Structural verification of petromyzestrosterol

by total syntheses of both C14-epimers of its 3-*O*-methyl derivative

Atsuo Nakazaki,*[a,b] Maho Kawai,[a] and Toshio Nishikawa[a]

[a]Graduate School of Bioagricultural Sciences, Nagoya University,

Furo-cho, Chikusa, Nagoya 464-8601 (Japan).

[b]Faculty of Science and Engineering, Iwate University,

Ueda, Morioka 020-8551 (Japan).

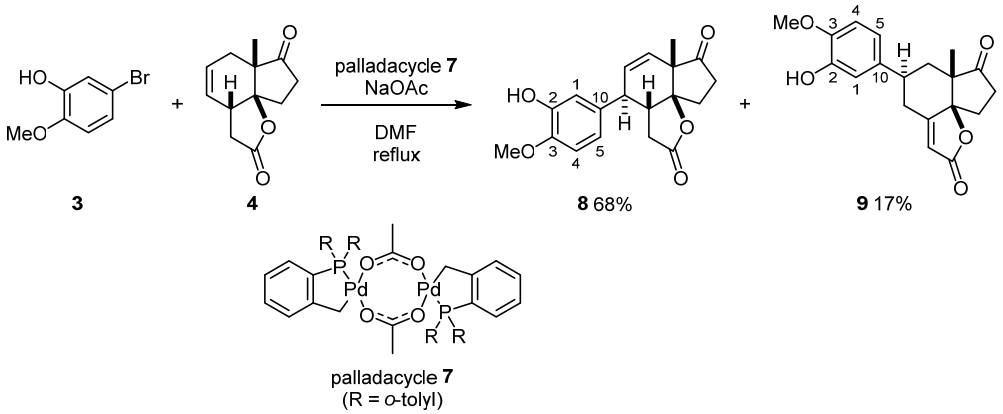
E-mail: nakazaki@iwate-u.ac.jp

Contents:

General Techniques

Infrared spectra (IR) were recorded on a JASCO FT/IR-4100 type A spectrophotometer and are reported in wavenumber (cm^{-1}). Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts of all compounds are reported in ppm relative to the residual undeuterated solvent ($CDCl_3$ as δ = 7.26, CD_3OD as δ = 3.31, acetone-d_6 as δ = 2.05). Data were reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broadened), coupling constant(s), and assignment. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Avance-400 (100 MHz) spectrometer. Chemical shifts of all compounds are reported in ppm relative to the solvent ($CDCl_3$ as δ = 77.16, CD_3OD as δ = 49.00, pyridine-d_5 as δ = 123.87, acetone-d_6 as δ = 29.84). All NMR were measured at 300 K. High-resolution mass spectra (HRMS) were record on an Aglient technologies 6220 LC/TOF-MS spectrometer for ESI-MS, and reported in *m*/*z*. Melting points (mp) were recorded on a Yanaco MP-S3 melting point apparatus and are not corrected.

All reactions were monitored by thin layer chromatography (TLC) on 0.25 mm silica gel-coated glass plates $60F_{254}$ (Merck, #1.05715.0001). Visualization was achieved by using UV light (254 nm) and appropriate reagent (ethanolic phosphomolybdic acid or *p*-anisaldehyde solution in H_2SO_4/AcOH/EtOH), followed by heating. Silica gel 60N (neutral, particle size 0.063-0.200 mm, Kanto, #37565-84) was used for neutral silica gel open column chromatography. Silica gel 60N (spherical, neutral, particle size 0.04-0.05 mm, Kanto, #37563-84) was used for neutral silica gel flash column chromatography. Chromatorex-DIOL (particle size MB 100-75/200, Fuji Silysia Chemical Ltd. HU200602) was used for Chromatorex DIOL silica gel open column chromatography. Dry THF and CH_2Cl_2 were purchased from Kanto Chemical Co., Inc. Dry DMF was distilled from CaH_2. Celite (Hyflo Super-Cel Celite) was purchased from Nacalai Tesque, Inc. Florisil was purchased from Kanto Chemical Co., Inc. All other commercially available reagents were used as received.

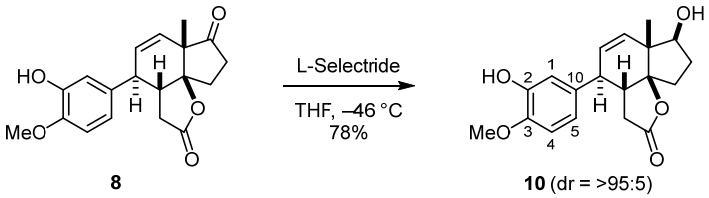


Mizoroki-Heck reaction of 3 and 4: To a solution of **4** (2.07 g, 10.0 mmol) and **3** (3.06 g, 15.1 mmol) in dry DMF (40.2 mL) was added NaOAc (2.15 g, 26.2 mmol) under Ar atmosphere at room temperature. And then to the resulting mixture was added Herrmann palladacycle **7** (286 mg, 0.305 mmol). After being heated to reflux, the resulting mixture was stirred for 2 h. The reaction mixture was cooled to room temperature and diluted with H_2O. The reaction mixture was filtered through a pad of Florisil. The aqueous layer was extracted with CH_2Cl_2 (3 x). The combined organic layer was washed with H_2O (3 x) and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane:EtOAc = 1:1) to afford **8** (2.23 g, 68% yield) as a white solid and **9** (17% yield, calculated based on the amount of **8**) as a white solid. A part of the mixture was purified by preparative TLC for spectral analysis of **9**. Relative stereochemistry of **8** and **9** were determined by ^{1}H NMR and NOESY correlations (Figure 3).

8: IR (KBr) ν_{max} 3445, 1784, 1743, 1511, 1281 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H, s, C*H*$_3$), 2.06 (1H, br dd, J = 13, 9 Hz, C*H*), 2.25-2.61 (6H, m, 6 x C*H*), 3.31 (1H, m, C*H*CH=CH), 3.89 (3H, s, C*H*$_3$O), 5.46 (1H, dd, J = 10, 2 Hz, CH=C*H*), 5.68 (1H, br s, O*H*), 5.77 (1H, dd, J = 10, 2 Hz, C*H*=CH), 6.64 (1H, dd, J = 8, 2 Hz, aryl H-5), 6.73 (1H, d, J = 2 Hz, aryl H-1), 6.82 (1H, d, J = 8 Hz, aryl H-4). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 26.4, 32.3, 34.4, 44.3, 45.2, 55.6, 56.2, 92.6, 111.1, 113.6, 118.9, 130.2, 132.9, 134.1, 146.1, 146.2, 174.7, 215.5. ^{1}H NMR (400 MHz, acetone-d_6) δ 1.18 (3H, s, C*H*$_3$), 2.11-2.27 (2H, m, 2 x C*H*), 2.36-2.47 (3H, m, 3 x C*H*), 2.53-2.75 (2H, m, 2 x C*H*), 3.53 (1H, br d, J = 11 Hz, C*H*CH=CH), 3.84 (3H, s, C*H*$_3$O), 5.38 (1H, dd, J = 9.5, 2 Hz, CH=C*H*), 5.78 (1H, dd, J = 9.5, 1.5 Hz, C*H*=CH), 6.70-6.77 (2H, m, aryl H-5, aryl H-1), 6.92 (1H, d, J = 8 Hz, aryl

H-4) , 7.63 (1H, br s, O*H*). ^{13}C NMR (100 MHz, acetone-d_6) δ 15.9, 26.8, 32.4, 34.7, 44.5, 45.5, 56.0, 56.3, 92.9, 112.7, 115.2, 119.4, 130.3, 134.5, 135.4, 147.5, 147.7, 174.8, 215.8. HRMS-ESI (*m*/*z*): $[M + Na]^+$ calcd for $C_{19}H_{20}O_5Na$, 351.1203; found, 351.1203. mp 166-167 °C.

9: IR (KBr) ν_{max} 3420, 1741, 1513, 1443 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70 (3H, s, CH_3), 1.74 (1H, dd, J = 14, 7 Hz, $CH_3CCH_AH_BCH$), 2.08 (1H, dd, J = 14, 4 Hz, $CH_3CCH_AH_BCH$), 2.20 (1H, dd, J = 14, 10 Hz, C*H*), 2.45 (1H, ddd, J = 14, 13, 9 Hz, C*H*), 2.59 (1H, ddd, J = 19, 8, 1 Hz, C*H*), 2.74 (1H, ddd, J = 18.5, 12.5, 9.5 Hz, C*H*), 2.91 (1H, ddd, J = 18.5, 9, 2 Hz, CH_AH_BC=CH), 3.14-3.21 (2H, m, $CHCH_AH_BC$=CH), 3.87 (3H, s, CH_3O), 5.63 (1H, br s, O*H*), 6.03 (1H, d, J = 2 Hz, C*H*=C), 6.66 (1H, dd, J = 8, 2 Hz, aryl H-5), 6.75 (1H, d, J = 8 Hz, aryl H-4), 6.76 (1H, d, J = 2 Hz, aryl H-1). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.7, 30.5, 31.2, 35.3, 37.4, 39.0, 55.2, 56.1, 93.3, 110.7, 113.1, 116.6, 118.1, 136.4, 145.5, 145.9, 169.9, 171.8, 217.7. HRMS-ESI (*m*/*z*): $[M + Na]^+$ calcd for $C_{19}H_{20}O_5Na$, 351.1203; found, 351.1205. mp 65-67 °C.

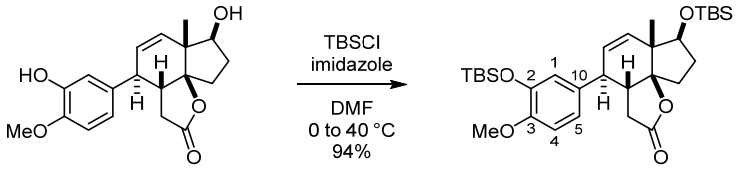


8 **10** (dr = >95:5)

Reduction of ketone 8: To a solution of **8** (1.93 g, 5.88 mmol) in dry THF (39.0 mL) was added dropwise L-Selectride (1.0 M solution in THF, 23.0 mL, 23.0 mmol) at –46 °C. After being stirred at –46 °C for 20 min, to this solution was added dropwise L-Selectride (1.0 M solution in THF, 6.4 mL, 6.4 mmol) at –46 °C. After being stirred at –46 °C for 15 min, the reaction was quenched with a saturated aqueous solution of NH_4Cl and 1 N aqueous solution of HCl at –46 °C. The aqueous layer was extracted with EtOAc (3 x). The combined organic layer was dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by Chromatorex DIOL silica gel open column chromatography (hexane:EtOAc:CH_2Cl_2 = 6:2:1) to afford 17β-alcohol **10** (1.51 g, 78% yield, dr = >95:5 determined by ^{1}H NMR analysis) as a white solid. Relative stereochemistry was

determined by NOESY correlations (Figure 4).

17β-alcohol 10: IR (KBr) ν_{max} 3434, 1776, 1510, 1279 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (3H, s, C*H*$_3$), 1.84 (1H, m, C*H*), 1.90-2.05 (2H, m, 2 x C*H*), 2.23-2.46 (4H, m, 4 x C*H*), 3.32 (1H, dt, J = 10, 2 Hz, C*H*CH=CH), 3.88 (3H, s, C*H*$_3$O), 3.92 (1H, d, J = 3 Hz, C*H*OH), 5.49 (1H, dd, J = 10, 2 Hz, CH=C*H*), 5.60 (1H, dd, J = 10, 2 Hz, C*H*=CH), 5.71 (1H, br s, O*H*), 6.63 (1H, dd, J = 8, 2 Hz, aryl H-5), 6.72 (1H, d, J = 2 Hz, aryl H-1), 6.80 (1H, d, J = 8 Hz, aryl H-4). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 30.0, 31.7, 32.6, 44.9, 45.5, 52.1, 56.2, 80.0, 95.2, 111.0, 113.6, 118.9, 130.6, 134.9, 135.2, 145.9, 146.1, 175.5. HRMS-ESI (m/z): $[M + Na]^+$ calcd for $C_{19}H_{22}O_5Na$, 353.1359; found, 353.1356. mp 174-176 °C.

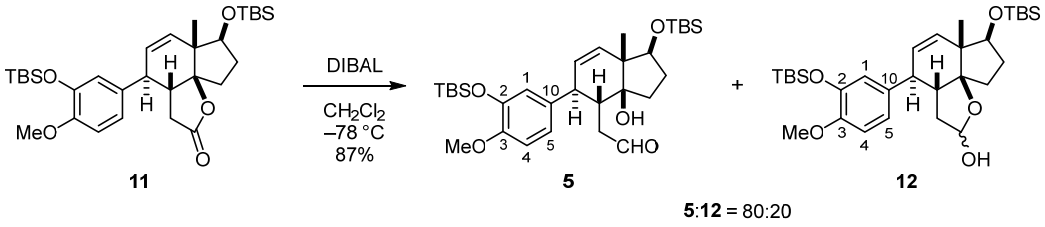


10 **11**

Silylation of 10: To a solution of **10** (953 mg, 2.88 mmol) in dry DMF (7.2 mL) were added imidazole (1.57 g, 23.1 mmol) and TBSCl (1.76 g, 11.5 mmol) at 0 °C. After being heated to 40 °C, the resulting mixture was stirred for 2 h. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ and then 1 N aqueous solution of HCl at 0 °C. The aqueous layer was extracted with EtOAc (3 x). The combined organic layer was washed with H_2O (3 x), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane:EtOAc = 7:1) to afford **11** (1.51 g, 94% yield) as a white solid.

11: IR (KBr) ν_{max} 1782, 1509, 1253 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.06 (3H, s, C*H*$_3$Si), 0.08 (3H, s, C*H*$_3$Si), 0.14 (6H, s, (C*H*$_3$)$_2$Si), 0.91 (9H, s, (C*H*$_3$)$_3$C), 0.99 (9H, s, (C*H*$_3$)$_3$C), 1.15 (3H, s, C*H*$_3$CCH), 1.70 (1H, m, C*H*), 1.85-1.97 (2H, m, 2 x C*H*), 2.10-2.23 (2H, m, 2 x C*H*), 2.25-2.38 (2H, m, 2 x C*H*), 3.22 (1H, br d, J = 9 Hz, C*H*CH=CH), 3.78 (3H, s, C*H*$_3$O), 3.90 (1H, dd, J = 4, 3 Hz, C*H*OSi), 5.46 (1H, dd, J = 10, 2 Hz, CH=C*H*), 5.58 (1H, dd, J = 10, 1 Hz, C*H*=CH), 6.62 (1H, d, J =

2 Hz, aryl H-1), 6.68 (1H, dd, J = 8, 2 Hz, aryl H-5), 6.80 (1H, d, J = 8 Hz, aryl H-4). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.8, -4.5, -4.4, 15.7, 18.2, 18.6, 25.8, 25.9, 30.2, 32.4, 32.7, 44.1, 46.5, 52.3, 55.7, 79.4, 95.1, 112.5, 120.2, 120.3, 130.2, 134.6, 136.3, 145.3, 150.1, 176.3. HRMS-ESI (m/z): [M + Na]$^+$ calcd for $C_{31}H_{50}O_5Si_2Na$, 581.3089; found, 581.3086. mp 104-105 °C.



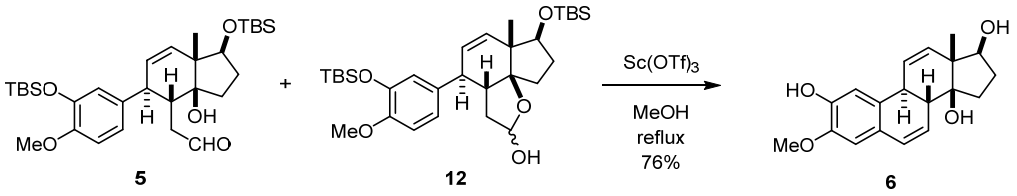
11 **5** **12**

5:**12** = 80:20

Reduction of lactone 11: To a solution of **11** (3.47 g, 6.21 mmol) in dry CH_2Cl_2 (62.0 mL) was added dropwise DIBAL (1.0 M solution in hexane, 14.0 mL, 14.0 mmol) at –78 °C. After being stirred at –78 °C for 15 min, the reaction was quenched with 1 N aqueous solution of HCl at –78 °C. The aqueous layer was extracted with CH_2Cl_2 (3 x). The combined organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane:EtOAc:CH_2Cl_2 = 8:1:1) to afford a mixture of hydroxyaldehyde **5** and lactol **12** (3.02 g, 87% yield, **5**:**12** = 80:20 determined by ^{1}H NMR analysis) as a white solid.

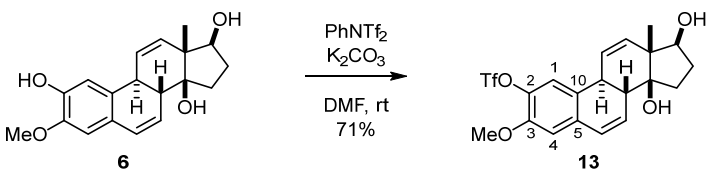
Hydroxyaldehyde 5 and lactol 12: IR (KBr) ν_{max} 3409, 1725, 1509 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (1.2H, br s, (CH_3)$_2$Si), 0.10 (4.8H, s, (CH_3)$_2$Si), 0.14 (3H, s, CH_3Si), 0.15 (3H, s, CH_3Si), 0.90 (7.2H, s, (CH_3)$_3$C), 0.91 (1.8H, s, (CH_3)$_3$C), 0.99 (9H, s, (CH_3)$_3$C), 1.22 (2.4H, s, CH_3CCH), 1.25 (0.6H, br s), 1.55-1.92 (4.0H, m), 2.10 (1H, m), 2.23 (0.8H, dd, J = 15, 3 Hz), 2.37-2.53 (1.6H, m), 2.97 (0.8H, br d, J = 10 Hz, CHCH=CH), 3.07 (0.2H, m), 3.70 (0.8H, s, OH), 3.78 (3H, s, CH_3O), 3.86 (0.2H, m, CHOSi), 3.91 (0.8H, d, J = 3.5 Hz, CHOSi), 5.32 (0.8H, dd, J = 10, 2 Hz, CH=CH), 5.41 (1H, dd, J = 10, 1 Hz, CH=CH), 5.46 (0.2H, m), 6.63-6.73 (2H, m, aryl), 6.77 (1H, m, aryl), 9.32 (0.8H, d, J = 3 Hz, CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.9, -4.6, -4.4, 17.6, 18.1, 18.6, 25.87, 25.94, 31.5, 33.0, 42.0, 44.1, 47.8, 51.7, 55.7, 82.6, 82.8, 112.2, 121.2, 122.0, 130.1, 132.9, 135.4, 145.3, 150.2, 203.0 (Signals of ^{13}C NMR are only shown for the major hydroxyaldehyde **5**). HRMS-ESI

(*m*/*z*): [M + Na]$^+$ calcd for $C_{31}H_{52}O_5Si_2Na$, 583.3245; found, 583.3240. mp 112-113 °C.



Friedel-Crafts-type cyclodehydration of 5 and 12: To a solution of a mixture of **5** and **12** (492 mg, 0.874 mmol) in MeOH (14.8 mL) was added $Sc(OTf)_3$ (87.7 mg, 0.178 mmol) at room temperature. After being heated to reflux, the resulting mixture was stirred for 4 h. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ and then 1 N aqueous solution of HCl at 0 °C. The aqueous layer was extracted with EtOAc (3 x). The combined organic layer was dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by Chromatorex DIOL silica gel open column chromatography (hexane:EtOAc = 2:1) to afford tetracycle **6** (209 mg, 76% yield) as a white solid.

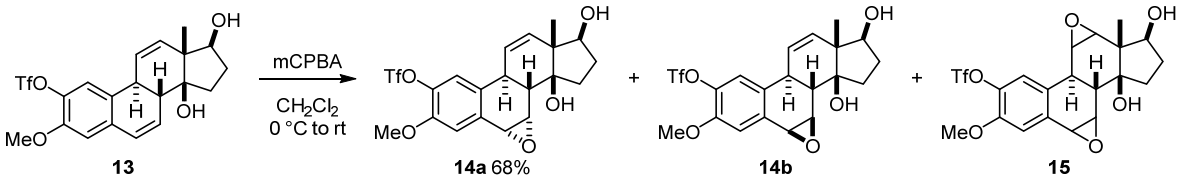
Tetracycle 6: IR (KBr) ν_{max} 3464, 1569, 1507, 1298 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD) δ 1.10 (3H, s, C*H*$_3$), 1.76 (1H, m, C*H*), 1.80-1.90 (2H, m, 2 x C*H*), 2.17 (1H, m, C*H*), 2.32 (1H, dt, *J* = 15, 2.5 Hz, C*H*CH=CH), 3.19 (1H, br d, *J* = 15 Hz, C*H*CH=CH), 3.82-3.87 (4H, m, 4 x C*H*), 5.51 (1H, dd, *J* = 10, 2.5 Hz, CH=C*H*), 6.10 (1H, d, *J* = 10 Hz, C*H*=CH), 6.24 (1H, dd, *J* = 10, 2.5 Hz, C*H*=CH), 6.53 (1H, dd, *J* = 10, 2.5 Hz, CH=C*H*), 6.75 (1H, s, aryl), 6.83 (1H, s, aryl). ^{13}C NMR (100 MHz, pyridine-d_5) δ 18.4, 32.9, 34.2, 39.9, 42.8, 53.3, 56.5, 80.6, 82.3, 112.0, 113.0, 124.6, 127.2, 129.06, 129.13 132.0, 137.1, 147.1, 147.9. HRMS-ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{19}H_{22}O_4Na$, 337.1410; found, 337.1405. mp 226-228 °C.



Sulfonylation of 6: To a solution of **6** (160 mg, 0.510 mmol) in dry DMF (5.6 mL) were added K_2CO_3

(89.2 mg, 0.645 mmol) and $PhNTf_2$ (225 mg, 0.629 mmol) at room temperature. The reaction mixture was stirred at room temperature for 18.5 h. The reaction was quenched with 1 N aqueous solution of HCl. The aqueous layer was extracted with EtOAc (4 x). The combined organic layer was washed with H_2O (3 x) and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane:EtOAc = 2:1) to afford **13** (162 mg, 71% yield) as a light brown solid.

13: IR (KBr) ν_{max} 3421, 1497, 1421, 1211 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.17 (3H, s, CH_3), 1.79-2.00 (3H, m, 3 x C*H*), 2.11 (1H, d, J = 4 Hz, CHO*H*), 2.26 (1H, ddd, J = 15, 10, 4 Hz, CH_AH$_B$COH), 2.43 (1H, dt, J = 15, 2 Hz, COHC*H*CH=CH), 2.72 (1H, s, CO*H*), 3.31 (1H, br d, J = 15 Hz, C*H*CH=CH), 3.91 (3H, s, CH_3O), 3.96 (1H, br s, C*H*OH), 5.50 (1H, dd, J = 10, 3 Hz, CH_3CC*H*=CH), 6.02 (1H, dd, J = 10, 1 Hz, CH_3CCH=C*H*), 6.54 (1H, dd, J = 10, 2 Hz, COHCHC*H*=CH), 6.58 (1H, dd, J = 10, 2 Hz, COHCHCH=C*H*), 6.81 (1H, s, aryl H-4), 7.11 (1H, s, aryl H-1). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.8, 31.9, 33.1, 38.7, 41.0, 52.8, 56.4, 80.9, 82.0, 111.4, 117.4, 118.9 (q, J = 319 Hz), 123.4, 127.9, 130.2, 132.8, 135.5, 135.7, 137.2, 149.8. HRMS-ESI (m/z): $[M + Na]^+$ calcd for $C_{20}H_{21}F_3O_6SNa$, 469.0903; found, 469.0904. mp 65-66 °C.



Epoxidation of 13: To a solution of **13** (435 mg, 0.974 mmol) in CH_2Cl_2 (8.9 mL) was added mCPBA (171 mg, 0.991 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 6.5 h. The reaction was diluted with CH_2Cl_2. The resulting mixture was washed with 10% aqueous solution of Na_2SO_3 and a saturated aqueous solution of $NaHCO_3$ and H_2O, dried over Na_2SO_4, and concentrated under reduced pressure to afford a crude mixture of diastereomers **14a** and **14b** and diepoxide **15** (**14a**:**14b**:**15** = 80:11:9 determined by ^1H NMR analysis). The residue was purified by silica gel flash column chromatography (hexane:EtOAc = 1:1) to afford α-epoxide **14a** (308 mg, 68% yield) as a light

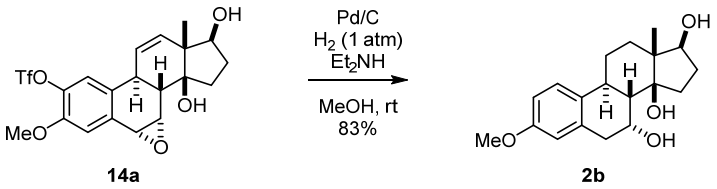
brown solid and a mixture of β-epoxide **14b** and diepoxide **15** (**14b**:**15** = 49:51 determined by ^{1}H NMR analysis) as a solid. A part of the mixture was purified by silica gel flash column chromatography (CH_2Cl_2:EtOAc = 1:2) and preparative TLC for spectral analysis of **14b** and **15**. The newly generated stereogenic centers in **14a** were determined by NOESY correlation of **2b** (Figure 5).

α-epoxide **14a:** IR (KBr) ν_{max} 3457, 1508, 1422, 1214 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (3H, s, C*H*$_3$), 1.79-1.86 (2H, m, 2 x C*H*), 1.89 (1H, d, *J* = 12 Hz, C*H*COH), 2.06 (1H, dt, *J* = 15, 9 Hz, C*H*), 2.18 (1H, br s, O*H*), 2.34 (1H, ddd, *J* = 15, 9, 5 Hz, C*H*), 3.17 (1H, br s, O*H*), 3.45 (1H, br d, *J* = 12 Hz, C*H*CH=CH), 3.89 (1H, d, *J* = 4 Hz, CHC*H*), 3.94 (3H, s, C*H*$_3$O), 3.99 (1H, br s, C*H*OH), 4.17 (1H, d, *J* = 4 Hz, C*H*CH), 5.44 (1H, dd, *J* = 10, 3 Hz, CH=C*H*), 6.01 (1H, d, *J* = 10 Hz, C*H*=CH), 7.12 (1H, s, aryl), 7.14 (1H, s, aryl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.7, 32.0, 32.8, 33.2, 40.2, 52.6, 53.0, 53.5, 56.6, 80.8, 82.0, 115.1, 118.2, 118.8 (q, *J* = 319 Hz), 123.6, 131.9, 133.7, 134.7, 138.4, 149.6. HRMS-ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{20}H_{21}F_3O_7SNa$, 485.0852; found, 485.0862. mp 74-76 °C.

