SUPPLEMENTARY MATERIAL FOR:

Tandem isobenzofuran formation-Diels Alder reactions in the coupling of carbene complexes with 2-alkynylbenzaldehyde derivatives featuring an alkyne-dienophile tether

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General Experimental. . Nuclear Magnetic Resonance (^1H and ^{13}C NMR) spectra were recorded on a Varian AF (200 or 400 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) relative to an internal chloroform reference. Coupling constants (J values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Infrared spectra were recorded on a Perkin-Elmer model 1720 spectrometer. Band positions are reported in reciprocal centimeters (cm^{-1}). Band intensities are reported relative to the most intense band and are listed as: br (broad), vs (very strong), s (strong), m (medium), w (weak); only diagnostic bands (excluding C-H stretches) above 1500 cm^{-1} are reported. Mass spectra (MS) were obtained on a VG 7070E spectrometer using electron impact (El) or chemical ionization (CI) or on a Waters HPLC-MS with CI and ESI capabilitites: m/e value is reported, followed by the relative intensity in parentheses. Melting points were taken on a Fisher-Johns melting point apparatus (Model 12-144) equipped with a calibrated thermometer. Flash column chromatography was performed using thick-walled glass columns and “flash grade” silica gel (Sorbtech 230-400 mesh). Preparative thin layer chromatography was performed using precoated 1000 micron 20 x 20 silica gel plates purchased from Sorbtech. Routine thin layer chromatography (TLC) was performed using precoated 0.25mm silica gel plates purchased from Sorbtech. Combustion analysis results were obtained from Desert Analytics Laboratory or Galbraith Laboratories.

Starting Materials. The following compounds were prepared according to literature procedures: 1-hepten-6-yne (**10a**),[1] allyl propargyl ether (**10bc**),[2] dimethyl allyl(propargyl)malonate (**10d**),[3] dimethyl methallyl(propargyl)malonate (**10e**),[4] N-allyl-N-propargyl-p-toluenesulfonamide (**10f**), and dimethyl 3-butenyl(propargyl)malonate (**10g**).[3]

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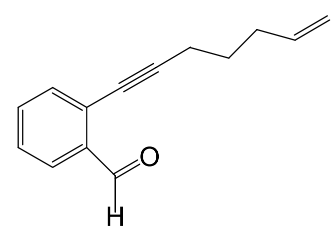
[1] Negishi, E; Holmes, S.J.; Tour, J.M.; Miller, J.A.; Cederbaum, F.E.; Swanson, D.R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336-3346.
[2] Guermont, J.P.. *Bull. Soc. Chim. France* **1953**, 386-390.
[3] Miura, K.; Saito, H.; Fujisawa, N.; Hosomi, A. *J. Org. Chem.* **2000**, *65*, 8119-8122.
[4] Gomez, A.M.; Company, M.D.; Valverde, S.; Lopez, J.C. *Org. Lett.* **2002**, *4*, 383-386.

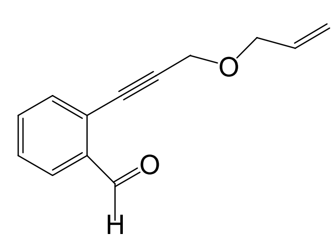
Synthesis of 6a. A mixture of palladium(II) chloride (0.080g, 0.45 mmol) and triphenylphosphine (0.235 g, 0.74 mmol) in diethylamine (10 mL) was stirred at room temperature for 10 min, then 2-bromobenzaldehyde (3.700 g, 20.00 mmol), 1-hepten-6-yne (2.256 g, 24 mmol), copper (I) iodide (0.080 g, 0.42 mmol) and diethylamine (30 mL) were added. The mixture was refluxed for 12 h. The solvent was evaporated, and the residue was diluted with ethyl acetate and filtered through a pad of Celite, and the pad rinsed with ethyl acetate (3×30 mL. The combined ethyl acetate solution was concentrated, and the crude residue was then purified by flash column chromatography with ethyl acetate/hexane (1:10) to afford **6a** (3.837 g, 97%).

Compound **6a**: ^{1}H NMR ($CDCl_3$): δ 10.55 (s, 1 H), 7.92 (d, 1 H, J = 7.6 Hz), 7.55 (m, 2 H), 7.44 (m, 1 H), 5.94 (ddt, 1 H J = 17.0, 10.3, 6.6 Hz), 5.15 (dq, 1 H, J = 17.0, 1.6 Hz), 5.04 (dq, 1 H, J = 10.3, 1.5 Hz), 2.55 (t, 2 H, J = 7.0 Hz), 2.24 (br q, 2 H, J = 7.2 Hz,), 1.82 (quintet, 2 H, J =7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 192.0, 137.6, 136.1, 133.7, 133.4, 128.0, 127.9, 127.0, 115.6, 97.8, 76.7, 33.0, 27.8, 19.0; IR (neat, cm^{-1}) 2224 (m), 1789 (m),1776 (m), 1698 (s), 1642 (m), 1595 (m); MS (EI): *m/e*; 198 (M^+, 62), 183 (49), 170 (84), 155 (18), 144 (48), 128 (63), 115 (100), 102 (10), 89 (18); HRMS calcd for $C_{14}H_{14}O$ for 198.104465, found 198.104582.



Synthesis of 6b. A mixture of palladium(II) chloride (0.060g, 0.34 mmol) and triphenylphosphine (0.177 g, 0.68 mmol) in triethylamine (10 mL) was stirred at room temperature for 10 min, then 2-bromobenzaldehyde (0.740 g, 4.00 mmol), ally propargyl ether (0.528 g, 5.50 mmol), copper (I) iodide (0.080 g, 0.42 mmol), triethylamine (25 mL) were added. The mixture was refluxed for 12 h. The solvent was evaporated, and the residue was treated as described above to afford an oil, which was purified by flash column chromatography with ethyl acetate/hexane (1:6), afford **6b** (0.429 g, 54%).

Compound **6b**: ^{1}H NMR ($CDCl_3$): δ 10.51 (s, 1 H), 7.93 (dm, 1 H, J = 7.6 Hz), 7.57 (t, 1 H, J = 1.4 Hz), 7.53 (m, 2 H), 7.45 (m, 1 H), 6.04 (dddd, 1 H, J = 17.2, 10.2, 5.7, 0.6

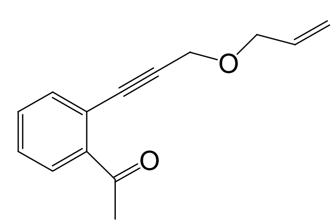


Hz), 5.40(dt, 1 H, J =17.2, 3.0 Hz), 5.28 (dm, 1 H, J =10.2 Hz), 4.44 (s, 2 H), 4.15 (br d, 2 H, J = 5.7 Hz); ^{13}C NMR ($CDCl_3$): δ 191.4, 136.2, 134.0, 133.7, 133.6, 128.9, 127.3, 126.1, 118.0, 92.6, 81.9, 71.0, 57.9; IR (neat, cm^{-1}) 2215 (w), 1698 (s), 1648 (m), 1595 (m); MS (CI): *m/e* 201 (MH^+, 15), 170 (61), 143 (100), 131 (10), 115 (9), 103 (10), 77 (4); HRMS calcd for $C_{13}H_{13}O_2$ 201.091555, found 201.091524.

This reaction was unsuccessful if the diethylamine was used as the solvent.

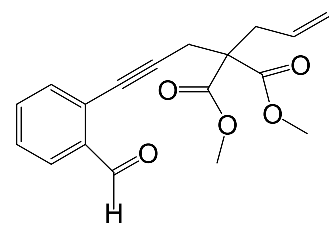
Synthesis of 6c. To a solution **6b** (0.400g, 2.00 mmol) in diethyl ether (15 mL) was added methylmagnesium iodide (3.00 mmol) in diethyl ether (10 mL) dropwise at room temperature (methylmagnesium iodide was freashly prepared from iodomethane and magnesium turnings). After 1 h, the reaction was quenched with saturated aqueous ammonium chloride solution, and the aqueous layer was extracted with diethyl ether. The combined organic layers dried over sodium sulfate, the solvent was removed under reduced pressure, the residues was purified via column chromatography with ethyl acetate / hexane (1:6) to afford an intermediate alcohol (0.377 g, 87%). Pridinium chlorochrmate (0.563 g, 2.61 mmol) and sodium acetate (0.043g, 0.52 mmol) were suspended in dichloromethane (10 mL) and stirred vigorously. A solution of the above alcohol (0.377 g, 1.74 mmol) in dichloromethane (5 mL) was added dropwise, and the mixture was left stirring overnight. After 14 h, it was diluted with ethyl acetate and filtered through a short pad of slica gel; the residue was rinsed with ethyl acetate three times. The solvent was removed and the residue was purified with ethyl acetate/ hexanes (1: 5) to yield 0.322 g (86%) pure ketone **6c**.

Intermediate Alcohol: ^{1}H NMR ($CDCl_3$): δ 7.55 (d, 1 H, J = 8.0 Hz), 7.43 (m, 3 H), 6.02 (ddt, 1 H, J = 16.9,10.2, 5.8 Hz), 5.36 (m, 3 H), 4.37 (s, 2 H), 4.12 (d, 2 H, J = 5.8 Hz); 2.86 (s, 1 H), 1.48 (d, 3 H, J = 6.0 Hz).



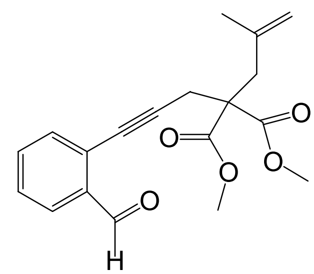
Compound **6c:** ^{1}H NMR ($CDCl_3$): 7.67 (dm, 1 H, J = 7.4 Hz), 7.52 (dm, 1 H, J = 7.4 Hz), 7.41 (m, 2 H), 6.00 (ddt, 1 H, J = 17.3, 10.2, 5.8 Hz), 5.31 (dq, 1 H, J =17.3, 1.8 Hz), 5.22 (ddt, 1 H, J = 10.2, 1.8, 1.0 Hz), 4.37 (s, 2 H), 4.11 (br d, 2H, J = 5.8 Hz), 2.64 (s, 3 H); ^{13}C NMR ($CDCl_3$): δ 200.3, 141.1, 134.3, 134.1, 131.3, 128.5, 121.1, 118.0, 91.1, 85.2, 70.9, 58.0, 29.8; IR (neat, cm^{-1}) 2234 (m), 1771 (m), 1688 (s); MS (EI): *m/e* 213 (M-1, 3.3), 184 (100), 157 (52), 145 (22.8), HRMS calcd for $C_{14}H_{13}O_2$, 213.091555 found 213.090833; calcd for $C_{13}H_{12}O$ 184.088815 found 184.089483.

Synthesis of 6d. A mixture of palladium(II) chloride (0.060g, 0.34 mmol) and triphenylphosphine (0.177 g, 0.68 mmol) in THF (10 mL) was stirred at room temperature for 10 min. Then 2-bromobenzaldehyde (2.405 g, 13.00 mmol), dimethyl allyl(propargyl)malonate (2.640 g, 12.45 mmol), copper(I) iodide (0.080 g, 0.42 mmol), triethylamine (2.53 mL, 18.20 mmol), and THF (20 mL) were added. The mixture was refluxed for 12 h. The solvent was evaporated, and the residue was treated as described above to afford an oil, which was purified by column chromatography with ethyl acetate / hexanes (1:6), assigned as **6d** (3.735 g, 95%).



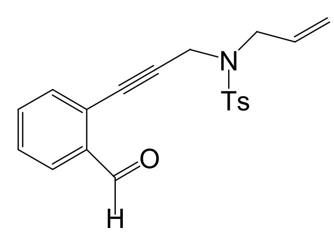
Compound **6d**: ^{1}H NMR ($CDCl_3$): δ 10.43 (s, 1 H), 7.90 (d, 1 H, J = 7.6Hz), 7.55 (m, 2 H), 7.44 (td, 1 H, J = 7.6, 0.8 Hz), 5.94 (ddt, 1 H, J = 17.2, 10.0, 7.4 Hz), 5.20 (dd, 1 H, J = 17.2, 1.2 Hz), 5.16 (dt, 1 H, J =10.4, 1.4 Hz), 3.76 (s, 3 H), 3.73 (s, 3 H), 3.08 (s, 2 H), 2.87 (br d, 2 H, J = 7.6 Hz,); ^{13}C NMR ($CDCl_3$): δ 191.7, 170.2, 136.3, 133.8, 133.7, 131.7, 128.6, 127.2, 126.8, 120.2, 92.0, 79.4, 57.2, 53.0, 37.1, 24.1; IR (neat, cm^{-1}) 2226 (w), 1732 (s), 1698 (s); MS (EI): *m/e* 314 (M$^+$, 3), 254 (21), 223 (15), 195 (100), 167 (12), 115 (13), 59 (4); HRMS calcd for $C_{18}H_{18}O5$ 314.115424, found 314.115498.

Synthesis of 6e. Treatment of 2-bromobenzaldehyde (1.295 g, 7.00 mmol) and Dimethyl (2-methyl-2-propenyl)(propargyl)malonate (1.130g, 5.00 mmol) as described in preparation of **6d,** afforded a yellow oil**,** which was purified by flash column chromatography using ethyl acetate / hexanes (1:6), and identified as **6e** (1.513 g, 92%). Compound **6e**: ^{1}H NMR ($CDCl_3$): δ 10.44 (s, 1 H), 7.91 (ddd, 1 H, J = 7.6, 2.8, 1.4 Hz), 7.53 (m, 3 H), 4.94 (br s, 1 H), 4.85 (br s, 1 H), 3.76 (s, 6 H), 3.13 (s, 2 H), 2.89 (br s, 2 H), 1.56 (br s, 3 H); ^{13}C NMR ($CDCl_3$): δ 192.0, 170.9, 140.2, 136.7, 134.1, 134.0, 128.9, 127.5, 127.2, 116.9, 92.7, 80.0, 57.2, 53.3, 40.5, 24.5, 23.6; IR (neat, cm^{-1}) 2226 (w), 1737 (s), 1698 (s); MS (EI): *m/e* 328 (M^+, 12), 313 (13), 296 (38), 269 (56), 209 (92), 191 (36), 144 (100), 115 (48), 59 (19); HRMS calcd for $C_{19}H_{20}O5$ 328.131074, found 328.130128.



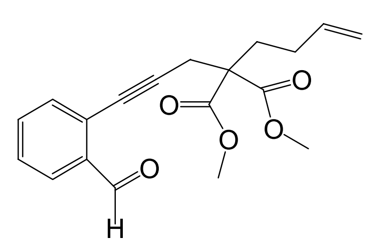
Synthesis of 6f. Reaction of 2-bromobenzaldehyde (0.925 g, 5.00 mmol) and N-ally-N-propargyl *p*-toluenesulfonamide (0.724 g, 2.90 mmol) as described in preparation of **6b,** afforded a yellow oil**,** which was purified by flash column chromatography with ethyl acetate / hexanes (1:5), which was assigned as **6f** (0.890 g, 91%).

Compound **6f**: ^{1}H NMR ($CDCl_3$): δ 9.92 (s, 1 H), 7.93 (dd, 1 H, J = 7.8, 1.6 Hz), 7.77 (t, 1 H, J = 1.6 Hz), 7.73 (d, 2 H, J = 7.6 Hz), 7.48 (td, 1 H J = 7.6, 1.6 Hz), 7.39 (t, 1 H, J = 7.6 Hz), 7.19 (d, 1 H, J = 7.6 Hz), 7.18(d, 2 H, J = 7.6 Hz), 5.87 (ddt, 1 H, J =17.2, 10.0, 6.4 Hz), 5.30 (dt, 1 H, J =17.2, 1.6 Hz), 5.26 (d, 1 H, J =10.0 1.6 Hz), 4.36 (s, 2 H), 3.88 (br d, 2 H, J = 6.4 Hz), 2.27 (s, 3 H); ^{13}C NMR ($CDCl_3$): δ 190.9, 144.0, 135.9, 135.8, 133.8, 133.5, 132.1, 130.0, 129.0, 127.8, 127.2, 125.7, 120.3, 89.2, 81.6, 49.7, 36.8, 21.5; IR (neat, cm^{-1}) 1698 (s)1349 (s), 1163 (s); LC-MS (CI): 354 ($M+H^+$, 100), 321 ($M-CH_3OH$, 20); LC-MS (Electrospray): 376 (M+Na, 100). Shipment to an external MS facility resulted in decomposition.



