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Supporting Information

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Supporting information

Gold(I)-Catalyzed Cycloisomerization of 3-Methoxy-1,6-enynes Featuring Tandem Cyclization and [3,3]-Sigmatropic Rearrangement**

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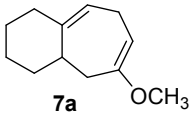
Representative Experimental Procedure for the cycloisomerization and the conversion to the cyclohept-4-en-1-ones, and copies of ^{1}H and ^{13}C spectra for all new compounds.

I. General information

All solvents were dried and distilled according to the standard methods before use. $Au(PPh_3)Cl$ and $AgSbF_6$ were purchased from Aldrich Chemicals and stored in a dry-keeper. $Au(P(C_6F_5)_3)Cl$ was prepared according to the literature procedures.[1] Experiments were performed in flame-dried glasswares with rubber septa under a positive pressure of nitrogen. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as a visualizing agent and acidic *p*-anisaldehyde, and heat as developing agent. Flash chromatography was carried out on Merck 60 silica gel (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded with Bruker (300 MHz) spectrometer. ^{1}H NMR spectra were referenced to residual TMS (0 ppm) and reported as follows; chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet). Chemical shifts of the ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.23 ppm). Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer.

II. General procedure for the cycloisomerization

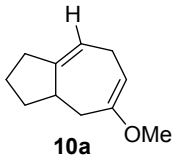
Compound 7a



7a

To a stirred solution of gold complex $Au(P(C_6F_5)_3Cl$ (5.1mg, 0.0067 mmol) and $AgSbF_6$ (2.3 mg, 0.0067 mmol) was added methylene chloride (10 mL) and the solution was stirred for 10 min. The resulting solution was filtered through a pad of Celite and concentrated. The residue was dried over high vacuum for 2 hours, and then cooled to -15°C. To this residue was added a solution of **6** (120 mg, 0.67 mmol) in CH_2Cl_2 (13. 4 mL, 0.05M, pre-cooled to -15°C). The resulting colorless solution was stirred for 2 min. Triethylamine (1 mL) was added and the solution was stirred for 5 min. The resulting solution was passed through a pad of Celite and concentrated. The residual oil was purified by flash chromatography on silica gel (deactivated by triethylamine before use, eluted with pentane: ether = 95:5) to give the compound **7a** as a colorless oil (117 mg, 0.65 mmol, 97% yield). R_f = 0.45 (pentane: ether = 95:5);
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14-1.47 (m, 3H), 1.66-1.77 (m, 3H), 1.87-1.95 (m, 1H), 2.04-2.14 (m, 2H), 2.38-2.40 (m, 2H), 2.45-2.57 (m, 1H), 2.64-2.74 (m, 1H), 3.47 (s, 3H), 4.79 (app t, *J* = 6.4 Hz, 1H), 5.45 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6, 27.0, 28.9, 35.7, 37.5, 38.8, 39.2, 54.6, 95.7, 120.3, 143.8, 159.4; IR: (cm^{-1}) ν 3070, 2925, 2852, 1666, 1155; HRMS calcd for $C_{12}H_{18}O$: 178.1358. found: 178. 1358.

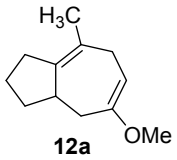
Compound 10a



10a

Using the representative procedure, a mixture of **9** (105 mg, 0.64 mmol), gold complex $Au(P(C_6F_5)_3Cl$ (4.9 mg, 0.0064 mmol) and $AgSbF_6$ (2.2 mg, 0.0064 mmol) were reacted to give **10a** as a colorless oil. (101 mg, 0.61 mmol, 96 % yield). R_f = 0.63 (hexane : ethyl acetate = 95:5);
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25-1.35 (m, 1H), 1.51-1.71 (m, 2H), 1.91-1.96 (m, 1H), 2.18 - 2.35 (m, 4H), 2.65 - 2.82 (m, 3H), 3.46 (s, 3H), 4.60 (app t, *J* = 5.4 Hz, 1H), 5.51 - 5.54 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.9, 25.2, 34.3, 35.0, 37.6, 39.8, 54.3, 94.1, 118.4, 148.5, 157.8; IR: (cm^{-1}) ν 3071, 2945, 2856, 2829, 1668, 1144; HRMS calcd for $C_{11}H_{16}O$: 164.1201. found: 164.1202.

Compound 12a

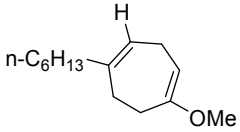


12a

Using the representative procedure, a mixture of **11** (30 mg, 0.17 mmol), gold complex $Au(P(C_6F_5)_3Cl$ (6.4 mg, 0.0084 mmol) and $AgSbF_6$ (2.9 mg, 0.0084 mmol) were reacted to give **12a** as a colorless oil. (29 mg, 0.16 mmol, 95 % yield). R_f = 0.45 (pentane: ether = 95:5);

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25-1.38 (m, 1H), 1.52-1.76 (m, 2H), 1.68 (s, 3H), 1.85-1.96 (m, 1H), 2.15 - 2.22 (m, 2H), 2.25 - 2.32 (m, 2H), 2.45 (dd, *J* = 18.0, 7.2 Hz, 1H), 2.67-2.83 (m, 1H), 2.89 - 3.04 (m, 1H), 3.45 (s, 3H), 4.63 (dd, *J* = 6.8, 4.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2, 25.3, 31.3, 31.8, 35.0, 37.4, 39.8, 54.1, 93.9, 126.8, 141.0, 157.5; IR: (cm^{-1}) ν 2938, 2856, 2830, 1667, 1158; HRMS calcd for $C_{12}H_{18}O$: 178.1358. found: 178.1358.

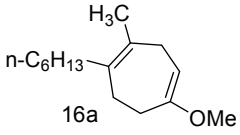
Compound **14a**



Using the representative procedure, a mixture of **13** (73 mg, 0.35 mmol), gold complex $Au(P(C_6F_5)_3Cl$ (2.7 mg, 0.0035 mmol) and $AgSbF_6$ (1.2 mg, 0.0035 mmol) were reacted to give **14a** as a colorless oil. (66 mg, 0.32 mmol, 90 % yield). R_f = 0.45 (pentane: ether = 95:5);

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3 H), 1.26-1.43 (m, 8H), 1.97 (app t, *J* = 7.3 Hz, 2H), 2.21 - 2.27 (m, 2H), 2.28 - 2.31 (m, 2H), 2.69 (app t, *J* = 5.7 Hz, 1H), 3.46 (s, 3H), 4.66 (t, *J* = 5.8 Hz, 1H), 5.54 (t, *J* = 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4, 23.0, 23.7, 28.4, 28.5, 29.5, 30.5, 32.1, 39.5, 54.3, 94.6, 123.5, 142.8, 158.9; IR: (cm^{-1}) ν 2927, 2856, 2829, 1668, 1160; HRMS calcd for $C_{14}H_{24}O$: 208.1827. found: 208.1829.

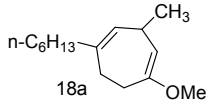
Compound **16a**



Using the representative procedure, a mixture of **15** (80 mg, 0.36 mmol), gold complex $Au(P(C_6F_5)_3Cl$ (2.7 mg, 0.0036 mmol) and $AgSbF_6$ (1.2 mg, 0.0036 mmol) were reacted to give **16a** as a colorless oil. (68 mg, 0.31 mmol, 85 % yield). R_f = 0.43 (pentane: ether = 95:5);

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3 H), 1.22-1.38 (m, 8H), 1.71 (s, 3H), 2.05 (app t, *J* = 7.4 Hz, 2H), 2.12 - 2.19 (m, 2H), 2.26 - 2.30 (m, 2H), 2.66 (d, *J* = 6.0Hz, 2H), 3.45 (s, 3H), 4.68 (t, *J* = 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 20.8, 23.0, 28.9, 29.5, 29.7, 30.4, 30.6, 32.2, 34.2, 54.0, 94.3, 132.6, 134.7, 157.7; IR: (cm^{-1}) ν 2927, 2856, 1666, 1162; HRMS calcd for $C_{15}H_{26}O$: 222.1984. found: 222.1981.

Compound 18a

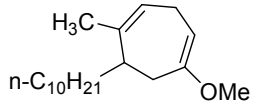


(a) From the reaction of **17**
Using the representative procedure, a mixture of **17** (67 mg, 0.30 mmol), gold complex $Au(P(C_6F_5)_3Cl$ (2.3 mg, 0.0030 mmol) and $AgSbF_6$ (1.0 mg, 0.0030 mmol) were reacted to give **18a** as a colorless oil. (60 mg, 0.27 mmol, 89 % yield). R_f = 0.45 (pentane: ether = 95:5);

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3 H), 1.13 (d, *J* = 7.4 Hz, 3H), 1.21-1.42 (m, 8H), 1.96 (app t, *J* = 7.5 Hz, 2H), 2.01 - 2.18 (m, 2H), 2.31 - 2.43 (m, 2H), 3.11 - 3.22 (m, 1H), 3.46 (s, 3H), 4.42 (d, *J* = 3.3 Hz, 1H), 5.29 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 23.0, 23.9, 28.4, 28.4, 28.6, 29.5, 30.2, 32.1, 39.4, 54.2, 102.6, 131.5, 141.0, 157.4; IR: (cm^{-1}) ν 2956, 2928, 2856, 1659, 1202; HRMS calcd for $C_{15}H_{26}O$: 222.1984. found: 222.1988.

(b) From the reaction of **19**
Using the representative procedure, a mixture of **19** (120 mg, 0.54 mmol), gold complex $Au(P(C_6F_5)_3Cl$ (4.1 mg, 0.0054 mmol) and $AgSbF_6$ (1.8 mg, 0.0054 mmol) were reacted to give **18a** as a colorless oil. (114 mg, 0.51 mmol, 95 % yield). R_f = 0.77 (hexane : ethyl acetate = 95:5);

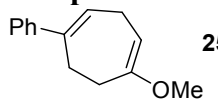
Compound 23a



23a

Using the representative procedure, a mixture of **22** (38 mg, 0.14 mmol), gold complex $Au(P(C_6F_5)_3Cl$ (5.2 mg, 0.0068 mmol) and $AgSbF_6$ (2.3 mg, 0.0068 mmol) were reacted to give **23a** as a colorless oil. (36 mg, 0.13 mmol, 94 % yield). R_f = 0.45 (pentane: ether = 95:5);
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 1.19 -1.57 (m, 18H), 1.69 (d, *J* = 1.2 Hz, 3H), 2.12 - 2.23 (m, 2H), 2.51 - 2.62 (m, 2H), 2.74-2.90 (m. 1H), 3.46 (s, 3H), 4.62 - 4.65 (m, 1H), 5.43 (app t, *J* = 4.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 23.0, 24.7, 24.9, 28.1, 29.7, 29.9, 30.0, 30.2, 32.3, 32.5, 35.0, 40.1, 54.3, 94.3, 123.0, 141.2, 157.9; IR: (cm^{-1}) ν 2924, 2854, 1672, 1145; Anal calcd for $C_{19}H_{34}O$: C, 81.95; H, 12.31; found: C, 81.94; H, 12.09.

Compound 25a

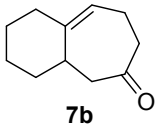


25a

Using the representative procedure, a mixture of **24** (60 mg, 0.30 mmol), gold complex $Au(P(C_6F_5)_3Cl$ (4.5 mg, 0.0060 mmol) and $AgSbF_6$ (2.1 mg, 0.0060 mmol) were reacted to give **25a** as a colorless oil. (58 mg, 0.29 mmol, 97 % yield). R_f = 0.45 (pentane: ether = 95:5);

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 - 2.45 (m, 2H), 2.72 - 2.77 (m, 2H), 2.90 (app t, *J* = 6.0 Hz, 2H), 3.49 (s, 3H), 4.70 (t, *J* = 5.8Hz, 1H), 6.15 (t, *J* = 6.2 Hz, 1H), 7.17 – 7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.2, 28.2, 30.6, 54.3, 93.9, 125.9, 126.9, 128.2, 128.6, 142.3, 143.7, 158.6; IR: (cm^{-1}) ν 2950, 2850, 1734, 1704, 1491, 1446, 1105, 758, 699; HRMS calcd for $C_{14}H_{16}O$: 200.1201. found: 200.1204.

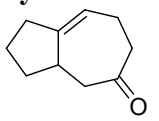
Representative procedure for the conversion into the cyclohept-4-en-1-one
(b) Conversion of 7a to 7b:



7b

To a solution of **7a** (22mg, 0.12 mmol) in THF (1 mL) at 0^{o}C was added water (0.1 mL) and p-toluenesulfonic acid (2.3 mg, 0.012 mmol). The reaction mixture was stirred for 7 h at 0^{o}C, and then diluted with ether (20 mL). This solution was washed with saturated aq. $NaHCO_3$ solution (2 x 10 mL), water (10 mL), dried over anh. Na_2SO_4 and concentrated. The residual oil was purified by flash chromatography on silica gel (eluted with pentane : ether = 85:15) to give the compound **7b** as a colorless oil (18 mg, 0.11 mmol, 90% yield). The spectral data are in complete agreement with those in the literature.[2]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16-1.44 (m, 3H), 1.75-1.80 (m, 3H), 1.93 (m, 1H), 2.14 (m, 1 H), 2.32 (m, 2H), 2.46 (m, 1H), 2.54 (m, 2H), 2.74 (dd, *J* = 4.5, 4.5 Hz, 1H), 2.82 (dd, *J* = 15, 9 Hz, 1H), 5.57 (m, 1H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.1, 26.9, 28.8, 36.5, 38.6, 41.2, 44.4, 47.5, 120.7, 144.1, 213.6; IR: (cm^{-1}) ν 3053, 1700, 1419, 1265, 739, 704.

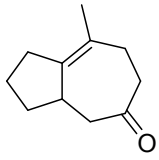
Synthesis of 10b



10b

Using the repesentative procedure, **10a** (33 mg, 0.20 mmol) was converted to **10b** (27 mg, 0.18 mmol, 90% yield). The spectral data are in complete agreement with the literature value.[2]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27-1.40 (m, 1H), 1.50-1.74 (m, 2H), 2.04 (m, 1H), 2.26-2.48 (m, 6H), 2.63 (dd, *J* = 2.7, 2.7 Hz, 1H), 2.76-2.90 (m, 2H), 5.61 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.3, 25.9, 35.1, 35.6, 38.4, 42.7, 49.9, 119.6, 148.5, 213.5; IR: (cm^{-1}) ν 3053, 2986, 2932, 2856, 2685, 2410, 1305, 1702, 1422, 1261, 895, 828.

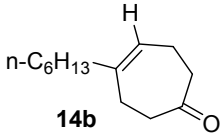
Synthesis of 12b



12b

Using the repesentative procedure, **12a** (32 mg, 0.18 mmol) was converted to **12b** (26 mg, 0.16 mmol, 88% yield). The spectral data are in complete agreement with the literature value. [3]
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24-1.35 (m, 1H), 1.50-1.56 (m, 1H), 1.66 (s, 3H), 1.69-1.77 (m, 1H), 1.92-1.98 (m, 1H), 2.30-2.43 (m, 6H), 2.58 (dd, *J* = 3, 3 Hz, 1H), 2.79-2.92 (m, 2H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.1, 25.3, 32.2, 32.9, 36.1, 39.0, 42.4, 49.7, 126.4, 140.6, 213.6; IR: (cm-^{1}) ν 3053.8, 2986, 2685, 2410, 2305,1702, 1551, 1421, 1271, 895; HRMS calcd for $C_{11}H_{16}O$: m/z 164.1201. found 164.1202.

Synthesis of 14b

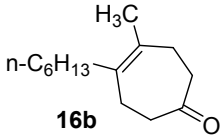


14b

Using the representative procedure, **14a** (31 mg, 0.15 mmol) was converted to **14b** (24 mg, 0.013 mmol, 84 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.9 (t, *J* = 6.6 Hz, 3H), 1.27-1.41(m, 8H), 2.00 (t, *J* = 7.5 Hz, 2H), 2.27-2.34 (m, 4H), 2.56-2.62 (m, 4H), 5.56 (t, *J* = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 23.0, 24.1, 28.0, 28.4, 29.3, 32.1, 40.4, 42.7, 43.1, 123.7, 142.3, 214.0; IR: (cm-^{1}) ν 3053, 2928, 2856, 2685, 2305, 1702, 1422, 1378, 1263, 895, 738; Anal. calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. found: C, 80.39; H, 11.32.

Synthesis of 16b

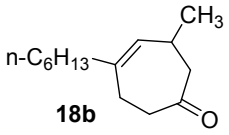


16b

Using the representative procedure, **16a** (26 mg, 0.12 mmol) was converted to **16b** (21 mg, 0.010 mmol, 85 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 1.28 -1.38 (m, 8H), 1.74 (s, 3H), 2.06 (t, *J* = 7.3 Hz, 2H), 2.24 - 2.30 (m, 4H), 2.43 - 2.50 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4, 20.9, 23.0, 28.6, 29.0, 29.6, 31.1, 32.2, 35.5, 42.7, 43.6, 130.6, 135.2, 213.4; IR: (cm^{-1}) ν 2954, 2926, 2856, 1738, 1710, 1464, 1377; HRMS calcd for $C_{14}H_{24}O$: 208.1827. found: 208.1829.

Synthesis of 18b

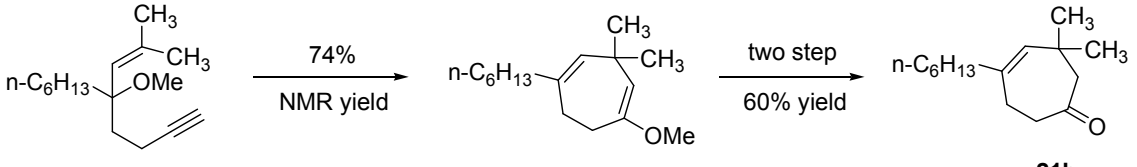


18b

Using the representative procedure, **18a** (44 mg, 0.20 mmol) was converted to **18b** (33 mg, 0.16 mmol, 80 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.5 Hz, 3H), 1.09 (d, *J* = 6.8 Hz, 3H), 1.28-1.40 (m, 8H), 1.97-2.02 (m, 2H), 2.26-2.53 (m, 5H), 2.58-2.74 (m, 2H), 5.31 (d, *J* = 3.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 23.0, 23.3, 27.7, 28.4, 29.3, 30.5, 32.1, 40.6, 42.9, 50.9, 130.7, 140.6, 213.1; IR: (cm^{-1}) ν 2957, 2927, 2856, 1708, 1457, 1405, 1277, 1120, 962, 830; HRMS calcd for $C_{14}H_{24}O$: m/z 208.1827. found 208.1824.

Synthesis of 21b

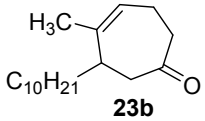


20 **21a** **21b**

Using the representative procedure, a mixture of **20** (68 mg, 0.29 mmol), gold complex $Au(P(C_6F_5)_3Cl$ (4.4 mg, 0.0057 mmol) and $AgSbF_6$ (2.0 mg, 0.0057 mmol) were reacted to give **21a** as a colorless oil. (51 mg, 0.22 mmol, 74 % yield). The yield of this reaction was approximated as 74%, which was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. Crude reaction mixture was treated with catalytic p-TsOH (10 %) to give **21b** as a colorless oil (38 mg, 0.17 mmol, 60 % yield for two step conversion)

R_f = 0.45 (pentane: ether = 95:5);^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.6 Hz, 3H), 1.05 (s, 6H), 1.27-1.37 (m, 8H), 1.95-2.00 (m, 2H), 2.31-2.35 (m, 2H), 2.46-2.66 (m, 2H), 2.66 (s, 2H), 5.13 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 26.3, 28.0, 28.8, 31.2, 31.7, 35.6, 41.4, 43.3, 53.8, 133.9, 137.0, 212.7; IR: (cm^{-1}) ν 2957, 2928, 2857, 1707, 1466, 1389, 1363, 1232, 918; HRMS calcd for $C_{15}H_{26}O$: m/z 222.1984. found 222.1987.

Synthesis of 23b

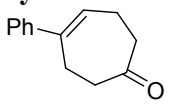


23b

Using the repesentative procedure, **23a** (28 mg, 0.10 mmol) was converted to **23b** (24 mg, 0.090 mmol, 90 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 3 H), 1.19 -1.41 (m, 18H), 1.74 (s, 3H), 2.27 - 2.33 (m, 3H), 2.45 - 2.49 (m, 2H), 2.63 - 2.75 (m, 2H), 5.59 (app t, *J* = 6.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 22.9, 23.0, 25.4, 27.4, 29.7, 29.9, 30.0, 32.3, 33.5, 41.5, 44.3, 46.0, 124.1, 141.6, 213.7; IR: (cm^{-1}) ν 2925, 2854, 1745, 1709, 1465, 1378; HRMS calcd for $C_{18}H_{32}O$: m/z 264.2453. found 264.2455.

Synthesis of 25b

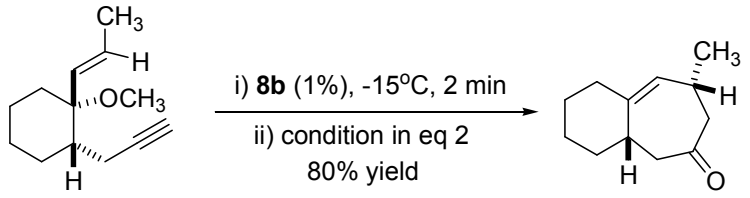


25b

Using the representative procedure, compound **25a** (40 mg, 0.20 mmol) was converted into **25b** (28 mg, 0.15 mmol, 74 % yield). The spectral data are in full accord with those in the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.50-2.56 (m, 2H), 2.67-2.71 (m, 2H), 2.74-2.82 (m, 4H), 6.11 (t, *J* = 5.9 Hz, 1H), 7.26-7.27 (m, 1H), 7.29-7.34 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.7, 28.1, 42.8, 43.1, 126.2, 127.4, 128.0, 128.8, 142.5,144.2,213.1; IR: (cm^{-1}) ν 3079, 3054, 3028, 1706, 1597, 1356, 1324, 1242, 763, 698.

Synthesis of 27

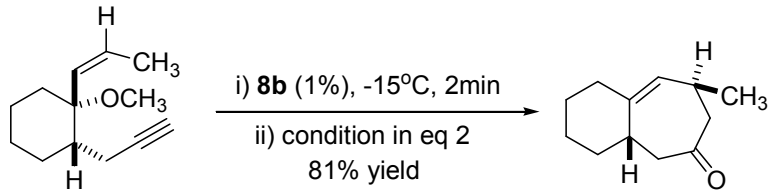


26 **27**

Using the representative procedure, a mixture of **26** (125 mg, 0.65 mmol), gold complex $Au(P(C_6F_5)_3Cl$ (5.0 mg, 0.0065 mmol) and $AgSbF_6$ (2.2 mg, 0.0065 mmol) were reacted in CH_2Cl_2 (13 mL) to give the crude cycloheptadiene as a colorless oil. The yield of this reaction was approximated as 90%, which was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The crude reaction mixture was treated with catalytic p-TsOH (10 %) for 7 hours at 0°C to give **27** as a white solid (93 mg, 0.52 mmol, 80 % yield for two step conversion)

R_f = 0.45 (pentane: ether = 95:5); m. p 30-31°C (from ether/pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (d, *J* = 7.1 Hz, 3H), 1.08-1.48 (m, 3H), 1.62-1.82 (m, 3H), 1.88-2.03 (m, 1H), 2.07-2.22 (m, 2H), 2.25-2.52 (m, 3H), 2.85-3.04 (m, 1H), 3.47 (dd, *J* = 12.2, 4.9 Hz, 1H), 5.22 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.3, 26.8, 27.7, 28.7, 35.3, 38.6, 40.3, 47.0, 53.4, 128.4, 142.7, 212.7; IR: (cm^{-1}) ν 2928, 2855, 1704, 1444; HRMS calcd for $C_{12}H_{18}O$: m/z 178.1358. found 178.1358.

Synthesis of 29

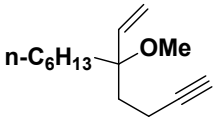


28 29

Using the representative procedure, a mixture of **28** (150 mg, 0.78 mmol), gold complex $Au(P(C_6F_5)_3Cl$ (6.0 mg, 0.0078 mmol) and $AgSbF_6$ (2.7 mg, 0.0078 mmol) were reacted in CH_2Cl_2 (16 mL) to give the crude cycloheptadiene as a colorless oil. The yield of this reaction was approximated as ~90%, which was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The crude reaction mixture was treated with catalytic p-TsOH (10 %) for 7 hours at 0^oC to give **29** as a colorless oil (113 mg, 0.63 mmol, 81 % yield for two step conversion)

R_f = 0.45 (pentane: ether = 95:5);^1H NMR (300 MHz, $CDCl_3$): δ = 1.03 (d, *J* = 7.0 Hz, 3H), 1.18-1.46 (m, 3H), 1.70-1.82 (m, 3H), 1.83-1.95 (m, 1H), 2.10-2.16 (m, 1H), 2.18-2.34 (m, 3H), 2.43-2.51 (m, 1H), 2.99-3.19 (m, 2H), 5.19 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.0, 26.6, 27.3, 28.6, 36.8, 38.4, 41.5, 47.9, 52.5, 128.3, 142.2, 212.8; IR: (cm^{-1}) ν 2928, 2854, 1709, 1446; HRMS calcd for $C_{12}H_{18}O$: m/z 178.1358. found 178.1358.

Representative procedure for the preparation of substrates
Synthesis of 5-methoxy-5-vinylundec-1-yne (13).



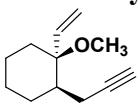
13

To a solution of sodium hydride (185 mg, 4.64 mmol, 60% in oil) in 15 mL of DMF was added a solution of 5-vinylundec-1-yn-5-ol (600 mg, 3.09 mmol) in DMF dropwise at 0^0C under nitrogen. The reaction was maintained at 0^0C for 1 h prior to the slow addition of methyl iodide (578 µl, 9.27 mmol). The resulting reaction mixture was stirred for 6 h before being quenched with ice-water.

