Supporting Information

Total Synthesis of (±)-Chondrosterin I Using Desymmetric Intramolecular Aldol Reaction

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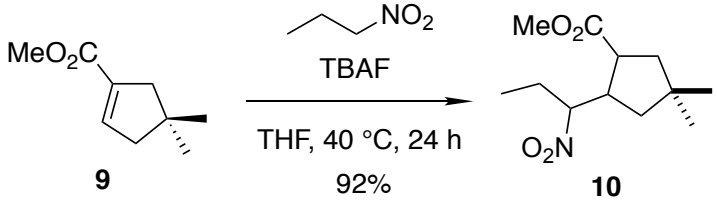
General

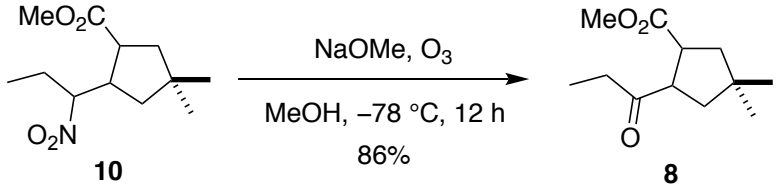
All reactions involving air- and moisture-sensitive reagents were carried out using standard syringe-septum cap techniques. Unless otherwise noted, all solvents and reagents were obtained from commercial suppliers and used without further purification. Routine monitoring of reactions was carried out Merck silica gel 60 F254 TLC plates. Column chromatography was performed on Kanto Chemical Silica Gel 60N (spherical, neutral 60–230 μm) with the solvents indicated. Melting points were taken on a Yanako MP-S3 micro melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a JASCO ECZ 400S (400 MHz) spectrometer. Chemical shifts were expressed in ppm using $CHCl_3$ (7.26 ppm for ^{1}H NMR, 77.0 ppm for ^{13}C NMR) in $CDCl_3$ as internal standard. Infrared spectral measurements were carried out with a JASCO FT/IR-4700 and only noteworthy absorptions were listed. HRMS spectra measured on a Micromass LCT spectrometer. X-ray crystallographic analysis was taken with Burker APEX2 Ultra TXS.

Methyl 4,4-dimethyl-2-(1-nitropropyl)cyclopentane-1-carboxylate (**10**)



To a stirred solution of **9** (2.00 g, 13.0 mmol) in 1-nitropropane (1.20 ml, 13.4 mmol) were added dropwise TBAF (1.0 M in THF, 13.0 ml, 13.0 mmol) at room temperature under Ar atmosphere, and the reaction mixture was stirred at 40 ˚C for 24 h. After cooling to room temperature the reaction mixture was quenched with 1 M HCl, and extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane-AcOEt, 5:1) to afford **10** (2.90 g, 92%) as a colorless oil and a mixture of 2 diastereomers. IR (neat) 2955, 2871, 1737, 1550, 1463, 1437, 1370, 1314, 1261, 1245, 1199, 1171, 808 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88-0.96 (3H, m), 0.99-1.05 (6H, m), 1.21-1.42 (1H, m), 1.62-2.04 (5H, m), 2.61-3.05 (2H, m), 3.66, 3.71 (3H, s) 4.29-4.41 (1H, m); ^{13}C NMR (400 MHz, $CDCl_3$) δ 10.4, 10.5, 25.3, 25.4, 28.6, 29.0, 29.5 (overlapping of 2 diastereomers), 38.4, 38.6, 43.1, 44.2, 45.0, 45.2, 45.2, 45.3, 46.2, 46.4, 52.0, 52.1, 93.7, 93.9, 175.5, 175.6; HRMS (ESI-TOF) Calcd for $C_{12}H_{21}NO_4Na$ $[M+Na]^+$ 266.1368. Found 266.1361.

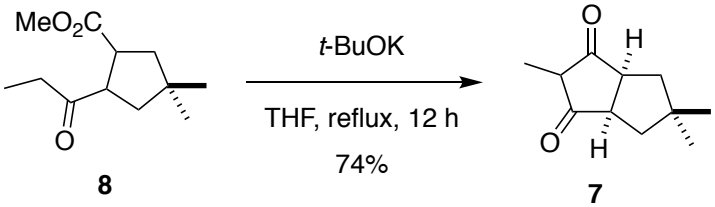
Methyl 4,4-dimethyl-2-propionylcyclopentane-1-carboxylate (**8**)



10 **8**

To a stirred solution of **10** (1.00 g, 4.11 mmol) in MeOH (20 ml) was added dropwise sodium methoxide (28% in MeOH, 1.50 ml, 6.17 mmol) at room temperature under Ar atmosphere, the reaction mixture was stirred at the same temperature for 30 min, and then was bubbled ozone at −78 ˚C for 5 h. The reaction mixture was quenched with dimethyl sulfide and allowed to room temperature for over night. The mixture was partitioned between AcOEt and sat. NH_4Cl aqueous solution, the combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resultant residue was purified by silica gel column chromatography (hexane-AcOEt, 10:1) to afford **8** (750 mg, 86%) as a colorless oil. IR (neat) 2954, 2870, 1734, 1714, 1462, 1437, 1369, 1350, 1248, 1200, 1175, 1117 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94-1.08 (9H, m), 1.43-1.52 (1H, m), 1.64-1.72 (1H, m), 1.77-1.88 (2H, m), 2.37-2.53 (2H, m), 3.30-3.44 (2H, m), 3.63 (3H, s); ^{13}C NMR (400 MHz, $CDCl_3$) δ 7.6, 28.8, 28.9, 35.3, 39.5, 44.2, 44.3, 44.8, 51.8, 53.4, 175.8, 211.8; HRMS (ESI-TOF) Calcd for $C_{12}H_{20}O_3Na$ $[M+Na]^+$ 235.1310. Found 235.1304.

(3a*R*,6a*S*)-2,5,5-Trimethyltetrahydropentalene-1,3(2*H*,3a*H*)-dione (**7**)

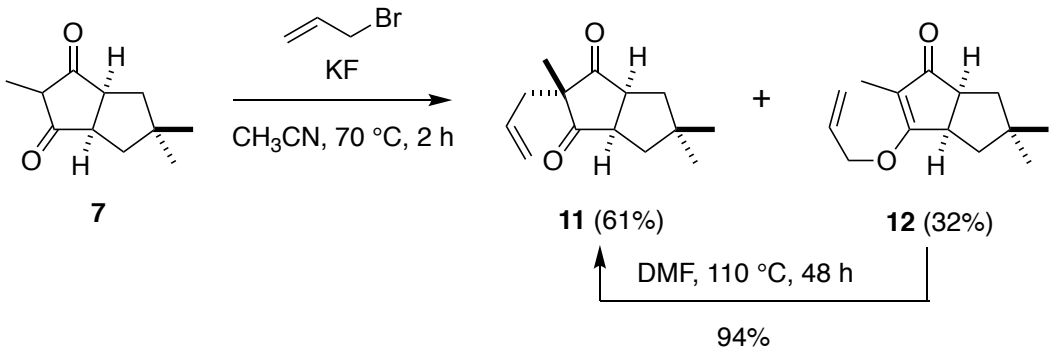


8 **7**

To a stirred solution of **8** (135 mg, 0.640 mmol) in THF (5 ml) was added potassium *tert*-butoxide (1.0 M in THF, 1.90 ml, 1.90 mmol) at room temperature under Ar atmosphere, and the mixture was stirred at 80 ˚C for 12 h. After cooling to room temperature the reaction mixture was quenched with 1 M HCl, and extracted with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resultant residue was purified by silica gel column chromatography (AcOEt, 100%) to afford **7** (85 mg, 74%) as a colorless amorphous. IR (neat) 2955, 2867, 1775, 1732, 1575, 1465, 1446, 1395, 1360, 1245, 1220, 1111, 1084, 983 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (6H, s), 1.43 (2H, dd, J = 13.2, 6.0 Hz), 1.62 (3H, s), 1.80 (2H, dd, J = 13.2, 9.2 Hz), 3.20 (2H, ddd, J = 12.0, 6.2, 5.6 Hz), 10.68 (1H, br); ^{13}C NMR (400 MHz, $CDCl_3$) δ 5.8, 28.1, 28.5, 42.1, 43.5, 48.1, 111.0, 201.2; HRMS (ESI-TOF)

Calcd for $C_{11}H_{17}O_2$ $[M+H]^+$ 181.1229. Found 181.1222.

(2*r*,3a*R*,6a*S*)-2-Allyl-2,5,5-trimethyltetrahydropentalene-1,3(2*H*,3a*H*)-dione (**11**) and (3a*R*,6a*S*)-3-(Allyloxy)-2,5,5-trimethyl-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (**12**)



To a stirred solution of **7** (470 mg, 2.61 mmol) in CH_3CN (50 ml) was added allyl bromide (0.442 ml, 5.22 mmol) and potassium fluoride (758 mg, 13.1 mmol) at room temperature under Ar atmosphere, and the mixture was stirred at 70 ˚C for 2 h. After cooling to room temperature the reaction mixture was quenched with 1 M HCl, and extracted with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resultant residue was purified by silica gel column chromatography (hexane-AcOEt, 3:1) to afford **11** (350 mg, 61%) as a yellow oil and **12** (185 mg, 32%) as an orange oil. A solution of **12** (50.0 mg, 0.227 mmol) in DMF (2 ml) was stirred at 110 ˚C for 48 h under Ar atmosphere. After cooling to room temperature the mixture was quenched with H_2O, and extracted with diethyl ether. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resultant residue was purified by silica gel column chromatography (hexane-AcOEt, 10:1) to afford **11** (47 mg, 94%) as a yellow oil.

Data for **11**

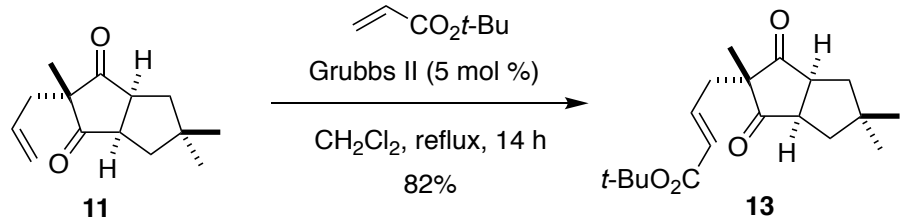
IR (neat) 2956, 2932, 2868, 1760, 1719, 1464, 1450, 1370, 1209, 924 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.73 (3H, s), 0.98 (3H, s), 1.10 (3H, s), 1.74-1.88 (4H, m), 2.28 (2H, d, *J* = 7.2 Hz), 3.26-3.35 (2H, m), 5.00-5.12 (2H, m), 5.51-5.63 (1H, m); ^{13}C NMR (400 MHz, $CDCl_3$) δ 17.2, 27.4, 27.8, 40.8, 42.4, 44.6, 51.6, 59.6, 120.0, 131.0, 218.6; HRMS (ESI-TOF) Calcd for $C_{14}H_{19}O_2$ $[M-H]^-$ 219.1385. Found 219.1390.

