Synthesis of Pentyn- or Hexynamide. To a solution of corresponding amine (2.0 mmol, 1 equiv) in MeCN (10 mL) was added *N*-Hydroxysuccinimide-activated 4-Pentynoic or 5-Hexynoic acid (2.4 mmol, 1.2 equiv) at room temperature. After stirring at room temperature for 1 h, the resulting solution was treated with saturated aqueous NH_4Cl . The aqueous layer was extracted with EtOAc (20 mL x 2) and the combined organic layer was washed with brine (10 mL x 2) and dried over Na_2SO_4 . After filtration followed by evaporation, the crude product was purified by flash column chromatography on silica gel to provide the title compounds.

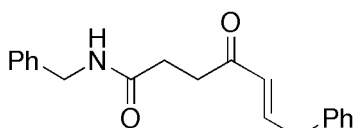
General Procedure for Intermolecular Reaction of Alkynamides and Alkenes. To a solution of $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ (15.7 mg, 0.045 mmol, 15 mol%) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (10.2 mg, 0.060 mmol, 20 mol%) in MeCN:H₂O 5:1 (1.5 mL) was added alkene (0.45 mmol, 1.5 eq). The reaction vessel was capped and placed under 1 atm of oxygen. A solution of alkyne (0.30 mmol, 1.0 eq) in MeCN:H₂O 5:1 (1.5 mL) was added dropwise over 8-12 h at room temperature or 40 °C. After the dropwise addition was completed, the reaction mixture was poured into saturated aqueous NH_4Cl (5 mL). The aqueous layer was extracted with EtOAc (5 mL x 3), and then the organic layer was washed with brine (5 mL x 2). The combined organic layers were dried over Na_2SO_4 and filtered, and the solvent was removed by rotary evaporation. The crude product was purified by flash

chromatography with a mobile phase consisting of a mixture of hexanes and ethyl acetate and a solid phase consisting of a layer of Florisil on top of a layer of silica gel. In all cases below, the *E* isomer was the only isomer observed by NMR analysis. Note that amide isomers in some cases cause the appearance of two very closely spaced resonances in both protein and carbon NMR spectra.



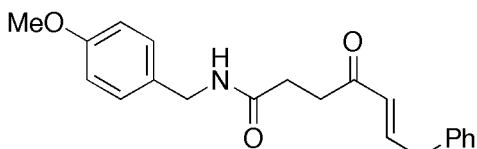
(*E*)-*N*-Benzyl-*N*-methyl-4-oxo-7-phenylhept-5-enamide.

TLC R_f = 0.15 (2:1 hexane: ethyl acetate); ^1H NMR (CDCl_3 , 500 MHz) δ 7.17-7.38 (m, 10H, Ar-*H*), 7.01-7.07 (m, 1H, CH), 6.13, 6.15 (dt, 1H, J = 15.5, 1.5 Hz, CH), 4.58, 4.59 (s, 2H, CH_2), 3.55 (t, J = 5.0 Hz, 2H, CH_2), 2.93, 2.96 (s, 3H, CH_3), 2.92-2.99 (m, 2H, CH_2), 2.68-2.71 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 199.1 (C=O), 199.2 (C=O), 171.8 (NC=O), 172.0 (NC=O), 145.5 (CH), 145.6 (CH), 137.3, 136.5, 130.9 (CH), 131.1 (CH), 128.9, 128.8 (2C), 128.7 (2C), 128.5, 127.9, 127.5, 127.2, 126.7, 126.4, 53.2, 50.9, 38.9, 38.7, 34.9, 34.8, 33.9, 27.1, 26.8; MS (ESI) Exact mass calculated for $\text{C}_{21}\text{H}_{23}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 322.1729. Found: 322.1663.



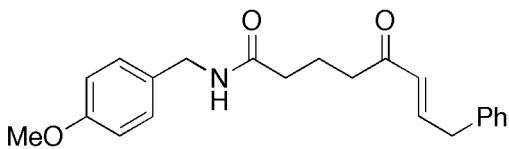
(*E*)-*N*-Benzyl-4-oxo-7-phenylhept-5-enamide.

TLC R_f = 0.26 (1:1 hexane: ethyl acetate); ^1H NMR (CDCl_3 , 500 MHz) δ 7.29-7.33 (m, 4H, Ar-*H*), 7.25-7.26 (m, 4H, Ar-*H*), 7.16-7.17 (d, 2H, J = 6.5 Hz, Ar-*H*), 6.99 (dt, 1H, J = 16.0, 6.5 Hz, CH), 6.10 (d, 1H, J = 15.5 Hz), 6.03 (br, 1H, NH), 4.41 (d, 2H, J = 6.0 Hz, CH_2), 3.54 (d, 2H, J = 6.5 Hz, CH_2), 2.95 (t, 2H, J = 7.0 Hz, CH_2), 2.50 (t, 2H, J = 7.0 Hz, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 199.3, 171.9, 146.1, 138.2, 137.5, 130.7, 128.8 (2C), 128.7 (2C), 128.6 (2C), 127.7 (2C), 127.4, 126.7, 43.6, 38.7, 35.2, 29.9; MS (ESI) Exact mass calculated for $\text{C}_{20}\text{H}_{21}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 308.1572. Found: 308.1519.



(*E*)-*N*-(4-methoxybenzyl)-4-oxo-7-phenylhept-5-enamide.

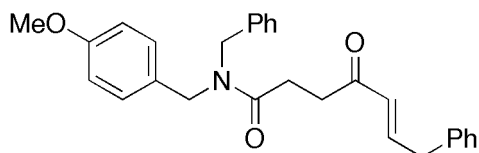
TLC R_f = 0.25 (1:1 hexane: ethyl acetate); ^1H NMR (CDCl_3 , 500 MHz) δ 7.32 (t, 2H, J = 7.5 Hz, Ar-*H*), 7.25 (t, 1H, J = 7.5 Hz, Ar-*H*), 7.19 (d, 2H, J = 9.0 Hz), 7.16 (d, 2H, J = 8.0 Hz, Ar-*H*), 7.00 (dt, 1H, J = 15.5, 7.0 Hz, CH), 6.85 (d, 2H, J = 9.0 Hz, Ar-*H*), 6.10 (dt, 1H, J = 15.5, 1.5 Hz, CH), 5.98 (br, 1H, NH), 4.34 (d, 2H, J = 6.0 Hz, CH_2), 3.78 (s, 3H, OCH_3), 3.54 (d, 2H, J = 7.0 Hz, CH_2), 2.94 (t, 2H, J = 6.5 Hz, CH_2), 2.48 (t, 2H, J = 6.5 Hz, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 199.0, 171.7, 158.9, 146.0, 137.5, 130.7, 130.3, 129.0 (2C), 128.8 (2C), 128.7 (2C), 126.7, 114.0 (2C), 55.2, 43.1, 38.7, 35.2, 30.0; MS (ESI) Exact mass calculated for $\text{C}_{21}\text{H}_{23}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 338.1678. Found: 338.1638.



(*E*)-*N*-(4-methoxybenzyl)-5-oxo-8-phenyloct-6-enamide.

TLC R_f = 0.18 (1:1 hexane: ethyl acetate); ^1H NMR (CDCl_3 , 500 MHz) δ 7.32 (t, 2H, J = 7.5 Hz, Ar-*H*), 7.25 (t, 1H, J = 7.0 Hz, Ar-*H*), 7.19 (d, 2H, Ar-*H*, J = 9.0 Hz), 7.16 (d, 2H, Ar-*H*, J = 8.0 Hz), 6.95 (dt, 1H, J =

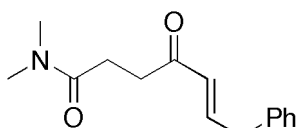
15.5, 7.0 Hz, *CH*), 6.84 (d, 2H, $J = 8.5$ Hz, *Ar-H*), 6.06 (d, 1H, $J = 16.0$ Hz, *CH*), 5.78 (br, 1H, *NH*), 4.34 (d, 2H, $J = 5.5$ Hz, CH_2), 3.78 (s, 3H, OCH_3), 3.52 (d, 2H, $J = 7.0$ Hz, CH_2), 2.62 (t, 2H, $J = 7.0$ Hz, CH_2), 2.22 (t, 2H, $J = 7.5$ Hz, CH_2), 1.92-1.98 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 172.1, 158.9, 145.6, 137.5, 130.9, 130.4, 129.1 (2C), 128.7 (2C), 128.6 (2C), 126.7, 114.0 (2C), 55.2, 42.9, 38.7, 38.6, 35.4, 19.9; MS (ESI) Exact mass calculated for $C_{22}H_{25}NO_3$ ($M+H$) $^+$: 352.1834. Found: 352.1852.



(*E*)-*N*-Benzyl-*N*-(4-methoxybenzyl)-4-oxo-7-phenyloct-5-enamide. TLC $R_f = 0.16$ (2:1 hexane: ethyl acetate); 1H NMR ($CDCl_3$, 500 MHz) δ 7.11-7.37 (m, 10H, *Ar-H*), 7.00-7.06 (m,

1H, *CH*), 6.88 (d, 1H, $J = 8.0$ Hz, *ArH*), 6.82 (d,

1H, $J = 8.0$ Hz, *ArH*), 6.84 (d, 2H, $J = 8.5$ Hz, *Ar-H*), 6.14 (dt, 1H, $J = 16.0, 1.5$ Hz, *CH*), 4.55, 4.51, 4.47, 4.43 (s, 4H, CH_2), 3.80, 3.78 (s, 3H, OCH_3), 3.54 (d, 2H, $J = 7.0$ Hz, CH_2), 2.97 (q, 2H, $J = 7.5$ Hz, CH_2), 2.75 (t, 1H, $J = 6.5$ Hz, CH_2), 2.71 (t, 1H, $J = 6.5$ Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 172.1, 158.9, 145.6, 137.6, 137.3, 136.4, 130.9, 129.6 (2C), 129.3, 128.8 (2C), 128.7 (2C), 128.6 (2C), 128.1, 127.9, 127.5, 127.3, 126.7 (2C), 126.5 (2C), 114.3 (2C), 113.9 (2C), 55.2, 49.6, 49.2, 48.0, 47.0, 38.8, 34.8, 27.0; MS (ESI) Exact mass calculated for $C_{28}H_{29}NO_3$ ($M+H$) $^+$: 428.2147. Found: 428.2087.



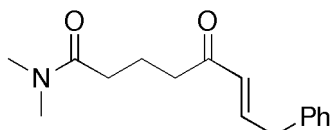
(*E*)-*N,N*-Dimethyl-4-oxo-7-phenylhept-5-enamide. TLC $R_f =$

0.15 (1:2 hexane: ethyl acetate); 1H NMR ($CDCl_3$, 500 MHz)

δ 7.32 (t, 2H, $J = 7.5$ Hz, *Ar-H*), 7.24 (t, 1H, $J = 7.5$ Hz, *Ar-H*),

7.18 (d, 2H, $J = 7.0$ Hz, *Ar-H*), 7.02 (dt, 1H, $J = 16.0, 6.5$ Hz,

CH), 6.14 (dt, 1H, $J = 16.0, 1.5$ Hz, *CH*), 3.54 (dd, 2H, CH_2 , $J = 5.5, 1.5$ Hz), 3.04 (s, 3H, CH_3), 2.93 (s, 3H, CH_3), 2.91 (t, 2H, $J = 6.5$ Hz, CH_2), 2.63 (t, 2H, $J = 7.0$ Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 171.6, 145.6, 137.6, 131.0, 128.8 (2C), 128.7 (2C), 126.7, 38.8, 37.1, 35.5, 34.8, 27.0; MS (ESI) Exact mass calculated for $C_{15}H_{19}NO_2$ ($M+H$) $^+$: 246.1416. Found: 246.1433.



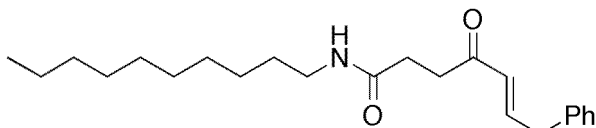
(*E*)-*N,N*-Dimethyl-5-oxo-8-phenyloct-6-enamide. TLC $R_f =$

0.18 (1:2 hexane: ethyl acetate); 1H NMR ($CDCl_3$, 500 MHz)

δ 7.32 (t, 2H, $J = 7.5$ Hz, *Ar-H*), 7.24 (t, 1H, $J = 7.5$ Hz, *Ar-*

H), 7.16 (d, 2H, $J = 7.5$ Hz, *Ar-H*), 6.97 (dt, 1H, $J = 16.0, 6.5$

Hz, *CH*), 6.08 (d, 1H, $J = 15.5$ Hz, *CH*), 3.53 (d, 2H, CH_2 , $J = 6.5$ Hz), 2.98 (s, 3H, CH_3), 2.92 (s, 3H, CH_3), 2.66 (t, 2H, $J = 7.0$ Hz, CH_2), 2.34 (t, 2H, $J = 7.0$ Hz, CH_2), 1.94 (t, 2H, $J = 7.0$ Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 172.4, 145.4, 137.6, 131.0, 128.8 (2C), 128.7 (2C), 126.7, 39.0, 38.7, 37.1, 35.3, 32.2, 19.3; MS (ESI) Exact mass calculated for $C_{16}H_{21}NO_2$ ($M+H$) $^+$: 260.1572. Found: 260.1551.

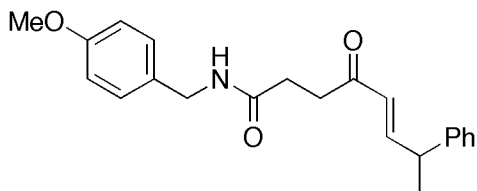


(*E*)-*N*-Decyl-4-oxo-7-phenylhept-5-enamide. TLC $R_f = 0.18$ (2:1 hexane: ethyl acetate); 1H NMR ($CDCl_3$, 500 MHz) δ 7.32 (t, 2H, $J = 7.0$ Hz, *Ar-H*),

7.24 (t, 1H, $J = 7.5$ Hz, *Ar-H*), 7.16 (d, 2H, $J = 7.0$ Hz, *Ar-H*), 6.97 (dt, 1H, $J = 16.0, 6.5$

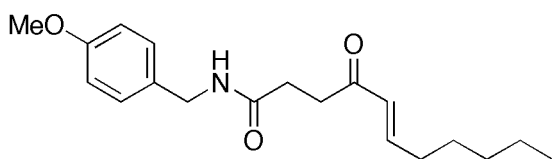
Hz, *CH*), 6.08 (d, 1H, $J = 15.5$ Hz, *CH*), 3.53 (d, 2H, CH_2 , $J = 6.5$ Hz), 2.98 (s, 3H, CH_3), 2.92 (s, 3H, CH_3), 2.66 (t, 2H, $J = 7.0$ Hz, CH_2), 2.34 (t, 2H, $J = 7.0$ Hz, CH_2), 1.94 (t, 2H, $J = 7.0$ Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 172.4, 145.4, 137.6, 131.0, 128.8 (2C), 128.7 (2C), 126.7, 39.0, 38.7, 37.1, 35.3, 32.2, 19.3; MS (ESI) Exact mass calculated for $C_{16}H_{21}NO_2$ ($M+H$) $^+$: 260.1572. Found: 260.1551.

Hz, CH), 6.10 (d, 1H, $J = 16.0$ Hz, CH), 5.77 (br, 1H, NH), 3.53 (d, 2H, CH_2 , $J = 6.5$ Hz), 3.20 (q, 2H, $J = 6.5$ Hz, CH_2), 2.92 (t, 2H, $J = 6.5$ Hz, CH_2), 2.45 (t, 2H, $J = 7.0$ Hz, CH_2), 1.46 (br, 2H, CH_2), 1.25 (br, 14H, CH_2), 0.88 (t, 3H, $J = 7.0$ Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 171.9, 146.0, 137.5, 130.7, 128.8 (2C), 128.7 (2C), 126.7, 39.6, 38.7, 35.3, 31.8, 30.1, 29.5 (2C), 29.3 (2C), 29.2, 26.8, 22.6, 14.1; MS (ESI) Exact mass calculated for $C_{23}H_{35}NO_2$ (M+H) $^+$: 358.2668. Found: 358.2655.