β-epoxide **14b:** IR (KBr) ν_{max} 3055, 1422, 1265 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (3H, s, C*H*$_3$), 1.81-1.93 (3H, m, 3 x C*H*), 2.12 (1H, m, C*H*), 2.19-2.28 (2H, m, 2 x C*H*), 2.81 (1H, s, O*H*), 3.54 (1H, br d, *J* = 12 Hz, C*H*CH=CH), 3.79 (1H, d, *J* = 4 Hz, C*H*), 3.86 (1H, t, *J* = 4 Hz, C*H*), 3.94 (3H, s, C*H*$_3$O), 3.96 (1H, m, C*H*), 5.52 (1H, dd, *J* = 10, 3 Hz, CH=C*H*), 5.92 (1H, dd, *J* = 10, 2 Hz, C*H*=CH), 7.06 (1H, s, aryl), 7.29 (1H, s, aryl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.5, 31.9, 32.8, 37.7, 46.5, 48.8, 52.8, 55.0, 56.5, 80.8, 82.0, 116.4, 118.6, 123.0, 133.7, 134.0, 136.4, 138.7, 150.1. (CF_3 group is missing due to weak signal). HRMS-ESI (*m*/*z*): [M + Na]$^+$ calcd for $C_{20}H_{21}F_3O_7SNa$, 485.0852; found, 485.0864. mp 125-126 °C.

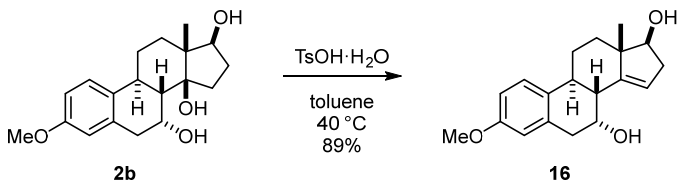
Diepoxide **15:** IR (KBr) ν_{max} 3459, 1510, 1422, 1222 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H, s, C*H*$_3$), 1.84 (1H, d, *J* = 12 Hz), 1.95-2.10 (3H, m), 2.40 (1H, m), 2.77 (1H, d, *J* = 1 Hz), 2.81 (1H, d, *J* = 4 Hz), 3.19 (1H, d, *J* = 12 Hz, ArC*H*), 3.65 (1H, d, *J* = 4 Hz), 3.86 (1H, d, *J* = 4 Hz), 3.95 (3H, s, C*H*$_3$O), 4.06 (1H, m), 4.09 (1H, d, *J* = 4 Hz), 7.13 (1H, s, aryl), 7.27 (1H, s, aryl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.2, 32.0, 33.2, 33.7, 36.6, 49.2, 52.1, 53.5, 53.9, 56.6, 58.4, 80.9, 81.2, 114.8, 119.0,

130.3, 134.1, 138.5, 150.1 (CF_3 group is missing due to weak signal). HRMS-ESI (*m*/*z*): $[M + Na]^+$ calcd for $C_{20}H_{21}F_3O_8SNa$, 501.0801; found, 501.0800.



Hydrogenolysis of 14a: To a solution of **14a** (283 mg, 0.612 mmol) in MeOH (6.1 mL) were added Et_2NH (0.080 ml, 0.77 mmol) and Pd/C (5%, 143 mg) at room temperature. The reaction mixture was stirred under an atmosphere of hydrogen (1 atm) at room temperature for 17 h. The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by Chromatorex DIOL silica gel open column chromatography (hexane:EtOAc = 2:1) to afford **2b** (162 g, 83% yield) as a white solid.

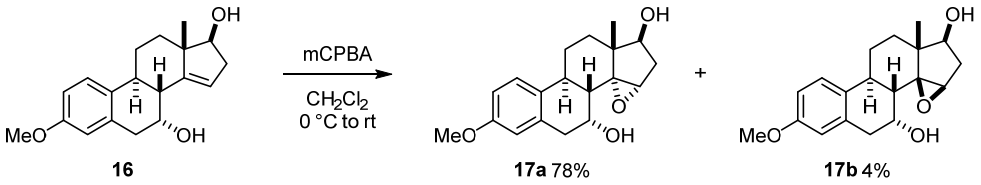
2b: IR (KBr) ν_{max} 3406, 1608, 1501, 1235 cm^{-1}. ^1H NMR (400 MHz, CD_3OD) δ 1.07 (3H, s, C*H*$_3$), 1.30 (1H, m, C*H*), 1.35-1.49 (2H, m, 2 x C*H*), 1.63 (1H, d, *J* = 12 Hz,C*H*COH), 1.80 (1H, m, C*H*), 1.97 (1H, ddd, *J* = 14, 10, 3 Hz, C*H*), 2.20-2.41 (3H, m, 3 x C*H*), 2.80-2.90 (2H, m, 2 x C*H*), 3.03 (1H, d, *J* = 17 Hz, CH_AH$_B$CHOHCH), 3.66 (1H, d, *J* = 6 Hz, C*H*OHCCH$_3$), 3.74 (3H, s, C*H*$_3$O), 4.54 (1H, br s, C*H*OHCH), 6.62 (1H, d, *J* = 2 Hz, aryl H-4), 6.70 (1H, dd, *J* = 9, 2 Hz, aryl H-2), 7.22 (1H, d, *J* = 9 Hz, aryl H-1). ^{13}C NMR (100 MHz, CD_3OD) δ 14.2, 28.1, 32.1, 33.5, 34.0, 35.2, 41.1, 48.3, 50.8, 55.5, 63.8, 82.8, 85.3, 113.0, 115.4, 128.1, 133.1, 136.1, 159.1. HRMS-ESI (*m*/*z*): $[M + Na]^+$ calcd for $C_{19}H_{26}O_4Na$, 341.1723; found, 341.1728. mp 128-129 °C.



Dehydration of 2b: To a solution of **2b** (49.6 mg, 0.156 mmol) in toluene (6.4 mL) was added TsOH·H_2O (176 mg, 0.927 mmol) at room temperature. After being heated to 40 °C, the resulting mixture

was stirred for 4.5 h. The reaction mixture was cooled to room temperature and diluted with H_2O. The aqueous layer was extracted with EtOAc (3 x). The combined organic layer was washed with H_2O (2 x), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane:EtOAc = 1:1) to afford alkene **16** (41.6 mg, 89% yield) as a white solid.

16: IR (KBr) ν_{max} 3396, 1610, 1502, 1254, 1070 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (3H, s, CH_3), 1.45 (1H, td, J = 14, 3.5 Hz, CH), 1.61 (1H, m, CH), 2.04 (1H, dt, J = 13, 3 Hz, CH), 2.21-2.31 (2H, m, 2 x CH), 2.46 (1H, dddd, J = 13, 3, 3, 3 Hz, CH), 2.59-2.71 (2H, m, 2 x CH), 2.97 (1H, d, J = 18 Hz, CH_AH$_B$CHOHCH), 3.15 (1H, dd, J = 18, 3 Hz, CH$_A$$H_B$CHOHCH), 3.78 (3H, s, C$H_3$O), 4.13 (1H, m, C$H$OHCCH$_3$), 4.54 (1H, br s, C$H$OHCH), 5.39 (1H, d, J = 2 Hz, CH=C), 6.66 (1H, d, J = 2 Hz, aryl H-4), 6.76 (1H, dd, J = 9, 2 Hz, aryl H-2), 7.28 (1H, d, J = 9 Hz, aryl H-1). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0, 27.0, 36.1, 37.9, 38.4, 39.1, 43.3, 47.4, 55.4, 65.1, 83.4, 112.4, 114.6, 116.0, 127.0, 130.9, 134.6, 149.0, 158.0. HRMS-ESI (m/z): $[M + Na]^+$ calcd for $C_{19}H_{24}O_3Na$, 323.1618; found, 323.1622. mp 161-163 °C.



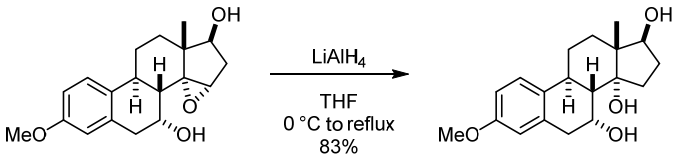
16 **17a** 78% **17b** 4%

Epoxidation of 16: To a solution of **16** (29.8 mg, 0.0992 mmol) in CH_2Cl_2 (0.90 mL) was added mCPBA (21.5 mg, 0.125 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 10 min. The reaction was diluted with EtOAc. The resulting mixture was washed with 10% aqueous solution of Na_2SO_3 (2 x) and a saturated aqueous solution of $NaHCO_3$ and H_2O (2 x) and brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford a crude mixture of diastereomers (**17a**:**17b** = 95:5 determined by ^1H NMR analysis). The residue was purified by silica gel flash column chromatography (hexane:EtOAc = 1:1) to afford α-epoxide **17a** (24.4 mg, 78% yield) as a white solid and β-epoxide **17b** (1.2 mg, 4% yield) as a white solid. Relative stereochemistry of **17a**

was determined by comparison of ^{1}H NMR spectra of **2b** and **1b** after reduction with $LiAlH_4$.

α-epoxide **17a:** IR (KBr) ν_{max} 3430, 1610, 1504, 1258 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (3H, s, CH_3), 1.59-1.75 (4H, m, 4 x C*H*), 1.93 (1H, m, $CH_3CCH_AH_B$), 2.27 (1H, d, J = 12 Hz, CHOHC*H*CH), 2.45 (1H, dd, J = 14, 7 Hz, $CH_AH_BCHOHCCH_3$), 2.52 (1H, m, $CH_3CCH_2CH_AH_B$), 2.87 (1H, d, J = 18 Hz, $CH_AH_BCHOHCH$), 3.01 (1H, d, J = 18 Hz, $CH_AH_BCHOHCH$), 3.10 (1H, td, J = 12, 3 Hz, C*H*CHCHOH), 3.57 (1H, d, J = 1 Hz, O*H*), 3.73 (1H, m, C*H*OHCCH$_3$), 3.77 (3H, s, CH_3O), 3.94 (1H, s, C*H*CH$_2$CHOH), 4.10 (1H, br s, C*H*OHCH), 6.64 (1H, d, J = 2 Hz, aryl H-4), 6.76 (1H, dd, J = 9, 2 Hz, aryl H-2), 7.28 (1H, d, J = 9 Hz, aryl H-1). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 26.0, 32.9, 33.7, 34.3, 37.1, 38.4, 41.9, 55.4, 59.2, 65.1, 74.8, 75.9, 112.3, 114.6, 126.8, 130.7, 134.8, 158.0. HRMS-ESI (m/z): $[M + Na]^+$ calcd for $C_{19}H_{24}O_4Na$, 339.1567; found, 339.1558. mp 185-187 °C.

β-epoxide **17b:** IR (KBr) ν_{max} 3423, 1609, 1500, 1235 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (3H, s, CH_3), 1.25 (1H, m), 1.32 (1H, m), 1.60-1.70 (2H, m), 2.01-2.14 (3H, m), 2.27 (1H, dd, J = 16, 6 Hz, C*H*), 2.42 (1H, m, C*H*), 2.78-2.91 (2H, m, 2 x C*H*), 3.12 (1H, d, J = 17 Hz, $CH_AH_BCHOHCH$), 3.48 (1H, dd, J = 12, 6 Hz, C*H*), 3.78 (3H, s, CH_3O), 4.06 (1H, s, C*H*), 4.25 (1H, br s, C*H*), 6.64 (1H, d, J = 2 Hz, aryl H-4), 6.78 (1H, dd, J = 8, 2 Hz, aryl H-2), 7.25 (1H, d, J = 8 Hz, aryl H-1). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 26.8, 34.6, 35.9, 36.3, 39.8, 40.2, 46.1, 55.4, 62.4, 62.8, 72.7, 112.7, 115.0, 127.1, 130.8, 134.1, 158.2. (one sp^3 carbon is missing due to overlap with $CDCl_3$). HRMS-ESI (m/z): $[M + Na]^+$ calcd for $C_{19}H_{24}O_4Na$, 339.1567; found, 339.1574. mp 177-180 °C.

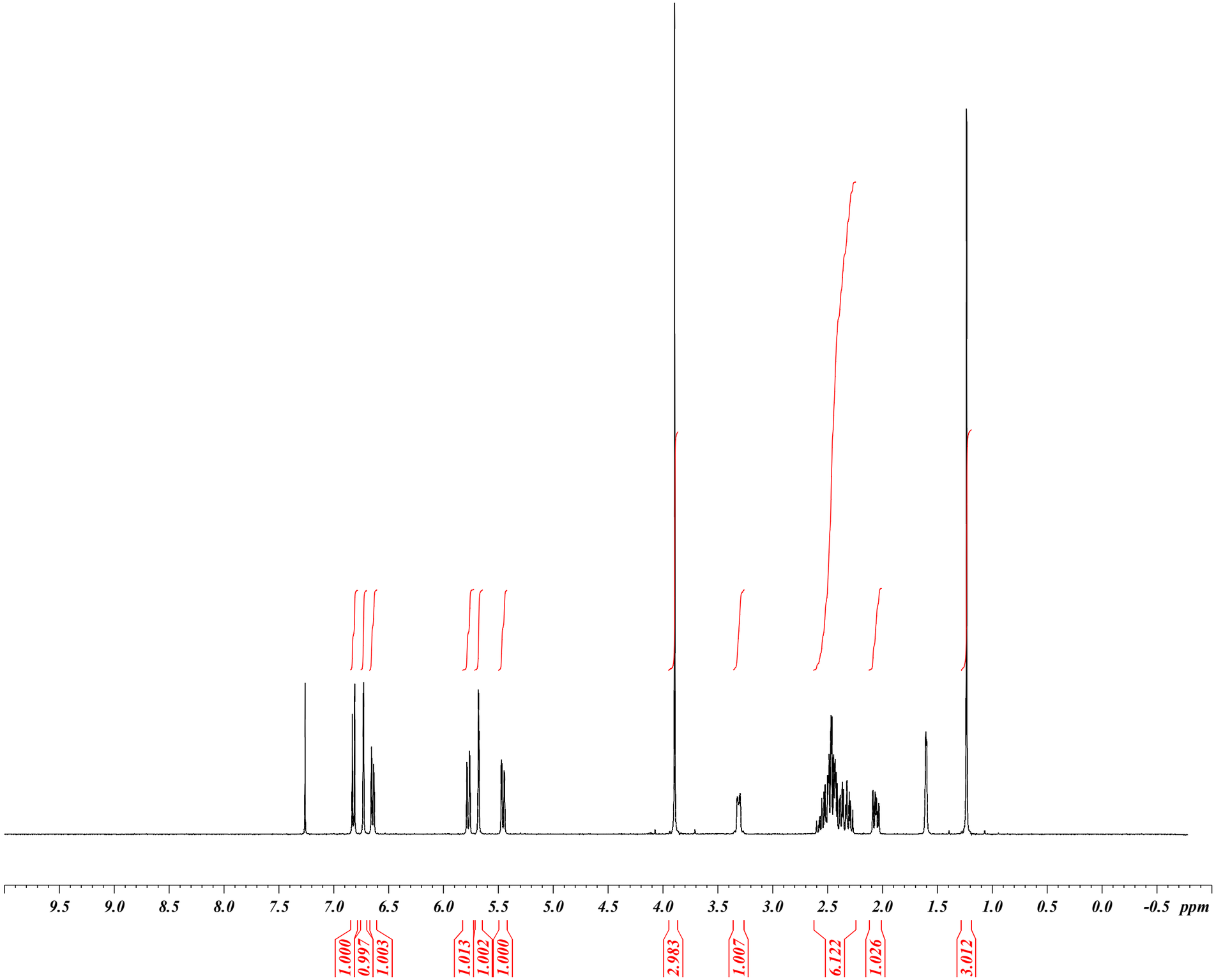


17a **1b**

Reduction of 17a: To a solution of **17a** (109 mg, 0.344 mmol) in dry THF (4.7 mL) were added $LiAlH_4$ (109 mg, 2.88 mmol) and dry THF (3.0 mL) at 0 °C. After being heated to reflux, the resulting mixture was stirred for 5 h. The reaction was quenched with 1 N aqueous solution of HCl at 0 °C. The aqueous layer was extracted with EtOAc (3 x). The combined organic layer was

washed with H_2O (2 x), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (CH_2Cl_2:MeOH = 20:1) to afford **1b** (90.9 mg, 83% yield) as a white solid.

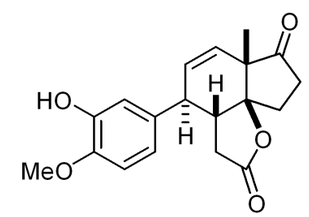
1b: IR (KBr) ν_{max} 3367, 1501, 1056 cm^{-1}. ^1H NMR (400 MHz, CD_3OD) δ 0.86 (3H, s, CH_3), 1.45-1.63 (3H, m, 3 x CH), 1.73 (1H, m, CH_AH$_B$COH), 1.78 (1H, d, J = 13 Hz, CHCOH), 1.87 (1H, td, J = 13, 6 Hz, CH$_A$$H_B$COH), 2.20 (1H, td, J = 13, 4 Hz, CH$_3$CCH_AH$_B$), 2.26 (1H, m, CH_AH$_B$CH$_2$COHCCH$_3$), 2.41 (1H, m, CH$_3$CCH$_2$CH_AH$_B$), 2.79 (1H, d, J = 19 Hz, CH_AH$_B$CHOHCH), 3.08 (1H, dd, J = 19, 3 Hz, CH$_A$$H_B$CHOHCH), 3.25 (1H, m, C$H$CHCHOH), 3.74 (3H, s, C$H_3$O), 4.23 (1H, t, J = 8 Hz, CHOHCCH$_3$), 4.39 (1H, br s, CHOHCH), 6.61 (1H, d, J = 2 Hz, aryl H-4), 6.71 (1H, dd, J = 9, 2 Hz, aryl H-2), 7.25 (1H, d, J = 9 Hz, aryl H-1). ^{13}C NMR (100 MHz, CD_3OD) δ 15.8, 26.8, 30.0, 30.5, 31.0, 33.1, 39.6, 44.9, 48.4, 55.5, 67.5, 79.1, 85.8, 112.9, 115.1, 127.7, 133.6, 135.7, 159.0. HRMS-ESI (m/z): $[M + Na]^+$ calcd for $C_{19}H_{26}O_4Na$, 341.1723; found, 341.1726. mp 185-186 °C.



Current Data Parameters
NAME kawaiA400
EXPNO 85
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200817
Time 12.12 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 4901.961 Hz
FIDRES 0.149596 Hz
AQ 6.6846719 sec
RG 1024
DW 102.000 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
SFO1 400.1321477 MHz
NUC1 1H
P1 15.00 usec

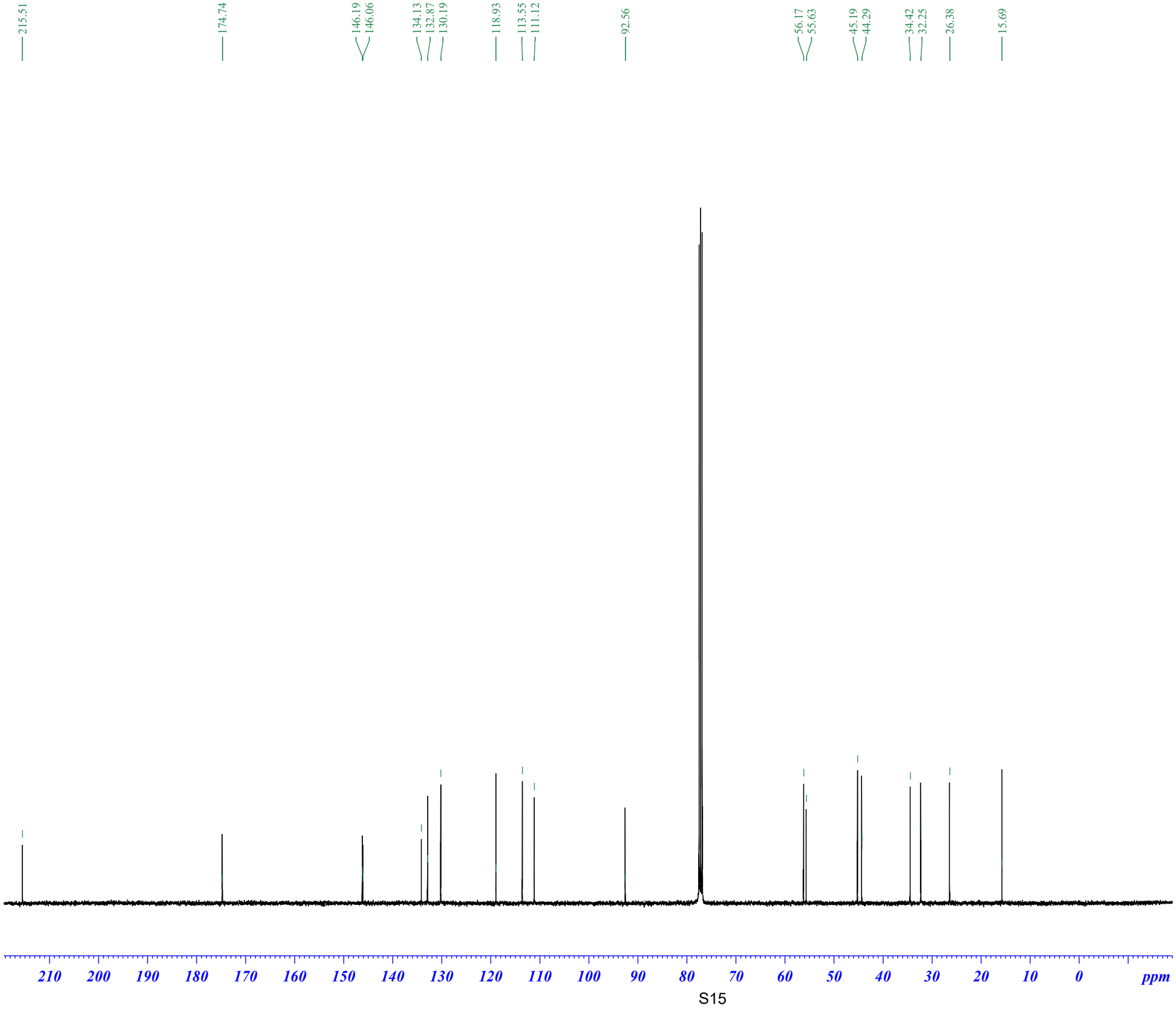
F2 - Processing parameters
SI 32768
SF 400.1300093 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



8

^{1}H NMR (400 MHz, $CDCl_3$)

13C kawai 2077 20 08 17



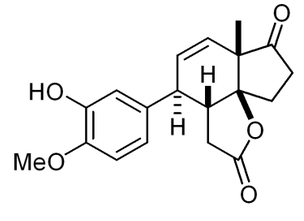
Current Data Parameters
NAME kawaiB400
EXPNO 245
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200817
Time 13.40
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2000
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 2580.3
DW 20.850 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 =======
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

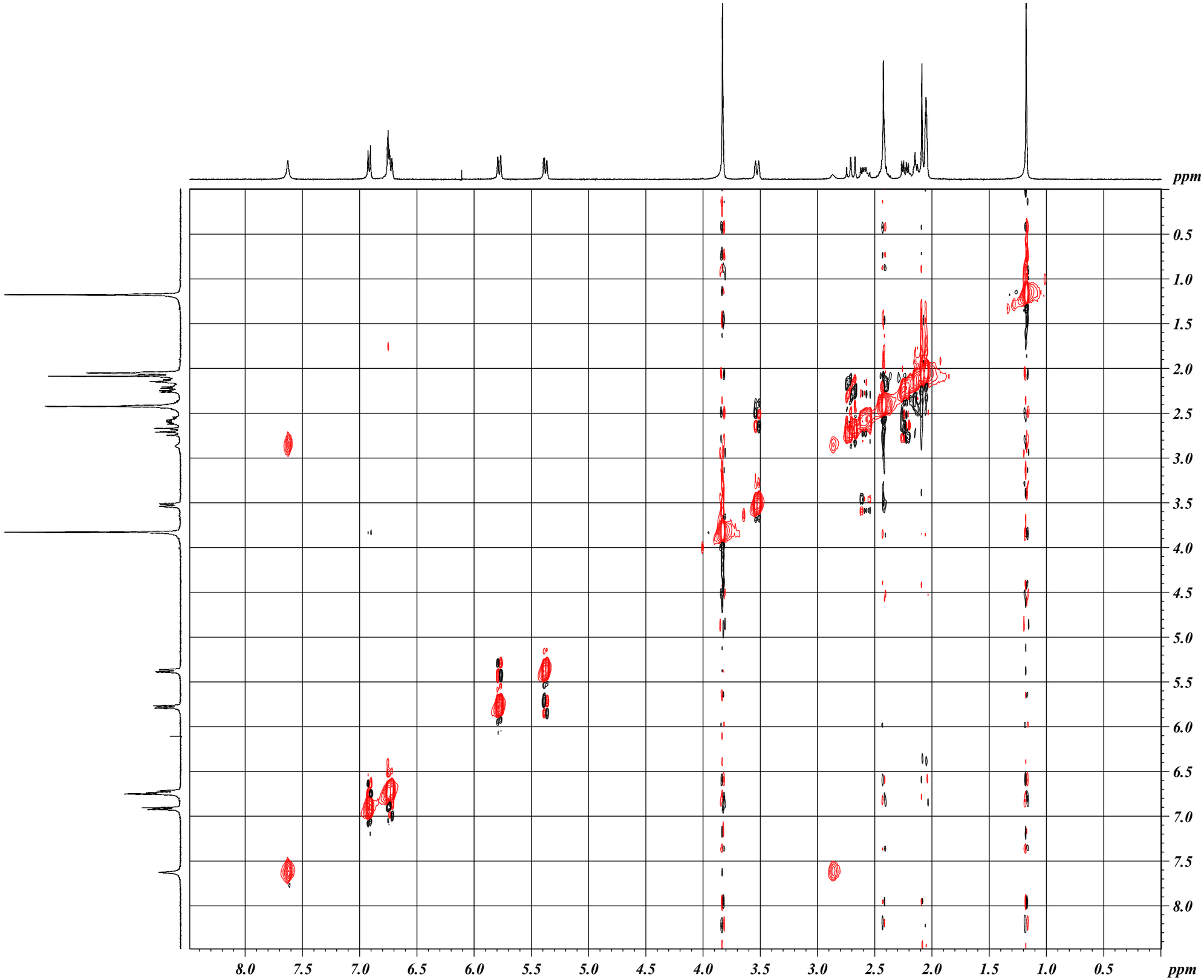
======== CHANNEL f2 =======
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 10.30 dB
PL12 25.00 dB
PL13 25.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127561 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

