

Supporting Information

An unprecedented stereoselective [2+2] cycloreversion of cyclobutanones

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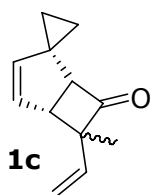
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1. Generals: ^1H and ^{13}C NMR spectra were recorded with AW 300 and AV2 400 MHz Bruker spectrometer instruments in CDCl_3 . Chemical shifts in CDCl_3 and CD_2Cl_2 are reported in δ (ppm) relative to tetramethylsilane (TMS), chloroform and dichloromethane as internal reference unless otherwise stated. In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 , or CH_3) was determined by recording the DEPT-90 and DEPT-135 experiments, and is given in parentheses. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, bs = broad singlet, sept = septet. Solvents for extraction and chromatography were technical grade and used without further purification. Flash chromatography was performed using Tsingdao Haiyang Chemical silica gel (200 ± 300 mesh) and silica gel Merck grade (60 Å). Unless otherwise noted, a mixture of hexane:MTBE (50:1) was used as eluent. IR spectra were recorded with a Bruker Tensor 27 and a Jasco FT/IR-4100. High resolution MS were obtained with a Finnigan MAT 95 (San Jose, CA; USA) double-focusing magnetic sector mass spectrometer (geometry BE) and GC/MS spectral data were obtained from an Agilent 6890 N and MSD 5975 using a column HP-5 MS, 30 m, 0.25 mm, 0.25 μm . All solvents were dried over standard drying agent and freshly distilled prior to use. All other reagents were used as received. Substrates **1a**, **b**, **d** and **8** were synthesized according to literature protocols,^[1] *endo/exo* isomers could be conveniently separated by chromatography on Ag-doped silica gel.^[2]

2. Experimental Procedures



6-Methyl-6-vinylspiro[bicyclo[3.2.0]hept[3]ene-2,1'-cyclopropan]-7-one (**1c**)

Freshly prepared tigloyl chloride (23.7 g, 0.20 mol in 200 mL of dry CH_2Cl_2) was added dropwise to a solution of triethylamine (30.36 g, 0.30 mol) and spiro[2.4]hepta-4,6-diene^[3] (27.64 g, 0.30 mol) in CH_2Cl_2 (300 mL) at 0 °C during 1.5 h. The mixture was stirred for 2 h at room temperature, was filtered and concentrated in vacuo. The residue was diluted with hexane (300 mL), washed with water and brine, dried (MgSO_4), concentrated in vacuo and purified by column chromatography to give 20.2 g (58%) of **1c** (mixture of *endo*: *exo*-isomers, ratio 1: 3).

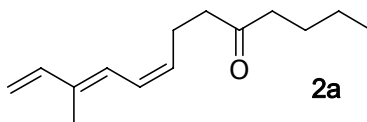
The *exo* isomer: ^1H NMR (300 MHz, CDCl_3): δ 5.94 (dd, $J = 10.5, 17.3$ Hz, 1H), 5.72-5.62 (m, 1H), 5.47-5.34 (m, 1H), 5.21-5.04 (m, 2H), 3.65 (d, $J = 6.9$ Hz, 1H), 3.45-3.35 (m, 1H), 1.27-1.18 (m, 1H), 1.16 (s, 3H), 0.84-0.73 (m, 1H), 0.71-0.57 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 213.6 (s), 141.5 (d), 139.4 (d), 127.2 (d), 113.7 (t), 71.6 (s), 64.3 (d), 48.9 (d), 31.0 (s), 15.9 (q), 13.4 (t), 8.7 (t). The *endo* isomer: ^1H NMR (300 MHz, CDCl_3): δ 5.82 (dd, $J = 10.7, 17.5$ Hz, 1H), 3.51-3.45 (m, 1H), 1.40 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 214.1 (s), 140.9 (d), 135.3 (d), 128.0 (d), 115.5 (t), 70.5 (s), 63.7 (d), 51.6 (d), 31.1 (s), 21.9 (q), 13.7 (t), 8.7 (t). IR (neat): 3082, 3002, 2969, 1774, 1451, 1144, 962, 922, 763 cm^{-1} . MS (EI): m/z (%): 174 [M]⁺ (9), 159 (36), 146 (25), 131 (64), 91 (100), 82 (30). HRMS (EI): m/z calcd. for $\text{C}_{12}\text{H}_{14}\text{O}$ (M)⁺ 174.1045, found: 174.1026.

General Procedure for the Synthesis of Ketones **2** and **10**

A solution of alkyl lithium (0.01 mol in hexane) was added dropwise to a solution of ketone **1** or **9**

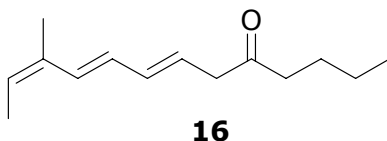
(0.01 mol) and 5 mol% of DMPU (or HMPT) in dry THF (20 mL) with stirring at $-78\text{ }^{\circ}\text{C}$ under argon during 10-15 min. The reaction mixture was then heated to reflux temperature. The conversion was monitored by GC-MS or TLC. After 1 to 12 h, the resulting mixture was allowed to cool to room temperature and quenched with water (20 mL). The mixture was extracted with MTBE ($3 \times 30\text{ mL}$), and the combined organic phases were washed with water and brine, dried with MgSO_4 and concentrated in vacuo. The residue was purified by column chromatography or by bulb-to-bulb distillation.

(8Z,10E)-11-Methyltrideca-8,10,12-trien-5-one (2a)



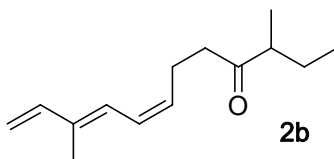
This compound was purified by column chromatography to yield 1.61 g (79%) of a colorless liquid. Odor: fruity, floral, pineapple, peppery, diffusive. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 6.44 (dd, $J = 10.7\text{ Hz}$, 17.3 Hz , 1H), 6.37-6.27 (m, 2H), 5.56-5.39 (m, 1H), 5.23 (d, $J = 17.3\text{ Hz}$, 1H), 5.06 (d, $J = 10.7\text{ Hz}$, 1H), 2.57-2.46 (m, 4H), 2.40 (t, $J = 7.4\text{ Hz}$, 2H), 1.85 (s, 3H), 1.62-1.52 (m, 2H), 1.39-1.22 (m, 2H), 0.89 (t, $J = 3.6\text{ Hz}$, 3H). $^1\text{H NMR}$ (400 MHz, C_6D_6): δ 6.43 (dd, $J = 10.8\text{ Hz}$, 17.4 Hz , 1H), 6.40-6.39 (m, 1H), 6.30 (ddt, $J = 10.6\text{ Hz}$, 10.6 Hz , 1.56 Hz , 1H), 5.41 (dt, $J = 10.6\text{ Hz}$, 7.7 Hz , 1H), 5.14 (d, $J = 17.4\text{ Hz}$, 1H), 4.97 (d, $J = 10.8\text{ Hz}$, 1H), 2.46-2.38 (m, 2H), 2.04 (t, $J = 7.4\text{ Hz}$, 2H), 1.94 (t, $J = 7.4\text{ Hz}$, 2H), 1.71 (s, 3H), 1.46-1.40 (m, 2H), 1.16-1.09 (m, 2H), 0.78 (t, $J = 7.3\text{ Hz}$, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 210.4 (s), 141.4 (d), 135.7 (s), 131.1 (d), 125.9 (d), 125.4 (d), 112.7 (t), 42.6 (t), 42.1 (t), 25.9 (t), 22.3 (t), 22.1 (t), 13.8 (q), 11.7 (q). $^{13}\text{C NMR}$ (75 MHz, C_6D_6): δ 210.4 (s), 141.4 (d), 135.7 (s), 131.0 (d), 125.9 (d), 125.4 (d), 112.6 (t), 42.3 (t), 42.2 (t), 26.1 (t), 22.6 (t), 22.4 (t), 14.0 (q), 11.8 (q). IR (neat): 3031, 2959, 2933, 2873, 1714, 1612, 1577, 1456, 1410, 1378, 988, 894 cm^{-1} . MS (EI): m/z (%): 206 [M] $^+$ (45), 149 (10), 121 (96), 106 (100), 91 (61), 85 (84), 79 (43), 57 (87). HRMS (EI): m/z calcd. for $\text{C}_{14}\text{H}_{22}\text{O}$ (M) $^+$ 206.1671, found 206.1664.

(7E,9E,11Z)-11-Methyltrideca-7,9,11-trien-5-one (16)



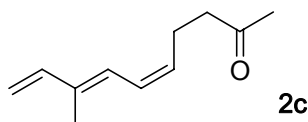
Vinyl cyclobutanone *endo*-**1a** was used as the substrate to afford the [1,7]-H shift product trienone **16** (1.01 g, 50%) of a yellowish liquid. Odor: fruity, fatty, pineapple weak. $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 6.58 (d, $J = 15.2\text{ Hz}$, 1H), 6.20 (dd, $J = 10.4\text{ Hz}$, 15.2 Hz , 1H), 6.01 (dd, $J = 10.4\text{ Hz}$, 14.9 Hz , 1H), 5.80-5.63 (m, 1H), 5.35-5.20 (m, 1H), 2.77 (d, $J = 7.2\text{ Hz}$, 2H), 1.95 (t, $J = 7.2\text{ Hz}$, 2H), 1.71 (s, 3H), 1.56 (d, $J = 7.0\text{ Hz}$, 3H), 1.44-1.35 (m, 2H), 1.12-1.02 (m, 2H), 0.73 (t, $J = 7.0\text{ Hz}$, 3H). $^{13}\text{C NMR}$ (75 MHz, C_6D_6): δ 206.4 (s), 134.8 (d), 133.1 (s), 129.3 (d), 128.7 (d), 126.1 (d), 125.5 (d), 46.8 (t), 41.8 (t), 26.0 (t), 22.5 (t), 20.5 (q), 14.0 (q), 13.1 (q). IR (neat): 3033, 2959, 2933, 2873, 1715, 1458, 1377 cm^{-1} . MS (EI): m/z (%): 206 [M] $^+$ (40), 121 (83), 85 (98), 57 (100).

(7Z, 9E)-3, 10-Dimethyldodeca-7,9,11-trien-4-one (2b)



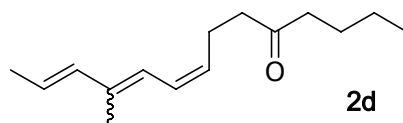
This compound was purified by column chromatography to yield 1.45 g (71%) of a yellowish liquid. Odor: fruity, floral, citrus, pineapple, green, metallic. ^1H NMR (300 MHz, CDCl_3): δ 6.45 (dd, $J = 10.7$ Hz, 17.3 Hz, 1H), 6.38-6.26 (m, 2H), 5.57-5.39 (m, 1H), 5.23 (d, $J = 17.3$ Hz, 1H), 5.05 (d, $J = 10.7$ Hz, 1H), 2.67-2.34 (m, 5H), 1.85 (s, 3H), 1.77-1.67 (m, 1H), 1.43-1.33 (m, 1H), 1.06 (d, $J = 6.9$ Hz, 3H), 0.87 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 213.9 (s), 141.5 (d), 135.7 (s), 131.3 (d), 125.9 (d), 125.3 (d), 112.7 (t), 47.9 (d), 40.8 (t), 25.9 (t), 22.0 (t), 15.8 (q), 11.7 (q), 11.7 (q). IR (neat): 3091, 2964, 2934, 2877, 1713, 1612, 1459, 1261, 1075, 1019, 795 cm^{-1} . MS (EI): m/z (%): 206 [M] $^+$ (44), 149 (24), 131 (18), 121 (16), 106 (100), 91(60), 85 (35), 79 (40), 57 (76). HRMS (EI): m/z calcd. for $\text{C}_{14}\text{H}_{22}\text{O}$ (M) $^+$ 206.1671, found 206.1677.

(5Z,7E)-8-Methyldeca-5,7,9-trien-2-one (2c)



This compound was purified by column chromatography to yield 0.74 g (46%) of a colorless liquid. Odor: fruity, pear-like, rosy, metallic. ^1H NMR (300 MHz, CDCl_3): δ 6.45 (dd, $J = 10.6$ Hz, 17.3 Hz, 1H), 6.37-6.28 (m, 2H), 5.58-5.38 (m, 1H), 5.23 (d, $J = 17.3$ Hz, 1H), 5.06 (d, $J = 10.6$ Hz, 1H), 2.66-2.37 (m, 4H), 2.15 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 208.0 (s), 141.4 (d), 135.8 (s), 130.8 (d), 125.8 (d), 125.5 (d), 112.8 (t), 43.4 (t), 29.9 (q), 22.0 (t), 11.8 (q). IR (neat): 3090, 3031, 2921, 1717, 1611, 1577, 1513, 1363, 1161 cm^{-1} . MS (EI): m/z (%): 164 [M] $^+$ (31), 121 (12), 106 (100), 91 (90), 79 (48). HRMS (EI): m/z calcd. for $\text{C}_{11}\text{H}_{16}\text{O}$ (M) $^+$ 164.1201, found 164.1194.

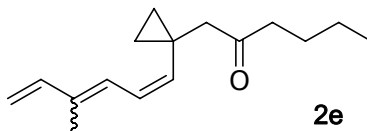
(8Z)-11-Methyltetradeca-8,10,12-trien-5-one (2d)



This compound was purified by column chromatography to yield 0.69 g (31%) of a yellow liquid ($E: Z = 8: 2$). Odor: Fruity, fatty, metallic, weak. Major (E)-isomer: ^1H NMR (300 MHz, CDCl_3): δ 6.77-6.07 (m, 3H), 5.87-5.62 (m, 1H), 5.51-5.28 (m, 1H), 2.58-2.43 (m, 4H), 2.40 (t, $J = 7.4$ Hz, 2H), 1.95-1.73 (m, 6H), 1.63-1.48 (m, 2H), 1.41-1.21 (m, 2H), 0.90 (t, $J = 7.2$ Hz, 3H). ^1H NMR (300 MHz, C_6D_6): δ 6.73-6.21 (m, 2H), 6.21-5.88 (m, 1H), 5.76-5.40 (m, 1H), 5.39-5.16 (m, 1H), 2.48-2.32 (m, 2H), 2.04 (t, $J = 6.2$ Hz, 2H), 3.69 (t, $J = 7.3$ Hz, 2H), 1.65 (s, 3H), 1.56 (d, $J = 6.5$ Hz, 3H), 1.42-1.27 (m, 2H), 1.14-0.95 (m, 2H), 0.69 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 210.6 (s), 136.2 (d), 135.6 (s), 129.6 (d), 125.6 (d), 124.7 (d), 123.3 (d), 42.6 (t), 42.5 (t), 25.9 (t), 22.3 (t), 22.0 (t), 18.4 (q), 13.8 (q), 12.5 (q). Minor (Z)-isomer: ^1H NMR (300 MHz, C_6D_6): δ 1.91 (d, $J = 7.3$ Hz, 2H), 0.82 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 209.0 (s), 134.9 (d), 133.6 (d), 131.3 (s), 129.5 (d), 128.1 (d), 125.0 (d), 46.9 (t), 42.1 (t), 25.8 (t), 22.3

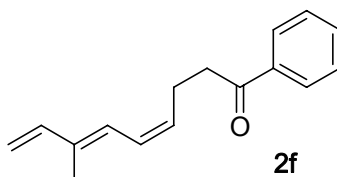
(t), 20.8 (t), 20.3 (q), 14.4 (q), 13.8 (q). IR (neat): 3024, 2959, 2932, 2873, 1715, 1448, 1383, 963 cm^{-1} . MS (EI): m/z (%): 220 [M]⁺ (64), 163 (5), 135 (36), 120 (100), 105 (68), 93 (48), 85 (56), 79 (21), 57 (60). HRMS (EI): m/z calcd. for $\text{C}_{15}\text{H}_{24}\text{O}$ (M)⁺ 220.1827, found 220.1830.

1-((1Z,3E)-4-Methylhexa-1,3,5-trienyl)cyclopropyl)hexan-2-one (2e)



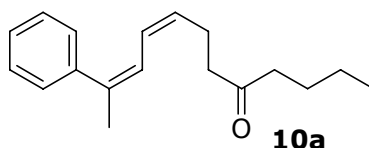
This compound was purified by distillation under reduced pressure to yield 1.40 g (60%) of a yellow liquid ($E:Z = 8:2$). Odor: fruity, green, floral, quite weak. Major (E)-isomer: ^1H NMR (300 MHz, CDCl_3): δ 6.56-6.39 (m, 2H), 6.29 (dd, $J = 11.3$ Hz, 10.9 Hz, 1H), 5.74 (d, $J = 10.9$ Hz, 1H), 5.25 (d, $J = 17.3$ Hz, 1H), 5.07 (d, $J = 10.6$ Hz, 1H), 2.49 (s, 2H), 2.39 (t, $J = 7.4$ Hz, 2H), 1.83 (s, 3H), 1.58-1.43 (m, 2H), 1.36-1.19 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H), 0.75-0.64 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3): δ 210.0 (s), 141.6 (d), 136.0 (s), 134.8 (d), 127.0 (2d), 112.9 (t), 52.5 (t), 42.8 (t), 25.7 (t), 22.3 (t), 16.5 (s), 13.9 (t), 13.9 (t), 13.8 (q), 11.6 (q). Minor (Z)-isomer: ^1H NMR (300 MHz, CDCl_3): δ 6.90 (dd, $J = 10.8$ Hz, 17.2 Hz, 1H), 5.67 (d, $J = 7.5$ Hz, 1H), 5.27 (d, $J = 17.2$ Hz, 1H), 5.16 (d, $J = 11.4$ Hz, 1H), 1.93 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 210.0 (s), 134.8 (s), 134.4 (d), 133.0 (d), 125.7 (d), 125.2 (d), 114.9 (t), 20.3 (q), 16.3 (s). IR (neat): 3065, 3018, 2958, 2929, 2861, 1729, 1600, 1580, 1455, 1378, 1286, 1121, 1075, 758 cm^{-1} . MS (EI): m/z (%): 232 [M]⁺ (22), 175 (16), 147 (57), 132 (17), 117 (18), 105 (34), 91 (28), 85 (72), 57 (100). HRMS (EI): m/z calcd. for $\text{C}_{16}\text{H}_{24}\text{O}$ (M)⁺ 232.1827, found 232.1828.