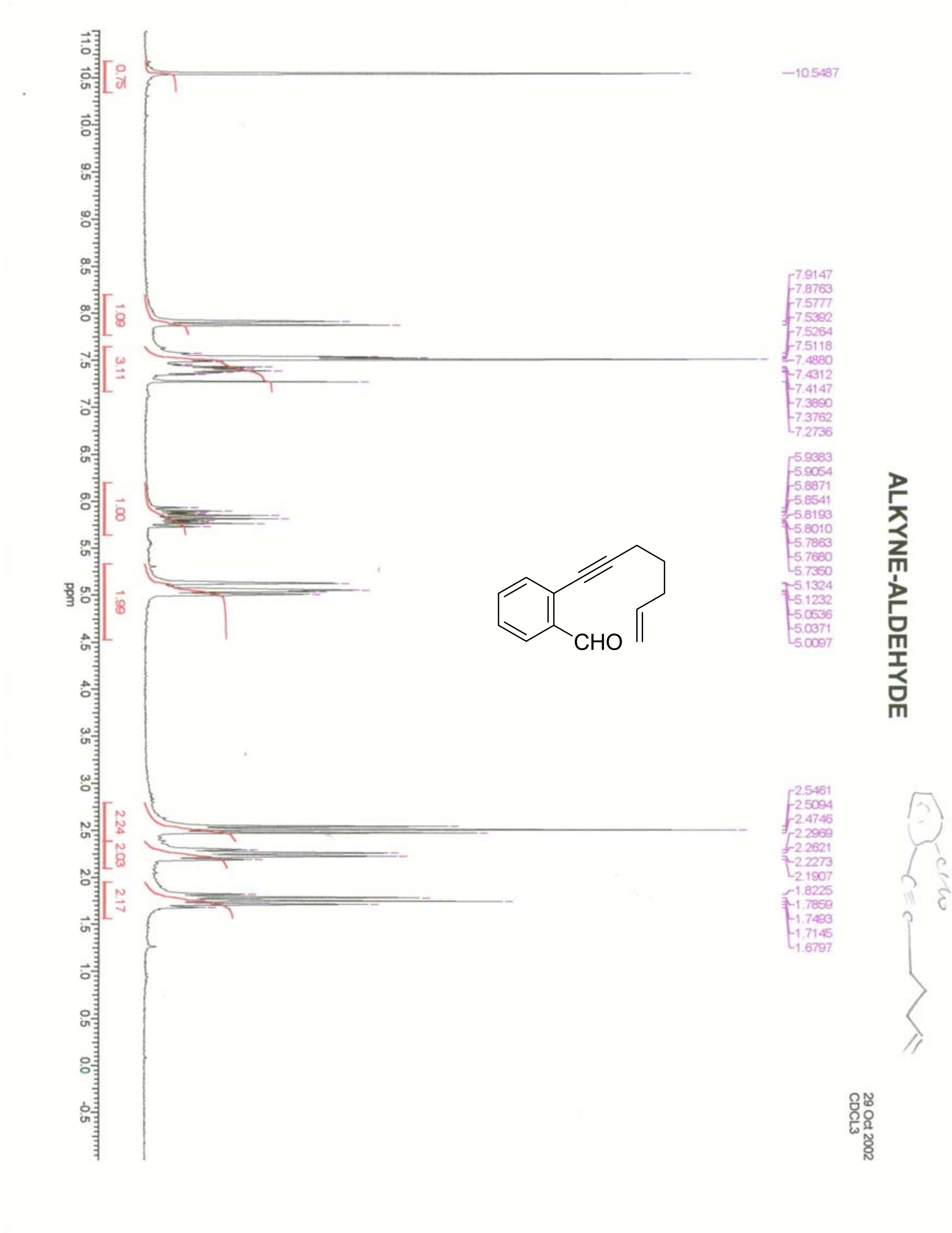
Synthesis of 6g: Treatment of 2-bromobenzaldehyde (0.789 g, 4.31 mmol) and dimethyl (2-butenenyl)propargylmalonate (0.752 g, 3.36 mmol) as described in preparation of **6d,** afforded a yellow oil**,** which was purified by flash column chromatography with ethyl acetate/ hexanes (1:5), which was assigned as **6g** (0.928 g, 84%).

Compound **6g**: ^{1}H NMR ($CDCl_3$): δ 10.41 (s, 1 H), 7.86 (d, 1 H, J = 7.6 Hz), 7.51 (m, 2 H), 7.40 (t, 1 H, J = 7.2 Hz), 5.82 (ddt, 1 H, J =16.8, 10.0, 6.8 Hz), 5.07 (dt, 1 H, J

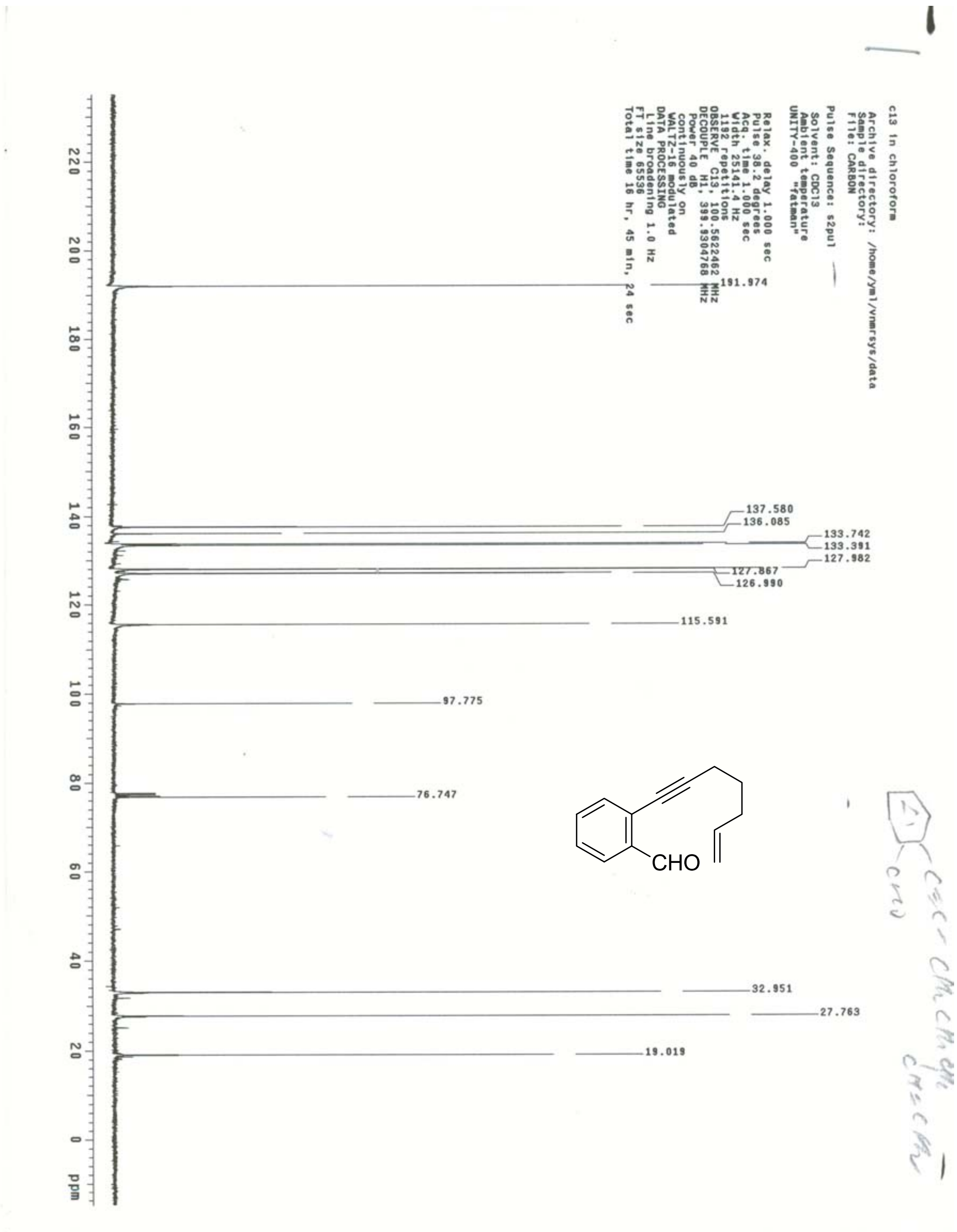


=17.2, 1.6 Hz), 4.98 (d, 1 H, J =10.0 Hz), 3.75 (s, 6 H), 3.13 (s, 2 H), 2.22 (m, 2 H), 2.04 (br q, 2 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 191.8, 170.7, 137.1, 136.3, 133.8, 133.7, 131.7, 128.6, 127.2, 126.8, 91.9, 79.4, 57.0, 53.0, 31.8, 28.6, 24.3; IR (neat, cm^{-1}) 2241 (w), 1735 (s), 1698 (s); MS (EI): *m/e* 328 (M^+, 12), 313 (13), 296 (38), 269 (56), 209 (92), 191 (36), 144 (100), 115 (48), 59 (19); HRMS calcd for $C_{18}H_{18}O5$ 328.131074, found 328.130128.

Proton NMR for Compound **6a**.



Carbon-13 NMR for Compound **6a**.



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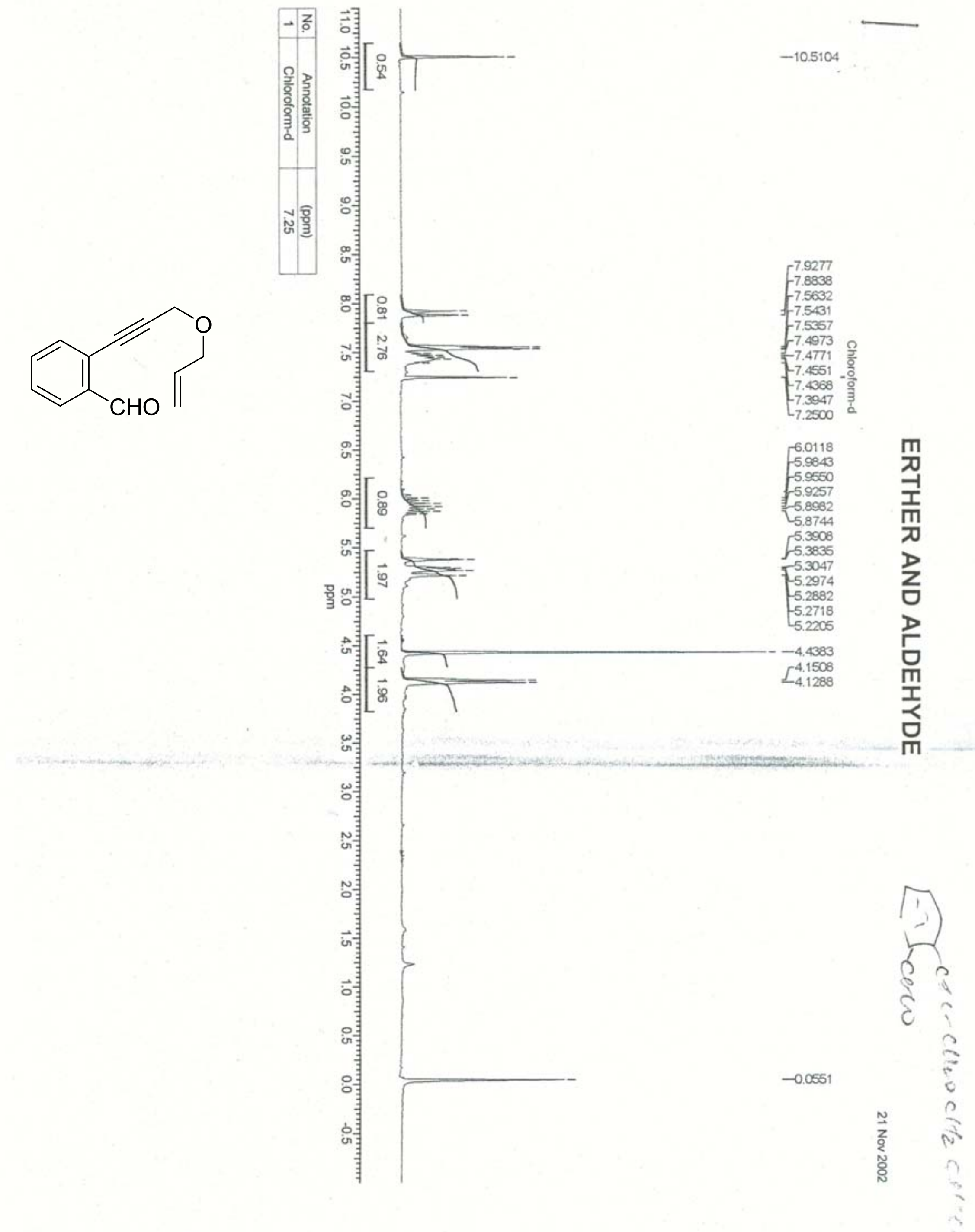
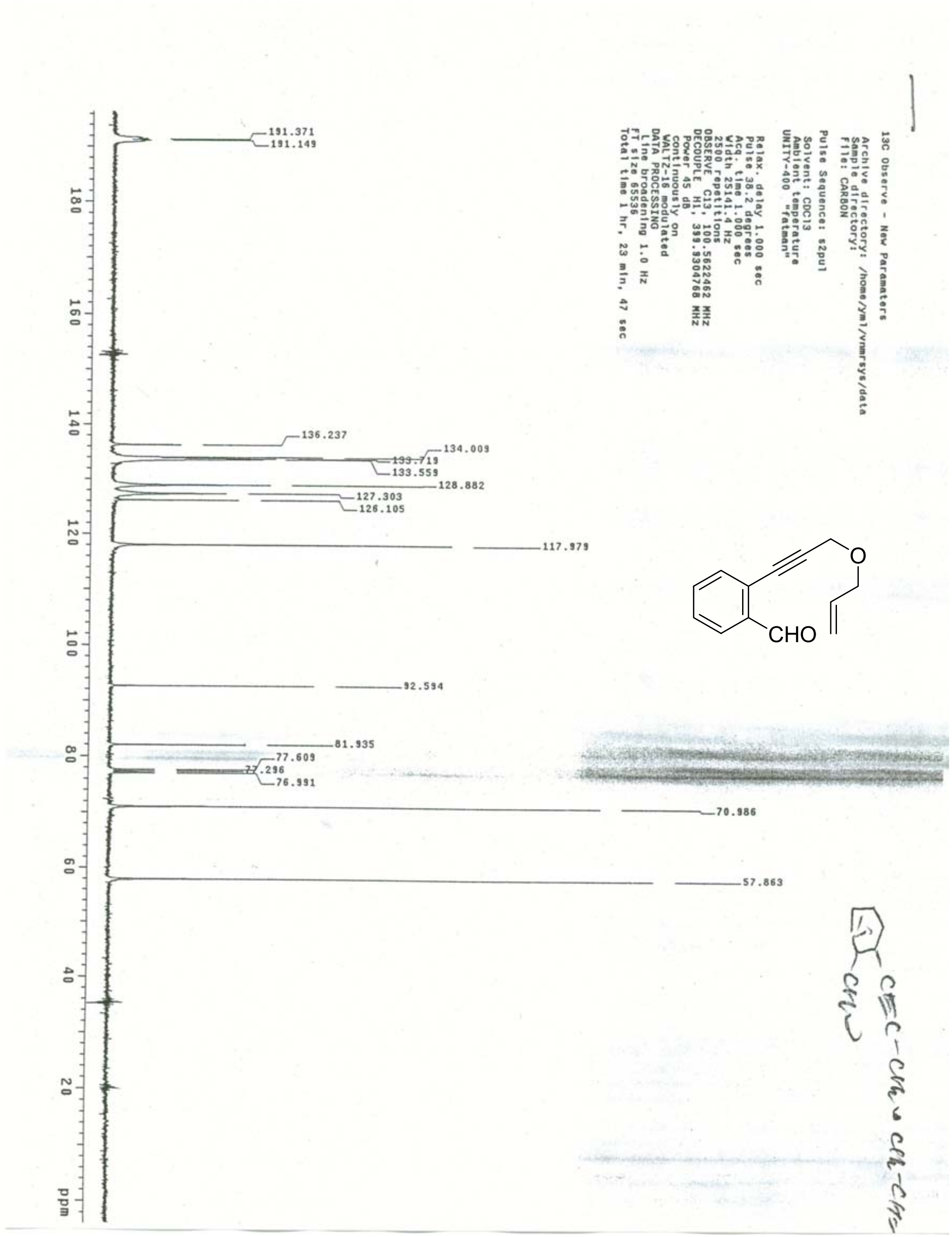
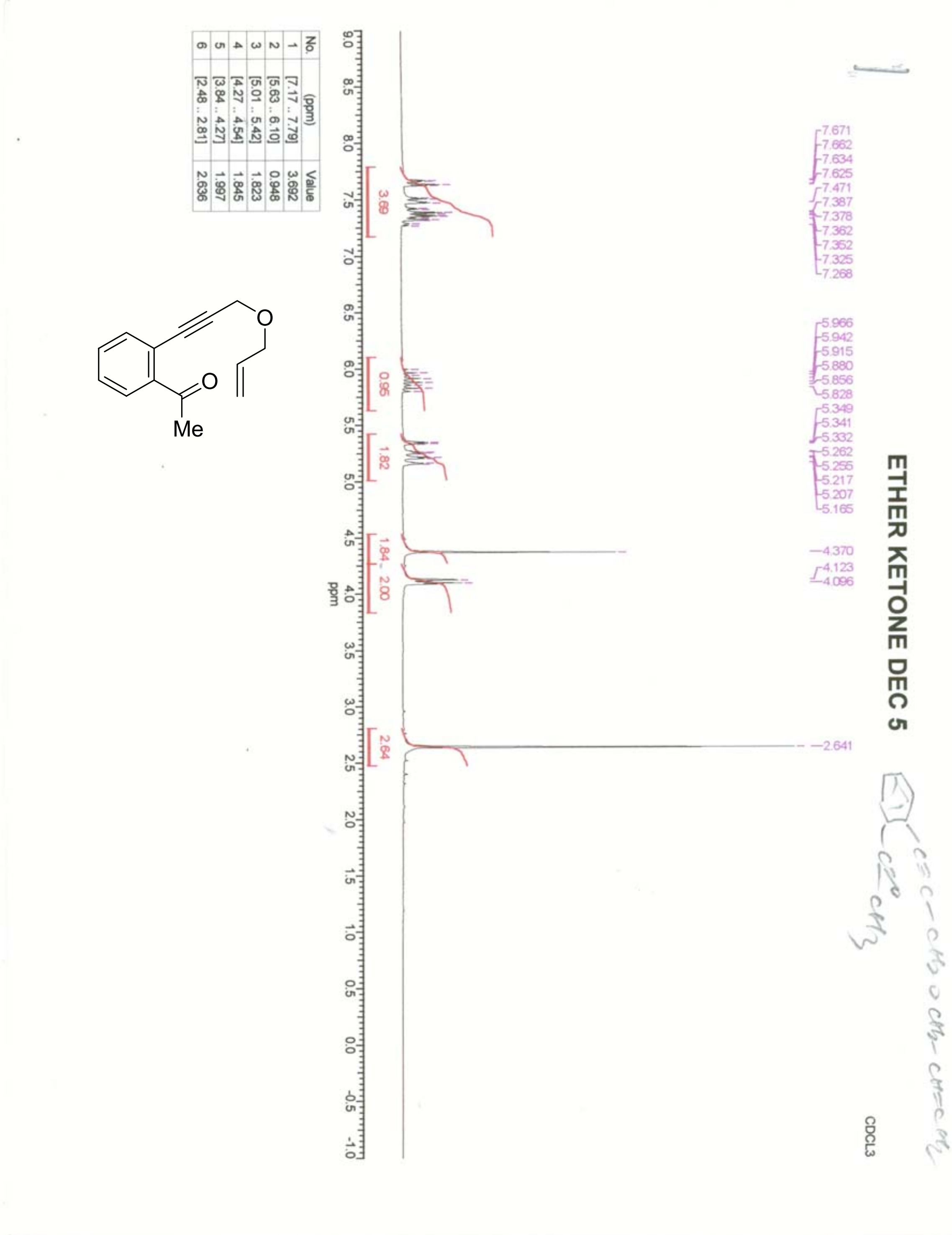