The reaction mixture was diluted with water and extracted with ether (3 x 10 ml). The combined organic layers were washed with brine (10 ml), dried (Na_2SO_4) and concentrated to give a crude compound. Crude thus obtained was purified by silica gel column chromatography (eluted with EA : Hexane = 5 : 95) to afford 400 mg (62% yield) of **13** as colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.4 Hz, 3H), 1.46-1.51 (m, 2H), 1.26 (m, 8H), 1.80-1.86 (m, 2H), 1.93 (t, *J* = 2.6 Hz, 1H), 2.11-2.17 (m, 2H), 3.12 (s, 3H), 5.11-5.17 (dd, *J* = 1.3, 17.6 Hz, 1H), 5.20-5.24 (dd, *J* = 1.3, 11.0 Hz, 1H), 5.59-5.68 (dd, *J* = 11.1, 17.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.5, 14.1, 22.6, 23.0, 29.7, 31.8, 33.7, 35.2, 49.4, 69.9, 78.6, 84.9, 115.7, 141.3; IR: (cm^{-1}) ν 3312, 2934, 2858, 2826, 2119, 1462, 1414, 1136, 1000, 925, 629; HRMS calcd for $C_{14}H_{24}O$: m/z 208.1827. found 208.1825.

1-methoxy-2-(prop-2-ynyl)-1-vinylcyclohexane (6)

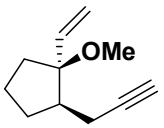


6

Yield: 91%. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.20-1.34 (m, 3H), 1.42-1.56 (m, 3H), 1.69-1.76 (m, 1H), 1.88-1.20 (m, 3H), 2.02-2.11 (m, 1H), 2.44-2.51 (m, 1H), 3.10 (s, 3H), 5.06-5.12 (dd, *J* = 1.4, 17.7 Hz, 1H), 5.20-5.24 (dd, *J* = 1.4, 11.0 Hz, 1H), 5.65-5.75 (dd, *J* = 11.1, 17.7 Hz, 1H); ^{13}C NMR (75 MHz,

$CDCl_3$): δ = 19.1, 21.6, 25.7, 27.0, 31.3, 45.6, 49.7, 68.7, 77.9, 85.4, 115.9, 141.7; IR: (cm^{-1}) ν 3309, 2941, 2857, 2826, 1638, 1449, 1148, 620; HRMS calcd for $C_{12}H_{18}O$: m/z 178.1358. found 178.1362.

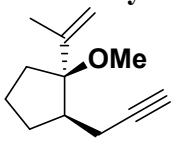
1-methoxy-2-(prop-2-ynyl)-1-vinylcyclopentane (9)



9

Yield: 42 %. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.55-1.71 (m, 4H), 1.83-1.93 (m, 2H), 2.00-2.06 (m, 2H), 2.07-2.19 (m, 1H), 2.31-2.40 (m, 1H), 3.10 (s, 3H), 5.11-5.21 (m, 2H), 5.71-5.80 (dd, *J* = 10.98, 17.43 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.5, 21.0, 29.7, 32.0, 49.3, 50.8, 68.2, 85.3, 86.5, 115.5, 139.8; IR: (cm^{-1}) ν 3310, 3086, 2964, 2875, 2826, 2118, 1640, 1449, 1181, 1164, 1071, 627; HRMS calcd for $C_{11}H_{16}O$: m/z 164.1201. found 164.1205.

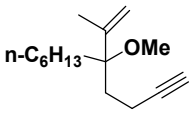
1-methoxy-1-(prop-1-en-2-yl)-2-(prop-2-ynyl)cyclopentane (11)



11

Yield: 61%. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.56-1.68 (m, 3H), 1.70 (s, 3H), 1.80-1.93 (m, 3H), 1.96-2.10 (m, 2H), 2.10-2.16 (m, 1H), 2.32-2.40 (m, 1H), 3.06 (s, 3H), 4.91 (d, *J* = 1.1 Hz, 1H), 4.99 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1, 19.7, 21.2, 29.3, 31.2, 46.5, 50.6, 67.8, 85.1, 88.4, 112.8, 144.2; IR: (cm^{-1}) ν 3309, 2964, 2874, 2117, 1640, 1448, 1216, 1168, 1105, 1077, 906, 626; HRMS calcd for $C_{12}H_{18}O$: m/z 178.1358. found 178.1357.

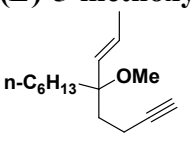
5-methoxy-5-(prop-1-en-2-yl)undec-1-yne (15)



15

Yield: 47%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.4 Hz, 3H), 1.13-1.16 (m, 2H), 1.26 (m, 6H), 1.46-1.52 (m, 2H), 1.67 (s, 3H), 1.82-1.88 (m, 2H), 1.93 (t, *J* = 2.61 Hz, 1H), 2.04-2.08 (m, 2H), 3.05 (s, 3H), 4.93 (s, 1H), 5.03 (d, *J* = 1.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.6, 14.1, 18.9, 22.7, 23.1, 29.7, 31.4, 31.8, 32.8, 49.2, 67.9, 80.7, 84.9, 114.3, 145.6; IR (cm^{-1}): ν 3312, 2935, 2872, 2858, 2824, 2119, 1641, 1466, 1451, 1376, 1192, 1128, 1082, 905, 629; Anal. calcd for $C_{15}H_{26}O$: C 81.29; H 11.94. found: C 81.12 H 11.86.

(*E*)-5-methoxy-5-(prop-1-enyl)undec-1-yne (17)

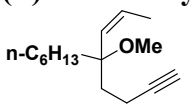


17

Yield: 41%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3H), 1.19-1.33 (m, 8H), 1.44-1.49 (m, 2H), 1.74-1.71 (dd, *J*=6.4, 1.6 Hz, 3H), 1.82-1.75 (m, 2H), 1.93 (t, *J* = 2.64 Hz, 1H), 2.10-2.16 (m, 2H), 3.09 (s, 3H), 5.23-5.28 (dq, *J* = 15.8, 1.44 Hz, 1H), 5.50-5.60 (dq, *J* = 6.5, 15.8 Hz, 1H); ^{13}C NMR (75

MHz, $CDCl_3$): δ = 12.6, 14.1, 18.0, 22.7, 23.1, 29.8, 31.8, 34.1, 35.5, 49.3, 67.8, 78.2, 85.0, 126.4, 134.3; IR: (cm^{-1}) ν 3312, 2935, 2857, 2824, 1460, 1377, 1195, 1080, 627; Anal. calcd for $C_{15}H_{26}O$: C 81.04; H 11.83. found: C 81.02; H 11.79.

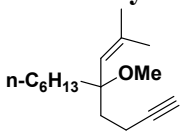
(*Z*)-5-methoxy-5-(prop-1-enyl)undec-1-yne (19)



19

Yield: 63%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.5 Hz, 3H), 1.27 (m, 8H), 1.52-1.55 (m, 2H), 1.76-1.79 (dd, *J* = 7.3, 1.8 Hz, 3H), 1.83-1.89 (m, 2H), 1.93 (t, *J* = 2.6 Hz, 1H), 2.15-2.21 (m, 2H), 3.12 (s, 3H), 5.02-5.07 (dq, *J* = 1.7, 11.9 Hz, 1H), 5.23-5.61 (dq, *J* = 7.2, 11.9 Hz,1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8, 14.1, 14.2, 22.7, 23.4, 29.8, 31.8, 35.4, 36.5, 49.1, 67.8, 79.9, 85.0, 127.6, 131.9; IR: (cm^{-1}) ν 3312, 3013, 2933, 2859, 2829, 2119, 1651, 1463, 1377, 1263, 1102, 724, 689; Anal. calcd for $C_{15}H_{26}O$ C 81.02; H 11.79. found: C 81.16 H 12.12.

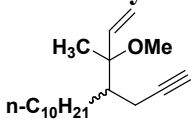
5-methoxy-5-(2-methylprop-1-enyl)undec-1-yne (20)



20

Yield = 60%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.3 Hz, 3H), 1.26 (m, 8H), 1.50-1.55 (m, 2H), 1.70 (s, 3H), 1.78 (s, 3H), 1.81-1.86 (m, 2H), 1.93 (t, *J* = 2.6 Hz, 1H), 2.18-2.12 (m, 2H), 3.08 (s, 3H), 4.85 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.3, 14.5, 19.1, 23.1, 23.8, 27.7, 30.2, 32.2, 36.0, 37.0, 49.4, 68.1, 79.5, 85.5, 126.5, 136.2; IR: (cm^{-1}) ν 3313, 2932, 2859, 2823, 2119, 1664, 1454, 1377, 1268, 1235, 1188, 1088, 830, 628; HRMS calcd for $C_{16}H_{28}O$: m/z 236.2140. found 236.2141.

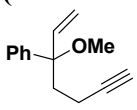
3-methoxy-3-methyl-4-(prop-2-ynyl)tetradec-1-ene (22)



22

Yield: 60 %. (A mixture of diastereomers). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.4 Hz, 3H) 1.20-1.26 (m, 19H), 1.32-1.49 (m, 2H), 1.61-1.63 (m, 1H), 1.91 (t, *J* = 2.7 Hz, 1H), 2.26-2.48 (m, 2H), 3.13 (s, 3H), 5.10-5.17 (dd, *J* =1.2, 17.6 Hz, 1H), 5.23-5.28 (dd, *J* = 1.4, 10.9 Hz, 1H), 5.60-5.70 (dd, *J* = 10.9, 17.61 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 16.5, 19.1, 23.1, 29.0, 29.5, 29.7, 29.9, 30.0, 30.3, 30.4, 32.3, 46.5, 50.2, 69.4, 80.3, 84.9, 116.7, 142.2; IR: (cm^{-1}) ν 3312, 3084, 2925, 2854, 2825, 2117, 1465, 1412, 1375, 1157, 1107, 1059, 1002, 924, 864, 721, 628; Anal. calcd for $C_{19}H_{34}O$: C 81.95; H 12.31. found: C 81.93 H 12.56.

(3-methoxyhept-1-en-6-yn-3-yl)benzene (24)

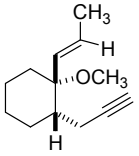


24

Yield: 67%. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.90-1.95 (m, 2H), 2.15-2.27 (m, 3H), 3.14 (s, 3H), 5.27-5.36 (m, 2H), 5.82-5.91 (dd, *J* = 10.6, 17.6 Hz, 1H), 7.21-7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ =

12.9, 34.8, 50.5, 68.0, 80.7, 84.7, 115.6, 126.5, 127.1, 128.1, 140.9, 142.3; IR: (cm^{-1}) ν 3301, 2939, 2827, 1492, 1446, 1092, 1077, 899, 724, 700, 633; HRMS calcd for $C_{14}H_{16}O$: m/z 200.1201. found 200.1201.

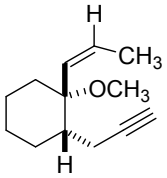
Synthesis of compound 26



26

Yield : 81%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21-1.55 (m, 6H), 1.67-1.76 (m, 4H), 1.82-1.96 (m, 3H), 2.00-2.11 (m, 1H), 2.45-2.53 (m, 1H), 3.07 (s, 3H), 5.30-5.36 (m, 1H), 5.45 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.3, 19.0, 21.5, 25.6, 27.0, 31.6, 45.9, 49.4, 68.5, 77.1, 85.5, 126.4, 134.5; IR: (cm^{-1}) ν 3310, 2935, 2856, 2825, 2117, 1448, 1075, 625; HRMS calcd for $C_{13}H_{20}O$: m/z 192.1514 found 192.1513.

Synthesis of compound 28

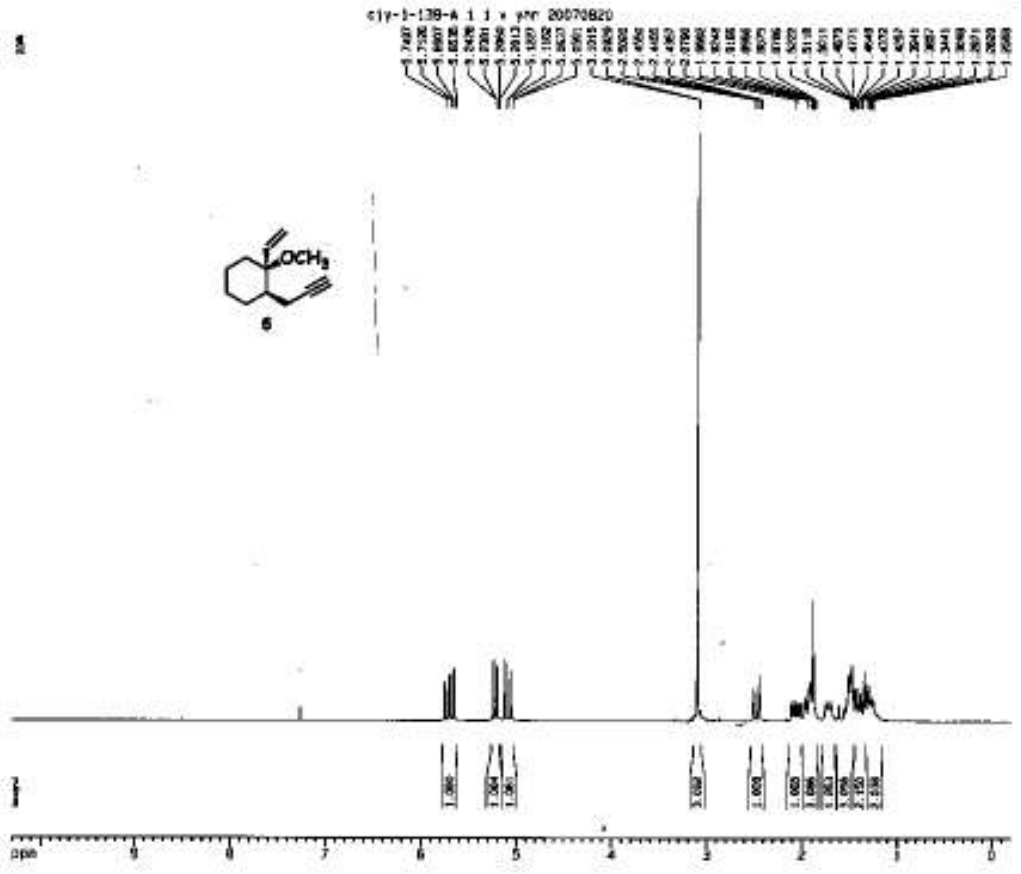


28

Yield : 84%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23-1.71 (m, 7H), 1.76 (dd, *J* = 7.2, 1.8 Hz, 3H), 1.85-2.02 (m, 3H), 2.07-2.19 (m, 1H), 2.48 (dt, *J* = 16.7, 2.9 Hz, 1H), 3.10 (s, 3H), 5.00-5.07 (m, 1H), 5.51-5.63 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.6, 19.1, 21.5, 25.1, 26.4, 33.6, 44.8, 49.5, 68.5, 79.3, 85.4, 127.3, 132.2; IR: (cm^{-1}) ν 3309, 2934, 2857, 2826, 2117, 1652, 1448, 1161, 1078, 743; HRMS calcd for $C_{13}H_{20}O$: m/z 192.1514 found 192.1513.

References:

