Electronic Supplementary Information

Total synthesis of antimalarial diterpenoid (+)-kalihinol A

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Experimental Section

General

Optical rotations were measured using a Jasco P-1030 polarimeter. Melting points (mp) were measured using a Yazawa melting point apparatus BY-2 and are uncorrected. IR spectra were recorded using a Jasco FT-IR/620 spectrometer. UV spectra were recorded using a Jasco V-550 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 or Bruker Biospin AV-600 spectrometer. Chemical shifts are given on the δ (ppm) scale using tetramethylsilane (TMS) as the internal standard (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; br, broad). High resolution ESIMS (HRESIMS) spectra were obtained using a Micromass LCT spectrometer. Elemental analysis data were obtained using an Elemental Vavio EL. Flash column chromatography was performed using Kanto Chemical Silica Gel 60N (spherical, neutral) 40-50 μm.

(2*R*,3*R*,6*R*)-6-(*tert*-Butyldiphenylsilanyloxy)-2,3-epoxy-3,7-dimethyloct-7-en-1-ol (3). To a solution of diol **2** (6.20 g, 36.5 mmol) in CH_2ClCH_2Cl (95 mL) were added Et_3N (7.63 mL, 54.8 mmol), DMAP (450 mg, 3.65 mmol) and TBSCl (6.05 g, 40.1 mmol) at r.t. After stirring for 1 hr at an ambient temperature, the mixture was diluted with Et_2O, washed with H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue which was then filtered through silica gel pad using hexane/AcOEt = 6:1 as a eluent. The filtrate was concentrated to give crude TBS ether. The crude TBS ether was used next reaction without further purification.

To a solution of the above crude TBS ether in DMF (37 mL) were added imidazole (4.07 g, 73.0 mmol) and TBDPSCl (14.3 g, 54.8 mmol) at r.t. After stirring for 5 hr at an ambient temperature, the mixture was diluted with Et_2O, washed with H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue which was then filtered through silica gel pad using hexane/AcOEt = 13:1 as a eluent. The filtrate was concentrated to give crude TBDPS ether. The crude TBDPS ether was used next reaction without further purification.

To a solution of the above crude TBDPS ether in MeOH (360 mL) was added PPTS (3.60 g, 14.3 mmol) at r.t. After stirring for 9 hr at an ambient temperature, the mixture was concentrated under reduced pressure to give a residue which was then purified by silica gel column chromatography (hexane/AcOEt = 7 : 2) to generate allylic alcohol (12.4 g, 83% yield, three steps) as a colorless oil. $[\alpha]_D^{28}$ -23.5 (*c* 0.89, $CHCl_3$); IR (neat) 3333, 2931 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.70-7.63 (4H, m), 7.37 (6H, m), 5.23 (1H, dt, *J* = 6.9, 1.2 Hz), 4.77 (1H, d, *J* = 1.5 Hz), 4.75 (1H, d, *J* = 0.7 Hz), 4.09 (1H, t, *J* = 6.1 Hz), 4.05 (2H, d, *J* = 6.9 Hz), 1.78 (2H, m), 1.70 (3H, s), 1.56 (2H, m), 1.50 (3H, s), 1.07 (9H, s); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 145.7, 139.5, 135.7, 135.7, 134.4, 133.7, 129.3, 129.3, 127.3, 127.2, 122.8, 111.7, 76.9, 59.4, 34.7, 33.4, 27.2, 19.6, 17.4, 16.4; EIMS *m/z*: 351 (M^+-^{t}Bu, 9), 135 (100); HREIMS *m/z*: 351.1798 (Calcd for $C_{22}H_{27}O_2Si$: M^+-^{t}Bu, 351.1780).

To a cold (-20 °C) suspension of 4A molecular sieves (12 g) in CH_2Cl_2 (53.0 mL) were added D-(-)-DET (230 mg, 1.10 mmol), $Ti(OiPr)_4$ (220 mg, 0.790 mmol) and TBHP (16.8 mL, 31.6 mmol,

2.52 M in CH_2Cl_2 solution). After stirring for 1 hr at the same temperature, a solution of the above allylic alcohol (6.45 g, 15.8 mol) in CH_2Cl_2 (10.0 mL) was added over 30 min. After stirring at -20 °C for 30 min, NaOH (5.0 mL, 30% in saturated aqueous NaCl) was added. The mixture was diluted with Et_2O, warmed to r.t. and stirred for 10 min. $MgSO_4$ (69 g) and celite (10 g) were then added and after stirring for 15 min, the mixture was filtered through a celite pad and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt = 5 : 2) to give epoxyalcohol **3** (6.37 g, 95% yield) as a colorless oil. $[\alpha]_D^{29}$ -19.7 (*c* 0.97, $CHCl_3$); IR (neat) cm^{-1}: 3418, 2932; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.70-7.61 (4H, m), 7.38 (6H, m), 4.79 (1H, d, *J* = 0.6 Hz), 4.77 (1H, d, *J* =1.3 Hz), 4.11 (1H, t, *J* = 5.5 Hz), 3.75 (1H, dd, *J* = 12.0, 4.4 Hz), 3.61 (1H, dd, *J* = 12.0, 6.6 Hz), 2.79 (1H, dd, *J* = 6.6, 4.4 Hz), 1.66 (3H, s), 1.50 (2H, m), 1.31 (2H, m), 1.12 (3H, s), 1.07 (9H, s); ^{13}C-NMR 100 MHz, $CDCl_3$) δ: 145.6, 135.9, 135.9, 134.5, 133.8, 129.6, 129.5, 127.5, 127.4, 111.9, 76.6, 62.6, 61.3, 61.1, 33.3, 30.3, 27.0, 19.3, 17.5, 17.2, 16.7.; EIMS *m/z*: 367 (M^+-^{t}Bu, 2), 199 (100); HREIMS *m/z*: 367.1741 (Calcd for $C_{22}H_{27}O_2Si$: M^+-^{t}Bu, 367.1729).

(2*S*,3*R*,6*R*)-2-{3-(Benzyloxy)propyl}-6-(*tert*-butyldiphenylsilyloxy)-3,7-dimethyloct-7-ene-1,3-diol (5). Grignard reagent **4** (2.70 ml, 1.89 mmol, 0.7 M in THF) was added dropwise to CuI (7.2 mg, 37.7 μmol) at -78 °C under Ar atmosphere. After stirring for 30 min at the same temperature, a solution of epoxyalcohol **3** (160 mg, 377 μmol) in THF (3.07 mL) was added. The mixture was warmed to r.t. After stirring for 3 hr, the reaction mixture was diluted with Et_2O, washed with sat. NH_4Cl aqueous solution, H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 5 : 2) to generate diol **5** (240 mg, 94% yield) as a colorless oil. $[\alpha]_D^{28}$ -8.4 (*c* 0.91, $CHCl_3$); IR (neat) cm^{-1}: 3357, 2931; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.70-7.62 (4H, m), 7.43-7.25 (11H, m), 4.82 (1H, d, *J* = 0.6 Hz), 4.79 (1H, d, *J* = 1.3 Hz), 4.47 (2H, s), 4.13 (1H, t, *J* = 5.7 Hz), 3.68 (2H, m), 3.42 (2H, m), 1.68 (2H, m), 1.67 (3H, s), 1.48 (4H, m), 1.34-1.22 (2H, m), 1.07 (9H, s), 0.99 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 145.9, 138.4, 136.0, 135.9, 134.6, 133.8, 129.6, 129.6, 128.4, 127.6, 127.5, 127.4, 111.8, 77.1, 76.4, 72.9, 70.3, 63.0, 46.6, 36.2, 28.6, 28.4, 27.0, 23.5, 23.3, 19.3, 17.6; ESIMS *m/z*: 575 (100); HRESIMS *m/z*: 575.3531 (Calcd for $C_{36}H_{50}O_4Si$: M^++H, 575.3557); *Anal*.: Calcd for $C_{36}H_{50}O_4Si$: C, 75.22; H, 8.77. Found: C, 74.92; H, 8.83.

(2*S*,3*R*,6*R*)-3-Acetoxy-2-(3-benzyloxypropyl)-6-chloro-3,7-dimethyl-7-octenyl acetate (6). To a solution of diol **5** (20.0 mg, 34.8 μmol) in pyridine (35 μL) was added Ac_2O (21.3 mg, 209 μmol) at r.t. After stirring for 3 hr at an ambient temperature, DMAP (0.4 mg, 3.5 μmol) was added and stirred at 60 °C for 24 hr. The reaction mixture was concentrated under reduced pressure to give a residue which was then purified by silica gel column chromatography (hexane/AcOEt = 4 : 1) to generate diacetate (18.8 mg, 82% yield) as a colorless oil. $[\alpha]_D^{22}$ -17.4 (*c* 0.81, $CHCl_3$); IR (neat) cm^{-1}: 2932, 1738; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.69-7.61 (4H, m), 7.42-7.26 (11H, m), 4.77 (2H, s), 4.47 (2H, s), 4.14 (1H, dd, *J* =11.6, 4.8Hz), 4.10 (1H, m), 4.00 (1H, dd, *J* = 11.7, 4.7Hz), 3.41

(2H, m), 2.40 (1H, m), 1.99 (3H, s), 1.87 (3H, s), 1.71 (2H, m), 1.67 (3H, s), 1.55-1.33 (4H, m), 1.30-1.20 (2H, m), 1.24 (3H, s), 1.07 (9H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 170.9, 170.0, 145.8, 138.6, 135.9, 134.6, 134.0, 129.6, 128.3, 127.6, 127.4, 111.9, 85.9, 72.8, 70.2, 64.0, 43.7, 31.1, 28.7, 28.1, 27.0, 23.9, 22.2, 21.4, 21.0, 19.3, 17.2; EIMS *m/z*: 599 (M^+-OAc, 24), 541 (100); HREIMS *m/z*: 599.3548 (Calcd for $C_{38}H_{51}O_4Si$: M^+-OAc, 599.3557).

TBAF (1.0 M in THF, 8.64 mL, 8.64 mmol) and AcOH (520 mg, 8.64 mmol) were added to the above diacetate (570 mg, 865 μmol). The mixture stirred at 60 °C for 48 hr. The reaction mixture was diluted with Et_2O, washed with sat. $NaHCO_3$ aqueous solution, H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 3 : 2) to generate alcohol (344 mg, 95% yield) as a colorless oil. $[\alpha]_D^{22}$ +1.5 (*c* 0.75, $CHCl_3$); IR (neat) cm^{-1} : 3445, 2944, 1734; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.34-7.27 (5H, m), 4.92 (1H, t, *J* = 0.7 Hz), 4.84 (1H, t, *J* = 1.4 Hz), 4.49 (2H, s), 4.24 (1H, dd, *J* =11.7, 4.8 Hz), 4.08 (1H, ,dd, *J* = 0.7 Hz), 4.01 (1H, br t, *J* = 1.70, 5.8 Hz), 3.47 (2H, t, *J* = 6.1 Hz), 2.46 (1H, m), 2.02 (3H, s), 1.98 (3H, s), 1.75 (2H, m), 1.70 (3H, s), 1.62-1.49 (4H, m), 1.38 (3H, s), 1.34 (2H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 171.0, 170.3, 147.0, 138.5, 128.3, 127.6, 127.5, 111.5, 86.0, 75.8, 72.8, 70.1, 64.0, 43.7, 31.9, 28.4, 28.1, 24.0, 22.3, 21.4, 21.0, 17.4; EIMS *m/z*: 361 (M^+-OAc, 100); HREIMS *m/z*: 443.2399 (Calcd for $C_{24}H_{36}O_6$: M^++Na, 443.2410); *Anal*.: Calcd for $C_{24}H_{36}O_6$: C, 68.54 ; H, 8.63. Found: C, 68.52; H, 8.62.

To a cold (0 °C) solution of the above alcohol (44.6 g, 106 mmol) in CH_2Cl_2 (212 mL) were added hexachloroacetone (19.3 mL, 127 mmol) and Ph_3P (33.3 g, 127 mmol). After stirring for 5 min at the same temperature, the reaction mixture was concentrated under reduced pressure to give a residue which was then purified by silica gel column chromatography (hexane/AcOEt = 3 : 1) to generate allylic chloride **6** (41.9 g, 90% yield) as a colorless oil. $[\alpha]_D^{23}$ -1.3 (*c* 0.78, $CHCl_3$); IR (neat) cm^{-1}: 2951, 1732; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.35-7.27 (5H, m), 5.00 (1H, s), 4.89 (1H, q, *J* = 1.5 Hz), 4.49 (2H, s), 4.31 (1H, t, *J* =11.7, 4.4 Hz), 3.47 (2H, t, *J* = 6.1 Hz), 2.50 (1H, m), 2.03 (3H, s), 1.98 (3H, s), 1.97-1.74 (4H, m), 1.79 (3H, s), 1.56 (2H, m), 1.38 (3H, s), 1.35 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 170.9, 170.2, 144.0, 138.5, 128.3, 127.6, 127.5, 114.5, 85.7, 72.8, 70.0, 66.9, 63.8, 43.7, 33.7, 30.6, 28.1, 24.1, 22.3, 21.4, 21.0, 16.9; EIMS *m/z*: 437 (M^+-H, 10), 379 (M^+-OAc, 100); HREIMS *m/z*: 378.2025 (Calcd for $C_{22}H_{31}O_3Cl$: M^+-AcOH, 378.1962); *Anal*.: Calcd for $C_{36}H_{50}O_4Si$: C, 65.66 ; H, 8.04. Found: C, 65.60; H, 8.11.

(2*S*)-5-Benzyloxy-2-[(2*R*,5*S*)-(5-chloro-2,6,6-trimethyltetrahydropyran-2-yl)]-pentyl pivalate (7). To a cold (-78 °C) solution of diacetate **6** (208 mg, 473 μmol) in toluene (4.70 mL) was added DIBAH (1.05 mL, 945 μmol, 0.9 M in hexane). After stirring for 10 min at the same temperature, the reaction mixture was diluted with Et_2O, warmed to r.t. and stirred for 3 hr. The mixture was dried over $MgSO_4$. Removal of the solvent gave crude diol, which was used the next reaction without further purification.

To a solution of the above crude diol in pyridine (500 μL) was added PivCl (65.4 mg, 567 μmol) at r.t. After stirring for 30 min at an ambient temperature, the reaction mixture was diluted with

Et_2O, washed with sat. $NaHCO_3$ aqueous solution, H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 4 : 1) to generate pivalate (161 mg, 78% yield, two steps) as a colorless oil. $[\alpha]_D^{22}$ +1.6 (*c* 1.27, $CHCl_3$); IR (neat) cm^{-1}: 3491, 2971, 1726; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.35-7.28 (5H, m), 5.00 (1H, s), 4.88 (1H, m), 4.49 (2H, s), 4.35 (1H, t, *J* = 7.2 Hz), 4.28 (1H, dd, *J* = 11.7, 5.0 Hz), 4.18 (1H, dd, *J* = 11.79, 3.9 Hz), 3.48 (2H, t, *J* = 6.1 Hz), 1.99-1.91 (3H, m), 1.80 (3H, s), 1.71-1.57 (4H, m), 1.47 (1H, m), 1.36 (1H, m), 1.19 (9H, s), 1.15 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 178.4, 144.3, 138.4, 128.3, 127.6, 127.5, 114.2, 74.0, 72.9, 70.1, 67.3, 64.2, 47.0, 38.7, 37.7, 30.5, 28.2, 27.2, 24.3, 24.1, 17.1; EIMS *m/z*: 439 (M^+-H, 0.1), 421 (M^+-OH, 4), 125 (100); HREIMS *m/z*: 420.2424 (Calcd for $C_{25}H_{39}O_4Cl$: M^+-H_2O, 420.2431).

To a solution of the above pivalate (14.9 g, 34.0 mmol) in CH_2Cl_2 (340 mL) was added IDCP (120 g, 255 mmol) at r.t. After stirring for 4 hr at an ambient temperature, the reaction mixture was diluted with Et_2O, washed with sat. $Na_2S_2O_3$ aqueous solution, H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave crude iodoether, which was used the next reaction without further purification.

To a cold (-78 °C) solution of the above crude iodoether in THF (175 mL) were added Bu_3SnH (28.3 mL, 105 mmol) and Et_3B (7.61 mL, 52.6 mmol). After stirring for 1 hr at the same temperature, the reaction mixture was diluted with Et_2O, warmed to r.t. and added sat. KF aqueous solution (50 mL). After stirring for 30 min at the same temperature, the reaction mixture was washed with H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 10 : 1) to generate tetrahydropyran **7** (10.8 g, 72% yield, two steps) as a colorless oil. $[\alpha]_D^{22}$ -13.4 (*c* 0.71, $CHCl_3$); IR (neat) cm^{-1}: 2957, 1727; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.36-7.27 (5H, m), 4.49 (2H, s), 4.24 (1H, dd, *J* = 11.5, 4.1 Hz), 4.13 (1H, dd, *J* = 11.4, 4.4 Hz), 3.69 (1H, dd, *J* = 12.2, 4.3 Hz), 3.46 (2H, t, *J* = 6.2 Hz), 2.08 (1H, m), 1.98 (1H, m), 1.80-1.50 (5H, m), 1.35 (2H, m), 1.32 (3H, s), 1.25 (3H, s), 1.18 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 178.6, 138.6, 128.3, 127.6, 127.5, 75.4, 75.1, 72.8, 70.4, 65.1, 63.7, 50.1, 38.7, 35.6, 30.5, 28.3, 27.2, 27.0, 23.5, 22.6, 22.4; EIMS *m/z*: 438 (M^+, 12), 161 (100); HREIMS *m/z*: 438.2527 (Calcd for $C_{25}H_{39}O_4Cl$: M^+, 438.2537); *Anal.*: Calcd for $C_{25}H_{39}O_4Cl$: C, 68.39 ; H, 8.95. Found: C, 68.56; H, 8.78.

(2*S*,5*RS*)-5-(*tert*-Butyldimethylsilanyloxy)-2-[(2*R*,5*S*)-(5-chloro-2,6,6-trimethyltetrahydropyran-2-yl)]-5-hydroxy-6-heptenyl pivalate (8). A solution of benzyl ether **7** (3.80g, 8.66 mmol) in MeOH (28.9 mL) in the presence of 10% Pd/C (866 mg) was stirred at r.t. for 2.5 hr under a hydrogen atmosphere. The reaction mixture was diluted with AcOEt and filtered through silica gel pad and filtrate was concentrated under reduced pressured. The residue was purified by silica gel column chromatography (hexane : AcOEt = 2 : 1) to generate alcohol (3.00 g, 99% yield) as a colorless oil. $[\alpha]_D^{28}$ -16.9 (*c* 0.78, $CHCl_3$); IR (neat) cm^{-1}: 3434, 2957, 1726; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 4.24 (1H, dd, *J* = 11.5, 4.3 Hz), 4.11 (1H, dd, *J* = 11.5, 4.7 Hz), 3.70 (1H, dd, *J* = 12.2, 4.2 Hz), 3.64 (2H, t, *J* = 6.1 Hz), 2.08 (1H, m), 2.01 (1H, m), 1.74-1.51 (7H, m), 1.34 (3H, s), 1.27

(3H, s), 1.25 (3H, s), 1.19 (9H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 178.7, 75.6, 75.4, 65.0, 63.8, 63.0, 49.9, 38.8, 35.0, 31.2, 30.5, 27.2, 27.0, 23.2, 22.9, 22.6; EIMS *m/z*: 349 (M^++H, 15), 331 (M^+-OH, 2), 161 (100); HREIMS *m/z*: 349.2147 (Calcd for $C_{18}H_{33}O_4Cl$: M^++H, 349.2146); *Anal*.: Calcd for $C_{18}H_{33}O_4Cl$: C, 61.96 ; H, 9.53. Found: C, 62.18; H, 9.59.

To a solution of the above alcohol 19.7 mg, 56.5 μmol) in CH_2Cl_2 (753 μL) were added $NaHCO_3$ (17.1 mg, 203 μmol) and Dess-Martin periodinane (28.8 mg, 67.8 μmol) at r.t. After stirring for 10 min at an ambient temperature, the reaction mixture was diluted with Et_2O and added sat. $NaHCO_3$ aqueous solution and sat. $Na_2S_2O_3$ aqueous solution. After stirring for 15 min at the same temperature, the reaction mixture was washed with H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 4 : 1) to generate aldehyde (19.2 mg, 98% yield) as a colorless oil. $[\alpha]_D^{27}$ -19.6 (*c* 0.89, $CHCl_3$); IR (neat) cm^{-1}: 2976, 1726; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.78 (1H, t, *J* = 1.2 Hz), 4.26 (1H, dd, *J* = 11.6, 3.8 Hz), 4.07 (1H, dd, *J* = 11.6, 4.4 Hz), 3.69 (1H, dd, *J* = 12.2, 4.2 Hz), 2.56 (2H, m), 2.15-1.97 (2H, m), 1.87 (1H, m), 1.69-1.54 (4H, m), 1.33 (3H, s), 1.25 (6H, s), 1.18 (9H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 202.0, 178.5, 75.6, 75.1, 64.8, 63.5, 49.4, 42.6, 38.8, 35.0, 30.4, 27.2, 27.0, 22.9, 22.6, 19.3; EIMS *m/z*: 347 (M^+, 4), 331 (M^+-Me, 1), 161 (100); HREIMS *m/z*: 331.1646 (Calcd for $C_{18}H_{31}O_4Cl$: M^+-Me, 331.1676).

To a cold (0 °C) solution of the above aldehyde (184 mg, 530 μmol) in THF (5.30 mL) was added CH_2=CHMgBr (1.09 mL, 1.06 mmol, 0.97 M in THF). After stirring for 10 min at the same temperature, the reaction mixture was diluted with Et_2O, washed with sat. NH_4Cl aqueous solution, H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 2 : 1) to generate diastereomeric mixture of alcohol (198 mg, 99% yield) as a colorless oil. IR (neat) cm^{-1}: 3439, 2958, 1727; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.84 (1H, m), 5.21 (1H, d, *J* = 17.2 Hz), 5.10 (1H, d, *J* = 10.4 Hz), 4.23 (1H, m), 4.13 (1H, m), 4.10 (1H, m), 3.70 (1H, dd, *J* = 12.3, 4.2 Hz), 2.09 (1H, m), 1.98 (1H, m), 1.80-1.48 (6H, m), 1.33 (3H, s), 1.30 (2H, m), 1.27 (3H, s), 1.22 (3H, s), 1.19 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 178.6, 141.0, 114.8, 114.6, 75.6, 75.4, 73.7, 72.7, 65.0, 63.8, 63.7, 38.8, 35.8, 35.4, 35.2, 35.1, 30.5, 29.7, 27.2, 27.0, 22.9, 22.8, 22.7, 22.6, 22.3; EIMS *m/z*: 375 (M^++H, 0.3), 359 (M^+-Me, 0.2), 161 (100); HREIMS *m/z*: 359.1995 (Calcd for $C_{20}H_{35}O_4Cl$: M^+-Me, 359.1989); *Anal*.: Calcd for $C_{20}H_{35}O_4Cl$: C, 64.07 ; H, 9.41. Found: C, 64.17; H, 9.28.

To a solution of the above alcohol (15.1 mg, 40.3 μmol) in DMF (40.3 μL) were added imidazole (4.12 mg, 60.5 μmol) and TBSCl (6.68 mg, 44.3 μmol) at r.t. After stirring for 1 hr at an ambient temperature, the mixture was diluted with Et_2O, washed with H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 10 : 1) to generate diastereomeric mixture of TBS ether **8** (19.5 mg, 99% yield) as a colorless oil. IR (neat) cm^{-1}: 2957, 1729; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.77 (1H, m), 5.13 (1H, m), 5.01 (1H, d, *J* = 10.4 Hz), 4.22 (1H, m), 4.15-4.01 (2H, m), 3.69 (1H, dd, *J* = 12.2, 4.2 Hz), 2.08 (1H, m), 1.99 (1H, m), 1.65-1.39 (6H, m), 1.32 (3H, s), 1.25 (3H, s), 1.21 (3H, s), 1.18 (9H, s), 0.89 (9H, s), 0.04 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 141.4, 141.2, 113.9,

79.9, 76.5, 73.7, 73.5, 64.3, 63.6, 53.1, 53.0, 37.3, 37.3, 37.0, 36.8, 30.5, 27.0, 25.8, 22.3, 21.8, 19.9, 19.8, -4.4, -4.8; EIMS *m/z*: 489 (M^++H, 10), 357 (M^+-OTBS, 25), 161 (100); HREIMS *m/z*: 488.3098 (Calcd for $C_{26}H_{49}O_4SiCl$: M^+, 488.3089); *Anal*.: Calcd for $C_{26}H_{49}O_4SiCl$: C, 63.83 ; H, 10.10. Found: C, 63.89; H, 10.07.

