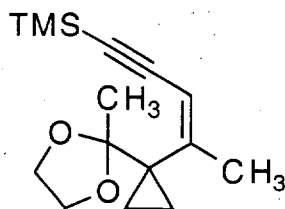
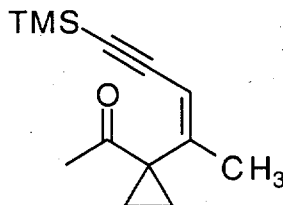


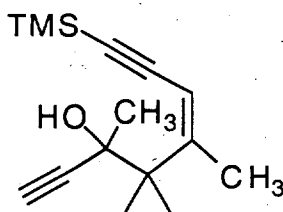
Supporting Information  
JACS Full Paper**(Z)-Trimethyl-{4-[1-(2-methyl-[1,3]dioxolan-2-yl)-cyclopropyl]-pent-3-en-1-ynyl}silane (8):**

To a flame-dried 100 mL round bottomed flask was added a solution of 1,3-bis(trimethylsilyl)propyne (2.12 g, 11.5 mmol) in THF (25 mL). The solution was stirred at rt and then cooled to -78 °C, and treated with *t*-BuLi (1.7 M, 6.2 mL, 10.6 mmol) dropwise. The resulting yellow solution was stirred at -78 °C for 1 h. A solution of ketone **7** (1.50 g, 8.85 mmol) in THF (15 mL) was first cooled to -78 °C and then added dropwise via canula. The reaction was stirred and allowed to warm gradually to -40 °C over a period of 4 h. The reaction was quenched with sat. NH<sub>4</sub>Cl (10 mL) at -40 °C, and then warmed to rt. The mixture was partitioned between Et<sub>2</sub>O (40 mL) and H<sub>2</sub>O (30 mL) and the aqueous layer was separated and extracted with Et<sub>2</sub>O (40 mL). The combined organic layers were dried with MgSO<sub>4</sub>; filtered and concentrated to afford a yellow crude mixture, which was purified by silica gel chromatography. The excess reagent was removed by eluting with 0.5% EtOAc/Hex and elution with 1% EtOAc/Hex afforded the desired product **8** as a yellow oil (0.976 g, 3.69 mmol, 42%); *R*<sub>f</sub>: 0.36 (Hexane : EtOAc = 95:5); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz) 0.18 (s, 9H), 0.71 (dd, *J* = 5.9, 4.0 Hz, 2H), 0.87 (dd, *J* = 5.9 4.0 Hz, 2H), 1.49 (s, 3H), 1.94 (d, *J* = 1.5 Hz, 3H), 3.89-4.00 (m, 4H), 5.50 (q, *J* = 1.5 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.9 MHz) 153.4, 111.2, 110.6, 103.9, 99.9, 65.2, 31.2, 24.0, 23.9, 10.6, -0.1; IR (neat): 2144, 1692, 1605, 1440, 1374, 1292, 1176, 1094, 1050 cm<sup>-1</sup>; HRMS calcd for C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>Si MH<sup>+</sup>: 265.1627. Found: 265.1624.



**(Z)-1-{1-[1-methyl-4-(trimethylsilyl)-but-1-en-3-ynyl]-cyclopropyl}-ethanone (9):**

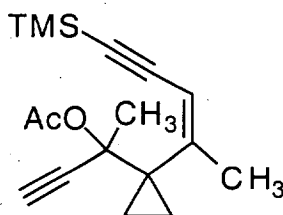
The ketal **8** (0.976 g, 3.69 mmol) was dissolved in acetone (10 mL) and H<sub>2</sub>O (10 mL), and treated with PTSA•H<sub>2</sub>O (106 mg, 0.55 mmol). The reaction was stirred at rt for 3 h. The organic solvent was removed *in vacuo* and the aqueous residue was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with saturated NaHCO<sub>3</sub> (20 mL), H<sub>2</sub>O (20 mL), then dried with MgSO<sub>4</sub>, and concentrated. The crude product was purified by silica gel chromatography (1% EtOAc/Hex) to yield a clear oil (0.771 g, 3.51 mmol, 95%); R<sub>f</sub>: 0.33 (Hexane : EtOAc = 95:5); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz) 0.17 (s, 9H), 1.09 (dd, *J* = 7.2, 3.7 Hz, 2H), 1.44 (dd, *J* = 7.2, 3.7 Hz, 2H), 1.91 (d, *J* = 1.5 Hz, 3H), 2.24 (s, 3H), 5.64 (q, *J* = 1.5 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.9 MHz) 207.3, 150.8, 112.3, 102.4, 100.3, 36.3, 27.7, 23.4, 19.5, 18.3, -0.2; IR (neat): 2140, 1693, 1621, 1349, 1278, 1249 cm<sup>-1</sup>; HRMS calcd for C<sub>13</sub>H<sub>20</sub>OSi MH<sup>+</sup>: 221.1362. Found: 221.1361.



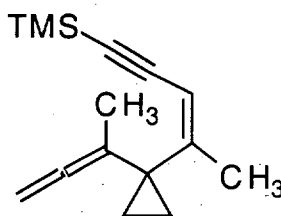
**(Z)-2-{1-[1-methyl-4-(trimethylsilyl)-but-1-en-3-ynyl]-cyclopropyl}-but-3-yn-2-ol**

**(10):** CeCl<sub>3</sub>•7H<sub>2</sub>O (4.28 g, 11.5 mmol) was dried as described in the literature and suspended in THF (100 mL). The milky suspension was stirred at rt overnight, and then cooled to 0 °C. The suspension was treated with ethynylmagnesium bromide (0.5 M, 23 mL, 11.5 mmol) at 0 °C and stirred for 1.5 h. A solution of the ketone **9** (0.508 g, 2.31 mmol) in THF (10 mL) was added and the reaction was stirred at 0 °C for 1 h. The reaction was quenched with 10% citric acid (50 mL), and extracted with Et<sub>2</sub>O (3 x 50 mL). The combined organic layers were washed with sat. NaHCO<sub>3</sub> (100 mL), H<sub>2</sub>O (100 mL) and brine (100 mL) then dried with MgSO<sub>4</sub>, filtered and concentrated. The crude product was purified by silica gel chromatography, eluting with 5-10% EtOAc/hex to afford a clear oil (0.539 g, 2.19 mmol, 95%); R<sub>f</sub>: 0.16 (Hexane : EtOAc, 95:5); <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 270 MHz) 0.20 (s, 9H), 0.72-0.88 (m, 2H), 1.03-1.11 (m, 1H), 1.21-1.28 (m, 1H), 1.59 (s, 3H), 1.96 (d,  $J = 1.5$  Hz, 3H), 2.39 (s, 1H), 2.78 (s, 1H), 5.59 (q,  $J = 1.5$  Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.9 MHz) 152.2, 112.4, 104.1, 99.1, 85.6, 73.9, 71.6, 31.5, 27.9, 24.7, 12.1, 12.0, -0.2; IR (neat): 3446, 3303, 2133, 1641, 1241, 1095 cm<sup>-1</sup>; HRMS calcd for C<sub>15</sub>H<sub>22</sub>OSi: 246.1440; Found: 246.1435.

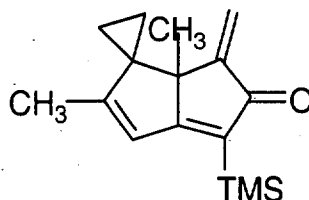


**(Z)-Acetic acid, 1-methyl-1-{1-[1-methyl-4-(trimethylsilyl)-but-1-en-3-ynyl]-cyclopropyl}-prop-2-ynyl ester (11):** Alcohol **10** (0.128 g, 0.519 mmol) was dissolved in Et<sub>3</sub>N (0.73 mL, 5.2 mmol). The solution was treated with DMAP (0.063 g, 0.516 mmol), and then acetic anhydride (0.25 mL, 2.6 mmol). The reaction was stirred at rt for 1 h then filtered through a column of Florisil eluting with Et<sub>2</sub>O (30 mL). The solvent was removed *in vacuo* and the resulting crude mixture was quickly purified by chromatography using Florisil (2% EtOAc/hex) to give a yellow oil (0.1410 g, 0.4896 mmol, 94%). This yellow oil was used immediately in the generation of the allene to prevent decomposition. R<sub>f</sub>: 0.40 (Hexane : EtOAc, 95:5), alumina TLC plate.



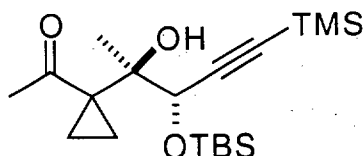
**(Z)-Trimethyl-4-[1-(1-methyl-prop-1,2-dienyl)-cyclopropyl]-pent-3-en-1-ynylsilane (12):** Following the general procedure for allene formation (*vide infra*), acetate **11** (0.141 g, 0.490 mmol) afforded allene **12** (0.043 g, 0.187 mmol, 38%) as a clear oil; R<sub>f</sub>: 0.71 (Hexane : EtOAc, 95:5); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz) 0.19 (s, 9H), 0.83 (dd,  $J = 6.6, 4.4$  Hz, 2H), 1.00 (dd,  $J = 6.6, 4.4$  Hz, 2H), 1.74 (t,  $J = 3.1$  Hz, 3H), 1.79 (d,  $J = 1.5$  Hz, 3H), 4.63 (q,  $J = 3.1$  Hz, 2H), 5.44 (q,  $J = 1.5$  Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.9 MHz) 206.7,

153.2, 108.5, 103.5, 102.2, 97.9, 74.5, 27.9, 22.5, 16.6, 14.5, -0.1; IR (neat): 3434, 2142, 1956, 1643, 1424, 1372, 1247  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{15}\text{H}_{22}\text{Si}$   $\text{MH}^+$ : 231.1569. Found: 231.1562.

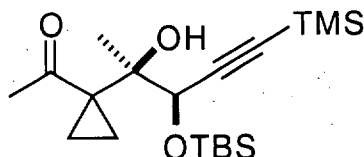


**5,7-Dimethyl-6-spiro-cyclopropyl-4-methylidenyl-2-trimethylsilyloxy-1,7-dien-3-one (14):** Following the general procedure for the P-K reaction, allene **12** (0.039 g, 0.170 mmol) yielded the  $\alpha$ -methylene cyclopentenone **14** (0.029 g, 0.113 mmol, 66%) as a pale yellow oil;  $R_f$ : 0.31 (Hexane : EtOAc, 90 : 10);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz) 0.24 (s, 9H), 0.74-0.96 (m, 3H), 1.10-1.18 (m, 1H), 1.26 (s, 3H), 1.72 (d,  $J = 1.2$  Hz, 3H), 4.73 (s, 1H), 5.80 (s, 1H), 6.46 (q,  $J = 1.2$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.9 MHz) 200.7, 195.9, 163.7, 149.9, 129.4, 123.3, 110.3, 56.7, 38.4, 30.1, 14.2, 13.6, 8.0, -1.0; IR (neat): 3080, 1675, 1643, 1570, 1372  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{16}\text{H}_{22}\text{OSi}$   $\text{MH}^+$ : 259.1518. Found: 259.1518.

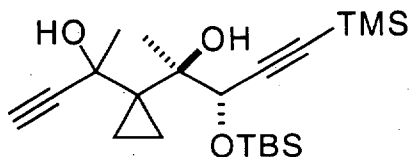
**Addition of 3-trimethylsilyl-1-[(1,1-dimethylethyl)dimethylsilyloxy]-2-propyne to 1,1-diacetylcyclopropane (16):** To a 10 mL round-bottomed flask was added a solution of 3-trimethylsilyl-1-[(1,1-dimethylethyl)dimethylsilyloxy]-2-propyne (271 mg, 1.12 mmol) in THF (2 mL). The solution was cooled to  $-78^\circ\text{C}$ , and  $t\text{-BuLi}$  (1.7 M, 0.61 mL, 1.0 mmol) was added dropwise. The resulting light yellow solution was stirred at  $-78^\circ\text{C}$  for 1 h. Crucial to the success of the reaction was to cool the solution of 1,1-diacetylcyclopropane (**15**) (100.0 mg, 0.794 mmol) in THF (2 mL) to  $-78^\circ\text{C}$  and then add it to the anion via canula over a period of 5 min. After the reaction had been stirred at  $-78^\circ\text{C}$  for 3 h, it was quenched with  $\text{H}_2\text{O}$  (3 mL) at  $-78^\circ\text{C}$  and then warmed to rt. The reaction was then partitioned between  $\text{Et}_2\text{O}$  (10 mL) and  $\text{H}_2\text{O}$  (7 mL) and the aqueous layer was extracted with  $\text{Et}_2\text{O}$  (3 x 10 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ), filtered and concentrated. The crude product was purified by silica gel flash chromatography eluting first with 2% then 5% EtOAc/hexane to give *anti*-**16** (94.5 mg, 0.256 mmol, 32%) and *syn*-**16** (72.7 mg, 0.198 mmol, 25%).



**1-{1-(1*R*\*,2*S*\*)-[2-(*tert*-Butyl-dimethylsilyloxy)-1-hydroxy-1-methyl-4-(trimethylsilyl)-but-3-ynyl]-cyclopropyl}-ethanone (*anti*-16)** pale yellow oil;  $R_f$  0.5 (90:10-hexane:EtOAc);  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  0.14 (s, 9H), 0.15 (s, 3H), 0.18 (s, 3H), 0.92 (s, 9H), 1.06-1.17 (m, 2H), 1.23-1.28 (m, 1H), 1.30 (s, 3H), 1.78-1.84 (m, 1H), 1.85 (s, 3H), 3.01 (bs, 1H), 5.06 (s, 1H);  $^{13}\text{C}$  NMR (67.9 MHz,  $\text{CDCl}_3$ )  $\delta$  208.2, 105.1, 90.6, 73.1, 68.6, 38.5, 25.8, 24.4, 23.8, 18.2, 13.8, 11.7, -0.3, -4.5, -5.1; IR (neat) 3549, 2174, 1682, 1467, 1410, 1359, 1318, 1251, 1062  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{19}\text{H}_{37}\text{O}_3\text{Si}_2$   $\text{MH}^+$ : 369.2281. Found: 369.2281. Anal. calcd for  $\text{C}_{19}\text{H}_{36}\text{O}_3\text{Si}_2$ : C, 61.92; H, 9.85. Found: C, 62.06; 9.84.

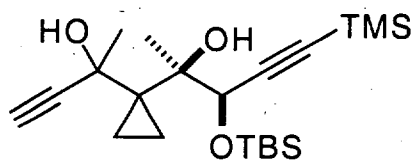


**1-{1-(1*R*\*,2*R*\*)-[2-(*tert*-Butyl-dimethylsilyloxy)-1-hydroxy-1-methyl-4-(trimethylsilyl)-but-3-ynyl]-cyclopropyl}-ethanone (*syn*-16)** white crystals, mp 84-86  $^\circ\text{C}$ ;  $R_f$  0.4 (90:10-hexane:EtOAc);  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  0.06 (s, 3H), 0.14 (s, 3H), 0.16 (s, 9H), 0.89 (s, 9H), 0.99-1.26 (m, 3H), 1.37 (s, 3H), 1.34-1.44 (m, 1H), 1.84 (s, 3H), 2.77 (bs, 1H), 5.21 (s, 1H);  $^{13}\text{C}$  NMR (67.9 MHz,  $\text{CDCl}_3$ )  $\delta$  208.3, 105.0, 91.0, 73.3, 68.3, 37.3, 25.7, 24.8, 22.5, 18.1, 13.4, 10.8, -0.2, -4.6, -5.0; IR (neat) 3436, 2164, 1662, 1467, 1354, 1318, 1246  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{19}\text{H}_{37}\text{O}_3\text{Si}_2$   $\text{MH}^+$ : 369.2281. Found: 369.2281. Anal. calcd for  $\text{C}_{19}\text{H}_{36}\text{O}_3\text{Si}_2$ : C, 61.92; H, 9.85. Found: C, 62.14; 9.77.



