Syntheses of dinor-*cis*/*iso*-12-oxo-phytodienoic acid (dn-*cis*/*iso*-OPDAs), ancestral jasmonate phytohormones of the bryophyte *Marchantia polymorpha* L., and their catabolites

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Supporting Information

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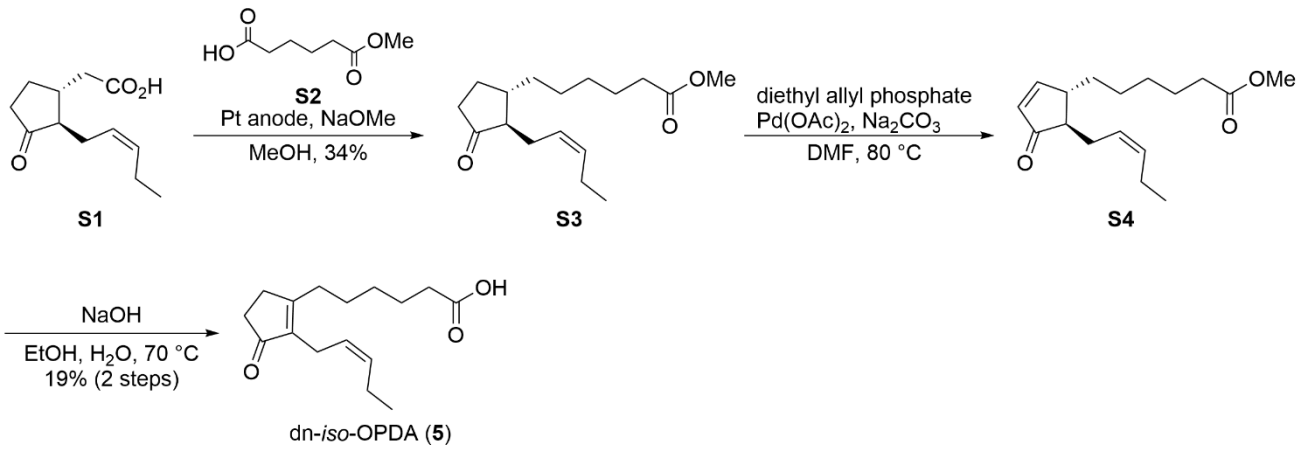
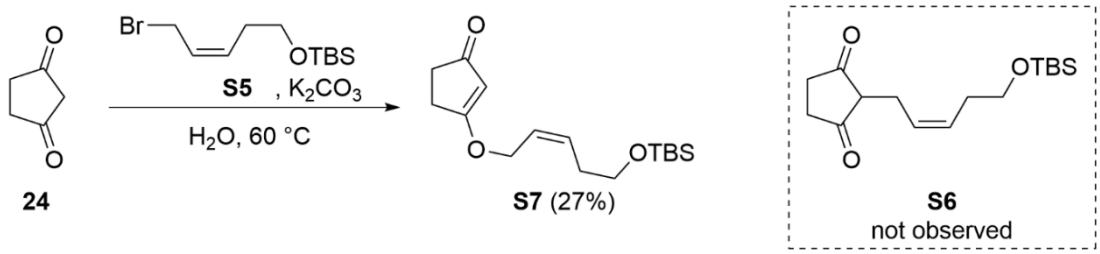


Scheme S1. Synthesis of dn-*iso*-OPDA (**5**) by Solano *et al*.



Scheme S2. Unsuccessful side chain introduction by allylation.

Experimental Section

General

All chemical reagents and solvents were obtained from commercial suppliers (Kanto Chemical Co. Ltd., Wako Pure Chemical Industries Co. Ltd., Nacalai Tesque Co. Ltd., Tokyo Chemical Industry Co. Ltd., Sigma-Aldrich Co. LLC., GE Healthcare) and used without further purification. All anhydrous solvents were either dried by standard techniques and freshly distilled before use, or purchased in anhydrous form and used as supplied. Reversed-phase high–performance liquid chromatography (HPLC) was carried out on a PU–4180 plus pump equipped with UV–4075 and MD–4010 detectors (JASCO, Tokyo, Japan). ^{1}H and ^{13}C NMR spectra were recorded on a JNM–ECS–400 spectrometer (JEOL, Tokyo, Japan) in deuterated chloroform using TMS as an internal standard. Fourier transform infrared (FT/IR) spectra were recorded on an FT/IR–4100 (JASCO, Tokyo, Japan). High–resolution (HR) electrospray ionization (ESI)–mass spectrometry (MS) analyses were conducted using a microTOF II (Bruker Daltonics Inc., Billerica, MA). Optical rotations were measured using a JASCO P–2200 polarimeter (JASCO, Tokyo, Japan). Flash chromatography was performed on an Isolera system (Biotage Ltd., North Carolina, US). TLC analyses were performed on Silica gel F254 (0.25 mm or 0.5 mm, MERCK, Germany) or RP–18F254S (0.25 mm, MERCK). All reactions were carried out under air unless stated otherwise.

Synthesis of dimethylamide (17). To a suspension of CuCN (65.5 mg, 731 μmol) in THF (14 mL) was added TBDPSO$(CH_2)_6$MgBr (27 mL, 0.52 M in THF, 14.1 mmol) at -30 °C under an argon atmosphere. The reaction mixture was stirred at -30 °C for 20 min, and a solution of **15** (670 mg, 4.72 mmol) in THF (7 mL) was added. After being stirred at -18 °C for 11 h, the reaction mixture was quenched with saturated aqueous NH_4Cl, and then extracted with EtOAc/*n*-hexane (2/8). The resulting organic layer was washed with saturated aqueous NaCl, dried over Na_2SO_4, and filtered. After evaporation, the residue was purified by medium-pressure chromatography (Isolera, eluent: 95:5 *n*-hexane/EtOAc to 60:40 *n*-hexane/EtOAc) to give a colorless oil (2.67 g, **16** and by-products). To a solution of the mixture (2.67 g), PPh_3 (2.48 g, 9.44 mmol) and AcOH (550 μL, 96.1 mmol) in THF (16 mL) was added DIAD (1.9 M in toluene, 5.3 mL, 10.1 mmol) at -78 °C under an argon atmosphere. The mixture was stirred at 0 °C for 1 h and the reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted with *n*-hexane. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was roughly purified by medium-pressure chromatography (Isolera, eluent: *n*-hexane to 94:6 *n*-hexane/EtOAc) to give a colorless oil (1.66 g, a desired acetate and by-products). To a solution of the mixture (1.66 g) in THF/MeOH (7/3, 50 mL) was added 1M-LiOH solution (14 mL 14.0 mmol) and the mixture was stirred for 3 h. MeOH and THF were removed under reduced pressure and the mixture was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product (1.48 g) was used for the next reaction without further purification. The mixture (1.48 g) and $MeC(OMe)_2NMe_2$ (3.8 mL) were dissolved in xylene (55 mL). The mixture was stirred at reflux temperature, and MeOH was removed in a Dean Stark apparatus with MS4A. After 5 h, the solvent was removed under reduced pressure. The crude product was purified by medium-pressure chromatography (Isolera, eluent: 95:5 *n*-hexane/EtOAc to 60:40 *n*-hexane/EtOAc) to afford **17** (1.64 g, 50% in 2 steps) as a red oil: $[\alpha]_D^{21}$ -55.8 (*c* 1.40, $CHCl_3$). ^{1}H

NMR (400 MHz, $CDCl_3$) δ_H: 7.69–7.64 (m, 4H), 7.34–7.44 (m, 6H), 5.82 (brs, 1H), 5.73 (brs, 1H), 5.66–5.57 (m, 1H), 3.66 (t, *J* =6.5 Hz, 2H), 3.12–3.04 (m, 1H), 2.98 (s, 3H), 2.95 (s, 3H), 2.45–2.20 (m, 4H), 2.12 (dd, *J* =14.7, 10.1 Hz, 1H), 1.96 (ddq, *J* =15.7, 8.5, 2.2 Hz, 1H), 1.59–1.50 (m, 2H), 1.44–1.20 (m, 8H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 172.68, 135.61, 135.53, 134.12, 130.25, 129.44, 127.53, 63.95, 43.51, 41.32, 37.44, 37.22, 35.42, 33.14, 32.57, 30.51, 29.69, 28.72, 26.87, 25.78, 19.22; IR (neat) cm^{-1}: 3047, 2927, 1651, 1103; HRMS (ESI, positive) *m/z* $[M+Na]^+$ Calcd. for $C_{31}H_{45}NNaO_2Si$: 514.3117, Found: 514.3092.

Synthesis of diol 18. To a solution of **17** (1.58 g 3.22 mmol), KH_2PO_4 (580 mg, 4.26 mmol) and $Na_2HPO_4 \cdot H_2O$ (136 mg, 853 µmol) in THF/H_2O (1/1, 46 mL) was added I_2 (1.63 g, 6.44 mmol) and the mixture was stirred for 14 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$ and the mixture was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by medium-pressure chromatography (Isolera, eluent: 95:5 *n*-hexane/EtOAc to 60:40 *n*-hexane/EtOAc) to give an iodolactone intermediate (1.58 g, 83%) as an orange oil. $[\alpha]_D^{20}$ +2.1 (*c* 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.68-7.63 (m, 4H), 7.44-7.34 (m, 6H), 5.26 (d, *J* = 6.4 Hz, 1H), 4.45 (d, *J* = 5.1 Hz, 1H), 3.65 (t, *J* = 6.6 Hz, 2H), 3.15-3.05 (m, 1H), 2.72-2.60 (m, 1H), 2.59 (dd, *J* = 18.8, 10.5 Hz, 1H), 2.49 (dd, *J* = 18.8, 3.9 Hz, 1H), 2.09 (dd, *J* = 14.7, 5.8 Hz, 1H), 1.64 (ddd, *J* = 14.7, 12.4, 5.1 Hz, 1H), 1.55 (quintet, *J* = 6.6 Hz, 1H), 1.42-1.18 (m, 8H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C:176.47, 135.53, 134.06, 129.48, 127.55, 92.72, 63.82, 40.38, 40.15, 38.83, 32.42, 29.96, 29.39, 28.70, 28.37, 28.19, 26.88, 25.63, 19.23; IR (neat) cm^{-1}: 3066, 2927, 1786, 1466, 1165, 1107; HRMS (ESI, positive) *m/z* $[M+Na]^+$ Calcd. for $C_{29}H_{39}INaO_3Si$: 613.1611, Found: 613.1587.
To a solution of the iodolactone intermediate (1.54 g 2.61 mmol) in THF (8 mL) was added DBU (480 µL, 3.21 mmol) and the mixture was stirred at reflux temperature for 8 h. The reaction mixture was cooled to -30 °C and $LiAlH_4$ (292 mg, 7.7 mmol) was added. After being stirred at 0 °C for 40 min, the reaction mixture was quenched with EtOAc and then a homogeneous mixture of $SiO_2/K_2CO_3/H_2O$ (10/1/3, 12.4 g) was added. The mixture was stirred for 40 min and the solids were removed by filtration and washed thoroughly with EtOAc. The filtrate was evaporated and the residue was purified by medium-pressure chromatography (Isolera, eluent: 88:12 *n*-hexane/EtOAc to EtOAc) to give **18** (1.11 g, 91%) as a pale yellow oil. $[\alpha]_D^{19}$ +34.5 (*c* 1.03, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.68-7.63 (m, 4H), 7.44-7.33 (m, 6H), 6.19 (dd, *J* = 5.8, 2.7 Hz, 1H), 5.96 (brd, *J* = 5.8 Hz, 1H), 4.60 (brd, *J* = 5.4 Hz, 1H), 3.89 (dt, *J* = 9.5, 5.0 Hz, 1H), 3.76 (td, *J* = 9.5, 4.1 Hz, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.50-2.42 (m, 1H), 2.10 (dq, *J* = 11.1, 7.4 Hz, 1H), 2.03-1.84 (m, 3H), 1.69 (dq, *J* = 14.1, 4.7 Hz, 1H), 1.55 (quintet, *J* = 7.4 Hz, 2H), 1.42-1.15 (m, 6H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 141.11, 135.53, 134.12, 131.77, 129.45, 127.53, 76.38, 63.94, 62.84, 46.79, 44.58, 33.53, 32.55, 29.63, 28.04, 28.01, 26.87, 25.74, 19.23; IR (neat) cm^{-1}: 3336, 2931, 2858, 1107, 702; HRMS (ESI, positive) *m/z* $[M+Na]^+$ Calcd. for $C_{29}H_{42}NaO_3Si$: 489.2801, Found: 489.2789.

Synthesis of bis-TES ether 19. To a solution of **18** (773 mg, 1.66 mmol) and imidazole (451 mg, 247 mmol) in DMF (10 mL) was added TESCl (832 µL, 4.97 mmol). The mixture was stirred for 13 h and the

reaction was quenched with saturated aqueous $NaHCO_3$. The mixture was extracted with *n*-hexane. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by medium-pressure chromatography (Isolera, eluent: *n*-hexane to 98:2 *n*-hexane/EtOAc) to give **19** (1.06 g, 92%) as a colorless oil. $[\alpha]_D^{20}$ -1.3 (*c* 1.18, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ_H: 7.66 (dd, *J* = 7.7, 1.5 Hz, 4H), 7.44-7.33 (m, 6H), 6.10 (dd, *J* = 5.8, 2.7 Hz, 1H), 5.82 (brd, *J* = 5.8 Hz, 1H), 4.47 (dd, *J* = 5.9, 2.3 Hz, 1H), 3.74-3.60 (m, 4H), 2.35 (brs, 1H), 2.07 (quintet, *J* = 7.0 Hz, 1H), 1.79 (dq, *J* = 13.8, 7.0 Hz, 1H), 1.64 (dq, *J* = 13.8, 7.0 Hz, 1H), 1.59-1.41 (m, 3H), 1.40-1.12 (m, 7H), 1.04 (s, 9H), 096 (t, *J* = 7.8 Hz, 9H), 0.93 (t, *J* = 7.8 Hz, 9H), 060 (q, *J* = 7.8 Hz, 6H), 0.56 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 140.21, 135.54, 134.17, 132.58, 129.43, 127.52, 76.18, 64.00, 62.04, 46.09, 42.79, 32.61, 32.52, 29.79, 28.79, 28.01, 26.87, 25.81, 19.22, 6.95, 6.84, 5.24, 4.45; IR (neat) cm^{-1}: 2951, 2877, 1103, 737; HRMS (ESI, positive) *m/z* $[M+Na]^+$ Calcd. for $C_{41}H_{70}NaO_3Si_3$: 717.4530, Found: 717.4511.

Synthesis of diene 20. To a solution of DMSO (210 µL, 2.96 mmol) in CH_2Cl_2 (2.2 mL) was added oxalyl chloride (120 µL, 1.40 mmol) at -78 °C under an argon atmosphere. After the reaction mixture was stirred at -78 °C for 15 min, a solution of **19** (187 mg, 269 µmol) in CH_2Cl_2 (2.5 mL) was slowly added. After the reaction mixture was stirred at -65 °C for 1 h, Et_3N (420 µL, 3.01 mmol) was slowly added. The mixture was gradually warmed to room temperature for 30 min with stirring. The reaction mixture was quenched with saturated aqueous NH_4Cl. The mixture was extracted with *n*-hexane. The organic layer was washed with saturated aqueous NaCl, dried over Na_2SO_4, and filtered. The reaction mixture was concentrated under reduced pressure to afford **11** (192 mg, mixture). The crude product was used for the next reaction without further purification. To a suspension of $[Ph_3P(CH_2)_2Me]^+Br^-$ (356 mg, 924 µmol) in THF (3.6 mL) was added NaHMDS (1.0 M in THF, 450 µL, 450 µmol). The mixture was stirred for 40 min and cooled to -78 °C. To this solution were added DMF (540 µL) and a solution of **11** (192 mg, mixture) in THF (3.3 mL). The reaction mixture was gradually warmed to room temperature for 2 h. Then, the reaction was quenched with saturated aqueous NH_4Cl and extracted with *n*-hexane. The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by medium-pressure chromatography (Isolera, eluent: *n*-hexane to 4:96 *n*-hexane/EtOAc) to give **20** (116 mg, 71% in 2 steps) as a colorless oil. $[\alpha]_D^{23}$ +1.6 (*c* 1.13, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ_H: 7.69-7.63 (m, 4H), 7.44-7.31 (m, 6H), 6.10 (dd, *J* = 5.9, 2.7 Hz, 1H), 5.83 (brd, *J* = 5.9 Hz, 1H), 5.48-5.30 (m, 2H), 4.49 (dd, *J* = 5.8, 2.3 Hz, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 2.38 (brs, 1H), 2.19 (t, *J* = 7.1 Hz, 1H), 2.08 (quintet, *J* = 7.1 Hz, 1H), 1.96 (quintet, *J* = 7.1 Hz, 1H), 1.60-1.45 (m, 5H), 1.40-1.14 (m, 7H), 1.04 (s, 9H), 0.97 (t, *J* = 7.5 Hz, 3H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.57 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 140.13, 135.54, 134.15, 132.67, 131.61, 129.43, 128.71, 127.53, 76.27, 63.99, 47.22, 46.03, 32.61, 32.36, 29.79, 28.04, 26.87, 25.82, 23.24, 20.79, 19.22, 14.29, 6.96, 5.22; IR (neat) cm^{-1}: 2931, 2877, 1107, 1011, 737, 706; HRMS (ESI, positive) *m/z* $[M+Na]^+$ Calcd. for $C_{38}H_{60}NaO_2Si_2$: 627.4030, Found: 627.4004.

Synthesis of diene 21. To a solution of DMSO (514 µL, 7.25 mmol) in CH_2Cl_2 (8.0 mL) was added oxalyl chloride (310 µL, 3.62 mmol) at -78 °C under an argon atmosphere. After the reaction mixture was stirred at -78 °C for 15 min, a solution of **19** (504 mg, 725 µmol) in CH_2Cl_2 (8.0 mL) was slowly added. After the

reaction mixture was stirred at -65 °C for 40 min, Et_3N (1.11 mL, 7.97 mmol) was slowly added. The mixture was gradually warmed to room temperature for 1 h with stirring. The reaction mixture was quenched with saturated aqueous NH_4Cl. The mixture was extracted with *n*-hexane. The organic layer was washed with saturated aqueous NaCl, dried over Na_2SO_4, and filtered. The reaction mixture was concentrated under reduced pressure to afford **11** (446 mg, mixture). The crude product was used for the next reaction without further purification. To a suspension of $[Ph_3P(CH_2)_3OTHP]^+Br^-$ (1.06 g, 2.18 mmol) in THF (12 mL) was added NaHMDS (1.0 M in THF, 1.14 mL, 1.14 mmol). The mixture was stirred for 40 min and cooled to -78 °C. To this solution were added DMF (1.32 mL) and a solution of **11** (446 mg, mixture) in THF (12 mL). The reaction mixture was gradually warmed to room temperature for 2 h. Then, the reaction was quenched with saturated aqueous NH_4Cl and extracted with *n*-hexane. The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by medium-pressure chromatography (Isolera, eluent: 99:1 *n*-hexane/EtOAc to 92:8 *n*-hexane/EtOAc) to give **21** (391 mg, 76% in 2 steps) as a paleyellow oil. $[\alpha]_D^{20}$ +34.8 (*c* 1.95, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ_H: 7.71-7.61 (m, 4H), 7.44-7.33 (m, 6H), 6.10 (dd, *J* = 5.8, 2.9 Hz, 1H), 5.83 (dq, *J* = 5.8, 1.4 Hz, 1H), 5.58 (brdt, *J* = 10.8, 7.1 Hz, 1H), 5.40 (brdt, *J* = 10.8, 7.1 Hz, 1H), 4.60 (dd, *J* = 4.2, 2.9 Hz, 1H), 4.49 (dd, *J* = 5.8, 2.4 Hz, 1H), 3.87 (ddd, *J* = 10.8, 7.3, 2.9 Hz, 1H), 3.75 (dt, *J* = 9.4, 7.3 Hz, 1H), 3.64 (t, *J* = 6.6 Hz, 2H), 3.54-3.45 (m, 1H), 3.42 (dt, *J* = 9.4, 7.1 Hz, 1H), 2.45-2.34 (m, 3H), 2.29-2.15 (m, 2H), 1.98 (quintet, *J* = 7.1 Hz, 1H), 1.89-1.76 (m, 1H), 1.75-1.66 (m, 1H), 1.66-1.43 (m, 6H), 1.42-1.14 (m, 8H), 1.04 (s, 9H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.57 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 140.10, 135.53, 134.14, 132.65, 131.34, 129.42, 127.52, 125.62, 98.70, 76.16, 67.07, 63.99, 62.24, 47.11, 46.02, 32.60, 32.43, 30.72, 29.79, 28.18, 28.04, 26.86, 25.83, 25.50, 23.44, 19.59, 19.21, 6.96, 5.20; IR (neat) cm^{-1}: 2935, 2873, 1107; HRMS (ESI, positive) *m/z* $[M+Na]^+$ Calcd. for $C_{43}H_{68}NaO_4Si_2$: 727.4544, Found: 727.4560.

Synthesis of diol 22. To a solution of **21** (201 mg, 285 μmol) in THF (10 mL) was added 1 M TBAF in THF (1.42 mL, 1.42 mmol). After being stirred at room temperature for 14 h, the solvent was removed under reduced pressure. The reaction mixture was quenched with saturated aqueous NH_4Cl. The mixture was extracted with EtOAc. The organic layer was washed with saturated aqueous NaCl, dried over Na_2SO_4, and filtered.The residue was purified by medium-pressure chromatography (Isolera, eluent: 88:12 n-hexane/EtOAc to EtOAc) to give **22** (97.9 mg, 72%) as a colorless oil. . $[\alpha]_D^{20}$ +127.1 (*c* 0.52, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ_H: 7.71 (dd, *J* = 5.8, 2.7 Hz, 1H), 6.18 (dd, *J* = 5.8, 1.7 Hz, 1H), 5.59 (dtt, *J* = 9.7, 7.2, 1.4 Hz, 1H), 5.45 (dtt, *J* = 9.7, 7.3, 1.7 Hz, 1H), 3.68 (t, *J* = 6.5 Hz, 2H), 3.04-2.95 (m, 1H), 2.56-2.44 (m, 2H), 2.43-2.27 (m, 4H), 2.27-2.14 (m, 1H), 1.79-1.56 (m, 3H), 1.51-1.29 (m, 4H), 1.28-1.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 211.01, 178.48, 167.04, 132.54, 130.66, 126.75, 62.01, 49.44, 44.30, 33.77, 30.94, 30.49, 29.10, 27.22, 24.39, 24.18; IR (film) cm^{-1}: 3433, 2935, 1705; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 141.15, 141.13, 132.06, 132.00, 130.91, 130.75, 127.16, 127.09, 99.17, 98.76, 75.49, 75.45, 67.26, 66.88, 62.93, 62.21, 62.10, 46.46, 46.41, 45.90, 45.88, 33.47, 33.42, 32.73, 30.38, 30.27, 29.68, 28.04, 25.68, 25.32, 25.29, 23.57, 23.49, 19.35 (a diastereomeric mixture derived from the THP group); IR (neat) cm^{-1}: 3409, 2931, 1030; HRMS (ESI, positive) *m/z* $[M+Na]^+$ Calcd. for $C_{21}H_{36}NaO_4$: 375.2511, Found: 375.2503.

Synthesis of triol 23. To a solution of **22** (75.0 mg, 213 μmol) in MeOH (20 mL) was added PPTS (18.0 mg, 717 μmol). After being stirred at 35 °C for 2 h, the solvent was removed under reduced pressure. The residue was purified by medium-pressure chromatography (Isolera, eluent: 99:1 $CHCl_3$/MeOH to 90:10 $CHCl_3$/MeOH) to give **23** (30.3 mg, 54%) as a colorless oil. $[\alpha]_D^{21}$ +72.0 (*c* 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 6.21 (dd, *J* = 5.8, 2.7 Hz, 1H), 5.93 (brd, *J* = 5.8 Hz, 1H), 5.60 (td, *J* = 10.5, 4.3 Hz, 1H), 5.42 (td, *J* = 10.5, 5.2 Hz, 1H), 4.47 (dd, *J* = 5.4, 2.7 Hz, 1H), 3.75 (dt, *J* = 10.1, 4.6 Hz, 1H), 3.65-3.55 (m, 3H), 2.88-2.37 (m, 4H), 2.24-2.13 (m, 1H), 2.12-1.98 (m, 2H), 1.63-1.49 (m, 3H), 1.47-1.19 (m, 6H), 1.19-1.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 141.50, 132.00, 131.82, 126.89, 75.59, 62.89, 61.71, 46.53, 45.91, 33.45, 32.69, 30.59, 29.65, 28.01, 25.63, 23.53; IR (neat) cm^{-1}: 3336, 2927, 2858, 1053; HRMS (ESI, positive) *m/z* $[M+Na]^+$ Calcd. for $C_{16}H_{28}NaO_3$: 291.1936, Found: 291.1926.