[1] J.-E. Kang, H.-B. Kim, J.-W. Lee, S. Shin, *Org. Lett.* 2006, *8*, 3537.
[2] X. Li, R. E. Kyne, T. V. Ovaska, *J. Org. Chem.* 2007, *72*, 6624 .
[3] C. E. McIntosh, I. Matinez, T. V. Ovaska, *synlett* 2004, 2579.
[4] P. A. Wender, H. Rieck, M. Fuji, *J. Am. Chem. Soc.* 1998, *120*, 10976.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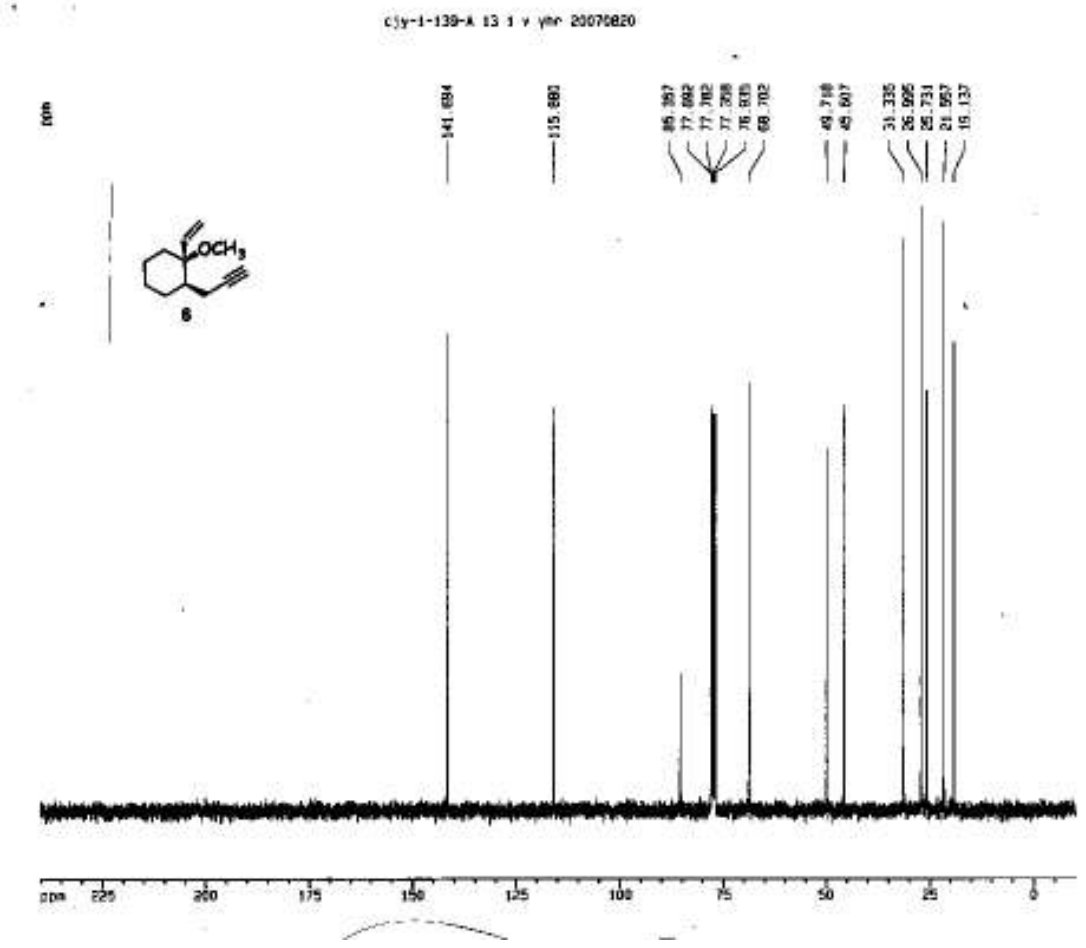
6
ppm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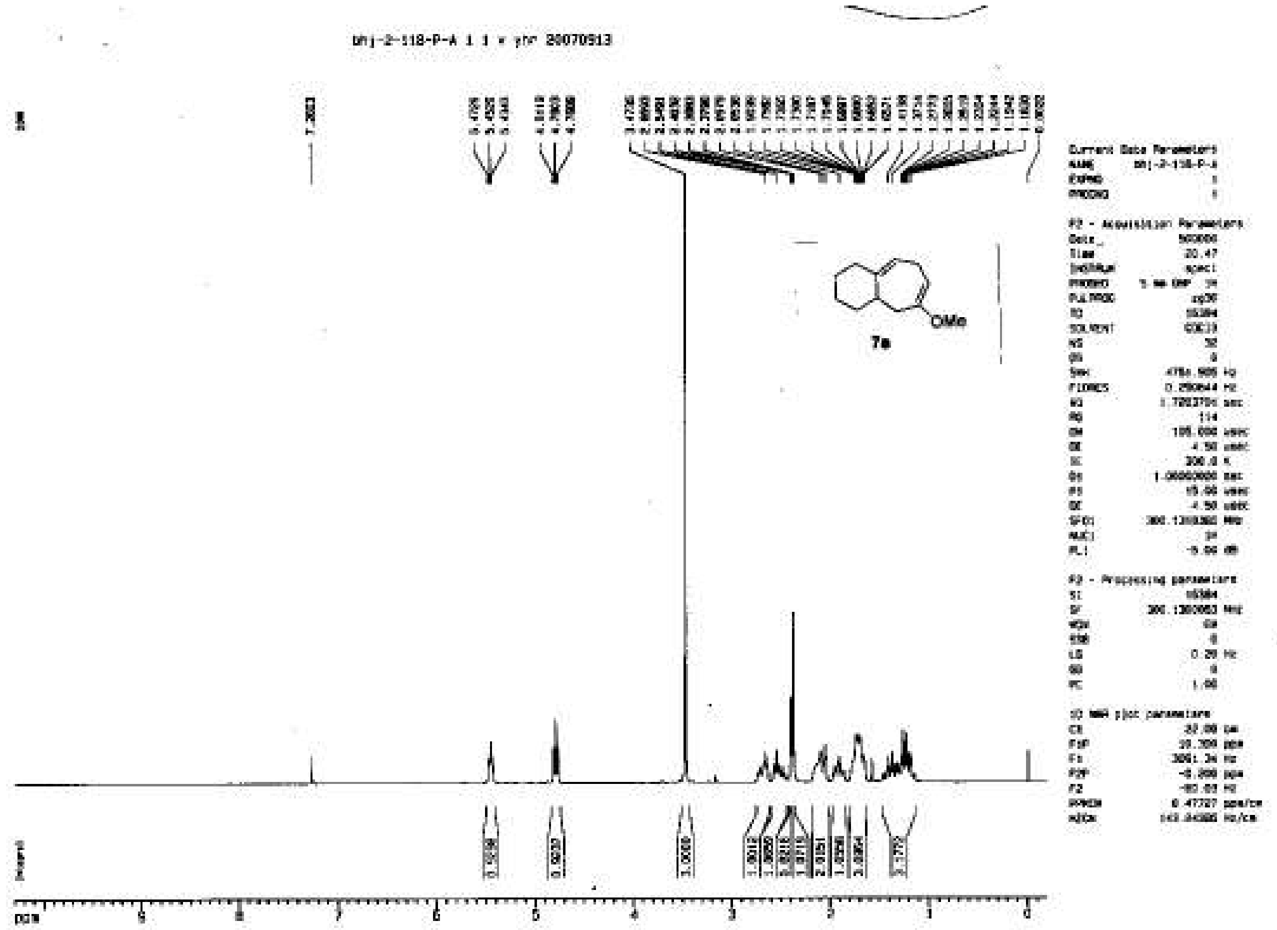
115.880
85.357
77.682
77.362
77.208
76.935
69.702
49.718
49.607
33.335
26.995
25.731
21.957
19.137
OCH3
6
ppm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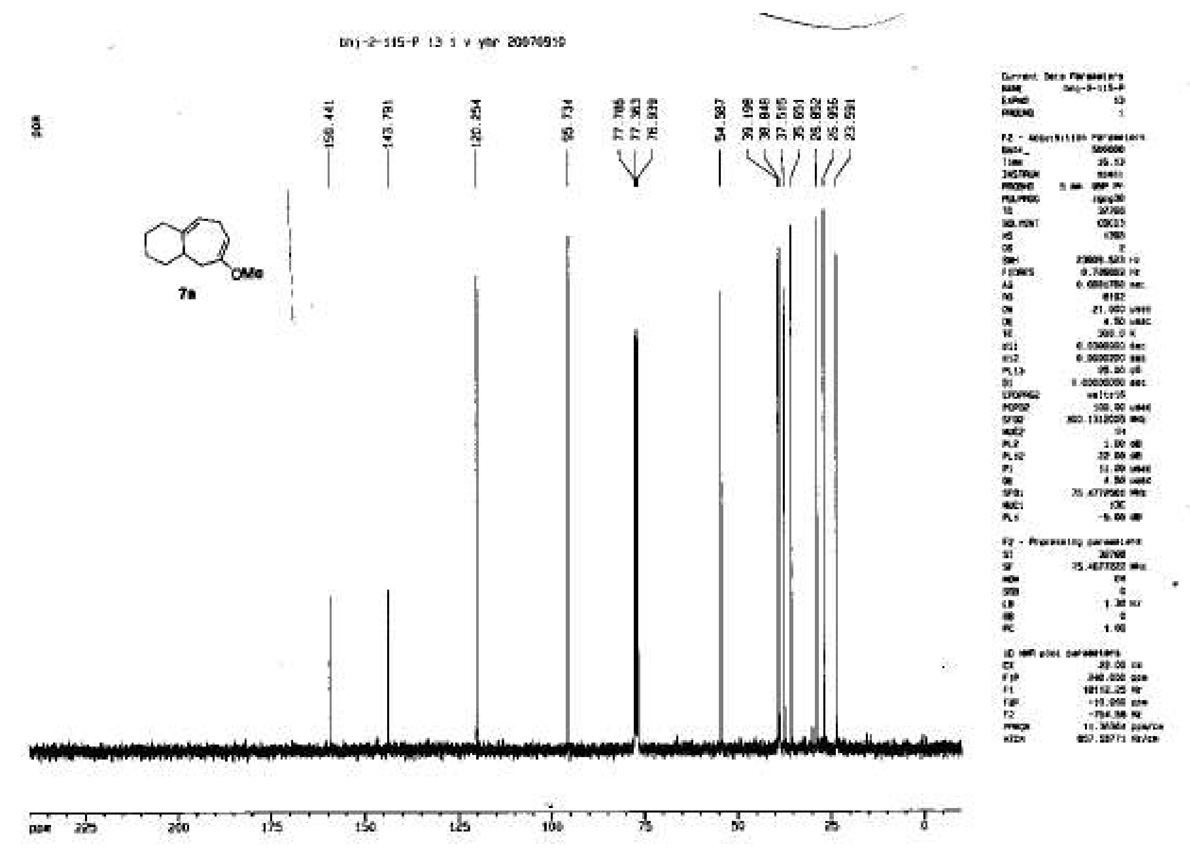
7a
ppm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143.791
120.254
95.734
77.786
77.363
76.939
54.587
39.198
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37.515
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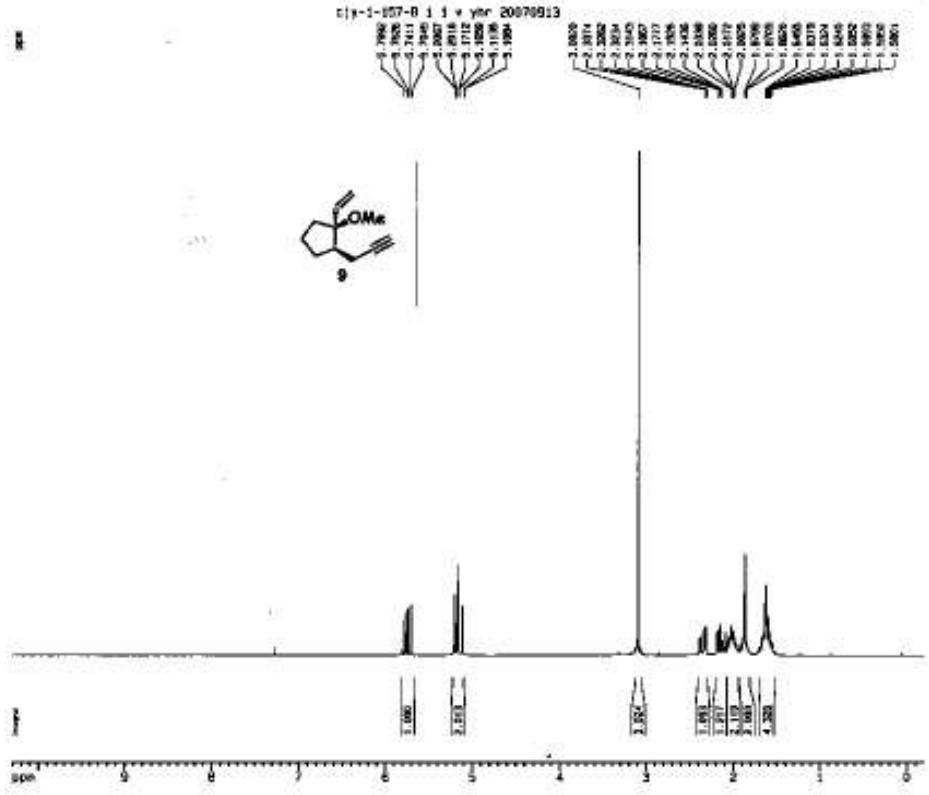
28.852
26.956
23.591
OMe
7a
ppm 225 200 175 150 125 100 75 50 25 0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9
