Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Protecting Group Free Enantiospecific Total Syntheses of Structurally Diverse Natural Products of Tetrahydrocannabinoid Family

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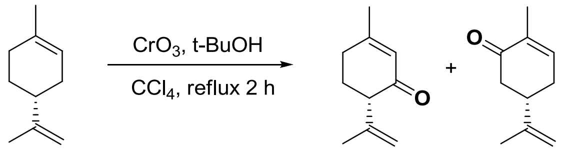
1. General Information:

General Aspects: All reactions were carried out under nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise mentioned. All the chemicals were purchased commercially, and used without further purification. Anhydrous THF and diethyl ether were distilled from sodium benzophenone, and dichloromethane was distilled from calcium hydride. Yields refer to chromatographically pure compounds, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as a visualizing agent and an p-anisaldehyde or ninhydrine stain, and heat as developing agents. Merck silica gel (particle size 100-200 and 230-400 mesh) was used for flash column chromatography. Neat coumpounds were used for record IR spectra. NMR spectra were recorded on either a Bruker Avance 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), Bruker Avance 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz), or JEOL DELTA (ECX) 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz). Mass spectrometric data were obtained using WATERS-Q-Tof-Premier-HAB213 and WATERS-Q-Tof-Premier-ESI-MS instruments. Melting points measurements were made using a hot stage apparatus. Optical rotations were measured using a polarimeter (AUTOPOL II) at 28 °C.

The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of a doublet of a doublet, dt = doublet of a triplet, td = triplet of a doublet, m = multiplet, br = broad.

2. Experimental Procedures:

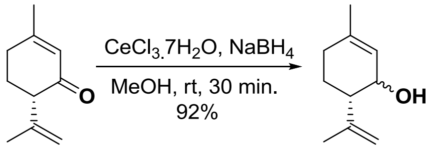
Synthesis of compound enone 14a:



14a 40% **Carvone** 55%

To a magnetically stirred solution of tertiary butyl alcohol (60 ml) was added chromium trioxide (24 g) in small portions and stirred for 15 min. Then the mixture was extracted with CCl_4 (160 ml). The organic layer was dried over sodium sulphate, concentrated to half of the volume. To this *R*-(+)-Limonene (8 g) was added and reflux for 2 h. Then reaction mixture was filtered and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:9) as eluent furnished the carvone (4.8 g, 55%) as colourless liquid; *Rf* = 0.6 (EtOAc-hexane 1:9); further elution of column using EtOAc-hexane (1:9) as eluent furnished the compound enone **14a** (3.5 g, 40%) as yellowish liquid; *Rf* = 0.5 (EtOAc-hexane 1:9); $[\alpha]_D^{28}$ = +27.88 (*c* 0.54, $CHCl_3$); **IR** (neat): ν_{max}/cm^{-1} 3076, 2927, 1667, 1435, 1379, 1201, 1087, 891 ; ^{1}**H NMR** ($CDCl_3$, 400 MHz): δ 5.89 (s, 1H), 4.93 (s, 1H), 4.74 (s, 1H), 2.94 (q, *J* = 6.0 Hz, 1H), 2.35-2.31 (m, 2H), 2.11-1.98 (m, 2H), 1.94 (s, 3H), 1.73 (s, 3H); ^{13}**C NMR** ($CDCl_3$, 100 MHz): δ 199.4, 161.9, 143.3, 126.7, 113.6, 53.8, 30.3, 27.6, 24.2, 20.6; **HRMS**: m/z calcd for $C_{10}H_{14}O$ $[M]^+$: 150.1045; found: 150.1043.

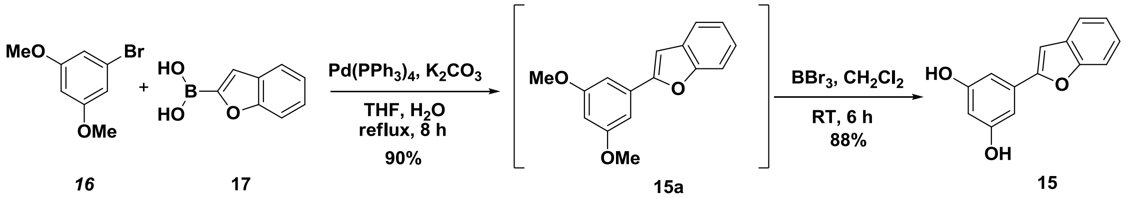
Synthesis of compound alcohol 14:



14a **14**

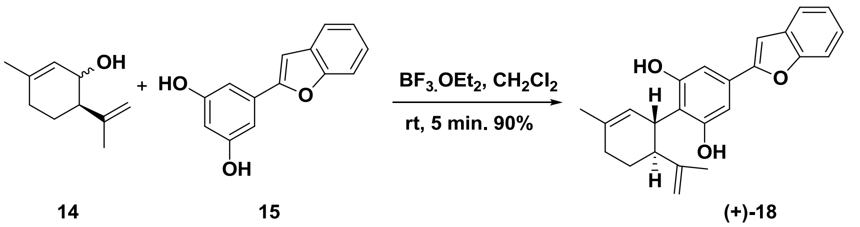
To a magnetically stirred solution of the enone **14a** (2 g, 13.3 mmol) in anhydrous MeOH (50 ml) was added $CeCl_3.7H_2O$ (1.91 g, 6.6 mmol) at RT and stirred for 10 min. Then $NaBH_4$ (608 mg, 16 mmol) was added portion wise at 0 °C. The reaction mixture was stirred for 30 min. at RT and quenched with water. Then it was extracted with CH_2Cl_2 (30 ml x 3), dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1: 9) as eluent furnished the alcohol **14** (1.84 g, 92%) as pale yellow liquid; *Rf* = 0.6 (EtOAc-hexane 1:9); **IR** (neat): ν_{max}/cm^{-1} 3396, 2925, 2854, 1453, 1375, 1035, 887; ^{1}**H NMR** ($CDCl_3$, 400 MHz): δ 5.67, 5.43(s, 1H), 4.84, 4.80 (s, 1H), 4.12 (s, 1H), 2.11-2.00(m, 3H), 1.83 (s, 3H), 1.71(s, 3H), 1.68 (s, 1H), 1.60-1.55 (m, 1H) ; ^{13}**C NMR** ($CDCl_3$, 100 MHz): δ 146.5, 146.4, 139.6, 136.6, 124.3, 122.3, 112.2, 111.6, 68.6, 63.7, 50.8, 46.0, 31.1, 30.1, 26.1, 23.4, 23.0, 22.5, 20.8, 19.3; **HRMS**: m/z calcd for $C_{10}H_{16}O$ $[M+H]^+$: 152.1201; found: 152.1209.

Synthesis of compound 15:



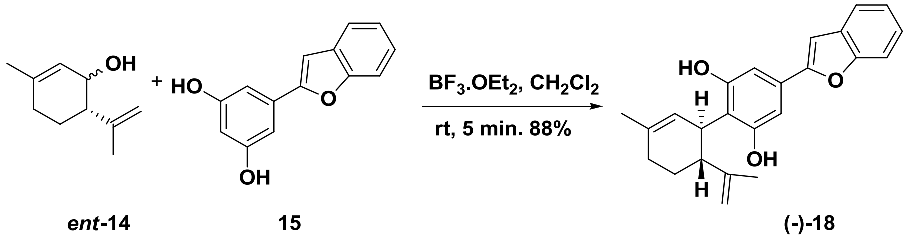
To a magnetically stirred solution of the resorcinol derivative **16** (651 mg, 3.0 mmol) and benzofuran boronic acid **17** (486 mg, 3.0 mmol) in THF/H_2O (15/15 ml) was added $Pd(PPh_3)_4$ (173 mg, 0.15 mmol) and K_2CO_3 (575 mg, 4.2 mmol). The reaction mixture was reflux for 8 h. Saturated aqueous solution of NH_4Cl (10 ml) was then added to the reaction mixture, extracted with EtOAc (20 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent furnished the compound **15a** (686 mg, 90%) as yellowish semi solid; *Rf* = 0.5 (EtOAc-hexane 1:9). Without purification, further compound **15a** was demethylated using BBr_3 (666 mg, 27 mmol) in CH_2Cl_2 (30 ml) and reactiom mixture was stirred at RT for 6 h. Crushed ice was then added to the reaction mixture, extracted with CH_2Cl_2 (20 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (2:3) as eluent furnished the compound **15** (672 mg, 88%) as yellowish semi solid; *Rf* = 0.4 (EtOAc-hexane 2:3). **IR** (neat): v_{max}/cm^{-1} 3337, 1611, 1575, 1450, 1155, 999, 953, 748;^{1}**H NMR** (CD_3OD, 400 MHz): δ 7.55 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.24 (td, *J* = 7.3 and 1.3 Hz, 1H), 7.18 (td, *J* = 7.5 and 1.1 Hz, 1H), 7.02 (s, 1H), 6.86 (d, *J* = 2.3 Hz, 2H), 6.32 (t, *J* = 2.1 Hz, 1H); ^{13}**C NMR** (CD_3OD, 100 MHz): δ 160.1, 157.5, 156.2, 133.6, 130.6, 125.4, 124.1, 122.0, 111.9, 104.6, 104.3, 102.4; **HRMS**: m/z calcd for $C_{14}H_{10}O_3$ $[M+H]^+$: 227.0708; found: 227.0700.

Synthesis of compound (+)-18:



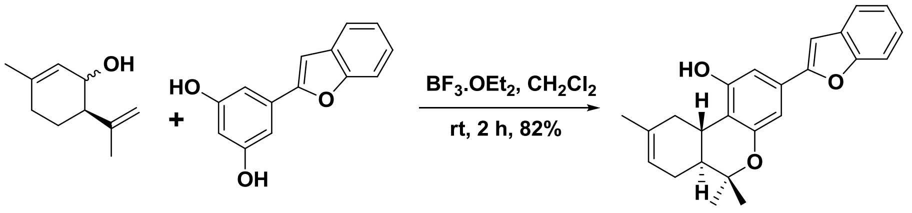
To a magnetically stirred solution of the resorcinol derivative **15** (500 mg, 2.21 mmol) and $BF_3 \cdot OEt_2$ (156 mg, 1.10 mmol) in anhydrous CH_2Cl_2 (10 ml) was added alcohol **14** (336 mg, 2.21 mmol) drop wise. The resulting purplish red solution was stirred for 5 min. at RT. Aq. $NaHCO_3$ (10 ml) was added to the reaction mixture, extracted with CH_2Cl_2 (20 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:4) as eluent furnished the diol **(+)-18** (720 mg, 90%) as yellowish liquid; *Rf* = 0.5 (EtOAc-hexane 1:4); $[\alpha]_D^{28}$ = +69 (*c* 0.46, $CHCl_3$); **IR** (neat): v_{max}/cm^{-1} 3418, 2925, 1626, 1567, 1453, 1246, 1029, 749; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.54 (d, *J* = 7.5 Hz, 1H), 7.47 (dd, *J* = 7.5 Hz, 1H), 7.27-7.18 (m, 2H), 6.95-6.86 (m, 3H), 6.17 (brs, 1H), 5.58 (s, 1H), 5.00 (brs, 1H), 4.65 (s, 1H), 4.55 (s, 1H), 3.97-3.93 (m, 1H), 2.46 (ddd, *J* = 14.4, 11.0 and 3.4 Hz, 1H), 2.26 (brs, 1H), 2.19-2.06 (m, 1H), 1.86-1.83 (m, 2H), 1.81 (s, 3H), 1.69 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 156.6, 155.4, 154.7, 154.5, 148.7, 140.7, 129.9, 129.1, 124.1, 123.4, 122.8, 120.8, 117.4, 111.2, 111.0, 106.5, 104.3, 101.3, 46.1, 37.1, 30.4, 28.2, 23.7, 20.1; **HRMS**: m/z calcd for $C_{24}H_{24}O_3$ $[M+H]^+$: 361.1805; found: 361.1802.

Synthesis of compound (-)-18:



To a magnetically stirred solution of the resorcinol derivative **15** (250 mg, 1.105 mmol) and $BF_3 \cdot OEt_2$ (78 mg, 0.55 mmol) in anhydrous CH_2Cl_2 (6 ml) was added alcohol ***ent*-14** (16 mg, 1.105 mmol) drop wise. The resulting purplish red solution was stirred for 5 min. at RT. Aq. $NaHCO_3$ (5 ml) was added to the reaction mixture, extracted with CH_2Cl_2 (20 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:4) as eluent furnished the diol **(-)-18** (360 mg, 88%) as yellowish liquid; *Rf* = 0.5 (EtOAc-hexane 1:4); $[\alpha]_D^{28}$ = -66 (*c* 0.46, $CHCl_3$).

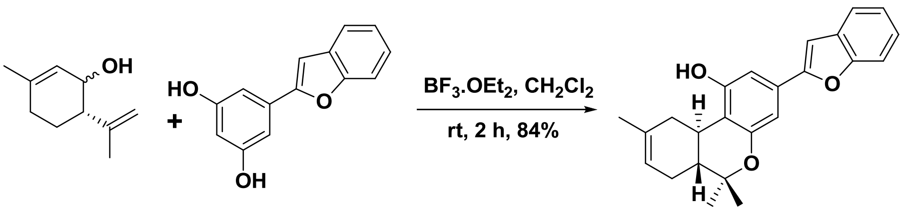
Synthesis of compound (+)-19:



14 **15** **(+)-19**

To a magnetically stirred solution of the dialcohol **15** (500 mg, 2.21 mmol) and $BF_3{\cdot}OEt_2$ (623 mg, 4.42 mmol) in anhydrous CH_2Cl_2 (10 ml) was added alcohol **14** (336 mg, 2.21 mmol) dropwise. The resulting purplish red solution was stirred for 2 h. at RT. Aq. $NaHCO_3$ (30 ml) was added to the reaction mixture, extracted with CH_2Cl_2 (20 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:4) as eluent furnished the compound **(+)-19** (655 mg, 82%) as yellowish semi solid; *Rf* = 0.55 (EtOAc-hexane 1:4); $[\alpha]_D^{28}$ = +143 (*c* 0.43, $CHCl_3$); **IR** (neat): v_{max}/cm^{-1} 3386, 2971, 2926, 1621, 1556, 1452, 1420, 1259, 1084, 964, 749; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.28 (td, *J* = 7.9 and 1.2 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.97 (s, 1H), 6.92 (s, 1H), 6.83 (s, 1H), 5.47 (s, 1H), 5.14 (brs, 1H), 3.25 (dd, *J* = 17.1 and 4.3 Hz, 1H), 2.81-2.76 (m, 1H), 2.20-2.17 (m, 1H), 1.92-1.85 (m, 3H), 1.73 (s, 3H), 1.44 (s, 3H), 1.16 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 155.5, 155.4, 155.3, 154.7, 134.6, 129.7, 129.2, 124.1, 122.8, 120.8, 119.3, 114.1, 111.0, 107.1, 103.9, 101.2, 77.1, 44.8, 35.8, 31.8, 27.8, 27.5, 23.5, 18.5; **HRMS**: m/z calcd for $C_{24}H_{24}O_3$ $[M+H]^+$: 361.1805; found: 361.1801.

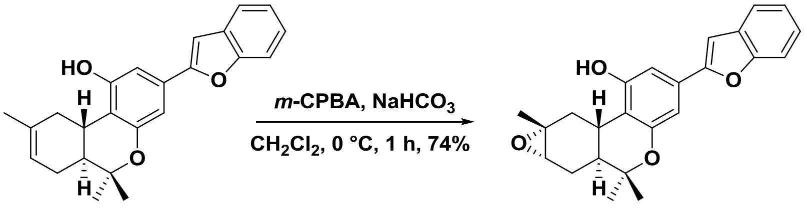
Synthesis of compound (-)-19:



***ent*-14** **15** **19**

To a magnetically stirred solution of the dialcohol **15** (250 mg, 1.105 mmol) and $BF_3{\cdot}OEt_2$ (312 mg, 2.21 mmol) in anhydrous CH_2Cl_2 (6 ml) was added alcohol ***ent*-14** (168 mg, 1.105 mmol) dropwise. The resulting purplish red solution was stirred for 2 h. at RT. Aq. $NaHCO_3$ (15 ml) was added to the reaction mixture, extracted with CH_2Cl_2 (15 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:4) as eluent furnished the compound **(-)-19** (328 mg, 84%) as yellowish semi solid; *Rf* = 0.55 (EtOAc-hexane 1:4); $[\alpha]_D^{28}$ = -149 (*c* 0.43, $CHCl_3$).

Synthesis of compound (+)-20:

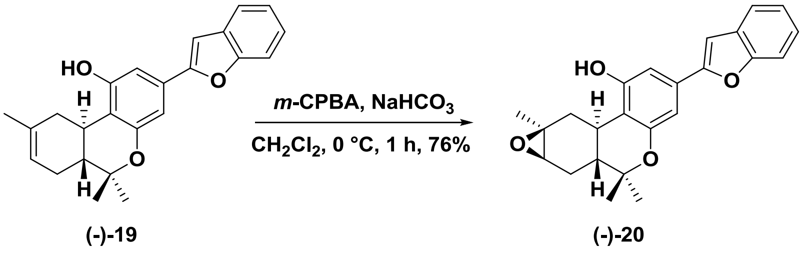


(+)-19

(+)-20

To a magnetically stirred solution of the compound **(+)-19** (200 mg, 0.55 mmol) in anhydrous CH_2Cl_2 (20 ml) was added $NaHCO_3$ (93 mg, 1.11 mmol) at 0 °C. After 10 min solution of *m*-CPBA (115 mg, 0.66 mmol) in CH_2Cl_2 (2 ml) was added and the mixture was stirred for next 1 h. Quenched the reaction with saturated solution of $NaHCO_3$, extracted with CH_2Cl_2 (15 ml x 3), organic layer was then washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (2:3) as eluent gave the epoxide **(+)-20** (155 mg, 74%) as yellowish waxy oil; *Rf* = 0.45 (EtOAc-hexane 2:3); $[\alpha]_D^{28}$ = +110 (*c* 0.20, $CHCl_3$); **IR** (neat): ν_{max}/cm^{-1} 3338, 2977, 2923, 1621, 1566, 1453, 1421, 1262, 1083, 750; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.55 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.27 (brt, *J* = 7.1 Hz, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.91 (s, 1H), 6.90 (s, 1H), 6.86 (s, 1H), 6.12 (brs, 1H), 3.47 (dd, *J* = 14.4 and 3.4 Hz, 1H), 3.20 (d, *J* = 5.5 Hz, 1H), 2.75 (brt, *J* = 8.9 Hz, 1H), 2.22-2.12 (m, 1H), 1.66 (d, *J* = 9.1 Hz, 2H), 1.49-1.44 (m, 1H), 1.41 (s, 3H), 1.37 (s, 3H), 1.03 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 155.5, 155.4, 155.2, 154.6, 129.6, 129.1, 124.1, 122.8, 120.8, 113.2, 111.0, 106.7, 104.3, 101.1, 77.2, 59.6, 59.4, 44.5, 34.8, 28.1, 27.3, 26.7, 22.9, 18.3; **HRMS**: m/z calcd for $C_{24}H_{24}O_4$ $[M+H]^+$: 377.1755; found: 377.1754.

Synthesis of compound (-)-20:

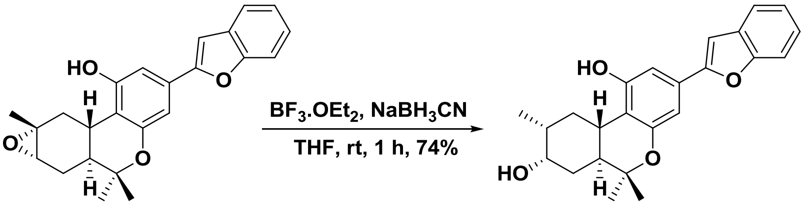


(-)-19

(-)-20

To a magnetically stirred solution of the compound **(-)-19** (100 mg, 0.275 mmol) in anhydrous CH_2Cl_2 (10 ml) was added $NaHCO_3$ (47 mg, 0.555 mmol) at 0 °C. After 10 min solution of *m*-CPBA (58 mg, 0.33 mmol) in CH_2Cl_2 (1 ml) was added and the mixture was stirred for next 1 h. Quenched the reaction with saturated solution of $NaHCO_3$, extracted with CH_2Cl_2 (15 ml x 3), organic layer was then washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (2:3) as eluent gave the epoxide **(-)-20** (78 mg, 76%) as yellowish waxy oil; *Rf* = 0.45 (EtOAc-hexane 2:3); $[\alpha]_D^{28}$ = -116 (*c* 0.20, $CHCl_3$);

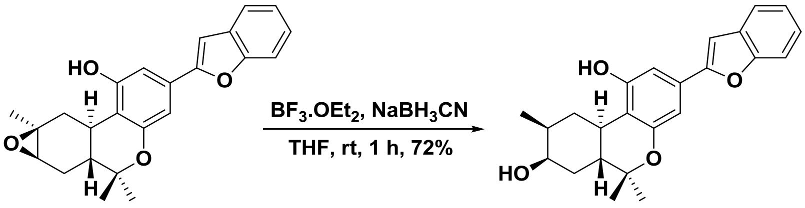
Synthesis of (+)-*epi*-machaeriol D 21:



(+)-20 **21 (+)-*Epi*-machaeriol D**

To a magnetically stirred solution of the compound (+)-**20** (100 mg, 0.26 mmol) in anhydrous THF (5 ml) was added $NaBH_3CN$ (32 mg, 0.53 mmol) at 0 °C followed by $BF_3{\cdot}OEt_2$ (75 mg, 0.53 mmol) and the mixture was stirred for 1 h at room temperature. Quenched the reaction with water, extracted with EtOAc (15 ml x 3), organic layer was then washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (2:3) as eluent gave the (+)- *epi*-machaeriol D **21** (74 mg, 74%) as yellowish semi solid; *Rf* = 0.5 (EtOAc-hexane 2:3); $[\alpha]_D^{28}$ = +115 (*c* 0.07, $CHCl_3$); **IR** (neat): ν_{max}/cm^{-1} 3368, 2925, 1620, 1564, 1452, 1260, 1134, 1041, 966, 750; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.56 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 6.8 Hz, 1H), 7.21 (t, *J* = 6.8 Hz, 1H), 6.93 (d, *J* = 1.1 Hz, 1H), 6.90 (s, 1H), 6.80 (d, *J* = 1.7 Hz, 1H), 5.28 (brs, 1H), 4.00 (s, 1H), 2.89 (dt, *J* = 13.1 and 3.4 Hz, 1H), 2.56 (td, *J* = 10.8 and 2.8 Hz, 1H), 2.01 (brt, 2H), 1.87-1.81 (m, 1H), 1.65 (brs, 2H), 1.42 (s, 3H), 1.12 (s, 3H), 1.06 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 155.5, 155.4, 155.3, 154.7, 129.6, 129.1, 124.1, 122.8, 120.8, 113.3, 111.0, 107.0, 103.8, 101.1, 77.1, 70.4, 41.4, 36.7, 35.7, 35.4, 31.7, 27.5, 18.9, 18.1; **HRMS**: m/z calcd for $C_{24}H_{26}O_4$ $[M+H]^+$: 379.1911; found: 379.1902.

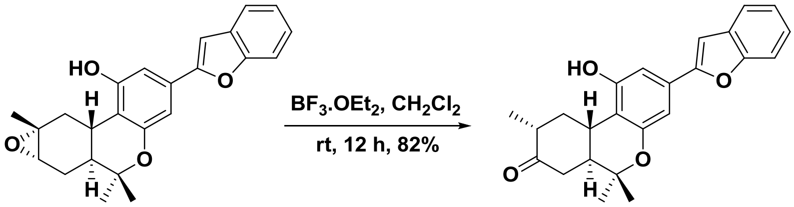
Synthesis of (-)-*epi*-machaeriol D 21:



(-)-20 **21 (-)-*Epi*-machaeriol D**

To a magnetically stirred solution of the compound (-)-**20** (50 mg, 0.13 mmol) in anhydrous THF (03 ml) was added $NaBH_3CN$ (16 mg, 0.265 mmol) at 0 °C followed by $BF_3{\cdot}OEt_2$ (38 mg, 0.265 mmol) and the mixture was stirred for 1 h at room temperature. Quenched the reaction with water, extracted with EtOAc (10 ml x 3), organic layer was then washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (2:3) as eluent gave the (-) - *epi*-machaeriol D **21** (37 mg, 72%) as yellowish semi solid; *Rf* = 0.5 (EtOAc-hexane 2:3); $[\alpha]_D^{28}$ = -119 (*c* 0.07, $CHCl_3$).

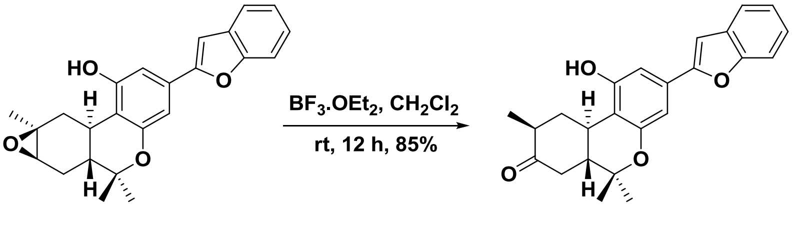
Synthesis of compound (+)-22:



(+)-20 **(+)-22**

To a magnetically stirred solution of the epoxide (+)-**20** (150 mg, 0.39 mmol) in anhydrous CH_2Cl_2 (05 ml) was added $BF_3{\cdot}OEt_2$ (112 mg, 0.79 mmol). The resulting purplish red solution was stirred for 12 h. at RT. Aq. $NaHCO_3$ (10 ml) was added to the reaction mixture, extracted with CH_2Cl_2 (10 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (2:3) as eluent furnished the ketone **22** (130 mg, 82%) as white solid; *Rf* = 0.45 (EtOAc-hexane 2:3); $[\alpha]_D^{28}$ = +91 (*c* 0.18, $CHCl_3$); **MP**: 204 °C; **IR** (neat): v_{max}/cm^{-1} 3416, 2968, 2929, 2874, 1694 (CO), 1622, 1566, 1453, 1089, 960, 802, 65; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.57 (d, *J* = 6.8 Hz, 1H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.28 (td, *J* = 5.7 and 1.3 Hz, 1H), 7.23 (td, *J* = 6.4 and 0.9 Hz, 1H), 6.96 (d, *J* = 1.6 Hz, 1H), 6.94 (d, *J* = 0.9 Hz, 1H), 6.85 (d, *J* = 1.6 Hz, 1H), 5.26 (s, 1H), 3.55-3.50 (m, 1H), 3.05 (td, *J* = 8.2 and 3.0 Hz, 1H), 2.66-2.54 (m, 2H), 2.22 (t, *J* = 14.2 Hz, 1H), 2.02-1.95 (m, 1H), 1.62 (s, 1H), 1.40 (s, 3H), 1.21 (s, 3H), 1.14 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 211.4, 155.3, 155.2, 155.1, 154.7, 130.2, 129.0, 124.3, 122.9, 120.9, 111.7, 111.1, 107.1, 104.0, 101.5, 76.7, 49.6, 44.9, 43.5, 37.6, 35.2, 27.2, 18.5, 14.4; **HRMS**: m/z calcd for $C_{24}H_{24}O_4$ $[M+H]^+$: 377.1753; found: 377.1759.

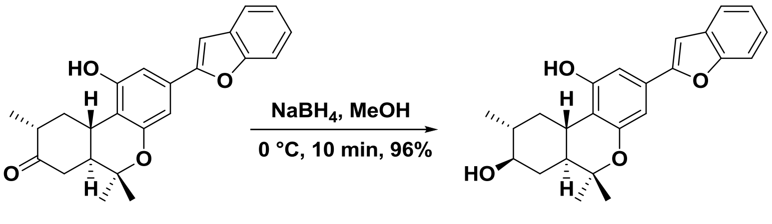
Synthesis of compound (-)-22:



(-)-20 (-)-22

To a magnetically stirred solution of the epoxide (-)-**20** (75 mg, 0.195 mmol) in anhydrous CH_2Cl_2 (4 ml) was added $BF_3 \cdot OEt_2$ (56 mg, 0.395 mmol). The resulting purplish red solution was stirred for 12 h. at RT. Aq. $NaHCO_3$ (5 ml) was added to the reaction mixture, extracted with CH_2Cl_2 (10 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (2:3) as eluent furnished the ketone (-)-**22** (65 mg, 85%) as white solid; *Rf* = 0.45 (EtOAc-hexane 2:3); $[\alpha]_D^{28}$ = -92 (*c* 0.18, $CHCl_3$).

