Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Asymmetric Epoxidation of Enones: Effect of Surfactants, Radical Scavengers and Morphology of Catalysts on Reaction Rates, Chemical Yields and Enantioselectivities in Phase-Transfer Catalysis

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General Information

All reagents purchased from commercial sources were used without further purification. Commercially available KOH pellet (99%) was grinded to prepare Solid KOH as powder form. 50% w/v aqueous KOH was used as stock solution. For the reactions that required heating, sand bath was used as heat source. Organic solvents were concentrated under reduced pressure using a Büchi rotary evaporator. Phase-transfer catalysts (3[1], 4[1], 6[3], 7[4], 8[4], 9[27]) were prepared according to the reported procedure. TLC analyses were performed using pre-coated TLC plate (silica gel 60 F_{254}, 0.25 mm). Flash column chromatography was carried out using E. Merck Silica gel 60 (0.040-0.063 mm). Hitachi (UV detector L-2130, Pump L-2130 and software LaChrome 890-8800-12) were used for HPLC. The values of enantiomeric excess (ee) of chiral products were determined by HPLC using 4.6 mm × 250 mm Daicel Chiralpak AD-H, Chiralpak ID-H, Chiralpak OD-H, Chiralpak OJ-H and Chiralcel AS-H. Nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were measured on JEOL JNM-LA 300 [300 MHz (^{1}H), 75 MHz (^{13}C)] JEOL JNM-ECZ400s [400 MHz (^{1}H), 101 MHz (^{13}C)], Bruker AVANCE 500 [500 MHz (^{1}H), 126 MHz (^{13}C)] ^{1}H-NMR spectra was recorded at 400 MHz or 500 MHz with reference to $CDCl_3$ (δ 7.24), CD_3OD (δ 3.31) or DMSO-d_6 (δ 2.50). ^{13}C-NMR spectra was obtained by 101 MHz or 126 MHz spectrometer relative to the central $CDCl_3$ (δ 77.0) or CD_3OD (δ 49.0) or DMSO-d_6 (δ 40.0) resonance. Coupling constants (*J*) in ^{1}H-NMR are in Hz. Low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were measured on JEOL JMS-700 spectrometers(double-focusing mass analyzer) or Agilent Q-TOF 6530 MS (ESI) spectrometer. Infrared (IR) spectra were recorded on JASCO FT/IR-4200 spectrometers. Optical rotations were measured on a JASCO P-2000 digital polarimeter and calibrated with pure solvent as blank. X-ray crystallographic data was collected by Agilent SuperNova X-ray Diffractometer using graphitemonochromated Mo Kα radiation.

Microscopic pictures of solid catalysts were obtained by Nikon SMZ1270 with an eye lens (C-W15X/16) and objective lens (total 90 times of magnification).

Preparation of PTC Catalysts

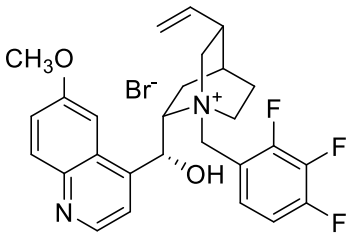
(*A) General procedure for PTC catalysts*

To a solution of (-)quinine (636.4 mg, 1.96 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (270 mg, 0.96 mmol) in a mixture of ethanol (7.6 mL), DMF (9.0 mL) and chloroform (3.0 mL) was stirred for overnight at rt. The resulting solution was poured into diethylether (100 mL) for solidification. The solid was filtered and washed with diethylether. The precipitate was dissolved into MeOH/CH_3Cl (1 : 1) and dried *in vacuo* to afford 1,3-bis(quininium-N-methyl)-2-fluorobenzene dibromide(**13**, 861.0 mg, 0.925 mmol, 97%) as ivory solid.

(*B) General procedure for anion exchange of PTC catalysts*

Preparation of anion exchanged PTC was performed by anion exchange of **13** according to the literature[5]. To a solution of **13** (100 mg, 0.107 mmol) in MeOH (1 mL) was added Amberlyst A-26 (OH^-)resin(about 100 mg). The mixture was stirred for 30min and filtered to remove the resin. To the filterate was added acids (1 N aq. solution, 1 mL) and stirred for 30min. The mixture was basified with NH_4OH aq. solution, extracted with dichloromethane twice, washed with water, dried over Na_2SO_4, filtered and concentrated to afford anion exchanged PTC as fine solid. Obtained PTC was re-dissolved into MeOH/CH_3Cl (1 : 1)and evaporated *in vacuo*.

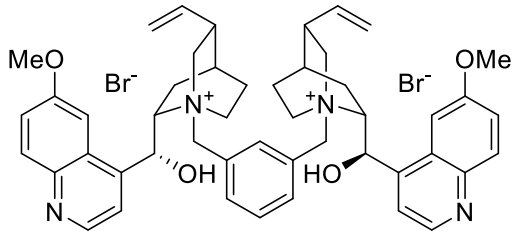
N-2,3,4-Trifluorobenzyl quininium bromide (5)



A mixture of quinine (1.00 g, 3.37 mmol) with 2,3,4-Trifluorobenzyl bromide (834 mg, 3.71 mmol) in a mixture of ethanol (2.3 mL), DMF (2.7 mL), and chloroform (1 mL) was stirred at 100 °C for 4 h. After cooling the reaction mixture to room temperature, the resulting suspension was diluted with methanol (5 mL) and ether (100 mL) and stirred for 1 h. The solids were filtered, washed with ether. The crude solid was recrystallized from methanol-ether to afford 1.67 g (95% yield) of desired product.

Light yellow solid; mp 158 °C (MeOH-Et_2O, decomp.); ^{1}H NMR (300 MHz, DMSO- d_6) δ 8.80 (d, J = 4.4 Hz, 1 H), 8.01 (d, J = 9.2 Hz, 1 H), 7.75-7.72 (m, 2 H), 7.61-7.56 (m, 1 H), 7.49 (dd, J = 9.1, 2.3 Hz, 1 H), 7.38 (d, J = 2.4 Hz, 1 H), 6.75 (d, J = 3.7 Hz, 1 H), 6.55 (s, 1H), 5.80-5.69 (m, 1 H), 5.51 (d, J = 12.7 Hz, 1 H), 5.14-4.99 (m, 2H), 4.75 (d, J = 12.9 Hz, 1 H), 4.24-4.21(m, 1 H), 4.00 (s, 3 H), 3.98-3.96 (m, 1 H), 3.76-3.67 (m, 1 H), 3.50-3.36 (m, 1 H), 2.70-2.65 (m, 1 H), 2.20-2.15 (m, 2 H), 2.00 (s, 1 H), 1.81-1.77 (m, 1 H), 1.46-1.38 (m, 1 H) ppm; ^{13}C NMR (75MHz, DMSO-d_6) δ 157.4, 147.4, 143.7, 137.9, 131.4, 131.3, 125.4, 121.5, 120.3, 116.7, 113.7, 102.2, 68.3, 63.8, 59.1, 56.4, 55.6, 50.9, 37.3, 25.8, 24.4, 20.4 ppm; IR (KBr) 3433, 1621, 1515, 1493, 1311, 1241, 1029, 827, 587 cm^{-1}; $[\alpha]^{20}_D$ = -199.0 (c 1.00, CH_3OH); MS (FAB): 469 $[M\text{-}Br]^+$; HRMS (FAB) calcd for $[C_{27}H_{28}F_3N_2O_2]^+$: 469.2097, found: 469.2123.

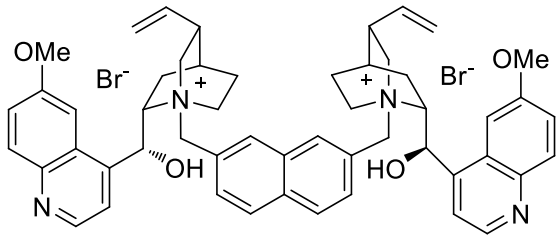
1,3-Bis(quininium-*N*-methyl)benzene dibromide (10)



According to the procedure **(A)**, from quinine(300mg, 0.925mmol) and 1,3-bis(bromomethyl)benzene (119.1mg, 0.451mmol), the compound **9** was obtained (402.7mg, 0.441mmol, 98%).

Pink solid; mp 213 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (300 MHz, DMSO-d_6) δ 8.82 (d, J = 4.7 Hz, 2H), 8.03 (d, J = 9.3 Hz, 2H), 7.94-7.71 (m, 5H), 7.52-7.39 (m, 4H), 6.69 (d, J = 3.7 Hz, 2H), 6.61 (s, 2H), 5.82-5.71 (m, 2H), 5.52 (d, J = 12.2 Hz, 2H), 5.12-4.99 (m, 4H), 4.74 (d, J = 12.0 Hz, 2H), 4.24-4.15 (m, 2H), 4.01 (s, 6H), 3.99-3.86 (m, 2H), 3.66-3.62 (m, 2H), 3.55-3.47 (m, 2H), 3.34-3.30 (m, 2H), 2.73-2.70 (m, 2H), 2.24-2.02 (m, 6H), 1.51-1.44 (m, 2H); ^{13}C-NMR (75 MHz, MeOH-d_6) δ 160.8, 149.0, 146.9, 145.6, 141.2, 139.5, 137.7, 132.6, 130.7, 128.2, 124.3, 122.5, 118.5, 103.3, 71.3, 66.6, 65.6, 62.5, 57.7, 53.7, 39.9, 29.0, 26.6, 22.9; IR (KBr) 3854, 3735, 3420, 1621, 1509, 1473, 1361, 1240, 1026 cm^{-1}; $[\alpha]^{20}_D$ = −202 (c 0.10, MeOH); MS (FAB): 831 $[M\text{-}Br]^+$; HRMS (FAB) calcd for $[C_{48}H_{56}BrN_4O_4]^+$: 831.3479, found: 831.3511.

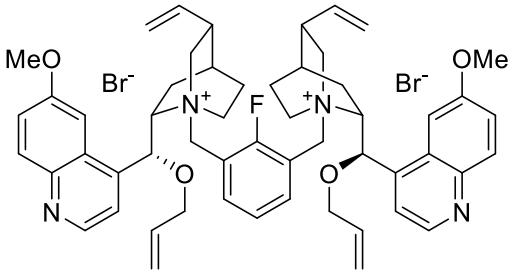
2,7-Bis(quininium-*N*-methyl)-naphthalene dibromide (11)



According to the procedure (**A**), from quinine (176.6 mg, 0.544 mmol) and 2,7-bis(bromomethyl)naphthalene (83.4 mg, 0.266 mmol), the compound **11** was obtained (240.0 mg, 0.249 mmol, 94%).

White solid; mp 204-205 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.79 (d, *J* = 4.6 Hz, 2H), 8.49 (s, 2H), 8.17 (d, *J* = 8.7 Hz, 2H), 8.04 (d, *J* = 9.6 Hz, 2H), 7.93 (d, *J* = 4.6 Hz, 2H), 7.90 (dd, *J* = 8.7, 1.4 Hz, 2H), 7.53 (dd, *J* = 9.1, 2.3 Hz, 2H), 7.49 (d, *J* = 2.3 Hz, 2H), 6.76 (s, 2H), 5.82-5.73 (m, 2H), 5.64 (d, *J* = 12.3 Hz, 2H), 5.17 (d, *J* = 17.4 Hz, 2H), 5.06 (d, *J* = 10.5 Hz, 2H), 5.02 (d, *J* = 12.3 Hz, 2H), 4.56-4.50 (m, 2H), 4.08 (s, 6H), 4.04-3.99 (m, 2H), 3.79-3.74 (m, 2H), 3.64-3.59 (m, 2H), 3.49-3.46 (m, 2H), 2.73-2.71 (m, 2H), 2.46-2.36 (m, 4H), 2.15-2.10 (m, 2H), 1.93-1.88 (m, 2H), 1.64-1.58 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 160.1, 148.3, 146.1, 144.8, 138.7, 136.1, 135.7, 134.2, 132.7, 131.9, 130.1, 127.4, 127.3, 123.3, 121.7, 117.7, 102.6, 70.3, 66.0, 65.5, 62.0, 56.6, 53.1, 39.3, 28.2, 25.9, 22.1 ppm; IR (neat) 3394, 1620, 1509, 1241, 1032 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{52}H_{58}BrN_4O_4]^+$ 881.3641; found 881.3628. $[\alpha]^{20}_D$ = -56.67 (*c* 1.0, MeOH).

1,3-Bis[O(9)-allylquininium-N-methyl]-2-fluorobenzene dibromide (12)

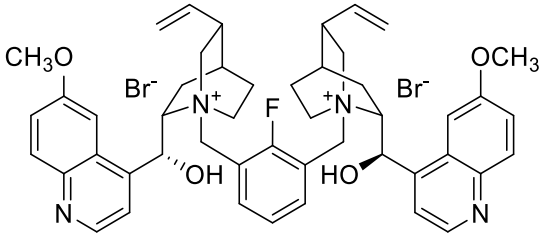


According to the procedure (**A**), the compound **12** was obtained (210.9 mg, 0.209 mmol, 91%).

Pink solid; mp 186 °C (CH_2Cl_2-Hexanes, decomp.); ^{1}H-NMR (300 MHz, DMSO-d_6) δ 8.84 (d,

J = 4.4 Hz, 2H), 8.07-8.02 (m, 4H), 7.66-7.39 (m, 7H), 6.52 (s, 2H), 6.16-6.07 (m, 2H), 5.84-5.72 (m, 4H), 5.46 (d, *J* = 17.3 Hz, 2H), 5.27 (d, *J* = 10.5 Hz, 2H), 5.11-5.02 (m, 6H), 4.76 (d, *J* = 12.5 Hz, 2H), 4.35-4.32 (m, 2H), 4.06-4.04 (m, 4H), 3.99 (s, 6H), 3.68-3.65 (m, 4H), 3.52-3.45 (m, 2H), 2.82-2.78 (m, 2H), 2.35-2.32 (m, 2H), 2.14-2.05 (m, 4H), 1.87-1.84 (m, 2H), 1.56-1.53 (m, 2H); ^{13}C-NMR (75 MHz, CDCl3) δ 163.3, 16.0, 158.5, 147.0, 144.6, 139.0, 136.9, 133.0, 131.7, 126.8, 125.6, 124.8, 122.2, 118.4, 116.0, 115.8, 101.4, 70.0, 68.6, 60.4, 56.5, 51.5, 49.3, 36.8, 26.3, 24.6, 22.2; IR (KBr) 3394, 2933, 1620, 1509, 1474, 1430, 1240, 1069, 1024, 926, 861, 828, 751, 663, 553, 465, 431, 404 cm-1; $[\alpha]^{20}_{D}$ = −110 (c 0.18, $CHCl_3$); MS (FAB): 929 $[M\text{-}Br]^+$; HRMS (FAB) calcd for $[C_{54}H_{63}BrFN_4O_4]^+$: 929.4011, found: 929.4089.

1,3-Bis(quininium-*N*-methyl)-2-fluorobenzene dibromide (13)

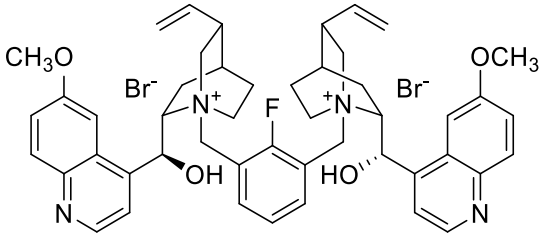


According to the procedure (**A**), the compound **13** was obtained (861.0 mg, 0.925 mmol, 97%).

Ivory solid; mp 208-209 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.82 (d, *J* = 4.6 Hz, 2H), 8.05-8.02 (m, 4H), 7.76 (d, *J* = 4.1 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.50 (dd, *J* = 9.2, 2.8 Hz, 2H), 7.42 (d, *J* = 2.3 Hz, 2H), 6.91 (s, 2H), 6.59 (s, 2H), 5.85-5.76 (m, 2H), 5.59 (d, *J* = 12.8 Hz, 2H), 5.11 (d, *J* = 17.4 Hz, 2H), 5.03 (d, *J* = 10.5 Hz, 2H), 4.77 (d, *J* = 12.8 Hz, 2H), 4.24-4.24 (m, 2H), 4.06-4.01 (m, 2H), 4.00 (s, 6H), 3.66-3.63 (m, 4H), 3.39-3.37 (m, 2H), 2.76-2.74 (m, 2H), 2.24-2.08 (m, 4H), 2.03-2.02 (m, 2H), 1.83-1.82 (m, 2H),

1.49-1.46 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 163.5, 158.7, 146.9, 144.6, 143.5, 138.7, 137.4, 130.5, 126.2, 122.0, 120.2, 116.6, 116.4, 116.3, 101.4, 68.9, 64.9, 60.7, 57.8, 55.3, 51.9, 48.3, 48.1, 47.9, 47.7, 47.5, 47.2, 47.0, 38.1, 26.7, 24.6, 21.0 ppm; IR (neat) 3230, 1620, 1509, 1240, 1032 cm^{-1}; HRMS (FAB) m/z: [M - Br]$^+$ calcd for $[C_{48}H_{55}BrFN_4O_4]^+$ 849.3391; found 849.3394. $[\alpha]^{20}_D$ = -28.90 (*c* 1.0, MeOH).

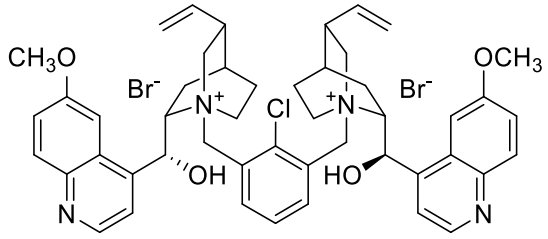
1,3-Bis(9-epi-quinidinium-N-methyl)-2-fluorobenzene dibromide (C(9)(*S*)-epi-13)



According to the procedure (**A**), the compound **C(9)(*S*)-epi-13** was obtained (501.5 mg, 0.539 mmol, 96%).

pink solid; mp 180 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, DMSO-d_6) δ 9.57 (d, *J* = 4.4 Hz, 2H), 8.90 (t, *J* = 7.2 Hz, 2H), 8.77-8.70 (m, 2H), 8.57-8.23 (m, 7H), 7.72 (d, *J* = 3.6 Hz, 2H), 6.84 (s, 2H), 6.62-6.54 (m, 2H), 6.20-6.16 (m, 2H), 5.95-5.80 (m, 4H), 5.44-5.43 (m, 2H), 5.16-5.14 (m, 2H), 4.80-4.74 (m, 4H), 4.61-4.45 (m, 6H), 4.16 (s, 6H), 3.60-3.57 (m, 2H), 2.84-2.65 (m, 6H), 1.80-1.76 (m, 2H); ^{13}C NMR (101MHz, DMSO-d_6) δ 157.7, 147.8, 144.6, 144.3, 138.3, 137.3, 131.5, 121.8, 117.1, 116.9, 116.8, 102.8, 69.1, 59.1, 58.9, 56.1, 48.8, 36.9, 36.4, 35.8, 25.6, 25.0, 24.2 IR (KBr) 3396, 2944, 1620, 1509, 1472, 1242, 1029, 853, 754 cm^{-1}; $[\alpha]^{20}_D$ = 6.9° (*c* 0.10, MeOH : CH_2Cl_2 = 1 : 1); MS (FAB): 849 [M-Br]$^+$; HRMS (FAB) calcd for $[C_{48}H_{55}BrFN_4O_4]^+$: 849.3391, found: 849.3394.

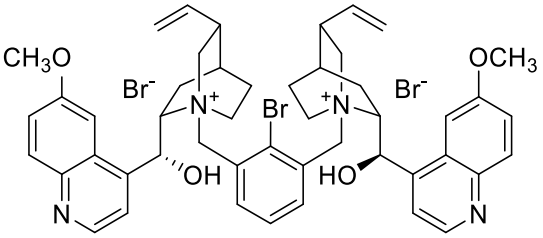
1,3-Bis(quininium-*N*-methyl)-2-chlorobenzene dibromide (14)



According to the procedure (**A**), from quinine (342.5 mg, 1.056 mmol) and 1,3-bis(bromomethyl)-2-chlorobenzene (150 mg 0.503 mmol), the compound **14** was obtained (471.1 mg, 0.497 mmol, 99%).

White solid; mp 192-193 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.76 (d, *J* = 4.6 Hz, 2H), 8.09 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 9.2 Hz, 2H), 7.90 (d, *J* = 4.6 Hz, 2H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.50 (dd, *J* = 9.4, 2.5 Hz, 2H), 7.43 (d, *J* = 2.3 Hz, 2H), 6.69 (s, 2H), 5.79-5.69 (m, 4H), 5.16-5.00 (m, 6H), 4.56-4.50 (m, 4H), 4.05 (s, 6H), 4.00-3.93 (m, 2H), 3.73-3.69 (m, 2H), 3.63-3.61 (m, 2H), 2.87-2.86 (m, 2H), 2.35-2.24 (m, 4H), 2.07-2.06 (m, 2H), 1.98-1.97 (m, 2H), 1.54-1.51 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 158.7, 147.0, 144.7, 143.4, 139.9, 138.8, 137.5, 130.6, 128.2, 127.9, 126.0, 122.0, 120.3, 116.3, 101.1, 69.3, 65.0, 61.7, 60.8, 55.3, 51.9, 38.0, 26.5, 24.7, 21.1 ppm; IR (neat) 3365, 1621, 1509, 1240, 1032, 827 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{48}H_{55}BrClN_4O_4]^+$ 865.3095; found 865.3074. $[\alpha]^{20}_D$ = -54.95 (*c* 1.0, MeOH).

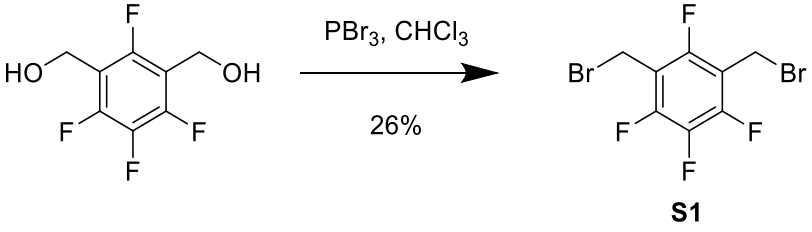
1,3-Bis(quininium-*N*-methyl)-2-bromobenzene dibromide (15)



According to the procedure (**A**), from quinine (397.4 mg, 1.225 mmol) and 2-bromo-1,3-bis(bromomethyl)benzene (200 mg 0.583 mmol), the compound **15** was obtained (548.7 mg, 0.553 mmol, 95%).

Ivory solid; mp 186-187 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.81 (d, *J* = 4.6 Hz, 2H), 8.13 (d, *J* = 7.8 Hz, 2H), 8.07 (d, *J* = 9.2 Hz, 2H), 7.96 (d, *J* = 4.6 Hz, 2H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 9.2, 2.3 Hz, 2H), 7.48 (d, *J* = 2.8 Hz, 2H), 6.73 (s, 2H), 5.84-5.75 (m, 4H), 5.19 (d, *J* = 17.0 Hz, 2H), 5.14-5.06 (m, 4H), 4.67-4.61 (m, 2H), 4.12-4.08 (m, 8H), 4.02-3.97 (m, 2H), 3.82-3.78 (m, 2H), 3.68-3.67 (m, 2H), 2.95-2.91 (m, 2H), 2.40-2.29 (m, 4H), 2.12-2.03 (m, 4H), 1.55-1.54 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 158.8, 147.0, 144.7, 143.4, 138.7, 137.5, 133.6, 130.6, 129.9, 128.8, 126.0, 122.0, 120.3, 116.2, 101.1, 69.4, 65.0, 64.4, 60.9, 55.3, 52.0, 38.0, 26.4, 24.7, 21.2 ppm; IR (neat) 3365, 1621, 1509, 1240, 1032 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{48}H_{55}Br_2N_4O_4]^+$ 829.3328; found 829.3309. $[\alpha]^{20}_D$ = -46.83 (*c* 1.0, MeOH).

1,3-Bis(bromomethyl)-2,4,5,6-tetrafluorobenzene (S1)

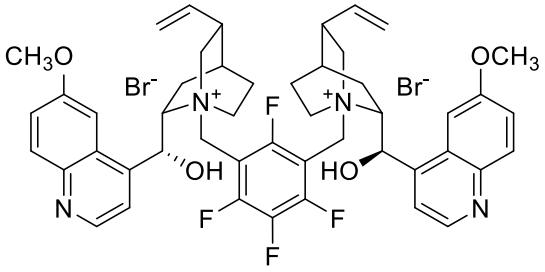


S1

To a solution of (perfluoro-1,3-phenylene)dimethanol[6] (100 mg, 0.476 mmol) in chloroform was added PBr3 (1 M in DCM, 0.952 mL, 0.952 mmol) slowly and stirred at rt for 3h. The resulting mixture was quenched with water, extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude was purified by column chromatography (silica gel, Hexane : DCM = 100:0 to 99:1) to afford **S1** (42.1 mg, 0.125 mmol, 26%).

Clear oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.43-4.48 (4H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 112.3, 112.1, 16.4 ppm; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -121.73 (d, *J* = 11.6 Hz, 1F), -133.88 (d, *J* = 23.1 Hz, 2F), -162.70 (td, *J* = 21.7, 11.6 Hz, 1F); IR (neat) 1499, 1107, 772 cm^{-1}

1,3-Bis(quininium-*N*-methyl)-2,4,5,6-tetrafluorobenzene dibromide (**16)**

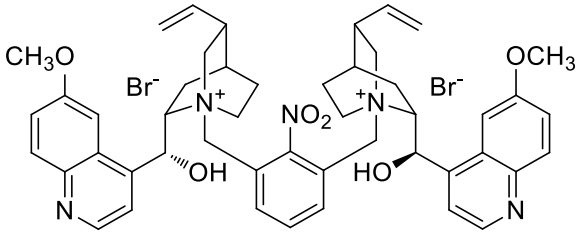


According to the procedure (**A**), from quinine (77.6 mg, 0.239 mmol) and **S1** (39.2 mg 0.117 mmol), the compound **16** was obtained (76.2 mg, 0.774 mmol, 66%).

White solid; mp 193-194 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.78 (d, *J* = 4.6 Hz, 2H), 8.04 (d, *J* = 9.6 Hz, 2H), 7.88 (d, *J* = 4.6 Hz, 2H), 7.53 (dd, *J* = 9.2, 2.8 Hz, 2H), 7.48-7.44 (m, 2H), 6.65 (s, 2H), 5.84-5.76 (m, 2H), 5.50 (d, *J* = 13.3 Hz, 2H), 5.16 (d, *J* = 17.0 Hz, 2H), 5.07 (d, *J* = 10.5 Hz, 2H), 4.62-4.62 (m, 4H), 4.34-4.30 (m, 2H), 4.13-4.09 (m, 2H), 4.07 (s, 6H), 3.76-3.70 (m, 2H), 3.62-3.60 (m, 2H), 2.96-2.90 (m, 2H), 2.37-2.27 (m, 4H), 2.12-2.01 (m, 4H), 1.61-1.60 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 159.6, 147.8,

145.2, 144.3, 138.1, 131.3, 126.9, 122.8, 121.1, 117.3, 102.2, 69.9, 65.9, 61.8, 56.2, 53.3, 52.9, 39.0, 27.1, 25.5, 21.9 ppm; IR (neat) 3375, 1621, 1506, 1241, 1031 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{48}H_{52}BrF_4N_4O_4]^+$ 903.3108; found 903.3100. $[\alpha]^{20}_D$ = -43.95 (*c* 1.0, MeOH).

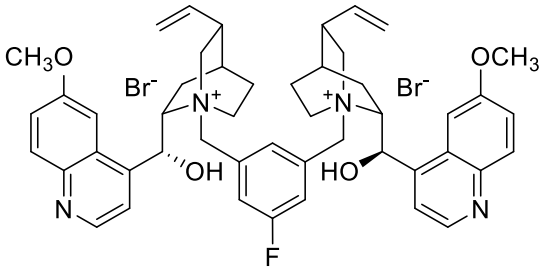
1,3-Bis(quininium-*N*-methyl)-2-nitrobenzene dibromide (17)



According to the procedure (**A**), from quinine (107.6 mg, 0.332 mmol) and 1,3-bis(bromomethyl)-2-nitrobenzene (50 mg, 0.162 mmol), the compound **17** was obtained (120.3 mg, 0.126 mmol, 78%).

Ivory solid; mp 188-189 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.78 (d, *J* = 4.6 Hz, 2H), 8.32 (d, *J* = 8.3 Hz, 2H), 8.06-8.02 (m, 3H), 7.91 (d, *J* = 4.6 Hz, 2H), 7.52 (dd, *J* = 9.2, 2.8 Hz, 2H), 7.37 (d, *J* = 2.8 Hz, 2H), 6.62 (s, 2H), 5.80-5.71 (m, 2H), 5.65 (d, *J* = 13.8 Hz, 2H), 5.18 (d, *J* = 17.0 Hz, 2H), 5.07 (d, *J* = 10.1 Hz, 2H), 4.92-4.90 (m, 2H), 4.46-4.41 (m, 2H), 4.09 (s, 6H), 4.05-4.00 (m, 2H), 3.94-3.88 (m, 2H), 3.67-3.59 (m, 4H), 2.88-2.80 (m, 2H), 2.33-2.26 (m, 4H), 2.11-2.10 (m, 2H), 2.04-2.01 (m, 2H), 1.51-1.45 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 160.2, 156.4, 148.3, 145.7, 144.8, 140.2, 138.6, 133.6, 131.9, 127.4, 123.6, 122.5, 121.7, 117.7, 102.2, 70.9, 66.4, 62.6, 60.7, 56.7, 53.8, 39.3, 27.7, 26.0, 22.6 ppm; IR (neat) 1536, 1471, 1358, 1240, 1024 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{48}H_{55}BrN_5O_6]^+$ 876.3336; found 876.3351. $[\alpha]^{20}_D$ = -49.87 (*c* 1.0, MeOH).

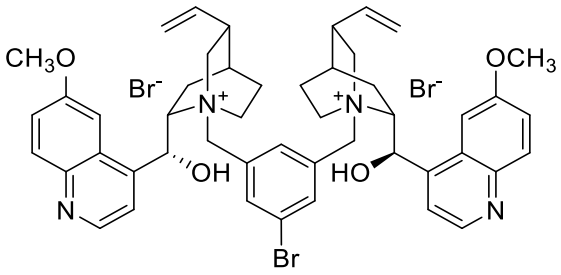
1,3-Bis(quininium-*N*-methyl)-5-fluorobenzene dibromide (18)



According to the procedure (**A**), from quinine (147.4 mg, 0.454 mmol) and 1,3-bis(bromomethyl)-5-fluorobenzene (62.5 mg, 0.222 mmol), the compound **18** was obtained (198.1 mg, 0.213 mmol, 96%).

Ivory solid; mp 214-215 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.77 (d, *J* = 4.6 Hz, 2H), 8.14 (s, 1H), 8.03 (d, *J* = 9.6 Hz, 2H), 7.90 (d, *J* = 4.6 Hz, 2H), 7.74-7.71 (m, 2H), 7.52 (dd, *J* = 9.4, 2.5 Hz, 2H), 7.44 (d, *J* = 2.3 Hz, 2H), 6.68 (s, 2H), 5.82-5.74 (m, 2H), 5.58 (d, *J* = 12.8 Hz, 2H), 5.21 (d, *J* = 17.0 Hz, 2H), 5.07 (d, *J* = 10.5 Hz, 2H), 4.63-4.60 (m, 2H), 4.46-4.40 (m, 2H), 4.08 (s, 6H), 3.99-3.94 (m, 2H), 3.86-3.80 (m, 2H), 3.74-3.70 (m, 2H), 3.62-3.55 (m, 2H), 2.87-2.80 (m, 2H), 2.42-2.37 (m, 2H), 2.31-2.30 (m, 2H), 2.11-2.10 (m, 2H), 2.00-1.95 (m, 2H), 1.63-1.57 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 160.1, 148.2, 146.0, 144.7, 138.6, 132.1, 132.0, 131.8, 127.4, 124.0, 123.8, 123.3, 121.7, 117.7, 102.6, 70.6, 65.9, 64.3, 61.9, 56.8, 53.1, 39.2, 28.1, 25.8, 22.1 ppm; IR (neat) 3382, 1620, 1509, 1240, 1024 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{48}H_{55}BrFN_4O_4]^+$ 849.3391; found 849.3405. $[\alpha]^{20}_D$ = -46.92 (*c* 1.0, MeOH).

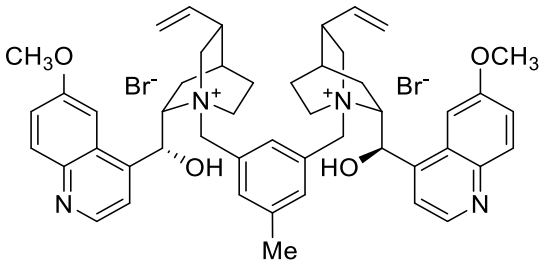
1,3-Bis(quininium-*N*-methyl)-5-bromobenzene dibromide (19)



According to the procedure (**A**), from quinine (48.5 mg, 0.150 mmol) and 1,3-bis(bromomethyl)-5-bromobenzene (25 mg, 0.073 mmol), the compound **19** was obtained (70.3 mg, 0.071 mmol, 97%).

Ivory solid; mp 201-202 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.77 (d, *J* = 5.0 Hz, 2H), 8.29 (s, 1H), 8.10 (d, *J* = 0.9 Hz, 2H), 8.03 (d, *J* = 9.6 Hz, 2H), 7.90 (d, *J* = 4.6 Hz, 2H), 7.52 (dd, *J* = 9.4, 2.5 Hz, 2H), 7.44 (d, *J* = 2.3 Hz, 2H), 6.67 (s, 2H), 5.83-5.74 (m, 2H), 5.56 (d, *J* = 12.4 Hz, 2H), 5.20 (d, *J* = 17.4 Hz, 2H), 5.07 (d, *J* = 10.5 Hz, 2H), 4.87-4.80 (m, 2H), 4.47-4.42 (m, 2H), 4.07 (s, 6H), 3.98-3.90 (m, 2H), 3.82-3.76 (m, 2H), 3.72-3.68 (m, 2H), 3.57-3.50 (m, 2H), 2.86-2.84 (m, 2H), 2.42-2.37 (m, 2H), 2.34-2.31 (m, 2H), 2.10-2.00 (m, 2H), 1.99-1.94 (m, 2H), 1.64-1.58 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 158.8, 146.9, 144.7, 143.5, 138.2, 137.9, 137.3, 130.7, 130.5, 126.1, 123.5, 121.9, 120.3, 116.4, 101.3, 69.2, 64.6, 62.8, 60.6, 55.4, 51.7, 37.9, 26.9, 24.5, 20.8 ppm; IR (neat) 1620, 1509, 1240, 1031, 719 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{48}H_{55}Br_2N_4O_4]^+$ 909.2615; found 909.2590. $[\alpha]^{20}_D$ = -46.85 (*c* 1.0, MeOH).

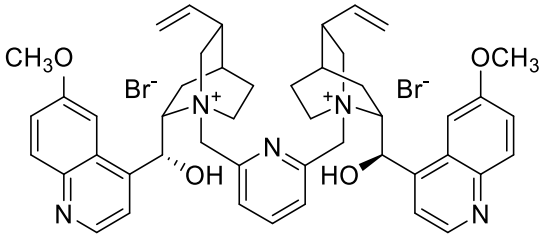
1,3-Bis(quininium-*N*-methyl)-5-methylbenzene dibromide (20)



According to the procedure (**A**), from quinine (59.8 mg, 0.1844 mmol) and 1,3-bis(bromomethyl)-5-bromobenzene (25 mg, 0.090 mmol), the compound **20** was obtained (78.5 mg, 0.085 mmol, 94%)

White solid; mp 208-209 °C (MeOH- Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.77 (d, *J* = 4.6 Hz, 2H), 8.04-8.02 (m, 3H), 7.90 (d, *J* = 4.6 Hz, 2H), 7.66 (s, 2H), 7.52 (dd, *J* = 9.2, 2.3 Hz, 2H), 7.45 (d, *J* = 2.8 Hz, 2H), 6.69 (s, 2H), 5.83-5.75 (m, 2H), 5.52 (d, *J* = 12.4 Hz, 2H), 5.20 (d, *J* = 17.0 Hz, 2H), 5.06 (d, *J* = 10.5 Hz, 2H), 4.85 (d, *J* = 12.4 Hz, 2H), 4.44-4.38 (m, 2H), 4.07 (s, 6H), 3.99-3.94 (m, 2H), 3.79-3.74 (m, 2H), 3.69-3.65 (m, 2H), 3.55-3.51 (m, 2H), 2.84-2.80 (m, 2H), 2.48 (s, 3H), 2.42-2.38 (m, 2H), 2.32-2.30 (m, 2H), 2.10-2.09 (m, 2H), 1.98-1.96 (m, 2H), 1.65-1.59 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 160.0, 148.2, 146.1, 144.7, 141.9, 138.7, 137.4, 137.2, 131.8, 129.7, 127.4, 123.3, 121.6, 117.6, 102.5, 70.3, 65.8, 64.9, 61.8, 56.6, 52.9, 39.2, 28.2, 25.8, 22.0, 21.2 ppm; IR (neat) 2948, 1620, 1509, 1240, 1054 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{49}H_{58}BrN_4O_4]^+$ 845.3641; found 845.3632. $[\alpha]^{20}_D$ = -46.70 (*c* 1.0, MeOH).

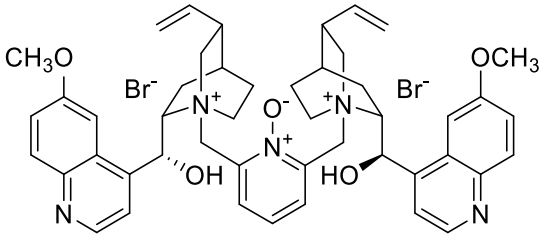
1,3-Bis(quininium-*N*-methyl)-pyridine dibromide (21)



According to the procedure (**A**), from quinine (88.5 mg, 0.273 mmol) and 2,6-bis(bromomethyl)pyridine (34.4 mg 0.130 mmol), the compound **21** was obtained (101.9 mg, 0.112 mmol, 86%).

Yellow solid; mp 223-224 °C (MeOH- Et_2O, decomp.); ^{1}H-NMR (400 MHz, DMSO-d_6) δ 9.64 (d, *J* = 4.6 Hz, 2H), 9.06 (t, *J* = 7.8 Hz, 1H), 8.88 (d, *J* = 7.8 Hz, 2H), 8.85 (d, *J* = 9.2 Hz, 2H), 8.59 (d, *J* = 4.6 Hz, 2H), 8.34 (dd, *J* = 9.2, 2.8 Hz, 2H), 8.25 (d, *J* = 2.8 Hz, 2H), 7.91 (s, 2H), 7.43 (s, 2H), 6.65-6.56 (m, 2H), 6.43 (d, *J* = 12.4 Hz, 2H), 5.92 (d, *J* = 17.4 Hz, 2H), 5.84 (d, *J* = 10.5 Hz, 2H), 5.67 (d, *J* = 12.4 Hz, 2H), 5.13-5.10 (m, 2H), 4.86 (s, 6H), 4.82-4.77 (m, 2H), 4.68-4.62 (m, 2H), 4.54-4.53 (m, 2H), 4.18-4.13 (m, 2H), 3.60-3.58 (m, 2H), 3.08-3.07 (m, 2H), 2.97-2.96 (m, 2H), 2.85-2.81 (m, 2H), 2.67-2.64 (m, 2H), 2.34-2.31 (m, 2H) ppm; ^{13}C-NMR (101 MHz, DMSO-d_6) δ 157.9, 150.1, 148.0, 144.5, 144.2, 139.7, 138.6, 132.0, 130.0, 126.0, 121.8, 120.9, 117.1, 103.0, 69.1, 64.4, 64.3, 60.2, 56.2, 51.8, 37.9, 26.5, 24.9, 20.9 ppm; IR (neat) 1621, 1508, 1032 cm^{-1}; HRMS (FAB) m/z: $[M - 2Br - H]^+$ calcd for $[C_{47}H_{54}N_5O_4]^+$ 752.4176; found 752.4164. $[\alpha]^{20}_D$ = -41.57 (*c* 1.0, DMSO).

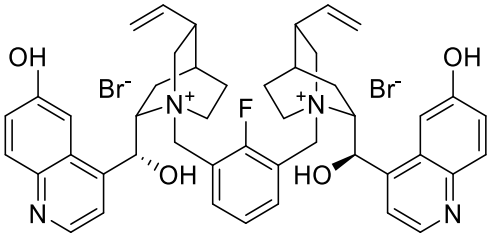
1,3-Bis(quininium-*N*-methyl)-pyridine-*N*-oxide dibromide (22)



According to the procedure (**A**), from quinine (363.7 mg, 1.1212 mmol) and 2,6-bis(bromomethyl)pyridine *N*-oxide (150 mg 0.5339 mmol), the compound **22** was obtained (484.2 mg, 0.52 mmol, 98%).

White solid; mp 206-207 °C (MeOH- Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.79 (d, *J* = 4.6 Hz, 2H), 8.23 (d, *J* = 7.8 Hz, 2H), 8.04 (d, *J* = 9.2 Hz, 2H), 7.88 (d, *J* = 4.6 Hz, 2H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.52 (dd, *J* = 9.4, 2.5 Hz, 2H), 7.44 (d, *J* = 2.3 Hz, 2H), 6.67 (s, 2H), 5.85-5.77 (m, 2H), 5.55 (d, *J* = 12.8 Hz, 1H), 5.35 (d, *J* = 12.4 Hz, 1H), 5.19-5.06 (m, 4H), 4.65-4.60 (m, 2H), 4.54-4.49 (m, 2H), 4.11-3.97 (m, 10H), 3.91-3.87 (m, 2H), 3.71-3.65 (m, 2H), 2.90-2.89 (m, 2H), 2.38-2.25 (m, 4H), 2.11-2.10 (m, 2H), 2.04-2.02 (m, 2H), 1.62-1.57 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 159.5, 147.8, 145.4, 144.2, 141.5, 138.3, 135.5, 131.4, 126.8, 126.8, 122.9, 120.8, 117.0, 101.7, 70.1, 65.8, 61.8, 59.0, 56.3, 53.9, 38.9, 26.9, 25.6, 21.8 ppm; IR (neat) 3365, 1620, 1508, 1240, 1023 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{47}H_{55}BrN_5O_5]^+$ 848.3387; found 848.3372. $[\alpha]^{20}_D$ = -46.26 (*c* 1.0, MeOH).

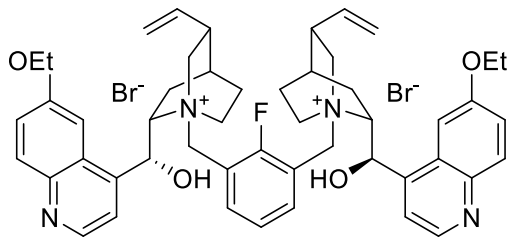
1,3-Bis(cupreinium-*N*-methyl)-2-fluorobenzene dibromide (23)



According to the procedure (**A**), from cupreine (synthesized according to the literatures)[8] (451.8 mg 1.456 mmol) and 1,3-frrbromomethyl)-2-fluorobenzene (200.2 mg, 0.710 mmol), the compound **23** was obtained (636.4 mg, 0.705 mmol, 99%)

Reddish solid; mp 218-219 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.61 (d, *J* = 4.6 Hz, 2H), 7.96 (t, *J* = 7.1 Hz, 2H), 7.88 (d, *J* = 9.6 Hz, 2H), 7.77 (d, *J* = 4.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.36-7.33 (m, 4H), 6.46 (s, 2H), 5.78-5.69 (m, 2H), 5.35 (d, *J* = 12.8 Hz, 2H), 5.17 (d, *J* = 17.0 Hz, 2H), 5.03 (d, *J* = 10.5 Hz, 2H), 4.95-4.95 (m, 2H), 4.39-4.39 (m, 2H), 4.05-4.01 (m, 2H), 3.85-3.79 (m, 2H), 3.63-3.61 (m, 2H), 3.48-3.46 (m, 2H), 2.84-2.84 (m, 2H), 2.31-2.22 (m, 4H), 2.07-2.06 (m, 2H), 1.97-1.95 (m, 2H), 1.53-1.47 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 160.1, 145.1, 143.2, 141.9, 138.7, 137.4, 130.2, 126.5, 125.6, 124.1, 119.6, 116.5, 116.3, 103.6, 68.7, 64.9, 60.8, 57.3, 51.6, 37.9, 26.5, 24.6, 20.9 ppm; IR (neat) 2965, 1619, 1487, 1238, 1053 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{46}H_{51}BrFN_4O_4]^+$ 742.3894; found 742.3891. $[\alpha]^{20}_D$ = -5.52 (*c* 1.0, MeOH).

1,3-Bis(6'-ethoxy-cinchonidium-*N*-methyl)-2-fluorobenzene dibromide (24)

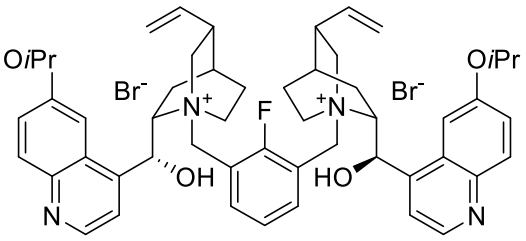


According to the procedure (**A**), from 6'-ethoxy-cinchonidine (synthesized according to the literatures)[7] (64.6 mg, 0.191 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (26.3 mg, 0.093 mmol), the compound **24** was obtained (89.0 mg, 0.093 mmol, quant.).

Light brown solid; mp 192-193 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ

8.73 (d, *J* = 4.6 Hz, 2H), 8.01 (d, *J* = 9.2 Hz, 2H), 7.97 (t, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 4.6 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.50 (dd, *J* = 9.2, 2.3 Hz, 2H), 7.46 (d, *J* = 2.3 Hz, 2H), 6.60 (s, 2H), 5.82-5.74 (m, 2H), 5.42 (d, *J* = 13.3 Hz, 2H), 5.14 (d, *J* = 17.4 Hz, 2H), 5.03 (d, *J* = 10.5 Hz, 2H), 4.84-4.82 (m, 2H), 4.36-4.25 (m, 6H), 4.04-3.90 (m, 4H), 3.62-3.54 (m, 4H), 2.89-2.81 (m, 2H), 2.34-2.22 (m, 4H), 2.07-1.96 (m, 4H), 1.63-1.57 (m, 2H), 1.45 (t, *J* = 6.9 Hz, 6H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 158.1, 146.9, 144.5, 143.4, 138.8, 137.5, 130.5, 126.3, 125.9, 122.0, 120.2, 116.6, 116.4, 116.4, 102.2, 68.7, 65.0, 64.1, 60.8, 57.6, 51.9, 38.1, 26.7, 24.7, 21.1, 13.9 ppm; IR (neat) 3202, 1619, 1509, 1240, 1039 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{50}H_{59}BrFN_4O_4]^+$ 877.3704; found 877.3692. $[\alpha]^{20}_D$ = -18.64 (*c* 1.0, MeOH).

1,3-Bis(6'-isopropoxy-cinchonidium-*N*-methyl)-2-fluorobenzene dibromide (25)

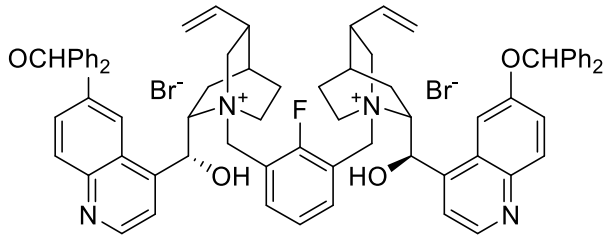


According to the procedure (**A**), from 6'-isopropoxy-cinchonidine (synthesized according to the literatures)[7] (149.8 mg, 0.425 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (58.5 mg, 0.207 mmol), the compound **25** was obtained (56.4 mg, 0.057 mmol, 28%).

Brown solid; mp 189-190 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.76 (d, *J* = 4.6 Hz, 2H), 8.05 (d, *J* = 9.2 Hz, 2H), 7.99 (t, *J* = 7.3 Hz, 2H), 7.85 (d, *J* = 4.6 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.54 (dd, *J* = 9.2, 2.8 Hz, 2H), 7.51 (d, *J* = 2.3 Hz, 2H), 6.59 (s, 2H), 5.85-5.76 (m, 2H), 5.42 (d, *J* = 12.8 Hz, 2H), 5.16 (d, *J* = 17.0 Hz, 2H), 5.06 (d, *J* = 10.5 Hz, 2H), 5.01-4.95 (m, 2H), 4.93-4.91 (m, 2H), 4.34-4.30 (m, 2H), 4.05-4.01 (m, 2H), 3.97-3.91

(m, 2H), 3.58-3.55 (m, 4H), 2.91-2.90 (m, 2H), 2.36-2.32 (m, 2H), 2.28-2.22 (m, 2H), 2.11-2.10 (m, 2H), 2.04-2.02 (m, 2H), 1.65-1.59 (m, 2H), 1.42 (dd, *J* = 8.3, 6.0 Hz, 12H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 158.3, 148.3, 145.7, 144.7, 140.1, 138.8, 132.0, 127.7, 127.3, 123.6, 121.6, 117.9, 117.7, 105.5, 71.8, 70.2, 66.5, 62.4, 59.0, 53.2, 39.4, 28.0, 26.0, 22.6, 22.5, 22.4 ppm; IR (neat) 1508, 1240, 1017 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{52}H_{63}BrFN_4O_4]^+$ 905.4017; found 905.4025. $[\alpha]^{20}_D$ = -7.01 (*c* 1.0, MeOH).

1,3-Bis(6'-diphenylmethoxy-cinchonidium-*N*-methyl)-2-fluorobenzene dibromide (26)

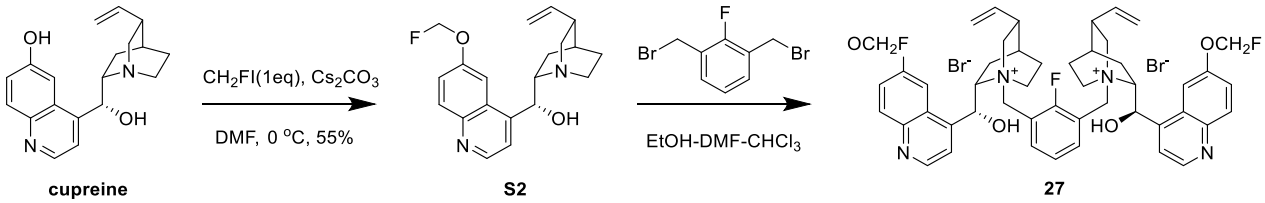


According to the procedure (**A**), from 6'- diphenylmethoxy-cinchonidine (synthesized according to the literatures)[8] (109.4 mg, 0.230 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (31.6 mg, 0.112 mmol), the compound **26** was obtained (114.0 mg, 0.092 mmol, 82%)

Pale yellow solid; mp 195-196 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.74 (d, *J* = 4.6 Hz, 2H), 8.03 (d, *J* = 9.6 Hz, 2H), 7.98 (t, *J* = 7.3 Hz, 2H), 7.80 (d, *J* = 4.6 Hz, 2H), 7.67-7.60 (m, 3H), 7.58-7.55 (m, 6H), 7.52-7.50 (m, 4H), 7.36 (t, *J* = 7.6 Hz, 4H), 7.28-7.18 (m, 8H), 6.97 (s, 2H), 6.35 (s, 2H), 5.65-5.56 (m, 2H), 5.13 (d, *J* = 13.3 Hz, 2H), 5.07 (d, *J* = 17.0 Hz, 2H), 4.99 (d, *J* = 10.1 Hz, 2H), 4.77 (d, *J* = 12.8 Hz, 2H), 4.27-4.20 (m, 2H), 4.02-3.96 (m, 2H), 3.80-3.76 (m, 2H), 3.58-3.55 (m, 2H), 3.39-3.36 (m, 2H), 2.88-2.80 (m, 2H), 2.24-2.19 (m, 2H), 2.12-2.10 (m, 2H), 2.02-2.01 (m, 4H), 1.53-1.47 (m, 2H) ppm; ^{13}C-NMR

(101 MHz, CD_3OD) δ 156.8, 147.2, 144.2, 143.5, 141.2, 141.1, 138.9, 137.5, 130.7, 128.5, 128.4, 127.8, 127.7, 126.9, 126.8, 126.1, 122.8, 120.5, 116.6, 116.4, 116.2, 104.6, 81.3, 68.3, 65.4, 61.3, 57.5, 51.9, 38.0, 26.6, 24.7, 21.5 ppm; IR (neat) 3383, 1619, 1508, 1238, 1004, 743 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{72}H_{71}BrFN_4O_4]^+$ 1153.4643; found 1153.4666. $[\alpha]^{20}_D$ = -39.83 (*c* 1.0, MeOH).

Procedure for 1,3-Bis(6'-fluoromethoxy-cinchonidium-N-methyl)-2-fluorobenzene dibromide(27)



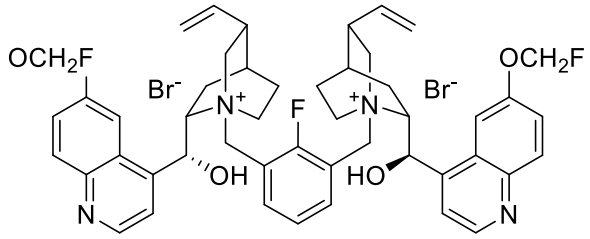
(*R*)-[6-(fluoromethoxy)quinolin-4-yl][(1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl]methanol (S2)

A mixture of cupreine (synthesized according to the literatures)[8] (213.0 mg, 0.686 mmol) and cesium carbonate (670.7 mg, 2.059 mmol) in DMF (4.3 mL) was added fluoroiodomethane (2 M in acetonitrile, 0.343 mL, 0.686 mmol) at 0 °C and stirred for 2h. The resulting mixture was quenched with water, extracted with dichloromethane, washed with ammonia water and brine, dried over $MgSO_4$, filtered and concentrated. The crude was purified by column chromatography (silica gel, DCM : MeOH = 100:0 to 90:10) to afford **S2** (125.2 mg, 0.366 mmol, 53%).

Pink solid; mp 197-198 °C ($MeOH-Et_2O$, decomp.); ^1H-NMR (400 MHz, CD_3OD) δ 8.76 (d,

J = 4.6 Hz, 1H), 8.06 (d, *J* = 9.6 Hz, 1H), 7.81 (d, *J* = 2.3 Hz, 1H), 7.72 (d, *J* = 4.6 Hz, 1H), 7.58 (dd, *J* = 9.1, 2.3 Hz, 1H), 6.08-5.89 (m, 2H), 5.83-5.74 (m, 1H), 5.54-5.53 (m, 1H), 5.01-4.91 (m, 2H), 3.64-3.59 (m, 1H), 3.18-3.06 (m, 2H), 2.70-2.66 (m, 2H), 2.35-2.30 (m, 1H), 1.90-1.82 (m, 3H), 1.63-1.51 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 156.10, 156.08, 151.51, 149.74, 145.84, 142.89, 132.12, 128.01, 123.06, 120.65, 115.01, 107.82, 102.67, 100.51, 72.69, 61.55, 57.64, 44.06, 41.06, 29.32, 28.39, 22.55 ppm; IR (neat) 2937, 1623, 1510, 1217, 1095, 758 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{20}H_{24}FN_2O_2]^+$ 343.1822; found 343.1825. $[\alpha]^{20}_D$ = -100.43 (*c* 1.0, $CHCl_3$).

1,3-Bis(6'-fluoromethoxy-cinchonidium-*N*-methyl)-2-fluorobenzene dibromide(27)

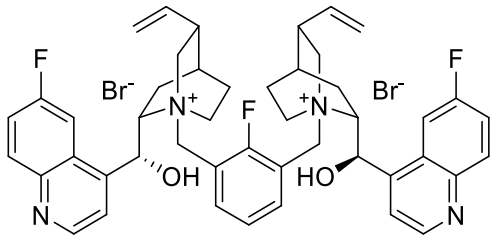


According to the procedure (**A**), from **S2** (95.5 mg, 0.280 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (38.5 mg, 0.136 mmol), the compound **27** was obtained (123.0 mg, 0.127 mmol, 93%).

Pink solid; mp 204-205 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.87 (d, *J* = 4.6 Hz, 2H), 8.12 (d, *J* = 9.1 Hz, 2H), 8.00 (t, *J* = 7.3 Hz, 2H), 7.93 (d, *J* = 4.6 Hz, 2H), 7.82 (d, *J* = 2.7 Hz, 2H), 7.64 (dd, *J* = 9.1, 2.7 Hz, 2H), 7.60 (d, *J* = 7.3 Hz, 1H), 6.70 (s, 2H), 6.10 (dd, *J* = 48.0, 3.7 Hz, 2H), 5.96 (dd, *J* = 46.7, 3.2 Hz, 2H), 5.84-5.75 (m, 2H), 5.53 (d, *J* = 12.8 Hz, 2H), 5.16 (d, *J* = 16.9 Hz, 2H), 5.05 (d, *J* = 10.5 Hz, 2H), 4.86-4.80 (m, 2H), 4.36-4.30 (m, 2H), 4.07-4.03 (m, 2H), 3.93-3.88 (m, 2H), 3.64-3.52 (m, 4H), 2.92-2.91 (m, 2H),

2.40-2.29 (m, 4H), 2.14-2.10 (m, 2H), 2.04-1.98 (m, 2H), 1.64-1.58 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 156.9, 156.9, 150.0, 147.0, 145.9, 140.2, 138.8, 132.6, 127.5, 127.2, 123.5, 121.9, 118.0, 117.9, 117.8, 107.6, 103.7, 101.5, 70.9, 66.2, 62.1, 59.4, 53.2, 39.5, 28.1, 26.0, 22.1 ppm; IR (neat) 1621, 1509, 1240, 1095, 770 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{48}H_{53}BrF_3N_4O_4]^+$ 885.3202; found 885.3227. $[\alpha]^{20}_D$ = -39.01 (*c* 1.0, MeOH).

1,3-Bis(6'-fluoro-cinchonidium-*N*-methyl)-2-fluorobenzene dibromide (28)

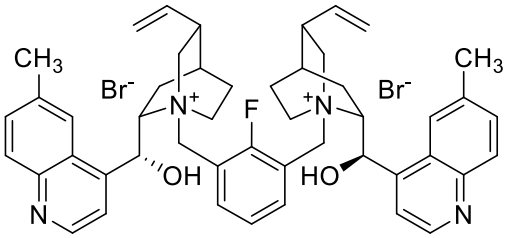


According to the procedure (**A**), from 6'-fluoro-cinchonidine (synthesized according to the literatures)[9] (33.7 mg, 0.108 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (14.8 mg, 0.053 mmol), the compound **28** was obtained (45.2 mg, 0.050 mmol, 95%).

Pale yellow solid; mp 196-197 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.90 (d, *J* = 4.6 Hz, 2H), 8.17 (dd, *J* = 9.4, 5.7 Hz, 2H), 8.03 (dd, *J* = 9.9, 2.5 Hz, 2H), 7.97 (t, *J* = 7.3 Hz, 2H), 7.91 (d, *J* = 4.6 Hz, 2H), 7.65-7.70 (m, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 6.52 (s, 2H), 5.82-5.74 (m, 2H), 5.24 (d, *J* = 12.8 Hz, 2H), 5.15 (d, *J* = 17.0 Hz, 2H), 5.05 (d, *J* = 7.8 Hz, 2H), 5.02 (d, *J* = 5.0 Hz, 2H), 4.30-4.24 (m, 2H), 4.08-4.03 (m, 2H), 3.96-3.90 (m, 2H), 3.69-3.65 (m, *J* = 3.4 Hz, 2H), 3.56-3.49 (m, 2H), 2.88-2.80 (m, 2H), 2.28-2.13 (m, 4H), 2.08-2.07 (m, 2H), 2.01-1.97 (m, 2H), 1.59-1.47 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 159.83, 149.20, 145.65, 145.59, 144.84, 138.74, 137.54, 132.01, 131.92, 125.83, 120.83, 120.10, 119.84, 116.44, 116.30, 106.81, 68.00, 65.24, 60.95, 57.15, 51.94, 38.03, 26.61, 24.72,

21.41 ppm; IR (neat) 1624, 1514, 1460, 1174, 921 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{46}H_{49}BrF_3N_4O_2]^+$ 825.2991; found 825.3002. $[\alpha]^{20}_D$ = -19.06 (*c* 1.0, MeOH).

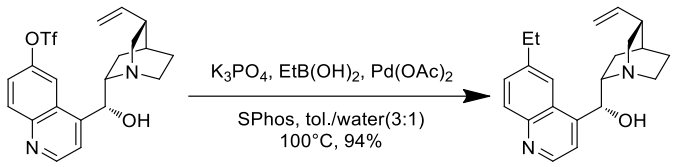
1,3-Bis(6'-methyl-cinchonidium-*N*-methyl)-2-fluorobenzene dibromide (29)



According to the procedure (**A**), from 6'-methyl-cinchonidine (synthesized according to the literatures)[10] (67.5 mg, 0.219 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (30.1 mg, 0.107 mmol), the compound **29** was obtained (51.9 mg, 0.058 mmol, 54%).

Ivory solid; mp 202-203 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.90 (d, *J* = 4.6 Hz, 2H), 8.12 (t, *J* = 7.1 Hz, 2H), 8.03-7.99 (m, 4H), 7.76 (d, *J* = 4.1 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 6.98 (s, 2H), 6.54 (s, 2H), 5.82-5.74 (m, 2H), 5.46 (d, *J* = 12.8 Hz, 2H), 5.18 (d, *J* = 17.4 Hz, 2H), 5.07-5.00 (m, 4H), 4.26-4.20 (m, 2H), 4.10-4.02 (m, 2H), 3.78-3.72 (m, 2H), 3.67-3.62 (m, 2H), 3.32-3.30 (m, 2H), 2.75-2.70 (m, 2H), 2.63 (s, 6H), 2.19-2.08 (m, 4H), 2.02-1.99 (m, 2H), 1.83-1.80 (m, 2H), 1.44-1.38 (m, 2H) ppm; ^{13}C-NMR (101 MHz, DMSO-d_6) δ 149.7, 146.8, 145.0, 138.9, 138.6, 137.3, 132.1, 130.2, 125.0, 122.7, 120.6, 117.2, 117.0, 68.3, 64.5, 56.8, 51.2, 37.9, 26.3, 24.9, 22.2, 21.4 ppm; IR (neat) 1747, 1508, 1217, 1031, 773 cm^{-1}; HRMS (ESI) m/z: $[M - 2Br - H]^+$ calcd for $[C_{48}H_{54}FN_4O_2]^+$ 737.4225; found 737.4256. $[\alpha]^{20}_D$ = -2.92 (*c* 1.0, MeOH).

6'-Ethyl-cinchonidine (S3)

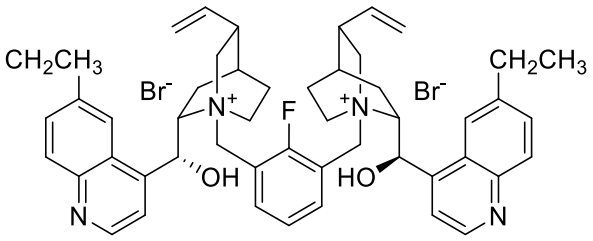


S3

A mixture of 6'-*O*-trifluoromethylsulfonyl-cinchonidine (synthesized according to the literatures)[8] (300 mg, 0.678 mmol), potassium phosphate tribasic (359.8, 1.695 mmol), ethyl boronic acid (77.5 mg, 1.017 mmol), palladium acetate (15.2 mg, 0.068 mmol) and SPhos (55.7 mg, 0.136 mmol) in toluene-water (3:1, 4.5 mL) was stirred at 100 °C for 2h. The resulting mixture was quenched with 1 N HCl, washed with dichloromethane. The aqueous layer was basified with NH_4OH solution, extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude was purified by column chromatography (silica gel, DCM : MeOH = 100:0 to 90:10) afford **S3** (206.2 mg, 0.639 mmol, 94%).

White solid; mp 168-169 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.1 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.78 (s, 1H), 7.53-7.50 (m, 2H), 5.76-5.68 (m, 2H), 4.97-4.89 (m, 2H), 3.50-3.45 (m, 1H), 3.18-3.07 (m, 2H), 2.77 (q, *J* = 7.5 Hz, 2H), 2.71-2.64 (m, 2H), 2.28 (s, 1H), 1.82-1.71 (m, 3H), 1.56-1.46 (m, 2H), 1.26 (t, *J* = 7.6 Hz, 3H) ppm ^{13}C-NMR (101 MHz, $CDCl_3$) δ 149.34, 148.27, 146.99, 143.08, 141.67, 130.30, 130.15, 125.72, 120.77, 118.19, 114.60, 77.43, 77.11, 76.80, 71.63, 60.31, 57.00, 43.37, 39.88, 29.33, 27.92, 27.52, 21.66, 15.99 ppm; IR (neat) 2931, 1589, 1507, 1101, 758 cm^{-1}; HRMS (FAB) m/z: [M + H]+ calcd for $[C_{21}H_{27}N_2O]^+$ 323.2123; found 323.2129. $[\alpha]^{20}_D$ = -75.24 (*c* 1.0, $CHCl_3$).

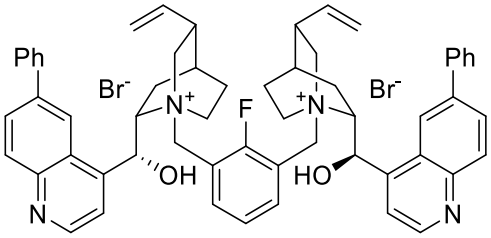
1,3-Bis(6'-ethyl-cinchonidium-*N*-methyl)-2-fluorobenzene dibromide (30)



According to the procedure (**A**), from 6'-ethyl-cinchonidine (**S3**) (150 mg, 0.465 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (64.0 mg 0.227 mmol), the compound **30** was obtained (201.9 mg, 0.218 mmol, 96%).

Ivory solid; mp 189-190 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (500 MHz, DMSO-d_6) δ 8.90 (d, *J* = 4.3 Hz, 2H), 8.12 (t, *J* = 7.3 Hz, 2H), 8.04-8.01 (m, 4H), 7.77 (d, *J* = 4.5 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.25 (s, 2H), 6.62 (s, 2H), 5.82-5.75 (m, 2H), 5.56 (d, *J* = 12.6 Hz, 2H), 5.17 (d, *J* = 17.3 Hz, 2H), 5.01-4.97 (m, 4H), 4.28-4.28 (m, 2H), 4.09-4.06 (m, 2H), 3.72-3.67 (m, 3H), 3.40-3.38 (m, 2H), 2.96-2.92 (m, 4H), 2.79-2.73 (m, 2H), 2.19-2.08 (m, 4H), 2.02-2.02 (m, 2H), 1.85-1.85 (m, 2H), 1.44-1.40 (m, 2H), 1.32 (t, *J* = 7.6 Hz, 6H) ppm; ^{13}C-NMR (126 MHz, DMSO-d_6) δ 161.3, 150.1, 147.4, 145.7, 143.7, 139.2, 138.9, 131.2, 130.7, 126.2, 125.4, 121.8, 120.9, 117.5, 117.4, 117.3, 69.0, 64.7, 60.0, 57.3, 51.5, 38.2, 29.3, 26.6, 25.2, 21.7, 16.4 ppm; IR (neat) 2965, 1508, 1032, 772 cm^{-1}; HRMS (ESI) m/z: $[M - 2Br - H]^+$ calcd for $[C_{50}H_{59}BrFN_4O_2]^+$ 845.3805; found 845.3792. $[\alpha]^{20}_D$ = -57.48 (*c* 1.0, MeOH).

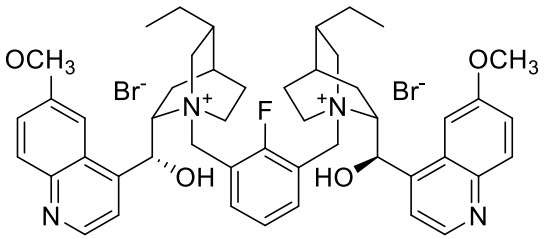
1,3-Bis(6'-phenyl-cinchonidium-*N*-methyl)-2-fluorobenzene dibromide (31)



According to the procedure (**A**), from 6'-phenyl-cinchonidine (synthesized according to the literatures)[8] (120.0 mg mg, 0.324 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (44.5 mg, 0.158 mmol), the compound **31** was obtained (161.8 mg, 0.158 mmol, quant.).

Brown solid; mp 193-194 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.94 (d, *J* = 4.6 Hz, 2H), 8.41 (s, 2H), 8.22 (d, *J* = 8.7 Hz, 2H), 8.15 (dd, *J* = 8.9, 1.6 Hz, 2H), 7.97-7.94 (m, 4H), 7.89 (d, *J* = 7.3 Hz, 4H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 4H), 7.39 (t, *J* = 7.3 Hz, 2H), 6.82 (s, 2H), 5.84-5.75 (m, 2H), 5.48 (d, *J* = 13.3 Hz, 2H), 5.14 (d, *J* = 17.4 Hz, 2H), 5.04 (d, *J* = 10.1 Hz, 2H), 4.85 (s, 2H), 4.37 (t, *J* = 10.8 Hz, 2H), 4.13 (t, *J* = 8.5 Hz, 2H), 3.85 (t, *J* = 11.5 Hz, 2H), 3.61-3.48 (m, 4H), 2.88 (d, *J* = 4.6 Hz, 2H), 2.39 (q, *J* = 6.4 Hz, 2H), 2.29 (s, 2H), 2.11 (d, *J* = 2.3 Hz, 2H), 2.02-1.96 (m, 2H), 1.70-1.64 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 149.6, 146.9, 146.3, 140.6, 140.2, 138.7, 137.4, 129.7, 129.6, 128.9, 127.9, 127.5, 125.4, 120.5, 120.2, 116.6, 116.4, 69.1, 64.9, 60.8, 57.6, 51.9, 38.1, 26.7, 24.7, 21.1 ppm; IR (neat) 3370, 1572, 1491, 756 cm^{-1}; HRMS (ESI) m/z: $[M - 2Br - H]^+$ calcd for $[C_{58}H_{58}FN_4O_2]^+$ 861.4553; found 861.4538. $[\alpha]^{20}_D$ = -21.61 (*c* 1.0, MeOH).

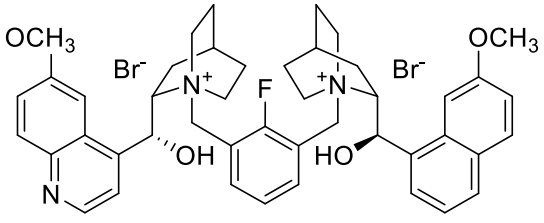
1,3-Bis(hydroquininium-*N*-methyl)-2-fluorobenzene dibromide (32)



According to the procedure (**A**), from hydroquinine (200 mg, 0.613 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (84.3 mg 0.299 mmol), the compound **32** was obtained. (177.2 mg, 0.190 mmol, 63%).

Yellow solid; mp 209-210 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.77 (d, *J* = 4.6 Hz, 2H), 8.04 (d, *J* = 9.2 Hz, 2H), 7.98 (t, *J* = 7.3 Hz, 2H), 7.88 (d, *J* = 4.6 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.52 (dd, *J* = 9.2, 2.8 Hz, 2H), 7.48 (d, *J* = 2.3 Hz, 2H), 6.67 (s, 2H), 5.48 (d, *J* = 12.8 Hz, 2H), 4.81 (d, *J* = 12.8 Hz, 2H), 4.62-4.60 (m, 2H), 4.32-4.30 (m, 2H), 4.07 (s, 6H), 4.03-3.99 (m, 2H), 3.92-3.87 (m, 2H), 3.53-3.52 (m, 2H), 3.40-3.38 (m, 2H), 2.38-2.33 (m, 2H), 2.25-2.24 (m, 2H), 2.07-2.00 (m, 4H), 1.94-1.92 (m, 2H), 1.63-1.48 (m, 2H), 1.40-1.30 (m, 4H), 0.84-0.80 (m, 6H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 158.7, 146.9, 144.7, 143.5, 138.6, 130.5, 126.2, 125.9, 122.0, 120.3, 116.6, 116.5, 101.4, 68.8, 64.9, 62.6, 57.7, 55.3, 51.9, 35.8, 25.8, 25.2, 24.4, 20.7, 10.3 ppm; IR (neat) 2957, 1620, 1509, 1240, 1024, 829 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{48}H_{59}BrFN_4O_4]^+$ 853.3704; found 853.3714. $[\alpha]^{20}_D$ = -36.86 (*c* 1.0, MeOH).

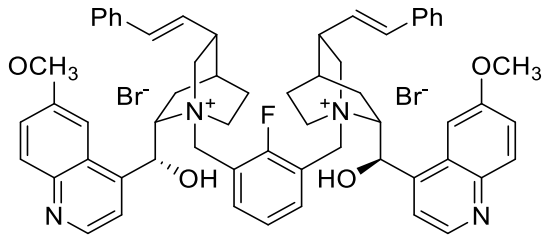
1,3-Bis(3-desvinyl-quininium-*N*-methyl)-2-fluorobenzene dibromide (33)



According to the procedure (**A**), from 3-desvinylquinine (synthesized according to the literatures)[11] (73.6 mg, 0.247 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (34.8 mg 0.120 mmol), the compound **33** was obtained (102.2 mg, 0.116 mmol, 97%).

Pale yellow solid; mp 215-216 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.80 (d, *J* = 5.0 Hz, 2H), 8.06 (d, *J* = 9.2 Hz, 2H), 8.01 (t, *J* = 7.3 Hz, 2H), 7.92 (d, *J* = 4.6 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 9.4, 2.5 Hz, 2H), 7.51 (d, *J* = 2.3 Hz, 2H), 6.69 (s, 2H), 5.40 (d, *J* = 13.3 Hz, 2H), 4.87-4.87 (m, 2H), 4.64 (s, 4H), 4.50-4.49 (m, 2H), 4.12-4.10 (m, 8H), 3.91-3.86 (m, 2H), 3.68-3.66 (m, 2H), 3.59 (d, *J* = 9.2 Hz, 2H), 2.46-2.41 (m, 2H), 2.16-2.09 (m, 4H), 1.97-1.88 (m, 6H), 1.44-1.38 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 158.7, 146.9, 144.6, 143.4, 138.6, 130.5, 126.1, 125.8, 121.9, 120.2, 116.7, 116.5, 101.5, 68.4, 65.2, 57.6, 57.1, 55.3, 52.0, 25.5, 23.8, 23.0, 20.6 ppm; IR (neat) 2912, 1621, 1508, 1032 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{44}H_{51}BrFN_4O_4]^+$ 797.3078; found 797.3079. $[\alpha]^{20}_D$ = -25.00 (*c* 1.0, MeOH).

1,3-Bis(11-*trans*-phenyl-quininium-*N*-methyl)-2-fluorobenzene dibromide (34)

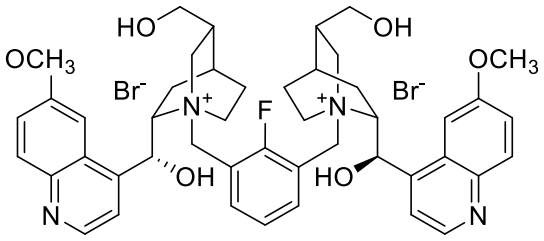


According to the procedure (**A**), from 11-(phenyl)-quinine (synthesized according to the literatures)[12] (99.0 mg, 0.247 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (34.0 mg 0.121 mmol), the compound **34** was obtained (102.2 mg, 0.116 mmol, 97%)

Pale yellow solid; mp 215-216 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ

8.75-8.72 (m, 2H), 7.99 (d, *J* = 8.7 Hz, 2H), 7.95 (t, *J* = 7.3 Hz, 2H), 7.82 (d, *J* = 4.6 Hz, 2H), 7.54-7.45 (m, 4H), 7.23 (d, *J* = 7.3 Hz, 3H), 7.18 (t, *J* = 7.3 Hz, 4H), 7.15-7.11 (m, 2H), 6.62 (s, 2H), 6.48 (d, *J* = 15.6 Hz, 2H), 6.24 (q, *J* = 7.9 Hz, 2H), 5.40 (d, *J* = 12.8 Hz, 2H), 4.23-4.16 (m, 2H), 4.01 (s, 6H), 3.68-3.58 (m, 4H), 3.08-3.06 (m, 2H), 2.34 (q, *J* = 5.8 Hz, 2H), 2.25-2.23 (m, 2H), 2.12-2.12 (m, 2H), 2.07-2.04 (m, 2H), 1.77-1.77 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 158.7, 147.0, 144.6, 143.5, 138.7, 136.6, 132.4, 130.5, 128.4, 128.3, 128.2, 127.4, 126.3, 126.0, 126.0, 121.9, 120.1, 101.6, 68.8, 64.9, 61.2, 57.8, 55.2, 52.1, 37.8, 27.2, 24.8, 21.2 ppm; IR (neat) 3394, 1621, 1509, 1240, 1026, 751 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{60}H_{63}BrFN_4O_4]^+$ 1001.4017; found 1001.4052. $[\alpha]^{20}_D$ = -47.06 (*c* 1.0, MeOH).

1,3-Bis(10-hydroxy-11-norquinnium-*N*-methyl)-2-fluorobenzene dibromide (35)

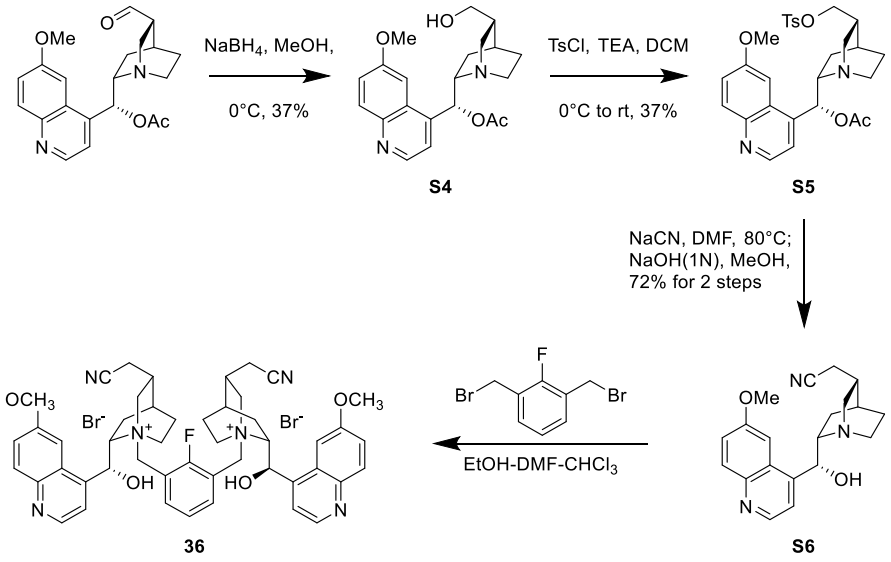


According to the procedure (**A**), from 10-hydroxy-11-norquinine (synthesized according to the literatures)[13] (38.1 mg, 0.116 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (16.0 mg 0.057 mmol), the compound **35** was obtained (19.7 mg, 0.021 mmol, 37%)

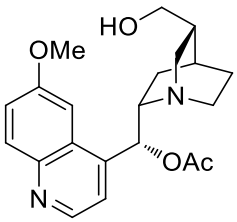
Brown solid; mp 195-196 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.81 (t, *J* = 4.1 Hz, 2H), 8.07 (d, *J* = 9.2 Hz, 2H), 8.01 (t, *J* = 7.3 Hz, 2H), 7.91 (d, *J* = 4.6 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.56 (dd, *J* = 9.4, 2.5 Hz, 2H), 7.47 (d, *J* = 2.8 Hz, 2H), 6.67 (s, 2H), 5.49 (d, *J* = 12.8 Hz, 2H), 4.67 (m, 2H), 4.51-4.45 (m, 2H), 4.15-4.08 (m, 8H), 3.74-3.68 (m,

2H), 3.51-3.44 (m, 8H), 2.38-2.33 (m, 2H), 2.28-2.28 (m, 4H), 2.19-2.19 (m, 2H), 1.95-1.88 (m, 4H), 1.62-1.56 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 158.7, 147.0, 144.6, 143.4, 138.6, 130.6, 126.1, 121.8, 120.2, 116.7, 116.5, 101.4, 69.1, 65.0, 62.2, 59.8, 57.7, 55.1, 36.6, 25.3, 23.1, 22.9, 21.6 ppm; IR (neat) 2951, 1621, 1510, 1219, 1019, 835 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{46}H_{55}BrFN_4O_6]^+$ 875.3296; found 875.3287. $[\alpha]^{20}_D$ = -187.77 (*c* 0.5, MeOH).

Procedure for 1,3-Bis*(*10-cyano-11-norquinnium-N-methyl)-2-fluorobenzene dibromide **(1f)**



(*R*)-[(1*S*,2*S*,4*S*,5*R*)-5-(hydroxymethyl)quinuclidin-2-yl](6-methoxyquinolin-4-yl)methyl acetate (S4)

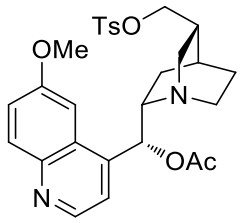


To a compound (1*S*,3*R*,4*S*,6*S*)-6-[(*R*)-hydroxy(6-methoxyquinolin-4-yl)methyl]quinuclidine-

3-carbaldehyde (synthesized according to the literatures)[14] (1.21g, 3.3 mmol) in dry MeOH (33 mL) was added slowly sodium borohydride (800.1 mg, 21.15 mmol) at 0 °C and stirred at rt for 2h. The reaction was quenched with water, extracted with DCM, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, DCM : MeOH = 100:0 to 80:20) to afford **S4** (445.4 mg, 1.202 mmol, 36%).

Pale yellow sticky caramel; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.6 Hz, 1H), 8.00 (d, *J* = 9.1 Hz, 1H), 7.42 (s, 1H), 7.36 (dd, *J* = 9.4, 2.5 Hz, 1H), 7.32 (d, *J* = 4.6 Hz, 1H), 6.52 (s, 1H), 3.96 (s, 3H), 3.55 (d, *J* = 7.3 Hz, 2H), 3.28-3.34 (m, 1H), 3.13-3.13 (m, 1H), 2.97-3.03 (m, 1H), 2.69-2.69 (m, 1H), 2.40-2.40 (m, 1H), 2.12 (s, 3H), 2.00-2.03 (m, 1H), 1.76-1.82 (m, 2H), 1.60-1.60 (m, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 158.02, 147.64, 146.79, 144.29, 131.80, 126.37, 121.74, 118.44, 118.38, 113.47, 101.02, 71.37, 59.85, 56.92, 55.92, 42.97, 32.61, 27.31, 25.76, 21.86, 20.41, 20.20 ppm ; IR (neat) 2942, 1620, 1509, 1230, 1027, 754 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{21}H_{27}N_2O_4]^+$ 371.1971; found 371.1978. $[\alpha]^{20}_D$ = -12.76 (*c* 1.0, $CHCl_3$).

(*R*)-(6-methoxyquinolin-4-yl)[(1*S*,2*S*,4*S*,5*R*)-5-[(tosyloxy)methyl]quinuclidin-2-yl]methyl acetate (S5)

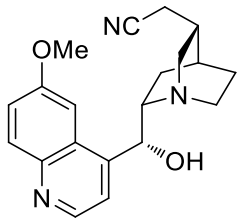


To a solution of a compound **S4** (300 mg, 0.81 mmol) in dichloromethane (8 mL) were added

tosyl chloride (209.2 mg, 1.215 mmol) and trimethylamine (0.23 mL, 1.62 mmol) at 0 °C. The mixture was stirred at rt for overnight. The resulting solution was quenched with water, extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude was purified by column chromatography (silica gel, DCM : MeOH = 100:0 to 95:5) afford **S5** (158.6 mg, 0.3025 mmol, 37%).

White sticky caramel; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.6 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.26-7.36 (m, 5H), 6.43-6.45 (m, 1H), 3.93 (s, 3H), 3.89-3.92 (m, 1H), 3.84-3.88 (m, 1H), 3.16-3.23 (m, 1H), 3.08-3.08 (m, 1H), 2.89-2.95 (m, 1H), 2.56-2.64 (m, 1H), 2.40 (s, 3H), 2.22-2.26 (m, 1H), 2.10 (s, 3H), 1.89-2.02 (m, 2H), 1.63-1.72 (m, 2H), 1.45-1.53 (m, 2H) ppm;^{13}C-NMR (101 MHz, $CDCl_3$) δ 170.04, 158.09, 147.48, 145.05, 144.85, 143.30, 132.87, 131.96, 129.98, 127.90, 126.99, 121.97, 118.84, 101.42, 73.48, 71.87, 59.10, 55.82, 53.51, 42.51, 34.68, 27.43, 23.90, 23.03, 21.76, 21.17 ppm; IR (neat) 2945, 1743, 1621, 1509, 1359, 1230, 1029, 838 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{28}H_{33}N_2O_6S]^+$ 525.2059; found 525.2053. $[\alpha]^{20}_D$ = -5.80 (*c* 1.0, $CHCl_3$).

2-[(1*S*,3*R*,4*S*,6*S*)-6-[(*R*)-hydroxy(6-methoxyquinolin-4-yl)methyl]quinuclidin-3-yl]acetonitrile (S6)

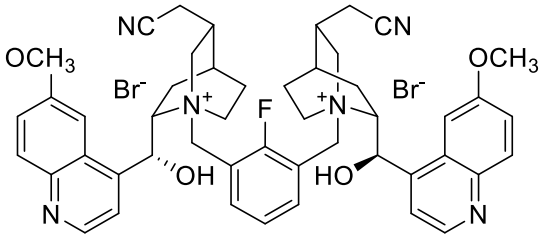


To a solution of a compound **S5** (80 mg, 0.153 mmol) in DMF (1 mL) was added sodium cyanide (15.0 mg, 0.305 mmol) and stirred at 80 °C for overnight. The resulting solution was

quenched with water, extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered and concentrated. To the crude in methanol (1.5 mL) was added potassium carbonate (105.7 mg, 0.765 mmol) and stirred for 2 h. The resulting mixture was quenched with water, extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude was purified by column chromatography (silica gel, DCM : MeOH = 100:0 to 90:10) afford **S6** (37.2 mg, 0.110 mmol, 72%)

Clear sticky caramel; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.8 Hz, 1H), 7.93 (d, *J* = 9.2 Hz, 1H), 7.44 (d, *J* = 4.6 Hz, 1H), 7.30 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.15 (d, *J* = 2.8 Hz, 1H), 5.49 (d, *J* = 4.1 Hz, 1H), 3.87 (s, 3H), 3.42-3.49 (m, 1H), 3.11-3.17 (m, 1H), 2.97-3.02 (m, 1H), 2.58-2.65 (m, 1H), 2.36-2.41 (m, 1H), 2.16-2.33 (m, 2H), 1.93-2.01 (m, 2H), 1.76-1.89 (m, 2H), 1.35-1.50 (m, 2H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 157.92, 147.60, 147.42, 144.21, 131.66, 126.52, 121.60, 118.67, 118.36, 101.25, 77.44, 77.33, 77.11, 76.80, 71.95, 59.87, 57.16, 55.80, 42.89, 32.78, 27.69, 25.87, 21.90, 20.76 ppm; IR (neat) 2932, 2349, 1620, 1508, 1230, 1027, 772 cm^{-1}; $[\alpha]^{20}_D$ = -35.29 (*c* 1.0, $CHCl_3$).

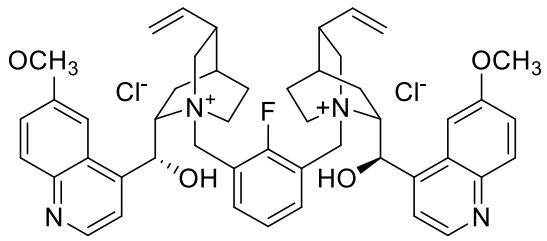
1,3-Bis(10-cyano-11-norquinnium-*N*-methyl)-2-fluorobenzene dibromide (36)



According to the procedure (**A**), from a compound **S6** (26.2 mg, 0.078 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (10.7 mg 0.038 mmol), the compound **36** was obtained (23.1 mg, 0.024 mmol, 63%).

Brown solid; mp 202-203 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.80 (d, *J* = 5.0 Hz, 2H), 8.06 (d, *J* = 9.2 Hz, 2H), 7.99 (t, *J* = 7.3 Hz, 2H), 7.90 (d, *J* = 4.6 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.55 (dd, *J* = 9.2, 2.3 Hz, 2H), 7.48 (d, *J* = 2.3 Hz, 2H), 6.69 (s, 2H), 5.53 (d, *J* = 12.8 Hz, 2H), 4.86-4.83 (m, 2H), 4.65-4.65 (m, 4H), 4.44-4.41 (m, 2H), 4.14-3.99 (m, 8H), 3.60-3.53 (m, 2H), 2.65-2.54 (m, 4H), 2.52-2.46 (m, 2H), 2.35-2.34 (m, 2H), 2.19-2.19 (m, 2H), 2.04-2.02 (m, 2H), 1.88 (s, 2H), 1.71-1.68 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 158.7, 147.0, 144.5, 143.5, 138.8, 130.5, 126.2, 126.1, 121.9, 120.3, 117.7, 116.4, 116.3, 101.5, 69.0, 64.7, 60.5, 57.9, 55.1, 52.1, 48.3, 48.1, 47.9, 47.7, 47.5, 47.2, 47.0, 31.5, 24.9, 22.9, 20.2, 19.5 ppm; IR (neat) 2349, 1621, 1509, 1240, 1032 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{48}H_{53}BrFN_6O_4]^+$ 875.3296; found 875.3304. $[\alpha]^{20}_D$ = -20.97 (*c* 1.0, MeOH).

1,3-Bis(quininium-*N*-methyl)-2-fluorobenzene dichloride (37)

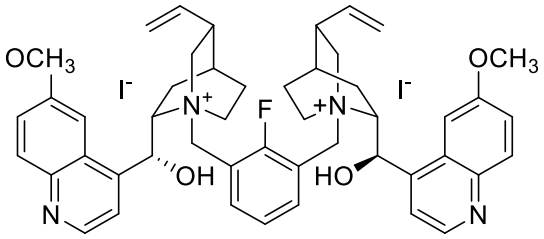


According to the procedure (**B**), from **13** (100.0 mg, 0.107 mmol) and hydrogen chloride (1 N aq. solution, 1 mL, 1.074 mmol), the compound **37** was obtained (67.0 mg, 0.080 mmol, 74%).

Ivory solid; mp 201-202 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.77 (d, *J* = 4.3 Hz, 2H), 7.98-8.04 (m, 4H), 7.87 (d, *J* = 4.3 Hz, 2H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.52 (dd, *J* = 9.5, 2.8 Hz, 2H), 7.47 (d, *J* = 2.4 Hz, 2H), 6.65 (s, 2H), 5.75-5.84 (m, 2H), 5.50 (d, *J* = 11.6 Hz, 2H), 5.16 (d, *J* = 17.1 Hz, 2H), 5.06 (d, *J* = 10.4 Hz, 2H), 4.85-4.85 (m, 2H), 4.33-4.39 (m,

2H), 4.05 (s, 6H), 4.01-4.03 (m, 2H), 3.82-3.88 (m, 2H), 3.61-3.63 (m, 2H), 3.47-3.54 (m, 2H), 2.87-2.87 (m, 2H), 2.34-2.39 (m, 2H), 2.27-2.27 (m, 2H), 2.09-2.10 (m, 2H), 1.95-2.00 (m, 2H), 1.59-1.65 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 160.08, 148.30, 145.92, 144.81, 140.06, 140.04, 138.73, 131.89, 127.48, 123.20, 121.54, 117.92, 117.78, 117.70, 102.76, 70.27, 66.18, 62.08, 58.99, 56.53, 54.83, 53.20, 39.43, 27.98, 25.99, 22.31 ppm; IR (neat) 1473, 1175, 1026, 769 cm^{-1}; HRMS (FAB) m/z: $[M - Cl]^+$ calcd for $[C_{48}H_{55}ClFN_4O_4]^+$ 805.3896; found 805.3889. $[\alpha]^{20}_D$ = -235.74 (*c* 1.0, MeOH).

1,3-Bis(quininium-*N*-methyl)-2-fluorobenzene diiodide(38)

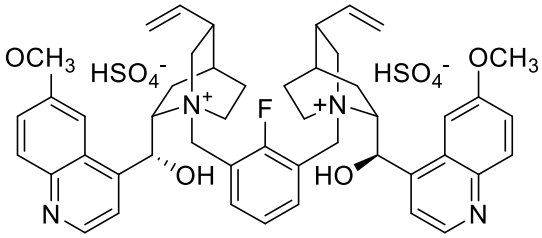


According to the procedure (**B**), from **13** (100.0 mg, 0.107 mmol) and hydrogen iodide (1 N aq. solution, 1 mL, 1.074 mmol), the compound **38** was obtained (29.1 mg, 0.028 mmol, 26%).

Yellow solid; mp 185-186 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.82 (d, *J* = 4.6 Hz, 2H), 8.03 (d, *J* = 9.2 Hz, 2H), 7.98 (t, *J* = 7.3 Hz, 2H), 7.76 (d, *J* = 4.6 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.51 (dd, *J* = 9.2, 2.8 Hz, 2H), 7.41 (d, *J* = 2.8 Hz, 2H), 6.71 (d, *J* = 3.7 Hz, 2H), 6.59 (d, *J* = 2.8 Hz, 2H), 5.84-5.75 (m, 2H), 5.51 (d, *J* = 12.8 Hz, 2H), 5.10 (d, *J* = 17.4 Hz, 2H), 5.02 (d, *J* = 10.1 Hz, 2H), 4.75 (d, *J* = 12.8 Hz, 2H), 4.16-4.10 (m, 2H), 4.01 (s, 6H), 3.97-3.97 (m, 2H), 3.73-3.71 (m, 2H), 3.65-3.65 (m, 2H), 3.50-3.47 (m, 2H), 2.87-2.85 (m, 2H), 2.25-2.21 (m, 2H), 2.12-2.08 (m, 2H), 2.04-2.04 (m, 2H), 1.90-1.85 (m, 2H), 1.50-1.44 (m, 2H) ppm; ^{13}C-NMR (101 MHz, DMSO-d_6) δ 157.9, 148.0, 144.3, 144.2, 139.0, 138.5,

132.0, 126.3, 125.9, 122.0, 120.8, 117.1, 117.0, 116.8, 102.8, 68.8, 64.5, 59.5, 57.5, 56.1, 51.3, 37.7, 26.3, 24.6, 21.0 ppm; IR (neat) 1621, 1509, 1259, 1038, 769 cm^{-1}; HRMS (FAB) m/z: [M - I]$^+$ calcd for $[C_{48}H_{55}FIN_4O_4]^+$ 897.3247; found 897.3271. $[\alpha]^{20}_D$ = -150.41 (*c* 1.0, DMSO).

