Total Synthesis of (+)-Lophirone H and Its Pentamethyl Ether Utilizing an Oxonium-Prins Cyclisation

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Supporting Information

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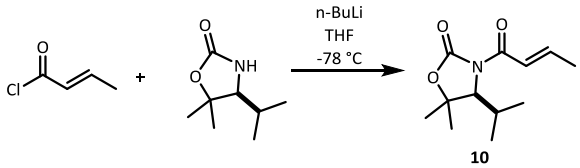
General Directions

All reactions were performed under nitrogen using oven-dried glassware unless stated otherwise. Yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogenous materials, unless otherwise indicated. MeCN, CH_2Cl_2, THF, Et_2O, DMF, and toluene were dried and deoxygenated with a Grubbs Pure-Solv 400 solvent purification system. The moisture content of the solvents was monitored by Karl Fischer coulometric titration (Mettler-Toledo DL39). ***Reagents:*** used as purchased from commercial sources, unless otherwise stated, and used according to COSHH regulations. ***Chromatography:*** Flash chromatography (FC) was performed on silica gel (Merck Kieselgel 60 F_{254} 230-400 mesh) unless otherwise stated. ***Melting Points:*** determined on a Stanford Research System OptiMelt. ***Thin Layer Chromatography (TLC):*** performed on Merck aluminium-backed plates pre-coated with silica (0.2 mm, 60 F_{254}) which were visualized either by quenching of ultraviolet fluorescence (λ_{max} = 254 and 366 nm) or staining with; potassium permanganate/Δ, bromoceresol green/Δ or phosphomolybdic acid/Δ TLC dips prepared according to general procedures. ***Optical Rotations:*** recorded on a Bellingham and Stanley ADP440+ polarimeter at 589 nm (Na D-line) with a path length of 0.5 dm. Concentrations (*c.*) are quoted in g/100 mL and specific rotations, $[\alpha]_D^T$, are quoted in units of 10^{-1}degcm^{2}g^{-1} at the specified temperature, T. ***Infra-red spectra:*** recorded as solids or neat liquids on a Perkin-Elmer FT-IR Spectrum BX, only selected absorbances (ν_{max}) are reported. ***^{1}H NMR spectra:*** recorded on a 400 or 500 MHz Bruker AMX-400/500 instrument. Chemical shifts (δ_H) are quoted in parts per million (ppm), referenced to the appropriate residual solvent peak. ***^{13}C NMR spectra:*** recorded at 101 MHz or 125 MHz on a Bruker AMX-400/500 instrument Chemical shifts (δ_C) are quoted in parts per million (ppm), referenced to the appropriate residual solvent peak. ***NOESY spectra:*** recorded on a 500 MHz Bruker AMX-500 instrument. ***High Resolution Mass Spectra:*** recorded on either a VG platform II or VG AutoSpec spectrometer, with only molecular ions ($[MH]^+$, $[MNa]^+$, $[MNH_4]^+$, $[MH_2O]^+$, $[MH]^-$) and major peaks being reported.

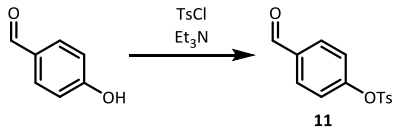
Experimental Procedures

(*S,E*)-3-(But-2-enoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one[1] (10)



According to the method of Davies,[1] to a solution of *n*-BuLi in THF (1.6 M, 1.91 mL, 3.06 mmol, 1.20 equiv.) was added dropwise to a solution of Davies' (*S*)-SuperQuat chiral auxiliary, (*S*)-(−)-4-isopropyl-5,5-dimethyl-2-oxazolidinone (400 mg, 2.60 mmol) in THF (5.00 mL) at -78 °C and allowed to stir for 1 hour. (*E*)-Crotonyl chloride (0.33 mL, 3.42 mmol, 1.30 equiv.) was added dropwise at -78 °C, allowed to warm to RT and allowed to stir for 1 hour. The reaction mixture was quenched with NH_4Cl solution (5 mL), extracted into EtOAc (2 x 10 mL), washed with brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography eluting with hexane/EtOAc (6:1) gave enone **10** as a white amorphous solid (430 mg, 75%); mp 63-64 °C; silica gel TLC R_f 0.35 (hexane/EtOAc, 4:1); $[\alpha]_D^{27}$ +46.0 (*c.* 1.0, $CHCl_3$) {lit.,[2] $[\alpha]_D^{23}$ +14.5 (*c.* 1.0, $CHCl_3$)}; ν_{max}/cm^{-1} (ATR-IR) 1754, 1686, 1360, 1175, 731; **^{1}H NMR** (400 MHz, chloroform-*d*) 7.31 (dq, *J* =15.2, 1.5 Hz, 1H), 7.14 (dq, *J* = 15.2, 6.8 Hz, 1H), 4.21 (d, *J* = 3.4 Hz, 1H), 2.23 – 2.08 (m, 1H), 1.95 (dd, *J* = 6.8, 1.5 Hz, 3H), 1.51 (s, 3H), 1.38 (s, 3H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, chloroform-*d*) 165.7, 153.6, 146.6, 122.0, 82.7, 66.3, 29.7, 28.8, 21.6, 21.6, 18.5, 17.1; ***m/z* HRMS** (ES^+) calc. 226.1443 $[MH]^+$, found 226.1437, $C_{12}H_{20}NO_3$, Δ = -2.7 ppm. [909731-28-8]. The spectroscopic data were in accordance with the literature.[1]

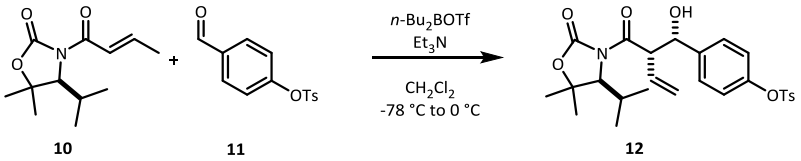
4-Formylphenyl 4-methylbenzenesulfonate (11)[3]



To a suspension of 4-hydroxybenzaldehyde (3.40 g, 27.8 mmol) in CH_2Cl_2 (50 mL) was added triethylamine (4.66 mL, 33.4 mmol, 1.2 equiv.) and *para*-toluenesulfonyloxy chloride (5.31 g, 27.8 mmol, 1.0 equiv.) and allowed to stir at RT for 24 hours. The reaction mixture was quenched with water (40 mL), extracted into EtOAc (3 x 40 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography eluting with hexane/EtOAc (4:1) gave aldehyde **11** as a white amorphous solid (6.13 g, 80%); mp 70-74 °C; silica gel TLC R_f 0.10 (hexane/EtOAc, 9:1); ν_{max}/cm^{-1} (ATR-IR) 2924, 2732, 1776, 1707, 1596, 1368, 1145; **^{1}H NMR** (400 MHz, chloroform-*d*) 9.97 (s, 1H), 7.86 – 7.80 (m, 2H), 7.75 – 7.68 (m, 2H), 7.36 – 7.29 (m, 2H), 7.21 –

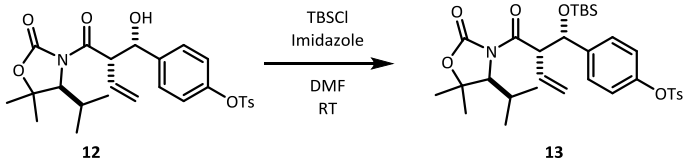
7.13 (m, 2H), 2.46 (s, 3H); **^{13}C NMR** (101 MHz, chloroform-*d*) 190.6, 153.9, 145.9, 134.8, 132.1, 131.3, 130.0, 128.5, 123.1, 21.8; ***m/z* HRMS** (ES^+) calc. 276.0456 $[M]^+$, found 276.0461, $C_{14}H_{12}O_4S$, Δ = 1.8 ppm. [80459-48-9]. The spectroscopic data were in accordance with the literature.[3]

4-((1*S*,2*S*)-2-((S)-4-Ethyl-5,5-dimethyl-2-oxooxazolidine-3-carbonyl)-1-hydroxybut-3-en-1-yl)phenyl 4-methylbenzenesulfonate (12)



According to the method of Evans,[4] to solution of enone **10** (1.80 g, 8.00 mmol) in CH_2Cl_2 (45.0 mL) at -78 °C was added a solution of *n*-Bu_2BOTf in CH_2Cl_2 (1M, 8.90 mL, 8.90 mmol, 1.10 equiv.) dropwise and stirred for 15 minutes. Triethylamine (1.70 mL, 12.2 mmol, 1.50 equiv.) was added dropwise and allowed to stir for: 2 hours at -78 °C, 15 minutes at 0 °C and then cooled down to -78 °C. A solution of aldehyde **11** (3.37 g, 12.2 mmol, 1.50 equiv.) in CH_2Cl_2 (29.0 mL) was added dropwise and allowed to stir at -78 °C for 1 hour then at 0 °C for 1 hour. The reaction mixture was quenched with $NaHCO_3$ solution (85 mL), extracted into hexane/EtOAc (1:1) (5 x 100 mL), the combined organics were concentrated *in vacuo*. The residue was dissolved in Et_2O (60 mL) and cooled to 0 °C, pH7 phosphate buffer (6.80 mL) and 30% H_2O_2 solution in H_2O (11.5 mL) were added and allowed to stir for 1 hour. The reaction mixture was quenched with water (100 mL), extracted into hexane/EtOAc (1:1) (3 x 150 mL), washed with brine (2 x 100 mL) dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography eluting with hexane/EtOAc (2:1) gave homoallylic alcohol **12** as a white amorphous solid (3.11 g, 78%); mp 95-96 °C; silica gel TLC R_f 0.40 (hexane/EtOAc, 2:1); $[\alpha]_D^{27}$ +12.0 (*c.* 0.4, Me_2CO); ν_{max}/cm^{-1} (ATR-IR) 1754, 1686, 1361, 1175, 731; **^{1}H NMR** (400 MHz, chloroform-*d*) 7.70 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 4H), 6.95 (d, *J* = 8.7 Hz, 2H), 5.97 (ddd, *J* = 17.2, 10.0, 8.9 Hz, 1H), 5.44 (d, *J* = 17.2 Hz, 1H), 5.39 (dd, *J* = 10.0, 1.0 Hz, 1H), 5.04 (dd, *J* = 6.6, 1.9 Hz, 1H), 4.96 (dd, *J* = 8.8, 6.6 Hz, 1H), 4.03 (d, *J* = 3.1 Hz, 1H), 2.95 (d, *J* = 2.2 Hz, 1H) 2.47 (s, 3H), 2.15 – 2.02 (m, 1H), 1.46 (s, 3H), 1.04 (s, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, chloroform-*d*) 173.1, 152.8, 149.2, 145.4, 139.7, 132.4, 132.2, 129.8, 128.5, 128.2, 122.4, 122.2, 82.8, 73.5, 66.0, 55.0, 29.7, 28.2, 21.7, 21.5, 21.2, 16.7; ***m/z* HRMS** (ES^+): calc. 502.1899 $[MH]^+$, found 502.1903, $C_{26}H_{32}NO_7S$, Δ = 0.8 ppm.

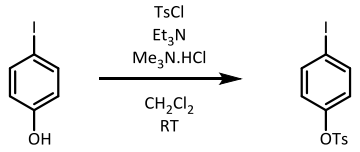
4-((1*S*,2*S*)-1-((*tert*-Butyldimethylsilyl)oxy)-2-((*S*)-4-isopropyl-5,5-dimethyl-2-oxooxazolidine-3-carbonyl)but-3-en-1-yl)phenyl 4-methylbenzenesulfonate (13)



12 **13**

To a solution of homoallylic alcohol **12** (3.08 g, 6.14 mmol) in DMF (15.0 mL) was added TBSCl (4.67g 31.0 mmol, 5.00 equiv.) in DMF (10.0 mL) and imidazole (1.05 g, 15.4 mmol, 2.50 equiv.) in DMF (10.0 mL) and allowed to stir at RT for 40 hours. The reaction mixture was quenched with water (20 mL), extracted into Et_2O (3 x 50 mL), washed with brine (2 x 40 mL), dried over $MgSO_4$ and concentrated *in vacuo.* Column chromatography eluting with hexane/CH_2Cl_2 (3:1) then CH_2Cl_2 gave protected alcohol **13** as a white amorphous solid (3.59 g, 95%); mp 110-111 °C; silica gel TLC R_f 0.25 (hexane/EtOAc, 4:1); $[\alpha]_D^{27}$ -10.6 (*c.* 0.2, Me_2CO); ν_{max}/cm^{-1} (ATR-IR) 1755, 1686, 1361, 1126, 732; **^{1}H NMR** (400 MHz, chloroform-*d*) 7.62 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.23 (m, 4H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.96 (ddd, *J* = 17.1, 10.1, 8.2 Hz, 1H), 5.39 (d, *J* = 17.1 Hz, 1H), 5.28 (dd, *J* = 10.1, 1.5 Hz, 1H), 4.99 (t, *J* = 8.7 Hz, 1H), 4.90 (d, *J* = 9.0 Hz, 1H), 3.84 (d, *J* = 3.3 Hz, 1H), 2.44 (s, 3H), 2.00 (ddq, *J* = 10.2, 6.9, 3.4 Hz, 1H), 1.36 (s, 3H), 0.92 (d, *J* = 7.1 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H), 0.77 (s, 9H), 0.71 (s, 3H), -0.02 (s, 3H), -0.30 (s, 3H); **^{13}C NMR** (101 MHz, chloroform-*d*) 172.2, 152.8, 149.0, 145.4, 142.0, 134.7, 132.2, 129.7, 128.7, 128.5, 122.1, 120.0, 82.5, 75.5, 65.9, 56.5, 29.6, 27.7, 25.7, 21.7, 21.5, 21.1, 18.1, 16.8, -4.7, -4.9; ***m/z* HRMS** (ES^+): calc. 638.2584 $[MNa]^+$, found 638.2598, $C_{32}H_{45}NO_7NaSSi$, Δ = 2.2 ppm.

4-Iodophenyl 4-methylbenzenesulfonate[5] (14)

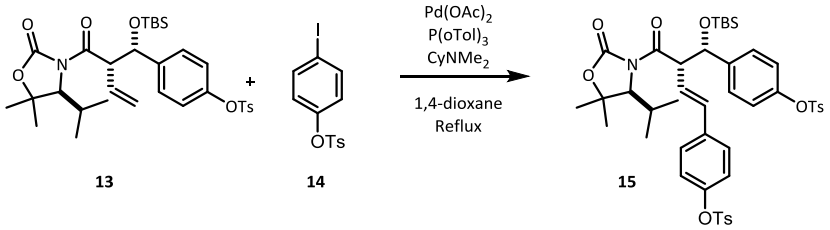


14

According to the method of Tanabe,[6] 4-iodophenol (2.00 g, 9.09 mmol), *para*-toluenesulfonyloxy chloride (3.48 g, 18.1 mmol, 2.00 equiv.), triethylamine (3.80 mL, 27.3 mmol, 3.00 equiv.) and trimethylamine hydrochloride (86.0 mg, 0.90 mmol, 0.10 equiv.) were dissolved in CH_2Cl_2 (36.0 mL) and allowed to stir for 3 hours at RT. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with 2.5 M NaOH solution (3 x 15 mL), dried over $MgSO_4$ and concentrated *in vacuo.* Column chromatography eluting with

hexane/CH_2Cl_2 (4:1) then CH_2Cl_2 gave aryl-iodide **14** as a white amorphous solid (3.23 g, 95%); silica gel TLC R_f 0.70 (hexane/EtOAc, 3:1); mp 96-98 °C; ν_{max}/cm^{-1} (ATR-IR) 1593, 1289, 1120, 830, 787; **^{1}H NMR** (400 MHz, chloroform-*d*) 7.70 (m, 2H), 7.60 (m, 2H), 7.32 (m, 2H), 6.73 (m, 2H), 2.46 (s, 3H); **^{13}C NMR** (101 MHz, chloroform-*d*) 149.5, 145.6, 138.7, 129.9, 128.5, 124.5, 91.7, 21.8; ***m/z* HRMS** (ES^-): calc. 372.9395 $[MH]^-$, found 372.9406, $C_{13}H_{10}IO_3S$, Δ = 2.9 ppm. [24962-55-8]. The spectroscopic data were in accordance with the literature.[5]

((3*S*,4*S*,*E*)-4-((*tert*-Butyldimethylsilyl)oxy)-3-((*S*)-4-isopropyl-5,5-dimethyl-2-oxooxazolidine-3-carbonyl)but-1-ene-1,4-diyl)*bis*(4,1-phenylene) *bis*(4-methylbenzenesulfonate) (15)



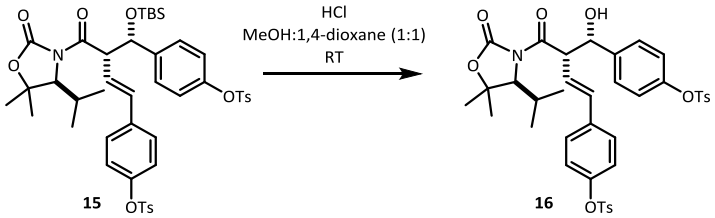
13 **14** **15**

According to the method of Aciro,[7] to a solution of alkene **13** (1.00 g, 1.62 mmol), aryl-iodide **14** (1.22 g, 3.24 mmol, 2.0 equiv.), palladium(II)acetate (72.0 mg, 0.32 mmol, 0.20 equiv.) and tri(*o*-tolyl)phosphine (100 mg, 0.32 mmol, 0.20 equiv.) in 1,4-dioxane (32.0 mL) was added *N*,*N*-dicyclohexylmethylamine (0.87 mL, 4.05 mmol, 2.50 equiv.) and refluxed for 17 hours. Palladium(II)acetate (72.0 mg, 0.32 mmol, 0.20 equiv.) and tri(*o*-tolyl)phosphine (100 mg, 0.32 mmol, 0.20 equiv.) were added and refluxed for a further 24 hours. The reaction mixture was concentrated *in vacuo,* diluted with CH_2Cl_2 (40 mL), washed with 1 M HCl (40 mL), extracted into CH_2Cl_2 (3 x 40 mL), dried over $MgSO_4$ and concentrated *in vacuo.* Column chromatography eluting with hexane/CH_2Cl_2 (1:1) then CH_2Cl_2 gave:

Alkene **15** as a white amorphous solid (666 mg, 48%); mp 65-66 °C; silica gel TLC R_f 0.65 (hexane/EtOAc, 2:1); $[\alpha]_D^{27}$ -28.1 (*c.* 0.4, Me_2CO); ν_{max}/cm^{-1} (ATR-IR) 1773, 1372, 1175, 1092, 861; **^{1}H NMR** (400 MHz, chloroform-*d*) 7.69 (m, 2H), 7.63 (m, 2H), 7.33 – 7.23 (m, 8H), 6.90 (m, 4H), 6.66 (d, *J* = 15.8 Hz, 1H), 6.24 (dd, *J* = 15.8, 8.8 Hz, 1H), 5.10 (*app.* t, *J* = 8.8 Hz, 1H), 4.94 (d, *J* = 9.0 Hz, 1H), 3.84 (d, *J* = 3.5 Hz, 1H), 2.45 (s, 3H), 2.44 (s, 3H), 2.07 – 1.92 (m, 1H), 1.36 (s, 3H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 6.7 Hz, 3H), 0.72 (s, 3H), 0.71 (s, 9H), -0.11 (s, 3H), -0.31 (s, 3H); **^{13}C NMR** (101 MHz, chloroform-*d*) 172.1, 152.8, 149.1, 148.9, 145.3, 141.8, 135.9, 133.7, 132.2, 129.7, 128.7, 128.5, 128.5, 127.4, 127.2, 122.5, 122.2, 110.0, 82.7, 75.8, 66.0, 55.9, 29.5, 27.7, 25.6, 21.7, 21.5, 21.2, 18.0, 16.9, -4.8, -4.9; ***m/z* HRMS** (ES^+): calc. 879.3380 $[MNH_4]^+$, found 879.3348, $C_{45}H_{59}N_2O_{10}S_2Si$, Δ = -3.6 ppm.

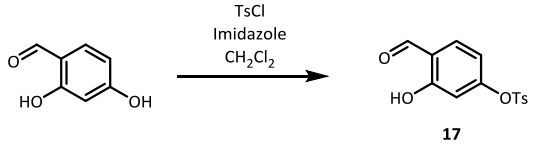
Alkene **13** as a white amorphous solid (460 mg, 46%). Spectroscopic data as above.

((3*S*,4*S*,*E*)-4-Hydroxy-3-((*S*)-4-isopropyl-5,5-dimethyl-2-oxooxazolidine-3-carbonyl)but-1-ene-1,4-diyl)*bis*(4,1-phenylene) bis(4-methylbenzenesulfonate) (16)



To a solution of protected-alcohol **15** (666 mg, 0.77 mmol) in MeOH (10.5 mL) and 1,4-dioxane (10.5 mL) was added concentrated HCl (0.64 mL, 7.70 mmol, 10.0 equiv.) and allowed to stir at RT for 40 hours. The reaction mixture was concentrated *in vacuo*, diluted with CH_2Cl_2 (20 mL), washed with $NaHCO_3$ (20 mL), extracted into CH_2Cl_2 (2 x 20 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give alcohol **16** as a white amorphous solid (568 mg, 98%); mp 78-79 °C; silica gel TLC R_f 0.40 (hexane/EtOAc, 1:1); $[\alpha]_D^{27}$ -10.2 (*c.* 0.2, Me_2CO); ν_{max}/cm^{-1} (ATR-IR) 2957, 1777, 1371, 1175, 860; **^{1}H NMR** (400 MHz, chloroform-*d*) 7.70 (m, 2H), 7.65 (m, 2H), 7.31 (d, *J* = 8.7 Hz, 4H), 7.27 – 7.24 (m, 4H), 6.92 (m, 4H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 15.9, 8.7 Hz, 1H), 5.12 – 5.02 (m, 2H), 4.02 (d, *J* = 3.4 Hz, 1H), 3.02 (d, *J* = 1.9 Hz, 1H), 2.45 (s, 3H), 2.43 (s, 3H), 2.11 – 2.00 (m, 1H), 1.44 (s, 3H), 1.05 (s, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, chloroform-*d*) 173.2, 152.9, 149.2, 145.4, 139.6, 135.4, 135.3, 129.8, 128.5, 128.5, 128.2, 127.6, 124.2, 122.6, 122.3, 83.0, 73.9, 66.1, 54.1, 29.6, 28.3, 21.7, 21.5, 21.2, 16.8; ***m/z* HRMS** (ES^-): calc. 770.2070 $[MNa]^+$, found 770.2092, $C_{39}H_{41}NO_{10}NaS_2$, Δ = 2.9 ppm.