(4Z,6E)-7-Methyl-1-phenylnona-4,6,8-trien-1-one (2f)



This compound was purified by column chromatography to yield 0.61 g (27%) of a colorless liquid. Odor: very weak. ^1H NMR (300 MHz, CDCl_3): δ 7.96 (d, $J = 7.3$ Hz, 2H), 7.63-7.37 (m, 3H), 6.44 (dd, $J = 10.7$ Hz, 17.3 Hz, 1H), 6.39-6.29 (m, 2H), 5.67-5.51 (m, 1H), 5.23 (d, $J = 17.3$ Hz, 1H), 5.05 (d, $J = 10.7$ Hz, 1H), 3.08 (t, $J = 7.2$ Hz, 2H), 2.76-2.58 (m, 2H), 1.86 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 199.4 (s), 141.5 (d), 136.9 (s), 135.8 (s), 133.0 (d), 131.1 (d), 128.6 (d), 128.6 (d), 128.0 (d), 128.0 (d), 125.9 (d), 125.6 (d), 112.7 (t), 38.4 (t), 22.4 (t), 11.8 (q). IR (neat): 3029, 2925, 2855, 1687, 1598, 1580, 1449, 1361, 1201, 746, 691 cm^{-1} . MS (EI): m/z (%): 226 [M]⁺ (21), 133 (8), 105 (100), 91 (30), 77 (37). HRMS (EI): m/z calcd. for $\text{C}_{16}\text{H}_{18}\text{O}$ (M)⁺ 226.1358, found 226.1357.

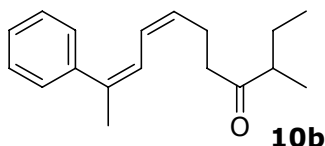
(8Z,10Z)-11-Phenyldodeca-8,10-dien-5-one (10a)



This compound was purified by column chromatography to yield 1.97 g (77%) of a yellow liquid.

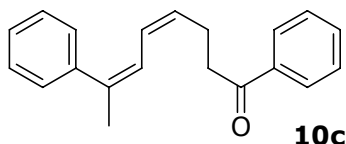
Odor: odorless. ^1H NMR (300 MHz, CDCl_3): δ 7.47-7.13 (m, 5H), 6.40 (d, $J = 11.4$ Hz, 1H), 6.02 (dd, $J = 11.4$ Hz, 11.4 Hz, 1H), 5.38-5.13 (m, 1H), 2.59-2.46 (m, 4H), 2.41 (t, $J = 7.4$ Hz, 2H), 2.14 (s, 3H), 1.70-1.48 (m, 2H), 1.41-1.23 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 210.7 (s), 141.5 (s), 139.2 (s), 128.8 (d), 128.3 (2d), 128.0 (2d), 126.9 (d), 126.7 (d), 122.0 (d), 42.7 (t), 42.5 (t), 25.9 (t), 25.7 (q), 22.4 (t), 22.1 (t), 13.8 (q). IR (neat): 3029, 2959, 2932, 2873, 1714, 1595, 1493, 1444, 1409, 769, 701 cm^{-1} . MS (EI): m/z (%): 256 [M] $^+$ (60), 181 (20), 156 (100), 142 (37), 129 (61), 85 (51), 77 (15), 57 (50). HRMS (EI): m/z calcd. for $\text{C}_{18}\text{H}_{24}\text{O}$ (M) $^+$ 256.1827, found 256.1836.

(7Z,9Z)-3-Methyl-10-phenylundeca-7,9-dien-4-one (10b)



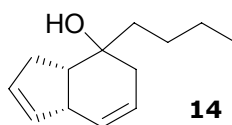
This compound was purified by bulb-to-bulb distillation (bp. 190 $^{\circ}\text{C}/0.09$ mbar) to yield 1.86 g (73%) of a colorless liquid. Odor: odorless. ^1H NMR (300 MHz, CDCl_3): δ 7.43-7.12 (m, 5H), 6.41 (d, $J = 11.4$ Hz, 1H), 6.02 (dd, $J = 11.4$ Hz, 11.4 Hz, 1H), 5.35-5.15 (m, 1H), 2.62-2.38 (m, 5H), 2.14 (s, 3H), 1.79-1.66 (m, 1H), 1.42-1.31 (m, 1H), 1.07 (d, $J = 6.9$ Hz, 3H), 0.88 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 214.1 (s), 141.5 (s), 139.1 (s), 129.0 (d), 128.3 (2d), 128.0 (2d), 126.9 (d), 126.7 (d), 122.0 (d), 47.9 (d), 40.9 (t), 25.9 (t), 25.7 (q), 21.9 (t), 15.8 (q), 11.7 (q). IR (neat): 3029, 2965, 2932, 1711, 1654, 1596, 1493, 1460, 1376, 1077, 1027, 769, 701 cm^{-1} . MS (EI): m/z (%): 256 [M] $^+$ (72), 199 (12), 181 (30), 156 (100), 142 (42), 129 (76), 77 (12), 57 (65). HRMS (EI): m/z calcd. for $\text{C}_{18}\text{H}_{24}\text{O}$ (M) $^+$ 256.1827, found 256.1839.

(4Z,6Z)-1,7-Diphenylocta-4,6-dien-1-one (10c)



This compound was purified by column chromatography to yield 1.41 g (51%) of a yellow liquid. Odor: odorless. ^1H NMR (300 MHz, CDCl_3): δ 7.97 (d, $J = 7.9$ Hz, 2H), 7.61-7.52 (m, 1H), 7.52-7.40 (m, 2H), 7.40-7.29 (m, 2H), 7.29-7.18 (m, 3H), 6.43 (d, $J = 11.4$ Hz, 1H), 6.06 (dd, $J = 11.4$ Hz, 11.4 Hz, 1H), 5.48-5.25 (m, 1H), 3.08 (t, $J = 7.4$ Hz, 2H), 2.78-2.59 (m, 2H), 2.14 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 199.6 (s), 141.5 (s), 139.2 (s), 136.9 (s), 133.0 (d), 128.9 (d), 128.6 (2d), 128.3 (2d), 128.1 (2d), 128.0 (2d), 126.9 (2d), 122.0 (d), 38.6 (t), 25.7 (q), 22.4 (t). IR (neat): 3057, 3029, 2962, 2930, 2909, 2849, 1686, 1597, 1448, 1202, 769, 749 cm^{-1} . MS (EI): m/z (%): 276 [M] $^+$ (30), 156 (84), 129 (43), 105 (100), 77 (37). HRMS (EI): m/z calcd. for $\text{C}_{20}\text{H}_{20}\text{O}$ (M) $^+$ 276.1514, found 276.1514.

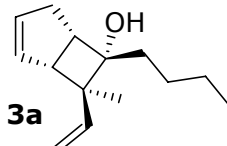
4-Butyl-3a,4,5,7a-tetrahydro-3H-inden-4-ol (14)



This compound was purified by column chromatography to yield 0.58 g (30%) of a colorless

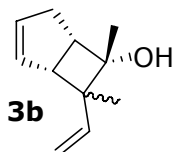
liquid. ^1H NMR (300 MHz, CDCl_3): δ 5.81-5.62 (m, 3H), 5.62-5.50 (m, 1H), 3.41-3.11 (m, 1H), 2.58-2.31 (m, 3H), 2.31-2.14 (m, 1H), 2.14-1.96 (m, 1H), 1.71-1.49 (m, 3H), 1.45-1.24 (m, 4H), 0.92 (t, $J = 6.2$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 132.8 (d), 130.3 (d), 129.0 (d), 123.1 (d), 72.8 (s), 46.4 (d), 45.2 (d), 39.2 (t), 34.1 (t), 33.0 (t), 25.5 (t), 23.3 (t), 14.1 (q). IR (neat): 3418, 2955, 2933, 2861, 1545, 1034 cm^{-1} . MS (EI): m/z (%): 192 [M] $^+$ (12), 174 (18), 135 (36), 117 (100), 107 (33), 92(64), 85(77), 79(35), 57(41). HRMS (EI): m/z calcd. for $\text{C}_{13}\text{H}_{20}\text{O}$ (M) $^+$ 192.1514, found 192.1513.

6-Butyl-7-methyl-7-vinylbicyclo[3.2.0]hept-2-en-6-ol (**3a**)



n-BuLi (0.05 mol, 1.6 M in hexane) was added dropwise to the solution of ketone **1a** (7.40 g, 0.05 mol) in dry THF (100 mL) with stirring at -78 $^{\circ}\text{C}$ under argon during 30 min. After the resulting mixture had been stirred for another 2 h at -78 $^{\circ}\text{C}$, it was quenched with water (100 mL), extracted with MTBE (3×100 mL). The organic phases were combined, washed with water and brine, dried with MgSO_4 and concentrated in vacuo. The residue was purified by distillation in kugelrohr (b.p. 150 $^{\circ}\text{C}$ / 9.5×10^{-2} mbar) to afford **3a** (8.76 g, 85%) as a colorless liquid. ^1H NMR (300 MHz, CDCl_3): δ 6.07 (dd, $J = 10.7$ Hz, 17.4 Hz, 1H), 5.93-5.84 (m, 1H), 5.80-5.71 (m, 1H), 5.00 (d, $J = 17.4$ Hz, 1H), 4.97 (d, $J = 10.7$ Hz, 1H), 3.09-3.00 (m, 1H), 2.79 (t, $J = 7.6$ Hz, 1H), 2.51-2.23 (m, 2H), 1.80 (brs, 1H), 1.38 (t, $J = 3.9$ Hz, 2H), 1.25-1.11 (m, 4H), 0.89 (s, 3H), 0.80 (t, $J = 6.5$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 144.8 (d), 134.6 (d), 133.2 (d), 110.7 (t), 80.4 (s), 52.2 (s), 50.6 (d), 43.3 (d), 37.9 (t), 32.1 (t), 25.0 (t), 23.2 (t), 15.3 (q), 14.1 (q). IR (neat): 3475, 3050, 2956, 2860, 1457, 1383, 907, 740 cm^{-1} . MS (EI): m/z (%): 206 [M] $^+$ (4), 147 (16), 140 (40), 131(28), 121 (37), 106 (45), 91 (57), 85 (100), 57 (99). HRMS (EI): m/z calcd. for $\text{C}_{14}\text{H}_{22}\text{O}$ (M) $^+$ 206.1671, found 206.1675.

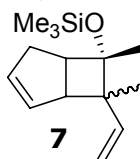
6,7-Dimethyl-7-vinylbicyclo[3.2.0]hept-2-en-6-ol (**3b**)



A solution of ketone **1a** (14.8 g, 0.10 mol) in dry THF (150 mL) was added dropwise to freshly prepared MeMgBr (0.10 mol in 100 mL dry THF) at 0 $^{\circ}\text{C}$ under argon. After the resulting mixture had been stirred for another 2 h at 0 $^{\circ}\text{C}$, the mixture was quenched with saturated *aq.* NH_4Cl (200 mL) and extracted with MTBE (3×200 mL). The organic phases were combined, washed with water and brine, dried with MgSO_4 and concentrated in vacuo. The residue was purified by distillation in kugelrohr (b.p. 85 $^{\circ}\text{C}$ / 6.5×10^{-2} mbar) to afford **3b** (3.17 g, 80%) as colorless liquid. The major *exo* isomer: ^1H NMR (300 MHz, CDCl_3): δ 6.09 (dd, $J = 10.7$ Hz, 17.4 Hz, 1H), 5.99-5.90 (m, 1H), 5.90-5.76 (m, 1H), 5.18-4.98 (m, 2H), 3.20-2.79 (m, 2H), 2.66-2.51 (m, 1H), 2.45-2.26 (m, 1H), 1.92 (s, 1H), 1.13 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 115.0 (d), 134.6 (d), 132.8 (d), 110.7 (t), 77.8 (s), 51.9 (s), 50.2 (d), 44.9 (d), 31.9 (t), 25.1 (q), 15.3 (q). The *endo* isomer: ^{13}C NMR (75 MHz, CDCl_3): δ 139.5 (d), 134.6 (d), 133.0 (d), 114.7 (t), 78.4 (s), 54.7 (d), 51.5 (s), 43.7 (d), 31.7 (t), 23.9 (q), 23.5 (q). IR (neat): 3455, 3050, 2960, 2926, 1450,

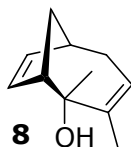
1384, 1077, 909, 742 cm^{-1} . MS (EI): m/z (%): 163 $[\text{M}-1]^+$ (48), 147 (29), 121 (46), 119 (70), 98 (100), 91 (78), 83 (96). HRMS (EI): m/z calcd. for $\text{C}_{11}\text{H}_{16}\text{O}$ (M) $^+$ 164.1201, found 164.1175.

6,7-Dimethyl-6-trimethylsilyloxy-7-vinylbicyclo[3.2.0]hept-2-ene (7)



A solution of triethylamine (4.55 g, 0.045 mol) in dry 2-methyltetrahydrofuran (2-MeTHF) (20 mL) was added dropwise to a solution of **3b** (4.92 g, 0.03 mol) and TMSCl (4.88 g, 0.045 mol) in dry THF (50 mL) with stirring at 0 $^{\circ}\text{C}$. After the resulting mixture was stirred overnight at room temperature, it was quenched with water (50 mL). The mixture was extracted with MTBE (3×60 mL). The organic phases were combined, washed with water and brine, dried with MgSO_4 and concentrated in vacuo. The residue was purified by distillation in kugelrohr (b.p. 110 $^{\circ}\text{C}/3.6 \times 10^{-2}$ mbar) to afford silylether **7** (6.01 g, 85%) as colorless liquid. The *exo* isomer: ^1H NMR (300 MHz, CDCl_3): δ 6.02 (dd, $J = 10.9$ Hz, 17.4 Hz, 1H), 5.94-5.78 (m, 1H), 5.66-5.50 (m, 1H), 5.04-4.80 (m, 2H), 3.07-2.98, 2.77-2.69 (m, 1H), 2.68-2.52 (m, 2H), 2.42-2.23 (m, 1H), 1.30 (s, 3H), 0.83 (s, 1H), 0.09 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ 143.4 (d), 132.9 (d), 128.3 (d), 108.9 (t), 74.6 (s), 50.1 (s), 45.8 (d), 45.4 (d), 31.8 (t), 25.7 (q), 16.1 (q), 0.0 (3q). The *endo* isomer: ^1H NMR (300 MHz, CDCl_3): δ 6.14 (dd, $J = 11.1$ Hz, 17.7 Hz, 1H), 1.19 (s, 3H), 0.06 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ 140.4 (d), 131.8 (d), 128.8 (d), 108.8 (t), 76.6 (s), 51.2 (d), 48.2 (s), 44.4 (d), 31.3 (t), 24.0 (q), 18.4 (q), 0.2 (3q). IR (neat): 3052, 2961, 2928, 1450, 1251, 990, 872 cm^{-1} . MS (EI): m/z (%): 236 $[\text{M}]^+$ (2), 221 (8), 170 (100), 155 (46), 73 (77). HRMS (EI): m/z calcd. for $\text{C}_{14}\text{H}_{24}\text{OSi}$ (M) $^+$ 236.1596, found 236.1583.

2,3-Dimethylbicyclo[4.2.1]nona-3,7-dien-2-ol (8)



Under an argon atmosphere, a solution of silane **7** (0.24 g, 0.001 mol) in dry hexane (20 mL) was added during 30 min dropwise into a quartz tube preheated to 300 $^{\circ}\text{C}$. The efflux was collected in a cold trap and treated with 1M HCl. The mixture was extracted with MTBE (3×20 mL). The organic phases were combined, washed with water and brine, dried with MgSO_4 and concentrated in vacuo. The residue was purified by column chromatography to afford **8** (0.13 g, 81%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 5.84-5.69 (m, 2H), 5.18-5.06 (m, 1H), 2.87-2.71 (m, 2H), 2.50-2.35 (m, 1H), 2.24-2.07 (m, 1H), 2.04-1.92 (m, 2H), 1.91-1.83 (m, 1H), 1.80 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 134.7 (s), 134.6 (d), 132.0 (d), 122.2 (d), 79.5 (s), 56.8 (d), 40.9 (d), 37.2 (t), 32.8 (t), 27.2 (q), 23.2 (q). IR (neat): 3423, 3054, 2934, 1710, 1648, 1450, 1092 cm^{-1} . MS (EI): m/z (%): 164 $[\text{M}]^+$ (8), 98 (100), 83 (64). HRMS (EI): m/z calcd. for $\text{C}_{11}\text{H}_{16}\text{O}$ (M) $^+$ 164.1201, found 164.1194.