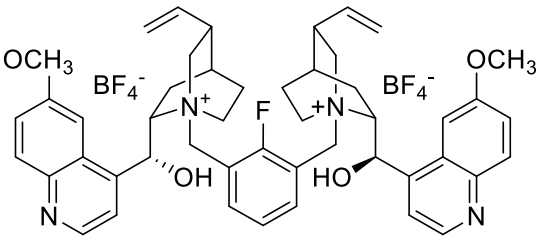
1,3-Bis(quininium-*N*-methyl)-2-fluorobenzene di(hydrogen sulfate) (39)



According to the procedure (**B**), from **13** (100.0 mg, 0.107 mmol) and sulfuric acid (1 N aq. solution, 1 mL, 1.074 mmol), the compound **39** was obtained (95.2 mg, 0.099 mmol, 92%).

White solid; mp 199-200 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.79 (d, *J* = 5.0 Hz, 2H), 8.10-8.03 (m, 6H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.49 (dd, *J* = 9.2, 2.3 Hz, 2H), 7.46 (s, 2H), 6.83 (s, 2H), 5.81-5.74 (m, 2H), 5.70 (d, *J* = 15.1 Hz, 2H), 5.16 (d, *J* = 17.0 Hz, 2H), 5.06 (d, *J* = 10.5 Hz, 2H), 4.82-4.82 (m, 2H), 4.52-4.49 (m, 2H), 4.08 (s, 6H), 3.99-3.93 (m, 2H), 3.72-3.69 (m, 2H), 3.59-3.58 (m, 2H), 3.46-3.45 (m, 2H), 2.83-2.81 (m, 2H), 2.32-2.28 (m, 4H), 2.09-2.09 (m, 2H), 2.00-1.93 (m, 2H), 1.57-1.52 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 159.5, 149.6, 143.9, 138.8, 138.6, 137.4, 127.2, 126.4, 125.8, 124.0, 120.6, 116.5, 116.4, 101.7, 69.0, 64.8, 60.7, 57.8, 55.5, 51.7, 38.0, 26.6, 24.6, 20.9 ppm; IR (neat) 1621, 1509, 1472, 1240, 1032, 829 cm^{-1}; HRMS (FAB) m/z: [M - HSO_4]$^+$ calcd for $[C_{48}H_{56}FN_4O_8S]^+$ 867.3803; found 867.3794. $[\alpha]^{20}_D$ = -42.40 (*c* 1.0, MeOH).

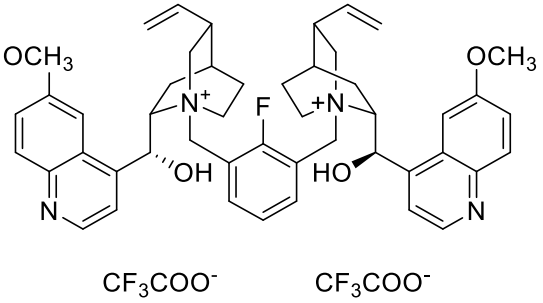
1,3-Bis(quininium-*N*-methyl)-2-fluorobenzene di(tetrafluoroborate) (40)



A mixture of **13** (50.0 mg, 0.054 mmol) and sodium tetrafluoroborate (17.7 mg, 0.161 mmol) in acetonitrile(1 mL) was stirred for overnight. The resulting suspension was filtered and washed with methanol and water. The solid was dried *in vacuo*. The compound **40** was obtained (43.1 mg, 0.046 mmol, 85%).

White solid; mp 228-229 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.81 (d, *J* = 4.6 Hz, 2H), 8.03-7.97 (m, 4H), 7.76 (d, *J* = 4.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.50 (dd, *J* = 9.2, 2.8 Hz, 2H), 7.40 (d, *J* = 2.3 Hz, 2H), 6.92 (s, 2H), 6.59 (s, 2H), 5.82-5.73 (m, 2H), 5.53 (d, *J* = 12.8 Hz, 2H), 5.10 (d, *J* = 17.0 Hz, 2H), 5.02 (d, *J* = 10.5 Hz, 2H), 4.77 (d, *J* = 12.4 Hz, 2H), 4.18-4.18 (m, 2H), 4.02-4.02 (m, 2H), 4.00 (s, 6H), 3.67-3.61 (m, 4H), 3.33-3.31 (m, 2H), 2.76-2.74 (m, 2H), 2.23-2.07 (m, 4H), 2.02-2.02 (m, 2H), 1.83-1.83 (m, 2H), 1.49-1.43 (m, 2H) ppm; ^{13}C-NMR (101 MHz, DMSO-d_6) δ 157.9, 148.0, 144.4, 144.2, 138.9, 138.5, 131.9, 126.1, 125.9, 122.1, 120.8, 117.2, 117.0, 116.9, 102.7, 68.7, 64.4, 59.6, 57.4, 56.0, 51.3, 37.8, 26.3, 24.8, 21.0 ppm; IR (neat) 1748, 1508, 1362, 1227, 1032, 772 cm^{-1}; HRMS (FAB) m/z: $[M - BF_4]^+$ calcd for $[C_{48}H_{55}BF_5N_4O_4]^+$ 857.4239; found 857.4222. $[\alpha]^{20}_D$ = -47.92 (*c* 1.0, DMSO).

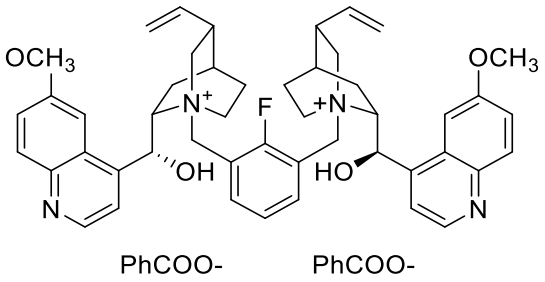
1,3-Bis(quininium-*N*-methyl)-2-fluorobenzene di(trifluoromethylacetate) (41)



According to the procedure (**B**), from **13** (100.0 mg, 0.107 mmol) and trifluoroacetic acid (0.08 mL, 1.074 mmol), the compound **41** was obtained (91.1 mg, 0.091 mmol, 85%).

Ivory solid; mp 208-209 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.79 (d, *J* = 4.6 Hz, 2H), 8.05 (d, *J* = 9.2 Hz, 2H), 8.00 (t, *J* = 7.4 Hz, 2H), 7.90 (d, *J* = 4.1 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 9.4, 2.5 Hz, 2H), 7.45 (d, *J* = 2.8 Hz, 2H), 6.67 (s, 2H), 5.82-5.73 (m, 2H), 5.53 (d, *J* = 12.9 Hz, 2H), 5.16 (d, *J* = 17.0 Hz, 2H), 5.08 (d, *J* = 10.6 Hz, 2H), 4.85-4.85 (m, 2H), 4.47-4.42 (m, 2H), 4.04 (s, 6H), 4.01-4.01 (m, 2H), 3.74-3.60 (m, 4H), 3.42-3.36 (m, 2H), 2.80-2.78 (m, 2H), 2.41-2.29 (m, 4H), 2.12-2.12 (m, 2H), 1.96-1.91 (m, 2H), 1.62-1.56 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 162.9 (q, *J* = 34.4 Hz), 160.1, 148.3, 145.9, 144.7, 140.0, 138.6, 131.9, 127.4, 127.3, 123.1, 121.6, 118.2 (q, *J* = 293.2 Hz), 117.9, 117.8, 117.7, 102.7, 70.4, 66.2, 62.1, 58.9, 56.4, 53.2, 49.8, 49.7, 49.6, 49.5, 49.4, 49.3, 49.2, 49.1, 49.0, 48.8, 48.6, 48.4, 39.4, 27.9, 26.0, 22.3 ppm; IR (neat) 1671, 1509, 1200, 1131, 1032, 721 cm^{-1}; HRMS (FAB) m/z: $[M - C_2F_3O_2]^+$ calcd for $[C_{50}H_{55}F_4N_4O_6]^+$ 883.4058; found 883.4072. $[\alpha]^{20}_D$ = -39.97 (*c* 1.0, MeOH).

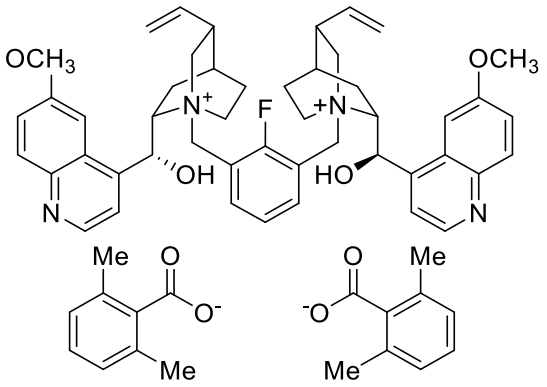
1,3-Bis(quininium-*N*-methyl)-2-fluorobenzene dibenzoate (42)



According to the procedure (**B**), from **13** (100.0 mg, 0.107 mmol) and benzoic acid (131.2 mg, 1.074 mmol), the compound **42** was obtained (105.1 mg, 0.104 mmol, 97%).

Brown solid; mp 166-167 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.77 (d, *J* = 4.6 Hz, 2H), 8.04 (d, *J* = 9.2 Hz, 2H), 7.98 (t, *J* = 7.3 Hz, 2H), 7.91-7.88 (m, 6H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 9.4, 2.5 Hz, 2H), 7.45 (d, *J* = 2.8 Hz, 2H), 7.42 (tt, *J* = 7.3, 1.8 Hz, 2H), 7.36-7.31 (m, 4H), 6.70 (s, 2H), 5.80-5.72 (m, 2H), 5.56 (d, *J* = 13.3 Hz, 2H), 5.14 (d, *J* = 17.0 Hz, 2H), 5.07 (d, *J* = 10.5 Hz, 2H), 4.84 (d, *J* = 12.8 Hz, 2H), 4.47-4.42 (m, 2H), 4.01 (s, 6H), 4.01-3.98 (m, 2H), 3.69-3.59 (m, 4H), 3.36-3.33 (m, 2H), 2.76-2.74 (m, 2H), 2.40-2.29 (m, 4H), 2.10-2.09 (m, 2H), 1.91-1.88 (m, 2H), 1.60-1.54 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 172.6, 158.7, 147.0, 144.7, 143.4, 138.7, 137.3, 135.9, 130.6, 129.0, 127.6, 126.1, 125.9, 121.6, 120.3, 116.7, 116.5, 116.4, 101.6, 69.2, 64.7, 60.7, 57.5, 55.0, 51.8, 38.1, 26.5, 24.7, 21.0 ppm; IR (neat) 1621, 1509, 1240, 1032, 721 cm^{-1}; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $[C_{62}H_{65}FN_4O_8Na]^+$ 1035.4679; found 1035.4736. $[\alpha]^{20}_D$ = -37.85 (*c* 1.0, MeOH).

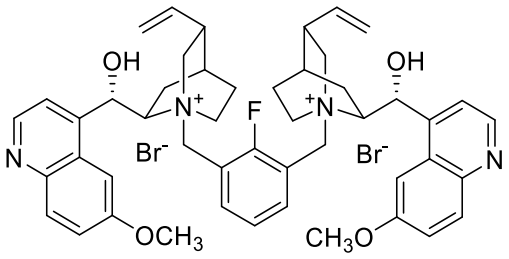
1,3-Bis(quininium-*N*-methyl)-2-fluorobenzene di(2,6-dimethylbenzoate) (43)



According to the procedure (**B**), from **13** (100.0 mg, 0.107 mmol) and 2,6-dimethyl benzoic acid (161.3 mg, 1.074 mmol), the compound **43** was obtained (114.0 mg, 0.107 mmol, 99%)

Ivory solid; mp 175-176 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.77 (d, *J* = 4.6 Hz, 2H), 8.04 (t, *J* = 7.3 Hz, 4H), 7.88 (d, *J* = 4.6 Hz, 2H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.56 (dd, *J* = 9.4, 2.5 Hz, 2H), 7.41 (d, *J* = 2.8 Hz, 2H), 6.96 (dd, *J* = 8.5, 6.6 Hz, 2H), 6.88 (d, *J* = 7.3 Hz, 4H), 6.62 (s, 2H), 5.81-5.73 (m, 2H), 5.59 (d, *J* = 12.8 Hz, 2H), 5.16 (d, *J* = 17.0 Hz, 2H), 5.09 (d, *J* = 10.1 Hz, 2H), 4.83 (d, *J* = 12.8 Hz, 2H), 4.54-4.49 (m, 2H), 4.03 (s, 6H), 4.00-3.98 (m, 2H), 3.65-3.62 (m, 4H), 3.36-3.34 (m, 2H), 2.76-2.74 (m, 2H), 2.40-2.33 (m, 4H), 2.24 (s, 12H), 2.11-2.11 (m, 2H), 1.89-1.89 (m, 2H), 1.56-1.56 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 178.6, 159.7, 148.1, 145.7, 144.4, 143.4, 139.7, 138.3, 132.9, 131.7, 127.6, 127.2, 127.1, 122.5, 121.4, 117.7, 117.6, 117.5, 102.7, 70.3, 65.7, 61.7, 58.5, 56.1, 52.8, 39.2, 27.6, 25.7, 22.0, 19.5 ppm; IR (neat) 1624, 1511, 1241, 1026 cm^{-1}; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $[C_{57}H_{64}FN_4O_6]^+$ 769.4129; found 769.4158. $[\alpha]^{20}_D$ = -37.07 (*c* 1.0, MeOH).

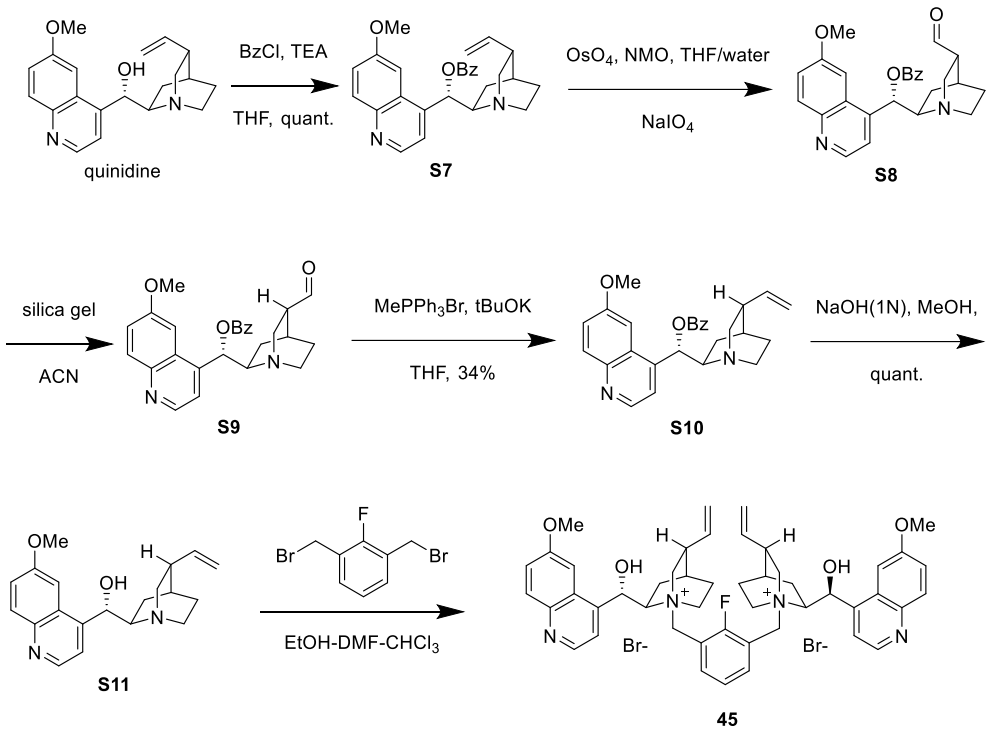
1,3-Bis(quinidinium-N-methyl)-2-fluorobenzene dibromide (44)



According to the procedure (**A**), from quinidine (100.0 mg 0.308 mmol) and 1,3-bis(bromomethyl)-2-fluorobenzene (42.4 mg, 0.150 mmol), the compound **44** was obtained (132.7 mg, 0.134 mmol, 89%).

White solid; mp 194-195 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.79 (d, *J* = 4.6 Hz, 2H), 8.11 (d, *J* = 7.8 Hz, 2H), 8.02-8.04 (m, 2H), 7.93 (d, *J* = 5.0 Hz, 2H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.50-7.55 (m, 4H), 6.72 (s, 2H), 6.04-6.13 (m, 2H), 5.65 (d, *J* = 12.8 Hz, 2H), 5.22-5.30 (m, 4H), 5.14-5.19 (m, 2H), 4.54-4.59 (m, 2H), 4.13 (s, 6H), 4.05-4.12 (m, 2H), 3.70-3.83 (m, 4H), 2.85-2.91 (m, 2H), 2.52-2.58 (m, 2H), 1.84-2.04 (m, 6H), 1.12-1.20 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 158.77, 146.91, 144.35, 143.44, 138.67, 136.60, 133.58, 130.43, 130.02, 128.74, 126.12, 122.03, 120.22, 116.56, 101.37, 68.31, 65.96, 63.78, 56.87, 55.39, 55.32, 37.63, 26.85, 23.43, 21.16 ppm; IR (neat) 1621, 1509, 1241, 1032, 829 cm^{-1}; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $[C_{48}H_{55}Br_2FN_4O_4]^+$ 952.2499; found 952.2444. $[\alpha]^{20}_D$ = +52.58 (*c* 1.0, MeOH).

Procedure for 1,3-Bis(3-epivinyl-quinidinium-N-methyl)-2-fluorobenzene dibromide (45)



(*S*)-(6-methoxyquinolin-4-yl)[(1*S*,2*R*,4*S*,5*R*)-5-vinylquinuclidin-2-yl]methyl benzoate (S7)

To a mixture of quinidine (2.0 g, 6.169 mmol) and trimethylamine (4.3 mL, 30.847 mmol) in dry THF (20 mL) was added benzoyl chloride (1.09 mL, 9.254 mmol) over 5 min at 0 °C and the reaction mixture was stirred for 2 h at rt. The resulting solution was quenched with water, extracted with dichloromethane, washed with ammonia water and brine, dried over $MgSO_4$, filtered and concentrated. The compound **S7** was obtained and used for without further purification.

(*S*)-[(1*S*,2*R*,4*S*,5*R*)-5-formylquinuclidin-2-yl](6-methoxyquinolin-4-yl)methyl benzoate (S8)

To a mixture of **S7** (2.64 g, 6.169 mmol) and N-methylmorpholine N-oxide (795 mg, 6.786 mmol) in THF/water (4:1, 30 mL) was added OsO_4 (in 2.5% *t*BuOH, 1.56 mL, 0.154 mmol) and stirred for overnight. To the resulting diol, was added $NaIO_4$ (3.95 g, 18.5 mmol) and stirred

for 2 h. The crude mixture was quenched with sodium bisulfite sat. solution and stirred for 30 min. The resulting solution was extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude was used for next step without further purification.

(*S*)-[(1*S*,2*R*,4*S*,5*S*)-5-formylquinuclidin-2-yl](6-methoxyquinolin-4-yl)methyl benzoate (S9)

A suspension of **S8** (900 mg, 2.091 mmol) and silica gel (3 g) in acetonitrile (40 mL) was stirred vigorously for overnight to racemization. The reaction was monitored by ^{1}H NMR. The crude was filtered to remove the silica gel and concentrated *in vacuo*. The mixture was purified by column chromatography (silica gel, EA : MeOH = 100:0 to 95:5) to afford **S9** (350 mg, 0.813 mmol, 39%). The TLC up spot was 3-epimer **S9** and down spot was normal form **S8**.

upspot 3-epi-**S9** : a sticky caramel; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.71 (d, *J* = 4.6 Hz, 1H), 8.08-8.06 (m, 2H), 8.01 (d, *J* = 9.2 Hz, 1H), 7.62-7.58 (m, 1H), 7.49-7.44 (m, 3H), 7.39-7.36 (m, 2H), 6.75 (d, *J* = 6.0 Hz, 1H), 3.96 (s, 3H), 3.54-3.47 (m, 1H), 3.33-3.28 (m, 1H), 3.23-3.16 (m, 1H), 2.79-2.72 (m, 2H), 2.65-2.62 (m, 1H), 2.48-2.48 (m, 1H), 1.99-1.94 (m, 1H), 1.88-1.82 (m, 1H), 1.48-1.40 (m, 2H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 203.45, 171.26, 165.37, 158.25, 147.44, 144.76, 143.41, 133.75, 131.93, 129.67, 128.85, 126.76, 122.15, 118.28, 101.33, 74.36, 60.49, 59.04, 55.86, 50.12, 49.57, 42.41, 29.00, 23.73, 21.51, 21.15, 14.28 ppm; IR (neat) 1746, 1620, 1509, 1263, 1108, 712 cm^{-1}; $[\alpha]^{20}_D$ = -27.29 (*c* 1.0, $CHCl_3$).

downspot **S8** : a white solid; mp 75-76 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 8.69 (t, *J* = 4.8 Hz, 1H), 8.06-8.08 (m, 2H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.63 (d, *J* = 2.8 Hz, 1H), 7.55-7.59 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35-7.39 (m, 2H), 6.79 (d, *J* = 6.9 Hz, 1H), 4.03 (s, 3H), 3.71-3.76 (m, 1H), 3.36-3.43 (m, 1H), 2.90-2.95 (m, 1H), 2.72-2.80 (m, 2H), 2.50-2.54 (m,

1H), 2.46-2.46 (m, 1H), 1.65-1.71 (m, 4H) ppm ^{13}C-NMR (101 MHz, $CDCl_3$) δ 203.15, 165.51, 158.25, 147.43, 144.74, 143.70, 133.57, 131.81, 129.91, 129.59, 128.66, 127.08, 122.36, 118.47, 101.24, 73.97, 59.08, 55.90, 50.39, 49.10, 42.45, 25.82, 25.12, 23.41 ppm

(*S*)-(6-methoxyquinolin-4-yl)[(1*S*,2*R*,4*S*,5*S*)-5-vinylquinuclidin-2-yl]methyl benzoate (S10)

To a suspension of methyltriphenylphosphonium bromide (187.6 mg 0.515 mmol) in dry THF (5 mL) was added potassium *tert*-butoxide (62.9 mg 0.515 mmol) at 0 °C and stirred for 1 h. To the yellow suspension was added **S9** in dry DCM (2.5 mL) at -78 °C and stirred for 2 h. The resulting solution was quenched with water, extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude was purified by column chromatography (silica gel, DCM : MeOH = 100:0 to 95:5) to afford **S10** (50.0 mg, 0.117 mmol, 34%).

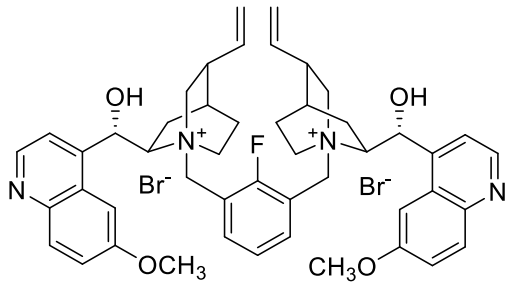
Sticky caramel; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.1 Hz, 1H), 8.08-8.10 (m, 2H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 2.3 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 4.6 Hz, 1H), 7.36 (dd, *J* = 9.2, 2.8 Hz, 1H), 6.77 (d, *J* = 5.5 Hz, 1H), 5.83-5.92 (m, 1H), 5.01-5.06 (m, 2H), 3.96 (s, 3H), 3.49-3.54 (m, 1H), 3.38-3.44 (m, 1H), 2.76-2.82 (m, 2H), 2.54-2.59 (m, 1H), 2.47-2.47 (m, 1H), 1.71-2.02 (m, 4H), 1.31-1.39 (m, 1H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.55, 158.11, 147.56, 144.87, 143.63, 141.57, 133.62, 131.98, 129.80, 129.74, 128.77, 126.92, 122.05, 118.60, 114.82, 101.44, 74.65, 58.83, 55.85, 50.96, 49.44, 40.83, 30.09, 27.83, 20.52 ppm; IR (neat) 1723, 1620, 1508, 1263, 1108, 711 cm^{-1}; $[\alpha]^{20}_D$ = -101.29 (*c* 1.0, $CHCl_3$).

3-Epivinyl-quinidine (S11)

To a solution of **S10** (43.5 mg, 0.102 mmol) in MeOH (1 mL) was added NaOH (1N aq. solution, 1 mL) and stirred for 2h. The resulting solution was extracted with dichloromethane, washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude was purified by column chromatography (silica gel, DCM : MeOH = 100:0 to 90:10) to afford **S11** (23.2 mg, 0.072 mmol, 70%)

White solid; mp 57-58 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.6 Hz, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.50 (d, *J* = 4.6 Hz, 1H), 7.21-7.23 (m, 1H), 7.11 (d, *J* = 2.8 Hz, 1H), 5.83 (d, *J* = 7.3 Hz, 1H), 5.66 (s, 1H), 5.00-5.05 (m, 2H), 3.77 (s, 3H), 3.74-3.82 (m, 1H), 3.09-3.14 (m, 1H), 2.79-2.82 (m, 2H), 2.47-2.57 (m, 2H), 1.87-1.92 (m, 1H), 1.79-1.79 (m, 1H), 1.66-1.73 (m, 1H), 1.22-1.33 (m, 2H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 157.79, 147.55, 147.50, 144.06, 141.52, 131.48, 126.40, 121.54, 118.57, 114.76, 101.15, 71.00, 59.26, 55.75, 50.95, 49.84, 40.02, 27.88, 27.05, 20.26 ppm; IR (neat) 1620, 1509, 1240, 1030, 756 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{20}H_{25}N_2O_2]^+$ 325.1916; found 325.1914. $[\alpha]^{20}_D$ = +113.83 (*c* 1.0, $CHCl_3$).

1,3-Bis(3-epivinyl-quinidinium-*N*-methyl)-2-fluorobenzene dibromide (45)



According to the procedure (**A**), from **S11** (21.9 mg, 0.068 mmol) and 1,3-bis(bromomethyl)-

2-fluorobenzene (9.3 mg 0.033 mmol), the compound **45** was obtained (17.0 mg, 0.017 mmol, 52%).

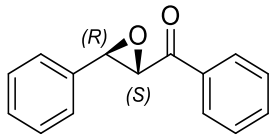
White solid; mp 201-202 °C (MeOH-Et_2O, decomp.); ^{1}H-NMR (400 MHz, CD_3OD) δ 8.78 (d, *J* = 4.6 Hz, 2H), 8.04-8.00 (m, 4H), 7.91 (d, *J* = 4.6 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.53 (dd, *J* = 9.4, 2.5 Hz, 2H), 7.42 (d, *J* = 2.8 Hz, 2H), 6.67 (s, 2H), 5.93-5.84 (m, 2H), 5.48 (d, *J* = 13.3 Hz, 2H), 5.13-5.09 (m, 4H), 4.84 (d, *J* = 13.3 Hz, 2H), 4.74-4.68 (m, 2H), 4.15-4.10 (m, 2H), 4.05 (s, 6H), 3.78-3.78 (m, 2H), 3.41-3.37 (m, 2H), 3.10-3.07 (m, 4H), 2.48-2.43 (m, 2H), 2.06-1.99 (m, 4H), 1.82-1.79 (m, 2H), 1.53-1.46 (m, 2H) ppm; ^{13}C-NMR (101 MHz, CD_3OD) δ 158.8, 147.0, 144.4, 143.4, 138.6, 137.9, 130.6, 126.0, 121.8, 120.3, 116.5, 116.5, 101.4, 68.6, 64.9, 57.9, 57.3, 57.1, 55.1, 38.8, 26.7, 26.4, 18.7 ppm; IR (neat) 1620, 1509, 1241, 1025, 769 cm^{-1}; HRMS (FAB) m/z: $[M - Br]^+$ calcd for $[C_{48}H_{55}BrFN_4O_4]^+$ 849.3391; found 849.3381. $[\alpha]^{20}_D$ = +92.84 (*c* 1.0, MeOH).

Procedure of Enantioselective PTC Epoxidation (C)

To a mixture of chalcone **1a** (25 mg, 0.120 mmol), chiral catalyst **13** (1.2 mg, 0.0012 mmol), N-*tert*-Butyl-α-phenylnitrone (2.1 mg, 0.012 mmol) and Span 20 (1% iPr_2O solution, 8.4 μL, 0.00024 mmol) in isopropyl ether (0.4 mL) was added 30% aqueous hydrogen peroxide (0.14 mL, 1.2 mmol) and 50% aqueous KOH (0.014 mL, 0.12 mmol) was added, and the reaction mixture was stirred vigorously at room temperature until starting material had been consumed. The suspension was diluted with ether (10 mL), washed with water (2 x 5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of residue by flash column chromatography on silica gel (hexanes : EtOAc = 50 : 1) afforded the desired product **2a** (26.9 mg, >99% yield) as a white solid. The enantioselectivity was determined by chiral HPLC

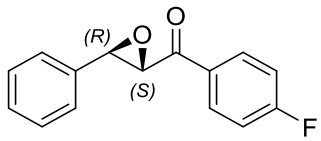
analysis (DAICEL Chiralpak AD, hexanes : ethanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ= 254 nm, retention times; 18.16 min(minor), 27.24 min(major), >99% ee). The absolute configuration was determined by comparison of the HPLC retention time with the reported data.

Phenyl[(2*S*,3*R*)-3-phenyloxiran-2-yl]methanone (2a)



According to the procedure (**C**), the compound **2a** was obtained (26.6 mg, 0.119 mmol, 99%). White solid; mp 61-62 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.35-7.41 (m, 5H), 4.29 (d, *J* = 1.8 Hz, 1H), 4.06 (d, *J* = 1.8 Hz, 1H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 193.19, 135.56, 134.13, 129.18, 128.99, 128.89, 128.46, 125.90, 61.12, 59.51 ppm; IR (neat) 1689, 1231, 696 cm^{-1}; The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak AD-H, hexane : ethanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ = 250 nm) retention time: minor isomer 18.16 min, major isomer 27.24 min, 99% ee, $[\alpha]^{20}_{D}$ = +229.30 (*c* 1.0, $CHCl_3$). The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[2],[15].

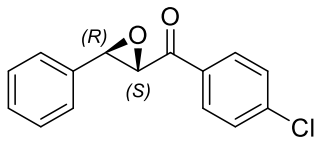
(4-Fluorophenyl)[(2*S*,3*R*)-3-phenyloxiran-2-yl]methanone (2b)



According to the procedure (**C**), the compound **2b** was obtained (27.4 mg, 0.113 mmol, 94%).

White solid; mp 77-78 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.09-8.04 (m, 2H), 7.43-7.35 (m, 5H), 7.19-7.14 (m, 2H), 4.24 (d, *J* = 2.3 Hz, 1H), 4.08 (d, *J* = 1.8 Hz, 1H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.6, 167.5, 164.9, 135.3, 131.9, 131.8, 131.2, 131.1, 129.1, 128.8, 125.8, 116.2, 116.0, 61.0, 59.3 ppm; IR (neat) 1688, 1231, 1157 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{15}H_{12}FO_2]^+$ 243.0821; found 243.0822. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak AD-H, hexane : 2-isopropanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ = 250 nm) retention time: minor isomer 11.69 min, major isomer 13.98 min, 97% ee, $[\alpha]^{20}_D$ = +207.66 (*c* 1.0, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[15],[16]

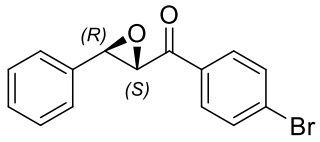
(4-Chlorophenyl)[(*2S,3R*)-3-phenyloxiran-2-yl]methanone (2c)



According to the procedure (**C**), the compound **2c** was obtained (21.1 mg, 0.082 mmol, 68%)

White solid; mp 93-94 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94 (dt, *J* = 8.9, 2.2 Hz, 2H), 7.44 (dt, *J* = 8.9, 2.2 Hz, 2H), 7.41-7.33 (m, 5H), 4.22 (d, *J* = 1.8 Hz, 1H), 4.05 (d, *J* = 1.8 Hz, 1H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.1, 140.7, 135.3, 133.8, 129.9, 129.3, 129.3, 128.9, 125.9, 61.2, 59.5 ppm; IR (neat) 1688, 1240, 697 cm^{-1}. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak AD-H, hexane : 2-isopropanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ = 250 nm) retention time: major isomer 12.92 min, minor isomer 14.49 min, 86% ee, $[\alpha]^{20}_D$ = +181.44 (*c* 1.0, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[17]

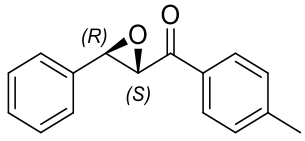
(4-Bromophenyl)[(*2S,3R*)-3-phenyloxiran-2-yl]methanone (2d)



According to the procedure (**C**), the compound **2d** was obtained (25.1 mg, 0.083 mmol, 69%).

White solid; mp 88-89 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.87 (dt, *J* = 9.0, 2.1 Hz, 2H), 7.61 (dt, *J* = 8.6, 2.1 Hz, 2H), 7.41-7.33 (m, 5H), 4.21 (d, *J* = 2.3 Hz, 1H), 4.05 (d, *J* = 1.8 Hz, 1H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.4, 135.3, 134.2, 132.3, 130.0, 129.5, 129.3, 128.9, 125.9, 61.1, 59.5 ppm; IR (neat) 1688, 1238, 696 cm^{-1}. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak OD-H, hexane : 2-isopropanol = 90 : 10, flow rate = 0.5 mL/min, 23 °C, λ = 250 nm) retention time: major isomer 25.71 min, minor isomer 26.92 min, 87% ee, $[\alpha]^{20}_{D}$ = +151.11 (*c* 1.0, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[17]

(4-Methylphenyl)[(2S,3R)-3-phenyl-2-oxiranyl]methanone (2e)

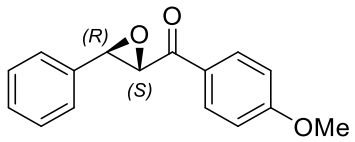


According to the procedure (**C**), the compound **2e** was obtained (28 mg, 0.118 mmol, 98%).

White solid; mp 61-62 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.41-7.34 (m, 5H), 7.26 (d, *J* = 7.8 Hz, 2H), 4.26 (d, *J* = 1.8 Hz, 1H), 4.05 (d, *J* = 1.8 Hz, 1H), 2.41 (s, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.5, 145.0, 135.6, 133.0, 129.5, 129.0, 128.7, 128.4,

125.8, 60.9, 59.3, 21.8 ppm; IR (neat) 1686, 1236 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{16}H_{15}O_2]^+$ 239.1072; found 239.1059. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak AD-H, hexane : 2-isopropanol = 95 : 5, flow rate = 1.0 mL/min, 23 °C, λ = 250 nm) retention time: major isomer 19.58 min, minor isomer 21.22 min, 97% ee, $[\alpha]^{20}_D$ = +259.7 (*c* 0.5, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[15]

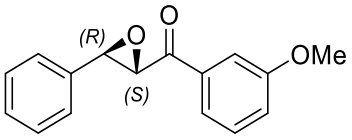
(4-Methoxyphenyl)[(*2S,3R*)-3-phenyl-2-oxiranyl]methanone (2f)



According to the procedure (**C**), the compound **2f** was obtained (30.2 mg, 0.119 mmol, 99%).

White solid; mp 62-63 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.99 (dt, *J* = 9.4, 2.4 Hz, 2H), 7.39-7.24 (m, 5H), 6.93 (d, *J* = 9.2 Hz, 2H), 4.24 (d, *J* = 1.8 Hz, 1H), 4.05 (d, *J* = 1.8 Hz, 1H), 3.85 (s, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.4, 164.3, 135.8, 130.9, 129.1, 128.8, 128.7, 125.9, 114.2, 61.0, 59.3, 55.7 ppm; IR (neat) 1678, 1240 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{16}H_{15}O_3]^+$ 255.1021; found 255.1010. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak AD-H, hexane : 2-isopropanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ = 250 nm) retention time: major isomer 23.05 min, minor isomer 25.57 min, 99% ee, $[\alpha]^{20}_D$ = +197.24 (*c* 1.0, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[15]

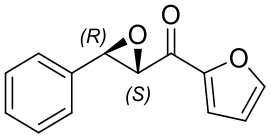
(3-Methoxyphenyl)[(*2S,3R*)-3-phenyl-2-oxiranyl]methanone (2g)



According to the procedure (**C**), the compound **2g** was obtained (18.9 mg, 0.074 mmol, 62%).

Clear oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 1H), 7.51 (t, *J* = 2.1 Hz, 1H), 7.41-7.34 (m, 6H), 7.16-7.13 (m, 1H), 4.27 (d, *J* = 1.8 Hz, 1H), 4.05 (d, *J* = 1.8 Hz, 1H), 3.83 (s, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 193.0, 160.1, 136.8, 135.5, 130.0, 129.2, 128.9, 125.9, 121.1, 120.7, 112.5, 61.1, 59.6, 55.6 ppm; IR (neat) 1689, 1266 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{16}H_{15}O_3]^+$ 255.1021; found 255.1010. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak OD-H, hexane : 2-isopropanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ = 250 nm) retention time: major isomer 12.26 min, minor isomer 13.22 min, 80% ee, $[\alpha]^{20}_D$ = +161.06 (*c* 1.0, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[18],[19].

Furan-2-yl[(2*S*,3*R*)-3-phenyloxiran-2-yl]methanone (2h)

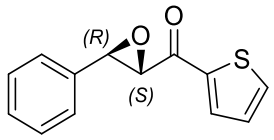


According to the procedure (**C**), the compound **2h** was obtained (22.1 mg, 0.103 mmol, 86%)

Pale yellow solid; mp 63-64 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 0.9 Hz, 1H), 7.44 (d, *J* = 3.7 Hz, 1H), 7.39-7.31 (m, 5H), 6.58 (q, *J* = 1.8 Hz, 1H), 4.13 (d, *J* = 1.8 Hz, 1H), 4.12 (d, *J* = 1.8 Hz, 1H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 182.0, 151.2, 147.6, 135.3, 129.0, 128.7, 125.8, 119.5, 112.6, 60.6, 59.6 ppm; IR (neat) 1674, 1272 cm^{-1}; HRMS (FAB) m/z: [M

+ H]$^+$ calcd for [$C_{13}H_{11}O_3$]$^+$ 215.0708; found 215.0713. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak AD-H, hexane : 2-isopropanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ = 250 nm) retention time: major isomer 13.00 min, minor isomer 14.91 min, 77% ee, $[\alpha]^{20}_D$ = +170.6 (*c* 0.5, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[20].

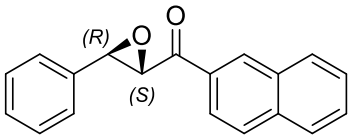
[(2*S*,3*R*)-3-Phenyl-2-oxiranyl]-2-thienylmethanone (2i)



According to the procedure (**C**), the compound **2i** was obtained (27.3 mg, 0.119 mmol, 99%).

White solid; mp 60-61 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.72 (dd, *J* = 4.8, 1.1 Hz, 1H), 7.40-7.31 (m, 5H), 7.16 (dd, *J* = 4.8, 3.9 Hz, 1H), 4.15 (d, *J* = 1.8 Hz, 1H), 4.06 (d, *J* = 1.8 Hz, 1H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 186.4, 140.9, 135.2, 133.6, 129.0, 128.7, 128.4, 125.7, 62.0, 59.4 ppm; IR (neat) 1664, 1243, 754 cm^{-1}; HRMS (FAB) m/z: [M + H]$^+$ calcd for [$C_{13}H_{11}O_2S$]$^+$ 231.048; found 231.0476. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak OD-H, hexane : 2-isopropanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ = 250 nm) retention time: minor isomer 12.62 min, major isomer 14.00 min, 99% ee, $[\alpha]^{20}_D$ = +313.64 (*c* 1.0, CH_2Cl_2) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[21].

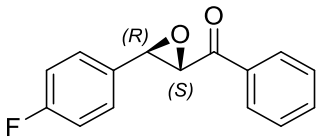
2-Naphthalenyl[(2*S*,3*R*)-3-phenyl-2-oxiranyl]methanone (2j)



According to the procedure (**C**), the compound **2j** was obtained (32.6 mg, 0.119 mmol, 99%).

White solid; mp 111-112 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.04 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.92 (t, *J* = 9.6 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.61 (t, *J* = 7.1 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 13.3 Hz, 6H), 4.43 (d, *J* = 1.4 Hz, 1H), 4.14 (d, *J* = 1.4 Hz, 1H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.7, 135.7, 135.4, 132.6, 132.2, 130.3, 129.5, 128.9, 128.7, 128.6, 127.7, 126.9, 125.7, 123.5, 60.9, 59.3 ppm; IR (neat) 1682, 1179, 752 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{19}H_{15}O_2]^+$ 275.1072; found 275.1057. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak AD-H, hexane : 2-isopropanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ = 250 nm) retention time: major isomer 15.55 min, minor isomer 18.09 min, 99% ee, $[\alpha]^{20}_D$ = +133.5 (*c* 0.5, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[16].

[(2*S*,3*R*)-3-(4-Fluorophenyl)-2-oxiranyl]phenylmethanone (2l)

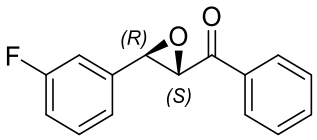


According to the procedure (**C**), the compound **2l** was obtained (27.4 mg, 0.113 mmol, 94%).

White solid; mp 79-80 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00-7.98 (m, 2H), 7.63-7.59 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.33 (dd, *J* = 8.7, 5.1 Hz, 2H), 7.08 (t, *J* = 8.5 Hz, 2H), 4.24 (d, *J* = 1.8 Hz, 1H), 4.05 (d, *J* = 1.8 Hz, 1H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.9, 164.4, 161.9, 135.4, 134.1, 131.2, 131.2, 128.9, 128.3, 127.6, 127.5, 116.0, 115.7, 60.9, 58.8 ppm; IR (neat) 1688, 1231, 754 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{15}H_{12}FO_2]^+$ 243.0821;

found 243.0815 ; The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak AD-H, hexane : 2-isopropanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ = 250 nm) retention time: major isomer 12.09 min, minor isomer 12.97 min, 72% ee, $[\alpha]^{20}_{D}$ = +271.29 (*c* 1.0, CH_2Cl_2) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[15].

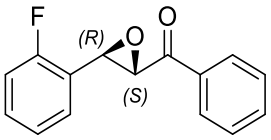
[(2*S*,3*R*)-3-(3-Fluorophenyl)-2-oxiranyl]phenylmethanone (2m)



According to the procedure (**C**), the compound **2m** was obtained (24.7 mg, 0.102 mmol, 85%).

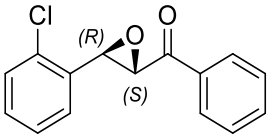
White solid; mp 75-76 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.99 (dt, *J* = 8.3, 1.6 Hz, 2H), 7.61 (tt, *J* = 7.4, 1.5 Hz, 1H), 7.51-7.46 (m, 2H), 7.38-7.33 (m, 1H), 7.16 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.08-7.03 (m, 2H), 4.24 (d, *J* = 1.8 Hz, 1H), 4.06 (d, *J* = 1.4 Hz, 1H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.6, 164.3, 161.9, 138.2, 138.1, 135.3, 134.1, 130.5, 130.4, 128.9, 128.4, 121.7, 121.6, 116.2, 115.9, 112.6, 112.4, 77.3, 60.8, 58.6, 58.6 ppm; IR (neat) 1689, 1233, 747 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{15}H_{12}FO_2]^+$ 243.0821; found 243.0827. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak AD-H, hexane : 2-isopropanol = 95 : 5, flow rate = 1.0 mL/min, 23 °C, λ = 250 nm) retention time: minor isomer 14.38 min, major isomer 16.82 min, 96% ee, $[\alpha]^{20}_{D}$ = +282.05 (*c* 1.0, CH_2Cl_2). The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[2],[21].

[(2*S*,3*R*)-3-(2-Fluorophenyl)-2-oxiranyl]phenylmethanone (2n)



According to the procedure (**C**), the compound **2n** was obtained (28.8 mg, 0.119 mmol, 99%) White solid; mp 77-78 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.36-7.31 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.11-7.06 (m, 1H), 4.33 (d, *J* = 1.8 Hz, 1H), 4.28 (d, *J* = 1.8 Hz, 1H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 193.0, 162.9, 160.4, 135.5, 134.2, 130.5, 130.4, 129.0, 128.5, 126.5, 126.5, 124.7, 124.7, 123.1, 123.0, 115.7, 115.5, 60.1, 54.3, 54.2 ppm; IR (neat) 1689, 1233, 758 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{15}H_{12}FO_2]^+$ 243.0821; found 243.0815; The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel AS-H, hexane : ethanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ = 250 nm) retention time: major isomer 9.27 min, minor isomer 18.11 min, 99% ee; $[\alpha]^{20}_D$ = +155.6 (*c* 1.0, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[2],[23].

[(2*S*,3*R*)-3-(2-Chlorophenyl)-2-oxiranyl]phenylmethanone (2o)

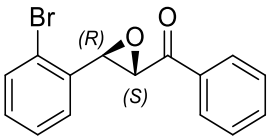


According to the procedure (C), the compound **2o** was obtained(24.3 mg, 0.094 mmol, 78%).

White solid; mp 81-82 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05-8.02 (m, 2H), 7. 63-7.59 (m, 1H), 7.51-7.47 (m, 2H), 7.39 (td, *J* = 4.6, 2.1 Hz, 2H), 7.33-7.29 (m, 2H), 4.39 (d, *J* = 1.8 Hz, 1H), 4.15 (d, *J* = 1.8 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.86, 135.44, 134.17, 133.87,

133.40, 129.86, 129.43, 128.98, 128.50, 127.36, 126.22, 60.14, 57.26; IR (neat) 1690, 1230, 754; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{15}H_{12}ClO_2]^+$ 259.0526; found 259.0536.; The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel AD-H, hexane : 2-isopropanol = 99 : 1, flow rate = 1.0 mL/min, 23 °C, λ = 254 nm) retention time: minor isomer 19.46 min, major isomer 21.79 min, 98% ee; $[\alpha]^{20}_D$ = -15.04 (*c* 1.0, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[24].

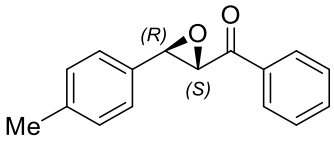
[(2*S*,3*R*)-3-(2-Bromophenyl)-2-oxiranyl]phenylmethanone (2p)



According to the procedure (C), the compound **2p** was obtained(8.5 mg, 0.029 mmol, 23%).

White solid; mp 76-77 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 2H), 7.64-7.60 (m, 1H), 7.57-7.55 (m, 1H), 7.51-7.47 (m, 2H), 7.39-7.34 (m, 2H), 7.25-7.22 (m, 1H), 4.33 (d, *J* = 2.3 Hz, 1H), 4.14 (d, *J* = 1.8 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.84, 135.53, 135.43, 134.16, 132.56, 130.15, 128.95, 128.55, 127.92, 126.56, 122.62, 60.09, 59.45; IR(KBr) 1689, 1229, 753; The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel AD-H, hexane : 2-isopropanol = 99 : 1, flow rate = 1.0 mL/min, 23 °C, λ = 254 nm) retention time: minor isomer 33.79 min, major isomer 37.50 min, 54% ee; $[\alpha]^{20}_D$ = -19.91 (*c* 1.0, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[24].

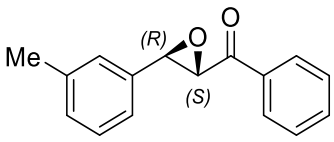
[(2*S*,3*R*)-3-(4-Methylphenyl)-2-oxiranyl]phenylmethanone (2q)



According to the procedure (**C**), the compound **2q** was obtained (6.3 mg, 0.026 mmol, 22%)

White solid; mp 78-79 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 4.28 (d, *J* = 1.8 Hz, 1H), 4.02 (d, *J* = 1.8 Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 193.3, 139.2, 135.6, 134.1, 132.5, 129.6, 129.0, 128.4, 125.9, 61.2, 59.6, 21.4 ppm; IR (neat) 1688, 1232, 753 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{16}H_{15}O_2]^+$ 239.1072; found 239.1079. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak OD-H, hexane : 2-isopropanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ = 250 nm) retention time: major isomer 8.73 min, minor isomer 9.48 min, 17% ee, $[\alpha]^{20}_D$ = +51.95 (*c* 1.0, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[25].

[(2*S*,3*R*)-3-(3-Methylphenyl)-2-oxiranyl]phenylmethanone (2r)

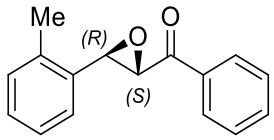


According to the procedure (**C**), the compound **2r** was obtained (14 mg, 0.059 mmol, 49%).

White solid; mp 50-51 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.19-7.17 (m, 3H), 4.28 (d, *J* =

1.2 Hz, 1H), 4.03 (d, *J* = 1.2 Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 193.2, 138.7, 135.6, 135.5, 134.1, 130.0, 129.0, 128.8, 128.5, 126.4, 123.1, 61.1, 59.6, 21.5 ppm; IR (neat) 1689, 1232, 775 cm^{-1}; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{16}H_{15}O_2]^+$ 239.1072; found 239.1076. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak OD-H, hexane : 2-isopropanol = 90 : 10, flow rate = 0.5 mL/min, 23 °C, λ = 250 nm) retention time: major isomer 18.74 min, minor isomer 19.57 min, 79% ee, $[\alpha]^{20}_D$ = +196.16 (*c* 1.0, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[25].

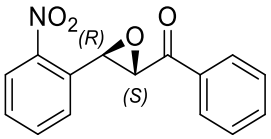
[(2*S*,3*R*)-3-(2-Methylphenyl)-2-oxiranyl]phenylmethanone (2s)



According to the procedure (**C**), the compound **2s** was obtained (20.5 mg, 0.086 mmol, 72%).

Clear oil; mp 50.6 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.13-8.10 (m, 2H), 7.72-7.68 (m, 1H), 7.59-7.55 (m, 2H), 7.42-7.39 (m, 1H), 7.34-7.31 (m, 2H), 7.27-7.25 (m, 1H), 4.29-4.27 (m, 2H), 2.43 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 193.49, 136.50, 135.60, 134.24, 134.08, 130.31, 129.10, 128.67, 128.50, 126.56, 124.38, 60.24, 57.92, 19.01; IR (neat) 1689, 1231, 752; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{16}H_{15}O_2]^+$ 239.1072; found 239.1089.; The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel OJ-H, hexane : 2-isopropanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ = 254 nm) retention time: major isomer 11.56 min, minor isomer 14.37 min, 93% ee; $[\alpha]^{20}_D$ = +55.37 (*c* 1.0, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[23].

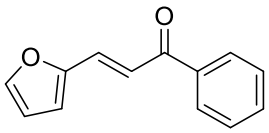
[(2*S*,3*R*)-3-(2-Nitrophenyl)-2-oxiranyl]phenylmethanone (2t)



According to the procedure (**C**), the compound **2t** was obtained (18.8 mg, 0.070 mmol, 58%).

White soild; mp 125-126 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.3 Hz, 1H), 8.01-7.99 (m, 2H), 7.73 (d, *J* = 4.1 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.49-7.45 (m, 2H), 4.62 (d, *J* = 1.8 Hz, 1H), 4.21 (d, *J* = 1.8 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 192.6, 147.6, 135.4, 134.7, 134.2, 132.7, 129.5, 128.9, 128.6, 127.5, 125.0, 59.7, 57.8; IR (neat) 1689, 1524, 1345, 1231; HRMS (FAB) m/z: $[M + H]^+$ calcd for $[C_{15}H_{12}NO_4]^+$ 270.0766; found 270.0773.; The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel OD-H, hexane : 2-isopropanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ = 254 nm) retention time: minor isomer 20.34 min, major isomer 22.47 min, 86% ee; $[\alpha]^{20}_D$ = +124.37 (*c* 1.0, $CHCl_3$) The configuration of the major enantiomer is (*2S,3R*), determined by comparison with literature data[26].

(*E*)-3-(furan-2-yl)-1-phenylprop-2-en-1-one[28] (1v)

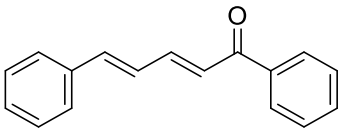


To a solution of furfural (0.21 mL, 2.50 mmol) and acetophenone (0.29 mL, 2.50 mmol) dissolved in ethanol (12.5 mL) was added NaOH (200 mg, 5.0 mmol). The mixture was stirred for at room temperature until starting material had been consumed. To the reaction mixture,

citric acid solution (10 % aq., 20 mL) was added. The suspension was diluted with dichloromethane (20 mL) and washed with brine (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane : EtOAC = 50 : 1) to afford the desired product (236.6 mg, 0.916 mmol, 37%) as a yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00-8.02 (m, 2H), 7.53-7.60 (m, 2H), 7.42-7.51 (m, 4H), 6.70 (d, *J* = 3.2 Hz, 1H), 6.49 (q, *J* = 1.7 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 189.91, 151.76, 145.03, 138.23, 132.86, 130.76, 128.70, 128.52, 119.39, 116.35, 112.78

(2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-one[29] (**1w**)

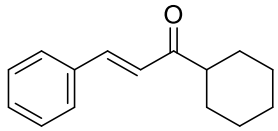


To a solution of cinnamaldehyde (0.104 mL, 0.832 mmol) and acetophenone (100mg, 0.832 mmol) dissolved in ethanol (1.7 mL) was added NaOH (67 mg, 1.665 mmol). The mixture was stirred for at room temperature until starting material had been consumed. To the reaction mixture, citric acid solution (10 % aq., 2 mL) was added. The suspension was diluted with dichloromethane (10 mL) and washed with brine (2 x 10 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane : EtOAC = 50 : 1) to afford the desired product (182.1 mg, 0.777 mmol, 93%) as a yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.62-7.54 (m, 2H), 7.50-7.46 (m, 4H), 7.34 (td, *J* = 14.3, 7.0 Hz, 3H), 7.08 (d, *J* = 14.6 Hz, 1H), 7.02 (d, *J* = 3.2 Hz, 1H), 7.01 (s, 1H); ^{13}C-

NMR (101 MHz, $CDCl_3$) δ 190.7, 145.0, 142.1, 138.3, 136.2, 132.8, 129.3, 129.0, 128.7, 128.5, 127.4, 127.0, 125.5

(*E*)-1-cyclohexyl-3-phenylprop-2-en-1-one[30] (1x)



To a solution of benzaldehyde (0.24 mL, 2.38 mmol) and cyclohexyl methyl ketone (0.33mL, 2.38 mmol) dissolved in ethanol (11.9 mL) was added NaOH (190.2 mg, 4.75 mmol). The mixture was stirred for at room temperature until starting material had been consumed. To the reaction mixture, citric acid solution (10 % aq., 20 mL) was added. The suspension was diluted with dichloromethane (10 mL) and washed with brine (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane : EtOAC = 50 : 1) to afford the desired product (471.9 mg, 2.20 mmol) as a clear oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.59-7.53 (m, 3H), 7.37-7.35 (m, 3H), 6.80 (d, *J* = 16.0 Hz, 1H), 2.64 (tt, *J* = 11.1, 3.4 Hz, 1H), 1.90-1.80 (m, 4H), 1.71-1.68 (m, 1H), 1.46-1.18 (m, 5H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 203.2, 142.3, 134.8, 130.4, 129.0, 128.4, 124.8, 49.5, 28.8, 26.0, 25.9

1 g Scale epoxidation of chalcone

To a mixture of chalcone **1a** (1.0 g, 4.8 mmol), chiral catalyst **13** (44.7 mg, 0.048 mmol), N-*tert*-Butyl-α-phenylnitrone (85.1 mg, 0.48 mmol) and Span 20 (1% *i*Pr_2O solution, 0.17 mL, 0.0096 mmol) in isopropyl ether (16 mL) was added 30% aqueous hydrogen peroxide (4.9 mL,

48 mmol) and 50% aqueous KOH (0.54 mL, 4.8 mmol) was added, and the reaction mixture was stirred vigorously at room temperature until starting material had been consumed. The suspension was diluted with ether (100 mL), washed with water (2 x 50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of residue by flash column chromatography on silica gel (hexanes : EtOAc = 50 : 1) afforded the desired product **2a** (1.07 g, >99% yield) as a white solid. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak AD, hexanes : ethanol = 90 : 10, flow rate = 1.0 mL/min, 23 °C, λ= 254 nm, retention times; 18.16 min(minor), 27.24 min(major), >99% ee). The absolute configuration was determined by comparison of the HPLC retention time with the reported data.

Computational Method

[MD Simulations for transition state] The initial geometry of catalyst **13** was build based on the X-ray crystallography. The substrate and peroxide anion were built by the LigPrep of Schrodinger Suite 2018-2. After preparing the complex consisting of substrate, peroxide anion, and catalyst **13**, molecular dynamics (MD) simulations of the complex were carried out using Macromodel v12.0 of of Schrodinger Suite 2018-2. OPLS3e force field parameters were used to describe molecules (No. of parameters, stretch: 151, bend: 268, torsion parameters: 426). Dielectric constant was 1.0, the Lennard–Jones (LJ) interactions were truncated at 12 Å, and van der waals interactions were truncated at 7 Å. Step wisely, conformational search, energy calculation, energy minimization of selected frame, and molecular dynamics were conducted. Atoms of catalyst **13** were frosen, and free movement of substrate and peroxide anion was allowed during MD simulation. For MD simulations, a temperature of 383 K was maintained under constant temperature velocity-Verlet algorithm, and time step of 1.5 fs, equilibration time of 1.0 ps, and simulation time of 10 ps with the SHAKE algorithm to constrain all covalent bonds containing hydrogen atoms. Two organic solvents, water and chloroform, were used for the MD simulations of the complex.

[DFT Calculations for transition state] After getting the optimized conformational complex resulting from MD simulations, density functional theory (DFT) calculations were carried out using the the Jaguar-v10.7 of Schrodinger Suite 2020-1 with density-functional theory. All the geometries of each species were optimized to respective minimum energy geometries using the functional **ωB97X-D** method with basis set **6–31++G(d,p)**. At the same computational level, frequency calculations were performed to see if the geometry optimization had found a minimum. After 65 iterative geometry optimizations, all criteria of convergence were satisfied

including the change of total energy, gradient maximum of the energy, gradient root mean square between geometries, and so on.

Cartesian coordinates of the optimized structure

SCF E(wB97XD) = -3285.724 a.u.

C1	-2.4188775944	1.1863791111	-3.2962911
C2	-1.1099509354	0.8519182617	-3.6413409
C3	-0.4960967446	-0.3322410781	-3.2375508
C4	-1.2496947752	-1.1837964847	-2.4215505
C5	-2.5631456714	-0.9006673208	-2.0918015
C6	-3.1436471692	0.2708829252	-2.5321845
C7	-4.3983235802	3.3462052728	0.8108423177
C8	-3.1152711941	2.4278671937	-3.7730366
C9	0.9551968522	-0.6756051936	-3.4643362
F10	-0.4178861670	1.7273456193	-4.3998214
C11	1.0130768293	-5.5101303656	-3.8149002
H12	-0.7740160923	-2.0699851001	-2.0084590
H13	-3.1226711444	-1.5835115093	-1.4632153
H14	-4.1759676513	0.4833715628	-2.2670664
N15	-3.0741537526	3.6671426422	-2.8558487
H16	-5.0730902947	3.3702394309	1.6588904323
N17	1.2512350000	-1.6592094558	-4.5930179
H18	-4.4388185319	2.4435751523	0.2068769058
C19	-4.4802370510	4.2221142711	-2.5189777
C20	-4.3170092502	5.6338556680	-1.9318876200
C21	-2.9053641508	5.7839760239	-1.3747959161
C22	-2.5775675949	4.5297575012	-0.5447074381
C23	-2.4320038911	3.3501271010	-1.5157972044
C24	-2.2349127526	4.7323287146	-3.5318107186
C25	-1.9208302402	5.8621480539	-2.5433725990
C26	1.3391026880	-0.9227760624	-5.9082441097
C27	1.3782912273	-1.9156489315	-7.0782812154

C28	1.7613012476	-3.2924968476	-6.5308765885
C29	0.5799980650	-3.8241733657	-5.6920235608
C30	0.1775936009	-2.7186553237	-4.6986738716
C31	2.5528811797	-2.4436772204	-4.3193790134
C32	2.9796541015	-3.1239587256	-5.6259668756
H33	-4.1606151014	2.1698790287	-3.8921856305
H34	-2.7442805939	2.7555538769	-4.7428635007
H35	1.2847325803	-1.1834619346	-2.5213334443
H36	1.5675268498	0.2011064022	-3.6648359487
H37	1.2473316760	-6.5355724769	-3.5494873790
C38	-3.5705794937	4.3565801808	0.5760837326
H39	0.9120103807	-4.8123223641	-2.9860989516
H40	-4.8192122520	3.5444226269	-1.7392299235
C41	-5.5532774246	4.1949341073	-3.6159264446
H42	-5.0668257053	5.7555058908	-1.1489522184
H43	-4.5092341548	6.3849432563	-2.7001600951
H44	-2.8320512774	6.6794735455	-0.7543067368
H45	-1.5902394903	4.6818855131	-0.0969103981
H46	-2.8885244579	2.4410423773	-1.1356982383
H47	-1.3788956984	3.1354822565	-1.7002153963
H48	-2.8200626657	5.0732892420	-4.3870137501
H49	-1.3315435506	4.2318851227	-3.8822949819
H50	-2.0084422867	6.8213144984	-3.0576219776
C51	0.8803885616	-5.1753583357	-5.0928524707
H52	-0.8942429284	5.7751424631	-2.1787309779
H53	2.2428195602	-0.3186799272	-5.8424845755
H54	0.4750375485	-0.2581560938	-5.9486338248
H55	2.1132387533	-1.5778262581	-7.8121377270
H56	0.4106576800	-1.9636179466	-7.5861852811
H57	1.9815810720	-3.9823642065	-7.3487566431
H58	-0.2628305984	-3.9647686821	-6.3790572953
H59	0.0223230354	-3.1017894417	-3.6920700332
H60	-0.7282277046	-2.2063564849	-5.0221326944
H61	2.2364926192	-3.1931256934	-3.5967756034
C62	3.6754412273	-1.6687832990	-3.6255695504

H63	3.4197466269	-4.0891402891	-5.3719711304
H64	3.7513779378	-2.5349198534	-6.1303115929
H65	-3.5942929253	5.2060818049	1.2582942135
H66	-5.5507736917	3.2351390804	-4.1416233129
O67	-5.2735395084	5.2280579097	-4.5312158044
C68	-6.9135976174	4.3096149561	-2.9338011461
H69	1.0141938633	-5.9503667702	-5.8474061713
C70	4.8743693556	-2.6002905640	-3.4662901158
H71	3.3203243129	-1.3835663672	-2.6311564754
O72	3.9800286904	-0.5196251085	-4.3919837899
H73	-5.9266258721	5.2031898252	-5.2368323550
H74	4.5594749209	0.0326684796	-3.8522629225
C75	-7.6454128256	5.4623328792	-2.9751698618
C76	-8.8953119400	5.5272434966	-2.3086392062
N77	-9.4105914038	4.5407364075	-1.6251878049
C78	-8.7017565628	3.3820542407	-1.5651566333
C79	-7.4480787200	3.1995134409	-2.2082981457
C80	5.9922998572	-2.4554013667	-4.2390466777
C81	7.0633564249	-3.3750056763	-4.1115783419
N82	7.0614660931	-4.4016525022	-3.3031893510
C83	5.9619792788	-4.5646464258	-2.5163398112
C84	4.8485279259	-3.6806992294	-2.5333498943
H85	-7.2719138590	6.3328559889	-3.5044391247
H86	-9.4735235530	6.4475669731	-2.3505981204
C87	-9.2452203543	2.3074964577	-0.8253382588
C88	-6.8023657973	1.9499143965	-2.0910993514
H89	6.0592681483	-1.6465095149	-4.9581520679
H90	7.9502488794	-3.2461788477	-4.7295505107
C91	5.9324608005	-5.6619377679	-1.6293273395
C92	3.7803090973	-3.8878984138	-1.6392388707
C93	-8.5968041583	1.1081431815	-0.7111992768
C94	-7.3516333708	0.9242119377	-1.3569444887
C95	4.8678522113	-5.8784244399	-0.7946732246
C96	3.7827408632	-4.9748642658	-0.8012959530
H97	-10.2039257001	2.4705881281	-0.3458146218

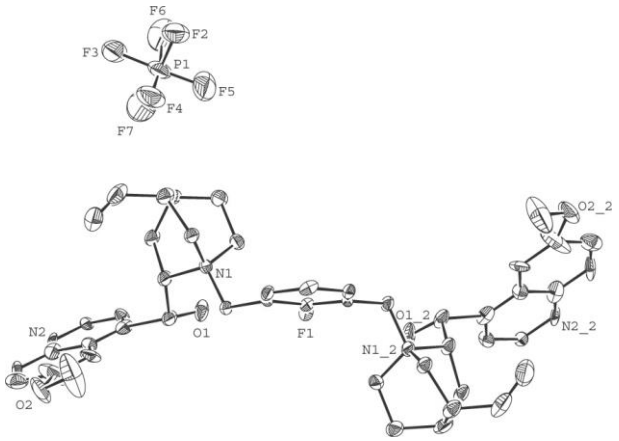
H98	-5.8672706069	1.7443385898	-2.5934527821
H99	6.7860914838	-6.3307602711	-1.6300254073
H100	2.9745197841	-3.1574249829	-1.5325813135
H101	-9.0463972731	0.3102558569	-0.1332857107
O102	-6.6334999307	-0.2192531170	-1.3069992583
H103	4.8786510183	-6.7349320446	-0.1308548659
O104	2.6899442543	-5.1045983303	0.0048286131
H105	1.7292005339	-6.0410772881	1.5014374675
C106	2.6625768781	-6.1549284749	0.9504735916
C107	-7.1718007998	-1.3346679981	-0.6177863762
H108	3.5023583928	-6.0856552901	1.6512236697
H109	2.6747548555	-7.1377634839	0.4645910129
H110	-8.1261506781	-1.6493244857	-1.0534810530
H111	-7.3059269812	-1.1202294852	0.4480490930
H112	-6.4441801267	-2.1369193519	-0.7331252478
C113	-0.2513607910	1.1546775081	0.4178286589
C114	0.7897536175	1.7550898337	-0.4703265619
C115	2.0045563789	0.9404797229	-0.633039157
O116	0.6479752099	2.8719221520	-0.9642755319
C117	-0.4052024499	-0.2314080099	0.5305790935
C118	-1.3698714824	-0.7456801257	1.3860120919
C119	-2.1577739212	0.1010883322	2.1551168842
C120	-1.9864124555	1.4781327385	2.0658757799
C121	-1.0443538707	1.9994905852	1.1933344703
C122	3.1591469243	1.4339985540	-1.0925535873
C123	4.4223091856	0.6887618534	-1.1299466237
C124	4.5700846088	-0.5629374503	-0.5131765347
C125	5.7896456805	-1.2174899207	-0.5435506896
C126	6.8796552106	-0.6535001202	-1.1985683707
C127	6.7447830824	0.5786309453	-1.8255292715
C128	5.5271622323	1.2483404684	-1.7828289577
H129	1.9507816892	-0.0864606252	-0.2939961576
H130	0.2203237073	-0.9238621523	-0.0428093187
H131	-1.4903526220	-1.8221457299	1.4605187230
H132	-2.8938026696	-0.3101014791	2.8397868975

H133	-2.5810599012	2.1443495223	2.6812475043
H134	-0.8840357565	3.0702077223	1.1313353501
H135	3.1797748462	2.4680553482	-1.4321671024
H136	3.7274863607	-1.0430674504	-0.0282956213
H137	5.8846012734	-2.1878991513	-0.0692569889
H138	7.8273734762	-1.1808565041	-1.2274651331
H139	7.5911978324	1.0250900250	-2.3373803954
H140	5.4310468768	2.2266273458	-2.24766902
O141	1.5010472123	-2.0557472881	-1.0742773553
O142	0.6973966943	-3.2414026595	-1.3596374124
H143	1.0775245045	-3.8825337013	-0.7422299

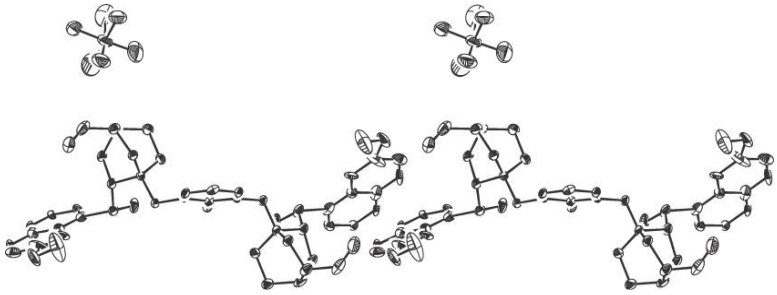
X-ray Crystallographic Data of 13

ORTEP diagram of 13-PF_6[2]

The solvent molecules (acetone and H_2O) and all hydrogen atoms are omitted for clarity.



Stereoview of 13-PF_6.



Crystal data and structure refinement for 13-PF_6.

Identification code	13-PF_6	
Empirical formula	C48 H55 F13 N4 O6 P2	
Formula weight	1092.90	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 16.396(4) Å	α= 90°.
	b = 13.046(3) Å	β= 107.386(4)°.
	c = 11.979(3) Å	γ= 90°.
Volume	2445.1(10) $Å^3$	
Z	2	
Density (calculated)	1.484 mg/m^3	
Absorption coefficient	0.192 mm^{-1}	
F(000)	1132	
Crystal size	1.30 x 0.50 x 0.15 mm^3	
Theta range for data collection	1.78 to 25.00°.	
Index ranges	-19<=h<=16, -15<=k<=15, -13<=l<=14	
Reflections collected	5780	
Independent reflections	3827 [R(int) = 0.0155]	
Completeness to theta = 25.00°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9717 and 0.7883	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3827 / 7 / 383	
Goodness-of-fit on F^2	1.044	

Final R indices [I>2sigma(I)]	R1 = 0.0813, wR2 = 0.2008
R indices (all data)	R1 = 0.0939, wR2 = 0.2134
Absolute structure parameter	0.1(3)
Largest diff. peak and hole	0.569 and -0.351 e.Å^{-3}

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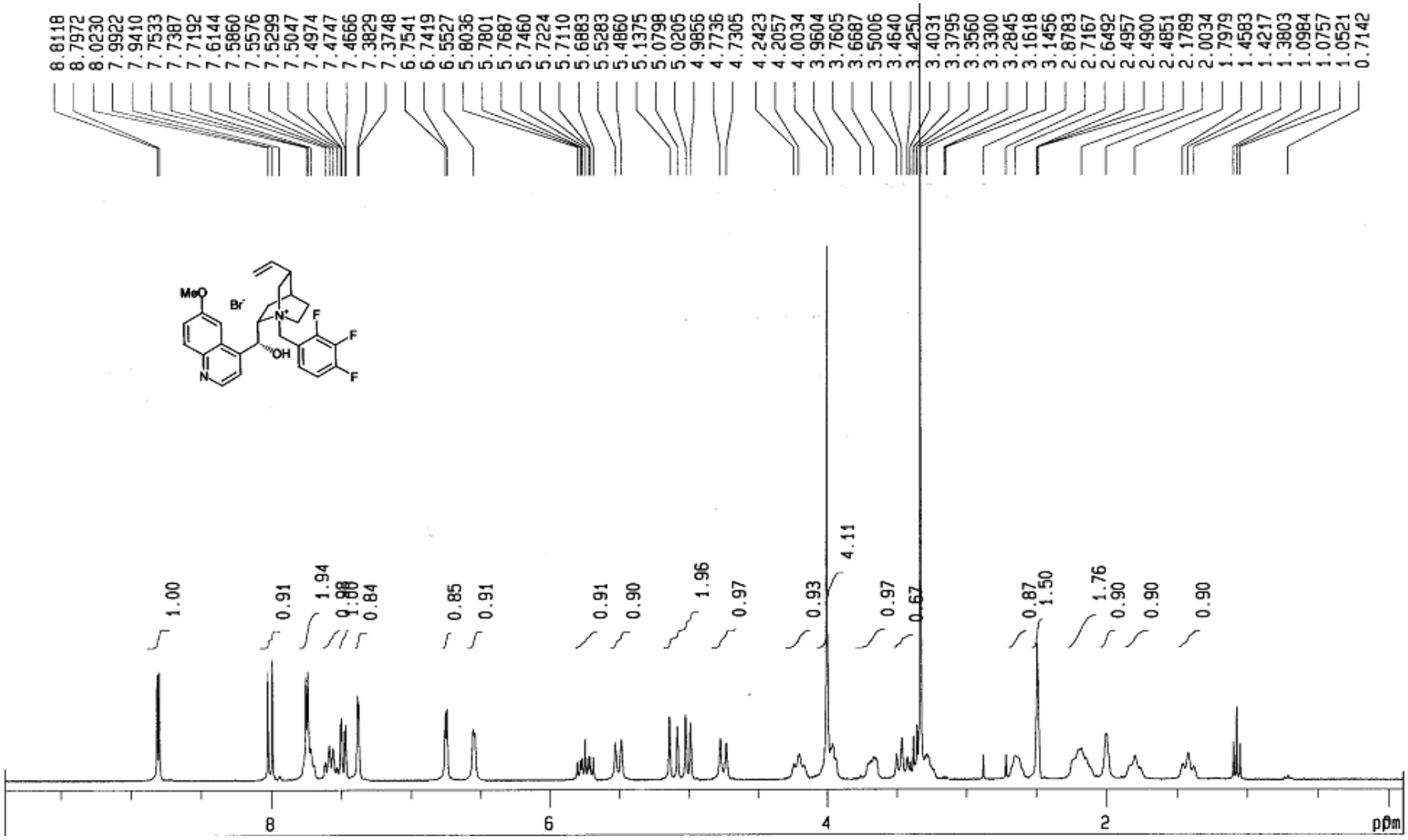
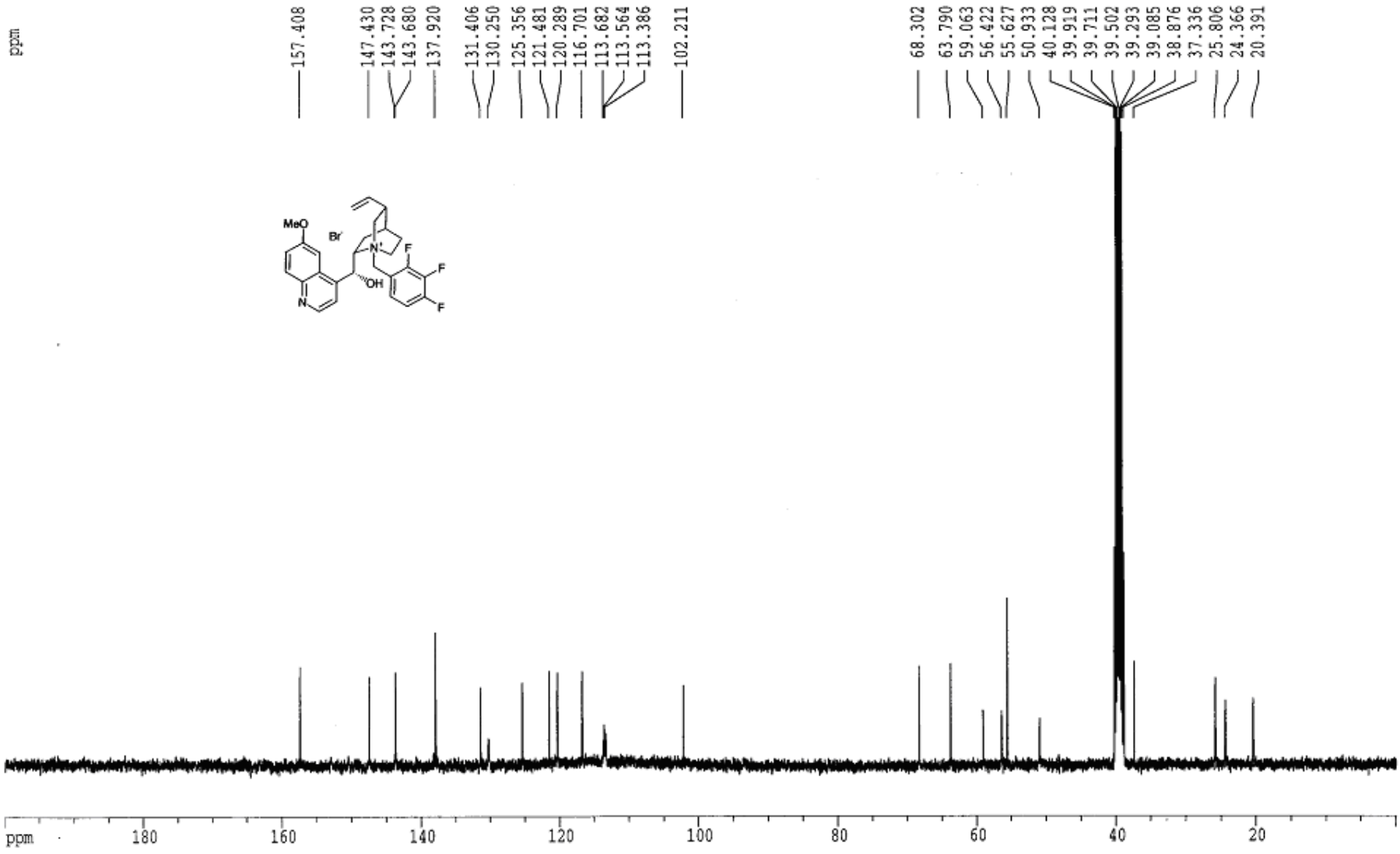
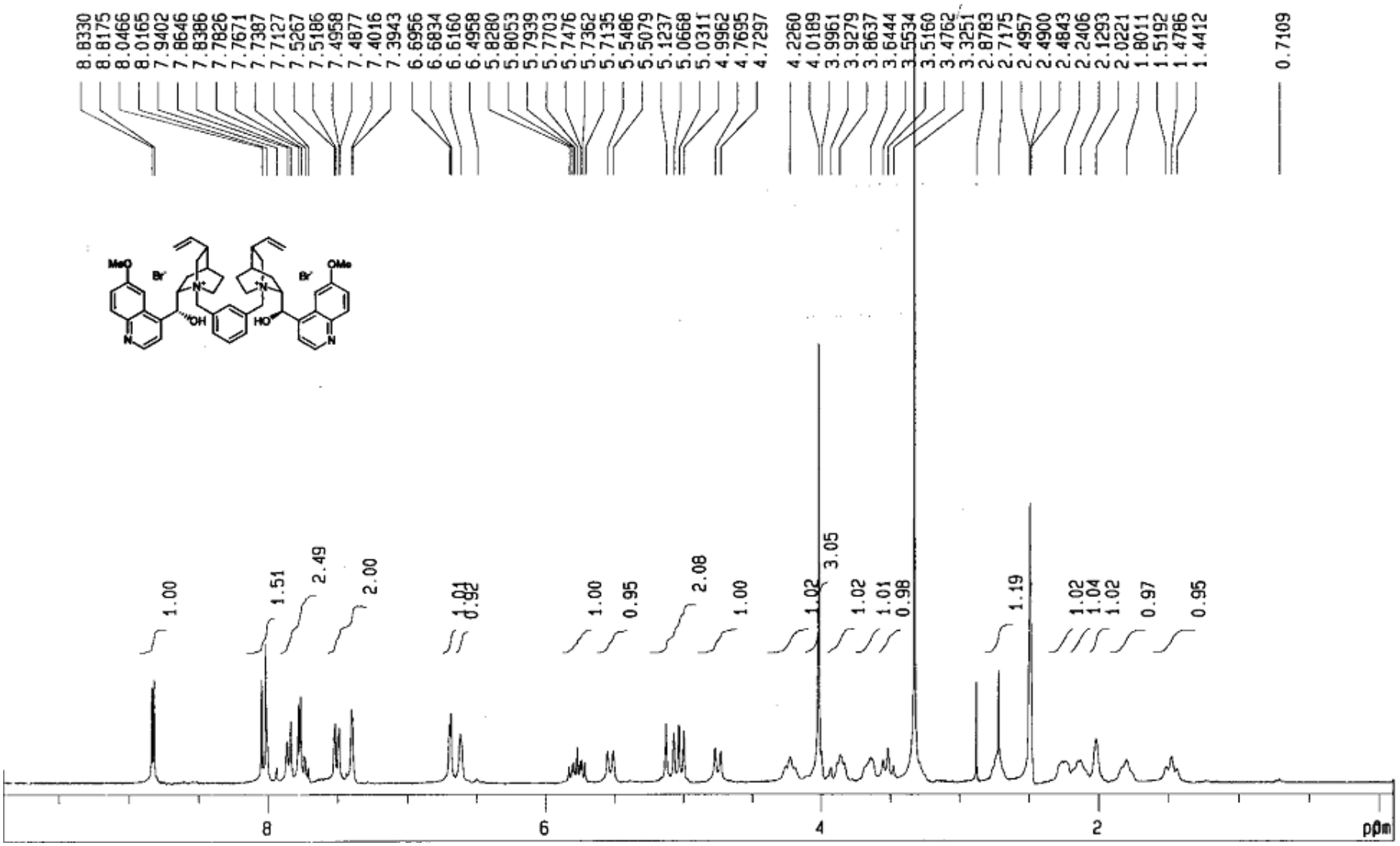
[1]H-NMR of compound **5** (DMSO-d_6, 300MHz)



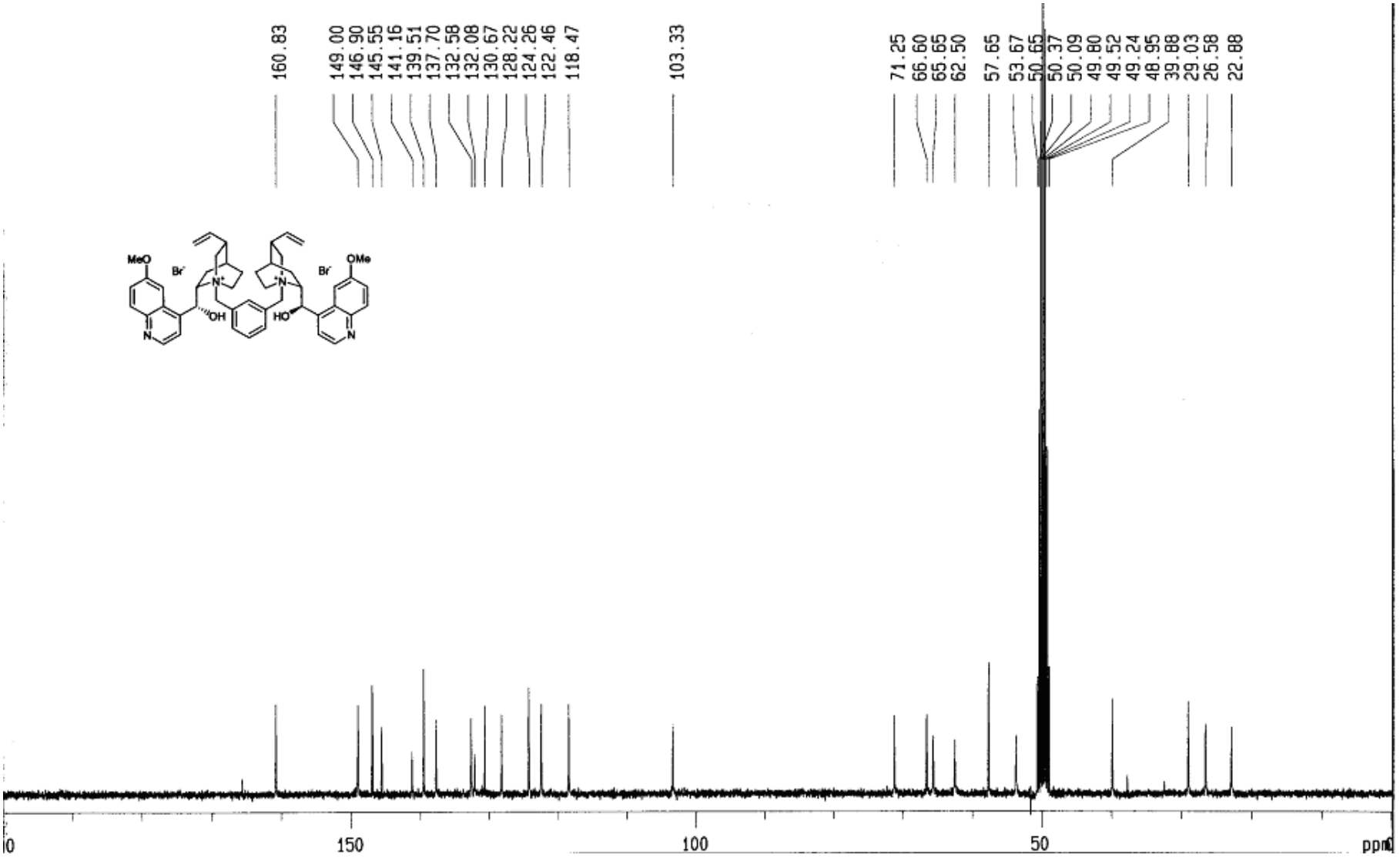
^{13}C-NMR of compound **5** (DMSO-d_6, 75MHz)



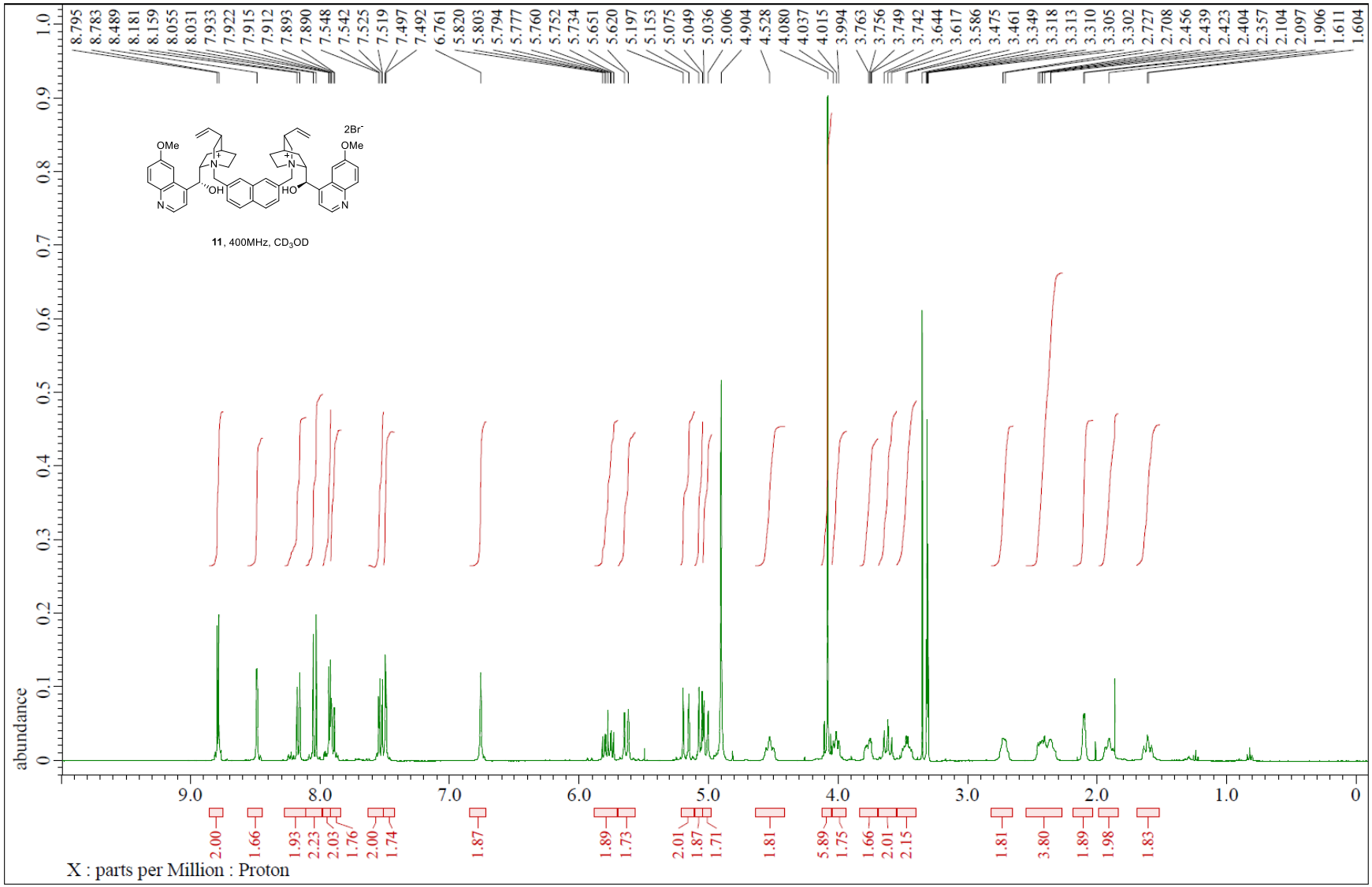
[1]H-NMR of compound **10** (DMSO-d_6, 300MHz)



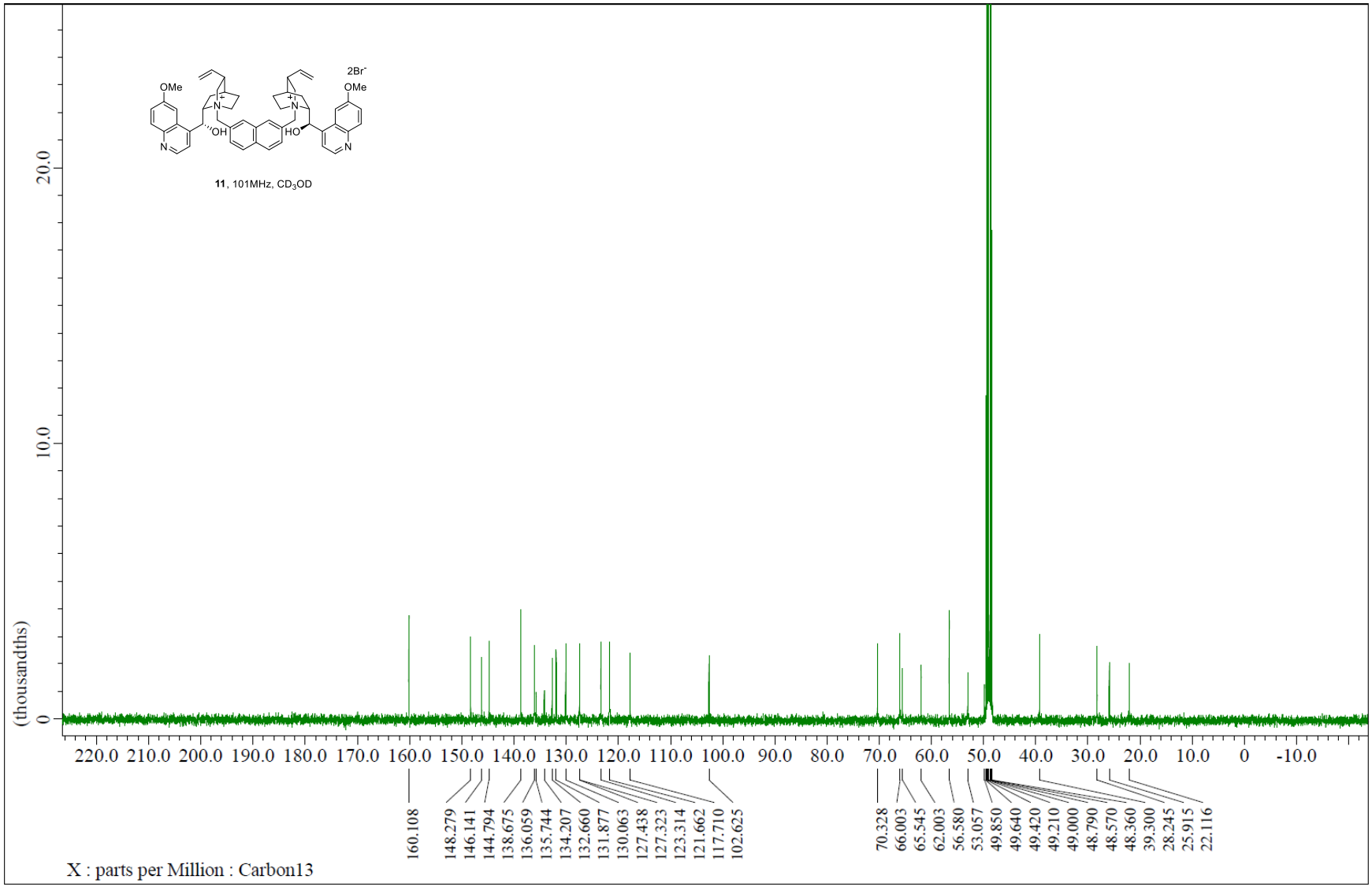
^{13}C-NMR of compound **10** (DMSO-d_6, 75MHz)



