Supporting Information for

Enantioselective Michael Addition of 3-Hydroxy-2-pyridone to Nitroolefins using *Cinchona*-derived Bifunctional Organocatalysts

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(1) General Information

All reagents purchased from commercial sources were used without further purification. TLC analyses were performed using pre-coated TLC plate (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on flash silica gel 230~400 mesh size. The values of enantiomeric excess (ee) of chiral products were determined by HPLC using 4.6 mm × 250 mm Daicel Chiralpak AD-H, Chiralcel OD-H, Chiralpak OJ-H and Chiralpak ID columns. Infrared analyses (KBr pellet) were performed by FT-IR. ^{1}H-NMR spectra were recorded at 400 MHz, 600 MHz or 800 MHz with reference to $CHCl_3$ (δ 7.24), CH_3OH (δ 3.31) and DMSO (δ 2.5) ^{13}C-NMR spectra were obtained by 101 MHz, 151 MHz or 201 MHz spectrometer relative to the central $CDCl_3$ (δ 77.0) or CD_3OD (δ 49.0) resonance. ^{19}F-NMR spectra were obtained by 376 MHz, 564 MHz or 753 MHz spectrometer. Coupling constants (*J*) in ^{1}H-NMR are in Hz. Low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were measured on positive-ion FAB or CI spectrometer. Melting points were measured on melting point apparatus and were uncorrected. Optical rotations were measured on polarimeter and calibrated with pure solvent as blank. The organocatalysts **3a**[1], **3b**[2], **4**[3] and **5a-d**[4] were prepared following the reported procedures. The crystal structure of **8o** was measured by Dr. Huiyeong Ju using a single-crystal X-ray diffractometer at the Korea Basic Science Institute (KBSI) Western Seoul Center

(2) General Procedures

(A) Procedure for preparation of 6.

a) 2,3-Dihydroxypyridine (220 mg, 1.98 mmol), imidazole (337 mg, 4.95 mmol) and anhydrous DMF (5 ml) were added to round bottom flask charged with argon gas. The reaction

mixture was stirred for 15 min and add TBDMSCl (239 mg, 2.18 mmol). The mixture was stirred for another 4 hours. After the reaction was finished, the mixture was diluted with diethyl ether (30 ml), washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Purification of the residue by recrystallization with diethyl ether and hexane to afford 3-((*tert*-butyldimethylsilyl)oxy)pyridin-2(1*H*)-one (400 mg, 90% yield) as a white clear crystal.

b) 3-((*tert*-Butyldimethylsilyl)oxy)pyridin-2(1*H*)-one (400 mg, 1.78 mmol) and diethyl ether (20 mL) were added to round bottom flask charged with argon gas. After lower the temperature to 0 °C, MeLi in ether (1.6 M in diethyl ether, 1.2 mL, 2.14 mmol) was added and stirred for 2 hours. Add 4-Toluenesulfonyl chloride (338 mg, 1.78 mmol) and the reaction was stirred another 30 hours for room temperature. After the reaction was finished, the mixture was diluted with diethyl ether (30 mL), washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Purification of the residue by recrystallization with diethyl ether and hexane to afford 3-((*tert*-butyldimethylsilyl)oxy)-1-tosylpyridin-2(1*H*)-one (492 mg, 73% yield) as a white solid.

c) 3-((*tert*-Butyldimethylsilyl)oxy)-1-tosylpyridin-2(1*H*)-one (1.37 g, 3.6 mmol) and dichloromethane (10 mL) was added to round bottom flask. After lower the temperature to 0 °C, boron trifluoro diethyl etherate (0.49 mL, 3.96 mmol) was added dropwise and the reaction mixture was stirred for 24 hours. After the reaction was finished, the mixture was diluted with dichloromethane (30 mL) and washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Purification of the residue by recrystallization with dichloromethane and hexane to afford **6** (1.01 g, 96% yield) as a white crystal.

(B) General procedure for nitroolefin

Aldehyde (15.0 mmol), nitromethane (0.9 mL, 16.6 mmol) and methanol (10 mL) were added to round bottom flask. After lower the temperature to 0 °C, NaOH (0.72 g, 18.1 mmol) was added portionwise and stirred. After an hour, 2 N HCl (15 mL, 30 mmol) was added slow and stirred for 15 min. After the reaction was finished, the mixture was diluted with dichloromethane and washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Purifications of the residue by flash column chromatography (ethyl acetate/ hexane, 1/100 ~ 1/10. v/v) to afford aliphatic nitroolefin **7**.

(C) Typical experimental procedure for asymmetric Michael reaction.

6 (20 mg, 0.08 mmol), nitroolefin **7** (0.16 mmol), catalyst **5a** (4.2 mg, 0.01 mmol) and dichloromethane (0.7 ml) were added to round bottom flask. At the designated temperature, the reaction mixture was stirred. After the reaction finished, the reaction mixture was concentrated. Purification of the residue by flash column chromatography (ethyl acetate/hexane, 1~100~4/10, v/v) to afford Michael adduct **8**.

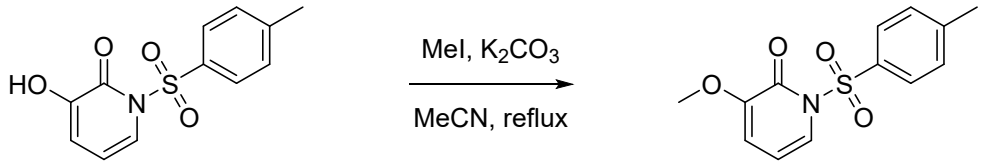
(3) Analytical data

3-Hydroxy-1-tosylpyridin-2(1H)-one (6)

Following the procedure (A) from 2,3-dihydroxypyridine (220 mg, 1.98 mmol), the moleculre **6** was obtained as a white solid (262 mg, overall 50% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.66 (dd, J = 7.5, 1.6 Hz, 1H), 7.36 (d, J = 8.7 Hz, 2H), 6.75 (dd, J = 7.1, 1.6 Hz, 1H), 6.53 (s, 1H), 6.23 (t, J = 7.3 Hz, 1H), 2.44 (s, 3H)ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.41, 147.27, 146.74, 133.12, 129.96, 129.75, 121.47, 114.41, 107.04, 77.43,

77.12, 76.80, 21.94 ppm, Compound **6** conforms to the reported data in the literature.[5]

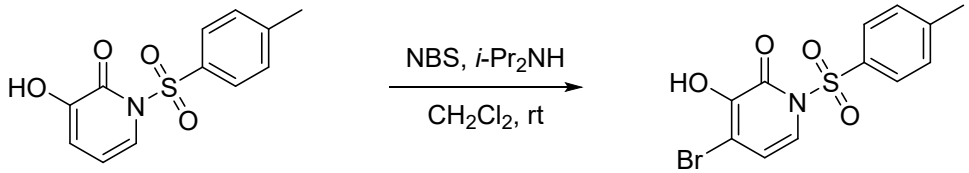
3-methoxy-1-tosylpyridin-2(1*H*)-one (6a)



6 **6a**

To a solution of compound **6** (50 mg, 0.19 mmol) and K_2CO_3 (78 mg, 0.57 mmol) dissolved in acetonitrile (1.9 mL) was added methyl iodide (12.9 μL, 0.21 mmol) in glass screw vial. The reaction mixture was heated at reflux for 3 h. After the reaction was finished, the mixture was quenched with water, extracted with EtOAc (10 mL). The organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the residue by flash column chromatography (ethyl acetate/ hexane, 1/5 to 2/1 gradient. v/v) to afford Synthesis of 3-methoxy-1-tosylpyridin-2(1*H*)-one as a white solid (37 mg, 70% yield), m.p. 146.2–148.6 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.71 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 6.49 (dd, *J* = 7.3, 1.4 Hz, 1H), 6.16 (t, *J* = 7.5 Hz, 1H), 3.72 (s, 3H), 2.41 (s, 3H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 151.0, 146.2, 133.3, 130.2, 129.5, 122.4, 112.4, 105.2, 77.4, 77.1, 76.8, 56.2, 21.9 ppm ; IR (KBr) 1680, 1370, 1175, 1087 cm^{-1}; HRMS (FAB) Calcd for $[C_{13}H_{14}NO_4S]^+$: 280.0644, found 280.0646.

4-bromo-3-hydroxy-1-tosylpyridin-2(1*H*)-one (6b)



6 **6b**

To a solution of compound **6** (50 mg, 0.19 mmol) and Diisopropylamine (2.66 μL, 0.019 mmol)

dissolved in DCM (500 μL) was added *N*-bromosuccinimide (37 mg, 0.21 mmol) portionwise under argon atmosphere. The reaction mixture was stirred for 1 h. After the reaction was finished, the mixture was quenched with water, extracted with DCM (10 mL). The organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the residue by flash column chromatography (ethyl acetate/ hexane, 1/10 to 1/1 gradient. v/v) to afford Synthesis of 4-bromo-3-hydroxy-1-tosylpyridin-2(1*H*)-one as a white solid (31 mg, 52% yield), m.p. 140.3–142.2 °C; ^{1}H-NMR (400 MHz, DMSO-*d*6) δ 10.62 (s, 1H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 6.59 (d, *J* = 7.8 Hz, 1H), 2.38 (s, 3H) ppm ; ^{13}C NMR (101 MHz, DMSO-*d*6) δ 155.1, 147.1, 146.3, 133.2, 130.4, 129.9, 121.2, 113.2, 111.6, 21.77 ppm ; IR (KBr) 1635, 1372, 1180, 668 cm^{-1}; HRMS (FAB) Calcd for $[C_{12}H_{11}BrNO_4S]^+$: 343.9592, found 343.9602.

(*E*)-1-Chloro-4-(3-nitroallyl)benzene (7l)

Following the general procedure (**B**) from the 2-(4-chlorophenyl)acetaldehyde (200 mg, 1.3 mmol), the molecule **7l** was obtained as a yellow oil (91 mg, 44% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30-7.40 (m, 3H), 7.11 (dt, *J* = 8.8, 2.2 Hz, 2H), 6.88 (dt, *J* = 13.3, 1.8 Hz, 1H), 3.55 (dd, *J* = 7.1, 1.6 Hz, 2H) ppm, ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 140.5, 134.2, 133.5, 130.2, 129.3, 34.0 ppm, IR (KBr) 1650, 1523, 1352cm^{-1}; HRMS (FAB) Calcd for $[C_9H_8ClNO_2]^+$: 197.0244, found 197.0247.

(*E*)-1-Methyl-4-(3-nitroallyl)benzene (7m)

Following the general procedure (**B**) from the 2-(*p*-tolyl)acetaldehyde (258 mg, 1.9 mmol), the molecule **7m** was obtained as a yellow oil (146 mg, 43% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37-7.43 (m, 1H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.89 (dt, *J* = 13.4, 1.7

Hz, 1H), 3.53 (dd, *J* = 6.9, 1.4 Hz, 2H), 2.34 (s, 3H) ppm, ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 140.3, 137.2, 132.6, 129.8, 128.7, 34.3, 21.2 ppm, IR (KBr) 1650, 1520, 1350 cm^{-1}; HRMS (FAB) Calcd for $[C_{10}H_{12}NO_2]^+$: 177.0790, found 177.0783.

(*E*)-1-Methoxy-4-(3-nitroallyl)benzene (7n)

Following the general procedure (**B**) from the 2-(4-methoxyphenyl)acetaldehyde (290 mg, 1.9 mmol), the molecule **7n** was obtained as a yellow oil (146 mg, 39% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.35-7.42 (m, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.85-6.89 (m, 3H), 3.79 (s, 3H), 3.51 (dd, *J* = 6.9, 1.8 Hz, 2H) ppm, ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 141.7, 140.3, 129.9, 127.6, 114.5, 55.4, 33.9 ppm, IR (KBr) 1649, 1513, 1351 cm^{-1}; HRMS (FAB) Calcd for $[C_{10}H_{11}NO_3]^+$: 193.0739, found 193.0739.

(*E*)-1-Chloro-4-(4-nitrobut-3-en-1-yl)benzene (7q)

Following the general procedure (**B**) from the 3-(4-chlorophenyl)propanal (672.1 mg, 4.0 mmol), the molecule **7q** was obtained as a yellow oil (616.2 mg, 73% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 4H), 7.09 (dt, *J* = 9.0, 2.3 Hz, 2H), 6.94 (dt, *J* = 13.4, 1.5 Hz, 1H), 2.80 (t, *J* = 7.3 Hz, 2H), 2.56 (qd, *J* = 7.5, 1.4 Hz, 2H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 140.2, 138.2, 132.4, 129.8, 128.9, 33.8, 33.3, 30.0 ppm ; IR (KBr) 1648, 1524, 1351 cm^{-1}; HRMS (FAB) Calcd for $[C_{10}H_{11}ClNO_2]^+$: 211.0400, found 211.0398.

(*E*)-1-Methyl-4-(4-nitrobut-3-en-1-yl)benzene (7s)

Following the general procedure (**B**) from the 3-(4-methylphenyl)propanal (592.4 mg, 4.0 mmol), the molecule **7s** was obtained as a yellow oil (443 mg, 58% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 1H), 7.10 (dd, *J* = 24.7, 7.8 Hz, 4H), 6.95 (d, *J* = 13.7 Hz, 1H), 2.79

(t, *J* = 7.5 Hz, 2H), 2.60-2.54 (m, 2H), 2.33 (s, 3H) ppm, ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 140.0, 136.6, 136.3, 129.5, 128.3, 33.6, 30.3, 21.1 ppm, IR (KBr) 1648, 1524, 1351 cm^{-1}; HRMS (CI) Calcd for $[C_{11}H_{14}NO_2]^+$: 192.1025, found 192.1028.

(*R*)-3-Hydroxy-4-(1-nitropentan-2-yl)-1-tosylpyridin-2(1H)-one (8a)

Following the general procedure (**C**) from **7a** (17.4 mg, 0.16 mmol), the molecule **8a** was obtained as a white solid (28.0 mg, 92% yield) m.p. 141–144 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 6.88 (s, 1H), 6.12 (d, *J* = 7.8 Hz, 1H), 4.72-4.51 (m, 2H), 3.63-3.55 (m, 1H), 2.46 (s, 3H), 1.77-1.55 (m, 3H), 1.26 (td, *J* = 15.1, 7.3 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 146.9, 144.5, 132.8, 130.1, 129.8, 126.8, 120.8, 107.7, 38.8, 32.3, 21.9, 20.3, 13.8 ppm ; IR (KBr) 1655, 1550, 1381, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{17}H_{22}N_2O_6S]^-$: 381.1120, found 381.1118. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak AD-H, hexane : 2-propanol = 80 : 20, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 75.2 min, major isomer 66.6 min, 96% ee, $[\alpha]^{25}_D$ = –3.8 (*c* 1.0, $CHCl_3$).

(*R*)-3-Hydroxy-4-(1-nitroheptan-2-yl)-1-tosylpyridin-2(1H)-one (8b)

Following the general procedure (**C**) from **7b** (21.6 mg, 0.16 mmol), the molecule **8b** was obtained as a yellow oil (27.4 mg, 84% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.12 (d, *J* = 7.8 Hz, 1H), 4.69 (dd, *J* = 12.8, 8.7 Hz, 1H), 4.53 (q, *J* = 6.4 Hz, 1H), 3.60-3.52 (m, 1H), 2.46 (s, 3H), 1.76-1.57 (m, 2H), 1.24 (dd, *J* = 7.5, 2.1 Hz, 7H), 0.85 (t, *J* = 6.6 Hz, 3H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 146.9, 144.5, 132.8, 130.1, 129.8, 126.8, 120.8, 107.7,

38.8, 32.3, 21.9, 20.3, 13.8 ppm ; IR (KBr) 1655, 1551, 1377, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{19}H_{25}N_2O_6S]^+$: 409.1433, found 409.1428. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 26.0 min, major isomer 34.1 min, 97% ee, $[\alpha]^{25}_D = -7.9$ (*c* 1.0, $CHCl_3$).

(*R*)-3-Hydroxy-4-(1-nitroundecan-2-yl)-1-tosylpyridin-2(1H)-one (8c)

Following the general procedure (**C**) from the compound **7c** (31.9 mg, 0.16 mmol), the molecule **8c** was obtained as a clear oil (29.7 mg, 80% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 6.85 (s, 1H), 6.12 (d, *J* = 7.8 Hz, 1H), 4.69 (dd, *J* = 13.0, 8.5 Hz, 1H), 4.53 (q, *J* = 6.4 Hz, 1H), 3.60-3.52 (m, 1H), 2.46 (s, 3H), 1.76-1.58 (m, 2H), 1.26-1.22 (m, 14H), 0.87 (t, *J* = 6.9 Hz, 3H)ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 147.0, 144.5, 132.8, 130.1, 129.8, 126.9, 120.8, 107.8, 39.1, 31.9, 30.2, 29.5, 29.4, 29.4, 29.3, 27.1, 22.7, 22.0, 14.2 ppm ; IR (KBr) 1654, 1552, 1378, 1176 cm^{-1}; HRMS (FAB) Calcd for $[C_{23}H_{33}N_2O_6S]^+$: 465.2059, found 465.2060. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 30.7 min, major isomer 22.3 min, 97% ee, $[\alpha]^{25}_D = -5.3$ (*c* 1.0, $CHCl_3$).

(*R*)-3-Hydroxy-4-(4-methyl-1-nitropentan-2-yl)-1-tosylpyridin-2(1H)-one (8d)

Following the general procedure (**C**) from the compound **7d** (19.5 mg, 0.16 mmol), the molecule **8d** was obtained as a white solid (27.1 mg, 86% yield), m.p. 152–155 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 6.99 (s, 1H), 6.14 (d, *J* = 7.8 Hz, 1H), 4.65 (dd, *J* = 12.9, 8.7 Hz, 1H), 4.50 (q, *J* = 6.3

Hz, 1H), 3.74-3.67 (m, 1H), 2.45 (s, 3H), 1.77-1.69 (m, 1H), 1.43-1.33 (m, 2H), 0.90 (t, *J* = 6.7 Hz, 6H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 147.0, 144.7, 135.1, 132.8, 132.5, 130.1, 129.9, 129.8, 126.8, 120.9, 107.6, 91.0, 78.7, 39.1, 36.8, 25.6, 23.3, 21.9, 21.6 ppm ; IR (KBr) 1655, 1551, 1378, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{18}H_{23}N_2O_6S]^+$: 395.1277, found 395.1278. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel OD-H, hexane : 2-propanol = 95 : 5, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 87.3 min, major isomer 69.3 min, 96% ee, $[\alpha]^{25}_D$ = –4.6 (*c* 1.0, $CHCl_3$).

(*R*)-3-Hydroxy-4-(3-methyl-1-nitrobutan-2-yl)-1-tosylpyridin-2(1H)-one (8e)

Following the general procedure (**C**) from the compound **7e** (17.4 mg, 0.16 mmol), the molecule **8e** was obtained as a white solid (18.0 mg, 59% yield). m.p. 150–151 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 6.72 (s, 1H), 6.09 (d, *J* = 7.8 Hz, 1H), 4.63-4.82 (m, 2H), 3.28 (td, *J* = 9.5, 4.6 Hz, 1H), 2.45 (s, 3H), 1.99-2.12 (m, 1H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.85 (d, *J* = 6.9 Hz, 3H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.66, 146.94, 144.58, 132.84, 130.07, 129.83, 126.61, 120.51, 120.47, 108.49, 76.02, 46.20, 29.36, 22.03, 20.92, 20.62 ppm ; IR (KBr) 1654, 1552, 1375, 1174 cm^{-1}; HRMS (FAB) Calcd for $[C_{17}H_{21}N_2O_6S]^+$: 381.1120, found 381.1123. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak ID, hexane : EtOH = 30 : 70, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 103.0 min, major isomer 115.6 min, 99% ee, $[\alpha]^{25}_D$ = –22.6 (*c* 1.0, $CHCl_3$).

(*R*)-4-(1-Cyclohexyl-2-nitroethyl)-3-hydroxy-1-tosylpyridin-2(1H)-one (8f)

Following the general procedure (**C**) from the compound **7f** (25.8 mg, 0.16 mmol), the

molecule **8f** was obtained as a white solid (21.2 mg, 63% yield), m.p. 191–194 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 2H), 6.63 (s, 1H), 6.07 (d, *J* = 7.8 Hz, 1H), 4.77 (t, *J* = 11.5 Hz, 1H), 4.66 (dd, *J* = 13.1, 4.8 Hz, 1H), 3.35-3.29 (m, 1H), 2.45 (s, 3H), 1.77-1.49 (m, 6H), 1.24-0.90 (m, 6H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 146.9, 144.5, 132.9, 130.1, 129.8, 126.7, 120.4, 108.6, 75.8, 45.1, 38.6, 31.1, 30.9, 26.0, 22.0 ppm ; IR (KBr) 1653, 1550, 1376, 1175, cm^{-1}; HRMS (FAB) Calcd for $[C_{20}H_{25}N_2O_6S]^+$: 421.1433, found 421.1424. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak OJ-H, hexane : EtOH = 90 : 10, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 60.3 min, major isomer 68.1 min, 84% ee, $[\alpha]^{25}_D$ = –3.8 (*c* 1.0, $CHCl_3$).

(*R*)-3-Hydroxy-4-(2-nitro-1-phenylethyl)-1-tosylpyridin-2(1H)-one (8h)

Following the general procedure (**C**) from the compound **7h** (36.5 mg, 0.16 mmol), the molecule **8h** as obtained as a white solid (20.3 mg, 62% yield). m.p. 68.3–72.7 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.26-7.39 (m, 7H), 7.00 (s, 1H), 6.09 (d, *J* = 7.8 Hz, 1H), 5.08-5.14 (m, 1H), 4.90-4.96 (m, 2H), 2.44 (s, 3H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 147.0, 144.0, 136.5, 132.7, 130.1, 129.8, 129.4, 128.5, 127.8, 126.2, 121.1, 107.5, 76.2, 44.0, 22.0 ppm ; IR (KBr) 1685, 1557, 1379, 1178 cm^{-1}; HRMS (FAB) Calcd for $[C_{20}H_{19}N_2O_6S]^+$: 415.0964, found 415.0964. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel OD-H, hexane : 2-propanol = 70 : 30, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 103.0 min, major isomer 115.6 min, 39% ee, $[\alpha]^{25}_D$ = –9.08 (*c* 1.0, $CHCl_3$).

(*R*)-4-(1-(4-Bromophenyl)-2-nitroethyl)-3-hydroxy-1-tosylpyridin-2(1H)-one (8i)

Following the general procedure (**C**) from the compound **7i** (55 mg, 0.16 mmol), the molecule **8i** was obtained as a white solid (22 mg, 56% yield), m.p. 125.4–129.5 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.2 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.94 (s, 1H), 6.05 (d, *J* = 7.8 Hz, 1H), 4.84-5.09 (m, 3H), 2.44 (s, 3H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 147.1, 144.0, 135.6, 132.6, 132.5, 130.1, 129.8, 129.5, 125.5, 122.5, 121.3, 107.2, 76.0, 43.6, 22.0 ppm ; IR (KBr) 1649, 1553, 1360, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{20}H_{18}BrN_2O_6S]^+$: 493.0063, found 493.0078. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel OD-H, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 240 nm) retention time: minor isomer 35.8 min, major isomer 43.6 min, 70% ee, $[\alpha]^{25}_D$ = –3.14 (*c* 1.0, $CHCl_3$).

(*R*)-3-Hydroxy-4-(2-nitro-1-(4-nitrophenyl)ethyl)-1-tosylpyridin-2(1H)-one (8j)

Following the general procedure (**C**) from the compound **7j** (47.5 mg, 0.16 mmol), the molecule **8j** was obtained as a white solid (18.7 mg, 51% yield), m.p. 138.8–142.3 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.2 Hz, H, 7.98 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 6.98 (s, 1H), 6.07 (d, *J* = 7.8 Hz, 1H), 5.00-5.15 (m, 3H), 2.44 (s, 3H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 147.8, 147.3, 144.3, 143.8, 132.5, 130.2, 129.9, 128.9, 124.5, 121.6, 106.9, 75.6, 43.8, 22.0 ppm ; IR (KBr) 1648, 1554, 1522, 1347, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{20}H_{18}N_3O_8S]^+$: 460.0815, found 460.0792. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel OD-H, hexane : 2-propanol : trifluoroacetic acid = 700 : 300 : 1, flow rate = 0.5 ml/min, 23 °C, λ = 240 nm) retention time: minor isomer 80.4 min, major isomer 94.7 min, 68% ee, $[\alpha]^{25}_D$ = –9.6 (*c* 1.0, $CHCl_3$).

(*R*)-3-Hydroxy-4-(1-nitro-3-phenylpropan-2-yl)-1-tosylpyridin-2(1H)-one (8k)

Following the general procedure (**C**) from the compound **7k** (24.6 mg, 0.16 mmol), the molecule **8k** was obtained as a white solid (28.0 mg, 82% yield), m.p. 68–71 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.33-7.24 (m, 4H), 7.16 (d, *J* = 6.4 Hz, 2H), 6.91 (s, 1H), 6.07 (d, *J* = 7.8 Hz, 1H), 4.83 (dd, *J* = 13.6, 9.0 Hz, 1H), 4.57 (dd, *J* = 13.3, 5.5 Hz, 1H), 3.83 (qd, *J* = 8.3, 5.6 Hz, 1H), 3.03 (ddd, *J* = 30.1, 13.8, 8.0 Hz, 2H), 2.49 (s, 3H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 147.0, 144.3, 137.2, 132.8, 130.0, 129.8, 128.9, 128.9, 127.2, 126.5, 120.8, 108.2, 76.0, 41.4, 36.2, 31.7, 22.8, 22.0, 14.2 ppm ; IR (KBr) 1656, 1551, 1376, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{21}H_{21}N_2O_6S]^+$: 429.1120, found 429.1127. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel OD-H, hexane : 2-propanol = 70 : 30, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 28.4 min, major isomer 37.5 min, 99% ee, $[\alpha]^{25}_D$ = –11.0 (*c* 1.0, $CHCl_3$).

(*R*)-4-(1-(4-Chlorophenyl)-3-nitropropan-2-yl)-3-hydroxy-1-tosylpyridin-2(1H)-one (8l)

Following the general procedure (**C**) from the compound **7l** (48.4 mg, 0.16 mmol), the molecule **8l** was obtained as a brown solid (29.7 mg, 80% yield), m.p. 66–71 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.85 (s, 1H), 5.97 (d, *J* = 7.8 Hz, 1H), 4.51-4.79 (m, 2H), 3.70-3.77 (m, 1H), 2.90-3.02 (m, 2H), 2.45 (s, 3H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 147.0, 144.4, 135.7, 133.1, 132.8, 130.3, 130.0, 129.9, 129.0, 125.9, 120.9, 108.1, 76.0, 41.3, 35.4, 22.0 ppm ; IR (KBr) 1654, 1552, 1377, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{21}H_{20}ClN_2O_6S]^+$: 463.0731, found 463.0721. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel OD-H, hexane : 2-propanol : trifluoroacetic acid =

700 : 300 : 1, flow rate = 0.5 ml/min, 23 °C, λ = 240 nm) retention time: major isomer 28.9 min, minor isomer 36.4 min, 99% ee, $[\alpha]^{25}_{D}$ = –104.9 (*c* 1.0, $CHCl_3$).

(*R*)-3-Hydroxy-4-(1-nitro-3-(p-tolyl)propan-2-yl)-1-tosylpyridin-2(1H)-one (8m)

Following the general procedure (**C**) from the compound **7m** (43.4 mg, 0.16 mmol), the molecule **8m** was obtained as a brown solid (33.6 mg, 95% yield), m.p. 132.9–137.6 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.87 (s, 1H), 6.04 (d, *J* = 7.8 Hz, 1H), 4.48-4.80 (m, 2H), 3.73-3.80 (m, 1H), 2.93 (m, 2H), 2.45 (s, 3H), 2.30 (s, 3H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 147.0, 144.3, 136.8, 134.0, 132.8, 130.0, 129.8, 129.6, 128.8, 126.7, 120.7, 108.2, 76.0, 41.4, 35.8, 22.0, 21.1 ppm ; IR (KBr) 1656, 1552, 1377, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{22}H_{23}N_2O_6S]^+$: 443.1277, found 443.1284. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak ID, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 52.3 min, major isomer 67.0 min, 98% ee, $[\alpha]^{25}_{D}$ = –75.0 (*c* 1.0, $CHCl_3$).

(*R*)-3-Hydroxy-4-(1-nitro-3-(p-tolyl)propan-2-yl)-1-tosylpyridin-2(1H)-one (8n)

Following the general procedure (**C**) from the compound **7n** (48.4 mg, 0.16 mmol), the molecule **8n** was obtained as a yellow solid (33.0 mg, 90% yield), m.p. 69.6–72.7 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.83 (s, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.02 (d, *J* = 7.8 Hz, 1H), 4.49-4.79 (m, 2H), 3.70-3.80 (m, 4H), 2.92 (m, 2H), 2.44 (s, 3H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 156.66, 147.0, 144.3, 132.8, 130.0, 130.0, 129.8, 129.1, 126.6, 120.7, 114.2, 108.2, 77.5, 77.1, 76.8, 76.0, 55.3, 41.6, 35.4, 22.0 ppm ; IR (KBr) 1657, 1552, 1377, 1175

cm^{-1}; HRMS (FAB) Calcd for $[C_{22}H_{23}N_2O_7S]^+$: 459.1226, found 459.1221. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak ID, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 240 nm) retention time: minor isomer 75.5 min, major isomer 92.3 min, 98% ee, $[\alpha]^{25}_D$ = –77.9 (*c* 1.0, $CHCl_3$).

(*R*)-3-Hydroxy-4-(1-nitro-4-phenylbutan-2-yl)-1-tosylpyridin-2(1H)-one (8o)

Following the general procedure (**C**) from the compound **7o** (26.7 mg, 0.16 mmol), the molecule **8o** was obtained as a white solid (31.9 mg, 90% yield), m.p. 110–112 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.27-7.23 (m, 2H), 7.19-7.15 (m, 1H), 7.11-7.09 (m, 2H), 7.04 (s, 1H), 6.11 (d, *J* = 7.8 Hz, 1H), 4.73-4.52 (m, 2H), 3.61-3.54 (m, 1H), 2.58-2.53 (m, 2H), 2.44 (s, 3H), 2.16-1.91 (m, 2H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 147.0, 144.7, 140.4, 132.8, 130.2, 129.9, 128.6, 128.4, 126.5, 126.4, 120.9, 108.0, 38.9, 33.3, 31.7, 22.0 ppm ; IR (KBr) 1653, 1551, 1377, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{22}H_{23}N_2O_6S]^+$: 443.1277, found 443.1273. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralcel OD-H, hexane : 2-propanol = 30 : 70, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 32.5 min, major isomer 44.0 min, 99% ee, $[\alpha]^{25}_D$ = –5.5 (*c* 1.0, $CHCl_3$).

(*R*)-4-(4-(4-Fluorophenyl)-1-nitrobutan-2-yl)-3-hydroxy-1-tosylpyridin-2(1H)-one (8p)

Following the general procedure (**C**) from the compound **7p** (29.4 mg, 0.16 mmol), the molecule **8p** was obtained as a white solid (31.0 mg, 84% yield), m.p. 124–126 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.05 (td, *J* = 6.0, 2.6 Hz, 2H), 6.97-6.92 (m, 2H), 6.09 (d, *J* = 7.8 Hz, 1H), 4.72-4.52 (m, 2H), 3.58-3.50 (m, 1H), 2.56-2.50 (m, 2H), 2.47 (s, 3H), 2.14-1.87 (m, 2H) ppm ; ^{13}C NMR

(101 MHz, $CDCl_3$) δ 161.44 (d, *J* = 244.7 Hz, CF), 156.5, 147.2, 147.0, 144.5, 135.9, 132.6, 130.0, 129.8, 129.7, 129.6, 125.9, 120.9, 115.4, 115.2, 107.8, 77.2, 38.8, 32.4, 31.6, 21.9, 14.1 ppm ; IR (KBr) 1655, 1551, 1376, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{22}H_{22}FN_2O_6S]^+$: 461.1183, found 461.1184. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak OJ-H, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 71.3 min, major isomer 85.1 min, > 99% ee, $[\alpha]^{25}_D$ = –19.0 (*c* 1.0, $CHCl_3$).

(*R*)-4-(4-(4-Chlorophenyl)-1-nitrobutan-2-yl)-3-hydroxy-1-tosylpyridin-2(1H)-one (8q)

Following the general procedure (**C**) from the compound **7q** (29.4 mg, 0.16 mmol), the molecule **8q** was obtained as a white solid (32.4 mg, 85% yield), m.p. 48–51 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.23 (dt, *J* = 8.9, 2.3 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.92 (s, 1H), 6.10 (d, *J* = 7.8 Hz, 1H), 4.69 (dd, *J* = 13.1, 8.5 Hz, 1H), 4.55 (q, *J* = 6.6 Hz, 1H), 3.58-3.51 (m, 1H), 2.55-2.49 (m, 2H), 2.46 (s, 3H), 2.14-1.88 (m, 2H)ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 147.1, 144.7, 138.8, 132.7, 132.2, 130.1, 129.9, 129.7, 128.8, 126.0, 121.0, 107.8, 38.8, 32.6, 31.5, 29.8, 22.0 ppm ; IR (KBr) 1653, 1551, 1377, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{22}H_{22}ClN_2O_6S]^+$: 477.0887, found 477.0884. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 40.4 min, major isomer 55.4 min, 99% ee, $[\alpha]^{25}_D$ = –25.0 (*c* 1.0, $CHCl_3$)

(*R*)-4-(4-(4-Bromophenyl)-1-nitrobutan-2-yl)-3-hydroxy-1-tosylpyridin-2(1H)-one (8r)

Following the general procedure (**C**) from the compound **7r** (38.6 mg, 0.16 mmol), the

molecule **8r** was obtained as a brown solid (38.4 mg, 92% yield), m.p. 48–51 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.35-7.39 (m, 5H), 6.94-6.97 (m, 2H), 6.79 (d, *J* = 23.9 Hz, 1H), 6.08 (d, *J* = 7.8 Hz, 1H), 4.50-4.71 (m, 2H), 3.49-3.56 (m, 1H), 2.41-2.51 (m, 2H), 2.45 (s, 3H), 1.83-2.12 (m, 2H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 147.1, 144.7, 138.8, 132.7, 132.2, 130.1, 129.9, 129.7, 128.8, 126.0, 121.0, 107.8, 38.8, 32.6, 31.5, 29.8, 22.0 ppm ; IR (KBr) 1653, 1551, 1377, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{22}H_{22}ClN_2O_6S]^+$: 477.0887, found 477.0884. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 40.4 min, major isomer 55.4 min, 97% ee, $[\alpha]^{25}_D$ = –25.0 (*c* 1.0, $CHCl_3$)

(*R*)-3-Hydroxy-4-(1-nitro-4-(*p*-tolyl)butan-2-yl)-1-tosylpyridin-2(1H)-one (8s)

Following the general procedure (**C**) from the compound **7s** (28.8 mg, 0.16 mmol), the molecule **8s** was obtained as a white solid (34.7 mg, 95% yield), m.p. 135 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.65 (t, *J* = 3.9 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.88 (s, 1H), 6.11 (d, *J* = 7.8 Hz, 1H), 4.73-4.51 (m, 2H), 3.59-3.52 (m, 1H), 2.56-2.49 (m, 2H), 2.46 (s, 3H), 2.32 (d, *J* = 7.3 Hz, 3H), 2.14-1.89 (m, 2H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 147.0, 144.6, 137.3, 136.0, 132.8, 130.1, 129.9, 129.3, 128.2, 126.4, 120.9, 108.1, 38.9, 32.8, 31.8, 22.0, 21.1 ppm ; IR (KBr) 1655, 1550, 1376, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{22}H_{22}N_2O_6S]^+$: 457.1433, found 457.1437. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 39.0 min, major isomer 50.5 min, 99% ee, $[\alpha]^{25}_D$ = –2.3 (*c* 1.0, $CHCl_3$).

(*R*)-3-Hydroxy-4-(4-(4-methoxyphenyl)-1-nitrobutan-2-yl)-1-tosylpyridin-2(1H)-one (8t)

Following the general procedure (**C**) from the compound **7t** (31.3 mg, 0.16 mmol), the molecule **8t** was obtained as a white solid (35.5 mg, 94% yield), m.p. 136–138 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (t, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.03-7.01 (m, 2H), 6.89 (s, 1H), 6.81 (dd, *J* = 6.6, 2.1 Hz, 2H), 6.10 (t, *J* = 7.1 Hz, 1H), 4.73-4.51 (m, 2H), 3.79 (d, *J* = 4.6 Hz, 3H), 3.58-3.51 (m, 1H), 2.54-2.49 (m, 2H), 2.46 (s, 3H), 2.13-1.87 (m, 2H) ppm ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 156.7, 147.0, 144.6, 132.8, 132.4, 130.1, 129.9, 129.3, 126.4, 120.9, 114.0, 108.1, 55.4, 38.9, 32.3, 31.9, 31.7, 22.8, 22.0, 14.2 ppm ; IR (KBr) 1655, 1550, 1376, 1175 cm^{-1}; HRMS (FAB) Calcd for $[C_{23}H_{25}N_2O_6S]^+$: 473.1382, found 473.1388. The enantioselectivity was determined by chiral HPLC analysis (DAICEL Chiralpak ID, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm) retention time: minor isomer 124.3 min, major isomer 173.0 min, 97% ee, $[\alpha]^{25}_D$ = –5.1 (*c* 1.0, $CHCl_3$).

(*R*)-4-(1-Nitro-4-phenylbutan-2-yl)-2-oxo-1-tosyl-1,2-dihydropyridin-3-yl trifluoromethanesulfonate (9)

To a solution of compound **8o** (500 mg, 1.13 mmol) and pyridine (225 μL, 2.82 mmol) dissolved in dry dichloromethane (11 mL) was added trifluoromethanesulfonic anhydride (285 μL, 1.70 mmol) slowly under argon atmosphere at 0°C. The reaction mixture was stirred for 5 min. After the reaction was finished, the mixture was quenched with water, extracted with dichloromethane. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Purification of the residue by flash column chromatography (ethyl acetate/ hexane, 1/4. v/v) to afford compound **9** as a white solid (650 mg, >99% yield),

m.p. 65.4–70.8 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.02-8.07 (m, 3H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.14-7.18 (m, 1H), 7.07 (d, *J* = 6.9 Hz, 2H), 6.10 (d, *J* = 7.8 Hz, 1H), 4.46-4.56 (m, 2H), 3.75-3.82 (m, 1H), 2.49-2.64 (m, 2H), 2.46 (s, 3H), 2.19-1.80 (2H) ppm ; ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.0, 147.4, 144.4, 139.5, 138.7, 132.1, 131.1, 130.4, 130.0, 128.8, 128.2, 126.8, 118.6 (q, *J* = 321.3 Hz, CF_3), 102.2, 76.9, 37.1, 33.1, 32.8, 22.0 ppm ; ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.97 ppm ; IR (KBr) 1685, 1557, 1379, 1178 cm^{-1}; HRMS (FAB) Calcd for $[C_{23}H_{22}F_3N_3O_8S_2]^+$: 575.0770, found 575.0766; $[\alpha]^{25}_D$ = +76.4 (*c* 1.0, $CHCl_3$).

(*R*)-4-(1-Nitro-4-phenylbutan-2-yl)-2-oxo-1,2-dihydropyridin-3-yl trifluoromethanesulfonate (10)

Compound **9** (250 mg, 0.44 mmol), bis(triphenylphosphine)palladium(II) dichloride (30.5 mg, 0.044 mmol), 1,3-bis(diphenylphosphino)propane (35.9 mg, 0.087 mmol) and dimethylformamide (10 mL) was added to glass screw vial charged with argon gas. The reaction mixture was stirred for 10 min and to the solution was added tributylamine (415 μL, 1.74 mmol) and formic acid (49 μL, 1.31 mmol). The mixture was stirred for another 1 hours at 80 °C. After the reaction was finished, the mixture was diluted with dichloromethane, washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Purification of the residue by flash column chromatography (ethyl acetate/ hexane, 90/10. v/v) to afford compound **10** as a white solid (165 mg, 90% yield), m.p. 51.9–55.4 °C; ^{1}H-NMR (400 MHz, CD_3OD) δ 7.44 (d, *J* = 6.9 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.13 (dd, *J* = 14.2, 7.8 Hz, 3H), 6.48 (d, *J* = 6.9 Hz, 1H), 4.71-4.89 (m, 2H), 3.80-3.88 (m, 1H), 2.46-2.63 (m, 2H), 1.86-2.10 (m, 2H) ppm ; ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.0, 145.0, 139.7, 138.2, 134.7, 128.8, 126.7, 118.7 (q, *J* = 320.8 Hz, CF_3), 103.7, 77.5, 36.8, 33.2, 33.0 ppm ; ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.43 ppm ; IR (KBr) 1667, 1557, 1378, 1137 cm^{-1}; HRMS (FAB) Calcd for

$[C_{16}H_{16}F_3N_2O_6S]^+$: 421.0681, found 421.0668; $[\alpha]^{25}_D$ = +57.8 (*c* 1.0, $CHCl_3$).

(*R*)-4-(1-Nitro-4-phenylbutan-2-yl)pyridine-2,3-diyl bis(trifluoromethanesulfonate) (11)

To a solution of compound **10** (124 mg, 0.30 mmol) and pyridine (59 µL, 0.74 mmol) dissolved in dry dichloromethane (3 mL) was added trifluoromethanesulfonic anhydride (74 µL, 0.44 mmol) slowly under argon atmosphere at 0 °C. The reaction mixture was stirred for 5 min. After the reaction was finished, the mixture was quenched with water, extracted with dichloromethane. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Purification of the residue by flash column chromatography (Ethyl acetate/ hexane, 1/3. v/v) to afford compound **11** as a yellow oil (105.3 mg, 65% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 5.0 Hz, 1H), 7.33 (d, *J* = 5.0 Hz, 1H), 7.25-7.28 (m, 2H), 7.18-7.22 (m, 1H), 7.06 (d, *J* = 6.9 Hz, 2H), 4.57-4.68 (m, 2H), 4.00 (dt, *J* = 14.9, 6.9 Hz, 1H), 2.52-2.66 (m, 2H), 2.00-2.21 (m, 2H) ppm ; ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.7, 148.3, 147.2, 139.2, 132.6, 128.9, 128.2, 126.9, 122.9, 118.5 (q, *J* = 321.0 Hz, CF_3), 118.4 (q, *J* = 321.0 Hz, CF_3), 77.7, 36.8, 34.2, 33.0 ppm ; ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.04, 72.26 ppm ; IR (KBr) 1559, 1378, 1150 cm^{-1}; HRMS (FAB) Calcd for $[C_{17}H_{15}F_6N_2O_8S_2]^+$: 553.0174, found 553.0180. $[\alpha]^{25}_D$ = +13.4 (*c* 1.0, $CHCl_3$).

(*R*)-4-(1-Nitro-4-phenylbutan-2-yl)-2-phenylpyridin-3-yl trifluoromethanesulfonate (12)

Compound **11** (10.3 mg, 0.018 mmol), Pd(dppf)Cl_2 CH_2Cl_2 (4.4 mg, 0.0054 mmol), phenyl boronic acid (6.6 mg, 0.054 mmol) and sodium carbonate (17.5 mg, 0.054 mmol) dissolved in 1,4-dioxane (0.5 mL) and water (0.1 mL) was added to a glass microwave vial. The reaction mixture was heated to 100 °C under microwave irradiation for 1 h. The resulting mixture was quenched with water, extracted with dichloromethane. The organic phase was washed with

brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Purification of the residue by flash column chromatography (ethyl acetate/ hexane, 1/3. v/v) to afford compound **12** as a pale yellow oil (5.6 mg, 62% yield), ^{1}H-NMR (400 MHz, CD_3OD) δ 9.92 (d, *J* = 5.5 Hz, 1H), 8.92 (d, *J* = 5.5 Hz, 1H), 8.88-8.90 (m, 2H), 8.76-8.79 (m, 3H), 8.51-8.55 (m, 2H), 8.44 (dd, *J* = 7.0, 5.4 Hz, 3H), 6.19 (ddd, *J* = 73.6, 13.7, 7.3 Hz, 2H), 5.28-5.35 (m, 1H), 3.86-3.99 (m, 2H), 3.34-3.53 (m, 2H) ppm ; ^{13}C NMR (201 MHz, CD_3OD) δ 13C-NMR (201 MHz, CD_3OD) δ 153.8, 149.0, 145.5, 142.0, 140.3, 135.6, 129.5, 129.2, 128.2, 128.0, 126.0, 122.2, 118.0 (q, *J* = 320.0 Hz, CF_3) 78.0, 36.9, 34.2, 32.8 ppm ; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.15 ppm ; IR (KBr) 1553, 1375, 1039 cm^{-1}; HRMS (FAB) Calcd for $[C_{22}H_{20}F_3N_2O_5S]^+$: 481.1045, found 481.1041. $[\alpha]^{25}_D$ = +47.8 (*c* 1.0, CH_3OH).

(4) References

(1) Medina, S.; Harper, M. J.; Balmond, E. I.; Miranda, S.; Crisenza, G. E. M.; Coe, D. M.; McGarrigle, E. M.; Galan, M. C. Stereoselective Glycosylation of 2-Nitrogalactals Catalyzed by a Bifunctional Organocatalyst. *Org. Lett.* **2016**, *18* (17), 4222–4225. https://doi.org/10.1021/acs.orglett.6b01962.

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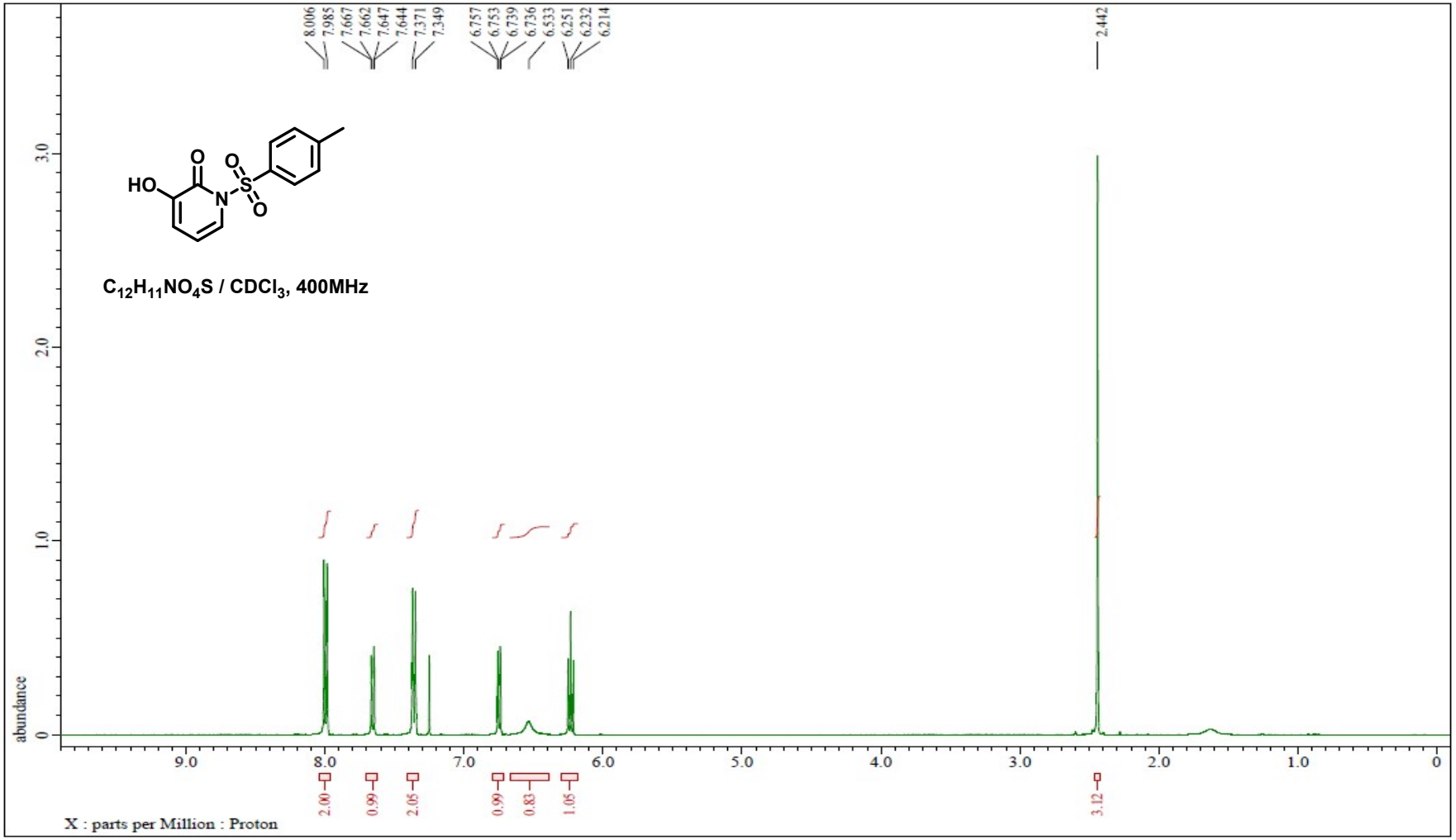
Activity, Enantioselectivity and Catalyst Recyclability in Dynamic Kinetic Resolution of Racemic Azlactones. *Chem. Commun.* **2009**, No. 46, 7224. https://doi.org/10.1039/b917882a.

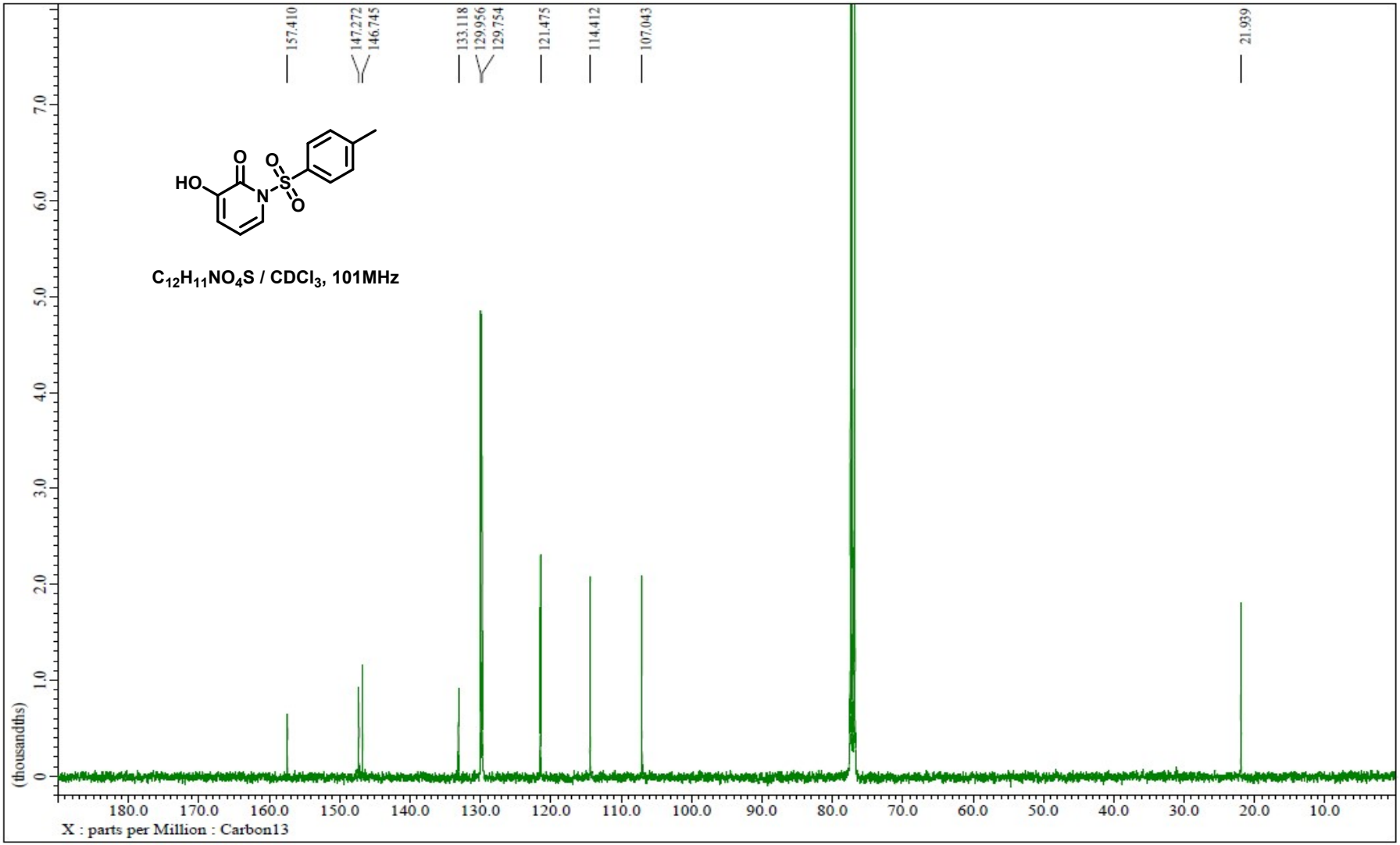
(5) Böhm, M.; Lorthiois, E.; Meyyappan, M.; Vasella, A. Synthesis and Evaluation as Glycosidase Inhibitors of Isoquinuclidines Mimicking a Distorted β -Mannopyranoside. *Helv. Chim. Acta* **2003**, *86* (11), 3787–3817. https://doi.org/10.1002/hlca.200390320.

