Benzotriazole as an efficient ligand in Cu-catalyzed Glaser reaction

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1. ^{1}H and ^{13}C NMR Spectrum of Symmetric dialkyne (**2a-u**).

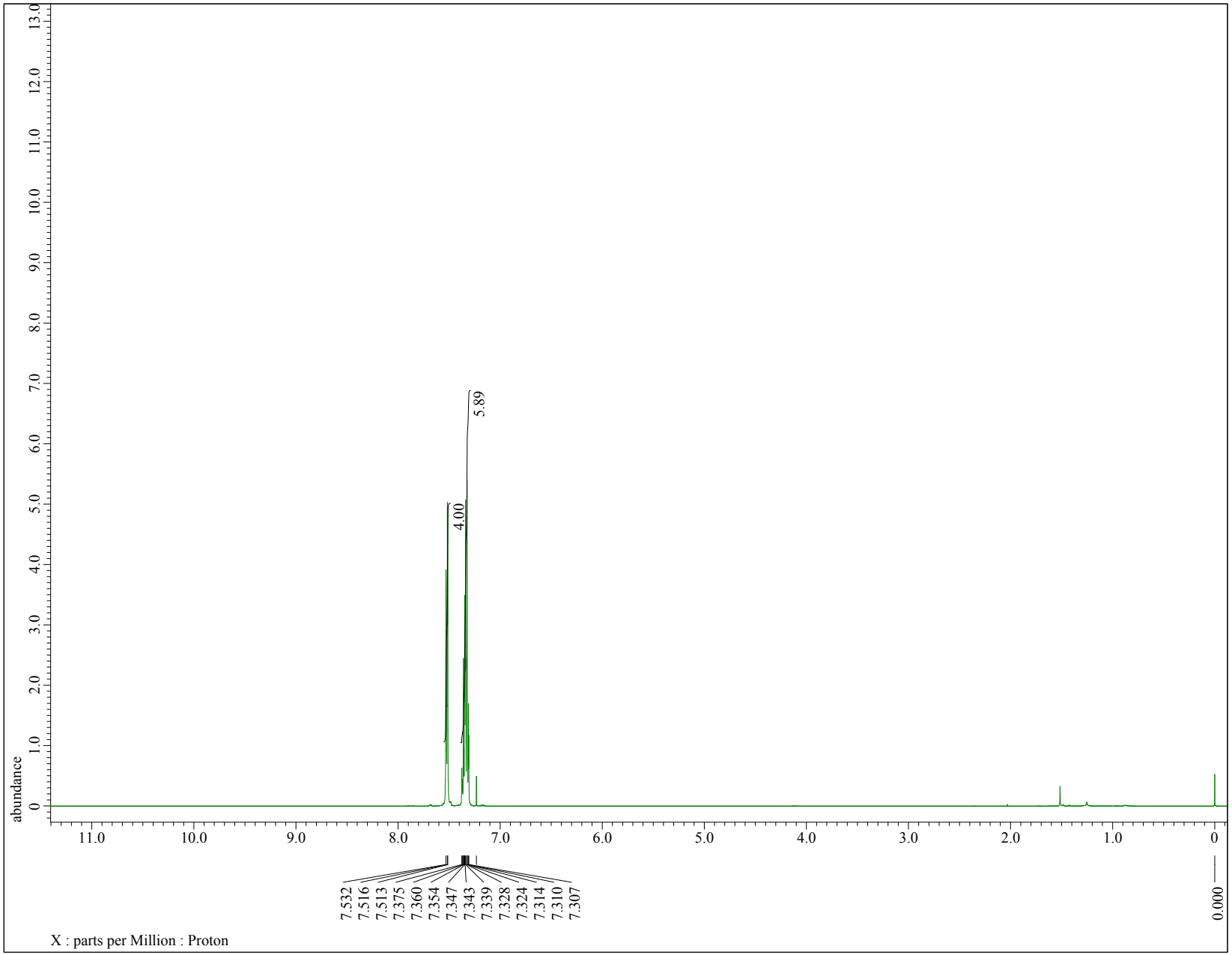

Figure S1: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2a**

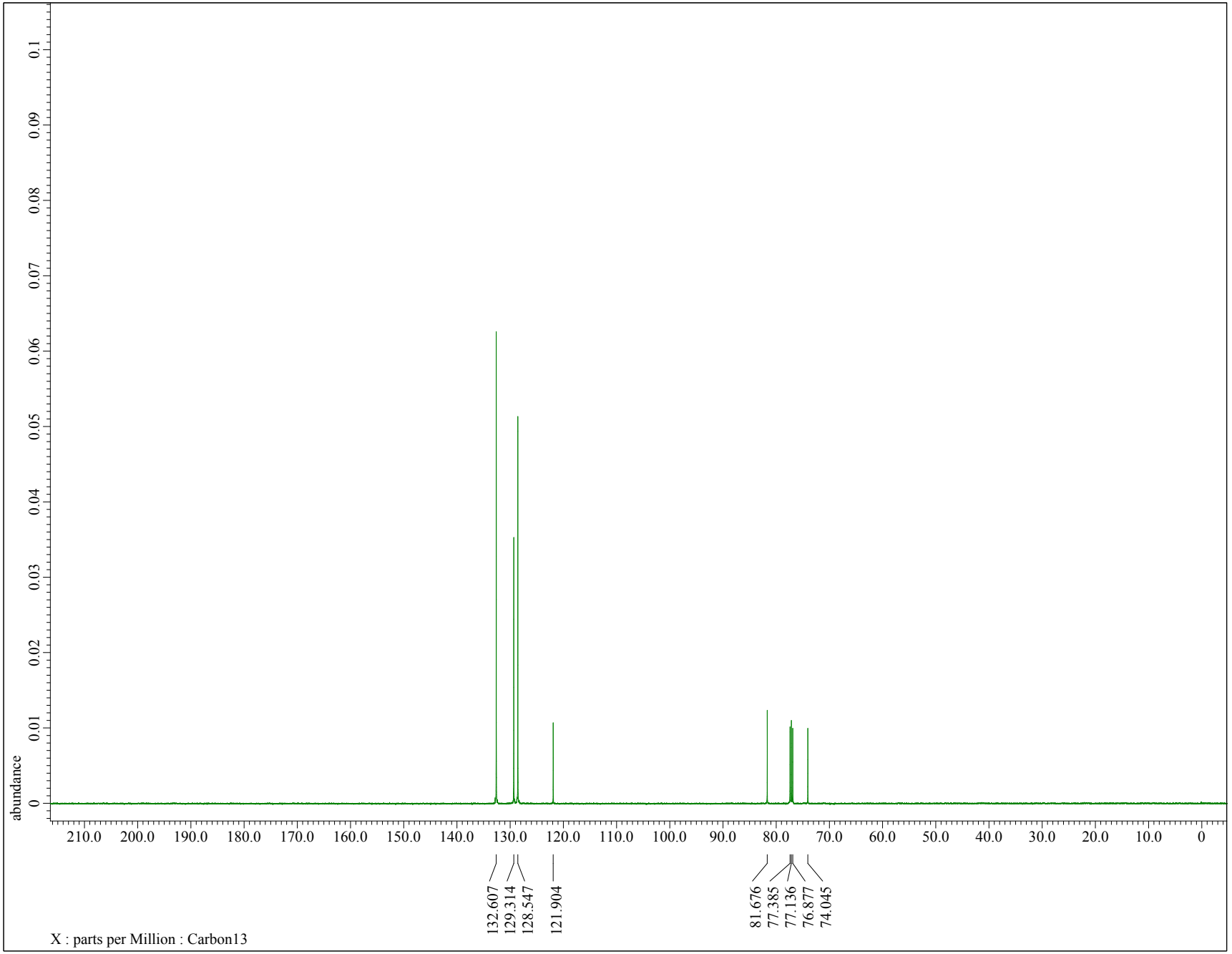

Figure S2: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