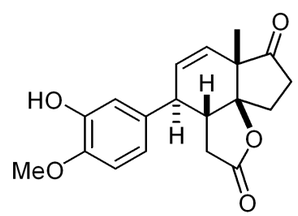


8

^{13}C NMR (100 MHz, $CDCl_3$)

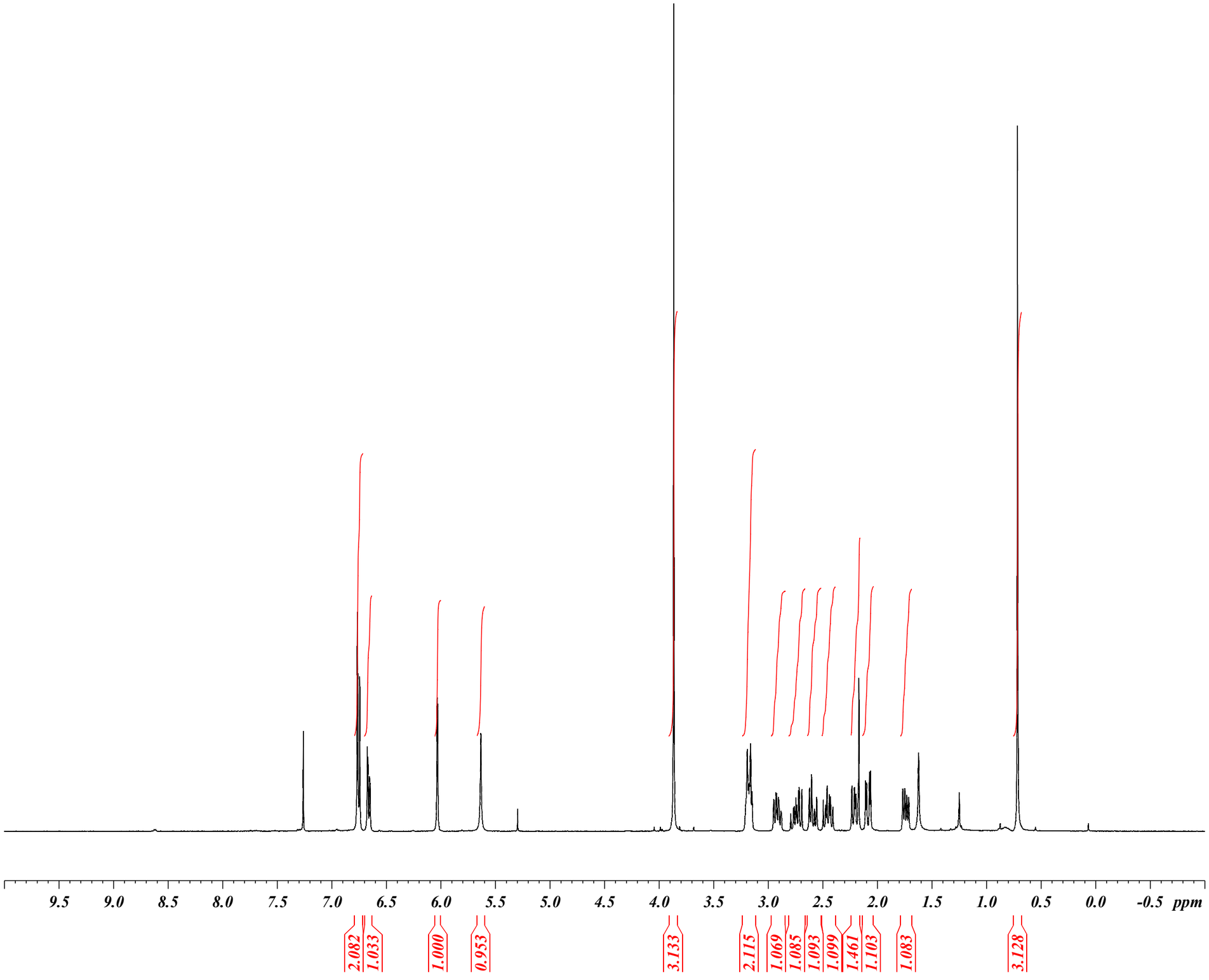



```
Current Data Parameters
NAME          kawaiB400
EXPNO               378
PROCNO                1

F2 - Acquisition Parameters
Date_          20210115
Time               8.54
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         noesyph
TD                 2048
SOLVENT         Acetone
NS                   28
DS                    2
SWH            3396.739 Hz
FIDRES         1.658564 Hz
AQ             0.3014656 sec
RG                645.1
DW              147.200 usec
DE                6.50 usec
TE                293.2 K
D0           0.00012810 sec
D1           2.00000000 sec
D8           0.60000002 sec
IN0          0.00029440 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.00 usec
PL1                10.30 dB
SFO1        400.1317028 MHz

F1 - Acquisition parameters
TD                  128
SFO1          400.1317 MHz
FIDRES       53.074062 Hz
SW                8.489 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                 1024
SF          400.1300068 MHz
WDW               QSINE
SSB                   2
LB        0 Hz
GB        0
PC                 1.00

F1 - Processing parameters
SI                 1024
MC2          States-TPPI
SF          400.1300076 MHz
WDW               QSINE
SSB                   2
LB        0 Hz
GB        0
```



8

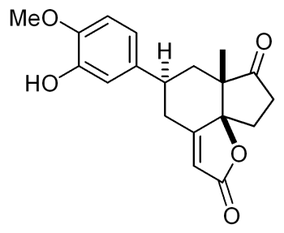
NOESY (acetone-d_6)



Current Data Parameters
NAME kawaiB400-2
EXPNO 13
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210303
Time 8.57 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.252629 Hz
AQ 3.9583745 sec
RG 322.5
DW 60.400 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324710 MHz
NUC1 1H
P1 15.00 usec

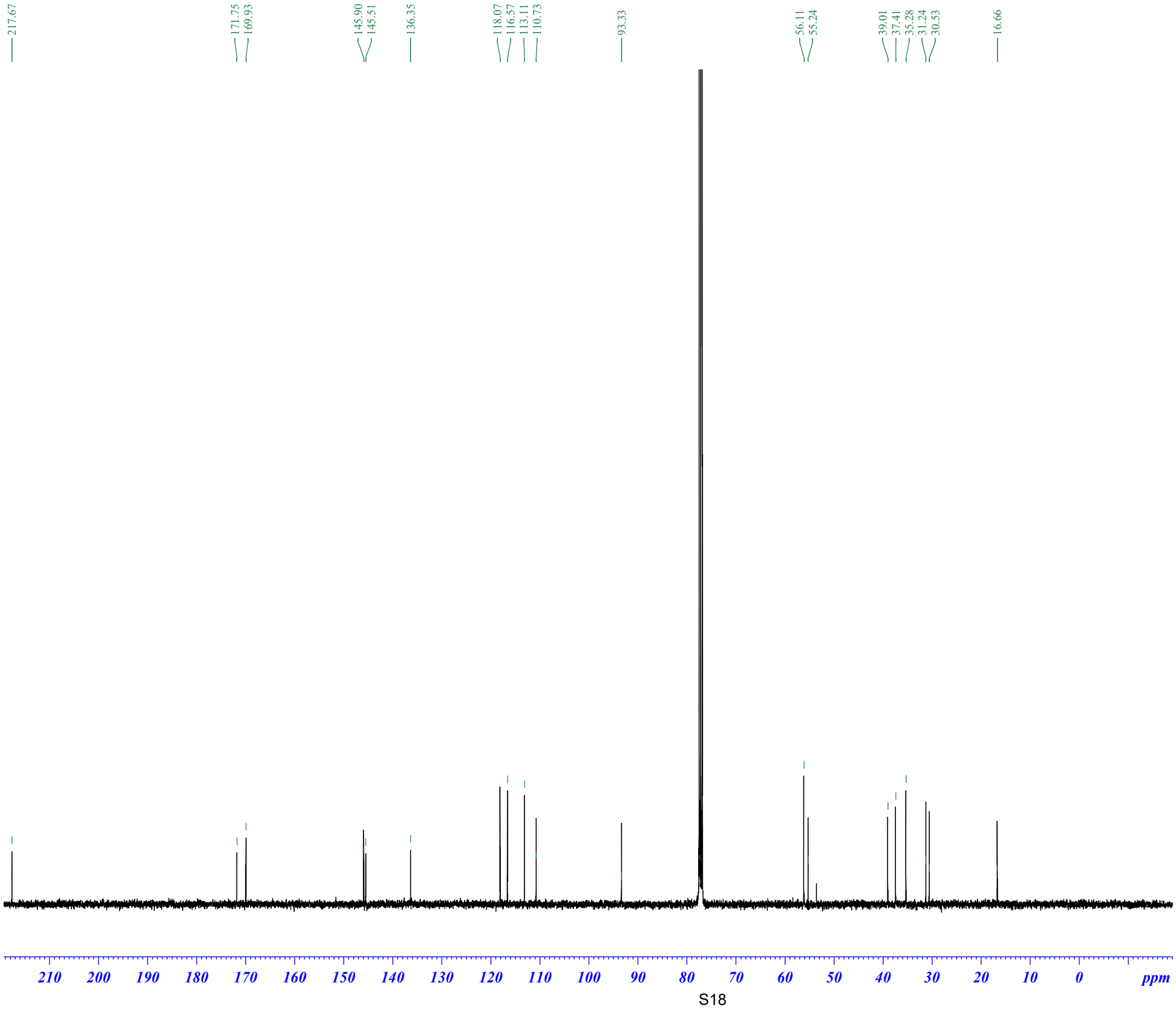
F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



9

^{1}H NMR (400 MHz, $CDCl_3$)

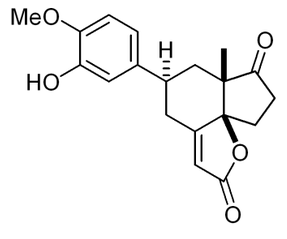
2077 bp 210301



Current Data Parameters
NAME kawaiB400-2
EXPNO 9
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210301
Time 17.41 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2000
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 362
DW 20.850 usec
DE 6.50 usec
TE 298.4 K
D1 1.20000005 sec
d11 0.03000000 sec
DELTA 1.10000002 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec

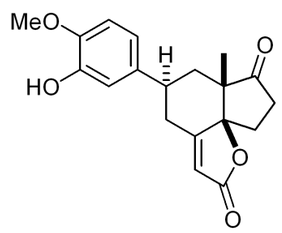
F2 - Processing parameters
SI 32768
SF 100.6127552 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



9

^{13}C NMR (100 MHz, $CDCl_3$)

2077 21 01 13 BP



9

COSY (acetone-d_6)

Current Data Parameters
NAME kawaiB400
EXPNO 370
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210113
Time 12.33
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG cosygpqf
TD 2048
SOLVENT Acetone
NS 1
DS 2
SWH 3255.208 Hz
FIDRES 1.589457 Hz
AQ 0.3145728 sec
RG 11585.2
DW 153.600 usec
DE 6.50 usec
TE 293.2 K
D0 0.00000300 sec
D1 1.48689198 sec
D13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00030720 sec

======== CHANNEL f1 ========
NUC1 1H
P0 15.00 usec
P1 15.00 usec
PL1 10.30 dB
SFO1 400.1316217 MHz

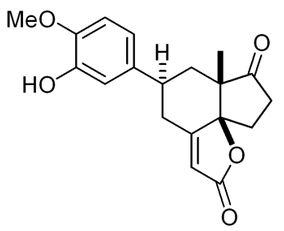
====== GRADIENT CHANNEL =====
GPNAM[1] SINE.100
GPZ1 10.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 256
SFO1 400.1316 MHz
FIDRES 25.431303 Hz
SW 8.135 ppm
FnMODE QF

F2 - Processing parameters
SI 1024
SF 400.1300069 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 QF
SF 400.1300069 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0

2077bp 210304 bc



9

HMBC (acetone-d_6)

Current Data Parameters
NAME kawaiB400-2
EXPNO 24
PROCNO 1

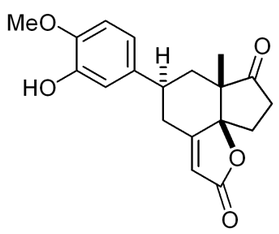
F2 - Acquisition Parameters
Date_ 20210304
Time 22.26 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG hmbcgplpndqf
TD 2048
SOLVENT Acetone
NS 32
DS 16
SWH 3787.879 Hz
FIDRES 3.699100 Hz
AQ 0.2703360 sec
RG 23170.5
DW 132.000 usec
DE 6.50 usec
TE 297.7 K
CNST2 145.0000000
CNST13 10.0000000
d0 0.00000300 sec
D1 1.07711995 sec
d2 0.00344828 sec
d6 0.05000000 sec
D16 0.00010000 sec
in0 0 sec
SFO1 400.1317102 MHz
NUC1 1H
P1 15.00 usec
p2 30.00 usec
SFO2 100.6228298 MHz
NUC2 13C
P3 10.00 usec
GPNAM[1] SINE.100
GPZ1 50.00 %
GPNAM[2] SINE.100
GPZ2 30.00 %
GPNAM[3] SINE.100
GPZ3 40.10 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 256
SFO1 100.6228 MHz
FIDRES 187.350113 Hz
SW 238.324 ppm
FnMODE QF

F2 - Processing parameters
SI 2048
SF 400.1299998 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 QF
SF 100.6126797 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0

2077bp 210304 qc



9

HMQC (acetone-d_6)

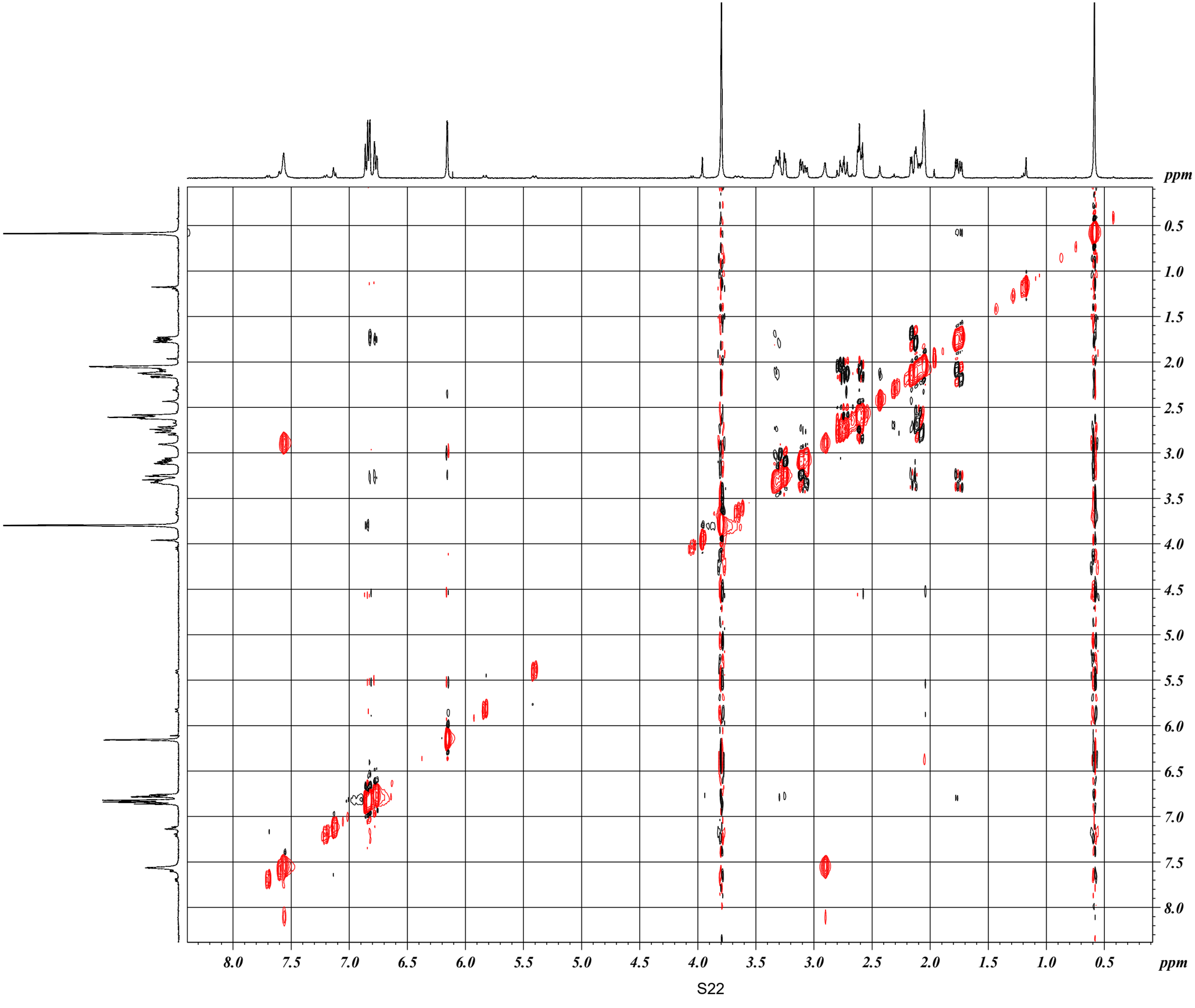
Current Data Parameters
NAME kawaiB400-2
EXPNO 25
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210305
Time 1.40 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG hmqcgpqf
TD 2048
SOLVENT Acetone
NS 32
DS 16
SWH 3787.879 Hz
FIDRES 3.699100 Hz
AQ 0.2703360 sec
RG 26008
DW 132.000 usec
DE 6.50 usec
TE 296.6 K
CNST2 145.0000000
d0 0.00000300 sec
D1 1.50000000 sec
d2 0.00344828 sec
d12 0.00002000 sec
d13 0.00000400 sec
D16 0.00010000 sec
DELTA1 0.00232428 sec
in0 0 sec
SFO1 400.1317102 MHz
NUC1 1H
P1 15.00 usec
p2 30.00 usec
SFO2 100.6228298 MHz
NUC2 13C
CPDPRG[2 garp
P3 10.00 usec
PCPD2 70.00 usec
GPNAM[1] SINE.100
GPZ1 50.00 %
GPNAM[2] SINE.100
GPZ2 30.00 %
GPNAM[3] SINE.100
GPZ3 40.10 %
P16 1000.00 usec

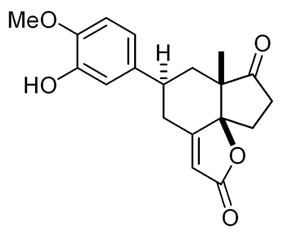
F1 - Acquisition parameters
TD 256
SFO1 100.6228 MHz
FIDRES 187.350113 Hz
SW 238.324 ppm
FnMODE QF

F2 - Processing parameters
SI 1024
SF 400.1300000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 QF
SF 100.6126690 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

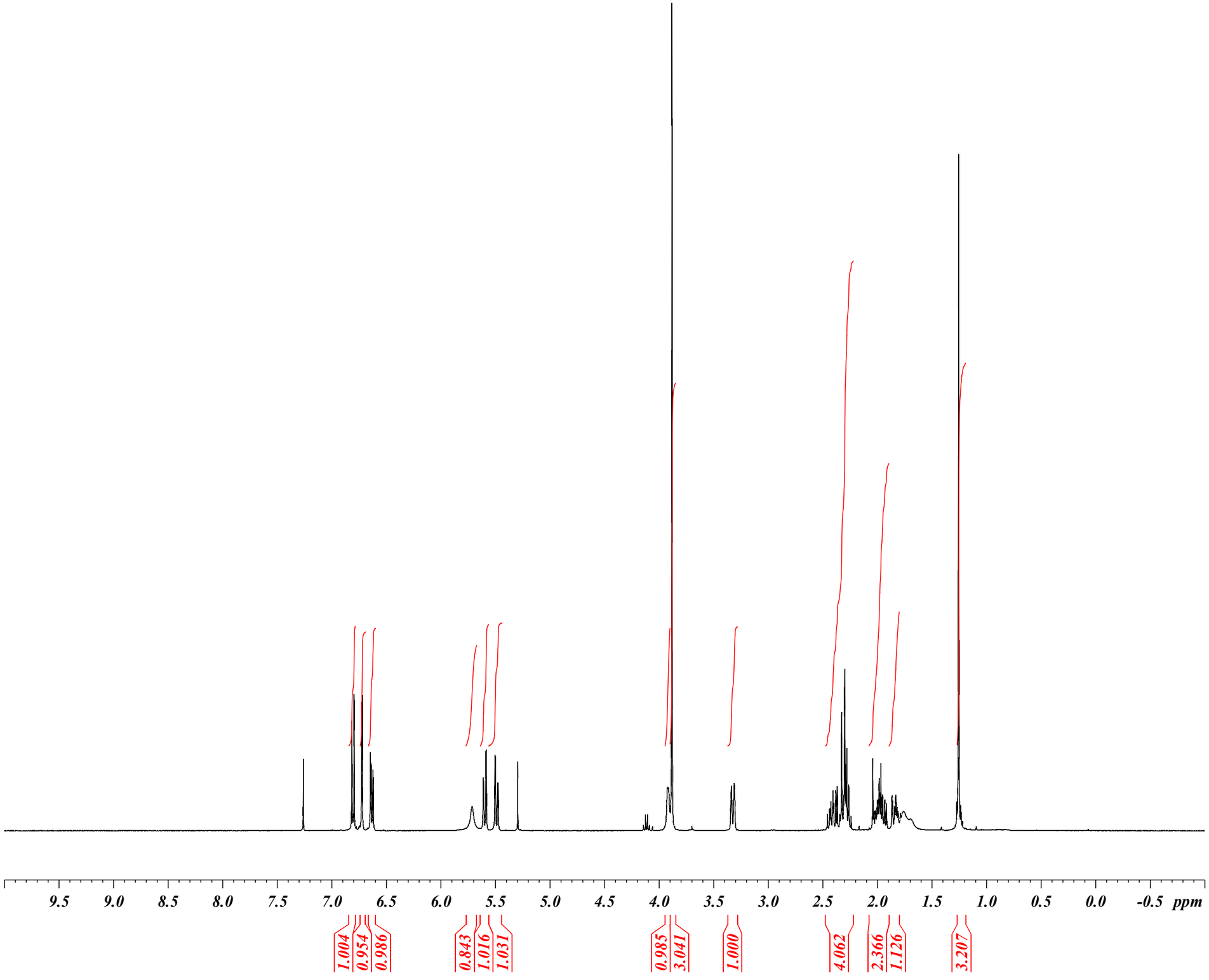



```
Current Data Parameters
NAME          kawaiB400
EXPNO               376
PROCNO                1

F2 - Acquisition Parameters
Date_          20210114
Time               9.10
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         noesyph
TD                 2048
SOLVENT         Acetone
NS                   24
DS                    2
SWH            3324.468 Hz
FIDRES         1.623275 Hz
AQ             0.3080192 sec
RG                 456.1
DW               150.400 usec
DE                 6.50 usec
TE                292.2 K
D0           0.00013130 sec
D1           2.00000000 sec
D8           0.60000002 sec
IN0          0.00030080 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.00 usec
PL1                10.30 dB
SFO1        400.1317028 MHz

F1 - Acquisition parameters
TD                  128
SFO1          400.1317 MHz
FIDRES       51.944813 Hz
SW                8.308 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI                 1024
SF          400.1300070 MHz
WDW                QSINE
SSB                    2
LB         0 Hz
GB         0
PC                 1.00

F1 - Processing parameters
SI                 1024
MC2         States-TPPI
SF          400.1300109 MHz
WDW                QSINE
SSB                    2
LB         0 Hz
GB         0
```



9

NOESY (acetone-d_6)

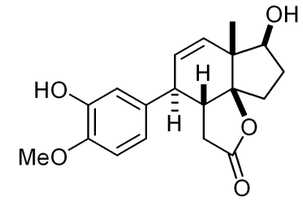


Current Data Parameters
NAME kawaiB400
EXPNO 288
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201029
Time 13.21
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9583745 sec
RG 161.3
DW 60.400 usec
DE 6.50 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 10.30 dB
SFO1 400.1324710 MHz