Synthesis of (+)-machaeriol D 7:



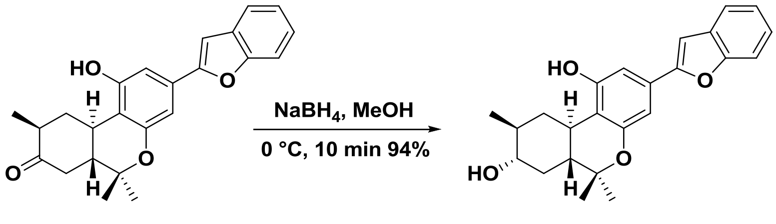
(+)-22 7 (+)-Machaeriol D

To a magnetically stirred solution of the compound (+)-**22** (100 mg, 0.26 mmol) in anhydrous MeOH (05 ml) was added $NaBH_4$ (20 mg, 0.53 mmol) at 0 °C and the mixture was stirred for 10 min. Quenched the reaction with crushed ice and then water, extracted with EtOAc (10 ml x 3), organic layer was then washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (2:3) as eluent gave the **machaeriol D 7** (96 mg, 96%) as white crystalline solid; *Rf* = 0.45 (EtOAc-hexane 2:3); $[\alpha]_D^{28}$ = +82 (*c* 0.13, $CHCl_3$); **IR** (neat): ν_{max}/cm^{-1} 3519, 3260, 2925, 1622, 1565, 1424, 1268, 1133, 1018, 788, 750; **^{1}H NMR**

(DMSO-d_6, 400 MHz): δ 9.71 (s, 1H, Ar-OH), 7.63-7.58 (m, 2H), 7.32-7.23 (m, 3H), 6.89 (s, 1H), 6.77 (s, 1H), 4.63 (d, *J* = 5.4 Hz, 1H), 3.16-3.08 (m, 1H), 2.41(t, *J* = 11.3 and 2.3 Hz, 1H), 2.00-1.96 (m, 1H), 1.52-1.43 (m, 2H), 1.35 (s, 3H), 1.05 (s, 3H), 0.99 (d, *J* = 6.3 Hz, 3H), 0.73 (dt, *J* = 12.3 and 11.6 Hz, 1H); **^{13}C NMR** (DMSO-d_6, 125 MHz): δ 157.3, 155.3, 154.9, 154.0, 128.9, 128.6, 124.3, 123.1, 121.0, 113.2, 111.0, 104.7, 103.4, 101.3, 76.6, 74.7, 47.0, 39.7, 37.0, 36.2, 35.0, 27.4, 18.9, 18.8; **HRMS**: m/z calcd for $C_{24}H_{26}O_4$ $[M+H]^+$: 379.1909; found: 379.1909.

^{1}H NMR ($CDCl_3$ 1 DropDMSO-d_6, 400 MHz): δ 7.51 (br d, *J* = 7.2 Hz, 1H), 7.40 (br d, *J* = 7.7 Hz, 1H), 7.23 (dd br, *J* = 7.4, 7.9 Hz, 1H), 7.19 (dd, *J* = 2.7, 7.2 and 7.4 Hz, 1H), 6.89 (s, 1H), 6.86 (br s, 1H), 6.80 (br s, 1H), 3.25 (br ddd, *J* = 4.1, 10.3 and 10.6 Hz, 1H), 3.22 (dt, *J* = 2.8, 13.1 Hz, 1H), 2.51 (ddd, *J* = 2.0, 9.7 and 11.2 Hz, 1H), 2.08 (m, 1H), 1.56 (br t, *J* = 10.8, 10.9 Hz, 1H), 1.53 (m, 1H), 1.38 (s, 3H), 1.12 (m, 1H), 1.09 (s, 3H), 1.05 (d, *J* = 6.5 Hz, 3H), 0.83 (br t, *J* = 11.9, 12.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$1 DropDMSO-d_6, 125 MHz): δ 157.4, 156.5, 155.5, 154.9, 129.6, 129.6, 124.2, 123.0, 121.1, 113.7, 111.3, 105.9, 104.4, 101.0, 77.5, 76.6, 47.9, 40.9, 37.4, 36.8, 35.7, 28.0, 19.4, 18.9.

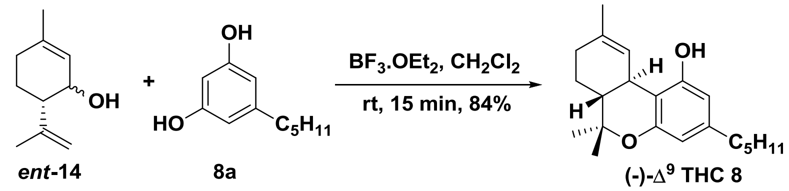
Synthesis of (-)-machaeriol D 7:



(-)-22 **7 (-)-Machaeriol D**

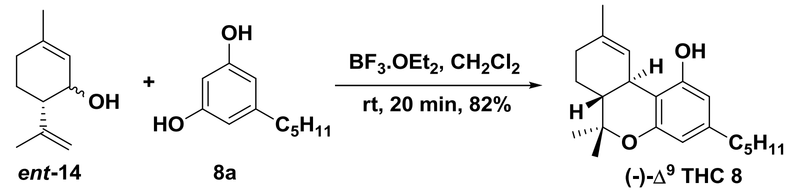
To a magnetically stirred solution of the compound (-)-**22** (50 mg, 0.13 mmol) in anhydrous MeOH (03 ml) was added $NaBH_4$ (10 mg, 0.265 mmol) at 0 °C and the mixture was stirred for 10 min. Quenched the reaction with crushed ice and then water, extracted with EtOAc (10 ml x 3), organic layer was then washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (2:3) as eluent gave the (-)-**machaeriol D 7** (47 mg, 94%) as white crystalline solid; *Rf* = 0.45 (EtOAc-hexane 2:3); $[\alpha]_D^{28}$ = -82 (*c* 0.13, $CHCl_3$).

Synthesis of (-)-Δ^9-THC 8:



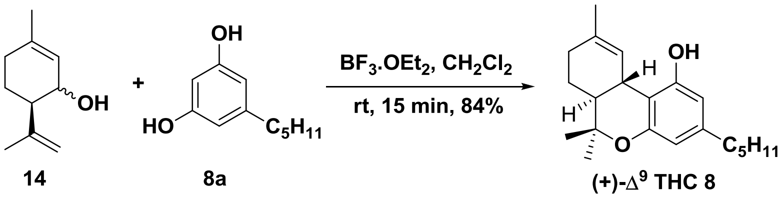
To a magnetically stirred solution of the commercially available olivetol **8a** (110 mg, 0.42 mmol) and alcohol ***ent*-14** (68 mg, 0.46 mmol) in anhydrous CH_2Cl_2 (8 ml), was added $BF_3{\cdot}OEt_2$ (14 mg, 0.10 mmol) in drop wise fashion. The resulting purplish red solution was stirred for 15 min at room temperature. Aq. $NaHCO_3$ (20 ml) was then added to the reaction mixture, extracted with CH_2Cl_2 (10 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:3) as eluent furnished **(-)-Δ^9-THC 8** (118 mg, 84%) as pale yellowish liquid; *Rf* = 0.5 (EtOAc-hexane 1:2); $[\alpha]_D^{28}$ = -68.5 (*c* 0.2,$CHCl_3$); lit -245 (*c* 0.78, $CHCl_3$); **IR** (neat): ν_{max}/cm^{-1} 3428, 2925, 2854, 1581, 1428, 1261, 1041; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 6.30 (s, 1H), 6.27 (s, 1H), 6.14 (s, 1H), 4.83 (brs, 1H), 3.19 (d, *J* = 11 Hz, 1H), 2.42 (t, *J* = 8.2 Hz, 2H), 2.16 (brs, 1H), 1.93-1.89 (m, 1H), 1.69 (s, 3H), 1.58-1.53 (m, 2H), 1.41 (s, 3H), 1.33-1.27 (m, 6H), 1.09 (s, 3H), 0.88 (t, *J* = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 154.8, 154.2, 142.8, 134.5, 123.8, 110.2, 109.1, 107.6, 77.2, 45.8, 35.5, 33.6, 31.6, 31.2, 30.7, 27.6, 25.1, 23.5, 22.6, 19.4, 14.1; **HRMS**: m/z calcd for $C_{21}H_{29}O_2$ $[M+H]^+$: 315.2326; found: 315.2320.

Gram Scale Synthesis of (-)-Δ^9-THC 8:



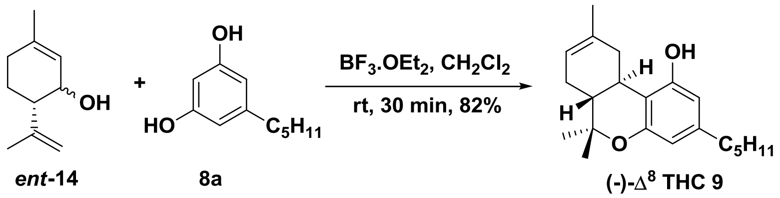
To a magnetically stirred solution of the commercially available olivetol **8a** (604 mg, 0.42 mmol) and alcohol ***ent*-14** (662 mg, 0.46 mmol) in anhydrous CH_2Cl_2 (30 ml), was added $BF_3{\cdot}OEt_2$ (136 mg, 0.10 mmol) in drop wise fashion. The resulting purplish red solution was stirred for 20 min at room temperature. Aq. $NaHCO_3$ (50 ml) was then added to the reaction mixture, extracted with CH_2Cl_2 (30 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:3) as eluent furnished **(-)-Δ^9-THC 8** (1.12 g, 82%).

Synthesis of (+)-Δ^9-THC 8:



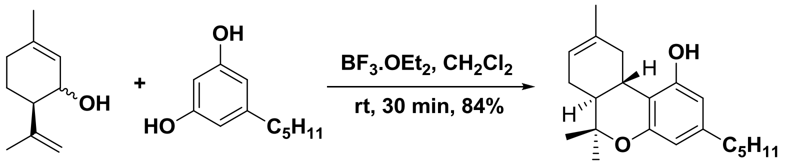
To a magnetically stirred solution of the commercially available olivetol **8a** (110 mg, 0.44 mmol) and alcohol **14** (69 mg, 0.46 mmol) in anhydrous CH_2Cl_2 (7 ml), was added $BF_3{\cdot}OEt_2$ (14 mg, 0.10 mmol) in drop wise fashion. The resulting purplish red solution was stirred for 15 min at room temperature. Aq. $NaHCO_3$ (10 ml) was then added to the reaction mixture, extracted with CH_2Cl_2, washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column using EtOAc-hexane (1:3) as eluent furnished the **(+)-Δ^9-THC 8** (130 mg, 85%) as pale yellowish liquid; *Rf* = 0.5 (EtOAc-hexane 1:2); $[\alpha]_D^{28}$ = +70.5 (*c* 0.26, $CHCl_3$).

Synthesis of (-)-Δ^8-THC 9:



To a magnetically stirred solution of the commercially available olivetol **8a** (100 mg, 0.44 mmol) and alcohol ***ent*-14** (67 mg, 0.44 mmol) in anhydrous CH_2Cl_2 (7 ml), was added $BF_3{\cdot}OEt_2$ (72 mg, 0.50 mmol) in drop wise fashion. The resulting purplish red solution was stirred for 30 min at room temperature. Aq. $NaHCO_3$ (10 ml) was then added to the reaction mixture, extracted with CH_2Cl_2 (10 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:3) as eluent furnished the **(-)-Δ^8-THC 9** (120 mg, 82%) as pale yellowish liquid; *Rf* = 0.5 (EtOAc-hexane 1:2); $[\alpha]_D^{28}$ = -132.5 (*c* 0.38, $CHCl_3$); lit -152 (*c* 0.46, $CHCl_3$); **IR** (neat): ν_{max}/cm^{-1} 3428, 2925, 2854, 1581, 1428, 1261, 1041; **^{1}H NMR** (CDCl3, 400 MHz): δ 6.28 (s, 1H), 6.12 (s, 1H), 5.41(brs, 1H), 4.85 (brs, 1H), 3.19 (dd, *J* = 16.4 Hz and 4.5 Hz, 1H), 2.67 (td, *J* = 10.5 and 4.5 Hz, 1H), 2.45 (td, *J* = 7.3 and 2.2 Hz, 1H), 2.18-2.10 (m, 1H), 1.86-1.78 (m, 3H), 1.57 (s, 3H), 1.61-1.54 (m, 2H), 1.38 (s, 3H), 1.34-1.29 (m, 4H), 1.11 (s, 3H), 0.89 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR**($CDCl_3$, 125 MHz): δ 154.6, 142.4, 134.5, 119.0, 110.2, 109.8, 107.3, 77.2, 44.6, 35.7, 35.17, 31.3, 30.3, 29.4, 27.6, 27.3, 23.2, 22.3, 18.2, 13.7; **HRMS**: m/z calcd for $C_{21}H_{29}O_2$ $[M+H]^+$: 315.2326; found: 315.2320.

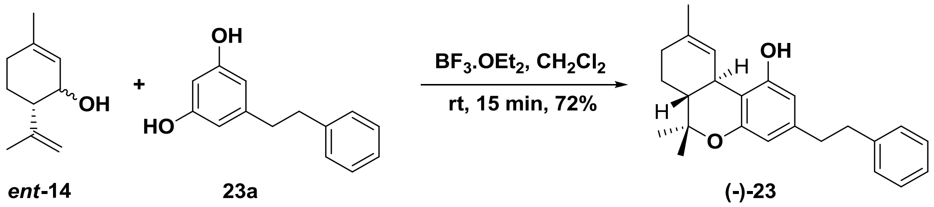
Synthesis of (+)-Δ^8-THC 9:



14 8a (+)-Δ^8-THC 9

To a magnetically stirred solution of the commercially available olivetol **8a** (110 mg, 0.44 mmol) and alcohol **14** (69 mg, 0.42 mmol) in anhydrous CH_2Cl_2 (7 ml), was added $BF_3{\cdot}OEt_2$ (72 mg, 0.50 mmol) in drop wise fashion. The resulting purplish red solution was stirred for 30 min at room temperature. Aq. $NaHCO_3$ (10 ml) was then added to the reaction mixture, extracted with CH_2Cl_2, washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column using EtOAc-hexane (1:3) as eluent furnished the **(+)-Δ^8-THC 9** (122 mg, 84%) as pale yellowish liquid; *Rf* = 0.5 (EtOAc-hexane 1:2); $[\alpha]_D^{28}$ = +135.4 (*c* 0.34, $CHCl_3$).

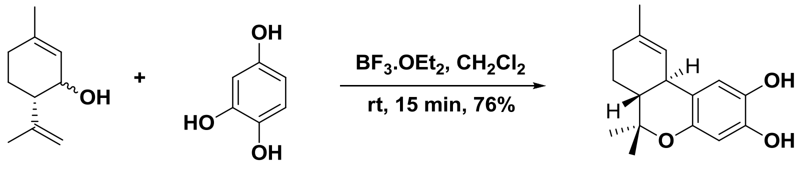
Synthesis of compound (-)-23:



ent-14 23a (-)-23

To a magnetically stirred solution of the compound **23a** (100 mg, 0.47 mmol) in CH_2Cl_2 was added $BF_3.OEt_2$ (22 mg, 0.10 mmol) in drop wise fashion. To the resulting solution alcohol ***ent*-14** (65 mg, 0.42 mmol) in anhydrous CH_2Cl_2 was added drop wise through syringe. The resulting purplish red solution was stirred for 15 min at room temperature. Aq. $NaHCO_3$ (10 ml) was then added to the reaction mixture, extracted with CH_2Cl_2 (10 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:3) as eluent furnished the compound (-)-**23** (130 mg, 72%) as pale yellowish liquid; *Rf* = 0.5 (EtOAc-hexane 1:2); $[\alpha]_D^{28}$ = -40.93 (*c* 0.17, $CHCl_3$); **IR** (neat): v_{max}/cm^{-1} 3428, 2925, 2854, 1581, 1428; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.31-7.28 (m, 2H), 7.21-7.19 (m, 3H), 6.34 (s, 1H), 6.31 (s, 1H), 6.17 (s, 1H), 4.94 (brs, 1H), 3.22 (d, *J* = 11 Hz, 1H), 2.90-2.86 (m, 2H), 2.78-2.75 (m, 2H), 2.17 (brs, 1H), 1.95-1.90 (m, 2H), 1.70 (s, 3H), 1.59-1.51 (m, 2H), 1.43 (s, 3H), 1.11 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 155.2, 154.6, 142.3, 141.9, 134.8, 128.6, 126.2, 123.9, 110.3, 109.7, 107.8, 77.3, 46.1, 37.8, 33.8, 31.4, 30.0, 27.8, 25.3, 23.7, 19.6; **HRMS**: m/z calcd for $C_{24}H_{28}O_2$ $[M+H]^+$: 349.2167; found: 349.2170.

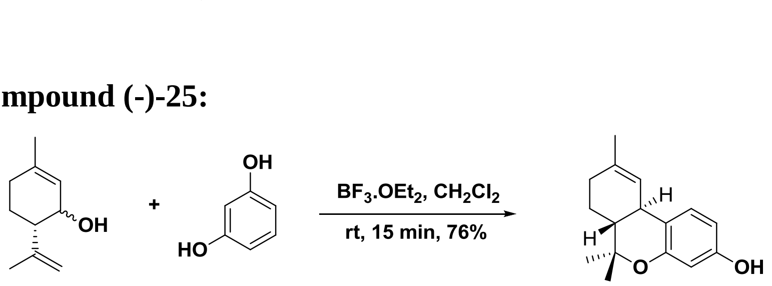
Synthesis of compound (-)-24:



***ent*-14** **24a** **(-)-24**

To a magnetically stirred solution of the compound **24a** (100 mg, 0.8 mmol) and alcohol ***ent*-14** (67 mg, 0.44 mmol) in anhydrous CH_2Cl_2 (7 ml), was added $BF_3{\cdot}OEt_2$ (22 mg, 0.10 mmol) in drop wise fashion. The resulting purplish red solution was stirred for 15 min at RT. Aq. $NaHCO_3$ (10 ml) was then added to the reaction mixture, extracted with CH_2Cl_2 (10 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:3) as eluent furnished the compound (-)-**24** (95 mg, 76%) as pale yellowish liquid; *Rf* = 0.3 (EtOAc-hexane 1:2); $[\alpha]_D^{28}$ = -15.20 (*c* 0.2, $CHCl_3$); **IR** (neat): ν_{max}/cm^{-1} 3428, 2925, 2854, 1581, 1261, 1041; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 6.82 (s, 1H), 6.38 (s, 1H), 5.76 (s, 1H), 3.06 (d, *J* = 8.7 Hz, 1H), 2.09 (d, *J* = 6.4 Hz, 2H) 1.87-1.82 (m, 1H), 1.71 (s, 3H), 1.57-1.50 (m, 2H), 1.40 (s, 3H), 1.14 (s, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 147.02, 142.9, 137.2, 134.8, 122.25, 112.5, 104.5, 78.1, 44.8, 33.8, 30.9, 27.9, 24.6, 23.6, 20.6, **HRMS**: m/z calcd for $C_{16}H_{20}O_3$ $[M-H]^-$: 259.1334; found: 259.1334.

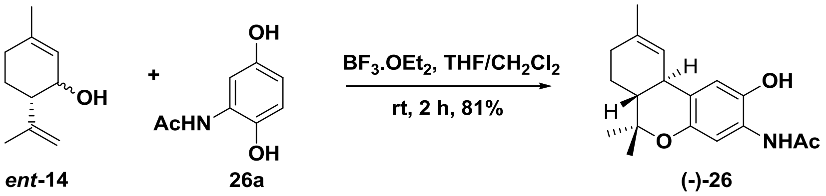
Synthesis of compound (-)-25:



***ent*-14** **25a** **(-)-25**

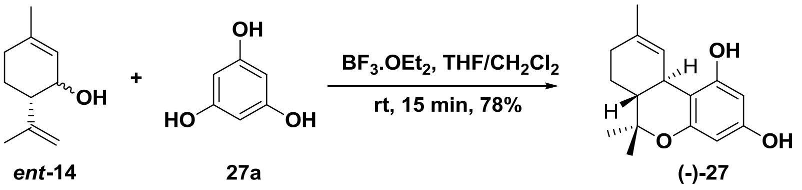
To a magnetically stirred solution of the compound **25a** (100 mg, 0.9 mmol) and alcohol ***ent*-14** (67 mg, 0.44 mmol) in anhydrous CH_2Cl_2 (7 ml), was added $BF_3{\cdot}OEt_2$ (22 mg, 0.10 mmol) in drop wise fashion. The resulting purplish red solution was stirred for 15 min at RT. Aq. $NaHCO_3$ (10 ml) was then added to the reaction mixture, extracted with CH_2Cl_2 (15 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:3) as eluent furnished the compound (-)-**25** (85 mg, 76%) as pale yellowish liquid; *Rf* = 0.3 (EtOAc-hexane 1:2); $[\alpha]_D^{28}$ = -3.82 (*c* 0.31,$CHCl_3$); **IR** (neat): vmax/cm-1 3428, 2925, 2854, 1581, 1261, 1041; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.15 (d, *J* = 8.2 Hz, 1H), 6.4 (dd, *J* = 8.2 and 2.5 Hz, 1H), 6.3 (d, *J* = 6.8 Hz, 1H), 5.9 (s, 1H), 4.81 (s, 1H), 3.11 (d, *J* = 11 Hz, 1H), 2.11 (brs, 1H), 1.89-1.85 (m, 2H), 1.74 (s, 3H), 1.59-1.53 (m, 2H), 1.43 (s, 3H), 1.17 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 154.9, 154.3, 134.8, 126.3, 122.2, 117.3, 107.2, 103.8, 78.3, 44.7, 33.6, 30.9, 28.0, 24.6, 23.6, 20.9; **HRMS**: m/z calcd for $C_{16}H_{20}O_2$ $[M+H]^+$ 245.1541; found: 245.1542.

Synthesis of compound (-)-26:



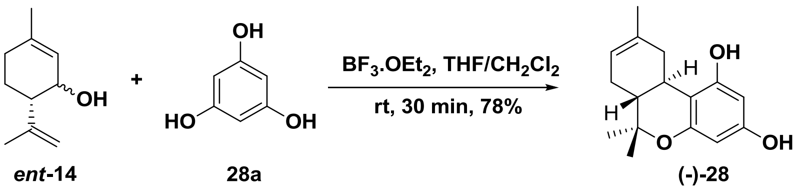
To a magnetically stirred solution of the compound **26a** (100 mg, 0.6 mmol) in THF/CH_2Cl_2 (1:3) was added $BF_3{\cdot}OEt_2$ (22 mg, 0.70 mmol) in drop wise fashion. To the resulting solution alcohol ***ent*-14** (67 mg, 0.44 mmol) in anhydrous CH_2Cl_2 was added drop wise through syringe. The resulting yellow brown solution was stirred for 2 h at RT. Aq. $NaHCO_3$ (10 ml) was then added to the reaction mixture, extracted with CH_2Cl_2 (15 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:3) as eluent furnished the compound (-)-**26** (108 mg, 81%) as pale yellowish liquid; *Rf* = 0.5 (EtOAc-hexane 1:2); $[\alpha]_D^{28}$ = -15.20 (*c* 0.2, $CHCl_3$); **IR** (neat): v_{max}/cm^{-1} 3428, 2925, 1660, 1522, 1421, 1366, 1173; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.12 (brs, 1H), 7.64 (brs, 1H), 6.96 (s, 1H), 6.46 (s, 1H), 5.84 (s, 1H), 3.14 (d, *J* = 10.8 Hz, 1H), 2.22 (s, 3H), 2.1 (brs, 1H), 1.89-1.84 (m, 2H), 1.72 (s, 3H), 1.58-1.51 (m, 2H), 1.4 (s, 3H), 1.14 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 170.4, 147.0, 141.8, 135.1, 124.3, 121.6, 119.1, 116.4, 110.0, 78.0, 44.5, 34.0, 30.7, 29.6, 27.9, 24.5, 23.4, 20.6; **HRMS**: m/z calcd for $C_{18}H_{23}NO_3$ $[M+H]^+$: 302.1756; found: 302.1757.

Synthesis of compound (-)-27:



To a magnetically stirred solution of the compound **27a** (100 mg, 0.8 mmol) in THF/CH_2Cl_2 (1:3) was added BF_3·OEt_2 (22 mg, 0.70 mmol) in drop wise fashion. To the resulting solution alcohol ***ent*-14** (65 mg, 0.42 mmol) in anhydrous CH_2Cl_2 was added dropwise through syringe. The resulting yellow brown solution was stirred for 15 min at RT. Aq. $NaHCO_3$ (10 ml) was then added to the reaction mixture, extracted with CH_2Cl_2 (10 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:3) as eluent furnished the compound (-)-**27** (100 mg, 78%) as pale yellowish liquid; *Rf* = 0.5 (EtOAc-hexane 1:2); $[\alpha]_D^{28}$ = -26.8 (*c* 0.32, $CHCl_3$); **IR** (neat): v_{max}/cm^{-1} 3428, 2925, 2854, 1581, 1428, 1261, 1041; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 6.82 (s, 1H), 6.36 (s, 1H), 5.80 (s, 1H), 3.08 (brd, 1H), 2.11-2.09 (m, 2H), 1.87-1.84 (m, 2H), 1.72 (s, 3H), 1.60-1.55 (m, 1H), 1.40 (s, 3H), 1.14 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz); δ 154.8, 154.2, 134.7, 126.2, 122.1, 117.2, 107.0, 103.7, 78.2, 44.6, 33.4, 30.8, 27.9, 24.5, 23.5, 20.7; **HRMS**: m/z calcd for $C_{16}H_{20}O_3$ $[M-H]^-$: 259.1334; found: 259.1331.

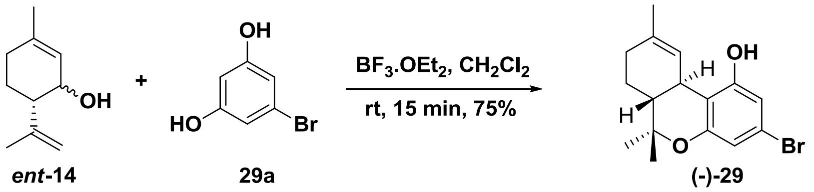
Synthesis of compound (-)-28:



To a magnetically stirred solution of the compound **28a** (100 mg, 0.8 mmol) in THF/CH_2Cl_2 (1:3) was added BF_3·OEt_2 (44 mg, 1.4 mmol) in drop wise fashion. To the resulting solution alcohol ***ent*-14** (65 mg, 0.42 mmol) in anhydrous CH_2Cl_2 was added dropwise through syringe. The resulting yellow brown solution was stirred for 15 min at RT. Aq. $NaHCO_3$ (10 ml) was then added to the reaction mixture, extracted with CH_2Cl_2 (10 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:3) as eluent furnished the compound (-)-**28** (96 mg, 75%) as pale yellowish liquid; *Rf* = 0.5 (EtOAc-hexane 1:2); $[\alpha]_D^{28}$ =

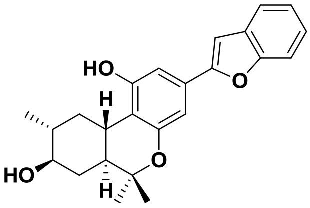
-94.5 (c 0.72, $CHCl_3$); **IR** (neat): ν_{max}/cm^{-1} 3380, 2973, 2926, 1623, 1458, 1374, 1263, 1148, 1130, 1035, 821, 758; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.95-5.77 (m, 4H), 5.41 (s, 1H), 3.16 (d, J = 13.7 Hz, 1H), 2.66-2.62 (m, 1H), 2.12 (brd, 1H), 1.86-1.75 (m, 2H), 1.68 (s, 3H), 1.63 (t, J = 8.0 Hz, 1H), 1.36 (s, 3H), 1.09 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz); δ 156.0, 155.5, 154.6, 134.7, 119.1, 106.4, 97.0, 96.0, 77.3, 44.8, 36.0, 31.2, 27.8, 27.4, 23.4, 18.4; **HRMS**: m/z calcd for $C_{18}H_{20}O_3$ $[M+H]^+$: 261.1491; found: 261.1493.