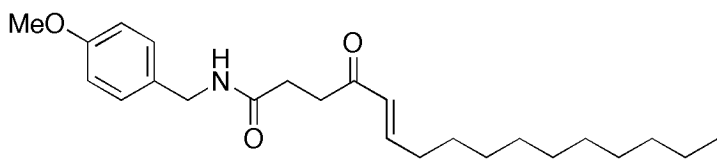
(E)-N-(4-methoxybenzyl)-4-oxo-7-phenyloct-5-enamide. TLC $R_f = 0.28$ (1:1 hexane: ethyl acetate); 1H NMR ($CDCl_3$, 500 MHz) δ 7.31 (t, 2H, $J = 7.0$ Hz, Ar-H), 7.23 (m, 1H, Ar-H), 7.17 (d, 4H, $J = 7.0$ Hz, Ar-H), 7.00 (dd, 1H, $J = 16.2$, 6.5 Hz, CH), 6.83 (dt, 2H, $J = 8.0$, 1.5 Hz, Ar-H),

6.08 (dd, 1H, $J = 16.0$, 2.0 Hz, CH), 5.92 (br, 1H, NH), 4.33 (d, 2H, $J = 5.5$ Hz, CH_2), 3.78 (s, 3H, OCH_3), 3.61 (quintet, 1H, $J = 7.0$ Hz, CH), 2.94 (t, 2H, $J = 6.5$ Hz, CH_2), 2.47 (t, 2H, $J = 6.5$ Hz, CH_2), 1.42 (d, 3H, $J = 7.0$ Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 171.8, 159.0, 151.3, 143.1, 130.3, 129.1 (2C), 128.8 (2C), 128.4, 127.3 (2C), 126.8, 114.0 (2C), 55.3, 43.1, 42.3, 35.3, 30.0, 20.1; MS (ESI) Exact mass calculated for $C_{22}H_{25}NO_3$ (M+H) $^+$: 352.1834. Found: 352.1781.



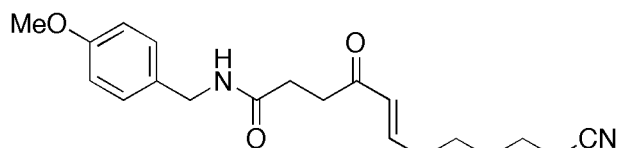
(E)-N-(4-Methoxybenzyl)-4-oxoundec-5-enamide. TLC $R_f = 0.30$ (1:1 hexane: ethyl acetate); 1H NMR ($CDCl_3$, 500 MHz) δ 7.19 (d, 2H, $J = 9.0$ Hz, Ar-H), 6.86-6.92 (m, 1H, CH), 6.86 (d, 2H, $J = 9.0$ Hz, Ar-H), 6.11 (d,

1H, $J = 14.0$ Hz, CH), 5.98 (brs, 1H, NH), 4.35 (d, 2H, $J = 5.5$ Hz, CH_2), 3.78 (s, 3H, OCH_3), 2.96 (t, 2H, $J = 7.0$ Hz, CH_2), 2.50 (t, 2H, $J = 6.5$ Hz, CH_2), 2.21 (q, 2H, $J = 6.0$ Hz, CH_2), 1.46 (q, 2H, $J = 7.0$ Hz, CH_2), 1.29-1.34 (m, 4H, CH_2), 0.897 (t, 3H, $J = 7.0$ Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 171.8, 158.9, 148.4, 130.3, 130.0, 129.0 (2C), 114.0 (2C), 55.3, 43.1, 35.1, 32.5, 31.3, 30.1, 27.7, 22.4, 13.9; MS (ESI) Exact mass calculated for $C_{19}H_{27}NO_3$ (M+H) $^+$: 318.1991. Found: 318.1960.



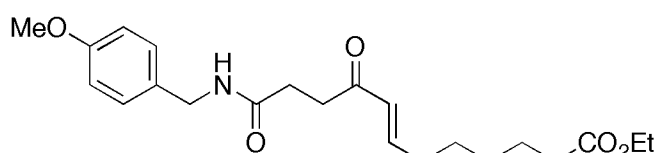
(E)-N-(4-Methoxybenzyl)-4-oxohexadec-5-enamide. TLC $R_f = 0.20$ (2:1 hexane: ethyl acetate); 1H NMR ($CDCl_3$, 500 MHz) δ 7.19 (d, 2H, $J = 8.5$ Hz,

Ar-H), 6.84-6.92 (m, 3H, CH, Ar-H), 6.11 (d, 1H, $J = 16.0$ Hz, CH), 5.96 (brs, 1H, NH), 4.35 (d, 2H, $J = 6.0$ Hz, CH_2), 3.79 (s, 3H, OCH_3), 2.95 (t, 2H, $J = 7.0$ Hz, CH_2), 2.50 (t, 2H, $J = 6.5$ Hz, CH_2), 2.21 (q, 2H, $J = 7.0$ Hz, CH_2), 1.44-1.47 (q, 2H, $J = 7.0$ Hz, CH_2), 1.26 (br, 14H, CH_2), 0.882 (t, 3H, $J = 6.5$ Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 171.9, 159.0, 148.4, 130.3, 130.0, 129.0 (2C), 114.0 (2C), 55.3, 43.1, 35.1, 32.5, 32.0, 30.3, 29.9, 29.6, 29.5 (2C), 29.4 (2C), 28.0, 22.7, 14.1; MS (ESI) Exact mass calculated for $C_{24}H_{37}NO_3$ (M+H) $^+$: 388.2773. Found: 388.2726.



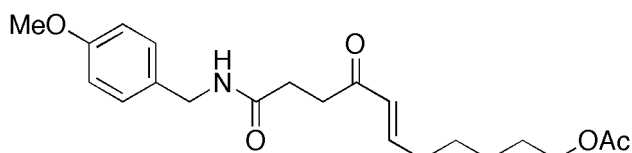
(E)-11-Cyano-N-(4-methoxybenzyl)-4-oxoundec-5-enamide. TLC R_f = 0.18 (40:1 CH_2Cl_2 : MeOH); ^1H NMR (CDCl_3 , 500 MHz) δ 7.21 (d, 2H, J = 9.0 Hz, Ar- H), 6.83-6.89 (m, 3H, CH,

Ar- H), 6.13 (d, 1H, J = 16.0 Hz, CH), 5.94 (brs, 1H, NH), 4.35 (d, 2H, J = 5.5 Hz, CH_2), 3.80 (s, 3H, OCH_3), 2.95 (t, 2H, J = 7.0 Hz, CH_2), 2.51 (t, 2H, J = 6.5 Hz, CH_2), 2.36 (t, 2H, J = 7.0 Hz, CH_2), 2.25 (q, 2H, J = 7.0 Hz, CH_2), 1.47-1.53 (m, 2H, CH_2), 1.61 (m, 2H, CH_2), 1.65-1.71 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 199.0, 171.8, 158.9, 147.0, 130.4, 130.3, 129.0 (2C), 119.5, 114.0 (2C), 55.3, 43.1, 35.1, 32.0, 30.0, 28.1, 27.2, 25.1, 17.0; MS (ESI) Exact mass calculated for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 343.1943. Found: 343.1904.



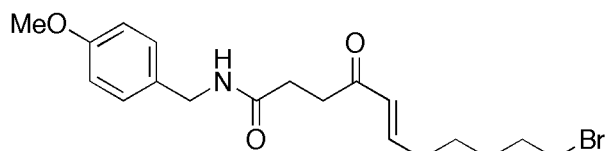
(E)-Ethy-12-(4-methoxybenzyl amino)-9,12-dioxododec-7-enoate. TLC R_f = 0.18 (1:1 hexane: ethyl acetate); ^1H NMR (CDCl_3 , 500 MHz) δ 7.20 (d, 2H, J = 9.0 Hz, Ar-

H), 6.84-6.90 (m, 3H, CH, Ar- H), 6.13 (d, 1H, J = 16.0 Hz, CH), 5.99 (brs, 1H, NH), 4.35 (d, 2H, J = 5.5 Hz, CH_2), 4.10-4.15 (m, 2H, CH_2), 3.80 (s, 3H, OCH_3), 2.95 (t, 2H, J = 6.5 Hz, CH_2), 2.44-2.54 (m, 4H, CH_2), 2.28-2.35 (m, 2H, CH_2), 1.60-1.67 (m, 2H, CH_2), 1.42-1.54 (m, 2H, CH_2), 1.32-1.40 (m, 2H, CH_2), 1.23-1.28 (m, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 199.1, 173.6, 171.8, 158.9, 147.8, 130.1, 129.0 (2C), 119.5, 114.0 (2C), 77.0, 60.2, 55.2, 43.0, 35.1, 34.1, 32.2, 30.0, 28.6, 27.6, 24.6, 14.2; MS (ESI) Exact mass calculated for $\text{C}_{22}\text{H}_{31}\text{NO}_5$ ($\text{M}+\text{H}$) $^+$: 390.2202. Found: 390.2221.



(E)-Ethy-11-(4-methoxybenzyl amino)-8,11-dioxododec-6-enyl acetate. TLC R_f = 0.13 (1:1 hexane: ethyl acetate); ^1H NMR (CDCl_3 , 500 MHz) δ 7.19 (d, 2H, J = 9.0 Hz, Ar- H),

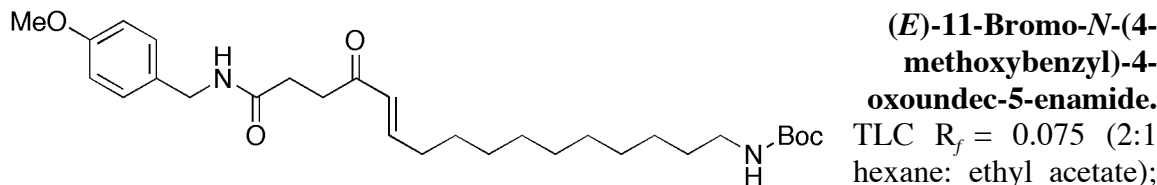
6.85-6.89 (m, 3H, CH, Ar- H), 6.13 (d, 1H, J = 16.0 Hz, CH), 6.02 (brs, 1H, NH), 4.35 (d, 2H, J = 5.5 Hz, CH_2), 4.06 (t, 2H, J = 6.5 Hz, CH_2), 3.79 (s, 3H, OCH_3), 2.95 (t, 2H, J = 7.0 Hz, CH_2), 2.50 (t, 2H, J = 7.0 Hz, CH_2), 2.23 (q, 2H, J = 7.5 Hz, CH_2), 2.05 (s, 3H, CH_3), 1.61-1.67 (m, 2H, CH_2), 1.47-1.53 (m, 2H, CH_2), 1.37-1.42 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 199.1, 171.8, 171.1, 158.9, 147.6, 130.1, 130.3, 129.0 (2C), 113.9 (2C), 64.2, 55.2, 43.0, 35.0, 32.2, 29.9, 28.3, 27.6, 25.5, 20.9; MS (ESI) Exact mass calculated for $\text{C}_{21}\text{H}_{29}\text{NO}_5$ ($\text{M}+\text{H}$) $^+$: 376.2046. Found: 376.2069.



(E)-11-Bromo-N-(4-methoxybenzyl)-4-oxoundec-5-enamide. TLC R_f = 0.18 (1:1 hexane: ethyl acetate); ^1H NMR (CDCl_3 , 500 MHz) δ 7.19 (d, 2H, J = 8.5 Hz, Ar- H), 6.84-6.90 (m, 3H, CH, Ar-

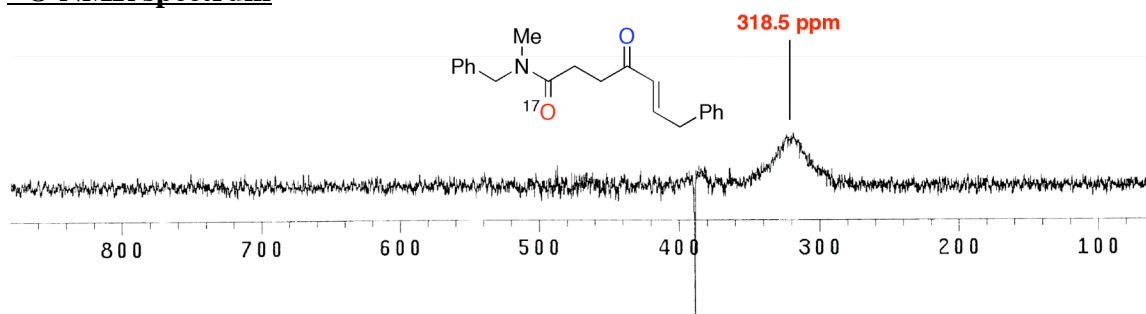
H), 6.12 (d, 1H, J = 16.5 Hz, CH), 5.95 (brs, 1H, NH), 4.35 (d, 2H, J = 6.0 Hz, CH_2), 3.80 (s, 3H, OCH_3), 3.41 (t, 2H, J = 7.0 Hz, CH_2), 2.96 (t, 2H, J = 6.5 Hz, CH_2), 2.51 (t,

2H, $J = 6.5$ Hz, CH_2), 2.24 (q, 2H, $J = 6.5$ Hz, CH_2), 1.86-1.89 (m, 2H, CH_2), 1.48-1.51 (m, 4H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 199.1, 171.8, 158.9, 147.5, 130.3, 130.2, 129.0 (2C), 114.0 (2C), 55.2, 43.1, 35.1, 33.5, 32.4, 32.2, 30.1, 27.7, 27.2; MS (ESI) Exact mass calculated for $\text{C}_{19}\text{H}_{26}\text{BrNO}_3$ ($\text{M}+\text{H}$) $^+$: 396.1096. Found: 396.1076.

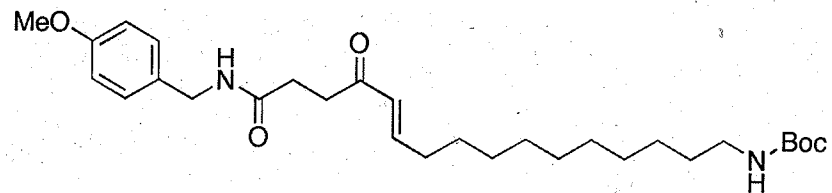


^1H NMR (CDCl_3 , 500 MHz) δ 7.19 (d, 2H, $J = 9.0$ Hz, Ar- H), 6.84-6.92 (m, 3H, CH, Ar- H), 6.10 (d, 1H, $J = 15.0$ Hz, CH), 5.97 (brs, 1H, NH), 4.51 (brs, 1H, NH), 4.35 (d, 2H, $J = 6.0$ Hz, CH_2), 3.80 (s, 3H, OCH_3), 3.10 (br, 2H, CH_2), 2.96 (t, 2H, $J = 6.5$ Hz, CH_2), 2.51 (t, 2H, $J = 6.5$ Hz, CH_2), 2.21 (q, 2H, $J = 6.5$ Hz, CH_2), 1.60-1.62 (br, 2H, CH_2), 1.44 (brs, 9H, $\text{C}(\text{CH}_3)_3$), 1.28 (brs, 14H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 199.2, 171.9, 158.9, 148.3, 130.4, 130.0, 129.0 (2C), 114.0 (2C), 78.1, 55.2, 43.1, 40.6, 35.0, 32.5, 30.1, 30.0, 29.4, 29.3 (2C), 29.2 (2C), 29.1, 28.4 (3C), 28.0, 26.8; MS (ESI) Exact mass calculated for $\text{C}_{29}\text{H}_{46}\text{NO}_5$ ($\text{M}+\text{H}$) $^+$: 503.3407. Found: 503.2653.