(2*S*,5*RS*)-5-(*tert*-Butyldimethylsilanyloxy)-2-[(2*R*,5*S*)-(5-chloro-2,6,6-trimethyltetrahydropyran-2-yl)]-6-hepten-1-ol (9). To a cold (-78 °C) solution of pivalate **8** (19.7 mg, 40.3 μmol) in CH_2Cl_2 (400 μL) was added DIBAH (52.0 μL, 48.4 μmol, 0.93 M in hexane). After stirring for 10 min at the same temperature, the reaction mixture was diluted with Et_2O, added with brine, warmed to r.t. and stirred for 3 hr. The mixture was dried with $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 4 : 1) to generate diastereomeric mixture of alcohol (15.8 mg, 97% yield) as a colorless oil. IR (neat) cm^{-1}: 3476, 2954; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.76 (1H, m), 5.13 (1H, d, *J* = 17.2 Hz), 5.02 (1H, d, *J* = 10.4 Hz), 4.05 (1H, m), 3.93 (1H, br d, *J* = 7.4 Hz), 3.76-3.67 (2H, m), 3.57 (1H, m), 2.16-1.98 (2H, m), 1.79(1H, m), 1.66-1.51 (4H, m), 1.42 (2H, m), 1.38 (3H, s), 1.32 (3H, s), 1.23 (3H, s), 0.88 (9H, s), 0.02 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 141.4, 141.2, 113.9, 79.9, 76.5, 73.7, 73.5, 64.3, 63.6, 53.1, 53.0, 37.3, 37.3, 37.0, 36.8, 30.5, 27.0, 25.8, 22.3, 21.8, 19.9, 19.8, -4.4, -4.8; EIMS *m/z*: 405 (M^++H, 1), 347 (M^+-^{t}Bu, 1), 59 (100); HREIMS *m/z*: 404.2521 (Calcd for $C_{21}H_{41}O_3SiCl$: M^+, 404.2514); *Anal*.: Calcd for $C_{21}H_{41}O_3SiCl$: C, 62.26 ; H, 10.20. Found: C, 62.45; H, 10.07.

To a solution of the above alcohol (240 mg, 592 μmol) in CH_2Cl_2 (6.00 mL) were added $NaHCO_3$ (300 mg, 3.55 mmol) and Dess-Martin periodinane (377 mg, 888 μmol) at r.t. After stirring for 30 min at an ambient temperature, the reaction mixture was diluted with Et_2O and added sat. $NaHCO_3$ aqueous solution and sat. $Na_2S_2O_3$ aqueous solution. After stirring for 15 min at the same temperature, the reaction mixture was washed with H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave crude aldehyde. The crude aldehyde was used next reaction without further purification.

To a cold (-78 °C) solution of CH_2=C(CH_3)CH_2P(O)Ph_2 (607 mg, 2.37 mmol) in THF (6.00 mL) were added HMPA (425 mg, 2.37 mmol) and BuLi (840 mL, 1.18 mmol. 1.41 M in hexane). After stirring for 1 hr at the same temperature, a solution of the above crude aldehyde in THF (1.00 mL) was added to the mixture. The mixture was warmed to r.t. over 2 hr. The reaction mixture was diluted with Et_2O, washed with sat. NH_4Cl aqueous solution, H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 40 : 1) to generate triene **9** (205 mg, 78% yield, two steps) as a colorless oil. IR (neat) cm^{-1}: 2928; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.05 (1H, d *J* = 15.7 Hz), 5.78 (1H, m), 5.37 (1H, dd, *J* = 15.8, 9.8 Hz), 5.13 (1H, m), 5.00 (1H, m), 4.87 (2H, s), 4.06 (1H, m), 3.64 (1H, dd, *J* = 12.4 Hz, 4.1 Hz), 2.14-1.92 (2H, m), 1.84 (2H, m), 1.82 (3H, s), 1.51-1.05 (5H, m), 1.33 (3H, s), 1.27 (3H, s), 1.22 (3H, s), 0.90 (9H, s), 0.03 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 142.0, 141.8, 135.5, 131.4, 131.3, 114.6, 113.4, 113.2, 77.2, 75.2, 74.1, 74.0, 65.5, 55.7, 55.5,

36.6, 33.3, 33.2, 30.4, 27.1, 25.9, 25.1, 24.0, 23.9, 22.4, 18.8, 18.3, -4.4, -4.4; EIMS *m/z*: 440 (M^+, 20), 383 (M^+-^{t}Bu, 16), 161 (100); HREIMS *m/z*: 440.2851 (Calcd for $C_{25}H_{45}O_2SiCl$: M^+, 440.2877).

(4*S*,4a*R*,8a*R*)-4-((2*R*,5*S*)-5-Chloro-2,6,6-trimethyltetrahydro-2*H*-pyran-2-yl)-6-methyl-3,4,4a,7,8,8a-hexahydronaphthalen-1-one (10). TBAF (3.00 mL, 3.00 mmol) and was added to trienen **9** (205 mg, 465 μmol). The mixture stirred at r.t. for 2 hr. The reaction mixture was diluted with Et_2O, washed with H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 5 : 1) to generate alcohol (146 mg, 96% yield) as a colorless oil. IR (neat) cm^{-1}: 3361, 2937; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.07 (1H, d *J* = 15.1 Hz), 5.85 (1H, m), 5.38 (1H, dd, *J* = 15.7, 9.7 Hz), 5.09 (1H, m), 4.88 (2H, s), 4.87 (2H, s), 4.09 (1H, br s), 3.66 (1H, m), 2.08 (1H,m), 1.98-1.75 (3H, m), 1.85 (3H, s), 1.61-1.48 (3H, m), 1.44-1.31 (3H, m), 1.33 (3H, s), 1.28 (3H, s), 1.24 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 141.9, 141.3, 141.2, 135.7, 135.7, 114.9, 114.5, 114.4, 75.5, 73.6, 55.7, 55.2, 35.6, 35.4, 33.2, 32.9, 30.3, 27.2, 25.2, 24.2, 22.4, 18.8; EIMS *m/z*: 327 (M^++H, 0.1), 161 (100).

To a solution of the above alcohol (146 mg, 447 μmol) in CH_2Cl_2 (5.00 mL) were added $NaHCO_3$ (230 mg, 2.68 mmol) and Dess-Martin periodinane (380 mg, 894 μmol) at r.t. After stirring for 30 min at an ambient temperature, the reaction mixture was diluted with Et_2O and added sat. $NaHCO_3$ aqueous solution and sat. $Na_2S_2O_3$ aqueous solution. After stirring for 15 min at the same temperature, the reaction mixture was washed with H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 9 : 1) to generate *cis*-decalin **10** (144 mg, 99% yield) as a colorless oil. $[\alpha]_D^{23}$ -82.5 (*c* 0.48, $CHCl_3$); IR (neat) cm^{-1}: 2927, 1721; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 5.17 (1H, s), 3.72 (1H, dd *J* = 12.4, 4.1 Hz), 2.85 (1H, m), 2.64 (1H, m), 2.40 (1H, td, *J* = 17.5, 4.5 Hz), 2.30 (1H, m), 2.20-1.98 (4H, m), 1.84-1.70 (4H, m), 1.57 (3H, s), 1.56 (1H, m), 1.51 (1H, m), 1.44 (1H, m), 1.44 (1H, m), 1.35 (3H, s), 1.29 (3H, s), 1.25 (3H, s); ^{1}H-NMR (125 MHz, $CDCl_3$) δ: 214.9, 134.0, 128.3, 76.4, 75.3, 65.1, 52.5, 44.3, 38.0, 35.3, 35.1, 30.5, 27.3, 26.3, 23.6, 22.6, 22.3, 21.3; EIMS *m/z*: 324 (M^+, 28), 189 (100); HREIMS *m/z*: 324.1852 (Calcd for $C_{19}H_{29}O_2Cl$: M^+, 324.1856); *Anal.*: Calcd for $C_{19}H_{29}O_2Cl$: C, 70.24; H, 9.00. Found: C, 70.32; H, 9.11.

(1a*R*,3a*R*,7*S*,7a*R*,7b*S*)-7-((2*R*,5*S*)-5-Chloro-2,6,6-trimethyltetrahydro-2*H*-pyran-2-yl)-1a-methyl-octahydronaphtho[2,1-*b*]oxiren-4(7b*H*)-one (11a) and (1a*S*,3a*R*,7*S*,7a*R*,7b*R*)-7-((2*R*,5*S*)-5-chloro-2,6,6-trimethyltetrahydro-2*H*-pyran-2-yl)-1a-methyl- octahydronaphtho[2,1-*b*]oxiren-4(7b*H*)-one (11b). To a cold (0 °C) solution of *cis*-decalin **10** (44.9 mg, 148 μmol) in CH_2Cl_2 (1.38 mL) were added Na_2HPO_4 (118 mg, 829 μmol) and *m*CPBA (110 mg, 415 μmol). After stirring for 3 hr at the same temperature, the reaction mixture was diluted with Et_2O, added with Me_2S and stirred for 10 min. The mixture was washed with 1 M NaOH aqueous solution, H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 3 : 1) to

generate α-epoxide **11a** (11.2 mg, 24% yield) as colorless needles and β-epoxide **11b** (33.5 mg, 71% yield) as a colorless oil. α-epoxide **11a**: mp: 164-168 °C; $[\alpha]_D^{27}$ -88.2 (*c* 0.76, $CHCl_3$); IR (KBr) cm^{-1}: 2927, 1712; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.74 (1H, dd, *J* = 12.1, 4.3 Hz), 2.82 (1H, s), 2.57-2.52 (1H, m), 2.48-2.41 (1H, m), 2.22-2.02 (3H, m), 2.00-1.93 (1H, m), 1.92-1.72 (5H, m), 1.67-1.54 (3H, m), 1.40-1.31 (7H, m), 1.26 (3H, s), 1.23 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 213.8, 76.2, 75.6, 66.0, 64.8, 58.3, 51.2, 42.5, 39.0, 36.2, 35.6, 30.4, 27.2, 25.5, 23.6, 22.6, 22.3, 21.6, 19.1; ESIMS *m/z*: 341 (100); HRESIMS *m/z*: 341.1889 (Calcd for $C_{19}H_{29}O_3Cl$: M^++H, 341.1883); *Anal*.: Calcd for $C_{19}H_{29}O_3Cl$: C, 66.94 ; H, 8.57. Found: C, 66.98; H, 8.53, β-epoxide **11b**: $[\alpha]_D^{27}$ -60.3 (*c* 1.21, $CHCl_3$); IR (neat) cm^{-1}: 2952, 1712; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.73 (1H, dd, *J* = 12.4, 4.3 Hz), 2.96 (1H, s), 2.63 (1H, ddd, *J* = 6.8, 4.0, 1.4 Hz), 2.36 (1H, dt, *J* = 18.0, 3.7 Hz), 2.28 (1H, dd, *J* = 13.6, 4.5 Hz), 2.22-2.11 (3H, m), 2.06-1.99 (2H, m), 1.86-1.80 (1H, m), 1.77-1.67 (3H, m), 1.63-1.52 (3H, m), 1.37 (3H, s), 1.28 (1H, s), 1.27 (6H, s), 1.25 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 212.3, 76.3, 75.5, 66.3, 65.0, 60.5, 51.4, 40.9, 38.1, 36.4, 35.6, 30.5, 27.3, 24.5, 23.6, 22.4, 21.0, 20.0, 20.0; ESIMS *m/z*: 359 (100), 341 (60); HRESIMS *m/z*: 341.1878 (Calcd for $C_{19}H_{29}O_3Cl$: M^++H, 341.1883); *Anal*.: Calcd for $C_{19}H_{29}O_3Cl$: C, 66.94; H, 8.57. Found: C, 67.13; H, 8.48.3

***tert*-Butyl((1a*R*,3a*R*,4*S*,7*S*,7a*S*,7b*S*)-7-((2*R*,5*S*)-5-chloro-2,6,6-trimethyltetrahydro-2*H*-pyran-2-yl)-1a-methyldecahydronaphtho[2,1-*b*]oxiren-4-yloxy)dimethylsilane (12).** To a cold (0 °C) solution of ketone **10** (19.1 mg, 58.8 μmol) in MeOH (588 μL) was added $NaBH_4$ (3.3 mg, 88.2 μmol). After stirring for 15 min at the same temperature, the reaction mixture was diluted with Et_2O, washed with sat. NH_4Cl aqueous solution, H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 9 : 1) to generate β-alcohol (15.0 mg, 79% yield) as colorless needles and α-alcohol (3.1 mg, 16% yield) as a colorless oil. β-alcohol: mp: 164-168 °C; $[\alpha]_D^{27}$ +67.6 (*c* 1.12, $CHCl_3$); IR (KBr) cm^{-1}: 3365, 2933; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 5.69 (1H, d, *J* = 4.8 Hz), 3.74 (1H, dt, *J* = 12.1, 4.6 Hz), 3.69 (1H, dd, *J* = 12.5, 4.2 Hz), 2.08 (1H, dq, *J* = 12.9, 4.2 Hz), 2.02-1.90 (4H, m), 1.77-1.74 (1H, m), 1.69-1.66 (2H, m), 1.62-1.49 (6H, m), 1.45-1.39 (3H, m), 1.35 (3H, s), 1.25 (1H, s), 1.22 (6H, s), 0.91 (1H, m); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 129.5, 127.9, 76.1, 75.0, 72.9, 65.3, 51.2, 41.6, 37.7, 37.3, 30.5, 30.3, 29.7, 27.6, 25.2, 23.6, 22.7, 20.8, 16.7; ESIMS *m/z*: 327 (100); HRESIMS *m/z*: 327.2096 (Calcd for $C_{19}H_{31}O_2Cl$: M^++H, 327.2091); *Anal*.: Calcd for $C_{19}H_{31}O_2Cl$: C, 69.81 ; H, 9.56. Found: C, 69.59 ; H, 9.53. α-alcohol: $[\alpha]_D^{27}$ +21.5 (*c* 0.97, $CHCl_3$); IR (neat) cm^{-1}: 3365, 2934; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.68 (1H, dd, *J* = 4.3, 1.2 Hz), 3.77-3.68 (2H, m), 2.15-1.90 (6H, m), 1.78-1.66 (3H, m), 1.62 (3H, brs), 1.61-1.51 (3H, m), 1.50-1.41 (2H, m), 1.39-1.34 (4H, m), 1.22 (6H, s), 0.92 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 127.9, 77.2, 76.1, 75.0, 72.8, 65.3, 50.9, 41.3, 37.8, 37.3, 30.5, 30.3, 29.7, 27.6, 25.3, 23.5, 22.8, 20.8, 16.7; ESIMS *m/z*: 327 (100); HRESIMS *m/z*: 327.2088 (Calcd for $C_{19}H_{31}O_2Cl$: M^++H, 327.2091); *Anal*.: Calcd for $C_{19}H_{31}O_2Cl$: C, 69.81; H, 9.56. Found: C, 69.57; H, 9.55.

To a solution of the above β-alcohol (495 mg, 1.51 mmol) in DMF (1.51 mL) were added imidazole (165 mg, 2.42 mmol) and TBSCl (274 mg, 1.82 mmol) at r.t. After stirring for 10 hr at an ambient temperature, the reaction mixture was diluted with Et_2O, washed with H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 10 : 1) to generate TBS ether (664 mg, quantitaitive yield) as a colorless oil. $[\alpha]_D^{27}$ +27.4 (*c* 1.37, $CHCl_3$); IR (neat) cm^{-1}: 2952, 1470, 1378, 1254; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.64 (1H, d, *J* = 5.6 Hz), 3.72-3.64 (2H, m), 2.84 (1H, dq, *J* = 12.6, 4.3 Hz), 2.00-1.77 (6H, m), 1.65-1.60 (4H, m), 1.59-1.39 (6H, m), 1.35 (3H, s), 1.26 (1H, s), 1.22 (3H, s), 1.21 (3H, s), 0.88 (9H, s), 0.03 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 129.8, 128.0, 77.2, 77.2, 76.1, 75.0, 73.4, 65.3, 50.9, 42.1, 37.9, 37.3, 30.6, 30.5, 30.3, 27.7, 25.9, 25.5, 23.6, 22.8, 20.8, 18.2, 16.9, -4.7, -4.7; ESIMS *m/z*: 309 (100), 441 (10); HRESIMS *m/z*: 441.2961 (Calcd for $C_{25}H_{45}ClO_2Si$: M^++H, 441.2956); *Anal.*: Calcd for $C_{25}H_{45}ClO_2Si$: C, 68.06; H, 10.28. Found: C, 67.84; H, 10.21.

To a cold (0 °C) solution of the above TBS ether (155 mg, 351 μmol) in $CHCl_3$ (3.51 mL) were added Na_2HPO_4 (125 mg, 878 μmol) and *m*CPBA (72.7 mg, 421 μmol). After stirring for 1 hr at the same temperature, the reaction mixture was diluted with Et_2O, added with Me_2S and stirred for 10 min. The mixture was washed with 1 M NaOH aqueous solution, H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 20 : 1) to generate epoxide **12** (150 mg, 99% yield) as a colorless oil. $[\alpha]_D^{25}$ +8.00 (*c* 1.11, $CHCl_3$); IR (neat) cm^{-1}: 2952, 1462, 1380, 1254; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.74 (1H, d, *J* = 2.3 Hz), 3.69 (1H, dd, *J* = 12.1, 4.3 Hz), 3.56-3.52 (1H, m), 2.10-1.97 (5H, m), 1.81-1.80 (2H, m), 1.64-1.61 (2H, m), 1.53-1.41 (5H, m), 1.32-1.22 (1H, m), 1.32 (3H, s), 1.26 (3H, s), 1.24 (3H, s), 1.22 (3H, s), 0.84 (9H, s), -0.01 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 76.4, 75.5, 72.7, 64.7, 63.6, 58.4, 46.5, 38.5, 38.0, 34.9, 30.8, 29.6, 27.8, 27.6, 25.8, 25.8, 25.8, 25.1, 22.6, 18.9, 18.0, 14.8, -4.7, -4.8; ESIMS *m/z*: 457 (100); HRESIMS *m/z*: 457.2904 (Calcd for $C_{25}H_{45}ClO_3Si$: M^++H, 457.2905); *Anal.*: Calcd for $C_{25}H_{45}ClO_3Si$: C, 65.68; H, 9.92. Found: C, 65.78; H, 9.78.

(4*S*,4a*R*,5*R*,6*R*,8a*R*)-5-Azido-4-((2*R*,5*S*)-5-chloro-2,6,6-trimethyltetrahydro-2*H*-pyran-2-yl)-6-hydroxy-6-methyloctahydronaphthalen-1(2*H*)-one (13) and (4*S*,4a*R*,5*R*,6*R*,8a*S*)-5-azido-4-((2*R*,5*S*)-5-chloro-2,6,6-trimethyltetrahydro-2*H*-pyran-2-yl)-6-hydroxy-6-methyloctahydronaphthalen-1(2*H*)-one (14). TBAF (1.0 M in THF, 15.6 mL, 15.6 mmol) was added to TBS ether **12** (712 mg, 1.56 mmol). The mixture stirred at 50 °C for 6 hr. The reaction mixture was diluted with Et_2O, washed with H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 1 : 1) to generate alcohol (497 mg, 93% yield) as a colorless oil. $[\alpha]_D^{26}$ +19.9 (*c* 1.20, $CHCl_3$); IR (neat) cm^{-1}: 3418, 2952, 1457; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.74 (1H, d, *J* = 2.8 Hz), 3.68 (1H, dd, *J* = 12.1, 4.3 Hz), 3.59 (1H, m), 2.18-2.16 (1H, m), 2.13-1.95 (3H, m), 1.86-1.82 (3H, m), 1.68-1.61 (3H, m), 1.56-1.36 (4H, m), 1.32 (3H, s), 1.32-1.26 (1H, m), 1.23 (3H, s), 1.21

(3H, s), 0.88 (1H, dq, *J* = 14.4, 4.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 76.3, 75.5, 72.1, 64.7, 63.6, 58.5, 46.3, 38.4, 37.9, 34.4, 30.8, 28.6, 27.5, 27.5, 25.6, 25.0, 22.5, 18.9, 14.6; ESIMS *m/z*: 343 (100); HRESIMS *m/z*: 343.2023 (Calcd for $C_{19}H_{31}ClO_3$: M^++H, 343.2016); *Anal.*: Calcd for $C_{19}H_{31}ClO_3$: C, 66.65; H, 9.11. Found: C, 66.55; H, 9.20.

To a solution of IBX (1.01 g, 3.62 mmol) in DMSO (7.25 mL) was added a solution of the above alcohol (497 mg, 1.45 mmol) in THF (7.25 mL) at r.t. After stirring for 20 min at an ambient temperature, the reaction mixture was diluted with Et_2O and filtered through celite pad. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 4 : 1) to generate ketone (467 mg, 95% yield) as colorless rod-like crystals. mp: 164-168 °C; $[\alpha]_D^{27}$ -88.2 (*c* 0.76, $CHCl_3$); IR (KBr) cm^{-1}: 2927, 1712; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.74 (1H, dd, *J* = 12.1, 4.3 Hz), 2.82 (1H, s), 2.57-2.52 (1H, m), 2.48-2.41 (1H, m), 2.22-2.02 (3H, m), 2.00-1.93 (1H, m), 1.92-1.72 (5H, m), 1.67-1.54 (3H, m), 1.40-1.31 (7H, m), 1.26 (3H, s), 1.23 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 213.8, 76.2, 75.6, 66.0, 64.8, 58.3, 51.2, 42.5, 39.0, 36.2, 35.6, 30.4, 27.2, 25.5, 23.6, 22.6, 22.3, 21.6, 19.1; ESIMS *m/z*: 341 (100); HRESIMS *m/z*: 341.1889 (Calcd for $C_{19}H_{29}ClO_3$: M^++H, 341.1883); *Anal.*: Calcd for $C_{19}H_{29}ClO_3$: C, 66.94; H, 8.57. Found: C, 66.98; H, 8.53.

To a solution of the above ketone (733 mg, 2.15 mmol) in MeOH/H_2O (8 : 1, 21.5 mL) were added NH_4Cl (1.04 g, 19.4 mmol) and NaN_3 (2.10 g, 32.3 mmol). The mixture was refluxed for 10 hr. The reaction mixture was filtered through silica gel pad. Removal of the solvent gave a residue, which was purified by silica gel column chromatography ($CHCl_3$: hexane : Et_2O = 4 : 1 : 1) to generate *trans*-decalin **13** (523 mg, 63% yield) as a pale yellow oil and *cis*-decalin **14** (261 mg, 32% yield) as a pale yellow oil. *trans*-decalin **13**: $[\alpha]_D^{25}$ +11.83 (*c* 1.07, $CHCl_3$); IR (neat) cm^{-1}: 3447, 2958, 2107, 1704; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 4.11 (1H, s), 3.74 (1H, dd, *J* = 12.4, 4.3 Hz), 2.49-2.25 (4H, m), 2.17-2.00 (3H, m), 1.90-1.77 (2H, m), 1.73-1.48 (6H, m), 1.37 (3H, s), 1.34 (3H, s), 1.33 (3H, s), 1.28 (3H, s), 0.88 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 212.7, 121.2, 77.6, 76.2, 72.9, 71.0, 64.5, 47.3, 44.9, 42.4, 39.1, 37.5, 32.9, 31.0, 29.7, 27.4, 25.7, 22.9, 21.0; ESIMS *m/z*: 384 (100); HRESIMS *m/z*: 384.2054 (Calcd for $C_{19}H_{30}ClN_3O_3$: M^++H, 384.2054); *Anal.*: Calcd for $C_{19}H_{30}ClN_3O_3$: C, 59.44 ; H, 7.88 ; N, 10.95. Found: C, 59.42 ; H, 7.81 ; N, 10.83. *cis*-decalin **14**: $[\alpha]_D^{25}$ -92.2 (*c* 1.75, $CHCl_3$); IR (neat) cm^{-1}: 3444, 2952, 2106, 1703; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 4.10 (1H, s), 3.73 (1H, dd, *J* = 12.4, 4.3 Hz), 2.49-2.24 (4H, m), 2.18-2.00 (3H, m), 1.90-1.84 (1H, m), 1.72-1.49 (7H, m), 1.37 (3H, s), 1.34 (3H, s), 1.32 (3H, s), 1.27 (3H, s), 0.97 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 212.8, 77.6, 76.2, 72.9, 71.0, 64.5, 47.2, 44.9, 42.3, 39.1, 37.4, 32.9, 31.0, 29.0, 27.4, 25.7, 22.9, 21.4, 21.0; ESIMS *m/z*: 384 (100); HRESIMS *m/z*: 384.2069 (Calcd for $C_{19}H_{30}ClN_3O_3$: M^++H, 384.2054); *Anal.*: Calcd for $C_{19}H_{30}ClN_3O_3$: C, 59.44 ; H, 7.88 ; N, 10.95. Found: C, 59.52; H, 7.91; N, 10.77.