Synthesis of dione 27. To a solution of K_2CO_3 (955 mg, 6.91 mmol) in water (8 mL) was slowly added 1,3-cyclopentanedione (678 mg, 6.91 mmol). The solution was heated to 60 °C and stirred as *cis*-1-bromopent-2-ene (1.03 g, 6.91 mmol) was added dropwise. After stirring for 23 h at 60 °C, the reaction mixture was allowed to cool to rt and 1M NaOH aq. was added until a pH of 12 was reached. The mixture was extracted with Et_2O. The aqueous layer was chilled, and 2M HCl aq. was slowly added until pH 1 was reached. The product was extracted with of $CHCl_3$, dried over Na_2SO_4, and filtered. After evaporation, the residue was purified by medium-pressure chromatography (Isolera, eluent: 98:2 $CHCl_3$/MeOH to 80:20 $CHCl_3$/MeOH) to give **27** (286 mg, 25%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 5.51 (dtt, *J* = 10.8, 6.9, 1.7 Hz, 1H), 5.44 (dtt, *J* = 10.8, 7.5, 1.4 Hz, 1H), 2.94 (d, *J* = 6.9 Hz, 2H), 2.54 (s, 4H), 2.17 (quintet, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 197.41, 134.12, 125.19, 116.63, 30.46, 20.65, 19.69, 14.23; IR (neat) cm^{-1}: 2962.12, 2869.56, 1685.48, 1623.77, 1357.64, 1261.22; HRMS (ESI, positive) *m/z* $[M + Na]^+$ Calcd. for $C_{10}H_{14}NaO_2$: 189.0891, found: 189.0887.

Synthesis of cyclopentenone 28. To a solution of **27** (279 mg, 1.68 mmol) in acetone (5 mL) were added K_2CO_3 (255 mg, 1.85 mmol) and Me_2SO_4 (193 μL, 2.02 mmol). After being stirred at reflux temperature for 4 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. Then the water layer was extracted with CH_2Cl_2. The resulting organic layer was washed with saturated aqueous NaCl, dried over Na_2SO_4, and filtered. After evaporation, the residue was purified by medium-pressure chromatography (Isolera, eluent: 99:1 $CHCl_3$/MeOH to 90:10 $CHCl_3$/MeOH) to give **28** (304 mg, quant.) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 5.38 (ddd, J = 10.7, 6.4, 1.6 Hz, 1H), 5.32 (ddd, *J* = 10.7, 6.9, 1.0 Hz, 1H), 3.95 (s, 3H), 2.88 (d, *J* = 6.4 Hz, 2H), 2.67-2.64 (m, 2H), 2.46-2.43 (m, 2H), 2.15 (quintetd, *J* = 6.9, 1.0 Hz, 2H), 0.97 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 204.52, 184.67, 132.27, 125.55, 119.80, 56.56, 33.59, 24.71, 20.57, 19.56, 14.32; IR (neat) cm^{-1}: 2962.13, 2931.27, 1550.49, 1353.78, 1257.36; HRMS (ESI, positive) *m/z* $[M + Na]^+$ Calcd. for $C_{11}H_{16}NaO_2$: 203.1048, found: 203.1037.

Synthesis of dione 31. A solution of allylpalladium (II) chloride dimer (138 mg, 377 μmol) and dppe (599 mg, 1.50 mmol) in degassed THF (37 mL) was treated successively with allyl acetate (1.6 mL, 15.0 mmol),

1,3-cyclopentadione (2.20 g, 22.5 mmol), BSA (5.5 mL, 22.5 mmol) and sodium acetate (51.5 mg, 628 µmol) at room temperature. After complete addition the reaction mixture was heated to reflux for 20 h. The solvent was removed under reduced pressure and the residue was taken up in dichloromethane (30 mL). The organic phase was washed with 1M HCl aq., the phases were separated and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried with Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was purified by medium-pressure chromatography (Isolera, eluent: 98:2 $CHCl_3$/MeOH to 80:20 $CHCl_3$/MeOH) to give **31** (1.66 g, 81%) as a pale yellow solid. All the analytical data are in the agreement with the reported data.[1-3]

Synthesis of cyclopentenone 32. To a solution of **31** (397 mg, 2.87 mmol) in acetone (8.5 mL) were added K_2CO_3 (437 mg, 3.16 mmol) and Me_2SO_4 (328 µL, 3.44 mmol). After being stirred at reflux temperature for 3 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. Then the mixture was extracted with CH_2Cl_2. The resulting organic layer was washed with saturated aqueous NaCl, dried over Na_2SO_4, and filtered. After evaporation, the residue was purified by medium-pressure chromatography (Isolera, eluent: 99:1 $CHCl_3$/MeOH to 90:10 $CHCl_3$/MeOH) to give **32** (429 mg, 98%) as a yellow oil. All the analytical data are in the agreement with the reported data.[4]

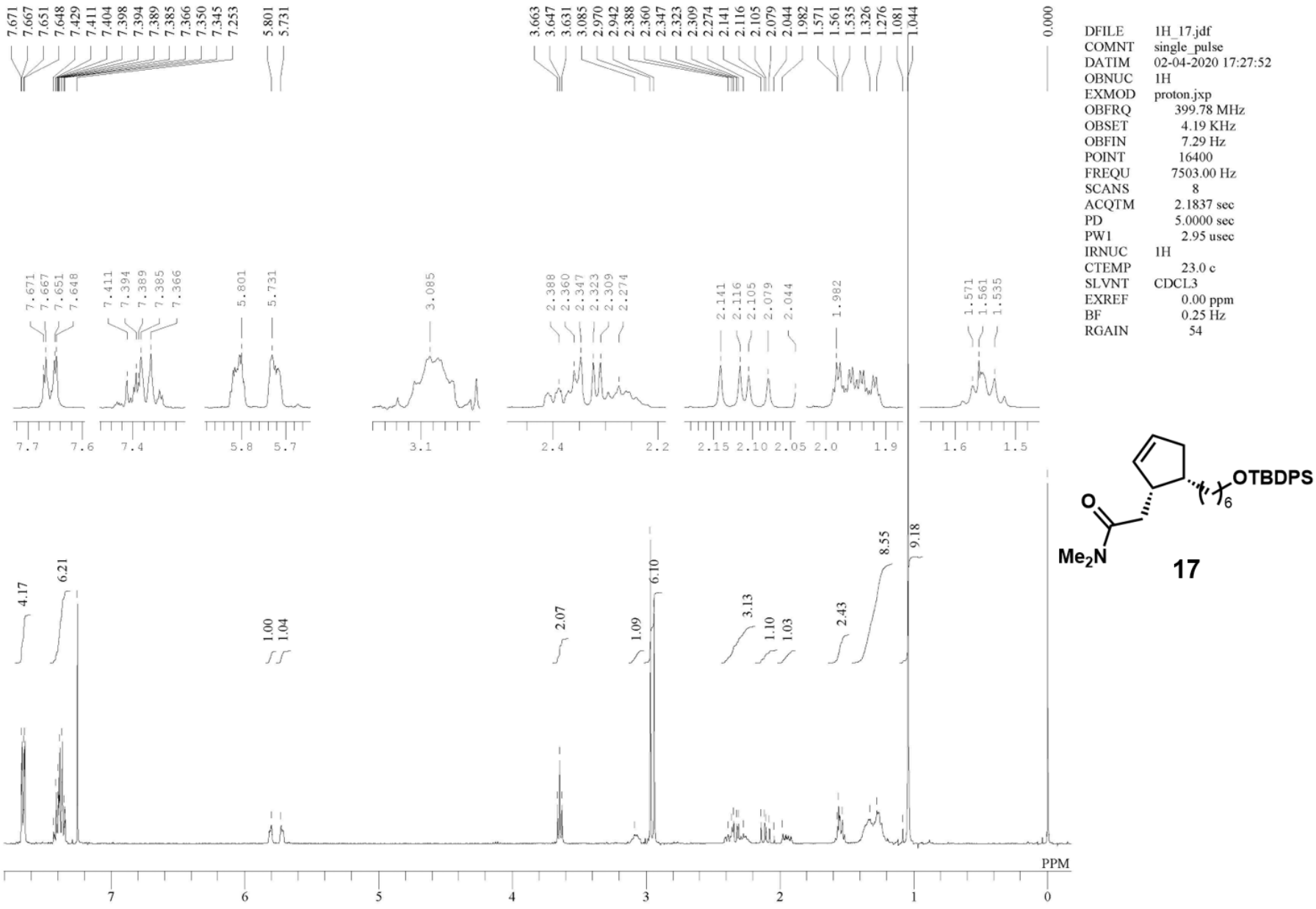
Synthesis of alcohol 33. To a solution of $THPO(CH_2)_6MgBr$ (1.0 M in THF, 7.0 mL, 7.00 mmol) was added to a solution of **32** (429 mg, 2.82 mmol) in THF (2.0 mL) at reflux temperature under an argon atmosphere. After being stirred at reflux temperature for 2 h, the reaction mixture was allowed to cool to rt and 10% HCl aq. (7 mL) was added. After 18 h of stirring at reflux temperature, H_2O was added and the water layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. After evaporation, the residue was purified by medium-pressure chromatography (Isolera, eluent: 88:12 *n*-hexane/EtOAc to EtOAc) to to give **33** (226 mg, 36%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 5.77 (ddt, J = 18.0, 9.4, 6.4 Hz, 1H), 4.96 (dq, J = 18.0, 2.0 Hz, 1H), 4.95 (dq, J = 9.4, 2.0 Hz, 1H), 3.65 (t, J = 6.4 Hz, 2H), 2.95 (d, J = 6.4 Hz, 2H), 2.54-2.52 (m, 2H), 2.43 (t, J = 7.8 Hz, 2H), 2.40-2.38 (m, 2H), 1.61-1.51 (m, 4H), 1.44-1.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 209.53, 175.43, 137.99, 135.06, 115.27, 62.91, 34.28, 32.68, 31.28, 29.63, 29.33, 27.45, 27.39, 25.68; IR (neat) cm^{-1}:3429, 2931, 2858, 1693, 1639; HRMS (ESI, positive) *m/z* $[M + Na]^+$ Calcd. for $C_{13}H_{20}NaO_2$: 245.1517, found: 245.1512.

Synthesis of diol 34. A 5 mL pear-shaped flask was charged with **33** (43.0 mg, 193 µmol), CH_2=$CHCH_2CH_2OAc$ (145 mg, 1.27 mmol) and Hoveyda-Grubbs Catalyst® M2001 Umicore (8.5 mg, 13.4 µmol). After 6 h of stirring, the residue was roughly purified by medium-pressure chromatography (Isolera, eluent: 99:1 $CHCl_3$/MeOH to 90:10 $CHCl_3$/MeOH) to give a mixture (26.7 mg). The crude mixture was used for the next reaction without further purification. To a solution of the mixture (26.7 mg) in MeOH (420 µL) was added 0.3M-NaOH solution (1.3 mL, 390 µmol) and the mixture was stirred at 50 ° for 1.5 h. The reaction mixture was quenched with 2M HCl aq. and the aqueous layer was extracted with EtOAc. The organic layer was washed with saturated aqueous NaCl, dried over Na_2SO_4, and filtered. After evaporation, the residue was purified medium-pressure chromatography (Isolera, eluent: 0.1:99:1 AcOH/$CHCl_3$/MeOH

to 0.1:86:14 AcOH/$CHCl_3$/MeOH) to give **34** (16.1 mg, 32% in 2 steps) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 5.43 (dtt, J = 10.8, 7.2, 1.5 Hz, 1H), 5.37 (dtt, J = 10.8, 6.8, 1.3 Hz, 1H), 3.69 (t, J = 6.2 Hz, 2H), 3.66 (t, J = 6.4 Hz, 2H), 2.98 (d, J = 6.8 Hz, 2H), 2.53-2.51 (m, 2H), 2.49-2.43 (m, 4H), 2.38-2.36 (m, 2H), 1.61-1.52 (m, 4H), 1.46-1.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 210.25, 175.16, 138.82, 128.96, 127.10, 62.89, 62.20, 34.36, 32.65, 31.30, 31.01, 29.54, 29.42, 27.58, 25.65, 21.89; IR (neat) cm^{-1}: 3410, 2931, 2862, 1686, 1635; HRMS (ESI, positive) *m/z* $[M + Na]^+$ Calcd. for $C_{16}H_{26}NaO_3$: 289.1780, found: 289.1775.