2a**

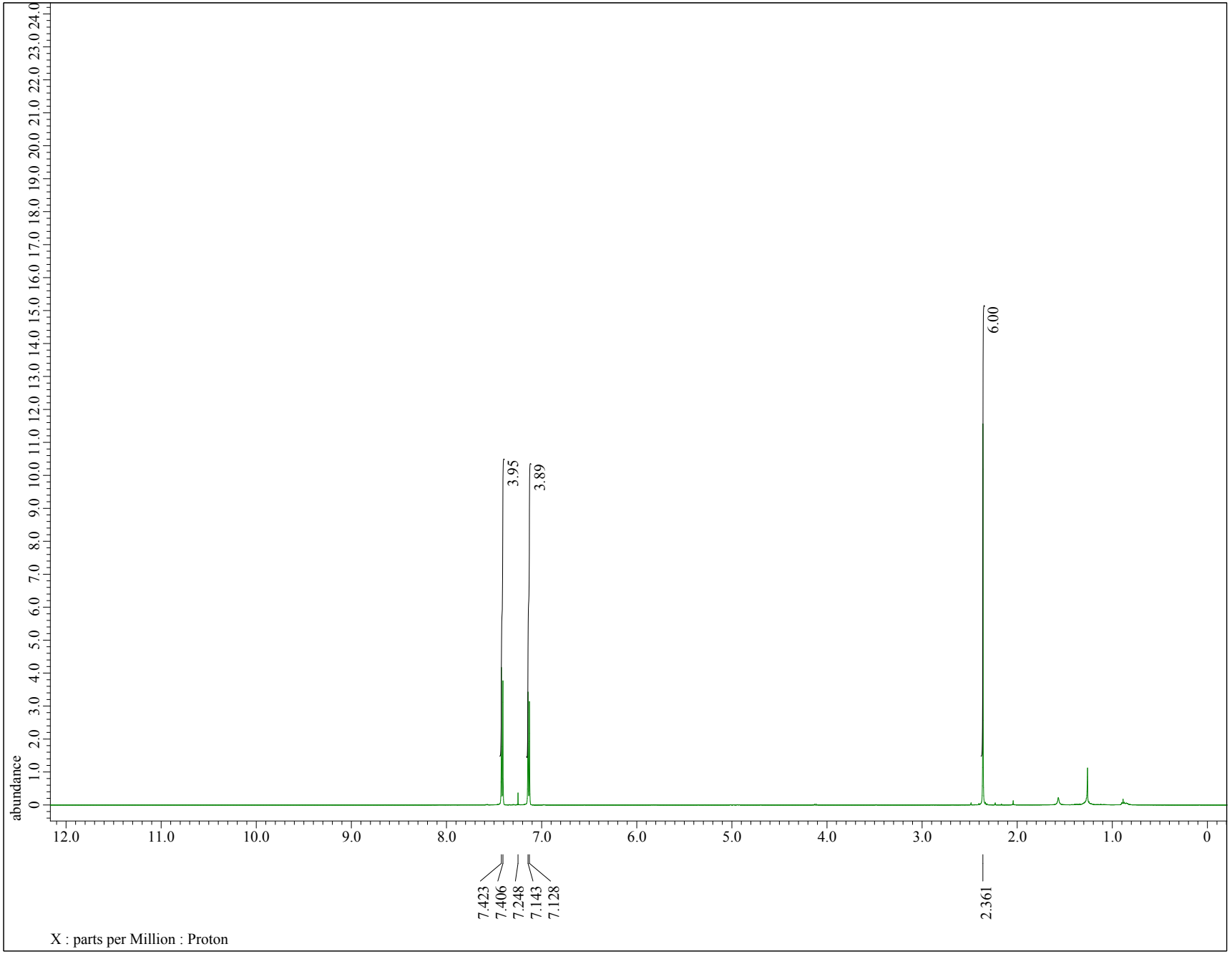

Figure S3: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2b**

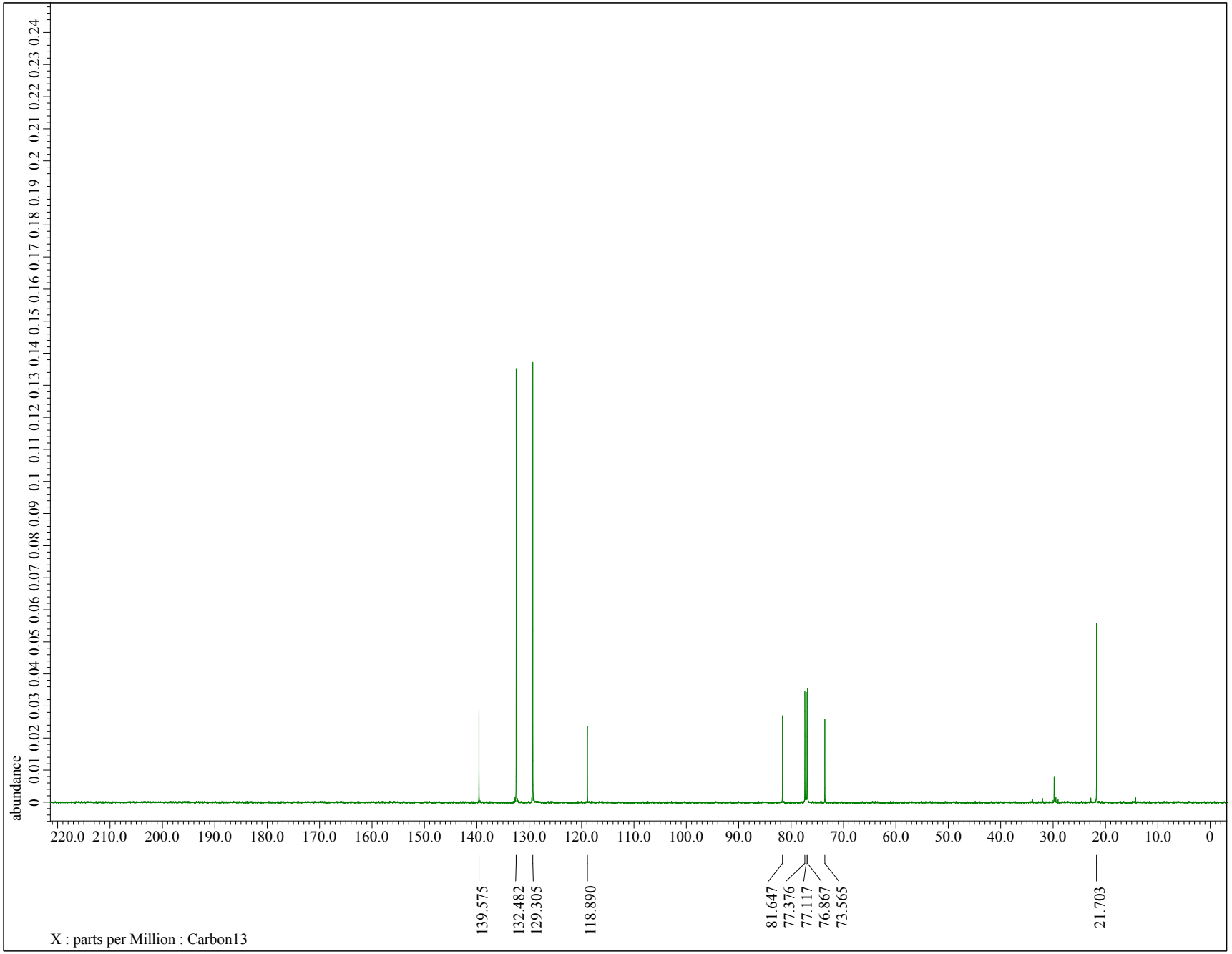