To a solution of *cis*-decalin **14** (18.7 mg, 48.7 μmol) in EtOH (974 μL) was added ^{t}BuOK (5.5 mg, 48.7 μmol). After stirring for 2 hr at an ambient temperature, the reaction mixture was diluted with Et_2O, washed with H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography ($CHCl_3$: hexane : Et_2O = 4 : 1 :

1) to generate *trans*-decalin **13** (11.0 mg, 59% yield) as a pale yellow oil and *cis*-decalin **14** (7.4 mg, 40% yield) as a pale yellow oil.

(1*R*,2*R*,4a*S*,8*S*,8a*S*)-1-Azido-8-((2*R*,5*S*)-5-chloro-2,6,6-trimethyltetrahydro-2*H*-pyran-2-yl)-2-methyl-5-methylenedecahydronaphthalen-2-ol (15). To a cold (-78 °C) solution of *trans*-decalin **13** (46.0 mg, 120 μmol) and 2-(methylsulfonyl)benzothiazole (102 mg, 480 μmol) in THF (1.20 mL) was added LiHMDS (218 μL, 240 μmol, 1.1 M in THF). After stirring for 3 hr at same temperature, the reaction mixture was diluted with Et_2O, washed with sat. NH_4Cl aqueous solution, H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 10 : 1) to generate *exo*-olefine **15** (40.3 mg, 88% yield) as colorless rod-like crystals. mp: 117-120 °C; $[\alpha]_D^{25}$ -13.6 (*c* 0.98, $CHCl_3$); IR (KBr) cm^{-1}: 3551, 2935, 2102, 1648, 896; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 4.64 (1H, d, *J* = 1.5 Hz), 4.53 (1H, s), 4.47 (1H, s), 3.77 (1H, dd, *J* = 12.4, 4.5 Hz), 2.25 (1H, dt, *J* = 12.6, 3.6 Hz), 2.15-1.75 (8H, m), 1.70-1.47 (6H, m), 1.38 (6H, s), 1.33 (3H, s), 1.22 (3H, s), 0.91 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 152.1, 104.3, 78.2, 76.2, 73.0, 69.0, 64.8, 48.6, 43.7, 38.4, 37.5, 35.7, 33.0, 31.5, 29.4, 29.1, 27.7, 24.7, 23.2, 19.7; ESIMS *m/z*: 339 (100), 382(5); HRESIMS *m/z*: 339.2086 (Calcd for $C_{20}H_{32}ClN_3O_2$: M^+-N_3, 339.2091); *Anal*.: Calcd for $C_{20}H_{32}ClN_3O_2$: C, 62.89; H, 8.44; N, 11.00. Found: C, 62.62; H, 8.41; N, 10.79.

(1'*S*,4'*S*,4a'*S*,5'*R*,6'*R*,8a'*S*)-5'-Azido-4'-((2*R*,5*S*)-5-chloro-2,6,6-trimethyltetrahydro-2*H*-pyran-2-yl)-6'-methyl-1-tosyloctahydro-2'*H*-spiro[aziridine-2,1'-naphthalen]-6'-ol (16). To a solution of *exo*-olefine **15** (24.0 mg, 62.8 μmol) and 4A MS (1.1 mg) in CH_3CN (3.14 mL) were added $Cu(OTf)_2$ (1.1 mg, 3.14 μmol) and PhI=NTs (47.0 mg, 126 μmol). After stirring for 3 hr at ambient temperature, the reaction mixture was diluted with Et_2O and then filtered through celite pad. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (hexane : AcOEt = 3 : 1) to generate aziridine **16** (15.9 mg, 46% yield) as colorless rod-like crystals. mp: 181-187 °C; $[\alpha]_D^{25}$ -29.2 (*c* 0.15, $CHCl_3$); IR (KBr) cm^{-1}: 3501, 2955, 2103, 1383; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.79 (2H, d, *J* = 8.1 Hz), 7.30 (2H, d, *J* = 8.1 Hz), 4.47 (1H, s), 3.77 (1H, dd, *J* = 12.1, 4.8 Hz), 2.47 (1H, s), 2.43 (3H, s), 2.35 (1H, d, *J* = 1.5 Hz), 2.23-2.18 (1H, m), 2.13-2.02 (5H, m), 1.95-1.91 (1H, m), 1.81-1.78 (1H, m), 1.69-1.49 (5H, m), 1.39 (3H, s), 1.37 (3H, s), 1.30 (3H, s), 1.25 (3H, s), 1.03-0.88 (3H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 143.6, 138.2, 129.4, 127.2, 78.0, 76.3, 72.8, 68.8, 64.5, 55.0, 47.9, 41.5, 38.3, 36.8, 36.1, 32.6, 31.5, 30.3, 29.2, 27.6, 26.9, 23.3, 21.6, 20.9, 19.8; ESIMS *m/z*: 551 (100); HRESIMS *m/z*: 551.2463 (Calcd for $C_{27}H_{39}ClN_4O_4S$: M^++H, 551.2459); *Anal*.: Calcd for $C_{27}H_{39}ClN_4O_4S$: C, 58.84; H, 7.13; N, 10.17. Found: C, 59.13; H, 7.17; N, 9.89.

***N*-((1*S*,4*S*,4a*S*,5*R*,6*R*,8a*S*)-5-Amino-4-((2*R*,5*S*)-5-chloro-2,6,6-trimethyltetrahydro-2*H*-pyran-2-yl)-6-hydroxy-1,6-dimethyldecahydronaphthalen-1-yl)-4-methylbenzenesulfonamide (17).**

To a cold (0 °C) solution of aziridine **16** (22.0 mg, 39.9 μmol) in MeOH/THF (3 : 1, 798 μL) were added $NiCl_2 \cdot 6H_2O$ (15.2 mg, 63.8 mmol) and $NaBH_4$ (6.8 mg, 180 μmol). After stirring for 10 min at the same temperature, the mixture stirred at r.t. for 3 hr. The reaction mixture was diluted with AcOEt, and then filtered through celite pad. The filtrate was washed with brine and phosphate buffer (pH 7.5, EDTA 10 mM), and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (AcOEt : MeOH = 10 : 1) to amine (17.6 mg, 84% yield) as colorless needles. mp: 198-201 °C; $[\alpha]_D^{25}$ -4.10 (*c* 0.95, $CHCl_3$); IR (KBr) cm^{-1}: 3377, 2926, 1383, 1157; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.79 (2H, d, *J* = 8.3 Hz), 7.29 (2H, d, *J* = 8.3 Hz), 3.73 (1H, dd, *J* = 12.1, 4.8 Hz), 3.24 (1H, s), 2.48 (1H, s), 2.42 (3H, s), 2.43-2.42 (1H, m), 2.26-2.21 (1H, dt, *J* = 13.2, 3.6 Hz), 2.14-1.89 (6H, m), 1.67-1.49 (6H, m), 1.36 (3H, s), 1.36-1.30 (2H, m), 1.30 (3H, s), 1.27 (3H, s), 1.27-1.22 (1H, m), 1.22 (3H, s), 1.10-0.95 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 143.6, 138.3, 129.4, 129.4, 127.2, 127.2, 77.5, 76.0, 72.4, 64.5, 57.6, 55.6, 49.1, 42.2, 38.6, 36.7, 36.5, 32.0, 31.3, 30.9, 29.6, 27.5, 27.0, 22.4, 21.6, 20.6, 18.9; ESIMS *m/z*: 525 (100); HRESIMS *m/z*: 525.2538 (Calcd for $C_{27}H_{41}ClN_2O_4S$: M^++H, 525.2554); *Anal.*: Calcd for $C_{27}H_{41}ClN_2O_4S$: C, 61.75; H, 7.87; N, 5.33. Found: C, 61.95; H, 8.07; N, 5.11.

To a cold (0 °C) solution of the above amine (16.5 mg, 31.4 μmol) in THF (628 μL) was added $LiBHEt_3$ (471 μL, 471 μmol, 1.0 M in THF). After stirring for 1.5 hr at 40 °C, the reaction mixture was cooled to 0 °C, added with H_2O, diluted with AcOEt, washed with brine, and then dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by silica gel column chromatography (AcOEt) to generate tosylamine **17** (13.7 mg, 83% yield) as a pale yellow oil. $[\alpha]_D^{25}$ -10.7 (*c* 0.15, $CHCl_3$); IR (neat) cm^{-1}: 3366, 2952, 1383, 1153; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.75 (2H, d, *J* = 8.4 Hz), 7.26 (2H, d, *J* = 8.3 Hz), 4.57 (1H, s), 3.68 (1H, dd, *J* = 12.1, 4.3 Hz), 3.20 (1H, d, *J* = 2.0 Hz), 2.41 (3H, s), 2.12-1.83 (4H, m), 1.62-1.34 (11H, m), 1.32 (4H, s), 1.27 (3H, s), 1.25 (3H, s), 1.17 (3H, s), 1.10 (3H, s), 0.88 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 142.8, 140.8, 129.4, 129.4, 127.0, 127.0, 77.5, 77.2, 75.9, 72.3, 64.5, 60.2, 57.7, 48.9, 41.5, 39.3, 38.6, 38.4, 32.5, 30.8, 29.6, 23.2, 22.4, 21.5, 21.4, 19.6, 18.9; ESIMS *m/z*: 527 (100); HRESIMS *m/z*: 527.2679 (Calcd for $C_{27}H_{43}ClN_2O_4S$: M^++H, 527.2710).

Kalihinol A (1). To a solution of naphthalene (10.3 mg, 80.6 μmol) in THF (3.06 mL) was added Li (11.1 mg, 161 mmol). The mixture was ultrasonicated till a color of the mixture turned into dark green and cooled to -78 °C. A solution of tosylamine **17** (42.5 mg, 80.6 μmmol) in THF (5.0 mL) was added to the mixture. The mixture was warmed to r.t., stirred for 1 hr and then added with H_2O. The mixture was filtered through celite pad. The filtrare was concentrated under reduced presser to give crude diamine, which was used the next reaction without further purification.

To a solution of the above crude diamine in CH_2Cl_2 (8.06 mL) was added acetic formic anhydride (5.0 mL). After stirring for 4 hr at r.t., the mixture was filtered through silica gel pad. The filtrare was concentrated under reduced presser to give crude formamide, which was used the next reaction without further purification.

To a solution of the above crude formamide in CH_2Cl_2 (537 μL) were added pyridine (6.52 μL, 80.6 μmol) and TsCl (15.4 mg, 80.6 μmol). After stirring for 12 hr at r.t., the reaction mixture was concentrated under reduced presser. The residue was purified by silica gel column chromatography (AcOEt : MeOH = 3 : 1) to give kalihinol A (**1**) (23.4 mg, 74% yield, three steps) as rod-like crystals. mp : 232-235 °C; $[\alpha]_D^{25}$ +12.4 (*c* 0.64, $CHCl_3$); IR (KBr) cm^{-1}: 3410, 2943, 2145, 1456, 1385; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 4.52 (1H, brs), 3.74 (1H, dd, *J* = 11.9, 4.8 Hz), 2.08-1.98 (4H, m), 1.87-1.73 (4H, m), 1.70-1.46 (7H, m), 1.41 (3H, s), 1.34 (6H, s), 1.30 (3H, s), 1.16 (3H, s), 0.97 (1H, ddd, *J* = 14.2, 14.1, 3.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 157.2 (t, *J* = 5.6 Hz), 153.0 (t, *J* = 4.0 Hz), 76.8, 75.9, 70.4, 64.1, 63.8 (t. *J* = 5.6 Hz), 59.8 (t, *J* = 5.6 Hz), 48.4, 42.3, 39.7, 37.9, 35.9, 32.5, 30.5, 28.8, 27.3, 22.8, 21.9, 21.6, 20.7, 19.1; ESIMS *m/z*: 366 (100), 393 (30); HRESIMS *m/z*: 393.2314 (Calcd for $C_{22}H_{33}ClN_2O_2$: M^++H, 393.2309); *Anal.*: Calcd for $C_{22}H_{33}ClN_2O_2$: C, 67.24; H, 8.46; N, 7.13. Found: C, 67.01; H, 8.48; N, 6.83.

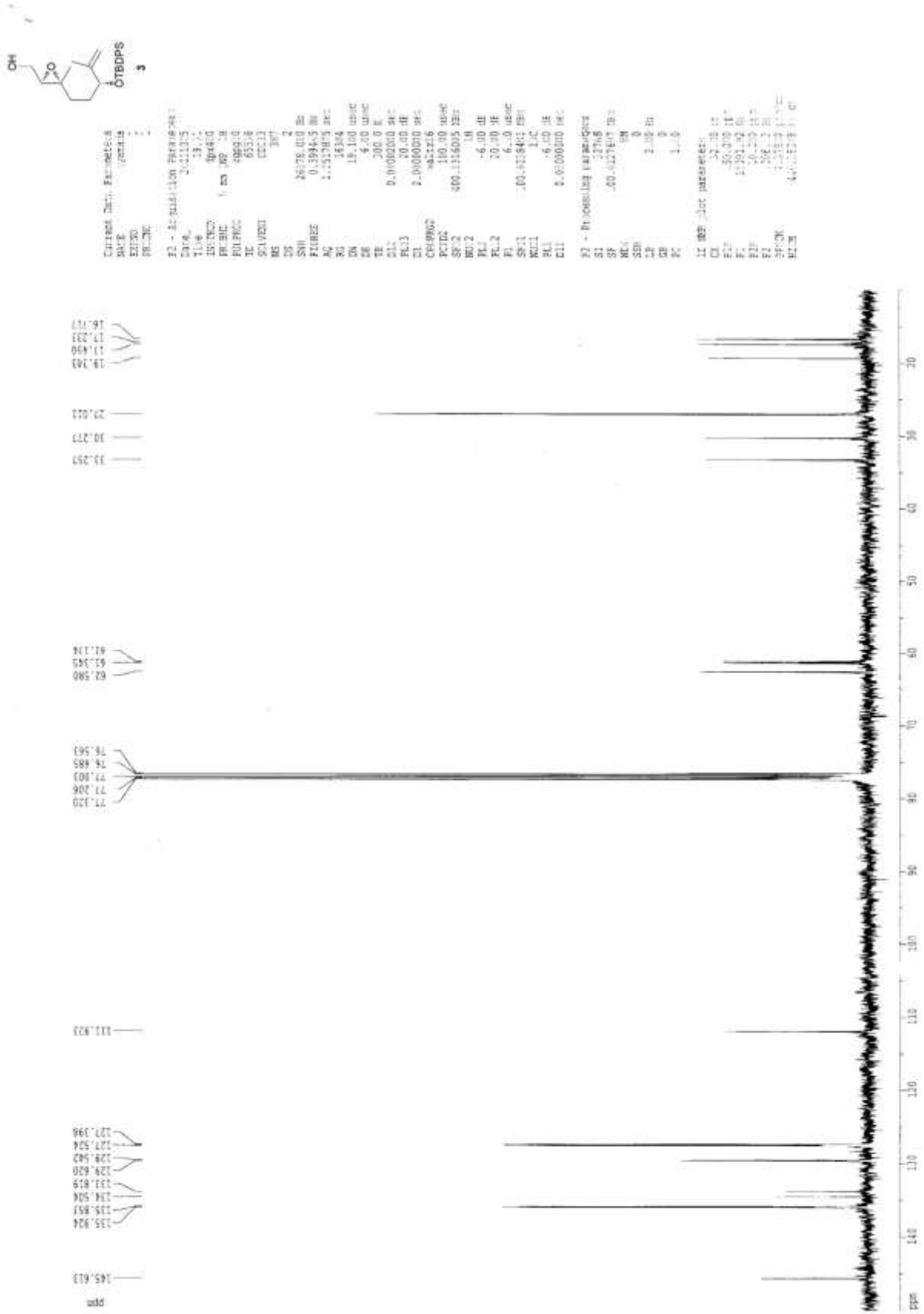
Ref.
mp : 233 °C; $[\alpha]_D$ +16 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) cm^{-1}: 3595, 3390, 2135, 2100, 1385, 1378, 1105; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 4.51 (1H, brs), 3.72 (1H, dd, *J* = 12, 5 Hz), 2.04-1.96 (3H, m), 1.72-1.44 (7H, m), 1.40 (3H, s), 1.33 (6H, s), 1.29 (3H, brt, *J* = 2 Hz), 1.24 (1H, m), 1.15 (3H, s), 0.98 (1H, ddd, *J* = 14, 14, 3 Hz); EILRMS *m/z*: 357 (4), 330 (7), 216 (9), 202 (8), 163 (71), 162 (18), 161 (94), 107 (58), 105 (22), 93 (34), 81 (41), 79 (25), 71 (36), 67 (53), 59 (45), 55 (40), 53 (31), 43 (58), 41 (100); EIHRMS *m/z*: 357.2561 (Calcd for $C_{22}H_{33}N_2O_2$: M^+-Cl, 357.2542), 330.2424 (Calcd for $C_{21}H_{32}NO_2$: M^+-Cl-HCN, 330.2433).

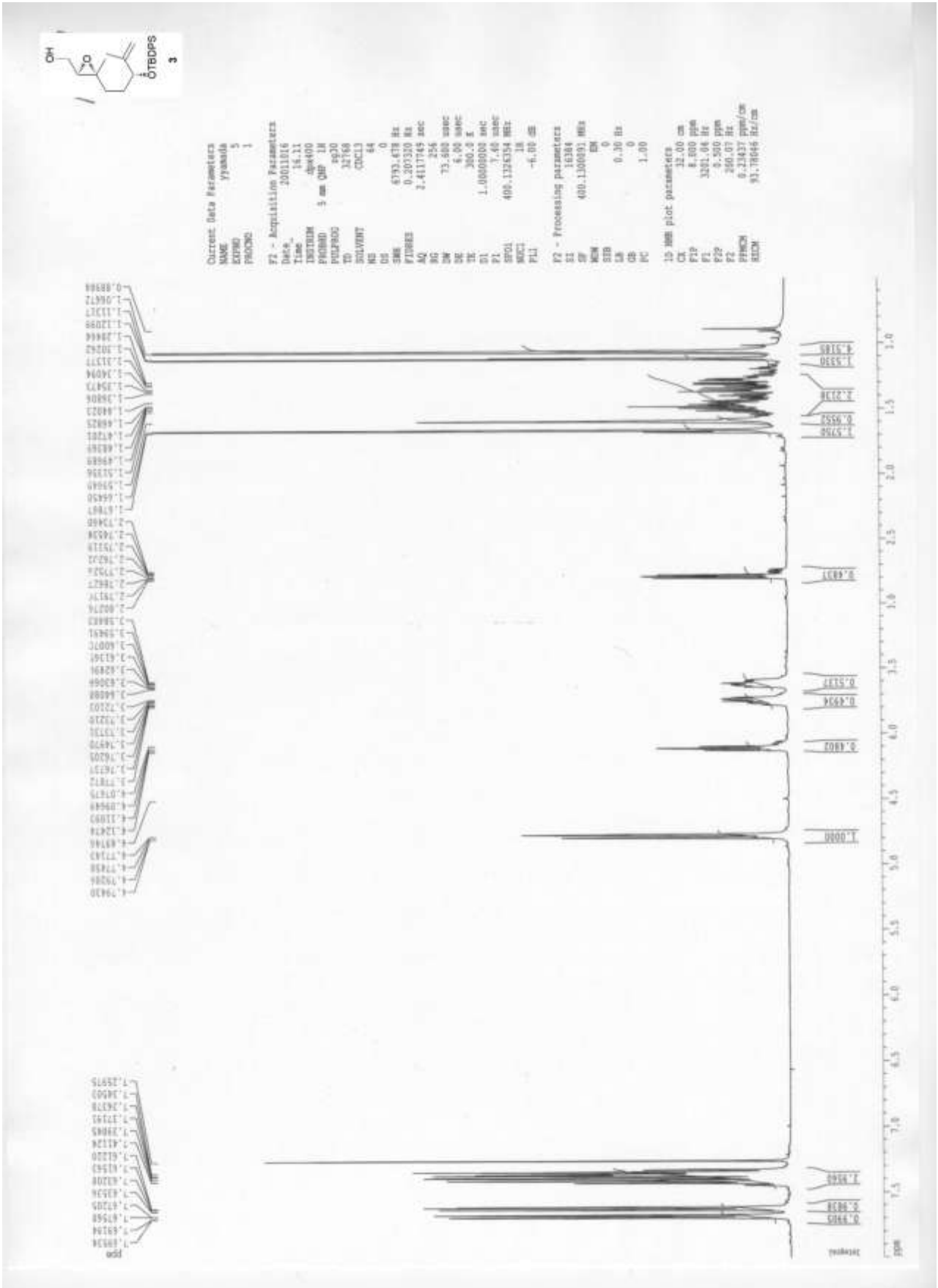
Crystal data and structure refinement for 11a.