Supplementary References

1. P. K. Ruprah, J.-P. Cros, J. E. Pease, W. G. Whittingham and J. M. J. Williams, *Eur. J. Org. Chem.* 2002, 3145-3152.
2. E. Lacoste, E. Vaique, M. Berlande, I. Pianet, J.-M. Vincent and Y. Landais, *Eur. J. Org. Chem.* 2007, 167-177.
3. X.-M. Zhang, M. Wang, Y.-Q. Tu, C.-A. Fan, Y.-J. Jiang, S.-Y. Zhang and F.-M. Zhang, *Synlett* 2008, 2831-2835.
4. P. K. Ruprah, J.-P. Cros, J. E. Pease, W. G. Whittingham, J. M. J. Williams, *Eur. J. Org. Chem.* 2002, 3145-3152.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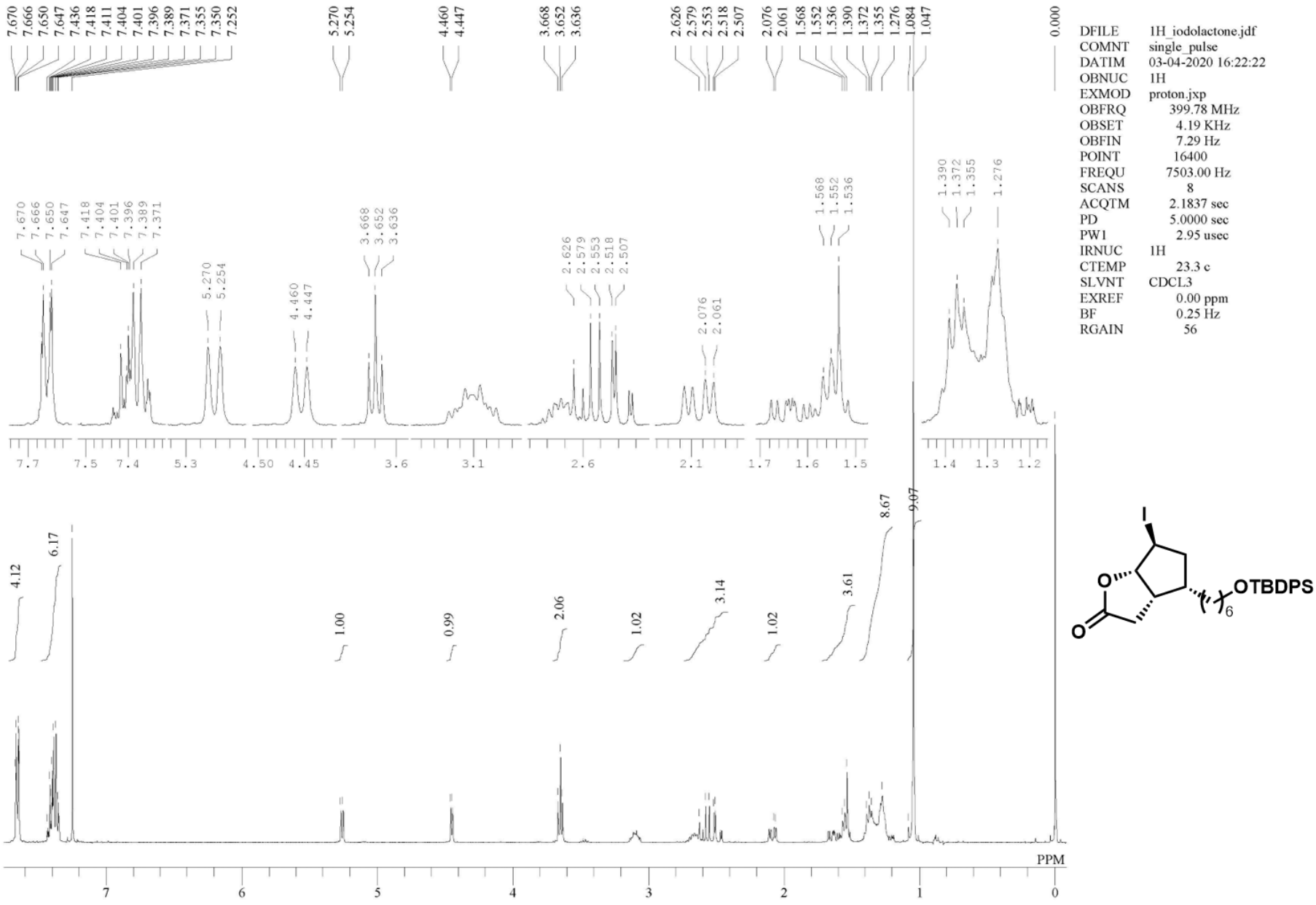
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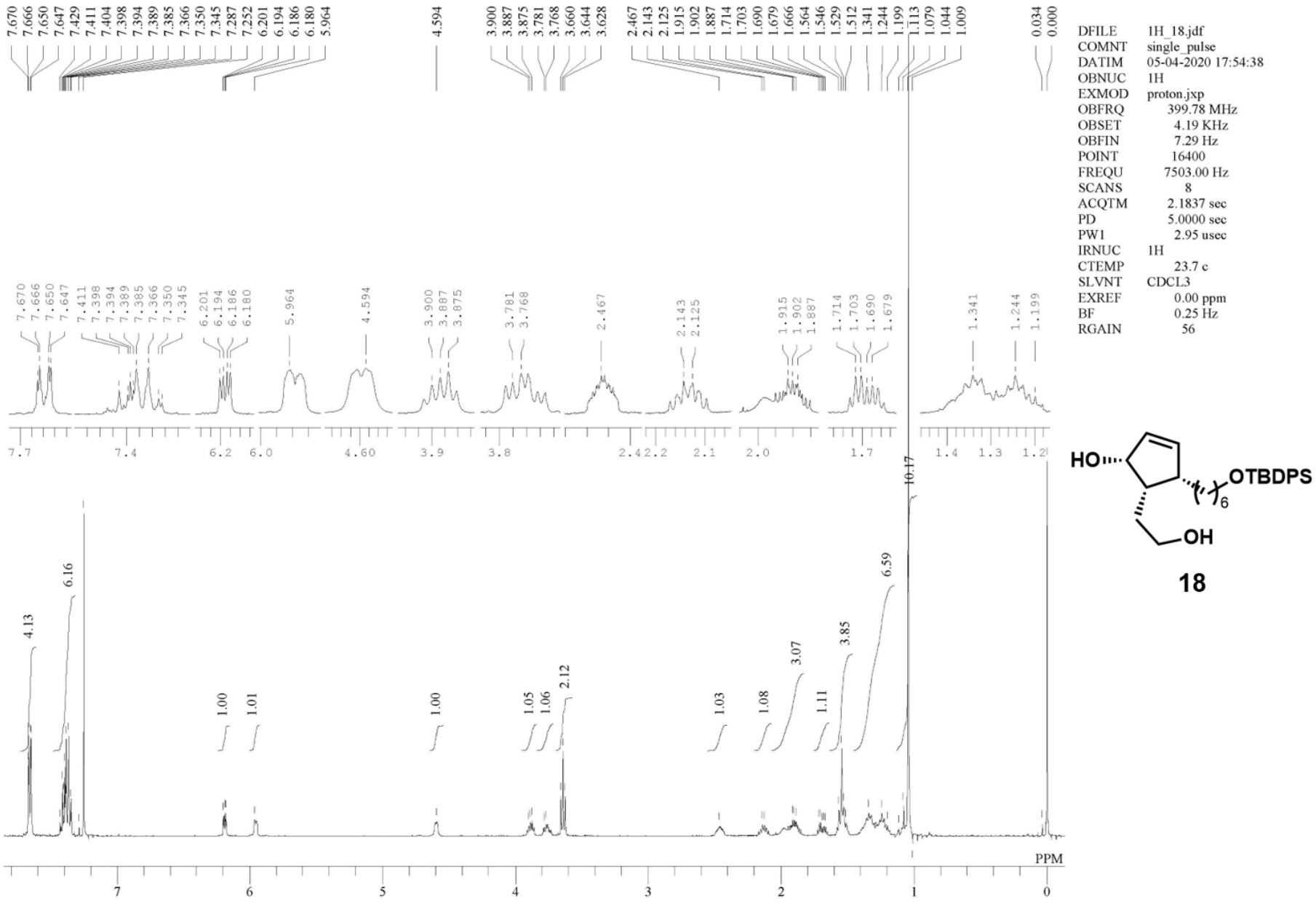
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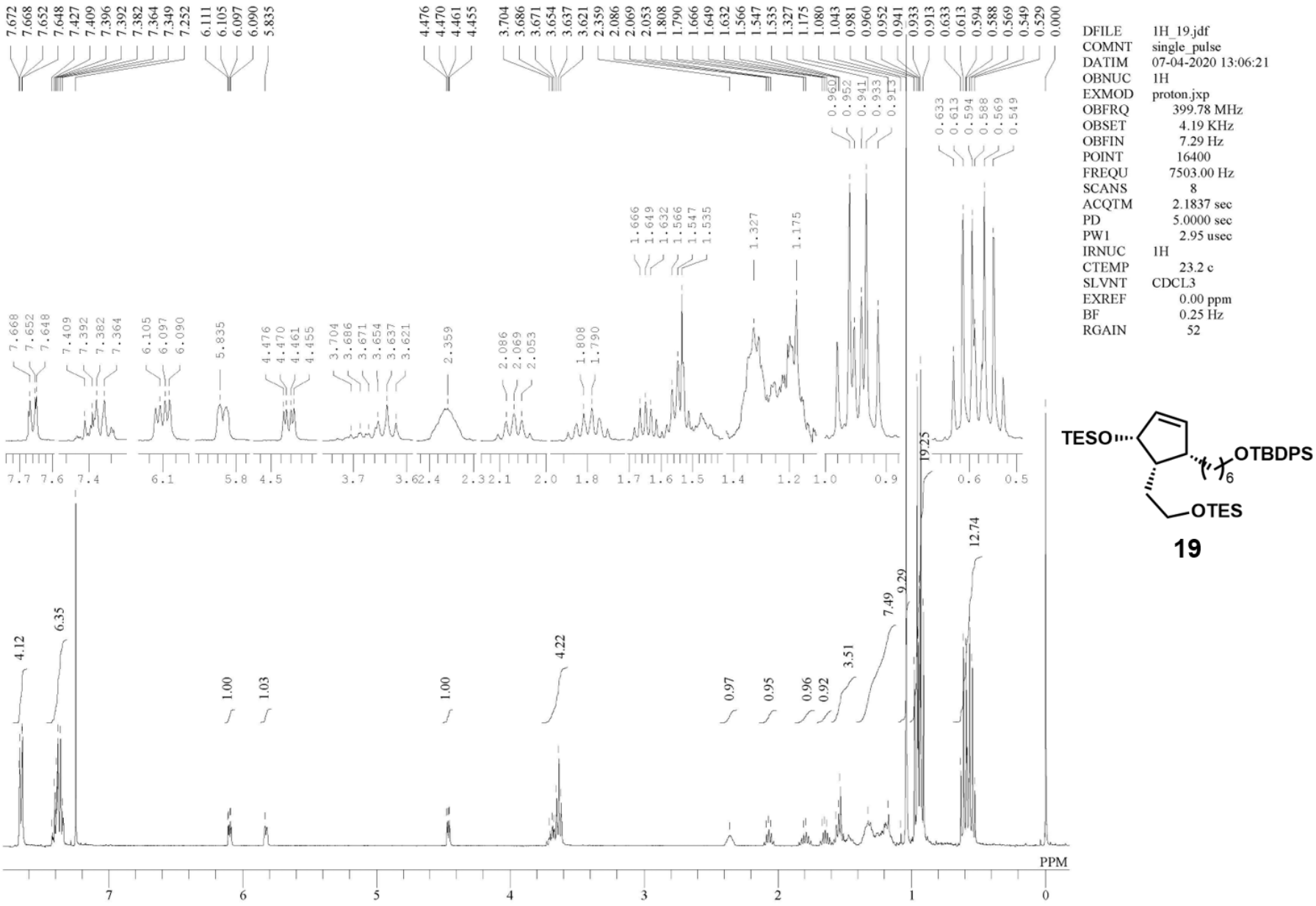
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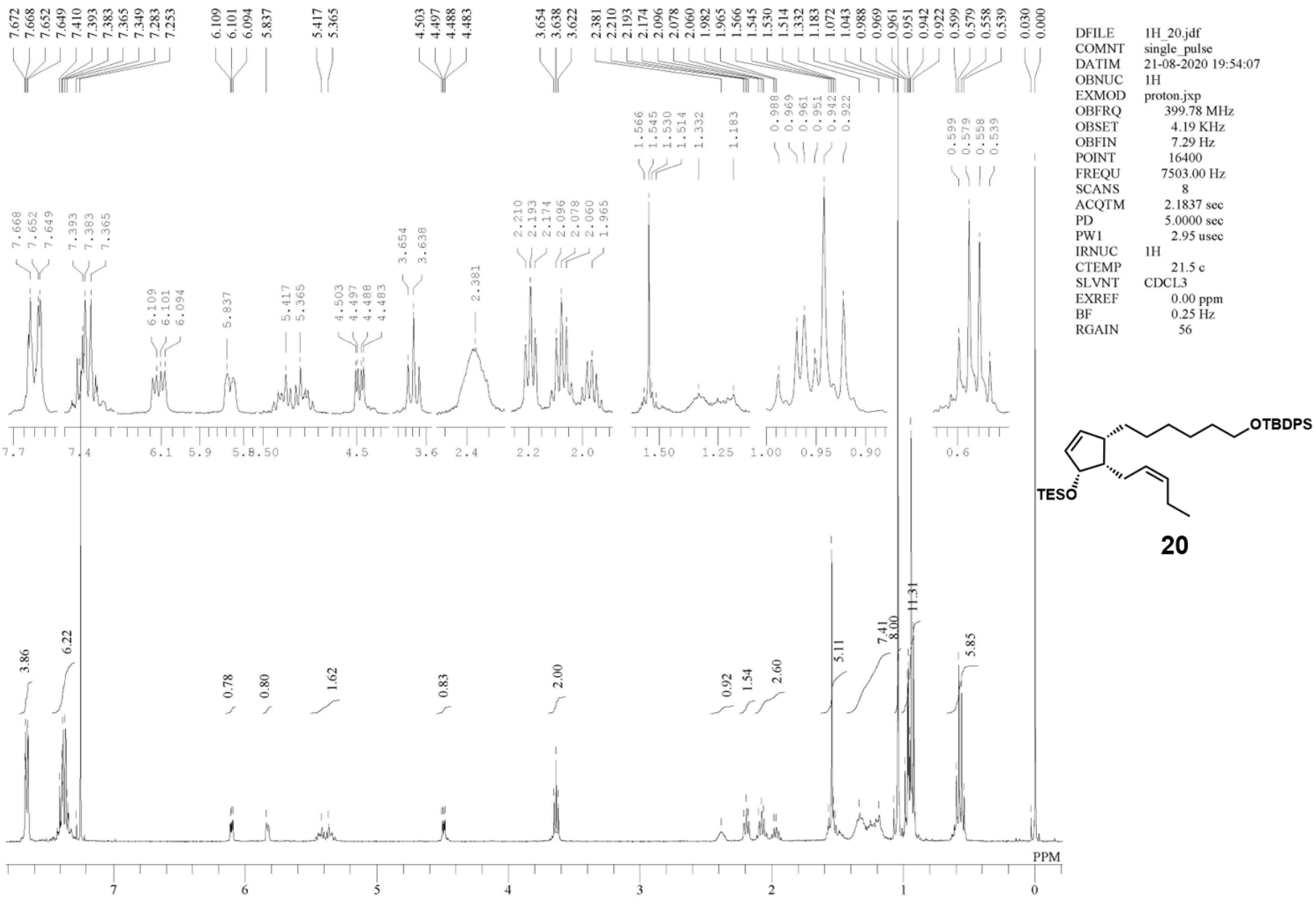
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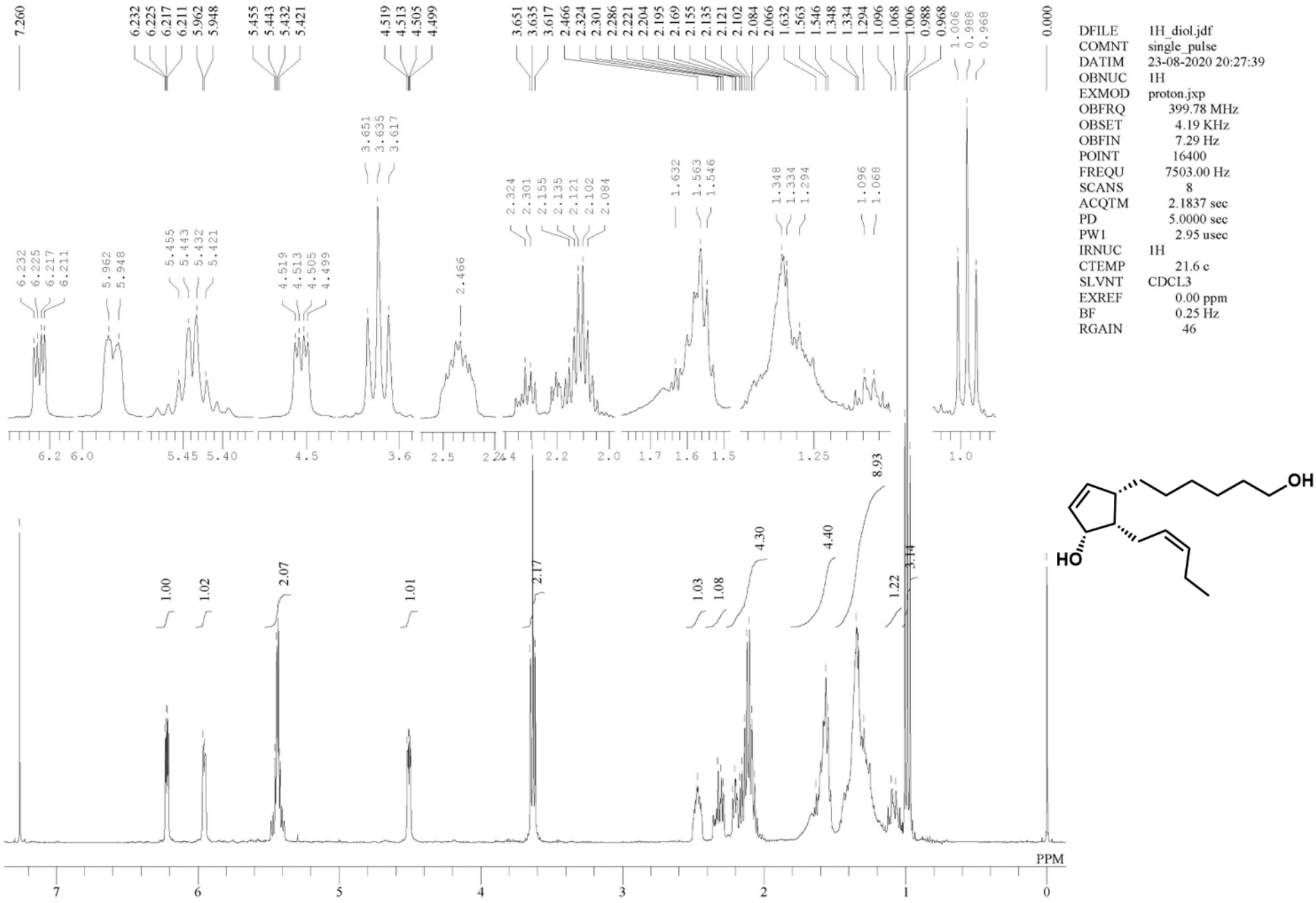
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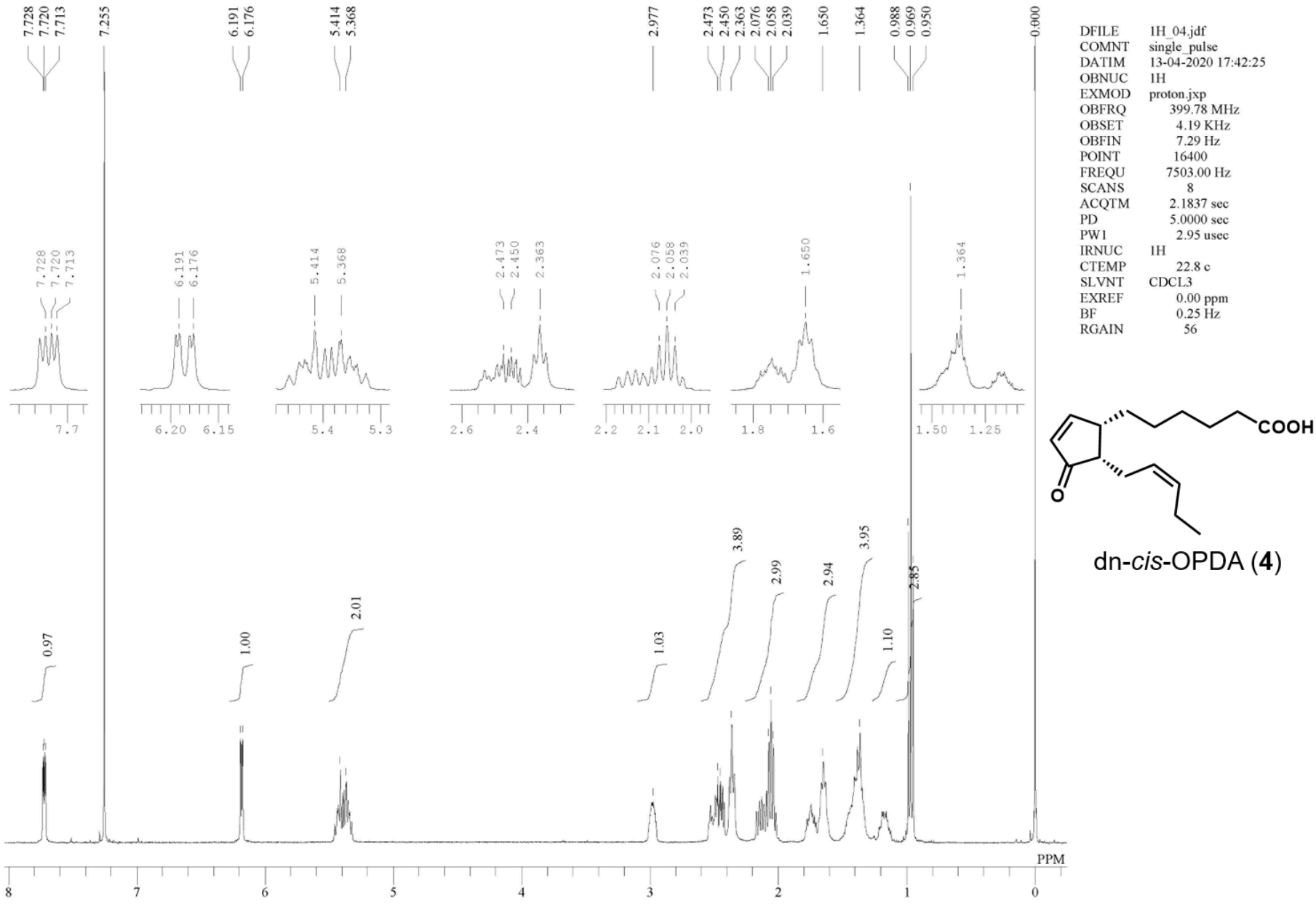
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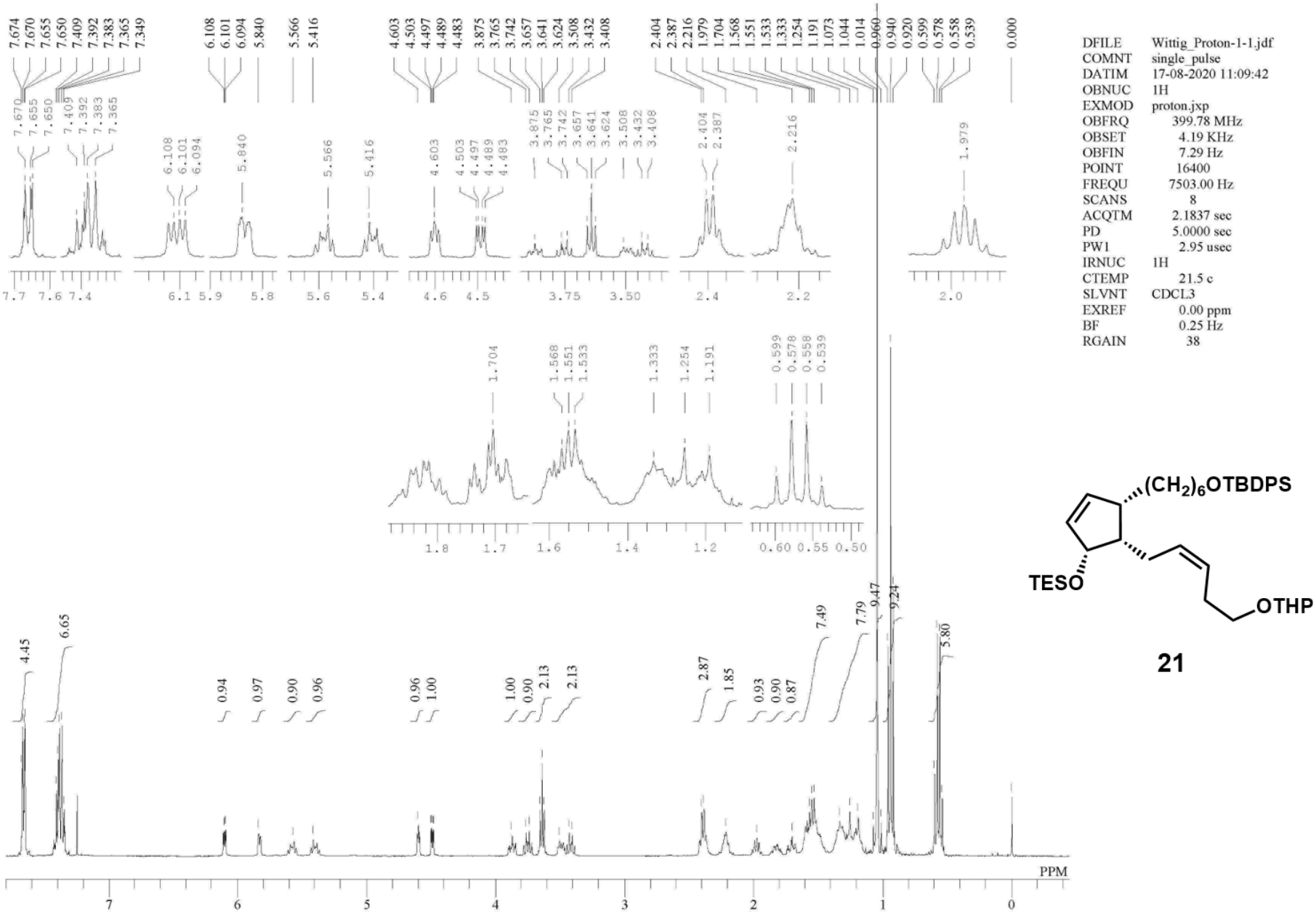
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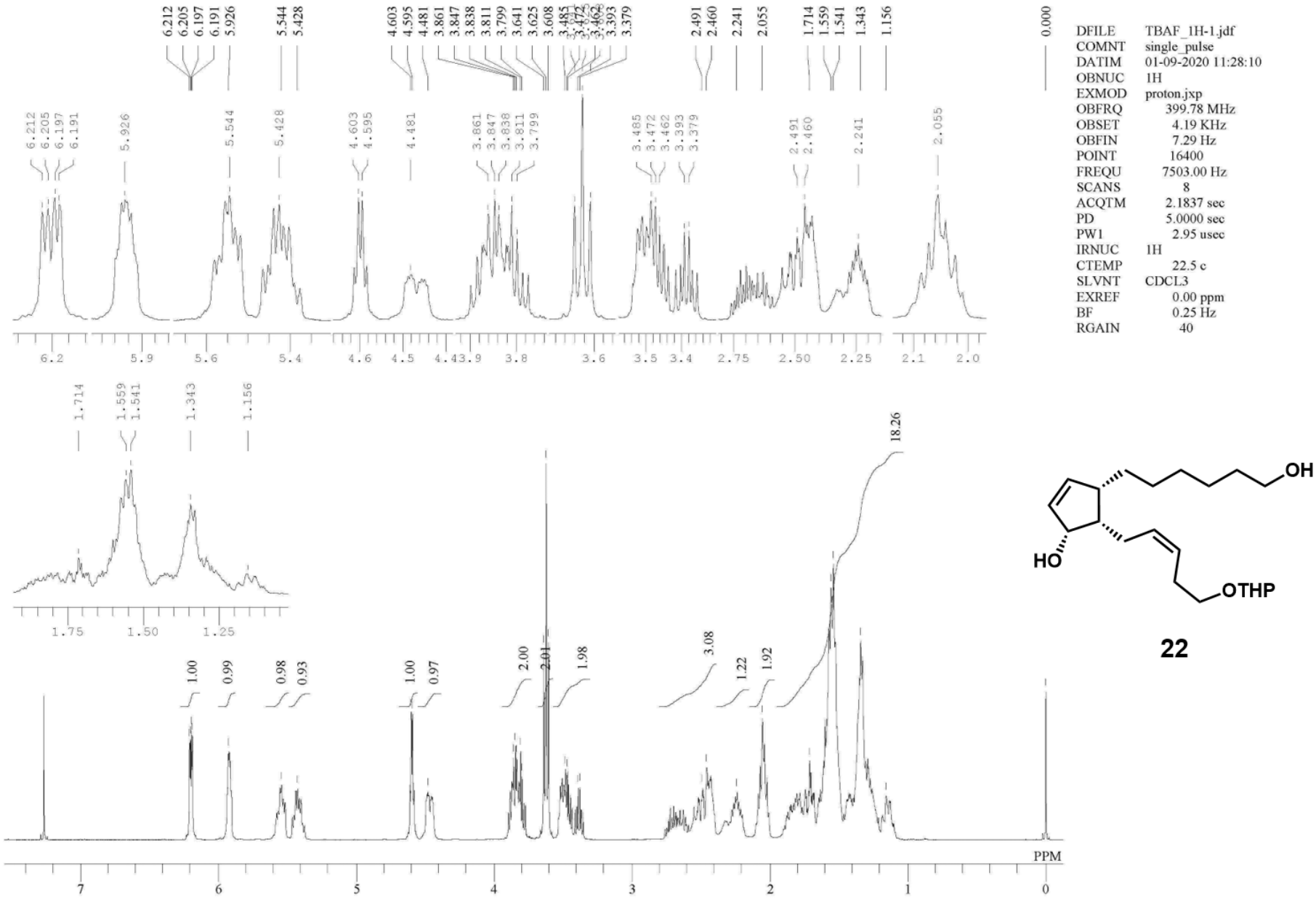
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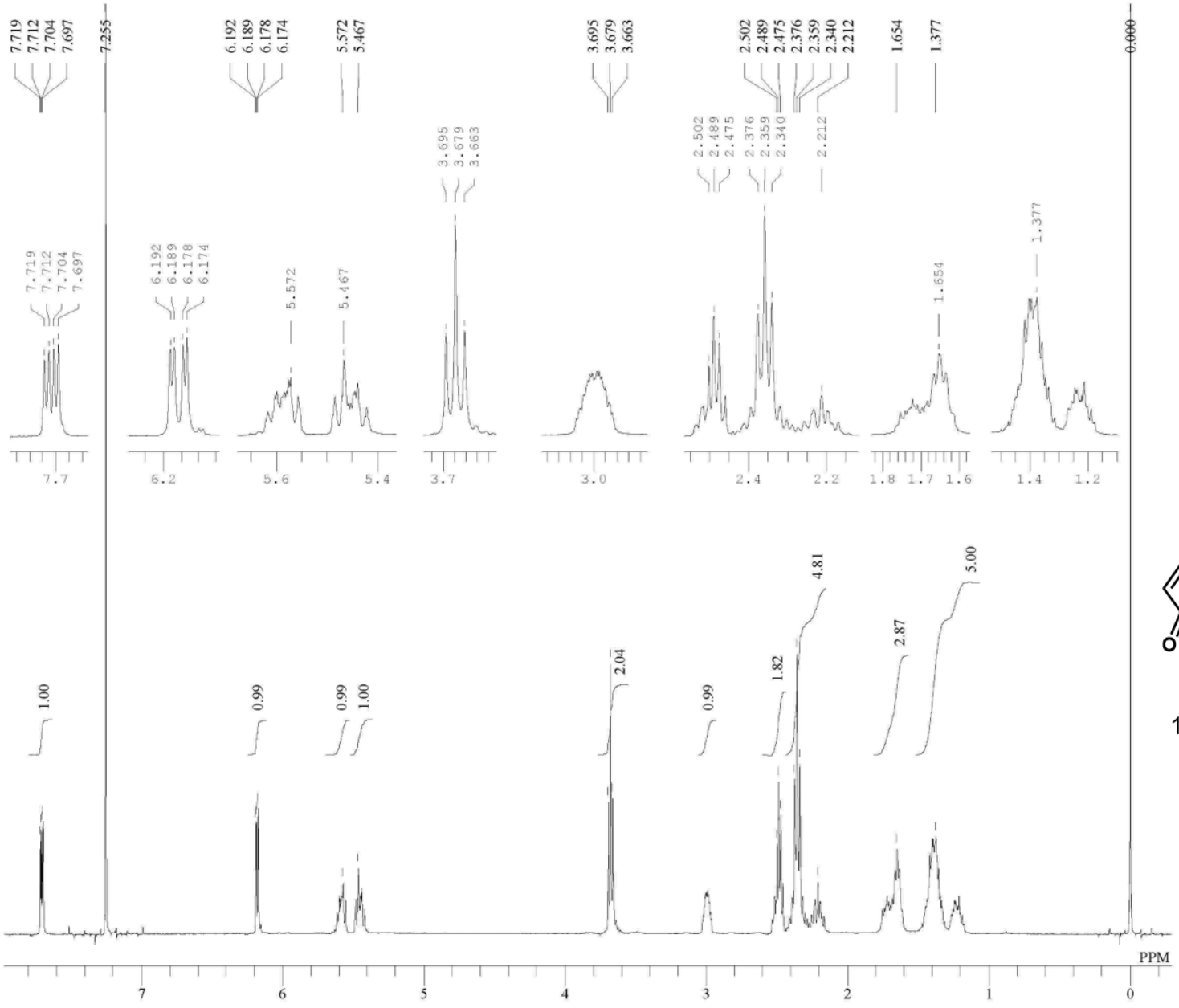

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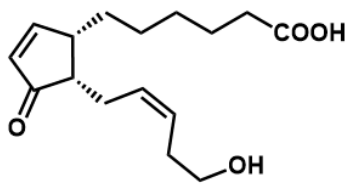