3. References

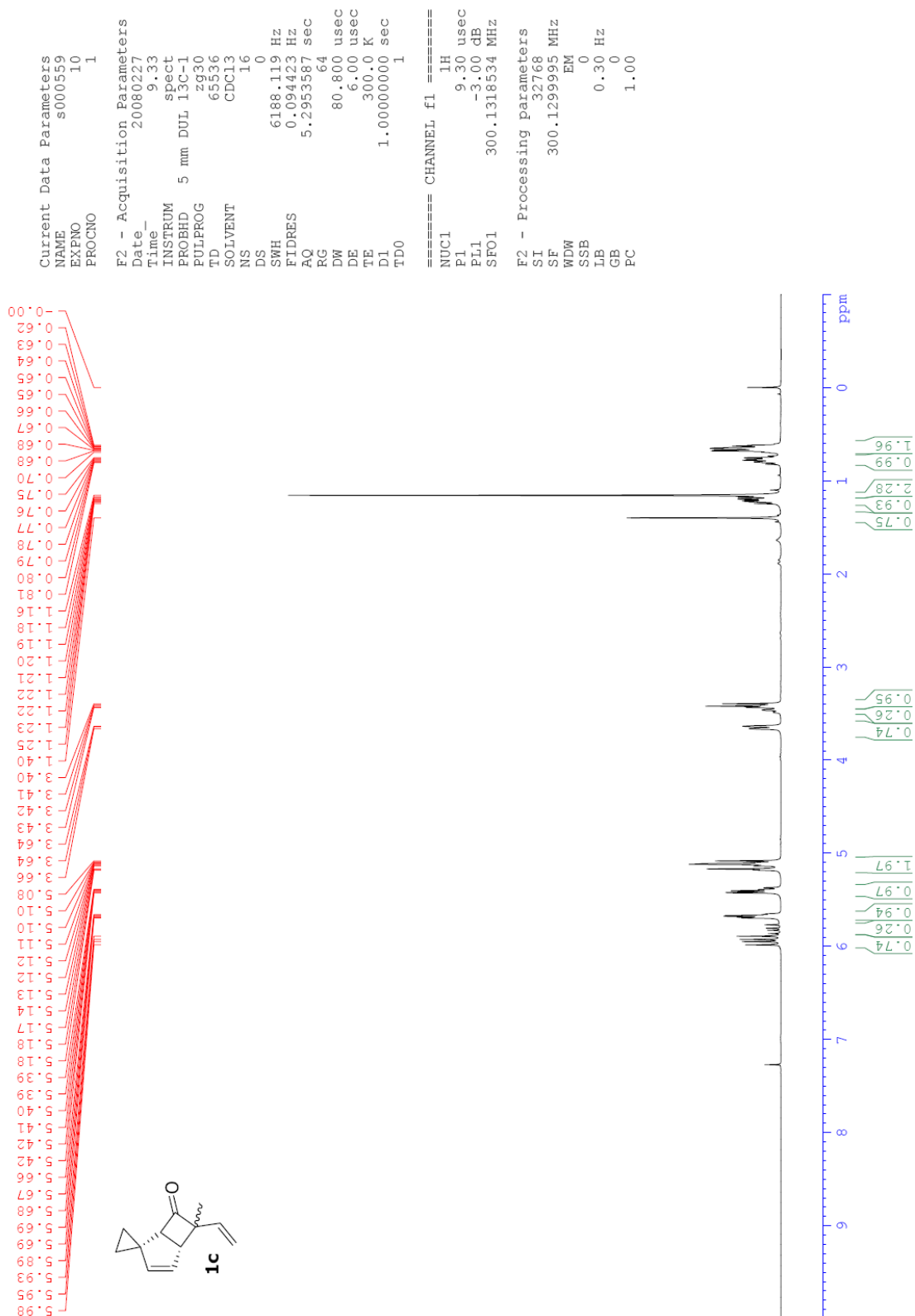
[1] (a) Rey, M.; Roberts, S. M.; Dieffenbacher, A.; Dreiding, A. S. *Helv. Chim. Acta* **1970**, *53*,

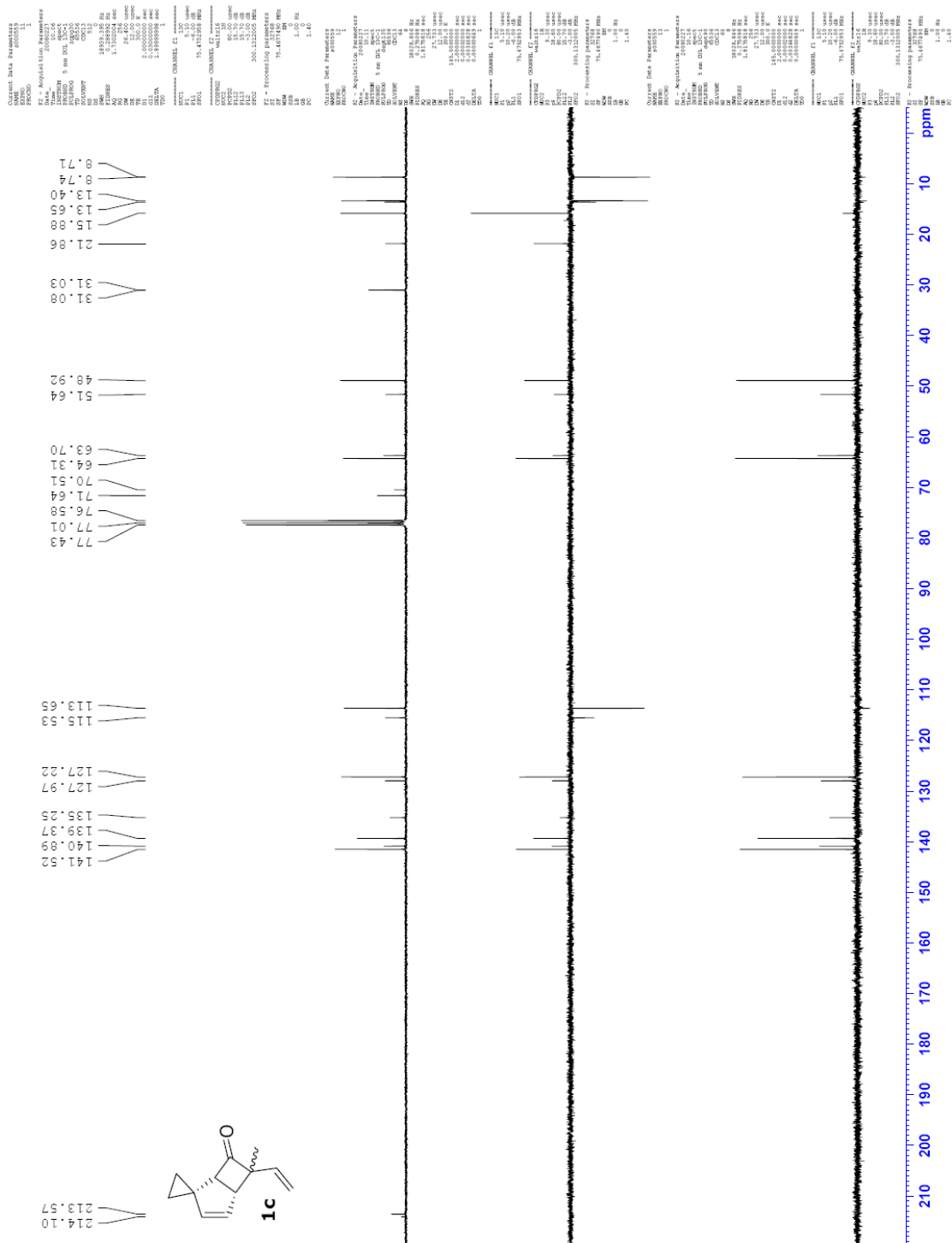
417-432; (b) Huston, R.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 1563-1575.

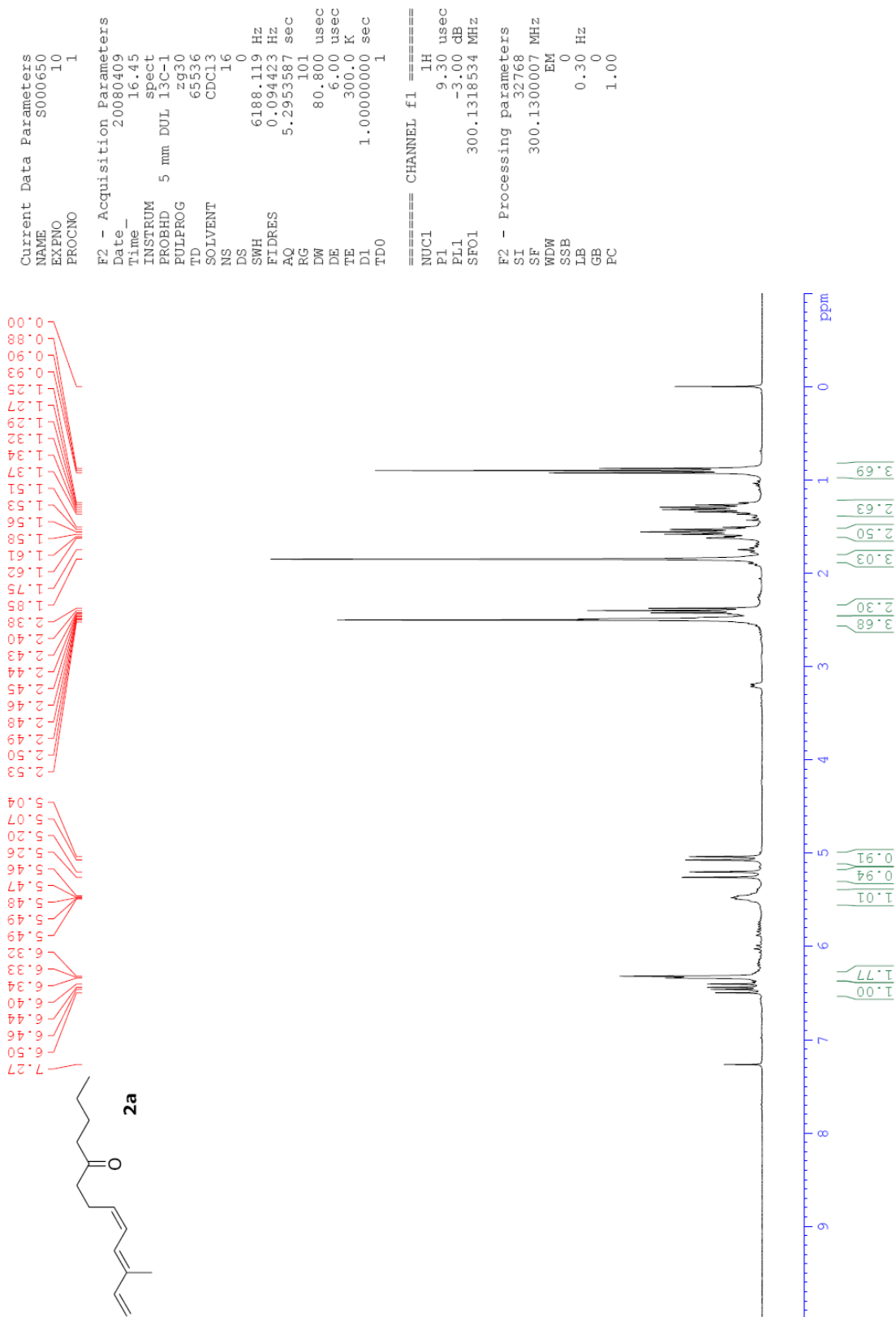
[2] Loev, B.; Bender, P. E.; Smith, R. *Synthesis* **1973**, 362.

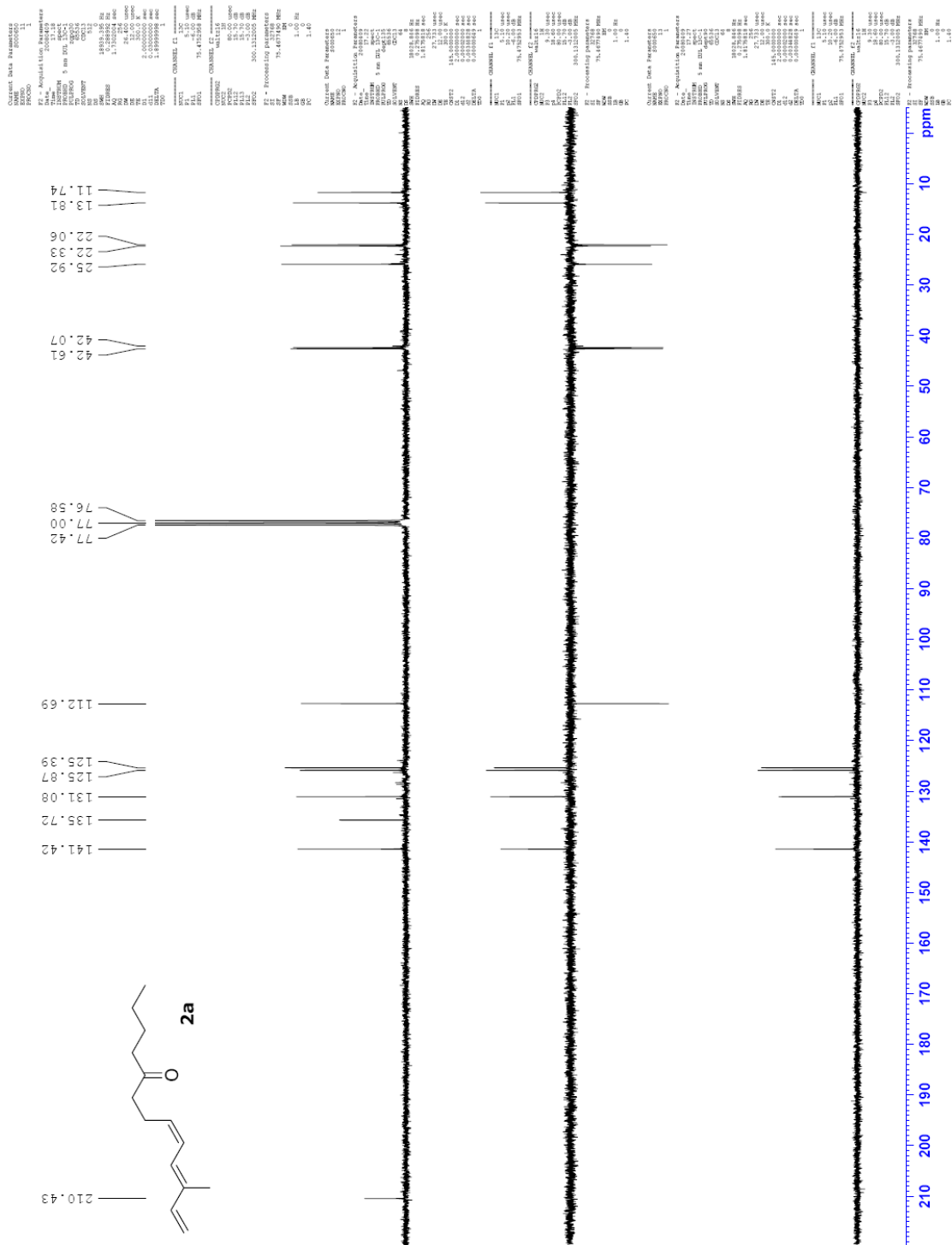
[3] Bartsch, R.; Lee, J. G. *J. Org. Chem.* **1991**, *56*, 2579-2582.