Synthesis of compound (-)-29:



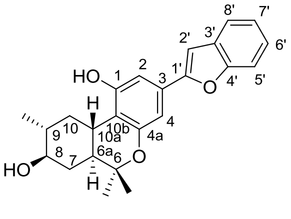
To a magnetically stirred solution of the compound **29a** (100 mg, 0.53 mmol) in anhydrous CH_2Cl_2 (7 ml), was added $BF_3{\cdot}OEt_2$ (22 mg, 0.10 mmol) in drop wise fashion. To this, solution of alcohol ***ent*-14** (65 mg, 0.42 mmol) in anhydrous CH_2Cl_2 (2 ml) was added slowly through syringe. The resulting yellow brown solution was stirred for 15 min at RT. Aq. $NaHCO_3$ (10 ml) was then added to the reaction mixture, extracted with CH_2Cl_2 (15 ml x 3), washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column chromatography using EtOAc-hexane (1:3) as eluent furnished the compound (-)-**29** (119 mg, 75%) as pale yellowish liquid; Rf = 0.3 (EtOAc-hexane 1:2); $[\alpha]_D^{28}$ = -145.5 (c 0.2, $CHCl_3$); **IR** (neat): vmax/cm^{-1} 3383, 2926, 1610, 1576, 1435, 1279, 1124, 1018, 833, 740; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ = 6.71 (d, J = 2.5 Hz, 1 H), 6.27 (d, J = 2.5 Hz, 1 H), 6.21 (s, 1 H), 4.85 (brs, 1 H), 3.12 (d, J = 11.0 Hz, 1 H), 2.27 - 2.12 (m, 2 H), 2.01 - 1.87 (m, 2 H), 1.73 (m, 1 H), 1.69 (s, 3 H), 1.41 (s, 3 H), 1.06 (s, 3 H);**^{13}C NMR** ($CDCl_3$, 125 MHz): δ 155.7, 154.9, 133.8, 125.2, 123.2, 117.4, 113.1, 103.9, 77.9, 46.8, 36.4, 30.8, 27.2, 25.0, 23.2, 18.7; **HRMS**: m/z calcd for $C_{16}H_{19}BrO_2$ $[M-H]^-$: 321.0490; found: 321.0492.

(+)-Machaeriol-D 7:



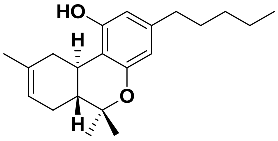
7 (+)-Machaeriol D

Entry	Machaeriol-D Q. Wang, Q. Huang, B. Chen, J. Lu, H. Wang, X. She and X. Pan, *Angew. Chem. Int. Ed*., **45**, 3651 (2006). ^{1}H-NMR	Synthesized (+)-Machaeriol-D **7** ^{1}H-NMR	Machaeriol-D Q. Wang, Q. Huang, B. Chen, J. Lu, H. Wang, X. She and X. Pan, *Angew. Chem. Int. Ed*., **45**, 3651 (2006). ^{13}C-NMR	Synthesized (+)-Machaeriol-D **7** ^{13}C-NMR
	δC (DMSO-d_6, 400 MHz)	δC (DMSO-d_6, 400 MHz)	δC (DMSO-d_6, 100 MHz)	δC (DMSO-d_6, 125 MHz)
1	9.78 (s, 1H, Ar-OH)	9.71 (s, 1H, Ar-OH)	157.3	157.3
2	7.58-7.63 (m, 2H)	7.63-7.58 (m, 2H)	155.3	155.3
3	7.23-7.32 (m, 3H)	7.32-7.23 (m, 3H)	154.9	154.9
4	6.90 (s, 1H)	6.89 (s, 1H)	154.0	154.0
5	6.77 (s, 1H)	6.77 (s, 1H)	128.8	128.9
6	4.66-4.67 (d, *J* = 3.6 Hz, 1H, -OH)	4.63 (d, *J* = 5.4 Hz, 1H)	128.5	128.6
7	3.10-3.17 (m, 2H)	3.16-3.08 (m, 1H)	124.2	124.3
8	2.37-2.43 (t, *J* = 11.2, 10.4 Hz, 1H)	2.41(t, *J* = 11.3 and 2.3 Hz, 1H)	123.1	123.1
9	1.96-1.99 (m, 1H)	2.00-1.96 (m, 1H)	120.9	121.0
10	1.43-1.52 (m, 2H)	1.52-1.43 (m, 2H)	113.2	113.2
11	1.35 (s, 3H)	1.35 (s, 3H)	110.9	111.0
12	1.10 (s, 3H)	1.05 (s, 3H)	104.6	104.7
13	0.98-0.99 (d, *J* = 6.0 Hz, 3H)	0.99 (d, *J* = 6.3 Hz, 3H)	103.4	103.4
14	0.66-0.75 ppm (dt, *J* = 12.0, 12.6 Hz, 1H)	0.99 ppm (dt, *J* = 12.3 and 11.6Hz, 1H)	101.2	101.3
15			76.5	76.6
16			74.7	74.7
17			47.0	47.0
18			39.7	39.7
19			37.0	37.0
20			36.1	36.2
21			35.0	35.0
22			27.4	27.4
23			18.9	18.9
24			18.8	18.8



(+)-Machaeriol D (**7**)

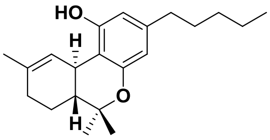
	Natural Machaeriol D I. Muhammad., X. C. Li., M. R. Jacob., B. L. Tekwani., D. C. Dunbar., D. Ferreira., *J. Nat. Prod.* **2003**, *66*, 804	Synthesized Machaeriol D **7**	Natural Machaeriol D I. Muhammad., X. C. Li., M. R. Jacob., B. L. Tekwani., D. C. Dunbar., D. Ferreira., *J. Nat. Prod.* **2003**, *66*, 804	Synthesized Machaeriol D **7**
Position C/H	δH ($CDCl_3$) (mult, *J* Hz)	δH ($CDCl_3$1 DropDMSO-d_6, 400 MHz) (mult, *J* Hz)	δC ($CDCl_3$)	δC ($CDCl_3$ 1 DropDMSO-d_6, 125 MHz)
1			157.5 s	157.4 s
2	6.78 br s	6.80 br s	106.5 s	105.9 s
3			129.8 s	129.6 s
4	6.80 br s	6.86 br s	104.0 s	104.4 s
4a			156.3 s	156.5 s
6			77.0 s	77.5 s
6a	1.56 br t (9.0, 11.2)	1.56 br t (10.8, 10.9)	48.0 d	47.9 d
7α	2.07 m	2.08 m	37.7 t	37.4 t
7β	1.13 m	1.12 m		
8	3.24 br ddd (4.7, 10.3, 10.4)	3.25 br ddd (4.1, 10.3, 10.6)	76.1 d	76.6 d
9	1.54 m	1.53 m	37.0 d	36.8 d
10α	0.83 br t (12.8, 13.4)	0.83 br t (11.9, 12.2)	40.7 t	40.9 t
10β	3.20 dt (2.6, 13.4)	3.22 dt (2.8, 13.1)		
10a	2.51 ddd (2.6, 11.1, 12.8)	2.51 ddd (2.0, 9.7, 11.2)	35.9 d	35.7 d
10b			113.9 s	113.7 s
6α-Me	1.09 s	1.09 s	18.7 q	18.9 q
6β-Me	1.38 s	1.38 s	27.5 q	28.0 q
9α-Me	1.04 d (6.5)	1.05 d (6.5)	18.9 q	19.4 q
1′			155.9 s	155.5 s
2′	7.09 s	6.89 s	101.4 d	101.0 d
3′			129.8 s	129.5 s
4′			155.1	154.9
5′	7.41 br d (8.1)	7.40 br d (7.7)	111.2 d	111.3 d
6′	7.24 dd br (7.3, 8.1)	7.23 dd br (7.4, 7.9)	124.6 d	124.2 d
7′	7.21 dd (1.2, 7.3, 7.7)	7.19 dd (2.7, 7.2, 7.4)	123.4 d	123.0 d
8′	7.50 br d (7.7)	7.51 br d (7.2)	121.3 d	121.1 d
OH	8.61 br s			



9 (-)-Δ^8 Tetrahydrocannabinol

(-)-Δ^8 Tetrahydrocannabinol **9:**

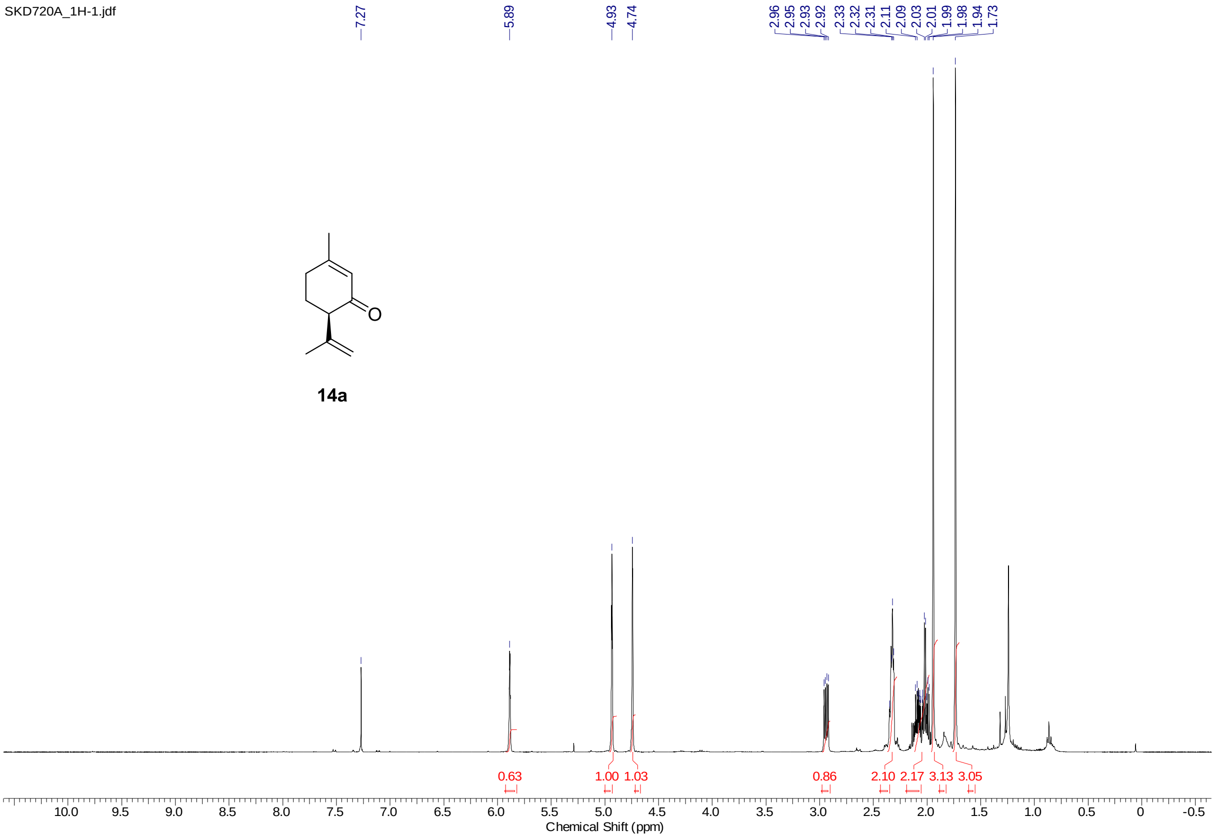
Entry	(-)-Δ^8 Tetrahydrocannabinol Cheng, L. J., Xie, J. H., Chen, Y., Wang, L. X., Zhou, Q. L. *Org. Lett.* **15**, 764-767 (2013). ^{1}H-NMR	Synthesized (-)-Δ^8 Tetrahydrocannabinol ^{1}H-NMR	(-)-Δ^8 Tetrahydrocannabinol Cheng, L. J., Xie, J. H., Chen, Y., Wang, L. X., Zhou, Q. L. *Org. Lett.* **15**, 764-767 (2013). ^{13}C-NMR	Synthesized (-)-Δ^8 Tetrahydrocannabinol ^{13}C-NMR
	δC (CDCl$_3$, 400 MHz)	δC (CDCl$_3$, 400 MHz)	δC (CDCl$_3$, 100 MHz)	δC (CDCl$_3$, 125 MHz)
1	6.29 (s, 1 H)	6.28 (s, 1H)	154.7	154.6
2	6.11 (d, J = 1.2 Hz, 1H)	6.12 (s, 1H)	142.7	142.4
3	5.43 (d, J = 4.5 Hz, 1H)	5.41(brs, 1H)	134.7	134.5
4	4.86 (s, 1H)	4.85(brs, 1H)	119.3	119.0
5	3.21 (dd, J = 16.0, 4.2 Hz, 1H)	3.19(dd, *J* =16.4 Hz, 4.5 Hz, 1H)	110.5	110.3
6	2.71 (td, J = 10.7, 4.5 Hz, 1H)	2.67(td, *J* = 10.53, 4.58 Hz, 1H)	110.0	109.8
7	2.44 (td, J = 7.3, 2.0 Hz, 1H)	2.45(td, *J* =7.3, 2.2 Hz, 1H)	107.7	107.3
8	2.19–2.10 (m, 1 H)	2.18-2.10(m, 1H)	44.8	44.6
9	1.82 (m, 3H)	1.86-1.78(m, 3H)	36.0	35.7
10	1.71 (s, 3H)	1.68(s, 3H)	35.4	35.2
11	1.61–1.52 (m, 1 H)	1.61-1.54(m, 2H)	31.5	31.3
12	1.39 (s, 3H)	1.35(s, 3H)	30.6	30.3
13	1.36–1.26 (m, 4H)	1.34-1.29(m, 4H)	27.9	29.4
14	1.11 (s, 3H)	1.08(s, 3H)	27.5	27.6
15	0.89 (t, J = 6.9 Hz, 3H)	0.89(t, *J* =6.87 Hz, 3H)	23.5	27.2
16			22.5	27.3
17			18.5	23.2
18			14.0	22.3
19				18.2
20				13.7



