Supporting Information
for
Phenylene-Bridged Bis(benzimidazolium) (BBIm^{2+}): a Dicationic Organic Photoredox Catalyst

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CONTENTS

I. General Information.

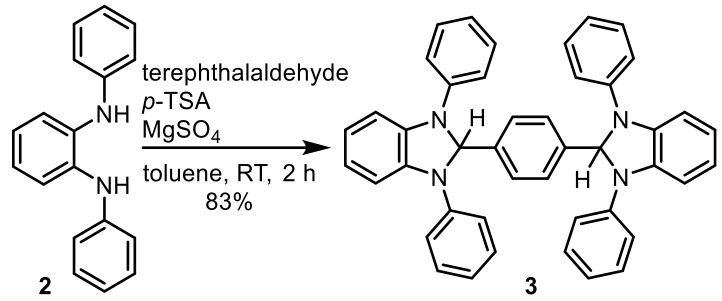
^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer (JEOL, Tokyo, Japan) in $CDCl_3$, CD_2Cl_2, or CD_3CN. NMR data have been reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (J) in Hz, and integration. Infrared spectra (IR) were obtained on a JASCO FT/IR-4000 spectrometer, and the absorptions have been reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). High resolution mass spectra (HRMS) were obtained using a JEOL JMS-700 and JMS-T100LP spectrometer. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed over SiO_2 (Silycycle Silica Flash F60 (230-400 mesh)) or NH_2 silica-gel (Kanto Chemical Co., Inc., NH_2 Silica Gel 60, spherical, particle size 40–50 μm). Data collection for X-ray crystal analysis were performed on a Rigaku / XtaLAB Pro P200 Hybrid Photon Counting diffractometer (Mo-Kα, λ = 0.71075 Å for $BBIm^{2+}\cdot 2[PF_6^-]$. The structures were solved with direct methods, using SHELXT-2018/3, and refined with full-matrix least-squares, using SHELXL-2018/3. Absorption spectra were measured on a JASCO V-670 spectrometer. Emission spectra were measured on a JASCO FP-8500 spectrometer. Cyclic voltammetric measurement was conducted with a BAS Model 612D electrochemical analyzer. Cyclic voltammogram of $BBIm^{2+}\cdot 2[PF_6^-]$ (5.0×10^{-4} M) and $\mathbf{1}^+\cdot[Br^-]$ (5.0×10^{-4} M) were recorded with a glassy carbon working electrode and a Pt counter electrode in acetonitrile containing 0.1 M $n Bu_4NPF_6$ as a supporting electrolyte. Photoirradiation was performed with 500 W xenon lamp (Ushio Optical ModelX SX-UID 500XAMQ), 60 W LED lamp (λ = 365 nm, dotAqua model), or 60 W LED lamp (λ = 405 nm, dotAqua model). All calculations were conducted using a Gaussian 09 suite program (G09 Rev D.01).[1] Optimization was performed at the ωB97XD/6-31G(d, p) level of theory. Harmonic vibration frequency analysis was conducted with the optimized structures at the same level of theory to verify all stationary points as local minima (with no imaginary frequency).

II. Materials

Acetonitrile (for Organic Synth.), toluene (for Organic Synth.), DMF (for Organic Synth.) and DME (for Organic Synth.) were purchased from Wako Chemicals and used as received. Terephthalaldehyde (TCI), *p*-toluenesulfonic acid (Wako), *N*-bromoacetamide (TCI), $AgPF_6$ (TCI), NaH (TCI), and methyl iodide (TCI), $Acr\text{-}Mes^+\cdot[ClO_4^-]$ (TCI), were purchased from commercial suppliers and used as received. Carboxylic acids **4a**–**4g** were supplied from TCI, Wako and Aldrich and used as received. N^1,N^2-diphenylbenzene-1,2-diamine **2** [CAS: 28394-83-4][2] was prepared according to the literature procedures.

III. Synthesis of Photocatalysts

Synthesis of phenylene-bridged bisaminal (3).



To a three-necked flask, **2** (2.0 g, 7.8 mmol) and terephthalaldehyde (0.54 g, 4.0 mmol) were added and dissolved in dry toluene (48 mL). *p*-Toluenesulfonic acid (0.16 g) and anhydrous $MgSO_4$ (0.48 g) were added and stirred at room temperature for 2 h. After removing insoluble materials by filtering through a pad of NH-silica (5 cm, eluent: toluene), the filtrate was concentrated in vacuo to ca. 5 mL. Et_2O was slowly added to the solution, giving a pale yellow crystal of **3** (2.0 g, 83%).

Mp 175.3–175.8 °C.

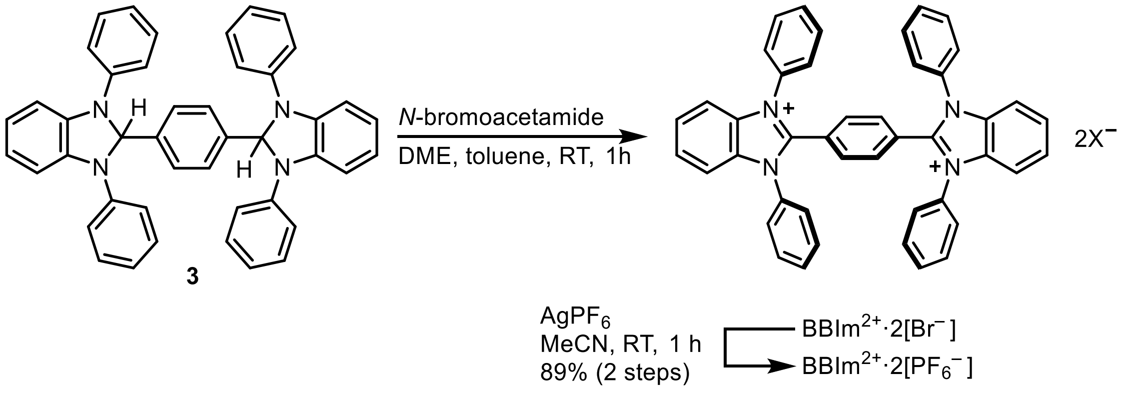
^{1}H-NMR ($CDCl_3$, 399.78 MHz) δ: 6.51 (s, 2H), 6.71–6.75 (m, 4H), 6.83–6.87 (m, 4H), 6.99–7.00 (m, 4H), 7.03–7.06 (m, 8H), 7.18–7.21 (m, 8H), 7.29 (s, 4H).

^{13}C-NMR ($CDCl_3$, 100.53 MHz) δ: 87.9, 108.1, 119.6, 121.6, 123.5, 127.7, 129.1, 137.9, 140.7, 142.1.

IR (KBr, cm^{-1}): 3063 w, 3035 w, 1586 m, 1506 s, 1484 s, 1462 m, 1433 w, 1393 m, 1364 m, 1340 m, 1306 m, 1282 w, 1263 m, 1228 m, 1160 w, 1092 w, 1077 w, 1020 w, 892.8 w, 844.6 w, 780.0 m, 768.4 m, 741.4 m, 727.9 m, 702.9 m, 695.2 m, 648.9 w, 508.1 m.

HRMS calcd for ([M$^+$]): 617.26997. Found: 617.27011.

Synthesis of BBIm^{2+}·2[PF_6^-].



To a suspension of **3** (1.5 g, 2.5 mmol) in dimethoxyethane (42 mL), *N*-bromoacetamide (0.35 g, 2.5 mmol) was added, and the suspension mixture was stirred at room temperature for 10 min. Additional *N*-bromoacetamide (0.35 g, 2.5 mmol) was added, and the mixture was stirred for additional 1 h. The colorless precipitate was filtered off and washed with ethanol to give BBIm^{2+}·2[Br^{-}] as a colorless solid (1.7 g). To a suspension of BBIm^{2+}·2[Br^{-}] (1.5 g, 1.9 mmol) in acetonitrile (250 mL), $AgPF_6$ (0.98 g, 3.9 mmol) was added, and the reaction mixture was stirred for 19 h. Insoluble AgBr was filtered off, and the filtrate was concentrated. The residue was recrystallized from acetonitrile/Et_2O to give BBIm^{2+}·2[PF_6^{-}] as a colorless crystal (1.7 g, 89%, 2 steps).

Mp >300 °C.

^{1}H-NMR ($CDCl_3$, 399.78 MHz) δ: 7.27 (s, 4H), 7.37–7.39 (m, 8H), 7.53–7.56 (m, 8H), 7.63–7.66 (m, 8H), 7.75–7.79 (m, 4H).

^{13}C-NMR ($CDCl_3$, 100.53 MHz) δ: 114.5, 126.0, 128.0, 129.4, 131.4, 132.1, 132.5, 132.8, 133.5, 149.1.

IR (KBr, cm^{-1}): 3855 w, 3677 w, 3650 w, 2369 w, 2345 w, 1593 w, 1509 s, 1490 m, 1471 m, 1458 m, 1471 m, 1458 m, 1448 m, 1079 w, 1025 w, 848.5 s, 835.0 s, 754.9 m, 693.2 m, 558.2 m, 505.2 w, 498.5 w.

HRMS calcd for ([M^{2+}]): 308.13080 (dication). Found: 308.13016.

X-ray crystallographic analysis of BBIm^{2+}·2[PF_6^{-}].

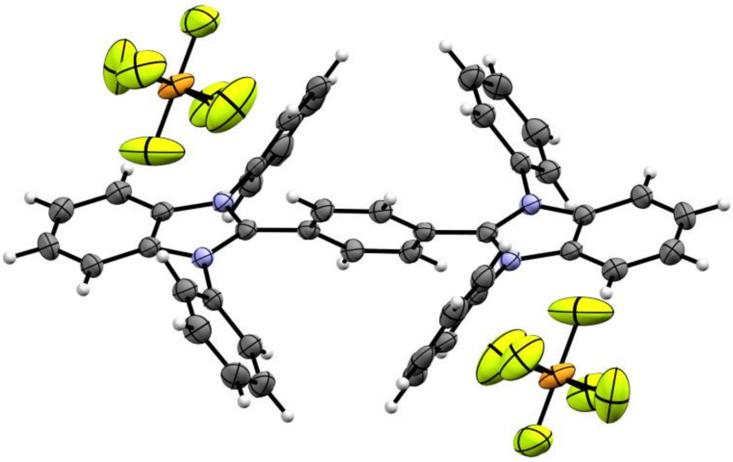
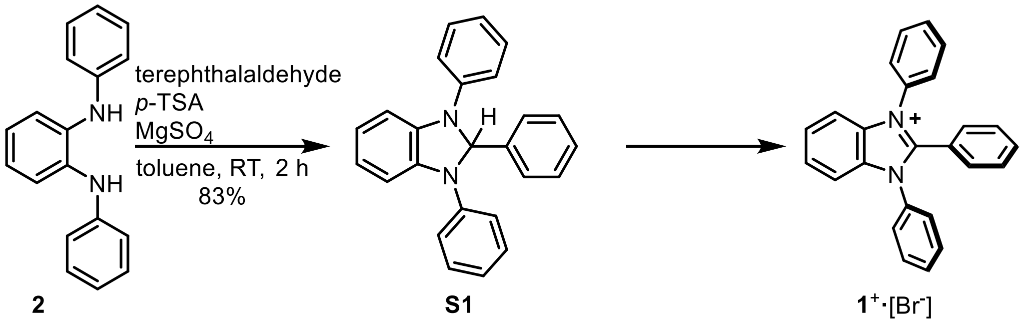


Fig. S1. ORTEP drawing of BBIm^{2+}·2[PF_6^{-}] (ellipsoids set at a 50% probability). Crystal data for BBIm^{2+}·2[PF_6^{-}], orthorhombic, space group *Ibca* (no. 73), a = 17.9121(6) Å, b = 22.9333(8) Å, c = 22.1479(11) Å, V = 9098.0(6) Å^3, T = 123 K, Z = 8, R_1 (wR_2) = 0.1005 (0.2714). CCDC 1992124.

Synthesis of $\mathbf{1}^{+}\cdot[\mathrm{Br}^{-}]$



Diamine **2** (0.52 g, 2.0 mmol) and benzaldehyde (0.21 g, 2.0 mmol) were added to a three-necked flask and dissolved in dry toluene (12 mL). *p*-Toluenesulfonic acid (38 mg) and anhydrous $MgSO_4$ (0.12 mg) were then added stirred at room temperature for 2 h. After removing insoluble materials by filtering through a pad of NH-silica (5 cm, eluent: toluene), the filtrate was concentrated in vacuo to ca. 5 mL. Et_2O was slowly added to the solution, giving pale yellow crystal of **S1** (0.34 g, 49%).

To a suspension of **S1** (0.28 g, 0.80 mmol) in dimethoxyethane (14 mL), *N*-bromoacetamide (0.11 g, 0.80 mmol) was added, and the suspension mixture was stirred at room temperature for 15 min. Additional *N*-bromoacetamide (0.11 g, 0.80 mmol) was added, and the mixture was stirred for additional 1 h. The pale yellow precipitate was filtered off and recrystallized from CH_2Cl_2/Et_2O to give $\mathbf{1}^{+}\cdot[\mathrm{Br}^{-}]$ as a colorless solid (0.20 g, 59%).

Mp >300 °C.

^{1}H-NMR ($CDCl_3$, 399.78 MHz) *δ*: 7.23 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.47–7.49 (m, 2H), 7.51–7.52 (m, 6H), 7.60–7.62 (m, 2H), 7.76 (d, *J* = 7.1 Hz, 2H), 7.93–7.95 (m, 4H).

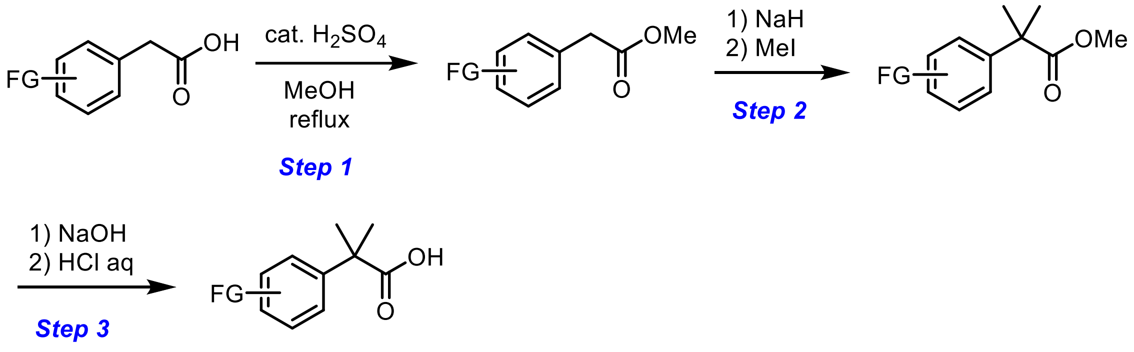
^{13}C-NMR ($CDCl_3$, 100.53 MHz) δ: 113.6, 121.2, 127.6, 128.1, 128.5, 130.0, 130.6, 132.0, 132.8, 133.0, 150.3.

IR (KBr, cm^{-1}): 3855 w, 3051 w, 3025 w, 3009 w, 2345 w, 1601 w, 1593 w, 1532 w, 1487 s, 1469 m, 1461 m, 1452 s, 1436 m, 1253 w, 1184 w, 1171 w, 1156 w, 1033 w, 771.3 m, 762.7 m, 753.0 m, 701.9 m, 689.4 m, 654.7 w, 615.1 w, 585.2 w, 502.3 w.

HRMS calcd for ([M+H^{+}]):347.15428. Found: 347.15433.

IV. Synthesis of Starting Materials.

Tertiary benzylic carboxylic acids were synthesized from the corresponding primary benzylic carboxylic acids via the synthetic sequence shown below.

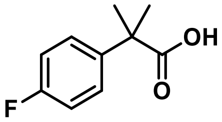


Esterification (Step 1). A two-necked flask was cooled to 0 °C using an ice/water bath. Benzylic carboxylic acid and MeOH were added to the flask (0.60 M). H_2SO_4 (a few drops) was added to the solution, and the mixture was refluxed overnight. The solution was cooled to room temperature and a saturated aqueous solution of $NaHCO_3$ was added. The mixture was extracted with EtOAc (5 times), and the organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The obtained methyl ester was used for the subsequent reaction without further purification.

Dimethylation (Step 2). A two-necked round-bottom flask equipped with a dropping funnel and a magnetic stirrer bar was flame-dried in *vacuo*, and then filled with N_2. NaH (oil dispersion, 5 equiv) and THF (3.6 M) were added to the flask and cooled to 0 °C using an ice/water bath. A THF solution of the methyl ester (1.5 M) and CH_3I (5 equiv) were added dropwise to the suspension and stirred overnight at room temperature before the reaction mixture was cooled to 0 °C. A saturated aqueous solution of NH_4Cl was added to the mixture. The resulting mixture was then extracted with EtOAc (5 times), and the organic layer was dried with Na_2SO_4. Filtration and concentration under reduced pressure gave the corresponding dimethylated methyl ester, which was used for the subsequent reaction without further purification.

Ester hydrolysis (Step 3). A round-bottom flask equipped with a magnetic stirrer bar was charged with the dimethylated methyl ester in MeOH (0.35 M), and NaOH (3 equiv) and distilled water (volume equal to MeOH) were then added to the flask. The reaction mixture was refluxed overnight and then concentrated under reduced pressure to remove MeOH. An aqueous solution of HCl (1 M) was added to the residue, and the resulting mixture was extracted with EtOAc (5 times). The organic layer was washed with brine, dried with Na_2SO_4 and filtered. The filtrate solution was concentrated under reduced pressure, and the resulting solid was recrystallized from hexane/EtOAc.

2-(4-Fluorophenyl)-2-methylpropanoic acid (6b) [CAS 20430-18-6].



The general procedure was followed using 2-(4-fluorophenyl)-2-methylpropanoic acid.

White solid (1.17 g, 37%). Mp 91.5–92.2 °C.

^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 1.62 (s, 6H), 2.17 (s, 1H), 6.99-7.05 (m, 2H), 7.34-7.39 (m, 2H).

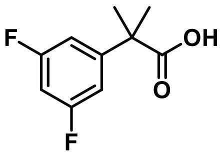
^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 26.3, 45.7, 115.2(d, J_{CF} = 21.0 Hz), 127.5(d, J_{CF} = 8.54 Hz), 139.5, 161.7 (d, J_{CF} = 245.3 Hz), 182.5.

^{19}F NMR (CDCl$_3$, 376.17 MHz) δ: -115.9.

IR (KBr, cm^{-1}): 3855 w, 3840 w, 3752 w, 3736 w, 3712 w, 3691 w, 3678 w, 3651 w, 3630 w, 2996 m, 1717 s, 1510 s, 1458 m, 1406 m, 1298 m, 1278 m, 1224 m, 1168 m, 1095 m, 1012 w, 935.3 m, 837.9 s, 813.8 m, 705.8 w, 597.8 m, 570.8 m, 522.6 m.

HRMS calcd for $C_{10}H_{11}FO_2$ ([M+H$^+$]): 182.0743. Found: 182.0741.

2-(3,5-Difluorophenyl)-2-methylpropanoic acid (6c) [CAS 879904-44-6].



The general procedure was followed using 2-(3,5-difluorophenyl)acetic acid.

White solid (911.9 mg, 27%). Mp 82.5–84.8 °C.

^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 1.58 (s, 6H), 6.69–6.74 (m, 1H), 6.91–6.94 (m, 2H).

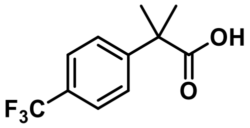
^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 26.0, 46.3, 102.5 (t, J_{CF} = 24.9 Hz), 109.2 (dd, J_{CF} = 18.5 Hz, 7.1 Hz), 147.6 (t, J_{CF} = 8.6 Hz), 162.9 (dd, J_{CF} = 247.7 Hz, 12.9 Hz), 182.0.

^{19}F NMR (CDCl$_3$, 376.17 MHz) δ: -109.3.

IR (KBr, cm^{-1}): 3855 m, 3840 w, 3751 w, 3736 w, 3712 w, 3691 w, 3677 w, 3650 w, 3630 w, 2979 s, 2345 w, 1702 s, 1626 s, 1458 m, 1436 m, 1293 m, 1174 m, 1120 s, 989.9 m, 900.5 s, 859.1 m, 696.1 m, 513.9 m.

HRMS calcd for $C_{11}H_{11}F_3O_2$ ([M+H$^+$]): 200.0649. Found: 200.0652.

2-Methyl-2-(4-(trifluoromethyl)phenyl)propanoic acid (6d) [CAS 32445-89-9].



The general procedure was followed using 2-(4-(trifluoromethyl)phenyl)acetic acid.

White solid (911.9 mg, 27%). Mp 73.6–74.2 °C.

^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 1.63 (s, 6H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H).

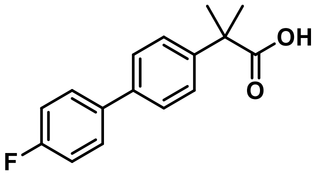
^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 26.2, 46.5, 122.8, 125.5, 126.4, 129.3 (d, J_{CF} = 32.4 Hz), 147.7, 182.3.

^{19}F NMR (CDCl$_3$, 376.17 MHz) *δ*: -62.2.

IR (KBr, cm^{-1}): 3904 w, 3855 w, 3841 w, 3752 w, 3736 w, 3712 w, 3691 w, 3678 w, 3651 w, 3630 w, 2982 m, 1701 s, 1618 m, 1542 w, 1509 w, 1472 m, 1409 m, 1327 s, 1168 s, 1106 s, 1068 s, 1012 m, 921.8 m, 837.9 m, 724.1 m, 655.7 m, 608.4 w, 506.2 m, 431.9 w

HRMS calcd for $C_{11}H_{11}F_3O_2$ ([M+H$^+$]): 232.0711. Found: 232.0714.

2-(4'-Fluoro-[1,1'-biphenyl]-4-yl)-2-methylpropanoic acid (6g) [CAS 1181290-87-8].



The general procedure was followed using 2-(4'-fluoro-[1,1'-biphenyl]-4-yl)acetic acid, which was synthesized following the literature procedure.[3] The spectra were in agreement with those reported in the literature.

White solid (948.8 mg, 35%). Mp 150.9–154.7 °C.

^{1}H NMR ((CD$_3$)$_2$CO, 399.78 MHz) δ: 1.59 (s, 6H), 7.21 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.69 (dd, *J* = 8.3 Hz, 5.7 Hz, 2H).

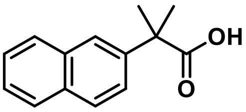
^{13}C NMR ((CD$_3$)$_2$SO, 100.3 MHz) δ: 26.2, 45.6, 115.7 (d, J_{CF} = 20.9 Hz), 119.6, 126.2, 126.5, 128.0, 129.7, 131.1, 144.5, 177.2.

^{19}F NMR ((CD$_3$)$_2$SO, 376.17 MHz) δ: -117.3.

IR (KBr, cm^{-1}): 3855 m, 3840 w, 3751 w, 3736 w, 3712 w, 3691 w, 3677 w, 3650 w, 3630 w, 2995 m, 2345 w, 1717 s, 1498 s, 1457 m, 1411 m, 1292 m, 1222 m, 1177 m, 1158 m, 1099 m ,923.7 m, 820.5 s, 521.6 w.

HRMS calcd for $C_{16}H_{15}FO_2$ ([M+H$^+$]): 258.1056. Found: 258.1058.

2-Methyl-2-(naphthalen-2-yl)propanoic acid (6h) [CAS 13365-41-8].



The general procedure was followed using 2-(naphthalen-2-yl)acetic acid.

White solid (1.09 g, 37%). Mp 150.5–151.2 °C.

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.17 (s, 6H), 7.46–7.48 (m,2H), 7.51–7.53 (m, 1H), 7.79–7.85 (m, 4H).

^{13}C NMR ($CDCl_3$, 100.3 MHz) δ: 26.2, 46.3, 124.0, 124.3, 125.9, 126.1, 127.4, 128.0, 128.1, 132.2, 133.1, 141.1, 182.2.

IR (KBr, cm^{-1}): 3855 w, 3841 w, 3752 w, 3736 w, 3712 w, 3691 w, 3678 w, 3651 w, 3630 w, 2989 m, 1700 s, 1542 w, 1508 w, 1458 w, 1296 m, 1157 w, 935.3 w, 818.6 m, 754.0 m, 481.1 m, 419.4 w.

HRMS calcd for $C_{14}H_{14}O_2$ ([M+H$^+$]): 214.0994. Found: 214.0994.

V. Set up used for the Photocatalytic Reaction

A 500 W xenon lamp (Ushio Optical ModelX SX-UID 500XAMQ) was used as the light source. The irradiation port was attached to Pyrex glass cylinder (ϕ50 mm × 200 mm) that was filled with water to eliminate light with wavelengths less than 300 nm. A test tube was fixed at a distance of 8 cm from the end of the Pyrex glass cylinder, and the temperature of the test tube was maintained at around 35 °C using a water bath (300 mL Pyrex glass beaker) and a circulator during the irrradiation.

Fig. S2 Photocatalytic reaction setup.

VI. Typical Procedures.

General procedure for the synthesis of alcohols from carboxylic acids.

To a test tube (*d* = 1.5 cm, *h* = 14.5 cm) with a magnetic stirrer bar, BBIm^{2+}·[2PF$_6^-$] (14 mg, 0.015 mmol), carboxylic acid (0.15 mmol), NaOH (3.6 mg) and acetonitrile (6 mL) were added. The test tube was capped with a septum rubber, and the oxygen gas was bubbled through the solution for 5 min using a needle (ϕ25). The rubber septum was removed and a glass cap was quickly applied to seal the tube. The contents of the flask were then stirred and irradiated with a 500 W xenon lamp for 18 h. After the reaction, methanol (6 mL) and $NaBH_4$ (20 mg) were added and the resulting solution was stirred for 30 min at room temperature. The reaction mixture was concentrated in vacuo to give a crude product, which was purified by column chromatography on silica gel.

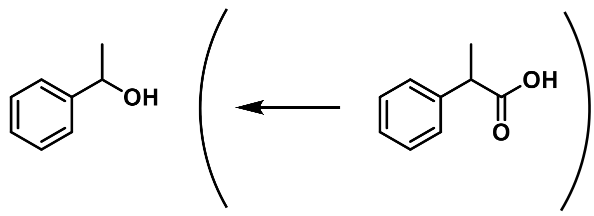
General procedure for the synthesis of dimers from carboxylic acids.

Procedure A. To a test tube (*d* = 1.5 cm, *h* = 14.5 cm) with a magnetic stirrer bar, BBIm^{2+}·[2PF$_6^-$] (14 mg, 0.015 mmol), carboxylic acid (0.15 mmol), NaOH aq. (0.09 M, 1 mL), distilled water (1 mL) and acetonitrile (4 mL) were added. The test tube was capped with a septum rubber, and the contents of the test tube were stirred and irradiated with 500 W xenon lamp for a period of 3 h. The reaction mixture was concentrated in vacuo to remove acetonitrile. To the resulting mixture, EtOAc (6 mL) and anhydrous Na_2SO_4 were added, and the mixture was filtered. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography on silica gel.

Procedure B. To a test tube (*d* = 1.5 cm, *h* = 14.5 cm) with a magnetic stirrer bar, BBIm^{2+}·[2PF$_6^-$] (14 mg, 0.015 mmol), carboxylic acid (0.15 mmol), NaOH aq. (0.09 M, 1 mL), distilled water (2 mL), and acetonitrile (3 mL) were added. The test tube was capped with a septum rubber, and the contents of the test tube were stirred and irradiated with 500 W xenon lamp for a period of 18 h. A dimerized product was precipitated from the solution and could be isolated by filtration. The product was washed with a mixture of acetonitrile/distilled water (1/1) and dried in vacuo.

VII. Spectroscopic Data of Products.

1-Phenylethan-1-ol (5a) [CAS: 98-85-1].



The typical procedure was followed using **4a** as the substrate.

Colorless oil (12.5 mg, 68% isolated yield).

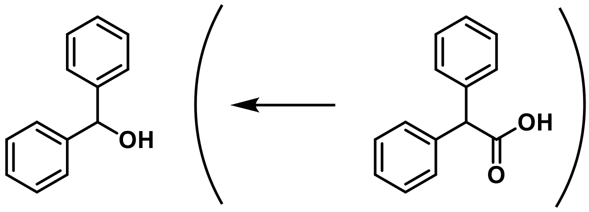
R_f 0.22 (SiO_2, hexane/EtOAc = 83/17).

^{1}H NMR (CD_2Cl_2, 399.78 MHz) *δ*: 1.45 (d, *J* = 6.3 Hz, 3H), 1.90 (s, 1H), 4.87 (q, *J* = 3.9 Hz, 1H), 7.25–7.27 (m, 1H), 7.32–7.38 (m, 4H).

^{13}C NMR (CD_2Cl_2, 100.53 MHz) *δ*: 25.5, 70.5, 125.7, 127.6, 128.7, 146.6.

HRMS Calcd for $C_{18}H_{10}O$ ([M$^+$]): 122.0726. Found: 122.0734.

Diphenylmethanol (5b) [CAS: 91-01-0].



The typical procedure was followed using **4b** as the substrate.

White solid (22.7 mg, 82% isolated yield).

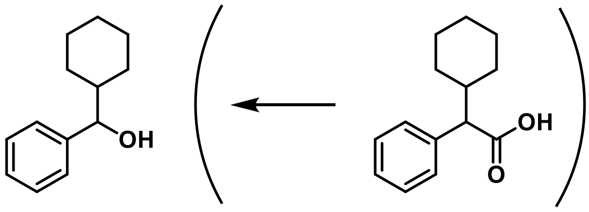
R*f* 0.22 (SiO_2, hexane/EtOAc = 83/17).

^{1}H NMR (CD_2Cl_2, 399.78 MHz) *δ*: 2.36 ((d, *J* = 3.2 Hz, 1H), 5.83 (d, *J* = 3.1 Hz, 1H), 7.25 (t, *J* = 6.9 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 4H), 7.38 (d, *J* = 6.7 Hz, 4H).