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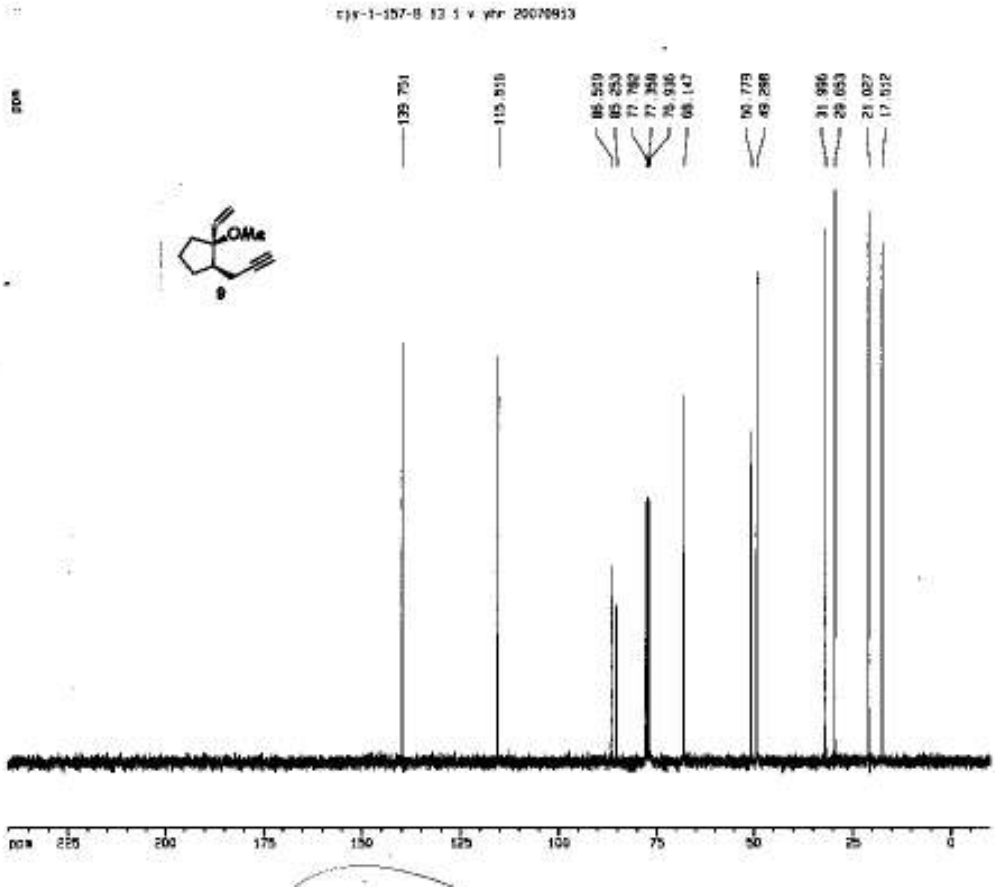
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29.053
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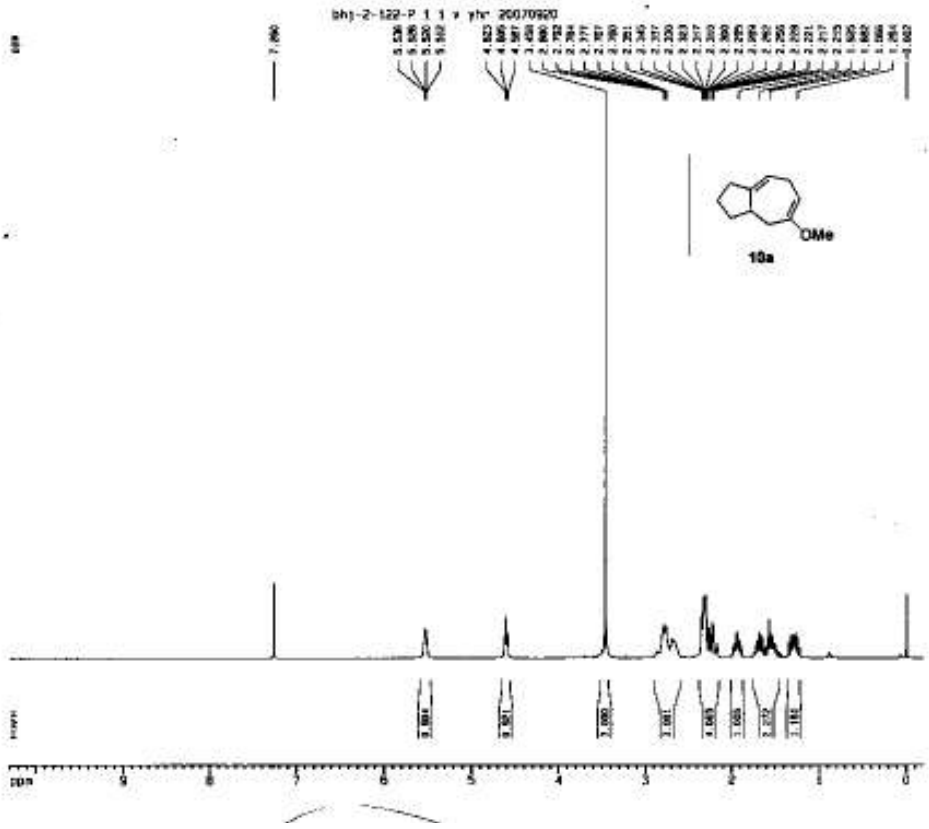
17.512
OMe
9
ppm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OMe
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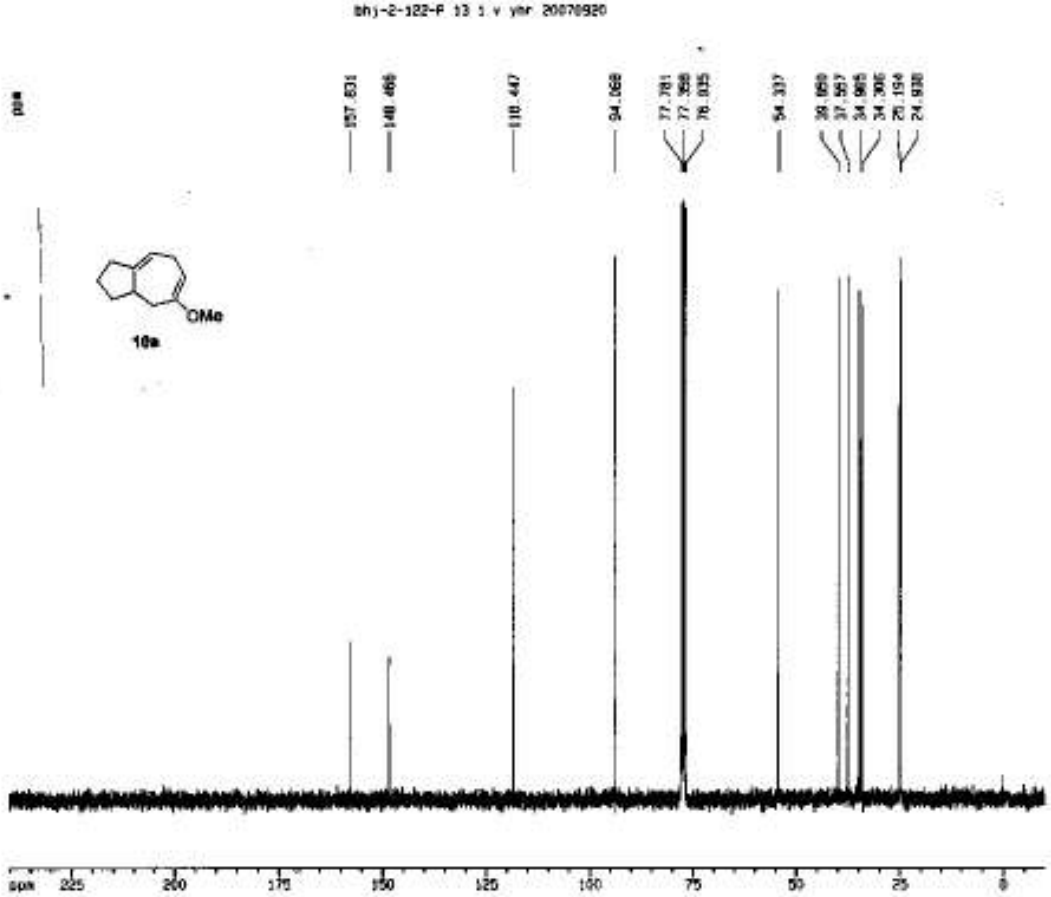
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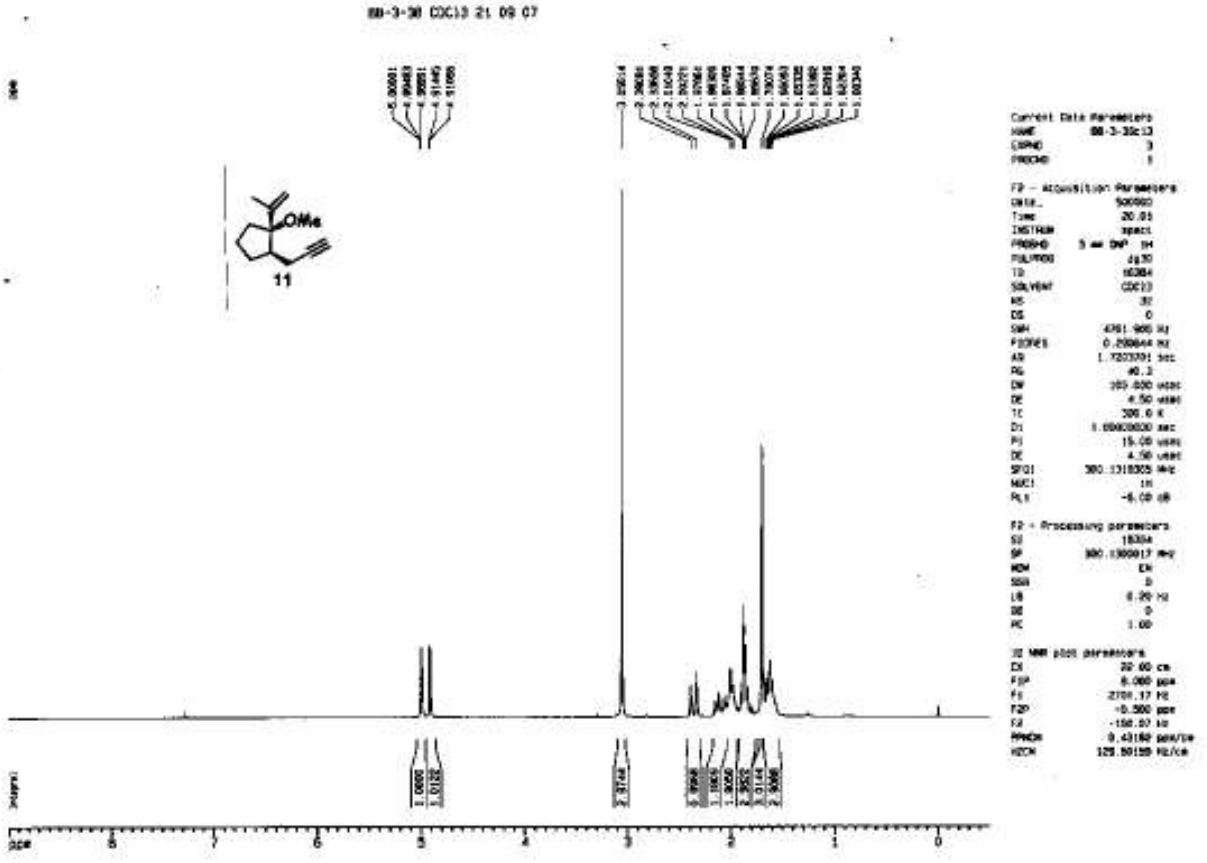
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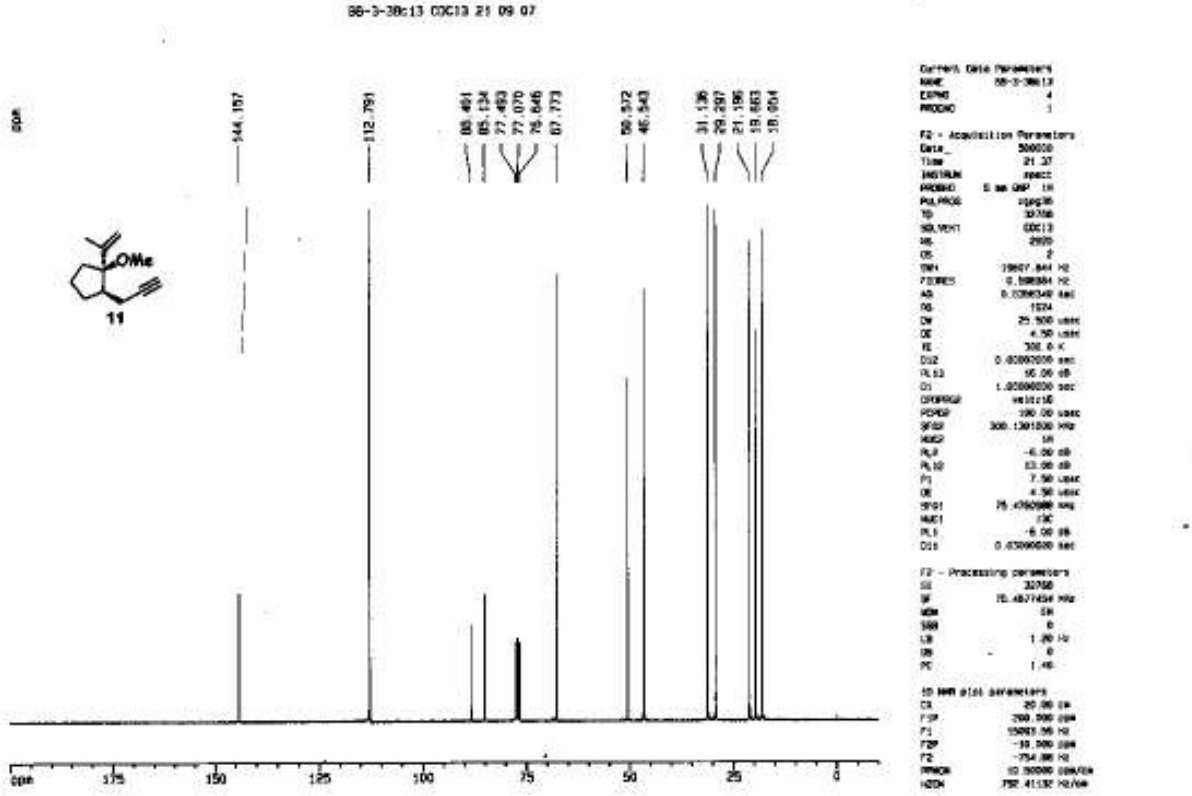
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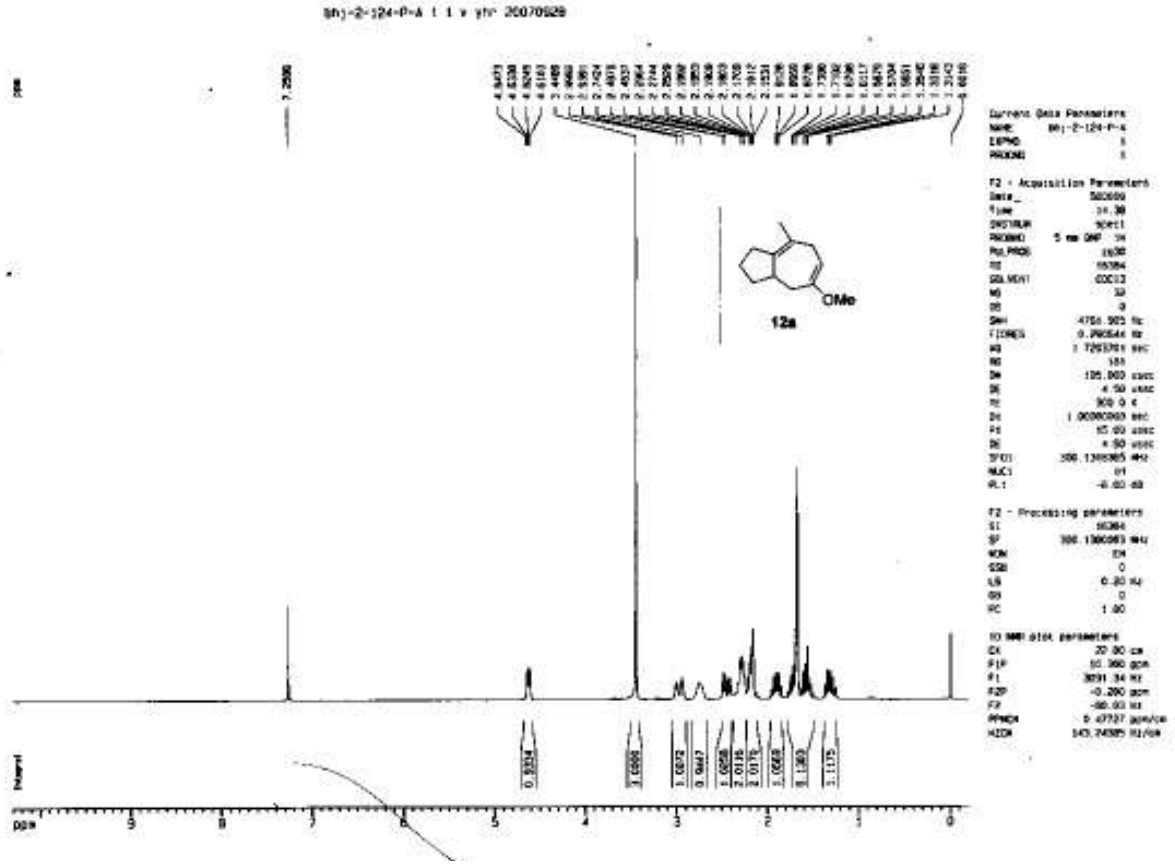
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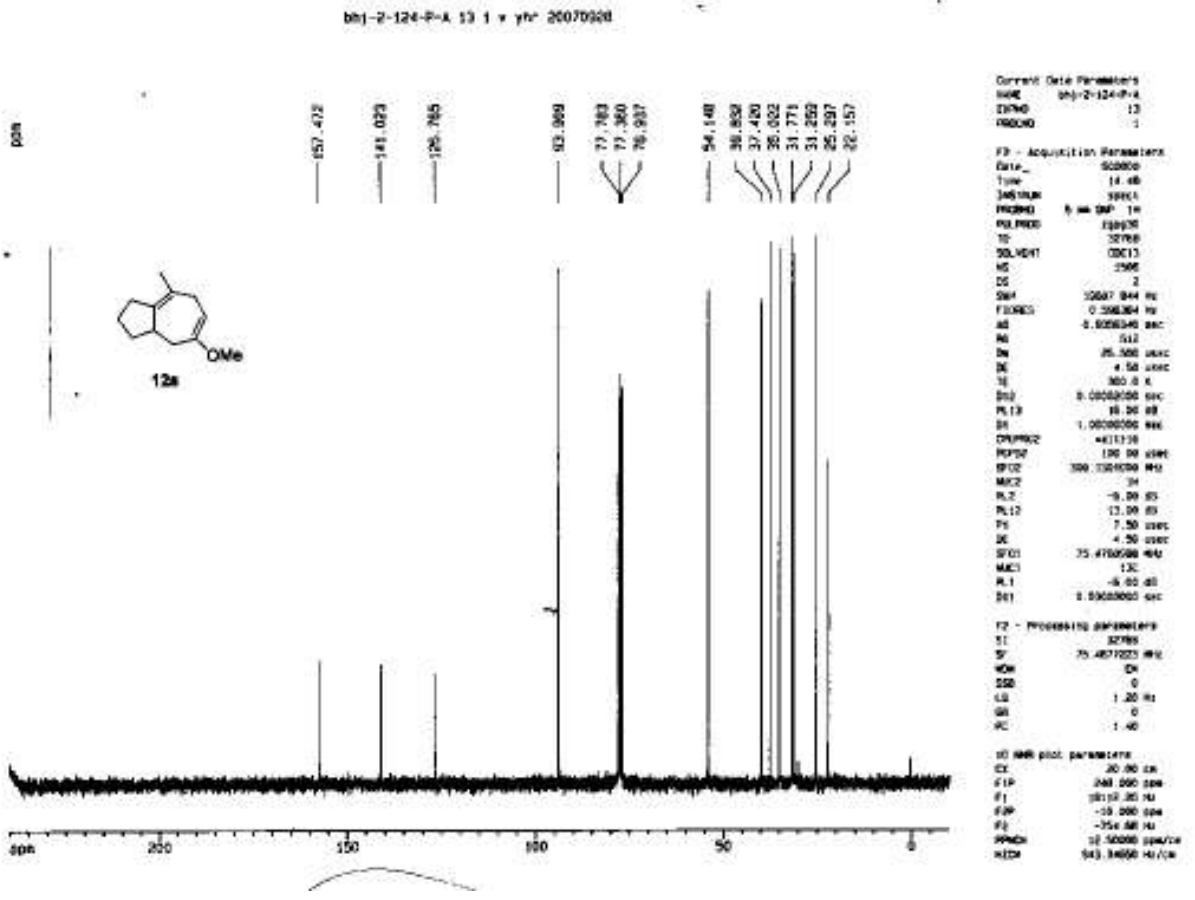
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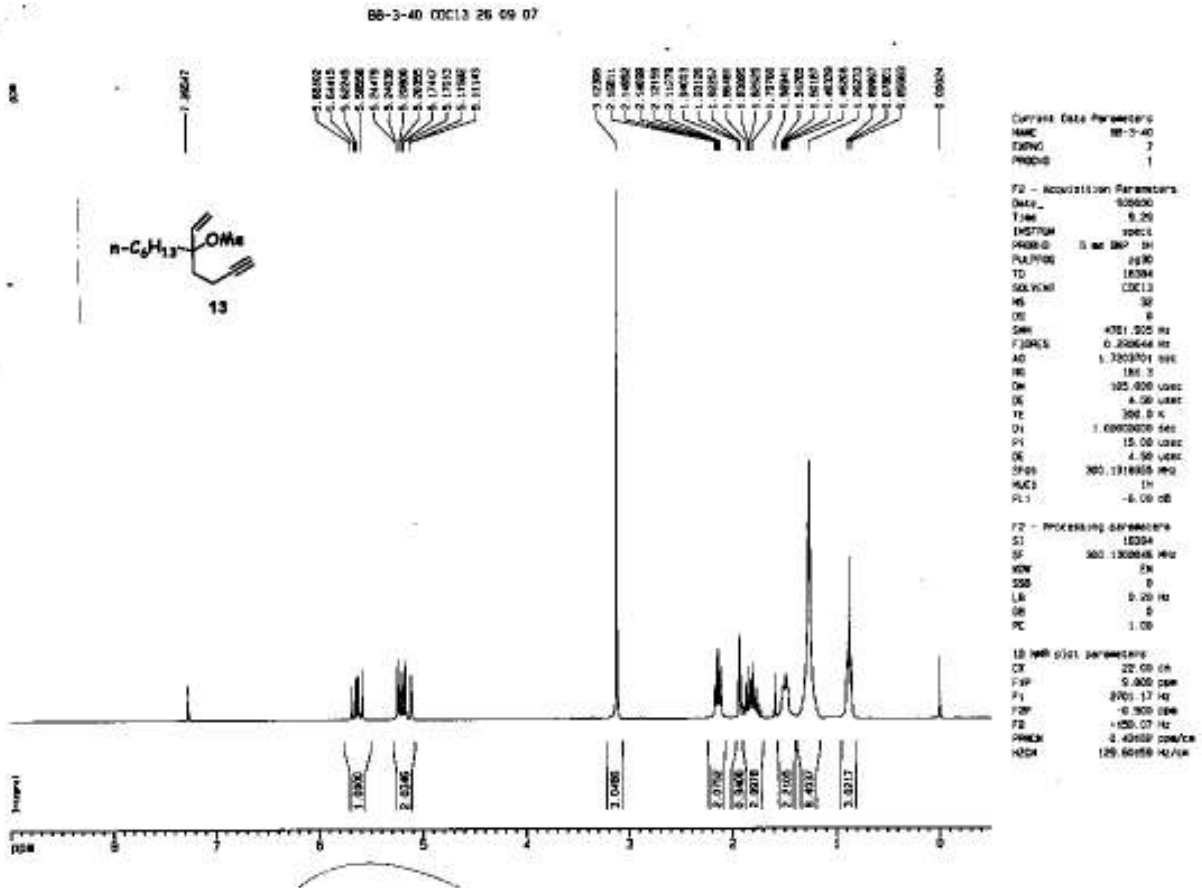
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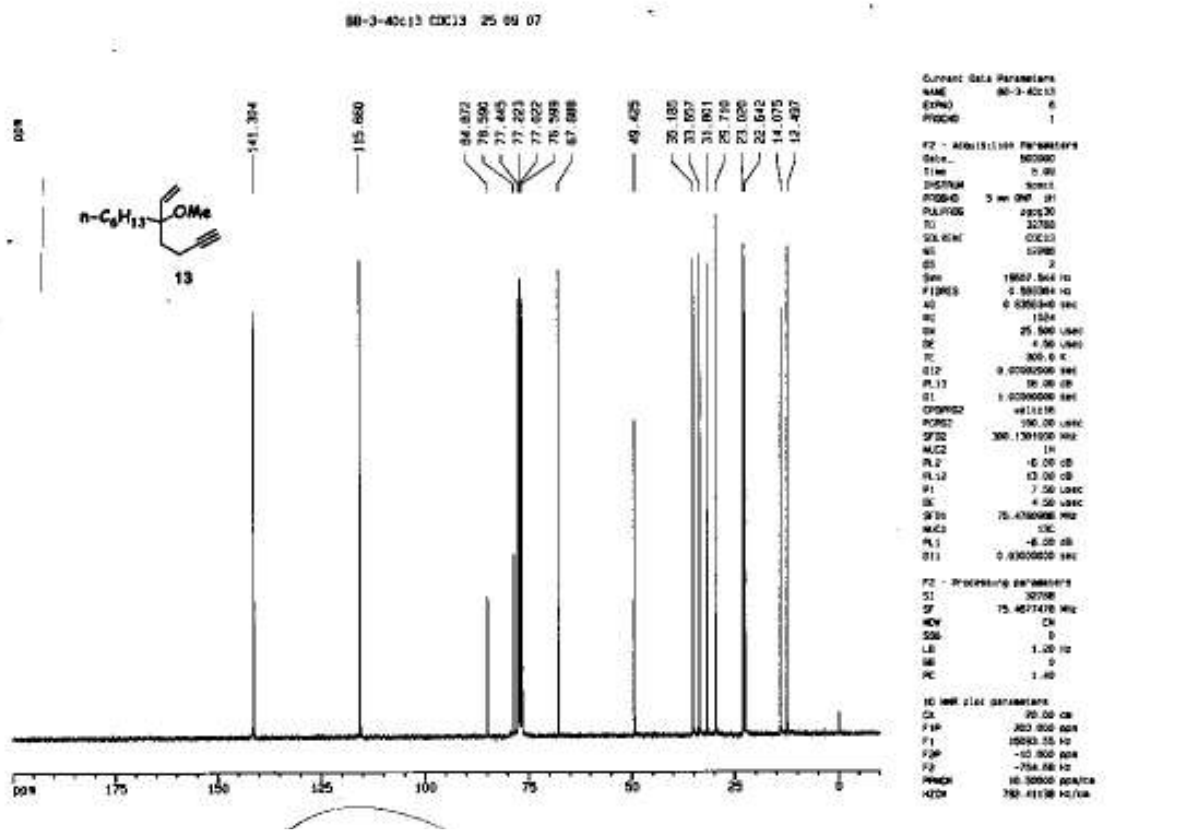
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13