(5) ^{1}H & ^{13}C NMR Spectra

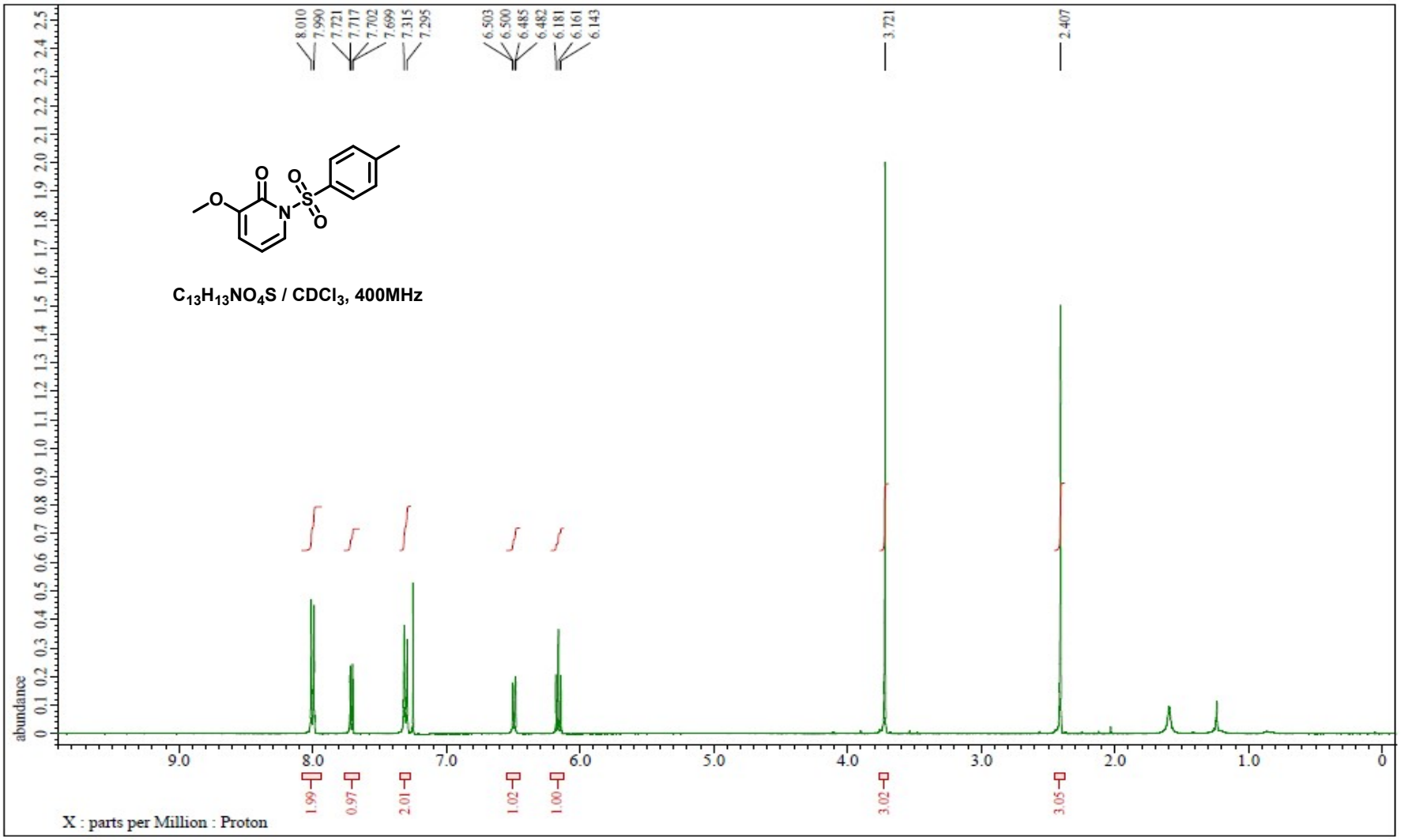
^{1}H-NMR of compound **(6)**



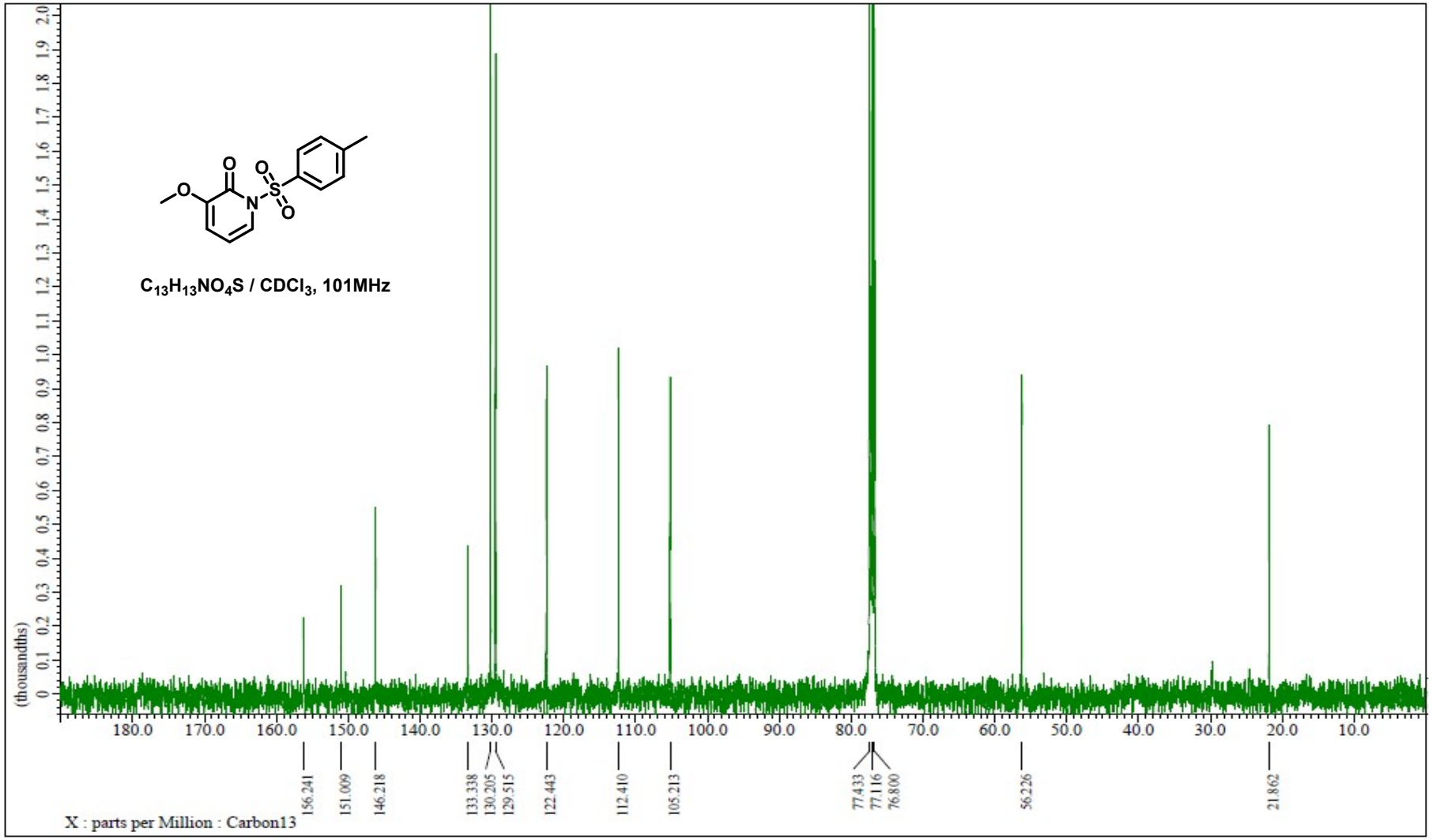
^{13}C -NMR of compound **(6)**



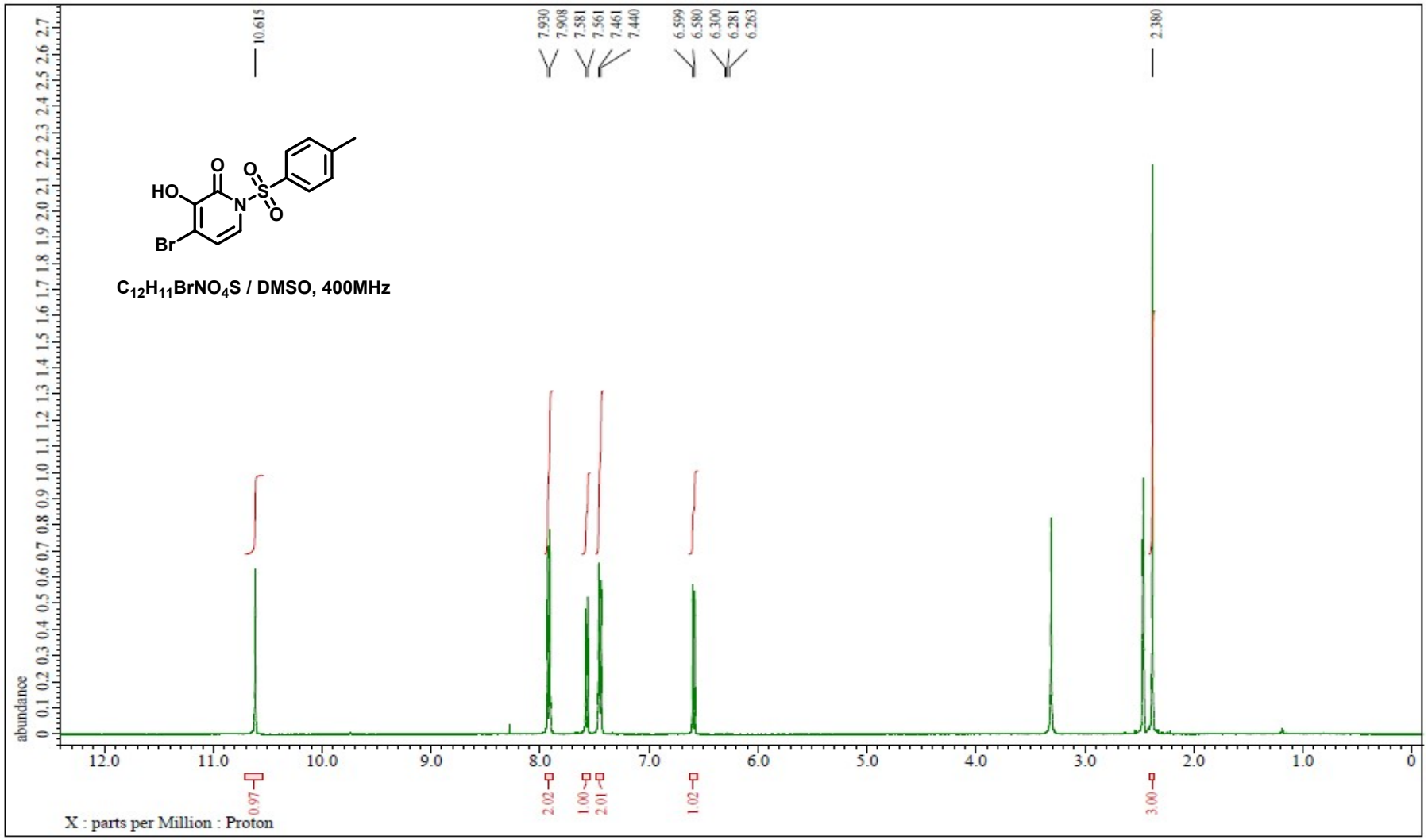
[1]H -NMR of compound **(6a)**



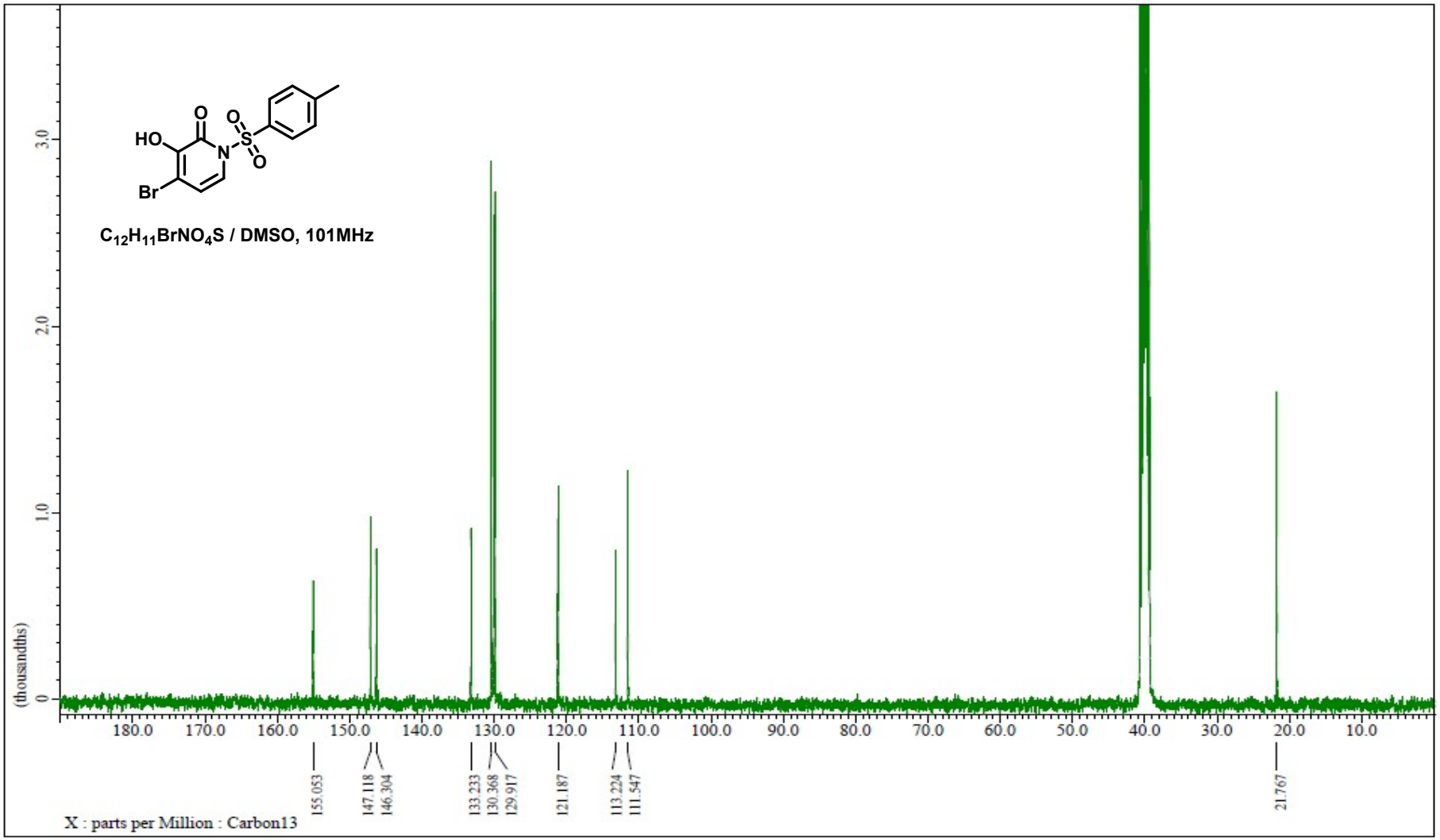
^{13}C -NMR of compound **(6a)**


C13H13NO4S / CDCl3, 101MHz
(thousandths)
X : parts per Million : Carbon13
156.241
151.009
146.218
133.338
130.205
129.515
122.443
112.410
105.213
77.433
77.116
76.800
56.226
21.862

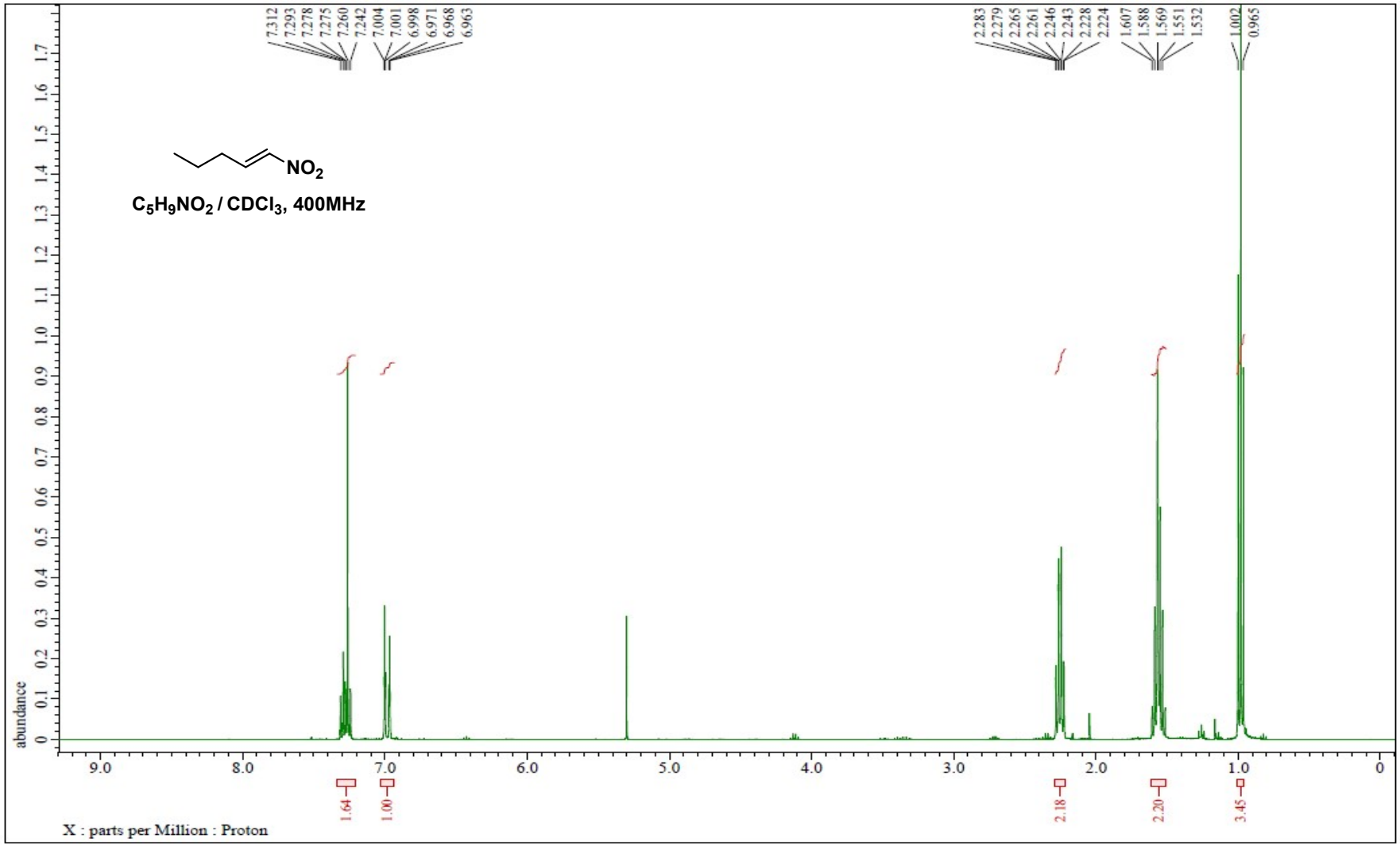
^{1}H -NMR of compound **(6b)**


10.615
7.930
7.908
7.581
7.561
7.461
7.440
6.599
6.580
6.300
6.281
6.263
2.380
HO
O
O
S
O
N
Br
C12H11BrNO4S / DMSO, 400MHz
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.97
2.02
1.00
2.01
1.02
3.00
X : parts per Million : Proton

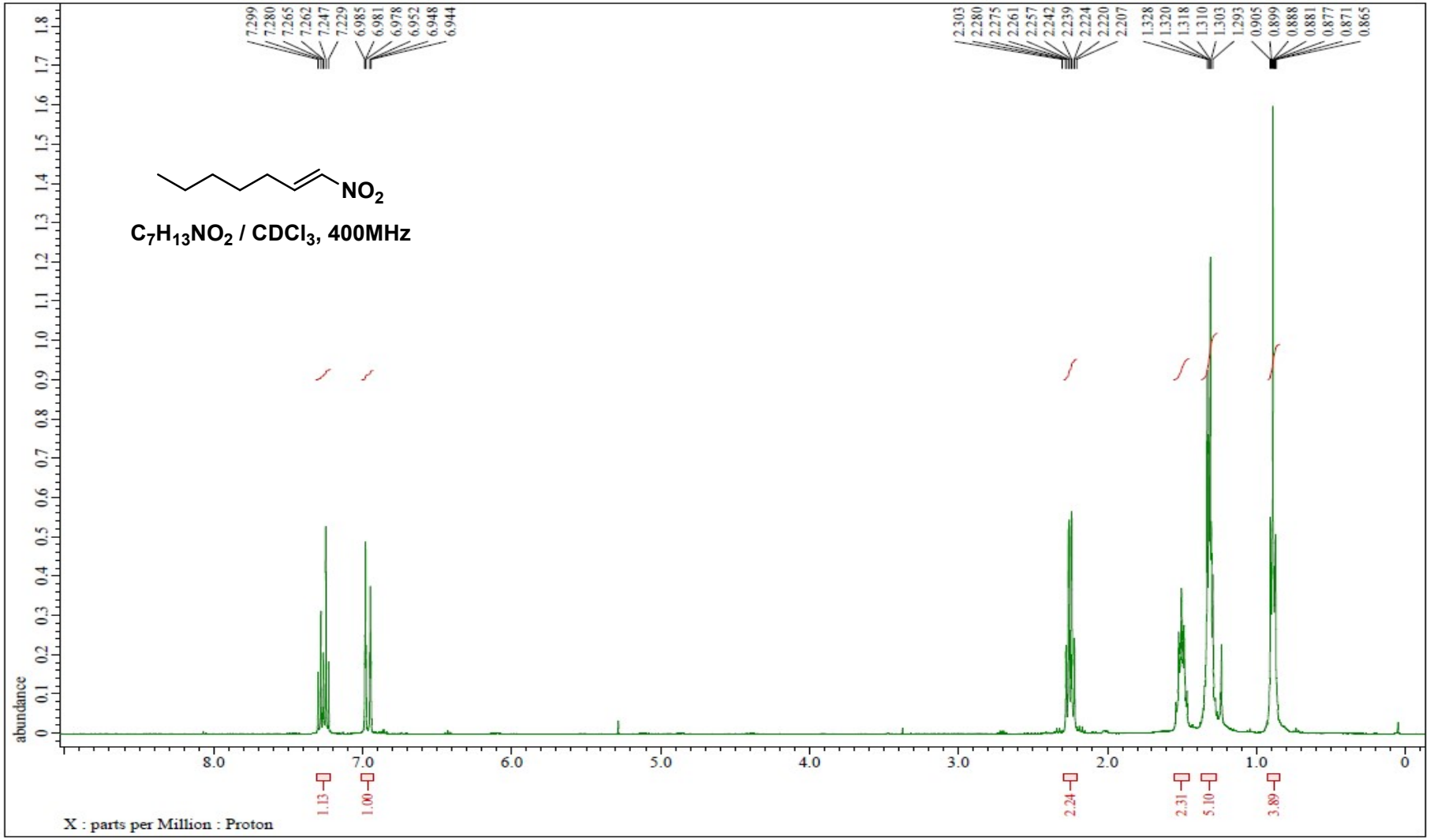
^{13}C -NMR of compound **(6b)**


HO
O
O
S
O
N
Br
C12H11BrNO4S / DMSO, 101MHz
(thousandths)
3.0
2.0
1.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
155.053
147.118
146.304
133.233
130.368
129.917
121.187
113.224
111.547
21.767
X : parts per Million : Carbon13