^{13}C NMR (CD_2Cl_2, 100.53 MHz) *δ*: 76.4, 126.7, 127.8, 128.8, 144.6.

HRMS Calcd for $C_{18}H_{10}ONa$ ([M+Na$^+$]): 207.0780. Found: 207.0781.

Diphenylmethanol (5c) [CAS: 945-49-3].



The typical procedure was followed using **4c** as the substrate.

White solid (22.3 mg, 78% isolated yield).

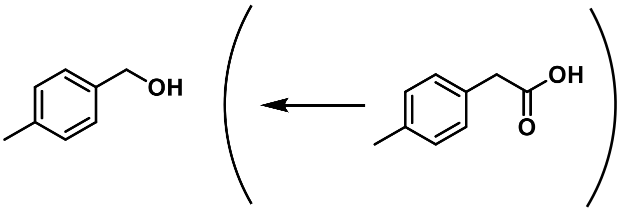
R*f* 0.31 (SiO_2, hexane/EtOAc = 83/17).

^{1}H NMR (CD_2Cl_2, 399.78 MHz) *δ*: 0.89–0.98 (m, 1H), 1.01–1.26 (m, 4H), 1.33–1.38 (m, 1H), 1.54–1.67 (m, 3H), 1.74–1.77 (m, 1H), 1.88 (d, *J* = 6.0 Hz, 1H), 1.92–1.96 (m, 1H), 4.34 (dd, *J* = 6.8 Hz, 2.4 Hz, 1H), 7.21–7.34 (m, 5H).

^{13}C NMR (CD_2Cl_2, 100.53 MHz) *δ*: 26.5, 26.5, 26.9, 29.1, 29.7, 45.4, 79.5, 127.0, 127.6, 128.4, 144.3.

HRMS Calcd for $C_{18}H_{10}ONa$ ([M+Na$^+$]): 213.1249. Found: 213.1252.

Diphenylmethanol (5d) [CAS: 589-18-4].



The typical procedure was followed using **4d** as the substrate.

Colorless oil (2.4 mg, 13% isolated yield).

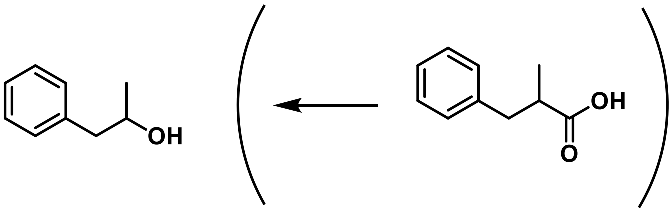
R*f* 0.14 (SiO_2, hexane/EtOAc = 83/17).

^{1}H NMR (CD_2Cl_2, 399.78 MHz) *δ*: 1.72 (s, 1H), 2.33 (s, 3H), 4.60 (d, *J* = 5.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H).

^{13}C NMR (CD_2Cl_2, 100.53 MHz) *δ*: 21.2, 65.3, 127.3, 129.4, 137.6, 138.6.

HRMS Calcd for $C_{18}H_{10}O$ ([M^+]): 122.0726. Found: 122.0729.

1-Phenylpropan-2-ol (5e) [CAS: 698-87-3].



The typical procedure was followed using **4e** as the substrate.

The yield was determined by GC using dodecane as an internal standard.

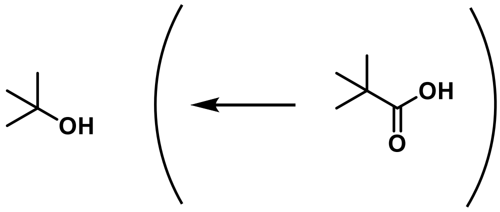
^{1}H NMR ($CDCl_3$, 399.78 MHz) *δ*: 1.20 (d, *J* = 6.0 Hz, 3H), 1.54 (d, *J* = 17.2 Hz, 1H), 2.66 (dd, *J* = 13.6 Hz, 8.0 Hz, 1H), 2.77 (dd, *J* = 13.6 Hz, 4.8 Hz, 1H), 3.97–4.00 (m, 1H), 7.20–7.24 (m, 3H), 7.28–7.32 (m, 2H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) *δ*: 23.1, 46.1, 69.2, 126.7, 128.8, 129.8, 139.3.

HRMS Calcd for $C_{18}H_{10}O$ ([[$M+Na^+$]): 159.0780. Found: 159.0776.

Spectroscopic data were consistent with those reported in the literature.[4]

2-Methylpropan-2-ol (5f) [CAS: 75-65-0].



The typical procedure was followed using **4f** as the substrate.

The yield was determined by NMR using 1,4–dioxane as an internal standard.

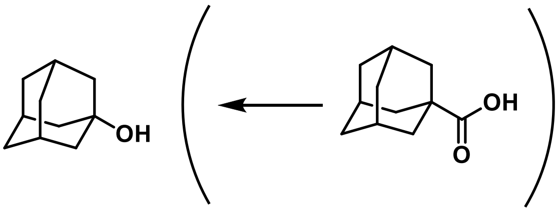
Spectroscopic data were consistent with those reported in the literature.[5]

^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 1.22 (s, 9H), 1.88 (br, 1H).

^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 31.2, 69.2.

HRMS Calcd for C$_4$H$_{10}$O ([M–Me$^+$]): 59.0875. Found: 59.0500.

(3s,5s,7s)-Adamantan-1-ol (5g) [CAS: 768-95-6].



The typical procedure was followed using **4g** as the substrate.

The yield was determined by GC using dodecane as an internal standard.

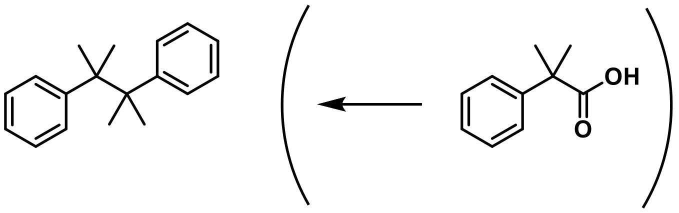
Spectroscopic data were consistent with those reported in the literature.[6]

^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 1.37 (s, 1H), 1.61 (dd, J = 20.0 Hz, 116 Hz, 6H), 1.71 (d, J = 2.8 Hz, 6H), 2.14 (s, 3H).

^{13}C NMR (CD$_2$Cl$_2$, 100.53 MHz) δ: 30.7, 36.0, 45.3, 68.2.

HRMS Calcd for C$_{18}$H$_{10}$O ([[M+Na$^+$]): 175.1093. Found: 175.1102.

(2,3-Dimethylbutane-2,3-diyl)dibenzene (7a) [CAS: 16483-40-2].



The typical procedure (Procedure A) was followed using **6a** as the substrate.

White solid (10.5 mg, 52% isolated yield). Mp 122.1–122.8 °C.

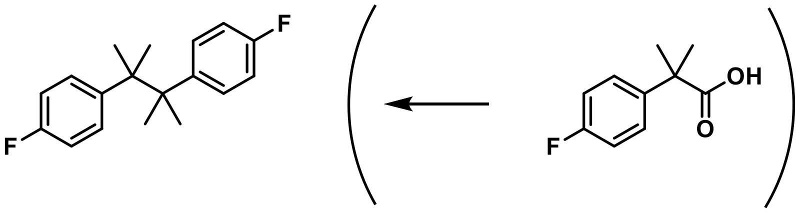
R*f* 0.34 (SiO_2, hexane/EtOAc = 100/0).

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.31 (s, 12H), 7.05–7.08 (m, 4H), 7.15–7.21 (m, 6H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 25.3 43.7, 125.6, 126.7, 128.7, 146.9.

HRMS Calcd for $C_{18}H_{22}$ ([M+H$^+$]): 238.1722. Found: 238.1724.

4,4'-(2,3-Dimethylbutane-2,3-diyl)bis(fluorobenzene) (7b) [CAS: 16483-40-2].



The typical procedure (Procedure A) was followed using **6b** (0.30 mmol) as the substrate.

White solid (27.4 mg, 67% isolated yield). Mp 122.1–122.8 °C.

R*f* 0.34 (SiO_2, hexane).

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.37 (s, 12H), 6.83–6.88 (m, 4H), 6.93–6.97 (m, 4H).

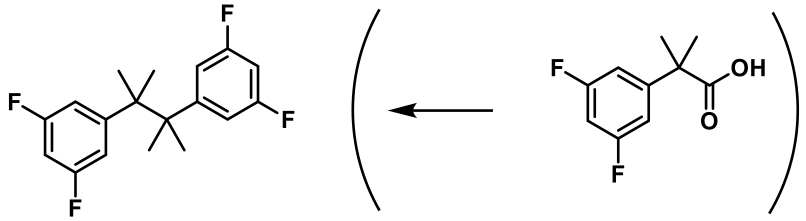
^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 25.4, 43.5, 113.4 (d, J_{CF} = 21.0 Hz), 130.2, 142.4, 161.1 (d, J_{CF} = 244.3 Hz).

^{19}F NMR ($CDCl_3$, 376.17 MHz) δ: -118.1.

IR (KBr, cm^{-1}): 3855 w, 3841 w, 3752 w, 3736 w, 3712 w, 3691 w, 3678 w, 3651 w, 3630 w, 2977 m, 1655 w, 1598 s, 1370 m, 1229 s, 1166 s, 1082 m, 1013 m, 836.0 m, 821.5 m, 685.6 m.

HRMS Calcd for $C_{18}H_{20}F_2$ ([M+H$^+$]): 274.1533. Found: 274.1529.

5,5'-(2,3-Dimethylbutane-2,3-diyl)bis(1,3-difluorobenzene) (7c).



The typical procedure (Procedure A) was followed using **6c** (0.30 mmol) as the substrate.

White solid (29.7 mg, 64% isolated yield). Mp 140.2–144.0 °C.

R_f 0.51 (SiO$_2$, hexane/CH$_2$Cl$_2$ = 4/1).

^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 1.29 (s, 12H), 6.57 (d, J = 8.0 Hz, 4H), 6.66 (t, J = 8.0 Hz, 2H).

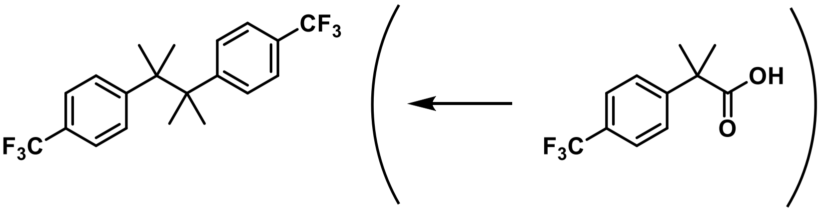
^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 24.9, 44.0, 25.3 (t, J_{CF} = 25.3 Hz), 111.5 (dd, J_{CF} = 18.6 Hz, 6.73 Hz).

^{19}F NMR (CDCl$_3$, 376.17 MHz) δ: -111.4.

IR (KBr, cm^{-1}): 2369 w, 2345 w, 1718 w, 1699 w, 1685 w, 1654 w, 1618 s, 1591 s, 1541 w, 1508 w, 1438 m, 1426 s, 1384 m, 1301 s, 1111 s, 978.6 m, 935.3 m, 869.7 s, 848.5 m, 703.8 m, 636.3 w.

HRMS Calcd for C$_{18}$H$_{18}$F$_4$ ([M+H$^+$]): 310.1345. Found: 310.1339.

4,4'-(2,3-Dimethylbutane-2,3-diyl)bis((trifluoromethyl)benzene) (7d) [CAS: 125847-20-3].



The typical procedure (Procedure A) was followed using **6d** (0.30 mmol) as the substrate.

White solid (20.1 mg, 36% isolated yield). Mp 73.3–75.4 °C.

R_f 0.51 (SiO$_2$, hexane/CH$_2$Cl$_2$ = 4/1).

^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 1.33 (s, 12H), 7.14 (d, J = 8.0 Hz, 4H), 7.44 (d, J = 8.4 Hz, 4H).

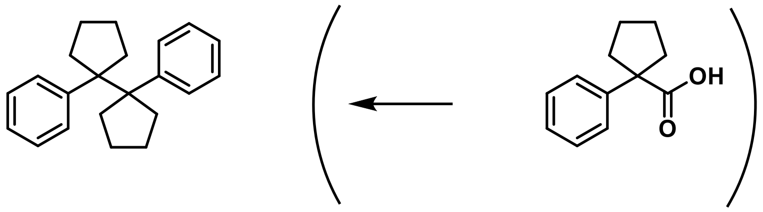
^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 25.1, 43.9, 123.6, 124.2 (q, J_{CF} = 271.8 Hz), 128.0 (q, J_{CF} = 32.2 Hz), 128.8, 150.4.

^{19}F NMR (CDCl$_3$, 376.17 MHz) δ: -62.1.

IR (KBr, cm^{-1}): 2367 w, 2345 w, 1718 w, 1699 w, 1685 w, 1654 w, 1637 w, 1618 m, 1560 m, 1541 m, 1508 m, 1457 m, 1410 m, 1328 s, 1166 m, 1117 s, 1090 s, 1068 s, 1016 m, 841.7 s, 621.9 m.

HRMS Calcd for C$_{20}$H$_{20}$F$_6$ ([M+H$^+$]): 374.1469. Found: 374.1463.

1,1'-Diphenyl-1,1'-bi(cyclopentane) (7e) [CAS: 59358-70-2].



The typical procedure (Procedure B) was followed using **6e** as the substrate.

White solid (14 mg, 65% isolated yield). Mp 140.4–141.1 °C.

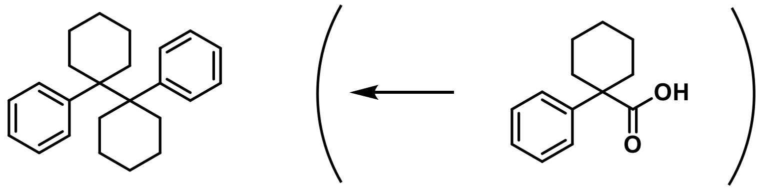
^{1}H NMR ($CDCl_3$, 399.78 MHz) *δ*: 1.22–1.27 (m, 4H), 1.53–1.57 (m, 4H), 1.83–1.88 (m, 4H), 2.18–2.23 (m, 4H), 6.92–6.94 (m, 4H), 7.09–7.10 (m, 6H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 22.5, 33.8, 58.0, 125.5, 126.9, 128.6, 144.2.

IR (KBr, cm^{-1}): 3905 m, 3855 s, 3841 m, 3752 m, 3736 m, 3712 m, 3691 m, 3678 m, 3651 s, 3630 m, 3569 m, 2923 m, 1655 m, 1542 m, 1458 m, 1035 m, 734,7 s, 705.8 s, 500.4 m.

HRMS Calcd for $C_{21}H_{13}$ ([1/2M$^+$]): 145.1012. Found: 145.1015.

1,1'-Diphenyl-1,1'-bi(cyclohexane) (7f) [CAS: 59358-71-3].



The typical procedure (Procedure B) was followed using **6f** as the substrate.

White solid (9.5 mg, 33% isolated yield). Mp 180.7–182.5 °C.

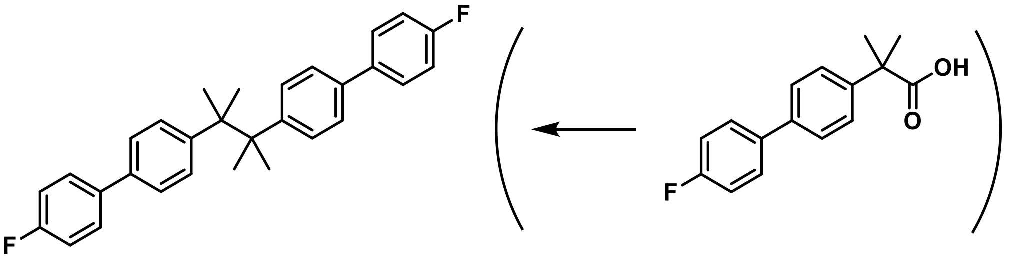
^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.00–1.15 (m, 6H), 1.35–1.48 (m, 10H), 2.30 (d, *J* = 11.9 Hz, 2H), 6.95 (d, *J* = 6.7 Hz, 4H), 7.16–7.26 (m, 6H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 22.6, 26.6, 30.2, 49.3, 125.1, 126.6, 130.7, 141.2.

IR (KBr, cm^{-1}): 2365 m, 2345 m, 1774 m, 1735 m, 1718 m, 1700 m, 1685 m, 1654 s, 1637 m, 1560 s, 1542 s, 1509 s, 1499 m, 1474 m, 1457 s, 1106 s, 880.3 s, 727,9 m, 704.8 s.

HRMS Calcd for $C_{24}H_{30}$ ([M+H$^+$]): 318.2348. Found: 318.2345.

4',4'''-(2,3-Dimethylbutane-2,3-diyl)bis(4-fluoro-1,1'-biphenyl) (7g).



The typical procedure (Procedure A) was followed using **6g** (0.30 mmol) as the substrate.

White solid (29.1 mg, 41% isolated yield). Mp 248.8–252.2 °C.

R_f 0.51 (SiO_2, hexane/CH_2Cl_2 = 4/1).

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.37 (s, 12H), 7.09−7.17 (m, 8H), 7.38 (d, *J* = 7.9 Hz, 4H), 7.55 (dd, *J* = 7.9 Hz, 4.1 Hz, 4H).

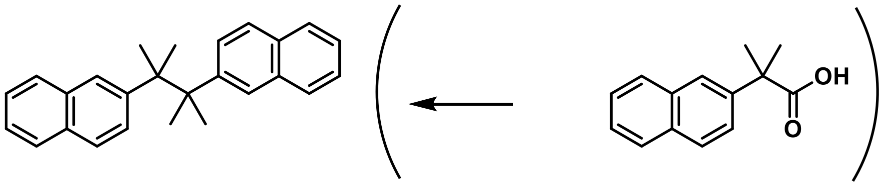
^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 25.2, 43.5, 115.5 (d, J_{CF} = 22.1 Hz), 125.1, 128.4 (d, J_{CF} = 8.6 Hz), 129.1, 137.0 (d, J_{CF} = 26.8 Hz), 145.9, 161.0, 163.5.

^{19}F NMR ($CDCl_3$, 376.17 MHz) δ: -115.7.

IR (KBr, cm^{-1}): 2368 m, 2345 m, 1773 w, 1734 m, 1718 m, 1700 m, 1685 m, 1654 m, 1637 m, 1617 w, 1560 m, 1541 m, 1523 w, 1508 m, 1491 m, 1475 m, 1458 m, 1398 m, 1094 s, 1009 s, 831.1 s, 624.8 w.

HRMS Calcd for $C_{30}H_{28}F_2$ ([M+H$^+$]): 426.2159. Found: 426.2158.

2,2'-(2,3-Dimethylbutane-2,3-diyl)dinaphthalene (7h) [CAS: 959053-73-7].



The typical procedure (Procedure B) was followed using **6h** (0.30 mmol) as the substrate.

White solid (23.0 mg, 41% isolated yield). Mp 215.4–220.3 °C.

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.46 (s, 12H), 7.17 (d, *J* =. 8.8 Hz, 2H), 7.42–7.44 (m, 4H), 7.55 (s, 2H), 7.59 (d, *J* =. 8.8 Hz, 2H), 7.68–7.71 (m, 2H), 7.78–7.80 (m, 2H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 25.5, 44.0, 125.3, 125.5, 125.6, 127.1, 127.3, 127.5, 128.1, 131.6, 132.5, 144.4.

IR (KBr, cm^{-1}): 2370 w, 2345 w, 1718 w, 1699 w, 1685 w, 1654 w, 1637 w, 1595 w, 1560 w, 1541 w, 1507 m, 1458 m, 1375 m, 1187 m, 1127 m, 1075 m, 862.0 m, 817.6 s, 750.1 s.

HRMS Calcd for $C_{26}H_{26}$ ([M+H$^+$]): 338.2035. Found: 338.2039.

VIII. Mechanistic Studies

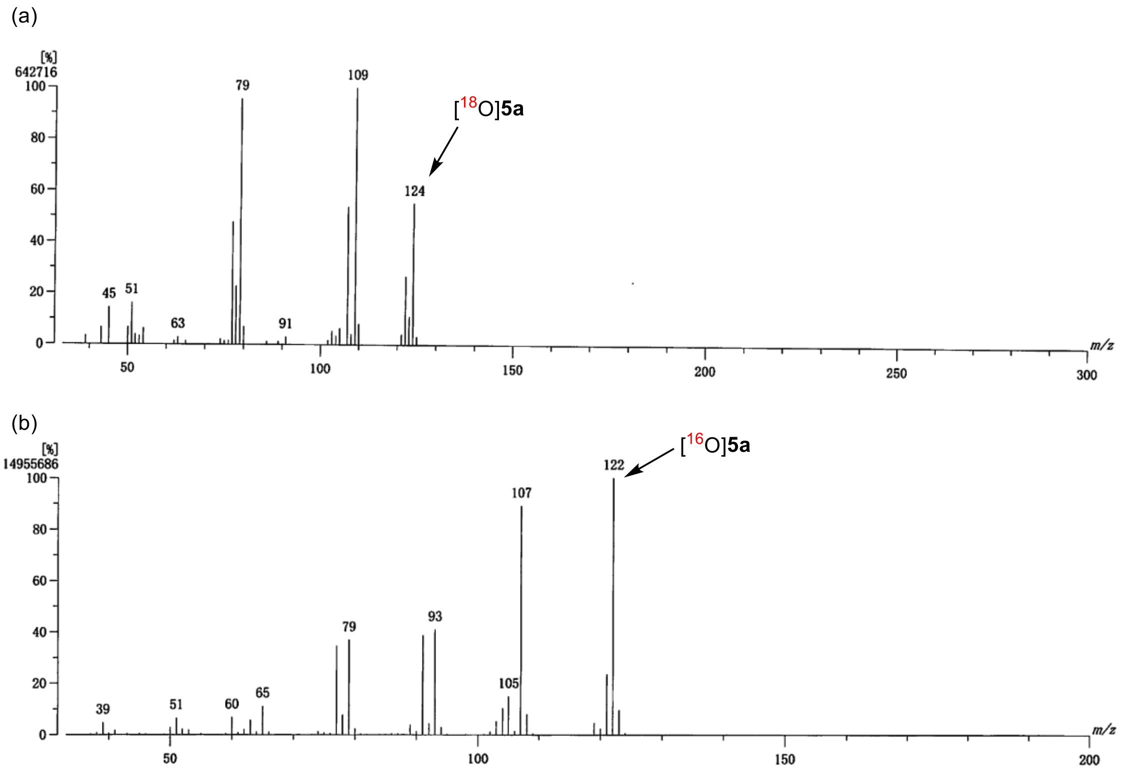
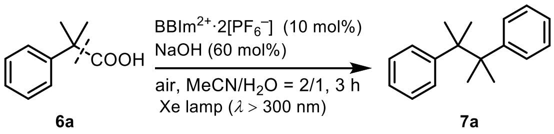


Fig. S3 HRMS spectra of **5a** for the photocatalytic hydroxylation reaction in (a) $^{18}O_2$- and (b) non-labeld O_2-saturated acetonitrile.

Table S1. Concentration dependency of photocatalytic decarboxylative dimerization of **6a**[a]



Entry	Amount of solvent (mL)	NMR yields (%)
1	6	57
2	30	45

[a]Reaction condition: **6a** (0.15 mmol), Cat. (0.015 mmol), NaOH (0.090 mmol), in acetonitrile / H_2O (2:1).

The yield of photocatalytic decarboxylative dimerization was not significantly affected by the concentration of BBI^{2+}, suggesting that the short-lived $^1BBIm^{2+*}$ is not an active species for the reaction.

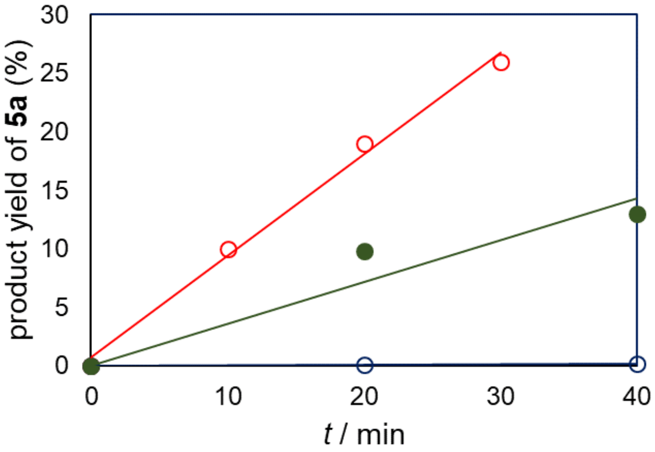


Fig. S4 Conversion/irradiation time profiles for the BBIm^{2+}·2[PF$_6^-$](red), **1**$^+$·[Br$^-$](blue) and Acr-Mes$^+$·[ClO$_4^-$](green) catalyzed decarboxylative hydroxylation reaction of **4a** (2.5 × 10^{-2} M) in oxygen-saturated acetonitrile.

The kinetic profiles for decarboxylative hydroxylation reaction of **4a** with photocatalysts BBIm^{2+}·2[PF$_6^-$], **1**$^+$·[Br$^-$] and Acr-Mes$^+$·[ClO$_4^-$] were compared under the same absorbance conditions [absorbance at 365 nm = 1.0, an LED lamp (365nm, 60 W)]. Coversion/irradiation time profiles are shown in Fig. S4, which clearly indicates the superior activity of BBIm^{2+}·2[PF$_6^-$] to **1**$^+$·[Br$^-$] and Acr-Mes$^+$·[ClO$_4^-$]. The quantum yields were estimated to be 0.60 (with BBIm^{2+}·2[PF$_6^-$]), 0.004 (with **1**$^+$·[Br$^-$]) and 0.23 (with Acr-Mes$^+$·[ClO$_4^-$]) (Table S2).

Table S2 Quantum yields for decarboxylative hydroxylation reaction of **4a** with photocatalysts.

Photocatalyst	BBIm^{2+}· 2[PF$_6^-$]	**1**$^+$· [Br$^-$]	Acr-Mes$^+$· [ClO$_4^-$]
Φ^a	0.60	0.004	0.23

[a]The quantum yield for photocatalytic oxygenation of *p*-xylene with Acr-Mes$^+$·[ClO$_4^-$]was used as a reference value.[7]

IX. Theoretical Calculations

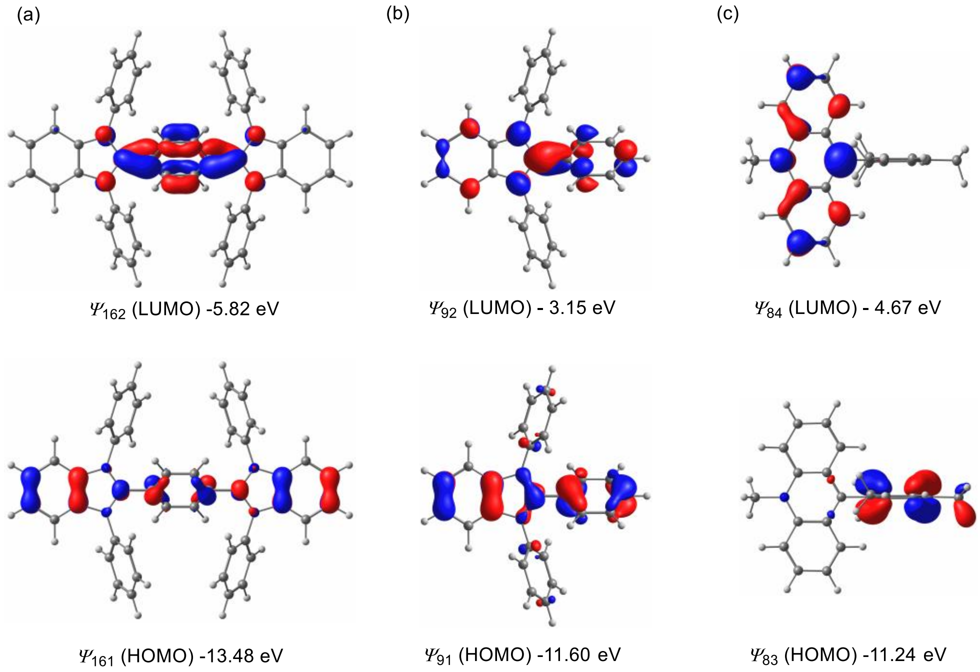


Fig. S5 Frontier orbitals (HOMO, LUMO) of (a) BBIm^{2+}, (b) **1**$^{+}$, and (c) Mes-Acr^{+} at ωB97XD/6-31G(d,p) level along with their energy levels.

X. Cyclic Voltammogram

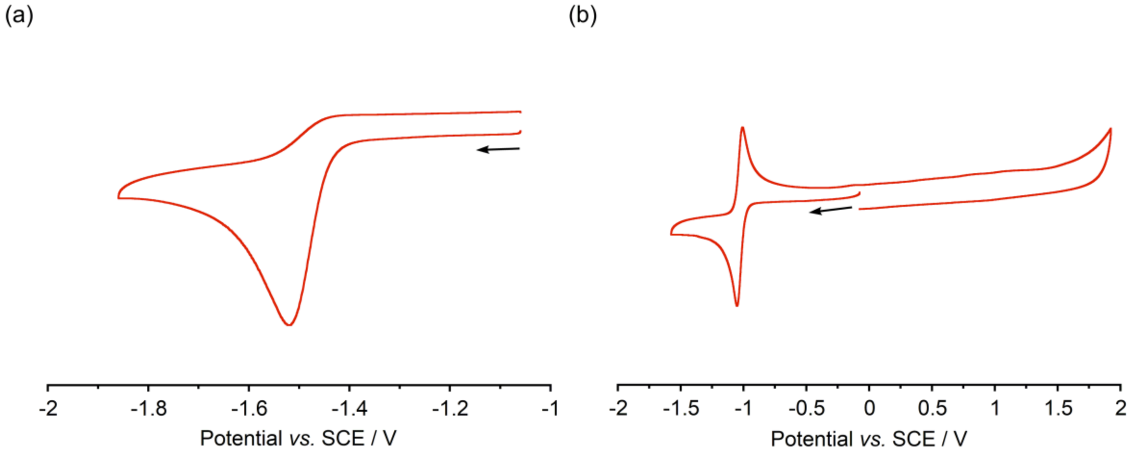


Figure S6. Cyclic voltammogram of (a) **1**$^{+}\cdot$[Br^{-}] and (b) BBIm$^{2+}\cdot$2[PF$_6^{-}$] (5.0 × 10^{-4} M in acetonitrile containing ^{n}Bu$_4$NPF$_6$, room temperature, scan rate = 0.5 V s^{-1}).