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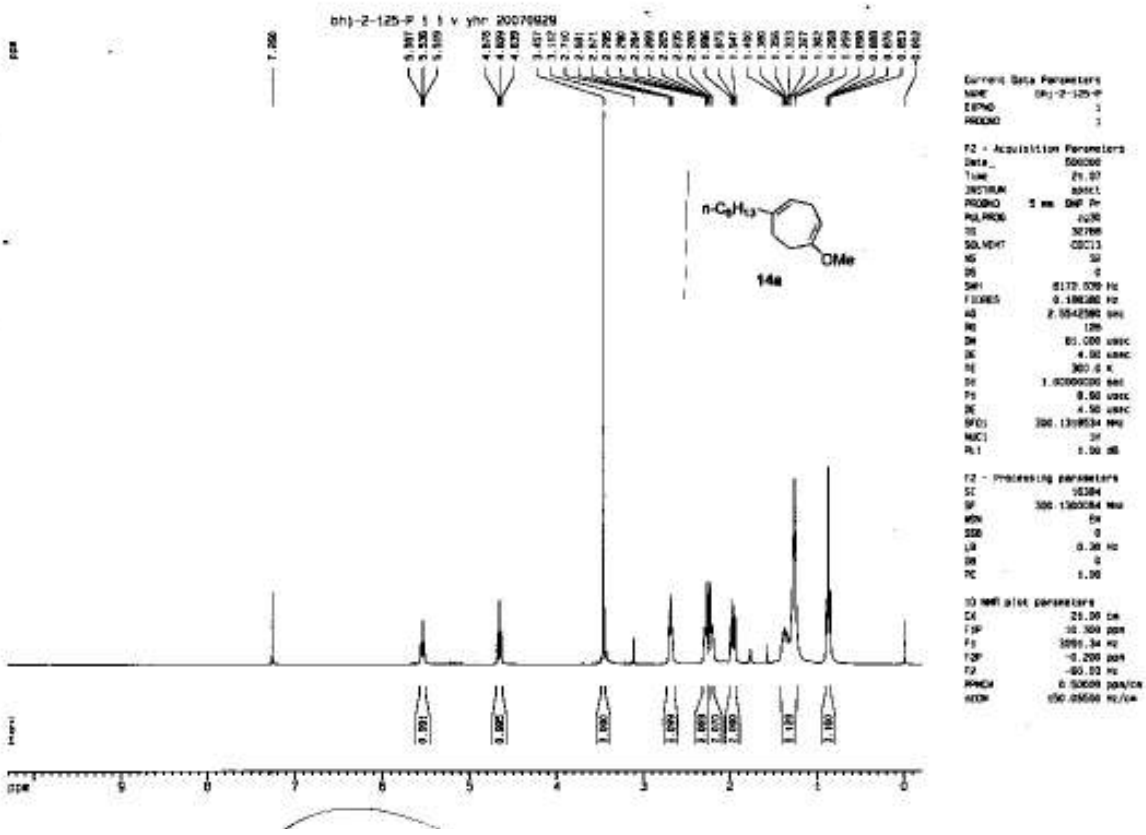
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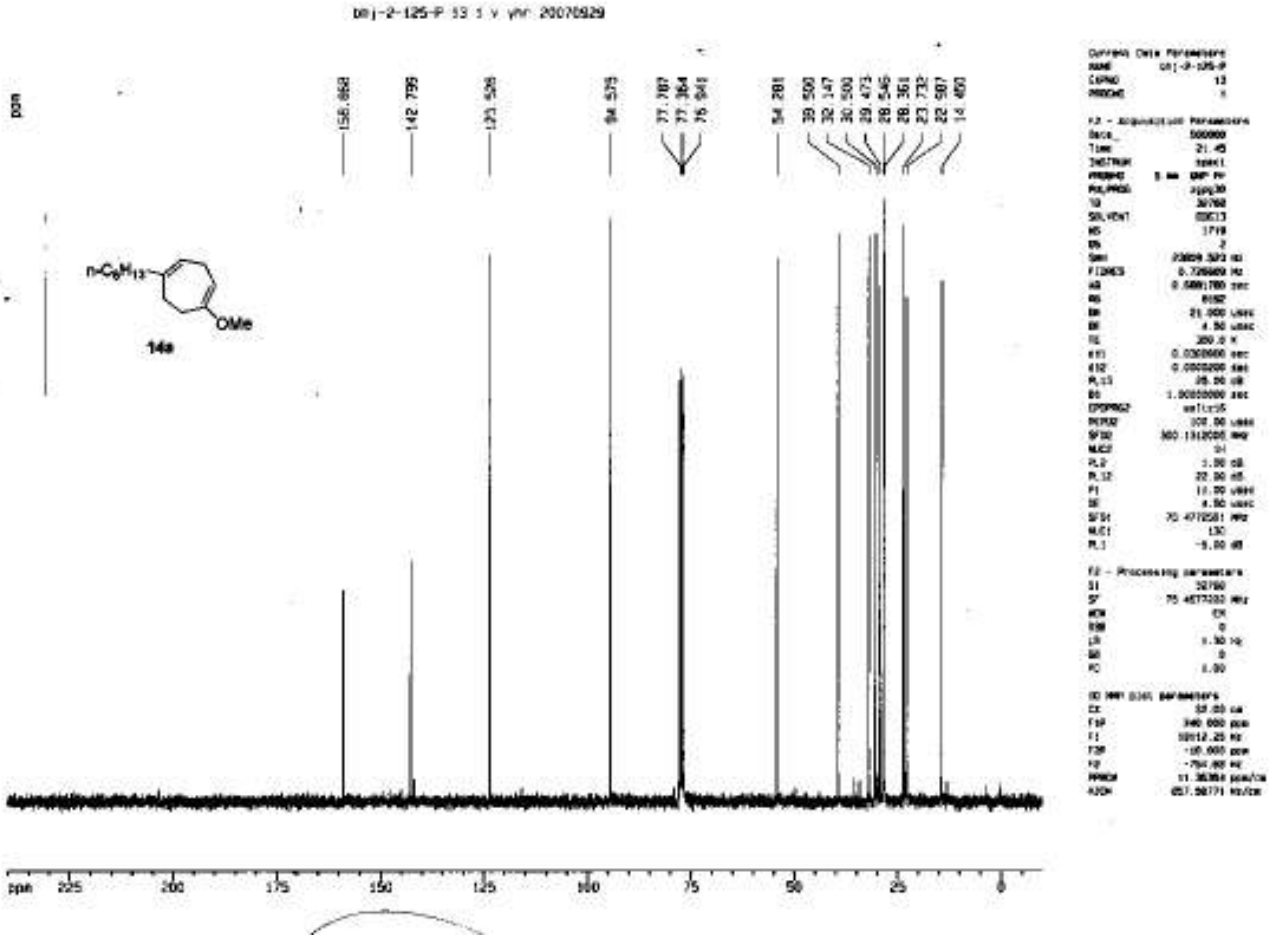
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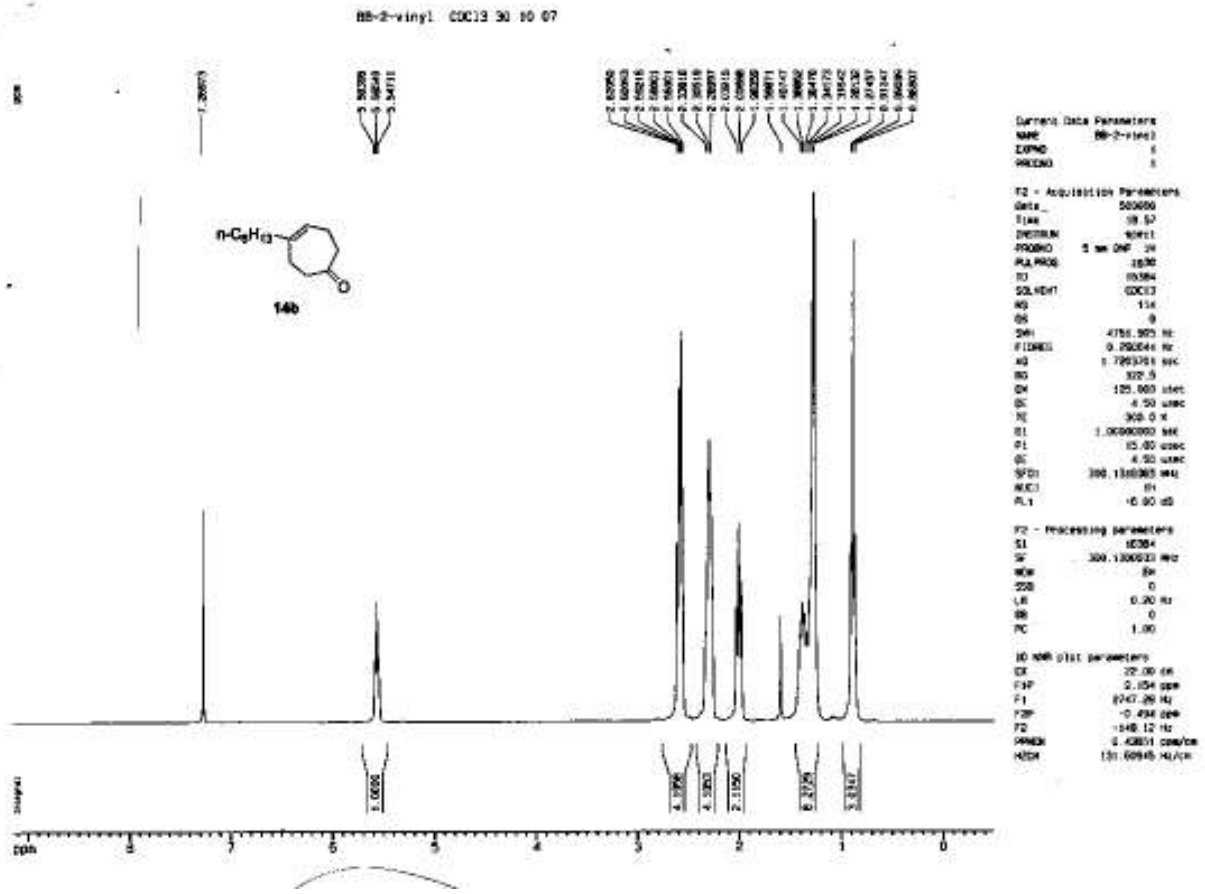
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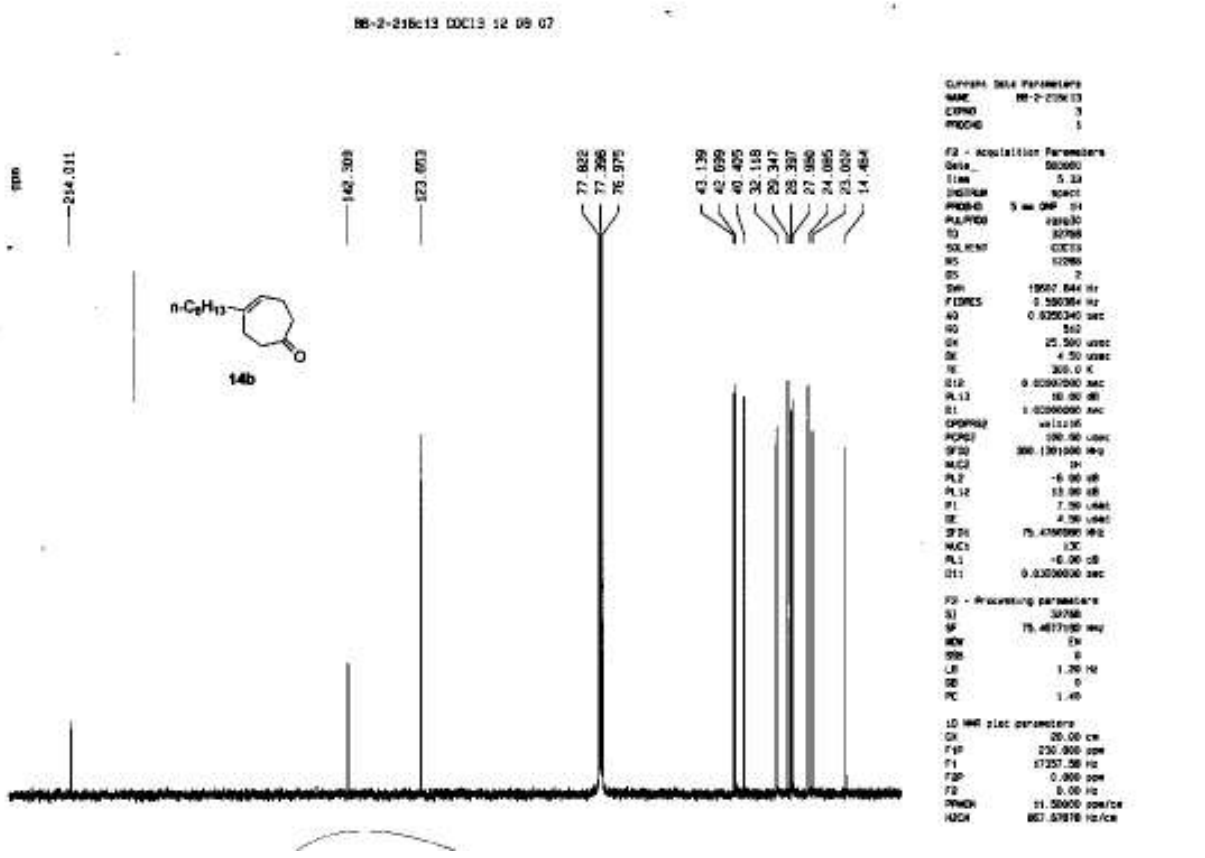
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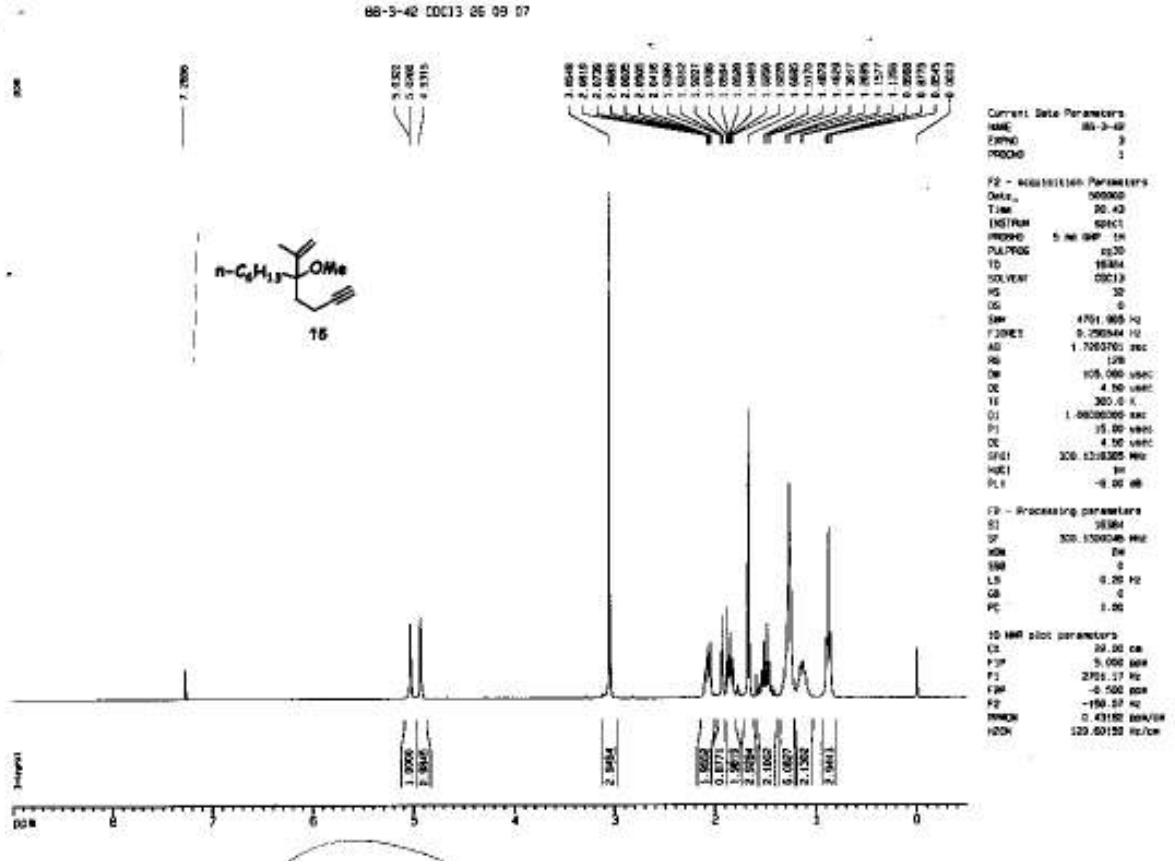
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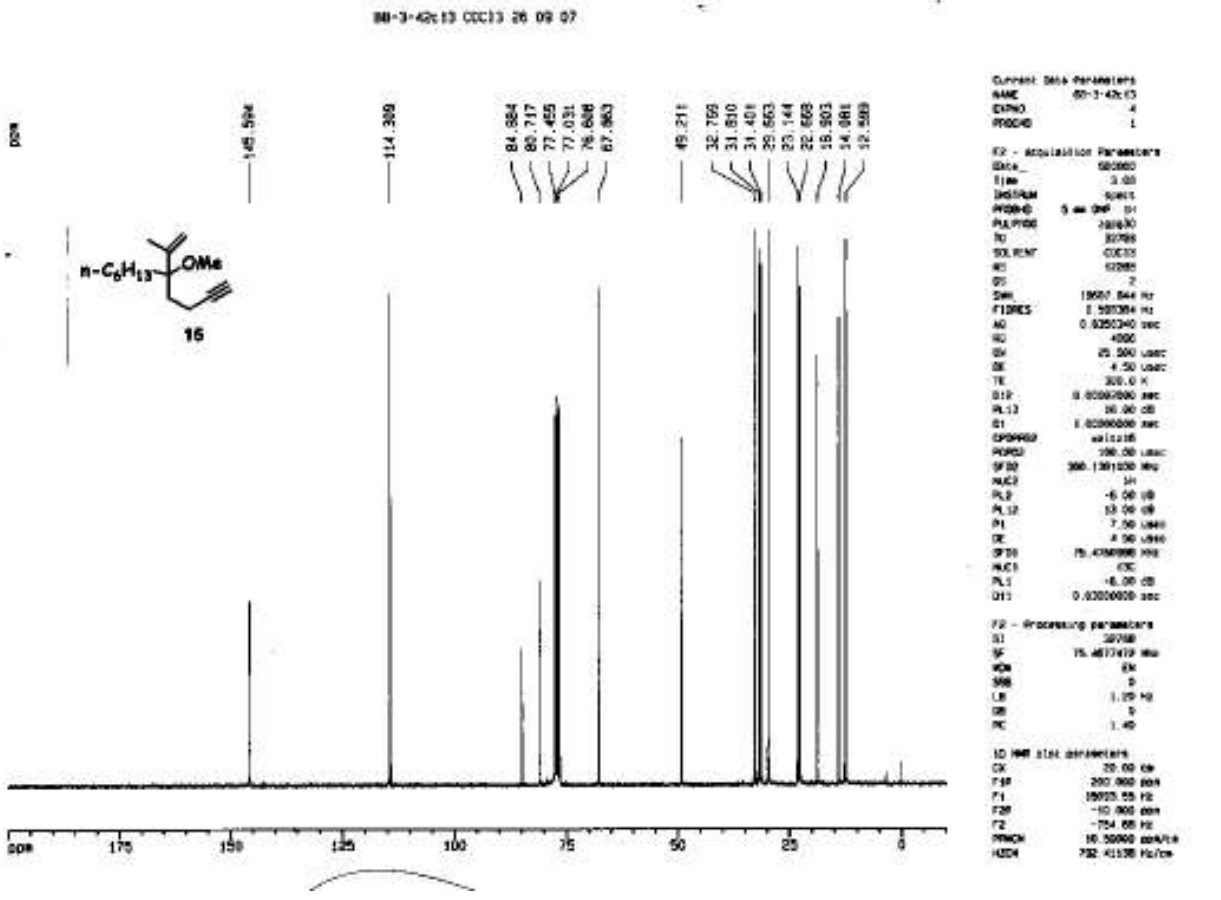
16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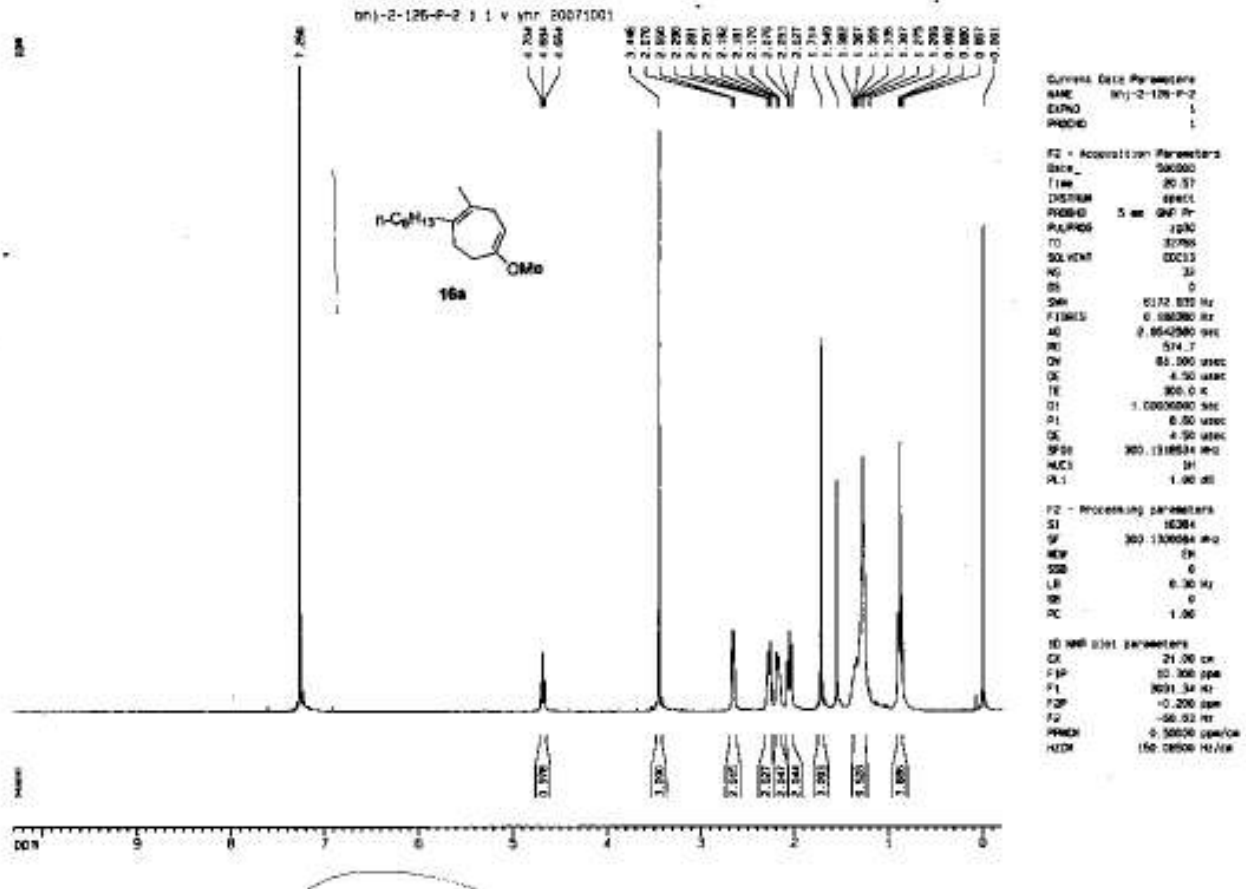
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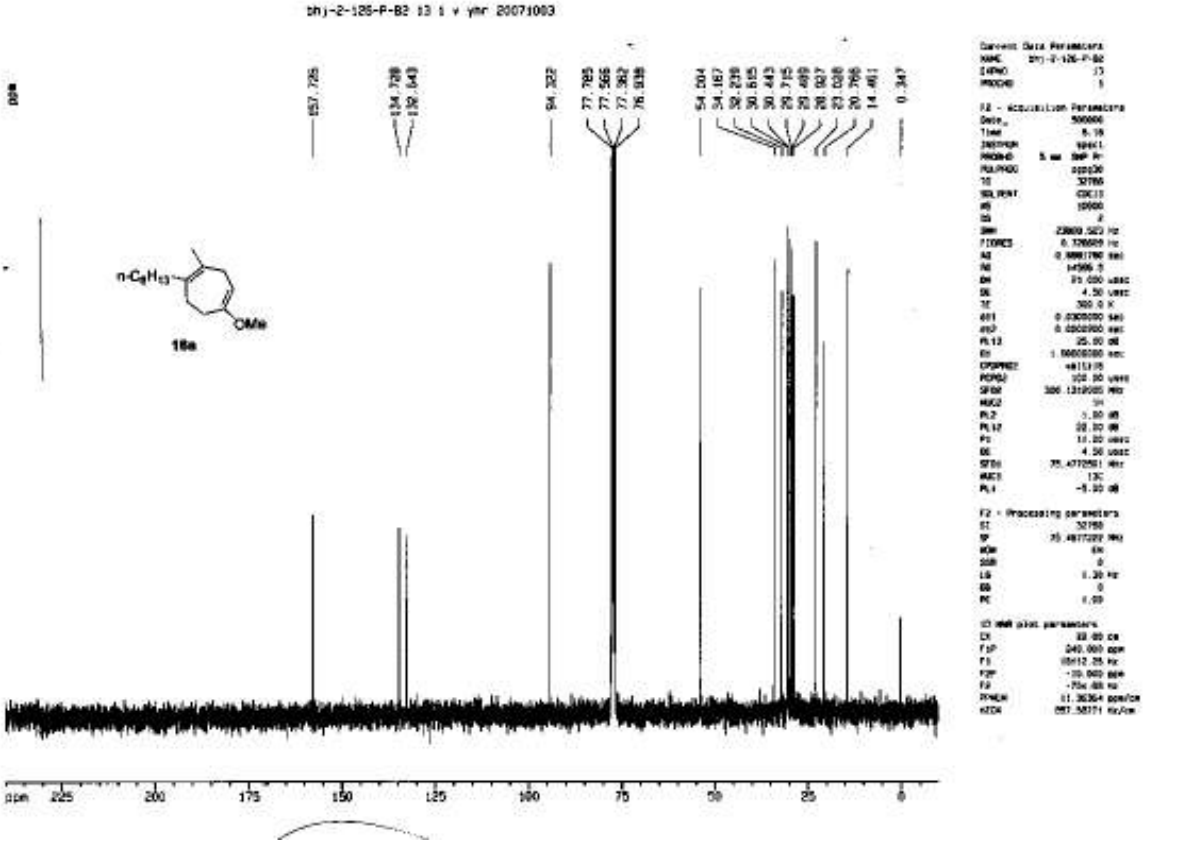
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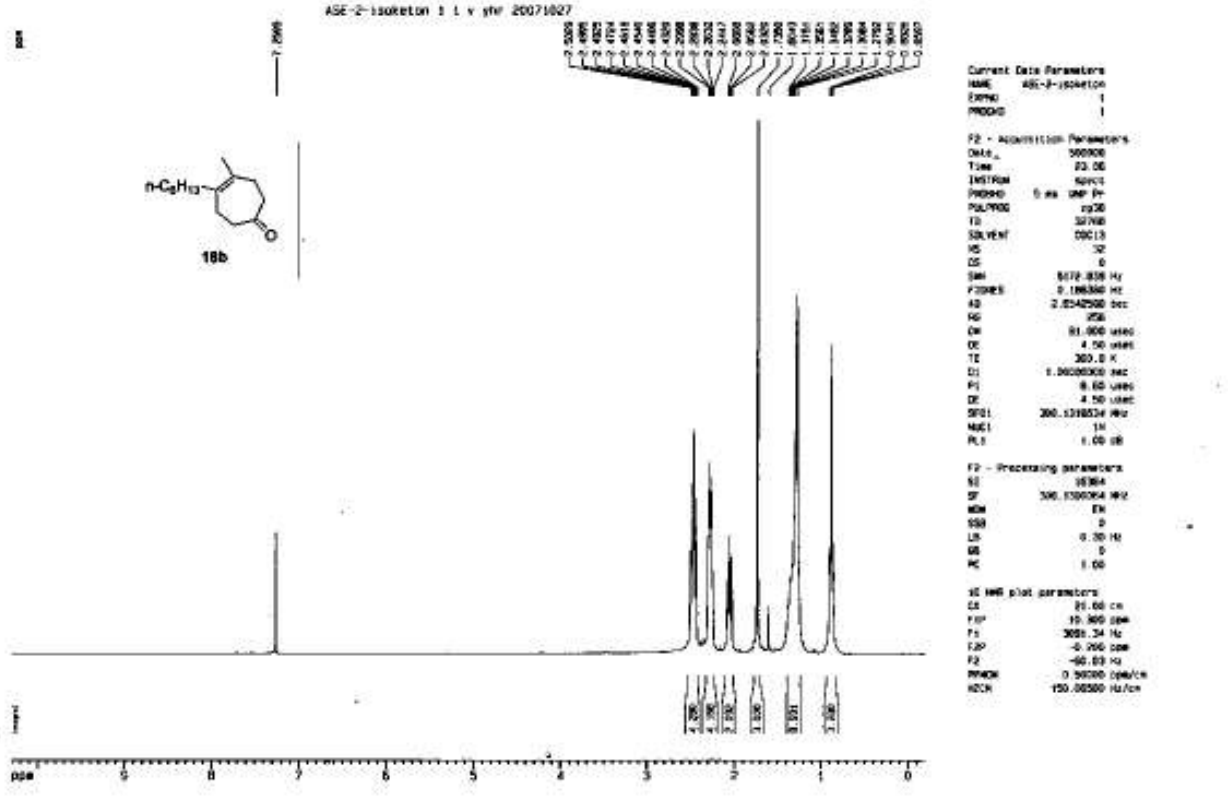
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16b
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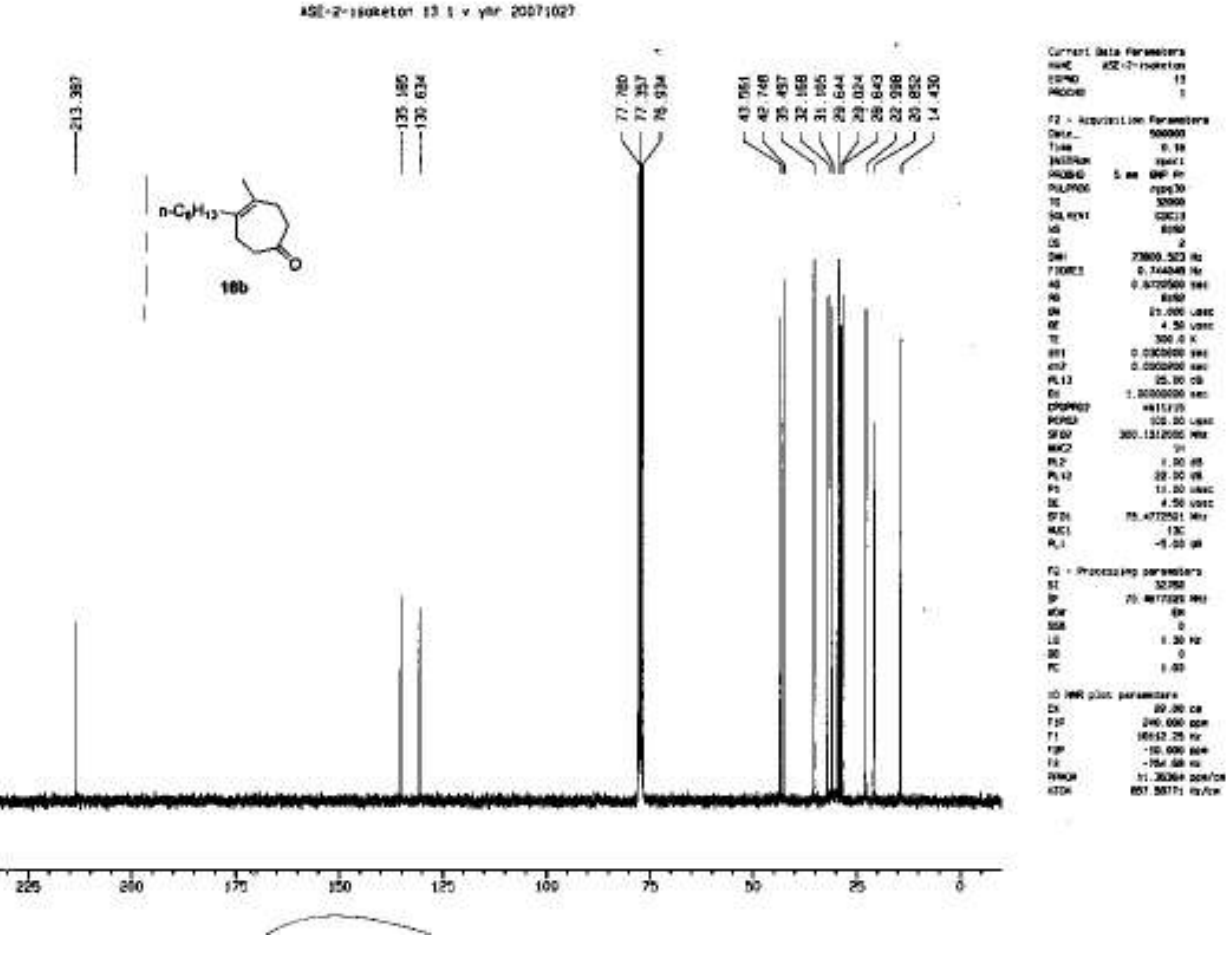
2
3
4
5
6
7
8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31.165
29.644