Carbon-13 NMR for Compound **6b**.



Proton NMR for Compound **6c**.



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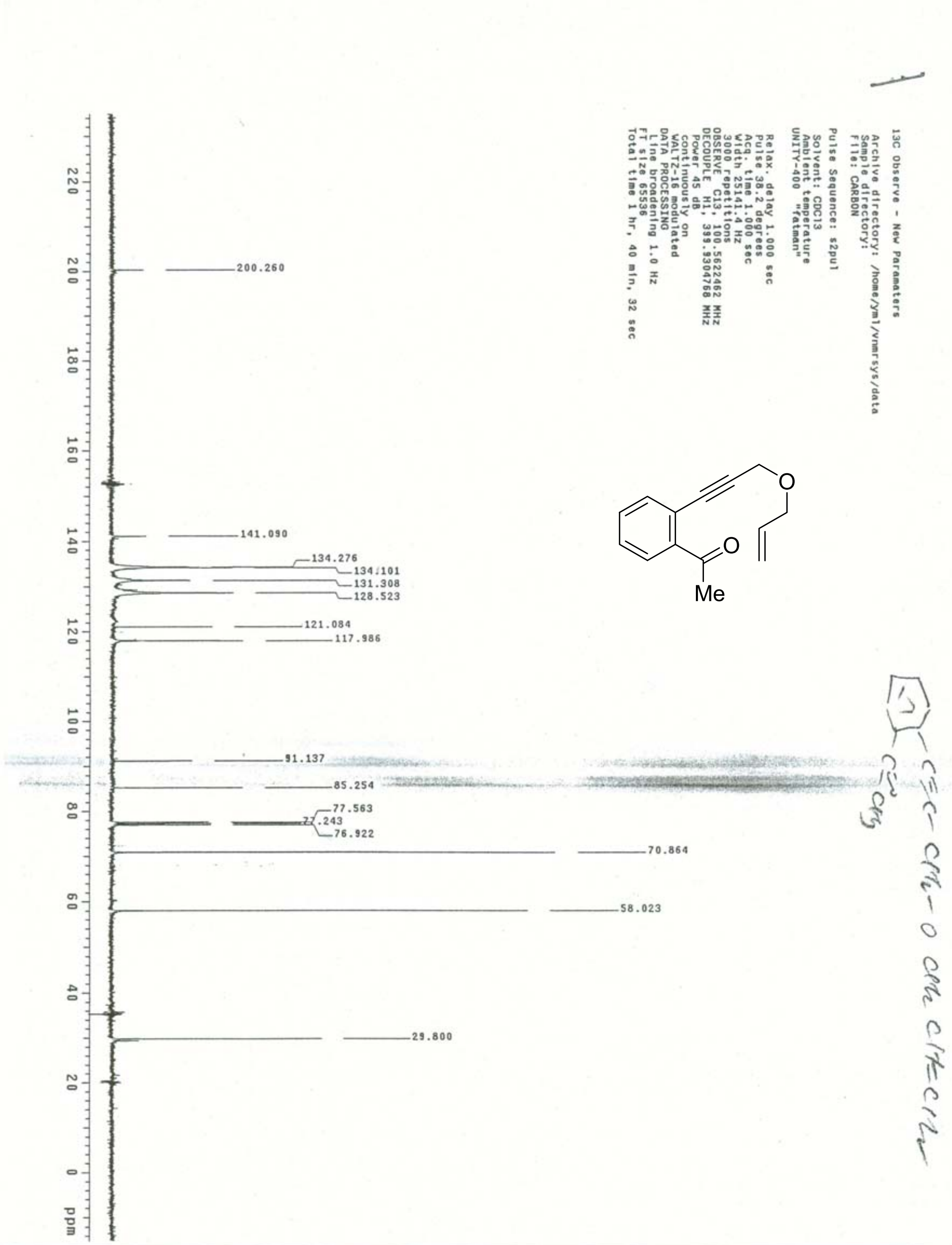

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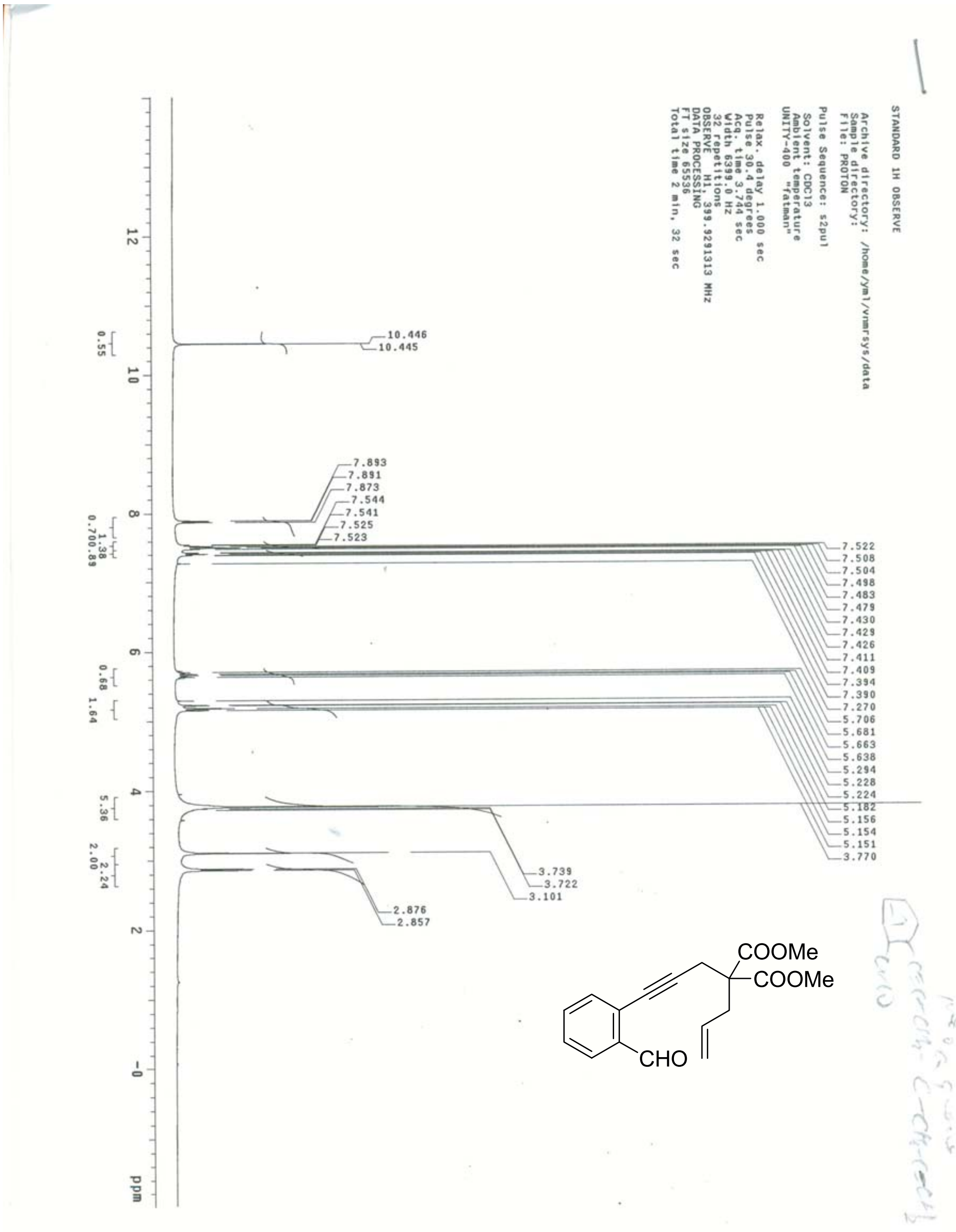
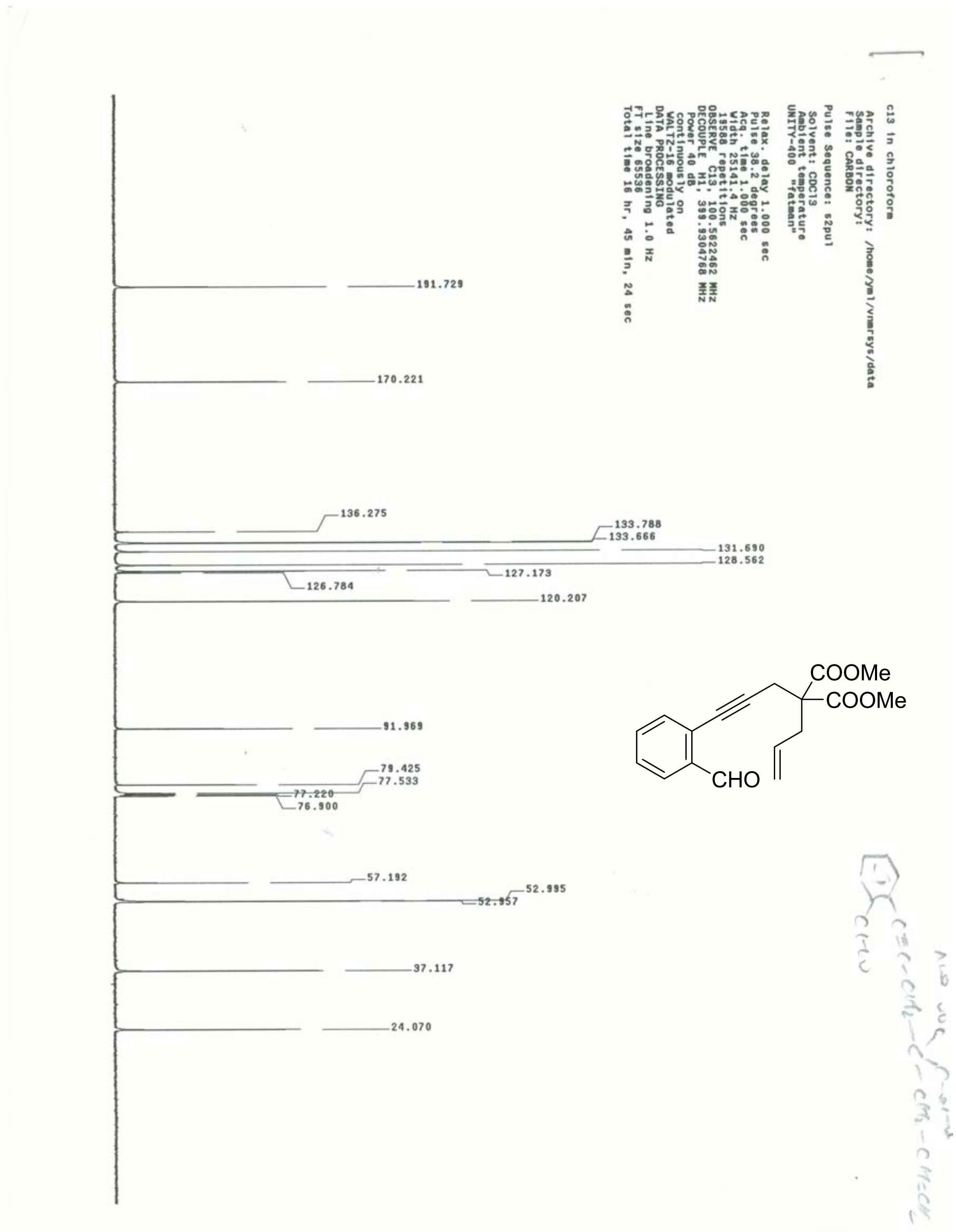
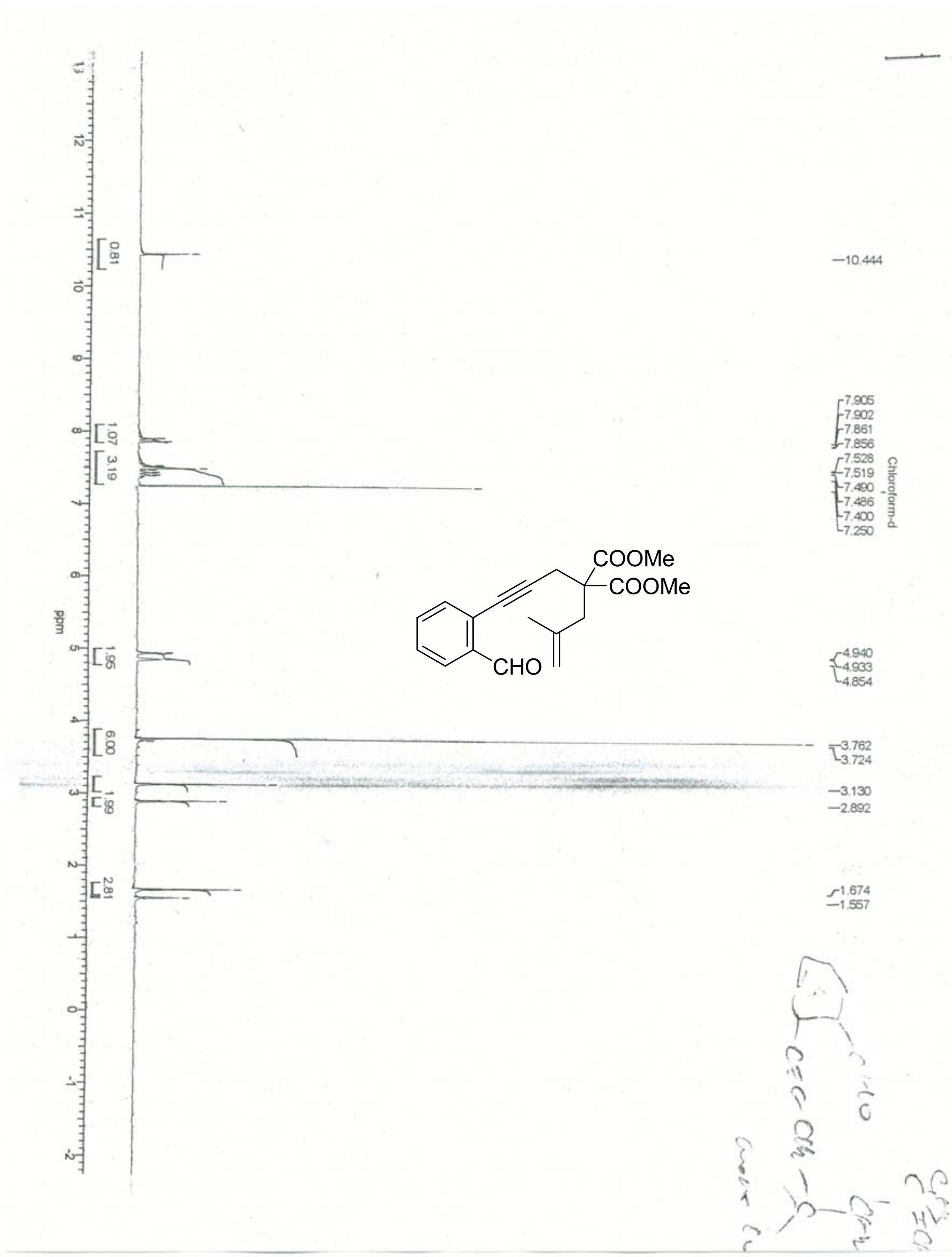