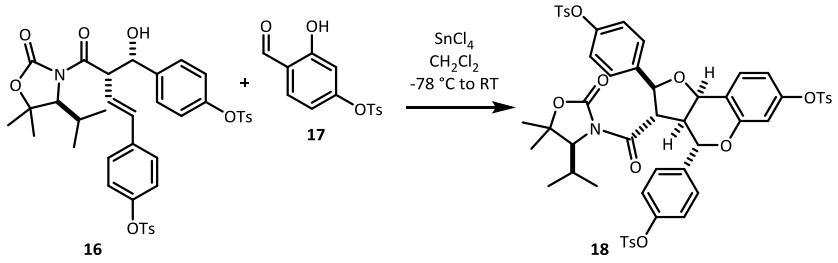
4-Formyl-3-hydroxyphenyl 4-methylbenzenesulfonate (17)



To a solution of 2,4-dihydroxybenzaldehyde (4.00 g, 29.0 mmol) and imidazole (2.17 g, 31.9 mmol, 1.1 equiv.) in CH_2Cl_2 (70 mL) was added *para*-toluenesulfonyloxy chloride (6.10 g, 31.9 mmol, 1.1 equiv.) in CH_2Cl_2 (45 mL) and allowed to stir at RT for 24 hours. The reaction mixture was diluted with CH_2Cl_2 (50 mL), extracted with water (2 x 50 mL), washed with brine (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography eluting with toluene gave aldehyde **17** as a white amorphous solid (2.55

g, 30%); mp 87-90 °C; silica gel TLC R_f 0.40 (hexane/CH_2Cl_2, 1:3); ν_{max}/cm^{-1} (ATR-IR) 1659, 1376, 1178, 1090, 973; **^{1}H NMR** (400 MHz, chloroform-*d*) 11.19 (s, 1H), 9.87 (s, 1H), 7.78 (m, 2H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.37 (m, 2H), 6.80 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.63 (d, *J* = 2.2 Hz, 1H), 2.49 (s, 3H); **^{13}C NMR** (101 MHz, chloroform-*d*) 195.5, 135.1, 130.0, 128.4, 119.3, 114.3, 111.2, 21.8; ***m/z* HRMS** (ES^-): calc. 291.0327 $[MH]^-$, found 291.0333, $C_{14}H_{11}O_5S$, Δ = 2.1 ppm.

((2*S*,3*S*,3*aS*,4*S*,9*bR*)-3-((*S*)-4-Isopropyl-5,5-dimethyl-2-oxooxazolidine-3-carbonyl)-7-(*para*-toluenesulfonyloxy)-2,3,3*a*,9*b*-tetrahydro-4H-furo[3,2-*c*]chromene-2,4-diyl)*bis*(4,1-phenylene) *bis*(4-methylbenzenesulfonate) (18)



According to the method of Spivey,[8] to a solution of aldehyde **17** (109 mg, 0.37 mmol, 1.40 equiv.) in CH_2Cl_2 (1.70 mL) at -78°C was added $SnCl_4$ in CH_2Cl_2 (1M, 0.32 mL, 0.32 mmol, 1.20 equiv.) and allowed to stir for 30 minutes. A solution of homoallylic alcohol **16** (200 mg, 0.27 mmol) in CH_2Cl_2 (3.60 mL) was added dropwise and allowed to stir at -78°C for 17 hours, allowed to stir at 0 °C for 24 hours, and then allowed to stir at RT for 23 hours. The reaction mixture was quenched with sat. $NaHCO_3$ solution (10 mL), extracted into CH_2Cl_2 (5 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography eluting with hexane/EtOAc (2:1 then 1:1 then 0:1) gave oxazolidinone **18** as a white amorphous solid (195 mg, 72%); mp 86-88 °C; silica gel TLC R_f 0.35 (DCM); $[\alpha]_D^{28}$ +36.5 (*c.* 0.4, Me_2CO); ν_{max}/cm^{-1} (ATR-IR) 1777, 1378, 1177, 865; **^{1}H NMR** (400 MHz, chloroform-*d*) 7.77 – 7.72 (m, 2H), 7.71 – 7.67 (m, 2H), 7.65 – 7.60 (m, 2H), 7.40 (d, J = 8.5 Hz, 1H), 7.39 – 7.27 (m, 8H), 7.25 – 7.21 (m, 2H), 6.96 (m, 2H), 6.91 (m, 2H), 6.72 (d, J = 2.4 Hz, 1H), 6.65 (dd, J = 8.4, 2.4 Hz, 1H), 5.05 (d, J = 6.4 Hz, 1H), 4.86 (d, J = 8.2 Hz, 1H), 4.56 – 4.51 (m, 2H), 3.92 (d, J = 3.5 Hz, 1H), 3.13 (ddd, J = 11.1, 6.4, 4.3 Hz, 1H), 2.46 – 2.42 (m, 9H), 1.86 (pd, J = 6.8, 3.5 Hz, 1H), 1.34 (s, 3H), 1.05 (s, 3H), 0.71 (d, J = 6.9 Hz, 3H), 0.38 (d, J = 6.8 Hz, 3H).; **^{13}C NMR** (101 MHz, chloroform-*d*) 172.7, 155.5, 151.6, 150.2, 150.1, 149.9, 145.6, 145.5, 145.3, 136.5, 132.5, 132.3, 132.0, 131.6, 129.9, 129.8, 129.4, 128.6, 128.5, 128.4, 128.2, 122.9, 122.8, 119.6, 116.0, 111.5, 85.3, 82.2, 78.7, 74.9, 66.6, 52.7, 50.9, 29.3, 28.3, 21.8, 21.4, 21.1, 16.5; ***m/z* HRMS** (ES^+) calc. 1044.2369 $[MNa]^+$, found 1044.2378, $C_{53}H_{51}NO_{14}NaS_3$, Δ = 0.9 ppm.

The relative stereochemistry of oxonium-Prins product **18** was determined by analysis of its NMR spectra. All coupling constants were in accord with expectation and additionally, the presence of a cross-peak between H_{3a} and H_{9b} in the NOESY spectrum suggested a 2,3-*cis* configuration for the fused bicycle. Other diagnostic signals included correlation between H_4 and H_3 and between H_{3a} and H_2 indicating these proton pairs were projecting from the same face of the bicycle respectively. As was the case for the pentamethyl ether derivative of lophirone H that was analysed by Bodo and Martin *et al*.[9], there was also a cross peak between H_9 on the aryl moiety of the benzopyran and H_{9b} of the fused bicycle (Figure 4).

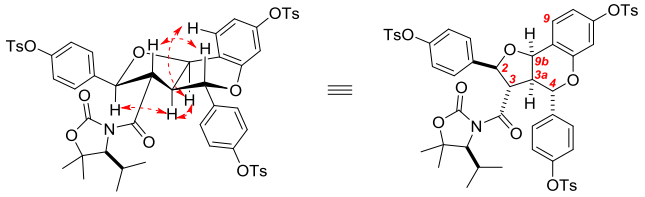
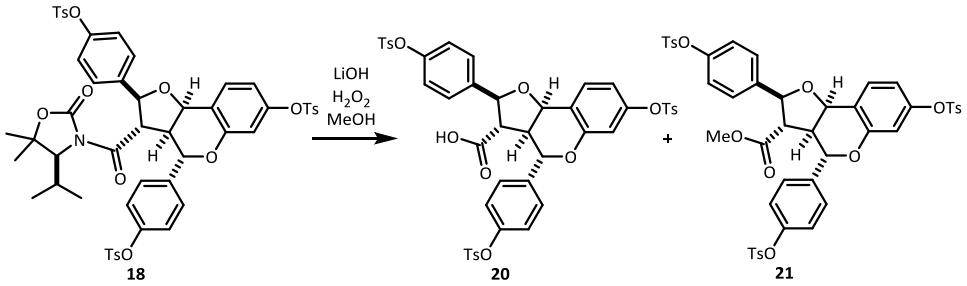


Figure S1. Key NOESY correlations observed in 4*H*-furo[3,2-*c*]benzopyran **18**.

(2*S*,3*S*,3*aS*,4*S*,9*bR*)-7-(*para*-Toluenesulfonyloxy)-2,4-*bis*(4-(*para*-toluenesulfonyloxy)phenyl)-2,3,3*a*,9*b*-tetrahydro-4H-furo[3,2-*c*]chromene-3-carboxylic acid (20) & methyl (2*S*,3*S*,3*aS*,4*S*,9*bR*)-7-(*para*-toluenesulfonyloxy)-2,4-*bis*(4-(*para*-toluenesulfonyloxy)phenyl)-2,3,3*a*,9*b*-tetrahydro-4H-furo[3,2-*c*]chromene-3-carboxylate (21)



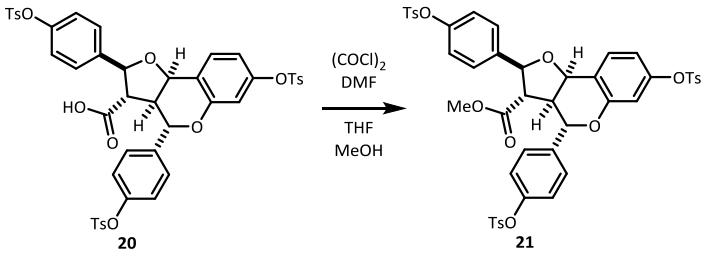
According to the method of Evans,[10] to a solution of oxazolidinone **18** (200 mg, 0.20 mmol) in methanol (20 mL) was added 30% H_2O_2 in water (20 µL, 0.20 mmol, 1.00 equiv.) and lithium hydroxide (8.2 mg, 0.20 mmol 1.00 equiv.) and allowed to stir at RT for 2 hours. The cloudy reaction mixture was concentrated *in vacuo*. Column chromatography eluting with hexane/EtOAc/formic acid (3:1:0.005) gave:

Acid **20** as a pale white amorphous solid (55 mg, 32%); mp 79-84 °C; silica gel TLC R_f 0.15 (hexane/EtOAc, 1:1); $[\alpha]_D^{27}$ +38.9 (*c.* 0.4, Me_2CO); ν_{max}/cm^{-1} (ATR-IR) 1494, 1371, 1177, 864; **^{1}H NMR** (400 MHz, acetone-d_6) 7.82 – 7.78 (m, 2H), 7.75 – 7.71 (m, 2H), 7.70 – 7.67 (m, 2H), 7.51 – 7.42 (m, 11H), 7.07 – 6.98 (m, 4H),

6.72 (dd, J = 8.4, 2.4 Hz, 1H), 6.69 (d, J = 2.4 Hz, 1H), 5.15 (d, J = 7.4 Hz, 1H), 4.98 (d, J = 5.4 Hz, 1H), 4.70 (d, J = 11.4 Hz, 1H), 3.14 (ddd, J = 11.4, 5.4, 3.0 Hz, 1H), 2.52 (dd, J = 7.4, 3.0 Hz, 1H), 2.46 (s, 3H), 2.45 (s, 3H), 2.43 (s, 3H).; **^{13}C NMR** (101 MHz, acetone-d_6) 156.9, 151.3, 151.0, 150.3, 147.0, 146.9, 146.9, 140.9, 137.6, 133.7, 133.5, 133.5, 133.3, 131.2, 131.0, 130.9, 129.5, 129.4, 129.4, 128.8, 123.6, 123.3, 120.8, 116.3, 111.8, 82.8, 79.0, 74.9, 56.4, 48.0, 21.8; ***m/z* HRMS** (ES^+) calc. 905.1372 $[MNa]^+$, found 905.1376, $C_{45}H_{38}O_{13}NaS_3$, Δ = 0.4 ppm.

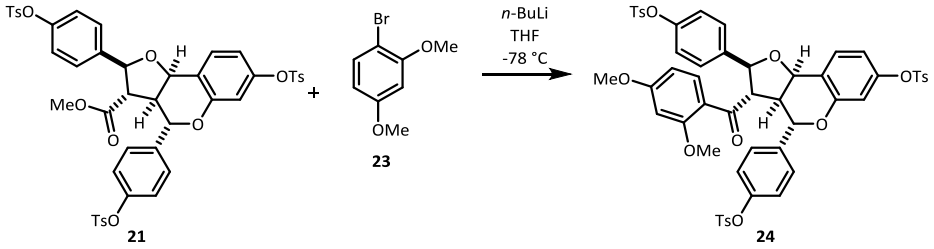
Methyl ester **21** as a white fluffy solid (119 mg, 67%); mp 95-98 °C; silica gel TLC R_f 0.29 (hexane/EtOAc, 3:2); ν_{max}/cm^{-1} (ATR-IR) 1735, 1597, 1504, 1372, 1195, 1177, 865; **^{1}H NMR** (400 MHz, chloroform-*d*) δ 7.81 – 7.66 (m, 6H), 7.42 – 7.27 (m, 9H), 7.24 – 7.17 (m, 2H), 7.01 (m, 2H), 6.97 (m, 2H), 6.71 (d, *J* = 2.3 Hz, 1H), 6.65 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.12 (d, *J* = 7.2 Hz, 1H), 4.93 (d, *J* = 5.3 Hz, 1H), 4.49 (d, *J* = 11.3 Hz, 1H), 3.55 (s, 3H), 2.97 (ddd, *J* = 11.3, 5.3, 3.0 Hz, 1H), 2.51 (dd, *J* = 7.2, 3.0 Hz, 1H), 2.48 – 2.42 (m, 9H); **^{13}C NMR** (101 MHz, chloroform-d) δ 172.1, 155.6, 150.3, 150.0, 149.3, 145.6, 145.5, 138.9, 135.8, 132.5, 132.4, 132.0, 129.9, 129.8, 129.4, 128.5, 128.4, 127.2, 122.8, 122.7, 118.9, 115.9, 111.4, 81.5, 77.9, 74.1, 55.0, 52.4, 47.2, 21.8; ***m/z* HRMS** (ES^+) calc. 914.1945 $[MNH_4]^+$, found 914.1975, $C_{46}H_{44}NO_{13}S_3$, Δ = -3.3 ppm.

Procedure for conversion of carboxylic acid 20 to methyl ester 21



To a solution of acid **20** (55 mg, 0.062 mmol) in tetrahydrofuran (6.8 mL) was added oxalyl chloride (8.8 µL, 0.10 mmol, 1.60 equiv.) and DMF (2.6 µL, 0.034 mmol, 0.55 equiv.). The reaction was allowed to stir at RT for 10 minutes before quenching with excess methanol (6 mL). The reaction mixture was concentrated *in vacuo*. Column chromatography eluting with hexane/EtOAc (3:2) gave methyl ester **21** as a white fluffy solid (45 mg, 80%). Spectroscopic data as above.

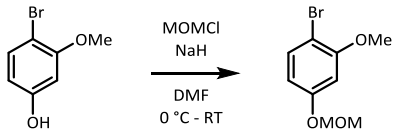
((2*S*,3*S*,3*aS*,4*S*,9*bR*)-3-(2,4-Dimethoxybenzoyl)-7-(*para*-toluenesulfonyloxy)-2,3,3*a*,9*b*-tetrahydro-4H-furo[3,2-*c*]chromene-2,4-diyl)*bis*(4,1-phenylene) *bis*(4-methylbenzenesulfonate) (24)



[0.098M Aryl-lithium stock solution: To a solution of 1-bromo-2,4-dimethoxybenzene **23** (146 µL, 1.02 mmol, 48 equiv.) in THF (9.9 mL) at -78 °C under Ar was added *n*-BuLi (2.5M, 420 µL, 1.05 mmol, 50 equiv.) and allowed to stir for 20 minutes.]

To a solution of methyl ester **21** (19 mg, 0.021 mmol) in THF (0.15 mL) at -78 °C under Ar was added (2,4-dimethoxyphenyl)lithium solution (0.35 mL, 0.034 mmol, 0.098M, 1.6 equiv.) in one portion to give a bright yellow solution which was allowed to stir at -78 °C for 3 hours. Based on ^{1}H NMR analysis of an aliquot of the reaction mixture the conversion was judged to be approximately 25%. (2,4-dimethoxyphenyl)lithium solution (0.35 mL, 0.034 mmol, 0.098M, 1.6 equiv.) was again added at -78 °C in one portion and the reaction mixture stirred for a further 1 hour. The reaction mixture was quenched with sat. NH_4Cl solution (3 mL), extracted into CH_2Cl_2 (5 x 3 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography eluting with hexane/EtOAc (9:1 → 1:1) gave aryl-ketone **24** as a white amorphous solid (10 mg, 47%); mp 82-85 °C; silica gel TLC R_f 0.33 (hexane/EtOAc, 3:2); ν_{max}/cm^{-1} (ATR-IR) 1598, 1504, 1372, 1265, 1177, 1091, 865, 735; **^{1}H NMR** (400 MHz, chloroform-*d*) δ 7.74 (m, 2H), 7.70 (m, 2H), 7.60 – 7.54 (m, 2H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.34 – 7.29 (m, 5H), 7.23 – 7.19 (m, 2H), 7.16 – 7.08 (m, 4H), 6.95 – 6.90 (m, 2H), 6.85 – 6.78 (m, 2H), 6.70 (d, *J* = 2.3 Hz, 1H), 6.62 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.40 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.07 (d, *J* = 2.2 Hz, 1H), 5.07 (d, *J* = 7.1 Hz, 1H), 4.99 (d, *J* = 5.2 Hz, 1H), 4.57 (d, *J* = 11.4 Hz, 1H), 3.94 (dd, *J* = 7.2, 2.8 Hz, 1H), 3.81 (s, 3H), 3.15 (s, 3H), 2.90 (ddd, *J* = 11.4, 5.3, 2.8 Hz, 1H), 2.46 – 2.41 (m, 9H); **^{13}C NMR** (101 MHz, chloroform-*d*) δ 200.0, 164.9, 159.9, 155.8, 150.2, 149.7, 145.6, 139.7, 136.1, 132.5, 132.3, 132.1, 129.9, 129.8, 129.8, 129.3, 128.4, 128.4, 128.4, 127.3, 122.4, 122.3, 120.1, 119.4, 115.7, 111.4, 105.7, 97.8, 83.1, 78.3, 74.6, 60.4, 55.6, 54.6, 48.3, 21.7; ***m/z* HRMS** (ES^+) calc. 1003.2128 $[MH]^+$, found 1003.2117, $C_{53}H_{47}O_{14}S_3$, Δ = -1.1 ppm.

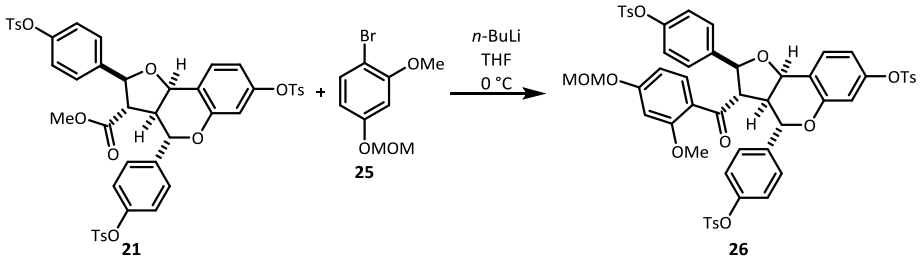
1-Bromo-2-methoxy-4-(methoxymethoxy)-benzene (25)[11]



25

According to the method of Snieckus,[11] to a suspension of NaH (60% dispersion in mineral oil, 132 mg, 3.29 mmol, 1.76 equiv.) in DMF (3 mL) at 0 °C under Ar was added a solution of 1-bromo-2-methoxy-4-hydroxy-benzene (380 mg, 1.87 mmol) in DMF (2.5 mL) dropwise (caution: H_2 evolution). The resultant brown solution was stirred at 0 °C for 30 minutes before adding chloromethyl methyl ether (0.24 mL, 3.14 mmol, 1.68 equiv.) dropwise. The pale yellow suspension was allowed to warm to RT and stirred for a further 2 hours. The reaction mixture was then poured into ice-cold H_2O, extracted into Et_2O (3 x 10 mL), washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography eluting with hexane/EtOAc (9:1 → 4:1) gave the MOM protected aryl-bromide **25** as a colourless oil (435 mg, 94%); silica gel TLC R_f 0.46 (hexane/EtOAc, 4:); **^{1}H NMR** (400 MHz, chloroform-*d*) δ 7.40 (d, *J* = 8.7 Hz, 1H), 6.62 (d, *J* = 2.7 Hz, 1H), 6.56 (dd, *J* = 8.7, 2.7 Hz, 1H), 5.16 (s, 2H), 3.87 (s, 3H), 3.48 (s, 3H); **^{13}C NMR** (101 MHz, chloroform-*d*) δ 158.0, 156.7, 133.4, 109.0, 103.8, 101.7, 94.8, 56.3, 56.3. The spectroscopic data were in accordance with the literature.[11]

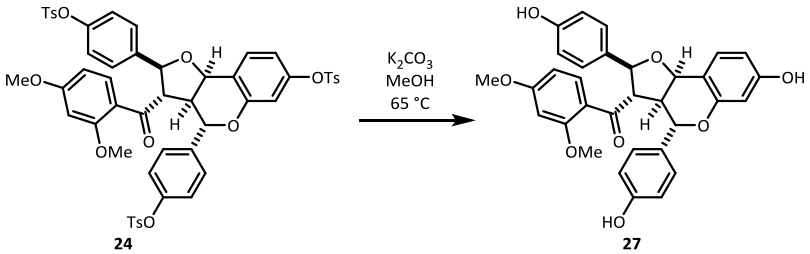
((2*S*,3*S*,3*aS*,4*S*,9*bR*)-3-(2-Methoxy-4-(methoxymethoxy)benzoyl)-7-(*para*-toluenesulfonyloxy)-2,3,3*a*,9*b*-tetrahydro-4H-furo[3,2-*c*]chromene-2,4-diyl) *bis*(4,1-phenylene) *bis*(4-methylbenzenesulfonate) (26)



[0.085M Aryl-lithium stock solution: To a solution of 1-bromo-2-methoxy-4-(methoxymethoxy)-benzene **25** (31 mg, 0.13 mmol, 19 equiv.) in THF (1.42 mL) at -78 °C under Ar was added *n*-BuLi (2.5M, 50 µL, 0.13 mmol, 19.05 equiv.) and allowed to stir for 15 minutes.]