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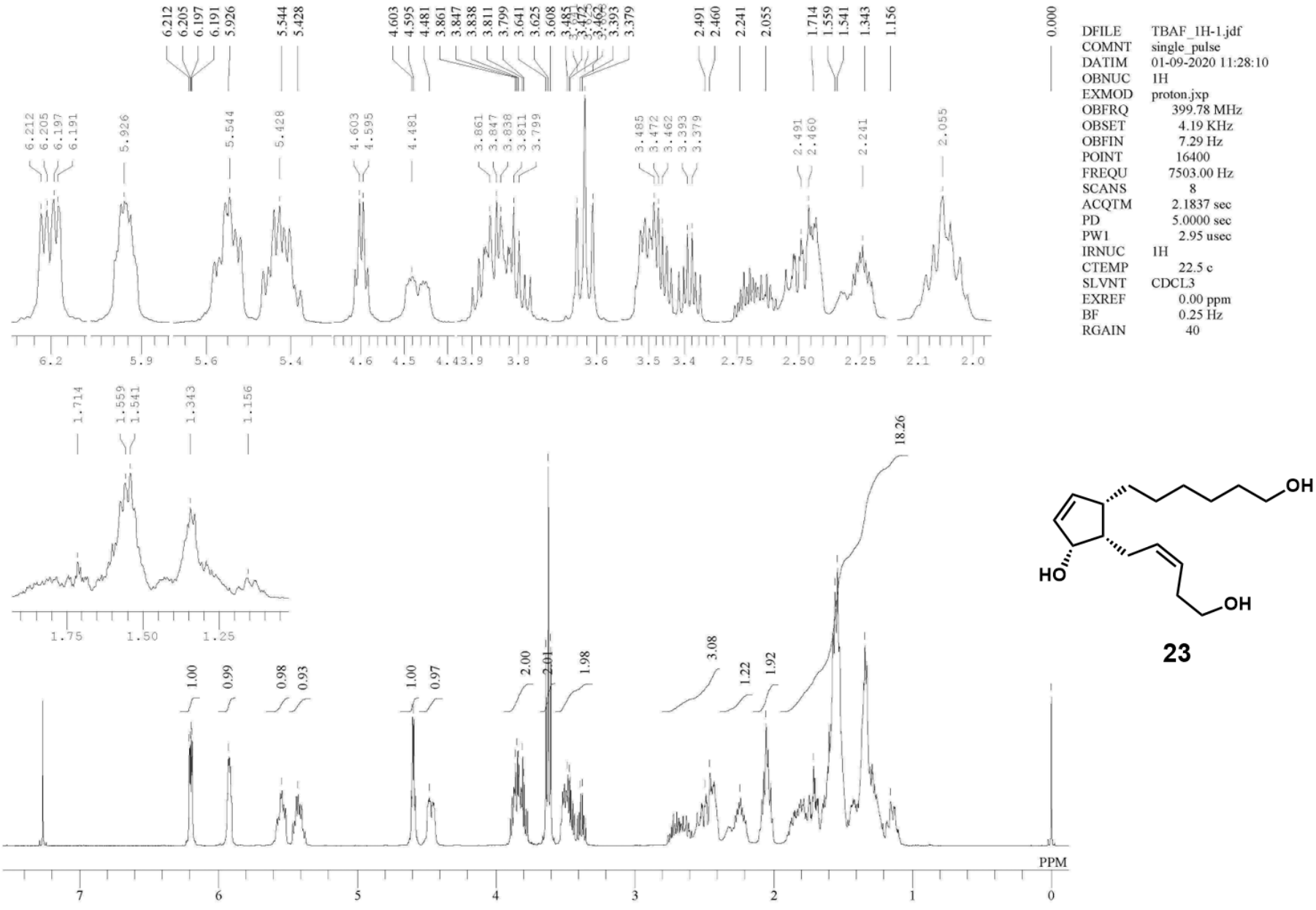
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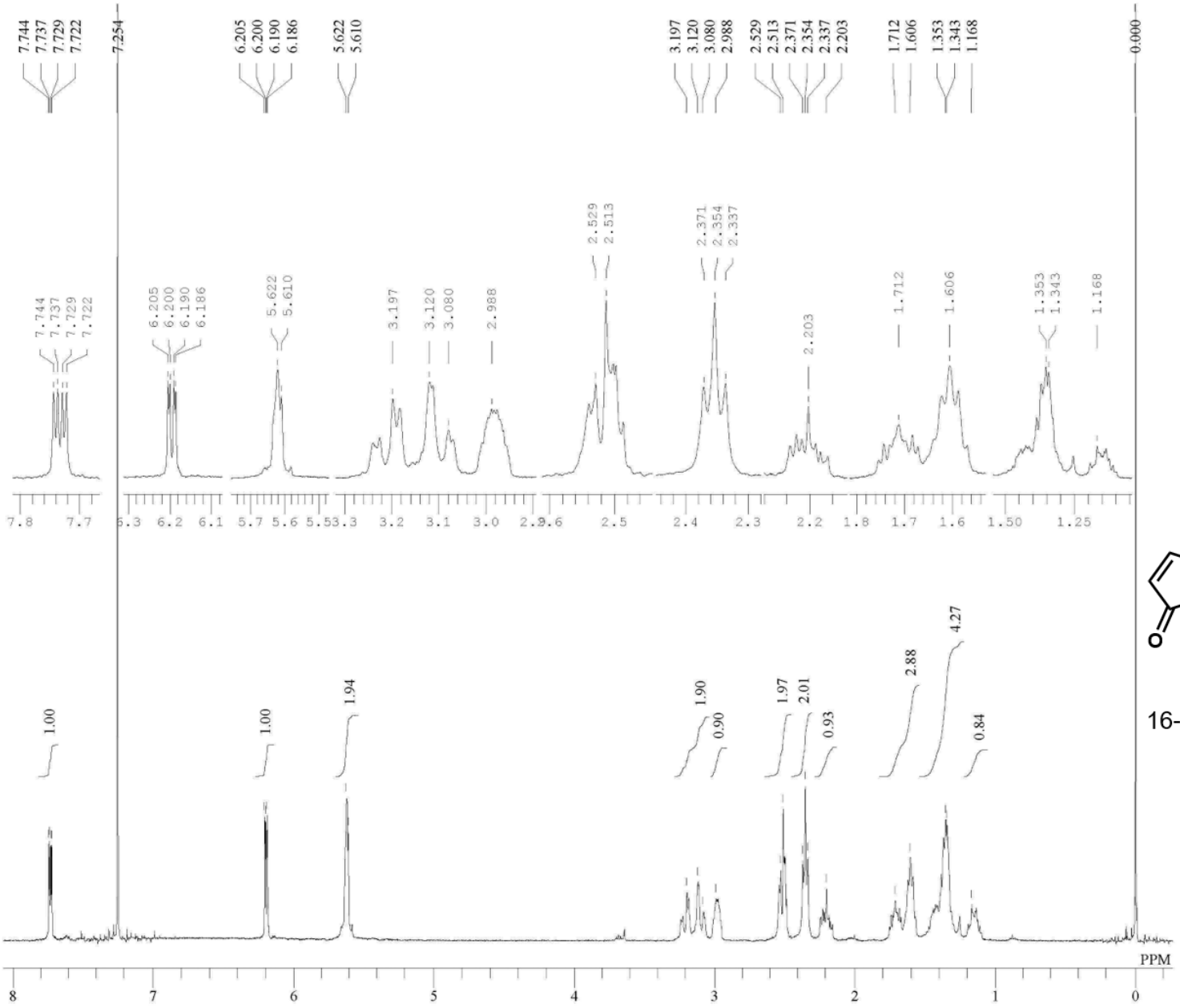

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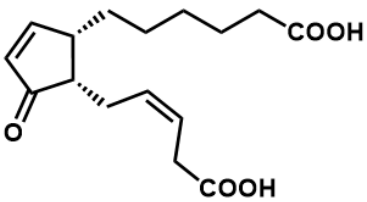
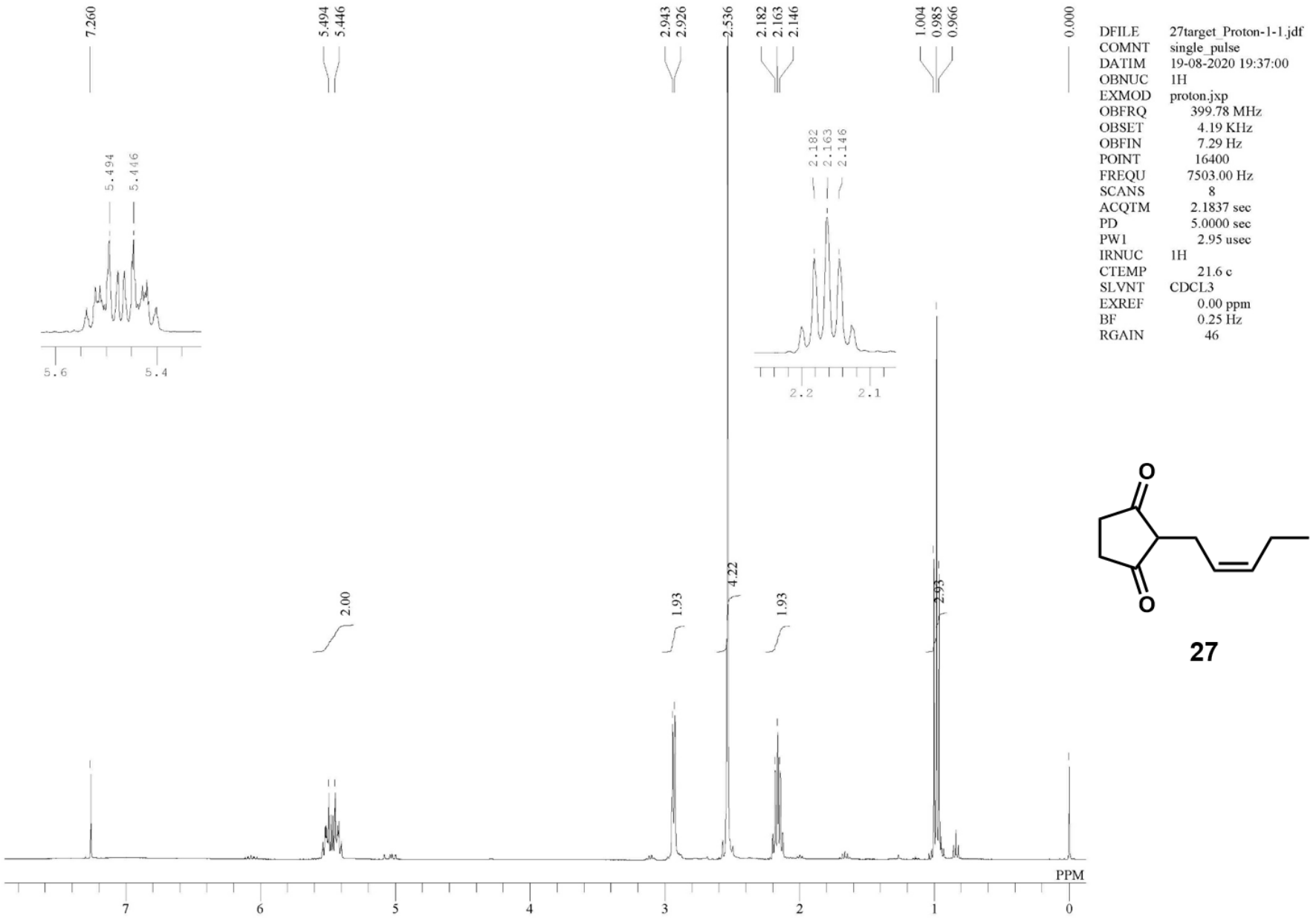
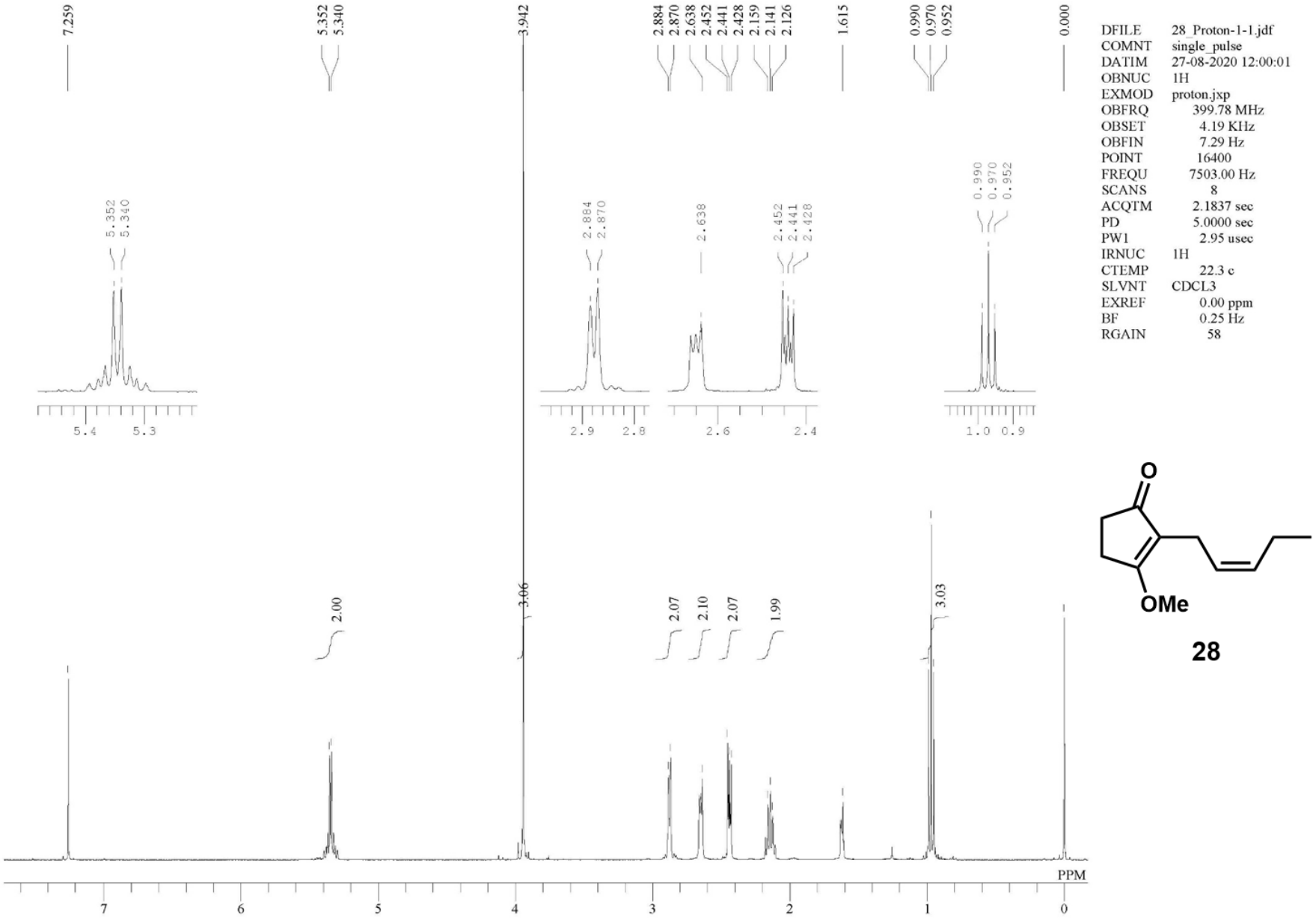
BF 0.25 Hz
RGAIN 58



16-COOH-dn-*cis*-OPDA (**7**)

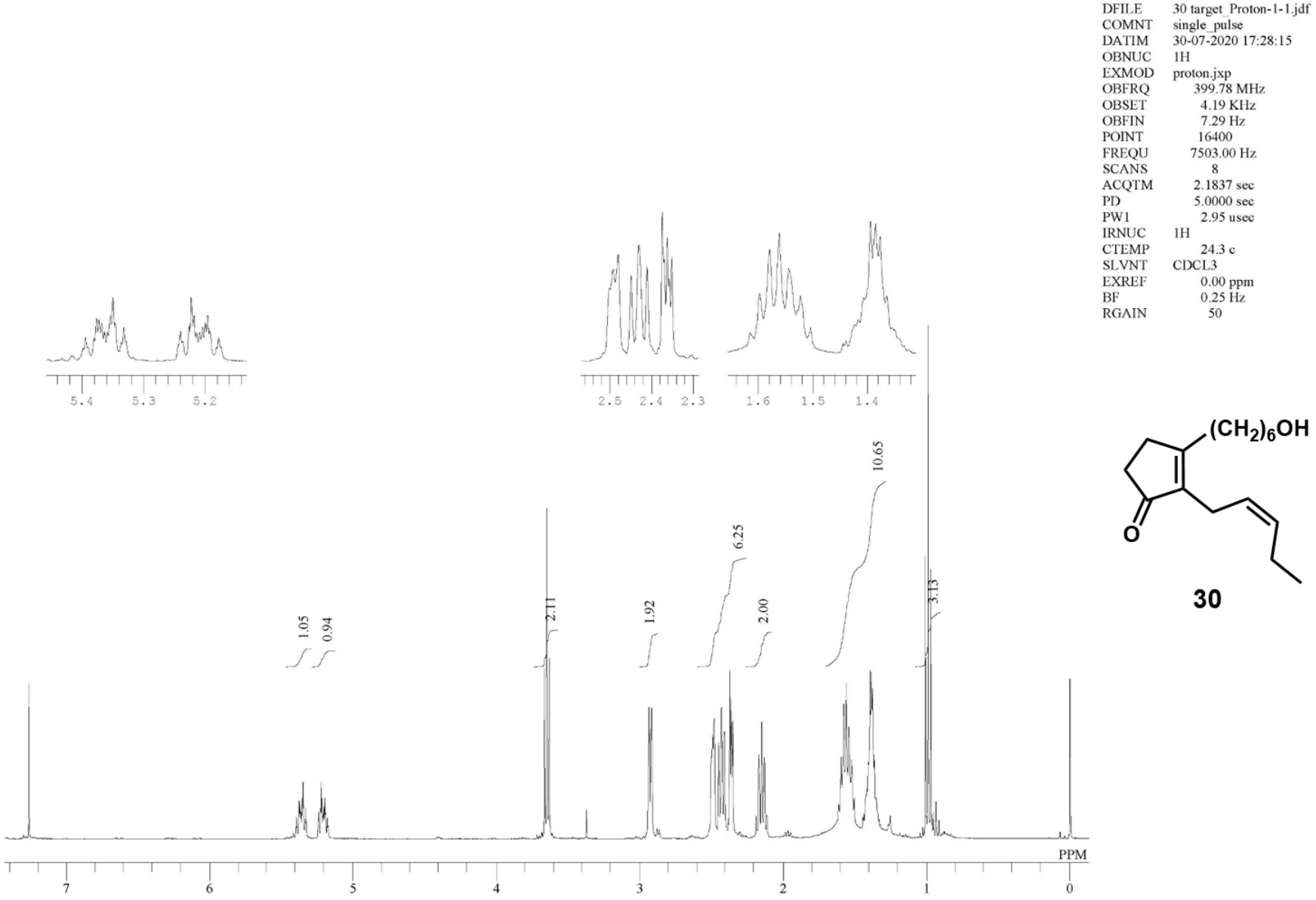

7.260
5.494
5.446
2.943
2.926
2.536
2.182
2.163
2.146
1.004
0.985
0.966
0.000
DFILE 27target_Proton-1-1.jdf
COMNT single_pulse
DATIM 19-08-2020 19:37:00
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 2.95 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.25 Hz
RGAIN 46
2.00
1.93
4.22
1.93
2.93
PPM
7
6
5
4
3
2
1
0
O
O

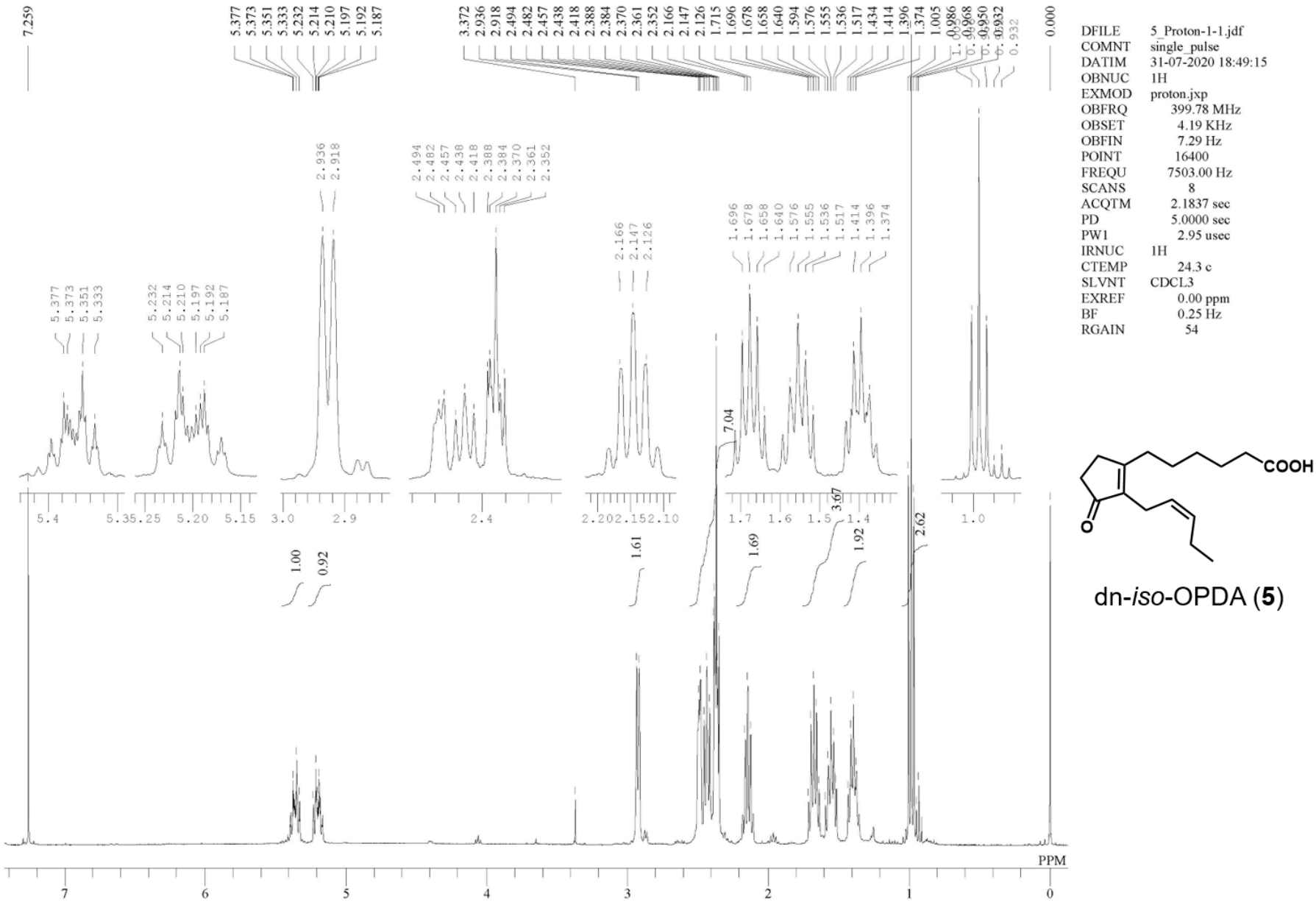
27


7.259
5.352
5.340
3.942
2.884
2.870
2.638
2.452
2.441
2.428
2.159
2.141
2.126
1.615
0.990
0.970
0.952
0.000
DFILE 28_Proton-1-1.jdf
COMNT single_pulse
DATIM 27-08-2020 12:00:01
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 2.95 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.25 Hz
RGAIN 58
2.00
3.06
2.07
2.10
2.07
1.99
3.03
PPM
7
6
5
4
3
2
1
0