XI. Stern–Volmer Analysis

Transient absorption measurements. The measurements of nanosecond transient absorption spectra in the photochemical reactions of $BBIm^{2+}$ with *t*BuCOO⁻ in MeCN were performed according to the following procedures. Typically, an Ar-saturated MeCN solution containing tBuCOO^{-} ($0 – 1.0 \times 10^{-4}$ M) and $BBIm^{2+}$ (1.0×10^{-5} M) was excited by a Nd:YAG laser (UNISOKU, TSP-1000-SLI10, 4-6 ns fwhm) at $\lambda = 355$ nm with a power of 20 mJ/pulse. Photoinduced events were measured by use of a continuous Xe lamp (150 W) and a photodiode (UNISOKU, USP-MK328-G3) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (UNISOKU, USP-OSC-LEC4024, 12bit, 4 ch, 200 MHz, 12.5 Mpoint/ch). The transient spectra were recorded for fresh solutions in each laser excitation. All experiments were performed at 298 K.

XII. References

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XIII. Cartesian Coordinates of Optimized Structures.

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6	0.704849580	-0.002164760	7.336137135
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6	-0.704849580	0.002164760	-7.336137135
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6	2.462497049	-0.034018496	3.197619230
6	2.462497049	-0.034018496	-3.197619230
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1	1.229298112	-0.006809288	8.284670473
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1	2.519066737	-0.002528691	-6.155080615
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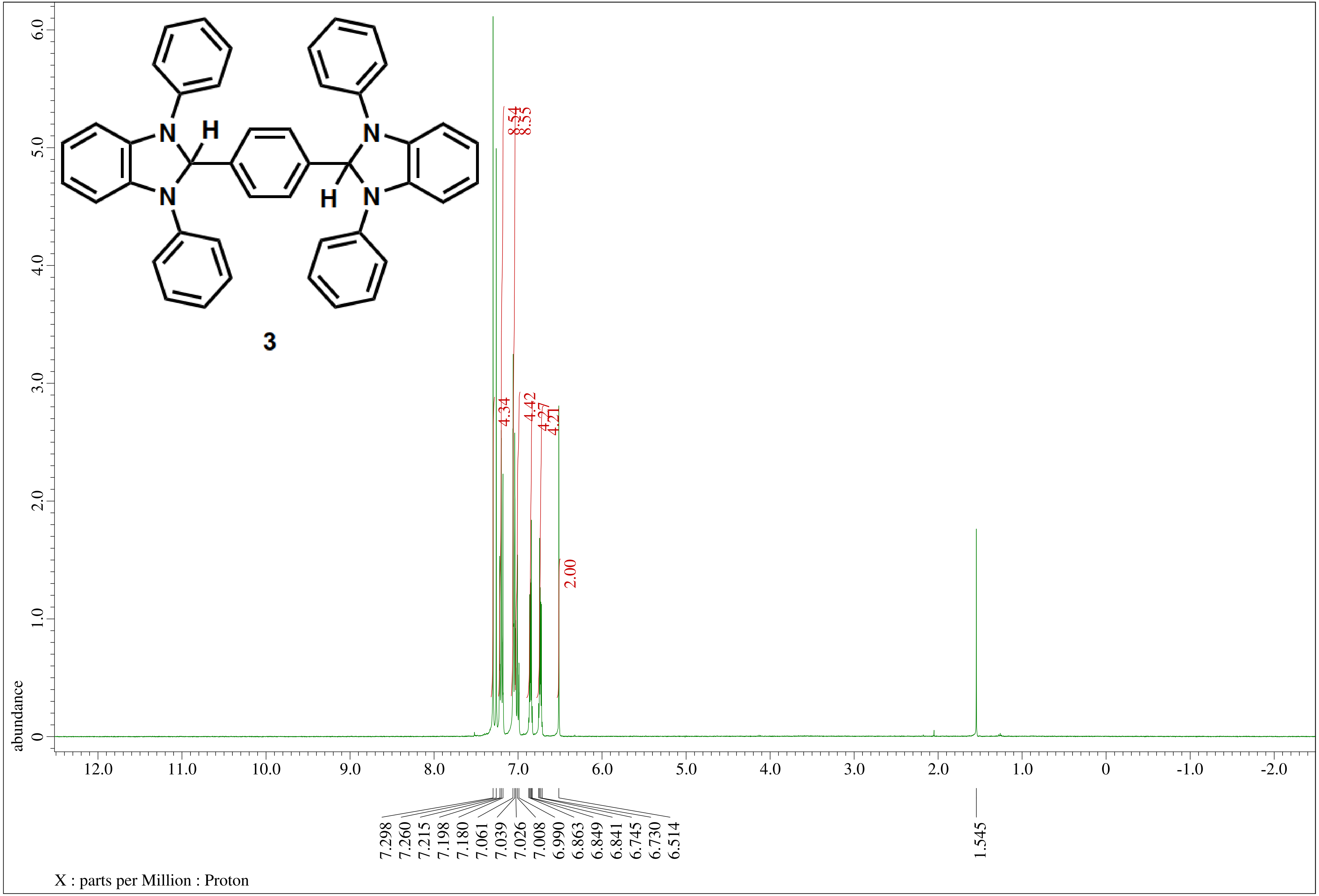
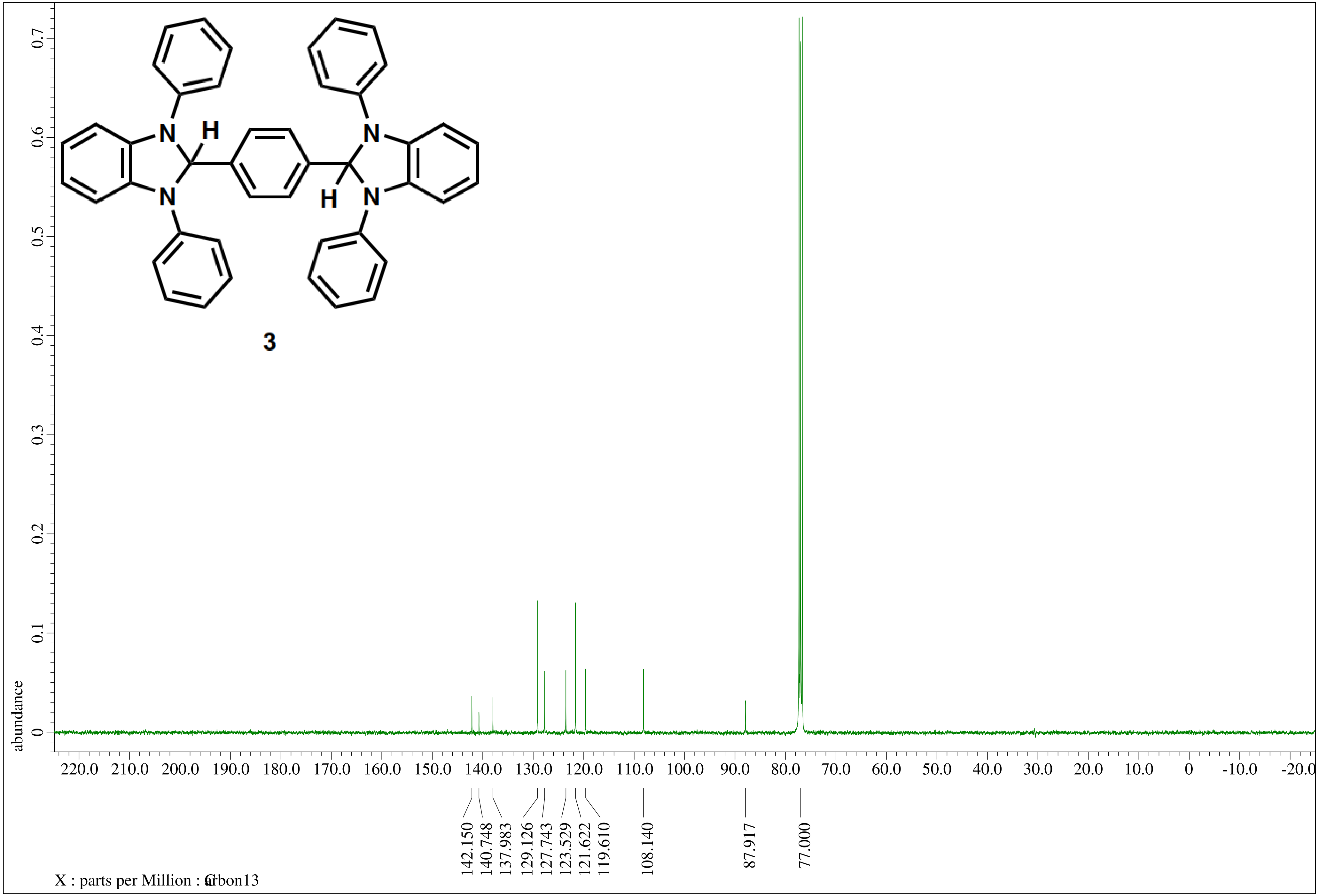
XIII. Copies of ^{1}H, ^{13}C, and ^{19}F NMR Spectra

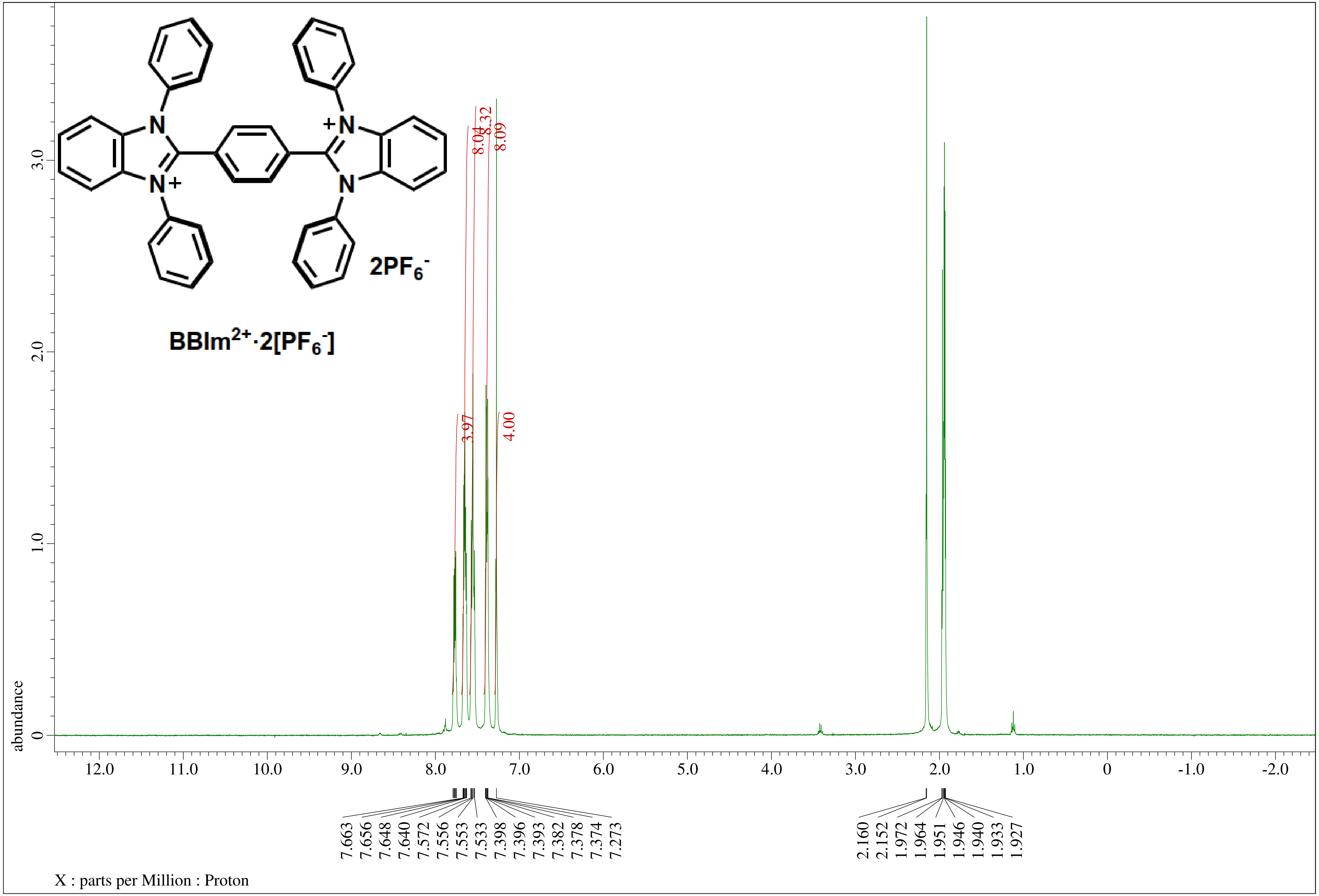
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3**



^{1}H NMR (400 MHz, CD$_3$CN) of BBIm^{2+}2[PF$_6^-$]



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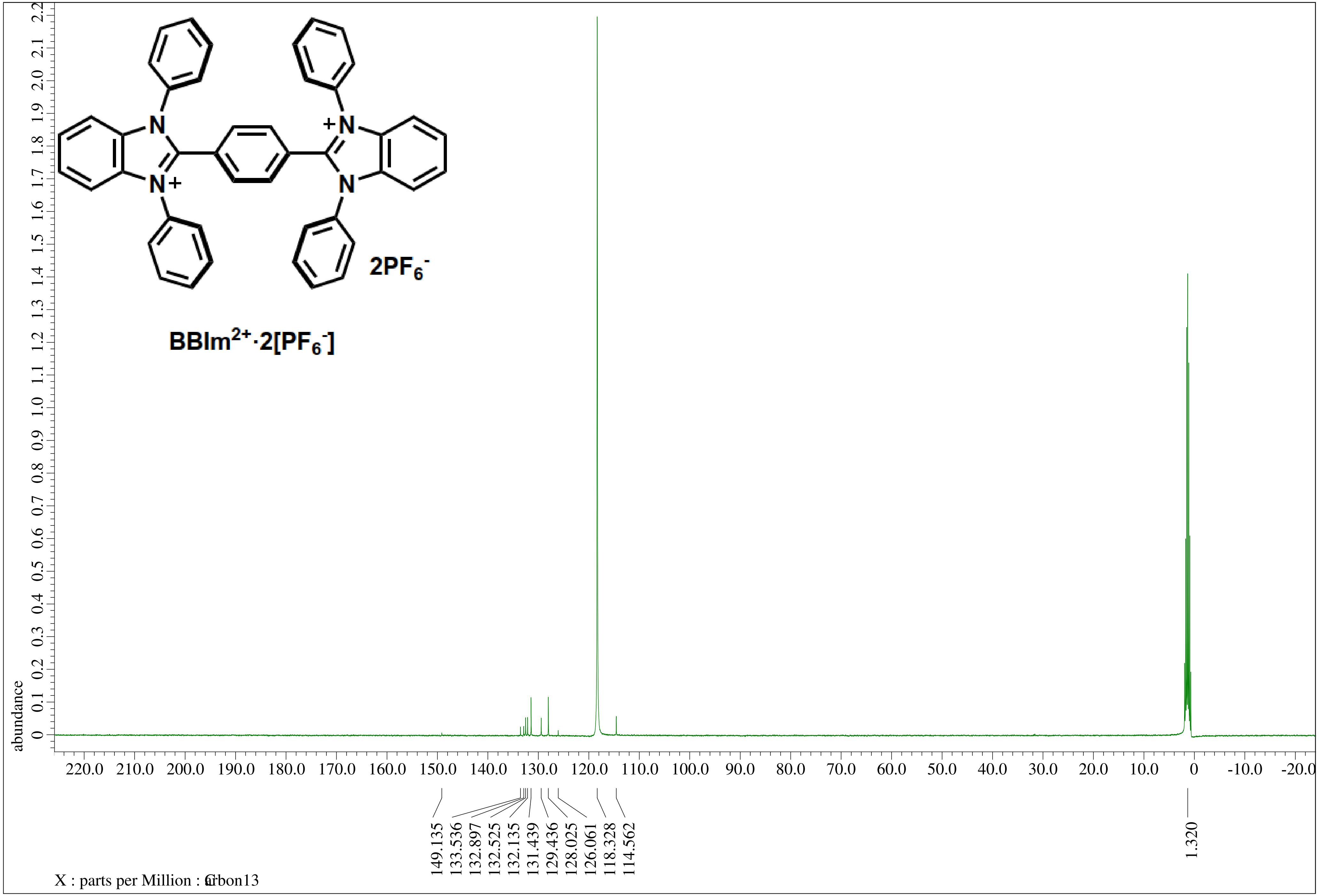
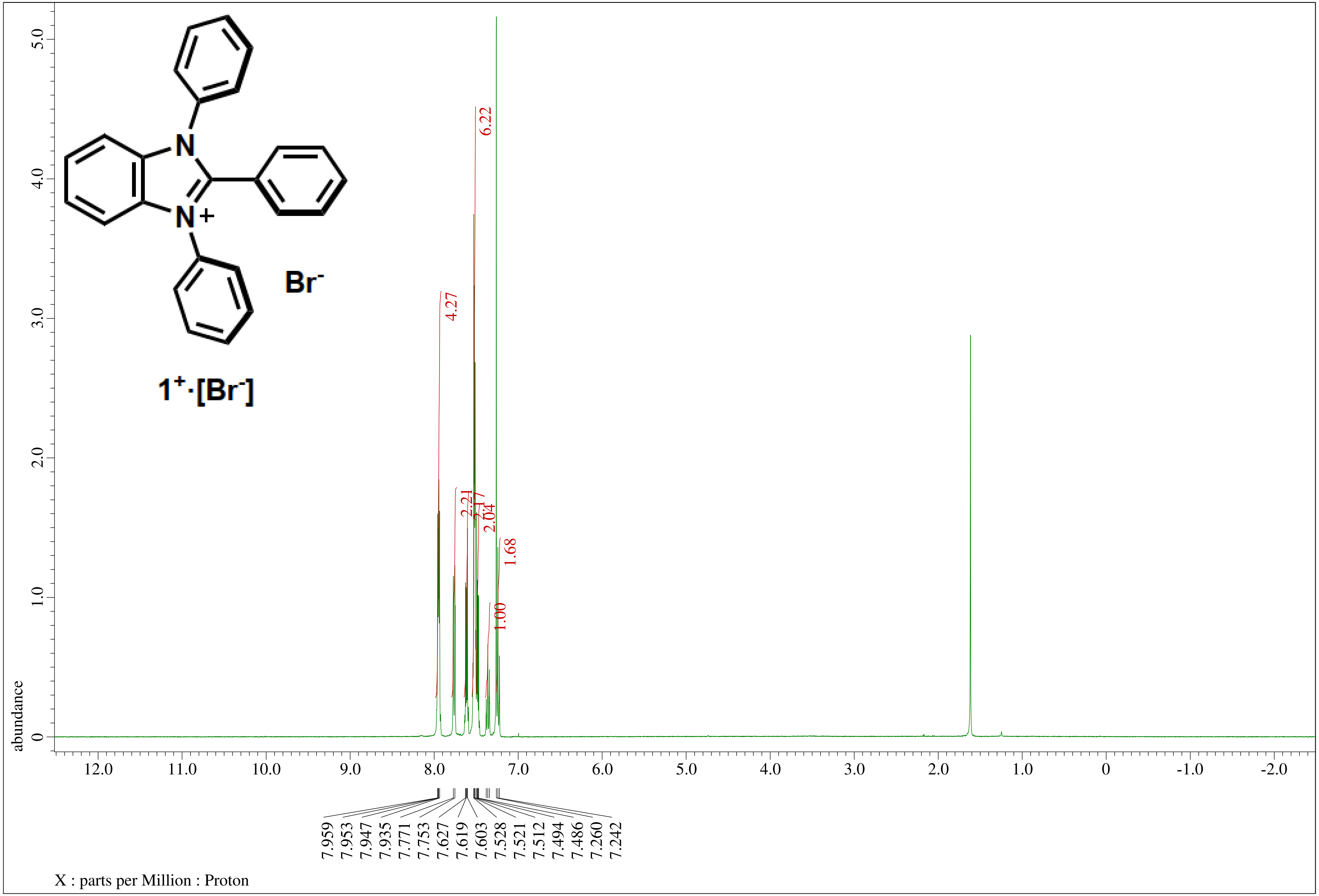
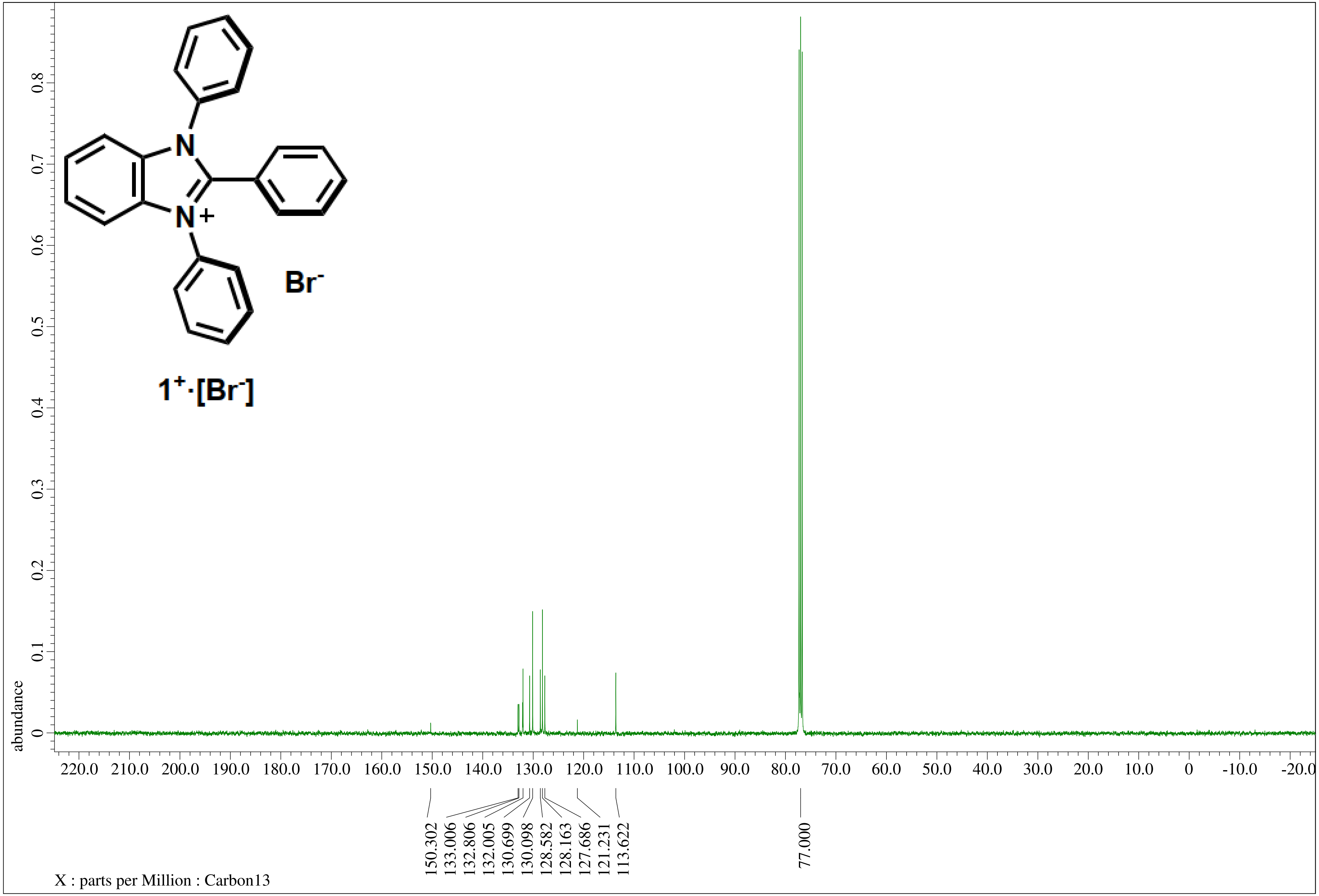


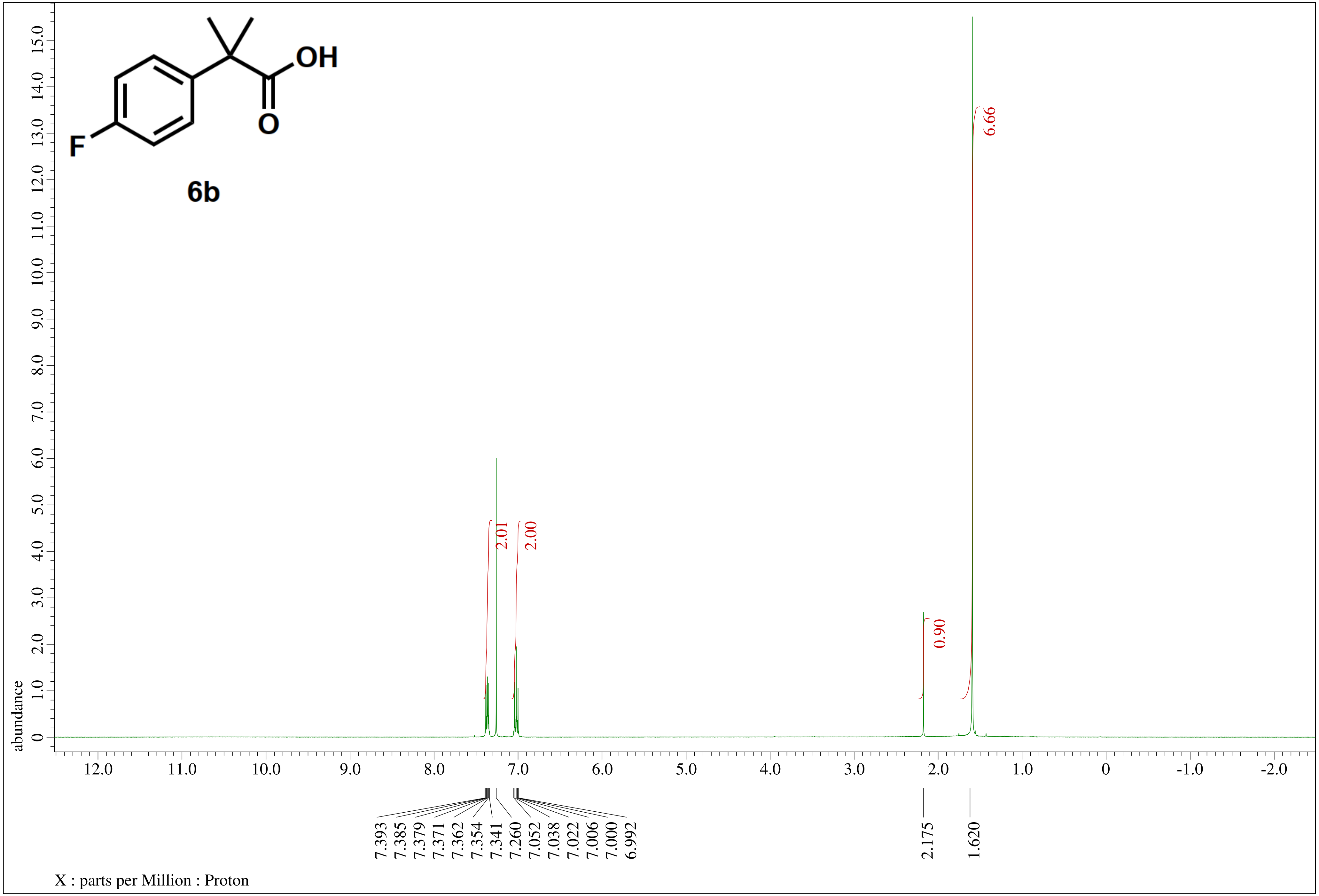
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **1$^+$[Br$^-$]**