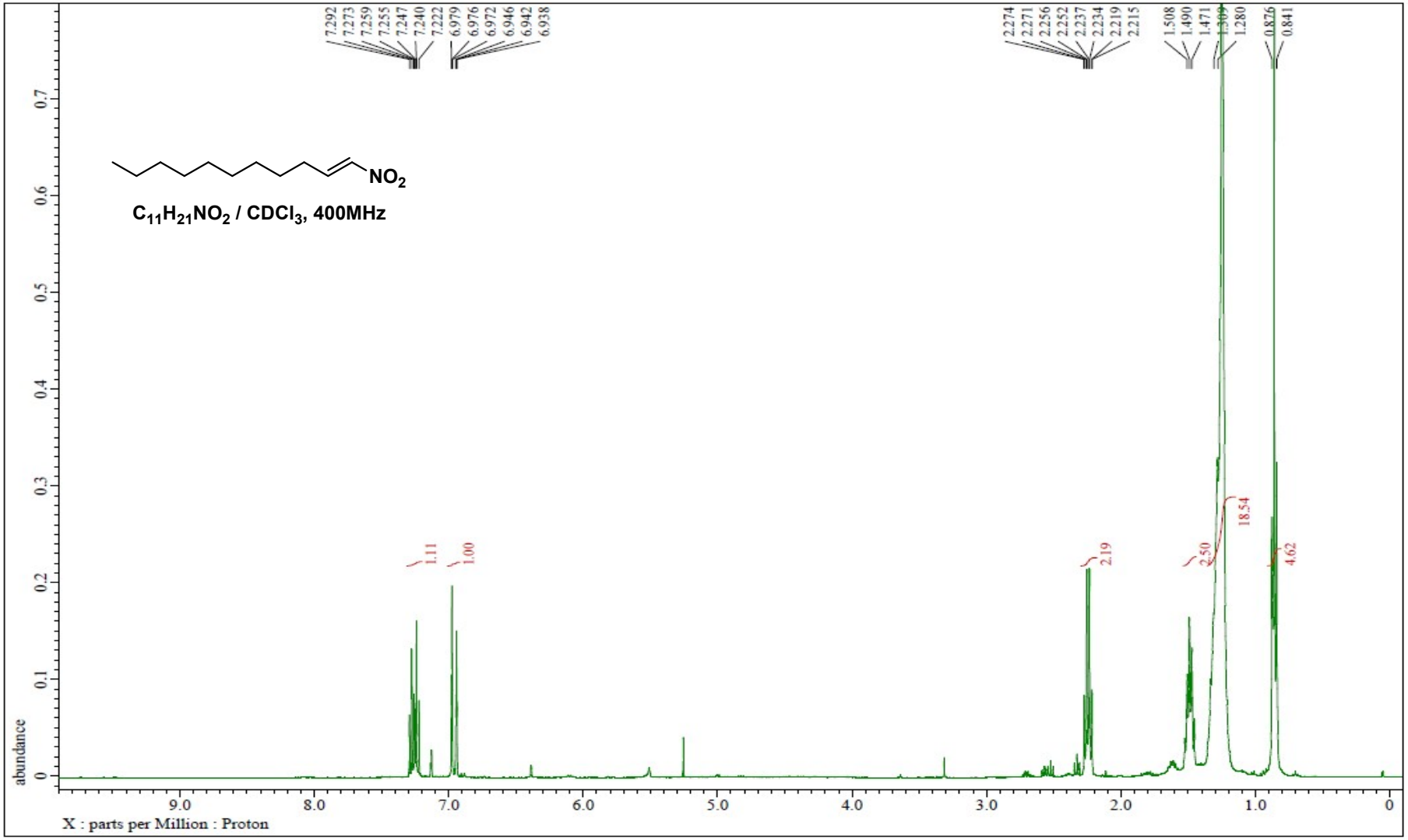
[1]H-NMR of compound **(7a)**



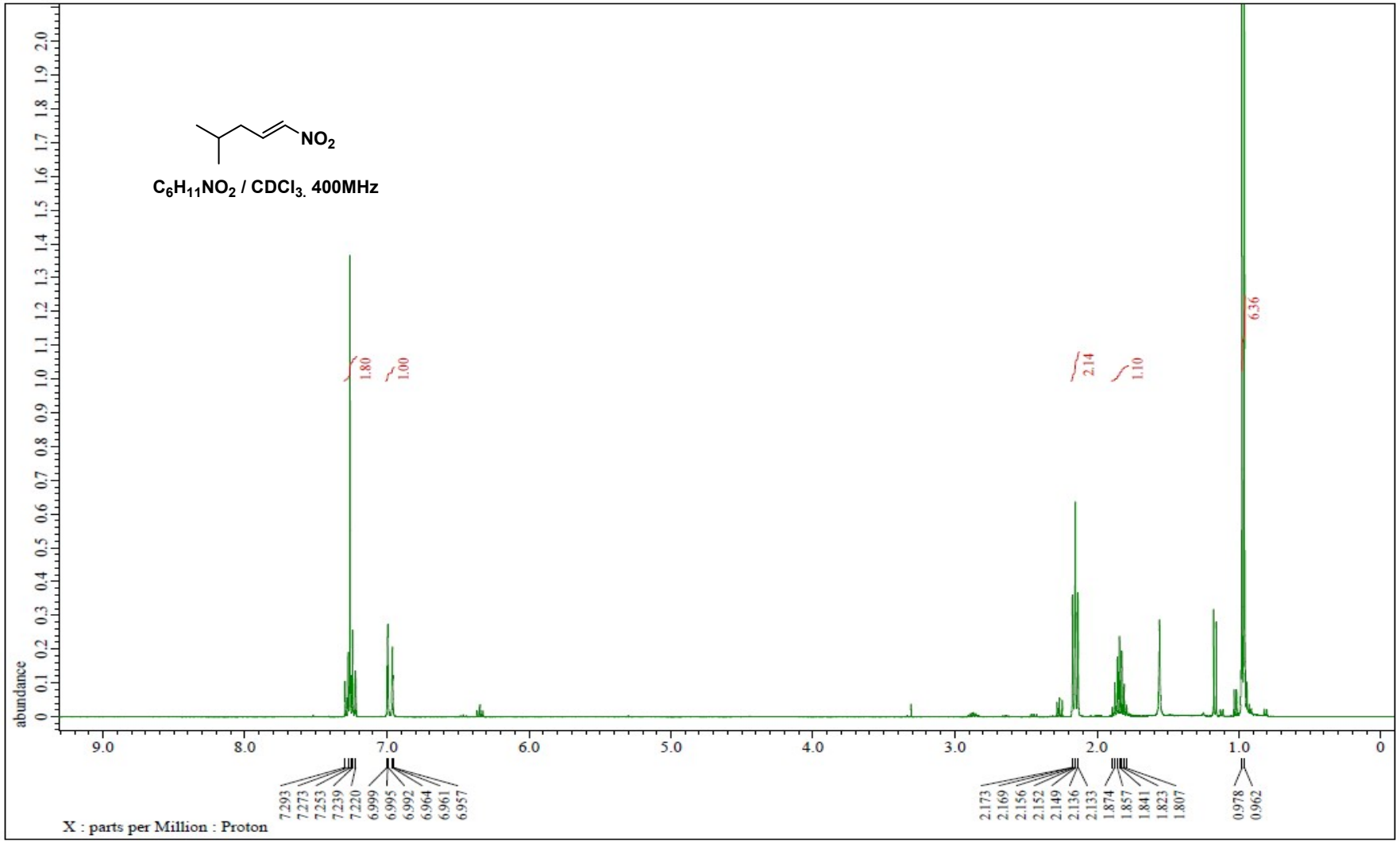
[1]H-NMR of compound **(7b)**



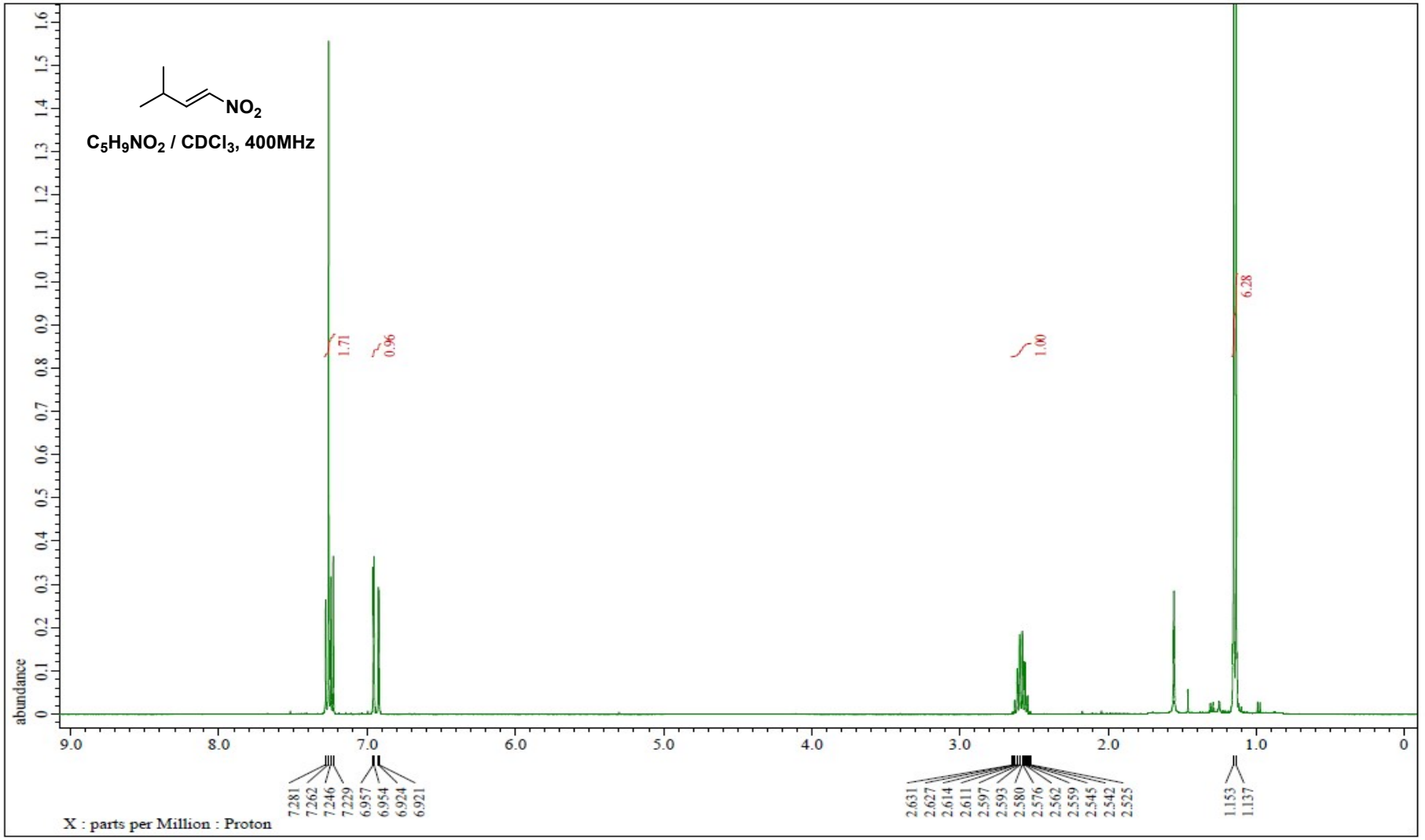
[1]H-NMR of compound **(7c)**



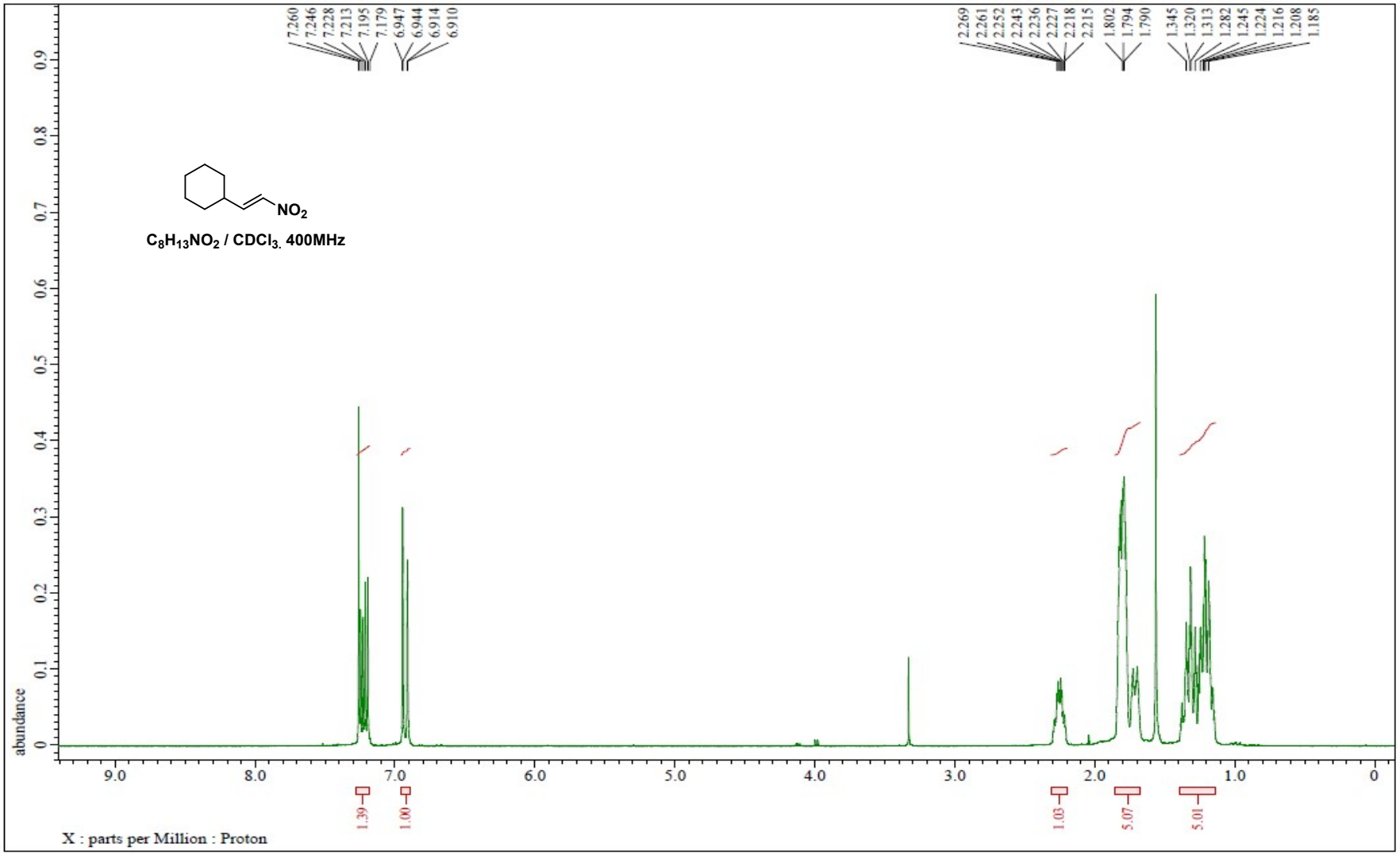
[1]H-NMR of compound **(7d)**



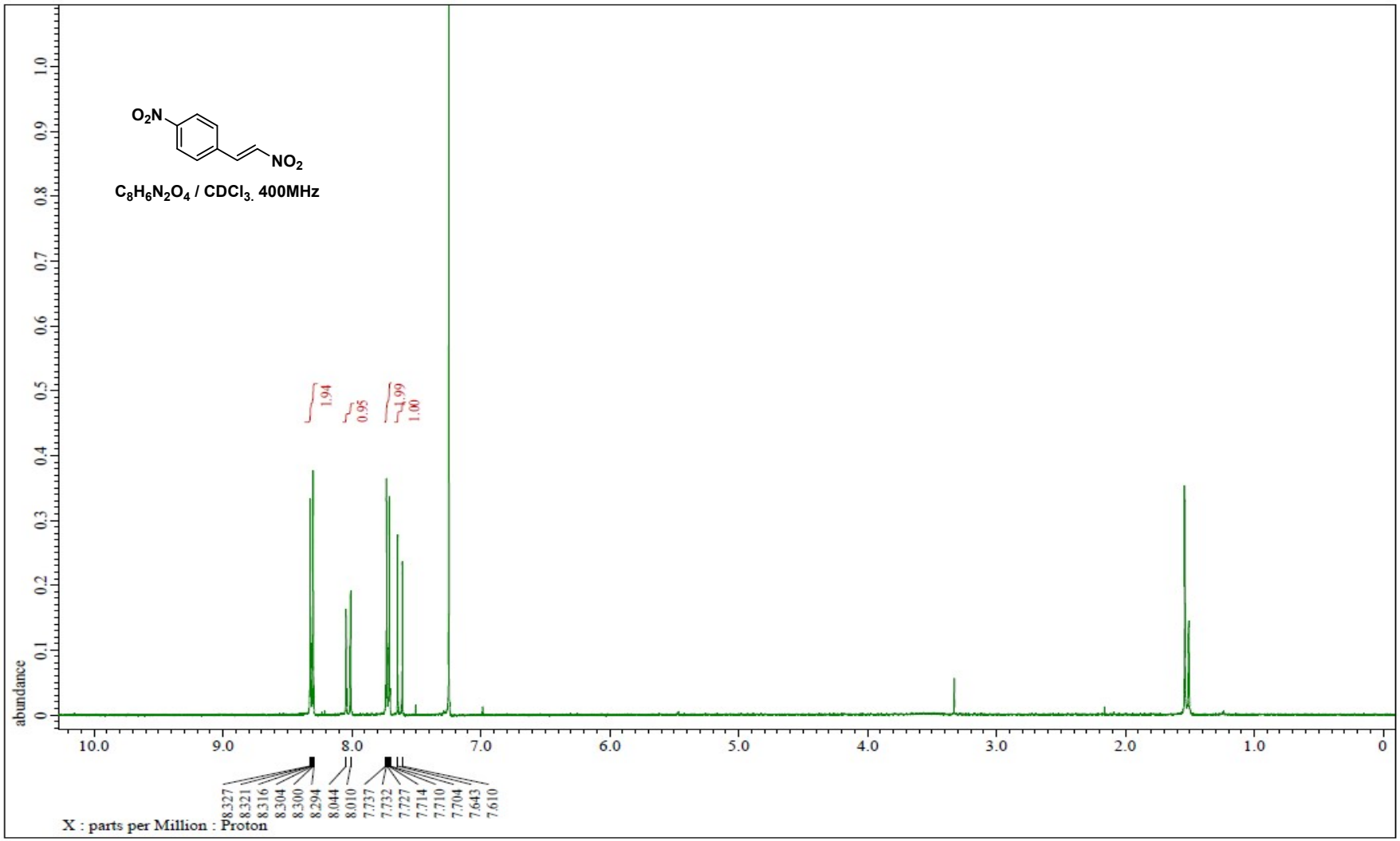
[1]H-NMR of compound **(7e)**



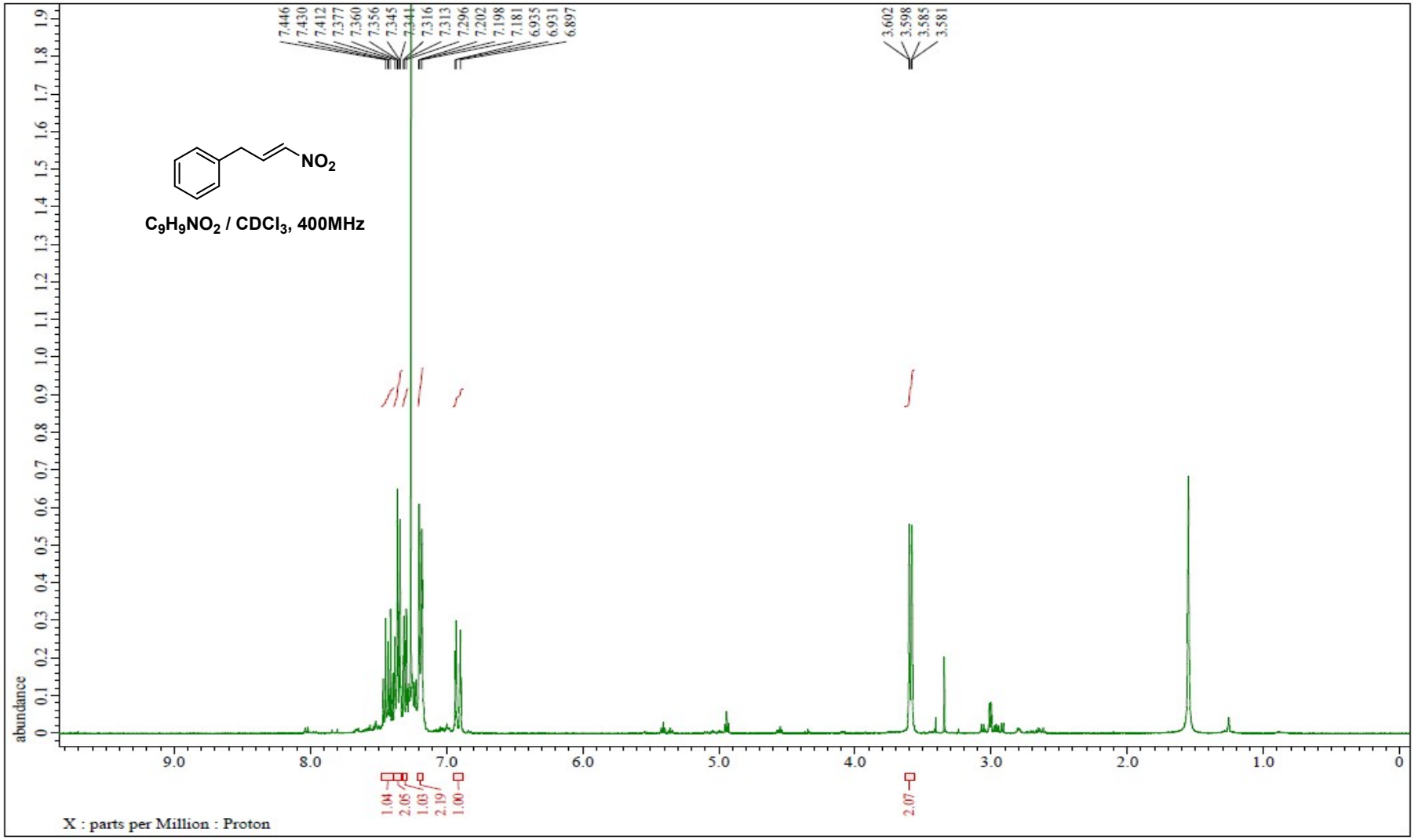
[1]H -NMR of compound **(7f)**



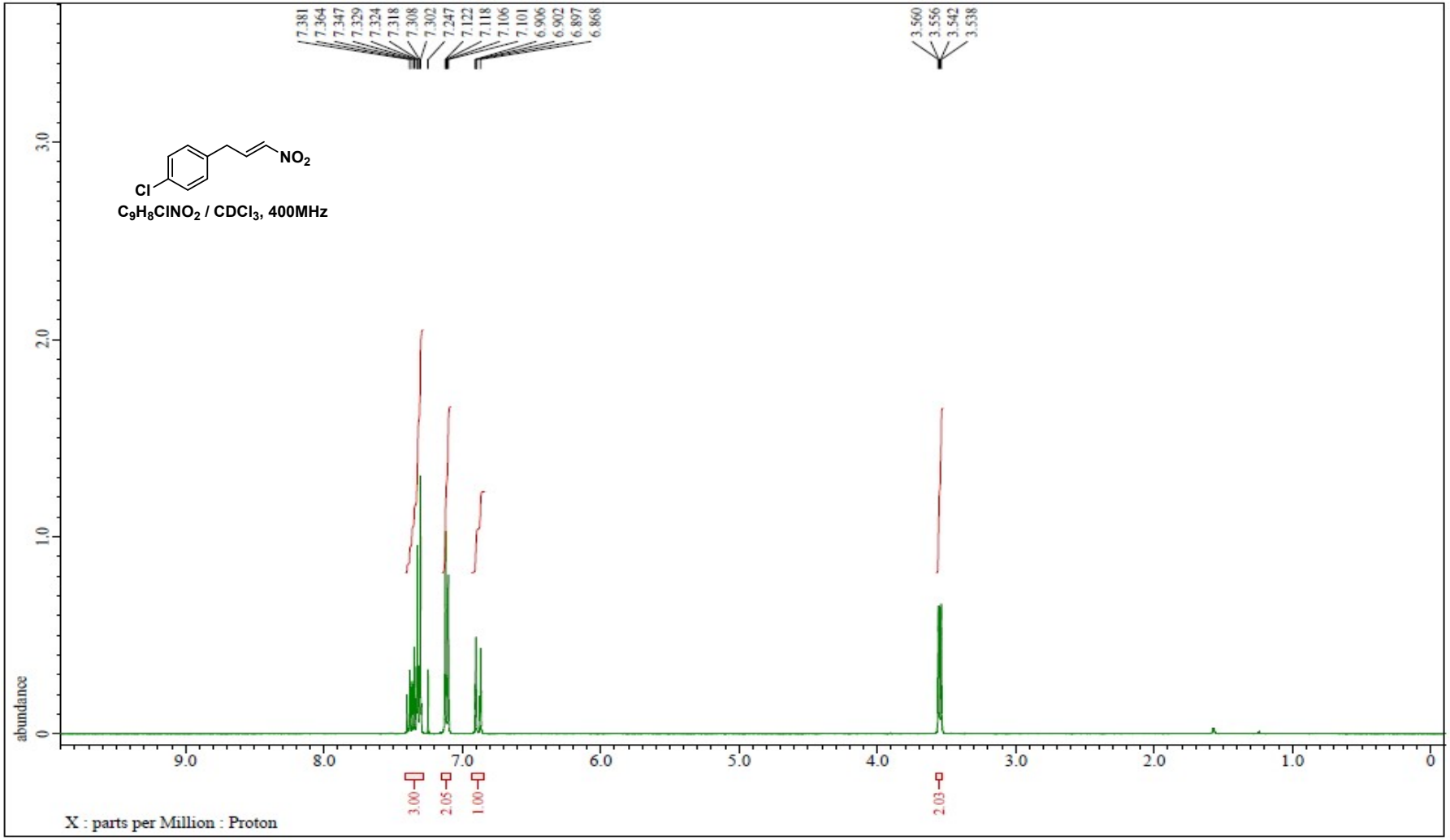
[1]H -NMR of compound **(7j)**



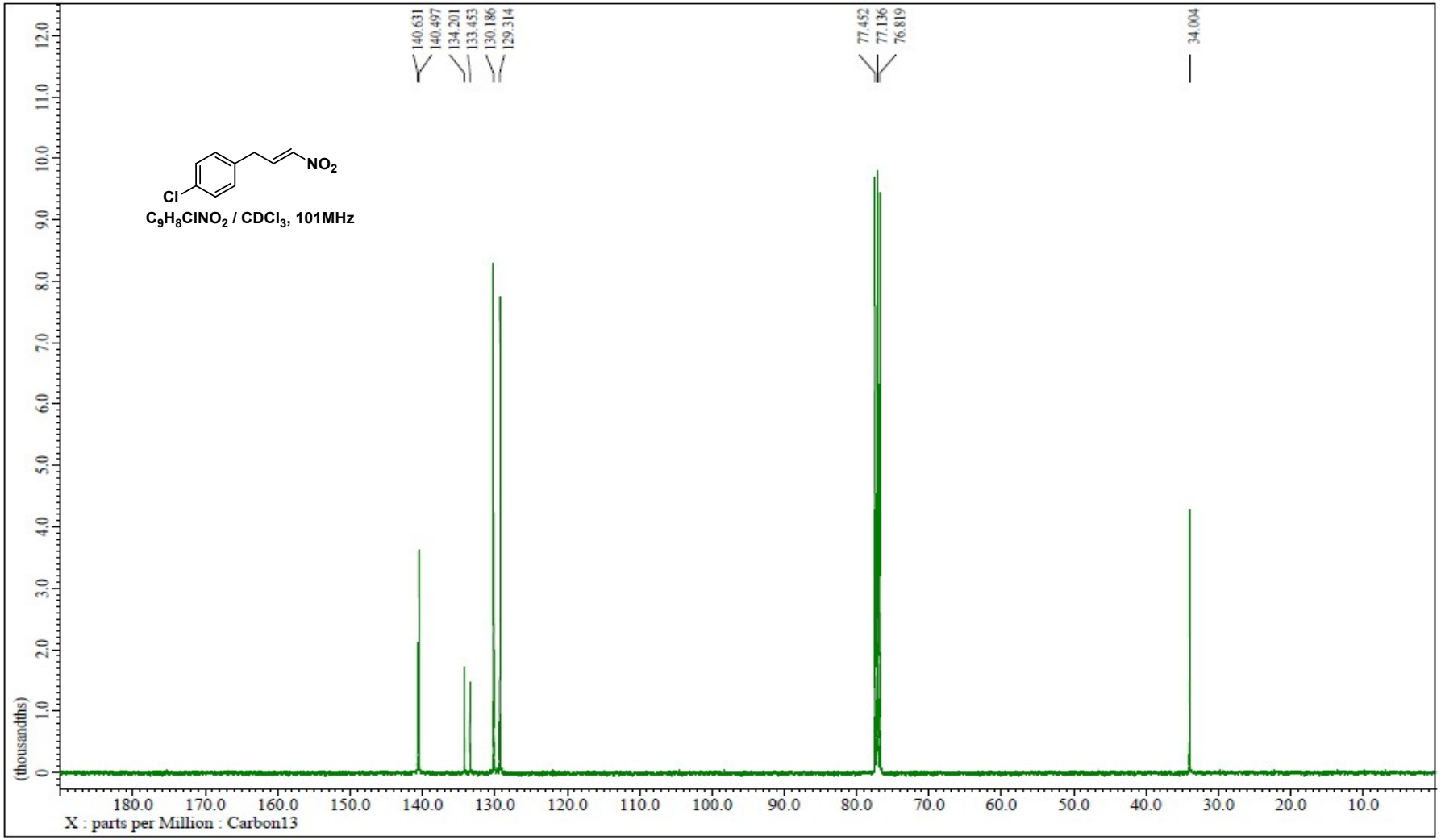
[1]H -NMR of compound **(7k)**



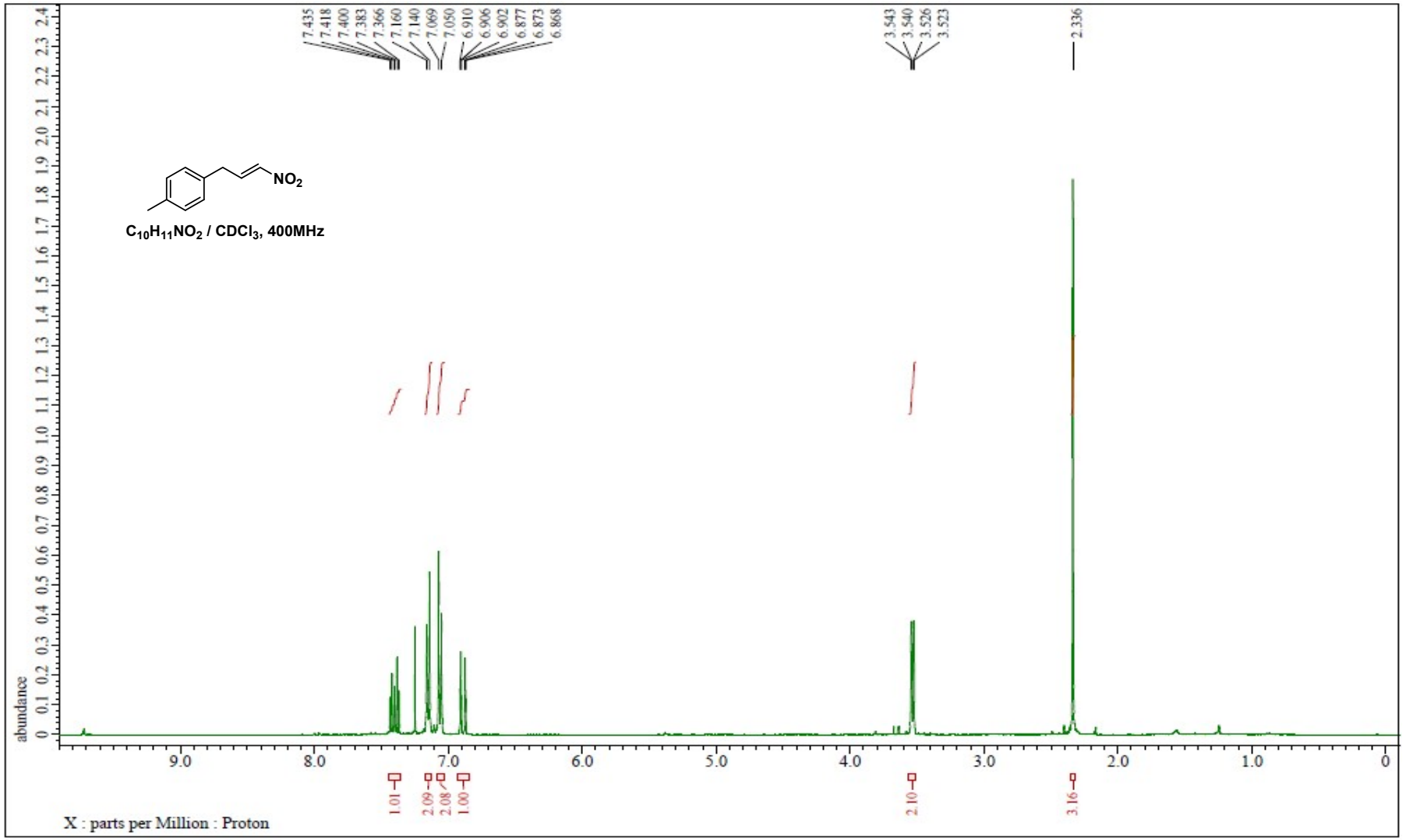
[1]H -NMR of compound **(7l)**



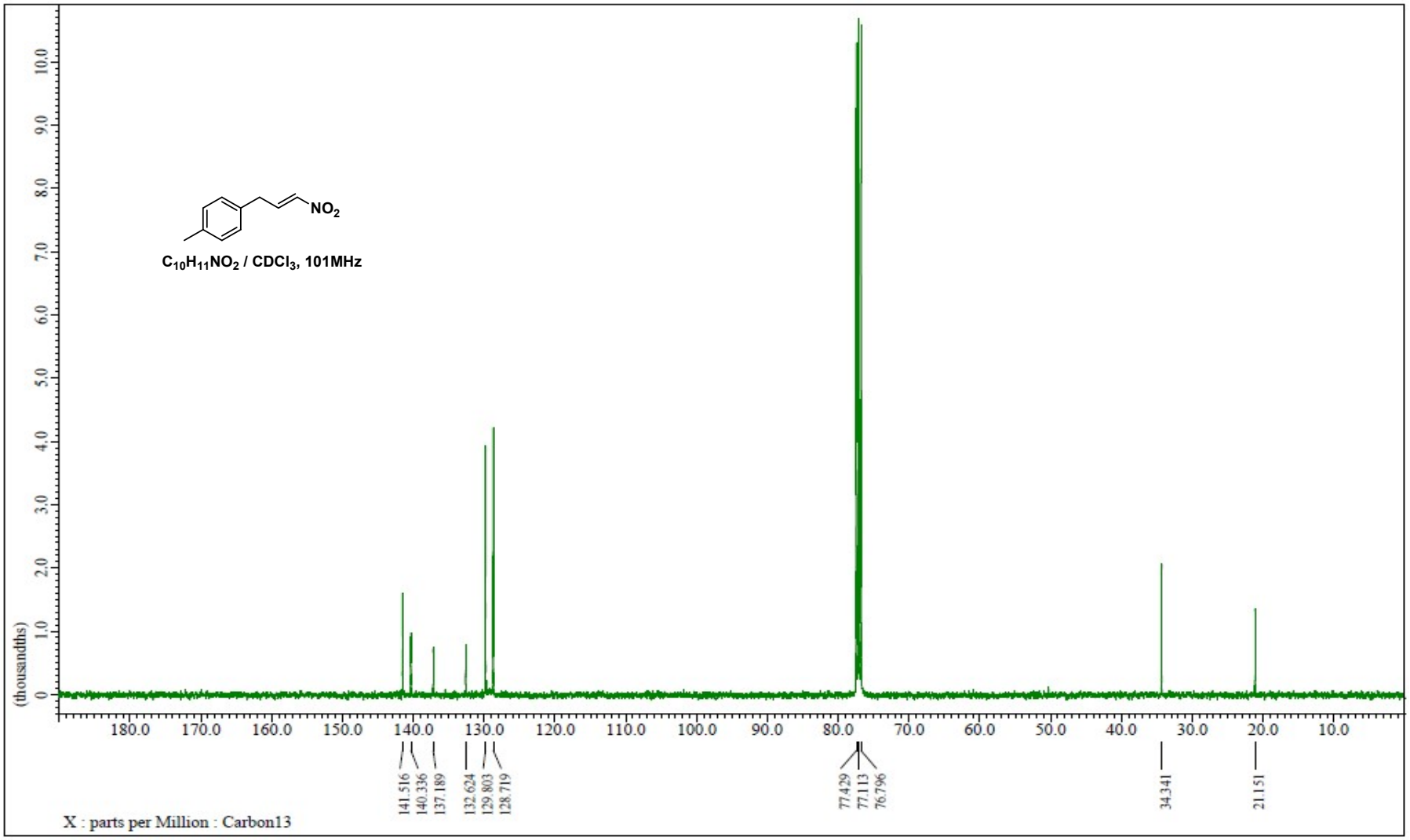
^{13}C -NMR of compound **(7l)**



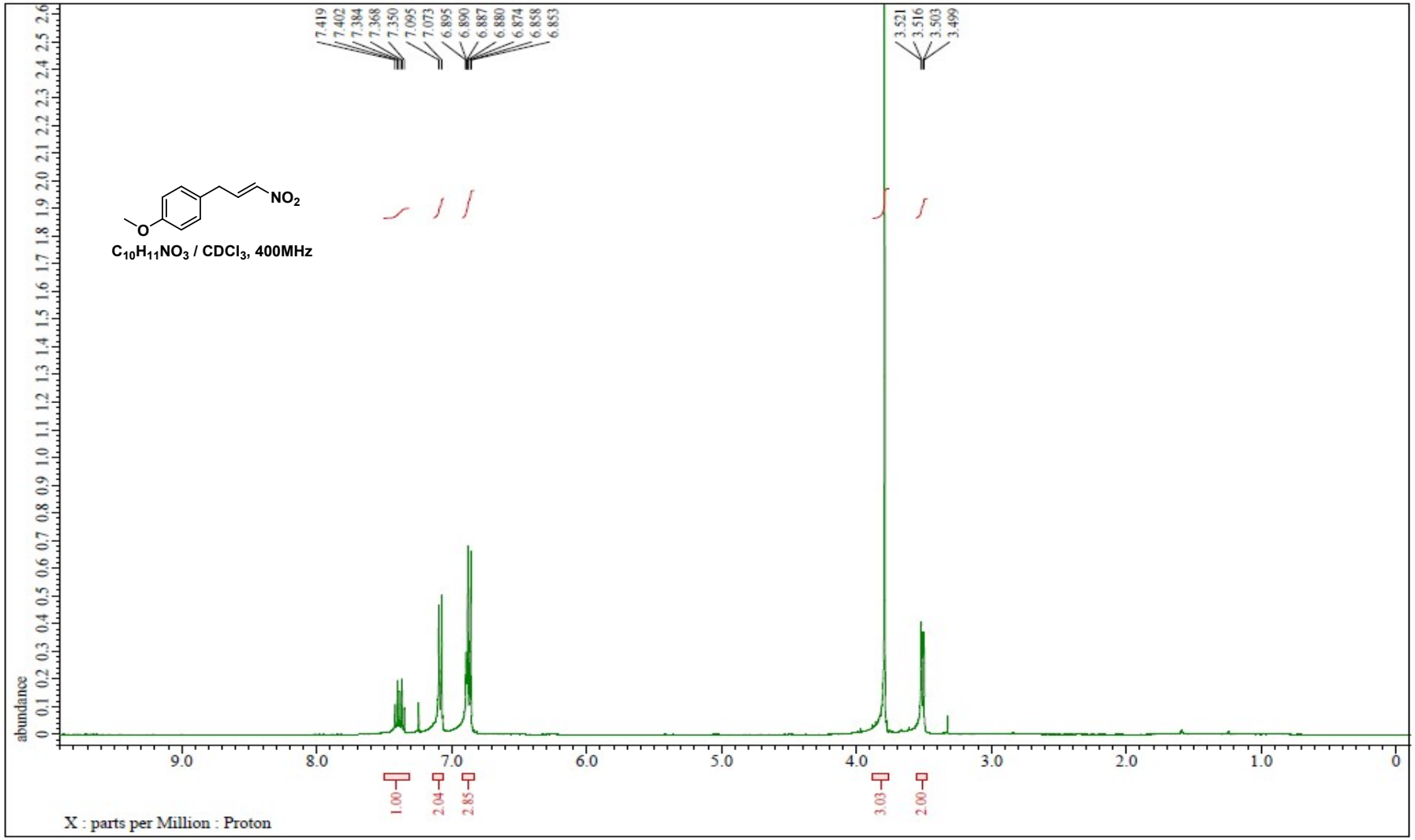
[1]H -NMR of compound **(7m)**



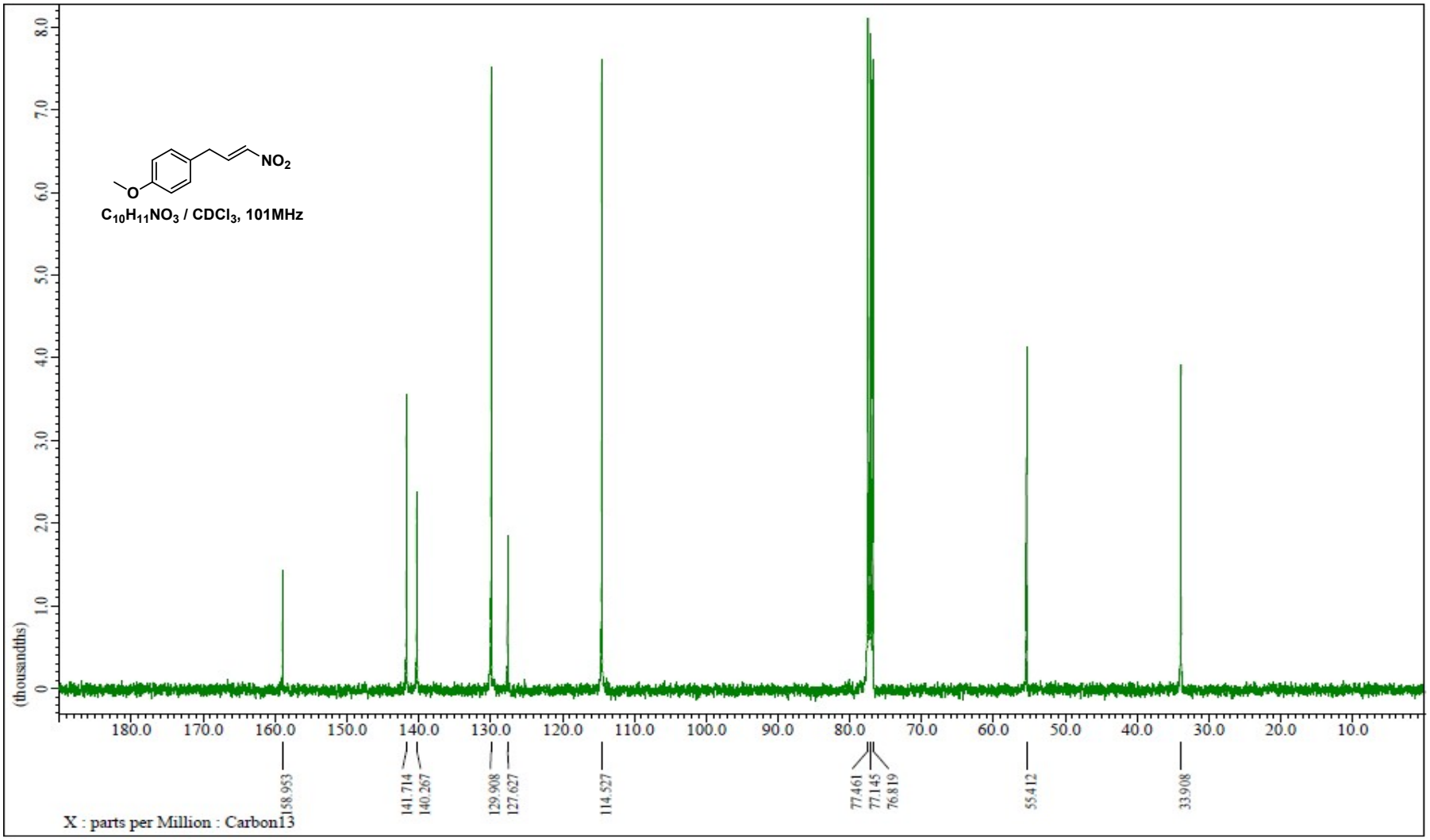
^{13}C -NMR of compound **(7m)**



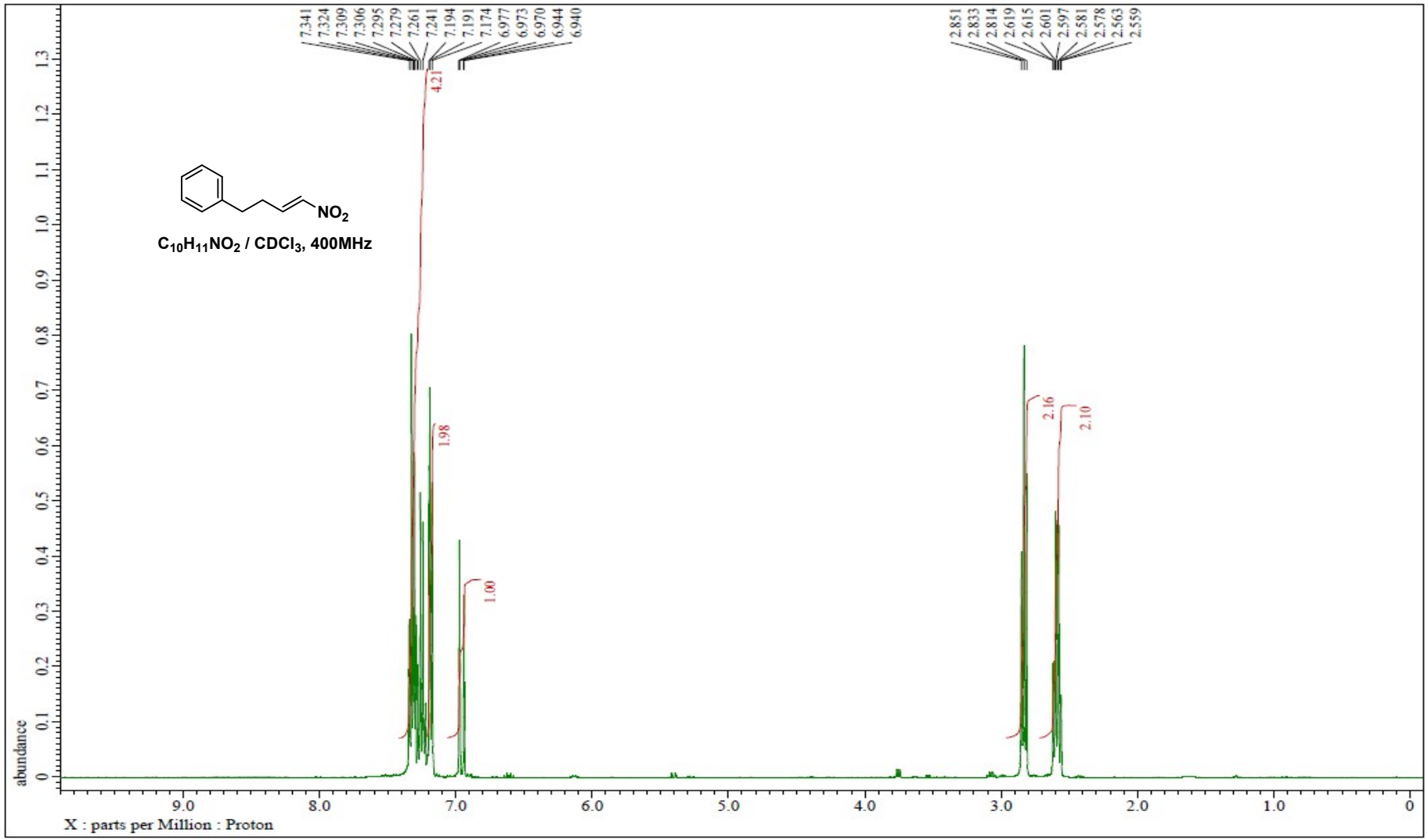
[1]H -NMR of compound **(7n)**



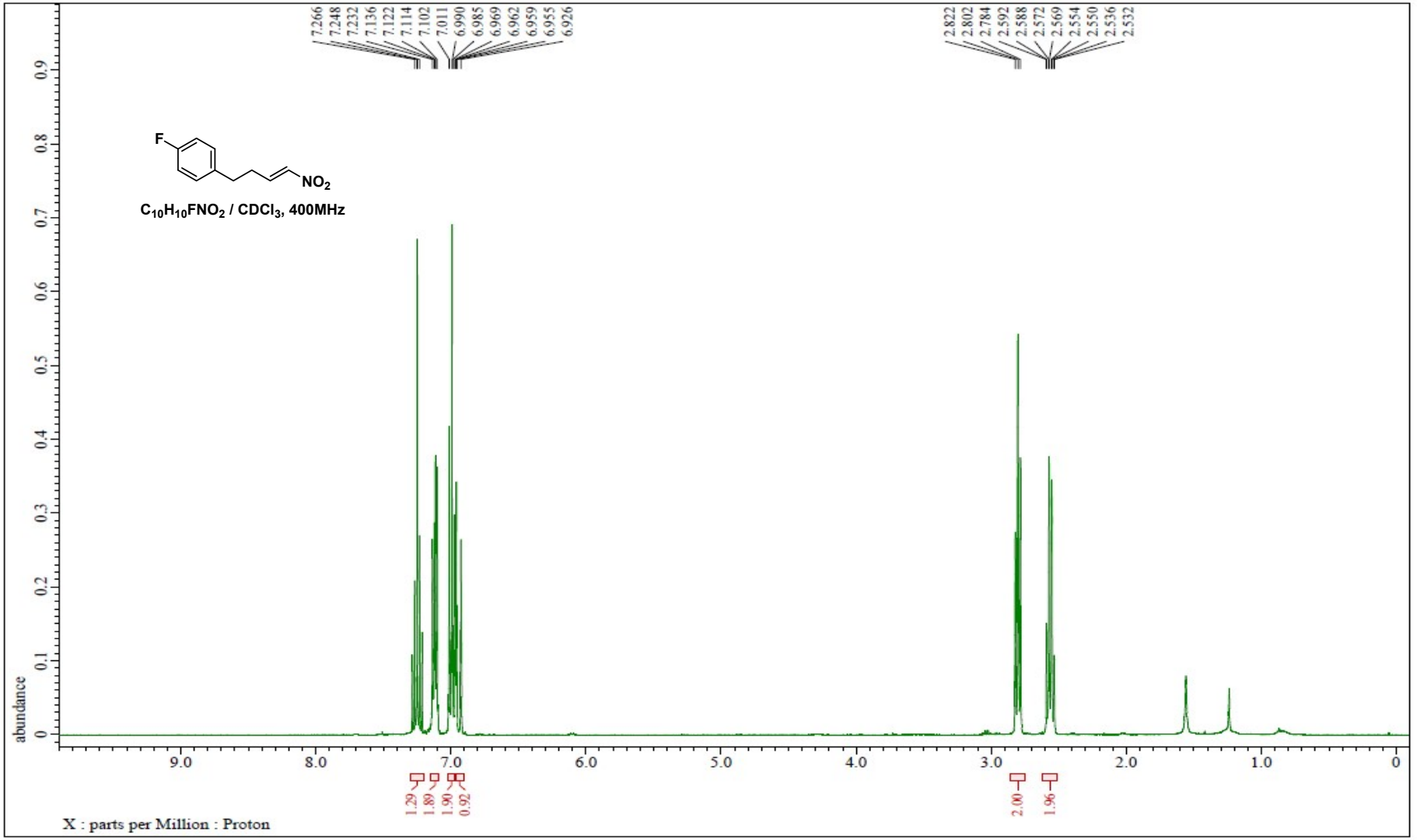
^{13}C -NMR of compound **(7n)**


NO2
O
C10H11NO3 / CDCl3, 101MHz
(thousandths)
X : parts per Million : Carbon13
158.953
141.714
140.267
129.908
127.627
114.527
77.461
77.145
76.819
55.412
33.908

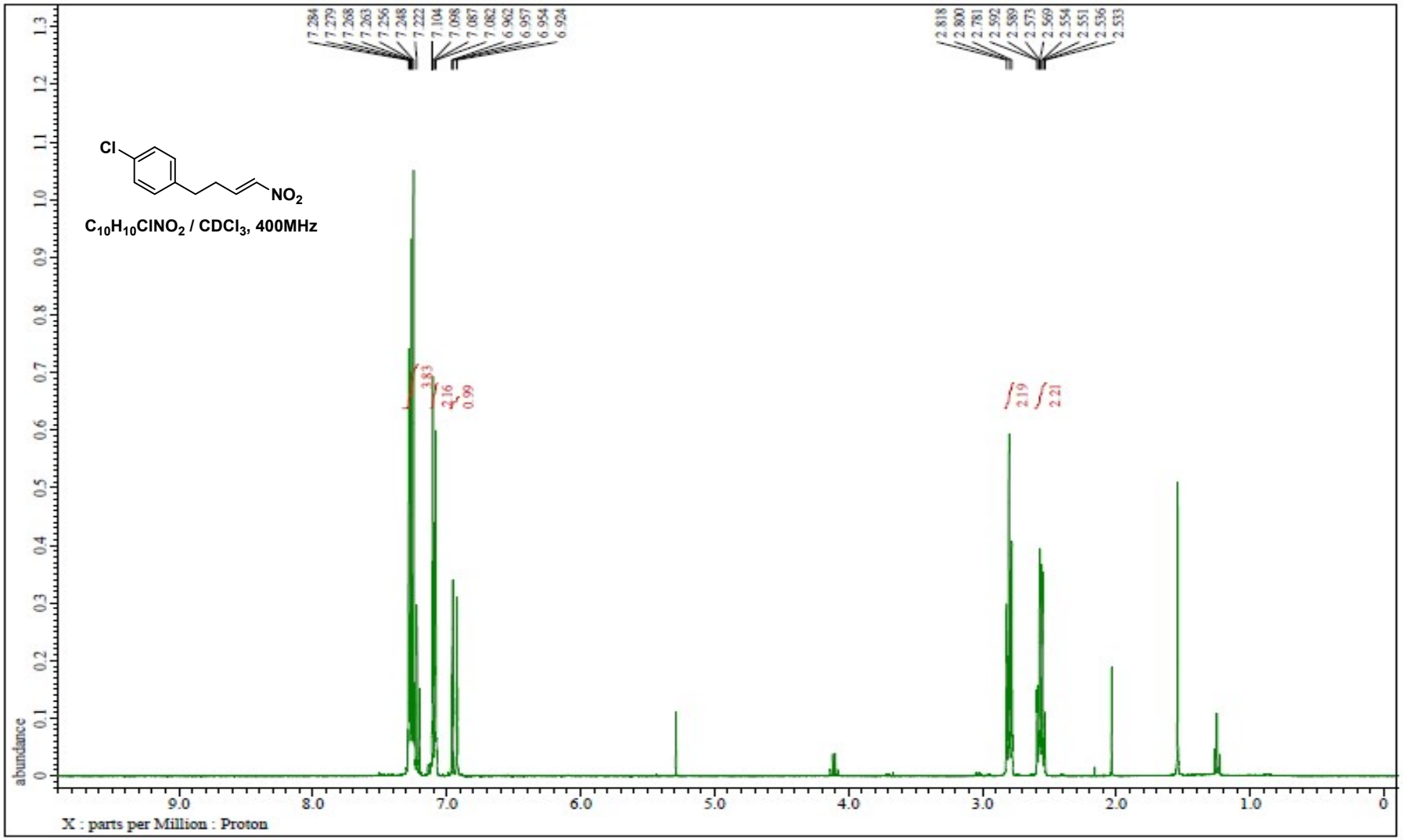
[1]H -NMR of compound **(7o)**



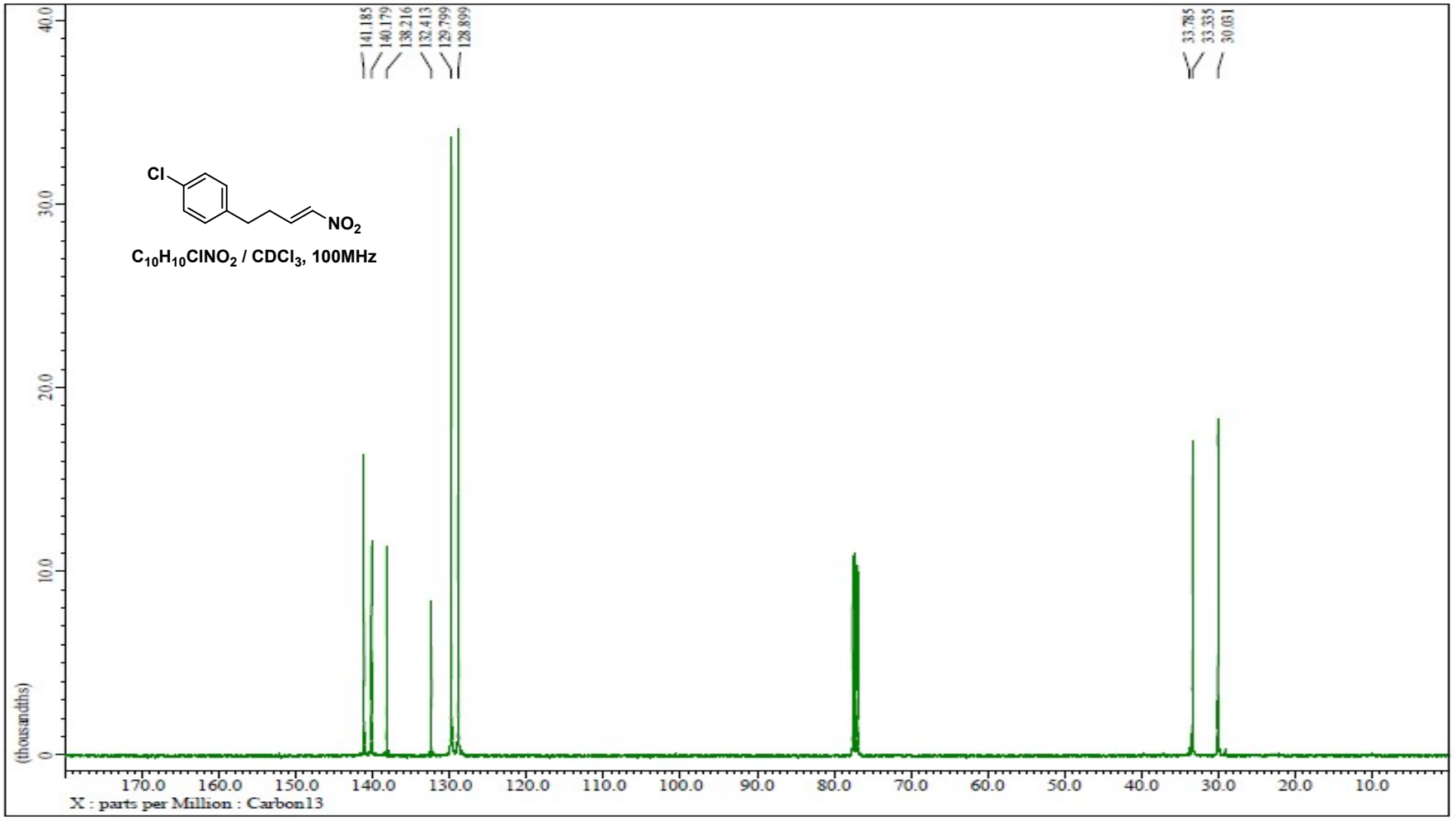
[1]H -NMR of compound **(7p)**



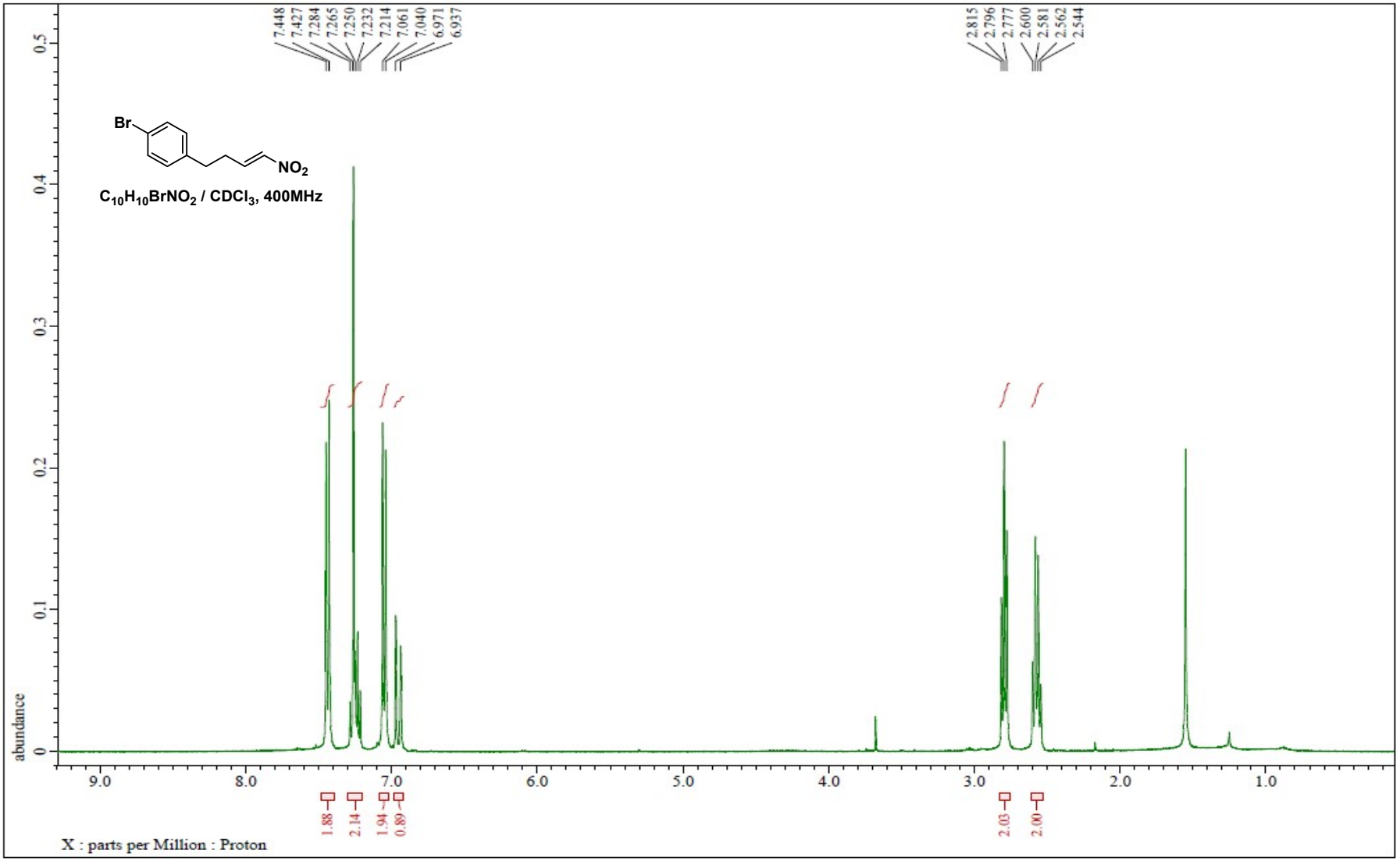
[1]H -NMR of compound **(7q)**



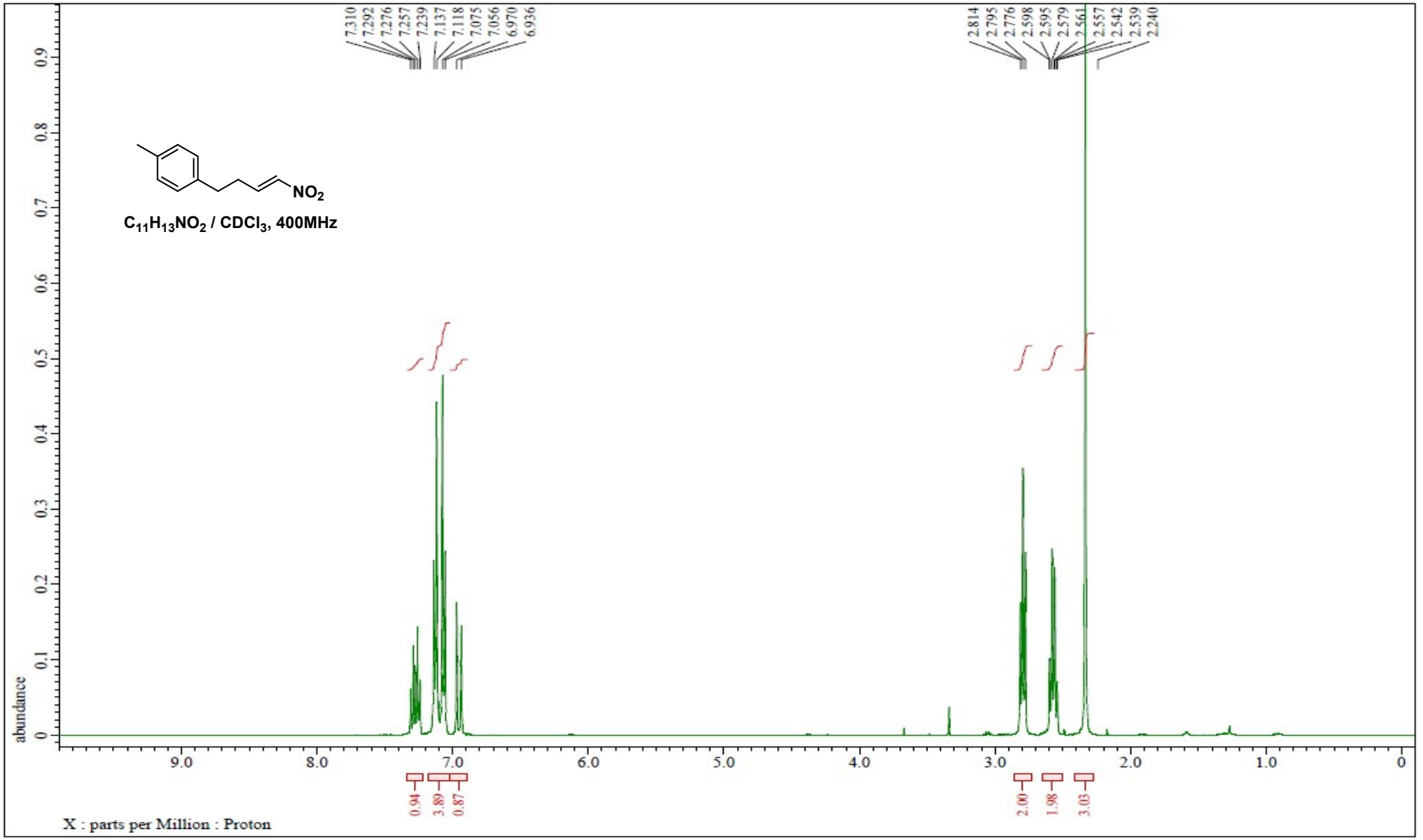
[13]C -NMR of compound **(7q)**



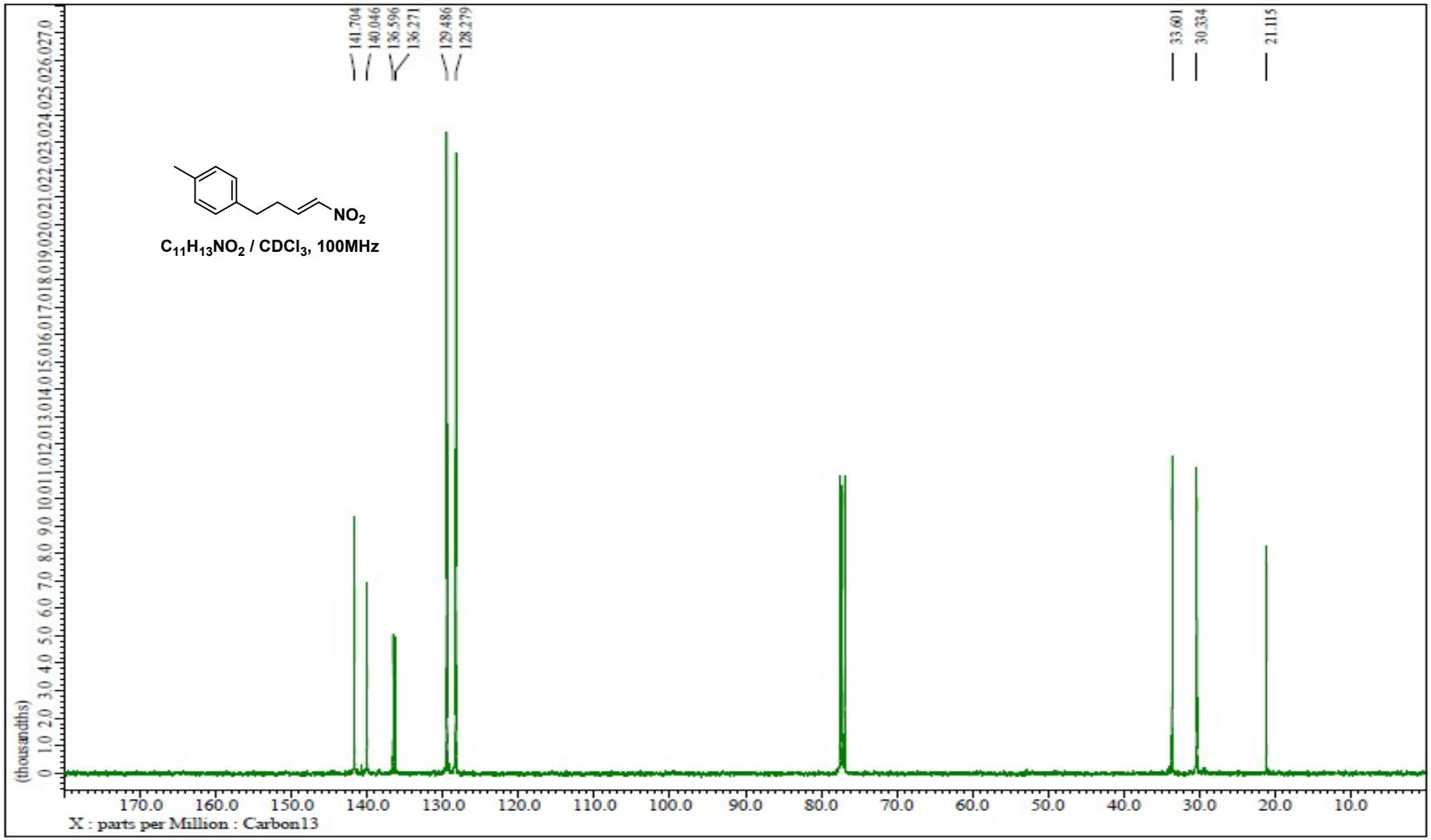
[1]H -NMR of compound **(7r)**


7.448
7.427
7.284
7.265
7.250
7.232
7.214
7.061
7.040
6.971
6.937
2.815
2.796
2.777
2.600
2.581
2.562
2.544
Br
NO2
C10H10BrNO2 / CDCl3, 400MHz
abundance
0
0.1
0.2
0.3
0.4
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
1.88
2.14
1.94
0.89
2.03
2.00
X : parts per Million : Proton