8 (-)-Δ^9 Tetrahydrocannabinol

(-)-Δ^9 Tetrahydrocannabinol **8:**

Entry	Natural (-)-Δ^9 Tetrahydrocannabinol Y.Gaoni,R.Mechoulam *J.Am.Chem.Soc*. **86**,1646-1647(1964) ^{1}H-NMR	(-)-Δ^9 Tetrahydrocannabinol Cheng, L. J., Xie, J. H., Chen, Y., Wang, L. X., Zhou, Q. L. *Org. Lett.* **15**, 764-767 (2013). ^{1}H-NMR	Synthesized (-)-Δ^9 Tetrahydrocannabinol ^{1}H-NMR	(-)-Δ^9 Tetrahydrocannabinol Cheng, L. J., Xie, J. H., Chen, Y., Wang, L. X., Zhou, Q. L. *Org. Lett.* **15**, 764-767 (2013). ^{13}C-NMR	Synthesized (-)-Δ^9 Tetrahydrocannabinol ^{13}C-NMR
	δC (CCl$_4$, 60 MHz)	δC (CDCl$_3$, 400 MHz)	δC (CDCl$_3$, 500 MHz)	δC (CDCl$_3$, 100 MHz)	δC (CDCl$_3$, 125 MHz)
1	6.35 (brs, 1H)	6.31 (s, 1H)	6.30 (s, 1H)	154.7	154.8
2	6.18 (d, *J*=2 Hz, 1H)	6.28 (s, 1H)	6.27 (s, 1H)	154.1	154.2
3	6.00(d, *J*=2 Hz, 1H)	6.14 (s, 1H)	6.14 (s, 1H)	142.8	142.8
4		4.86 (s, 1H)	4.83 (brs, 1H)	134.3	134.5
5	3.14 (brd, *J*=10 Hz, 1H)	3.21 (d, *J*= 10.4 Hz, 1H)	3.19(d, *J* = 11 Hz, 1H)	123.7	123.8
6		2.43 (t, *J*= 7.6 Hz, 2H)	2.43 (t, *J* = 8.2 Hz, 2H)	110.1	110.2
7		2.16 (brs, 1H)	2.16 (brs, 1H)	109.0	109.1
8		1.92 (m, 1H)	1.93-1.89 (m, 1H)	107.6	107.6
9	1.65 (s, 3H)	1.76–1.64 (m, 4H)	1.69 (s, 3H)	77.22	77.2
10		1.56 (m, 2H)	1.58-1.53 (m, 2H)	45.8	45.8
11	1.38 (s, 3H)	1.45–1.26 (m, 8H)	1.41 (s, 3H)	35.55	35.5
12		1.08 (s, 3H)	1.33-1.26 (m, 6H)	33.6	33.6
13	1.08 (s, 3H)	0.88 (t, *J*= 6.3 Hz, 3H)	1.09 (s, 3H)	31.5	31.6
14	0.88 (s, 3H)		0.86 (t, *J* = 6.4 Hz, 3H)	31.1	31.2
15				30.6	30.7
16				27.5	27.6
17				25.0	25.1
18				23.4	23.5
19				22.5	22.7
20				19.2	19.4
21				14.0	14.1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2.03
2.01
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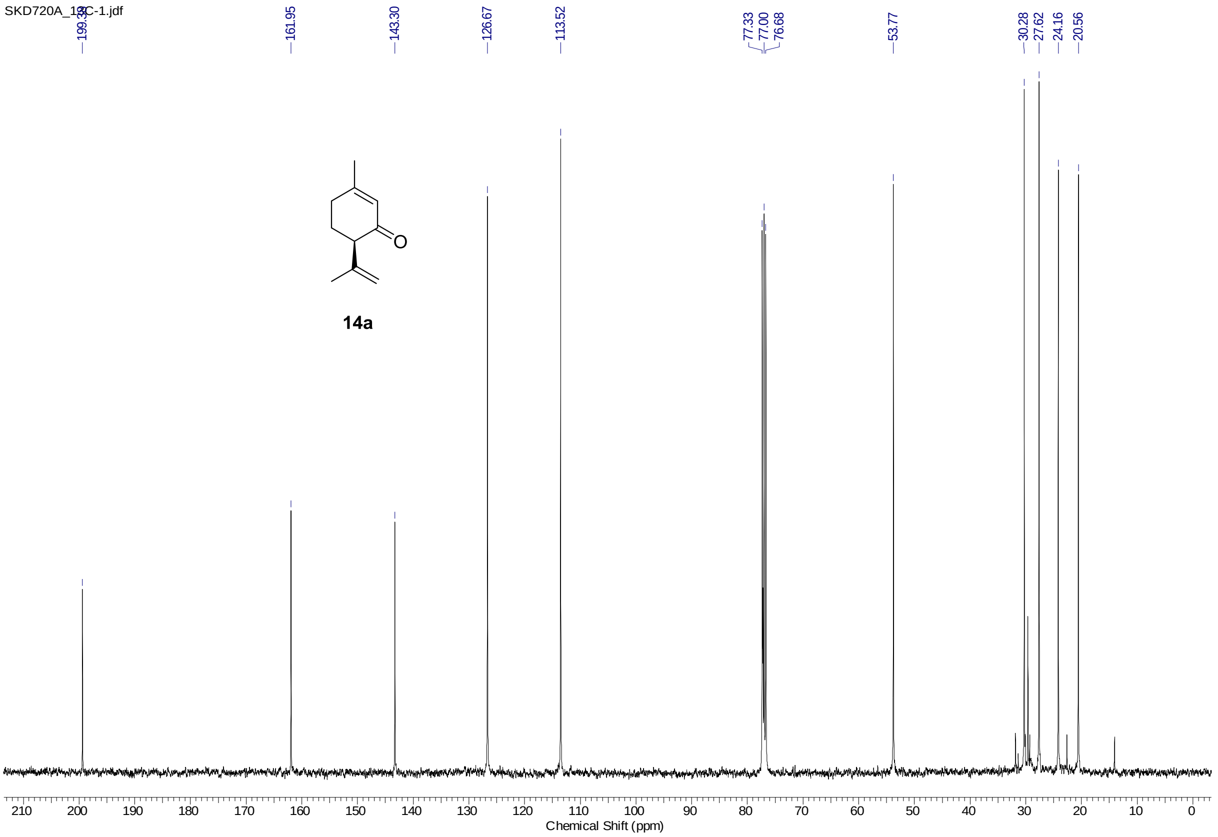
1.98
1.94
1.73
14a
0.63
1.00
1.03
0.86
2.10
2.17
3.13
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)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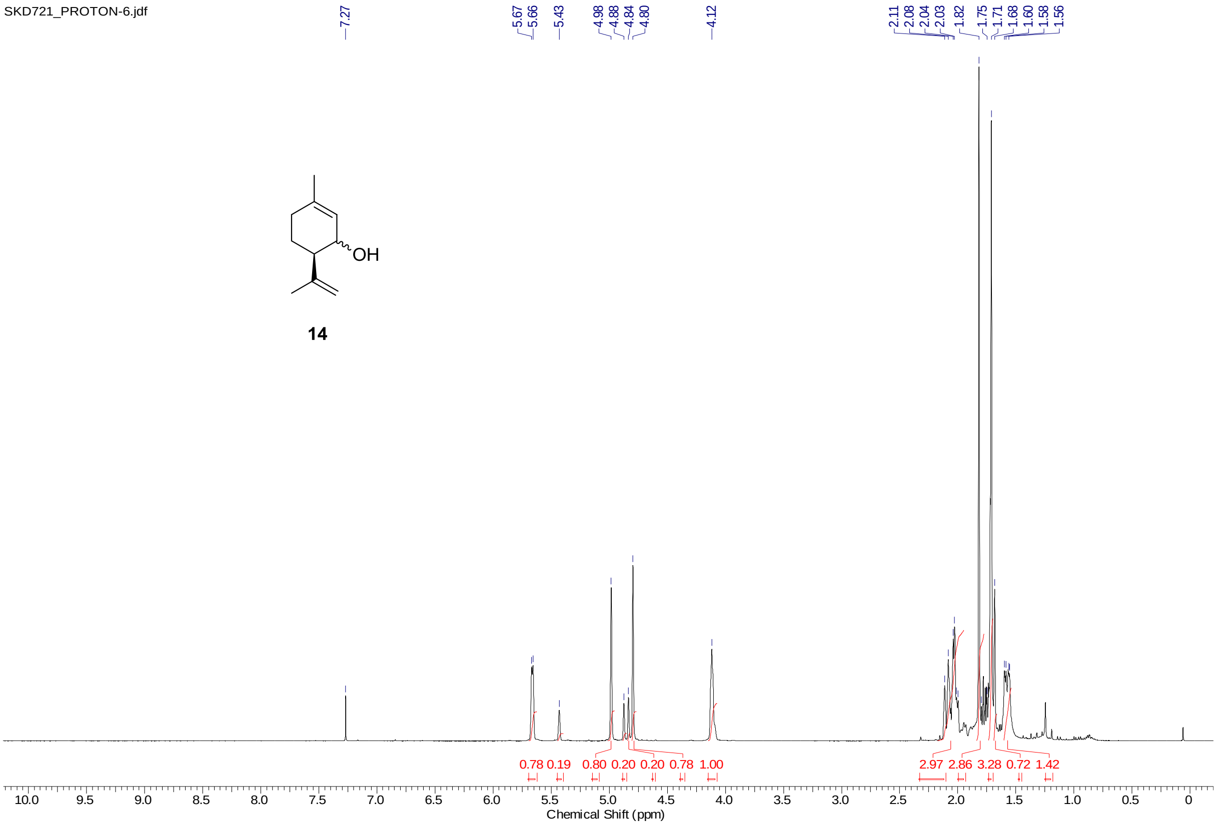
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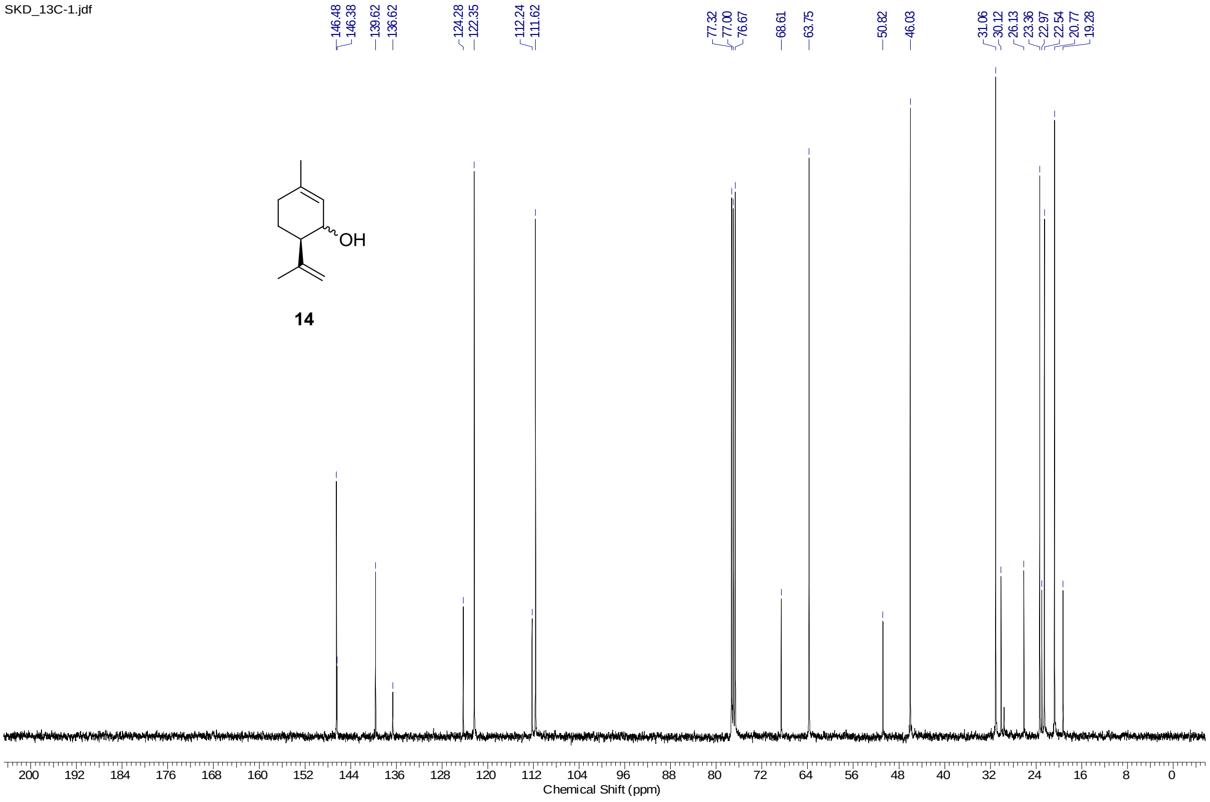
Chemical Shift (ppm)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160
152
144
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112
104
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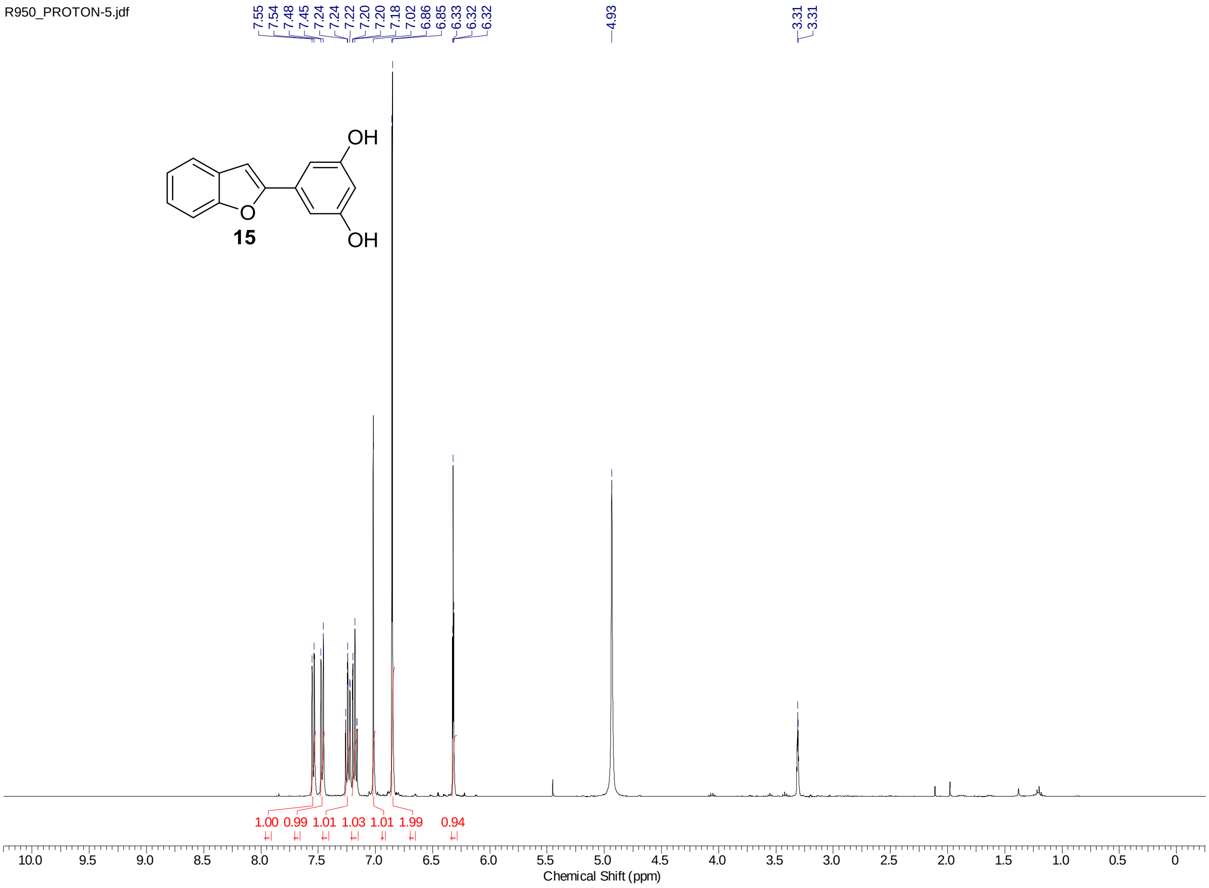
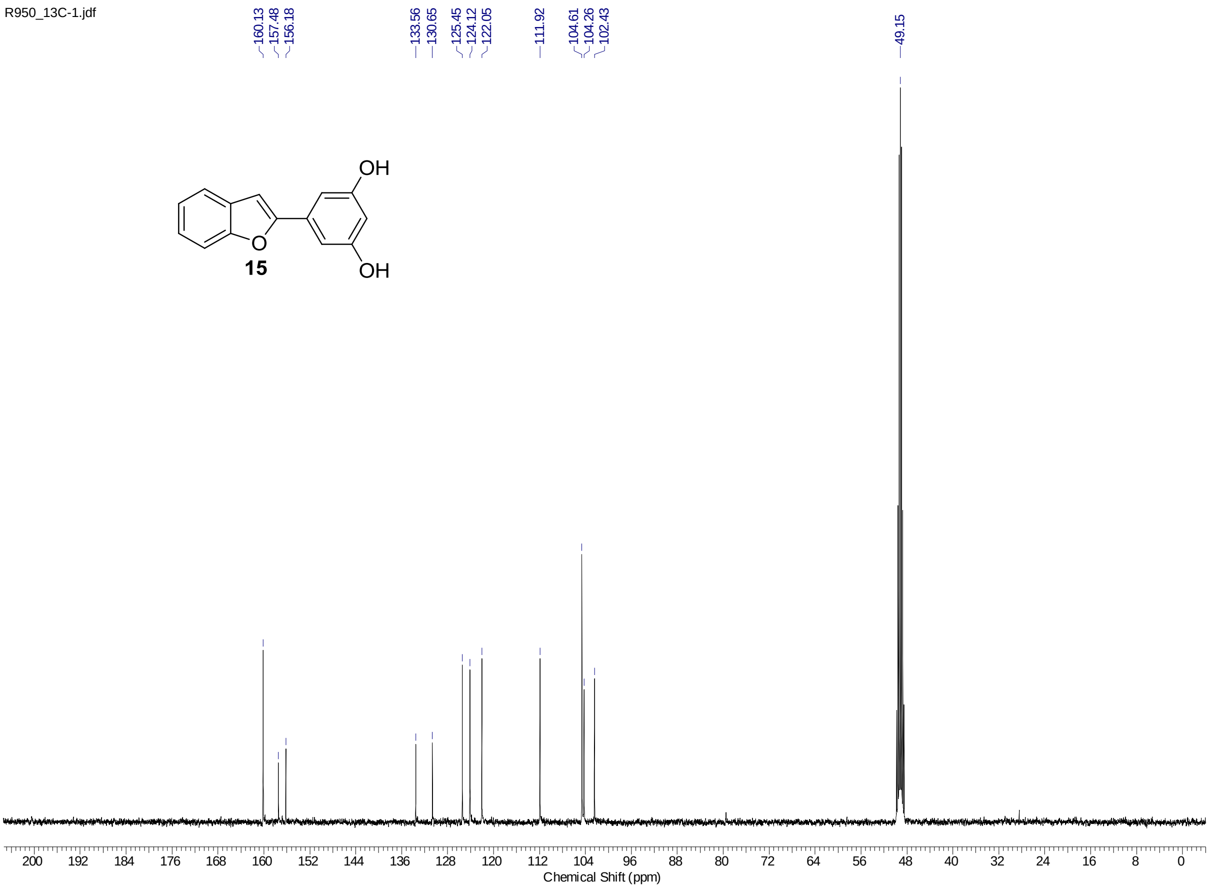
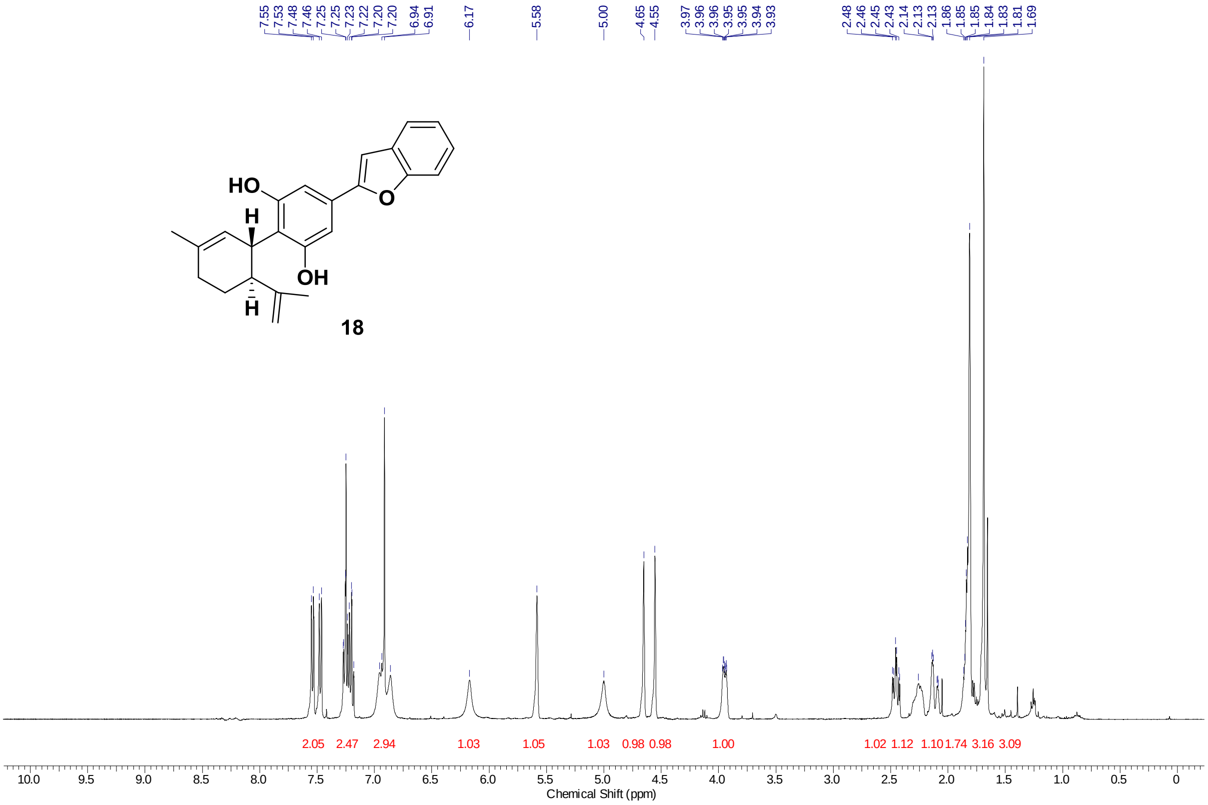
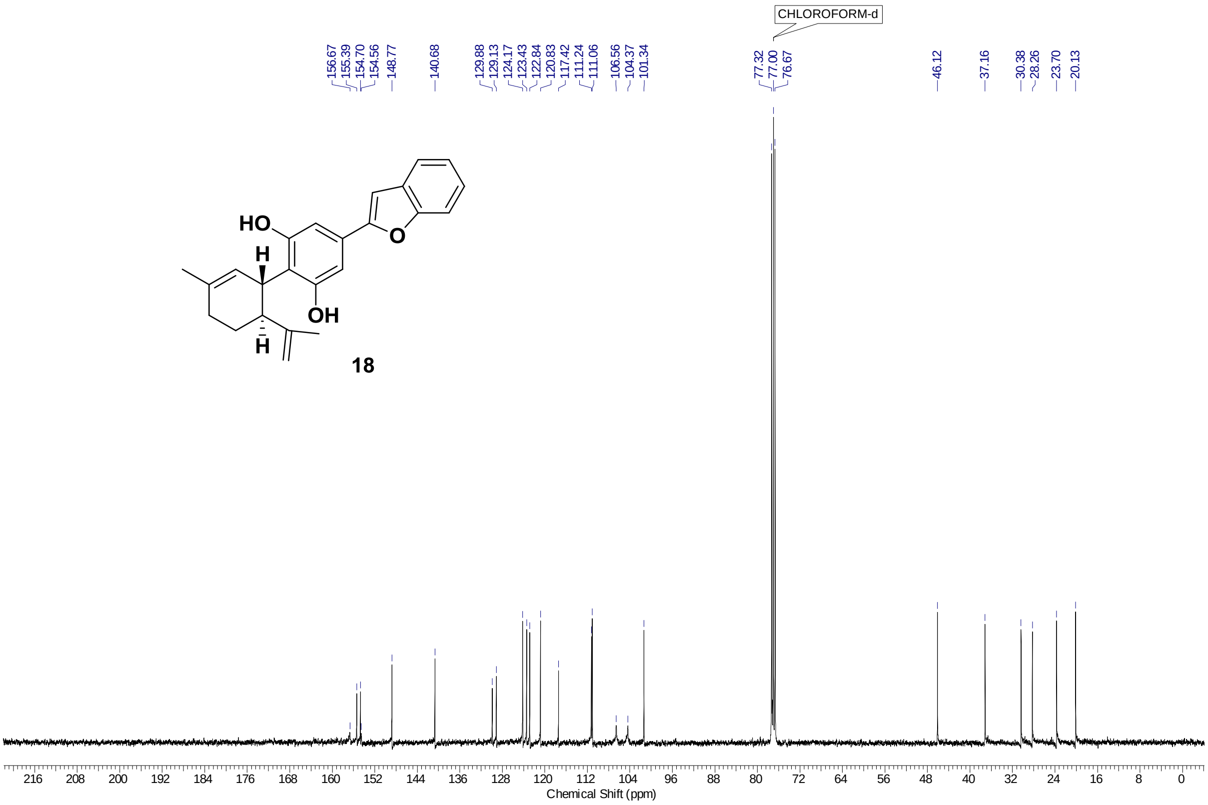
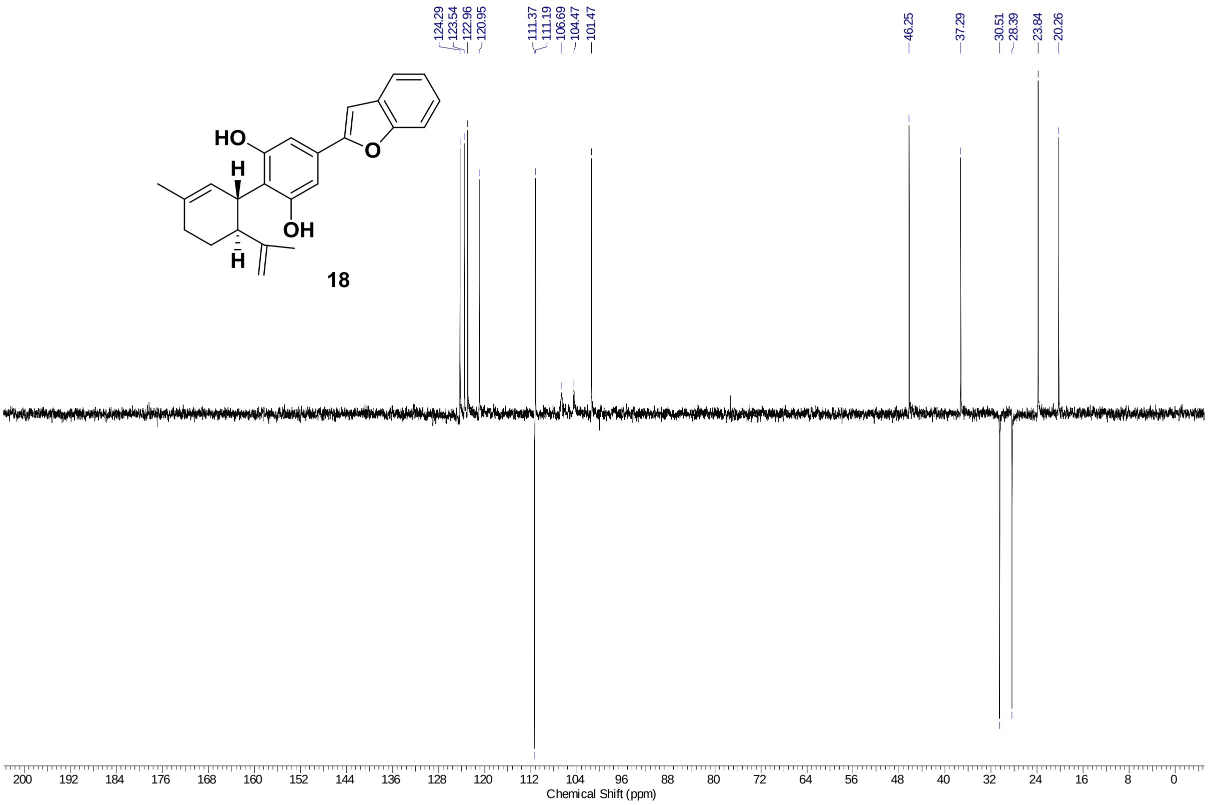
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

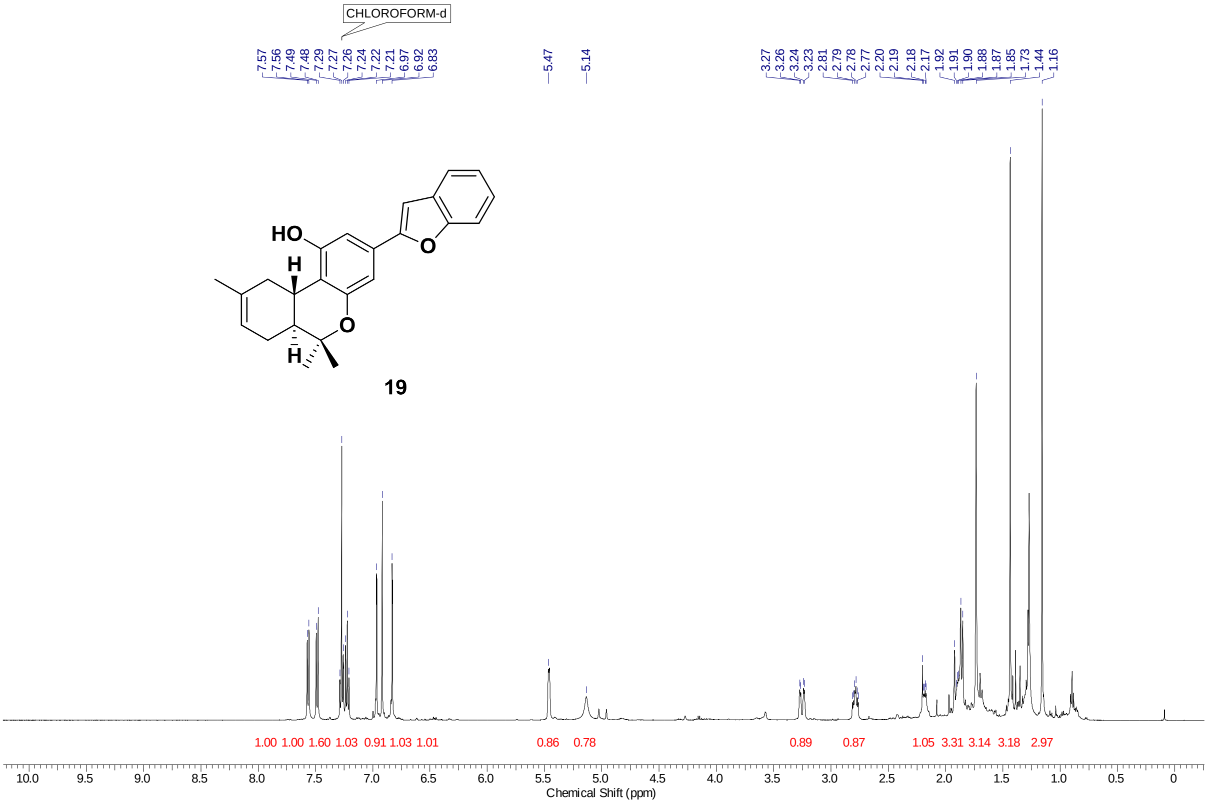

R950_PROTON-5.jdf
7.55
7.54
7.48
7.45
7.24
7.24
7.22
7.20
7.20
7.18
7.02
6.86
6.85
6.33
6.32
6.32
4.93
3.31
3.31
OH
O
OH
15
1.00
0.99
1.01
1.03
1.01
1.99
0.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

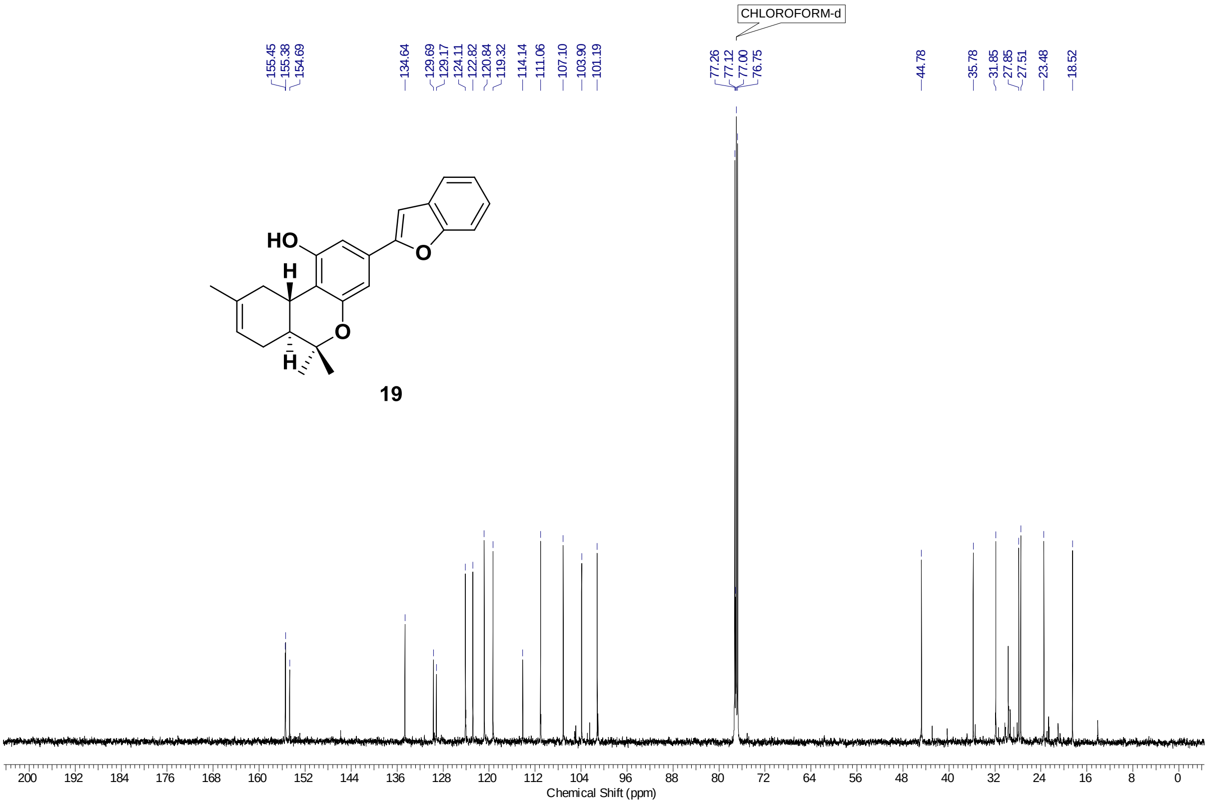

R950_13C-1.jdf
160.13
157.48
156.18
133.56
130.65
125.45
124.12
122.05
111.92
104.61
104.26
102.43
49.15
OH
O
OH
15
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

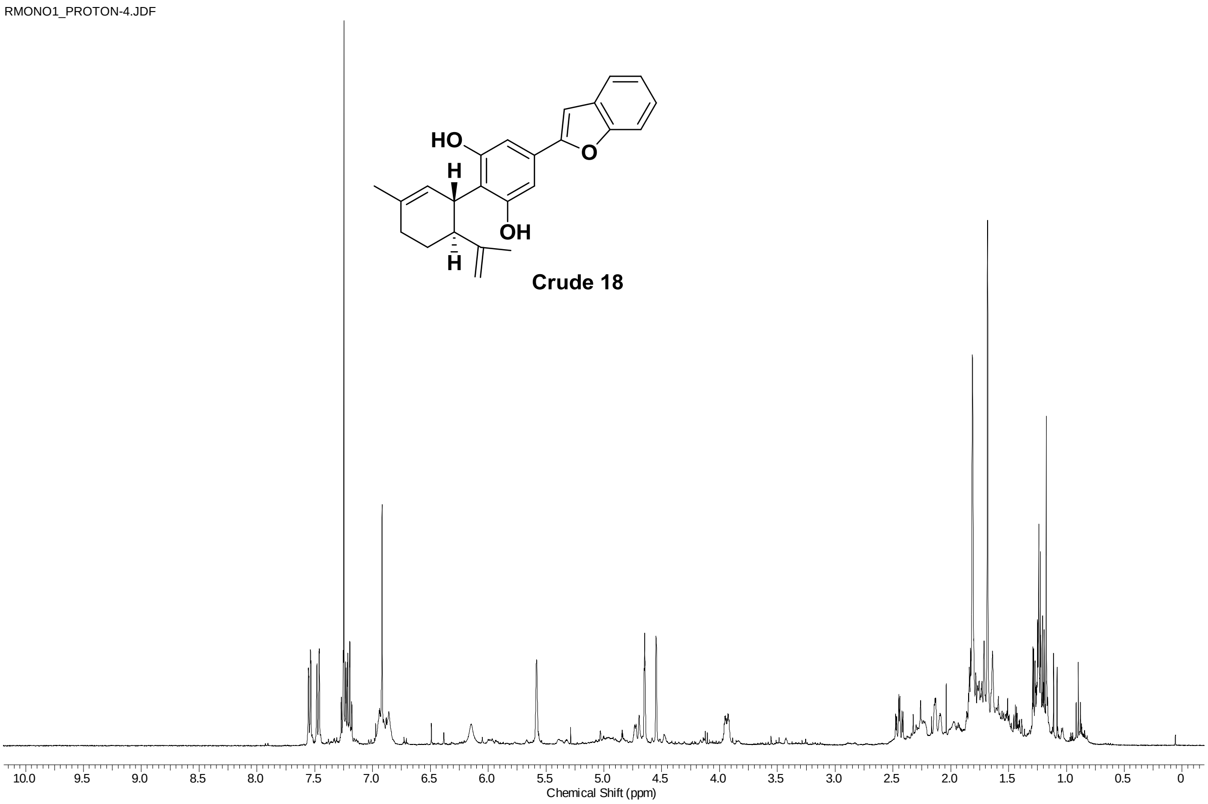

7.55
7.53
7.48
7.46
7.25
7.25
7.23
7.22
7.20
7.20
6.94
6.91
6.17
5.58
5.00
4.65
4.55
3.97
3.96
3.96
3.95
3.95
3.94
3.93
2.48
2.46
2.45
2.43
2.14
2.13
2.13
1.86
1.85
1.85
1.84
1.83
1.81
1.69
HO
H
OH
H
O
18
2.05
2.47
2.94
1.03
1.05
1.03
0.98
0.98
1.00
1.02
1.12
1.10
1.74
3.16
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

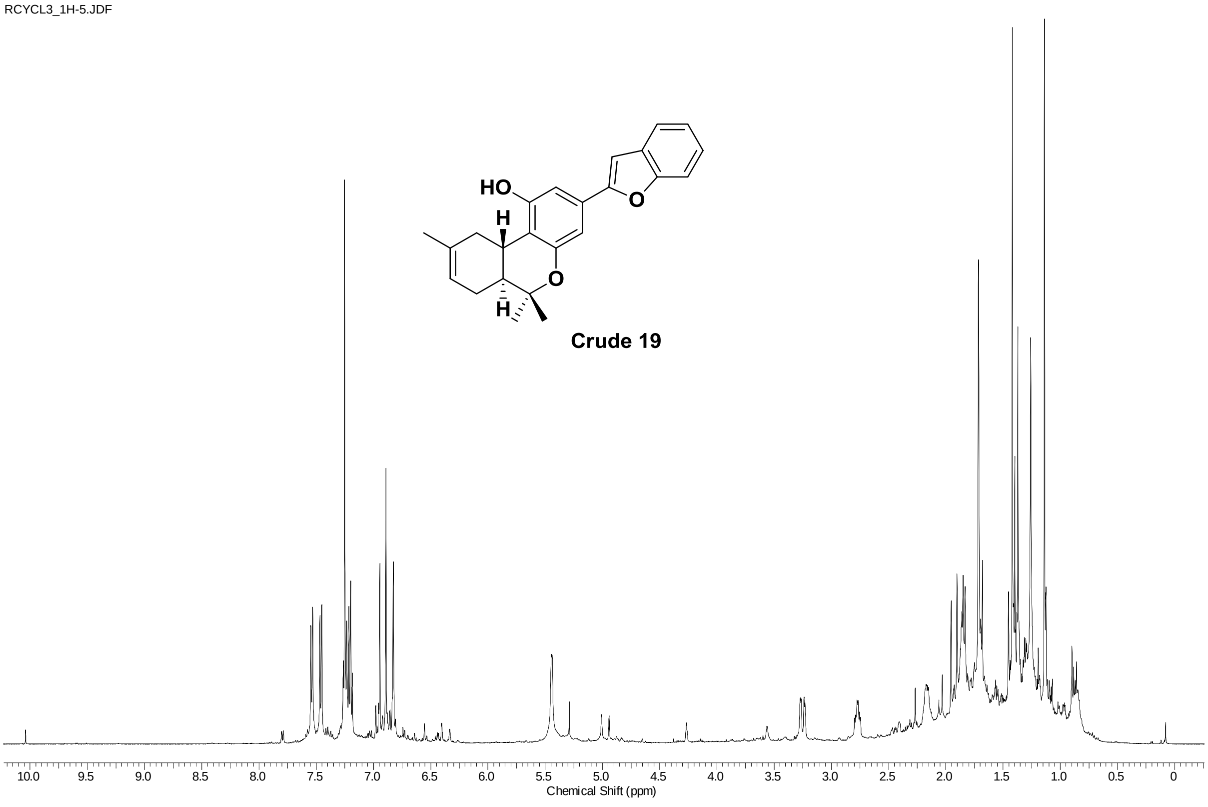

CHLOROFORM-d
156.67
155.39
154.70
154.56
148.77
140.68
129.88
129.13
124.17
123.43
122.84
120.83
117.42
111.24
111.06
106.56
104.37
101.34
77.32
77.00
76.67
46.12
37.16
30.38
28.26
23.70
20.13
HO
H
OH
H
O
18
216
208
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