**(1*R*\*,2*S*\*)-3-(*tert*-Butyl-dimethylsilyloxy)-2-[1-(1-hydroxy-1-methyl-prop-2-ynyl)-cyclopropyl]-5-trimethylsilyl-pent-4-yn-2-ol (*anti*-17):** To a 10 mL round-bottomed

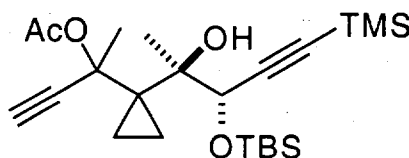
flask was added  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  (252 mg, 0.676 mmol). It was dried and suspended in THF (5 mL) as described in the literature. The suspension was stirred at rt overnight, then cooled to 0 °C and ethynylmagnesium bromide (0.5 M, 1.3 mL, 0.65 mmol) was added dropwise. The resulting clear solution was stirred at 0 °C for 1.5 h. A solution of **anti-16** (50.0 mg, 0.136 mmol) in THF (1 mL) was added at 0 °C. The reaction was complete in 15 min as determined by TLC. The reaction was partitioned between ice-water (10 mL) and  $\text{Et}_2\text{O}$  (10 mL). The aqueous layer was extracted with  $\text{Et}_2\text{O}$  (3 x 10 mL). The combined ether layers were dried with  $\text{MgSO}_4$ , filtered and concentrated. The crude product was purified by flash chromatography eluting with 10%  $\text{EtOAc}$ /hexane to give the non-separable diastereomers **anti-17** (*dr* 9.2/1, 52.0 mg, 0.132 mmol, 97%) as a pale yellow oil;  $R_f$  0.3 (90:10-hexane: $\text{EtOAc}$ );  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ) for the major isomer,  $\delta$  0.18 (s, 9H), 0.20 (s, 6H), 0.63-0.78 (m, 1H), 0.80-0.98 (m, 1H), 0.93 (s, 9H), 1.04-1.55 (m, 1H), 1.33 (s, 3H), 1.37-1.44 (m, 1H), 1.54 (s, 3H), 2.47 (s, 1H), 3.05 (s, 1H), 3.98 (s, 1H), 4.80 (s, 1H); for the minor isomer,  $\delta$  0.17 (s, 9H), 0.19 (s, 6H), 0.63-0.78 (m, 1H), 0.80-0.98 (m, 1H), 0.93 (s, 9H), 1.04-1.55 (m, 1H), 1.33 (s, 3H), 1.37-1.44 (m, 1H), 1.54 (s, 3H), 2.46 (s, 1H), 3.19 (s, 1H), 4.11 (s, 1H), 4.80 (s, 1H);  $^{13}\text{C}$  NMR (67.9 MHz,  $\text{CDCl}_3$ ) for the major isomer,  $\delta$  105.2, 92.7, 88.8, 75.9, 71.9, 71.5, 70.8, 31.4, 29.0, 25.8, 24.8, 18.2, 9.9, 8.0, -0.4, -4.2, -4.8; for the minor isomer,  $\delta$  104.8, 92.5, 88.2, 75.9, 71.4, 71.3, 70.5, 31.2, 28.3, 25.8, 24.5, 18.2, 9.4, 8.7, -0.4, -4.3, -4.9; IR (neat) 3549, 3426, 3303, 2164, 1463, 1369, 1245, 1059  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{21}\text{H}_{39}\text{O}_3\text{Si}_2$   $\text{MH}^+$  395.2438. Found: 395.2438.



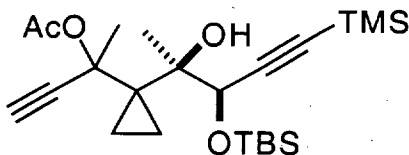
**(1R\*,2R\*)-3-(tert-Butyl-dimethylsilyloxy)-2-[1-(1-hydroxy-1-methyl-prop-2-ynyl)-cyclopropyl]-5-trimethylsilyl-pent-4-yn-2-ol (*syn-17*):** Following the above addition procedure, **syn-16** (62.0 mg, 0.168 mmol) gave the addition product **syn-17** (65.6 mg, 0.166 mmol, 99%) as a pale yellow oil;  $R_f$  0.3 (90:10-hexane: $\text{EtOAc}$ );  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  0.16 (s, 9H), 0.17 (s, 3H), 0.21 (s, 3H), 0.77-0.99 (m, 2H), 0.92 (s, 9H), 1.15-1.32 (m, 2H), 1.28 (s, 3H), 1.56 (s, 3H), 2.41 (s, 1H), 3.20 (s, 1H), 4.42 (s, 1H), 4.79 (s, 1H);  $^{13}\text{C}$  NMR (67.9 MHz,  $\text{CDCl}_3$ )  $\delta$  104.9, 92.5, 88.0, 72.5, 70.7, 68.7, 29.9, 29.4,

25.8, 22.6, 18.1, 9.1, 8.2, -0.5, -4.1, -4.9; IR (neat) 3436, 3303, 2174, 1467, 1374, 1246  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{21}\text{H}_{39}\text{O}_3\text{Si}_2 \text{MH}^+$  395.2438. Found: 395.2438.

**General procedure for the acylation of the propargylic alcohol:** According to the literature procedure, *anti*-**17** (72.8 mg, 0.185 mmol) was acylated with  $\text{Ac}_2\text{O}$  (87  $\mu\text{l}$ , 0.92 mmol) in the presence of DMAP (12.0 mg, 0.09 mmol) and neat  $\text{Et}_3\text{N}$  (0.25 mL, 1.84 mmol) at rt for 2 h. The reaction mixture was diluted with  $\text{Et}_2\text{O}$  (5 mL), filtered through a Florisil column, and washed with  $\text{Et}_2\text{O}$ . The crude product was quickly purified by flash chromatography using Florisil eluting with 2%  $\text{EtOAc}$ /hexane to give the desired product *anti*-**18**. The product was immediately converted into the corresponding allene to prevent decomposition. Extensive purification leads to the decomposition of the product.

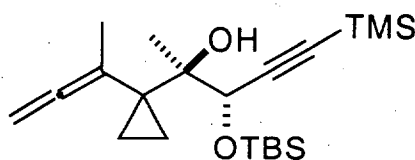


**Acetic acid, 1-{1-[(1*R*\*,2*S*\*)-2-(*tert*-butyldimethylsilyloxy)-1-hydroxy-1-methyl-4-(trimethylsilyl)-but-3-ynyl]-cyclopropyl}-1-methyl-prop-2-ynyl ester (*anti*-**18**)**  
Following the general procedure for the acylation of the propargylic alcohol, *anti*-**17** (72.8 mg, 0.185 mmol) was acylated to afford *anti*-**18** (80.3 mg, 0.183 mmol, 99%) as a pale yellow oil;  $R_f$  0.3 (90:10-hexane: $\text{EtOAc}$ , alumina plate).

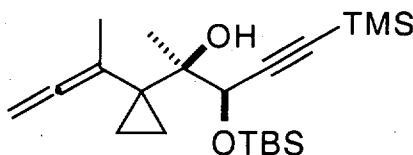


**Acetic acid, 1-{1-[(1*R*\*,2*R*\*)-2-(*tert*-butyldimethylsilyloxy)-1-hydroxy-1-methyl-4-(trimethylsilyl)-but-3-ynyl]-cyclopropyl}-1-methyl-prop-2-ynyl ester (*syn*-**18**):**  
Following the general procedure for the acylation of the propargylic alcohol, *syn*-**17** (50.1 mg, 0.127 mmol) was acylated to afford *syn*-**18** (54.2 mg, 0.124 mmol, 98%) as a pale yellow oil;  $R_f$  0.3 (90:10-hexane: $\text{EtOAc}$ , alumina plate).

**General procedure for the allene formation:** A solution of *anti*-**18** (0.353 g, 0.808 mmol), dissolved in deoxygenated toluene (20 mL) and H<sub>2</sub>O (73  $\mu$ L), was added to a flask containing [(Ph<sub>3</sub>P)CuH]<sub>6</sub> (0.791 g, 0.404 mmol) under N<sub>2</sub>. The reaction was stirred at rt for 20 min. The excess reagent was decomposed by allowing the reaction mixture to stir at rt open to the atmosphere for 3 h. The mixture was filtered through a short silica gel column, and washed with Et<sub>2</sub>O to remove the major by-products. The filtrate was concentrated and the crude product was purified by flash chromatography, eluting with 0.5% EtOAc/hexane to remove Ph<sub>3</sub>P followed by 1% EtOAc/hexane to provide and the desired product *anti*-**19** (164 mg, 0.430 mmol, 53%).



**(1*R*\*,2*S*\*)-3-(*tert*-Butyl-dimethylsilyloxy)-2-[1-(1-methyl-propa-1,2-dienyl)-cyclopropyl]-5-(trimethylsilyl)-pent-4-yn-2-ol (*anti*-**19**):** Following the general procedure for the allene formation reactions, *anti*-**18** (0.353 g, 0.808 mmol) gave *anti*-**19** (164 mg, 0.433 mmol, 54%) as a pale yellow oil; R<sub>f</sub> 0.5 (90:10-hexane:EtOAc); <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  0.13 (s, 3H), 0.15 (s, 9H), 0.16 (s, 3H), 0.37-0.45 (m, 1H), 0.49-0.56 (m, 1H), 0.81-0.89 (m, 1H), 0.90 (s, 9H), 1.08-1.13 (m, 1H), 1.22 (s, 3H), 1.75 (t, *J* = 3.2 Hz, 3H), 2.22 (s, 1H), 4.47 (s, 1H), 4.55 (q, *J* = 3.2 Hz, 2H); <sup>13</sup>C NMR (67.9 MHz, CDCl<sub>3</sub>)  $\delta$  210.2, 105.3, 100.2, 91.8, 75.2, 73.4, 69.9, 28.7, 25.8, 23.6, 18.9, 18.3, 11.1, 9.6, -0.4, -4.3, -5.1; IR (neat) 3569, 2174, 1949, 1467, 1364, 1246, 1062 cm<sup>-1</sup>; HRMS calcd for C<sub>21</sub>H<sub>38</sub>O<sub>2</sub>Si<sub>2</sub>: 378.2410. Found: 378.2410.

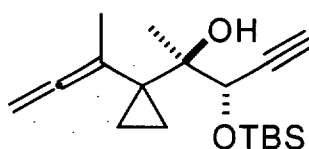




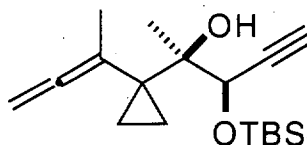
**(1*R*\*,2*R*\*)-3-(tert-Butyl-dimethylsilyloxy)-2-[1-(1-methyl-propa-1,2-dienyl)-**

**cyclopropyl]-5-(trimethylsilyl)-pent-4-yn-2-ol (*syn*-19):** Following the general procedure for the allene formation reactions, *syn*-18 (0.171 g, 0.390 mmol) gave *syn*-19 (81.6 mg, 0.216 mmol, 55%) as a pale yellow oil;  $R_f$  0.5 (90:10-hexane:EtOAc);  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  0.16 (s, 9H), 0.17 (s, 3H), 0.21 (s, 3H), 0.45-0.56 (m, 2H), 0.79-0.96 (m, 1H), 0.93 (s, 9H), 1.16-1.43 (m, 1H), 1.19 (s, 3H), 1.78 (t,  $J = 3.1$  Hz, 3H), 2.53 (s, 1H), 4.56 (q,  $J = 3.1$  Hz, 2H), 4.58 (s, 1H);  $^{13}\text{C}$  NMR (67.9 MHz,  $\text{CDCl}_3$ )  $\delta$  209.9, 105.1, 100.8, 91.2, 75.7, 73.4, 68.8, 28.3, 25.8, 21.9, 18.9, 18.2, 10.4, 10.2, -0.4, -4.1, -4.8; IR (neat) 3559, 2164, 1949, 1739, 1462, 1369, 1251, 1061  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{21}\text{H}_{38}\text{O}_2\text{Si}_2$ : 378.2410. Found: 378.2414.

**General procedure for the TMS deprotection:** A mixture containing the alkynyl allene *syn*-19 (97.4 mg, 0.258 mmol) with  $\text{K}_2\text{CO}_3$  (71 mg, 0.513 mmol) in  $\text{CH}_3\text{OH}$  (3 mL) and  $\text{H}_2\text{O}$  (0.75 mL) was stirred at 0 °C for 3 h. The reaction was partitioned between EtOAc (10 mL) and  $\text{H}_2\text{O}$  (5 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were concentrated. The residue was dissolved in EtOAc (15 mL), washed with  $\text{H}_2\text{O}$  (5 mL), dried ( $\text{MgSO}_4$ ) and concentrated. The crude product was purified by flash chromatography eluting with 5% EtOAc/hexane to afford the deprotected product *syn*-20 (75.3 mg, 0.246 mmol, 95%).

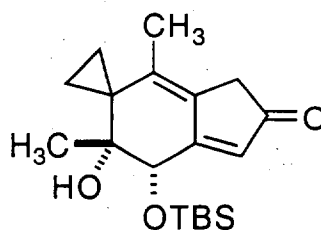
**(2*R*\*,3*S*\*)-3-(tert-Butyl-dimethylsilyloxy)-2-[1-(1-methyl-propa-1,2-dienyl)-**

**cyclopropyl]-pent-4-yn-2-ol (*anti*-20):** Following the general procedure for the TMS deprotection, *anti*-19 (0.147g, 0.389 mmol) yielded *anti*-20 (0.111 g, 0.363 mmol, 93%) as a yellow oil;  $R_f$  0.2 (95:5-hexane:EtOAc);  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  0.15 (s, 3H), 0.19 (s, 3H), 0.47 (ddd,  $J = 9.5, 5.8, 3.7$  Hz, 1H), 0.57 (ddd,  $J = 9.5, 5.8, 4.1$  Hz, 1H), 0.84-0.94 (m, 1H), 0.93 (s, 9H), 1.21-1.28 (m, 1H), 1.26 (s, 3H), 1.77 (t,  $J = 3.2$  Hz, 3H), 2.22 (s, 1H), 2.45 (d,  $J = 2.1$  Hz, 1H), 4.54 (d,  $J = 2.1$  Hz, 1H), 4.59 (q,  $J = 3.2$  Hz, 2H);  $^{13}\text{C}$  NMR (67.9 MHz,  $\text{CDCl}_3$ )  $\delta$  210.1, 100.1, 83.4, 76.5, 74.9, 73.6, 69.2, 28.6, 25.8, 23.5, 18.9, 18.2, 10.9, 9.5, -4.4, -5.2; IR (neat) 3569, 3303, 1954, 1471, 1359, 1251  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{18}\text{H}_{30}\text{O}_2\text{Si}$ : 306.2015. Found: 306.2015.



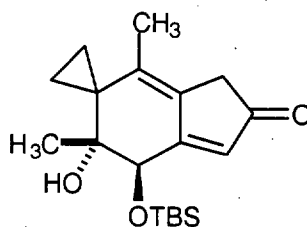
**(2*R*\*,3*R*\*)-3-(*tert*-Butyl-dimethylsilyloxy)-2-[1-(1-methyl-propa-1,2-dienyl)-cyclopropyl]-pent-4-yn-2-ol (*syn*-20):** Following the general procedure for the TMS deprotection, *syn*-19 (97.4 mg, 0.258 mmol) yielded *syn*-20 (75.3 mg, 0.246 mmol, 95%) as a pale yellow oil;  $R_f$  0.2 (95:5-hexane:EtOAc);  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  0.18 (s, 3H), 0.22 (s, 3H), 0.48-0.57 (m, 2H), 0.81-0.89 (m, 1H), 0.90-0.97 (m, 1H), 0.93 (s, 9H), 1.22 (s, 3H), 1.78 (t,  $J = 3.2$  Hz, 3H), 2.42 (d,  $J = 2.2$  Hz, 1H), 2.53 (s, 1H), 4.58 (q,  $J = 3.2$  Hz, 2H), 4.63 (d,  $J = 2.2$  Hz, 1H);  $^{13}\text{C}$  NMR (67.9 MHz,  $\text{CDCl}_3$ )  $\delta$  209.7, 100.7, 83.2, 75.6, 73.6, 68.0, 28.3, 25.8, 21.2, 18.9, 18.1, 10.2, 10.1, -4.2, -4.9; IR (neat) 3559, 3303, 1949, 1733, 1467, 1364, 1246  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{18}\text{H}_{31}\text{O}_2\text{Si}$ ,  $\text{MH}^+$ : 307.2093. Found: 307.2093.