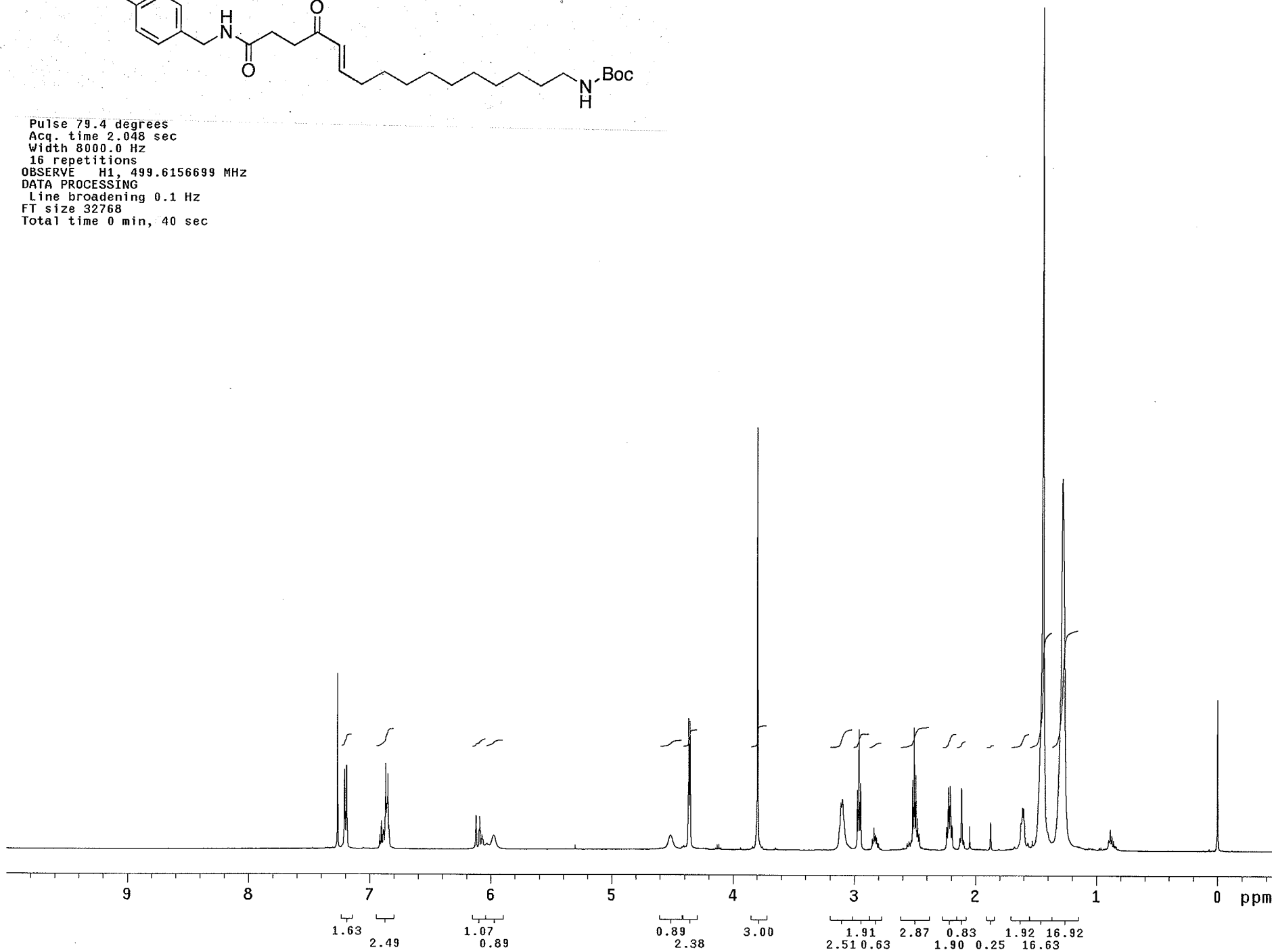
^{17}O NMR spectrum

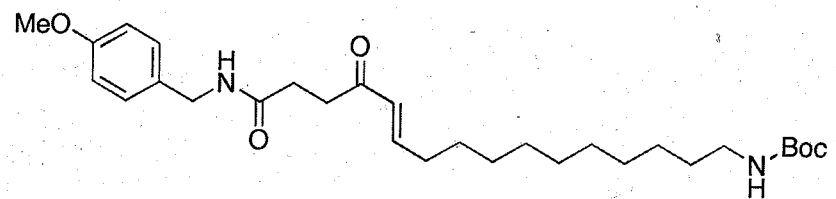


^1H and ^{13}C NMR spectrum for the above compounds appear on the following pages.

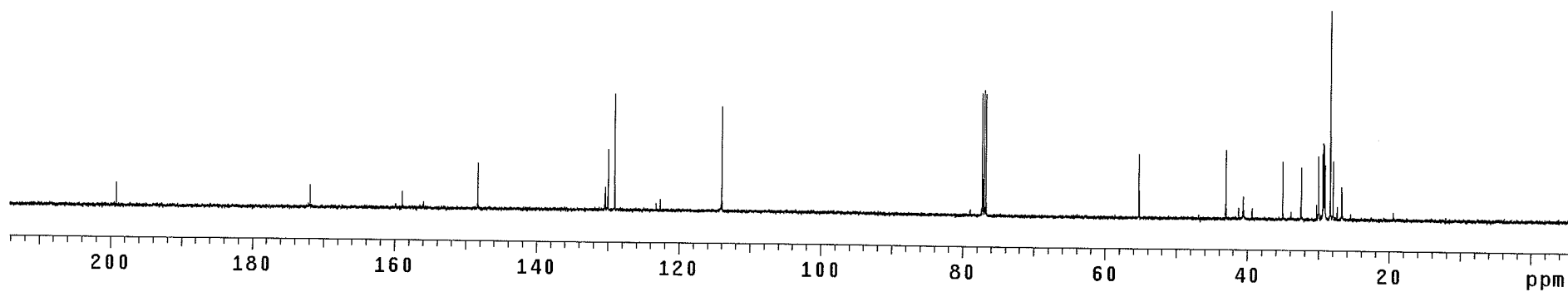


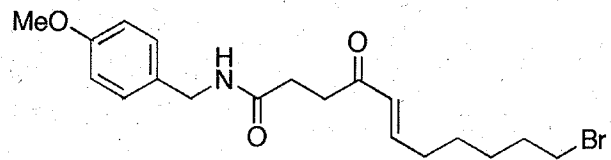
Pulse 79.4 degrees
 Acq. time 2.048 sec
 Width 8000.0 Hz
 16 repetitions
 OBSERVE H1, 499.6156699 MHz
 DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 32768
 Total time 0 min, 40 sec



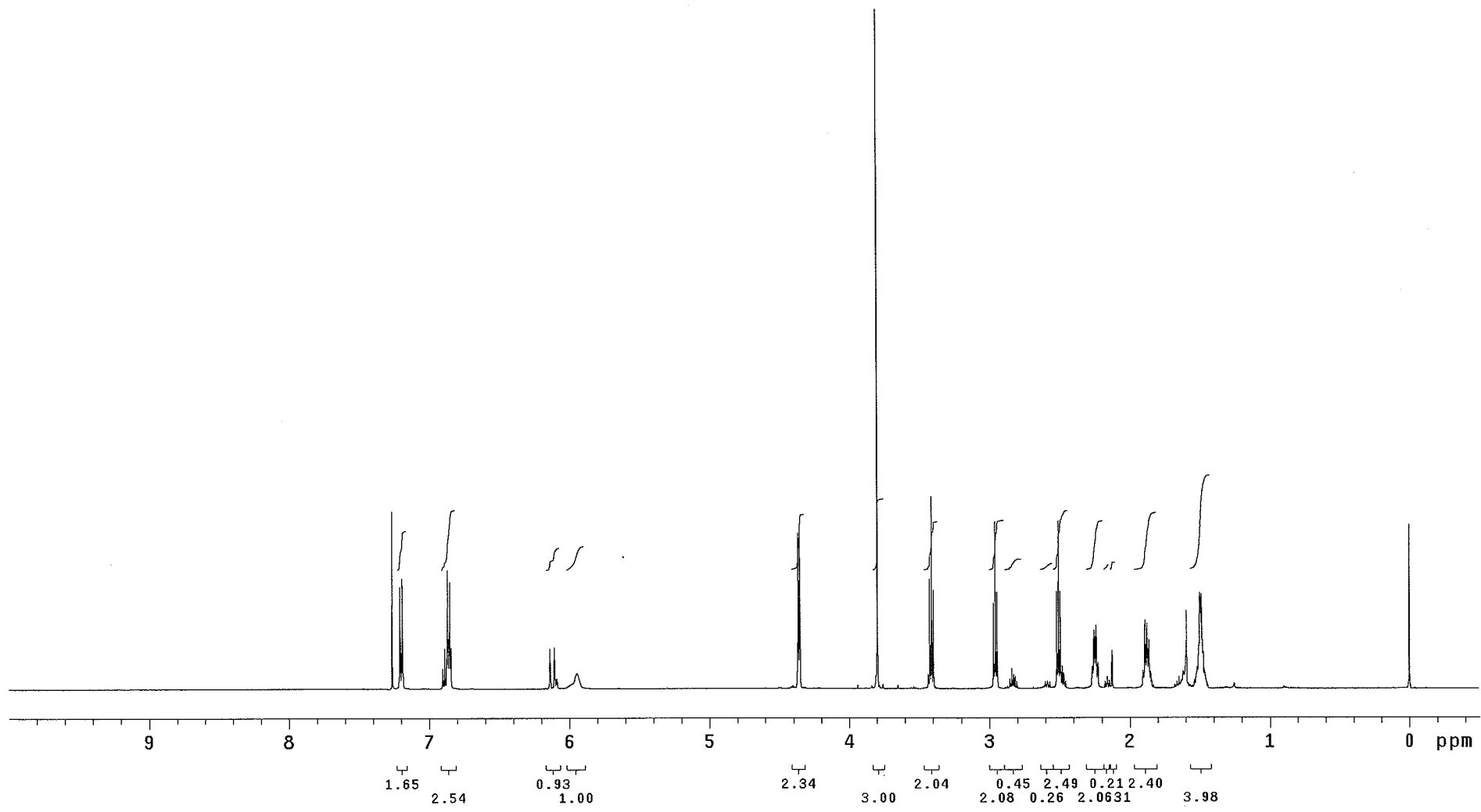


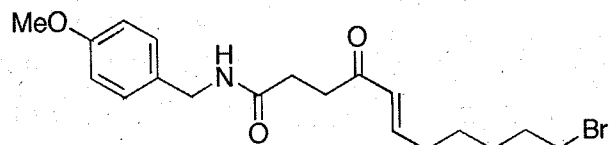
Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
10000 repetitions
OBSERVE C13, 125.6284643 MHz
DECOUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 3 min, 33 sec





Relax. delay 0.200 sec
 Pulse 79.4 degrees
 Acq. time 2.048 sec
 Width 8000.0 Hz
 16 repetitions
 OBSERVE H1, 499.6156699 MHz
 DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 32768
 Total time 0 min, 40 sec