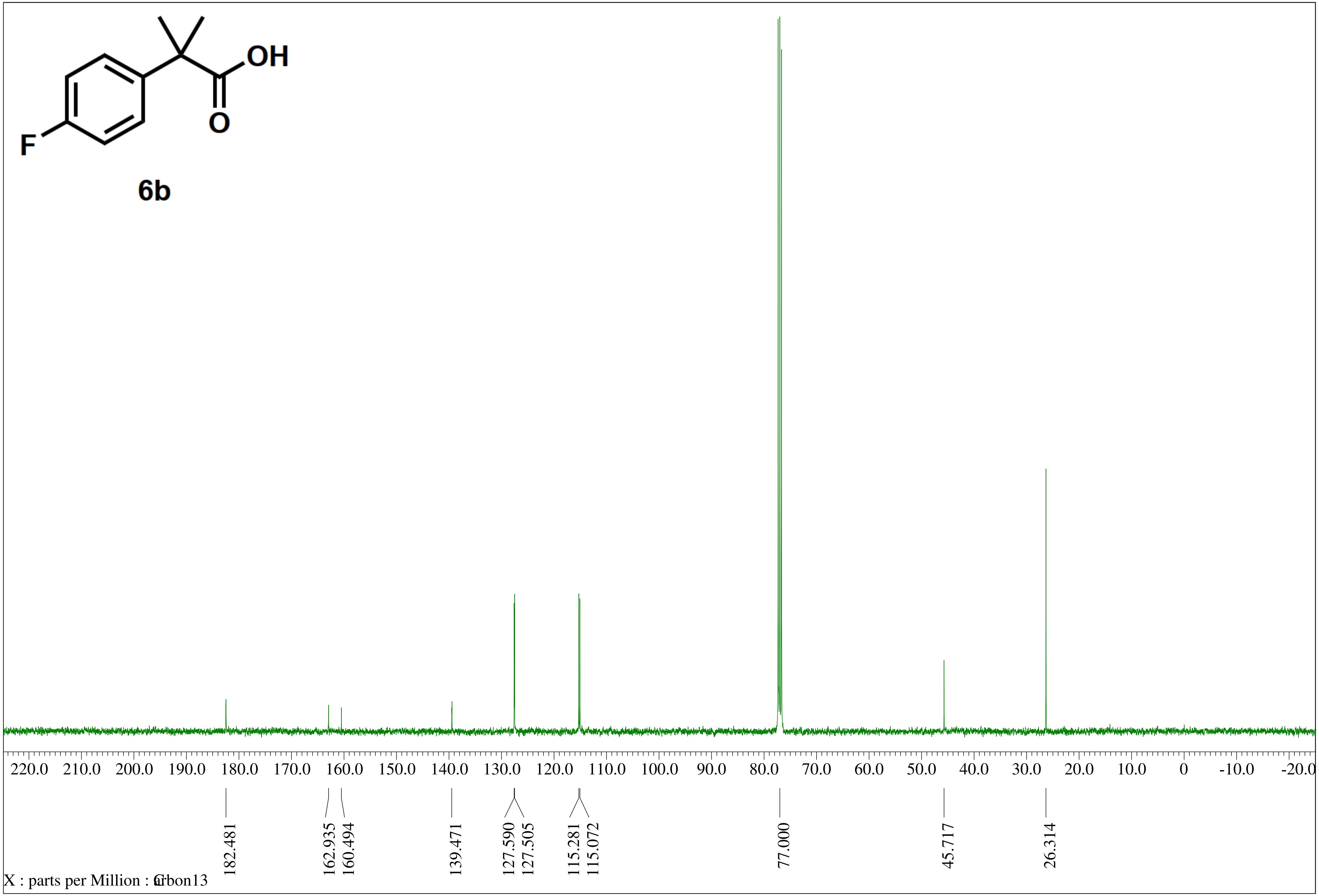
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **1$^+$[Br$^-$]**



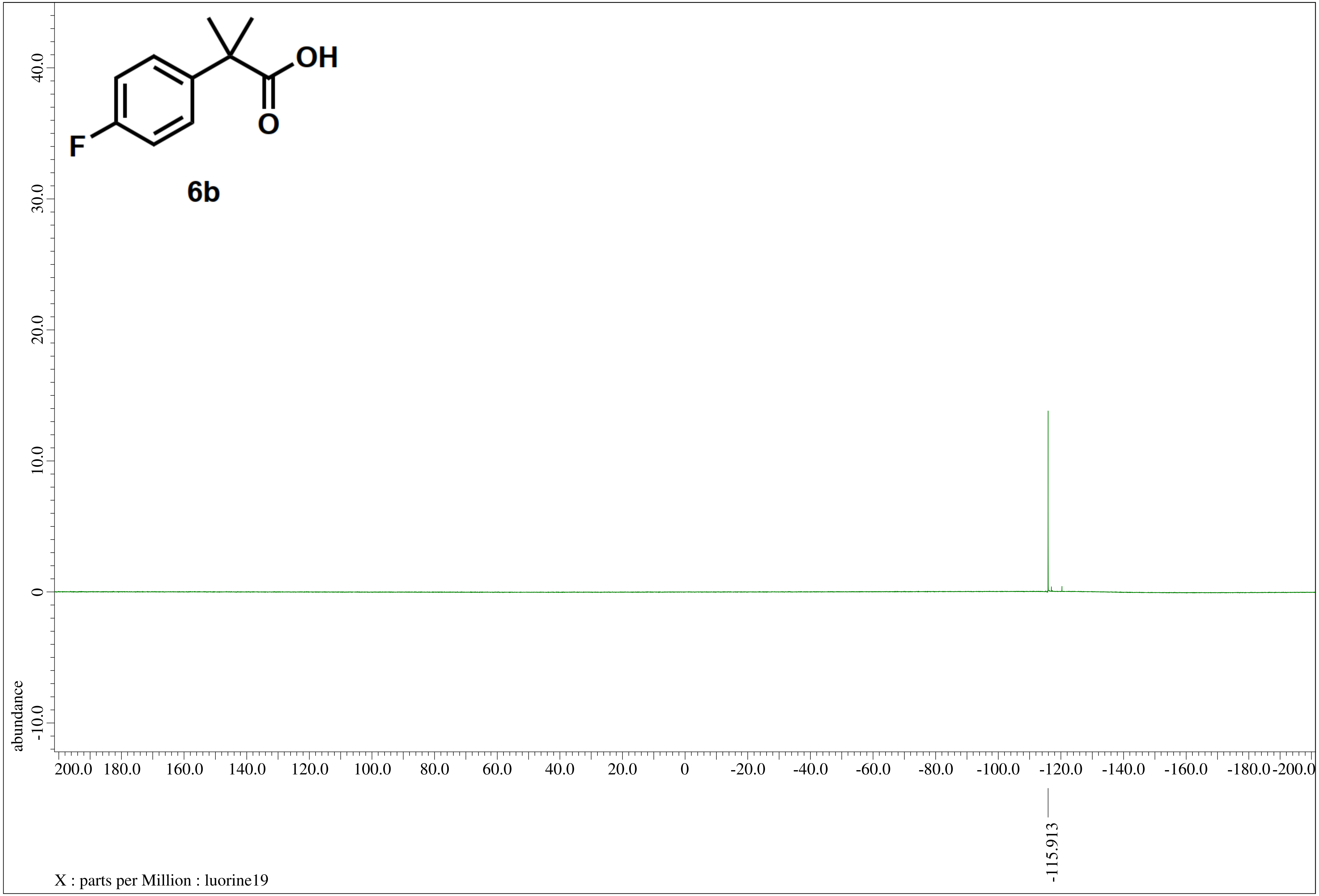
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6b**



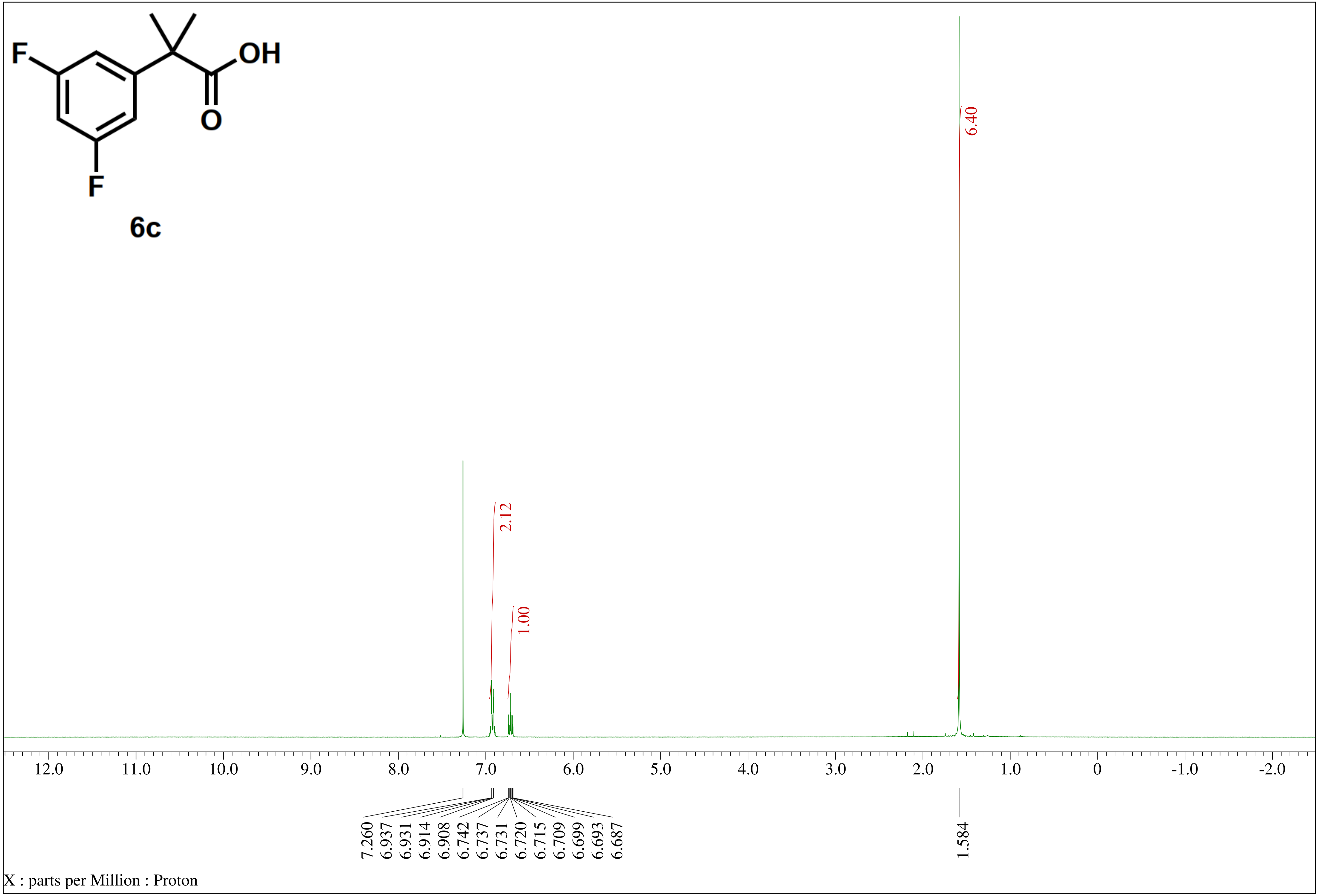
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **6b**



^{19}F NMR spectrum (375 MHz, CDCl$_3$) of **6b**



^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **6c**



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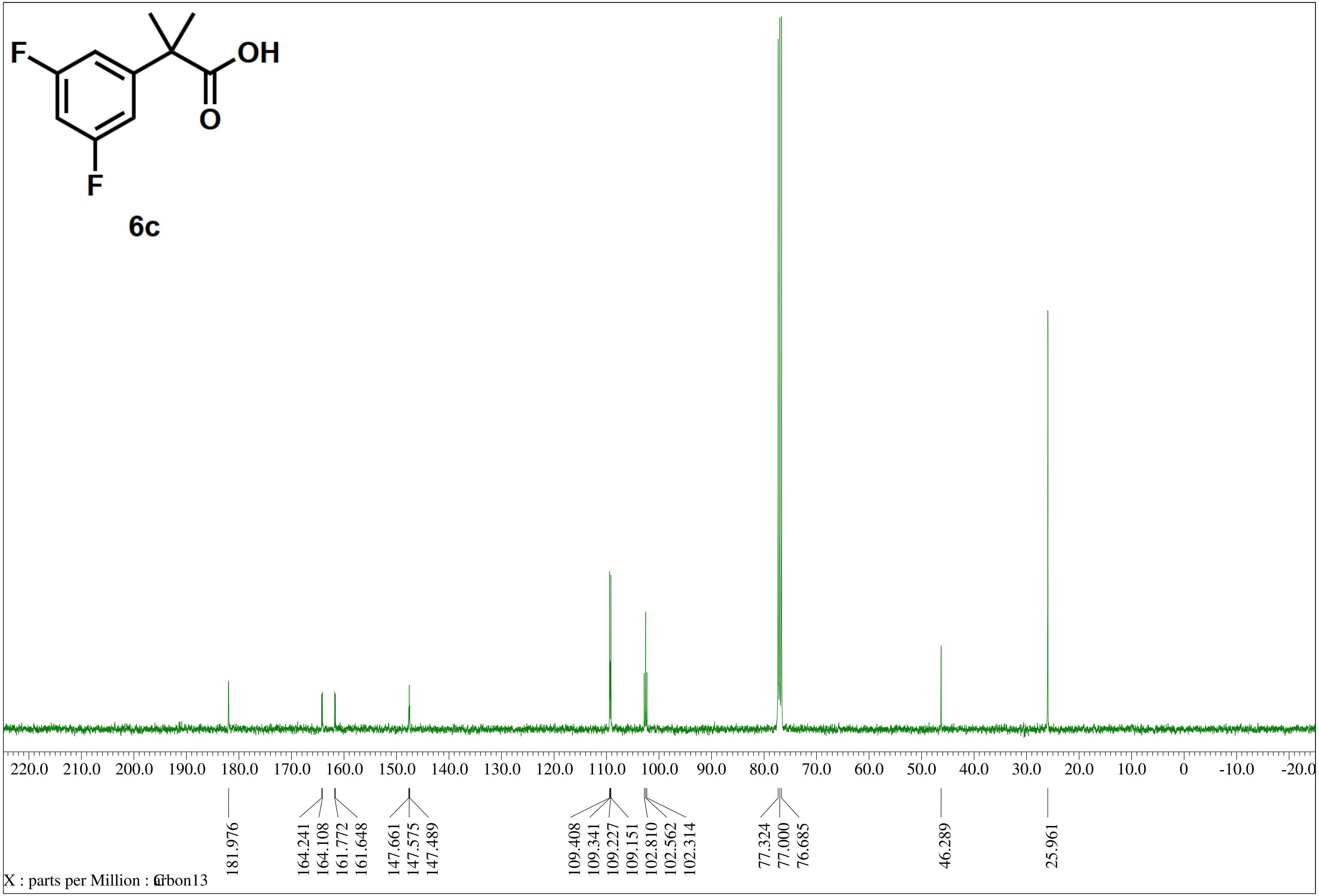

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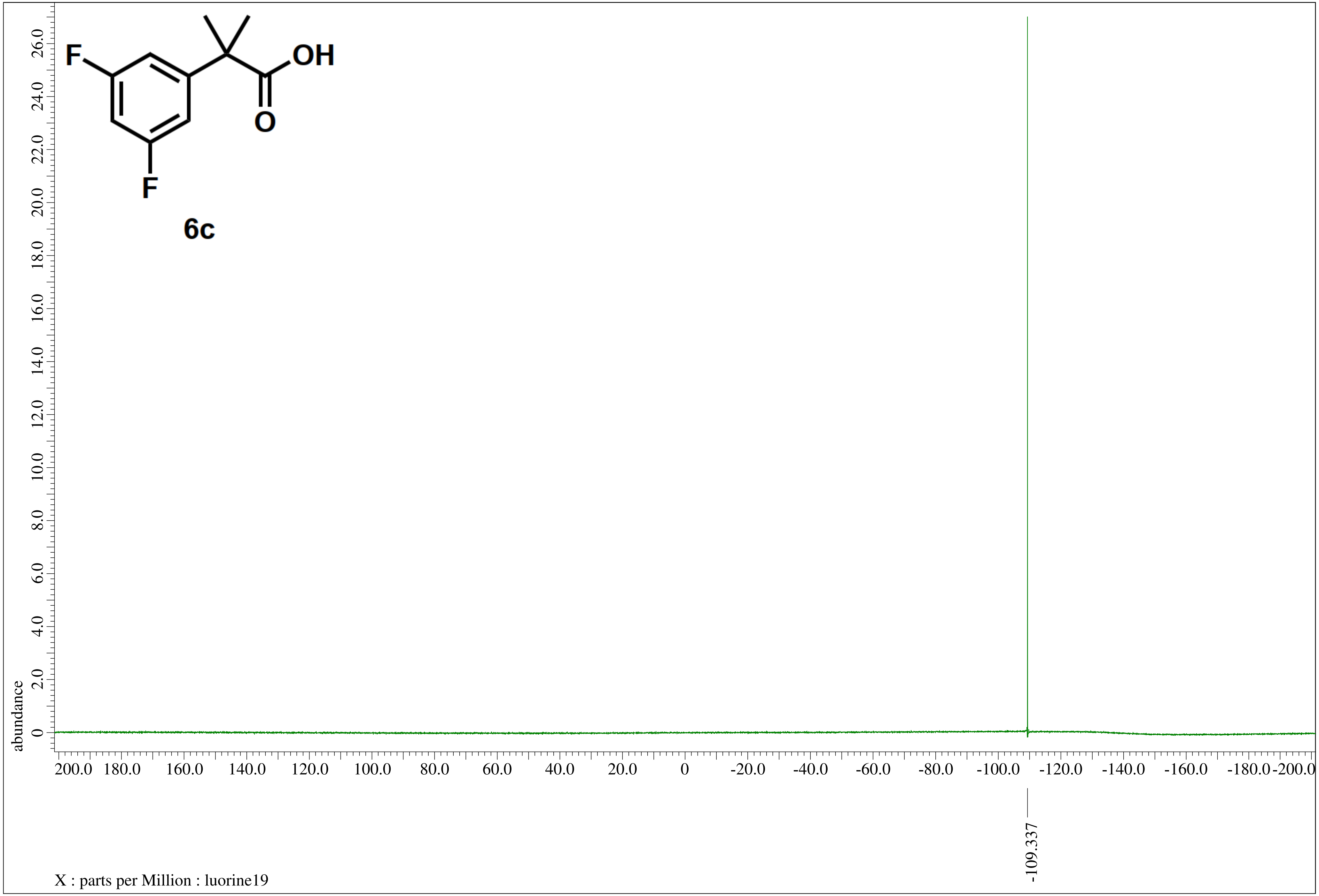
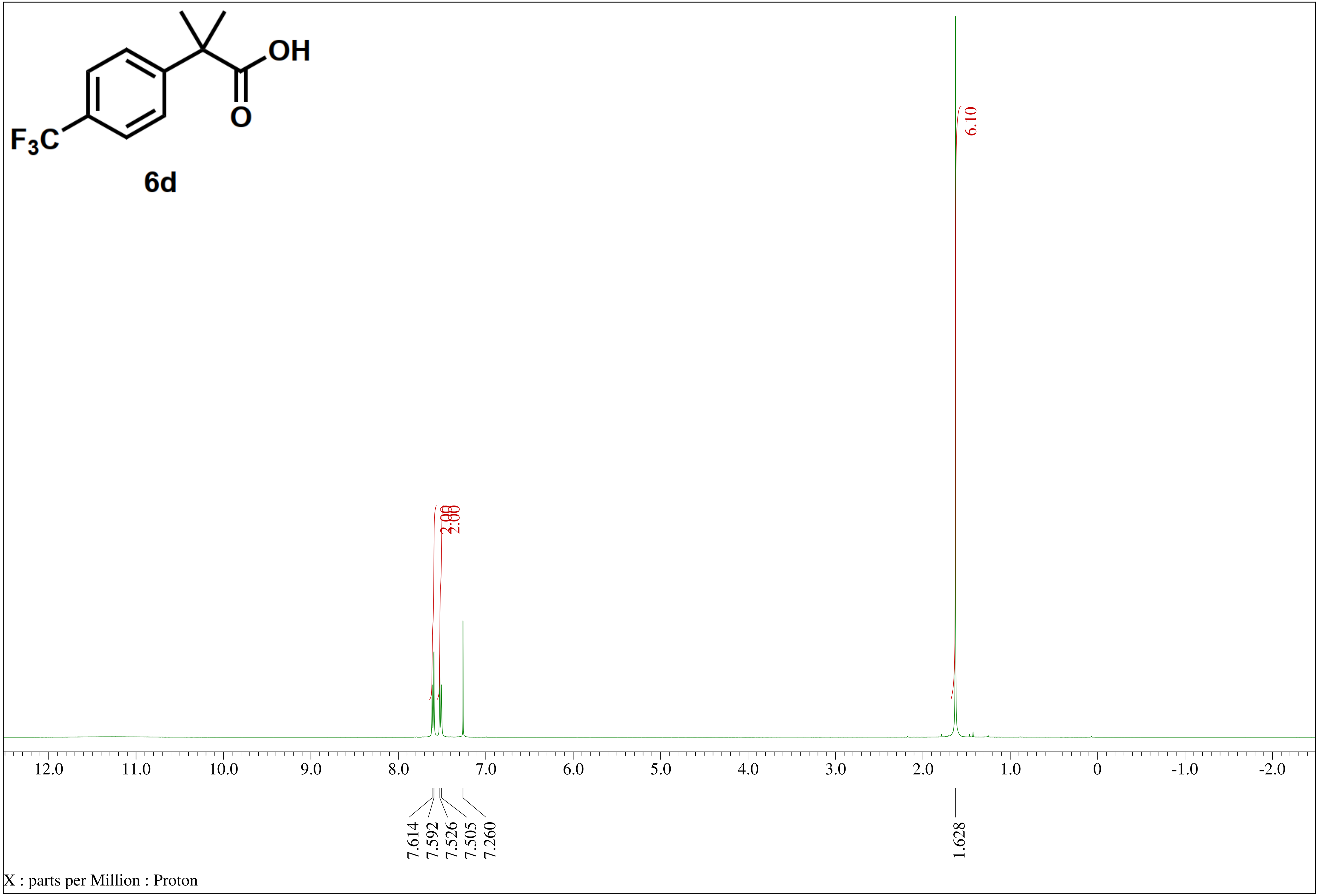
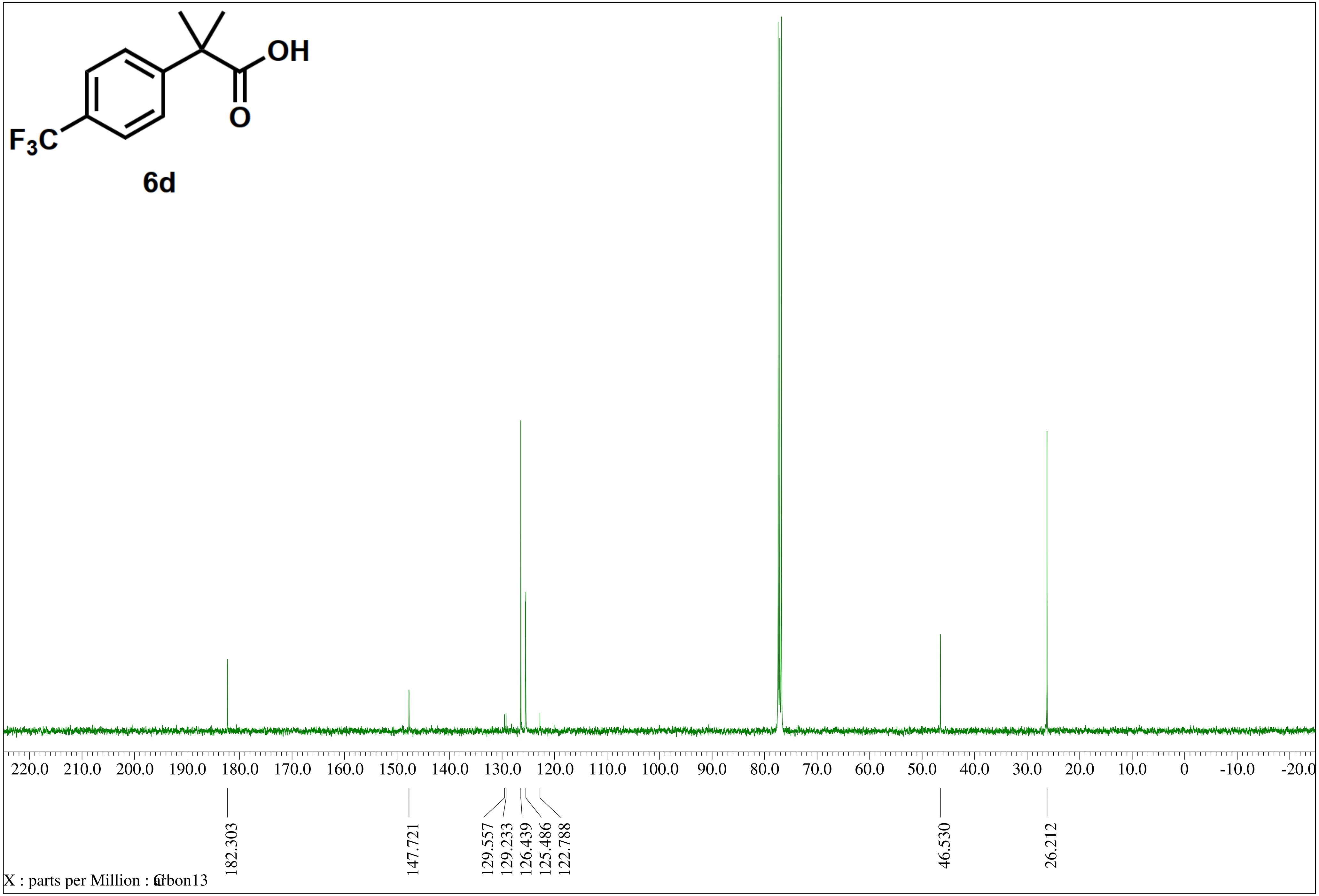


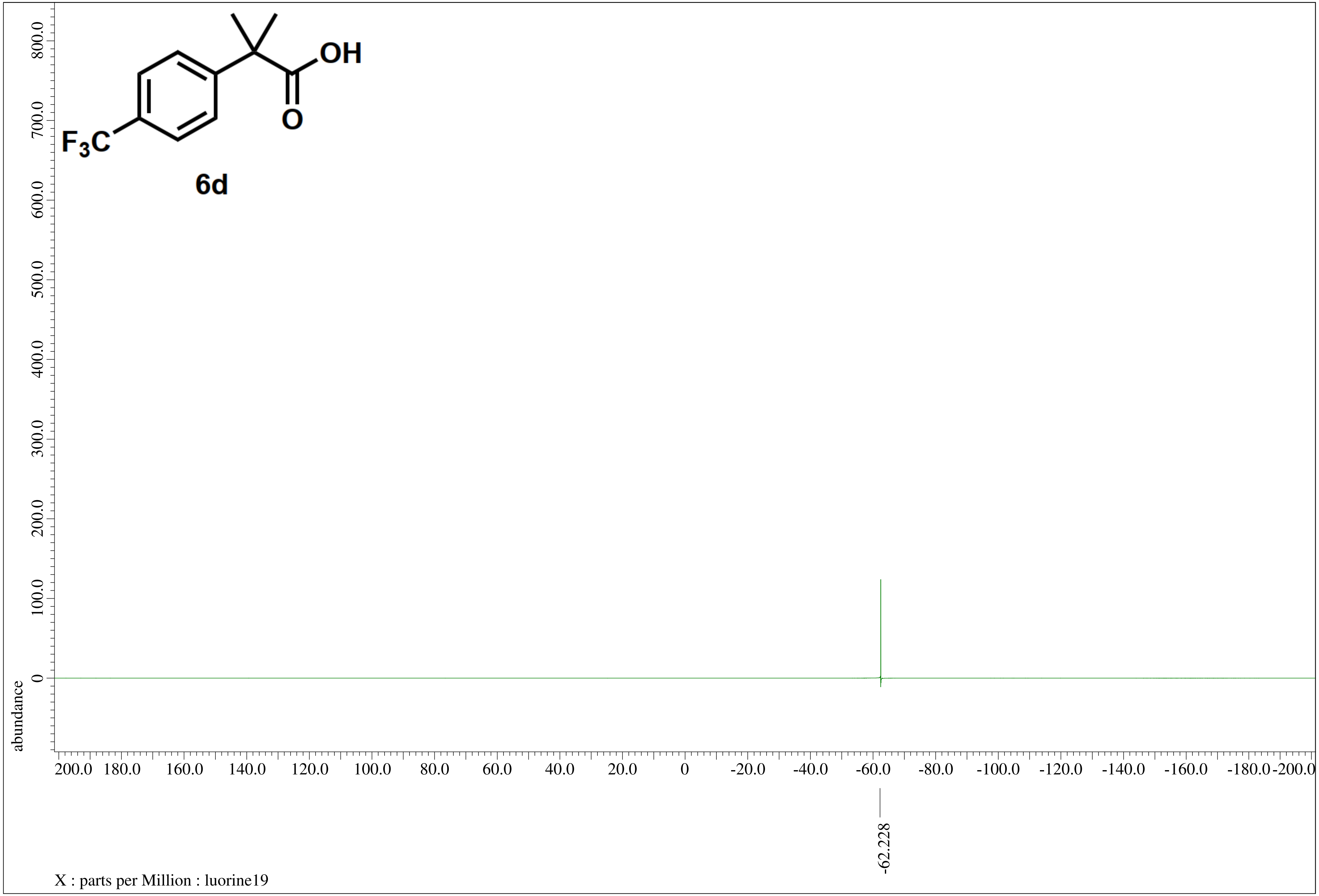
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6d**