**General procedure for the allenic Pauson-Khand cyclization reactions:** To a flame dried flask was added *anti*-20 (0.100 g, 0.327 mmol) in deoxygenated toluene (8 mL) and DMSO (0.23 mL, 3.3 mmol). The solution was transferred into a two-necked flask containing  $\text{Mo}(\text{CO})_6$  (130 mg, 0.491 mmol), equipped with a condenser under  $\text{N}_2$ . The reaction mixture was stirred in an oil-bath at 110  $^\circ\text{C}$  for 15 min, then cooled to rt, filtered through a plug of silica gel, and washed with  $\text{Et}_2\text{O}$  to remove the baseline material. The crude product was purified by flash chromatography eluting with 20% EtOAc/hexane to afford the desired product *cis*-21 (75.5 mg, 0.226 mmol, 69%).



**(8*R*\*,9*S*\*)-8-Hydroxy-6,8-dimethyl-7-spiro-cyclopropyl-9-[(1,1-dimethylethyl)-dimethylsilyloxy]-bicyclo[4.3.0]nona-1,5-dien-3-one (*cis*-21):** Following the general

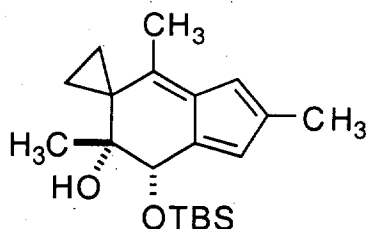
allenic Pauson-Khand procedure, *trans*-**20** (0.1002 g, 0.328 mmol) yielded the product *cis*-**21** (75.5 mg, 0.259 mmol, 69%) as white crystals, mp 95-96 °C; *R*<sub>f</sub> 0.2 (80:20-hexane:EtOAc); <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ 0.04 (s, 3H), 0.15 (s, 3H), 0.78-0.83 (m, 2H), 0.88-0.97 (m, 1H), 0.89 (s, 9H), 1.02-1.12 (m, 1H), 1.08 (s, 3H), 1.55 (s, 3H), 2.43 (s, 1H), 2.94 (d, *J* = 21.3 Hz, 1 H), 3.02 (d, *J* = 21.3 Hz, 1H), 4.39 (s, 1H), 6.08 (s, 1H); <sup>13</sup>C NMR (67.9 MHz, CDCl<sub>3</sub>) δ 204.8, 169.9, 137.7, 128.8, 128.7, 73.1, 72.7, 39.0, 28.9, 25.7, 21.9, 18.1, 15.7, 9.9, 6.2, -4.1, -4.7; IR (neat) 3436 (br), 1697, 1672, 1579, 1472, 1389, 1297, 1251, 1200 cm<sup>-1</sup>; HRMS calcd for C<sub>19</sub>H<sub>31</sub>O<sub>3</sub>Si MH<sup>+</sup> 335.2042. Found: 335.2042. Anal. calcd for C<sub>19</sub>H<sub>30</sub>O<sub>3</sub>Si: C, 68.22; H, 9.05. Found: C, 68.04; 9.07.



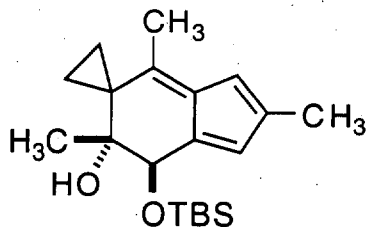
**(8R\*,9R\*)-8-Hydroxy-6,8-dimethyl-7-spiro-cyclopropyl-9-[(1,1-dimethylethyl)-dimethylsilyloxy]-bicyclo[4.3.0]nona-1,5-dien-3-one (*trans*-**21**):** Following the general allenic Pauson-Khand cyclization procedure, *syn*-**20** (60.1 mg, 0.196 mmol) afforded the product *trans*-**21** (44.8 mg, 0.134 mmol, 68%) as white crystals, mp 127-129 °C; *R*<sub>f</sub> 0.2 (80:20-hexane:EtOAc); <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ 0.14 (s, 6H), 0.45-0.53 (m, 1H), 0.55-0.73 (m, 0.26 H), 0.84-1.02 (m, 1H), 0.97 (s, 9H), 1.12 (s, 3H), 1.16-1.29 (m, 0.73 H), 1.33-1.40 (m, 1H), 1.54 (s, 3H), 1.61 (s, 1H), 2.92 (d, *J* = 21.2 Hz, 2H), 3.00 (d, *J* = 21.2 Hz, 1H), 4.58 (s, 1H), 6.09 (d, *J* = 1.7 Hz); <sup>13</sup>C NMR (67.9 MHz, CDCl<sub>3</sub>) δ 204.5, 174.3, 137.2, 129.8, 125.9, 75.9, 73.9, 39.1, 31.2, 25.8, 19.8, 18.2, 15.6, 8.6, 6.3, -4.5, -4.7; IR (neat) 3446 (br), 1697, 1667, 1579, 1471, 1456, 1374, 1251, 1230, 1169 cm<sup>-1</sup>; HRMS calcd for C<sub>19</sub>H<sub>31</sub>O<sub>3</sub>Si MH<sup>+</sup> 335.2042. Found: 335.2042. Anal. calcd for C<sub>19</sub>H<sub>30</sub>O<sub>3</sub>Si: C, 68.22; H, 9.05. Found: C, 68.00; 9.02.

**General procedure for the addition of CH<sub>3</sub>Li:** To a 25 mL round-bottomed flask was added CeCl<sub>3</sub>•7H<sub>2</sub>O (290 mg, 0.78 mmol). It was dried and suspended in THF (8 mL) as described in the literature. The suspension was stirred at rt overnight, then cooled to -78 °C. CH<sub>3</sub>Li (1.4 M, 0.56 mL, 0.78 mmol) was added and the resultant yellow solution

was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1.5 h. A solution of *cis*-**21** (26.0 mg, 0.078 mmol) in THF (1 mL) was added dropwise and the reaction was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h. The reaction was quenched with 0.1 M HCl (10 mL) at  $-78\text{ }^{\circ}\text{C}$  and warmed to rt. The mixture was partitioned between Et<sub>2</sub>O (15 mL) and H<sub>2</sub>O (4 mL). The aqueous layer was extracted with Et<sub>2</sub>O (3 x 10 mL). The combined organic layers were dried with MgSO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography eluting with 5% EtOAc/hexane to afford the product *cis*-**22** (24.8 mg, 0.075 mmol, 96%).



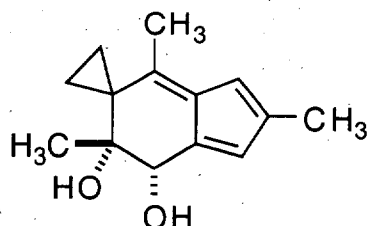
**(8*R*\*,9*S*\*)-8-Hydroxy-3,6,8-trimethyl-7-spiro-cyclopropyl-9-[(1,1-dimethylethyl)-dimethylsilyloxy]bicyclo[4.3.0]nona-1,3,5-triene (*cis*-**22**):** Following the general procedure for the addition of CH<sub>3</sub>Li, *cis*-**21** (26.0 mg, 0.078 mmol) yielded *cis*-**22** (24.8 mg, 0.075 mmol, 96%) as a yellow gum; *R*<sub>f</sub> 0.4 (95:5-hexane:EtOAc); <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  -0.16 (s, 3H), 0.13 (s, 3H), 0.75-1.00 (m, 2H), 0.84 (s, 9H), 1.05-1.33 (m, 2H), 1.10 (s, 3H), 1.81 (s, 3H), 2.06 (d, *J* = 1.2 Hz, 3H), 3.01 (s, 1H), 4.41 (s, 1H), 6.06 (t, *J* = 1.4 Hz, 1H), 6.19 (d, *J* = 1.2 Hz, 1H); <sup>13</sup>C NMR (67.9 MHz, CDCl<sub>3</sub>)  $\delta$  150.6, 140.6, 138.5, 133.2, 131.1, 114.3, 73.3, 73.2, 30.7, 25.9, 22.8, 18.1, 16.0, 15.6, 13.5, 6.1, -4.2, -4.6; IR (neat) 3415, 1733, 1626, 1441, 1369, 1338, 1251 cm<sup>-1</sup>; HRMS calcd for C<sub>20</sub>H<sub>32</sub>O<sub>2</sub>Si: 332.2172. Found: 332.2174.



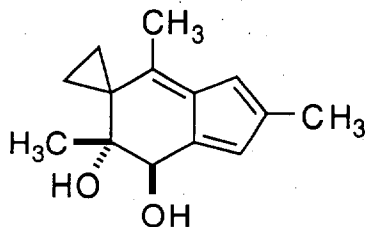
**(8*R*\*,9*R*\*)-8-Hydroxy-3,6,8-trimethyl-7-spiro-cyclopropyl-9-[(1,1-dimethylethyl)-dimethylsilyloxy]bicyclo[4.3.0]nona-1,3,5-triene (*trans*-**22**):** Following the general procedure for the addition of CH<sub>3</sub>Li, *trans*-**21** (36.0 mg, 0.108 mmol) yielded *trans*-**22**

(33.9 mg, 0.102 mmol, 94% ) as a yellow gum;  $R_f$  0.4 (95:5-hexane:EtOAc);  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  0.14 (s, 3H), 0.18 (s, 3H), 0.47-0.59 (m, 2H), 0.87-1.08 (m, 2H), 0.99 (s, 9H), 1.11 (s, 3H), 1.47-1.55 (m, 1H), 1.63 (bs, 1H), 1.78 (s, 3H), 2.07 (s, 3H), 4.66 (s, 1H), 5.98 (d,  $J = 1.0$  Hz, 1H), 6.05 (t,  $J = 1.9$  Hz, 1H);  $^{13}\text{C}$  NMR (67.9 MHz,  $\text{CDCl}_3$ )  $\delta$  148.4, 142.1, 140.2, 112.8, 76.0, 32.9, 26.0, 25.9, 19.9, 18.3, 16.0, 15.8, 9.5, -4.3, -4.7; IR (neat) 3518 (br), 1631, 1605, 1472, 1441, 1369, 1318, 1251  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{20}\text{H}_{33}\text{O}_2\text{Si}$ ,  $\text{MH}^+$ : 333.2249. Found: 333.2249.

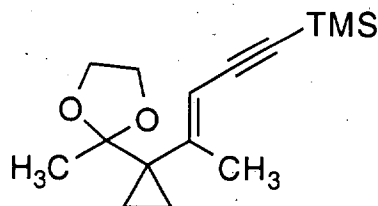
**General procedure for the TBS deprotection:** A solution of *cis*-22 (24.2 mg, 0.073 mmol) in THF (2 mL) with TBAF (1.0 M, 0.16 mL, 0.16 mmol) was stirred at 0 °C for 2 h. The solvent was evaporated and the residue was purified by flash chromatography eluting with 20% EtOAc/hexane to give diol *cis*-23 (15.3 mg, 0.070 mmol, 96%).



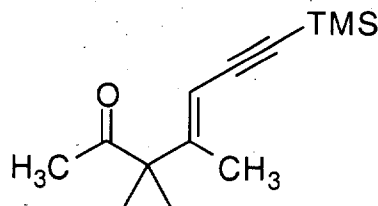
**(8*R*\*,9*S*\*)-8,9-Dihydroxy-3,6,8-trimethyl-7-spiro-cyclopropylbicyclo-[4.3.0]nona-1,3,5-triene (*cis*-23):** Following the general procedure for TBS deprotection, *cis*-22 (24.2 mg, 0.073 mmol) yielded *cis*-23 (15.3 mg, 0.070 mmol, 96%) as a yellow gum;  $R_f$  0.1 (80:20-hexane:EtOAc);  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  0.80-0.88 (m, 1H), 0.91-1.06 (m, 2H), 1.16 (s, 3H), 1.21-1.28 (m, 1H), 1.62 (d,  $J = 7.7$  Hz, 1H), 1.84 (s, 3H), 2.07 (d,  $J = 0.9$  Hz, 3H), 2.86 (s, 1H), 4.33 (d,  $J = 7.7$  Hz, 1H), 6.08 (t,  $J = 1.5$  Hz, 1H), 6.34 (s, 1H);  $^{13}\text{C}$  NMR (67.9 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 141.7, 138.4, 133.2, 130.1, 114.3, 73.1, 72.4, 30.1, 23.2, 16.1, 15.6, 12.9, 6.4; IR (neat) 3405, 1631, 1446, 1374, 1328  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{14}\text{H}_{19}\text{O}_2$   $\text{MH}^+$  219.1385. Found: 219.1385.



**(8*R*\*,9*R*\*)-8,9-Dihydroxy-3,6,8-trimethyl-7-spiro-cyclopropylbicyclo-[4.3.0]nona-1,3,5-triene (*trans*-23):** Following the general procedure for TBS deprotection, *trans*-22 (14.0 mg, 0.042 mmol) yielded *trans*-23 (8.9 mg, 0.041 mmol, 98%) as a yellow gum;  $R_f$  0.2 (65:35-hexane:EtOAc);  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  0.53-0.60 (m, 1H), 0.86-0.94 (m, 1H), 1.06-1.16 (m, 1H), 1.13 (s, 3H), 1.45-1.52 (m, 1H), 1.80 (s, 3H), 1.88 (bs, 1H), 1.97 (d,  $J$  = 6.6 Hz, 1H), 2.07 (s, 3H), 4.66 (d,  $J$  = 6.6 Hz, 1H), 6.01 (q,  $J$  = 1.6 Hz, 1H), 6.20 (t,  $J$  = 1.9 Hz, 1H);  $^{13}\text{C}$  NMR (67.9 MHz,  $\text{CDCl}_3$ )  $\delta$  149.0, 142.2, 140.3, 113.2, 76.5, 33.0, 19.5, 16.2, 15.7, 9.7; IR (neat) 3415, 1626, 1600, 1441, 1369, 1328, 1303, 1108  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{14}\text{H}_{19}\text{O}_2$   $\text{MH}^+$  219.1385. Found: 219.1385.

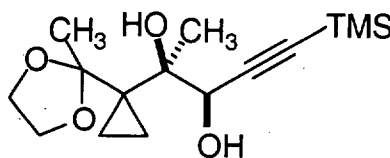


**(*E*)-Trimethyl-{4-[1-(2-methyl-[1,3]dioxolan-2-yl)-cyclopropyl]-pent-3-en-1-ynyl} silane (27):** A solution of the diethyl (3-trimethylsilyl-2-propynyl) phosphonate (4.12 g, 16.6 mmol) in THF (20 mL) in a flame-dried flask was cooled to  $-78^\circ\text{C}$ . It was treated with sodium hexamethyldisilazide (1.0 M, 15.4 mL, 15.4 mmol) and the resulting mixture was stirred at  $-78^\circ\text{C}$  for 1 h. A solution of ketone 7 (2.09 g, 12.3 mmol) in THF (20 mL) was cooled to  $-78^\circ\text{C}$ , then added via a canula. The reaction was stirred at  $-78^\circ\text{C}$  for 1 h, and then it was warmed gradually to rt over a period of 3 h. It was quenched with  $\text{H}_2\text{O}$  (10 mL), partitioned between EtOAc (60 mL) and  $\text{H}_2\text{O}$  (50 mL). The organic layer was washed with 0.5 M HCl (2 x 40 mL), 5%  $\text{NaHCO}_3$  (40 mL),  $\text{H}_2\text{O}$  (50 mL) and brine (60 mL) then it was dried with  $\text{MgSO}_4$ , filtered and concentrated. The crude mixture was purified by silica gel column chromatography, eluting first with 0.5% EtOAc/hex to remove the faster moving impurities, then the product was eluted with 1-2% EtOAc/hex to give the enyne 27 (2.85 g, 10.8 mmol, 88%) as a clear oil;  $R_f$  0.33 (hexane : EtOAc = 95:5);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz) 0.19 (s, 9H), 0.48 (dd,  $J$  = 6.1, 4.0 Hz, 2H), 0.82 (dd,  $J$  = 6.1, 3.8 Hz, 2H), 1.34 (s, 3H), 2.06 (d,  $J$  = 1.2 Hz, 3H), 3.92 (s, 4H), 5.57 (q,  $J$  = 1.2 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.9 MHz) 154.4, 110.3, 110.1, 103.1, 98.9, 65.1, 34.4, 23.5, 20.0, 9.6, 0.1; IR (neat): 2133, 1621, 1441, 1369, 1246  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{15}\text{H}_{24}\text{O}_2\text{Si}$   $\text{MH}^+$ : 265.1627. Found: 265.1624.