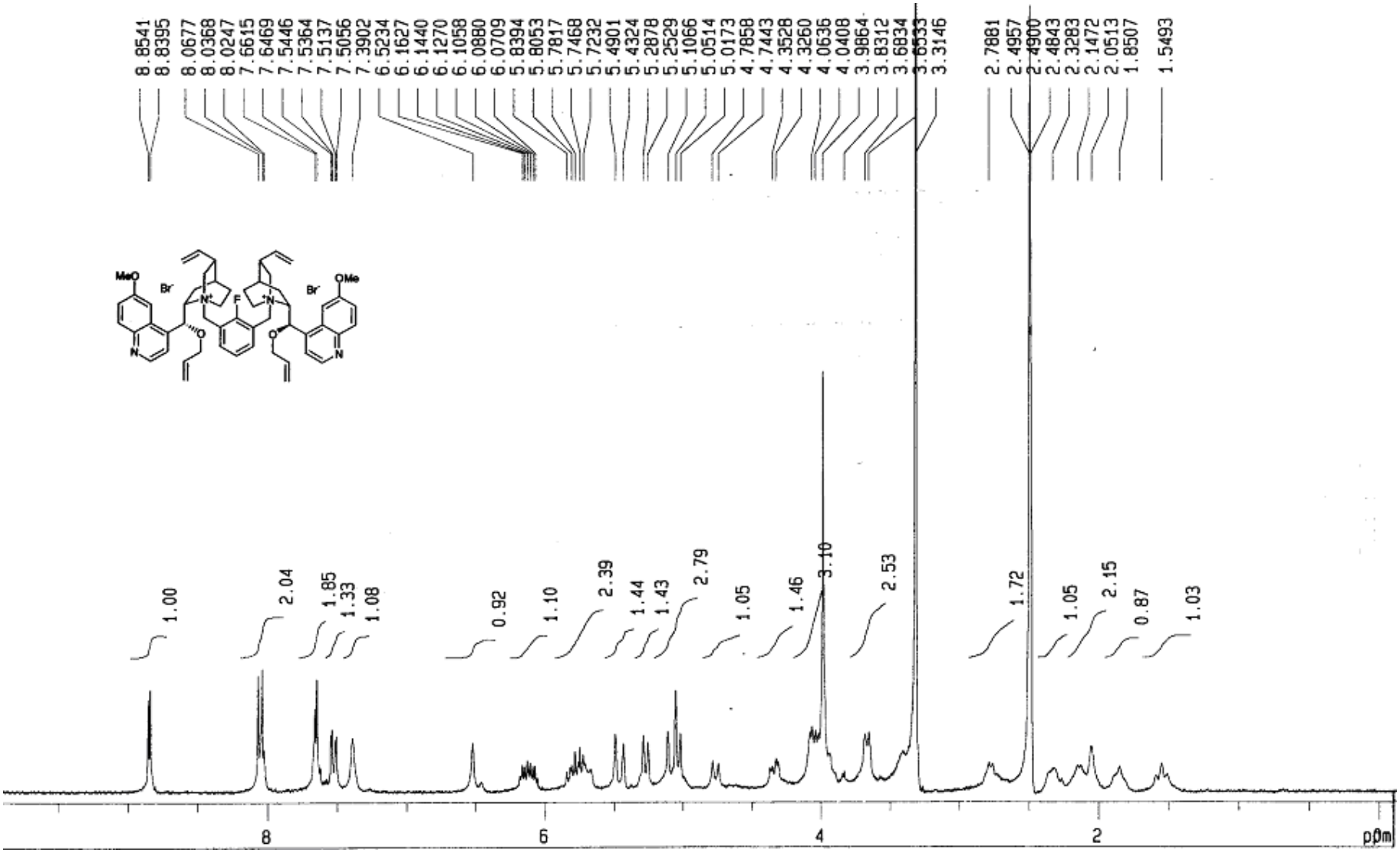
[1]H-NMR of compound **11**



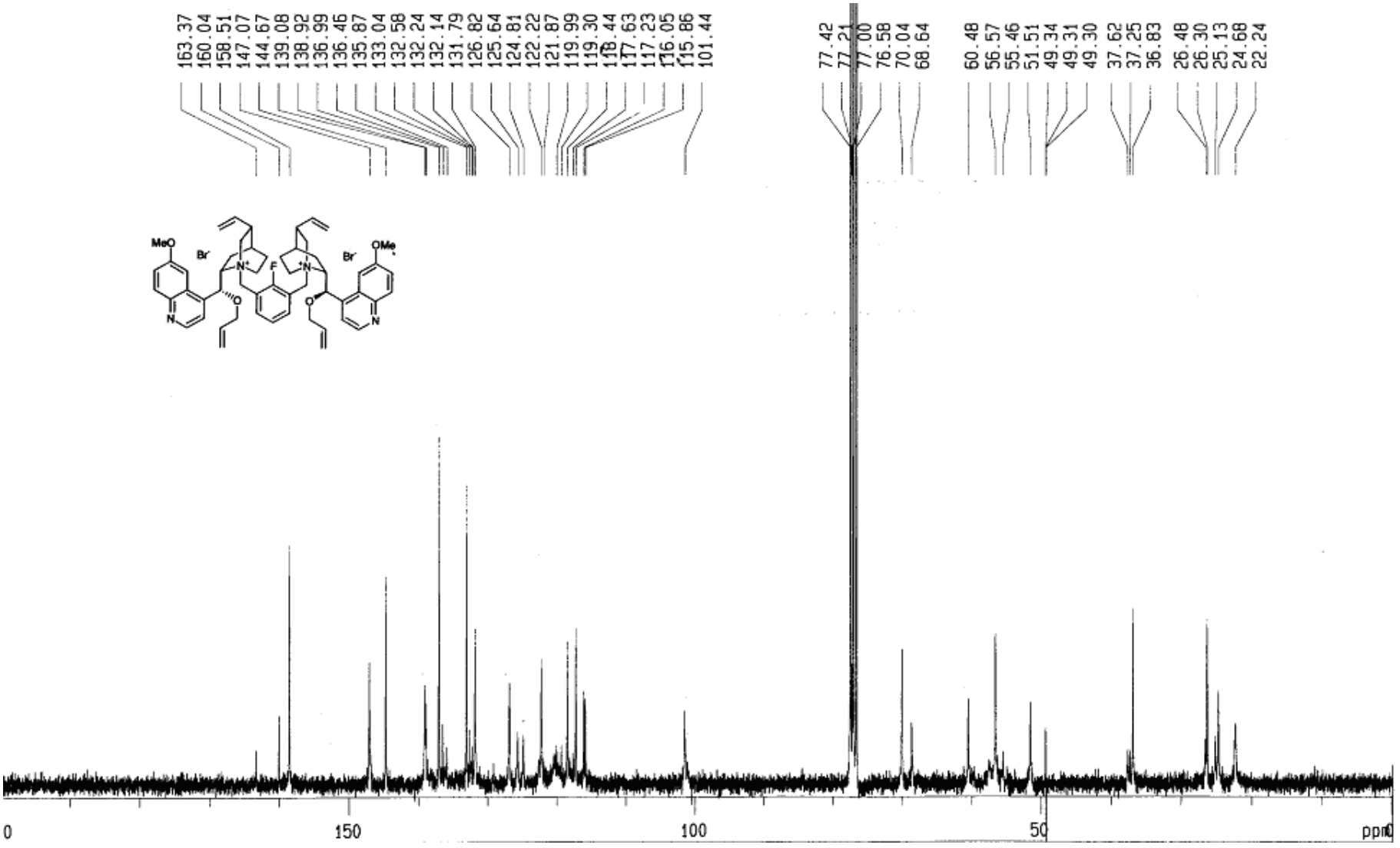
^{13}C-NMR of compound **11**



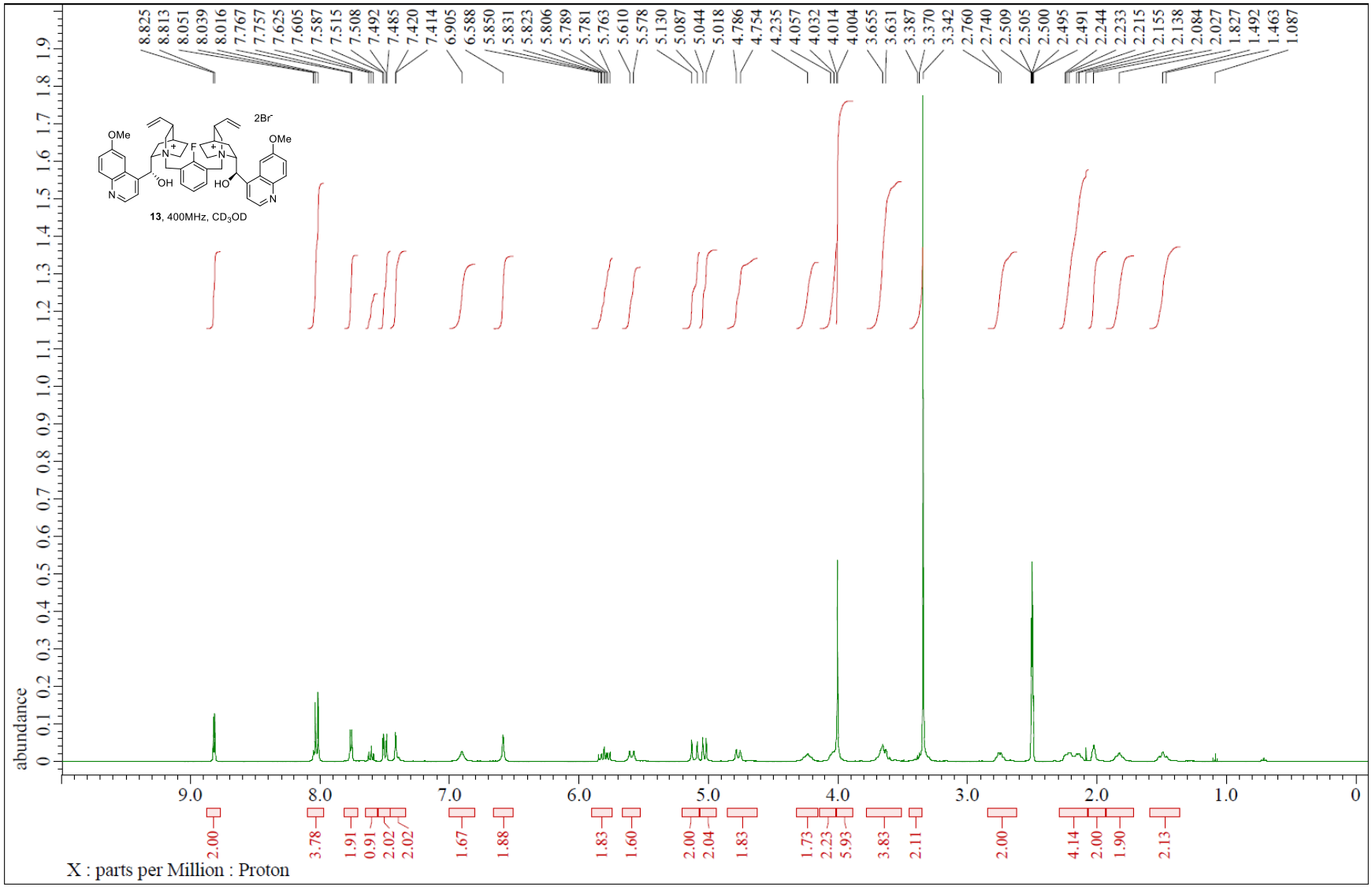
[1]H-NMR of compound **12** (DMSO-d_6, 300MHz)



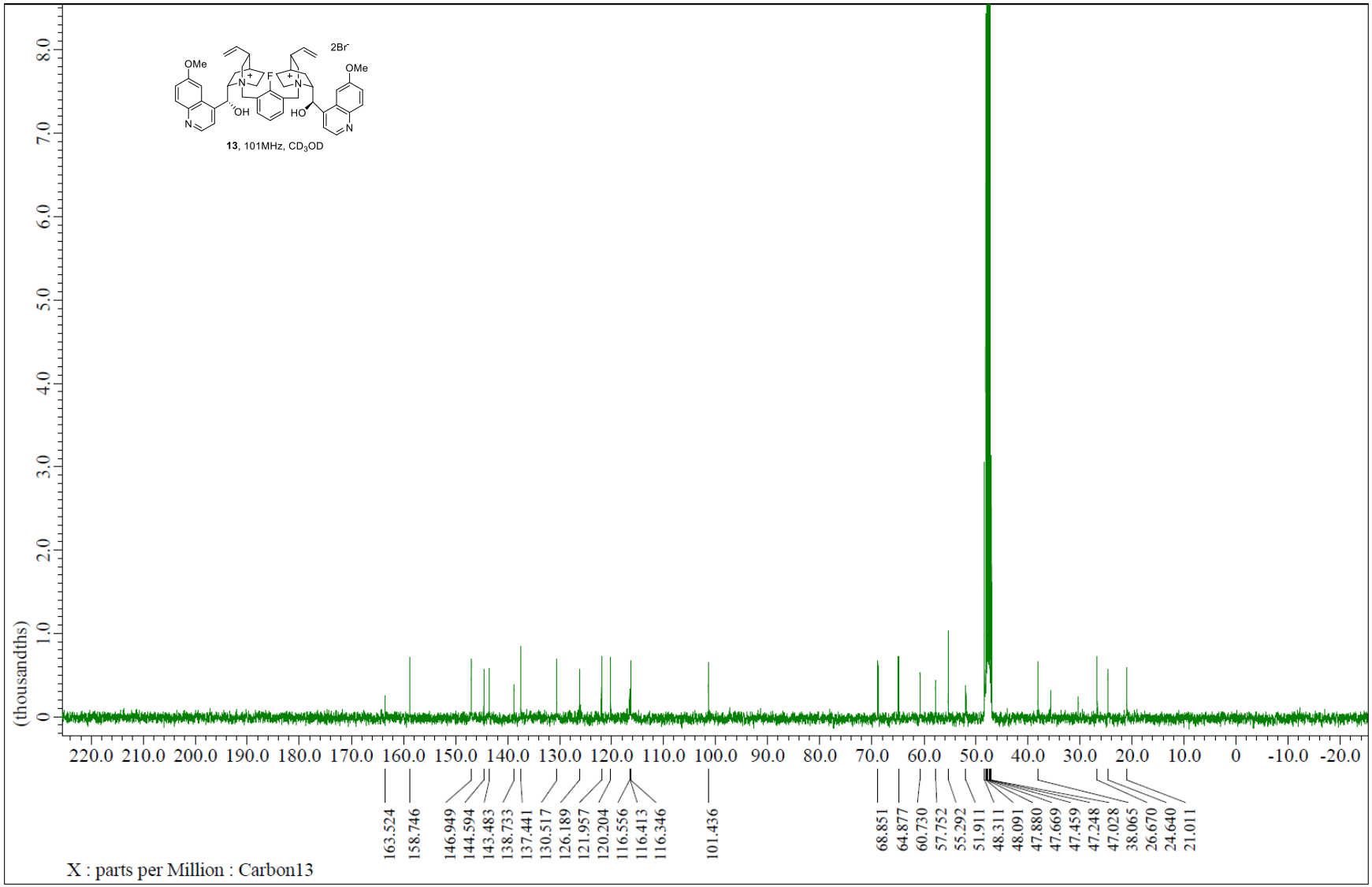
[13]C-NMR of compound **12** (DMSO-d_6, 75MHz)



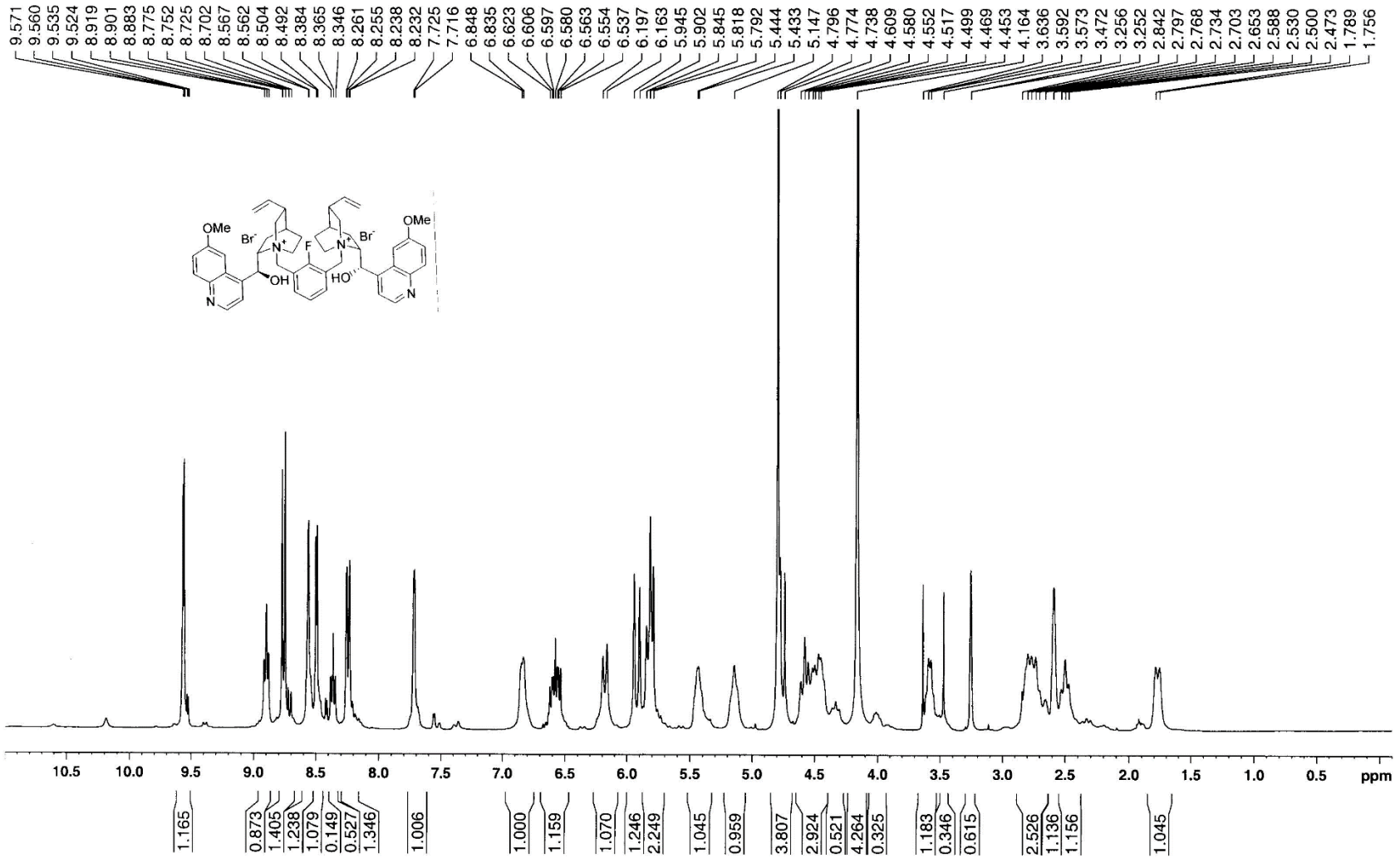
[1]H-NMR of compound **13**



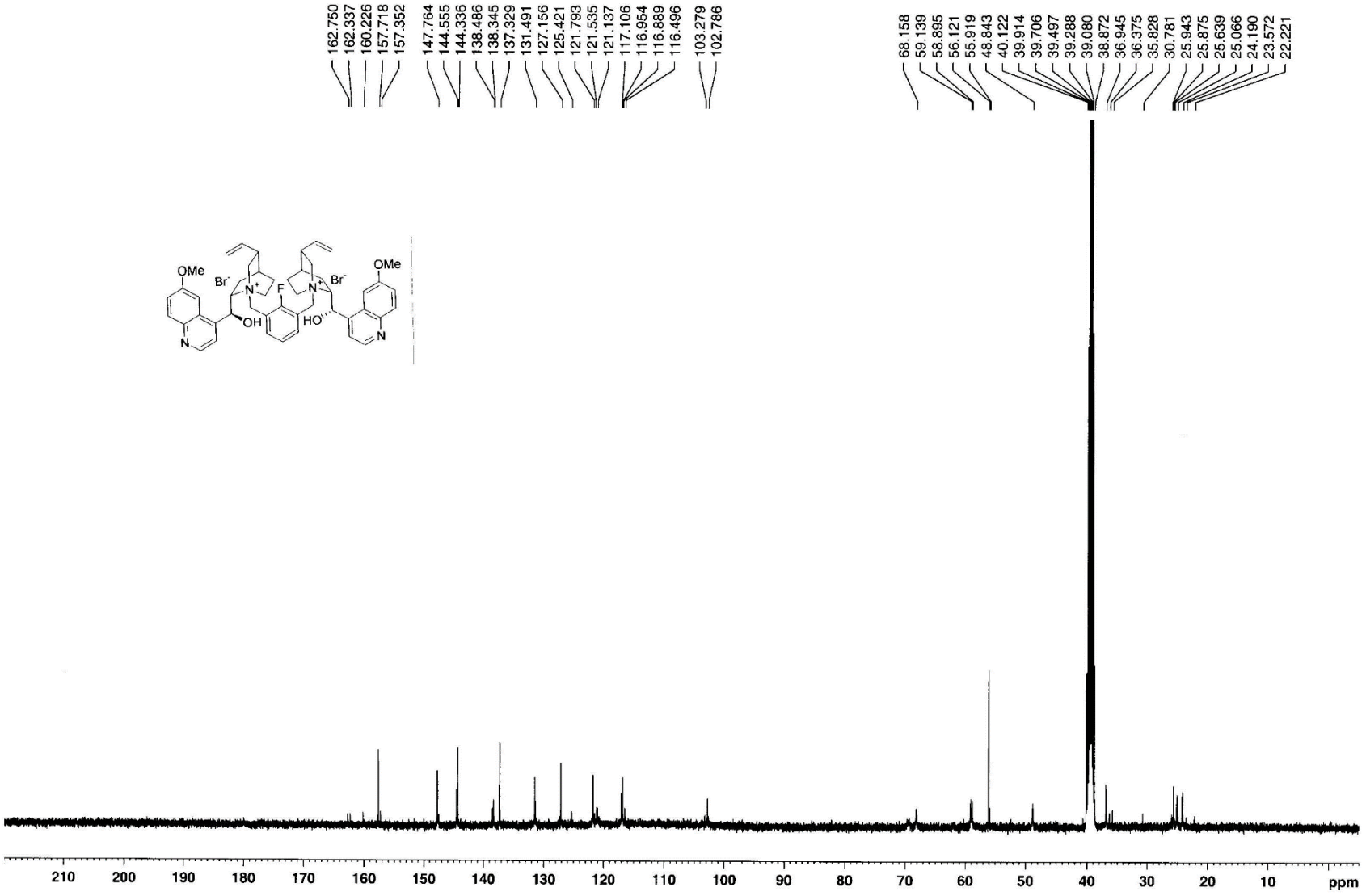
^{13}C-NMR of compound **13**



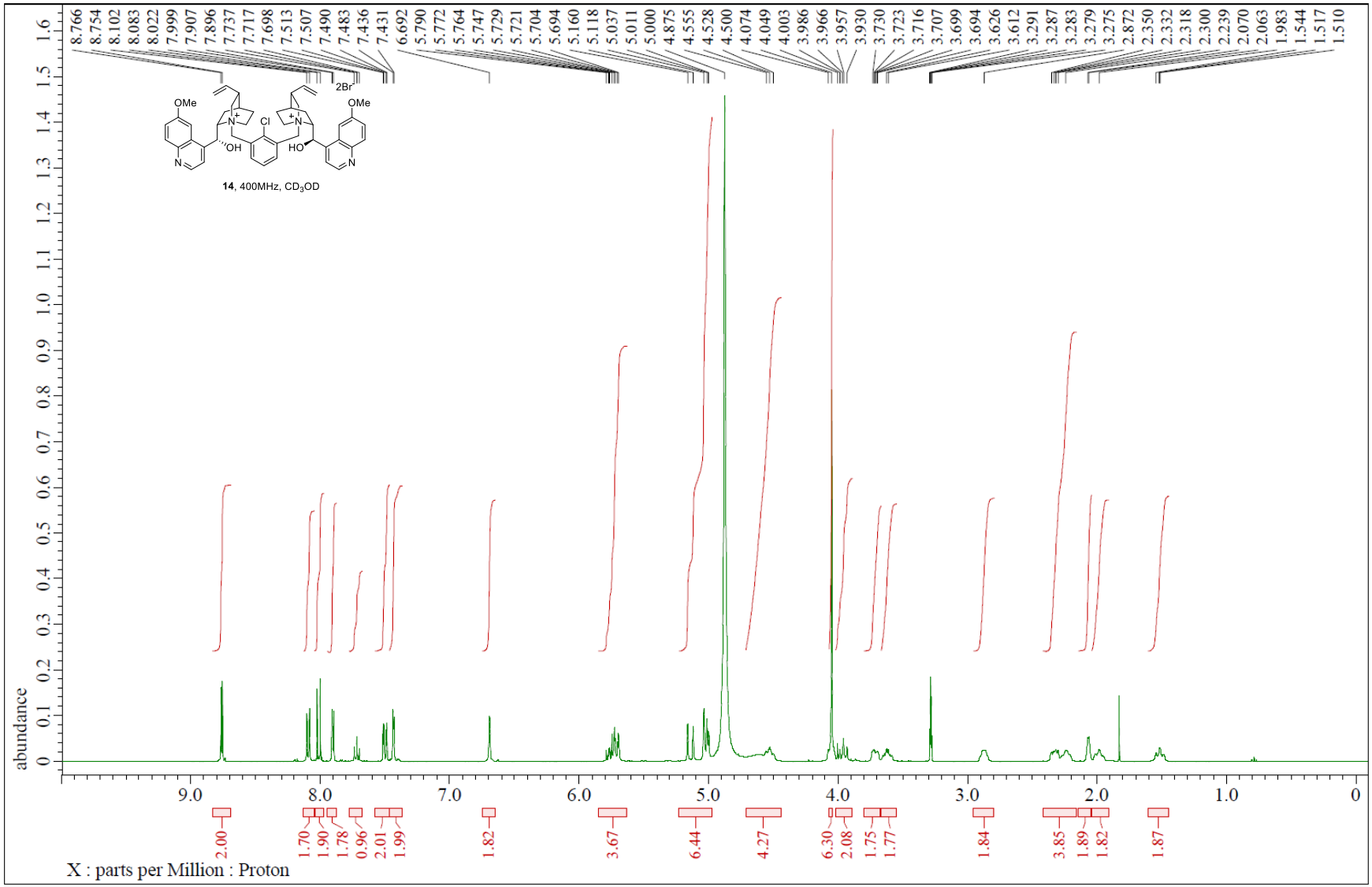
[1]*H-NMR of compound* **C(9)(*S*)-epi-13** (DMSO-d_6, 400MHz)



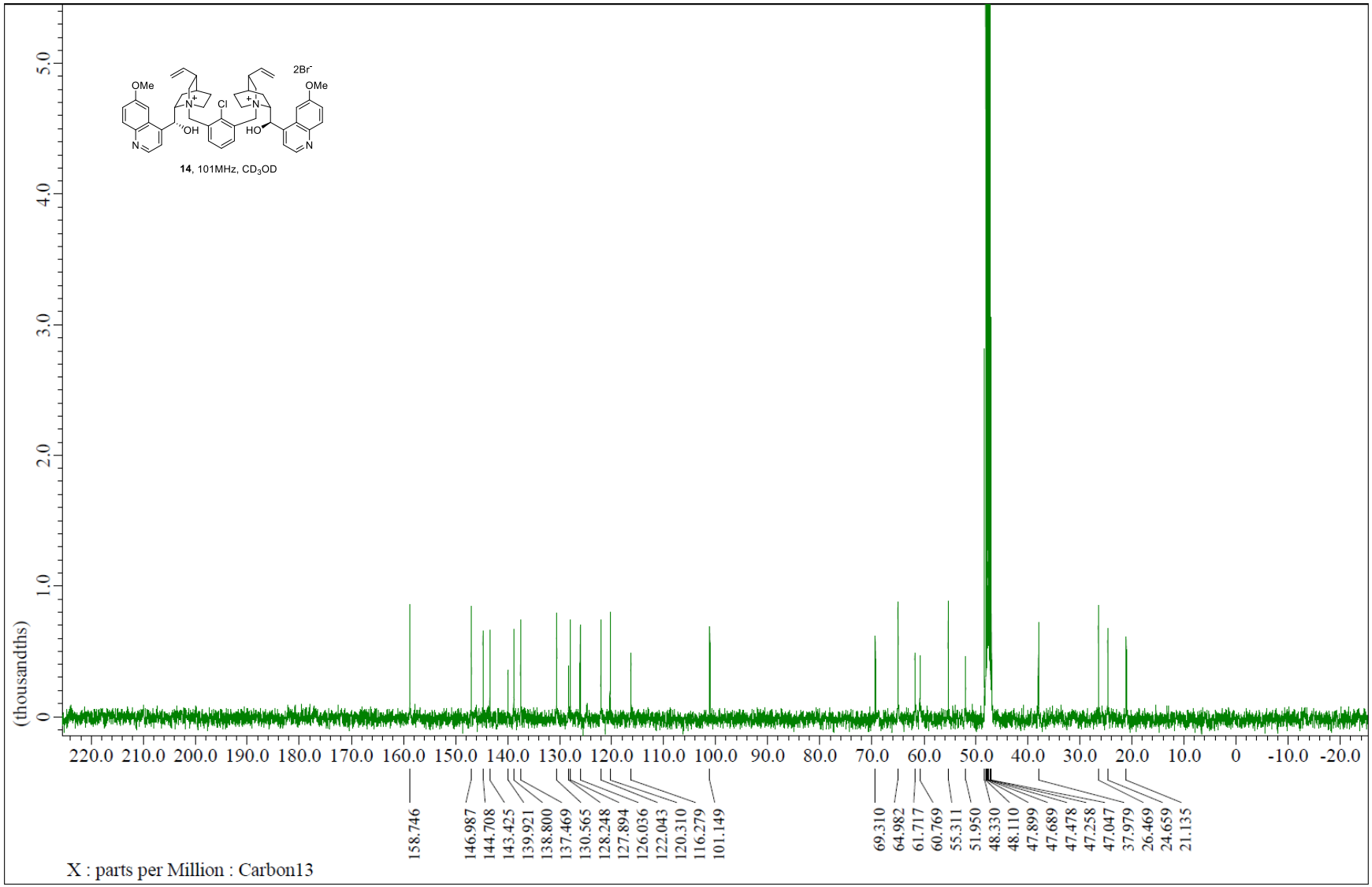
^{13}C-NMR of compound **C(9)(*S*)-epi-13** (DMSO-d_6, 101MHz)