Figure S4: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2b**

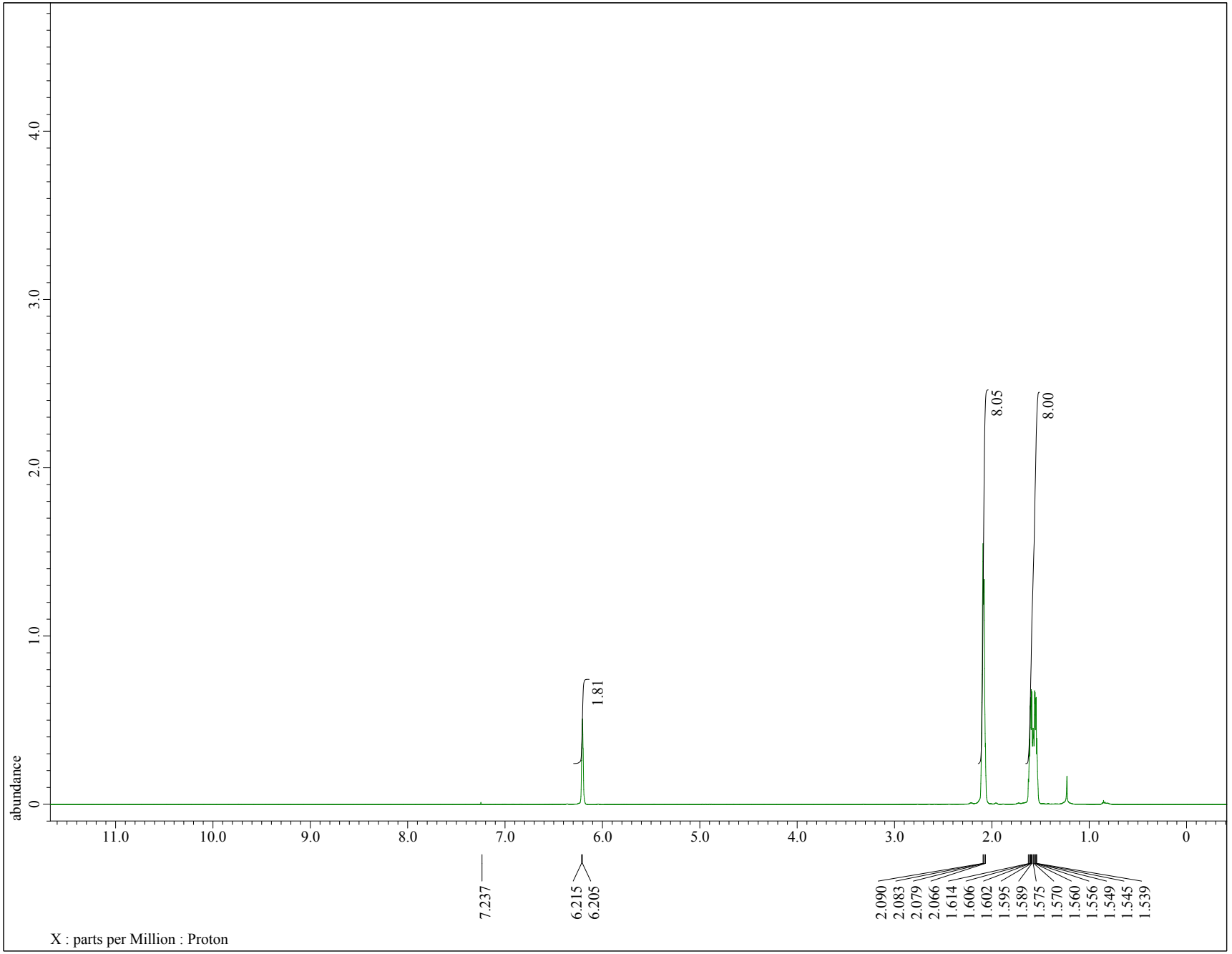

Figure S5: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2c**