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175
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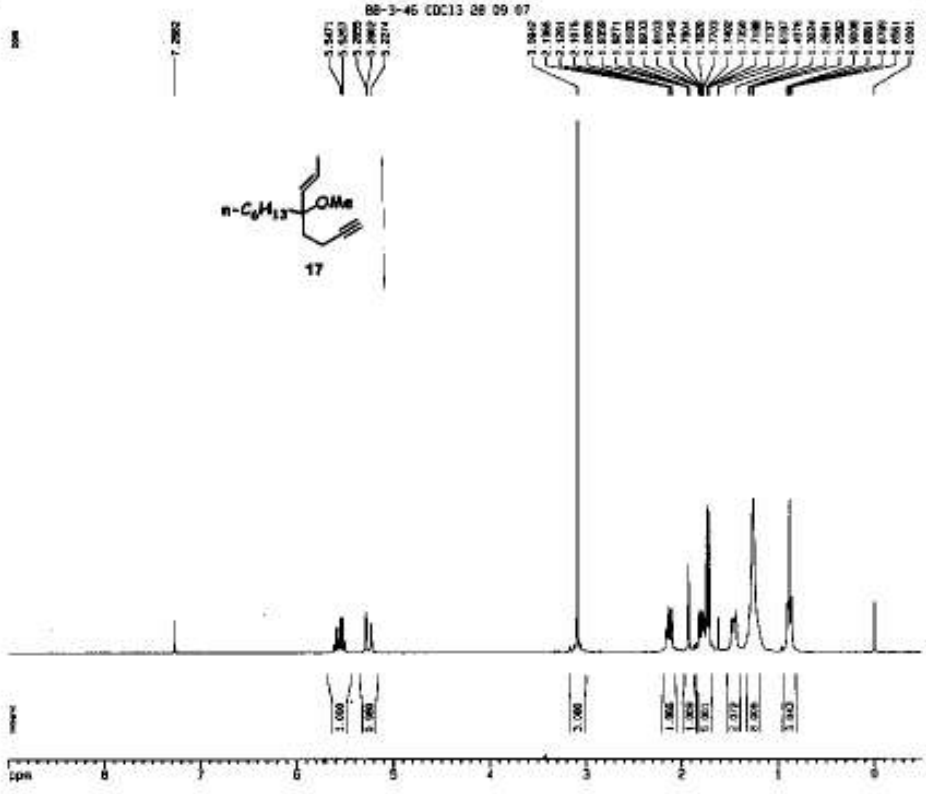
225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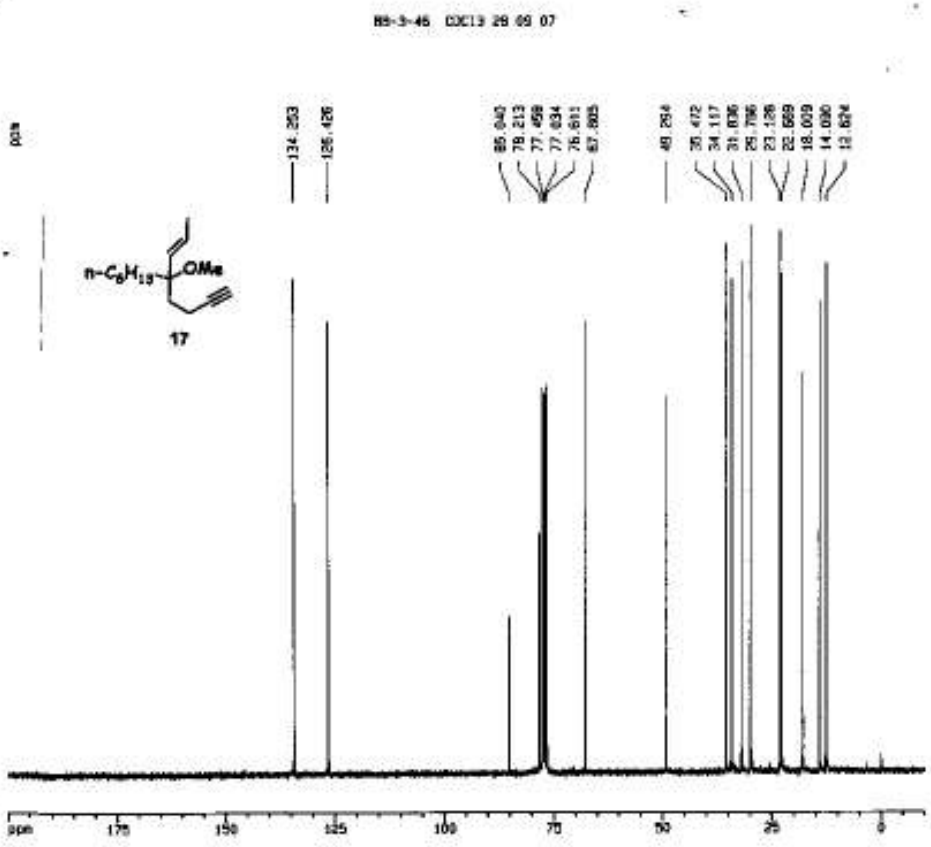
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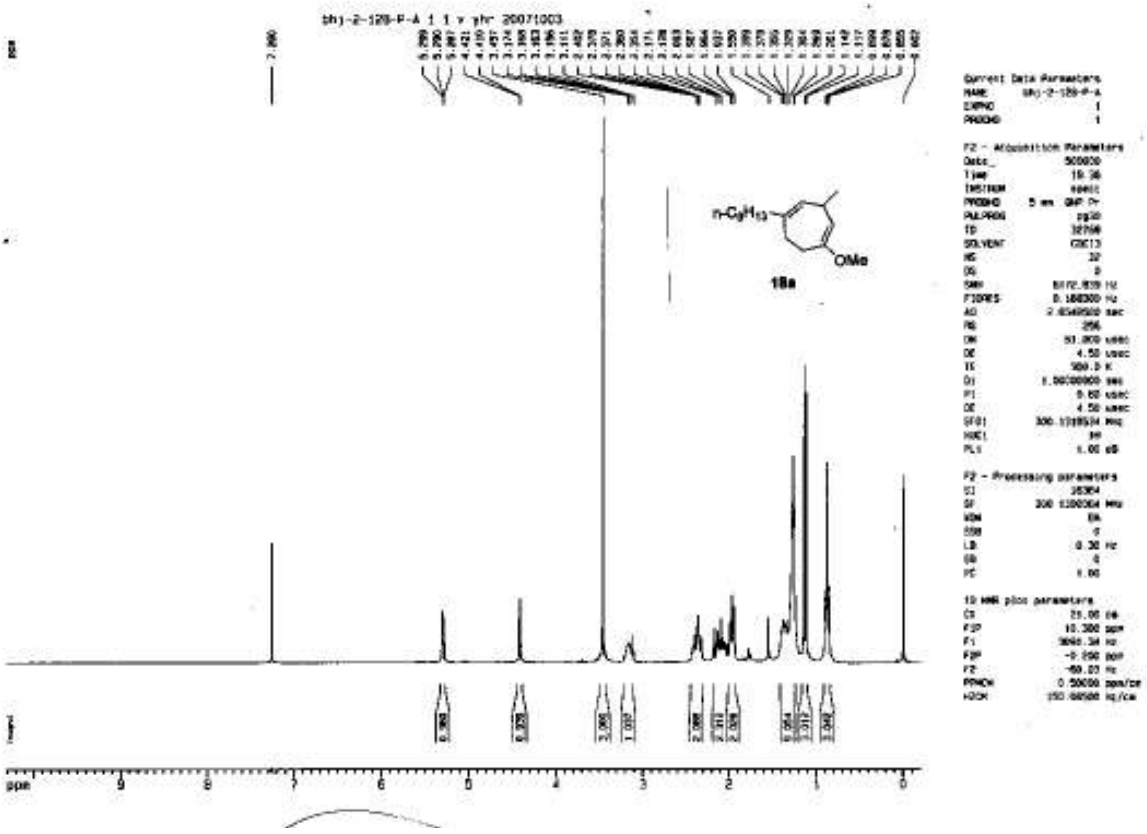
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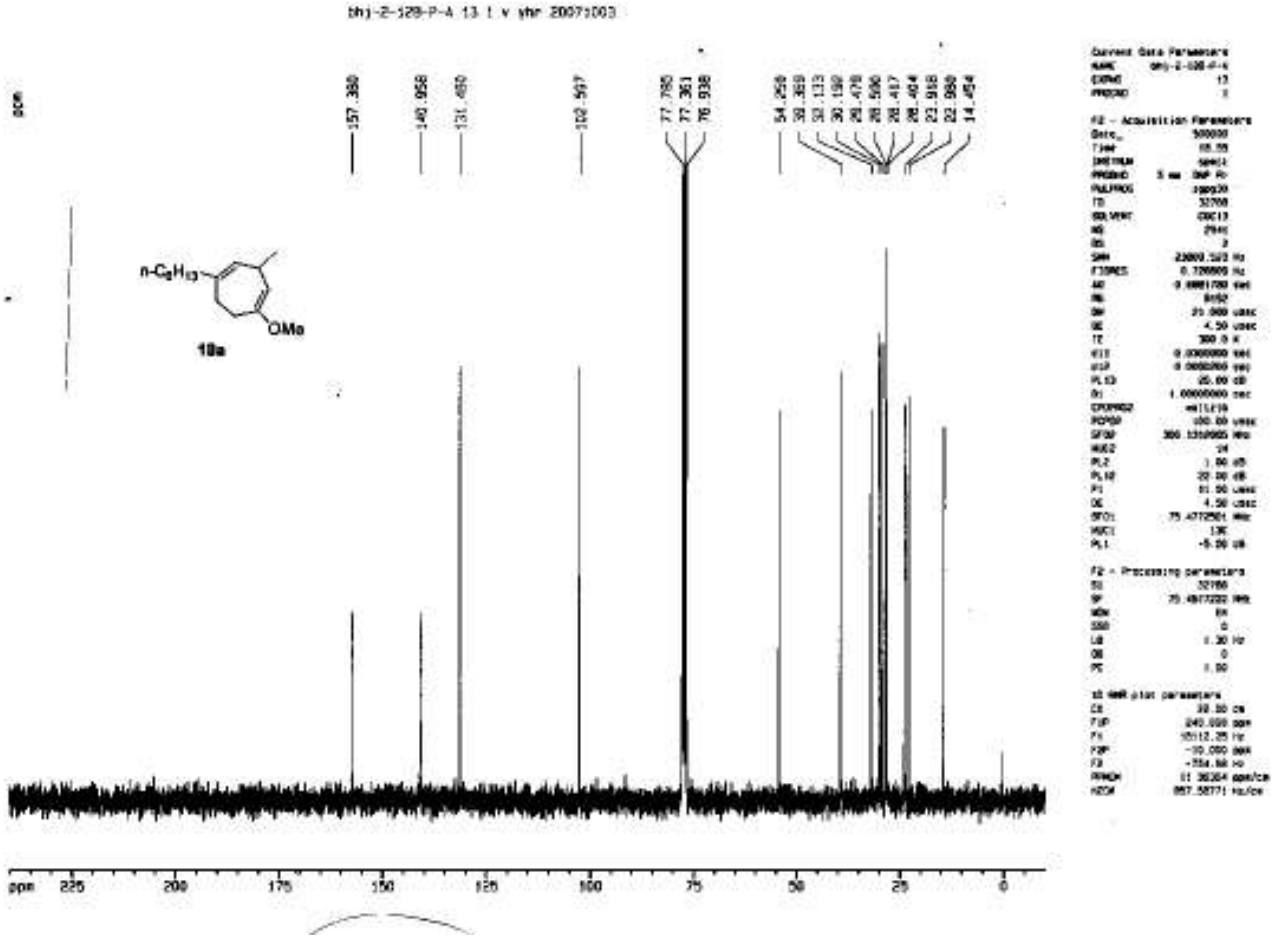
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OMe
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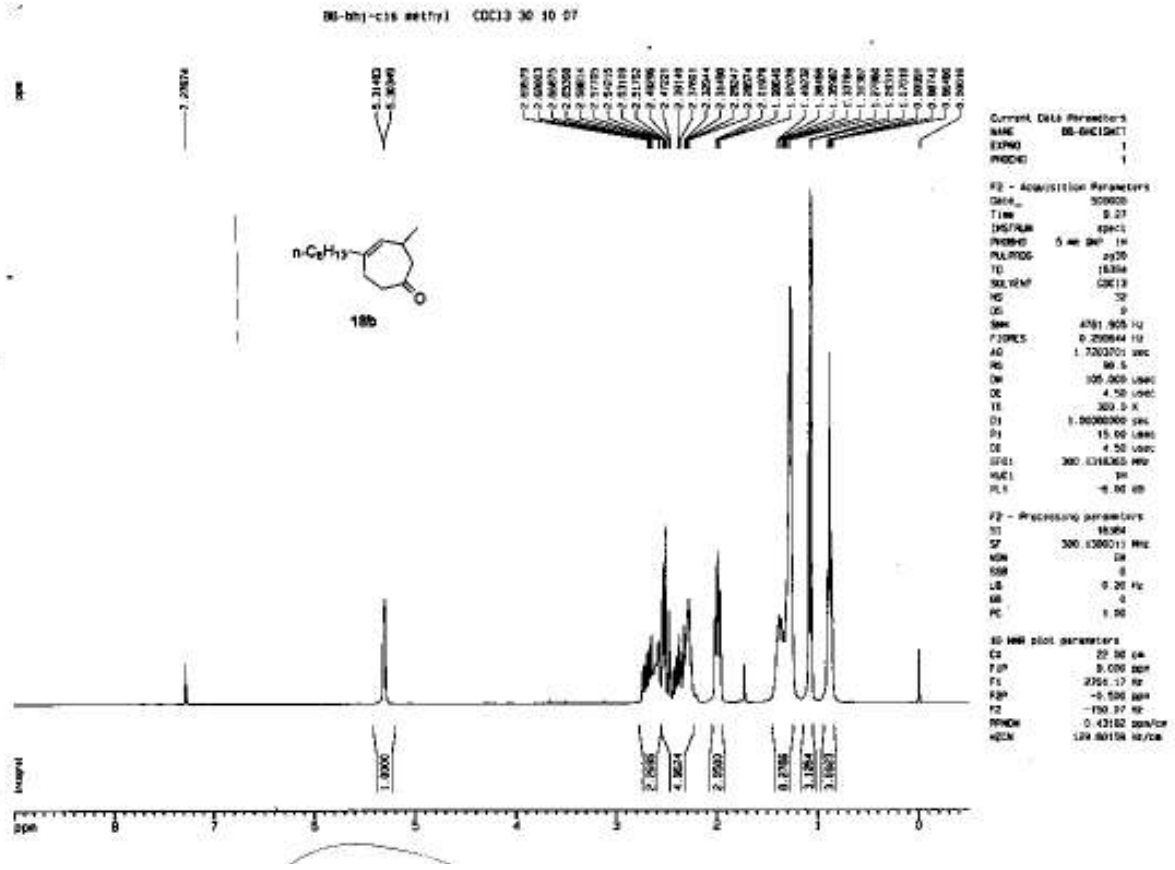
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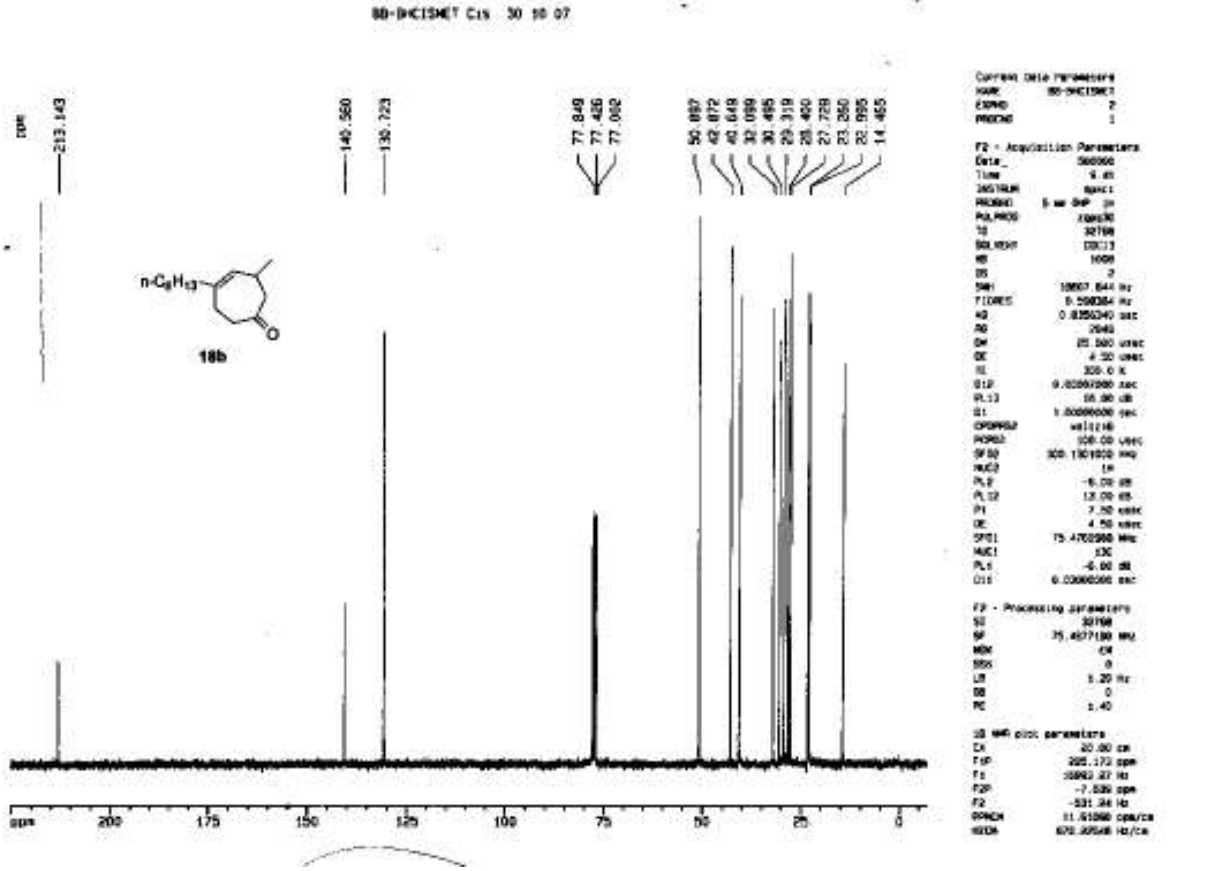
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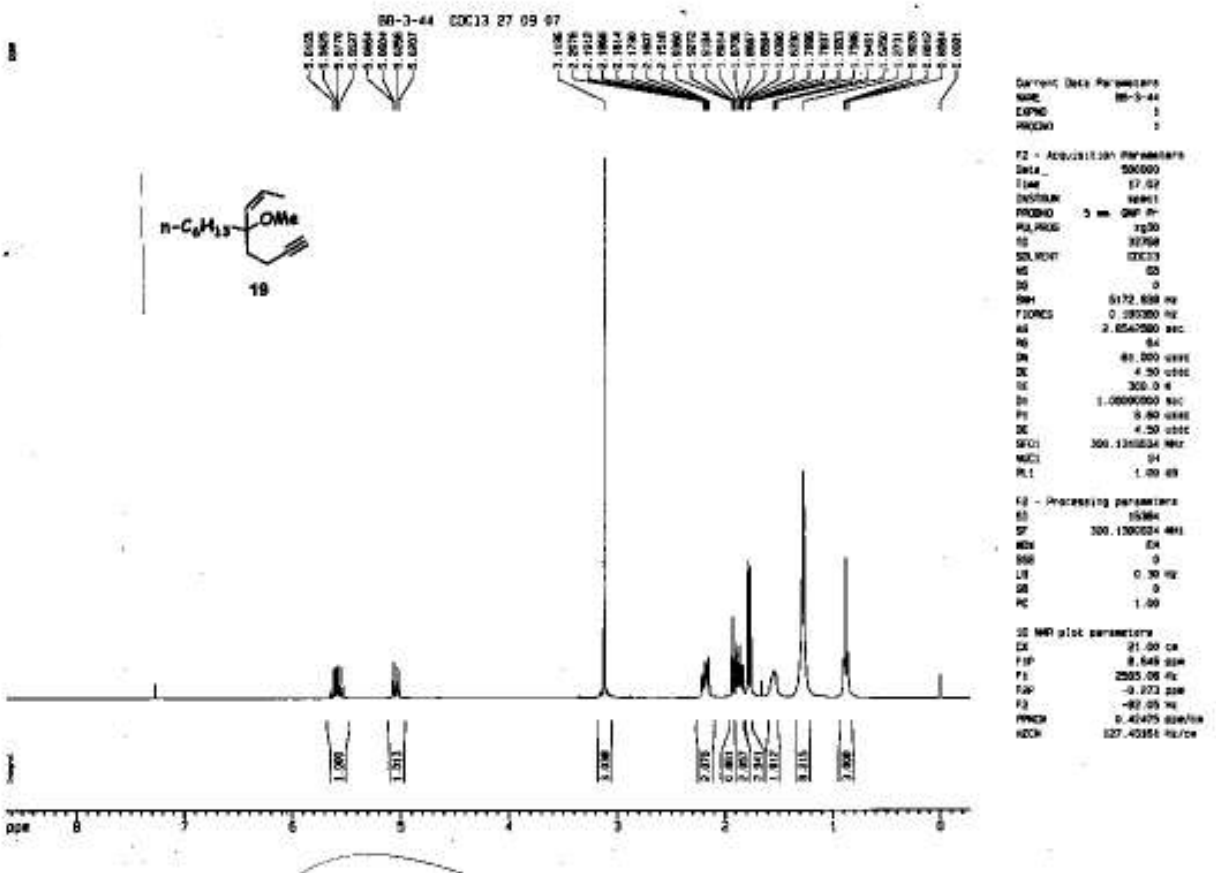
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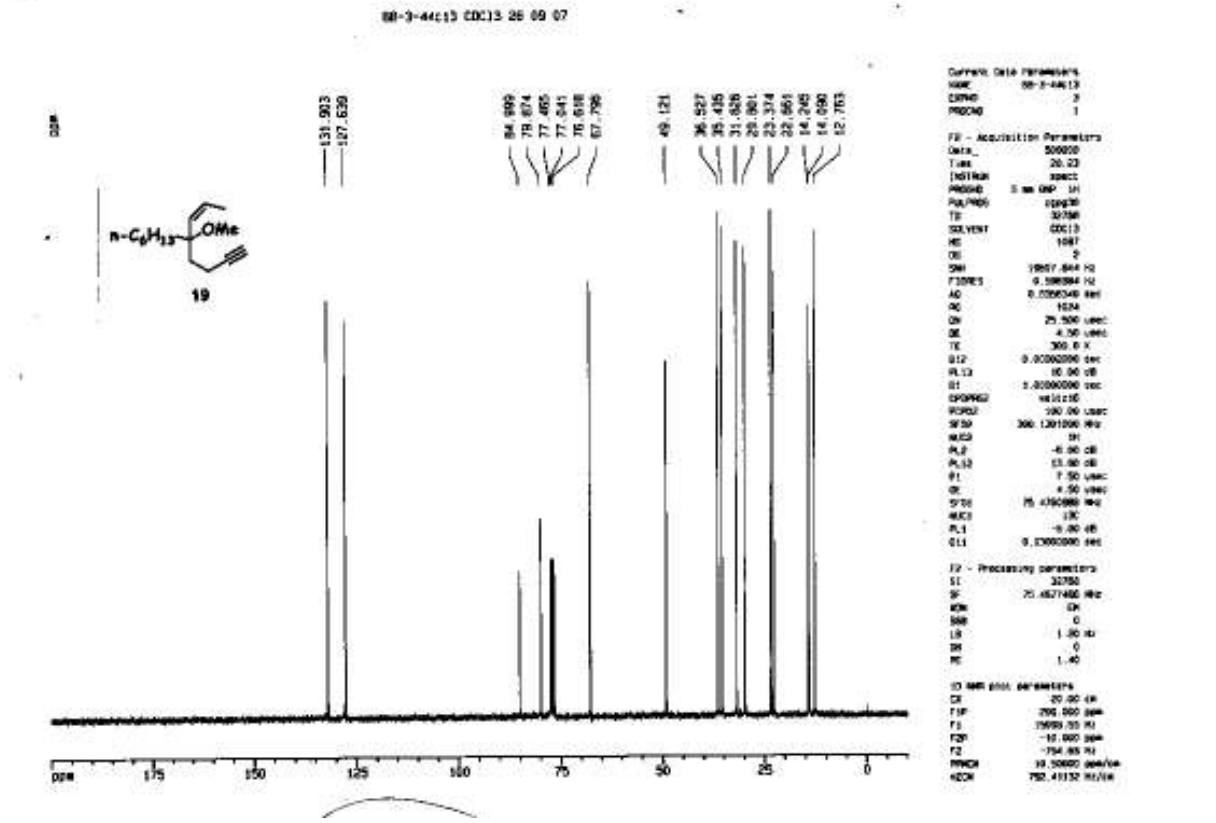
19
ppm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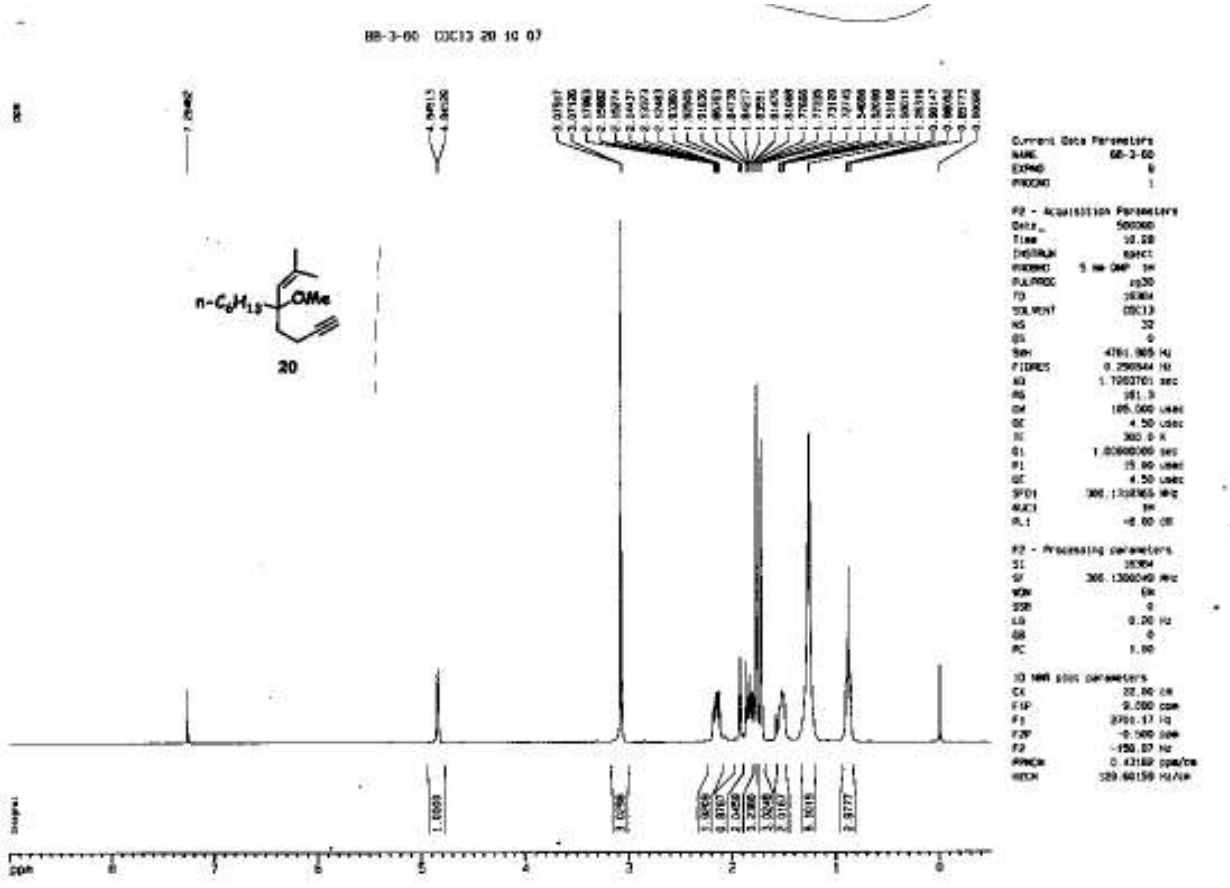
OMe
19
ppm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20