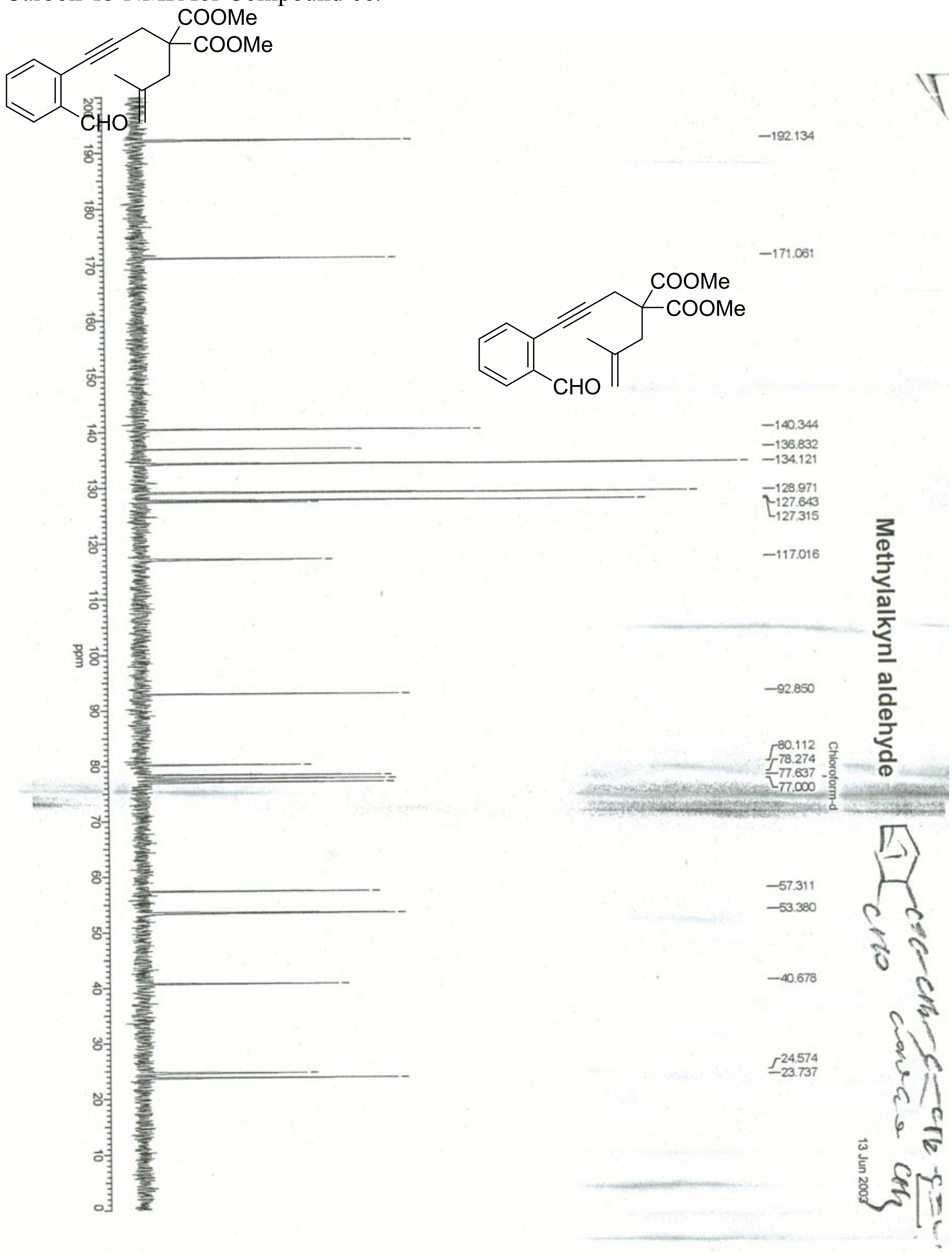
Carbon-13 NMR for Compound **6d**.



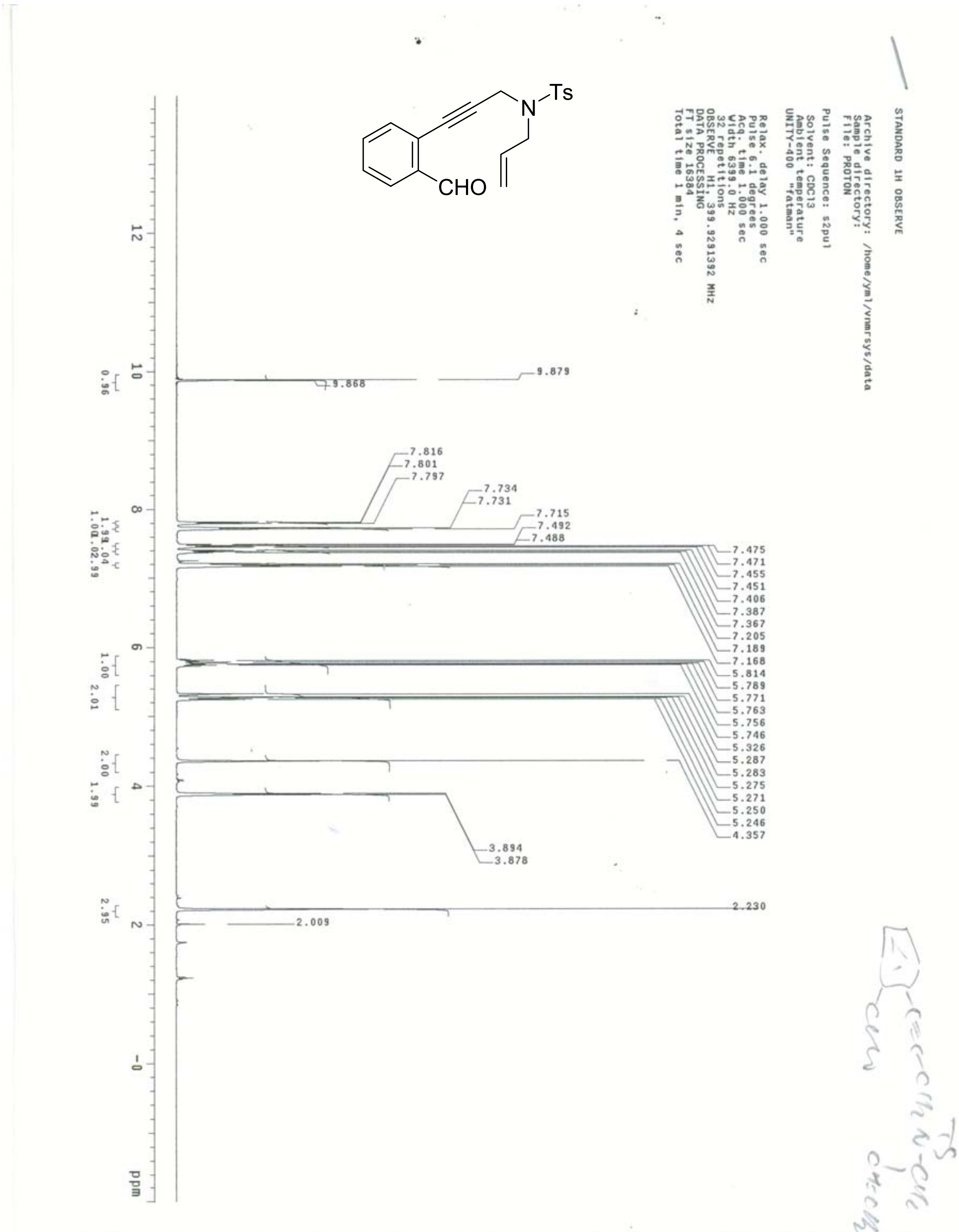
Proton NMR for Compound **6e**.



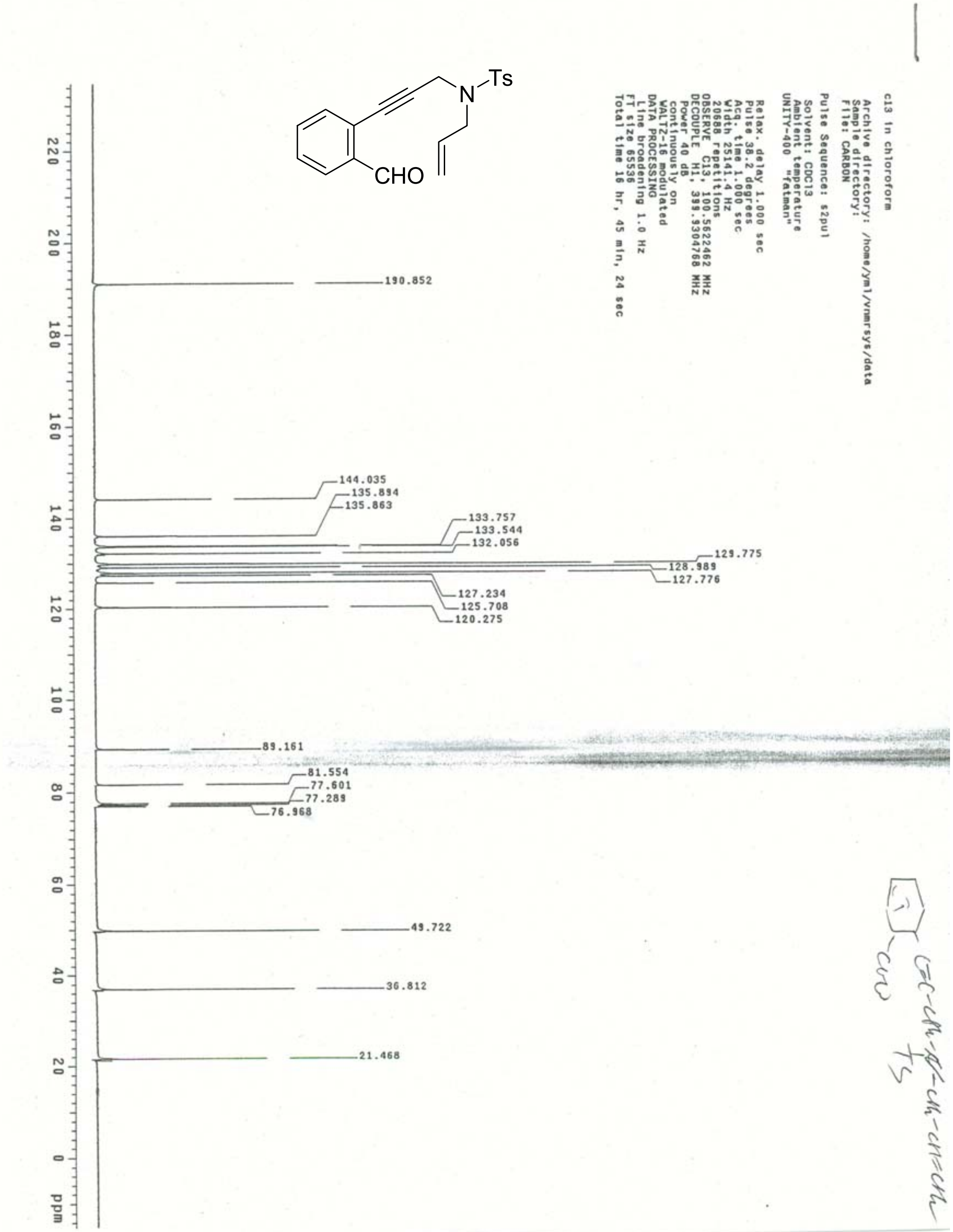
Carbon-13 NMR for Compound **6e**.



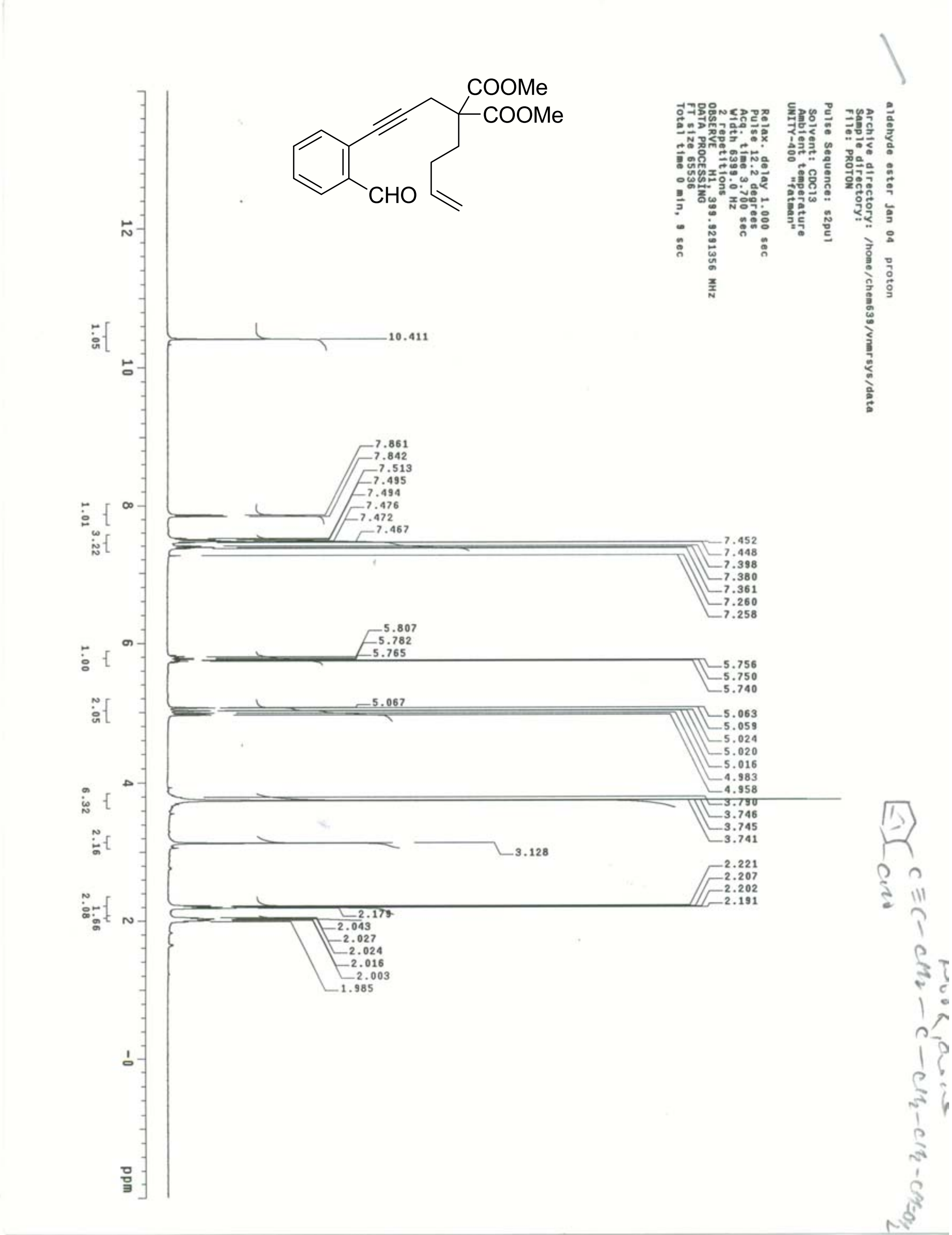
Proton NMR for Compound **6f**.