Data for **12**

IR (neat) 2953, 2864, 1686, 1627, 1388, 1336, 1285, 1240, 1222, 1124, 977, 935 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (3H, s), 1.00 (3H, s), 1.37 (1H, dd, *J* = 12.0, 8.0 Hz), 1.43 (1H, dd, *J* = 12.8, 8.0 Hz), 1.61 (3H, s), 1.72-1.89 (2H, m), 3.01-3.09 (1H, m), 3.30-3.38 (1H, m), 4.63-4.73

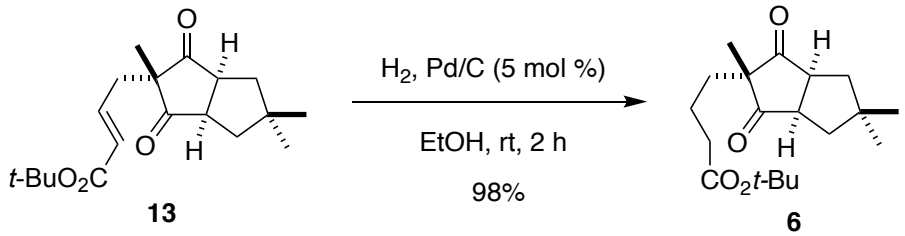
(2H, m), 5.25-5.40 (2H, m), 5.90-6.01 (1H, m); ^{13}C NMR (400 MHz, $CDCl_3$) δ 6.3, 27.7, 28.5, 41.7, 43.3, 43.9, 43.9, 51.1, 70.1, 113.8, 117.8, 132.3, 185.5, 207.9; HRMS (ESI-TOF) Calcd for $C_{14}H_{20}O_2Na$ $[M+Na]^+$ 243.1361. Found 243.1352.

tert-Butyl (*E*)-4-((2*r*,3a*R*,6a*S*)-2,5,5-trimethyl-1,3-dioxooctahydropentalen-2-yl)but-2-enoate (**13**)



To a stirred suspension of Grubbs II catalyst (58.0 mg, 0.0680 mmol) in CH_2Cl_2 at reflux under Ar atmosphere was added **11** (300 mg, 1.36 mmol) and *tert*-butyl acrylate (0.990 ml, 6.80 mmol), and the suspension was stirred at the same temperature for 14 h. After cooling to room temperature the reaction mixture was quenched with H_2O, and extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resultant residue was purified by silica gel column chromatography (hexane-AcOEt, 7:1) to afford **13** (356 mg, 82%) as a white crystal. Mp 90-93 °C; IR (KBr) 2957, 2934, 1757, 1714, 1655, 1366, 1336, 1301, 1280, 1167, 1151, 1132, 1029, 981 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 (3H, s), 0.98 (3H, s), 1.13 (3H, s), 1.43 (9H, s), 1.74-1.90 (4H, m), 2.37 (2H, dd, *J* = 8.0, 1.6 Hz), 3.26-3.35 (2H, m), 5.71 (1H, dt, *J* = 15.2, 1.2 Hz), 6.50-6.59 (1H, m); ^{13}C NMR (400 MHz, $CDCl_3$) δ 17.8, 27.3, 27.8, 28.0, 39.7, 40.8, 44.7, 51.6, 58.5, 80.5, 127.6, 139.1, 164.7, 218.0; HRMS (ESI-TOF) Calcd for $C_{19}H_{28}O_4Na$ $[M+Na]^+$ 343.1885. Found 343.1878.

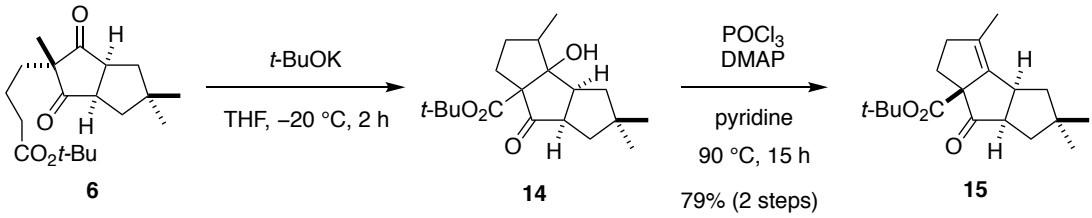
tert-Butyl 4-((2*r*,3a*R*,6a*S*)-2,5,5-trimethyl-1,3-dioxooctahydropentalen-2-yl)butanoate (**6**)



A suspension of **13** (280 mg, 0.873 mmol) and 10% Pd/C (47 mg, 0.0437 mmol) in EtOH was stirred at room temperature for 2 h under H_2 atmosphere. The insoluble material was removed by filtration, and concentrated in vacuo to afford **6** (280 mg, 98%) as a pink oil. IR (neat) 2961,

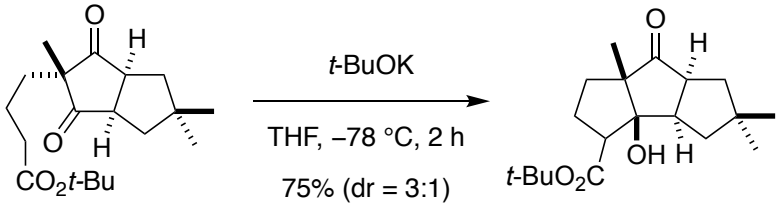
2930, 2868, 1722, 1712, 1366, 1260, 1148, 1073 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.70 (3H, s), 0.97 (3H, s), 1.09 (3H, s), 1.38 (9H, s), 1.41-1.61 (4H, m), 1.73-1.91 (4H, m), 2.05-2.16 (2H, m), 3.32-3.45 (2H, m); ^{13}C NMR (400 MHz, $CDCl_3$) δ 16.4, 19.5, 27.4, 27.8, 28.0, 34.9, 36.8, 40.8, 44.5, 51.3, 58.9, 80.7, 171.9, 218.6; HRMS (ESI-TOF) Calcd for $C_{19}H_{30}O_4Na$ $[M+Na]^+$ 345.2042. Found 345.2036.

tert-Butyl (3a*S*,7a*R*)-2,2,4-trimethyl-7-oxo-1,2,3,3a,5,6,7,7a-octahydro-6a*H*-cyclopenta[*a*]pentalene-6a-carboxylate (**15**)



To a stirred solution of **6** (20 mg, 0.0620 mmol) in THF (1 ml) was added potassium *tert*-butoxide (1.0 M in THF, 0.200 ml, 0.200 mmol) at −20 °C under Ar atmosphere, and the mixture was stirred at the same temperature for 2 h. The reaction mixture was quenched with sat. NH_4Cl aqueous solution, and extracted with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo to afford the crude **14**. To a stirred solution of the crude **14** and DMAP (10 mg, 0.0819 mmol) in pyridine (0.5 ml) was added $POCl_3$ (0.0700 ml, 0.751 mmol) at 0 °C, and the mixture was stirred at 90 °C for 15 h. After cooling to room temperature the reaction mixture was quenched with sat. $NaHCO_3$ aqueous solution, acidified with 1 M HCl, and extracted with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resultant residue was purified by silica gel column chromatography (hexane-AcOEt, 10:1) to afford **15** (15 mg, 79%) as a pale yellow crystal. Mp 72-75 °C; IR (KBr) 3449, 3000, 2928, 2867, 1712, 1465, 1444, 1367, 1246, 1221, 1133, 1095, 844, 827 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (3H, s), 1.08 (3H, s), 1.46 (9H, s), 1.41-1.52 (2H, m), 1.76 (3H, s), 1.60-1.87 (2H, m), 1.95-2.05 (1H, m), 2.16-2.30 (2H, m), 2.87-3.10 (2H, m), 3.28-3.37 (1H, m); ^{13}C NMR (400 MHz, $CDCl_3$) δ 14.2, 26.4, 27.9, 28.0, 34.1, 40.0, 40.3, 43.3, 43.6, 45.1, 57.7, 72.0, 81.9, 137.7, 138.6, 172.4, 214.8; HRMS (ESI-TOF) Calcd for $C_{19}H_{28}O_3Na$ $[M+Na]^+$ 327.1936. Found 327.1934.

tert-Butyl (3a*S*,3b*R*,6a*S*,7a*S*)-3a-hydroxy-5,5,7a-trimethyl-7-oxodecahydro-1*H*-cyclopenta[*a*]pentalene-3-carboxylate (**16**)



6 **16**

To a stirred solution of **6** (80 mg, 0.248 mmol) in THF (4 ml) was added potassium *tert*-butoxide (1.0 M in THF, 0.750 ml, 0.750 mmol) at −78 °C under Ar atmosphere, and the mixture was stirred at the same temperature for 2 h. The reaction mixture was quenched with sat. NH_4Cl aqueous solution, and extracted with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resultant residue was purified by silica gel column chromatography (hexane-AcOEt, 8:1) to afford **16** (60 mg, 75%) as a mixture of diastereomers (3:1).

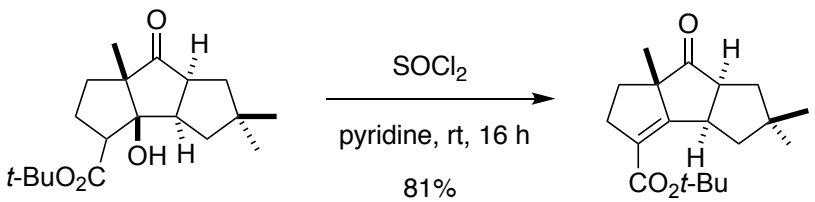
Data for less polar diastereomer (white crystal)

Mp 103-105 °C; IR (KBr) 3568, 2932, 1712, 1455, 1383, 1316, 1255, 1130, 1074, 1030, 845 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (3H, s), 1.03 (3H, s), 1.10 (3H, s), 1.50 (9H, s), 1.41-1.73 (5H, m), 1.78-1.96 (3H, m), 2.72-2.80 (1H, m), 2.80 (1H, s), 2.90-3.03 (2H, m); ^{13}C NMR (400 MHz, $CDCl_3$) δ 20.3, 27.2, 27.9, 28.2, 29.1, 36.8, 40.8, 43.0, 43.6, 48.8, 52.5, 56.7, 59.2, 81.9, 85.4, 173.4, 224.7; HRMS (ESI-TOF) Calcd for $C_{19}H_{30}O_4Na$ $[M+Na]^+$ 345.2042. Found 345.2032.

Data for polar diastereomer (white crystal)

Mp 104-108 °C; IR (KBr) 3478, 2955, 2868, 1732, 1706, 1454, 1380, 1302, 1258, 1219, 1157, 1101cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (3H, s), 1.07 (3H, s), 1.20 (3H, s), 1.48 (9H, s), 1.41-1.74 (4H, m), 1.81-2.15 (4H, m), 2.47-2.53 (1H, m), 2.88-3.06 (2H, m), 3.64 (1H, s); ^{13}C NMR (400 MHz, $CDCl_3$) δ 17.9, 23.8, 28.2, 28.7, 36.2, 41.0, 42.2, 42.3, 46.0, 52.6, 56.8, 60.2, 81.8, 86.0, 172.2, 222.6; HRMS (ESI-TOF) Calcd for $C_{19}H_{30}O_4Na$ $[M+Na]^+$ 345.2042. Found 345.2037.

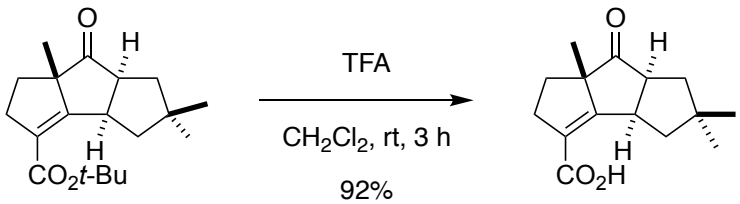
tert-Butyl (3b*R*,6a*S*,7a*S*)-5,5,7a-trimethyl-7-oxo-2,3b,4,5,6,6a,7,7a-octahydro-1*H*-cyclopenta[*a*]pentalene-3-carboxylate (**19**)



16 **19**

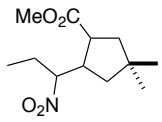
To a stirred solution of **16** (20 mg, 0.0650 mmol) in pyridine (1 ml) was added $SOCl_2$ (0.0500 ml, 0.650 mmol) at room temperature under Ar atmosphere, and the mixture was stirred at the same temperature for 16 h. The reaction mixture was quenched with 1 M HCl, and extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resultant residue was purified by silica gel column chromatography (hexane-AcOEt, 12:1) to afford **19** (16 mg, 81%) as a colorless oil. IR (neat) 3434, 2956, 1739, 1702, 1655, 1368, 1168, 1110 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (3H, s), 1.13 (3H, s), 1.39 (3H, s), 1.51 (9H, s), 1.53-1.69 (2H, m), 1.76-1.82 (1H, m), 1.90-2.05 (3H, m), 2.66 (1H, dd, *J* = 16, 8.4 Hz), 2.77-2.87 (1H, m), 3.18 (1H, ddd *J* = 9.6, 9.6, 9.6 Hz), 3.88 (1H, ddd, *J* = 9.6, 9.6, 9.6 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ 23.7, 26.3, 28.0, 28.2, 32.8, 35.6, 42.1, 43.3, 45.9, 46.3, 57.8, 63.4, 80.3, 128.9, 164.4, 164.7, 220.9; HRMS (ESI-TOF) Calcd for $C_{19}H_{28}O_3Na$ $[M+Na]^+$ 327.1936. Found 327.1927.