To a solution of methyl ester **21** (5.9 mg, 0.0066 mmol) in THF (0.1 mL) at -78 °C under Ar was added (2-methoxy-4-(methoxymethoxy)-phenyl)lithium solution (0.1 mL, 0.0086 mmol, 0.085M, 1.3 equiv.) was added in one portion to give a bright yellow solution and allowed to stir at -78 °C for 50 minutes. Based on ^{1}H NMR analysis of an aliquot of the reaction mixture the conversion was judged to be approximately 65%. (2-methoxy-4-(methoxymethoxy)-phenyl)lithium solution (0.05 mL, 0.0043 mmol, 0.085M, 0.65 equiv.) was again added at -78 °C in one portion and the reaction mixture stirred for a further 40 minutes. The reaction mixture was quenched with sat. NH_4Cl solution (2 mL), extracted into CH_2Cl_2 (5 x 3 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Preparative thin-layer chromatography eluting with hexane/EtOAc (3:2) gave aryl-ketone **26** as an off-white semisolid (3.8 mg, 56%); silica gel TLC R_f 0.35 (hexane/EtOAc, 1:1); ν_{max}/cm^{-1} (ATR-IR) 1656, 1600, 1504, 1372, 1260, 1177, 1153. **^{1}H NMR** (400 MHz, chloroform-*d*) δ 7.79 – 7.75 (m, 2H), 7.75 – 7.70 (m, 2H), 7.61 – 7.57 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.38 – 7.30 (m, 5H), 7.26 – 7.21 (m, 2H), 7.18 – 7.10 (m, 4H), 6.98 – 6.92 (m, 2H), 6.85 – 6.80 (m, 2H), 6.73 (d, *J* = 2.3 Hz, 1H), 6.64 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.56 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.24 (d, *J* = 2.2 Hz, 1H), 5.23 – 5.16 (*AB* m, 2H), 5.11 (d, *J* = 7.2 Hz, 1H), 5.02 (d, *J* = 5.3 Hz, 1H), 4.59 (d, *J* = 11.5 Hz, 1H), 3.94 (dd, *J* = 7.2, 2.8 Hz, 1H), 3.48 (s, 3H), 3.15 (s, 3H), 2.90 (ddd, *J* = 11.5, 5.3, 2.8 Hz, 1H), 2.51 – 2.42 (m, 9H). **^{13}C NMR** (101 MHz, chloroform-*d*) δ 200.2, 162.5, 150.2, 149.7, 148.9, 145.6, 145.5, 139.6, 137.3, 136.1, 132.5, 132.5, 132.1, 132.0, 129.9, 129.8, 129.2, 128.4, 128.4, 127.4, 122.4, 122.3, 121.0, 115.7, 111.4, 107.8, 99.5, 94.3, 83.1, 78.3, 74.6, 60.4, 56.4, 54.7, 48.4, 21.7; ***m/z* HRMS** (ES^+) calc. 1033.2250 $[MH]^+$, found 1033.2234, $C_{54}H_{49}O_{15}S_3$, Δ = 1.5 ppm.

(2,4-Dimethoxyphenyl)((2*S*,3*S*,3*aS*,4*S*,9*bR*)-7-hydroxy-2,4-*bis*(4-hydroxyphenyl)-2,3,3*a*,9*b*-tetrahydro-4H-furo[3,2-*c*]chromen-3-yl)methanone (27)

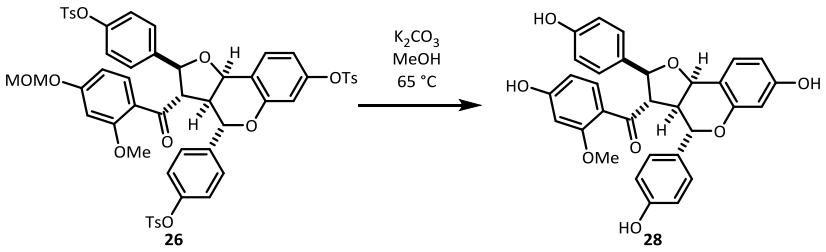


24 **27**

To a solution of aryl-ketone **24** (9.2 mg, 0.0092 mmol) in methanol (0.5 mL) was added K_2CO_3 (13 mg, 0.092 mmol, 10 equiv.) and the reaction was heated at 65 °C for 4 hours. The reaction mixture was quenched with 1M HCl (5 mL), extracted with EtOAc (6 x 5 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Preparative thin-layer chromatography eluting with hexane/EtOAc (2:3) gave triphenol **27** as an

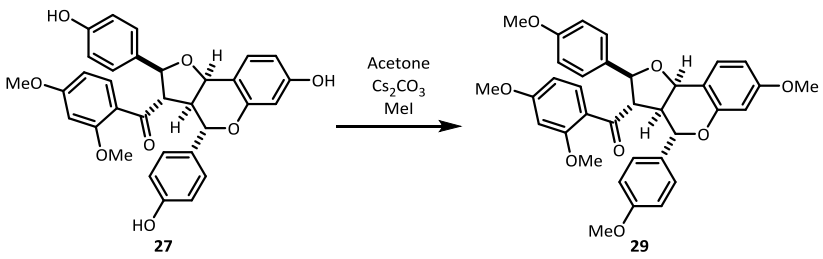
off-white semisolid (4 mg, 81%); silica gel TLC R_f 0.21 (hexane/EtOAc, 2:3); ν_{max}/cm^{-1} (ATR-IR) 3367, 1637, 1595, 1257, 1291, 1147, 1108; **^{1}H NMR** (400 MHz, acetone-d_6) δ 8.47 (*br.* s, 1H), 8.33 (*br.* s, 1H), 8.27 (*br.* s, 1H), 7.30 – 7.23 (m, 2H), 7.18 – 7.13 (m, 2H), 7.12 – 7.07 (m, 2H), 6.80 – 6.73 (m, 2H), 6.72 – 6.65 (m, 2H), 6.52 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.44 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.34 (d, *J* = 2.4 Hz, 1H), 6.19 (d, *J* = 2.3 Hz, 1H), 4.96 (d, *J* = 7.2 Hz, 1H), 4.86 (d, *J* = 5.1 Hz, 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.01 (dd, *J* = 7.2, 2.6 Hz, 1H), 3.81 (s, 3H), 3.26 (s, 3H), 2.90 (ddd, *J* = 11.5, 5.1, 2.6 Hz, 1H); **^{13}C NMR** (101 MHz, acetone-d_6) δ 202.1, 165.3, 160.8, 159.5, 158.6, 157.9, 157.8, 133.3, 133.2, 132.5, 130.6, 130.0, 128.9, 122.4, 115.9, 115.8, 113.6, 111.0, 110.1, 106.5, 103.8, 98.6, 84.4, 79.6, 75.9, 61.7, 56.0, 55.3, 49.3; ***m/z* HRMS** (ES^+) calc. 541.1862 $[MH]^+$, found 541.1875, $C_{32}H_{29}O_8$, Δ = 2.4 ppm.

((2*S*,3*S*,3*aS*,4*S*,9*bR*)-7-Hydroxy-2,4-*bis*(4-hydroxyphenyl)-2,3,3a,9b-tetrahydro-4H-furo[3,2-*c*]chromen-3-yl)(4-hydroxy-2-methoxyphenyl)methanone (28)



To a solution of aryl-ketone **26** (3.8 mg, 0.0037 mmol) in methanol (0.18 mL) was added K_2CO_3 (10.2 mg, 0.074 mmol, 20 equiv.) and the reaction was heated at 65 °C for 1 hour. The reaction mixture was quenched with 1M HCl (1 mL), extracted with EtOAc (6 x 3 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Preparative thin-layer chromatography eluting with hexane/EtOAc (3:7) gave tetraphenol **28** as an off-white semisolid (1.5 mg, 78%) which was not stable and was immediately taken through to the next stage; silica gel TLC R_f 0.10 (hexane/EtOAc, 3:7); ν_{max}/cm^{-1} (ATR-IR) 3325, 1630, 1459, 1260, 1166; **^{1}H NMR** (400 MHz, acetone-d_6) δ 8.97 (*br.* s, 1H), 8.49 (*br.* s, 1H), 8.37 (*br.* s, 1H), 8.28 (*br.* s, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.11 – 7.04 (m, 2H), 6.78 – 6.70 (m, 4H), 6.52 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.38 – 6.31 (m, 2H), 6.12 (d, *J* = 2.2 Hz, 1H), 4.89 – 4.84 (m, 2H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.06 (dd, *J* = 7.1, 2.5 Hz, 1H), 3.20 (s, 3H), 2.95 (ddd, *J* = 11.5, 5.1, 2.5 Hz, 1H). ***m/z* HRMS** (ES^-) calc. 525.1537 $[MH]^-$, found 525.1549, $C_{31}H_{25}O_8$, Δ = -2.3 ppm.

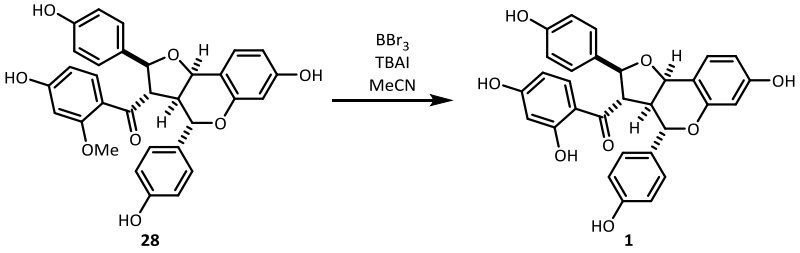
(2,4-Dimethoxyphenyl)((2*S*,3*S*,3*aS*,4*S*,9*bR*)-7-methoxy-2,4-*bis*(4-methoxyphenyl)-2,3,3*a*,9*b*-tetrahydro-4H-furo[3,2-*c*]chromen-3-yl)methanone (29)



27 **29**

To a solution of triphenol **27** (3.30 mg, 6.00 µmol) in acetone-d_6 (0.3 mL) was added Cs_2CO_3 (20.0 mg, 61.0 µmol, 10 equiv.) and methyl iodide (3.8 µL, 61.0 µmol, 10 equiv.) and allowed to stir for 19 hours at RT. The reaction mixture was concentrated in vacuo, diluted in water (3 mL), extracted with EtOAc (4 x 3 mL), dried over $MgSO_4$ and concentrated *in vacuo.* Column chromatography eluting with hexane/EtOAc (9:1 → 2:3) gave lophirone H pentamethyl ether **29** as an off-white semisolid (2.1 mg, 60%); silica gel TLC R_f 0.37 (hexane/EtOAc, 3:2); ν_{max}/cm^{-1} (ATR-IR) 1669, 1610, 1603, 1514, 1248, 1109, 1026, 829, 801; **^{1}H NMR** (400 MHz, acetone-d_6) δ 7.37 (d, *J* = 8.5 Hz, 1H), 7.27 – 7.19 (m, 5H), 6.91 – 6.85 (m, 2H), 6.77 – 6.71 (m, 2H), 6.61 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.43 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.43 (d, *J* = 2.5 Hz, 1H), 6.16 (d, *J* = 2.3 Hz, 1H), 5.07 (d, *J* = 7.4 Hz, 1H), 4.90 (d, *J* = 5.2 Hz, 1H), 4.66 (d, *J* = 11.5 Hz, 1H), 3.99 (dd, *J* = 7.4, 2.8 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.25 (s, 3H), 2.87 (ddd, *J* = 11.5, 5.2, 2.8 Hz, 1H); **^{13}C NMR** (101 MHz, acetone-d_6) δ 202.1, 165.1, 161.7, 160.7, 160.5, 160.2, 157.7, 134.2, 133.0, 132.4, 130.8, 130.3, 128.7, 122.3, 114.3, 109.2, 106.2, 101.9, 98.5, 84.1, 79.5, 75.6, 61.5, 55.8, 55.6, 55.6, 55.4, 55.2, 49.8, 29.8; ***m/z* HRMS** (ES^+) calc. 583.2332 $[MH]^+$, found 583.2323, $C_{35}H_{35}O_8$, Δ = -1.5 ppm.

(2,4-Dihydroxyphenyl)((2*S*,3*S*,3*aS*,4*S*,9*bR*)-7-hydroxy-2,4-*bis*(4-hydroxyphenyl)-2,3,3*a*,9*b*-tetrahydro-4H-furo[3,2-*c*]chromen-3-yl)methanone (1)

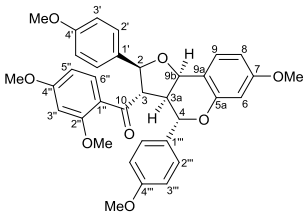


28 **1**

Tetraphenol **28** (1.5 mg, 0.0029 mmol) and tetrabutylammonium iodide (2.1 mg, 0.0057 mmol) were transferred to a dry microwave (Biotage®) vial which was thoroughly purged with Ar prior to sealing. The

contents were dissolved in dry MeCN (0.14 mL) to give a colourless solution. A solution of BBr_3 in CH_2Cl_2 (1M, 23 µL, 0.023 mmol, 8 equiv.) was added dropwise (cloudy fumes observed immediately) to give an orange solution with some white precipitate forming after ~2 mins. The reaction mixture was stirred for 15 mins at RT before it was quenched with sat. NaHCO3 (1 mL), extracted into EtOAc (5 x 2 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Preparative thin-layer chromatography eluting with hexane/EtOAc (1:4) gave (+)-lophirone H **1** as an off-white semisolid (0.8 mg, 54%); silica gel TLC R_f 0.51 (hexane/EtOAc, 1:4); ν_{max}/cm^{-1} (ATR-IR) 3361, 1656, 1615, 1513, 1464, 1259, 1013, 792; **^{1}H NMR** (400 MHz, acetone-d_6) 12.81 (s, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.22 – 7.18 (m, 2H), 6.83 – 6.78 (m, 4H), 6.55 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.38 (d, *J* = 2.4 Hz, 1H), 6.29 (d, *J* = 8.9 Hz, 1H), 6.21 (d, *J* = 2.4 Hz, 1H), 5.92 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.15 (d, *J* = 6.7 Hz, 1H), 5.00 (d, *J* = 5.3 Hz, 1H), 4.78 (d, *J* = 11.5 Hz, 1H), 3.58 (dd, *J* = 6.7, 2.6 Hz, 2H), 2.94 (ddd, *J* = 11.5, 5.3, 2.6); **^{13}C NMR** (101 MHz, acetone-d_6) δ 132.9, 132.4, 129.9, 127.9, 115.6, 115.2, 109.4, 107.9, 103.0, 102.7, 84.0, 78.3, 75.4, 57.2, 49.7 (peaks from HSQC spectrum as the sample decomposed during a standard ^{13}C acquisition ; quaternary carbons absent); ***m/z* HRMS** (ES^-) calc. 511.1388 $[MH]^-$, found 511.1396, $C_{30}H_{23}O_8$, Δ = -1.0 ppm.

Natural and Synthetic lophirone H pentamethyl ether: ^{1}H and ^{13}C NMR comparison



	Natural lophirone H pentamethyl ether[9]			Synthetic lophirone H pentamethyl ether (29)		
	^{1}H NMR (300 MHz, acetone-d_6)			^{1}H NMR (400 MHz, acetone-d_6)		
Position	δ	splitting	J values	δ	splitting	J values
3a	2.869	ddd	11.5, 5.2, 2.8	2.871	ddd	11.5, 5.2, 2.8
OMe	3.246	s		3.249	s	
OMe	3.739	s		3.744	s	
OMe	3.774	s		3.777	s	
OMe	3.777	s		3.78	s	
OMe	3.812	s		3.816	s	
3	3.991	dd	7.4, 2.8	3.99	dd	7.4, 2.8
4	4.658	d	11.5	4.656	d	11.5
9b	4.903	d	5.2	4.9	d	5.2
2	5.071	d	7.4	5.065	d	7.4
3''	6.158	d	2.3	6.16	d	2.3
5''	6.432	dd	8.5, 2.3	6.435	dd	8.6, 2.3
6	6.436	d	2.5	6.434	d	2.5
8	6.613	dd	8.5, 2.5	6.614	dd	8.5, 2.5
3'''	6.739	m		6.744	m	
5'''	6.739	m		6.744	m	
3'	6.875	m		6.878	m	
5'	6.875	m		6.878	m	
2'	7.223	m		7.227	m	
6'	7.223	m		7.227	m	
6''	7.223	d	8.5	7.227	d	8.6
2'''	7.223	m		7.227	m	
6'''	7.223	m		7.227	m	
9	7.327	d	8.5	7.371	d	8.5

Table S1. Comparison of ^{1}H NMR data for natural[9] and synthetic lophirone H pentamethyl ether.

	Natural lophirone H pentamethyl ether[9]		**Synthetic lophirone H pentamethyl ether (29)**	
Position	^{13}C NMR (75 MHz, acetone-d_6)		^{13}C NMR (101 MHz, acetone-d_6)	
	δ		δ	
3a	49.47	d	49.79	d
OMe	54.84	q	55.18	q
OMe	54.97	q	55.42	q
OMe	55.23	q	55.56	q
OMe	55.3	q	55.64	q
OMe	55.49	q	55.84	q
3	61.14	d	61.48	d
9b	75.23	d	75.57	d
4	79.21	d	79.5	d
2	83.77	d	84.11	d
3''	98.12	d	98.46	d
6	101.6	d	101.94	d
5''	105.91	d	106.24	d
8	108.88	d	109.22	d
3'	113.96	d	114.31	d
5'	113.96	d	114.31	d
3'''	113.96	d	114.31	d
5'''	113.96	d	114.31	d
1''	121.96	s	122.31	s
2'''	128.41	d	128.74	d
6'''	128.41	d	128.74	d
9a	128.62	s	128.74	s
2'	129.99	d	130.32	d
6'	129.99	d	130.32	d
1'''	130.42	s	130.79	s
6''	132.08	s	132.4	s
9	132.64	s	132.96	s
1'	133.81	s	134.15	s
5a	157.34	s	157.67	s
4'	159.82	s	160.17	s
4''	160.15	s	160.5	s
4'''	160.36	s	160.71	s
7	161.39	s	161.74	s
2''	164.72	s	165.05	s
10	201.83	s	202.11	s

Table S2. Comparison of ^{13}C NMR data for natural[9] and synthetic lophirone H pentamethyl ether.

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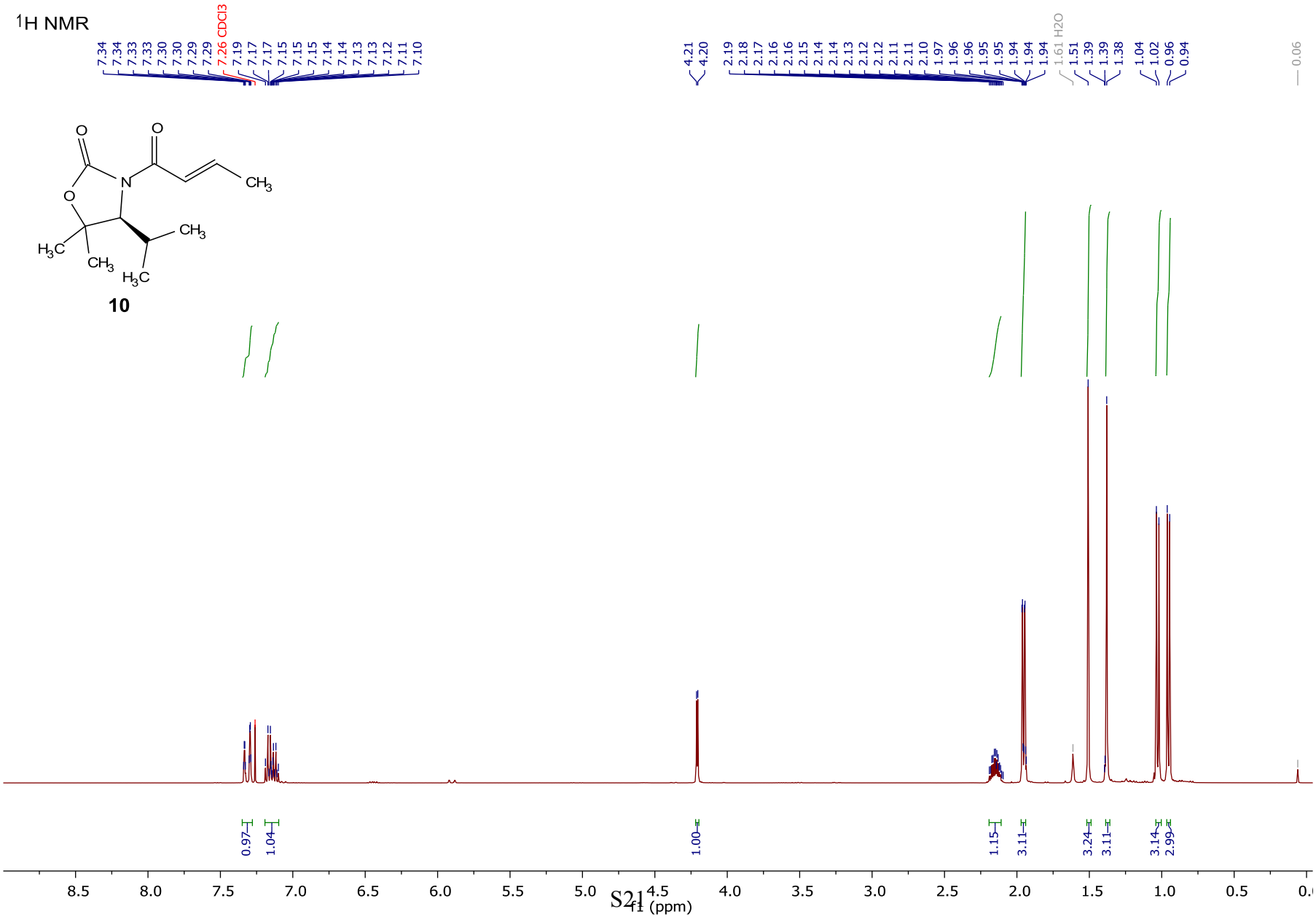
NMR Spectra