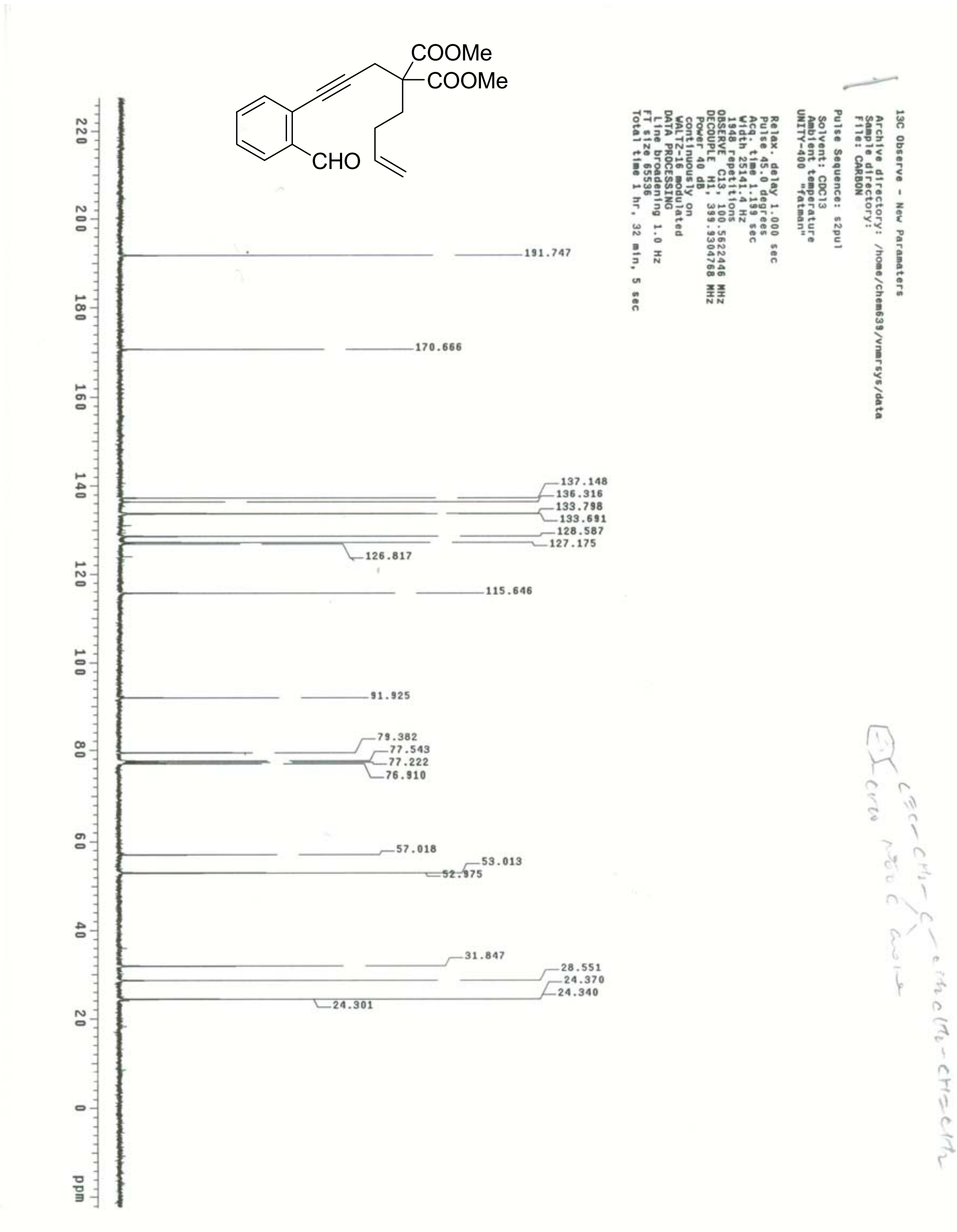
Carbon-13 NMR for Compound **6f**.



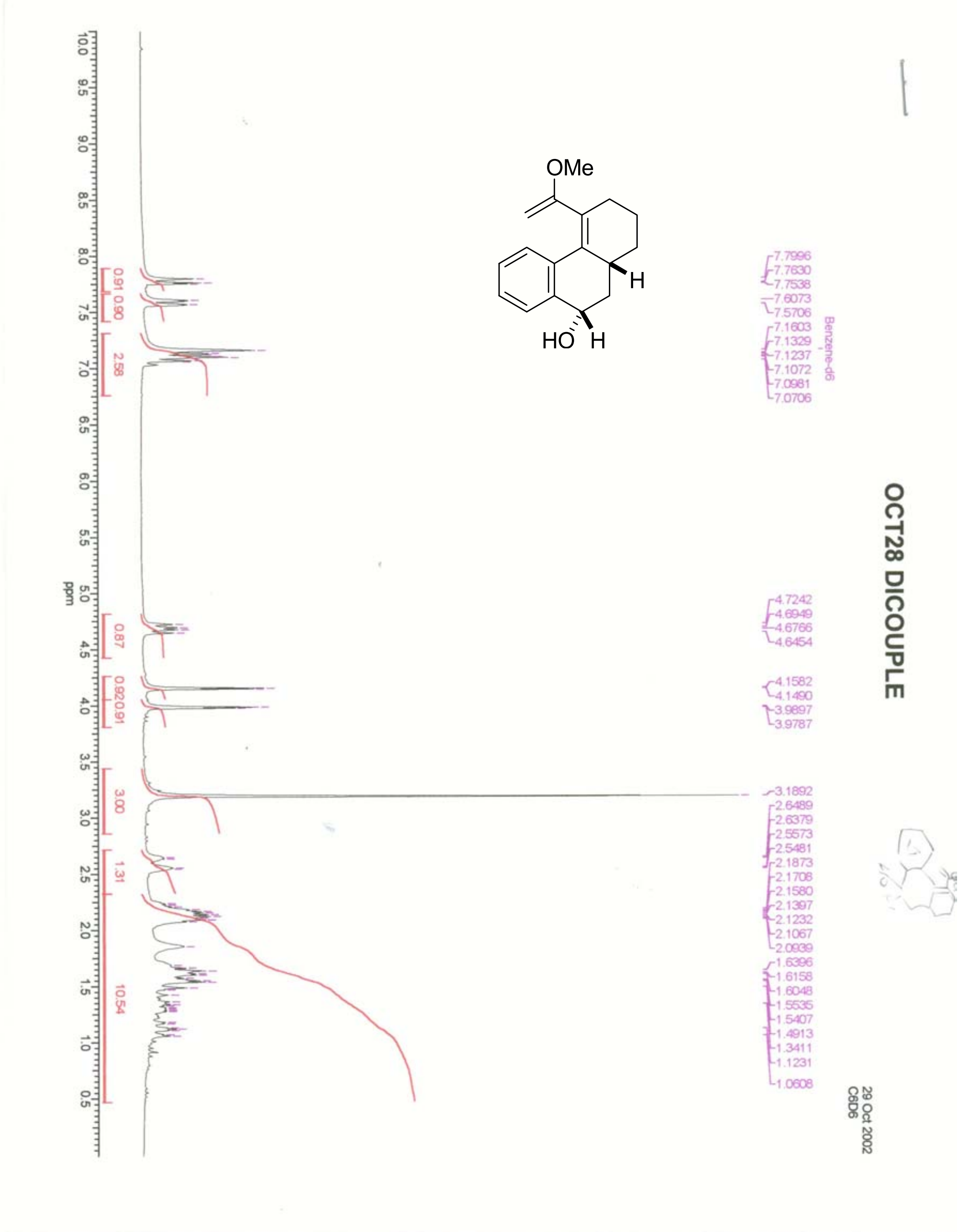
Proton NMR for Compound **6g**.



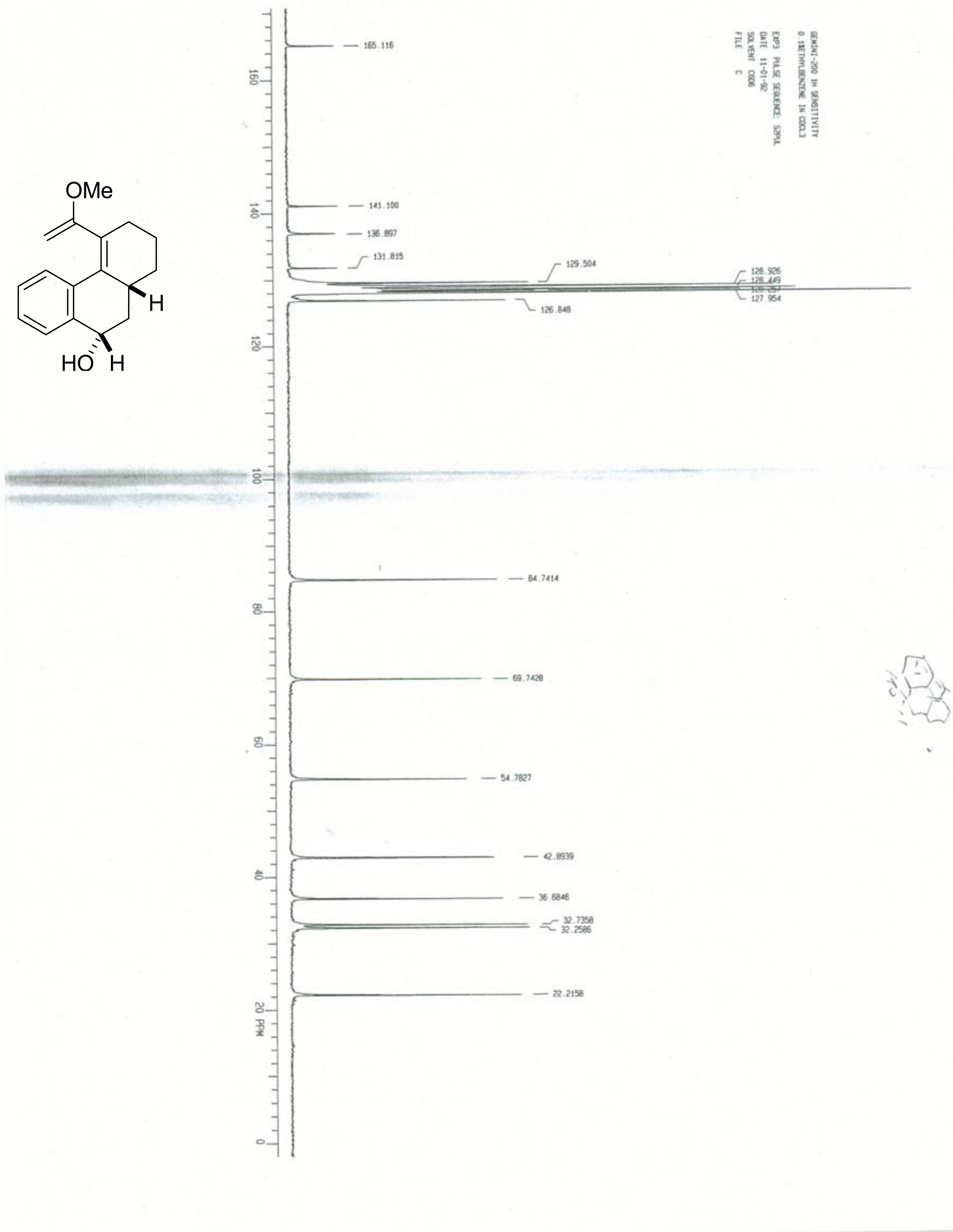
Carbon-13 NMR for Compound **6g**.



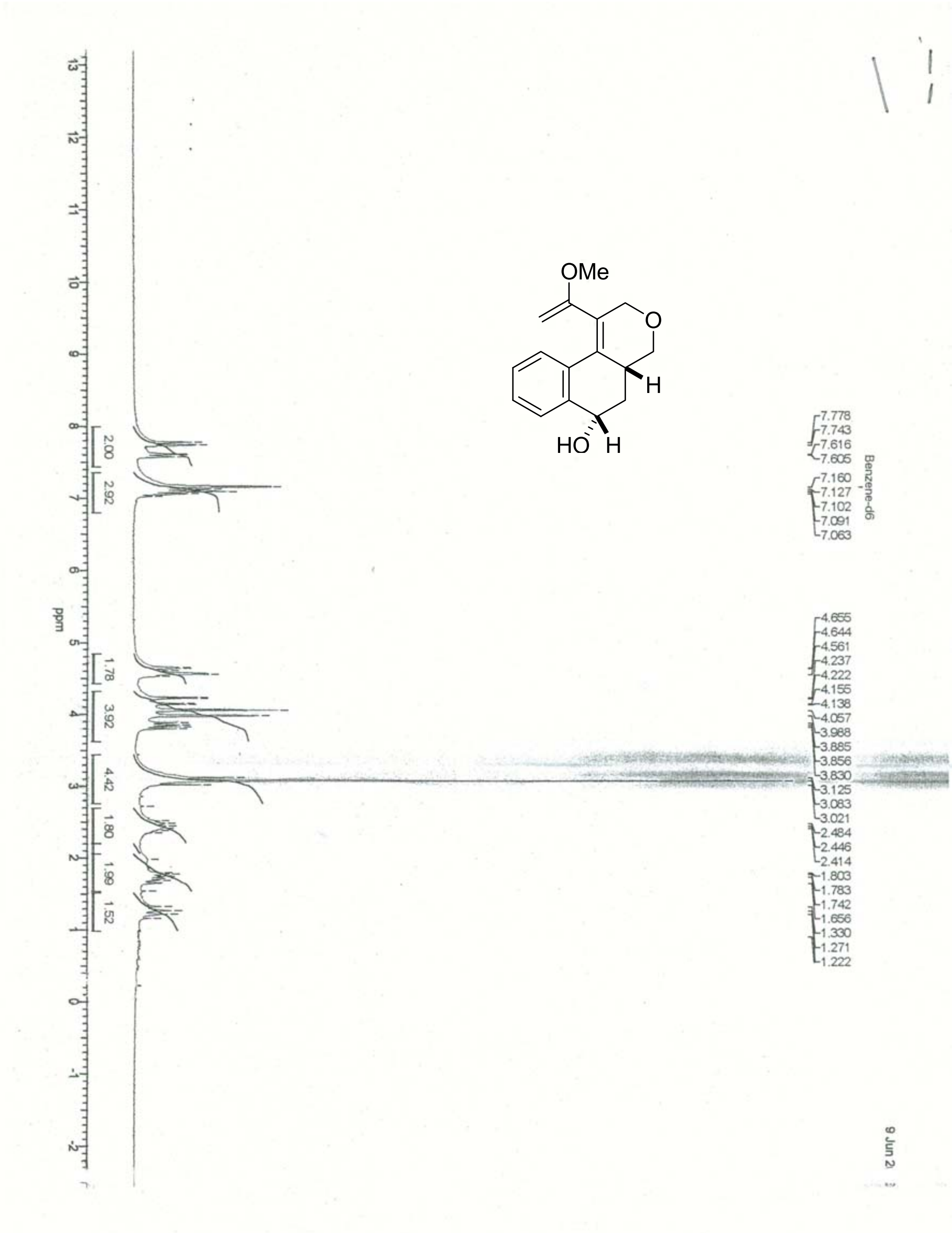
Proton NMR for Compound **14a**.



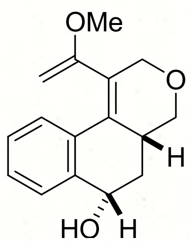
Carbon-13 NMR for Compound **14a**.

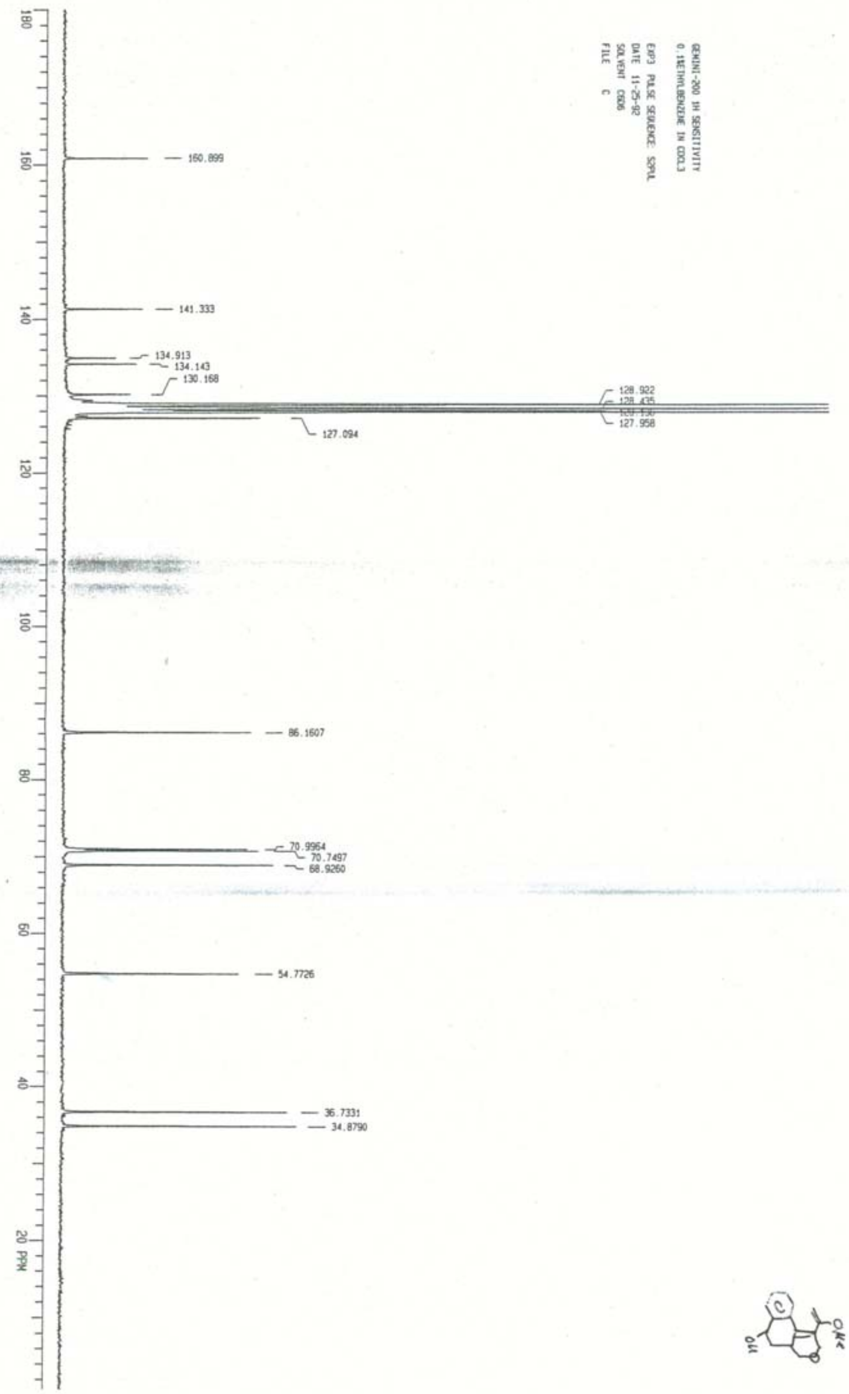


Proton NMR for Compound **14b**.