4. Copies of ^1H NMR and ^{13}C NMR Spectra of the New Compounds

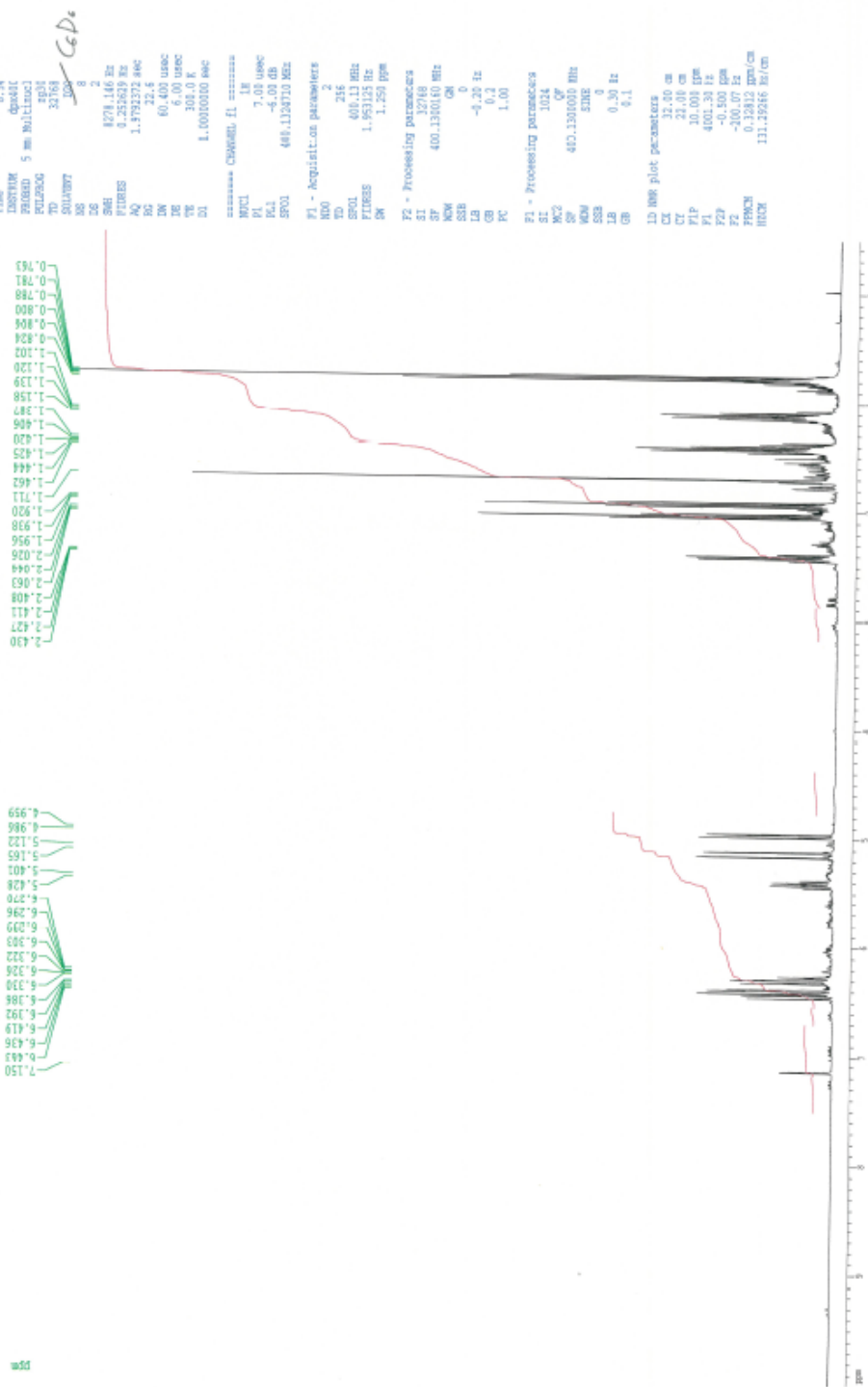








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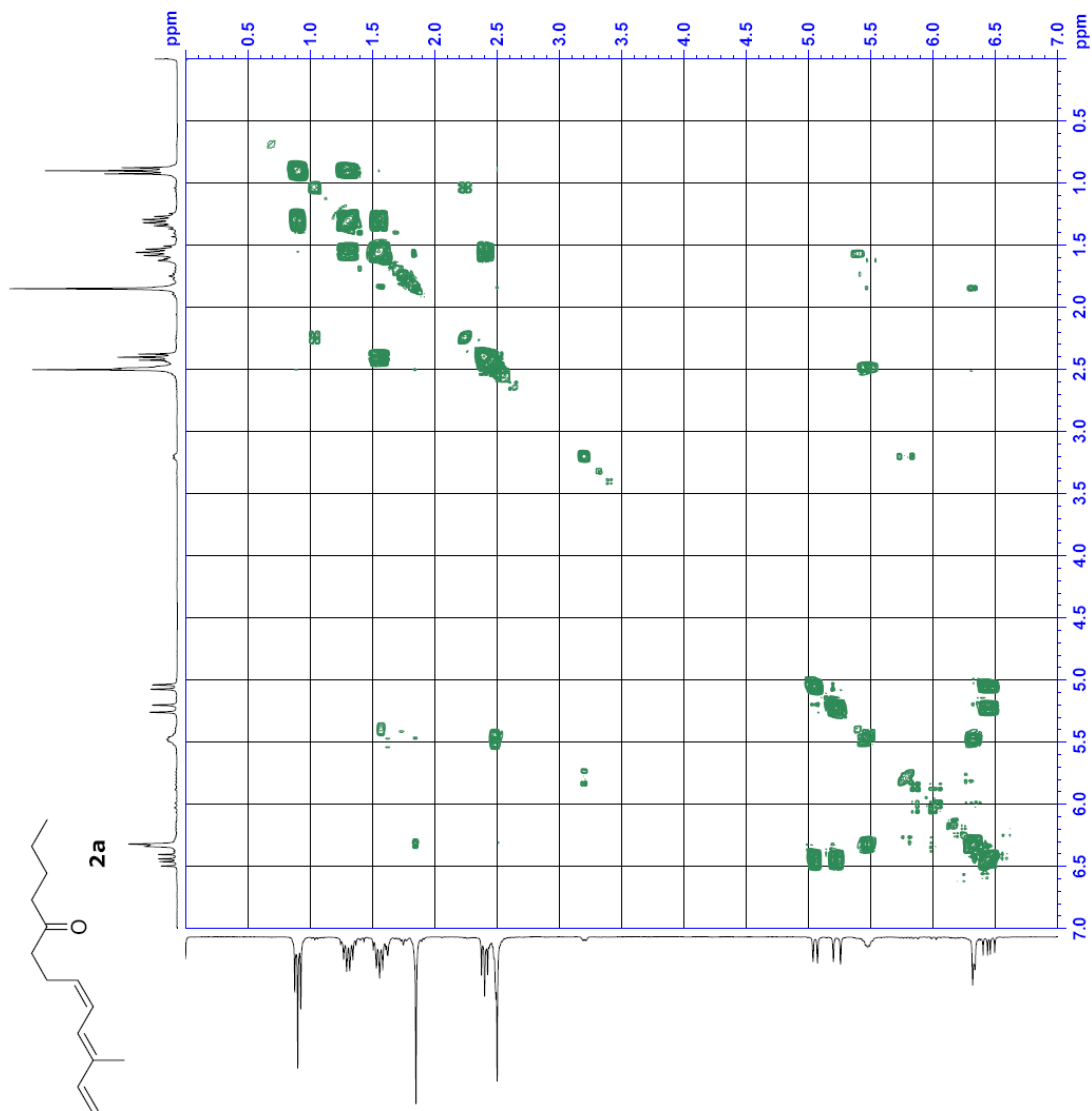
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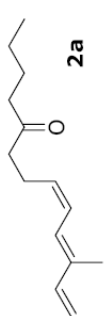
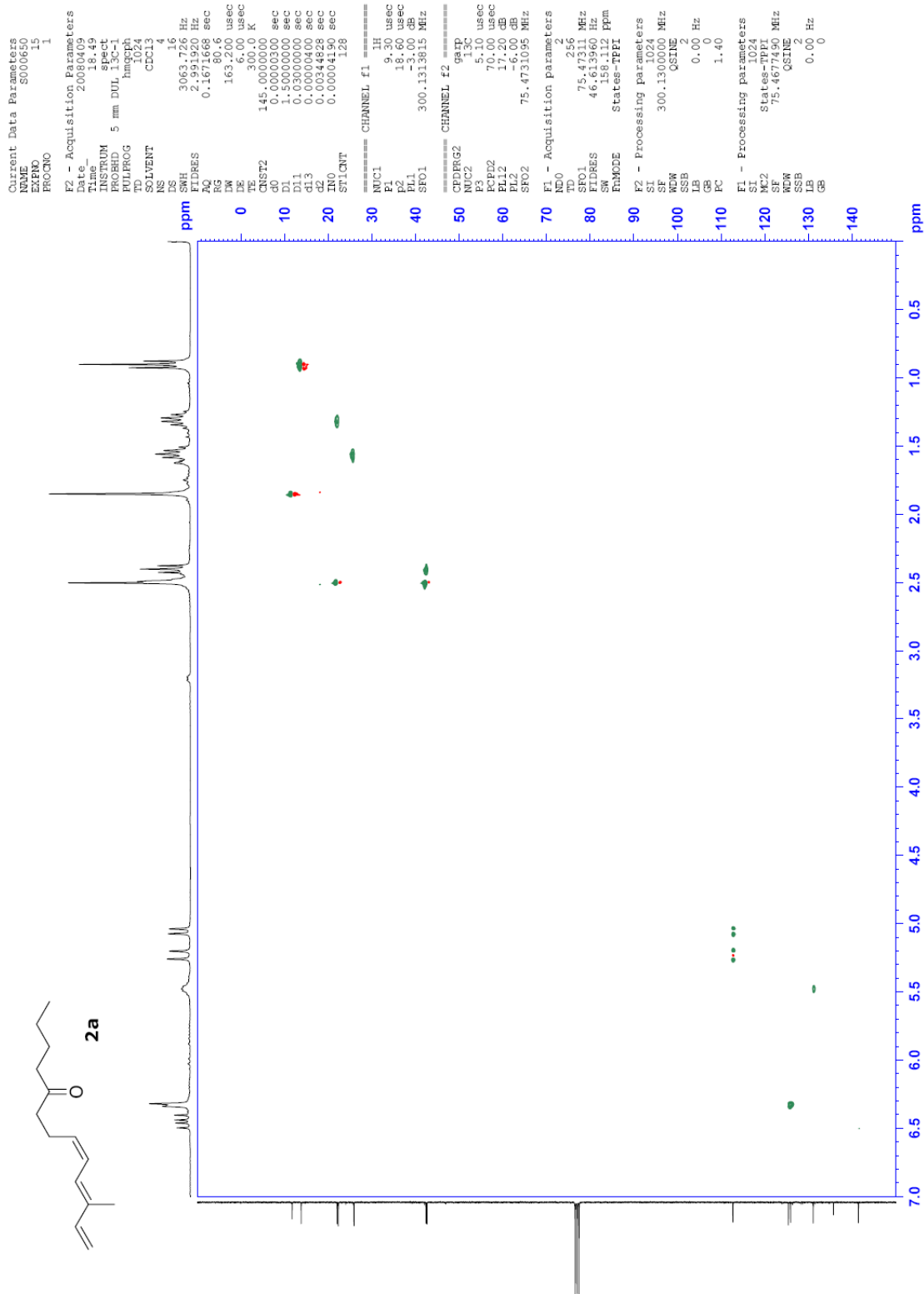
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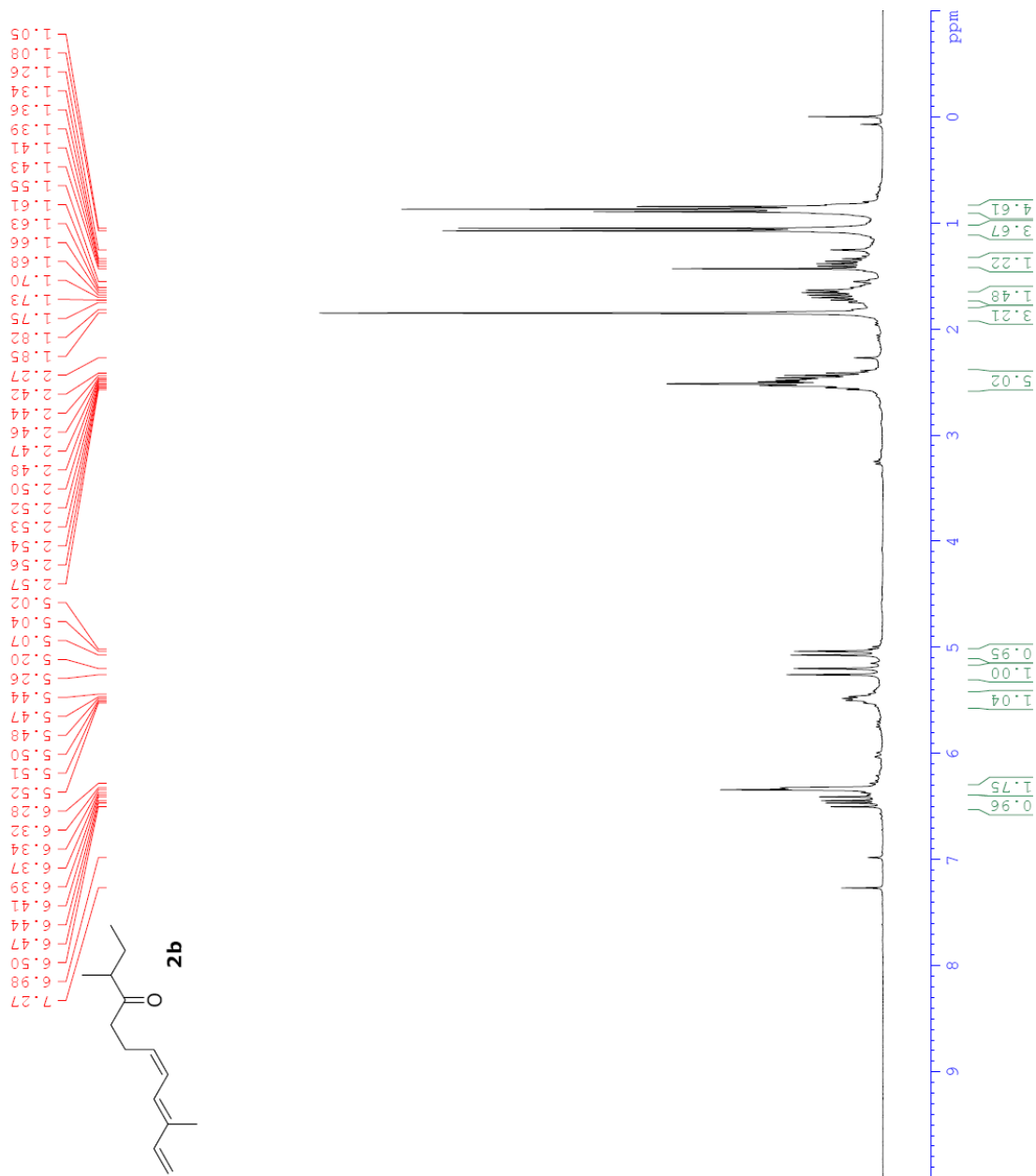
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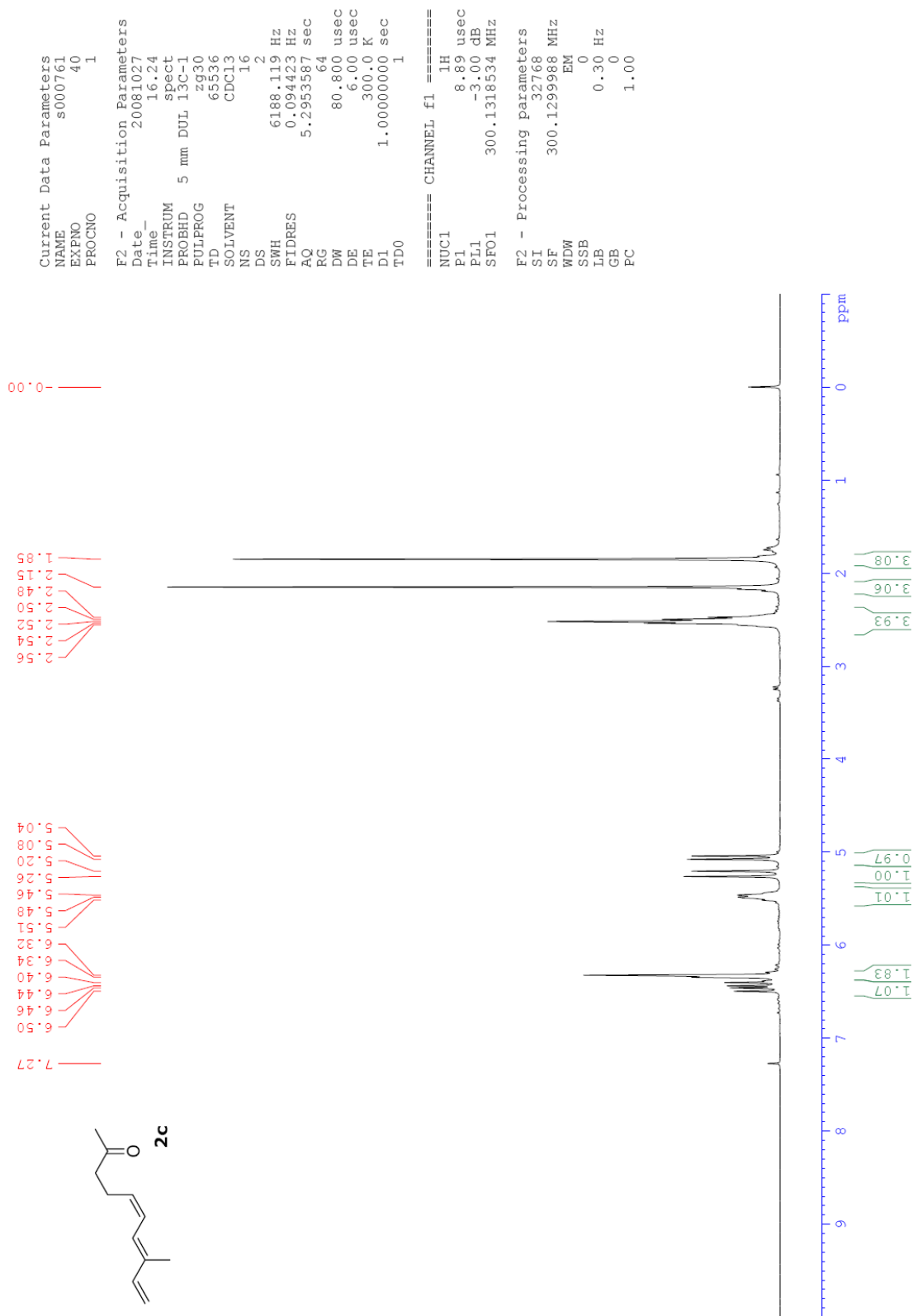
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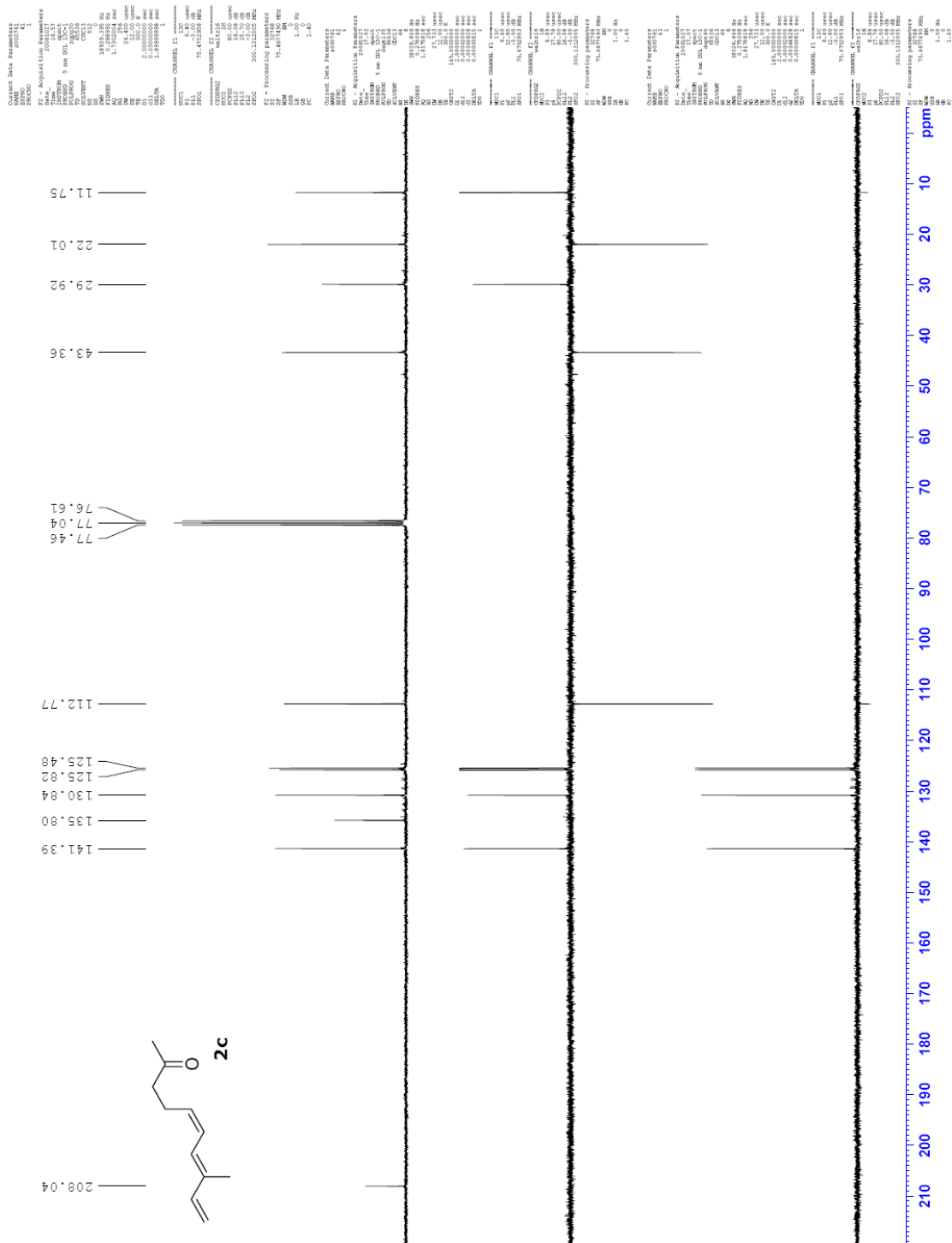
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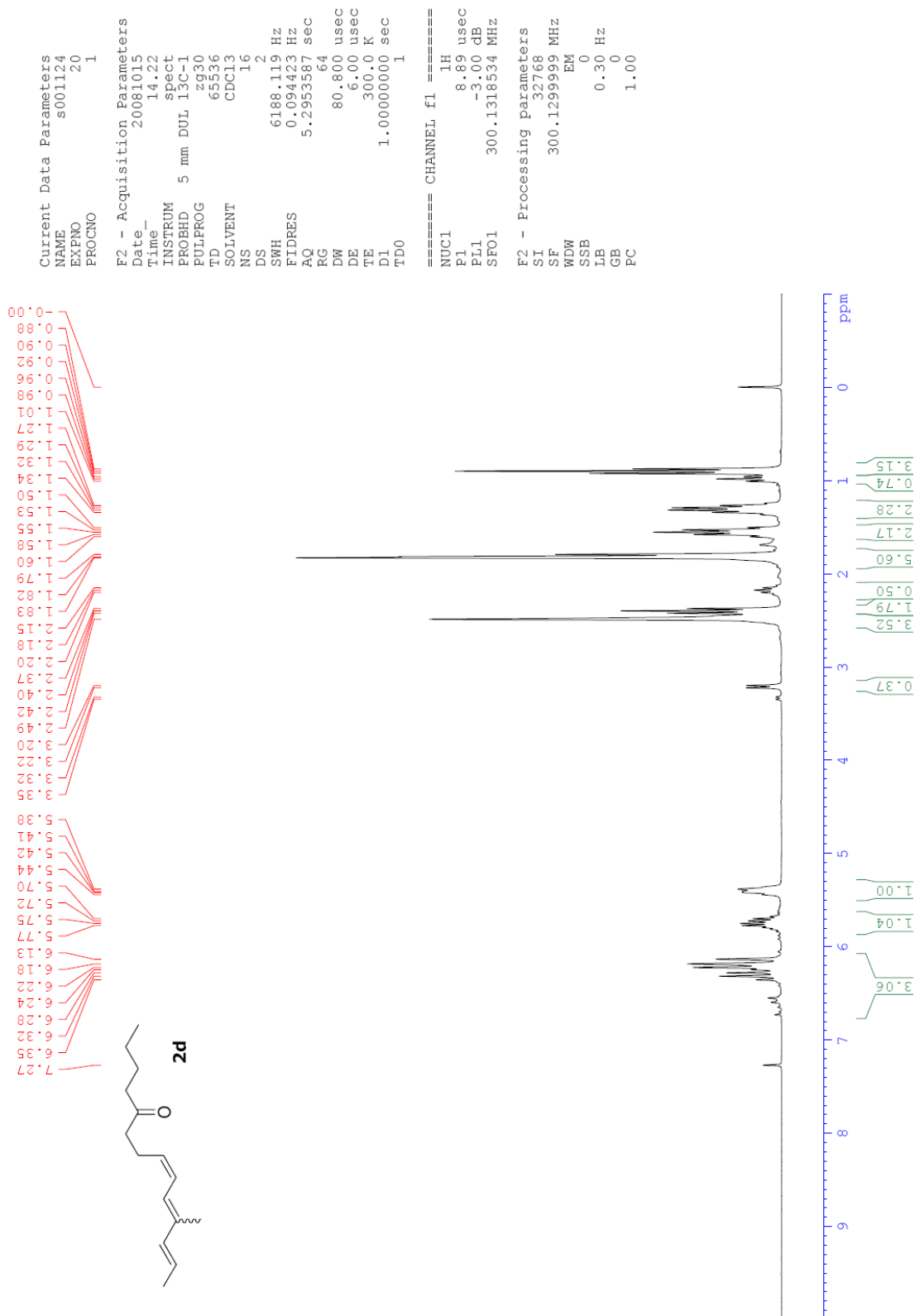