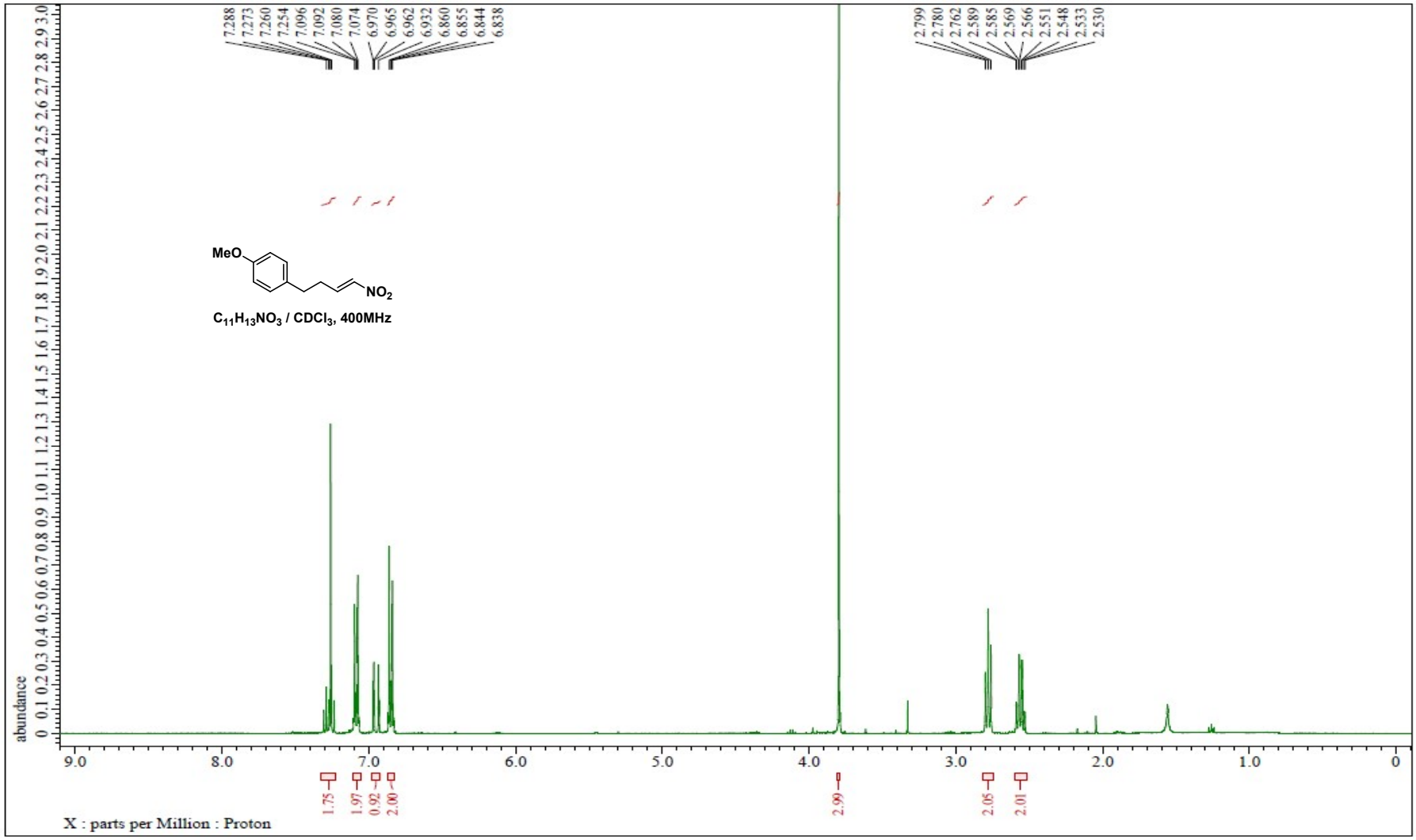
[1]H -NMR of compound **(7s)**



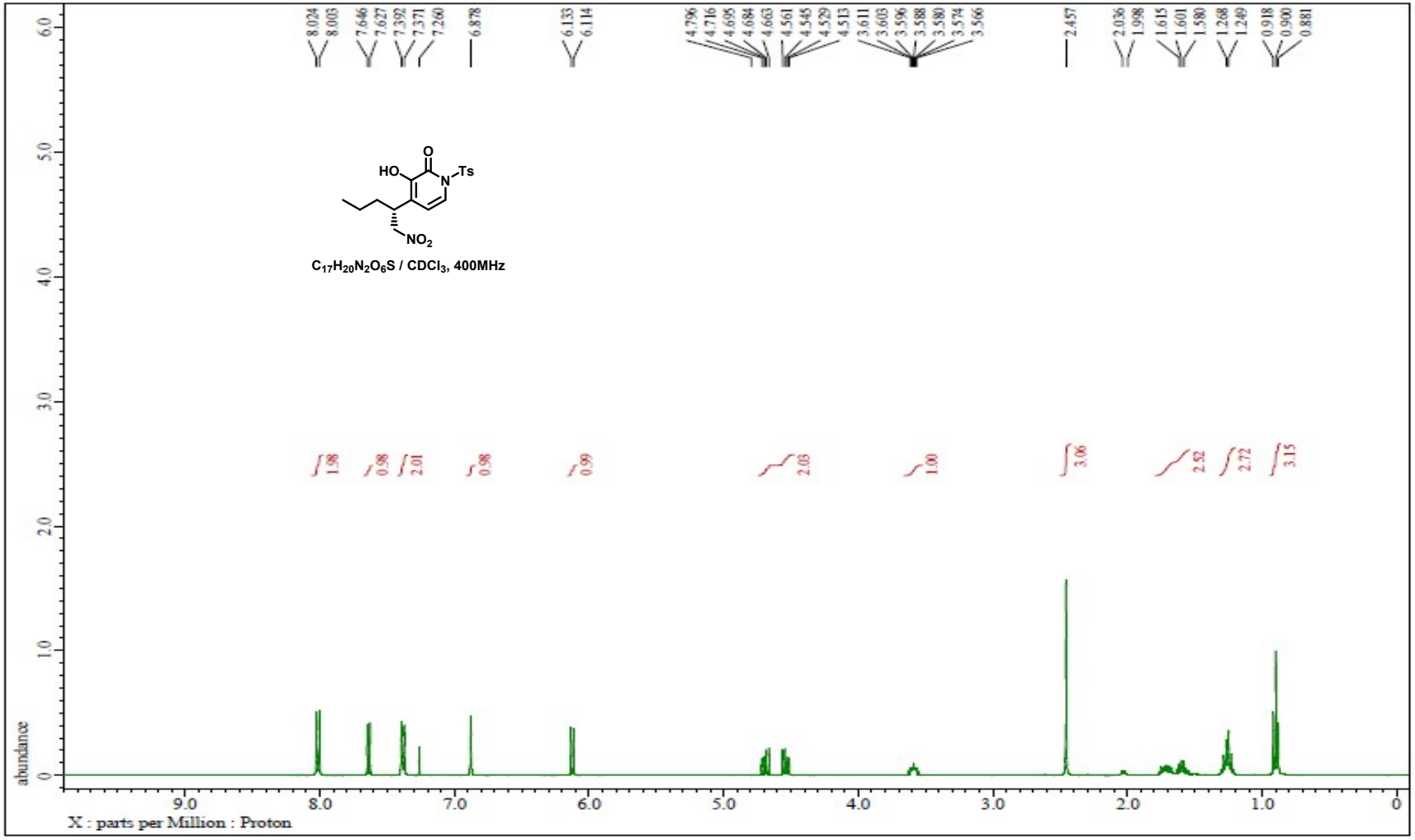
^{13}C -NMR of compound **(7s)**



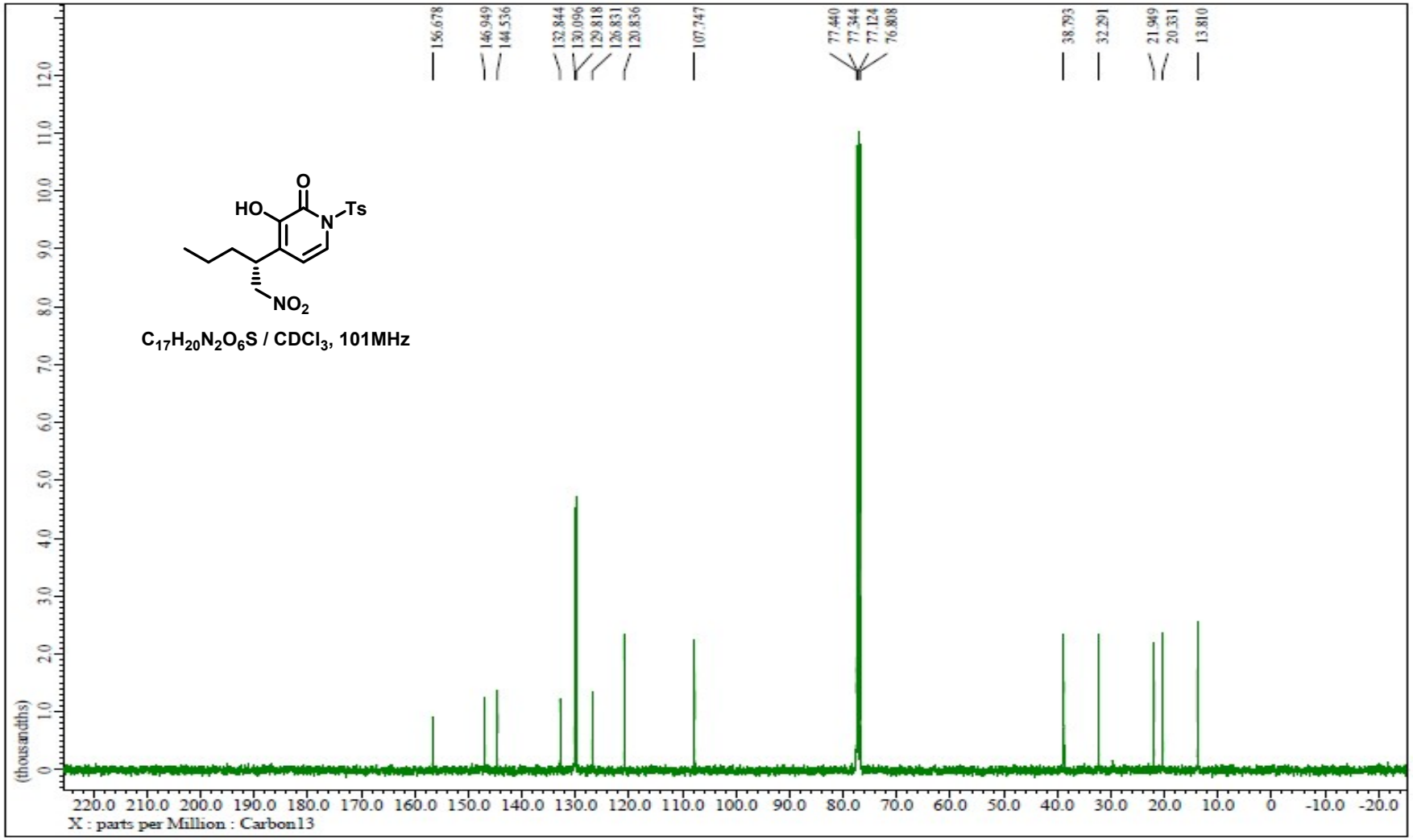
[1]H -NMR of compound **(7t)**



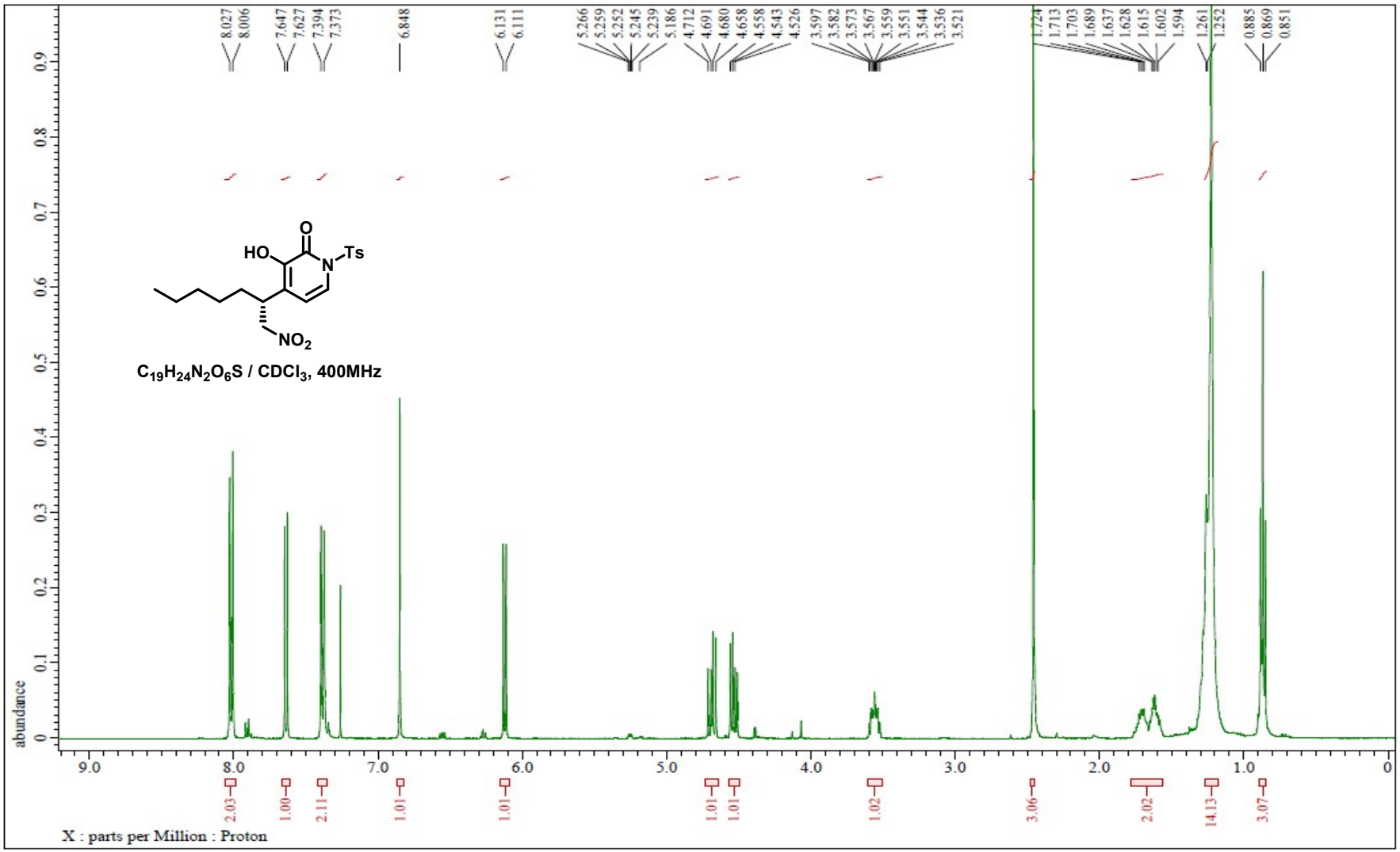
[1]H -NMR of compound **(8a)**



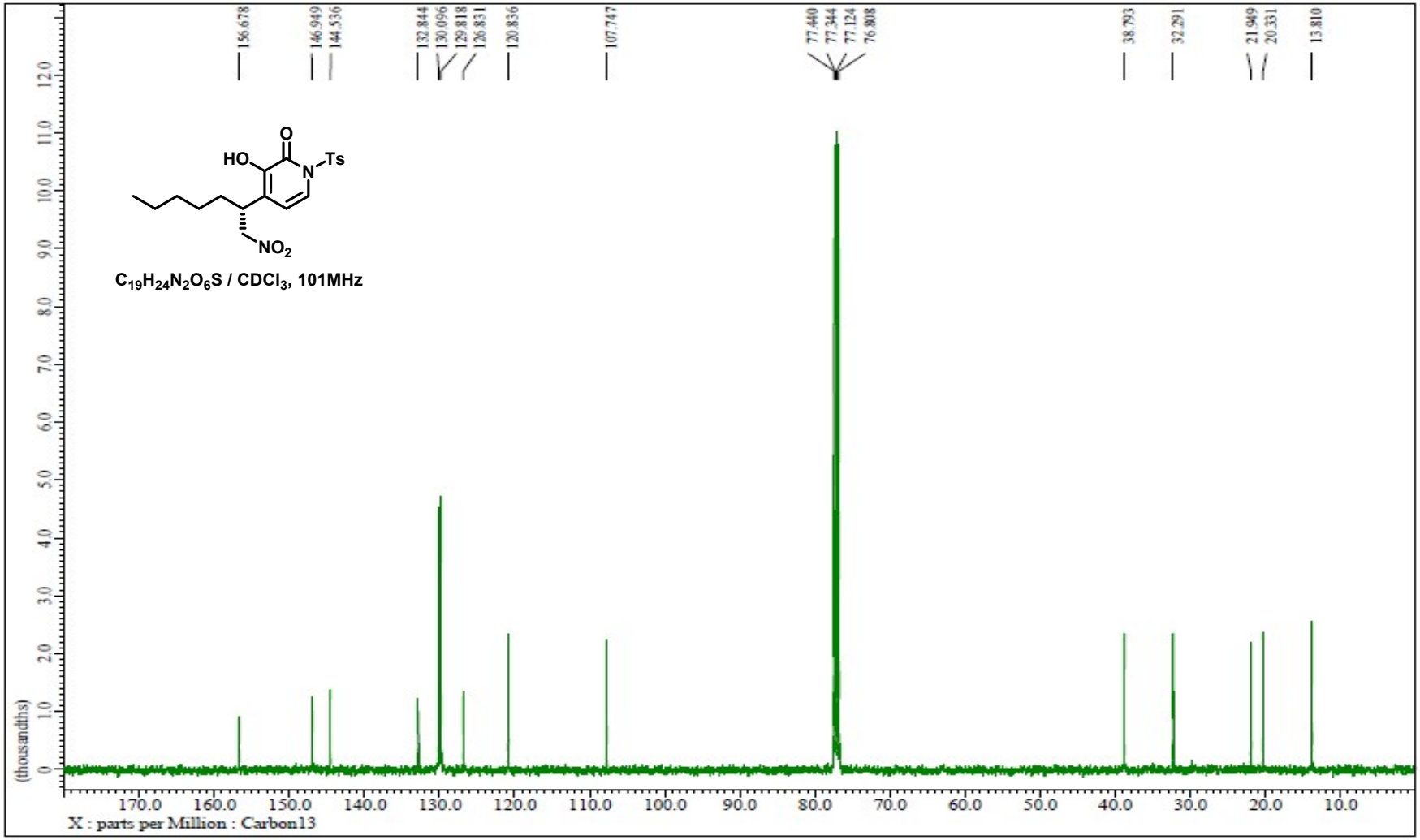
^{13}C -NMR of compound **(8a)**



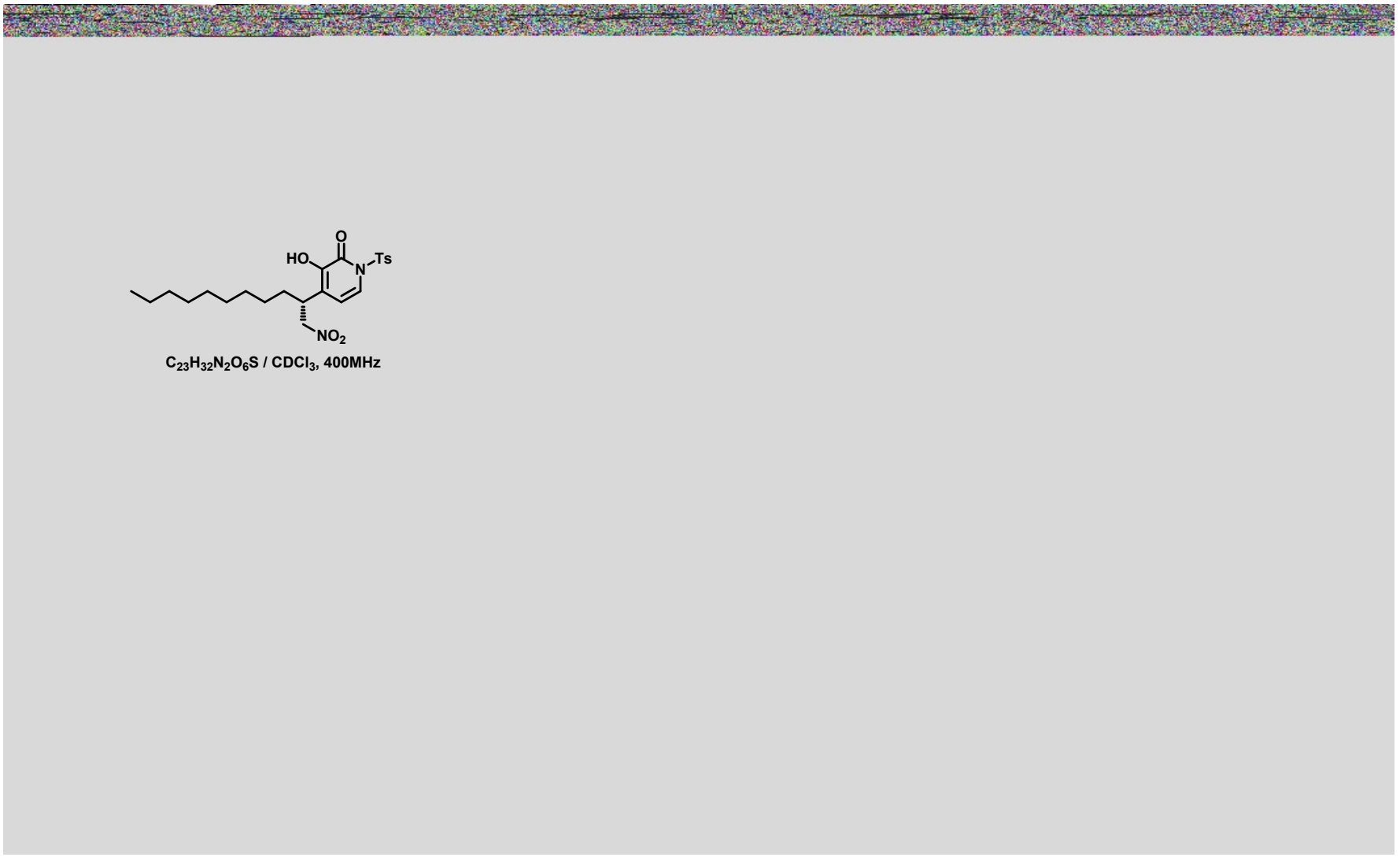
[1]H -NMR of compound **(8b)**



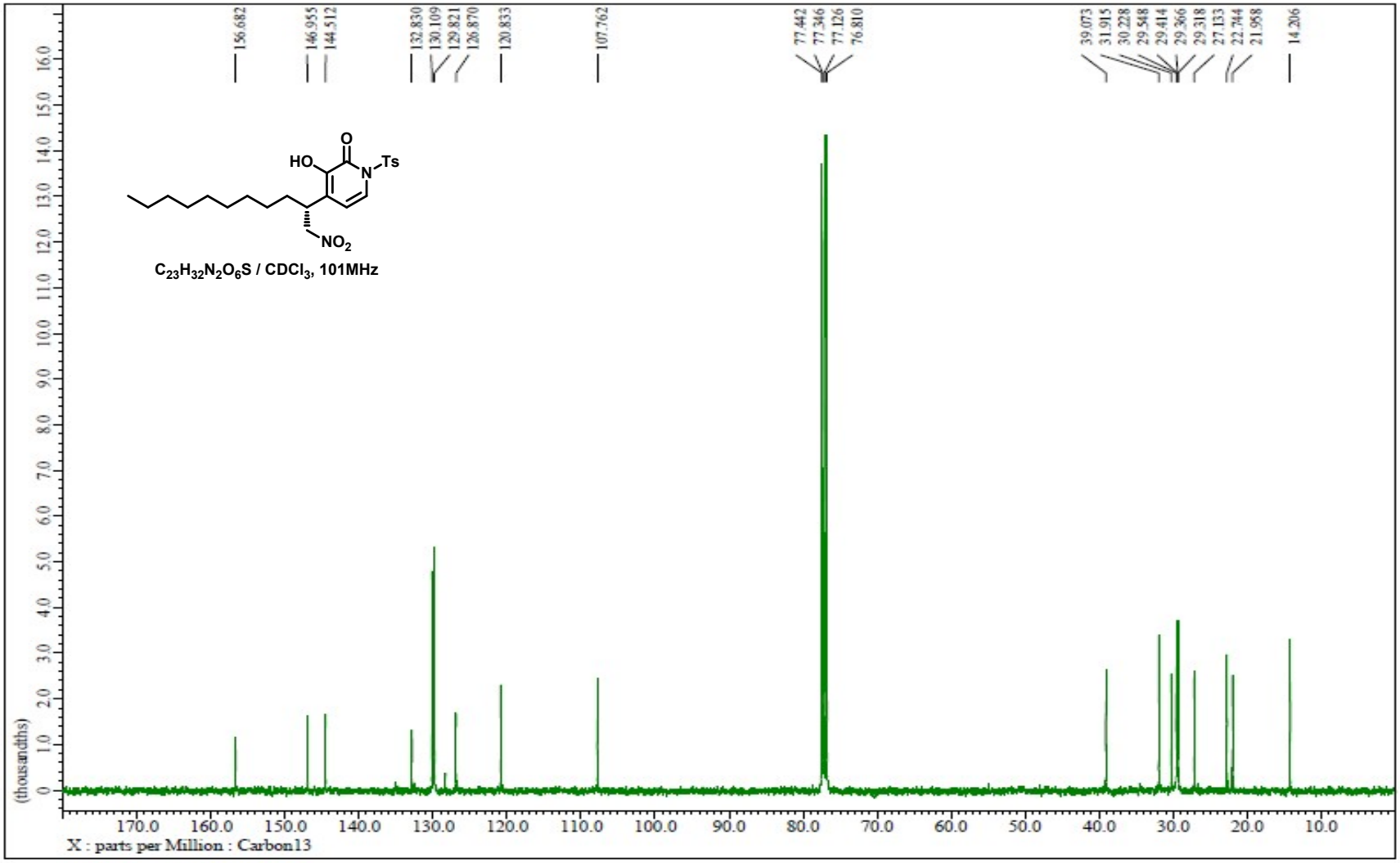
^{13}C -NMR of compound **(8b)**



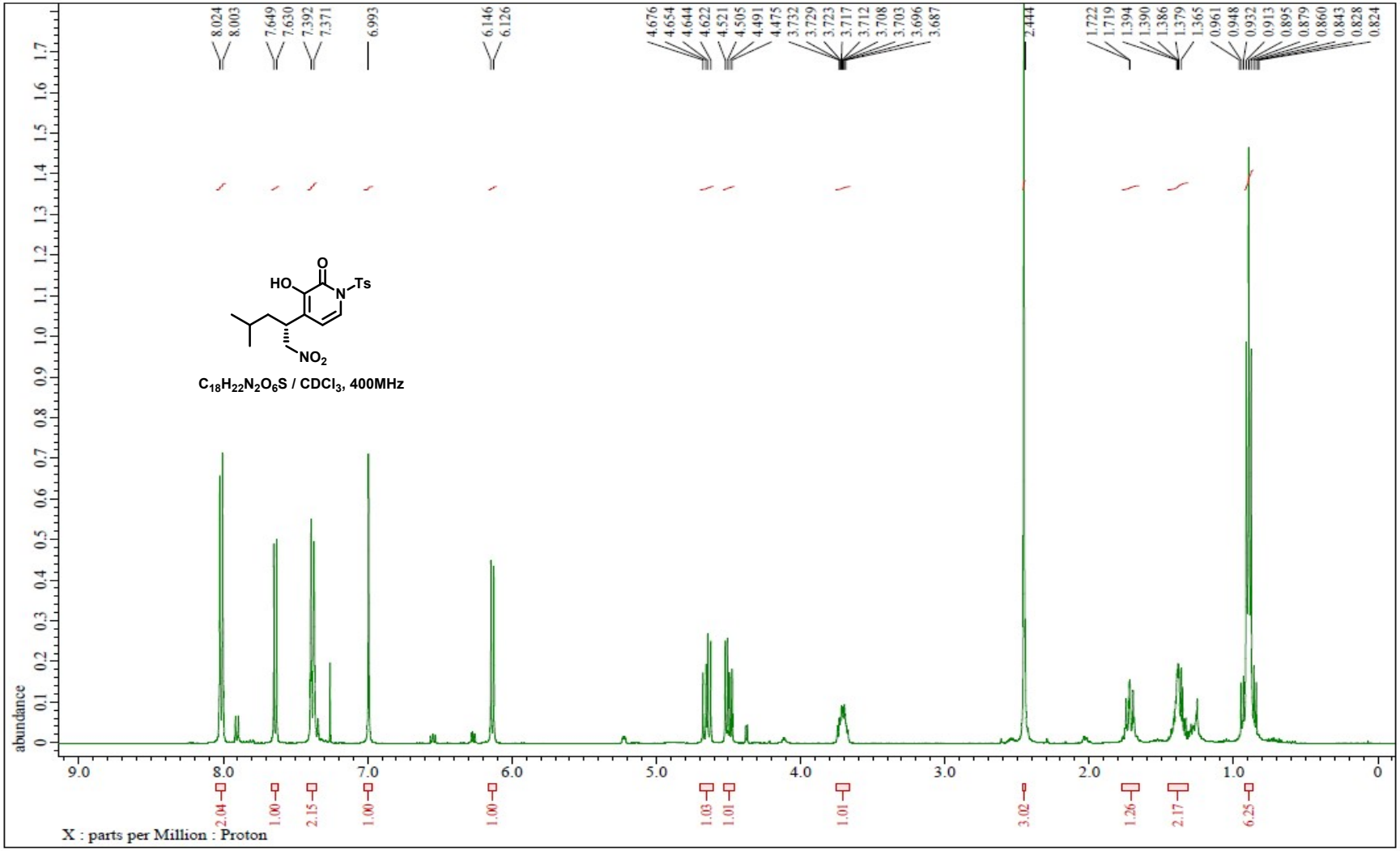
[1]H -NMR of compound **(8c)**



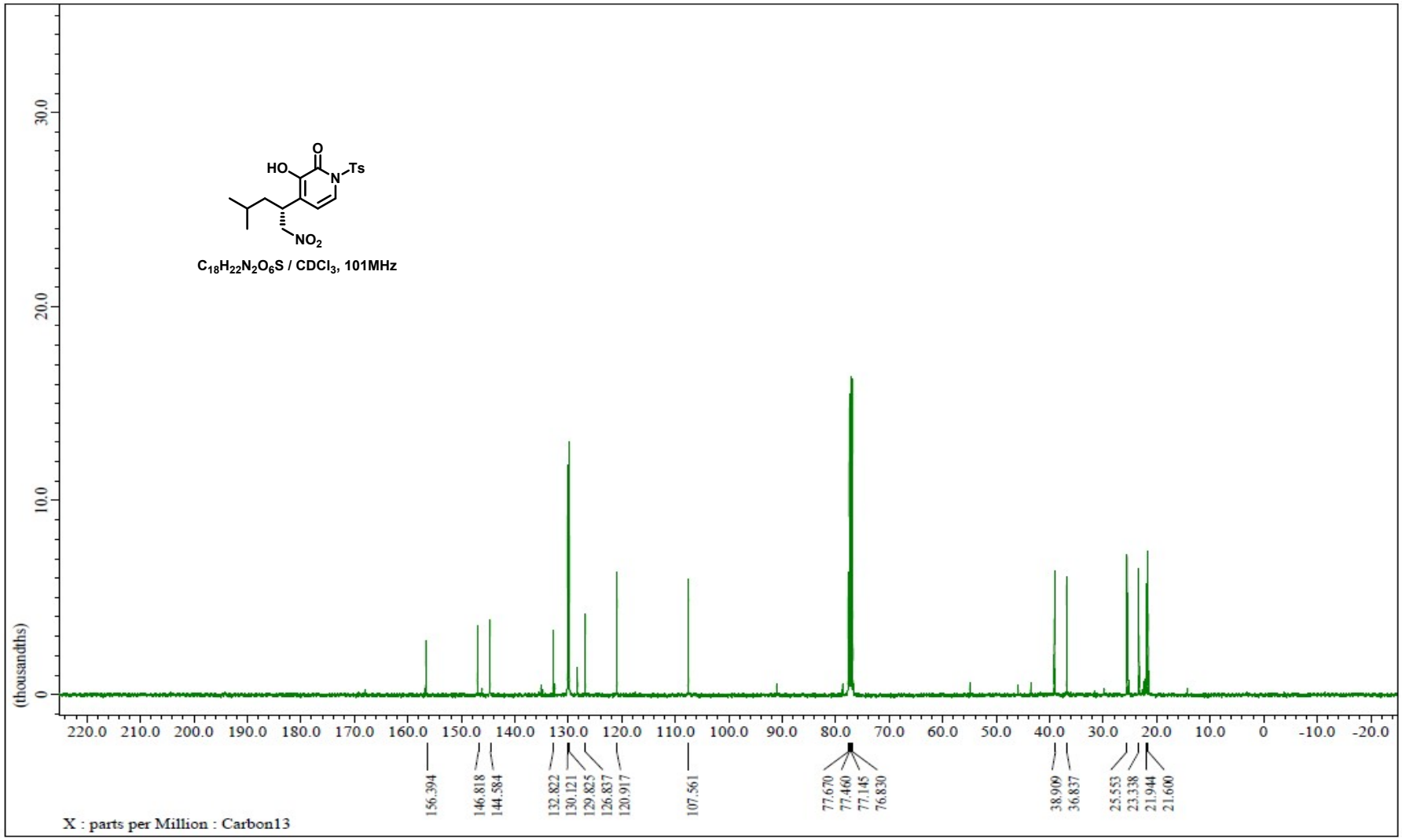
^{13}C -NMR of compound **(8c)**



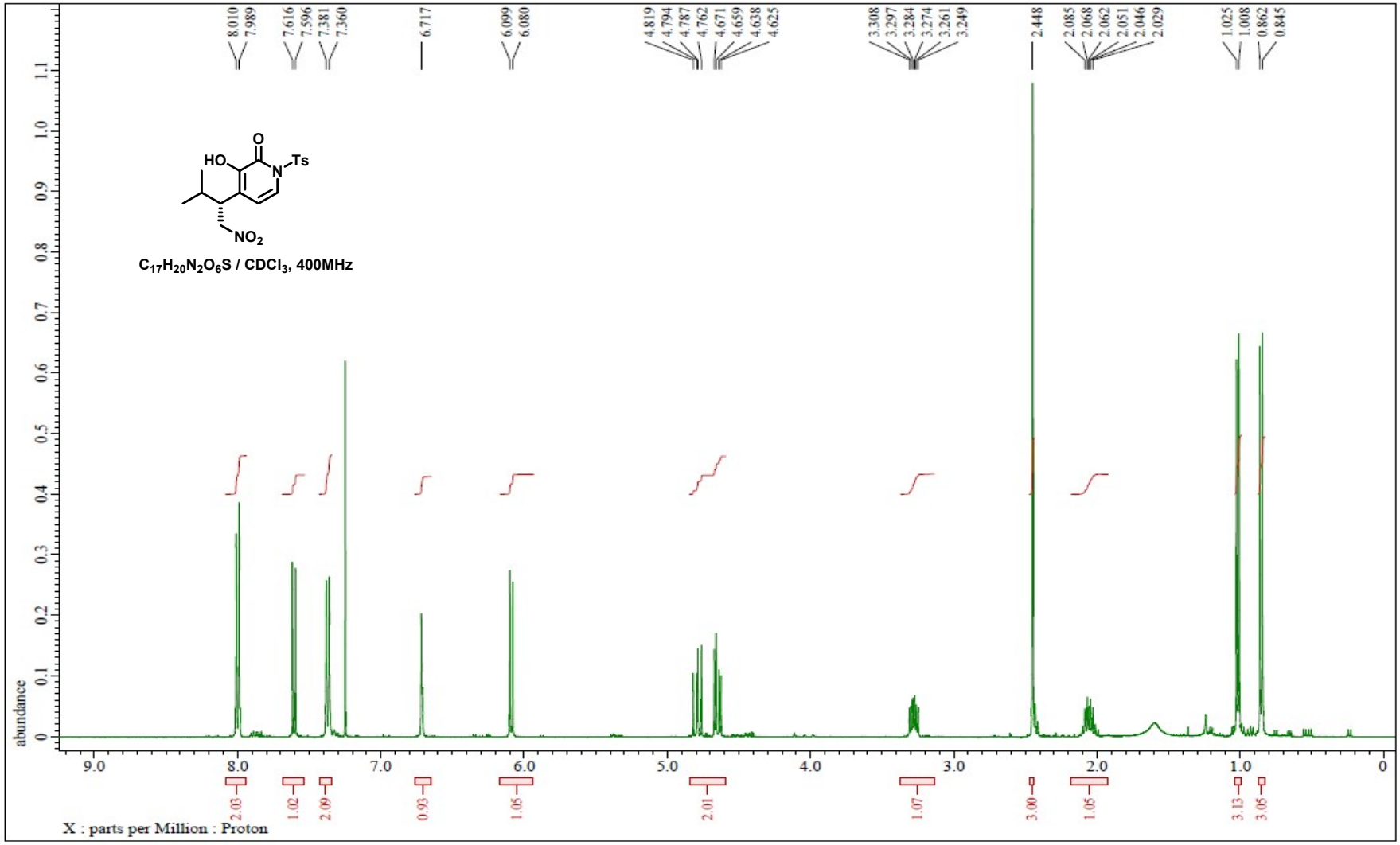
[1]H -NMR of compound **(8d)**



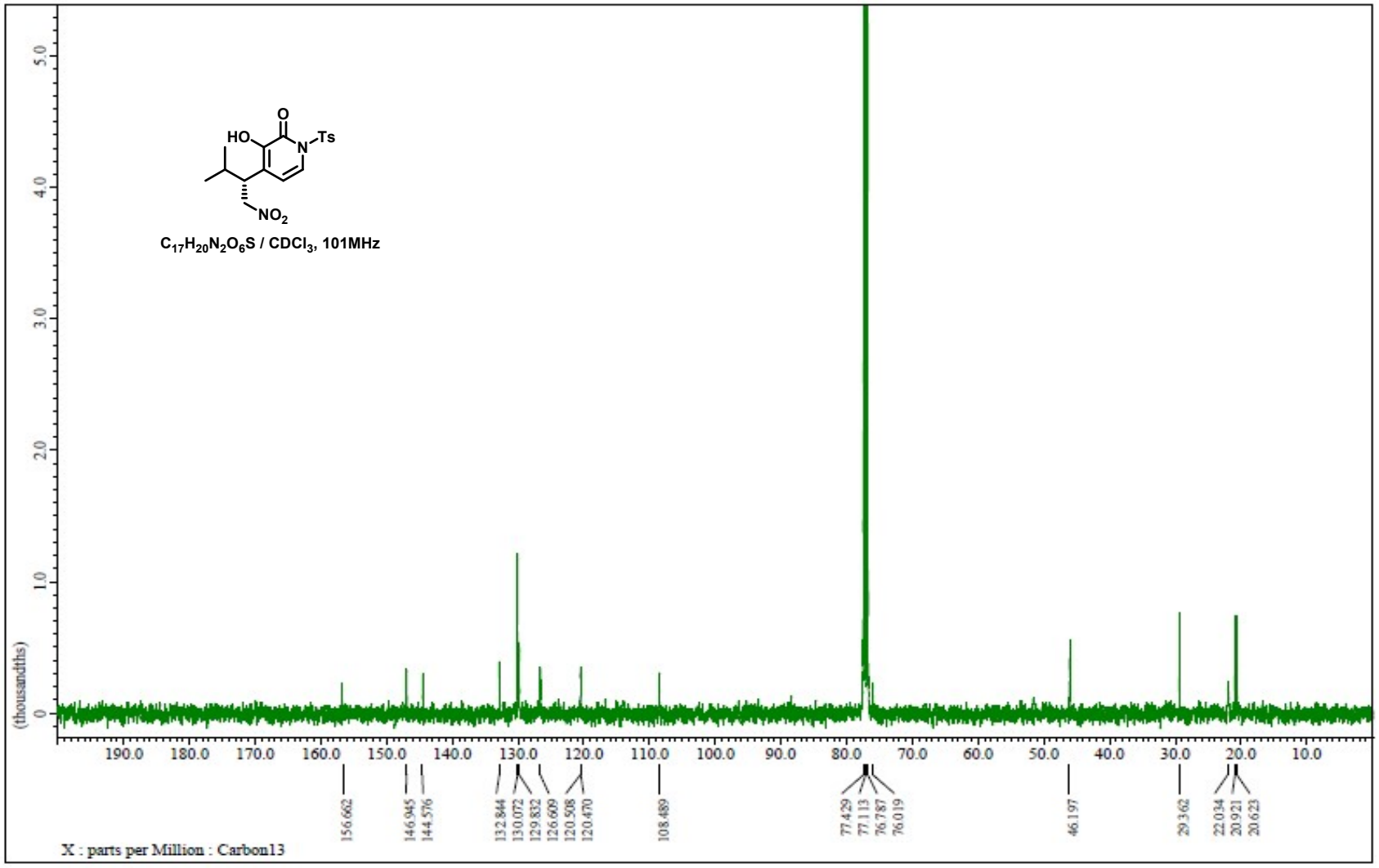
^{13}C -NMR of compound **(8d)**



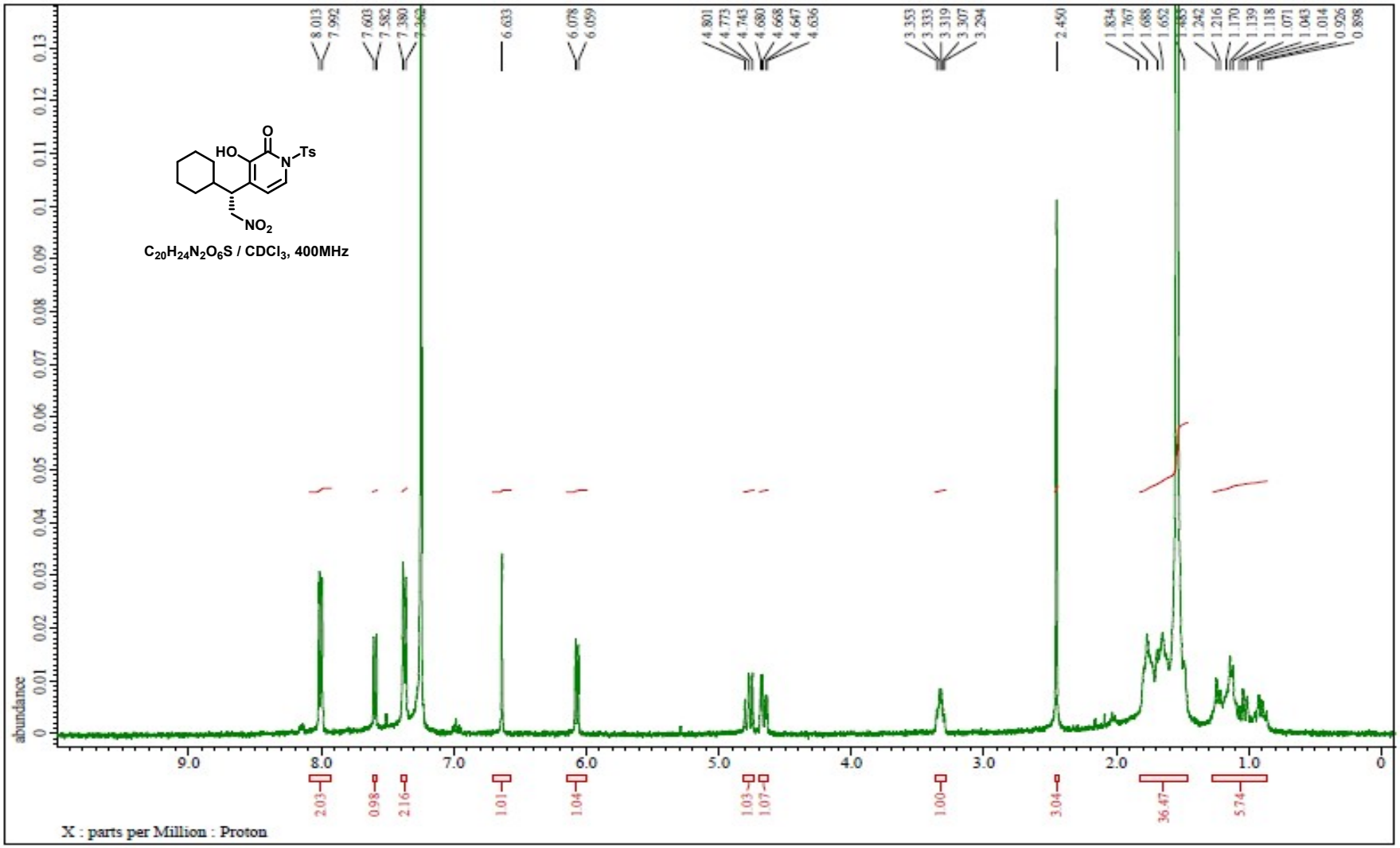
[1]H -NMR of compound **(8e)**



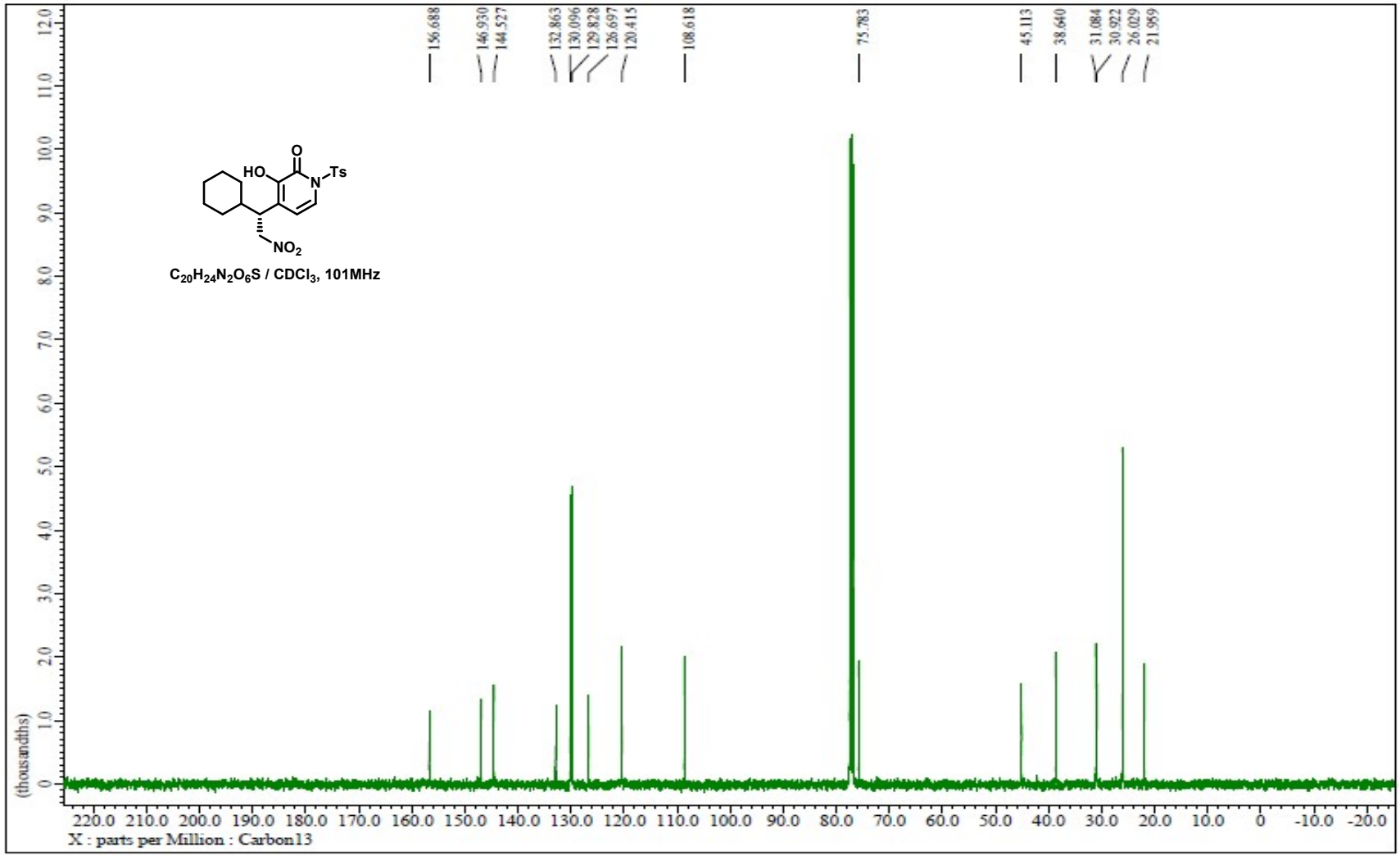
^{13}C -NMR of compound **(8e)**



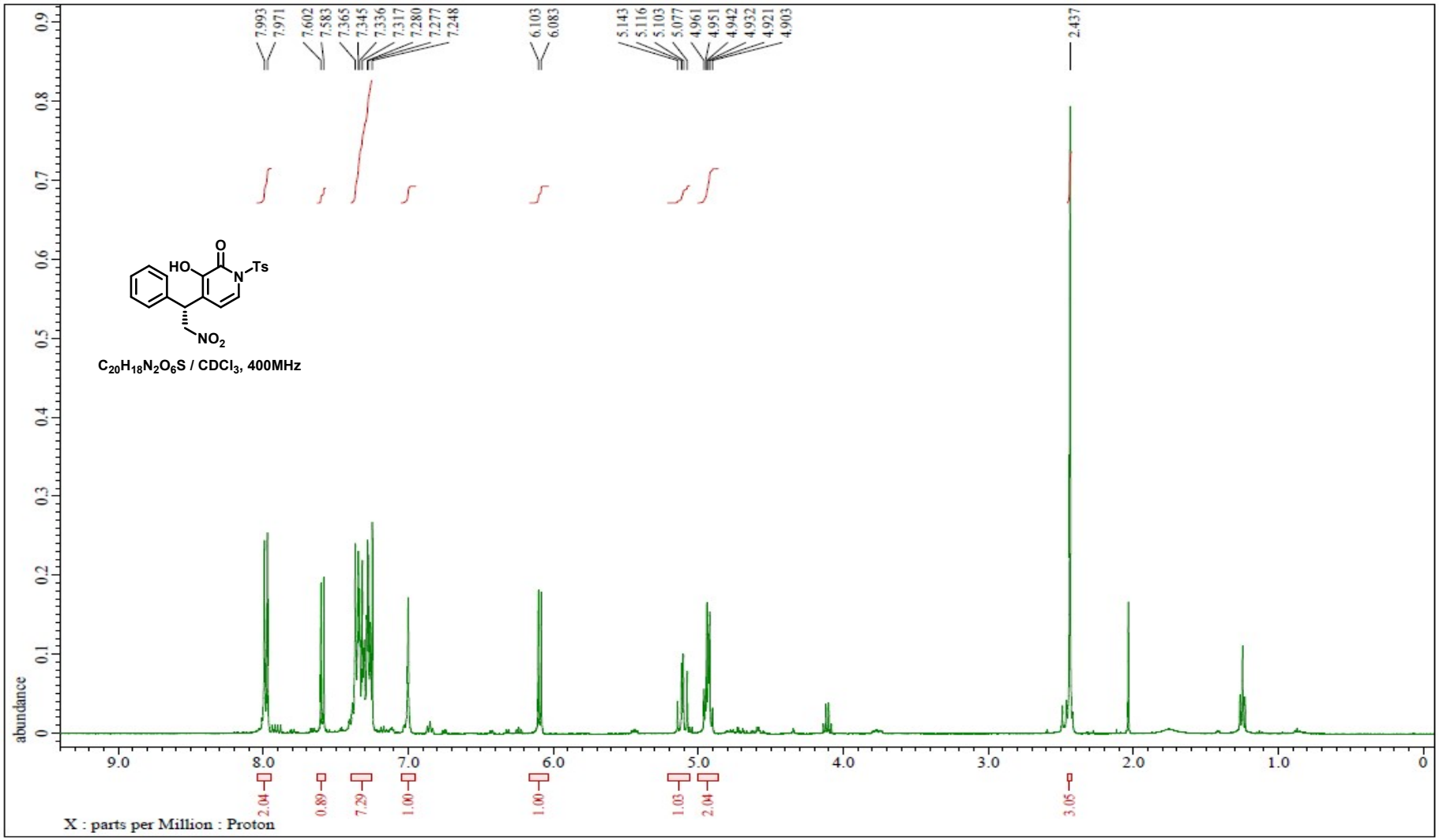
[1]H -NMR of compound **(8f)**



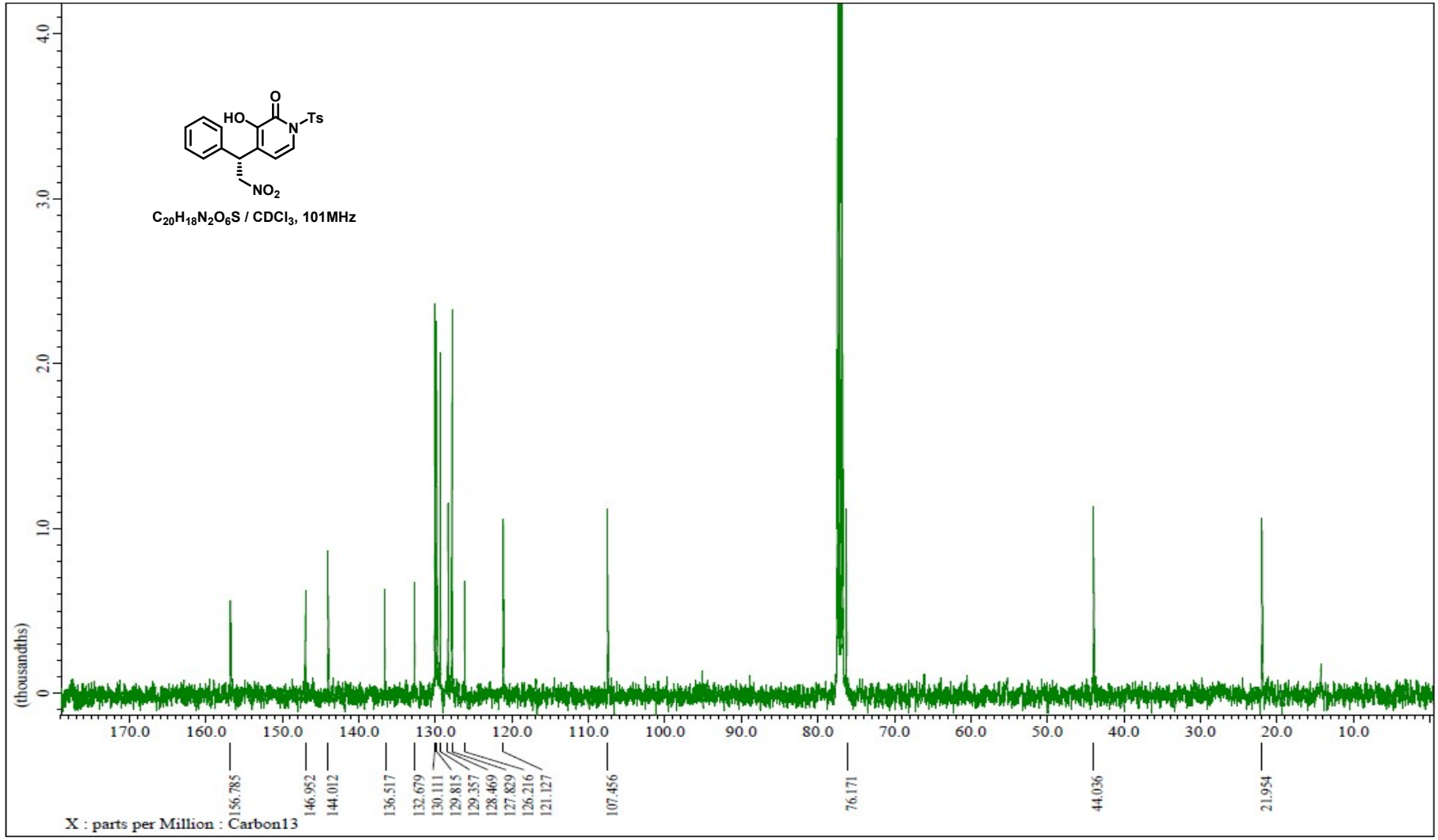
^{13}C -NMR of compound **(8f)**



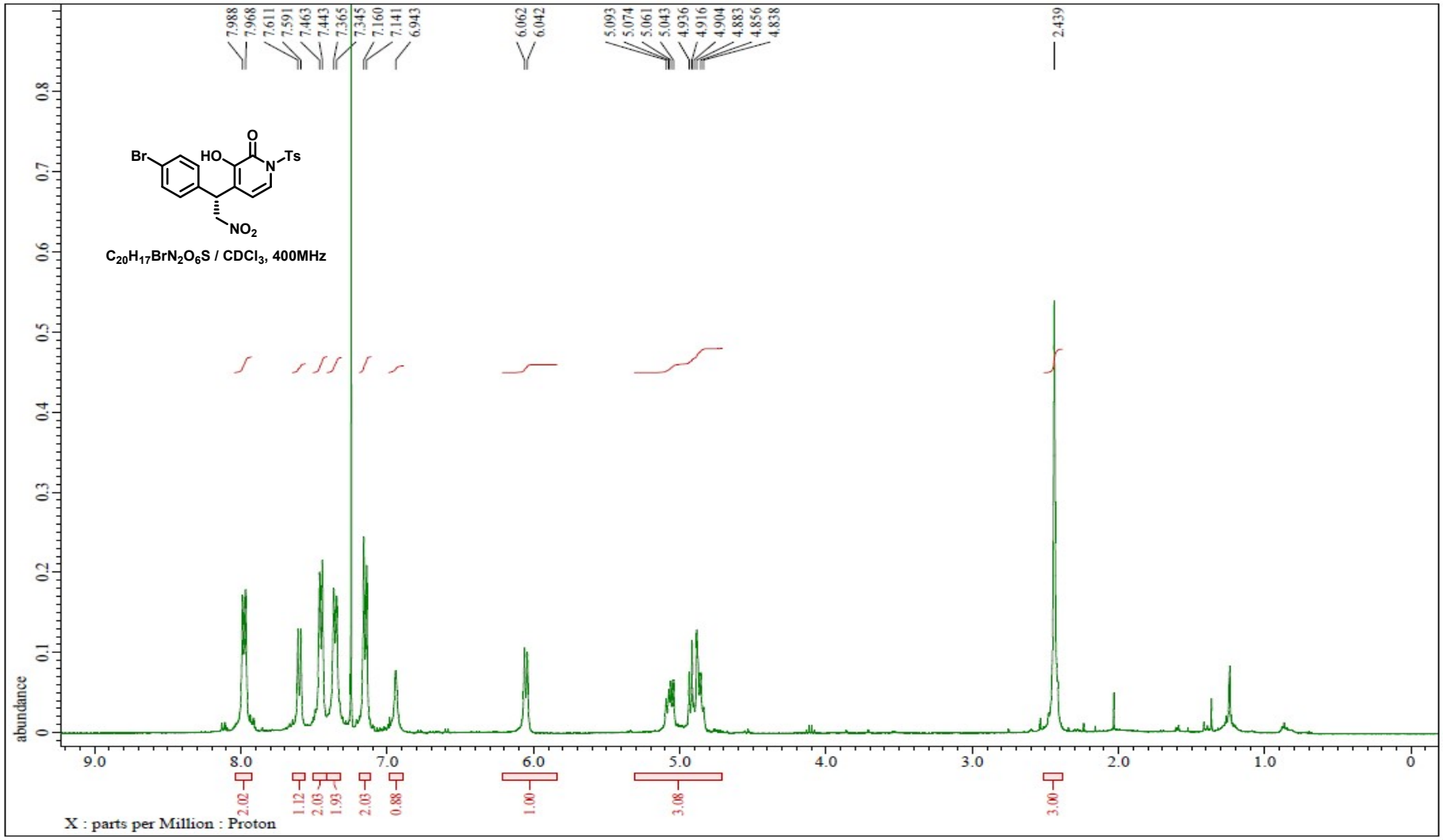
[1]H -NMR of compound **(8h)**



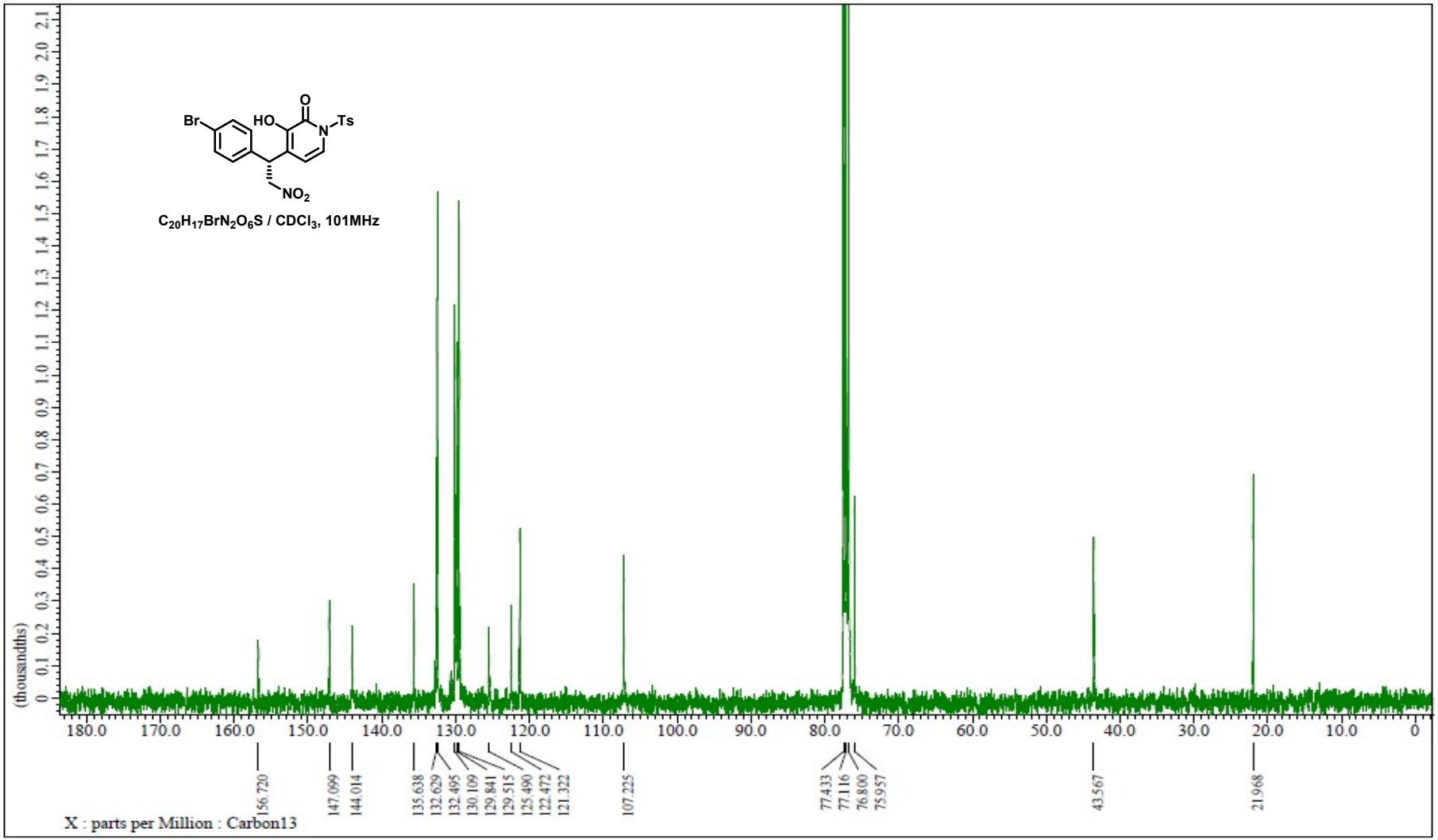
^{13}C -NMR of compound **(8h)**



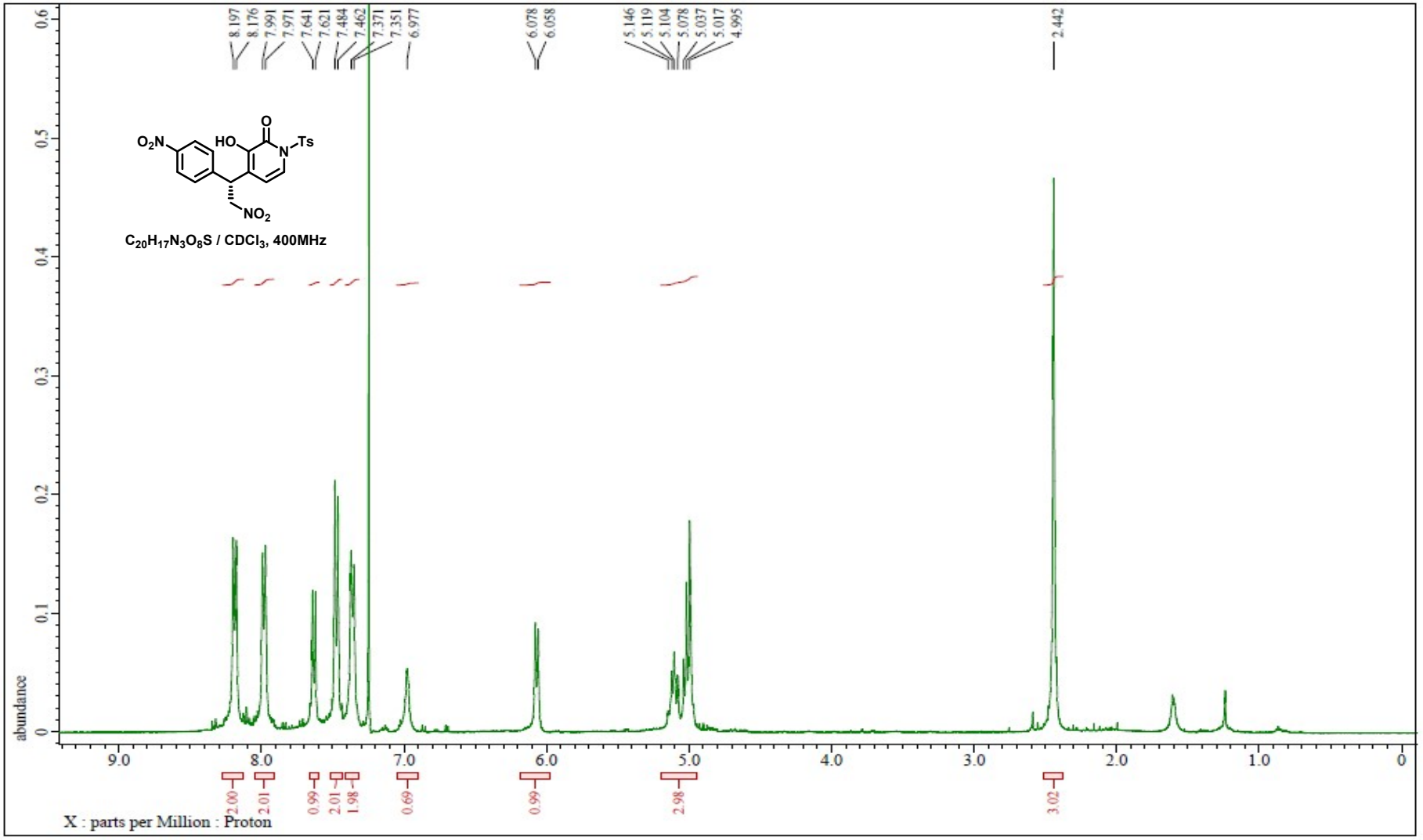
[1]H -NMR of compound **(8i)**



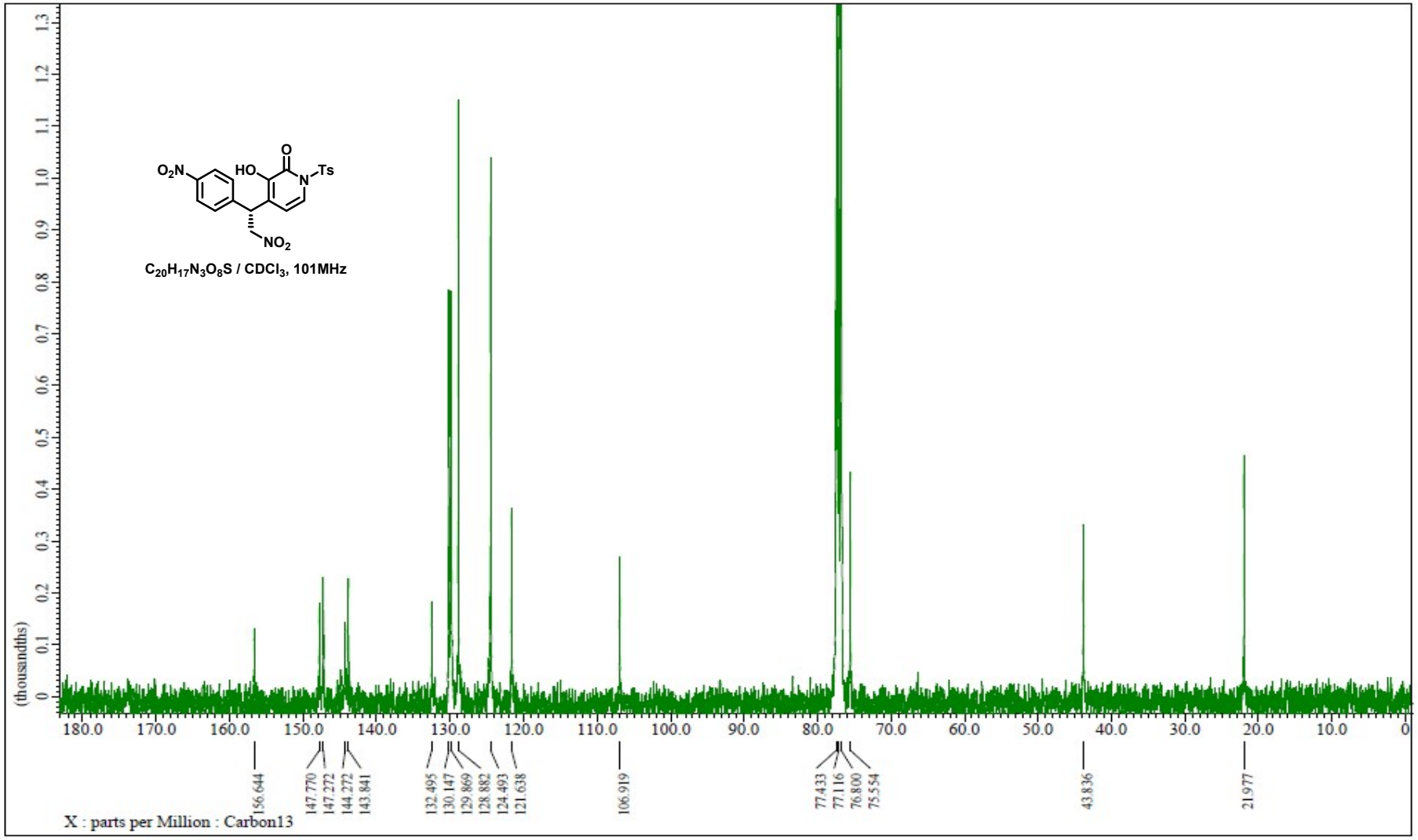
^{13}C -NMR of compound **(8i)**



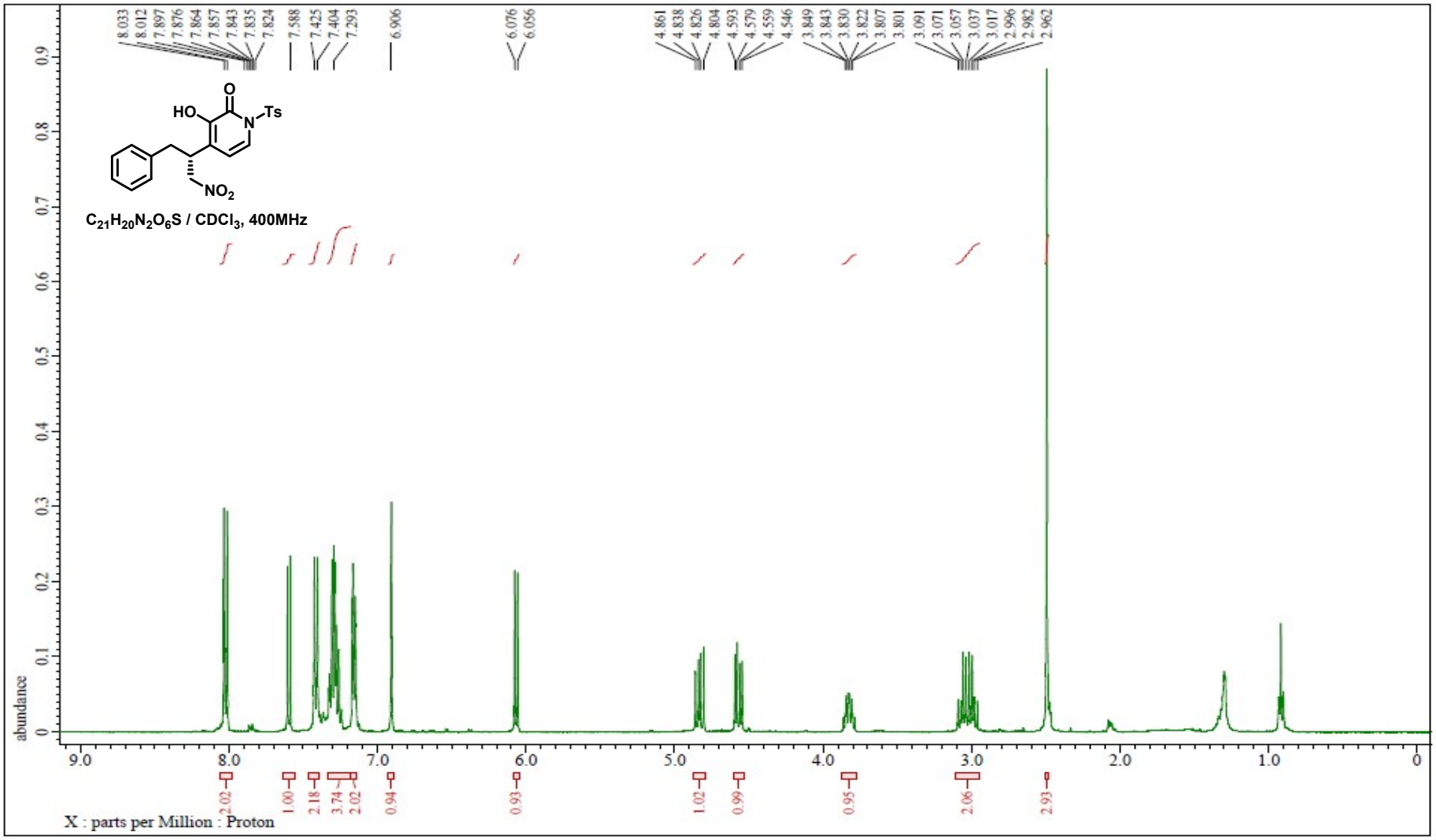
[1]H -NMR of compound **(8j)**



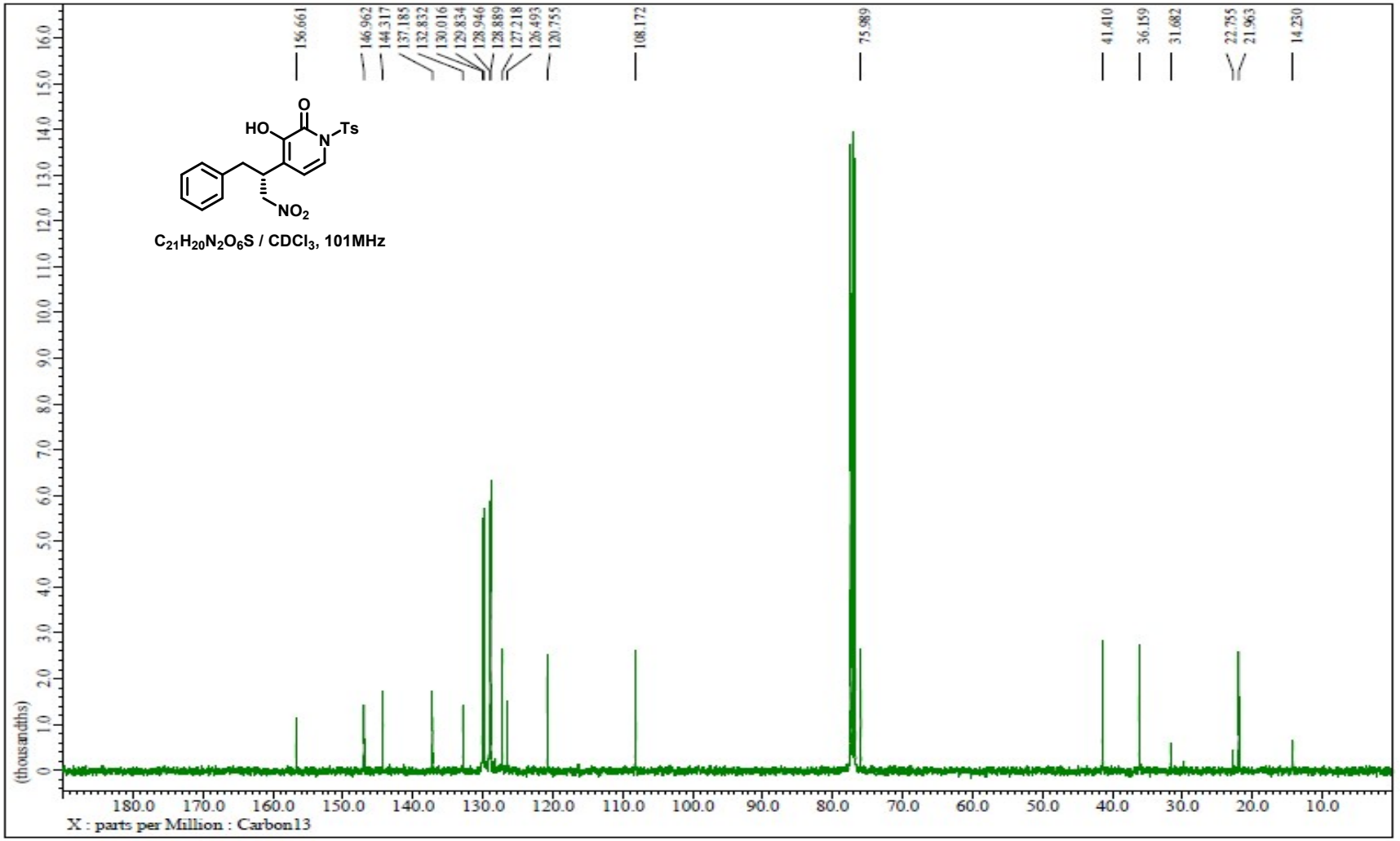
^{13}C -NMR of compound **(8j)**



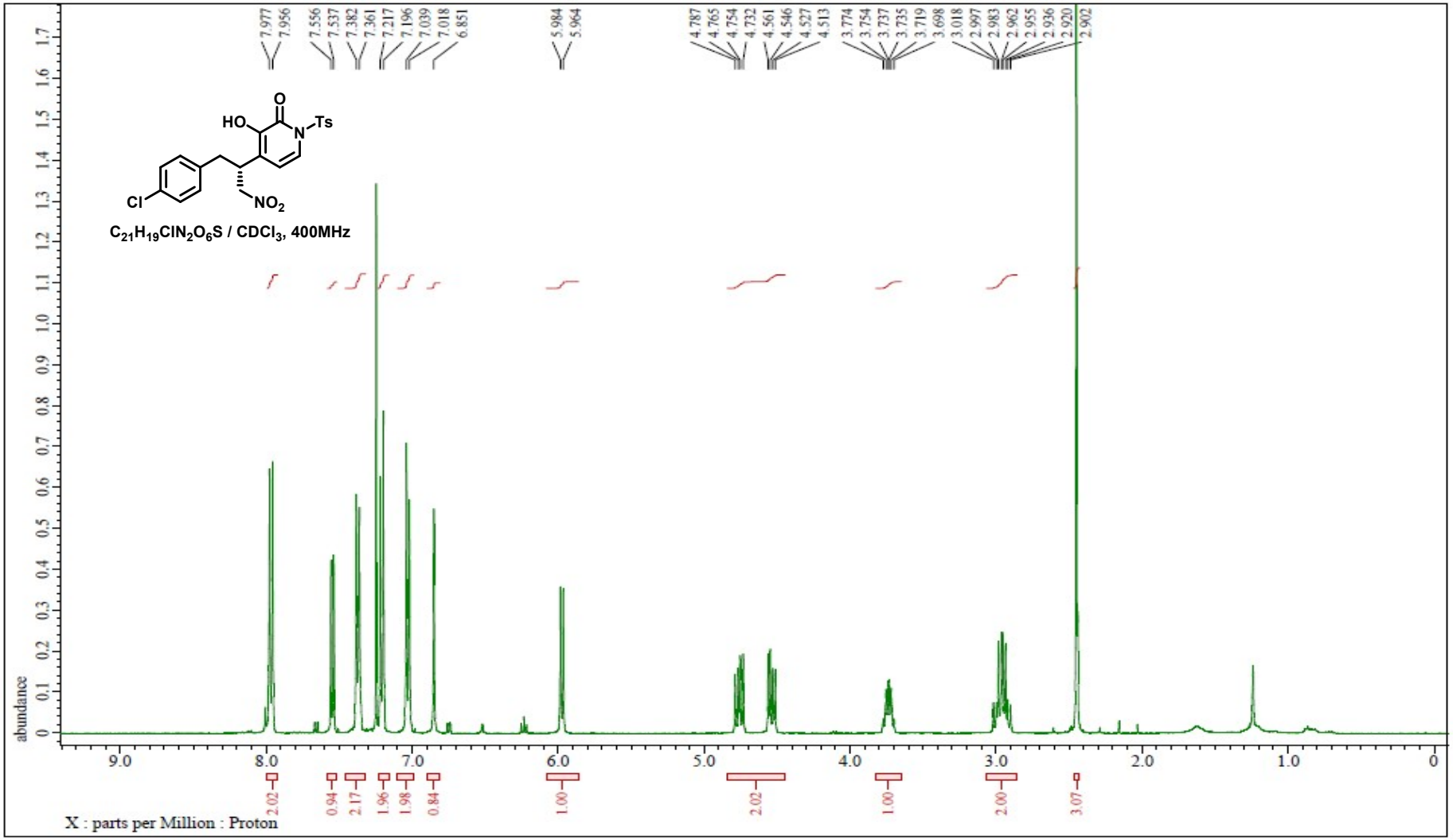
[1]H -NMR of compound **(8k)**



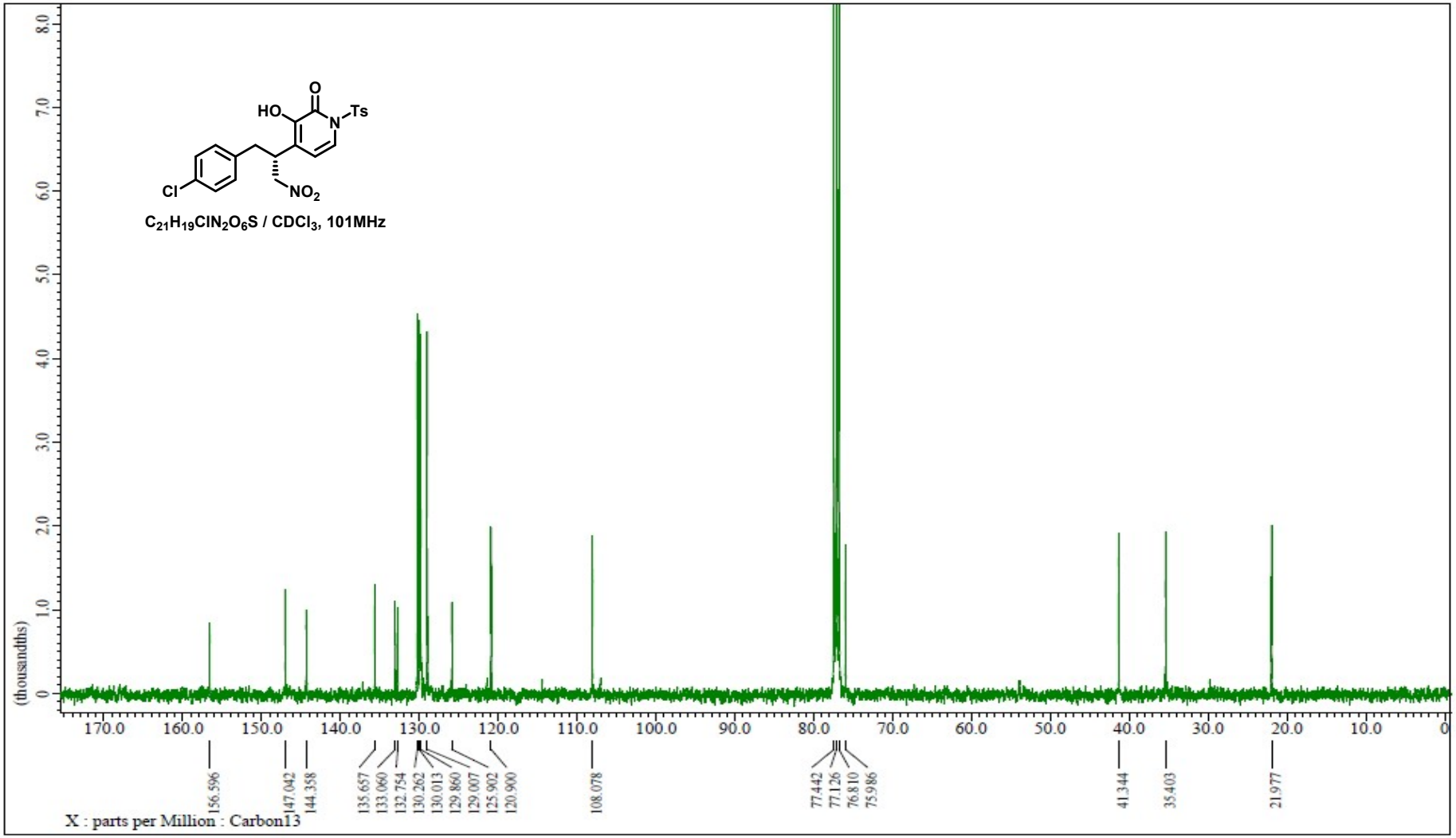
^{13}C -NMR of compound **(8k)**



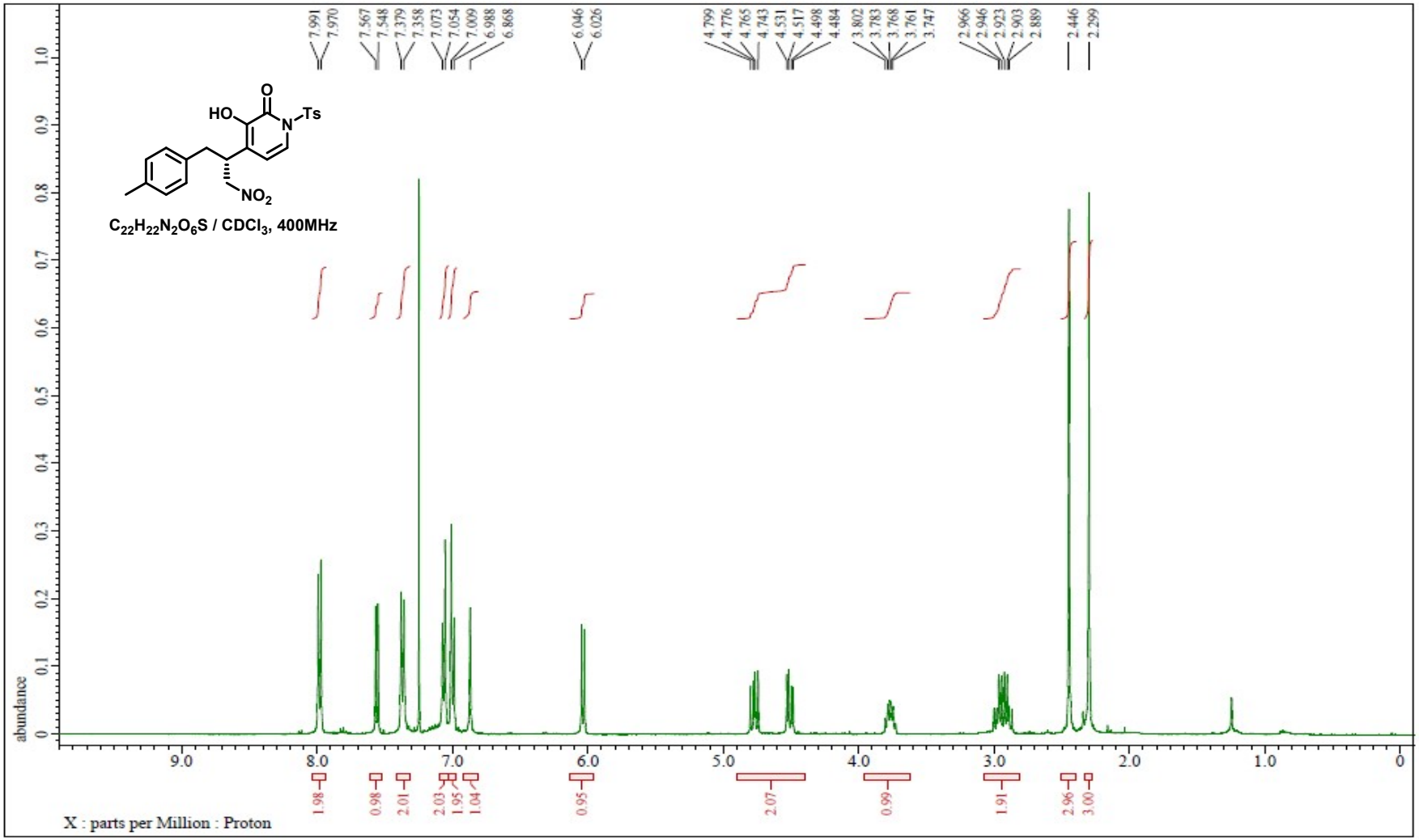
[1]H -NMR of compound **(8l)**



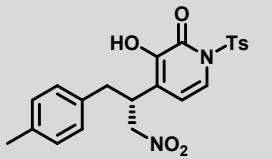
^{13}C -NMR of compound **(8l)**



[1]H -NMR of compound **(8m)**

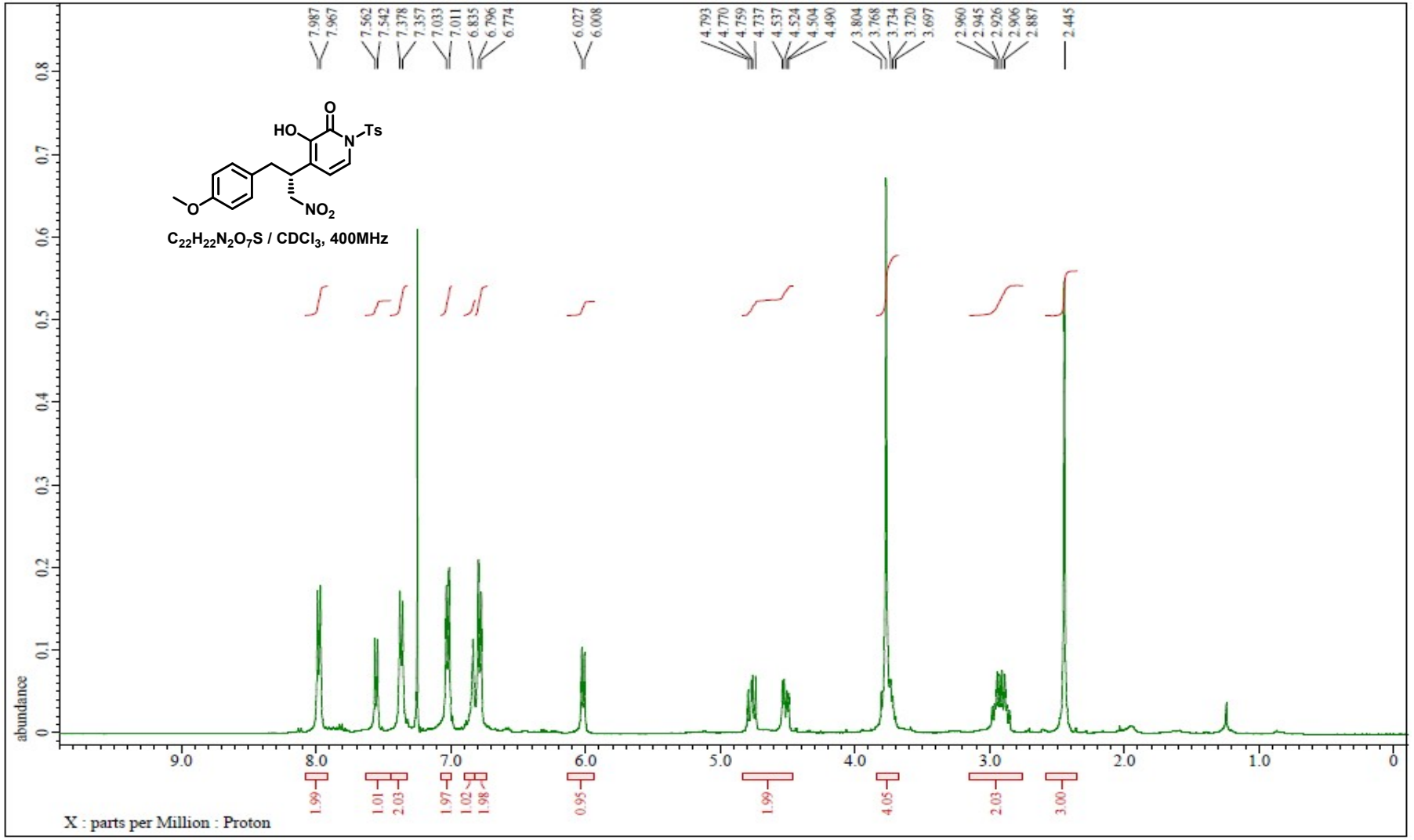


^{13}C -NMR of compound **(8m)**

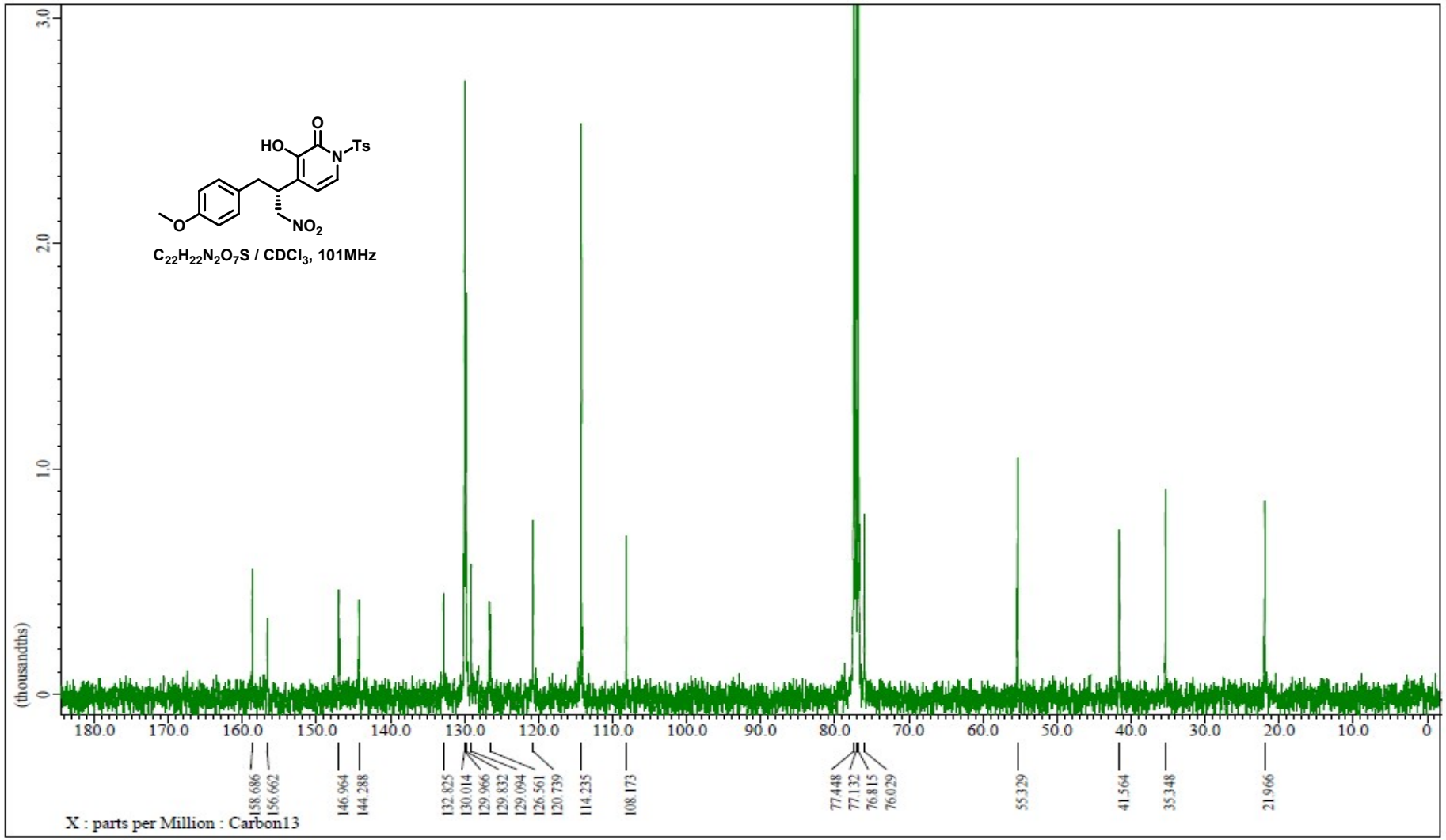


$C_{22}H_{22}N_2O_6S$ / $CDCl_3$, 101MHz

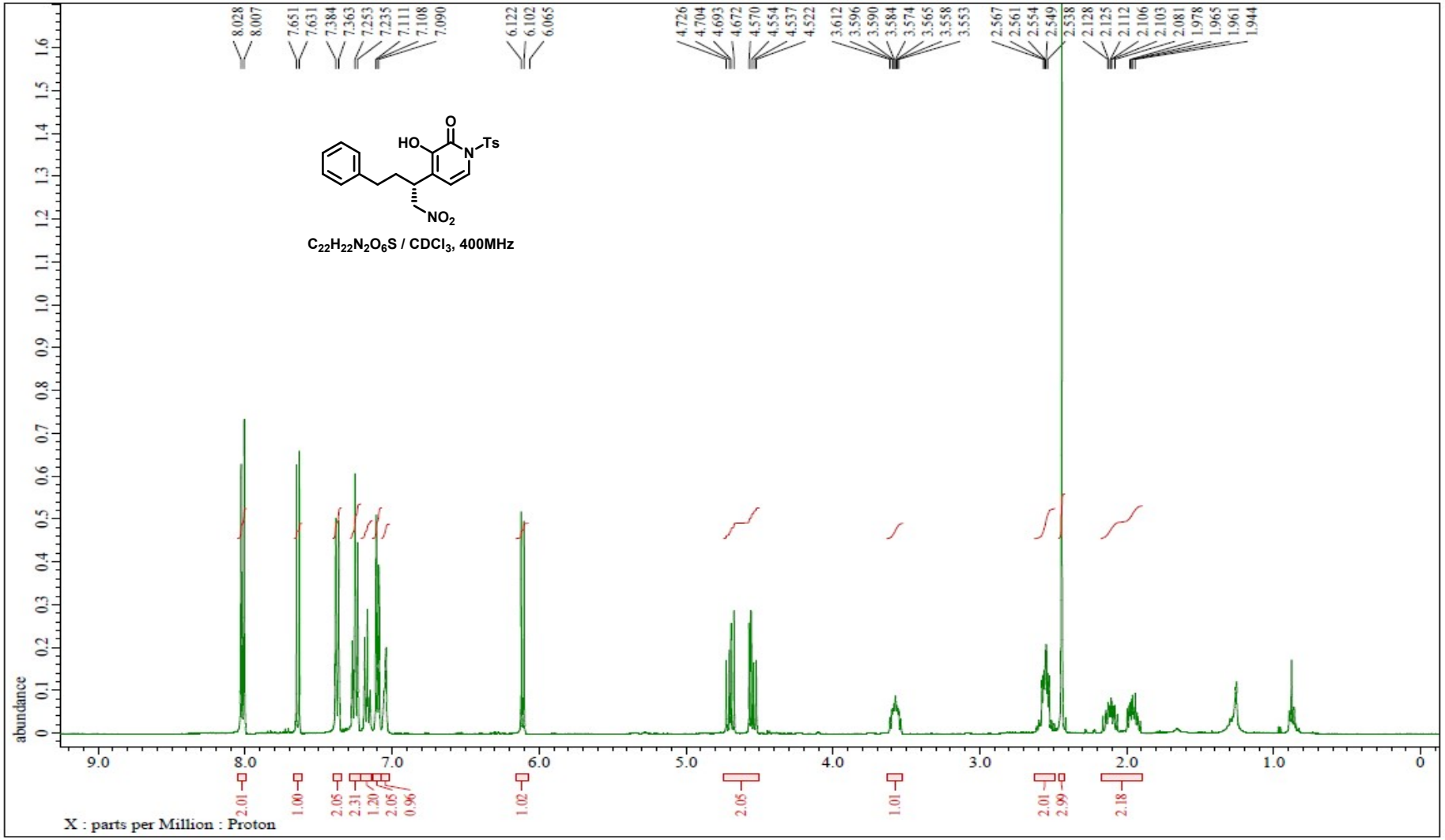
[1]H -NMR of compound **(8n)**



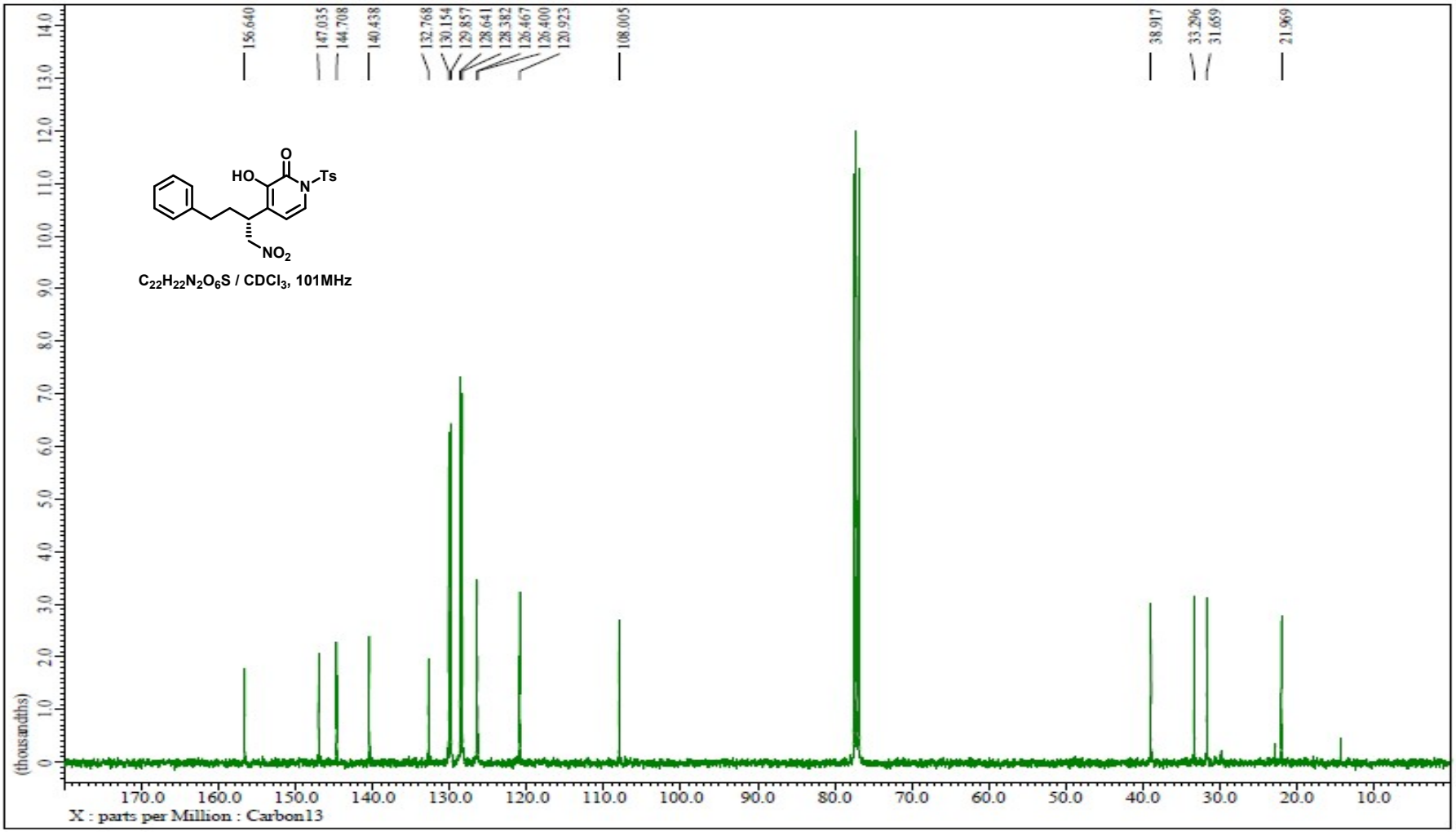
^{13}C -NMR of compound **(8n)**



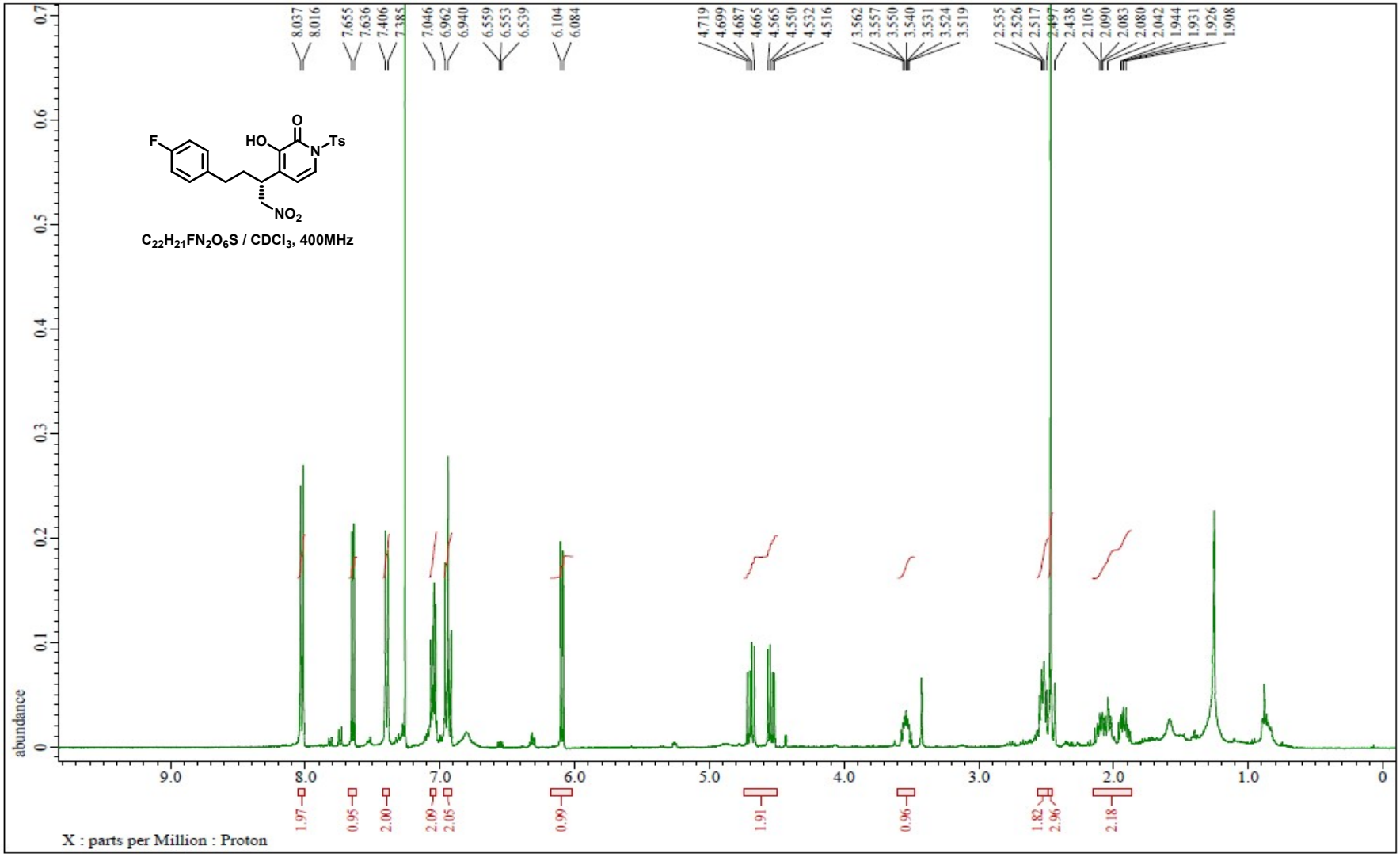
