Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Harnessing the potential diversity of resinic diterpenes through visible light-induced sensitized oxygenation coupled to Kornblum-DeLaMare and Hock reactions

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General Information

All reactions were carried out in oven-dried vessels under an atmosphere of argon and in anhydrous solvents unless stated otherwise. Resinic acids were obtained from our chemical collection as products from Helix Biotech Ltd company (Vancouver, Canada). Dichloromethane was distilled over calcium hydride. Commercial ethanol (HPLC grade) was directly used. Organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure on a Büchi rotary evaporator. Reactions were monitored by TLC on Merck silica gel 60-F_{254} aluminium sheets (ref.1.05554.0001), using UV absorption then vanillin-H_2SO_4 (1% vanillin in ethanol + 2% H_2SO_4) as a staining system. The products were purified by silica gel column chromatography (Geduran silica gel Si 60, 40-63 µm). NMR spectra were recorded on a Bruker 400 MHz Avance III or Bruker 600 MHz Avance III spectrometer. Chemical shifts (δ) are quoted in ppm with internal calibration from residual solvent peak ($CDCl_3$: 7.26, 77.0 ppm for ^1H and ^{13}C NMR, respectively). All coupling constants (*J*) are quoted in Hertz. The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). High resolution mass spectra (HR-MS) were measured on an Applied Biosystem QSTAR Pulsar-I spectrometer, using electrospray ionization. Infrared spectra were recorded on a Shimatzu 8400S FTIR spectrometer. Specific rotations were recorded on a Perkin Elmer 341 polarimeter at 20°C. Melting points were measured on a Büchi B-545 apparatus.

I: Experimental Procedures and Spectroscopic Data

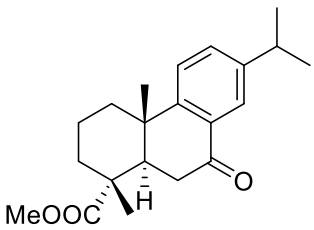
General procedure for methylation of resinic acids

To a stirred solution of acid **1**, **6** or **7** in toluene/methanol (3.6:1, c = 0.1 M) at 0 °C was added $TMSCHN_2$ (2.0 M in Et_2O, 1.1 equiv.) dropwise. The cooled bath was removed and the reaction mixture was stirred for 3h before being concentrated. The crude material was purified by chromatography on silica gel (100:5 cyclohexane/EtOAc) to afford the corresponding ester **8**, **10** or **11** (compound **11** was obtained as an inseparable 4:1 mixture with **10**).[1].

General procedure for hydroperoxidation of resinic derivatives

In a glass tube stopped with a septum, compound **3**, **4**, **8**, **10**, or **11** (1 equiv.) was dissolved in CH_2Cl_2 (c = 15 mM) and TPP (0.02 equiv) was added before bubbling oxygen (balloon) through the solution for 20 min. The reaction mixture was then exposed to visible light (XXCell spiral bulb, white daylight 7 W, 6500 K, 350 lumens). All was enveloped with an aluminum foil to minimize energy dispersion around the reaction. The reaction was monitored by TLC until disappearance of the starting material. At the end of the reaction, the mixture was concentrated under reduced pressure. The resulting crude material was purified by chromatography on silica gel (cyclohexane/EtOAc system) to afford peroxide compounds **12**, **13**, **14**, **15** or **16**.[2]

7-Oxodehydroabietic acid, methyl ester (17)



Into a reaction tube containing hydroperoxyde **14** (21 mg, 0.062 mmol) in CH_2Cl_2 (1 mL) was added pyridine (0.3 mL, 3.72 mmol), Ac_2O (0.3 mL, 3.17 mmol) and DMAP (0.15 mg, 0.0012 mmol). The reaction mixture was then stirred at room temperature for 24 hours before quenching with cold water. It was extracted three times with CH_2Cl_2, washed with a saturated

[1] (a) B. Zhou, X. Li, H. Feng, L. Yuanchao, *Tetrahedron* 2010, **66**, 5396; (b) M. Chu, R. M. Coates, *J. Org. Chem.* 1992, **57**, 4590; (c) W. A. Ayer, J. B. Macaulay, *Can. J. Chem.* 1987, **65**, 7.

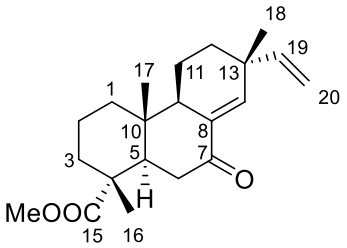
[2] (a) W. H. Schuller, R. V. Lawrence, *J. Am. Chem. Soc.*, 1961, **83**, 2563; (b) A. F. Barrero, J. F. Sanchez, E. J. Alvarez-Manzaneda R., M. Munoz Dorado, A. Haidour, *Phytochemistry* 1991, **30**, 593; (c) K. Krohn, E. Budianto, U. Florke, B. M. Hausen, *Liebigs Ann. Chem.* 1992, 911 (d) F. G. Cruz, M. D. Cerqueira, N. F. Roque, *J. Braz. Chem. Soc.*, 2003, **14**, 456.

solution of $CuSO_4$, brine, water, and dried over Na_2SO_4. The resulting crude material was purified by column chromatography on silica gel to afford **17** as a colorless resin (15 mg, 73%). Spectral data were consistent with those found in the literature.[1c,3] $[\alpha]^{25}_D$ = +11.4 (c 1, $CHCl_3$; lit.[4] +15.1, c 3.3, $CHCl_3$).

Procedure for the one-pot Schenck-ene hydroperoxidation/Kornblum-DeLaMare rearrangements of 10 or 11 into 18 or 19, respectively

In a reaction tube containing **10** or **11** (1.0 equiv.) in CH_2Cl_2 (0.06 M) was added TPP (0.02 equiv.), pyridine (60 equiv.), Ac_2O (50 equiv.) and DMAP (0.02 equiv.). Oxygen gas was passed through the solution during 20 min. The reaction mixture was then stirred under visible light (XXCell spiral bulb, white daylight 7 W, 6500 K, 350 lumens) at room temperature for 16 or 36 hours. The mixture was quenched with cold water, extracted three times with CH_2Cl_2, washed with a saturated solution of $CuSO_4$, brine, water, and dried over Na_2SO_4. The resulting crude material was purified by column chromatography on silica gel to afford products **18** or **19**.

(–)-7-Oxosandaracopimaric acid, methyl ester (18)



Compound **18** (13 mg) was obtained as a white solid from methyl isopimarate **10** (23 mg, 0.0073 mmol) following the general procedure (53% yield). Data were consistent with those partially described in the literature.[4,5] Complete data are given thereafter:

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.88 (*s*, 3H, 17-H), 1.11 (*s*, 3H, 18-H), 1.18-1.23 (*m*, 1H, 1-Ha), 1.25 (*s*, 3H, 16-H), 1.40-1.47 (*m*, 1H, 11-Ha), 1.50-1.54 (*m*, 1H, 12-Ha), 1.58-1.66 (*m*, 3H, 2-H and 12-Hb), 1.67-1.71 (*m*, 1H, 3-Ha), 1.73-1.80 (*m*, 2H, 3-Hb and 11-Hb), 1.81-1.85 (*m*, 1H, 1-Hb), 2.16-2.20 (*m*, 1H, 9-H), 2.21-2.26 (*m*, 1H, 6-Ha), 2.30-2.36 (*m*, 2H, 5-H and 6-

[3] See also for a complete assignment of NMR data: S. M. C. S. Monteiro, A. J. D. Silvestre, A. M. S. Silva, J. A. S. Cavaleiro, V. Félix, M. G. B. Drew, *New J. Chem.*, 2001, **25**, 1091.
[4] A. V. Vorob'ev, V. Aleksei, V. V. Grishko, I. B. Ivshina, E. N. Shmidt, L. M. Pokorvskii, M. S. Kuyukina, G. A. Tolstikov, *Mendeleev Comm.* 2001, **11**, 72.
[5] B. Esquivel, J. Cardenas, L. Rodriguez-Hahn, T. P. Ramamoorthy, *J. Nat. Prod.*, 1987, **50**, 738.

Hb), 3.65 (*s*, 3H, OCH_3), 4.99 (*dd*, *J* = 0.8, 10.3 Hz, 1H, 20-H^Z), 5.01 (*dd*, *J* = 0.8, 17.5 Hz, 1H, 20-H^E), 5.81 (*dd*, *J* = 10.3, 17.5 Hz, 1H, 19-H), 6.74 (*dd*, *J* = 1.8, 2.5 Hz, 1H, 14-H).

^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 14.2 (C-17), 16.3 (C-16), 17.9 (C-2), 18.8 (C-11), 25.8 (C-18), 34.0 (C-12), 35.6 (C-10), 36.9 (C-3), 37.9 (C-1), 38.7 (C-6), 38.7 (C-13), 44.6 (C-5), 46.3 (C-4), 51.0 (C-9), 52.1 (OCH_3), 111.9 (C-20), 135.1 (C-8), 144.8 (C-14), 146.3 (C-19), 178.1 (C-15), 199.4 (C-7).

IR (film on NaCl) ν cm^{-1}: 3019, 3005, 2978, 2934, 2874, 1598, 1445, 1383, 1352, 1217, 1112.

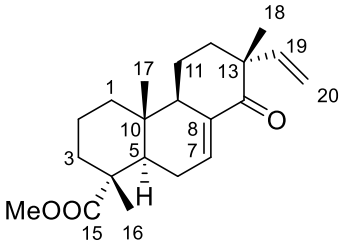
HRMS (ESI+) *m/z*: calculated for $C_{21}H_{31}O_3$: 331.2268 $[MH]^+$; found: 331.2271.

$[\alpha]_D^{25}$ = –9.0 (c 0.25, $CHCl_3$; lit.[4] –11, c 0.3, $CHCl_3$).

R_f (8:2 pentane/Et_2O): 0.26.

M.p. = 93-94 °C (lit. 89-90 °C).[5]

(–)-14-Oxoisopimaric acid, methyl ester (19)



Compound **19** (1.7 mg), was obtained as a colorless oil from methyl sandaracopimarate **11** (16 mg, 0.052 mmol) following the general procedure (10% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 0.88 (*s*, 3H, 17-H), 1.13-1.21 (*m*, 1H, 11-Ha), 1.18 (*s*, 3H, 18-H), 1.26 (*s*, 3H, 16-H), 1.54-1.67 (*m*, 4H, 2-H, 1-Ha and 3-Ha), 1.73-1.82 (*m*, 3H, 1-Hb, 3-Ha and 12-Hb), 1.83-1.90 (*m*, 2H, 11-Hb and 12-Hb), 1.90-1.96 (*m*, 1H, 6-Ha), 2.05 (*dd*, J = 4.3, 12.2 Hz, 1H, 5-H), 2.10-2.16 (*m*, 1H, 6-Hb), 2.23-2.30 (*m*, 1H, 9-H), 3.64 (*s*, 3H, OCH_3), 5.05 (*dd*, *J* = 1.0, 17.6 Hz, 1H, 20-H^E), 5.10, (*dd*, *J* = 1.0, 10.8 Hz, 1H, 20-H^Z), 6.18 (*dd*, *J* = 10.8, 17.6 Hz, 1H, 19-H), 6.88 (*m*, 1H, 7-H).

^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 14.2 (C-17), 16.8 (C-16), 18.0 (C-2), 18.3 (C-1), 23.9 (C-18), 26.3 (C-6), 33.9 (C-12), 34.9 (C-10), 36.8 (C-3), 37.9 (C-11), 43.9 (C-5), 46.2 (C-4), 48.6 (C-13), 52.0 (OCH_3), 52.5 (C-9), 112.5 (C-20), 135.7 (C-8), 137.4 (C-7), 143.6 (C-19), 178.5 (C-15), 203.1 (C-14).

IR (film on NaCl) ν cm^{-1}: 2947, 2926, 1726, 1684, 1615, 1558, 1456, 1387, 1367, 1245, 1189.

HRMS (ESI+) *m/z*: calculated for $C_{21}H_{30}NaO_3$ $[MNa]^+$: 353.2087; found: 353.2077.

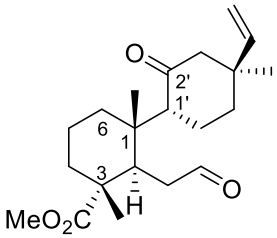
$[\alpha]_D^{25}$ = –29 (c 0.2, $CHCl_3$).

R_f (8:2 pentane/Et_2O): 0.25.

General procedure for the one-pot Schenck-ene oxygenation reaction/Hock rearrangement of 10/11 into 20/21

Esters **10** or **11** were dissolved in CH_2Cl_2 (0.01M) and TPP (0.02 equiv.) was added before oxygen was passed through for 20 min. The reaction mixture was then exposed to visible light for 16 or 36 hours, respectively, before adding TFA (3 equiv.) dropwise at 0°C and stirring for 3 hours at this temperature. The reaction was quenched with a saturated solution of $NaHCO_3$, extracted three times with CH_2Cl_2, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude material was purified by chromatography on silica gel to afford the compounds **20** and **21**, respectively.

(+)-(1*S*,1'*R*,2*R*,3*R*,4'*S*)-1,3,4'-trimethyl-2'-oxo-2-(2-oxoethyl)-4'-vinyl-[1,1'-bi(cyclohexane)]-3-carboxylic acid, methyl ester (20)



20 (7 mg) was obtained as a colorless oil from methyl isopimarate **10** (19 mg, 0.058 mmol) following the general procedure (35% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 0.95 (*s*, 3H, 4'-CH_3), 1.07 (*s*, 3H, 1-CH_3), 1.18 (*s*, 3H, 3-CH_3), 1.34-1.46 (*m*, 2H, 4-Ha and 6-Ha), 1.49-1.55 (*m*, 2H, 5-H), 1.62-1.79 (*m*, 4H, 6-Hb, 6'-Ha, 5'-H), 1.82-1.91 (*m*, 1H, 4-Hb), 2.00-2.08 (*m*, 2H, 6'-Hb, 3'-Ha), 2.25-2.37 (*m*, 3H, 2-CH_2a, 1'-H, 3'-Hb), 2.48 (*ddd*, *J* = 2.4, 5.4, 17.7 Hz, 1H, 2-CH_2b), 3.09 (*brs*, 1H, 2-H), 3.64 (*s*, 3H, OCH_3), 4.92 (*d*, *J* = 10.7 Hz, 1H, =CH_2^Z), 4.94 (*d*, *J* = 17.4 Hz, 1H, =CH_2^E), 5.79 (*dd*, *J* = 10.7, 17.4 Hz, 1H, –CH=), 9.75 (*pseudo-t*, *J* = 2.1 Hz, 1H, CHO).