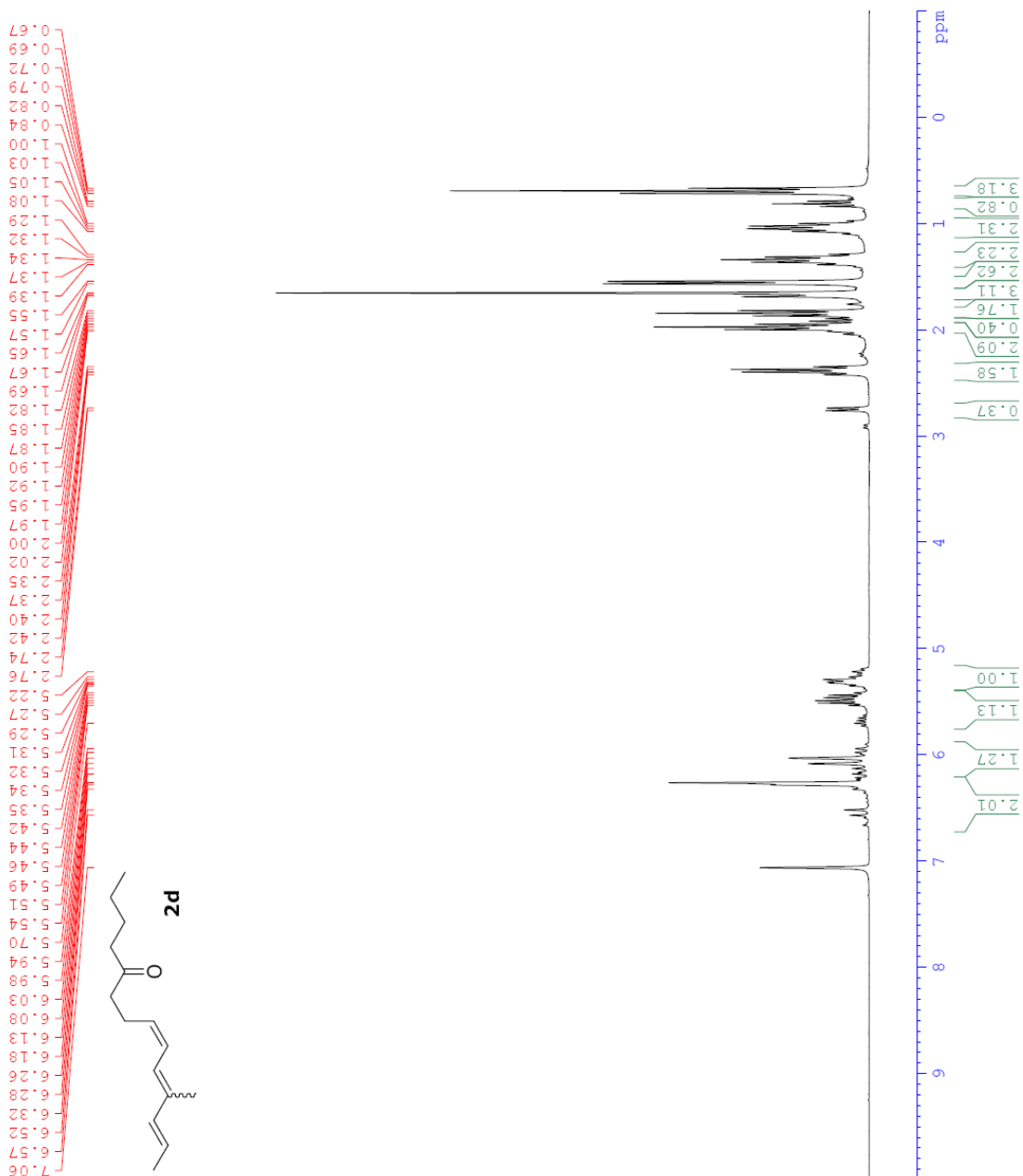


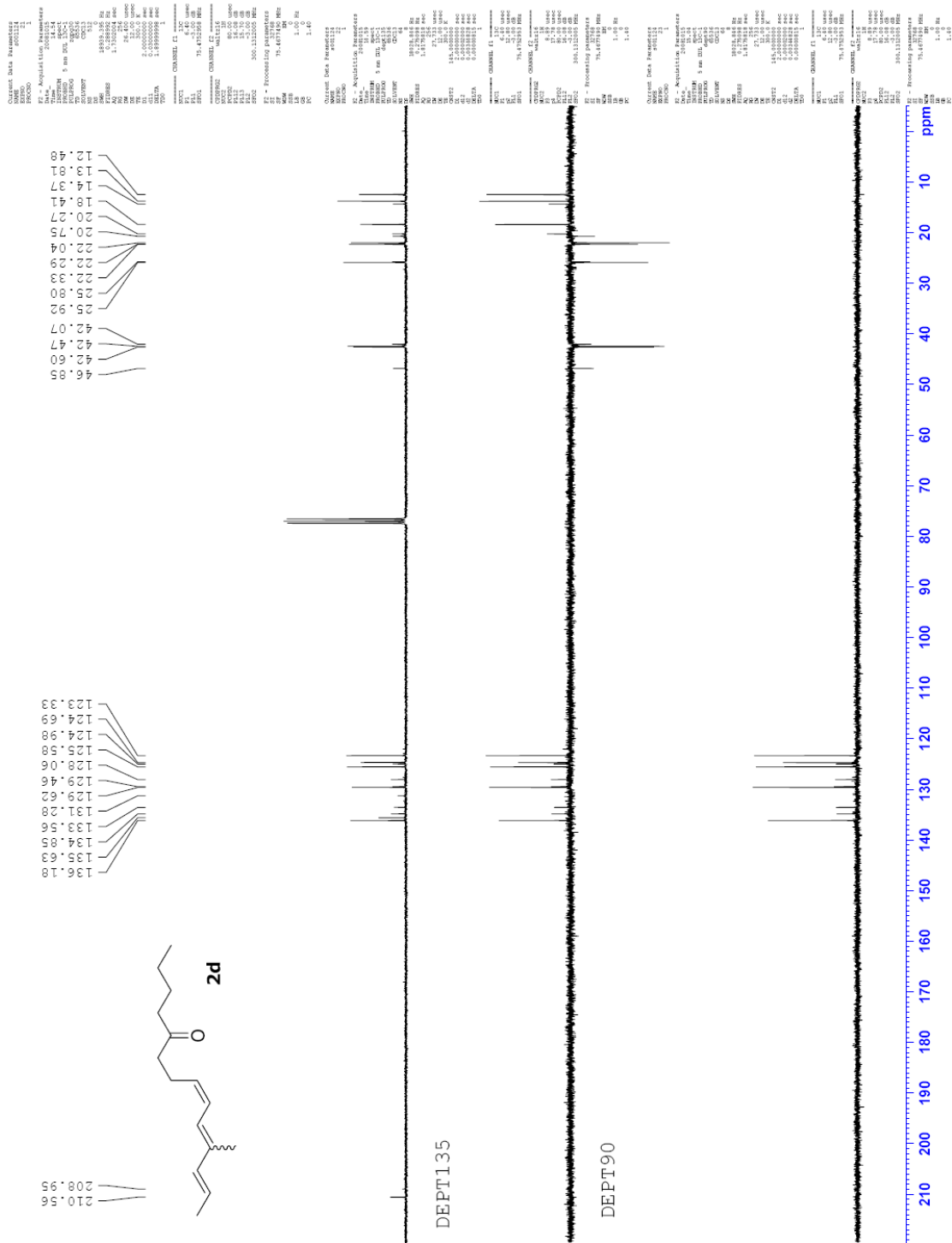


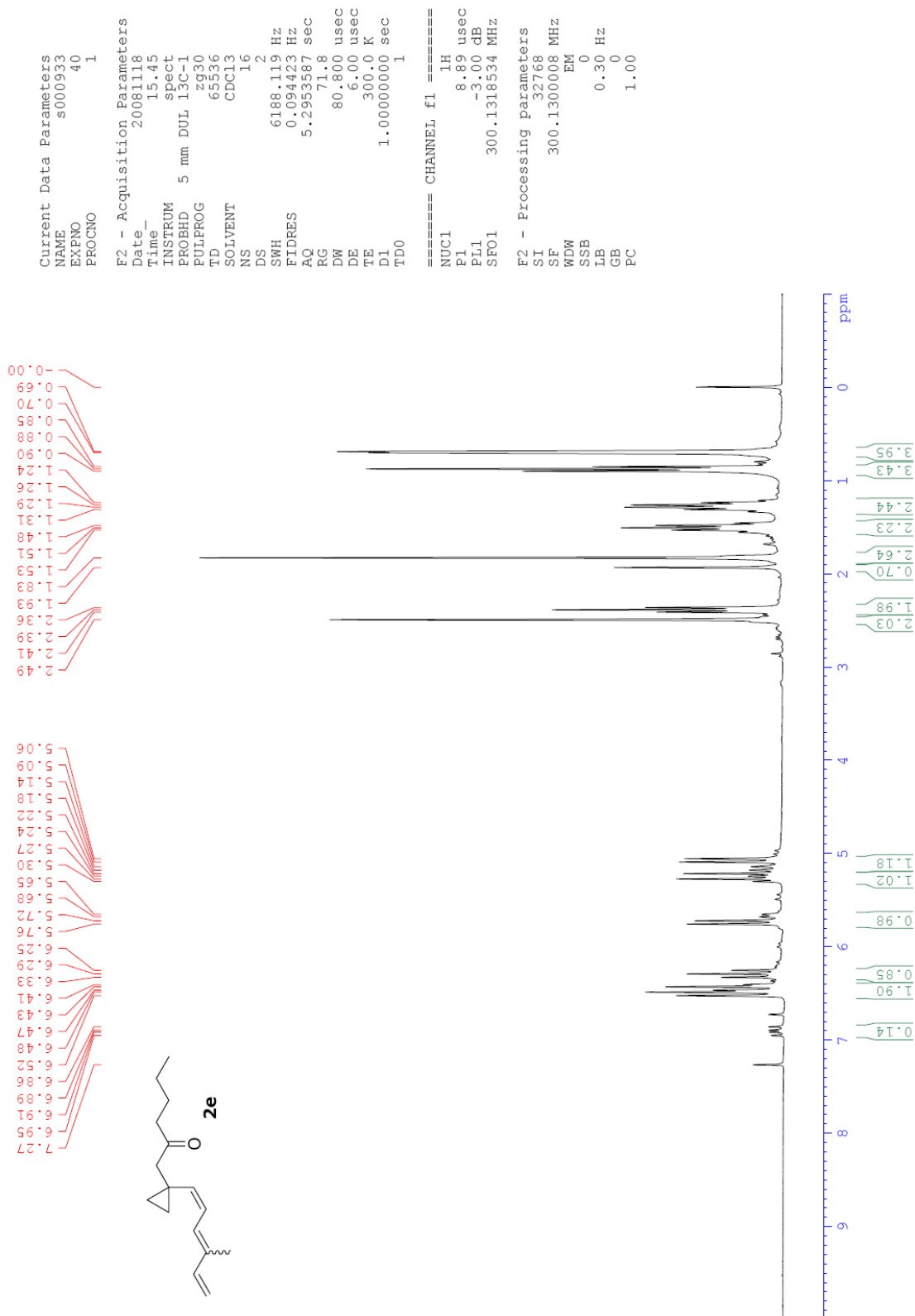













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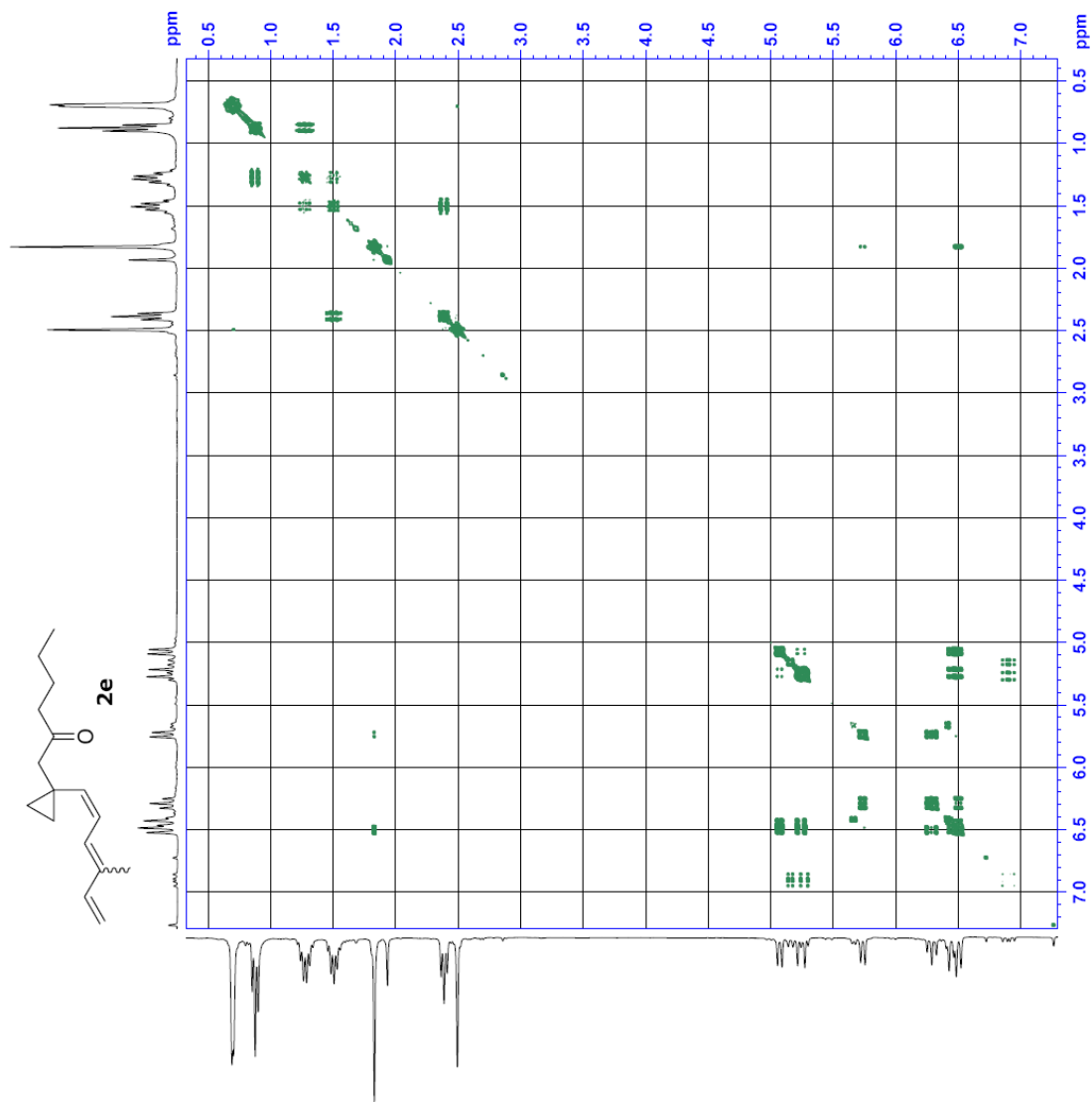
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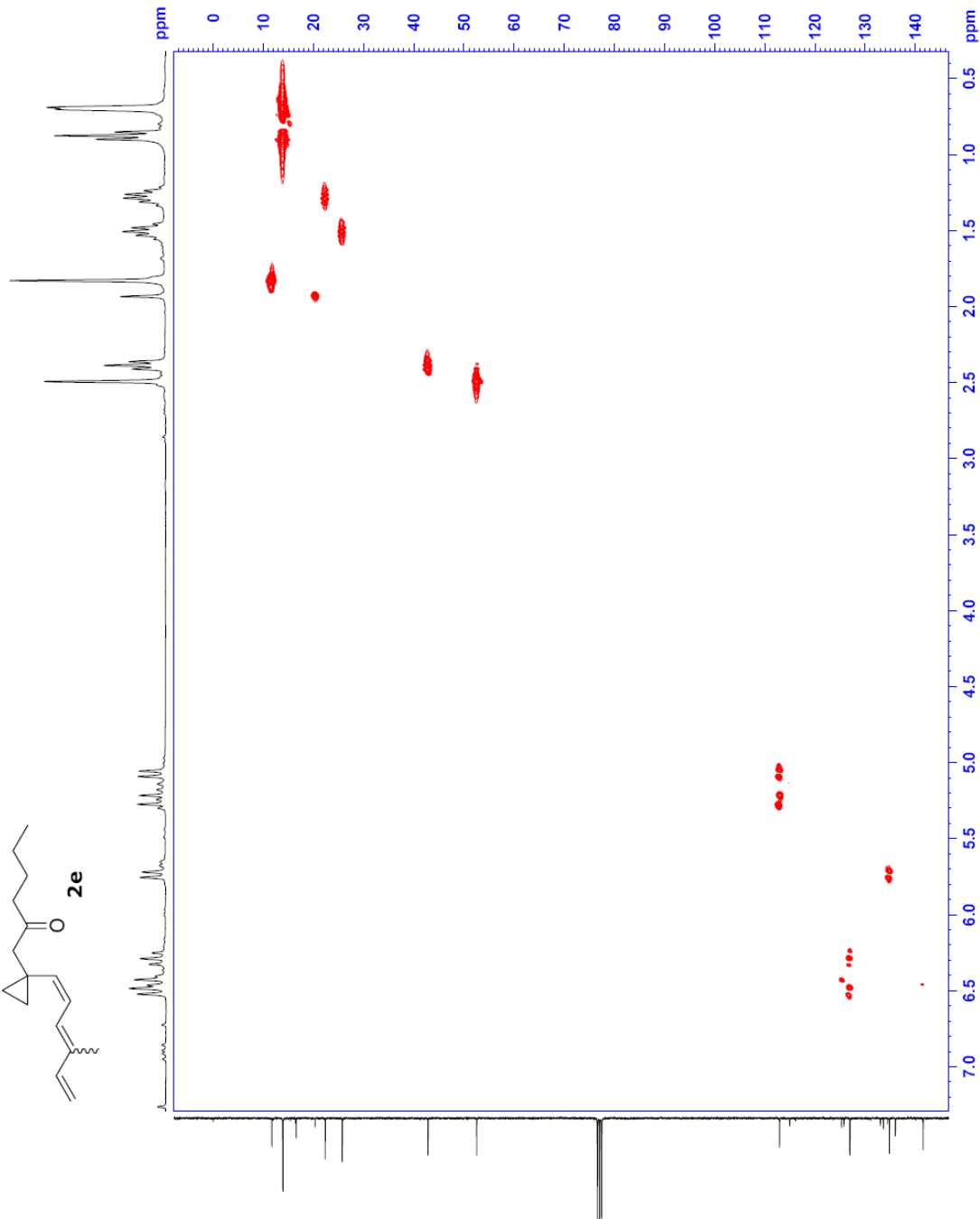