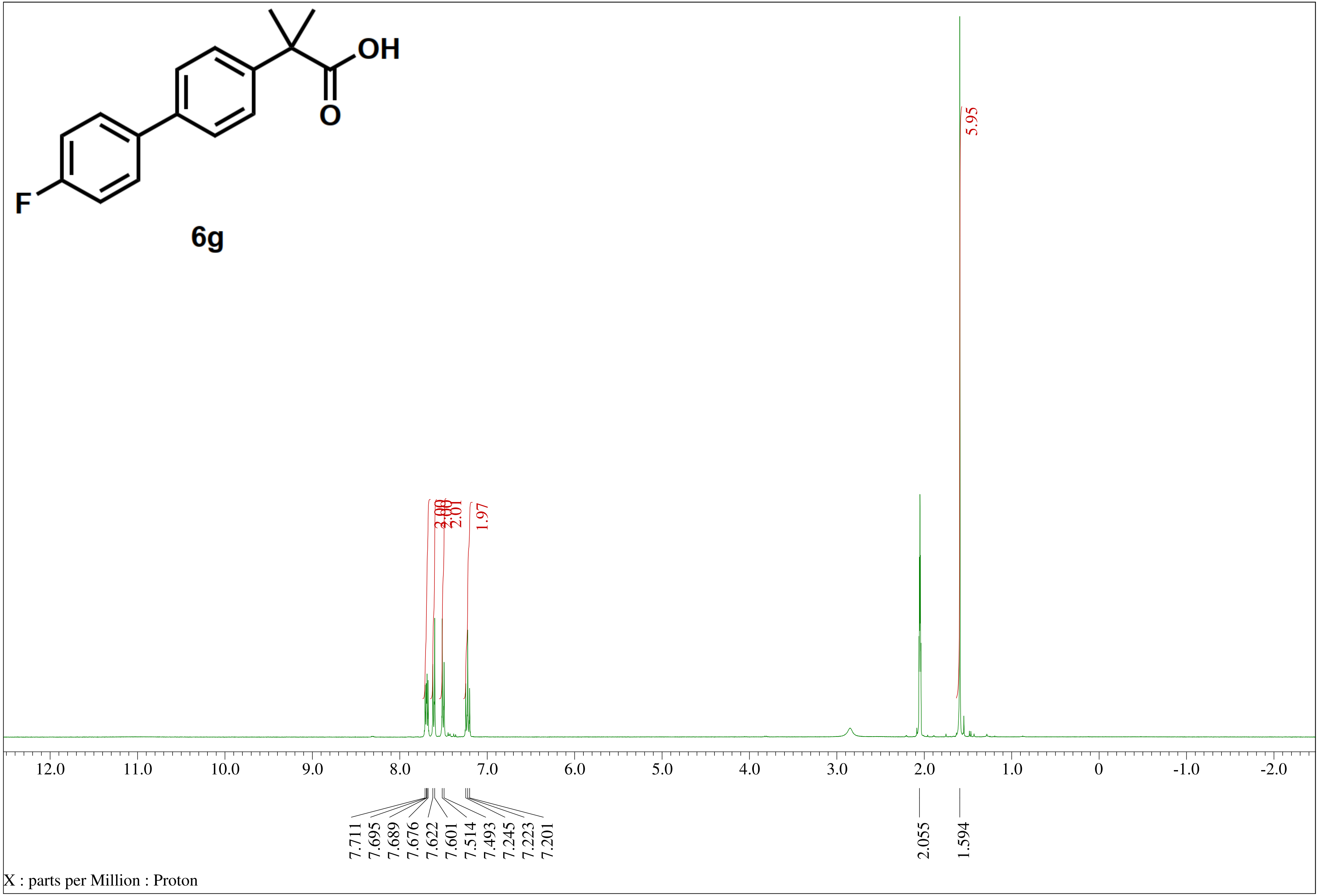
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **6d**



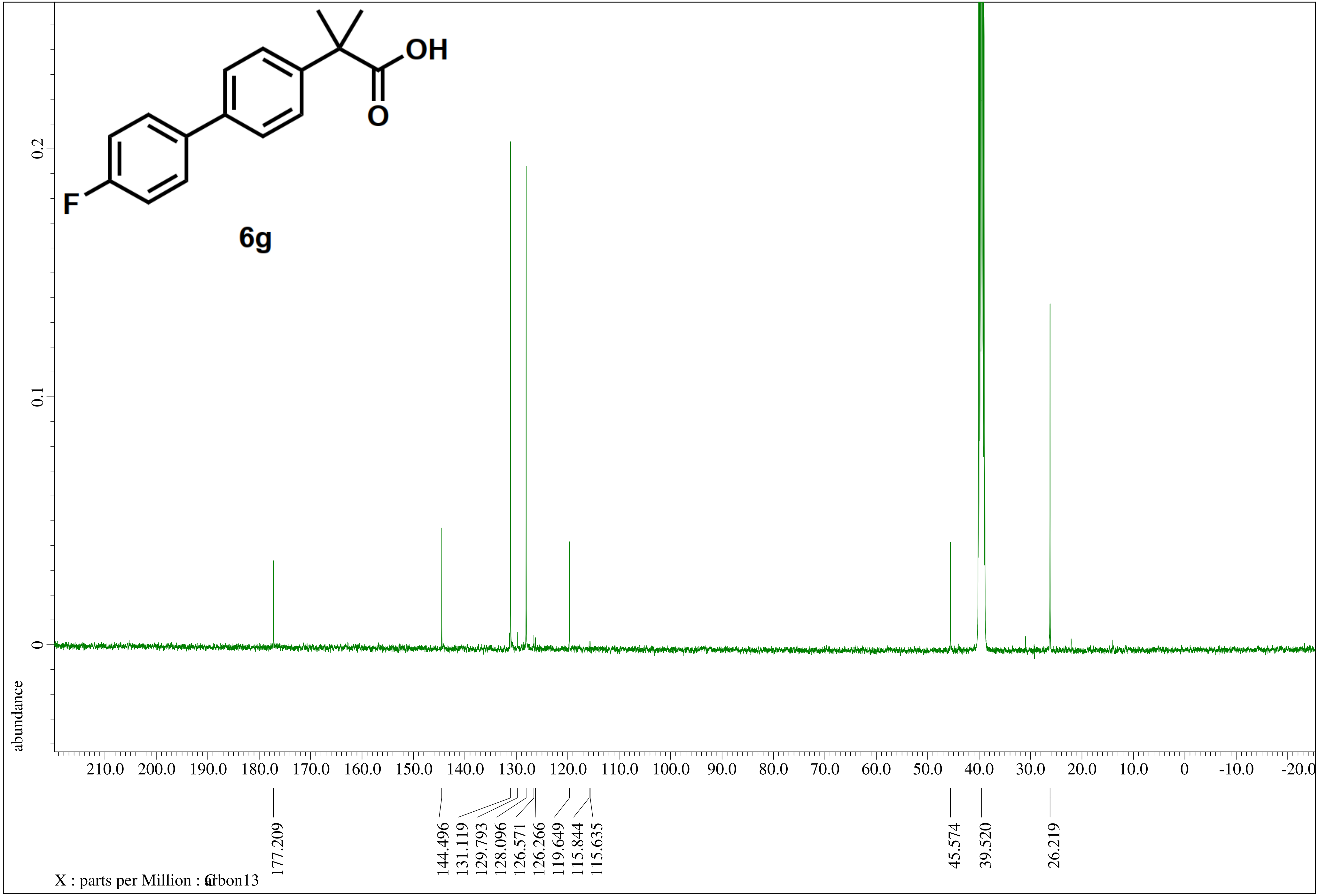
^{19}F NMR spectrum (375 MHz, CDCl$_3$) of **6c**



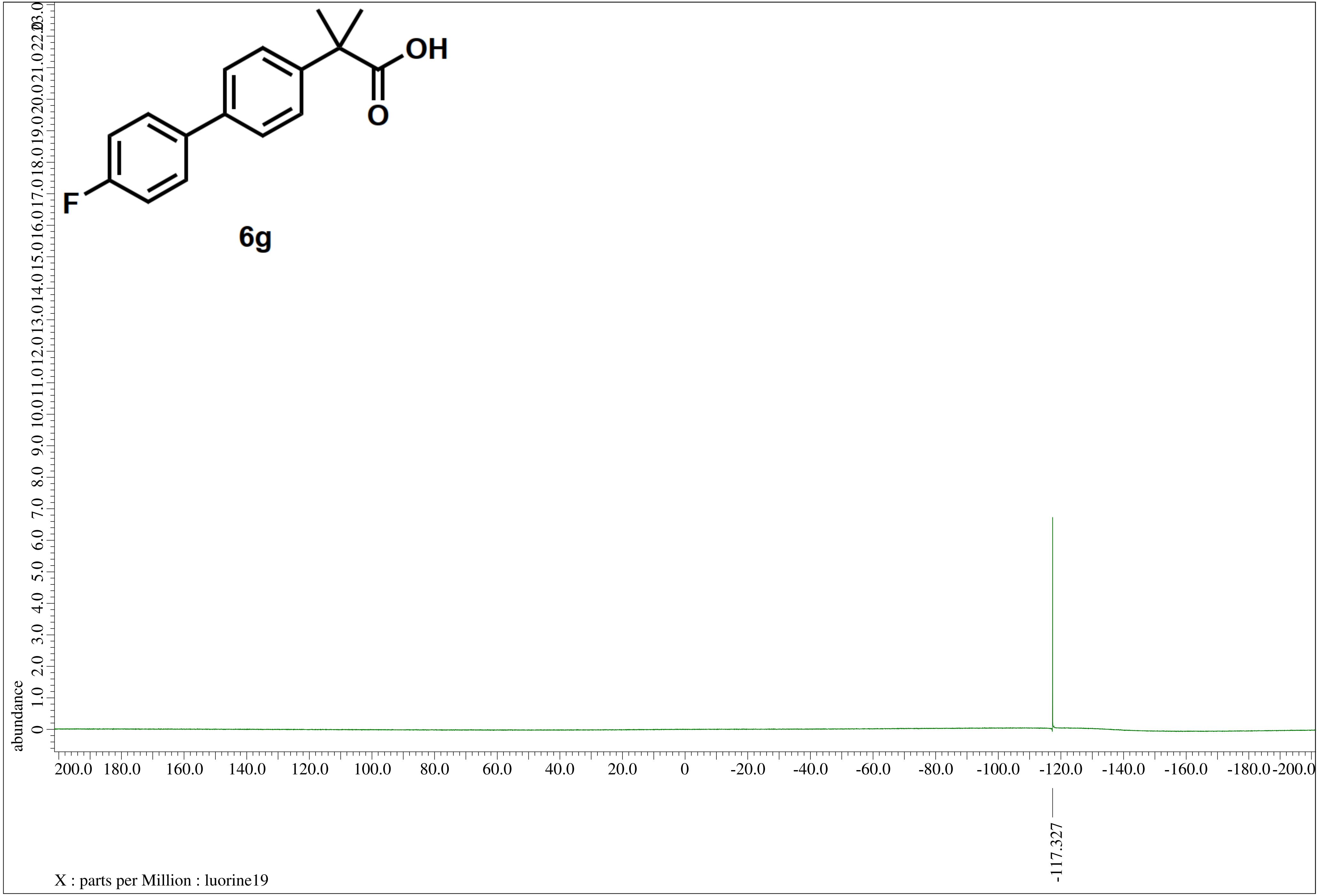
^{1}H NMR spectrum (400 MHz, $(CD_3)_2$ CO) of **6g**



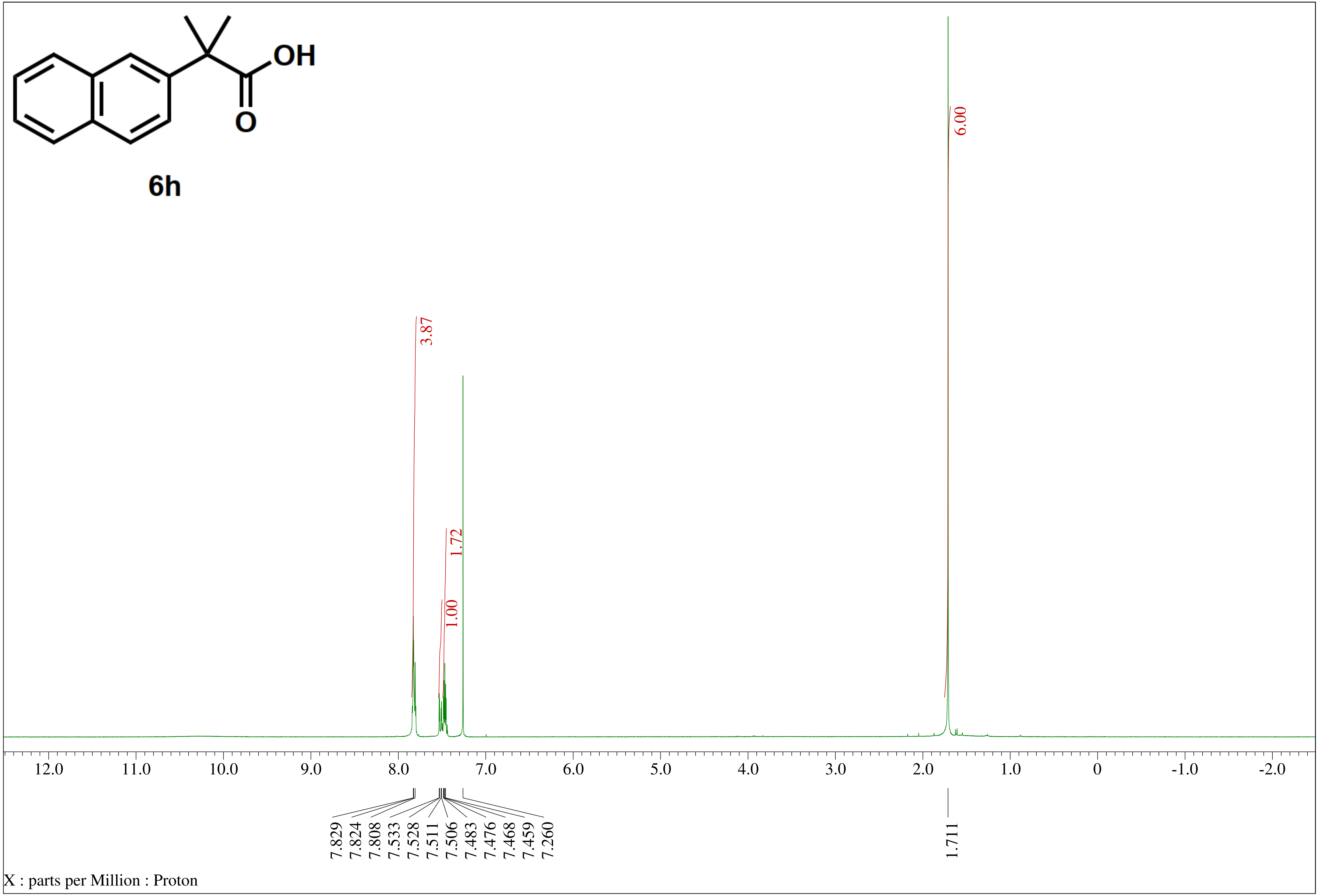
^{13}CNMR spectrum (100 MHz, (CD$_3$)$_2$ SO) of **6g**



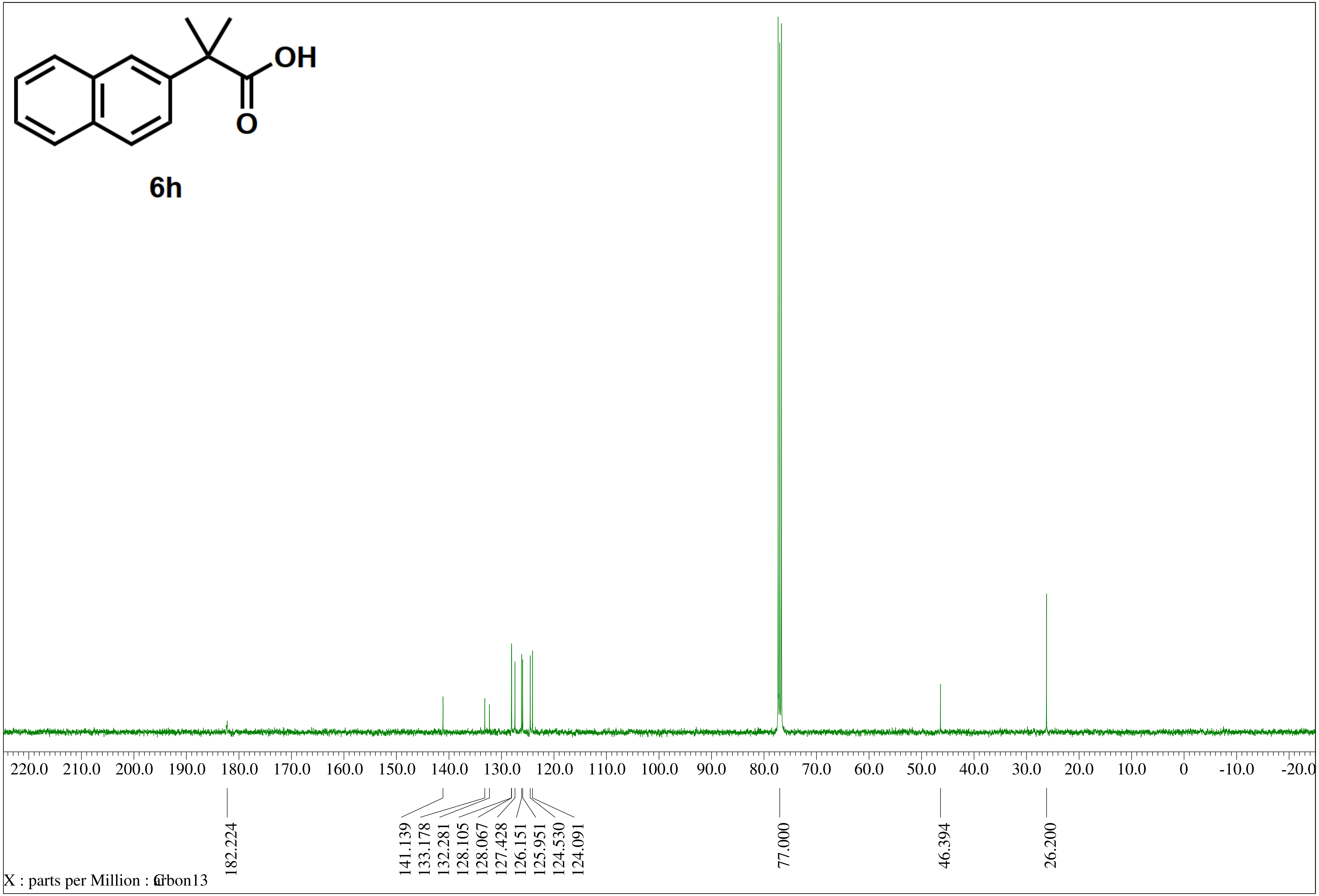
^{19}FNMR spectrum (375 MHz, $(CD_3)_2$ SO) of **6g**



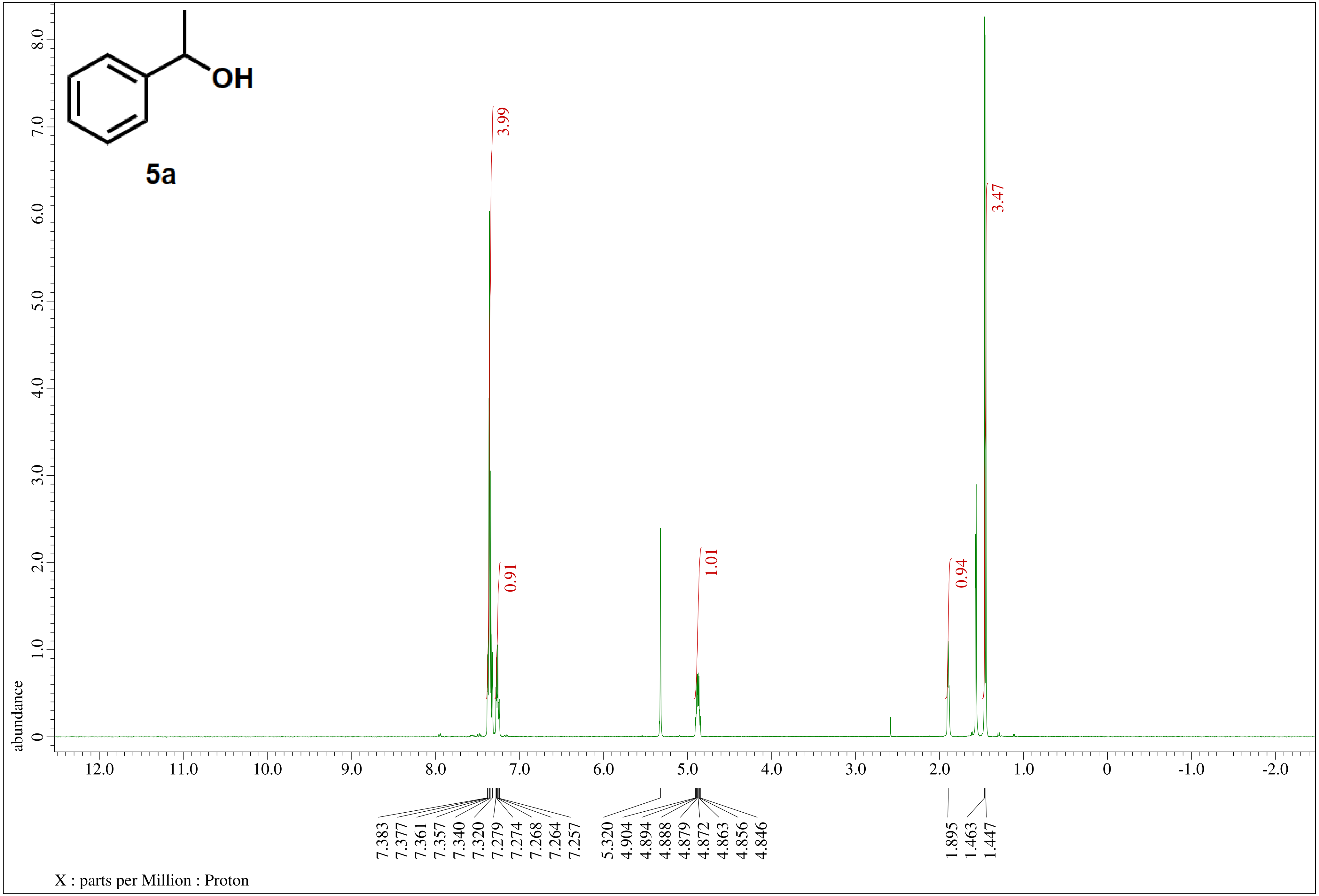
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6h**



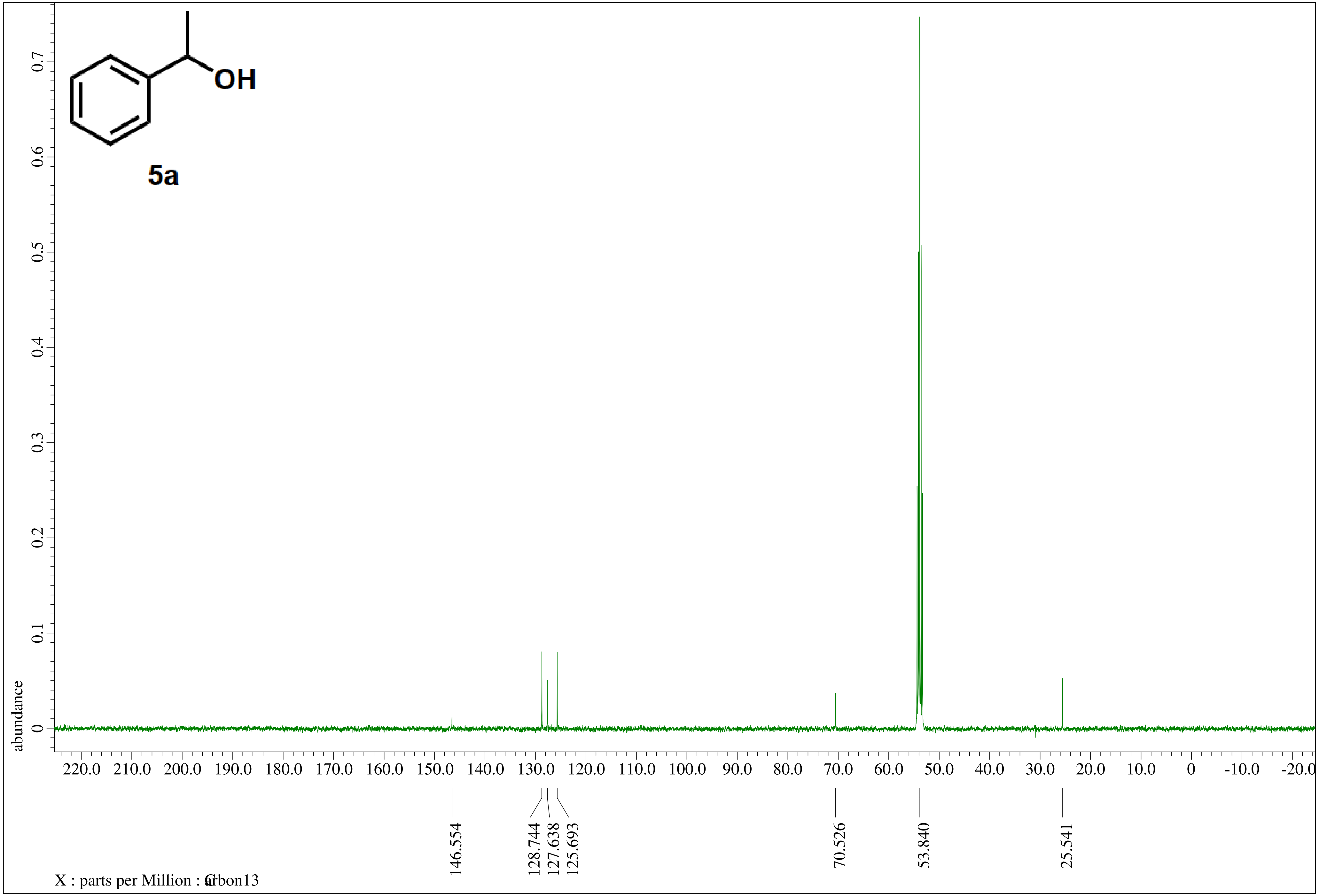
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **6h**



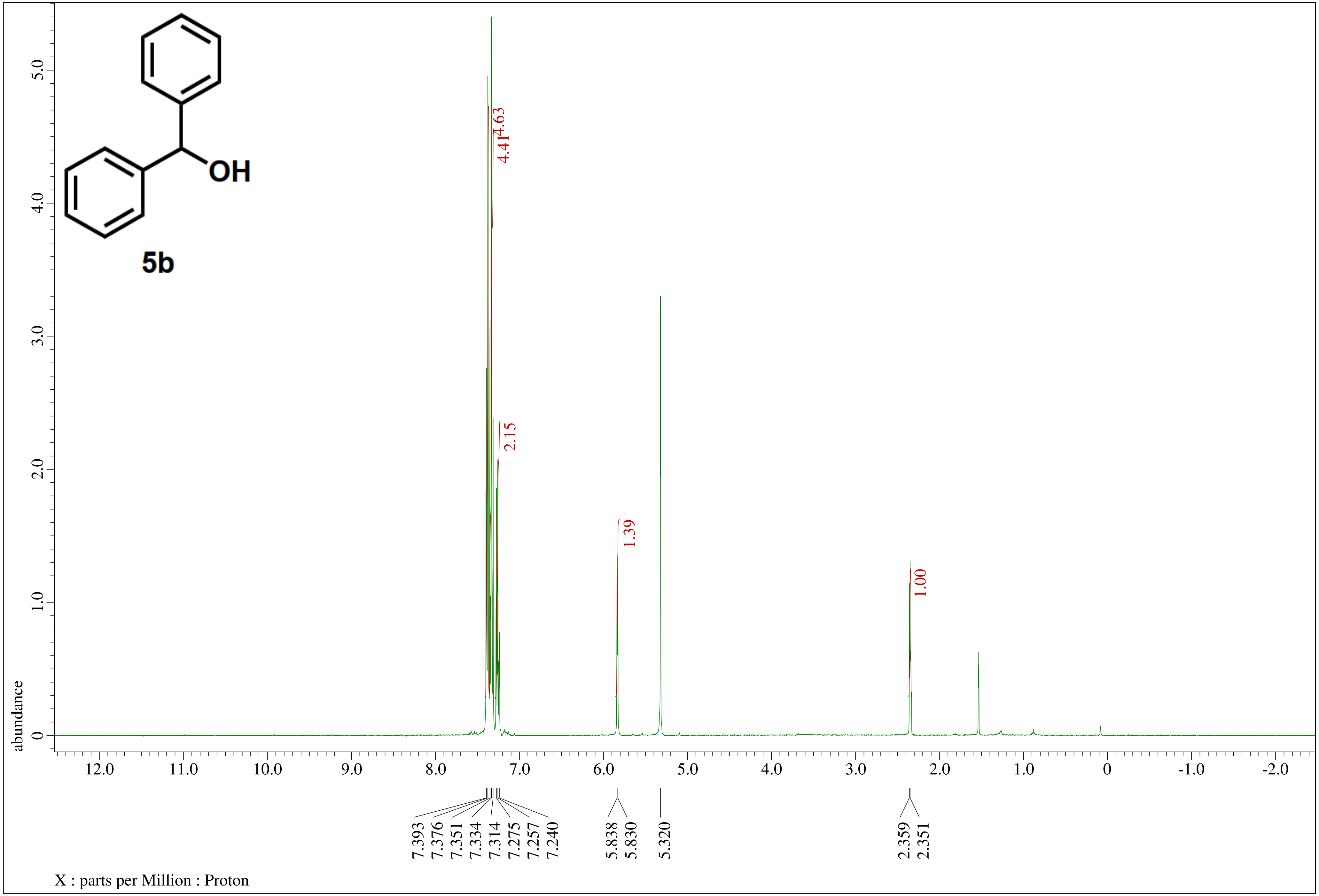
^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **5a**