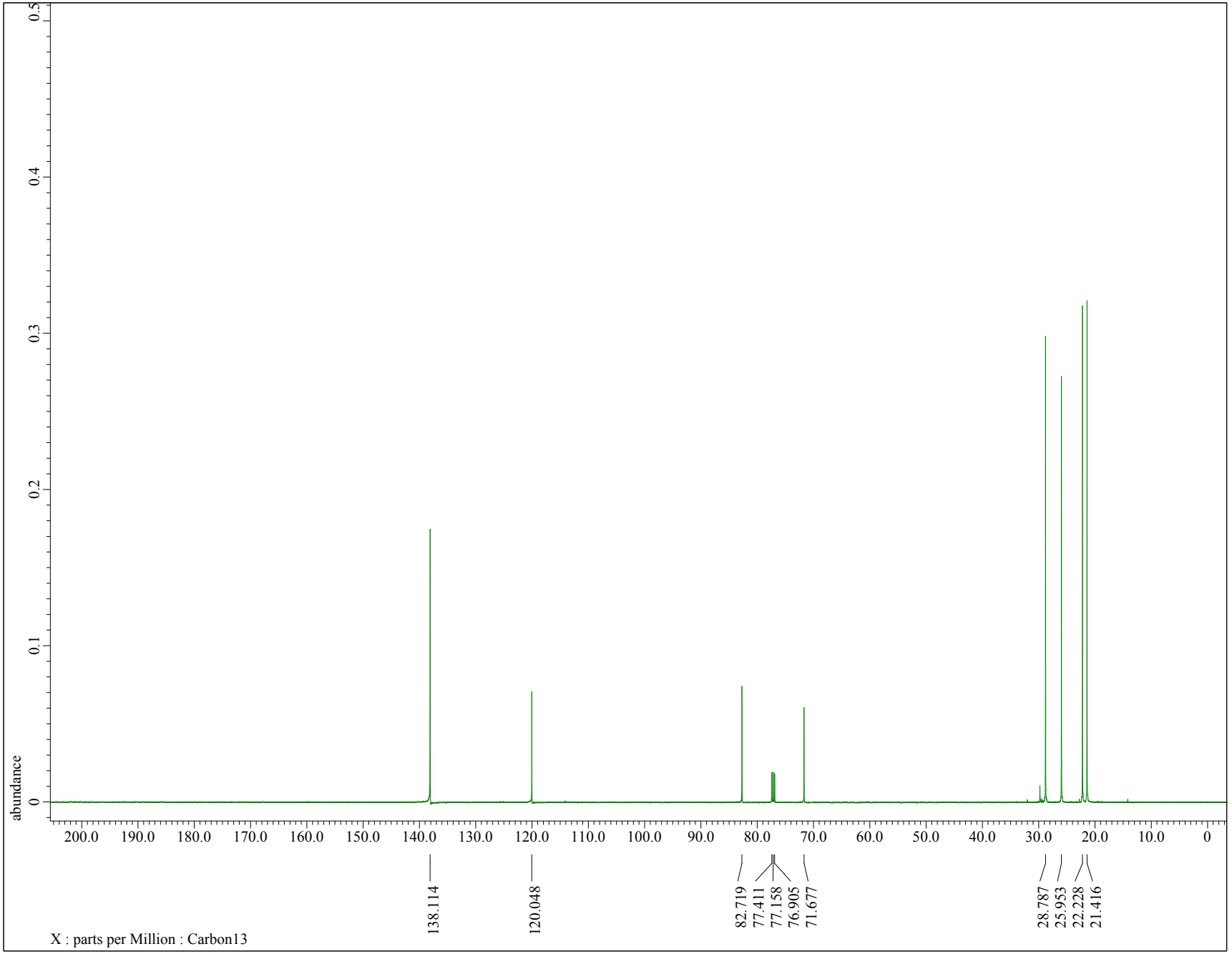

Figure S6: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2c**

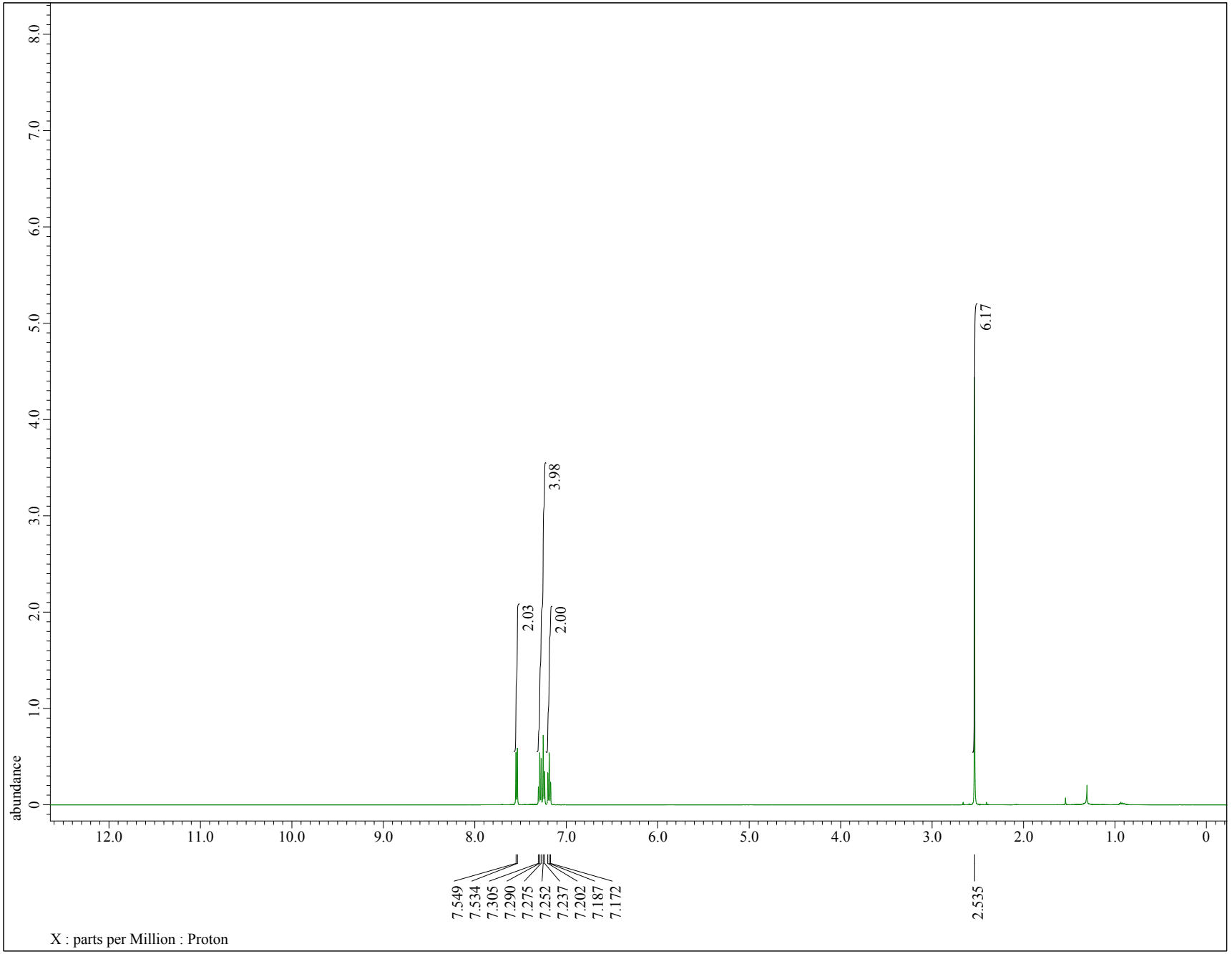

Figure S7: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2d**