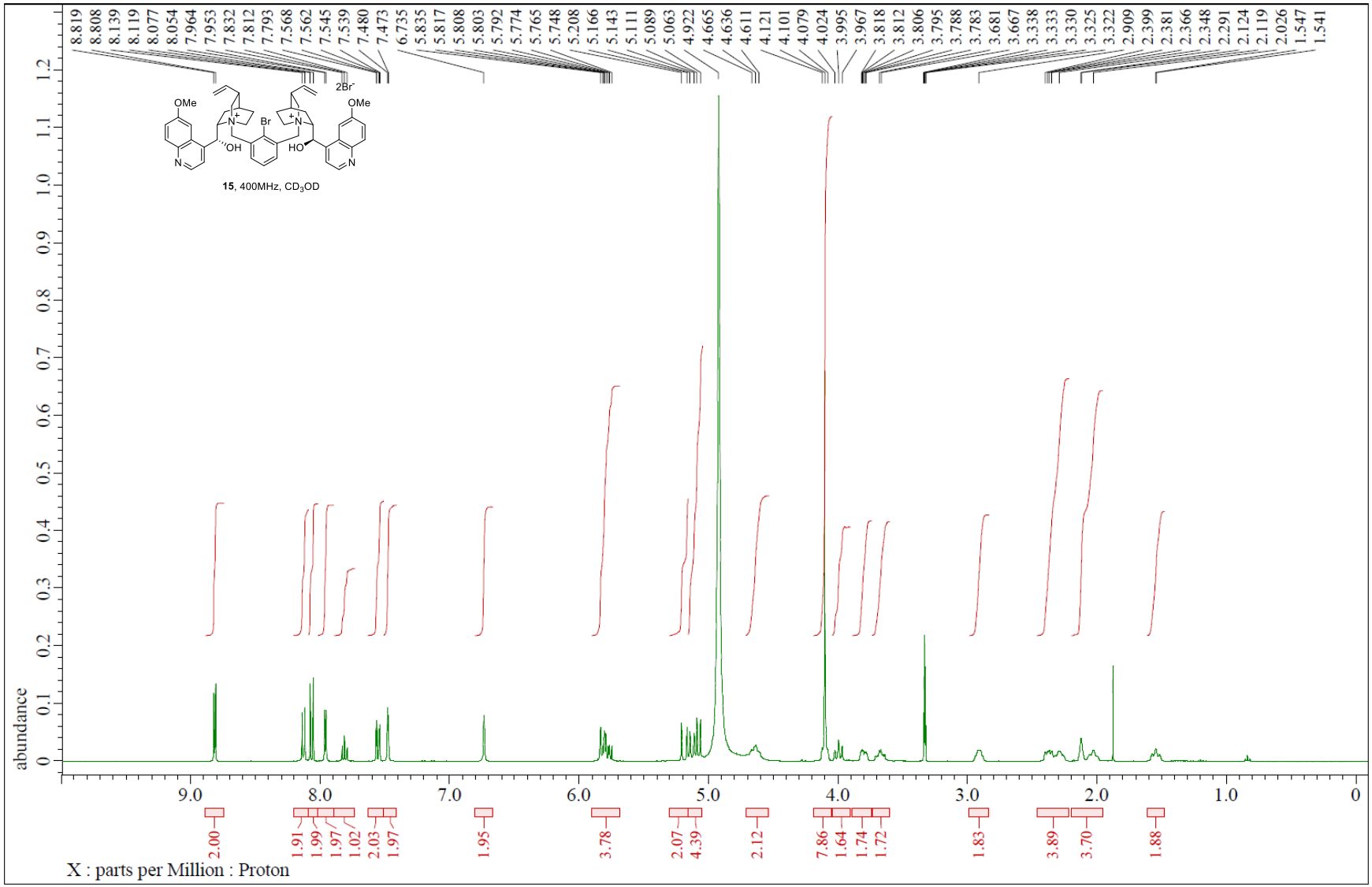
[1]H-NMR of compound **14**



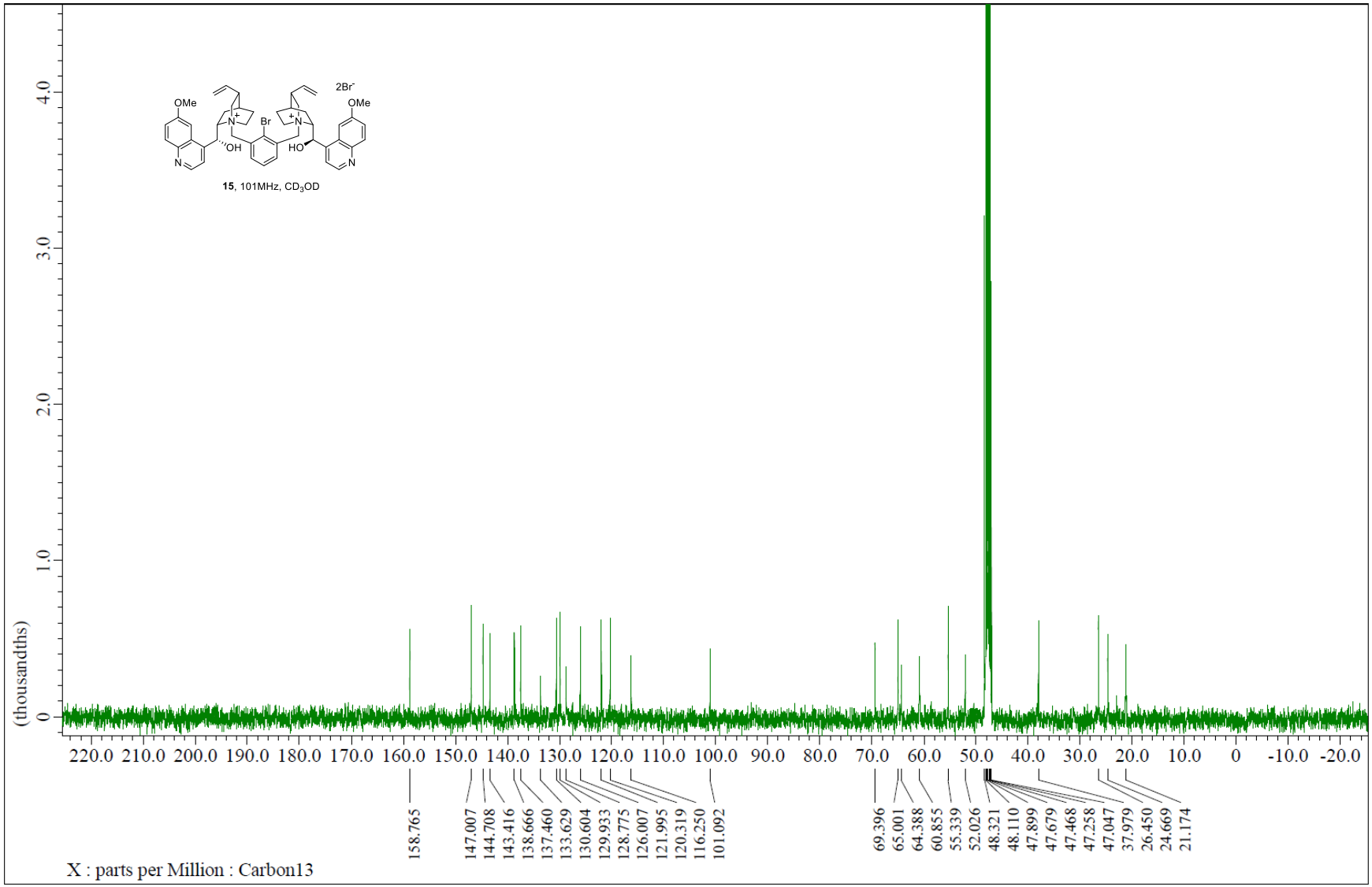
^{13}C-NMR of compound **14**



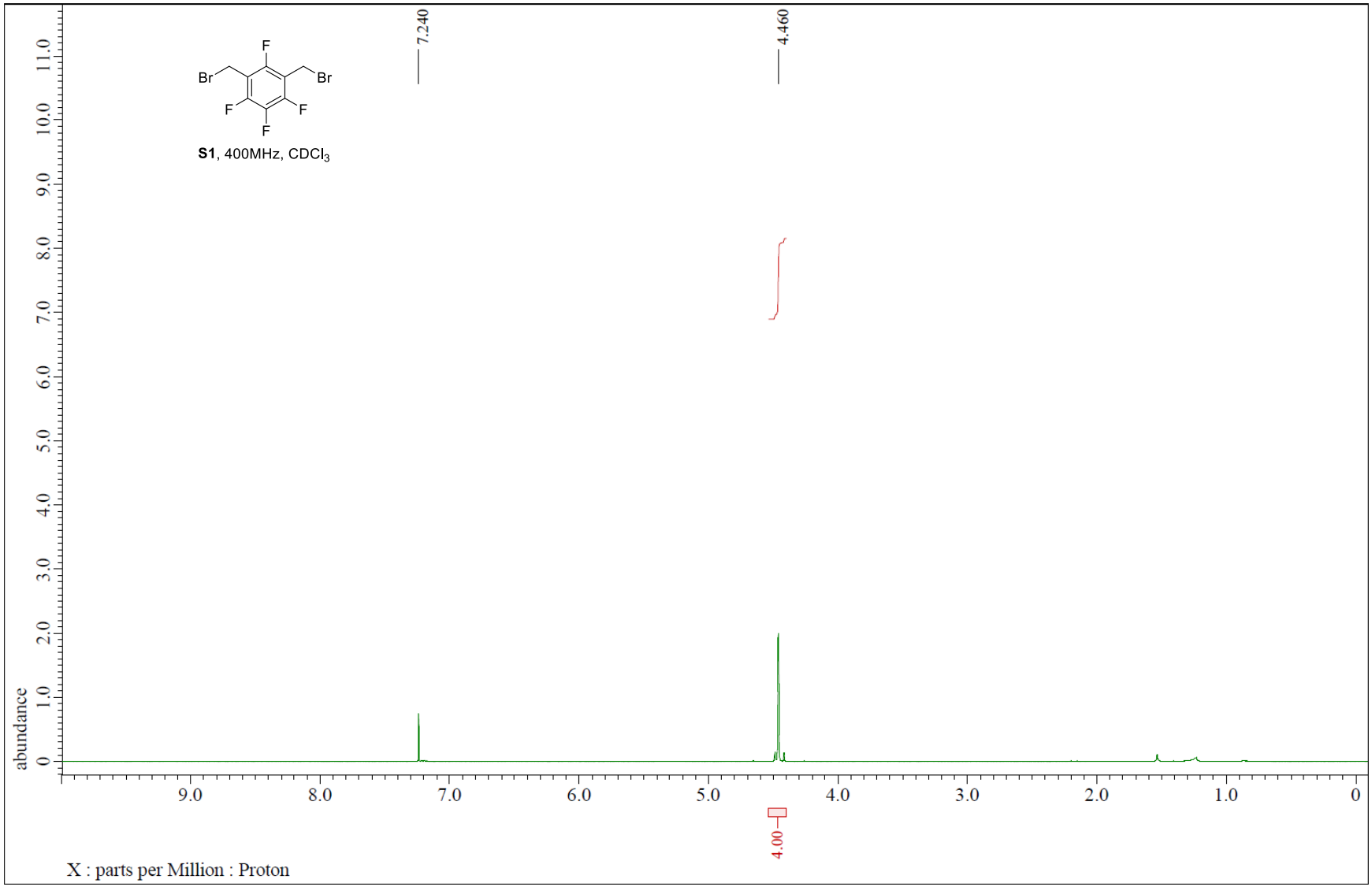
[1]H-NMR of compound **15**



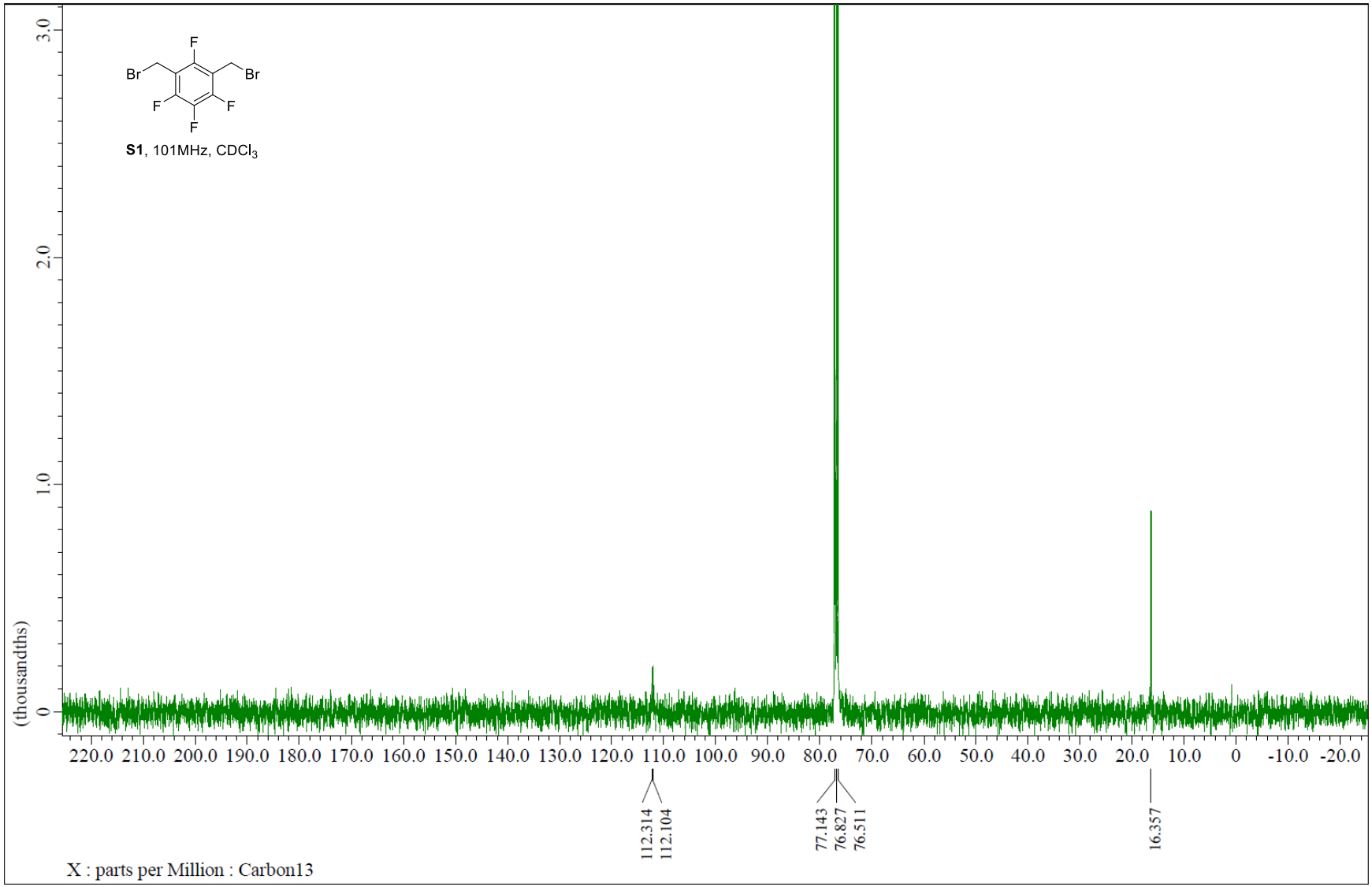
^{13}C-NMR of compound **15**



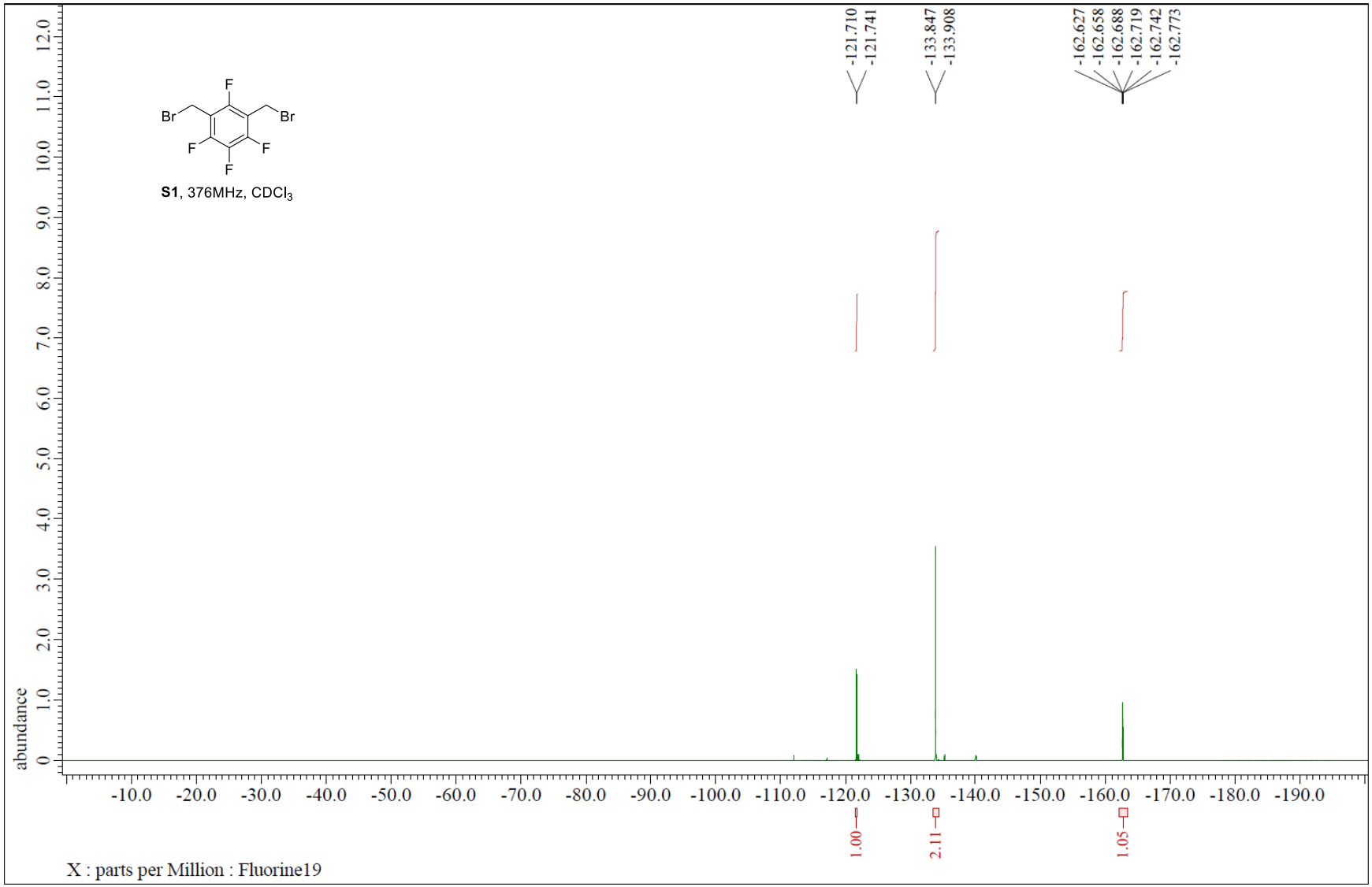
[1]H-NMR of compound **S1**



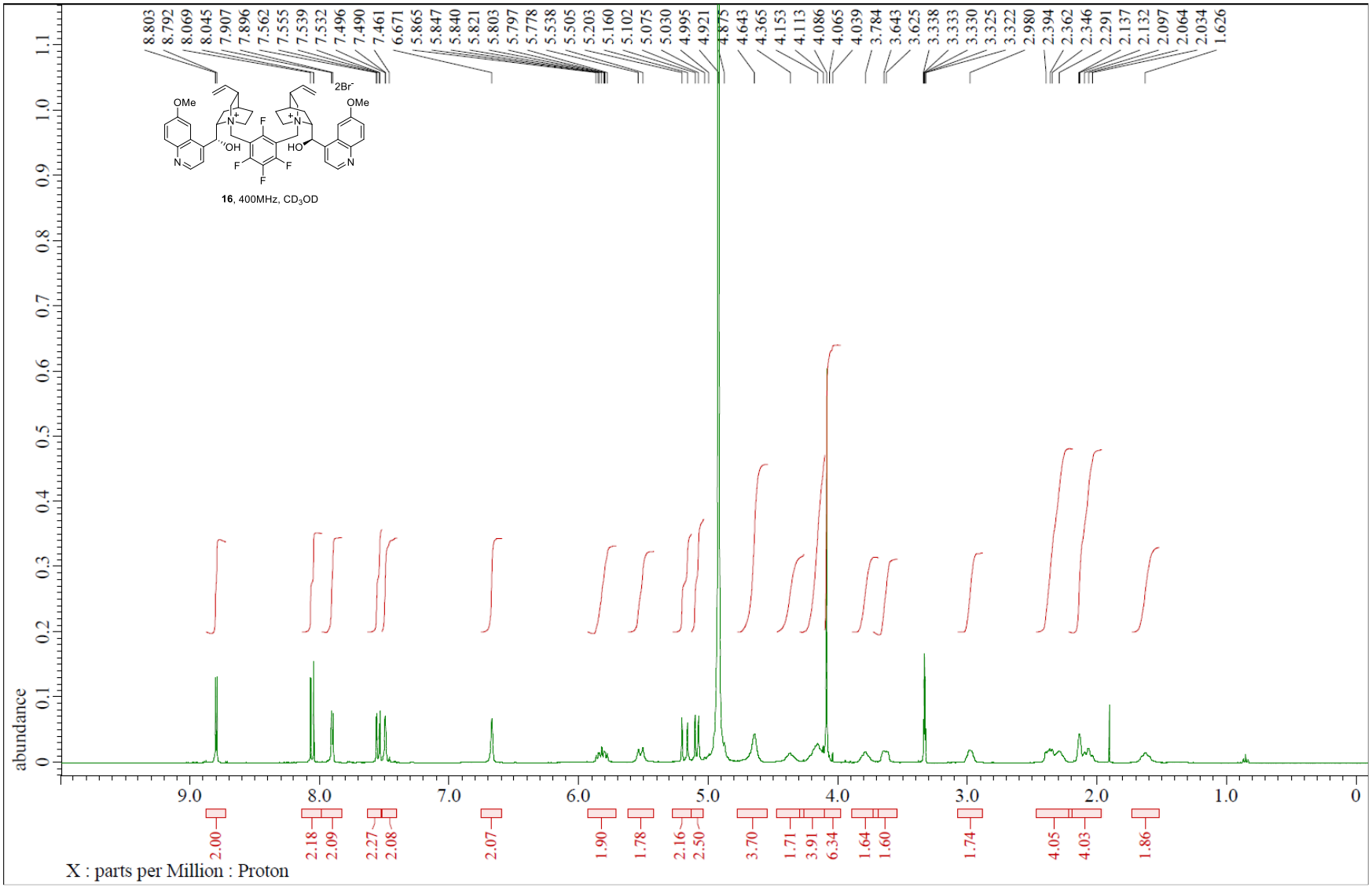
^{13}C-NMR of compound **S1**



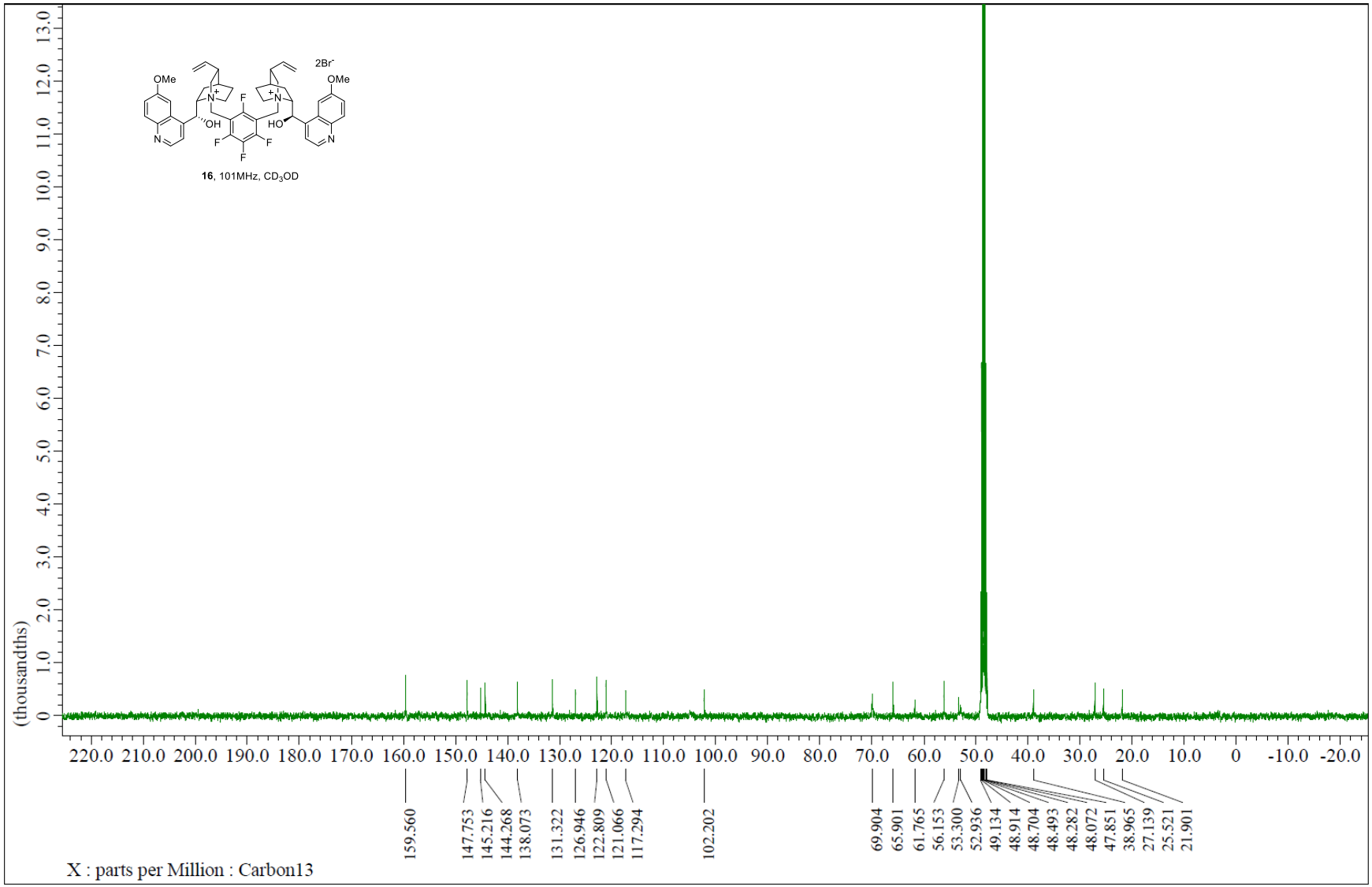
^{19}F-NMR of compound **S1**



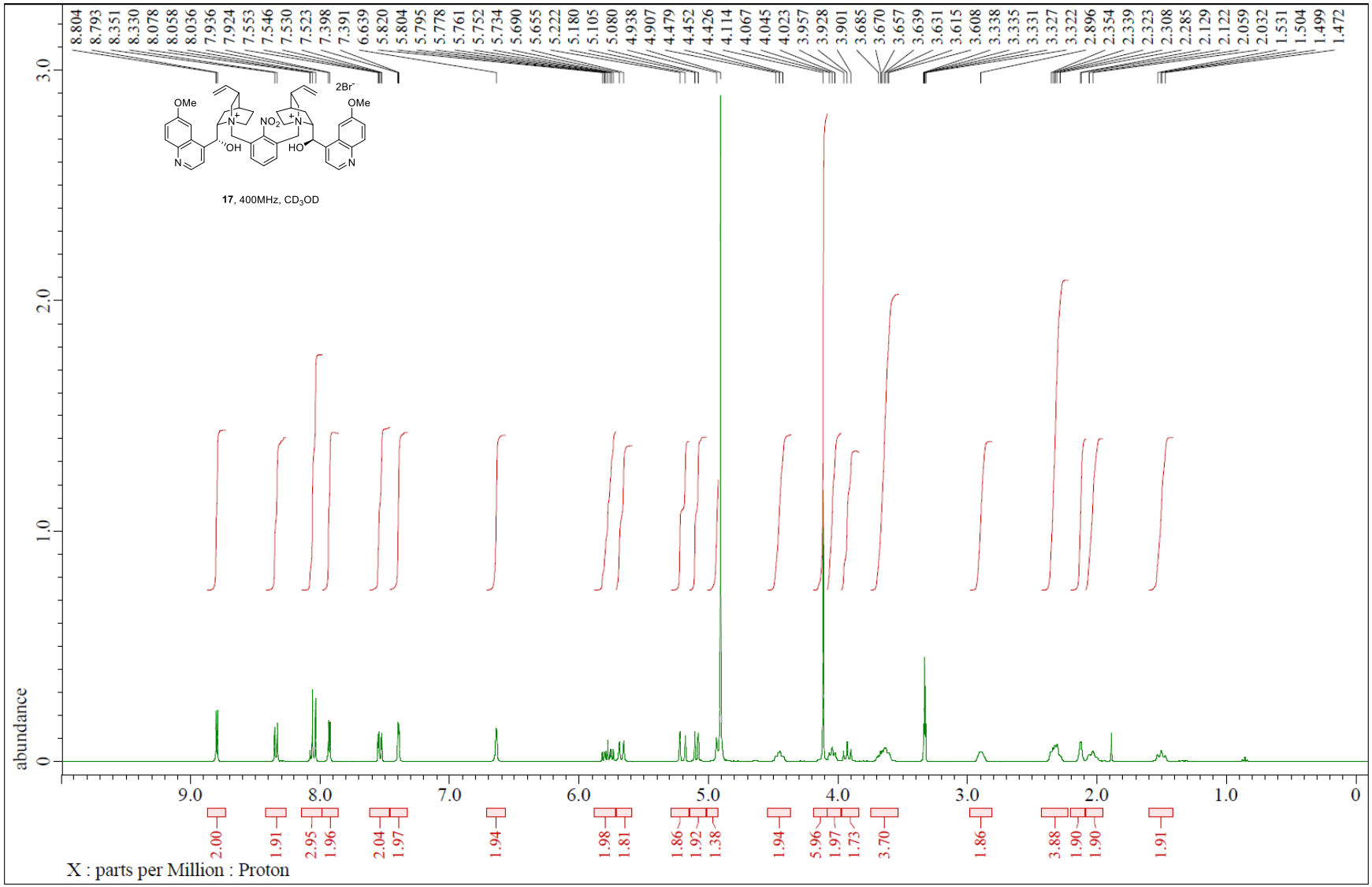
[1]H-NMR of compound **16**



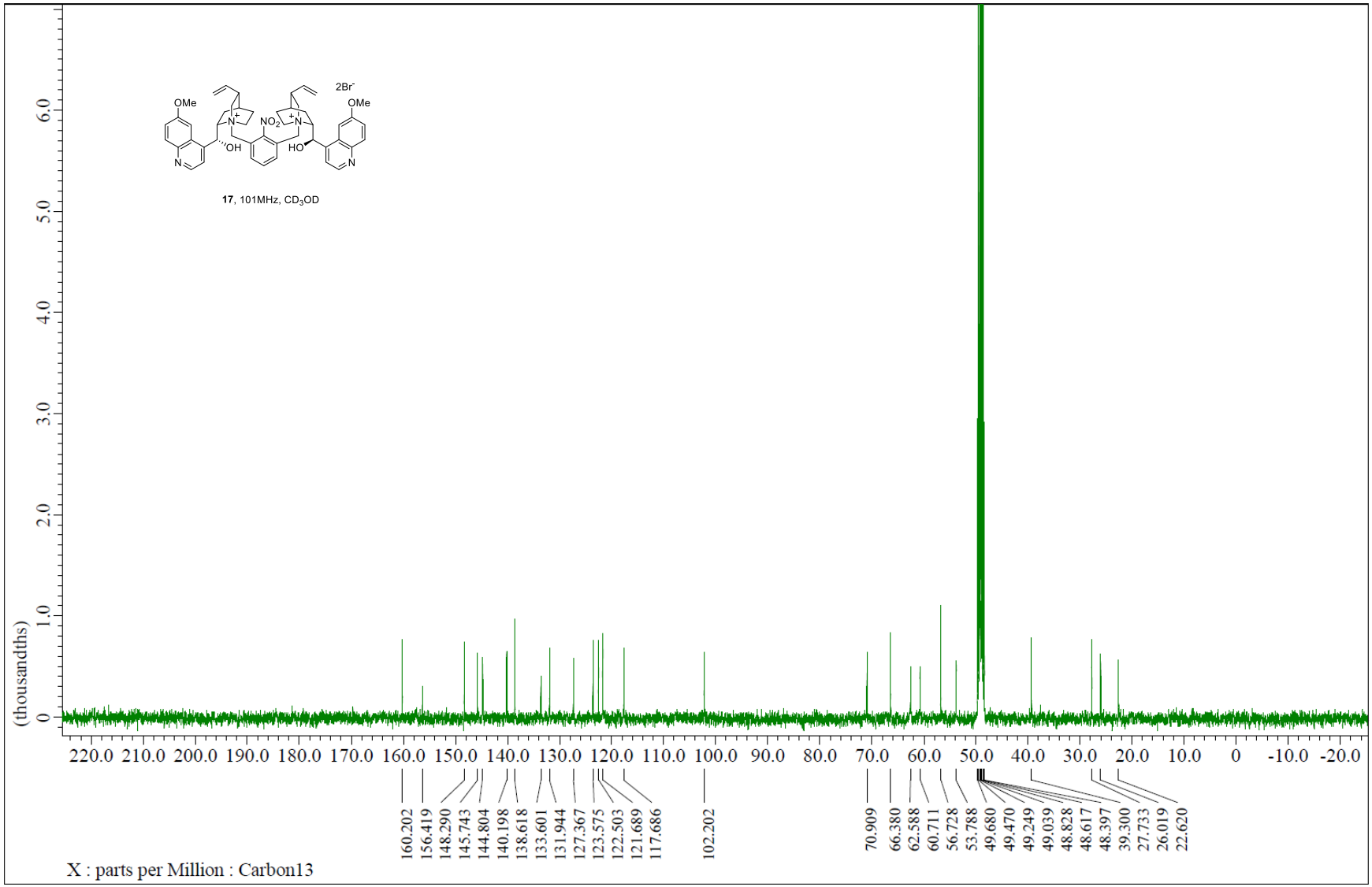
[1]H-NMR of compound **16**



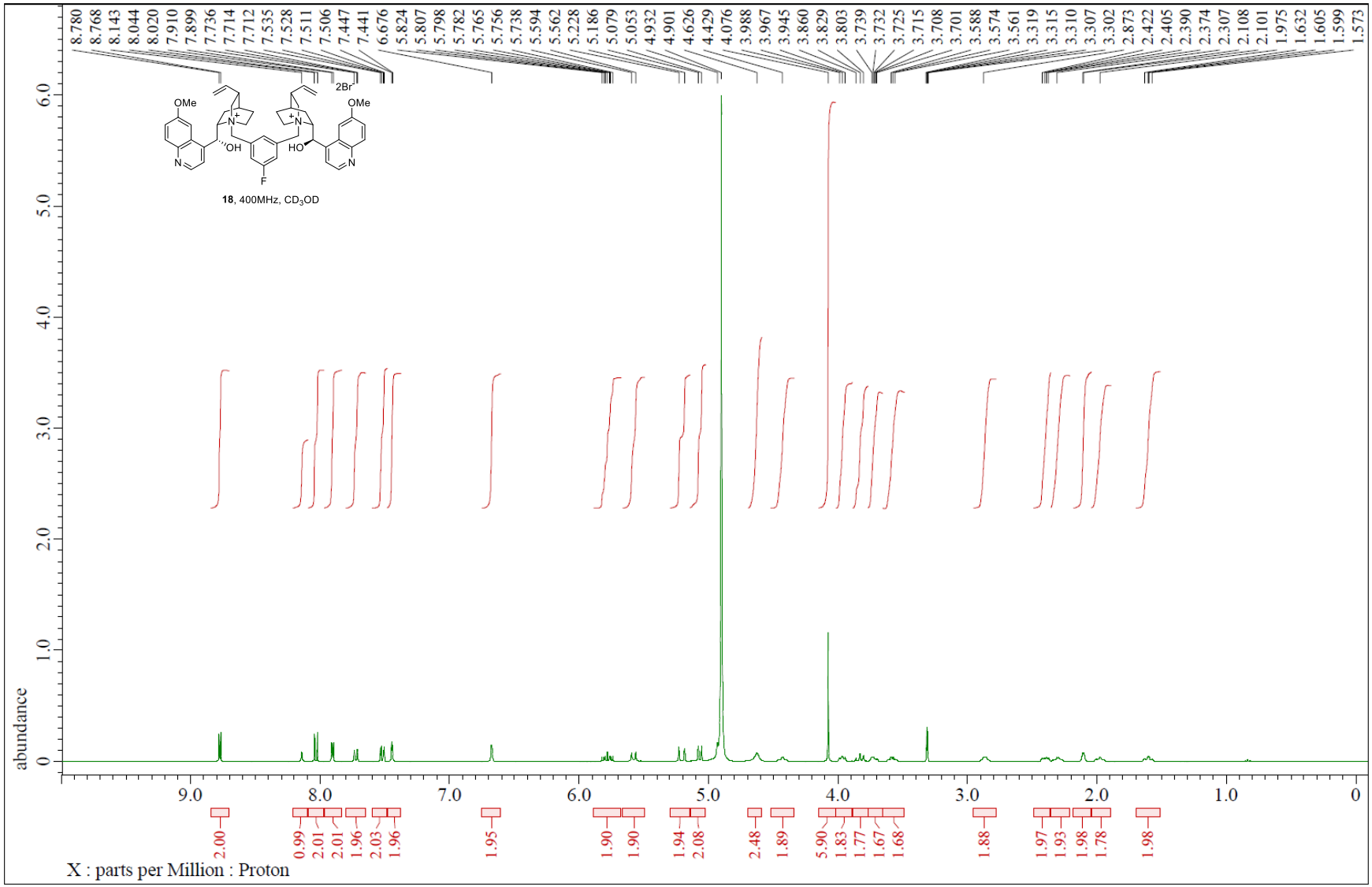
[1]H-NMR of compound **17**



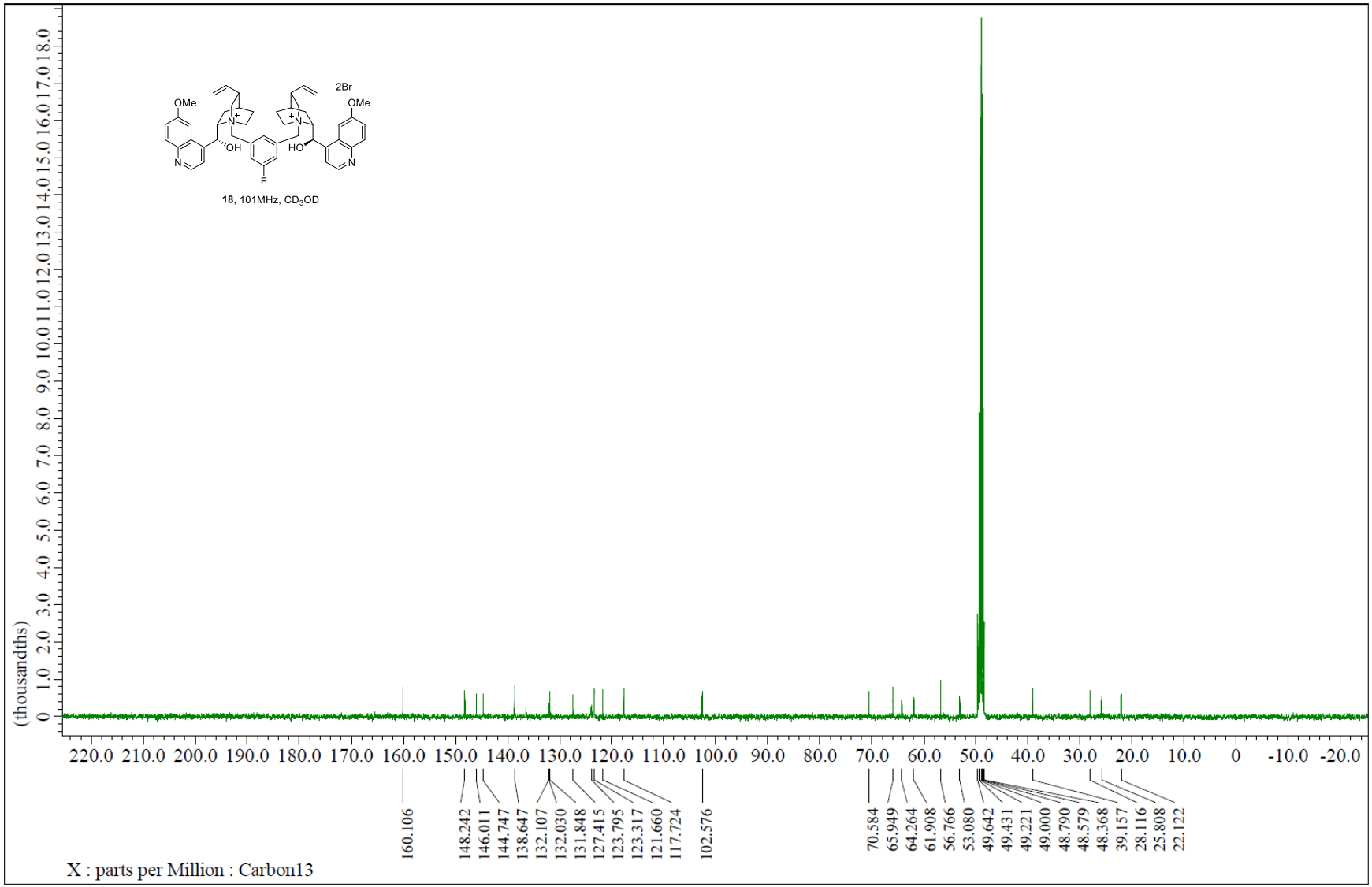
^{13}C-NMR of compound **17**



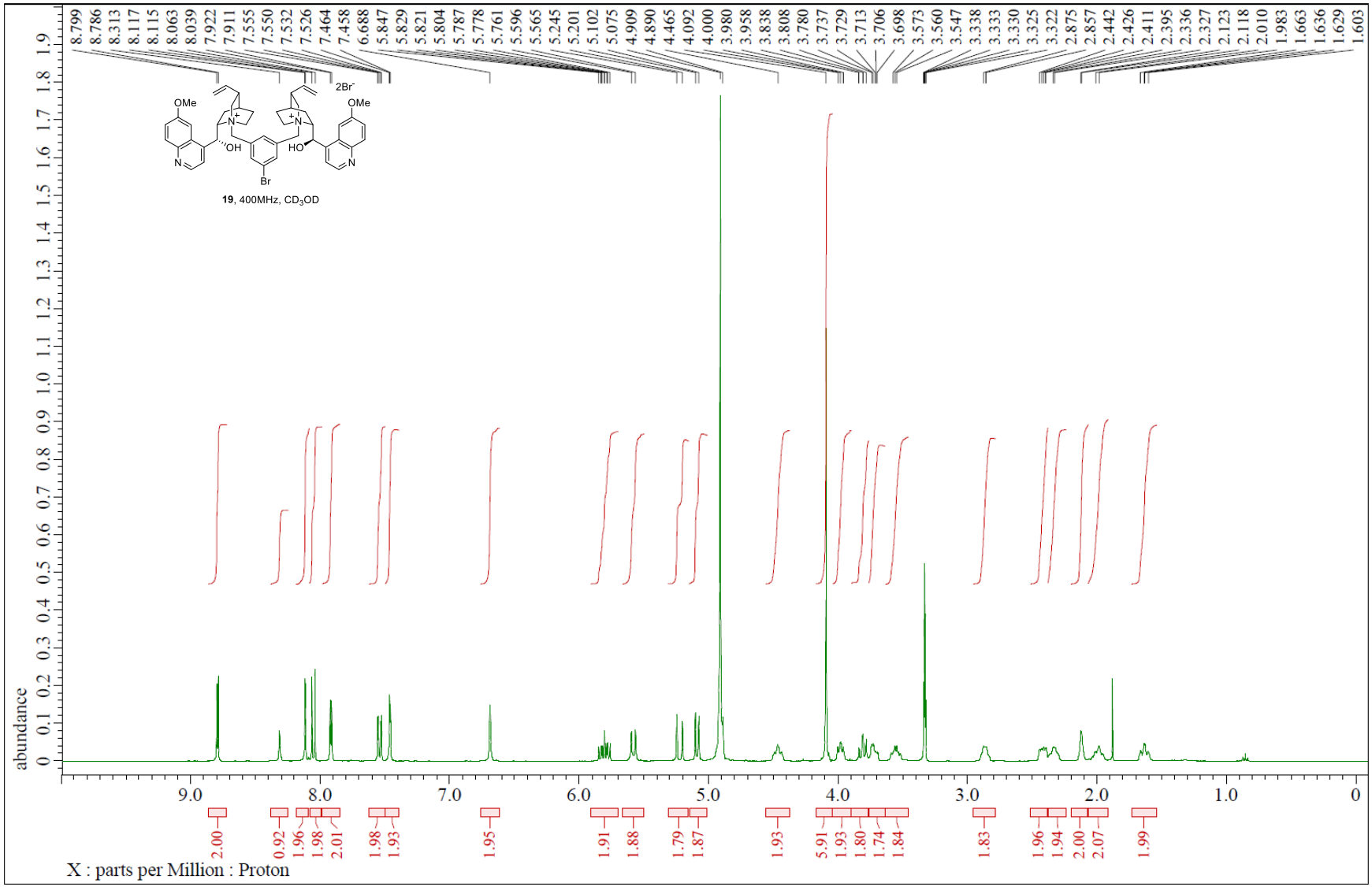
[1]H-NMR of compound **18**



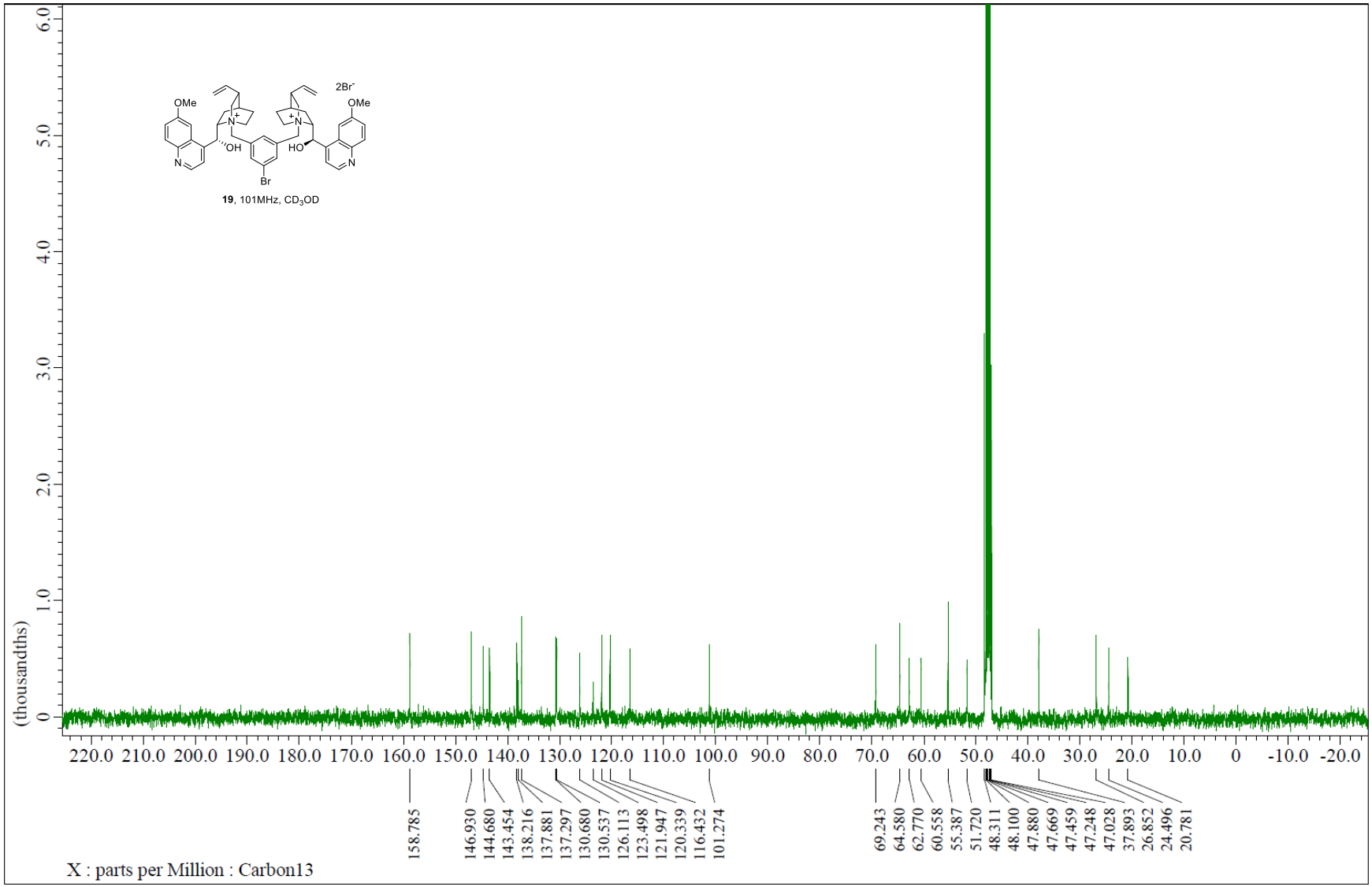
^{13}C-NMR of compound **18**



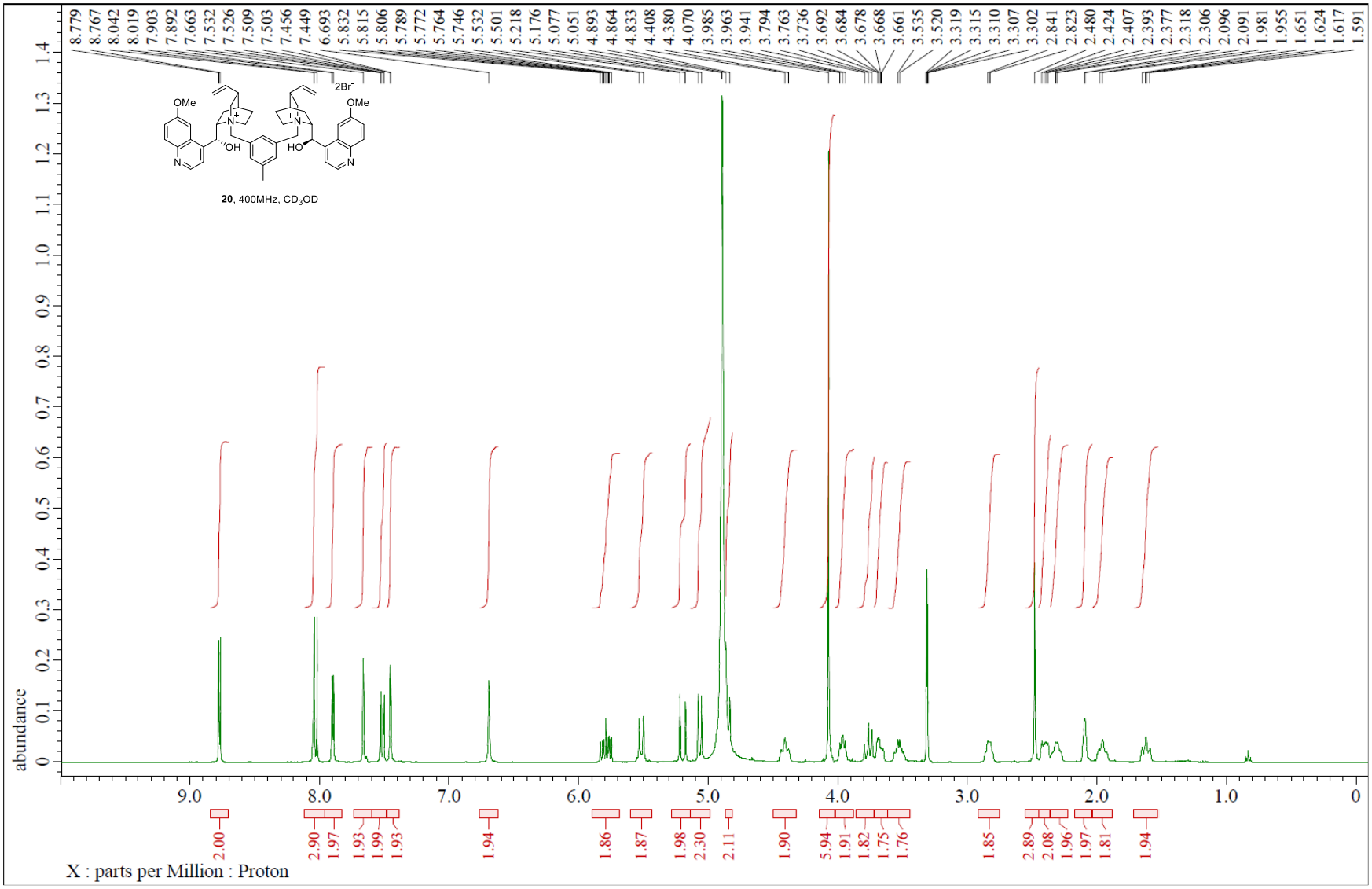
[1]H-NMR of compound **19**



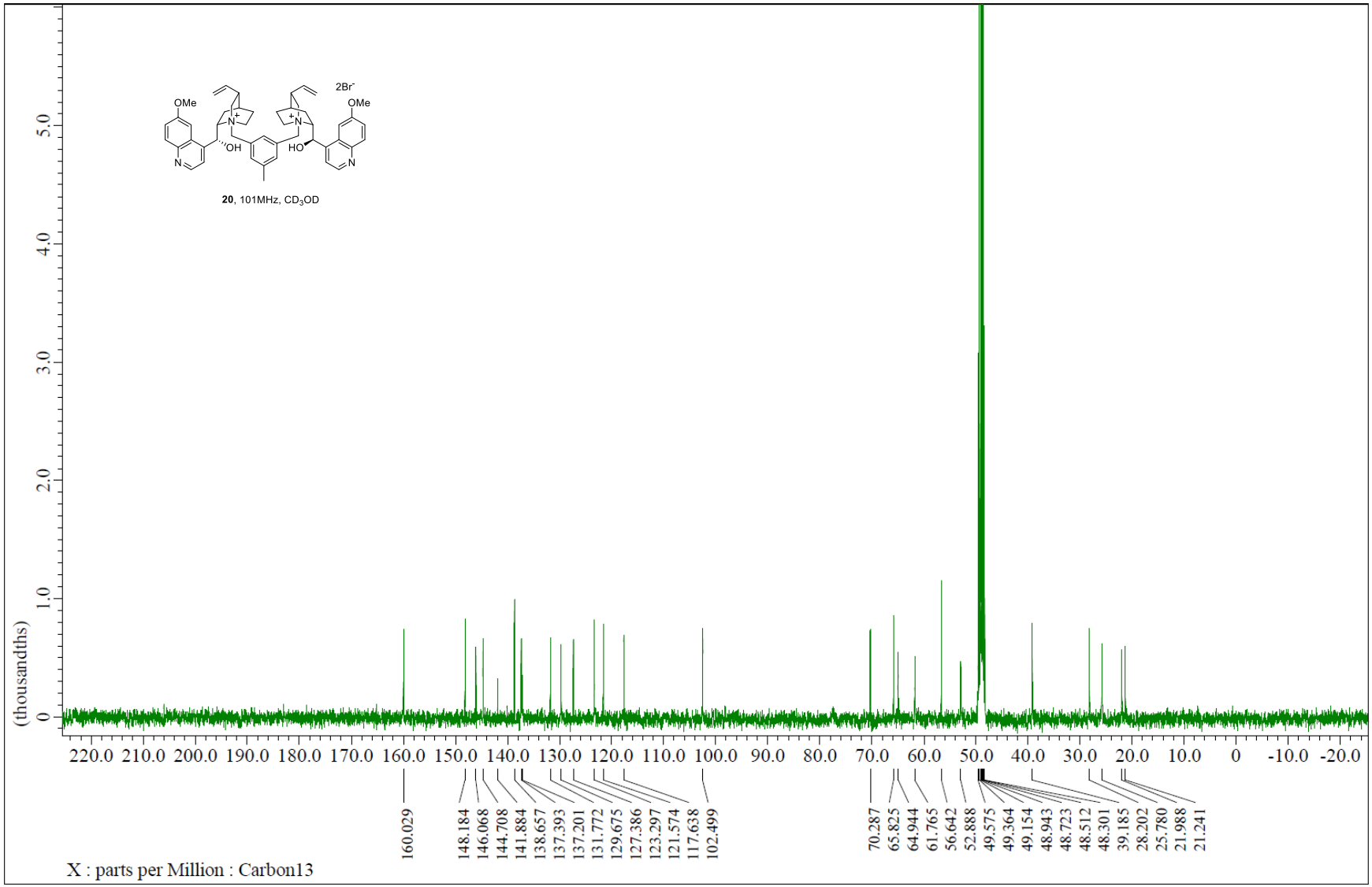
[13]C-NMR of compound **19**



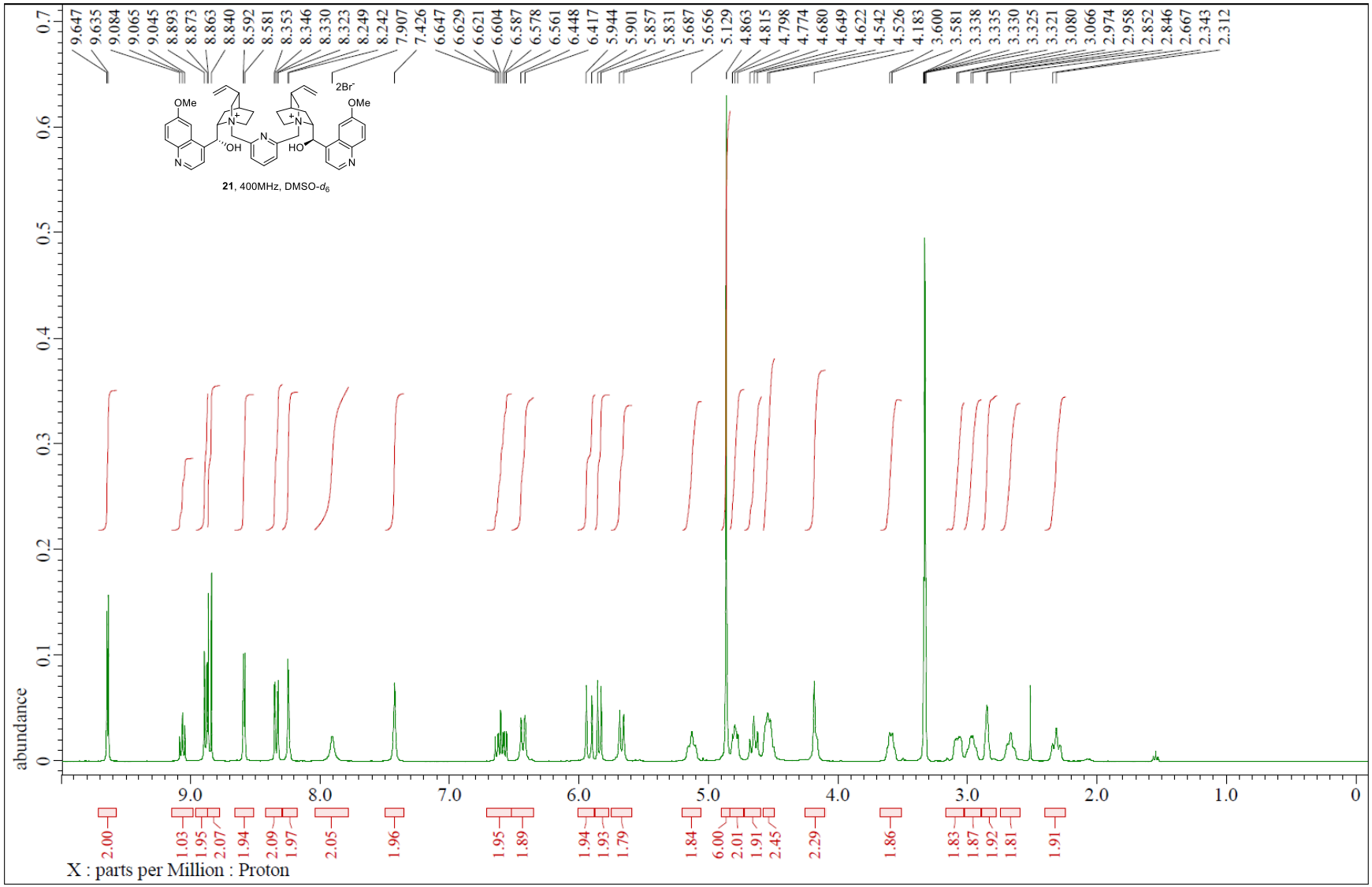
[1]H-NMR of compound **20**



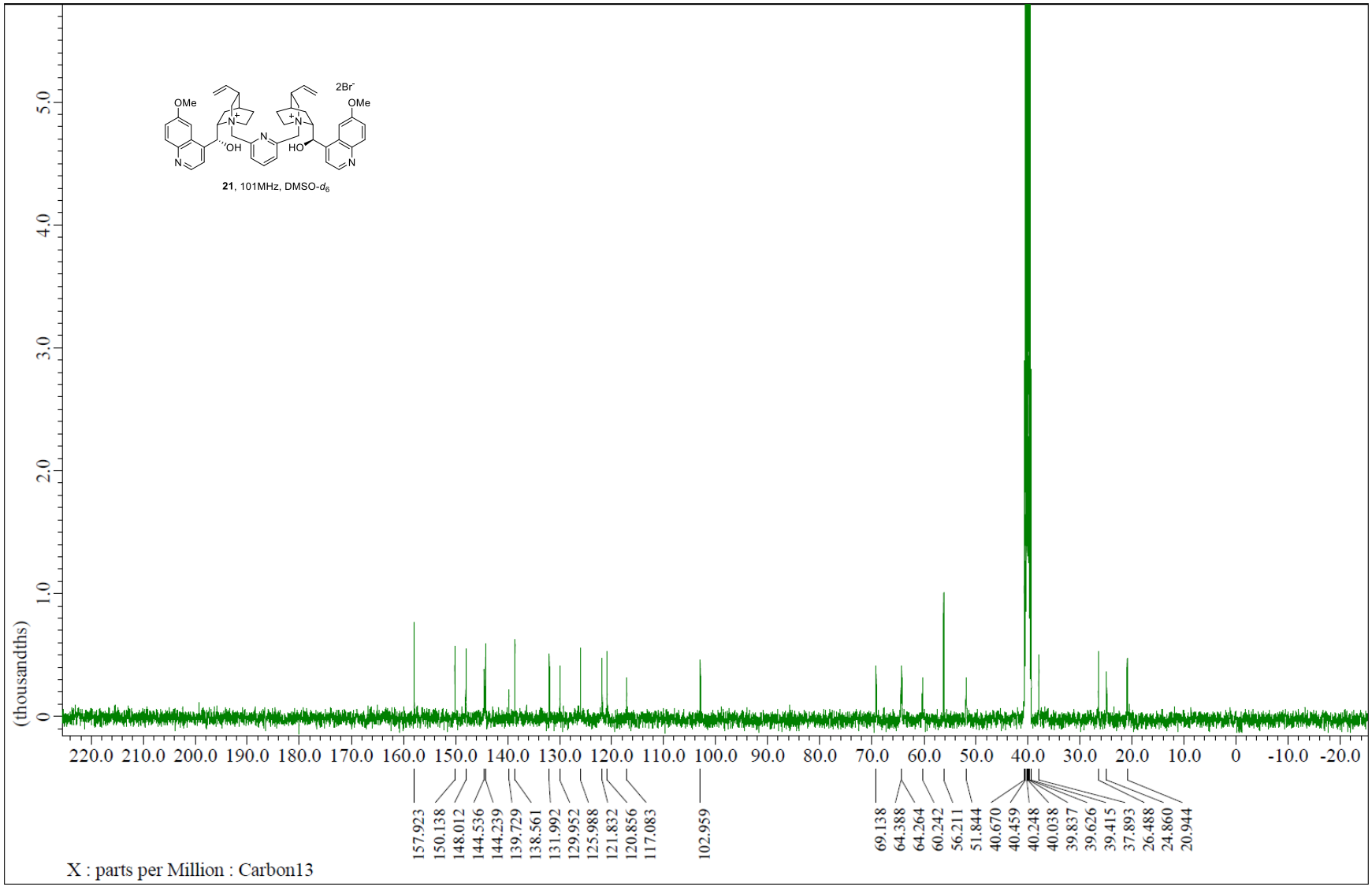
^{13}C-NMR of compound **20**



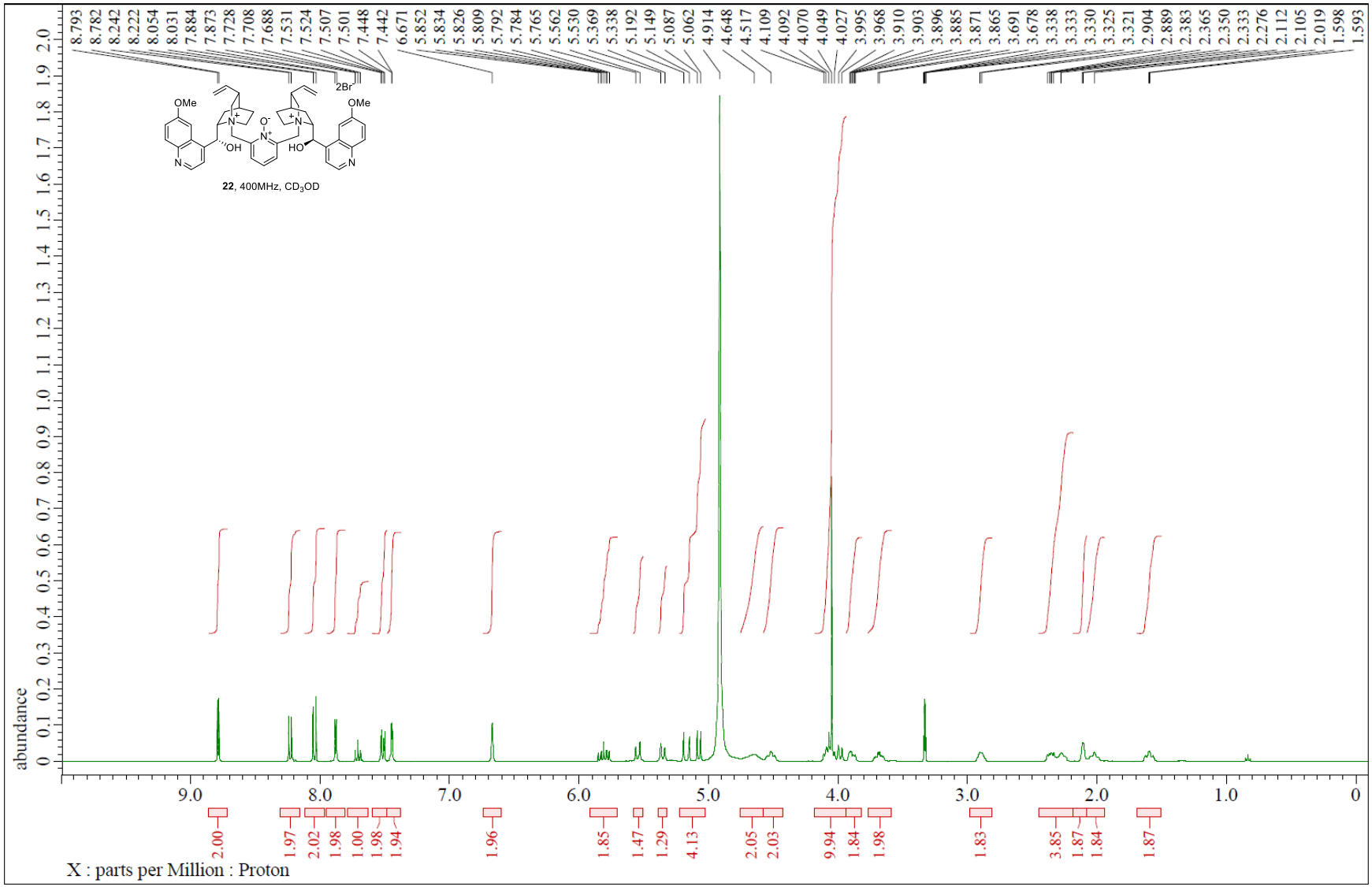
[1]H-NMR of compound **21**



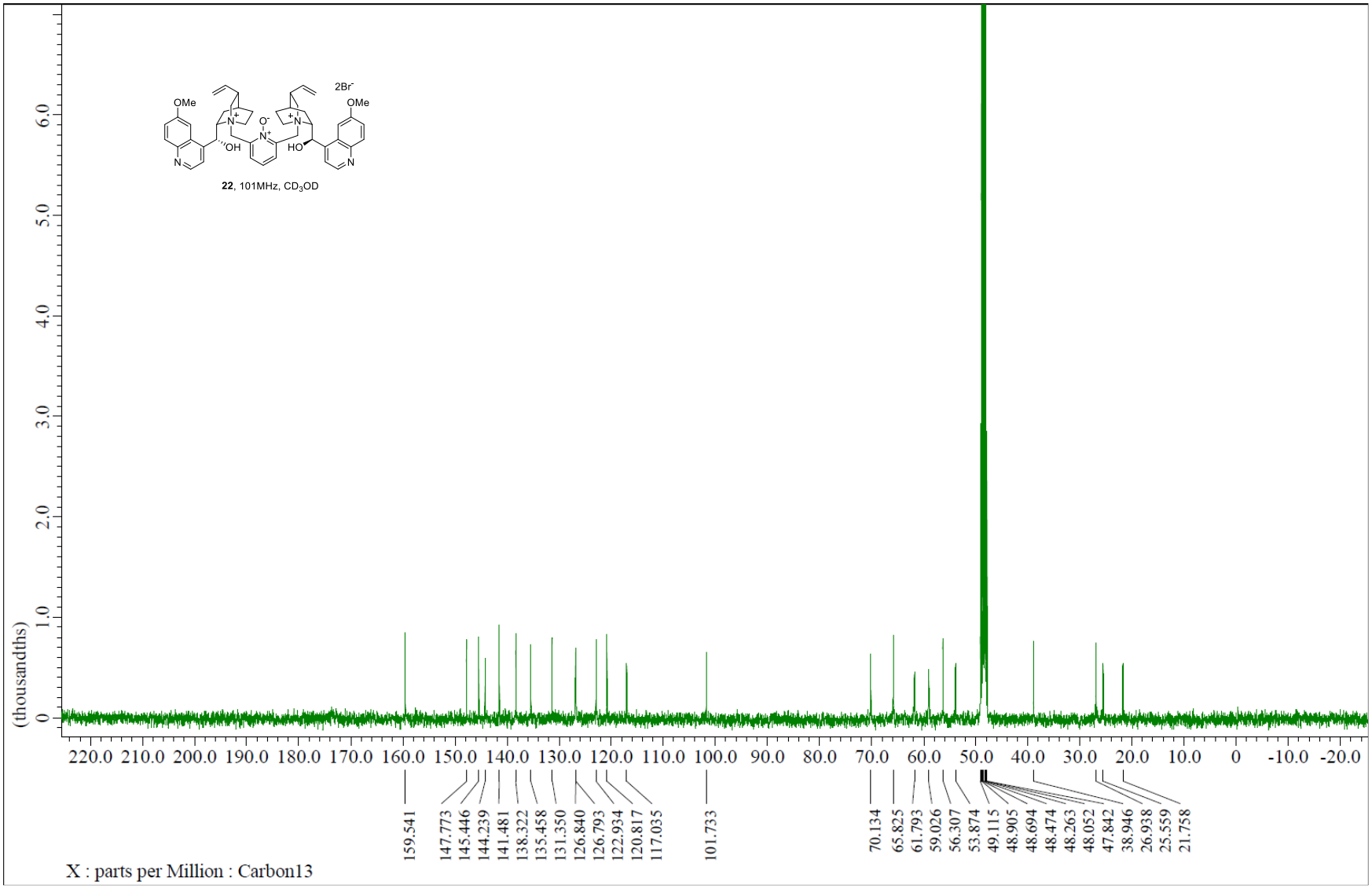
^{13}C-NMR of compound **21**



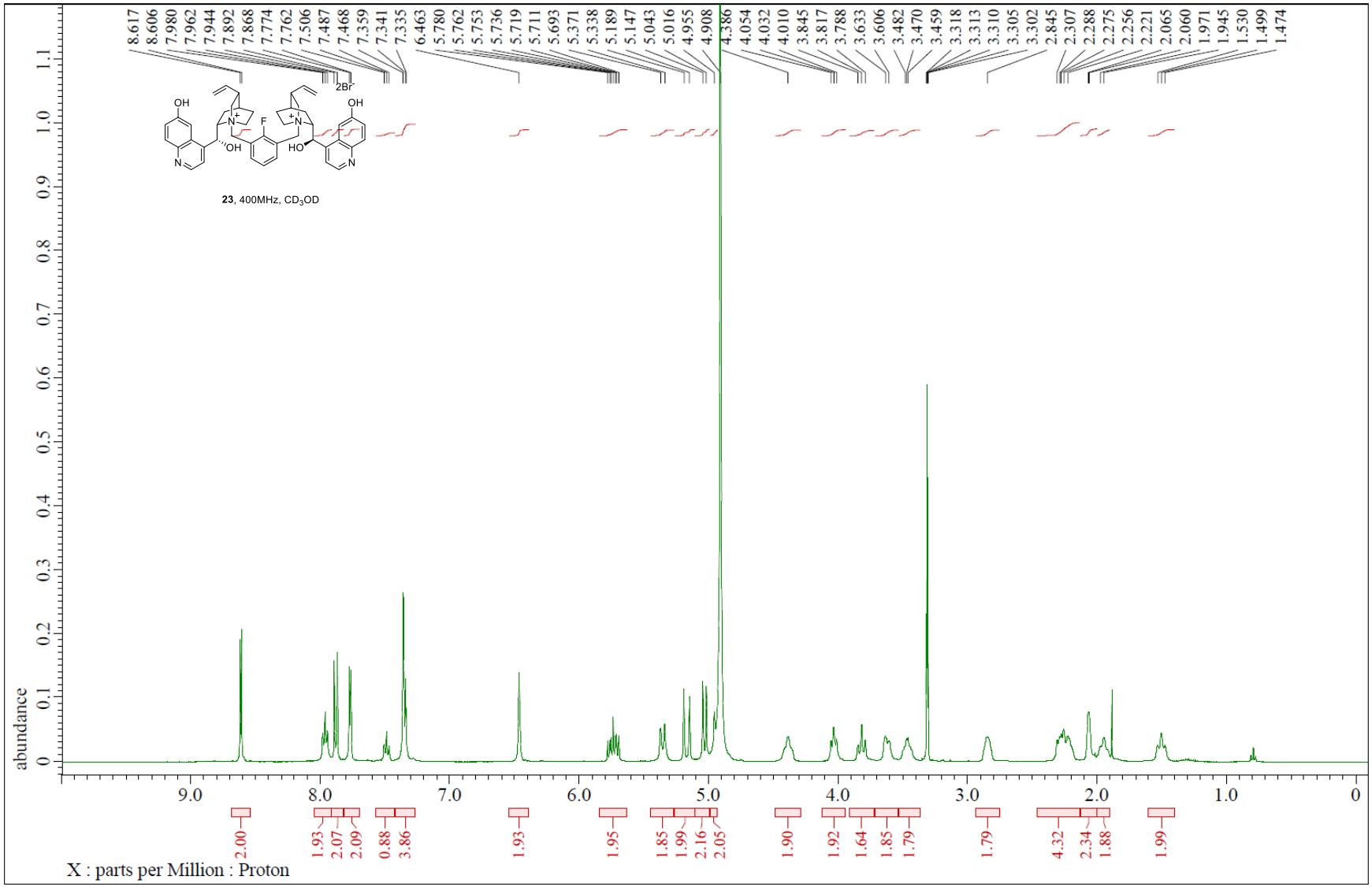
[1]H-NMR of compound **22**



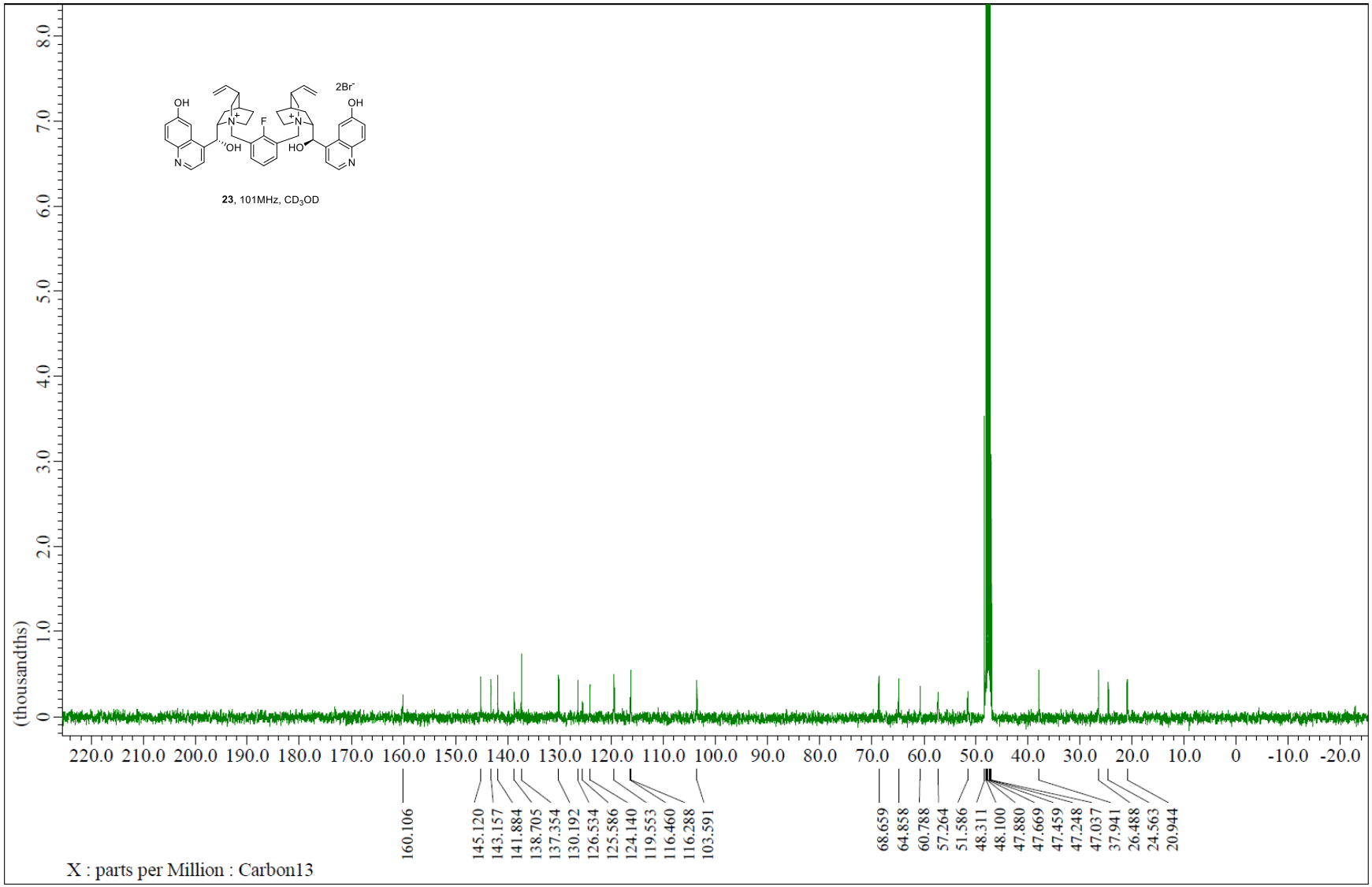
^{13}C-NMR of compound **22**



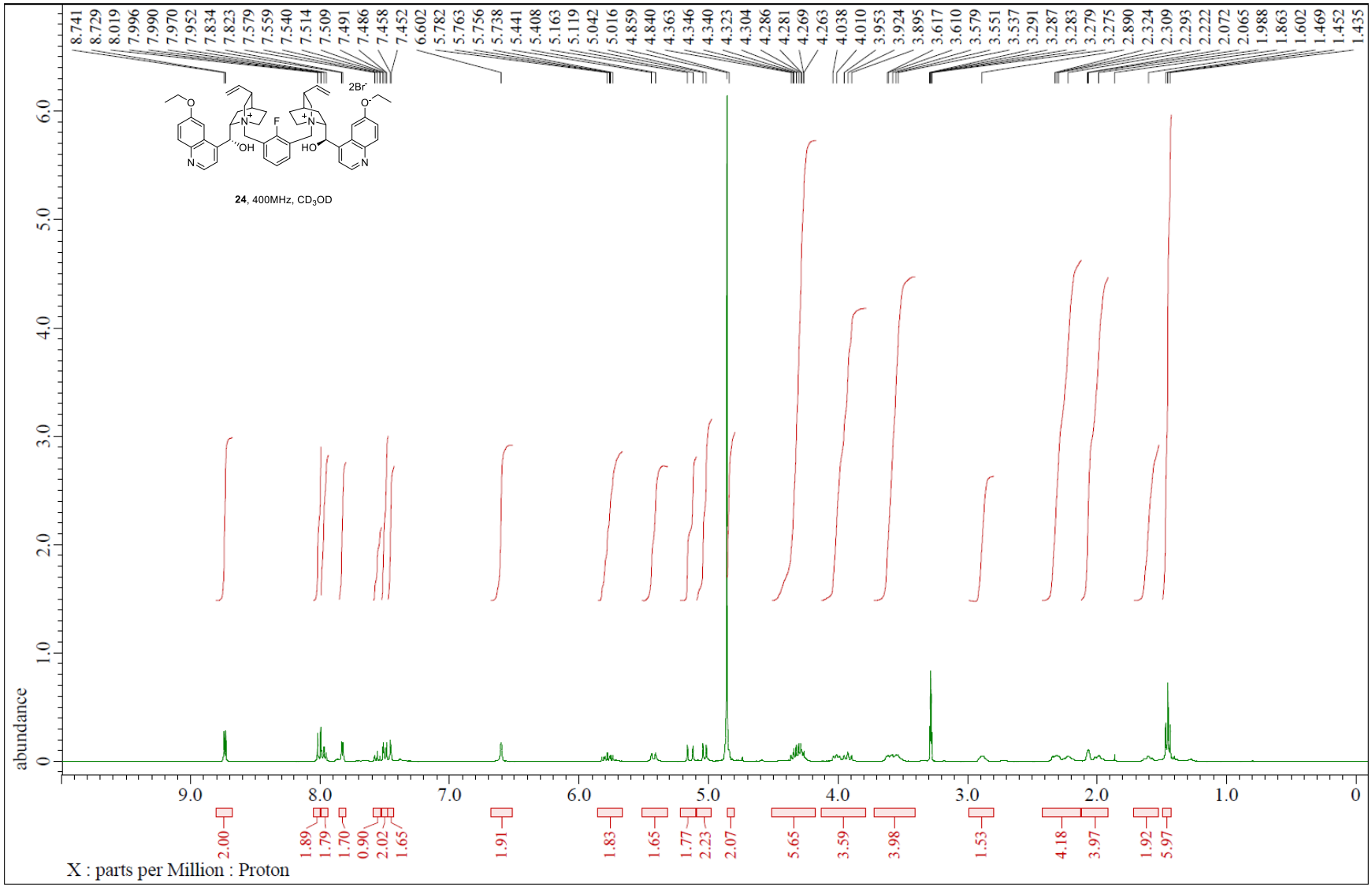
[1]H-NMR of compound **23**



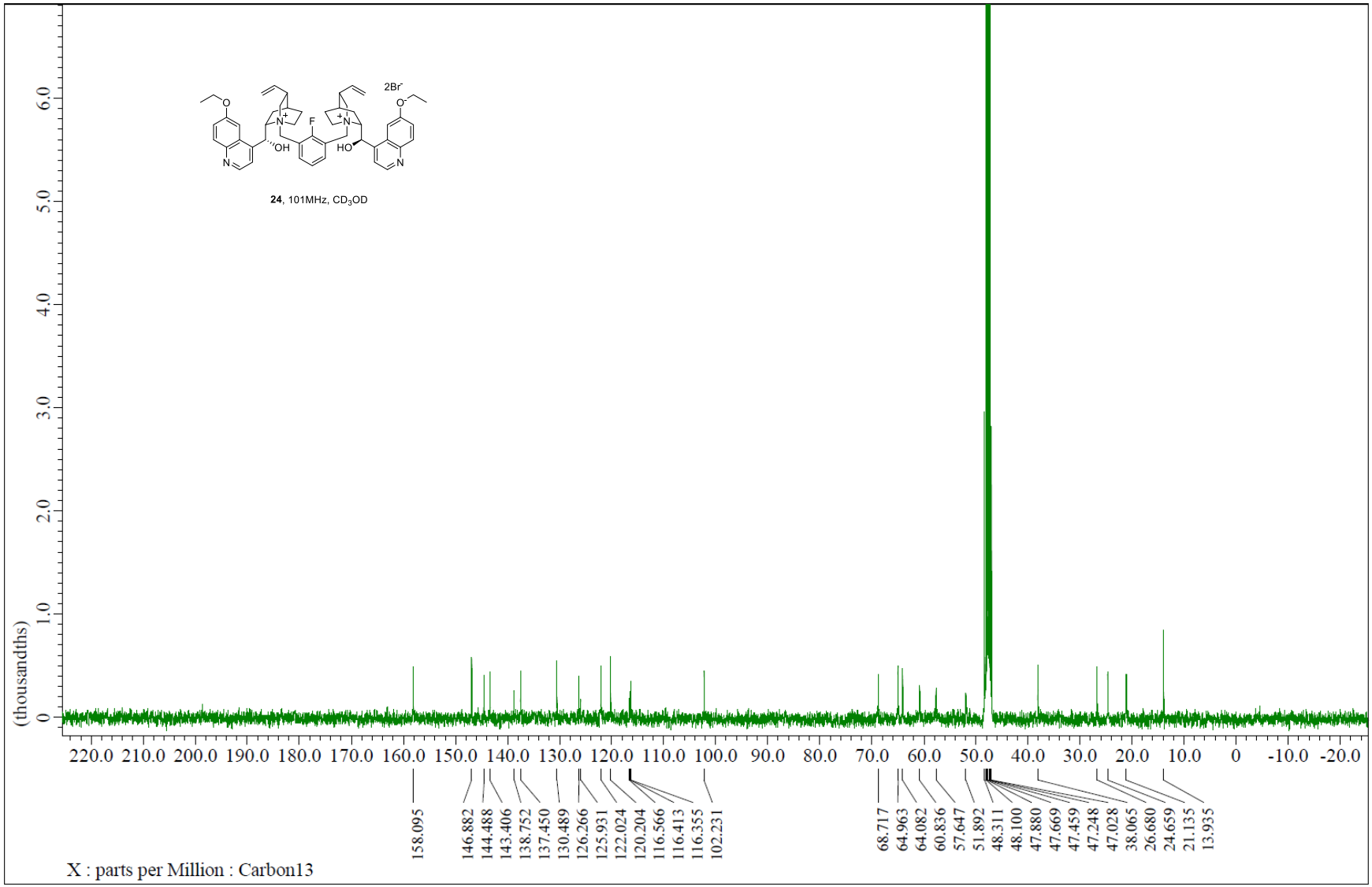
[1]H-NMR of compound **23**



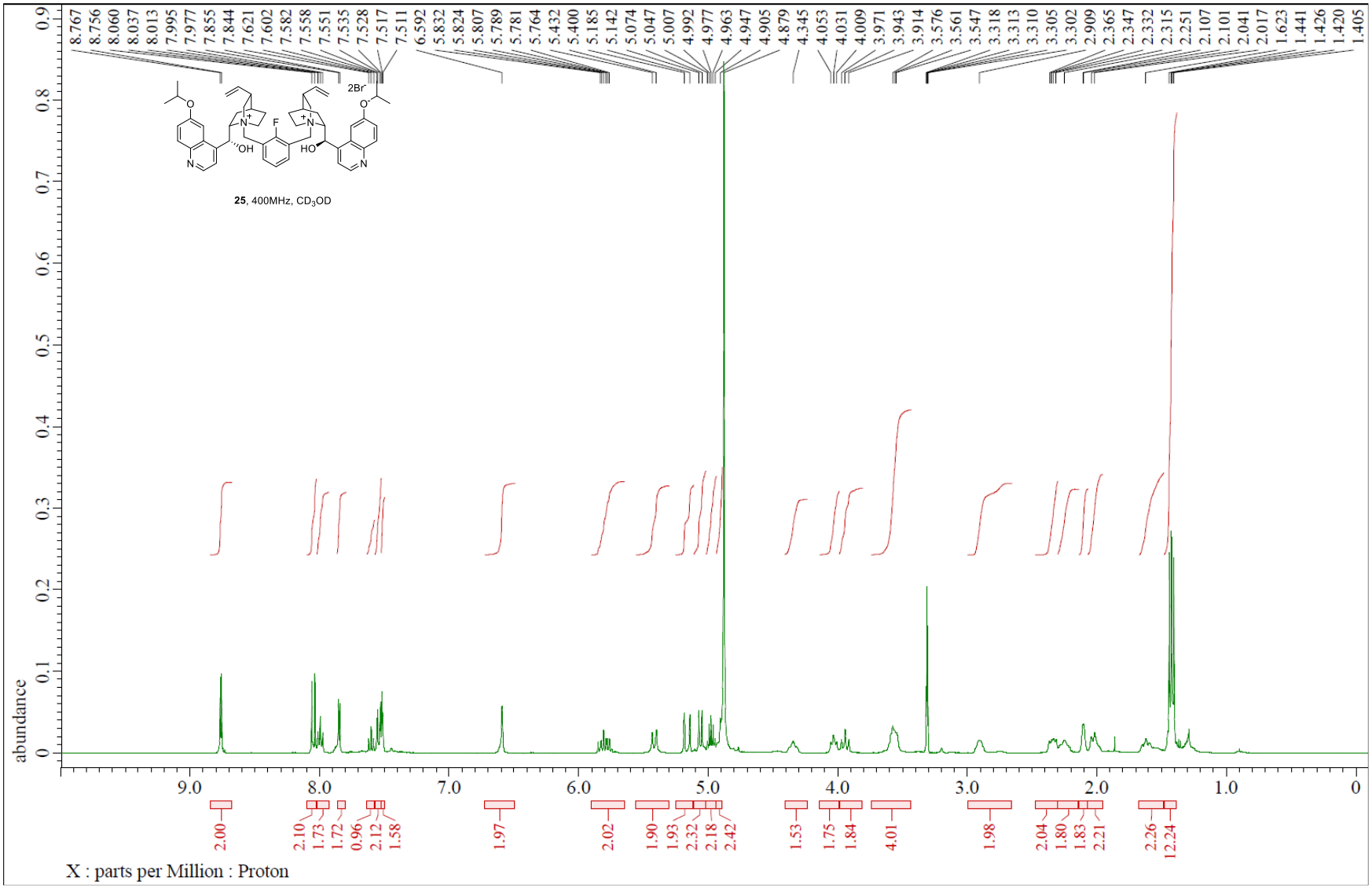
[1]H-NMR of compound **24**



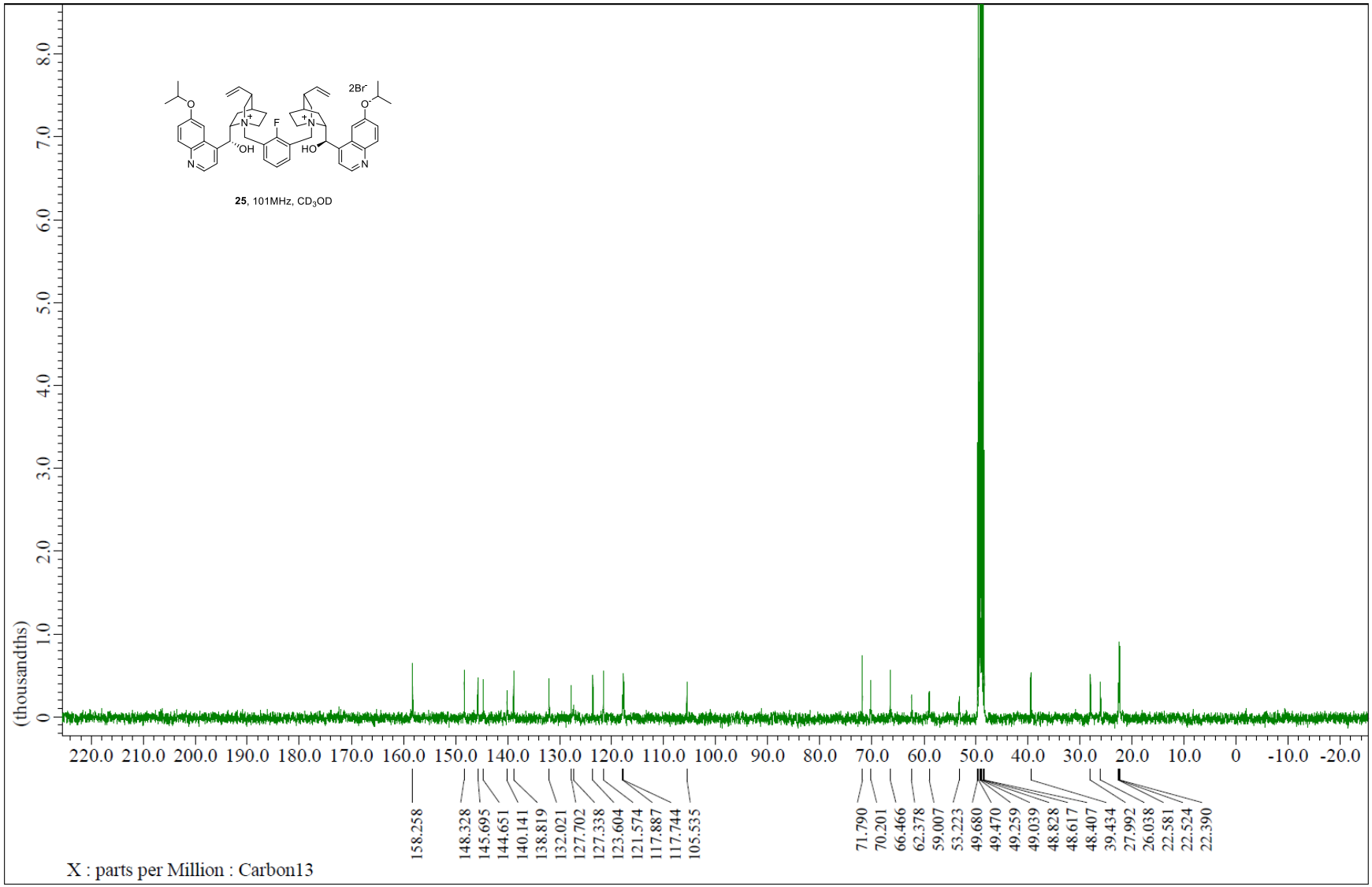
^{13}C-NMR of compound **24**



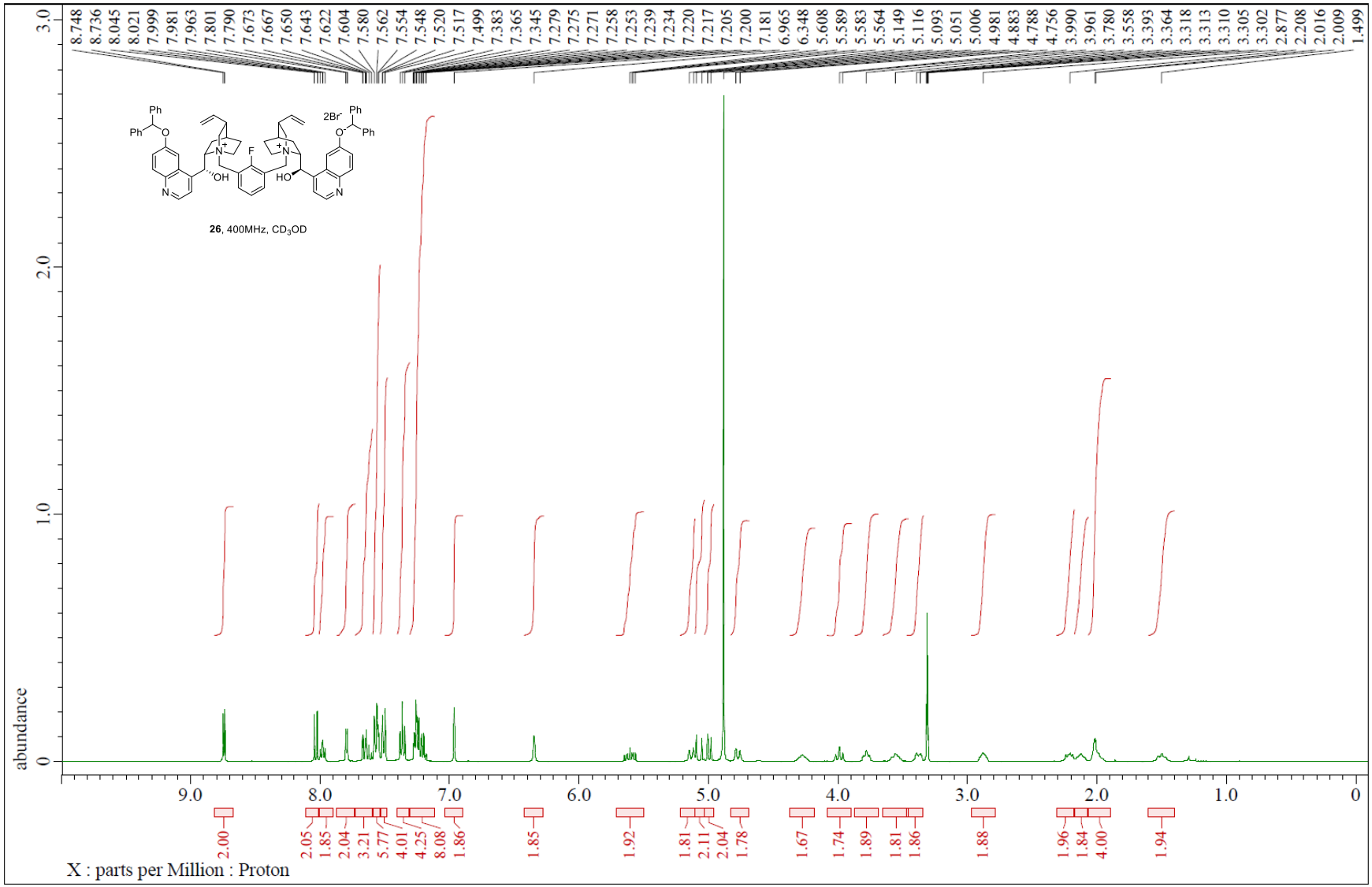
[1]H-NMR of compound **25**



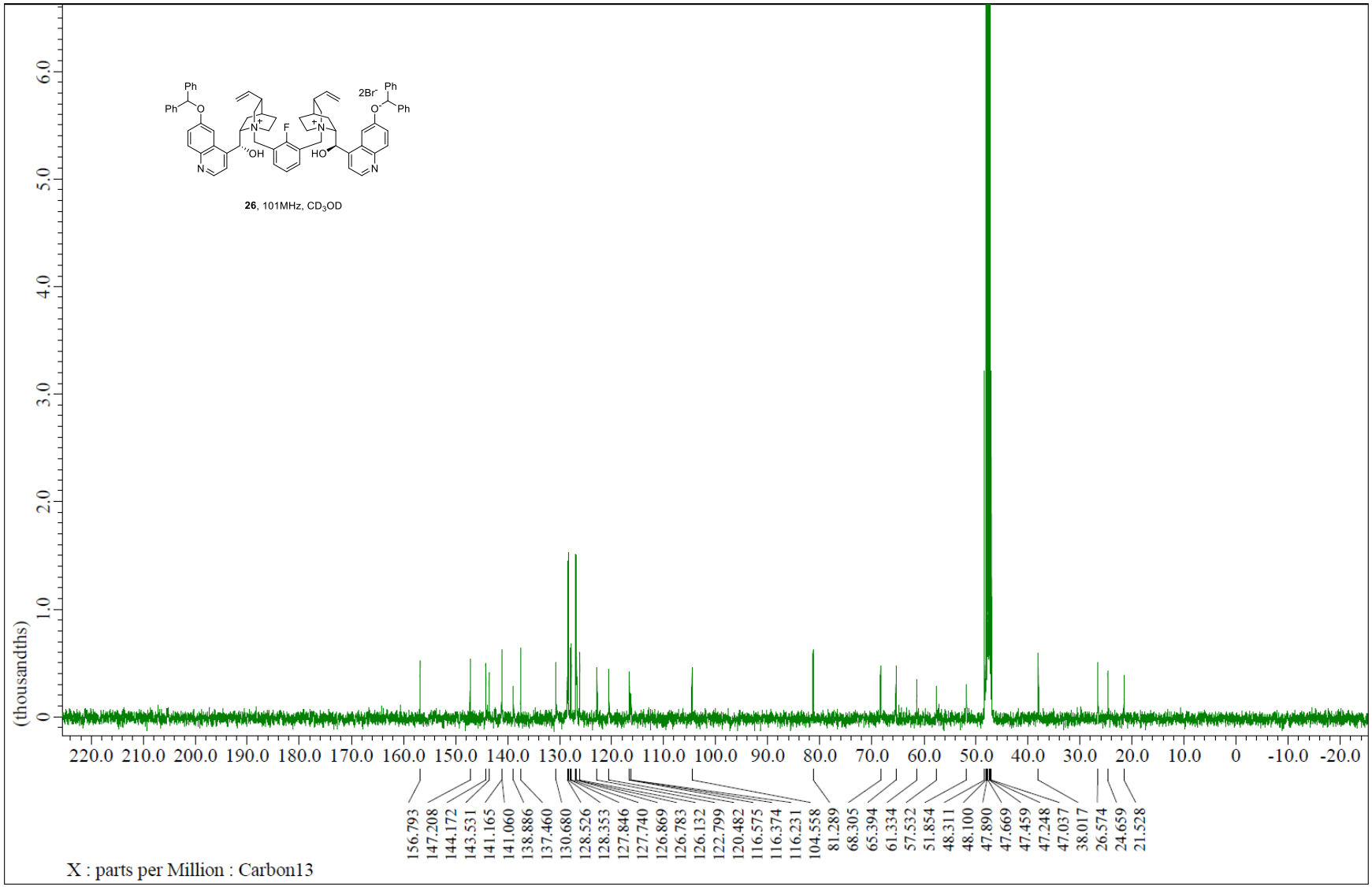
^{13}C-NMR of compound **25**



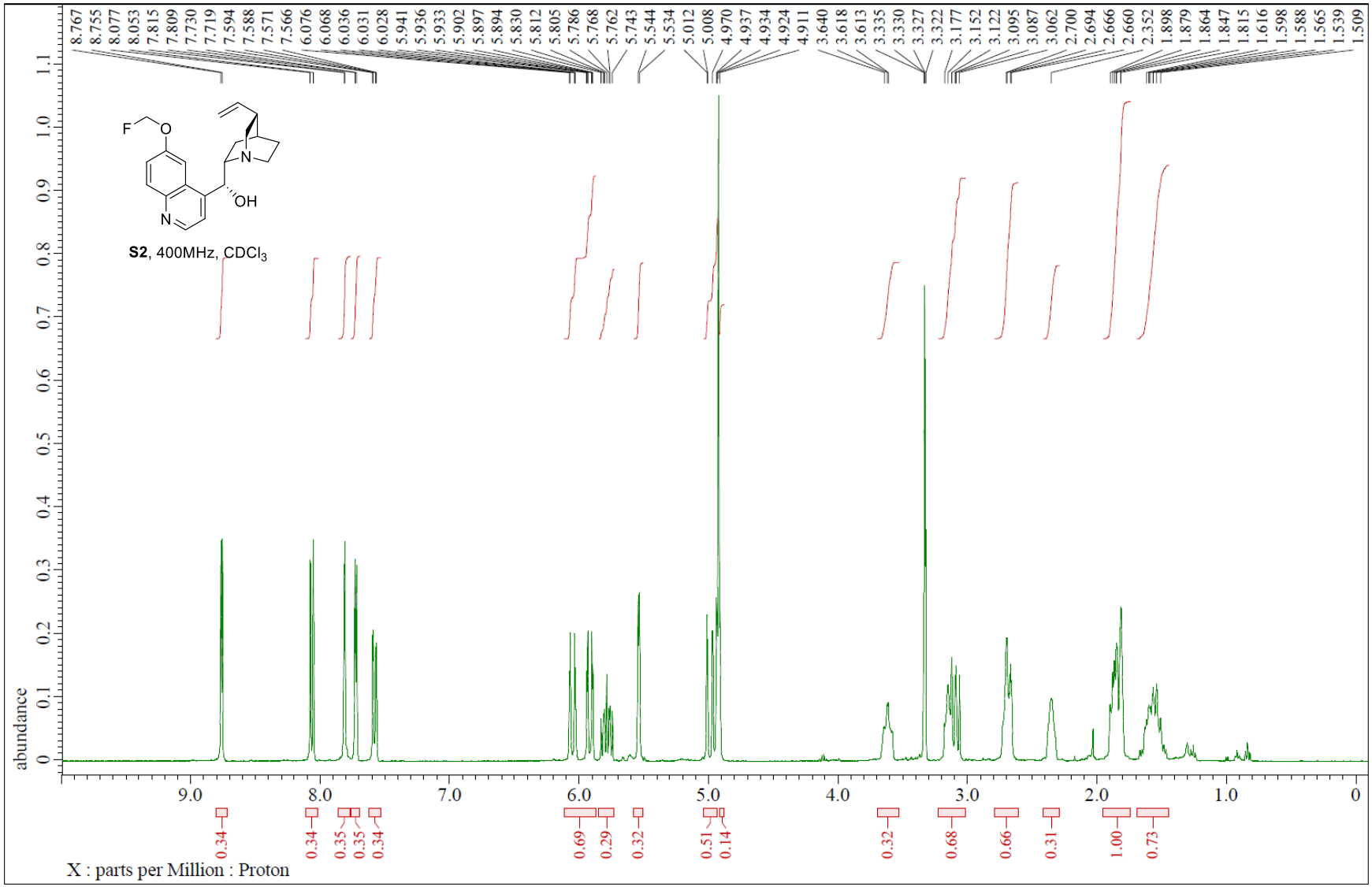
[1]H-NMR of compound **26**



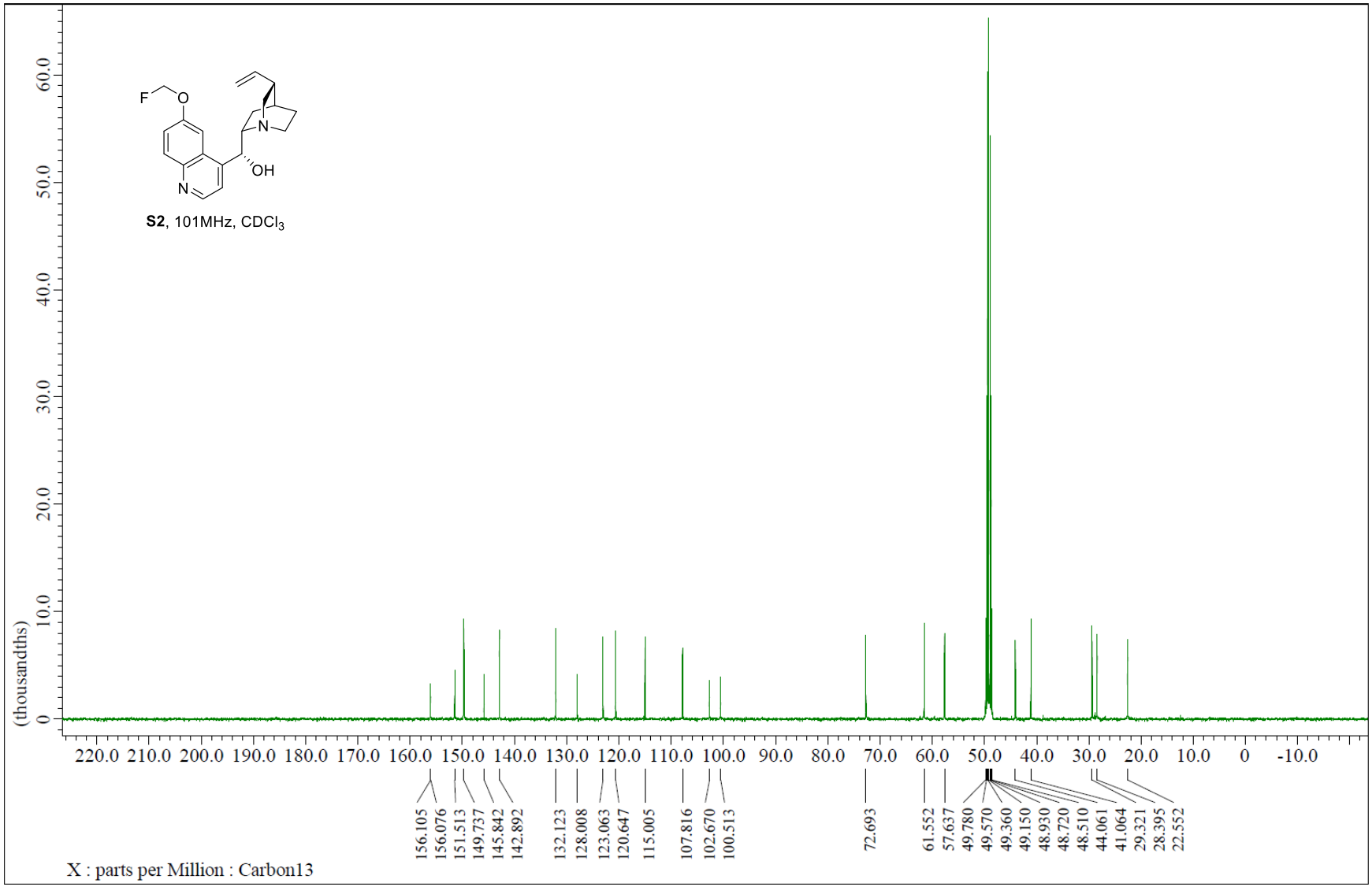
^{13}C-NMR of compound **26**



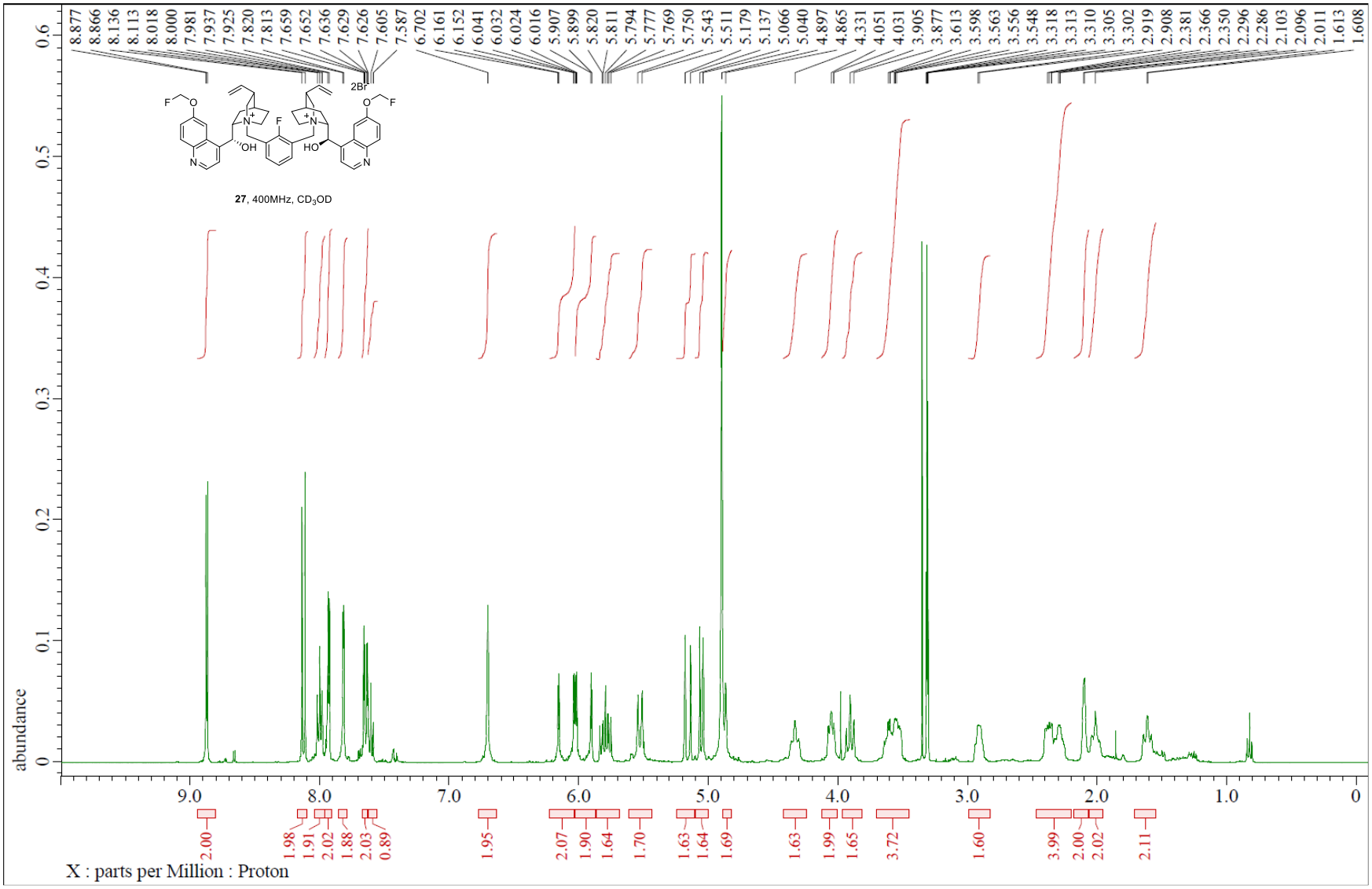
[1]H-NMR of compound **S2**



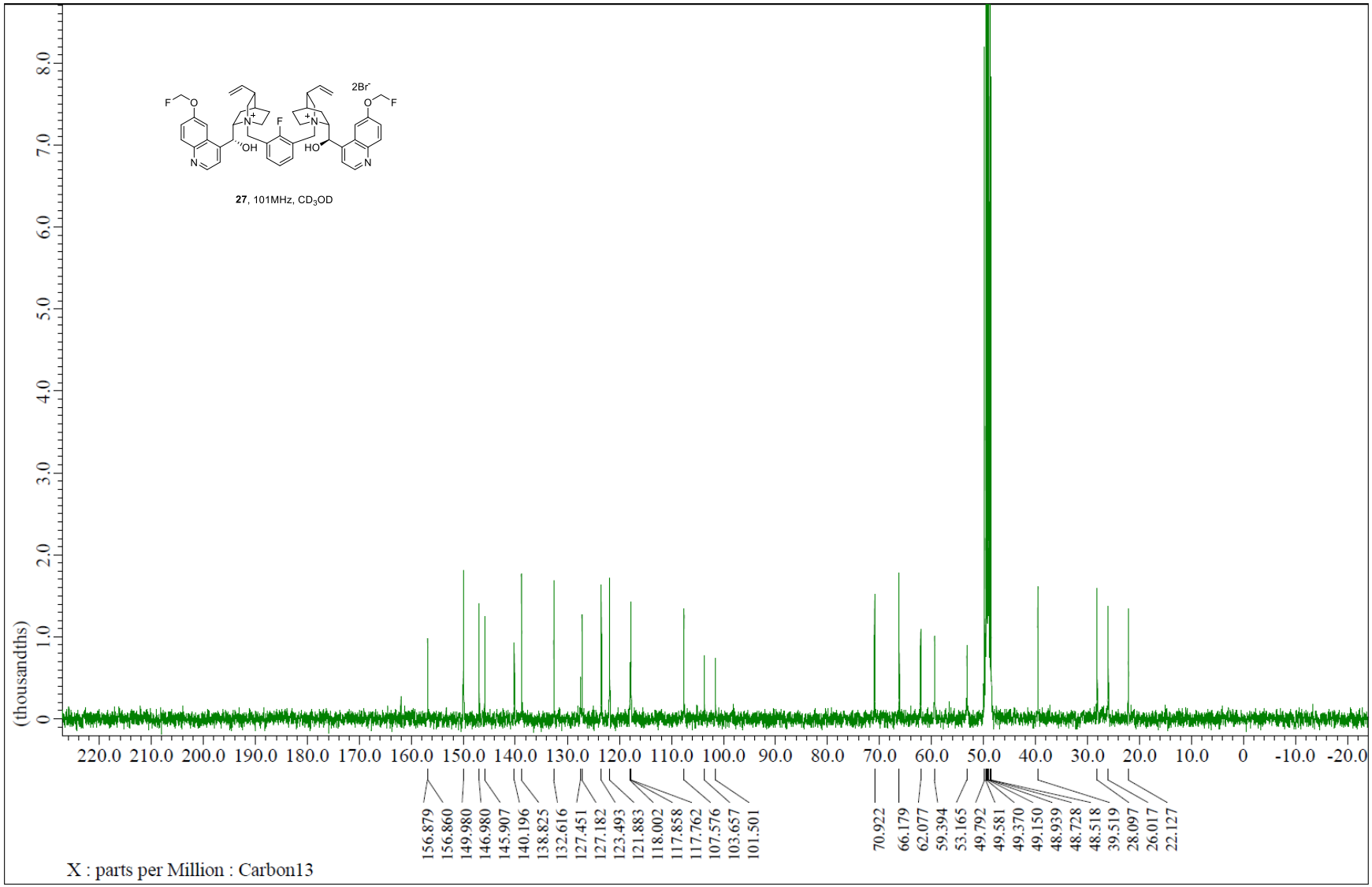
^{13}C-NMR of compound **S2**



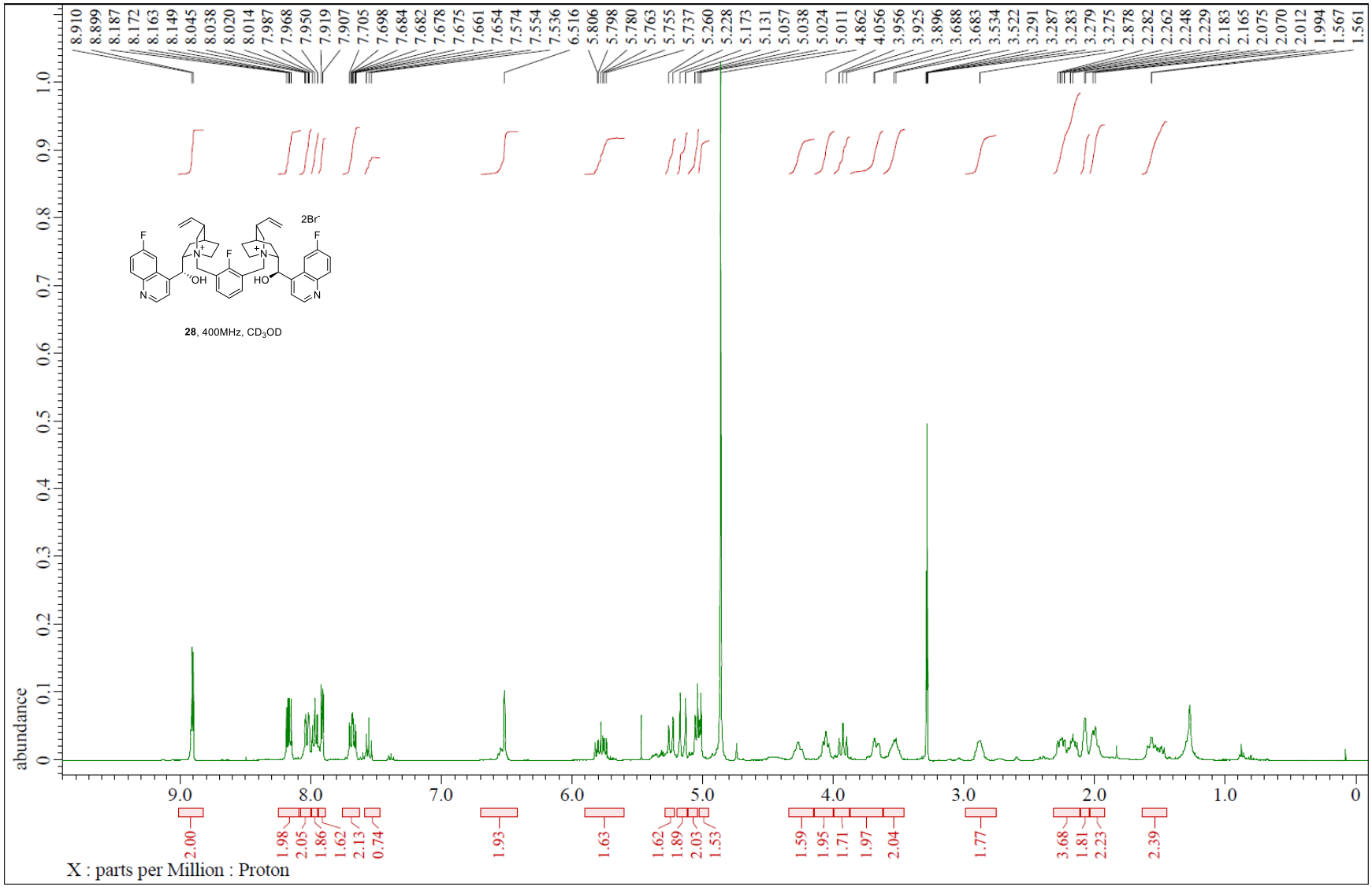
[1]H-NMR of compound **27**



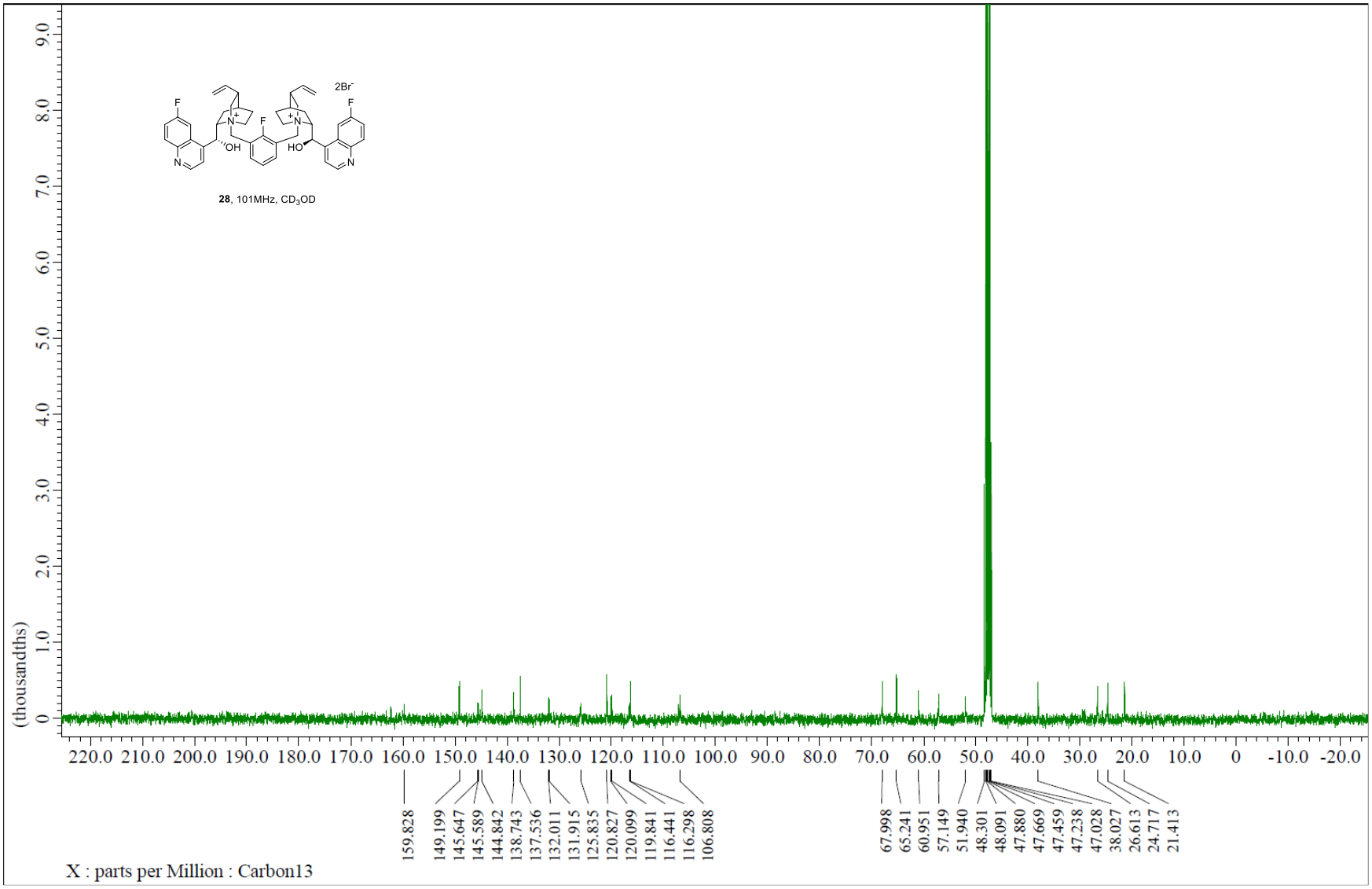
^{13}C-NMR of compound **27**



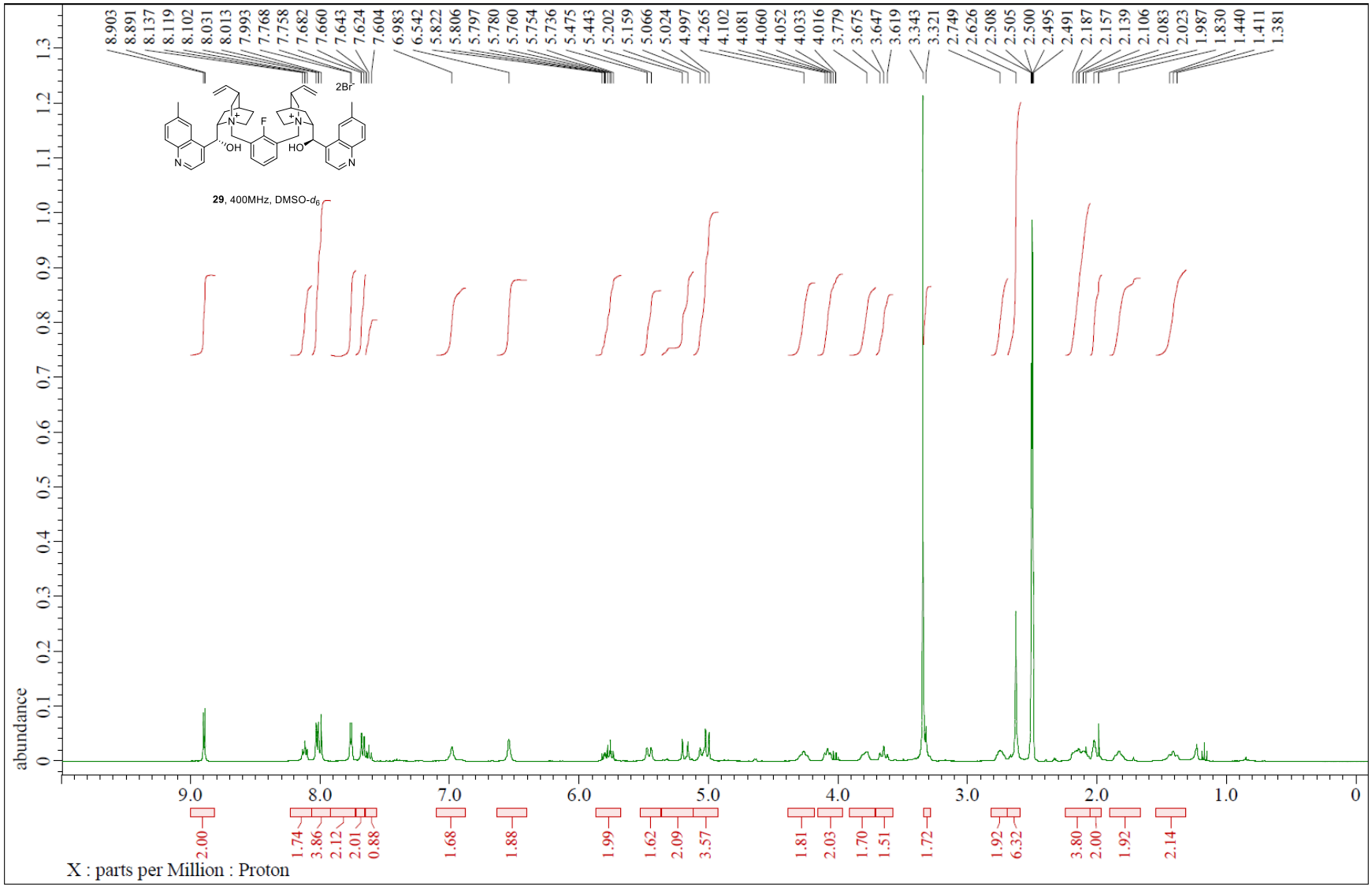
[1]H-NMR of compound **28**



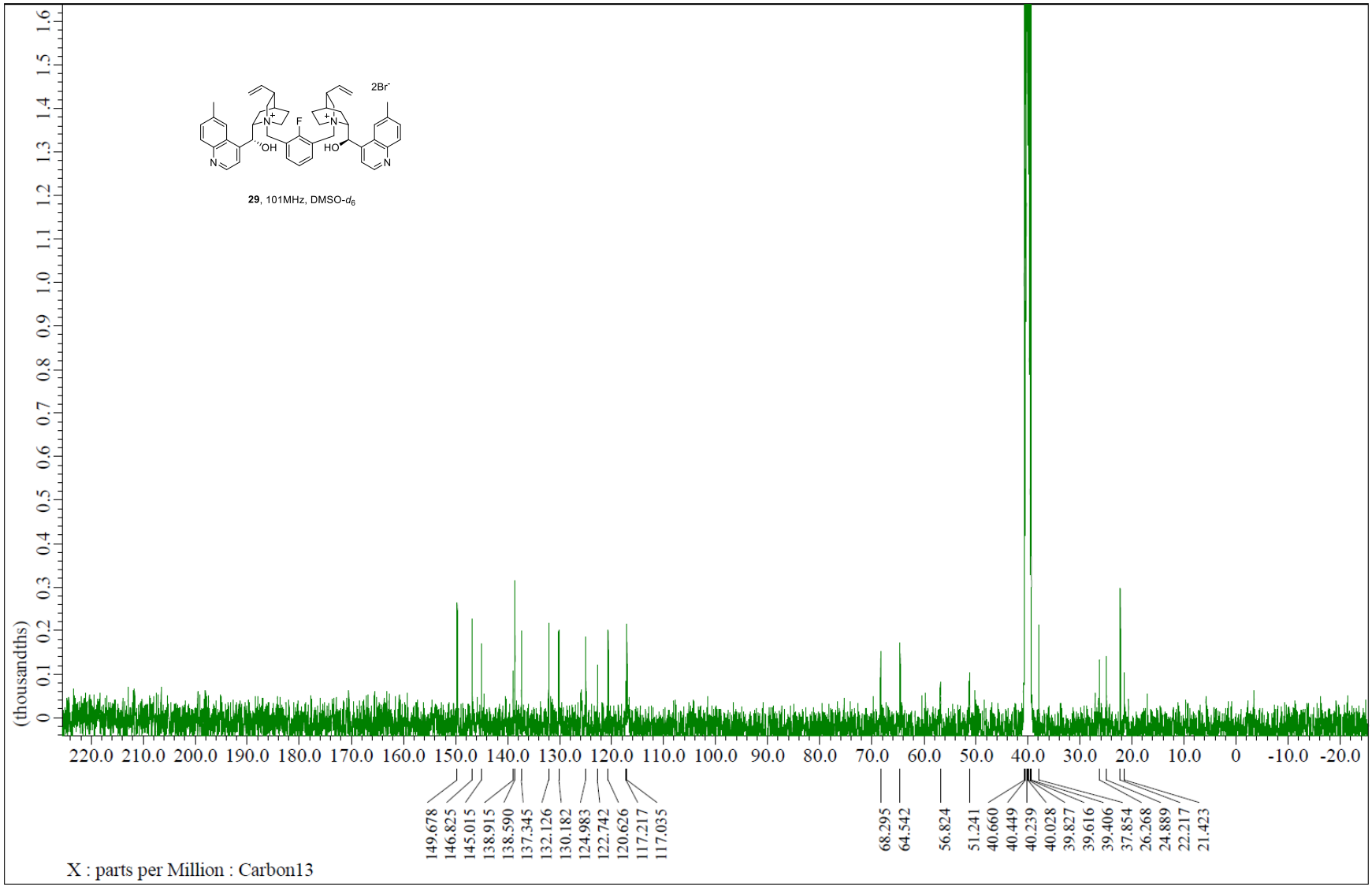
^{13}C-NMR of compound **28**



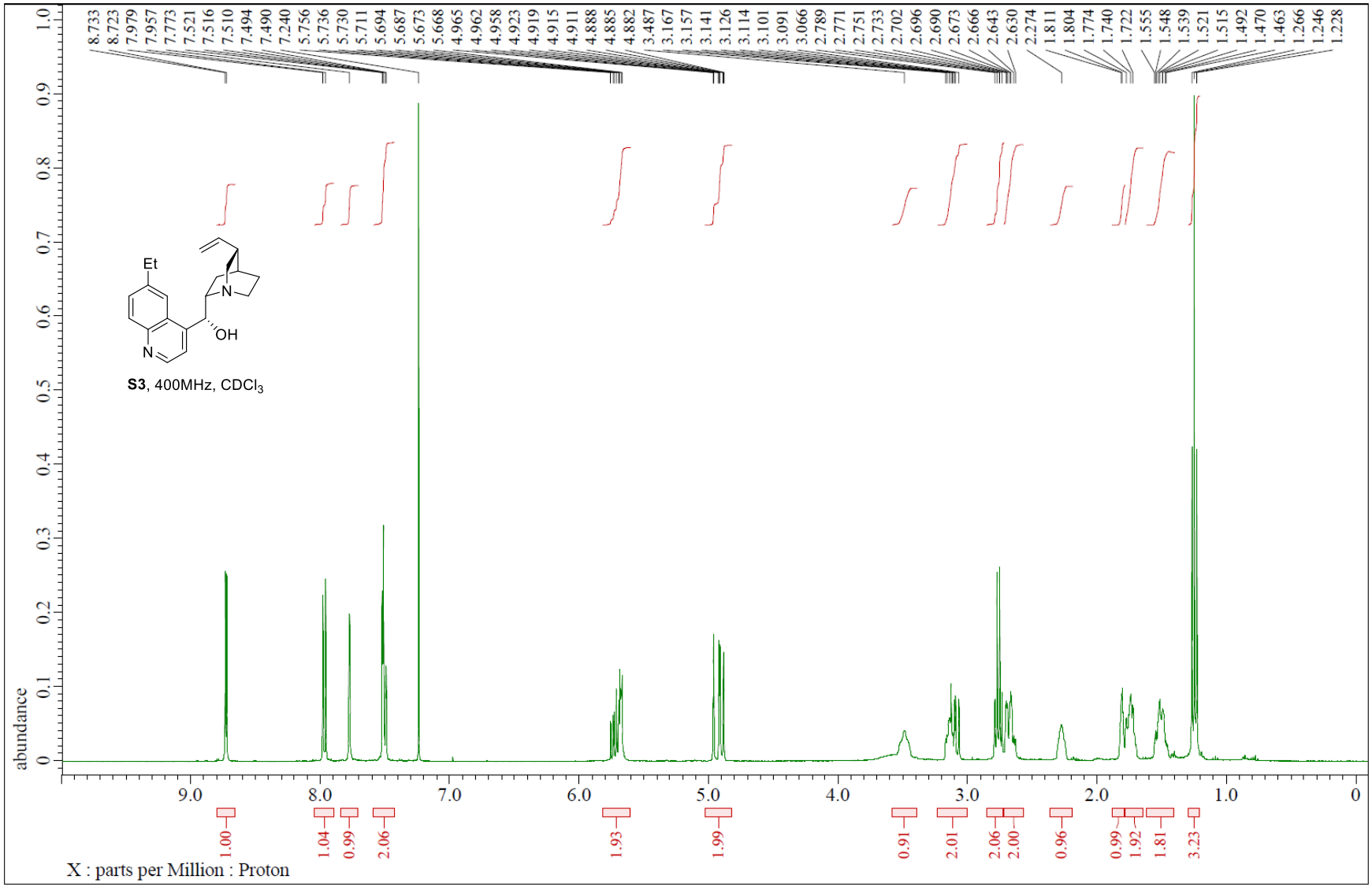
[1]H-NMR of compound **29**



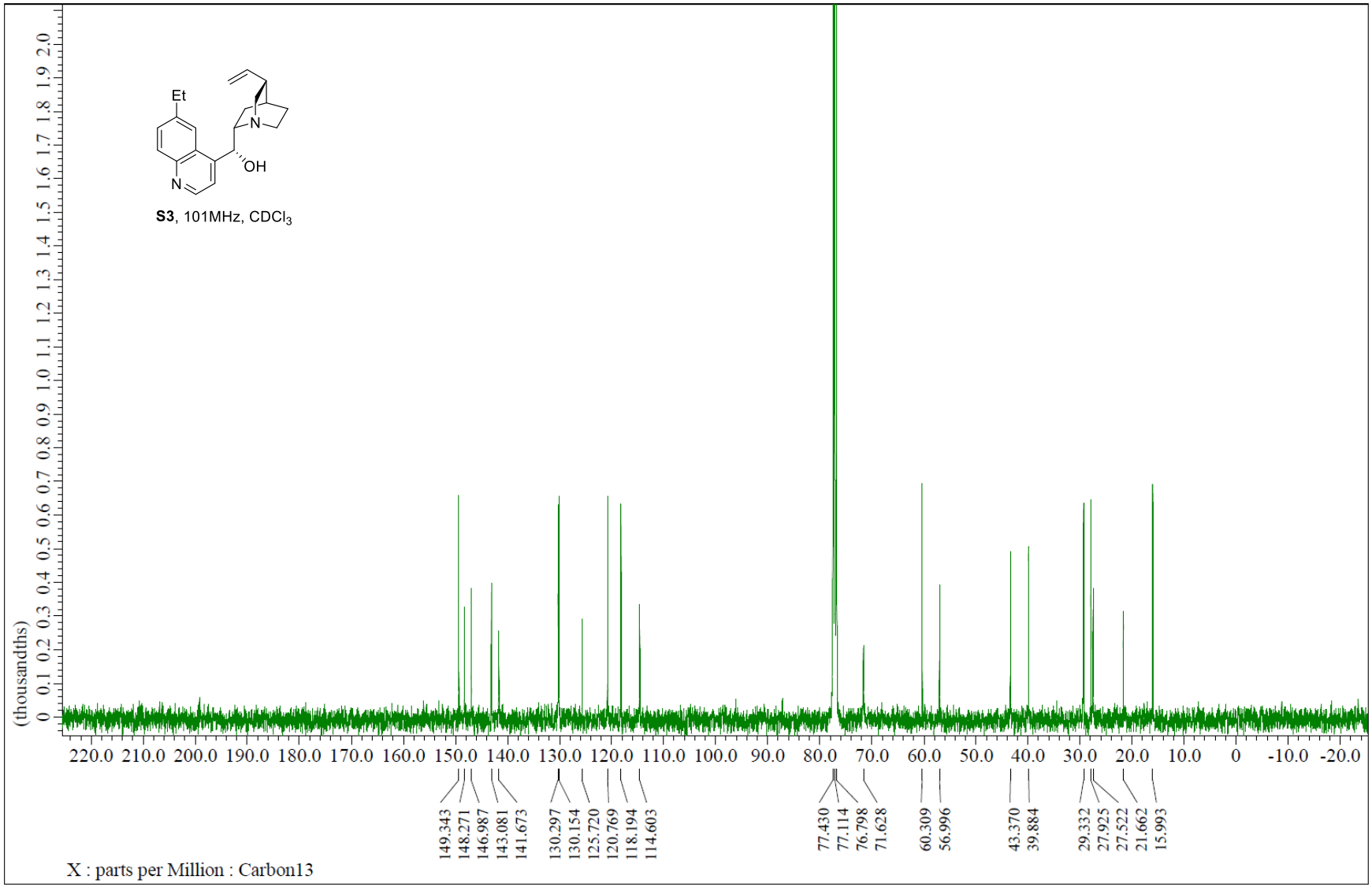
^{13}C-NMR of compound **29**



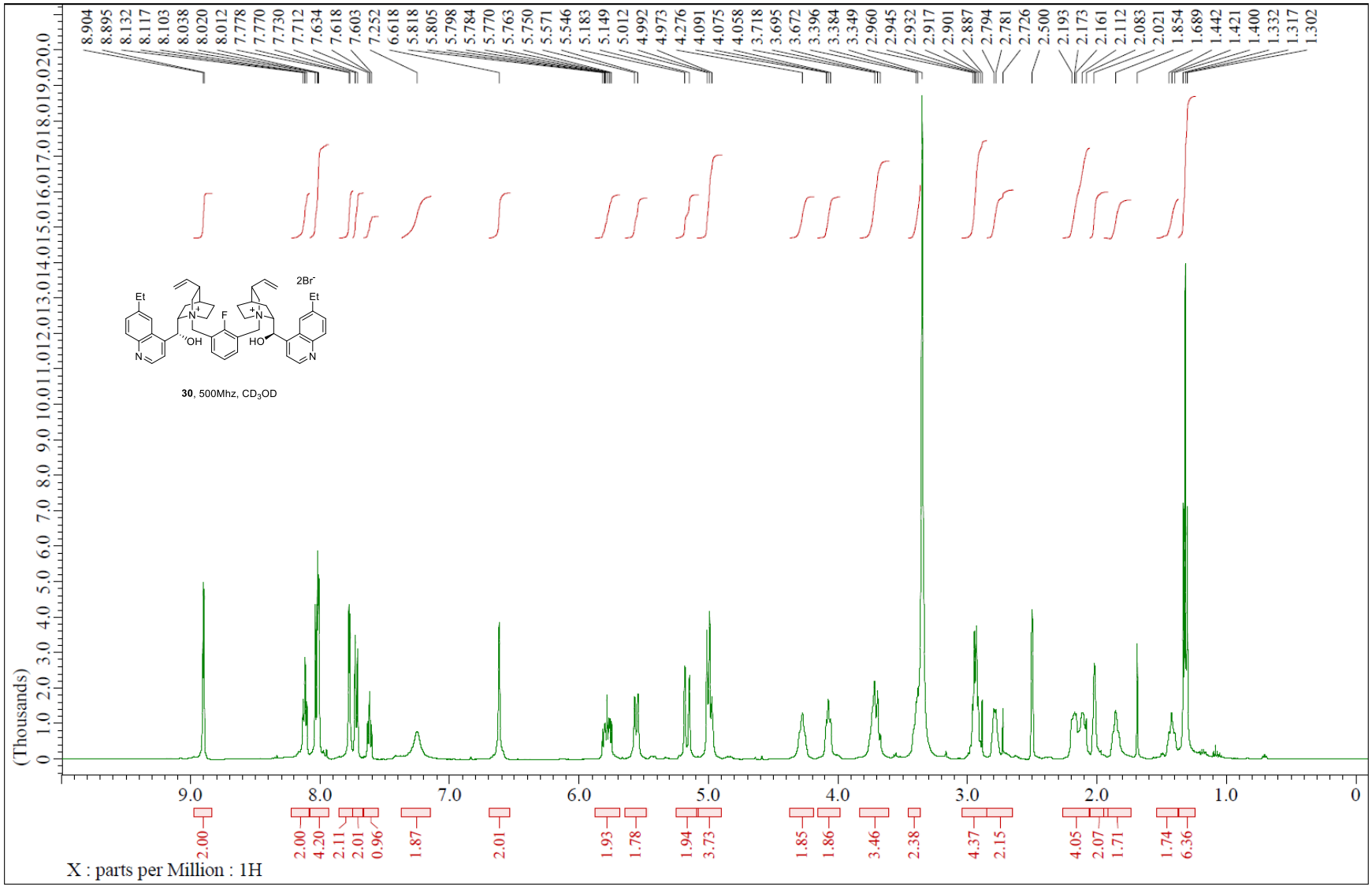
[1]H-NMR of compound **S3**



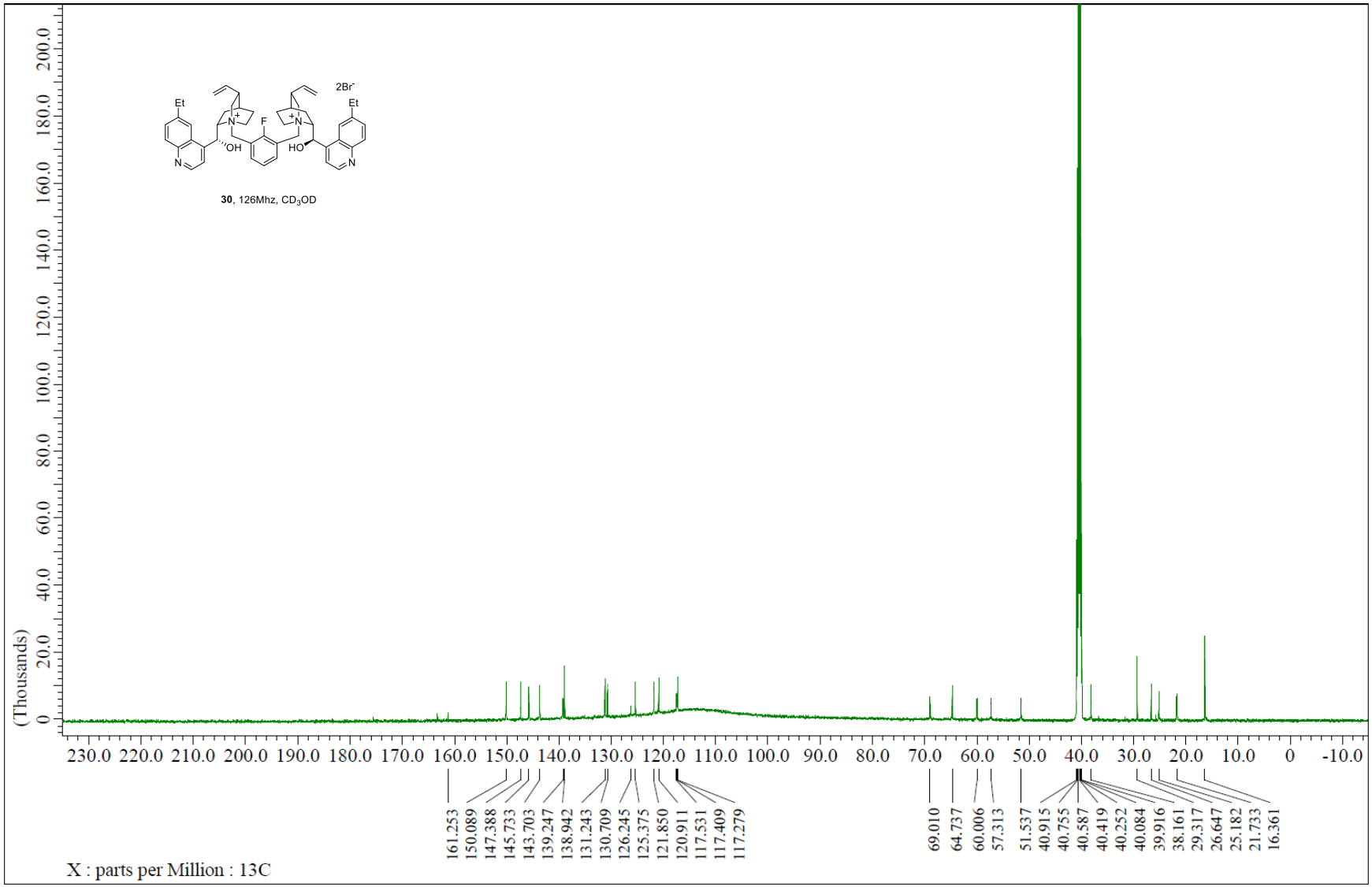
^{13}C-NMR of compound **S3**



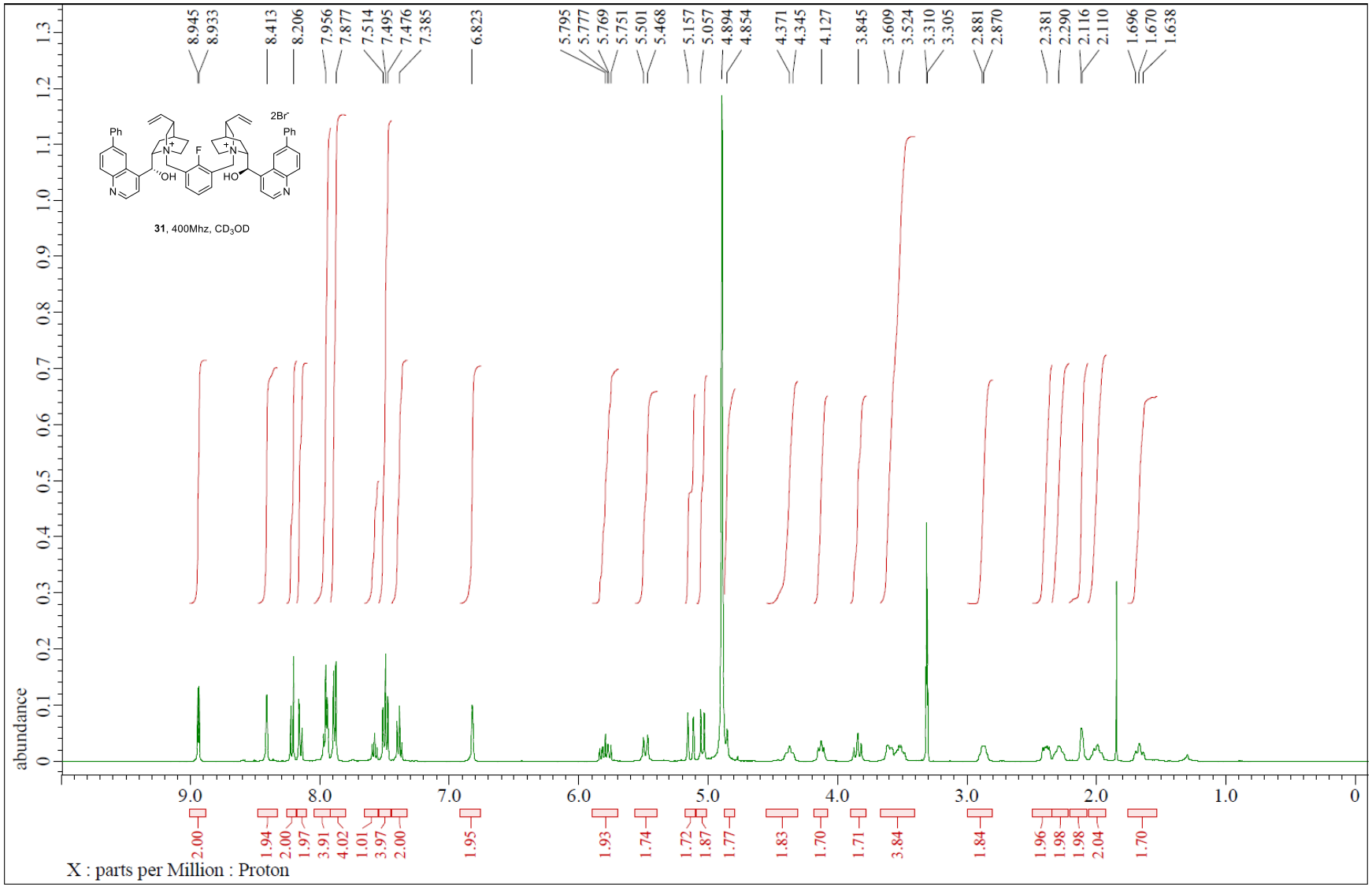
[1]H-NMR of compound **30**



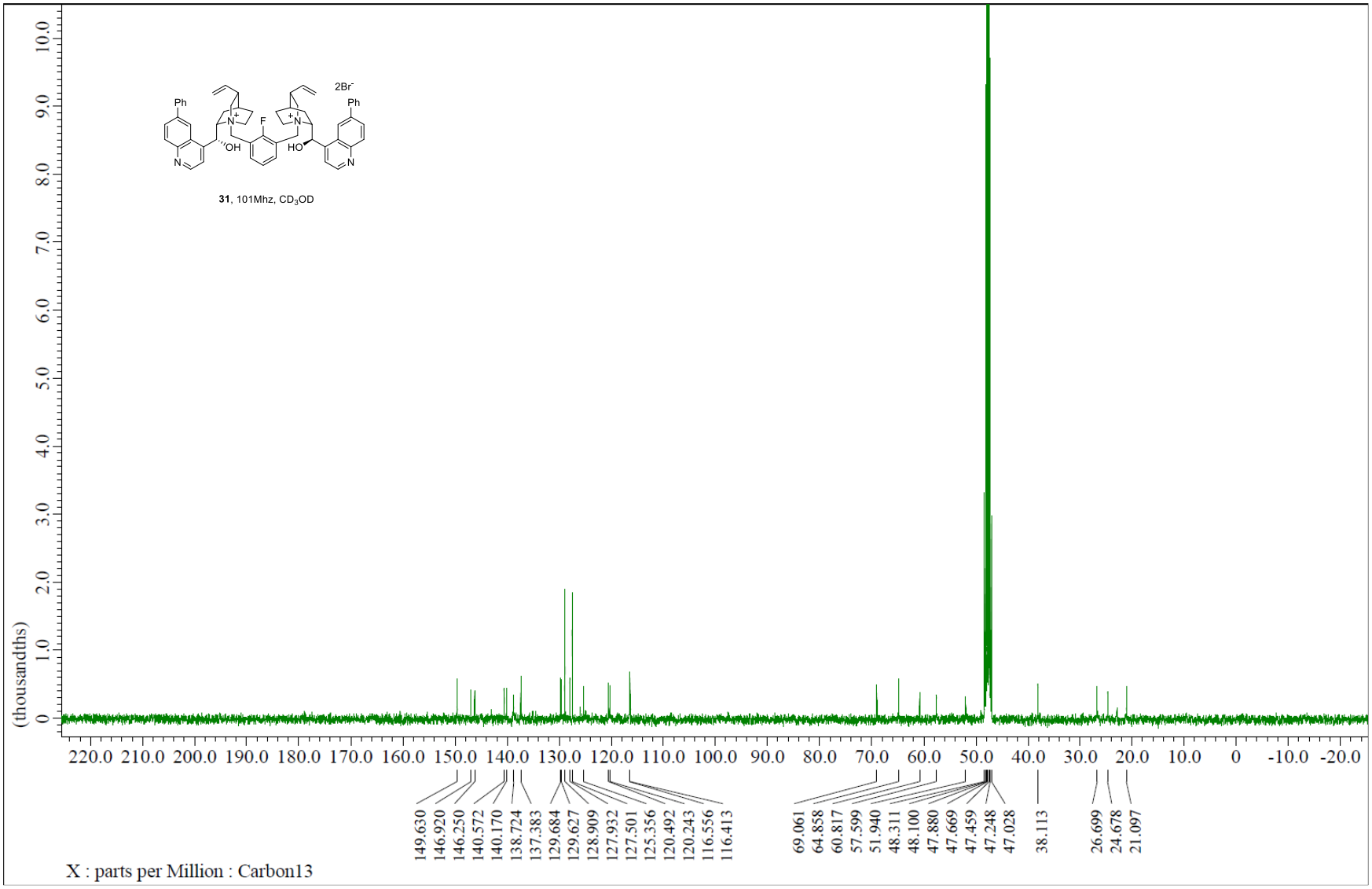
^{13}C-NMR of compound **30**



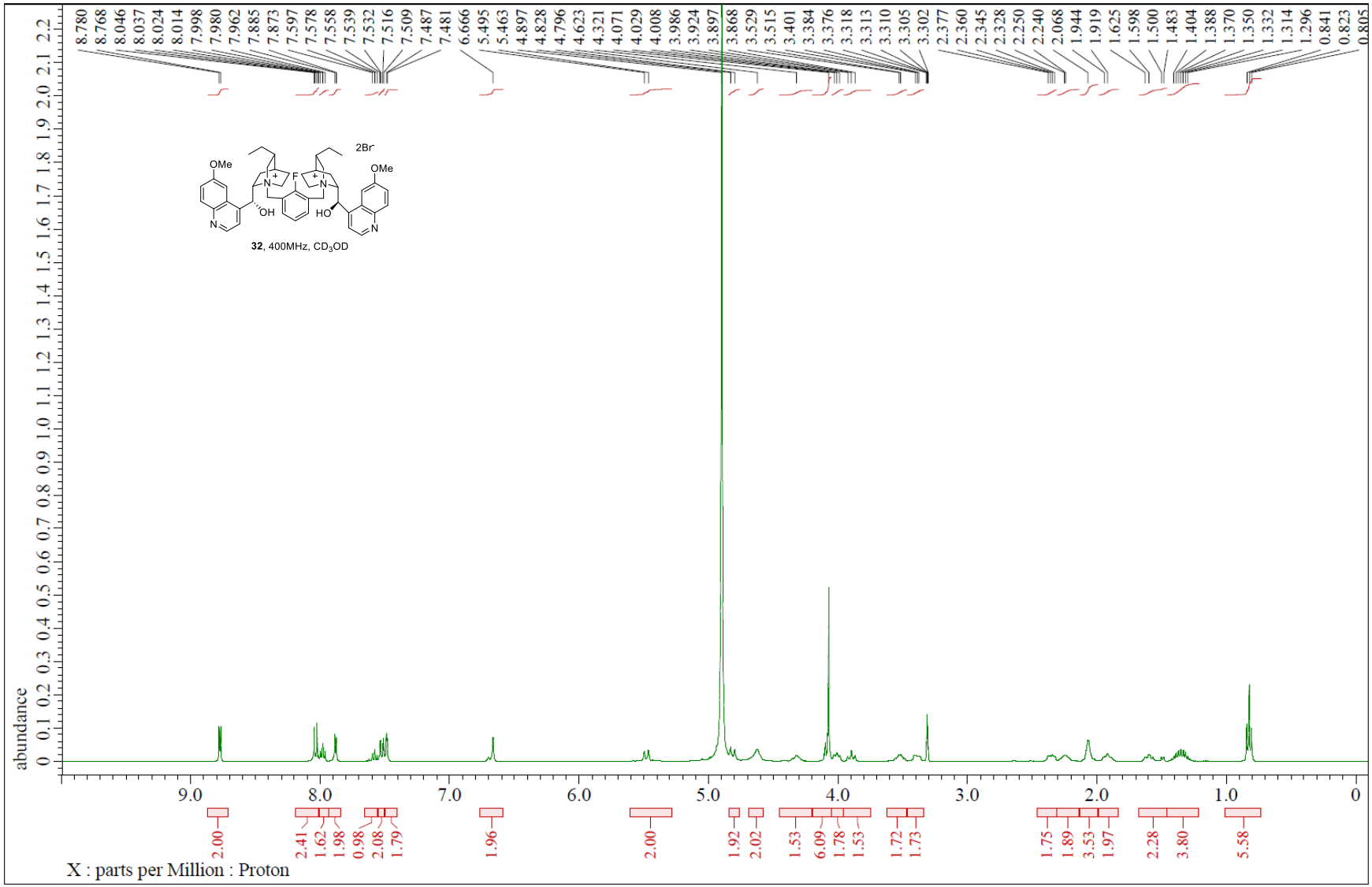
[1]H-NMR of compound **31**



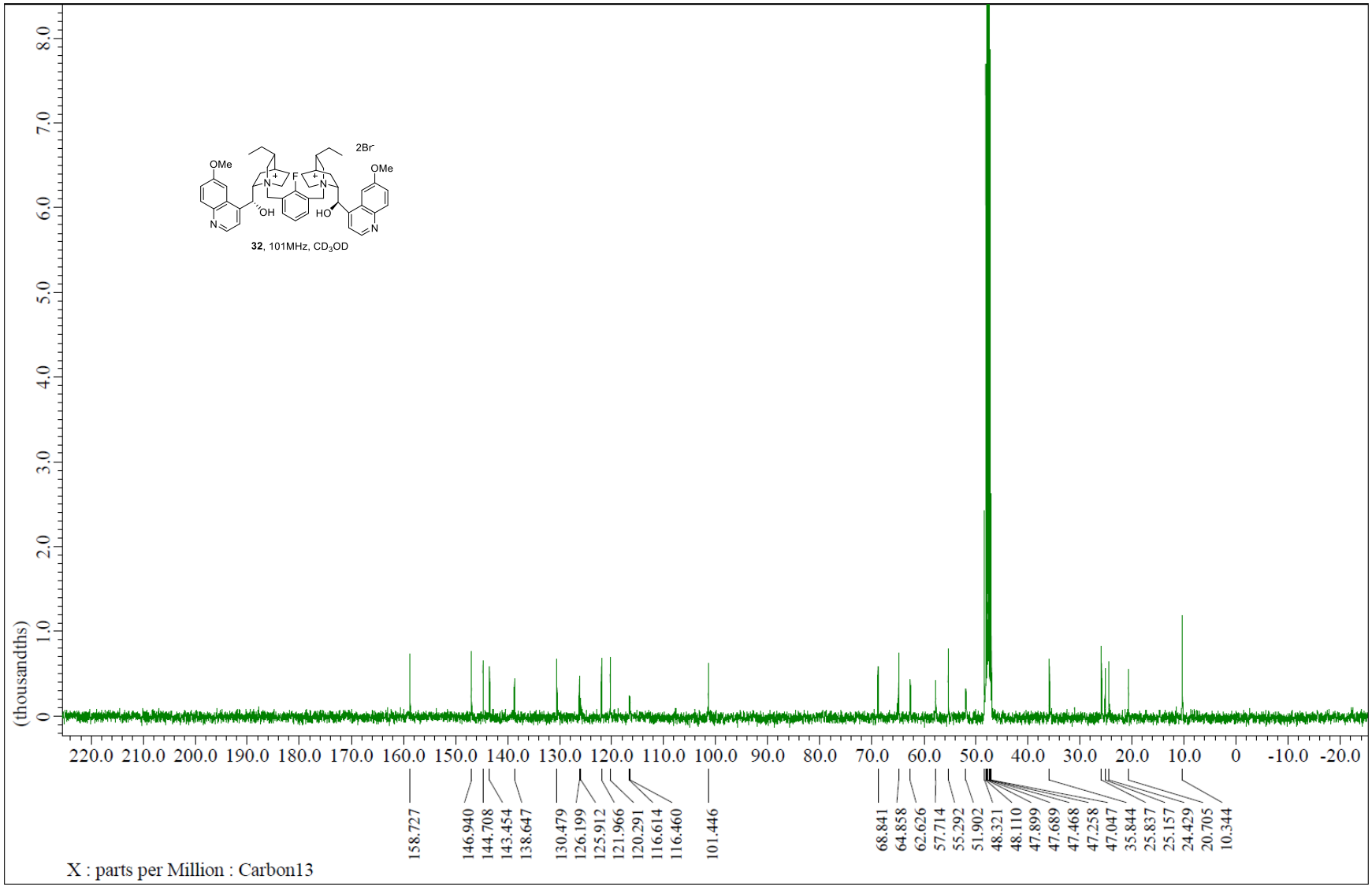
^{13}C-NMR of compound **31**



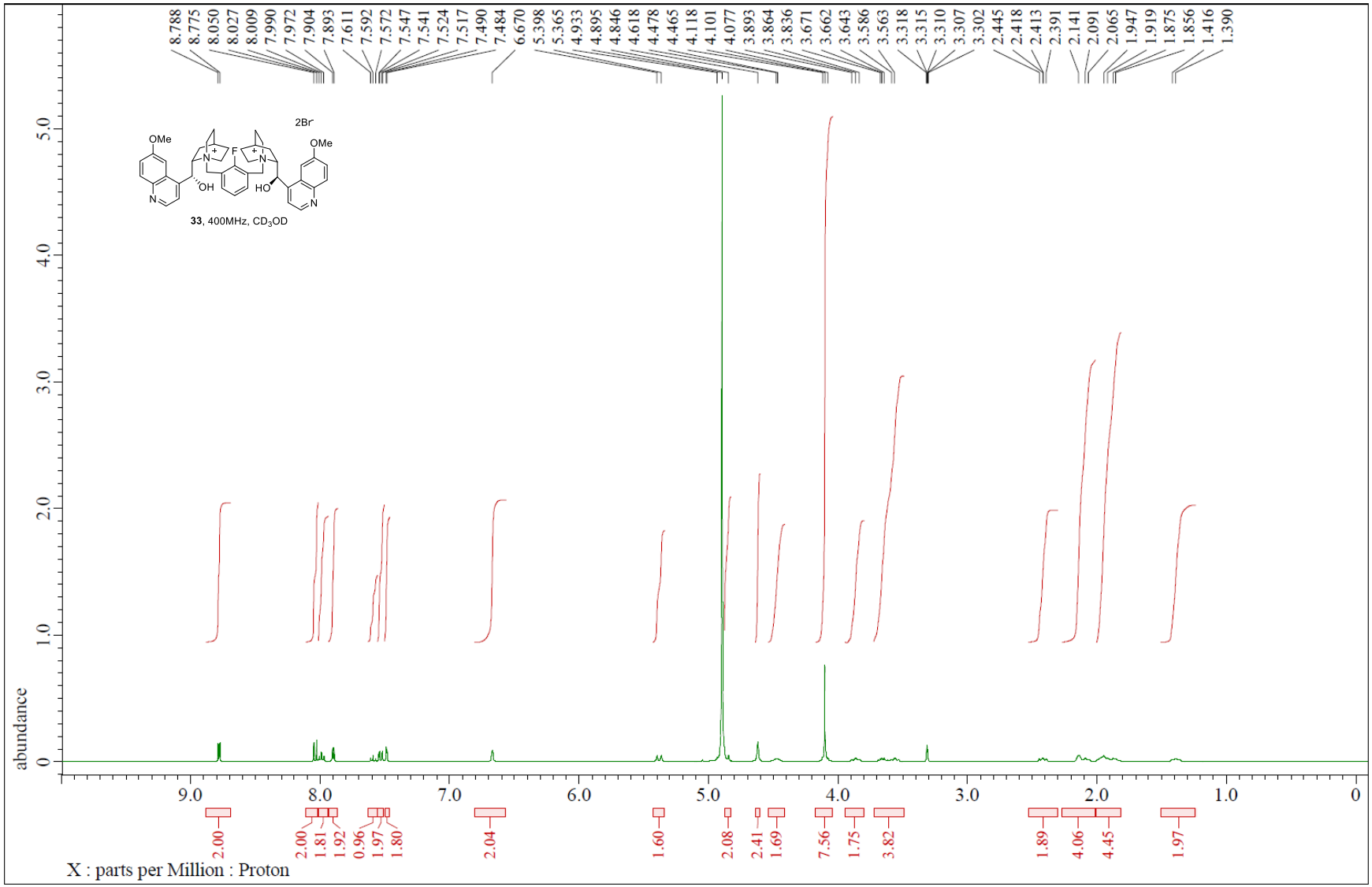
[1]H-NMR of compound **32**



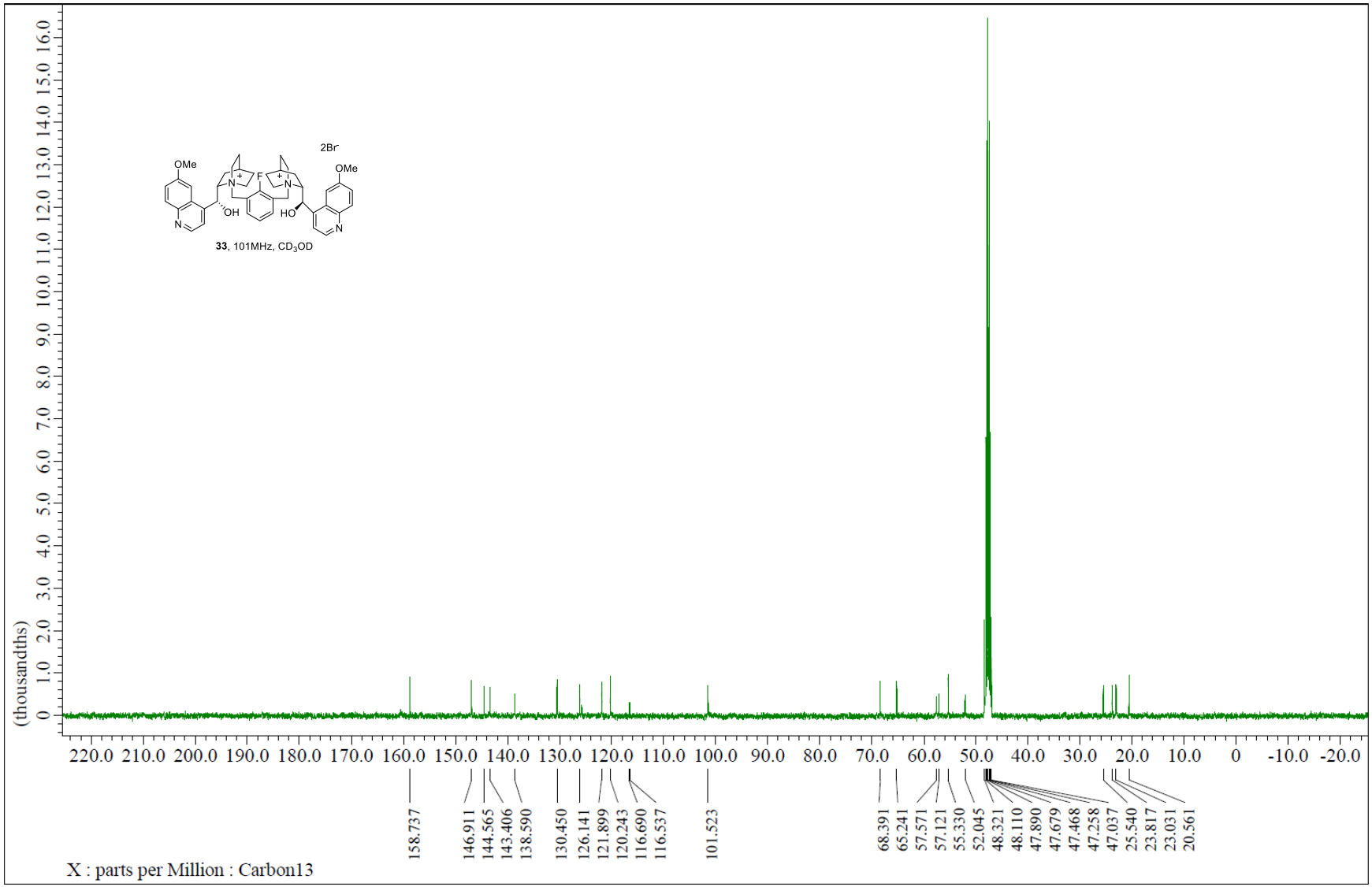
^{13}C-NMR of compound **32**



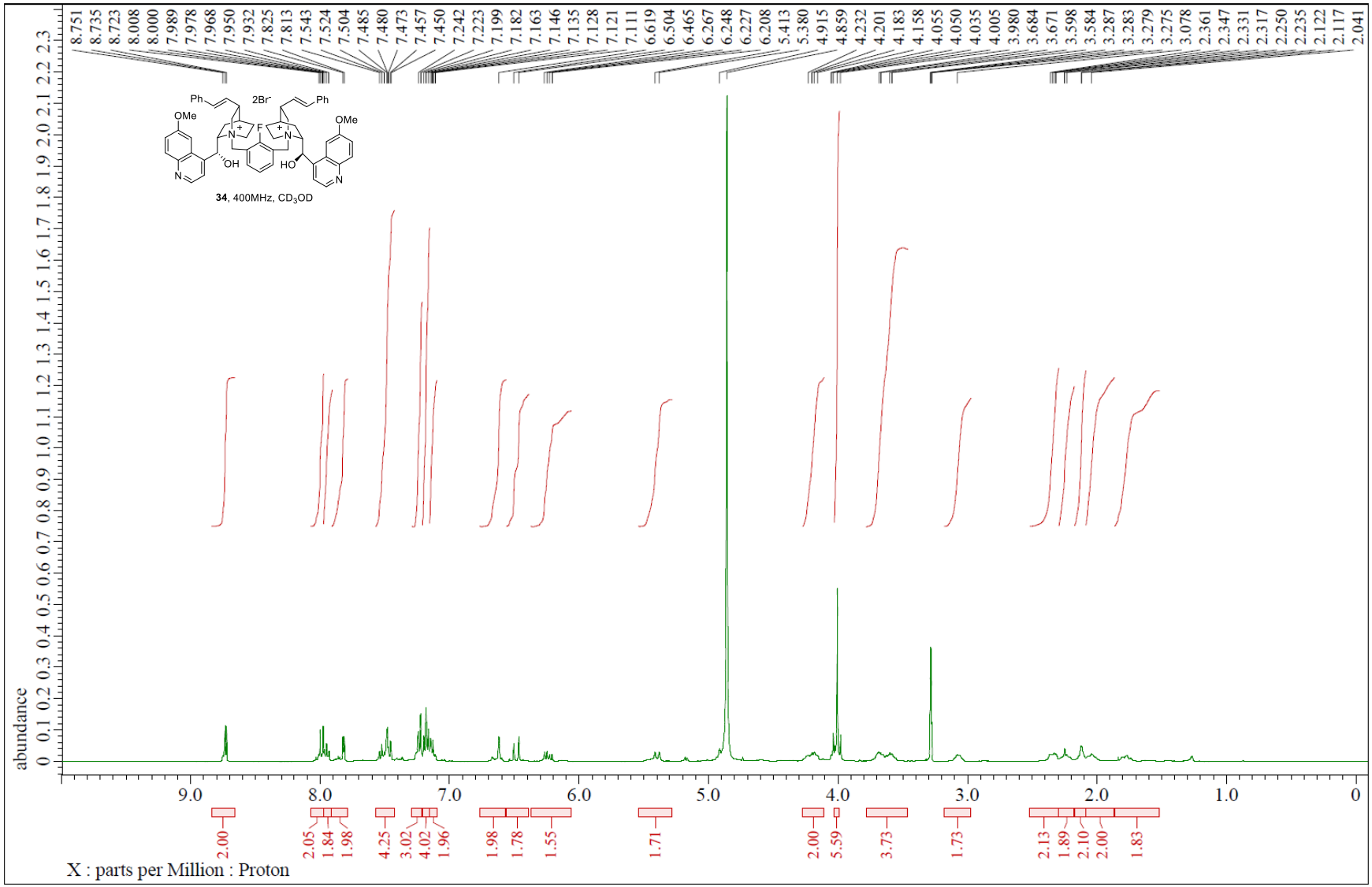
[1]H-NMR of compound **33**



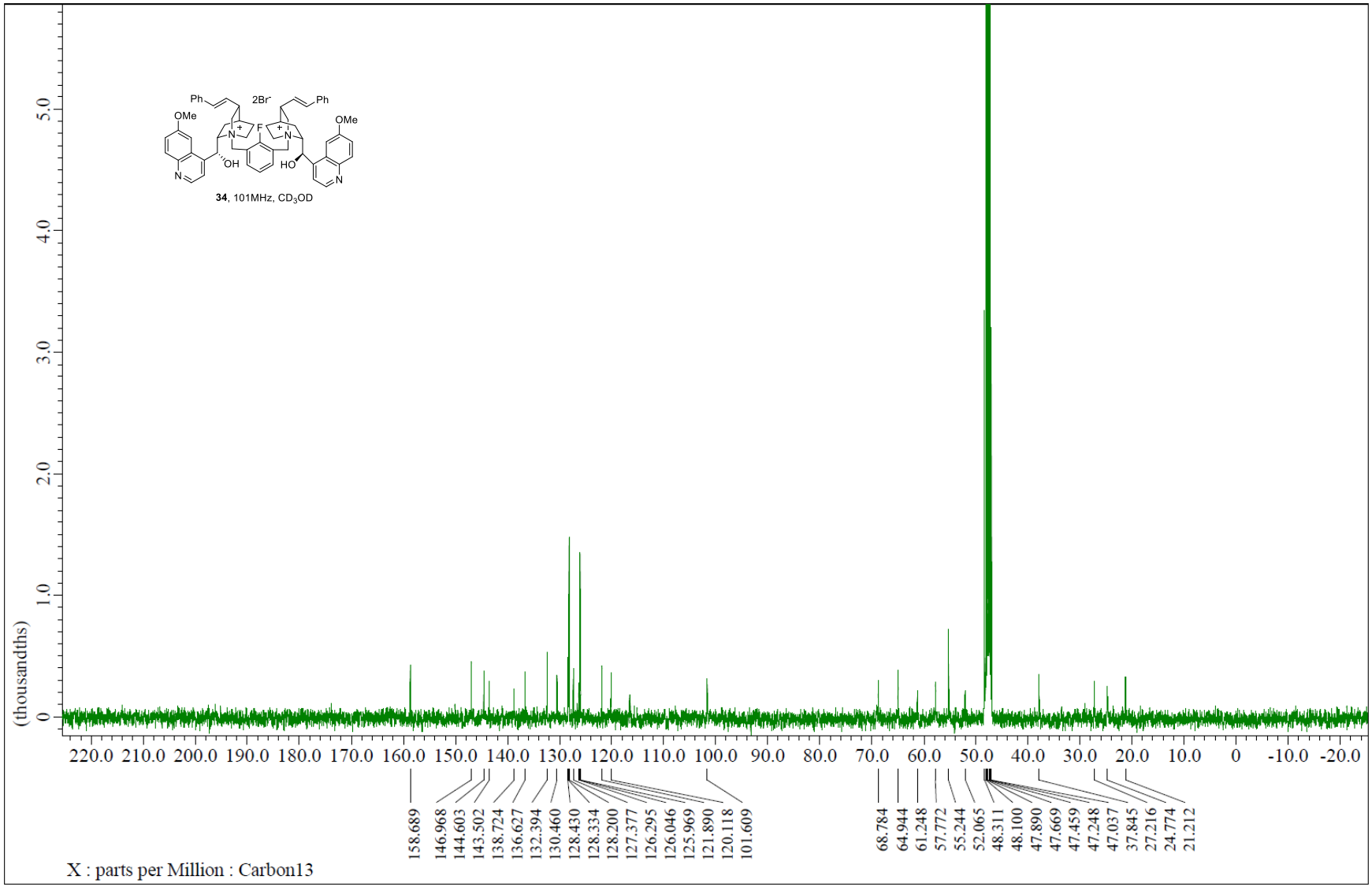
^{13}C-NMR of compound **33**



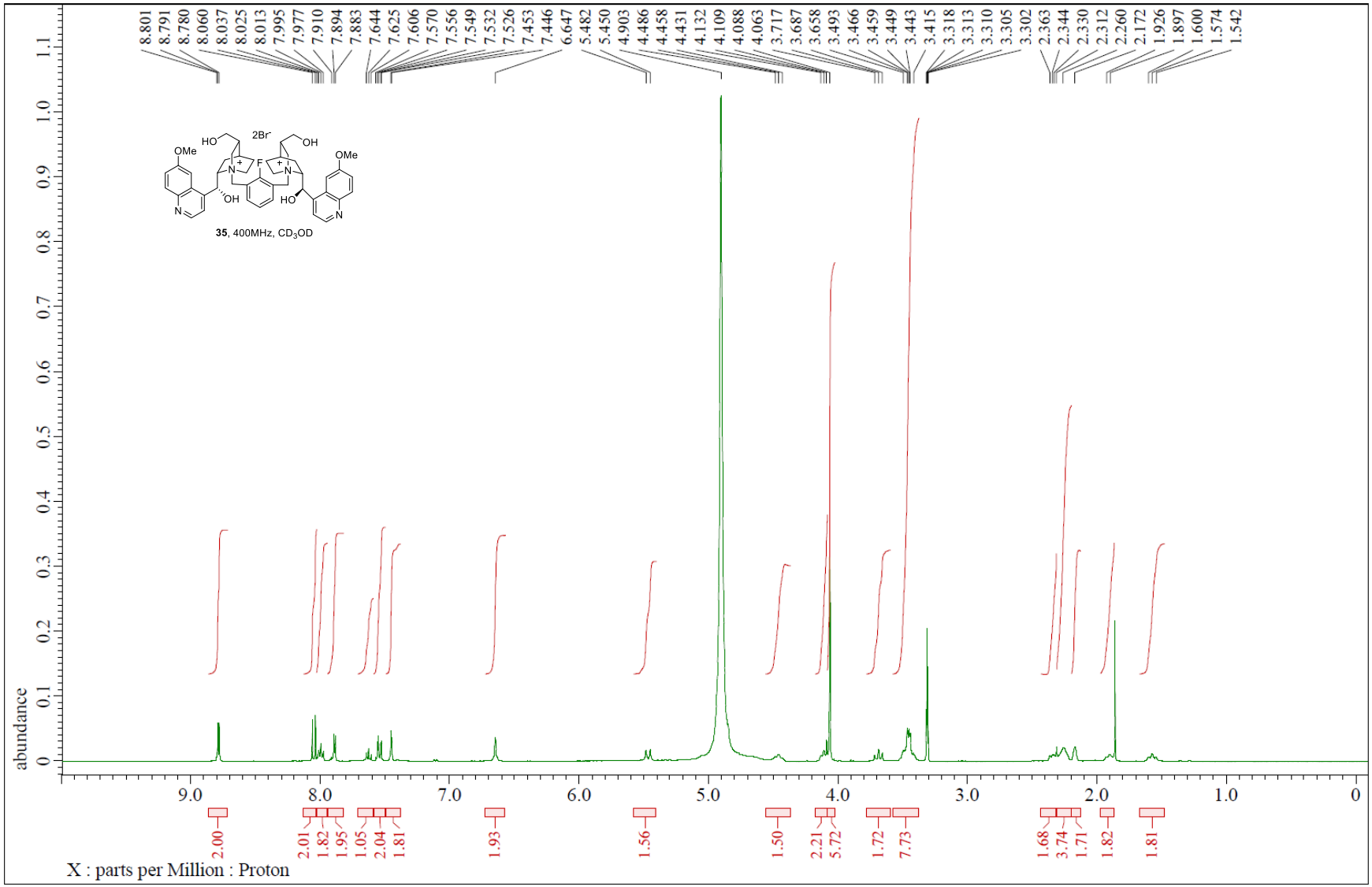
[1]H-NMR of compound **34**



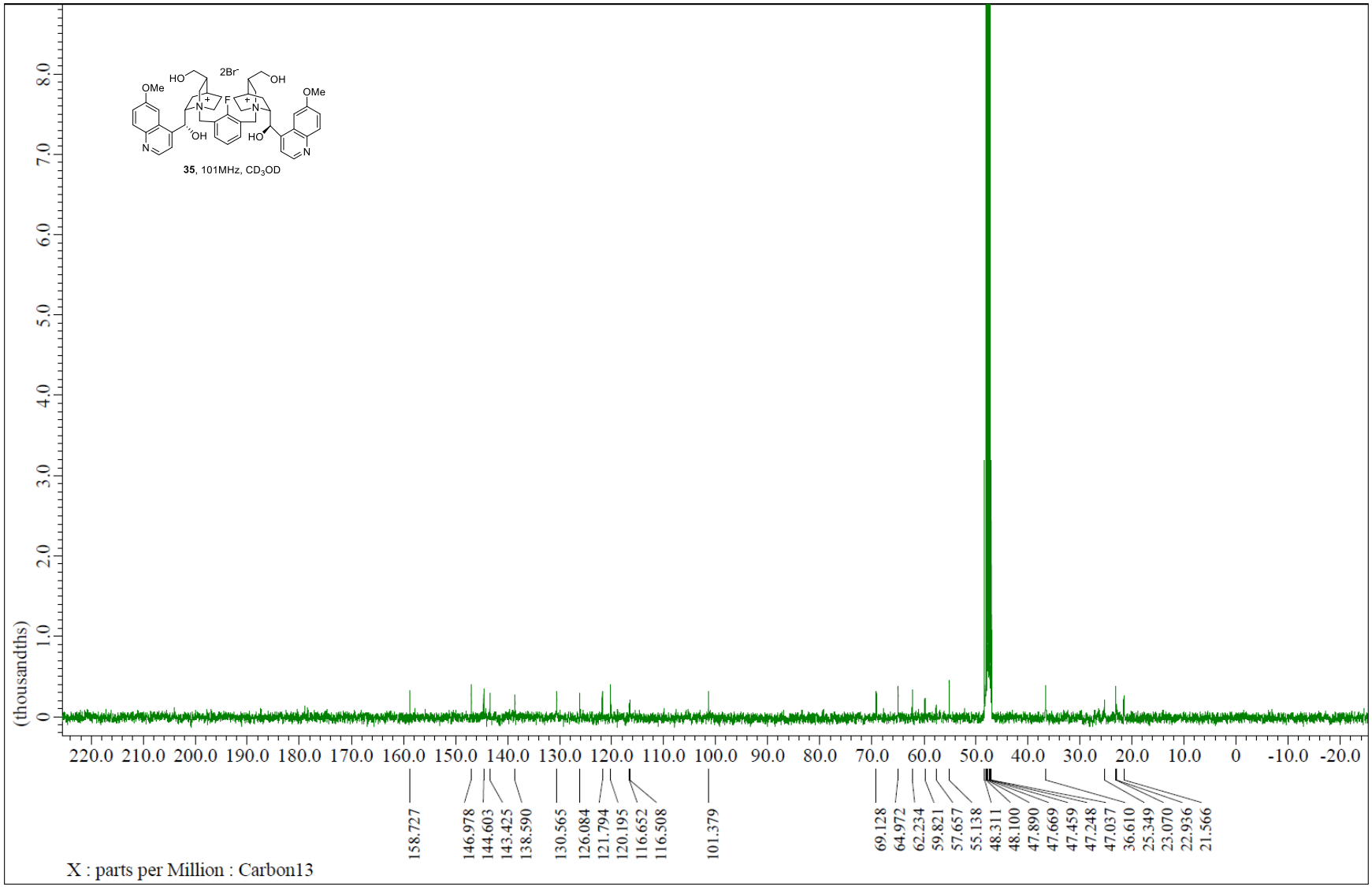
^{13}C-NMR of compound **34**



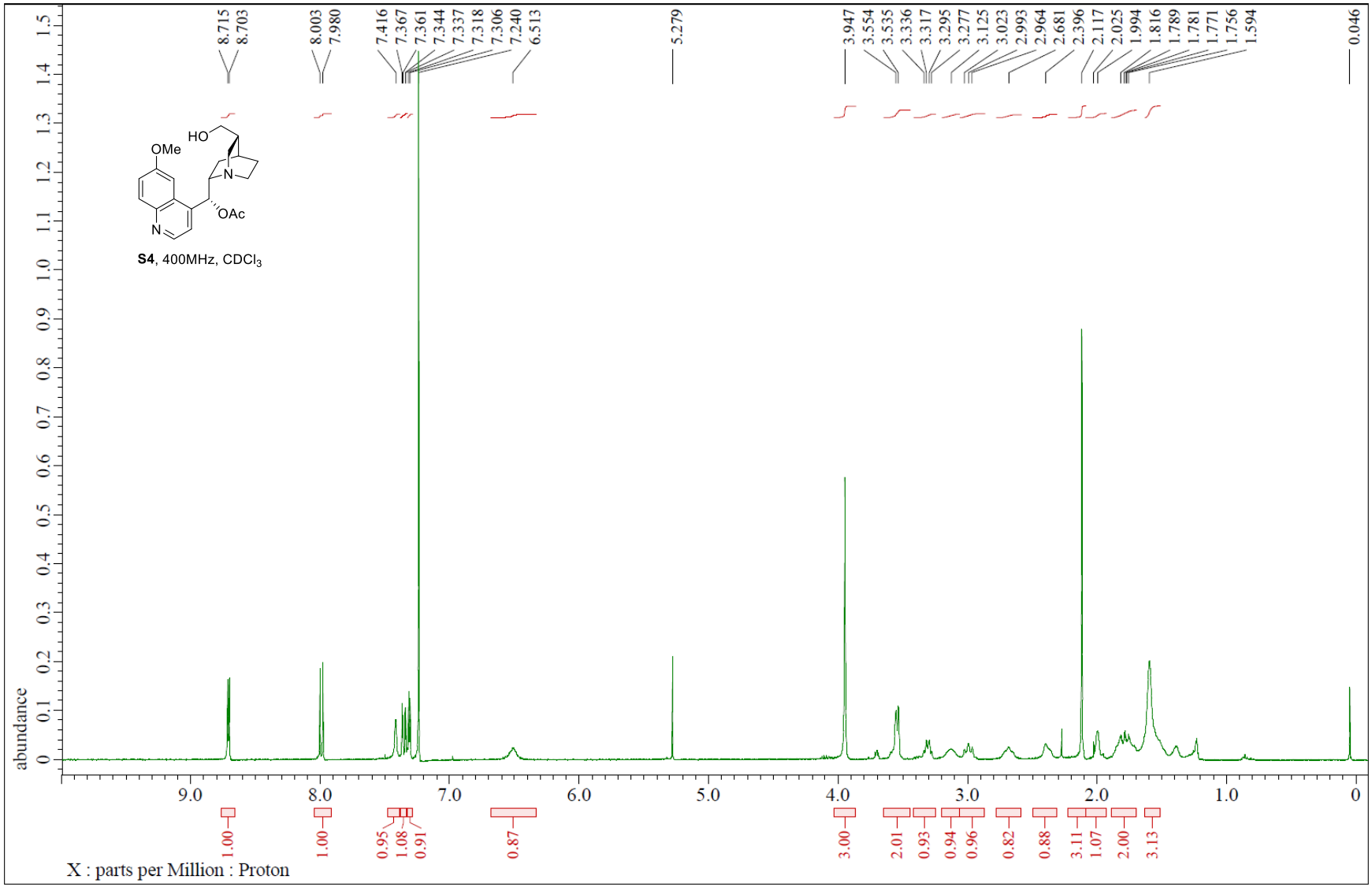
[1]H-NMR of compound **35**



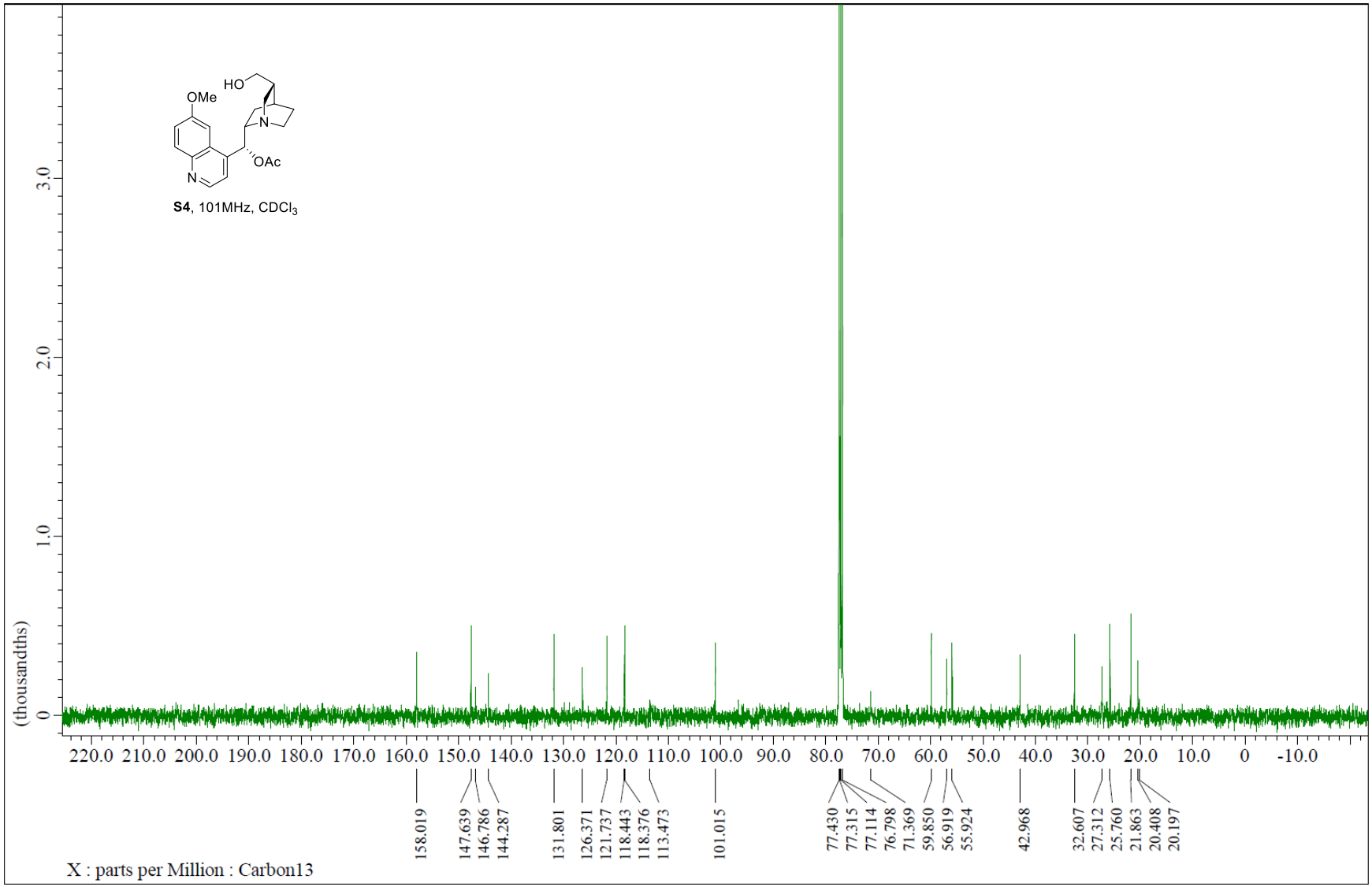
^{13}C-NMR of compound **35**



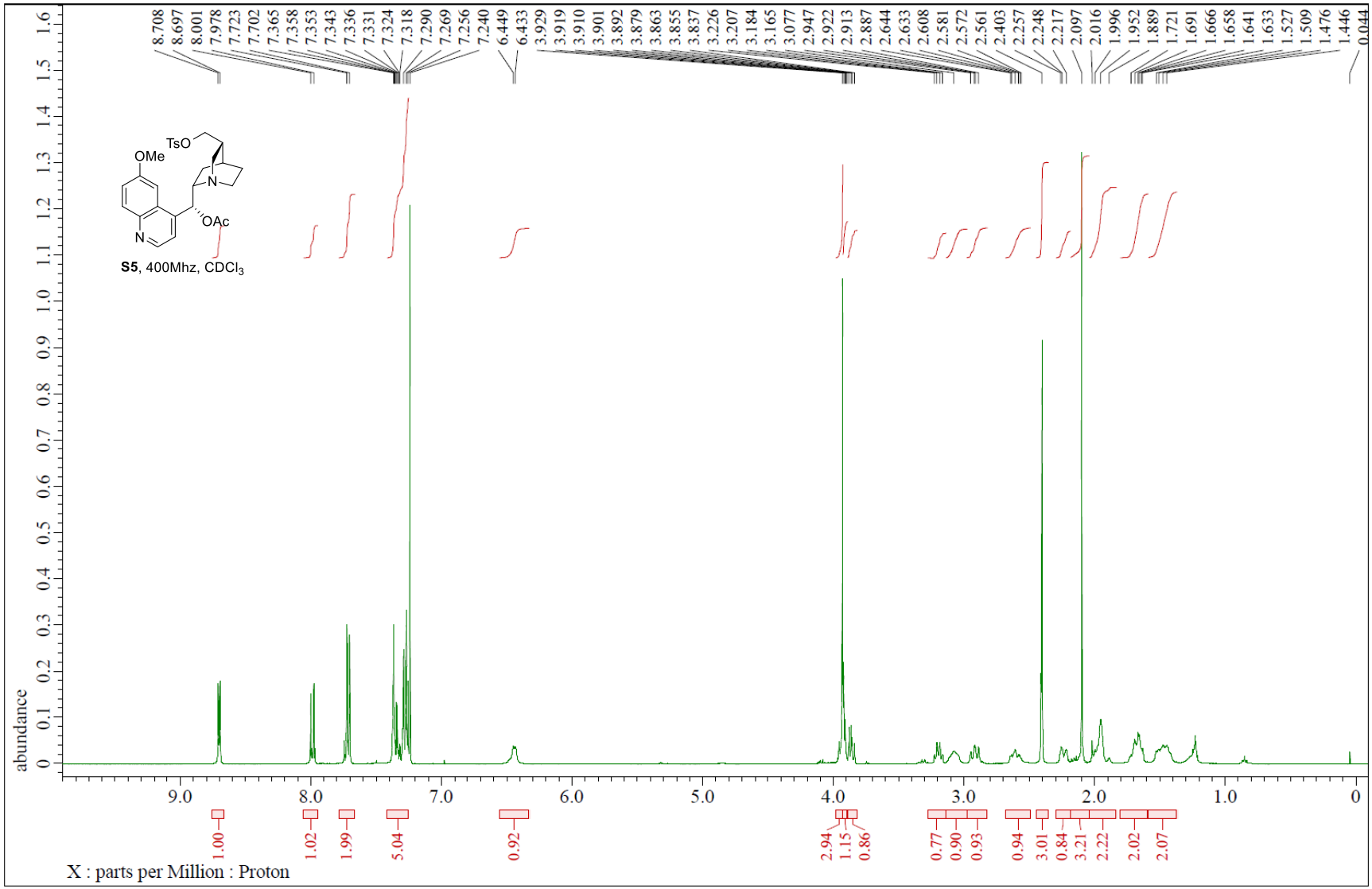
[1]H-NMR of compound **S4**



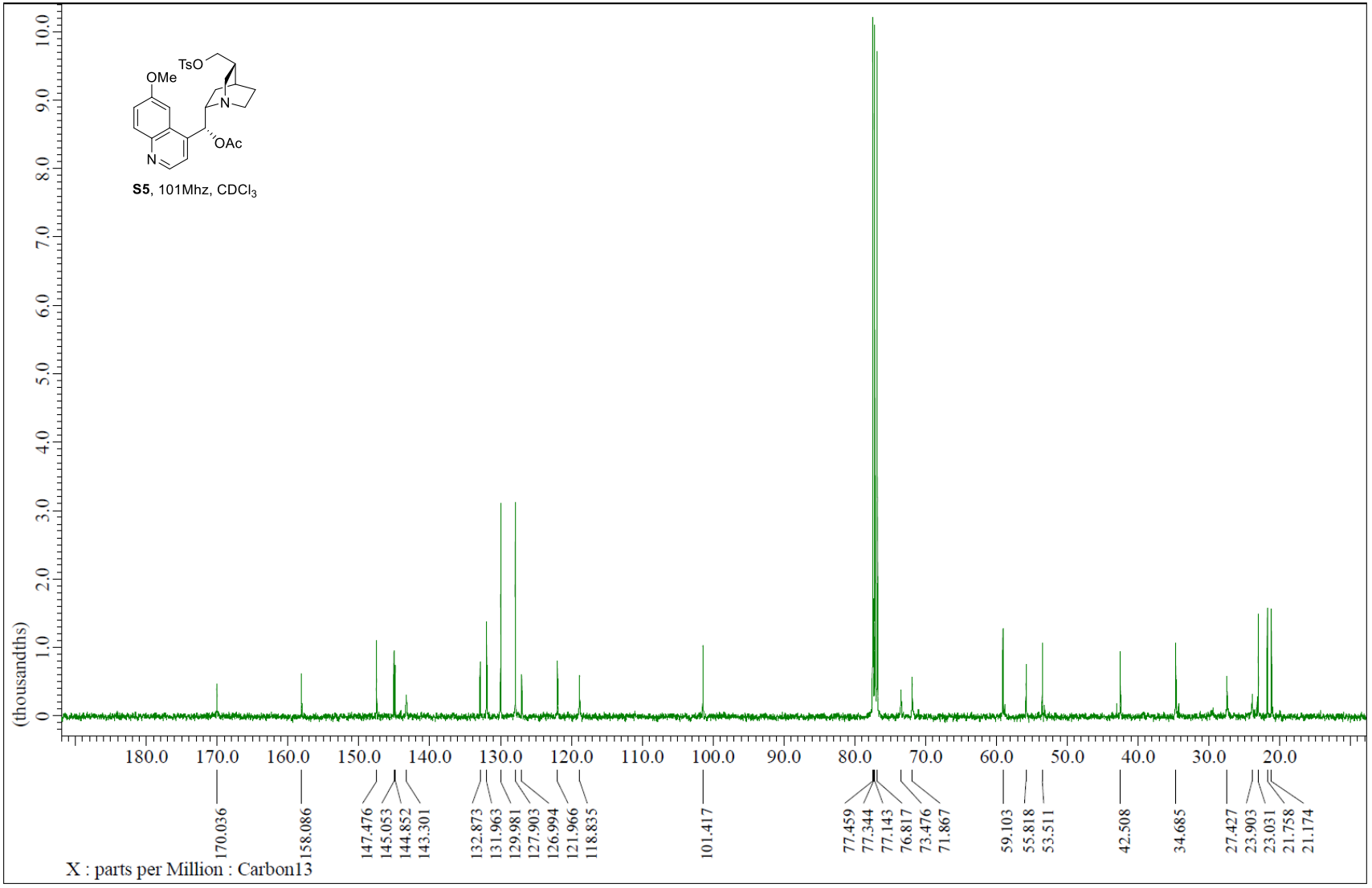
[13]C-NMR of compound **S4**



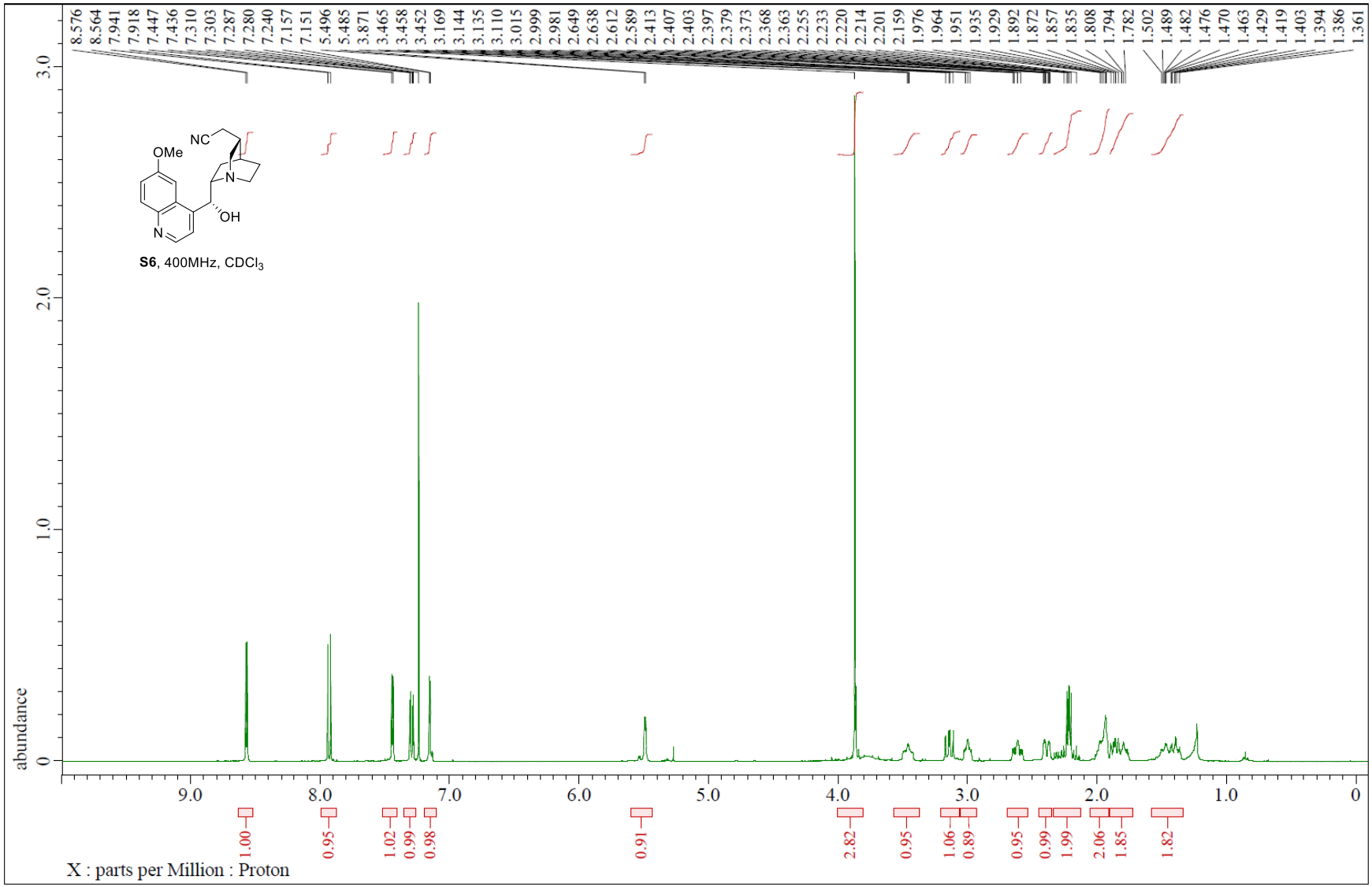
[1]H-NMR of compound **S5**



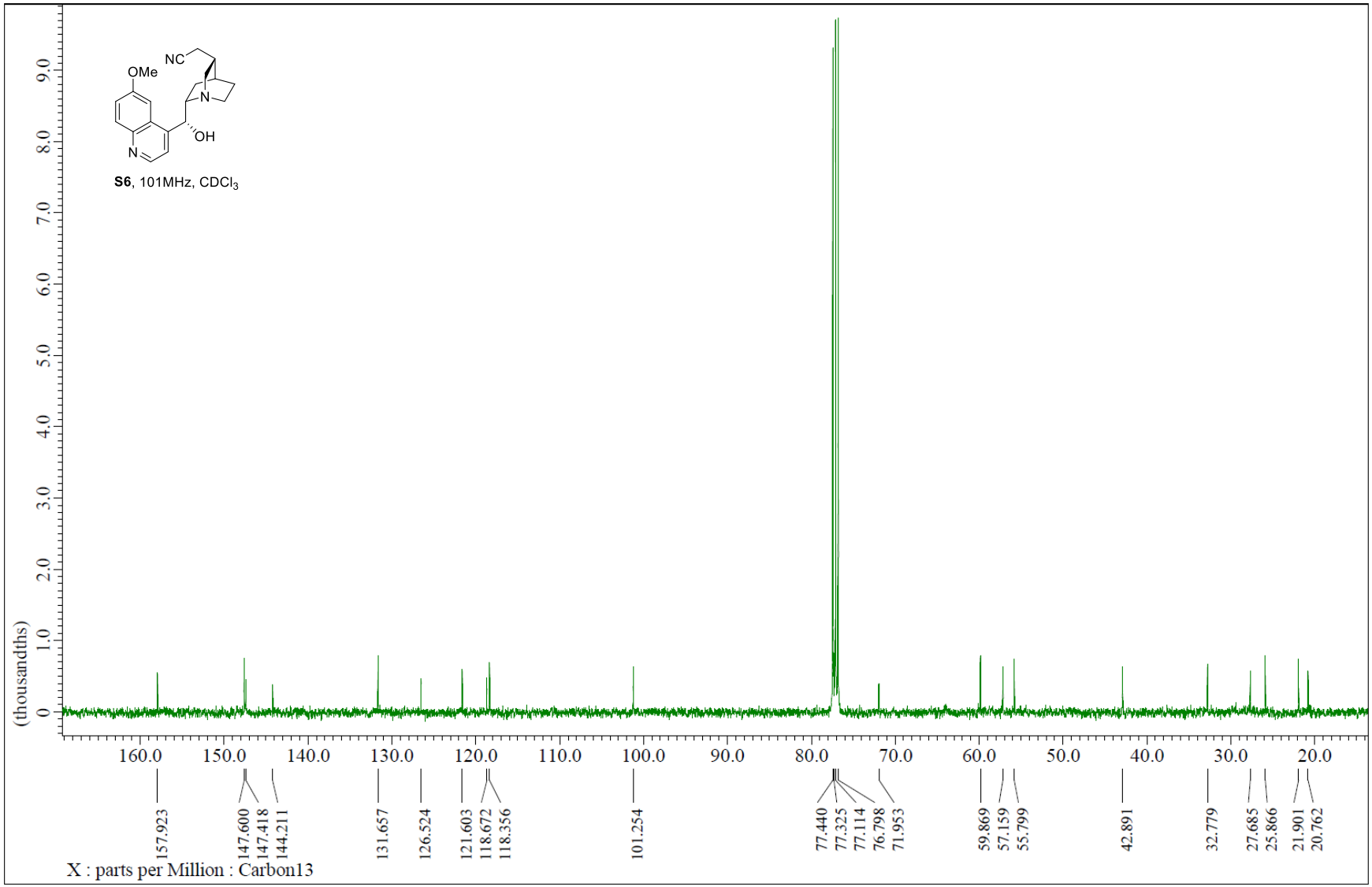
^{13}C-NMR of compound **S5**



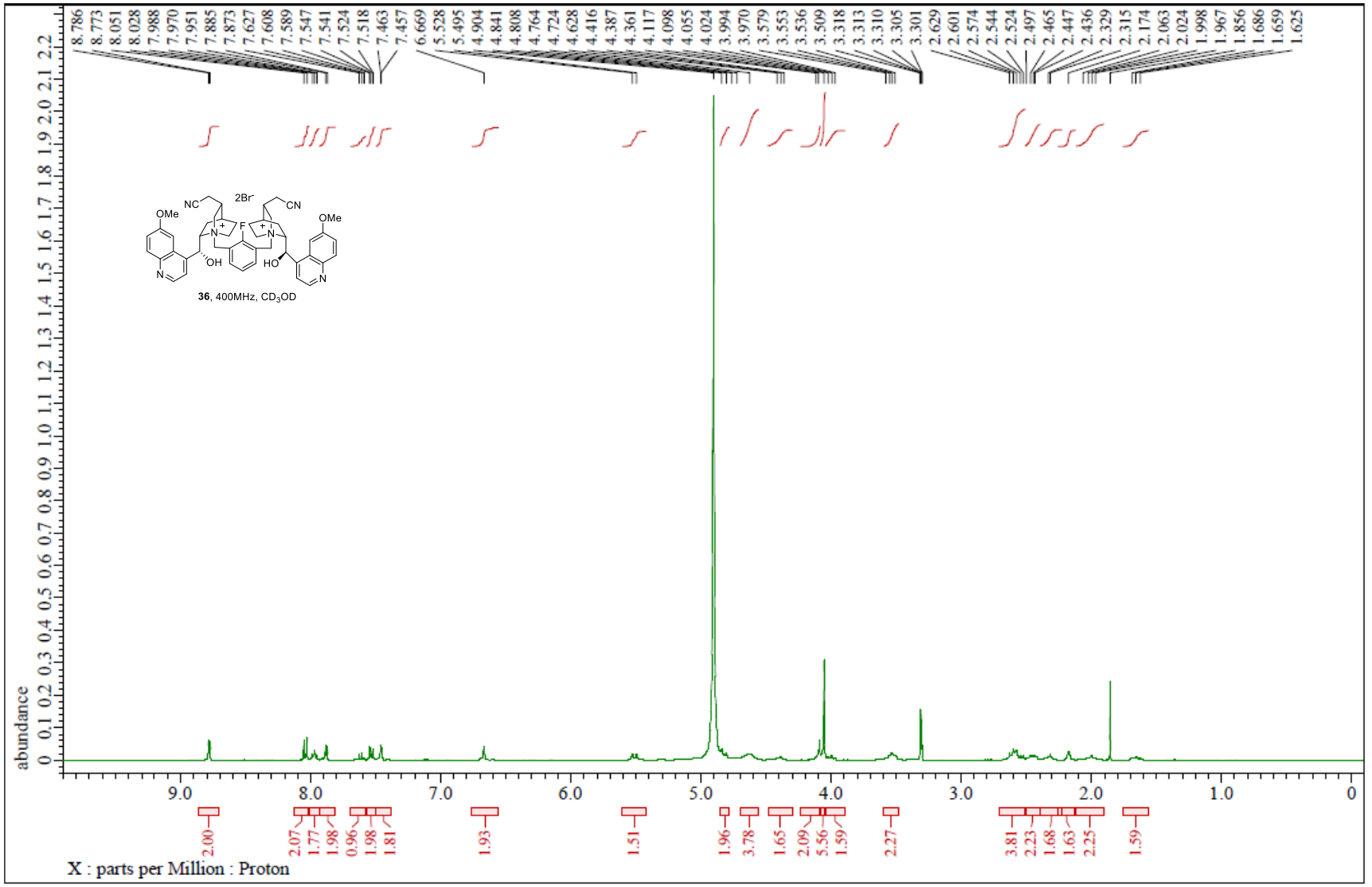
[1]H-NMR of compound **S6**



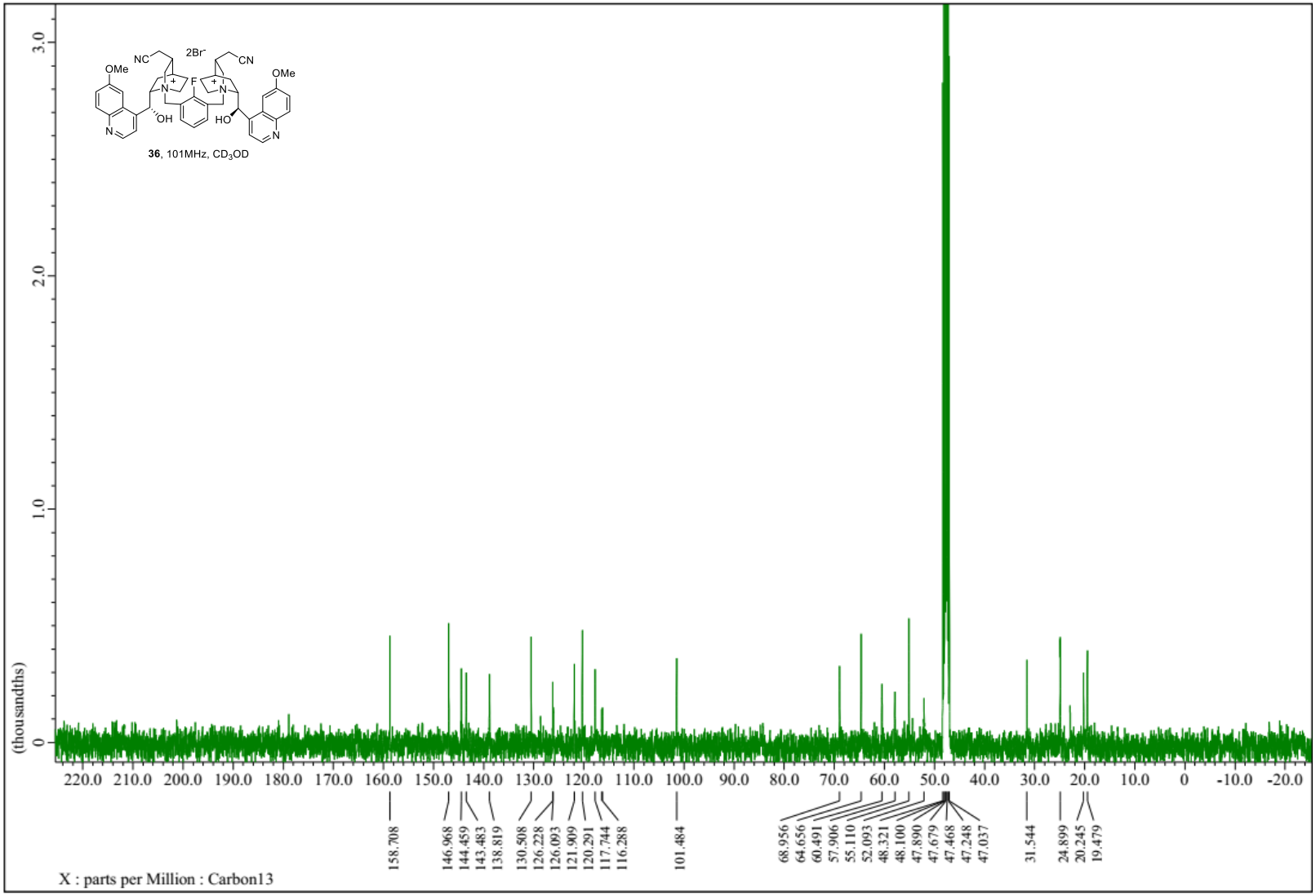
^{13}C-NMR of compound **S6**



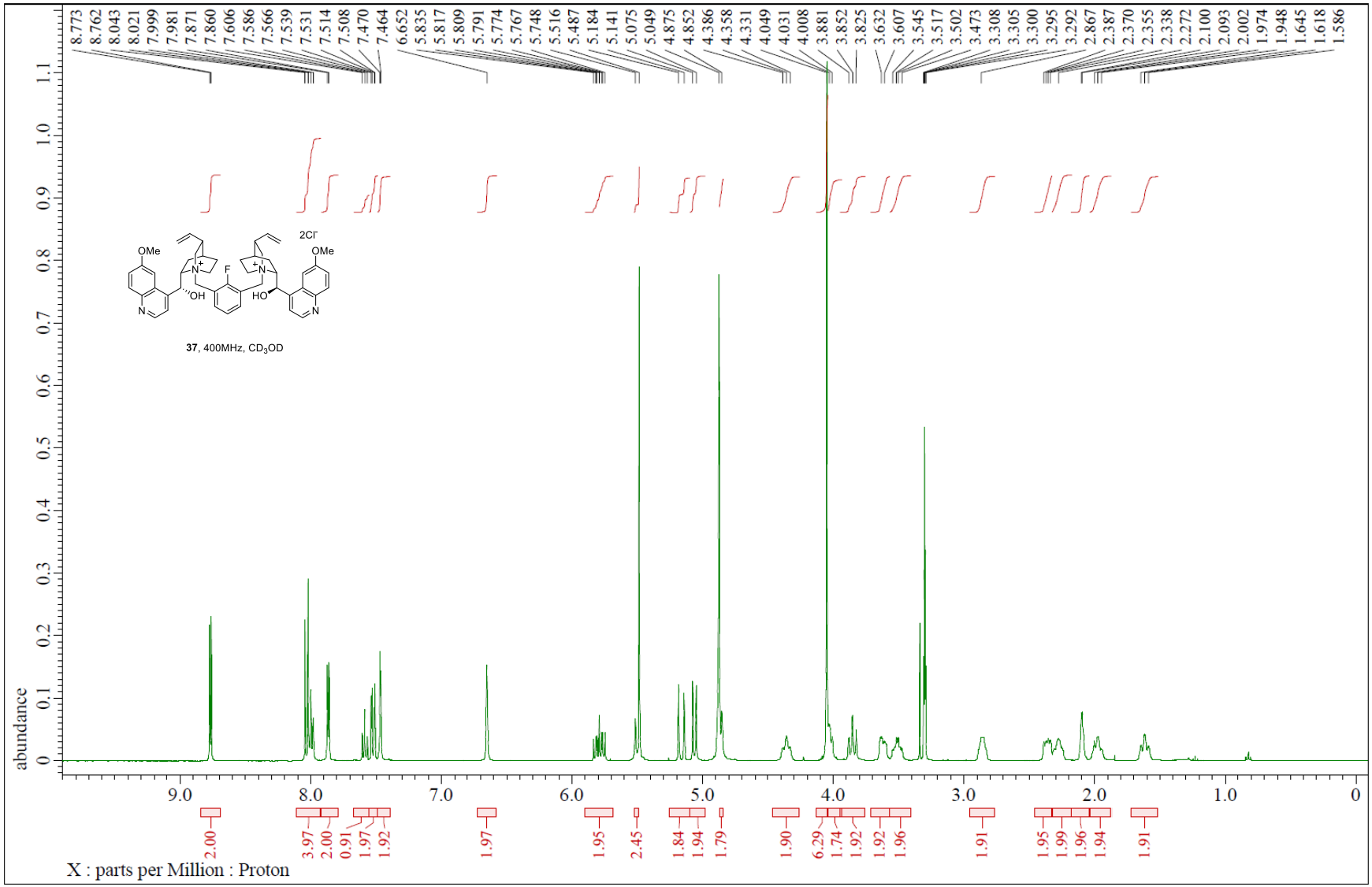
[1]H-NMR of compound **36**



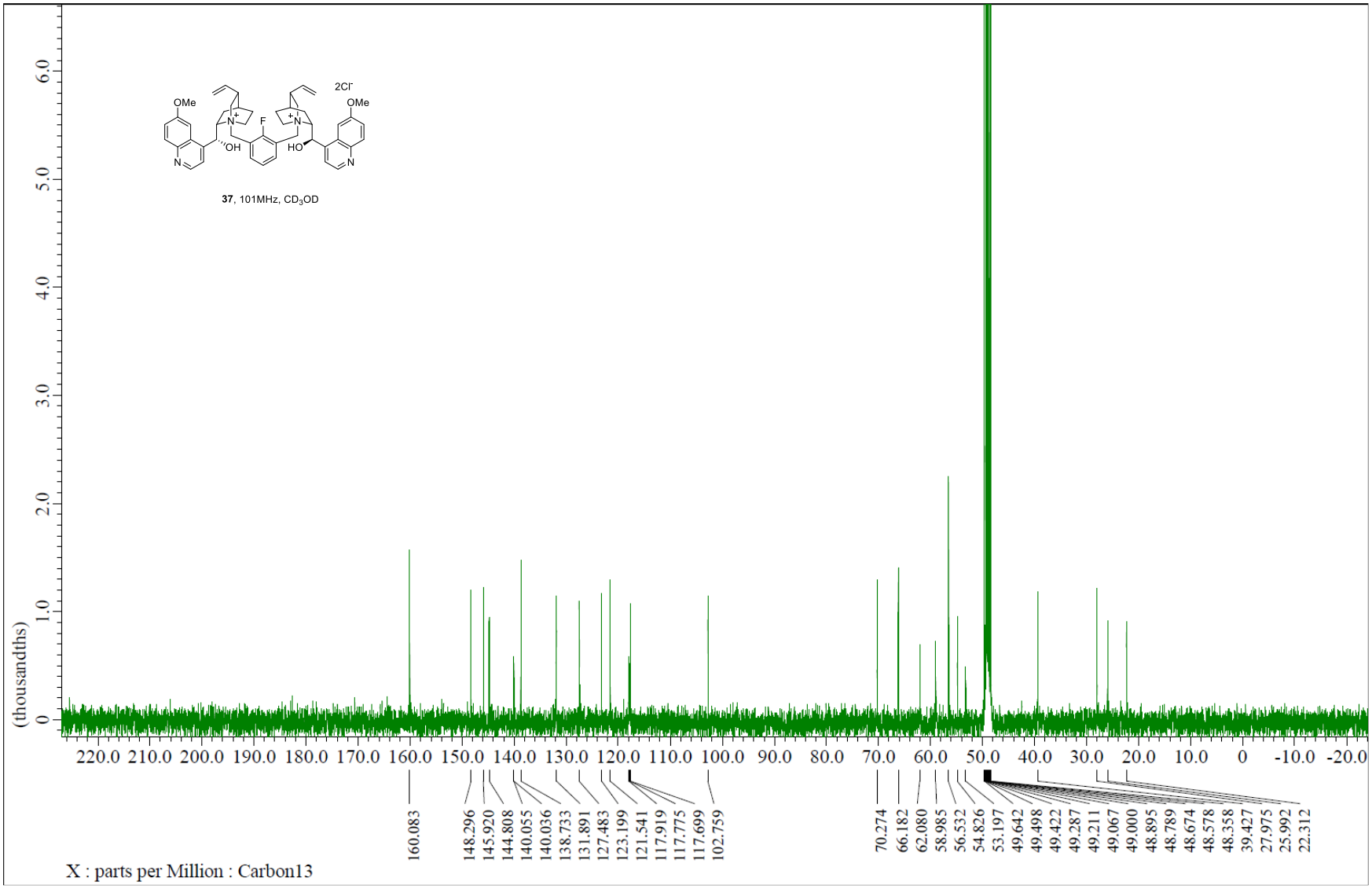
^{13}C-NMR of compound **36**



[1]H-NMR of compound **37**

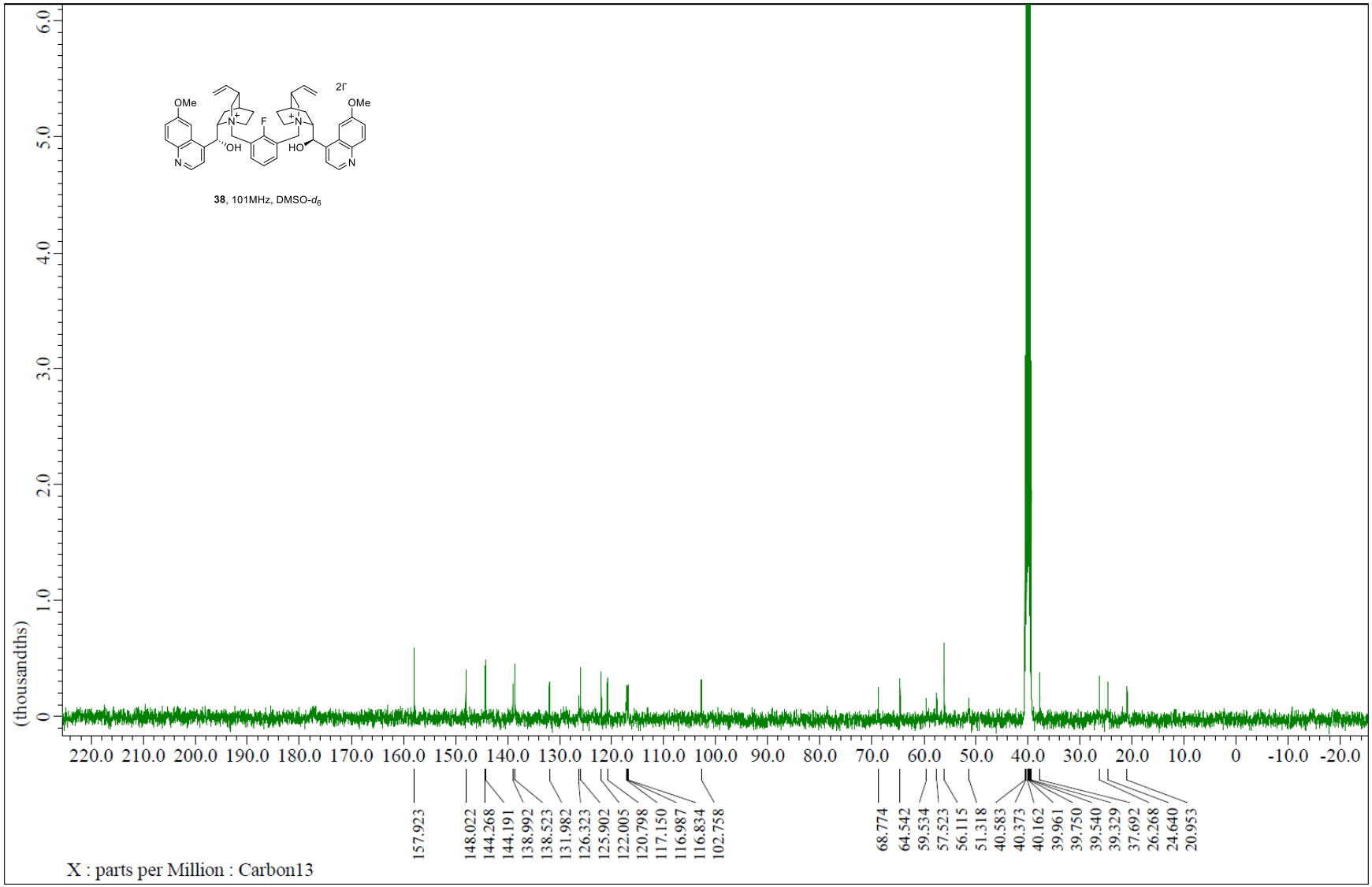


^{13}C-NMR of compound **37**

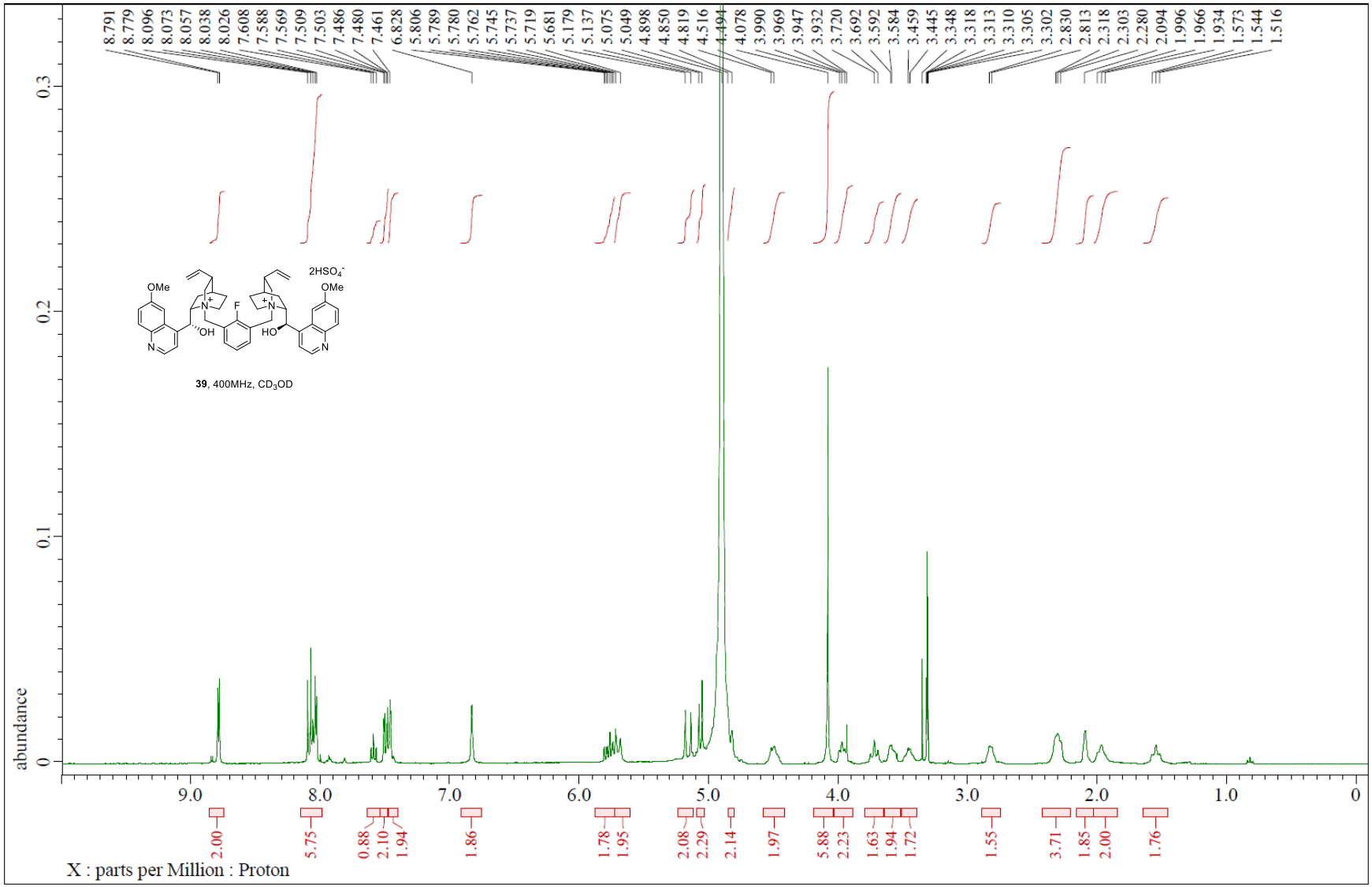


[1]H-NMR of compound **38**

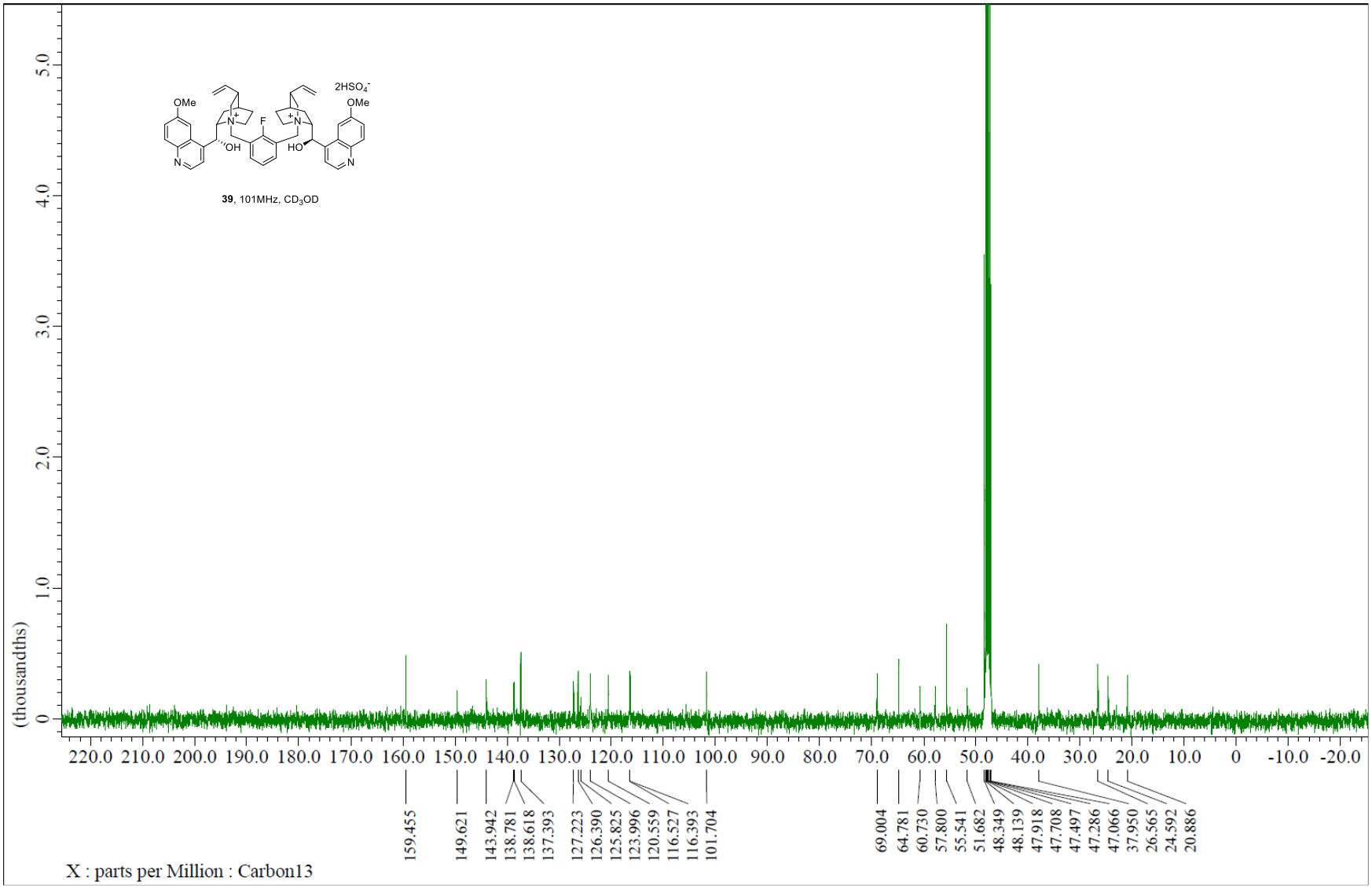
^{13}C-NMR of compound **38**



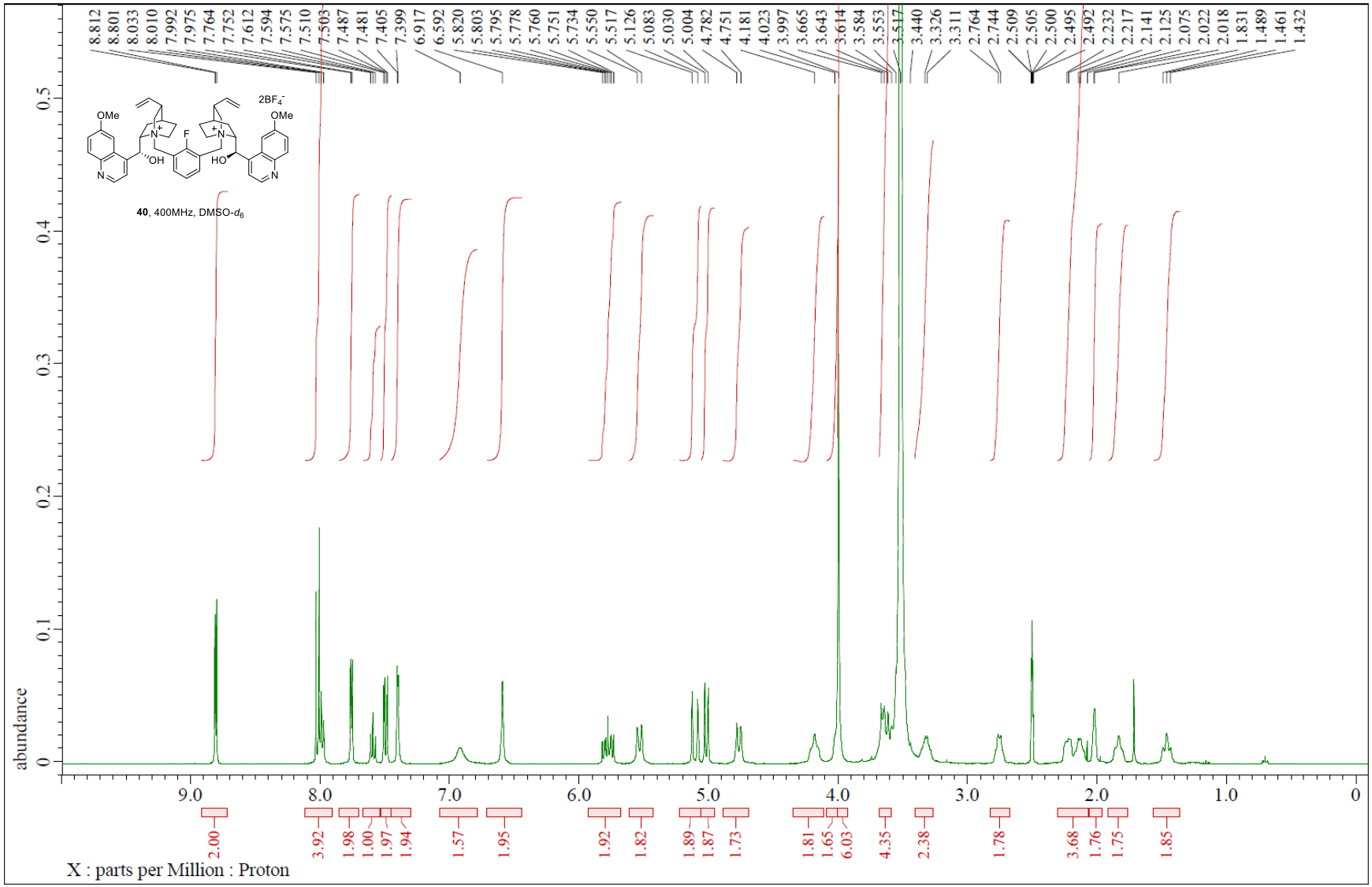
[1]H-NMR of compound **39**



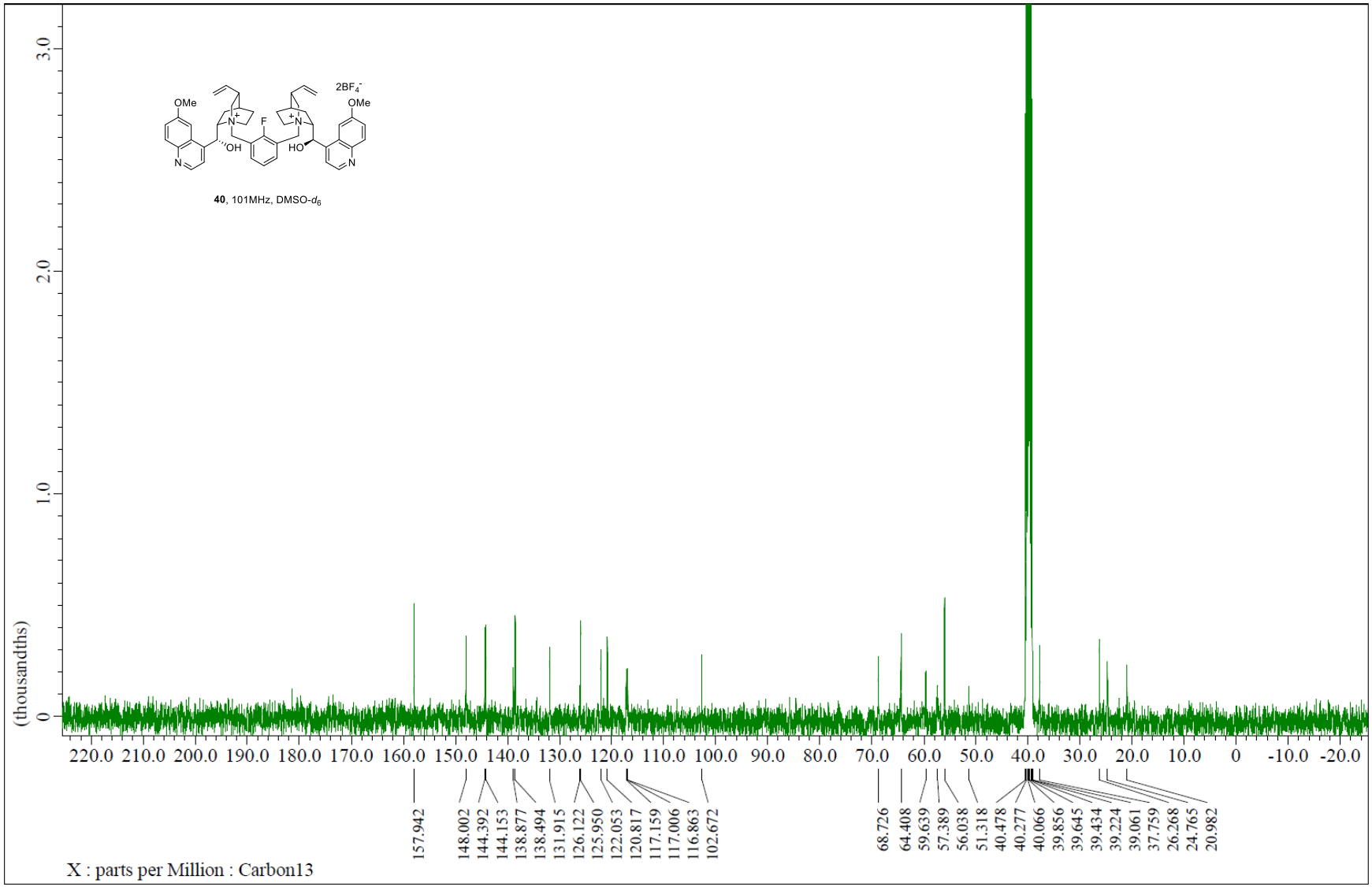
^{13}C-NMR of compound **39**



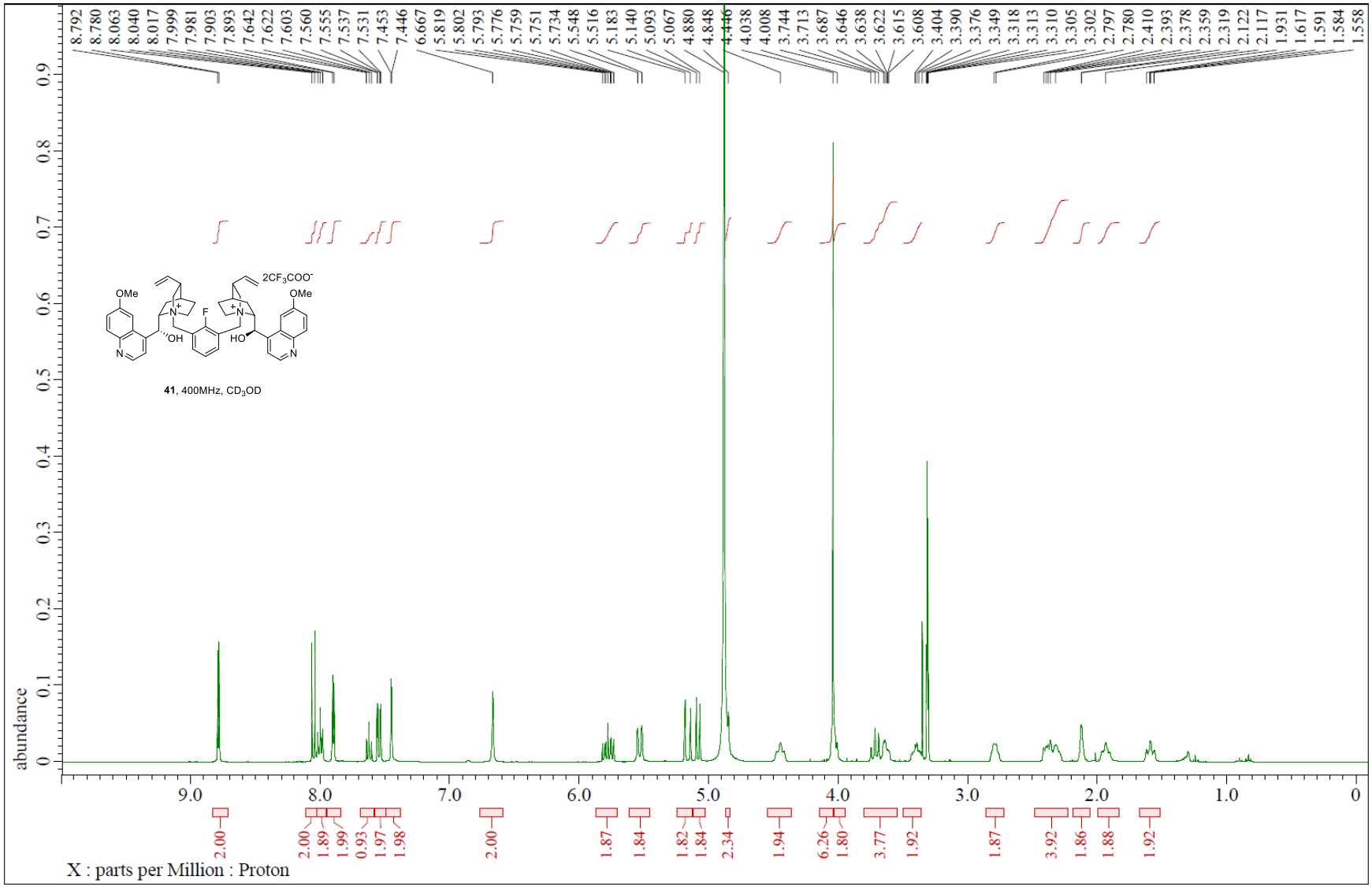
[1]H-NMR of compound **40**



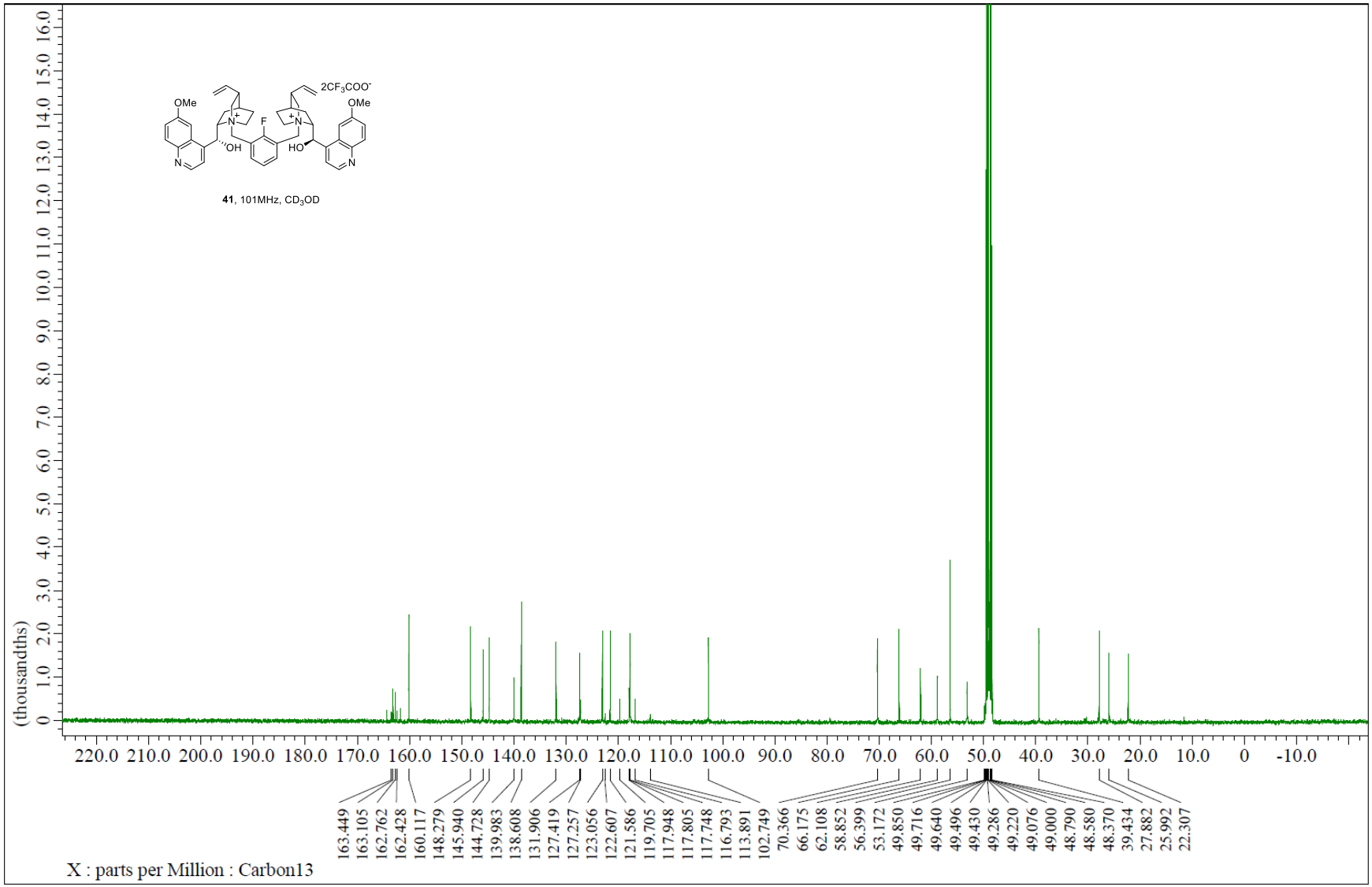
^{13}C-NMR of compound **40**



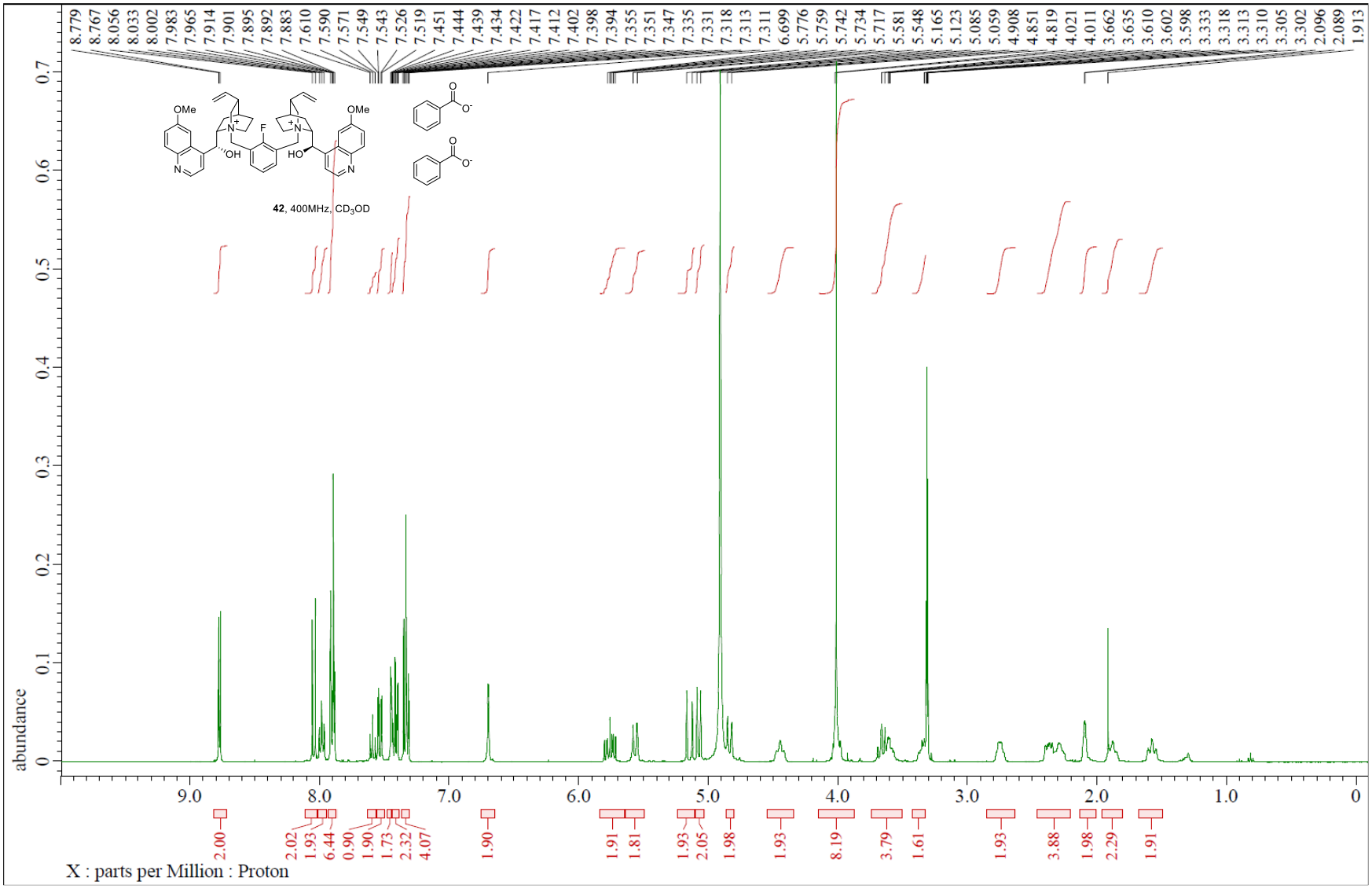
[1]H-NMR of compound **41**



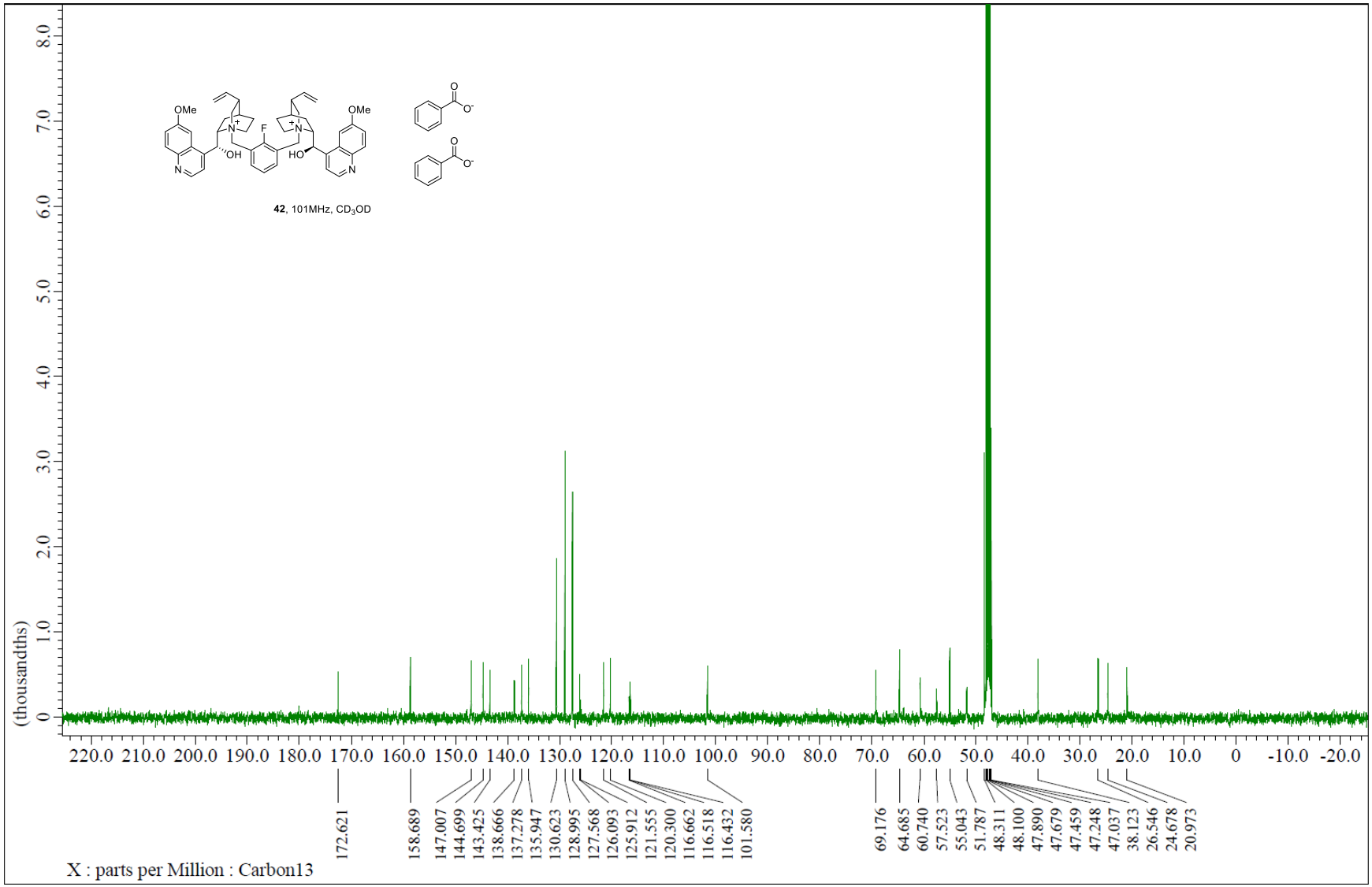
^{13}C-NMR of compound **41**



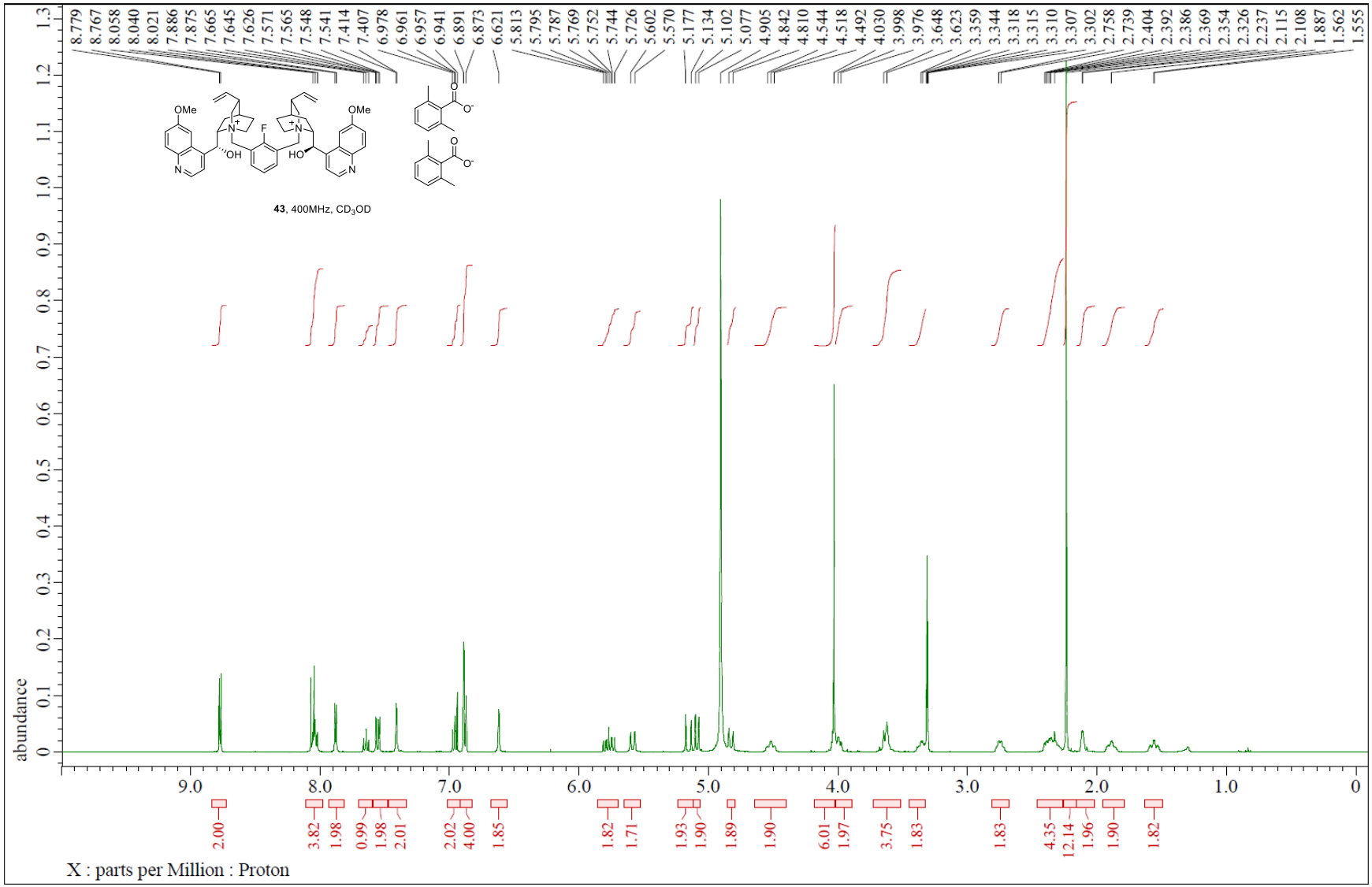
[1]H-NMR of compound **42**



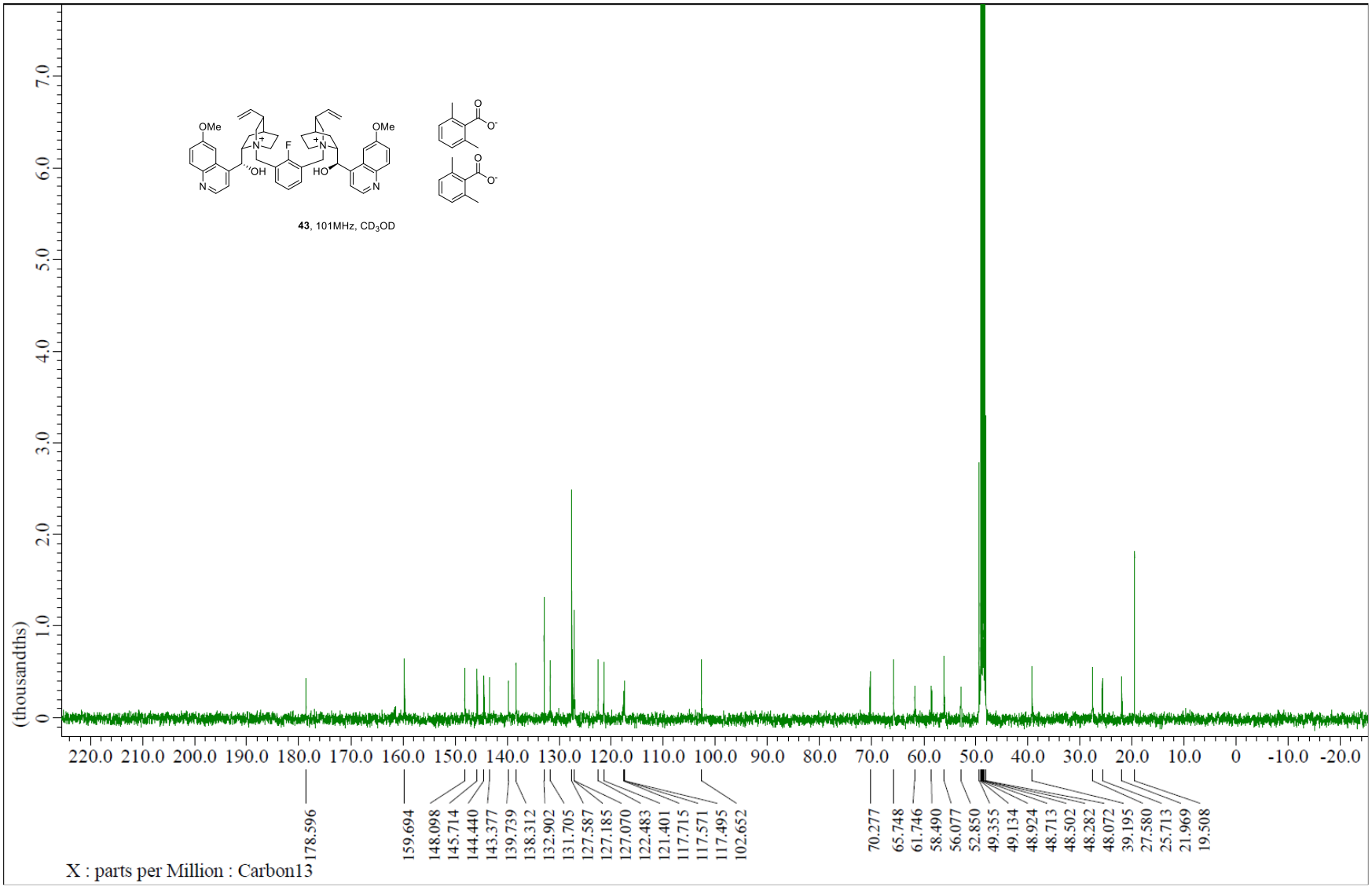
^{13}C-NMR of compound **42**



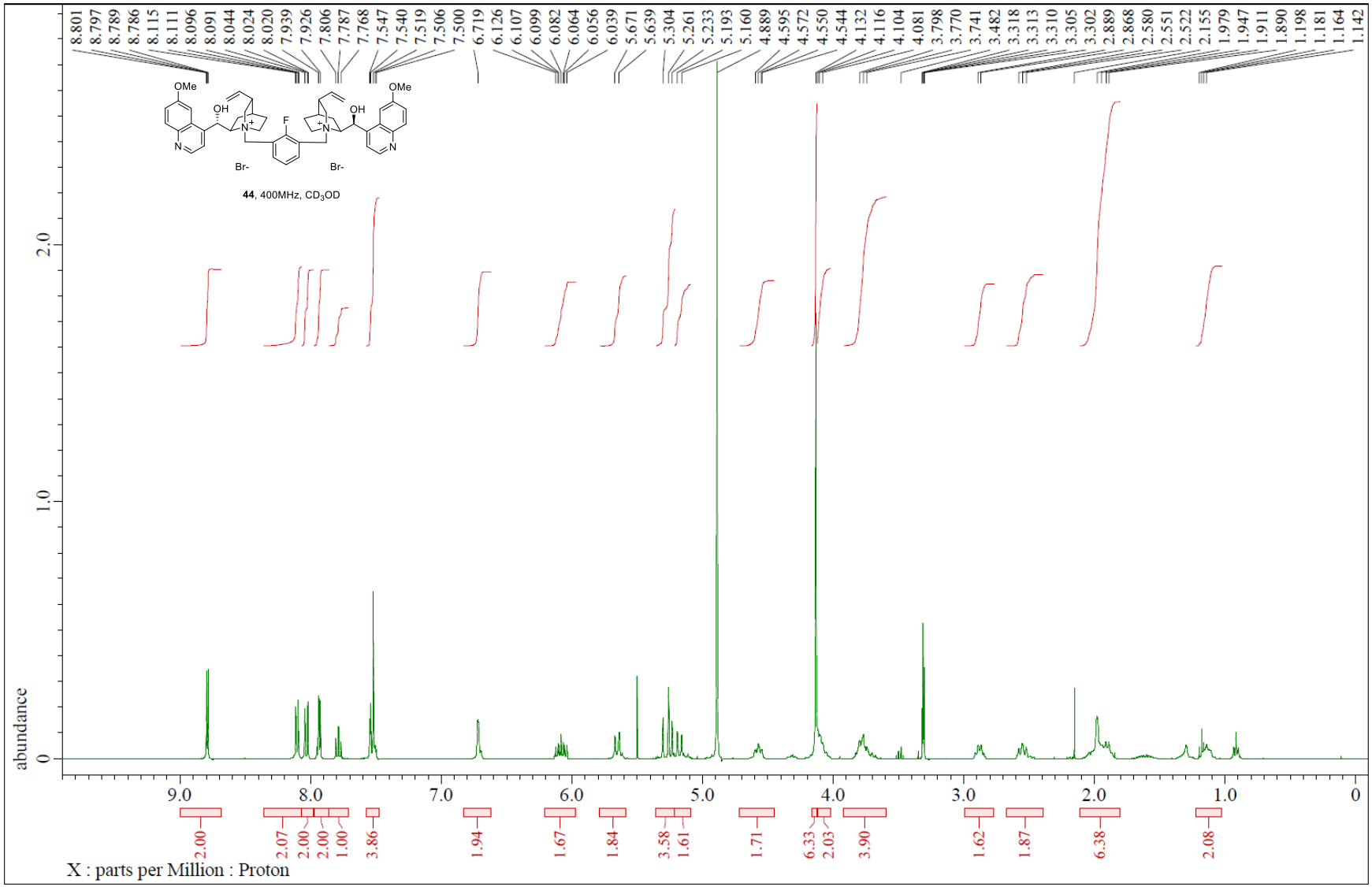
[1]H-NMR of compound **43**



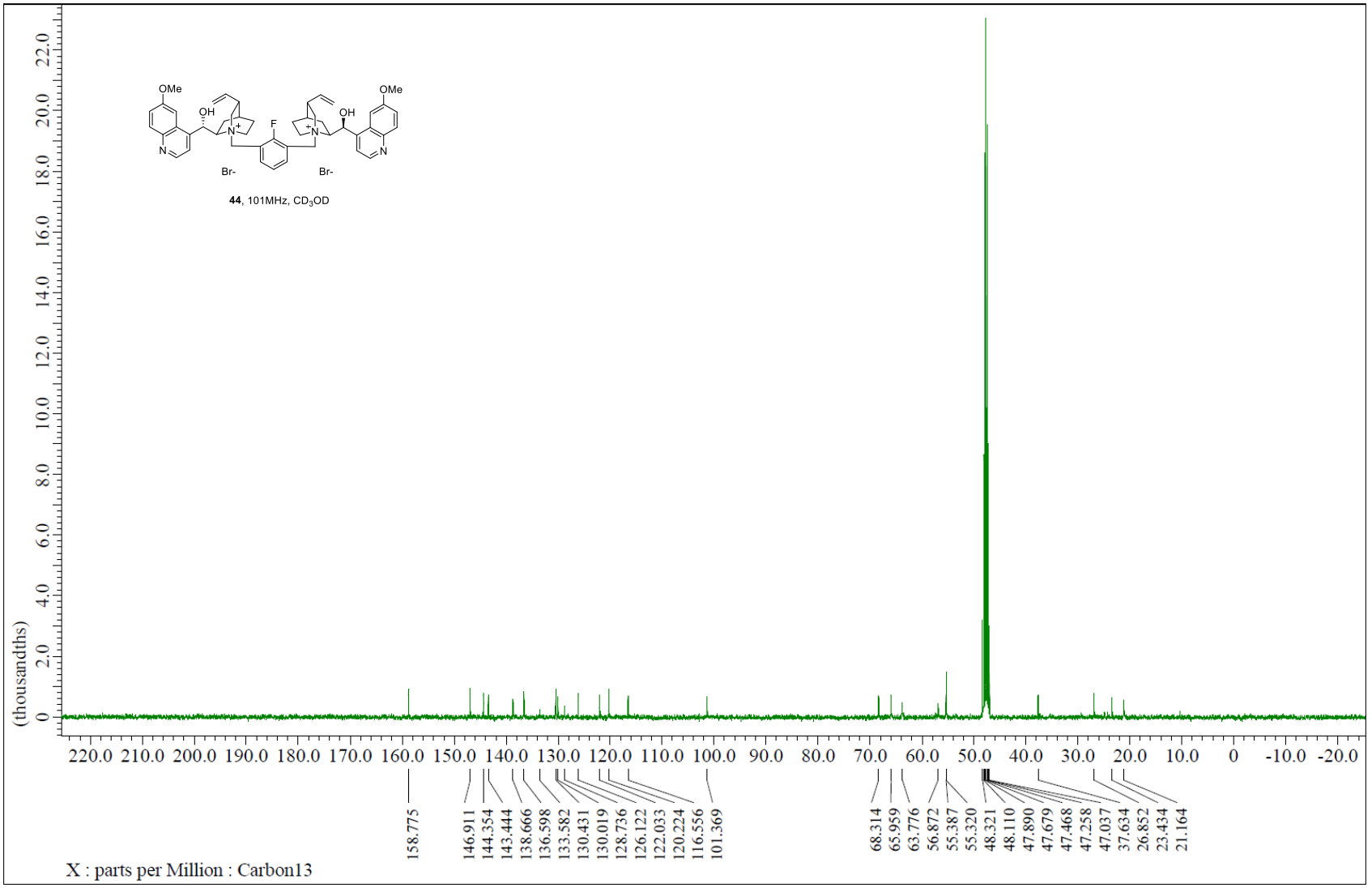
^{13}C-NMR of compound **43**



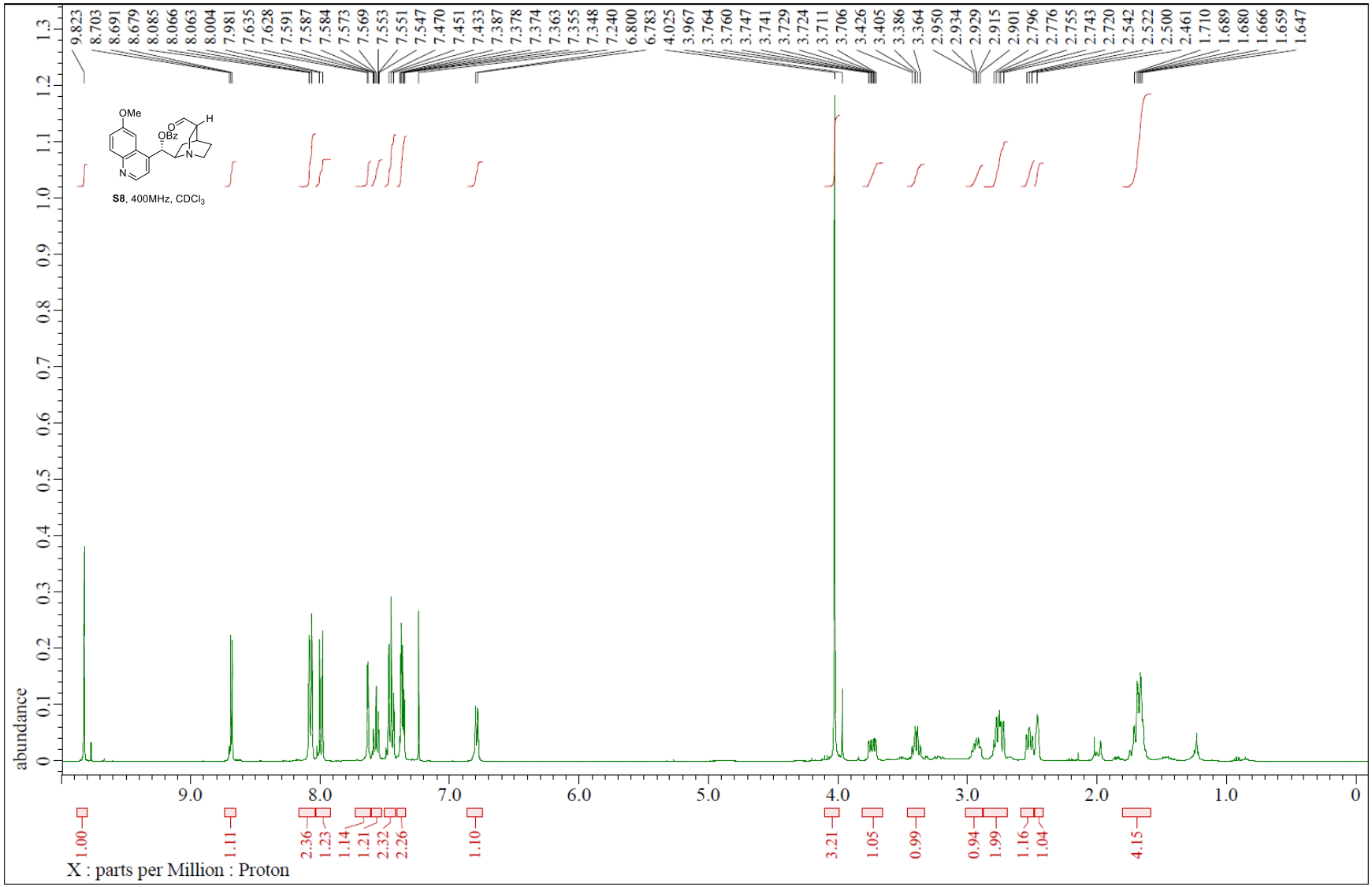
[1]H-NMR of compound **44**



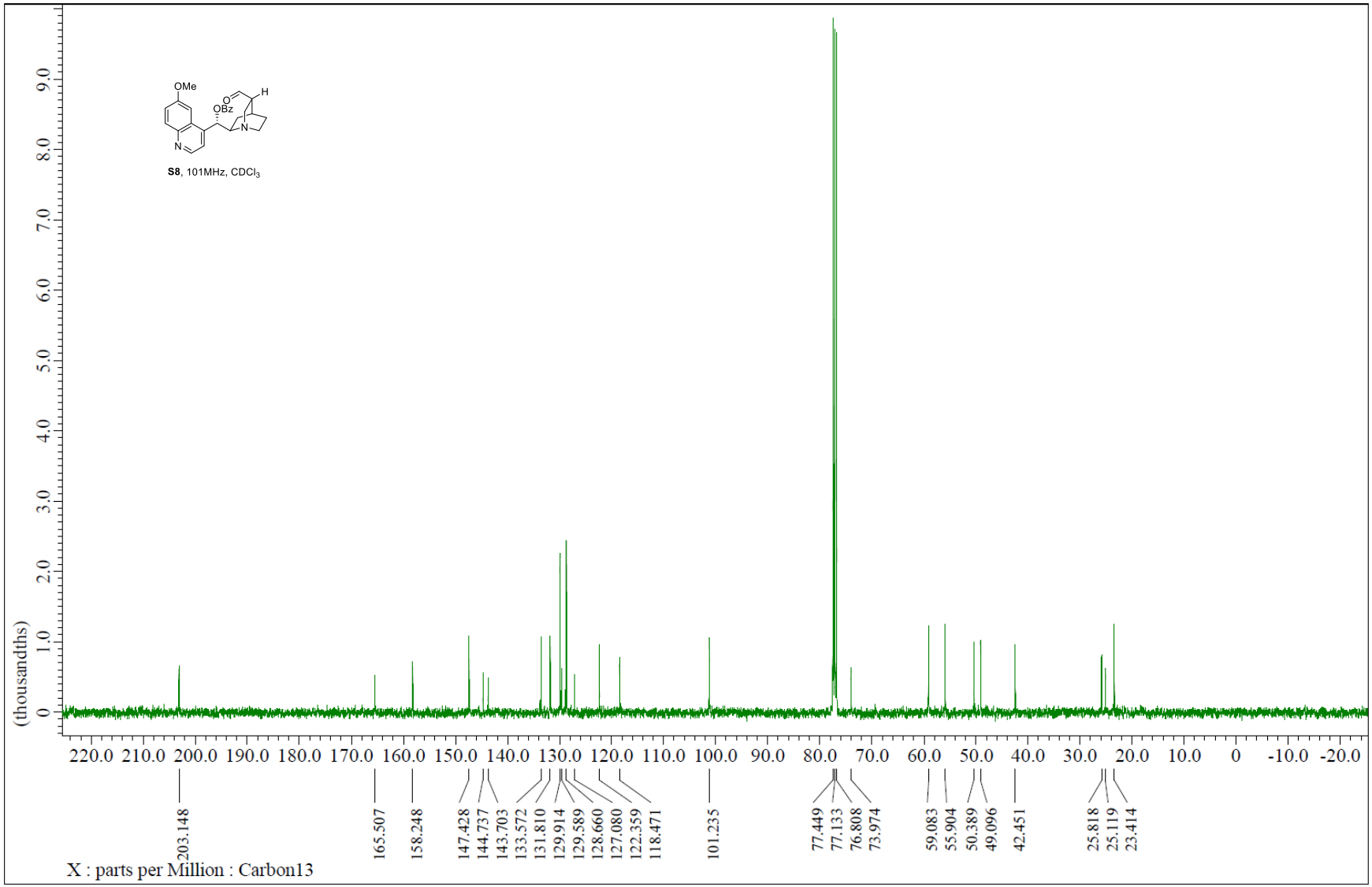
^{13}C-NMR of compound **44**



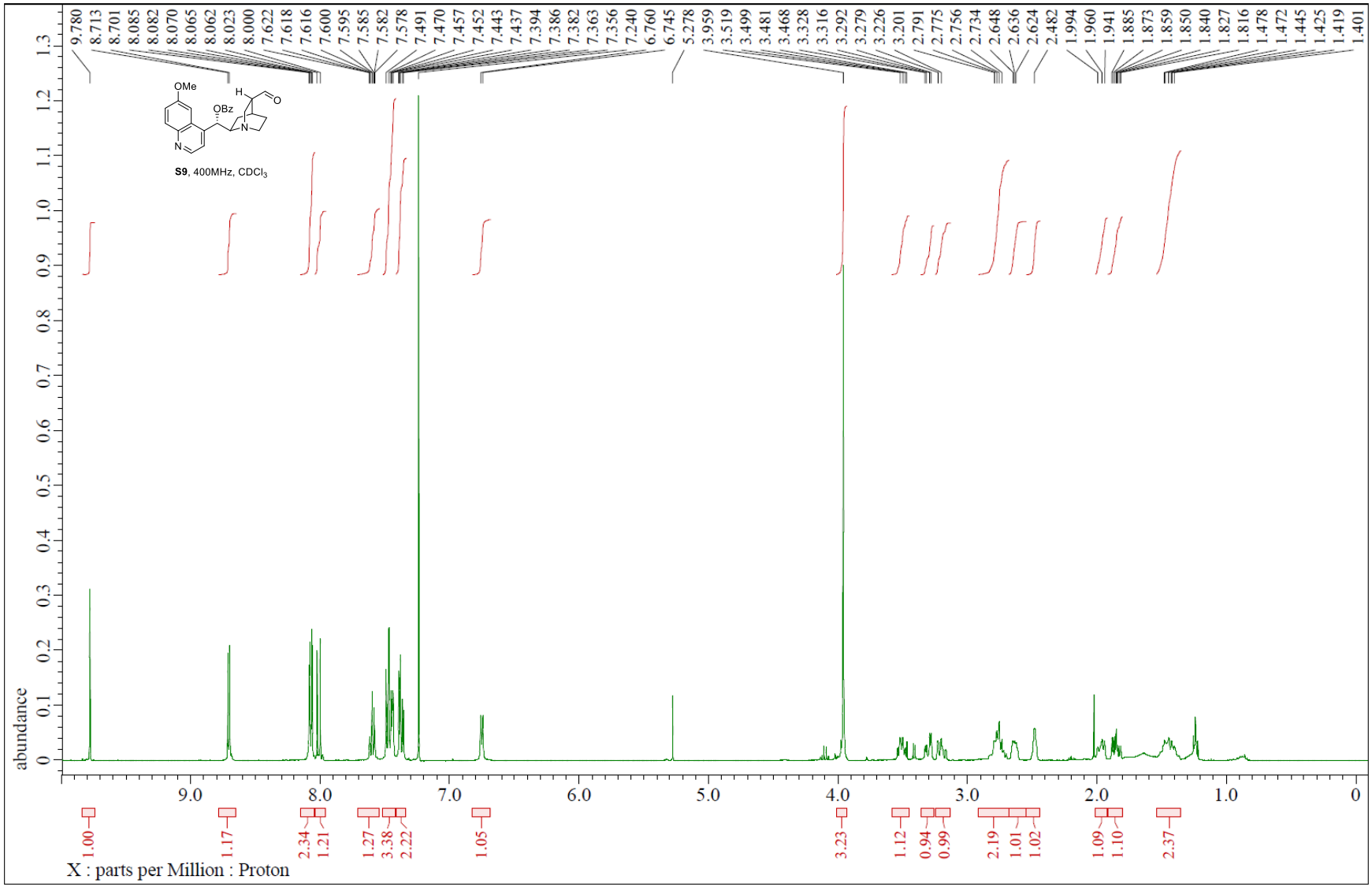
[1]H-NMR of compound **S8**



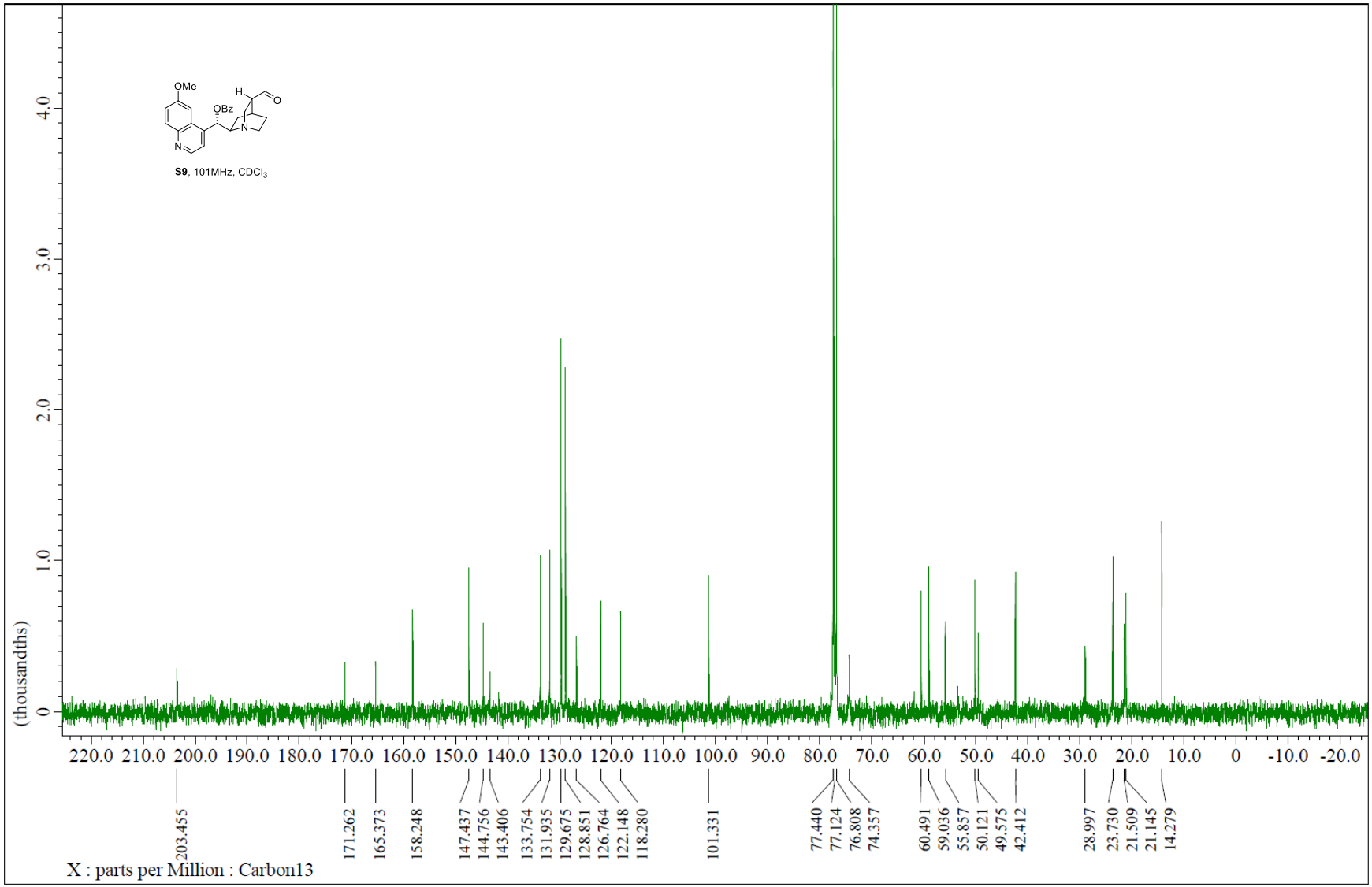