(3b*R*,6a*S*,7a*S*)-5,5,7a-Trimethyl-7-oxo-2,3b,4,5,6,6a,7,7a-octahydro-1*H*-cyclopenta[*a*]pentalene-3-carboxylic acid (**1**)



19 chondrosterin I (**1**)

To a stirred solution of **19** (60 mg, 0.197 mmol) in CH_2Cl_2 (0.5 ml) was added TFA (0.23 ml) at the room temperature, and the reaction mixture was stirred at the same temperature for 3 h. After concentration in vacuo, the residue was purified by silica gel column chromatography (hexane-AcOEt, 3:1) to afford **1** (45 mg, 92%) as a white crystal. Mp 186-189 °C; IR (KBr) 2957, 1737, 1683, 1432, 1369, 1336, 1296, 1279, 1207, 1119, 1075, 914, 714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (3H, s), 1.14 (3H, s), 1.43 (3H, s), 1.57-1.70 (2H, m), 1.81-1.87 (1H, m), 1.95-2.10 (3H, m), 2.72 (1H, dd, *J* = 16.0, 8.8 Hz), 2.83-2.95 (1H, m), 3.22 (1H, ddd, *J* = 9.6, 9.6, 9.6 Hz), 3.95 (1H, ddd, *J* = 9.6, 9.6, 9.6 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ 23.8, 26.5, 28.2, 32.5, 35.6, 42.2, 43.5, 46.1, 46.1, 58.2, 63.8, 126.6, 170.2, 170.2, 220.2; HRMS (ESI-TOF) Calcd for $C_{15}H_{19}O_3$ $[M-H]^-$ 247.1334. Found 247.1340.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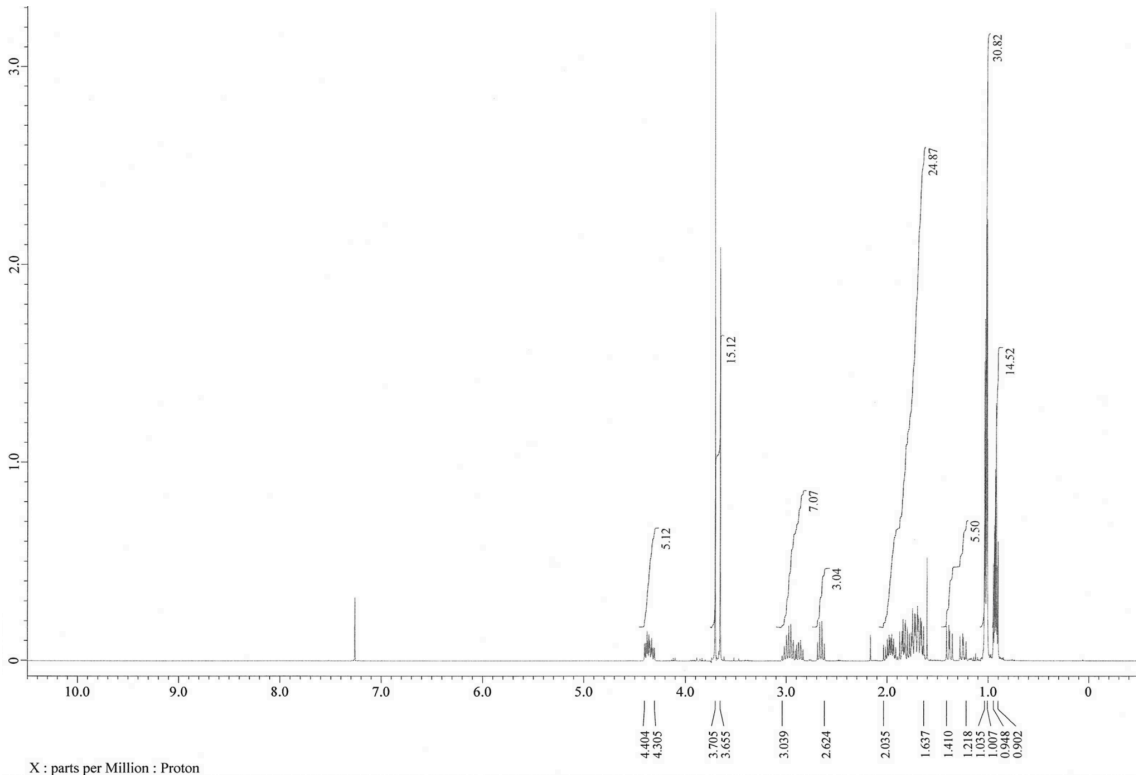
O2N

10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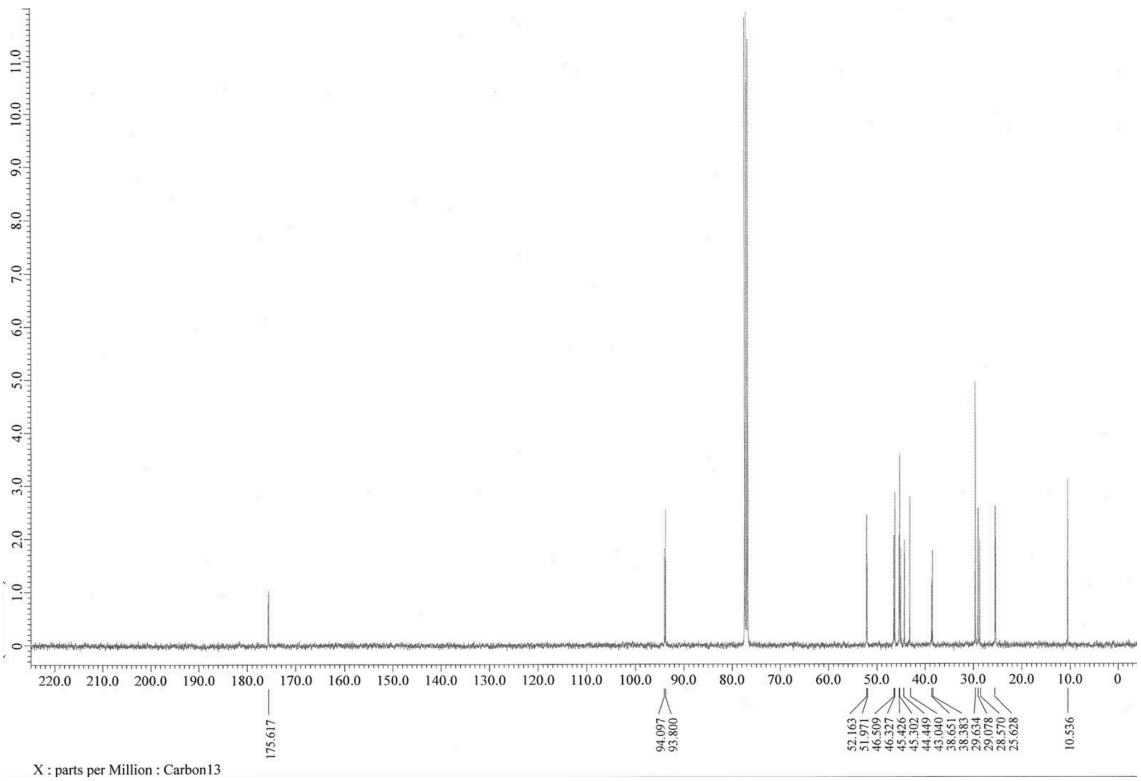
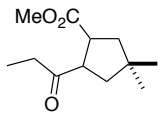
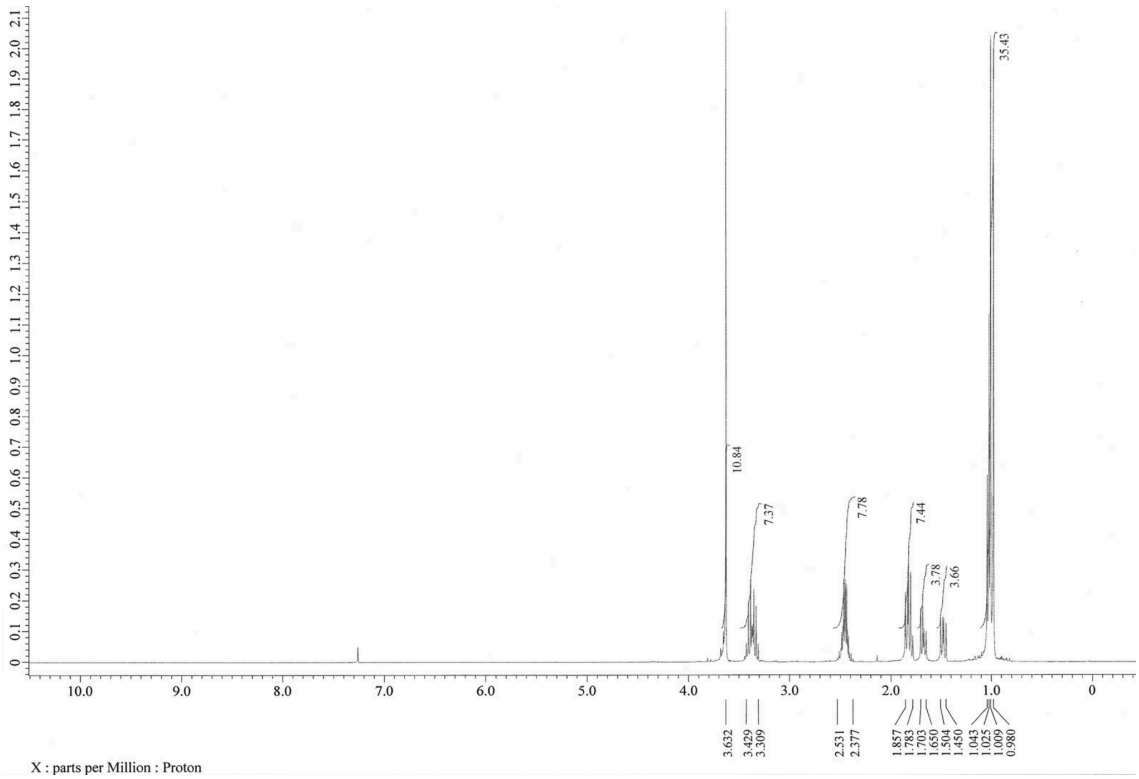
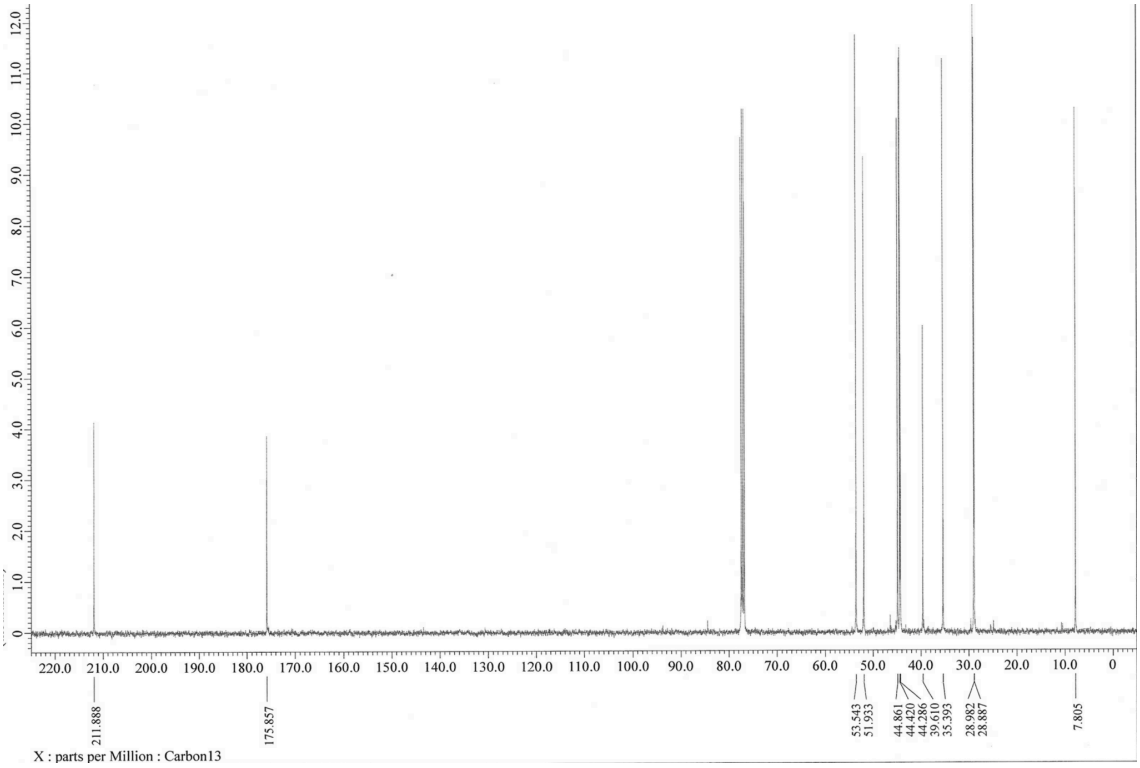
24.87
15.12
14.52
7.07
5.50
5.12
3.04
4.404
4.305
3.705
3.655
3.039
2.624
2.035
1.637
1.410
1.218
1.055
1.007
0.948
0.902
X : parts per Million : Proton