File: 6904-4-13C

Pulse Sequence: s2pu1

Solvent: CDC13

Temp. 23.0 C / 296.1 K

User: 1-14-87

Pulse 40.0 degrees

Acq. time 1.092 sec

Width 29996.3 Hz

100000 repetitions

OBSERVE C13, 125.6284634 MHz

DECOUPLE H1, 499.6181772 MHz

Power 34 dB

continuously on

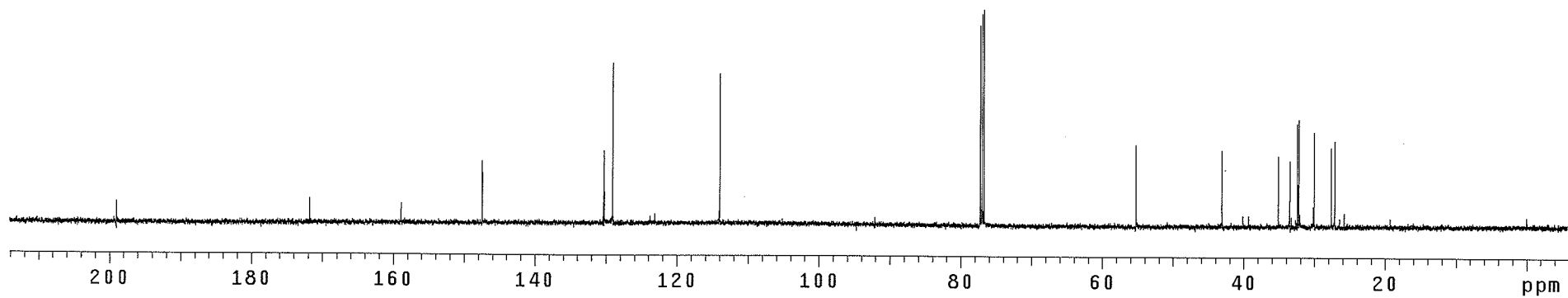
WALTZ-16 modulated

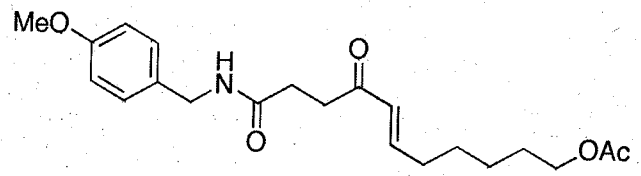
DATA PROCESSING

Line broadening 1.0 Hz

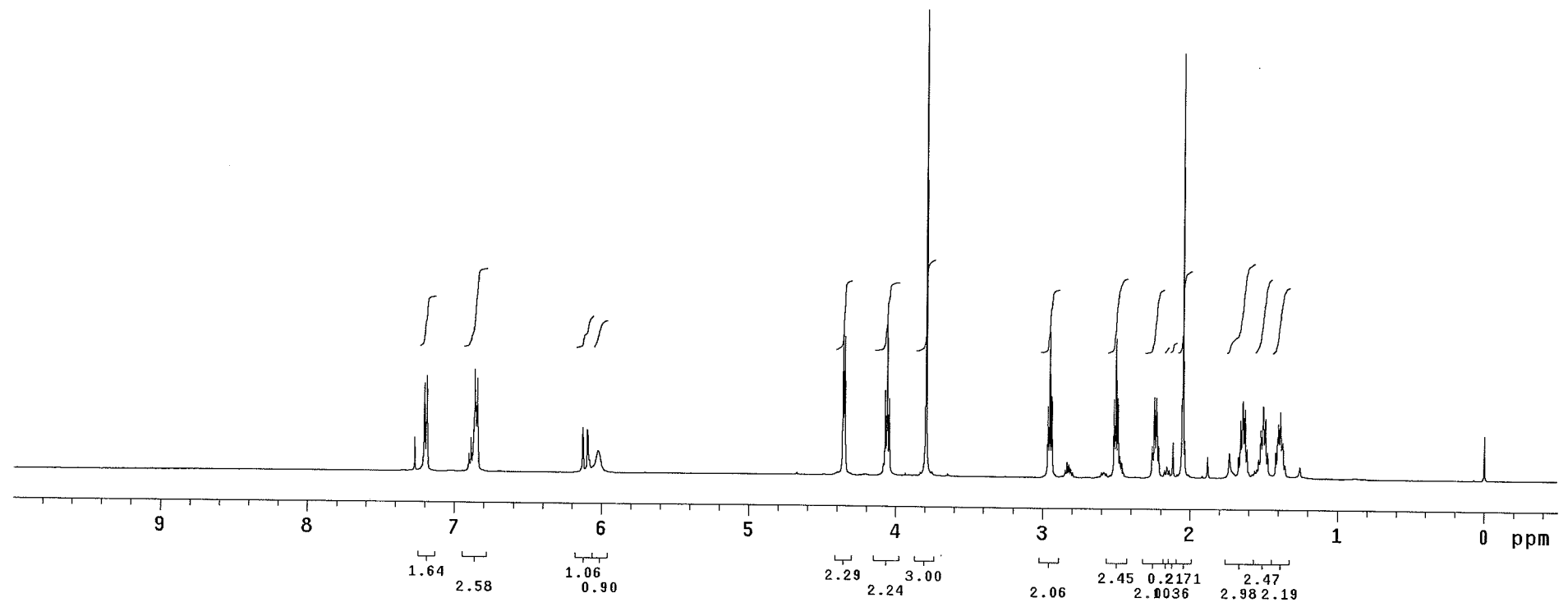
FT size 65536

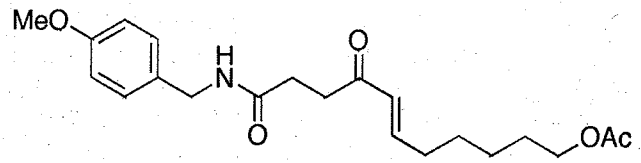
Total time 30 hr, 35 min



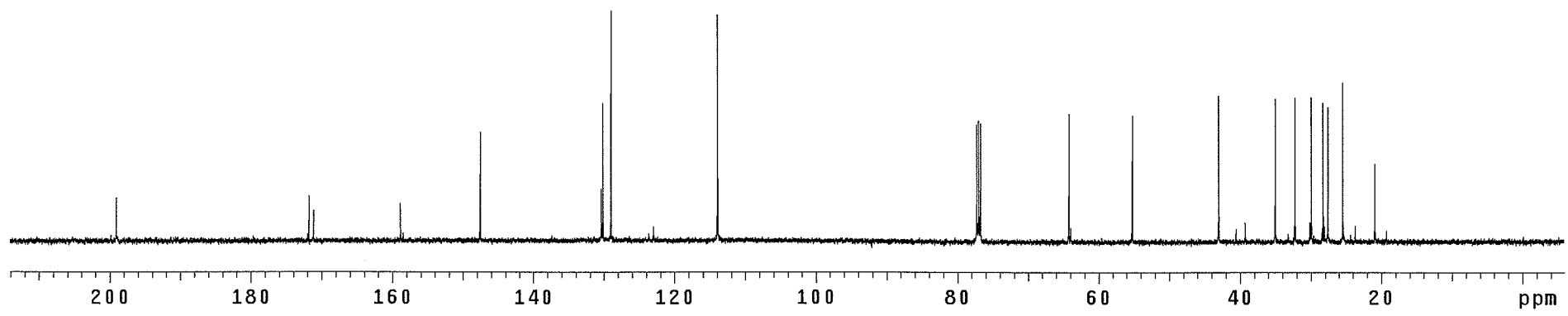


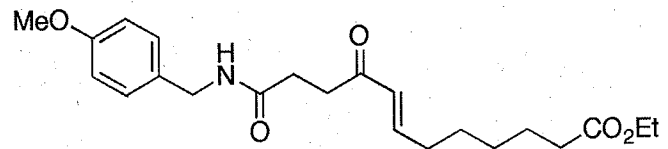
Relax. delay 0.200 sec
 Pulse 79.4 degrees
 Acq. time 2.048 sec
 Width 8000.0 Hz
 16 repetitions
 OBSERVE H1, 499.6156674 MHz
 DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 32768
 Total time 0 min, 40 sec



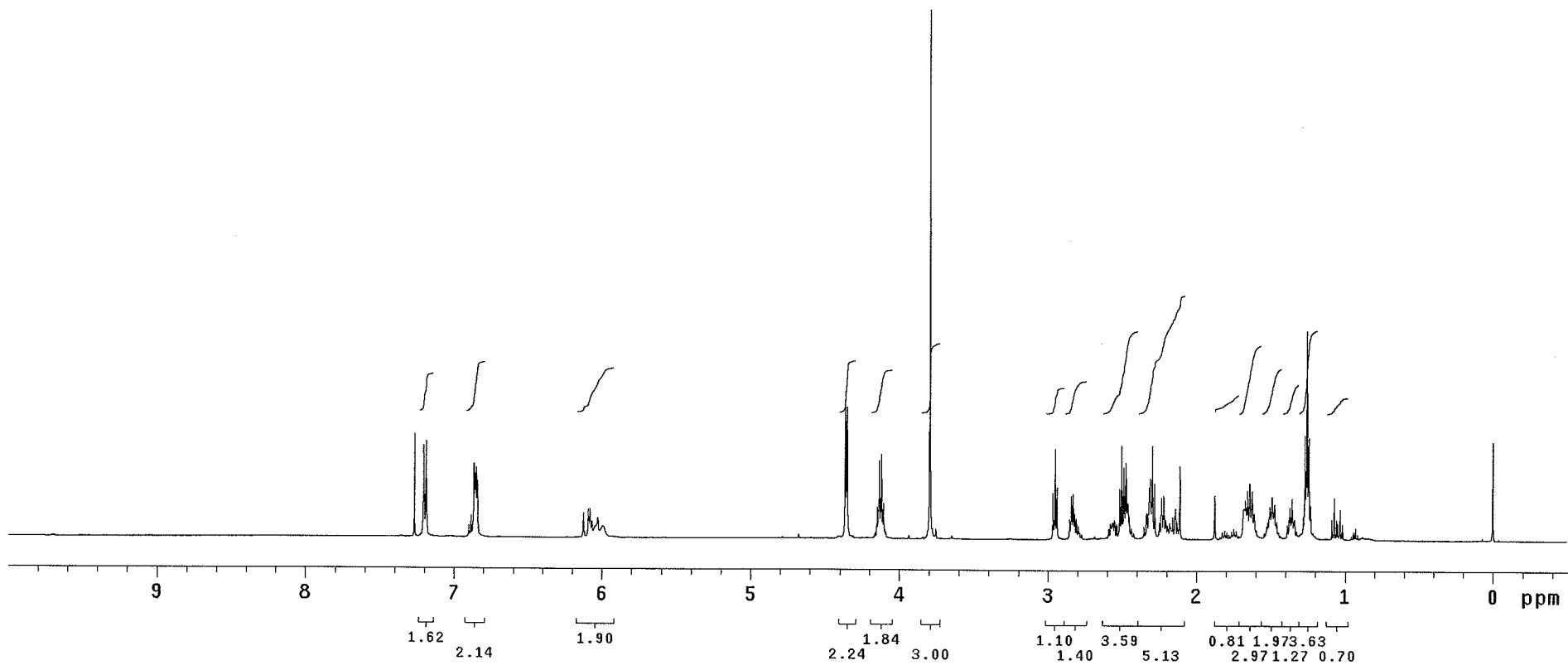


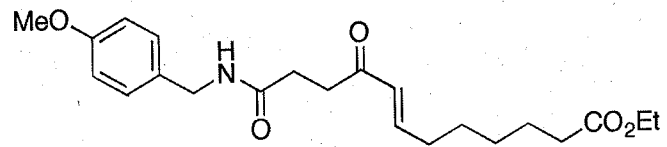
Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
10000 repetitions
OBSERVE C13, 125.6284689 MHz
DECOUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 3 min, 33 sec



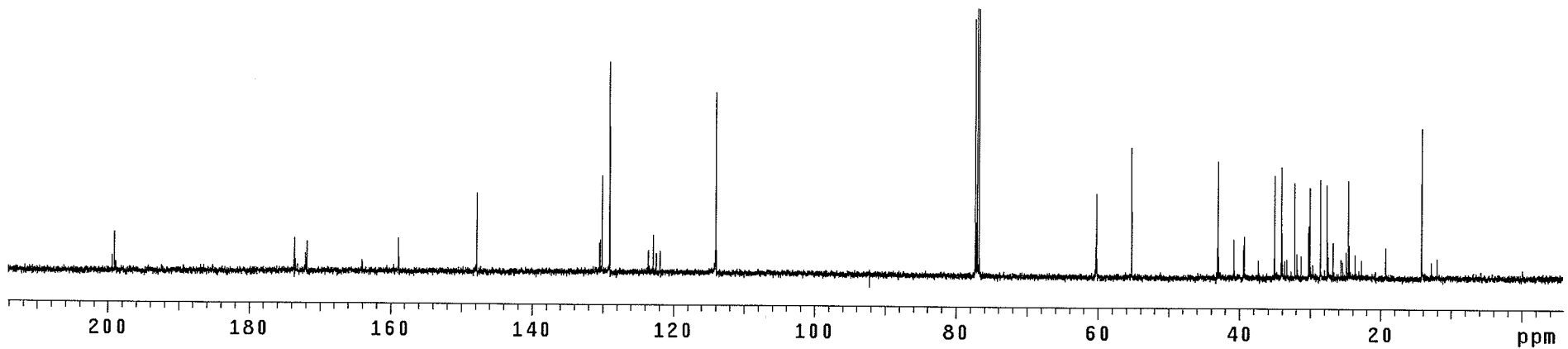


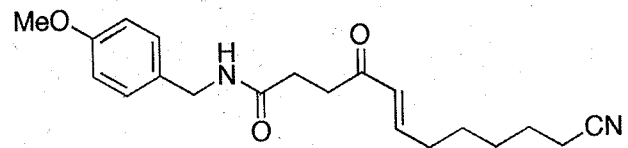
Relax. delay 0.200 sec
 Pulse 79.4 degrees
 Acq. time 2.048 sec
 Width 8000.0 Hz
 16 repetitions
 OBSERVE H1, 499.6156684 MHz
 DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 32768
 Total time 0 min, 40 sec



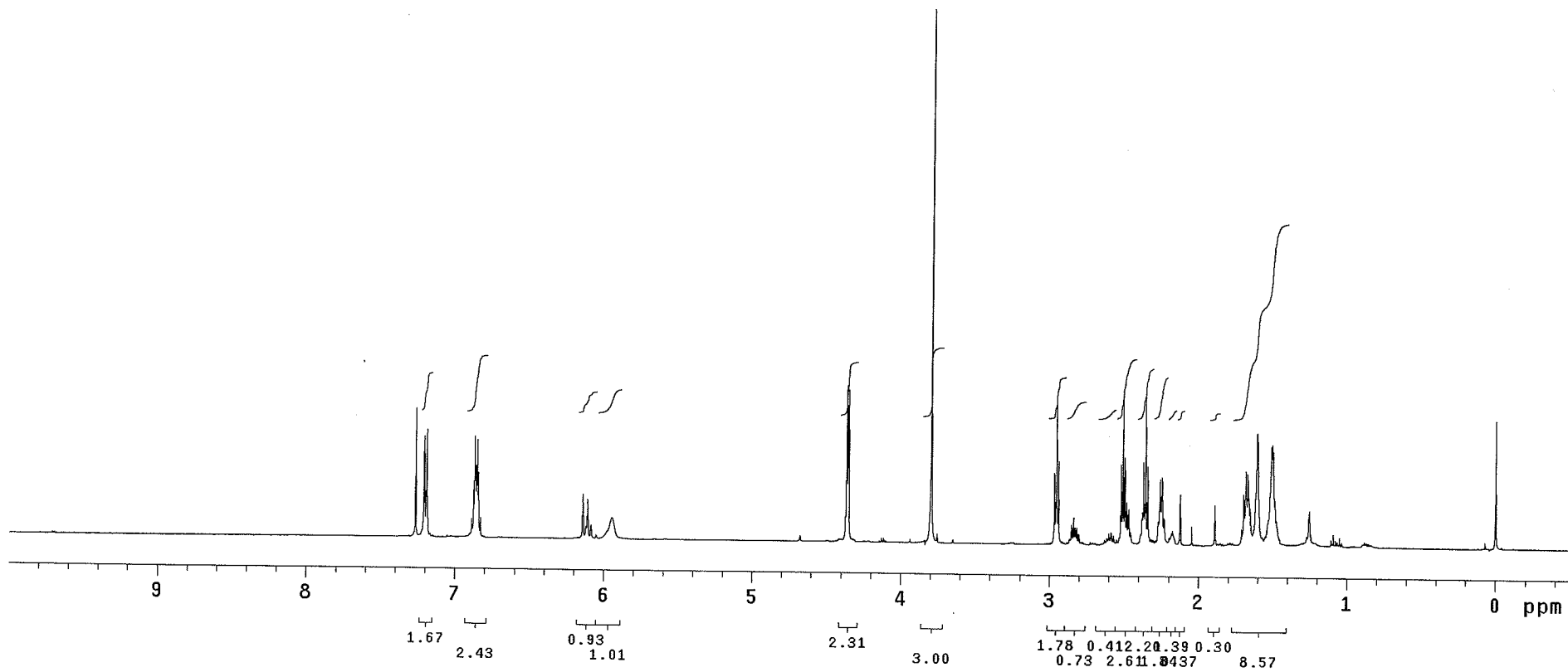


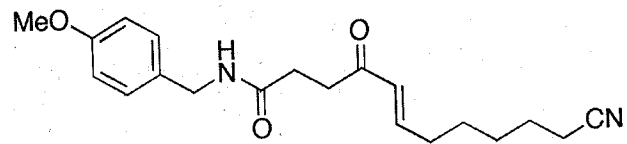
Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
6892 repetitions
OBSERVE C13, 125.6284653 MHz
DECOUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 3 min, 33 sec



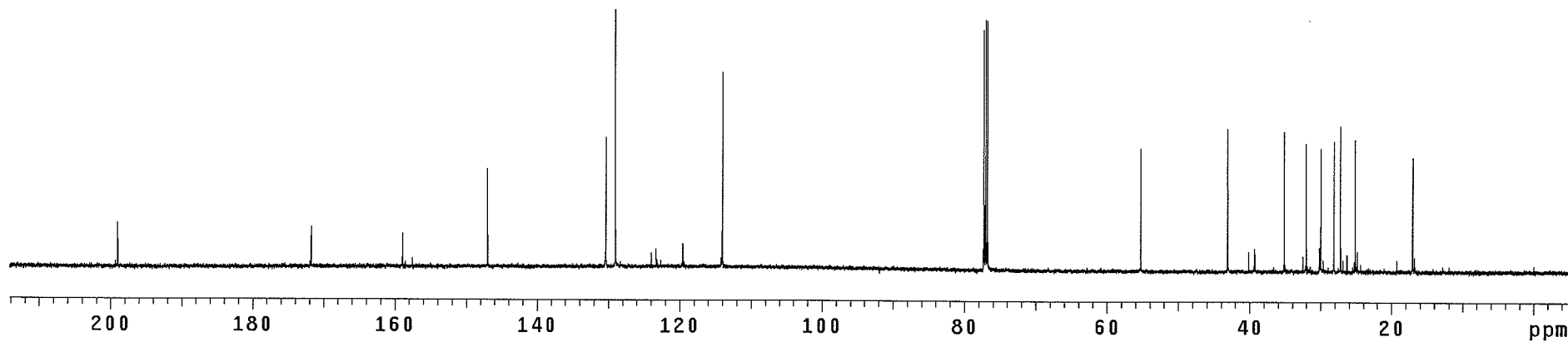


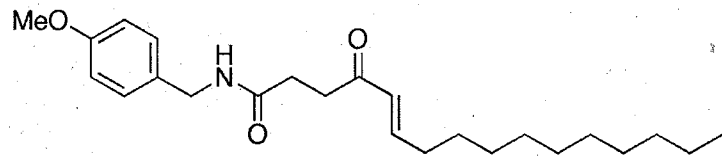
Relax. delay 0.200 sec
 Pulse 79.4 degrees
 Acq. time 2.048 sec
 Width 8000.0 Hz
 16 repetitions
 OBSERVE H1, 499.6156704 MHz
 DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 32768
 Total time 0 min, 40 sec