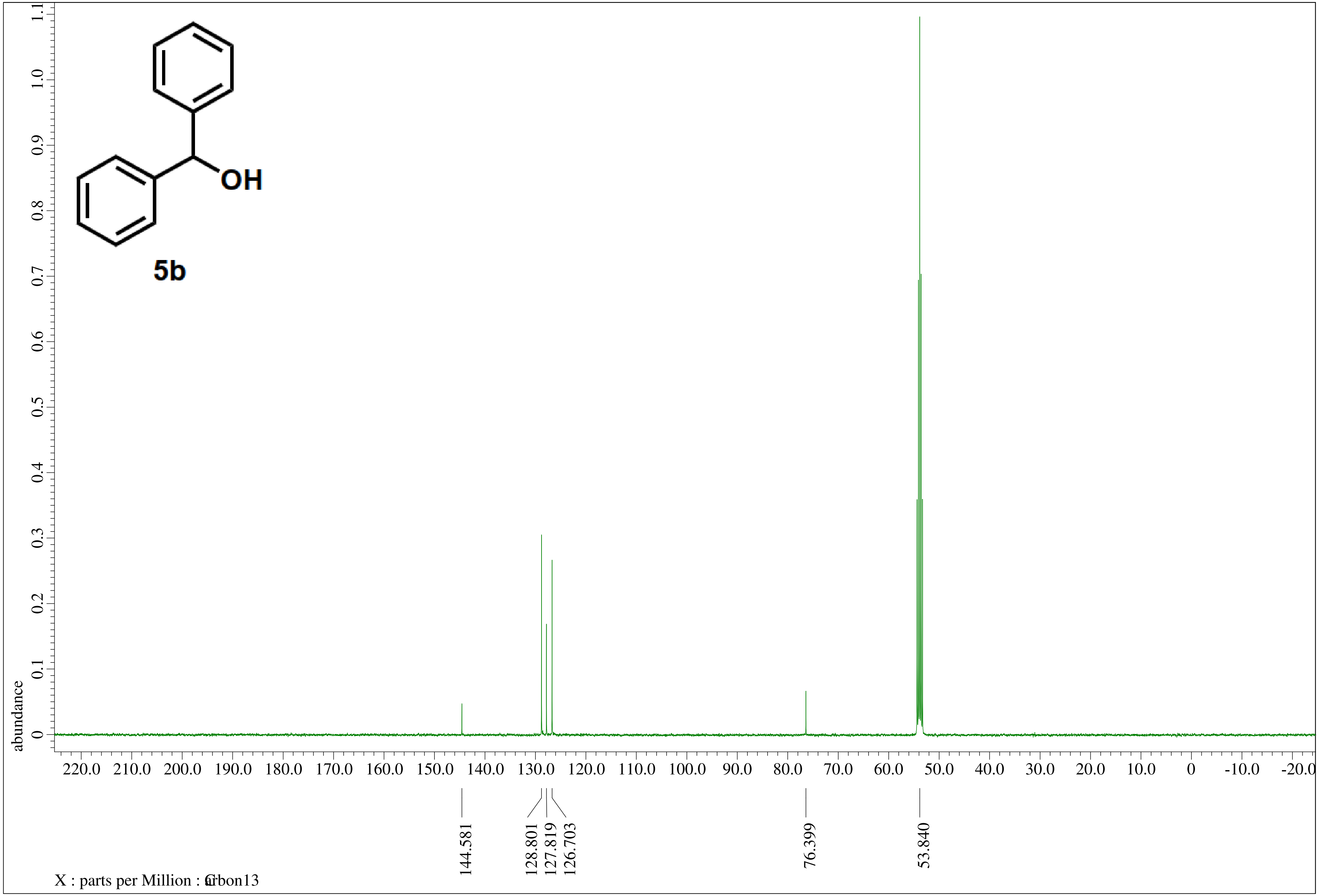
^{13}C NMR spectrum (100 MHz, CD_2Cl_2) of **5a**

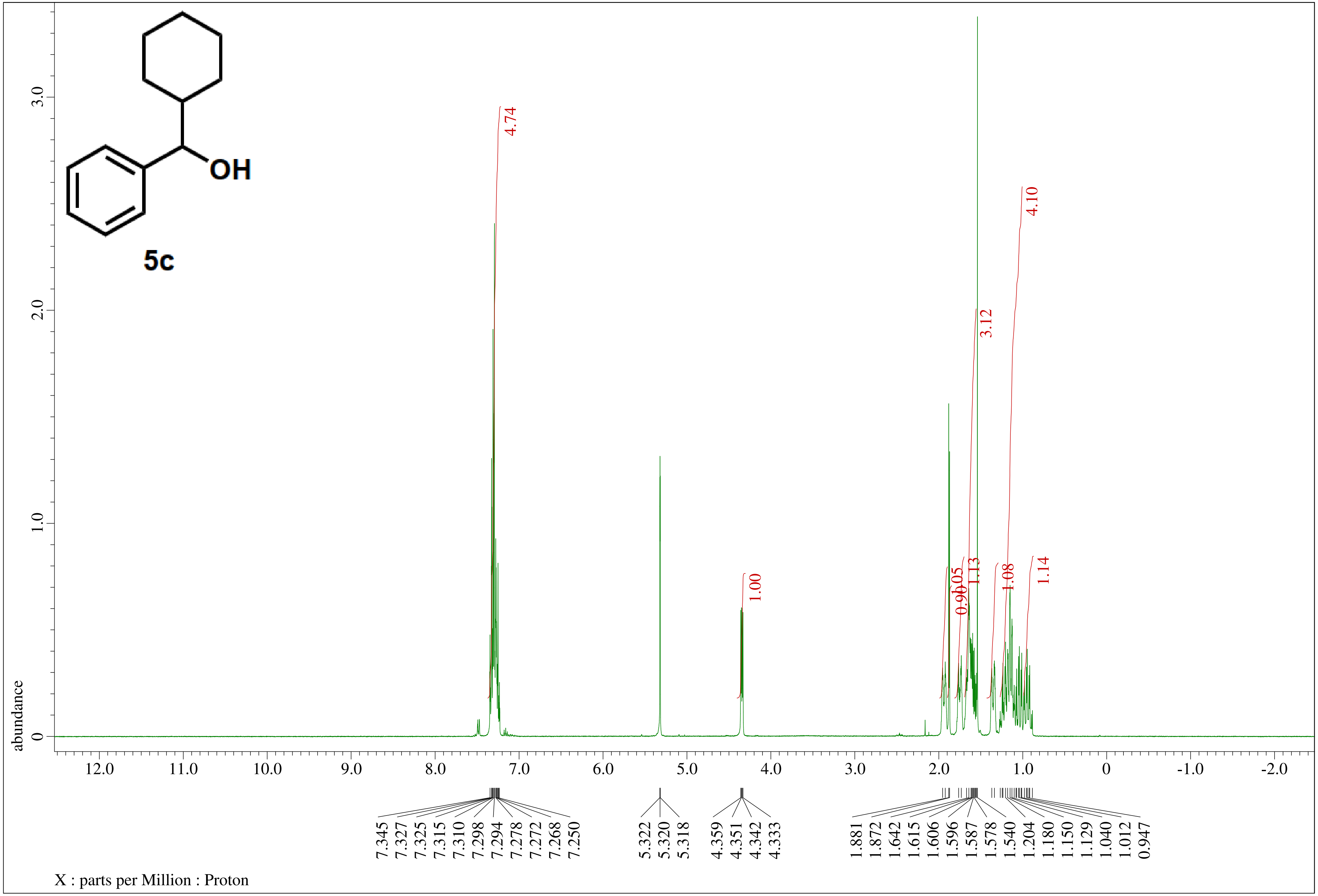


^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **5a**



^{13}C NMR spectrum (100 MHz, CD$_2$Cl$_2$) of **5b**

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5c
abundance
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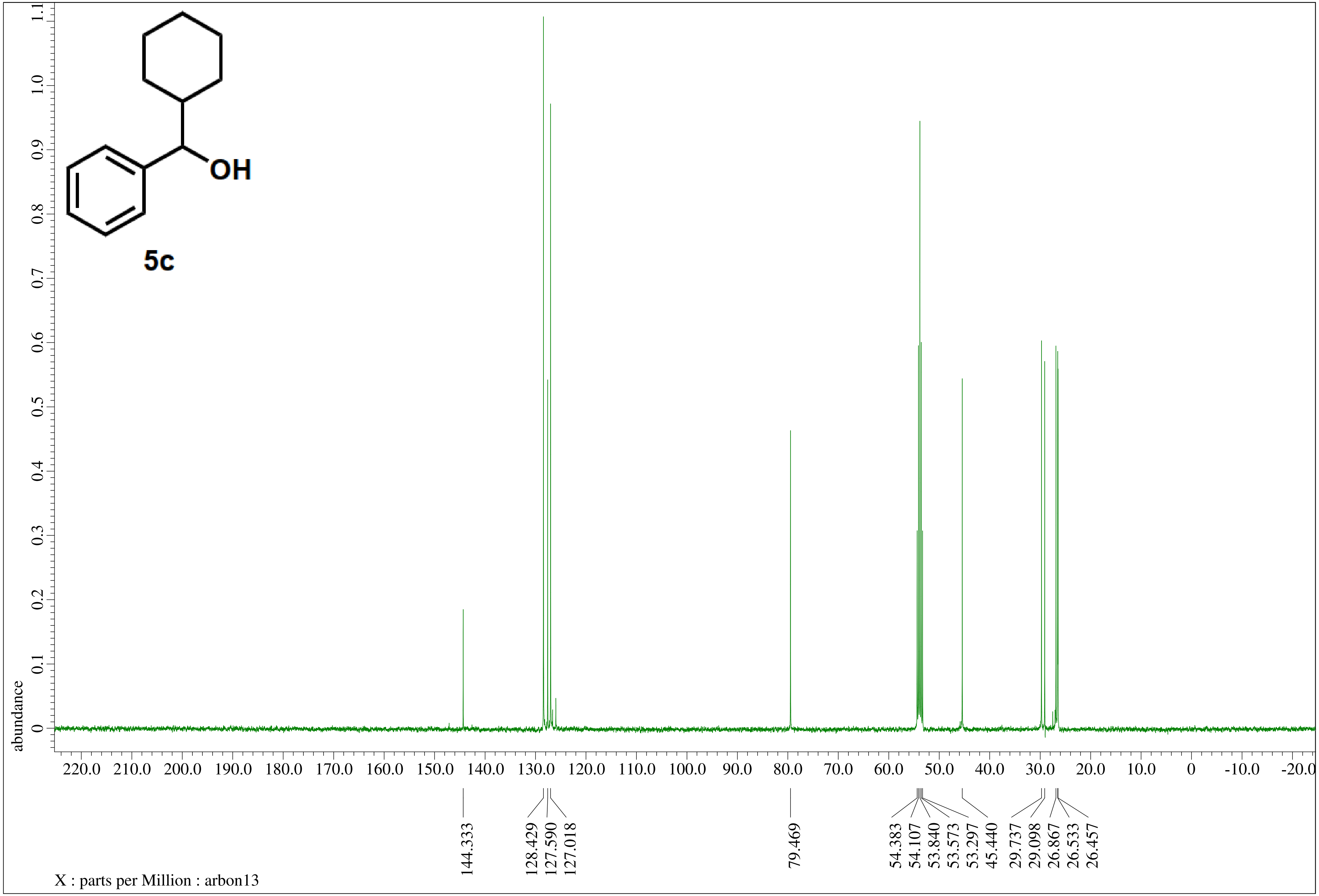
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
4.74
1.00
0.90
1.05
1.13
3.12
1.08
4.10
1.14
7.345
7.327
7.325
7.315
7.310
7.298
7.294
7.278
7.272
7.268
7.250
5.322
5.320
5.318
4.359
4.351
4.342
4.333
1.881
1.872
1.642
1.615
1.606
1.596
1.587
1.578
1.540
1.204
1.180
1.150
1.129
1.040
1.012
0.947
X : parts per Million : Proton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5c
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0.1
0
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210.0
200.0
190.0
180.0
170.0
160.0
150.0
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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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-20.0
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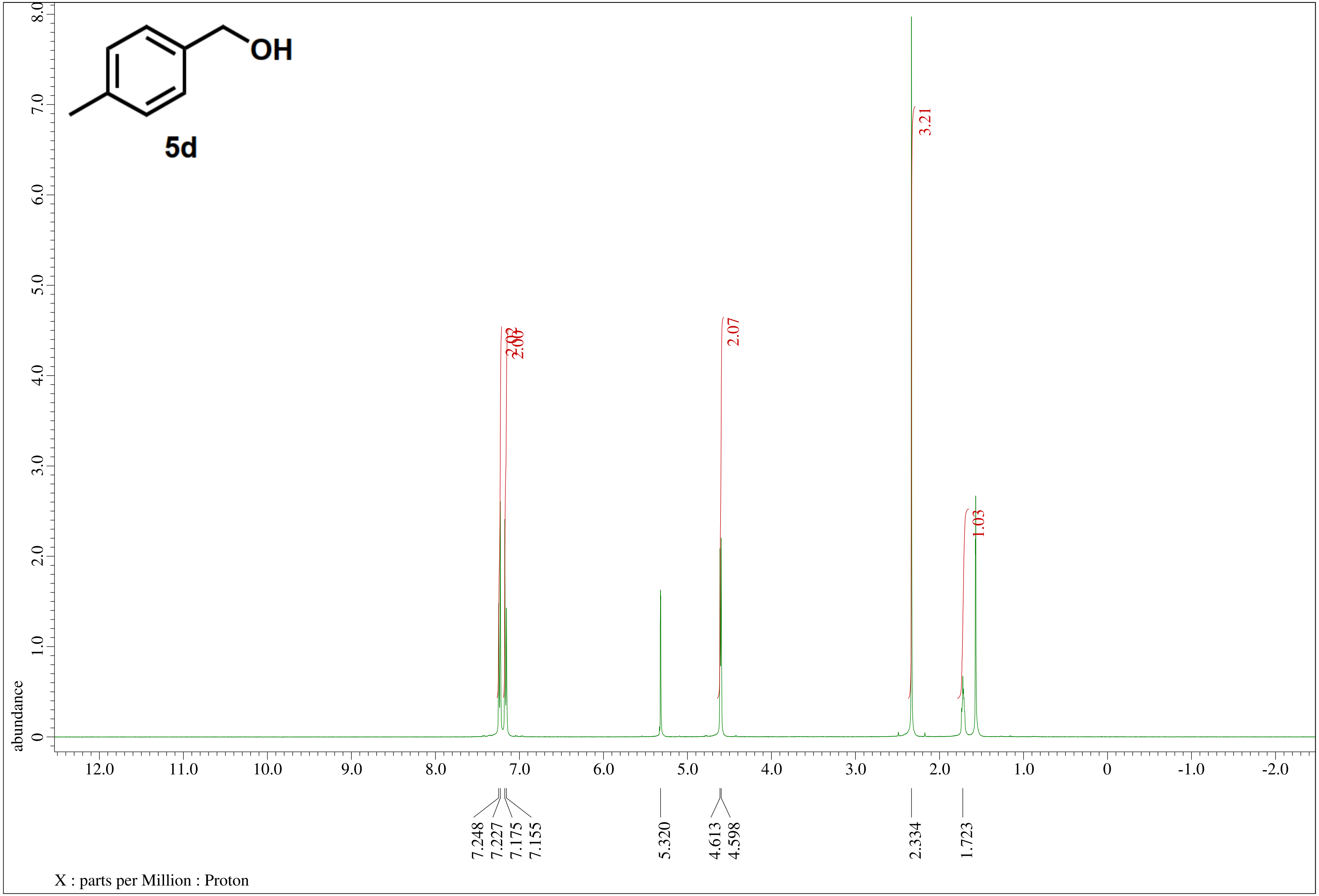
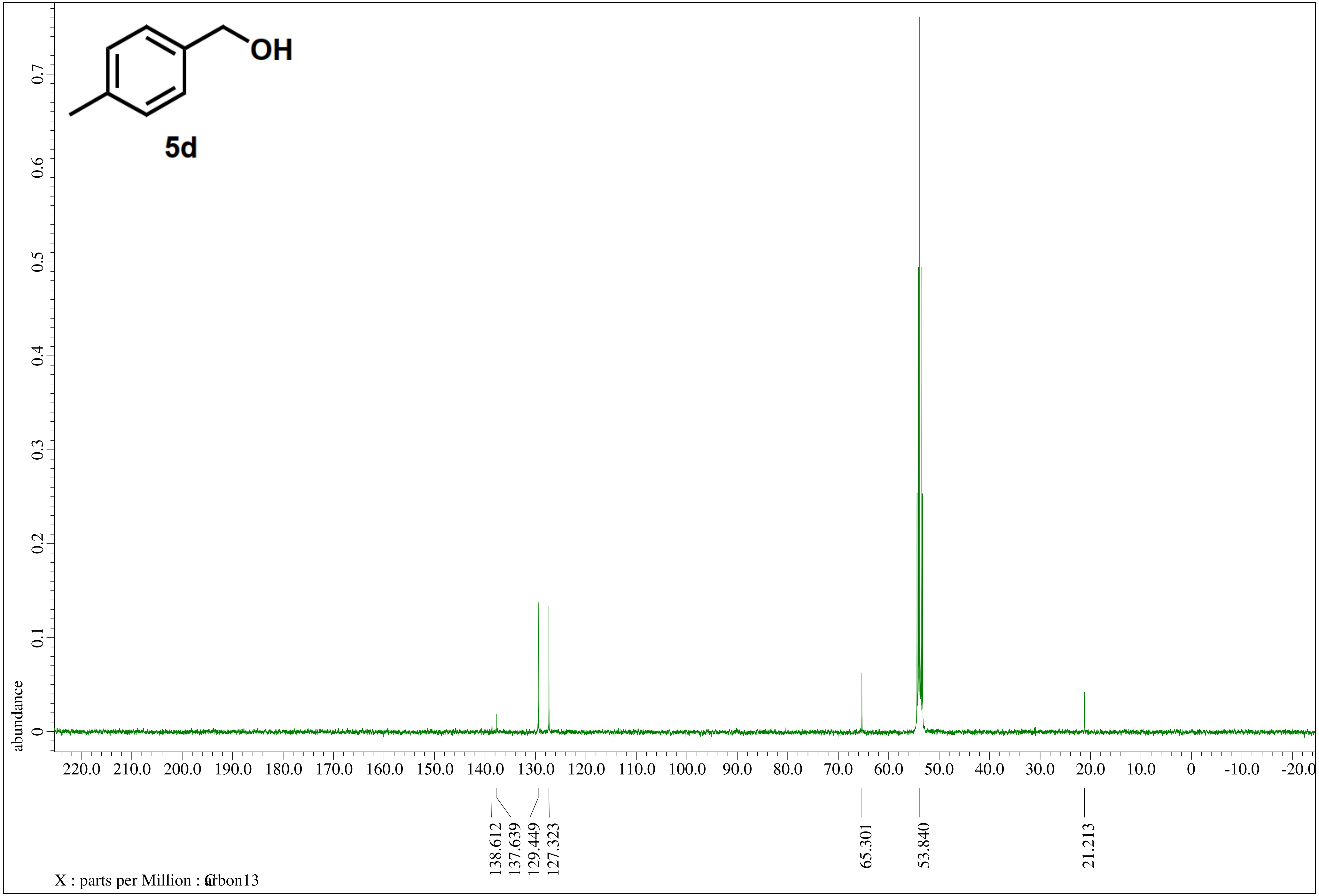
128.429
127.590
127.018
79.469
54.383
54.107
53.840
53.573
53.297
45.440
29.737
29.098
26.867
26.533
26.457
X : parts per Million : arbon13

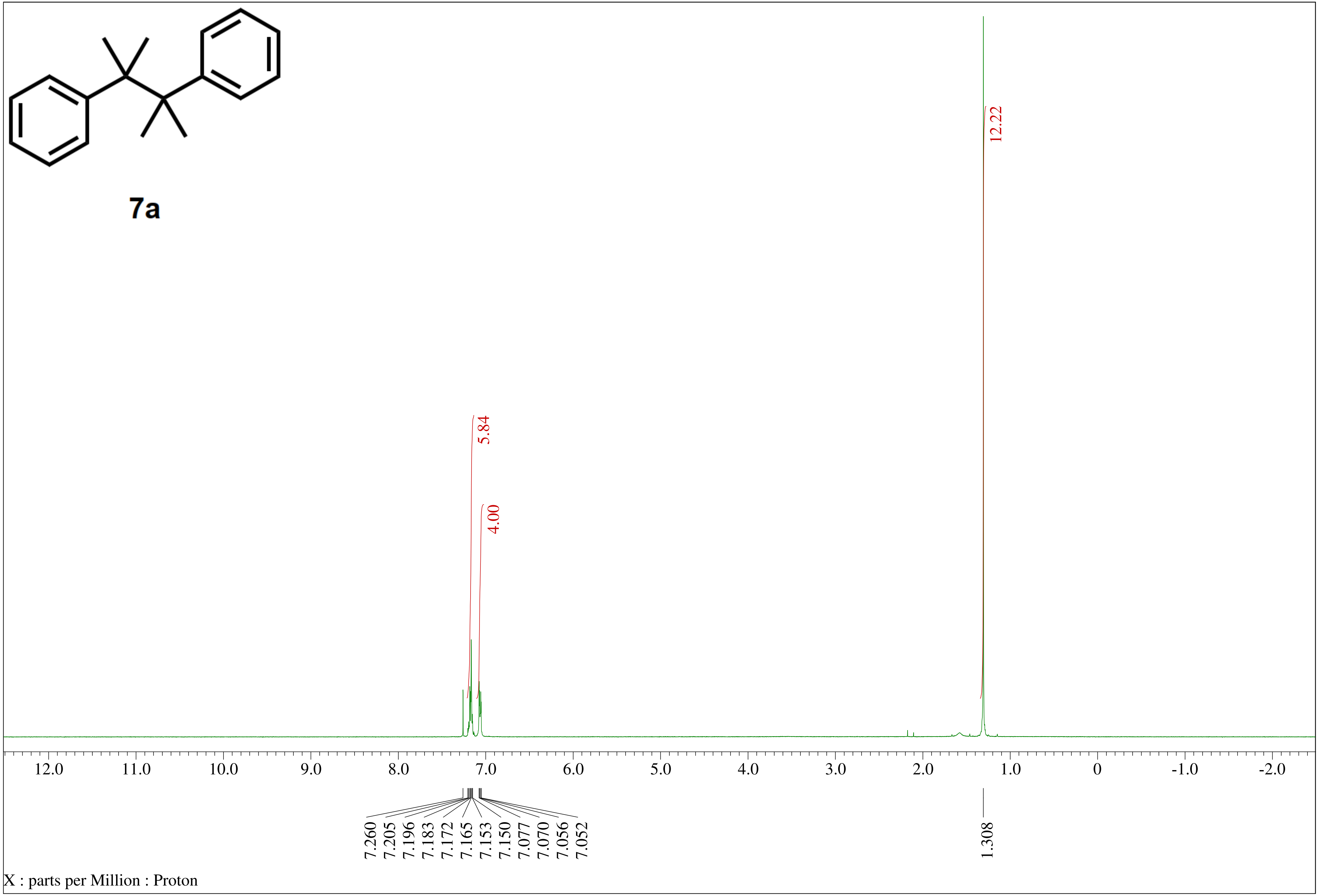
^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **5d**



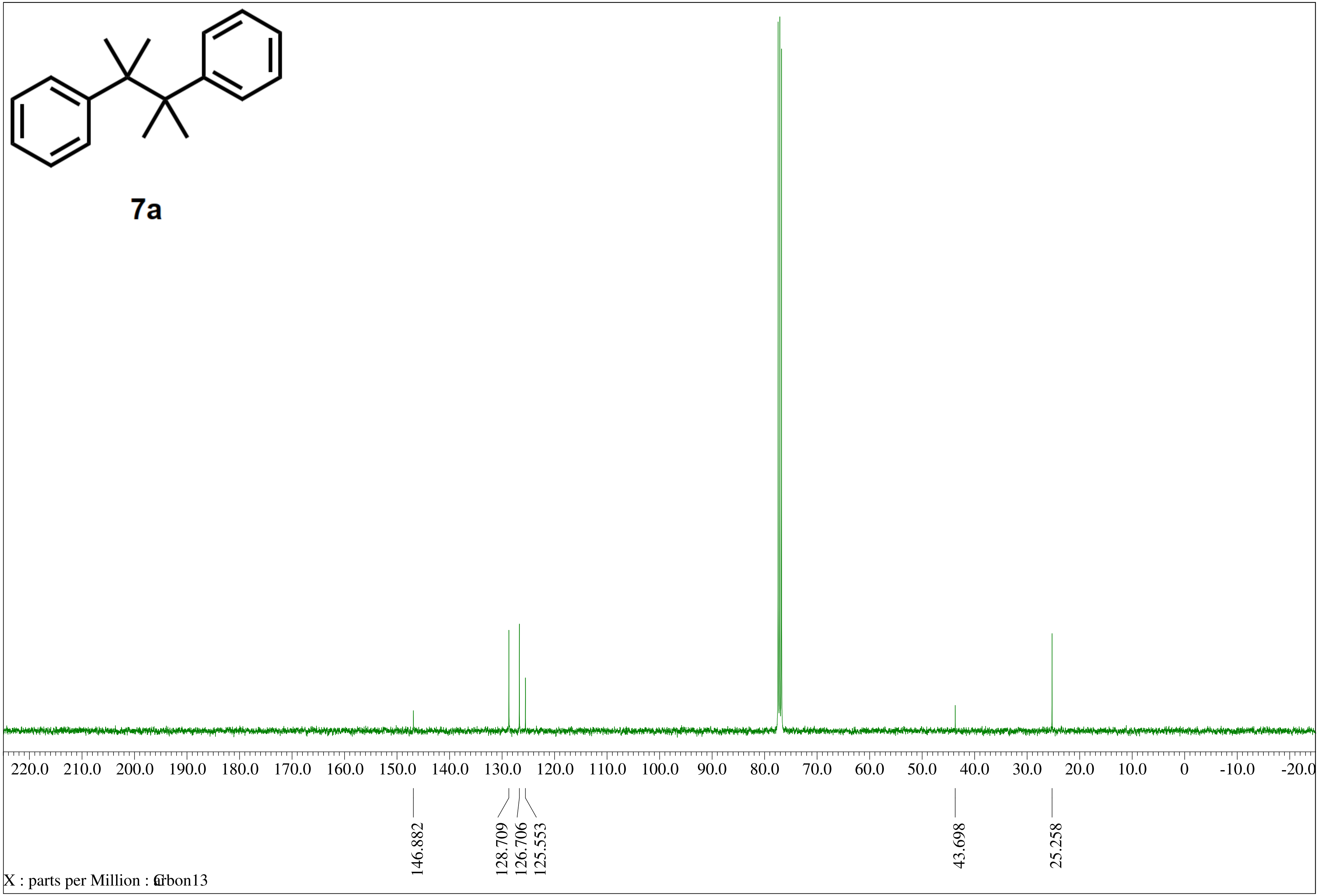
^{13}C NMR spectrum (100 MHz, CD_2Cl_2) of **5d**



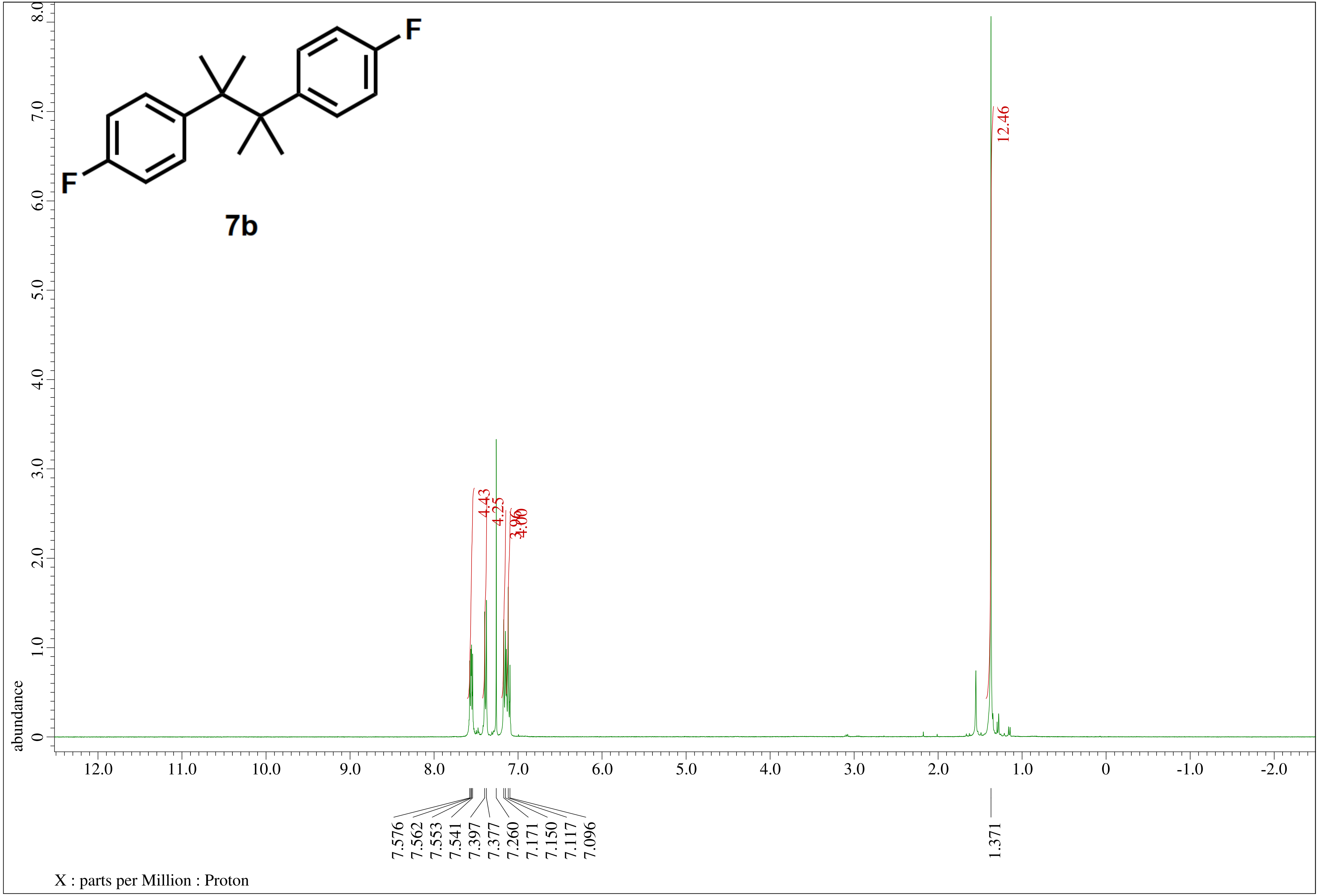
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **7a**