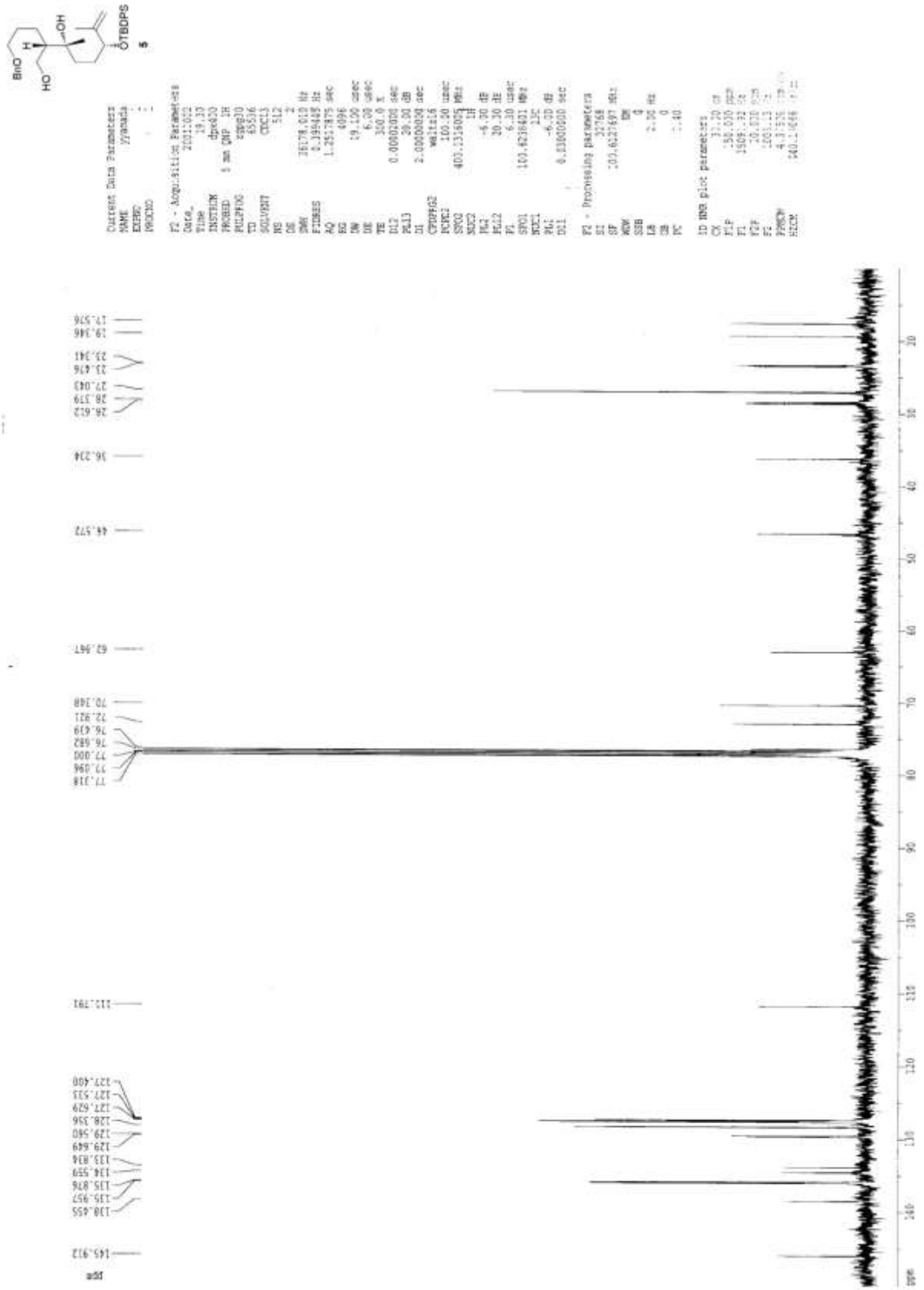
Identification code	compound 11a	
Empirical formula	C19 H29 Cl O3	
Formula weight	340.87	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.1306(15) Å	α= 90°.
	b = 18.463(5) Å	β= 90°.
	c = 31.983(8) Å	γ = 90°.
Volume	3620.1(16) $Å^3$	
Z	8	
Density (calculated)	1.251 Mg/m^3	
Absorption coefficient	0.224 mm^{-1}	
F(000)	1472	
Crystal size	0.18 x 0.10 x 0.06 mm^3	
Theta range for data collection	1.27 to 27.69°.	
Index ranges	-7<=h<=8, -23<=k<=24, -41<=l<=41	
Reflections collected	41645	
Independent reflections	8372 [R(int) = 0.0637]	
Completeness to theta = 27.69°	99.5 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9867 and 0.9608	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8372 / 0 / 423	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0373, wR2 = 0.0812	
R indices (all data)	R1 = 0.0495, wR2 = 0.0859	
Absolute structure parameter	-0.03(4)	
Largest diff. peak and hole	0.244 and -0.200 $e.Å^{-3}$	

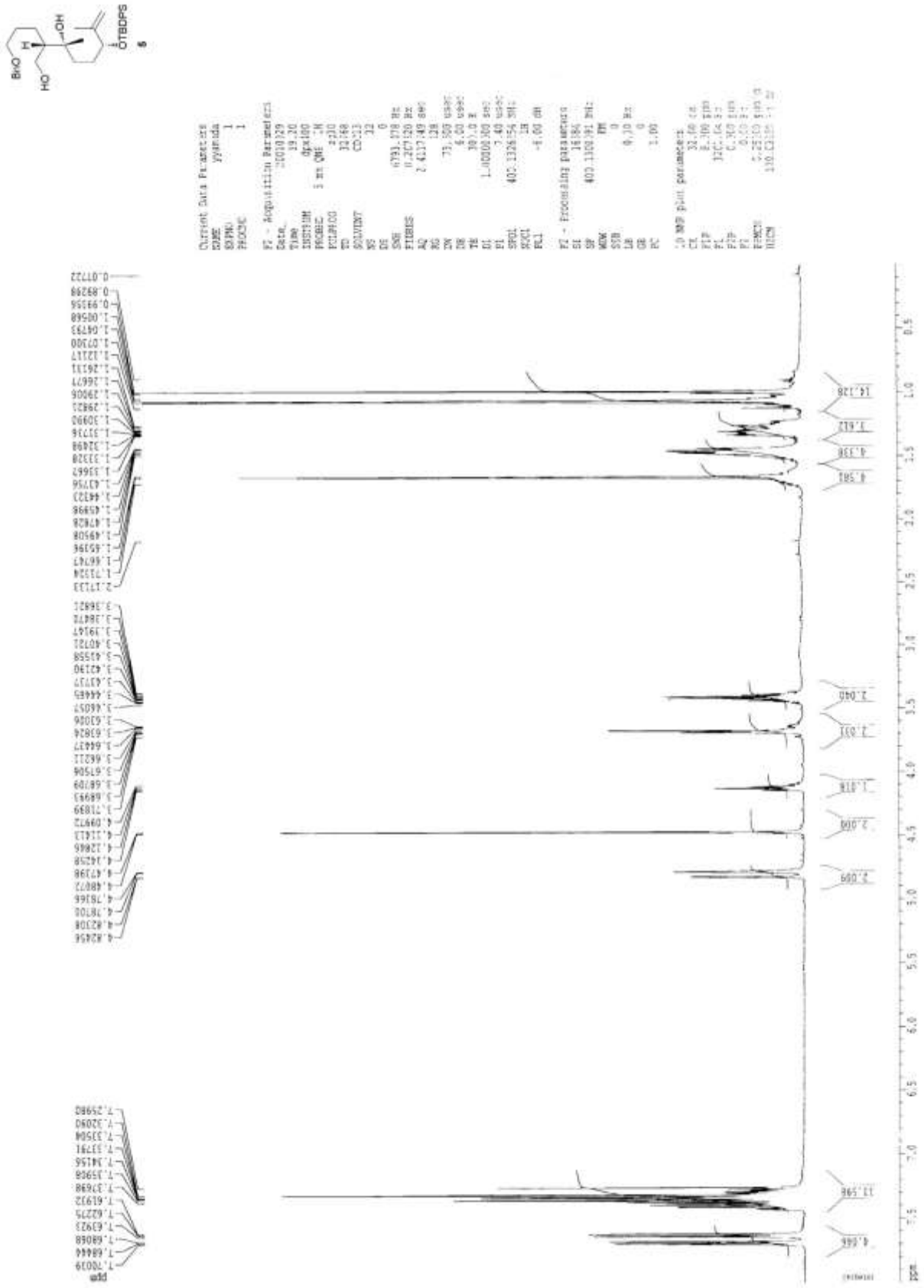
Crystal data and structure refinement for 16.

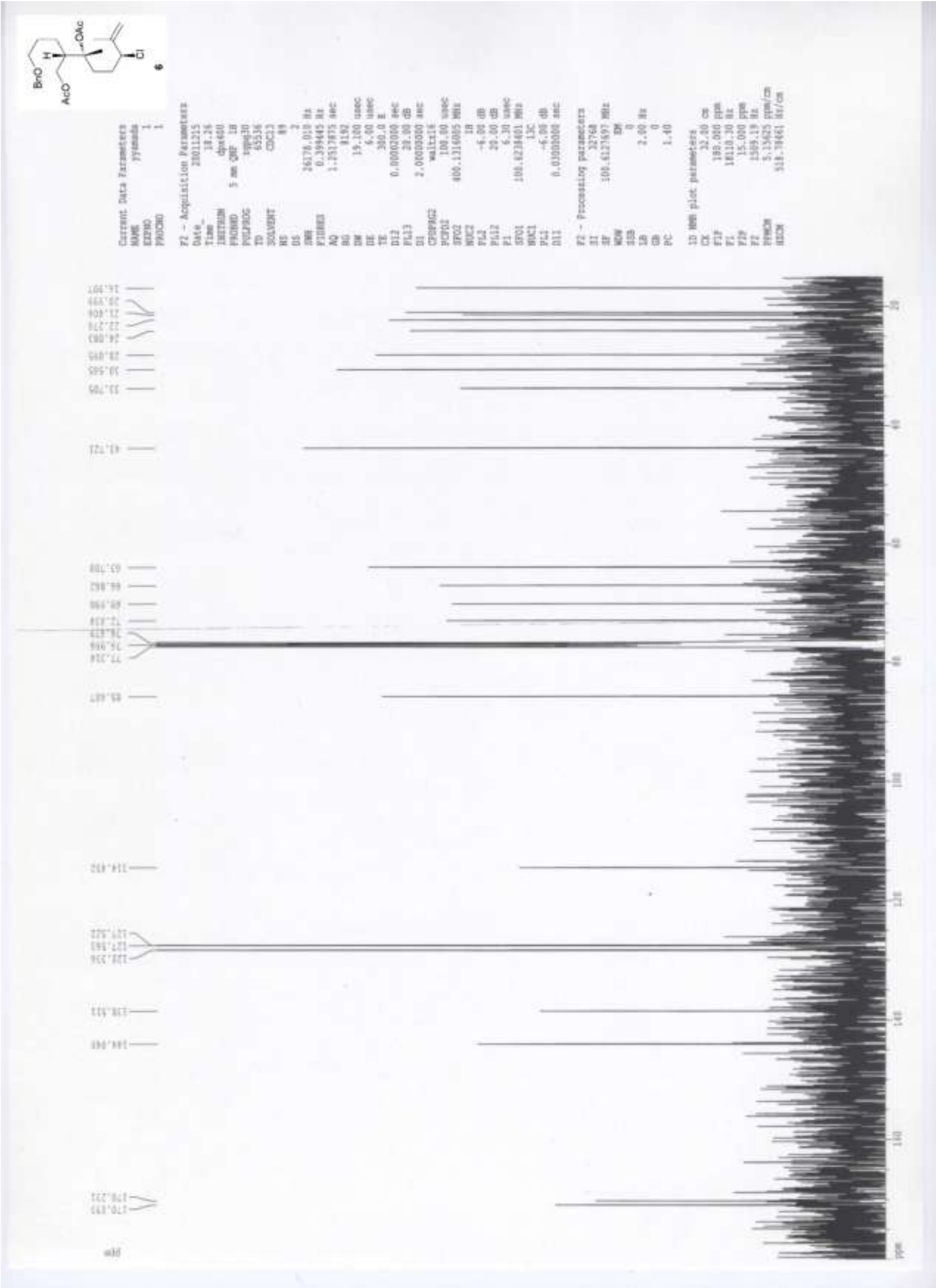
Identification code	compound 16	
Empirical formula	C27 H39 Cl N4 O4 S	
Formula weight	551.13	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 8.366(5) Å	α= 90°.
	b = 6.180(4) Å	β= 93.033(6)°.
	c = 26.368(15) Å	γ = 90°.
Volume	1361.4(13) $Å^3$	
Z	2	
Density (calculated)	1.344 Mg/m^3	
Absorption coefficient	0.258 mm^{-1}	
F(000)	588	
Crystal size	0.35 x 0.11 x 0.07 mm^3	
Theta range for data collection	1.55 to 27.66°.	
Index ranges	-10<=h<=10, -8<=k<=7, -34<=l<=34	
Reflections collected	13835	
Independent reflections	6037 [R(int) = 0.0692]	
Completeness to theta = 27.66°	97.2 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9822 and 0.9153	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6037 / 1 / 340	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1318	
R indices (all data)	R1 = 0.0599, wR2 = 0.1430	
Absolute structure parameter	0.03(6)	
Largest diff. peak and hole	0.498 and -0.626 e.$Å^{-3}$	