^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 17.9 (C-5), 20.7 (1-CH_3), 22.6 (3-CH_3 and 4'-CH_3), 23.9 (C-6'), 32.0 (C-6), 34.0 (C-4), 36.6 (C-5'), 38.4 (C-2), 38.5 (C-1), 42.4 (C-4'), 42.7 (2-CH_2), 42.9 (C-1'), 46.9 (C-3), 52.2 (OCH_3), 54.7 (C-3'), 110.4 (=CH_2), 147.5 (–C=), 178.8 (–CO_2), 202.7 (CHO), 210.7 (C-2').

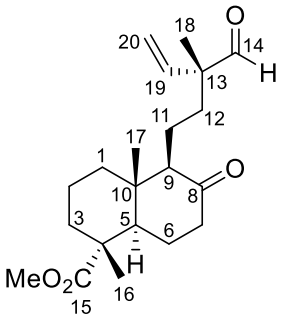
IR (film on NaCl) ν cm^{-1}: 3019, 2916, 2849, 1720, 1595, 1215, 1125.

HRMS (ESI+) *m/z*: calculated for $C_{21}H_{32}NaO_4$ $[MNa]^+$: 371.2193; found: 371.2206.

$[\alpha]_D^{25}$ = +5.2 (c 1, $CHCl_3$).

R_f (7:3 cyclohexane/Et_2O): 0.25.

(–)-(1*R*,4a*S*,5*R*,8a*R*)- 5-((*S*)-3-formyl-3-methylpent-4-en-1-yl)-1,4a-dimethyl-6-oxodecahydronaphtalene-1-carboxylic acid, methyl ester (21)



21 (4.2 mg) was obtained from methyl sandaracopimarate **11** (24 mg, 0.075 mmol) as a colorless oil (16% yield) and as an inseparable 3:1 mixture with isopimarate aldehyde **20**.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 0.72 (*s*, 3H, 17-H), 1.18 (*s*, 6H, 16-H and 18-H), 1.24-1.32 (*m*, 2H, 1-Ha and 12-Ha), 1.50-1.80 (*m*, 10H, 2-H, 3-H, 1-Hb, 6-H, 11-H, 12-Hb), 2.11 (*brd*, *J* = 10.0 Hz, 1H, 9-H), 2.33-2.40 (*m*, 3H, 5-H, 7-H), 3.70 (*s*, 3H, OCH_3), 5.15 (*d*, *J* = 17.4 Hz, 1H, 20-H^E), 5.28 (*d*, *J* = 10.6 Hz, 1H, 20-H^Z), 5.79 (*dd*, *J* = 10.6, 17.4 Hz, 1H, 19-H), 9.42 (*s*, 1H, 14-H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 15.0 (C-17), 16.2 (C-2), 16.6 (C-18), 17.7 (C-11), 17.8 (C-16), 25.9 (C-6), 34.8 (C-12), 37.0 (C-3), 38.1 (C-1), 42.0 (C-10), 42.3 (C-7), 47.3 (C-4), 48.5 (C-5), 52.2 (OCH_3), 53.1 (C-13), 64.9 (C-9), 116.7 (C-20), 138.7 (C-19), 178.8 (C-15), 203.1 (C-14), 210.9 (C-8).

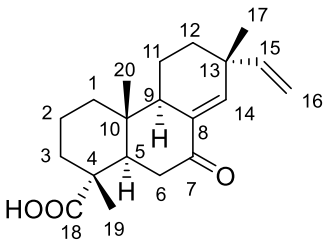
IR (film on NaCl) ν cm^{-1}: 3154, 2951, 2872, 2851, 1717, 1559, 1506, 1472, 1456, 1435, 1387, 1251.

HRMS (ESI+) *m/z*: calculated for $C_{21}H_{33}O_4$ $[MH]^+$: 349.2373; found: 349.2372.

$[\alpha]_D^{25}$ = –9.0 (c 0.5, $CHCl_3$).

R_f (7:3 cyclohexane/Et_2O): 0.25.

(–)-7-Oxo-13-*epi*-pimara-14,15-dien-18-oic acid (22)



Compound **18** (9 mg, 0.028 mmol) was dissolved into EtOH (0.3 mL), an aqueous solution of NaOH (14.8 M, 37 µL, 0.55 mmol) was added and the reaction mixture was refluxed for 16 hours. After cooling the mixture to room temperature, the reaction was quenched with water (1 mL), extracted with Et_2O (3 x 1 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude material was purified by chromatography on silica gel (95:5 CH_2Cl_2/Et_2O) to afford acid **22** as a colorless oil (6.6 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 0.88 (*s*, 3H, 20-H), 1.10 (*s*, 3H, 17-H), 1.17-1.24 (*m*, 1H, 1-Ha), 1.25 (*s*, 3H, 19-H), 1.39-1.48 (*m*, 1H, 11-Ha), 1.52 (*td*, *J* = 2.8, 13.5 Hz, 1H, 12-Ha), 1.57-1.69 (*m*, 3H, 3-H, 11-Hb,), 1.71-1.87 (*m*, 4H, 1-Hb, 2-H, 12-Hb), 2.08-2.17 (*m*, 1H, 9-H), 2.25-2.34 (*m*, 1H, 6-Ha), 2.34-2.45 (*m*, 3H, 5-H and 6-Hb), 4.98 (*dd*, *J* = 0.9 and 10.7 Hz, 1H, 16-H^Z), 4.99 (*dd*, *J* = 0.9, 17.5 Hz, 1H, 16-H^E), 5.80 (*dd*, *J* = 10.7, 17.5 Hz, 1H, 15-H), 6.74 (*s*, 1H, 14-H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 14.2 (C-20), 16.2 (C-19), 17.9 (C-2), 18.9 (C-11), 25.8 (C-17), 34.0 (C-12), 35.6 (C-10), 36.8 (C-3), 37.9 (C-6), 38.6 (C-13), 38.7 (C-1), 44.4 (C-5), 46.0 (C-4), 51.0 (C-9), 112.0 (C-16), 135.1 (C-8), 145.0 (C-14), 146.3 (C-15), 180.0 (C-18), 199.8 (C-7).

IR (film on NaCl) ν cm^{-1}: 3080, 2938, 2868, 1773, 1734, 1717, 1684, 1653, 1647, 1636, 1506, 1271, 1238.

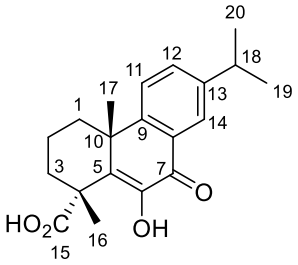
HRMS (ESI+) *m/z*: calculated for $C_{20}H_{29}O_3$ $[MH]^+$: 317.2111; found: 317.2118.

$[\alpha]_D^{25}$ = –30 (c 0.2, $CHCl_3$; lit.[7] +63.8, c 0.03, $CHCl_3$).[6]

R_f (CH_2Cl_2/MeOH 95:5) = 0.25.

[6] The observed discrepancy with the literature data was unexpected. It may indicate a wrong configuration assignment in the original work, where the absolute configuration of **22** was deduced from the analysis of CD spectra, without additional calculation.

(–)-(4*R*,10*R*)-6-Hydroxy-13-isopropyl-4,10-dimethyl-7-oxo-1,2,3,4,7,10-hexahydrophenanthrene-4-carboxylic acid (23)



Into a solution of ester **17** (15 mg, 0.045 mmol) in *t*-BuOH (1 mL) was added *t*-BuOK (126 mg, 1.12 mmol) under an oxygen atmosphere (balloon). The reaction mixture was stirred 24 hours at room temperature before quenching by cold water. The aqueous layer was acidified to pH 6 using an aqueous solution of HCl (1N) and extracted with $CHCl_3$ (3x3 mL), dried over Na_2SO_4 and concentrated. The resulting crude material was purified by column chromatography on silica gel (95:5 CH_2Cl_2/MeOH) to afford **23** (10 mg, 72%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.28 (two overlapped *d*, *J* = 6.9 Hz, 6H, 19-H and 20-H), 1.53 (*s*, 3H, 17-H), 1.62 (*s*, 3H, 16-H), 1.79-2.06 (*m*, 5H, 2-H, 3-H and 1-Ha), 2.39-2.48 (*m*, 1H, 1-Hb), 2.98 (*hept*, *J* = 6.9 Hz, 1H, 18-H), 6.90 (*brs*, 1H, 7-OH), 7.46 (*s*, 2H, 11-H and 12-H), 8.02 (*s*, 1H, 14-H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 17.6 (C-2), 22.1 (C-16), 23.8 (C-19 and C-20), 33.7 (C-17), 34.0 (C-1), 34.8 (C-3), 35.6 (C-18), 39.3 (C-10), 45.9 (C-4), 124.3 (C-14), 124.9 (C-11), 127.7 (C-6), 132.0 (C-12), 136.1 (C-5), 143.8 (C-8), 147.3 (C-13), 151.7 (C-9), 180.1 (C-15), 181.3 (C-7).

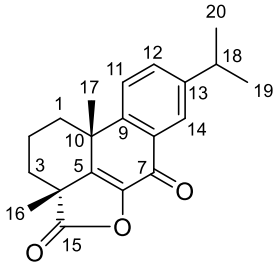
IR (film on NaCl) ν cm^{-1}: 3019, 2963, 2930, 2872, 2857, 1804, 1701, 1636, 1608, 1265, 1215.

HRMS (ESI+) *m/z*: calculated for $C_{20}H_{23}O_3$ $[MH]^+$: 311.4642; found: 311.4648.

$[\alpha]_D^{25}$ = –1.2 (c 1, $CHCl_3$).

R_f (95:5 CH_2Cl_2/MeOH) = 0.35.

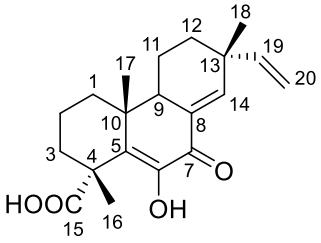
(–)-Picealactone A (24)



Lactone **24** (10 mg) was obtained as a white solid after spontaneous lactonisation of **23** in the freezer at –20 °C over one week (quantitative yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.29 (*d*, *J* = 6.9 Hz, 6H, H-19 and H-20), 1.36 (*td*, *J* = 3.6, 13.4 Hz, 1H, 1-Ha), 1.52 (*td*, *J* = 3.6, 13.4 Hz, 1H, 1-Hb), 1.61 (*s*, 3H, 17-H), 1.65 (*s*, 3H, 16-H), 1.80-1.91 (*m*, 1H, 2-Ha), 2.00-2.11 (*m*, 1H, 2-Hb), 2.11-2.19 (*m*, 1H, 3-Ha), 2.35-2.45 (*m*, 1H, 3-Hb), 3.00 (*hept*, *J* = 6.9 Hz, 1H, 18-H), 7.45 (*d*, *J* = 8.2 Hz, 1H, 11-H), 7.51 (*dd*, *J* = 2.0, 8.2 Hz, 1H, 12-H), 8.16 (*d*, *J* = 2.0 Hz, 1H, 14-H).
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 19.0 (C-2), 21.1 (C-16), 23.7/23.8 (C-19 and C-20), 24.4 (C-17), 33.8 (C-18), 36.0 (C-3), 38.9 (C-10), 42.4 (C-1), 47.1 (C-4), 124.7 (C-14), 125.8 (C-11), 130.7 (C-8), 131.8 (C-12), 142.4 (C-6), 145.6 (C-5), 148.1 (C-13), 148.4 (C-9), 174.0 (C-7), 179.7 (C-15).
IR (film on NaCl) ν cm^{-1}: 3028, 2959, 2930, 2870, 1805, 1674, 1653, 1001.
HRMS (ESI+) *m/z*: calculated for $C_{20}H_{23}O_3$ $[MH]^+$: 311.4642; found: 311.4648.
$[\alpha]_D^{25}$ = –16 (c 0.3, $CHCl_3$; lit.[7] –14.5, c 0.45, $CHCl_3$).
R_f (CH_2Cl_2) = 0.31.
M.p. = 189-192 °C (lit.: 191-192 °C[3]; 182-190 °C[7]).

(–)-7-Oxo-6-hydroxy-13-*epi*-pimara-5,14,15-trien-18-oic acid (25)



To a solution of ester **24** (15 mg, 0.045mmol) in *t*-BuOH (1 mL) was added *t*-BuOK (126 mg, 1.12 mmol). The reaction mixture was stirred under an oxygen atmosphere (balloon) during 24h at room temperature, before quenching by cold water. The aqueous phase was acidified to pH 6 using an aqueous solution of HCl (1N) and extracted with $CHCl_3$ (3 x 3 mL), dried over Na_2SO_4 and concentrated. The resulting crude material was purified by column chromatography on silica gel (CH_2Cl_2/MeOH 95:5), to afford **25** as a white powder after solvent removal (11 mg, 78% yield).

[7] Y.-H. Kuo, M.-H. Yeh, H.-C. Lin, *Chem. Pharm. Bull.*, 2004, **52**, 861.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.11 (*s*, 3H, 17-H), 1.16 (*s*, 3H, 18-H), 1.41 (*td*, *J* = 4.7, 13.0 Hz, 1H, 1-Ha), 1.49 (*s*, 3H, 16-H), 1.54 (*dd*, *J* = 3.3, 13.0 Hz, 1H, 12-Ha), 1.63 (*dt*, *J* = 2.3, 13.0 Hz, 1H, 11-Ha), 1.65-1.76 (*m*, 3H, 2-H and 12-Hb), 1.76-1.87 (*m*, 3H, 3-Ha, 1-Hb and 11-Hb), 1.93 (*td*, *J* = 4.7, 13.0 Hz, 1H, 3-Hb), 2.64-2.69 (*m*, 1H, 9-H), 5.02 (*d*, *J* = 10.6 Hz, 1H, 20-H^Z), 5.04 (*d*, J = 17.5 Hz, 1H, 20-H^E),5.84 (*dd*, J = 10.6, 17.5 Hz, 1H, 19-H), 7.01 (*s*, 1H, 14-H).