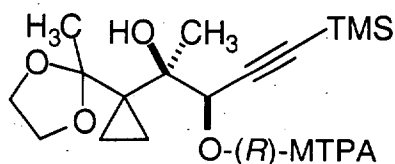
**(E)-{1-[1-Methyl-4-(trimethylsilyl)-but-1-en-3-ynyl]-cyclopropyl}-ethanone (29):**

Ketal **27** (0.409 g, 1.55 mmol) was dissolved in acetone (2 mL). The solution was treated with H<sub>2</sub>O (2 mL) and PTSA•H<sub>2</sub>O (0.044 g, 0.232 mmol), and stirred at rt for 3 h. Acetone was removed *in vacuo* and the aqueous residue was diluted with H<sub>2</sub>O (5 mL) and extracted with Et<sub>2</sub>O (3 x 10 mL). The combined organic layers were dried with MgSO<sub>4</sub>, filtered and concentrated to give a clear oil (0.330 g, 1.50 mmol, 97%), which solidified to a white solid upon setting in refrigerator; mp 36-37 °C; R<sub>f</sub>: 0.33 (Hexane : EtOAc = 95:5); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz) 0.21 (s, 9H), 0.94 (dd, *J* = 6.7, 3.7 Hz, 2H), 1.36 (dd, *J* = 6.7, 3.7 Hz, 2H), 2.04 (d, *J* = 1.2 Hz, 3H), 2.17 (s, 3H), 5.59 (q, *J* = 1.2 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.9 MHz) 207.1, 151.1, 110.8, 102.1, 100.2, 39.4, 27.7, 20.1, 17.5, 0.0; IR (neat): 2133, 1697, 1615, 1415, 1354, 1272, 1246, 1144, 1082 cm<sup>-1</sup>; HRMS calcd for C<sub>13</sub>H<sub>20</sub>OSi MH<sup>+</sup>: 221.1362. Found: 221.1362.



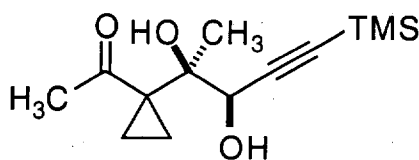
**(2R,3R)-2-[1-(2-Methyl-[1,3]dioxolan-2-yl)-cyclopropyl]-5-(trimethylsilyl)-pent-4-yn-2,3-diol (28):** This compound was prepared using the general procedure for the asymmetric dihydroxylation of enynes (*vide infra*). White solid, mp 75-77 °C; R<sub>f</sub>: 0.21 (Hexane : EtOAc = 80:20); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz) 0.17 (s, 9H), 0.56-0.69 (m, 3H), 0.83-1.00 (m, 1H), 1.33 (s, 6H), 2.79 (s, 1H), 3.64 (d, *J* = 3.8 Hz, 1H), 3.83-4.13 (m, 4H), 4.68 (d, *J* = 3.8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.9 MHz) 111.5, 103.6, 91.0, 74.9, 68.8, 64.5, 63.6, 30.3, 23.4, 23.1, 7.4, 6.8, -0.2; IR (neat): 3467, 3323, 2164, 1410, 1374, 1312, 1241 cm<sup>-1</sup>; [α]<sub>D</sub><sup>25</sup> = -15.243 ° (c 1.00, CH<sub>2</sub>Cl<sub>2</sub>); HRMS calcd for C<sub>15</sub>H<sub>26</sub>O<sub>4</sub>Si MH<sup>+</sup>: 299.1679. Found: 299.1676. The enantiomeric excesses were established by the <sup>1</sup>H NMR

of the corresponding Mosher ester (spectra for racemic and optically pure samples are included in the supporting information section).



$R_f$ : 0.35 (Hexane : EtOAc = 80:20);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.15 (s, 9H), 0.66-0.74 (m, 2H), 0.78-0.86 (m, 2H), 1.14 (s, 3H), 1.43 (s, 3H), 3.64 (d,  $J$  = 1.0 Hz, 3H), 3.87 (s, 1H), 3.91-4.12 (m, 4H), 6.23 (s, 1H), 7.39-7.41 (m, 3H), 7.62-7.64 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.9 MHz)  $\delta$  165.8, 132.4, 129.5, 128.5, 128.2, 127.7, 112.0, 100.2, 92.9, 76.2, 71.5, 64.3, 64.2, 55.7, 29.9, 24.3, 19.5, 9.5, 6.4, -0.5.

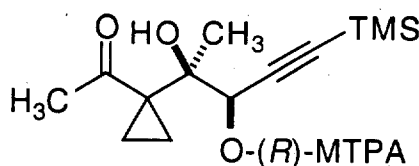
#### General Procedure for the Asymmetric Dihydroxylation of Enynes.



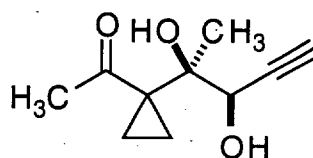
**1-[(1*R*,2*R*)-1-[1,2-Dihydroxy-1-methyl-4-(trimethylsilyl)-but-3-ynyl]-cyclopropyl] ethanone (30):** To a 10 mL round bottomed flask was added  $\text{K}_2\text{OsO}_2(\text{OH})_4$  (3.4 mg,  $9.2 \times 10^{-3}$  mmol),  $(\text{DHQD})_2\text{PYR}$  (40.7 mg,  $4.17 \times 10^{-2}$  mmol),  $\text{K}_3\text{Fe}(\text{CN})_6$  (456 mg, 1.39 mmol),  $\text{K}_2\text{CO}_3$  (191 mg 1.39 mmol), *t*-BuOH (2 mL) and  $\text{H}_2\text{O}$  (2 mL). The bi-phasic mixture was stirred at rt for 10 min, then  $\text{CH}_3\text{SO}_2\text{NH}_2$  (48.3 mg, 0.5081 mmol) was added and the mixture was stirred at rt 5 min. Enyne **29** (101.6 mg, 0.4619 mmol) was added to the AD-mix- $\beta$  mixture and stirred at rt for 48 h. The reaction mixture was partitioned between EtOAc (20 mL) and  $\text{H}_2\text{O}$  (10 mL). The aqueous layer was separated and extracted with EtOAc (2 x 10 mL) and the combined organic layers were washed with KOH (1 M, 10 mL),  $\text{H}_2\text{O}$  (10 mL) then dried with  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The crude product was purified by silica gel chromatography, eluting (20% EtOAc/Hex) to give the diols **30** and **31**. Diol **30**: (57.9 mg, 0.228 mmol, 49%) white solid, mp 81-82.5 °C;  $R_f$ : 0.19 (Hexane : EtOAc = 80 : 20);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 270 MHz) 0.09 (s, 9H), 0.11 (s, 18H), 0.12 (s, 9H), 0.15-0.22 (m, 2H), 0.30-0.38 (m, 2H), 0.42-0.55



(m, 2H), 0.60-0.67 (m, 6H), 0.69 (s, 6H), 0.71-0.84 (m, 2H), 0.91 (s, 3H), 1.04-1.11 (m, 1H), 1.07 (s, 6H), 1.25 (s, 3H), 1.27-1.30 (m, 1H), 1.32 (s, 3H), 1.39 (s, 3H), 2.16 (bs, 1H), 2.17 (bs, 1H), 2.92 (bs, 0.5 H), 2.94 (bs, 0.5 H), 3.07 (s, 2H), 3.18 (s, 1H), 4.24 (bs, 2H), 4.39 (s, 2H), 4.74 (s, 1H), 5.14 (s, 0.5), 5.17 (s, 0.5H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 67.9 MHz) 209.2, 107.2, 106.1, 104.9, 102.2, 101.6, 93.4, 90.6, 79.6, 78.9, 78.4, 76.8, 74.7, 68.5, 38.2, 37.0, 36.7, 27.0, 24.3, 23.2, 22.0, 21.6, 19.6, 12.6, 11.4, 8.8, 8.3, 7.0, 4.1, -0.1, -0.2, -0.3; IR (KBr): 3481, 3427, 2177, 1749, 1398, 1312, 1279, 1242  $\text{cm}^{-1}$ ;  $[\alpha]^{25}_{\text{D}} = -8.10^\circ$  (c 1.00,  $\text{CH}_2\text{Cl}_2$ , 1 h); HRMS calcd for  $\text{C}_{13}\text{H}_{22}\text{O}_3\text{Si}$   $\text{MH}^+$ : 255.1416. Found: 255.1416. The enantiomeric excesses were established by the  $^1\text{H}$  NMR of the corresponding Mosher ester (spectra for racemic and optically pure samples are included in the supporting information section).

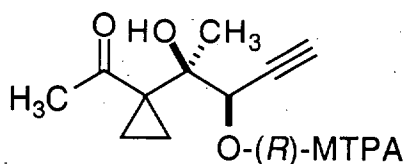


$R_f$ : 0.28 (Hexane : EtOAc = 80:20);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.16 (s, 9H), 0.92-1.00 (m, 1H), 1.22 (s, 3H), 1.25-1.33 (m, 2H), 1.40-1.48 (m, 1H), 1.87 (s, 3H), 3.54 (d,  $J = 1.0$  Hz, 3H), 3.62 (bs, 1H), 6.29 (s, 1H), 7.37-7.43 (m, 3H), 7.54-7.56 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.9 MHz)  $\delta$  209.7, 165.4, 132.0, 129.5, 128.3, 127.8, 99.0, 93.9, 85.4, 85.0, 84.6, 74.1, 71.3, 55.4, 36.6, 24.6, 20.3, 12.9, 12.3, -0.4.



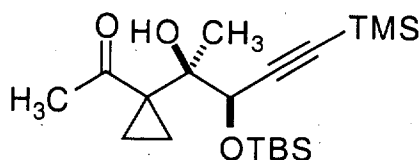
**1-((1R,2R)-1-[1,2-Dihydroxy-1-methyl-3-butynyl]-cyclopropyl) ethanone (31):** (9.1 mg, 0.05 mmol, 11%); white solid; mp 103-105  $^\circ\text{C}$ ;  $R_f$ : 0.19 (Hexane : EtOAc = 65 : 35);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 270 MHz) 0.09-0.17 (m, 1H), 0.27-0.44 (m, 2H), 0.48 (s, 2H), 0.51-0.71 (m, 9H), 0.80 (s, 1H), 0.94-0.99 (m, 1.5H), 1.04 (s, 3H), 1.18-1.23 (m, 2.5H), 1.26 (s, 3H), 1.32 (s, 4H), 1.70 (s, 0.36H), 1.84 (s, 0.36H), 1.94 (d,  $J = 2.2$  Hz, 1.52H), 1.98 (d,  $J = 2.2$  Hz, 0.36H), 2.01 (d,  $J = 2.2$  Hz, 1H), 2.56 (s, 0.76H), 2.59 (s, 0.76H), 2.68 (s, 1H),

2.84 (s, 1.52H), 4.02 (s, 1H), 4.24 (d,  $J = 2.2$  Hz, 1H), 4.57 (d,  $J = 2.2$  Hz, 0.36H), 5.06 (d,  $J = 2.2$  Hz, 0.76H), 5.08 (d,  $J = 2.2$  Hz, 0.76H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 67.9 MHz) 107.2, 104.9, 83.5, 80.1, 79.6, 79.4, 79.0, 77.6, 76.4, 76.3, 76.0, 74.4, 74.3, 67.9, 38.1, 36.9, 36.6, 26.9, 24.2, 23.1, 22.1, 21.2, 19.3, 14.8, 12.5, 11.1, 8.8, 8.3, 6.9, 4.0; IR (neat): 3415, 3292, 2113, 1667, 1451, 1425, 1369, 1322  $\text{cm}^{-1}$ ;  $[\alpha]^{25}_{\text{D}} = -15.40^\circ$  (c 1.00,  $\text{CH}_2\text{Cl}_2$ , 1 h); The enantiomeric excesses were established by the  $^1\text{H}$  NMR of the corresponding Mosher ester (spectra for racemic and optically pure samples are included in the supporting information section).



$R_f$ : 0.2 (Hexane : EtOAc = 80:20);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.89-1.01 (m, 1H), 1.21-1.34 (m, 2H), 1.28 (s, 3H), 1.39-1.47 (m, 1H), 1.86 (s, 3H), 2.56 (d,  $J = 2.2$  Hz, 1H), 3.41 (s, 1H), 3.57 (d,  $J = 0.7$  Hz, 3H), 6.34 (d,  $J = 2.2$  Hz, 1H), 7.39-7.43 (m, 3H), 7.54-7.57 (m, 2H).

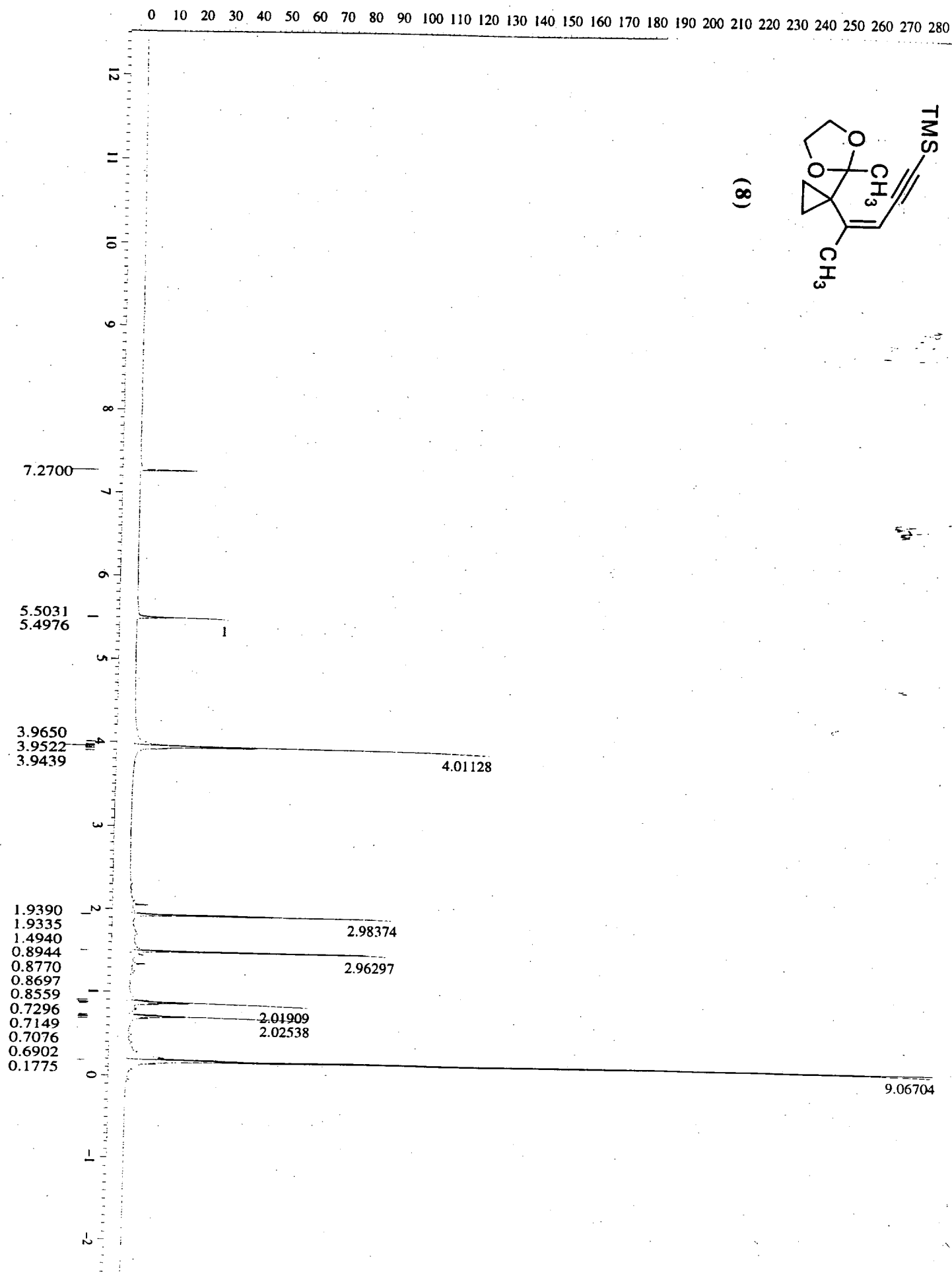
**Conversion of the terminal alkyne 31 to TMS protected alkyne 30:** Alkyne 31 (0.92 g, 5.1 mmol) was dissolved in THF (20 mL) in a flame-dried flask, and cooled to  $0^\circ\text{C}$ . This solution was treated with freshly prepared LDA (1.0 M, 22.8 mL, 22.8 mmol) and stirred at  $0^\circ\text{C}$  for 1 h. The resulting solution was treated with TMSCl (2.90 mL, 22.8 mmol) at  $0^\circ\text{C}$ , and allowed to stir at  $0^\circ\text{C}$  for 1 h. The reaction was quenched with sat.  $\text{NH}_4\text{Cl}$  (50 mL) and partitioned between  $\text{Et}_2\text{O}$  (60 mL) and  $\text{H}_2\text{O}$  (40 mL). The aqueous layer was separated and extracted with  $\text{Et}_2\text{O}$  (2 x 40 mL). The combined organic layers were concentrated and the residue was dissolved in THF (15 mL) and the solution was treated with 1.0 M HCl (15 mL). This mixture was stirred at rt for 1.5 h. It was then diluted with  $\text{Et}_2\text{O}$  (50 mL). The organic layer was washed with sat.  $\text{NaHCO}_3$  (20 mL),  $\text{H}_2\text{O}$  (20 mL) and brine (20 mL), dried with  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. Purification of the crude product by silica gel chromatography (20% EtOAc/Hex) afforded the TMS protected product 30 (0.940 g, 3.70 mmol, 73%).