Complete NMR data files in MestreNova mnova and mnpub formats are available at DOI: 10.14469/hpc/2017 for analysis using Mestrenova V11 or higher software. For further details of the mnpub method of publishing NMR datasets, see DOI: 10.14469/hpc/1053. In addition, static versions of all spectra are available below in this PDF document.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4.21 4.20 2.19 2.18 2.17 2.16 2.16 2.15 2.14 2.14 2.13 2.12 2.12 2.11 2.11 2.10 1.97 1.96 1.96 1.95 1.95 1.94 1.94 1.94 1.61 H2O 1.51 1.39 1.39 1.38 1.04 1.02 0.96 0.94 0.06
O
O
N
O
CH3
H3C
CH3
CH3
H3C
10
0.97 1.04 1.00 1.15 3.11 3.24 3.11 3.14 2.99
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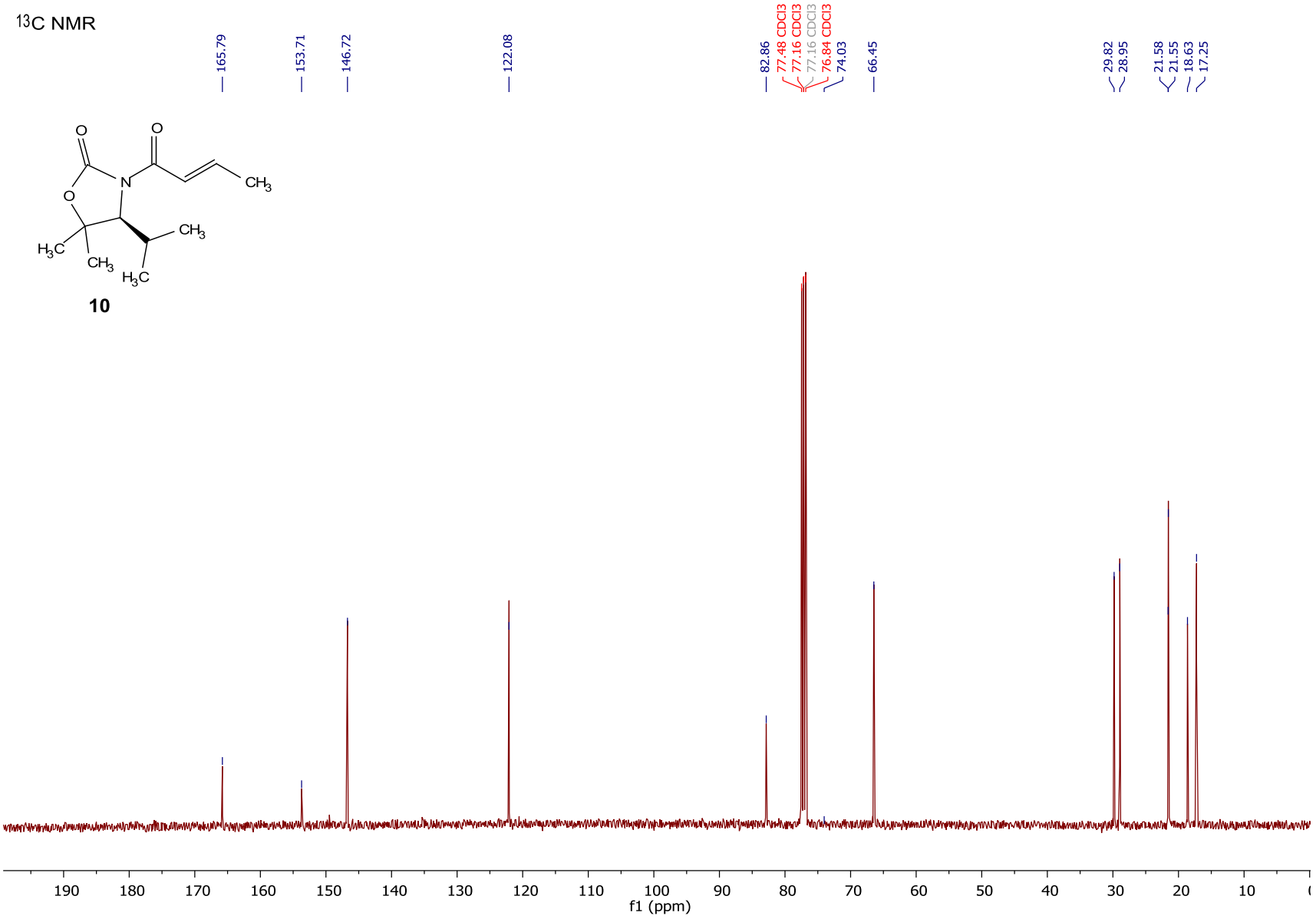
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H3C
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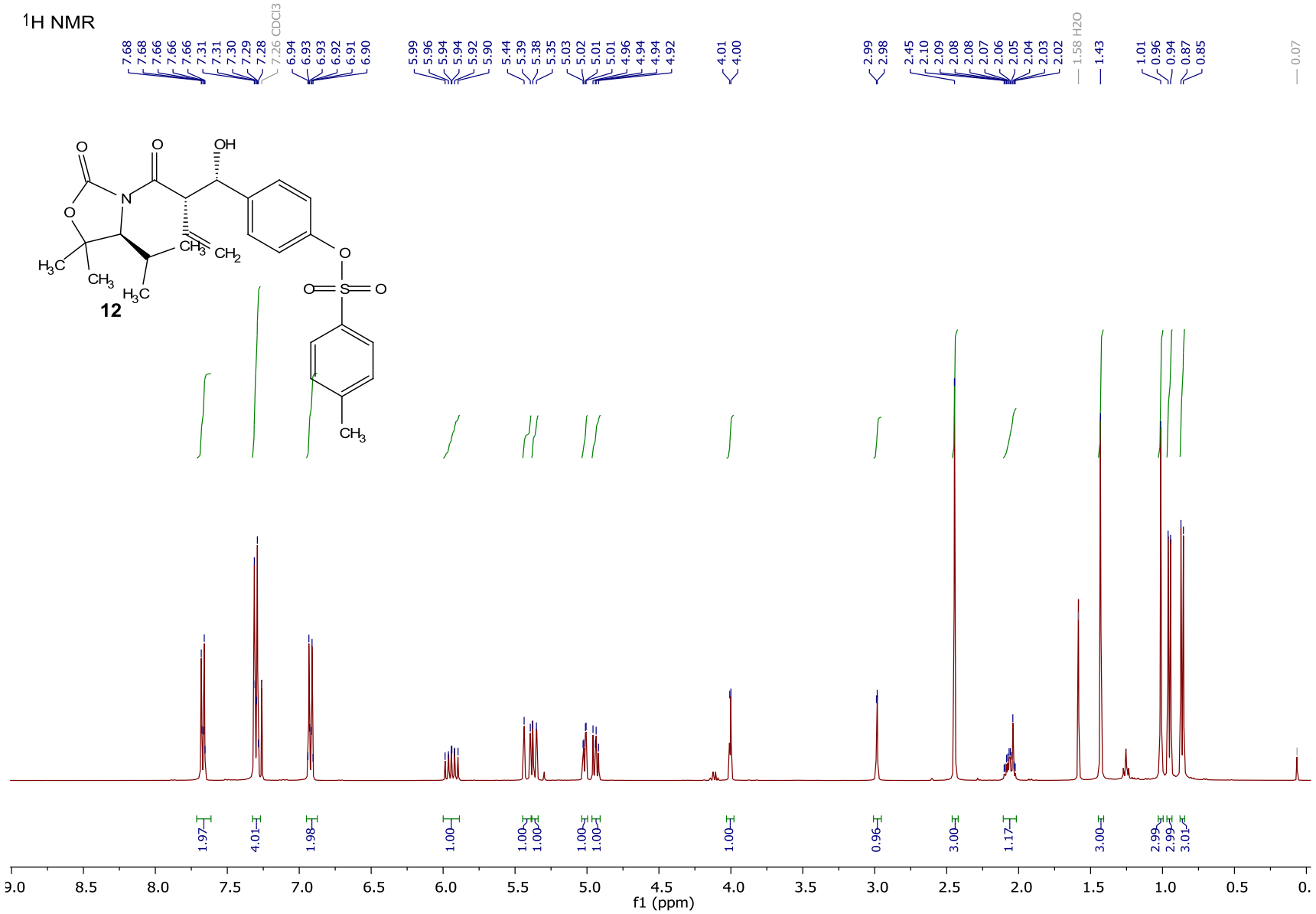
f1 (ppm)