[1]H -NMR of compound **(8o)**



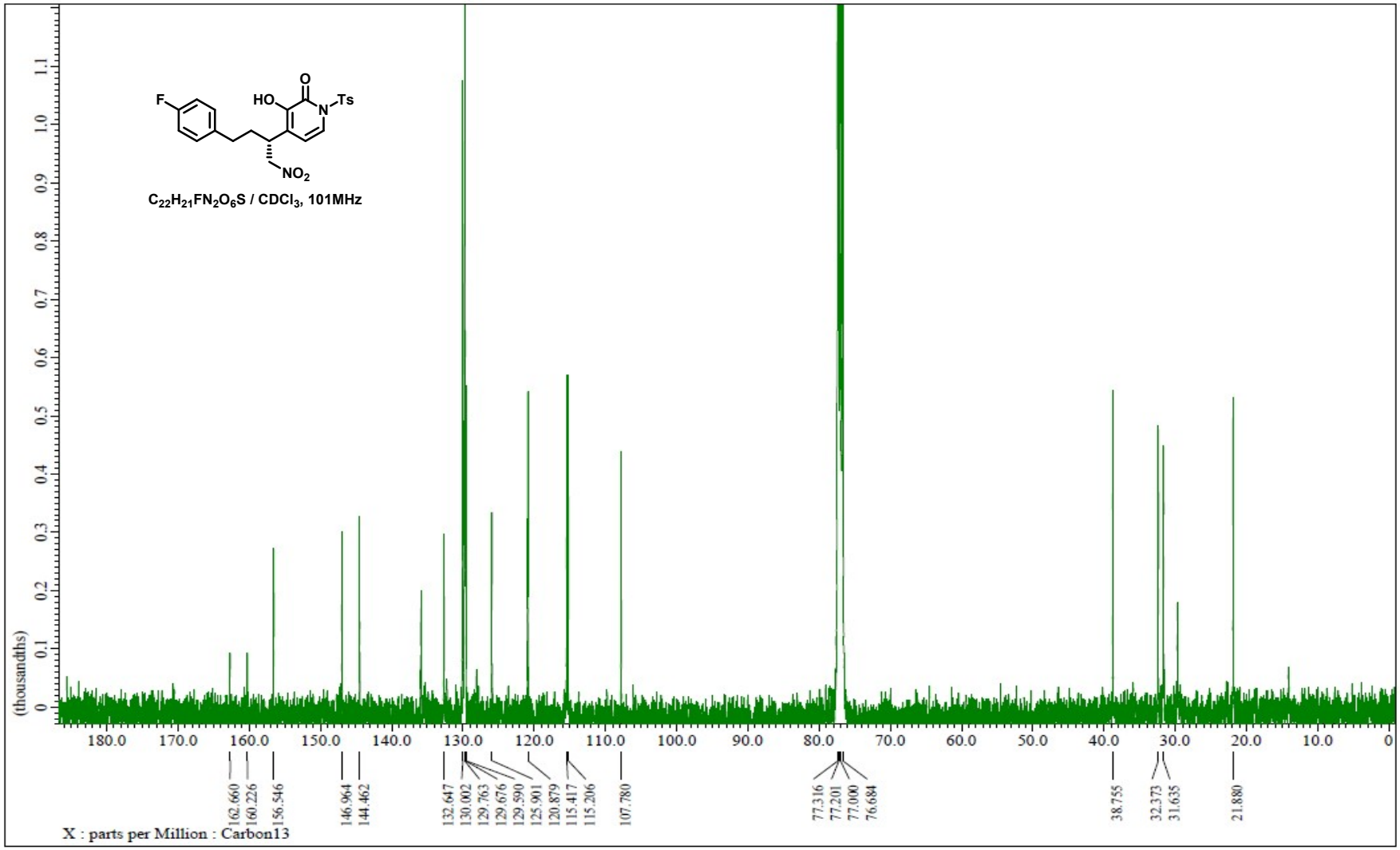
^{13}C -NMR of compound **(8o)**



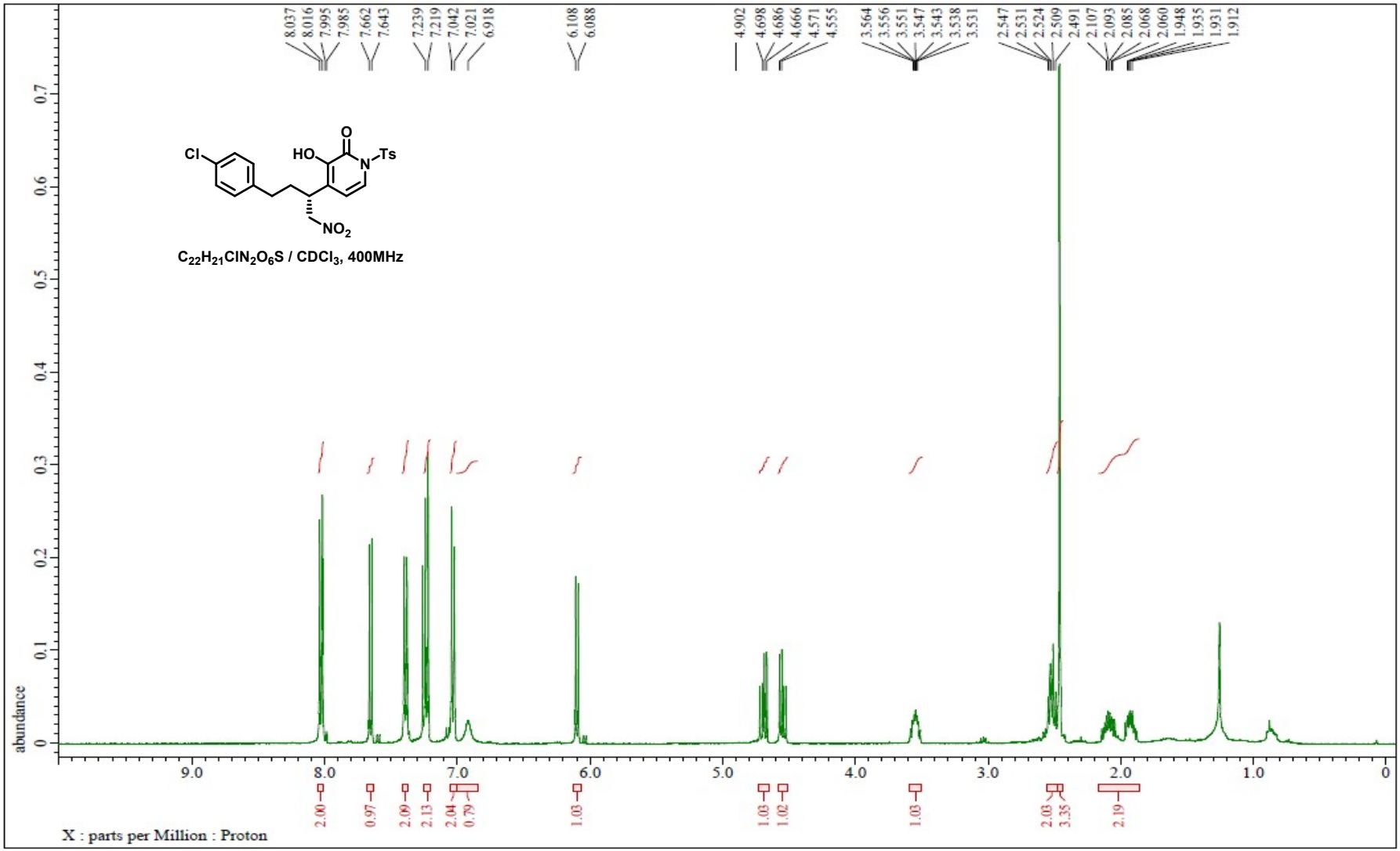
[1]H -NMR of compound **(8p)**



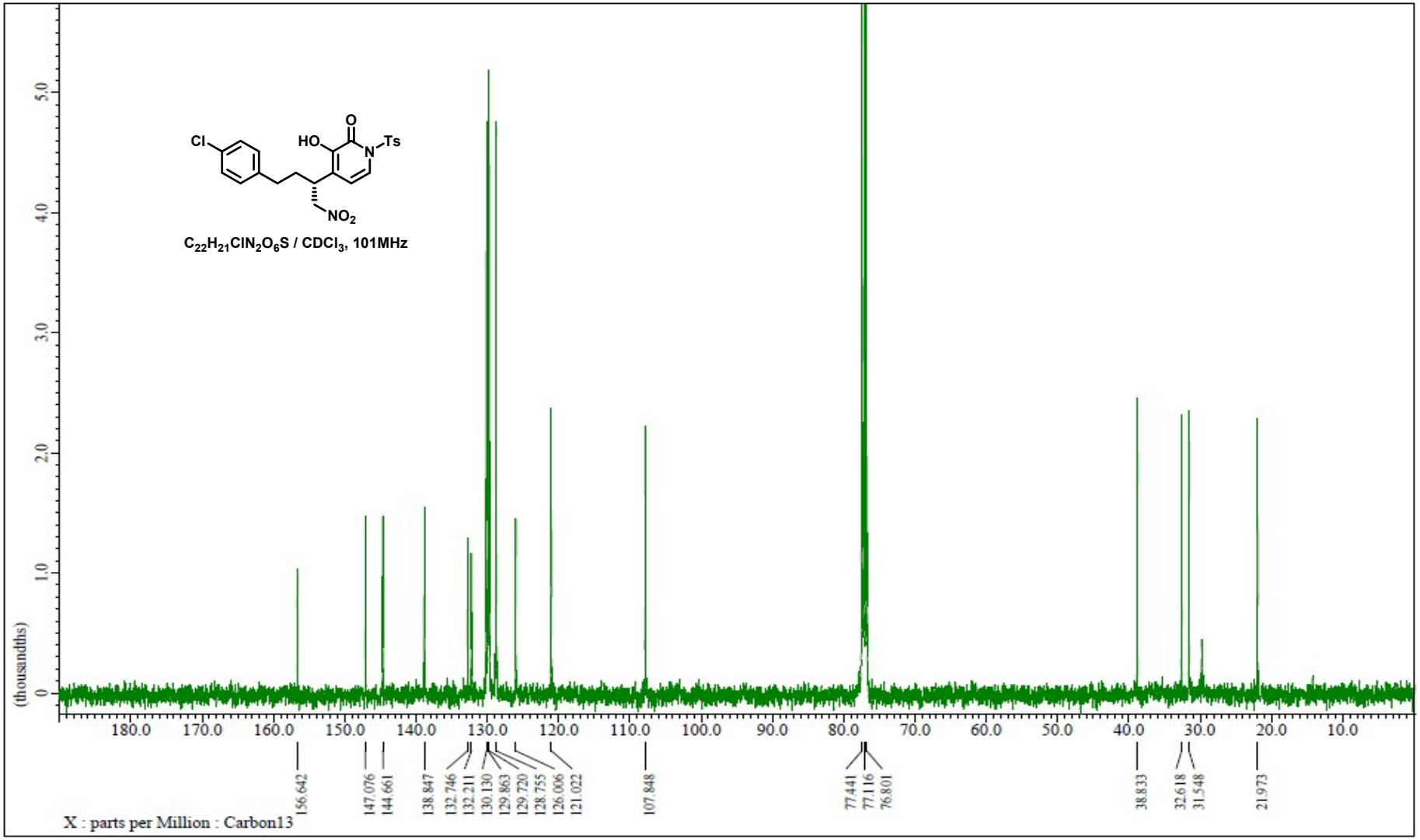
^{13}C -NMR of compound **(8p)**



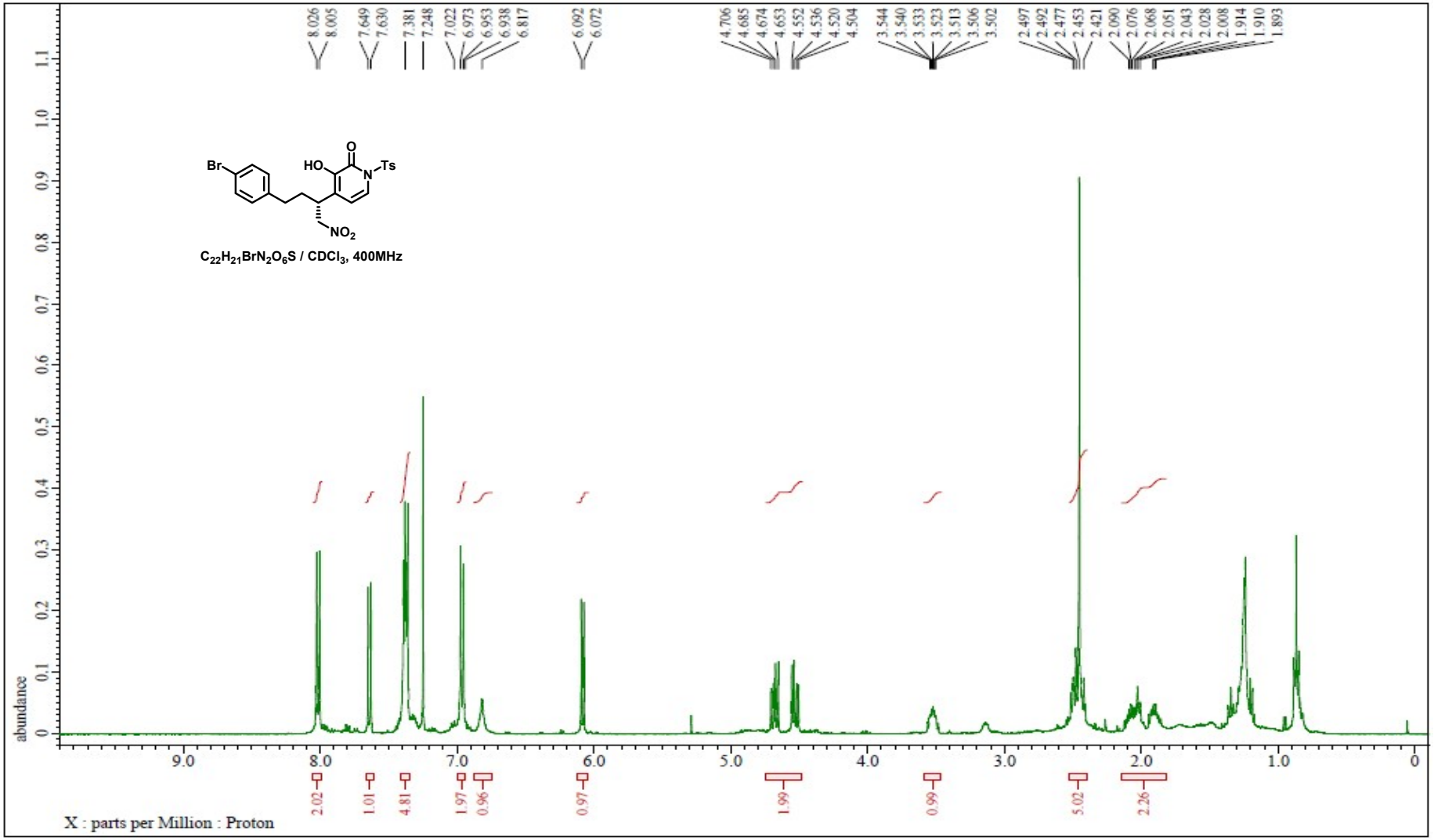
[1]H -NMR of compound **(8q)**



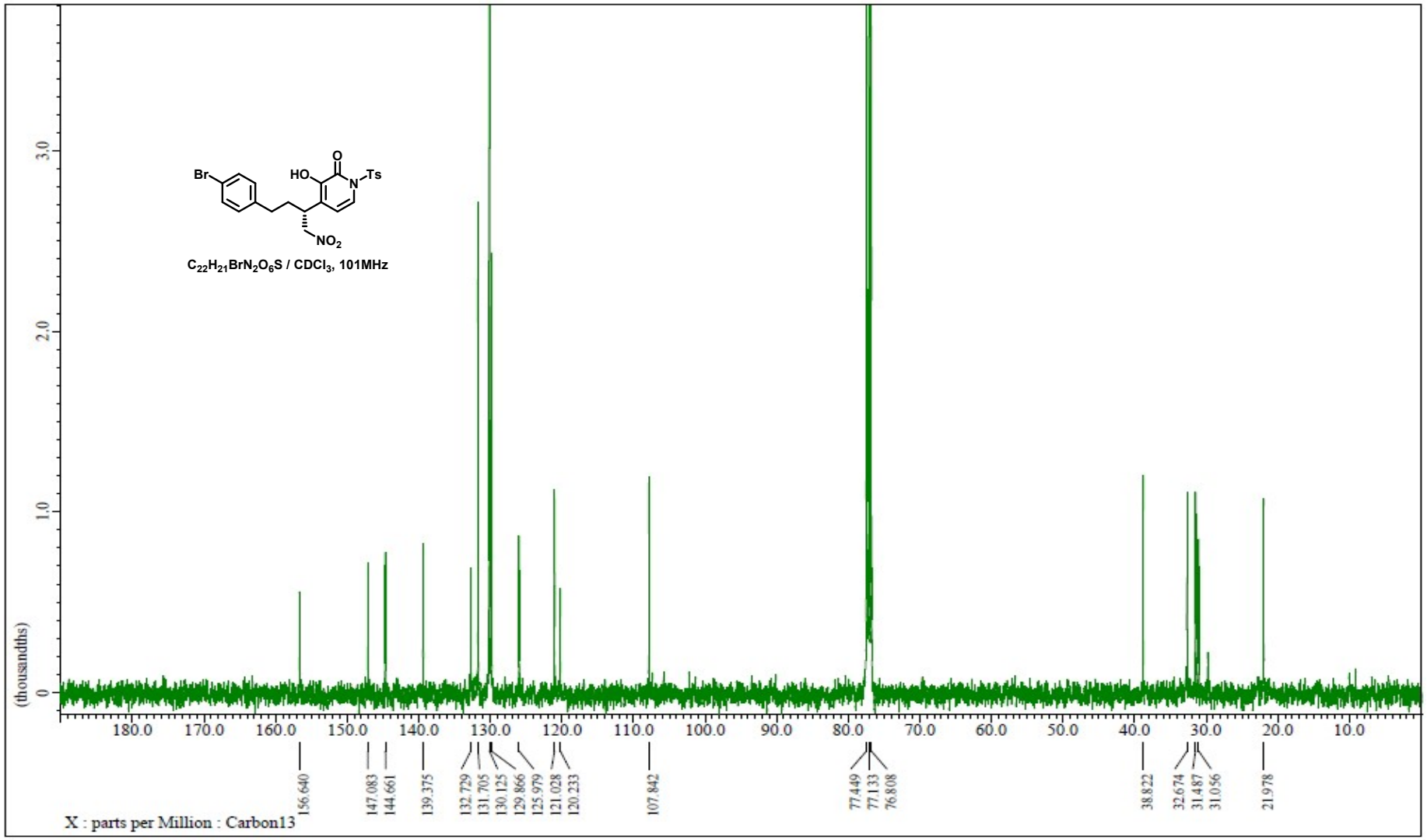
^{13}C -NMR of compound **(8q)**



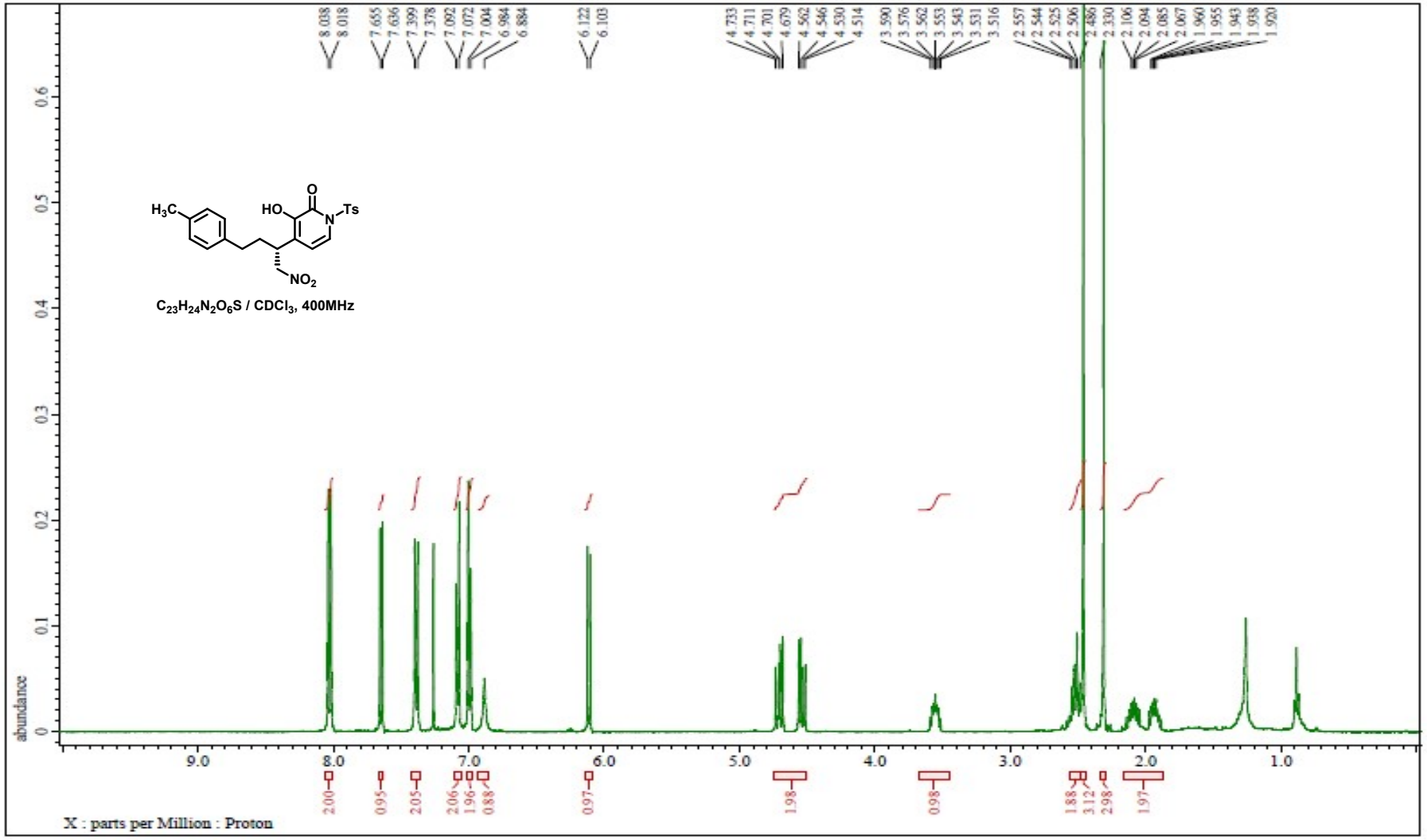
[1]H -NMR of compound **(8r)**



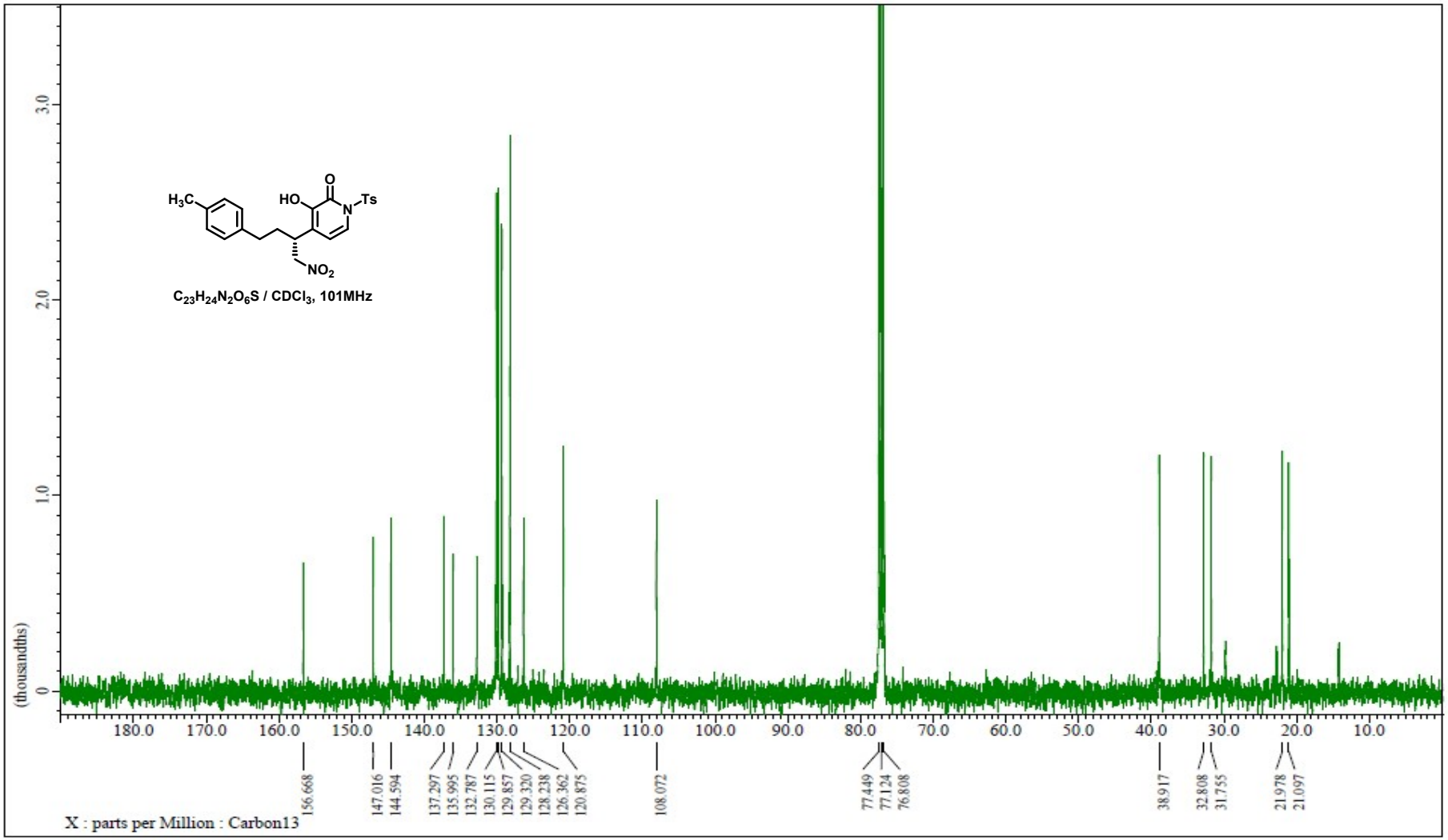
^{13}C -NMR of compound **(8r)**



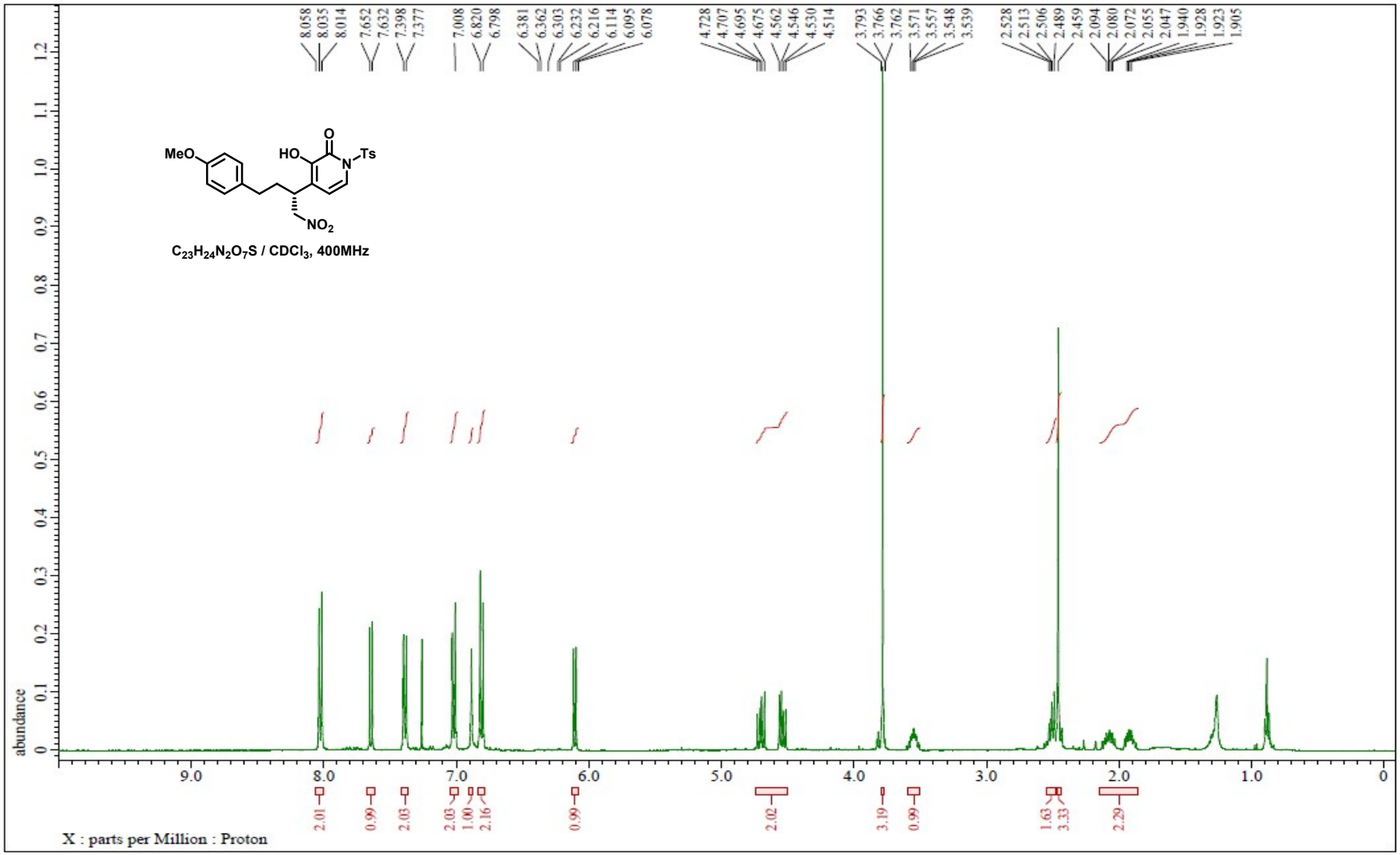
[1]H -NMR of compound **(8s)**



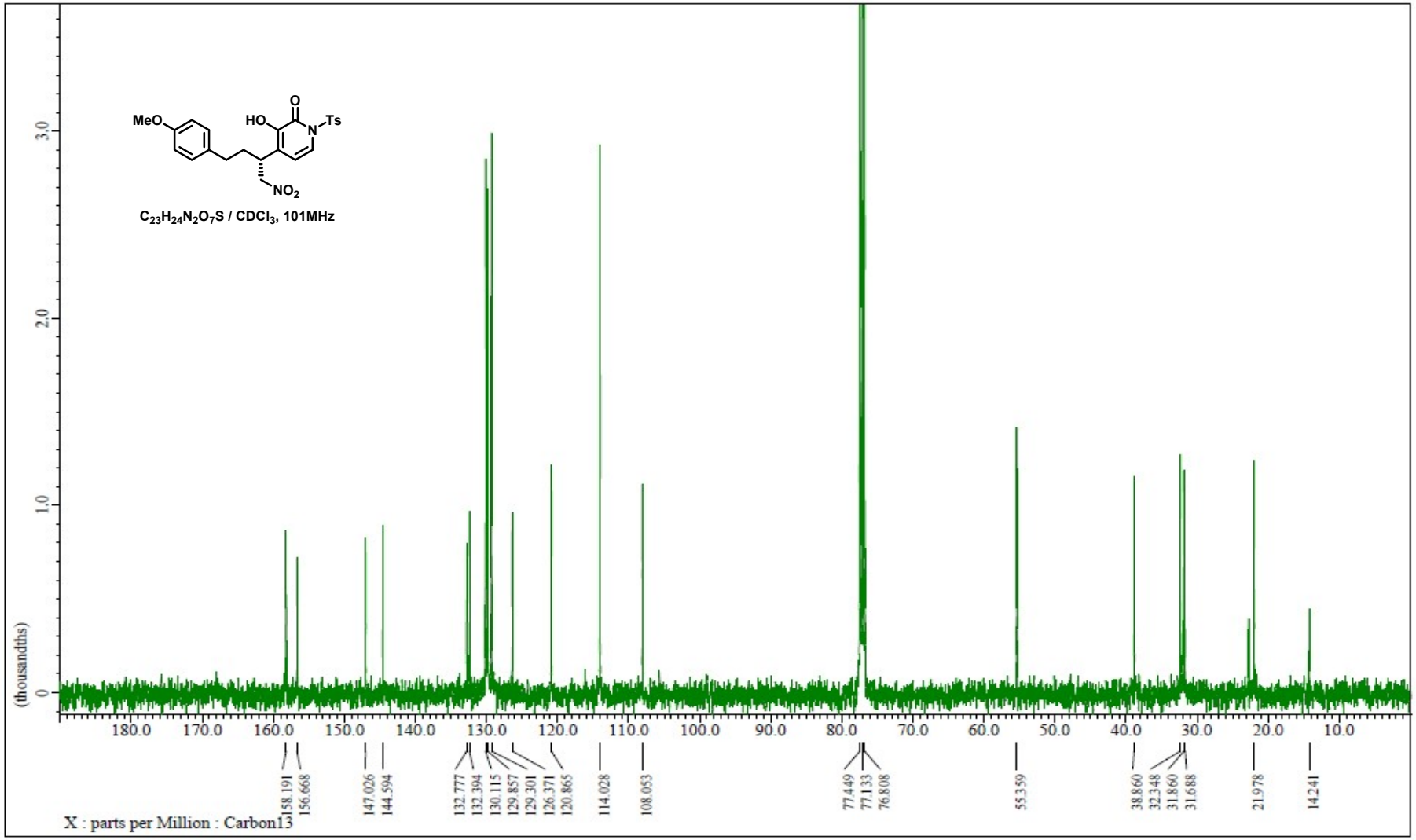
^{13}C -NMR of compound **(8s)**



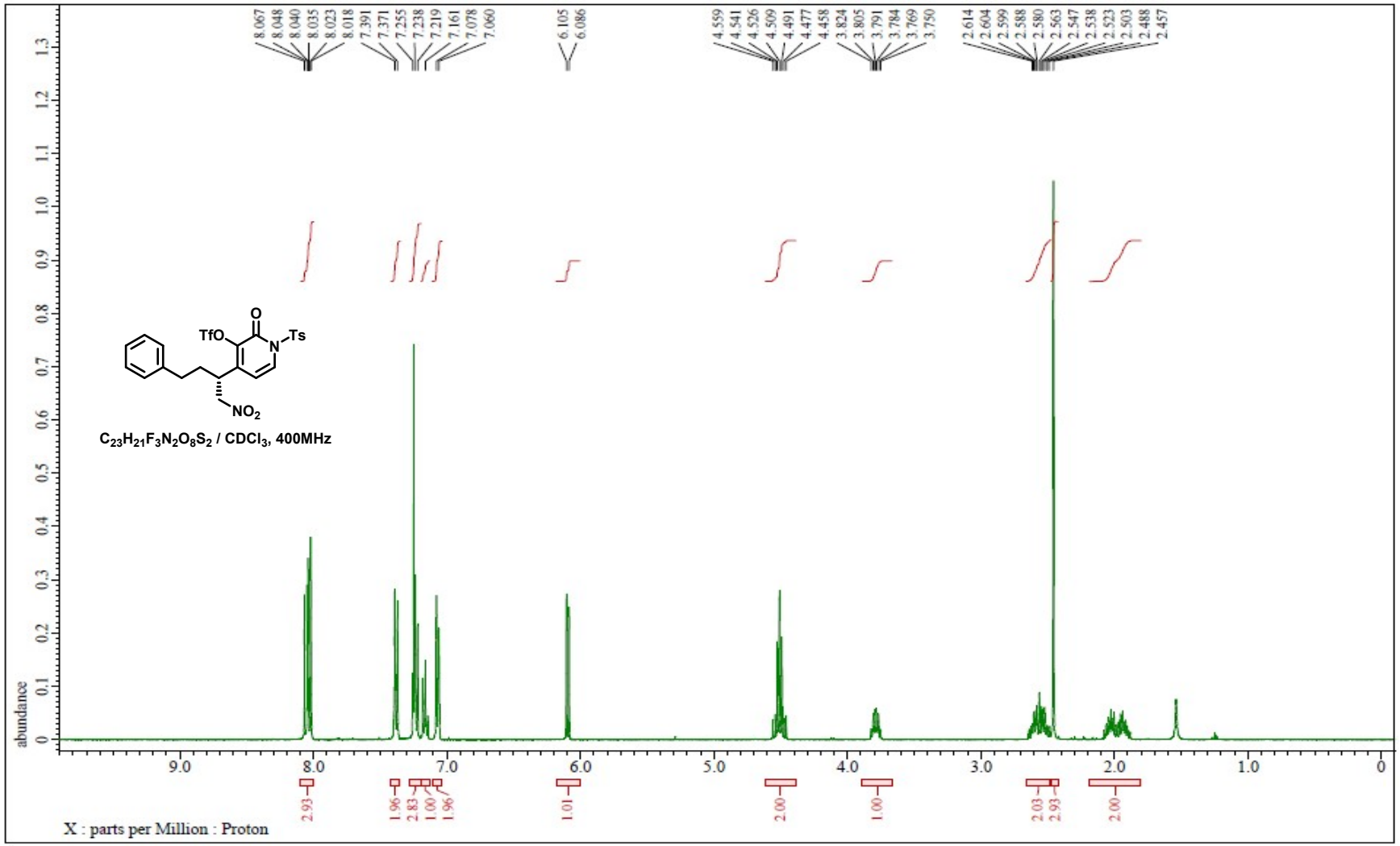
[1]H -NMR of compound **(8t)**



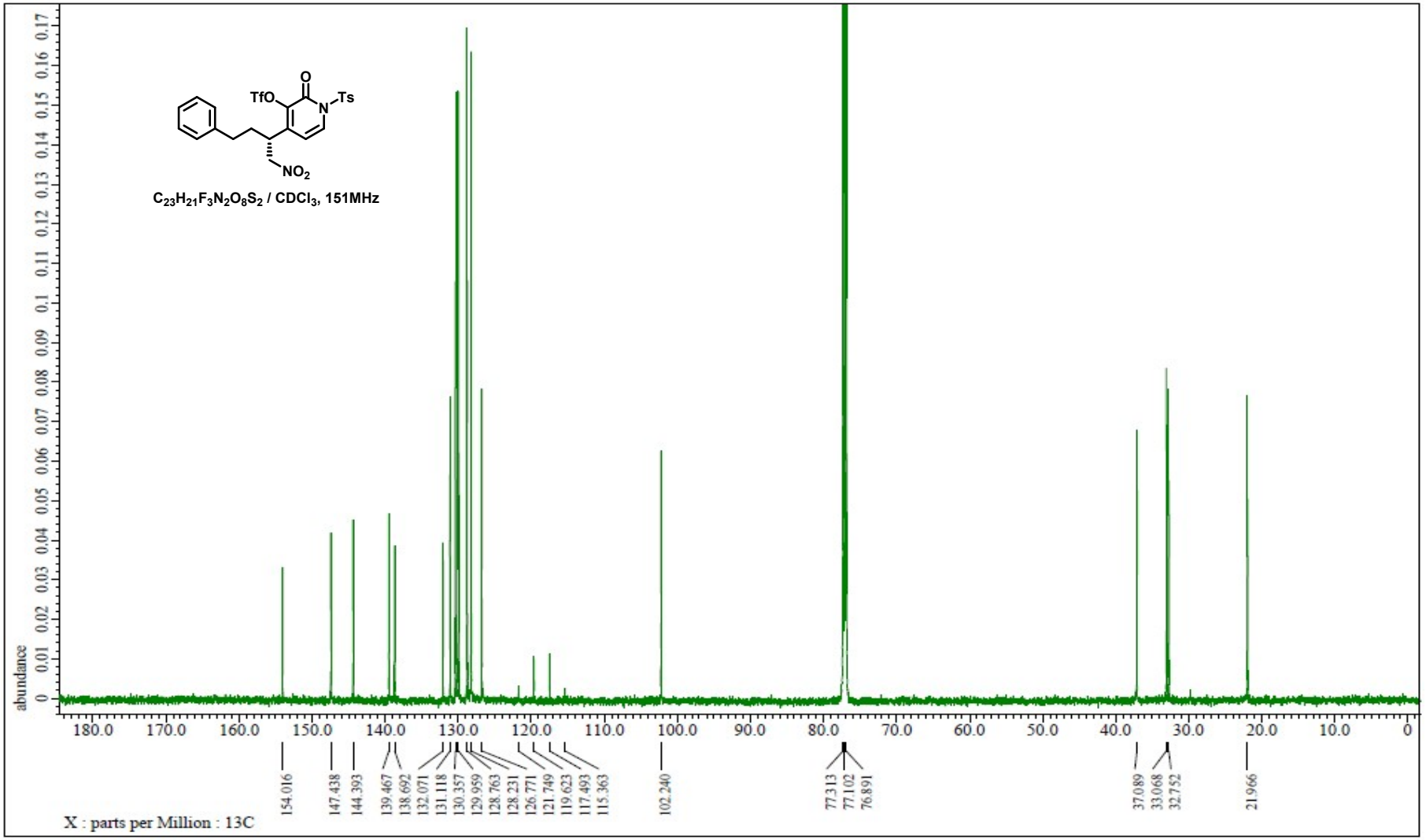
^{13}C -NMR of compound **(8t)**



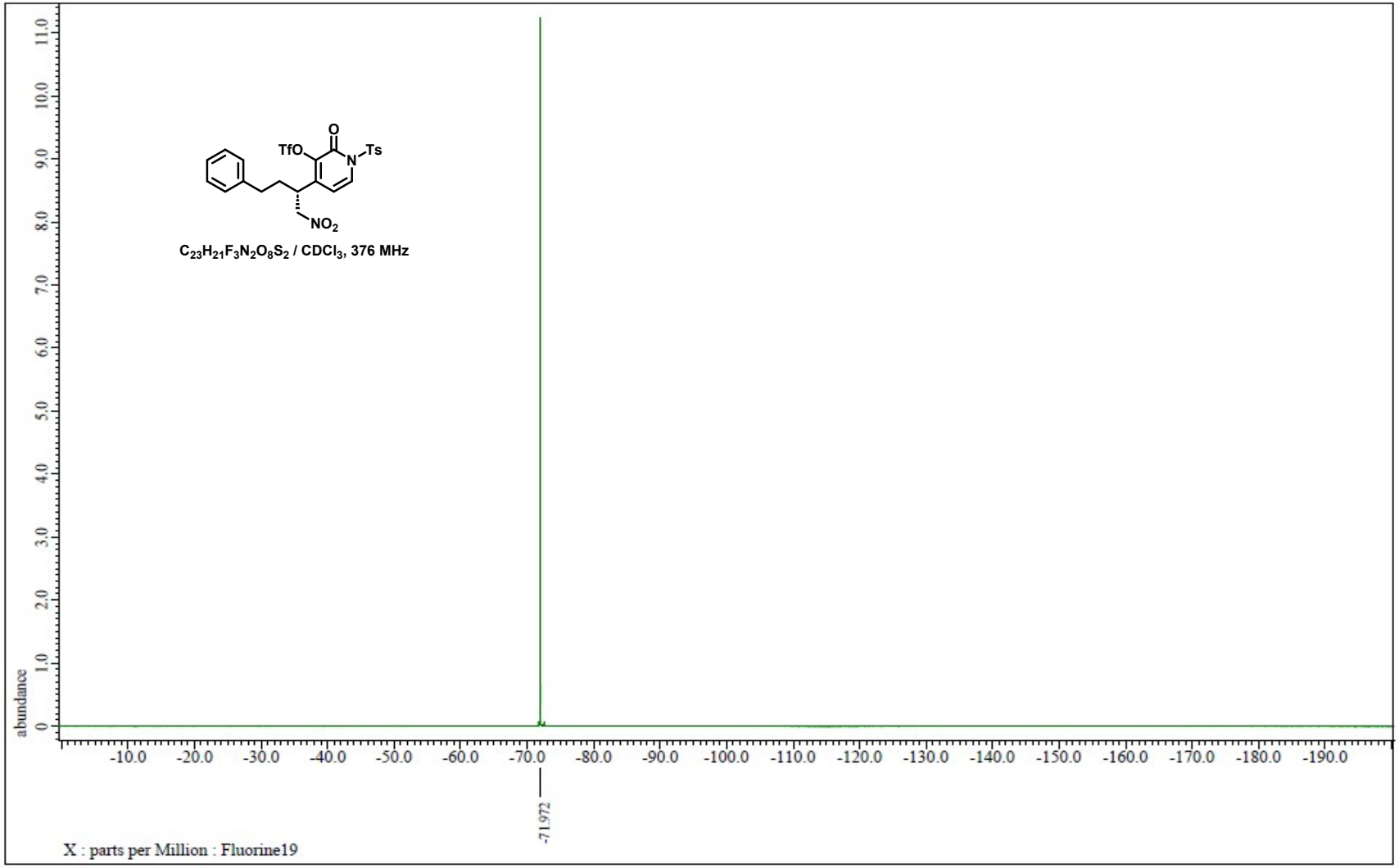
[1]H -NMR of compound **(9)**



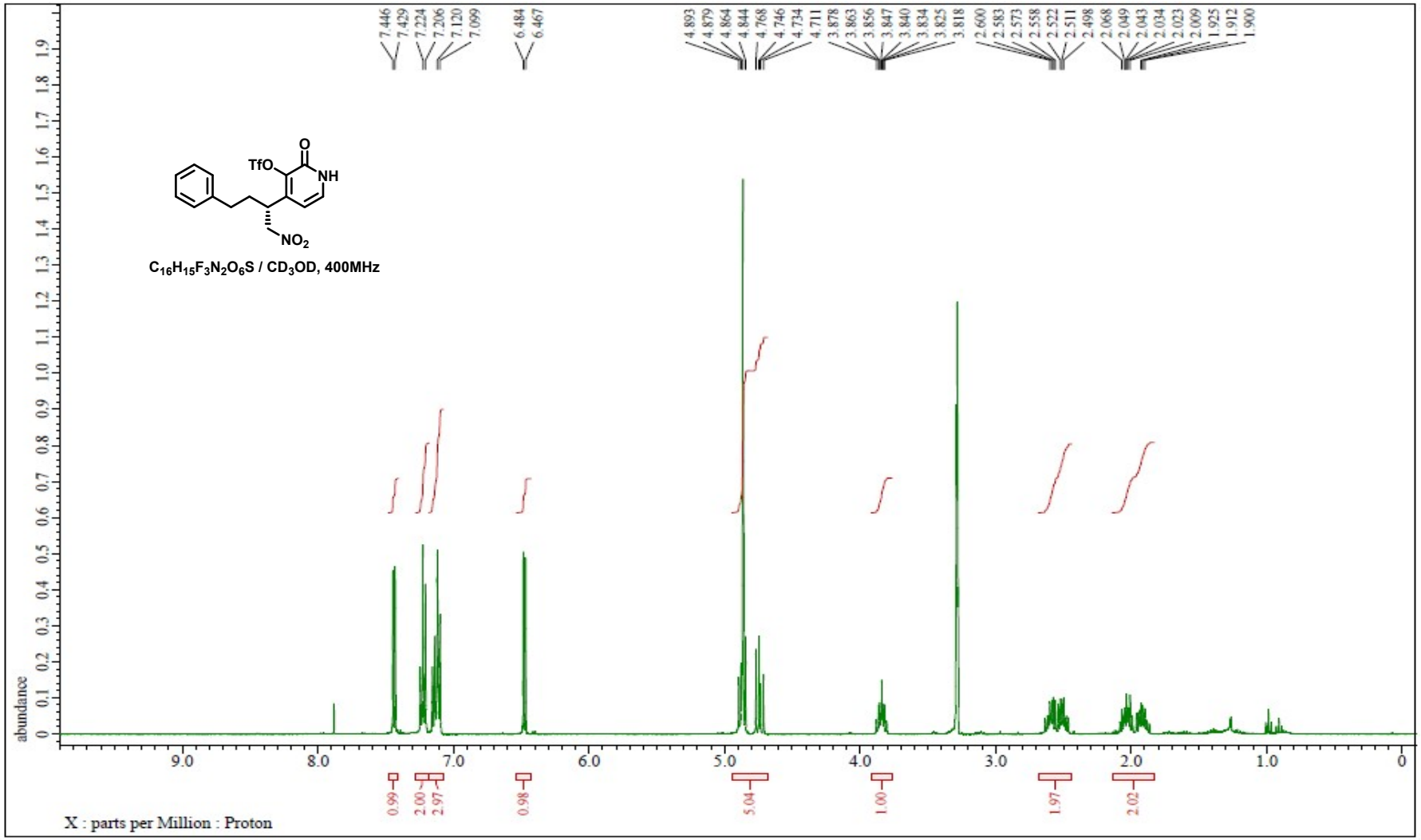
^{13}C -NMR of compound **(9)**



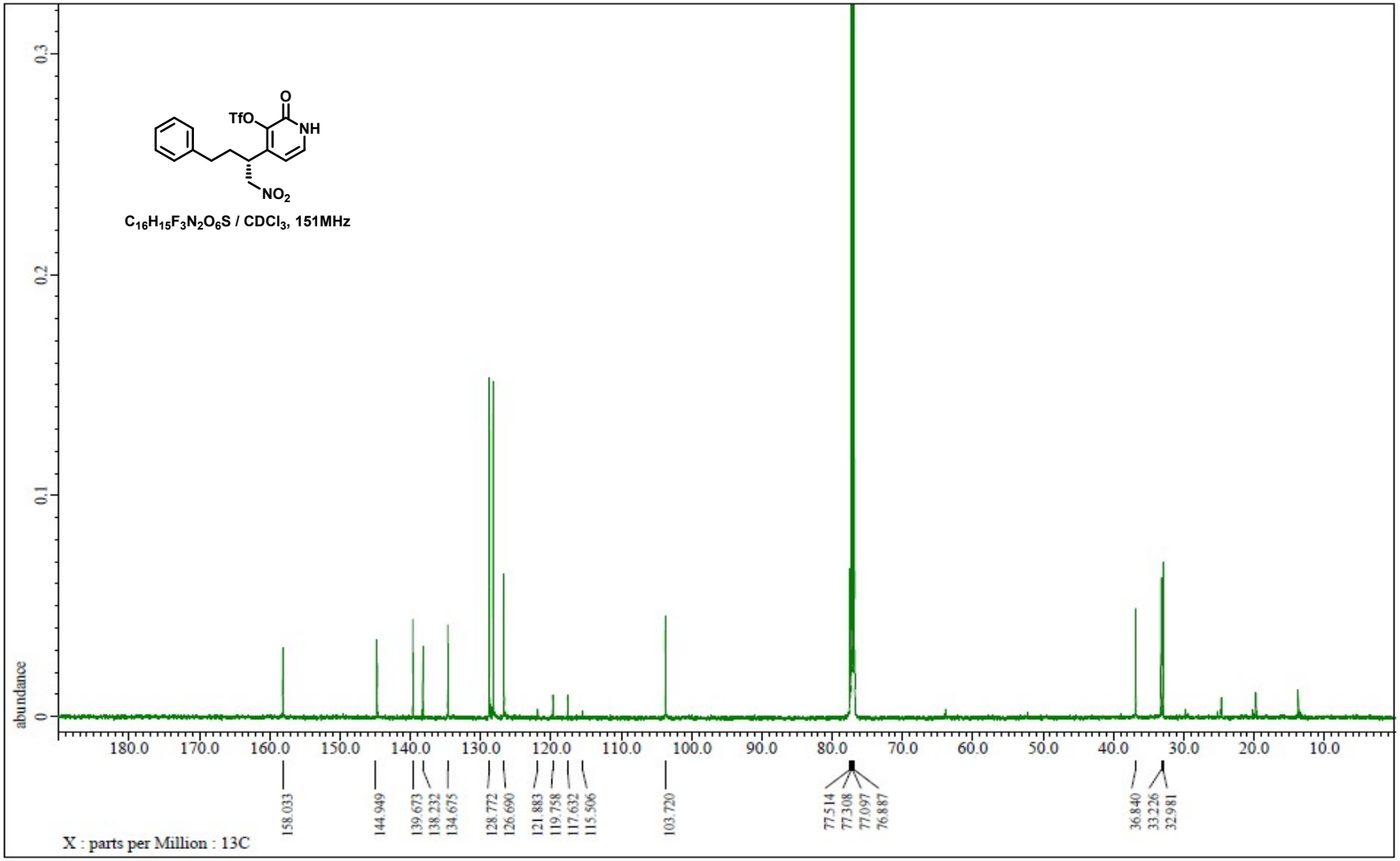
^{19}F -NMR of compound **(9)**



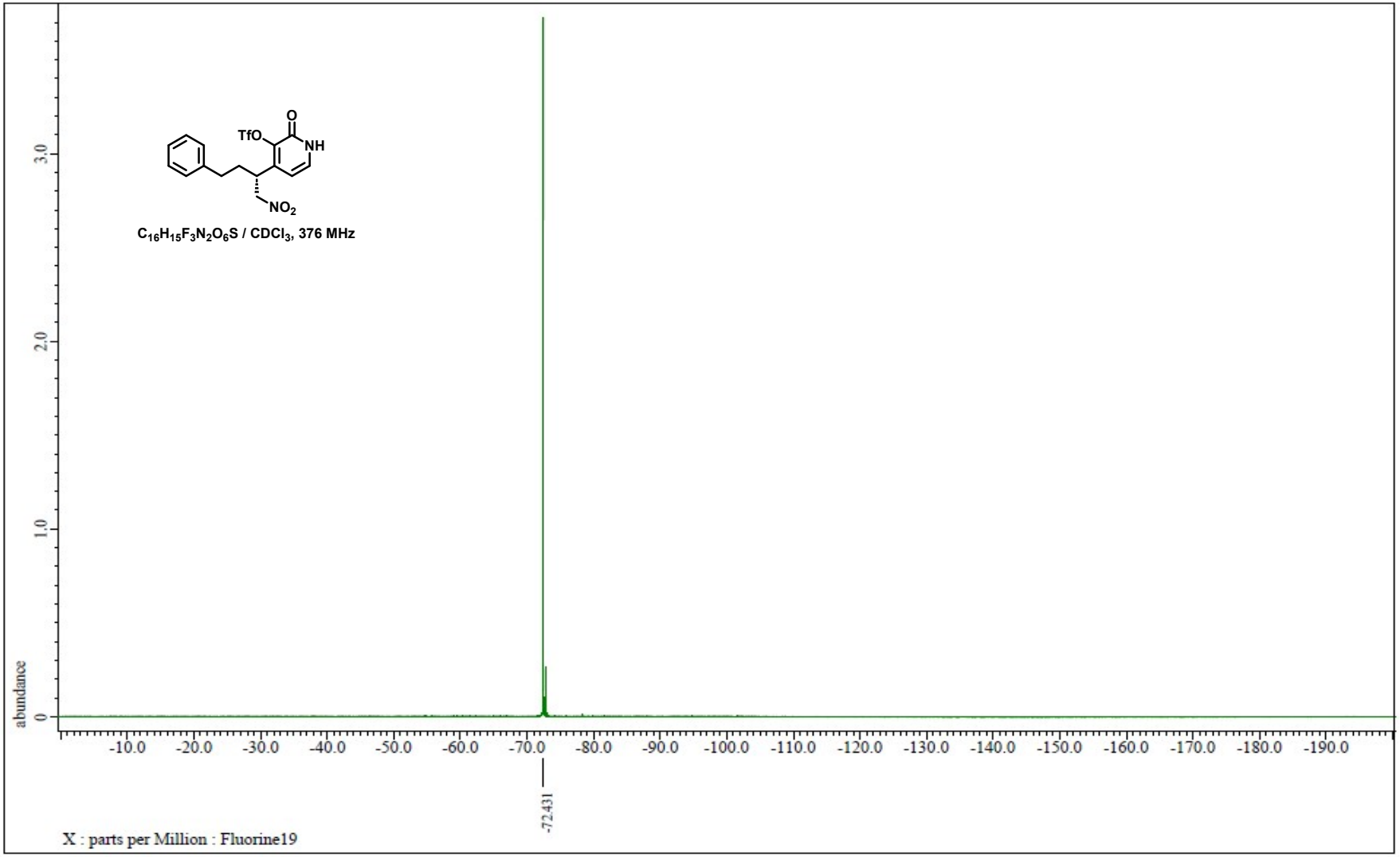
[1]H -NMR of compound **(10)**



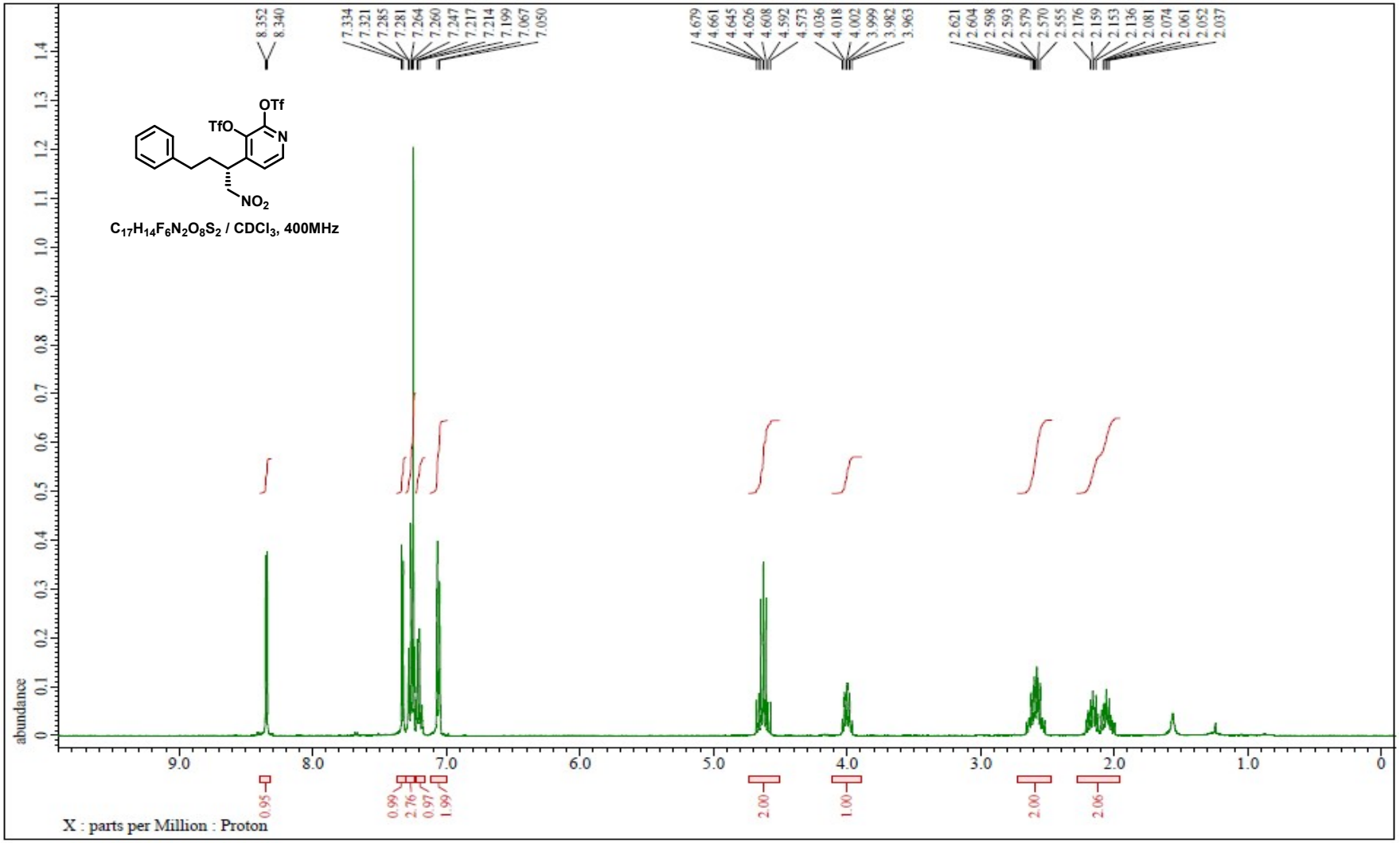
^{13}C -NMR of compound **(10)**



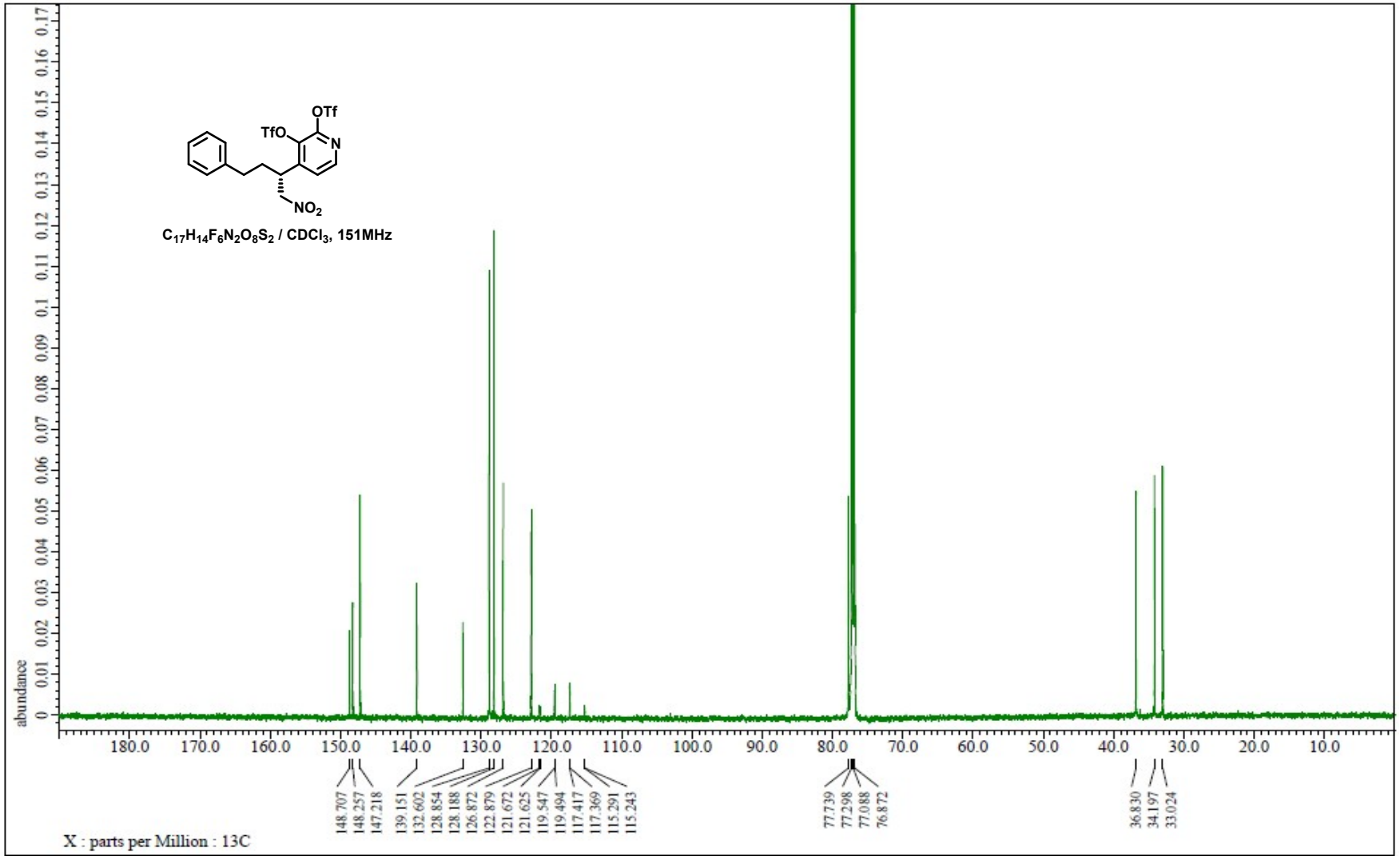
^{19}F -NMR of compound **(10)**



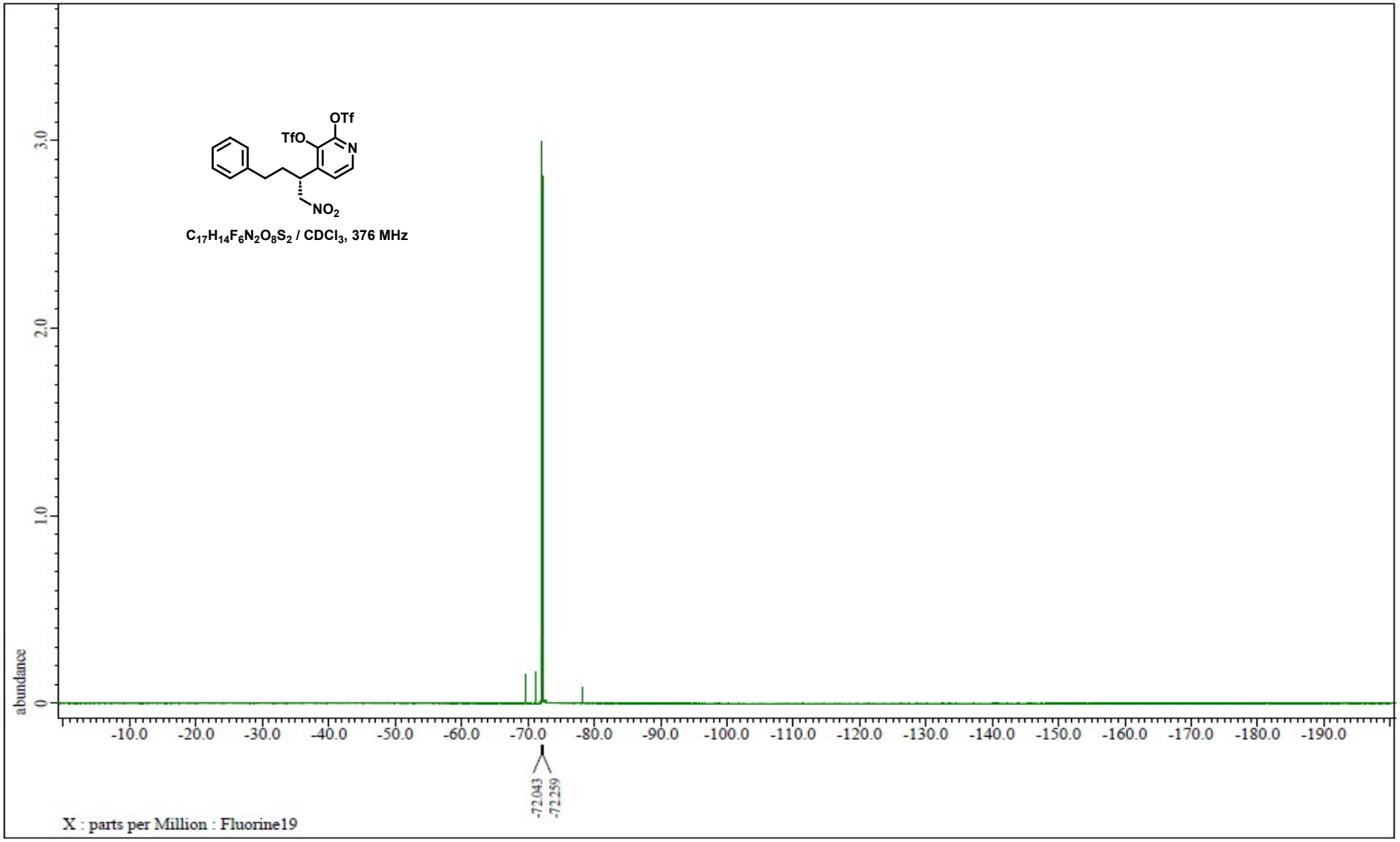
[1]H -NMR of compound **(11)**



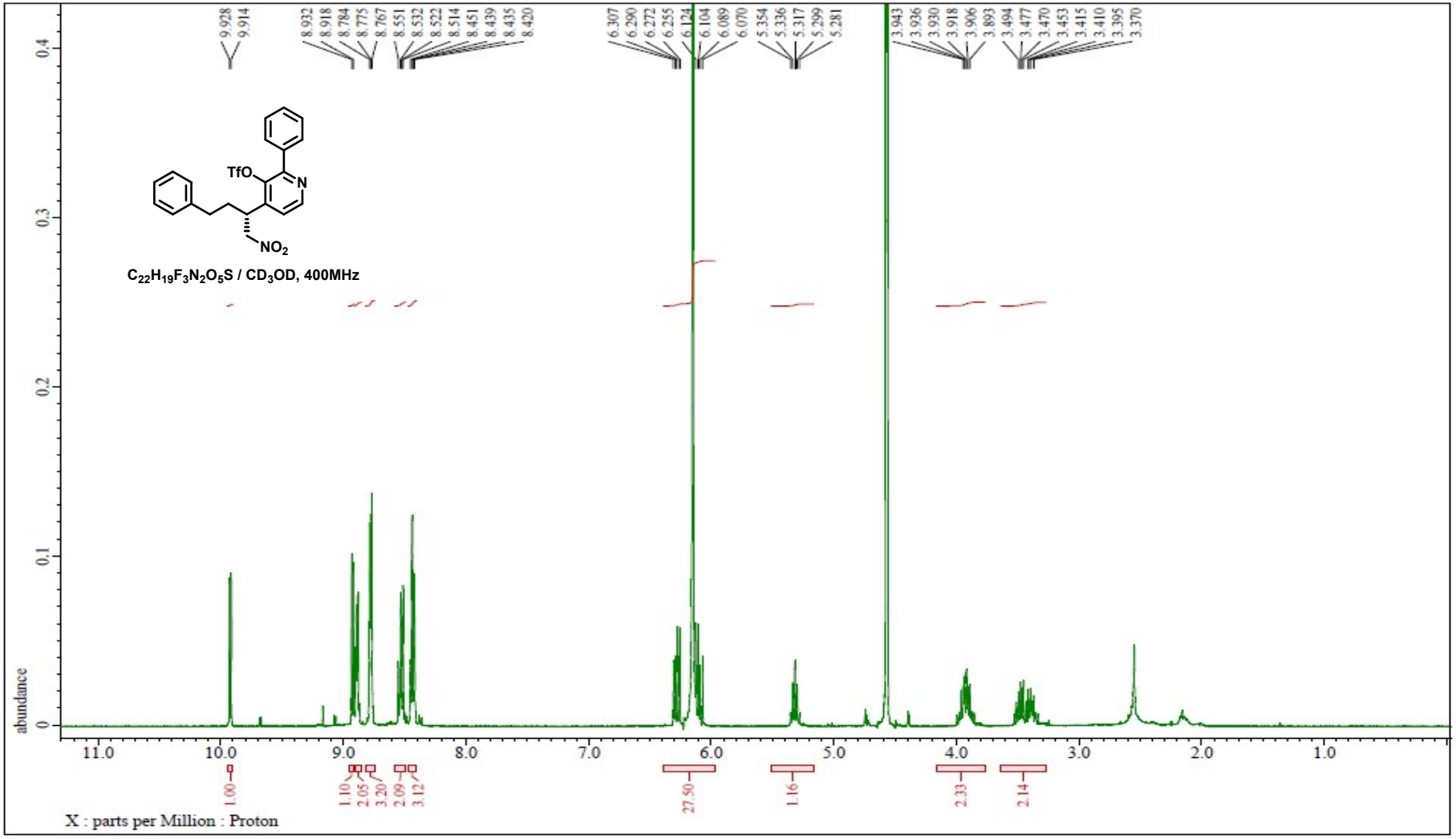
^{13}C -NMR of compound **(11)**



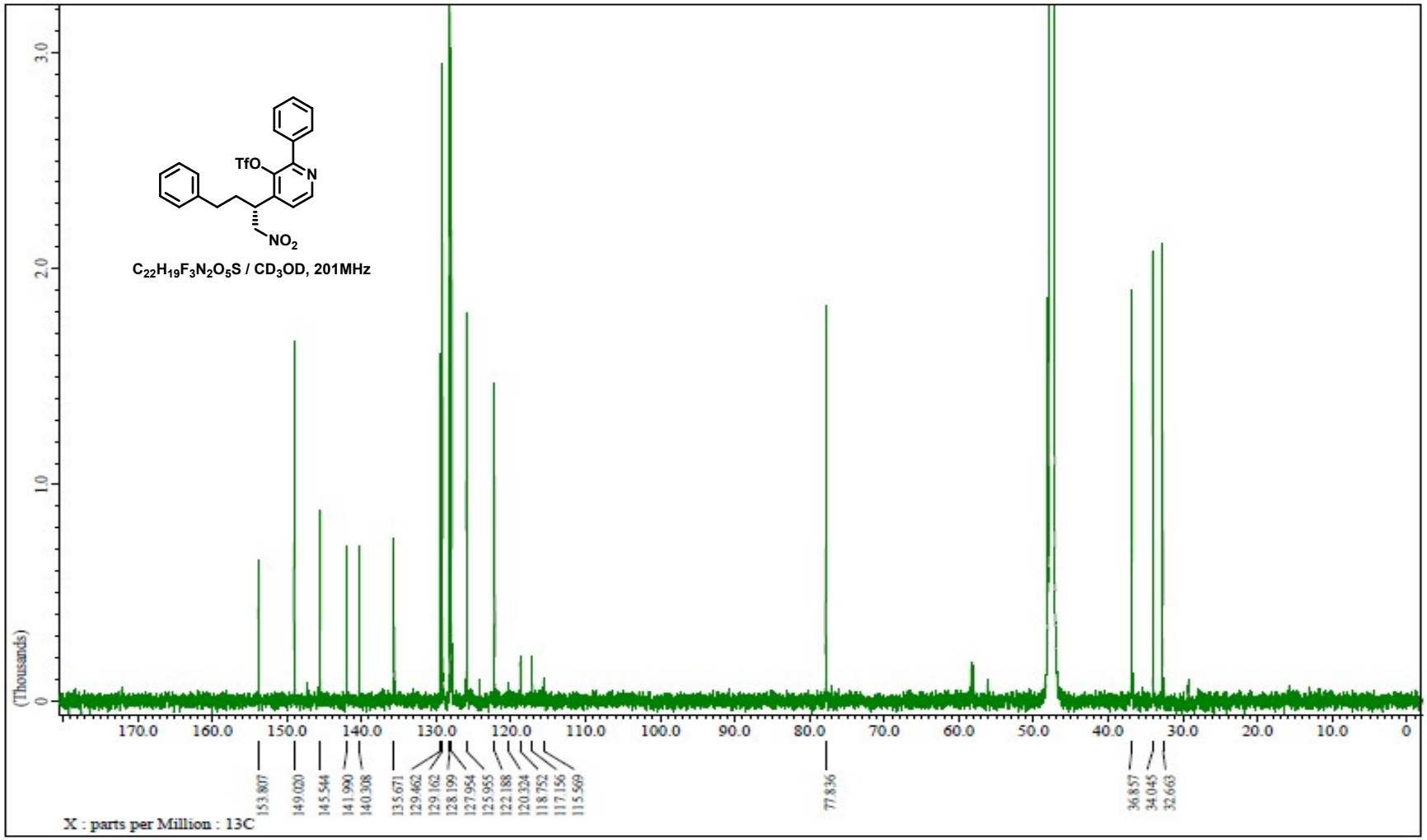
^{19}F -NMR of compound **(11)**



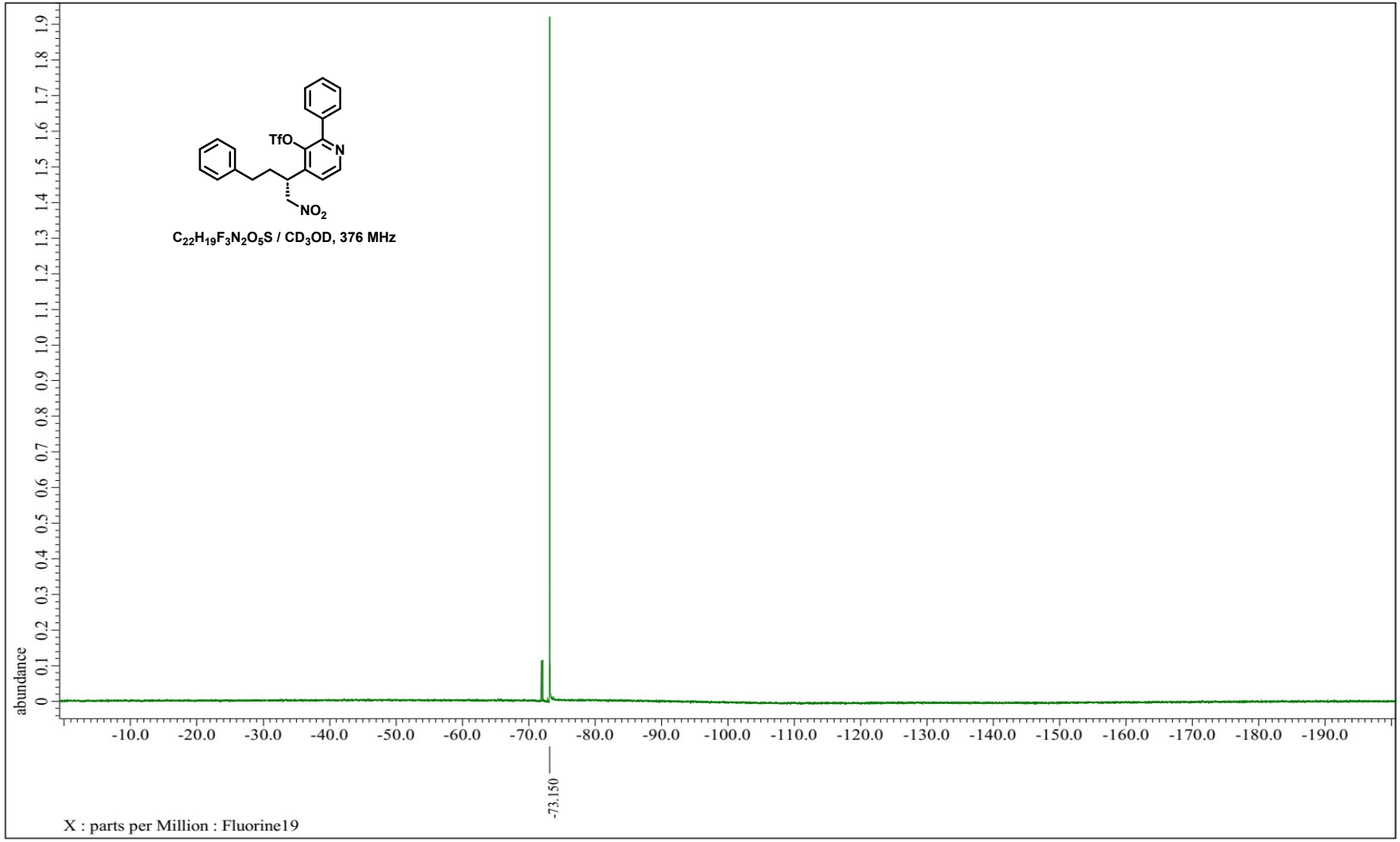
[1]H -NMR of compound **(12)**



^{13}C -NMR of compound **(12)**



^{19}F -NMR of compound **(12)**



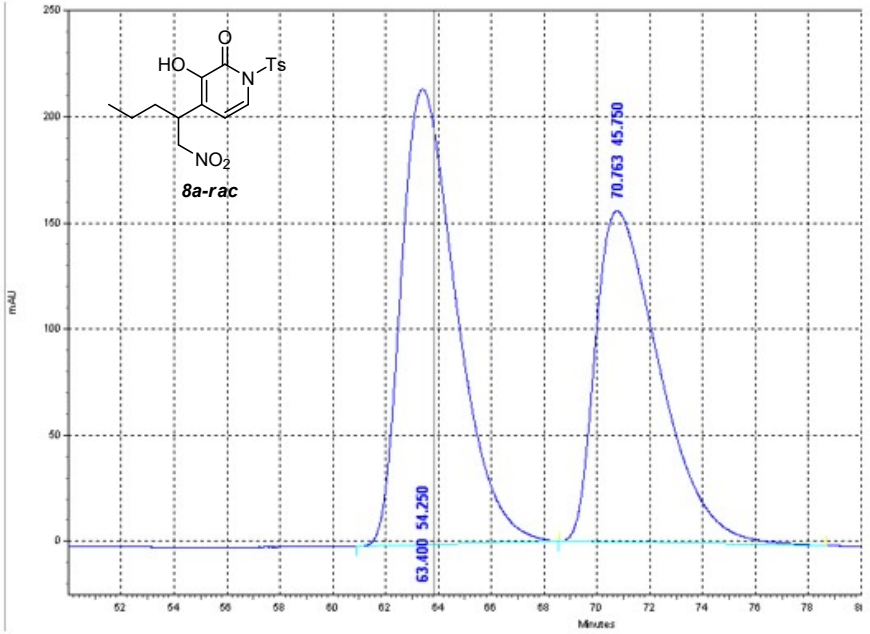
(6) Chiral HPLC spectra

As the racemate products could not obtained by using trimethylamine (TEA), the LC data of racemates were obtained by using catalyst **1a** which gave almost racemates.

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak AD-H, hexane : 2-propanol = 80 : 20, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8a-rac***



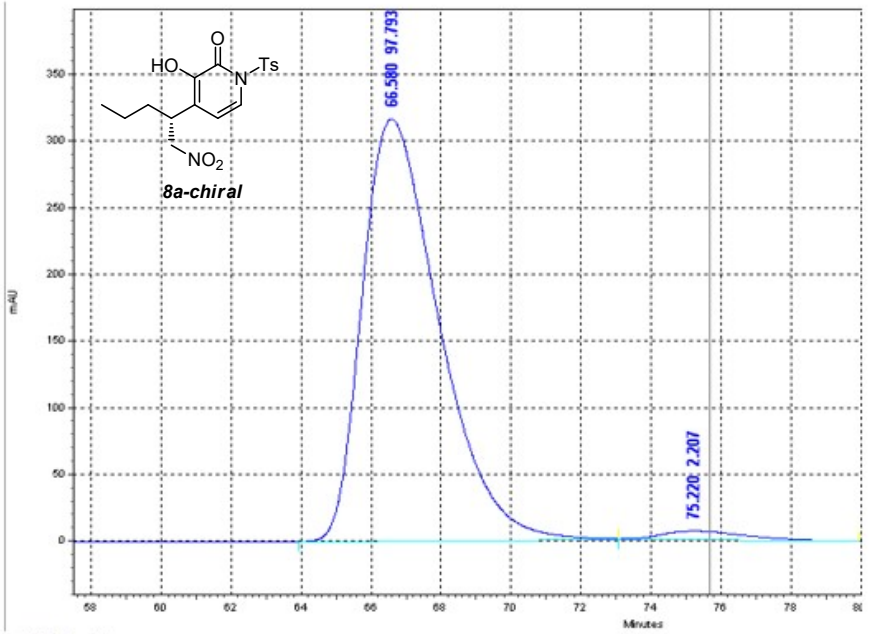
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	63.400	124770310	54.250	MM
	70.763	105222249	45.750	MM