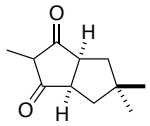

175.617
94.097
93.800
52.163
51.971
46.509
46.327
45.426
45.302
44.449
43.040
38.651
38.383
29.634
29.078
28.570
25.628
10.536
X : parts per Million : Carbon13


MeO2C
O

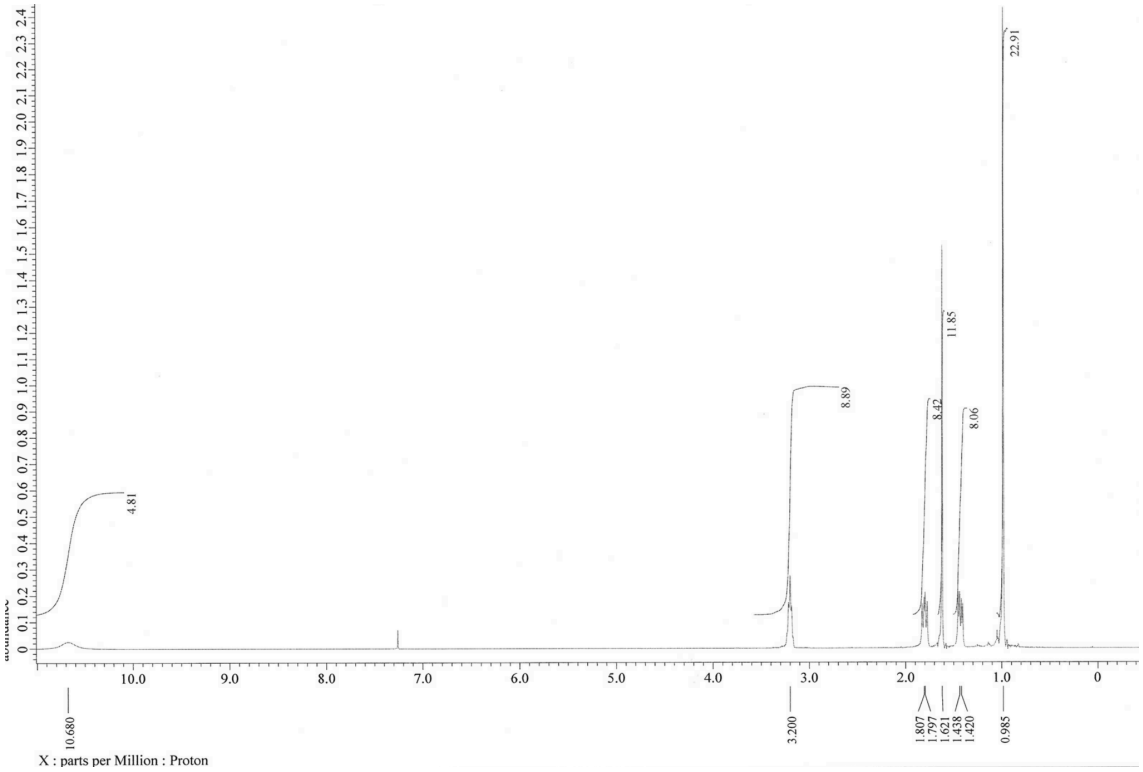
8

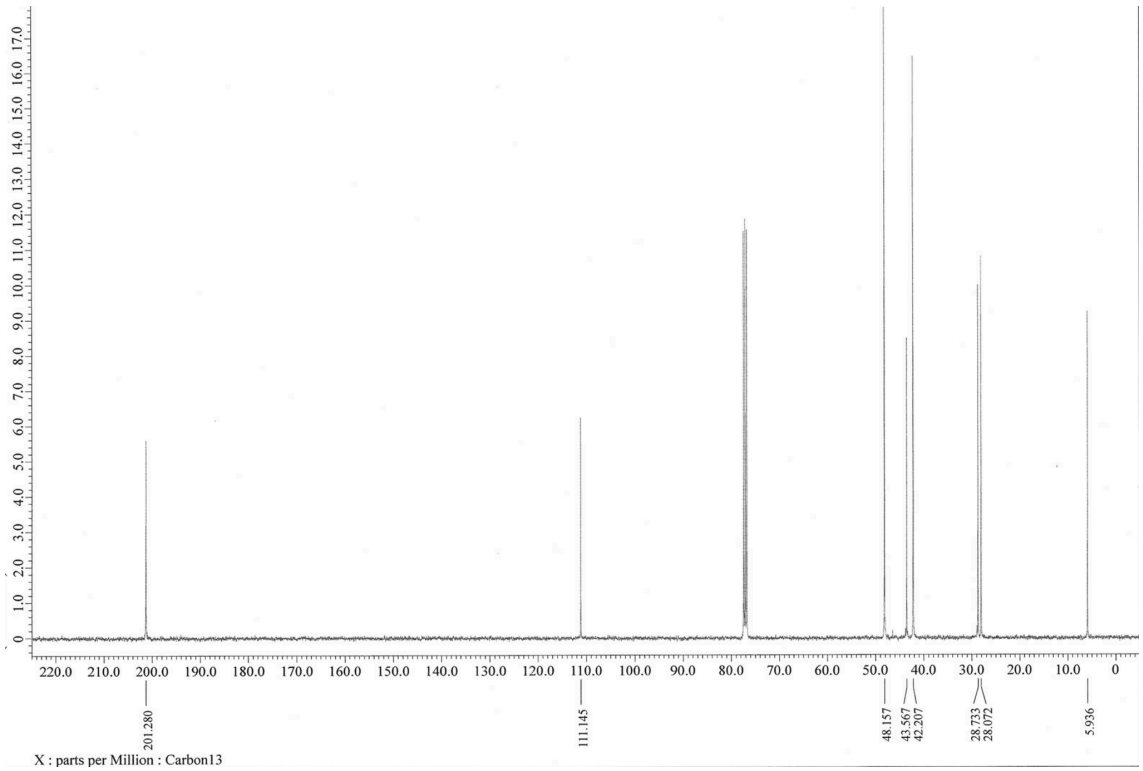

10.84
7.37
7.78
7.44
3.78
3.66
35.43
3.632
3.429
3.309
2.531
2.377
1.857
1.793
1.703
1.650
1.504
1.450
1.043
1.025
1.009
0.980
X : parts per Million : Proton

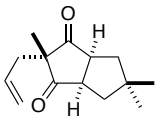

211.888
175.857
53.543
51.933
44.861
44.420
44.236
39.610
35.393
28.982
28.887
7.805
X : parts per Million : Carbon13