^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 17.3 (C-2), 19.0 (C-11), 22.0 (C-16), 24.5 (C-17), 25.1 (C-18), 33.2 (C-12), 36.2 (C-1), 36.7 (C-1), 37.3 (C-10), 38.5 (C-13), 45.6 (C-4), 47.2 (C-9), 112.2 (C-20), 132.2 (C-6), 139.2 (C-5), 143.8 (C-8), 145.8 (C-14), 146.0 (C-19), 181.8 (C-15), 182.4 (C-7).

IR (film on NaCl) ν cm^{-1}: 3047, 2942, 2868, 1734, 1695, 1684, 1653, 1647, 1506, 1457, 1270, 1028, 992.

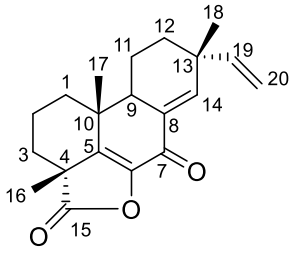
HRMS (ESI+) *m/z*: calculated for $C_{20}H_{25}O_3$ $[MH]^+$: 313.1798; found: 313.1792.

$[\alpha]_D^{25}$ = –114 (c 0.2, $CHCl_3$).

M.p.: 93.5-94.5 °C.

R_f (95:5 CH_2Cl_2/MeOH): 0.21.

***iso*-Dabeshanensin B (26)**



Compound **25** (4.5 mg, 0.014 mmol) was dissolved in EtOH (150 µL) and H_2O (15µL) under Argon before adding $RhCl_3 \cdot 3H_2O$ (0.4 mg, 0.0014 mmol). The mixture was heated at 100 °C for 2h before quenching the reaction with water (0.5 mL). The mixture was extracted using Et_2O (3x0.5 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude material was purified by column chromatography on silica gel (100% CH_2Cl_2) to afford **26** as a white solid (3.0 mg, 67%).

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 1.19 (*s*, 3H, 18-H), 1.20 (*s*, 3H, 17-H), 1.29 (*td*, *J* = 4.7, 13.1 Hz, 1H, 1-Ha), 1.53 (*s*, 3H, 16-H), 1.55-1.59 (*m*, 3H, 3-Ha and 12-H), 1.72-1.87 (*m*, 4H, 3-H and 11-H), 2.04-2.12 (*m*, 2H, 1-Hb and 3-Hb), 2.51 (*dt*, *J* = 2.6, 6.6 Hz, 1H, 9-H), 4.94 (*dd*,

J = 0.9, 17.4 Hz, 1H, 20-H^{E}), 5.03 (*dd*, *J* = 0.9, 10.6 Hz, 1H, 20-H^{Z}), 5.76 (*dd*, *J* = 10.6, 17.4 Hz, 1H, 19-H), 6.91 (*d*, *J* = 2.6 Hz, 1H, 14-H).

^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 18.3 (C-2), 18.6 (C-11), 19.3 (C-17), 23.9 (C-16), 26.7 (C-18), 32.7 (C-3), 33.1 (C-12), 38.0 (C-8), 38.5 (C-13), 39.9 (C-1), 46.0 (C-4), 46.8 (C-9), 113.3 (C-20), 133.5 (C-10), 143.0 (C-6), 144.8 (C-14), 144.9 (C-19), 148.8 (C-5), 177.3 (C-15), 179.7 (C-7).

IR (film on NaCl) ν cm^{-1}: 2926, 2855, 1805, 1716, 1678, 1633, 1464, 1383, 1236, 1184, 1070, 983.

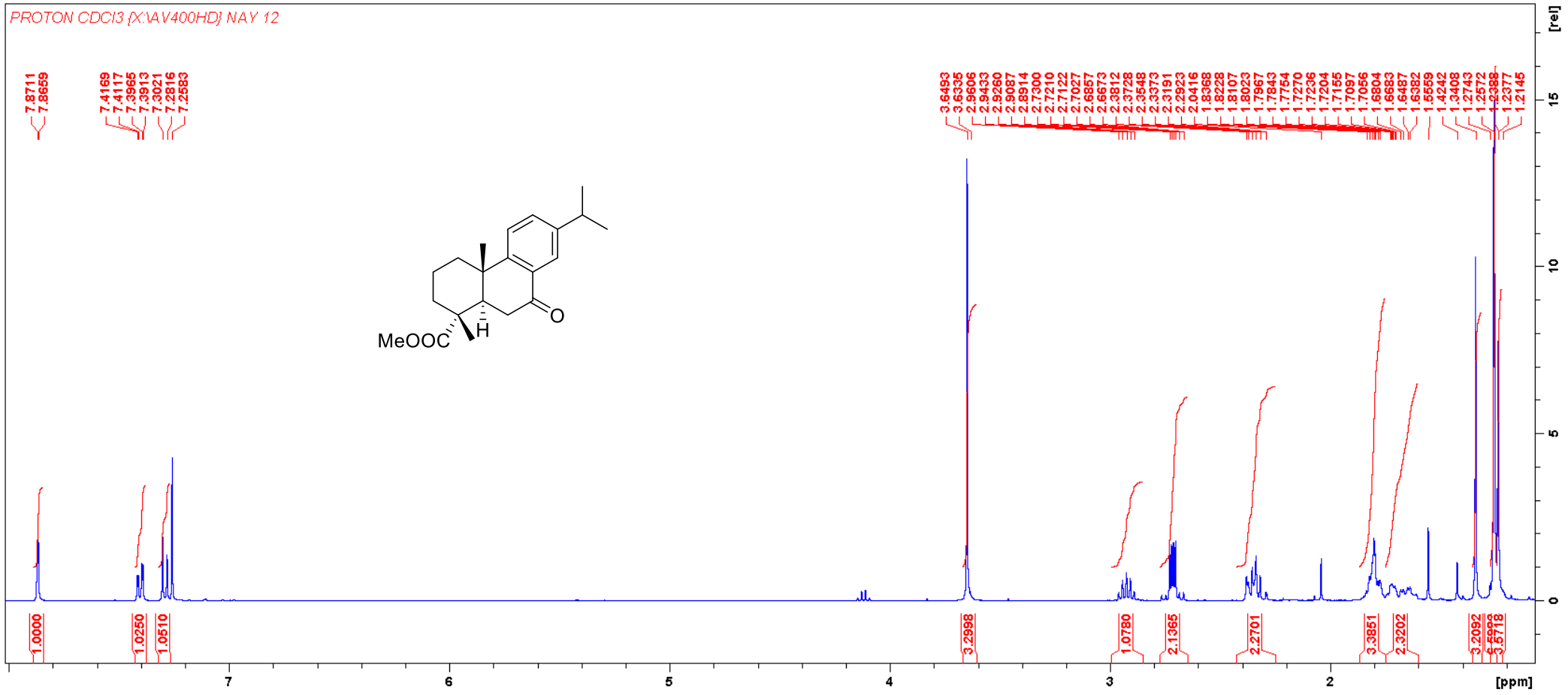
HRMS (EI+) *m/z*: calculated for $C_{20}H_{24}O_3$: 312.1725; found: 312.1722.

$[\alpha]_D^{25}$ = –117 (c 0.24, CH_2Cl_2).

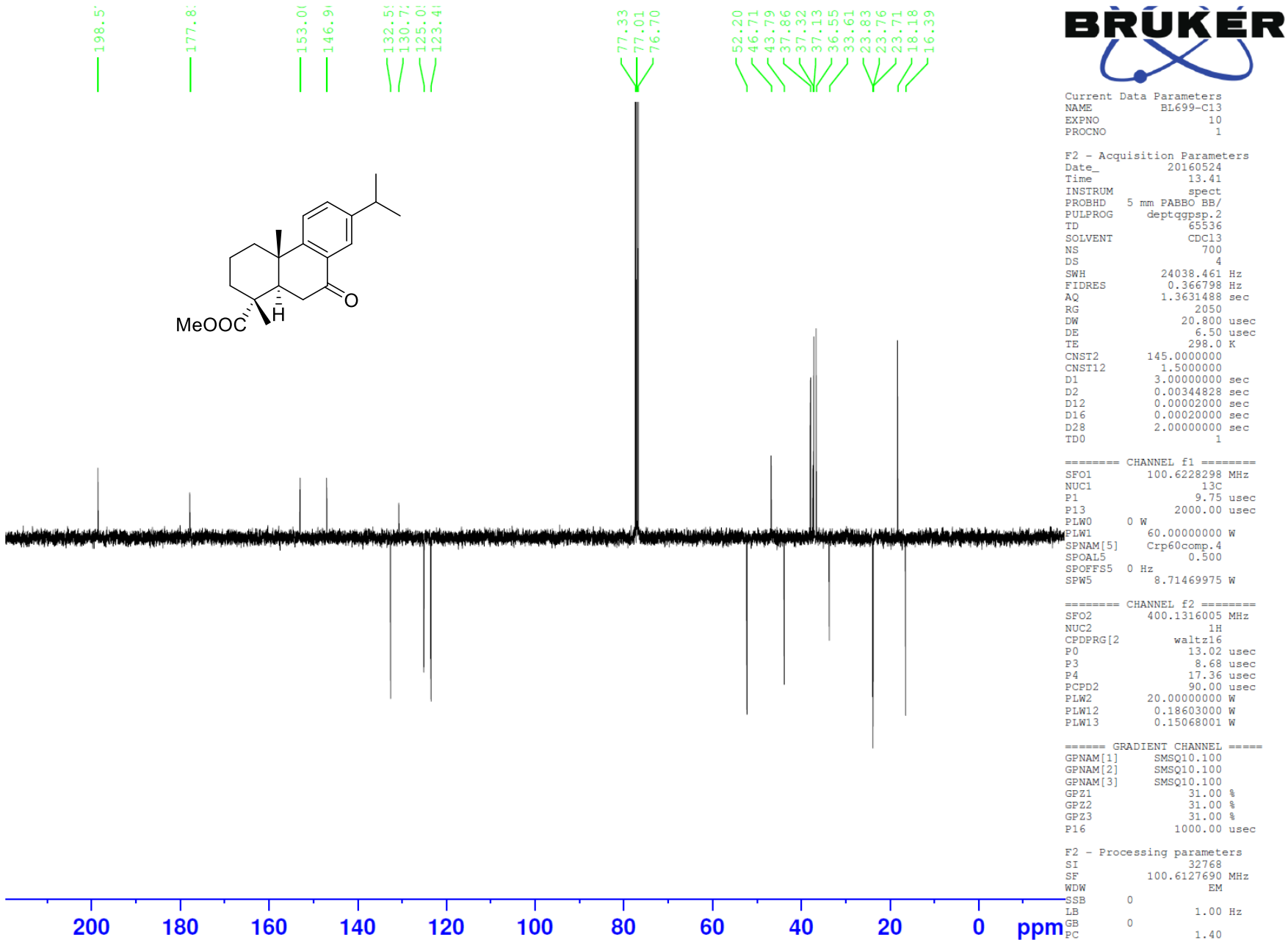
M.p. = 134-136°C.

R_f (CH_2Cl_2): 0.41.

^{1}H NMR spectrum of compound 17 (400 MHz, $CDCl_3$, 298 K)



^{13}C NMR spectrum (DEPTQ) of compound 17 (100 MHz, $CDCl_3$, 298 K)

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PROCNO                  1

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INSTRUM             spect
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PULPROG     deptqgpsp.2
TD                  65536
SOLVENT             CDCl3
NS                    700
DS                      4
SWH             24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631488 sec
RG                   2050
DW                20.800 usec
DE                 6.50 usec
TE                298.0 K
CNST2          145.0000000
CNST12           1.5000000
D1             3.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
D16            0.00020000 sec
D28            2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6228298 MHz
NUC1                  13C
P1                   9.75 usec
P13               2000.00 usec
PLW0       0 W
PLW1         60.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5    0 Hz
SPW5          8.71469975 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                  1H
CPDPRG[2          waltz16
P0                  13.02 usec
P3                   8.68 usec
P4                  17.36 usec
PCPD2               90.00 usec
PLW2         20.00000000 W
PLW12         0.18603000 W
PLW13         0.15068001 W

====== GRADIENT CHANNEL =====
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GPNAM[3]      SMSQ10.100
GPZ1                31.00 %
GPZ2                31.00 %
GPZ3                31.00 %
P16               1000.00 usec