^{13}C-NMR of compound **S8**



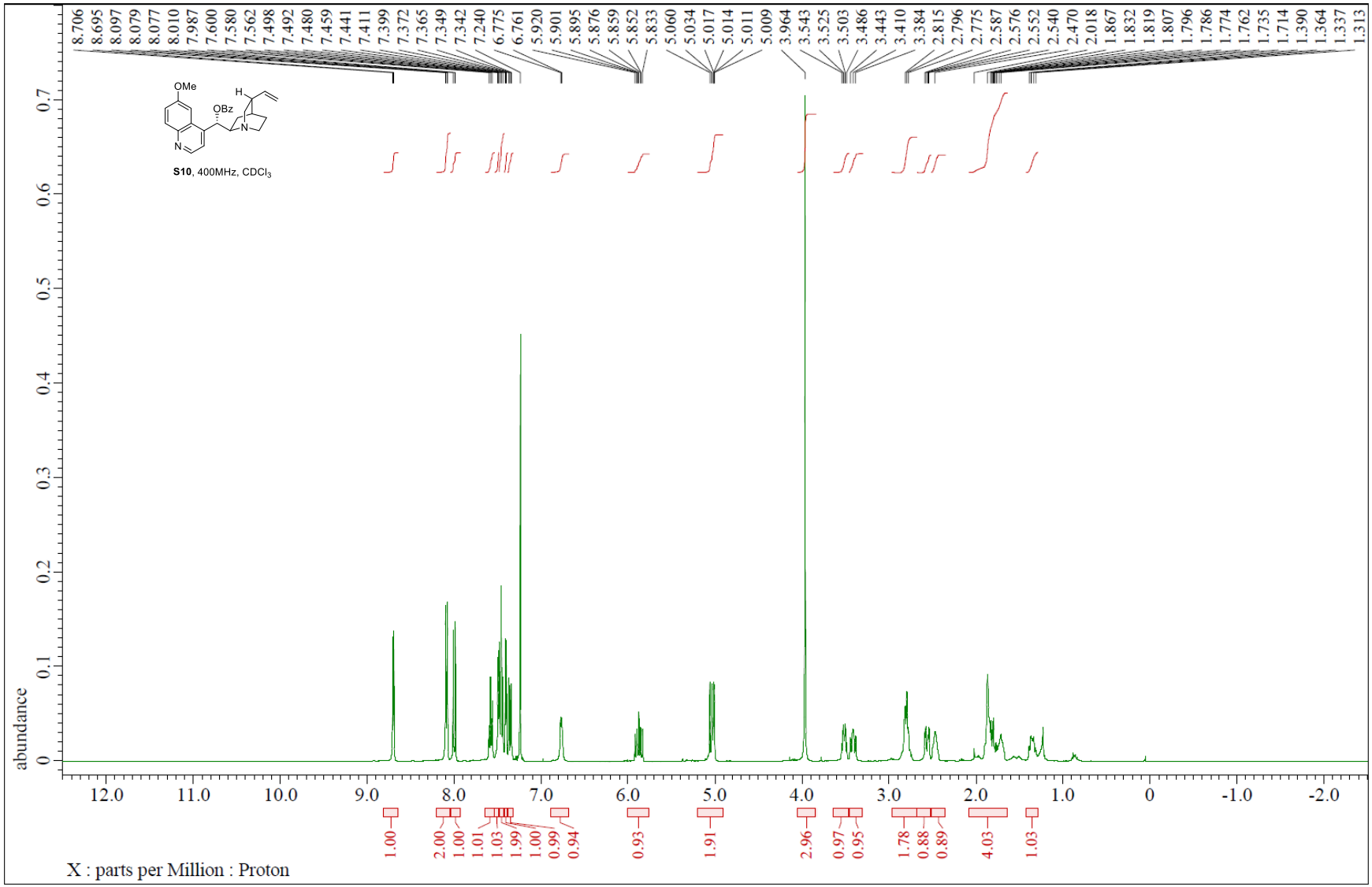
[1]H-NMR of compound **S9**



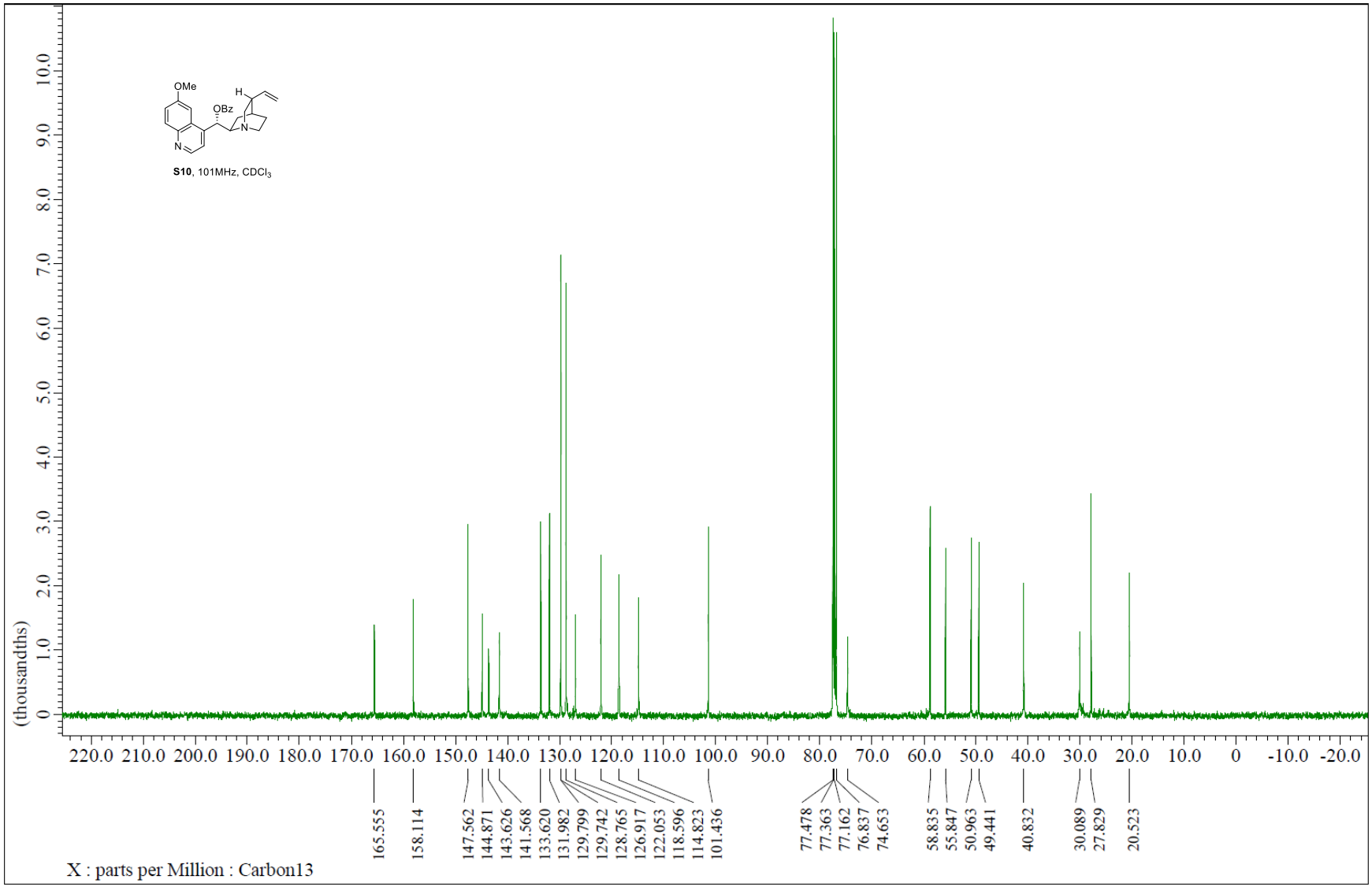
^{13}C-NMR of compound **S9**



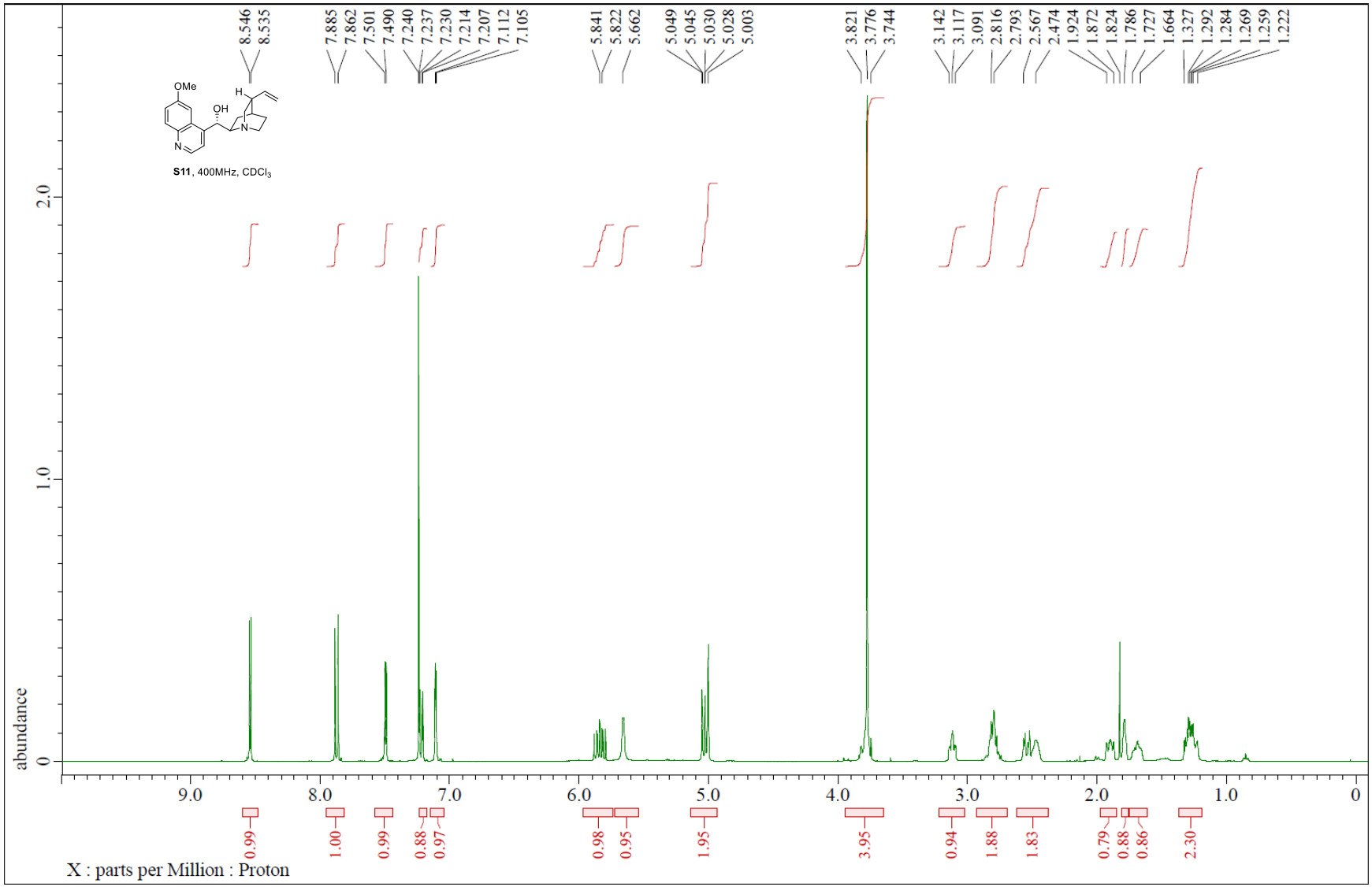
[1]H-NMR of compound **S10**



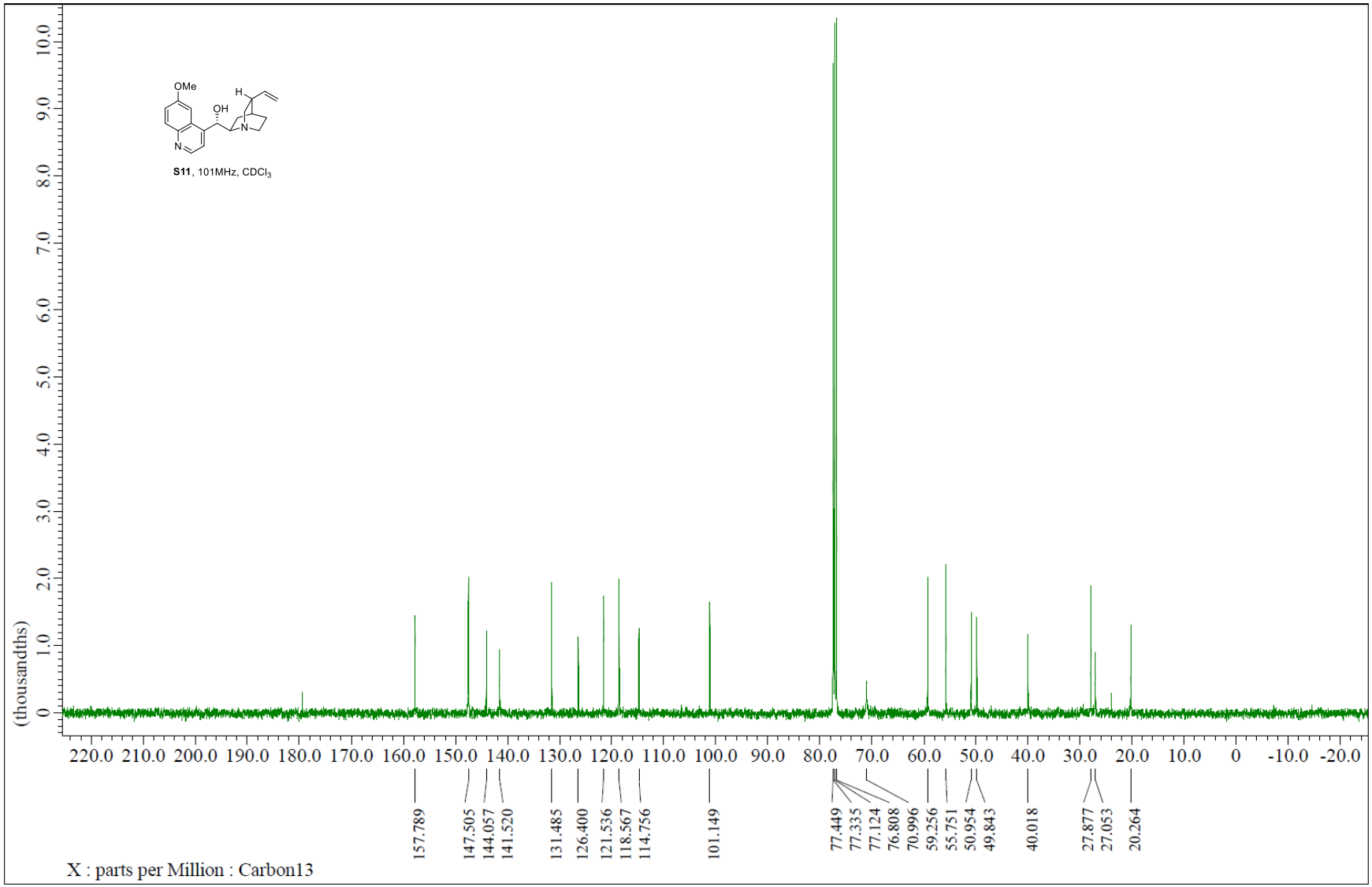
^{13}C-NMR of compound **S10**



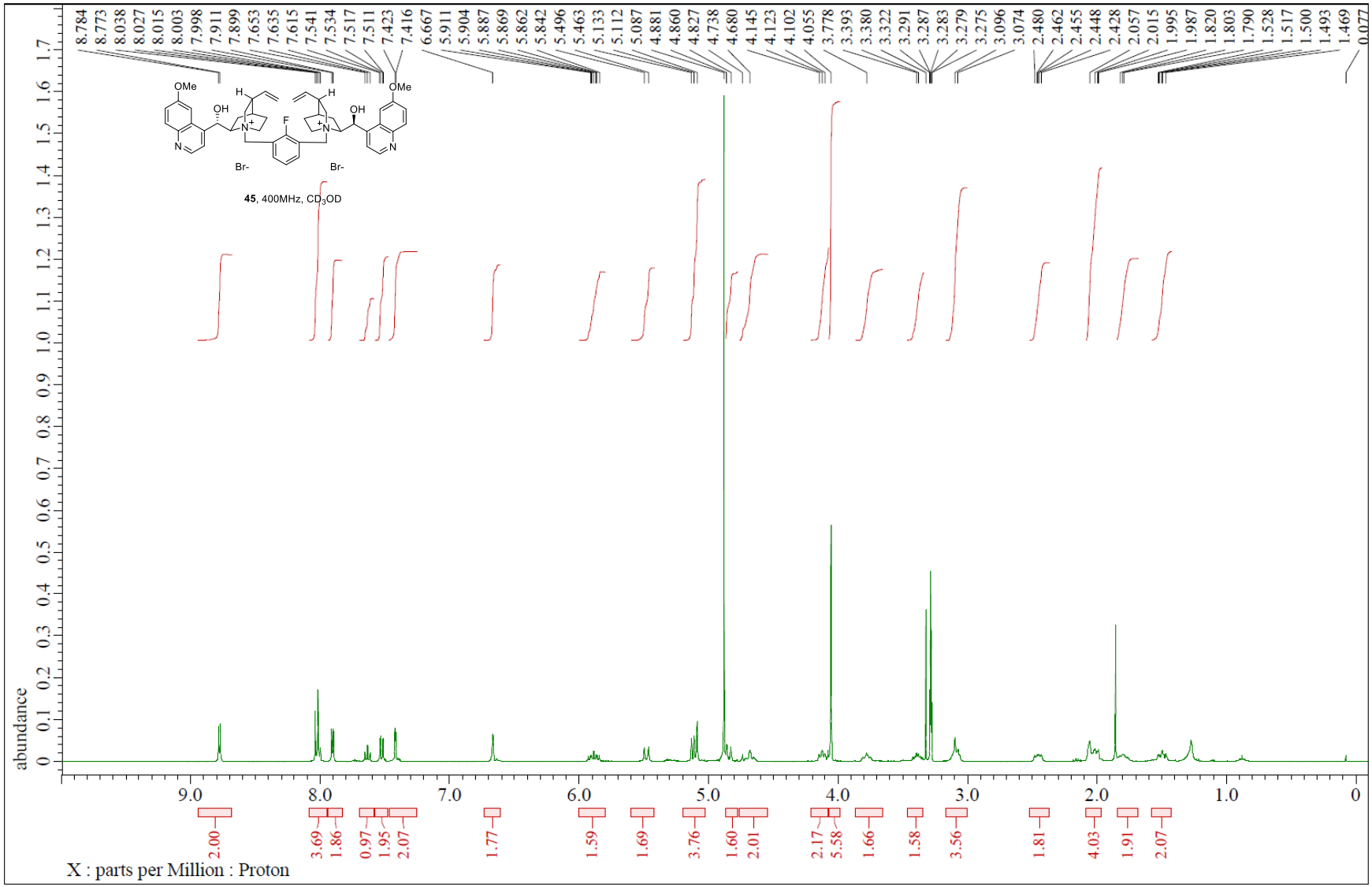
[1]H-NMR of compound **S11**



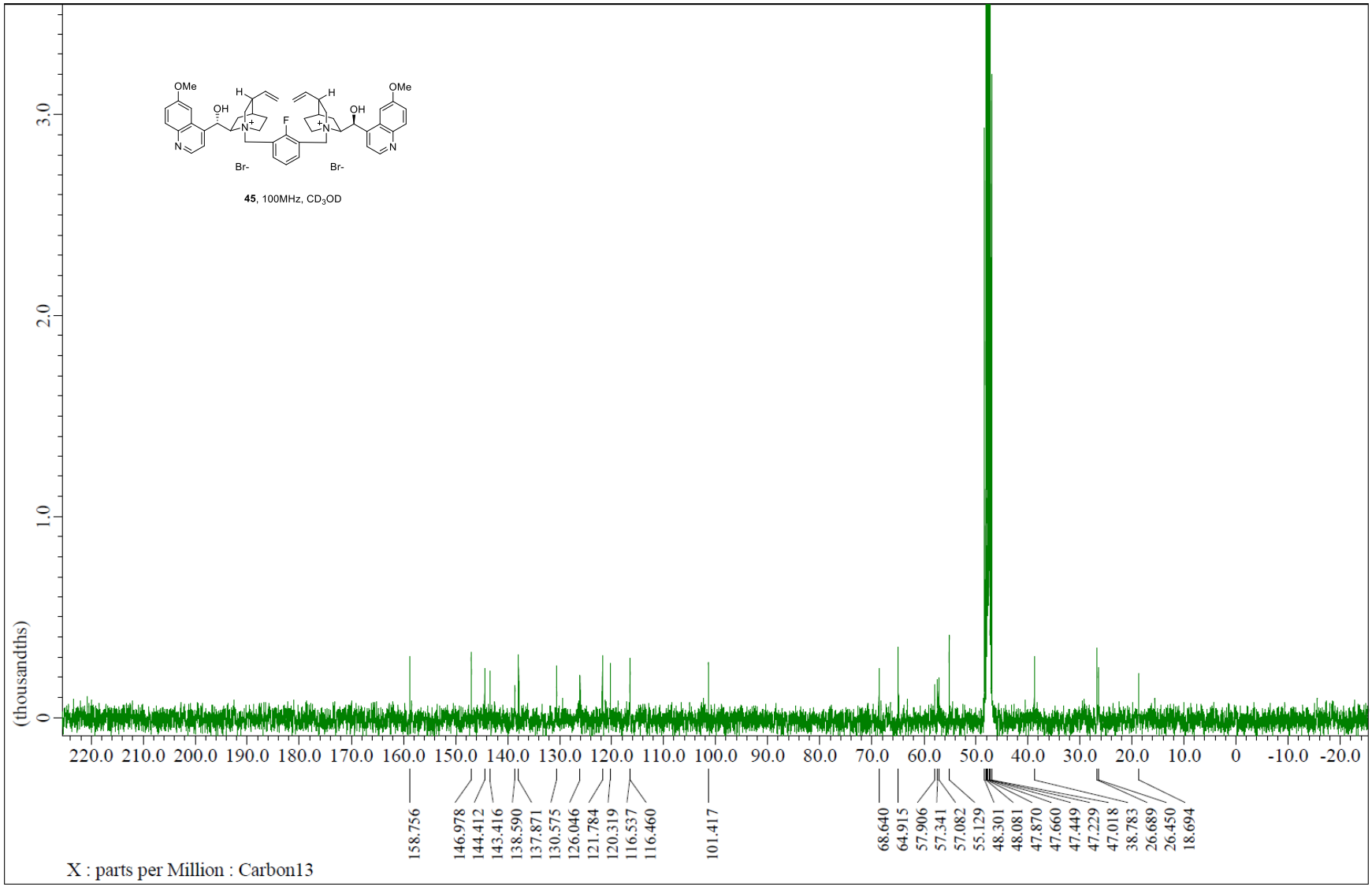
^{13}C-NMR of compound **S11**



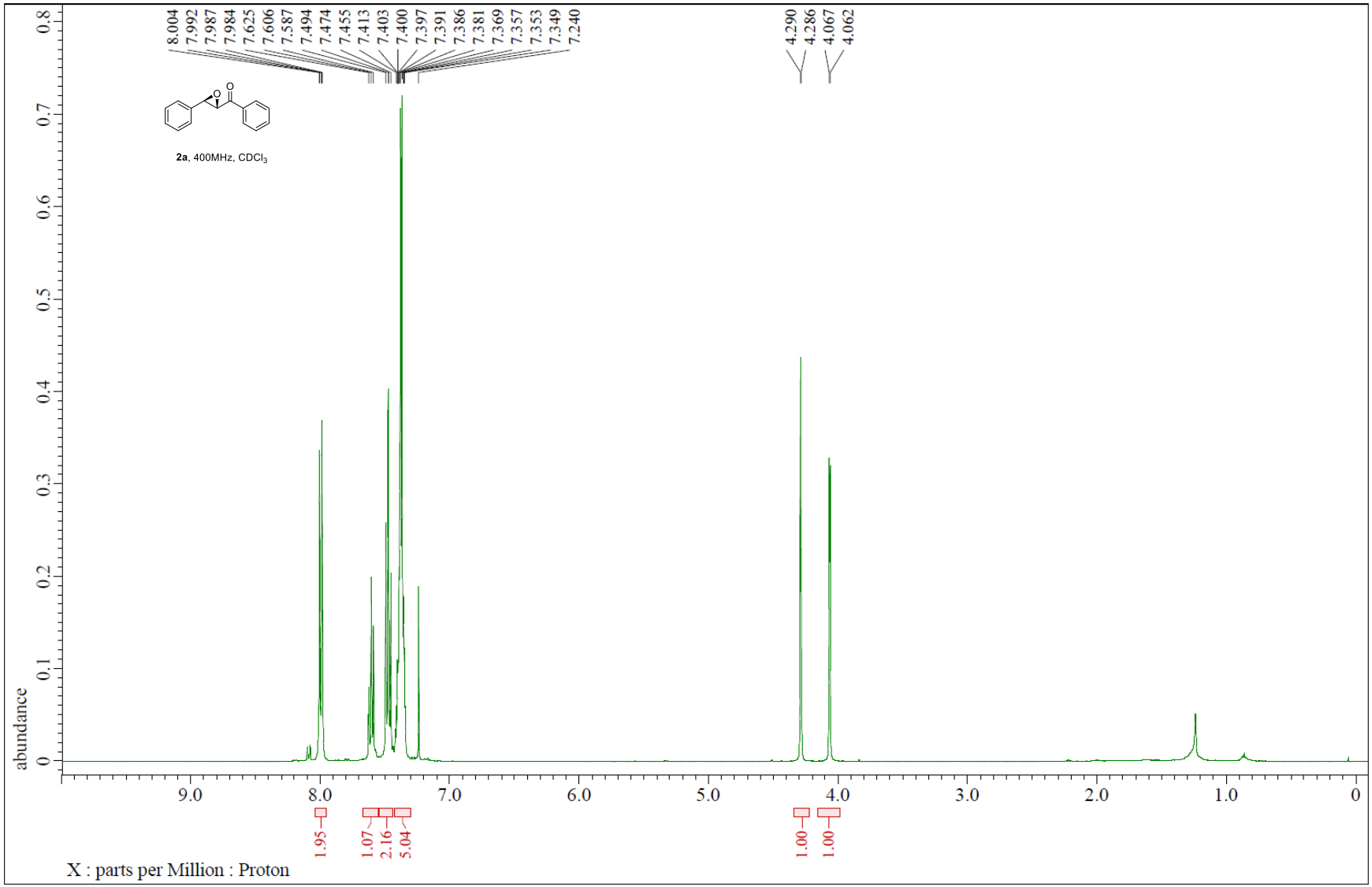
[1]H-NMR of compound **45**



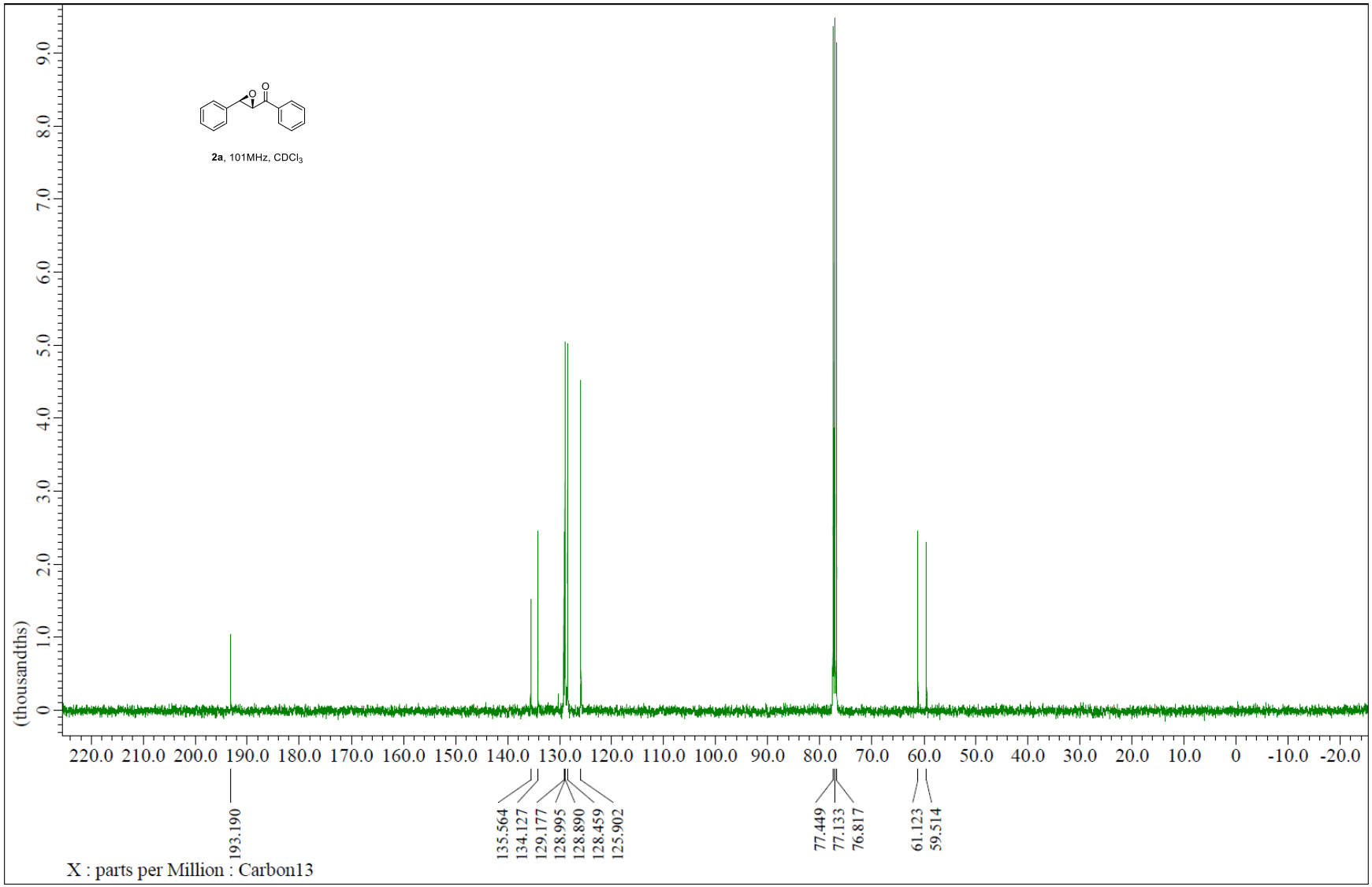
^{13}C-NMR of compound **45**



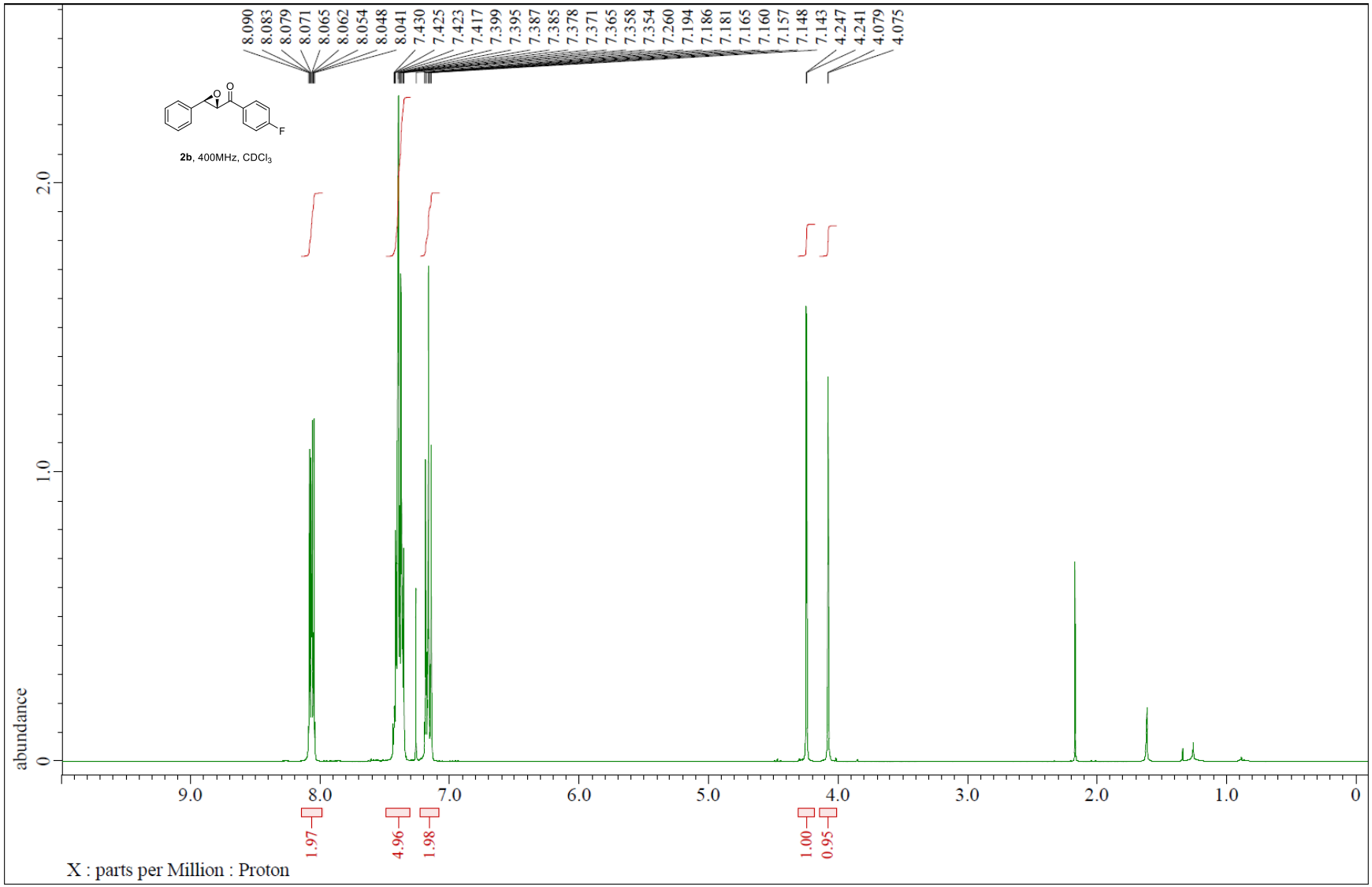
[1]H-NMR of compound **2a**



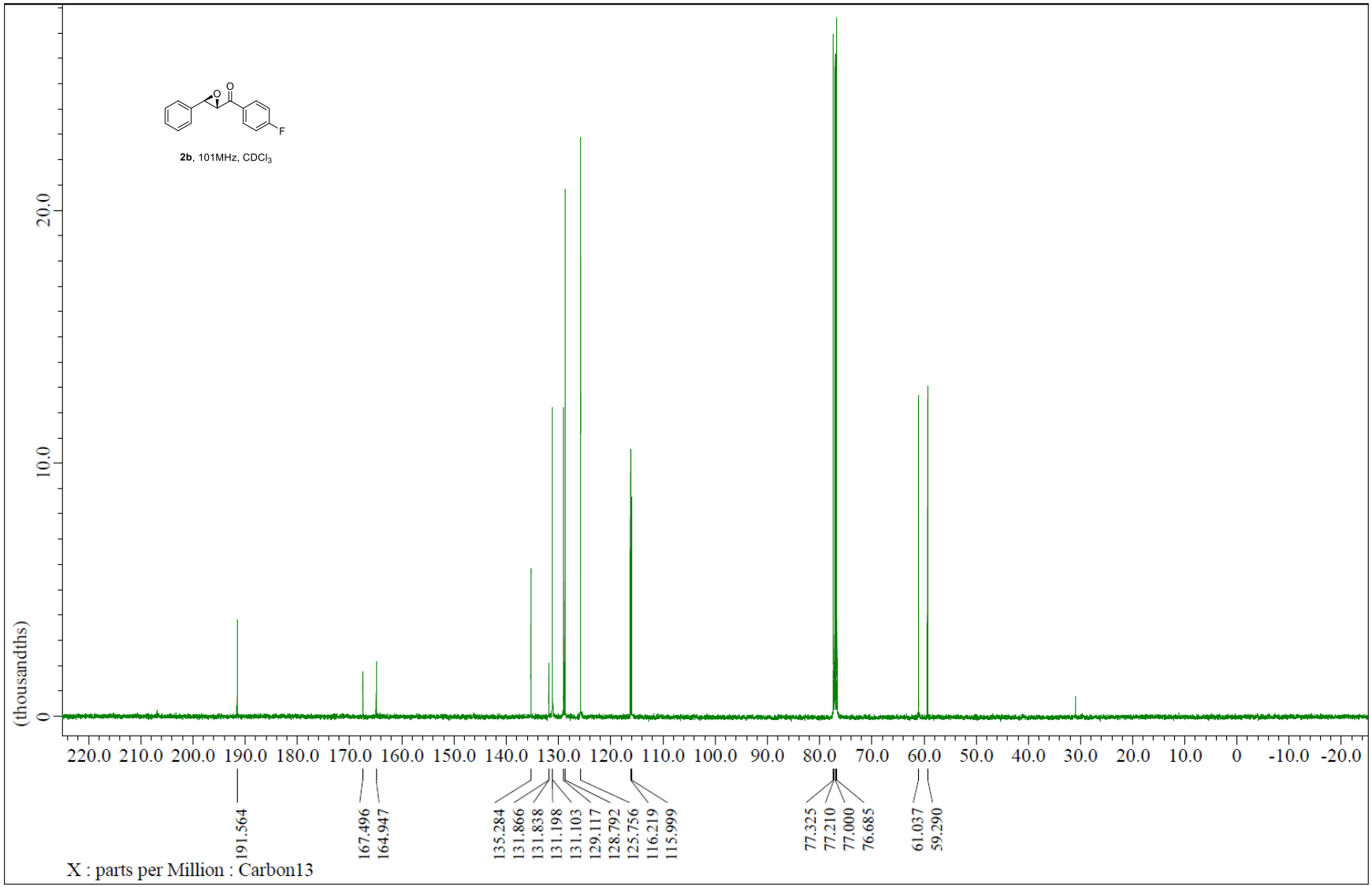
^{13}C-NMR of compound **2a**



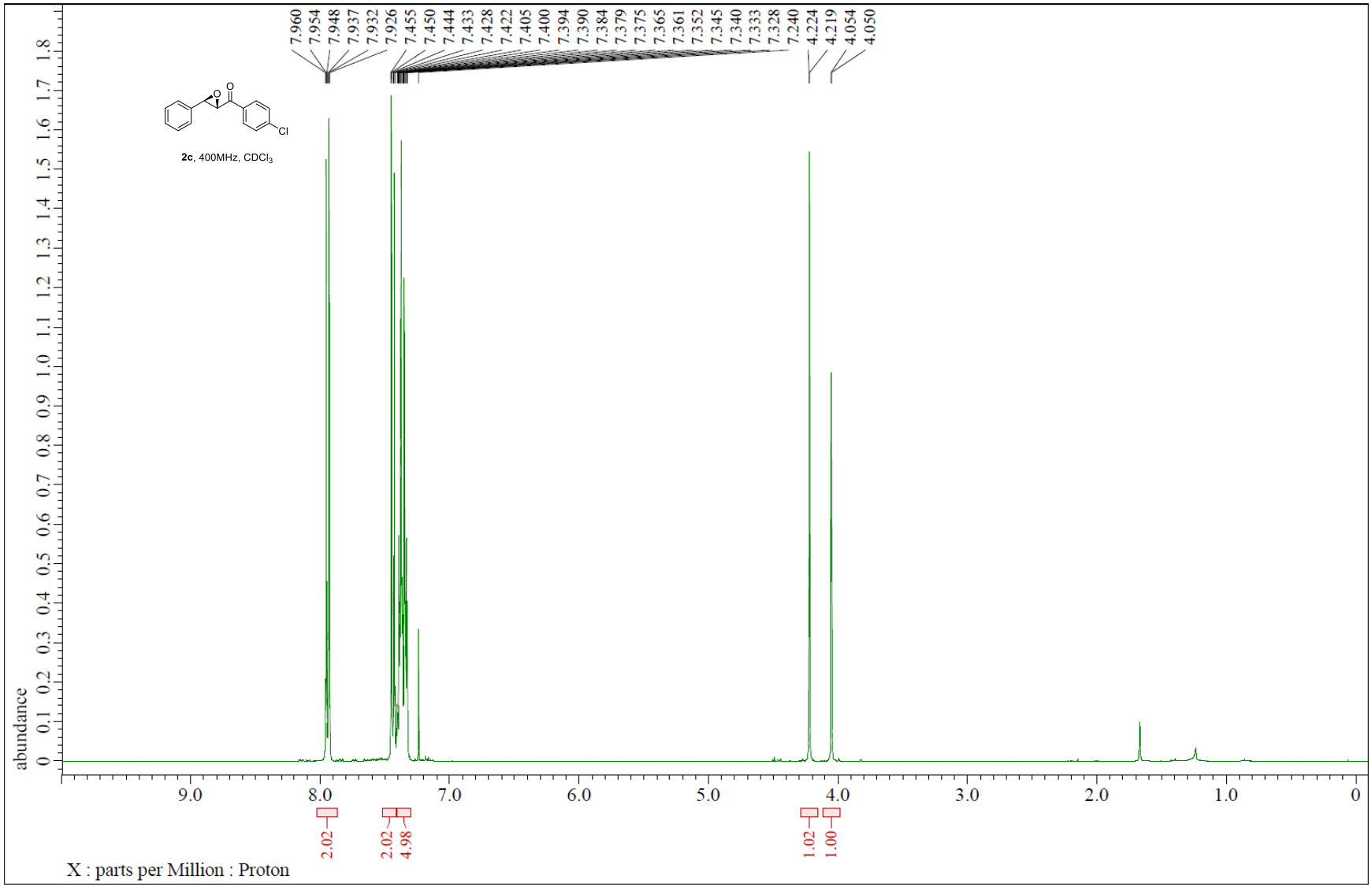
[1]H-NMR of compound **2b**



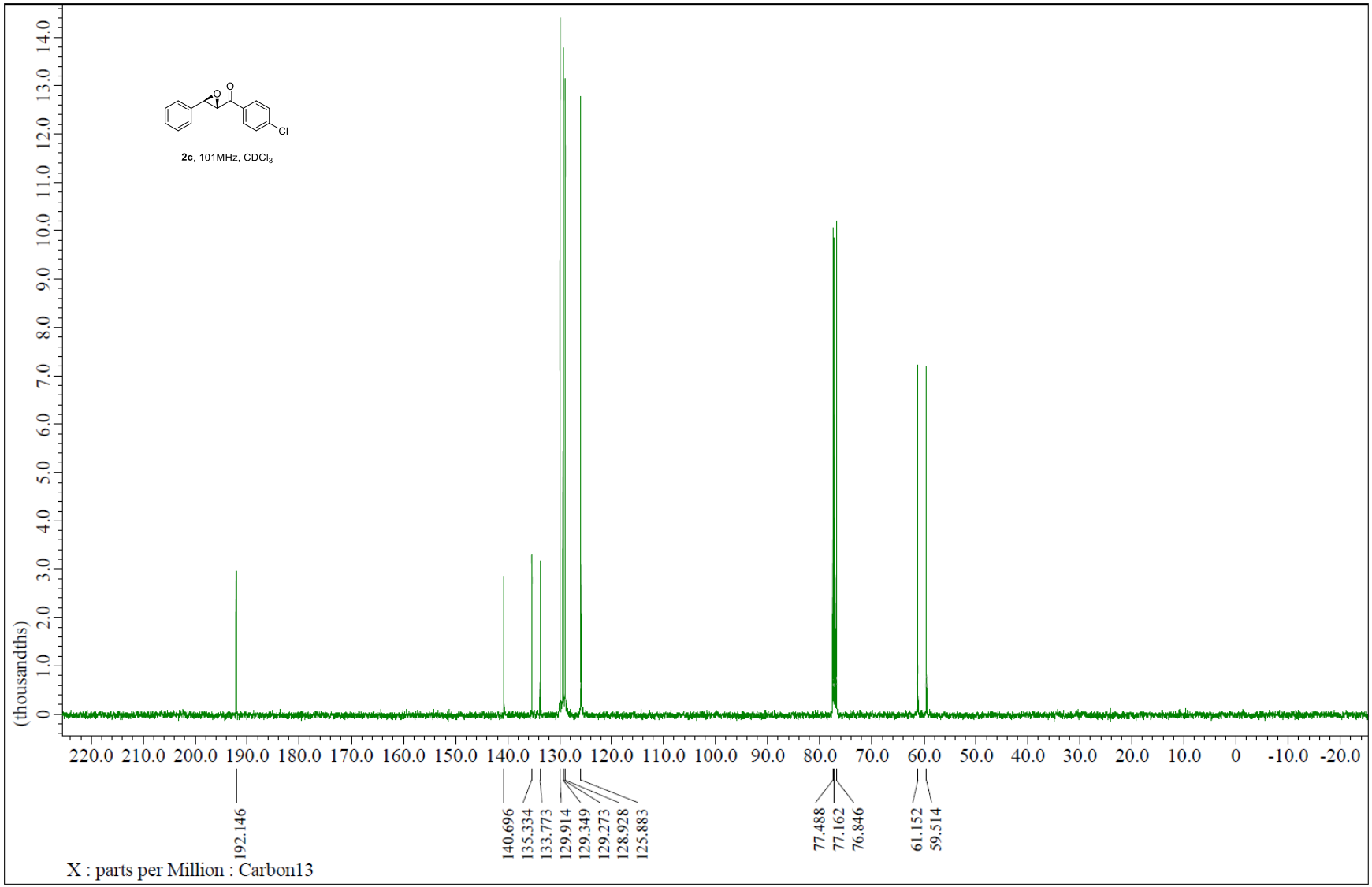
^{13}C-NMR of compound **2b**



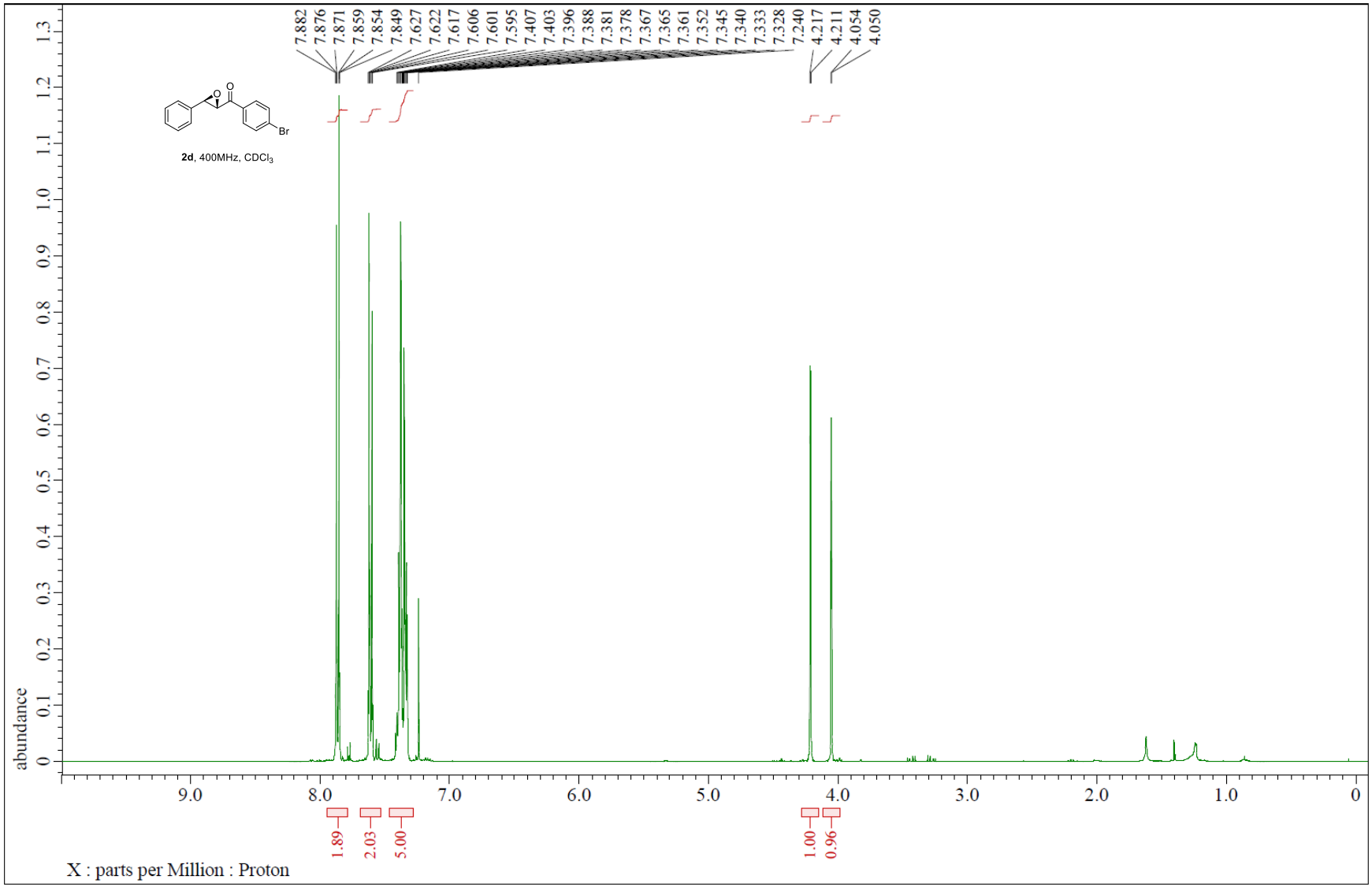
[1]H-NMR of compound **2c**



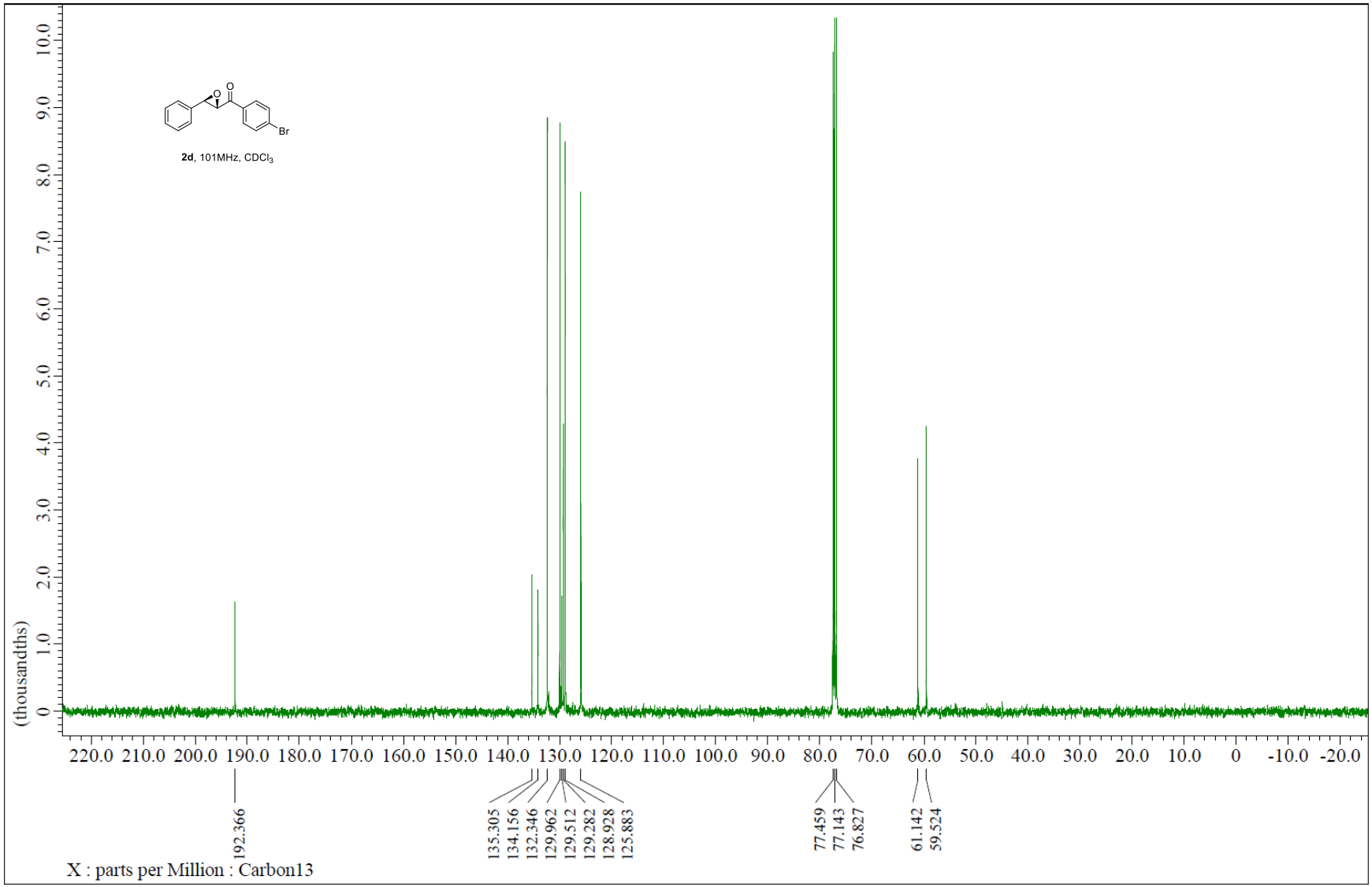
^{13}C-NMR of compound **2c**



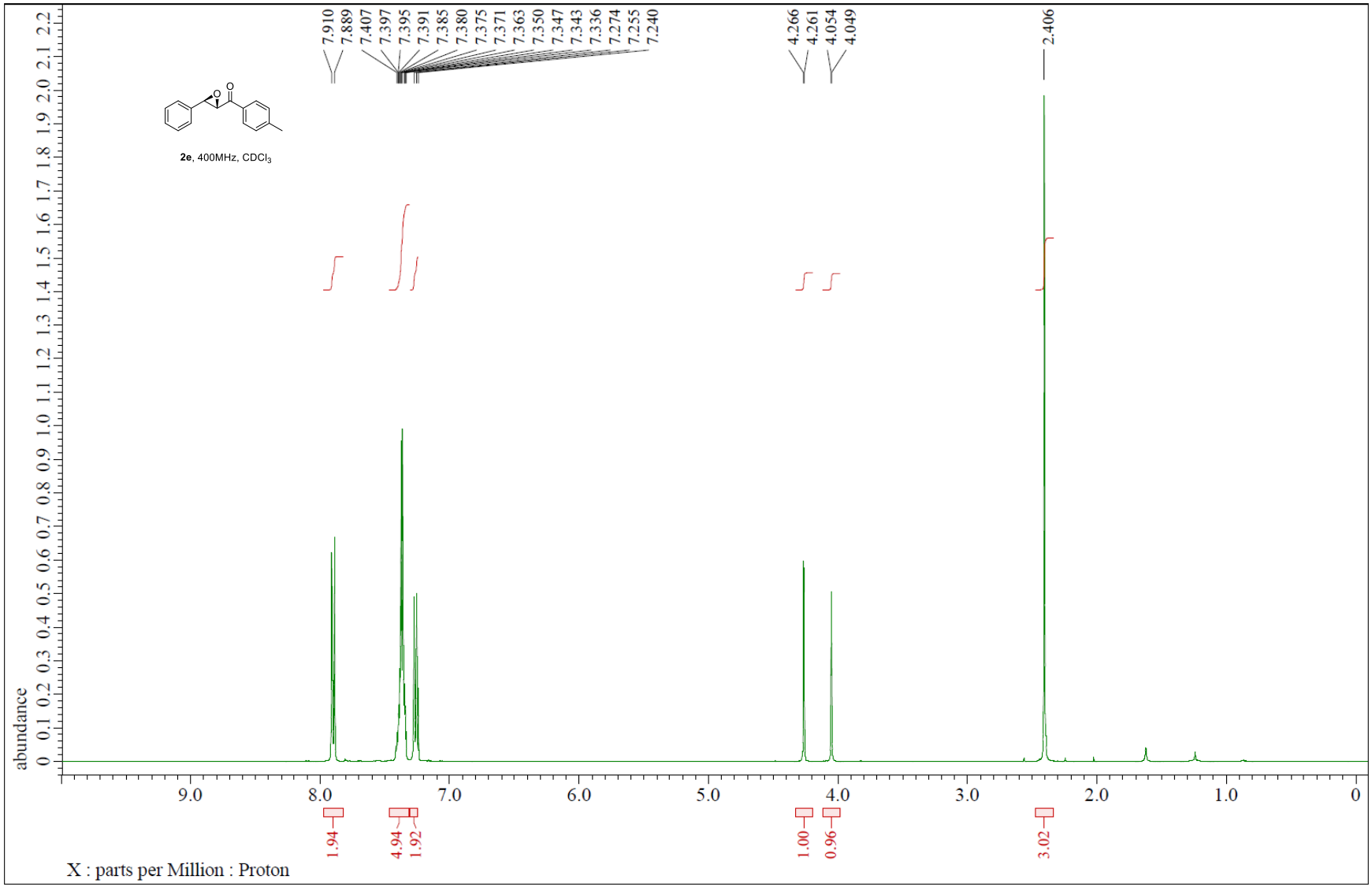
[1]H-NMR of compound **2d**



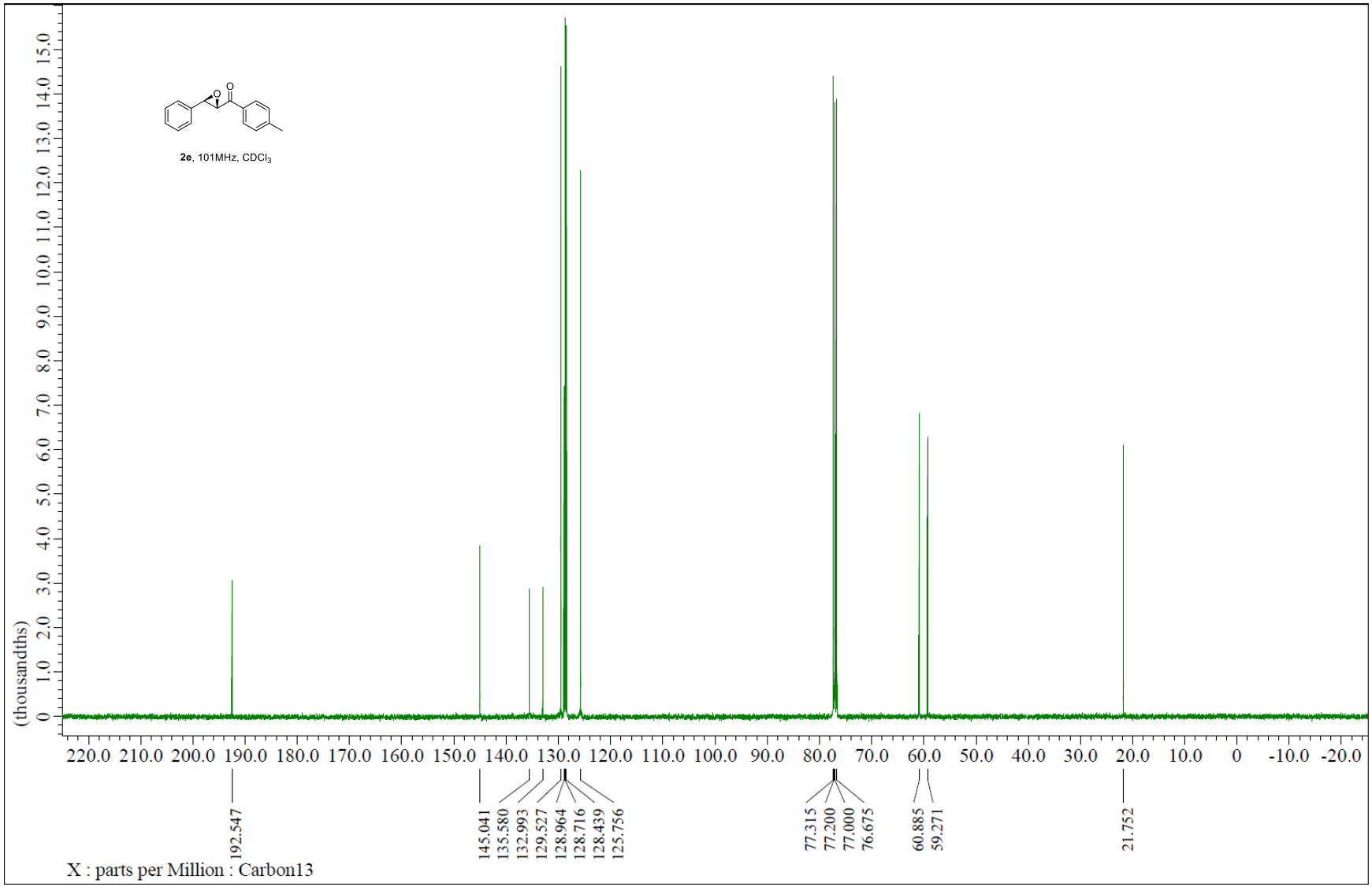
^{13}C-NMR of compound **2d**



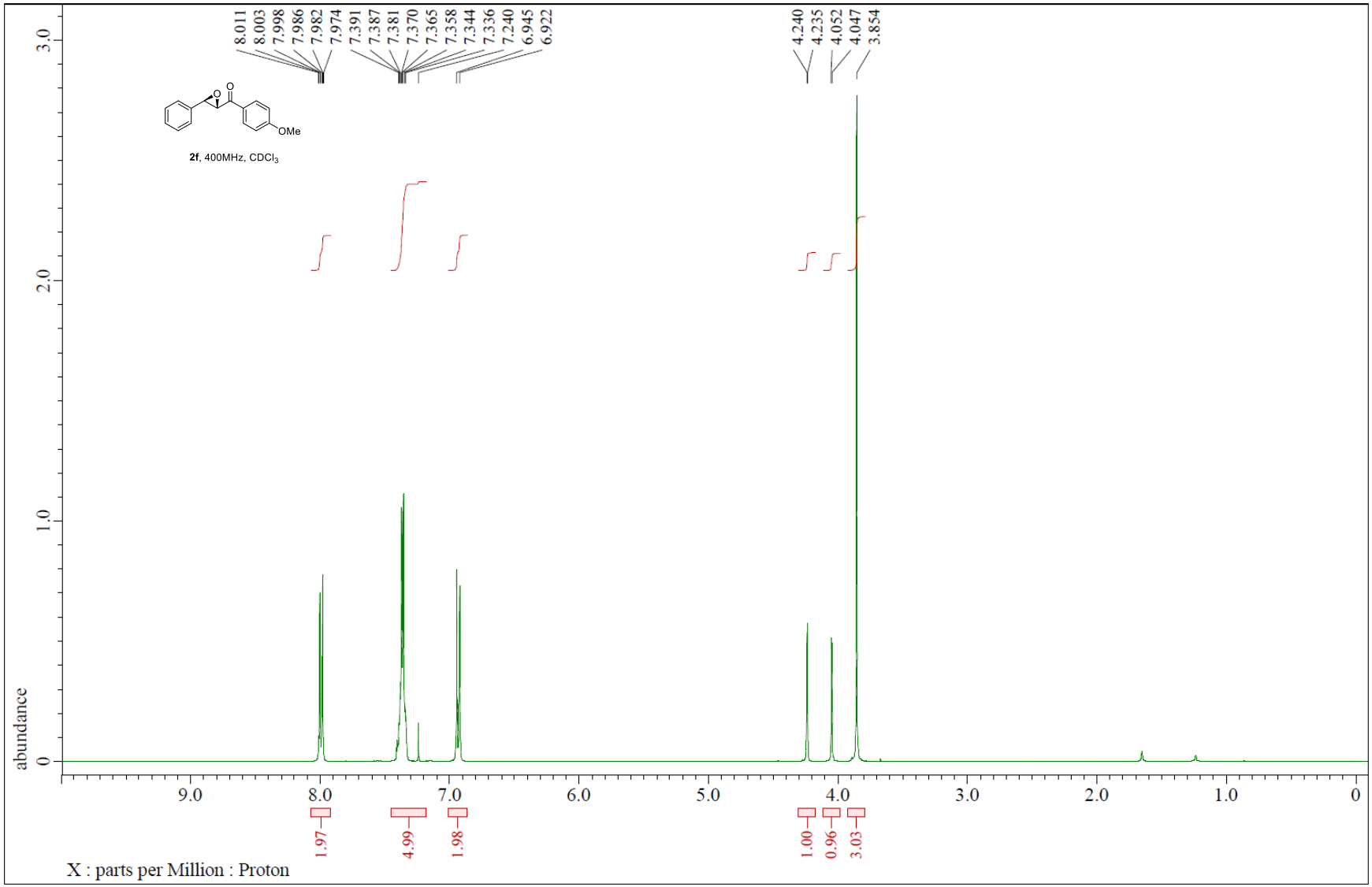
[1]H-NMR of compound **2e**



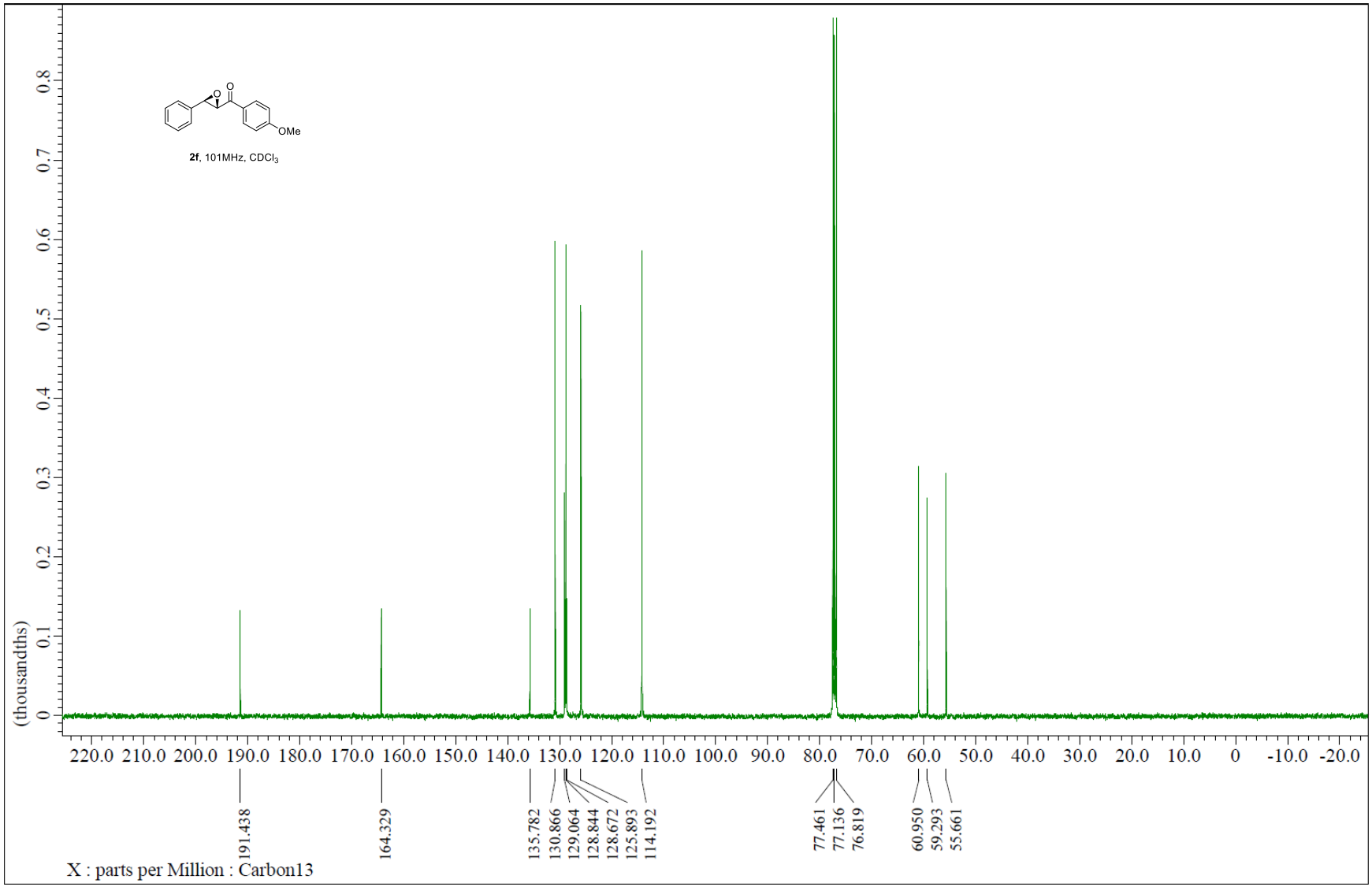
^{13}C-NMR of compound **2e**



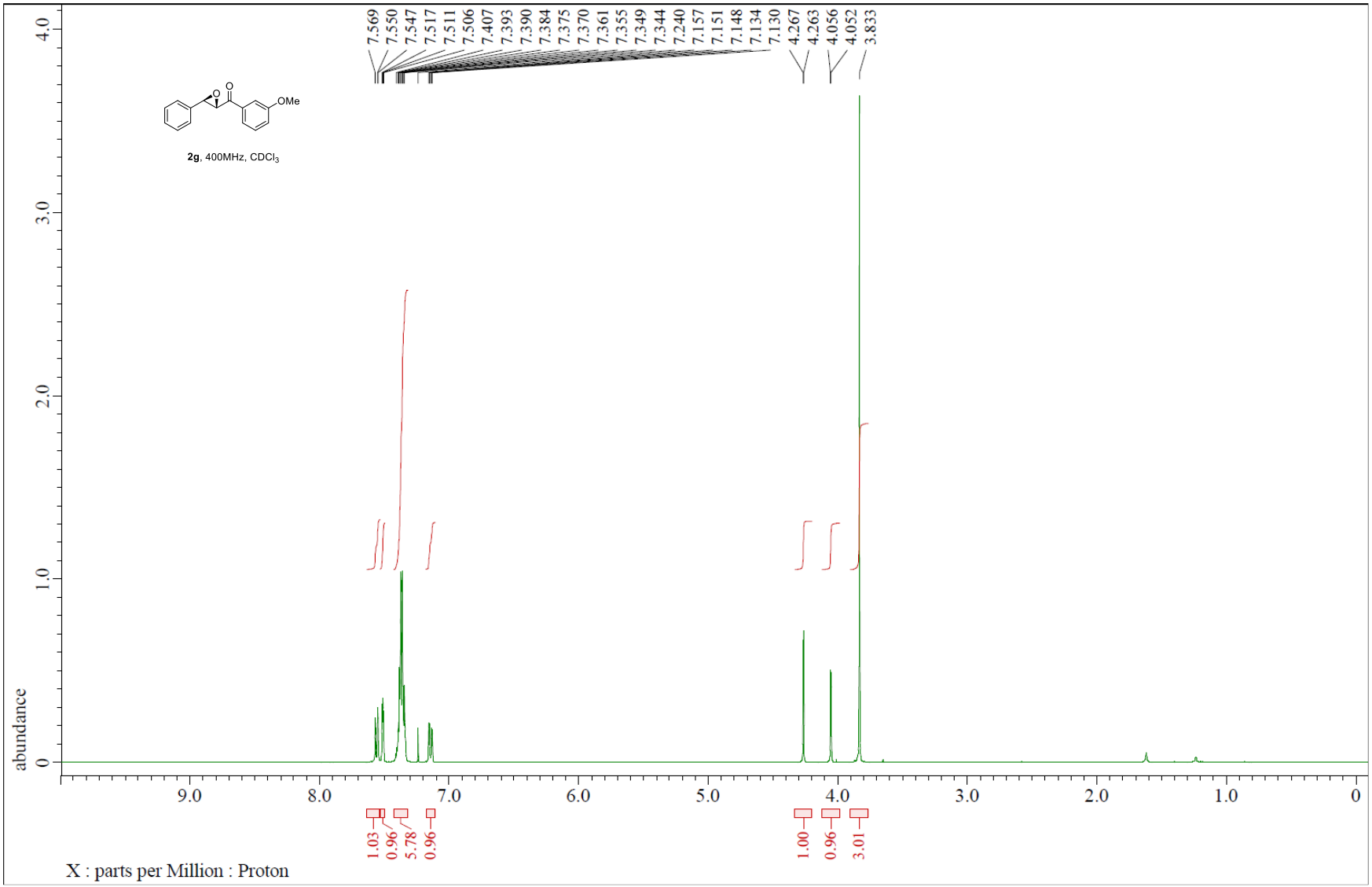
[1]H-NMR of compound **2f**



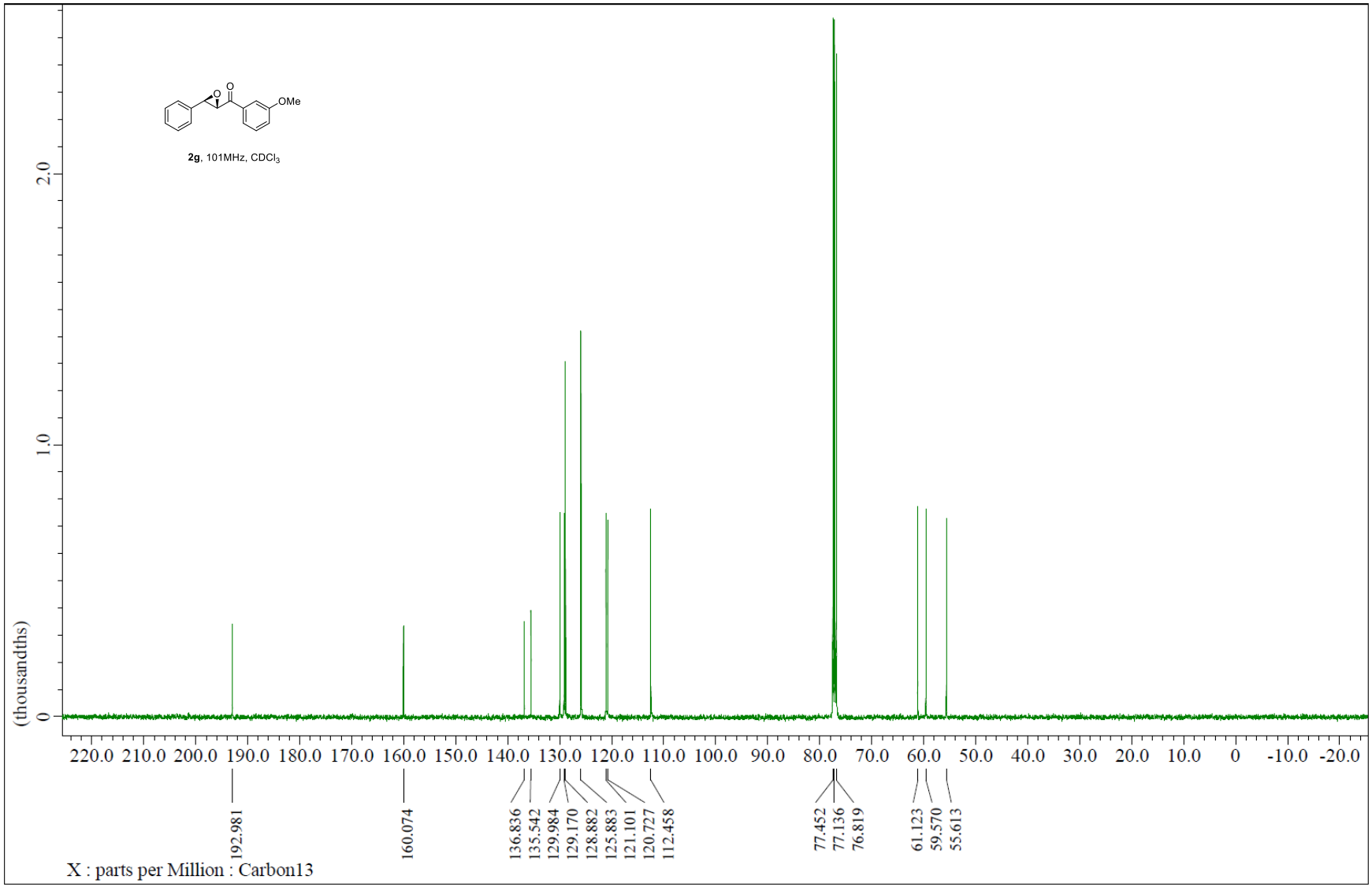
^{13}C-NMR of compound **2f**



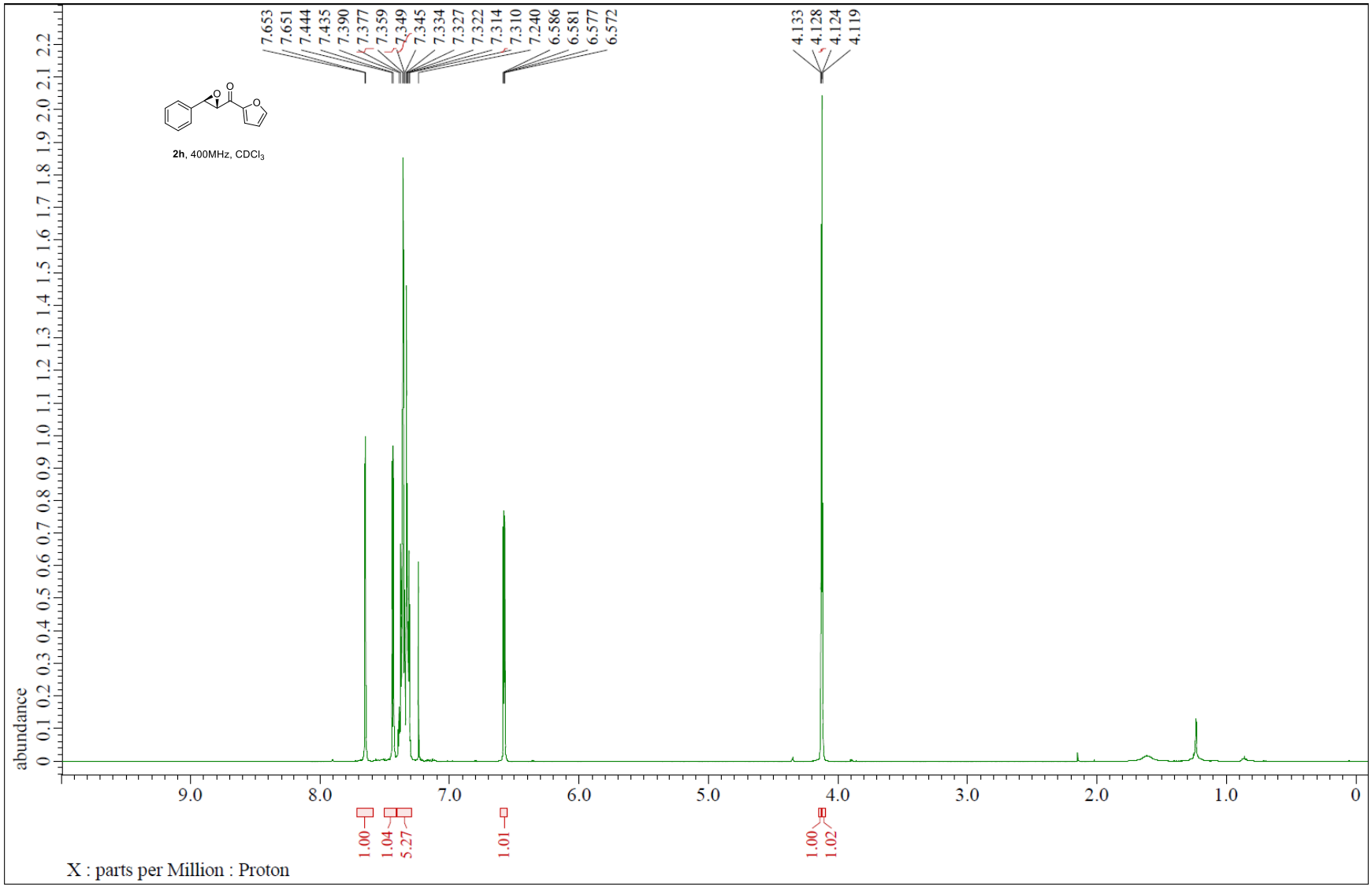
[1]H-NMR of compound **2g**



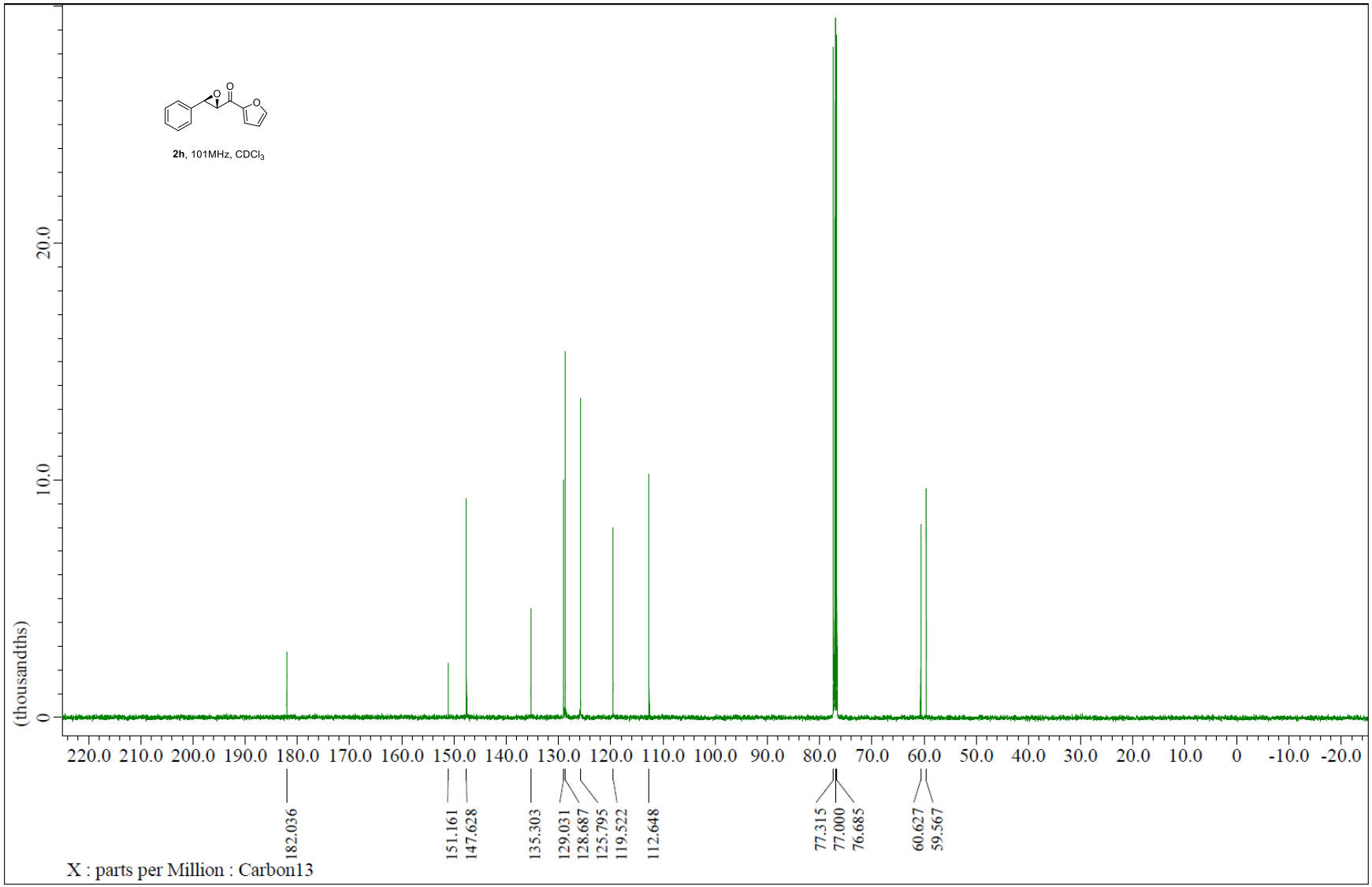
[1]H-NMR of compound **2g**



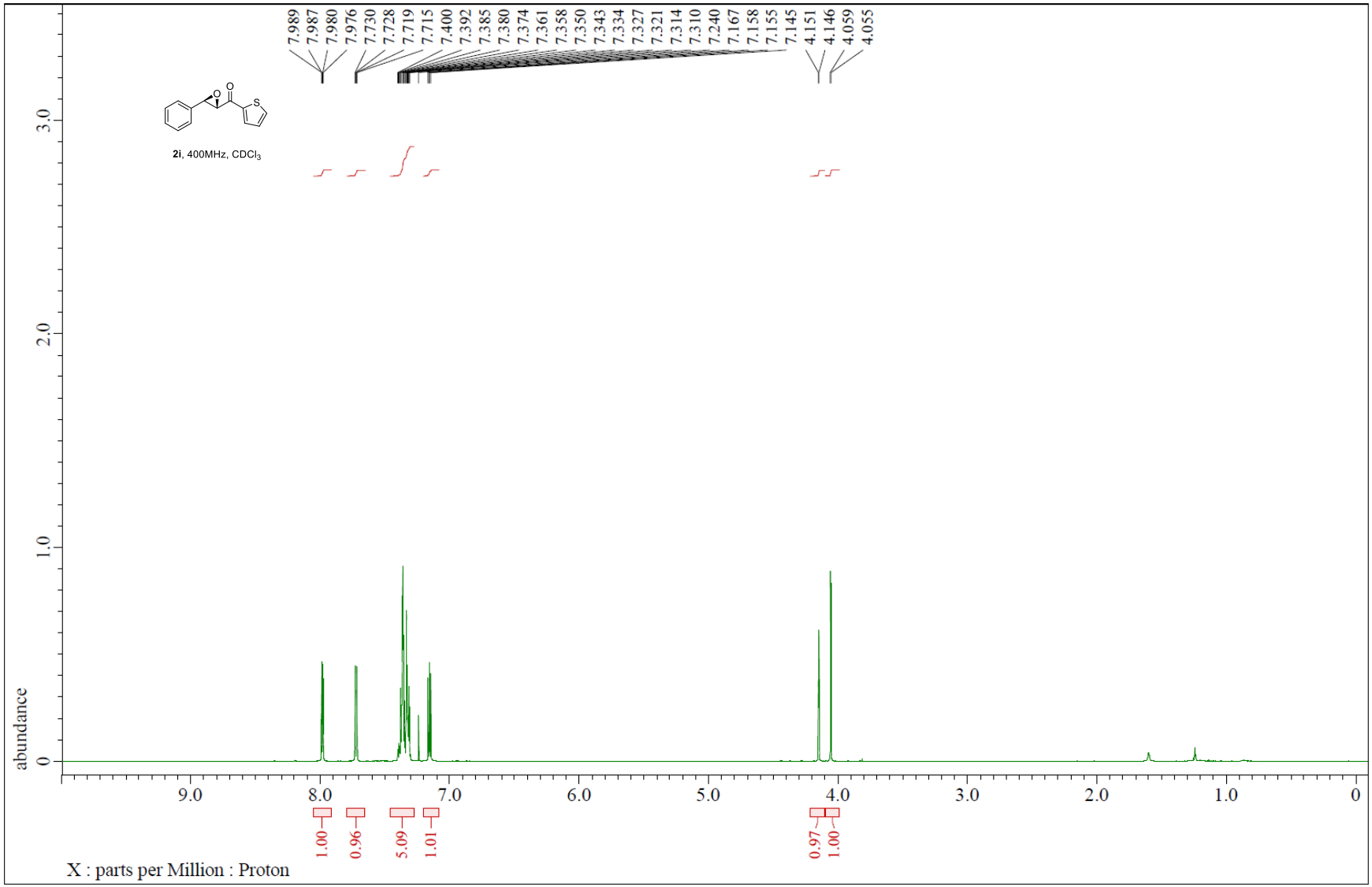
[1]H-NMR of compound **2h**



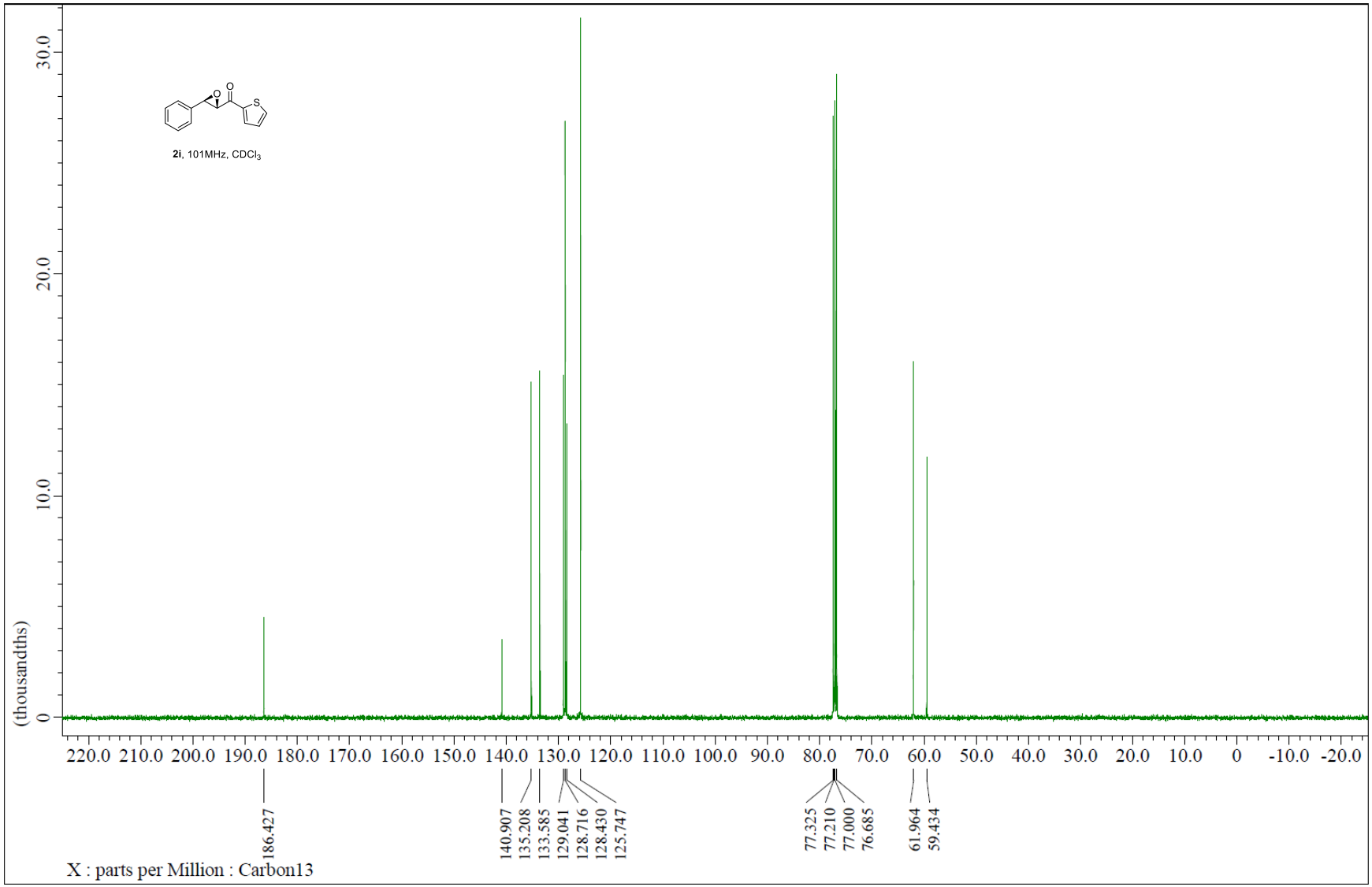
^{13}C-NMR of compound **2h**



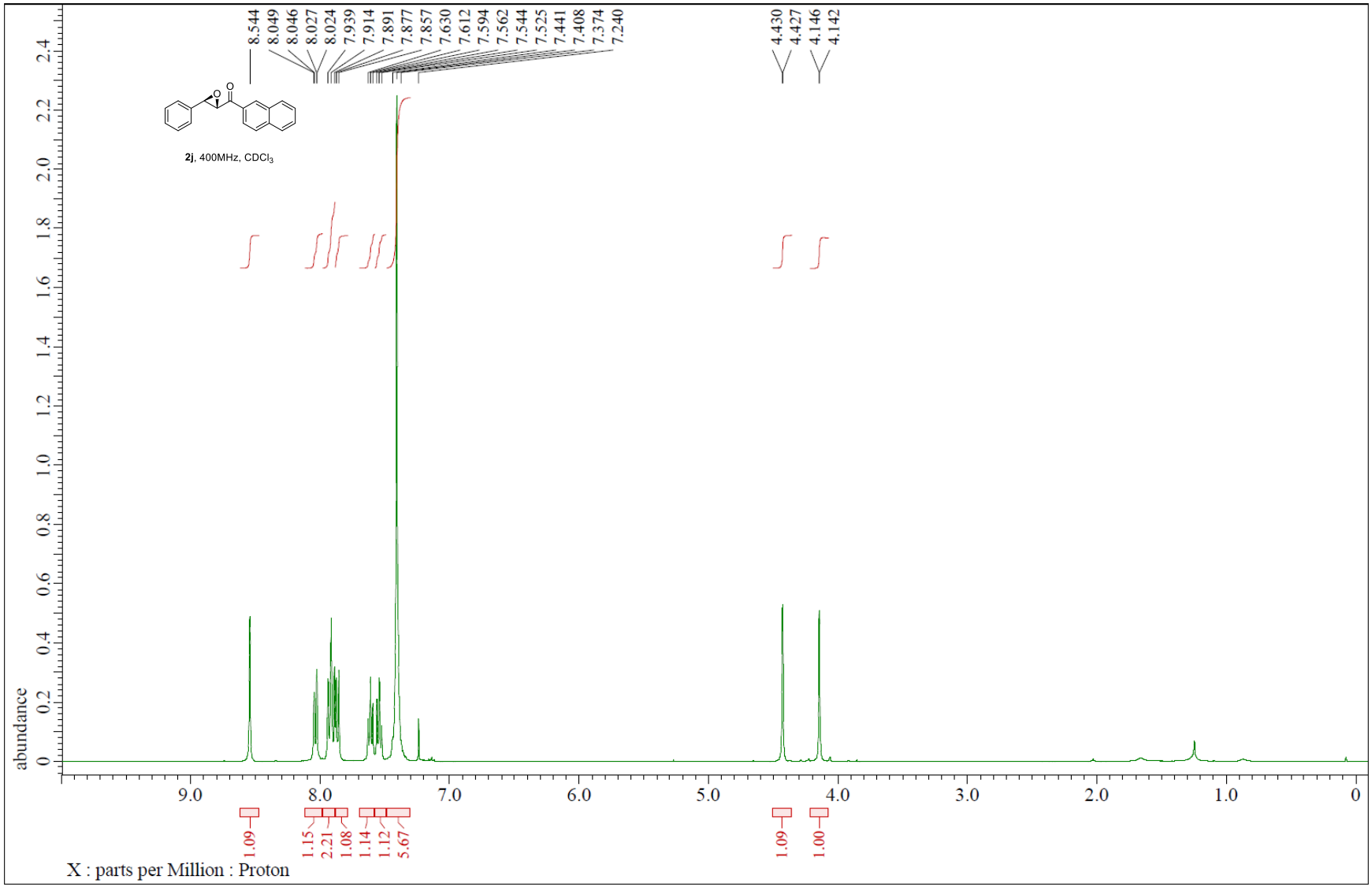
[1]H-NMR of compound **2i**



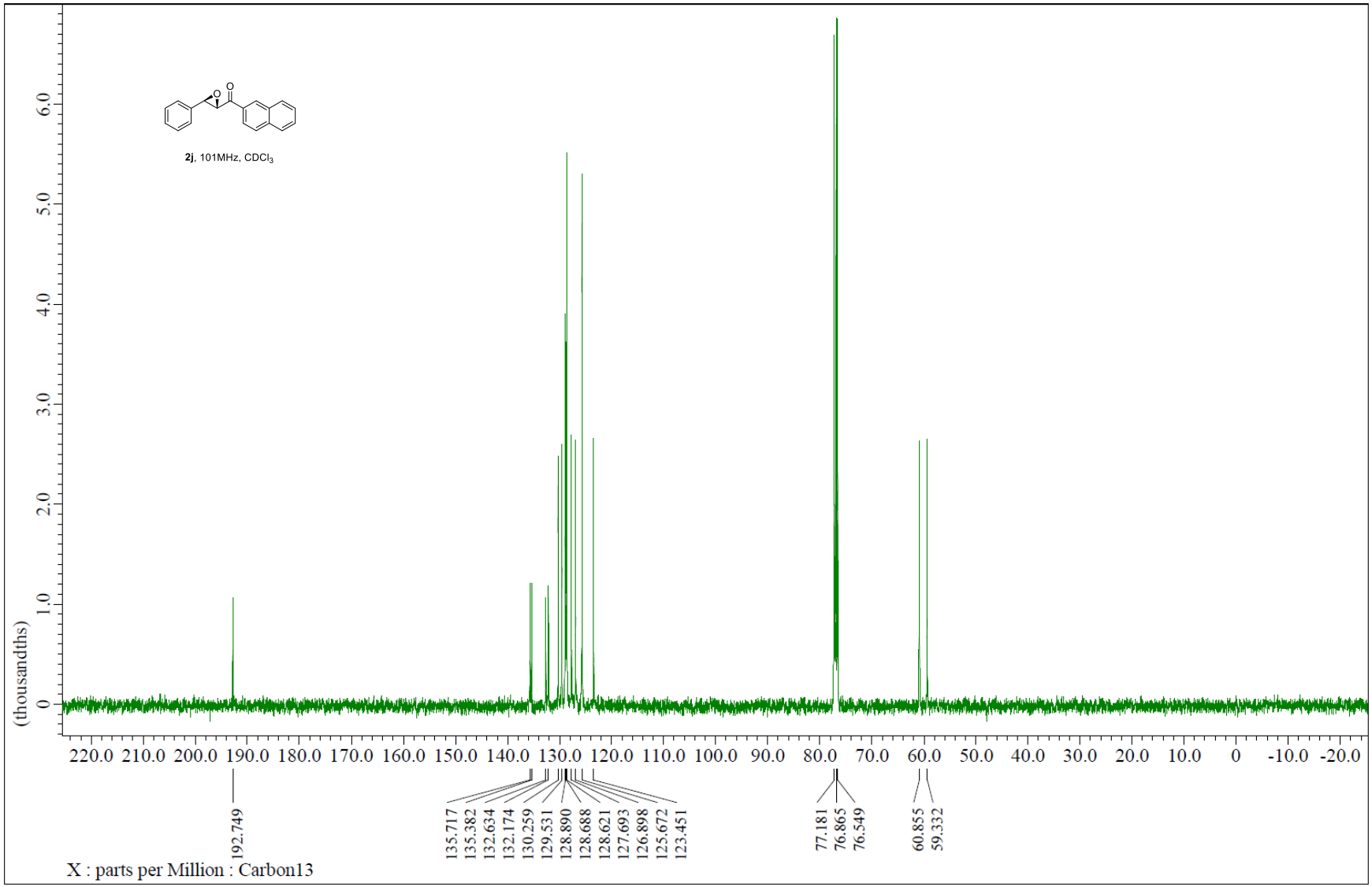
^{13}C-NMR of compound **2i**



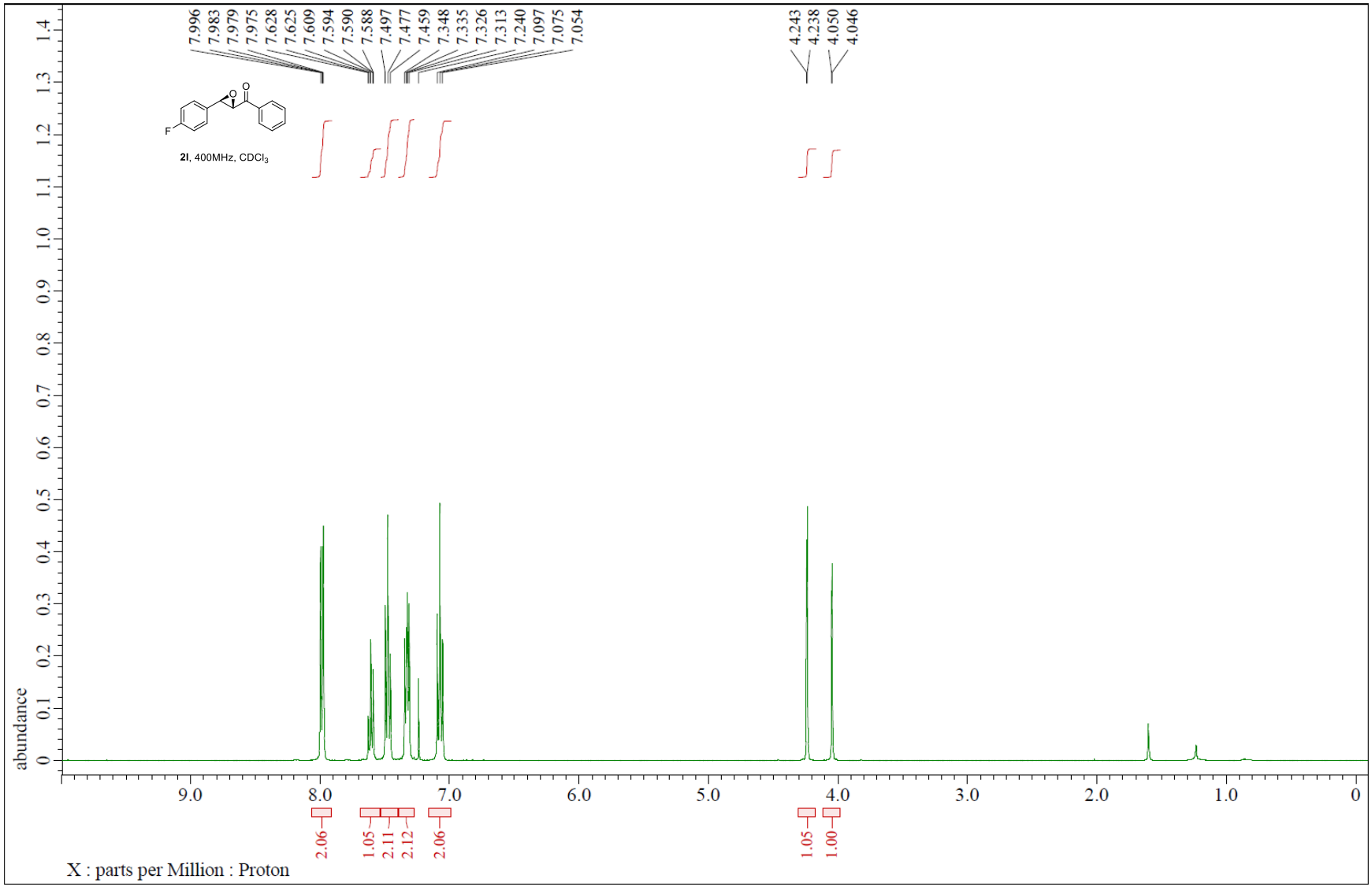
[1]H-NMR of compound **2j**



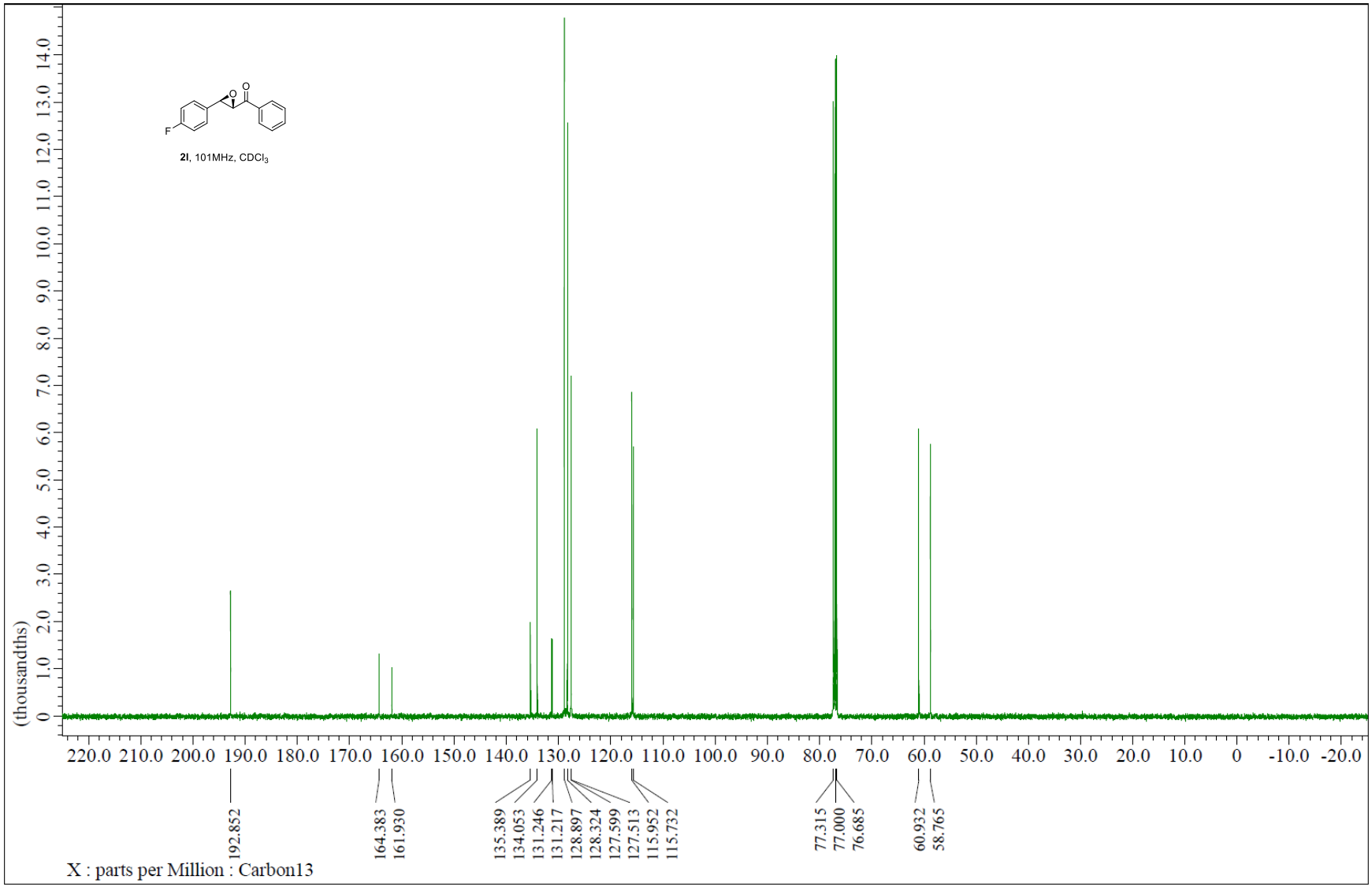
^{13}C-NMR of compound **2j**



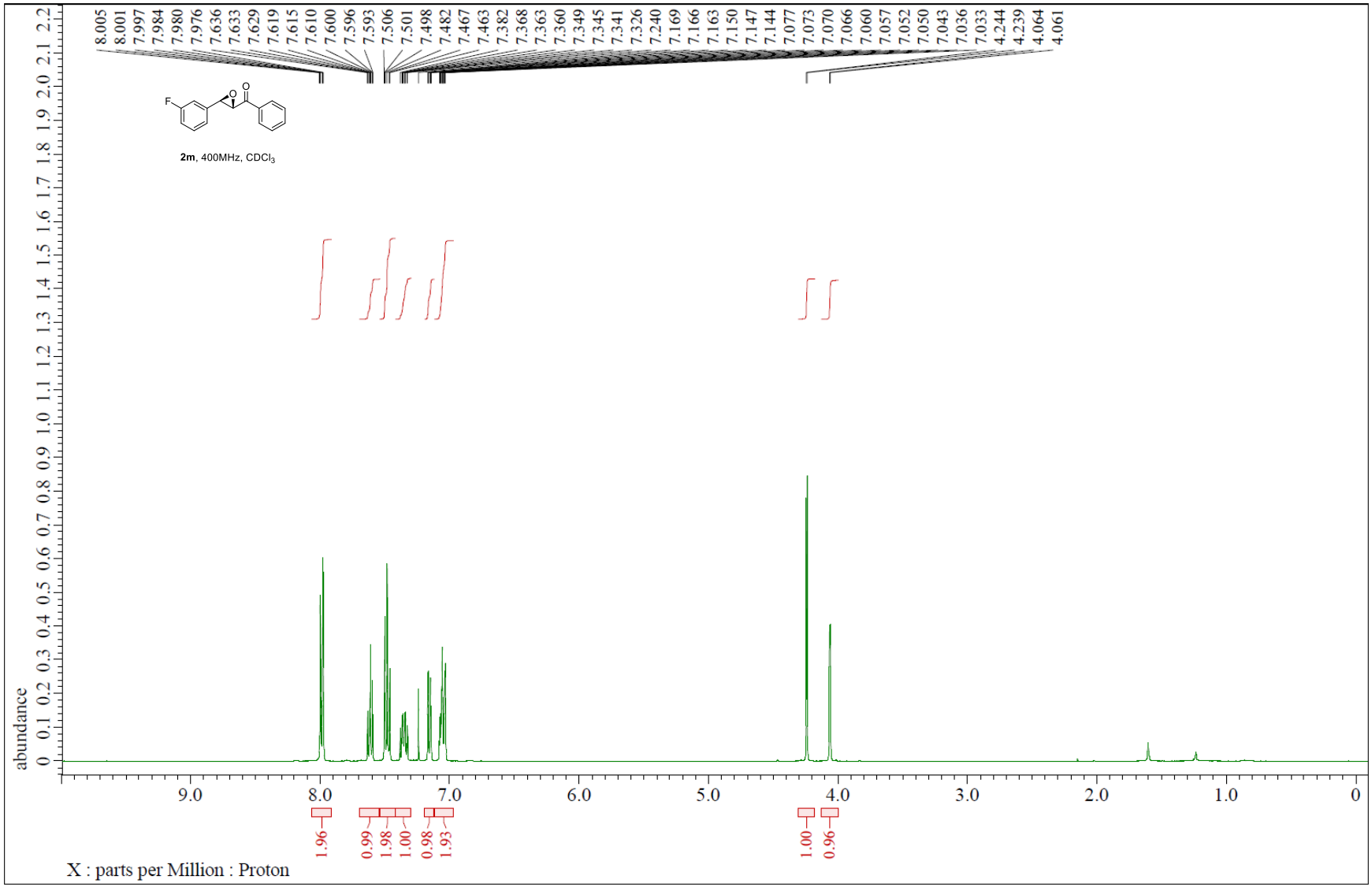
[1]H-NMR of compound **2l**



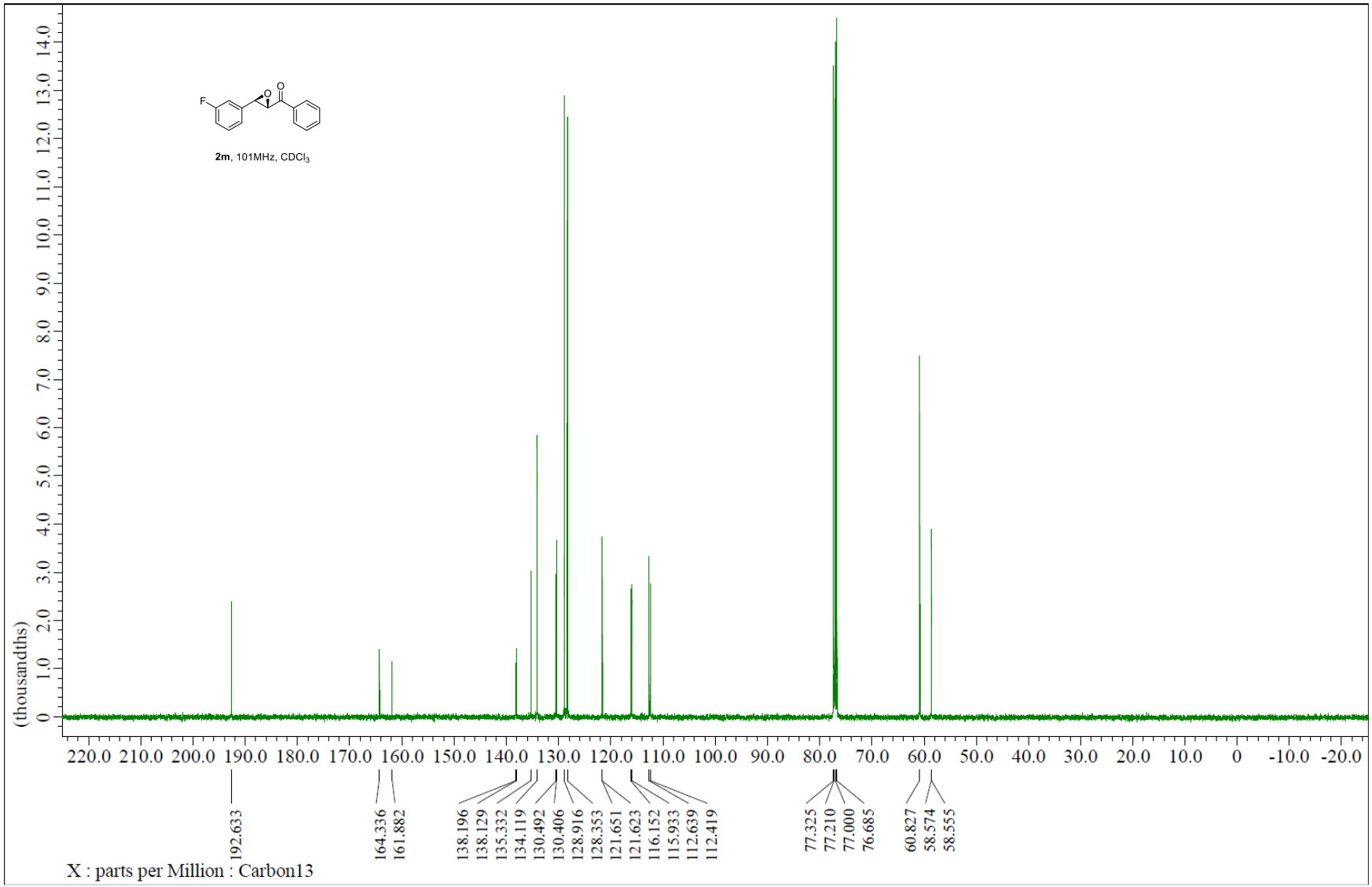
^{13}C-NMR of compound **2l**



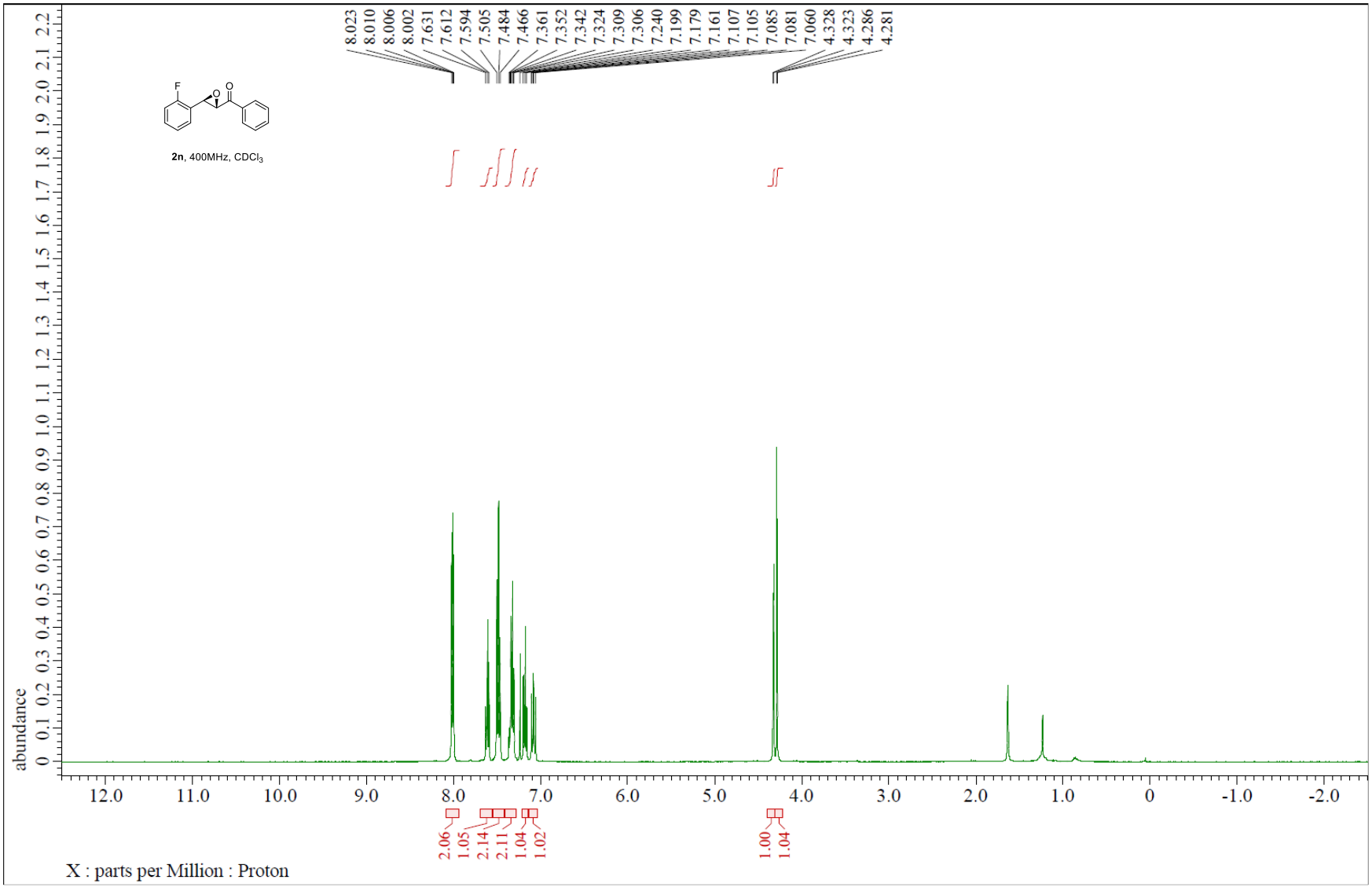
[1]H-NMR of compound **2m**



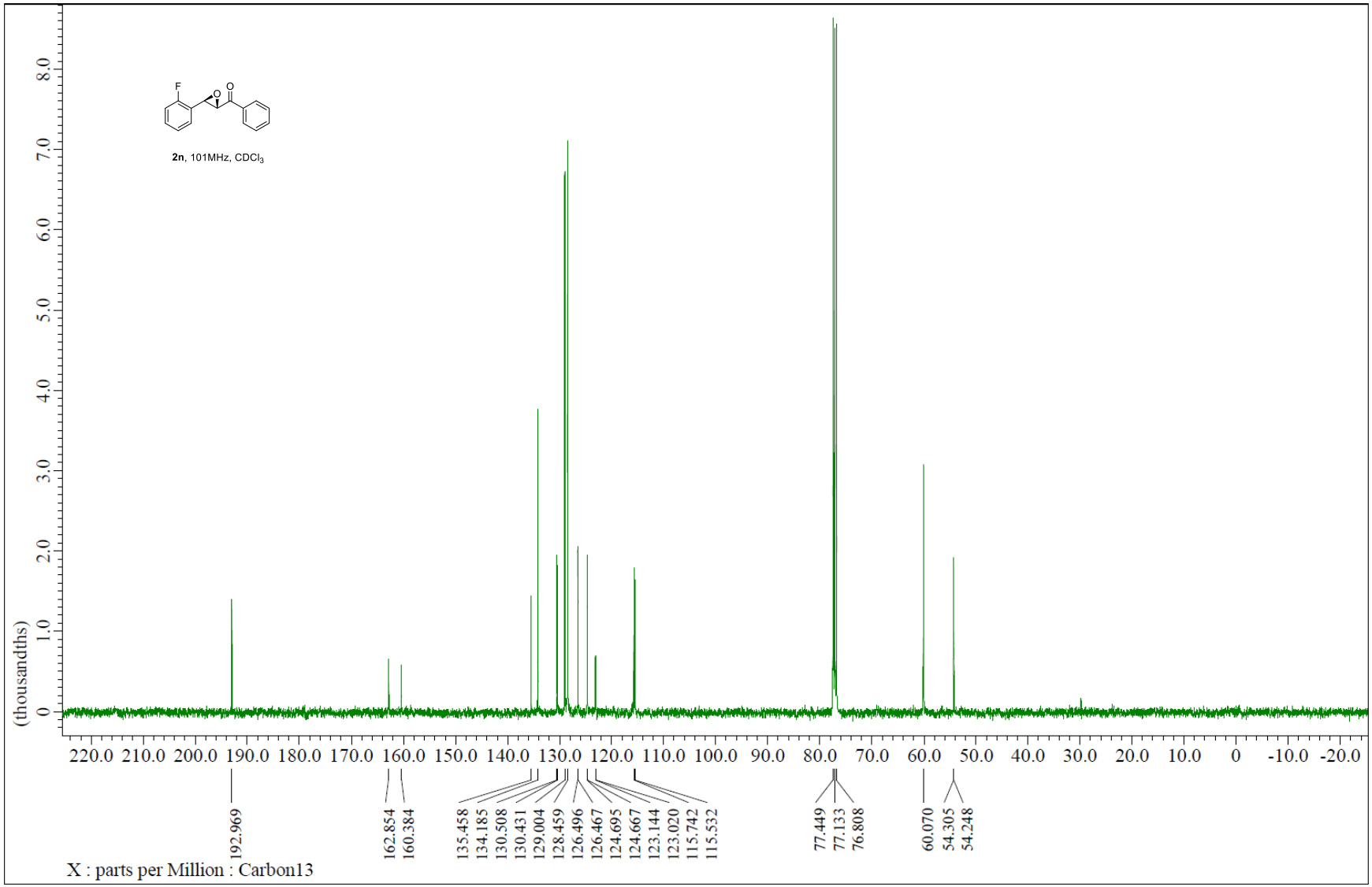
^{13}C-NMR of compound **2m**



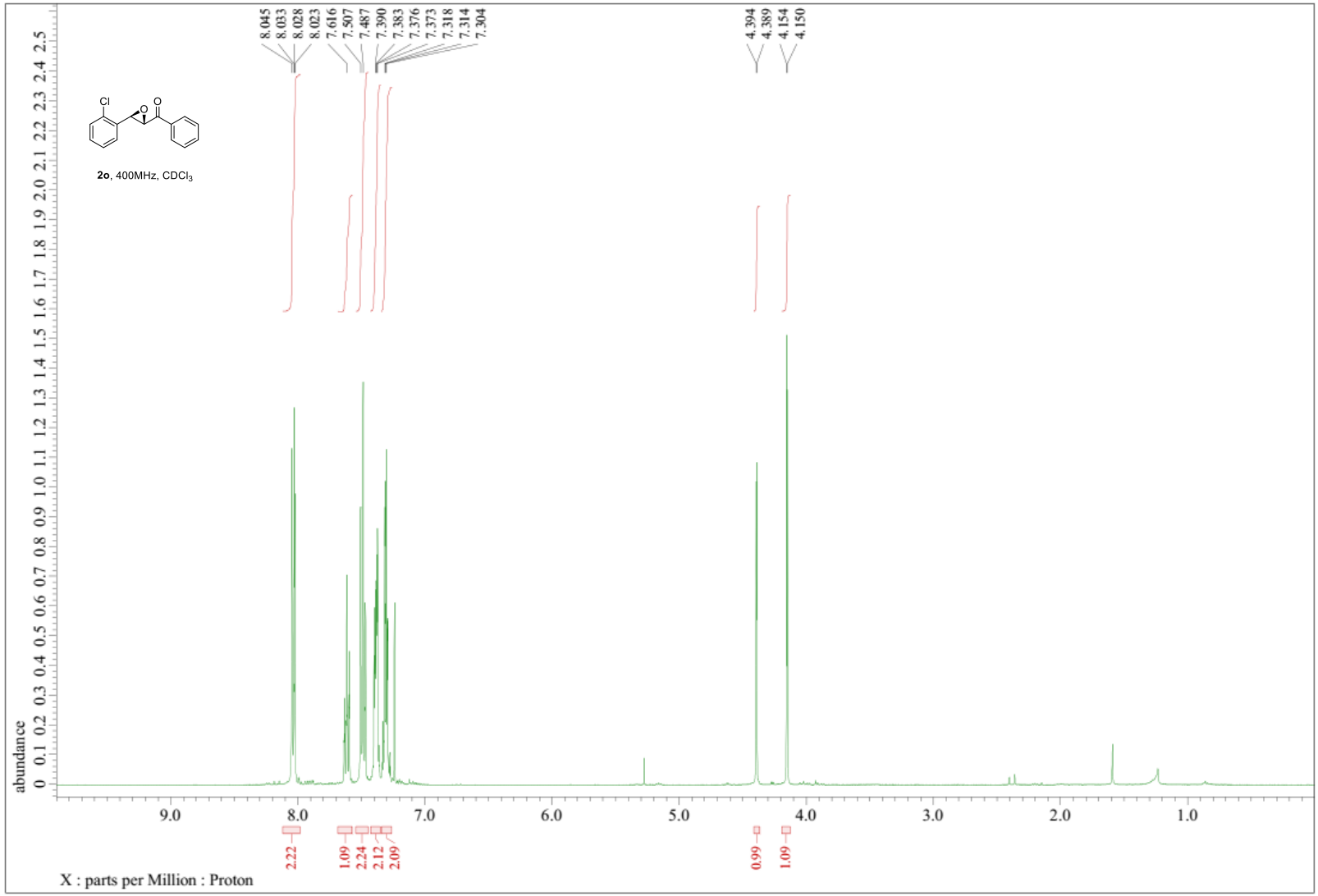
[1]H-NMR of compound **2n**



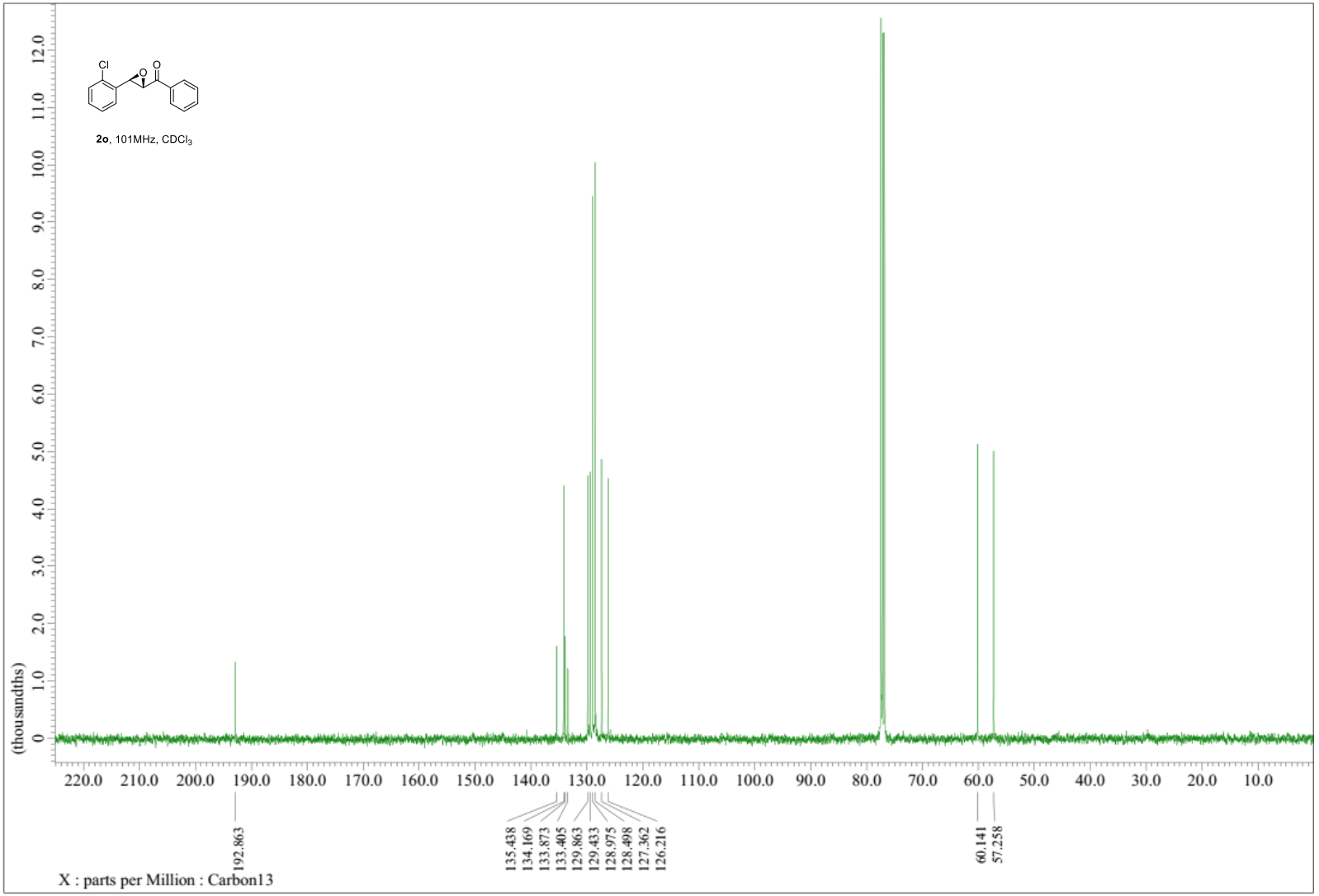
^{13}C-NMR of compound **2n**



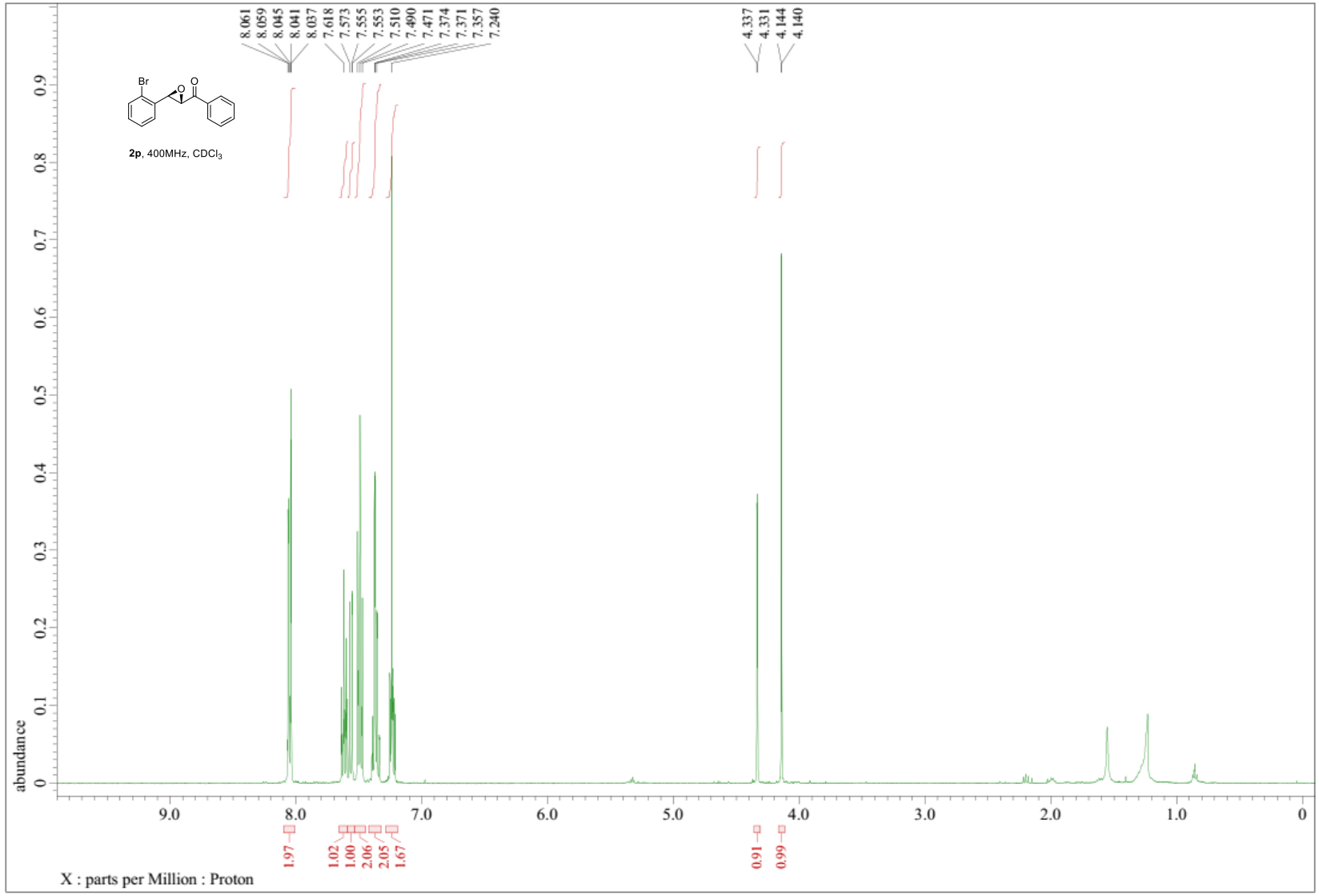
[1]H-NMR of compound **2o**



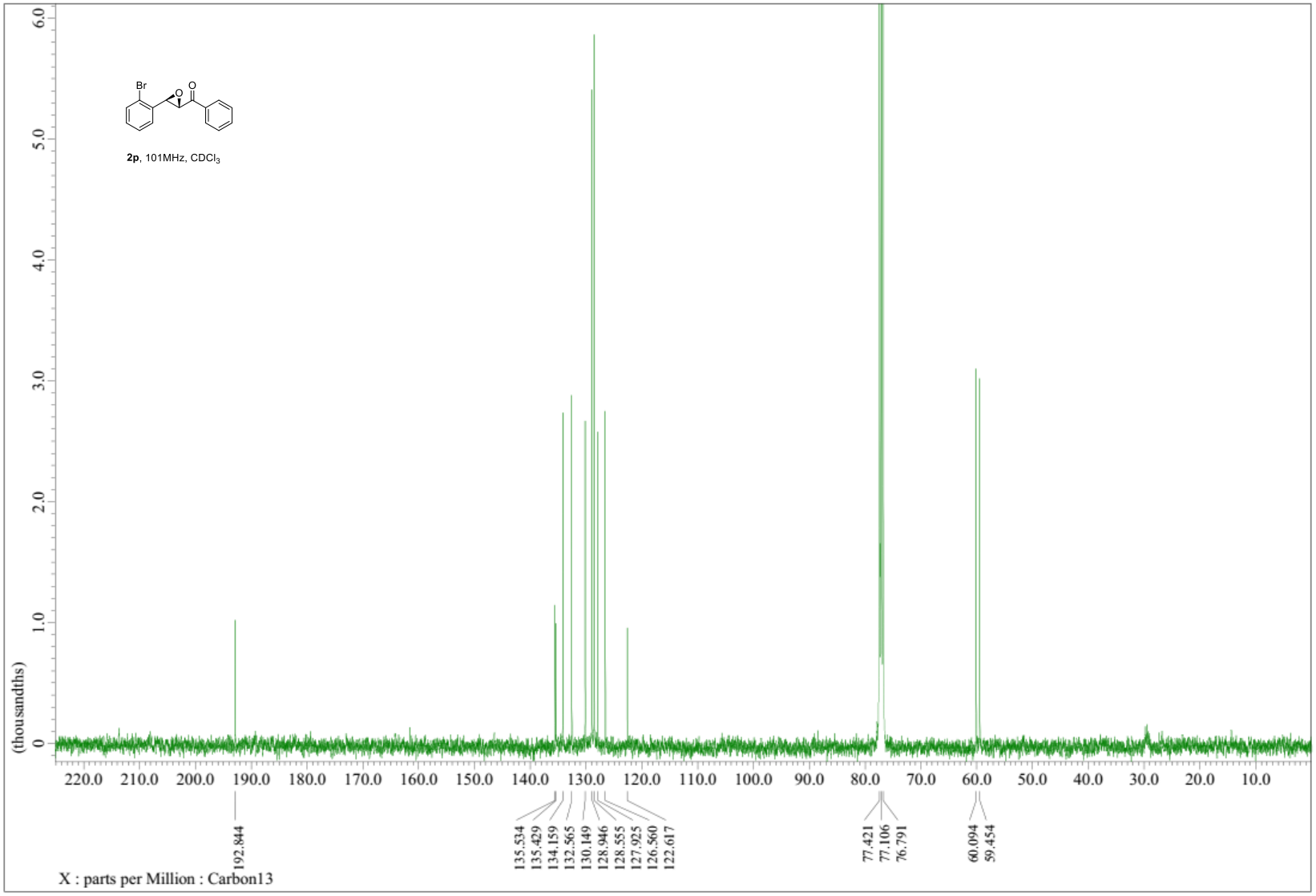
^{13}C-NMR of compound **2o**



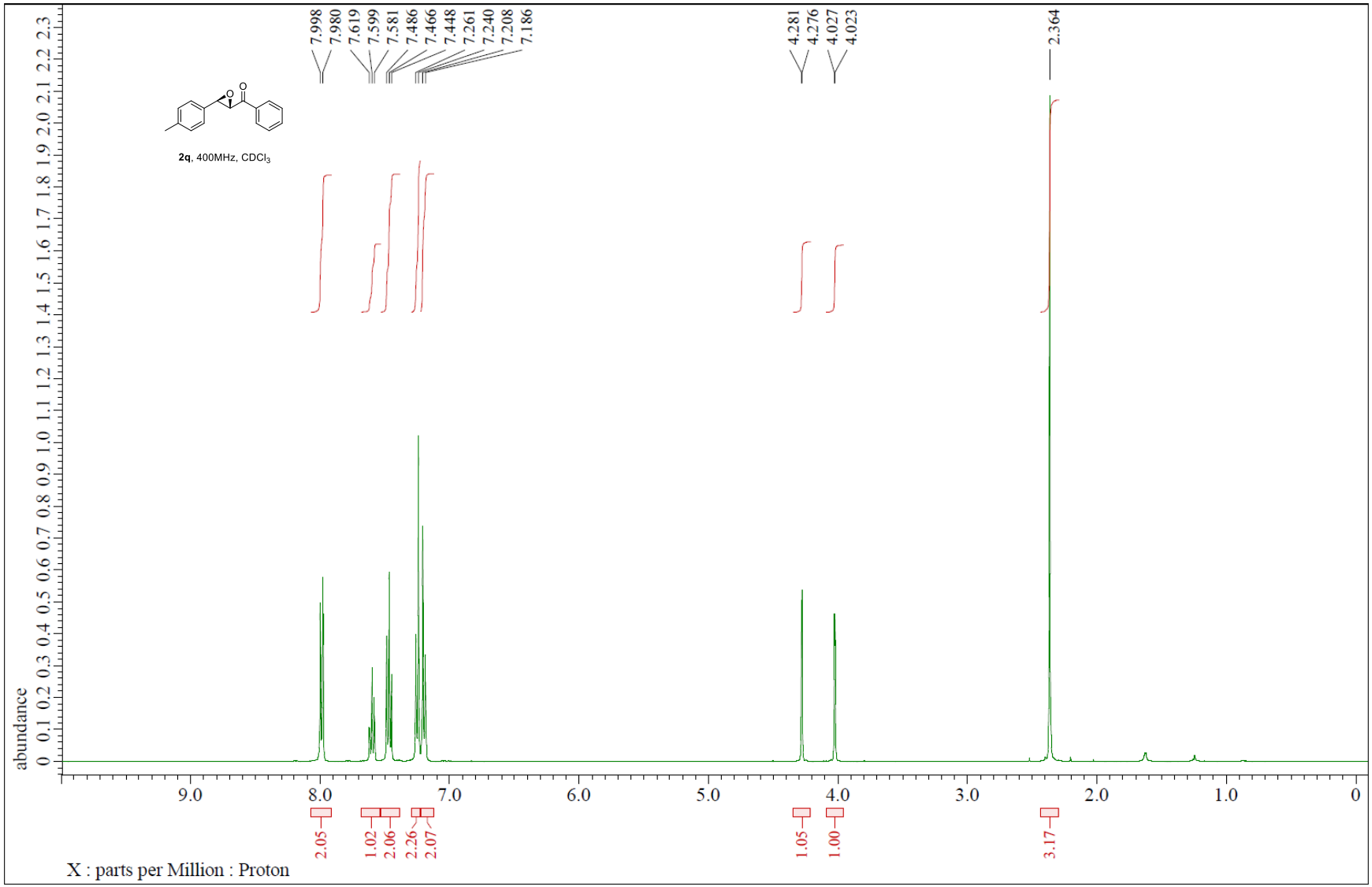
[1]H-NMR of compound **2p**



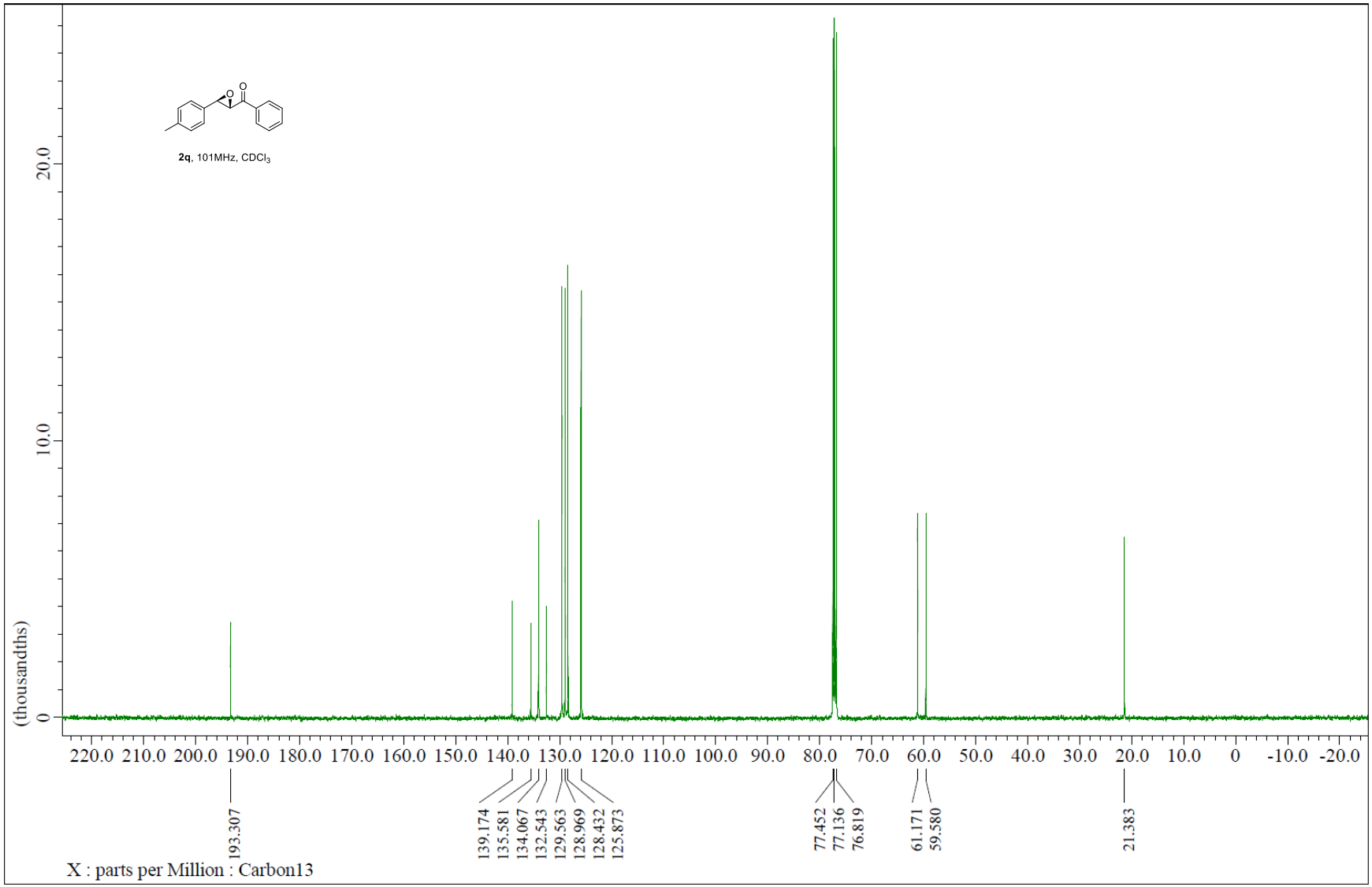
^{13}C-NMR of compound **2p**



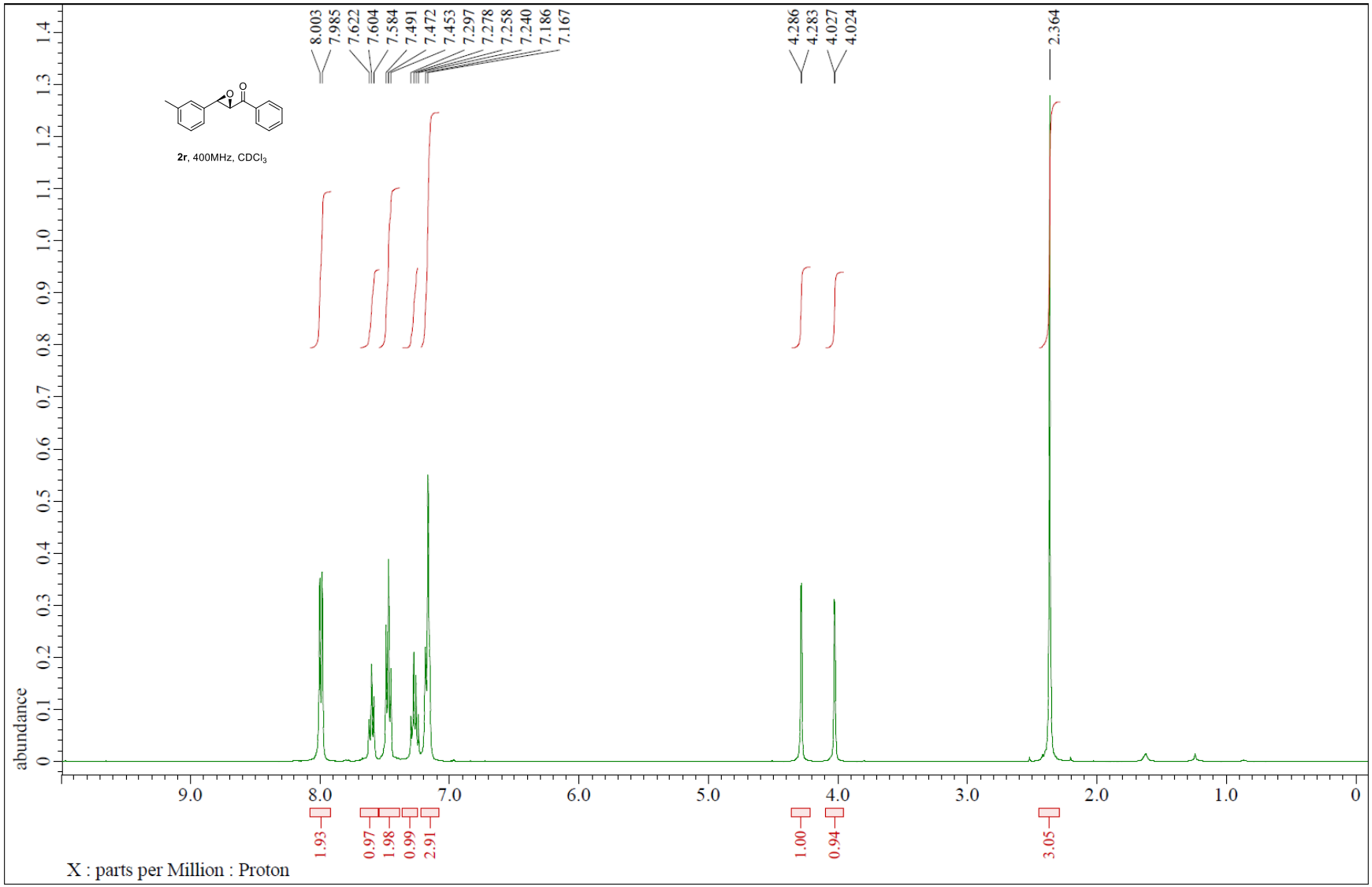
[1]H-NMR of compound **2q**



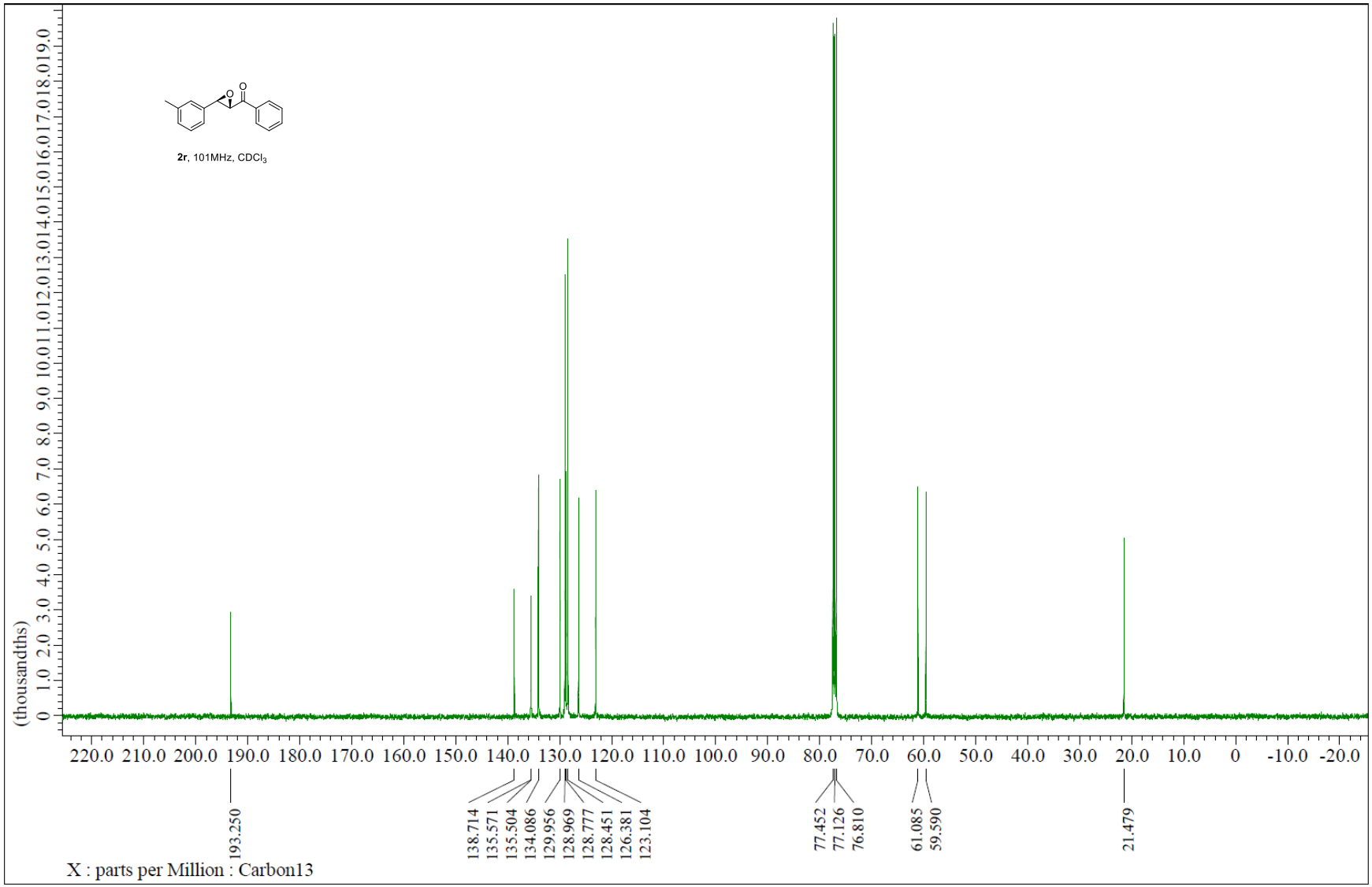
^{13}C-NMR of compound **2q**



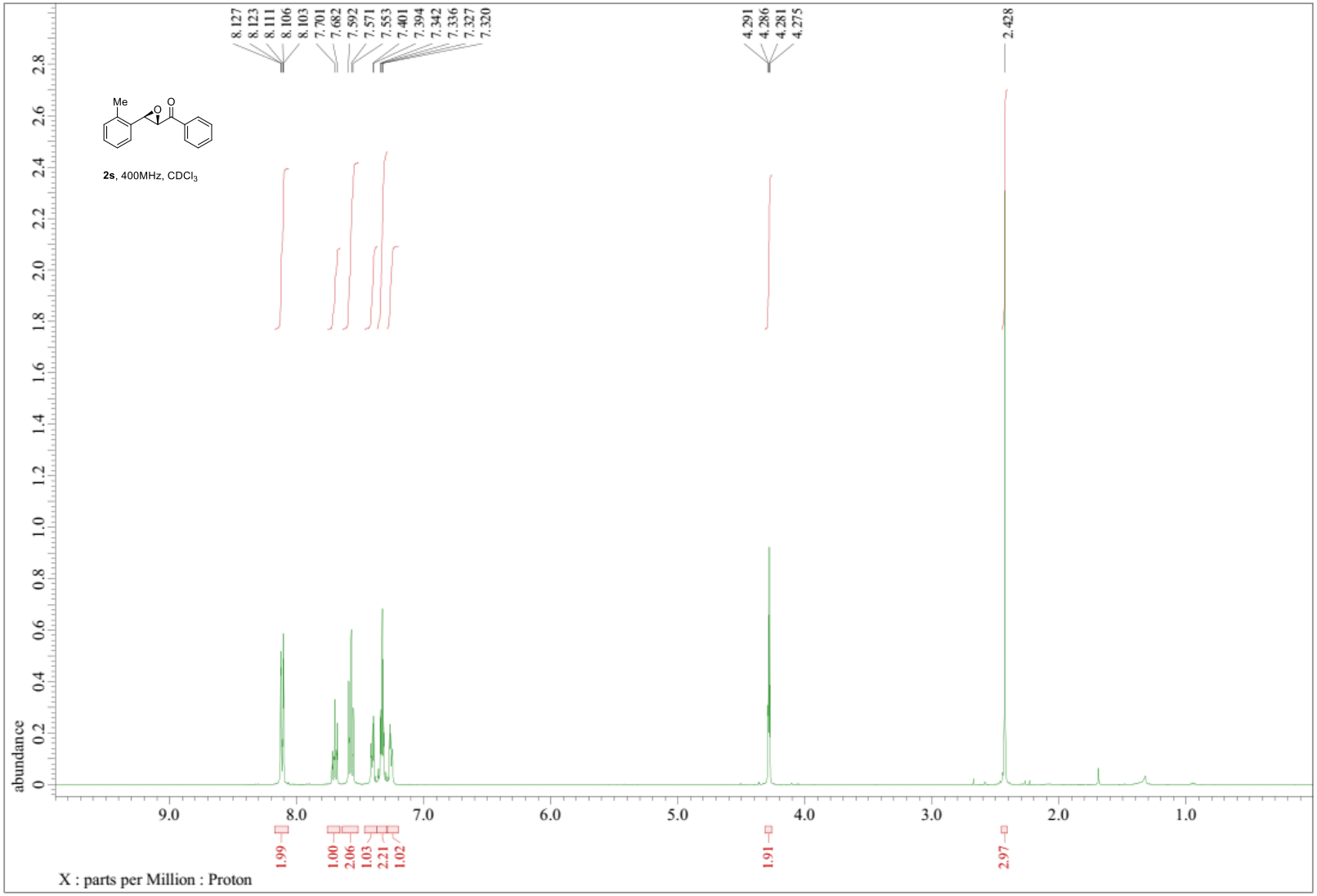
[1]H-NMR of compound **2r**



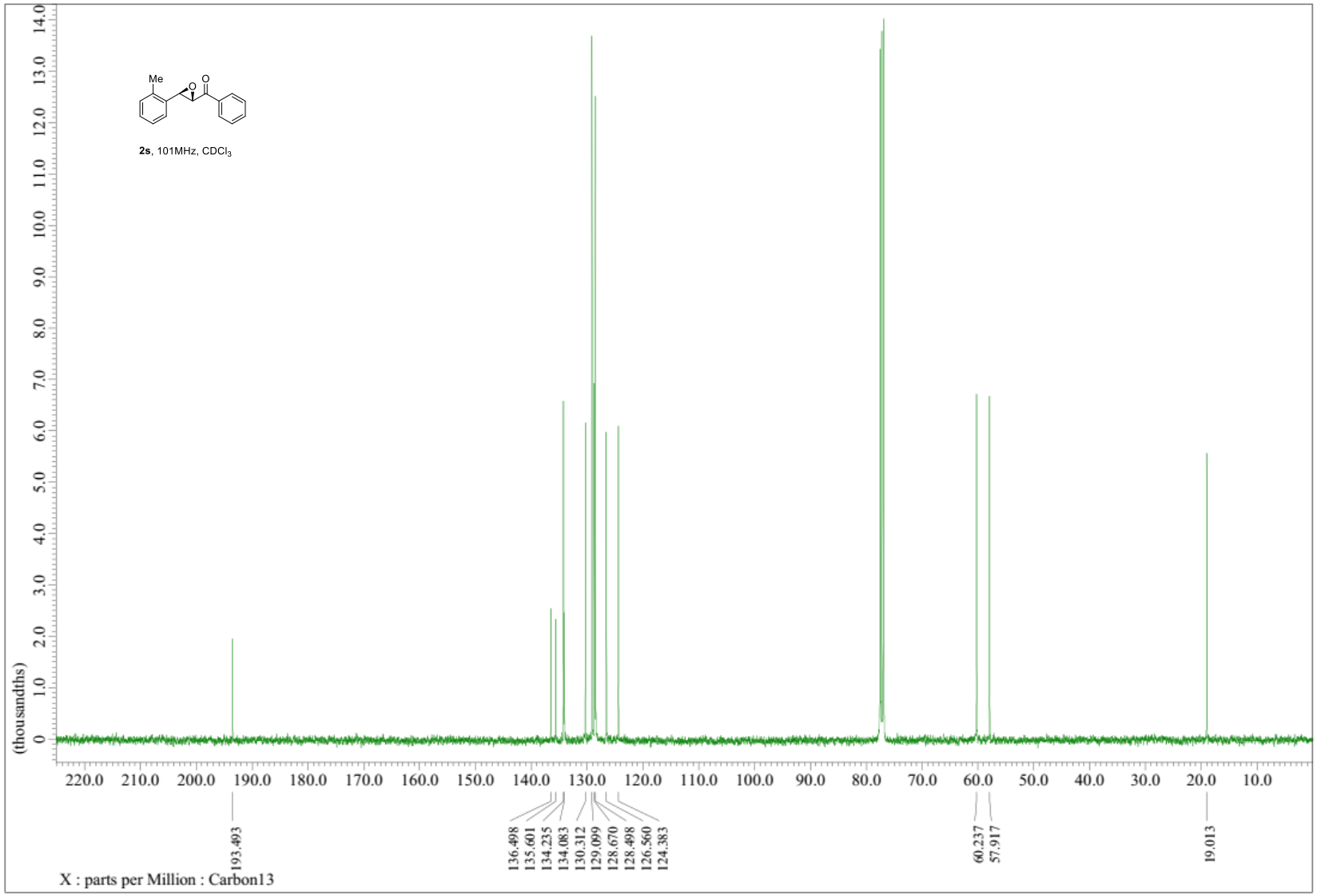
[1]H-NMR of compound **2r**



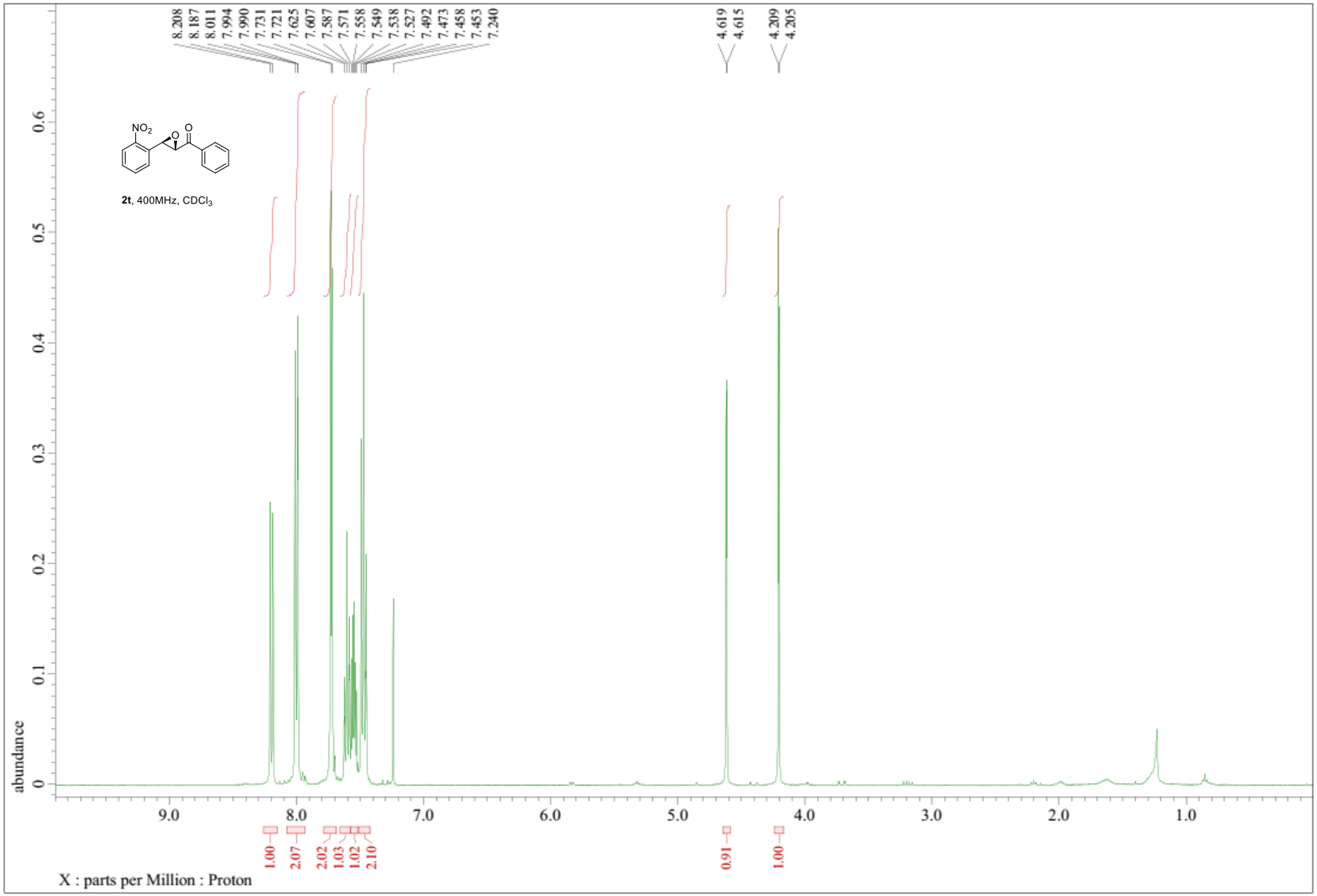
[1]H-NMR of compound **2s**



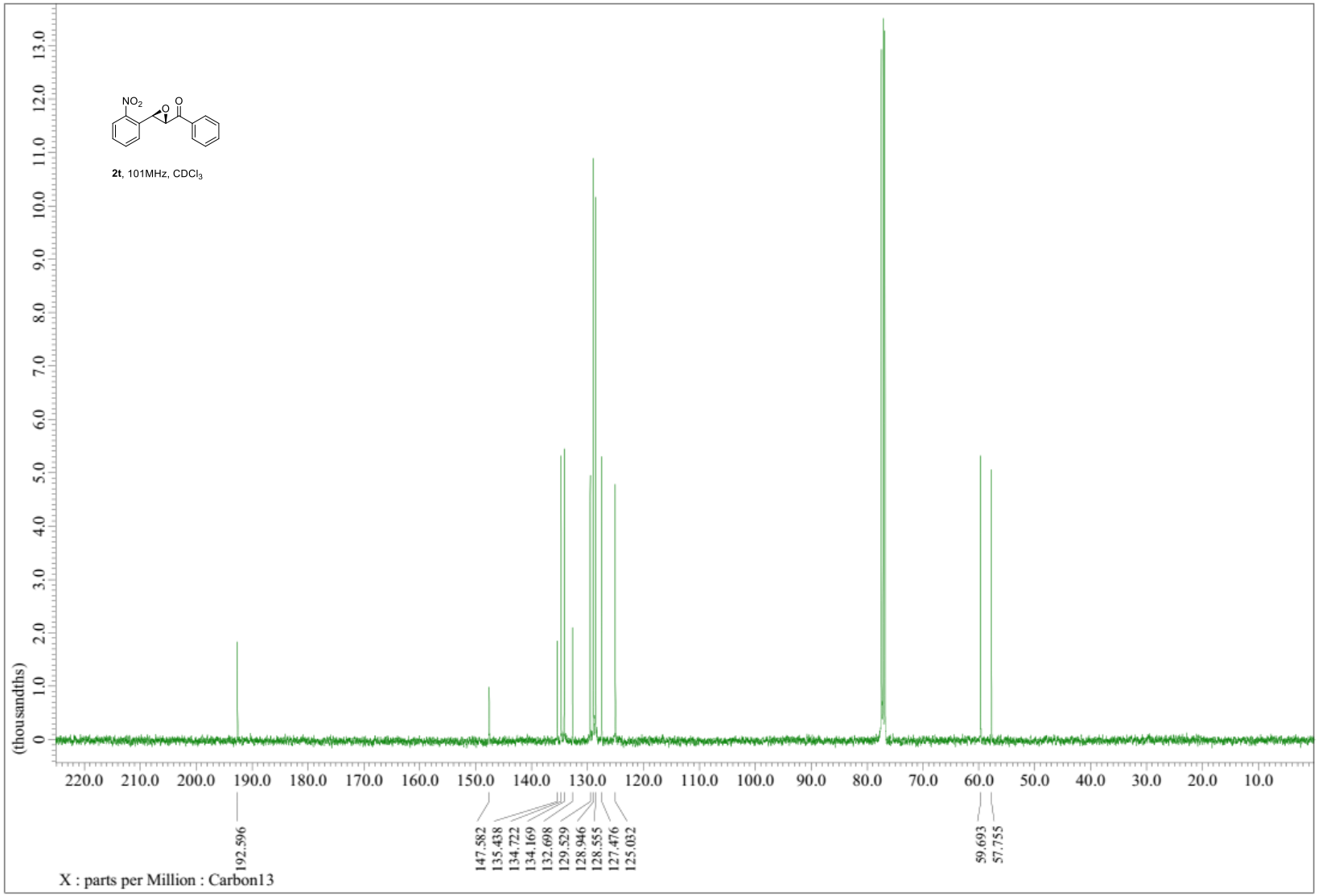
^{13}C-NMR of compound **2s**



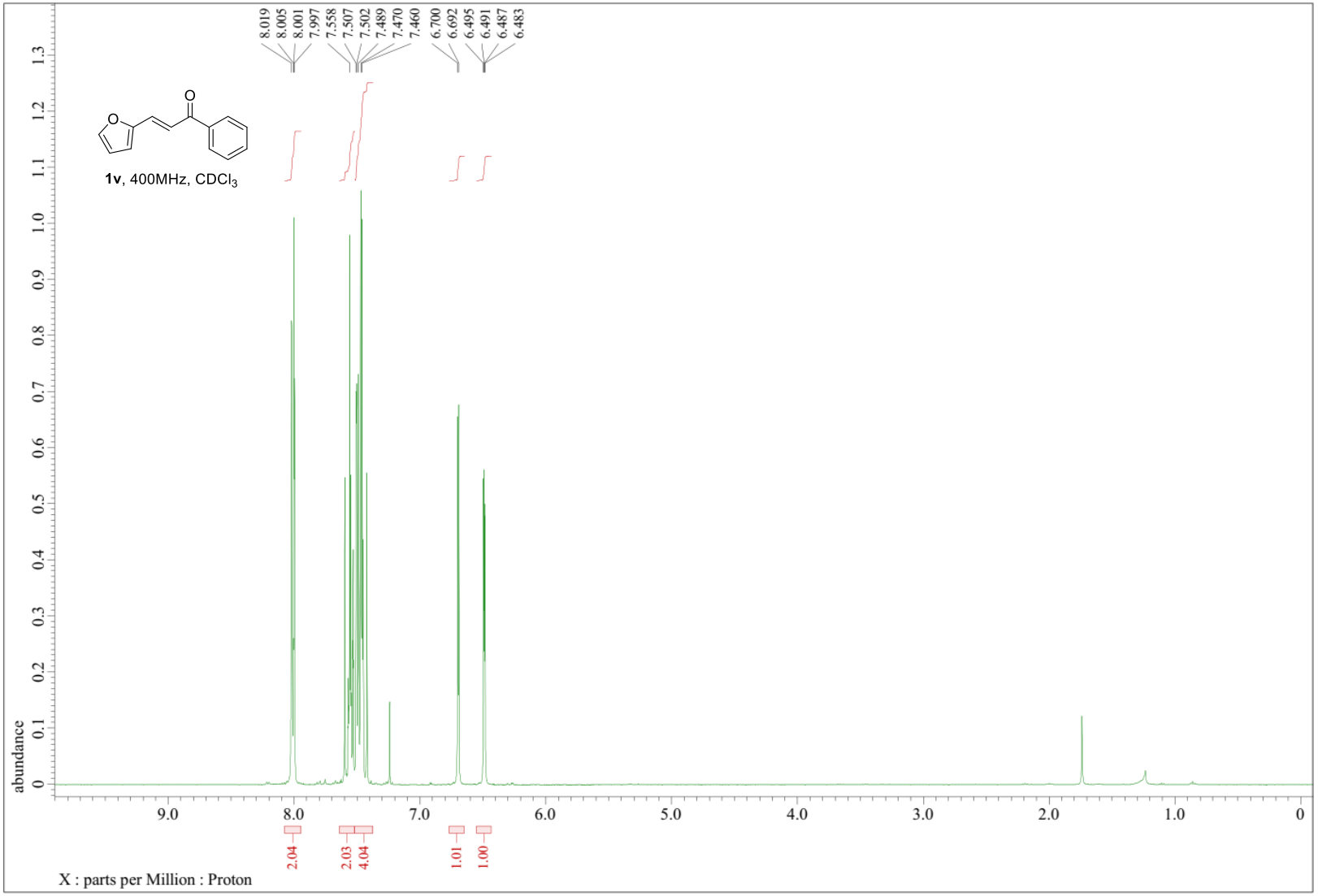
[1]H-NMR of compound **2t**



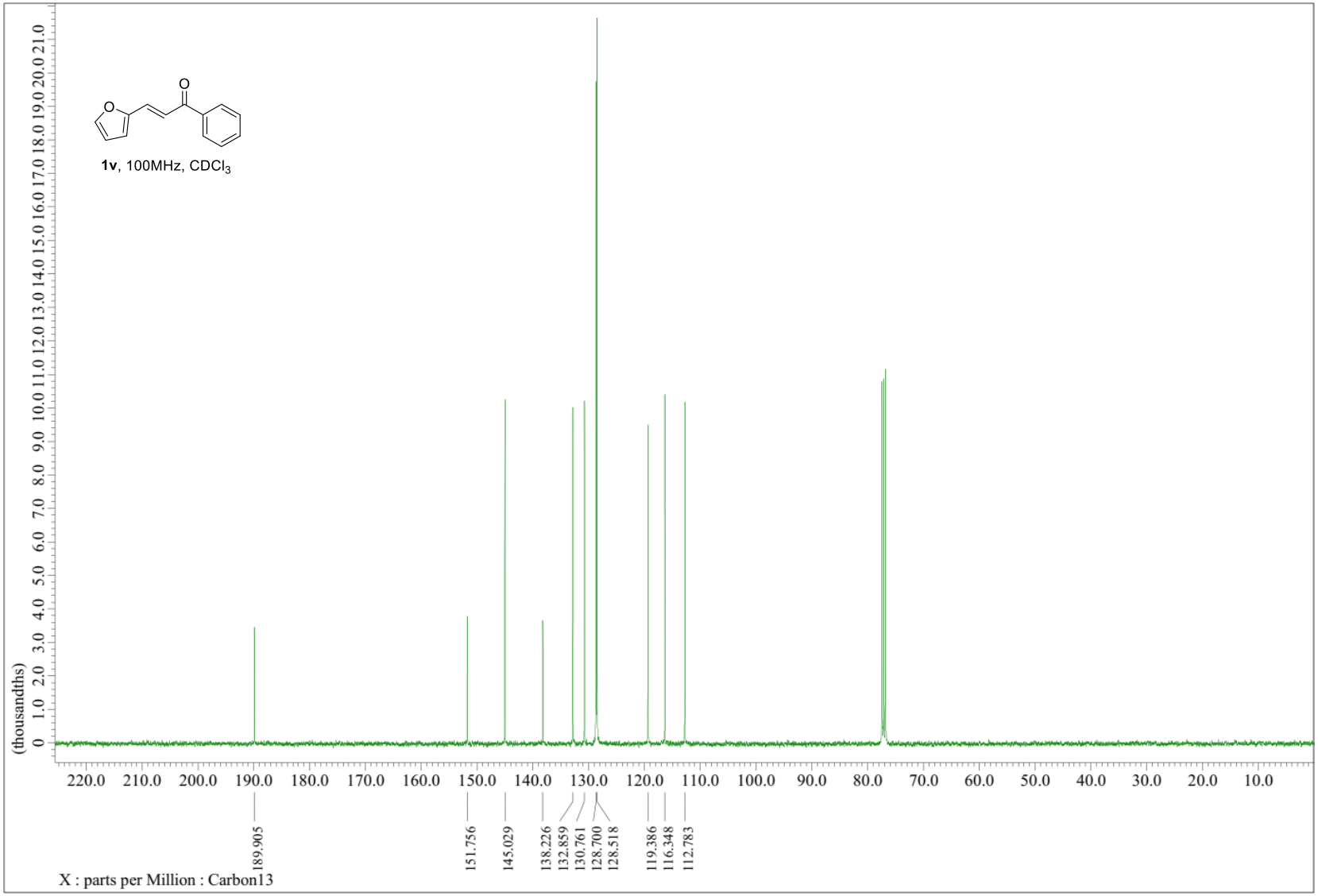
^{13}C-NMR of compound **2t**



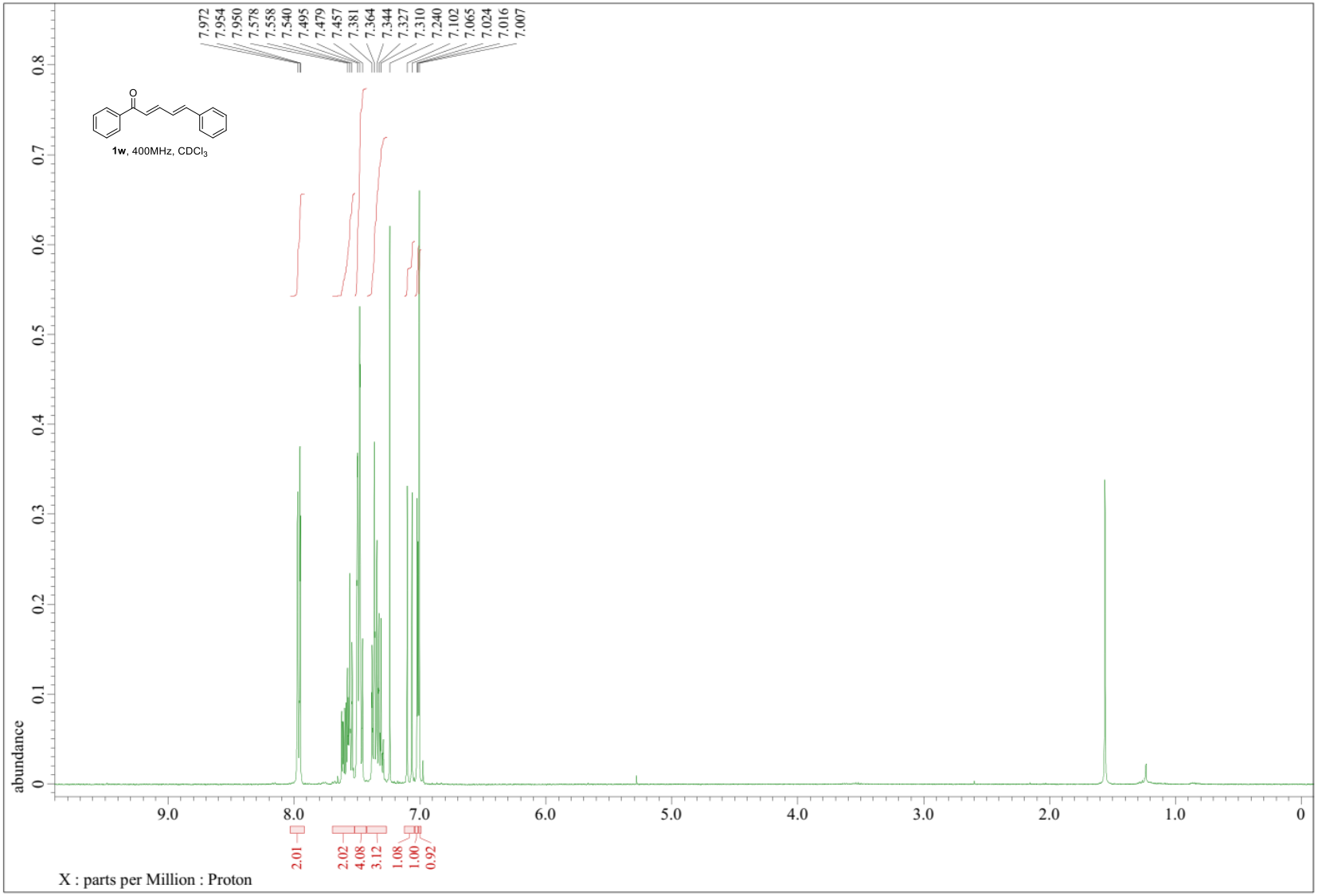
[1]H-NMR of compound **1v**



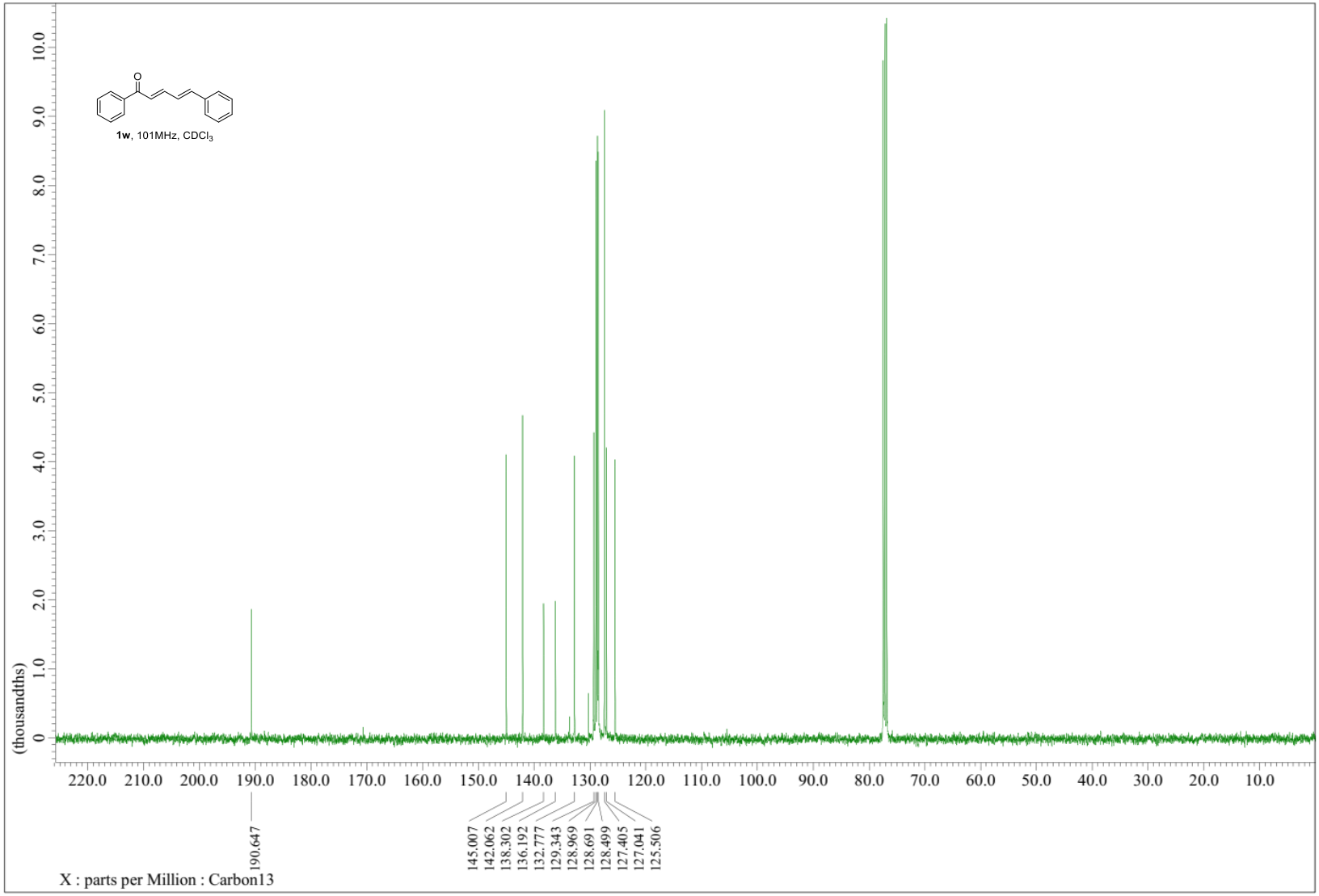
^{13}C-NMR of compound **1v**



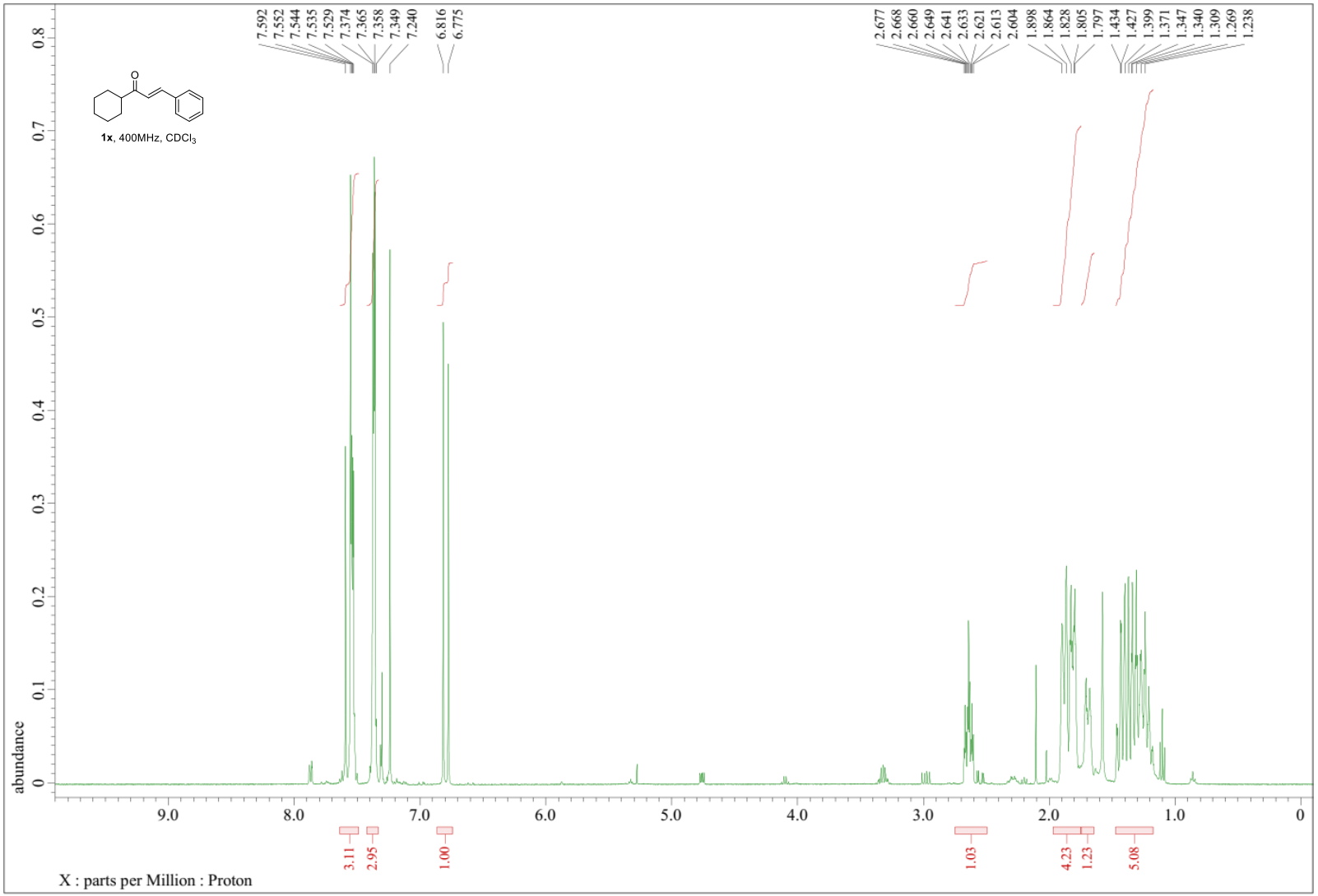
[1]H-NMR of compound **1w**



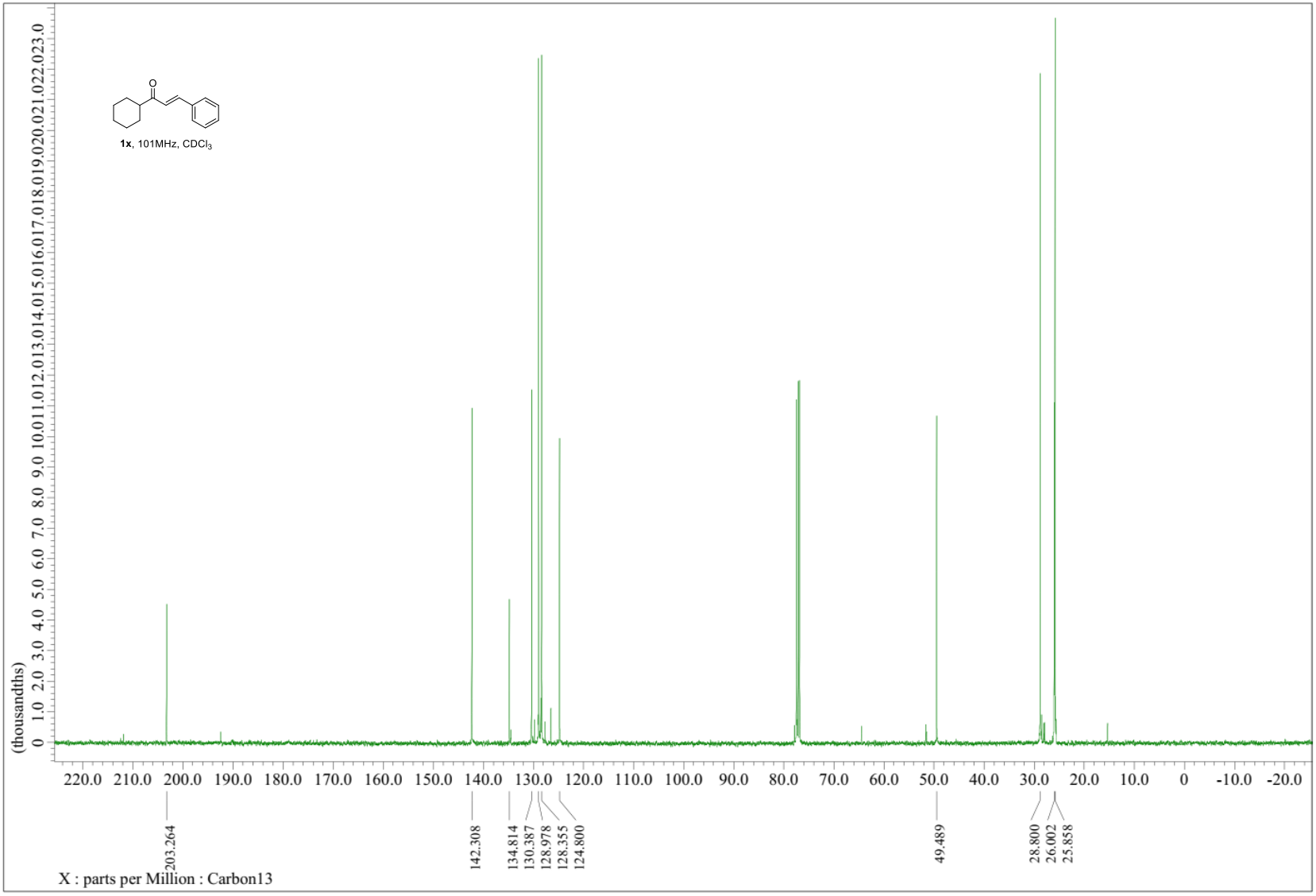
^{13}C-NMR of compound **1w**



[1]H-NMR of compound **1x**



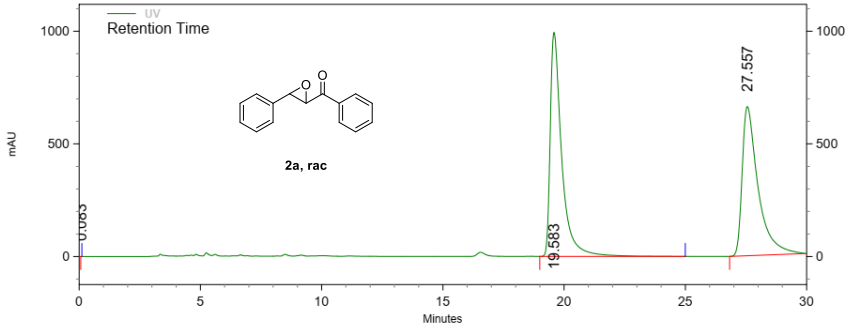
^{13}C-NMR of compound **1x**



Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-2-27 (AD H Hx EtOH (90 10) 1flow 30min 250nm) 180612.dat
Acquired: 2018-06-12 오후 3:15:17 **Printed:** 2018-06-12 오후 3:50:59

Analyst: System
Sample ID: lgw-2-27 **Vial:** N/A **Injection Volume:** 0



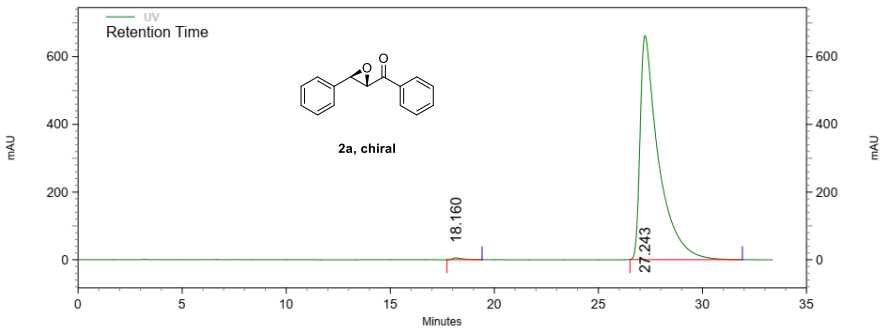
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	0.083	27	0.000	BI
	19.583	130735966	51.936	BI
	27.557	120988839	48.064	IE
Totals		251724832	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-7-21(AD H EtOH Hx 10 90 1flow 250nm 30 min) 20.11.05.dat
Acquired: 2020-11-05 오후 3:59:54 **Printed:** 2020-11-05 오후 4:34:47

Analyst: System
Sample ID: lgw-7-21(AD H EtOH Hx 10 90 1flow 250nm 30 min) 20.11.05 **Vial:** N/A
Injection Volume: 0



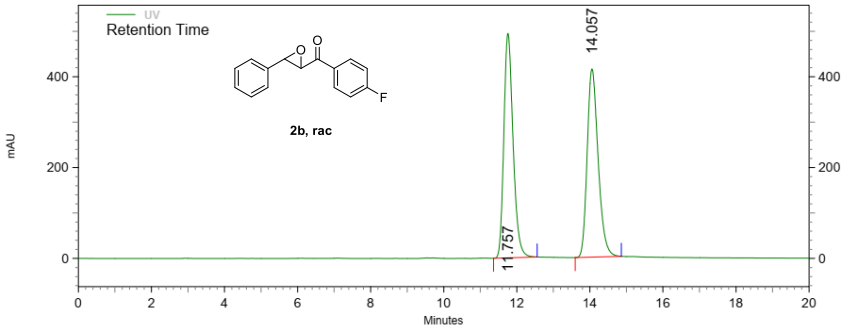
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	18.160	745117	0.457	MM
	27.243	162320906	99.543	mm
Totals		163066023	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-8-4 rac (AD H Hx iPrOH (90 10) 1flow 20min 254nm) 210304.dat
Acquired: 2021-03-04 오후 4:42:38 **Printed:** 2021-03-04 오후 5:05:37

Analyst: System
Sample ID: lgw-8-4 rac (AD H Hx iPrOH (90 10) 1flow 20min 254nm) 210304 **Vial:** N/A
Injection Volume: 0



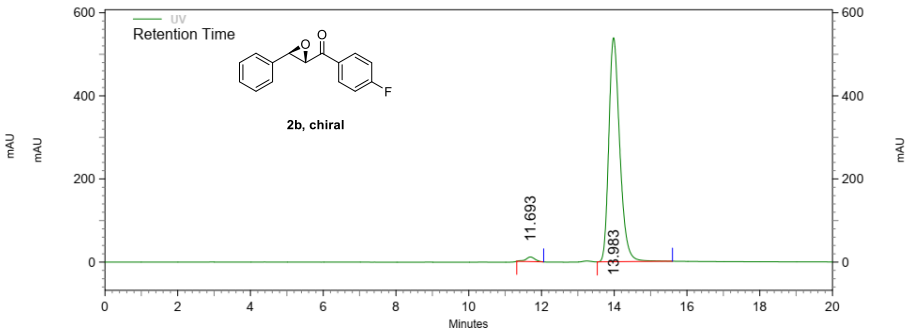
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	11.757	34609982	50.073	MM
	14.057	34508818	49.927	MM
Totals		69118800	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-8-28-chiral (AD H Hx iPrOH (90 10) 1flow 20min 254nm) 210304.dat
Acquired: 2021-03-04 오후 5:07:43 **Printed:** 2021-03-04 오후 5:28:09

Analyst: System
Sample ID: lgw-8-28-chiral (AD H Hx iPrOH (90 10) 1flow 20min 254nm) 210304 **Vial:** N/A
Injection Volume: 0



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	11.693	787698	1.718	MM