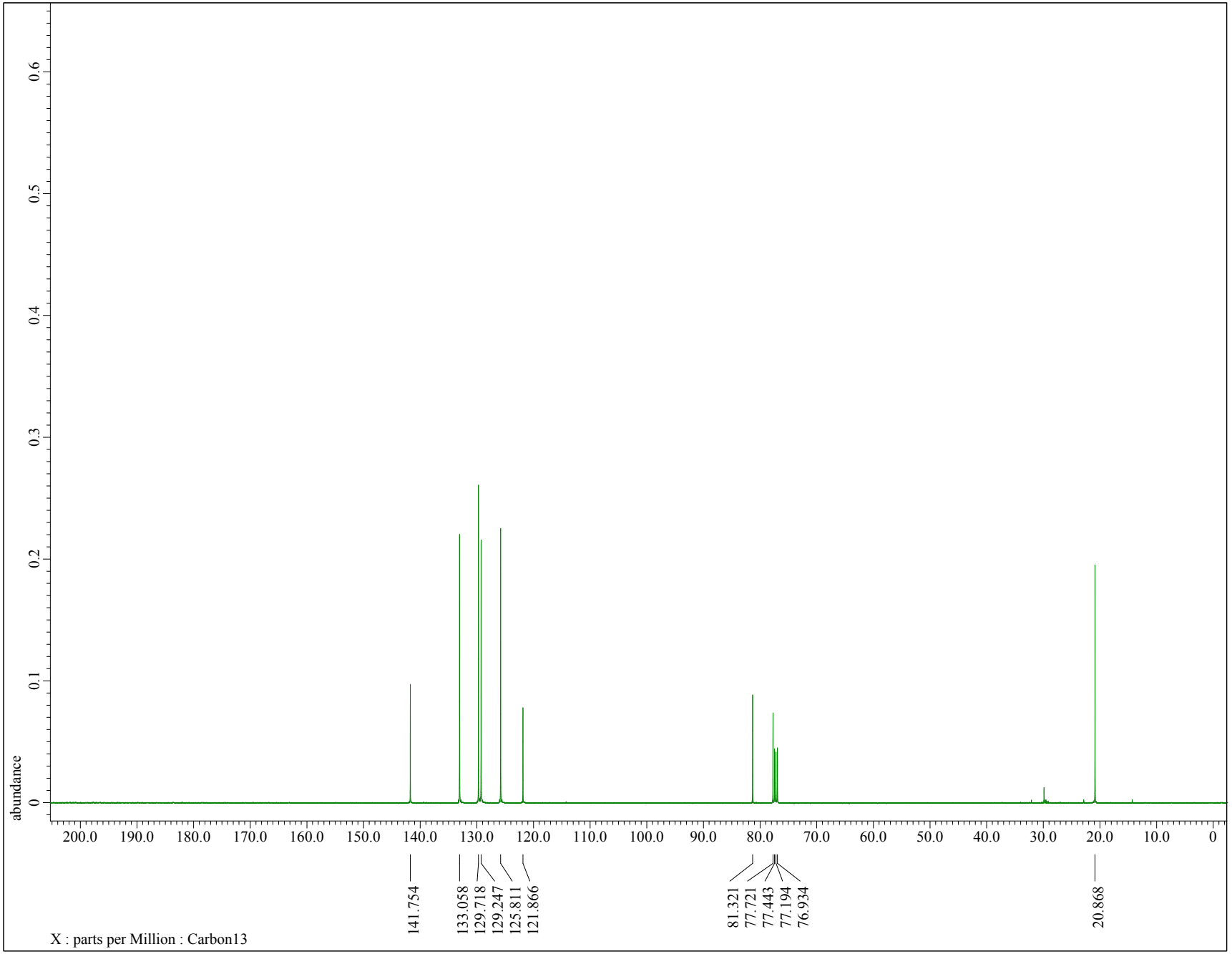

Figure S8: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2d**

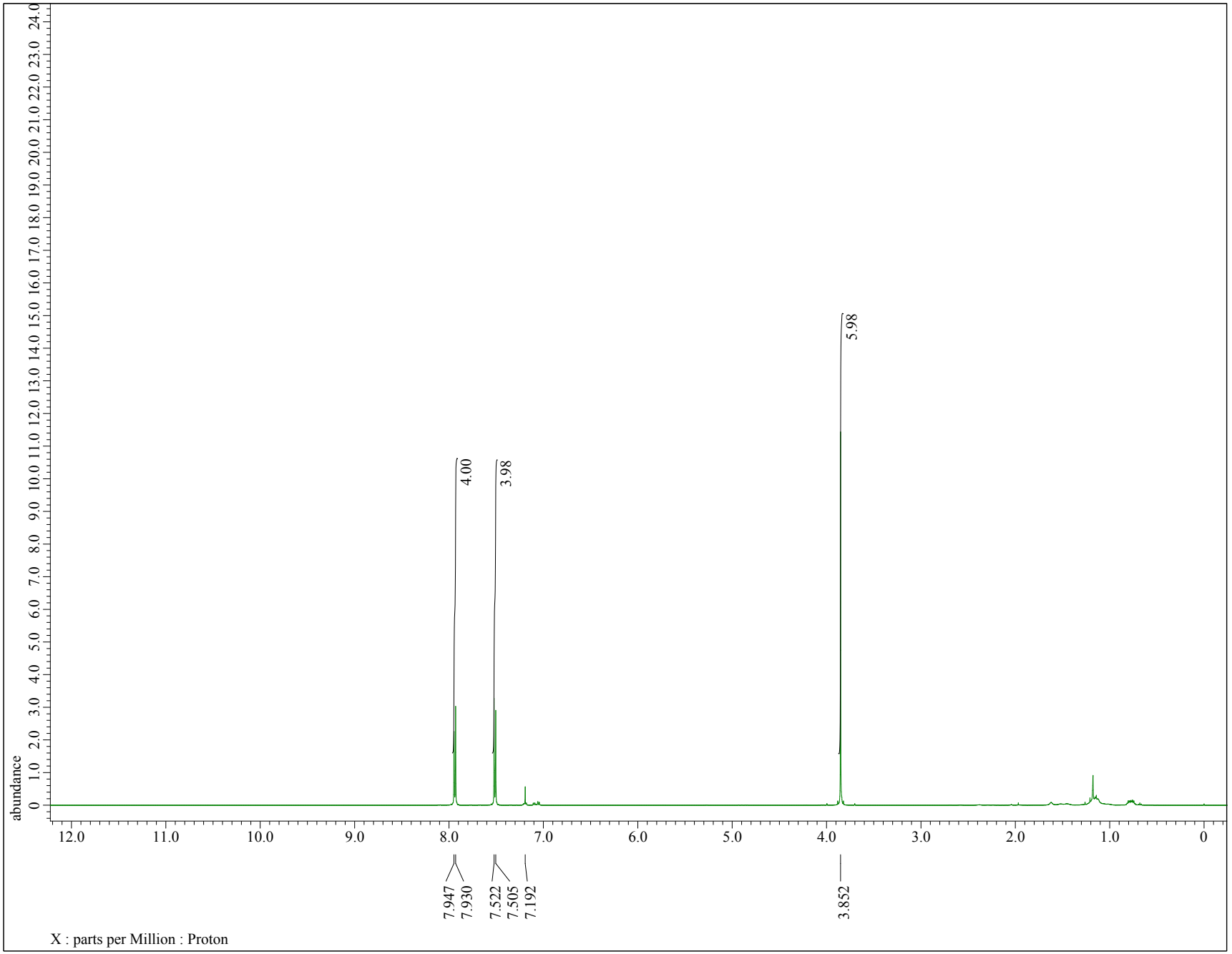