F2 - Processing parameters
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
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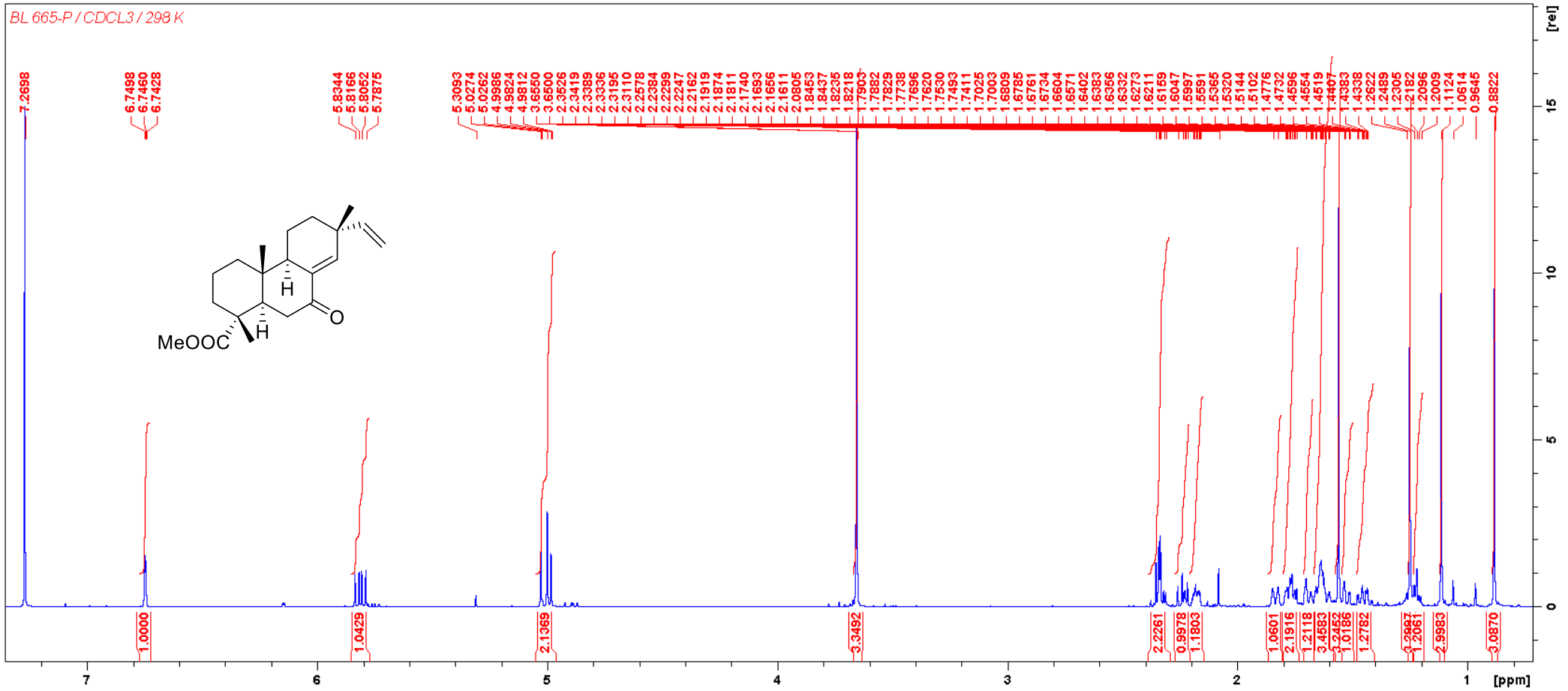
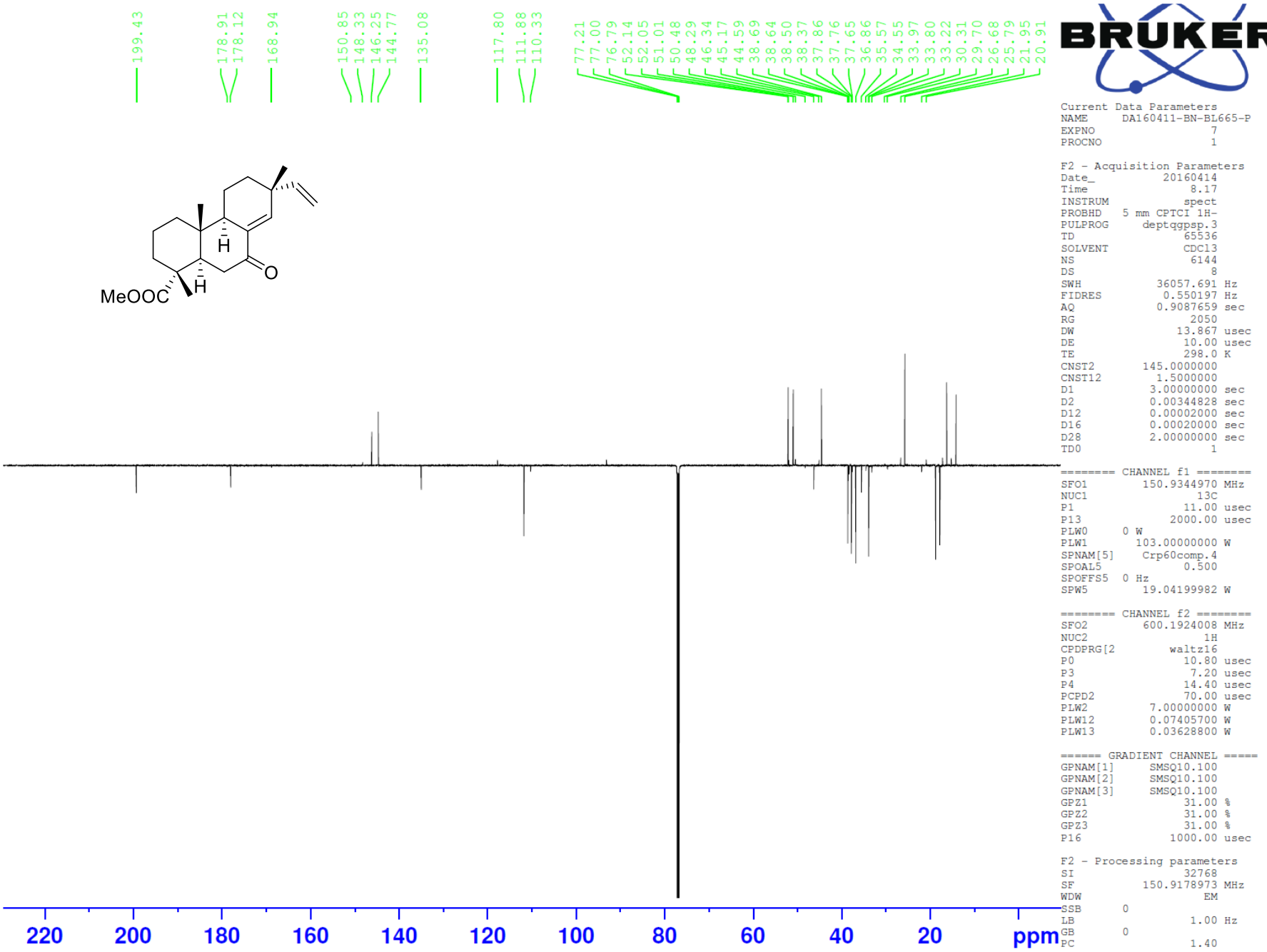
^{1}H NMR spectrum of compound 18 (600 MHz, $CDCl_3$, 298 K)



^{13}C NMR spectrum (DEPTQ) of compound 18 (150 MHz, $CDCl_3$, 298 K)

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Current Data Parameters
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EXPNO                       7
PROCNO                      1

F2 - Acquisition Parameters
Date_           20160414
Time               8.17
INSTRUM           spect
PROBHD   5 mm CPTCI 1H-
PULPROG     deptqgpsp.3
TD               65536
SOLVENT          CDCl3
NS                6144
DS                   8
SWH          36057.691 Hz
FIDRES        0.550197 Hz
AQ            0.9087659 sec
RG                2050
DW              13.867 usec
DE              10.00 usec
TE              298.0 K
CNST2        145.0000000
CNST12         1.5000000
D1           3.00000000 sec
D2           0.00344828 sec
D12          0.00002000 sec
D16          0.00020000 sec
D28          2.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         150.9344970 MHz
NUC1                  13C
P1                11.00 usec
P13             2000.00 usec
PLW0      0 W
PLW1       103.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5   0 Hz
SPW5         19.04199982 W

======== CHANNEL f2 ========
SFO2         600.1924008 MHz
NUC2                  1H
CPDPRG[2          waltz16
P0                10.80 usec
P3                 7.20 usec
P4                14.40 usec
PCPD2             70.00 usec
PLW2          7.00000000 W
PLW12         0.07405700 W
PLW13         0.03628800 W

====== GRADIENT CHANNEL =====
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GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPZ1               31.00 %
GPZ2               31.00 %
GPZ3               31.00 %
P16              1000.00 usec

F2 - Processing parameters
SI                32768
SF           150.9178973 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
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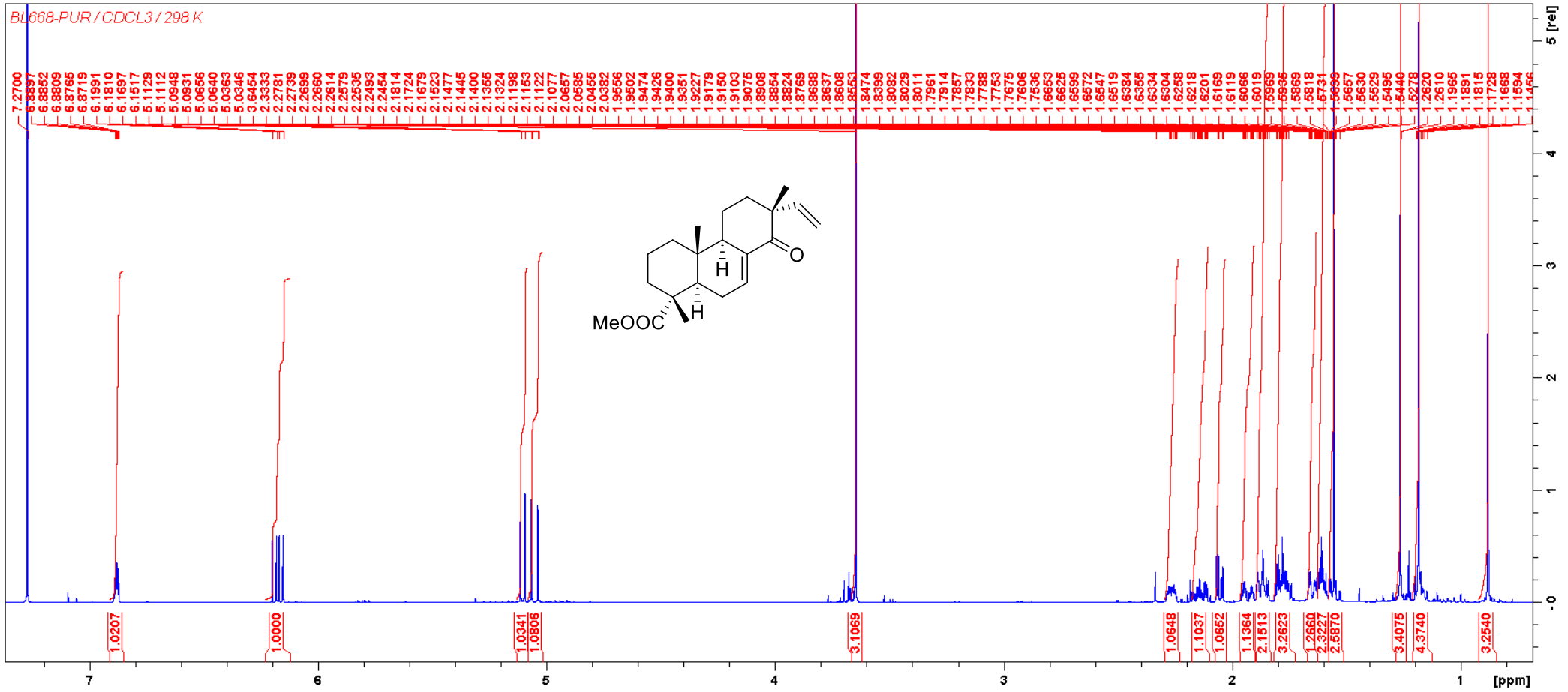
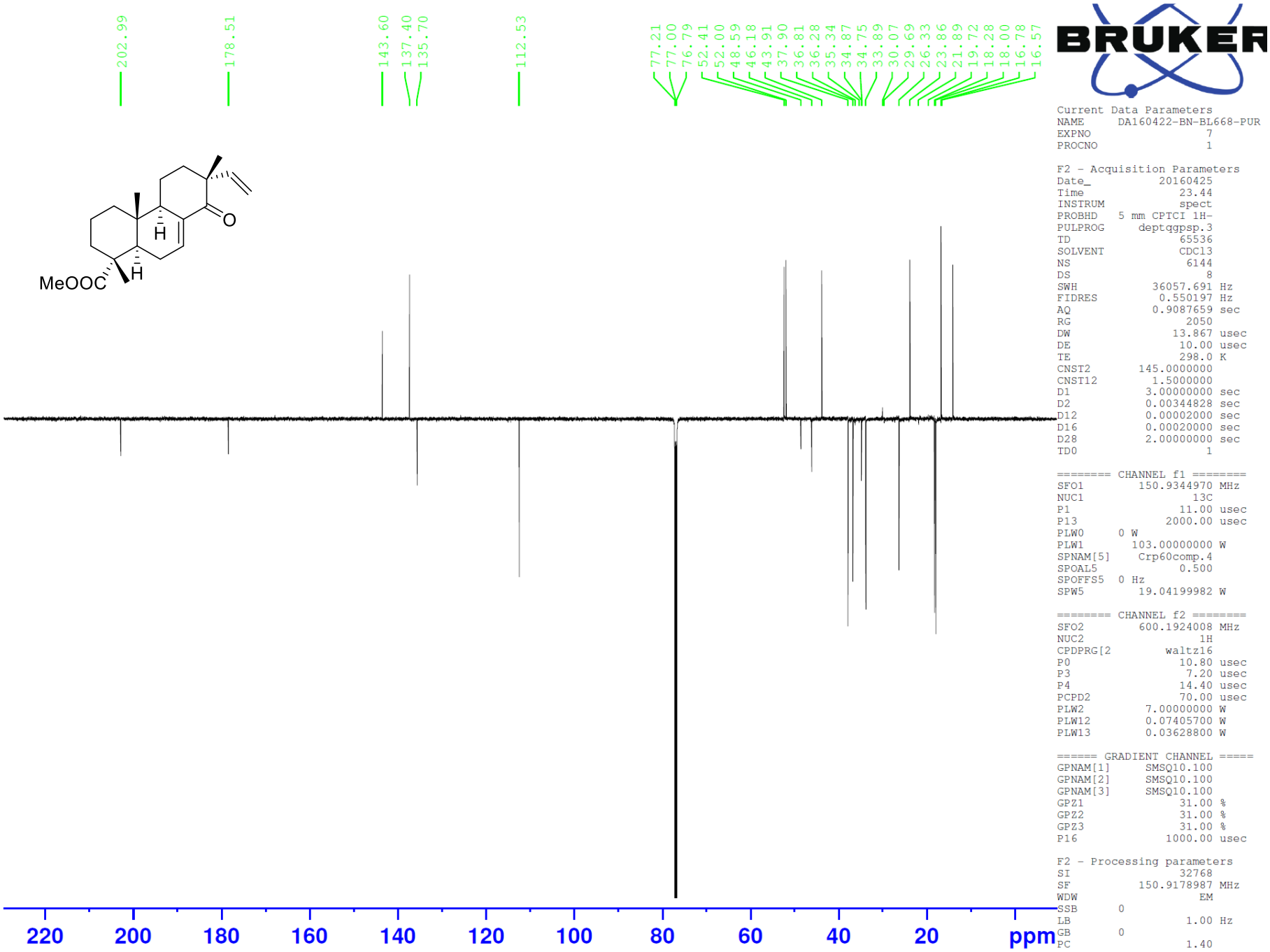
^{1}H NMR spectrum of compound 19 (600 MHz, $CDCl_3$, 298 K)