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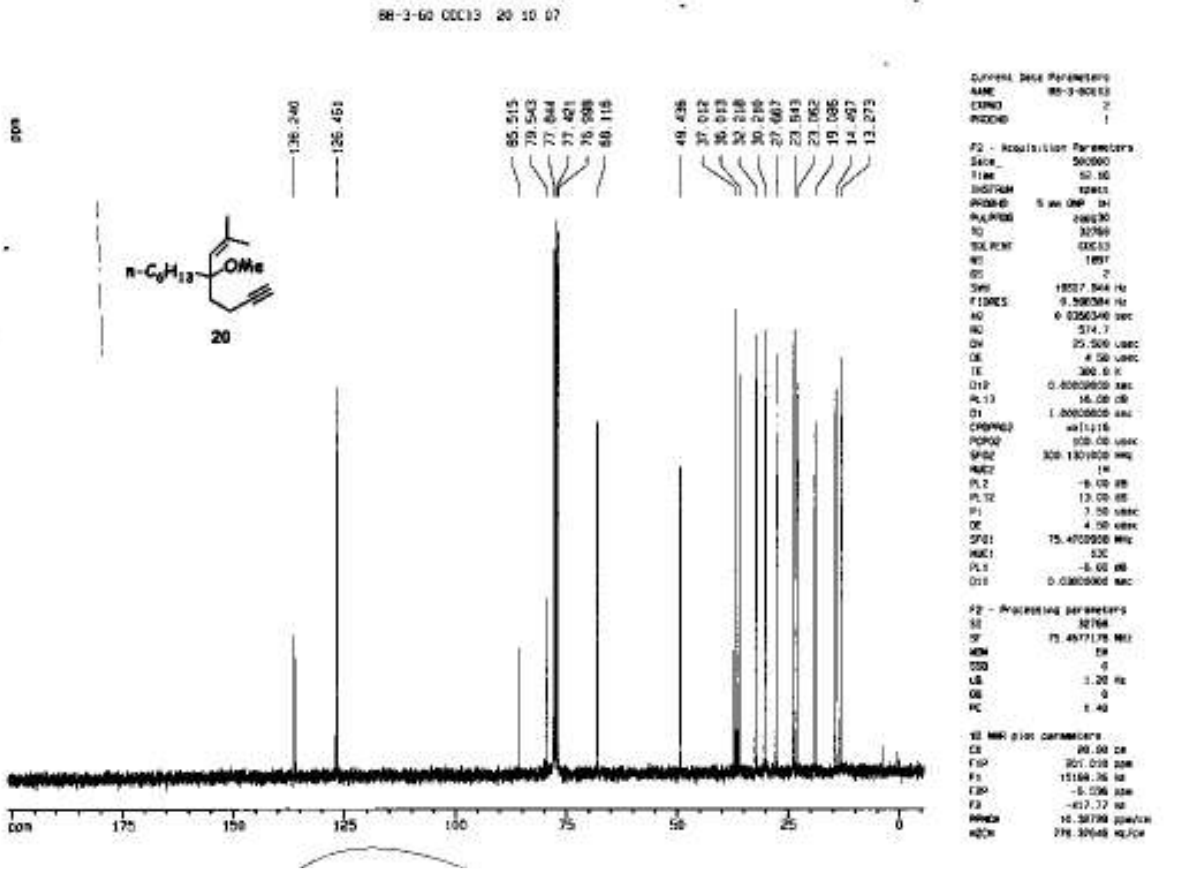
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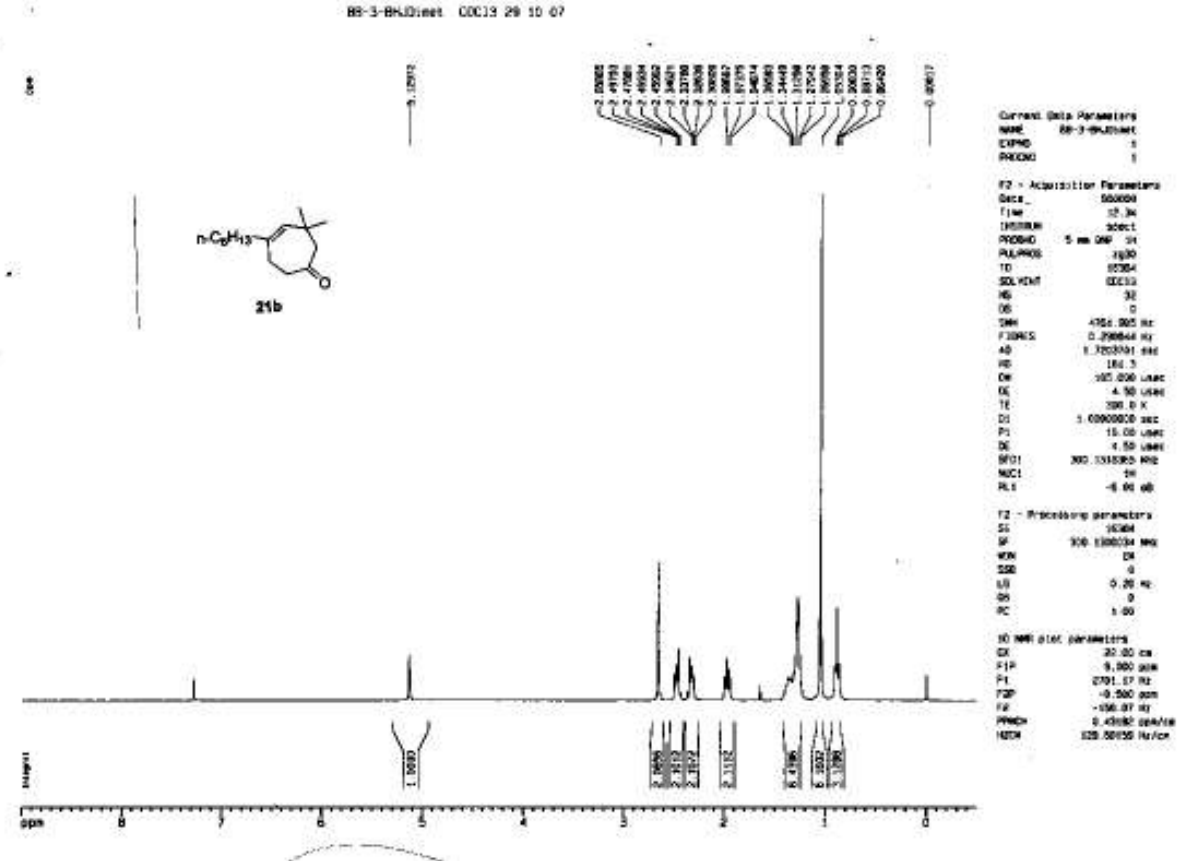
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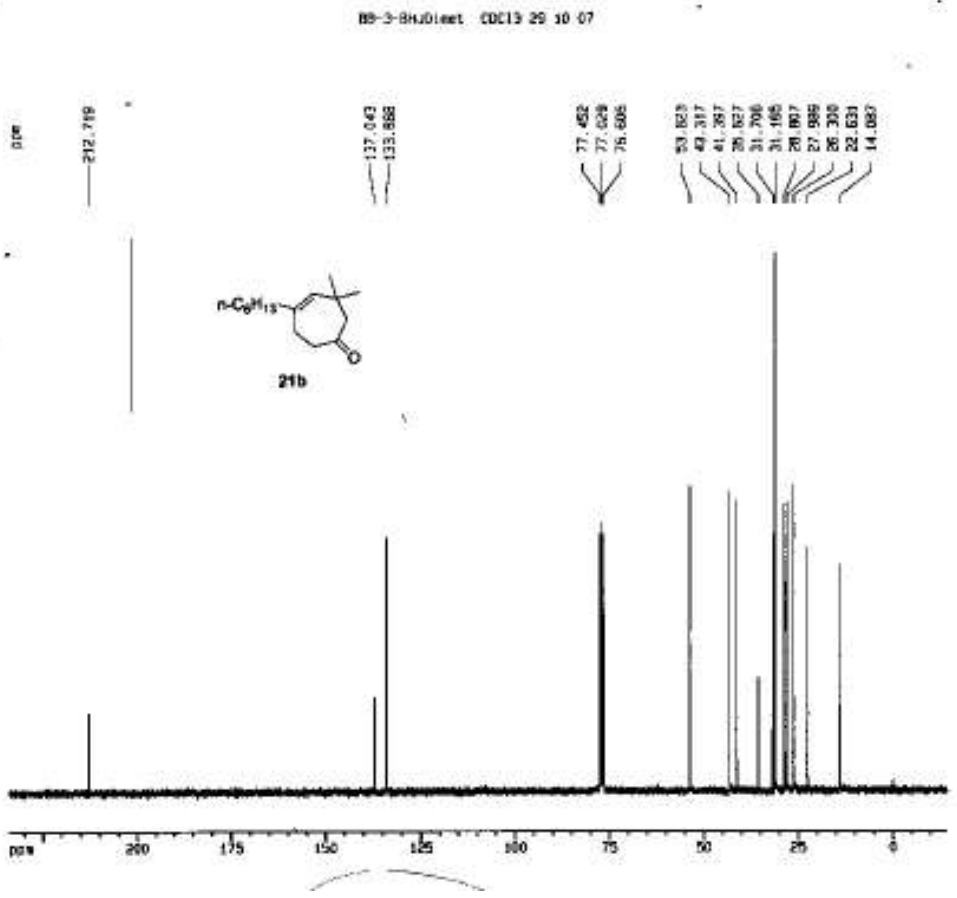
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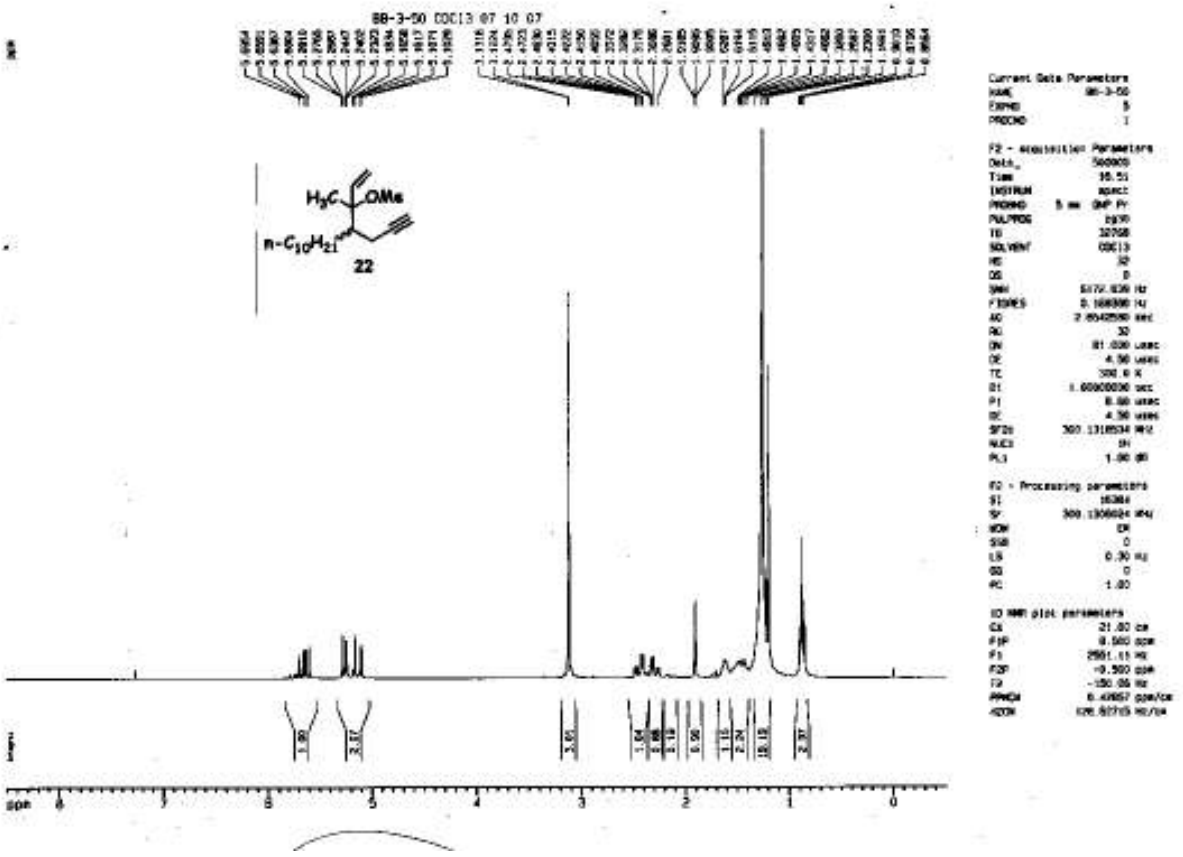
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OMe
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22
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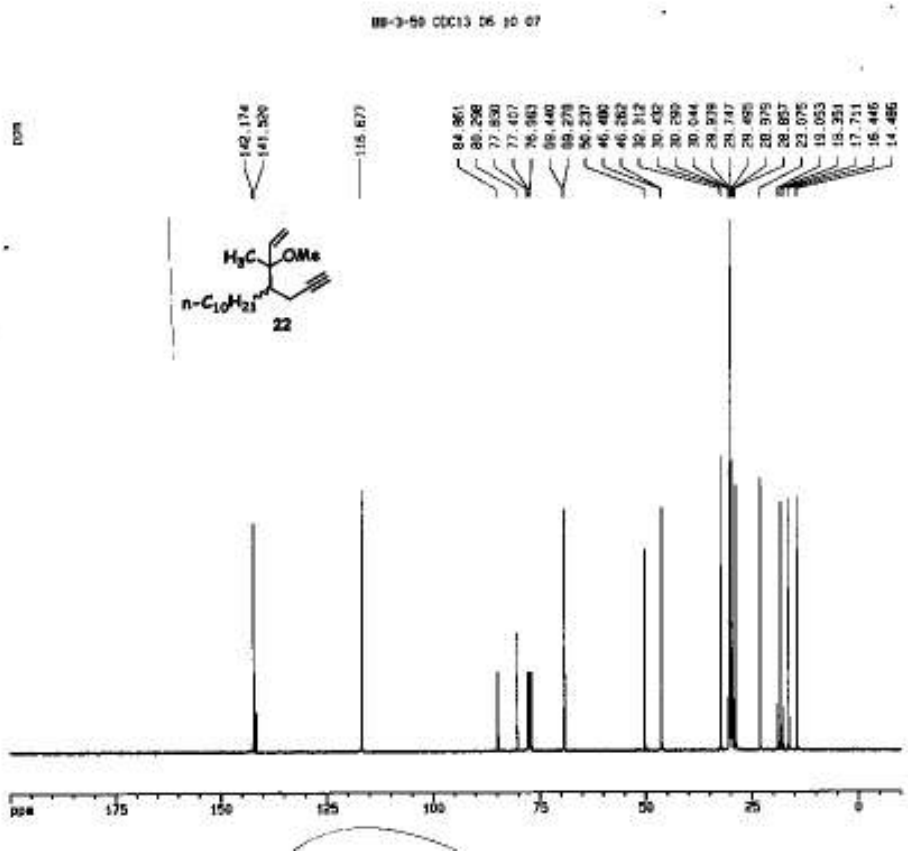
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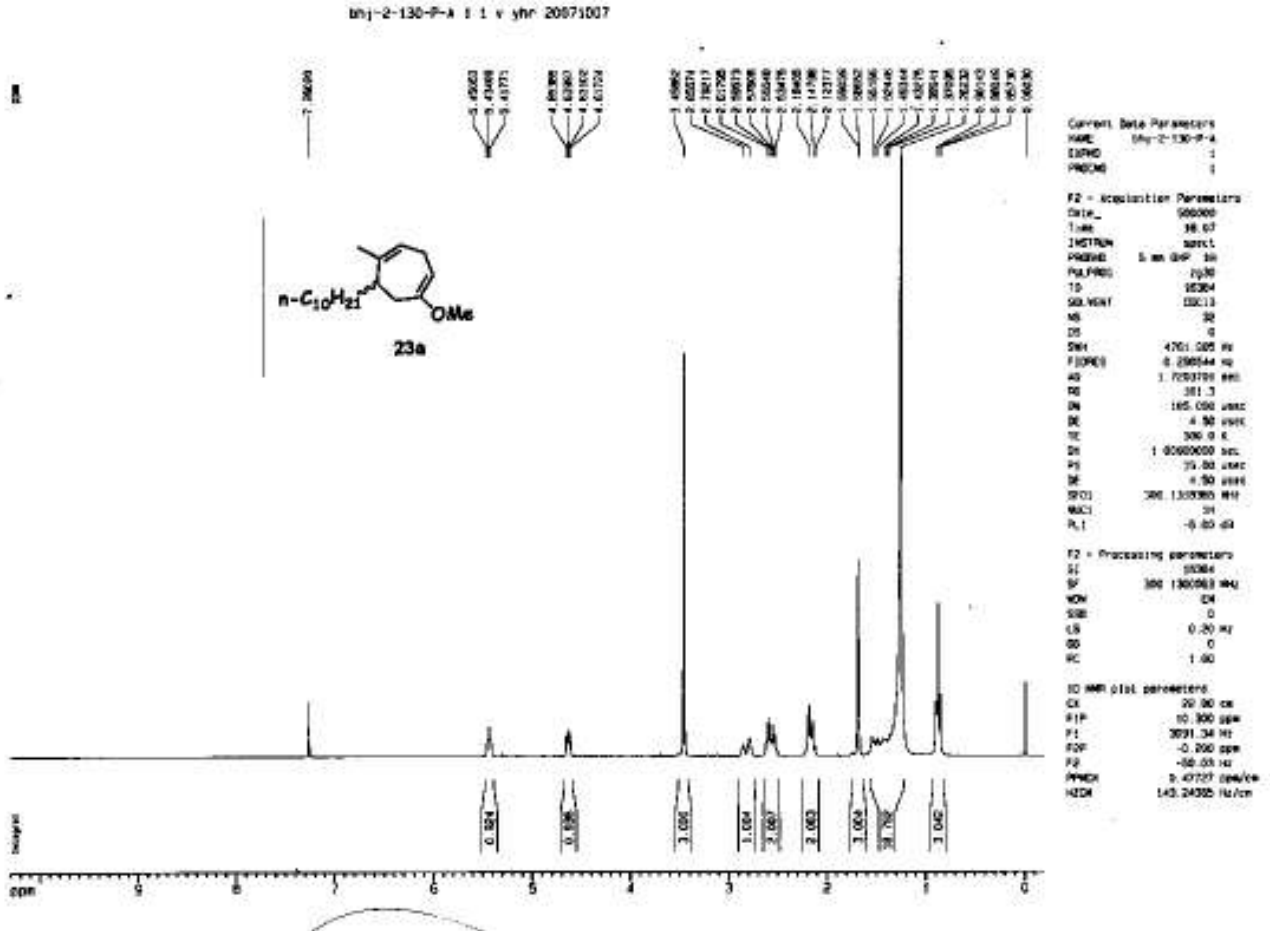
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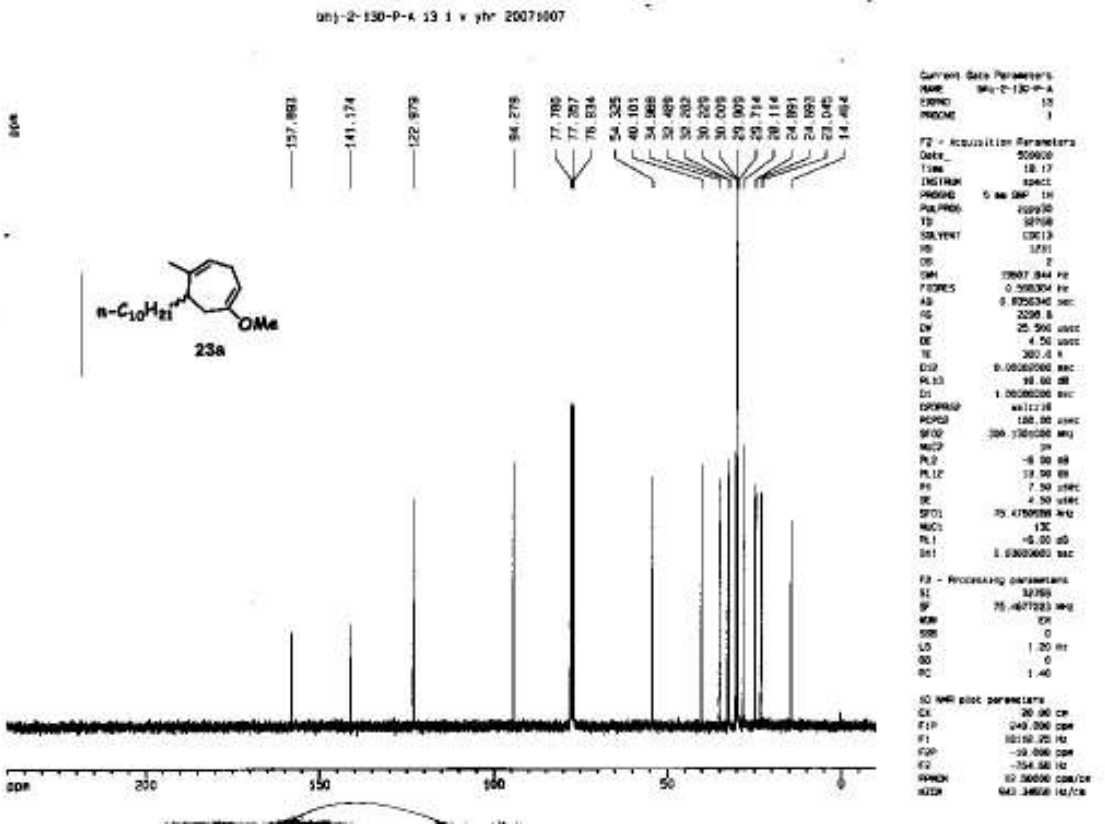
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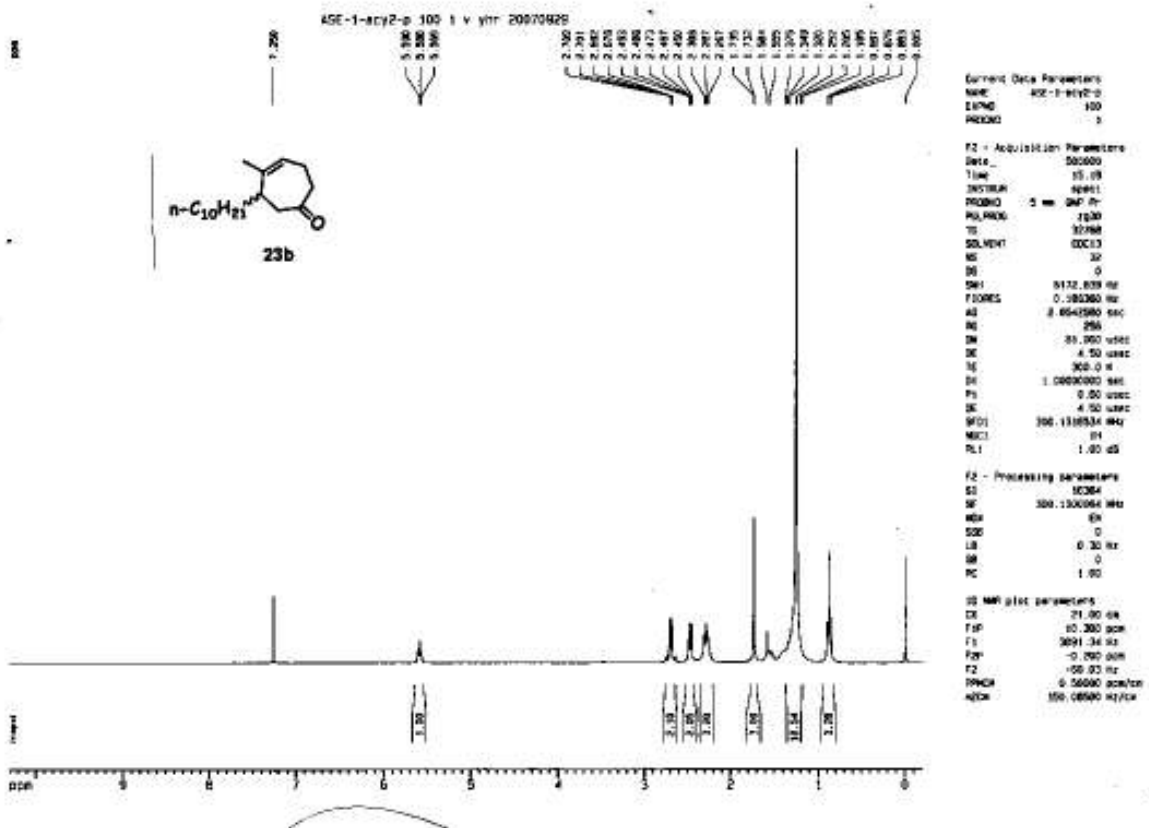
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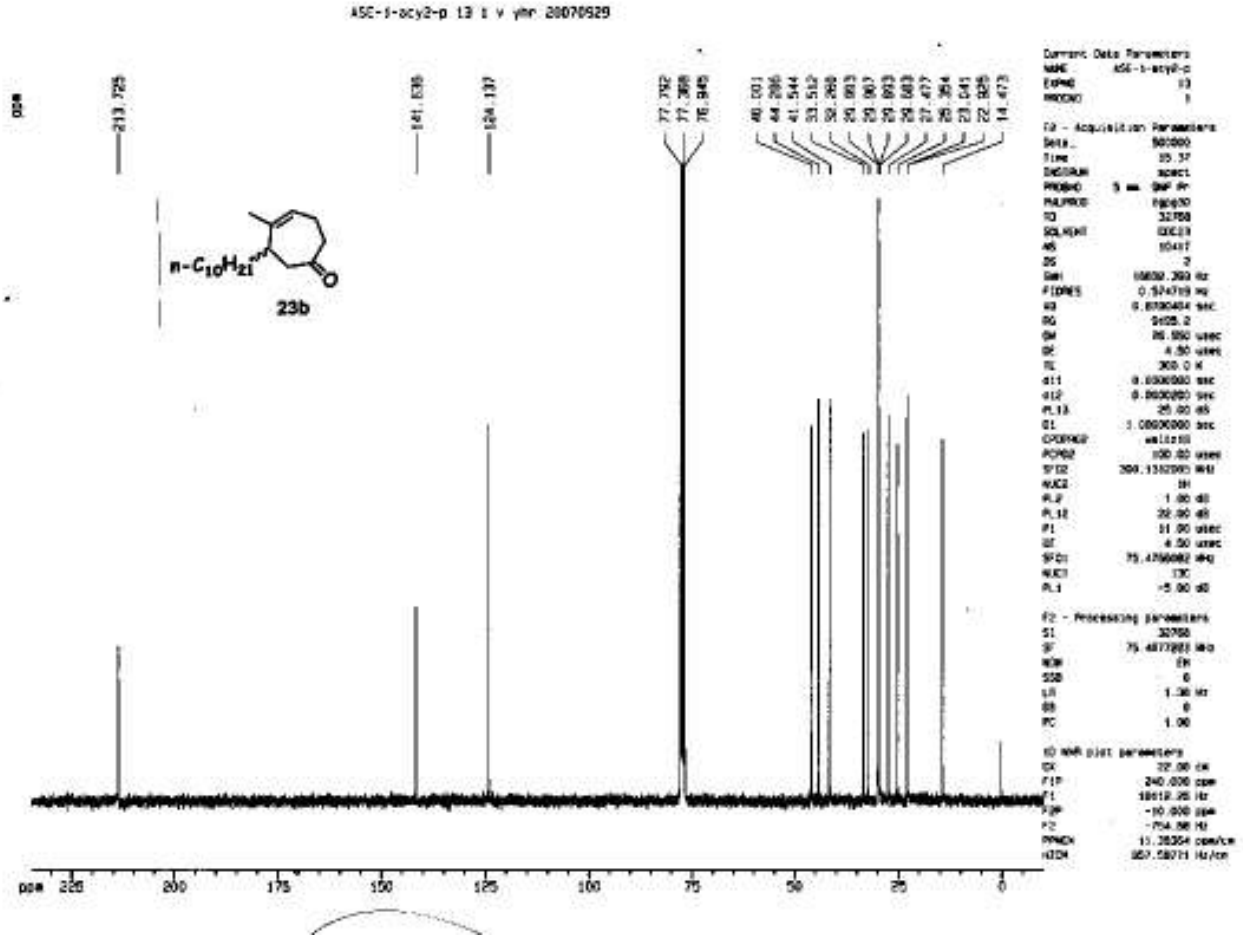
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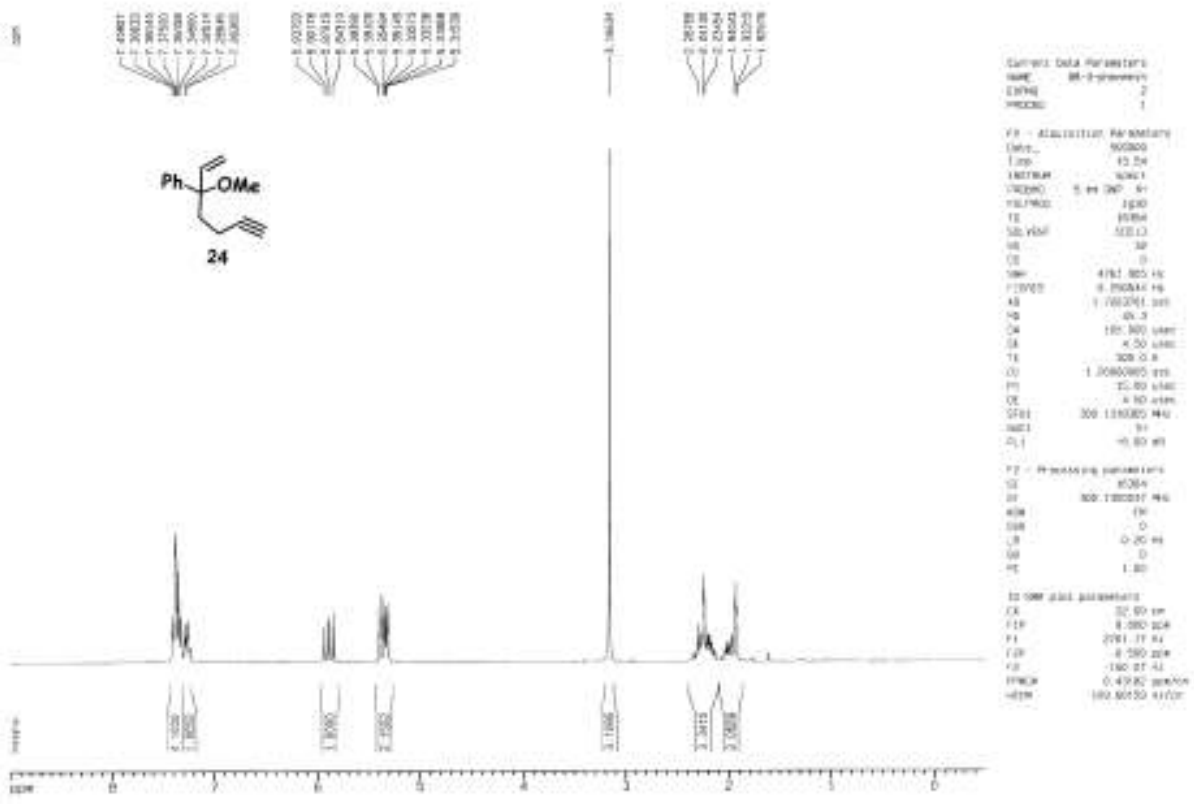
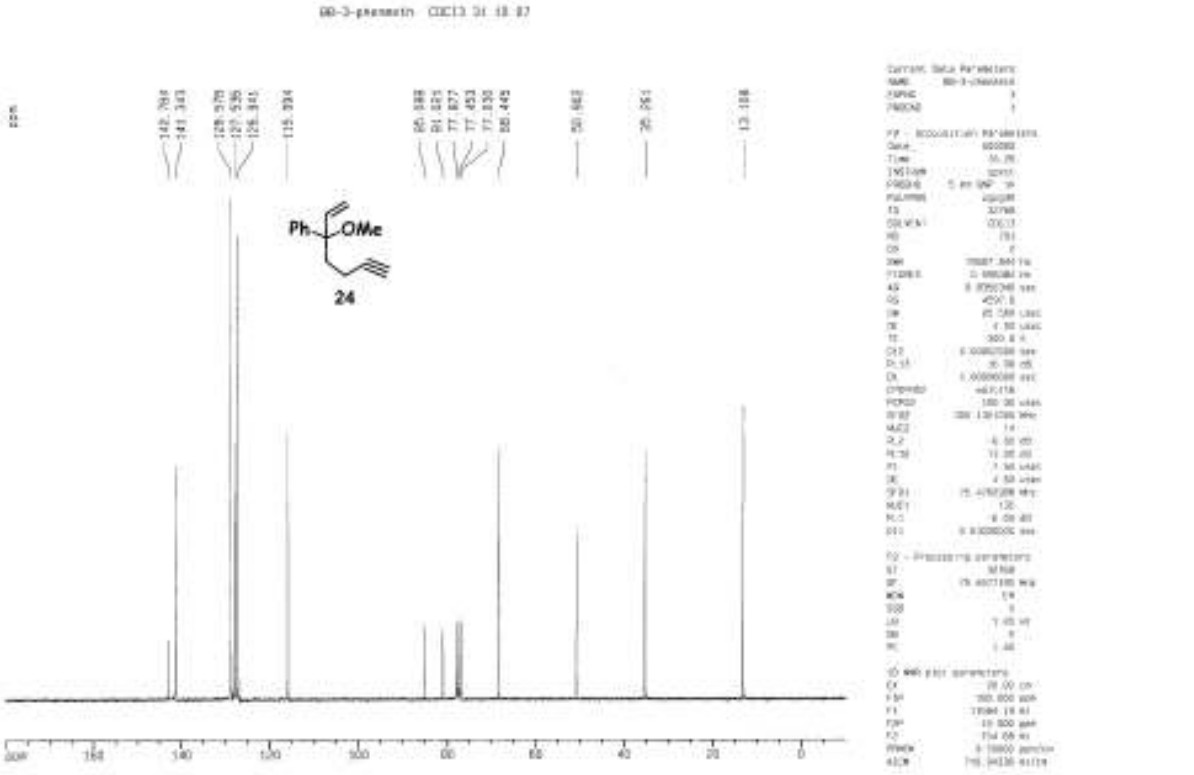
23b