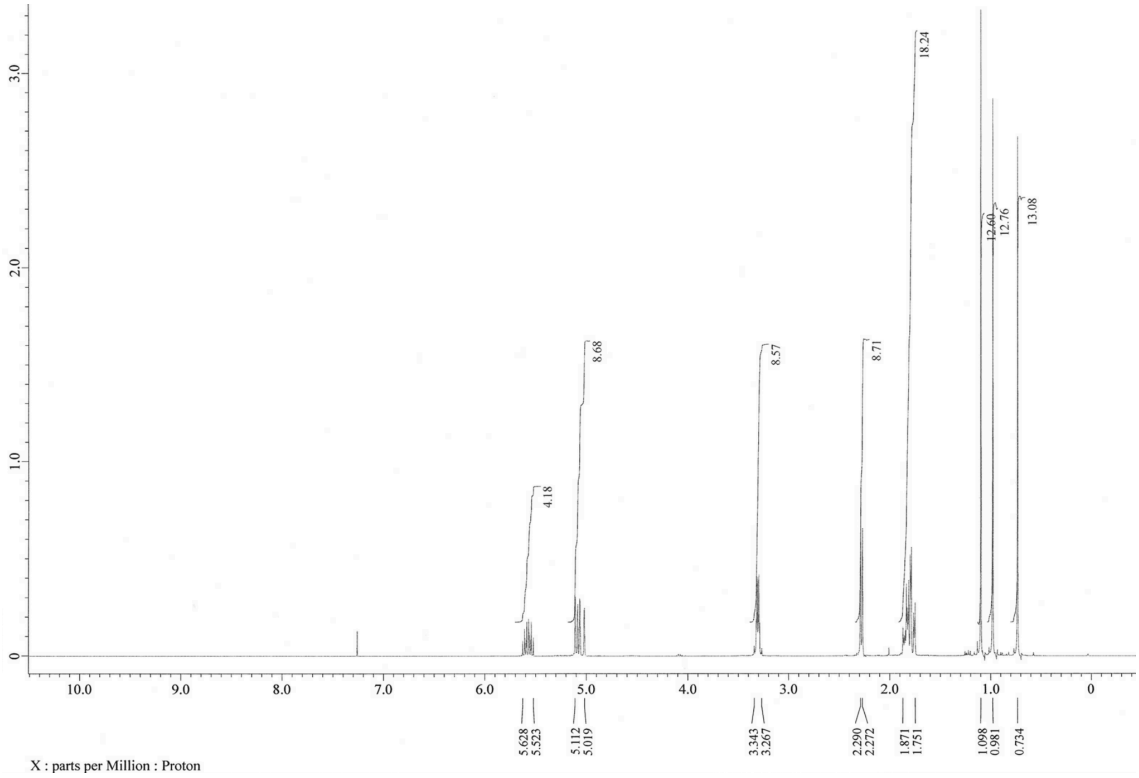
7

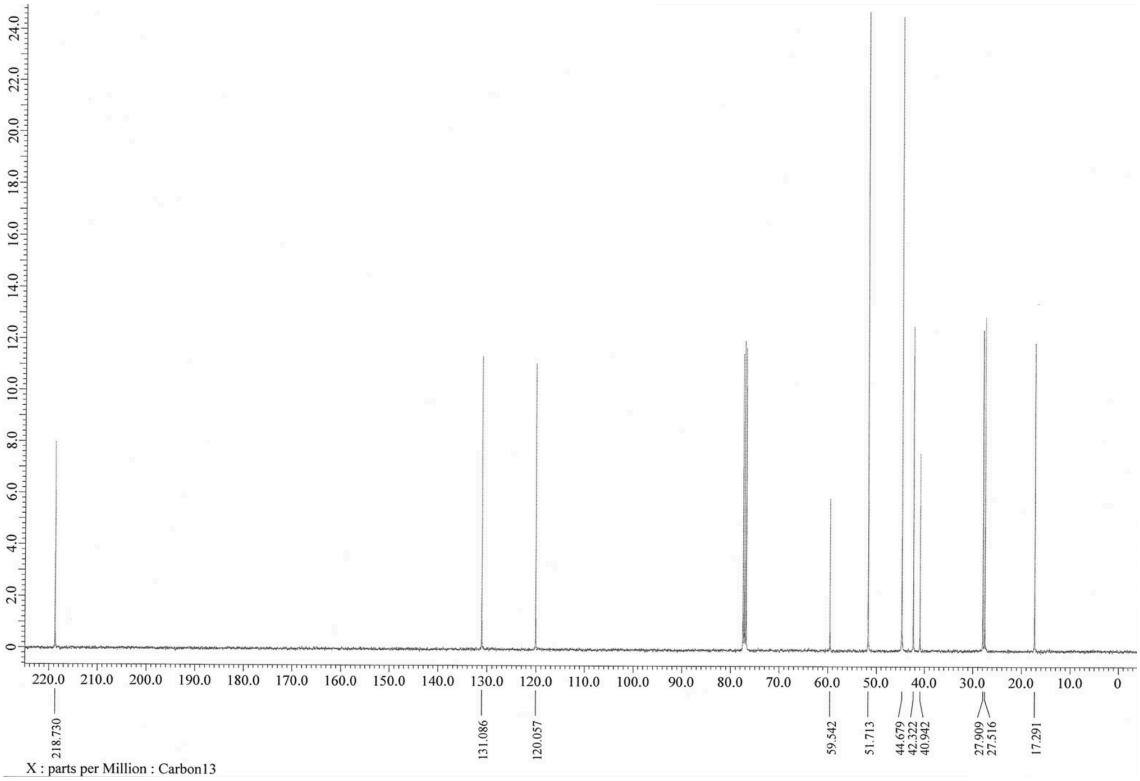

22.91
11.85
8.89
8.42
8.06
4.81
10.680
3.200
1.807
1.797
1.621
1.438
1.420
0.985
X : parts per Million : Proton

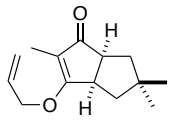

201.280
111.145
48.157
43.567
42.207
28.733
28.072
5.936
X : parts per Million : Carbon13



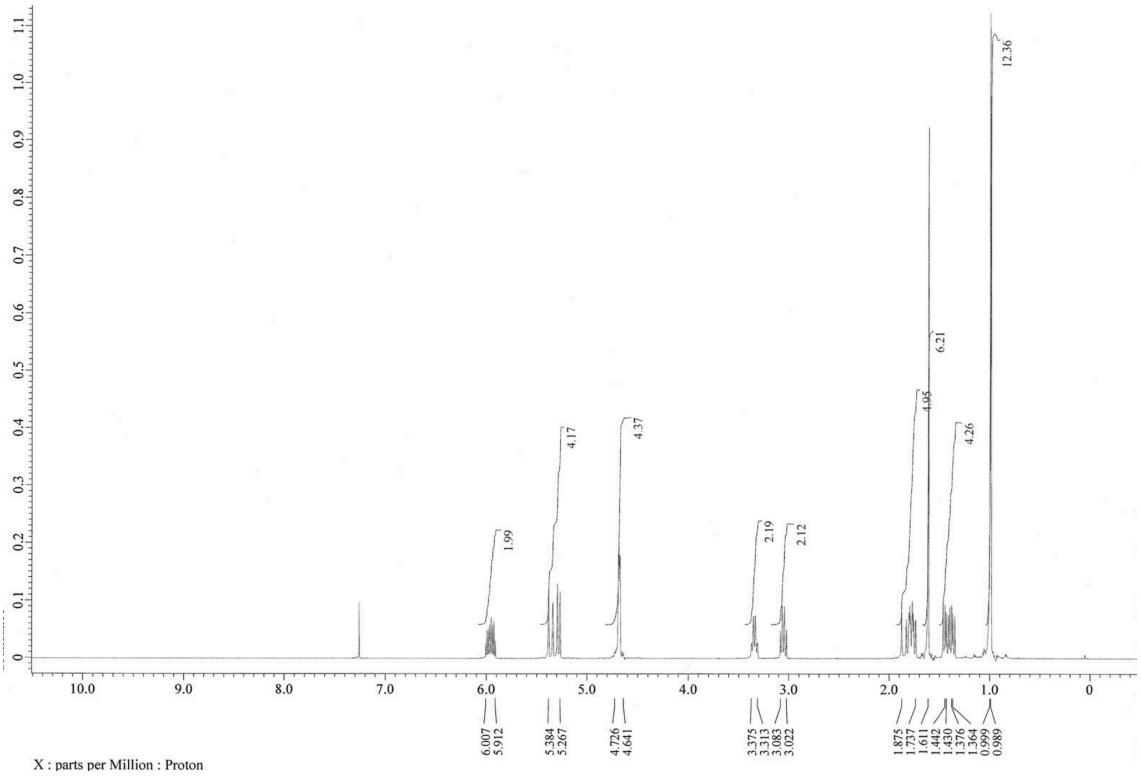
11

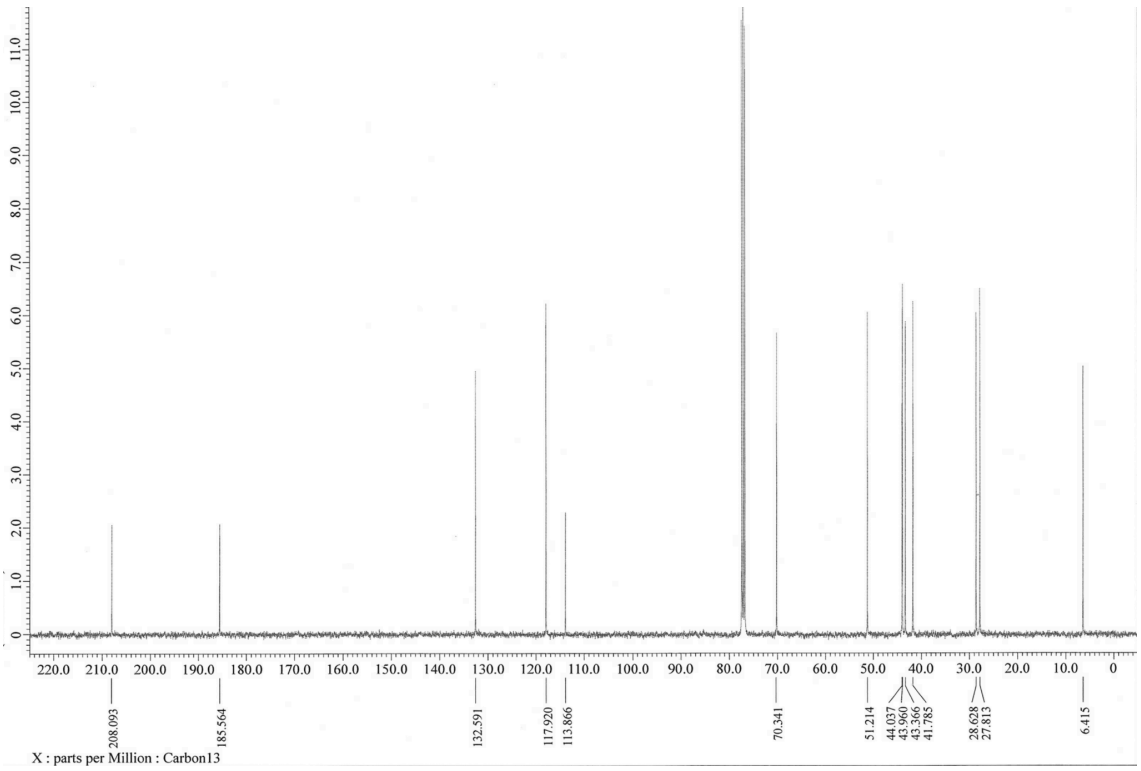

18.24
13.08
12.76
12.60
8.68
8.57
8.71
4.18
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.628
5.523
5.112
5.019
3.343
3.267
2.290
2.272
1.871
1.751
1.098
0.981
0.734
X : parts per Million : Proton

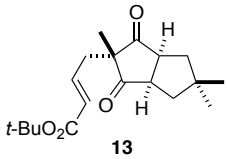

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
218.730
131.086
120.057
59.542
51.713
44.679
42.322
40.942
27.909
27.516
17.291
X : parts per Million : Carbon13