Figure S9: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2e**

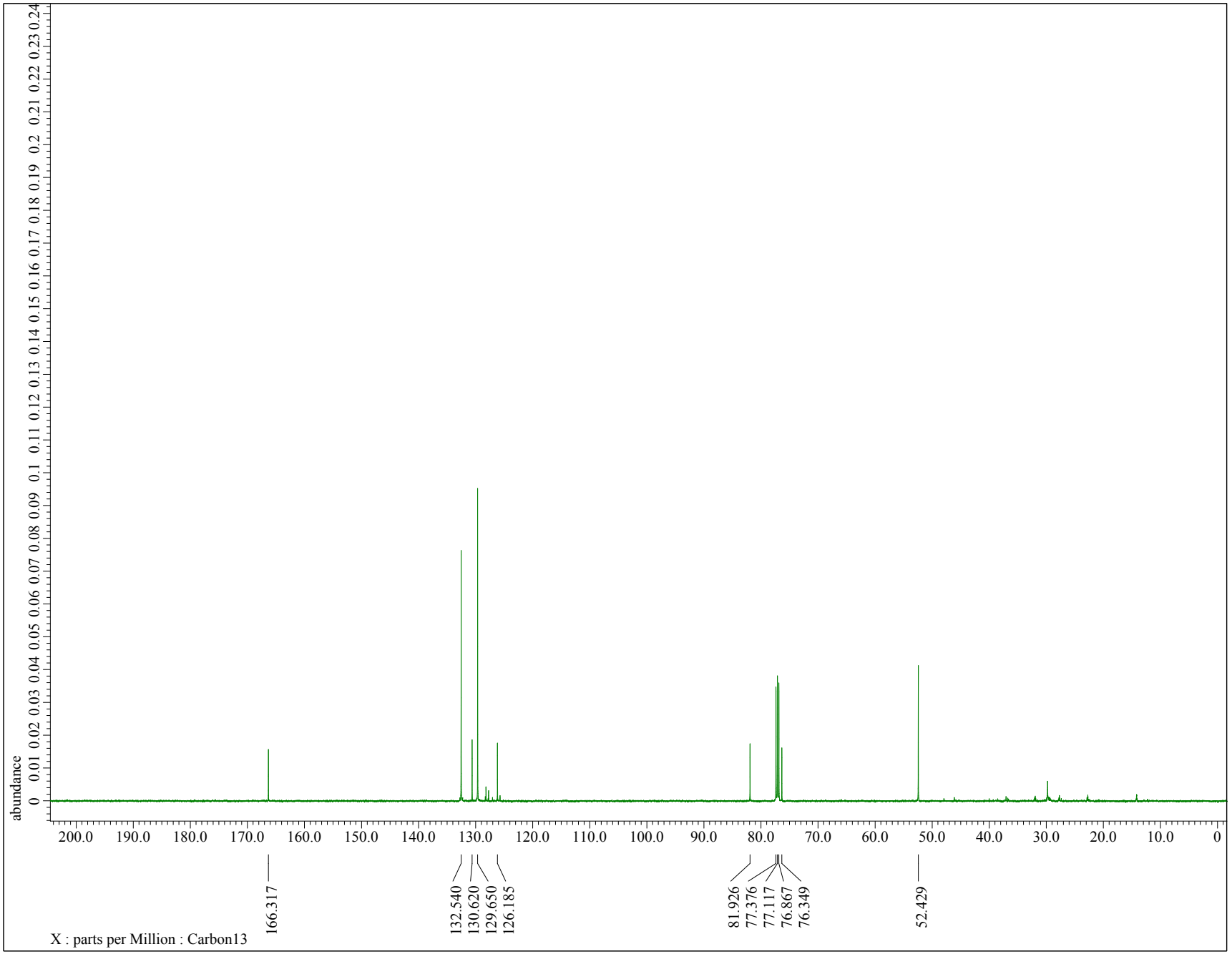

Figure S10: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2e**

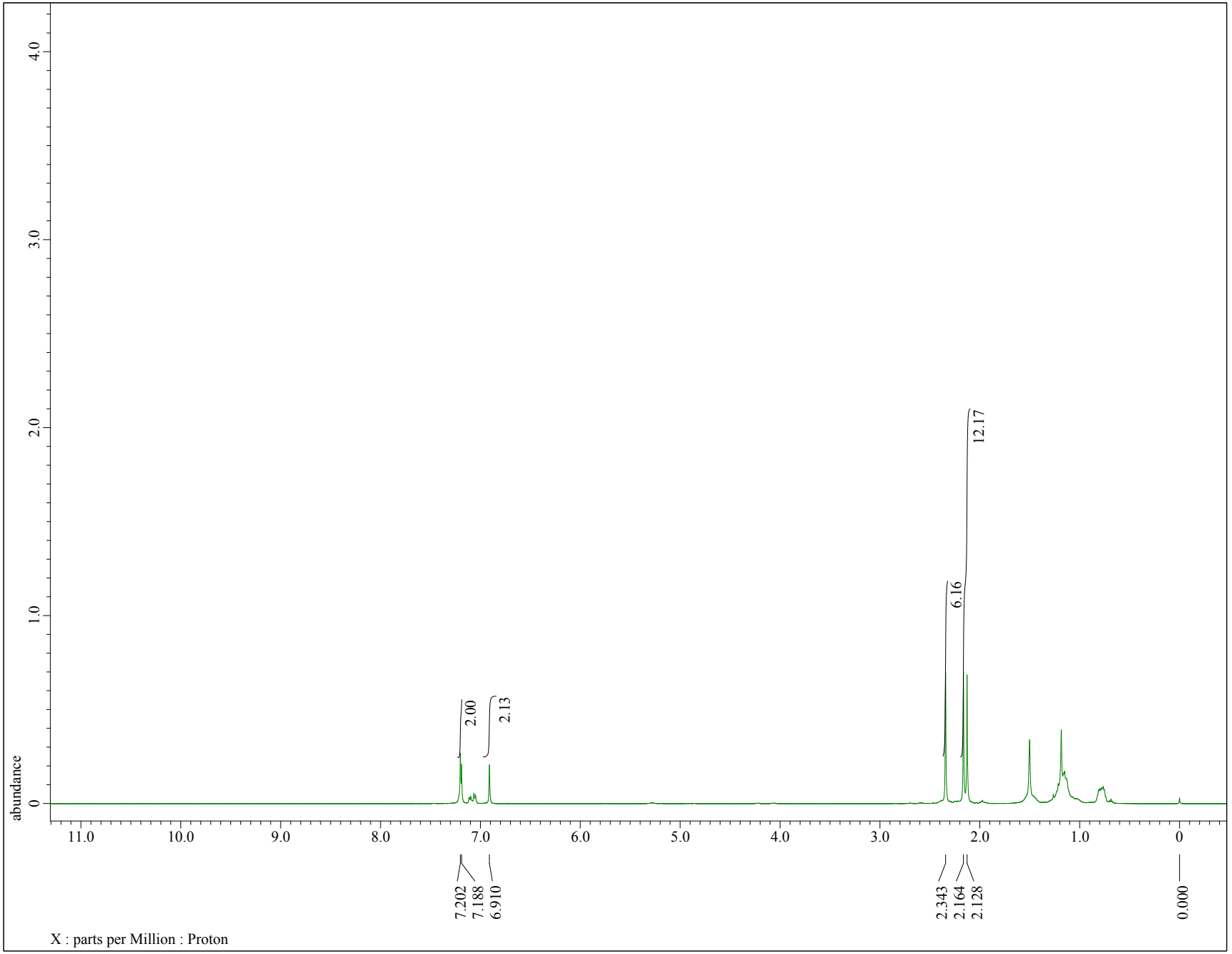