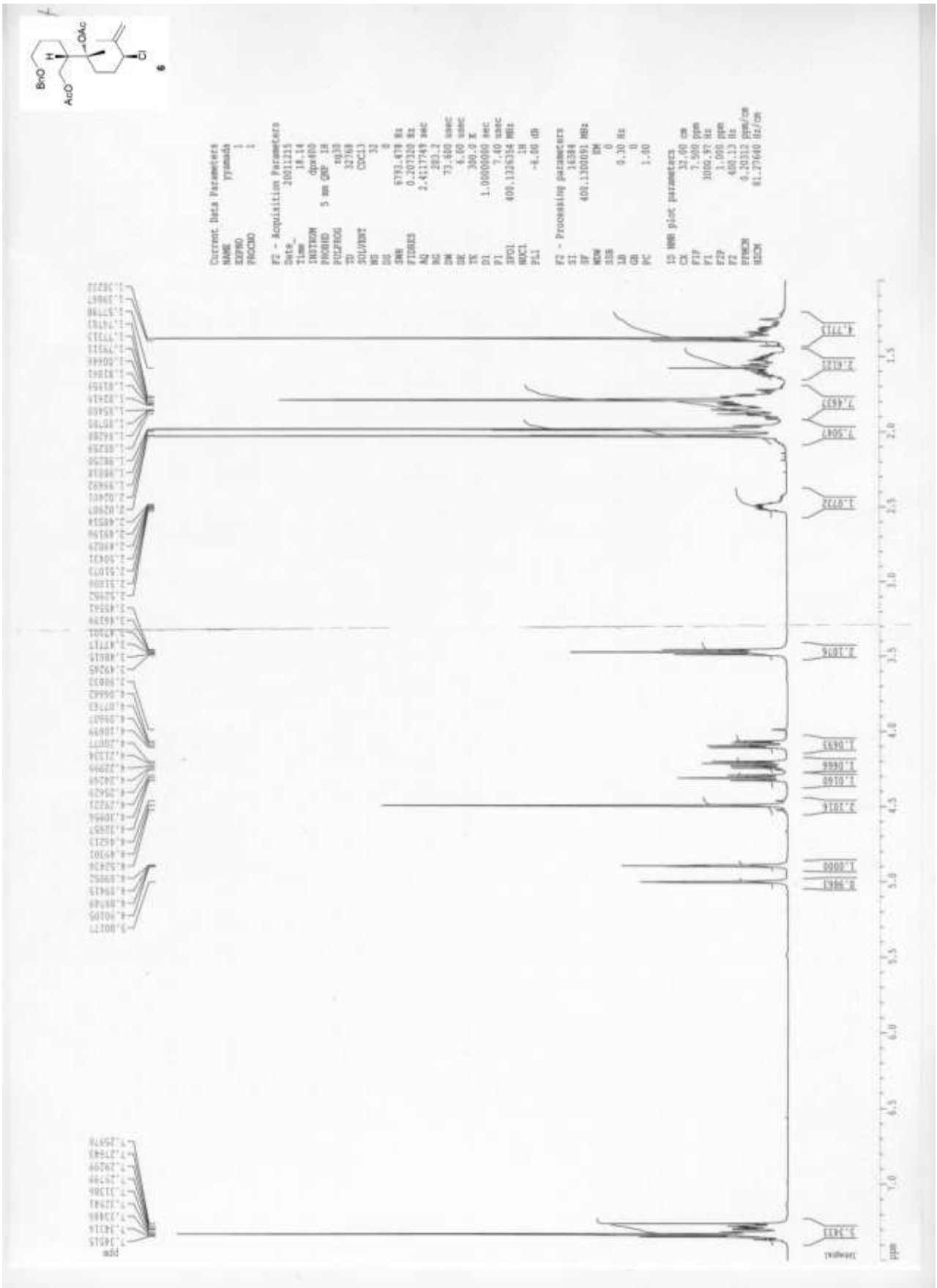

OH
OTBDPS
3

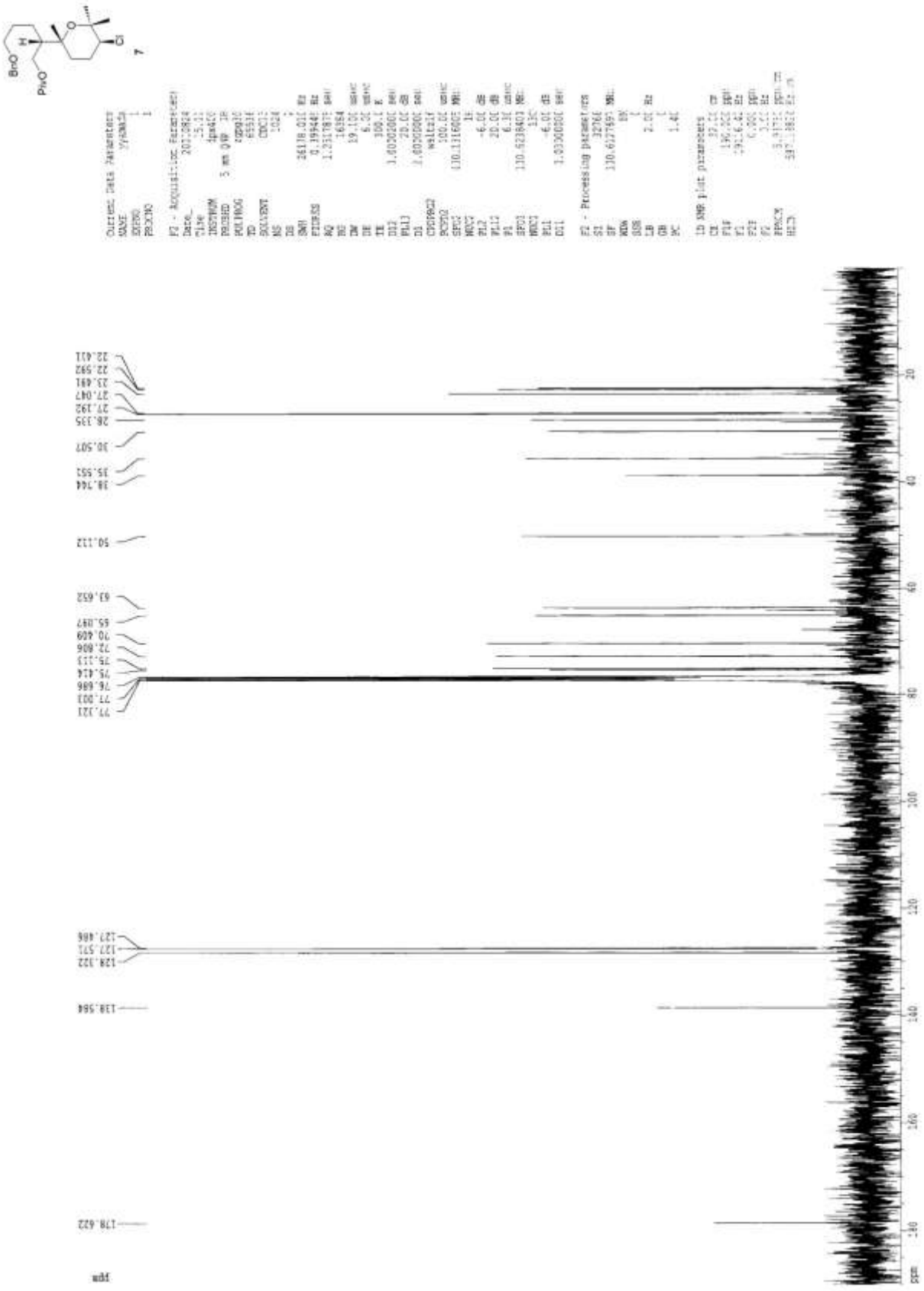

OH
O
OTBDPS
3

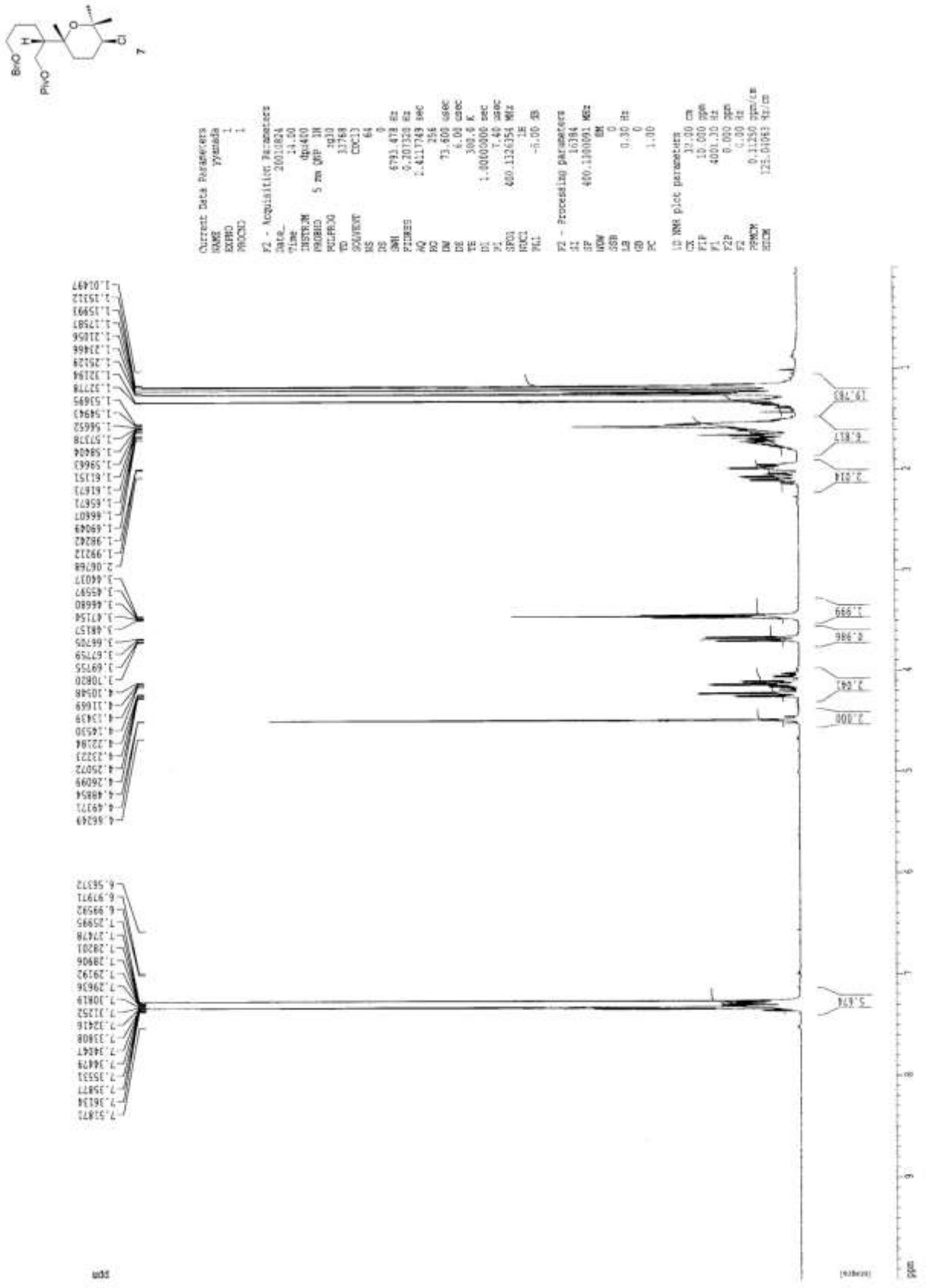

BnO
H
OH
HO
OTBDPS
5

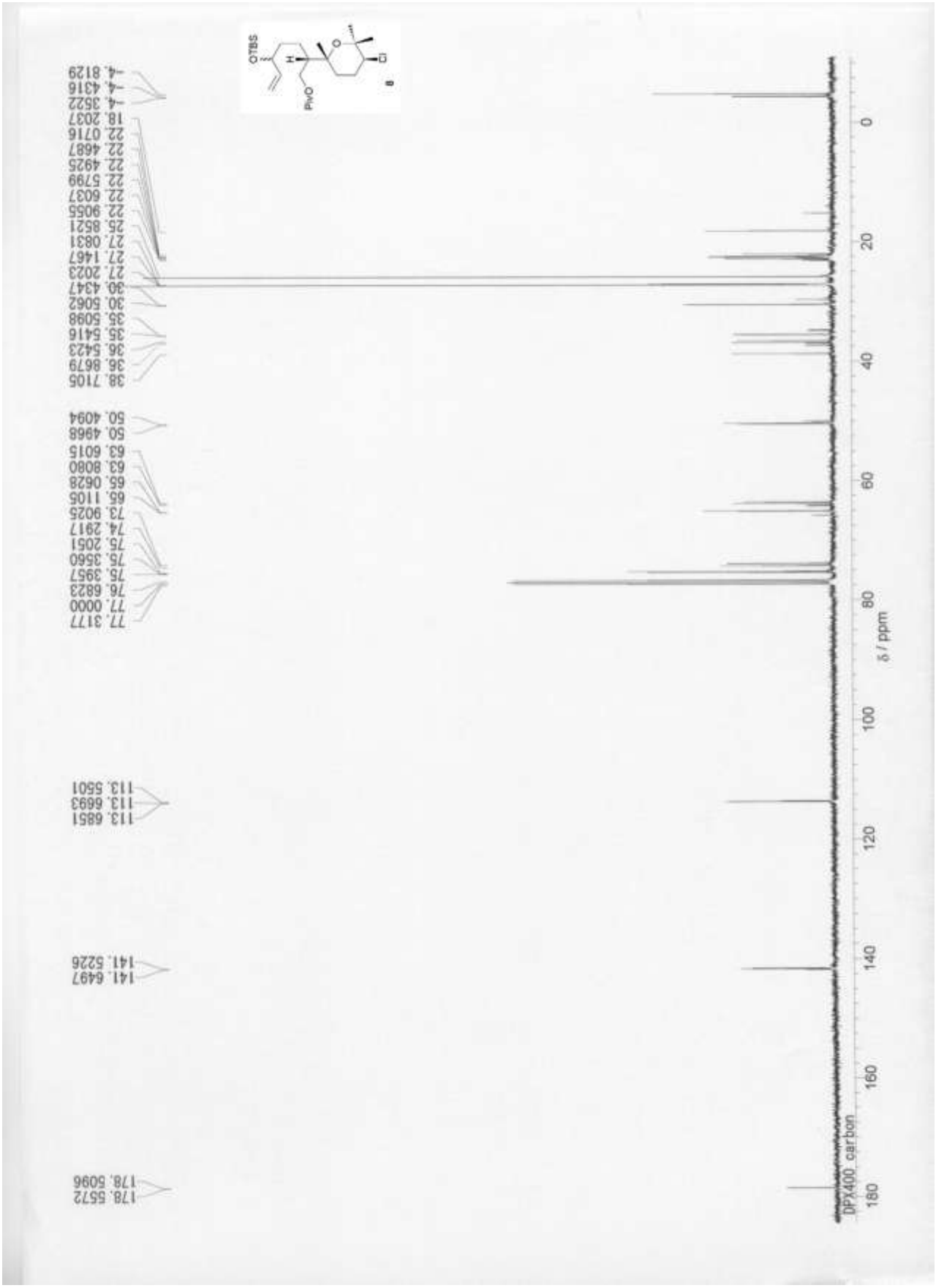

BnO
H
OH
HO
OTBDPS
5

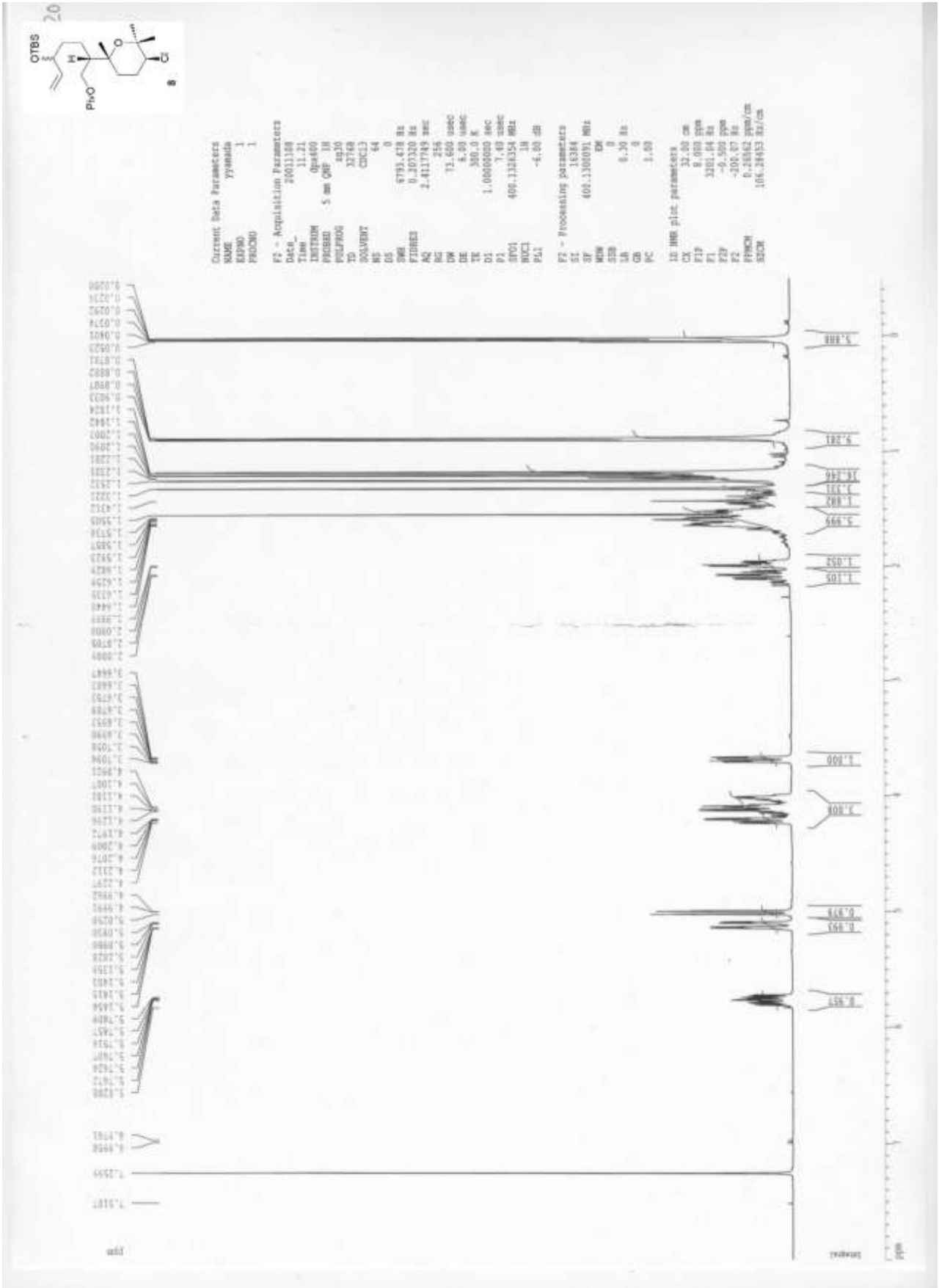


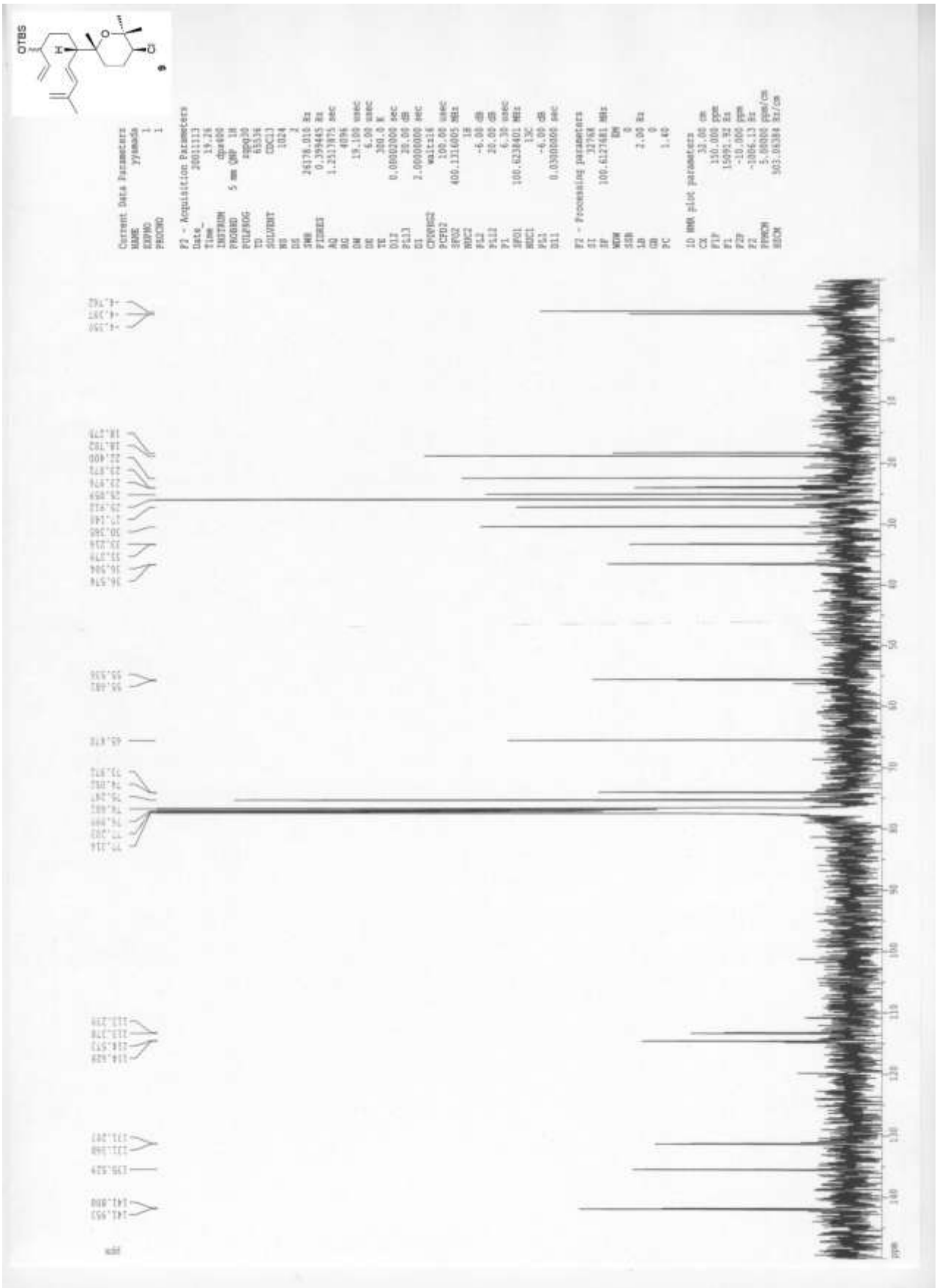

BnO
H
OAc
Cl
AcO
6
Current Data Parameters
NAME yamada
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20011215
Time 18.14
INSTRUM dpx400
PROBHD 5 mm GNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6793.479 Hz
FIDRES 0.207320 Hz
AQ 2.4117749 sec
RG 203.2
DW 73.600 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 7.40 usec
SFO1 400.1326354 MHz
NUC1 1H
PL1 -4.00 dB
F2 - Processing parameters
SI 16384
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 32.00 cm
F1P 7.500 ppm
F1 3000.97 Hz
F2P 1.000 ppm
F2 400.13 Hz
PPMCM 0.20312 ppm/cm
HZCM 81.27640 Hz/cm
8.7113
2.4121
3.4631
3.5067
1.0732
2.1076
1.0691
1.0666
1.0160
2.1014
1.2000
0.9861
3.2611
ppm

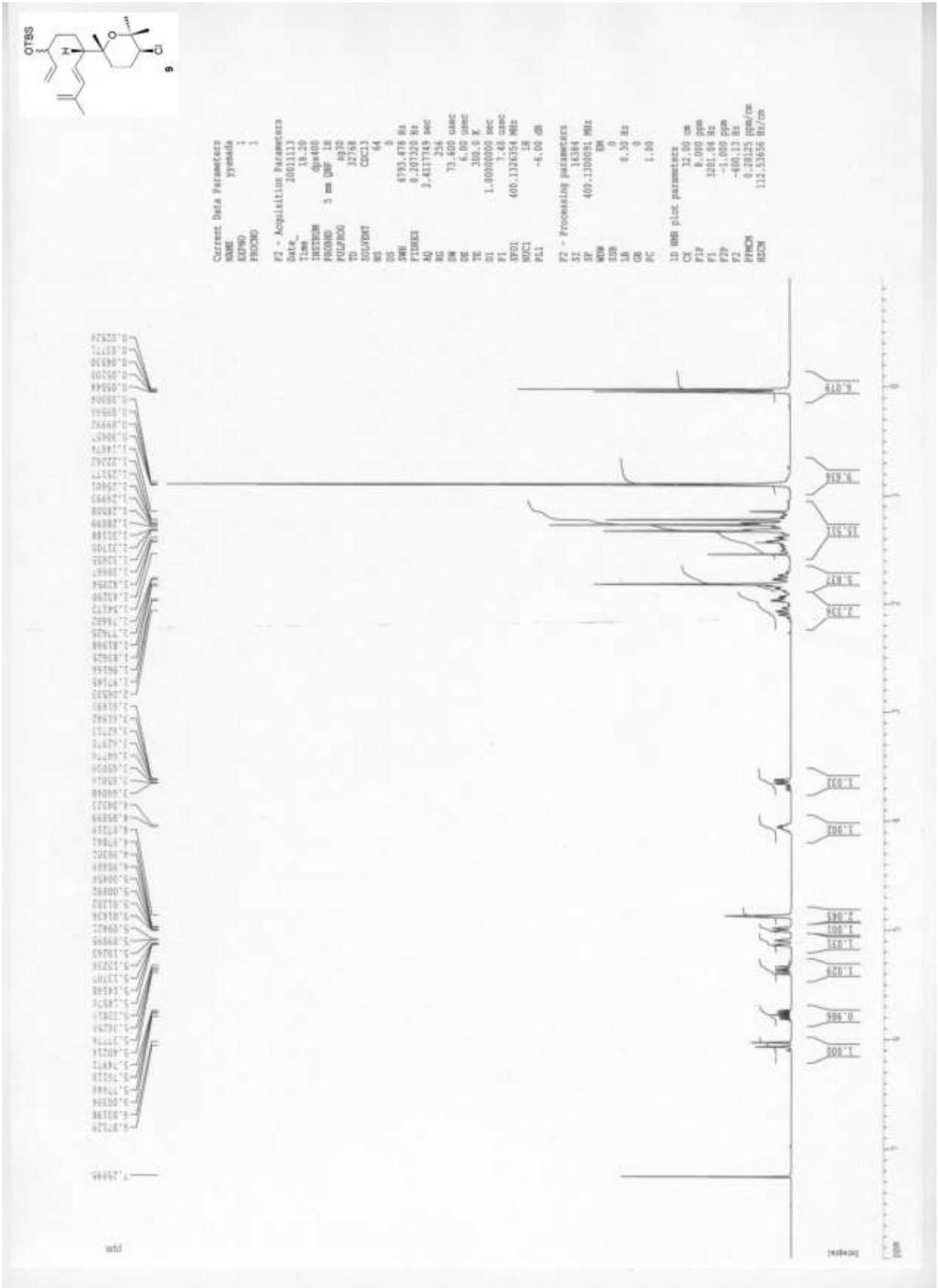

BnO
H
O
Cl
PivO
7
32.611
22.592
25.691
27.047
27.192
28.195
30.507
35.551
38.744
50.112
63.652
65.097
70.409
72.806
75.113
75.414
76.686
77.003
77.321
127.486
127.571
128.122
138.564
178.622
ppm

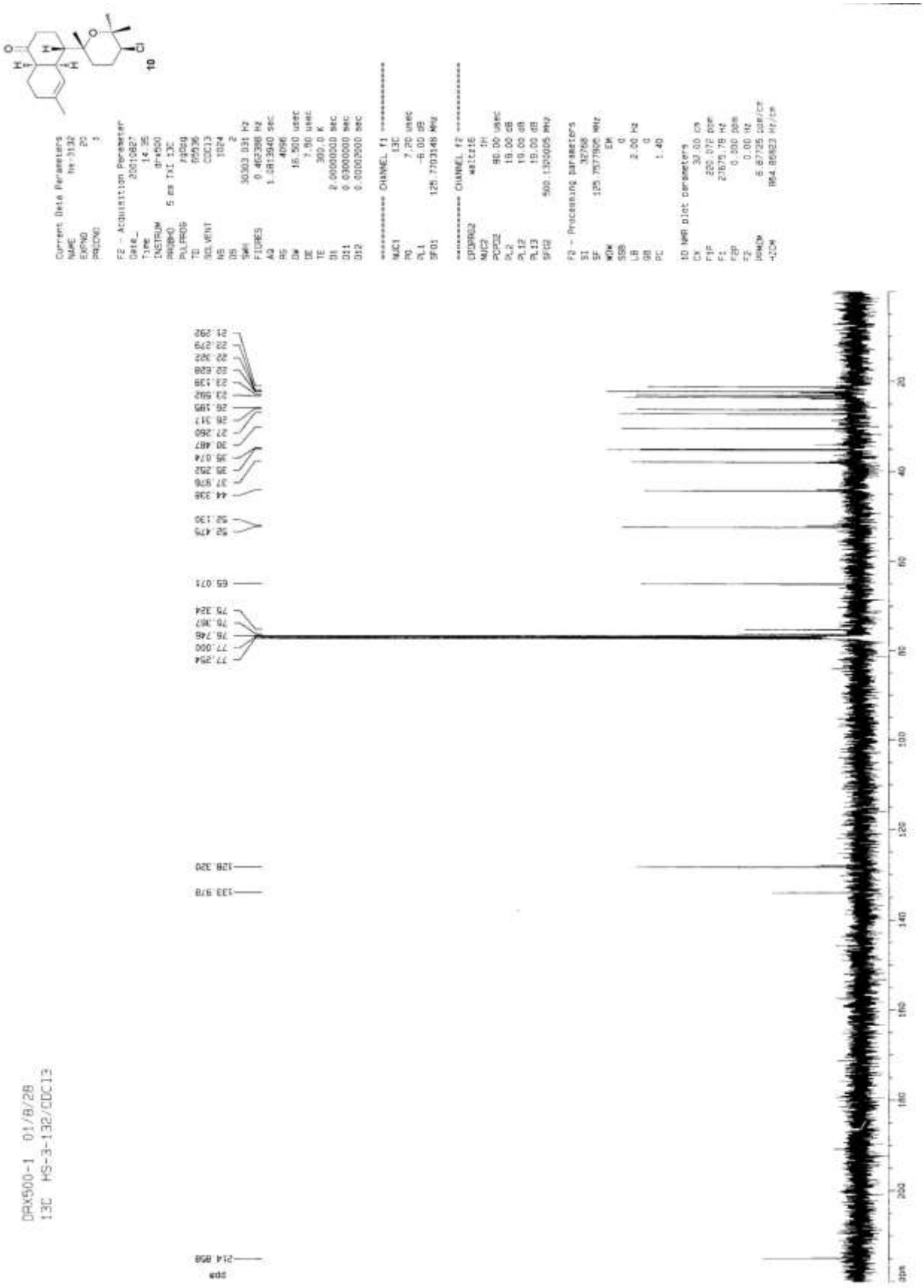


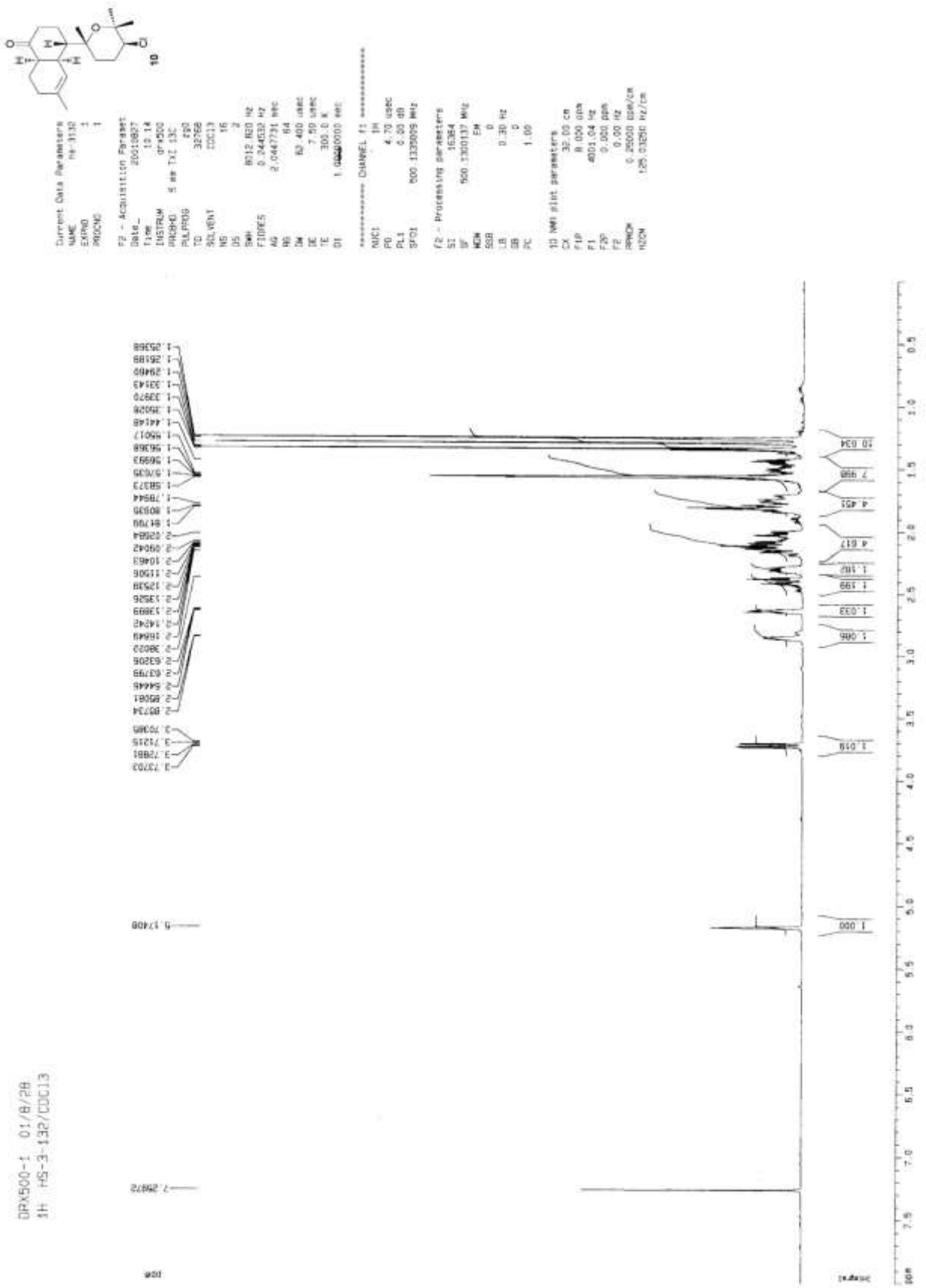

OTBS
H
O
Cl
PivO
8
-4.8129
-4.4316
-4.3522
18.2037
22.0716
22.4687
22.4925
22.5799
22.6037
22.9055
25.8521
27.0831
27.1467
27.2023
30.4347
30.5062
35.5098
35.5416
36.5423
36.8679
38.7105
50.4094
50.4968
63.6015
63.8080
65.0628
65.1105
73.9025
74.2917
75.2051
75.3560
75.3957
76.6823
77.0000
77.3177
113.5501
113.6693
113.6851
141.5226
141.6497
178.5096
178.5572
DPX400 carbon
δ / ppm
0
20
40
60
80
100
120
140
160
180

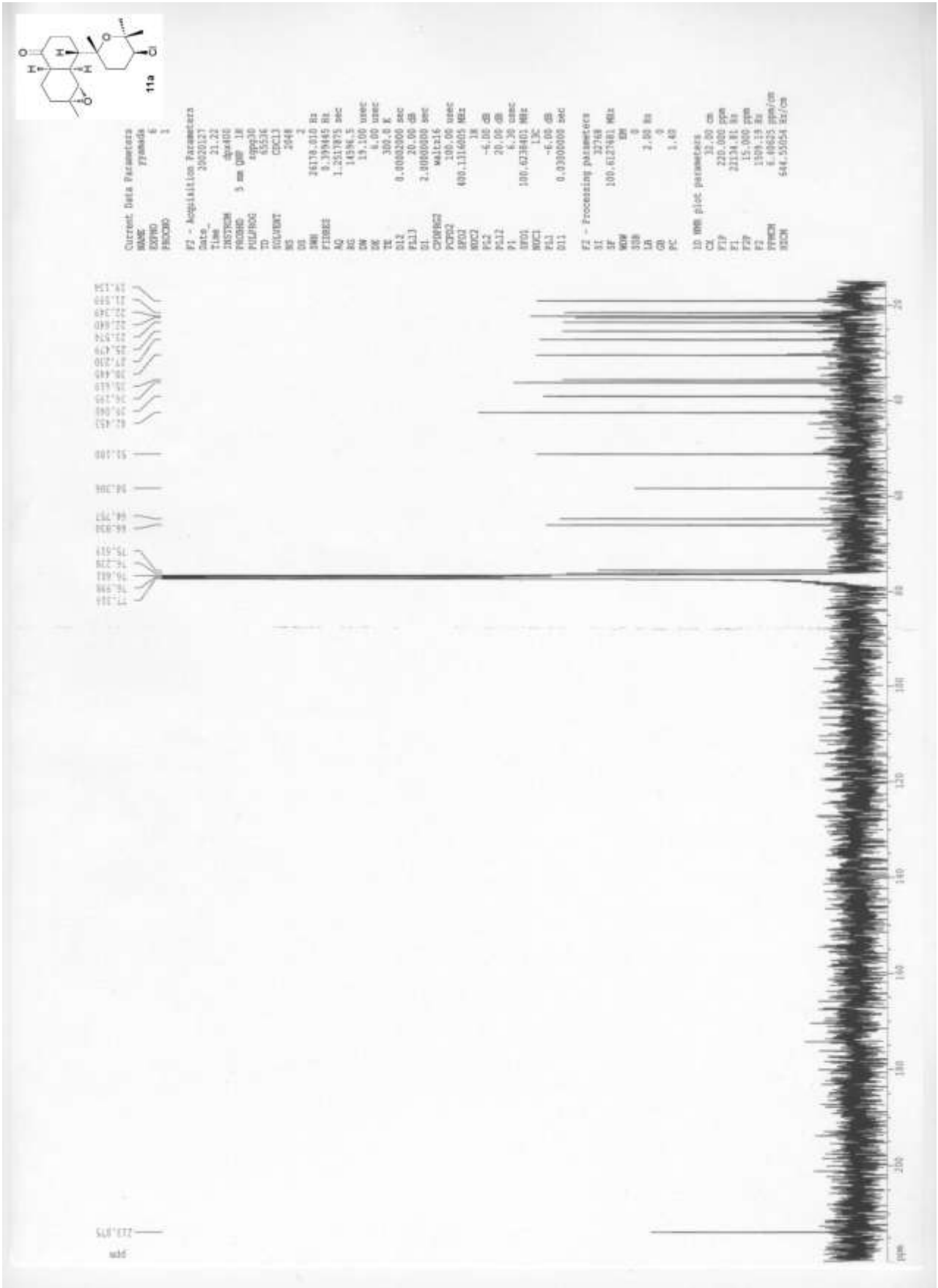

OTBS
H
O
O
PhO
8
Current Data Parameters
NAME yyamada
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20011108
Time 11.21
INSTRUM spa400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 6735.478 Hz
FIDRES 0.107320 Hz
AQ 2.4117749 sec
RG 256
DW 73.600 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 7.49 usec
SFO1 400.1324354 MHz
NUC1 1H
PL1 -6.00 dB
F2 - Processing parameters
SI 16384
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 32.00 cm
F1P 8.000 ppm
F1 3201.64 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.25562 ppm/cm
HZCM 102.28453 Hz/cm
5.888
2.281
1.886
1.052
1.000
3.008
0.979
0.951
8.957
ppm

