Supporting Information

Enantioselective total synthesis of sagittacin E and related natural products

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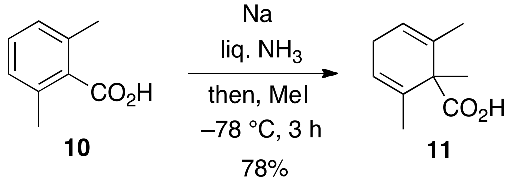
General

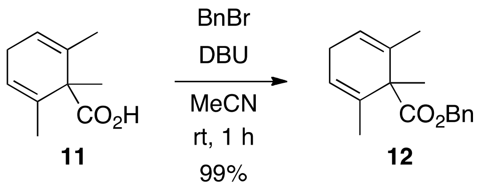
All reactions involving air- and moisture-sensitive reagents were carried out using standard syringe-septum cap techniques. Unless otherwise noted, all solvents and reagents were obtained from commercial suppliers and used without further purification. Routine monitoring of reactions were carried out 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. Measurement of optical rotations was performed with a JASCO P-2200 automatic digital polarimeter. 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 were measured on a Micromass LCT spectrometer. X-ray crystallographic analysis was taken with Burker APEX2 Ultra TXS.

1,2,6-Trimethylcyclohexa-2,5-diene-1-1carboxylic acid (**11**).



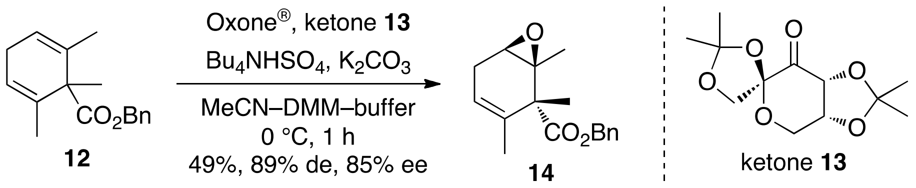
To a stirred solution of 2,6-dimethylbenzoic acid (**10**) (13.0 g, 86.6 mmol) in liquid ammonia (300 mL) and THF (80 mL) was added portionwise sodium metal (9.02 g, 390 mmol) at –78 °C, and then iodomethane (32.1 mL, 73.3 g, 520 mmol) was added dropwise. After stirred for 3 h at –78 °C, the reaction mixture was allowed to warm to room temperature, ammonia gas was removed. To this resulting mixture was added water and conc. H_2SO_4. The mixture was extracted with hexane (3 × 300 mL), and the combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by recrystallization from hexane to afford **11** (11.2 g, 78%) as colorless needles. Mp 113–115 ºC (from hexane); IR (KBr) 3077, 2980, 2944, 2921, 2822, 2642, 2516, 1703, 1561, 1446, 1432, 1404 1273, 1144, 1096, 1036 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (3H, s), 1.73 (6H, s), 2.62–2.80 (2H, m), 5.60–5.64 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4 (2C), 20.9, 27.0, 51.1, 121.7 (2C), 132.8 (2C), 178.9; HRMS (ESI–TOF) calcd for $C_{10}H_{15}O_2$ ([M+H]$^+$) 167.1072, found 167.1068.

Benzyl 1,2,6-trimethylcyclohexa-2,5-diene-1-carboxylate (**12**).



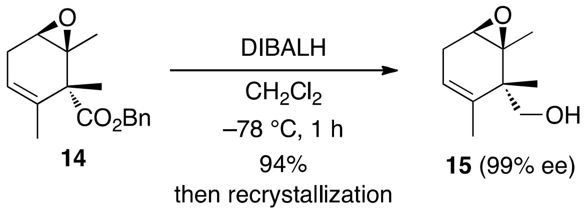
To a stirred solution of **11** (1.22 g, 7.35 mmol) and DBU (1.32 mL, 1.34 g, 8.82 mmol) in MeCN (15 mL) was added dropwise benzyl bromide (1.48 mmol, 2.14 g, 12.5 mmol) at 0 °C, and the mixture was stirred for 1 h at room temperature. The reaction was quenched with sat. K_2CO_3 aqueous solution, and the mixture was extracted with AcOEt (3 × 100 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 70:1) to afford **12** (1.85 g, 99%) as colorless oil. IR (neat) 3034, 2975, 2943, 2919, 2881, 2859, 2817, 1953, 1882, 1730, 1696, 1660, 1587, 1497, 1454, 1383, 1370, 1223, 1132, 1093, 1034, 964 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (3H, s) 1.58–1.60 (6H, m), 2.58–2.77 (2H, m), 5.14 (2H, s), 5.53–5.57 (2H, m), 7.27–7.35 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3 (2C), 21.3, 27.0, 51.2, 66.4, 120.9 (2C), 128.0, 128.1 (2C), 128.3 (2C), 133.3 (2C), 136.1, 174.6; HRMS (ESI–TOF) calcd for $C_{17}H_{21}O_2$ ($[M+H]^+$) 257.1542, found 257.1548.

Benzyl (1*S*,2*R*,6*R*)-1,2,3-trimethyl-7-oxabicyclo[4.1.0]hept-3-ene-2-carboxylate (**14**).



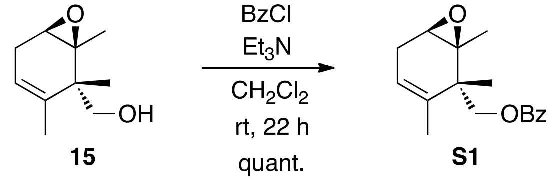
To a stirred solution of **12** (128 mg, 0.500 mmol), tetra-*n*-butylammonium hydrosulfate (6.8 mg, 20.0 μmol) and Shi ketone **13** (38.7 mg, 0.150 mmol) in MeCN–DMM [formaldehyde dimethylacetal] (1:2, 7.8 mL) and 0.05 M sodium tetraborate in 0.4 mM Na_2EDTA aqueous solution (3.8 mL) were added dropwise simultaneously, a solution of Oxone® (553 mg, 0.900 mmol) in 0.4 mM Na_2EDTA aqueous solution (2.3 mL) and a solution of K_2CO_3 (345 mg, 2.50 mmol) in 0.4 mM Na_2EDTA aqueous solution (2.3 mL) by using the syringe pump (0.24 mL/min) at 0 °C. After stirred for 1 h at 0 °C, H_2O was added to this mixture. The mixture was extracted with AcOEt (3 × 100 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt = 15:1) to afford **14** (66.5 mg, 49%, 85% ee) as colorless oil. $[\alpha]_D^{25}$ –120.9 (*c* = 0.98, $CHCl_3$); IR (neat) 3033, 2974, 2890, 2820, 1735, 1587, 1497, 1453, 1371, 1257, 1224, 1107, 1081, 1065, 1031, 955, 920, 886, 835, 802, 754, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (3H, s) 1.43 (3H, s), 1.59–1.61 (3H, m), 2.54–2.58 (2H, m), 3.14–3.16 (1H, m), 5.14 (2H, s), 5.30–5.35 (1H, m), 7.28–7.38 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8, 19.4, 19.8, 26.4, 51.9, 60.2, 61.3, 66.7, 120.2, 127.8 (2C), 128.2, 128.5 (2C), 131.5, 135.8, 173.4; HRMS (ESI–TOF) calcd for $C_{17}H_{20}NaO_3$ ($[M+Na]^+$) 295.1310, found 295.1304.

[(1*S*,2*S*,6*R*)-1,2,3-Trimethyl-7-oxabicyclo[4.1.0]hept-3-en-2-yl]methanol (**15**).



To a stirred solution of **14** (1.16 g, 4.30 mmol) in CH_2Cl_2 (43 mL) was added dropwise DIBALH (1.02 M in hexane, 12.6 mL, 12.9 mmol) at –78 °C, and the reaction mixture was stirred for 1 h at the same temperature. The reaction mixture was quenched with sat. potassium sodium tartrate aqueous solution, and extracted with $CHCl_3$ (3 × 100 mL). The combined organic layers was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt = 3:1) to afford **15** (682 mg, 94%) as colorless needles. Recrystallization from hexane gave the optically pure **15** (99% ee) as colorless needles. $[\alpha]_D^{22}$ +5.6 (*c* = 0.99, $CHCl_3$); Mp 74–75 ºC (from hexane); IR (KBr) 3454, 2974, 2919, 2892, 1482, 1453, 1376, 1294, 1211, 1054, 855, 791, 636 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (3H, s), 1.41 (3H, s), 1.65–1.68, (3H, m), 2.45–2.59 (2H, m), 3.10–3.12 (1H, m) 3.54 (2H, s), 5.43–5.47 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 18.8, 19.2, 26.4, 45.1, 60.0, 61.4, 66.2, 121.1, 133.2; HRMS (ESI–TOF) calcd for $C_{10}H_{17}O_2$ ($[M+H]^+$) 169.1229, found 169.1236.

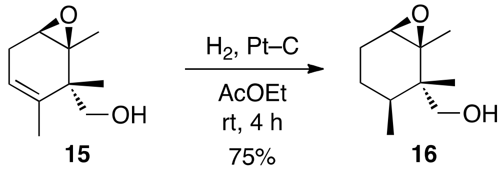
[(1*S*,2*S*,6*R*)-1,2,3-Trimethyl-7-oxabicyclo[4.1.0]hept-3-en-2-yl]methyl benzoate (**S1**).



To a stirred solution of **15** (61.0 mg, 0.363 mmol) and triethylamine (0.252 mL, 184 mg, 1.81 mmol) in CH_2Cl_2 (1.8 mL) was added dropwise benzoyl chloride (0.462 mL, 408 mg, 2.90 mmol) at room temperature, and the mixture was stirred for 22 h at the same temperature. The reaction was quenched with sat. NH_4Cl aqueous solution, and extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt = 5:1) to afford **S1** (98.7 mg, quant.) as colorless gum. $[\alpha]_D^{24}$ –102.2 (*c* = 0.15, $CHCl_3$); IR (neat) 2981, 2924, 2852, 1718, 1602, 1584, 1450, 1369, 1315, 1272, 1176, 1149, 1114, 1069, 1047, 1026, 983, 805, 711 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.15 (3H, s), 1.18 (3H, s), 1.72 (3H, d, *J* = 1.4 Hz), 1.93 (1H, dddq, *J* = 17.6, 10.1, 3.7, 1.4 Hz), 2.46 (1H, ddd, *J* = 17.6, 6.9, 5.5 Hz), 4.28 (1H, dd, *J* = 10.1, 6.9 Hz), 4.42 and

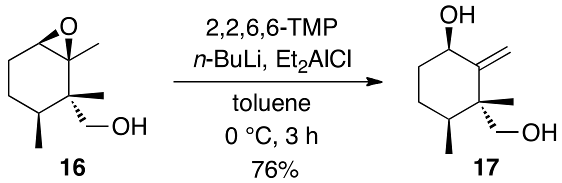
4.47 (2H, ABq, J = 11.9 Hz), 5.40–5.43 (1H, m), 7.44 (2H, dd, J = 8.2, 7.3 Hz), 7.57 (1H, t, J = 7.3 Hz), 7.99 (2H, d, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.2, 16.8, 19.5, 32.1, 47.0, 67.6, 69.7, 76.6, 122.3, 128.5 (2C), 129.5 (2C), 130.1, 133.1, 135.7, 166.3; HRMS (ESI–TOF) calcd for $C_{17}H_{21}O_3$ ([M+H]$^+$) 273.1491, found 273.1485.

[(1*S*,2*S*,3*S*,6*R*)-1,2,3-Trimethyl-7-oxabicyclo[4.1.0]heptan-2-yl]methanol (**16**).



To a stirred solution of **15** (162 mg, 0.964 mmol) in AcOEt (4.8 mL) were added 5% platinum on carbon (48.6), and the mixture was stirred for 4 h under H_2. After the catalyst was filtered off, the filtrate was concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt = 3:1) to afford **16** (123 mg, 75%) as colorless needles. $[\alpha]_D^{21}$ –46.4 (c = 1.04, $CHCl_3$); Mp 65–67 °C (from hexane–AcOEt); IR (KBr) 3464, 2964, 2932, 2879, 1464, 1450, 1439, 1375, 1278, 1218, 1147, 1069, 1006, 940, 874, 822, 749, 660 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (3H, s), 0.78 (3H, d, J = 6.9 Hz), 1.13 (1H, dddd, J = 12.8, 5.0, 2.7, 2.3 Hz), 1.32–1.46 (4H, m, including 3H, s, at δ 1.36), 1.58–1.70 (2H, m), 1.76 (1H, dddd, J = 14.6, 12.3, 5.0, 1.4 Hz), 2.00 (1H, dddd, J = 14.6, 4.1, 2.7, 2.3 Hz), 3.00–3.02 (1H, m), 3.53 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$); δ 12.9, 15.7, 20.6, 23.9, 25.8, 31.1, 40.6, 62.3, 62.5, 66.4; HRMS (ESI–TOF) calcd for $C_{10}H_{19}O_2$ ([M+H]$^+$) 171.1385, found 171.1391.

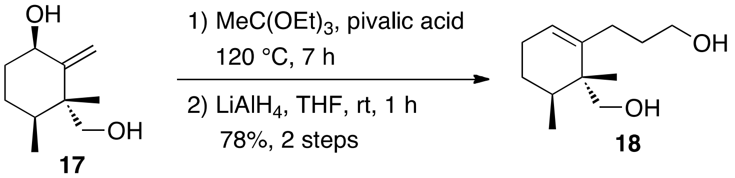
(1*R*,3*R*,4*S*)-3-(Hydroxymethyl)-3,4-dimethyl-2-methylenecyclohexan-1-ol (**17**).



To a stirred solution of 2,2,6,6-tetramethylpiperidine (10.9 mL, 9.07 g, 64.2 mmol) in toluene (32 mL) was added dropwise *n*-butyllithium (1.04 M in hexane, 38.3 mL, 64.2 mmol) at 0 °C under Ar, and the mixture was stirred for 30 min at 0 °C. To this mixture was added dropwise diethylaluminum chloride (1.04 M in hexane, 62.6 mL, 65.7 mmol) at 0 °C, and the mixture was stirred for 1 h at 0 °C. To this mixture was added dropwise **16** (2.49 g, 14.6 mmol) in toluene (29 mL) at 0 °C, and the reaction mixture was stirred for 3 h at the same temperature. The reaction was quenched with 1.0 M HCl aqueous solution, and extracted with AcOEt (3 × 300 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt = 1:1) to afford **17** (1.89 g, 76%)

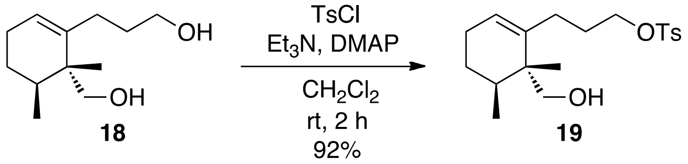
as colorless needles. $[\alpha]_D^{21}$ –6.4 (*c* = 1.11, $CHCl_3$); Mp 81–83 ºC (from hexane); IR (KBr) 3357, 2936, 2873, 1637, 1458, 1378, 1275, 1128, 1093, 1034, 1003, 971, 903 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, d, *J* = 6.8 Hz), 1.08 (3H, s), 1.45–1.64 (4H, m), 1.67–1.76 (1H, m), 1.82–1.92 (2H, m), 3.41 (1H, d, *J* = 11.2 Hz), 3.74 (1H, d, *J* = 11.2 Hz), 4.22–4.29 (1H, m), 4.96 (1H, s), 5.37 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 20.7, 27.0, 31.8, 34.7, 46.4, 68.1, 70.3, 109.5, 152.1; HRMS (ESI–TOF) calcd for $C_{10}H_{18}NaO_2$ ($[M+Na]^+$) 193.1204, found 193.1209.

3-((5*S*,6*R*)-6-(Hydroxymethyl)-5,6-dimethylcyclohex-1-en-1-yl)propan-1-ol (**18**).



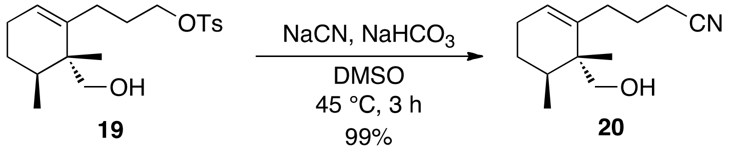
To a stirred solution of **17** (186 mg, 1.09 mmol) in triethyl orthoacetate (4 mL) were added pivalic acid (24.6 μL, 22.3 mg, 0.218 mmol) at room temperature under Ar, and the mixture was stirred for 7 h at 120 °C. The reaction was quenched with sat. $NaHCO_3$ aqueous solution, and the mixture was extracted with AcOEt (3 × 300 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by short column chromatography (hexane–AcOEt, 3:1) to afford the mixture of ester compounds. After this mixture was solved in THF (2 mL), lithium aluminum hydride (207 mg, 5.45 mmol) was added to this mixture at 0 °C. After stirred for 1 h at room temperature, the mixture was quenched with sat. potassium sodium tartrate aqueous solution. The mixture was extracted with AcOEt (3 × 30 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 1:2) to afford **18** (168 mg, 78% for 2 steps) as colorless oil. $[\alpha]_D^{19}$ –41.4 (*c* = 1.02, $CHCl_3$); IR (neat) 3335, 2957, 2923, 2879, 2838, 1456, 1435, 1380, 1271, 1231, 1171, 1046, 968, 924 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.79 (3H, s), 0.90 (3H, d, *J* = 7.3 Hz), 1.35–1.46 (1H, m), 1.52–1.59 (1H, m), 1.69–1.82 (2H, m), 1.88–1.98 (1H, m), 2.00–2.13 (4H, m), 3.47 (1H, d, *J* = 11.4 Hz), 3.60 (1H, d, *J* = 11.4 Hz), 3.62–3.75 (2H, m), 5.61–5.65 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.1, 16.7, 25.1, 25.9, 26.6, 31.0, 32.2, 43.3, 62.3, 65.7, 125.0, 139.7; HRMS (ESI-TOF) calcd for $C_{12}H_{22}NaO_2$ ($[M+Na]^+$) 221.1517, found 221.1511.

3-[(5*S*,6*R*)-6-Hydroxymethyl-5,6-dimethylcyclohex-1-en-1-yl]propyl 4-methylbenzenesulfonate (**19**).



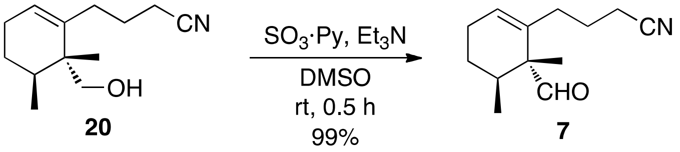
To a stirred solution of **18** (280 mg, 1.41 mmol), triethylamine (0.394 mL, 286 mg, 2.83 mmol) and 4-dimethylaminopyridine (17.3 mg, 0.141 mmol) in CH_2Cl_2 (14 mL) was added *p*-toluenesulfonyl chloride (404 mg, 2.12 mmol) at 0 °C, and the mixture was stirred for 2 h at room temperature. The reaction was quenched with H_2O, and the mixture was extracted with $CHCl_3$ (3 × 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 1:1) to afford **19** (462 mg, 92%) as pale yellow oil. $[\alpha]_D^{30}$ –23.8 (*c* = 1.00, $CHCl_3$); IR (neat) 3560, 3426, 2959, 2924, 2855, 1733, 1655, 1598, 1457, 1360, 1307, 1291, 1261, 1188, 1176, 1098, 1040, 1018, 964, 927, 834, 815, 741, 664 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.74 (3H, s), 0.87 (3H, d, *J* = 6.8 Hz), 1.24–1.42 (2H, m), 1.51–1.60 (1H, m), 1.75–2.03 (7H, m), 2.45 (3H, s), 3.43 and 3.47 (2H, ABq, *J* = 11.0 Hz), 4.06 (2H, t, *J* = 6.4 Hz), 5.46–5.51 (1H, m), 7.33–7.37 (2H, m), 7.78–7.81 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0, 16.8, 21.6, 24.9, 26.1, 26.4, 28.0, 32.0, 43.1, 65.8, 70.5, 125.3, 127.9 (2C), 129.8 (2C), 133.2, 139.0, 144.7; HRMS (ESI-TOF) calcd for $C_{19}H_{28}O_4NaS$ ($[M+Na]^+$) 375.1606, found 375.1604.

4-[(5*S*,6*R*)-6-Hydroxymethyl-5,6-dimethylcyclohex-1-en-1-yl]butanenitrile (**20**).



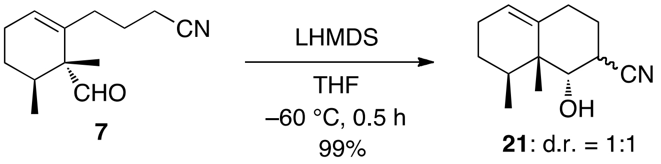
To a stirred solution of **19** (71.3 mg, 0.203 mmol) in DMSO (1 mL) was added $NaHCO_3$ (19.9 mg, 0.406 mmol) and sodium cyanide (34.1 mg, 0.406 mmol) at room temperature under Ar, and the mixture was stirred for 3 h at 45 °C. The reaction was quenched with sat. $NaHCO_3$ aqueous solution at 0 °C, and the mixture was extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 5:1) to afford **20** (41.8 mg, 99%) as colorless oil. $[\alpha]_D^{25}$ –49.4 (*c* = 1.01, $CHCl_3$); IR (neat) 3465, 2960, 2923, 2838, 2247, 1739, 1655, 1457, 1435, 1377, 1267, 1231, 1169, 1106, 1042, 1008, 965, 943, 791, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.80 (3H, s), 0.90 (3H, d, *J* = 7.5 Hz), 1.35–1.47 (2H, m), 1.54–1.61 (1H, m), 1.76–1.97 (3H, m), 2.01–2.08 (2H, m), 2.10–2.17 (2H, m), 2.38 (2H, t, *J* = 7.1 Hz), 3.50 and 3.56 (2H, ABq, *J* = 11.0 Hz), 5.56–5.60 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 16.9, 17.0, 24.5, 25.0, 26.4, 29.4, 32.0, 43.0, 65.8, 119.8, 125.7, 138,9; HRMS (ESI-TOF) calcd for $C_{13}H_{21}NNaO$ ($[M+Na]^+$) 230.1521, found 230.1521.

4-[(5*S*,6*R*)-6-Formyl-5,6-dimethylcyclohex-1-en-1-yl]butanenitrile (**7**)



To a stirred suspension of **20** (226 mg, 1.09 mmol) and triethylamine (1.22 mL, 882 mg, 8.72 mmol) in DMSO (11 mL) was added sulfur trioxide pyridine complex (520 mg, 3.27 mmol) at room temperature, and the mixture was stirred for 0.5 h at room temperature. The reaction was quenched with H_2O, and the mixture was extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulted residue was purified by column chromatography (hexane–AcOEt, 2:1) to afford **7** (222 mg, 99%) as colorless oil. $[\alpha]_D^{29}$ –104.5 (*c* = 1.01, $CHCl_3$); IR (neat) 2962, 2930, 2875, 2840, 2689, 2246, 1721, 1659, 1458, 1434, 1383, 1369, 1248, 1217, 1187, 1120, 1108, 1077, 1033, 968, 926, 904, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.78 (3H, d *J* = 7.5 Hz), 1.02 (3H, s), 1.31–1.43 (1H, m), 1.57–1.66 (1H, m), 1.68–1.78 (2H, m), 1.83–2.02 (3H, m), 2.08–2.15 (2H, m), 2.31 (2H, t, *J* = 7.3 Hz), 5.66–5.70 (1H, m), 9.27 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 15.9, 16.7, 24.5, 24,9, 25.1, 31.3, 31.9, 55.4, 119.4, 126.5, 134.6, 204.5; HRMS (ESI–TOF) calcd for $C_{13}H_{19}NNaO$ ($[M+Na]^+$) 228.1364, found 228.1362.

(1*S*,2*RS*,8*S*,8a*R*)-1-Hydroxy-8,8a-dimethyl-1,2,3,4,6,7,8,8a-octahydronaphthalene-2-carbonitrile (**21**)



To a stirred solution of **7** (801 mg, 3.90 mmol) in THF (39 mL) was added dropwise lithium bis (trimethylsilyl)amide (1.0 M in THF, 5.85 mL, 5.85 mmol) at –78 °C, and the mixture was stirred for 0.5 h at –78 °C. The reaction was quenched with sat. NH_4Cl aqueous solution, and the mixture was extracted with AcOEt (3 × 100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 3:1) to afford **21** (800 mg, 99%) as a mixture of 1:1 ratio.

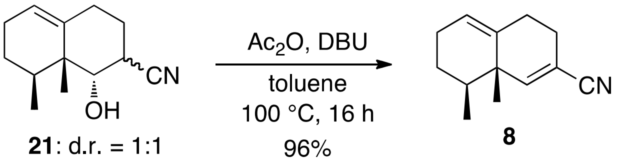
Data for (2*S*)-**21a**.

Colorless oil; $[\alpha]_D^{28}$ –22.7 (*c* = 1.04, $CHCl_3$); IR (neat) 3456, 2929, 2245, 1720, 1661, 1456, 1383, 1333, 1261, 1202, 1075, 1043, 979, 890, 839, 803, 758, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (3H, s), 1.12 (3H, d *J* = 6.9 Hz), 1.31–1.75 (5H, m), 1.94–2.05 (3H, m), 2.06–2.13 (1H, m), 2.15–2.26 (1H, m), 2.78 (1H, ddd, *J* = 13.2, 10.5, 4.1 Hz), 3.58 (1H, d, *J* = 10.5 Hz), 5.52–5.55 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.1, 18.6, 24.9, 28.3, 29.1, 30.7, 35.0, 38.7, 43.4, 79.4, 121.8, 125.0, 139.3; HRMS (ESI–TOF) calcd for $C_{13}H_{20}NO$ ($[M+H]^+$) 206.1545, found 206.1539.

Data for (2*R*)-**21b**.

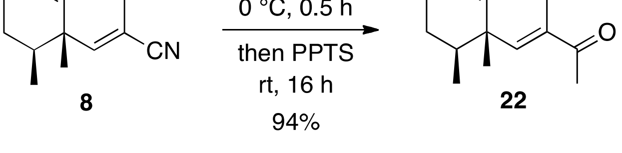
Colorless needles; $[\alpha]_D^{25}$ –121.0 (*c* = 0.95, $CHCl_3$); Mp 110–112 ºC (from hexane–$CHCl_3$); IR (KBr) 3472, 2936, 2907, 2861, 2236, 1449, 1446, 1432, 1381, 1360, 1273, 1165, 1062, 1044, 0133, 976, 928, 844, 831 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (3H, d, *J* = 6.9 Hz), 1.19 (3H, s), 1.36–1.44 (2H, m), 1.52–1.63 (3H, m), 1.94–2.09 (4H, m), 2.47–2.58 (1H, m), 3.10 (1H, dddd, *J* = 8.2, 5.5, 2.8, 1.4 Hz), 3.56 (1H, d, *J* = 5.5 Hz), 5.52–5.55 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 18.8, 25.4, 27.8, 28.1, 28.8, 34.7, 40.4, 44.3, 77.9, 121.2, 124.9, 139.9; HRMS (ESI–TOF) calcd for $C_{13}H_{20}NO$ ($[M+H]^+$) 206.1545, found 206.1539.

(8*S*,8a*S*)-8,8a-Dimethyl-3,4,6,7,8,8a-hexahydronaphthalene-2-carbonitrile (**8**).



To a stirred solution of the mixture of **21** (800 mg, 3.90 mmol) and DBU (1.75 mL, 1.78 g, 22.1 mmol) in toluene (8 mL) was added acetic anhydride (0.730 mL, 788 mg, 7.80 mmol) at room temperature, and the mixture was stirred for 1.5 h at the same temperature. After the reaction mixture was allowed to warm to 100 °C, DBU (7.80 mL, 5.94 g, 39.0 mmol) was added to this, and the stirring was continued for 16 h at 100 °C. The reaction was quenched with sat. NH_4Cl aqueous solution, and the mixture was extracted with AcOEt (3 × 100 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 10:1) to afford **8** (698 mg, 96%) as colorless oil. $[\alpha]_D^{24}$ –205.0 (*c* = 0.99, $CHCl_3$); IR (neat) 2964, 2925, 2217, 1736, 1673, 1631, 1454, 1434, 1388, 1371, 1260, 1220, 1098, 1066, 999, 886, 856, 810 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (3H, d, *J* = 6.4 Hz), 1.02 (3H, s), 1.50–1.54 (3H, m), 1.98–2.04 (2H, m), 2.15–2.40 (4H, m), 5.44–5.47 (1H, m), 6.58 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 19.7, 25.1, 26.6, 28.6, 29.3, 35.9, 39.7, 110.6, 119.7, 122.5, 138.2, 151.7; HRMS (ESI–TOF) calcd for $C_{13}H_{18}N$ ($[M+H]^+$) 188.1439, found 188.1435.

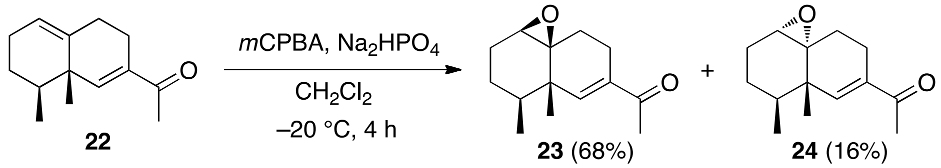
1-((8*S*,8a*S*)-8,8a-Dimethyl-3,4,6,7,8,8a-hexahydronaphthalen-2-yl)ethan-1-one (**22**).



To a stirred solution of **8** (431 mg, 2.30 mmol) in ether (12 mL) was added dropwise methyllitium (1.1 M in ether, 4.18 mL, 4.60 mmol) at 0 °C under Ar, and the mixture was stirred for 0.5 h at 0 °C. To this reaction mixture were added H_2O (6 mL) and PPTS (1.73 g, 6.90 mmol) at 0 °C, and the mixture was stirred for 16 h at room temperature. The mixture was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 20:1) to afford **21** (442 mg, 94%) as colorless oil. $[\alpha]_D^{26}$ –211.3 (*c* = 0.94, $CHCl_3$); IR (neat) 2965, 2932, 1669, 1633, 1460, 1434, 1393, 1377, 1352, 1265, 1241, 1211, 1172, 1066, 998, 968, 947, 875, 808 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.02 (3H, d, *J* = 2.7 Hz), 1.06 (3H, s), 1.50–1.60 (3H, m), 1.98–2.08 (3H, m), 2.17–2.32 (5H, m, including 3H, s, at δ 2.30), 2.57 (1H, ddd, *J* = 16.9, 5.5, 1.4 Hz), 5.42–5.45 (1H, m), 6.62 (1H, d, *J* = 2.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 20.1, 25.1, 25.4, 26.0, 26.9, 29.0, 36.2, 39.1, 120.9, 137.4, 140.5, 146.9, 199.8; HRMS (ESI–TOF) calcd for $C_{14}H_{21}O$ ($[M+H]^+$) 205.1592, found 205.1589.

1-((1a*R*,4*S*,4a*S*,8a*S*)-4,4a-Dimethyl-1a,2,4,4a,7,8-hexahydro-3*H*-naphtho[1,8a-*b*]oxiren-6-yl)ethan-1-one (**23**).

1-((1a*S*,4*S*,4a*S*,8a*R*)-4,4a-Dimethyl-1a,2,4,4a,7,8-hexahydro-3*H*-naphtho[1,8a-*b*]oxiren-6-yl)ethan-1-one (**24**).