10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4.01 4.00
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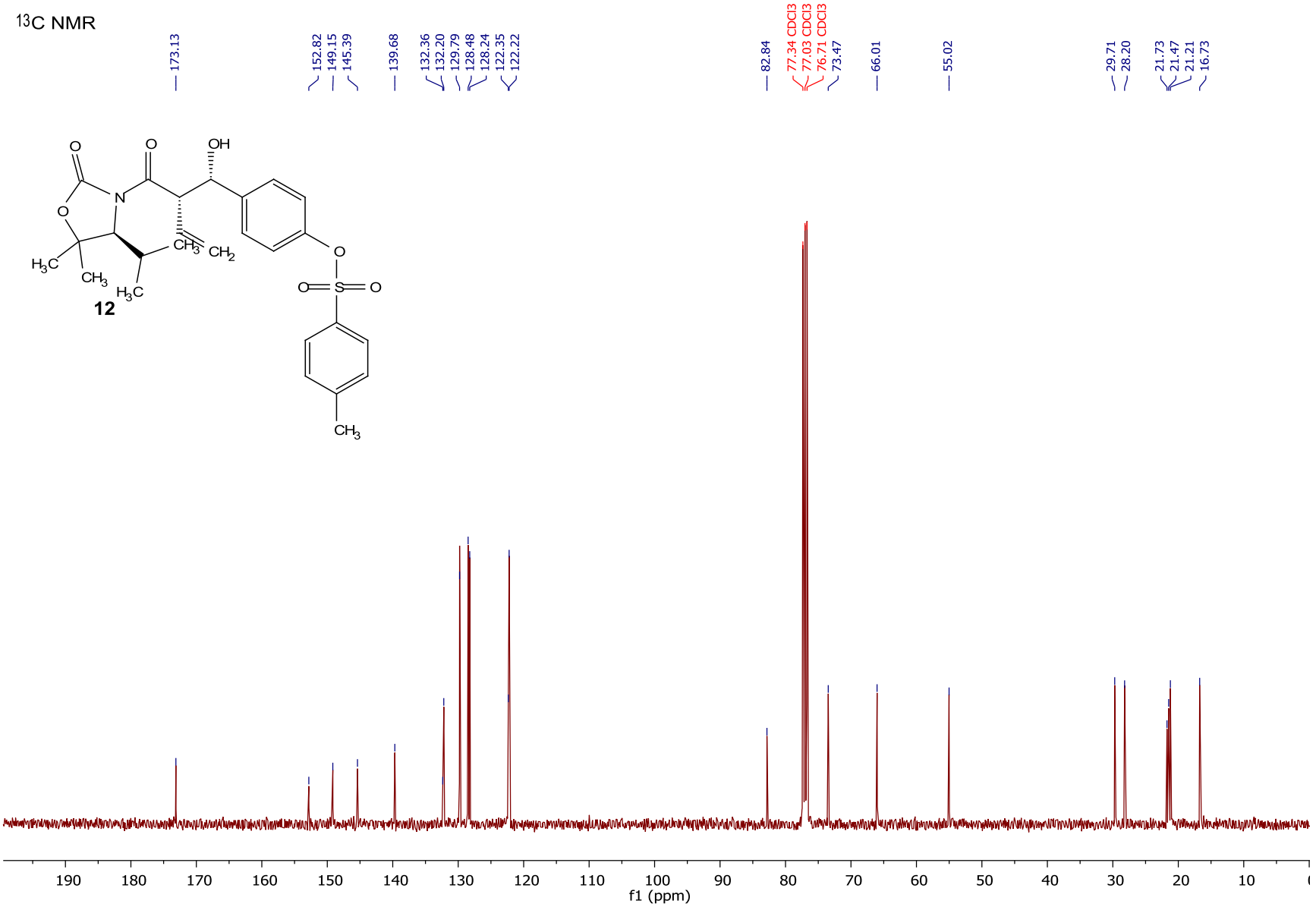
f1 (ppm)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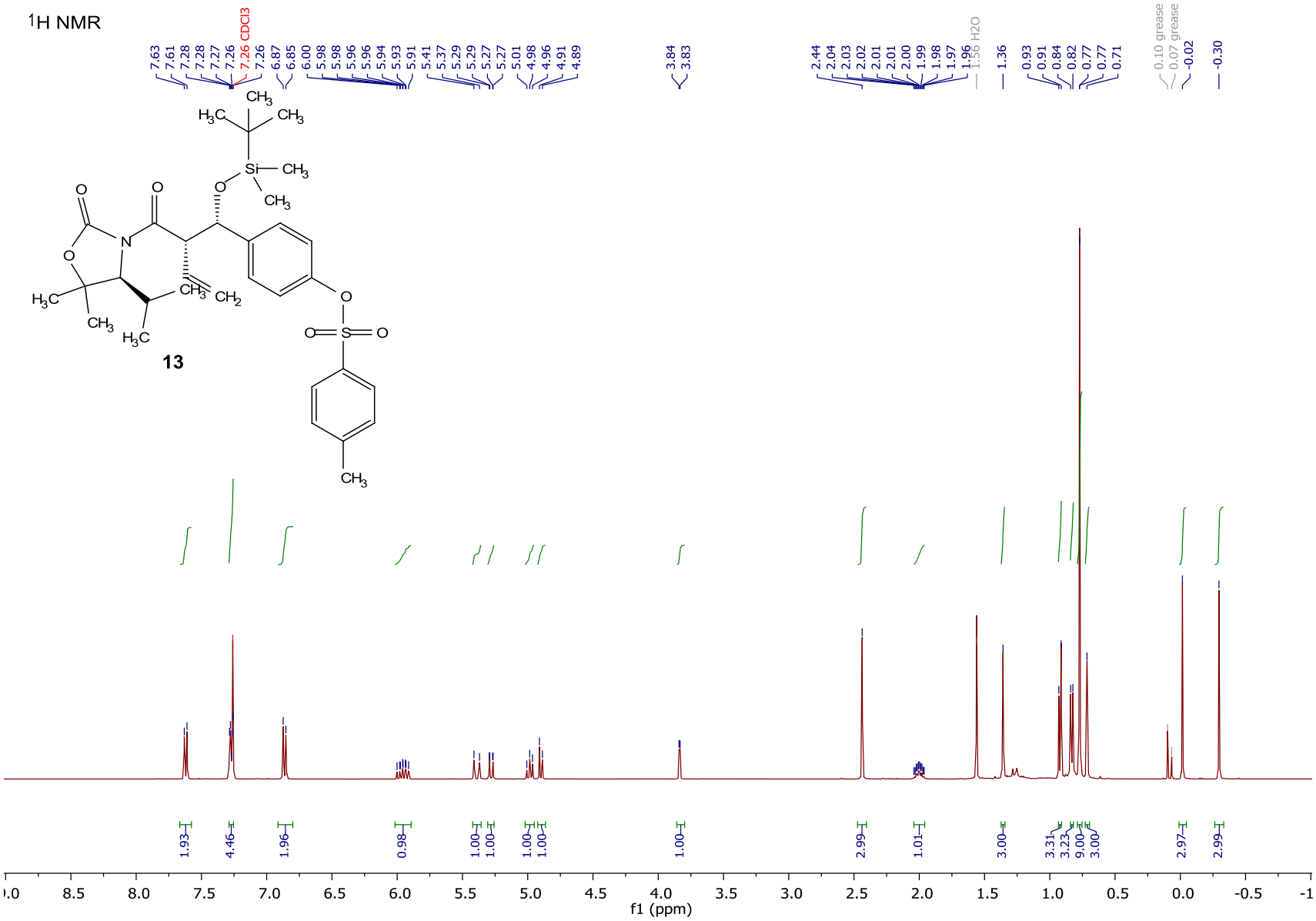
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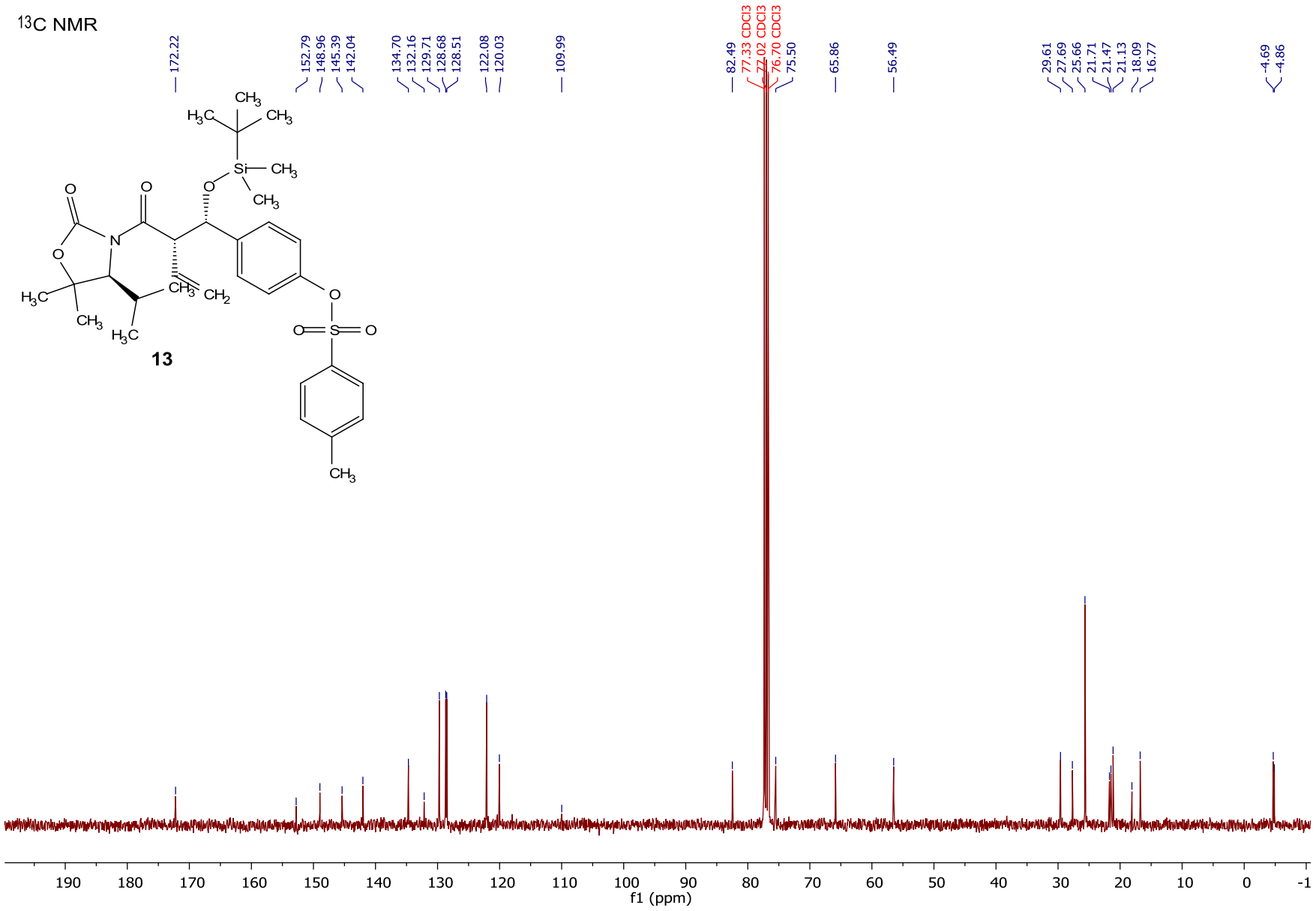
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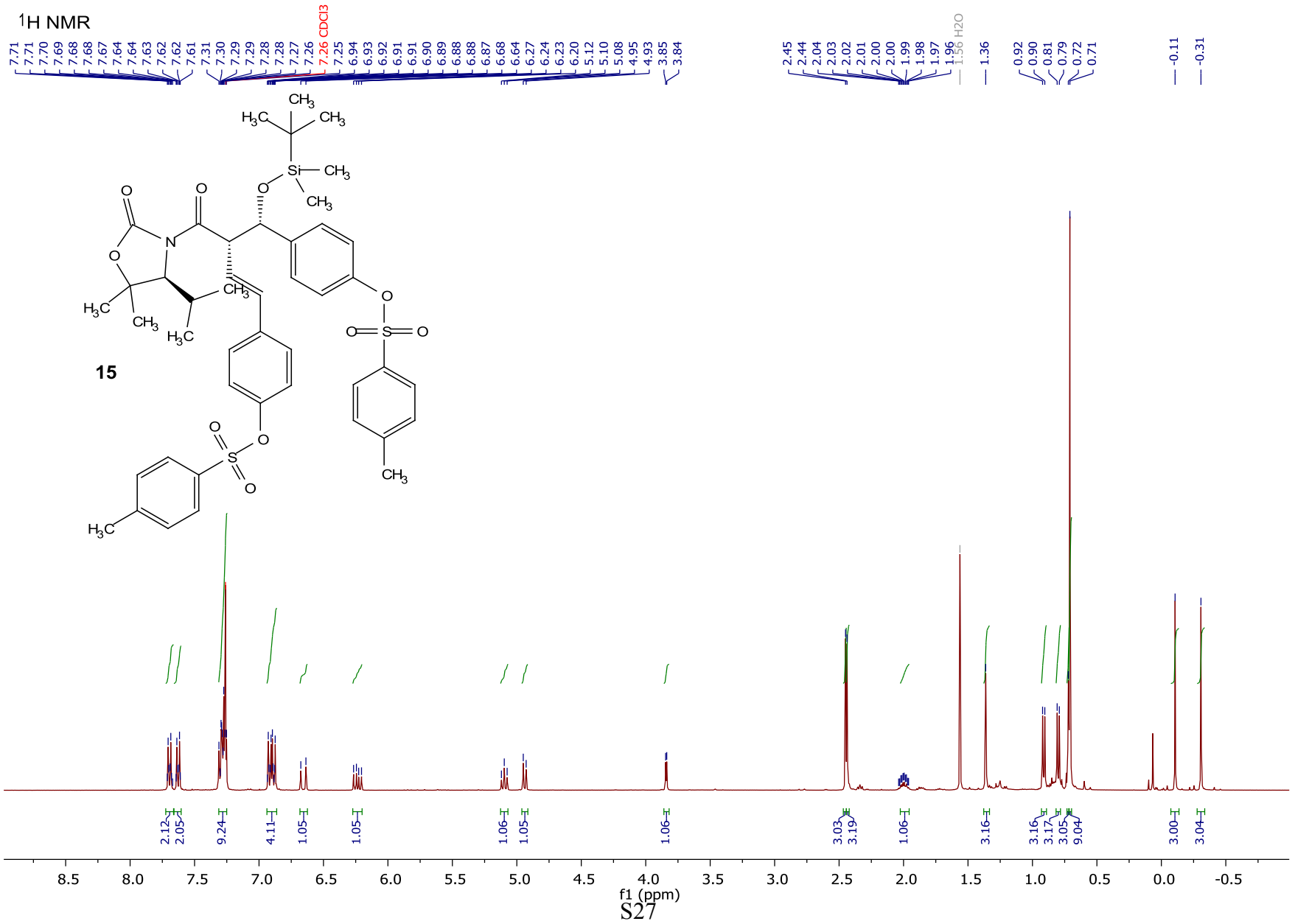
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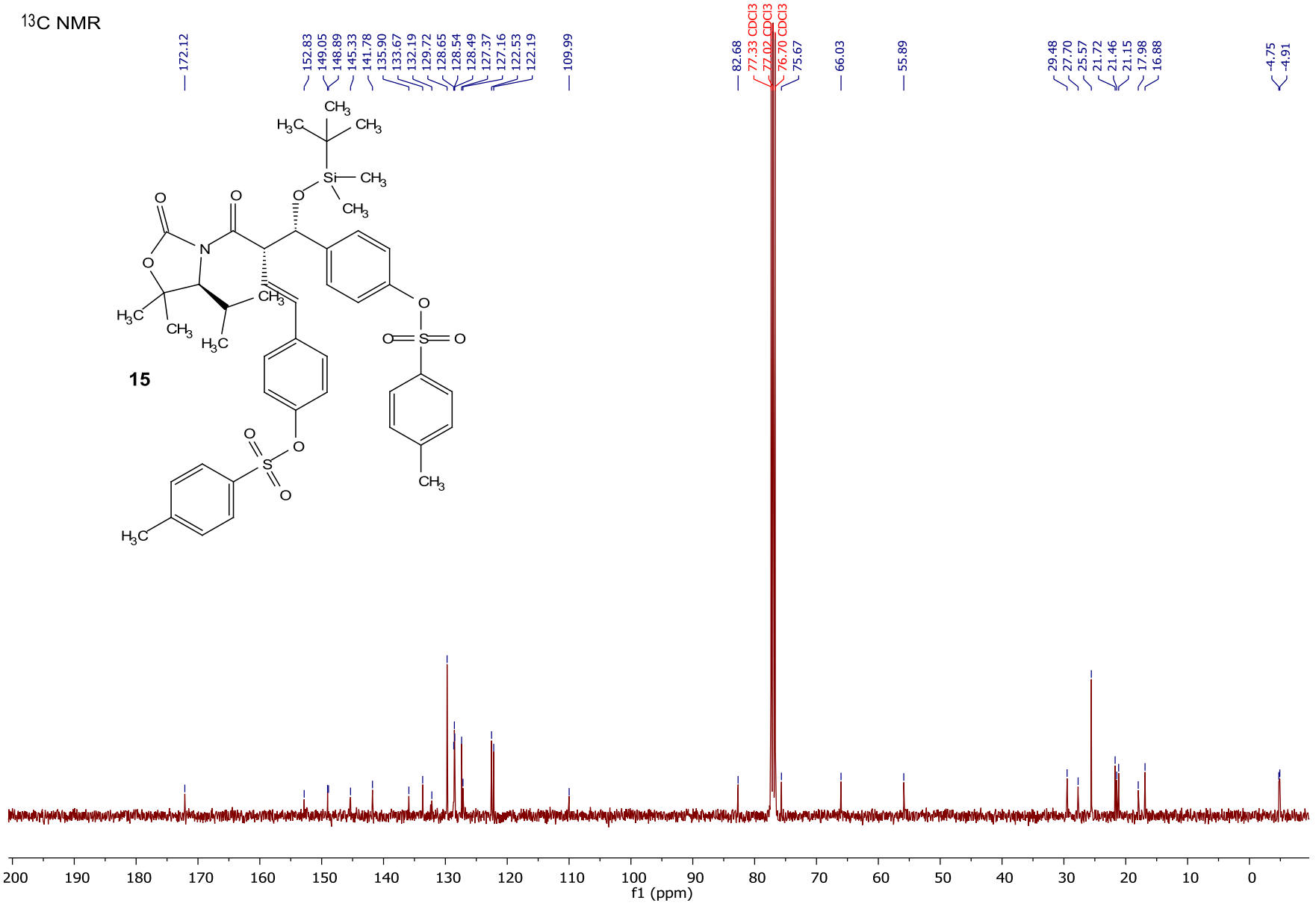
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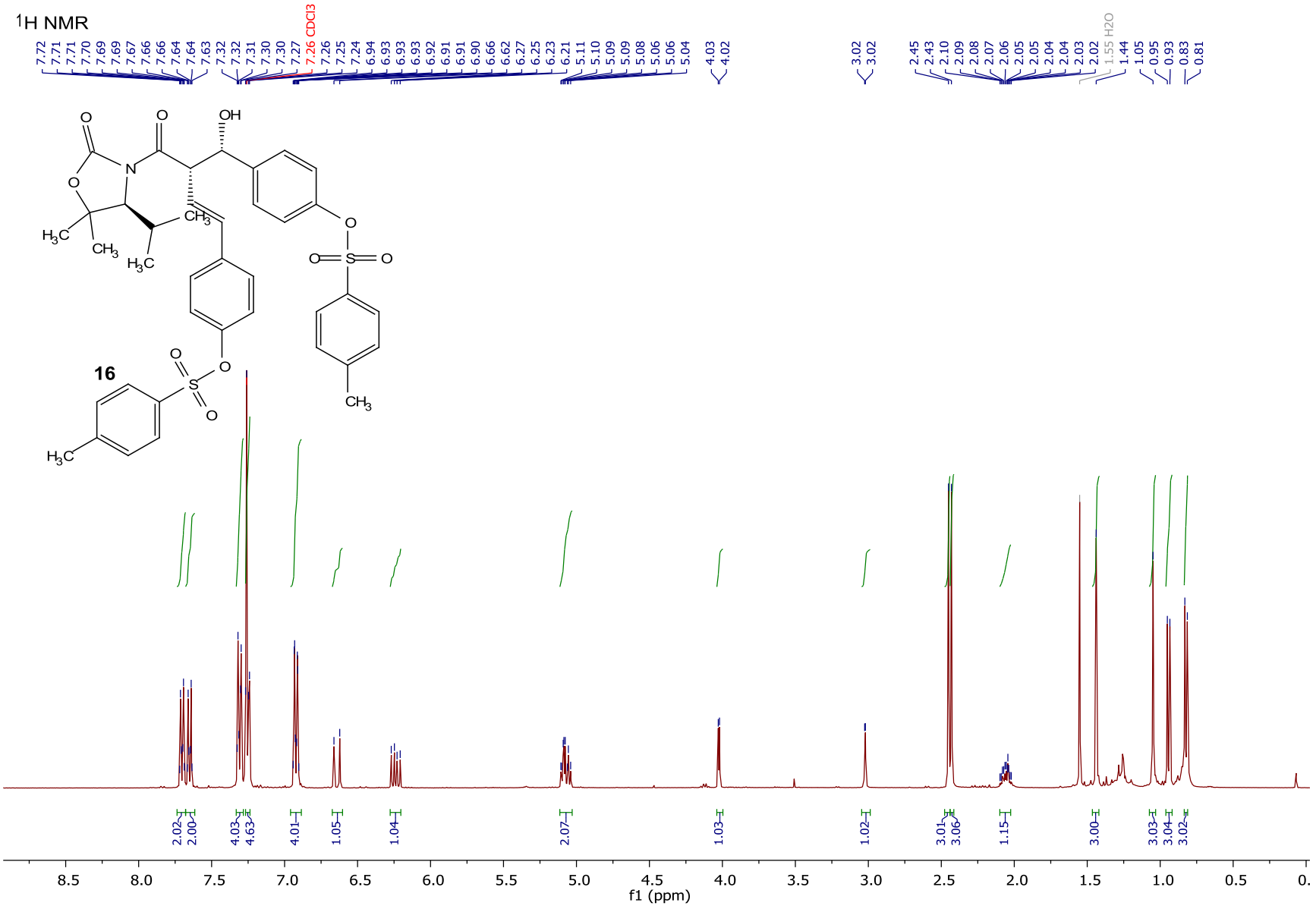
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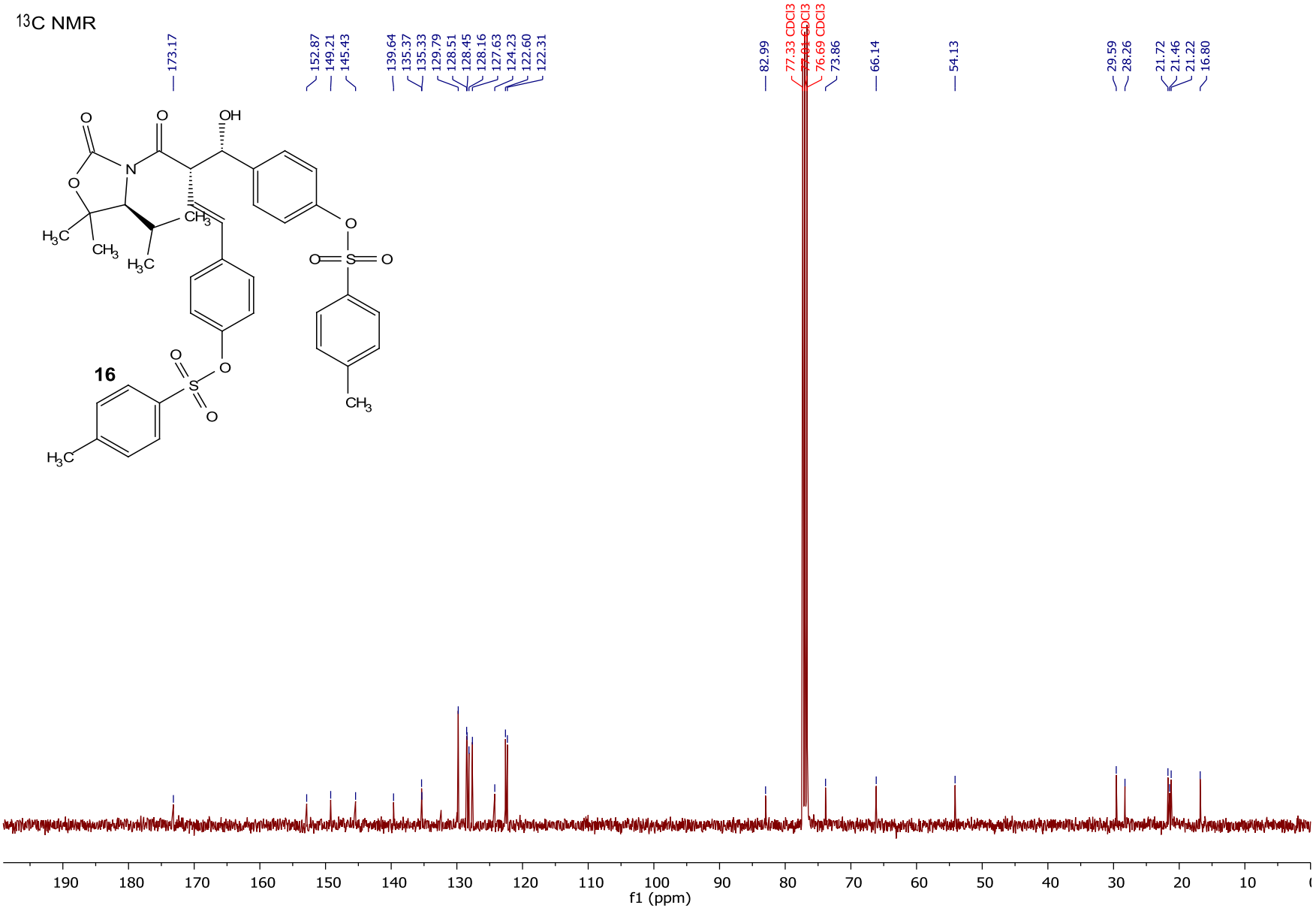
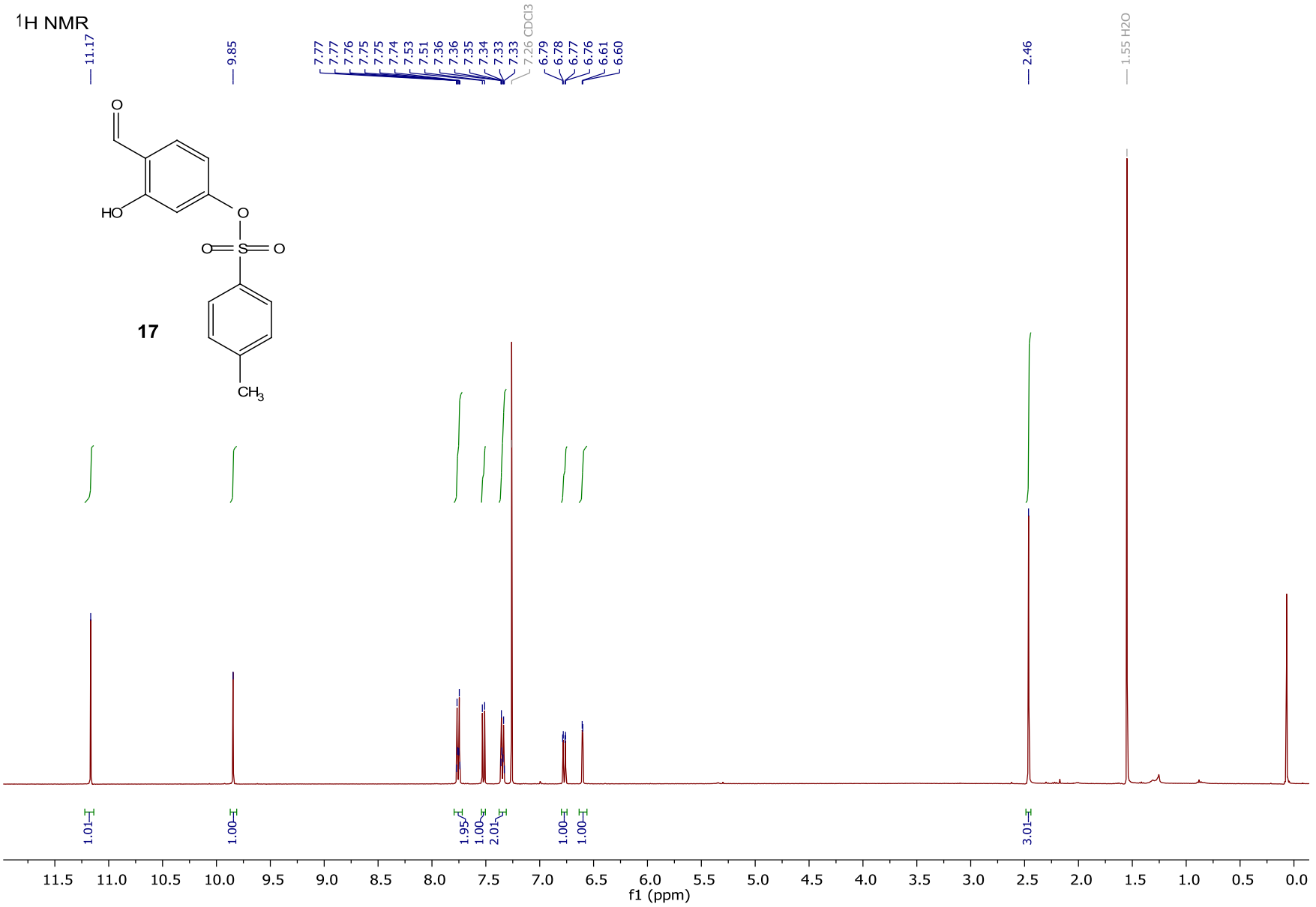
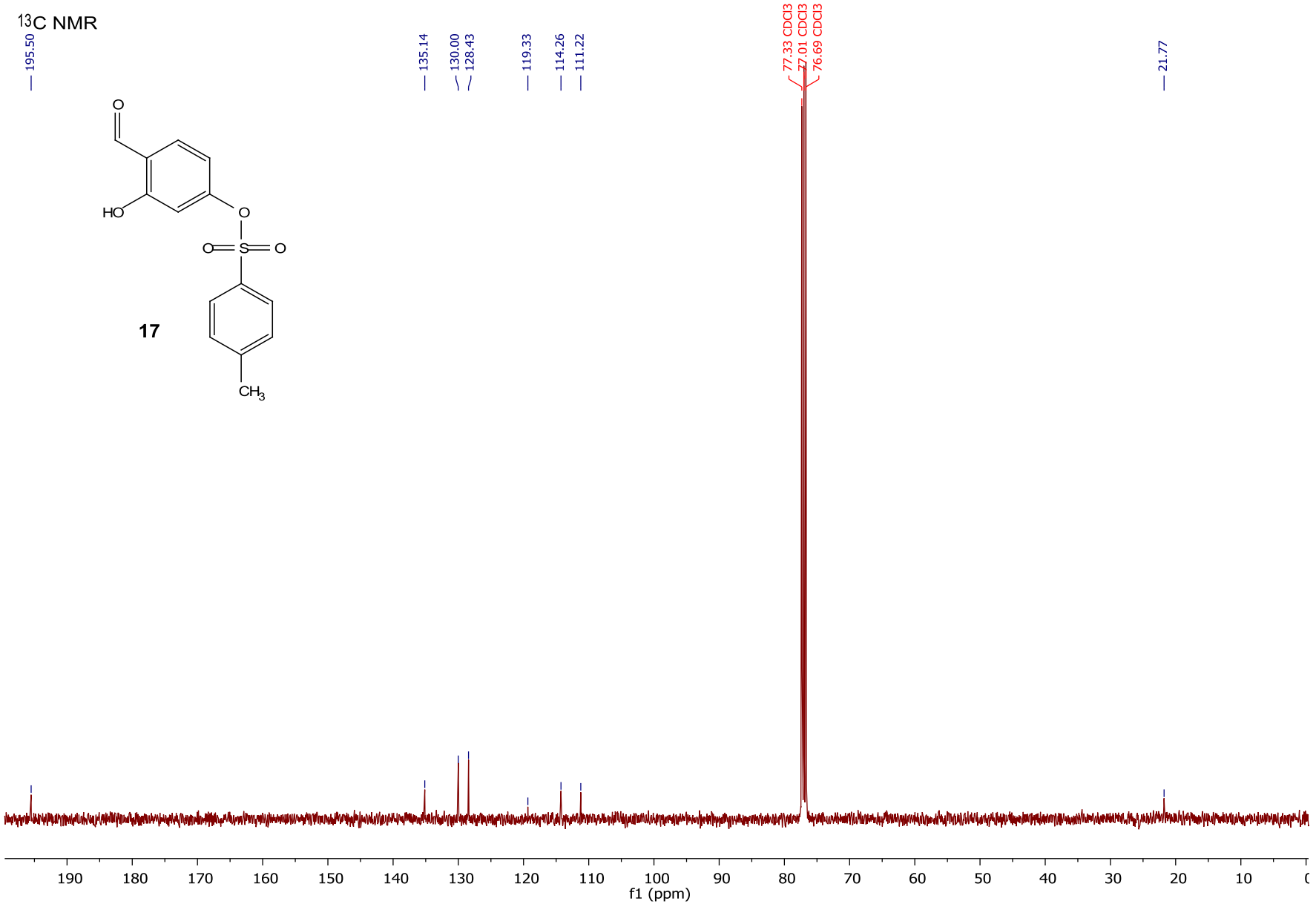
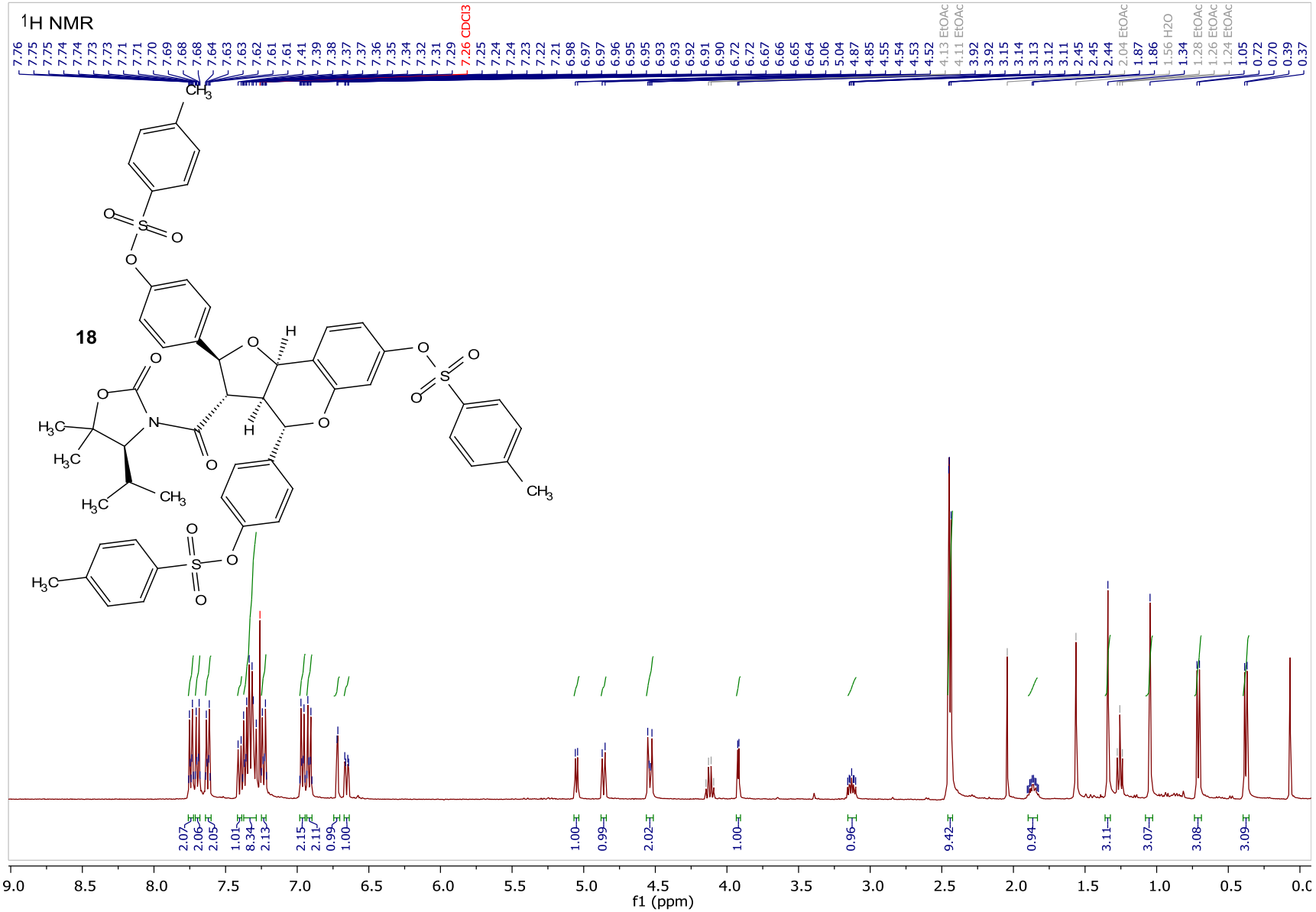
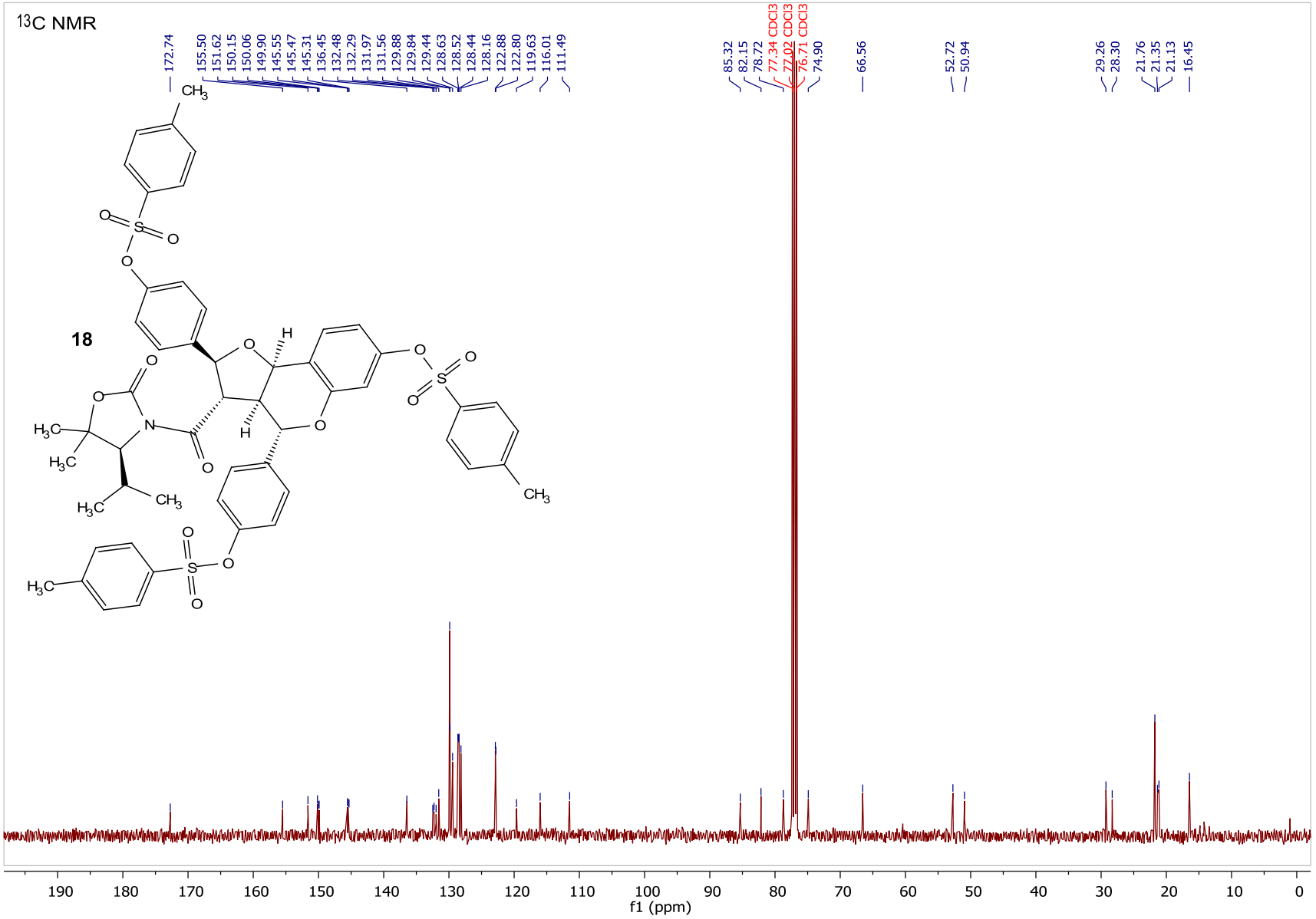
16
2.02 2.00 4.03 4.63 4.01 1.05 1.04 2.07 1.03 1.02 3.01 3.06 1.15 3.00 3.03 3.04 3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