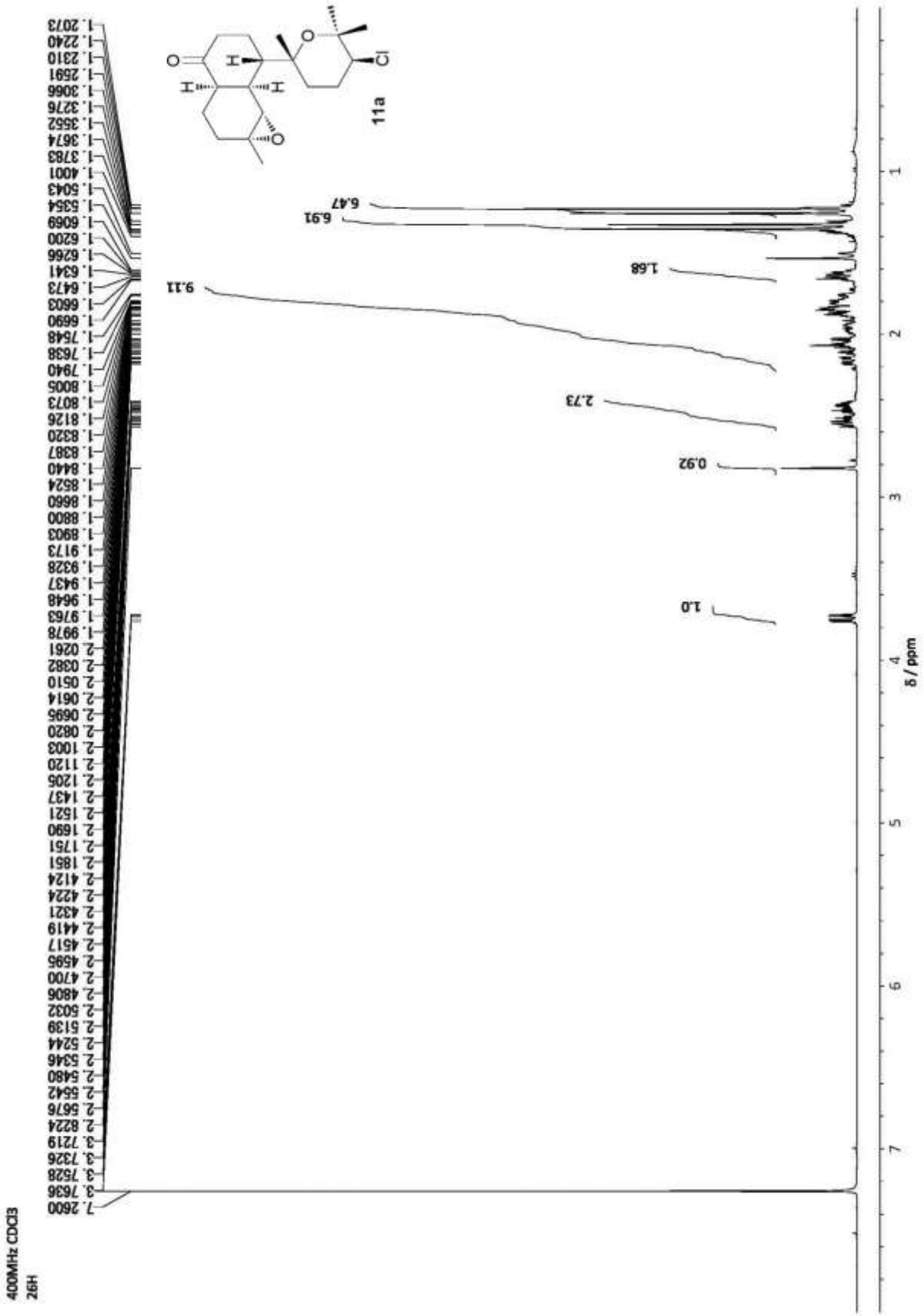

OTBS
O
H
O
9
Current Data Parameters
NAME yyamada 1
EXPNO 1 1
PROCNO
F2 - Acquisition Parameters
Date_ 20111113
Time 19.26
INSTRUM dpx400
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517375 sec
RG 4096
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
D11 0.08002000 sec
P13 20.00 dB
D1 2.00000000 sec
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 400.1316005 MHz
WDW2 1H
P12 -6.00 dB
P13 20.00 dB
P1 6.30 usec
SFO1 100.6230401 MHz
NUC1 13C
P11 -6.00 dB
D11 0.03000000 sec
F2 - Processing parameters
SI 32768
SF 100.6127681 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
10 mm plot parameters
CX 33.00 cm
F1P 150.000 ppm
F1 15091.92 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 5.00000 ppm/cm
HZCM 503.06384 Hz/cm

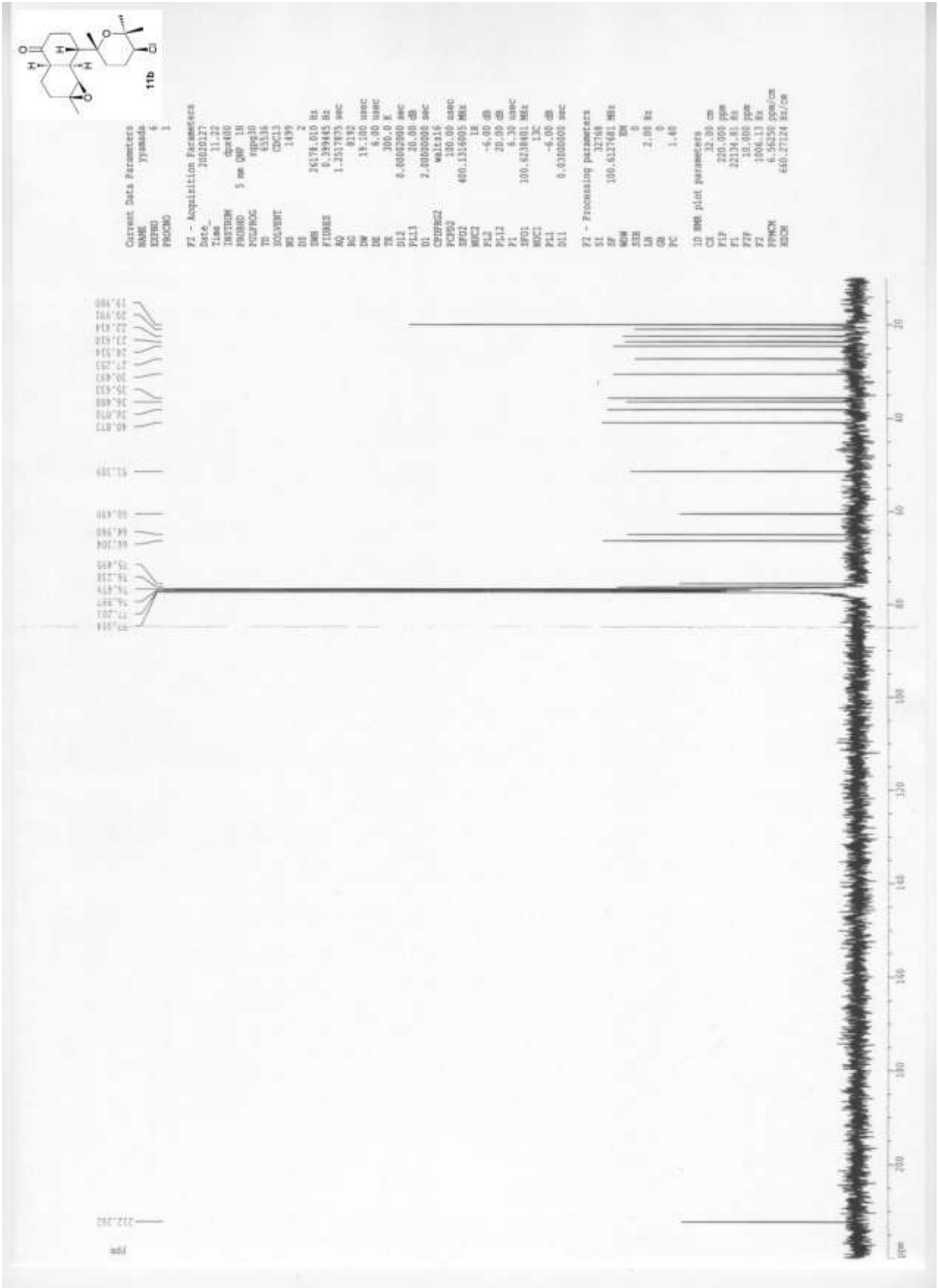

OTBS
H
O
Cl
9
Current Data Parameters
NAME yyma6a
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20011113
Time 18.20
INSTRUM dpx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 6793.478 Hz
FIDRES 0.207320 Hz
AQ 2.4117749 sec
RG 256
DW 73.600 usec
DE 6.00 usec
TE 302.5 K
D1 1.00000000 sec
P1 7.40 usec
SFO1 400.1326354 MHz
NUC1 1H
PL1 -6.00 dB
F2 - Processing parameters
SI 16384
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 12.00 cm
F1P 8.000 ppm
F1 3201.94 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.28125 ppm/cm
HZCM 112.53656 Hz/cm
6.079
9.636
15.511
5.857
2.336
1.931
1.000
2.065
1.000
1.031
1.029
0.966
1.000

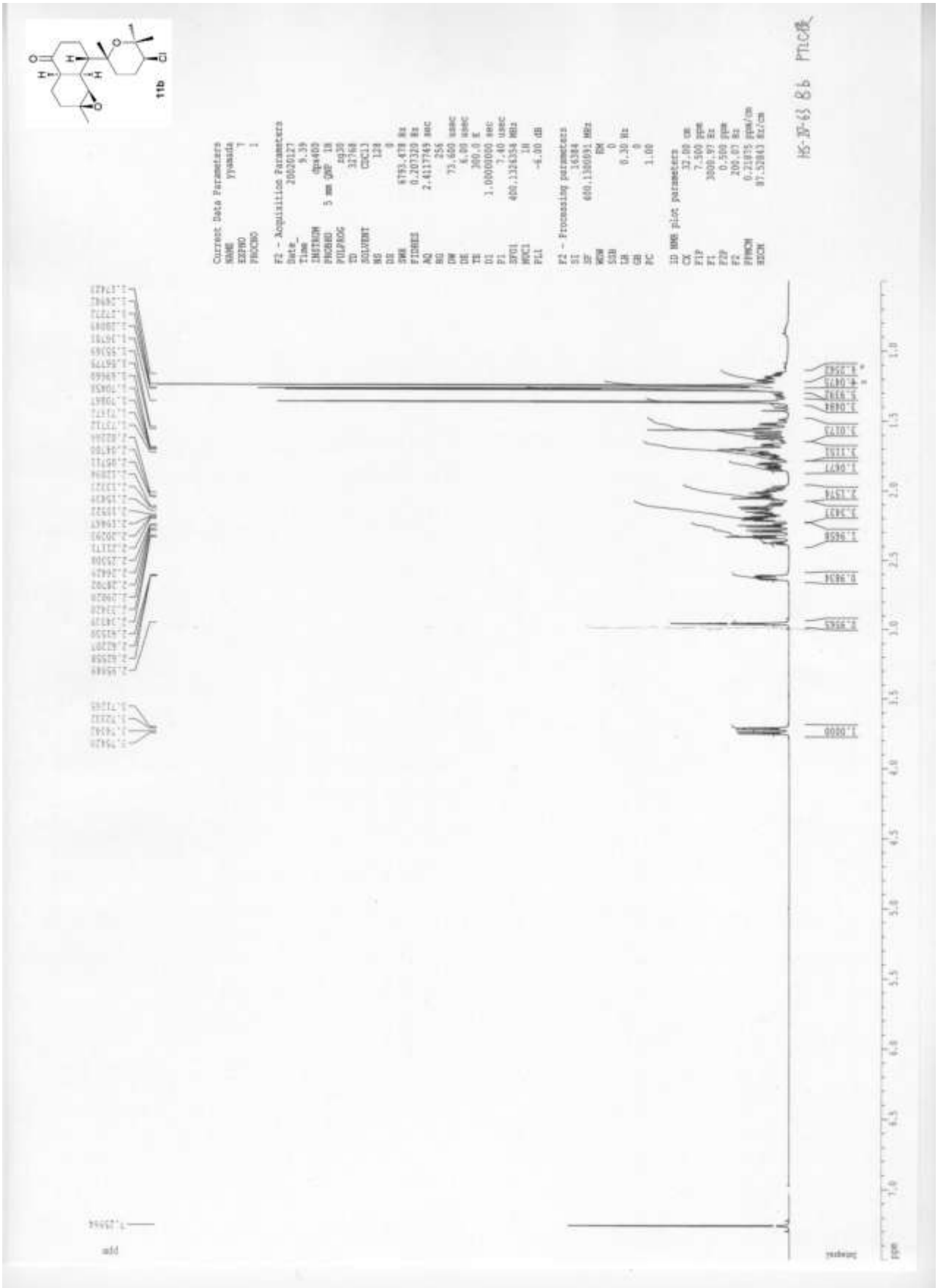

DRX500-1 01/8/28
13C HS-3-132/CDCl3
ppm

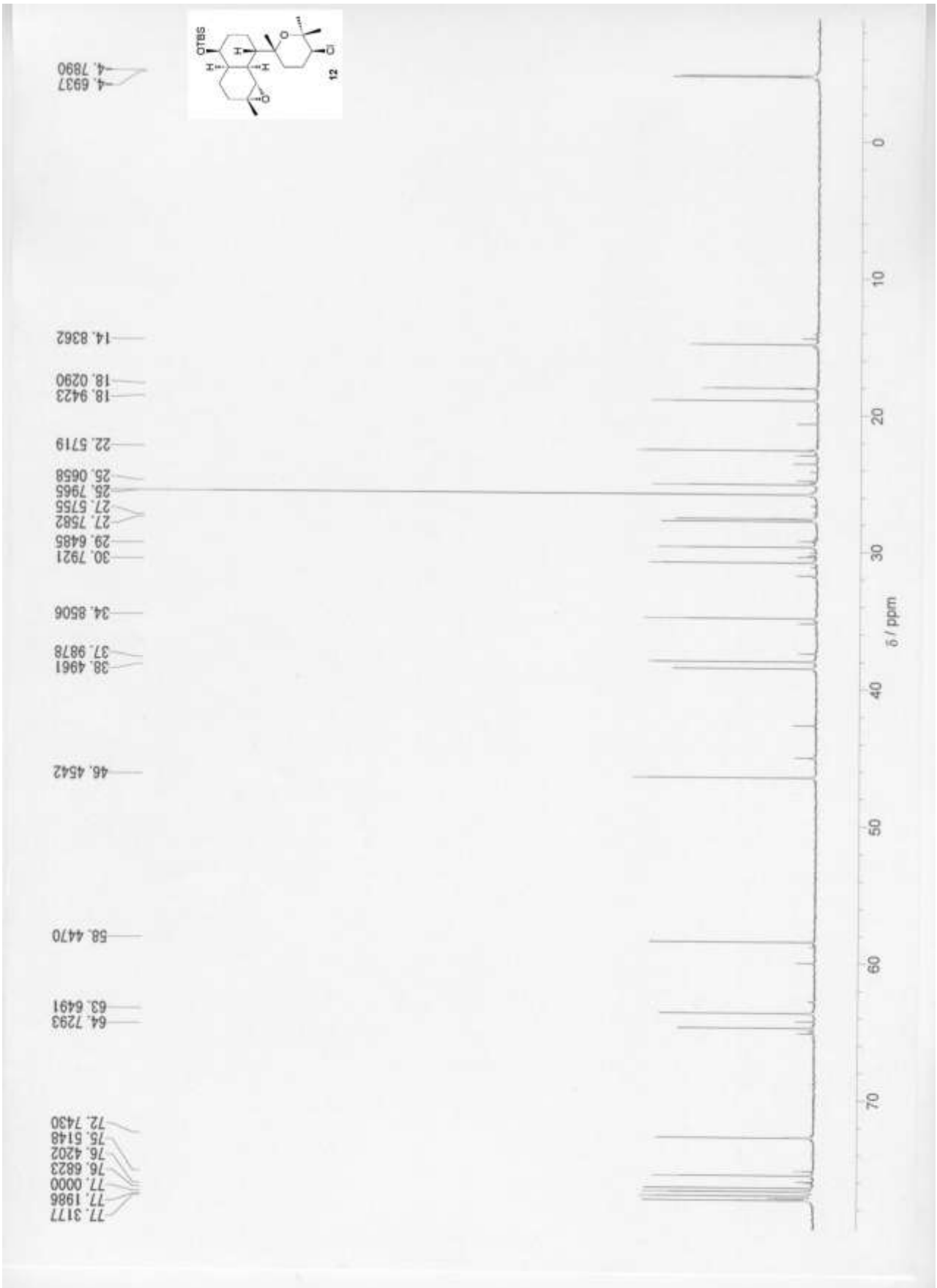

10
DPX500-1 01/8/2B
1H HS-3-132/CDCl3

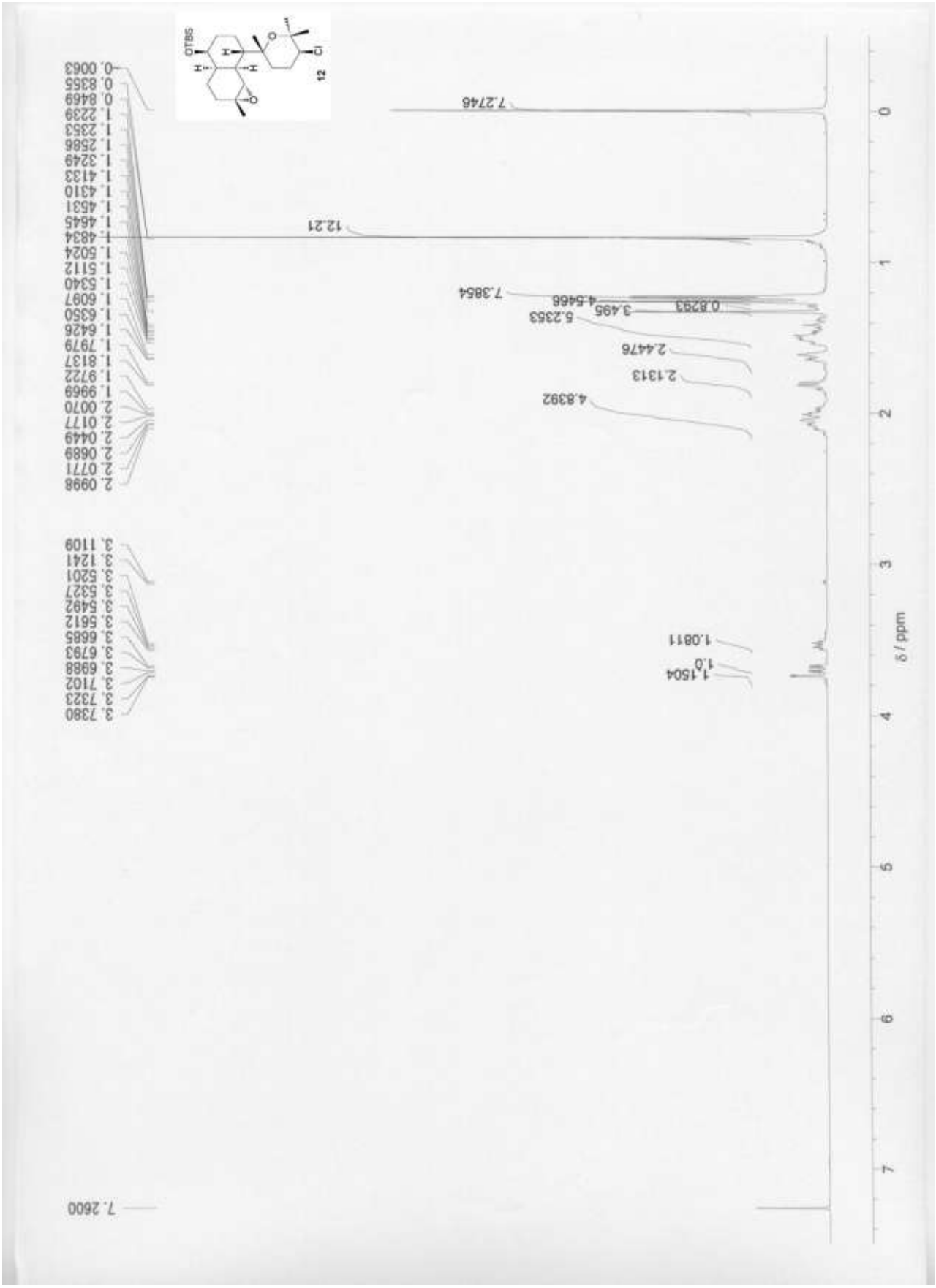

11a
Current Data Parameters
NAME
EXPNO
PROCNO
F2 - Acquisition Parameters
Date_
Time
INSTRUM
PROBHD
PULPROG
TD
SOLVENT
NS
DS
SWH
FIDRES
AQ
RG
DW
DE
TE
D12
P13
D1
CPDPRG2
PCPD2
SFO2
NUC2
P4
P12
P1
SFO1
NUC1
P3
D11
F2 - Processing parameters
SI
SF
WDW
SSB
LB
GB
PC
1D NMR plot parameters
CX
F1P
F1
F2P
F2
PPMCM
HZCM
5 mm QNP 1H
zgpg30
CDCl3
ppm
Hz