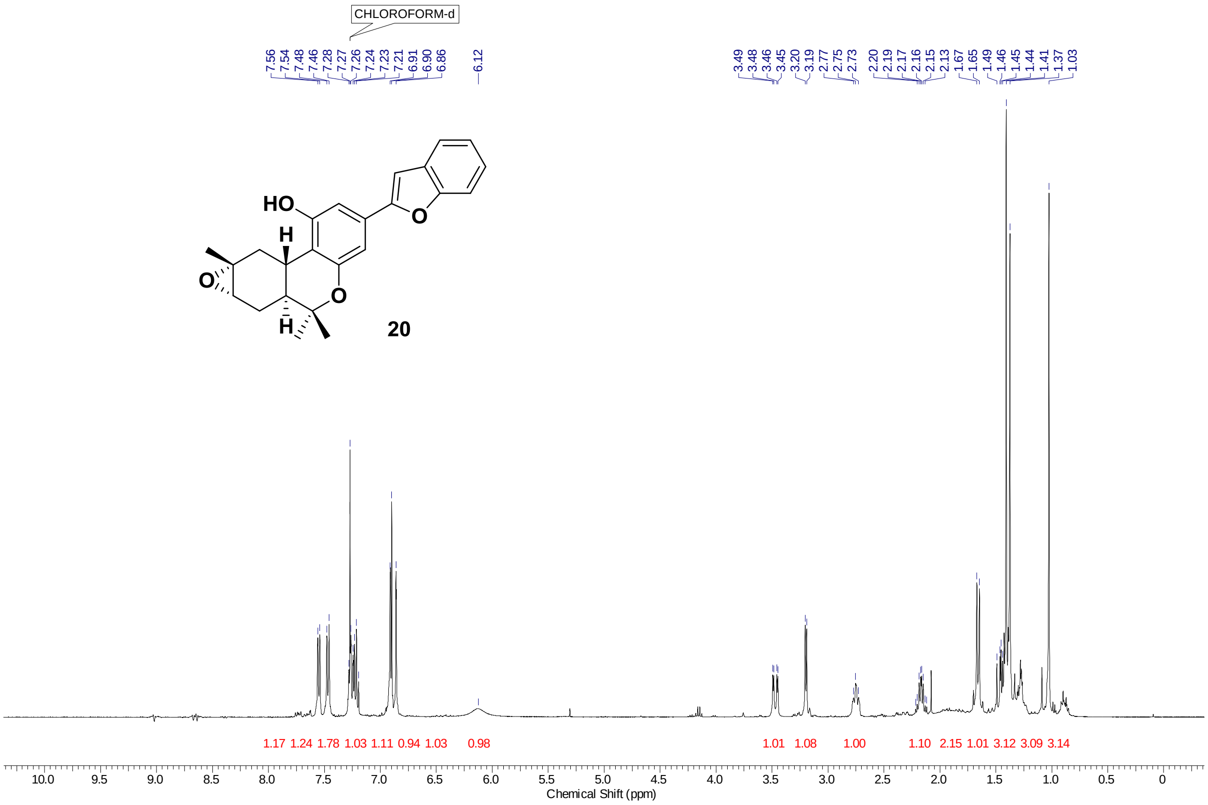

124.29
123.54
122.96
120.95
111.37
111.19
106.69
104.47
101.47
46.25
37.29
30.51
28.39
23.84
20.26
HO
H
OH
H
O
18
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

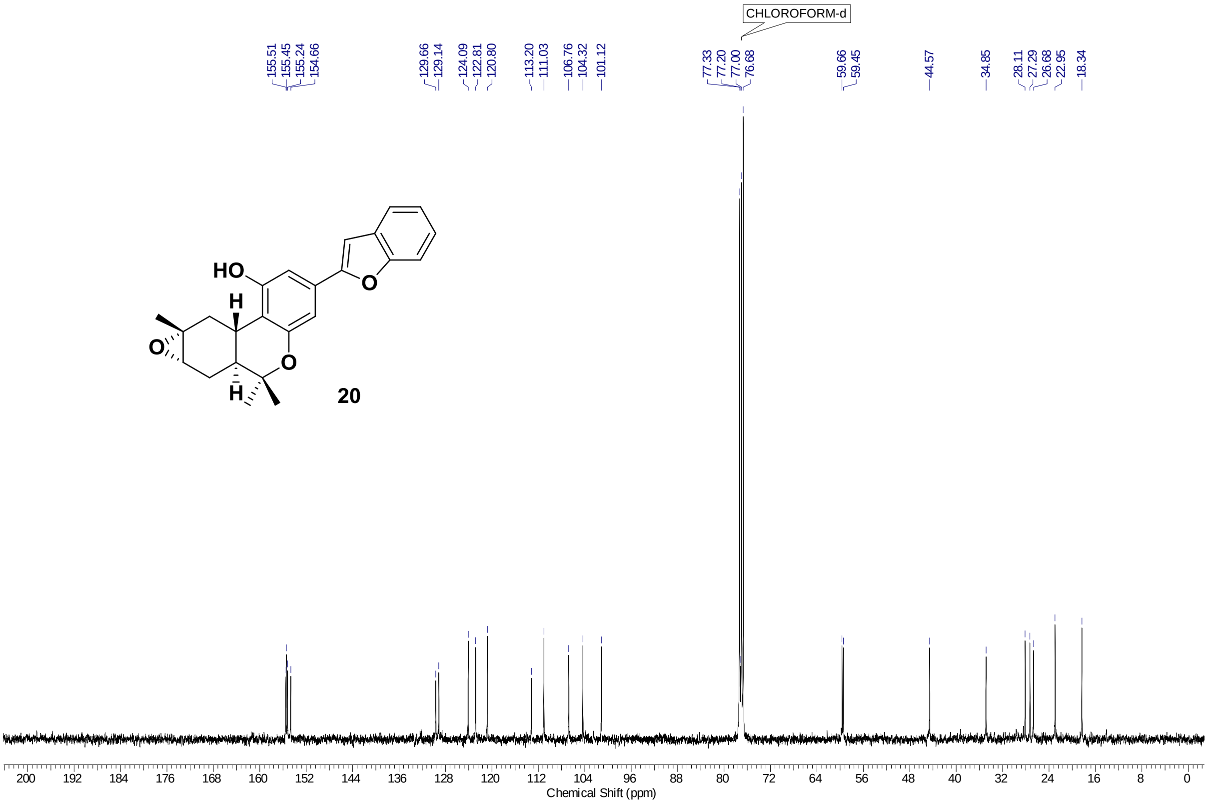

CHLOROFORM-d
7.57
7.56
7.49
7.48
7.29
7.27
7.26
7.24
7.22
7.21
6.97
6.92
6.83
5.47
5.14
3.27
3.26
3.24
3.23
2.81
2.79
2.78
2.77
2.20
2.19
2.18
2.17
1.92
1.91
1.90
1.88
1.87
1.85
1.73
1.44
1.16
HO
H
O
O
H
19
1.00
1.00
1.60
1.03
0.91
1.03
1.01
0.86
0.78
0.89
0.87
1.05
3.31
3.14
3.18
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

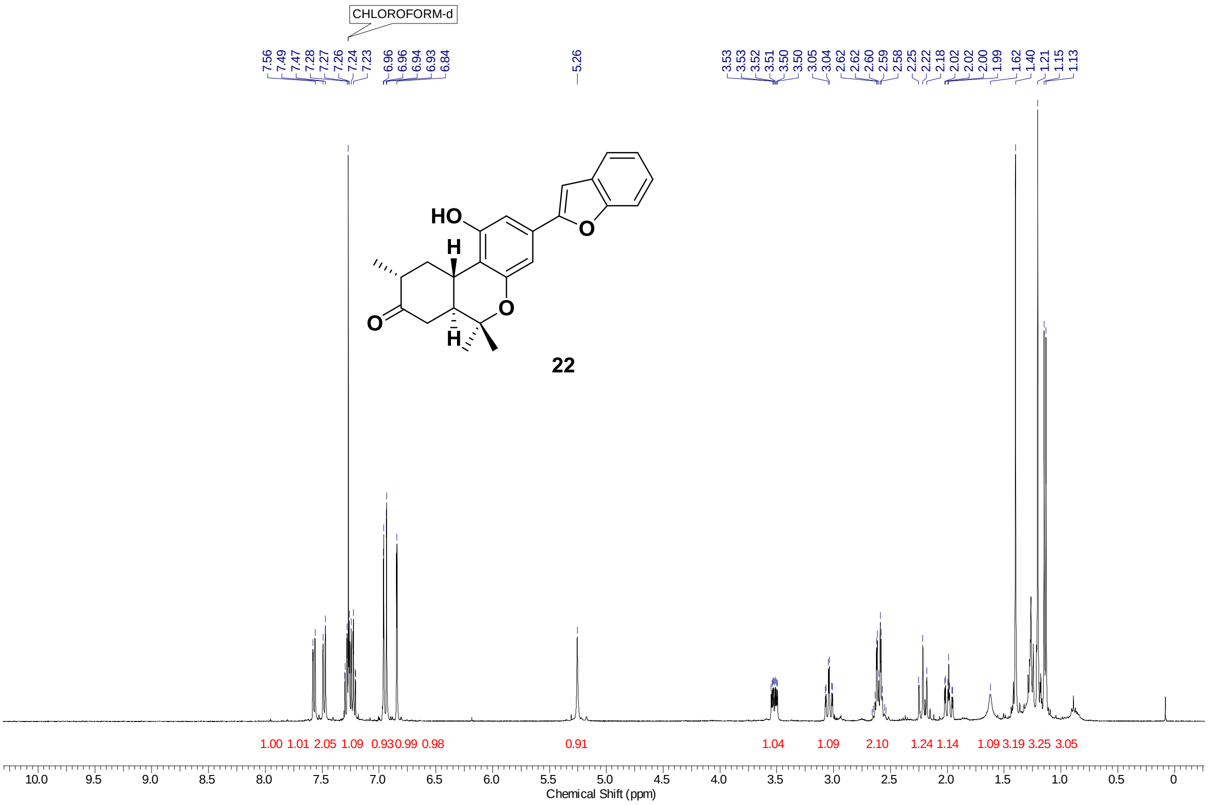

CHLOROFORM-d
155.45
155.38
154.69
134.64
129.69
129.17
124.11
122.82
120.84
119.32
114.14
111.06
107.10
103.90
101.19
77.26
77.12
77.00
76.75
44.78
35.78
31.85
27.85
27.51
23.48
18.52
HO
H
O
O
H
19
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

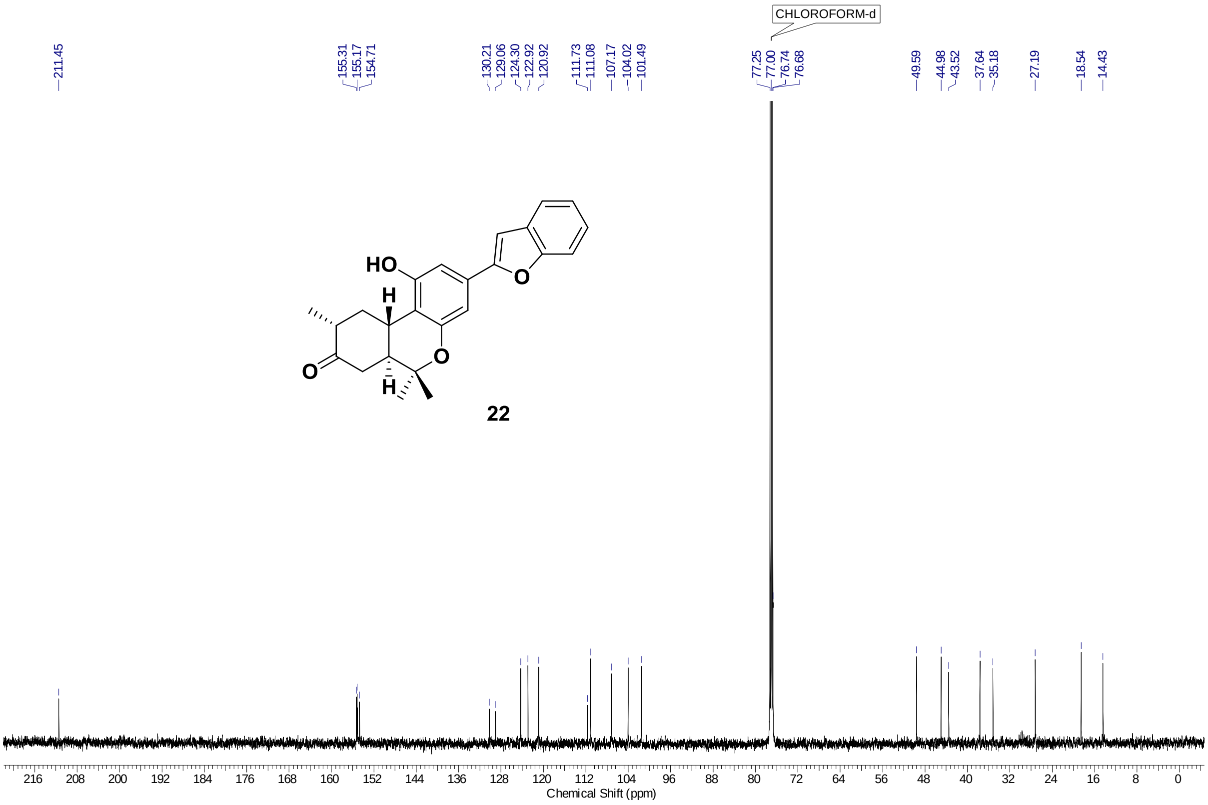

RMONO1_PROTON-4.JDF
HO
H
H
OH
O
Crude 18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

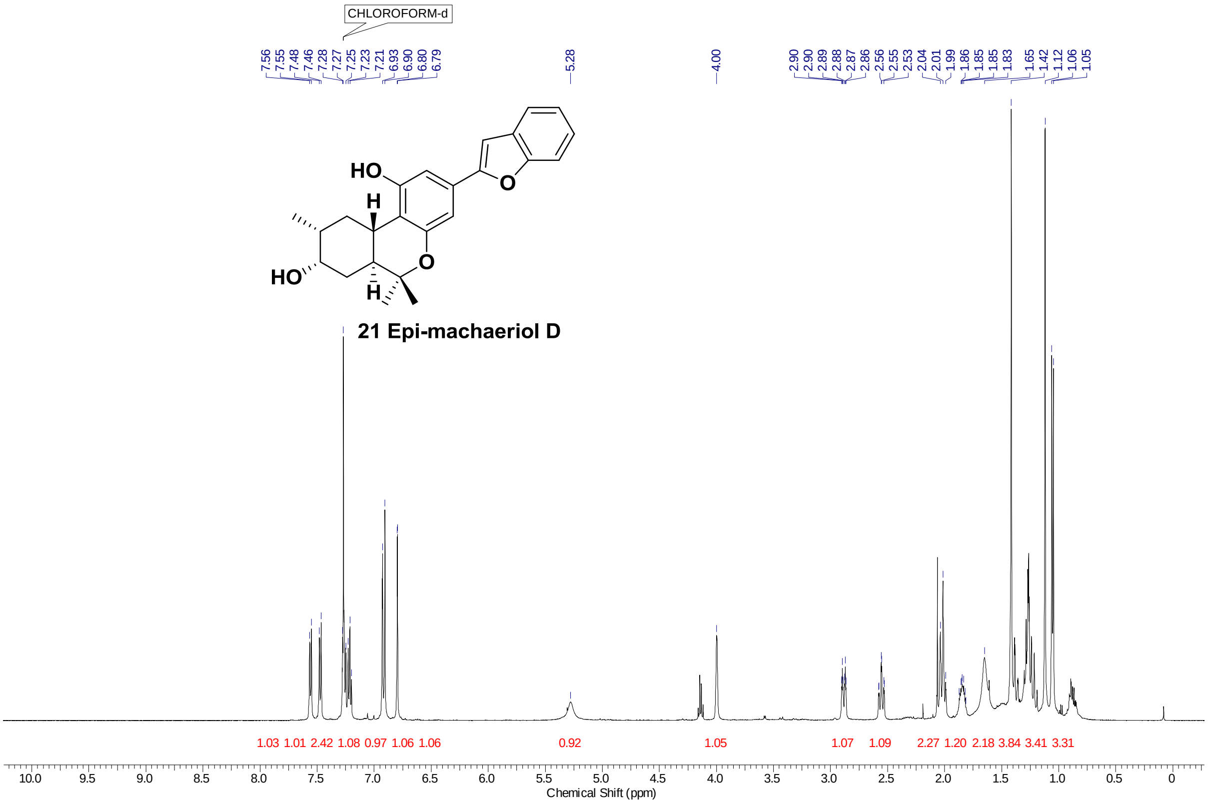

RCYCL3_1H-5.JDF
HO
H
O
H
O
Crude 19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


CHLOROFORM-d
7.56
7.54
7.48
7.46
7.28
7.27
7.26
7.24
7.23
7.21
6.91
6.90
6.86
6.12
3.49
3.48
3.46
3.45
3.20
3.19
2.77
2.75
2.73
2.20
2.19
2.17
2.16
2.15
2.13
1.67
1.65
1.49
1.46
1.45
1.44
1.41
1.37
1.03
HO
H
O
O
H
O
20
1.17
1.24
1.78
1.03
1.11
0.94
1.03
0.98
1.01
1.08
1.00
1.10
2.15
1.01
3.12
3.09
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

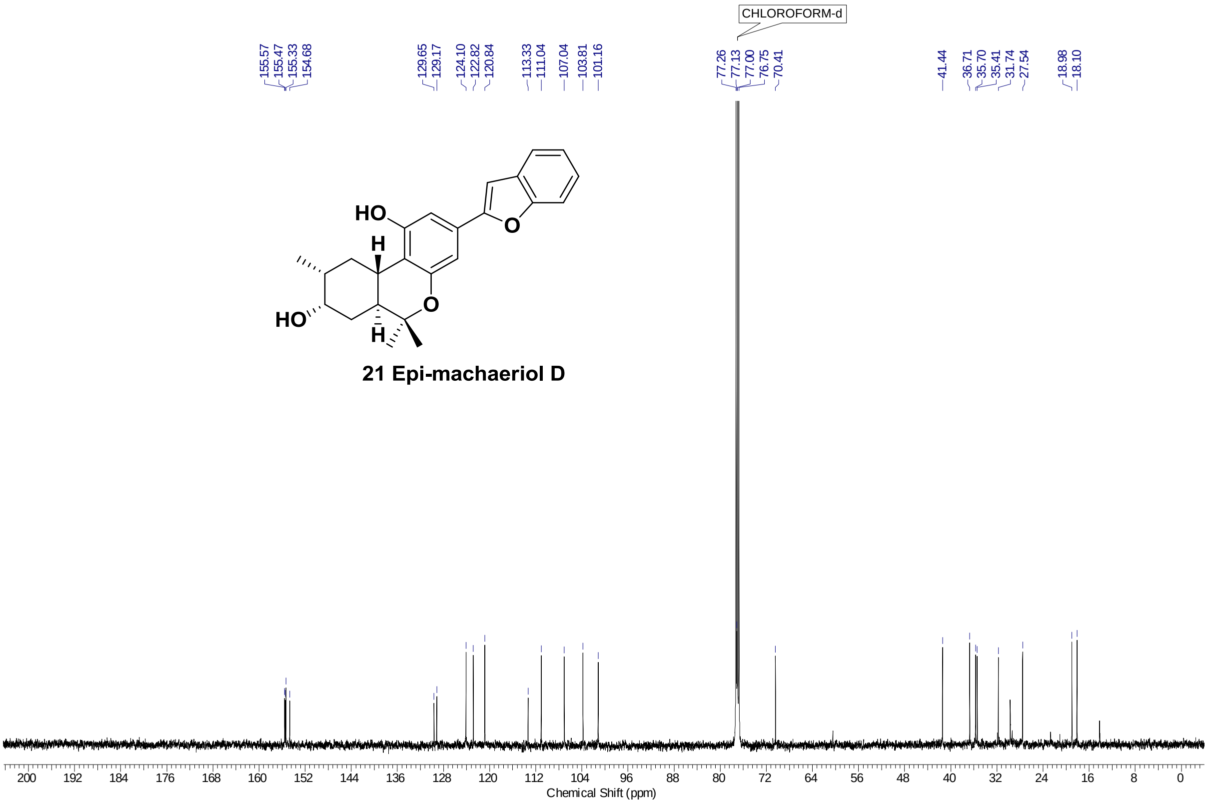

CHLOROFORM-d
155.51
155.45
155.24
154.66
129.66
129.14
124.09
122.81
120.80
113.20
111.03
106.76
104.32
101.12
77.33
77.20
77.00
76.68
59.66
59.45
44.57
34.85
28.11
27.29
26.68
22.95
18.34
HO
H
O
O
H
O
20
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


CHLOROFORM-d
7.56 7.49 7.47 7.28 7.27 7.26 7.24 7.23 6.96 6.96 6.94 6.93 6.84
5.26
3.53 3.53 3.52 3.51 3.50 3.50 3.05 3.04 2.62 2.62 2.60 2.59 2.58 2.25 2.22 2.18 2.02 2.02 2.00 1.99 1.62 1.40 1.21 1.15 1.13
HO
H
O
O
H
O
22
1.00 1.01 2.05 1.09 0.93 0.99 0.98
0.91
1.04 1.09 2.10 1.24 1.14 1.09 3.19 3.25 3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

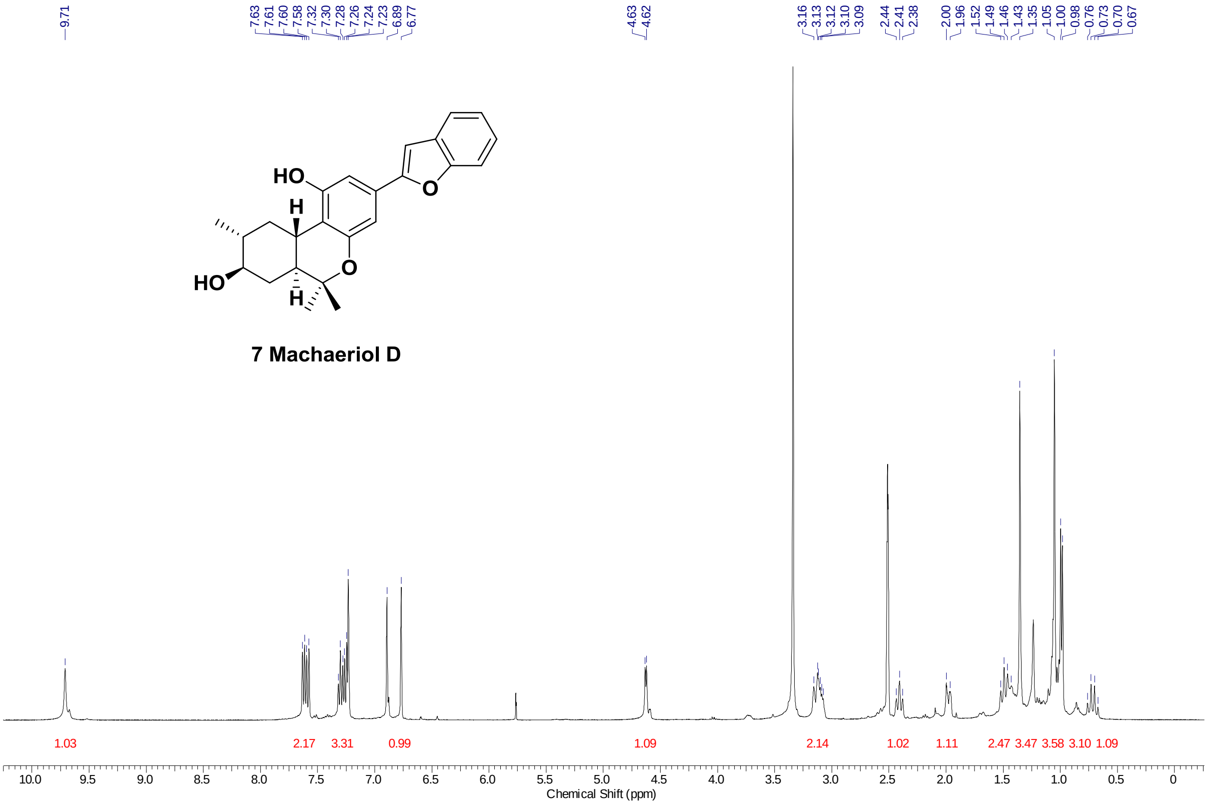

CHLOROFORM-d
211.45
155.31 155.17 154.71
130.21 129.06 124.30 122.92 120.92
111.73 111.08 107.17 104.02 101.49
77.25 77.00 76.74 76.68
49.59 44.98 43.52 37.64 35.18 27.19 18.54 14.43
HO
H
O
O
H
O
22
216 208 200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