Totals		229992559	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak AD-H, hexane : 2-propanol = 80 : 20, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8a-chiral***



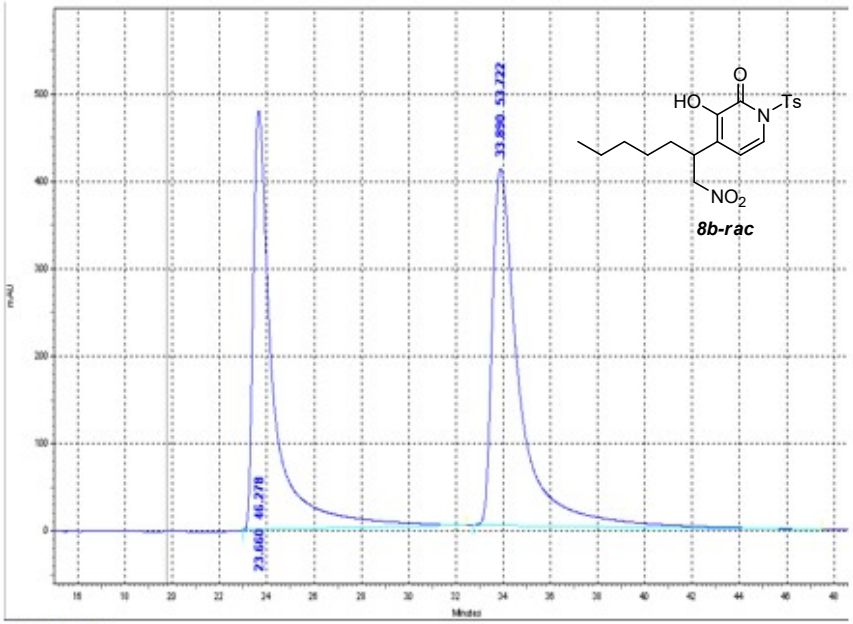
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	66.580	192443637	97.793	MM
	75.220	4342587	2.207	MM
Totals		196786224	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70,
flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8b-rac***



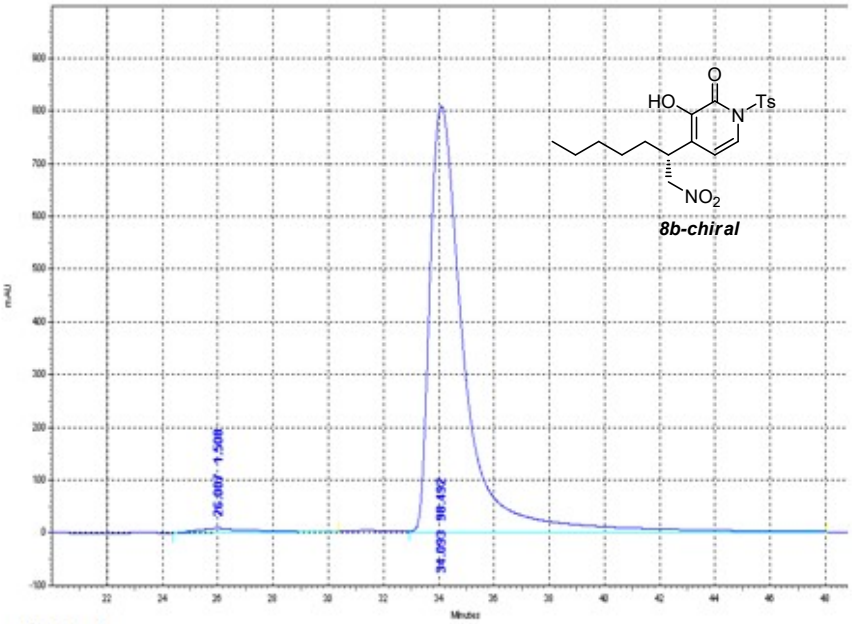
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	23.660	112768381	46.278	MM
	33.890	130908757	53.722	MM
Totals		243677138	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70,
flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8b-chiral***



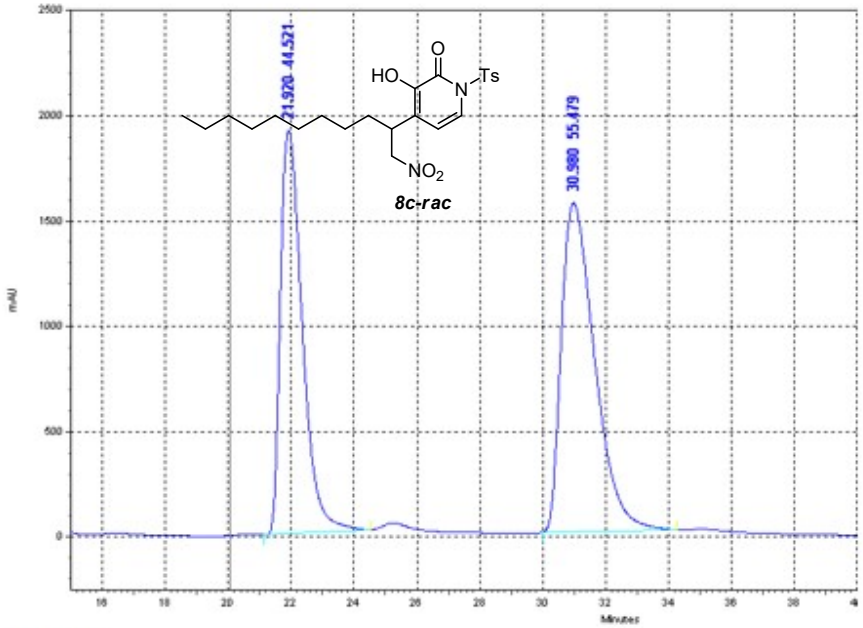
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	26.007	4236099	1.508	MM
	34.093	276754046	98.492	hh
Totals		280990145	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70,
flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8c-rac***



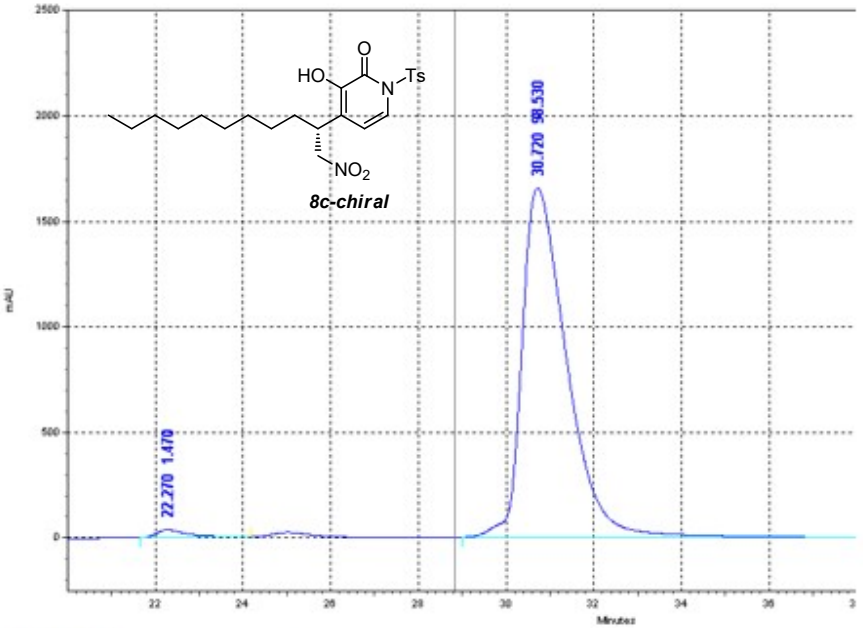
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	21.920	369823763	44.521	MM
	30.980	460849123	55.479	MM
Totals		830672886	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70,
flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8c-chiral***



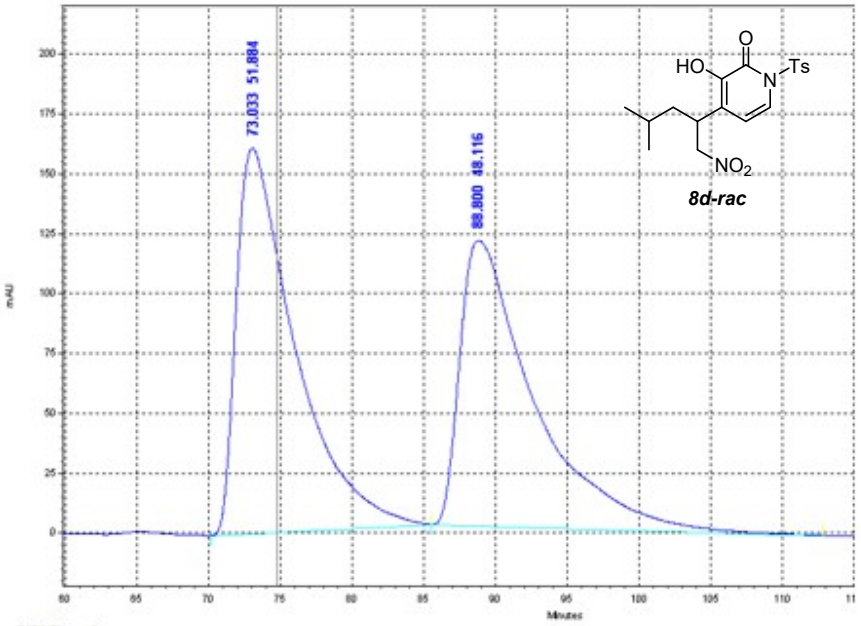
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	22.270	7022340	1.470	MM
	30.720	470638402	98.530	MM
Totals		477660742	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol = 95 : 05, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8d-rac***



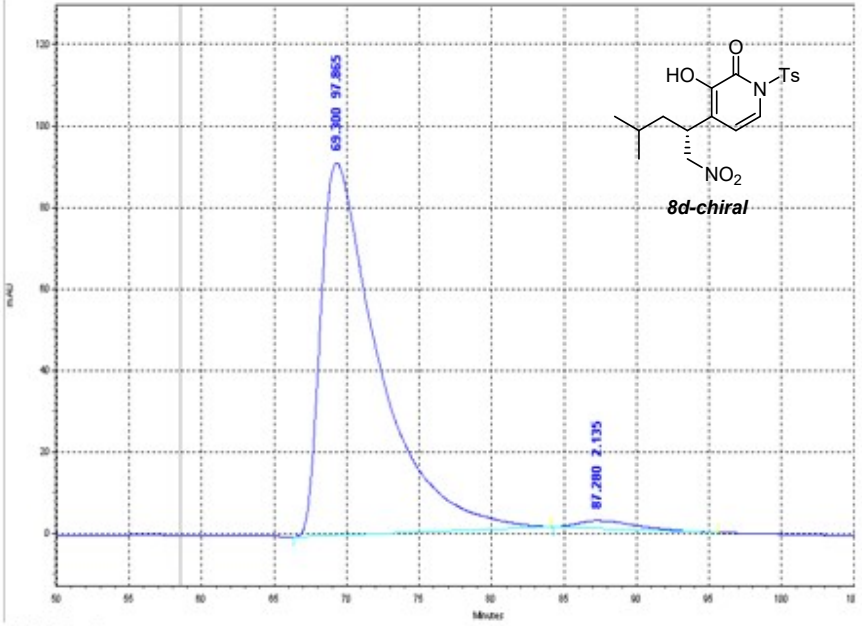
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	73.033	182898127	51.884	MM
	88.800	169615431	48.116	MM
Totals		352513558	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol = 95 : 05, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8d-chiral***



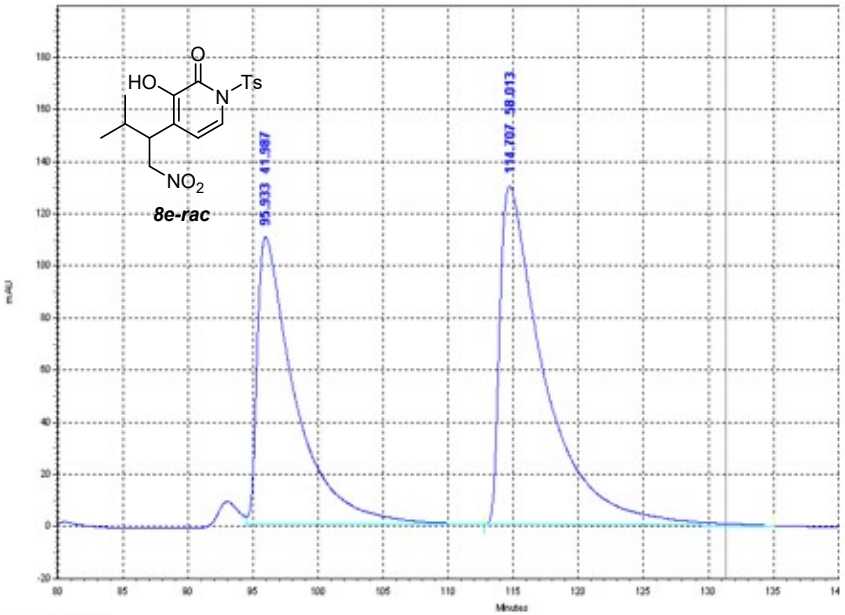
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	69.300	102000884	97.865	MM
	87.280	2225738	2.135	MM
Totals		104226622	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : ethanol= 30 : 70,
flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8e-rac***



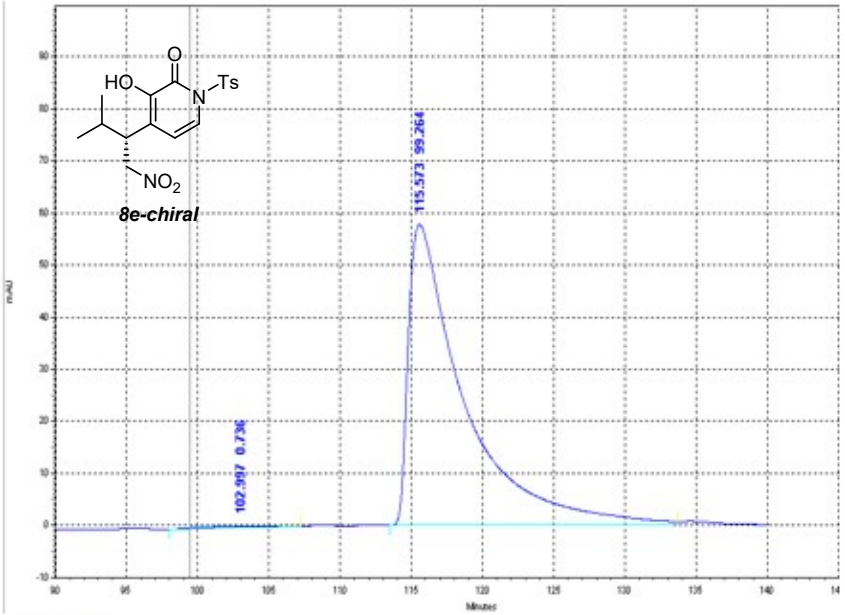
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	95.933	89537606	41.987	hh