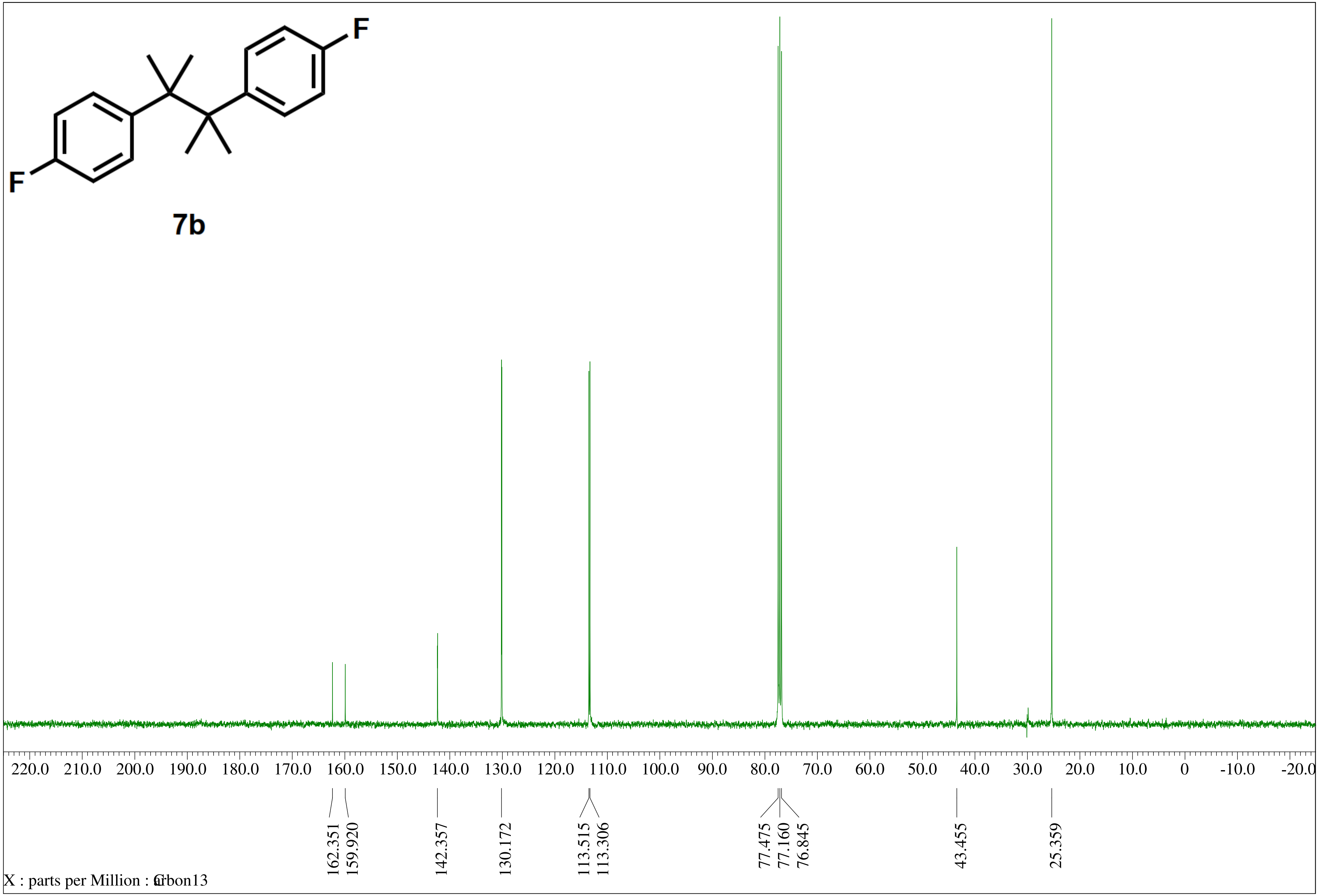
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **7a**



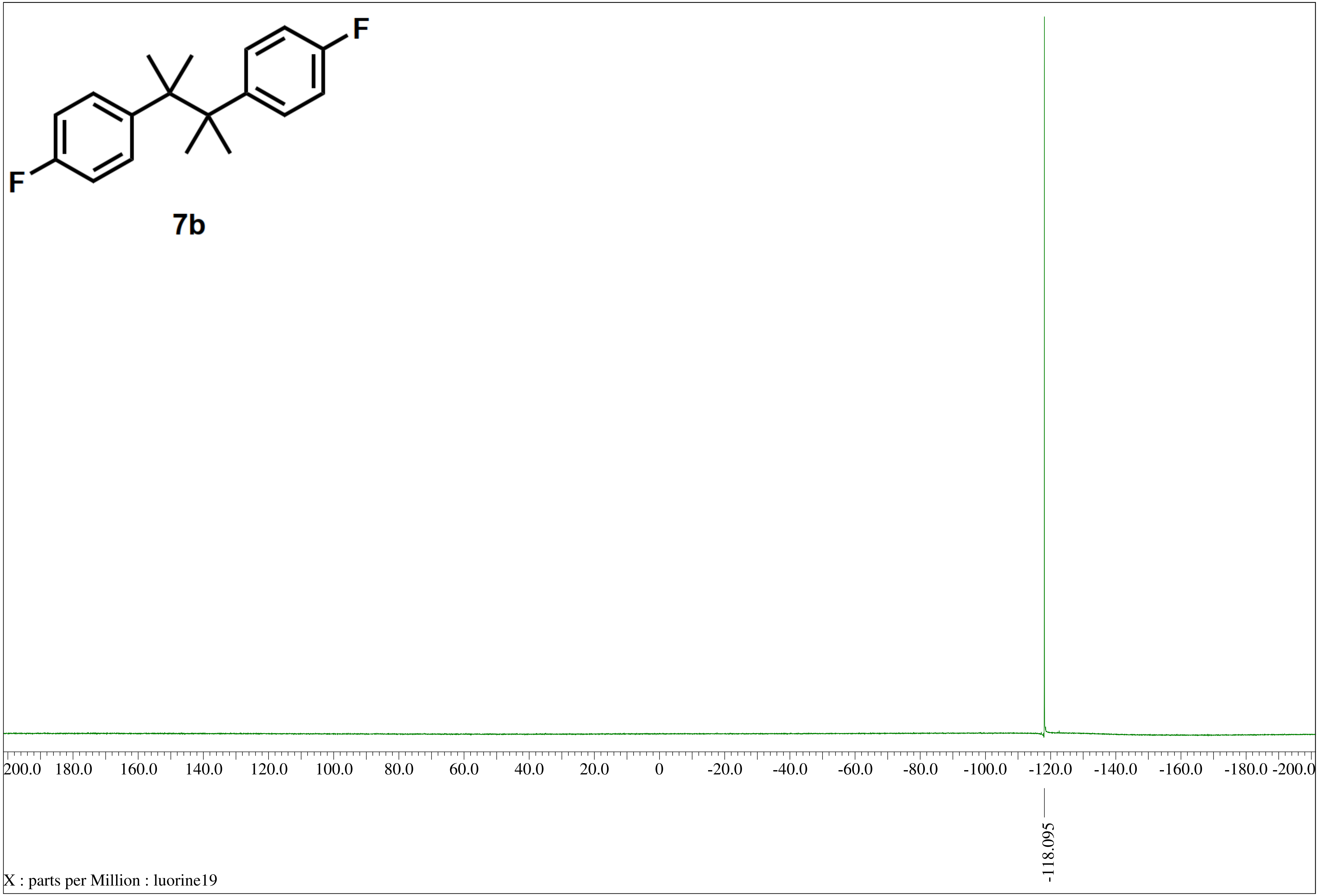
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **7b**



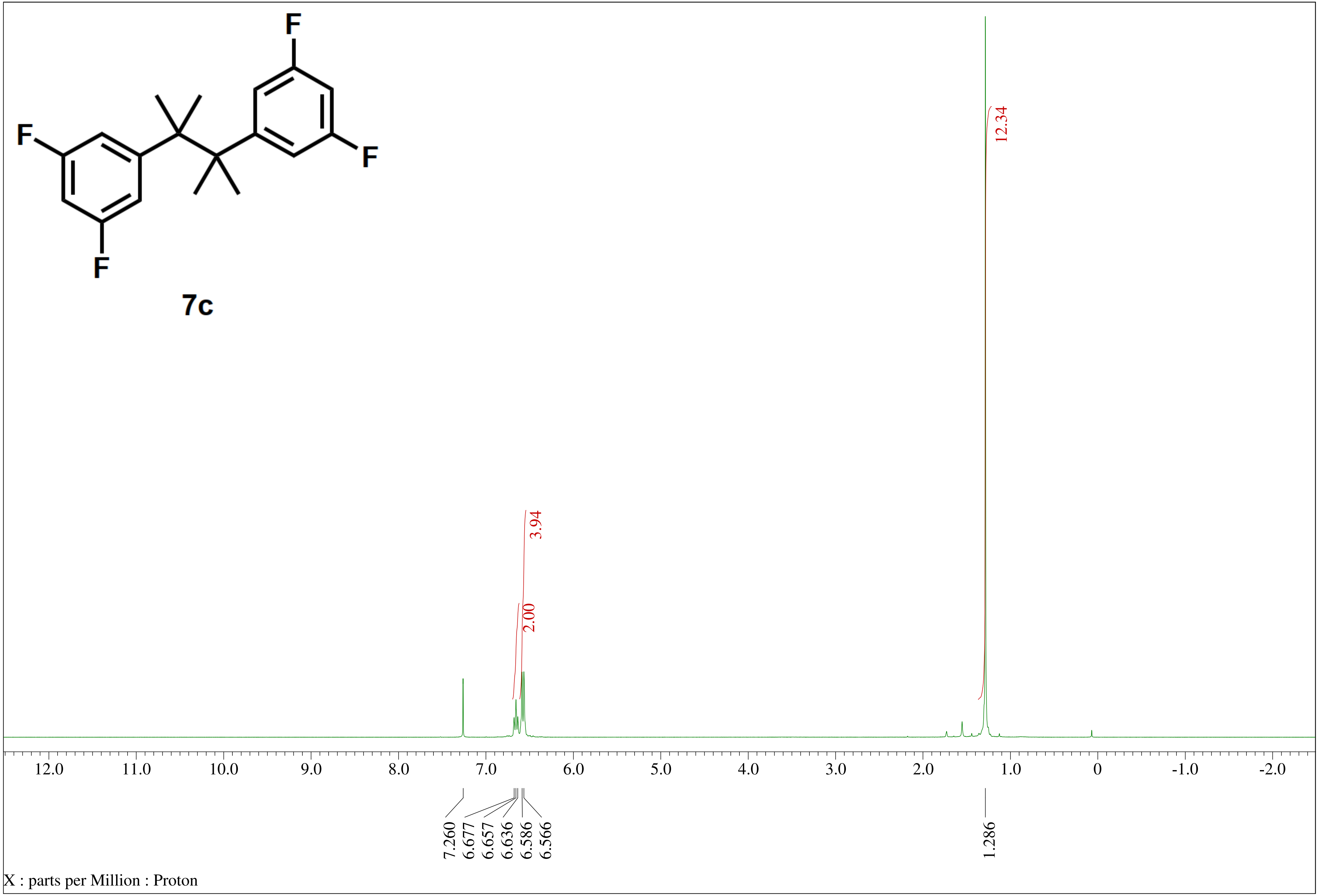
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **7b**



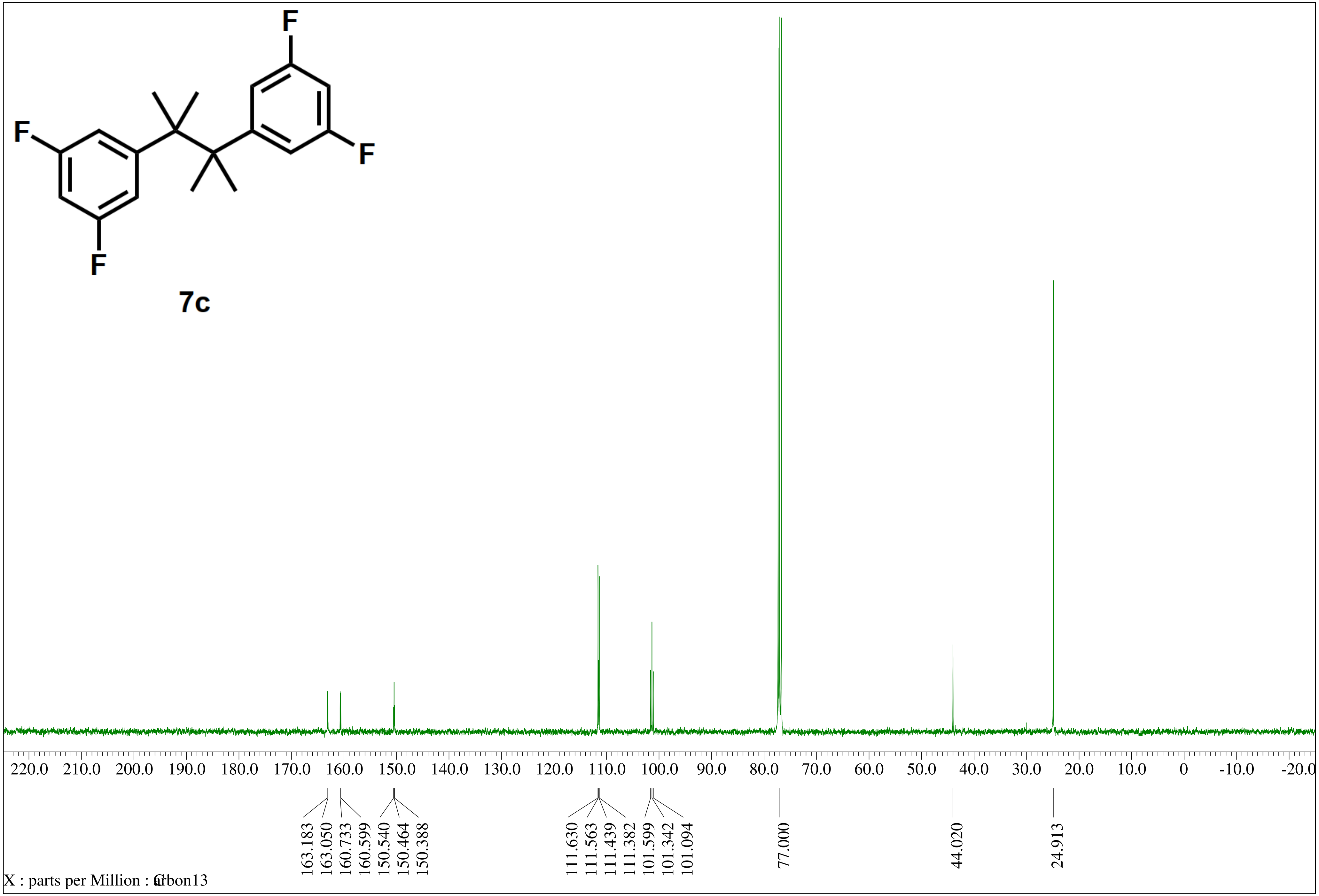
^{19}F NMR spectrum (375 MHz, $CDCl_3$) of **7b**



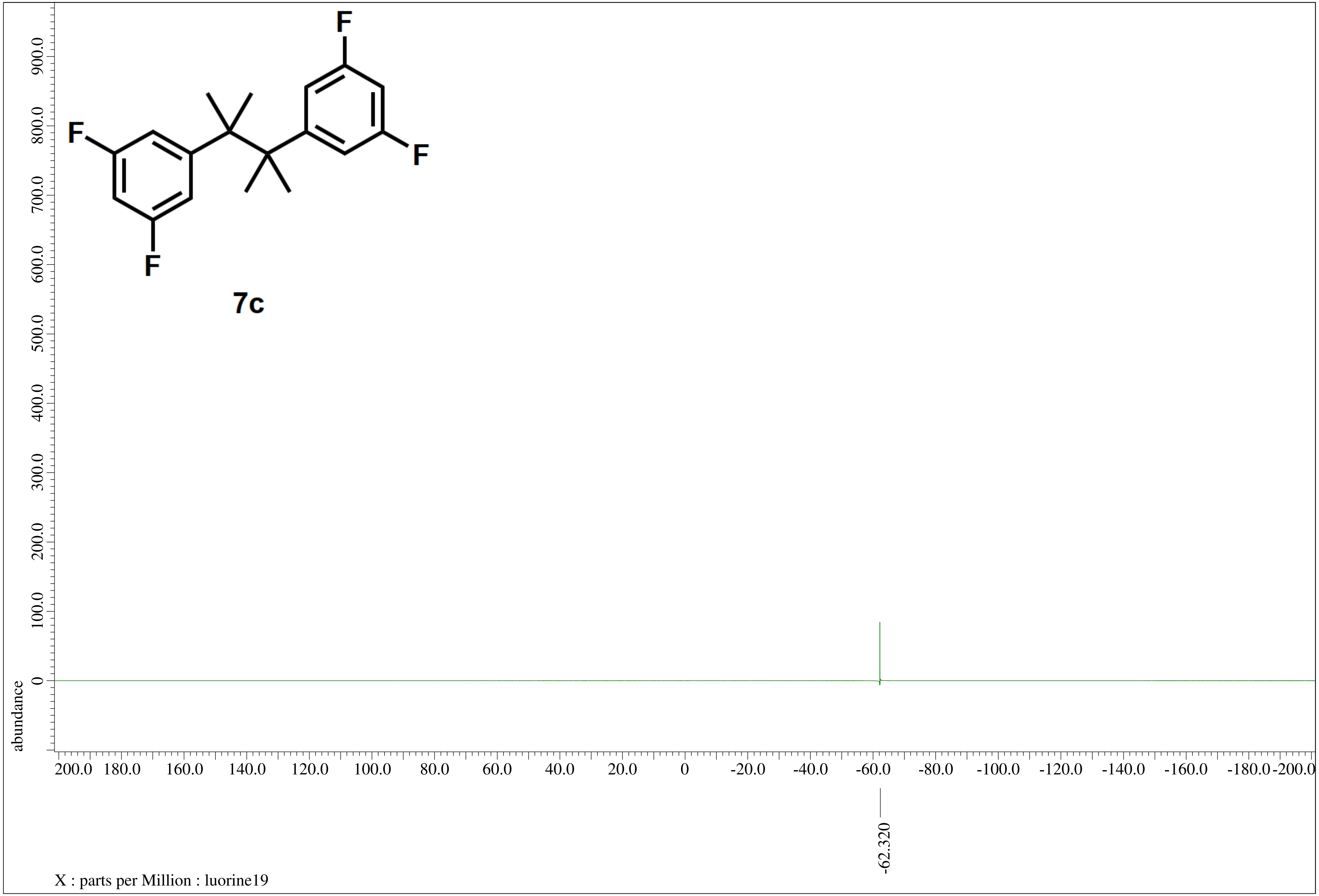
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7c**



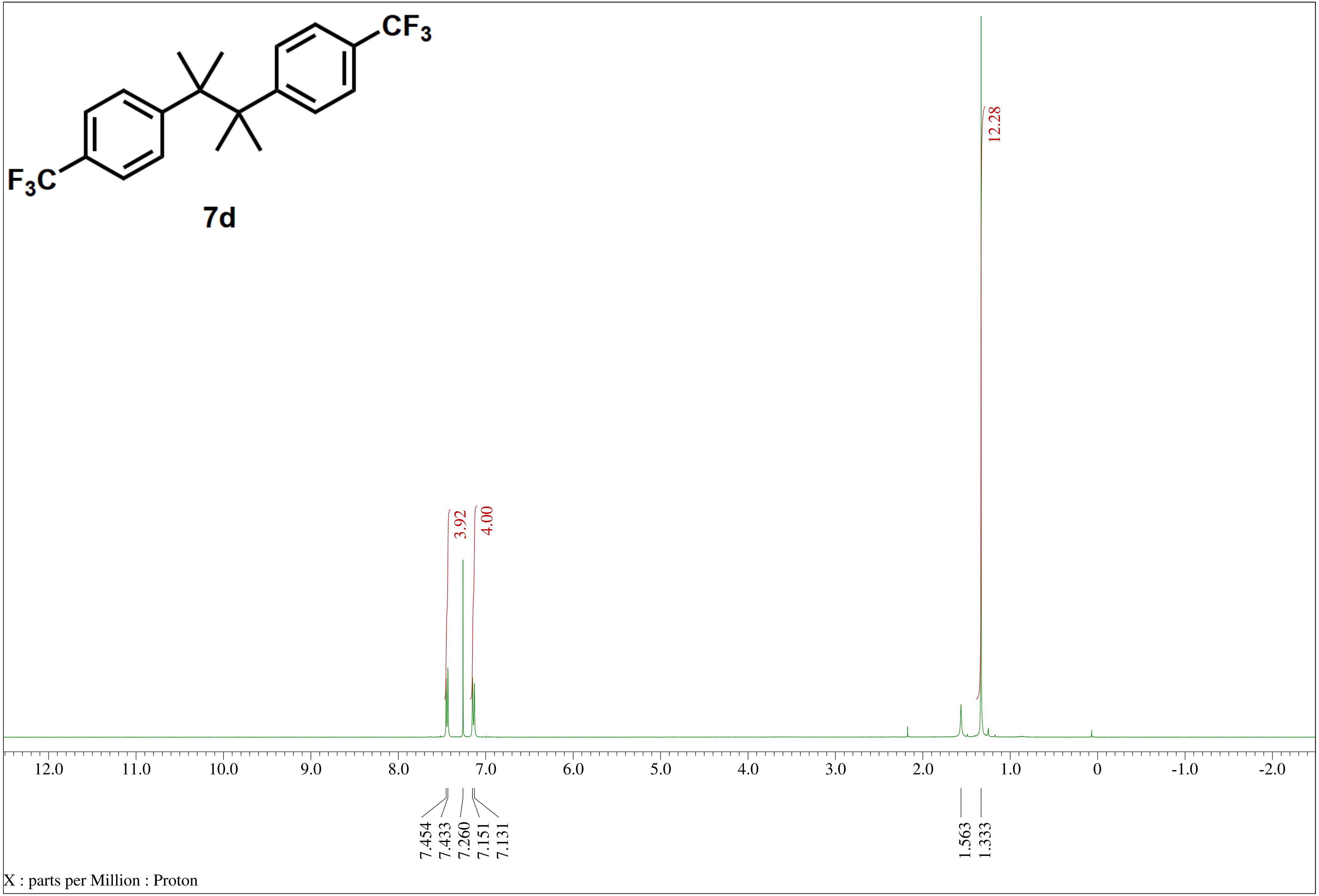
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **7c**



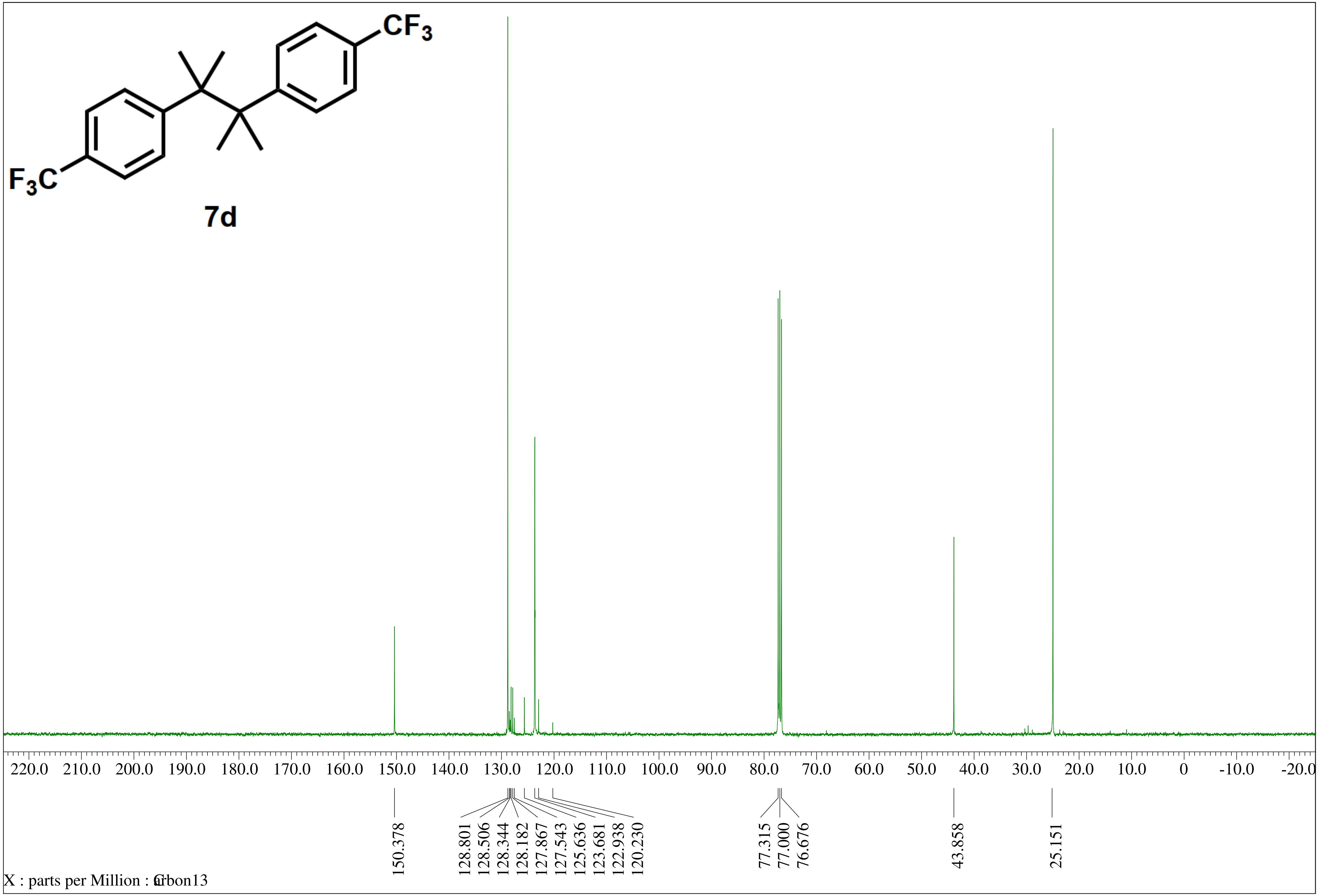
^{19}F NMR spectrum (375 MHz, CDCl$_3$) of **7c**



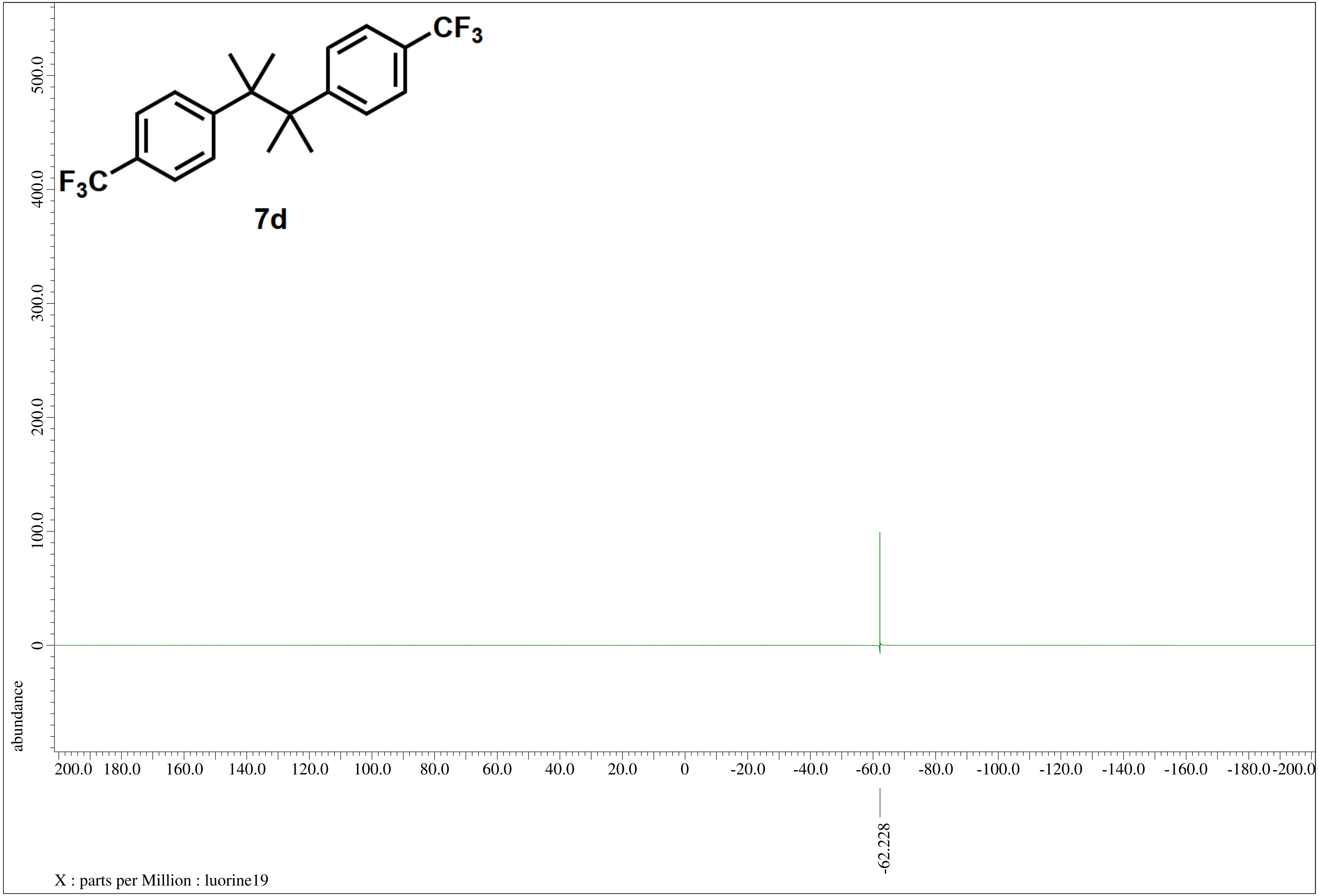
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **7d**