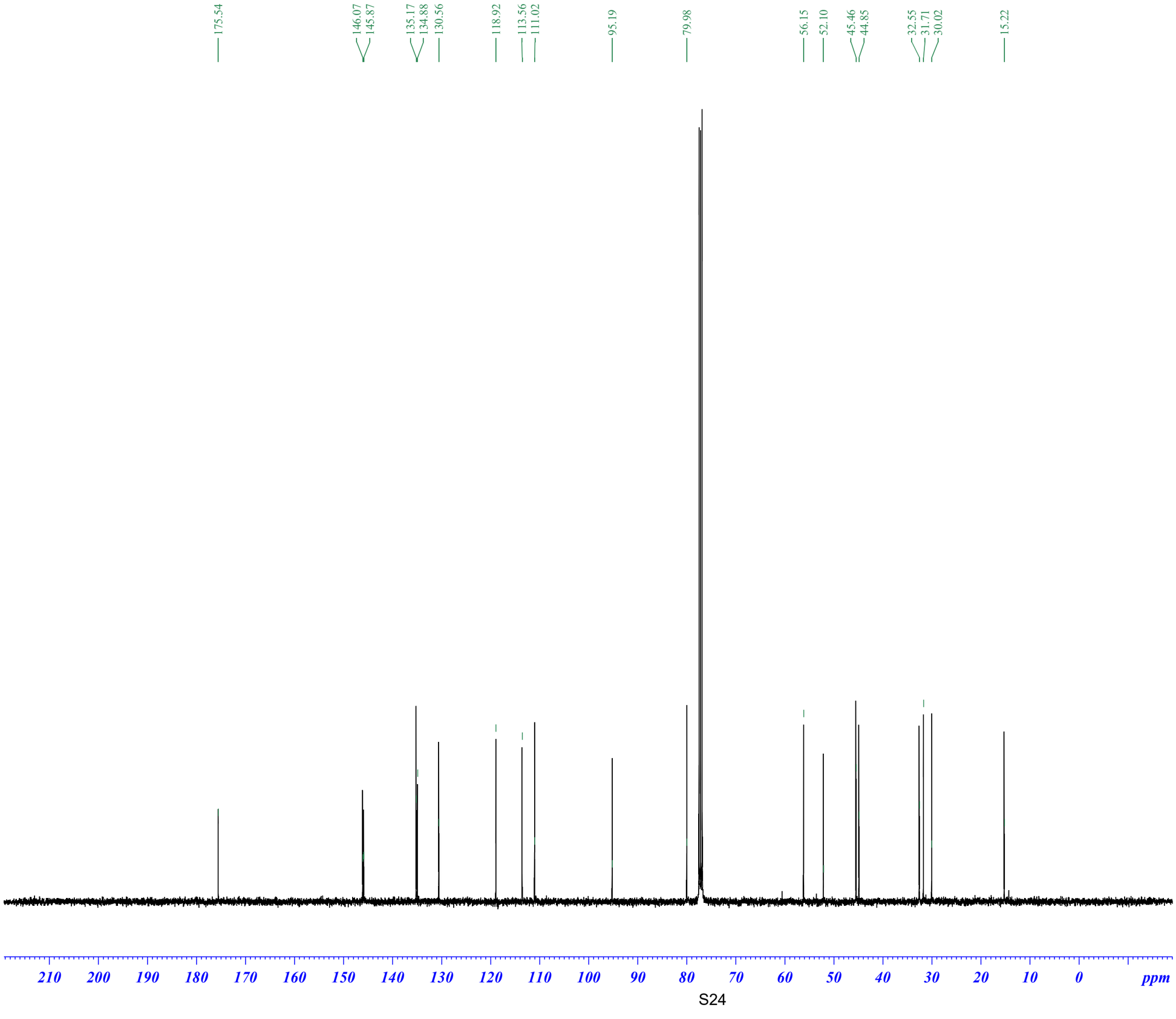
F2 - Processing parameters
SI 32768
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



10

^{1}H NMR (400 MHz, $CDCl_3$)

13C 2083 kawai 20 10 29



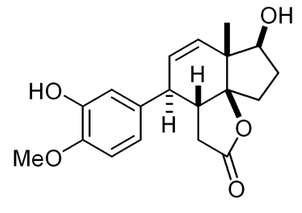
Current Data Parameters
NAME kawaiB400
EXPNO 289
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201029
Time 14.20
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1000
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 2580.3
DW 20.850 usec
DE 6.50 usec
TE 297.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 =======
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

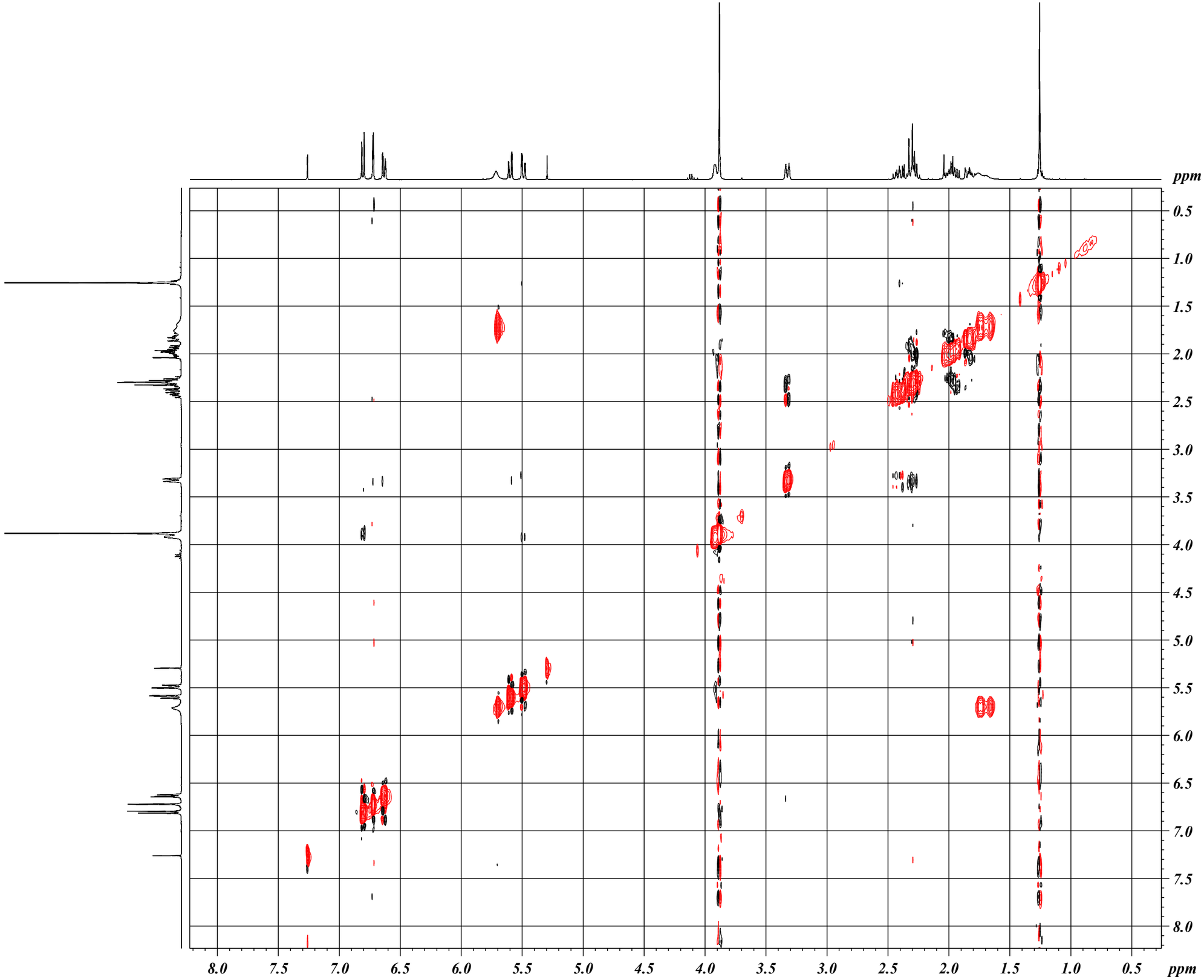
======== CHANNEL f2 =======
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 10.30 dB
PL12 25.00 dB
PL13 25.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127584 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

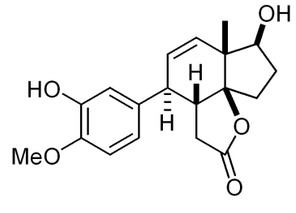


10

^{13}C NMR (100 MHz, $CDCl_3$)

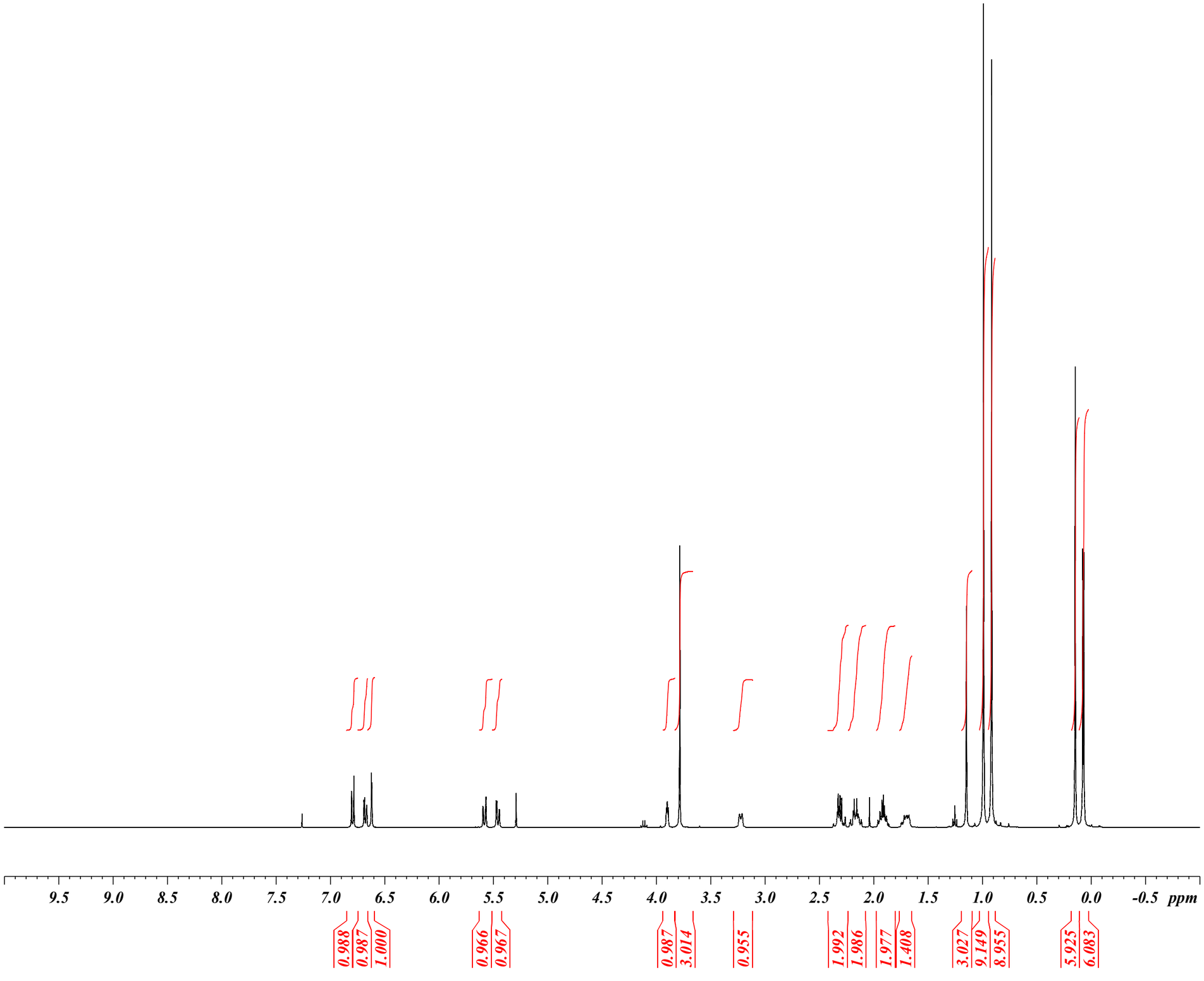



```
Current Data Parameters
NAME          kawaiB400
EXPNO               352
PROCNO                1

F2 - Acquisition Parameters
Date_          20210106
Time              12.20
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         noesyph
TD                2048
SOLVENT           CDCl3
NS                  24
DS                   2
SWH          3188.775 Hz
FIDRES       1.557019 Hz
AQ           0.3211264 sec
RG               812.7
DW             156.800 usec
DE               6.50 usec
TE              294.2 K
D0           0.00013770 sec
D1           2.00000000 sec
D8           0.60000002 sec
IN0          0.00031360 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PL1               10.30 dB
SFO1        400.1317065 MHz

F1 - Acquisition parameters
TD                  128
SFO1          400.1317 MHz
FIDRES       49.824306 Hz
SW               7.969 ppm
FnMODE      States-TPPI

F2 - Processing parameters
SI                 1024
SF          400.1300097 MHz
WDW                QSINE
SSB                    2
LB         0 Hz
GB         0
PC                 1.00

F1 - Processing parameters
SI                 1024
MC2         States-TPPI
SF          400.1300071 MHz
WDW                QSINE
SSB                    2
LB         0 Hz
GB         0
```



10

NOESY ($CDCl_3$)

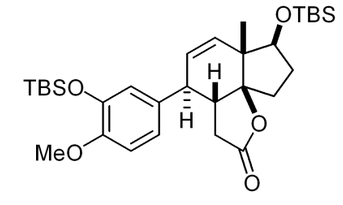


Current Data Parameters
NAME kawaiB400
EXPNO 255
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200825
Time 15.21
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9583745 sec
RG 35.9
DW 60.400 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 10.30 dB
SFO1 400.1324710 MHz

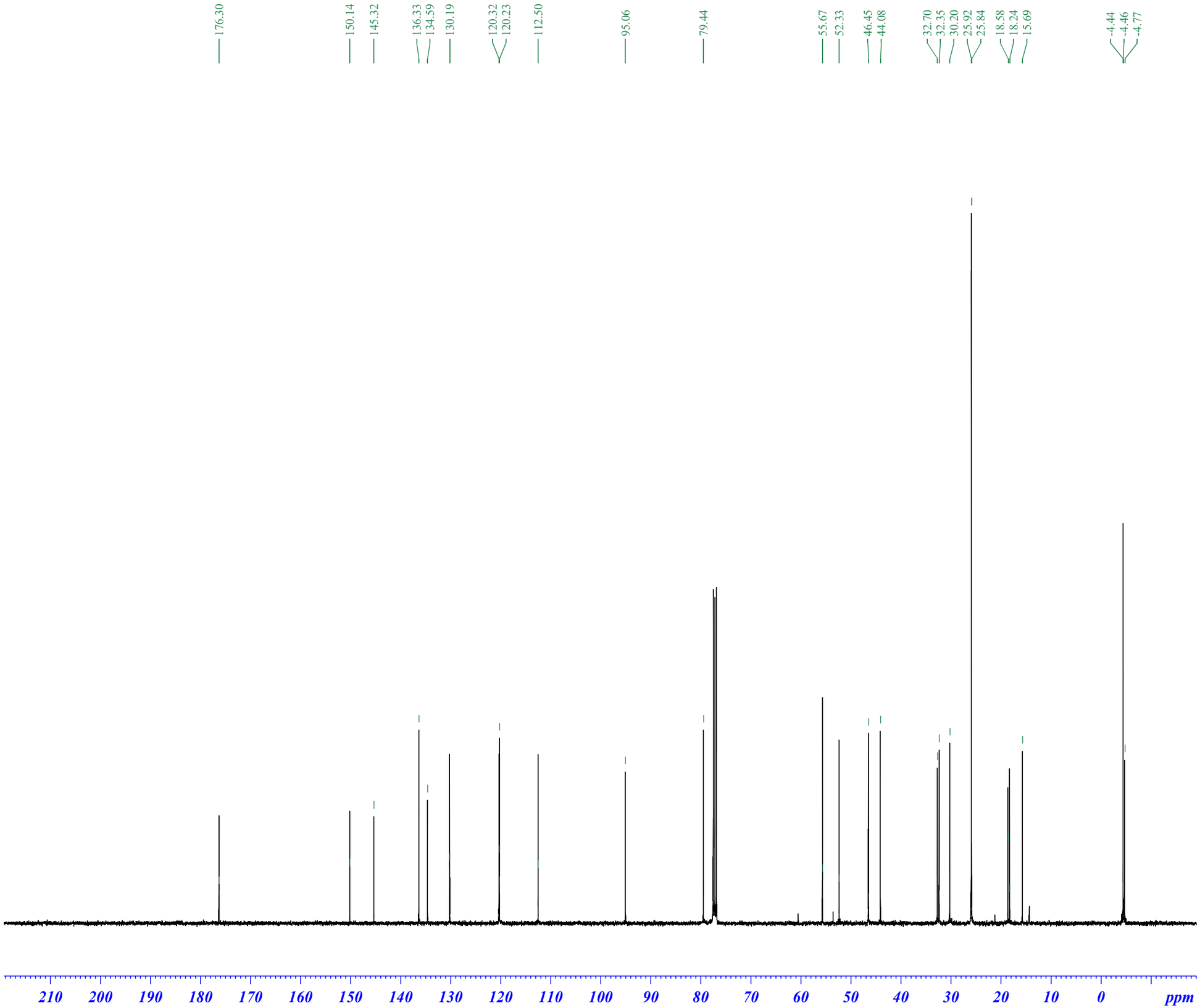
F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



11

^{1}H NMR (400 MHz, $CDCl_3$)

13C kawai 2086 20 08 25



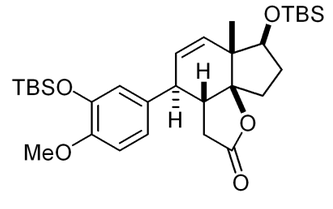
Current Data Parameters
NAME kawaiB400
EXPNO 256
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200825
Time 16.20
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1000
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 2048
DW 20.850 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 =======
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

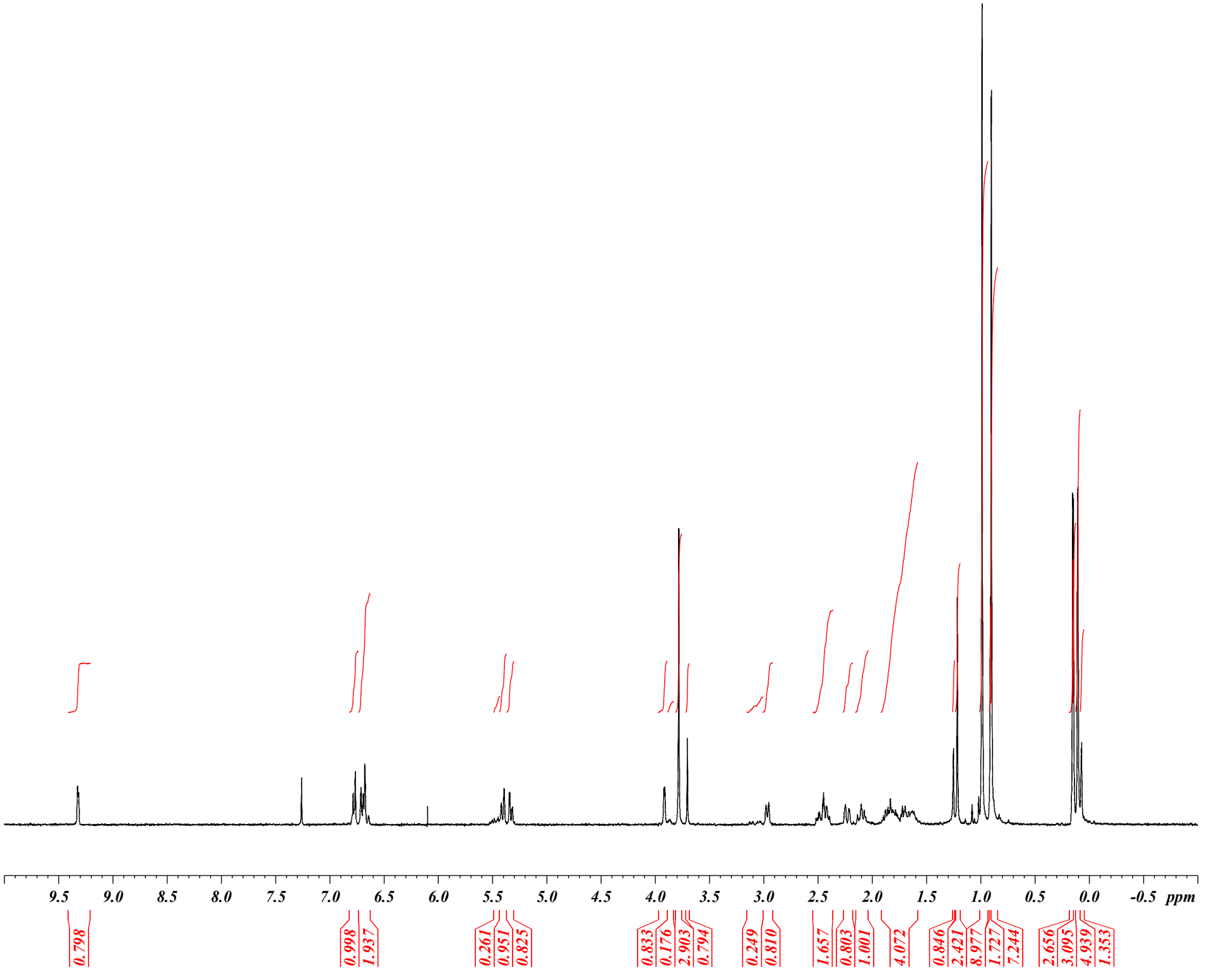
======== CHANNEL f2 =======
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 10.30 dB
PL12 25.00 dB
PL13 25.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127578 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