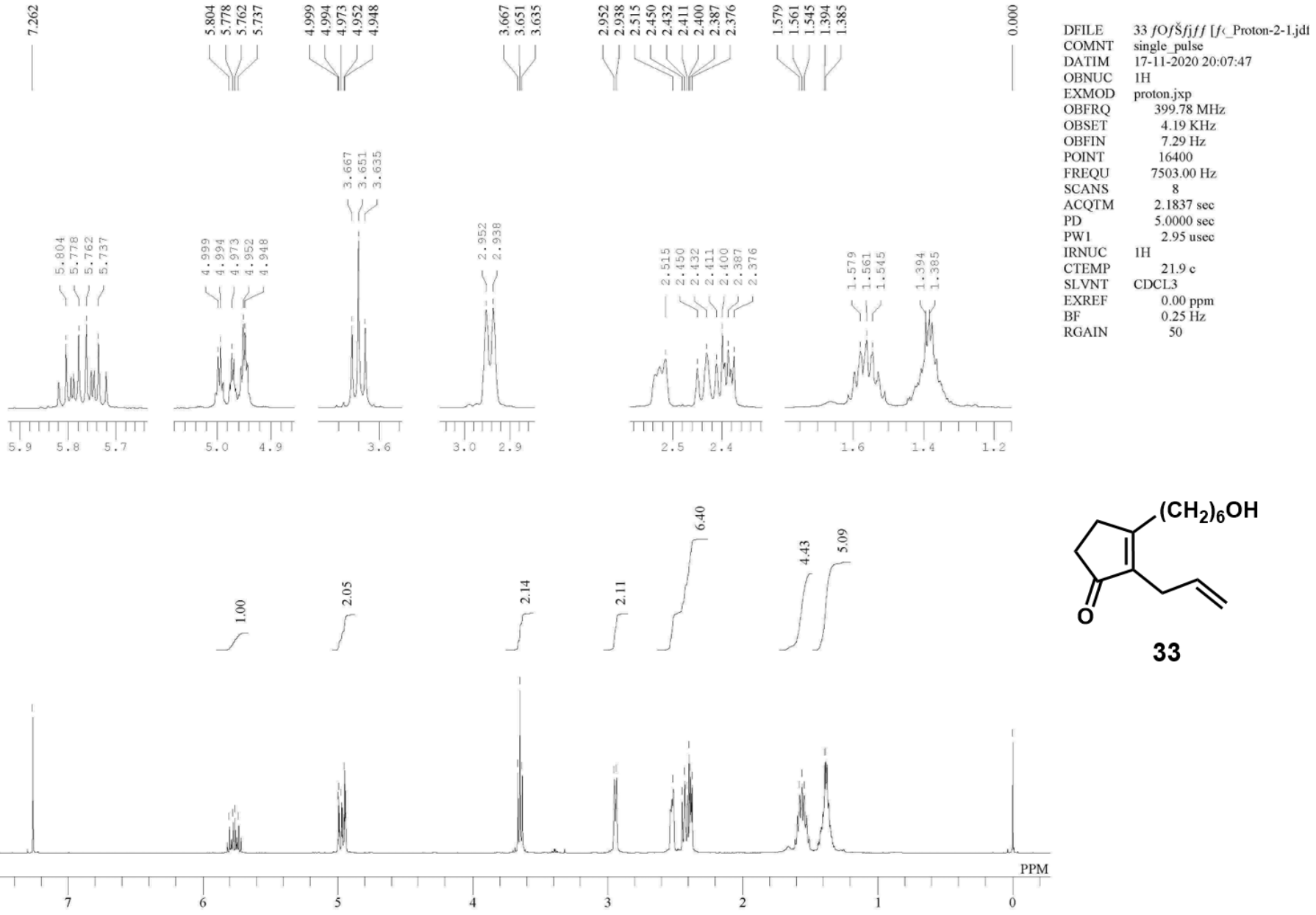
O
OMe

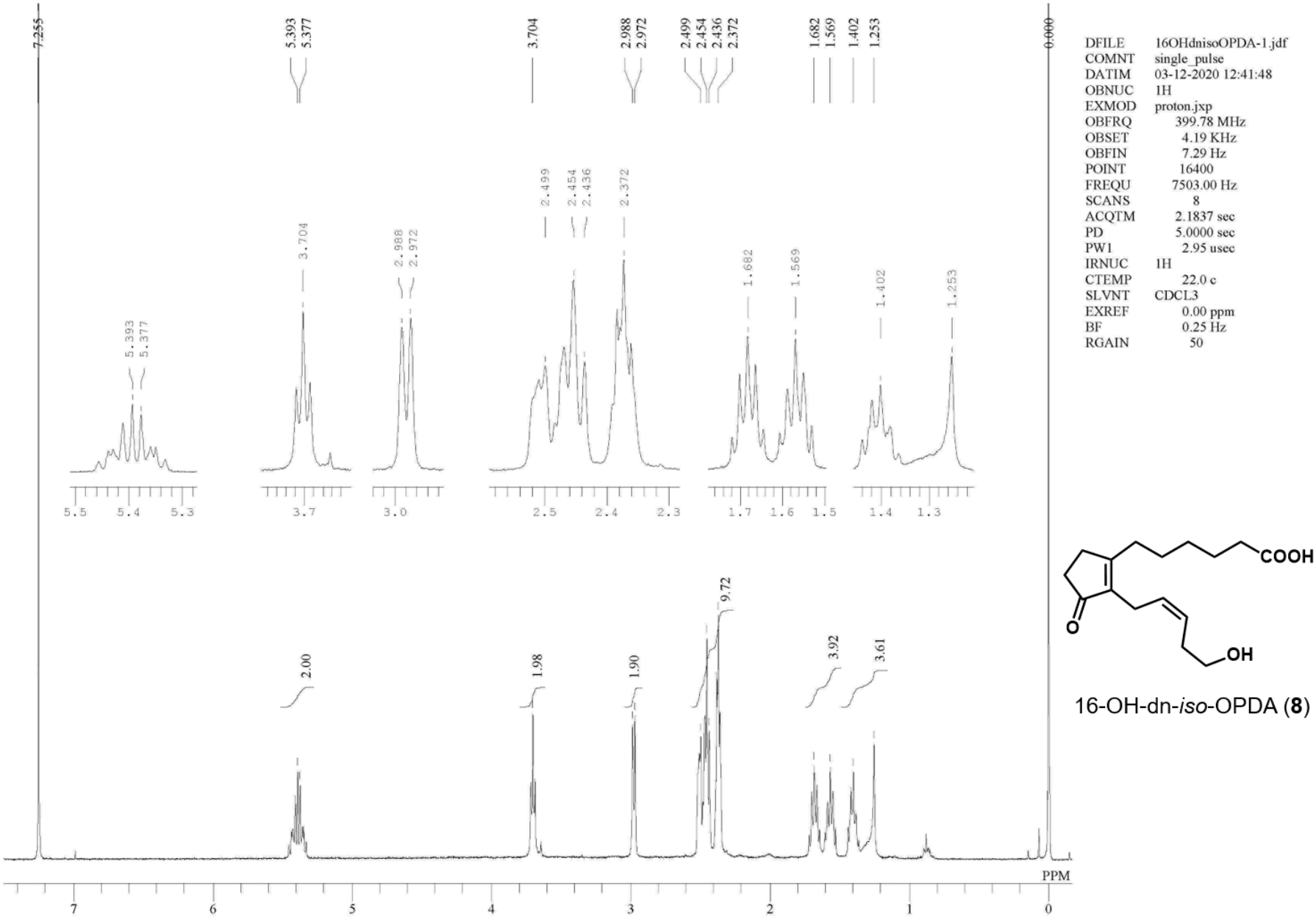
28


DFILE 30 target_Proton-1-1.jdf
COMNT single_pulse
DATIM 30-07-2020 17:28:15
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 2.95 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.25 Hz
RGAIN 50
5.4 5.3 5.2
2.5 2.4 2.3
1.6 1.5 1.4
1.05
0.94
2.11
1.92
6.25
2.00
10.65
3.13
PPM
7 6 5 4 3 2 1 0
(CH2)6OH
O
30

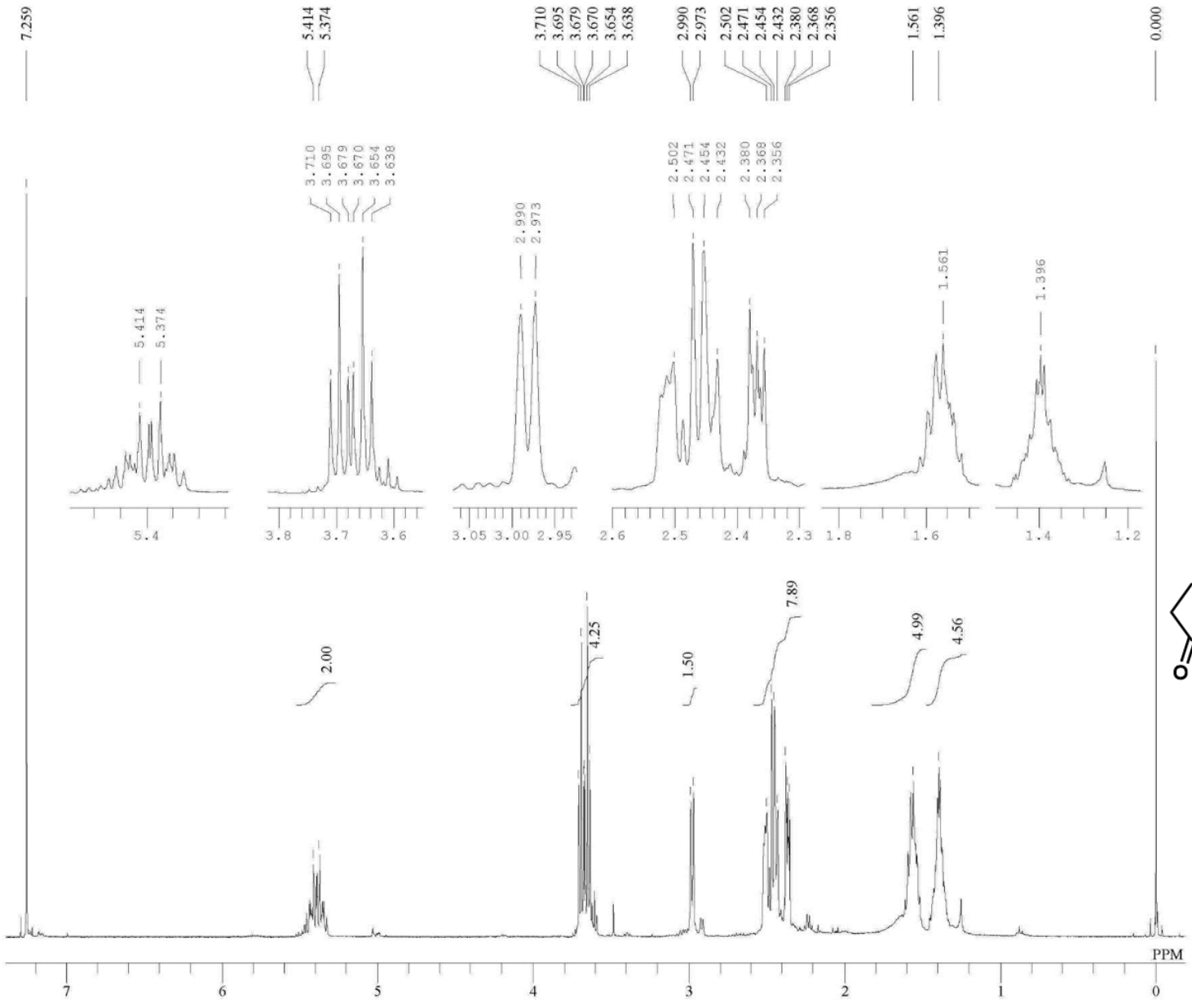

DFILE 5_Proton-1-1.jdf
COMNT single_pulse
DATIM 31-07-2020 18:49:15
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 2.95 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.25 Hz
RGAIN 54
PPM
COOH
O

dn-*iso*-OPDA (**5**)

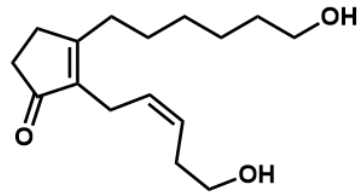

7.262
5.804
5.778
5.762
5.737
4.999
4.994
4.973
4.952
4.948
3.667
3.651
3.635
2.952
2.938
2.515
2.450
2.432
2.411
2.400
2.387
2.376
1.579
1.561
1.545
1.394
1.385
0.000
DFILE 33 fOfŠfjff [f‹_Proton-2-1.jdf
COMNT single_pulse
DATIM 17-11-2020 20:07:47
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 2.95 usec
IRNUC 1H
CTEMP 21.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.25 Hz
RGAIN 50
1.00
2.05
2.14
2.11
6.40
4.43
5.09
PPM
(CH2)6OH
O
33



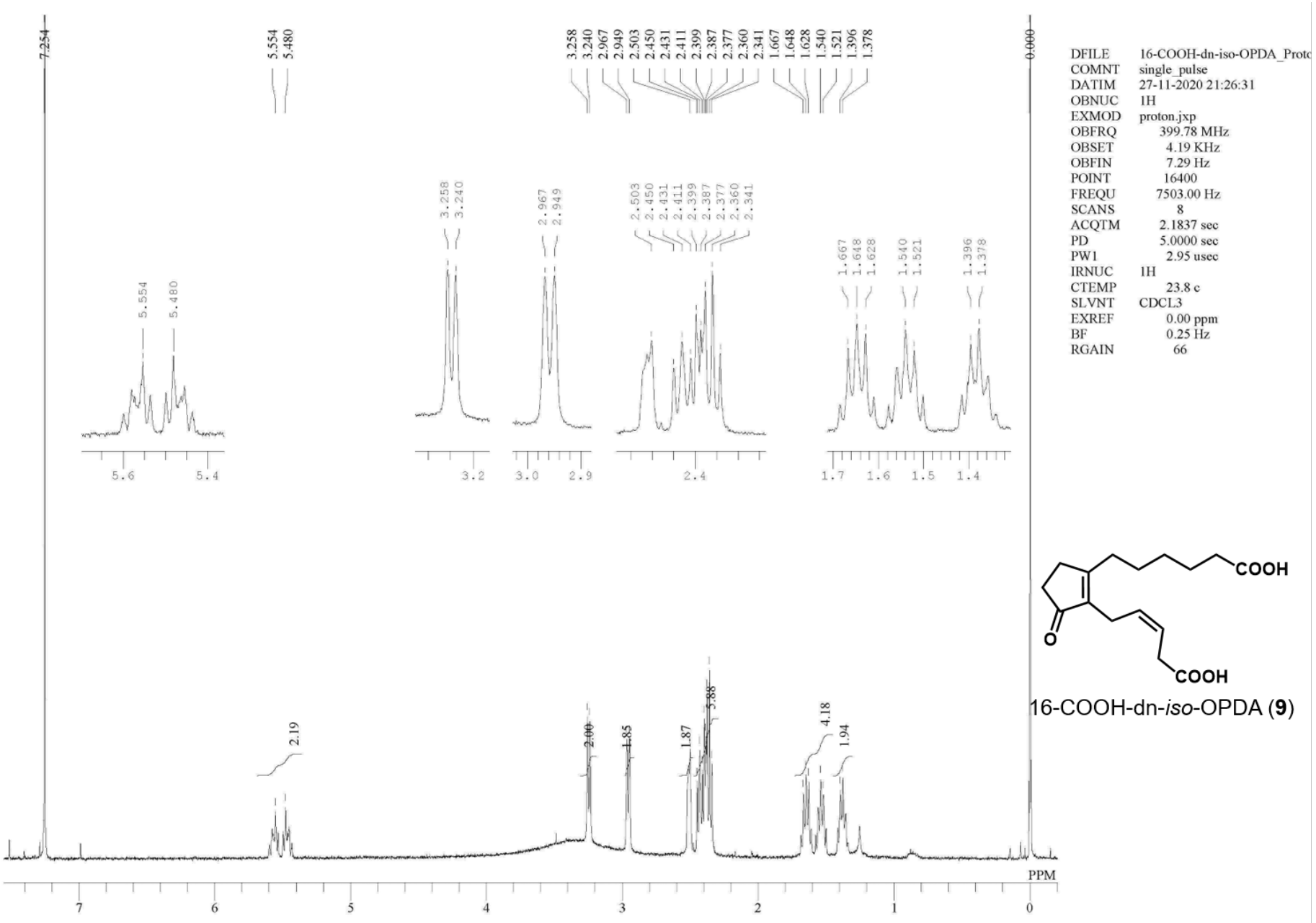
16-OH-dn-*iso*-OPDA (**8**)



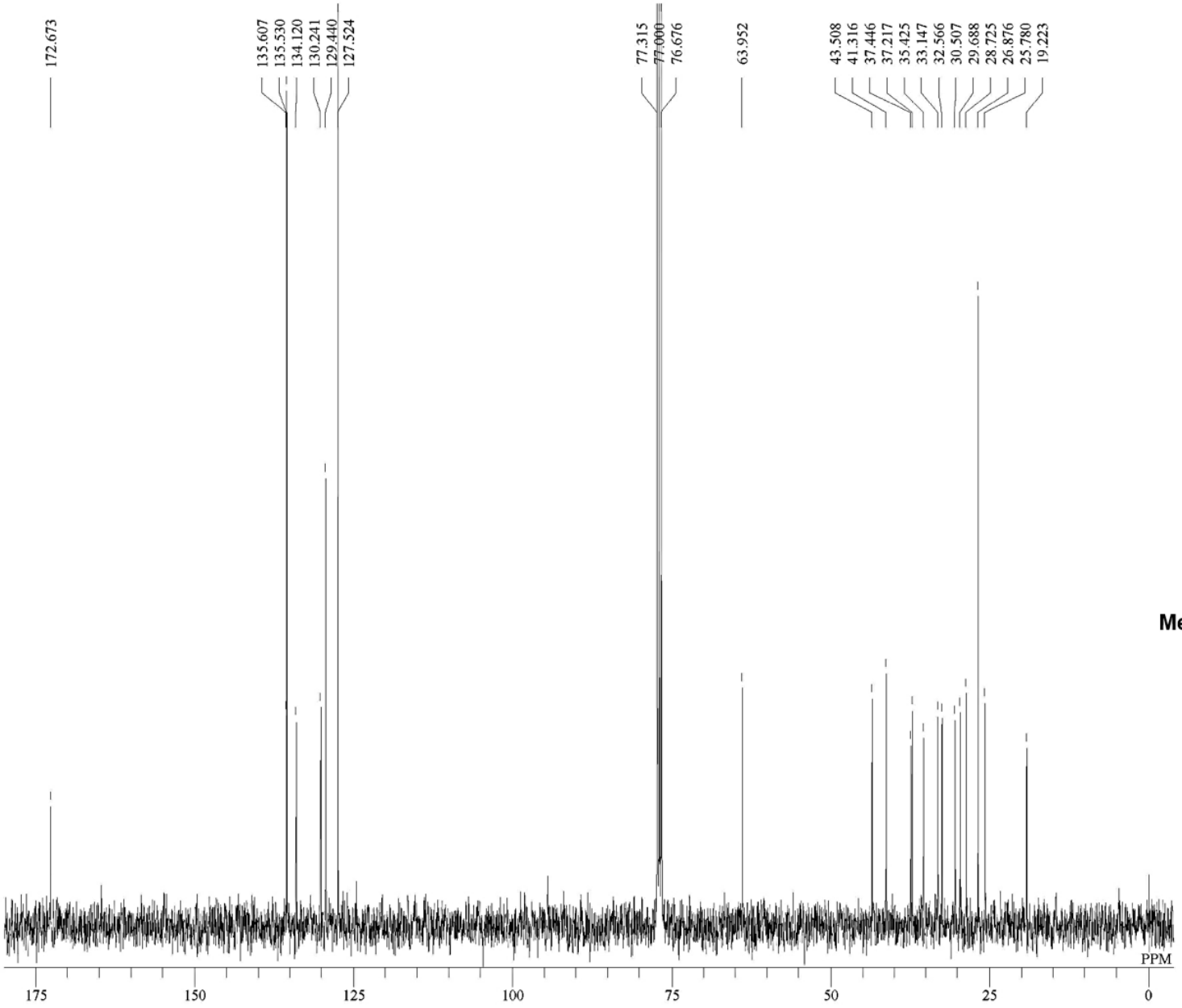
DFILE 35 fWfqfhf fLfV2OH_Proton
COMNT single_pulse
DATIM 10-11-2020 17:15:42
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 2.95 usec
IRNUC 1H
CTEMP 21.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.25 Hz
RGAIN 62



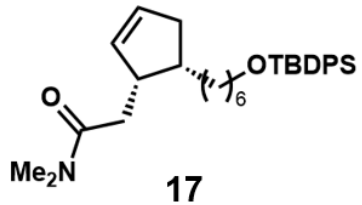
34



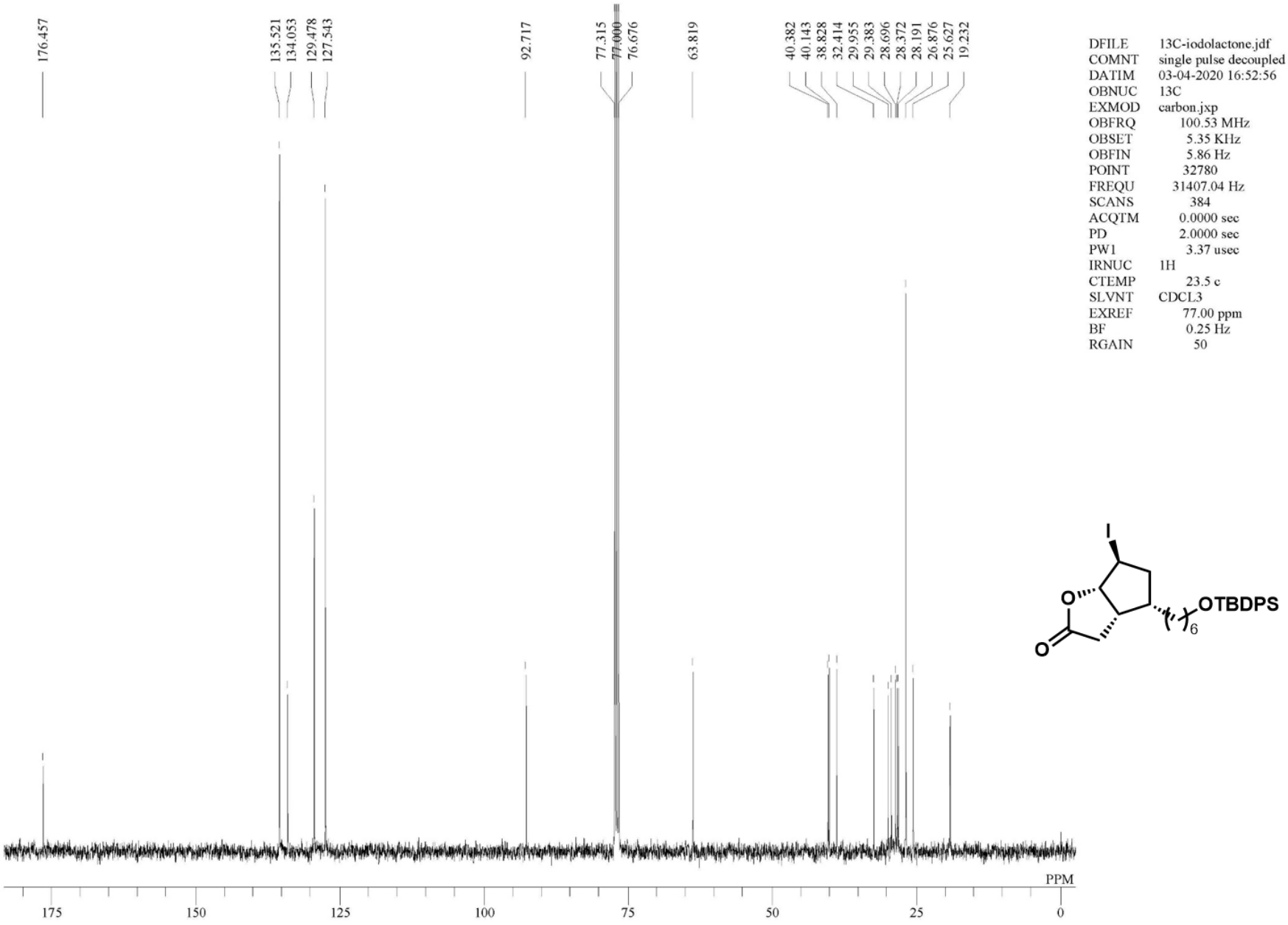
16-COOH-dn-*iso*-OPDA (**9**)

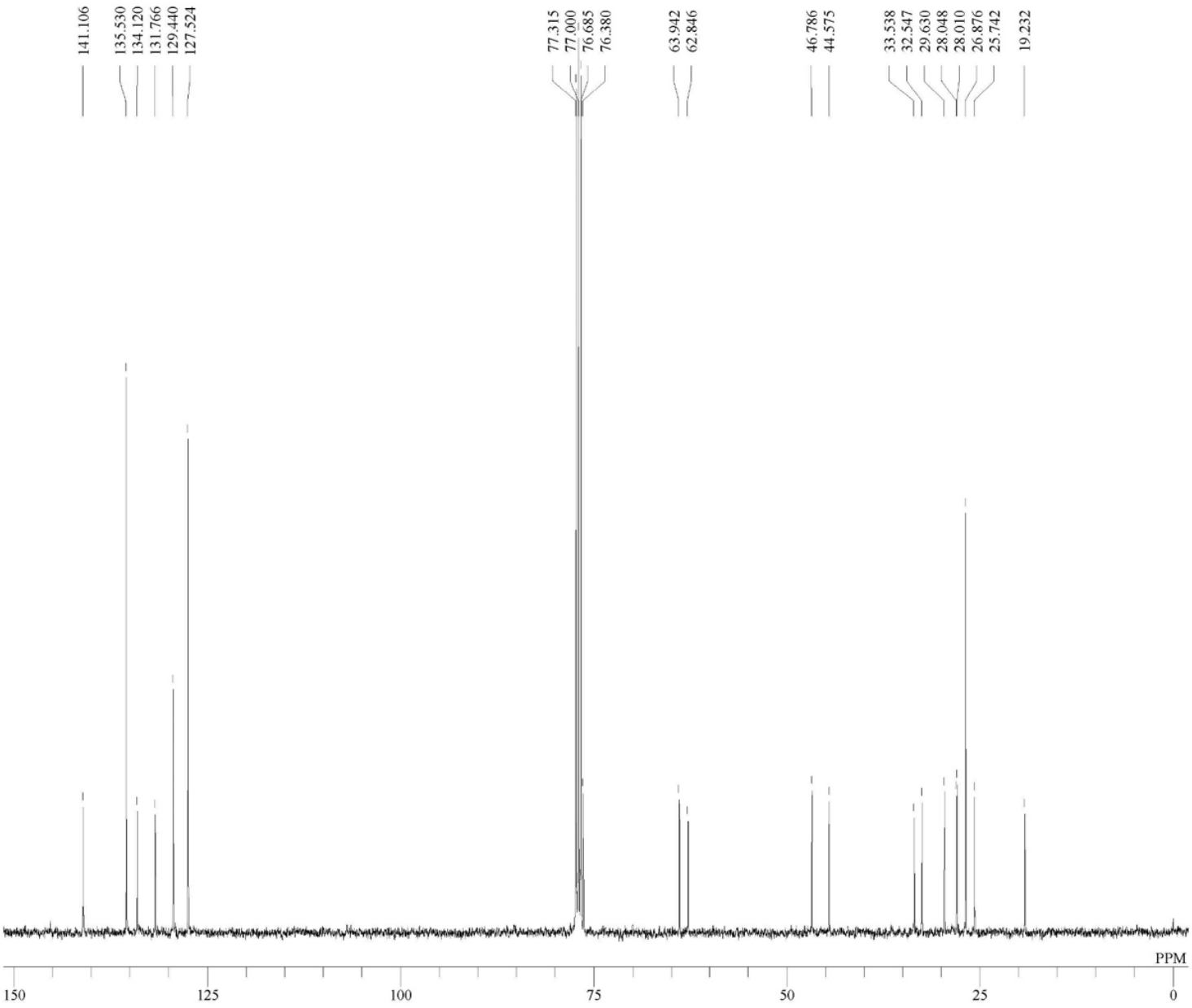


DFILE	13C_17.jdf
COMNT	single pulse decoupled gated N
DATIM	02-04-2020 17:35:19
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	190
ACQTM	0.0000 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	22.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50