	13.983	45071422	98.282	MM
Totals		45859120	100.000	

Area Percent Report

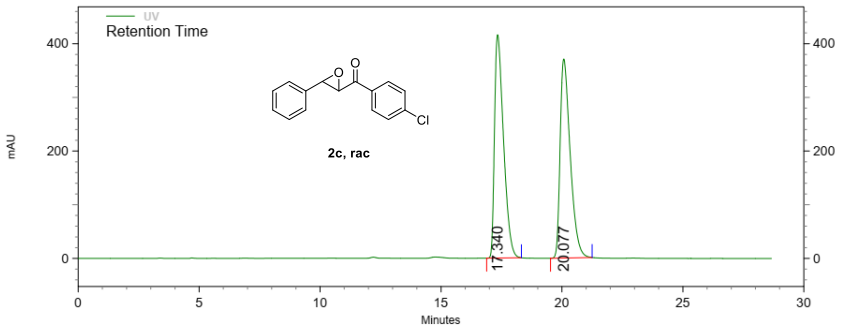
File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw 10-53 (ID-H Hx iPrOH 90 10 1flow 30min 250nm) 211026.dat

Acquired: 2021-10-26 오후 7:18:38 Printed: 2021-10-26 오후 7:47:32

Analyst: System

Sample ID: lgw 10-53 (ID-H Hx iPrOH 90 10 1flow 30min 250nm) 211026 Vial: N/A

Injection Volume: 0



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	17.340	43065326	50.105	MM
	20.077	42884567	49.895	MM
Totals		85949893	100.000	

Area Percent Report

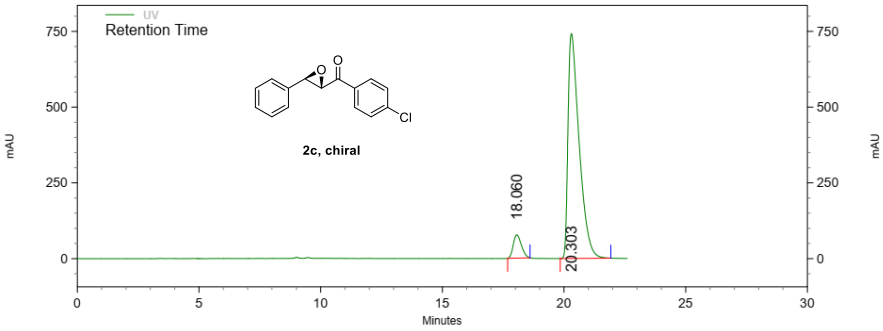
File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw 10-61 c(ID-H Hx iPrOH 90 10 1flow 30min 250nm) 211026.dat

Acquired: 2021-10-26 오후 8:21:11 Printed: 2021-10-26 오후 8:44:12

Analyst: System

Sample ID: lgw 10-61 c(ID-H Hx iPrOH 90 10 1flow 30min 250nm) 211026 Vial: N/A

Injection Volume: 0



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	18.060	7143654	7.041	MM
	20.303	94314885	92.959	MM
Totals		101458539	100.000	

Area Percent Report

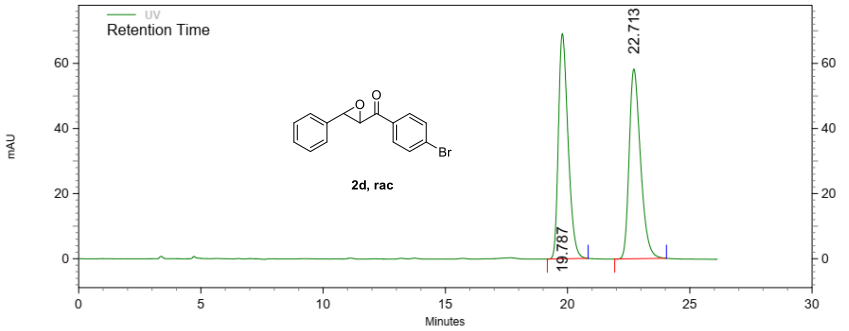
File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw 10-52 (ID-H Hx iPrOH 90 10 1flow 30min 250nm) 211026.dat

Acquired: 2021-10-26 오후 6:50:50 **Printed:** 2021-10-26 오후 7:17:21

Analyst: System

Sample ID: lgw 10-52 (ID-H Hx iPrOH 90 10 1flow 30min 250nm) 211026 **Vial:** N/A

Injection Volume: 0



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	19.787	7593575	50.190	MM
	22.713	7536218	49.810	MM
Totals		15129793	100.000	

Area Percent Report

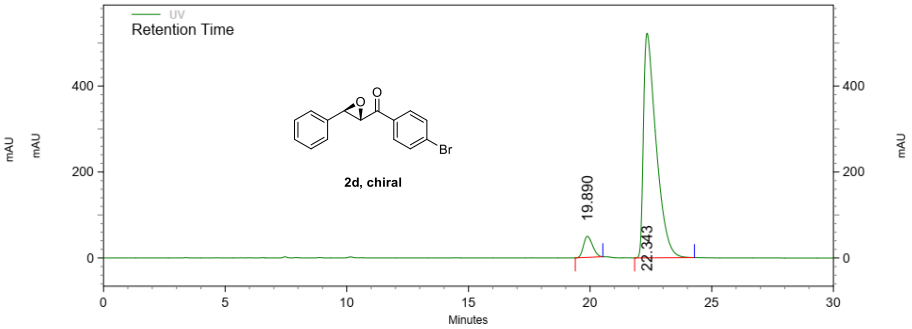
File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw 10-60 c(ID-H Hx iPrOH 90 10 1flow 30min 250nm) 211026.dat

Acquired: 2021-10-26 오후 7:49:42 **Printed:** 2021-10-26 오후 8:20:12

Analyst: System

Sample ID: lgw 10-60 c(ID-H Hx iPrOH 90 10 1flow 30min 250nm) 211026 **Vial:** N/A

Injection Volume: 0



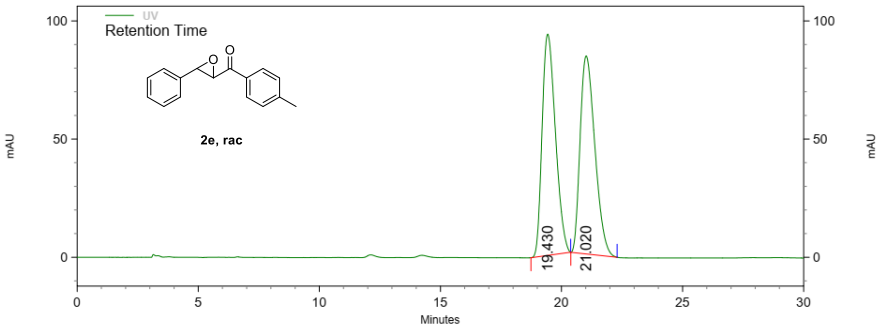
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	19.890	5099848	6.322	MM
	22.343	75574213	93.678	MM
Totals		80674061	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-7-90 racemic(AD H Hx iPrOH (95 5) 1flow 30min 254nm) 210806.dat
Acquired: 2021-08-06 오후 12:38:25 **Printed:** 2021-08-06 오후 1:19:57

Analyst: System
Sample ID: lgw-7-90 racemic(AD H Hx iPrOH (95 5) 1flow 30min 254nm) 210806 **Vial:** N/A **Injection Volume:** 0



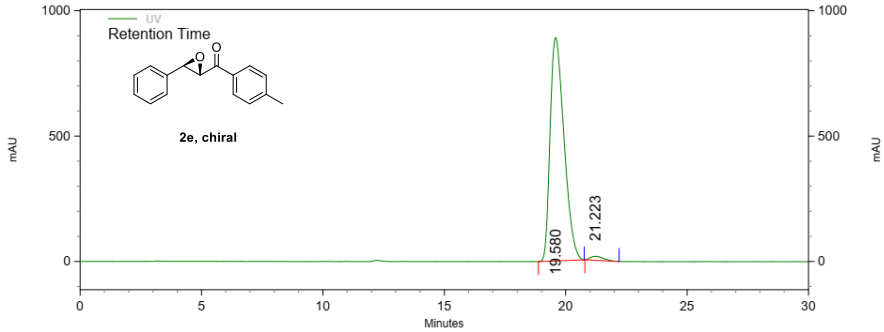
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	19.430	14308839	50.200	MM
	21.020	14194584	49.800	MM
Totals		28503423	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-9-95 chiral(AD H Hx iPrOH (95 5) 1flow 30min 254nm) 210806.dat
Acquired: 2021-08-06 오전 11:59:52 **Printed:** 2021-08-06 오후 12:36:15

Analyst: System
Sample ID: lgw-9-95 chiral(AD H Hx iPrOH (95 5) 1flow 30min 254nm) 210806 **Vial:** N/A **Injection Volume:** 0



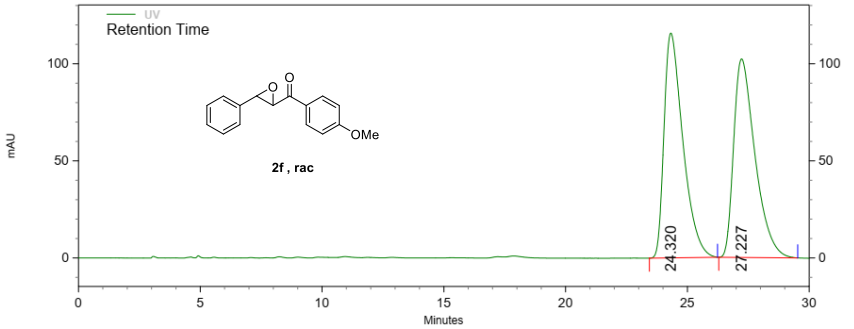
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	19.580	141875019	98.305	MM
	21.223	2446063	1.695	MM
Totals		144321082	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-7-100 rac(AD H iPrOH Hx 10 90 1flow 254nm 30 min) 210517.dat
Acquired: 2021-05-17 오후 4:17:16 **Printed:** 2021-05-17 오후 4:48:31

Analyst: System
Sample ID: lgw-7-100 rac(AD H iPrOH Hx 10 90 1flow 254nm 30 min) 210517 **Vial:** N/A
Injection Volume: 0



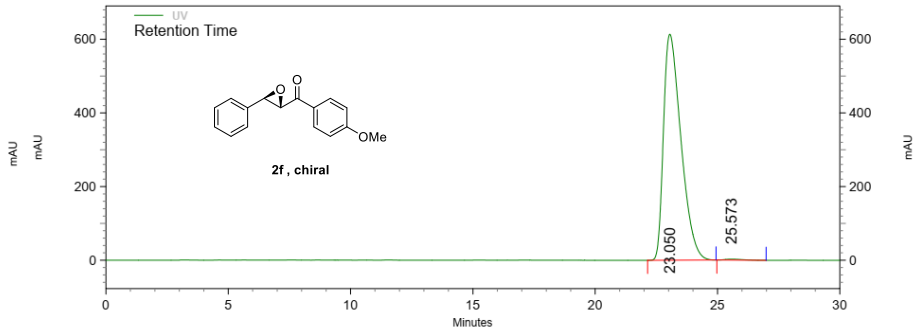
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	24.320	24927629	50.022	MM
	27.227	24905572	49.978	MM
Totals		49833201	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-9-61 chiral (AD H iPrOH Hx 10 90 1flow 254nm 30 min) 210708.dat
Acquired: 2021-07-08 오후 3:25:39 **Printed:** 2021-07-08 오후 4:01:55

Analyst: System
Sample ID: lgw-9-61 chiral (AD H iPrOH Hx 10 90 1flow 254nm 30 min) 210708 **Vial:** N/A
Injection Volume: 0



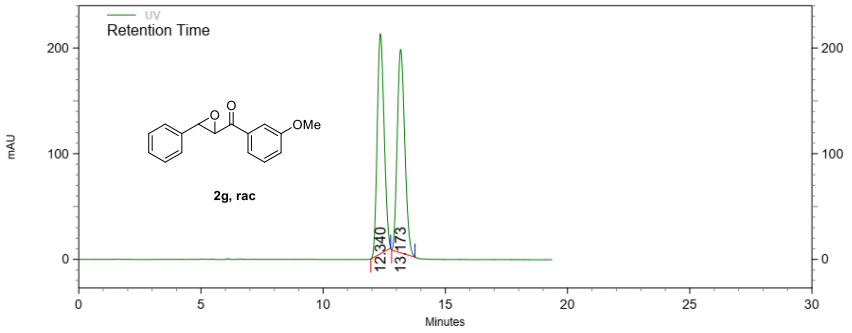
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	23.050	121635327	99.573	MM
	25.573	521899	0.427	MM
Totals		122157226	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw 7-99 rac (OD-H Hx iPrOH 90 10 1flow 30min 250nm) 211026.dat
Acquired: 2021-10-26 오후 11:36:22 **Printed:** 2021-10-26 오후 11:56:13

Analyst: System
Sample ID: lgw 7-99 rac (OD-H Hx iPrOH 90 10 1flow 30min 250nm) 211026 **Vial:** N/A
Injection Volume: 0



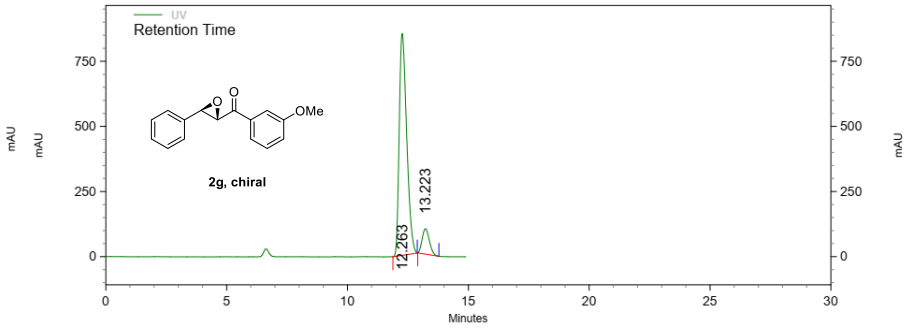
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	12.340	16359410	49.754	MM
	13.173	16521492	50.246	MM
Totals		32880902	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw 10- 2_3OMe (OD-H Hx iPrOH 90 10 1flow 30min 250nm) 211026.dat
Acquired: 2021-10-27 오전 12:15:14 **Printed:** 2021-10-27 오전 12:30:29

Analyst: System
Sample ID: lgw 10- 2_3OMe (OD-H Hx iPrOH 90 10 1flow 30min 250nm) 211026 **Vial:** N/A
Injection Volume: 0



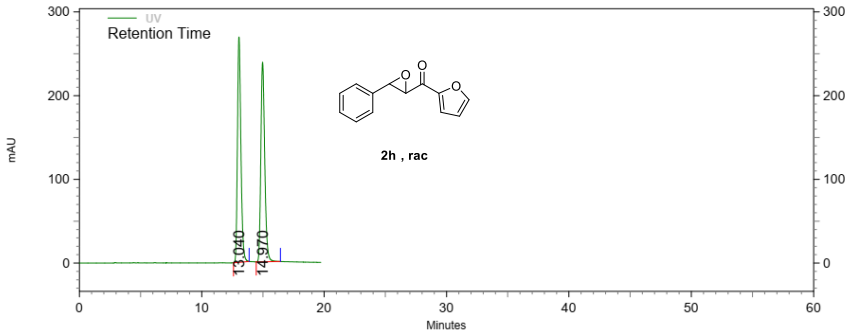
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	12.263	73056759	90.048	MM
	13.223	8074575	9.952	MM
Totals		81131334	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-8-2 rac-4 (AD H Hx iPrOH (90 10) 1flow 60min 254nm) 210304.dat
Acquired: 2021-03-04 오후 3:55:05 **Printed:** 2021-03-04 오후 4:38:32

Analyst: System
Sample ID: lgw-8-2 rac-4 (AD H Hx iPrOH (90 10) 1flow 60min 254nm) 210304 **Vial:** N/A **Injection Volume:** 0



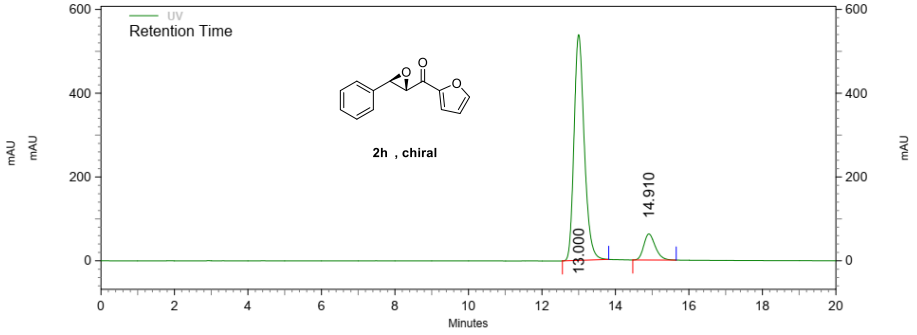
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	13.040	21013534	49.851	MM
	14.970	21139566	50.149	MM
Totals		42153100	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-8-27 chiral(AD H Hx iPrOH (90 10) 1flow 20min 254nm) 210304.dat