To a stirred solution of **8** (175 mg, 0.857 mmol) in CH_2Cl_2 (9 mL) was added Na_2HPO_4 (365 mg, 2.57 mmol) and *m*CPBA (65%, 250 mg, 0.943 mmol) at –20 °C, and the mixture was stirred for 4 h at –20 °C. The reaction was quenched with sat. $NaHCO_3$ aqueous solution, and the mixture was extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 15:1) to afford **23** (129 mg, 68%) and **24** (29.3 mg, 16%) as colorless oil, each.

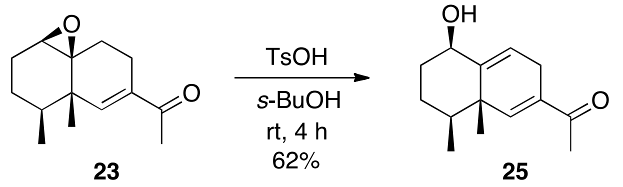
Data for **23**

$[\alpha]_D^{28}$ –164.7 (*c* = 0.98, $CHCl_3$); IR (neat) 2964, 2936, 2878, 2858, 1755, 1669, 1637, 1455, 1435, 1378, 1354, 1270, 1235, 1176, 1035, 1011, 972, 878 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (3H, d, *J* = 6.9 Hz), 1.08 (3H, s), 1.13–1.26 (3H, m), 1.43–1.54 (1H, m), 1.17 (1H, dddd, *J* = 14.6, 12.2, 5.0, 1.8 Hz), 2.00–2.17 (3H, m), 2.33 (3H, s), 2.63–2.69 (1H, m), 3.05–3.07 (1H, m), 6.80 (1H, d, *J* = 2.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 16.1, 22.8, 24.5, 25.4, 25.9, 29.8, 37.6, 38.2, 62.4, 63.4, 136.6, 147.9, 199.1; HRMS (ESI–TOF) calcd for $C_{14}H_{21}O_2$ ($[M+H]^+$) 221.1542, found 221.1542.

Data for **24**

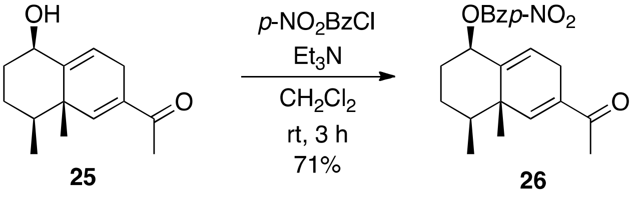
[α]$_D^{16}$ –155.3 (*c* = 1.05, $CHCl_3$); IR (neat) 2938, 2880, 1668, 1631, 1469, 1440, 1377, 1352, 1269, 1250, 1232, 1003, 962, 901 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (3H, d, *J* = 6.9 Hz), 1.09 (3H, s), 1.23–1.43 (3H, m), 1.88–2.09 (1H, m), 2.21 (1H, ddd, *J* = 13.3, 11.9, 6.9 Hz), 2.31–2.41 (4H, m, including 3H, s, at δ 2.31), 2.56 (1H, dd, *J* = 17.9, 6.4 Hz), 3.11 (1H, d, *J* = 3.2 Hz), 6.90 (1H, d, *J* = 2.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 18.1, 21,1, 21.8, 24.3, 25.3, 26.1, 29.7, 37.7, 60.4, 64.4, 137.6, 145.0, 199.4; HRMS (ESI–TOF) calcd for $C_{14}H_{20}NaO_2$ ([M+Na]$^+$) 243.1361, found 243.1354.

1-((5*R*,8*S*,8a*S*)-5-Hydroxy-8,8a-dimethyl-3,5,6,7,8,8a-hexahydronaphthalen-2-yl)ethan-1-one (**25**).



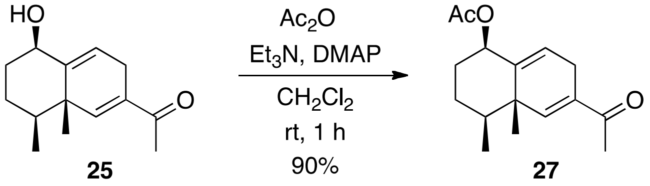
To a stirred solution of **23** (31.0 mg, 0.141 mmol) in *s*-BuOH (0.7 mL) was added *p*-toluenesulfonic acid monohydrate (26.8 mg, 0.141 mmol) ar room temperature, and the mixture was stirred for 4 h at the same remperature. The reaction was quenched with sat. NH_4Cl aqueous solution, and the mixture was extracted with AcOEt (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 5:1) to afford **25** (19.1 mg, 62%) as colorless needles. [α]$_D^{27}$ +29.4 (*c* = 0.96, $CHCl_3$); Mp 74–75 ºC (from hexane-AcOEt); IR (KBr) 3387, 2959, 2931, 2865, 1666, 1634, 1421, 1379, 1355, 1261, 1110, 1054, 1007, 991, 957, 930, 914 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (3H, d, *J* = 6.9 Hz), 1.25 (3H, s), 1.39–1.45 (1H, m), 1.54–1.65 (3H, m), 1.85–1.97 (2H, m), 2.34 (3H, s), 2.79 (1H, A part of ABXX', *J* = 22.9, 2.7, 1.9 Hz), 2.91 (1H, B part of ABXX', *J* = 22.9, 4.6, 0.0 Hz), 4.35 (1H, dd, *J* = 2.8, 2.7 Hz), 5.74 (1H, dd, *J* = 4.1, 2.7 Hz), 6.81 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 21.4, 24.8, 25.2, 25.5, 33.4, 39.6, 40.2, 74.5, 122.5, 133.7, 141.8, 145.9, 199.3; HRMS (ESI–TOF) calcd for $C_{14}H_{21}O_2$ ([M+H]$^+$) 221.1542, found 221.1534.

(1*R*,4*S*,4a*S*)-6-Acetyl-4,4a-dimethyl-1,2,3,4,4a,7-hexahydronaphthalen-1-yl 4-nitrobenzoate (**70**).



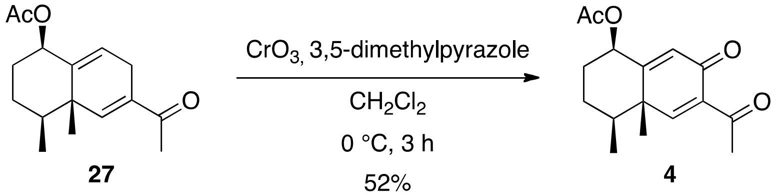
To a stirred solution of **25** (15.7 mg, 0.0713 mmol) in CH_2Cl_2 (0.7 mL) was added triethylamine (49.7 μL, 36.1 mg, 0.357 mmol), 4-dimethylaminopyridine (0.9 mg, 7.13 μmol), and 4-nitrobenzoyl chloride (26.5 mg, 0.143 mmol) in 0 °C, and the mixture was stirred for 3 h at room temperature. The reaction was quenched with sat. NH_4Cl aqueous solution, and the mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 3:1) to afford **26** (18.7 mg, 71%) as colorless needles. $[\alpha]_D^{26}$ –26.5 (*c* = 0.97, $CHCl_3$); Mp 156–158 °C (from hexane); IR (KBr) 2962, 2932, 2867, 1720, 1667, 1635, 1607, 1527, 1343, 1272, 1097, 1014, 1000, 955, 874, 861, 718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (3H, d, *J* = 6.4 Hz), 1.22 (3H, s), 1.55–1.64 (1H, m), 1.67–1.81 (2H, m), 1.89 (1H, dddd, *J* = 13.2, 12.3, 12.3, 2.7 Hz), 2.09–2.15 (1H, m), 2.34 (3H, s), 2.85 (1H, A part of ABXX’, *J* = 23.3, 2.3, 2.3 Hz), 2.97 (1H, B part of ABXX’, *J* = 23.3, 4.1, 0.0 Hz), 5.65–5.68 (1H, m), 6.00–6.03 (1H, m), 6.82 (1H, s), 8.18 (2H, d, *J* = 8.2 Hz), 8.29 (2H, d, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 20.9, 25.0, 25.2, 26.1, 31.4, 39.4, 39.9, 78.0, 123.6 (2C), 126.6, 130.5 (2C), 133.7, 136.2, 136.7, 144.8, 150.4, 163.8, 198.9; HRMS (ESI–TOF) calcd for $C_{21}H_{23}NNaO_5$ ($[M+Na]^+$) 392.1474, found 392.1468.

(1*R*,4*S*,4a*S*)-6-Acetyl-4,4a-dimethyl-1,2,3,4,4a,7-hexahydronaphthalen-1-yl acetate (**27**).



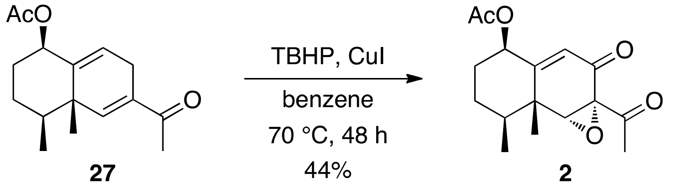
To a stirred solution of **25** (196 mg, 0.890 mmol) in CH_2Cl_2 (9 mL) was added triethylamine (0.620 □L, 450 mg, 4.45 mmol), 4-dimethylaminopyridine (10.9 mg, 89.0 μmol), and acetic anhydrate (0.168 mL, 182 mg, 1.78 mmol) in 0 °C, and the mixture was stirred for 1 h at room temperature. The reaction was quenched with saturated NH_4Cl aqueous solution, and the mixture was extracted with $CHCl_3$ (3 × 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 3:1) to afford **27** (210 mg, 90%) as colorless needles. $[\alpha]_D^{30}$ –29.8 (*c* = 0.98, $CHCl_3$); Mp 60–62 °C (from hexane); IR (KBr) 2959, 2937, 2866, 1733, 1669, 1635, 1435, 1369, 1244, 1218, 1205, 1104, 1017, 1002, 956, 871, 817 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (3H, d, *J* = 6.9 Hz), 1.15 (3H, s), 1.48 (1H, dddd, *J* = 13.2, 3.2, 3.2, 3.2 Hz), 1.56–1.68 (2H, m), 1.79 (1H, dddd, *J* = 13.3, 12.3, 12.3, 3.2 Hz), 1.94 (1H, dddd, *J* = 14.2, 3.2, 2.7, 2.7 Hz), 2.03 (3H, s), 2.33 (3H, s), 2.82 (1H, A part of ABXX’, *J* = 23.3, 2.8, 2.3 Hz), 2.91 (1H, B part of ABXX’, *J* = 23.3, 4.1, 0.0 Hz), 5.36–5.38 (1H, m), 5.88 (1H, dd, *J* = 4.1, 2.8 Hz), 6.79 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 20.5, 21.6, 24.9, 25.2, 26.1, 31.4, 39.5, 40.0, 75.9, 125.3, 133.6, 137.2, 145.3, 170.2, 199.2; HRMS (ESI–TOF) calcd for $C_{16}H_{22}NaO_3$ ($[M+H]^+$) 285.1467, found 285.1460.

(1*R*,4*S*,4a*S*)-6-Acetyl-4,4a-dimethyl-7-oxo-1,2,3,4,4a,7-hexahydronaphthalen-1-yl acetate (**4**).



To a stirred solution of chromium trioxide (387 mg, 3.87 mmol) in CH_2Cl_2 (0.7 mL) was added 3,5-dimethylpyrazole (372 mg, 3.87 mmol) at –20 °C, and the mixture was stirred for 20 min at –20 °C. To this mixture was added dropwise a solution of **27** (67.6 mg, 0.258 mmol) in CH_2Cl_2 (2 mL) at –20 °C, and the stirring was continued for 3 h at 0 °C. The reaction was quenched with solid $NaHCO_3$, and the mixture was filtered through a Celite pad. The filtrate was extracted with Et_2O (2 × 30 mL). The combined organic layers were washed with sat. $NaHCO_3$ aqueous solution, 1.0 M HCl aqueous solution, H_2O, and brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 4:1) to afford **4** (36.8 mg, 52%) as colorless crystals. $[\alpha]_D^{26}$ –33.3 (c = 0.50, $CHCl_3$); Mp 122–124 ºC (from hexane); IR (KBr) 2971, 2938, 2925, 2880, 1747, 1691, 1659, 1631, 1366, 1248, 1217, 1099, 1019, 962, 921, 875 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (3H, d, J = 6.4 Hz), 1.29 (3H, s), 1.54–1.65 (2H, m), 1.68 (1H, ddd, J = 14.2, 3.6, 3.6 Hz), 1.86 (1H, dddd, J = 13.2, 12.8, 12.8, 2.7 Hz), 2.06 (3H, s), 2.11 (1H, dddd, J = 14.2, 2.7, 2.7, 2.3 Hz), 2.56 (3H, s), 5.50 (1H, dd, J = 2.7, 2.7 Hz), 6.35 (1H, s), 7.66 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0, 17.8, 21.2, 25.4, 31.0, 31.9, 40.5, 43.8, 74.3, 129.3, 136.1, 159.4, 160.8, 169.7, 183.8, 198.6; HRMS (ESI–TOF) calcd for $C_{16}H_{20}NaO_4$ ($[M+Na]^+$) 299.1259, found 299.1258.

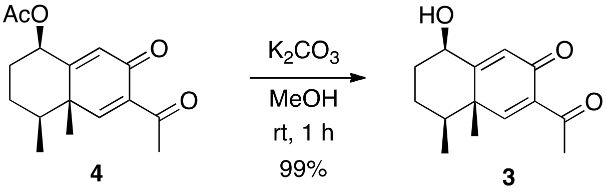
(1a*S*,4*R*,7*S*,7a*R*,7b*R*)-1a-Acetyl-7,7a-dimethyl-2-oxo-1a,2,4,5,6,7,7a,7b-octahydronaphtho[1,2-*b*]oxiren-4-yl acetate (**2**).



To a stirred solution of **27** (9.2 mg, 0.0351 mmol) in benzene (0.4 mL) was added copper iodide (2.0 mg, 0.0105 mmol) and *tert*-butyl hydroperoxide (5 M in decane, 49.1 μL, 0.246 mmol) at room temperature, and the mixture was stirred for 48 h at 70 °C. The reaction was quenched with sat. $Na_2S_2O_3$ aqueous solution, and the mixture was extracted with AcOEt (2 × 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 3:1) to afford **2** (4.5 mg, 44%) as colorless crystals. $[\alpha]_D^{25}$ +52.1 (c = 0.40, $CHCl_3$); Mp 82–84 ºC (from hexane); IR (KBr) 2963, 2932, 2879, 1733, 1677, 1629, 1456, 1369, 1240, 1107, 1019, 960, 882, 871 cm^{-1}; ^{1}H NMR (400

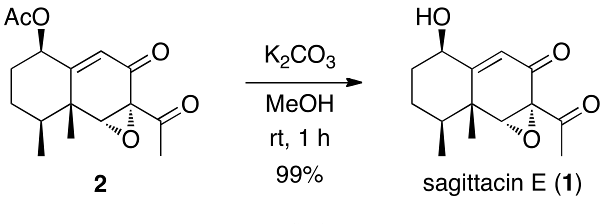
MHz, $CDCl_3$) δ 1.14 (3H, d, *J* = 6.4 Hz), 1.29 (3H, s), 1.59–1.66 (1H, m), 1.70 (1H, ddd, *J* = 13.7, 3.2, 3.2 Hz), 1.79 (1H, dddd, *J* = 13.3, 13.3, 13.3, 2.7 Hz), 1.90–1.99 (1H, m), 2.01 (1H, dddd, *J* = 14.2, 2.7, 2.7, 2.7 Hz), 2.05 (3H, s), 2.35 (3H, s), 3.50 (1H, s), 5.43 (1H, dd, *J* = 2.7 Hz), 6.06 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 18.5, 21.3, 25.0, 28.2, 30.8, 37.4, 40.7, 63.4, 66.5, 74.3, 125.8, 157.8, 169.5, 190.9, 200.5; HRMS (ESI–TOF) calcd for $C_{16}H_{20}NaO_5$ ($[M+Na]^+$) 315.1208, found 315.1202.

(4a*S*,5*S*,8*R*)-3-Acetyl-8-hydroxy-4a,5-dimethyl-5,6,7,8-tetrahydronaphthalen-2(4a*H*)-one (**3**)

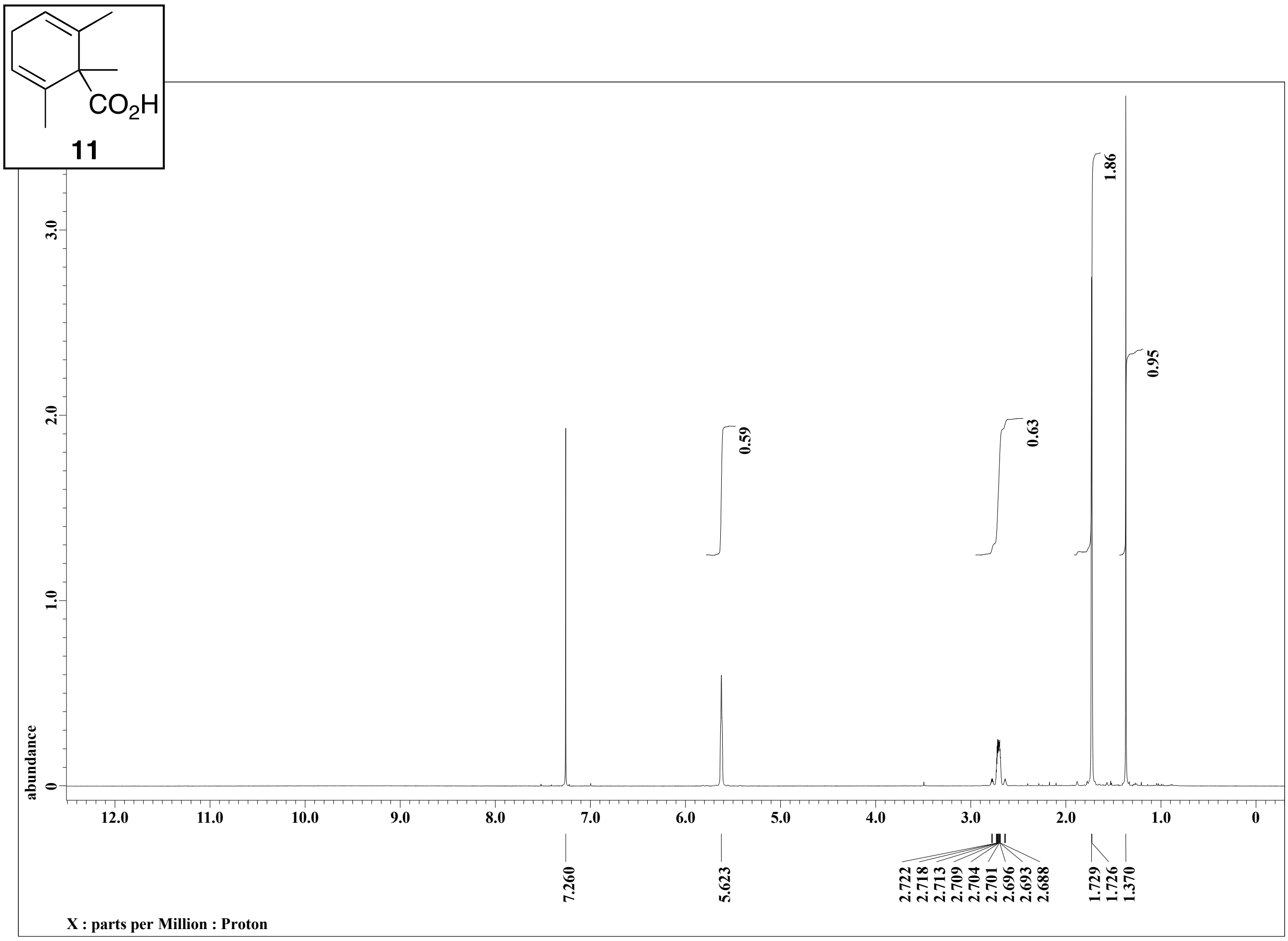


To a stirred solution of **4** (36.8 mg, 0.133 mmol) in MeOH (1.3 mL) was added K_2CO_3 (64.2 mg, 0.466 mmol) at 0 °C, and the mixture was stirred for 1 h at room temperature. The reaction was quenched with sat. NH_4Cl aqueous solution, and the mixture was extracted with $CHCl_3$ (3 × 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 1:1) to afford **3** (30.6 mg, 99%) as colorless crystals. $[\alpha]_D^{23}$ –43.3 (*c* = 1.01, $CHCl_3$); Mp 95–97 ºC (from hexane); IR (KBr) 3415, 2961, 2928, 2872, 1695, 1659, 1624, 1395, 1360, 1262, 1216, 1102, 1021, 924, 889 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (3H, d, *J* = 6.9 Hz), 1.39 (3H, s), 1.47–1.69 (4H, m), 1.98 (1H, dddd, *J* = 13.7, 13.7, 12.3, 3.7 Hz), 2.08 (1H, dddd, *J* = 14.2, 3.2, 2.7, 2.7 Hz), 2.56 (3H, s), 4.56 (1H, dd, *J* = 2.7, 2.7 Hz), 6.19 (1H, s), 7.68 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0, 18.6, 24.8, 31.0, 34.3, 40.8, 44.1, 73.4, 126.9, 135.9, 161.6, 164.7, 184.7, 198.7; HRMS (ESI–TOF) calcd for $C_{14}H_{18}NaO_3$ ($[M+Na]^+$) 257.1154, found 257.1149.

(1a*S*,4*R*,7*S*,7a*R*,7b*R*)-1a-Acetyl-4-hydroxy-7,7a-dimethyl-4,5,6,7,7a,7b-hexahydronaphtho[1,2-*b*]oxiren-2(1a*H*)-one [Sagittacin E] (**1**).



To a stirred solution of **2** (26.3 mg, 0.0900 mmol) in MeOH (0.9 mL) was added K_2CO_3 (31.0 mg, 0.225 mmol) at 0 °C, and the mixture was stirred for 1 h at room temperature. The reaction was quenched with sat. NH_4Cl aqueous solution, and the mixture was extracted with $CHCl_3$ (3 × 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 2:1) to afford **1** (22.3 mg, 99%) as colorless crystals. $[\alpha]_D^{28}$ +104.5 (*c* = 0.50, MeOH); Mp 82–84 ºC (from hexane–$CHCl_3$); IR (KBr) 3437, 2959, 2928, 2857, 1723, 1673, 1465, 1420, 1382, 1360, 1261, 1219, 1109, 1048, 1017, 886 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.13 (3H, d, *J* = 5.9 Hz), 1.39 (3H, s), 1.45–1.51 (1H, m), 1.61–1.72 (1H, m), 1.84–1.94 (2H, m), 1.95–2.02 (1H, m), 2.34 (3H, m), 3.49 (1H, s), 4.38–4.41 (1H, m), 5.90 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 19.4, 24.4, 28.1, 33.0, 37.8, 40.9, 63.6, 66.7, 73.6, 123.2, 163.5, 191.3, 200.7; HRMS (ESI–TOF) calcd for $C_{14}H_{18}NaO_4$ ($[M+Na]^+$) 273.1103, found 273.1098.


11
CO2H
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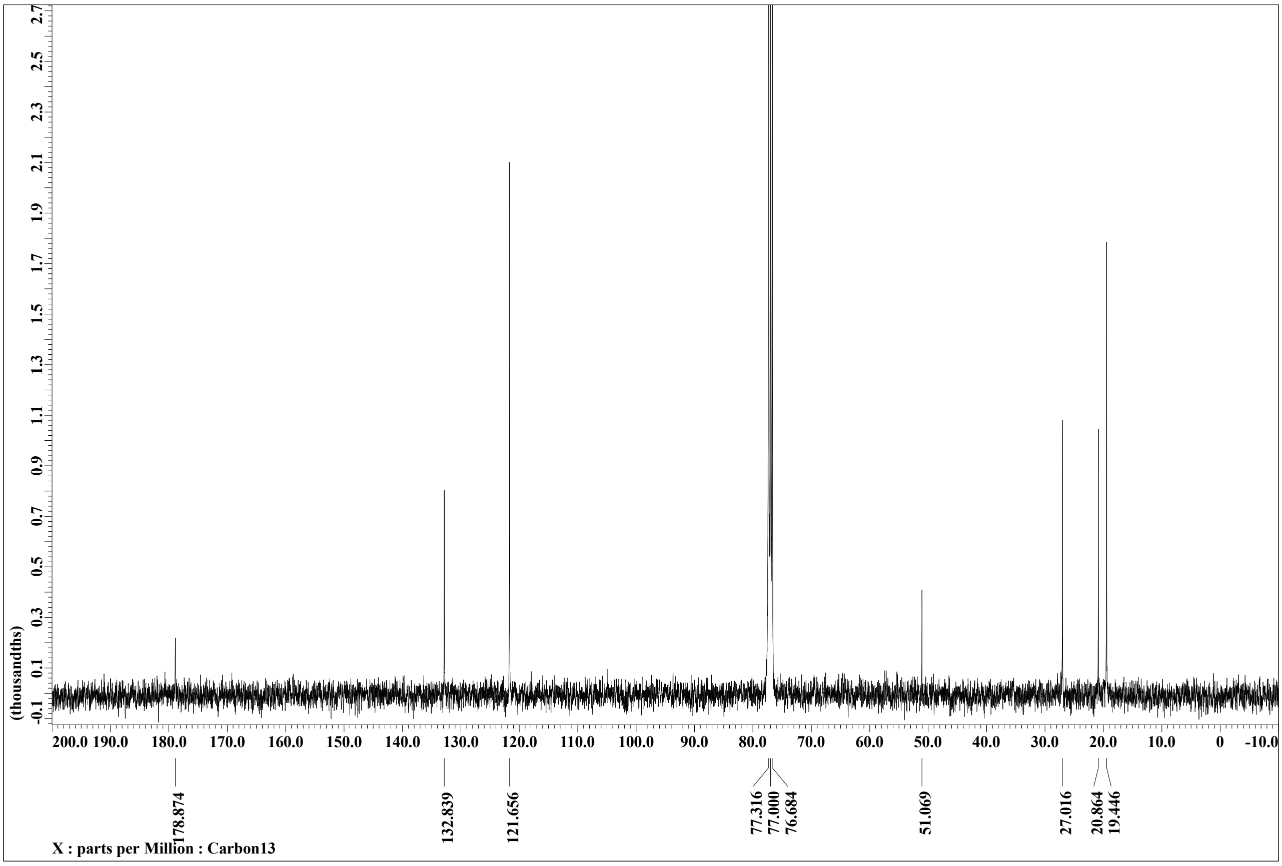
0.95
0.59
0.63
3.0
2.0
1.0
0
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
5.623
2.722
2.718
2.713
2.709
2.704
2.701
2.696
2.693
2.688
1.729
1.726
1.370
X : parts per Million : Proton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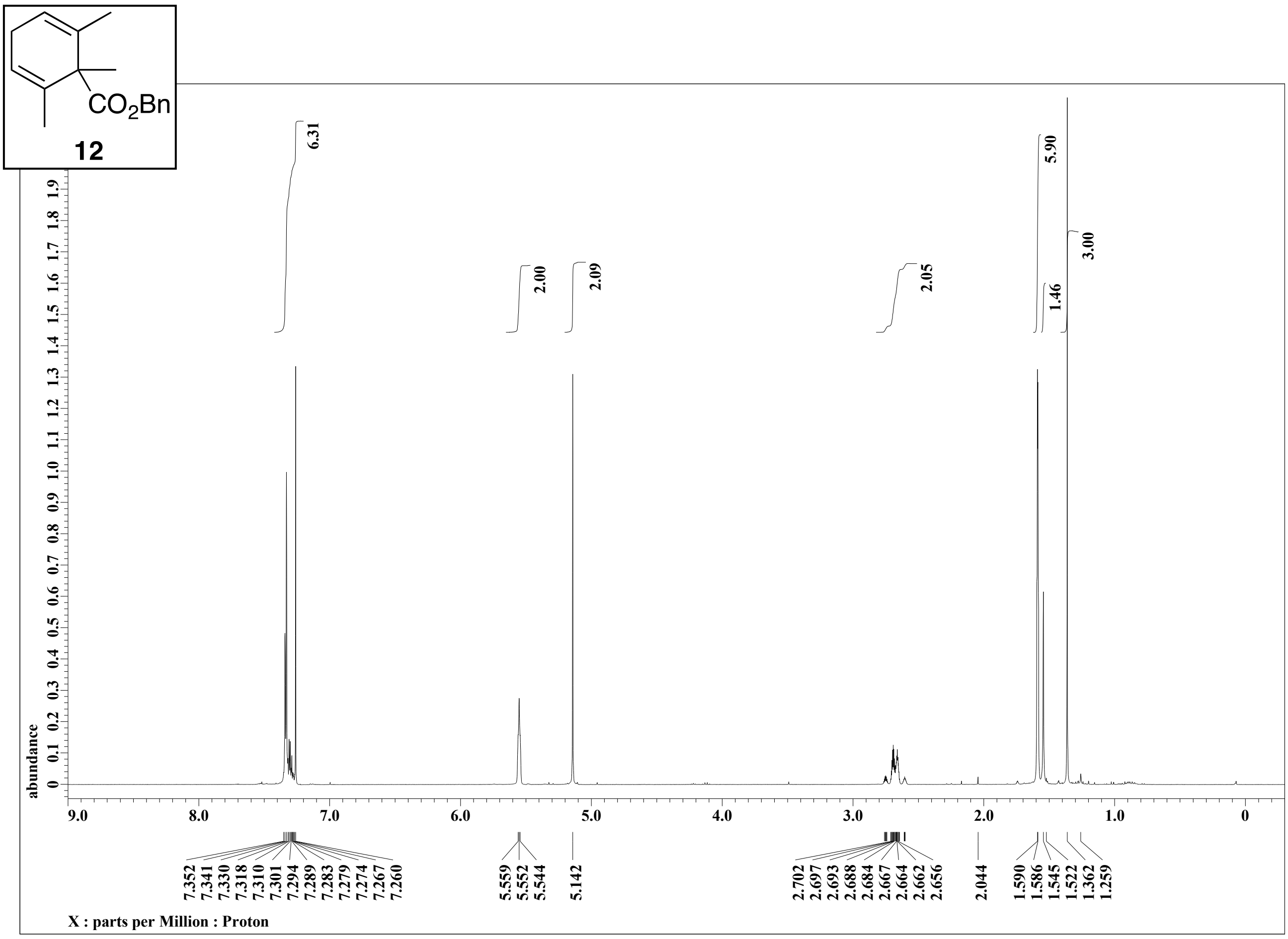
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
0.3
0.1
-0.1
(thousandths)
200.0 190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
178.874
132.839
121.656
77.316
77.000
76.684
51.069
27.016
20.864
19.446
X : parts per Million : Carbon13