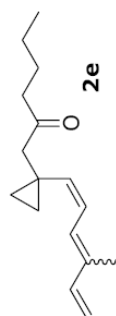
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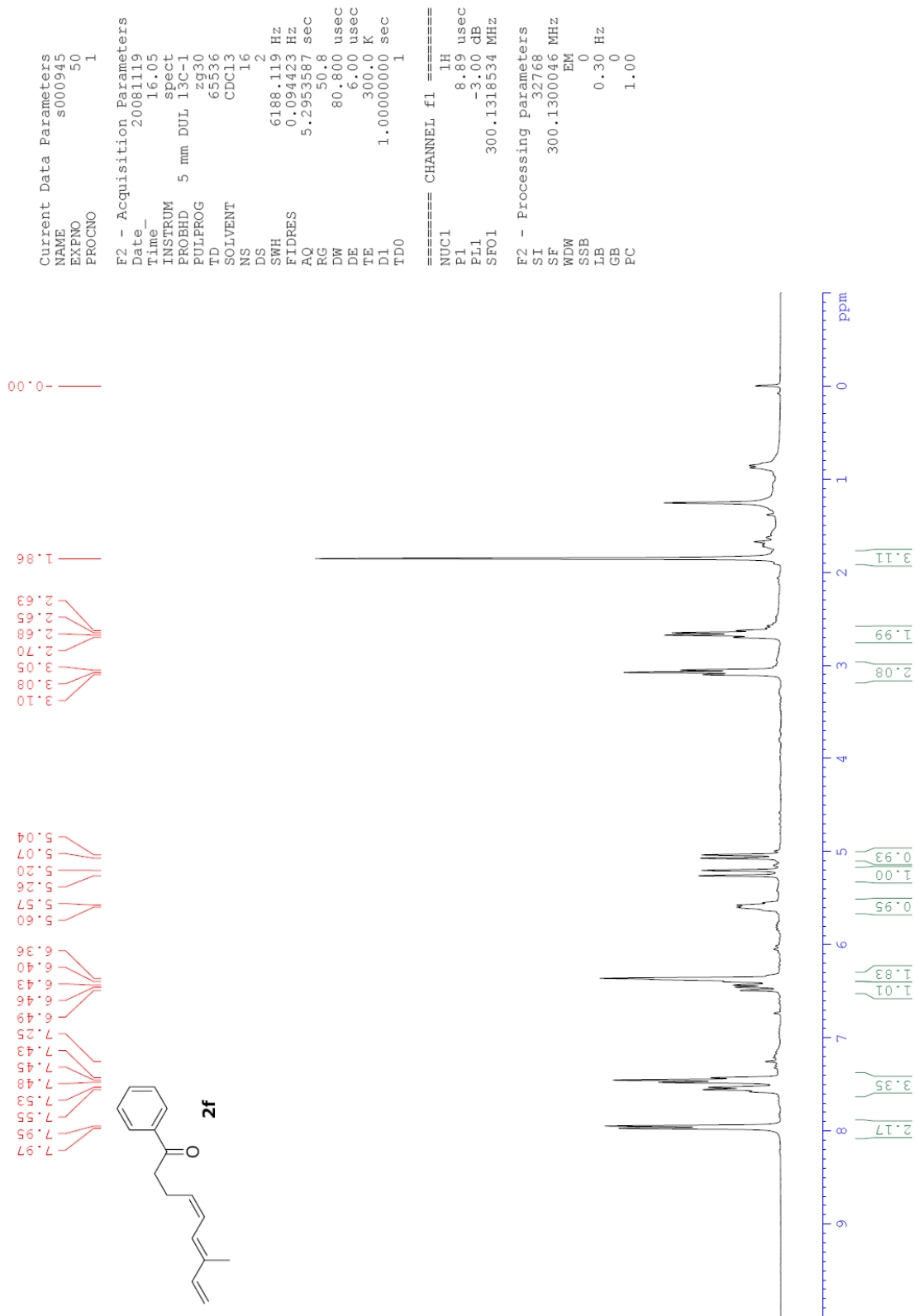
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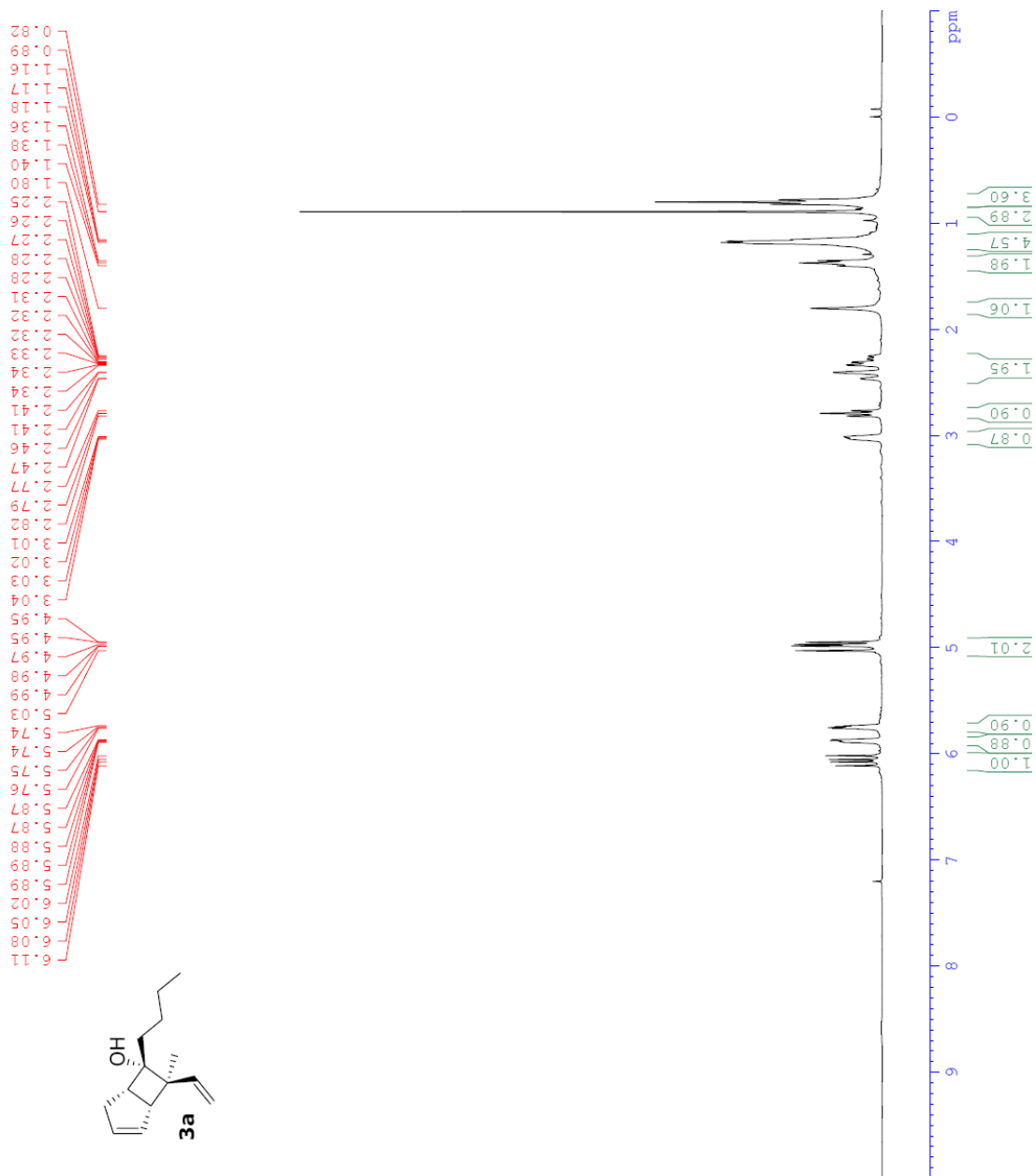
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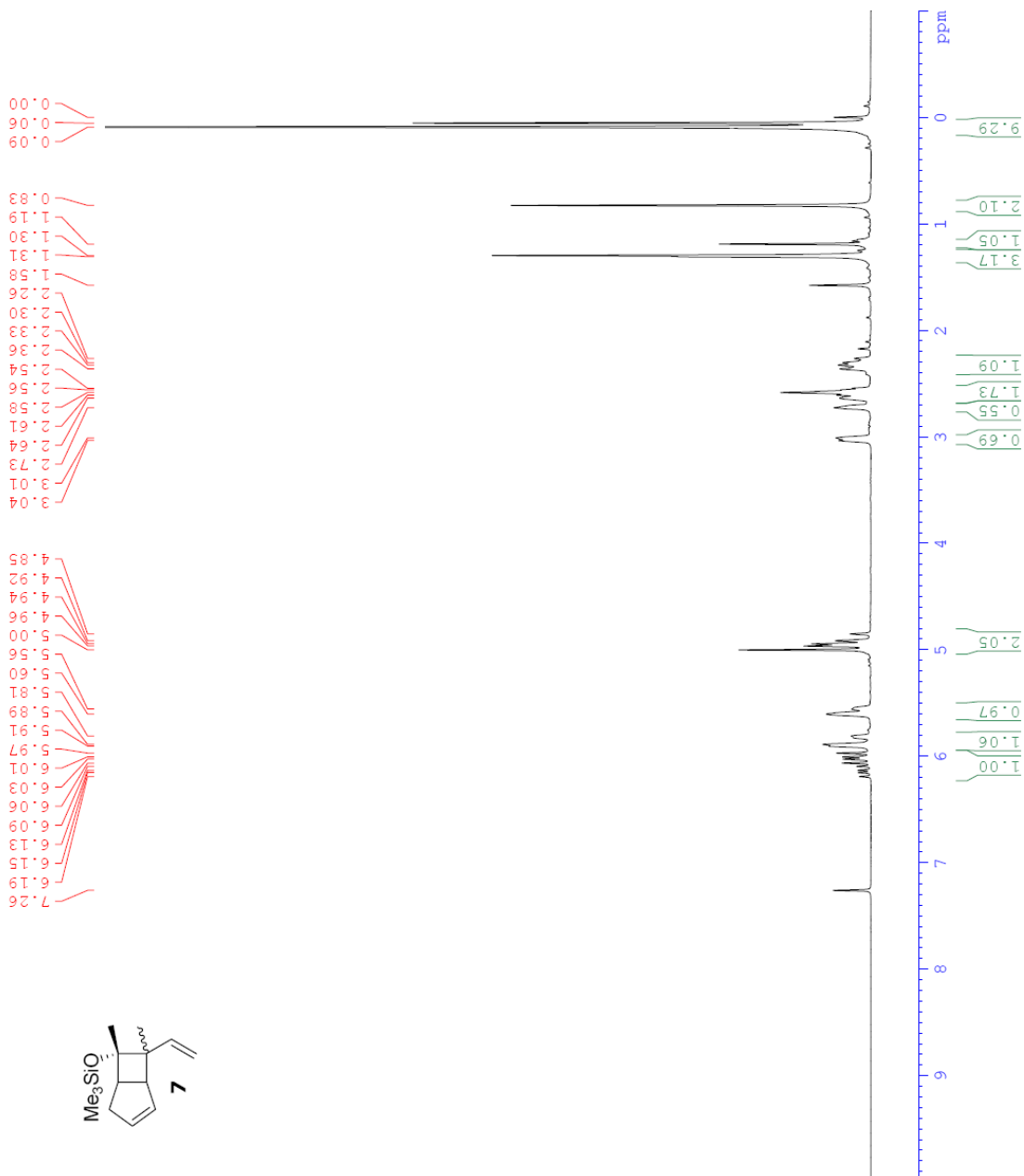