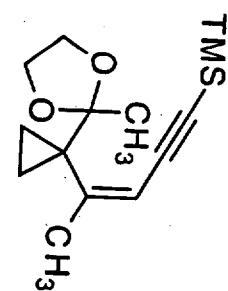


#### TBS protection of the Diol:

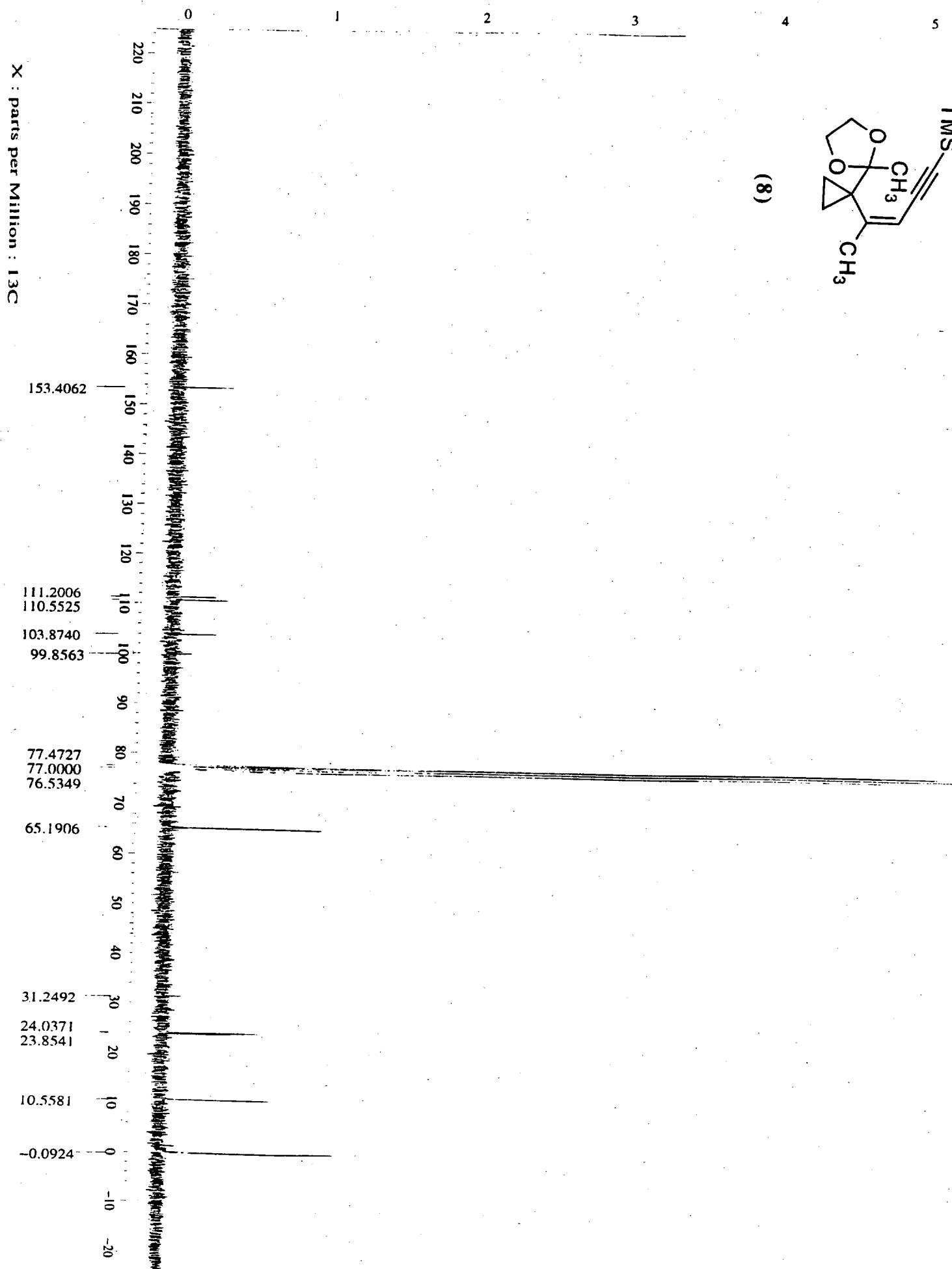
**1-{1-[2-(tert-butyl-dimethylsiloxy)-1-hydroxy-1-methyl-4-(trimethylsilyl)-but-3-ynyl-cyclopropyl] ethanone (*R,R*-16):** To a flame dried flask was added diol **30** (263 mg, 0.104 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL). It was stirred at rt until a homogeneous solution formed then cooled to  $-78^\circ\text{C}$ . The solution was then treated with freshly distilled 2,6-lutidine (24  $\mu\text{l}$ , 0.21 mmol) and followed by the addition of freshly distilled TBSOTf (29  $\mu\text{l}$ , 0.12 mmol). The reaction was stirred at  $-78^\circ\text{C}$  for 1h, and it was warmed gradually to  $0^\circ\text{C}$ . It was quenched with 0.1 M HCl (10 mL), partitioned between  $\text{Et}_2\text{O}$  (20 mL) and  $\text{H}_2\text{O}$  (5 mL). The aqueous layer was extracted with  $\text{Et}_2\text{O}$  (2 x 10 mL). The combined organic layers were washed with 0.1 M HCl (20 mL),  $\text{H}_2\text{O}$  (10 mL) and brine (30 mL) then dried with  $\text{MgSO}_4$ , filtered and concentrated. The crude mixture was purified by silica gel chromatography (10% EtOAc/Hex) to afford the TBS protected product (29.3 mg, 0.079 mmol, 77%).  $[\alpha]_D^{25} = -47.342^\circ$  (c 0.997,  $\text{CH}_2\text{Cl}_2$ )

X : parts per Million : 1H





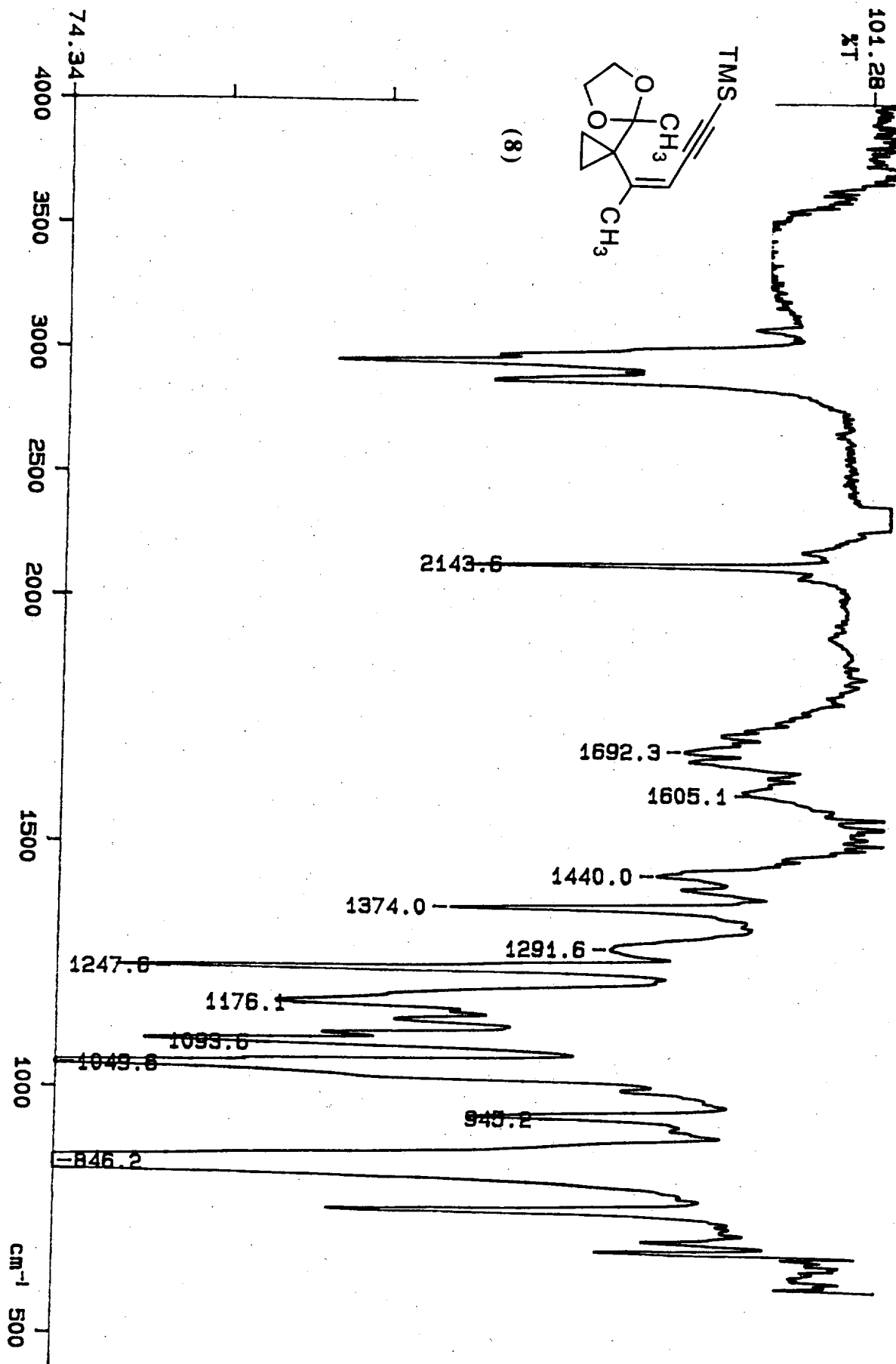
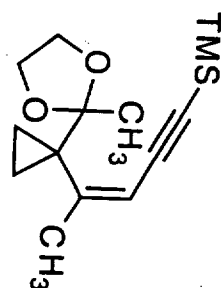
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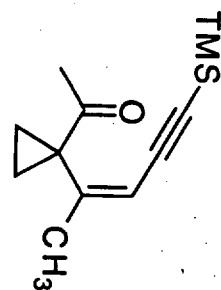
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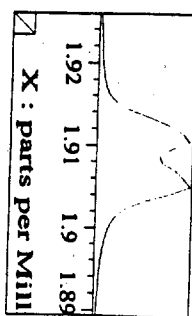
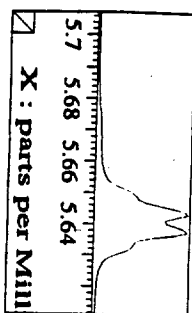
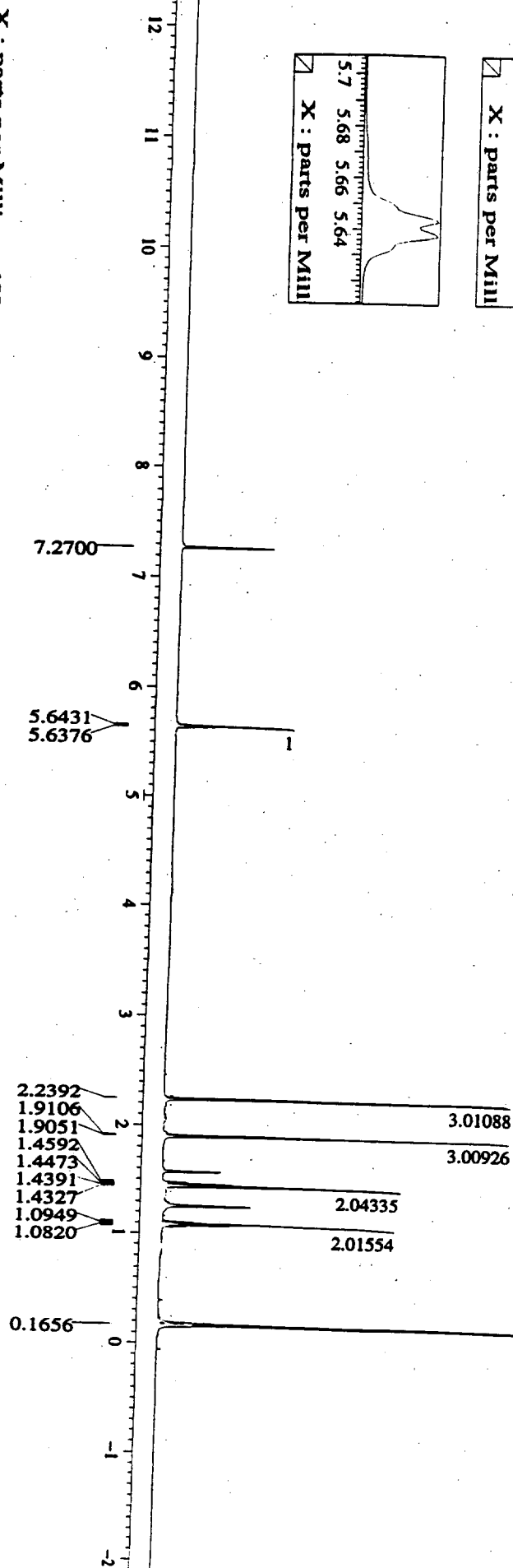