12

CO$_2$Bn
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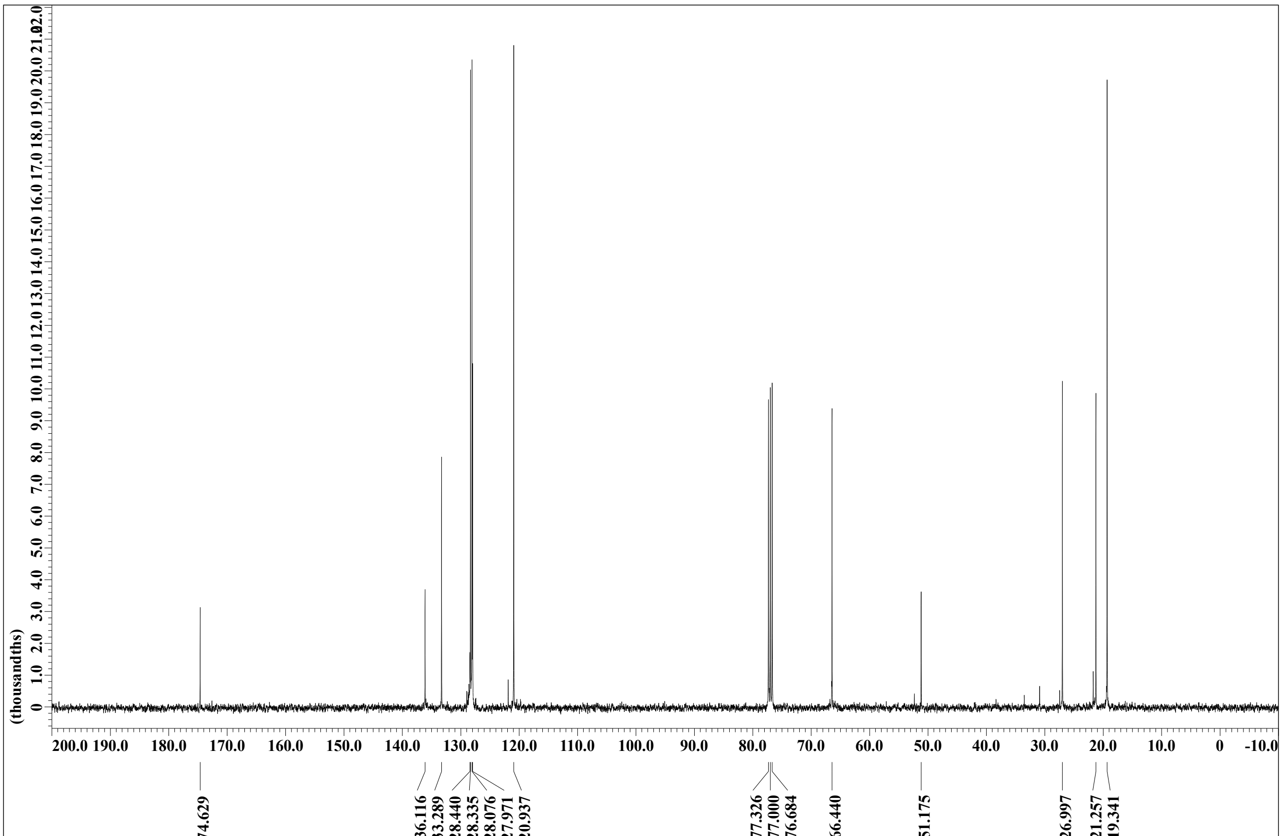
6.31
2.00
2.09
2.05
5.90
1.46
3.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.352 7.341 7.330 7.318 7.310 7.301 7.294 7.289 7.283 7.279 7.274 7.267 7.260
5.559 5.552 5.544
5.142
2.702 2.697 2.693 2.688 2.684 2.667 2.664 2.662 2.656
2.044
1.590 1.586 1.545 1.522 1.362 1.259
X : parts per Million : Proton



(thousandths)
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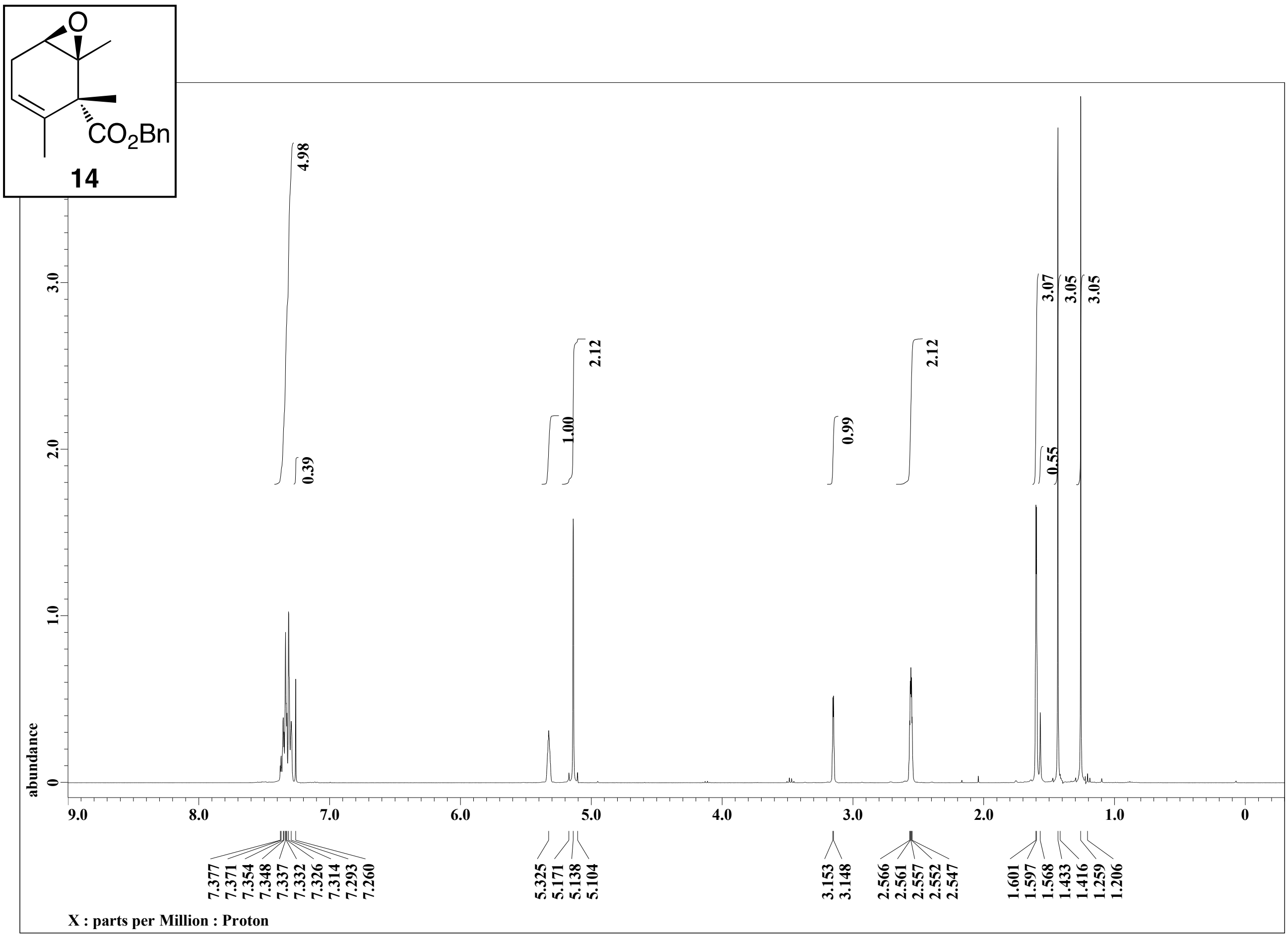
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
174.629
136.116 133.289 128.440 128.335 128.076 127.971 120.937
77.326 77.000 76.684
66.440
51.175
26.997
21.257 19.341
X : parts per Million : Carbon13


O
CO$_2$Bn
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1.00
2.12
0.99
2.12
3.07
0.55
3.05
3.05
abundance
0
1.0
2.0
3.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.377
7.371
7.354
7.348
7.337
7.332
7.326
7.314
7.293
7.260
5.325
5.171
5.138
5.104
3.153
3.148
2.566
2.561
2.557
2.552
2.547
1.601
1.597
1.568
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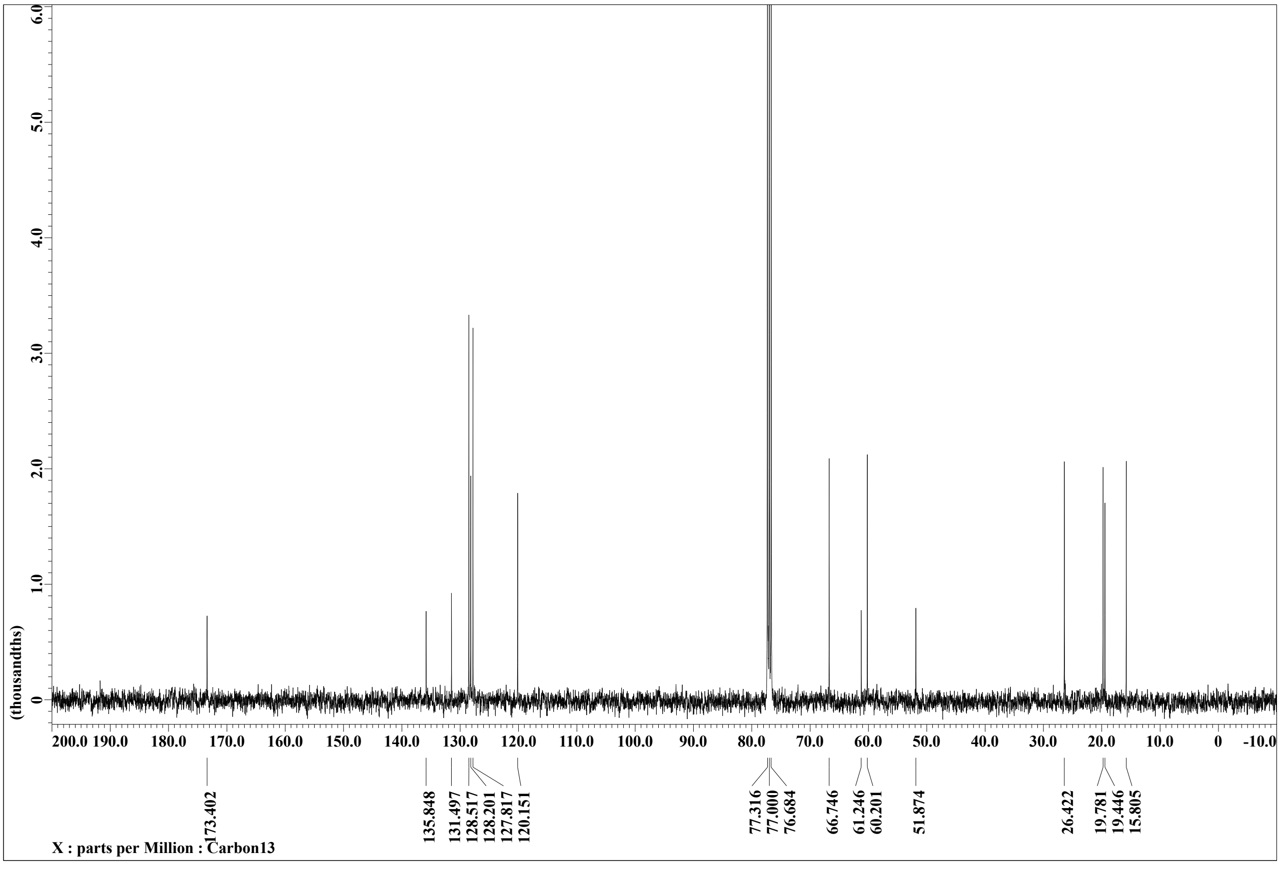
1.259
1.206
X : parts per Million : Proton

14


(thousandths)
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2.0
3.0
4.0
5.0
6.0
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 -10.0
173.402
135.848
131.497
128.517
128.201
127.817
120.151
77.316
77.000
76.684
66.746
61.246
60.201
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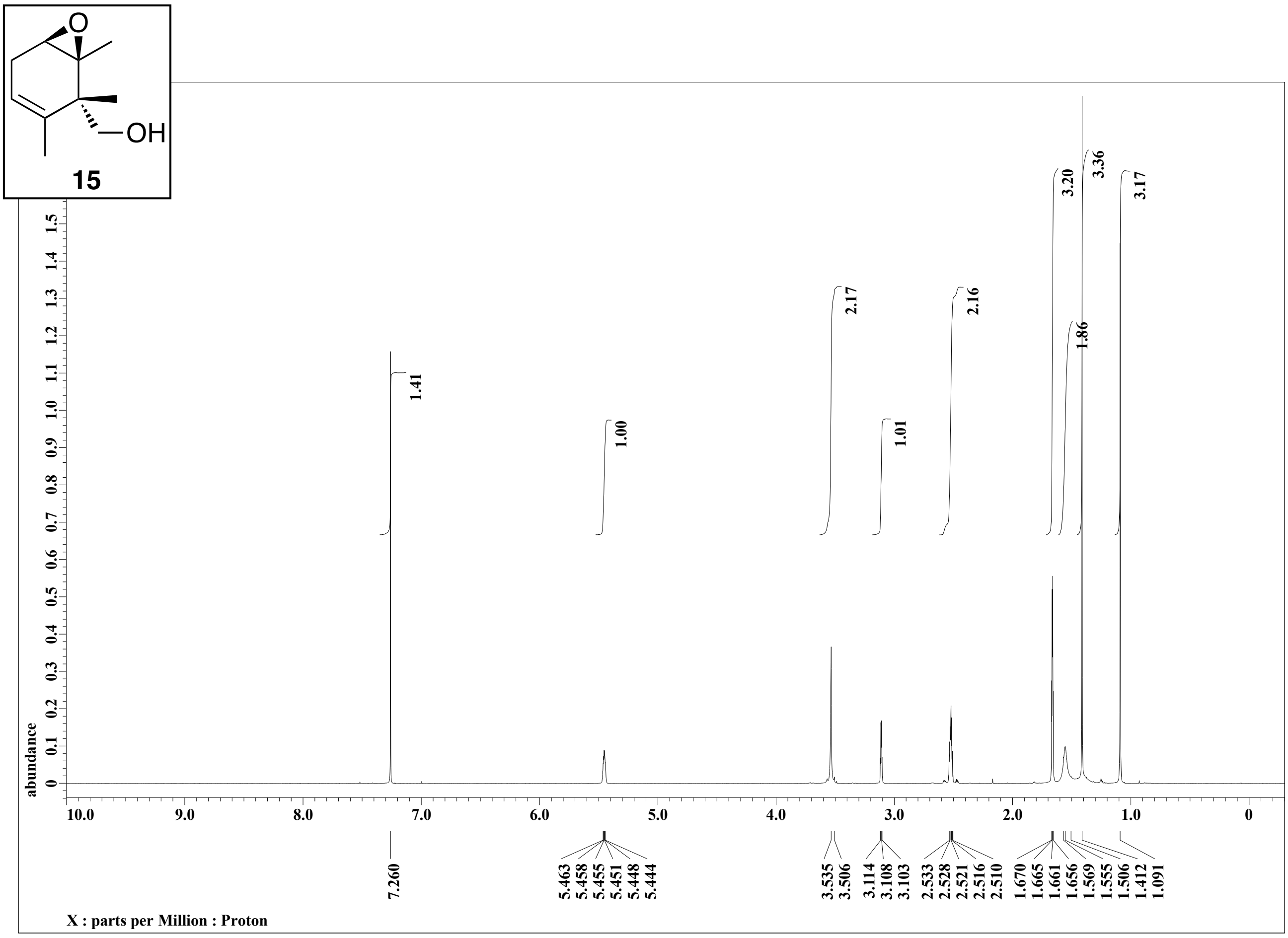
19.446
15.805
X : parts per Million : Carbon13


15
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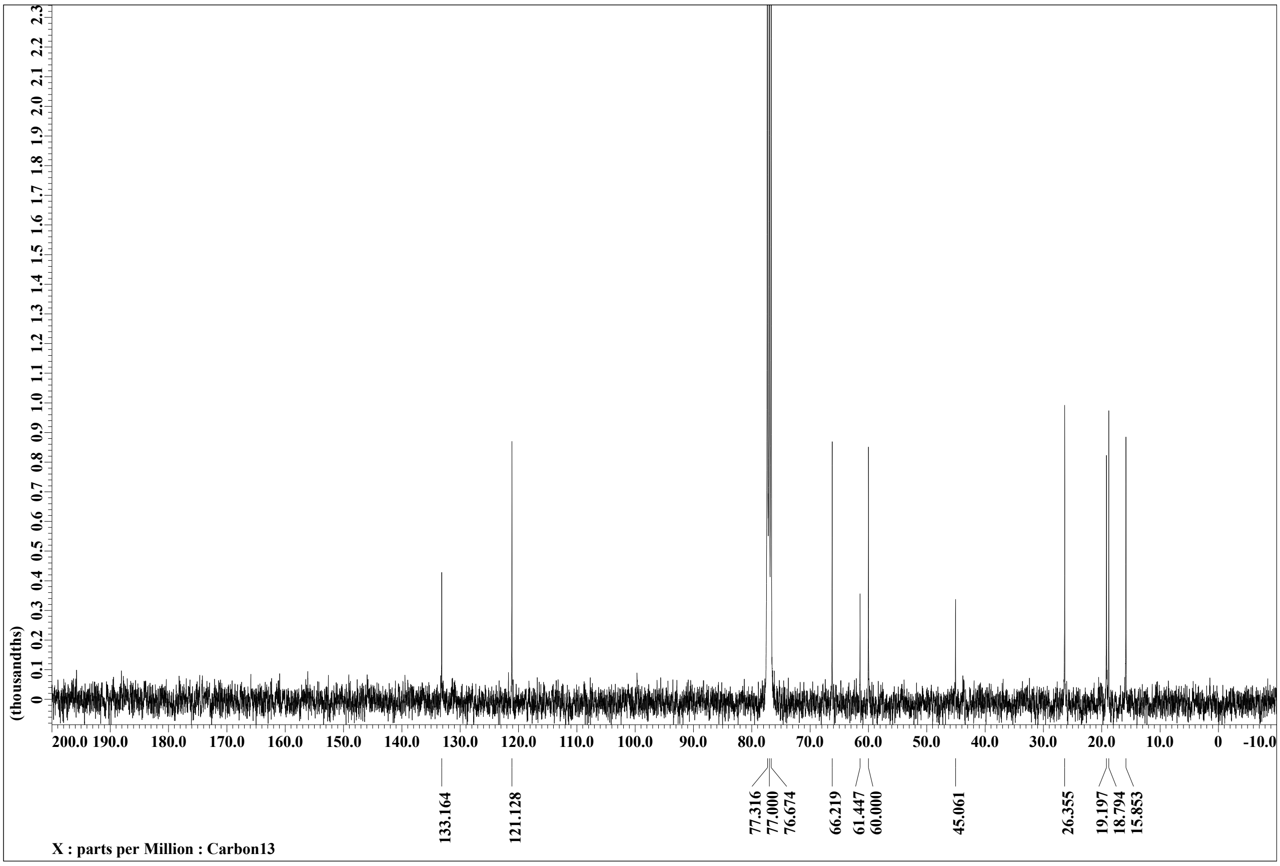
2.17
1.01
2.16
3.20
1.86
3.36
3.17
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.260
5.463
5.458
5.455
5.451
5.448
5.444
3.535
3.506
3.114
3.108
3.103
2.533
2.528
2.521
2.516
2.510
1.670
1.665
1.661
1.656
1.569
1.555
1.506
1.412
1.091
X : parts per Million : Proton


(thousandths)
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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 -10.0
133.164
121.128
77.316
77.000
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66.219
61.447
60.000
45.061
26.355
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18.794
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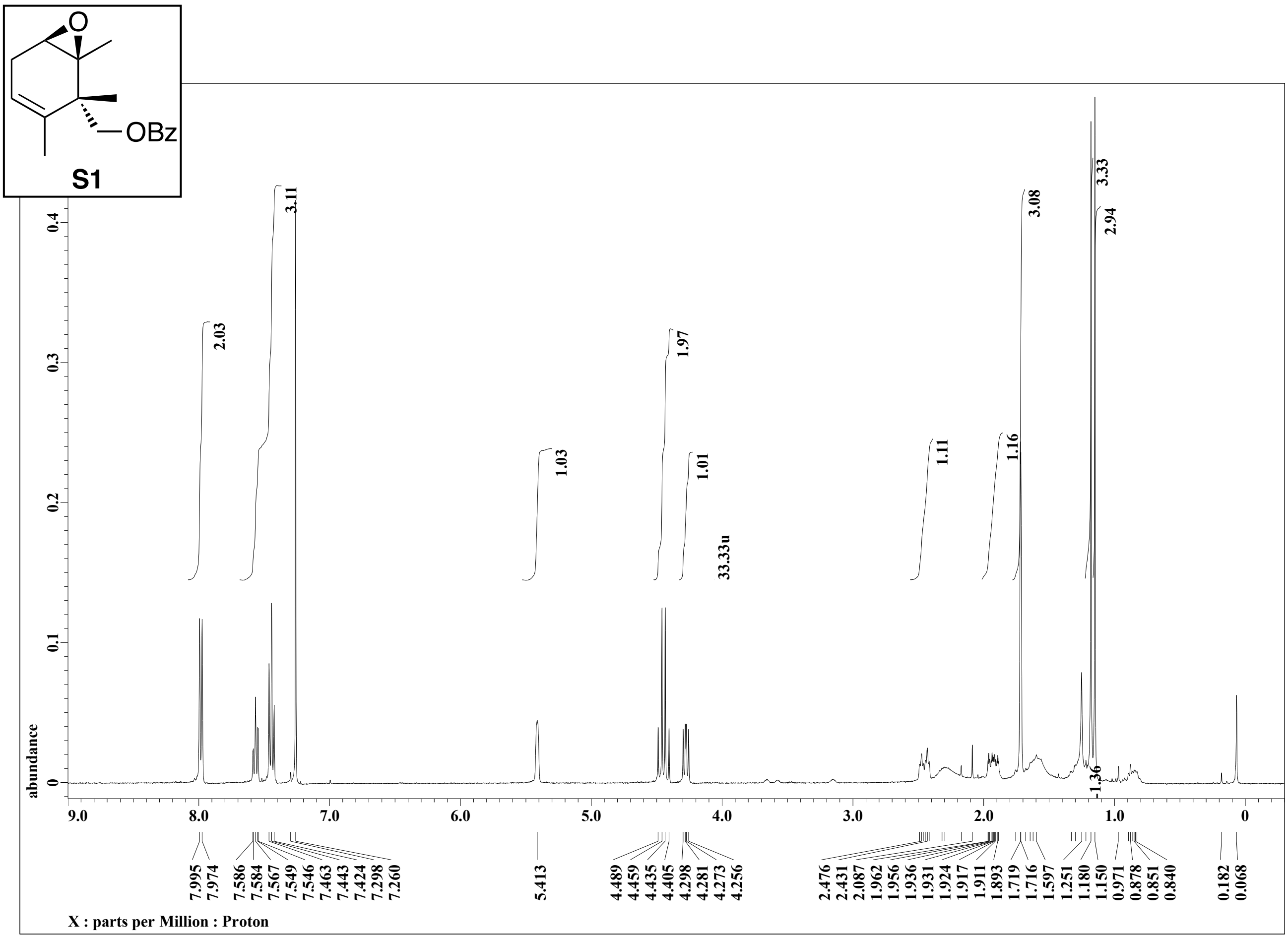
X : parts per Million : Carbon13


O
OBz
abundance
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0.3
0.4
2.03
3.11
1.03
1.97
1.01
33.33u
1.11
1.16
3.08
3.33
2.94
-1.36
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.995
7.974
7.586
7.584
7.567
7.549
7.546
7.463
7.443
7.424
7.298
7.260
5.413
4.489
4.459
4.435
4.405
4.298
4.281
4.273
4.256
2.476
2.431
2.087
1.962
1.956
1.936
1.931
1.924
1.917
1.911
1.893
1.719
1.716
1.597
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1.150
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0.851
0.840
0.182
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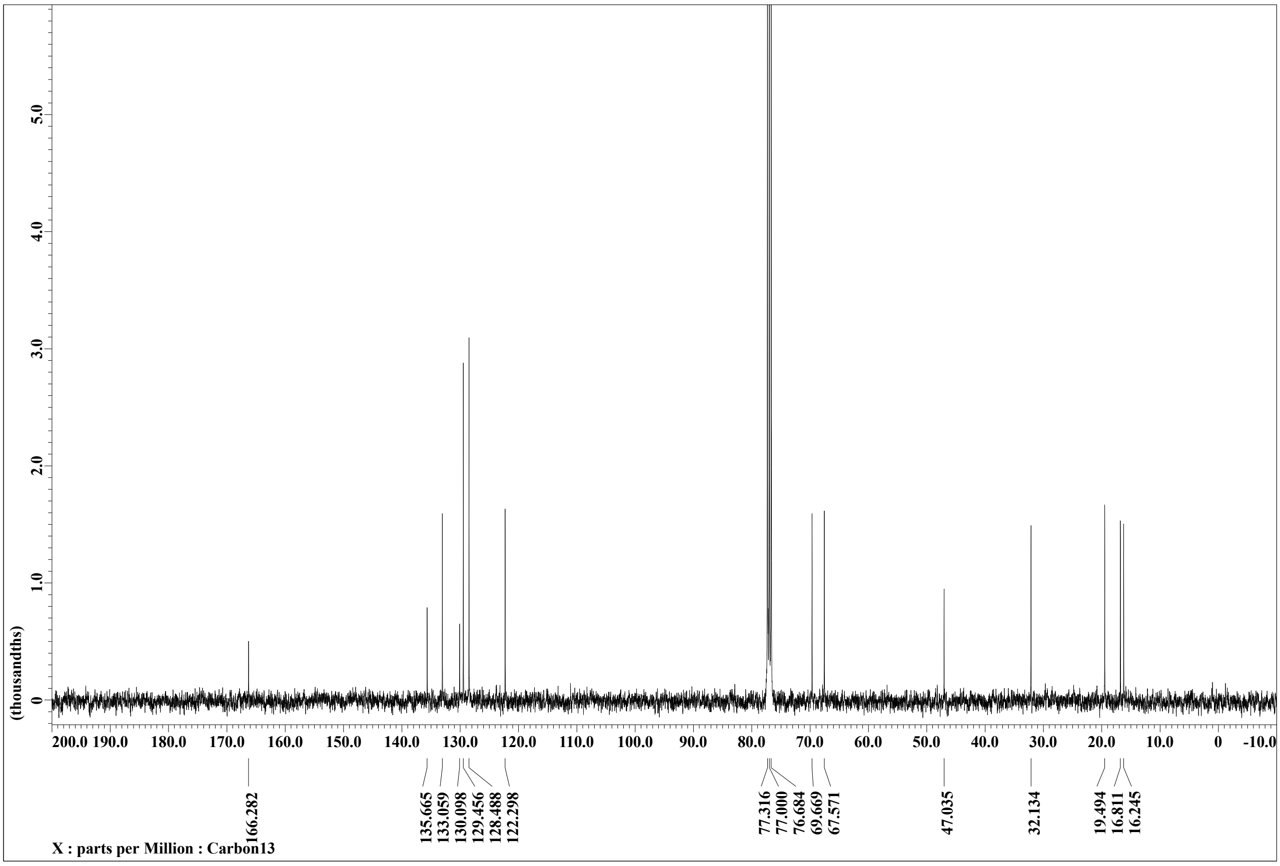
X : parts per Million : Proton

S1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5.0
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
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166.282
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133.059
130.098
129.456
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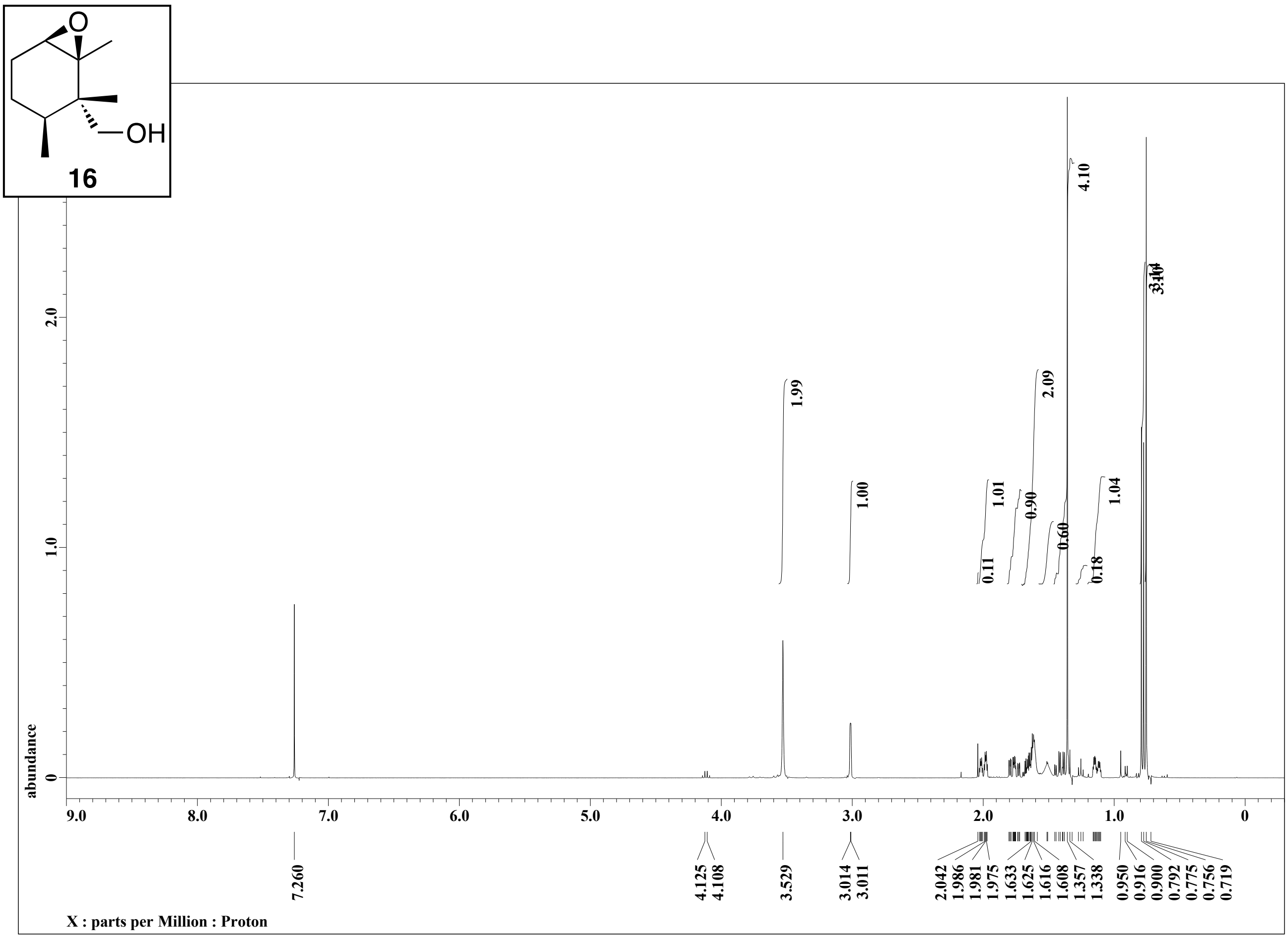