^{13}C NMR spectrum (DEPTQ) of compound 19 (150 MHz, $CDCl_3$, 298 K)



BRUKER

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Current Data Parameters
NAME      DA160422-BN-BL668-PUR
EXPNO                         7
PROCNO                        1

F2 - Acquisition Parameters
Date_              20160425
Time                  23.44
INSTRUM               spect
PROBHD    5 mm CPTCI 1H-
PULPROG      deptqgpsp.3
TD                    65536
SOLVENT               CDCl3
NS                     6144
DS                        8
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                     2050
DW                  13.867 usec
DE                  10.00 usec
TE                  298.0 K
CNST2          145.0000000
CNST12           1.5000000
D1               3.00000000 sec
D2               0.00344828 sec
D12              0.00002000 sec
D16              0.00020000 sec
D28              2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           150.9344970 MHz
NUC1                    13C
P1                  11.00 usec
P13               2000.00 usec
PLW0       0 W
PLW1         103.00000000 W
SPNAM[5]      Crp60comp.4
SPOAL5              0.500
SPOFFS5    0 Hz
SPW5           19.04199982 W

======== CHANNEL f2 ========
SFO2           600.1924008 MHz
NUC2                    1H
CPDPRG[2          waltz16
P0                  10.80 usec
P3                   7.20 usec
P4                  14.40 usec
PCPD2               70.00 usec
PLW2            7.00000000 W
PLW12           0.07405700 W
PLW13           0.03628800 W

====== GRADIENT CHANNEL =====
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GPNAM[2]       SMSQ10.100
GPNAM[3]       SMSQ10.100
GPZ1                31.00 %
GPZ2                31.00 %
GPZ3                31.00 %
P16               1000.00 usec

F2 - Processing parameters
SI                    32768
SF             150.9178987 MHz
WDW                      EM
SSB        0
LB                   1.00 Hz
GB         0
PC                   1.40
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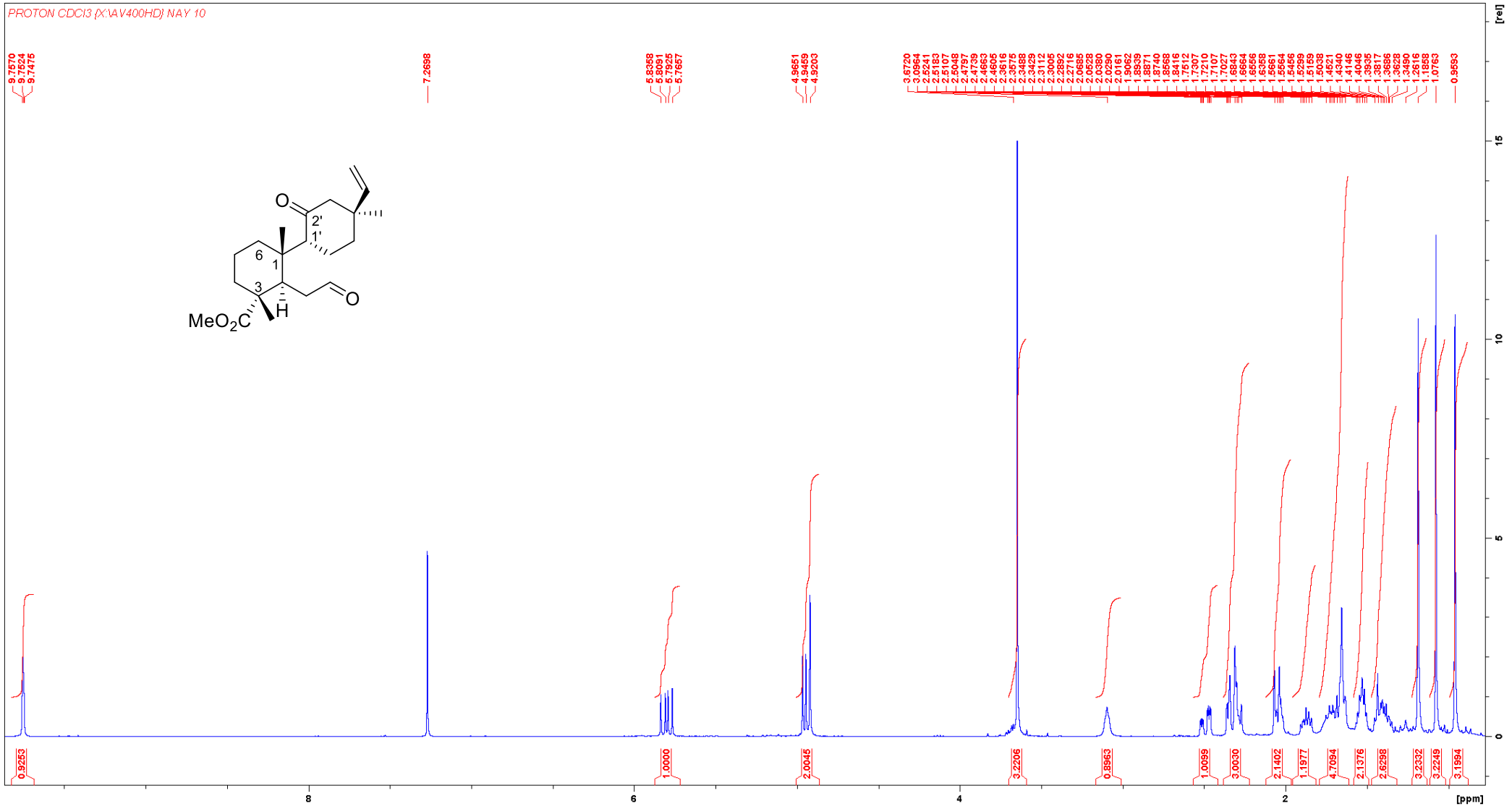
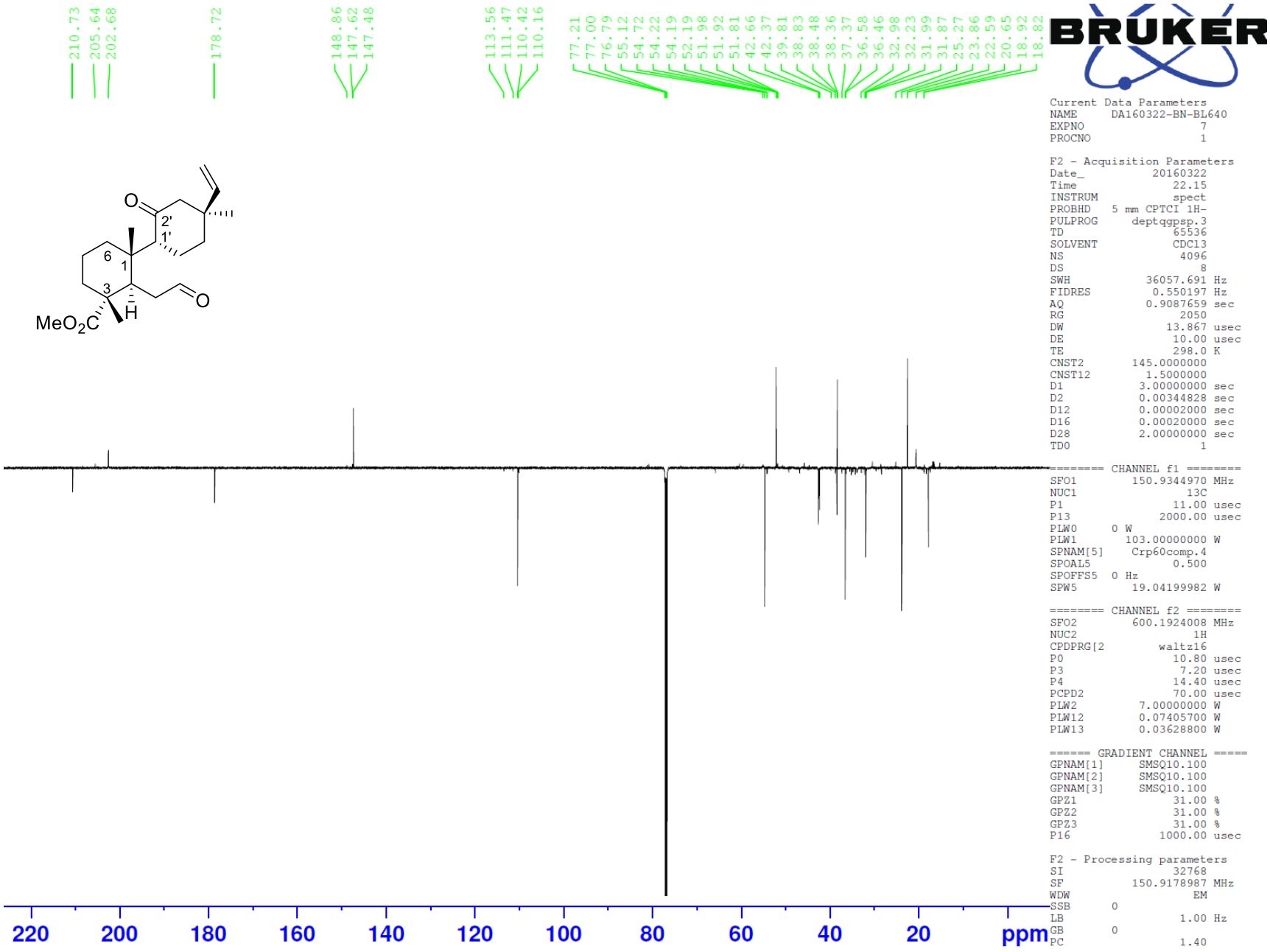
^{1}H NMR spectrum of compound 20 (400 MHz, $CDCl_3$, 298 K)



^{13}C NMR spectrum (DEPTQ) of compound 20 (150 MHz, $CDCl_3$, 298 K)



BRUKER

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Current Data Parameters
NAME      DA160322-BN-BL640
EXPNO                    7
PROCNO                   1

F2 - Acquisition Parameters
Date_           20160322
Time              22.15
INSTRUM           spect
PROBHD   5 mm CPTCI 1H-
PULPROG     deptqgpsp.3
TD                65536
SOLVENT           CDCl3
NS                 4096
DS                    8
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9087659 sec
RG                 2050
DW               13.867 usec
DE               10.00 usec
TE               298.0 K
CNST2        145.0000000
CNST12         1.5000000
D1           3.00000000 sec
D2           0.00344828 sec
D12          0.00002000 sec
D16          0.00020000 sec
D28          2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         150.9344970 MHz
NUC1                13C
P1                11.00 usec
P13             2000.00 usec
PLW0      0 W
PLW1       103.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5         19.04199982 W

======== CHANNEL f2 ========
SFO2         600.1924008 MHz
NUC2                1H
CPDPRG[2          waltz16
P0                10.80 usec
P3                 7.20 usec
P4                14.40 usec
PCPD2             70.00 usec
PLW2          7.00000000 W
PLW12         0.07405700 W
PLW13         0.03628800 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPZ1               31.00 %
GPZ2               31.00 %
GPZ3               31.00 %
P16              1000.00 usec