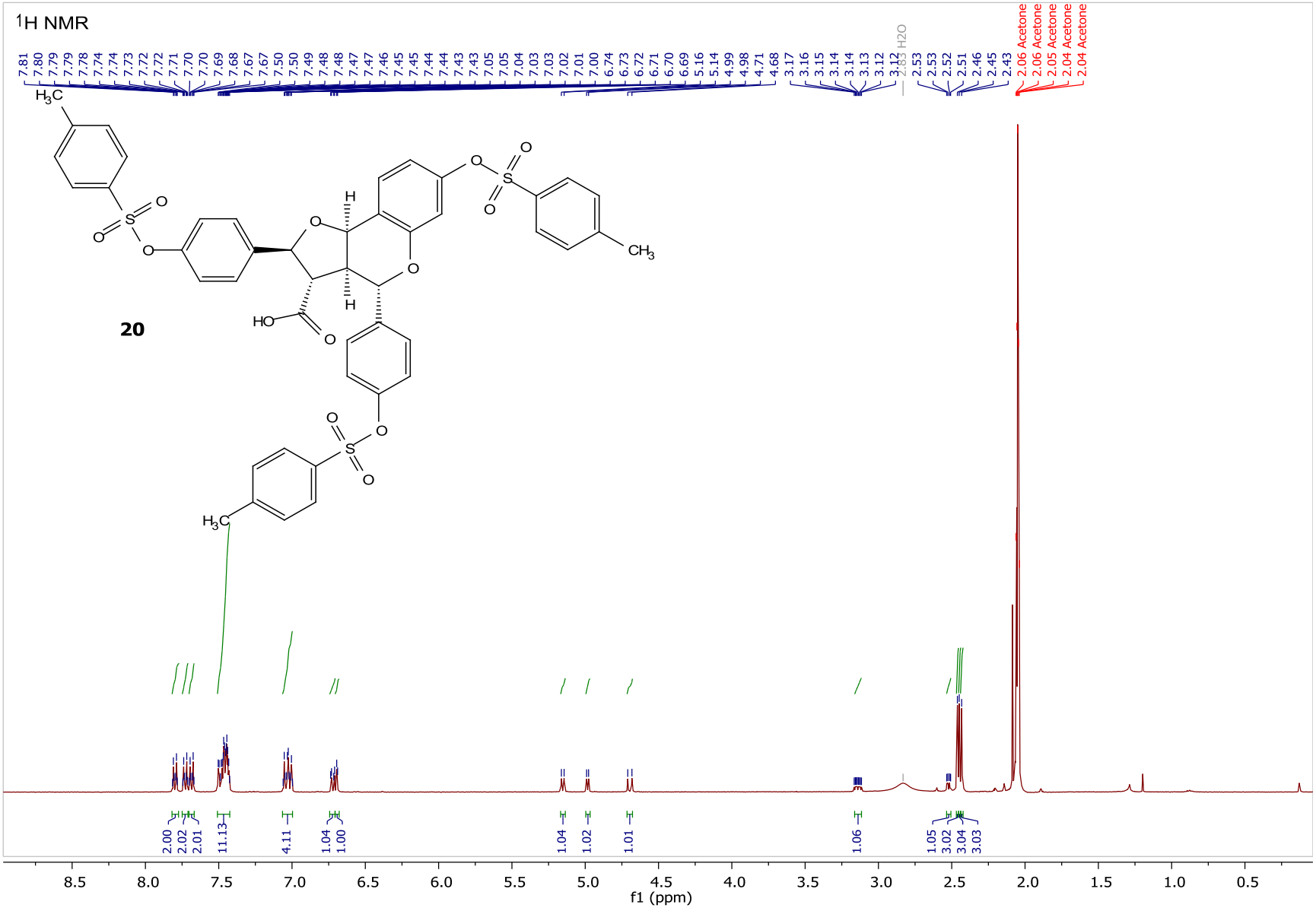

13C NMR
173.17
152.87
149.21
145.43
139.64
135.37
135.33
129.79
128.51
128.45
128.16
127.63
124.23
122.60
122.31
82.99
77.33 CDCl3
77.01 CDCl3
76.69 CDCl3
73.86
66.14
54.13
29.59
28.26
21.72
21.46
21.22
16.80
16
f1 (ppm)

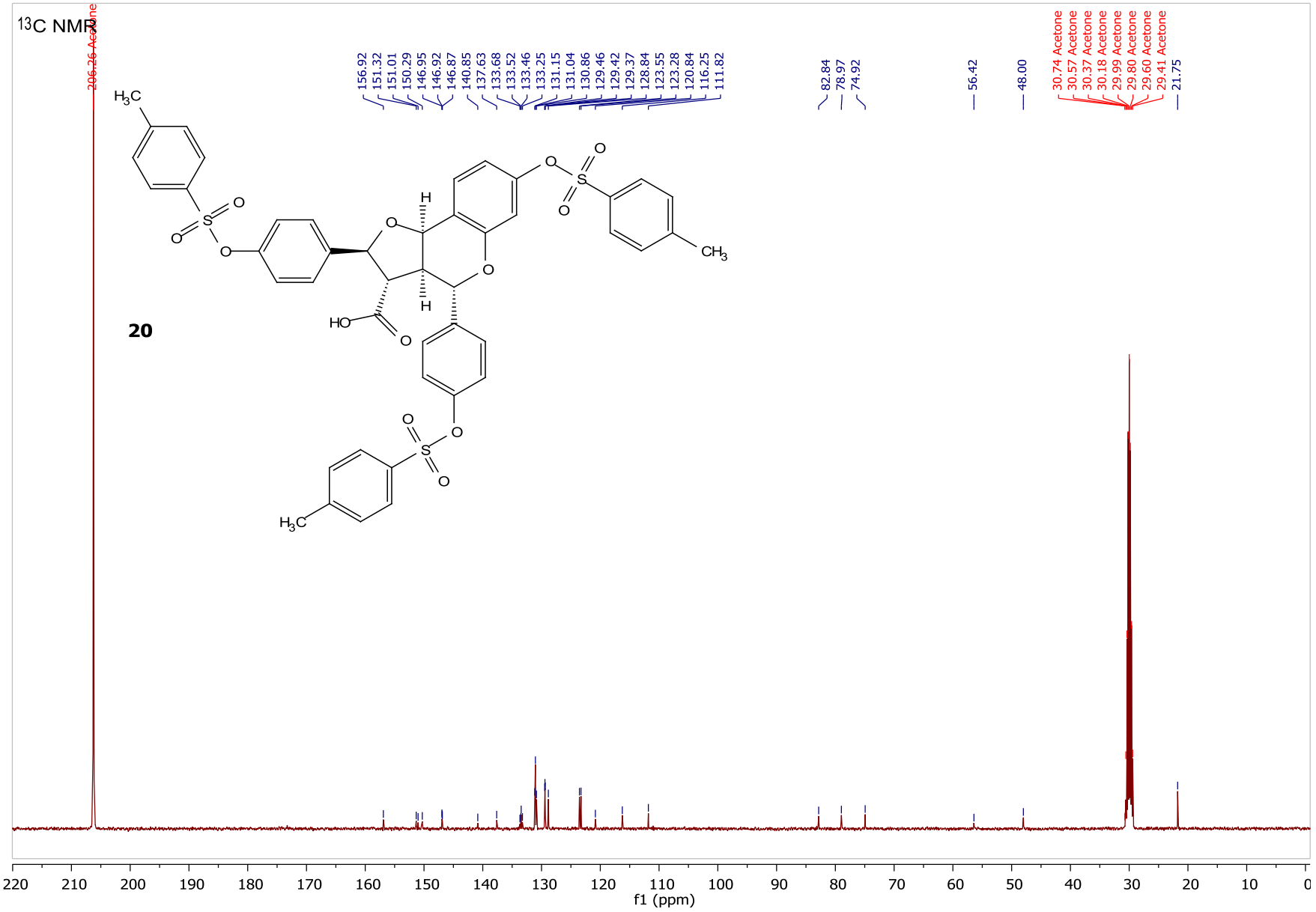

1H NMR
11.17
9.85
7.77
7.77
7.76
7.75
7.75
7.74
7.53
7.51
7.36
7.36
7.35
7.34
7.33
7.33
7.26 CDCl3
6.79
6.78
6.77
6.76
6.61
6.60
2.46
1.55 H2O
HO
O
O
S
O
O
CH3
17
1.01
1.00
1.95
1.00
2.01
1.00
1.00
3.01
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

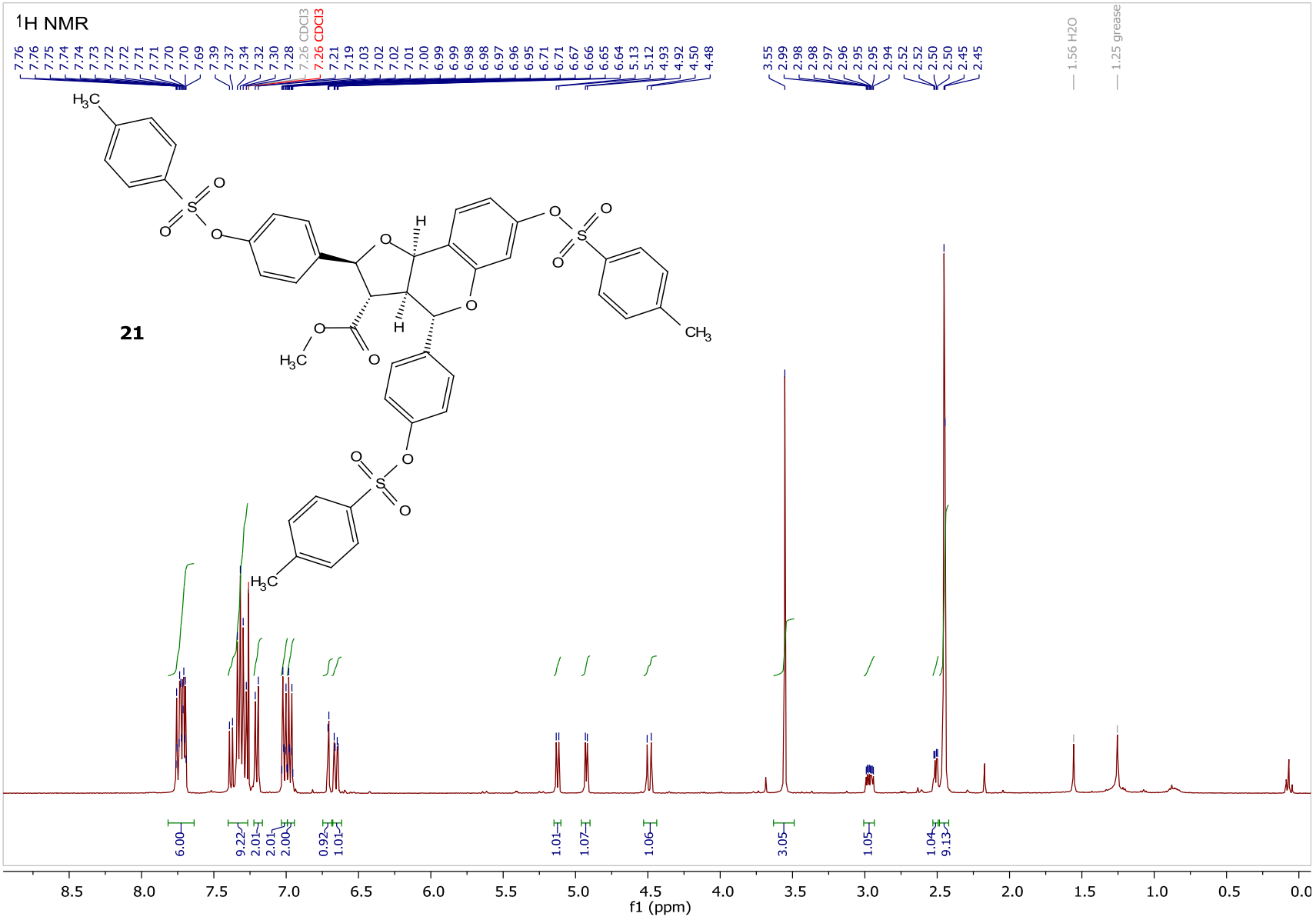

13C NMR
195.50
135.14
130.00
128.43
119.33
114.26
111.22
77.33 CDCl3
77.01 CDCl3
76.69 CDCl3
21.77
O
HO
O
O
S
O
CH3
17
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

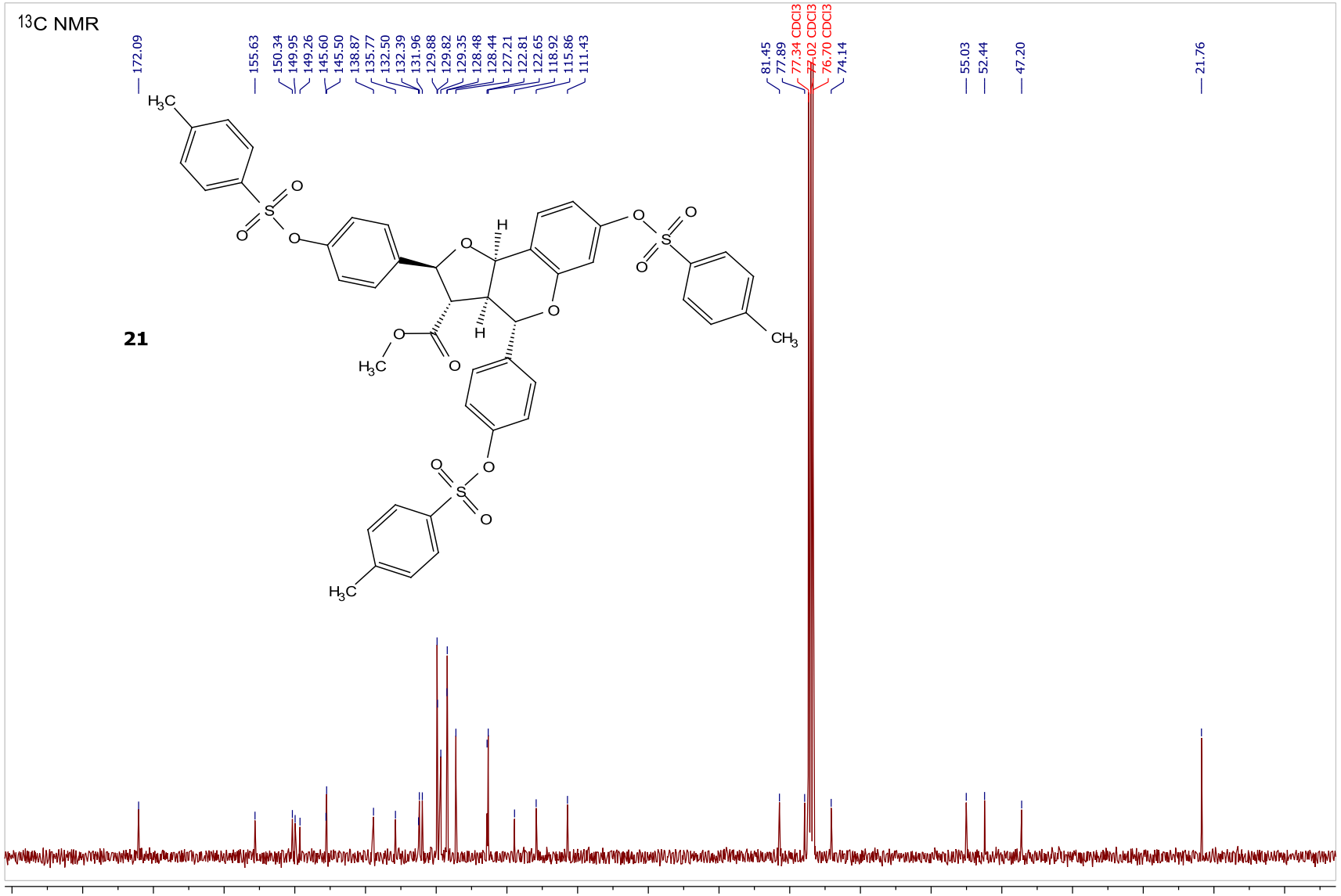

1H NMR
18
f1 (ppm)

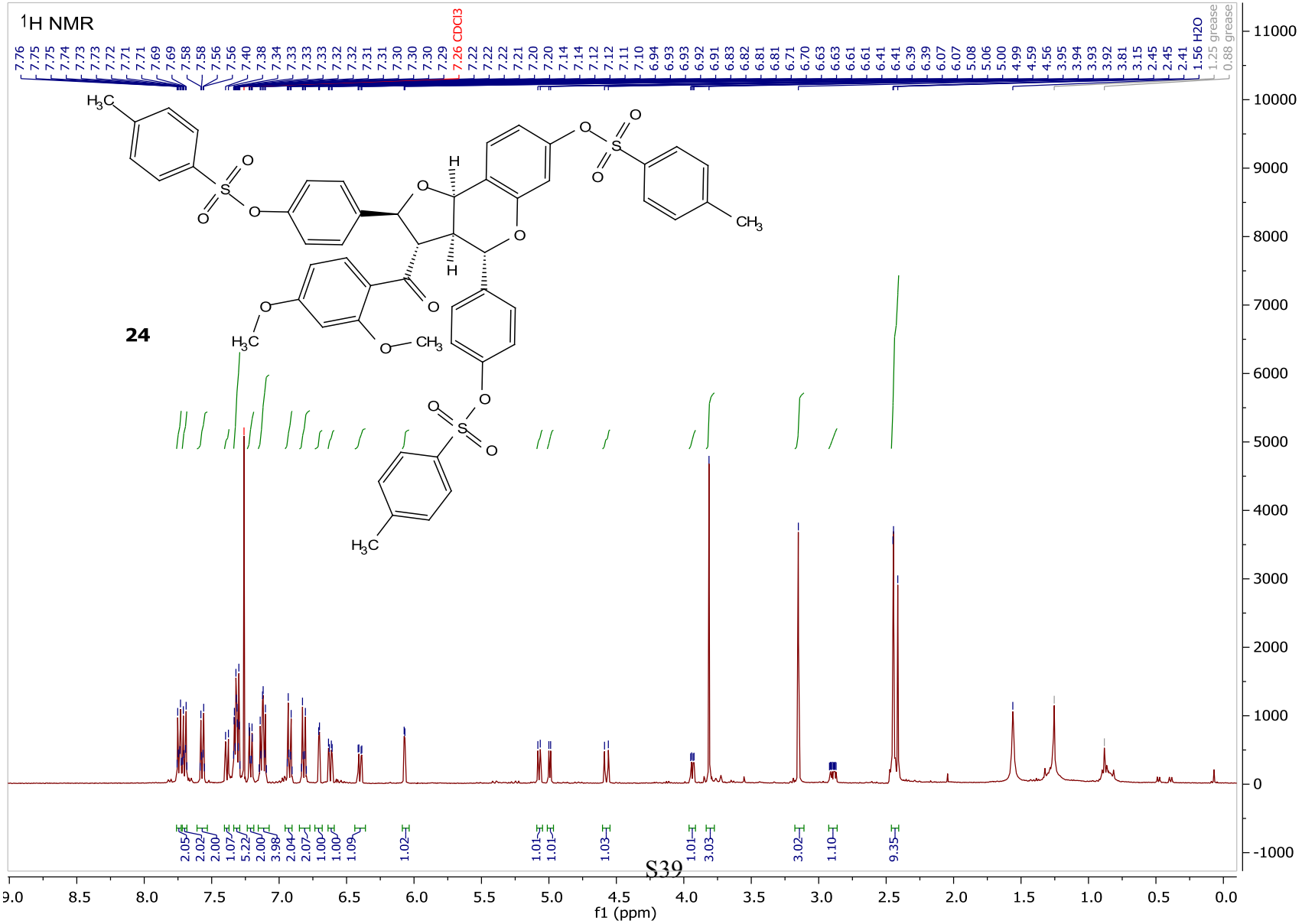

13C NMR
18
172.74
155.50
151.62
150.15
150.06
149.90
145.55
145.47
145.31
136.45
132.48
132.29
131.97
131.56
129.88
129.84
129.44
128.63
128.52
128.44
128.16
122.88
122.80
119.63
116.01
111.49
85.32
82.15
78.72
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
74.90
66.56
52.72
50.94
29.26
28.30
21.76
21.35
21.13
16.45
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