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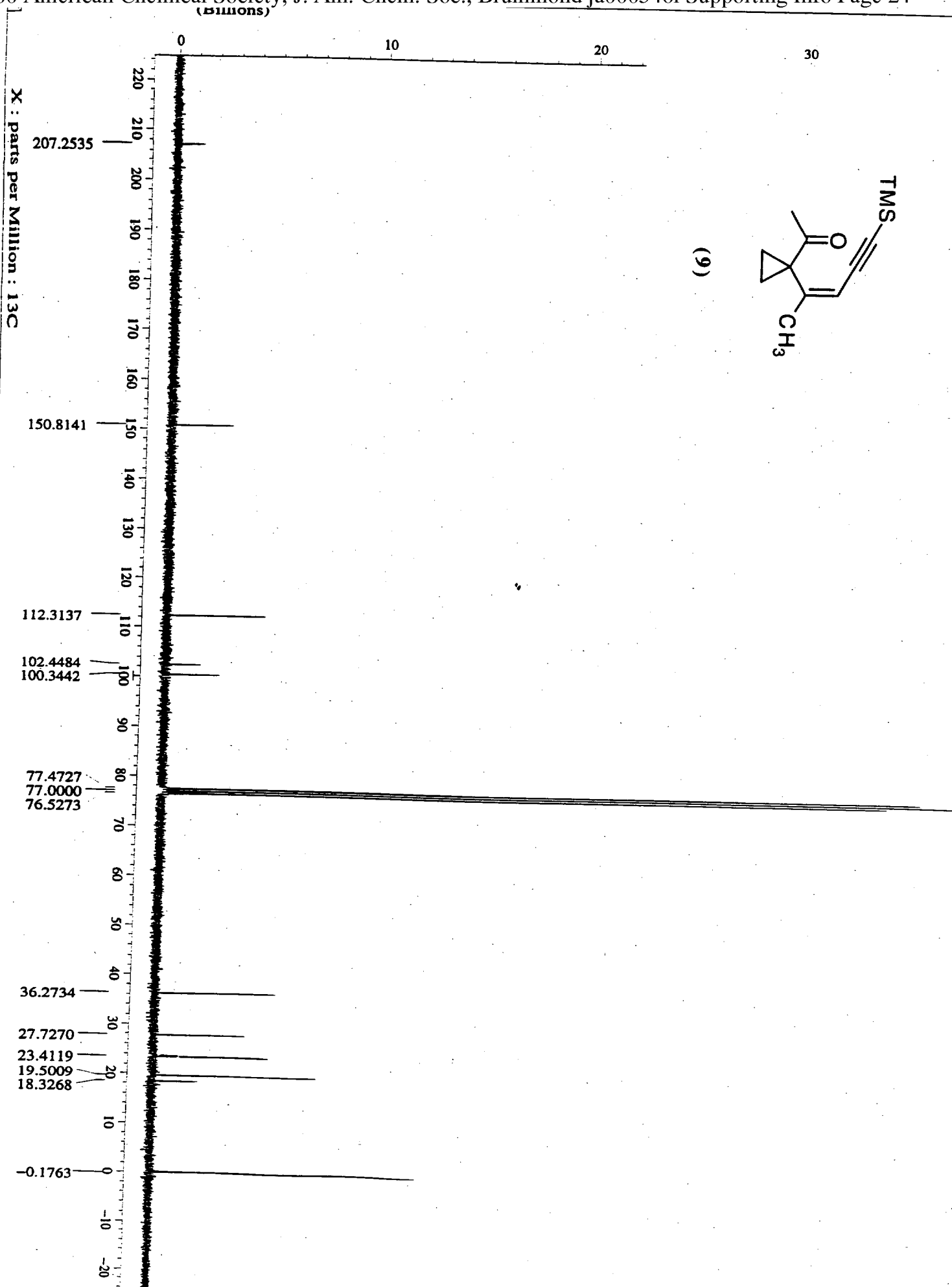


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X : parts per Million : 1H



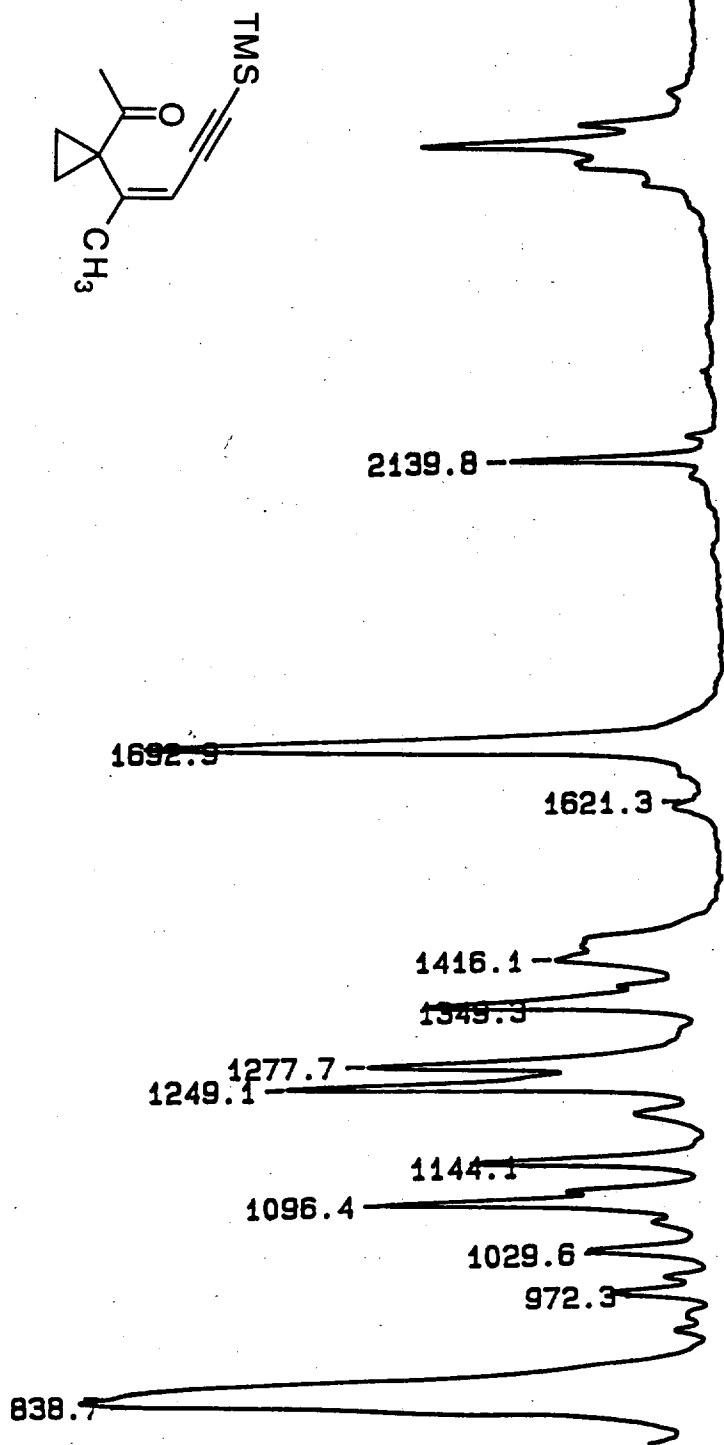
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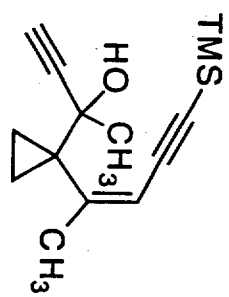
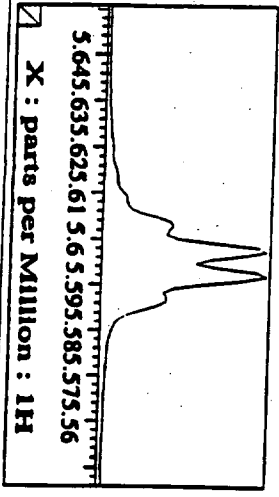
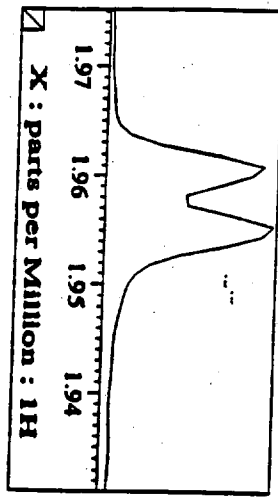
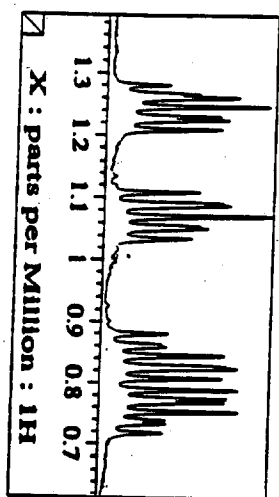
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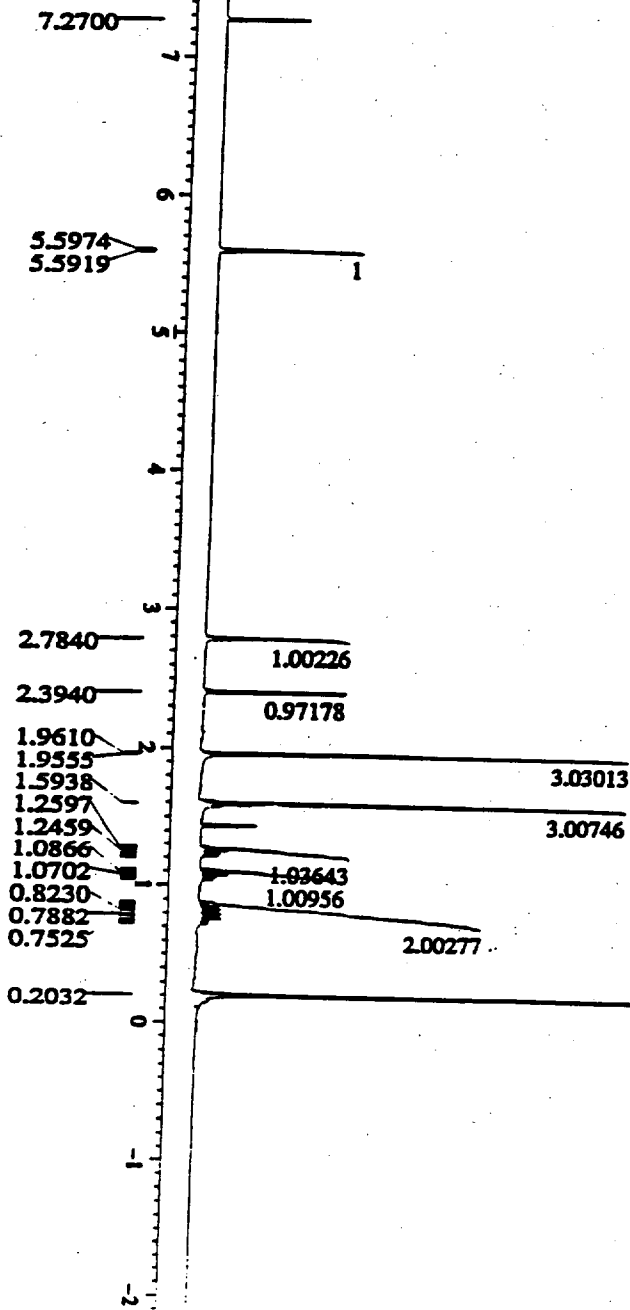
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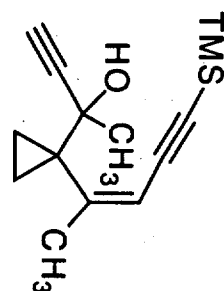
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parts per Million : 1H

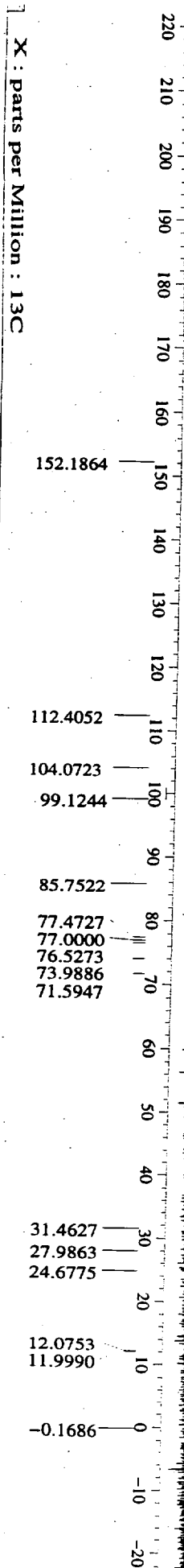
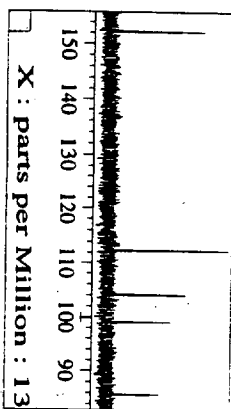
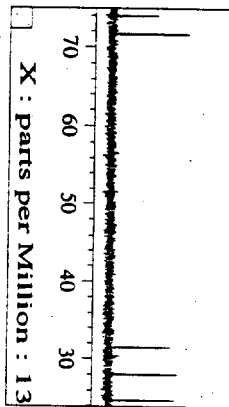
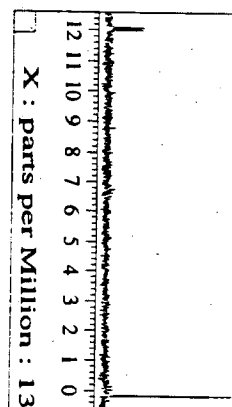


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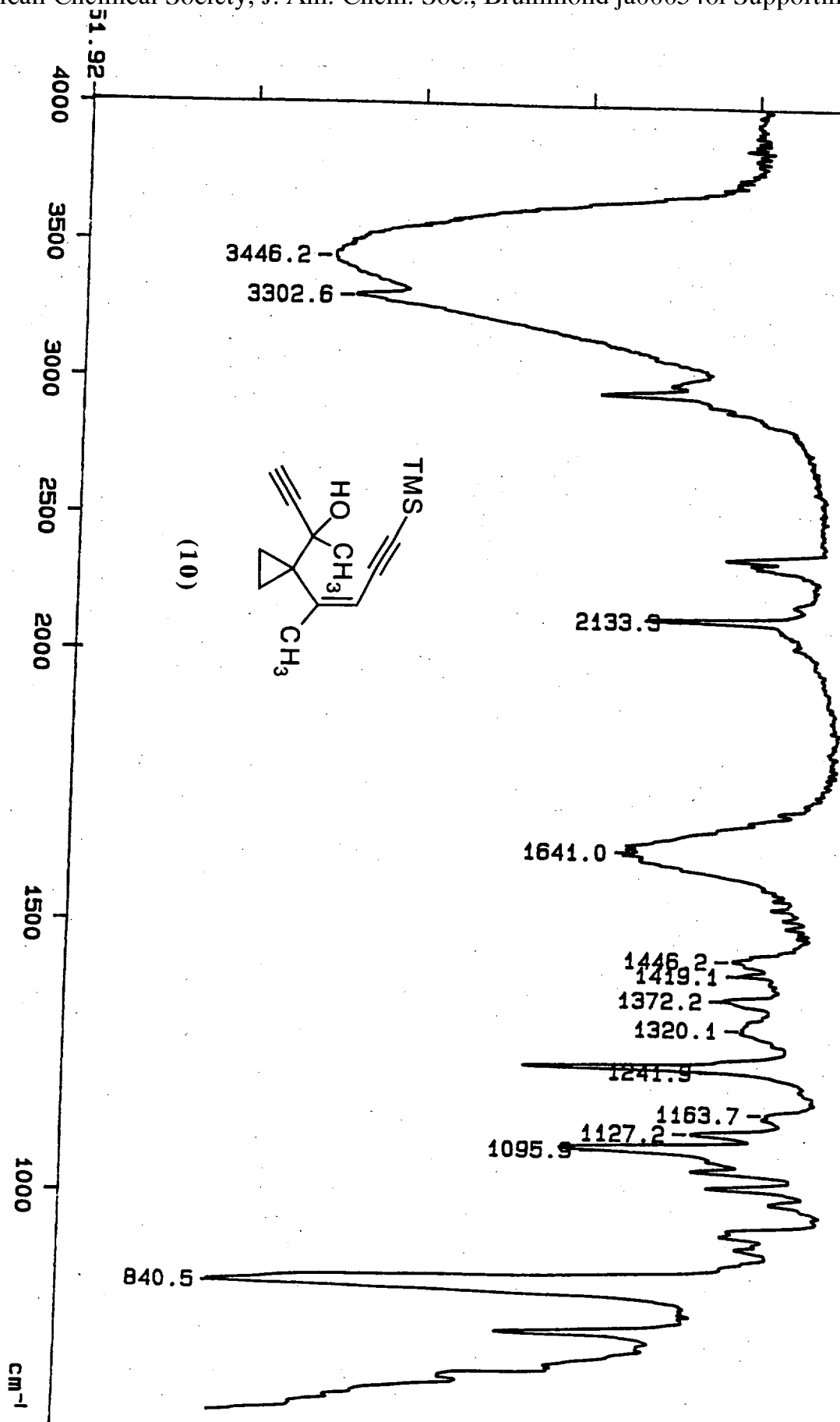


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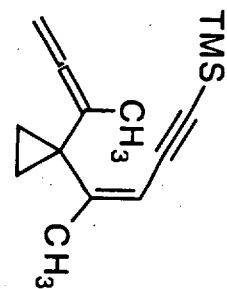