F2 - Processing parameters
SI                 32768
SF           150.9178987 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
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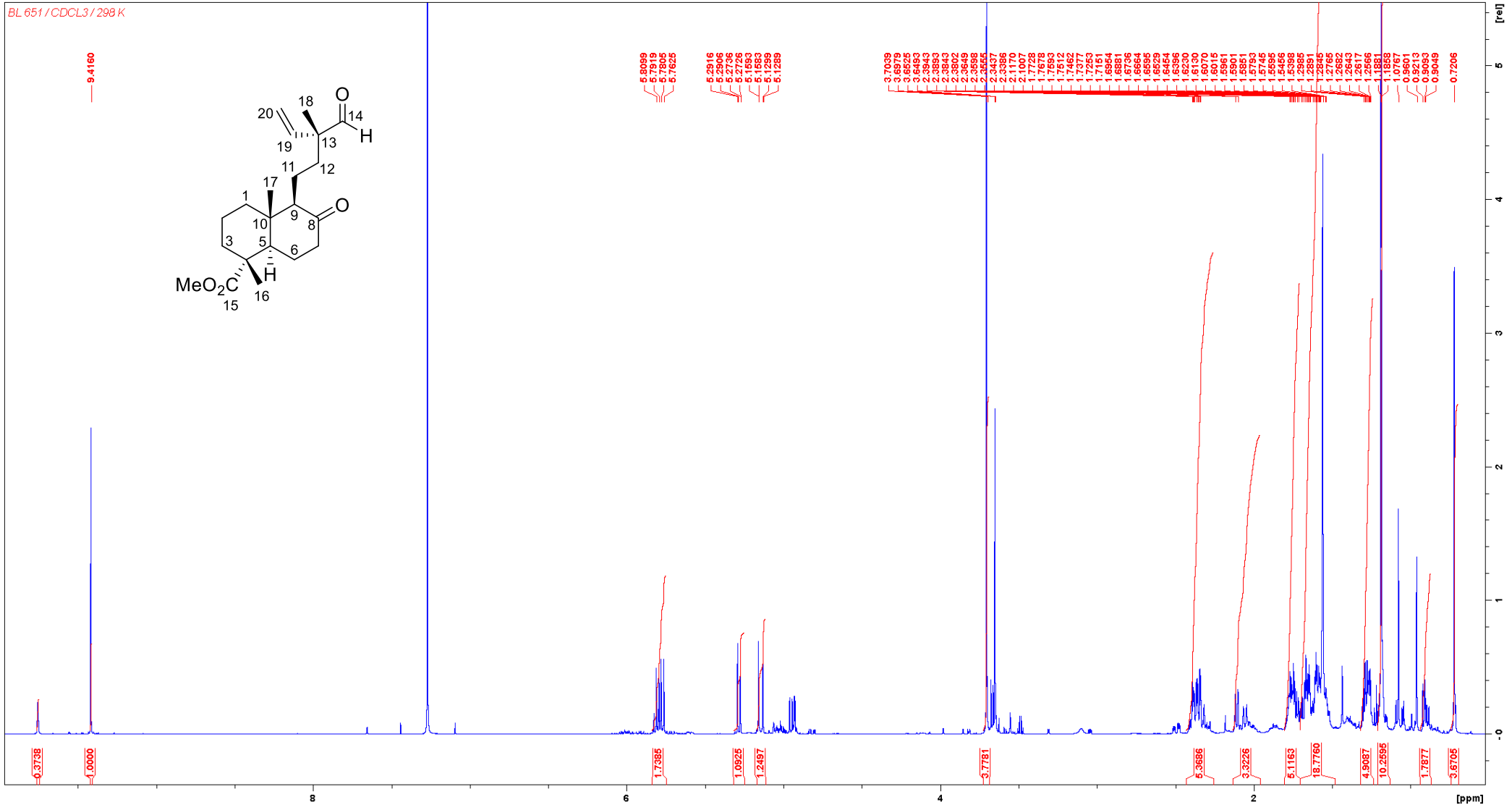
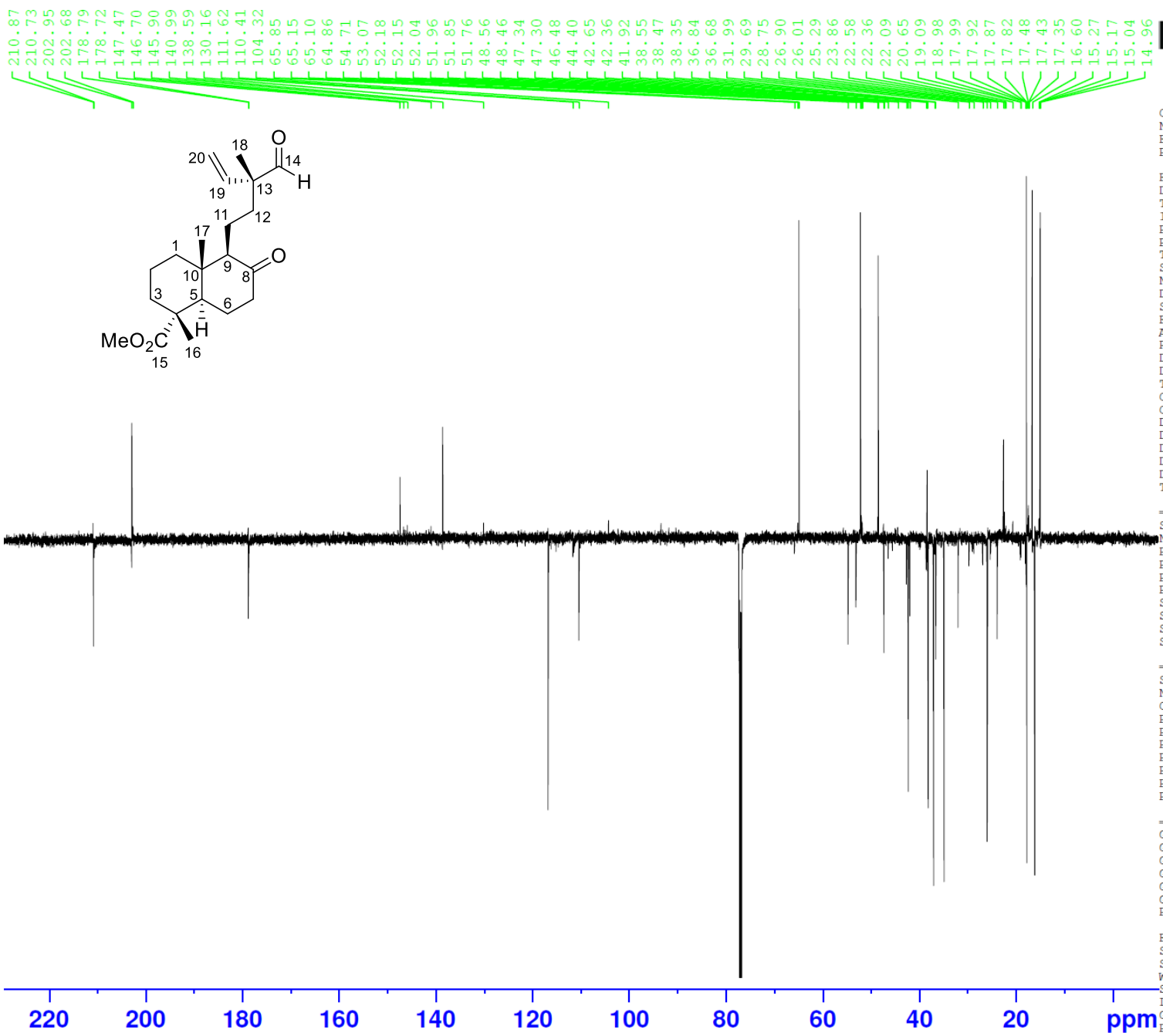
^{1}H NMR spectrum of compound 21 (600 MHz, $CDCl_3$, 298 K)



^{13}C NMR spectrum (DEPTQ) of compound 21 (150 MHz, $CDCl_3$, 298 K)

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Current Data Parameters
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EXPNO                    7
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160622
Time                 21.19
INSTRUM              spect
PROBHD   5 mm CPTCI 1H-
PULPROG      deptqqpsp.3
TD                   65536
SOLVENT              CDCl3
NS                    4096
DS                       8
SWH              36057.691 Hz
FIDRES           0.550197 Hz
AQ               0.9087659 sec
RG                    2050
DW                 13.867 usec
DE                 10.00 usec
TE                 298.0 K
CNST2           145.0000000
CNST12            1.5000000
D1                3.00000000 sec
D2                0.00344828 sec
D12               0.00002000 sec
D16               0.00020000 sec
D28               2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           150.9344970 MHz
NUC1                    13C
P1                   11.00 usec
P13                2000.00 usec
PLW0       0 W
PLW1         103.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5    0 Hz
SPW5           19.04199982 W

======== CHANNEL f2 ========
SFO2           600.1924008 MHz
NUC2                    1H
CPDPRG[2          waltz16
P0                   10.80 usec
P3                    7.20 usec
P4                   14.40 usec
PCPD2                70.00 usec
PLW2            7.00000000 W
PLW12           0.07405700 W
PLW13           0.03725000 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPZ1                 31.00 %
GPZ2                 31.00 %
GPZ3                 31.00 %
P16                1000.00 usec

F2 - Processing parameters
SI                   32768
SF             150.9179003 MHz
WDW                     EM
SSB        0
LB                    1.00 Hz
GB         0
PC                    1.40
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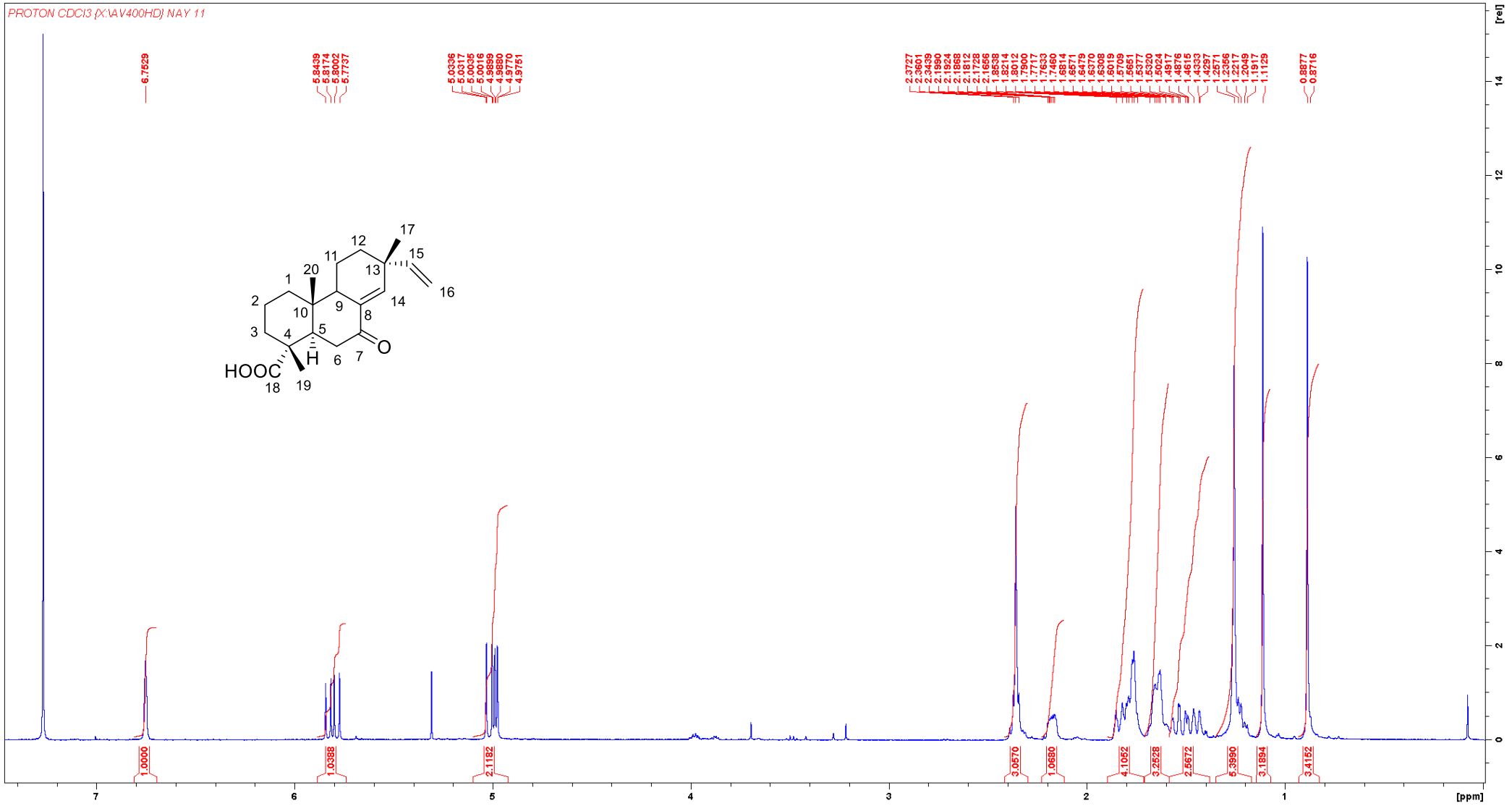
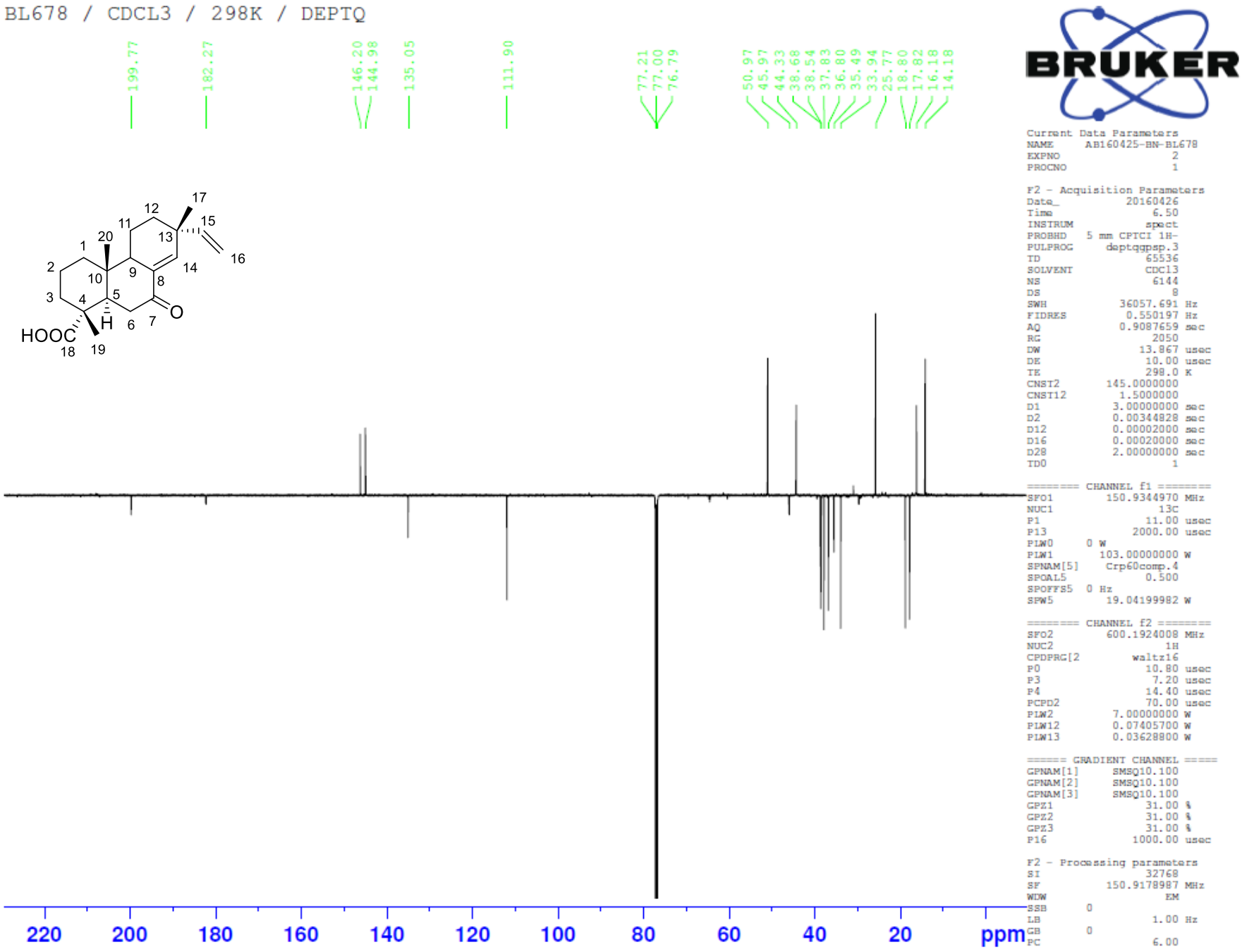
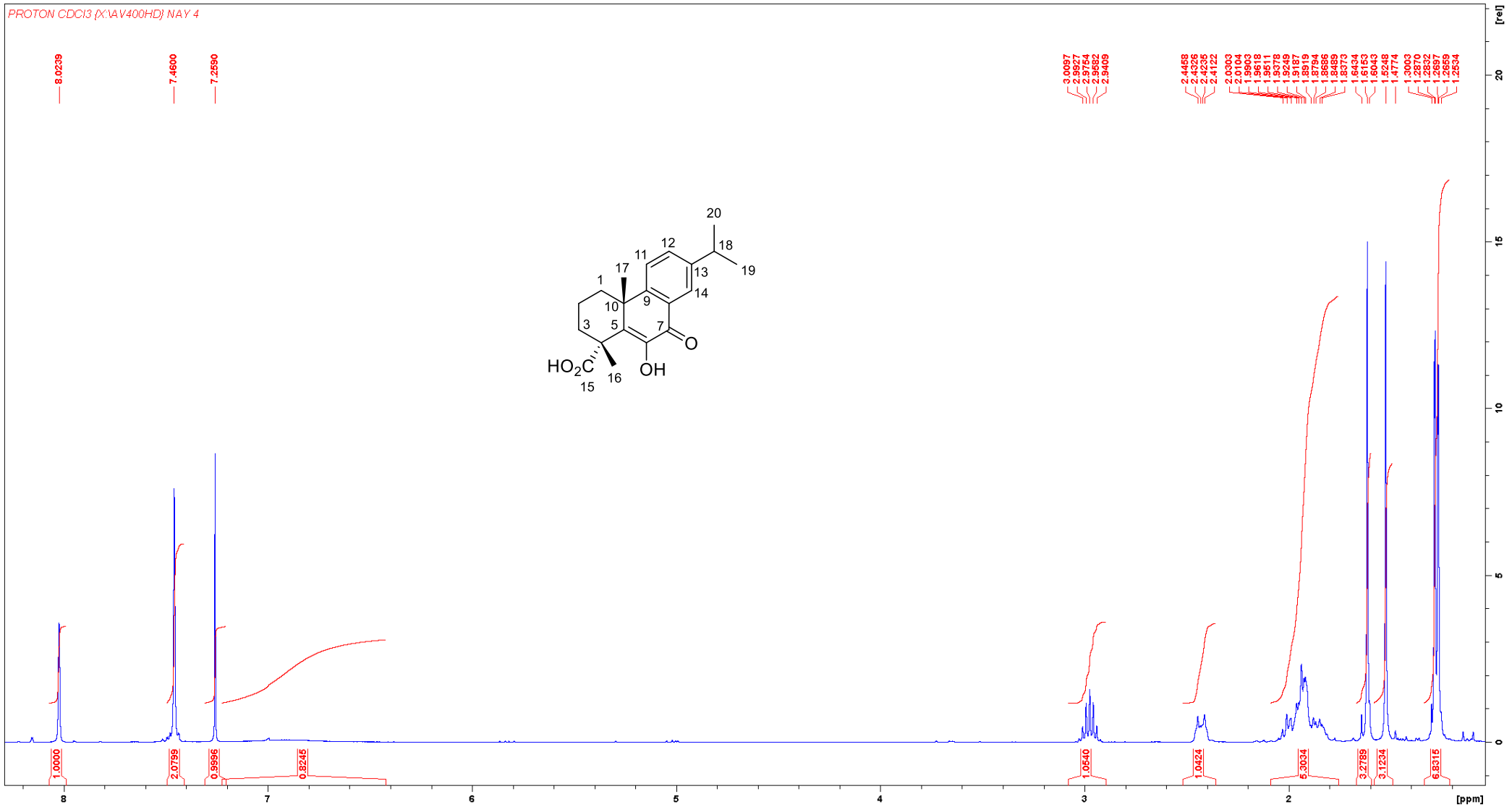
^{1}H NMR spectrum of compound 22 (400 MHz, $CDCl_3$, 298 K)