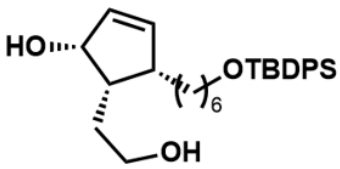


17

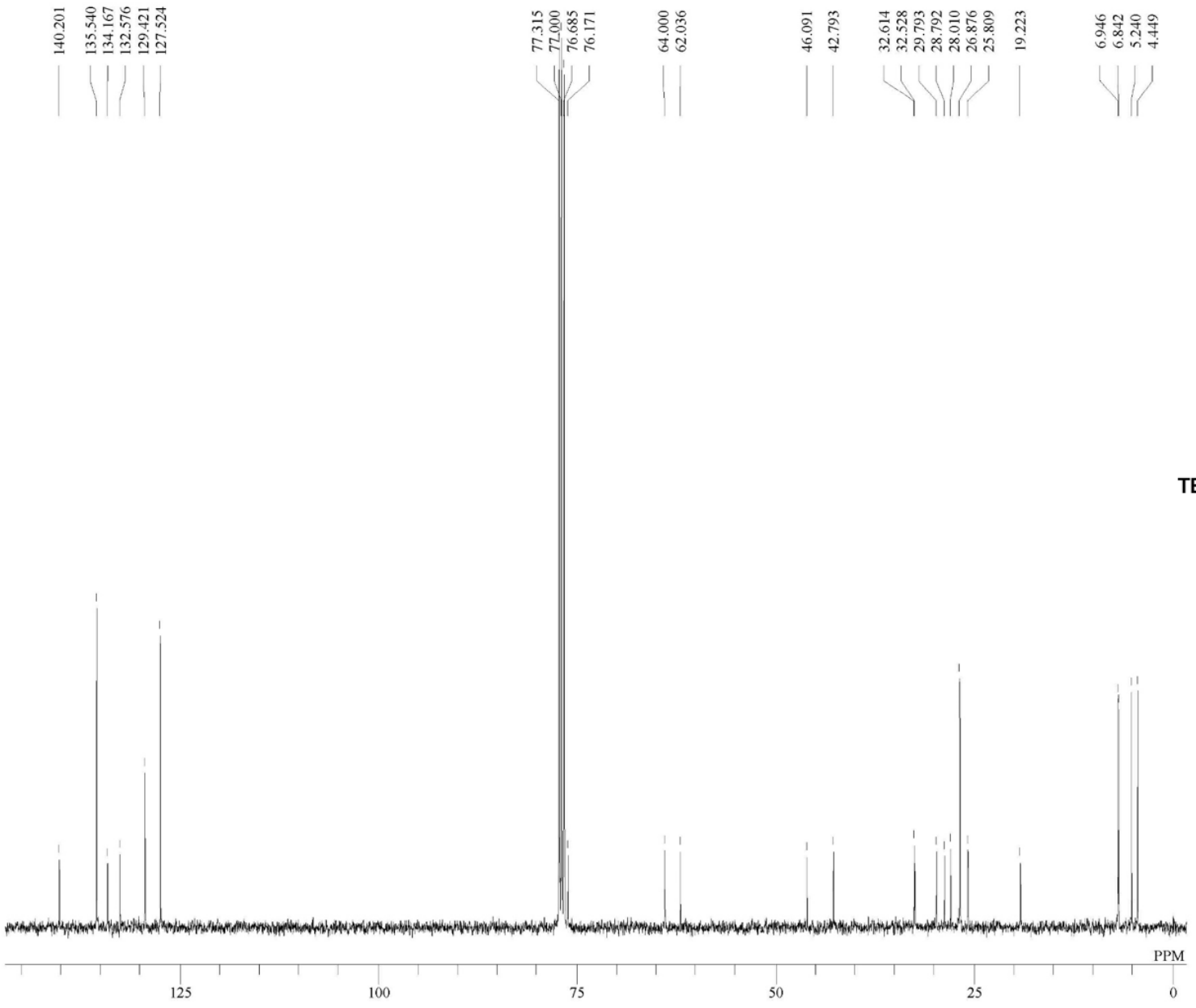

176.457
135.521
134.053
129.478
127.543
92.717
77.315
77.000
76.676
63.819
40.382
40.143
38.828
32.414
29.955
29.383
28.696
28.372
28.191
26.876
25.627
19.232
DFILE 13C-iodolactone.jdf
COMNT single pulse decoupled gated N
DATIM 03-04-2020 16:52:56
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32780
FREQU 31407.04 Hz
SCANS 384
ACQTM 0.0000 sec
PD 2.0000 sec
PW1 3.37 usec
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.25 Hz
RGAIN 50
I
O
O
OTBDPS
6
PPM
175
150
125
100
75
50
25
0



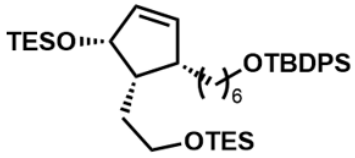
DFILE	13C_18.jdf
COMNT	single pulse decoupled gated N
DATIM	05-04-2020 18:10:58
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	784
ACQTM	0.0000 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	23.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50



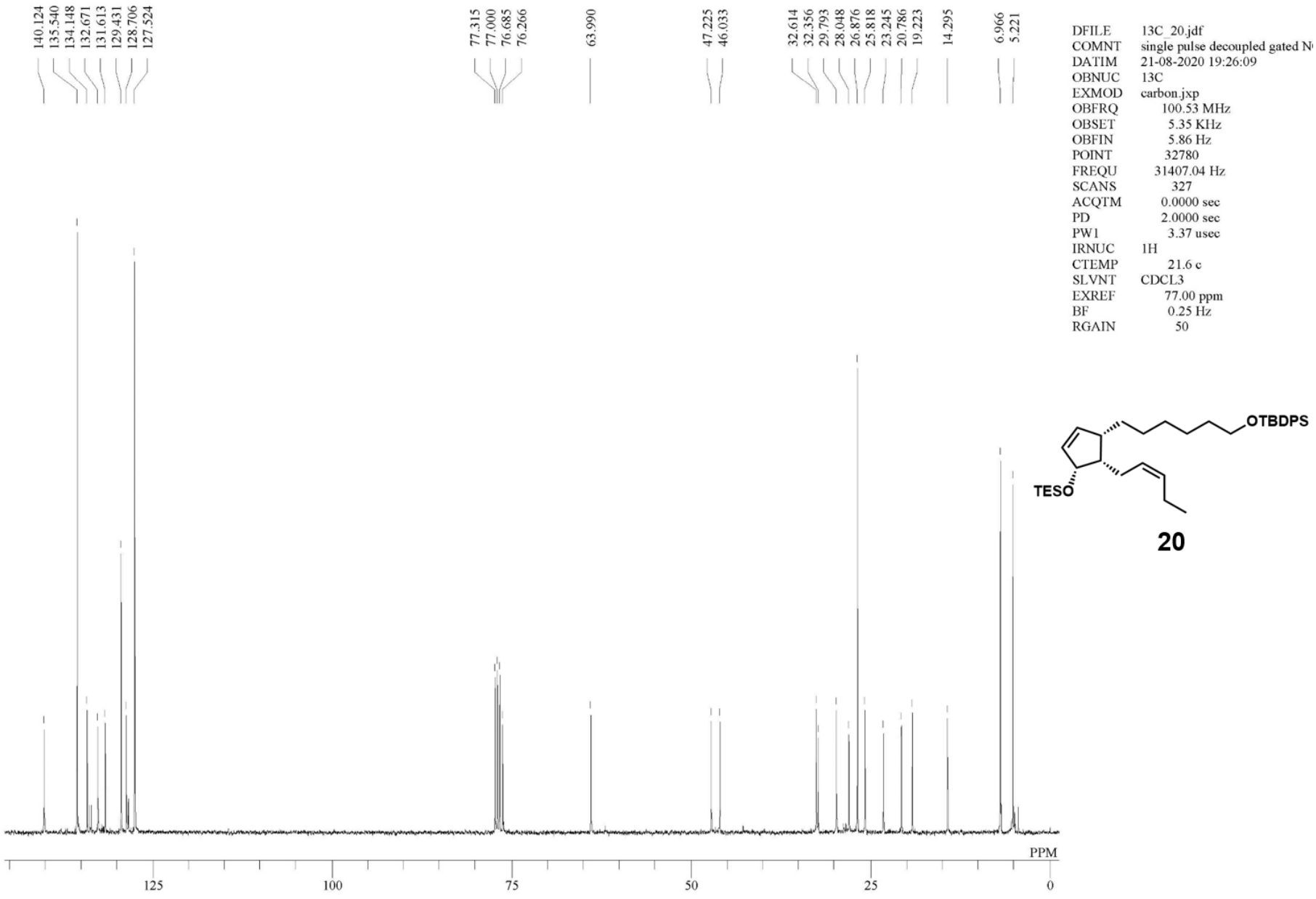
18

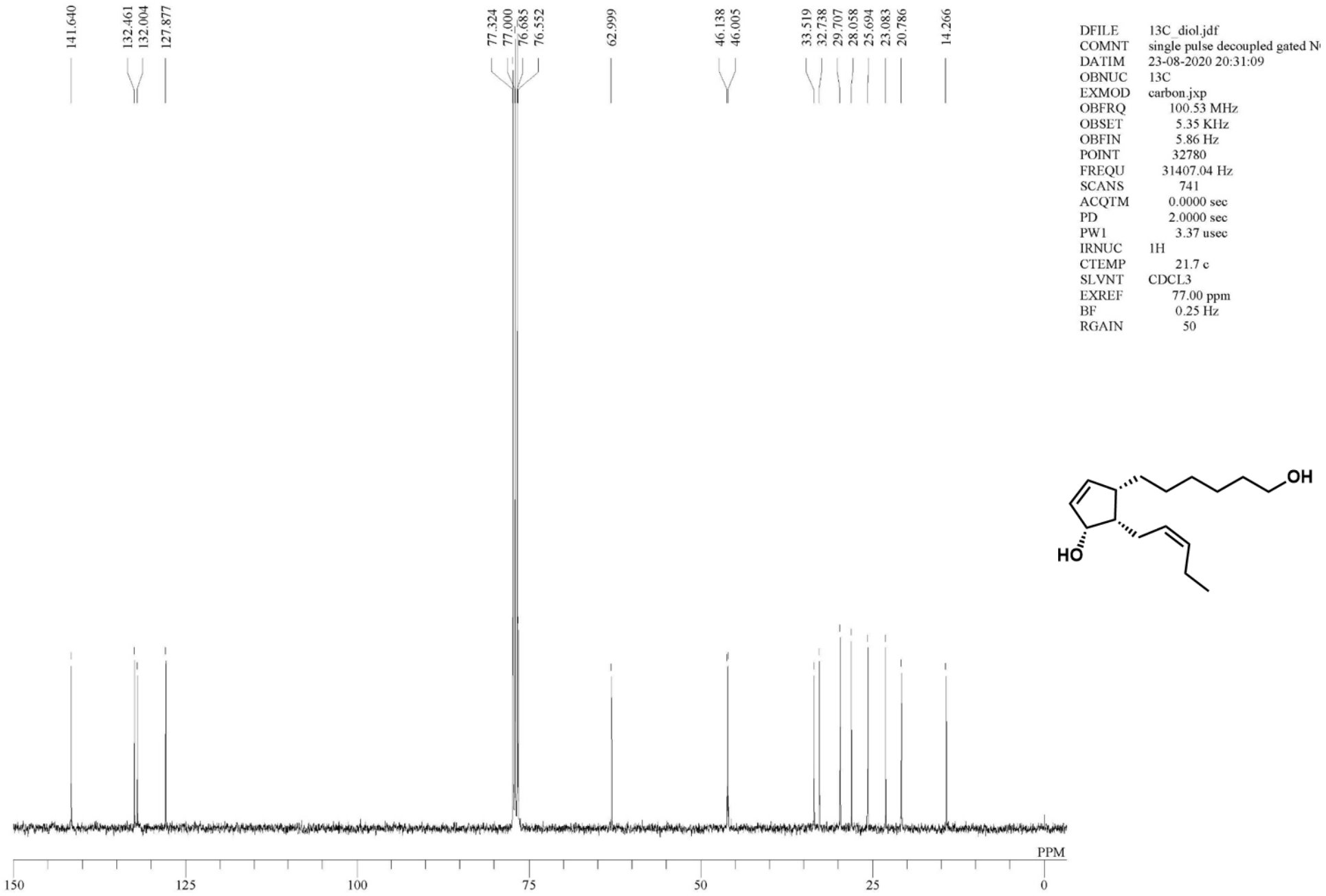


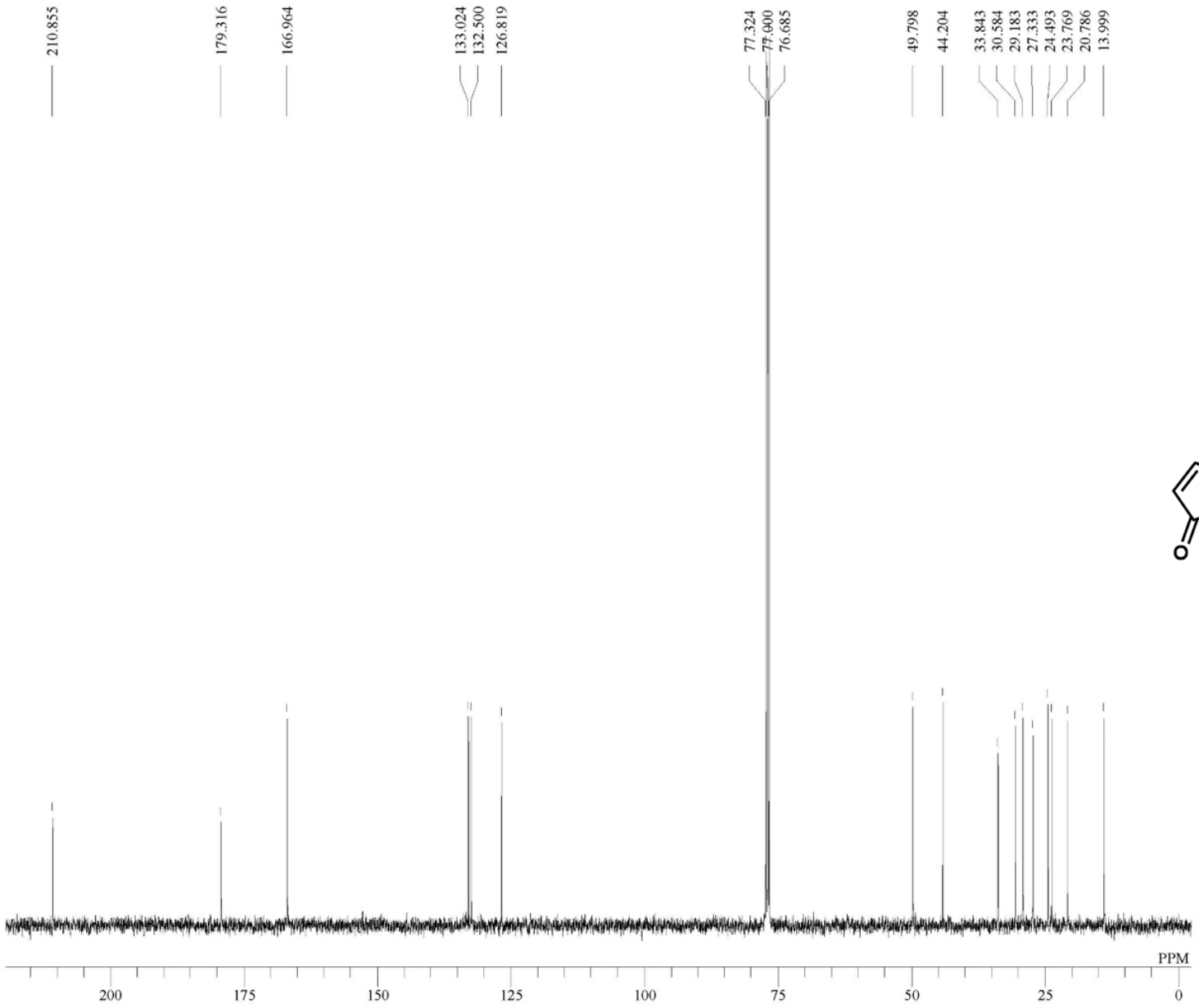
DFILE	13C_19.jdf
COMNT	single pulse decoupled gated N
DATIM	07-04-2020 17:36:05
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	523
ACQTM	0.0000 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50



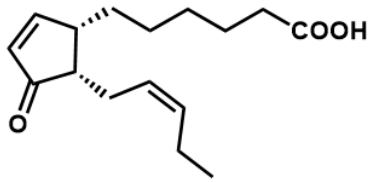
19


140.124
135.540
134.148
132.671
131.613
129.431
128.706
127.524
77.315
77.000
76.685
76.266
63.990
47.225
46.033
32.614
32.356
29.793
28.048
26.876
25.818
23.245
20.786
19.223
14.295
6.966
5.221
DFILE 13C_20.jdf
COMNT single pulse decoupled gated N
DATIM 21-08-2020 19:26:09
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32780
FREQU 31407.04 Hz
SCANS 327
ACQTM 0.0000 sec
PD 2.0000 sec
PW1 3.37 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.25 Hz
RGAIN 50
OTBDPS
TESO
20
PPM
125
100
75
50
25
0

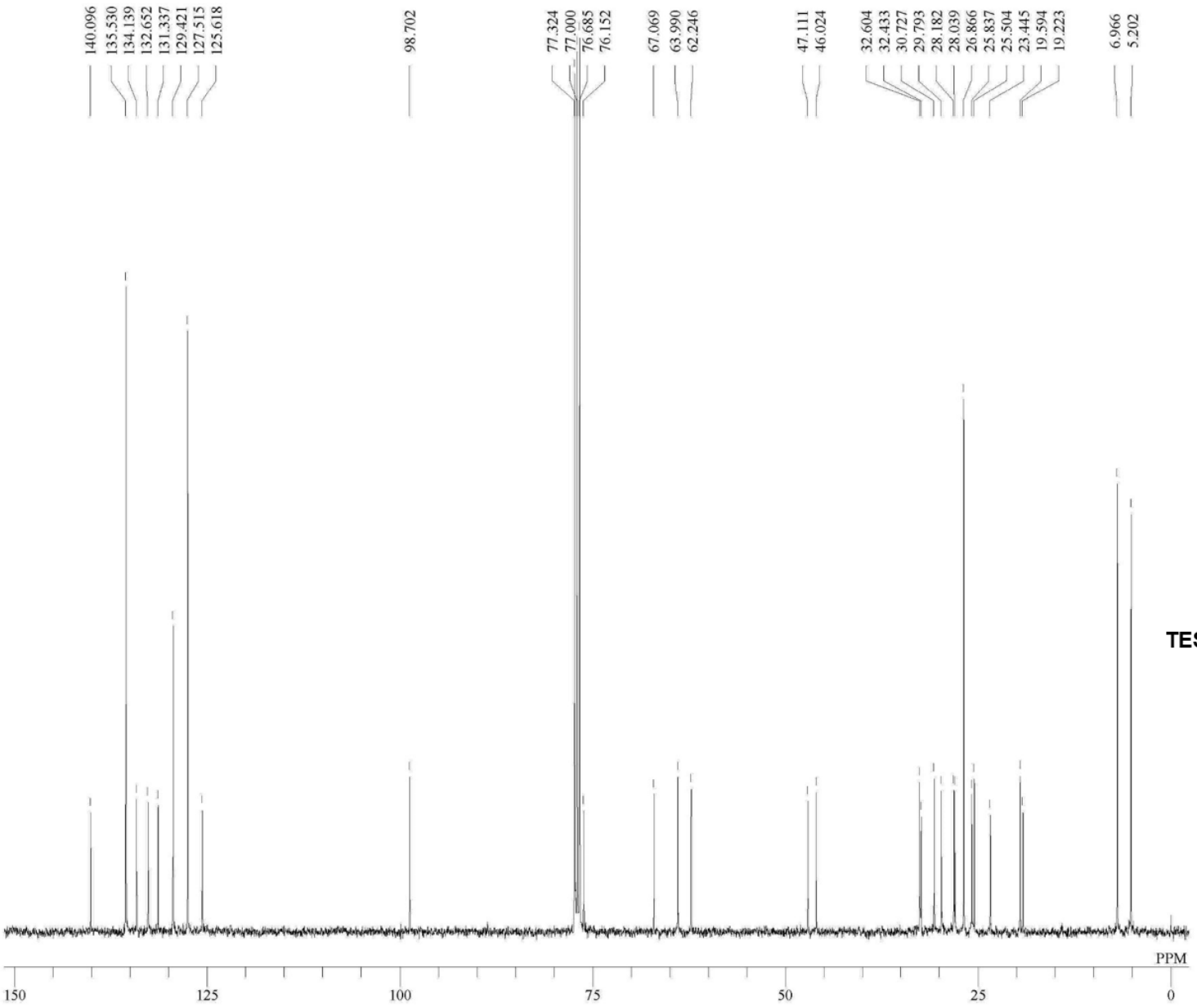

141.640
132.461
132.004
127.877
77.324
77.000
76.685
76.552
62.999
46.138
46.005
33.519
32.738
29.707
28.058
25.694
23.083
20.786
14.266
DFILE 13C_diol.jdf
COMNT single pulse decoupled gated N
DATIM 23-08-2020 20:31:09
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32780
FREQU 31407.04 Hz
SCANS 741
ACQTM 0.0000 sec
PD 2.0000 sec
PW1 3.37 usec
IRNUC 1H
CTEMP 21.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.25 Hz
RGAIN 50
OH
HO
PPM
150
125
100
75
50
25
0



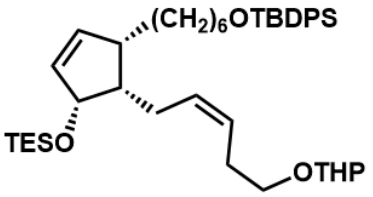
DFILE	13C_04.jdf
COMNT	single pulse decoupled gated N
DATIM	24-08-2020 18:58:19
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	337
ACQTM	0.0000 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	21.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50