Acquired: 2021-03-04 오후 4:17:10 **Printed:** 2021-03-04 오후 4:37:37

Analyst: System
Sample ID: lgw-8-27 chiral (AD H Hx iPrOH (90 10) 1flow 20min 254nm) 210304 **Vial:** N/A **Injection Volume:** 0



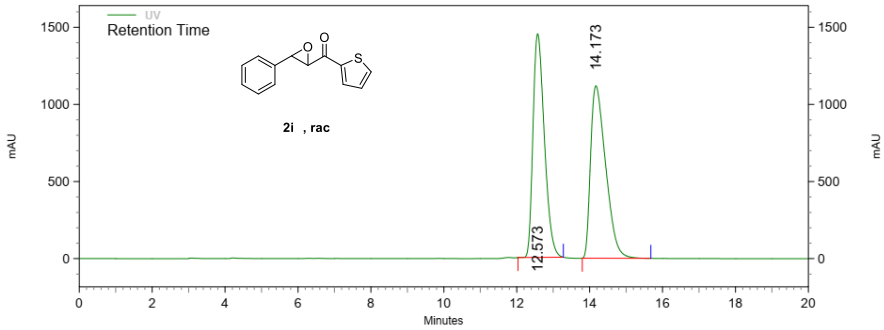
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	13.000	41708889	88.512	MM
	14.910	5413178	11.488	MM
Totals		47122067	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-8-1 rac (OD H Hx iPrOH (90 10) 1flow 20min 254nm) 210216.dat
Acquired: 2021-02-16 오후 5:00:01 **Printed:** 2021-02-16 오후 5:21:21

Analyst: System
Sample ID: lgw-8-1 rac (OD H Hx iPrOH (90 10) 1flow 20min 254nm) 210216 **Vial:** N/A
Injection Volume: 0



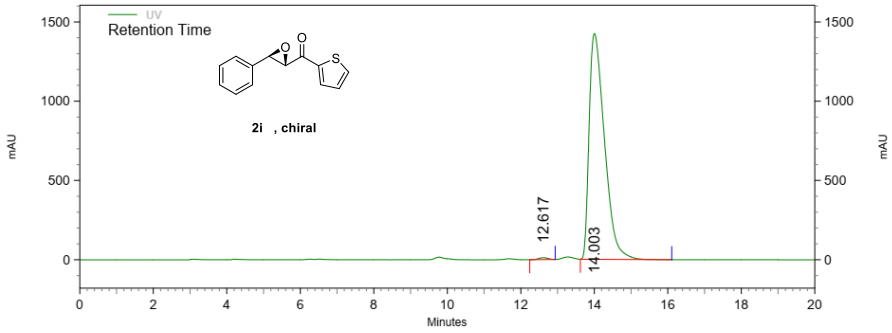
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	12.573	125852655	49.452	MM
	14.173	128642460	50.548	MM
Totals		254495115	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-8-12 (OD H Hx iPrOH (90 10) 1flow 20min 254nm) 210216.dat
Acquired: 2021-02-16 오후 5:22:42 **Printed:** 2021-02-16 오후 5:45:11

Analyst: System
Sample ID: lgw-8-12 (OD H Hx iPrOH (90 10) 1flow 20min 254nm) 210216 **Vial:** N/A
Injection Volume: 0



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	12.617	841996	0.508	mm
	14.003	165052156	99.492	mm
Totals		165894152	100.000	

Area Percent Report

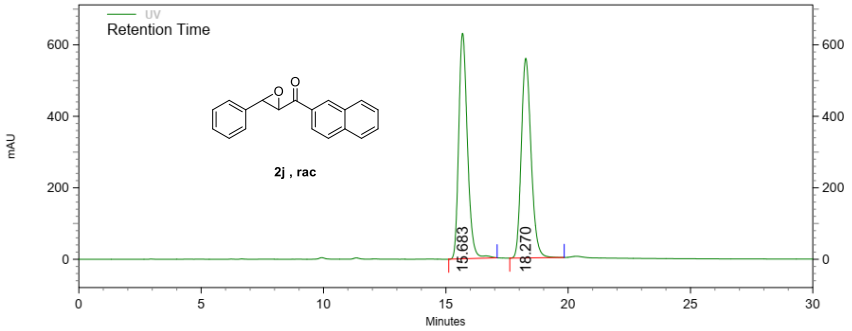
File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-8-5 rac (AD H Hx iPrOH (90 10) 1flow 30min 254nm) 210310.dat

Acquired: 2021-03-10 오후 3:06:30 **Printed:** 2021-03-10 오후 3:36:59

Analyst: System

Sample ID: lgw-8-5 rac (AD H Hx iPrOH (90 10) 1flow 30min 254nm) 210310 **Vial:** N/A

Injection Volume: 0



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	15.683	62337736	50.032	MM
	18.270	62258471	49.968	MM
Totals		124596207	100.000	

Area Percent Report

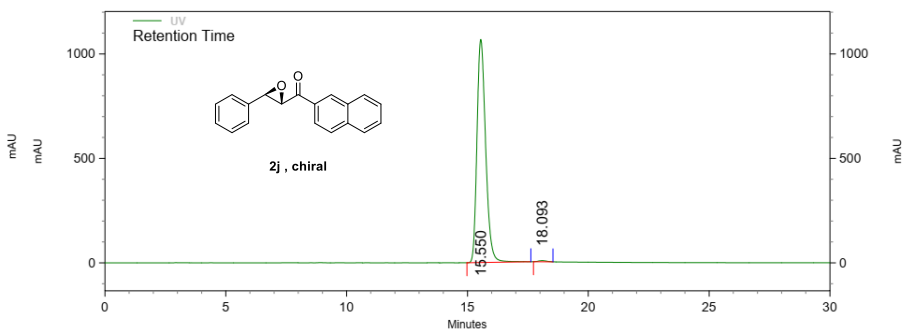
File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-8-22 chiral (AD H Hx iPrOH (90 10) 1flow 30min 254nm) 210310.dat

Acquired: 2021-03-10 오후 3:38:20 **Printed:** 2021-03-10 오후 4:14:47

Analyst: System

Sample ID: lgw-8-22 chiral (AD H Hx iPrOH (90 10) 1flow 30min 254nm) 210310 **Vial:** N/A

Injection Volume: 0



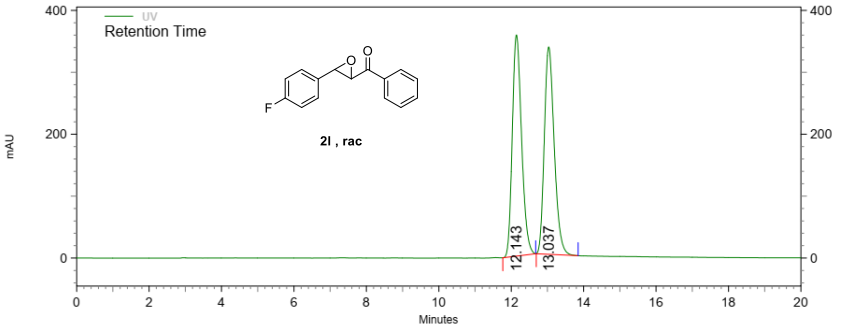
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	15.550	106836338	99.538	mm
	18.093	495984	0.462	MM
Totals		107332322	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-7-91 rac (AD H Hx iPrOH (90 10) 1flow 20min 254nm) 210310.dat
Acquired: 2021-03-10 오후 4:18:12 **Printed:** 2021-03-10 오후 4:40:10

Analyst: System
Sample ID: lgw-7-91 rac (AD H Hx iPrOH (90 10) 1flow 20min 254nm) 210310 **Vial:** N/A **Injection Volume:** 0



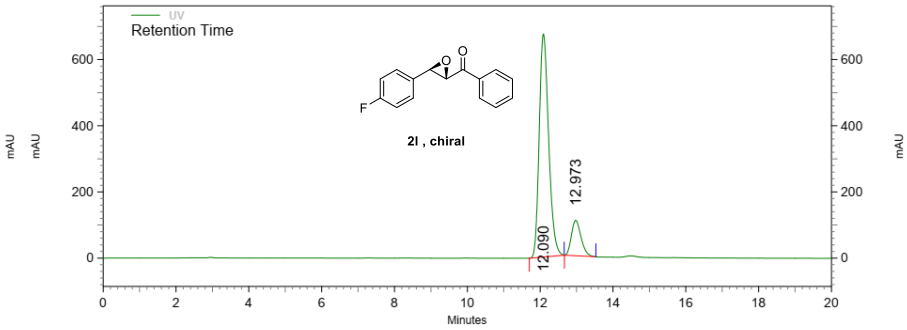
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	12.143	25429965	49.945	MM
	13.037	25485919	50.055	MM
Totals		50915884	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-8-31 chiral (AD H Hx iPrOH (90 10) 1flow 20min 254nm) 210310.dat
Acquired: 2021-03-10 오후 4:41:24 **Printed:** 2021-03-10 오후 5:06:58

Analyst: System
Sample ID: lgw-8-31 chiral (AD H Hx iPrOH (90 10) 1flow 20min 254nm) 210310 **Vial:** N/A **Injection Volume:** 0



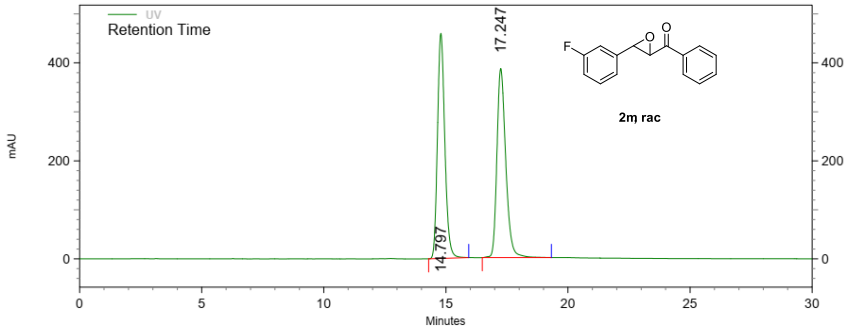
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	12.090	48393887	86.015	MM
	12.973	7868428	13.985	MM
Totals		56262315	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-7-95 rac (AD H Hx iPrOH (95 5) 1flow 30min 254nm) 210312.dat
Acquired: 2021-03-12 오후 4:11:49 **Printed:** 2021-03-12 오후 4:46:38

Analyst: System
Sample ID: lgw-7-95 rac (AD H Hx iPrOH (95 5) 1flow 30min 254nm) 210312 **Vial:** N/A
Injection Volume: 0



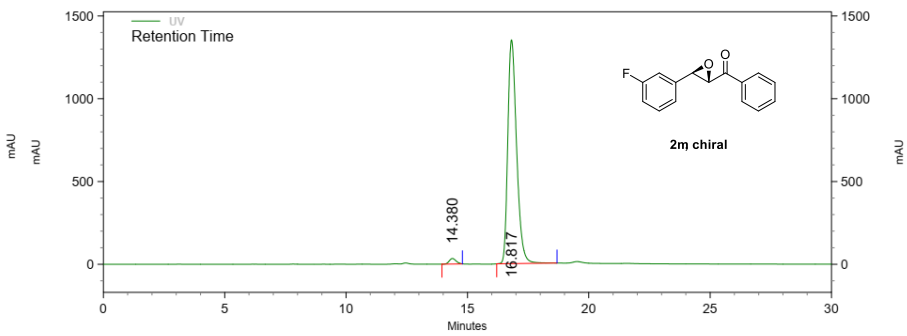
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	14.797	38404297	49.711	MM
	17.247	38850056	50.289	MM
Totals		77254353	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-8-36 chiral (AD H Hx iPrOH (95 5) 1flow 30min 254nm) 210312.dat
Acquired: 2021-03-12 오후 4:49:56 **Printed:** 2021-03-12 오후 5:20:56

Analyst: System
Sample ID: lgw-8-36 chiral (AD H Hx iPrOH (95 5) 1flow 30min 254nm) 210312 **Vial:** N/A
Injection Volume: 0



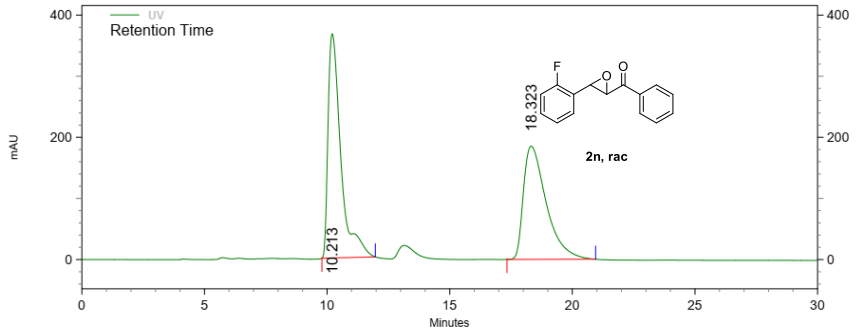
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	14.380	2621472	1.886	BI
	16.817	136342432	98.114	MM
Totals		138963904	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-7-94 rac (AS H Hx EtOH (90 0) 1flow 30min 250nm) 210315.dat
Acquired: 2021-03-15 오후 2:08:36 **Printed:** 2021-03-15 오후 2:40:29

Analyst: System
Sample ID: lgw-7-94 rac (AS H Hx EtOH (90 0) 1flow 30min 250nm) 210315 **Vial:** N/A
Injection Volume: 0



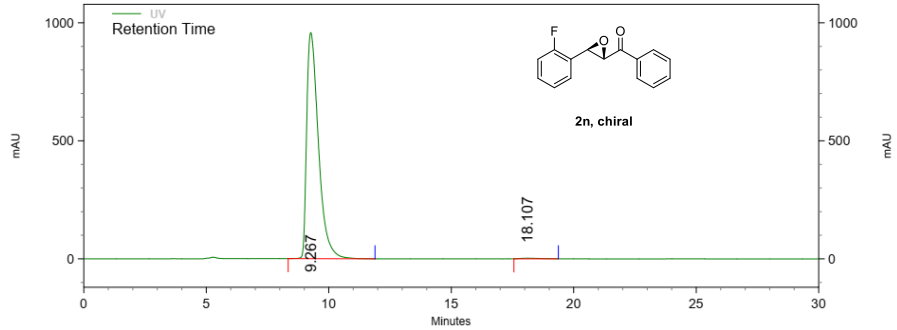
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	10.213	53156554	52.595	MM
	18.323	47910389	47.405	MM
Totals		101066943	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-8-35 chiral (AS H Hx EtOH (90 0) 1flow 30min 250nm) 210315.dat
Acquired: 2021-03-15 오후 2:42:54 **Printed:** 2021-03-15 오후 3:13:50

Analyst: System
Sample ID: lgw-8-35 chiral (AS H Hx EtOH (90 0) 1flow 30min 250nm) 210315 **Vial:** N/A
Injection Volume: 0



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	9.267	127662814	99.547	MM
	18.107	580923	0.453	MM
Totals		128243737	100.000	

Area Percent Report

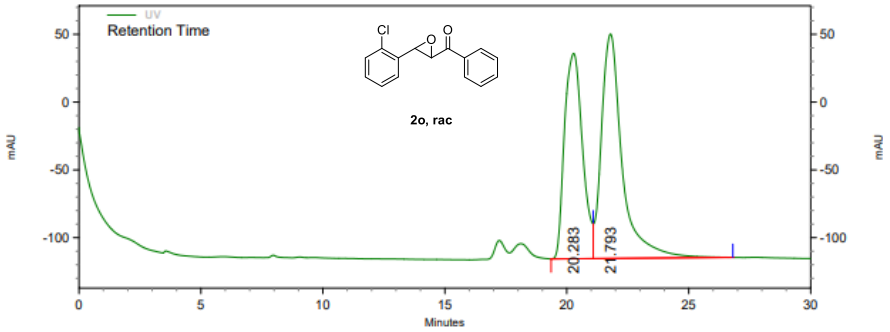
File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-11-83 rac(AD H Hx EtOH 99 1 1flow 254nm 30min) 220330.dat

Acquired: 2022-03-30 오후 2:55:59 **Printed:** 2022-03-30 오후 3:28:36

Analyst: System

Sample ID: lgw-11-83 rac(AD H Hx EtOH 99 1 1flow 254nm 30min) 220330 **Vial:** N/A