16

OH
abundance
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2.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.99
1.00
0.11
1.01
0.90
2.09
0.60
0.18
1.04
4.10
3.04
7.260
4.125
4.108
3.529
3.014
3.011
2.042
1.986
1.981
1.975
1.633
1.625
1.616
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0.756
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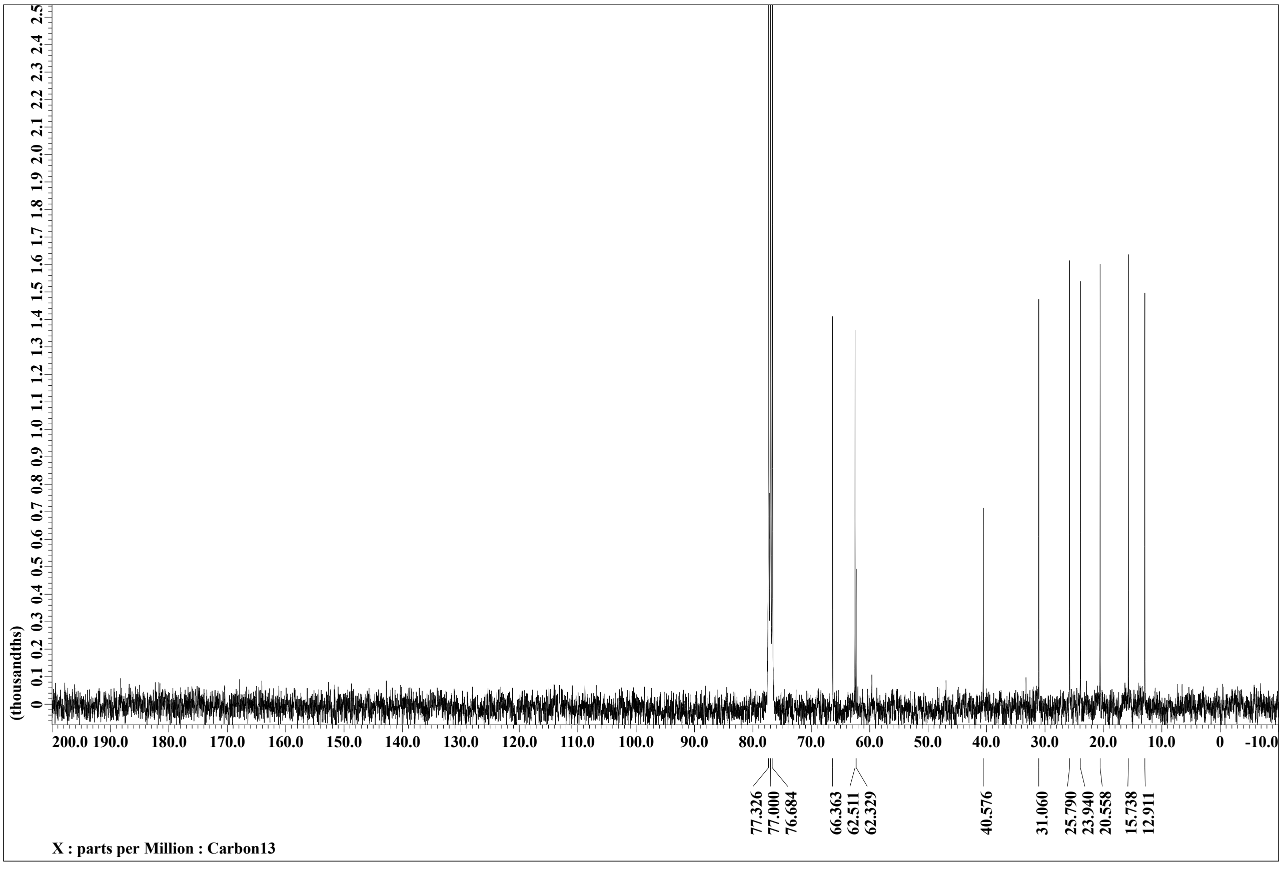
X : parts per Million : Proton



(thousandths)
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0.6
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0.8
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1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
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
-10.0
77.326
77.000
76.684
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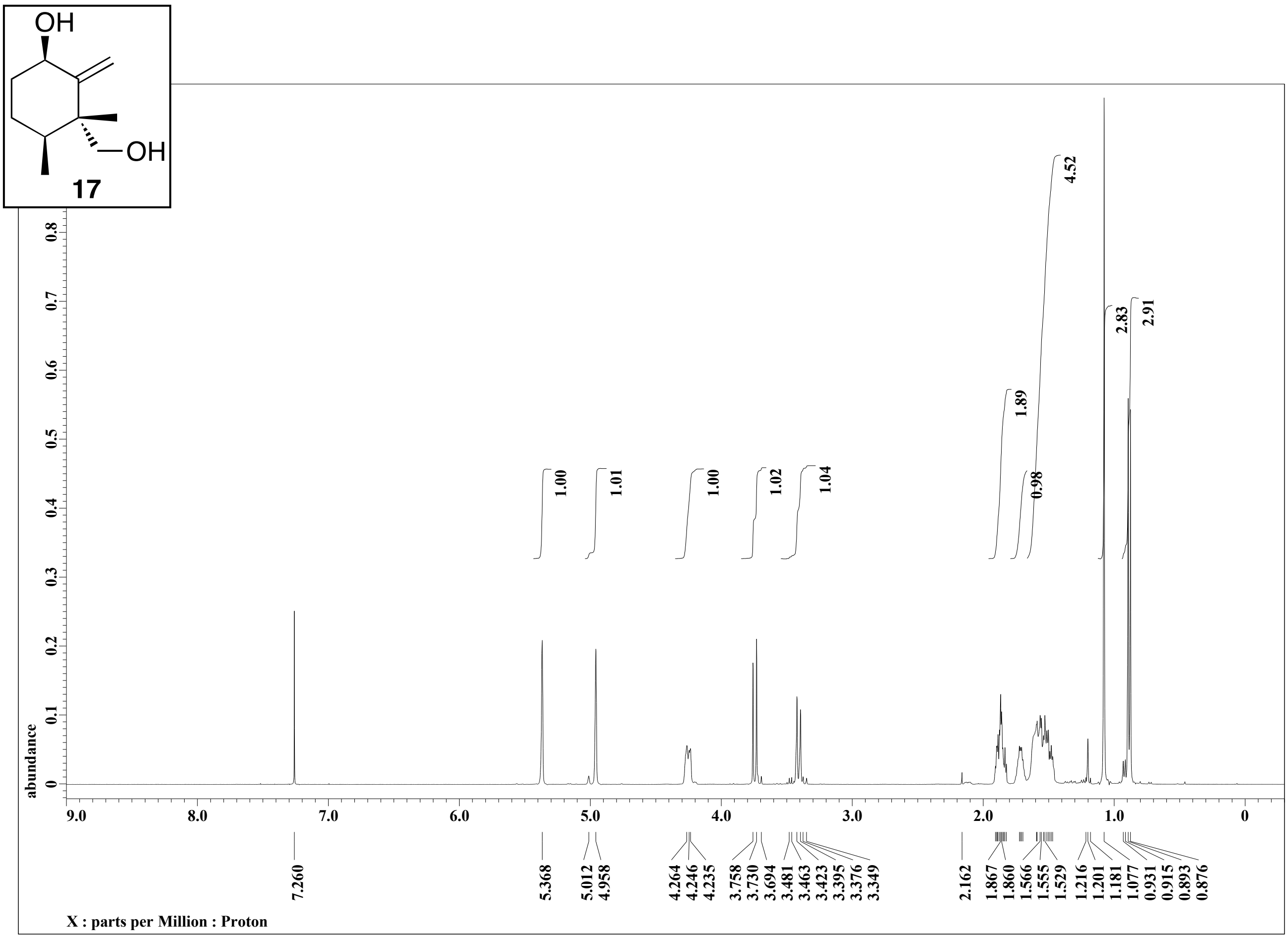
15.738
12.911
X : parts per Million : Carbon13


OH
OH
17
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1.01
1.00
1.02
1.04
1.89
0.98
4.52
2.83
2.91
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
5.368
5.012
4.958
4.264
4.246
4.235
3.758
3.730
3.694
3.481
3.463
3.423
3.395
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2.162
1.867
1.860
1.566
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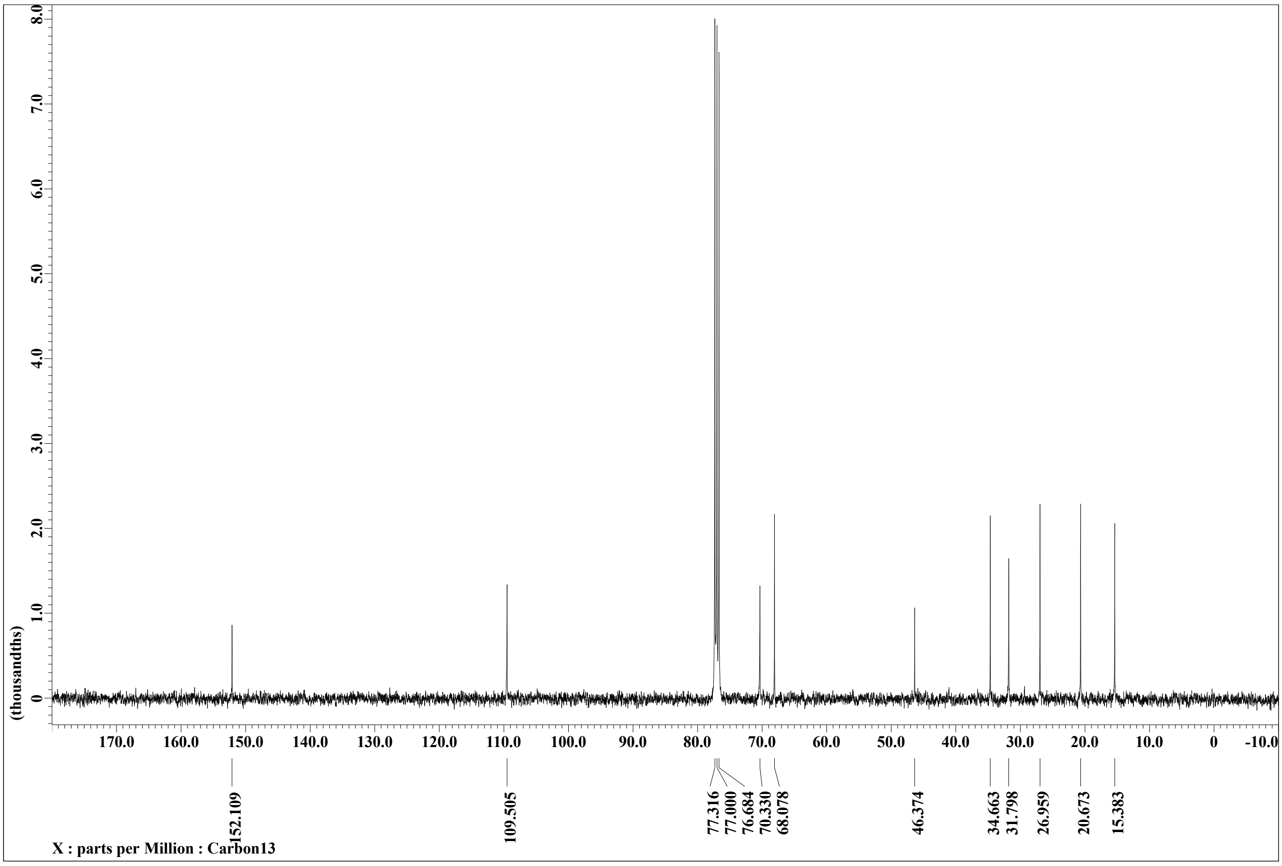
X : parts per Million : Proton


(thousandths)
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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
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152.109
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77.316
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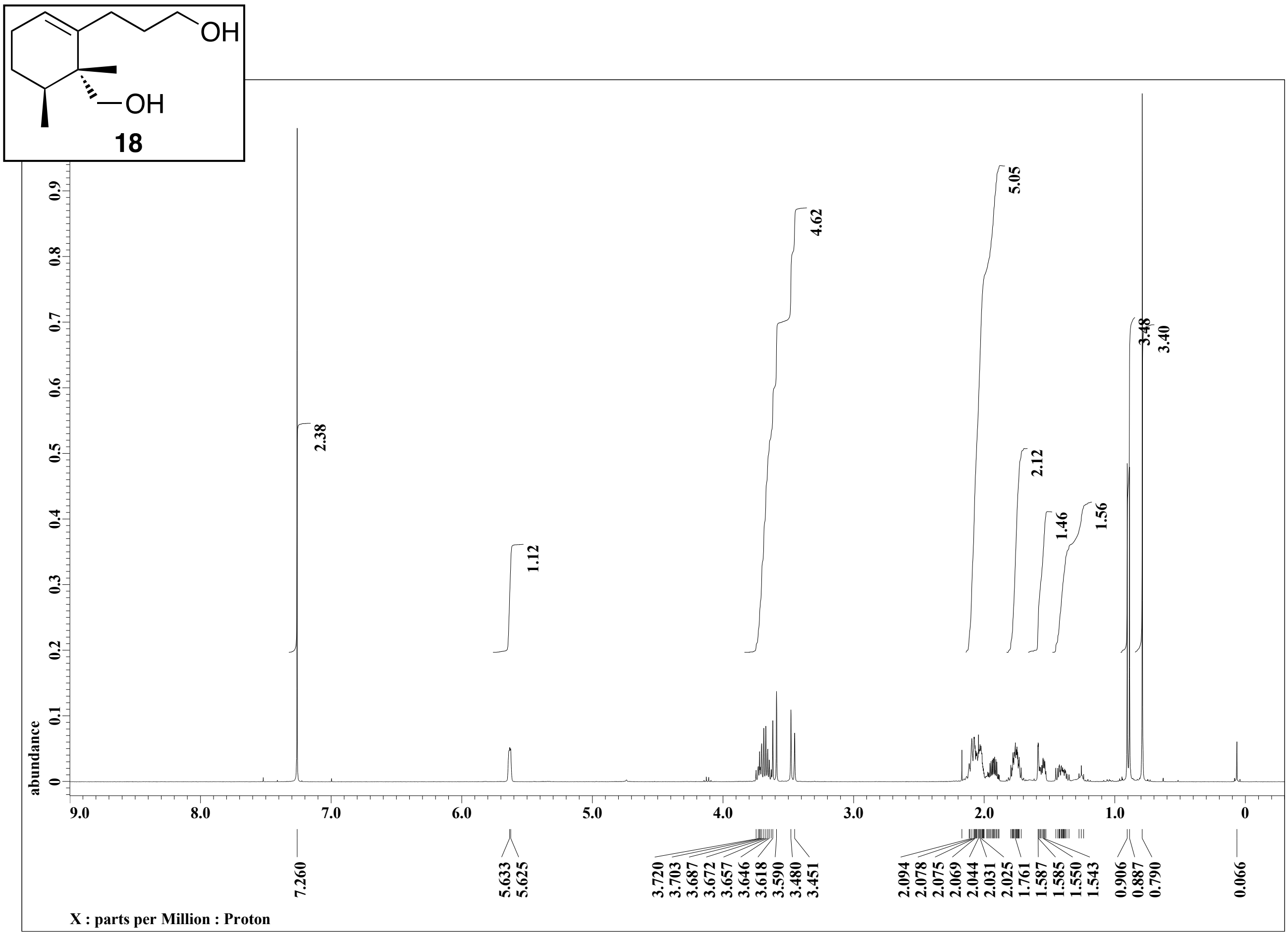
18

OH
OH
abundance
X : parts per Million : Proton
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2.38
1.12
4.62
5.05
2.12
1.46
1.56
3.48
3.40
7.260
5.633
5.625
3.720
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2.075
2.069
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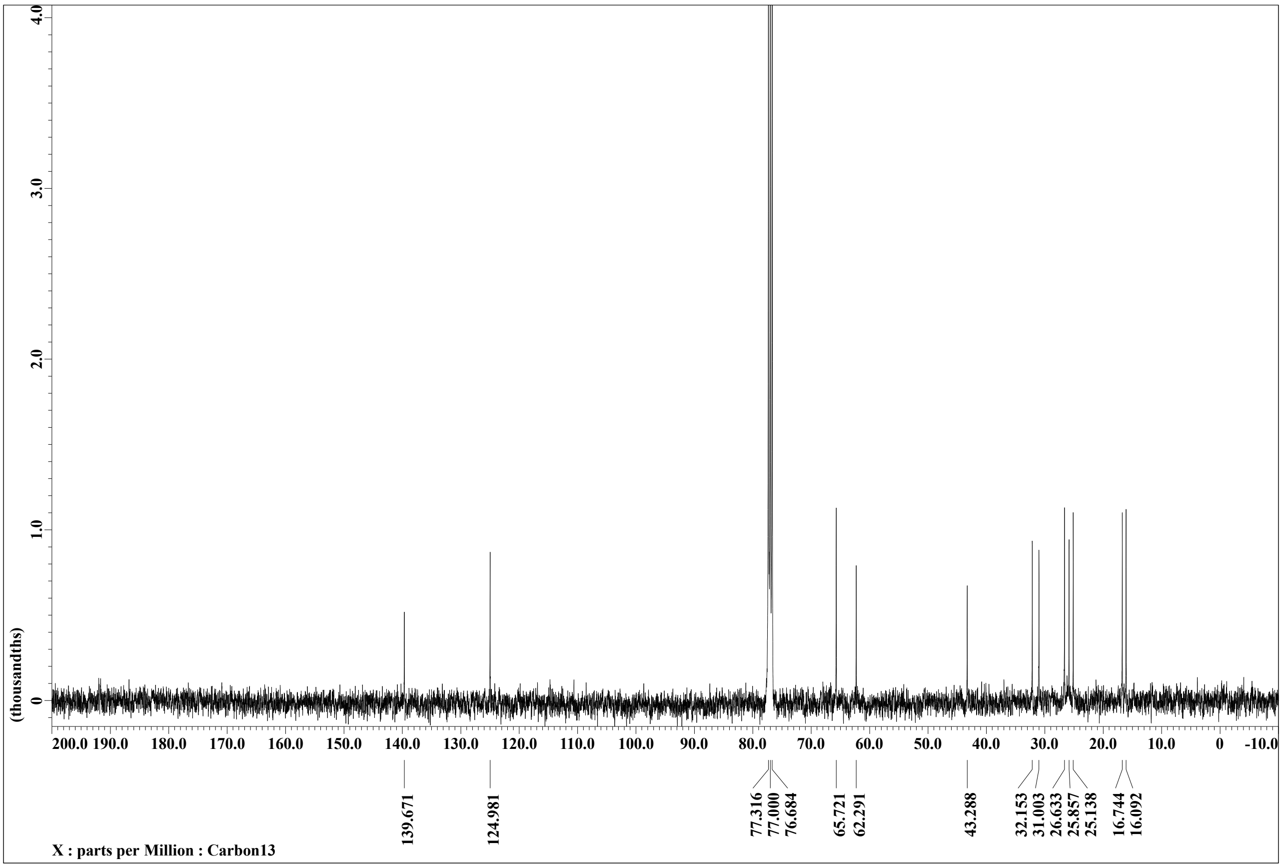
0.066



(thousandths)
X : parts per Million : Carbon13
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 -10.0
0 1.0 2.0 3.0 4.0
139.671
124.981
77.316
77.000
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43.288
32.153
31.003
26.633
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25.138
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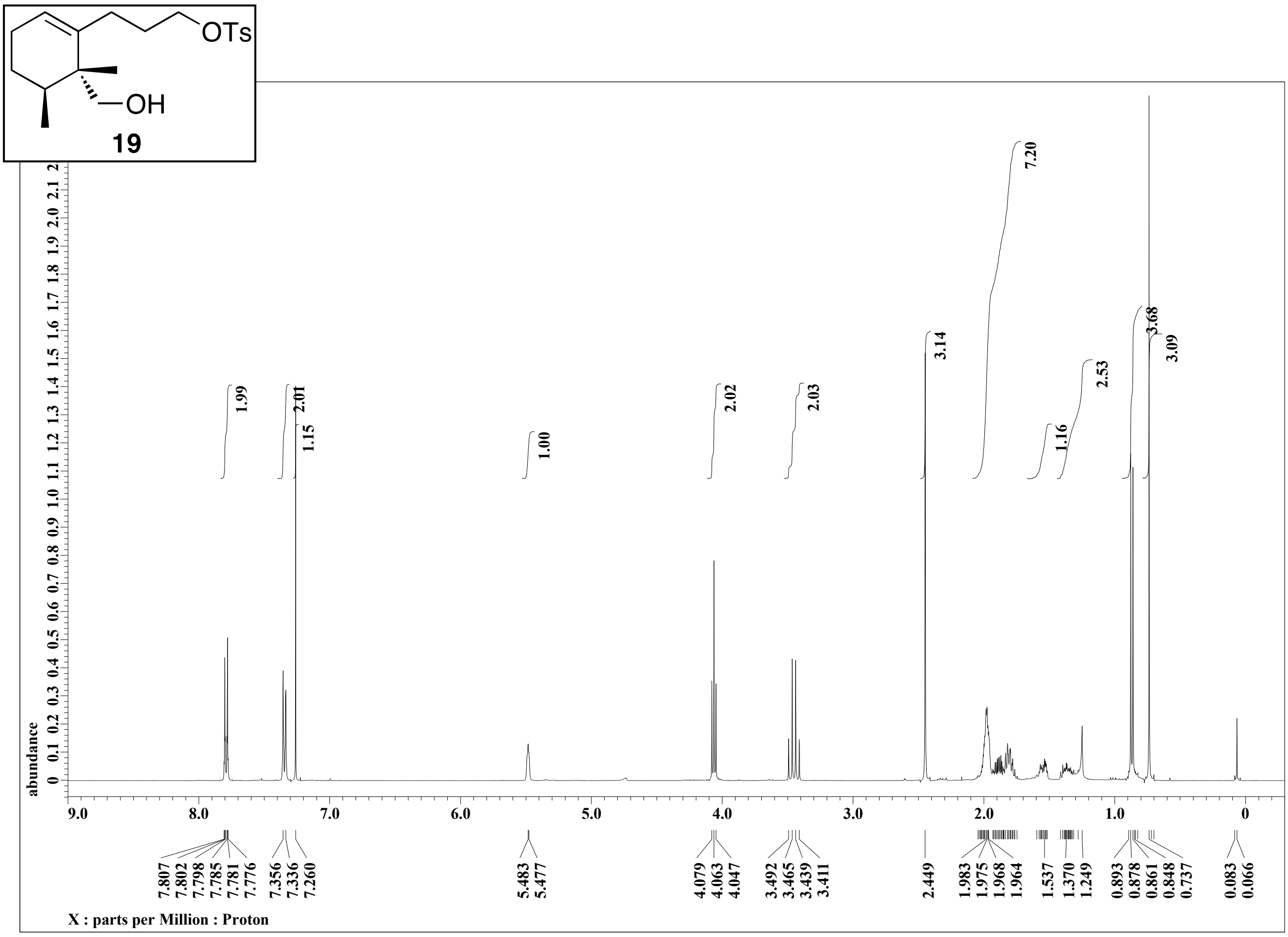
16.092


OTs
OH
abundance
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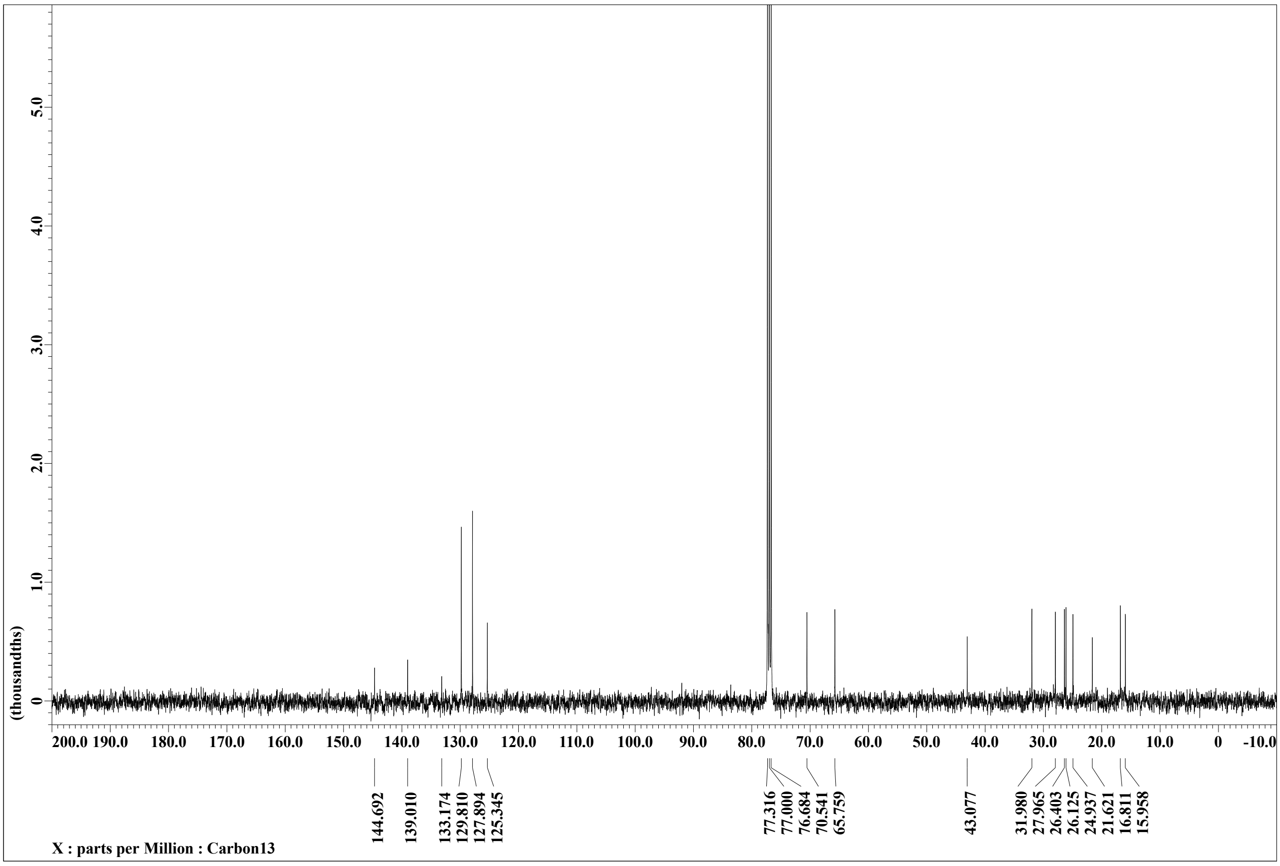
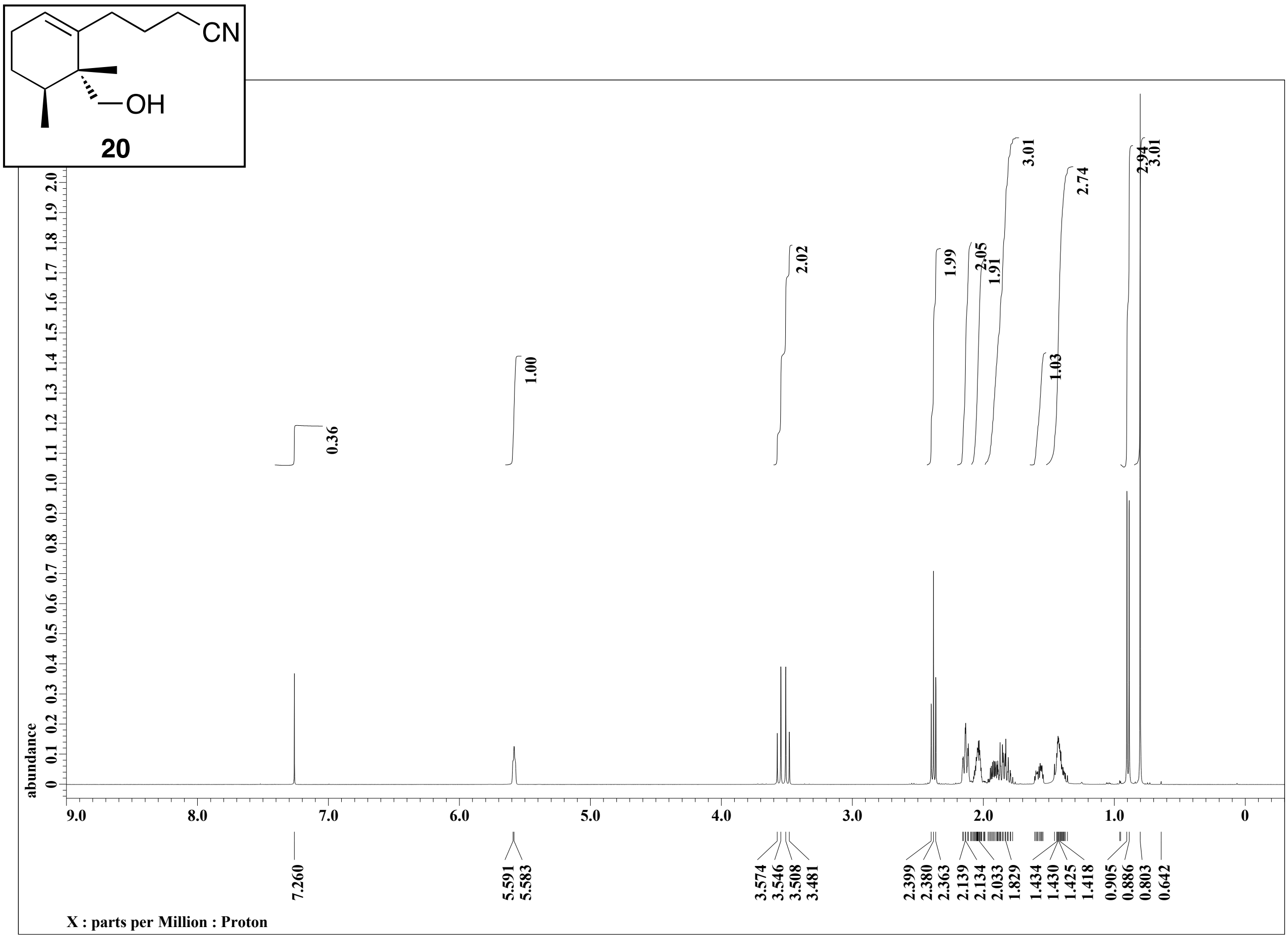
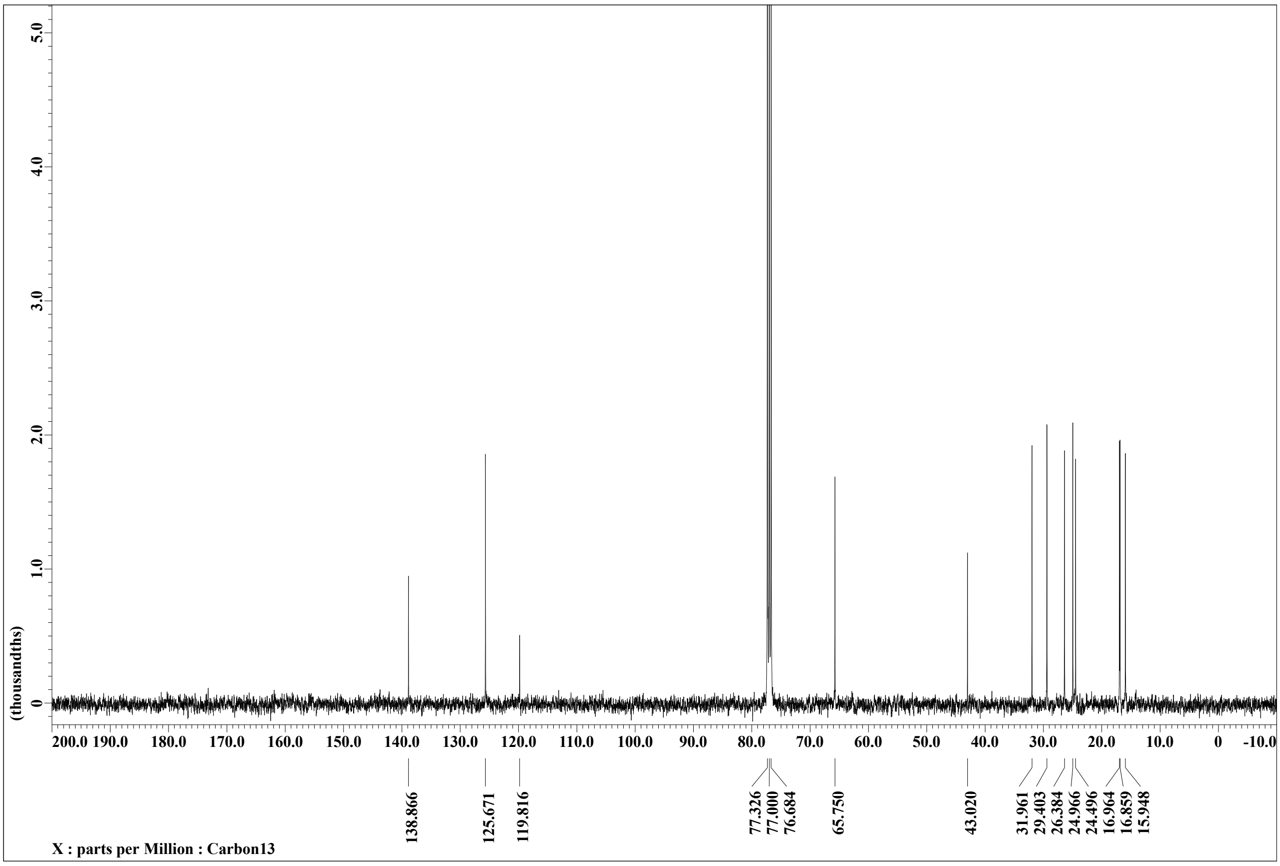
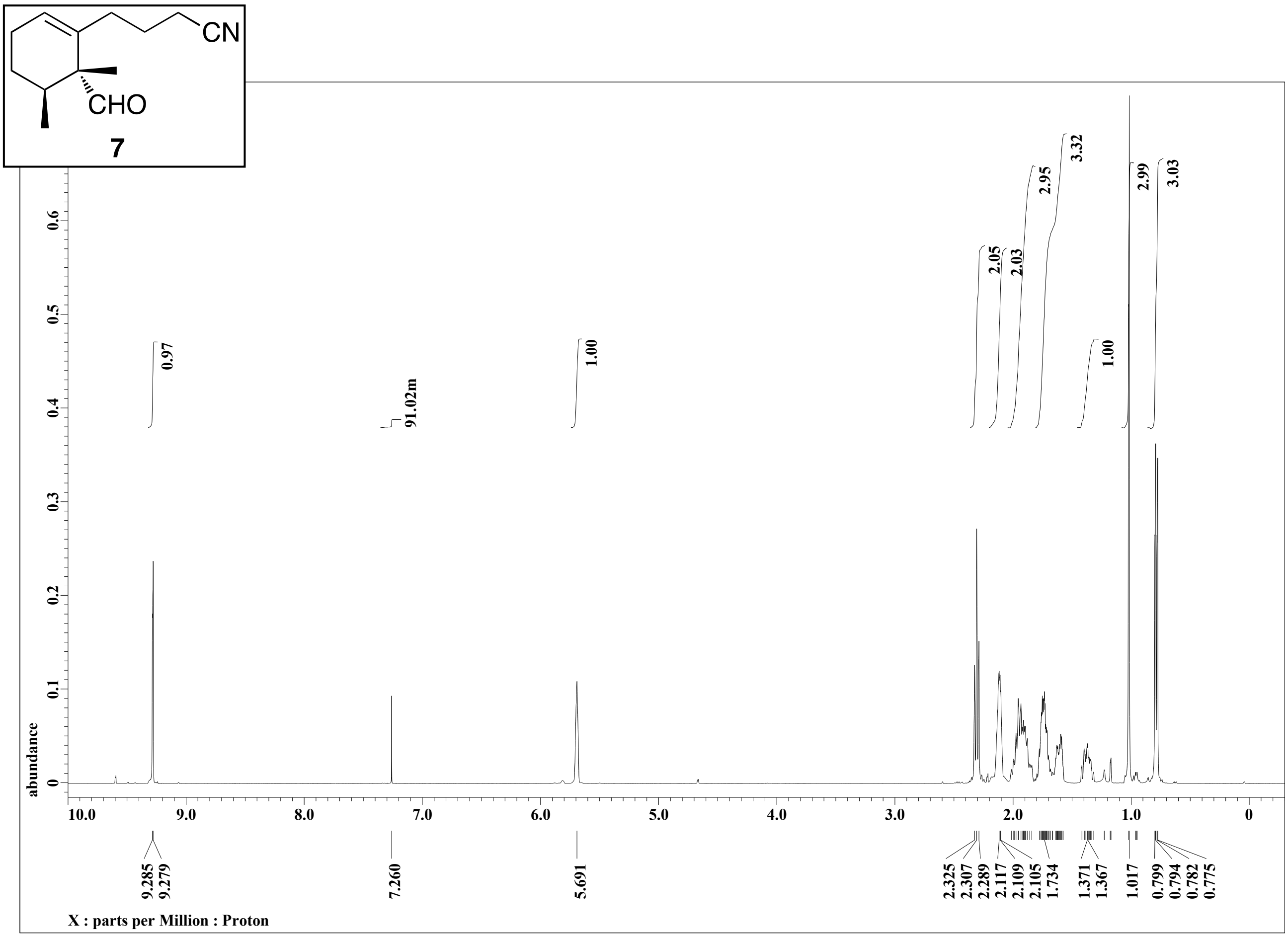
1.99
2.01
1.15
1.00
2.02
2.03
3.14
7.20
1.16
2.53
3.68
3.09
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.807 7.802 7.798 7.785 7.781 7.776
7.356 7.336 7.260
5.483 5.477
4.079 4.063 4.047
3.492 3.465 3.439 3.411
2.449
1.983 1.975 1.968 1.964
1.537 1.370 1.249
0.893 0.878 0.861 0.848 0.737
0.083 0.066
X : parts per Million : Proton