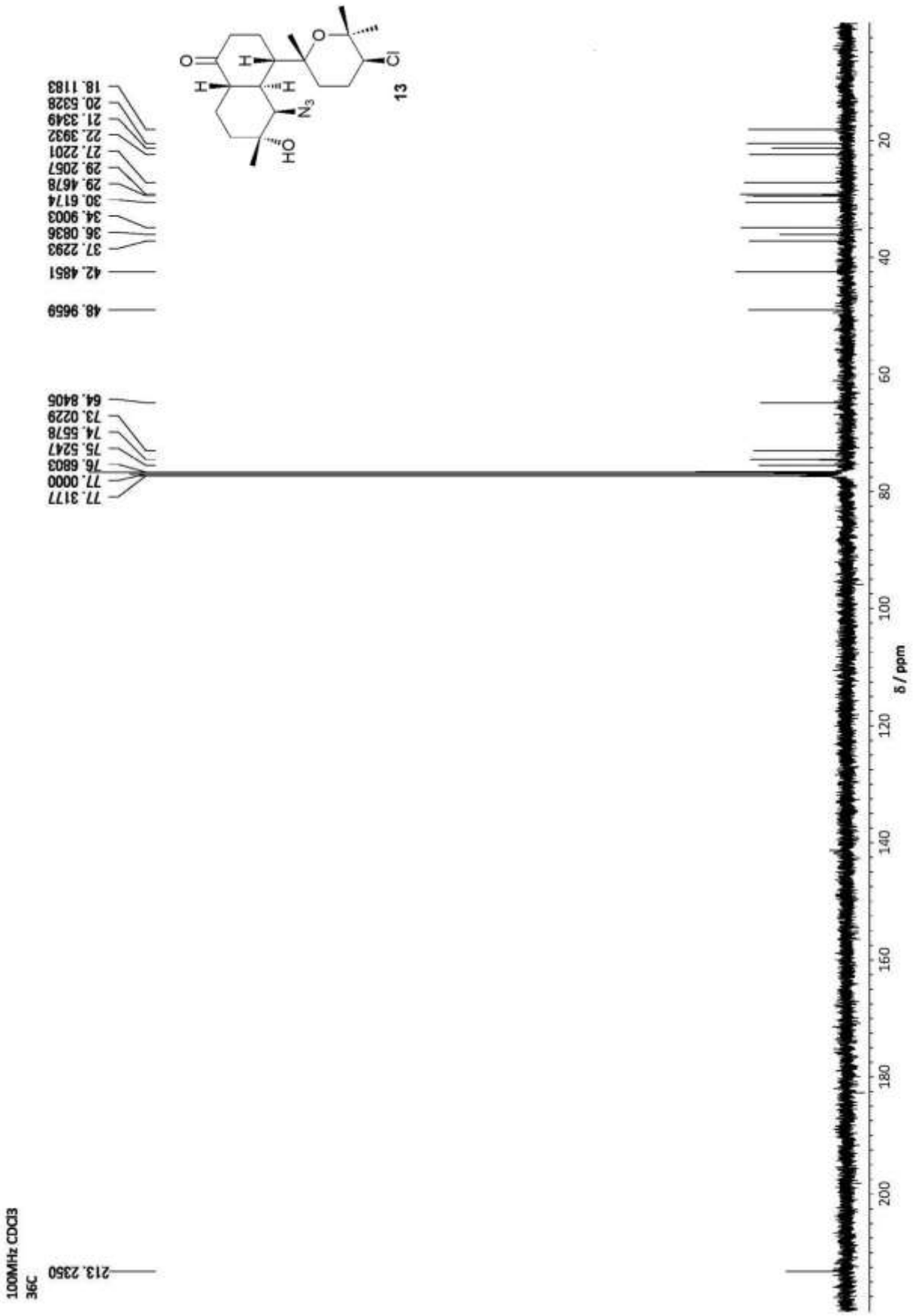

400MHz CDCl3
26H
11a
6.47
6.91
1.68
9.11
2.73
0.92
1.0
δ / ppm

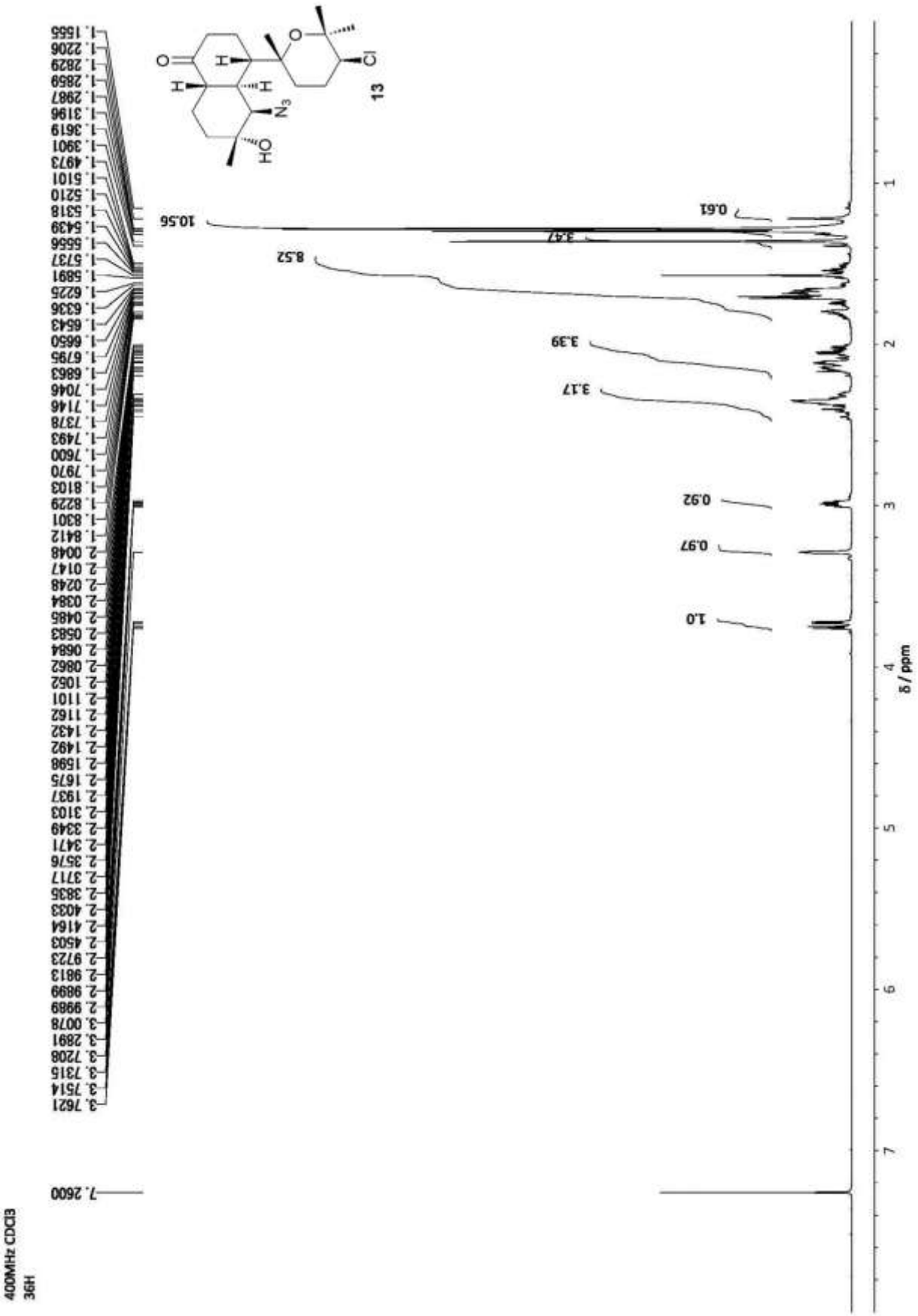

11b
Current Data Parameters
NAME yamada
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20020127
Time 11.22
INSTRUM dpx400
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1499
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.3517835 sec
RG 8192
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
D11 6.00002000 sec
PL13 20.00 dB
D1 2.00000000 sec
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 400.1316005 MHz
NUC2 1H
PL2 -6.00 dB
PL12 20.00 dB
P1 6.30 usec
SFO1 100.6238401 MHz
NUC1 13C
PL1 -6.00 dB
D11 0.03000000 sec
F2 - Processing parameters
SI 32768
SF 100.6127681 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 32.00 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P 10.000 ppm
F2 1006.13 Hz
PPMCM 6.56250 ppm/cm
HZCM 660.27124 Hz/cm

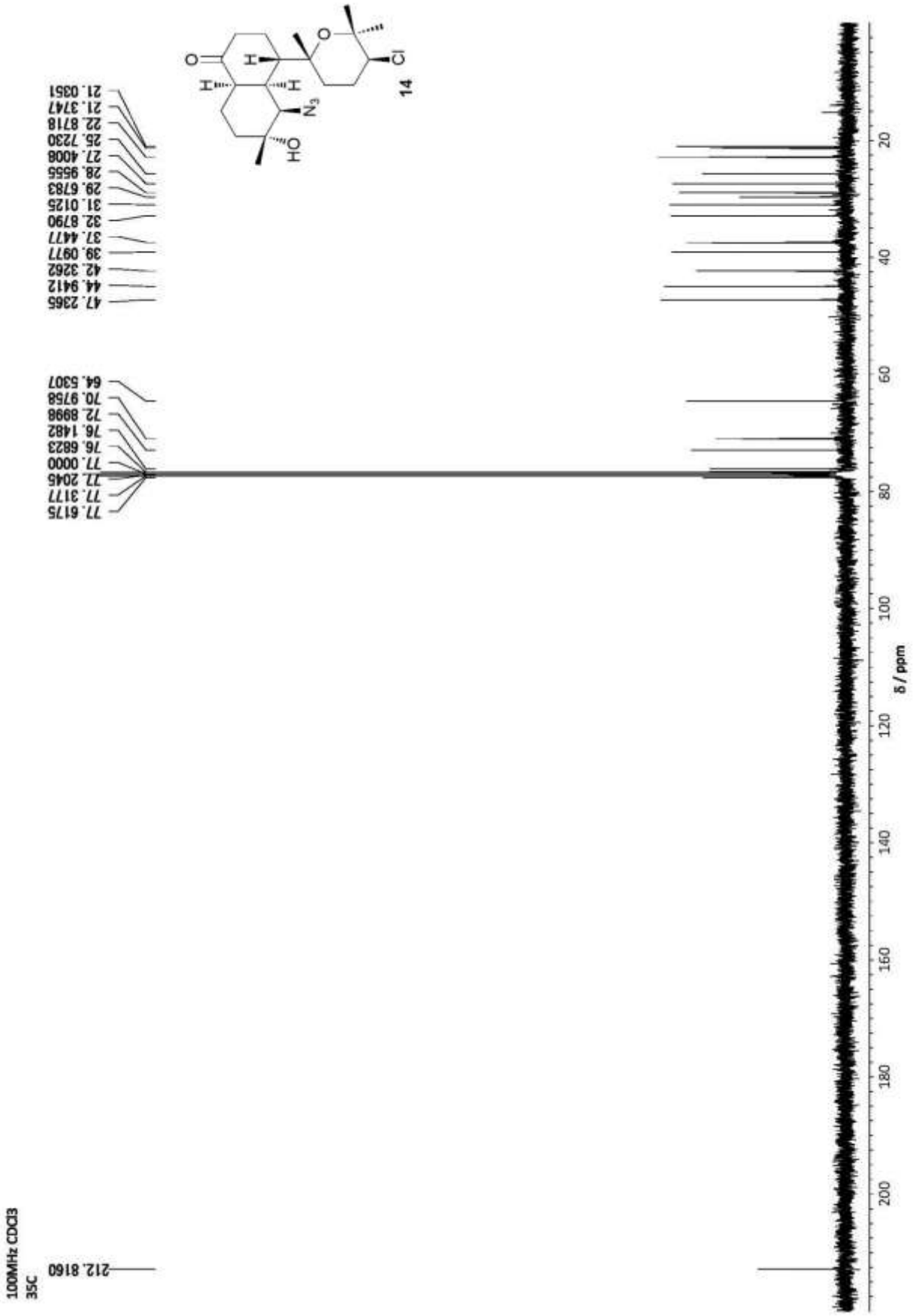

11b
Current Data Parameters
NAME yyasuda
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20020127
Time 9.39
INSTRUM dpx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 128
DS 0
SWH 6793.478 Hz
FIDRES 0.207320 Hz
AQ 2.4117749 sec
RG 256
DW 73.600 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 7.40 usec
SFO1 400.1316354 MHz
NUC1 1H
PL1 -6.00 dB
F2 - Processing parameters
SI 16384
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 32.00 cm
F1P 7.500 ppm
F1 3000.97 Hz
F2P 0.500 ppm
F2 200.07 Hz
PPMCM 0.21875 ppm/cm
HZCM 97.52843 Hz/cm
MS-JF-63 86 PTLCfr
1.0000
0.9614
0.9658
1.3437
1.1574
1.0671
1.1151
1.0173
1.0884
0.9716
0.9750
1.0000
ppm

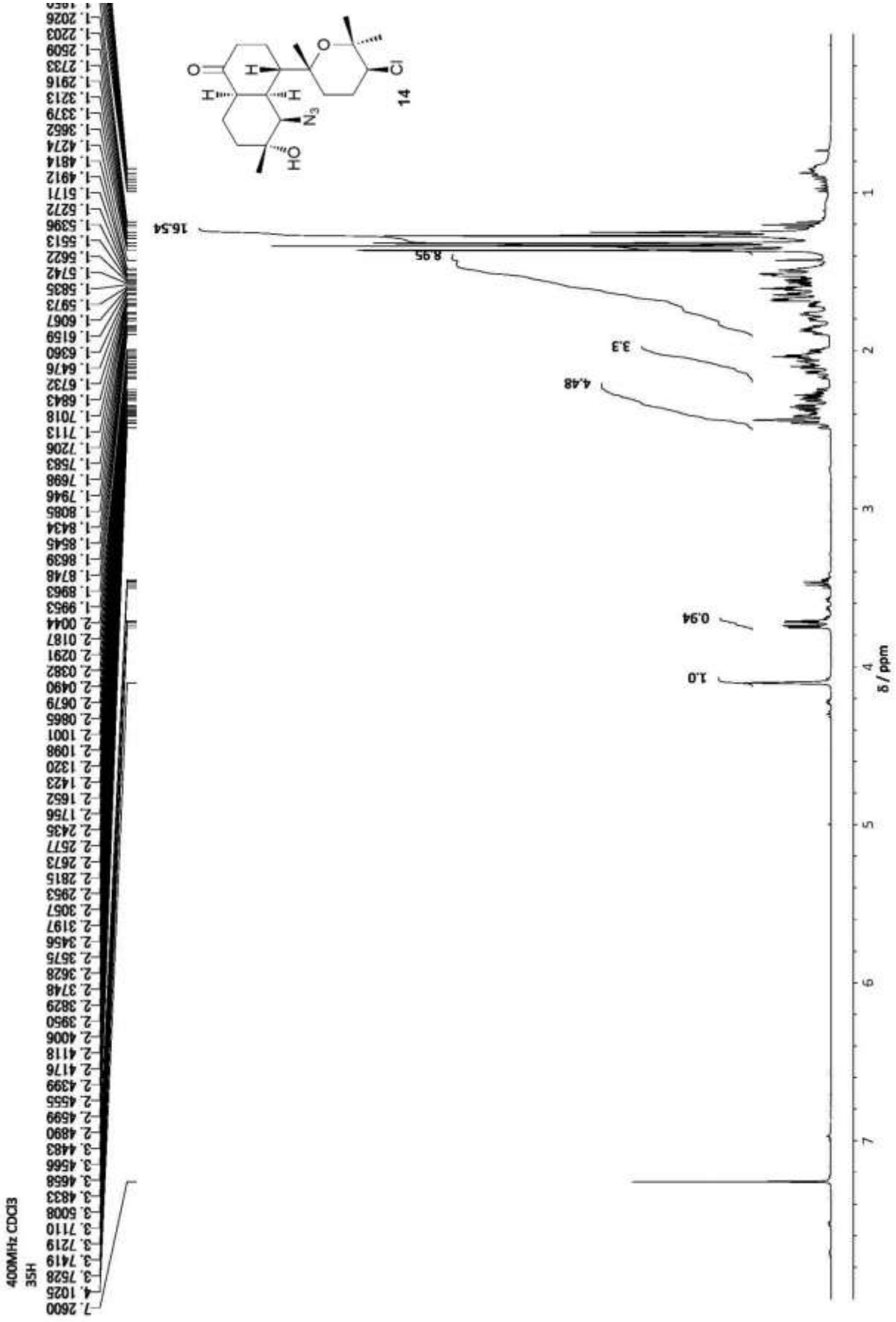

OTBS
H
H
O
Cl
12
4.7890
4.6937
14.8362
18.0290
18.9423
22.5719
25.0658
25.7965
27.5755
27.7582
29.6485
30.7921
34.8506
37.9878
38.4961
46.4542
58.4470
63.6491
64.7293
72.7430
75.5148
76.4202
76.6823
77.0000
77.1986
77.3177
0
10
20
30
40
50
60
70
δ / ppm

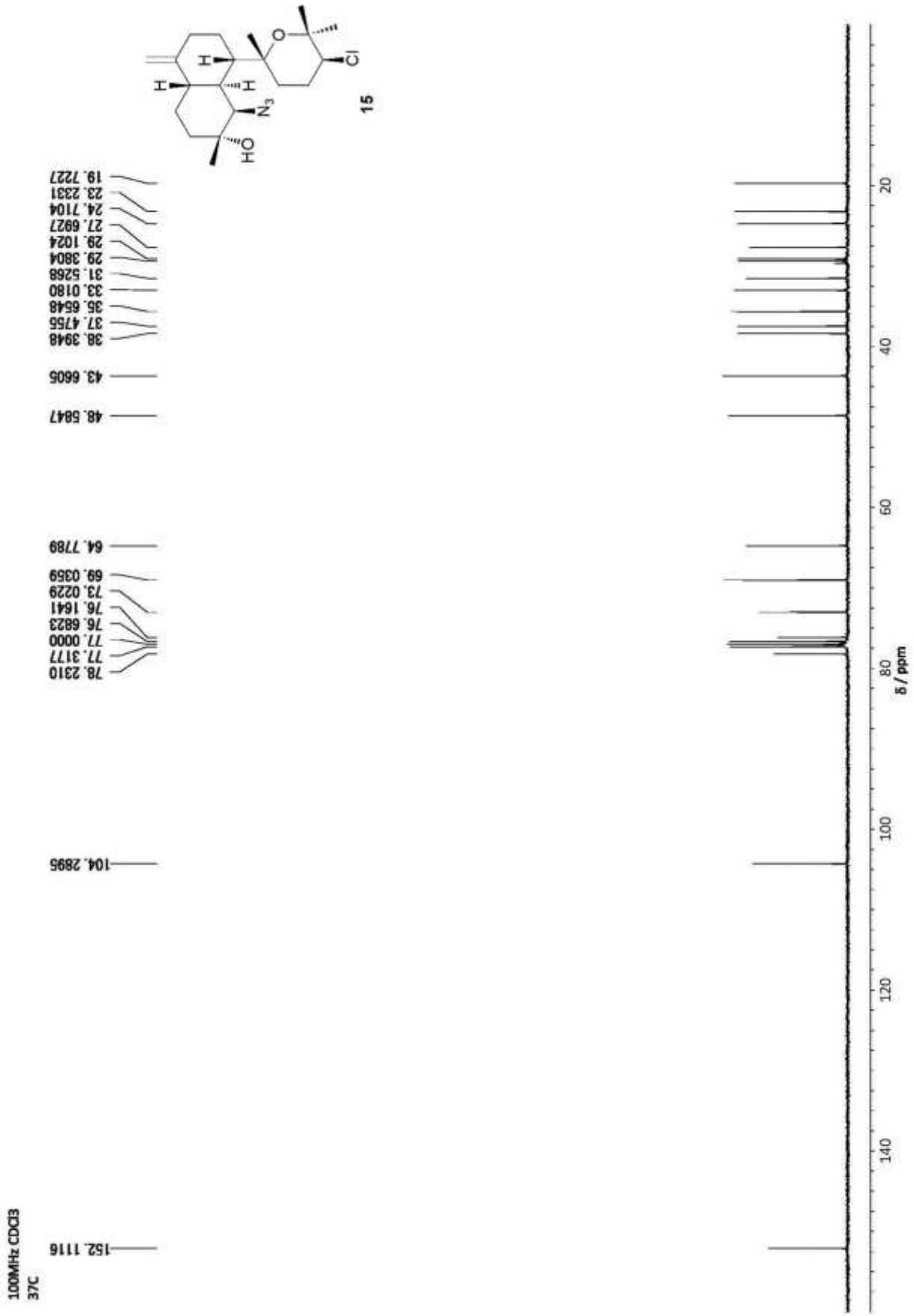

OTBS
H
H
H
O
O
Cl
12
7.2746
12.21
7.3854
4.5466
3.495
0.8293
5.2353
2.4476
2.1313
4.8392
1.0811
1.1504
1.0
7.2600
δ / ppm

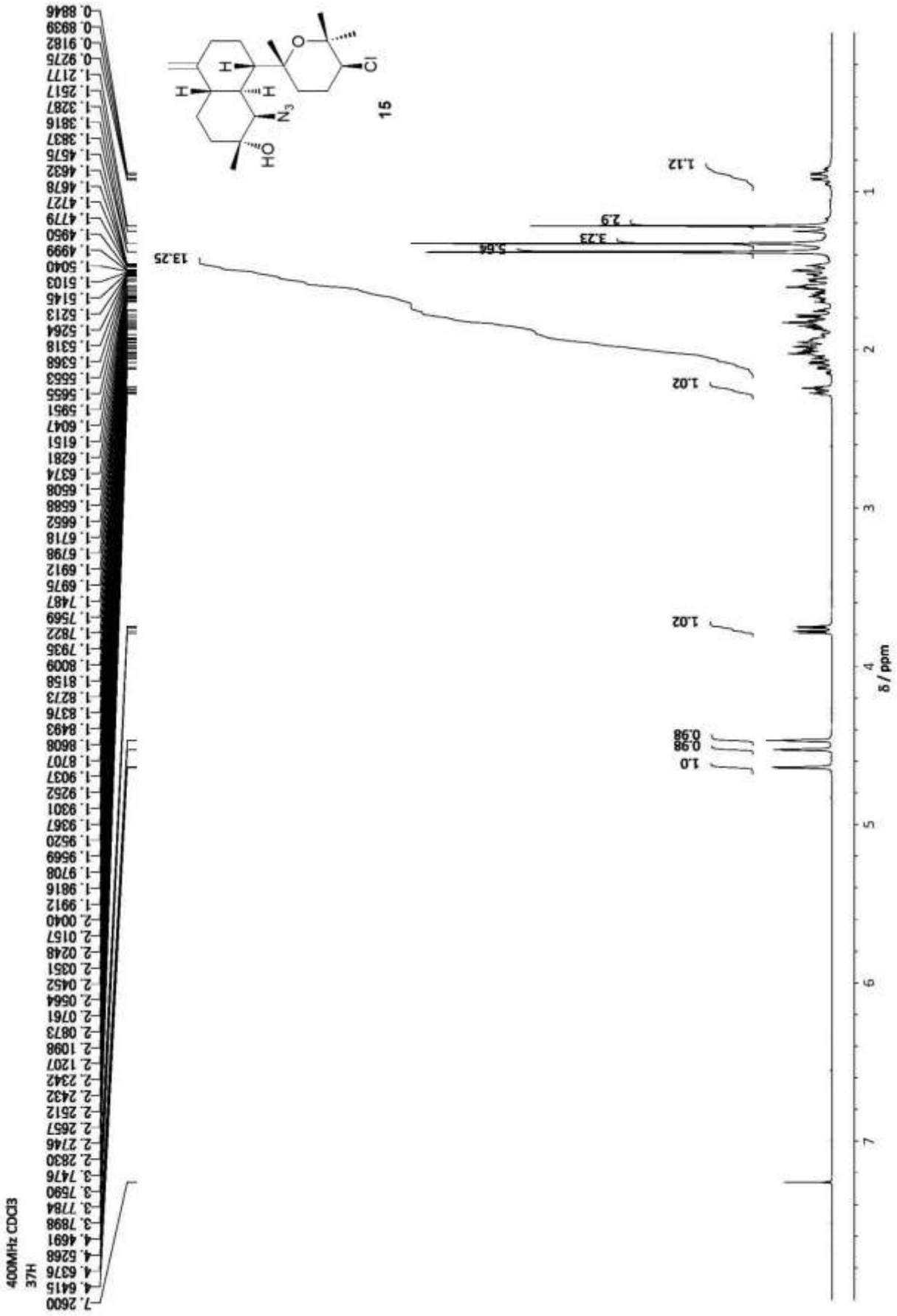

18.1183
20.5328
21.3349
22.3932
27.2201
29.2057
29.4678
30.6174
34.9003
36.0836
37.2293
42.4851
48.9659
64.8405
73.0229
74.5578
75.5247
76.6803
77.0000
77.3177
213.2350
100MHz CDCl3
36C
δ / ppm
13