	114.707	123715610	58.013	MM
Totals		213253216	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : ethanol= 30 : 70,
flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8e-chiral***



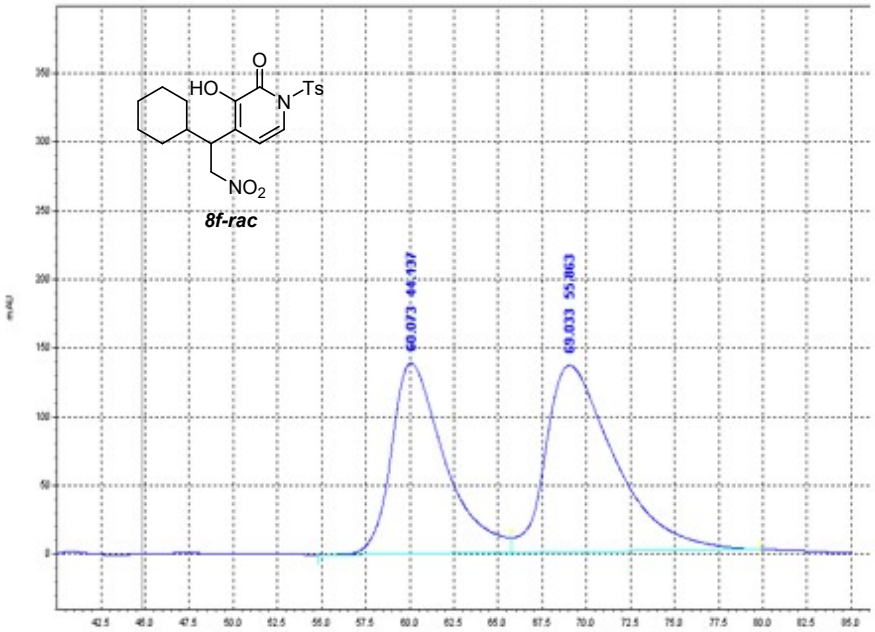
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	102.997	467299	0.736	MM
	115.573	63009558	99.264	HH
Totals		63476857	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak OJ-H, hexane : ethanol = 90 : 10, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8f-rac***



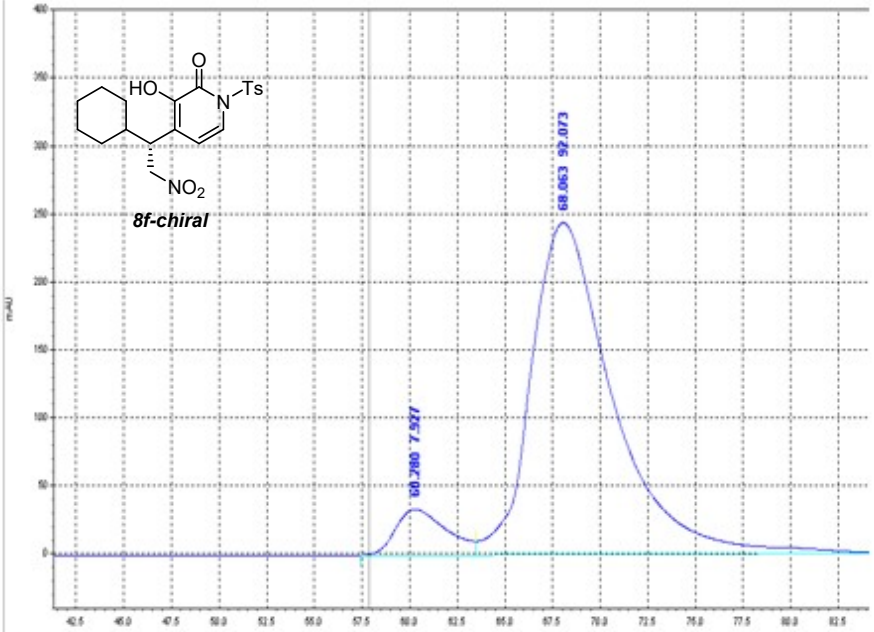
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	60.073	116269302	44.137	Mx
	69.033	147161719	55.863	xM
Totals		263431021	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak OJ-H, hexane : ethanol = 90 : 10, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8f-chiral***



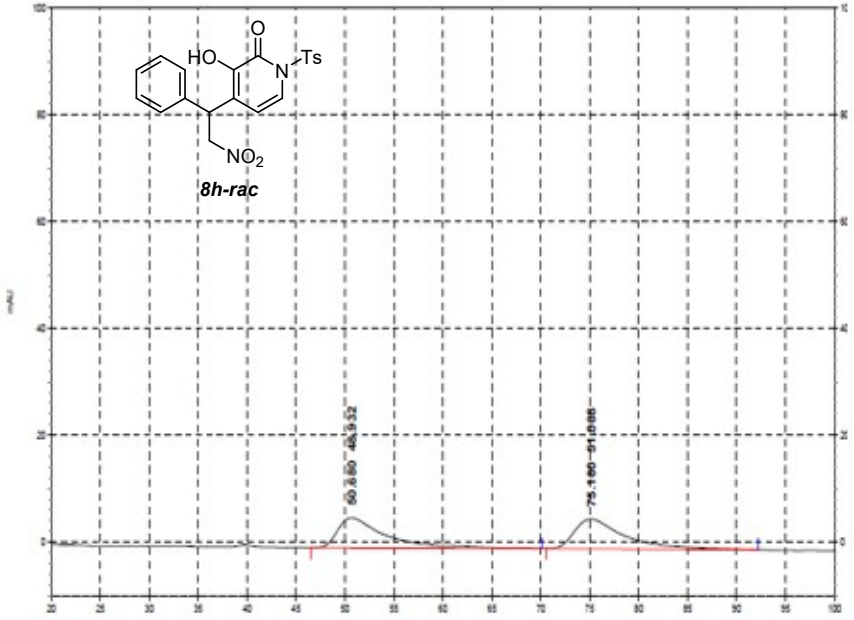
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	60.280	25156356	7.927	Mx
	68.063	292212393	92.073	xM
Totals		317368749	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol = 70 : 30, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8h-rac***



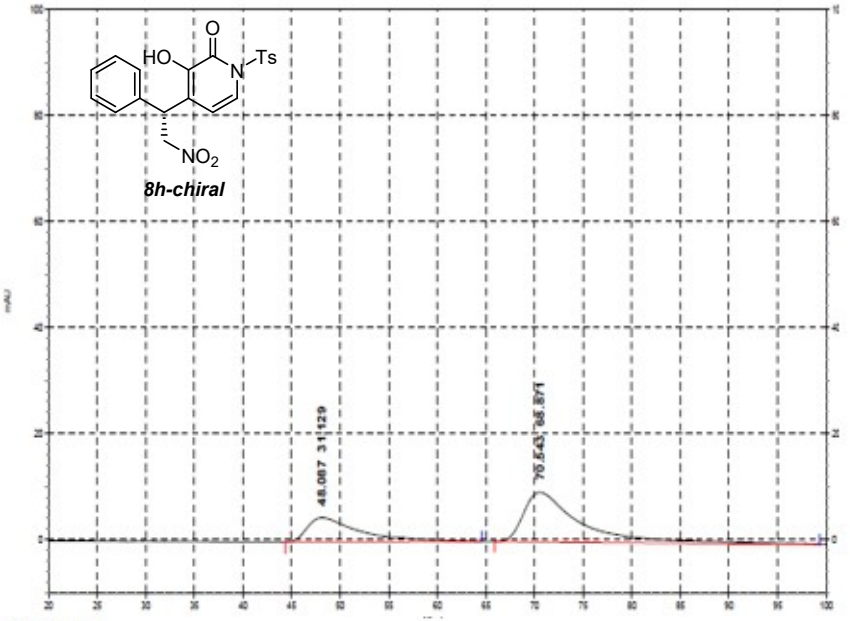
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	50.680	7595574	48.932	mm
	75.160	7927217	51.068	MM
Totals		15522791	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol = 70 : 30, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8h-chiral***



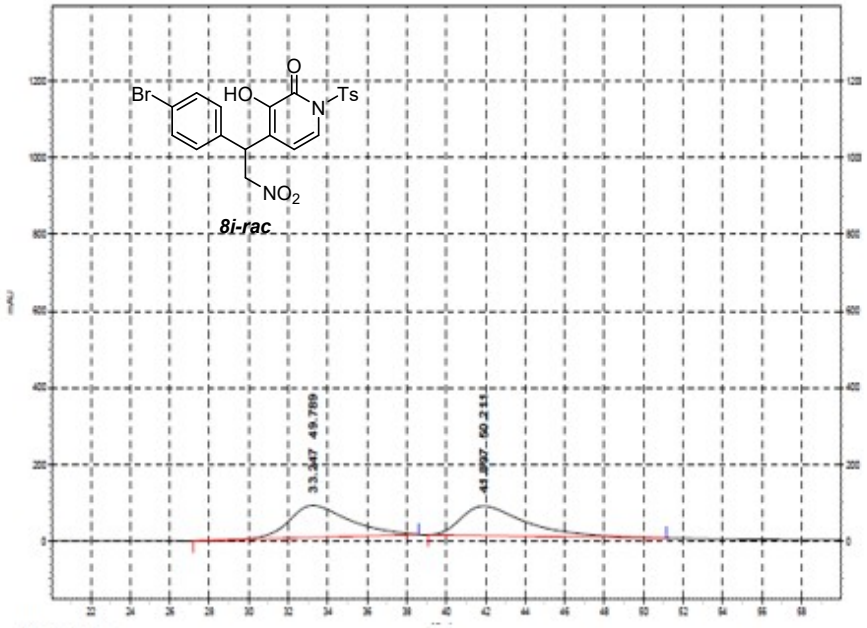
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	48.087	6888133	31.129	MM
	70.543	15239302	68.871	MM
Totals		22127435	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 240 nm

Sample ID: ***8i-rac***



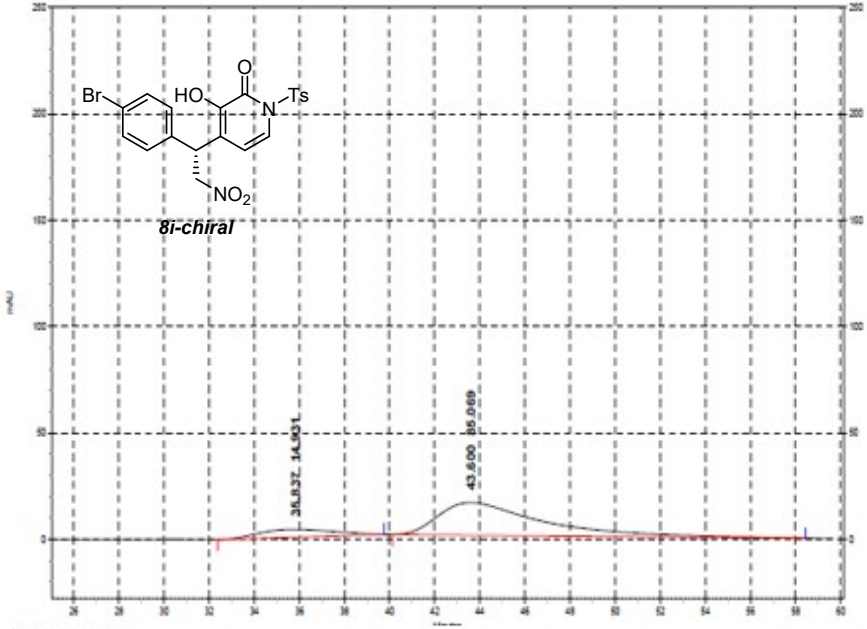
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	33.247	69622663	54.658	mm
	41.897	57756586	45.342	mm
Totals		127379249	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 240 nm

Sample ID: ***8i-chiral***

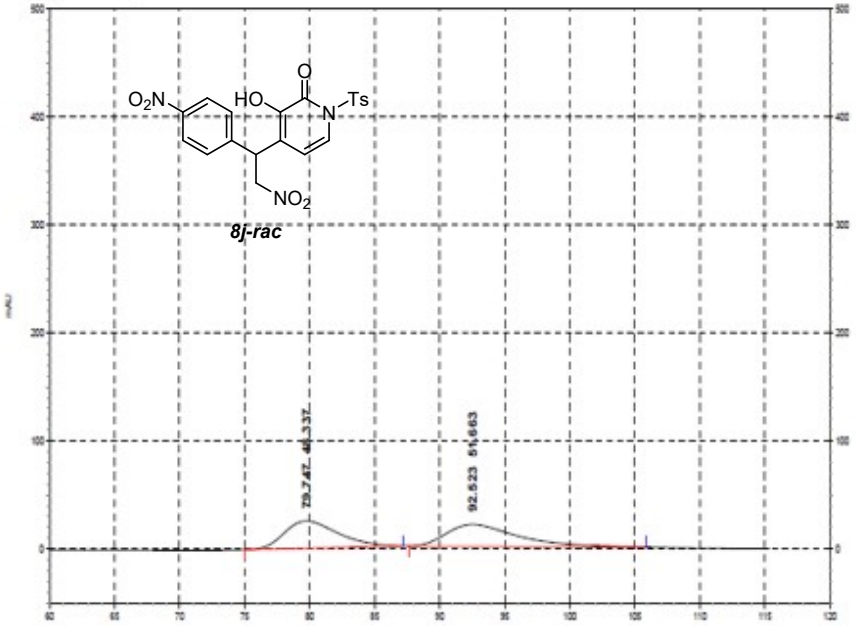


UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	35.837	3406715	14.931	MM
	43.600	19409995	85.069	MM
Totals		22816710	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol : trifluoroacetic acid = 700 : 300 : 1,
flow rate = 0.5 ml/min, 23 °C, λ = 240 nm
Sample ID: ***8j-rac***