IRKIN ELMET

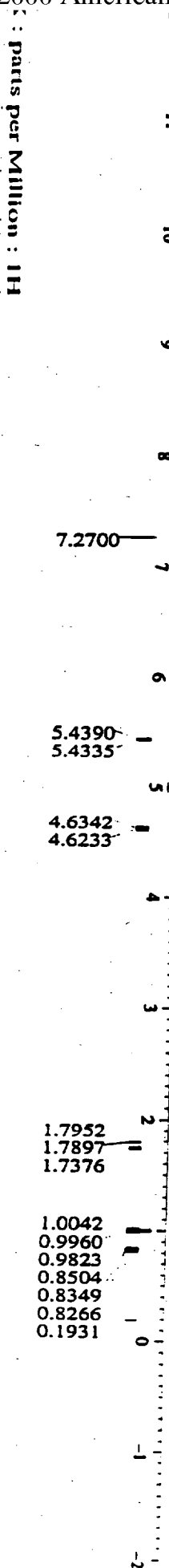
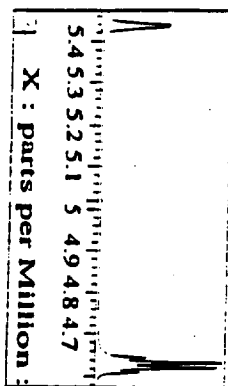
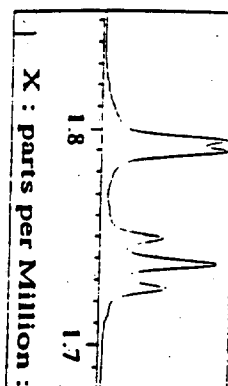
85.64  
%T

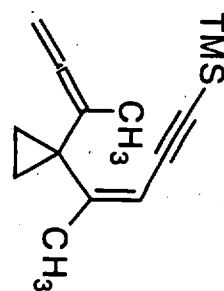


99/08/09 04:35  
X: 16 scans. 4.0cm-1



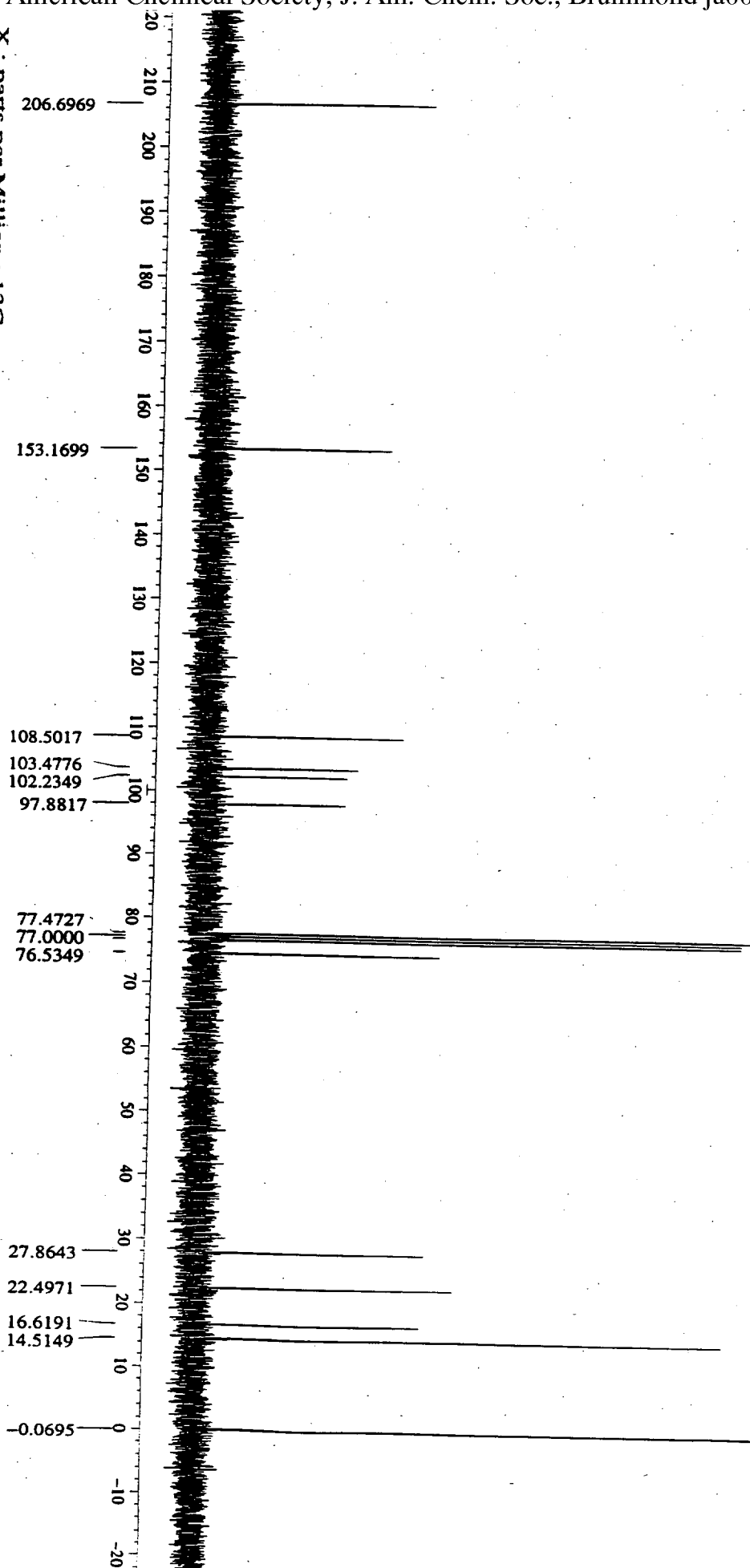
(12)



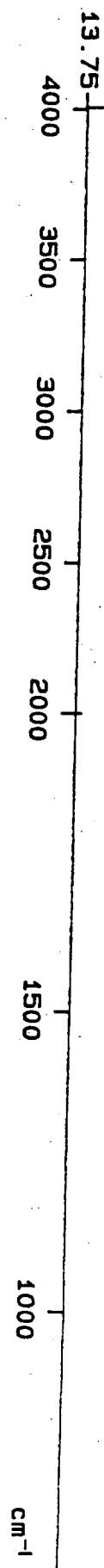


(12)

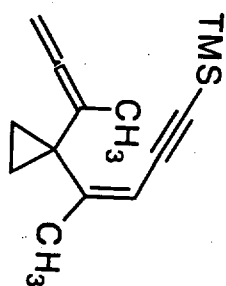
X : parts per Million :  $^{13}\text{C}$



89.12-  
%T



(12)



2141.5

1956.1

1643.3

1424.4

1372.2

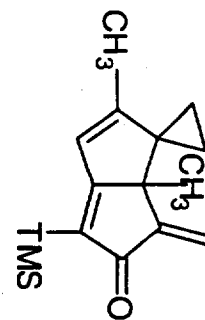
1247.1

1095.9

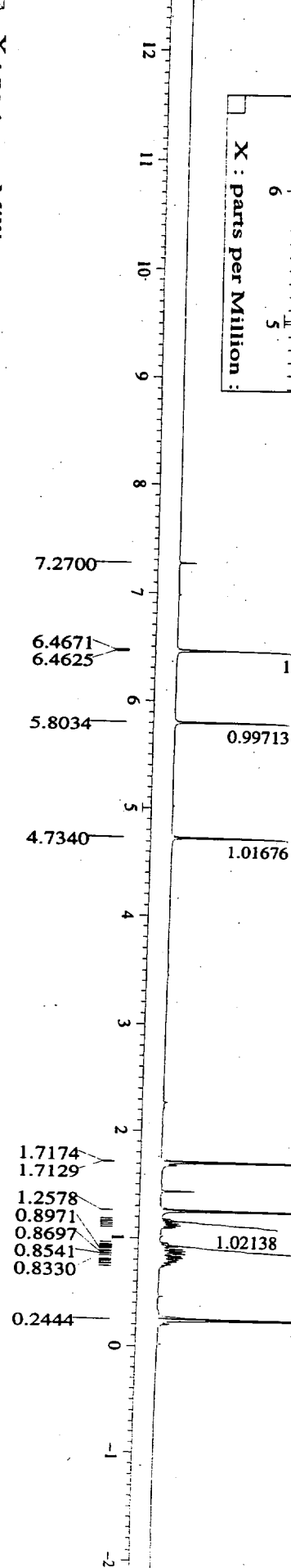
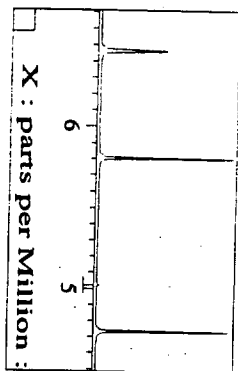
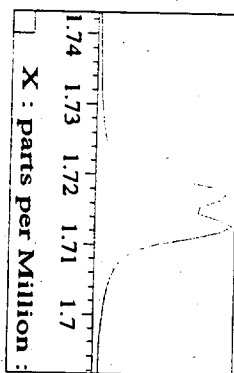
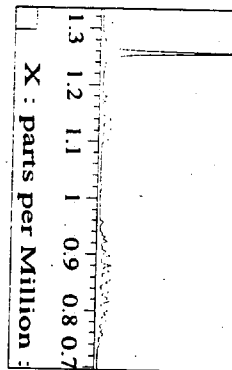
1022.9

840.5

99/08/09 08:34  
X: 16 scans, 4.0cm-1

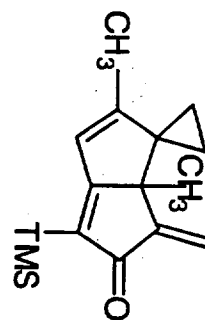


(14)

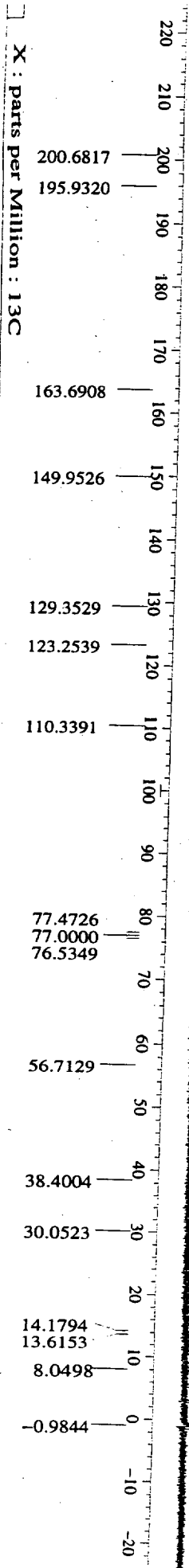
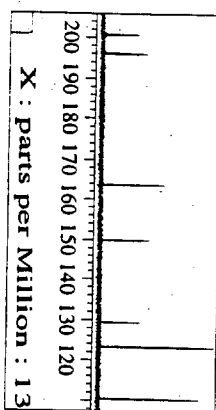
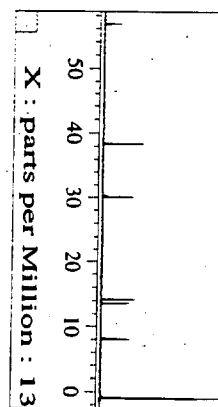


8.96829

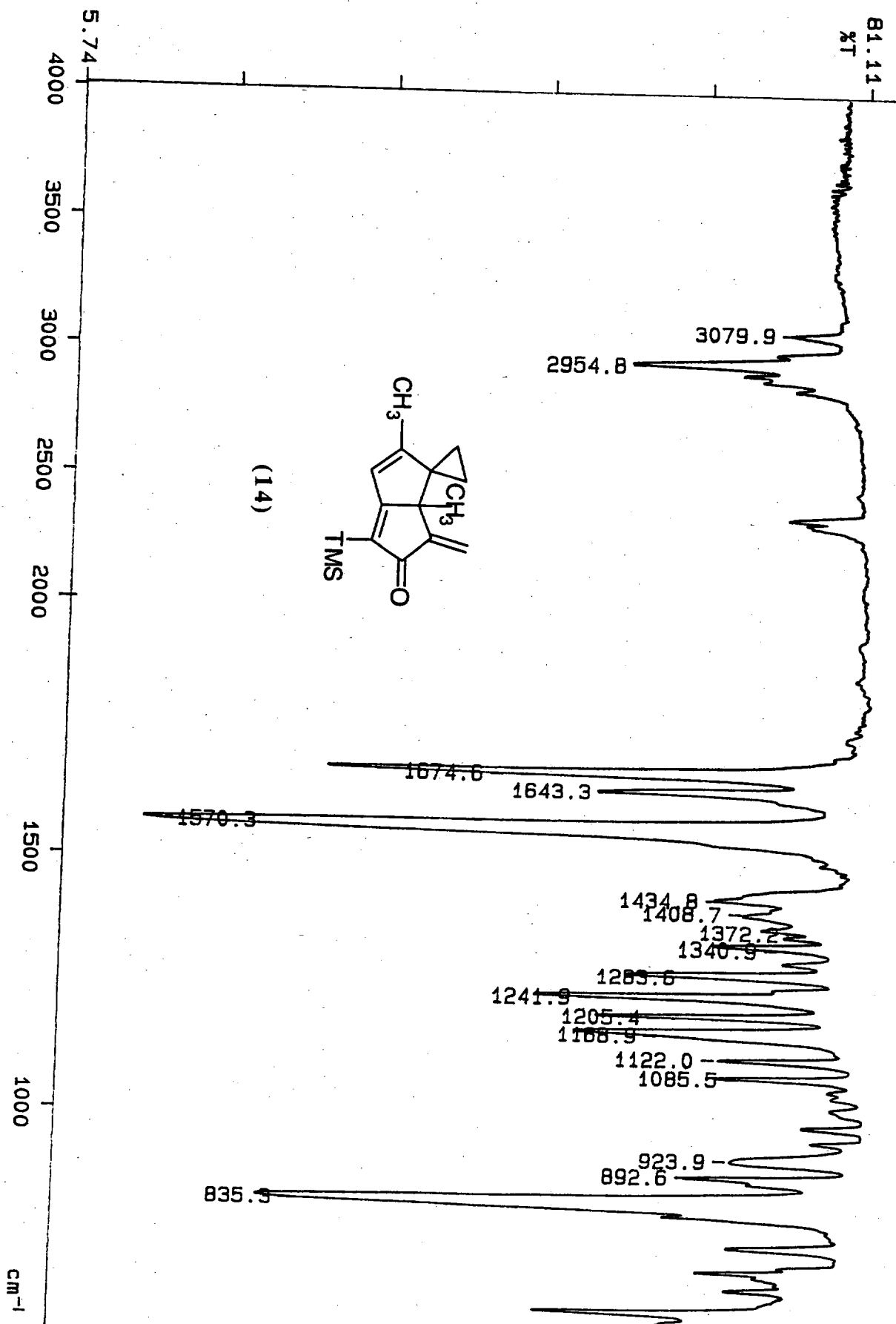




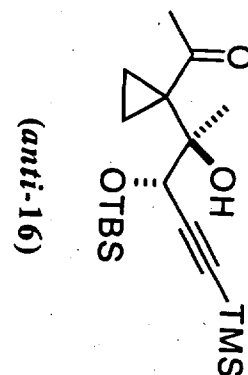
(14)