19


(thousandths)
0 1.0 2.0 3.0 4.0 5.0
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 -10.0
144.692
139.010
133.174 129.810 127.894 125.345
77.316 77.000 76.684 70.541 65.759
43.077
31.980 27.965 26.403 26.125 24.937 21.621 16.811 15.958
X : parts per Million : Carbon13

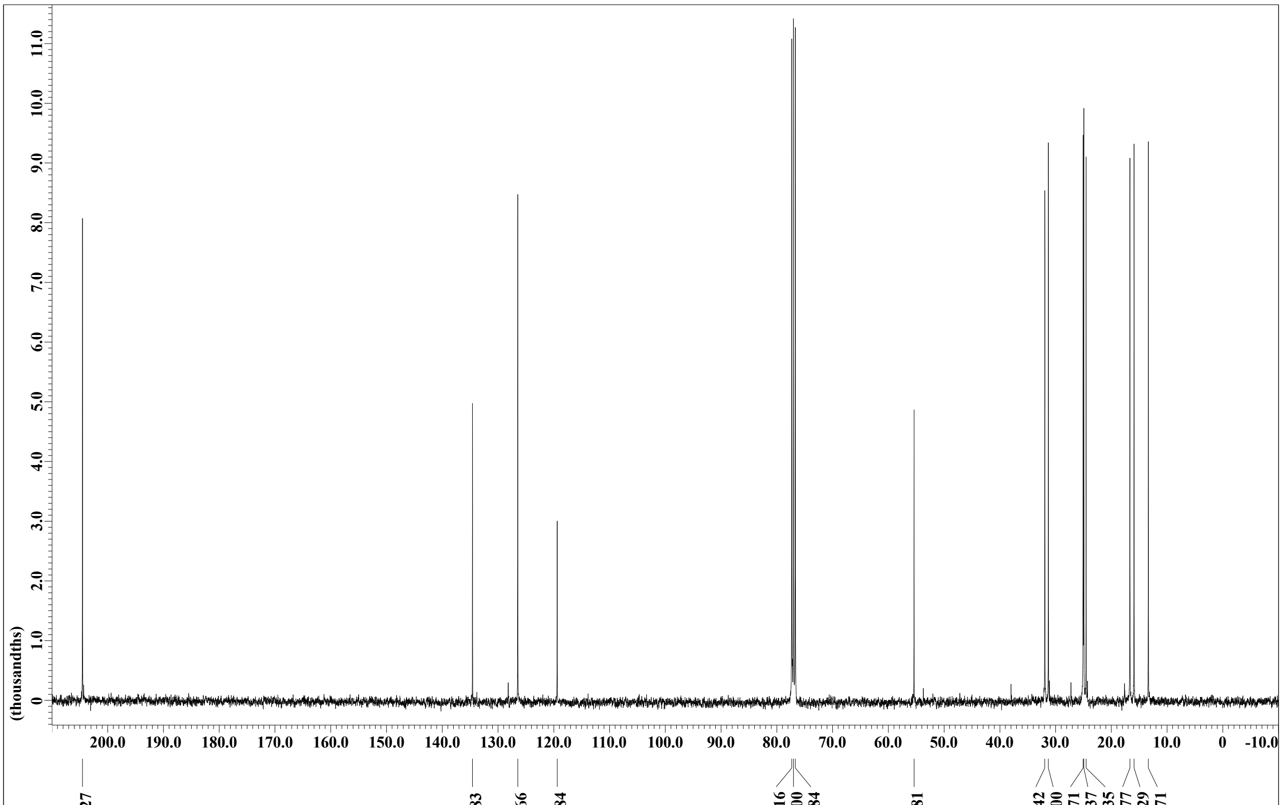

CN
OH
20
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0
0.36
1.00
2.02
1.99
2.05
1.91
3.01
1.03
2.74
2.94
3.01
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.260
5.591
5.583
3.574
3.546
3.508
3.481
2.399
2.380
2.363
2.139
2.134
2.033
1.829
1.434
1.430
1.425
1.418
0.905
0.886
0.803
0.642
X : parts per Million : Proton


(thousandths)
0 1.0 2.0 3.0 4.0 5.0
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 -10.0
138.866
125.671
119.816
77.326
77.000
76.684
65.750
43.020
31.961
29.403
26.384
24.966
24.496
16.964
16.859
15.948
X : parts per Million : Carbon13

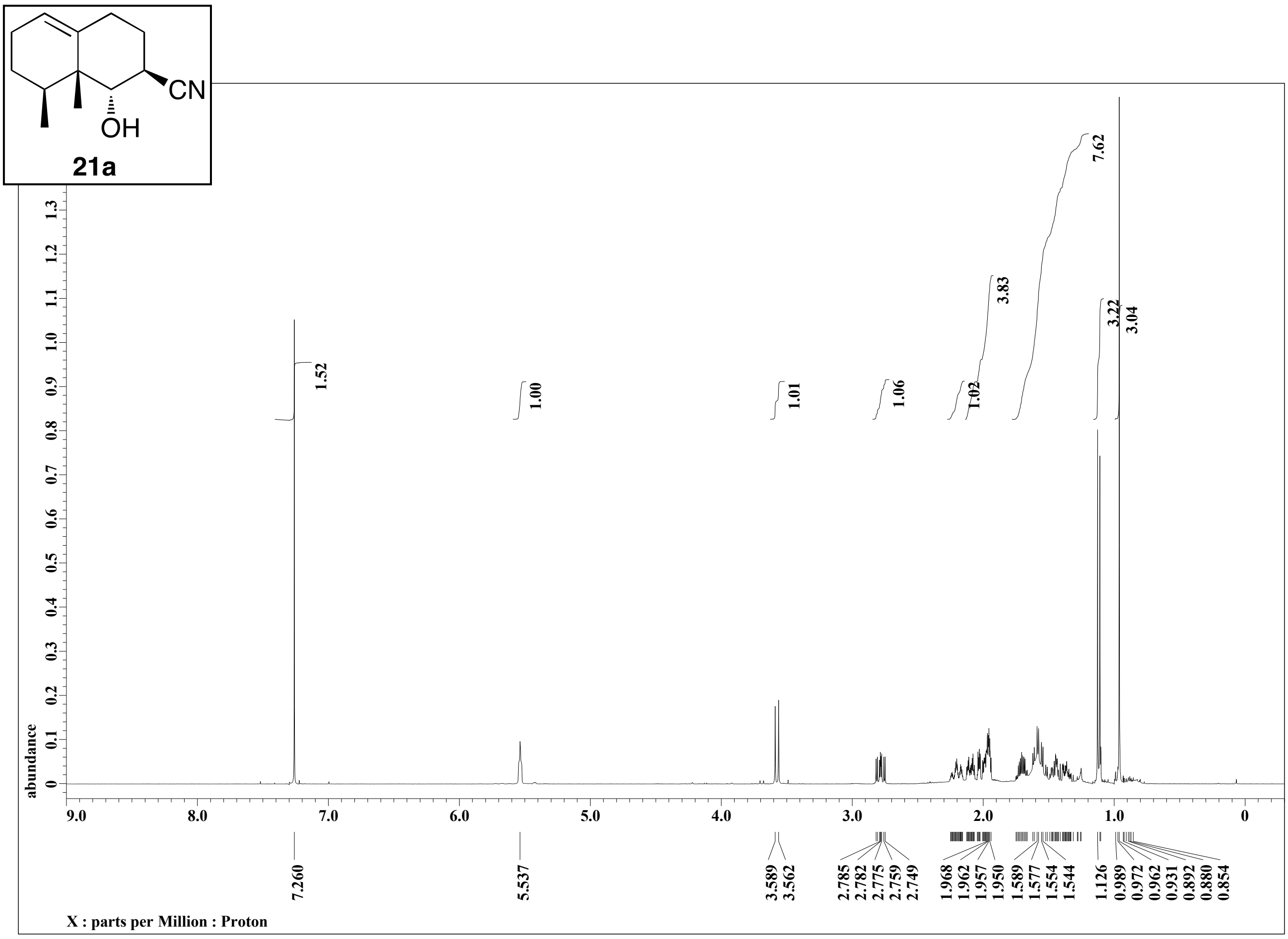


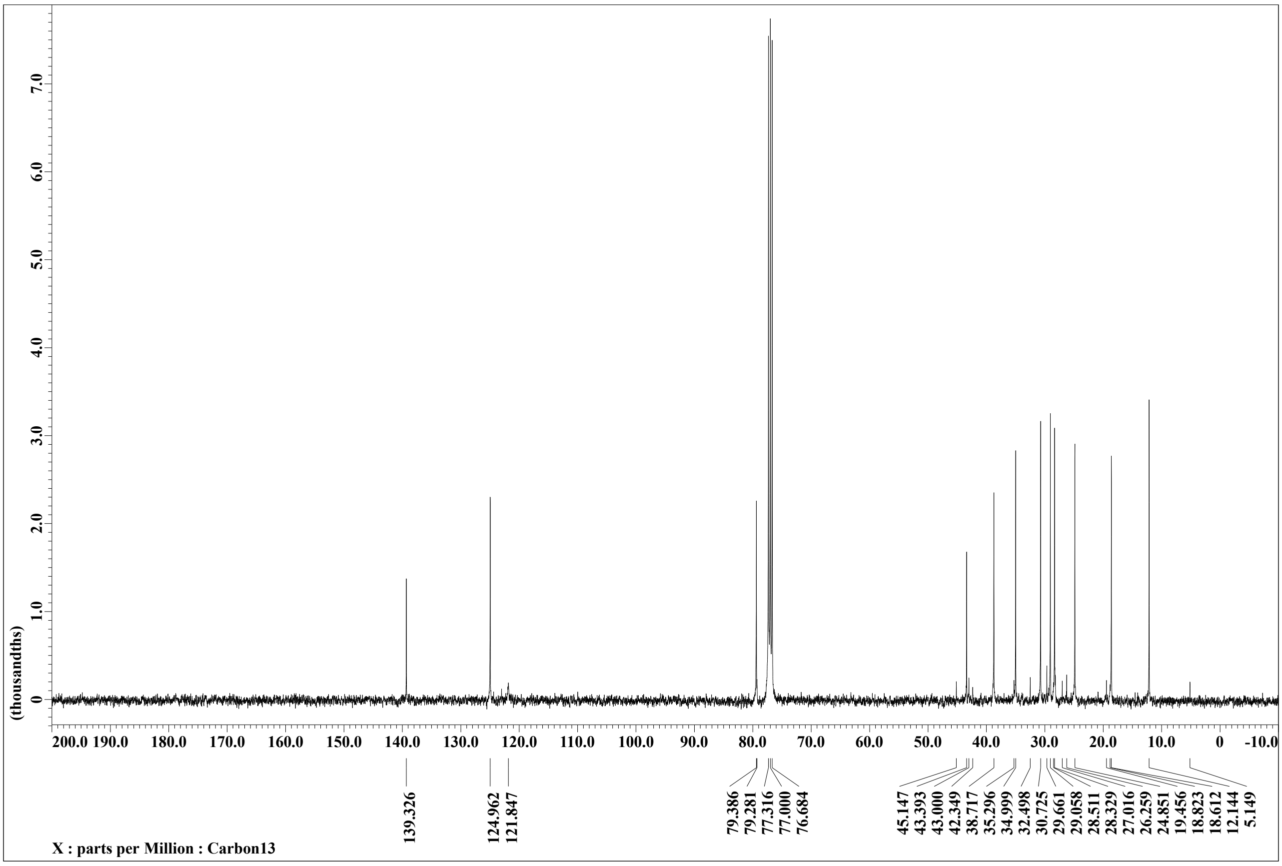
7

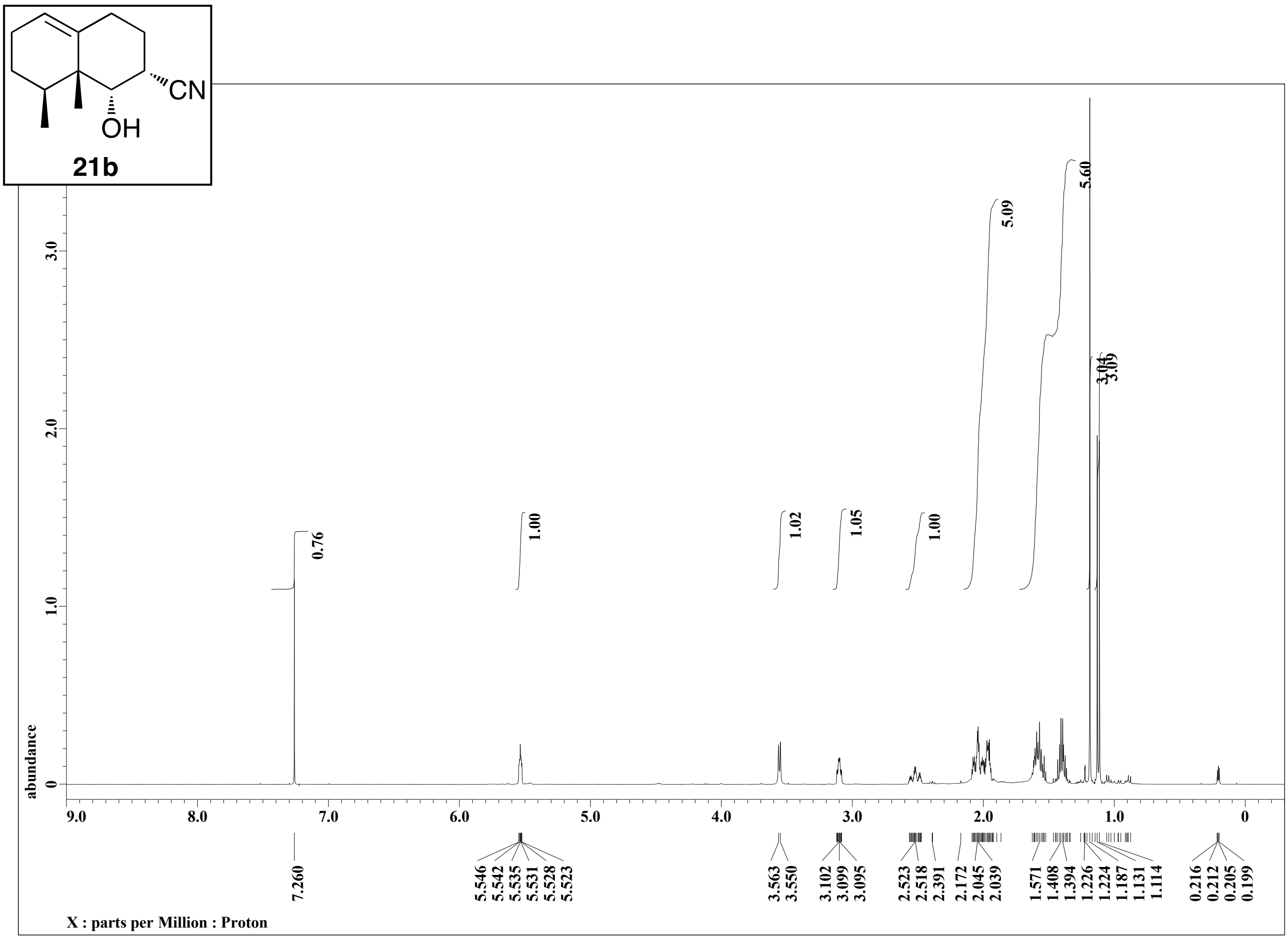
CN
CHO
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.97
91.02m
1.00
2.05
2.03
2.95
3.32
1.00
2.99
3.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.285
9.279
7.260
5.691
2.325
2.307
2.289
2.117
2.109
2.105
1.734
1.371
1.367
1.017
0.799
0.794
0.782
0.775
X : parts per Million : Proton

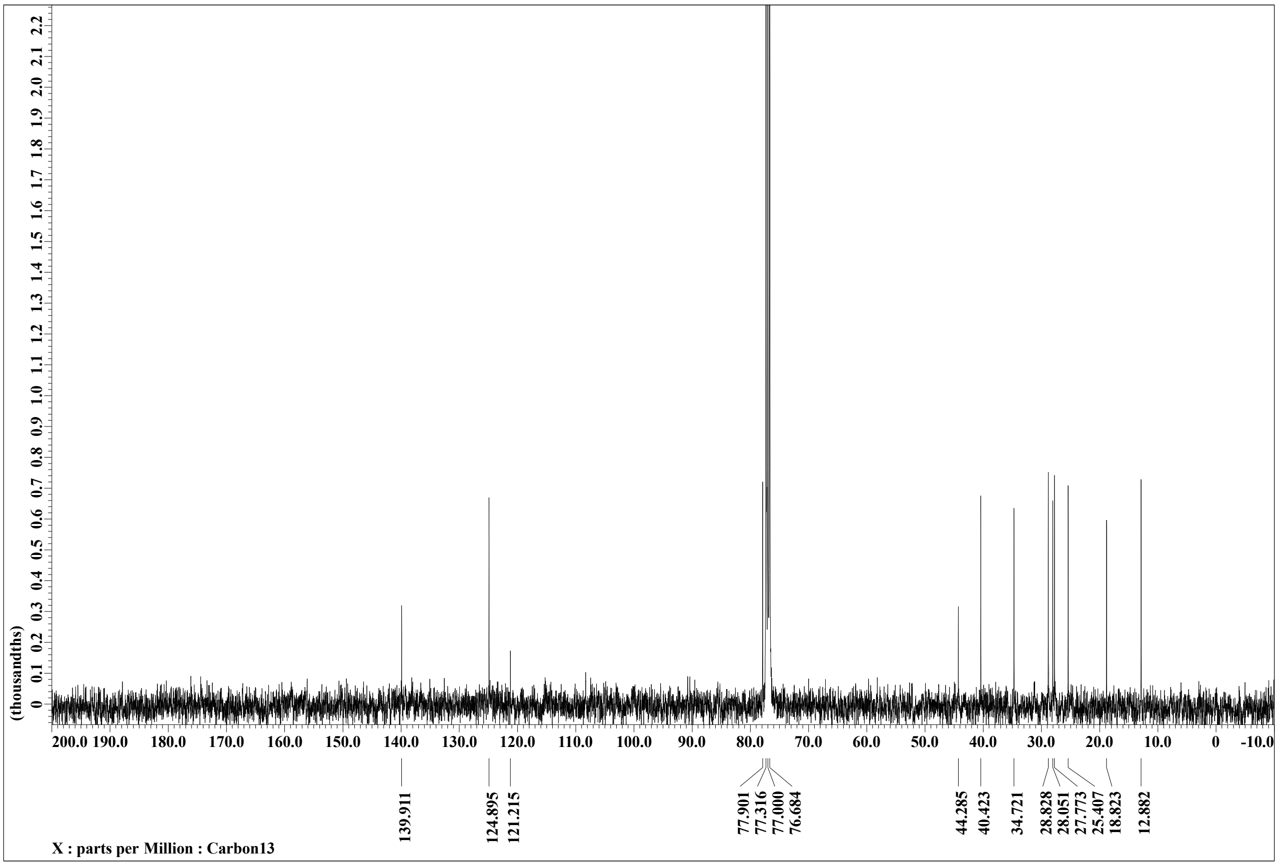


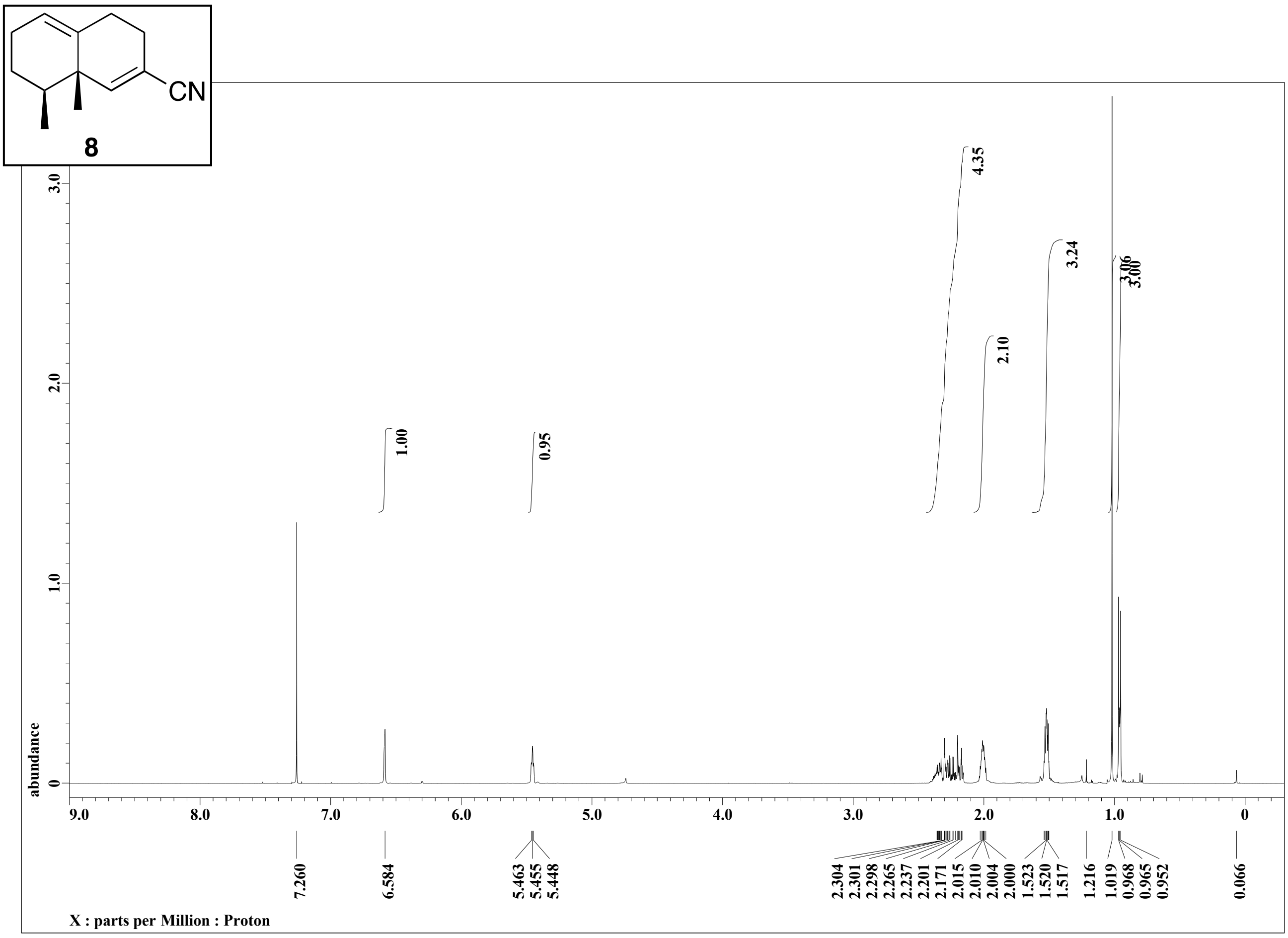
(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
204.527
134.583
126.466
119.384
77.316
77.000
76.684
55.381
31.942
31.300
25.071
24.937
24.535
16.677
15.929
13.371
X : parts per Million : Carbon13

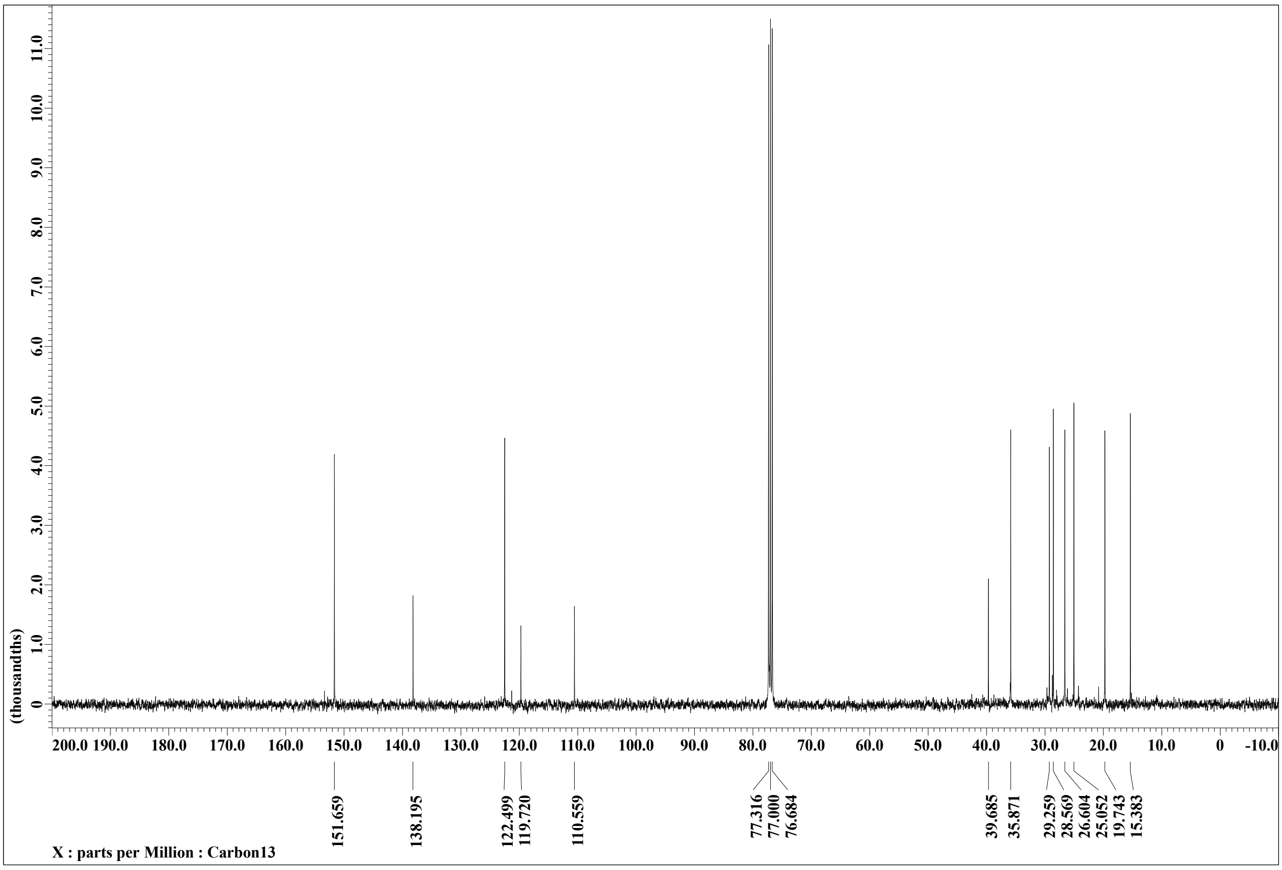

CN
OH
21a
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.52
1.00
1.01
1.06
1.02
3.83
7.62
3.22
3.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
5.537
3.589
3.562
2.785
2.782
2.775
2.759
2.749
1.968
1.962
1.957
1.950
1.589
1.577
1.554
1.544
1.126
0.989
0.972
0.962
0.931
0.892
0.880
0.854
X : parts per Million : Proton