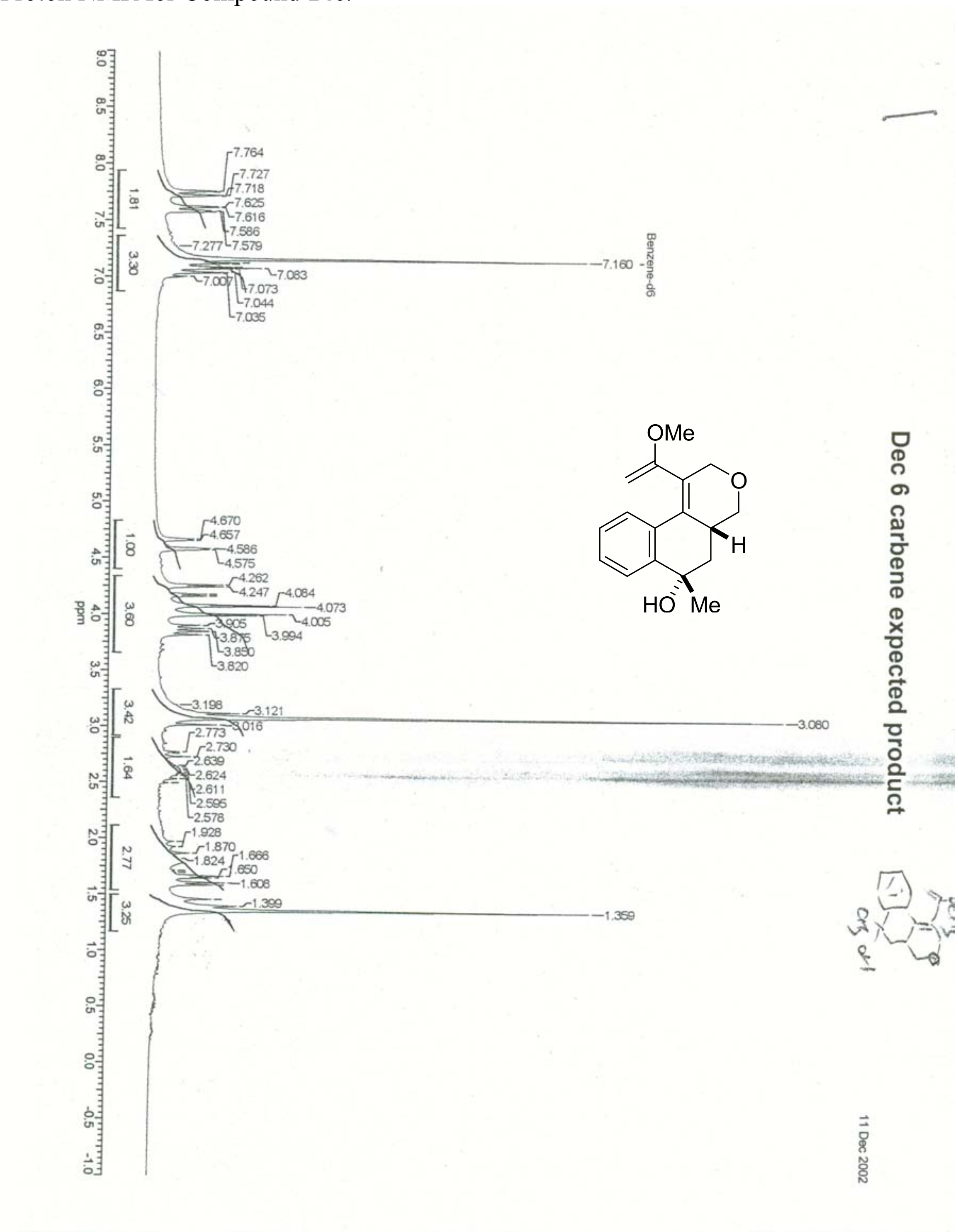


Carbon-13 NMR for Compound **14b**.

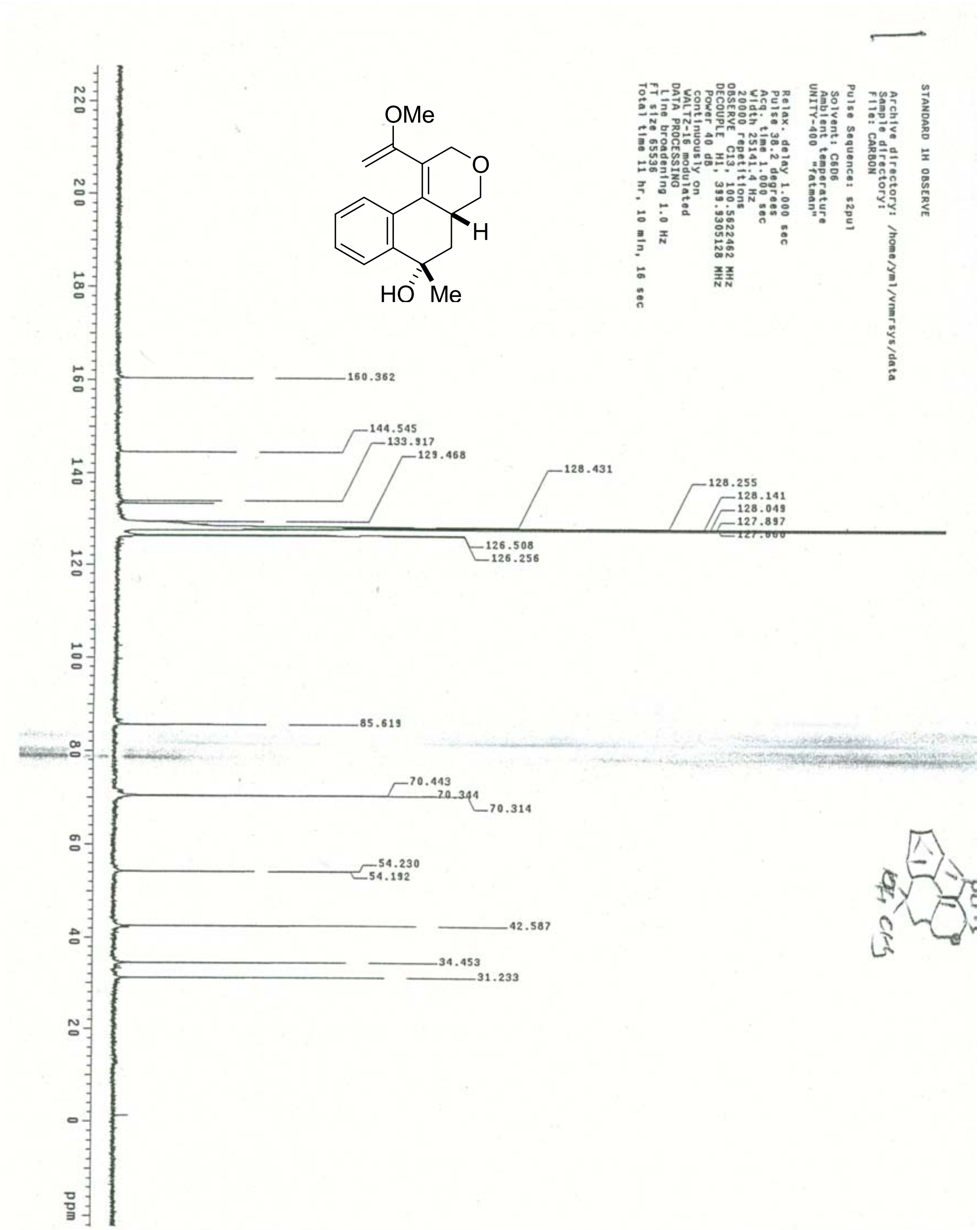




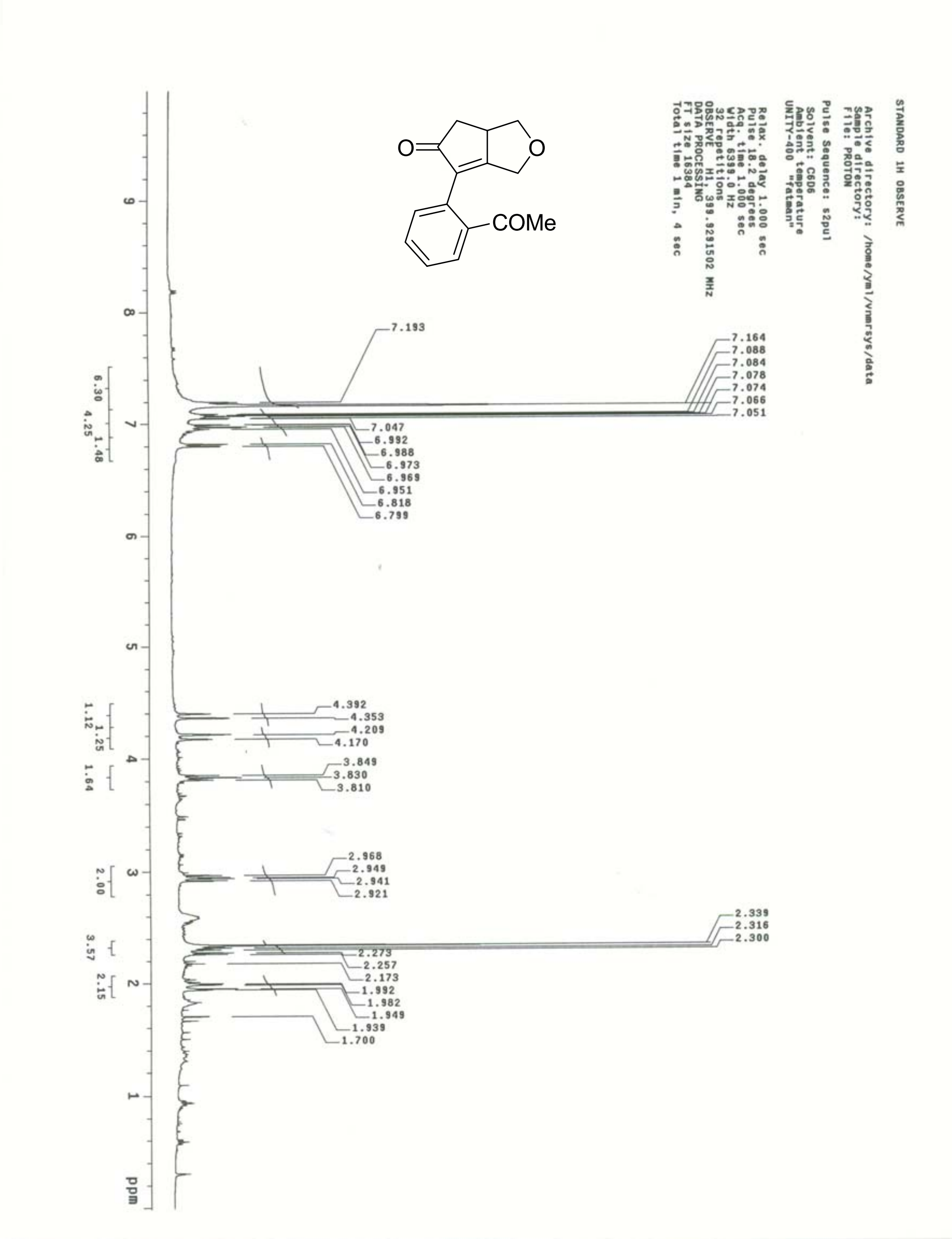
Proton NMR for Compound **14c**.



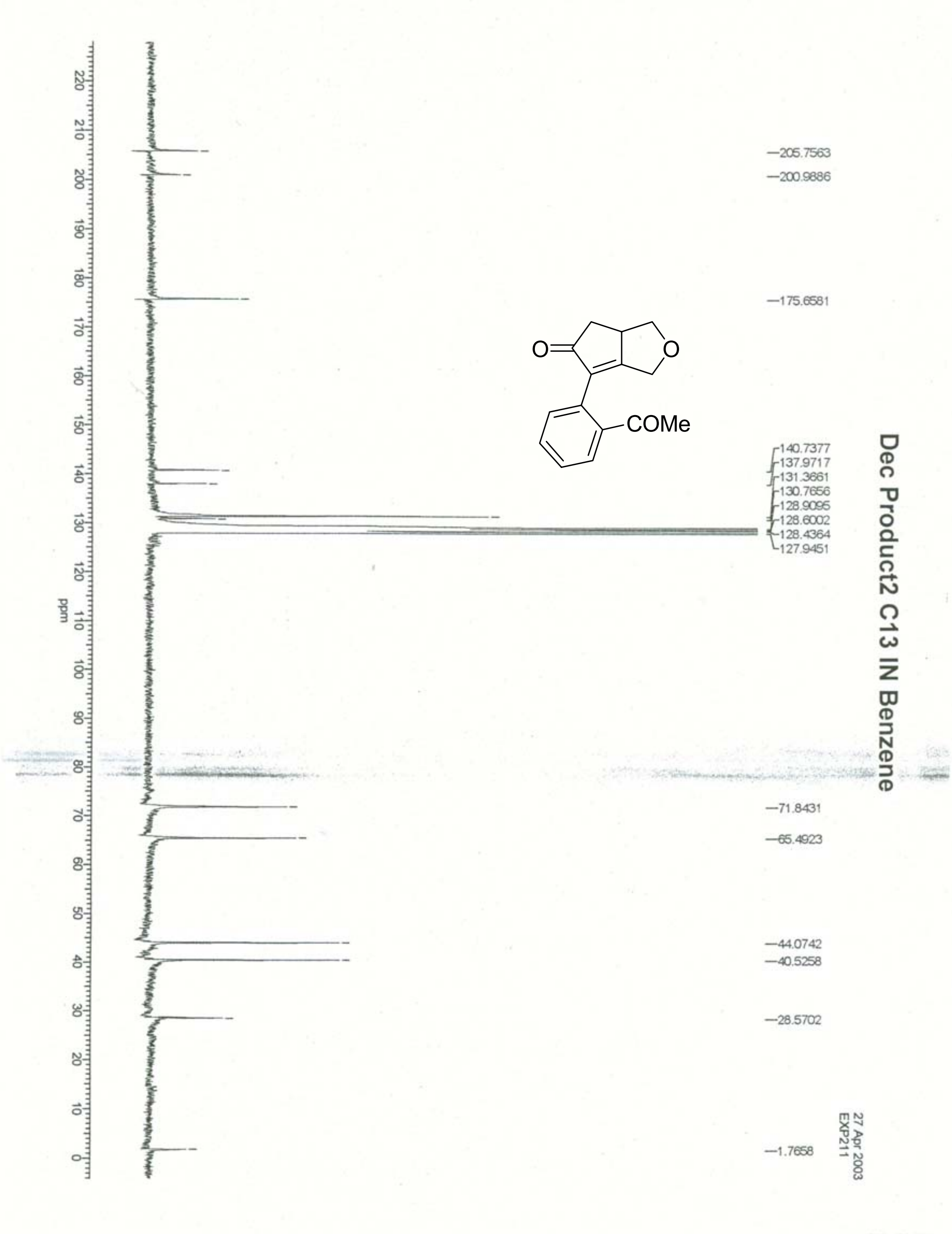
Carbon-13 NMR for Compound **14c**.