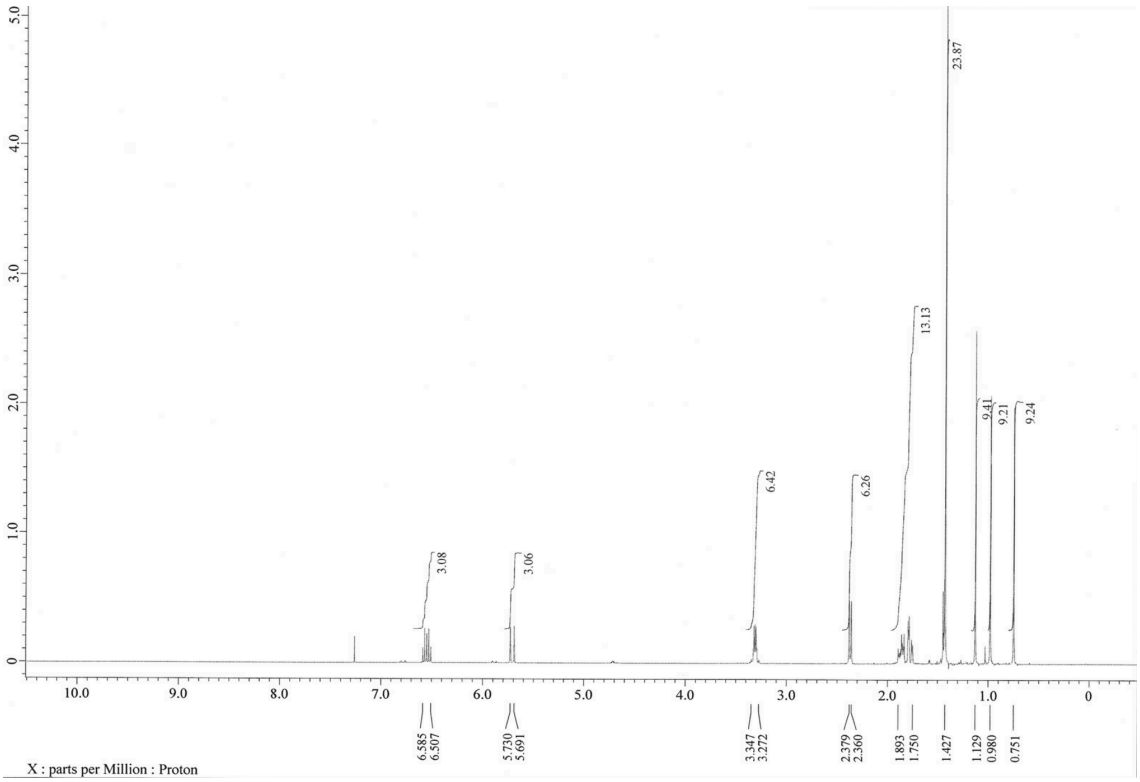
12

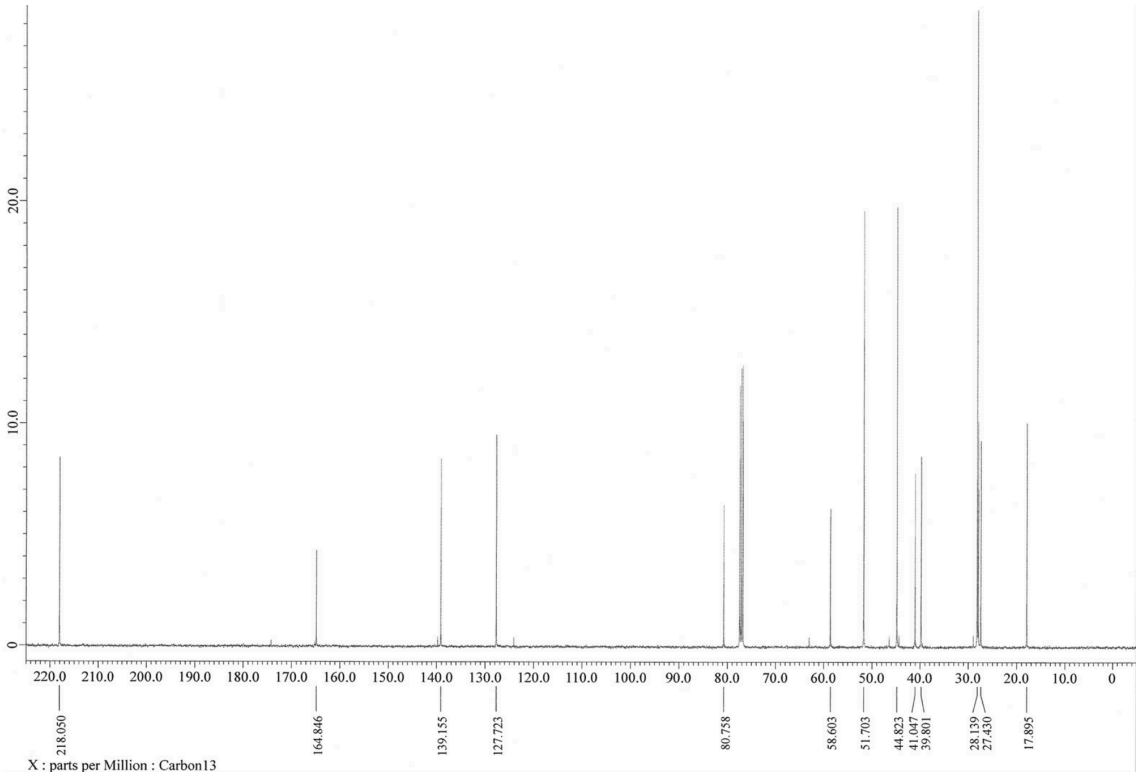

12.36
6.21
4.96
4.37
4.26
4.17
2.19
2.12
1.99
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
6.007
5.912
5.384
5.267
4.726
4.641
3.375
3.313
3.083
3.022
1.875
1.737
1.611
1.442
1.430
1.376
1.364
0.999
0.989
X : parts per Million : Proton

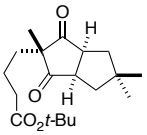

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
208.093
185.564
132.591
117.920
113.866
70.341
51.214
44.037
43.960
43.366
41.785
28.628
27.813
6.415
X : parts per Million : Carbon13


O
H
O
H
t-BuO2C

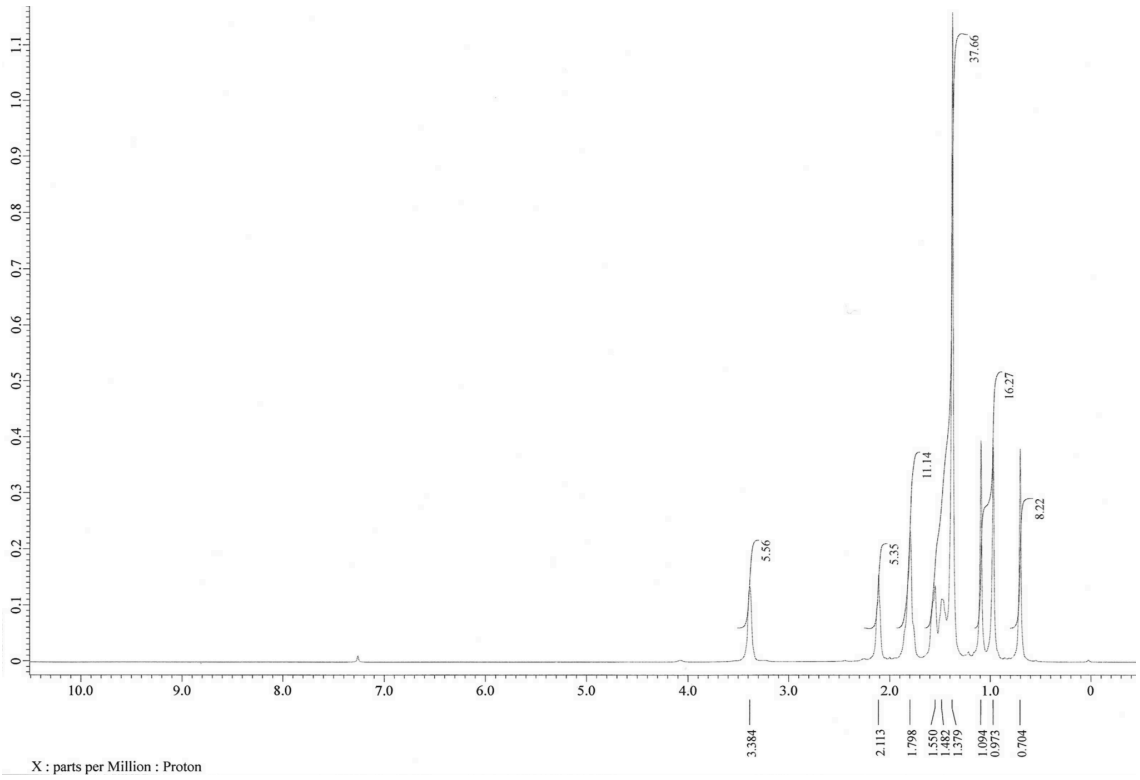
13

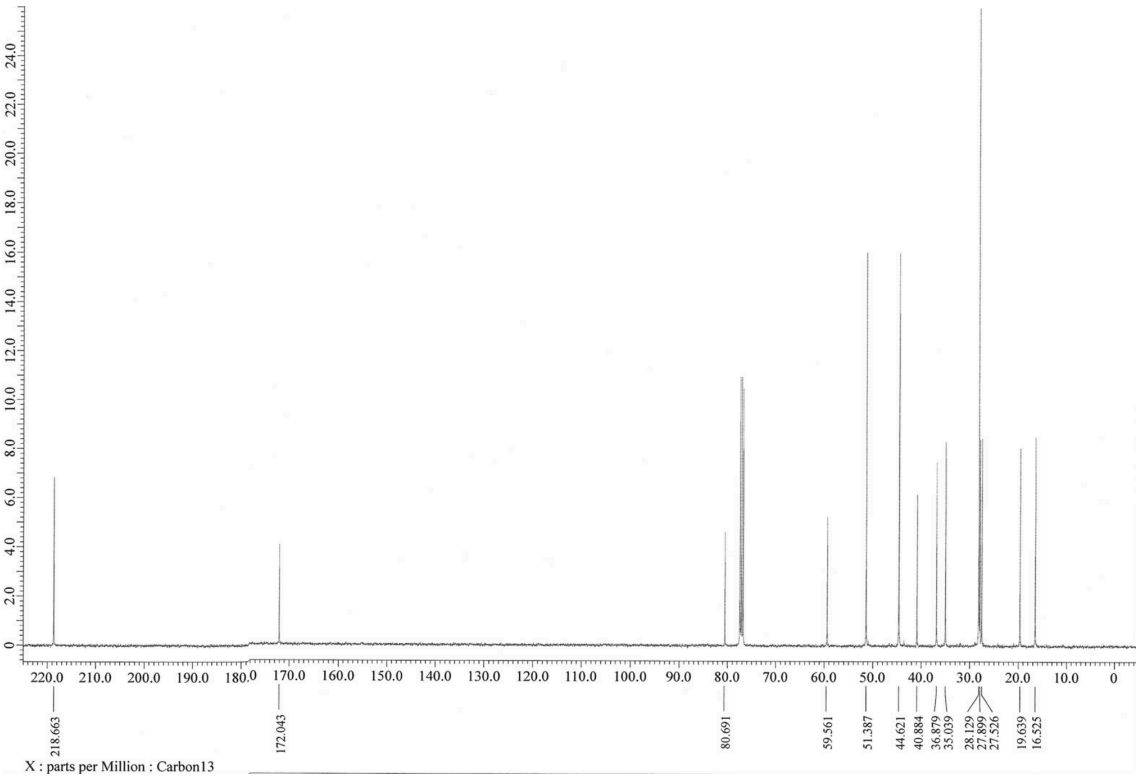

23.87
13.13
9.41
9.21
9.24
6.42
6.26
3.08
3.06
6.585
6.507
5.730
5.691
3.347
3.272
2.379
2.360
1.893
1.750
1.427
1.129
0.980
0.751
X : parts per Million : Proton

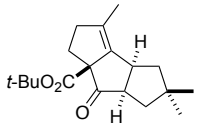

218.050
164.846
139.155
127.723
80.758
58.603
51.703
44.823
41.047
39.801
28.139
27.430
17.895
X : parts per Million : Carbon13