Injection Volume: 0



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	20.283	31046592	44.228	BV
	21.793	39149745	55.772	VI
Totals		70196337	100.000	

Area Percent Report

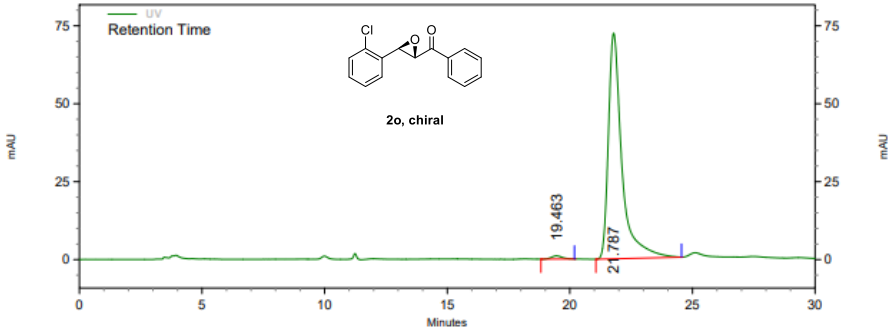
File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-12-2 chiral(AD H Hx EtOH 99 1 1flow 254nm 30min) 220330.dat

Acquired: 2022-03-30 오후 2:23:04 **Printed:** 2022-03-30 오후 2:54:34

Analyst: System

Sample ID: lgw-12-2 chiral(AD H Hx EtOH 99 1 1flow 254nm 30min) 220330 **Vial:** N/A

Injection Volume: 0



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	19.463	125030	1.116	BI
	21.787	11081332	98.884	BB
Totals		11206362	100.000	

Area Percent Report

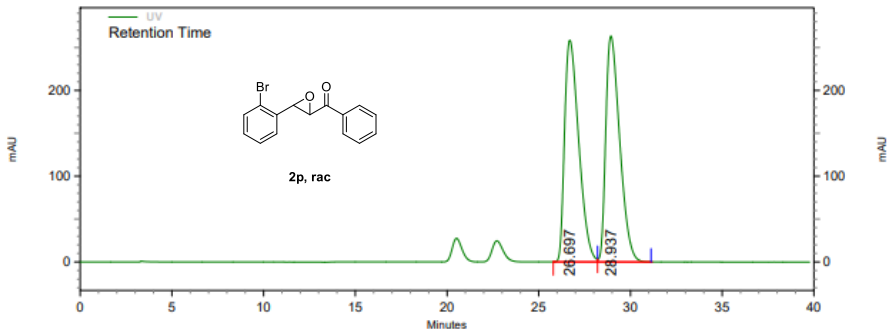
File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-12-46 rac ADH Hx IPrOH 99 1 254nm 1flow 220413.dat

Acquired: 2022-04-13 오후 2:39:44 **Printed:** 2022-04-13 오후 3:20:57

Analyst: System

Sample ID: lgw-12-46 rac ADH Hx IPrOH 99 1 254nm 1flow 220413 **Vial:** N/A

Injection Volume: 0



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	26.697	55528402	49.920	IV
	28.937	55705559	50.080	VI
Totals		111233961	100.000	

Area Percent Report

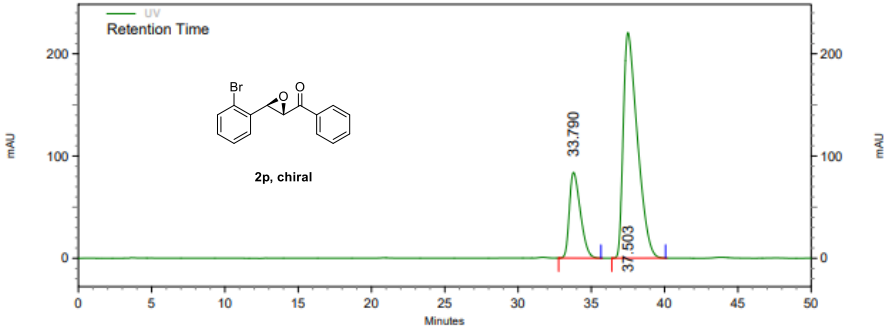
File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-12-46 chiral ADH Hx IPrOH 99 1 254nm 1flow 220413.dat

Acquired: 2022-04-13 오후 3:21:53 **Printed:** 2022-04-13 오후 4:12:49

Analyst: System

Sample ID: lgw-12-46 chiral ADH Hx IPrOH 99 1 254nm 1flow 220413 **Vial:** N/A

Injection Volume: 0



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	33.790	17497647	22.830	II
	37.503	59144444	77.170	BI
Totals		76642091	100.000	

Area Percent Report

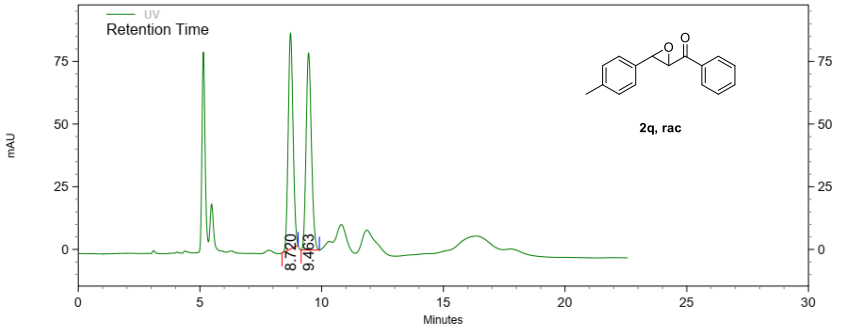
File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw 7-97 rac (OD-H Hx iPrOH 90 10 1flow 30min 250nm) 211026.dat

Acquired: 2021-10-26 오후 11:12:16 **Printed:** 2021-10-26 오후 11:35:12

Analyst: System

Sample ID: lgw 7-97 rac (OD-H Hx iPrOH 90 10 1flow 30min 250nm) 211026 **Vial:** N/A

Injection Volume: 0



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	8.720	4786046	49.826	MM
	9.463	4819490	50.174	MM
Totals		9605536	100.000	

Area Percent Report

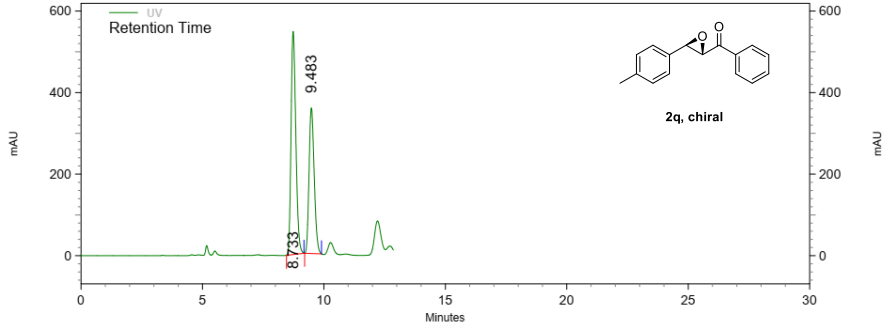
File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw 9-83 1_4Me (OD-H Hx iPrOH 90 10 1flow 30min 250nm) 211026.dat

Acquired: 2021-10-26 오후 11:57:36 **Printed:** 2021-10-27 오전 12:10:49

Analyst: System

Sample ID: lgw 9-83 1_4Me (OD-H Hx iPrOH 90 10 1flow 30min 250nm) 211026 **Vial:** N/A

Injection Volume: 0



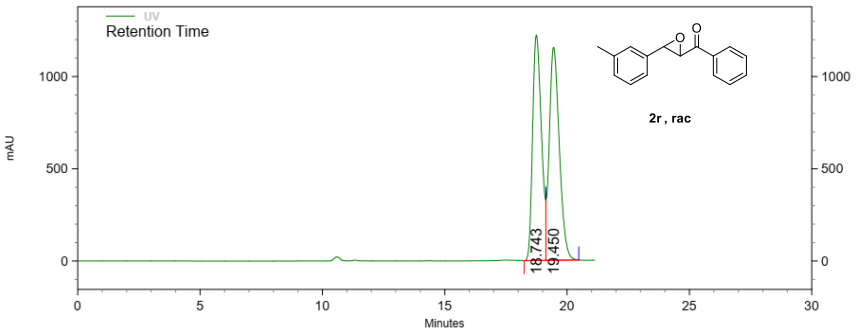
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	8.733	29878968	58.620	MM
	9.483	21091470	41.380	MM
Totals		50970438	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw 7-96 rac (OD-H Hx iPrOH 90 10 05flow 30min 250nm) 211026.dat
Acquired: 2021-10-27 오전 12:36:04 **Printed:** 2021-10-27 오전 12:57:33

Analyst: System
Sample ID: lgw 7-96 rac (OD-H Hx iPrOH 90 10 05flow 30min 250nm) 211026 **Vial:** N/A
Injection Volume: 0



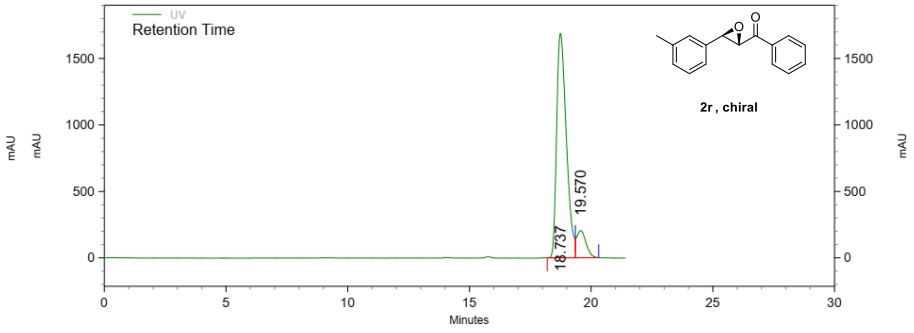
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	18.743	122243995	48.096	Mx
	19.450	131920227	51.904	xM
Totals		254164222	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw 10- 1_4Me (OD-H Hx iPrOH 90 10 05flow 30min 250nm) 211026.dat
Acquired: 2021-10-27 오전 12:59:09 **Printed:** 2021-10-27 오전 1:22:11

Analyst: System
Sample ID: lgw 10- 1_4Me (OD-H Hx iPrOH 90 10 05flow 30min 250nm) 211026 **Vial:** N/A
Injection Volume: 0



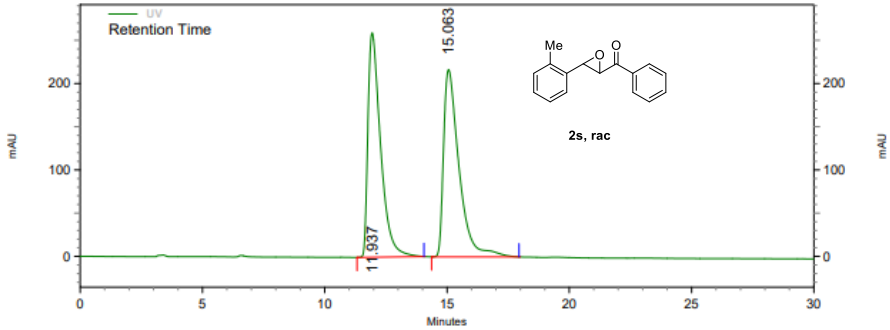
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	18.737	186426011	89.534	Mx
	19.570	21792824	10.466	xM
Totals		208218835	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-11-85 rac (OJ-H Hx i-Pr 90 10 254nm 30min) 220328.dat
Acquired: 2022-03-28 오후 1:26:38 **Printed:** 2022-03-28 오후 2:03:45

Analyst: System
Sample ID: lgw-11-85 rac (OJ-H Hx i-Pr 90 10 254nm 30min) 220328 **Vial:** N/A
Injection Volume: 0



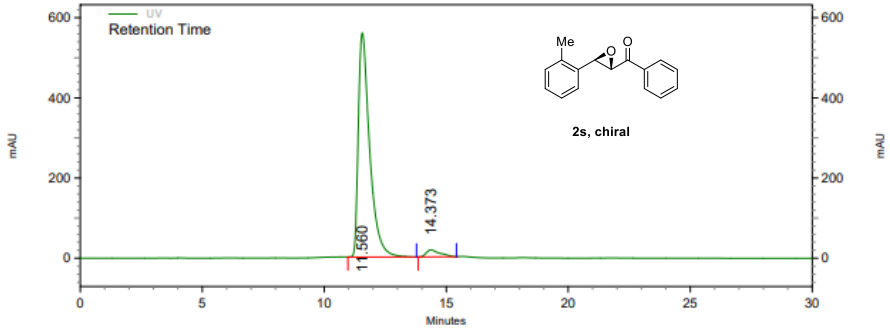
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	11.937	37380107	49.502	MM
	15.063	38132454	50.498	MM
Totals		75512561	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-12-3 chiral(OJ H Hx EtOH 90 10 1flow 254nm 30min) 220330.dat
Acquired: 2022-03-30 오후 3:45:40 **Printed:** 2022-03-30 오후 4:15:53

Analyst: System
Sample ID: lgw-12-3 chiral(OJ H Hx EtOH 90 10 1flow 254nm 30min) 220330 **Vial:** N/A
Injection Volume: 0



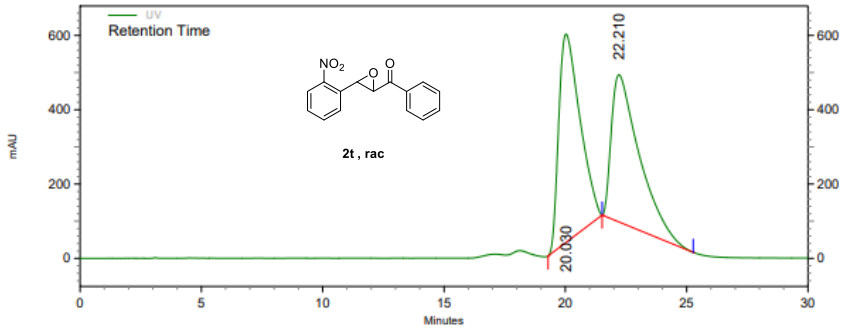
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	11.560	72224032	96.384	MM
	14.373	2709767	3.616	MM
Totals		74933799	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-12-24 rac(OD-H Hx i-PrOH (90 10) 1flow 30min 254nm) 220406.dat
Acquired: 2022-04-06 오전 11:18:51 Printed: 2022-04-06 오전 11:49:15

Analyst: System
Sample ID: lgw-12-24 rac(OD-H Hx i-PrOH (90 10) 1flow 30min 254nm) 220406 Vial: N/A
Injection Volume: 0



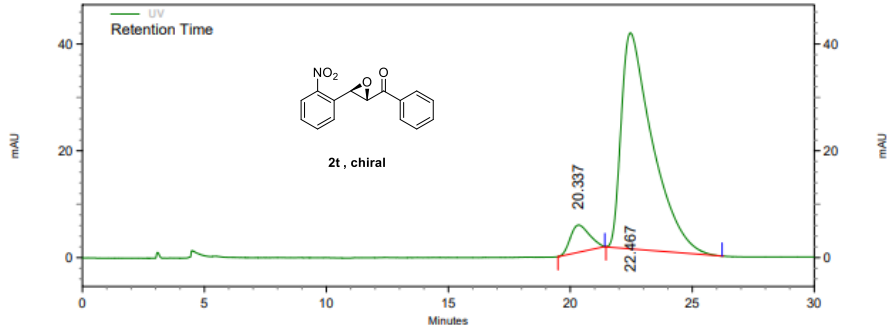
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	20.030	135609117	51.491	MM
	22.210	127755077	48.509	MM
Totals		263364194	100.000	

Area Percent Report

File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\GWLEE\lgw-12-25 chiral(OD-H Hx i-PrOH (90 10) 1flow 30min 254nm) 220406.dat
Acquired: 2022-04-06 오전 11:50:44 Printed: 2022-04-06 오후 12:20:58

Analyst: System
Sample ID: lgw-12-25 chiral(OD-H Hx i-PrOH (90 10) 1flow 30min 254nm) 220406 Vial: N/A
Injection Volume: 0



UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	20.337	1103271	7.093	MM
	22.467	14450583	92.907	MM
Totals		15553854	100.000	