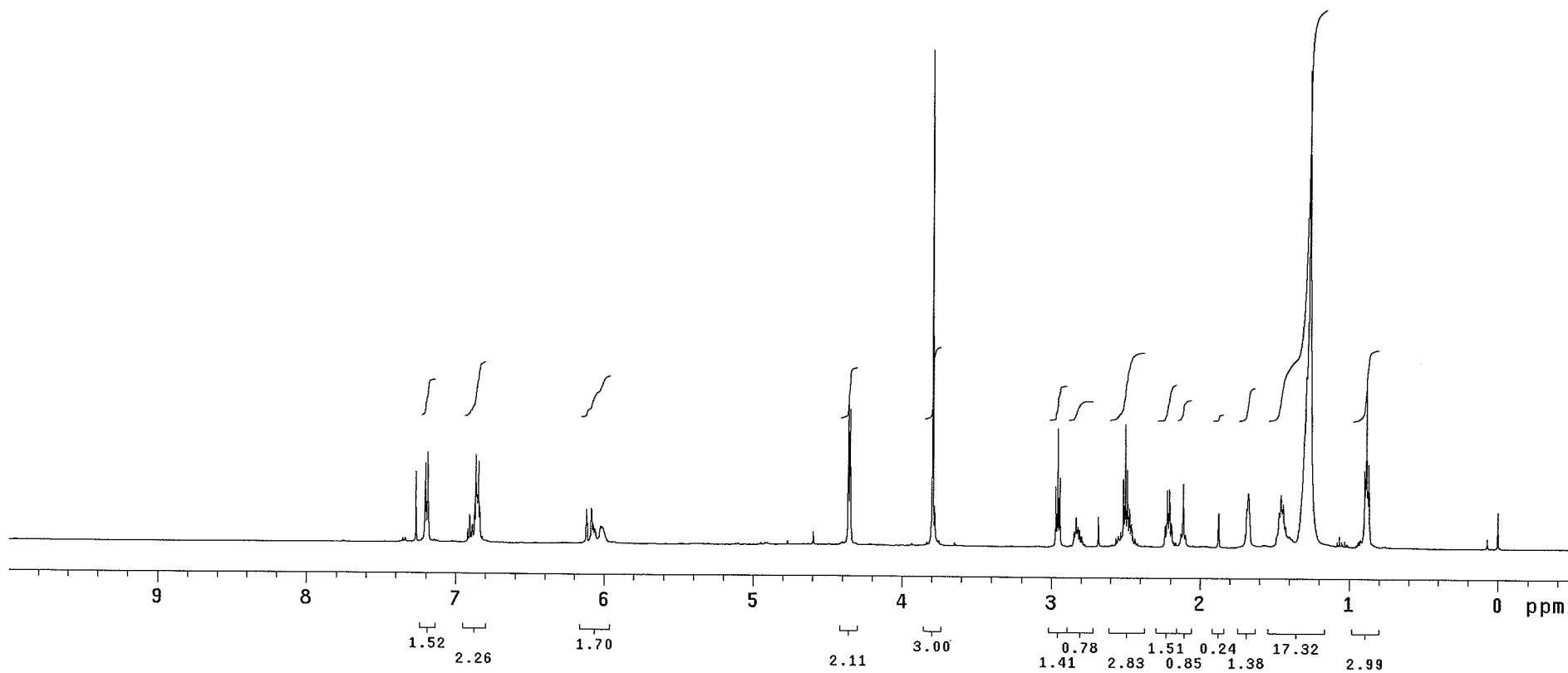


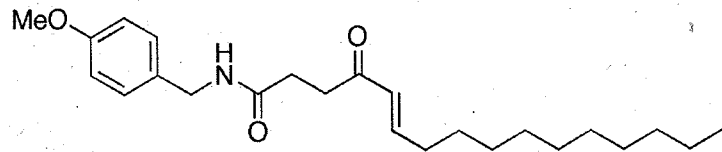
Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
25523 repetitions
OBSERVE C13, 125.6284653 MHz
DECOUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 30 hr, 35 min, 30 sec



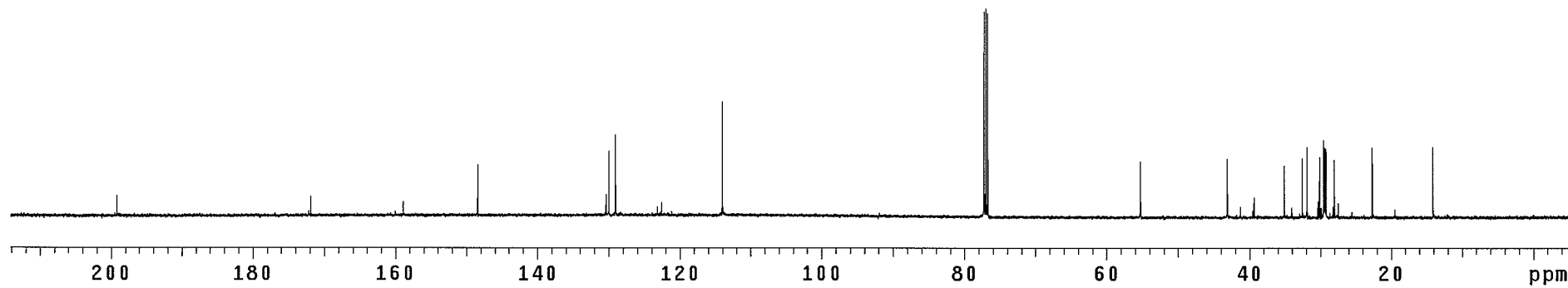


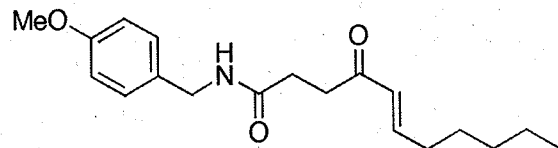
Relax. delay 0.200 sec
 Pulse 79.4 degrees
 Acq. time 2.048 sec
 Width 8000.0 Hz
 16 repetitions
 OBSERVE H1, 499.6156694 MHz
 DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 32768
 Total time 0 min, 40 sec



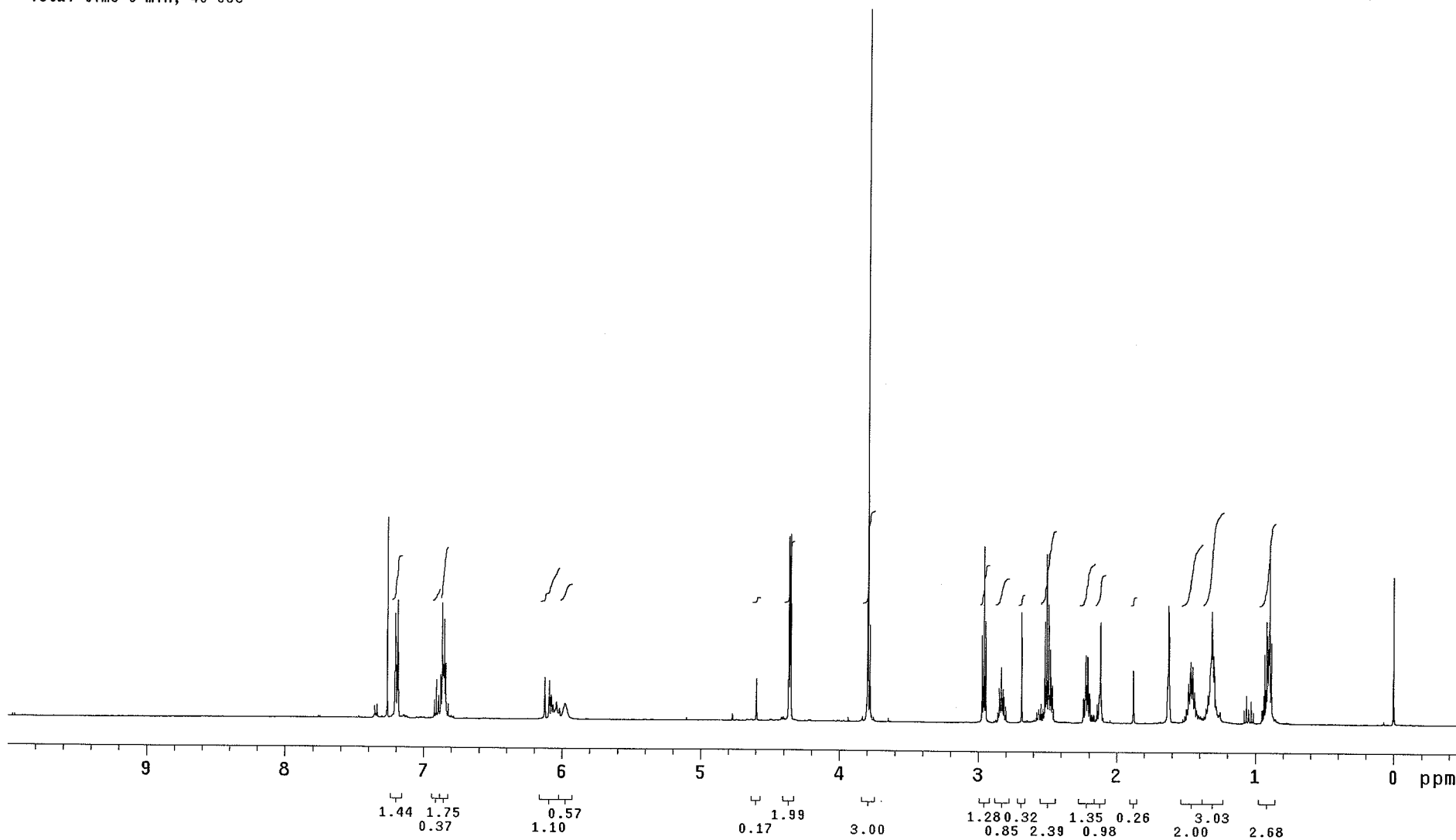


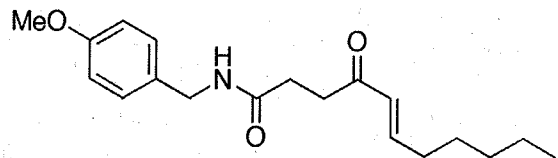
Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
25720 repetitions
OBSERVE C13, 125.6284625 MHz
DECOUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 30 hr, 35 min, 30 sec



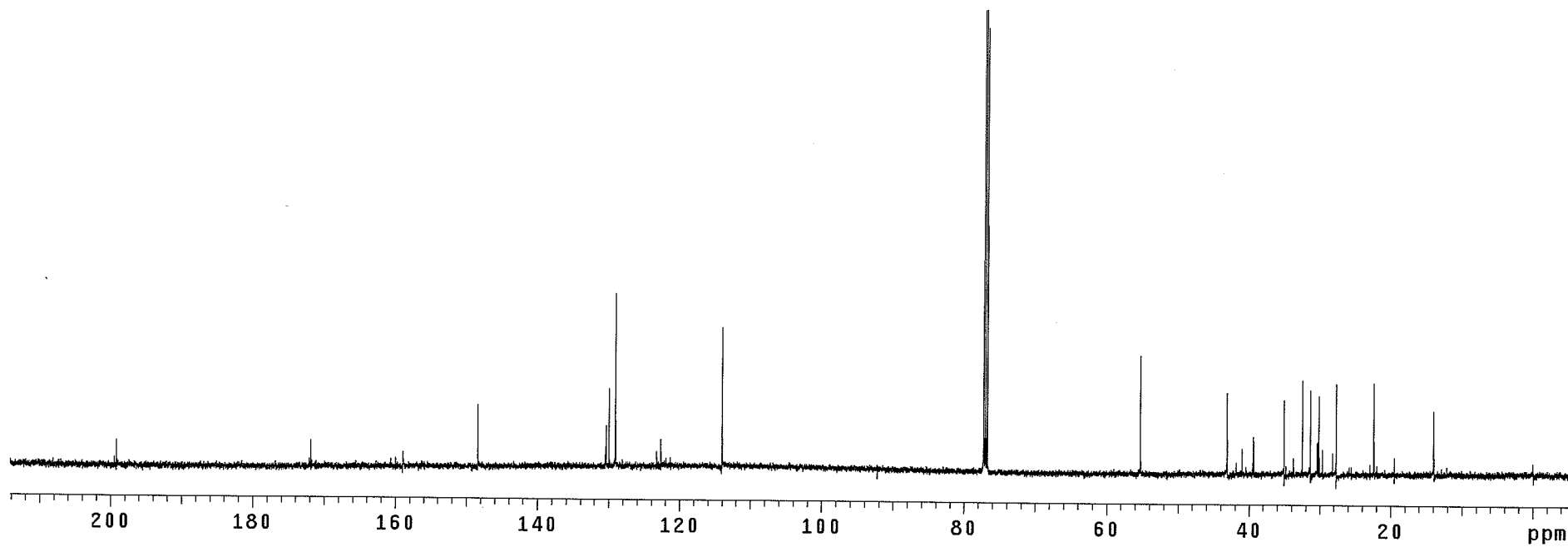


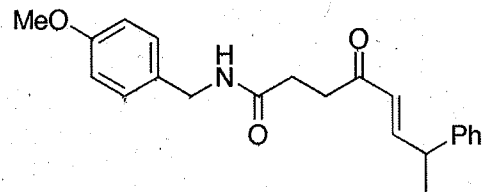
Pulse 79.4 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.6156699 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 40 sec





Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
23735 repetitions
OBSERVE C13, 125.6284616 MHz
DECOUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 30 hr, 35 min, 30 sec



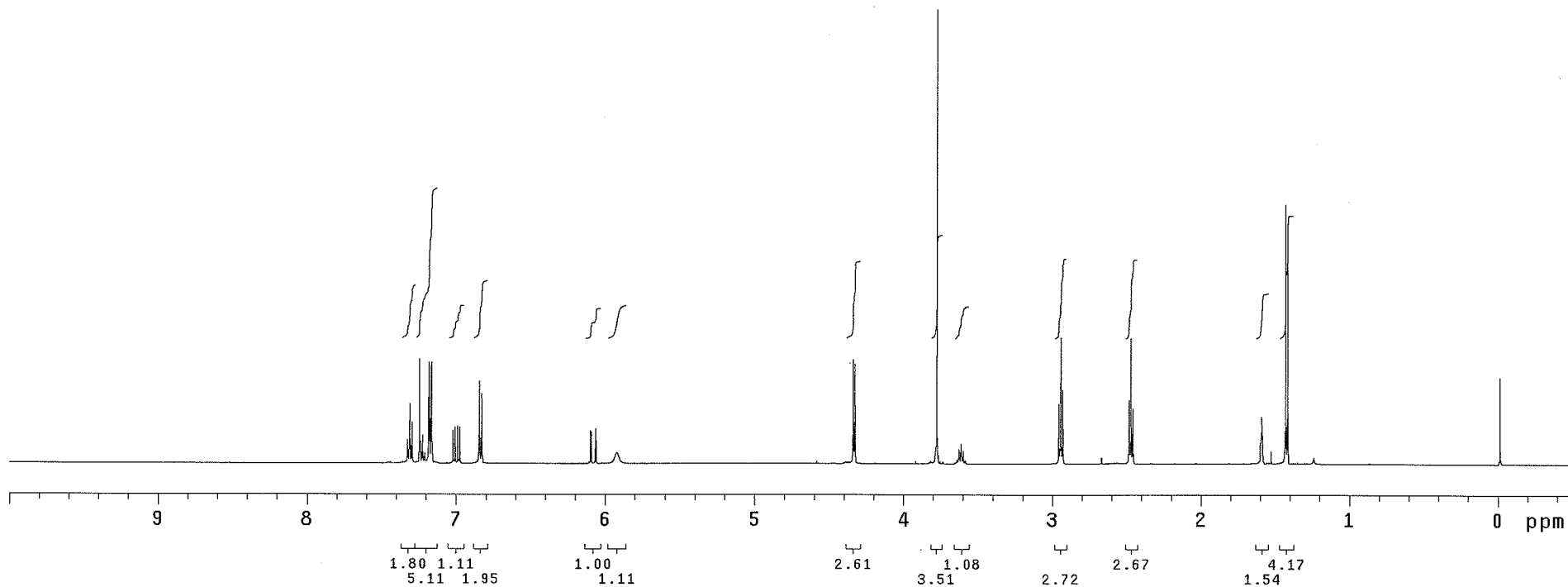


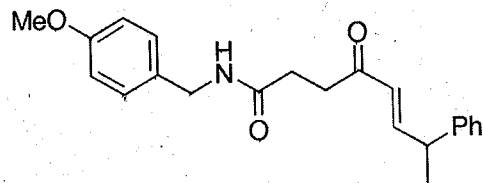
File: 6901-2-1H

Pulse Sequence: s2pu1
Solvent: CDC13

Temp. 23.0 C / 296.1 K

Relax. delay 0.200 sec
Pulse 79.4 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.6156790 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min