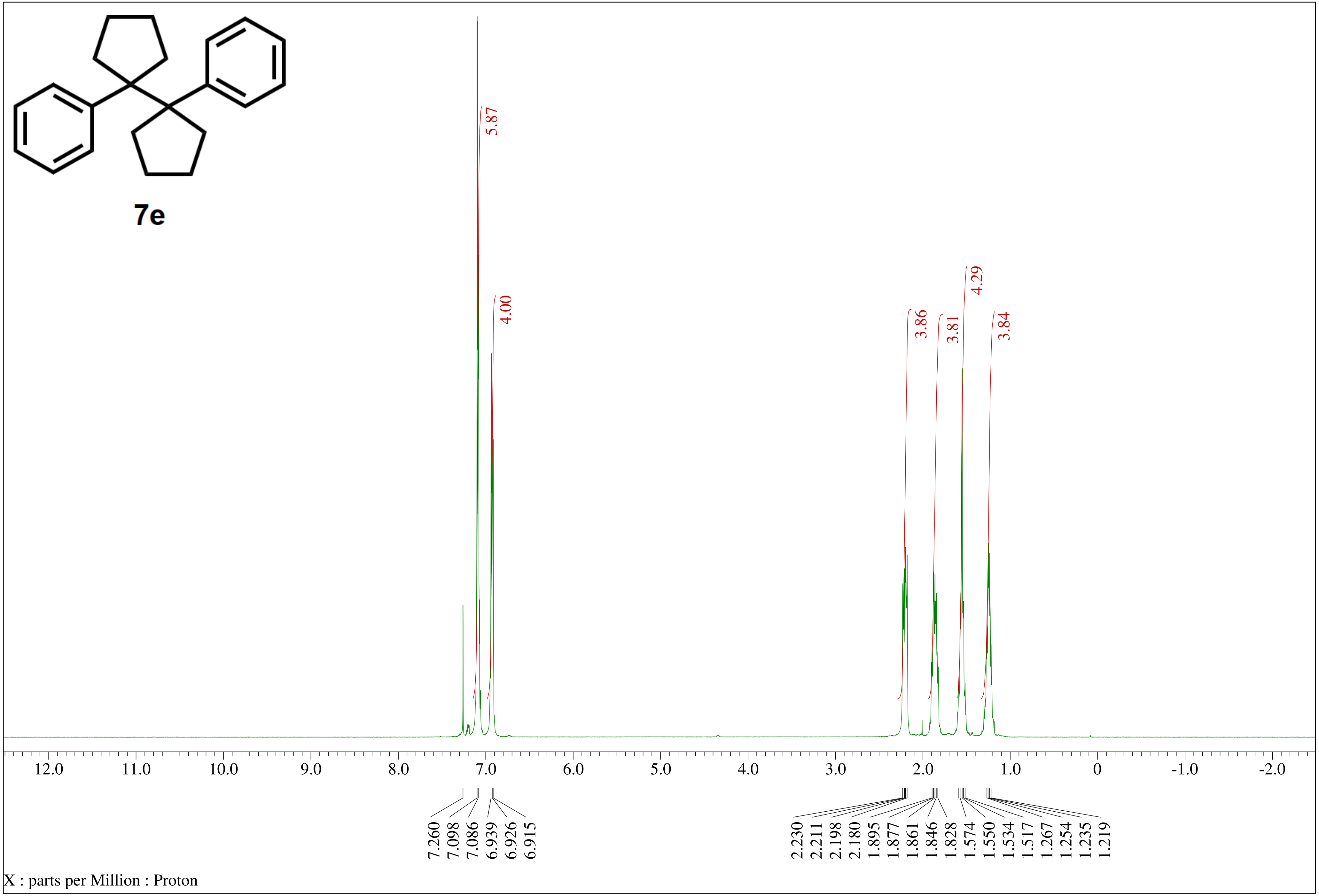
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **7d**



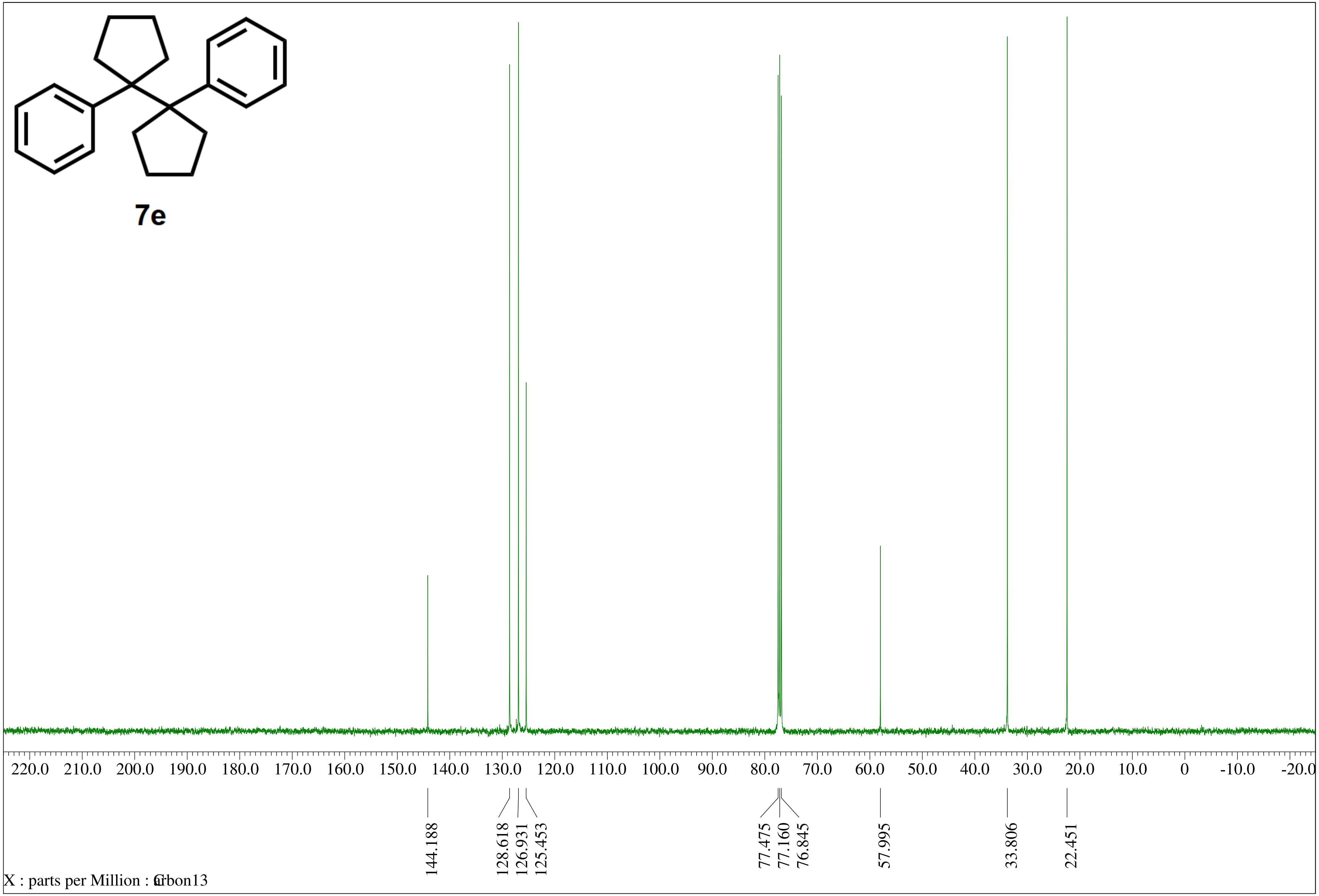
^{19}F NMR spectrum (375 MHz, $CDCl_3$) of **7d**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7e**

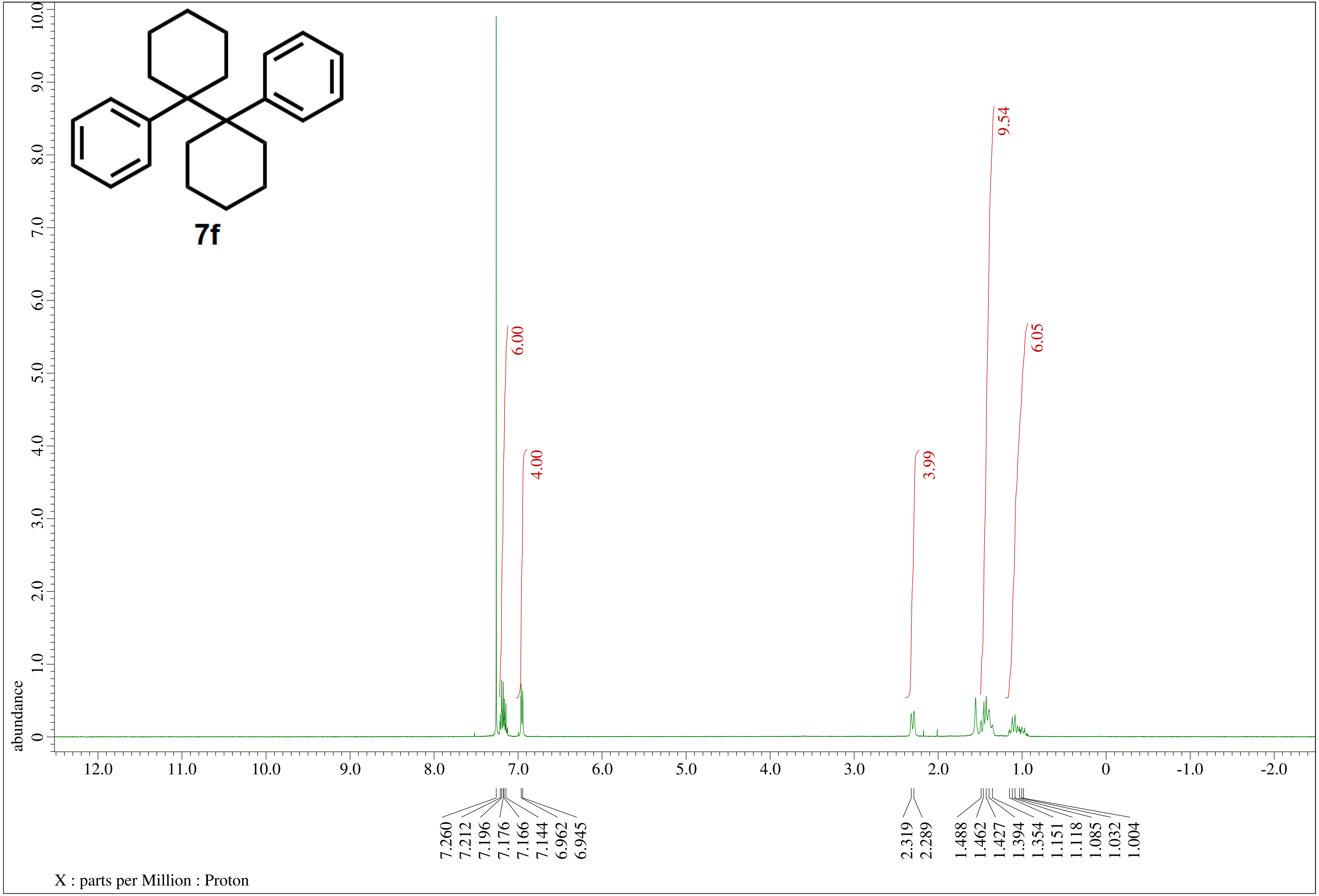


^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **7e**

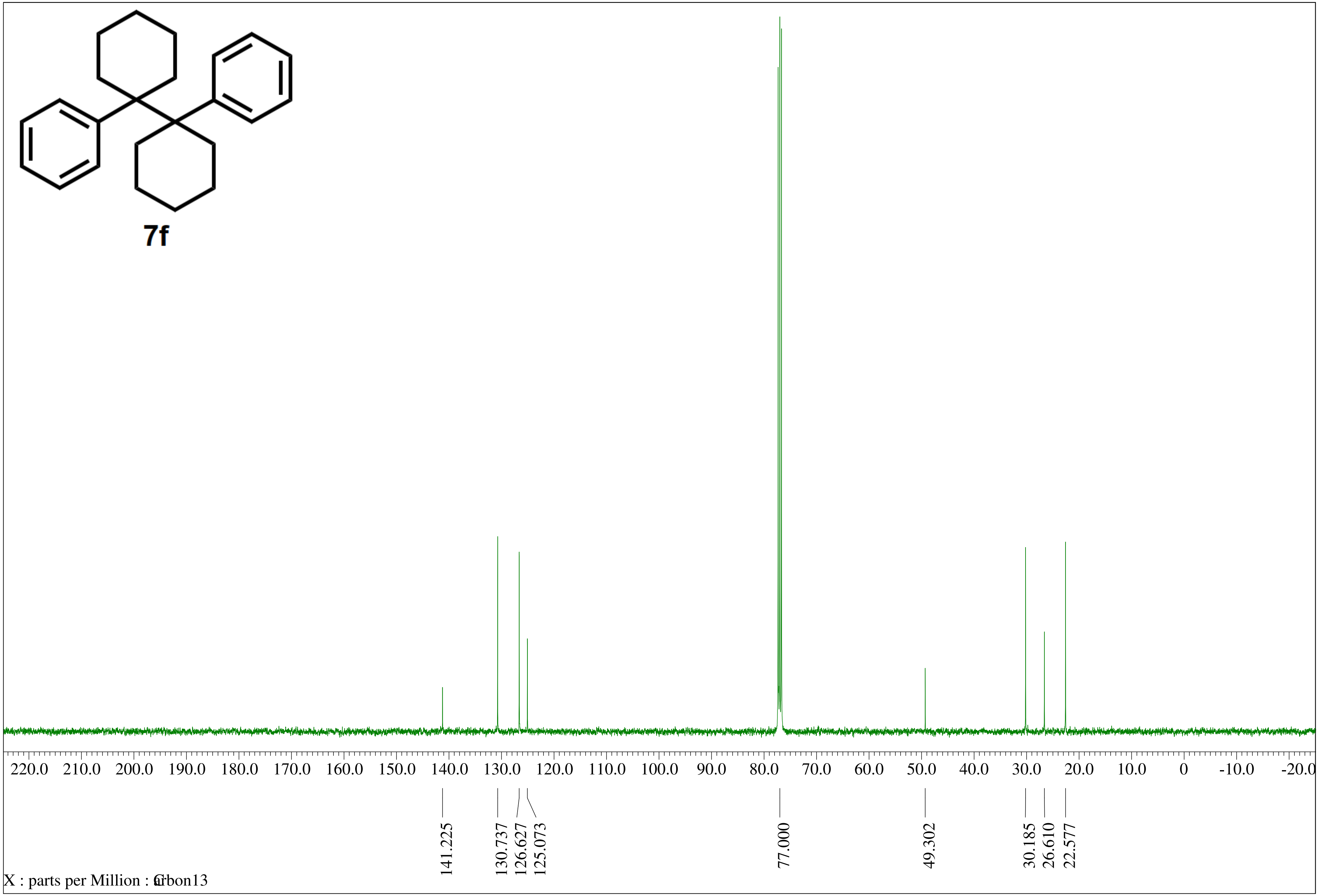


7e

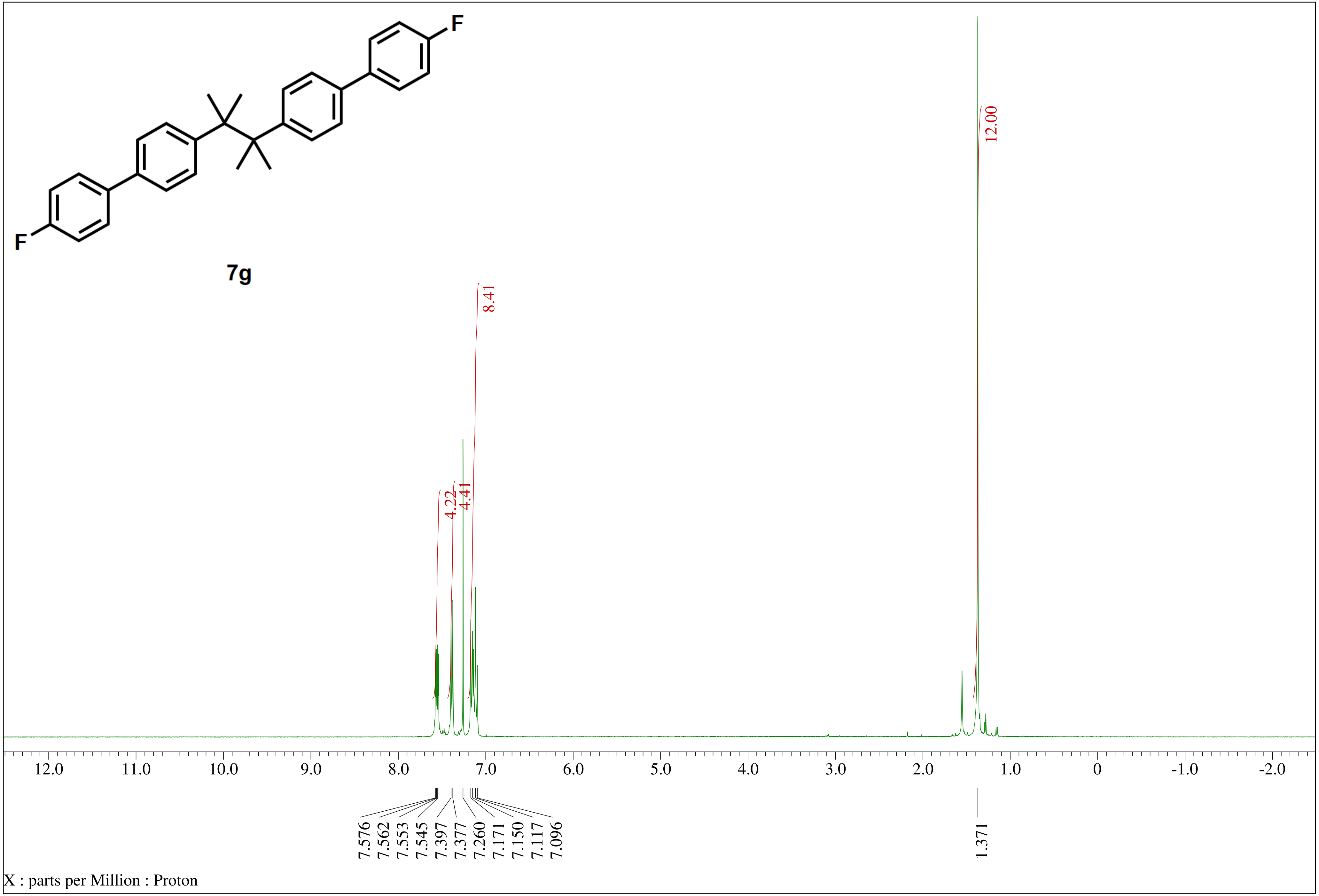
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7f**



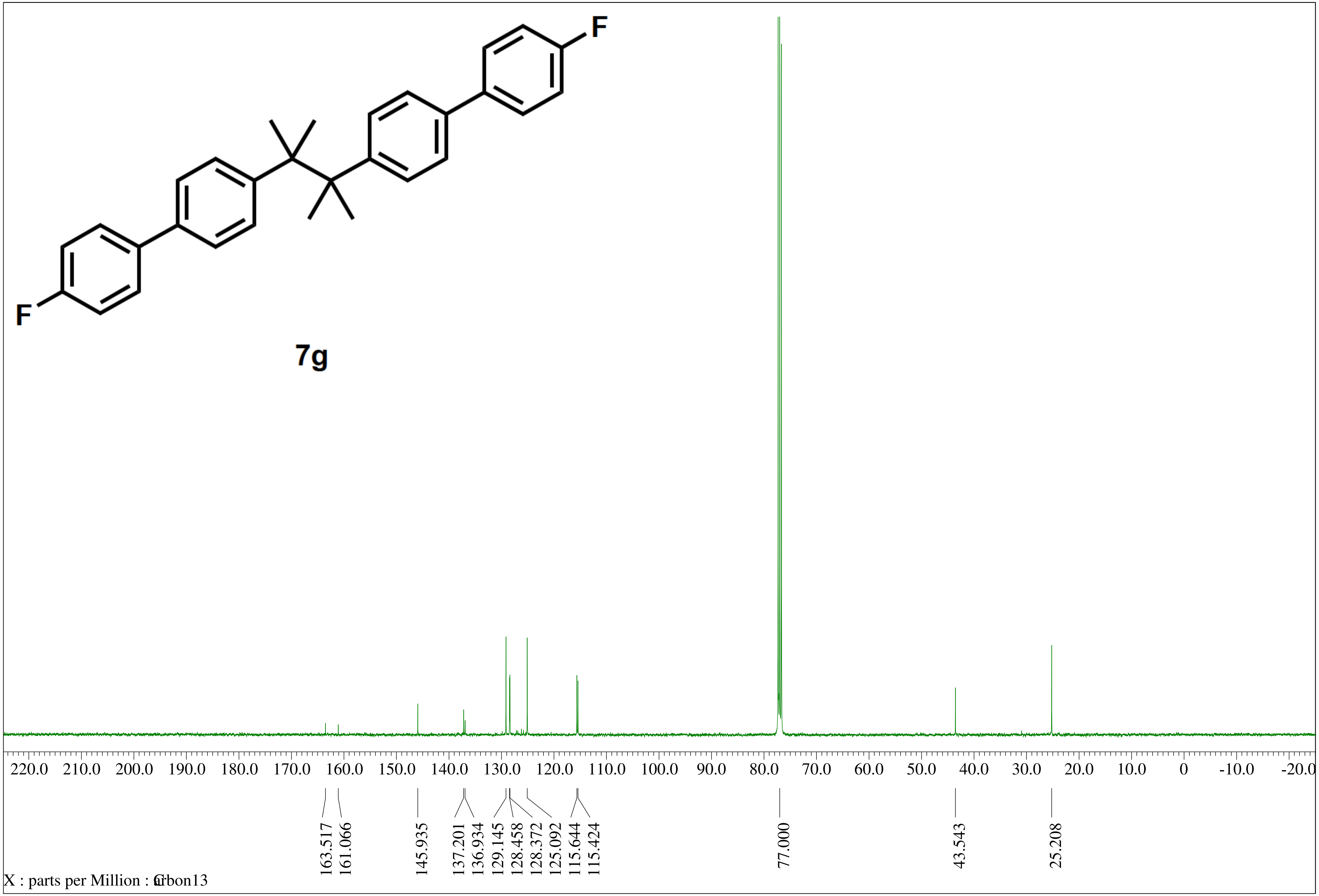
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **7f**



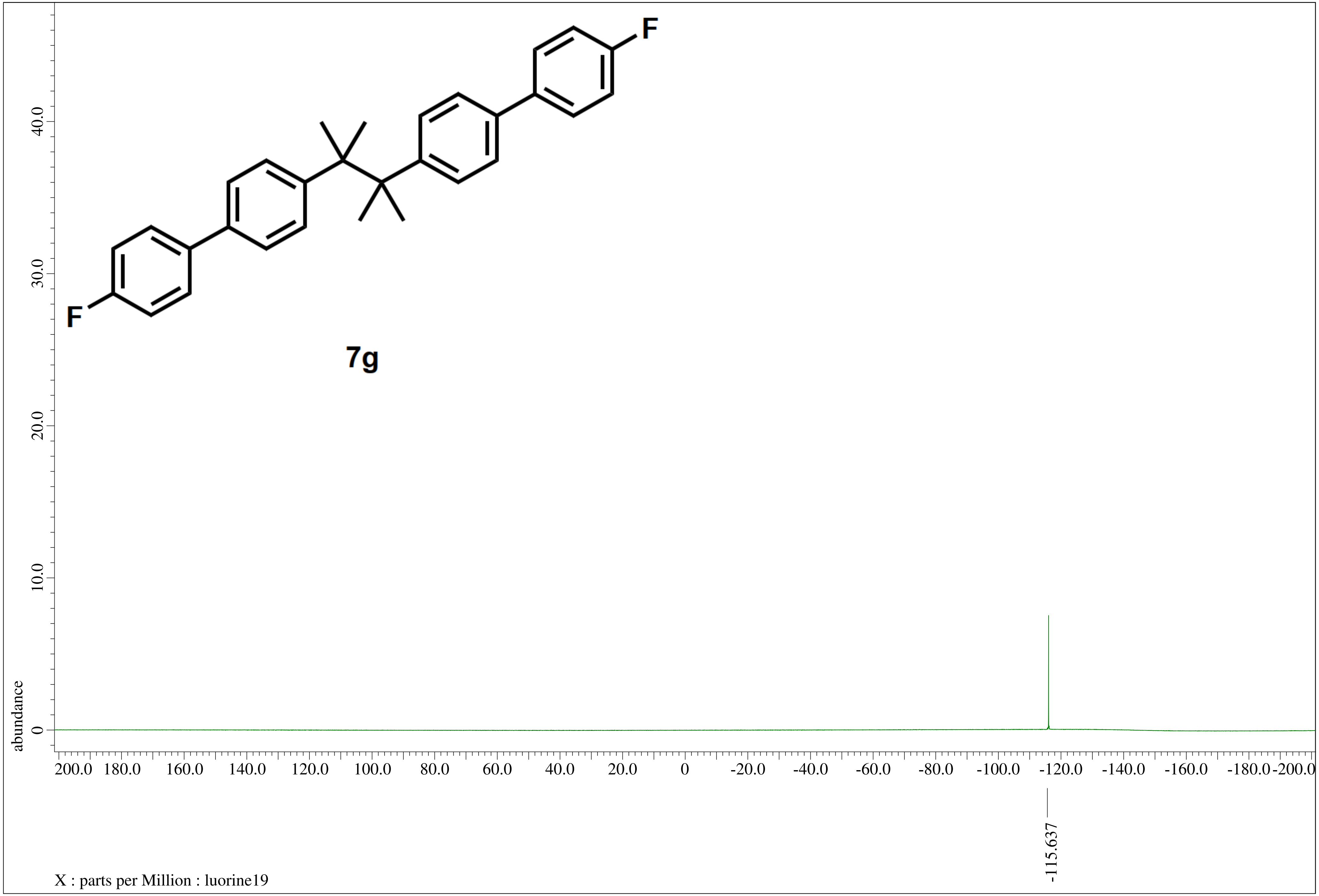
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7g**



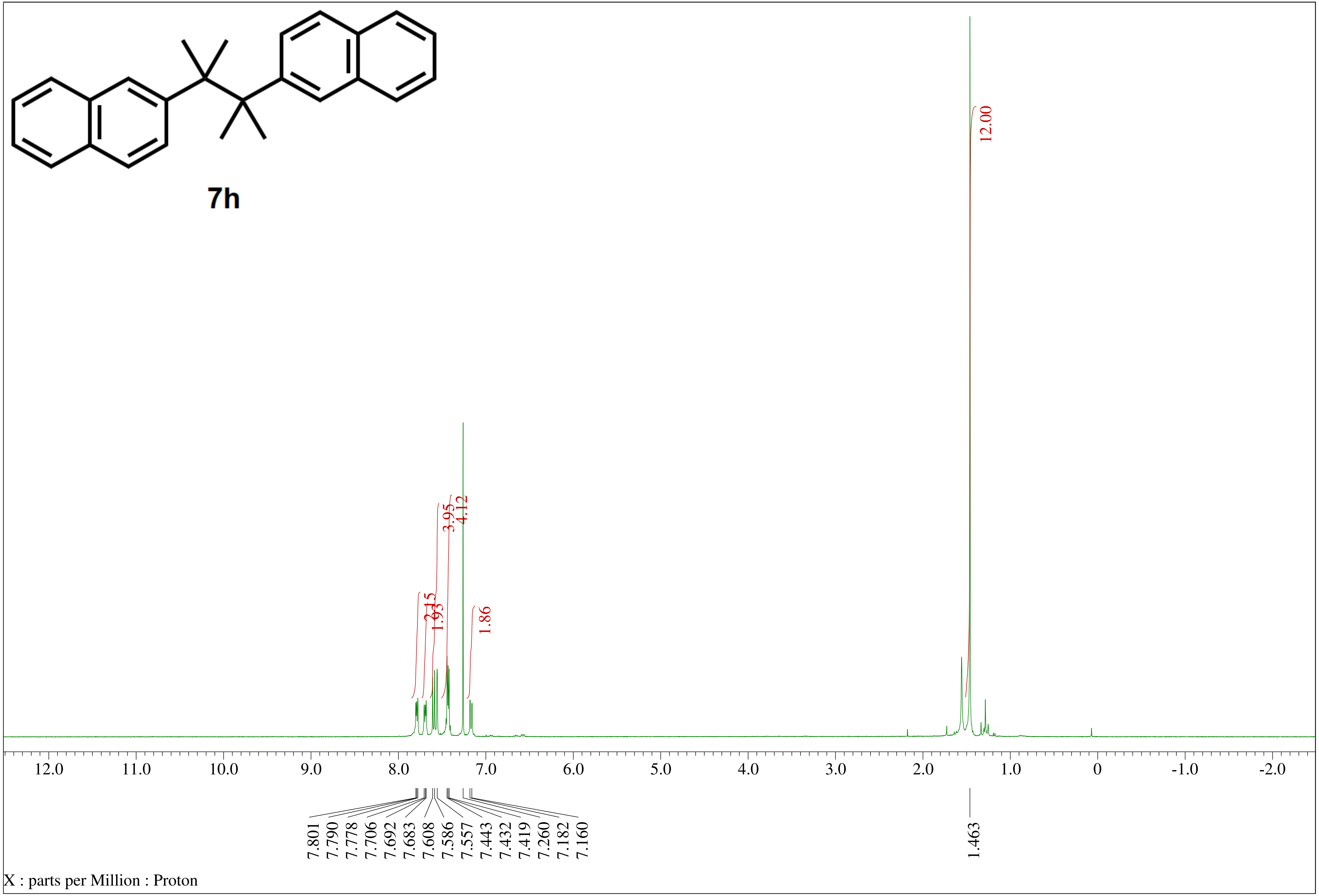
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **7g**



^{19}F NMR spectrum (375 MHz, $CDCl_3$) of **7g**



^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **7h**



^{13}C NMR spectrum (100 MHz, CDCl$_3$) of **7h**