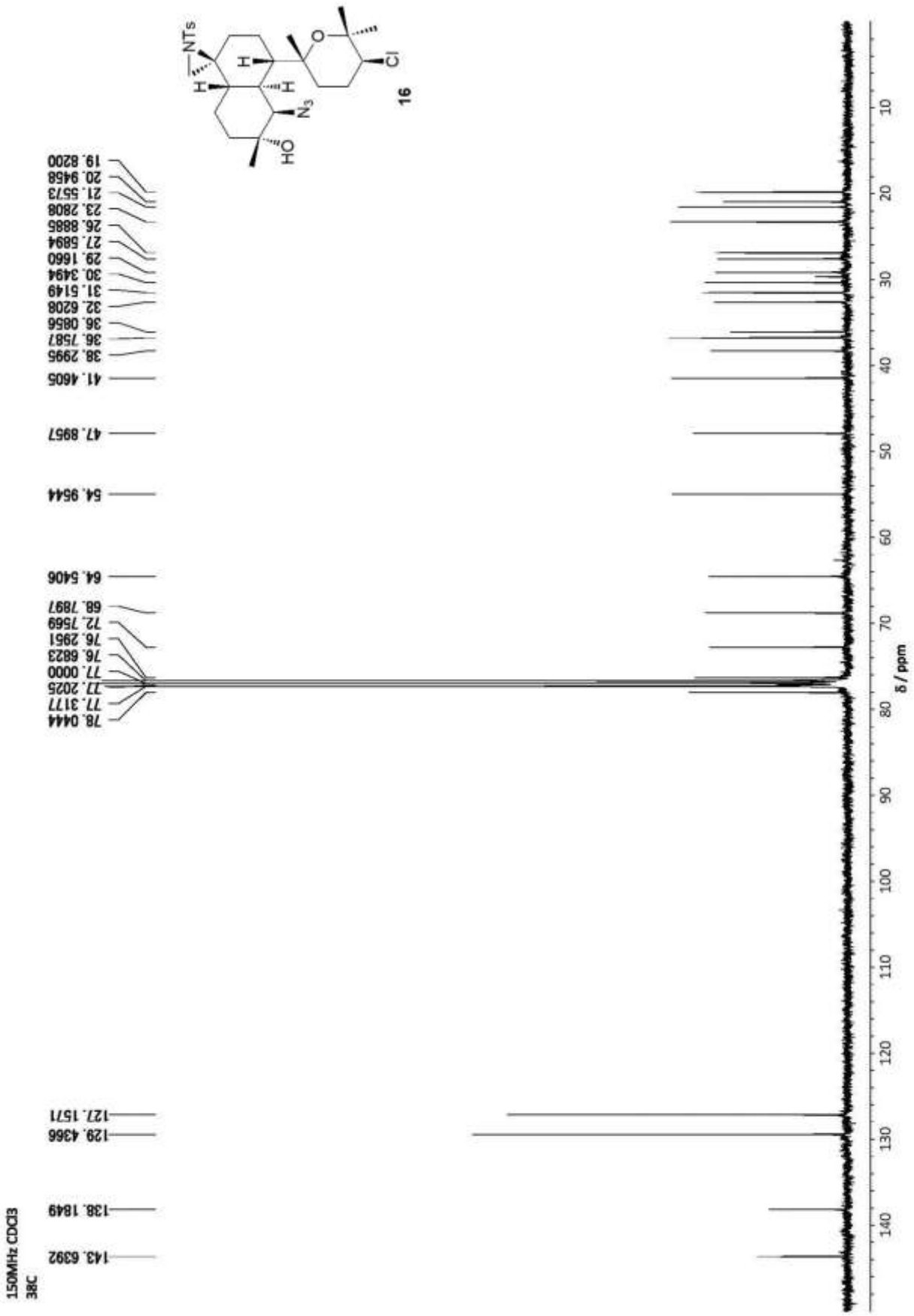

400MHz CDCl3
36H
δ / ppm
13
10.56
8.52
3.47
3.39
3.17
1.0
0.97
0.92
0.61

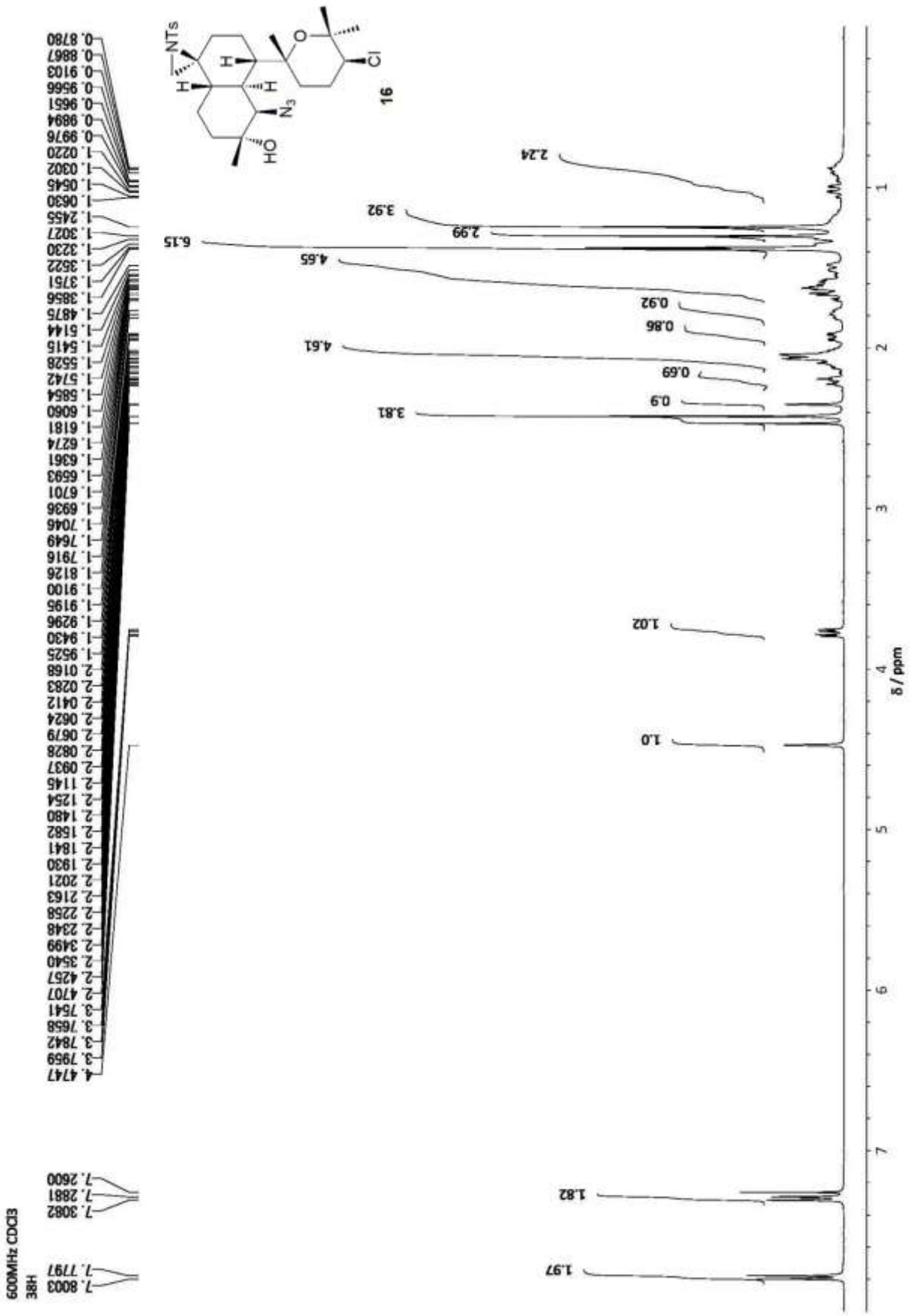

14
21.0351
21.3747
22.8718
25.7230
27.4008
28.9555
29.6783
31.0125
32.8790
37.4477
39.0977
42.3262
44.9412
47.2365
64.5307
70.9758
72.8998
76.1482
76.6823
77.0000
77.2045
77.3177
77.6175
212.8160
100MHz CDCl3
35C
δ / ppm

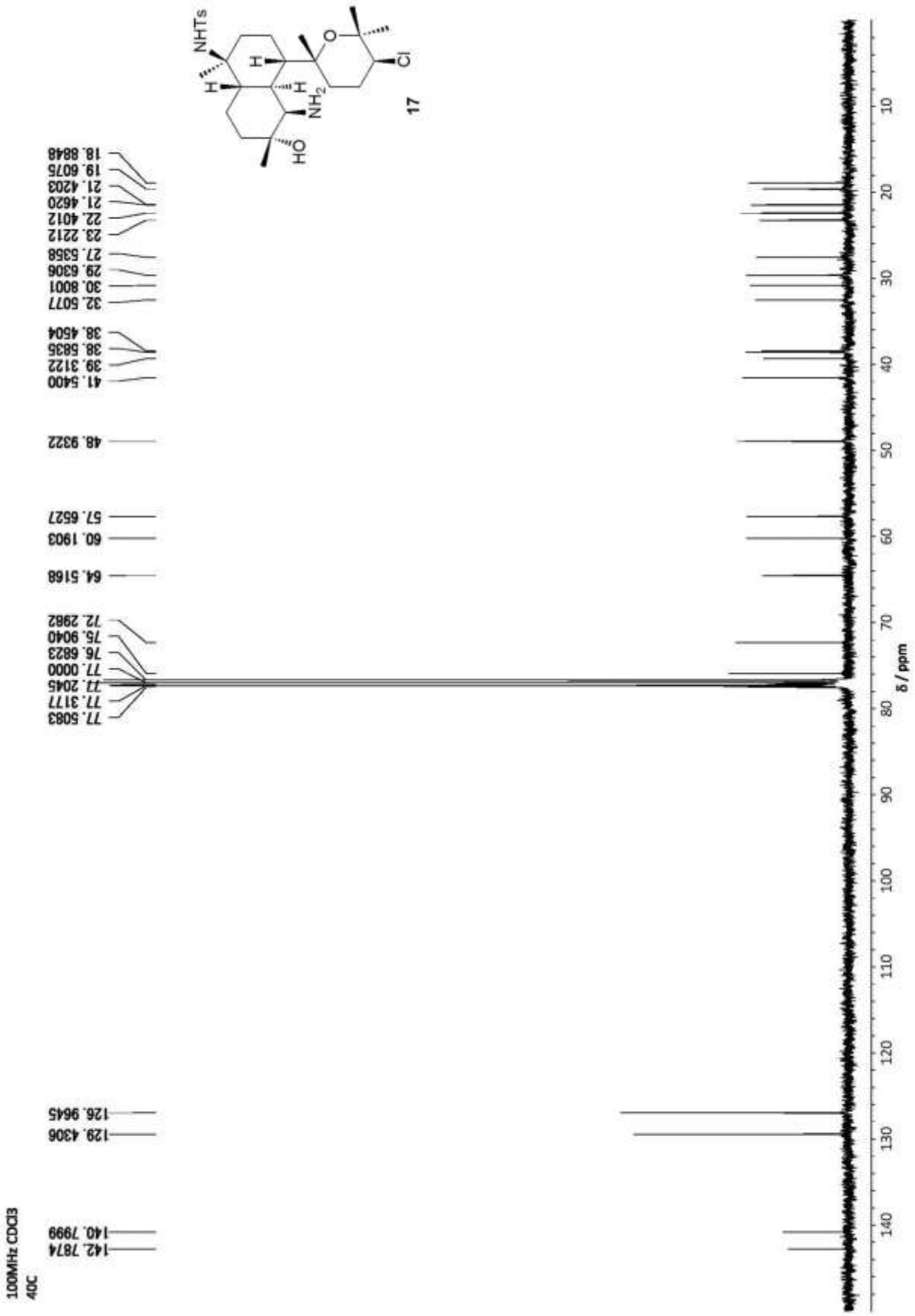

400MHz CDCl3
35H
16.54
8.95
3.3
4.48
0.94
1.0
δ / ppm
14

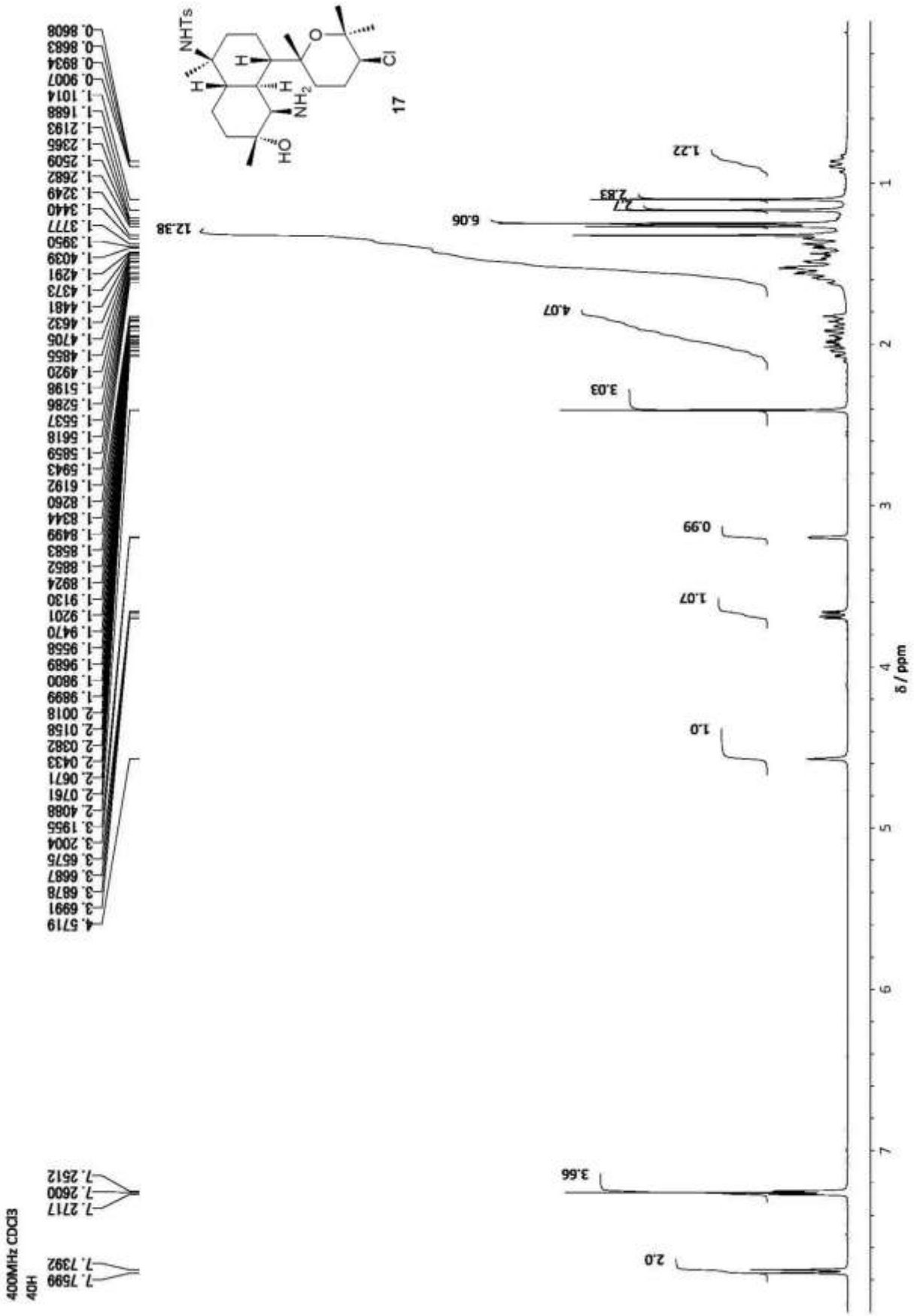

15
100MHz CDCl3
37C
δ / ppm
20
40
60
80
100
120
140
19.7227
23.2331
24.7104
27.6927
29.1024
29.3804
31.5268
33.0180
35.6548
37.4755
38.3948
43.6605
48.5847
64.7789
69.0359
73.0229
76.1641
76.6823
77.0000
77.3177
78.2310
104.2895
152.1116

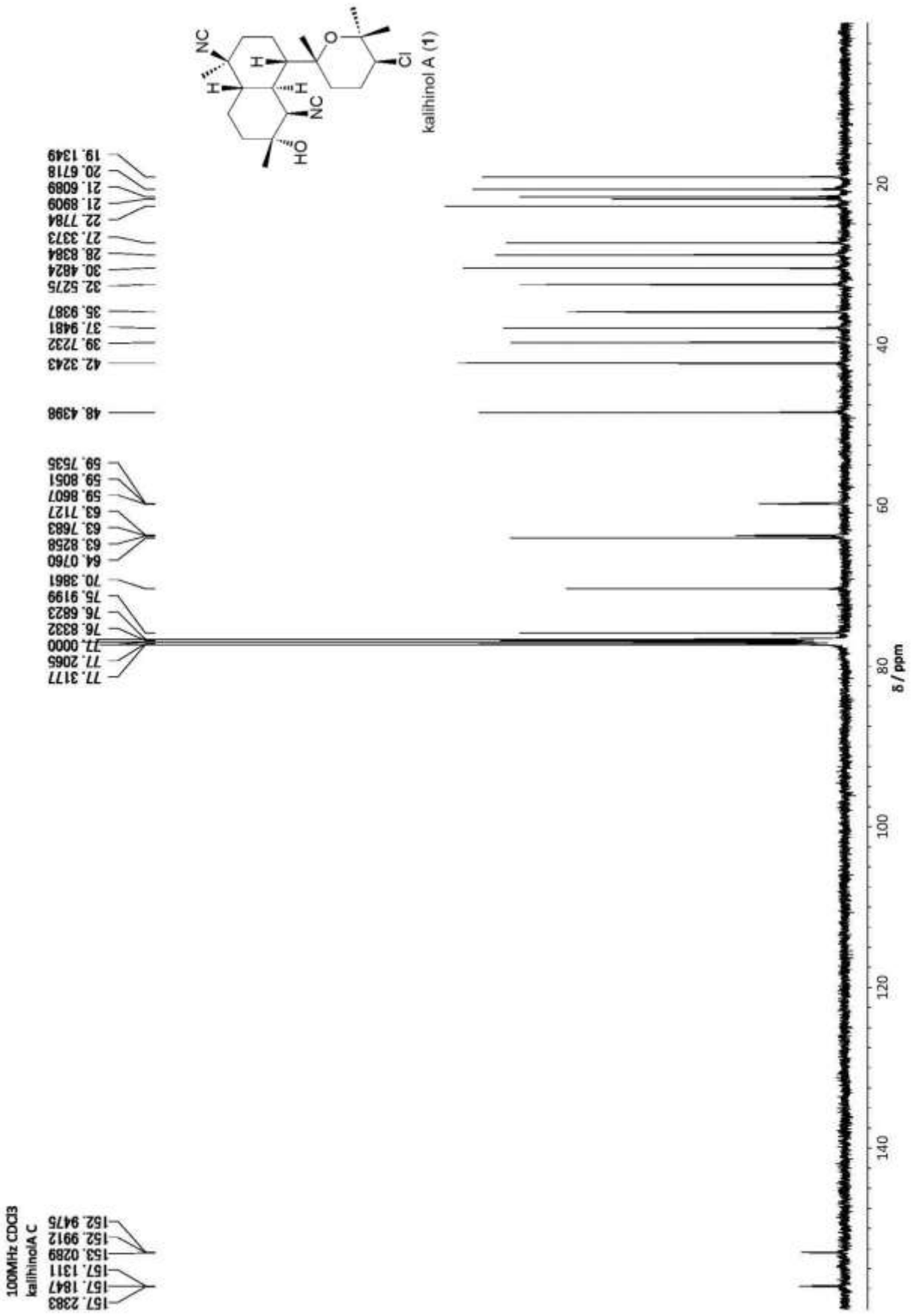

400MHz CDCl3
37H
15
13.25
5.64
3.23
2.9
1.12
1.02
1.02
0.98
0.98
1.0
δ / ppm

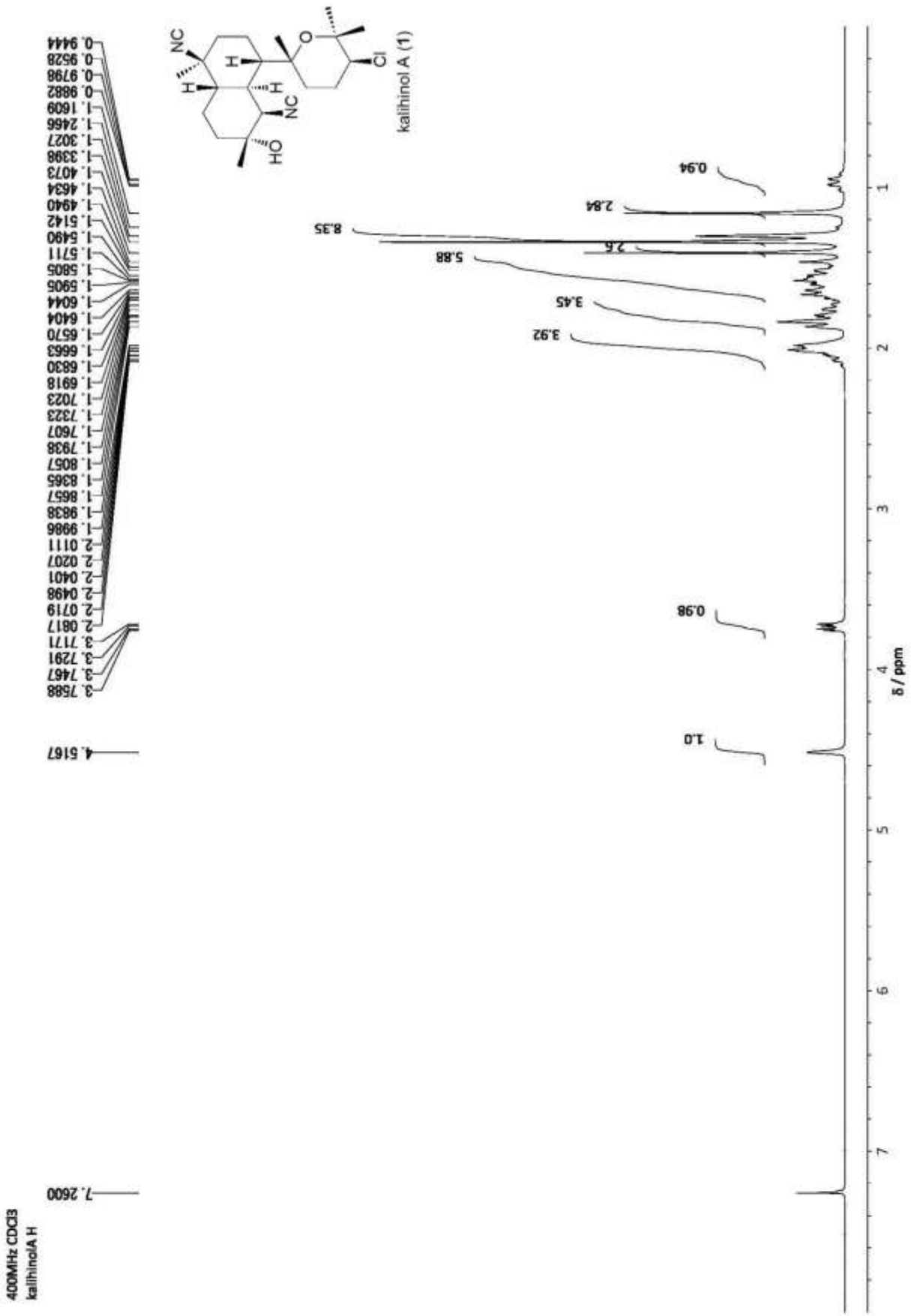

NTs
H
H
H
O
Cl
N3
HO
16
19.8200
20.9458
21.5573
23.2808
26.8885
27.5894
29.1660
30.3494
31.5149
32.6208
36.0856
36.7587
38.2995
41.4605
47.8957
54.9544
64.5406
68.7897
72.7569
76.2951
76.6823
77.0000
77.2025
77.3177
78.0444
127.1571
129.4366
138.1849
143.6392
150MHz CDCl3
38C
δ / ppm


NTs
H
H
H
O
Cl
N3
OH
16
2.24
3.92
2.99
6.15
4.65
0.92
0.86
4.61
0.69
0.9
3.81
1.02
1.0
1.82
1.97
600MHz CDCl3
38H
δ / ppm


NHTs
H
H
O
Cl
H
NH2
HO
17
18.8848
19.6075
21.4203
21.4620
22.4012
23.2212
27.5358
29.6306
30.8001
32.5077
38.4504
38.5835
39.3122
41.5400
48.9322
57.6527
60.1903
64.5168
72.2982
75.9040
76.6823
77.0000
77.2045
77.3177
77.5083
126.9645
129.4306
140.7999
142.7874
100MHz CDCl3
40C
δ / ppm


NHTs
H
H
H
NH2
O
Cl
HO
17
400MHz CDCl3
40H
12.38
6.06
4.07
3.03
2.83
2.7
1.22
0.99
1.07
1.0
3.66
2.0
δ / ppm


kalihinol A (1)
δ / ppm
100MHz CDCl3
kalihinolA C


400MHz CDCl3
kalihinolA H
kalihinol A (1)
δ / ppm
0.94
2.84
8.35
2.6
5.88
3.45
3.92
0.98
1.0