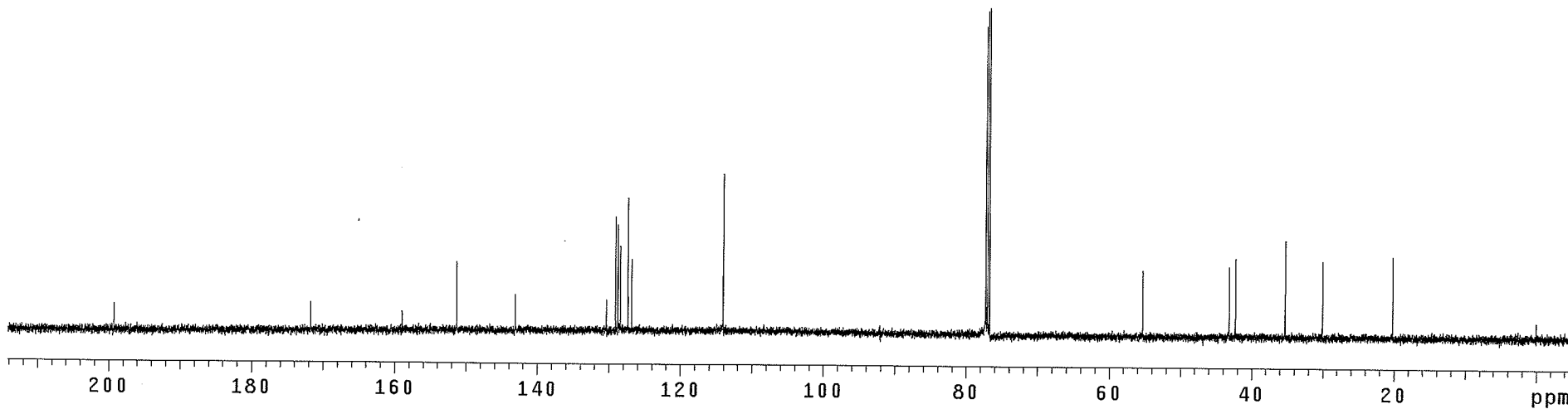


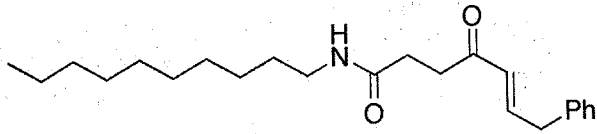
FILE: 6901-2-13C

Pulse Sequence: s2pu1
Solvent: CDC13

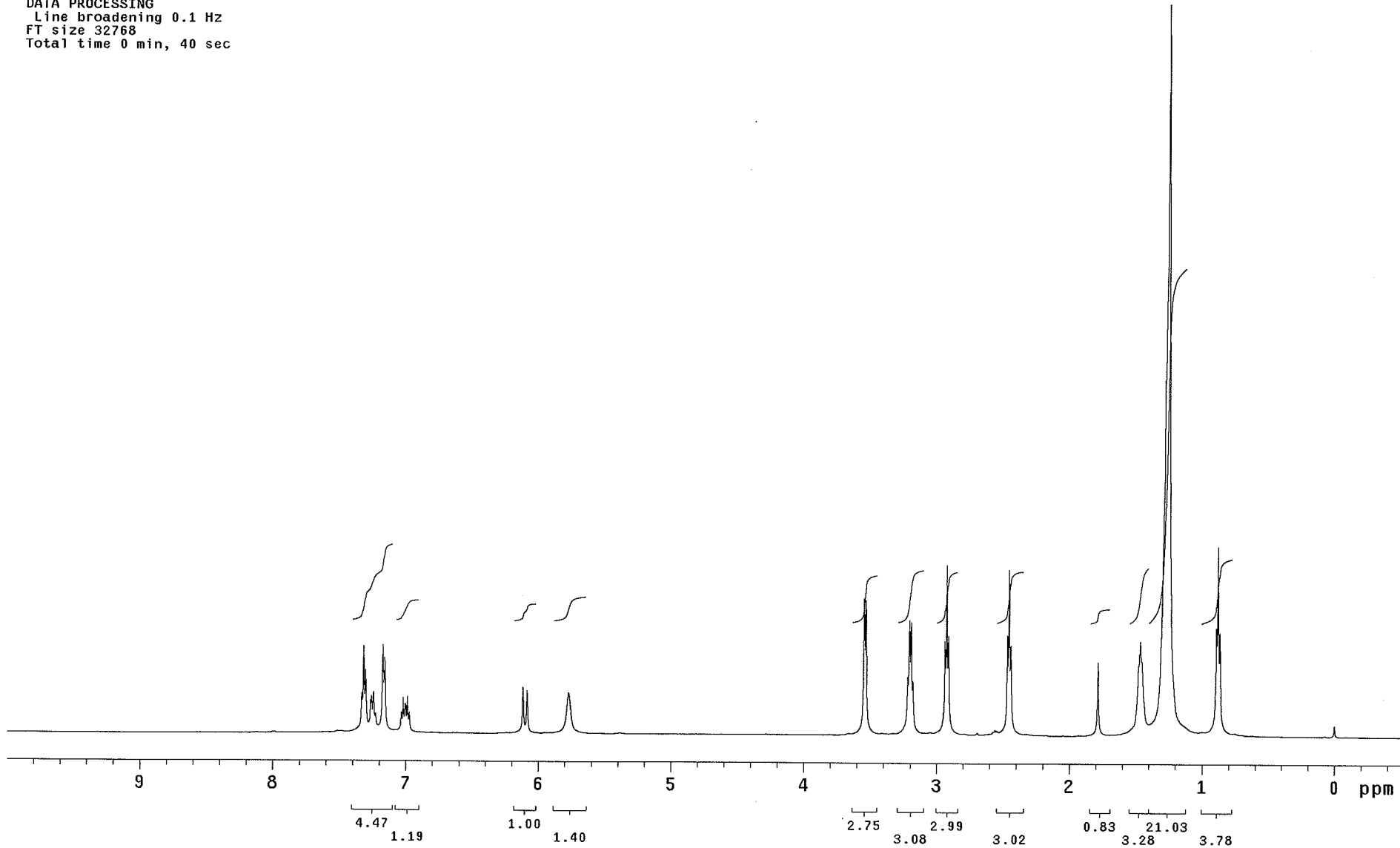
Temp. 23.0 C / 296.1 K
User: 1-14-87

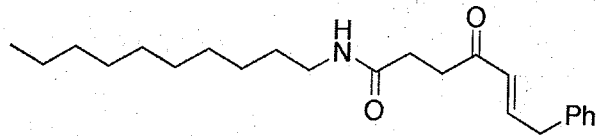
Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
6228 repetitions
OBSERVE C13, 125.6284616 MHz
DECOUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 30 hr, 35 min





Relax. delay 0.200 sec
Pulse 79.4 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.6156689 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 40 sec





Sample directory:

File: 6901-1-13C

Pulse Sequence: s2pu1

Solvent: CDCl3

Temp. 23.0 C / 296.1 K

User: 1-14-87

Pulse 40.0 degrees

Acq. time 1.092 sec

Width 29996.3 Hz

5501 repetitions

OBSERVE C13, 125.6284653 MHz

DECOUPLE H1, 499.6181772 MHz

Power 34 dB

continuously on

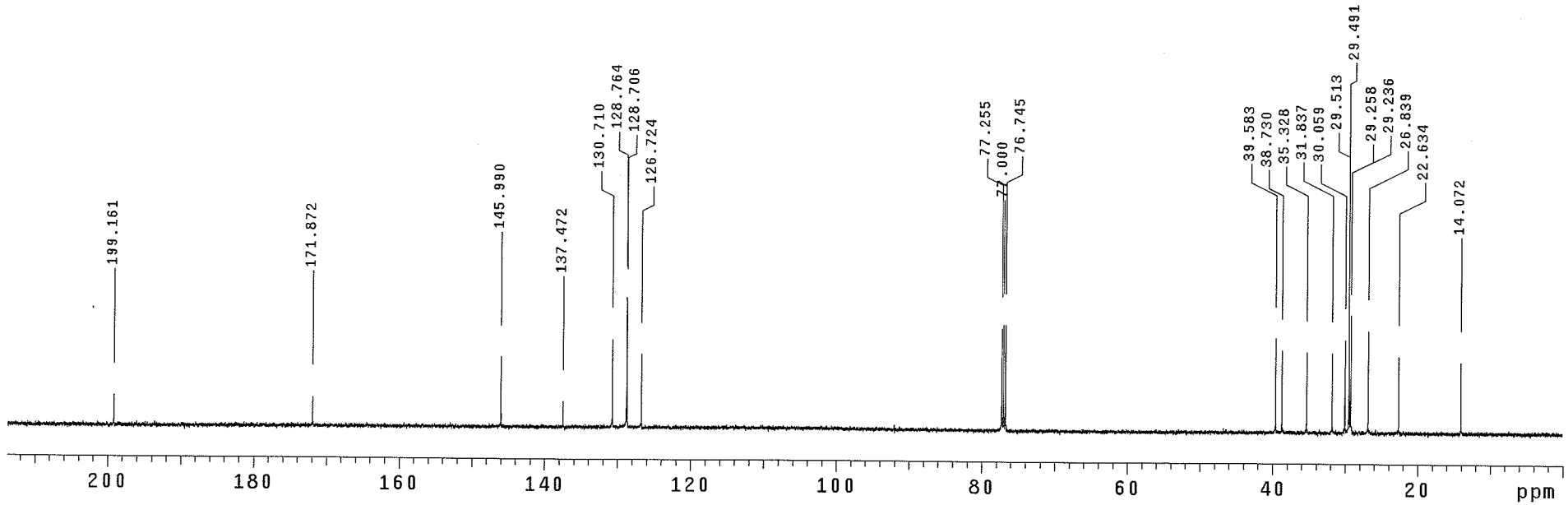
WALTZ-16 modulated

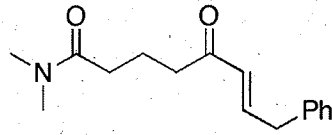
DATA PROCESSING

Line broadening 1.0 Hz

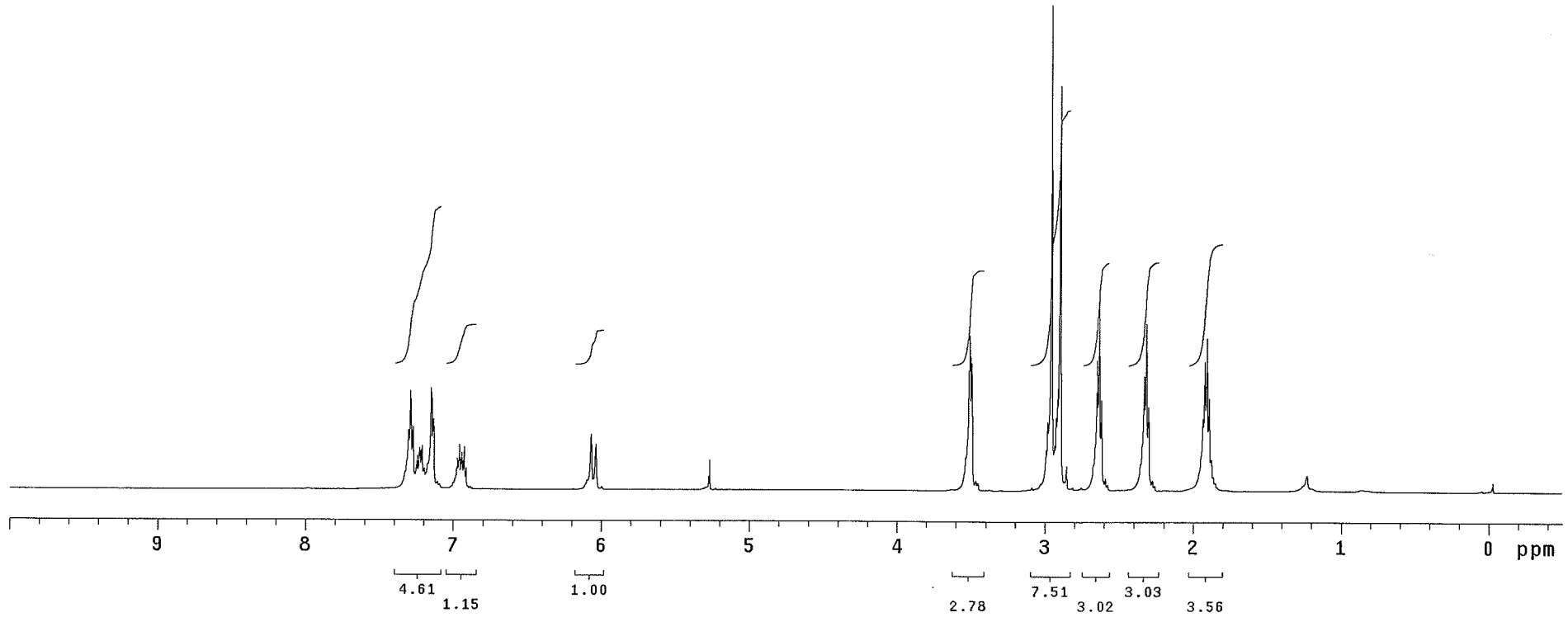
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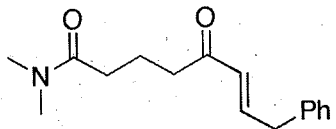
Total time 3 hr, 3 min





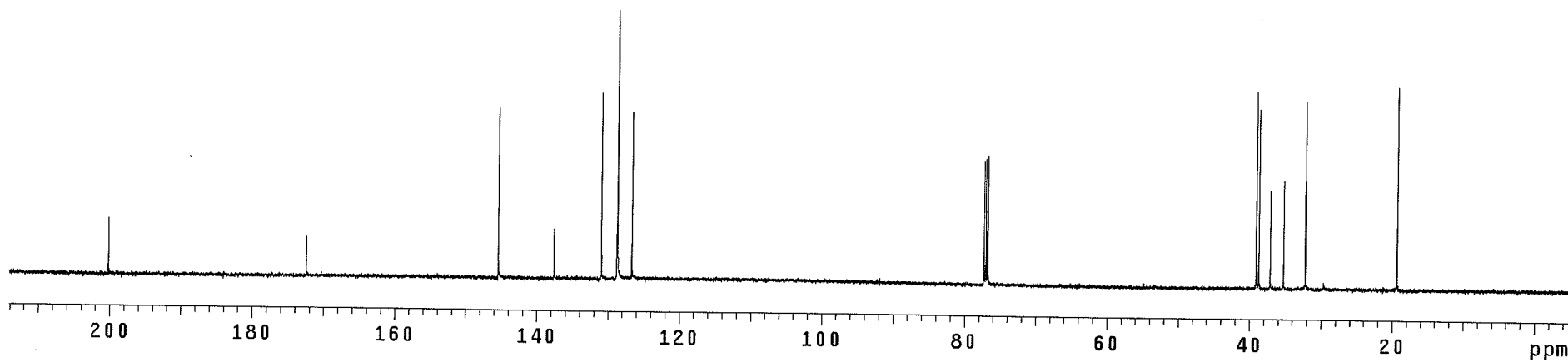
Relax. delay 0.200 sec
Pulse 79.4 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.6156790 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 40 sec

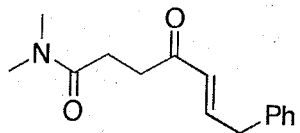




INOVA-500 "inova500"