O
H
O
H
CO2t-Bu

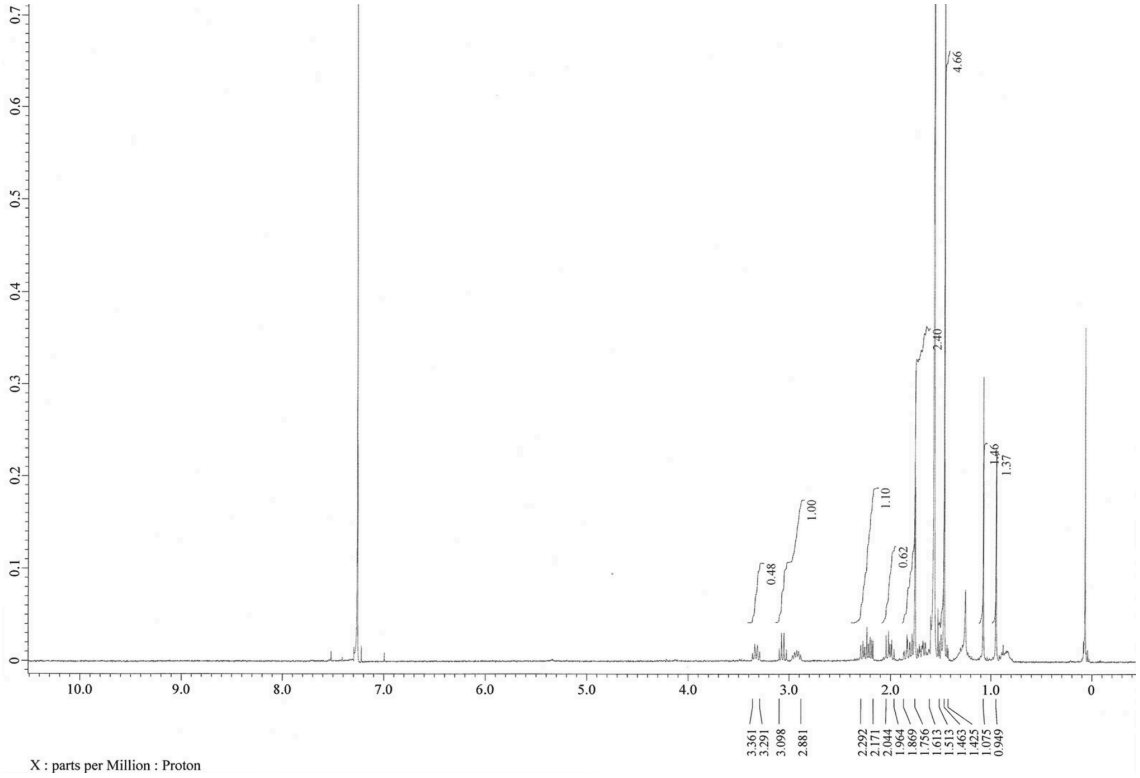
6

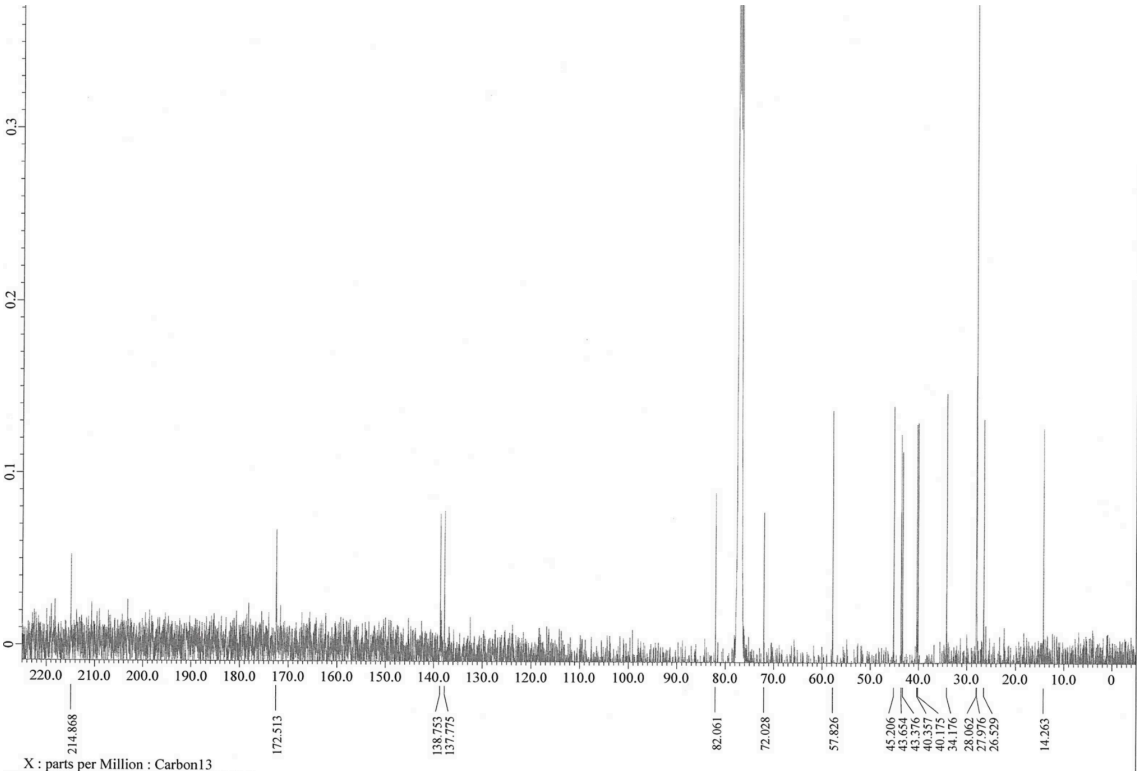

37.66
16.27
11.14
8.22
5.56
5.35
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3.384
2.113
1.798
1.550
1.482
1.379
1.094
0.973
0.704
X : parts per Million : Proton

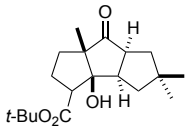

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
218.663
172.043
80.691
59.561
51.387
44.621
40.884
36.879
35.039
28.129
27.899
27.526
19.639
16.525
X : parts per Million : Carbon13


t-BuO2C
O
H
H

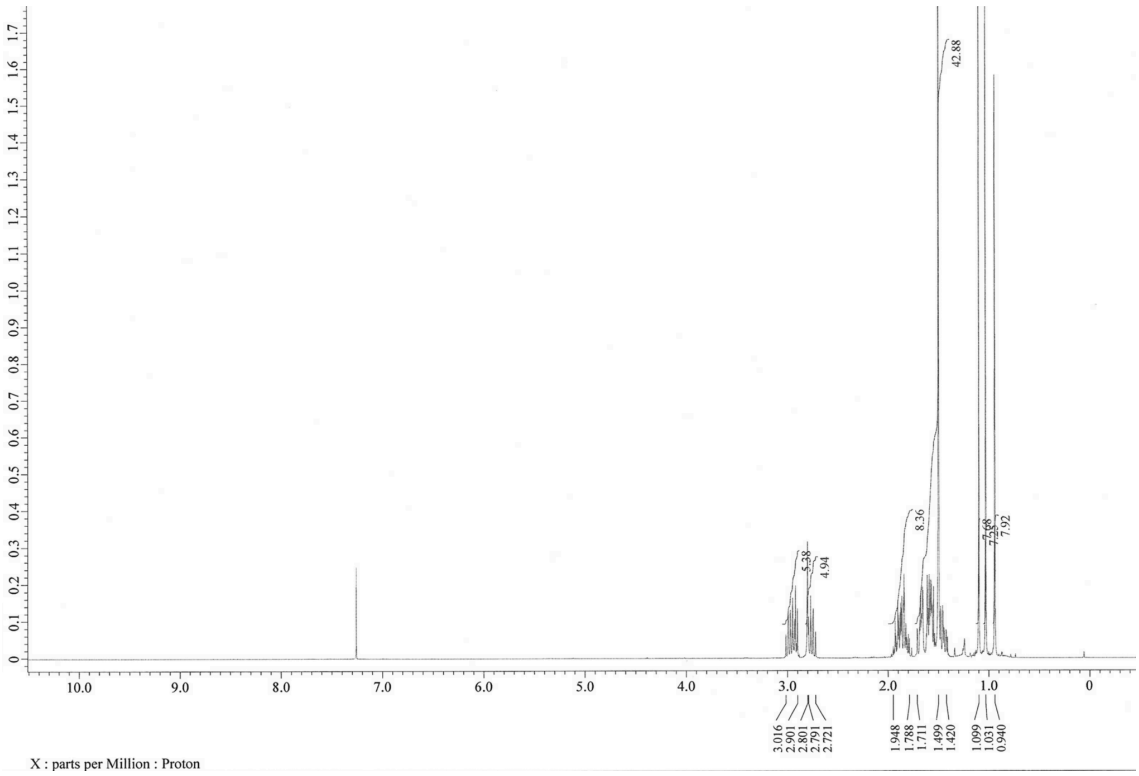
15

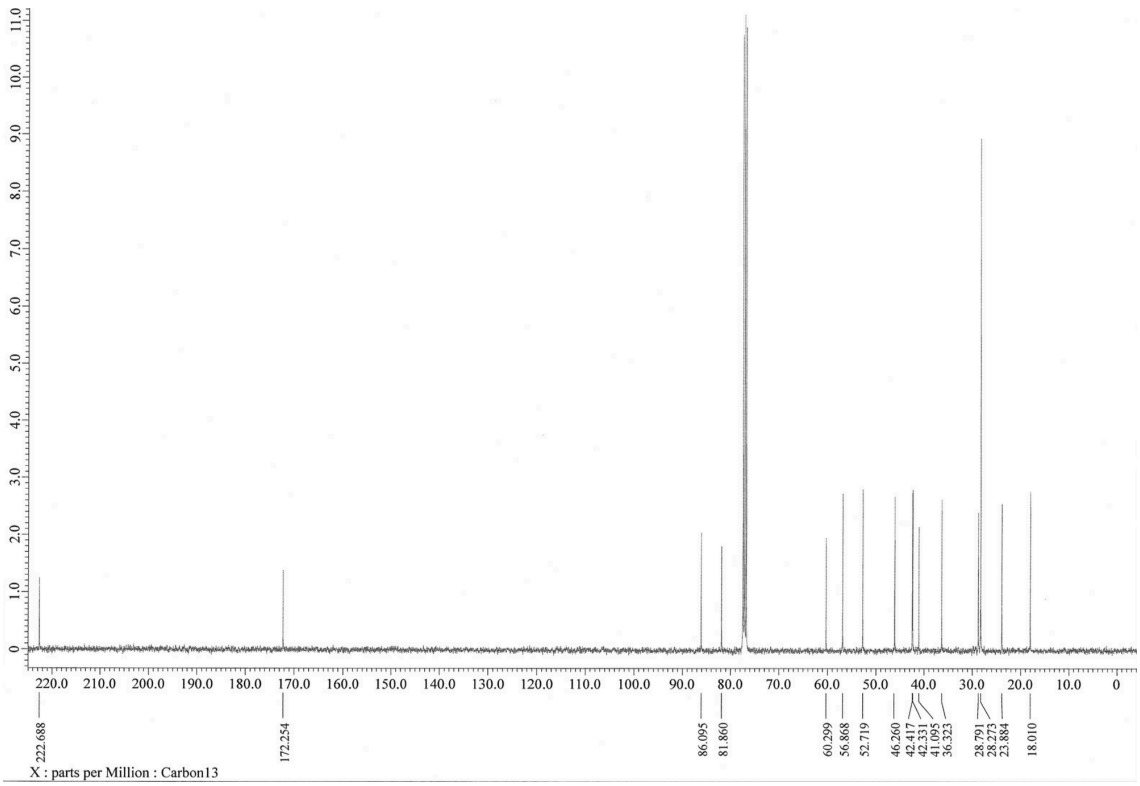

4.66
2.40
1.46
1.37
1.10
1.00
0.62
0.48
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3.361
3.291
3.098
2.881
2.292
2.171
2.044
1.964
1.869
1.736
1.613
1.513
1.463
1.425
1.075
0.949
X : parts per Million : Proton

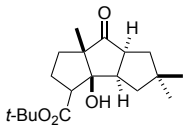

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
214.868
172.513
138.753
137.775
82.061
72.028
57.826
45.206
43.654
43.376
40.357
40.175
34.176
28.062
27.976
26.529
14.263
X : parts per Million : Carbon13