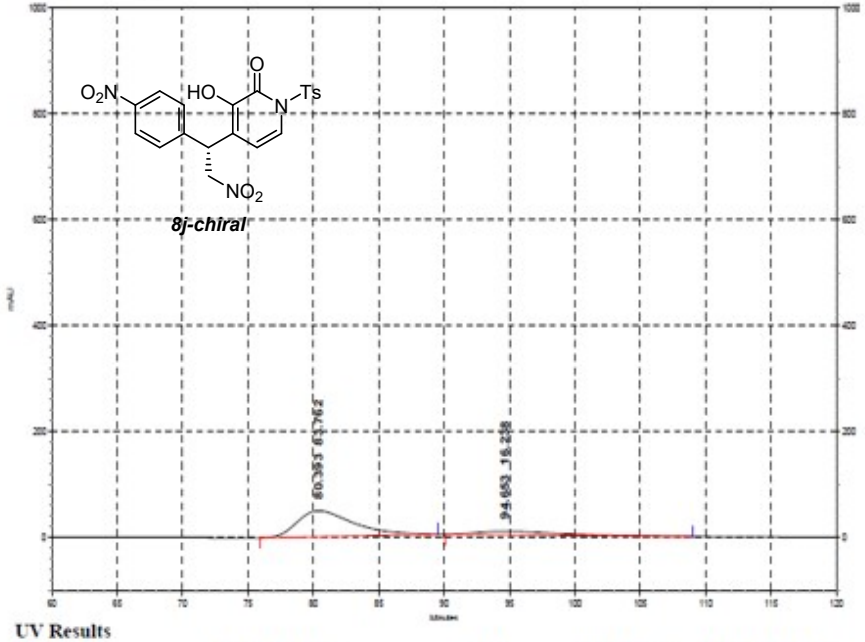


UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	79.747	28948097	48.337	MM
	92.523	30940502	51.663	mm
Totals		59888599	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol : trifluoroacetic acid = 700 : 300 : 1,
flow rate = 0.5 ml/min, 23 °C, λ = 240 nm
Sample ID: ***8j-chiral***



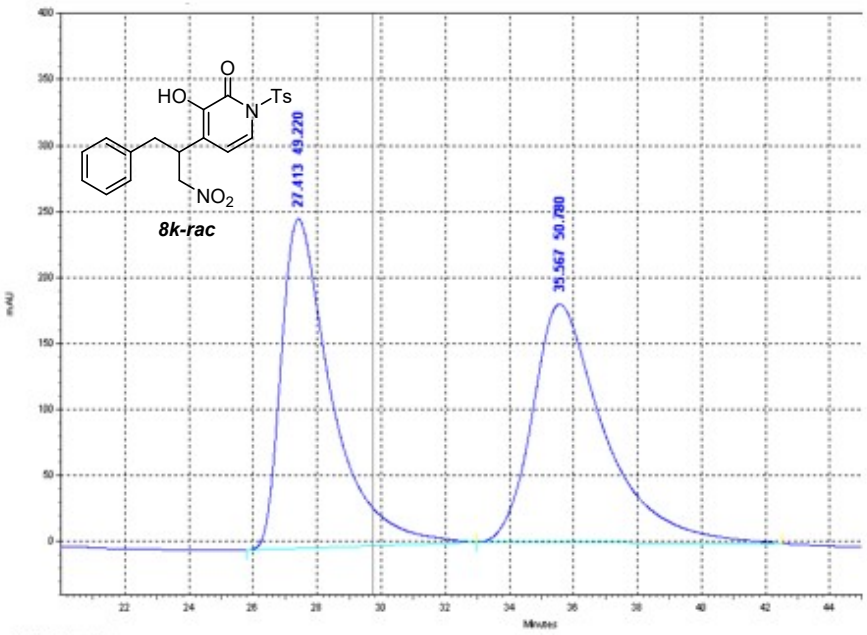
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	80.393	58252067	83.762	MM
	94.653	11292331	16.238	MM
Totals		69544398	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol = 70 : 30, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8k-rac***



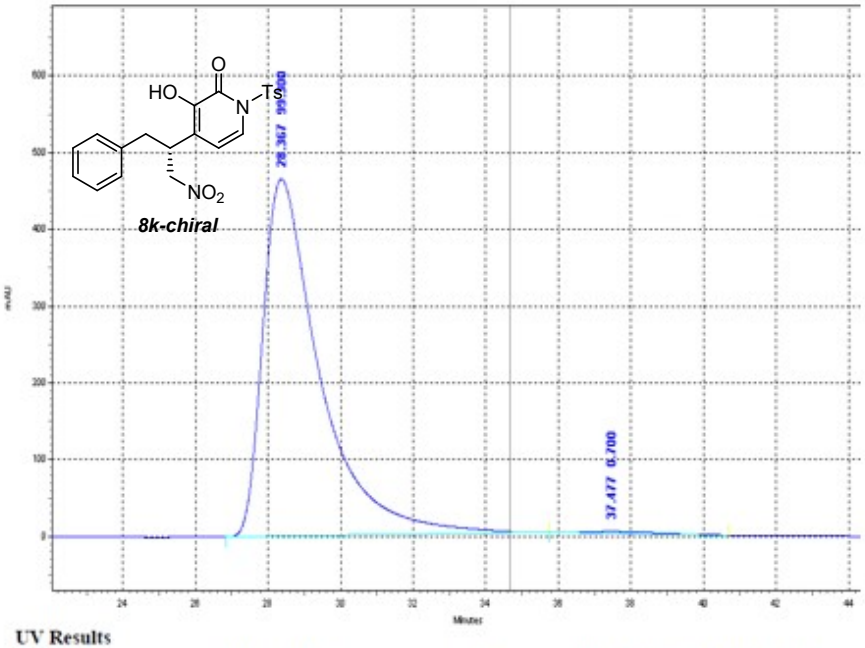
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	27.413	109164241	49.220	MM
	35.567	112623173	50.780	MM
Totals		221787414	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol = 70 : 30, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8k-chiral***

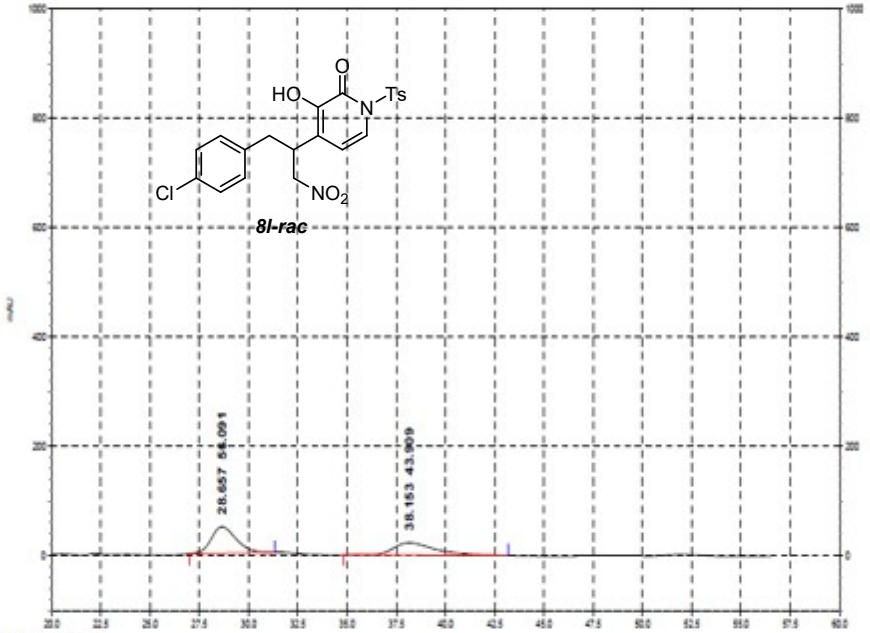


UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	28.367	204245403	99.300	MM
	37.477	1439612	0.700	MM
Totals		205685015	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol : trifluoroacetic acid = 700 : 300 : 1,
flow rate = 0.5 ml/min, 23 °C, λ = 240 nm
Sample ID: ***8l-rac***

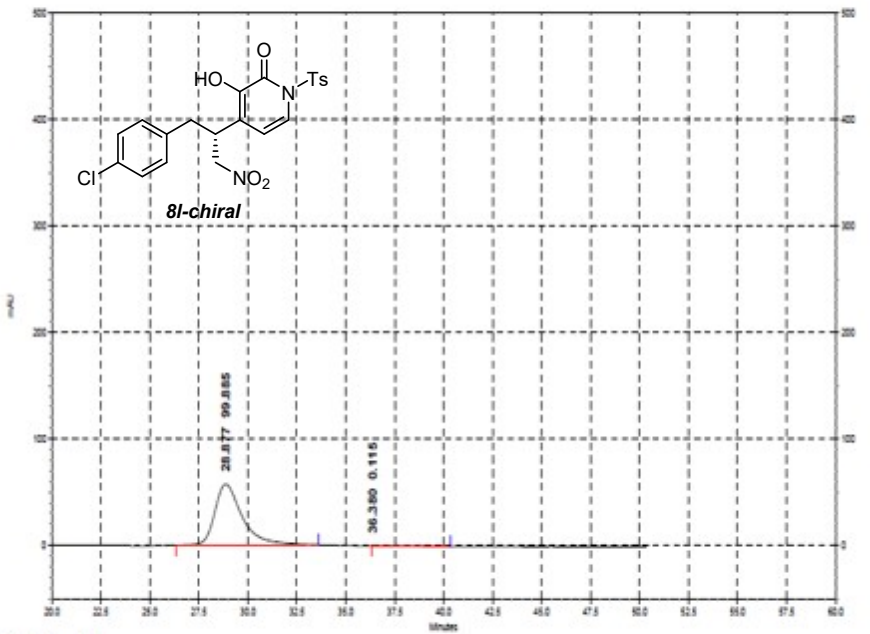


UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	28.657	17121447	56.091	mm
	38.153	13402702	43.909	MM
Totals		30524149	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol : trifluoroacetic acid = 700 : 300 : 1,
flow rate = 0.5 ml/min, 23 °C, λ = 240 nm
Sample ID: ***8l-chiral***



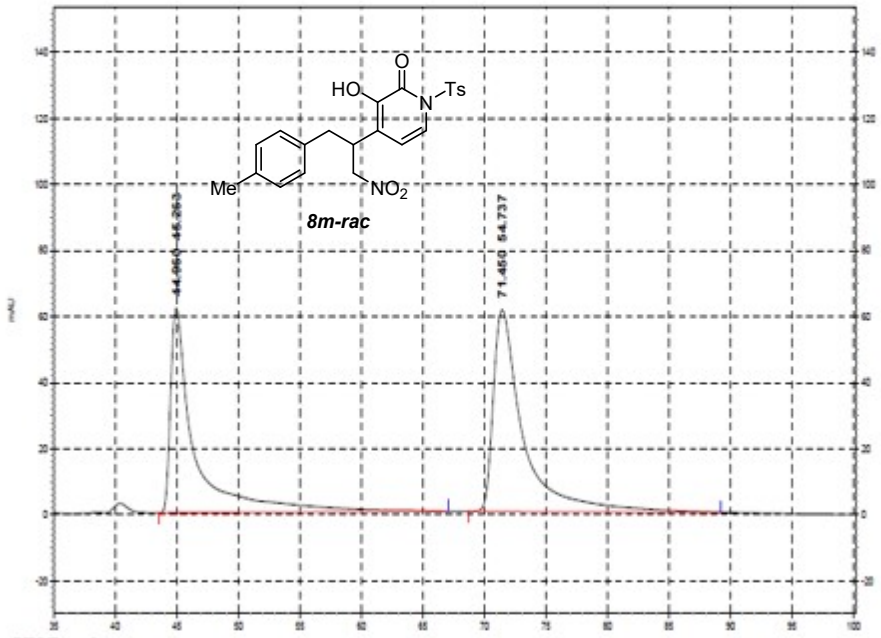
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	28.877	22324191	99.885	MM
	36.380	25720	0.115	MM
Totals		22349911	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8m-rac***



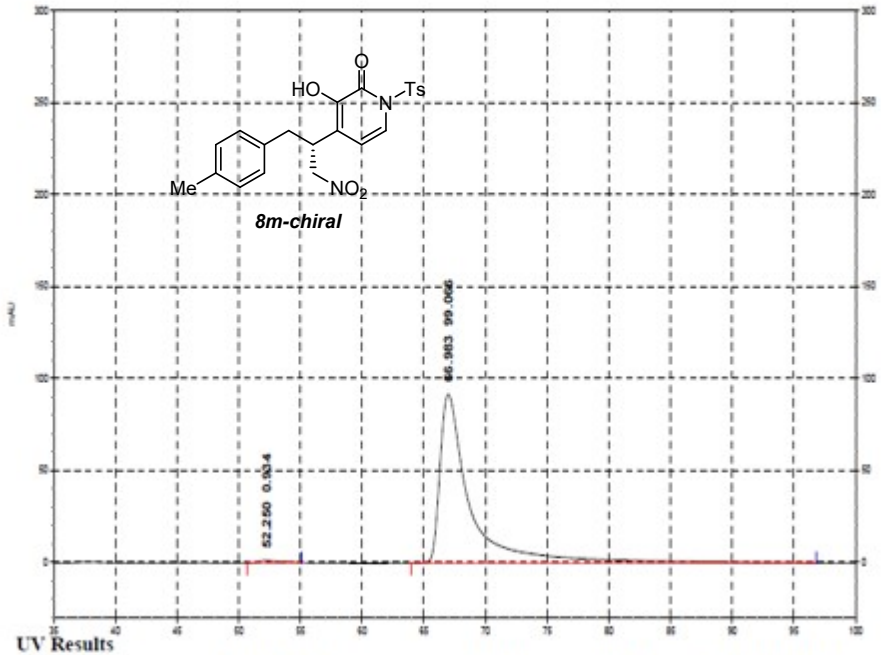
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	44.960	34107801	45.263	mm
	71.450	41246905	54.737	mm
Totals		75354706	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8m-chiral***



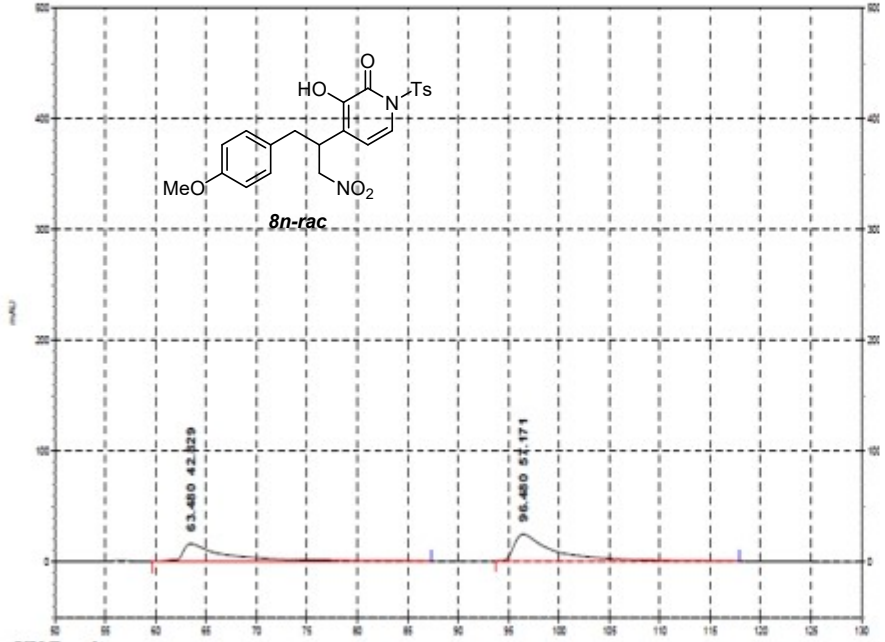
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	52.250	593006	0.934	II
	66.983	62881129	99.066	MM
Totals		63474135	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8n-rac***



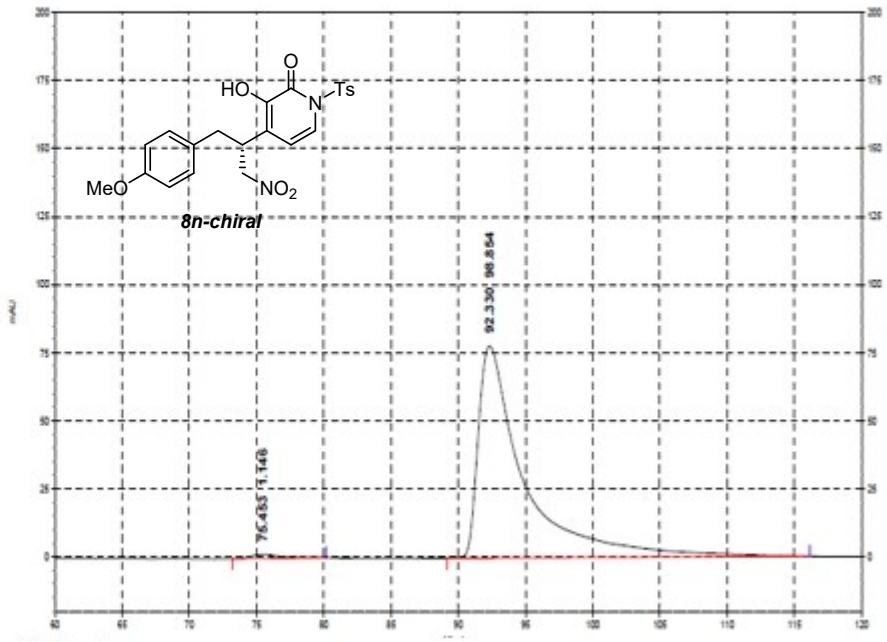
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	63.480	20113113	42.829	MM
	96.480	26848159	57.171	MM
Totals		46961272	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8n-chiral***



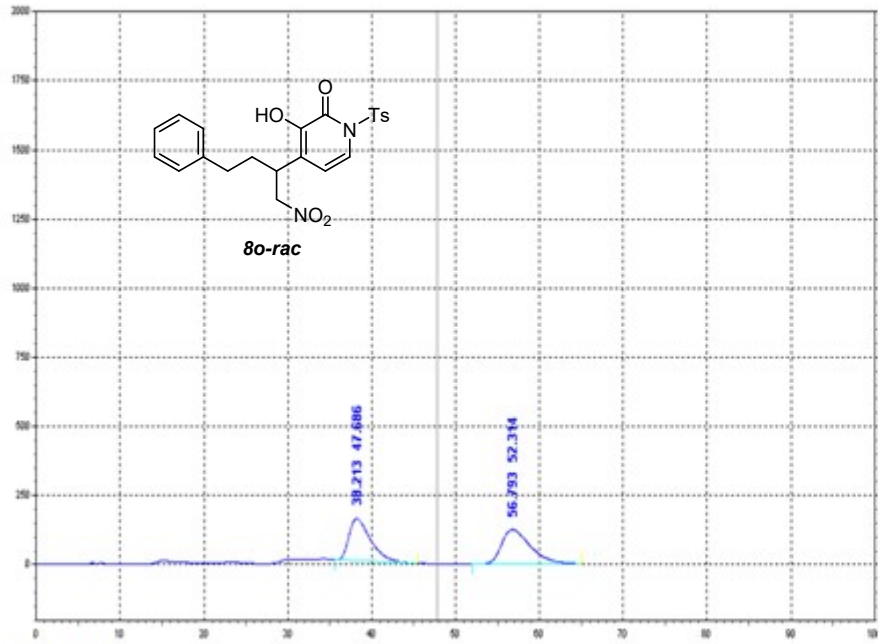
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	75.453	854146	1.146	MM
	92.330	73664999	98.854	MM
Totals		74519145	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol = 30 : 70, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8o-rac***



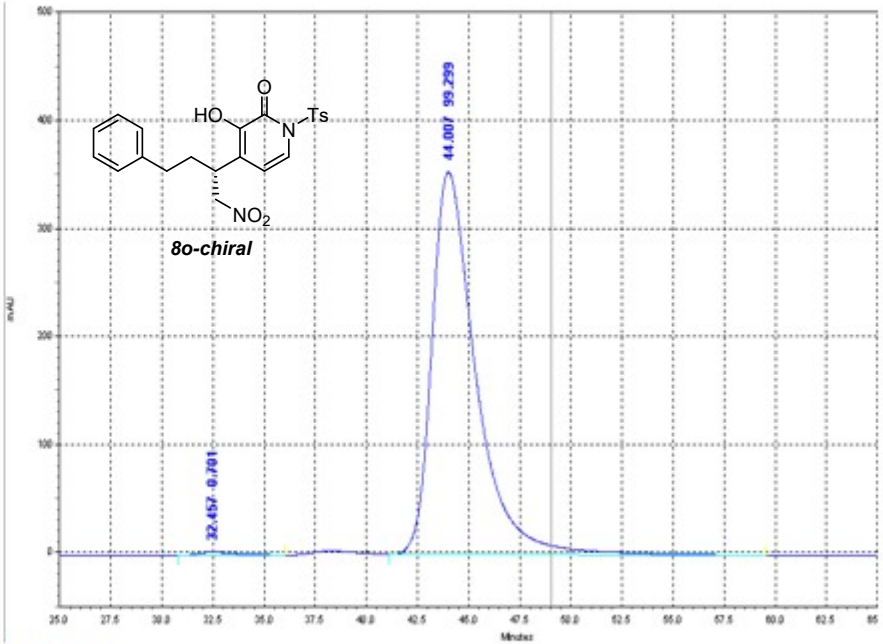
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	38.213	110314886	47.686	MM
	56.793	121021670	52.314	MM
Totals		231336556	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralcel OD-H, hexane : 2-propanol = 30 : 70, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8o-chiral***



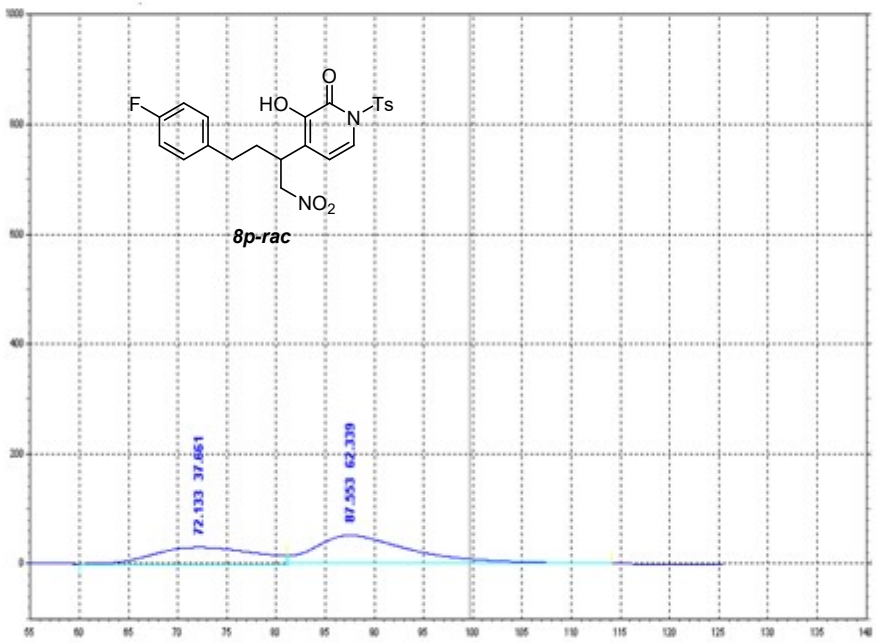
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	32.457	1499459	0.699	MM
	44.007	212992166	99.301	MM
Totals		214491625	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak OJ-H, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8p-rac***



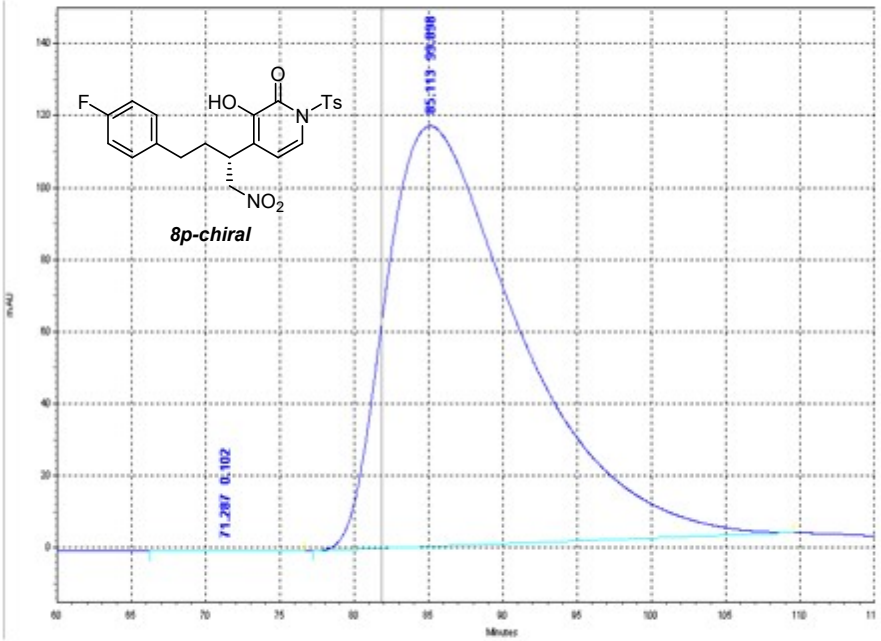
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	72.133	86075395	37.661	HH
	87.553	142475517	62.339	hh
Totals		228550912	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak OJ-H, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8p-chiral***



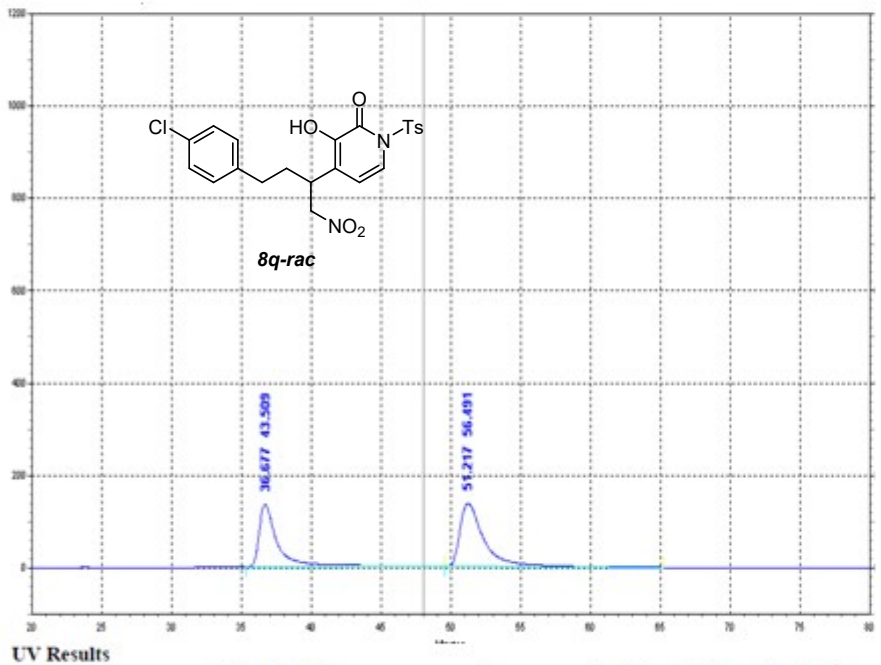
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	71.287	302046	0.102	MM
	85.113	295929093	99.898	MM
Totals		296231139	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70,
flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8q-rac***



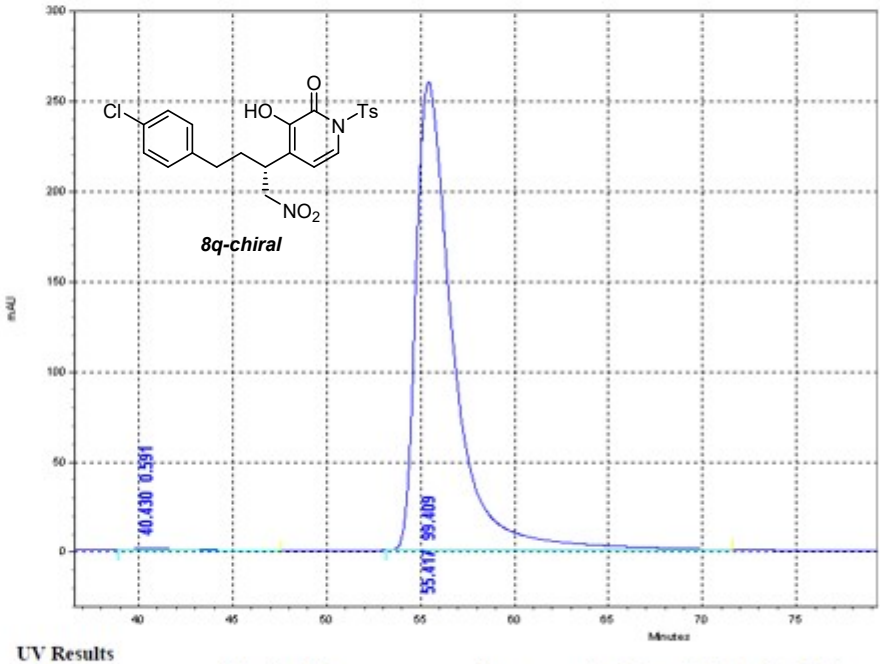
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	36.677	50643725	43.509	MM
	51.217	65755207	56.491	MM
Totals		116398932	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70,
flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8q-chiral***



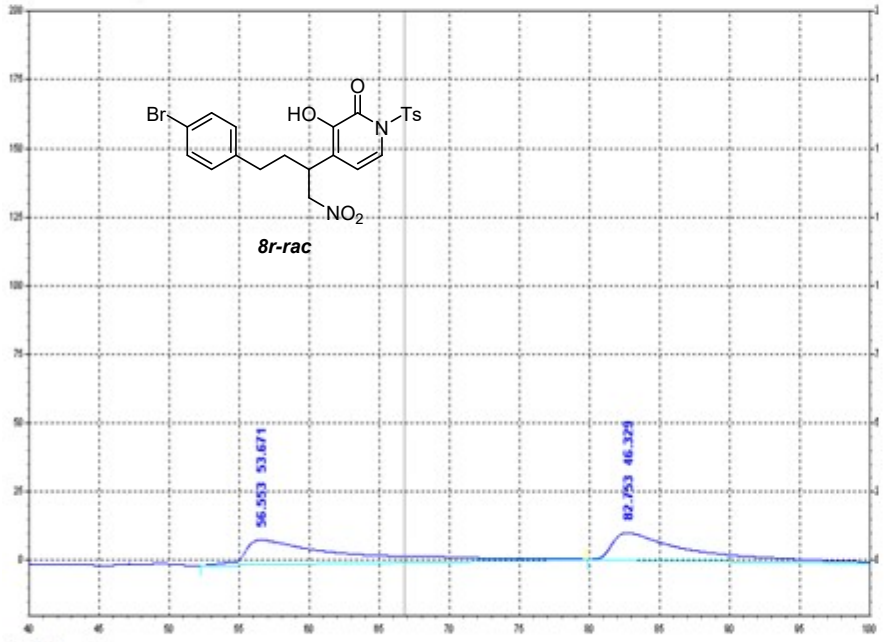
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	40.430	849704	0.591	MM
	55.417	142910529	99.409	MM
Totals		143760233	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8r-rac***



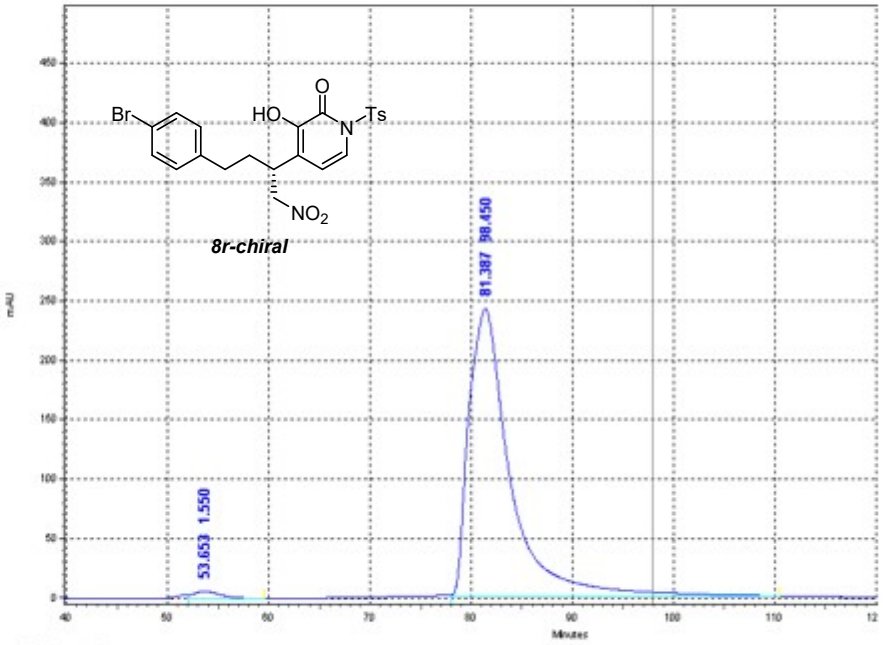
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	56.553	17203800	53.671	MM
	82.753	14850167	46.329	MM
Totals		32053967	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8r-chiral***



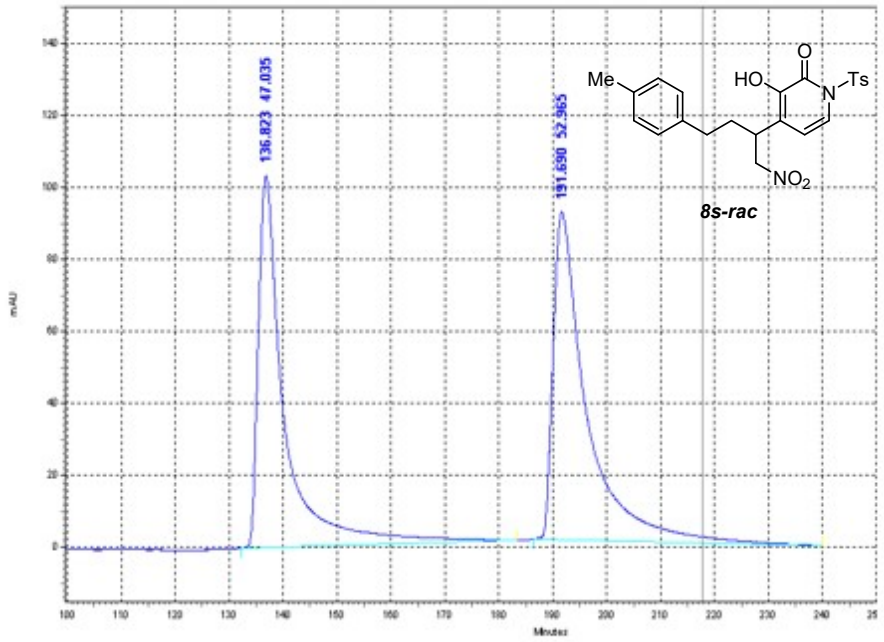
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	53.653	4341143	1.550	hh
	81.387	275807991	98.450	hh
Totals		280149134	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8s-rac***



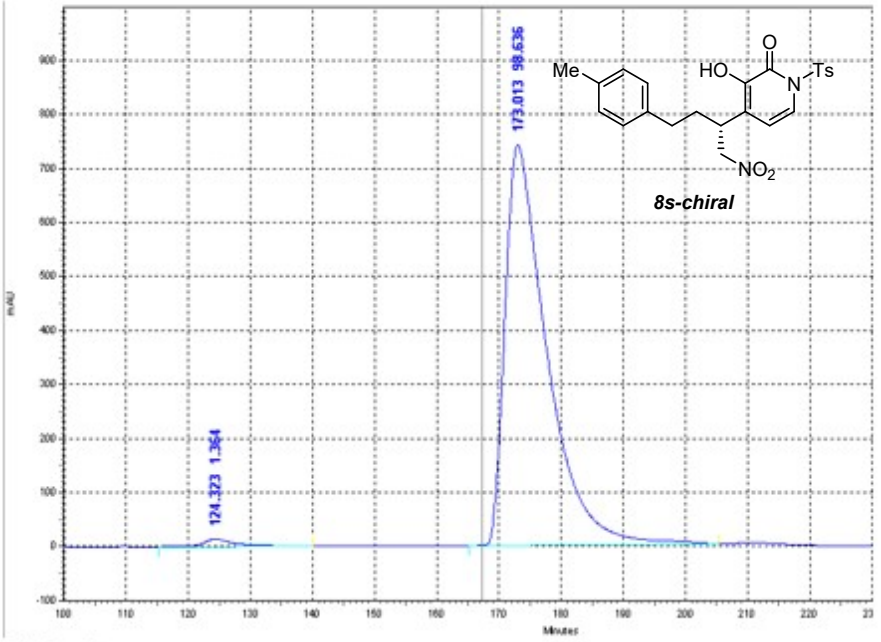
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	136.823	139482596	47.035	MM
	191.690	157067662	52.965	MM
Totals		296550258	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 30 : 70, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8s-chiral***



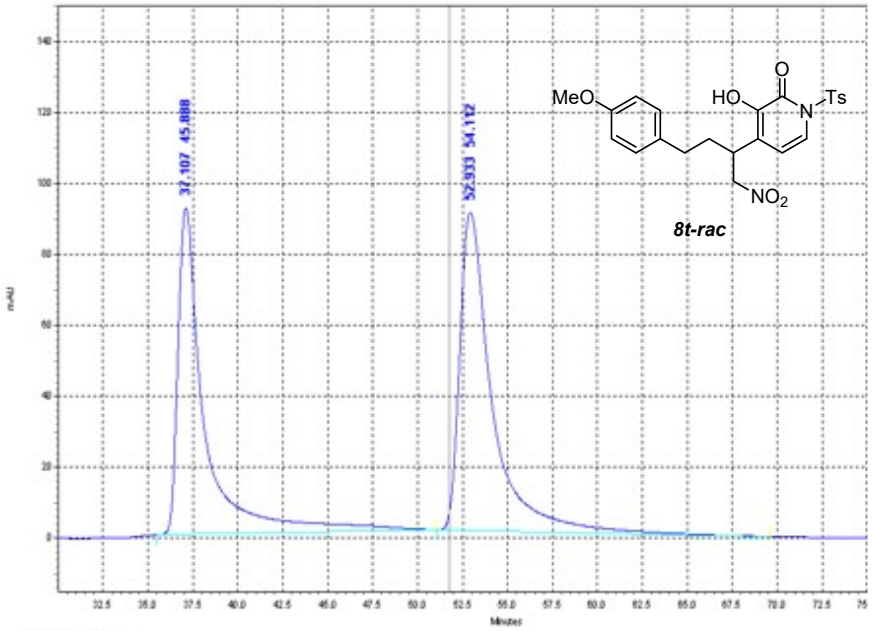
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	124.323	19200214	1.364	MM
	173.013	1388506134	98.636	MM
Totals		1407706348	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8t-rac***



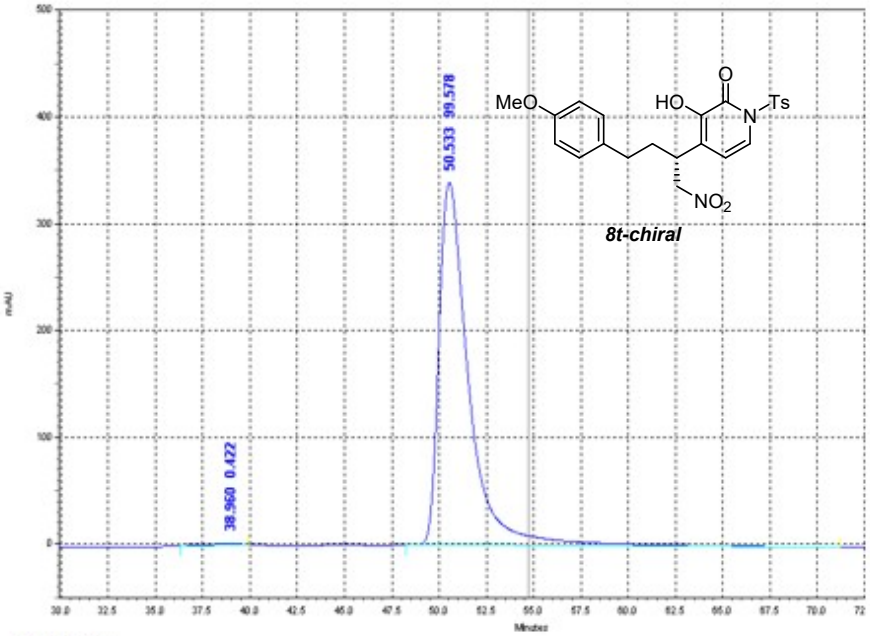
UV Results

Name	Retention Time	Area	Area Percent	Integration Codes
	37.107	38258486	45.888	MM
	52.933	45115051	54.112	MM
Totals		83373537	100.000	

Area Percent Report

Instrument Name: L-2000 Software
Version: Version LaChrom 890-8800-12
Acquisition Method: DAICEL Chiralpak ID, hexane : 2-propanol = 50 : 50, flow rate = 0.5 ml/min, 23 °C, λ = 243 nm

Sample ID: ***8t-chiral***

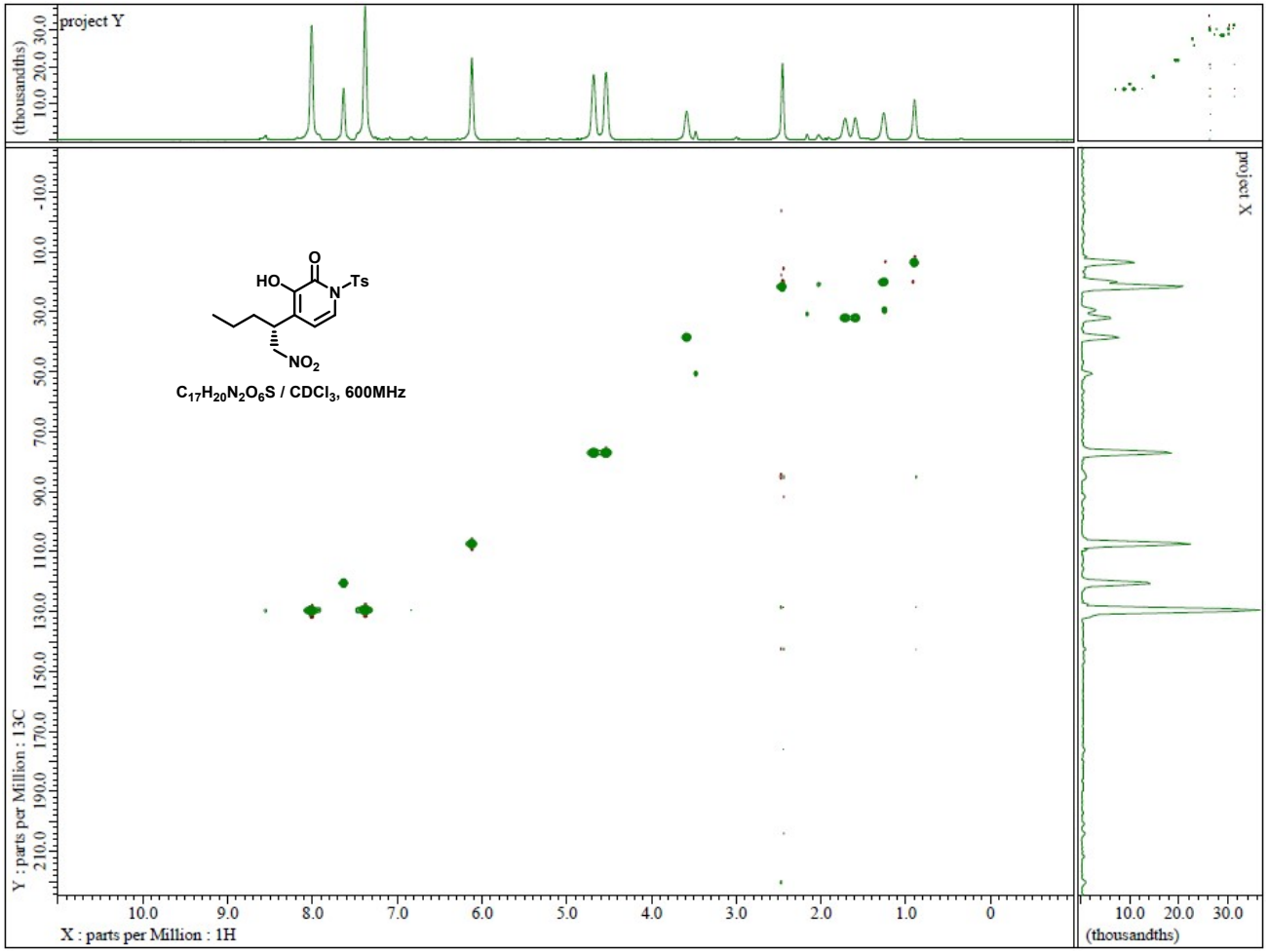


UV Results

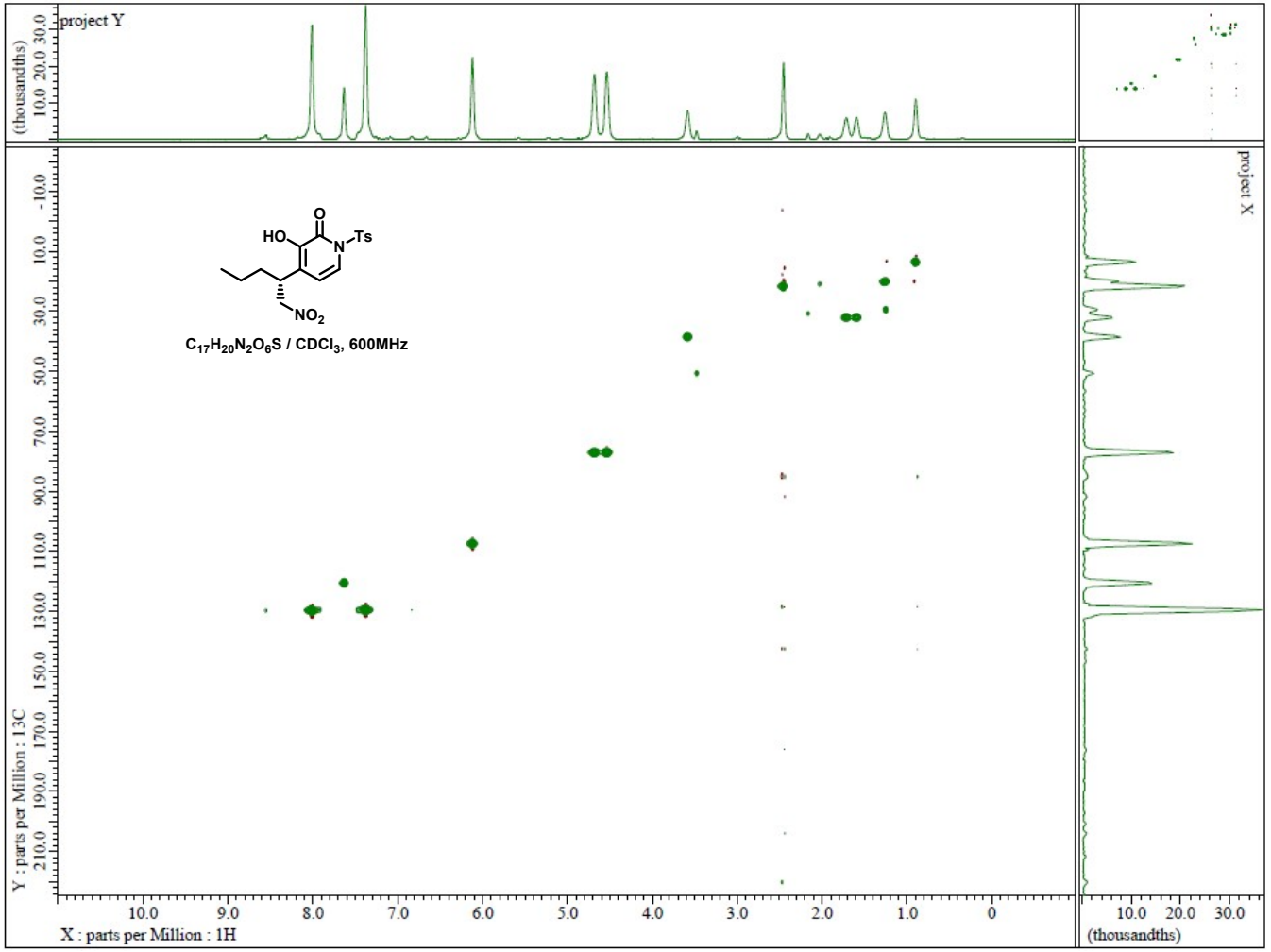
Name	Retention Time	Area	Area Percent	Integration Codes
	38.960	637133	0.422	MM
	50.533	150415292	99.578	MM
Totals		151052425	100.000	

(7) COSY & ^{1}H-^{13}C HSQC

COSY of compound **(8a)**

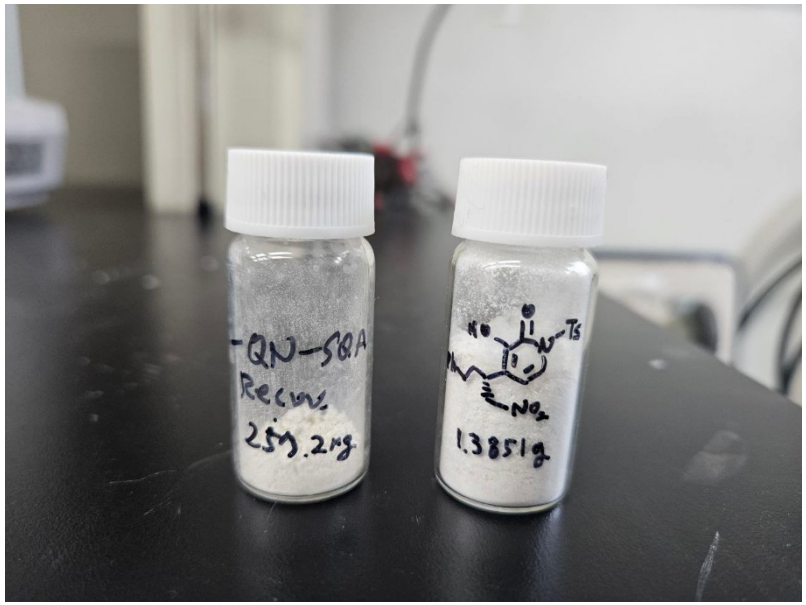


^{1}H-^{13}C *HSQC of compound* **(8a)**



(8) Gram-scale procedure of compound (8o)

To a solution of **6** (1.00 g, 3.77 mmol) and catalyst **5a** (273.3 mg, 0.377 mmol) dissolved in dichloromethane (38 mL) was added nitroolefin **7o** (1.34 g, 7.54 mmol) at -20 ℃ and the solution was stirred for 48 h. After the reaction finished, the reaction quenched with 1 N HCl and extracted with DCM. The aqueous phase was basified with NH_4OH solution, the precipitate was collected by filtration and the catalyst **5a** was recovered as white solid (257.2 mg, recovery yield 94%). The organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo.* The residue was purified by flash column chromatography (ethyl acetate/hexane, 1/3, v/v) to afford Michael adduct **8o**



as white solid (1.39g, 83%).

(9) X-ray Crystallographic Data of 8o

The compound **8o** was dissolved in ethanol with heating, followed by recrystallization slowly at 40 °C bath. The crystals obtained were then used for X-ray crystallography.

Identification code	**8o**	
Empirical formula	C22 H22 N2 O6 S	
Formula weight	442.47	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.8856(10) Å	a= 90°.
	b = 13.443(2) Å	b= 90°.
	c = 26.710(5) Å	g = 90°.
Volume	2113.3(6) $Å^3$	
Z	4	
Density (calculated)	1.391 Mg/m^3	
Absorption coefficient	0.196 mm^{-1}	
F(000)	928	
Crystal size	0.330 x 0.035 x 0.033 mm^3	
Theta range for data collection	2.150 to 28.331°.	
Index ranges	-7<=h<=6, -17<=k<=17, -35<=l<=35	
Reflections collected	43950	

Independent reflections	5242 [R(int) = 0.1348]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6353
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5242 / 24 / 318
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0572, wR2 = 0.1368
R indices (all data)	R1 = 0.1510, wR2 = 0.1797
Absolute structure parameter	-0.01(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.294 and -0.363 e.$Å^{-3}$