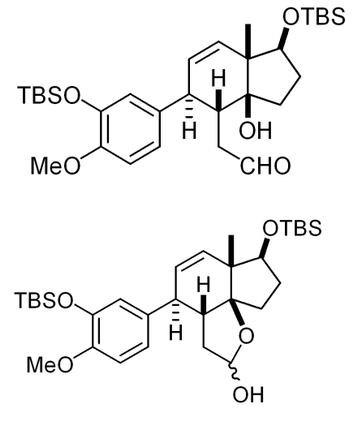


11

^{13}C NMR (100 MHz, $CDCl_3$)




```
Current Data Parameters
NAME          kawaiB400
EXPNO             373
PROCNO              1

F2 - Acquisition Parameters
Date_         20210113
Time             13.05
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           zg30
TD             65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH           8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9583745 sec
RG               1625.5
DW               60.400 usec
DE                6.50 usec
TE               293.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1               15.00 usec
PL1              10.30 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300095 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

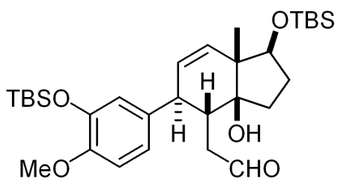


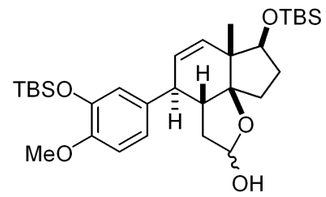
5 and **12**

^{1}H NMR (400 MHz, $CDCl_3$)

2139 21 01 13 TM

203.02
150.19
145.31
135.38
132.87
130.10
122.00
121.21
112.20
82.84
82.61
55.69
51.70
47.77
44.07
41.95
33.00
31.52
25.94
25.87
18.61
18.13
17.58
-4.43
-4.62
-4.92





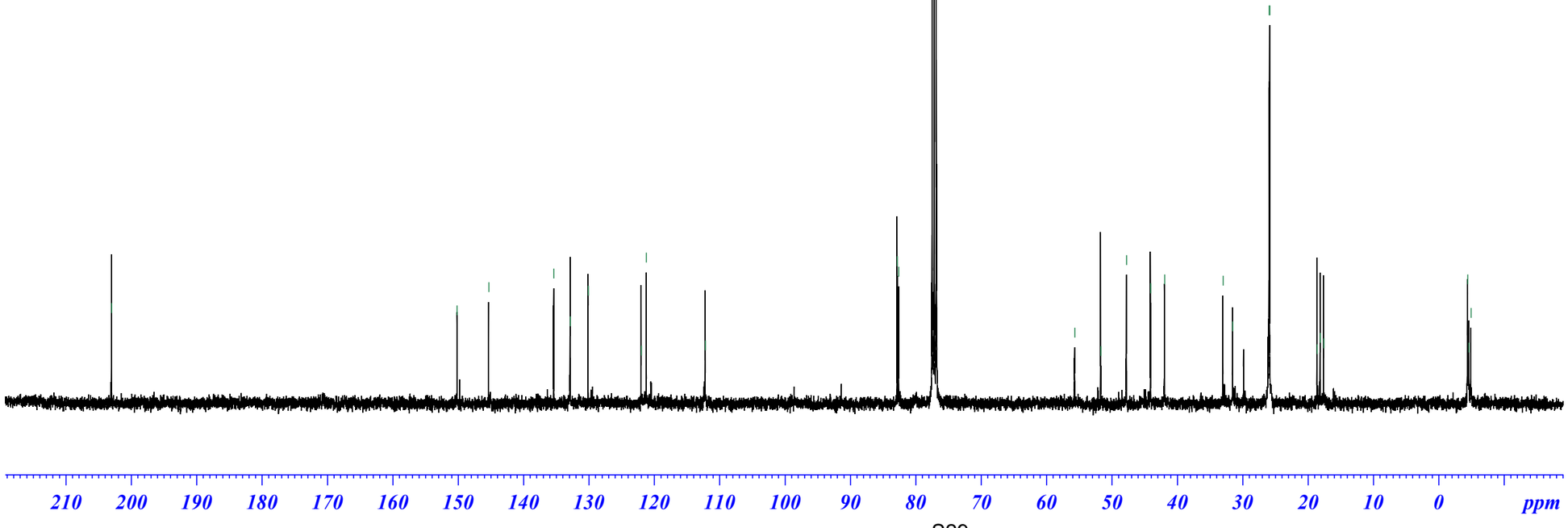
Current Data Parameters
NAME kawaiB400
EXPNO 374
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210113
Time 14.53
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2400
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 5792.6
DW 20.850 usec
DE 6.50 usec
TE 294.2 K
D1 1.20000005 sec
D11 0.03000000 sec
TD0 1

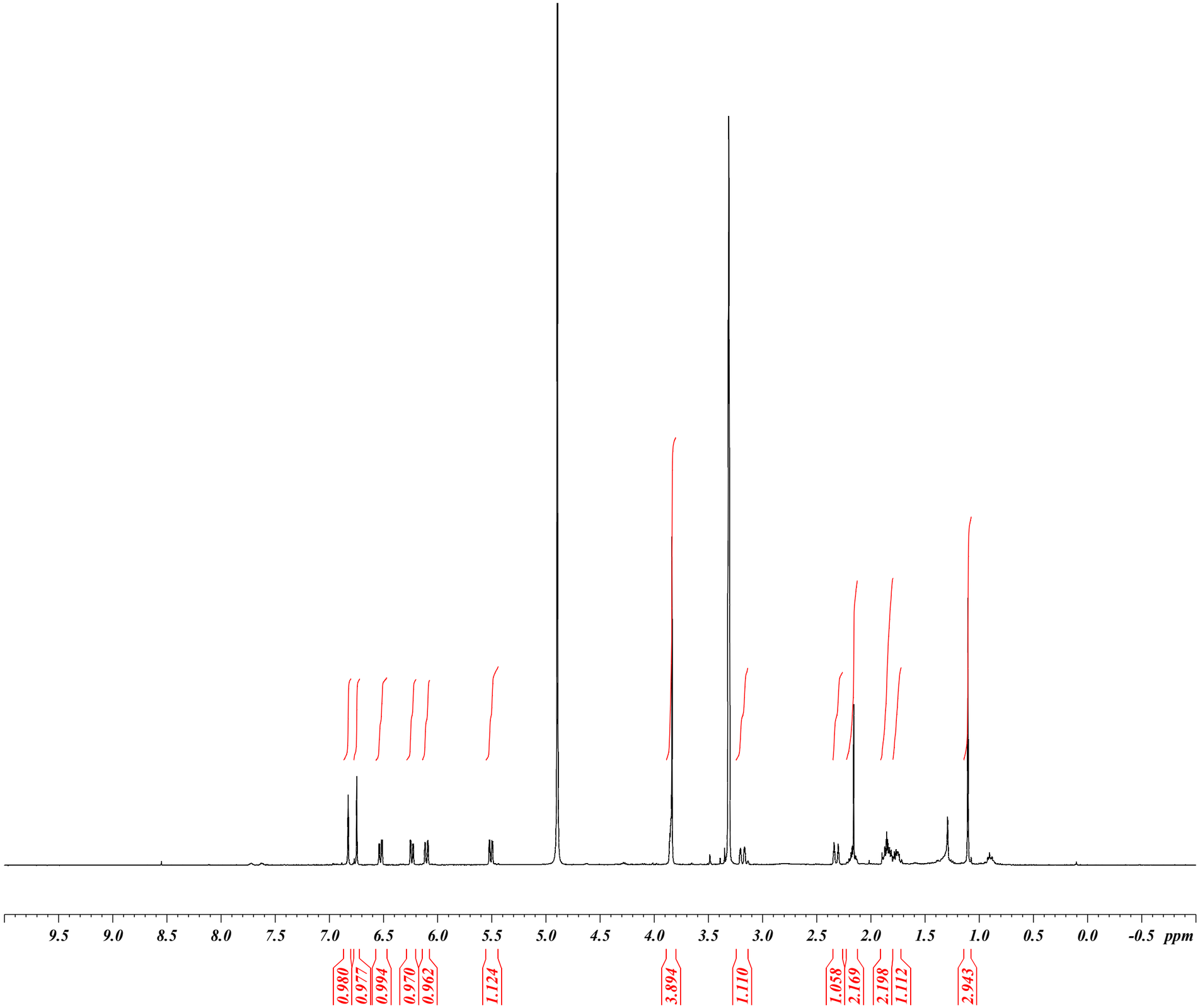
======== CHANNEL f1 =======
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 =======
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 10.30 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127563 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



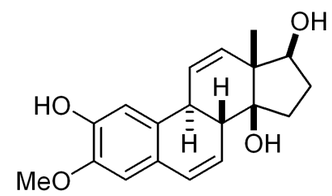
5 and **12**
^{13}C NMR (100 MHz, $CDCl_3$)



Current Data Parameters
NAME kawaiB400
EXPNO 388
PROCNO 1

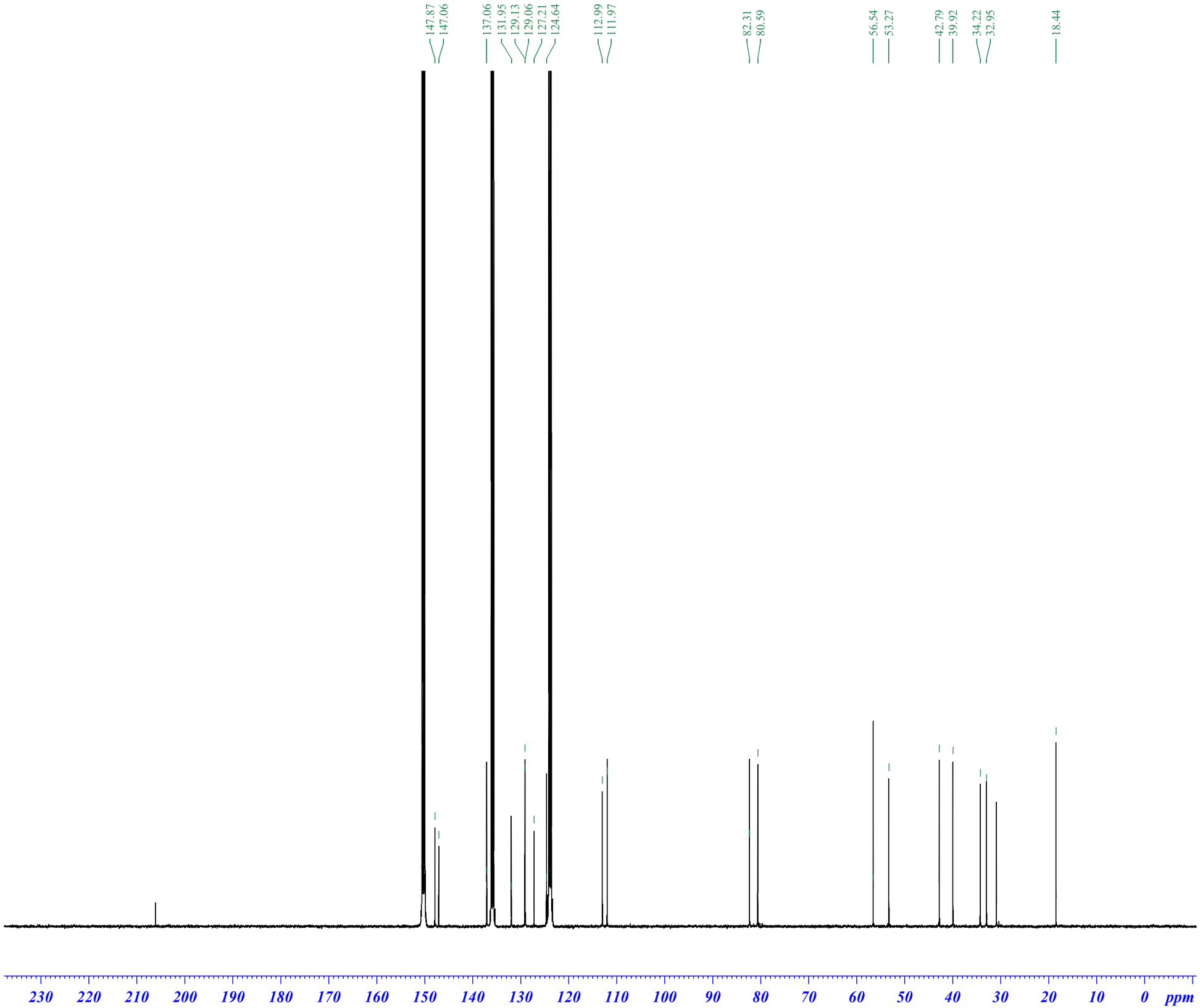
F2 - Acquisition Parameters
Date_ 20210121
Time 10.11 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 128
DS 2
SWH 8278.146 Hz
FIDRES 0.252629 Hz
AQ 3.9583745 sec
RG 645.1
DW 60.400 usec
DE 6.50 usec
TE 294.4 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324710 MHz
NUC1 1H
P1 15.00 usec

F2 - Processing parameters
SI 32768
SF 400.1300075 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



6

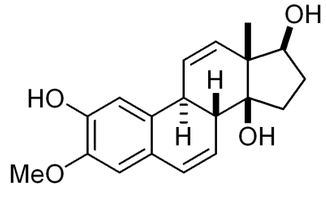
^{1}H NMR (400 MHz, CD_3OD)



Current Data Parameters
NAME kawai 400AN
EXPNO 12
PROCNO 1

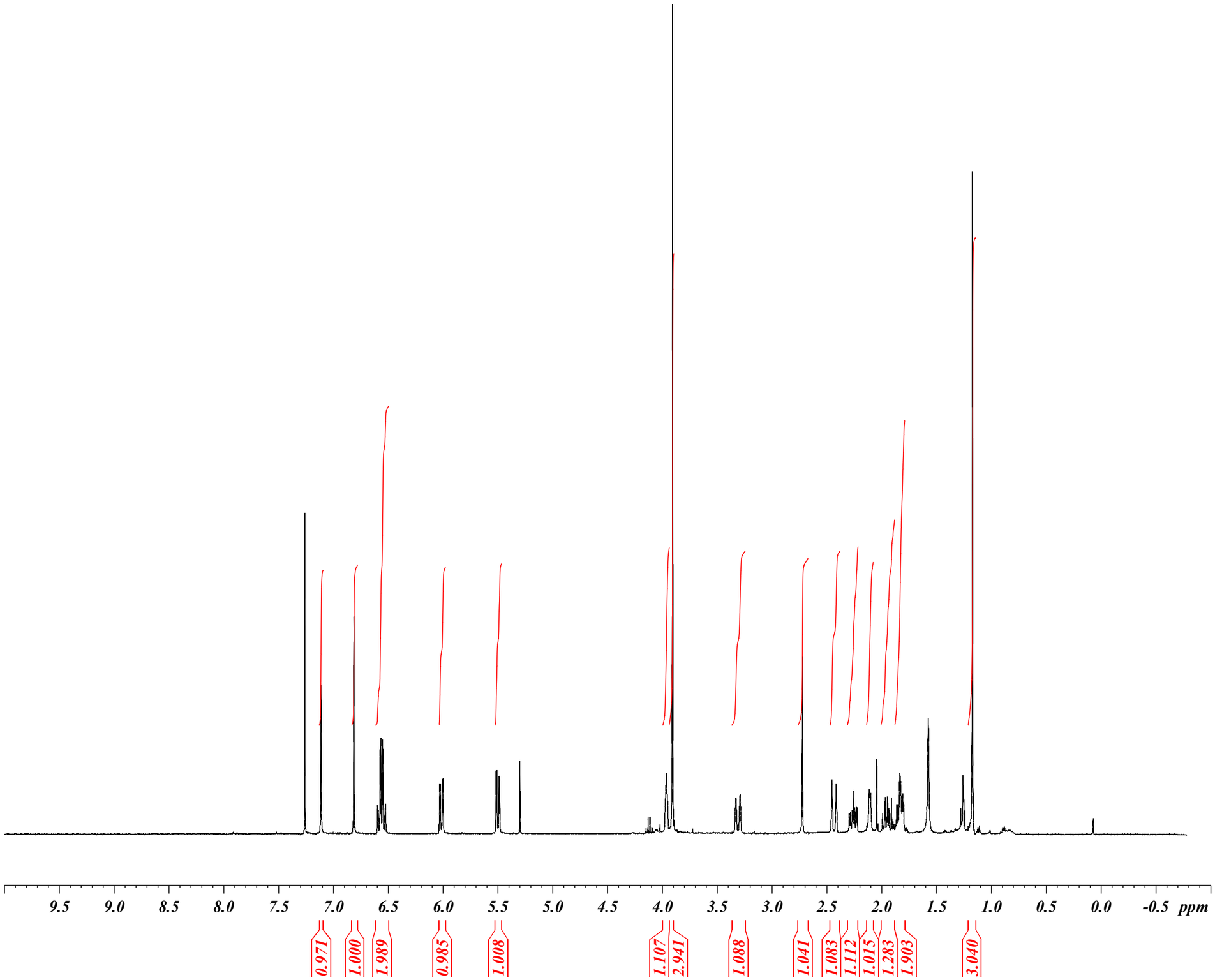
F2 - Acquisition Parameters
Date_ 20210312
Time 8.15 h
INSTRUM Avance
PROBHD Z163739_0304 (
PULPROG zgpg30
TD 65536
SOLVENT Pyr
NS 14000
DS 2
SWH 25000.000 Hz
FIDRES 0.762939 Hz
AQ 1.3107200 sec
RG 101
DW 20.000 usec
DE 8.64 usec
TE 300.0 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6241209 MHz
NUC1 13C
P0 2.67 usec
P1 8.00 usec
PLW1 92.79299927 W
SFO2 400.1326008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 22.60000038 W
PLW12 0.17857000 W
PLW13 0.08981800 W

F2 - Processing parameters
SI 65536
SF 100.6127078 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



6

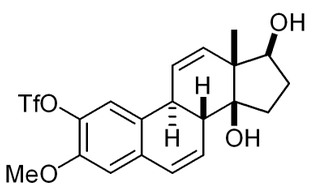
^{13}C NMR (100 MHz, pyridine-d_5)



Current Data Parameters
NAME kawaiA400
EXPNO 175
PROCNO 1

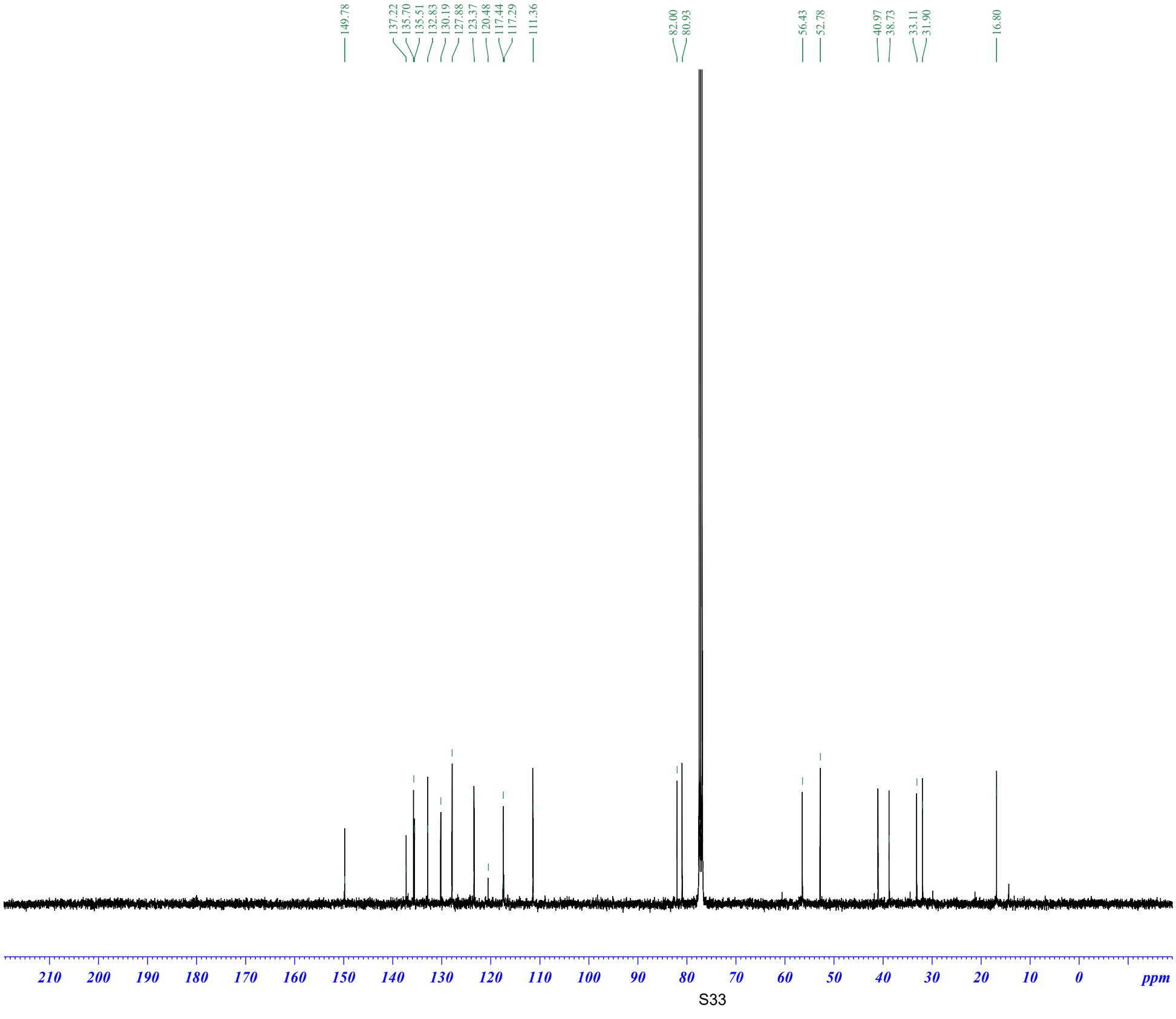
F2 - Acquisition Parameters
Date_ 20201123
Time 14.48 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 4901.961 Hz
FIDRES 0.149596 Hz
AQ 6.6846719 sec
RG 812.7
DW 102.000 usec
DE 6.50 usec
TE 297.4 K
D1 1.00000000 sec
TD0 1
SFO1 400.1321477 MHz
NUC1 1H
P1 15.00 usec

F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



13

^{1}H NMR (400 MHz, $CDCl_3$)



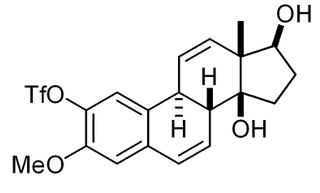
Current Data Parameters
NAME kawaiB400
EXPNO 341
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201227
Time 12.16
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3600
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 5792.6
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 1.20000005 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 =======
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

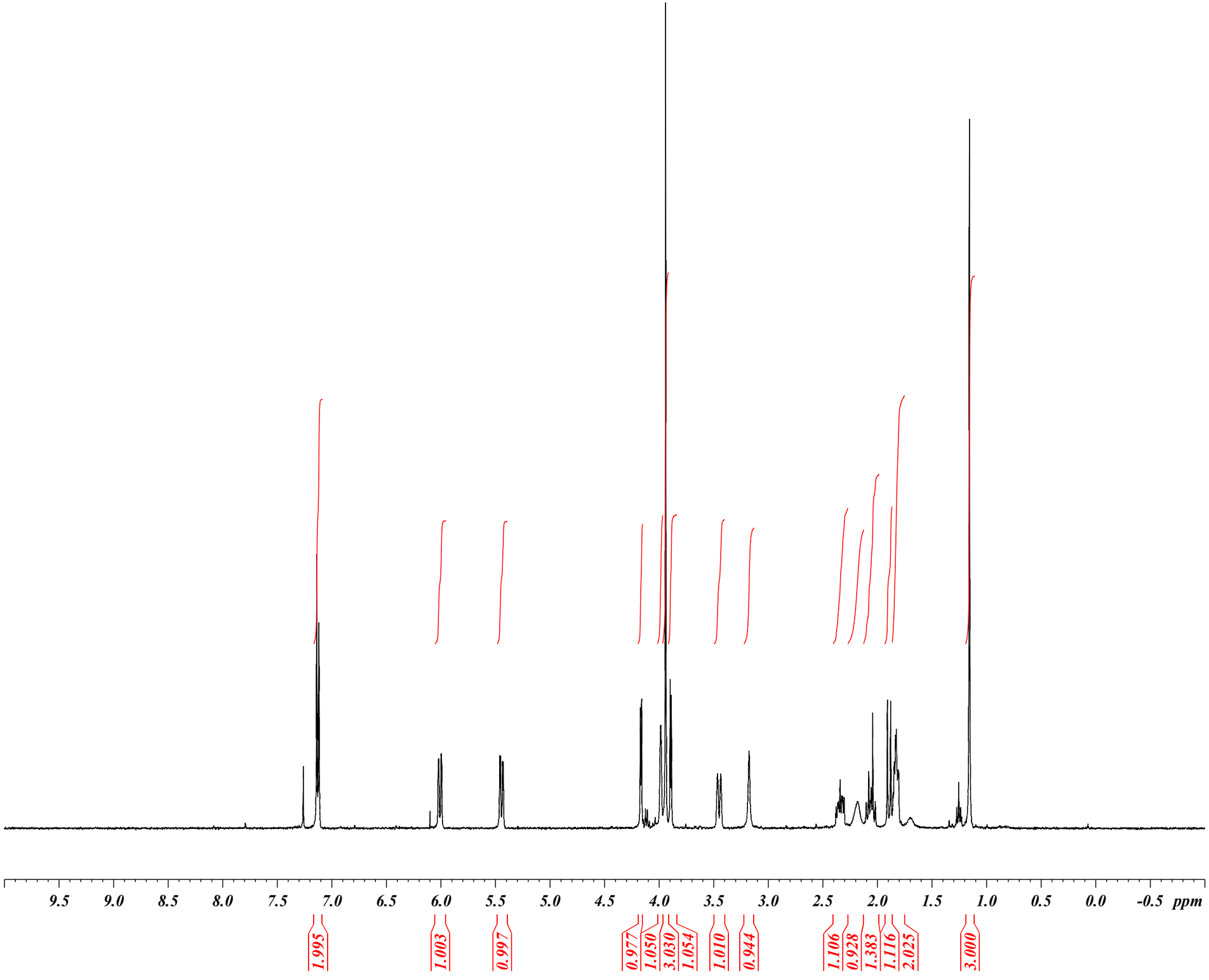
======== CHANNEL f2 =======
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 10.30 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127561 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

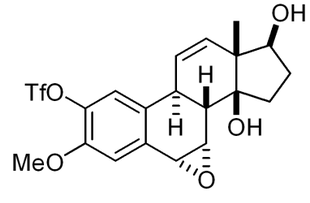


13

^{13}C NMR (100 MHz, $CDCl_3$)

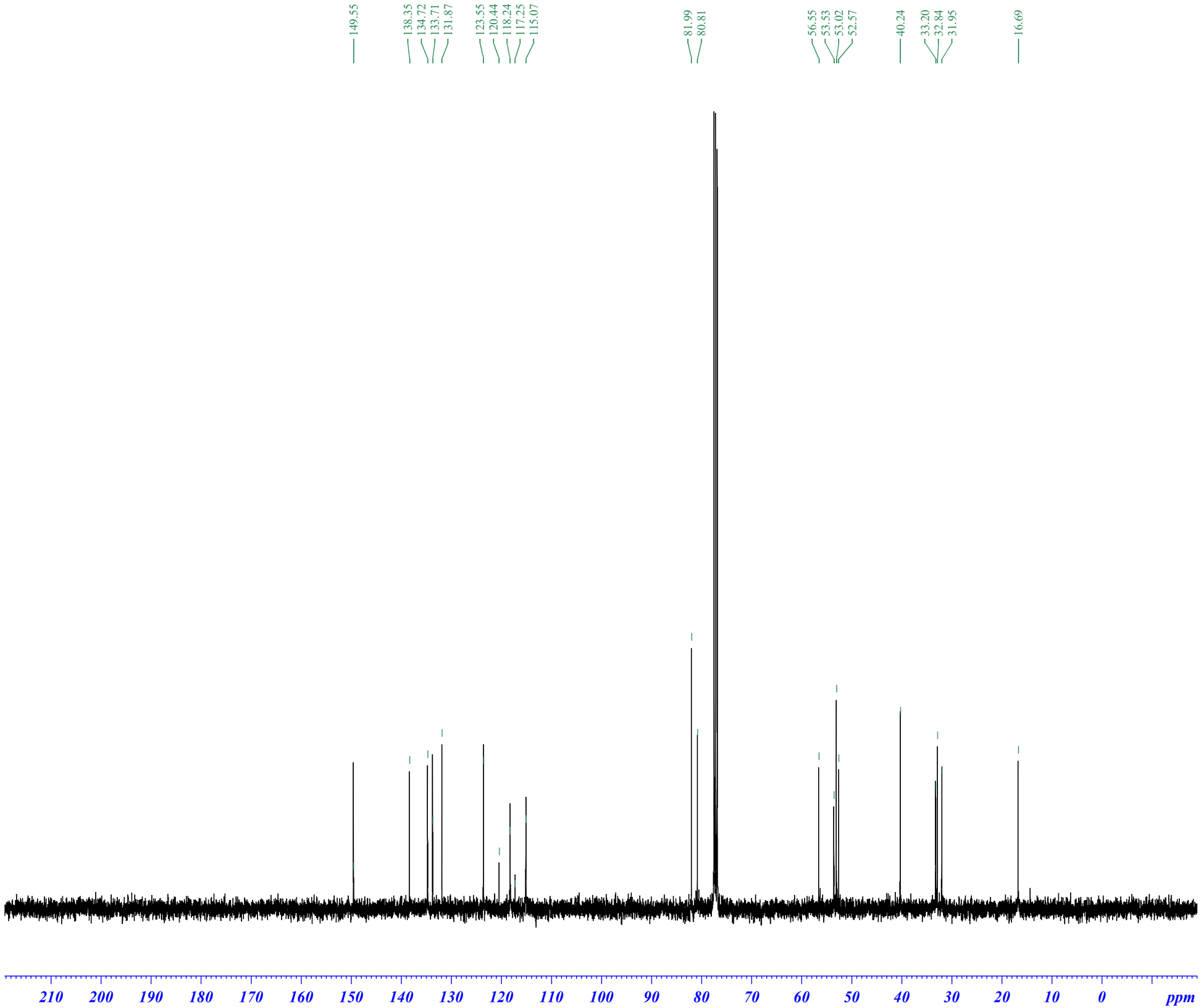



```
Current Data Parameters
NAME          kawaiB400
EXPNO              309
PROCNO               1