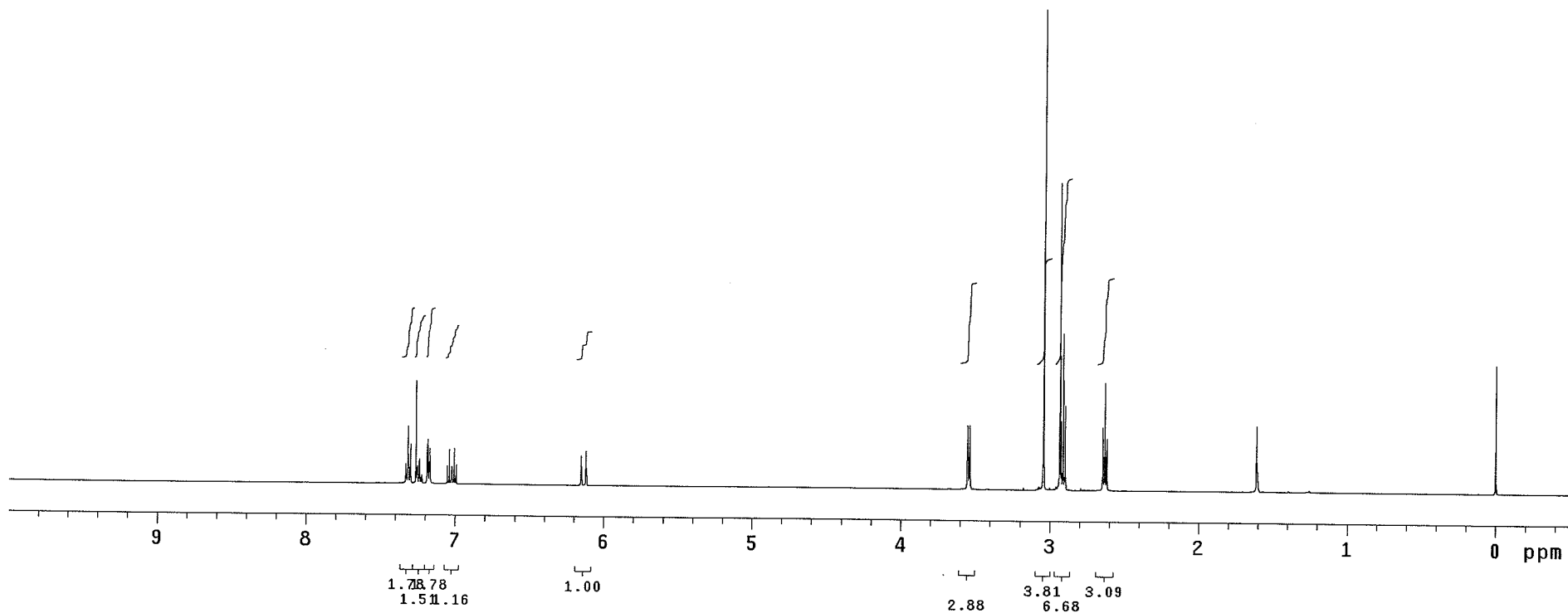
Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
12915 repetitions
OBSERVE C13, 125.6284680 MHz
DECOUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 30 hr, 35 min, 30 sec

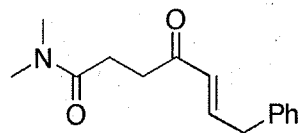




Temp. 25.00 °C
INOVA-500 "inova500"

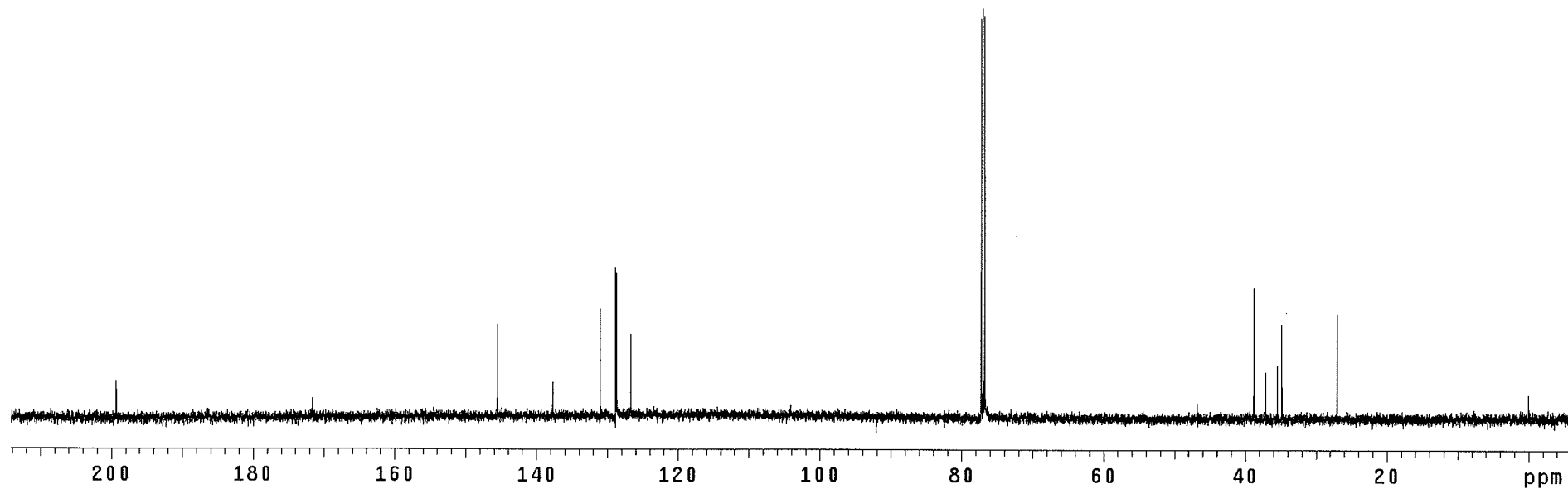
Relax. delay 0.200 sec
Pulse 79.4 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.6156704 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 40 sec

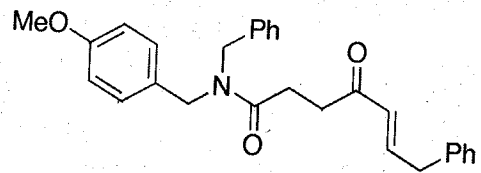




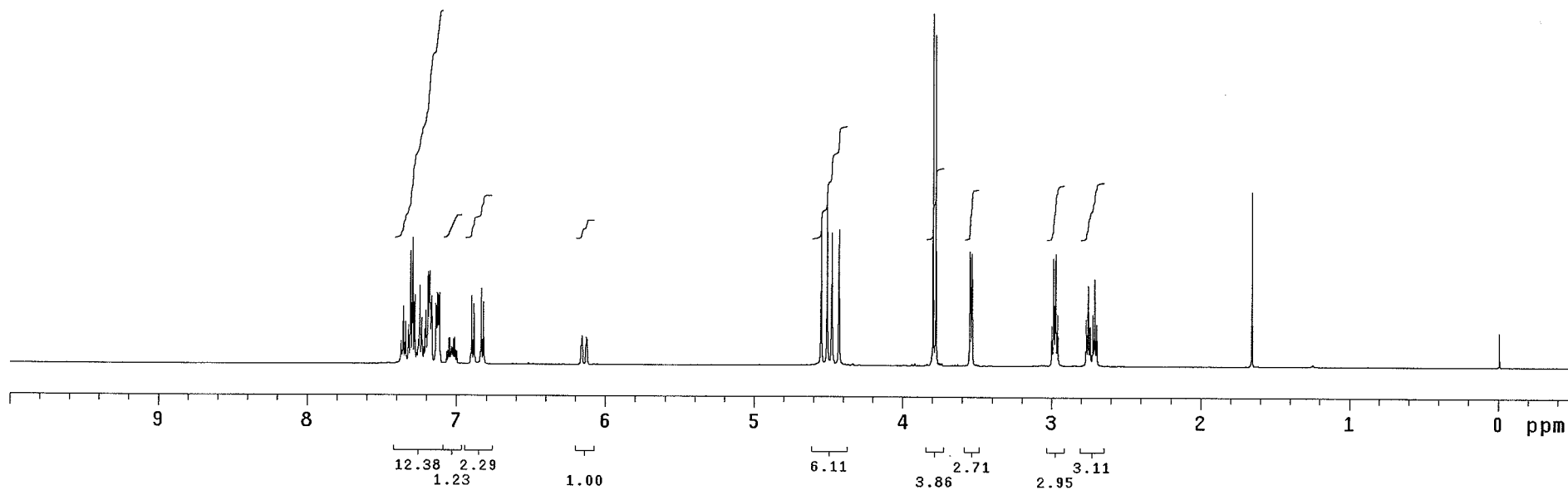
User: 1-14-87
INOVA-500 "inova500"

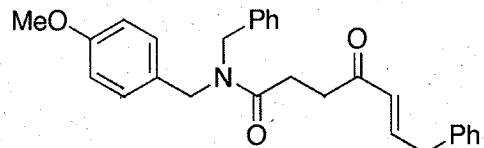
Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
5390 repetitions
OBSERVE C13, 125.6284616 MHz
DECOUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 30 hr, 35 min, 30 sec





Relax. delay 0.200 sec
Pulse 79.4 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.6156790 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 40 sec



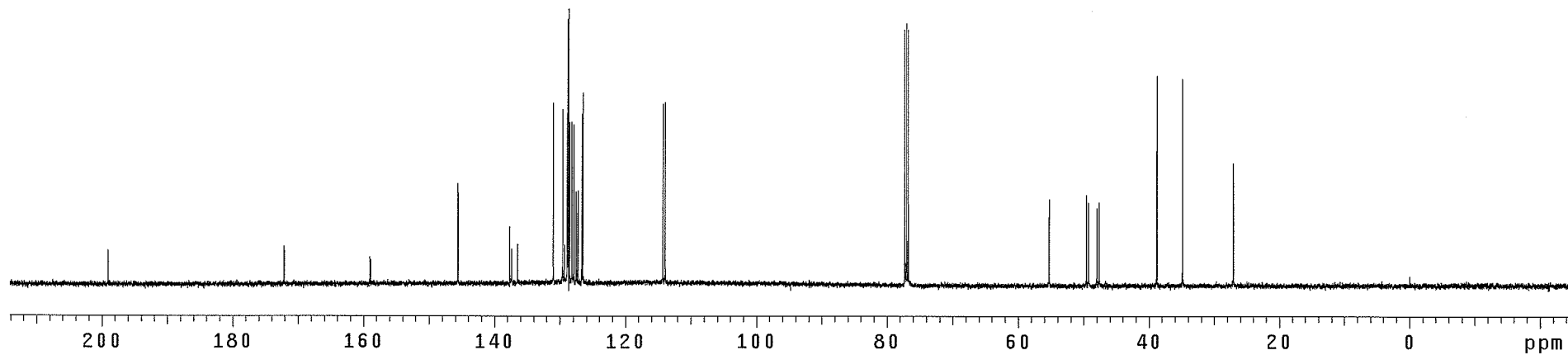


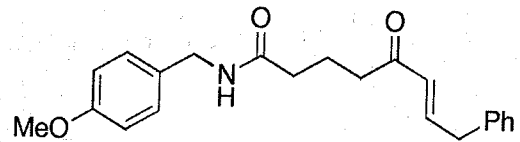
File: 6810-2-13C

Pulse Sequence: s2pu1
Solvent: CDC13

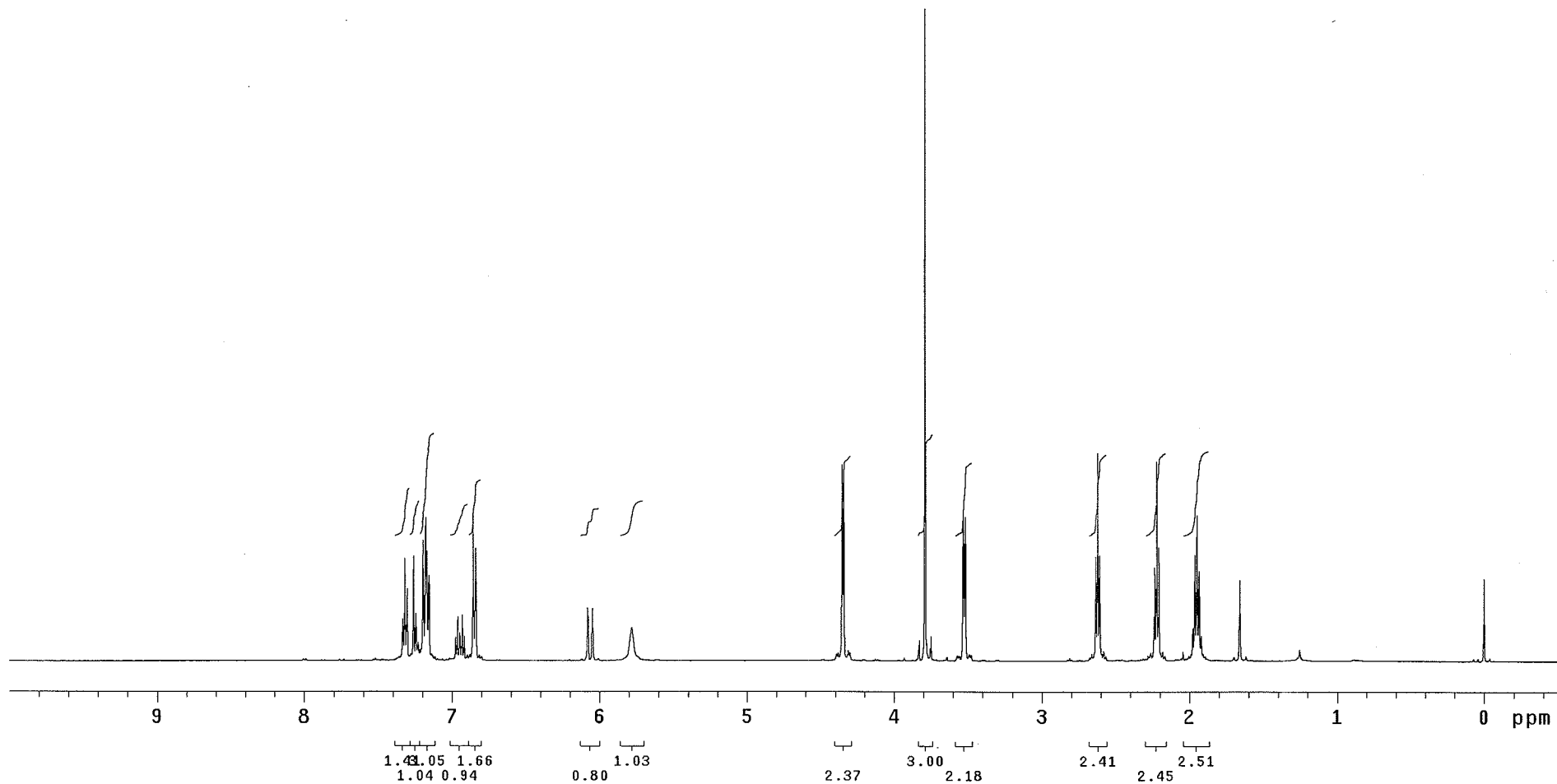
Temp. 23.0 C / 296.1 K
User: 1-14-87

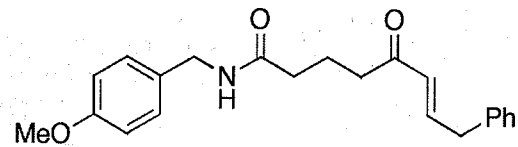
Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
14388 repetitions
OBSERVE C13, 125.6284653 MHz
DECOUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 305 hr, 55 min