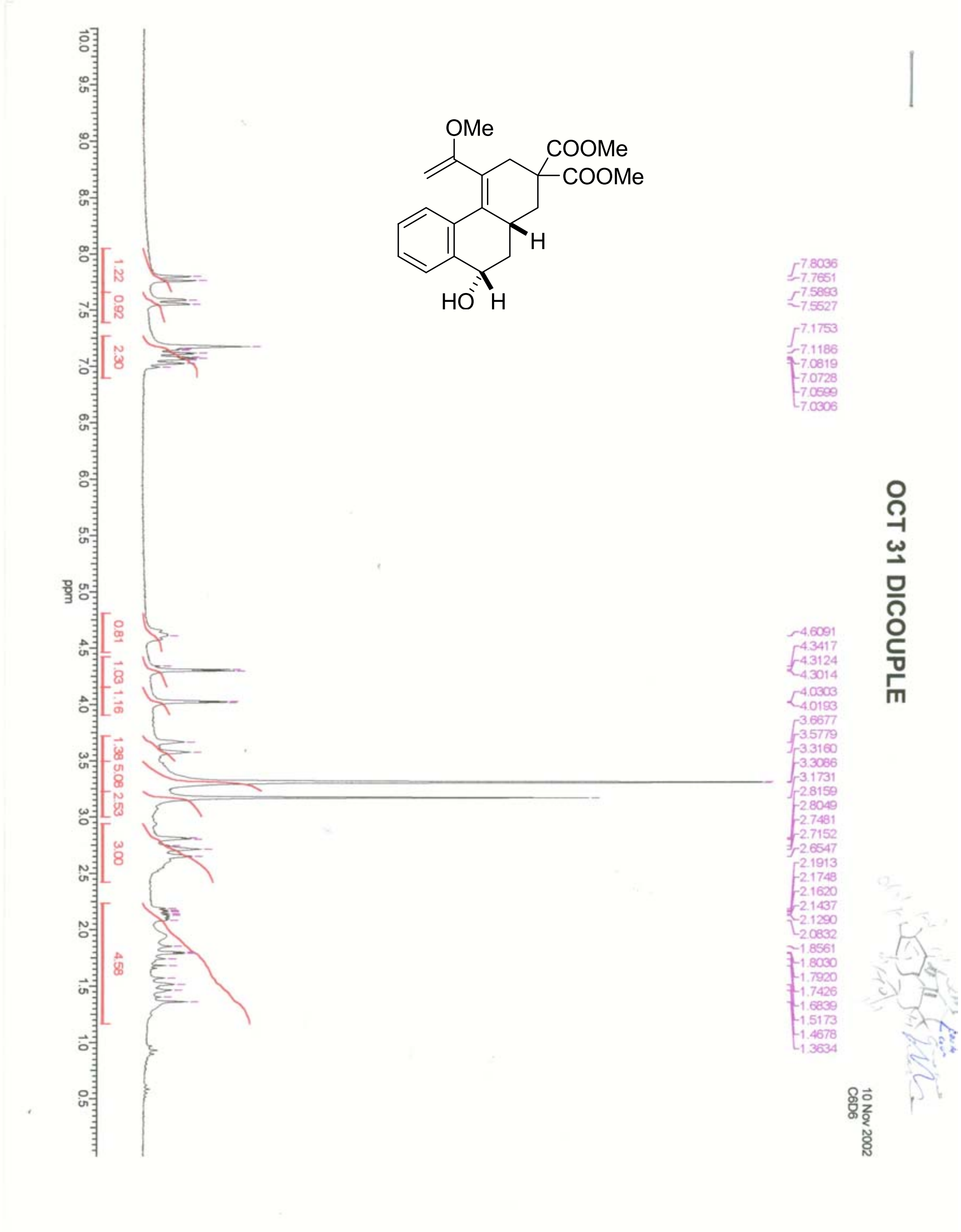
Proton NMR for Compound **15c**.



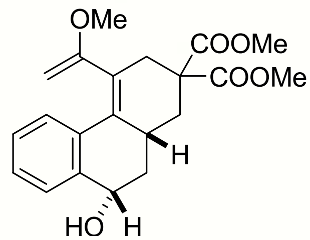
Carbon-13 NMR for Compound **15c**.

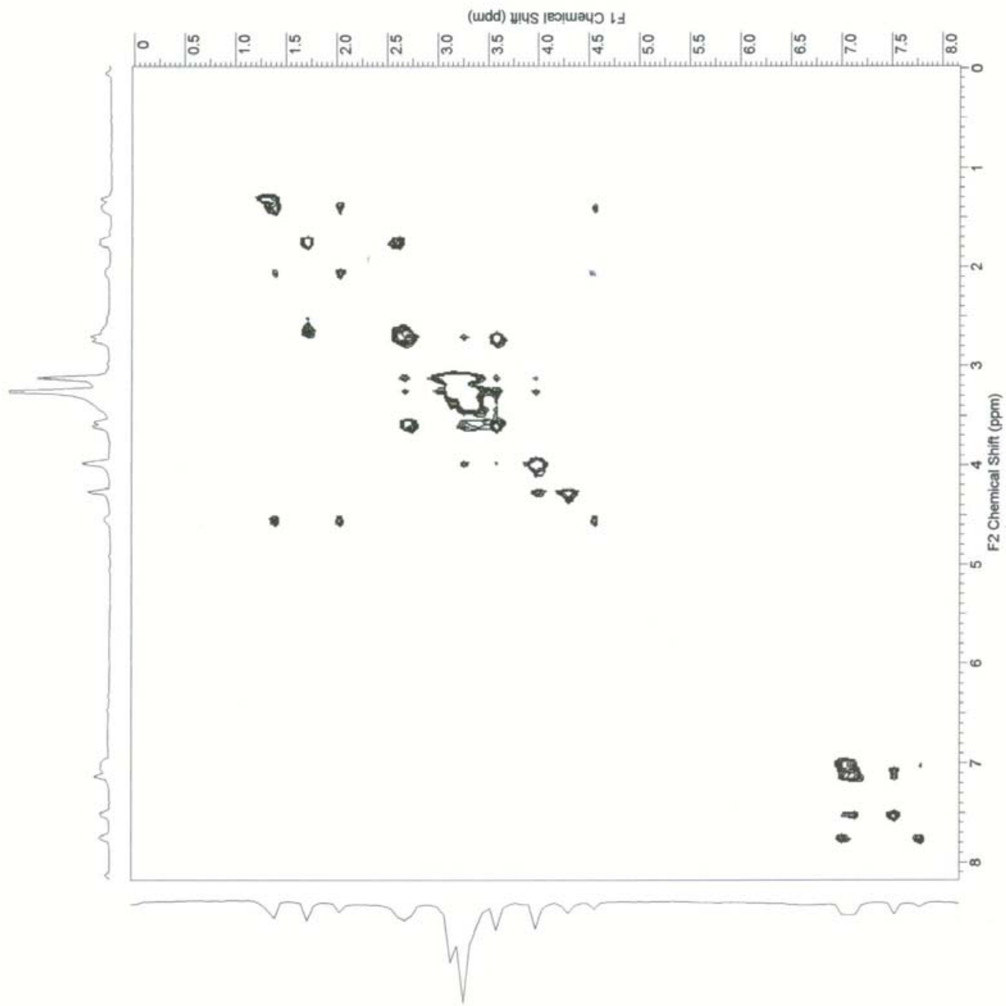


Proton NMR for Compound **14d**.

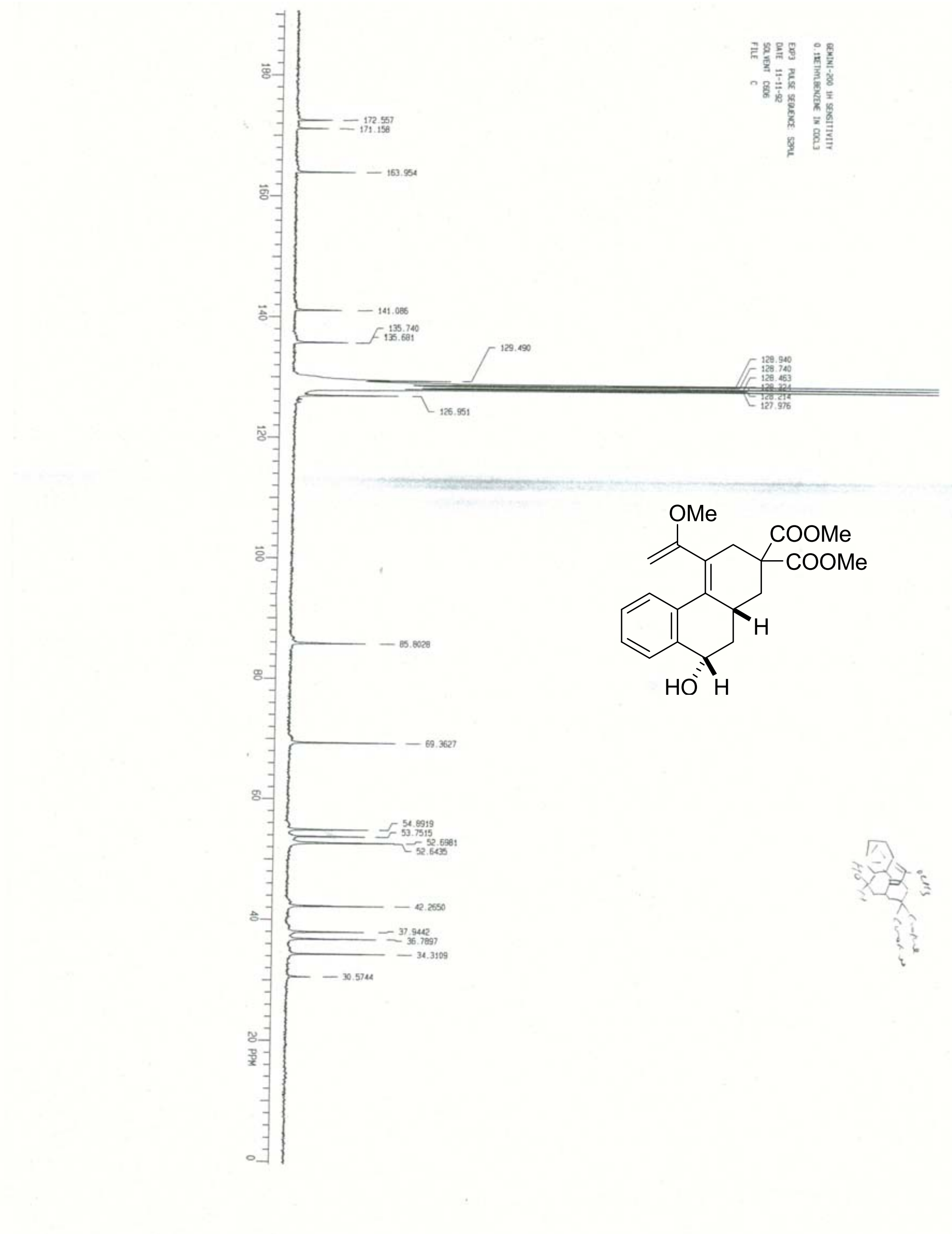


COSY Spectrum for Compound **14d**.

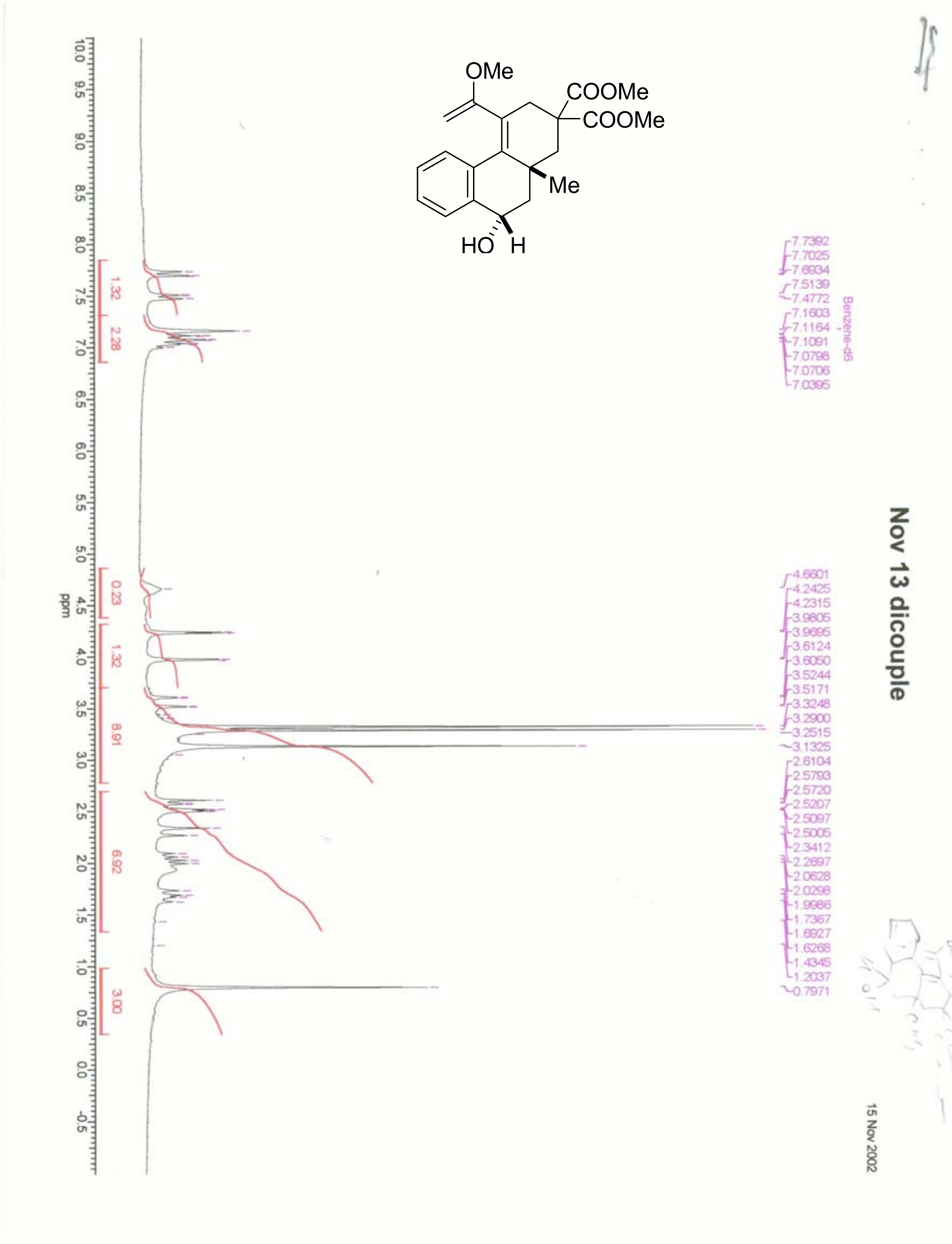




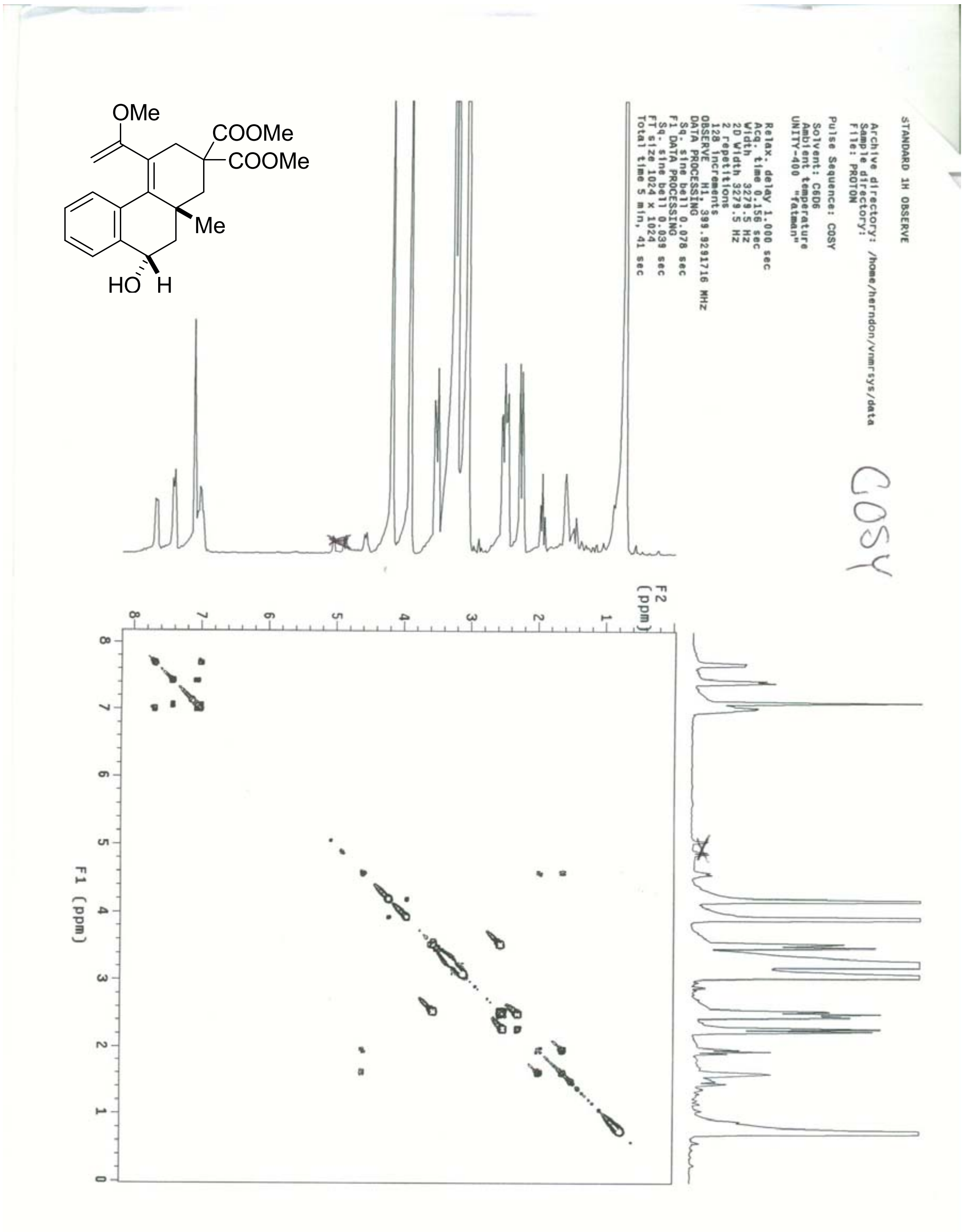
Carbon-13 NMR for Compound **14d**.