Ph
OMe
24


Ph
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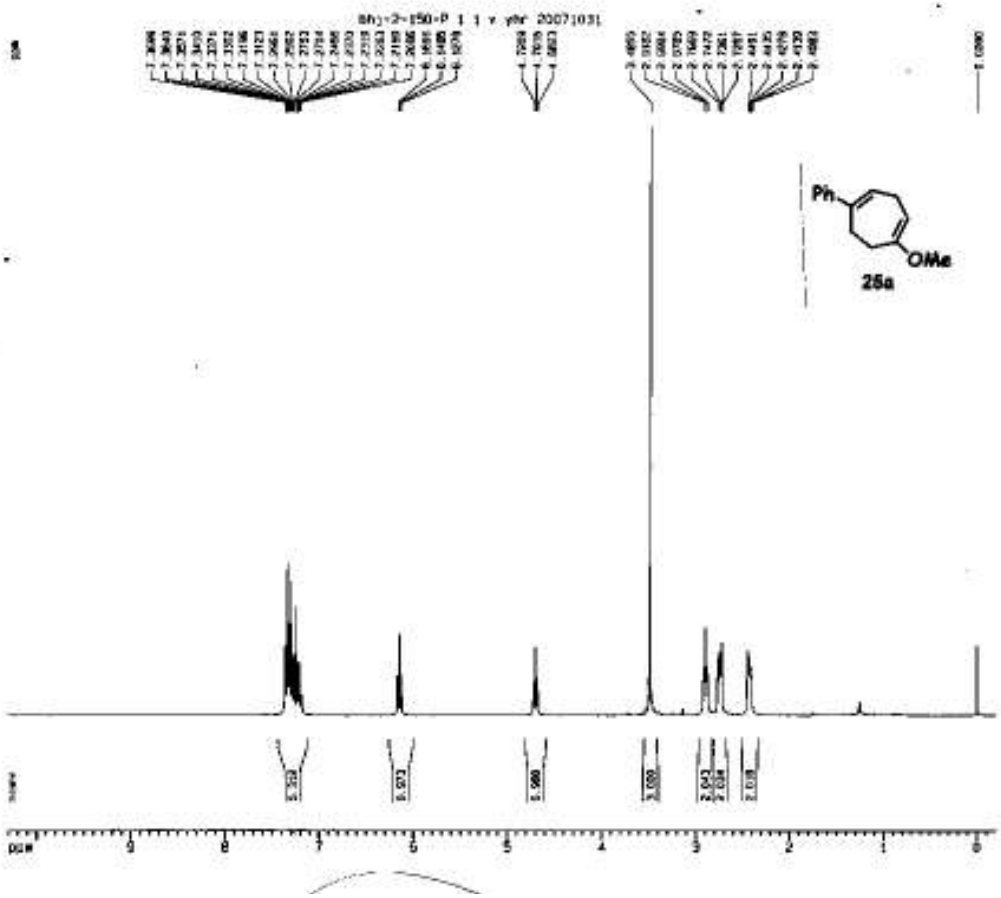
24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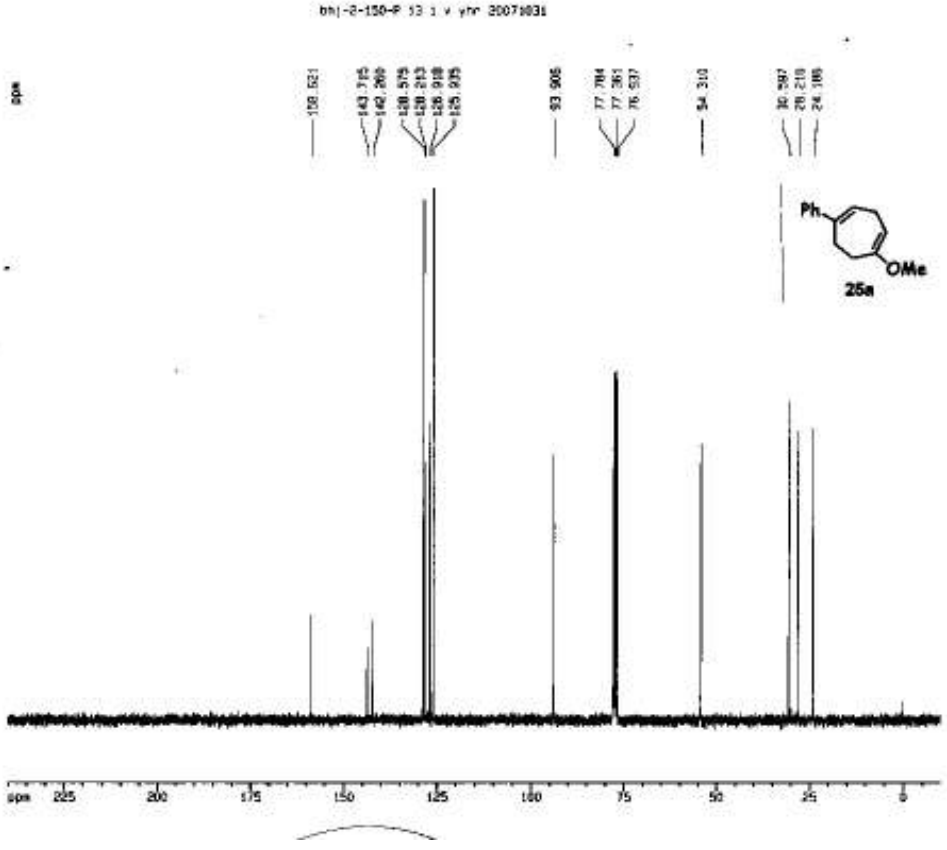
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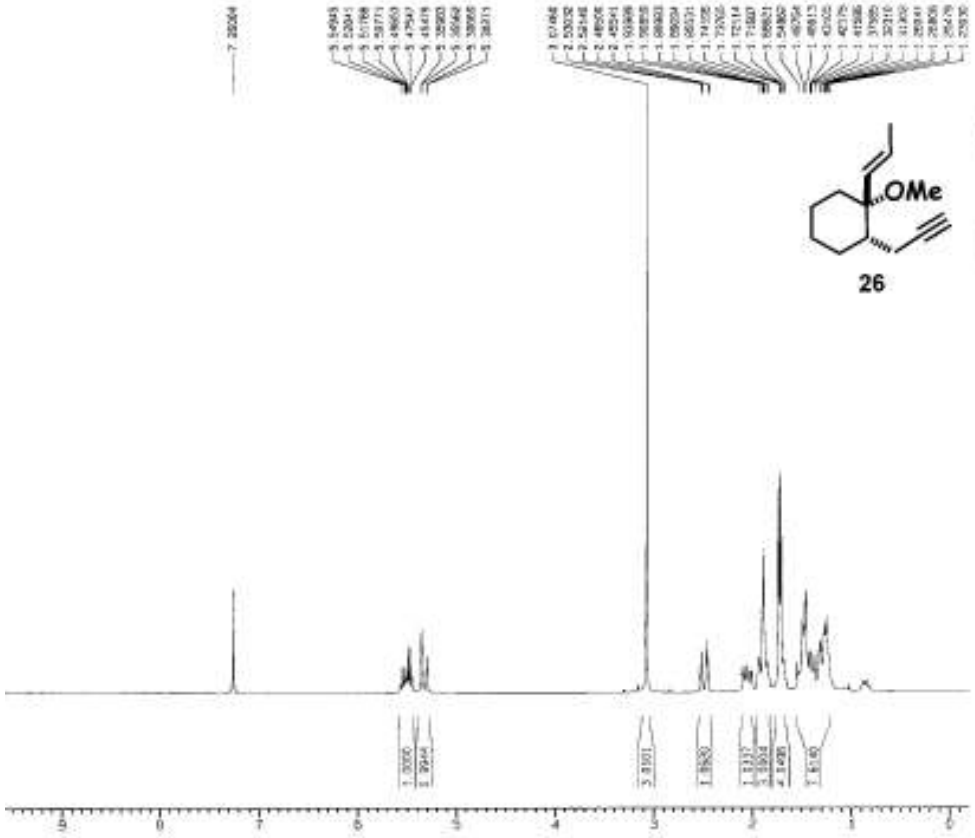

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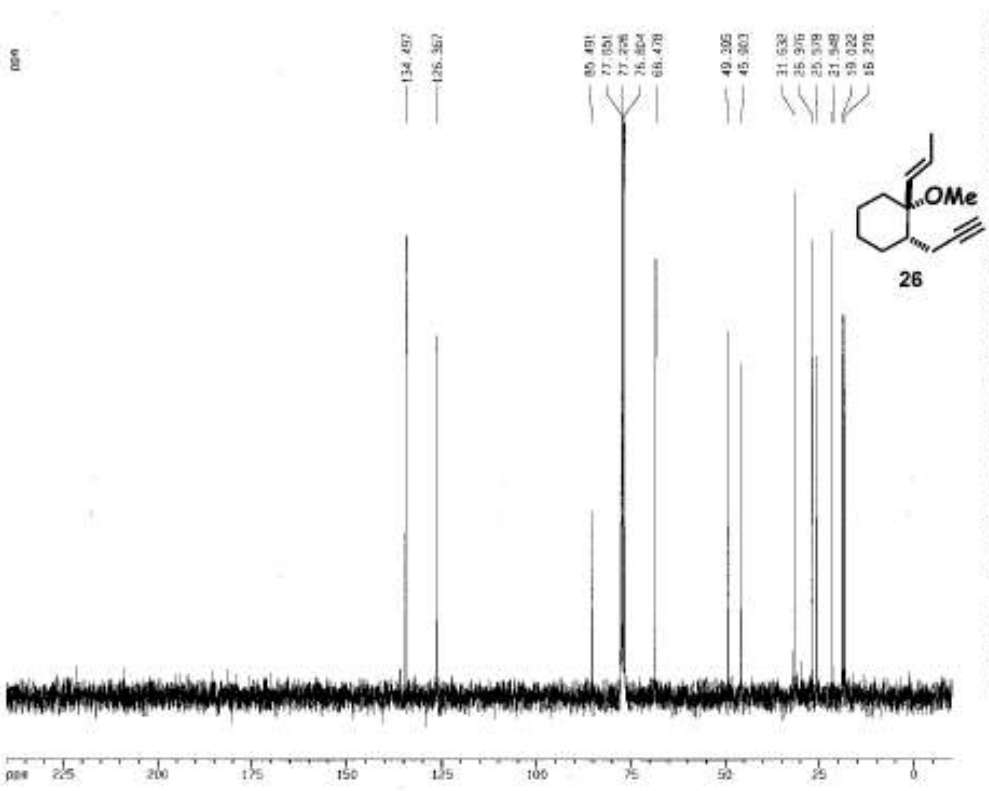

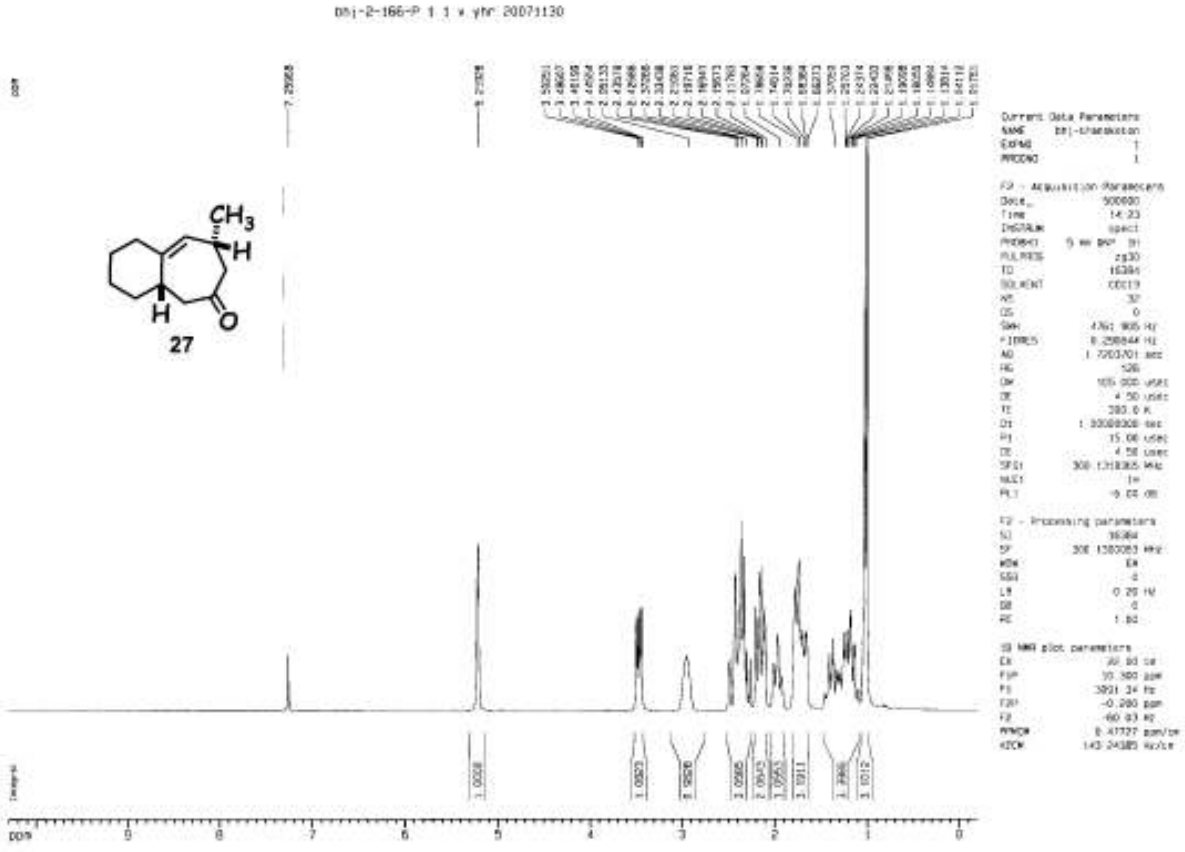
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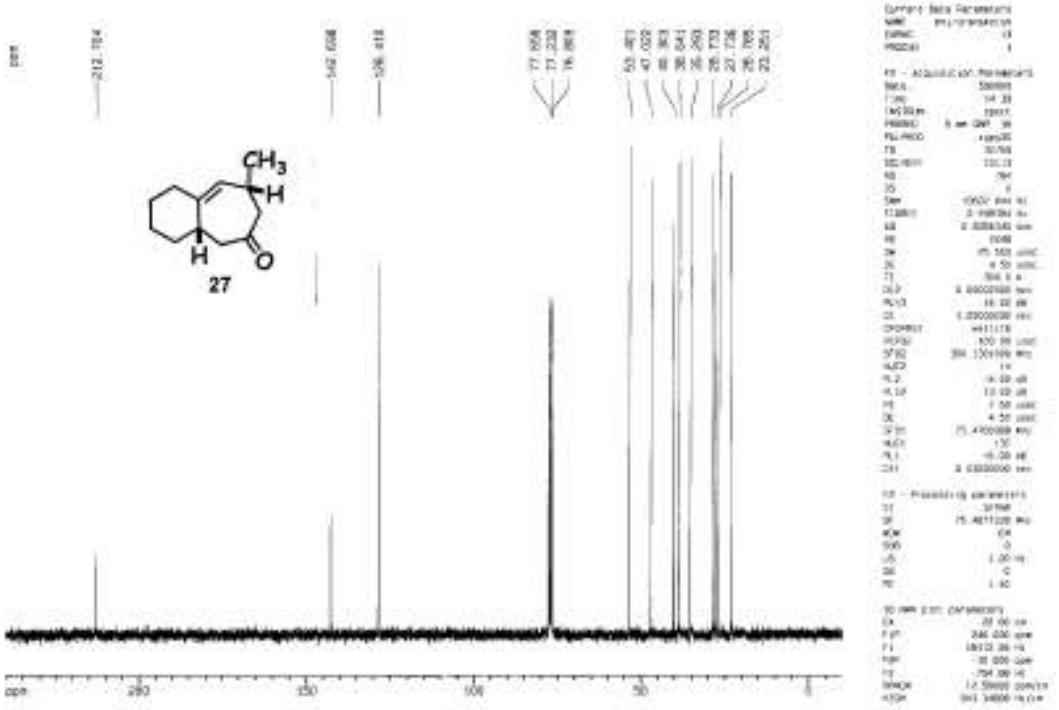
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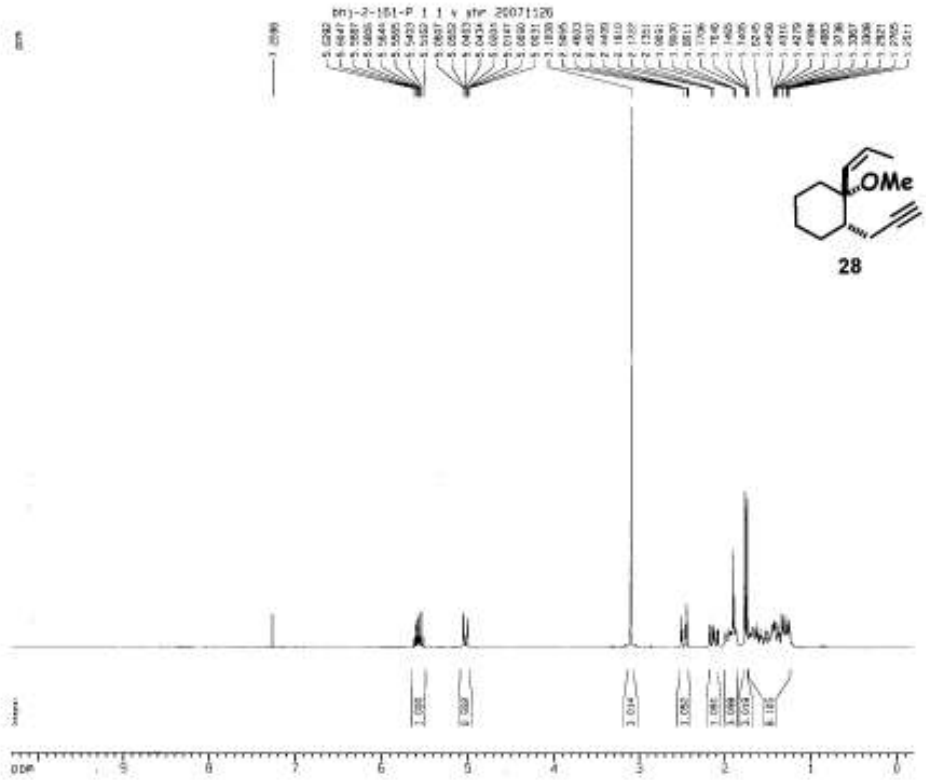
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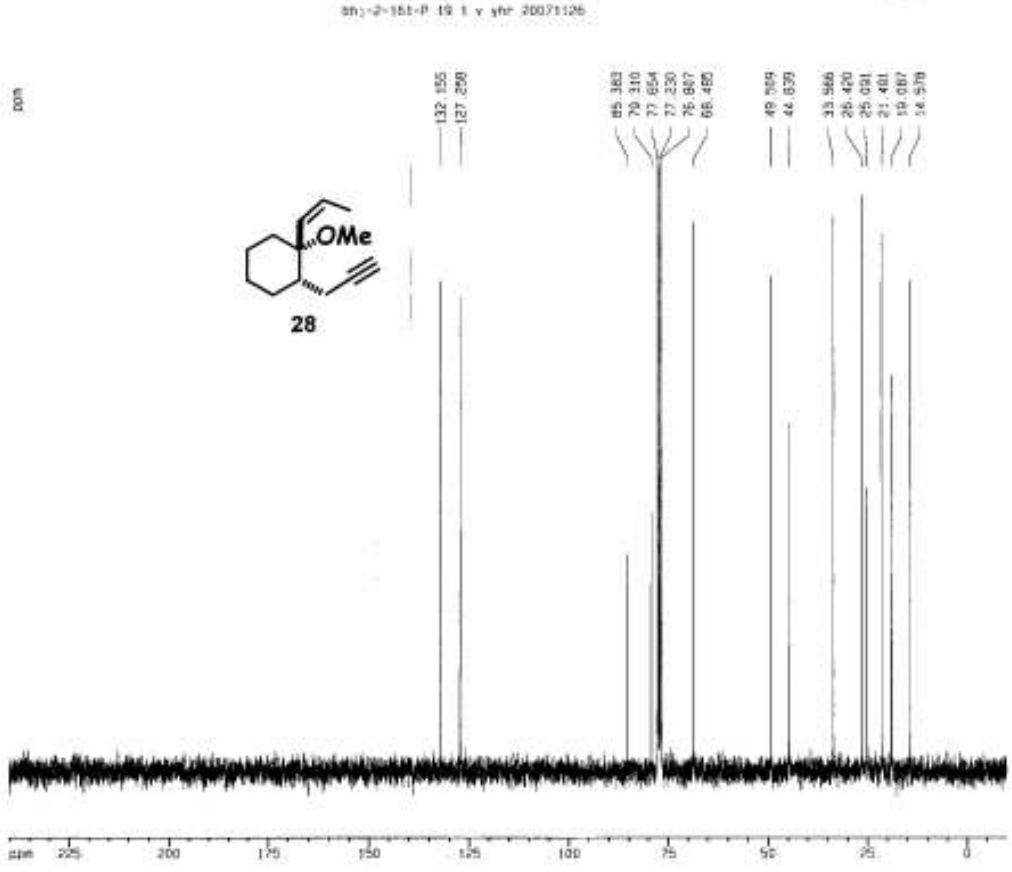
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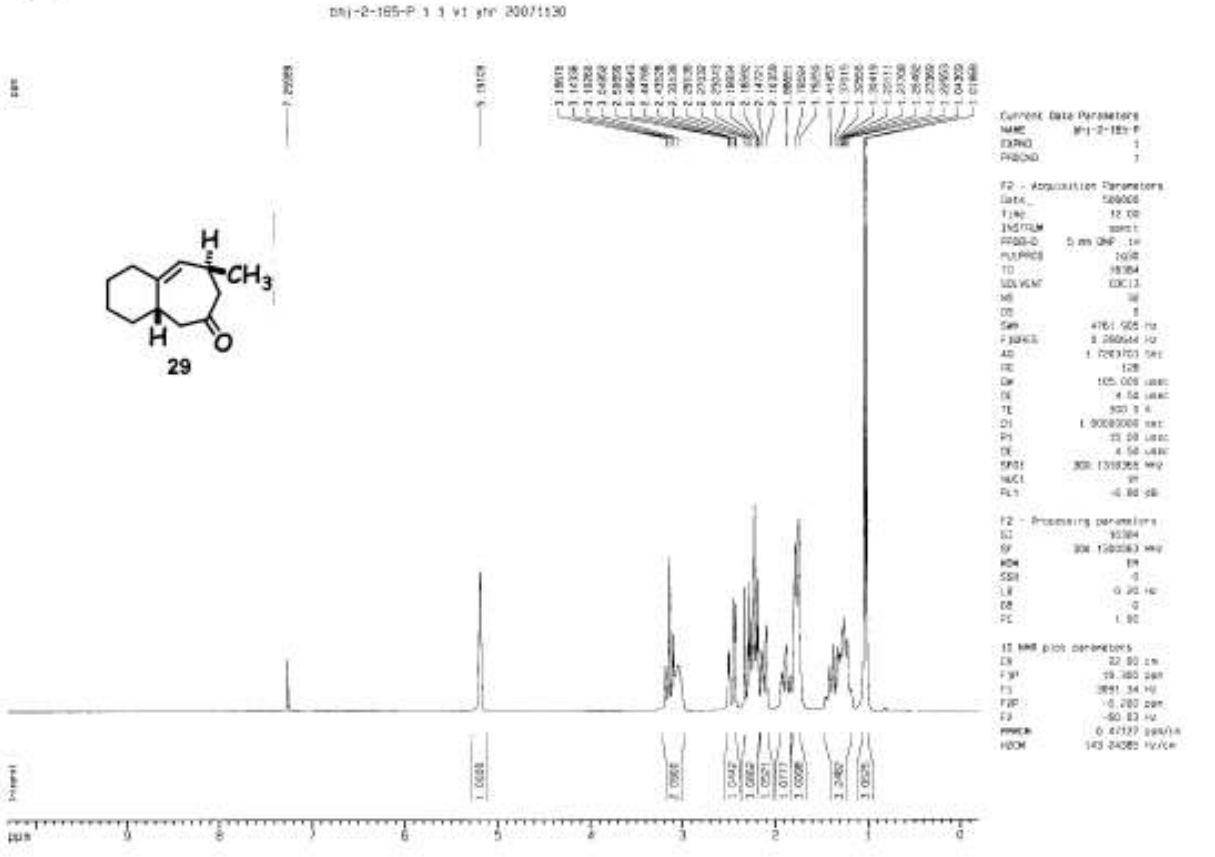
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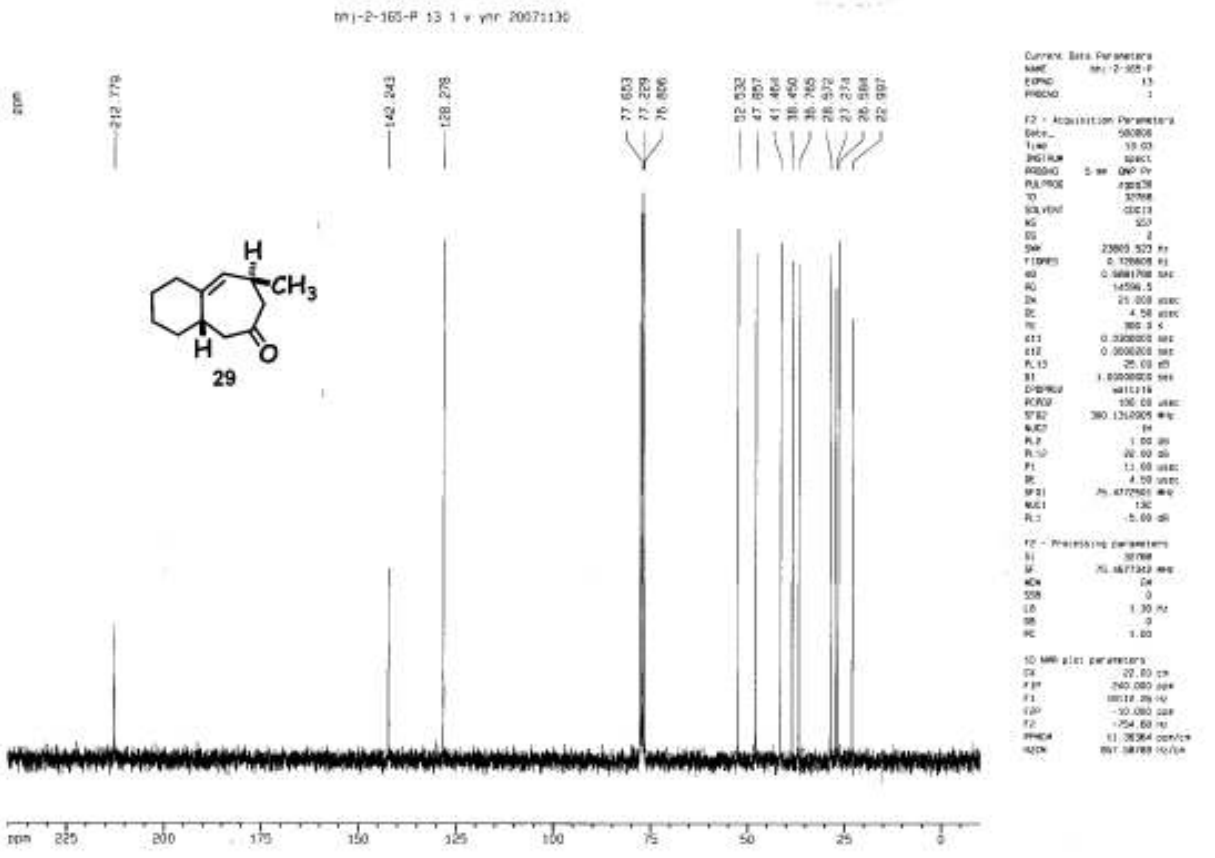
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