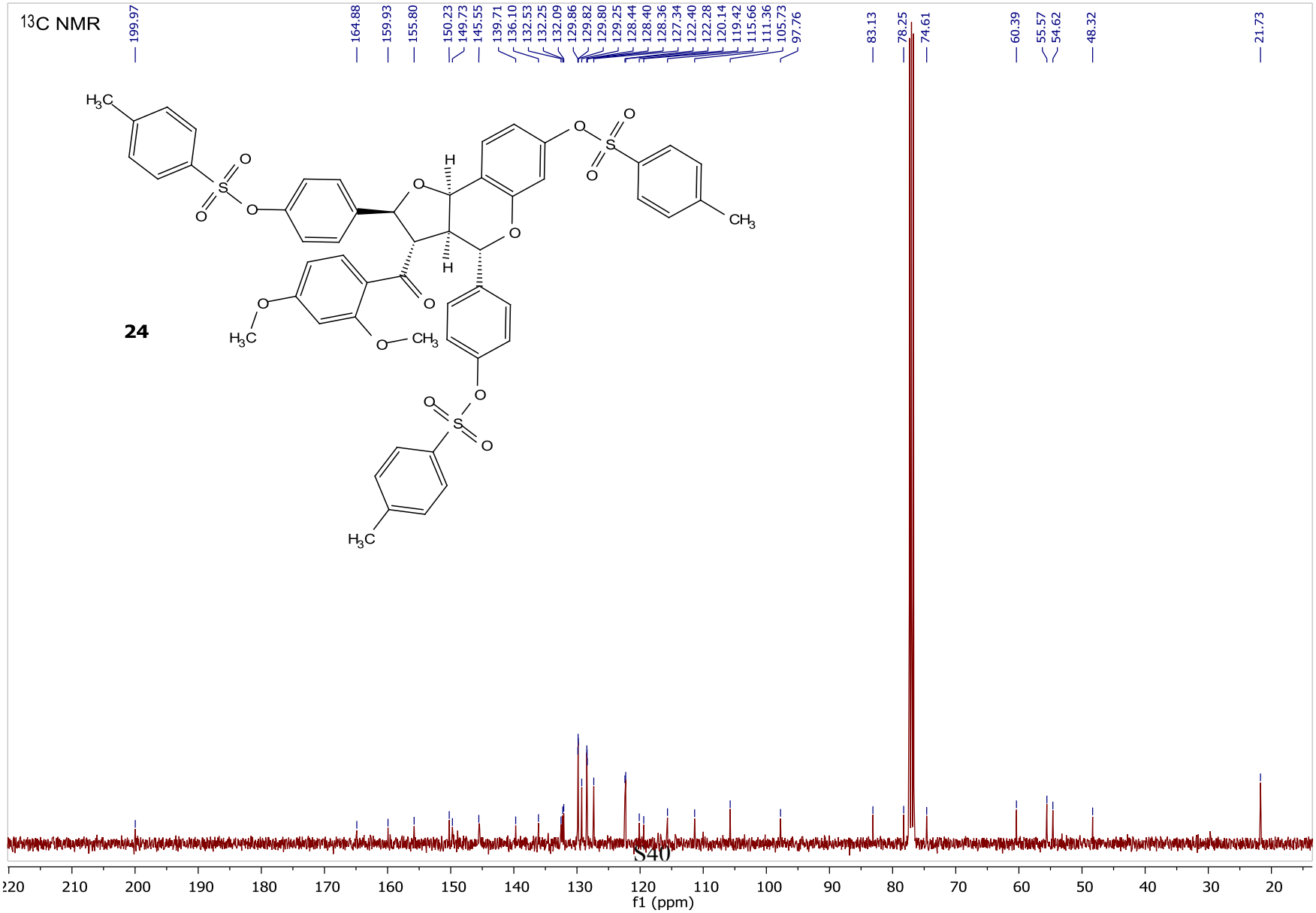

1H NMR
20
f1 (ppm)


13C NMR
206.26 Acetone
156.92
151.32
151.01
150.29
146.95
146.92
146.87
140.85
137.63
133.68
133.52
133.46
133.25
131.15
131.04
130.86
129.46
129.42
129.37
128.84
123.55
123.28
120.84
116.25
111.82
82.84
78.97
74.92
56.42
48.00
30.74 Acetone
30.57 Acetone
30.37 Acetone
30.18 Acetone
29.99 Acetone
29.80 Acetone
29.60 Acetone
29.41 Acetone
21.75
20
f1 (ppm)


1H NMR
21
f1 (ppm)


13C NMR
172.09
155.63
150.34
149.95
149.26
145.60
145.50
138.87
135.77
132.50
132.39
131.96
129.88
129.82
129.35
128.48
128.44
127.21
122.81
122.65
118.92
115.86
111.43
81.45
77.89
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
74.14
55.03
52.44
47.20
21.76
21
f1 (ppm)


1H NMR
24
f1 (ppm)


13C NMR
199.97
164.88
159.93
155.80
150.23
149.73
145.55
139.71
136.10
132.53
132.25
132.09
129.86
129.82
129.80
129.25
128.44
128.40
128.36
127.34
122.40
122.28
120.14
119.42
115.66
111.36
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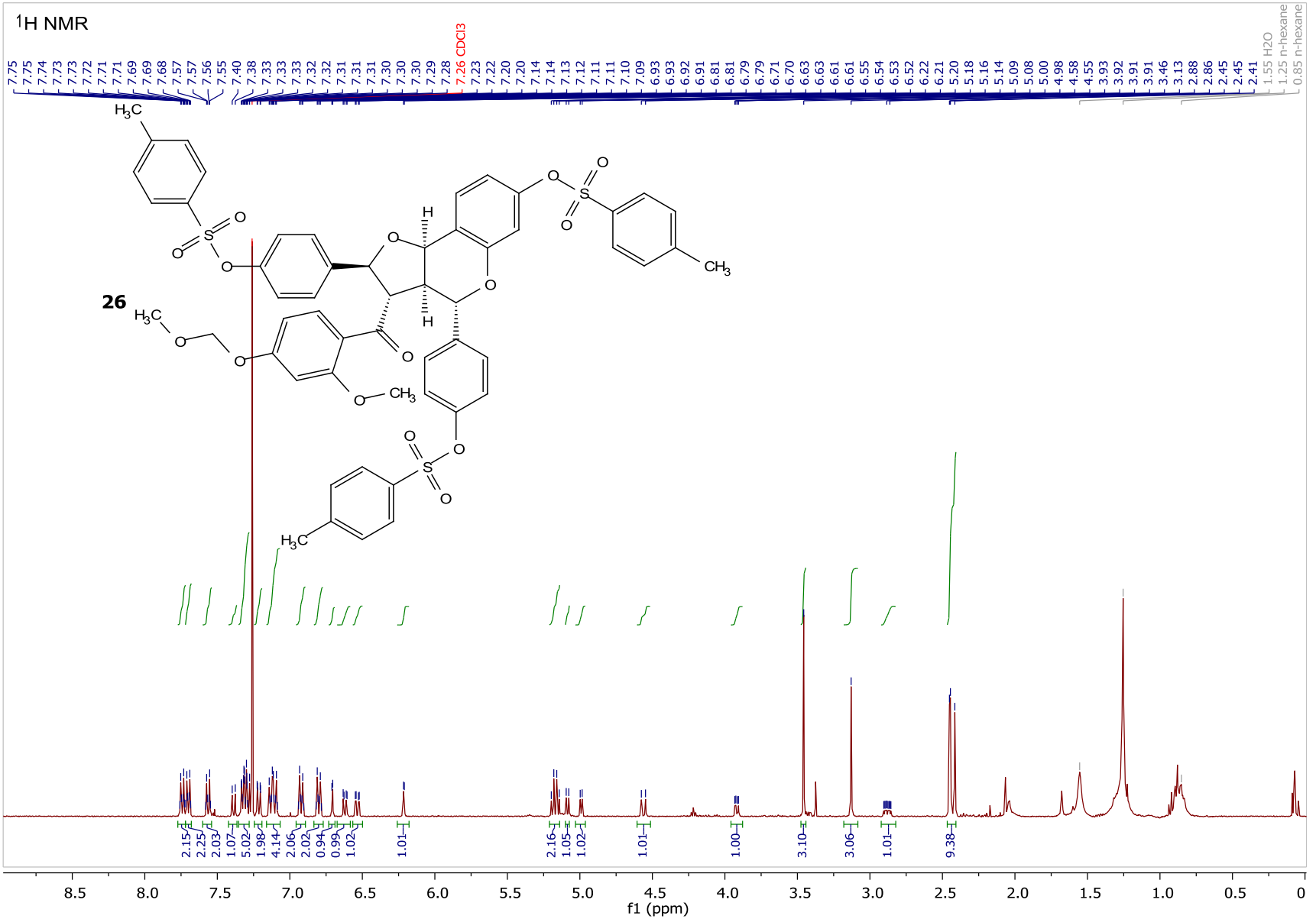
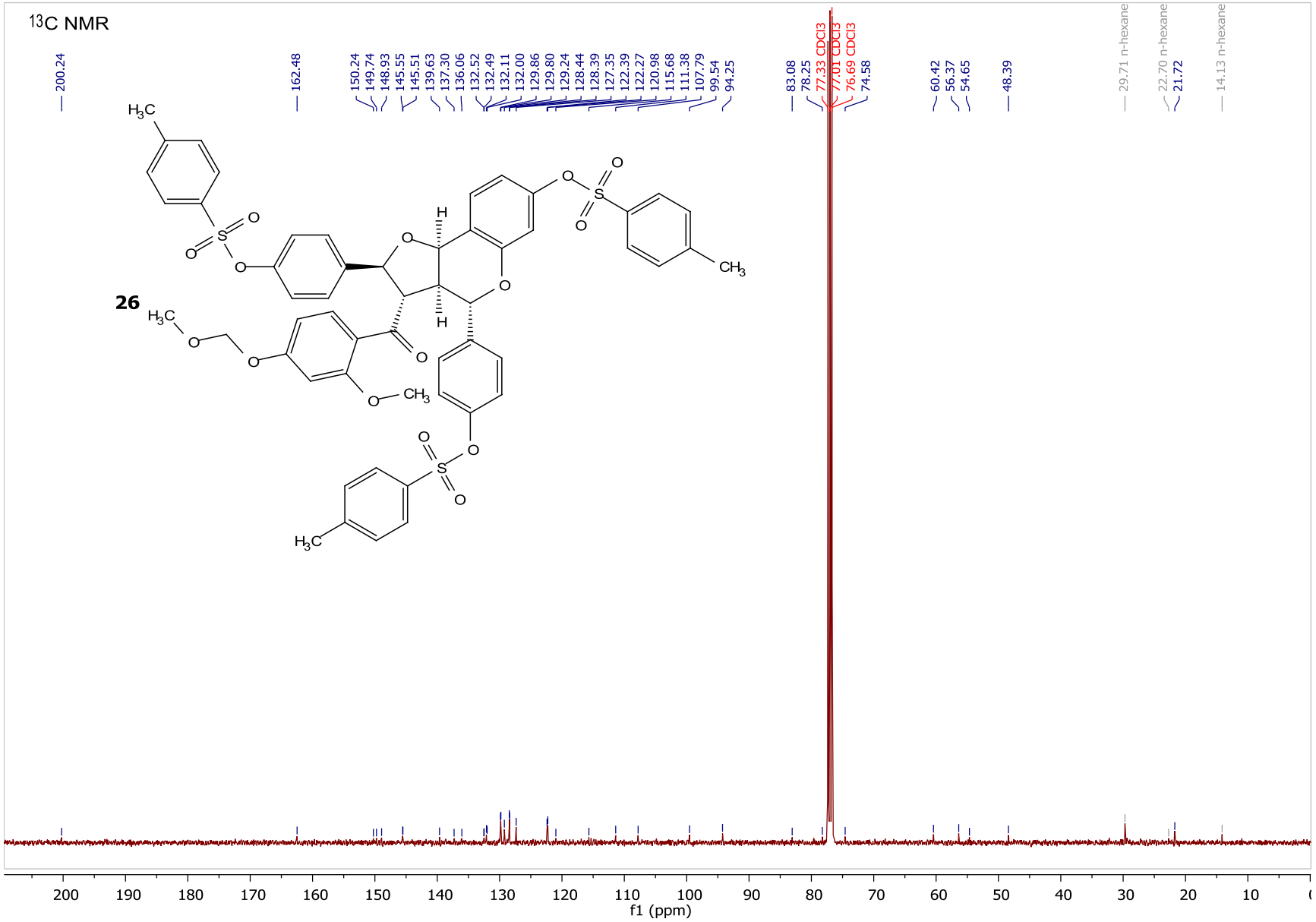
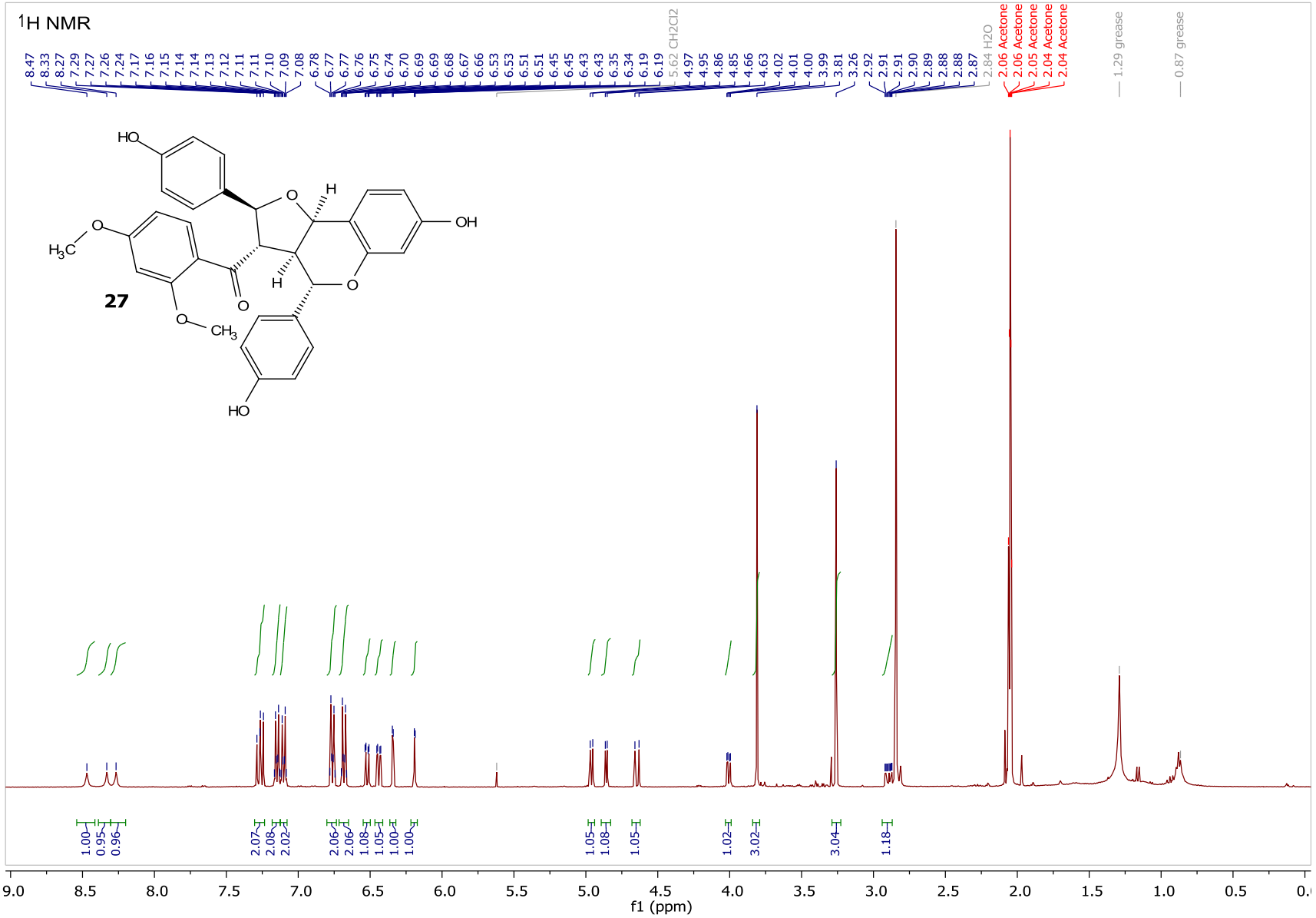
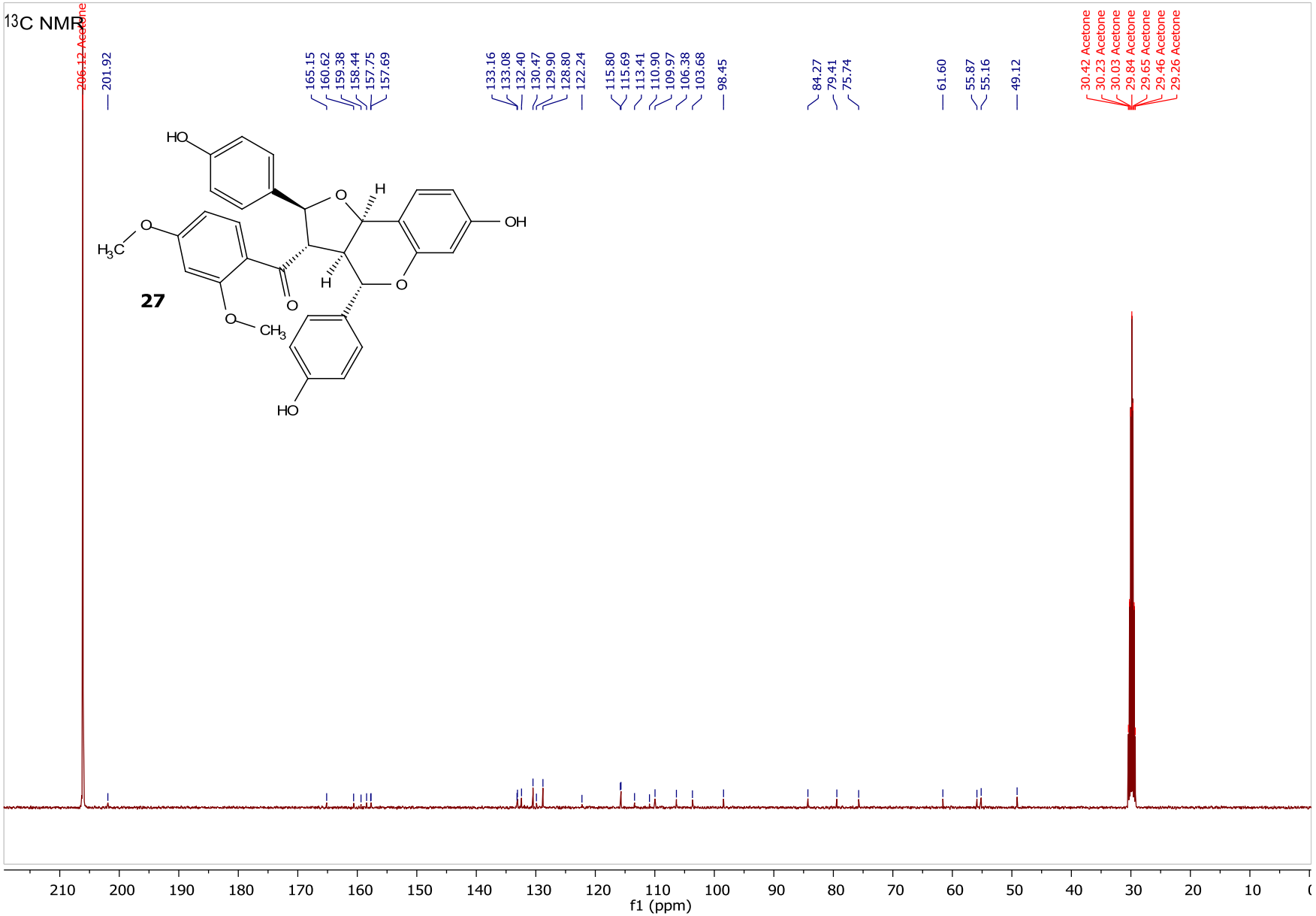
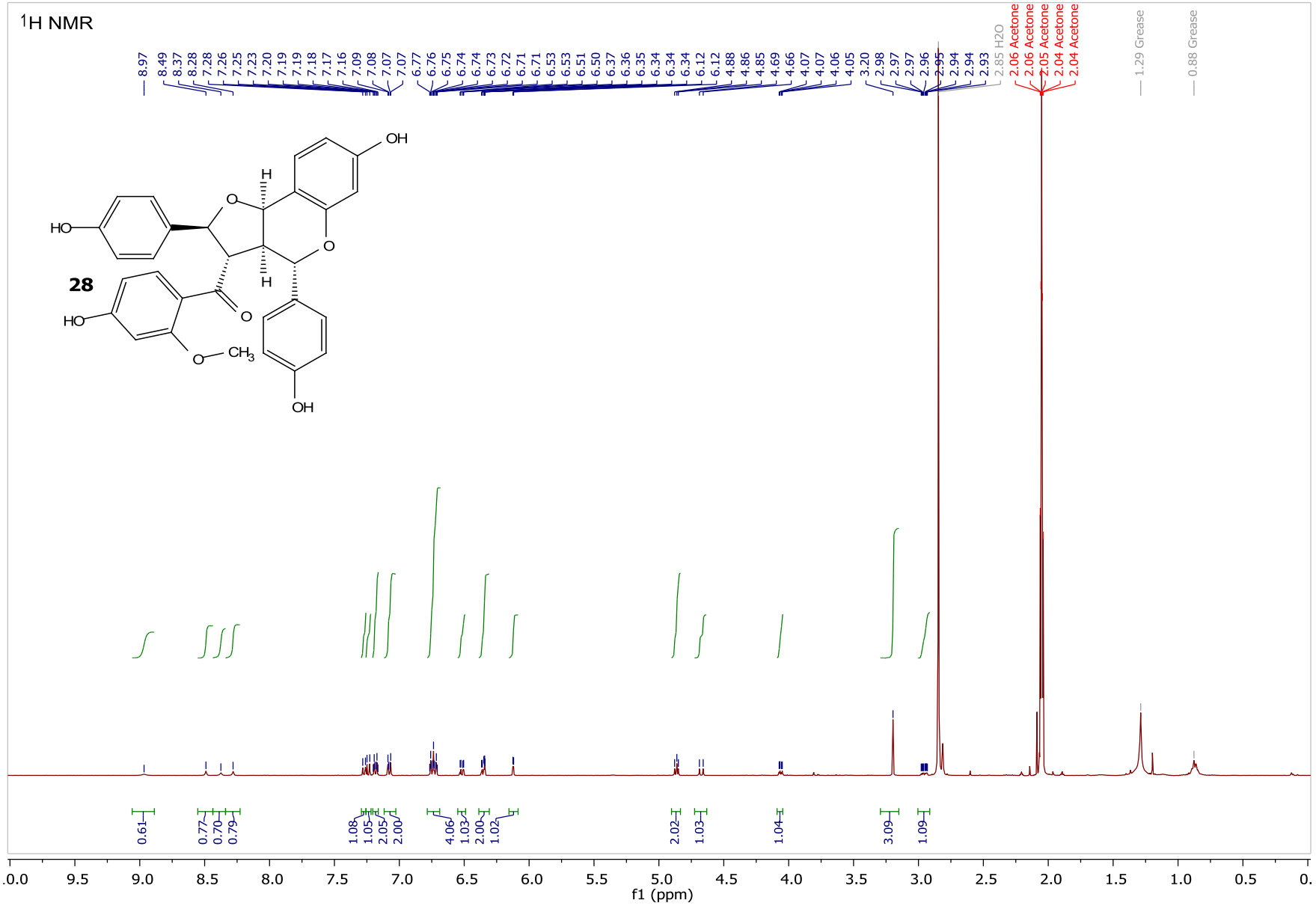
55.57
54.62
48.32
21.73
24
f1 (ppm)