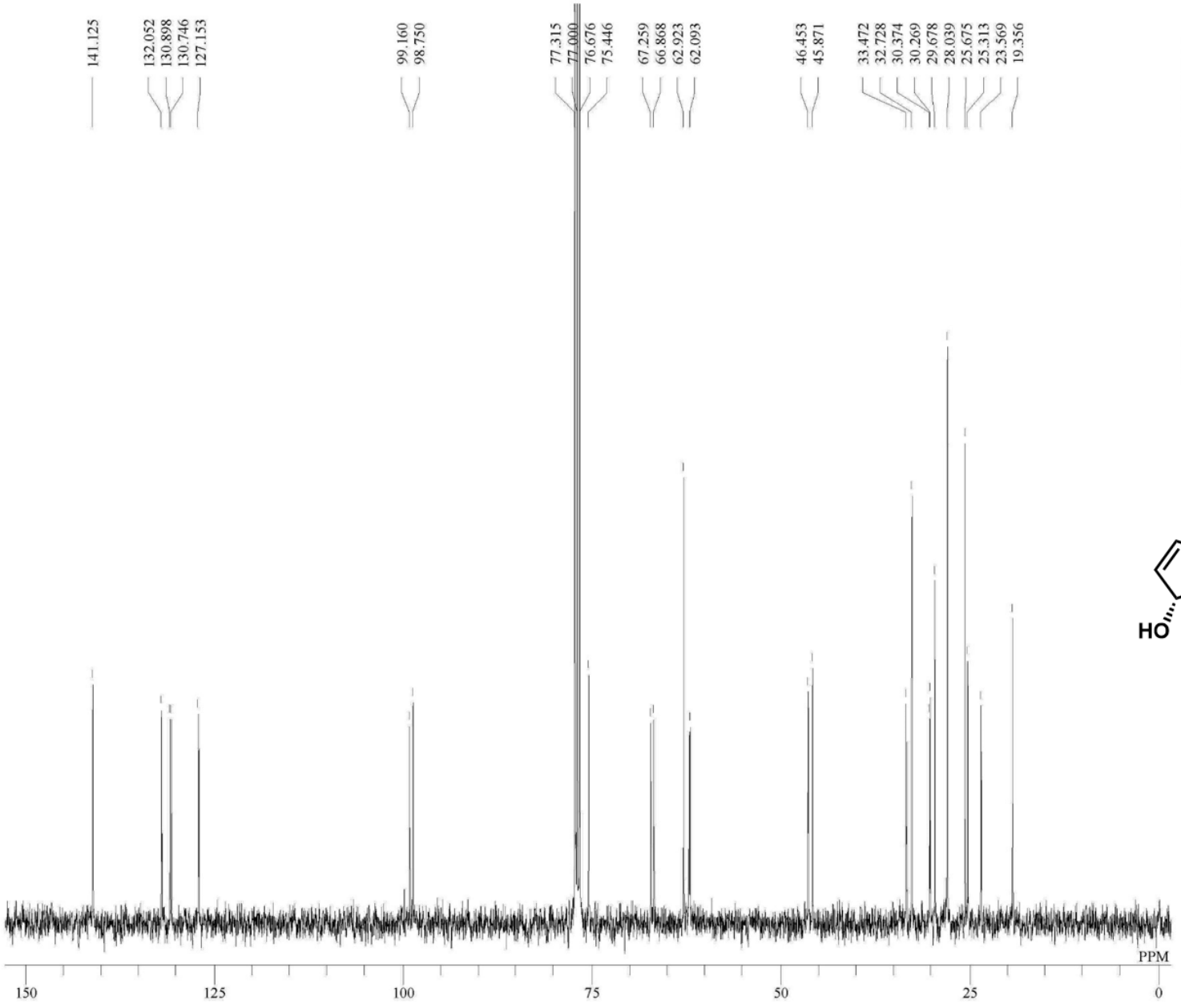
dn-*cis*-OPDA (**4**)



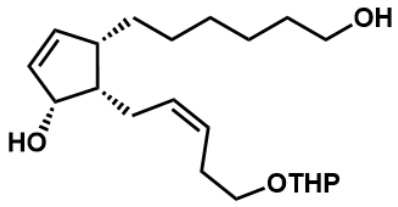
DFILE	Wittig_Carbon-1-1.jdf
COMNT	single pulse decoupled gated N
DATIM	17-08-2020 11:11:59
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	1024
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	21.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50



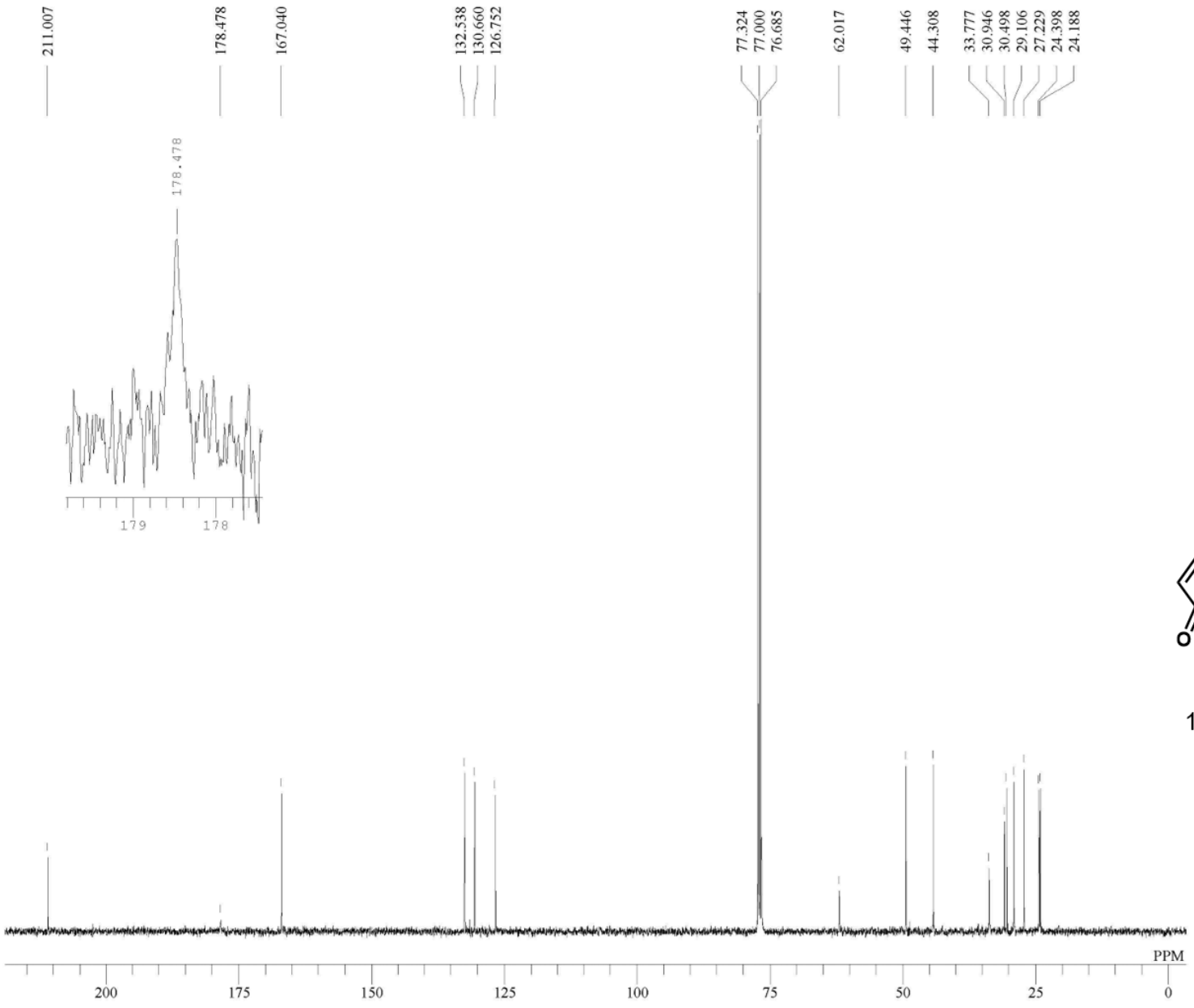
21



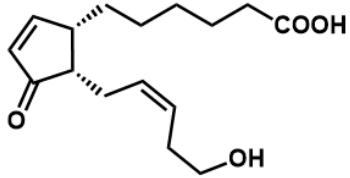
DFILE	TBAF_13C-1.jdf
COMNT	single pulse decoupled gated N
DATIM	01-09-2020 11:29:24
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	201
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	22.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50



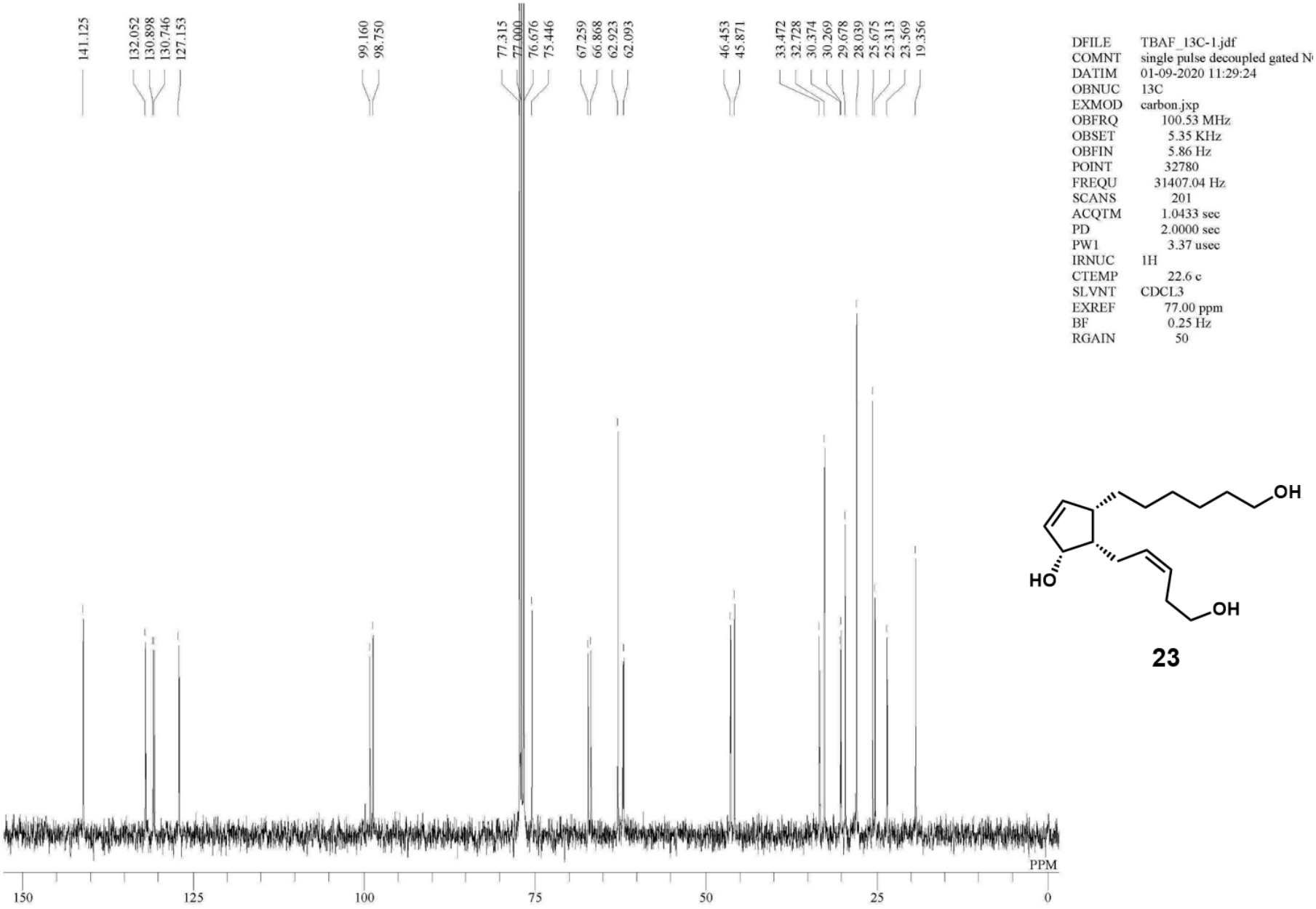
22



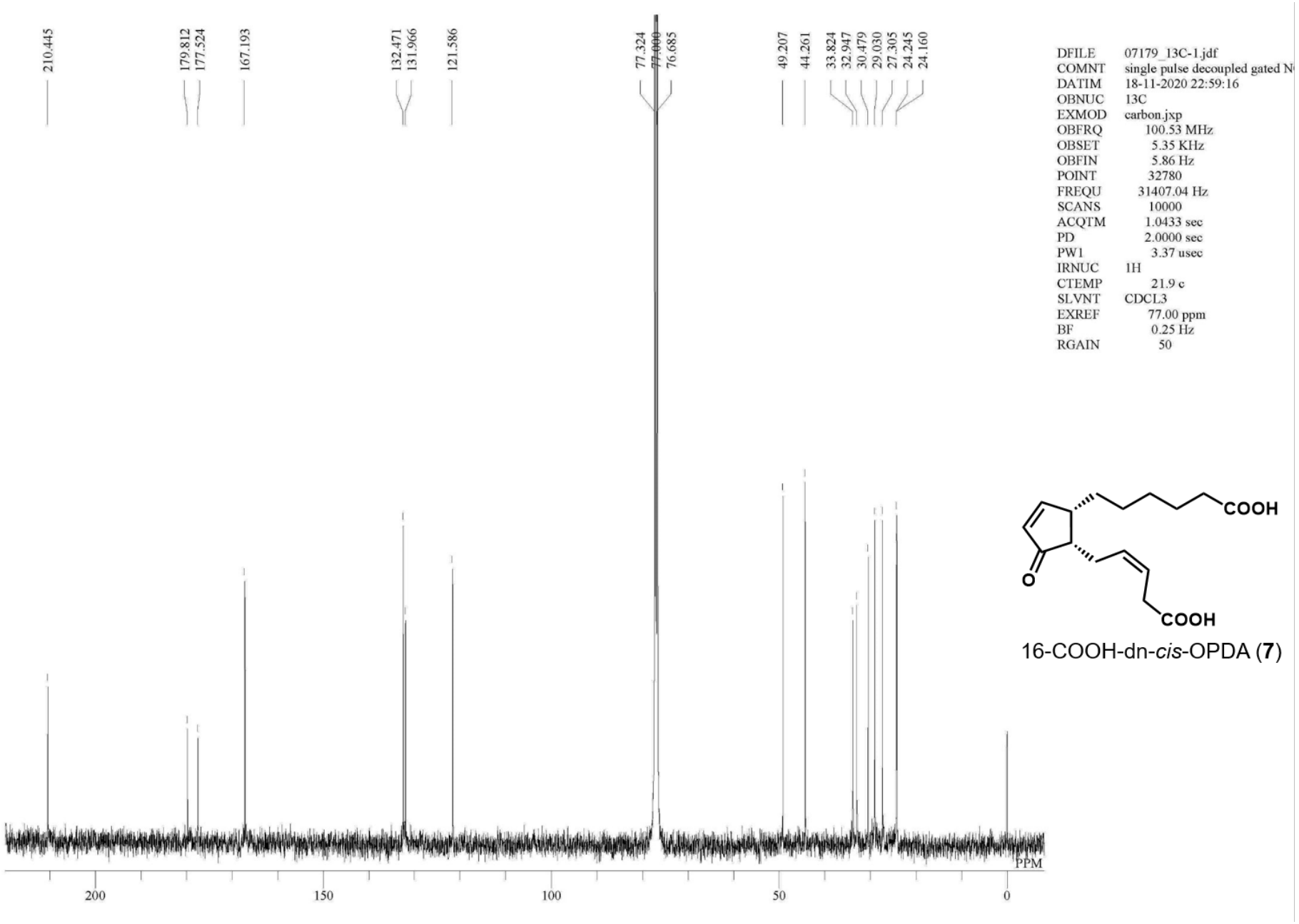
DFILE	16OHdncisOPDA_Carbon-1.jd
COMNT	single pulse decoupled gated N
DATIM	02-12-2020 17:35:13
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	1024
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	23.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50



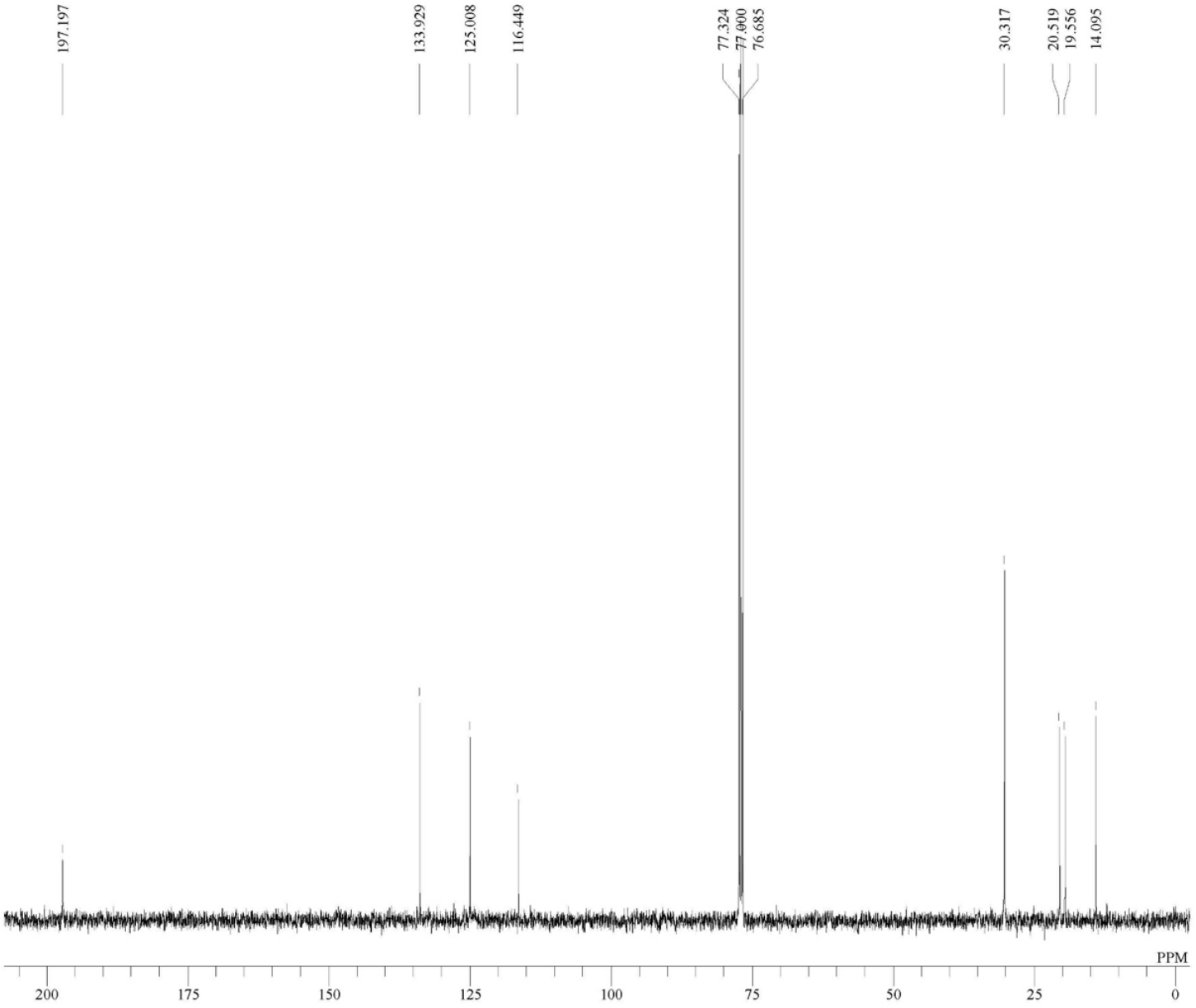
16OH-dn-*cis*-OPDA (**6**)


141.125
132.052
130.898
130.746
127.153
99.160
98.750
77.315
77.000
76.676
75.446
67.259
66.868
62.923
62.093
46.453
45.871
33.472
32.728
30.374
30.269
29.678
28.039
25.675
25.313
23.569
19.356
DFILE TBAF_13C-1.jdf
COMNT single pulse decoupled gated N
DATIM 01-09-2020 11:29:24
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32780
FREQU 31407.04 Hz
SCANS 201
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.37 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.25 Hz
RGAIN 50
OH
HO
OH
PPM
150
125
100
75
50
25
0

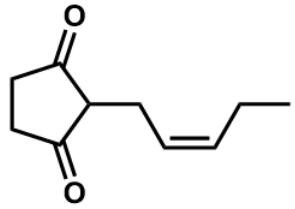
23



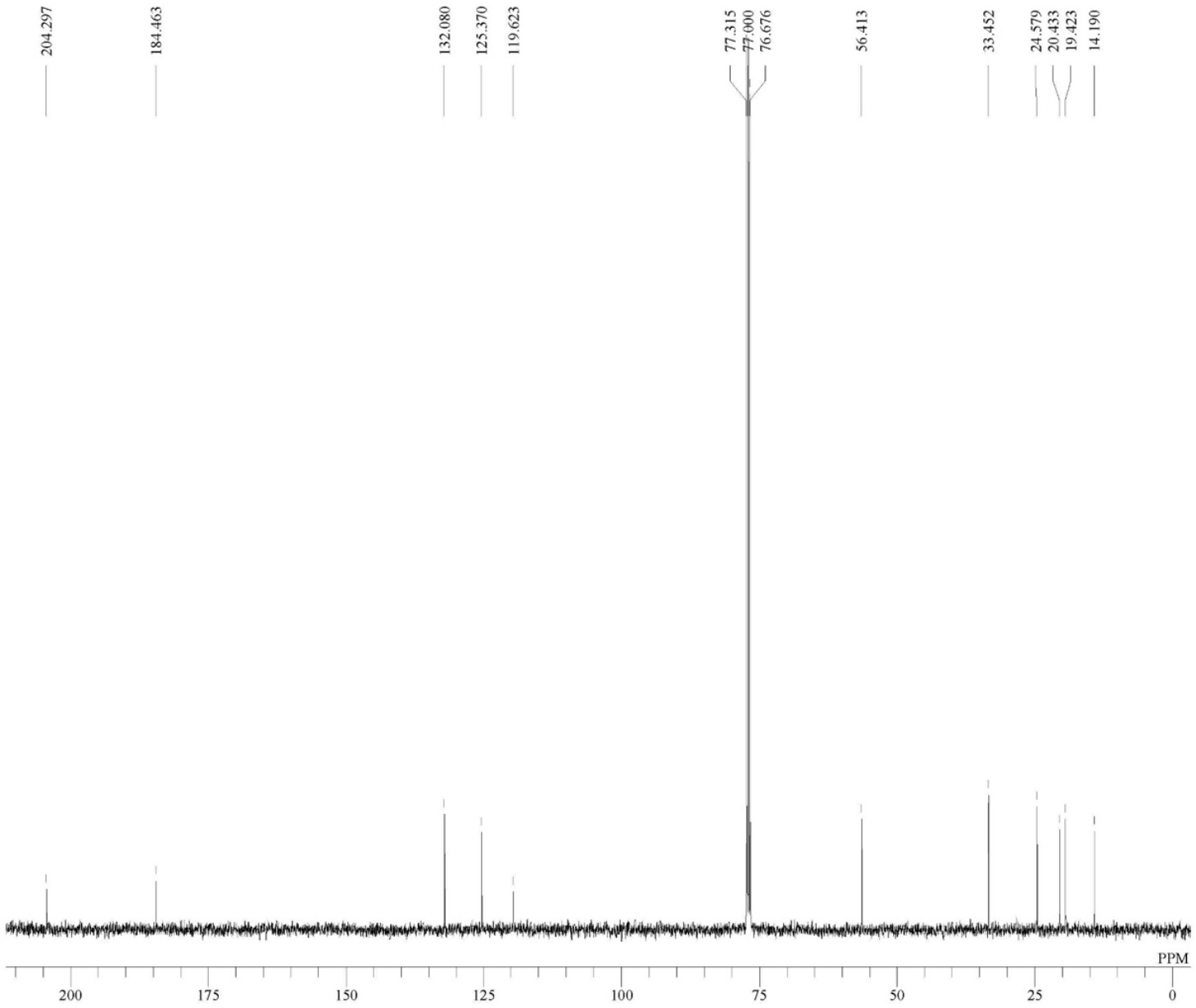
16-COOH-dn-*cis*-OPDA (**7**)



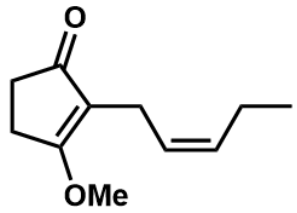
DFILE	27_Carbon-1-1.jdf
COMNT	single pulse decoupled gated N
DATIM	19-08-2020 19:38:27
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	208
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	21.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50