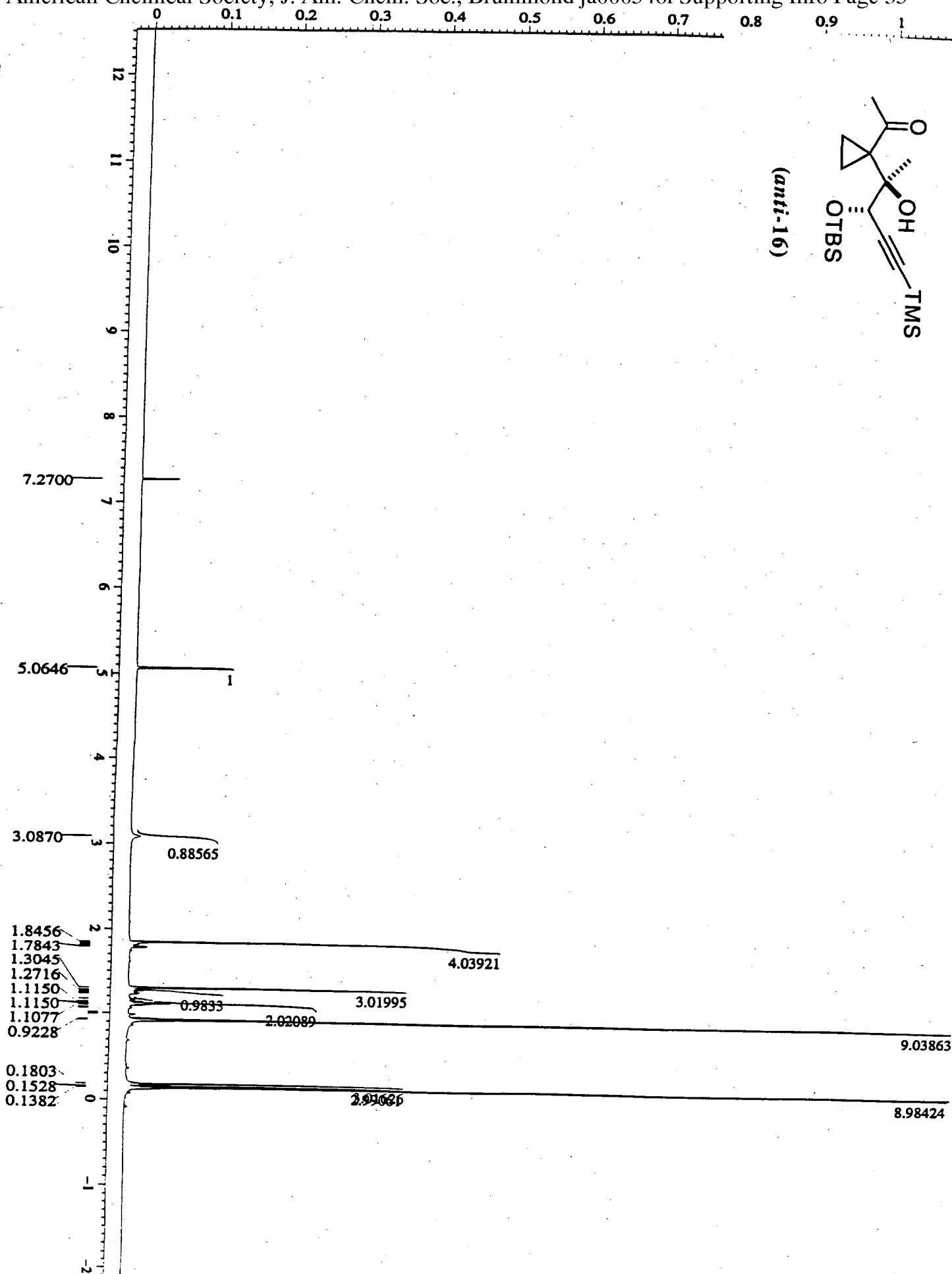
PERKIN ELMER



99/08/10 04:20  
X: 16 scans. 4.0cm-1

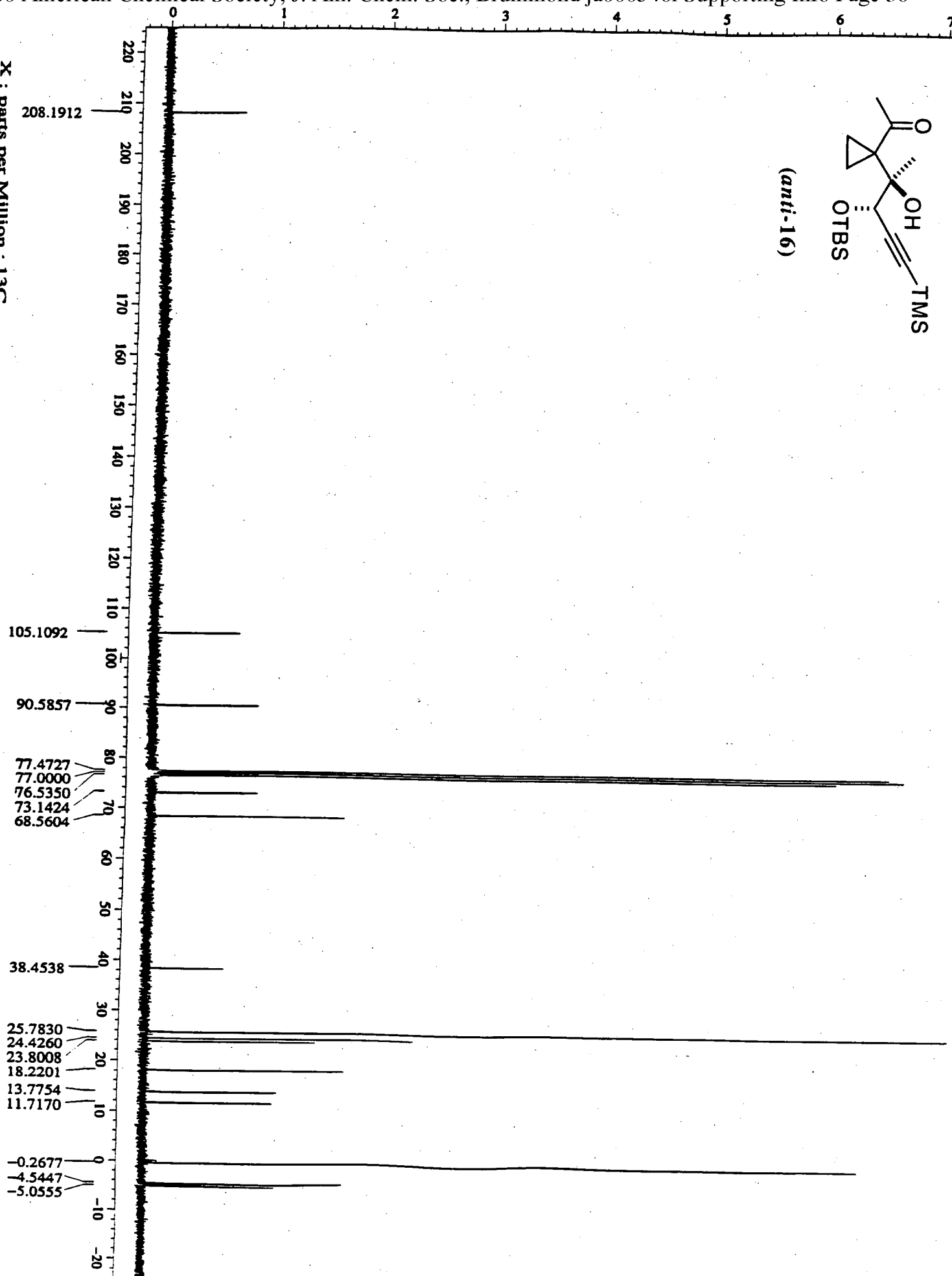
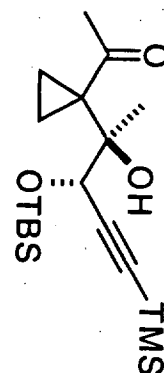


X : parts per Million : 1H



X : parts per Million : 13C

(anti-16)



37 "来い 来い"

**XT**

**XT**

11:74

4000

**3500**

3000

**2500**

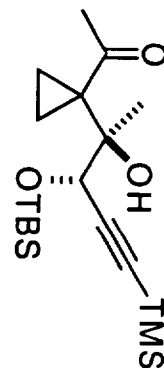
200

**1500**

**1000**

1-30

**(anti-16)**



98/10/08 15:23  
X: 3 scans, 4.0cm-1

**3548.7**

2943.0

~~2851.9~~

**2174.4**

**1682.1**

1466.7

**1410.3**

**1359.0**

1317.9

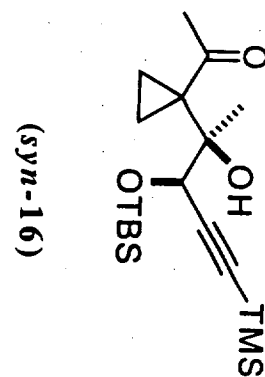
**1251.3**

1064-5

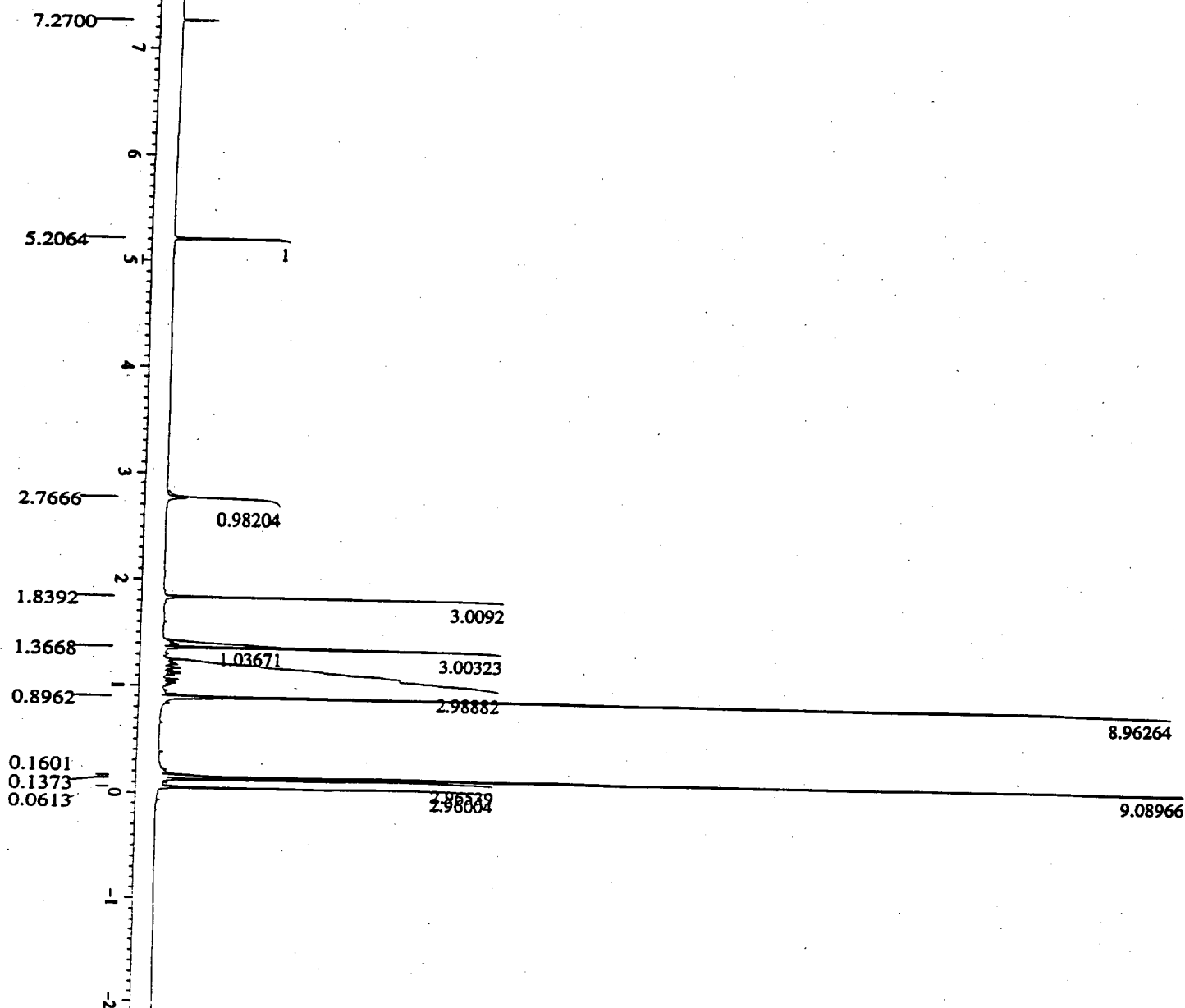
**-1035.5**

**846.2**

98/10/08 15:23  
X: 3 scans, 4.0cm-1



X : parts per Million : 1H



X : parts per Million : 13C

208.2598

105.0253

91.0355

77.4727

77.0000

76.5273

73.3482

68.3164

37.2798

25.7372

24.7766

22.4742

18.0829

13.3790

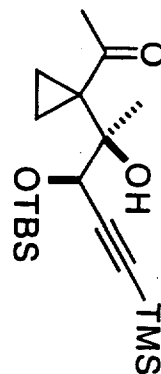
10.7640

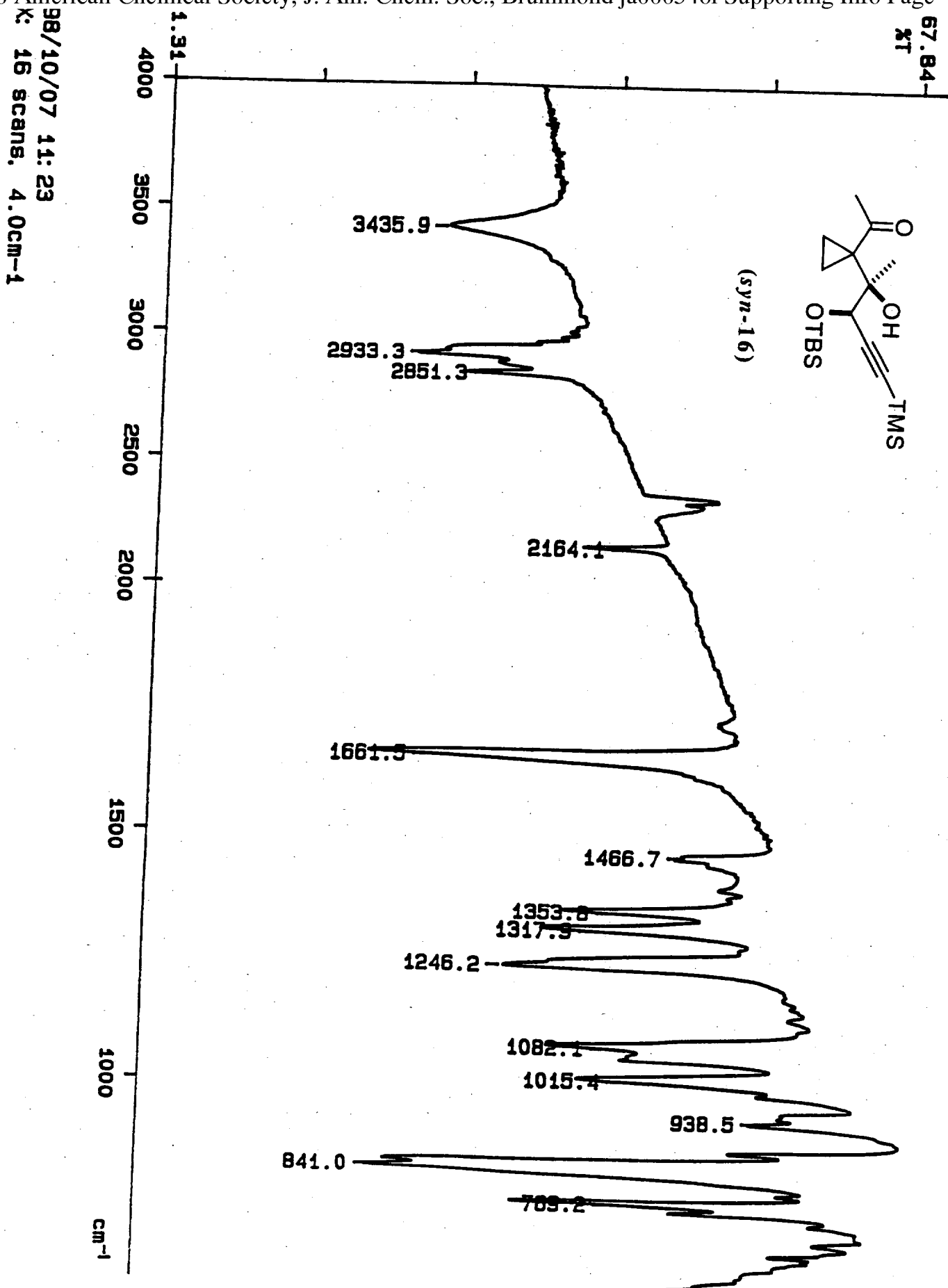
-0.2448

-4.6209

-5.0174

(syn-16)





98/10/07 11:23  
K: 16 scans. 4.0cm-1