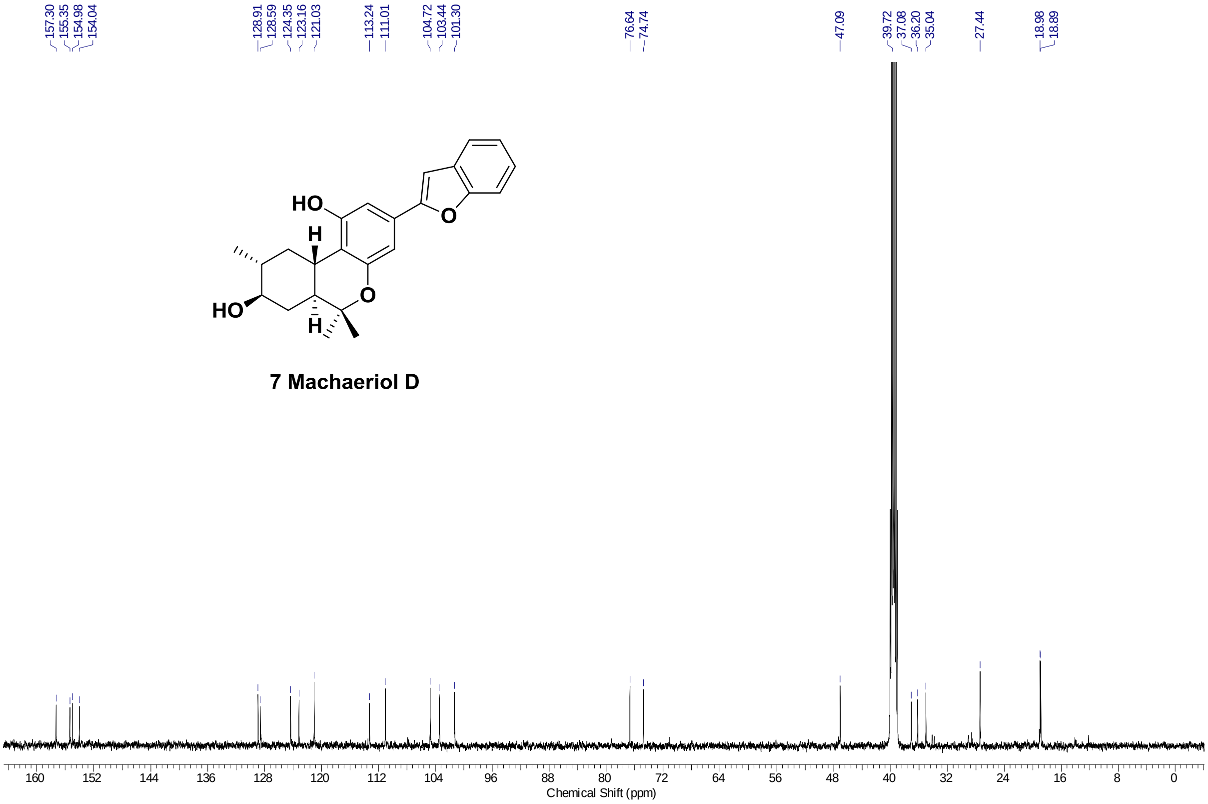


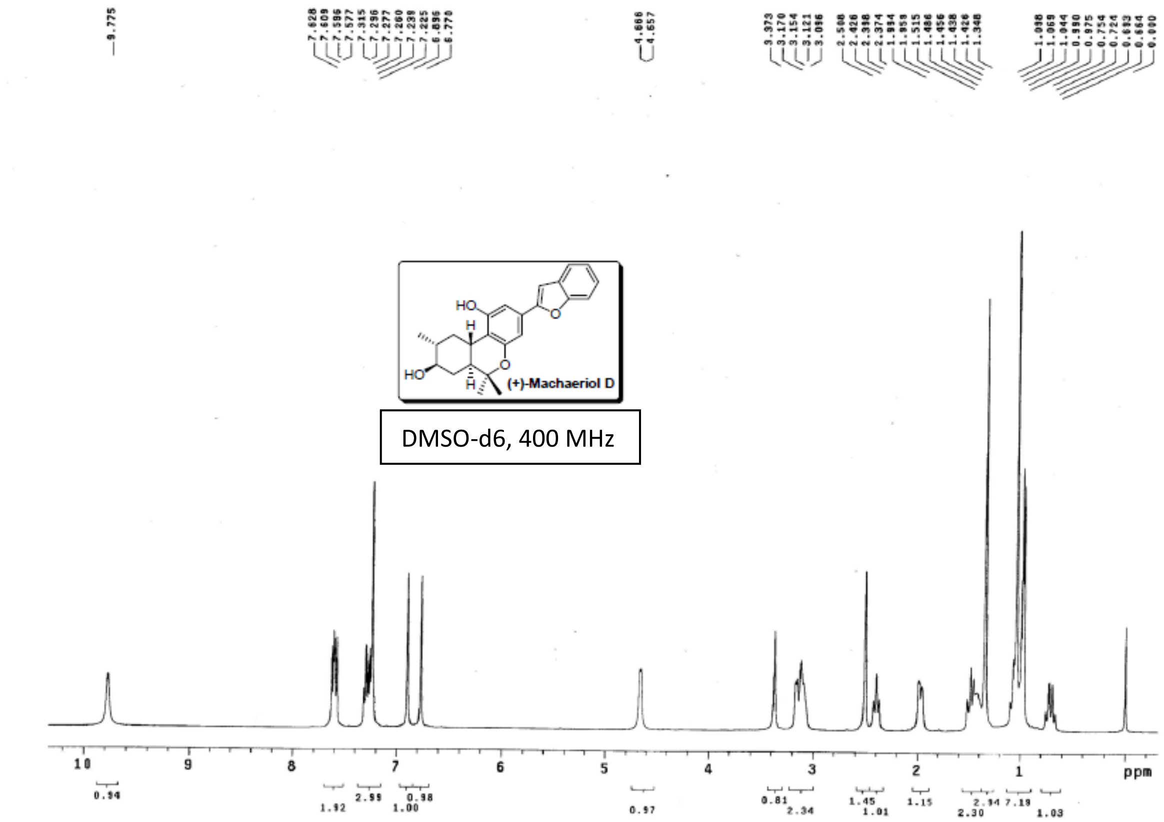
21 Epi-machaeriol D

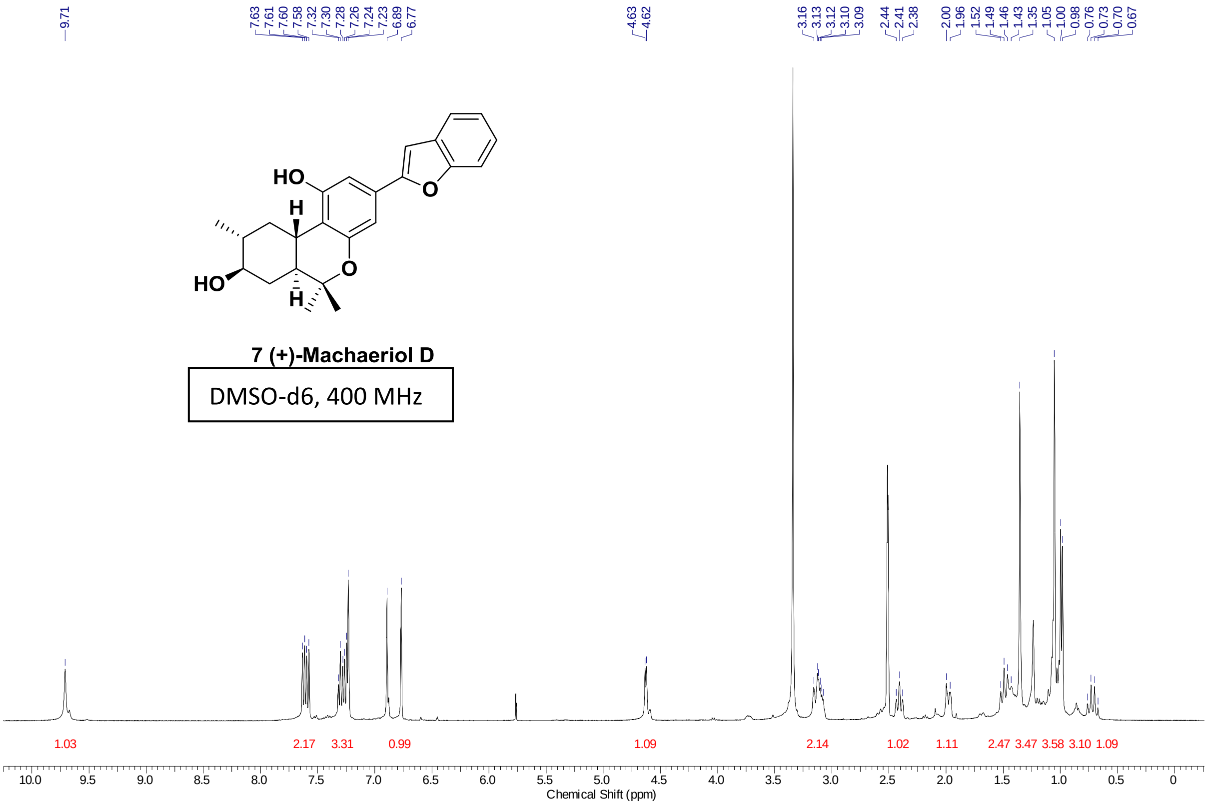


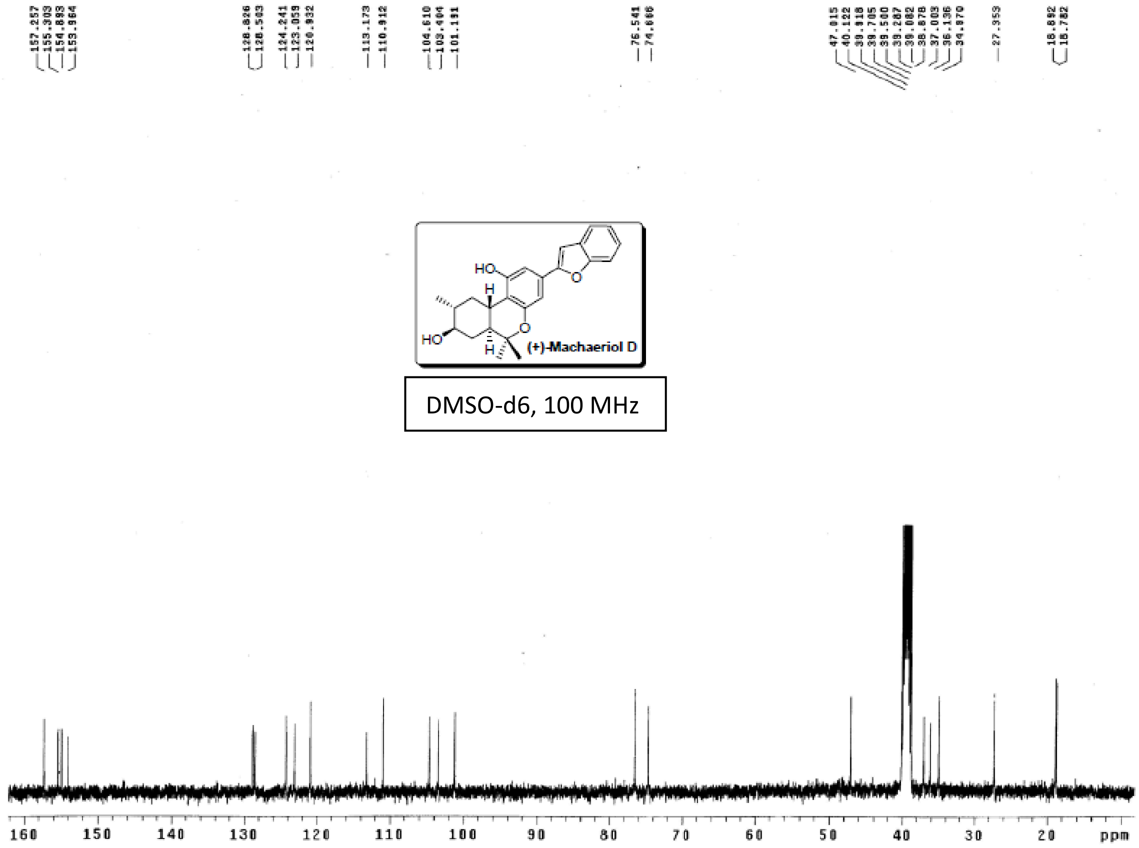
21 Epi-machaeriol D

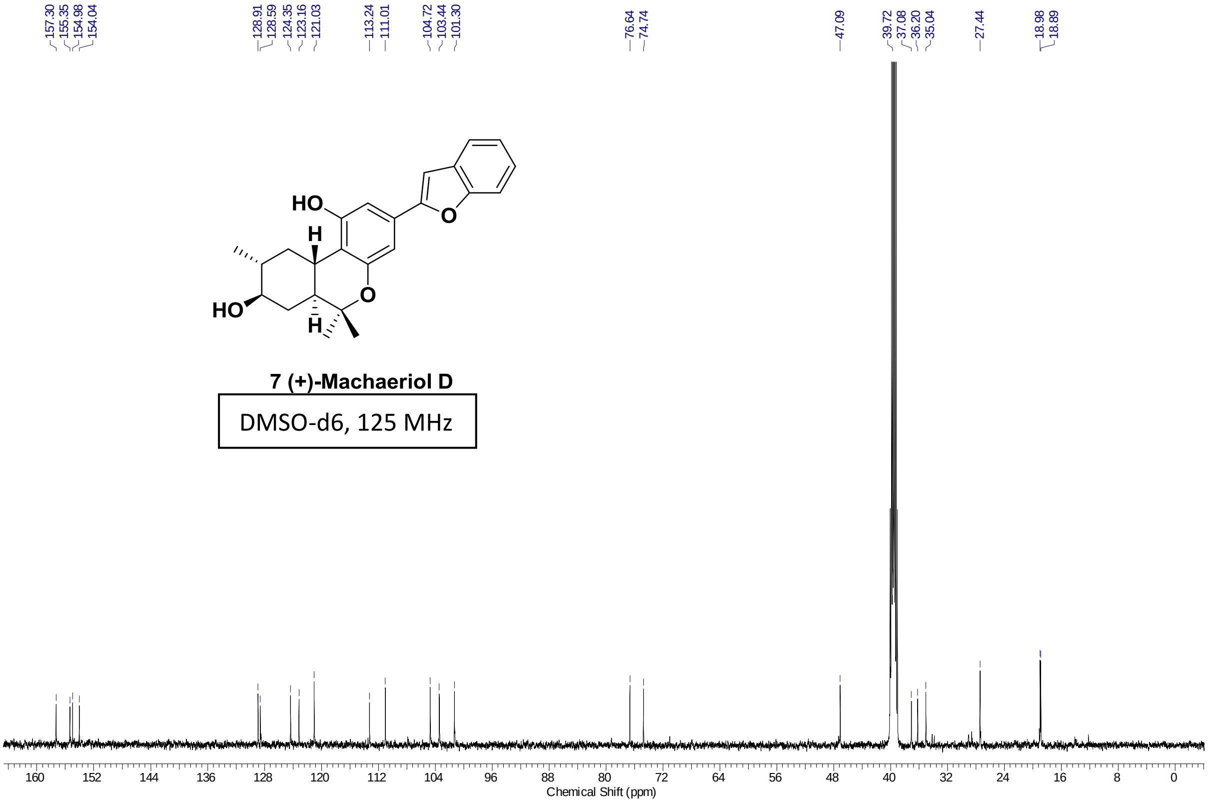

9.71
7.63 7.61 7.60 7.58 7.32 7.30 7.28 7.26 7.24 7.23 6.89 6.77
4.63 4.62
3.16 3.13 3.12 3.10 3.09 2.44 2.41 2.38 2.00 1.96 1.52 1.49 1.46 1.43 1.35 1.05 1.00 0.98 0.76 0.73 0.70 0.67
HO
H
HO
O
O
H
7 Machaeriol D
1.03
2.17 3.31 0.99
1.09
2.14 1.02 1.11 2.47 3.47 3.58 3.10 1.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

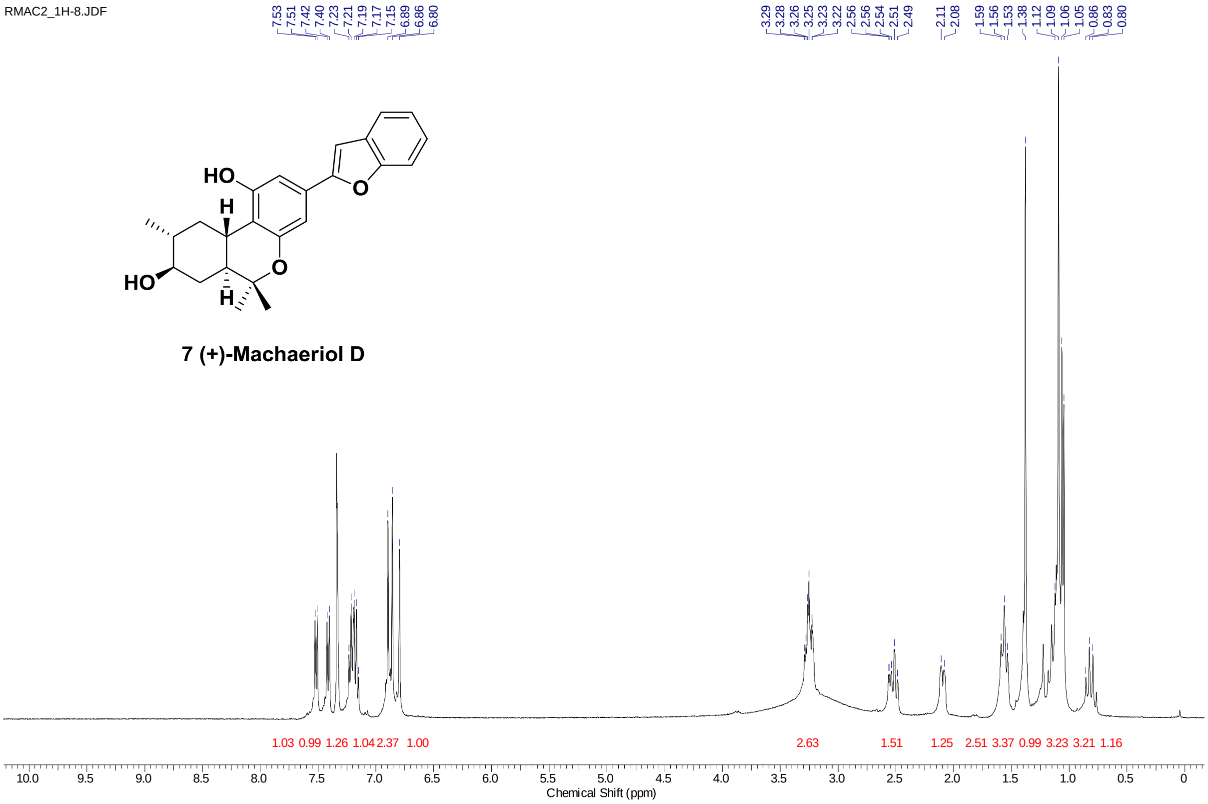

157.30 155.35 154.98 154.04
128.91 128.59 124.35 123.16 121.03
113.24 111.01
104.72 103.44 101.30
76.64 74.74
47.09
39.72 37.08 36.20 35.04
27.44
18.98 18.89
HO
H
HO
O
O
H
7 Machaeriol D
160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

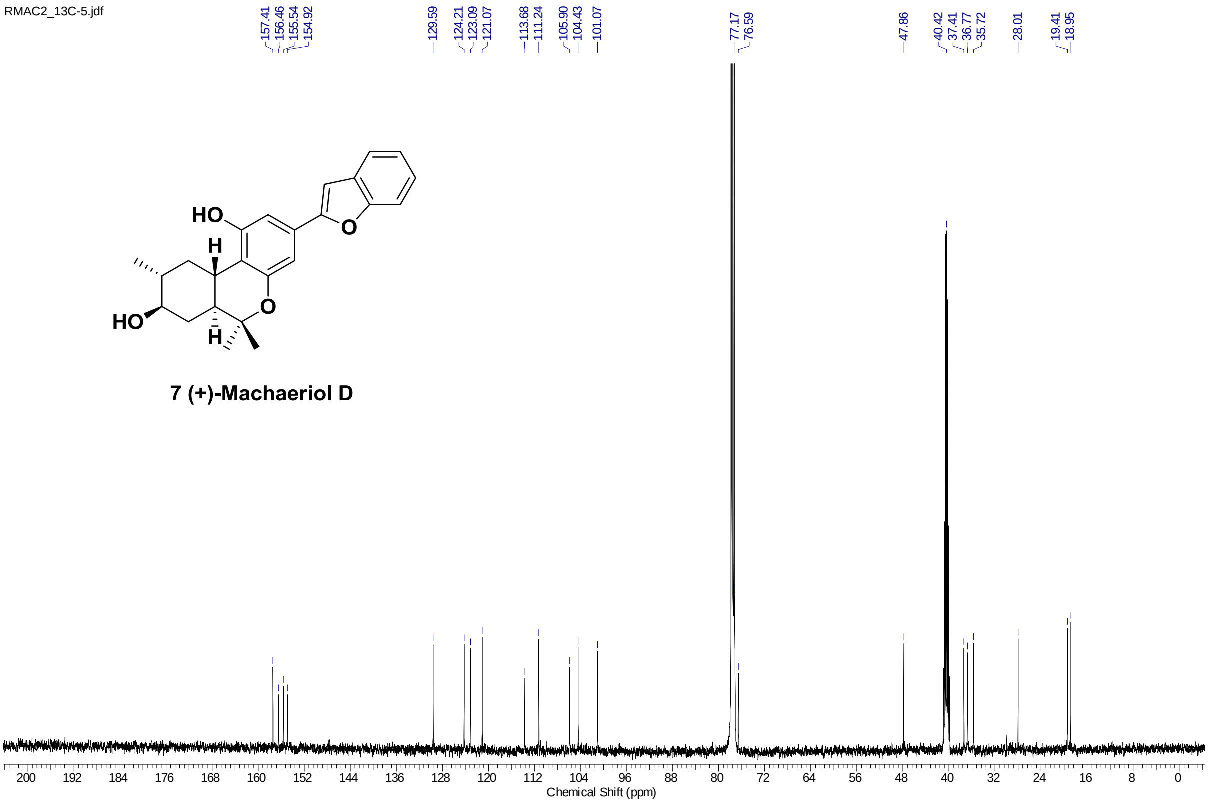

(+)-Machaeriol D
DMSO-d6, 400 MHz
ppm
10
9
8
7
6
5
4
3
2
1
0.94
1.92
2.99
1.00
0.98
0.97
0.81
2.34
1.45
1.01
1.15
2.30
2.34
7.19
1.03

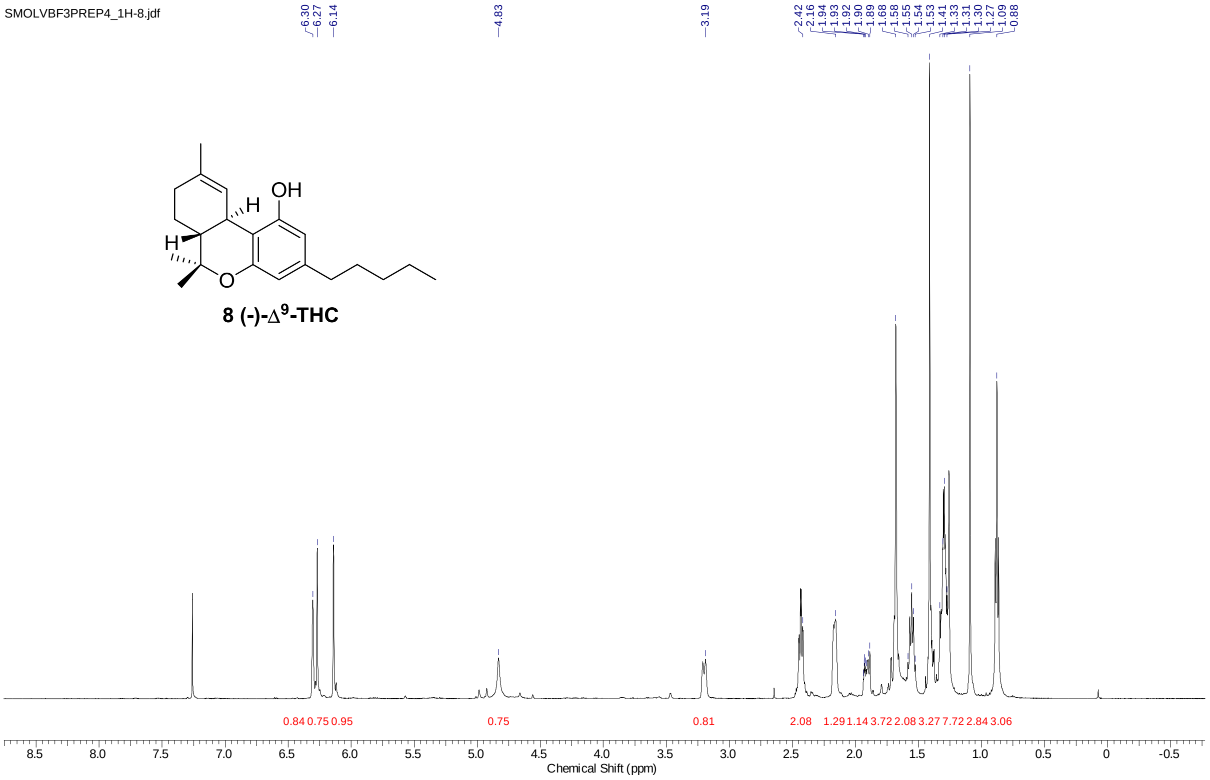

9.71
7.63
7.61
7.60
7.58
7.32
7.30
7.28
7.26
7.24
7.23
6.89
6.77
4.63
4.62
3.16
3.13
3.12
3.10
3.09
2.44
2.41
2.38
2.00
1.96
1.52
1.49
1.46
1.43
1.35
1.05
1.00
0.98
0.76
0.73
0.70
0.67
7 (+)-Machaeriol D
DMSO-d6, 400 MHz
1.03
2.17
3.31
0.99
1.09
2.14
1.02
1.11
2.47
3.47
3.58
3.10
1.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


157.257
155.303
154.893
153.964
128.826
128.503
124.241
123.059
120.932
113.173
110.912
104.610
103.404
101.191
76.541
74.666
47.015
40.122
39.918
39.705
39.500
39.287
39.082
38.878
37.003
36.136
34.970
27.353
18.892
18.782
HO
H
O
HO
H
(+)-Machaeriol D
DMSO-d6, 100 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

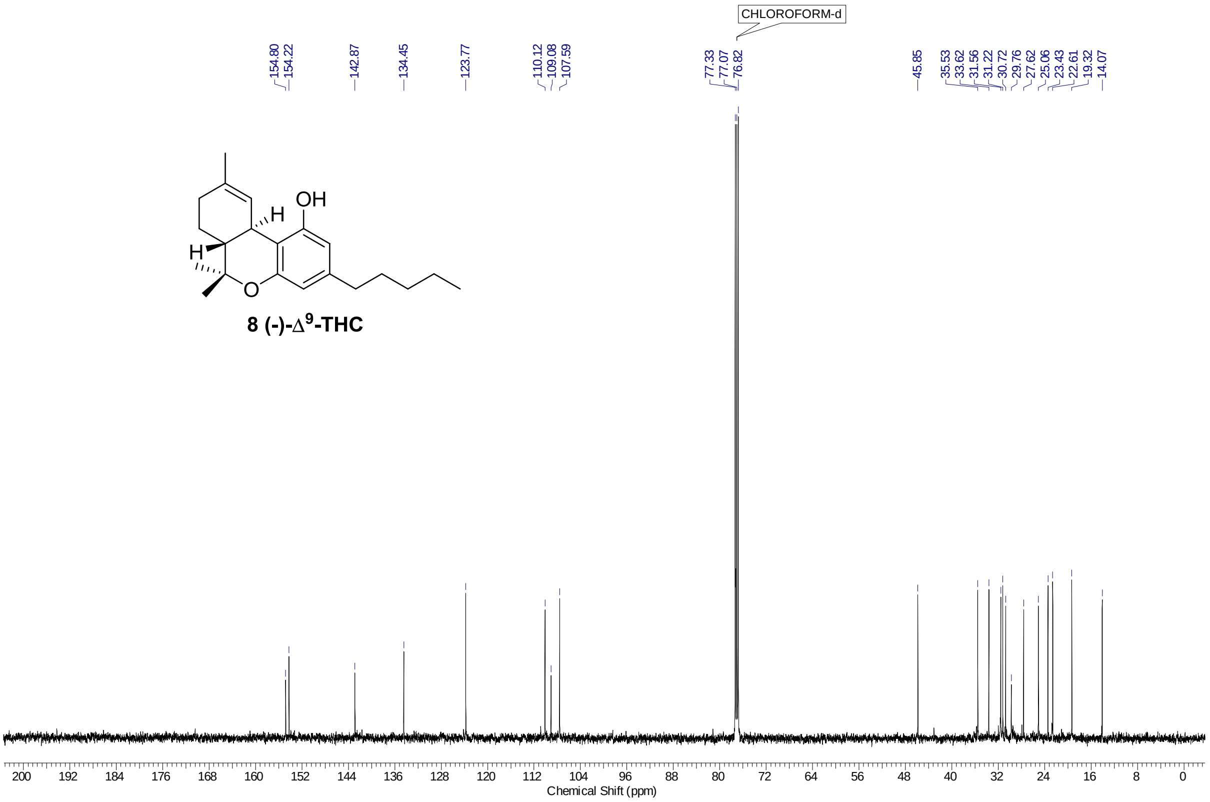

157.30
155.35
154.98
154.04
128.91
128.59
124.35
123.16
121.03
113.24
111.01
104.72
103.44
101.30
76.64
74.74
47.09
39.72
37.08
36.20
35.04
27.44
18.98
18.89
HO
H
O
HO
H
7 (+)-Machaeriol D
DMSO-d6, 125 MHz
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