F2 - Acquisition Parameters
Date_         20201202
Time             15.47
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9583745 sec
RG               1625.5
DW               60.400 usec
DE                6.50 usec
TE               296.2 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                 1H
P1               15.00 usec
PL1              10.30 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                32768
SF         400.1300094 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
```



14a

^{1}H NMR (400 MHz, $CDCl_3$)



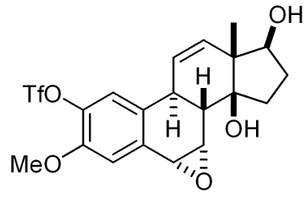
Current Data Parameters
NAME kawaiB400
EXPNO 310
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201202
Time 16.00
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 250
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 5792.6
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 1.20000005 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 =======
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

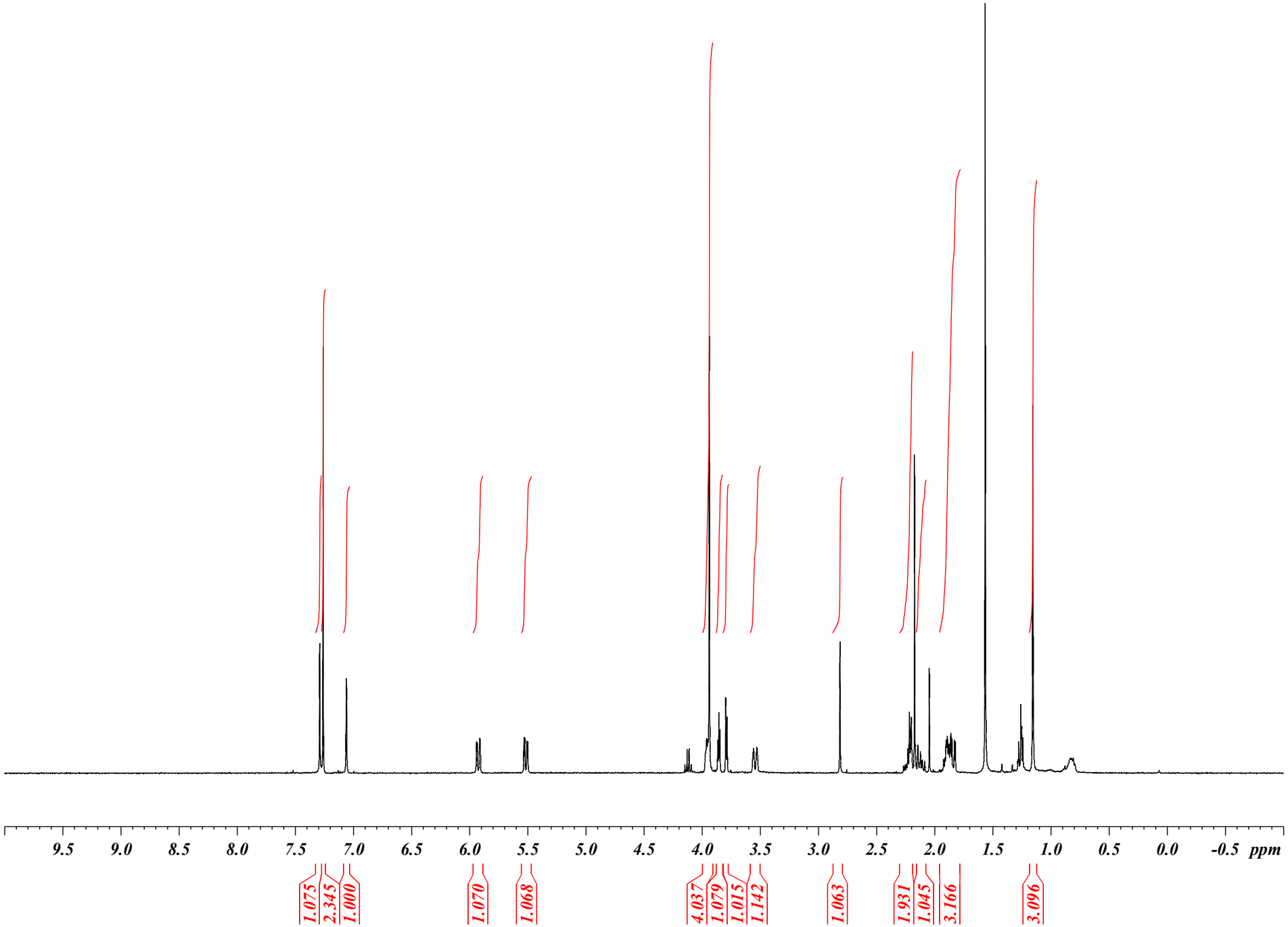
======== CHANNEL f2 =======
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 10.30 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127572 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



14a

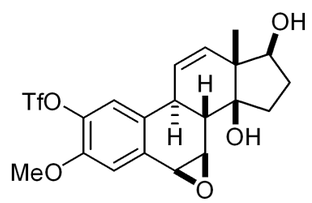
^{13}C NMR (100 MHz, $CDCl_3$)



Current Data Parameters
NAME kawaiB400-2
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210304
Time 13.03 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.252629 Hz
AQ 3.9583745 sec
RG 1024
DW 60.400 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324710 MHz
NUC1 1H
P1 15.00 usec

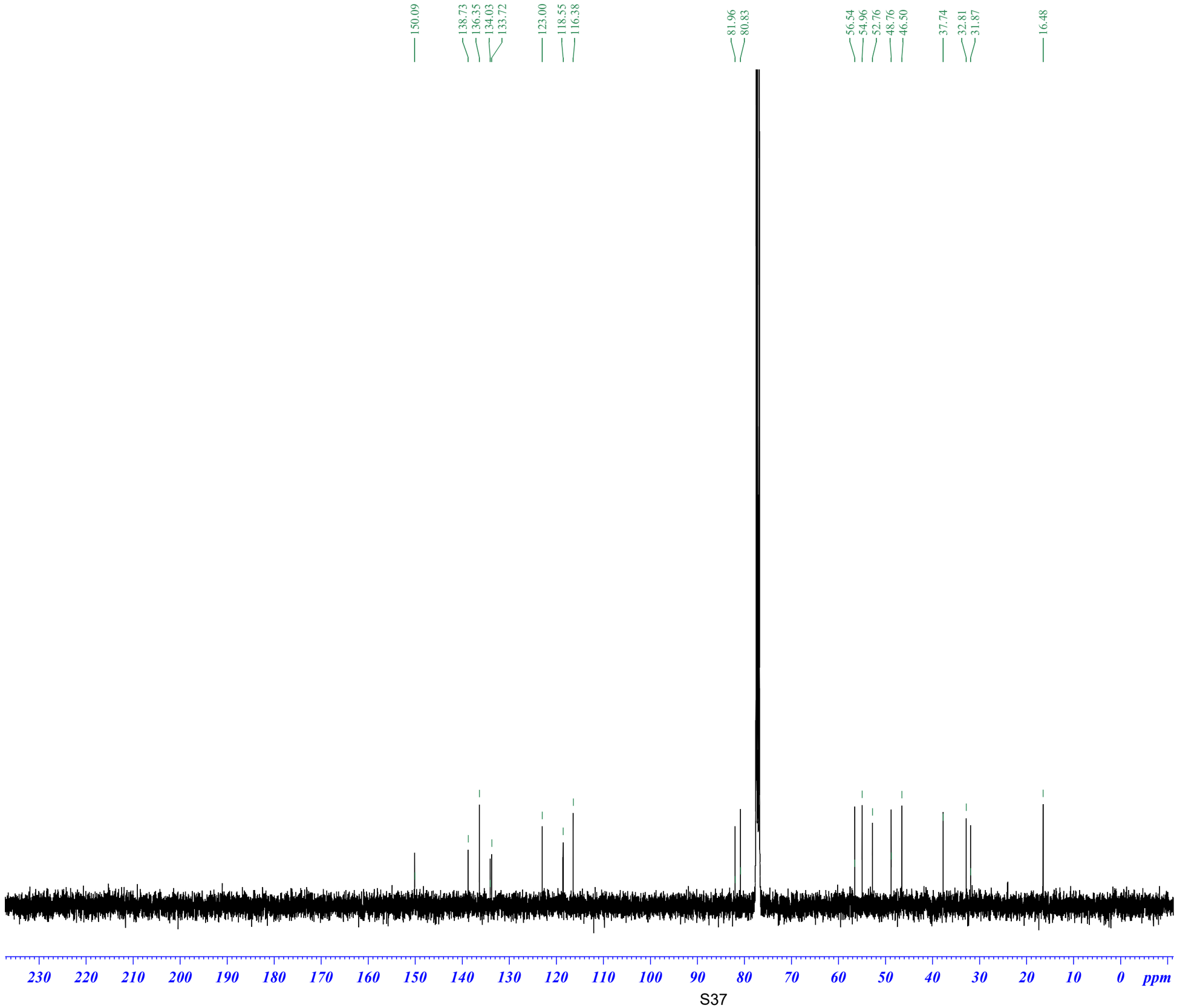
F2 - Processing parameters
SI 32768
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



14b

^{1}H NMR (400 MHz, $CDCl_3$)

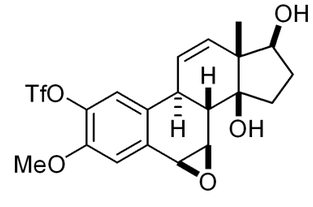
[2144] bp



Current Data Parameters
NAME kawai 400 AN
EXPNO 8
PROCNO 1

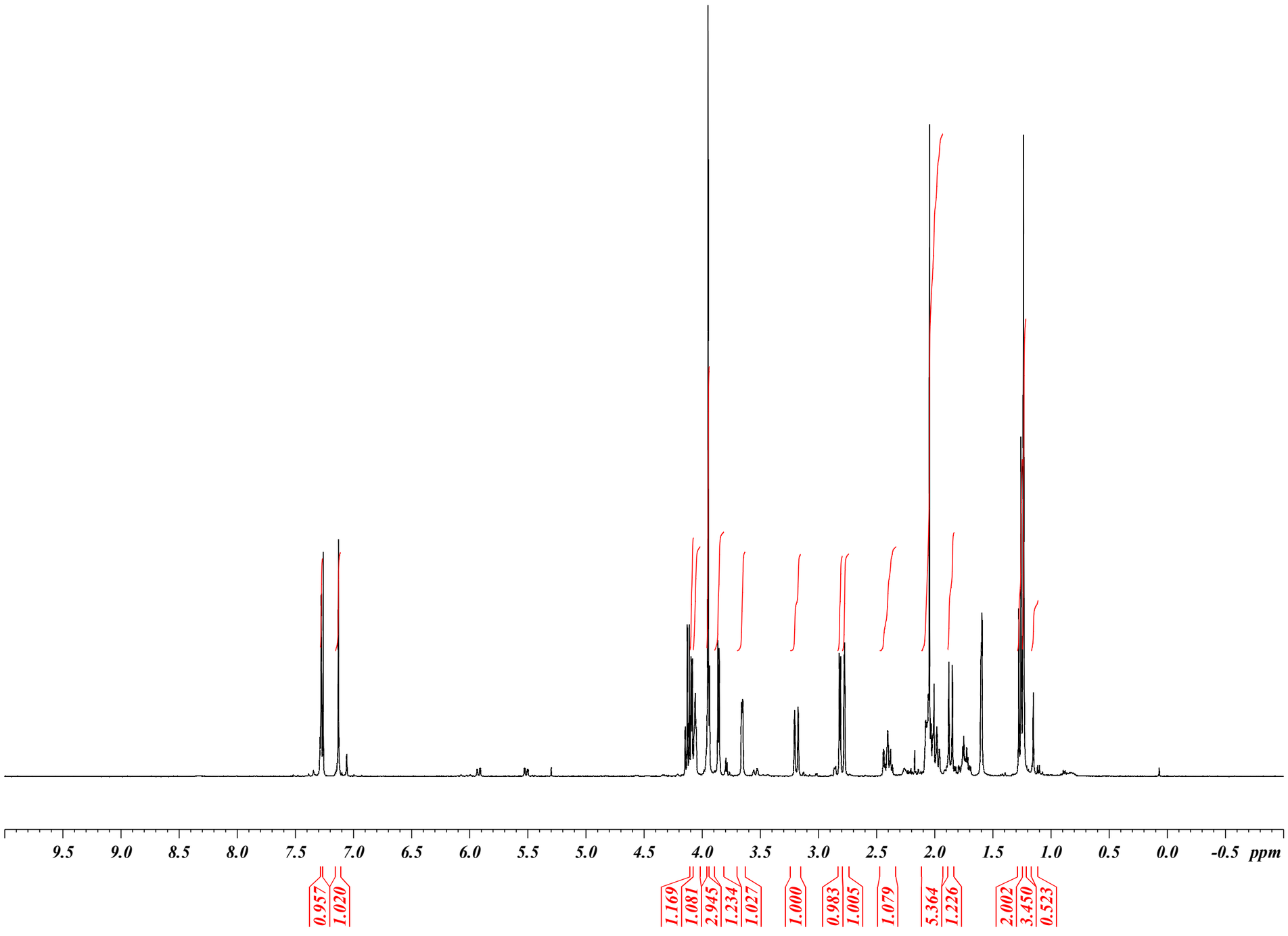
F2 - Acquisition Parameters
Date_ 20210311
Time 14.45 h
INSTRUM Avance
PROBHD Z163739_0304 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3200
DS 2
SWH 25000.000 Hz
FIDRES 0.762939 Hz
AQ 1.3107200 sec
RG 101
DW 20.000 usec
DE 8.64 usec
TE 300.0 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6241209 MHz
NUC1 13C
P0 2.67 usec
P1 8.00 usec
PLW1 92.79299927 W
SFO2 400.1326008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 22.60000038 W
PLW12 0.17857000 W
PLW13 0.08981800 W

F2 - Processing parameters
SI 65536
SF 100.6127537 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



14b

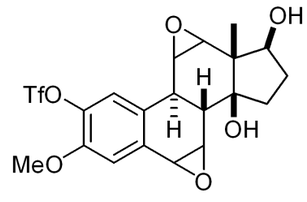
^{13}C NMR (100 MHz, $CDCl_3$)



Current Data Parameters
NAME kawaiB400-2
EXPNO 18
PROCNO 1

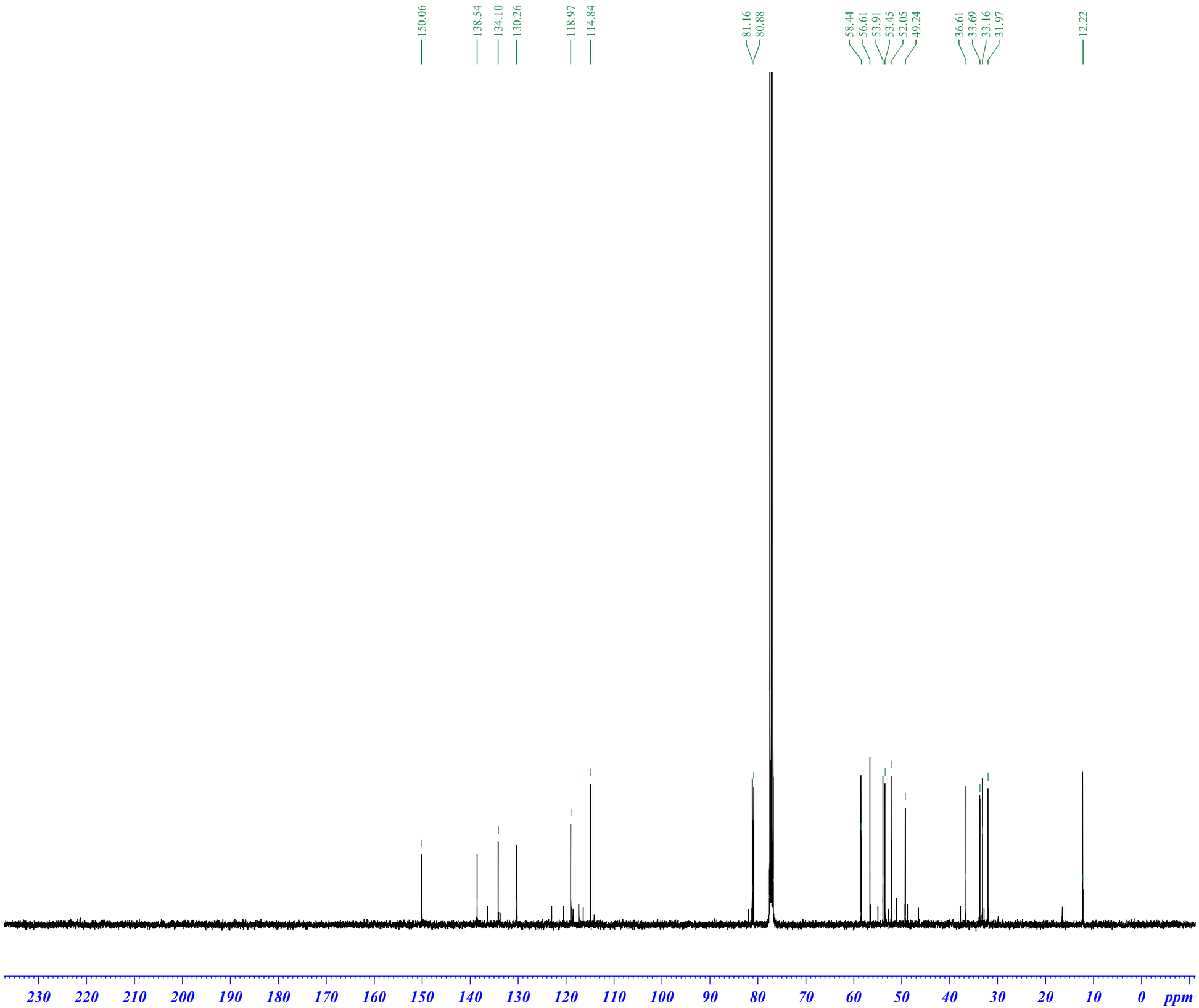
F2 - Acquisition Parameters
Date_ 20210303
Time 15.45 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.252629 Hz
AQ 3.9583745 sec
RG 456.1
DW 60.400 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324710 MHz
NUC1 1H
P1 15.00 usec

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



15

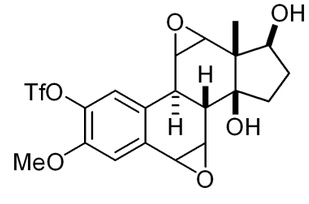
^{1}H NMR (400 MHz, $CDCl_3$)



Current Data Parameters
NAME kawai 400AN
EXPNO 3
PROCNO 1

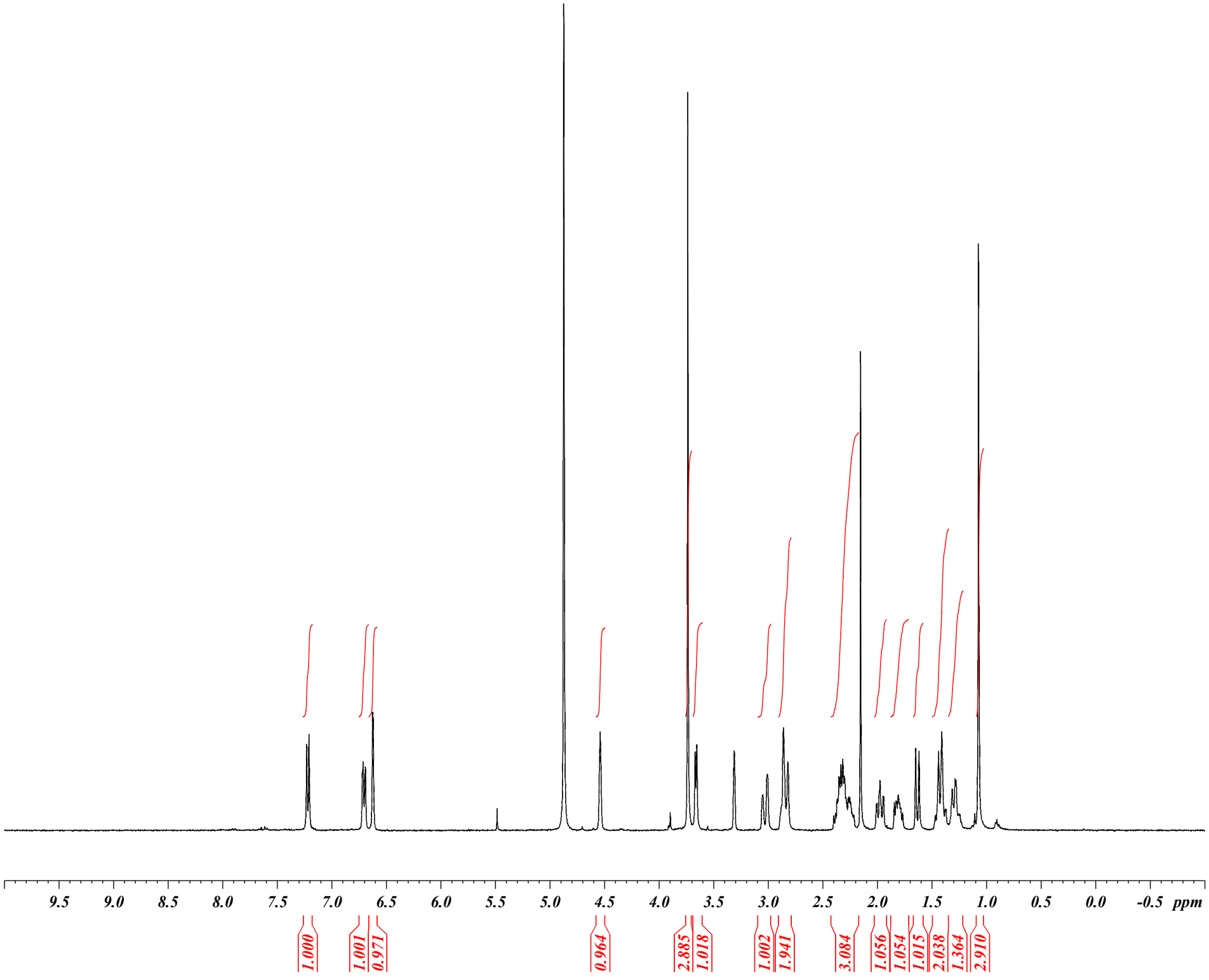
F2 - Acquisition Parameters
Date_ 20210309
Time 11.42 h
INSTRUM Avance
PROBHD Z163739_0304 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3000
DS 2
SWH 25000.000 Hz
FIDRES 0.762939 Hz
AQ 1.3107200 sec
RG 101
DW 20.000 usec
DE 8.64 usec
TE 300.0 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6241209 MHz
NUC1 13C
P0 2.67 usec
P1 8.00 usec
PLW1 92.79299927 W
SFO2 400.1326008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 22.60000038 W
PLW12 0.17857000 W
PLW13 0.08981800 W

F2 - Processing parameters
SI 65536
SF 100.6127543 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

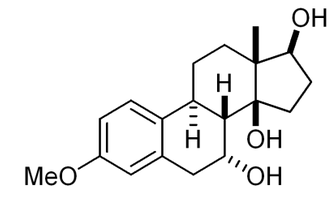


15

^{13}C NMR (100 MHz, $CDCl_3$)



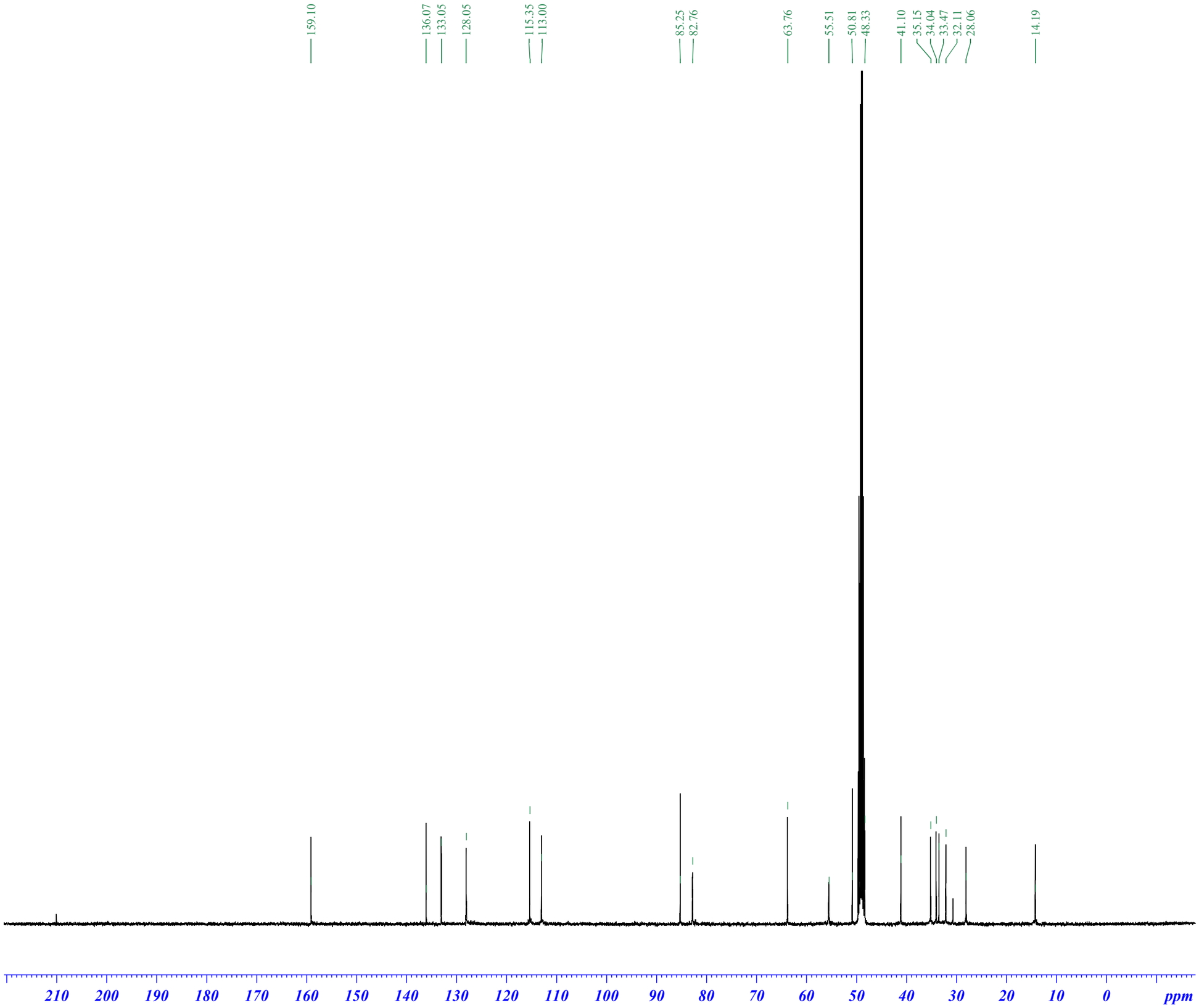

```
Current Data Parameters
NAME          kawaiB400
EXPNO              338
PROCNO               1

F2 - Acquisition Parameters
Date_         20201224
Time             14.08
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           zg30
TD               65536
SOLVENT           MeOD
NS                  16
DS                   2
SWH           8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9583745 sec
RG                1024
DW              60.400 usec
DE               6.50 usec
TE              296.2 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                 1H
P1              15.00 usec
PL1             10.30 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                32768
SF         400.1300075 MHz
WDW                EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```



2b

^{1}H NMR (400 MHz, CD_3OD)

2146 20 12 24



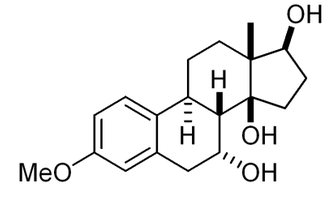
Current Data Parameters
NAME kawaiB400
EXPNO 339
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201224
Time 15.38
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 2000
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 1625.5
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 1.20000005 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 =======
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