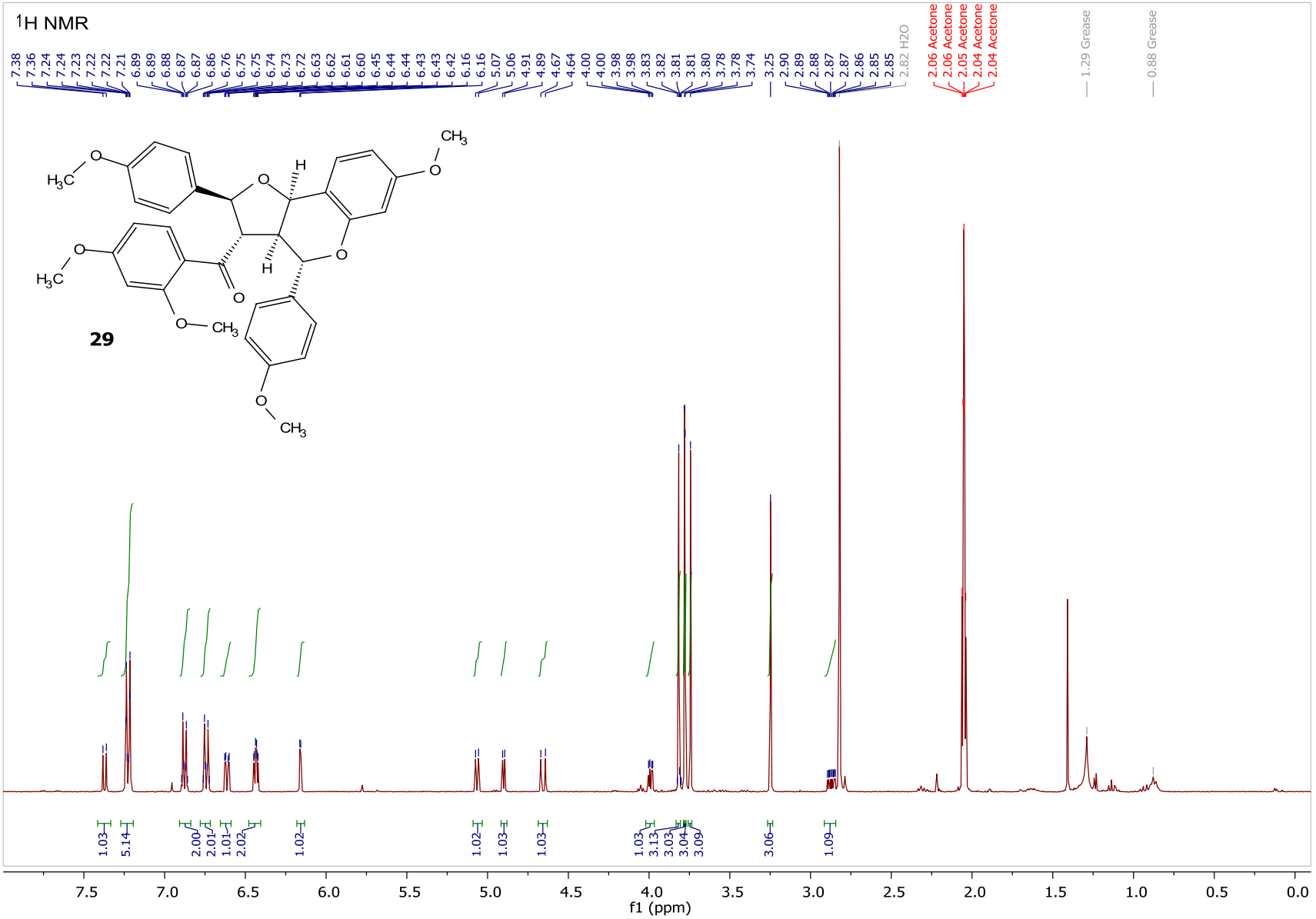

1H NMR
7.75 7.75 7.74 7.73 7.73 7.72 7.71 7.71 7.69 7.69 7.68 7.57 7.57 7.56 7.55 7.40 7.38 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.28 7.26 CDCl3 7.23 7.22 7.20 7.20 7.14 7.14 7.13 7.12 7.11 7.11 7.10 7.09 6.93 6.93 6.92 6.91 6.81 6.81 6.79 6.79 6.71 6.70 6.63 6.63 6.61 6.61 6.55 6.54 6.53 6.52 6.22 6.21 5.20 5.18 5.16 5.14 5.09 5.08 5.00 4.98 4.58 4.55 3.93 3.92 3.91 3.91 3.46 3.13 2.88 2.86 2.45 2.45 2.41 1.55 H2O 1.25 n-hexane 0.85 n-hexane
26
2.15 2.25 2.03 1.07 5.02 1.98 4.14 2.06 2.02 0.94 0.99 1.02 1.01 2.16 1.05 1.02 1.01 1.00 3.10 3.06 1.01 9.38
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
f1 (ppm)

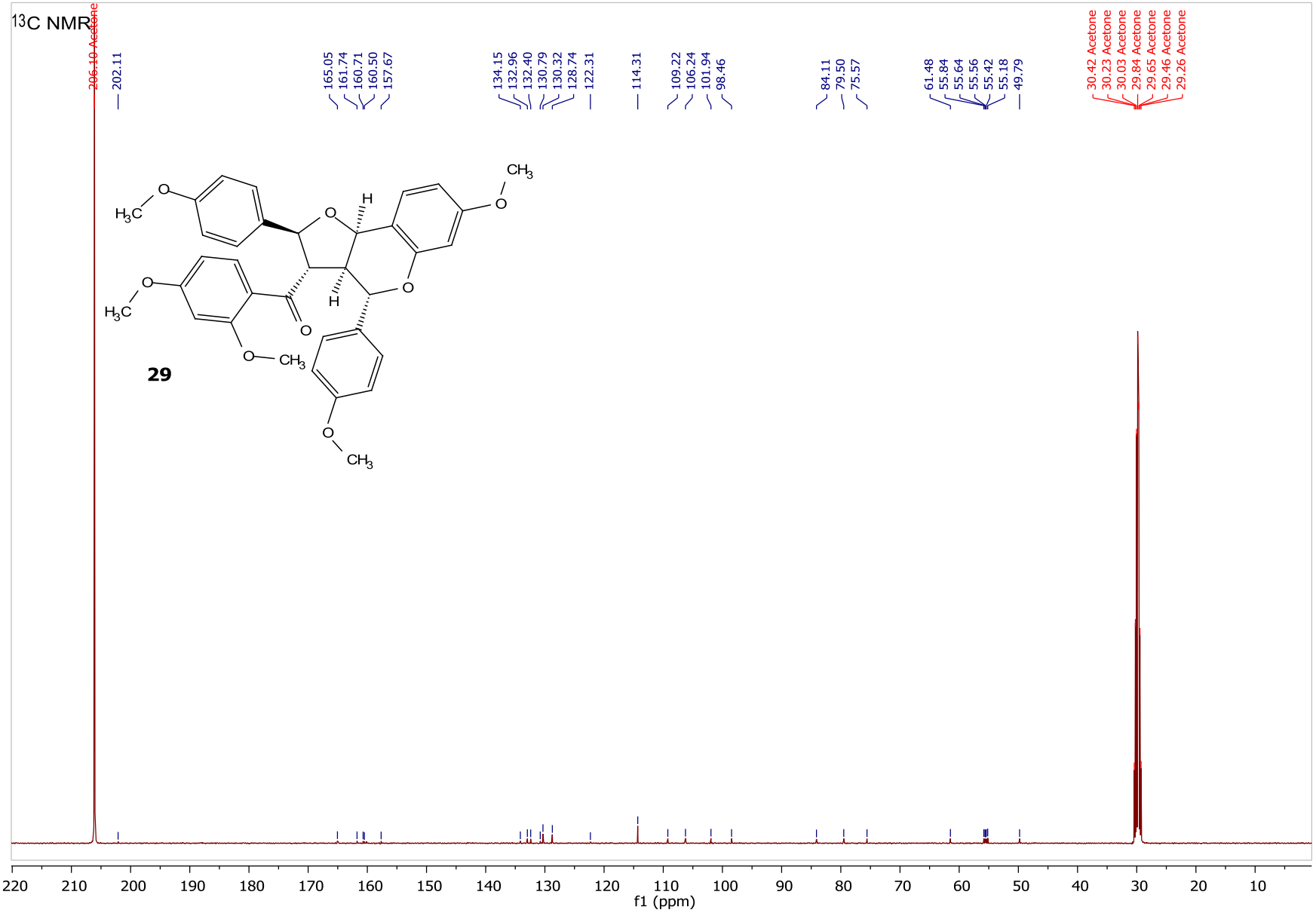

13C NMR
200.24
162.48
150.24
149.74
148.93
145.55
145.51
139.63
137.30
136.06
132.52
132.49
132.11
132.00
129.86
129.80
129.24
128.44
128.39
127.35
122.39
122.27
120.98
115.68
111.38
107.79
99.54
94.25
83.08
78.25
77.33 CDCl3
77.01 CDCl3
76.69 CDCl3
74.58
60.42
56.37
54.65
48.39
29.71 n-hexane
22.70 n-hexane
21.72
14.13 n-hexane
26
f1 (ppm)

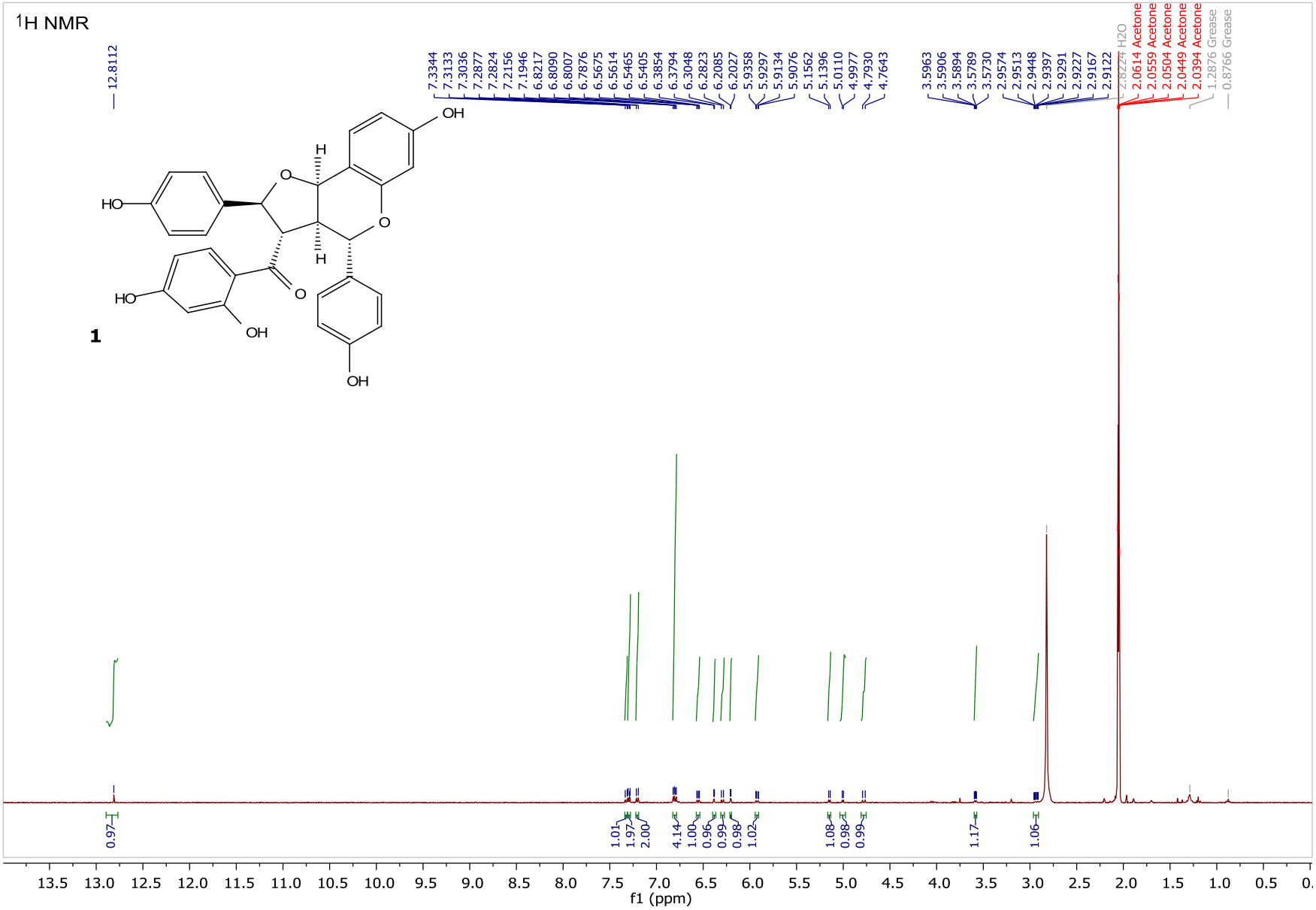

1H NMR
8.47 8.33 8.27 7.29 7.27 7.26 7.24 7.17 7.16 7.15 7.14 7.14 7.13 7.12 7.11 7.11 7.10 7.09 7.08 6.78 6.77 6.77 6.76 6.75 6.74 6.70 6.69 6.69 6.68 6.67 6.66 6.53 6.53 6.51 6.51 6.45 6.45 6.43 6.43 6.35 6.34 6.19 6.19 5.62 CH2Cl2 4.97 4.95 4.86 4.85 4.66 4.63 4.02 4.01 4.00 3.99 3.81 3.26 2.92 2.91 2.91 2.90 2.89 2.88 2.88 2.87 2.84 H2O 2.06 Acetone 2.06 Acetone 2.05 Acetone 2.04 Acetone 2.04 Acetone 1.29 grease 0.87 grease
HO
O
H
OH
O
H3C
O
H
O
27
O
O
CH3
HO
1.00 0.95 0.96 2.07 2.08 2.02 2.06 2.06 1.08 1.05 1.00 1.00 1.05 1.08 1.05 1.02 3.02 3.04 1.18
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
f1 (ppm)


13C NMR
206.12 Acetone
201.92
165.15
160.62
159.38
158.44
157.75
157.69
133.16
133.08
132.40
130.47
129.90
128.80
122.24
115.80
115.69
113.41
110.90
109.97
106.38
103.68
98.45
84.27
79.41
75.74
61.60
55.87
55.16
49.12
30.42 Acetone
30.23 Acetone
30.03 Acetone
29.84 Acetone
29.65 Acetone
29.46 Acetone
29.26 Acetone
HO
O
H
OH
H3C
O
H
O
O
O
CH3
HO
27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


1H NMR
28
f1 (ppm)


1H NMR
7.38 7.36 7.24 7.24 7.23 7.22 7.22 7.21 6.89 6.89 6.88 6.87 6.87 6.86 6.76 6.75 6.75 6.74 6.73 6.72 6.63 6.62 6.61 6.60 6.45 6.44 6.44 6.43 6.43 6.42 6.16 6.16 5.07 5.06 4.91 4.89 4.67 4.64 4.00 4.00 3.98 3.98 3.83 3.82 3.81 3.81 3.80 3.78 3.78 3.74 3.25 2.90 2.89 2.88 2.87 2.87 2.86 2.85 2.85 2.82 H2O
2.06 Acetone 2.06 Acetone 2.05 Acetone 2.04 Acetone 2.04 Acetone
1.29 Grease
0.88 Grease
29
1.03 5.14 2.00 2.01 1.01 2.02 1.02 1.02 1.03 1.03 1.03 3.13 3.03 3.04 3.09 3.06 1.09
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
f1 (ppm)


13C NMR
206.10 Acetone
202.11
165.05
161.74
160.71
160.50
157.67
134.15
132.96
132.40
130.79
130.32
128.74
122.31
114.31
109.22
106.24
101.94
98.46
84.11
79.50
75.57
61.48
55.84
55.64
55.56
55.42
55.18
49.79
30.42 Acetone
30.23 Acetone
30.03 Acetone
29.84 Acetone
29.65 Acetone
29.46 Acetone
29.26 Acetone
29
f1 (ppm)


1H NMR
12.8112
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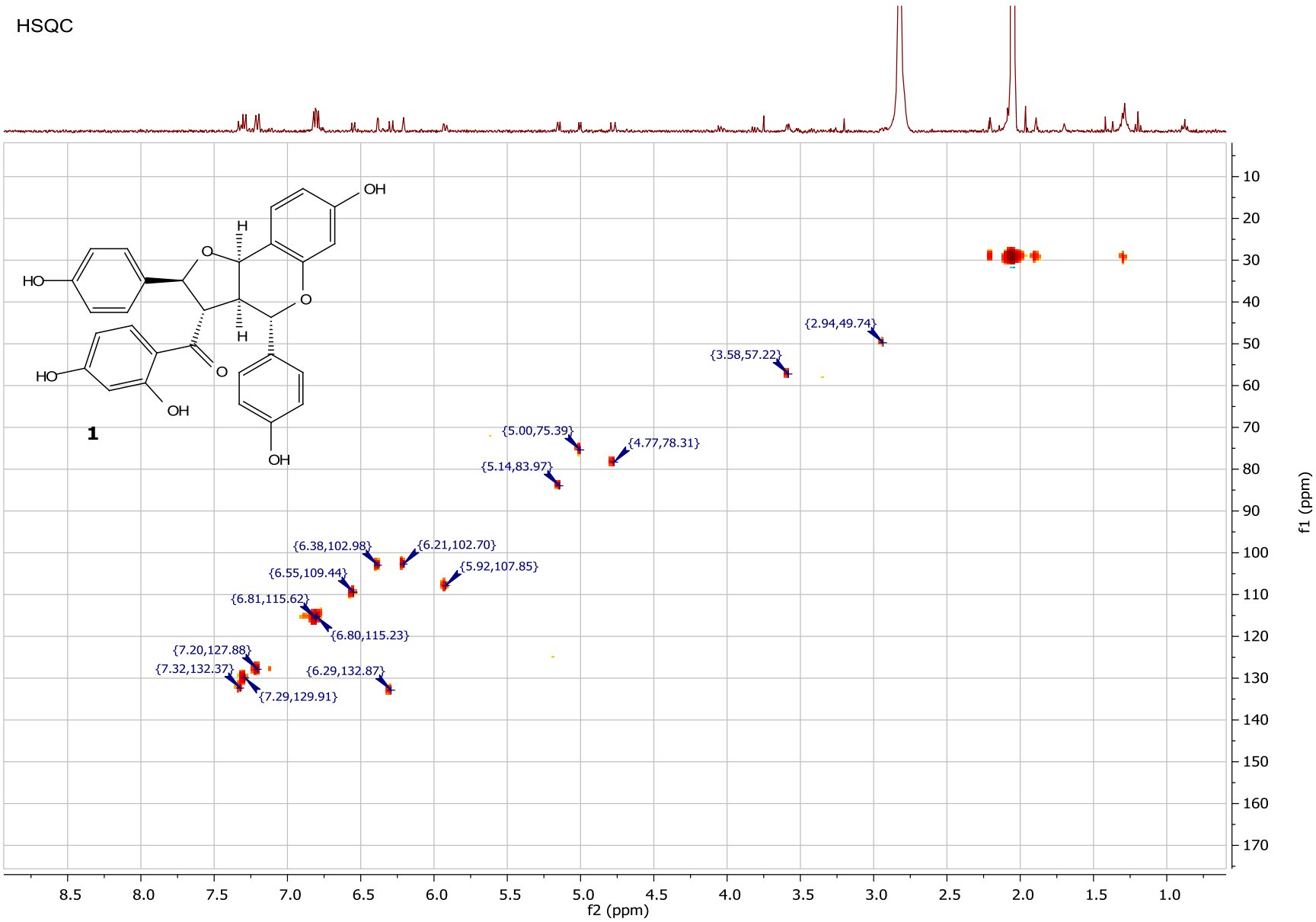
7.3133
7.3036
7.2877
7.2824
7.2156
7.1946
6.8217
6.8090
6.8007
6.7876
6.5675
6.5614
6.5465
6.5405
6.3854
6.3794
6.3048
6.2823
6.2085
6.2027
5.9358
5.9297
5.9134
5.9076
5.1562
5.1396
5.0110
4.9977
4.7930
4.7643
3.5963
3.5906
3.5894
3.5789
3.5730
2.9574
2.9513
2.9448
2.9397
2.9291
2.9227
2.9167
2.9122
2.8224 H2O
2.0614 Acetone
2.0559 Acetone
2.0504 Acetone
2.0449 Acetone
2.0394 Acetone
1.2876 Grease
0.8766 Grease
HO
O
H
OH
O
H
HO
O
OH
OH
1
0.97
1.01
1.97
2.00
4.14
1.00
0.96
0.99
0.98
1.02
1.08
0.98
0.99
1.17
1.06
13.5 13.0 12.5 12.0 11.5 11.0 10.5 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.
f1 (ppm)


HSQC
OH
H
O
HO
O
H
HO
O
OH
1
OH
{2.94,49.74}
{3.58,57.22}
{5.00,75.39}
{4.77,78.31}
{5.14,83.97}
{6.38,102.98}
{6.21,102.70}
{6.55,109.44}
{5.92,107.85}
{6.81,115.62}
{6.80,115.23}
{7.20,127.88}
{7.32,132.37}
{6.29,132.87}
{7.29,129.91}
f2 (ppm)
f1 (ppm)