RMAC2_1H-8.JDF
7.53
7.51
7.42
7.40
7.23
7.21
7.19
7.17
7.15
6.89
6.86
6.80
3.29
3.28
3.26
3.25
3.23
3.22
2.56
2.56
2.54
2.51
2.49
2.11
2.08
1.59
1.56
1.53
1.38
1.12
1.09
1.06
1.05
0.86
0.83
0.80
HO
H
HO
H
O
O
7 (+)-Machaeriol D
1.03 0.99 1.26 1.04 2.37 1.00
2.63
1.51
1.25 2.51 3.37 0.99 3.23 3.21 1.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

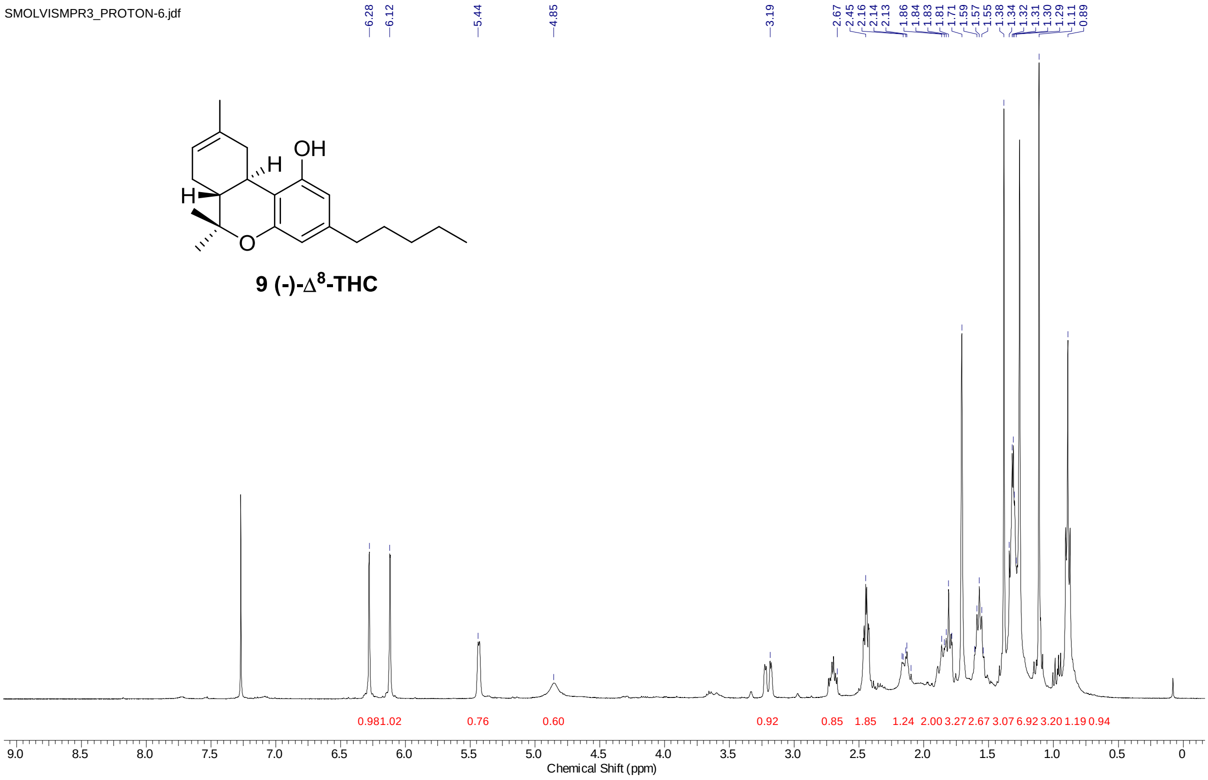

RMAC2_13C-5.jdf
157.41
156.46
155.54
154.92
129.59
124.21
123.09
121.07
113.68
111.24
105.90
104.43
101.07
77.17
76.59
47.86
40.42
37.41
36.77
35.72
28.01
19.41
18.95
HO
H
HO
H
O
O
7 (+)-Machaeriol D
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)



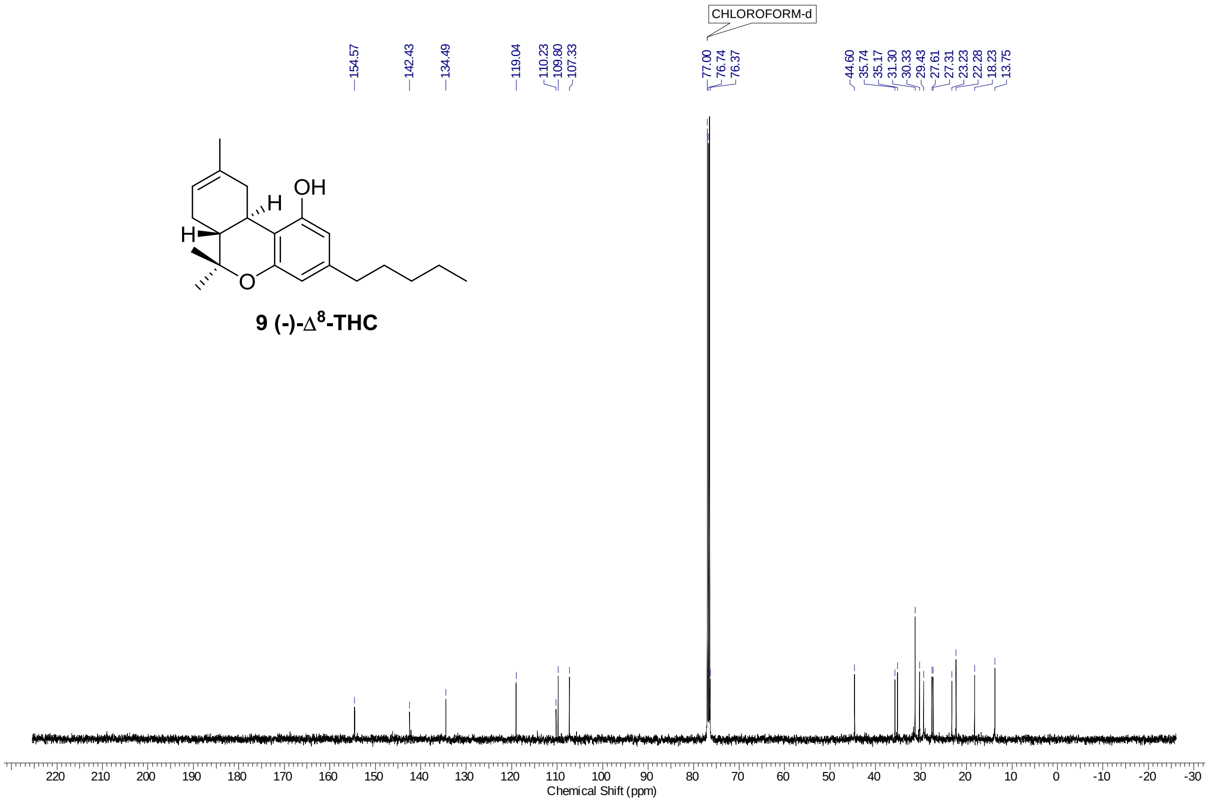
8 (-)-Δ⁹-THC



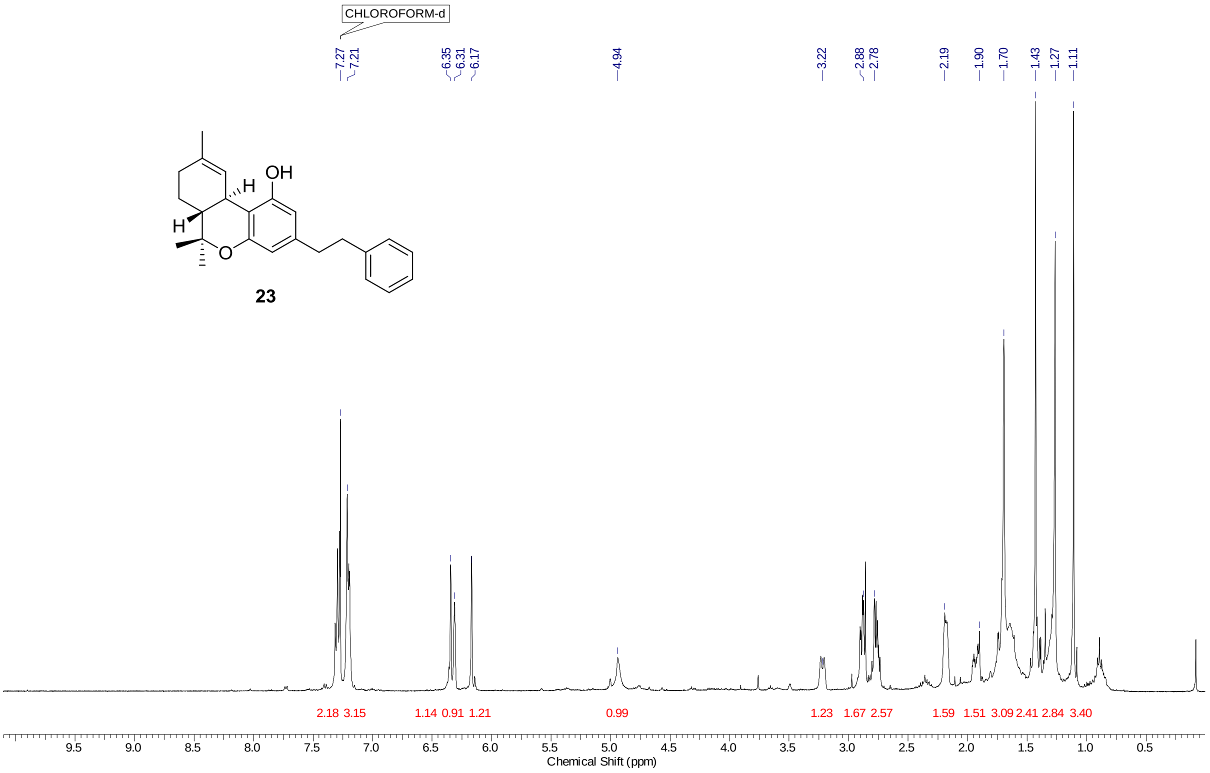
8 (-)-Δ⁹-THC



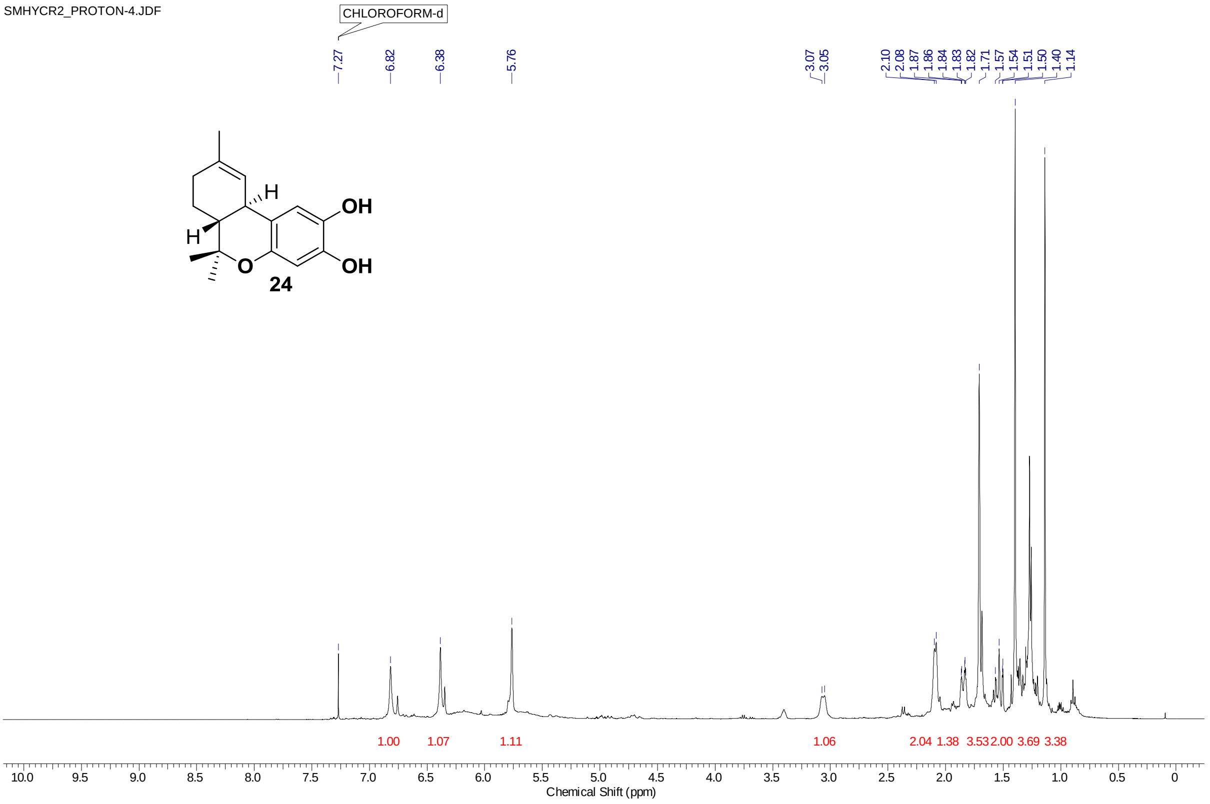
9 (-)-Δ^8-THC



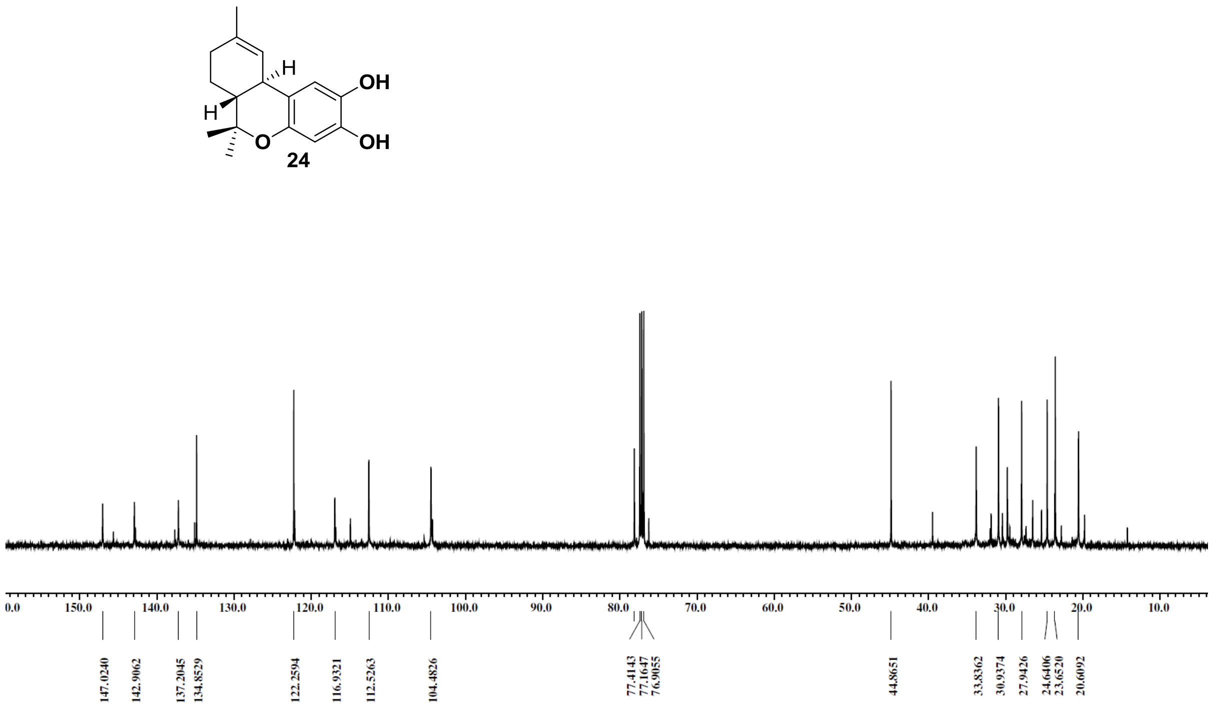
9 (-)-Δ^8-THC


CHLOROFORM-d
7.27
7.21
6.35
6.31
6.17
4.94
3.22
2.88
2.78
2.19
1.90
1.70
1.43
1.27
1.11
OH
H
H
O
23
2.18 3.15
1.14 0.91 1.21
0.99
1.23 1.67 2.57
1.59 1.51 3.09 2.41 2.84 3.40
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)

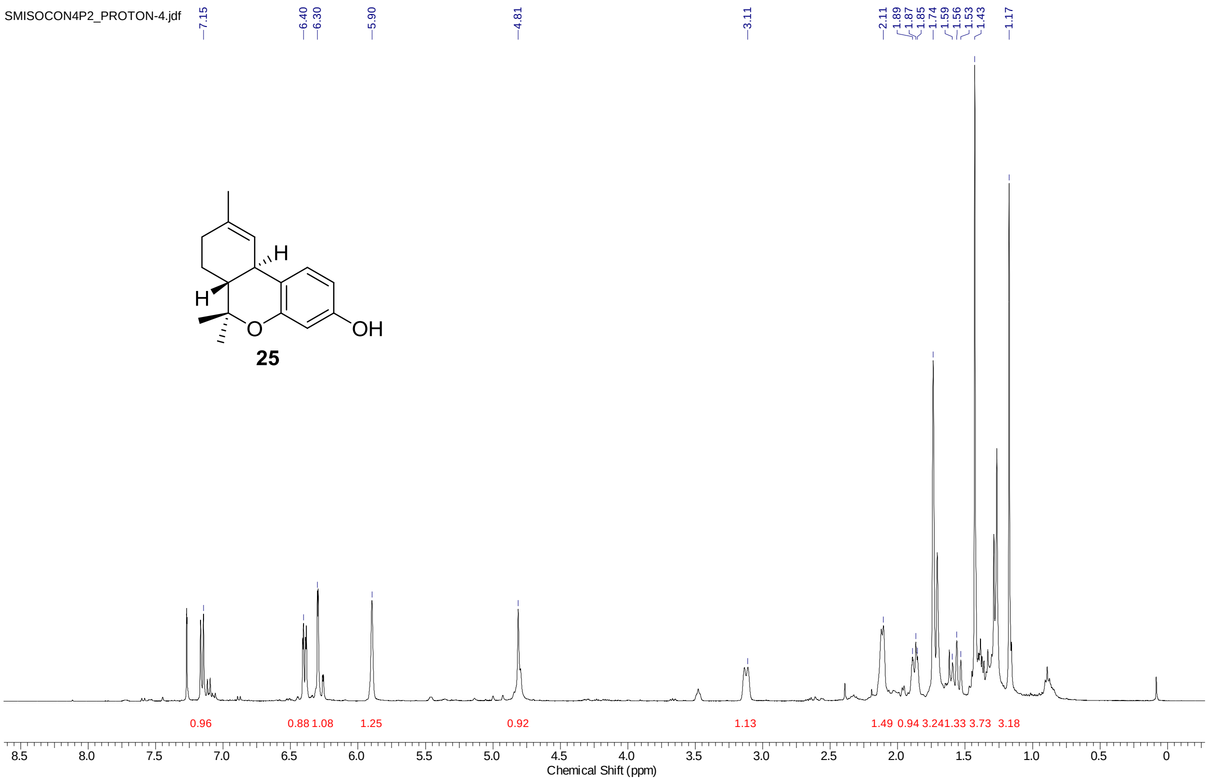

CHLOROFORM-d
155.22
154.62
142.27
141.99
134.78
128.65
126.18
123.91
110.30
109.74
107.79
77.64
77.53
77.32
77.00
46.07
37.81
33.88
31.46
30.01
27.86
25.31
23.69
19.57
OH
H
H
O
23
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16
Chemical Shift (ppm)

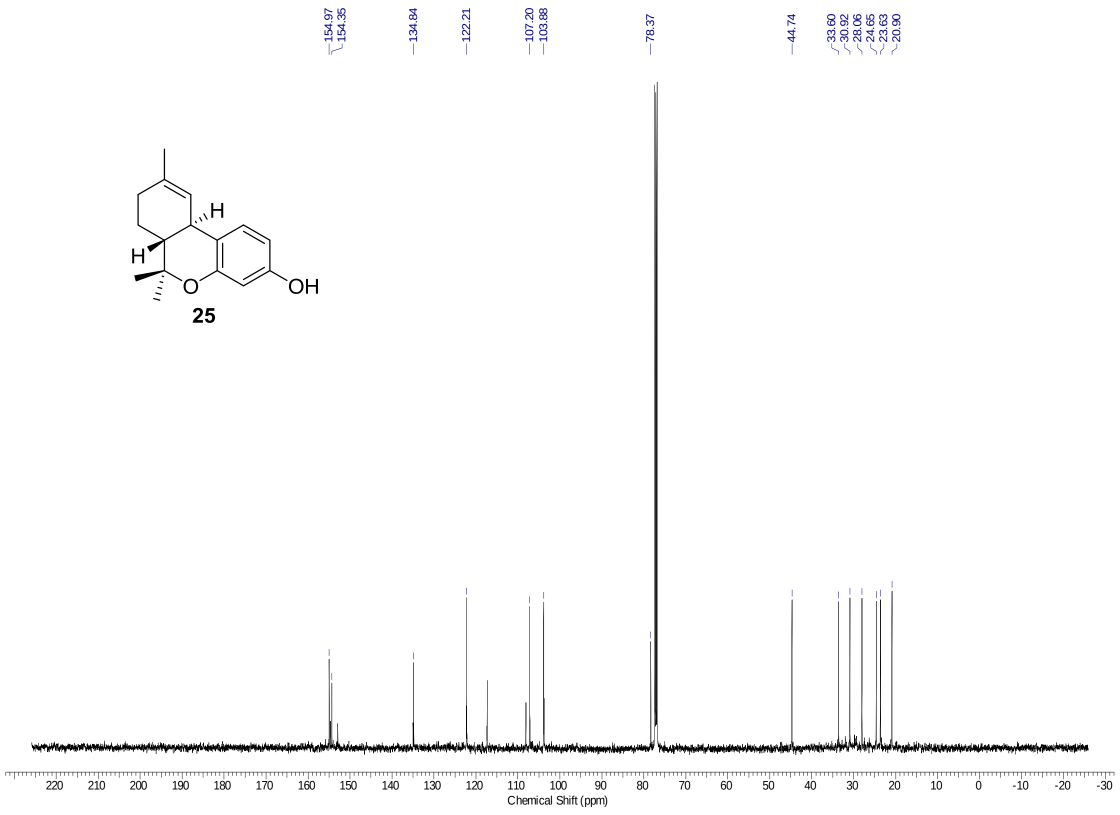

SMHYCR2_PROTON-4.JDF
CHLOROFORM-d
7.27
6.82
6.38
5.76
3.07
3.05
2.10
2.08
1.87
1.86
1.84
1.83
1.82
1.71
1.57
1.54
1.51
1.50
1.40
1.14
OH
OH
H
H
O
1.00
1.07
1.11
1.06
2.04
1.38
3.53
2.00
3.69
3.38
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

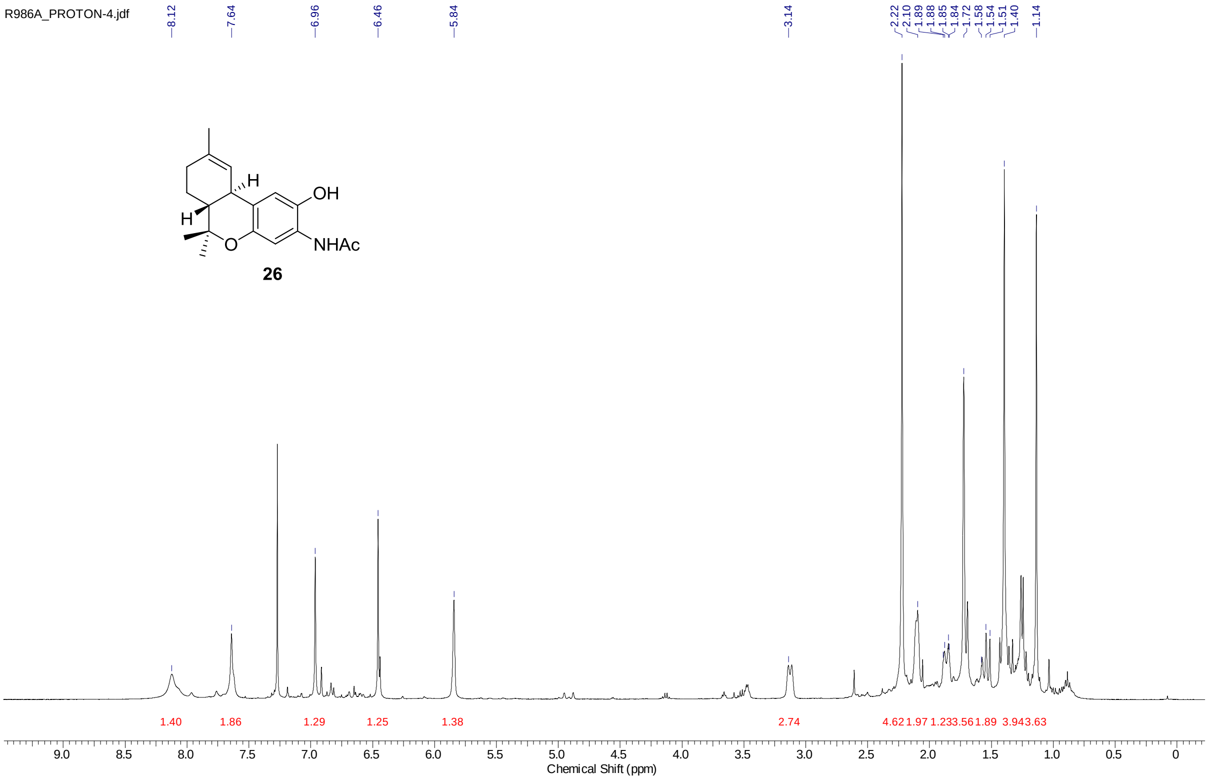
24

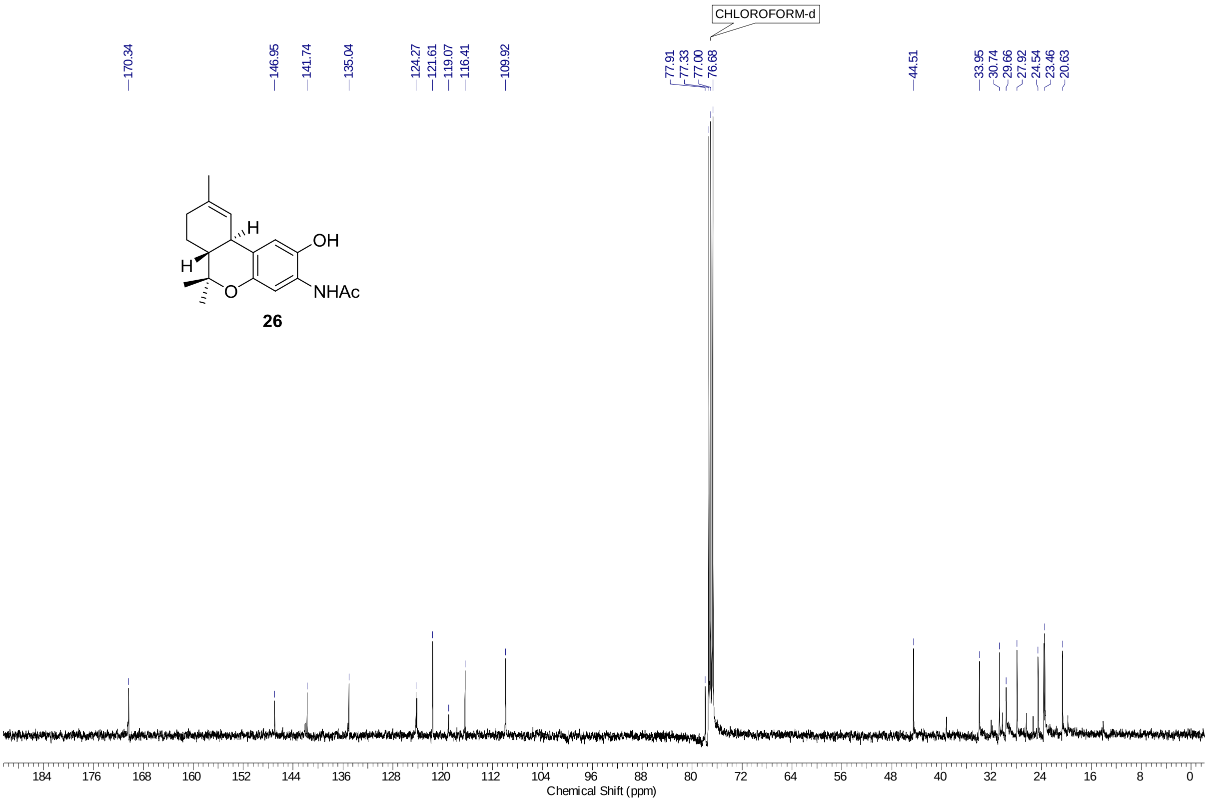

OH
OH
H
H
O
0.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
147.0240
142.9062
137.2045
134.8529
122.2594
116.9321
112.5263
104.4826
77.4143
77.1647
76.9055
44.8651
33.8362
30.9374
27.9426
24.6406
23.6520
20.6092