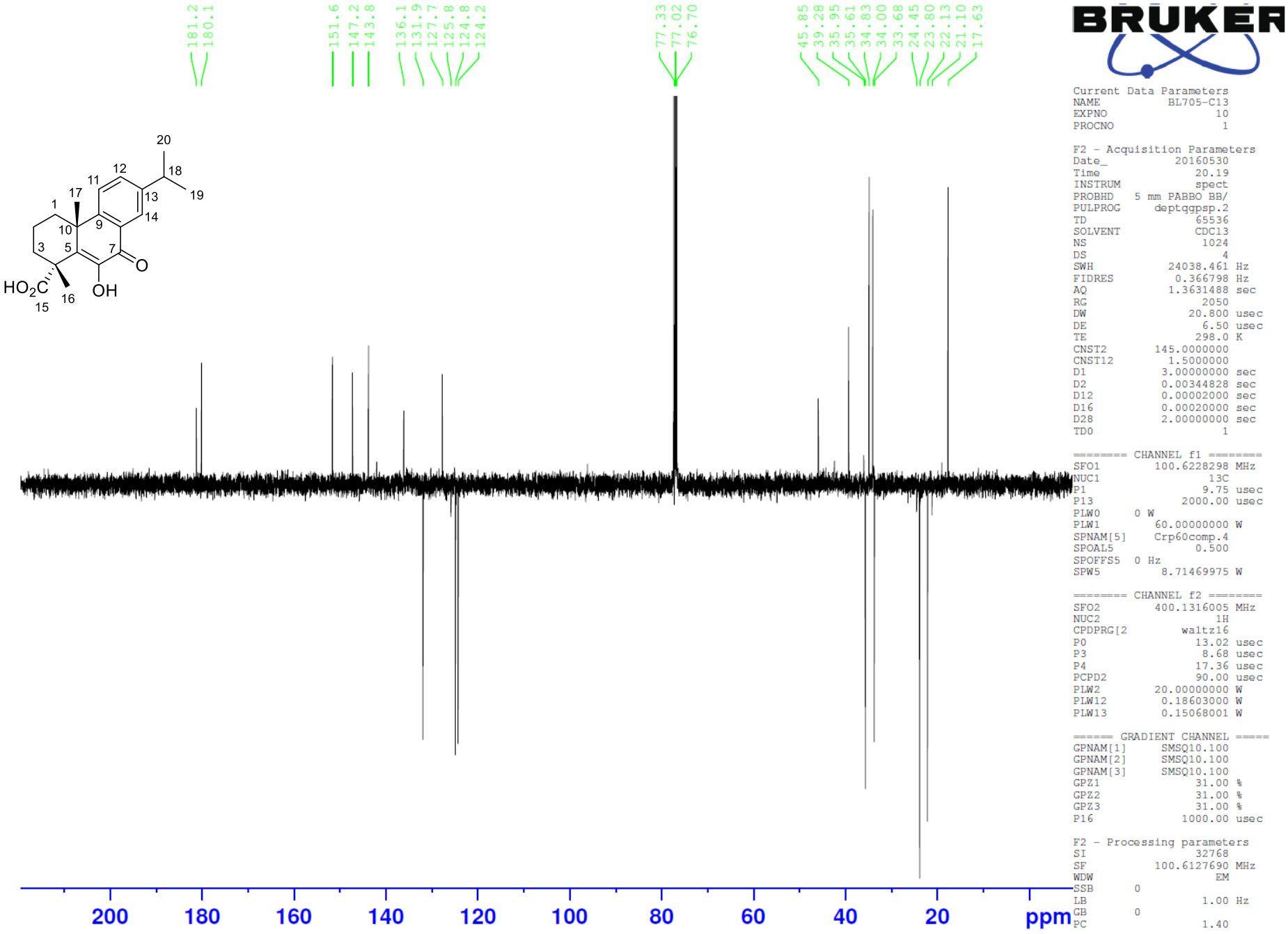
^{13}C NMR spectrum (DEPTQ) of compound 22 (100 MHz, $CDCl_3$, 298 K)



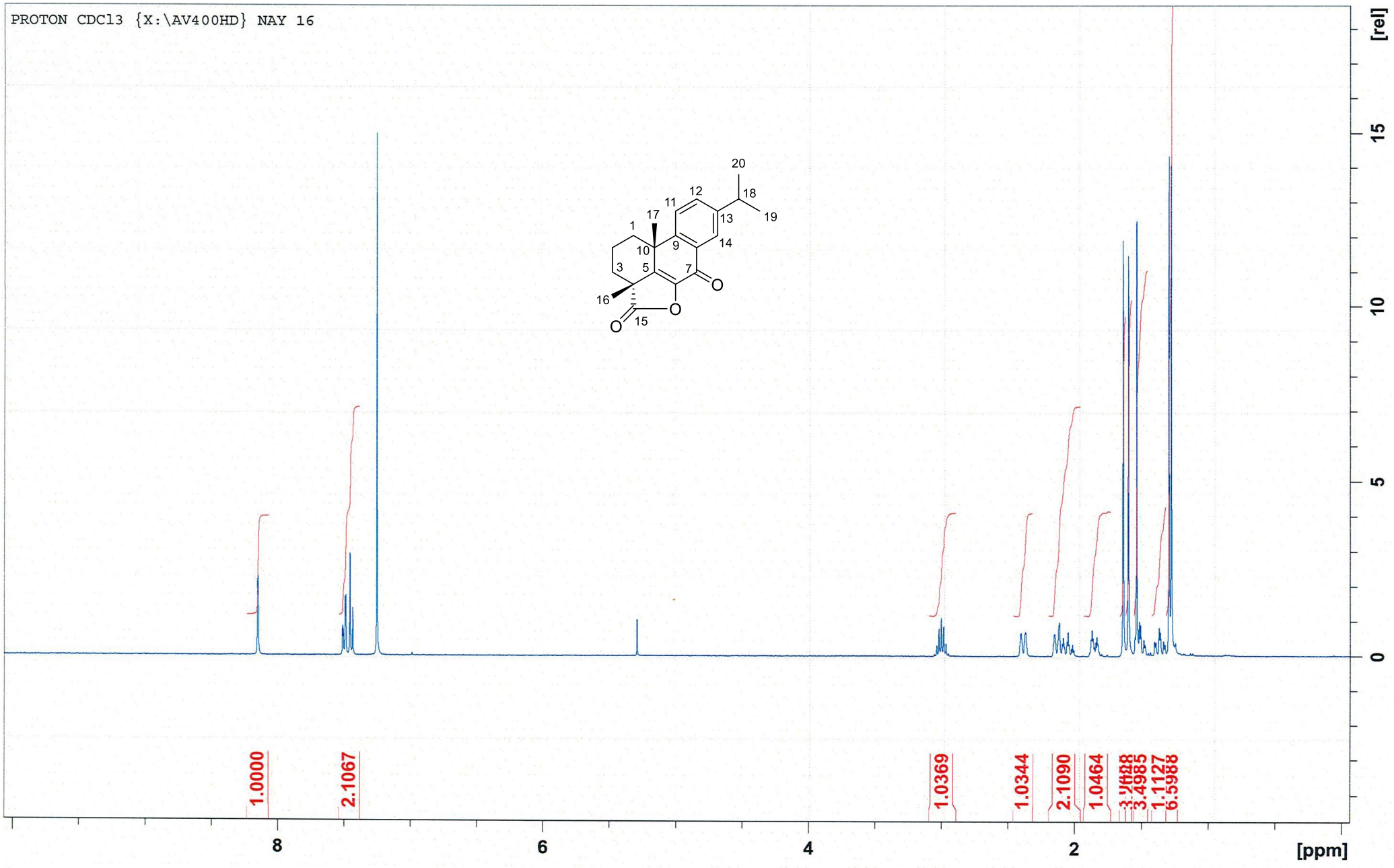
^{1}H NMR spectrum of compound 23 (400 MHz, $CDCl_3$, 298 K)