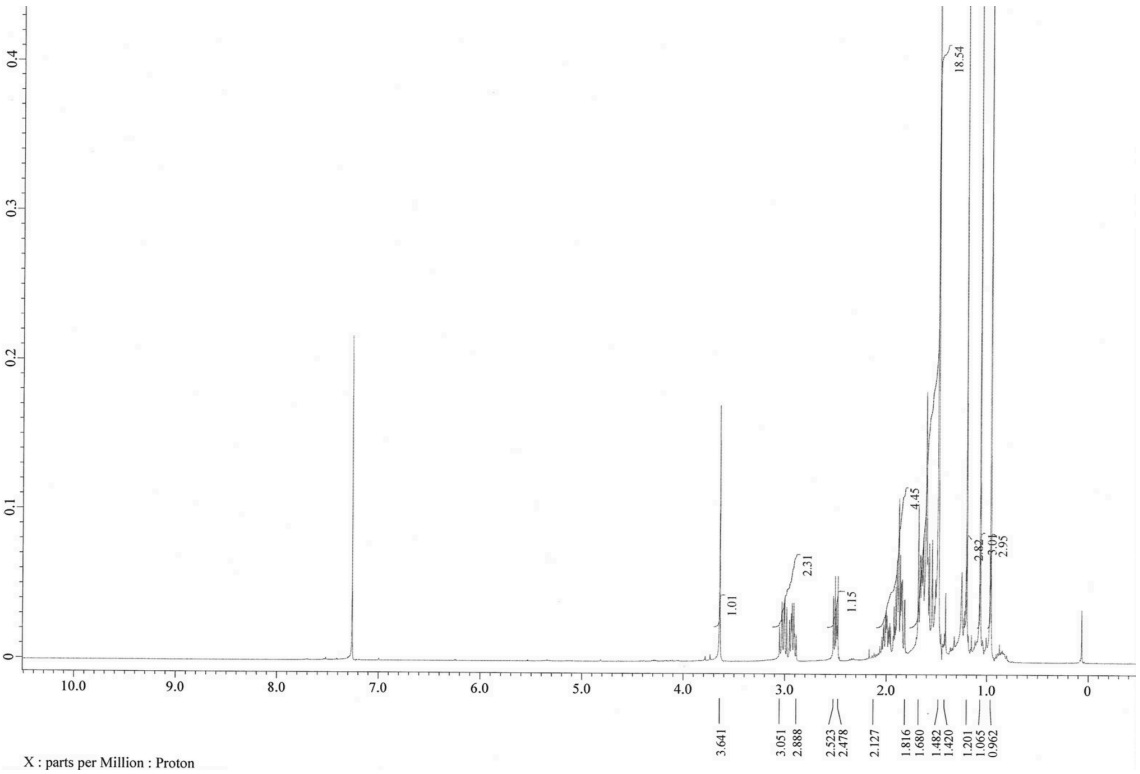
16 (less polar)

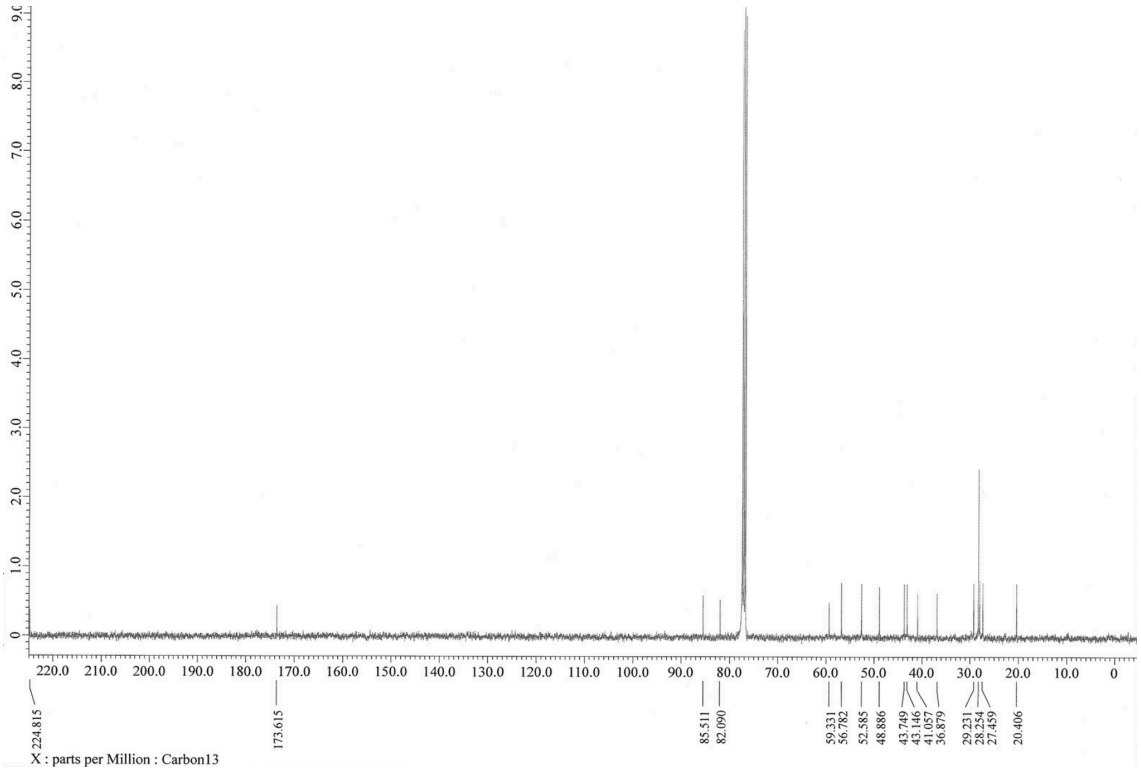


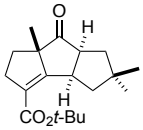



O
H
OH H
t-BuO2C

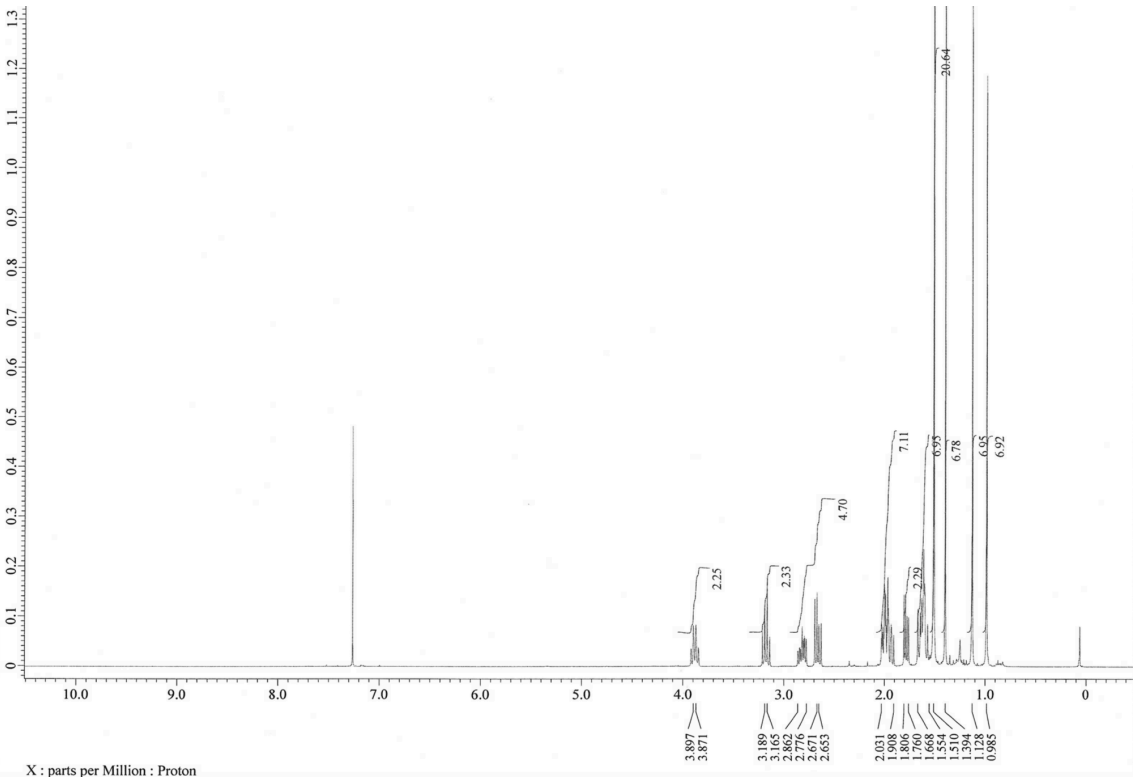
16 (polar)

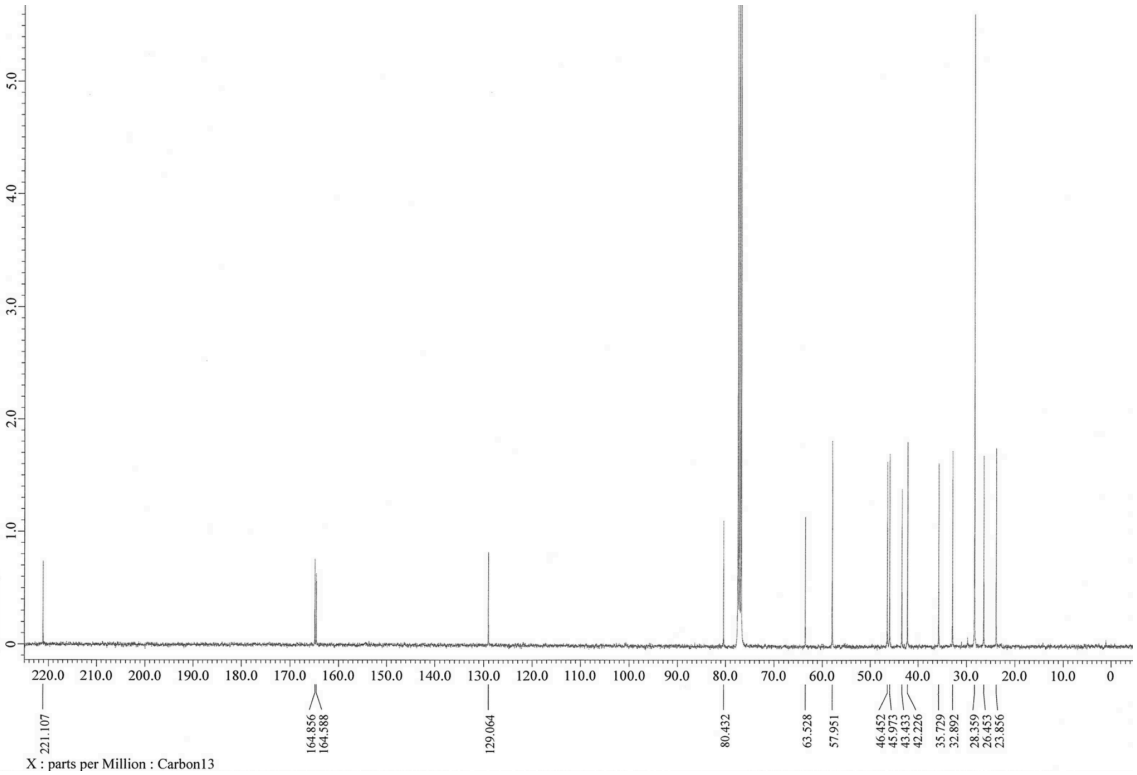

18.54
4.45
2.82
2.40
2.95
2.31
1.15
1.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3.641
3.051
2.888
2.523
2.478
2.127
1.816
1.680
1.482
1.420
1.201
1.065
0.962
X : parts per Million : Proton

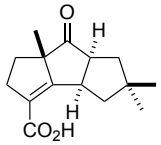

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
224.815
173.615
85.511
82.090
59.331
56.782
52.585
48.886
43.749
43.146
41.057
36.879
29.231
28.254
27.459
20.406
X : parts per Million : Carbon13


O
H
H
CO2t-Bu

19


20.64
7.11
6.93
6.78
6.95
6.92
4.70
2.25
2.33
2.29
3.897
3.871
3.189
3.165
2.862
2.776
2.671
2.653
2.031
1.908
1.806
1.760
1.668
1.554
1.510
1.394
1.128
0.985
X : parts per Million : Proton


221.107
164.856
164.588
129.064
80.432
63.528
57.951
46.452
45.973
43.433
42.226
35.729
32.892
28.359
26.453
23.856
X : parts per Million : Carbon13



chondrosterin I (**1**)