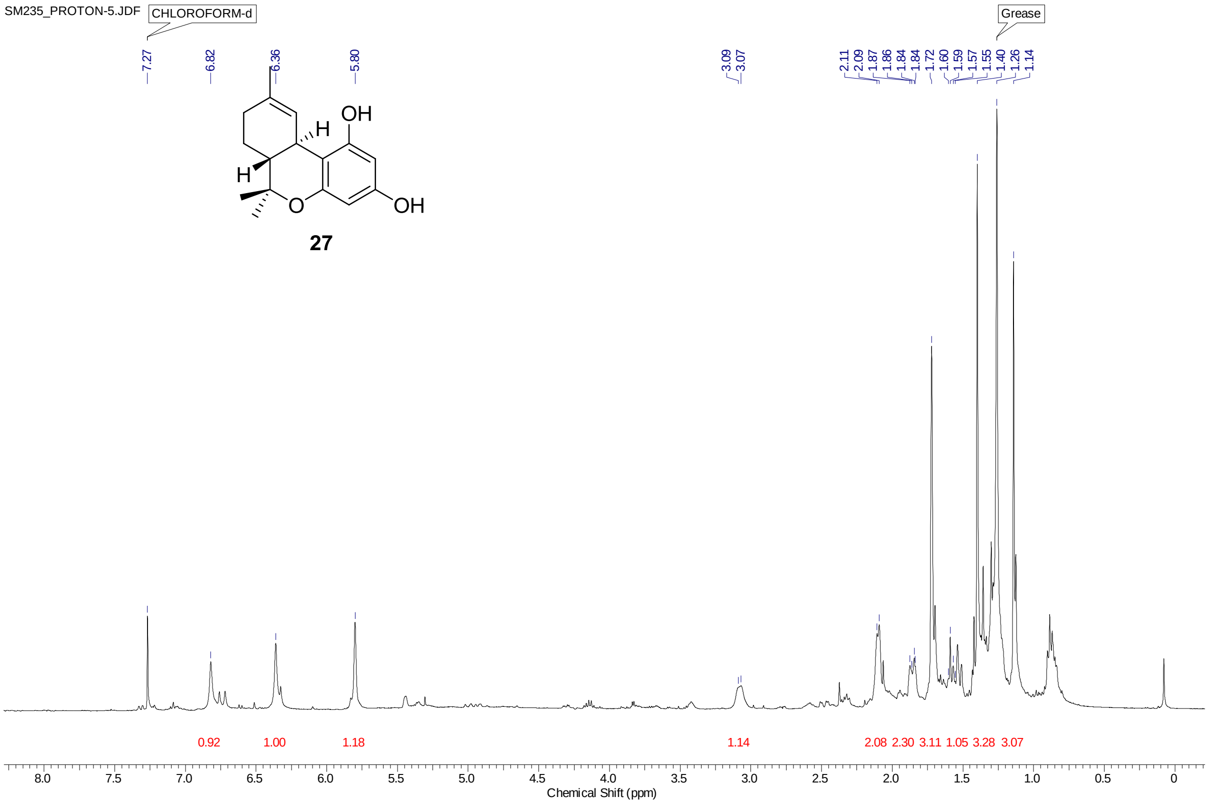
24

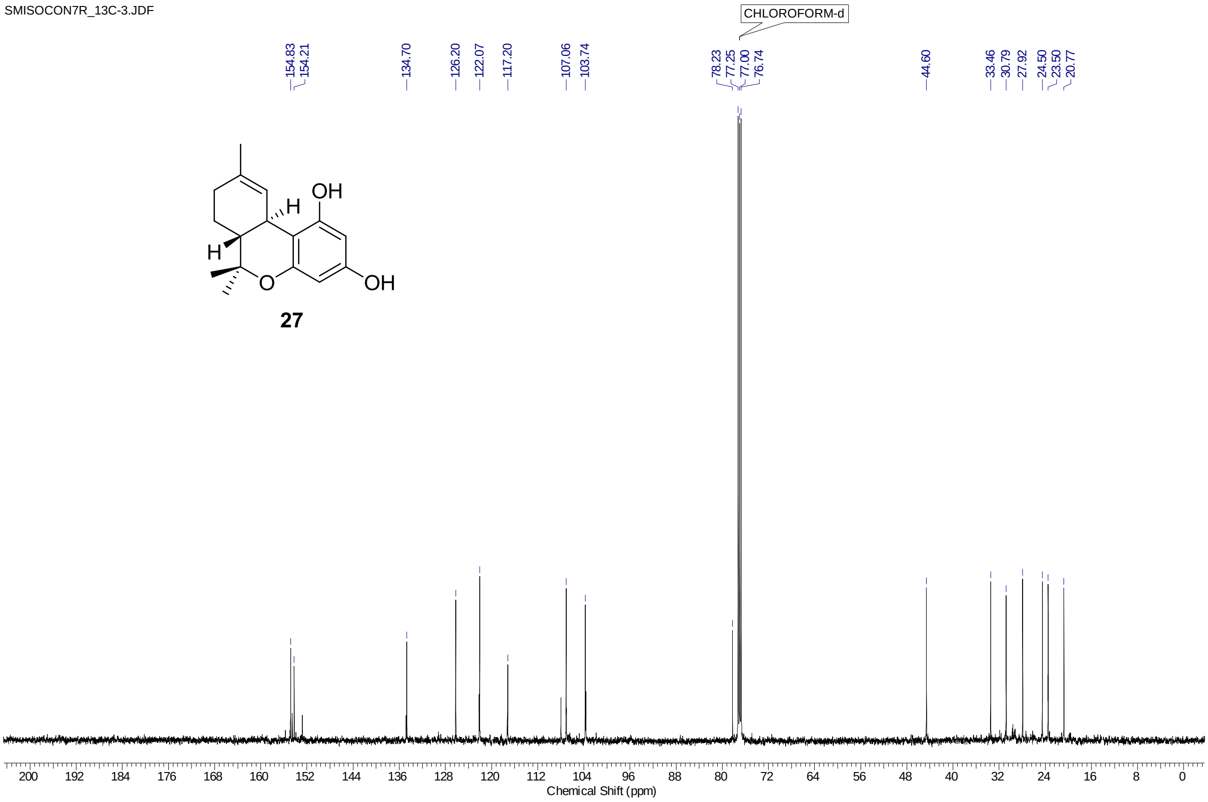

SMISOCON4P2_PROTON-4.jdf
7.15
6.40
6.30
5.90
4.81
3.11
2.11
1.89
1.87
1.85
1.74
1.59
1.56
1.53
1.43
1.17
H
H
O
OH
25
0.96
0.88
1.08
1.25
0.92
1.13
1.49
0.94
3.24
1.33
3.73
3.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

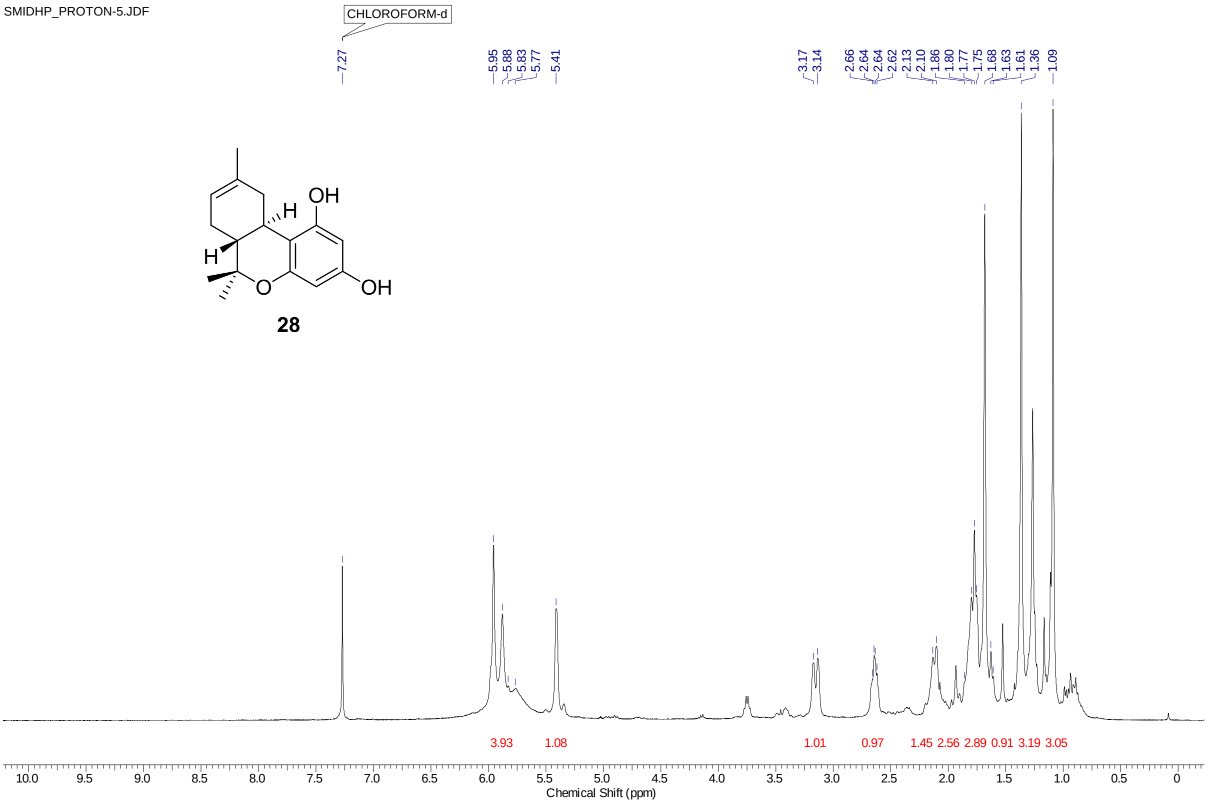

154.97
154.35
134.84
122.21
107.20
103.88
78.37
44.74
33.60
30.92
28.06
24.65
23.63
20.90
H
H
O
OH
25
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
Chemical Shift (ppm)

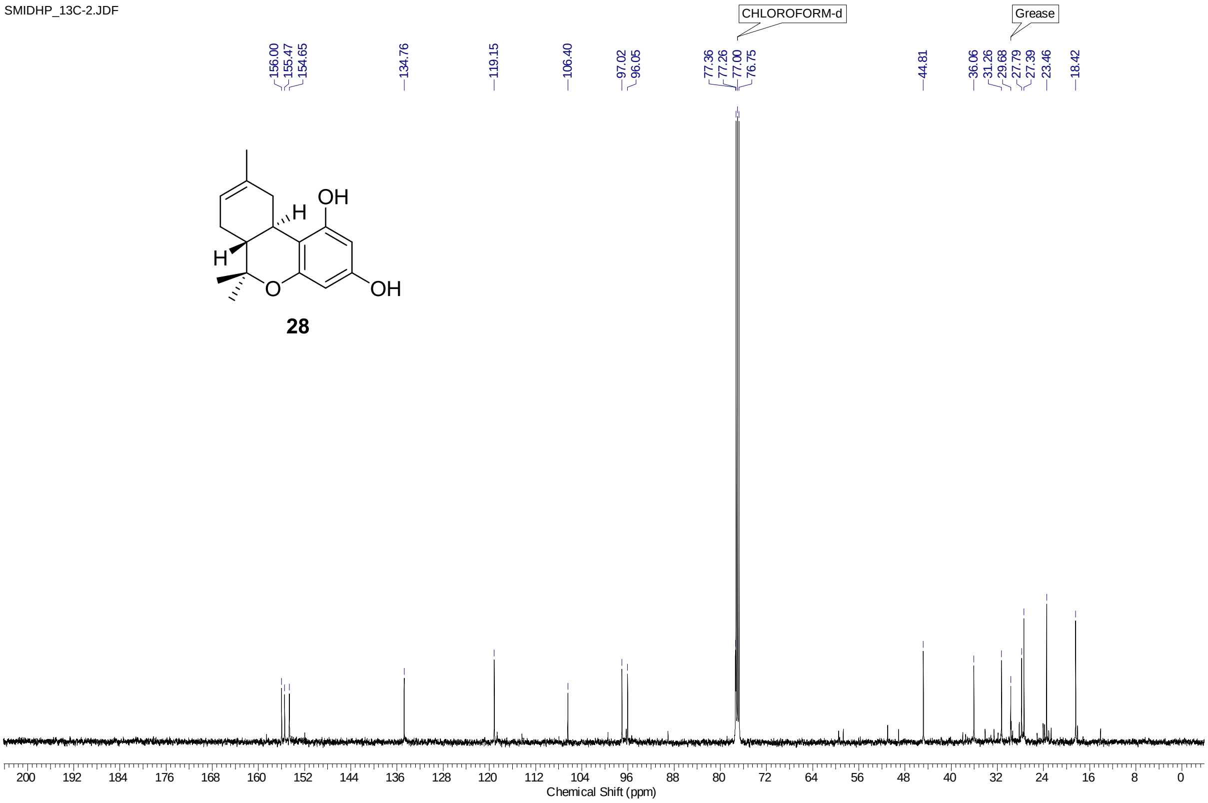

R986A_PROTON-4.jdf
8.12
7.64
6.96
6.46
5.84
3.14
2.22
2.10
1.89
1.88
1.85
1.84
1.72
1.58
1.54
1.51
1.40
1.14
H
OH
H
O
NHAc
26
1.40
1.86
1.29
1.25
1.38
2.74
4.62
1.97
1.23
3.56
1.89
3.94
3.63
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

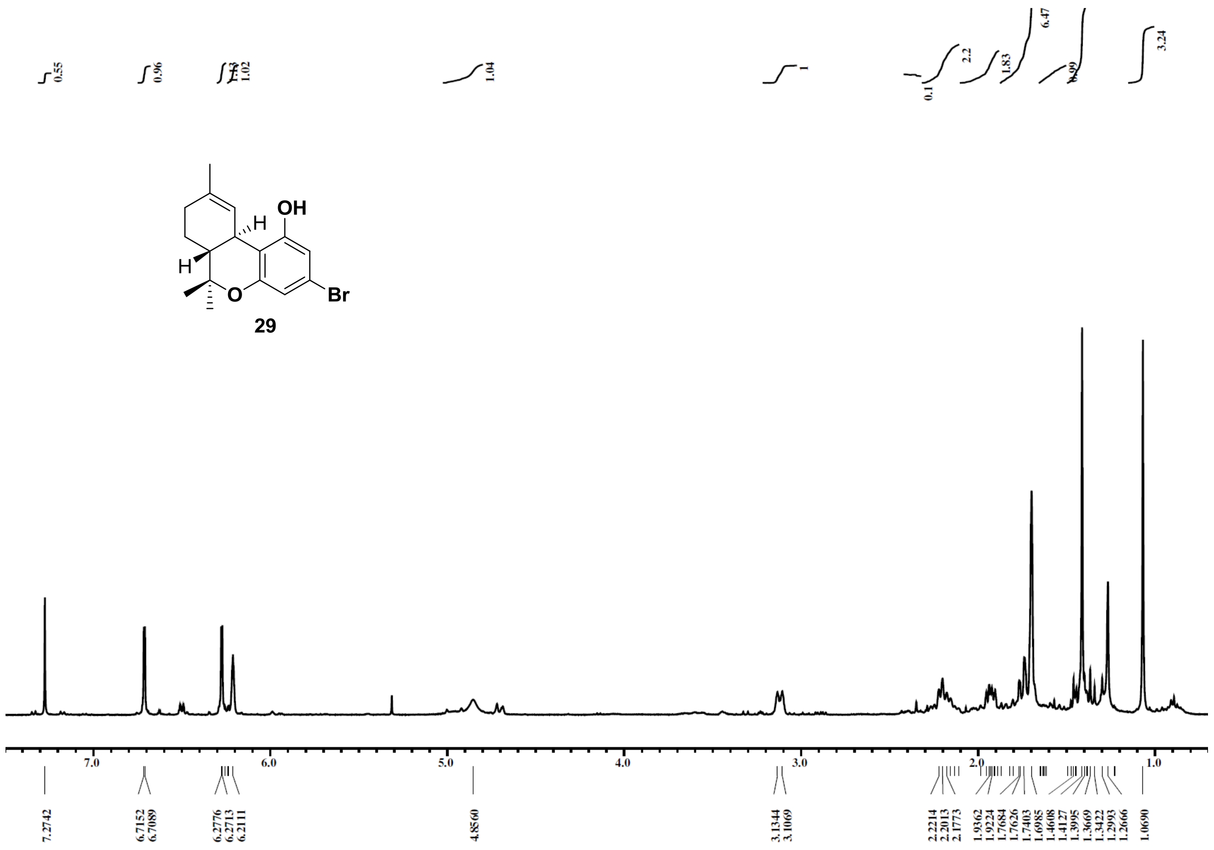

CHLOROFORM-d
170.34
146.95
141.74
135.04
124.27
121.61
119.07
116.41
109.92
77.91
77.33
77.00
76.68
44.51
33.95
30.74
29.66
27.92
24.54
23.46
20.63
H
OH
H
O
NHAc
26
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

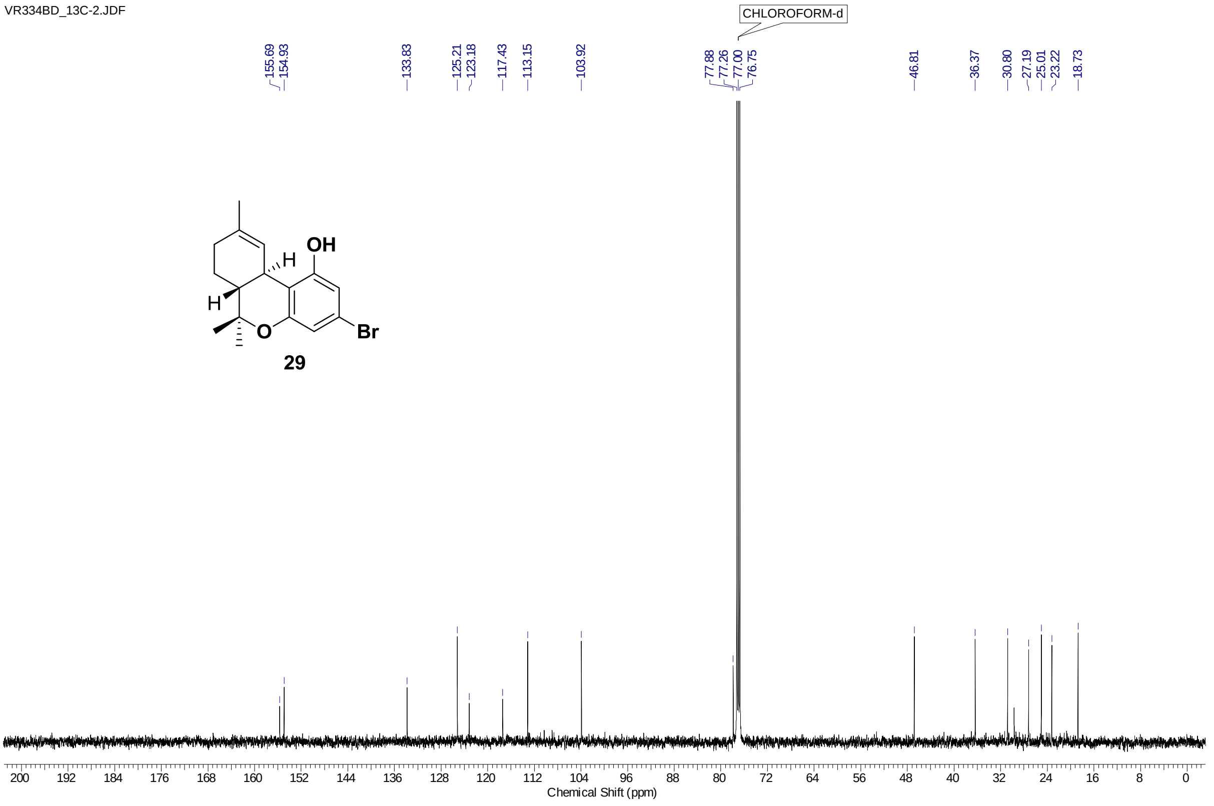

SM235_PROTON-5.JDF
CHLOROFORM-d
Grease
7.27
6.82
6.36
5.80
3.09
3.07
2.11
2.09
1.87
1.86
1.84
1.84
1.72
1.60
1.59
1.57
1.55
1.40
1.26
1.14
OH
H
H
O
OH
27
0.92
1.00
1.18
1.14
2.08
2.30
3.11
1.05
3.28
3.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


SMISOCON7R_13C-3.JDF
CHLOROFORM-d
154.83
154.21
134.70
126.20
122.07
117.20
107.06
103.74
78.23
77.25
77.00
76.74
44.60
33.46
30.79
27.92
24.50
23.50
20.77
OH
H
H
O
OH
27
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


SMIDHP_PROTON-5.JDF
CHLOROFORM-d
7.27
5.95
5.88
5.83
5.77
5.41
3.17
3.14
2.66
2.64
2.64
2.62
2.13
2.10
1.86
1.80
1.77
1.75
1.68
1.63
1.61
1.36
1.09
OH
H
H
O
OH
28
3.93
1.08
1.01
0.97
1.45
2.56
2.89
0.91
3.19
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

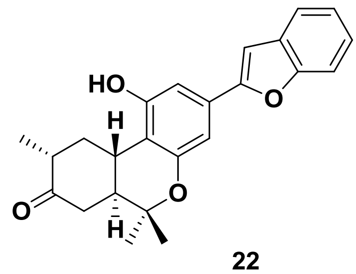

SMIDHP_13C-2.JDF
CHLOROFORM-d
Grease
156.00
155.47
154.65
134.76
119.15
106.40
97.02
96.05
77.36
77.26
77.00
76.75
44.81
36.06
31.26
29.68
27.79
27.39
23.46
18.42
OH
H
H
O
OH
28
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


0.55
0.96
1.02
1.04
0.1
2.2
1.83
6.47
0.99
3.24
OH
H
H
O
Br
29
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.2742
6.7152
6.7089
6.2776
6.2713
6.2111
4.8560
3.1344
3.1069
2.2214
2.2013
2.1773
1.9362
1.9224
1.7684
1.7626
1.7403
1.6985
1.4608
1.4127
1.3995
1.3669
1.3422
1.2993
1.2666
1.0690

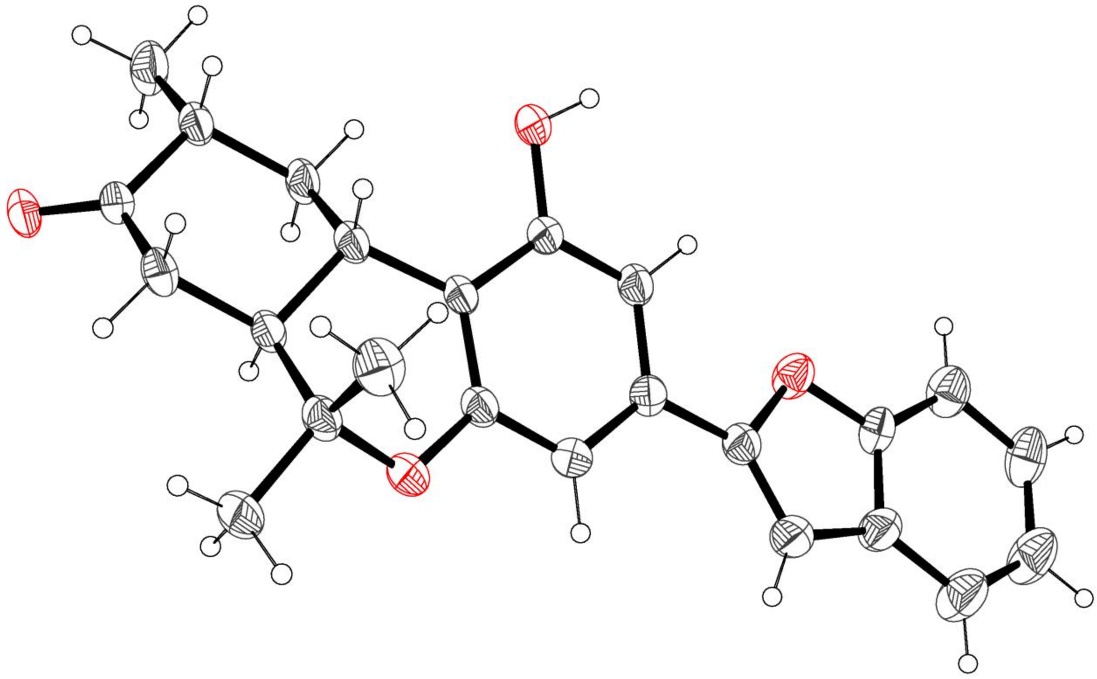

VR334BD_13C-2.JDF
CHLOROFORM-d
155.69
154.93
133.83
125.21
123.18
117.43
113.15
103.92
77.88
77.26
77.00
76.75
46.81
36.37
30.80
27.19
25.01
23.22
18.73
OH
H
H
O
Br
29
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

X-ray crystallographic data:

Compound **(+)-22:**



22



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) c__docume~1_admini~1_desktop_rohan_30julb

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: c__docume~1_admini~1_desktop_rohan_30julb

```
Bond precision:  C-C = 0.0043 A          Wavelength=0.71073

Cell:               a=8.814(2)       b=9.199(3)       c=24.640(7)
                    alpha=90         beta=90          gamma=90
Temperature:        173 K

                 Calculated                 Reported
Volume           1997.8(10)                 1997.8(10)
Space group      P 21 21 21                 P2(1)2(1)2(
Hall group       P 2ac 2ab                  ?
Moiety formula   C24 H24 O4                 C24 H23 O4
Sum formula      C24 H24 O4                 C24 H24 O4
Mr               376.43                     376.43
Dx,g cm-3        1.252                      1.252
Z                4                          4
Mu (mm-1)        0.084                      0.084
F000             800.0                      800.0
F000'            800.40
h,k,lmax         10,11,29                   10,11,29
Nref             3713[ 2145]                3712
Tmin,Tmax        0.978,0.981                0.978,0.981
Tmin'            0.978

Correction method= EMPIRICAL

Data completeness= 1.73/1.00       Theta(max)= 25.490

R(reflections)= 0.0526( 2450)      wR2(reflections)= 0.1227( 3712)

S = 1.083                    Npar= 257
```