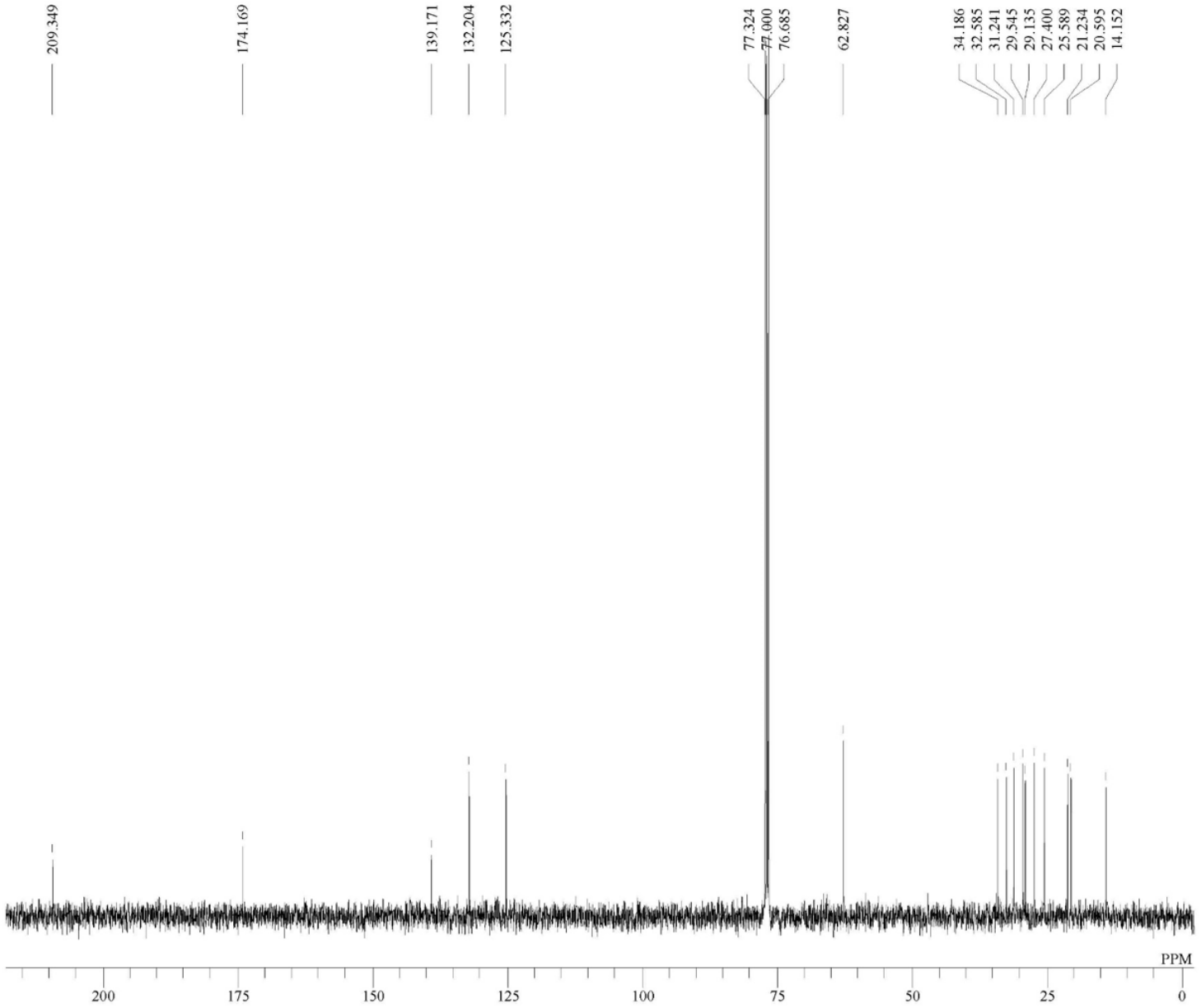
27



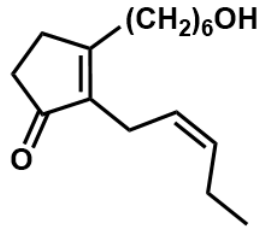
DFILE	28_Carbon-2-1.jdf
COMNT	single pulse decoupled gated N
DATIM	25-08-2020 12:04:35
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	520
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50



28



DFILE	30 target_Carbon-1-1.jdf
COMNT	single pulse decoupled gated N
DATIM	30-07-2020 17:29:56
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	99
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	24.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50



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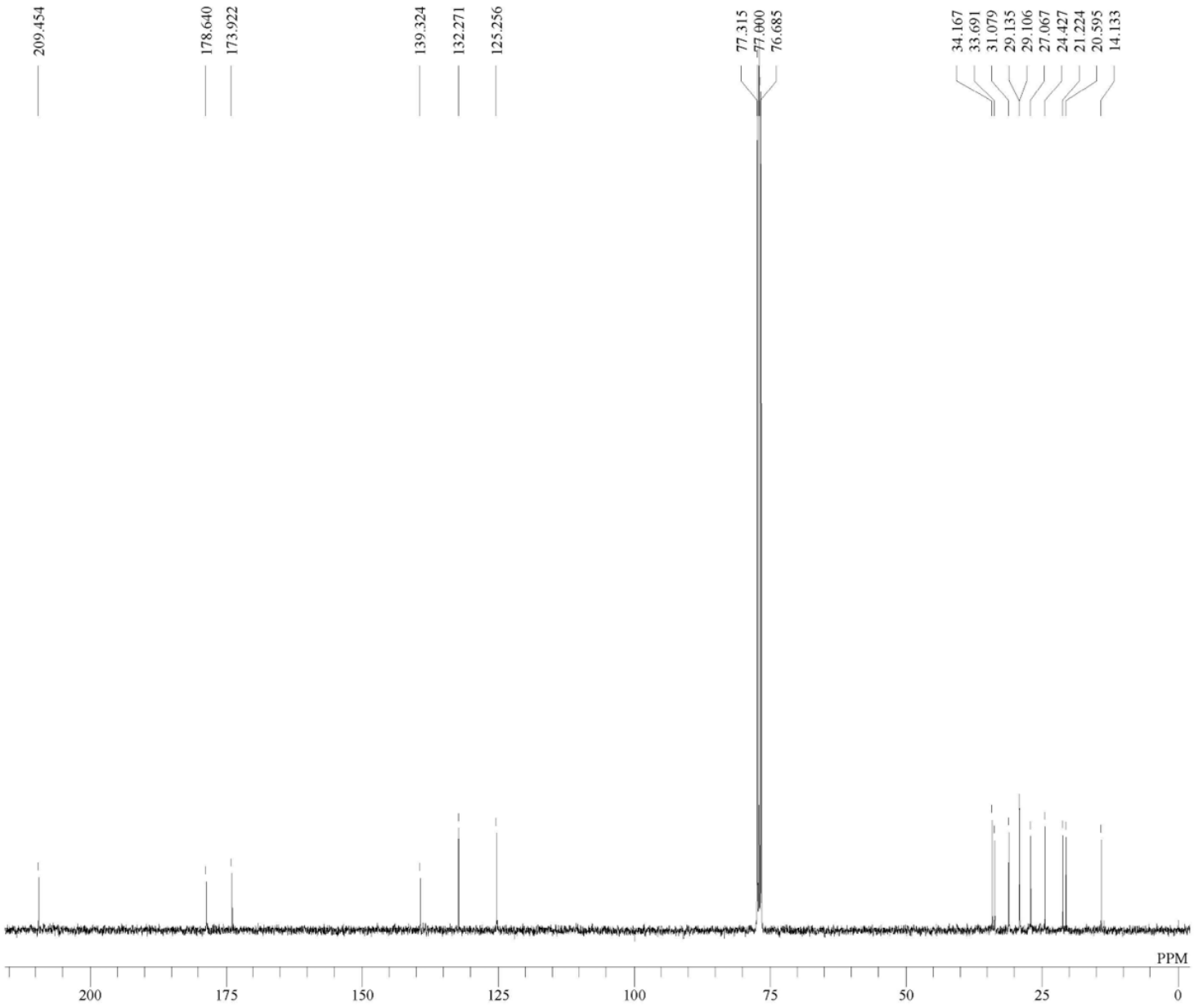
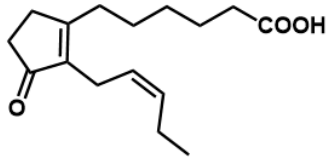
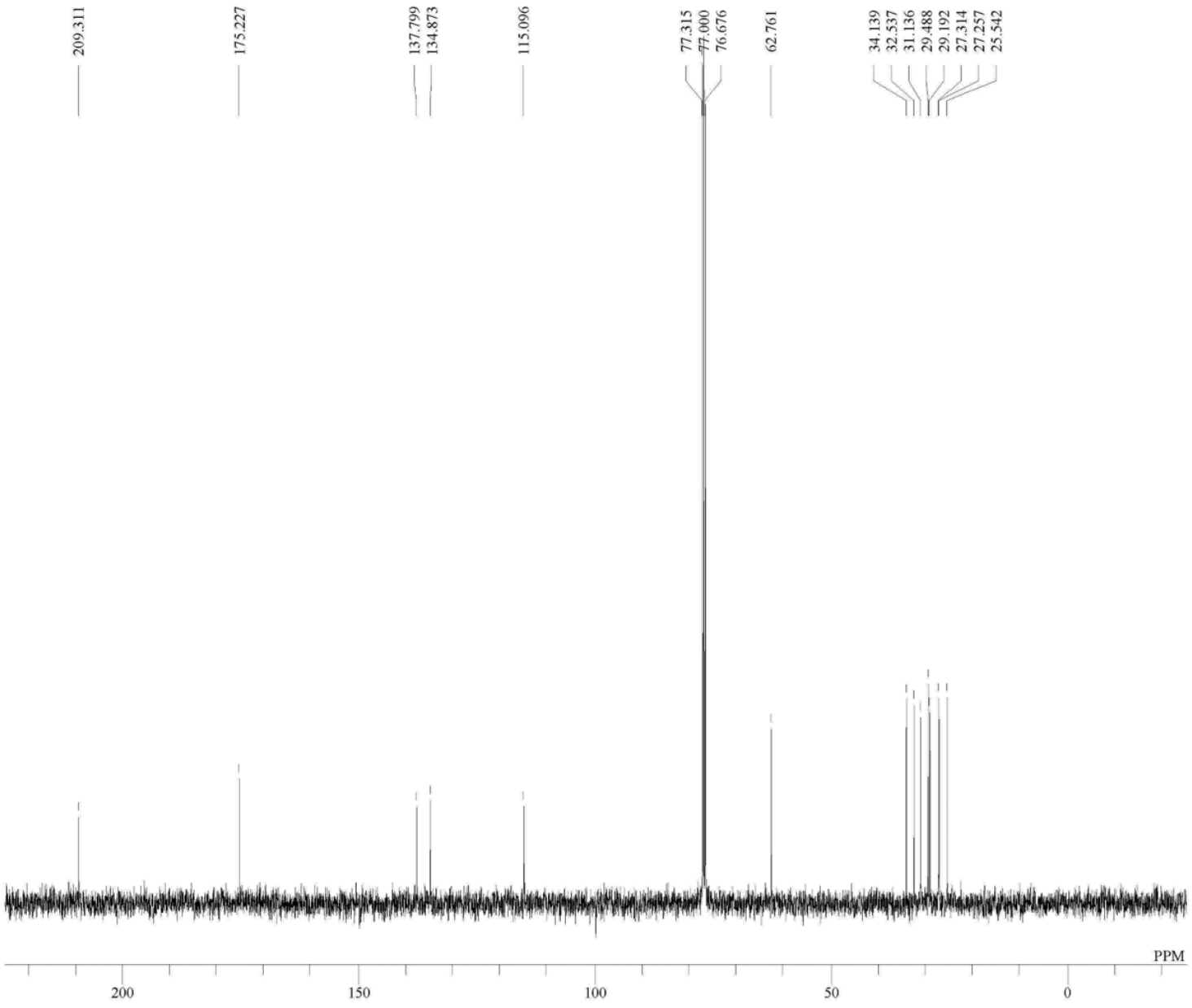


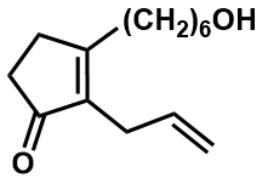
DFILE	5_Carbon-1-1.jdf
COMNT	single pulse decoupled gated N
DATIM	31-07-2020 18:50:42
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	1032
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	24.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50



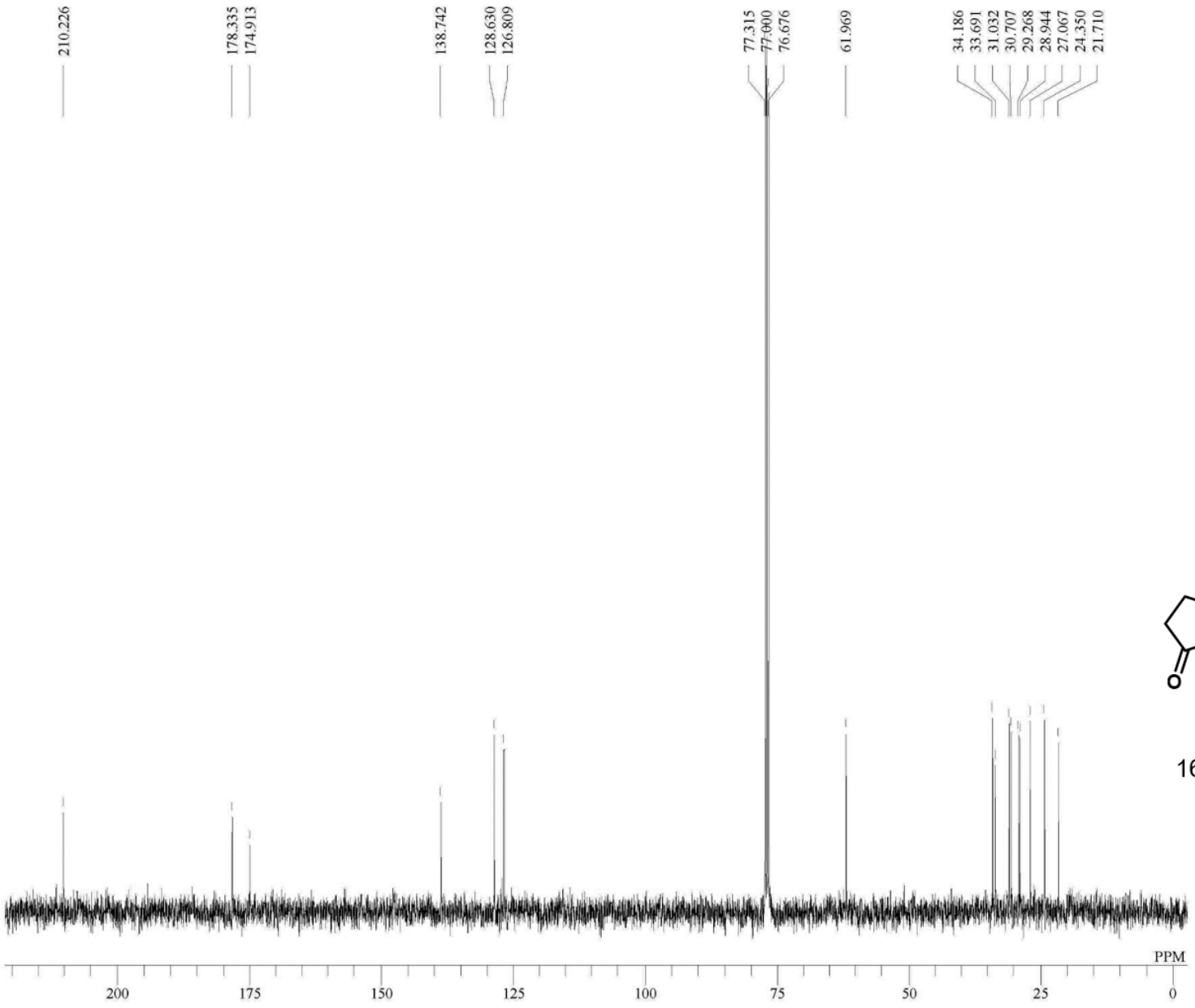
dn-*iso*-OPDA (**5**)



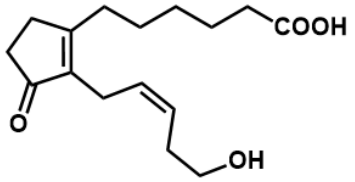
DFILE	33 *fOfŠfjff [f<_*Carbon-1-1.jd
COMNT	single pulse decoupled gated N
DATIM	30-10-2020 20:59:35
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	74
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50



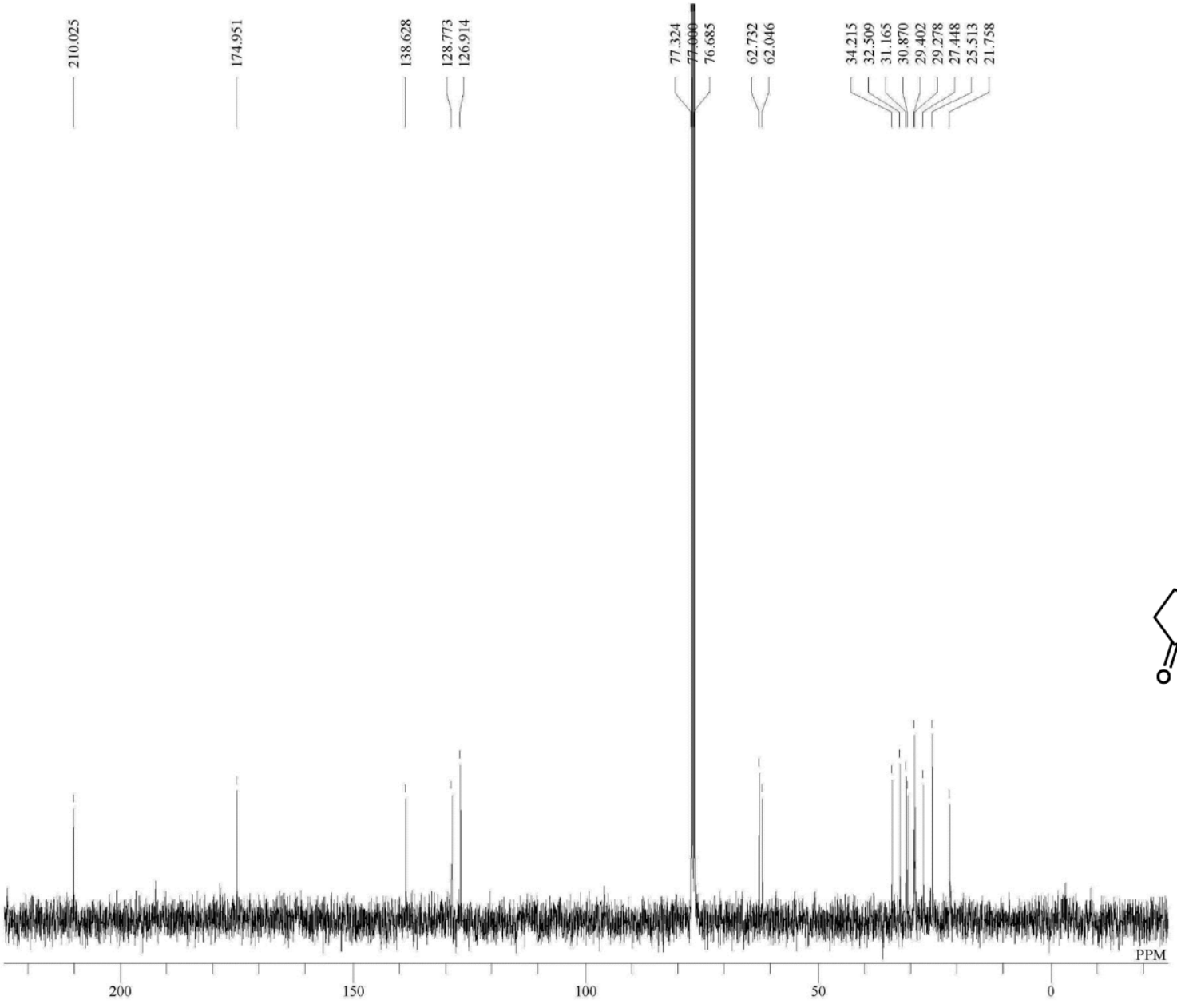
33



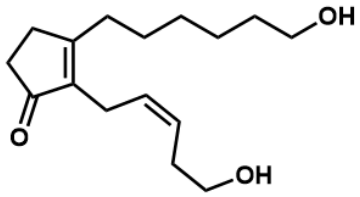
DFILE	07195_Carbon_64-1.jdf
COMNT	single pulse decoupled gated N
DATIM	12-12-2020 22:42:08
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	65
ACQTM	0.0000 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50



16-OH-dn-*iso*-OPDA (**8**)



DFILE	35 fWfqfhf fLfV_Carbon-1-1
COMNT	single pulse decoupled gated N
DATIM	30-10-2020 20:43:38
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32780
FREQU	31407.04 Hz
SCANS	174
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.37 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.25 Hz
RGAIN	50



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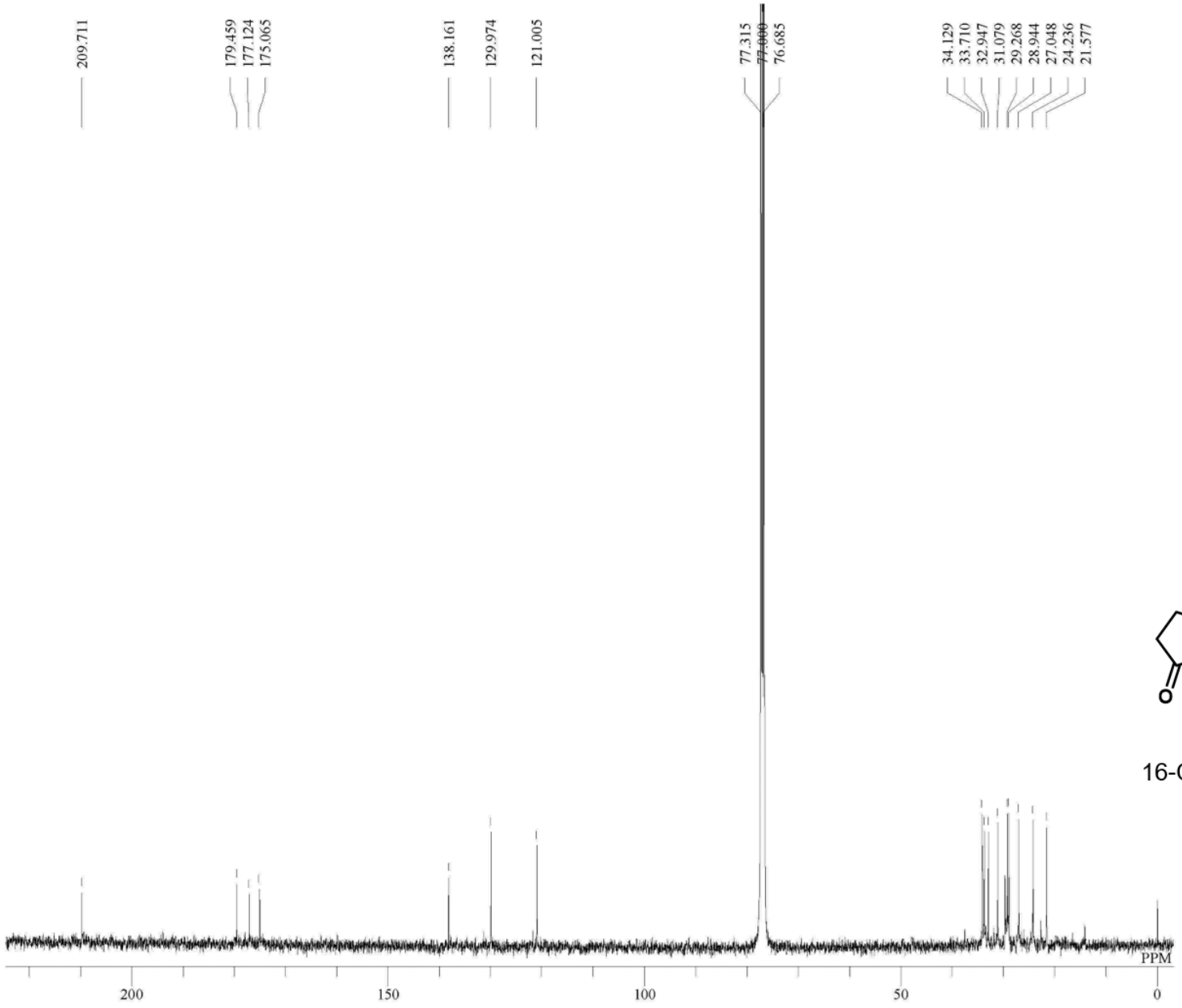
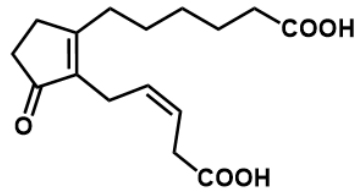


DFILE 07197_Carbon-1-1.jdf
COMNT single pulse decoupled gated N
DATIM 13-12-2020 18:01:10
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32780
FREQU 31407.04 Hz
SCANS 15000
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.37 usec
IRNUC 1H
CTEMP 19.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.25 Hz
RGAIN 50



16-COOH-dn-*iso*-OPDA (**9**)