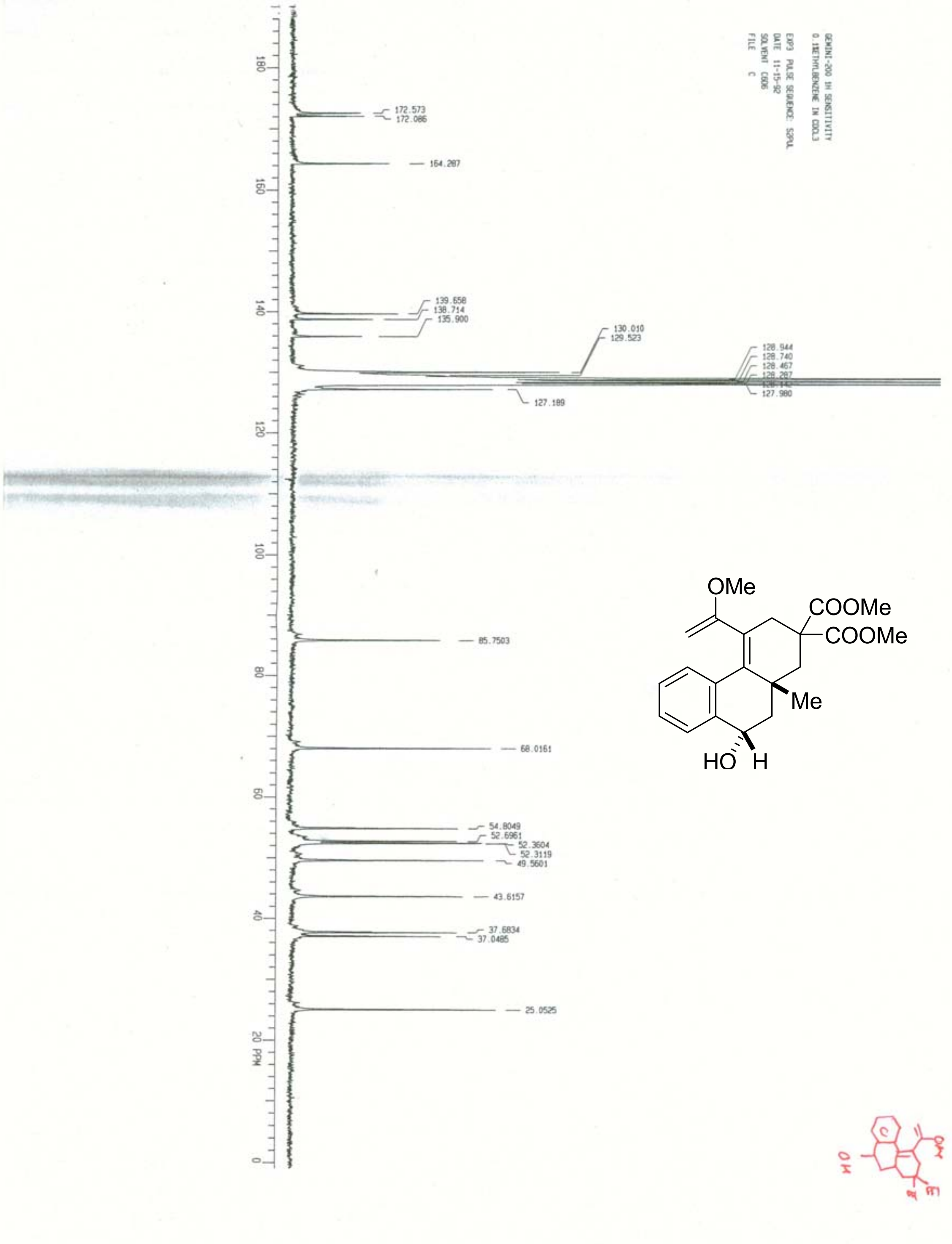
Proton NMR for Compound **14e**.



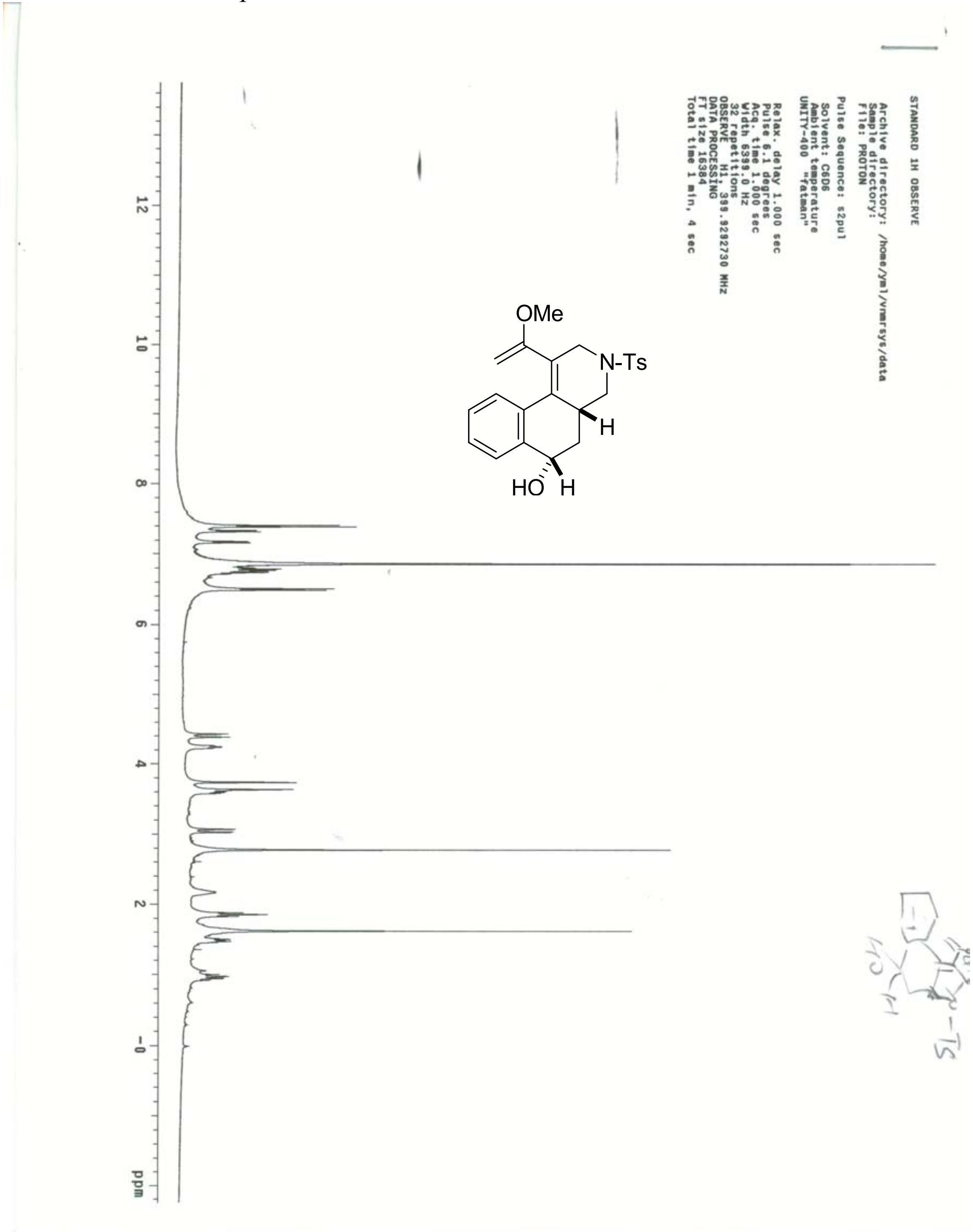
COSY Spectrum for Compound **14e**.



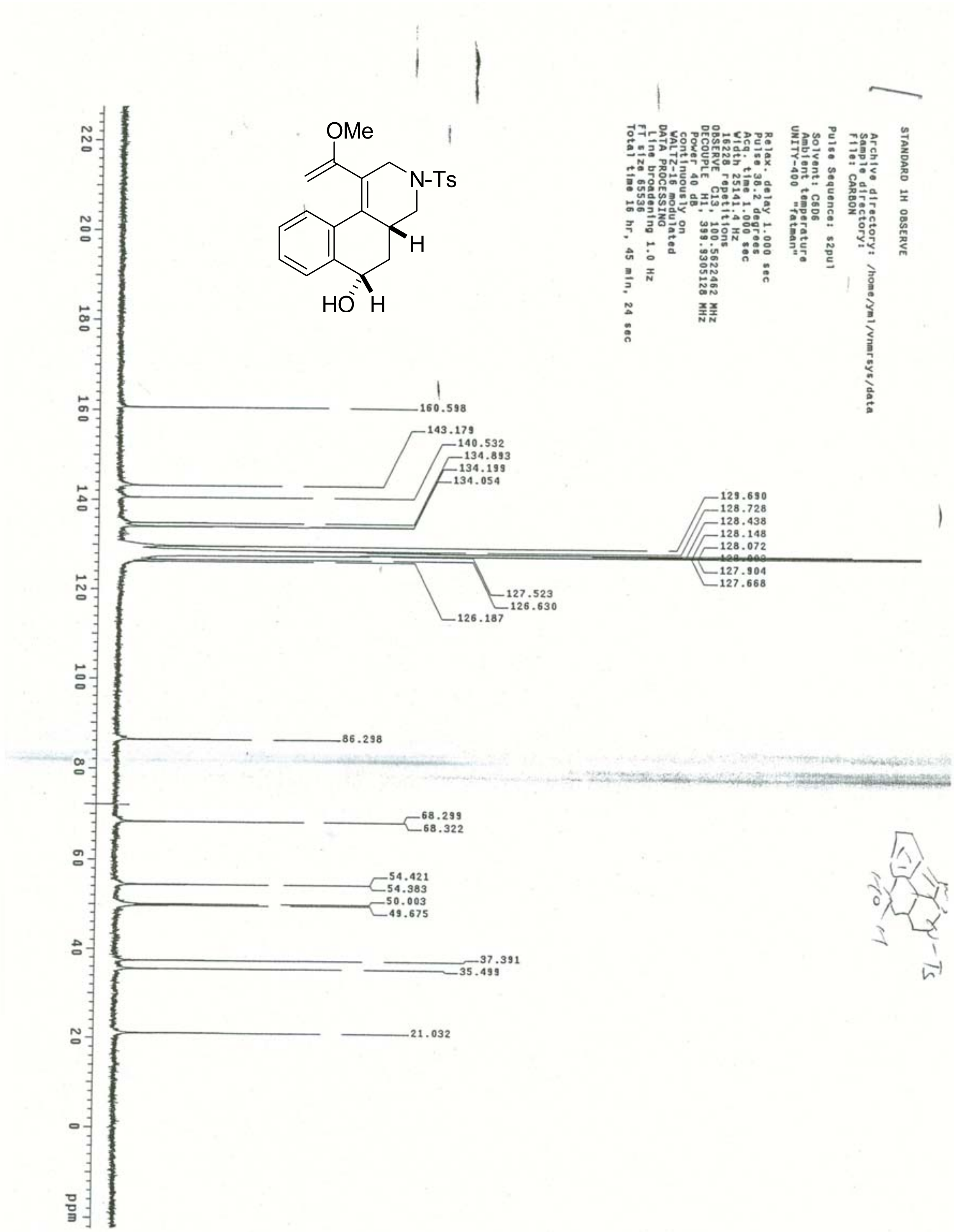
Carbon-13 NMR for Compound **14e**.



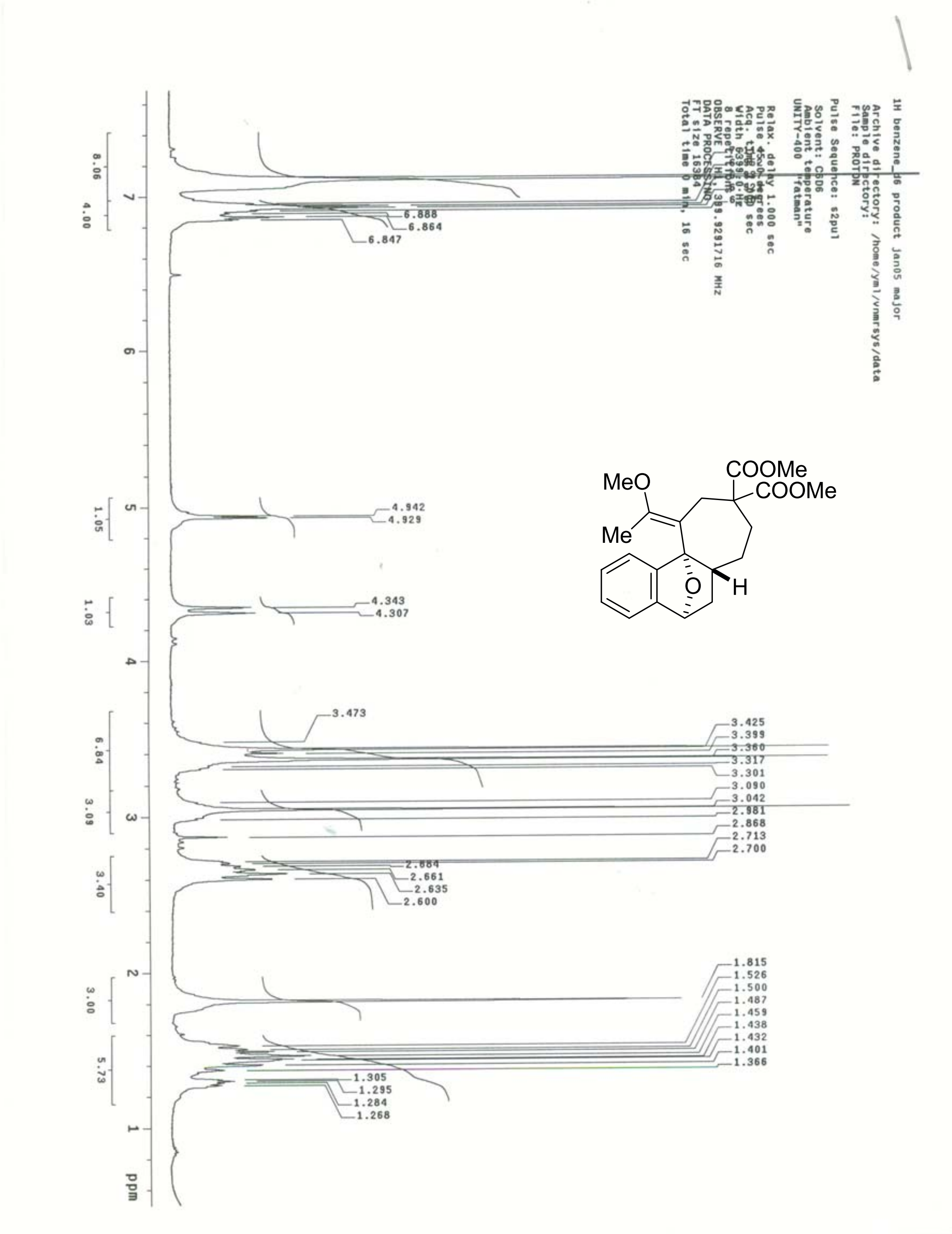
Proton NMR for Compound **14f**.



Carbon-13 NMR for Compound **14f**.



Proton NMR for Compound **9g**.



Carbon-13 NMR for Compound **9g**.