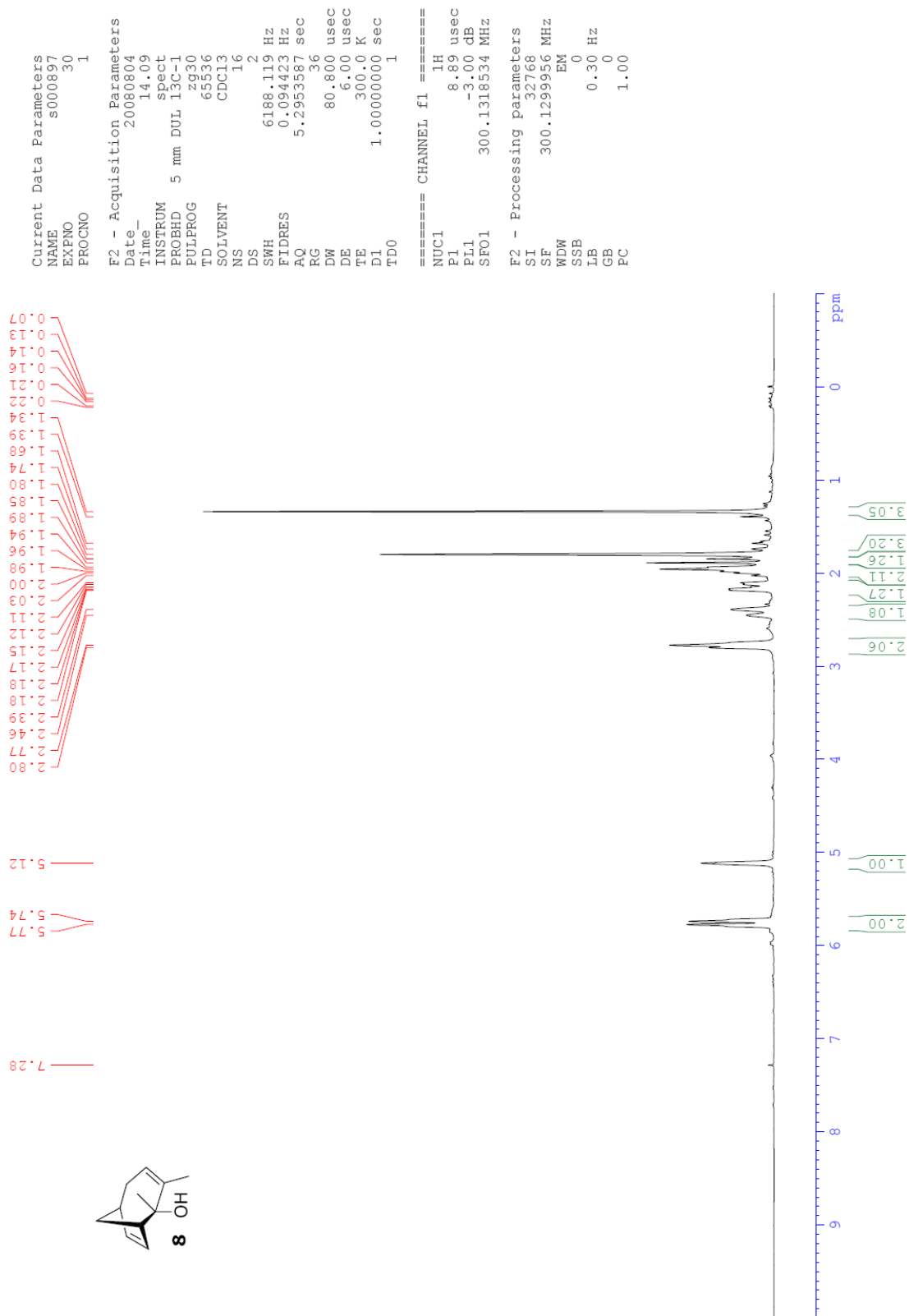
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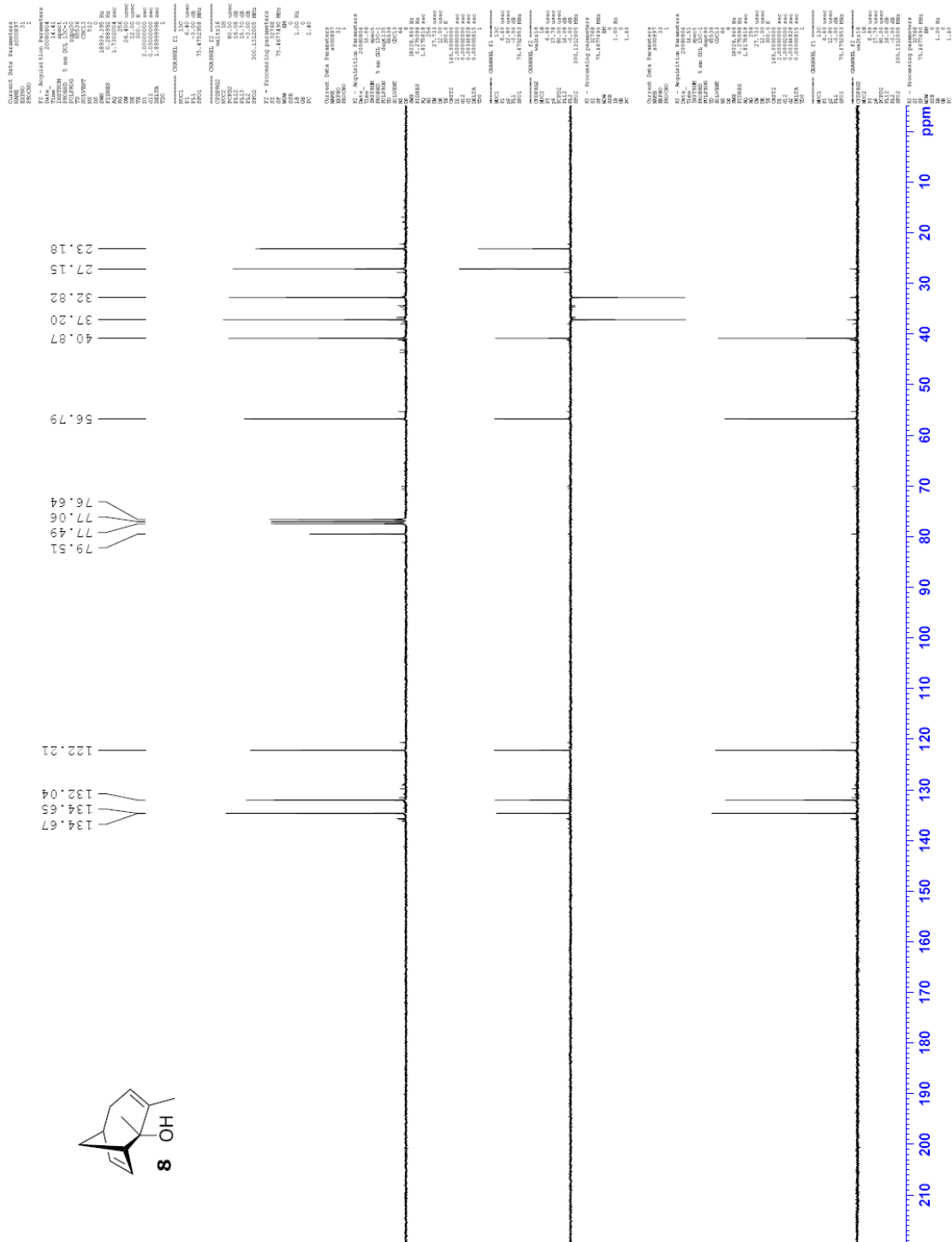
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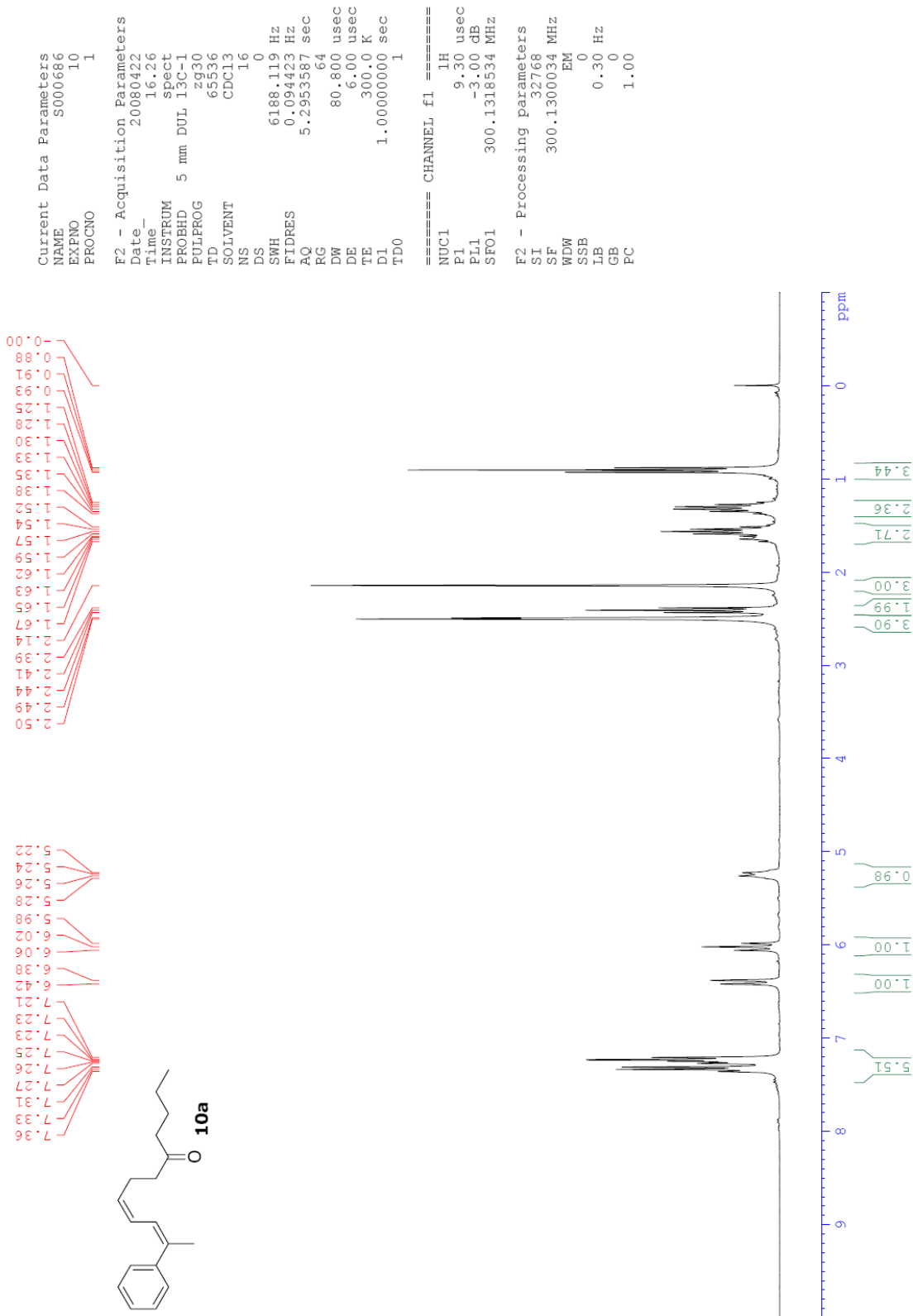
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EXPNO 14
PROCNO 1

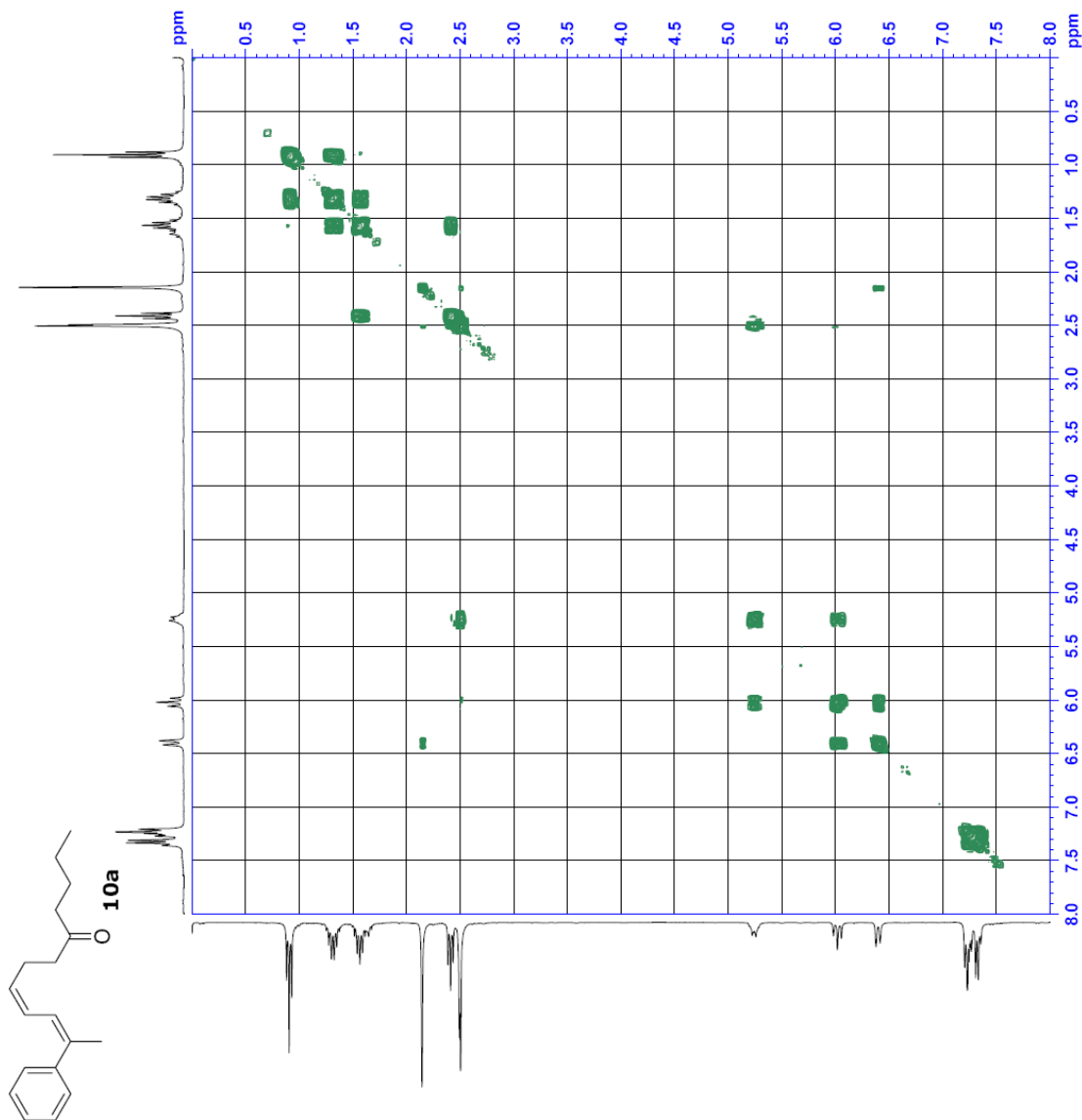
F2 - Acquisition Parameters
Date_ 20080422
Time 17.09
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG cosydrif
TD 2048
SOLVENT CDCl3
NS 8
DS 16
SWH 3605.769 Hz
FIDRES 1.760630 Hz
AQ 0.2840393 sec
RG 64
DW 138.667 usec
DE 6.00 usec
TE 300.0 K
d0 0.0000300 sec
d1 2.0000000 sec
d13 0.0000400 sec
d20 0.0000000 sec
IN0 0.0002735 sec

==== CHANNEL f1 =====
NUC1 1H
P1 9.30 usec
PL1 -3.00 dB
SFO1 300.1313901 MHz

F1 - Acquisition parameters
ND0 1
TD 256
SFO1 300.1314 MHz
FIDRES 14.084189 Hz
SW 12.013 ppm
F1MODE QF