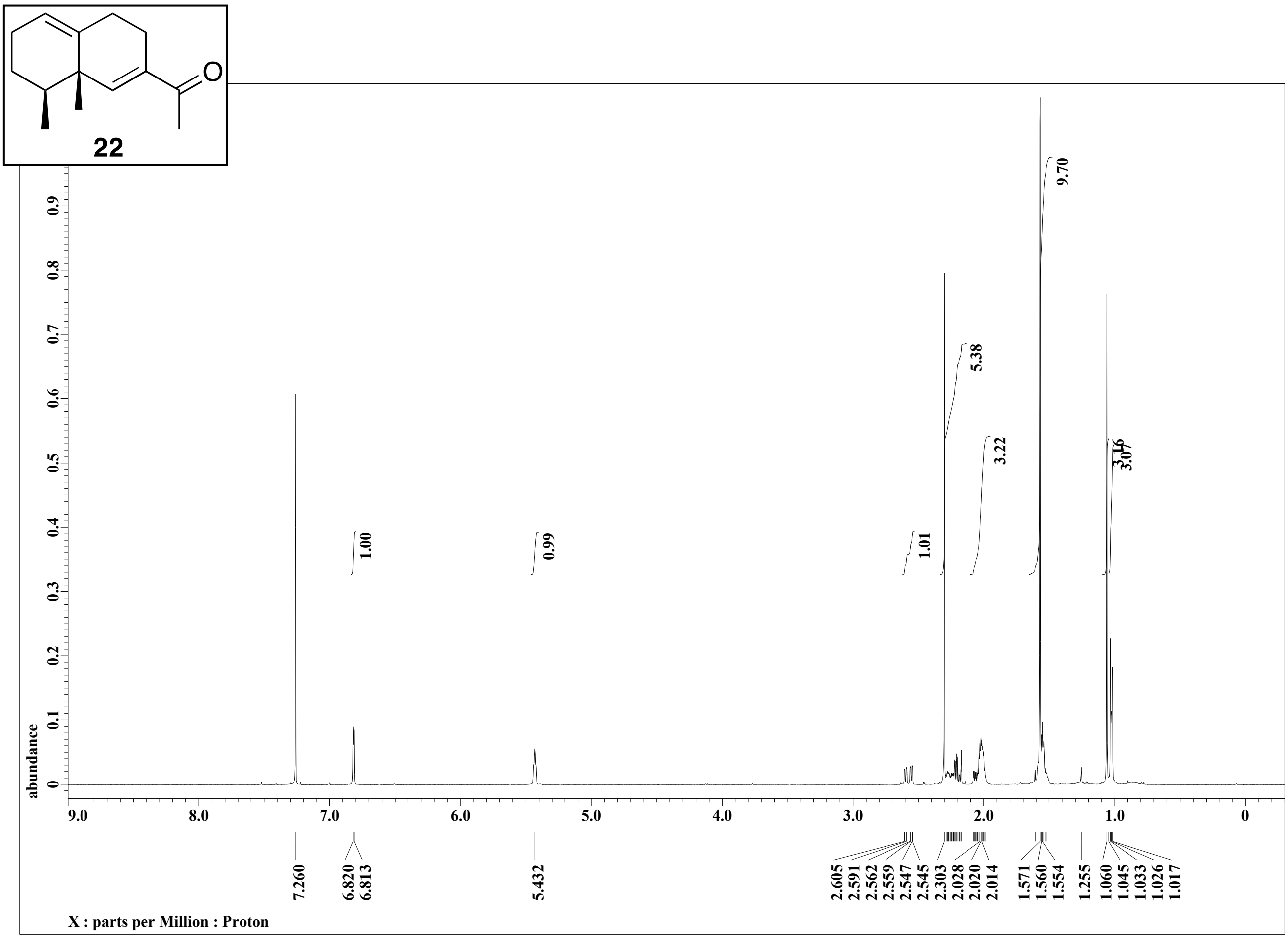

(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
139.326
124.962
121.847
79.386
79.281
77.316
77.000
76.684
45.147
43.393
43.000
42.349
38.717
35.296
34.999
32.498
30.725
29.661
29.058
28.511
28.329
27.016
26.259
24.851
19.456
18.823
18.612
12.144
5.149
X : parts per Million : Carbon13

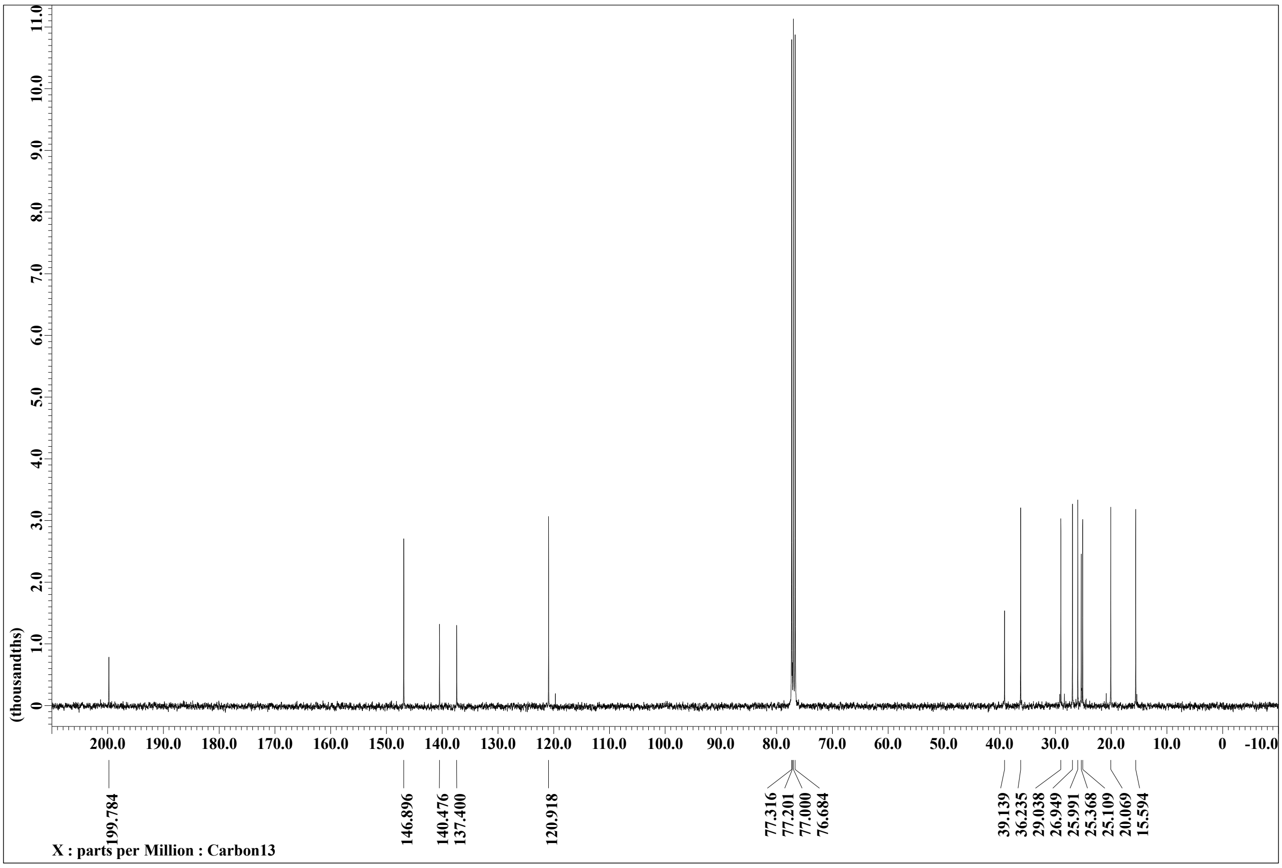

CN
OH
21b
abundance
0
1.0
2.0
3.0
0.76
1.00
1.02
1.05
1.00
5.09
5.60
3.04
3.09
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
5.546
5.542
5.535
5.531
5.528
5.523
3.563
3.550
3.102
3.099
3.095
2.523
2.518
2.391
2.172
2.045
2.039
1.571
1.408
1.394
1.226
1.224
1.187
1.131
1.114
0.216
0.212
0.205
0.199
X : parts per Million : Proton

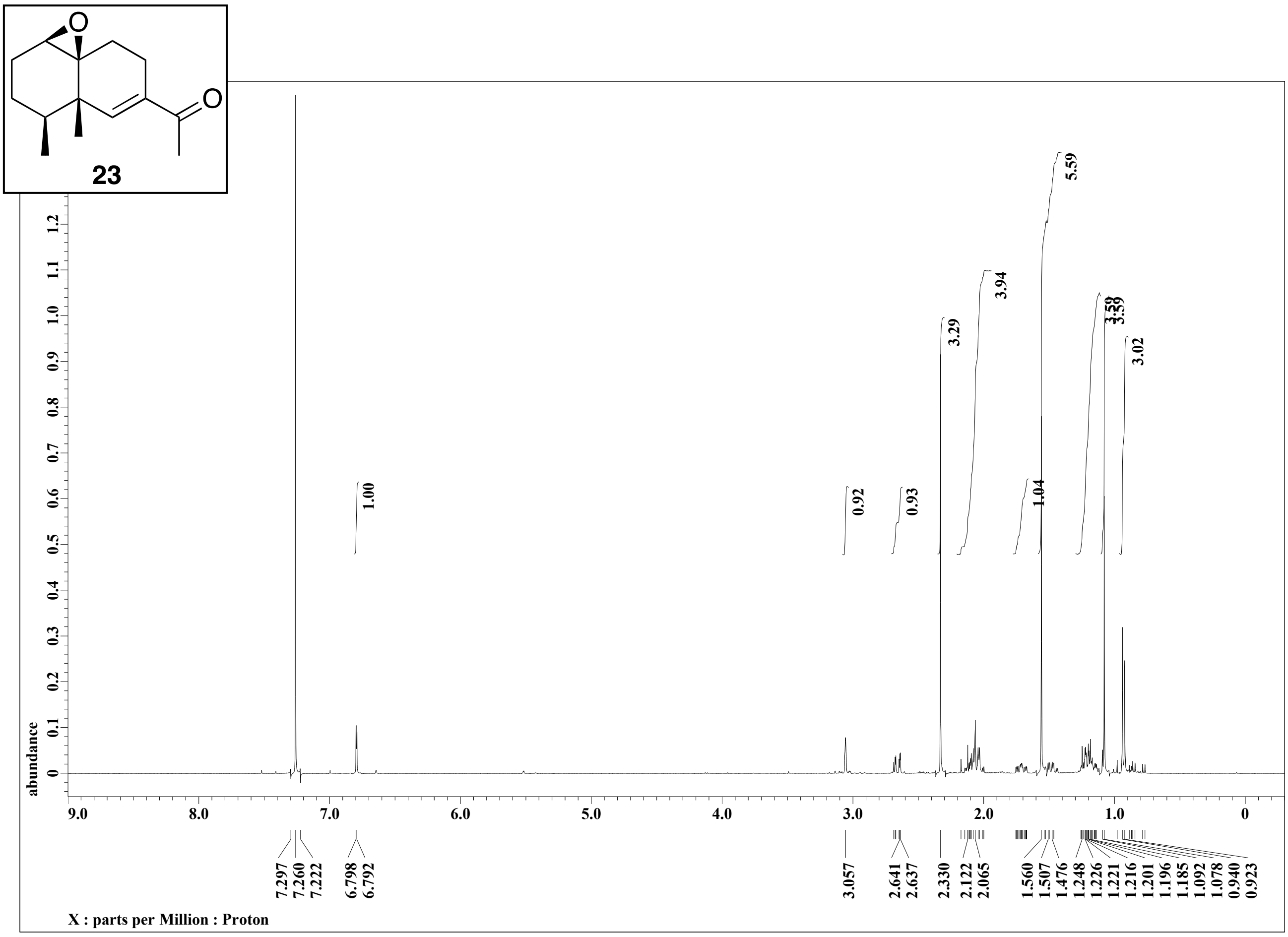

(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
139.911
124.895
121.215
77.901
77.316
77.000
76.684
44.285
40.423
34.721
28.828
28.051
27.773
25.407
18.823
12.882
X : parts per Million : Carbon13

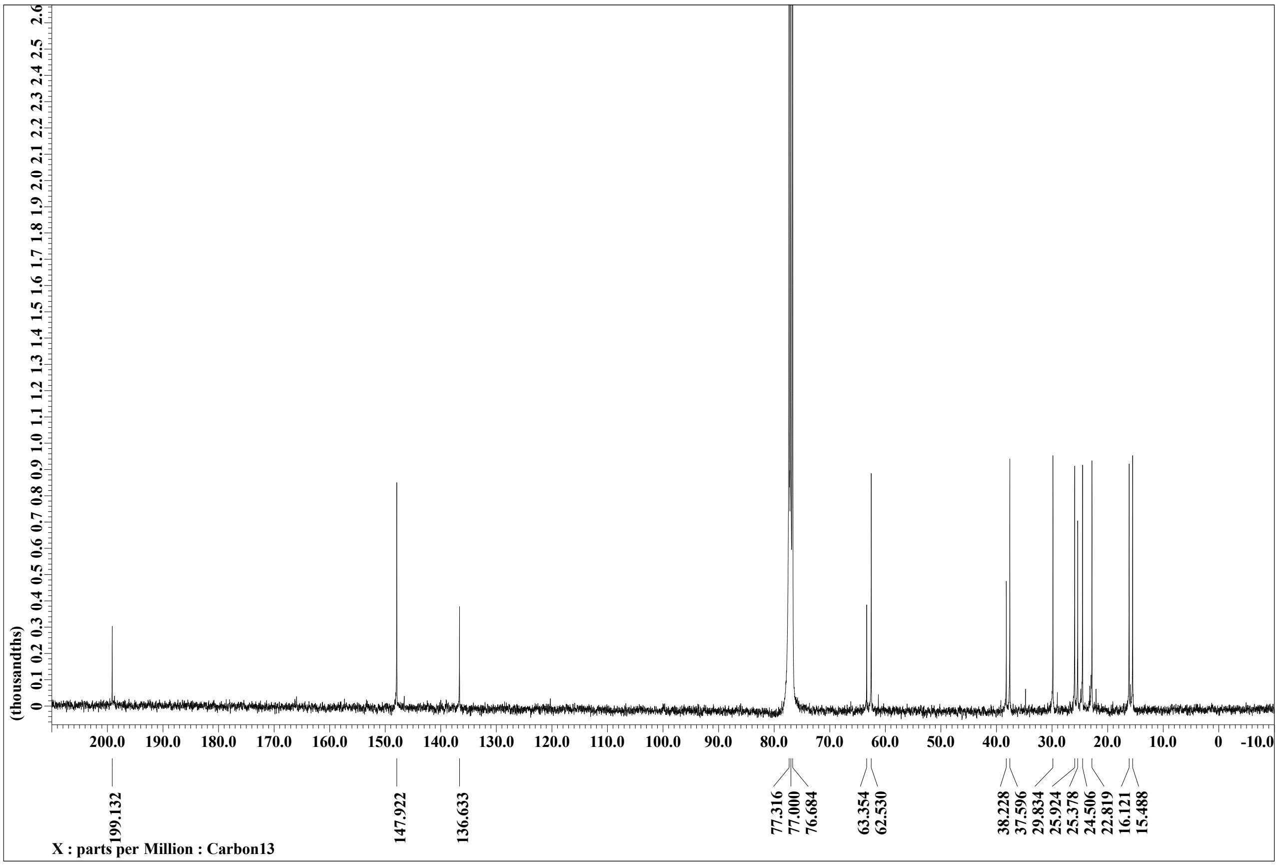

CN
8
abundance
0
1.0
2.0
3.0
1.00
0.95
4.35
2.10
3.24
3.06
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
6.584
5.463
5.455
5.448
2.304
2.301
2.298
2.265
2.237
2.201
2.171
2.015
2.010
2.004
2.000
1.523
1.520
1.517
1.216
1.019
0.968
0.965
0.952
0.066
X : parts per Million : Proton

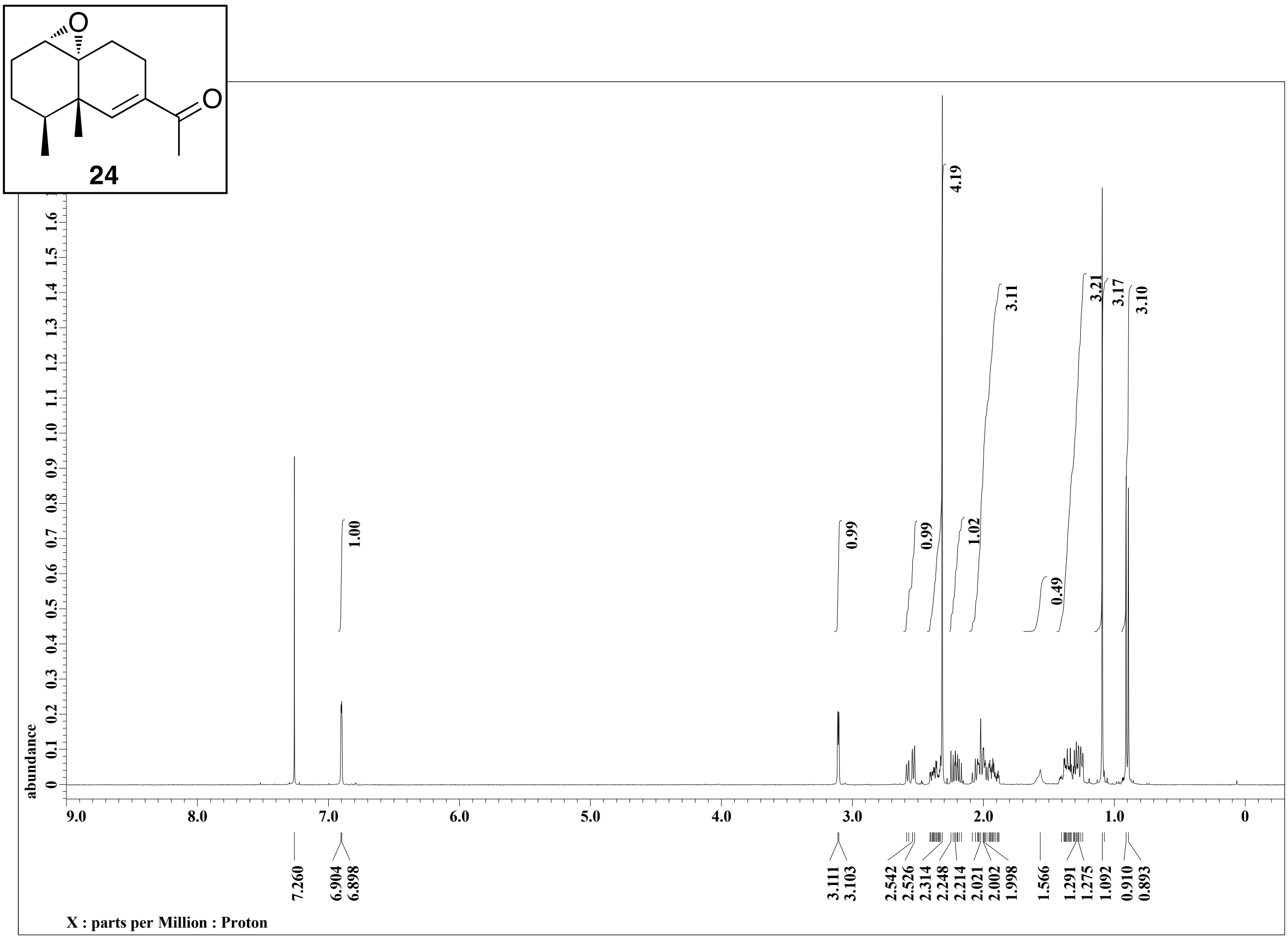

(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
151.659
138.195
122.499
119.720
110.559
77.316
77.000
76.684
39.685
35.871
29.259
28.569
26.604
25.052
19.743
15.383
X : parts per Million : Carbon13


O
22
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.00
0.99
1.01
5.38
3.22
9.70
3.16
3.07
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
6.820
6.813
5.432
2.605
2.591
2.562
2.559
2.547
2.545
2.303
2.028
2.020
2.014
1.571
1.560
1.554
1.255
1.060
1.045
1.033
1.026
1.017
X : parts per Million : Proton


(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
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
-10.0
199.784
146.896
140.476
137.400
120.918
77.316
77.201
77.000
76.684
39.139
36.235
29.038
26.949
25.991
25.368
25.109
20.069
15.594
X : parts per Million : Carbon13

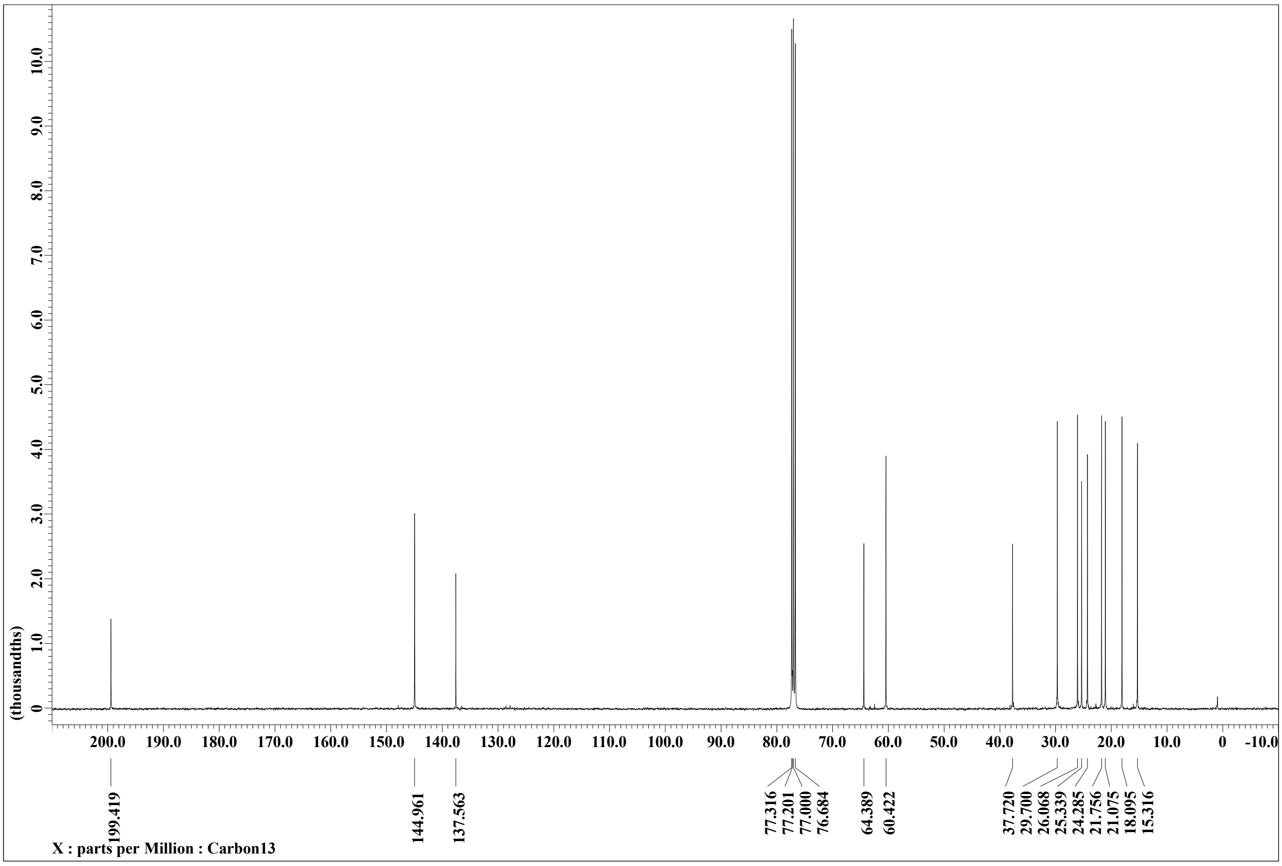

23
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.00
0.92
0.93
3.29
3.94
1.04
5.59
3.59
3.59
3.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.297
7.260
7.222
6.798
6.792
3.057
2.641
2.637
2.330
2.122
2.065
1.560
1.507
1.476
1.248
1.226
1.221
1.216
1.201
1.196
1.185
1.092
1.078
0.940
0.923
X : parts per Million : Proton


(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
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
-10.0
199.132
147.922
136.633
77.316
77.000
76.684
63.354
62.530
38.228
37.596
29.834
25.924
25.378
24.506
22.819
16.121
15.488
X : parts per Million : Carbon13