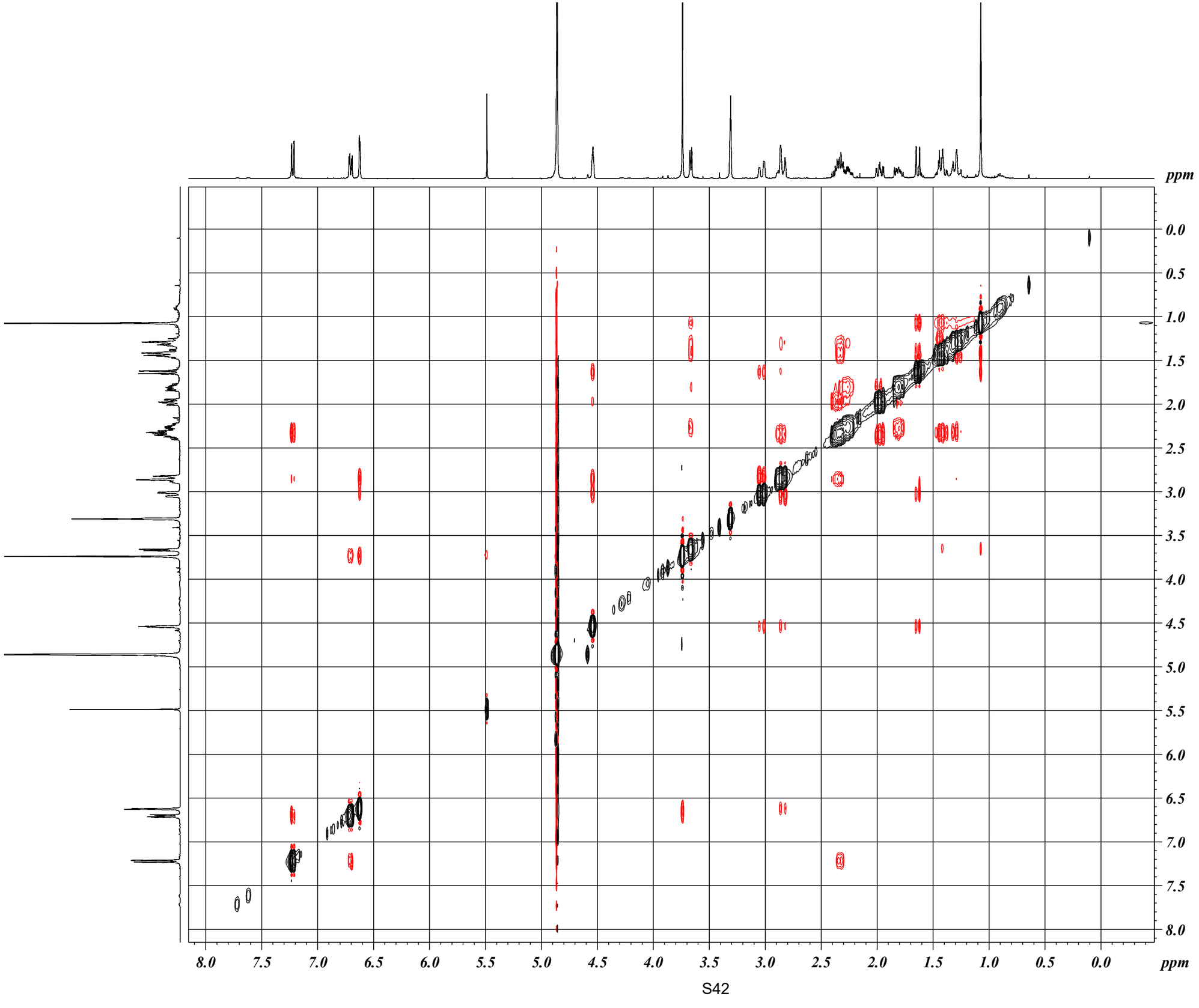
======== CHANNEL f2 =======
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 10.30 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6126301 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

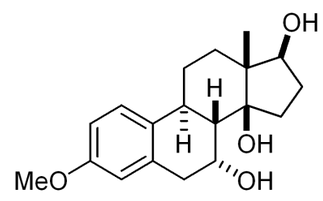


2b

^{13}C NMR (100 MHz, CD_3OD)




```
Current Data Parameters
NAME          kawaiB400
EXPNO               155
PROCNO                1

F2 - Acquisition Parameters
Date_          20190830
Time               2.19
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG         noesyph
TD                 2048
SOLVENT             MeOD
NS                   48
DS                    2
SWH            3453.039 Hz
FIDRES         1.686054 Hz
AQ             0.2965504 sec
RG                   256
DW               144.800 usec
DE                 6.50 usec
TE                297.2 K
D0             0.00012570 sec
D1             2.00000000 sec
D8             0.60000002 sec
IN0            0.00028960 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PL1               10.30 dB
SFO1        400.1315425 MHz

F1 - Acquisition parameters
TD                   128
SFO1          400.1315 MHz
FIDRES       53.953728 Hz
SW             8.630 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                  1024
SF          400.1300068 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                  1.00

F1 - Processing parameters
SI                  1024
MC2          States-TPPI
SF          400.1300092 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
```



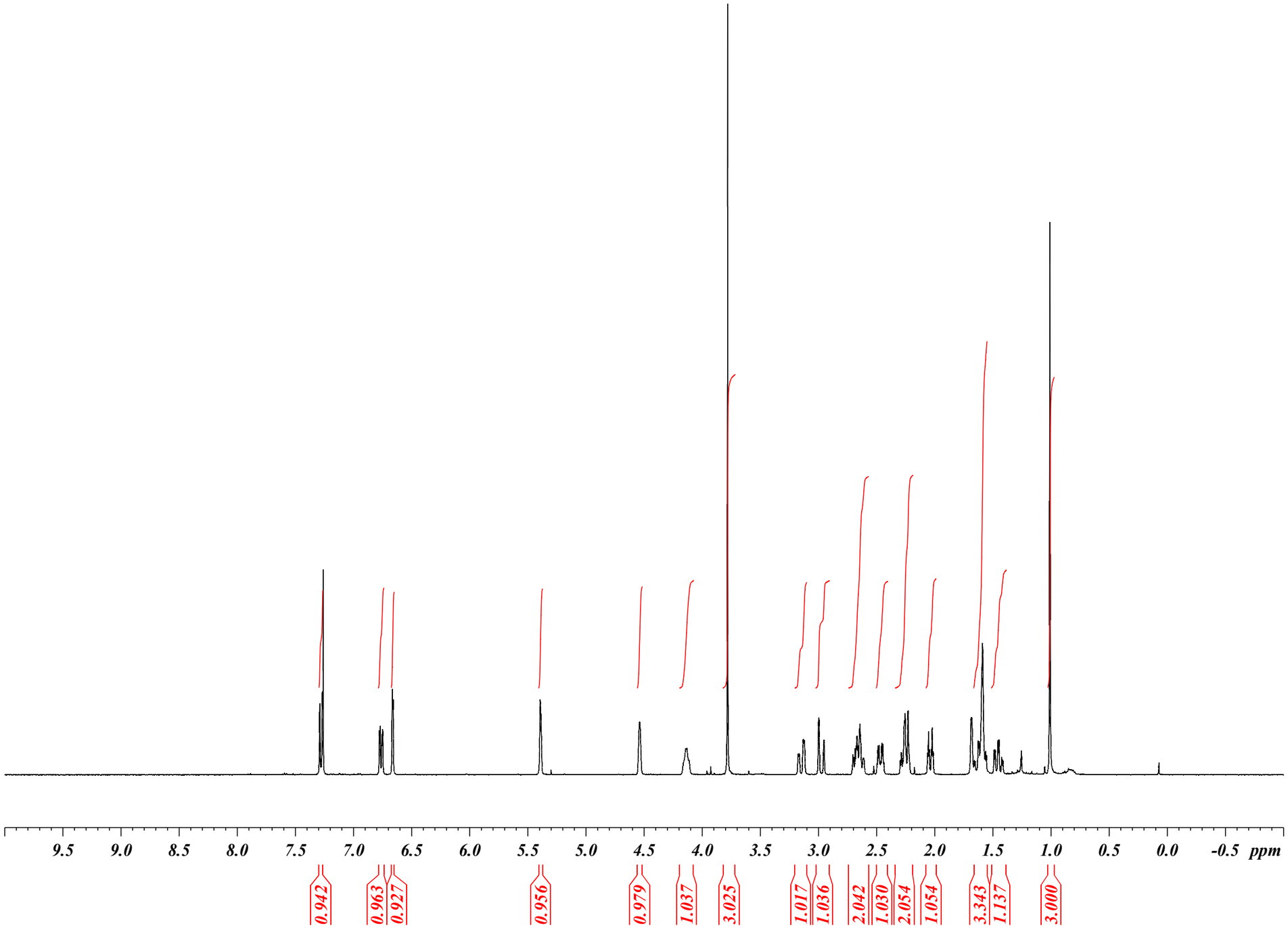
2b

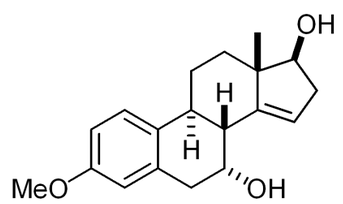
NOESY (CD_3OD)

Current Data Parameters
NAME kawaiB400-2
EXPNO 16
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210303
Time 12.55 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.252629 Hz
AQ 3.9583745 sec
RG 512
DW 60.400 usec
DE 6.50 usec
TE 295.5 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324710 MHz
NUC1 1H
P1 15.00 usec

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

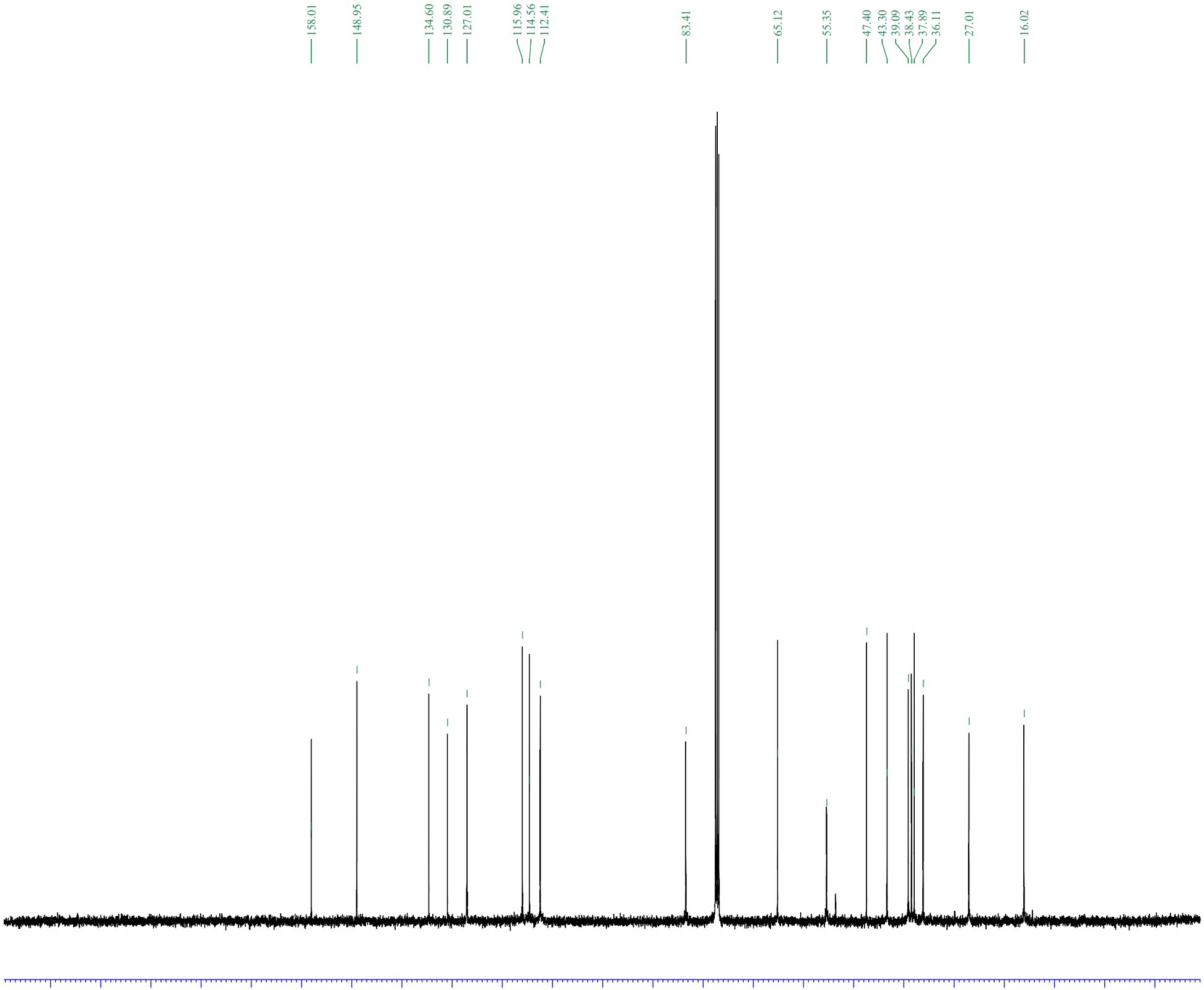




16

^{1}H NMR (400 MHz, $CDCl_3$)

2148 20 12 28



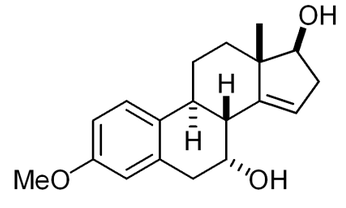
Current Data Parameters
NAME kawaiB400
EXPNO 350
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201228
Time 14.36
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1200
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 645.1
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 1.20000005 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 =======
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 =======
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 10.30 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 400.1316005 MHz

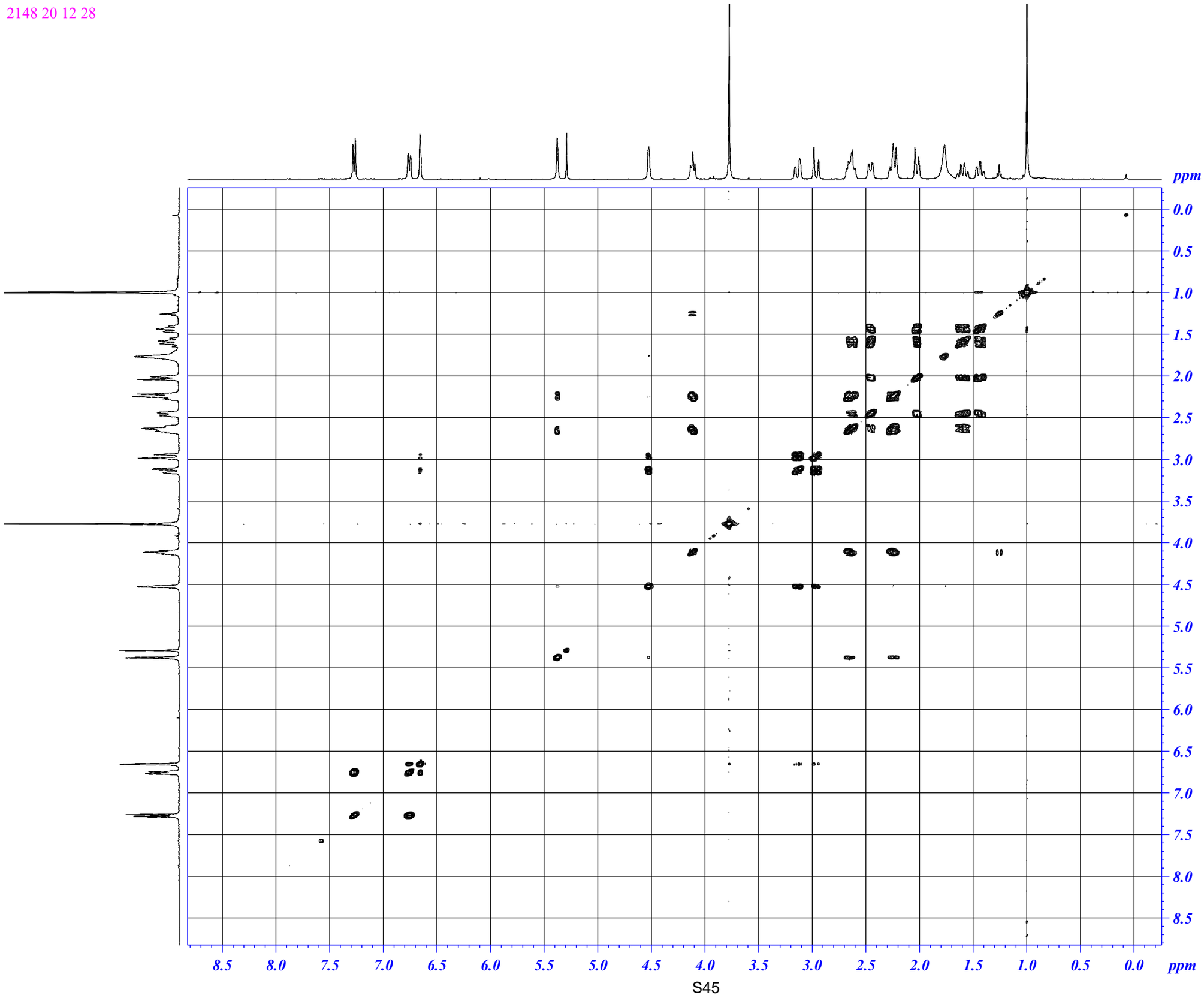
F2 - Processing parameters
SI 32768
SF 100.6127598 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



16

^{13}C NMR (100 MHz, $CDCl_3$)

2148 20 12 28



Current Data Parameters
NAME kawaiB400
EXPNO 349
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201228
Time 13.26
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG cosygpqf
TD 2048
SOLVENT CDCl3
NS 2
DS 16
SWH 3633.721 Hz
FIDRES 1.774278 Hz
AQ 0.2818048 sec
RG 7298.2
DW 137.600 usec
DE 6.50 usec
TE 296.2 K
D0 0.00000300 sec
D1 1.48689198 sec
D13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00027520 sec

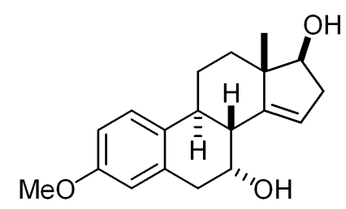
======== CHANNEL f1 ========
NUC1 1H
P0 15.00 usec
P1 15.00 usec
PL1 10.30 dB
SFO1 400.1317249 MHz

====== GRADIENT CHANNEL =====
GPNAM[1] SINE.100
GPZ1 10.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 256
SFO1 400.1317 MHz
FIDRES 28.388441 Hz
SW 9.081 ppm
FnMODE QF

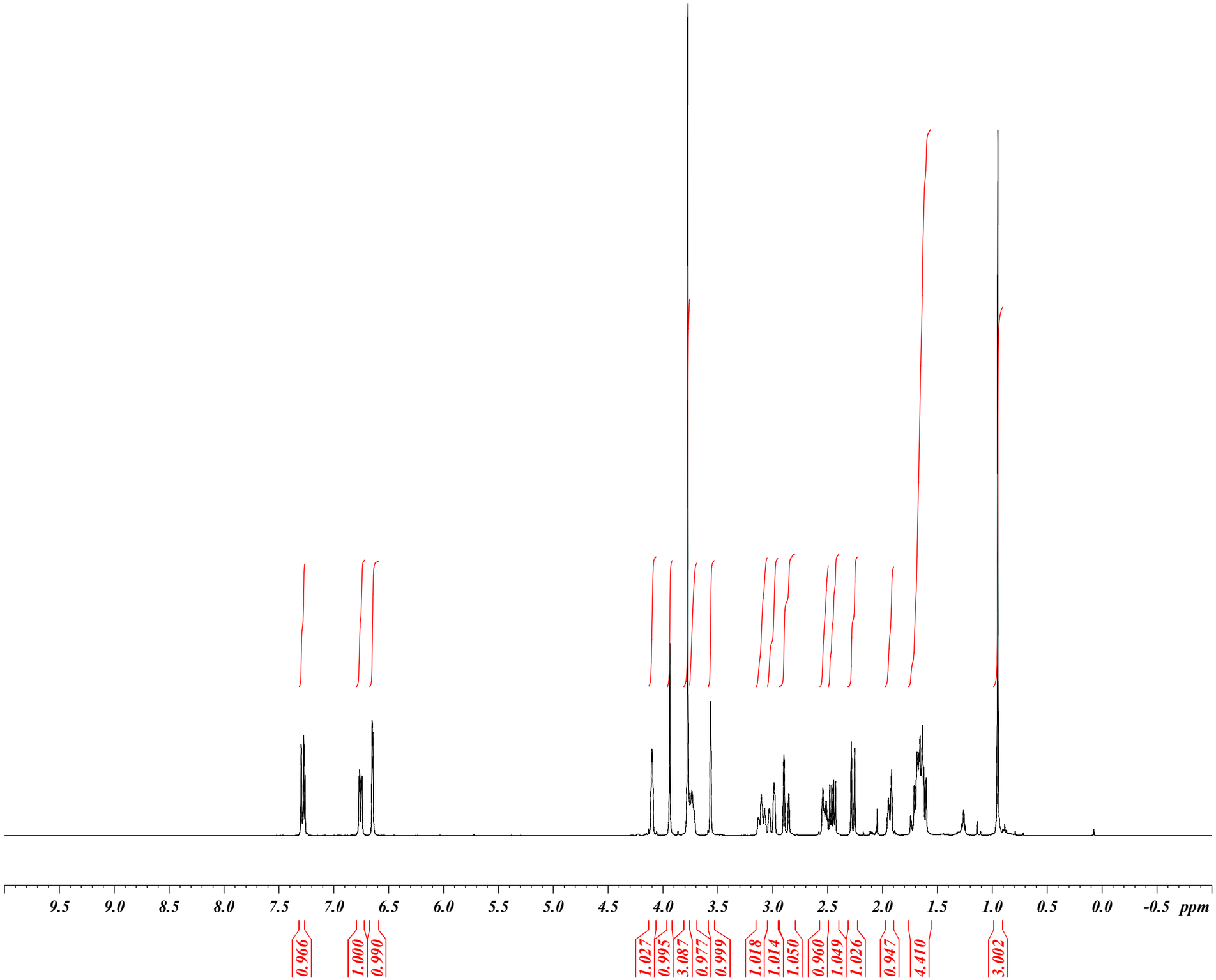
F2 - Processing parameters
SI 1024
SF 400.1300112 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 QF
SF 400.1300109 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0

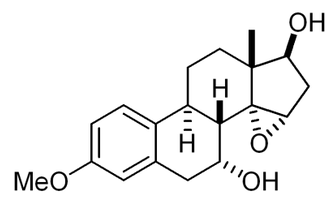


16

COSY ($CDCl_3$)