F2 - Processing parameters
SI 1024
SF 300.1300000 MHz
WDW QSINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
SF 300.1300000 MHz
WDW QSINE
SSB 0
LB 0.00 Hz
GB 0



```

Current Data Parameters
NAME      S000686
EXPNO    15
PROCNO   1

F2 - Acquisition Parameters
Date_    20080924
Time     18:29
INSTRUM  spect
PROBHD   5 mm DUL 13C-1
PULPROG  hmczph
TD        1024
SOLVENT  CDCl3
NS        16
DS        4
SWH       3063.726 Hz
FIDRES    2.591920 Hz
AQ        0.1671668 sec
RG         64
DW        163.200 usec
DE         6.00 usec
TE        300.2 K
CNST2     145.000000
d0         0.00000300 sec
d1         1.50000000 sec
d11        0.03000000 sec
d13        0.00000400 sec
d2         0.00344828 sec
IN0        0.00004150 sec
STCNT     128

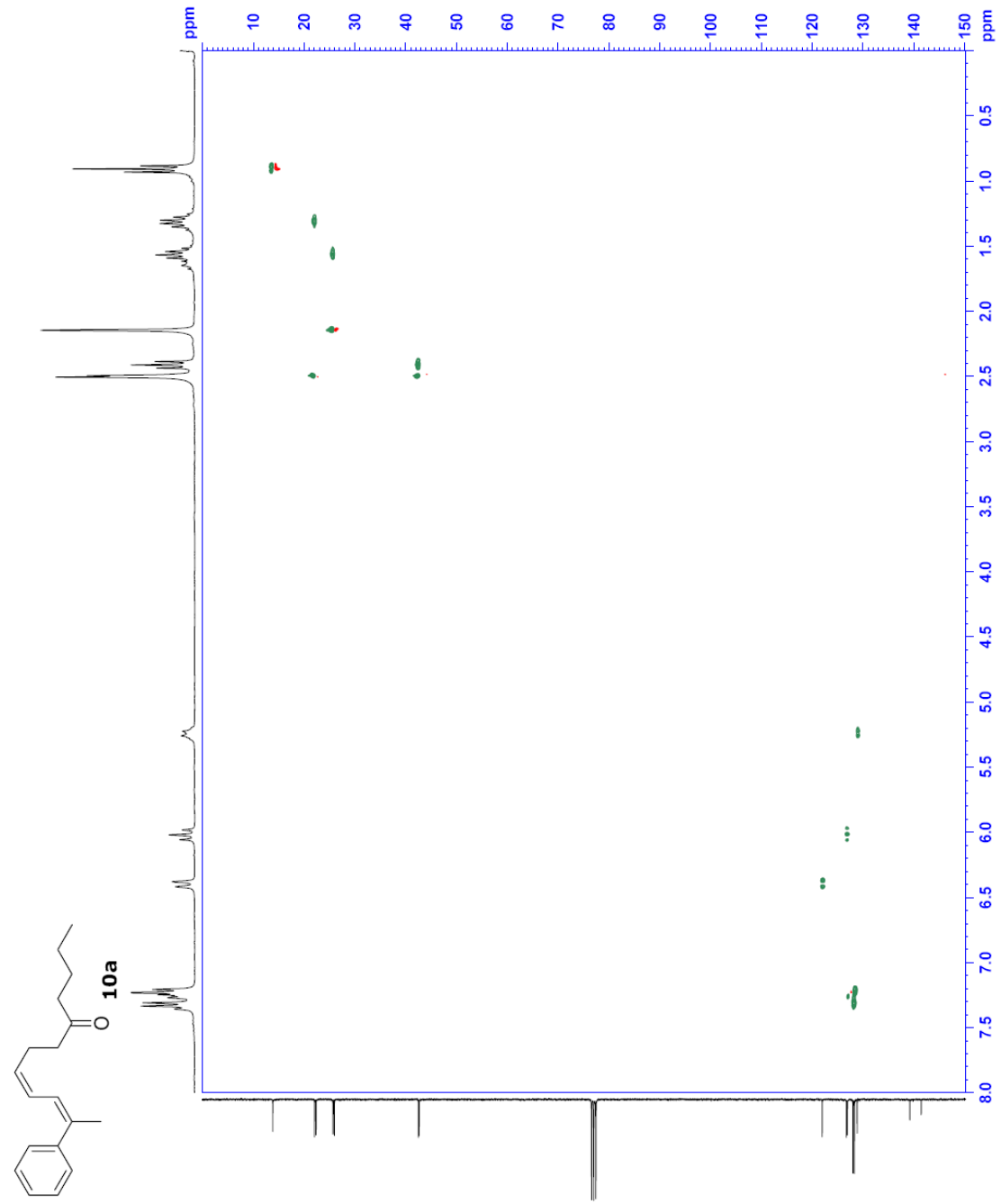
===== CHANNEL f1 =====
NUC1      1H
P1        9.30 usec
P2        18.60 usec
PL1       -3.00 dB
SFO1     300.1313815 MHz

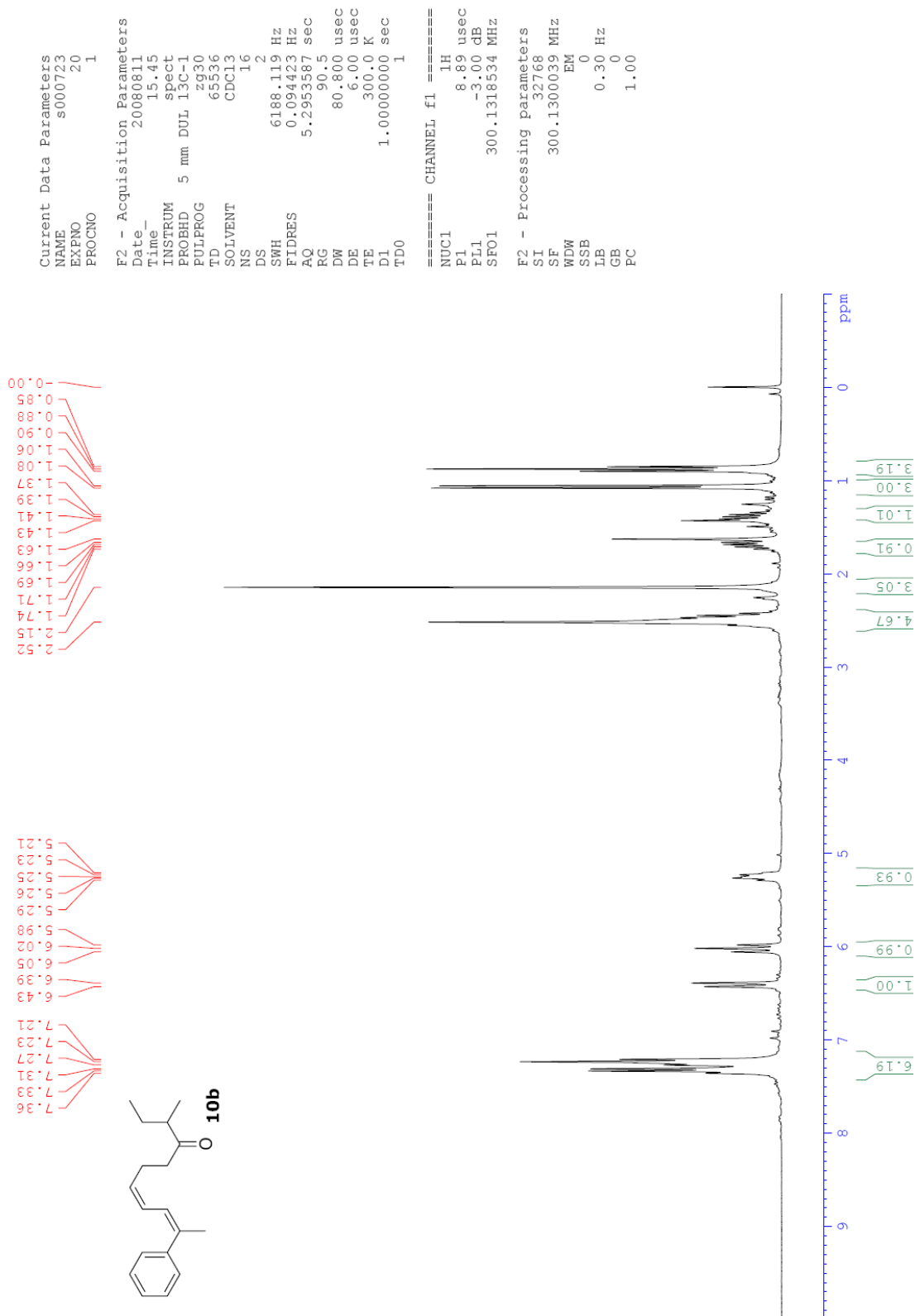
===== CHANNEL f2 =====
CDEPRG2   gap
NUC2      13C
P3        5.10 usec
PCPD2     70.00 usec
PL12      17.20 dB
PL2       6.00 dB
SFO2     75.4731095 MHz

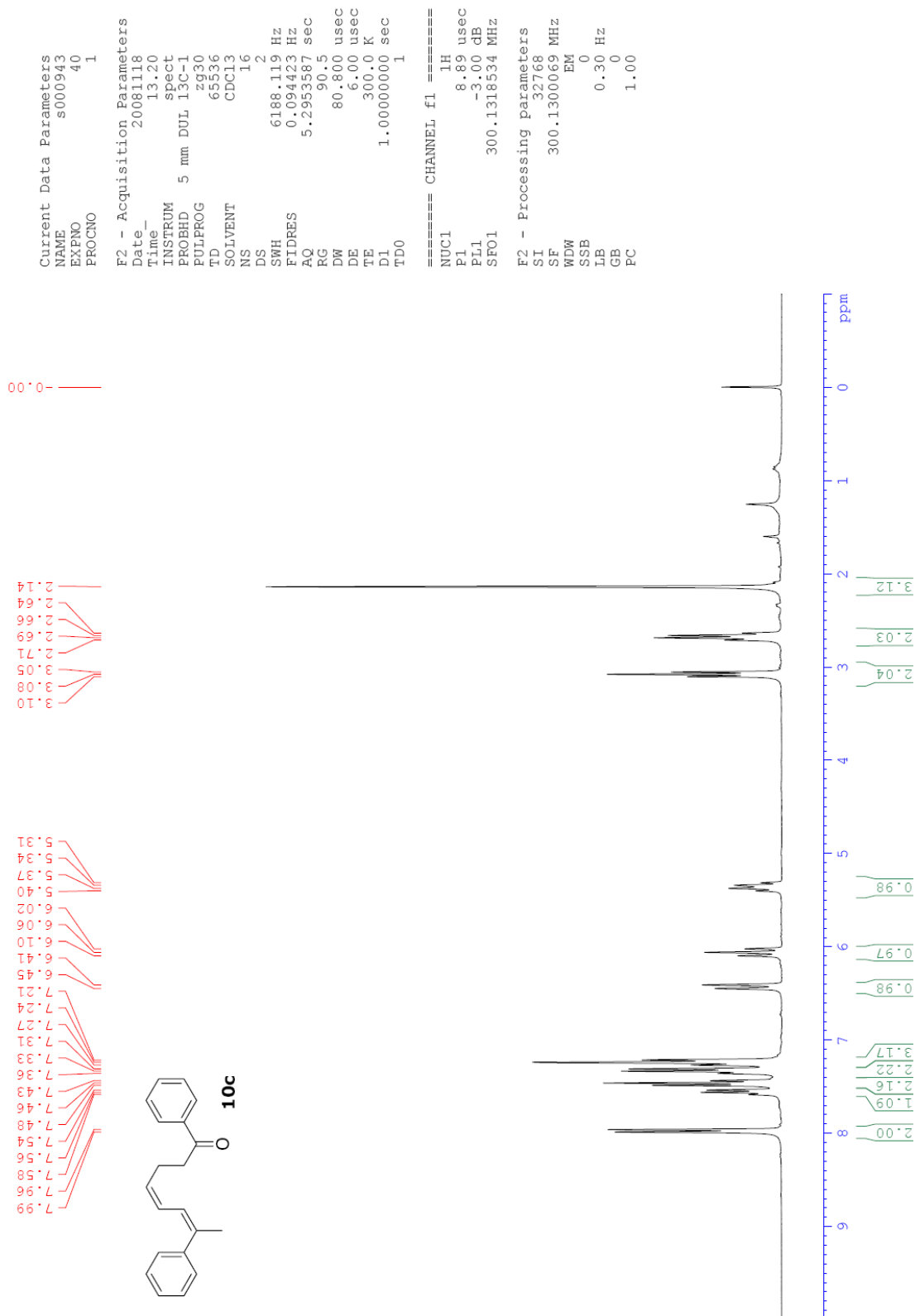
F1 - Acquisition Parameters
NUC0      2
TD        256
SFO1     75.47311 MHz
FIDRES    46.613960 Hz
AQ        0.1671668 sec
RG         64
SOLVENT  CDCl3
PC        1.40

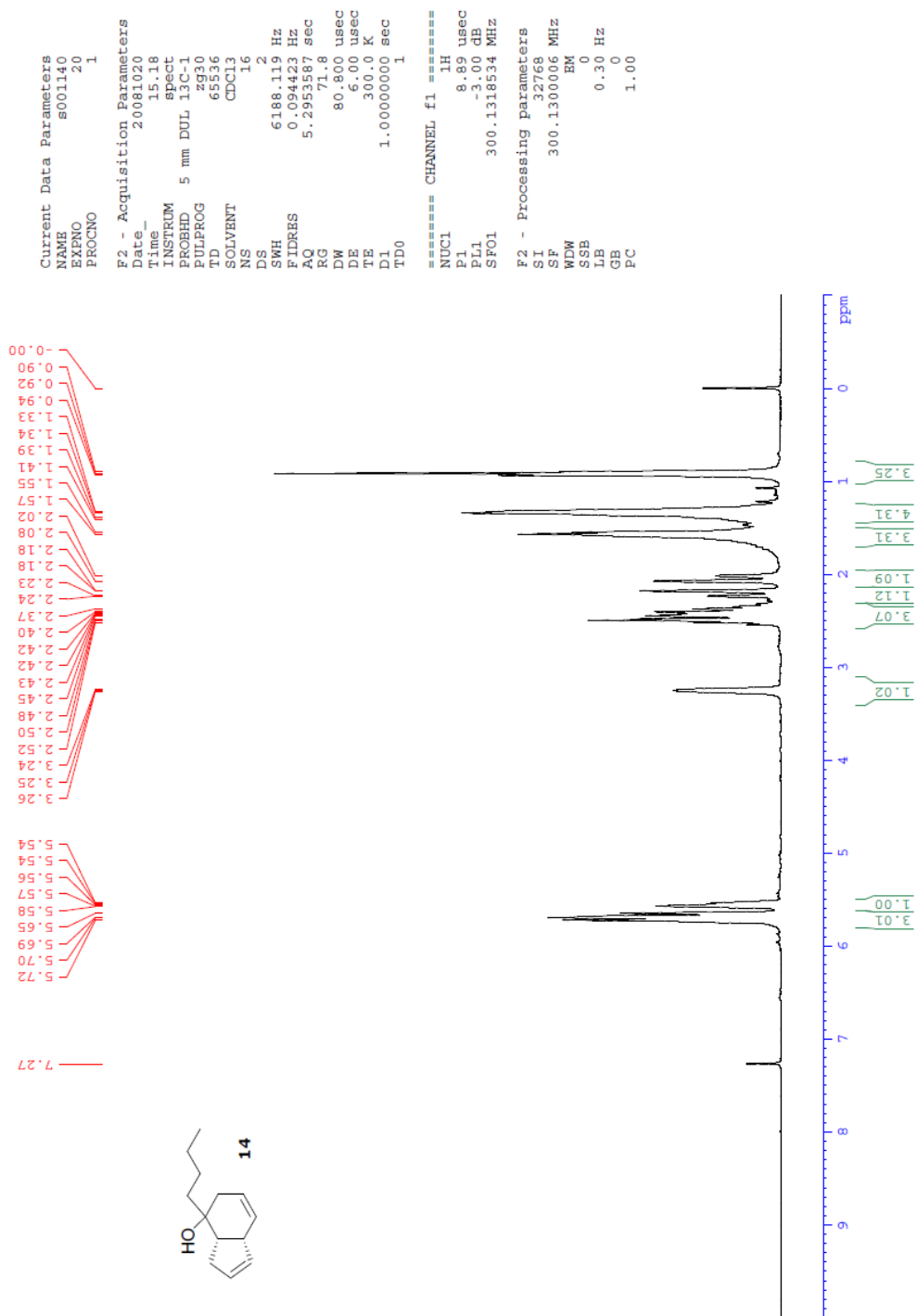
F2 - Processing parameters
SI        1024
SF        300.1300034 MHz
WDW       COSYME
SSB       0.0 Hz
GB        0
PC        1.40

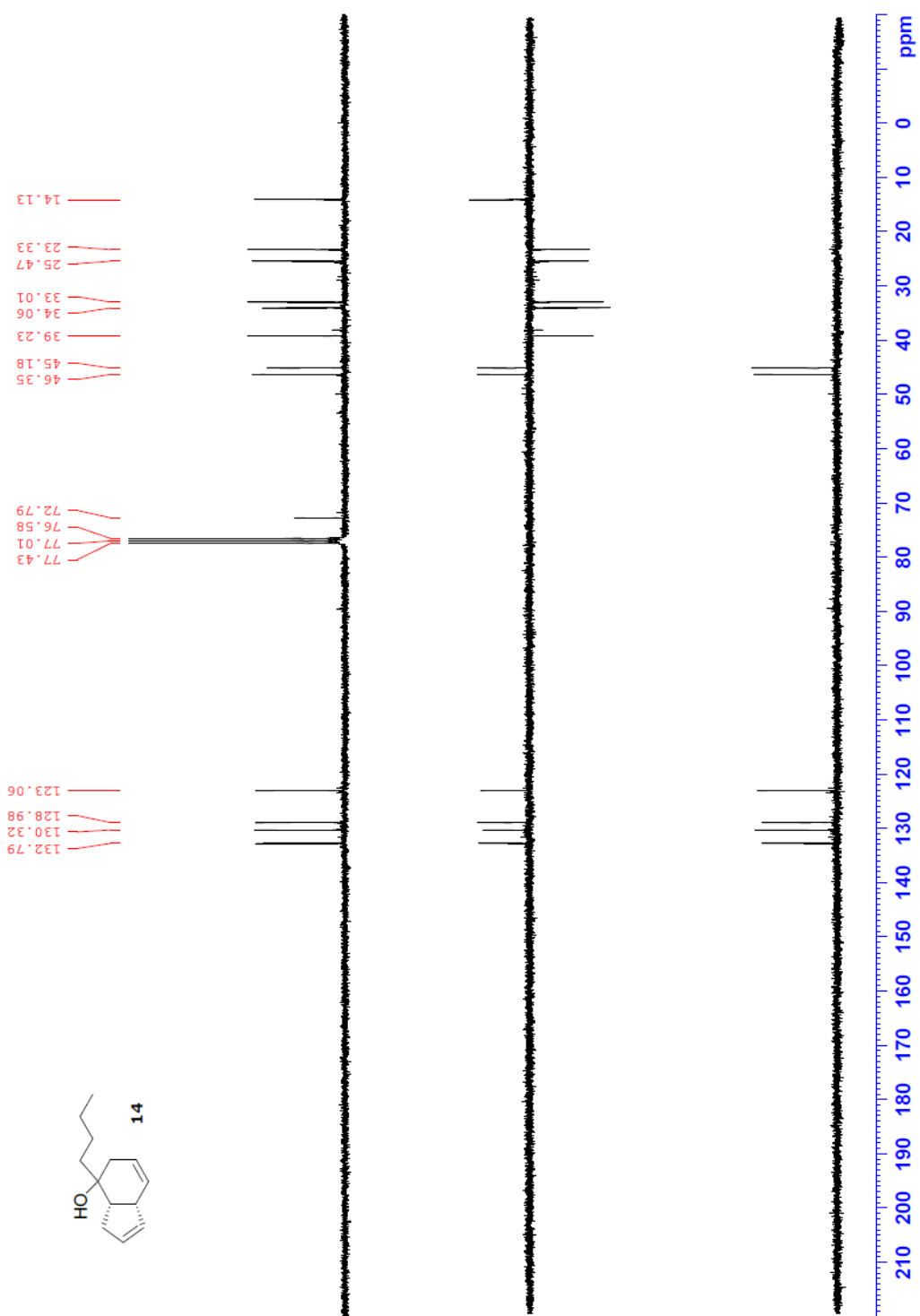
F1 - Processing parameters
SI        1024
SF        75.47311 MHz
WDW       States-TPP
SSB       0.0 Hz
GB        0
    
```











```
Current Data Parameters
NAME      S001482
EXPNO     40
PROCNO    1

F2 - Acquisition Parameters
Date_     20090320
Time      13.08
INSTRUM   spect
PROBHD    5 mm DUL 13C-1
PULPROG   zg30
TD         65536
SOLVENT   C6D6
NS         16
DS         2
SWH        6188.119 Hz
FIDRES     0.094423 Hz
AQ         5.2953587 sec
RG         71.8
DW         80.800 usec
DE         6.00 usec
TE         300.0 K
D1         1.0000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         8.89 usec
PL1        -3.00 dB
SFO1       300.1318534 MHz

F2 - Processing parameters
SI         32768
SF         300.1300513 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
```