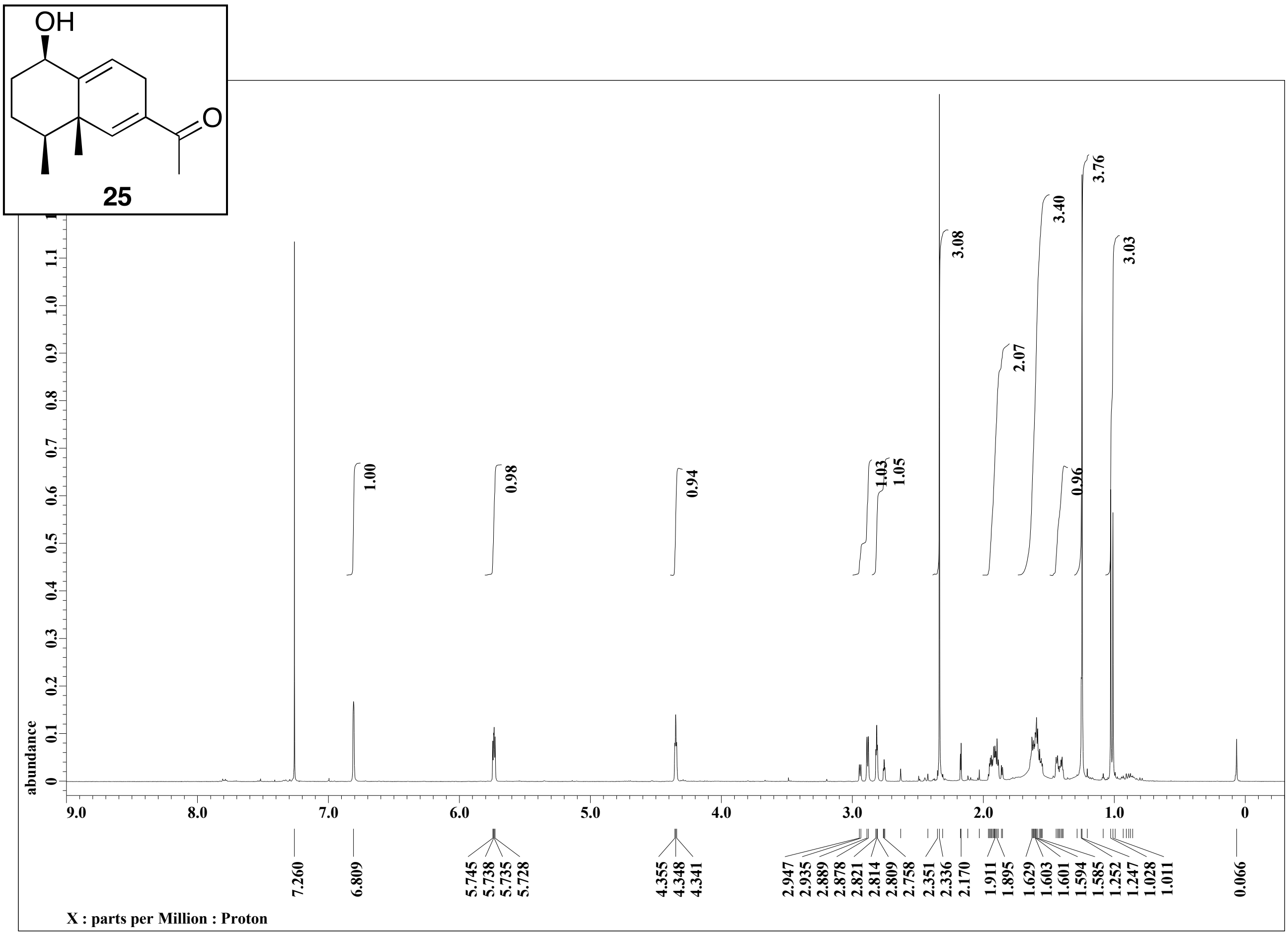


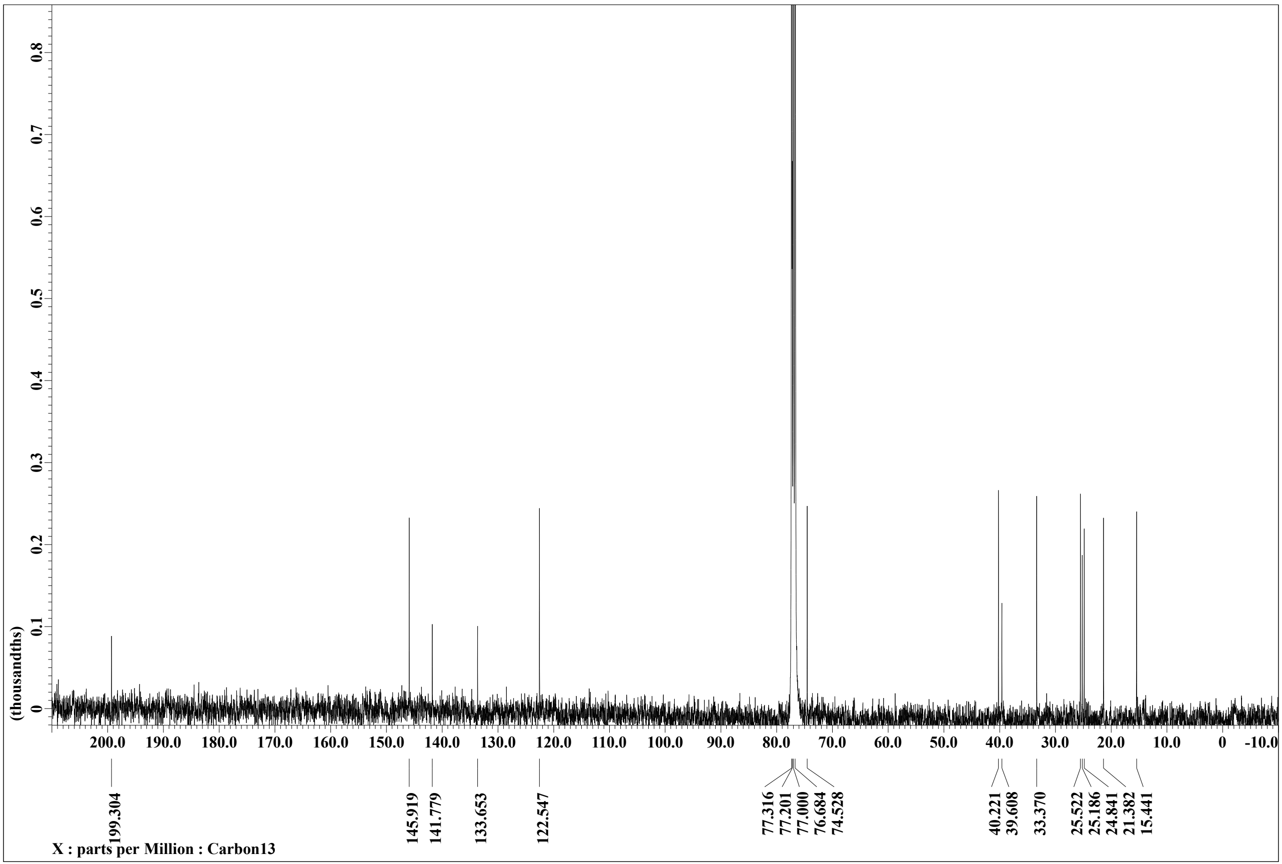
24

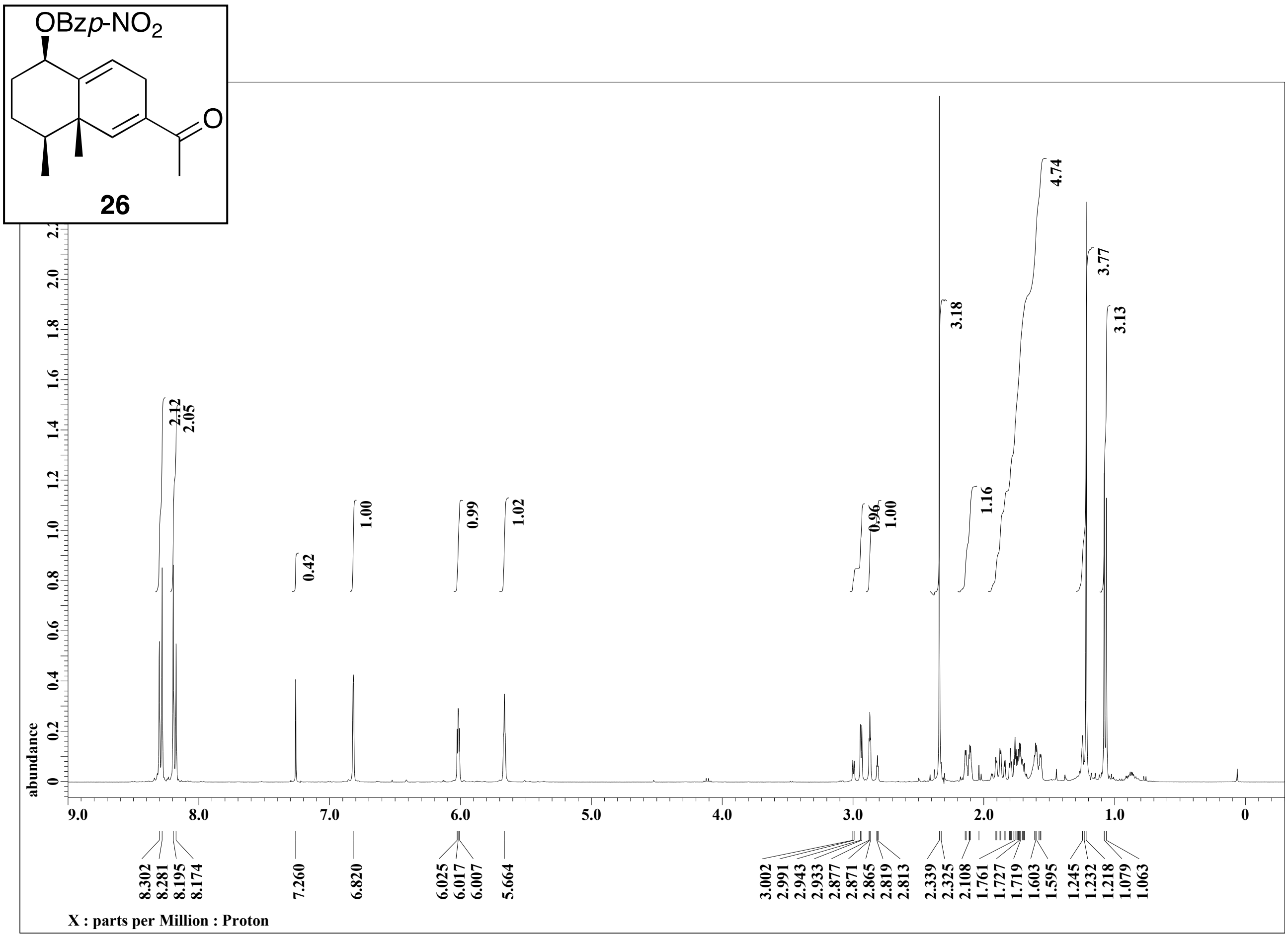
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.00
0.99
0.99
1.02
4.19
3.11
0.49
3.21
3.17
3.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
6.904
6.898
3.111
3.103
2.542
2.526
2.314
2.248
2.214
2.021
2.002
1.998
1.566
1.291
1.275
1.092
0.910
0.893
X : parts per Million : Proton

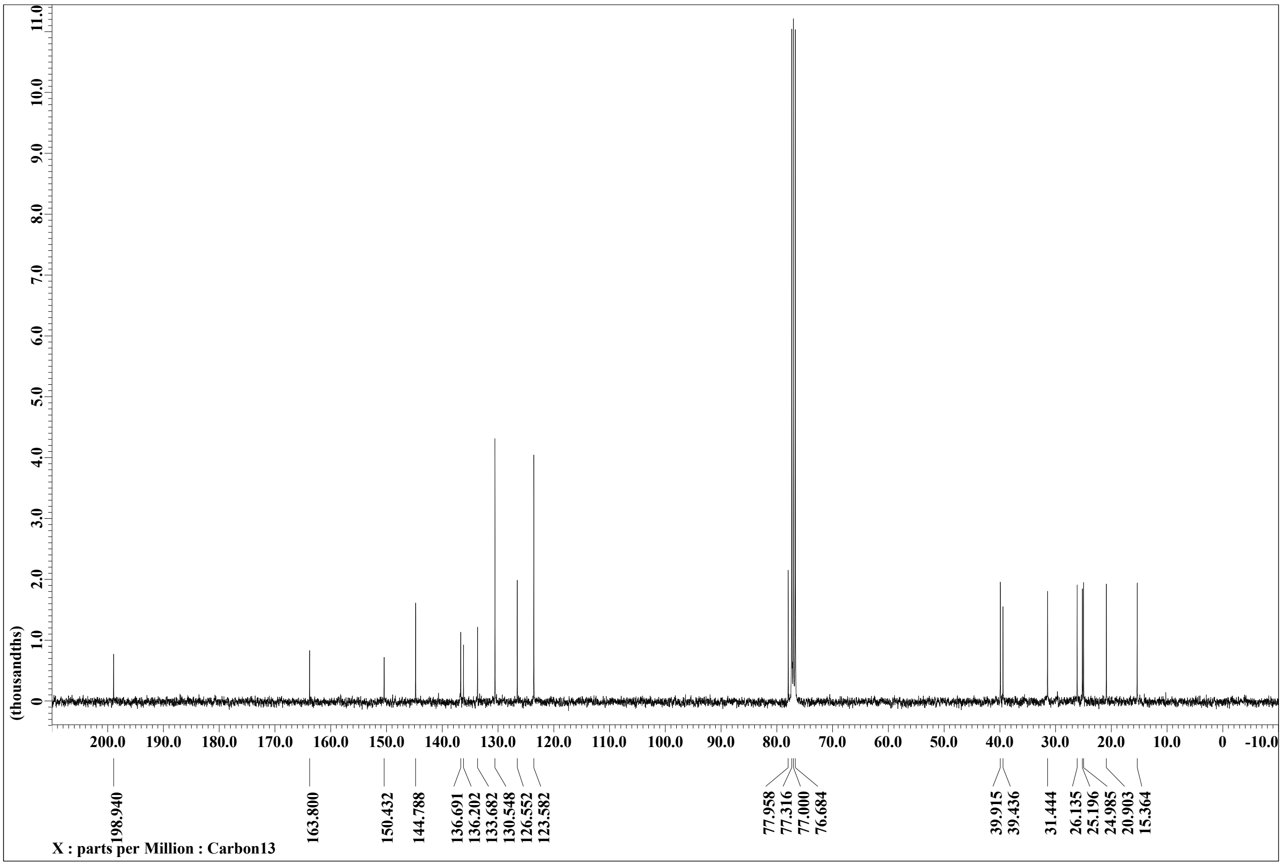


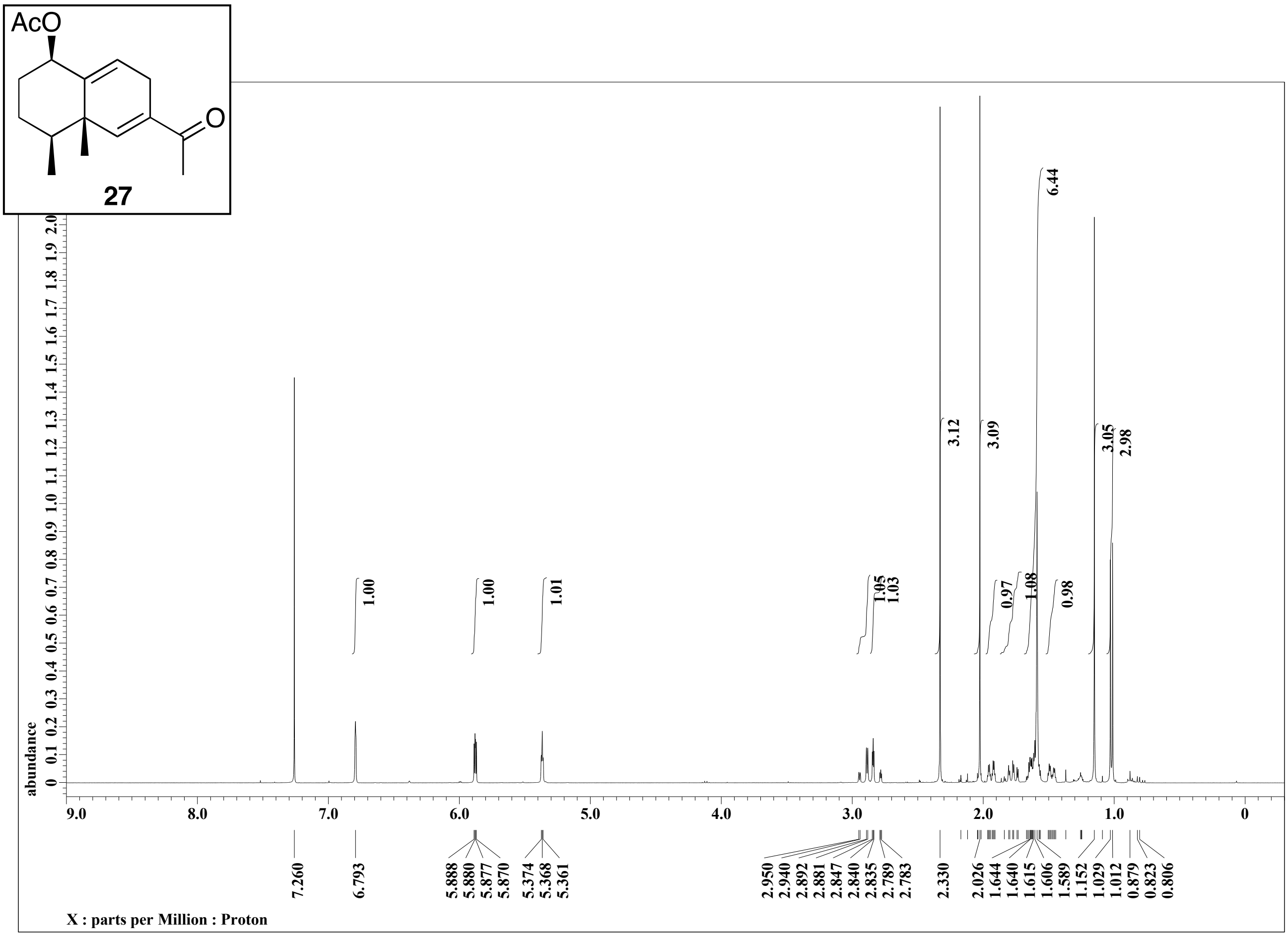
(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
199.419
144.961
137.563
77.316
77.201
77.000
76.684
64.389
60.422
37.720
29.700
26.068
25.339
24.285
21.756
21.075
18.095
15.316
X : parts per Million : Carbon13


25
OH
O
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.00
0.98
0.94
1.03
1.05
3.08
2.07
3.40
0.96
3.76
3.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
6.809
5.745
5.738
5.735
5.728
4.355
4.348
4.341
2.947
2.935
2.889
2.878
2.821
2.814
2.809
2.758
2.351
2.336
2.170
1.911
1.895
1.629
1.603
1.601
1.594
1.585
1.252
1.247
1.028
1.011
0.066
X : parts per Million : Proton


(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
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
-10.0
199.304
145.919
141.779
133.653
122.547
77.316
77.201
77.000
76.684
74.528
40.221
39.608
33.370
25.522
25.186
24.841
21.382
15.441
X : parts per Million : Carbon13


OBzp-NO2
O
26
abundance
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.12
2.05
0.42
1.00
0.99
1.02
0.96
1.00
3.18
1.16
4.74
3.77
3.13
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.302
8.281
8.195
8.174
7.260
6.820
6.025
6.017
6.007
5.664
3.002
2.991
2.943
2.933
2.877
2.871
2.865
2.819
2.813
2.339
2.325
2.108
1.761
1.727
1.719
1.603
1.595
1.245
1.232
1.218
1.079
1.063
X : parts per Million : Proton


(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
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
-10.0
198.940
163.800
150.432
144.788
136.691
136.202
133.682
130.548
126.552
123.582
77.958
77.316
77.000
76.684
39.915
39.436
31.444
26.135
25.196
24.985
20.903
15.364
X : parts per Million : Carbon13


AcO
O
27
abundance
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0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
1.00
1.00
1.01
1.05
1.03
3.12
3.09
0.97
1.08
0.98
6.44
3.05
2.98
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
6.793
5.888
5.880
5.877
5.870
5.374
5.368
5.361
2.950
2.940
2.892
2.881
2.847
2.840
2.835
2.789
2.783
2.330
2.026
1.644
1.640
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1.606
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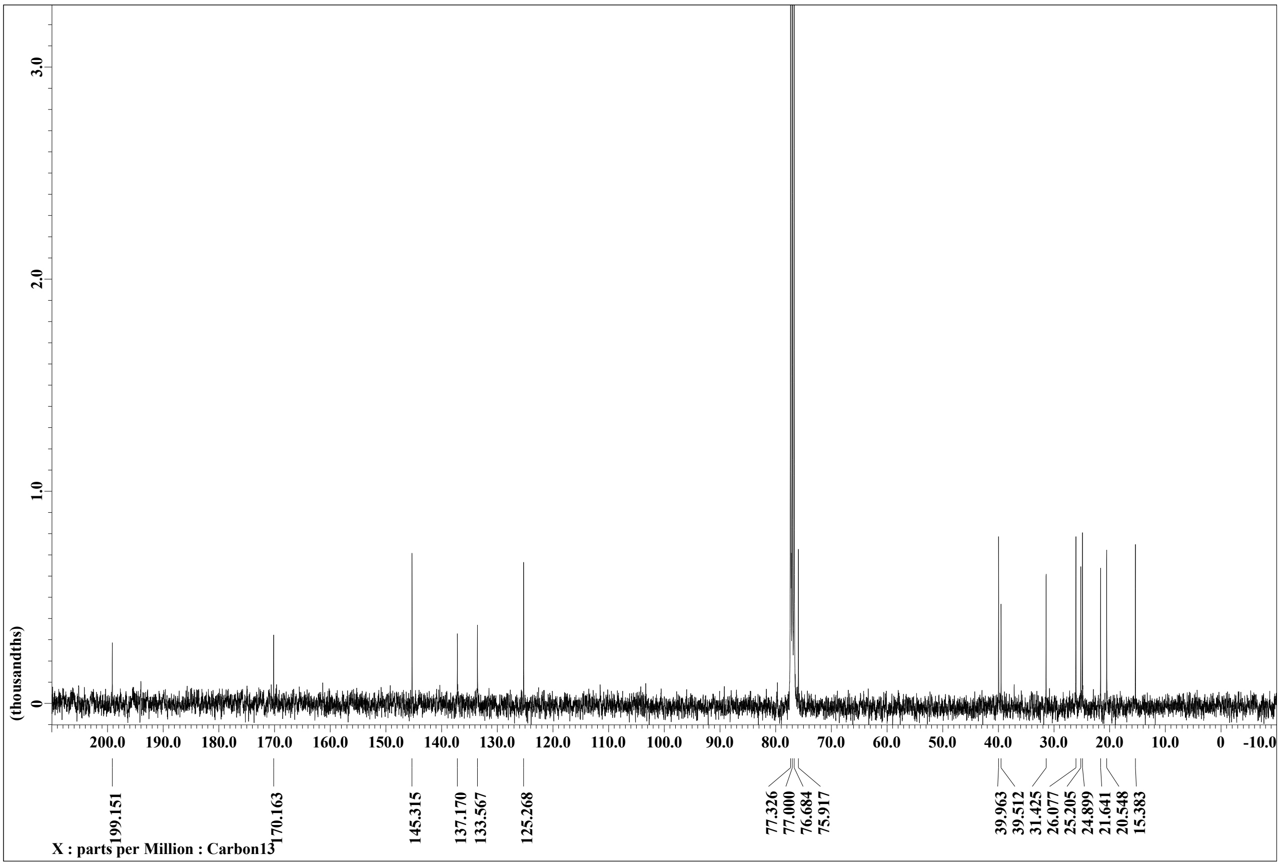
1.152
1.029
1.012
0.879
0.823
0.806
X : parts per Million : Proton


(thousandths)
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1.0
2.0
3.0
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
-10.0
199.151
170.163
145.315
137.170
133.567
125.268
77.326
77.000
76.684
75.917
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31.425
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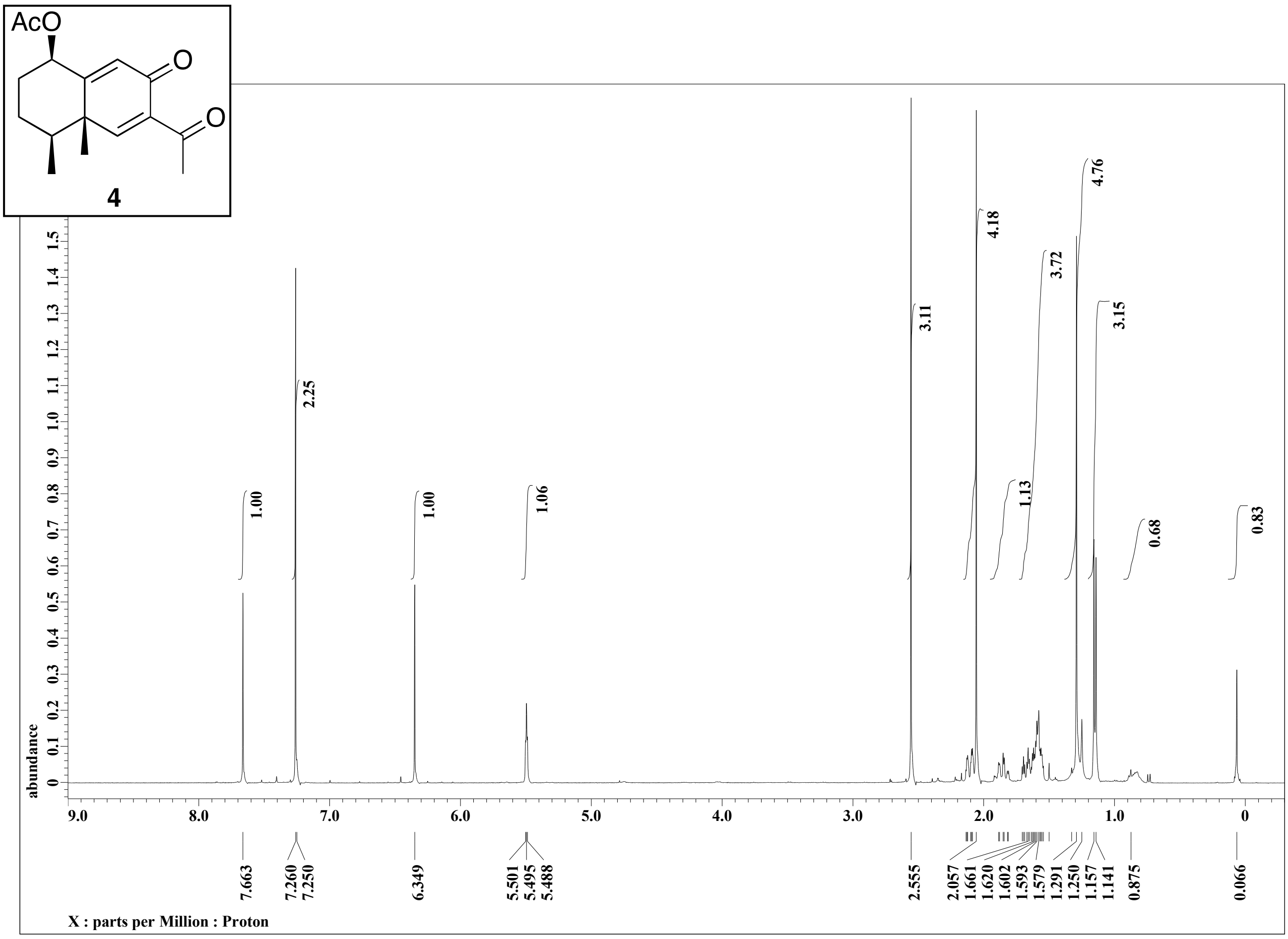
21.641
20.548
15.383
X : parts per Million : Carbon13


AcO
O
O
4
abundance
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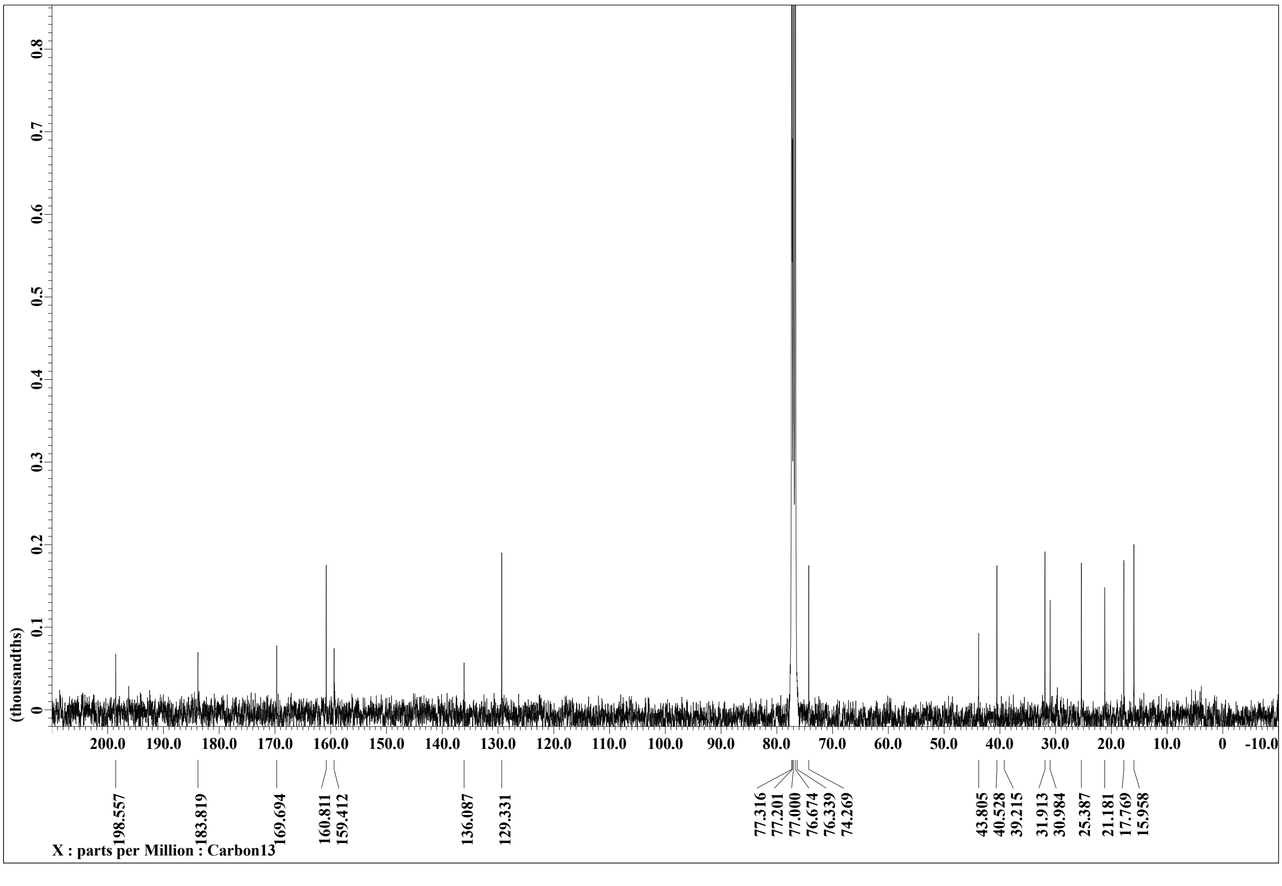
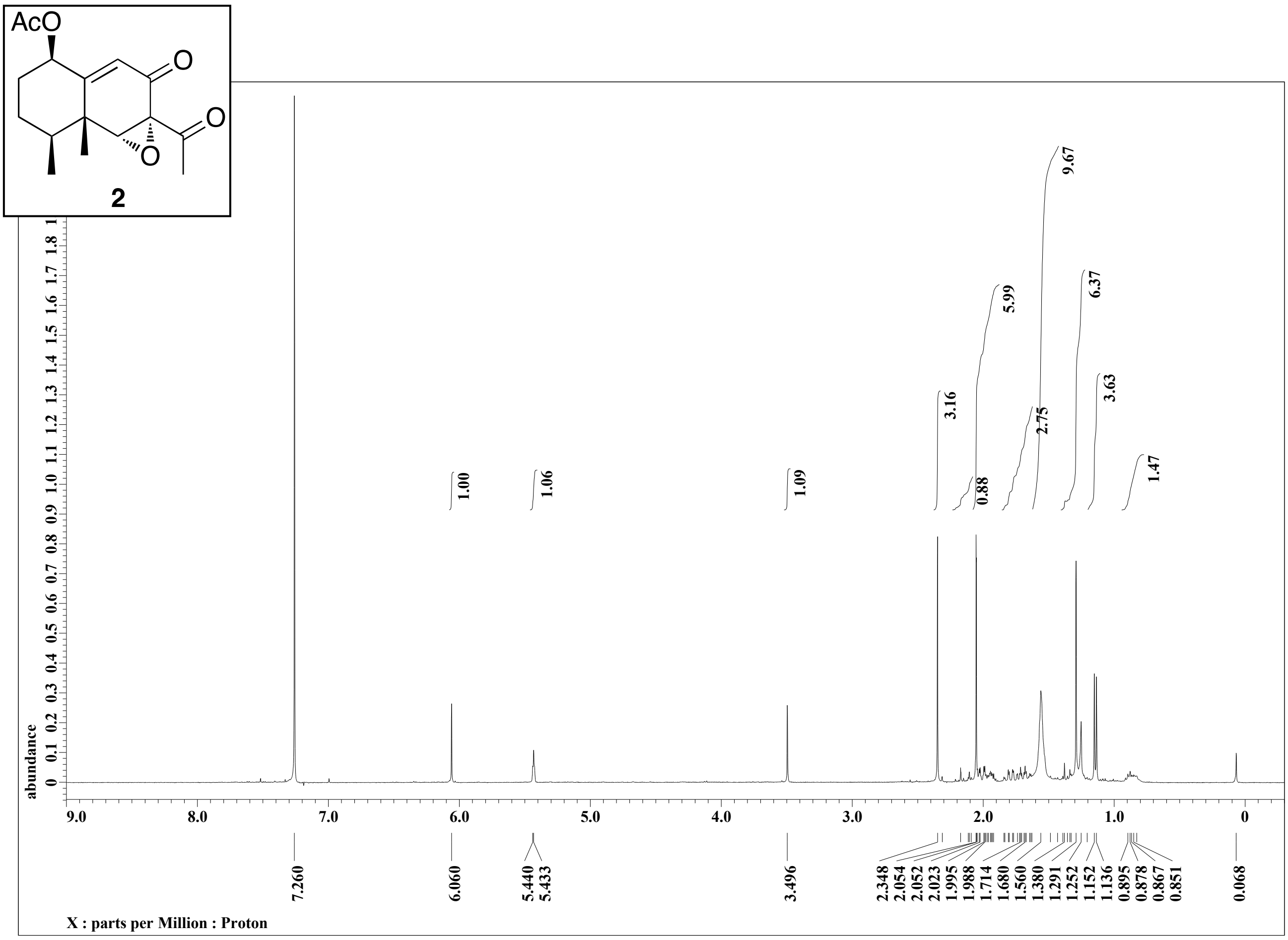
1.00
2.25
1.00
1.06
3.11
4.18
1.13
3.72
4.76
3.15
0.68
0.83
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.663
7.260
7.250
6.349
5.501
5.495
5.488
2.555
2.057
1.661
1.620
1.602
1.593
1.579
1.291
1.250
1.157
1.141
0.875
0.066
X : parts per Million : Proton


(thousandths)
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8
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 -10.0
198.557
183.819
169.694
160.811
159.412
136.087
129.331
77.316
77.201
77.000
76.674
76.339
74.269
43.805
40.528
39.215
31.913
30.984
25.387
21.181
17.769
15.958
X : parts per Million : Carbon13