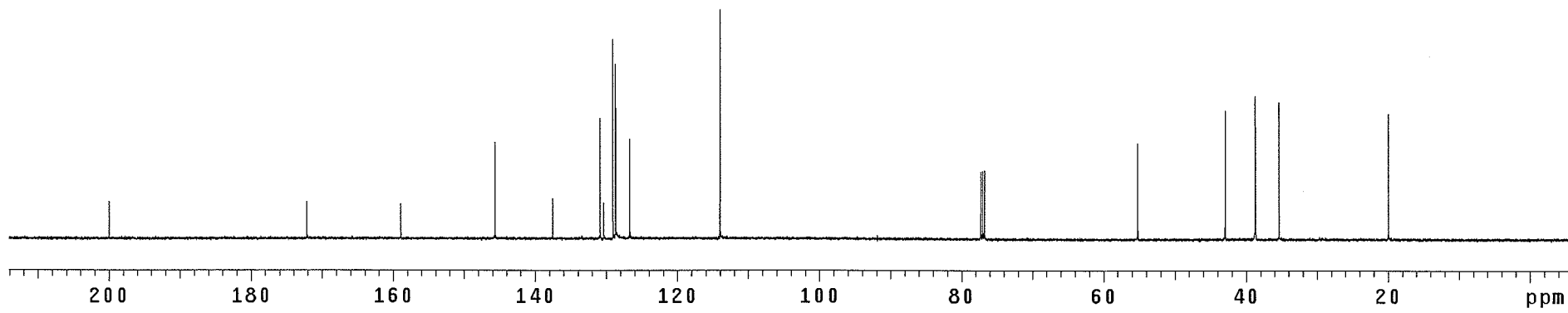


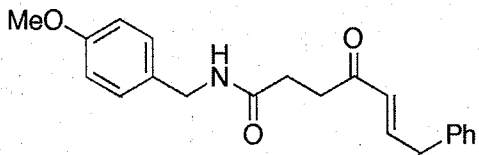
Relax. delay 0.200 sec
 Pulse 79.4 degrees
 Acq. time 2.048 sec
 Width 8000.0 Hz
 16 repetitions
 OBSERVE H1, 499.6156713 MHz
 DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 32768
 Total time 0 min, 40 sec



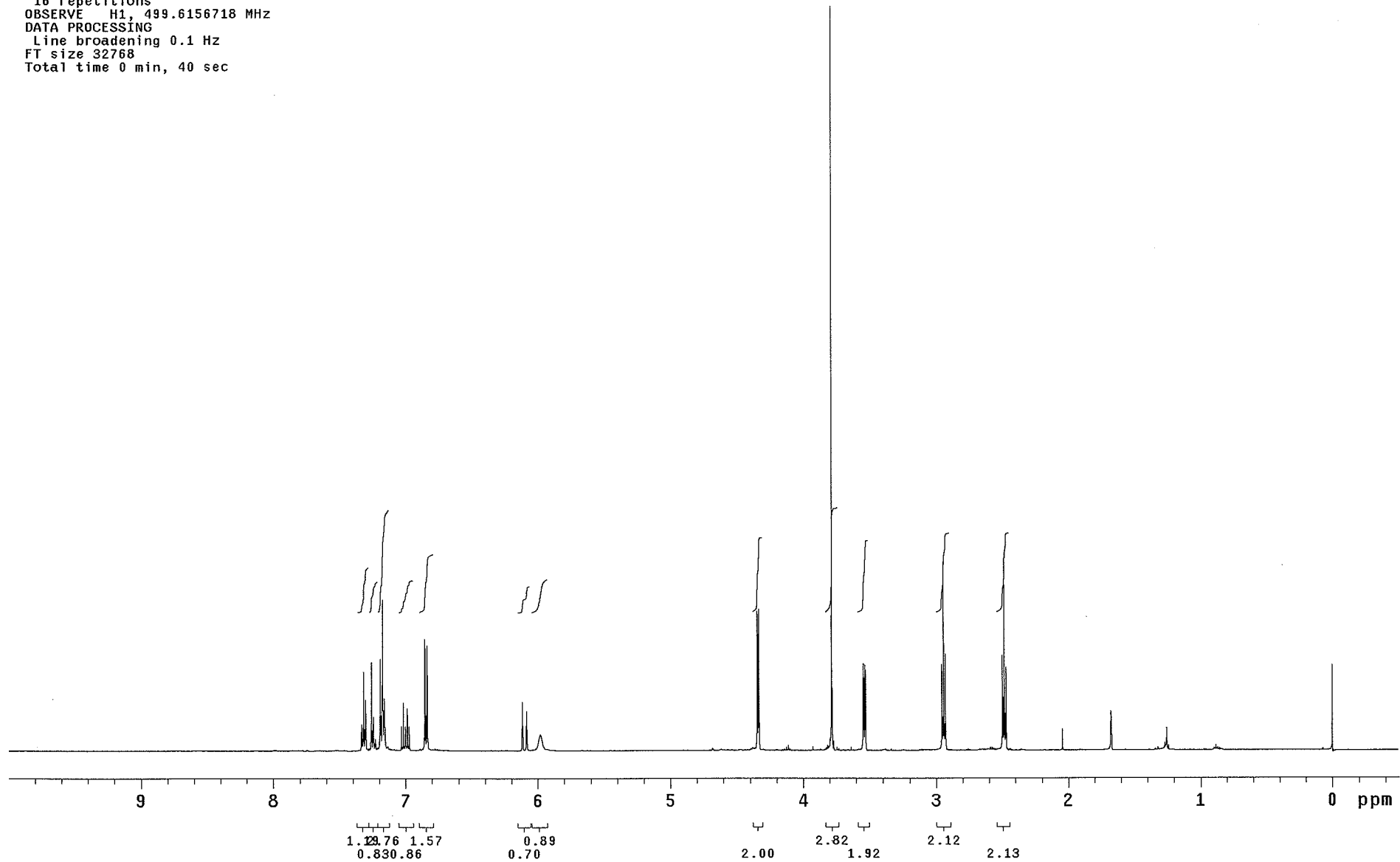


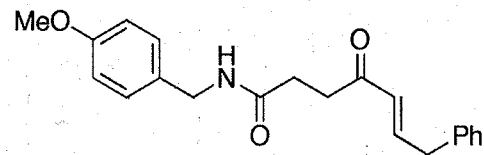
Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
4560 repetitions
OBSERVE C13, 125.6284698 MHz
DECUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 30 hr, 35 min, 30 sec



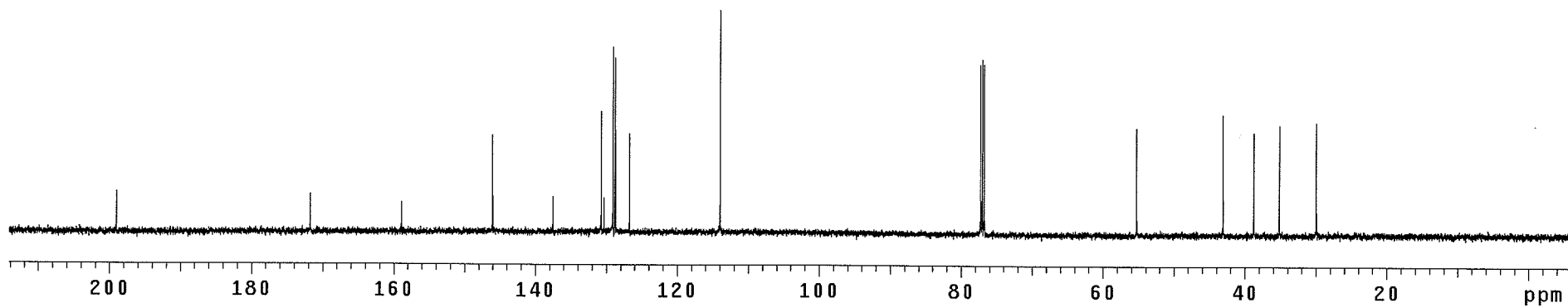


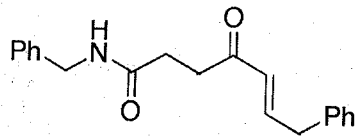
Relax. delay 0.200 sec
 Pulse 79.4 degrees
 Acq. time 2.048 sec
 Width 8000.0 Hz
 16 repetitions
 OBSERVE H1, 499.6156718 MHz
 DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 32768
 Total time 0 min, 40 sec





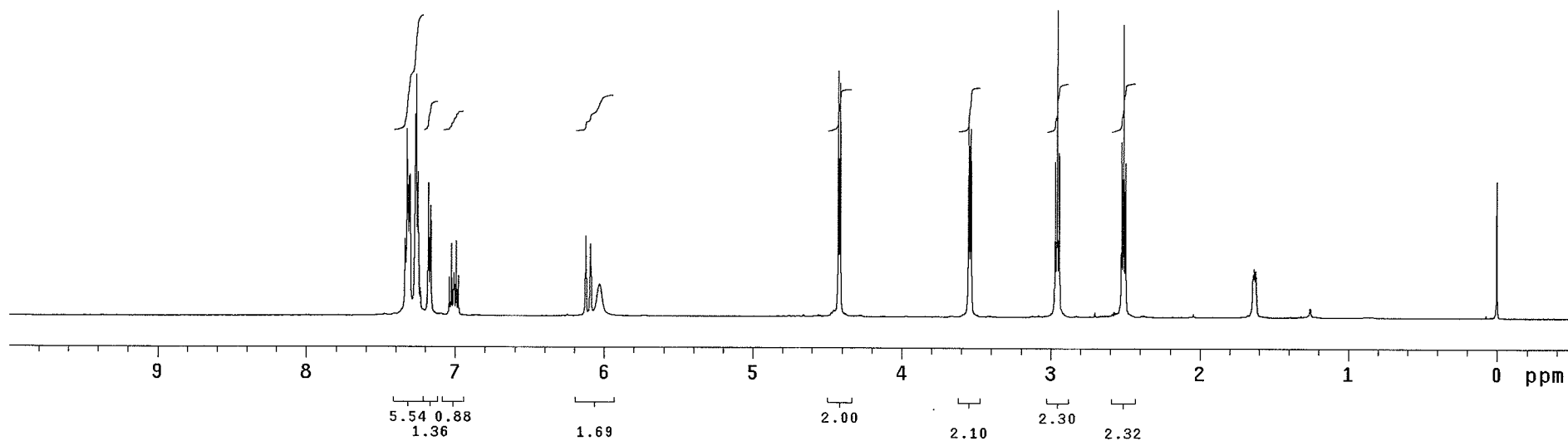
Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
3682 repetitions
OBSERVE C13, 125.6284653 MHz
DECOUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 30 hr, 35 min, 30 sec

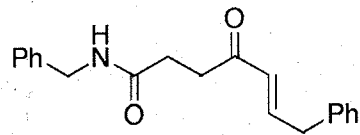




INOVA-500 "Inova500"

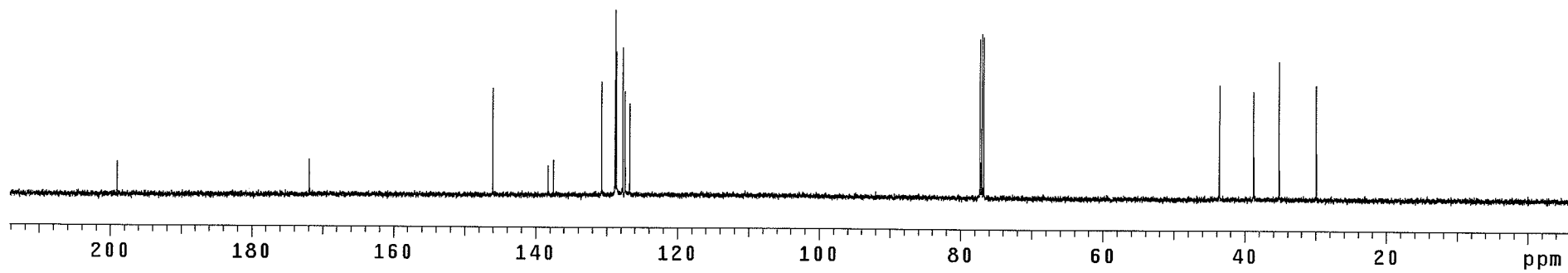
Relax. delay 0.200 sec
Pulse 79.4 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.6156718 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 40 sec

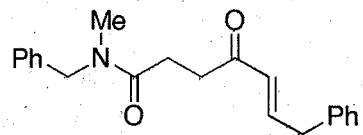




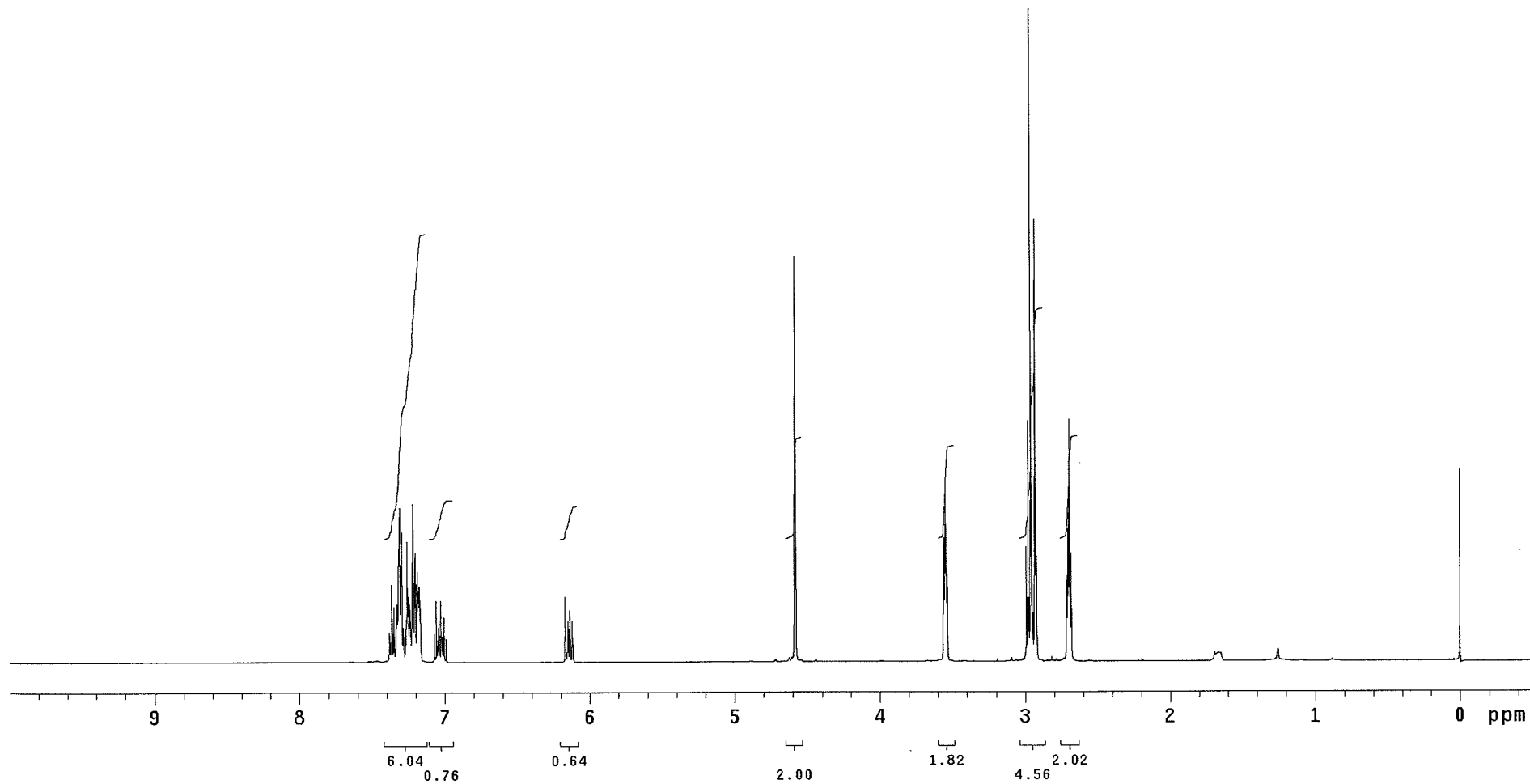
User: 1-14-87
INOVA-500 "inova500"

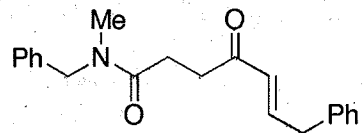
Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
4900 repetitions
OBSERVE C13, 125.6284653 MHz
DECOUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 30 hr, 35 min, 30 sec





Relax. delay 0.200 sec
Pulse 79.4 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.6156728 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 0 min, 40 sec





INOVA-500 "inova500"

Pulse 40.0 degrees
Acq. time 1.092 sec
Width 29996.3 Hz
4524 repetitions
OBSERVE C13, 125.6284653 MHz
DECOUPLE H1, 499.6181772 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3059 hr, 11 min, 32 sec