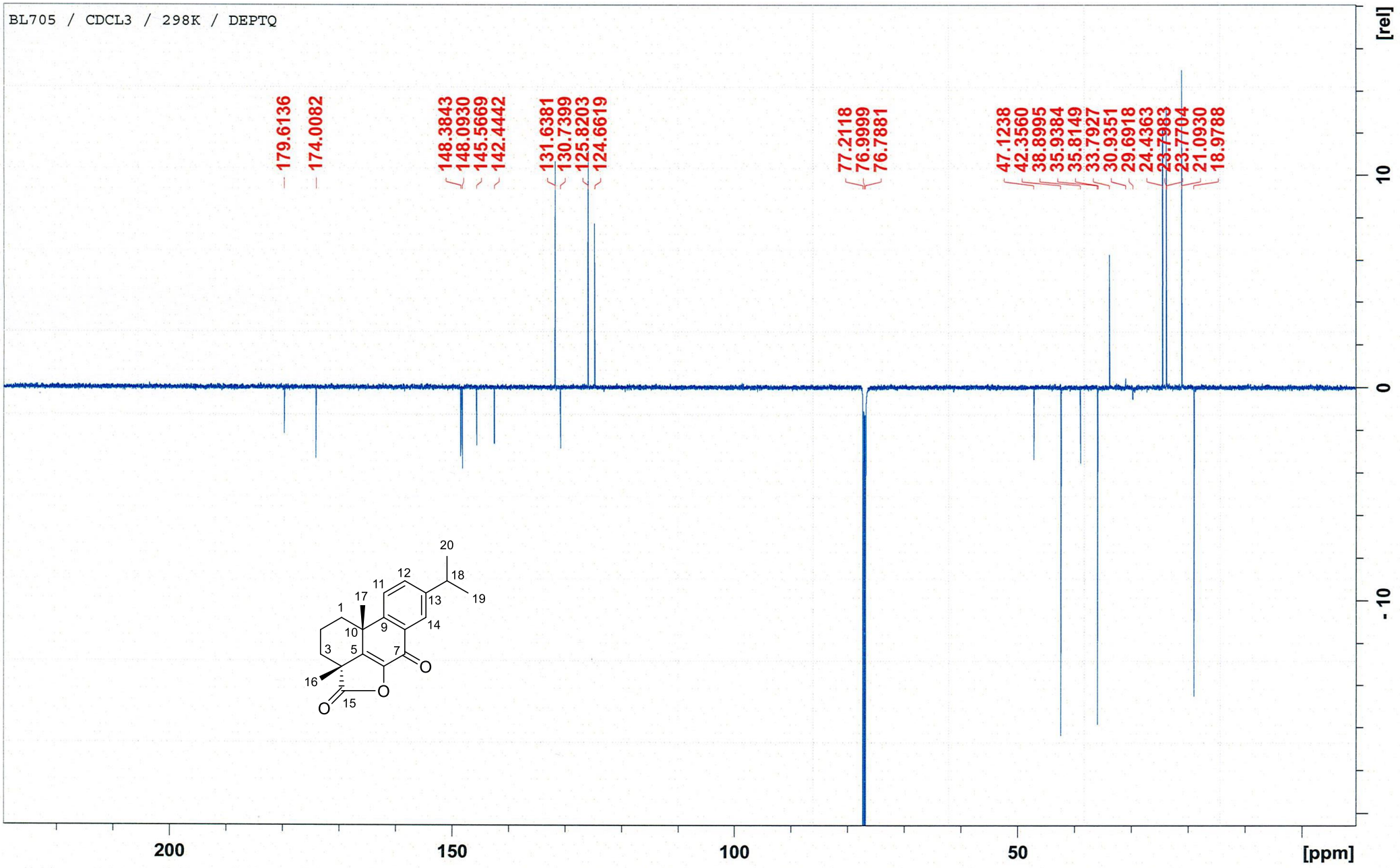
^{13}C NMR spectrum (DEPTQ) of compound 23 (100 MHz, $CDCl_3$, 298 K)



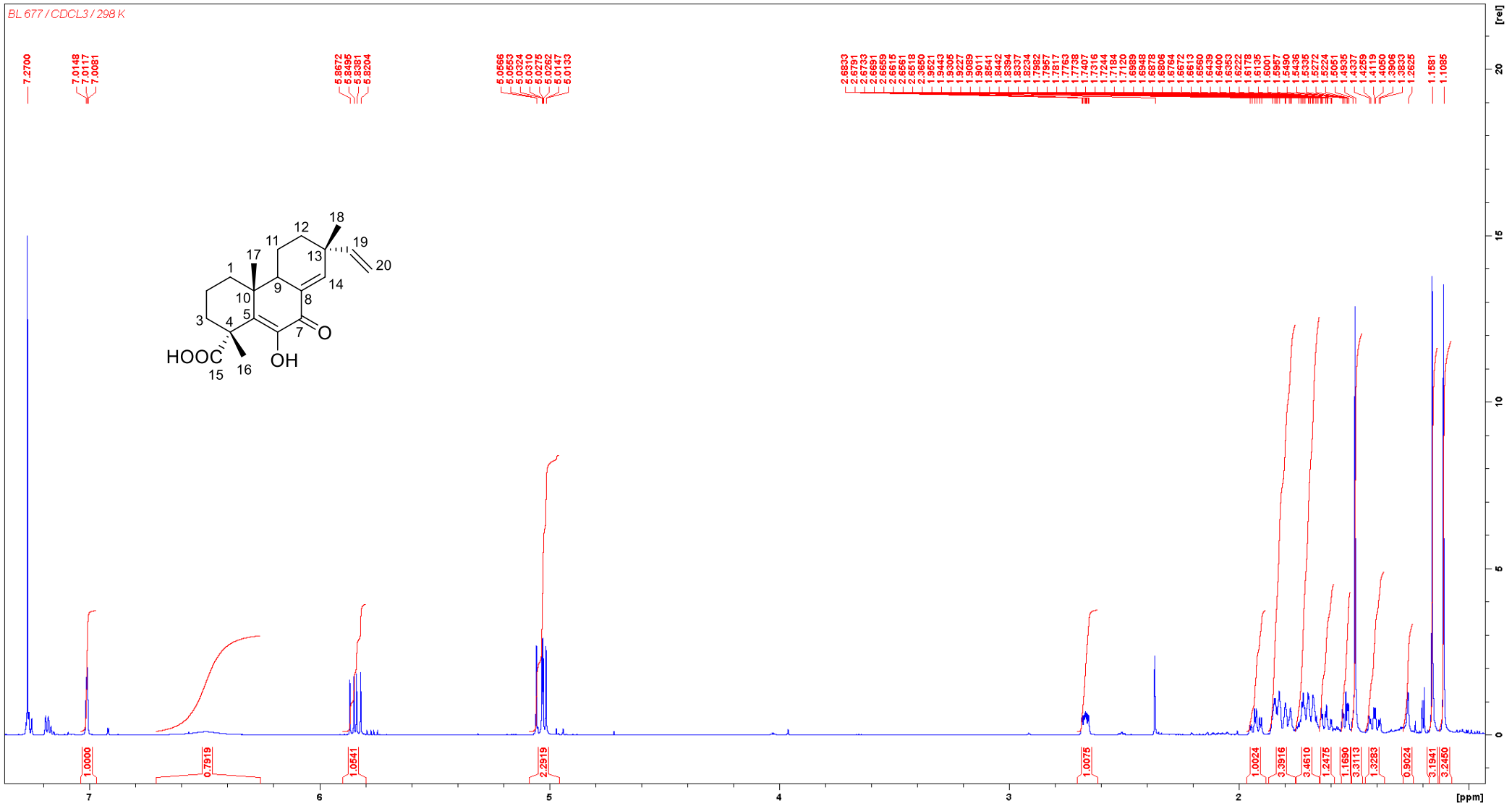
^{1}H NMR spectrum of compound 24 (400 MHz, $CDCl_3$, 298 K)



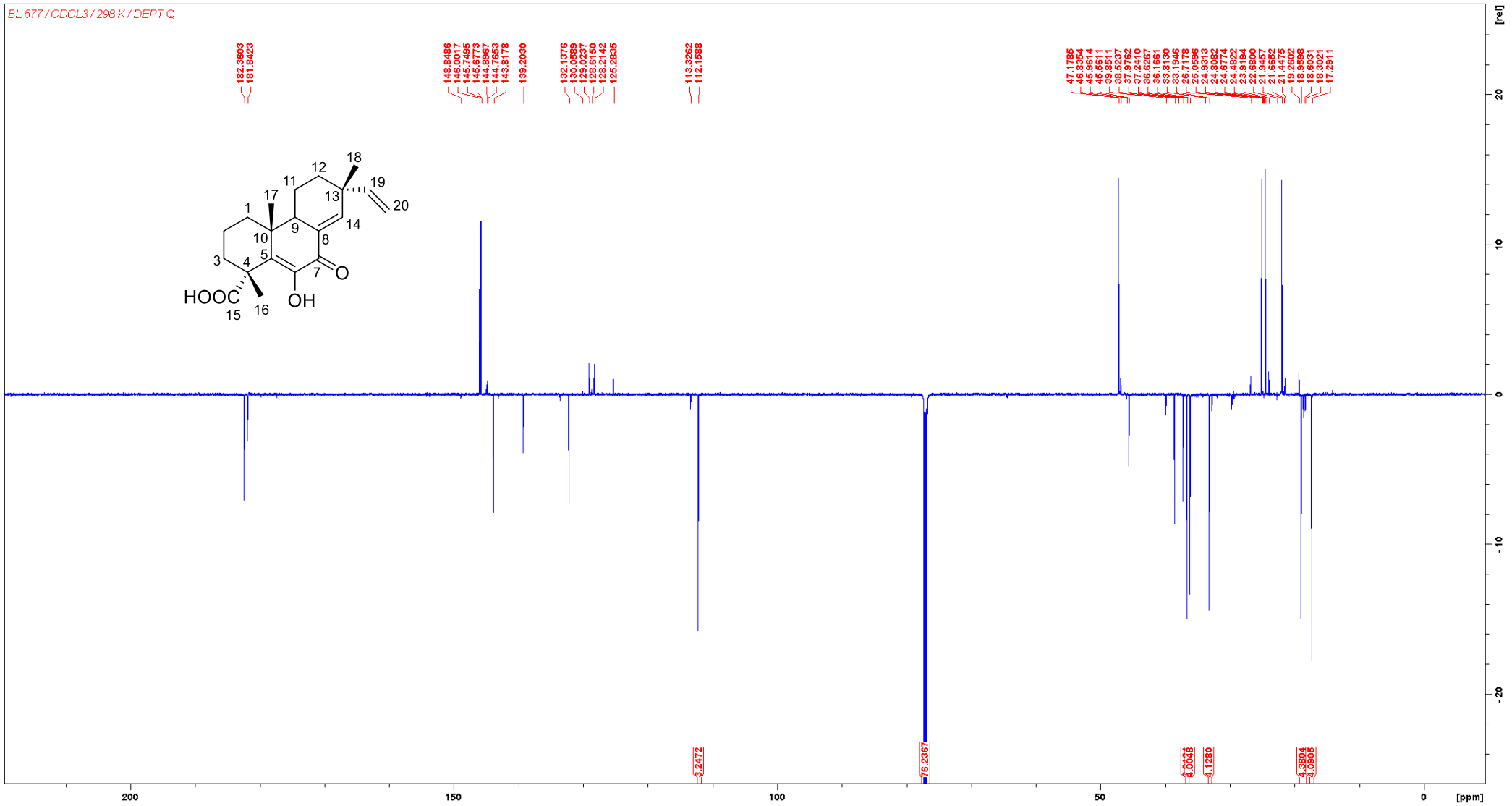
^{13}C NMR spectrum (DEPTQ) of compound 24 (100 MHz, $CDCl_3$, 298 K)



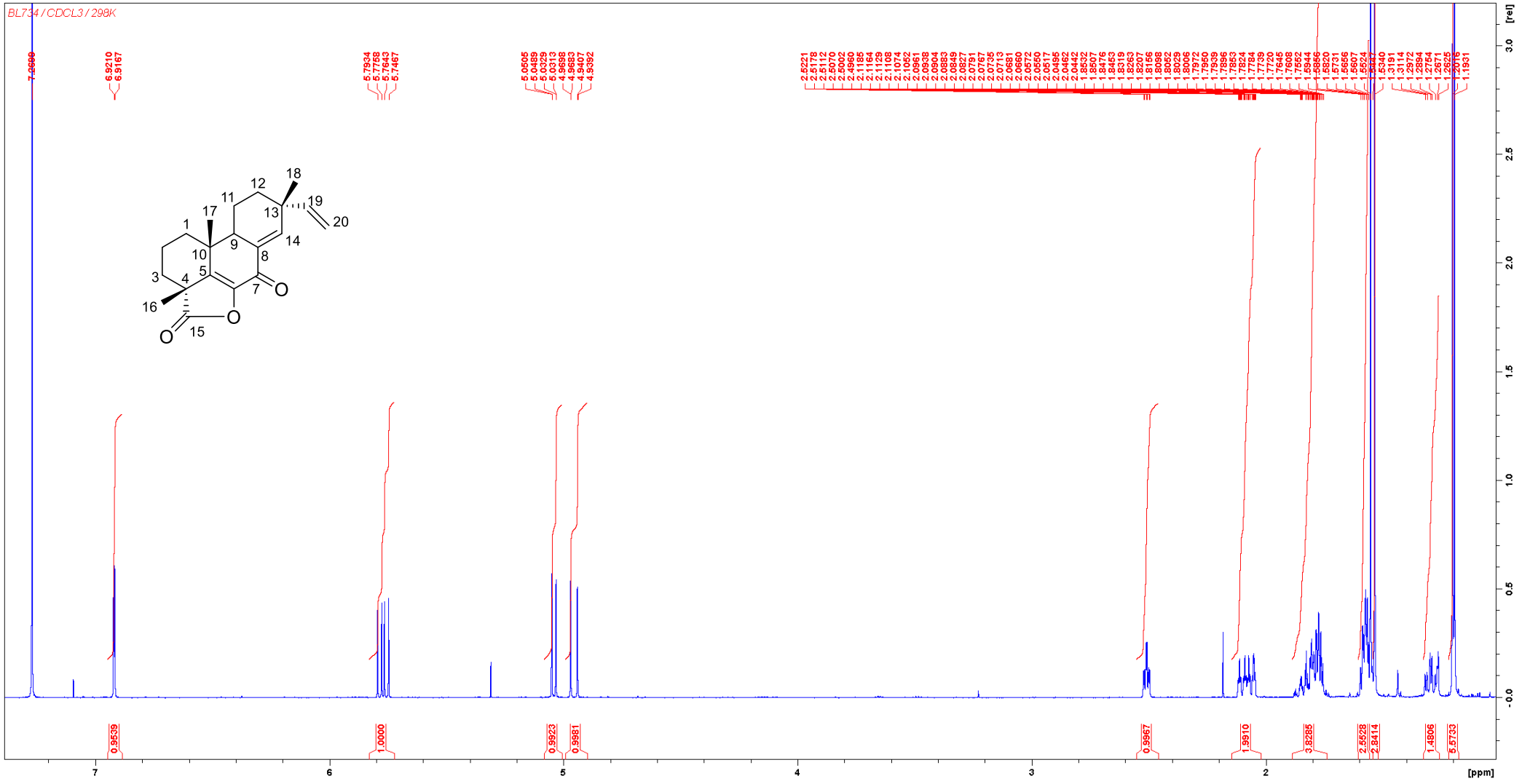
^{1}H NMR spectrum of compound 25 (600 MHz, $CDCl_3$, 298 K)



^{13}C NMR spectrum (DEPTQ) of compound 25 (150 MHz, $CDCl_3$, 298 K)



^{1}H NMR spectrum of compound 26 (600 MHz, $CDCl_3$, 298 K)



^{13}C NMR spectrum (DEPTQ) of compound 26 (150 MHz, $CDCl_3$, 298 K)