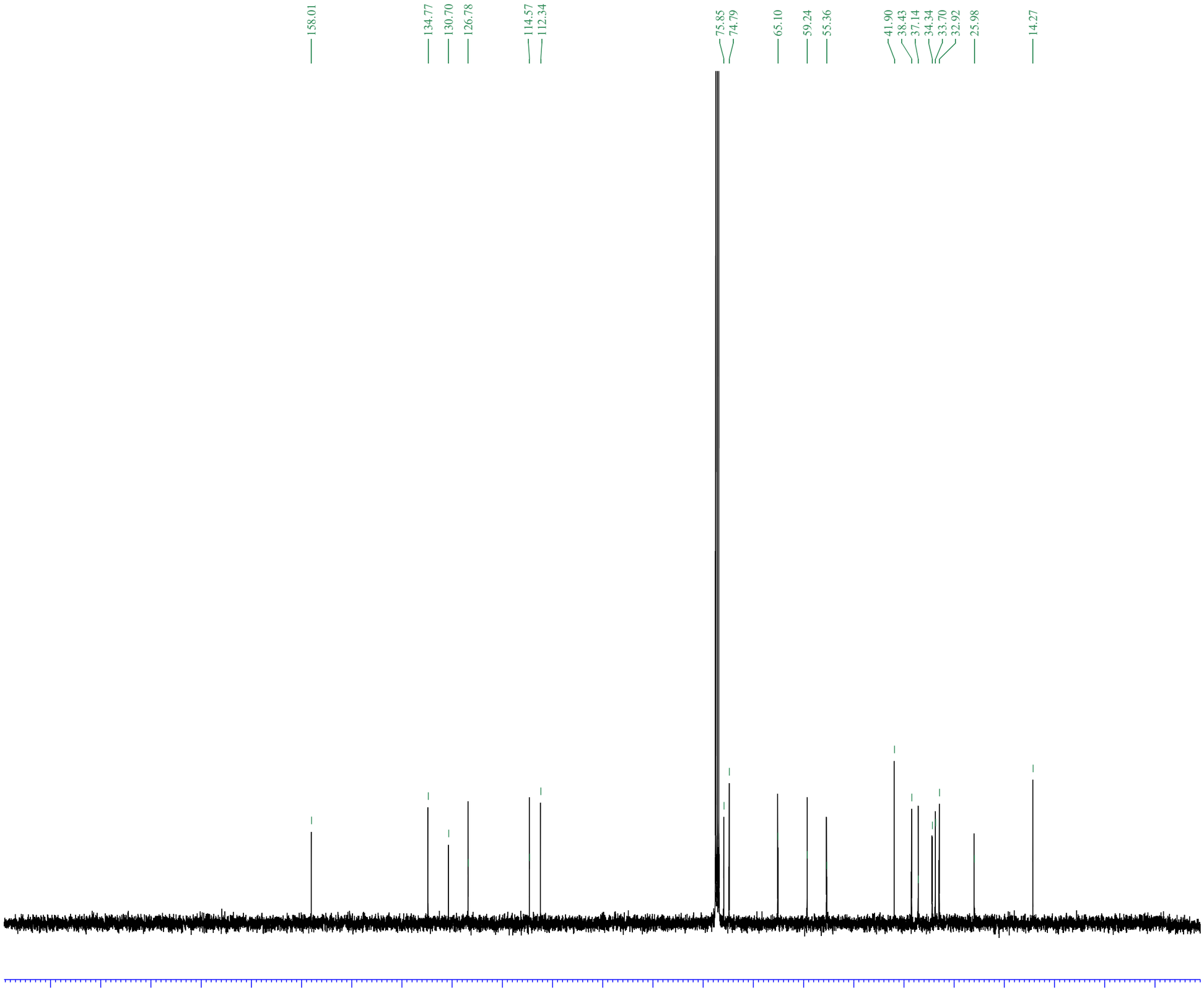

```
Current Data Parameters
NAME          kawaiB400
EXPNO              382
PROCNO               1

F2 - Acquisition Parameters
Date_         20210119
Time            14.54 h
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           zg30
TD               65536
SOLVENT           CDCl3
NS                  16
DS                   2
SWH           8278.146 Hz
FIDRES         0.252629 Hz
AQ            3.9583745 sec
RG                 181
DW              60.400 usec
DE               6.50 usec
TE              295.6 K
D1           1.00000000 sec
TD0                  1
SFO1         400.1324710 MHz
NUC1                1H
P1              15.00 usec

F2 - Processing parameters
SI                32768
SF          400.1300094 MHz
WDW                 EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```



17a

^{1}H NMR (400 MHz, $CDCl_3$)

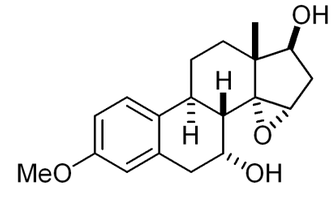
2150 21 01 19 TM



Current Data Parameters
NAME kawaiB400
EXPNO 384
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210119
Time 16.05 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1200
DS 4
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 1.3664256 sec
RG 1149.4
DW 20.850 usec
DE 6.50 usec
TE 296.1 K
D1 1.20000005 sec
d11 0.03000000 sec
DELTA 1.10000002 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 12.00 usec
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec

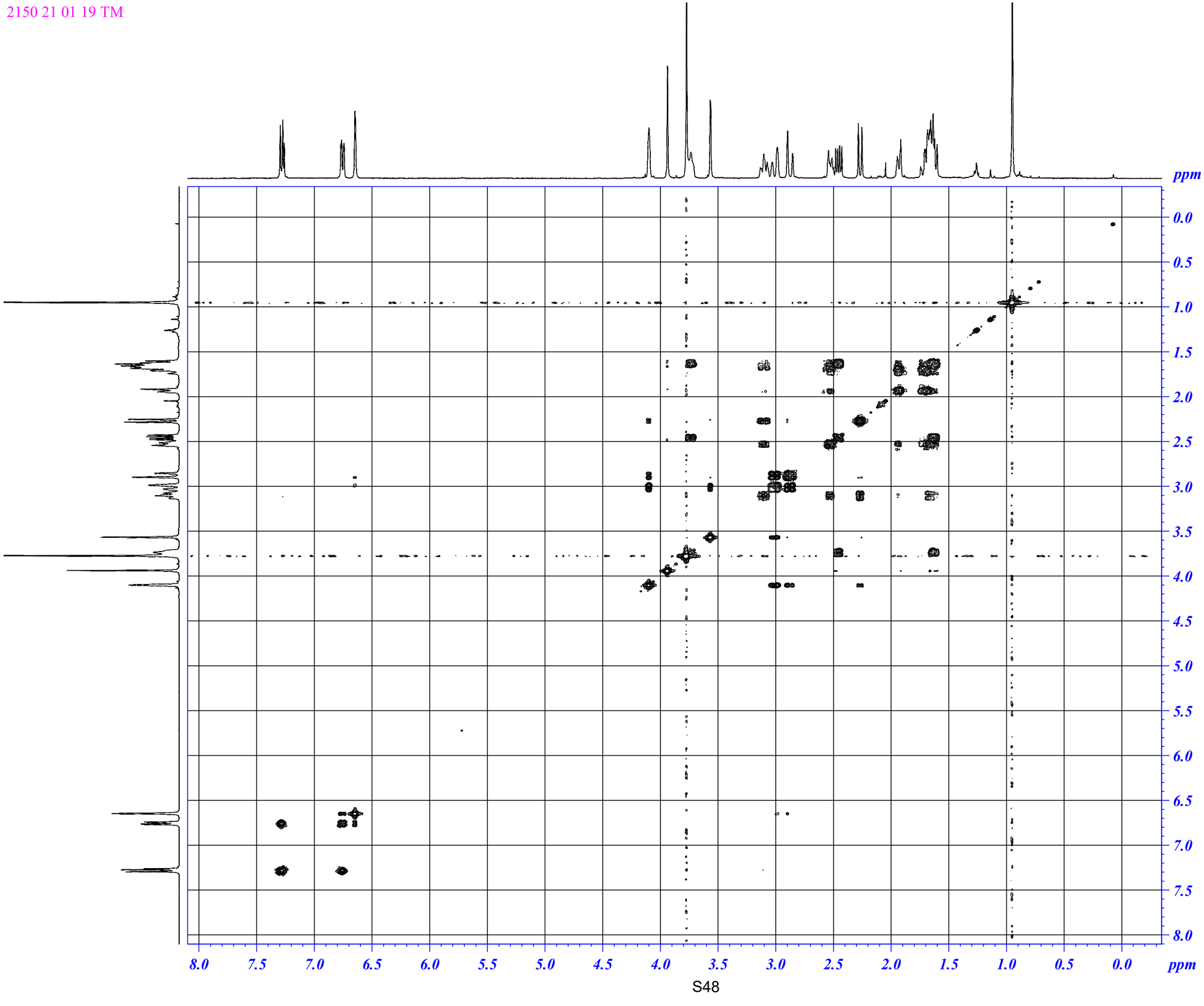
F2 - Processing parameters
SI 32768
SF 100.6127587 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



17a

^{13}C NMR (100 MHz, $CDCl_3$)

2150 21 01 19 TM



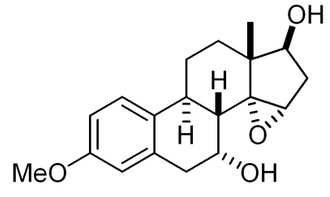
Current Data Parameters
NAME kawaiB400
EXPNO 383
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210119
Time 14.56 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG cosygpqf
TD 2048
SOLVENT CDCl3
NS 2
DS 2
SWH 3378.378 Hz
FIDRES 3.299198 Hz
AQ 0.3031040 sec
RG 181
DW 148.000 usec
DE 6.50 usec
TE 295.6 K
d0 0.00000300 sec
D1 1.48689198 sec
d13 0.00000400 sec
D16 0.00010000 sec
in0 0 sec
SFO1 400.1315591 MHz
NUC1 1H
P0 15.00 usec
P1 15.00 usec
GPNAM[1] SINE.100
GPZ1 10.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 256
SFO1 400.1316 MHz
FIDRES 26.393564 Hz
SW 8.443 ppm
FnMODE QF

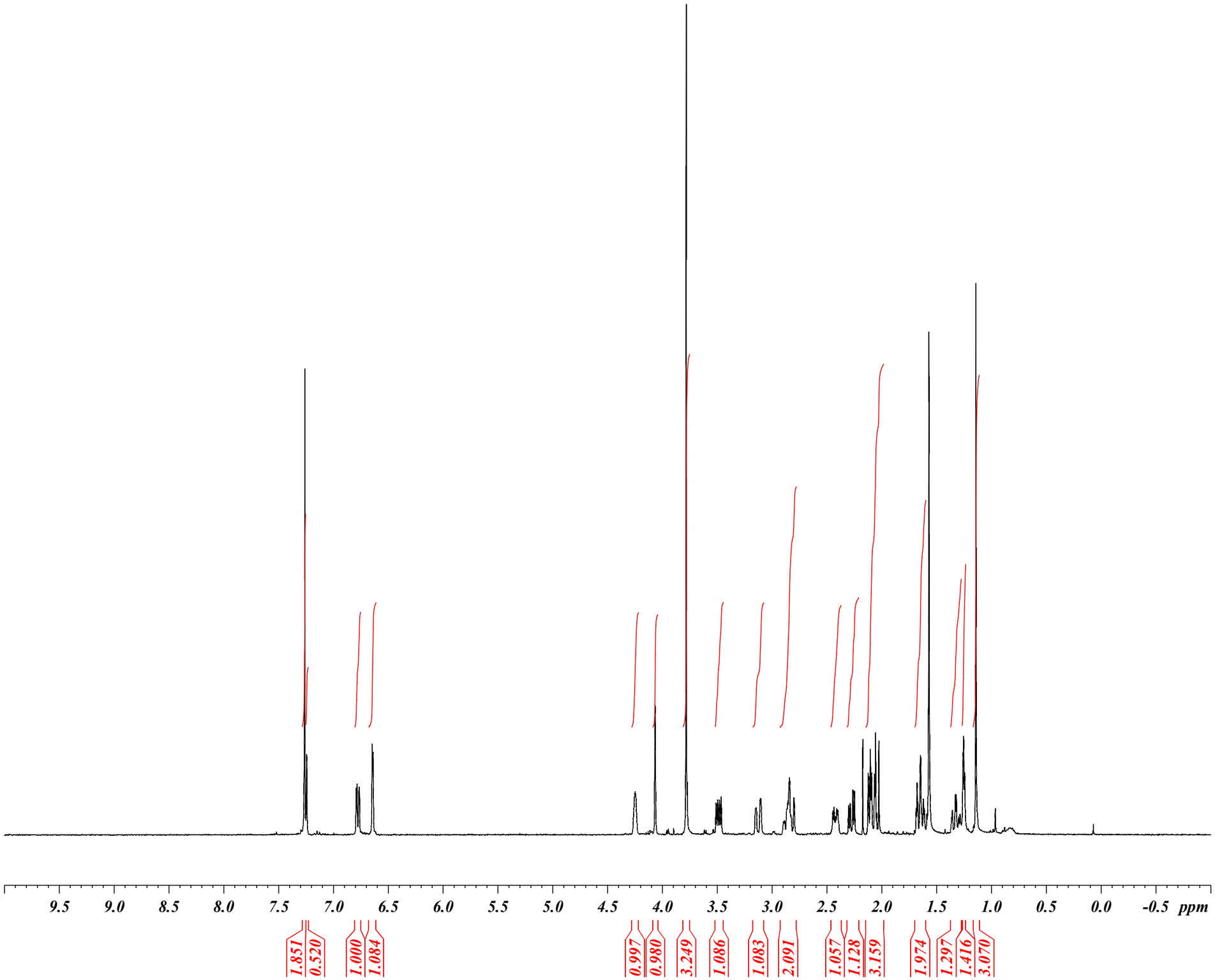
F2 - Processing parameters
SI 1024
SF 400.1300080 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 QF
SF 400.1300066 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0



17a

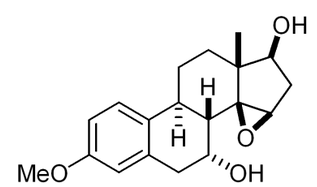
COSY ($CDCl_3$)



Current Data Parameters
NAME kawaiB400-2
EXPNO 21
PROCNO 1

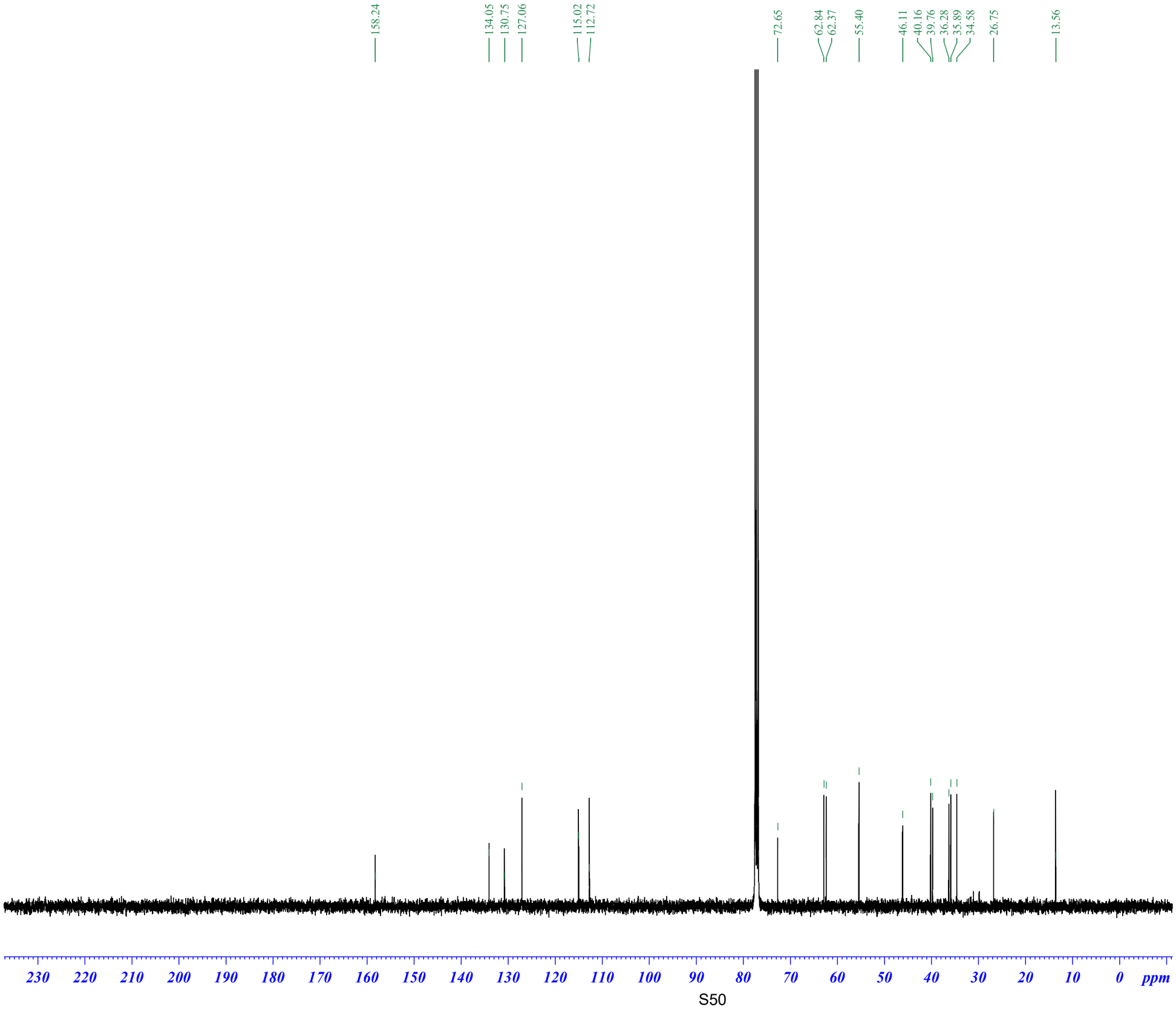
F2 - Acquisition Parameters
Date_ 20210304
Time 13.12 h
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.252629 Hz
AQ 3.9583745 sec
RG 812.7
DW 60.400 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324710 MHz
NUC1 1H
P1 15.00 usec

F2 - Processing parameters
SI 32768
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



17b

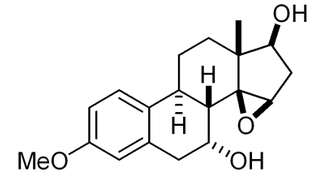
^{1}H NMR (400 MHz, $CDCl_3$)



Current Data Parameters
NAME kawai 400AN
EXPNO 15
PROCNO 1

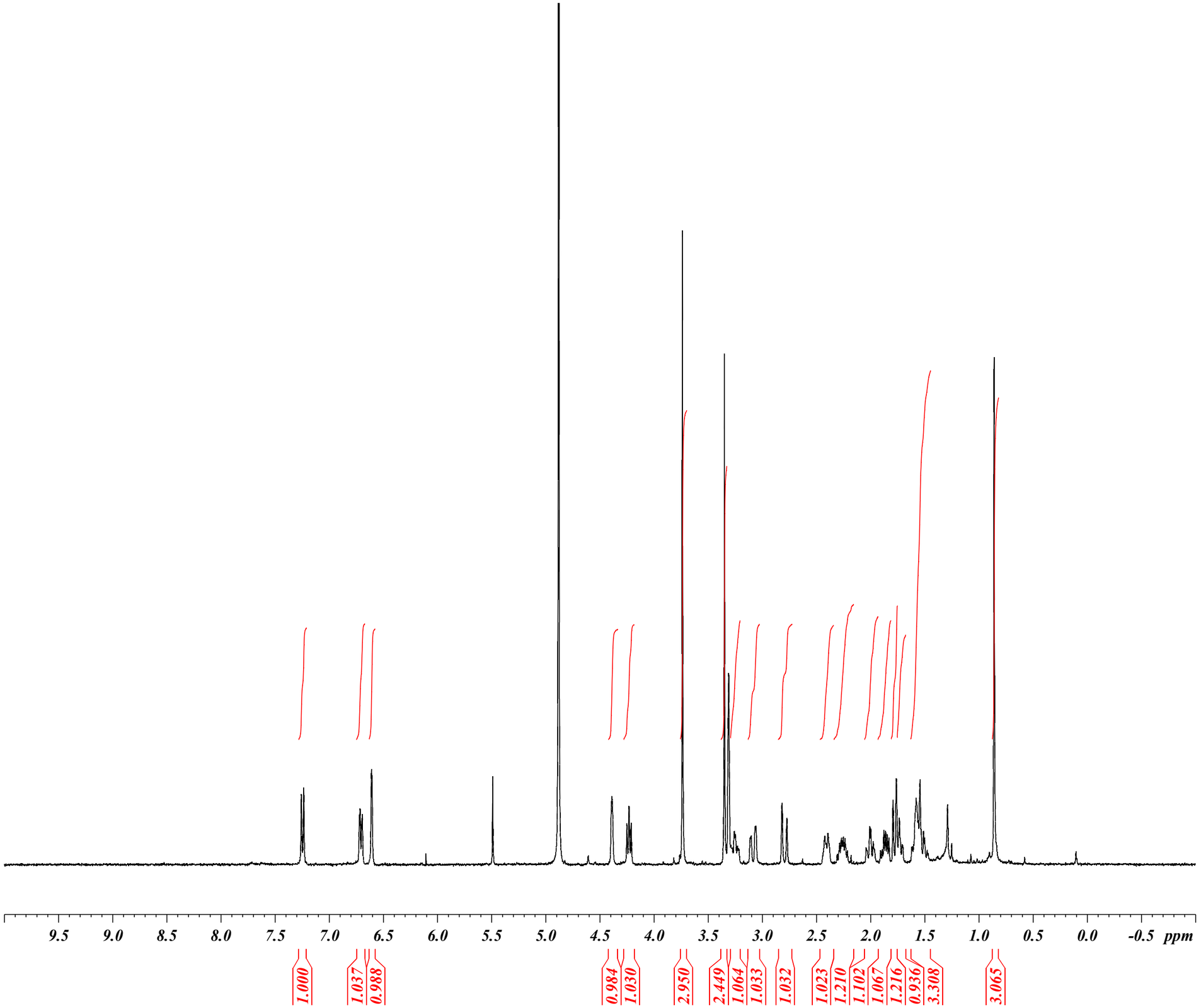
F2 - Acquisition Parameters
Date_ 20210312
Time 17.13 h
INSTRUM Avance
PROBHD Z163739_0304 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3200
DS 2
SWH 25000.000 Hz
FIDRES 0.762939 Hz
AQ 1.3107200 sec
RG 101
DW 20.000 usec
DE 8.64 usec
TE 300.0 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6241209 MHz
NUC1 13C
P0 2.67 usec
P1 8.00 usec
PLW1 92.79299927 W
SFO2 400.1326008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 22.60000038 W
PLW12 0.17857000 W
PLW13 0.08981800 W

F2 - Processing parameters
SI 65536
SF 100.6127540 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



17b

^{13}C NMR (100 MHz, $CDCl_3$)

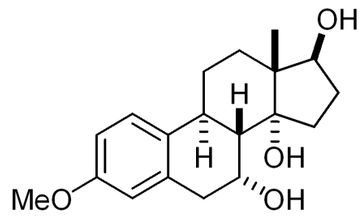


Current Data Parameters
NAME kawaiB400
EXPNO 346
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201228
Time 12.18
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 24
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9583745 sec
RG 2048
DW 60.400 usec
DE 6.50 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 10.30 dB
SFO1 400.1324710 MHz

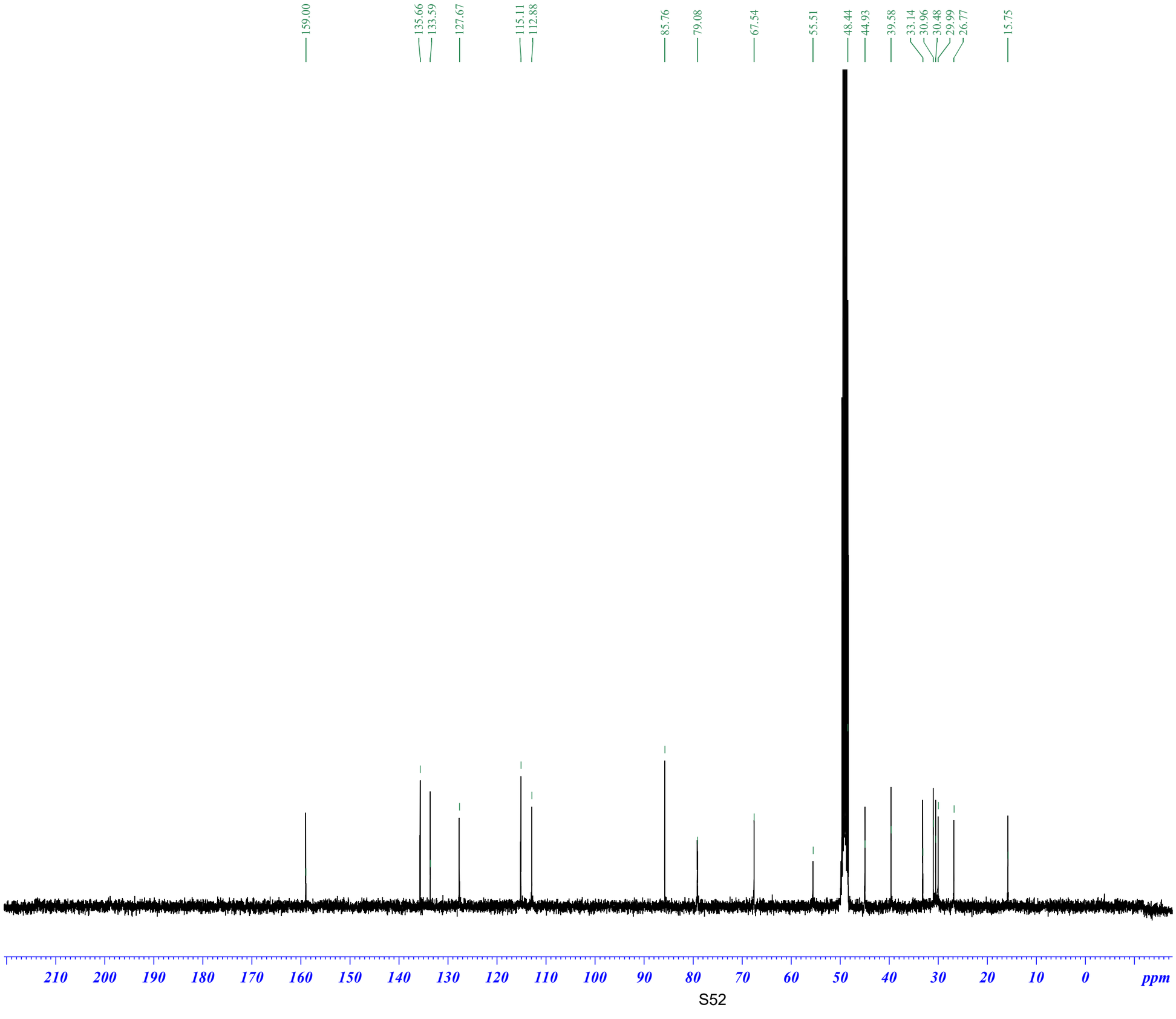
F2 - Processing parameters
SI 32768
SF 400.1300074 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



1b

^{1}H NMR (400 MHz, CD_3OD)

2121 20 12 28



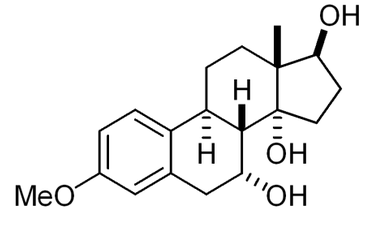
Current Data Parameters
NAME kawaiB400
EXPNO 347
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201228
Time 13.15
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 1200
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 1625.5
DW 20.850 usec
DE 6.50 usec
TE 296.2 K
D1 1.20000005 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 =======
NUC1 13C
P1 12.00 usec
PL1 7.50 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 =======
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 10.30 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 400.1316005 MHz

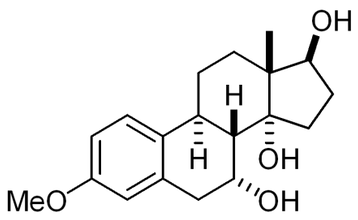
F2 - Processing parameters
SI 32768
SF 100.6126284 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



1b

^{13}C NMR (100 MHz, CD_3OD)

2121 21 01 08



1b

COSY (CD_3OD)

Current Data Parameters
NAME kawaiB400
EXPNO 360
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210108
Time 13.02
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG cosygpqf
TD 2048
SOLVENT MeOD
NS 1
DS 2
SWH 3396.739 Hz
FIDRES 1.658564 Hz
AQ 0.3014656 sec
RG 9195.2
DW 147.200 usec
DE 6.50 usec
TE 294.2 K
D0 0.00000300 sec
D1 1.48689198 sec
D13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00029440 sec

======== CHANNEL f1 ========
NUC1 1H
P0 15.00 usec
P1 15.00 usec
PL1 10.30 dB
SFO1 400.1314890 MHz

====== GRADIENT CHANNEL =====
GPNAM[1] SINE.100
GPZ1 10.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 256
SFO1 400.1315 MHz
FIDRES 26.537004 Hz
SW 8.489 ppm
FnMODE QF

F2 - Processing parameters
SI 1024
SF 400.1300078 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 QF
SF 400.1300077 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0