AcO
O
O
O
2
abundance
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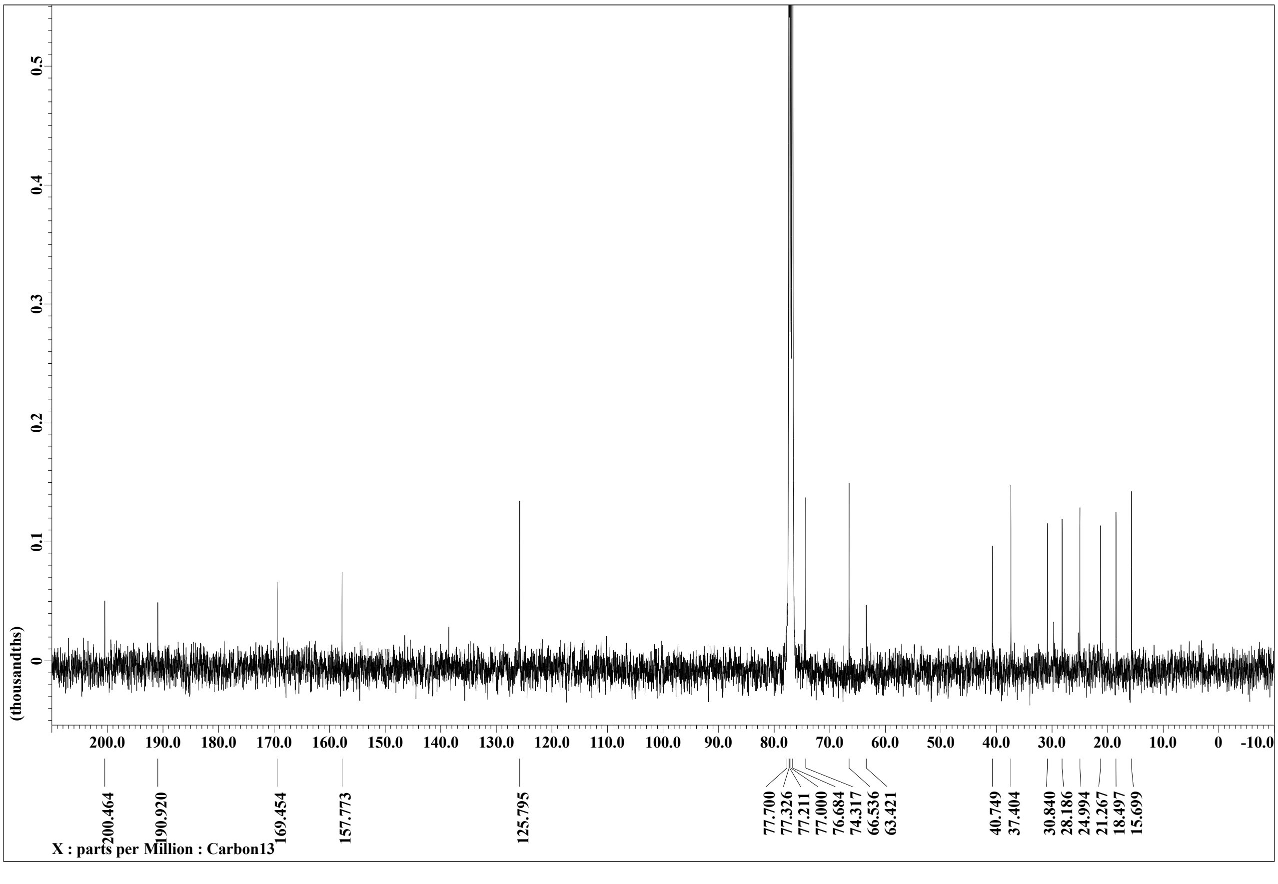
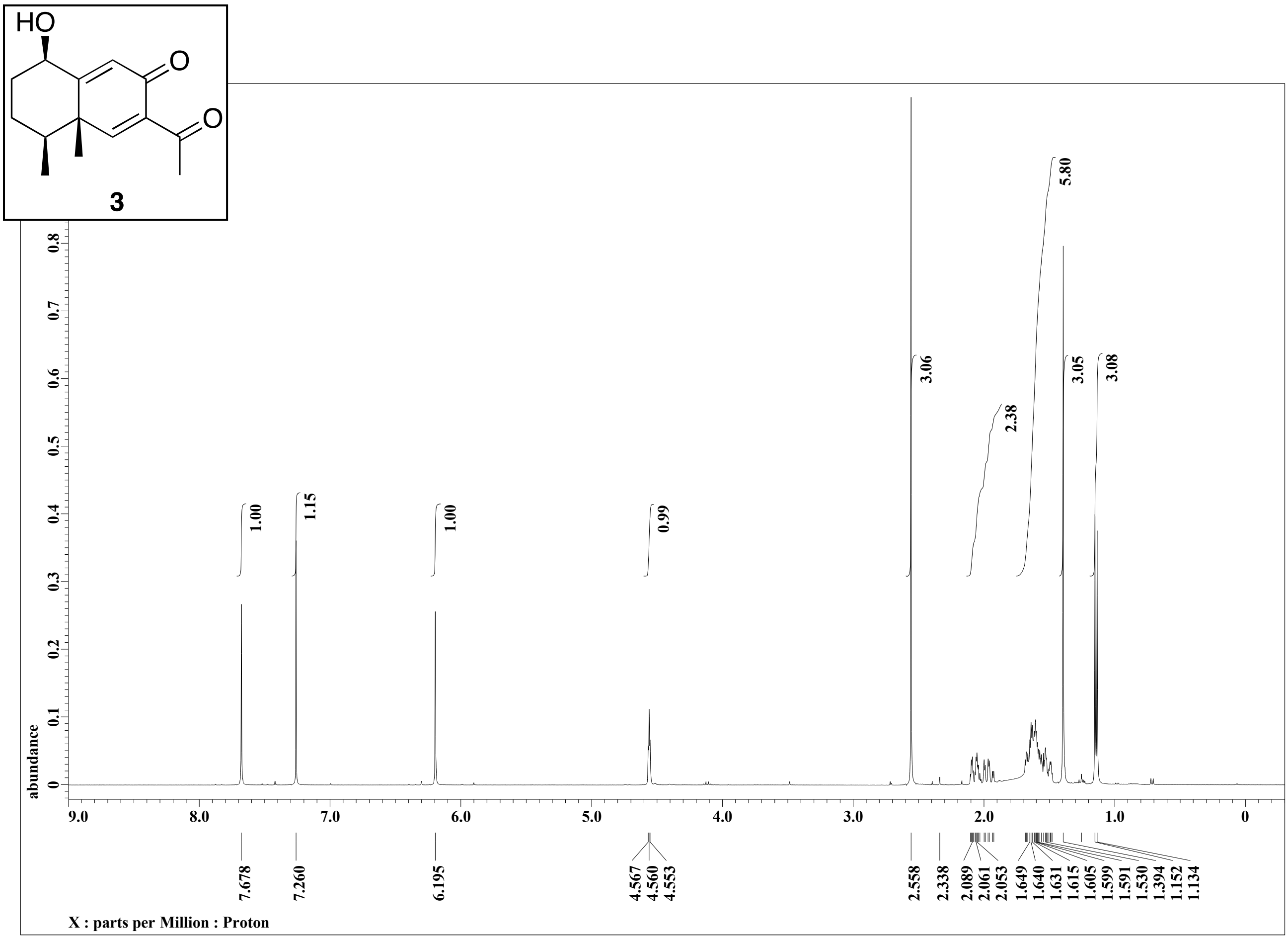
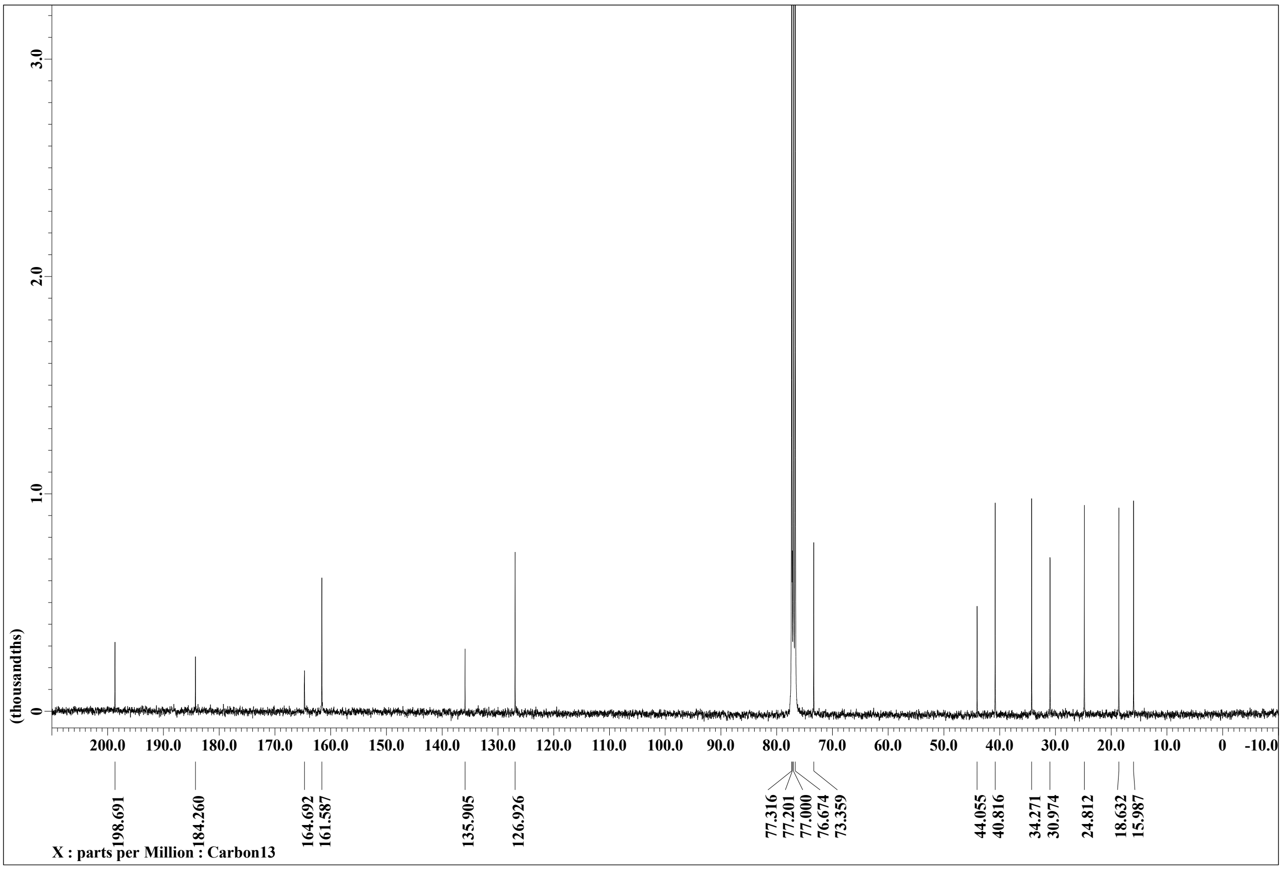
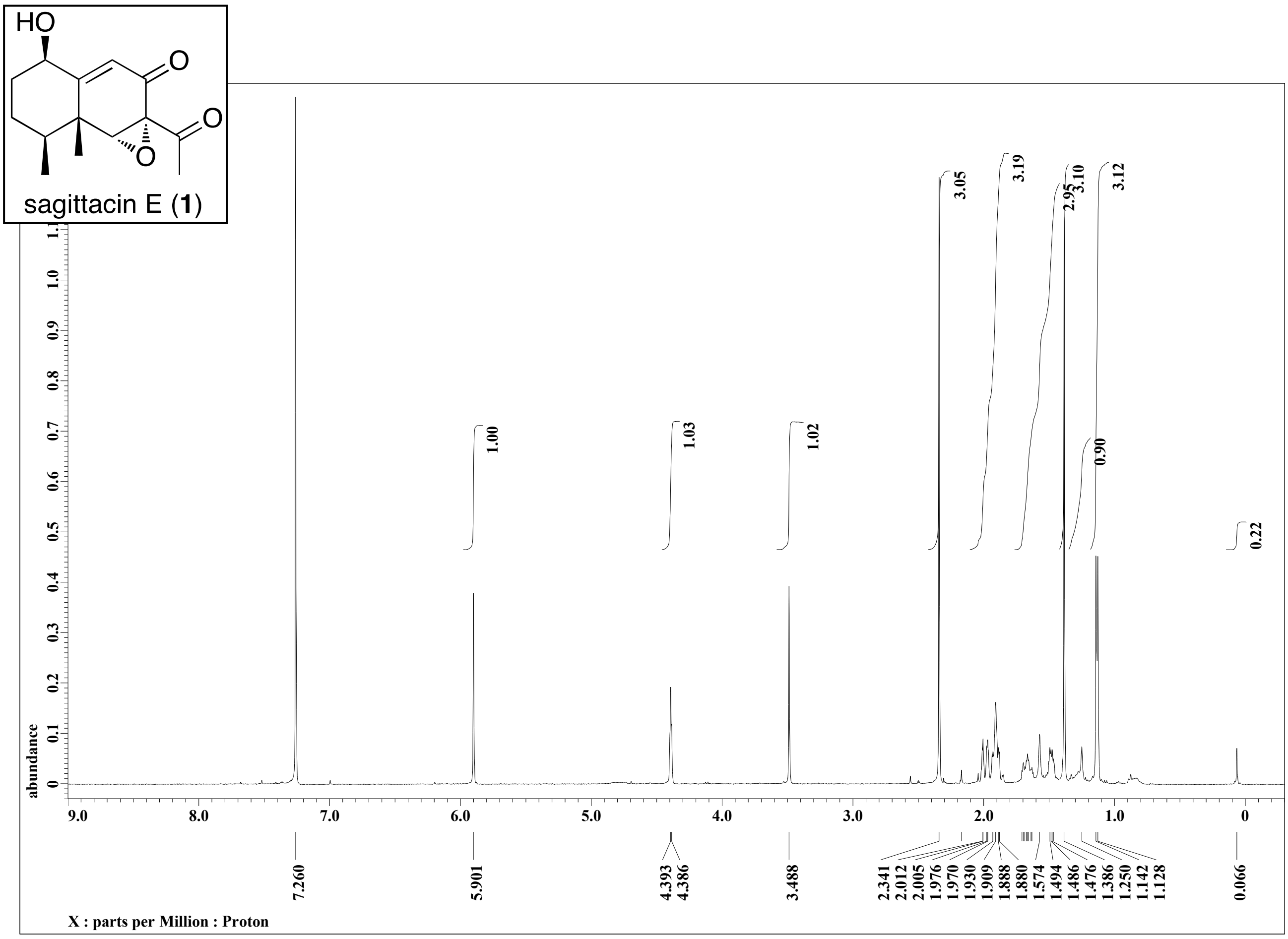
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.00
1.06
1.09
3.16
0.88
5.99
2.75
9.67
6.37
3.63
1.47
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
6.060
5.440
5.433
3.496
2.348
2.054
2.052
2.023
1.995
1.988
1.714
1.680
1.560
1.380
1.291
1.252
1.152
1.136
0.895
0.878
0.867
0.851
0.068
X : parts per Million : Proton


(thousandths)
0
0.1
0.2
0.3
0.4
0.5
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
-10.0
200.464
190.920
169.454
157.773
125.795
77.700
77.326
77.211
77.000
76.684
74.317
66.536
63.421
40.749
37.404
30.840
28.186
24.994
21.267
18.497
15.699
X : parts per Million : Carbon13


HO
O
O
3
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
1.00
1.15
1.00
0.99
3.06
2.38
5.80
3.05
3.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.678
7.260
6.195
4.567
4.560
4.553
2.558
2.338
2.089
2.061
2.053
1.649
1.640
1.631
1.615
1.605
1.599
1.591
1.530
1.394
1.152
1.134
X : parts per Million : Proton


(thousandths)
0
1.0
2.0
3.0
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
-10.0
198.691
184.260
164.692
161.587
135.905
126.926
77.316
77.201
77.000
76.674
73.359
44.055
40.816
34.271
30.974
24.812
18.632
15.987
X : parts per Million : Carbon13


sagittacin E (**1**)

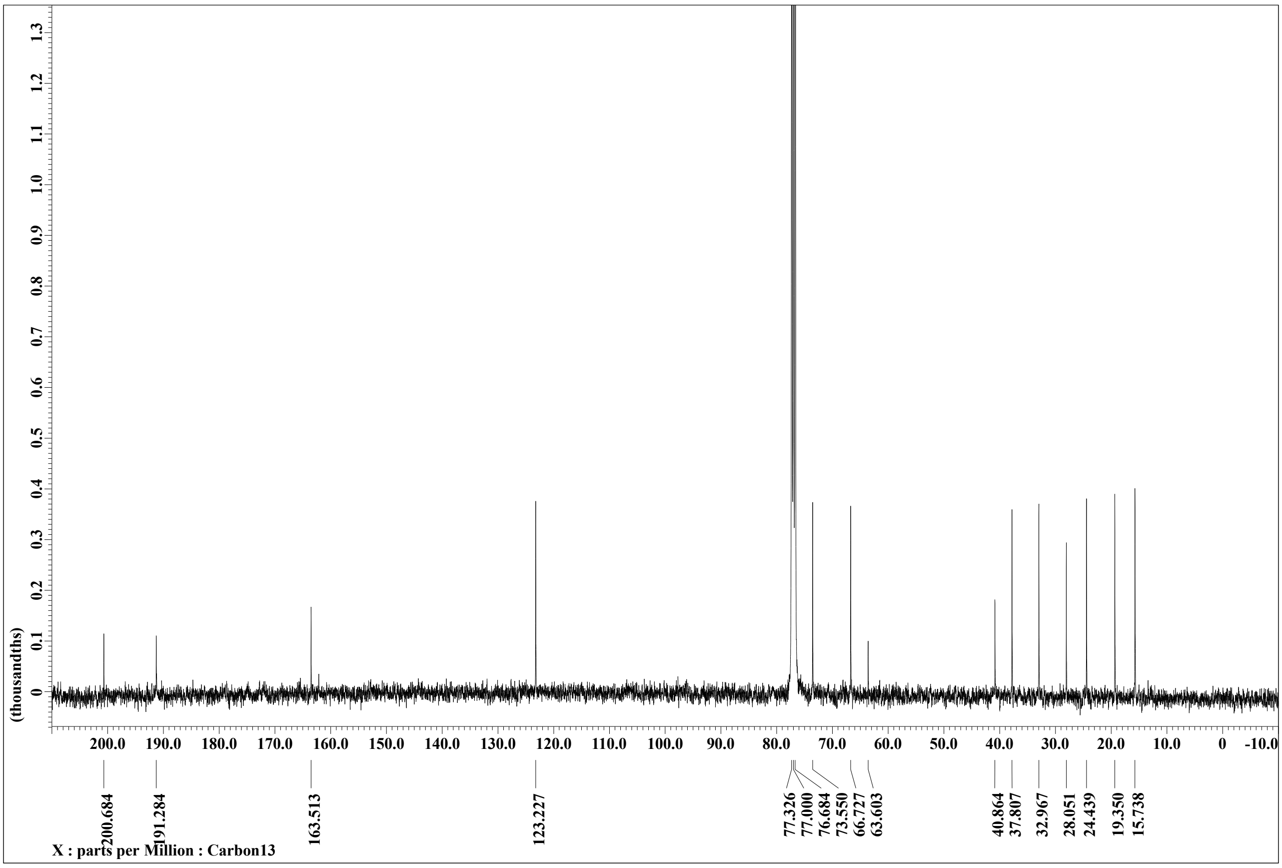


Figure S1. ORTEP drawing of X-ray crystallographic analysis of **26**.

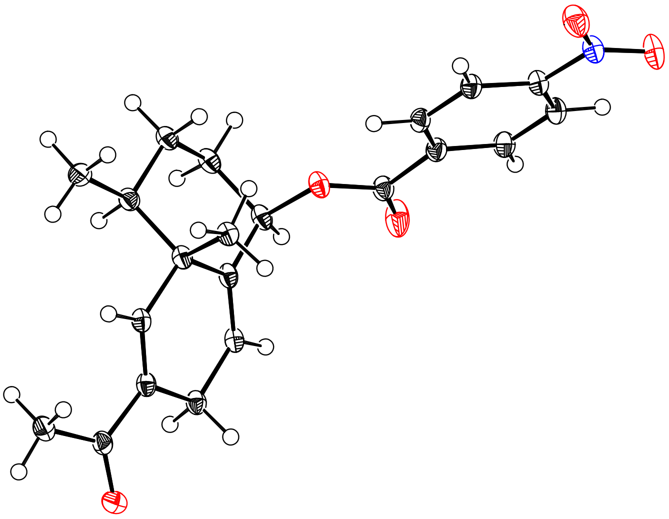


Figure S2. ORTEP drawing of X-ray crystallographic analysis of **4**.

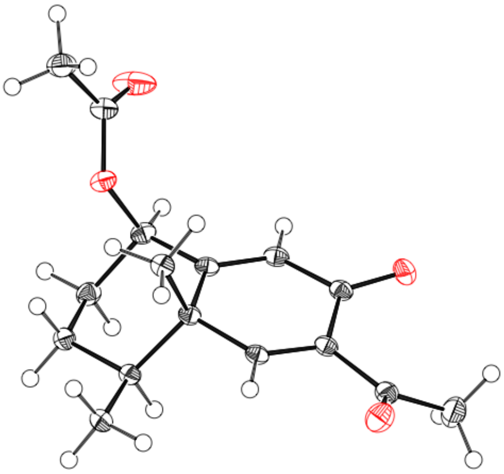


Figure S3. ORTEP drawing of X-ray crystallographic analysis of **2**.

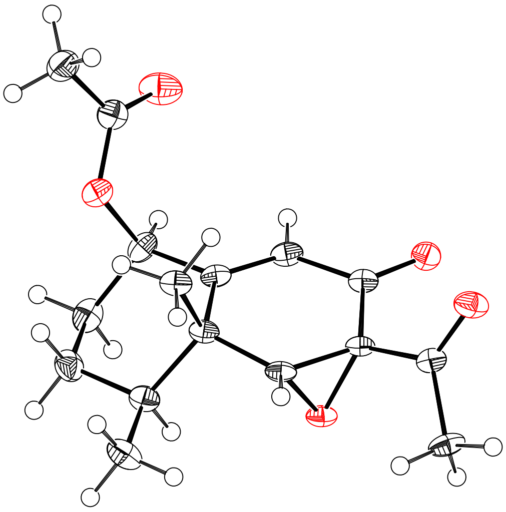
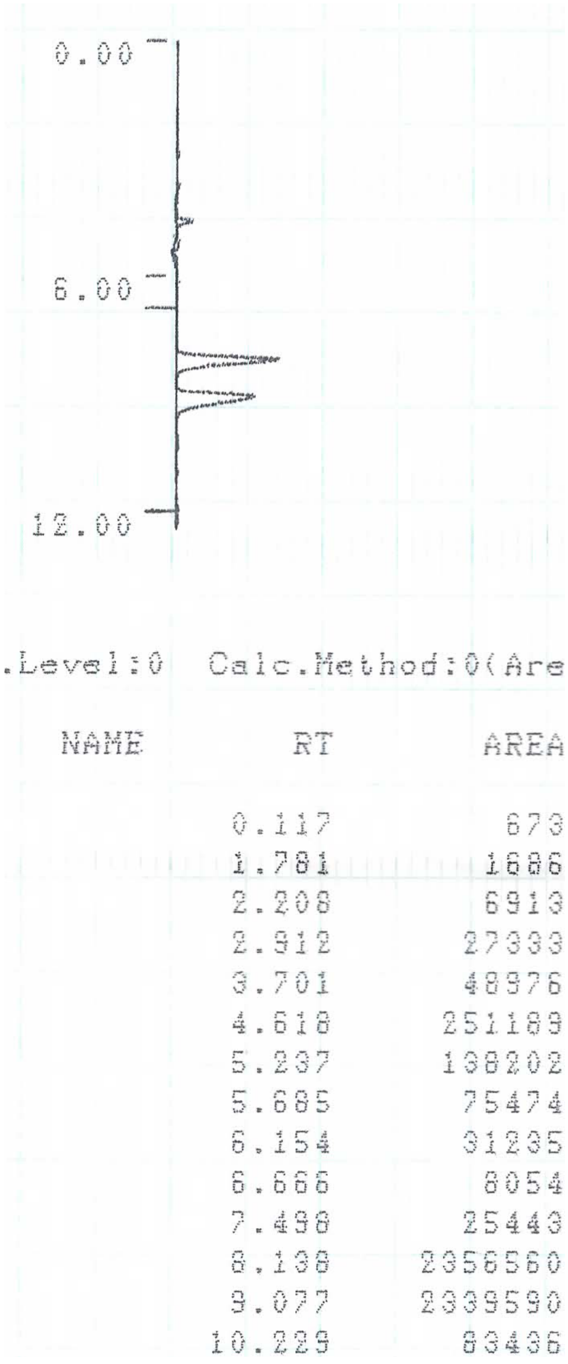


Figure S4. Chiral HPLC analysis of compound **14**.

Chiralcel AD-H column, hexane–*i*-PrOH, 150:1, 1.0 mL/min, 254 nm.

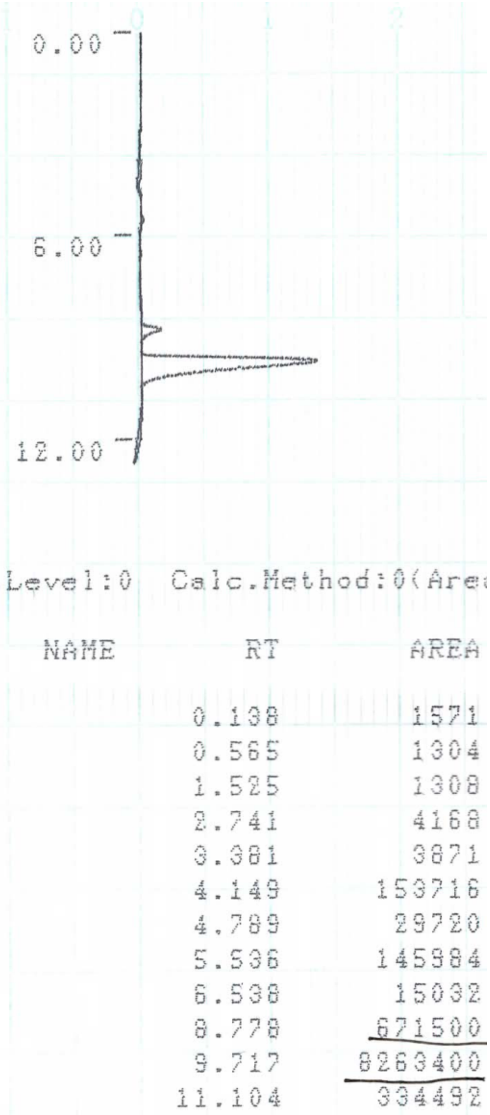
(+)-**14** (minor); t_R = 8.8 min, (–)-**14** (major); t_R = 9.7 min.

(±)-**14**



```
.Level:0   Calc.Method:0(Are

  NAME          RT          AREA

              0.117          673
              1.781         1686
              2.208         6913
              2.912        27333
              3.701        48976
              4.618       251189
              5.237       138202
              5.685        75474
              6.154        31235
              6.666         8054
              7.498        25443
              8.138      2356560
              9.077      2339590
             10.229        83436
```

(–)-**14**



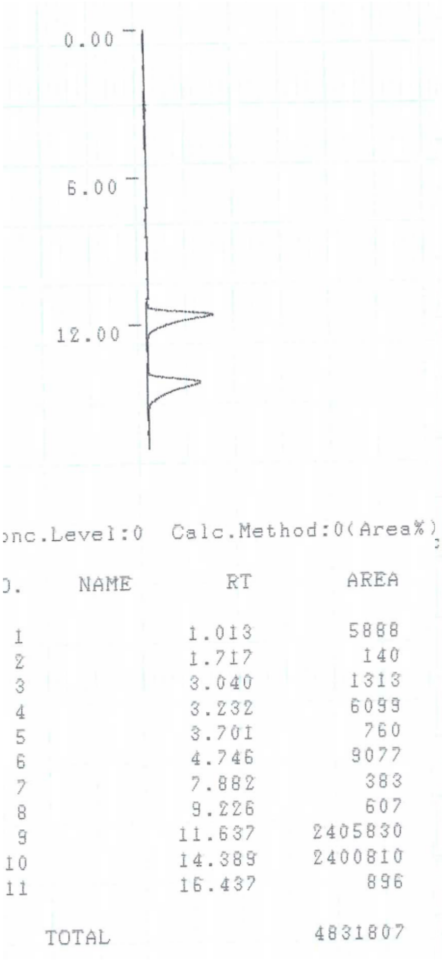
```
Level:0   Calc.Method:0(Are

  NAME          RT         AREA

              0.138         1571
              0.565         1304
              1.525         1308
              2.741         4168
              3.381         3871
              4.149       153716
              4.789        29720
              5.536       145984
              6.538        15032
              8.778       671500
              9.717      8263400
             11.104       334492
```

Figure S5. Chiral HPLC analysis of benzoate **S1**.

Chiralcel AD-H column, hexane–*i*-PrOH, 10:1, 1.0 mL/min, 254 nm.

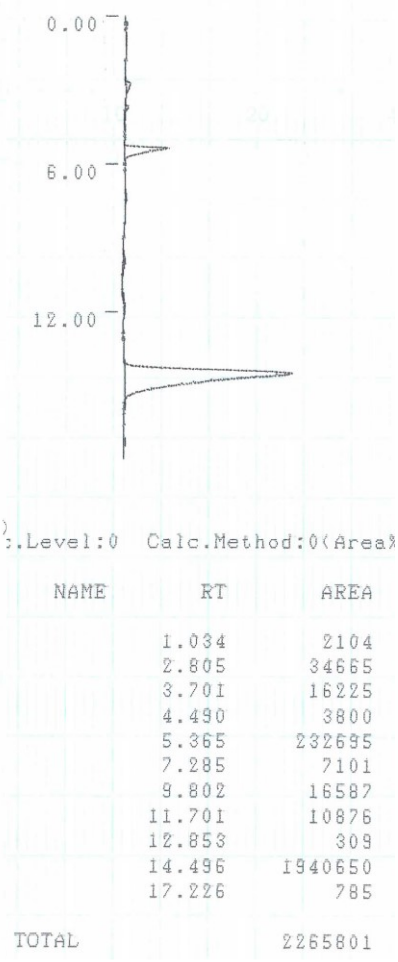
(+)-**S1** (minor); t_R = 11.8 min, (–)-**S1** (major); t_R = 14.6 min.

(±)-**S1**



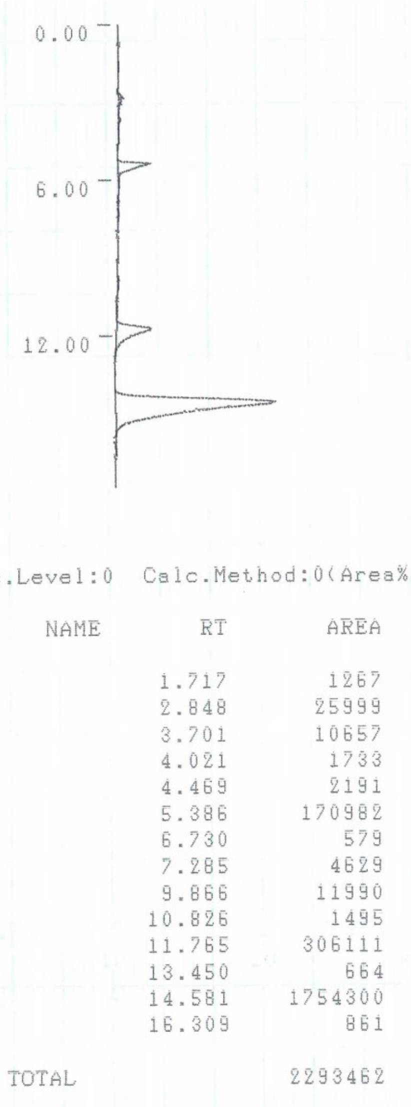
```
onc.Level:0  Calc.Method:0(Area%)

0.    NAME        RT        AREA

 1              1.013       5888
 2              1.717        140
 3              3.040       1313
 4              3.232       6099
 5              3.701        760
 6              4.746       9077
 7              7.882        383
 8              9.226        607
 9             11.637    2405830
10             14.389    2400810
11             16.437        896

   TOTAL                 4831807
```

Synthetic (–)-**S1**



```
:.Level:0  Calc.Method:0(Area%

   NAME        RT        AREA

             1.034       2104
             2.805      34665
             3.701      16225
             4.490       3800
             5.365     232695
             7.285       7101
             9.802      16587
            11.701      10876
            12.853        309
            14.496    1940650
            17.226        785

TOTAL                 2265801
```

Mixture of (±)- and (–)-**S1**



```
:.Level:0  Calc.Method:0(Area%

   NAME        RT        AREA

             1.717       1267
             2.848      25999
             3.701      10657
             4.021       1733
             4.469       2191
             5.386     170982
             6.730        579
             7.285       4629
             9.866      11990
            10.826       1495
            11.765     306111
            13.450        664
            14.581    1754300
            16.309        861

TOTAL                 2293462
```