Figure S11: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2f**

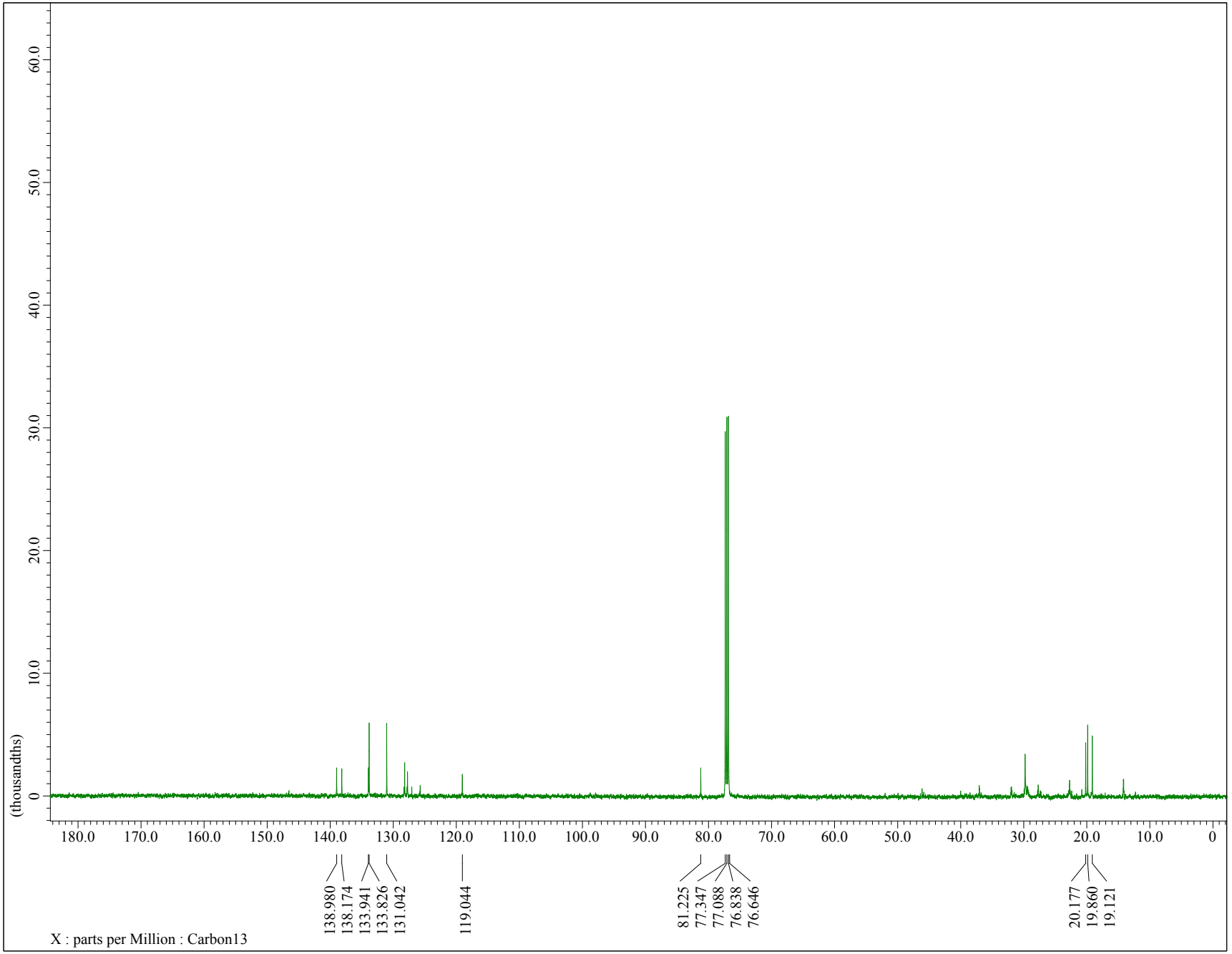

Figure S12: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2f**

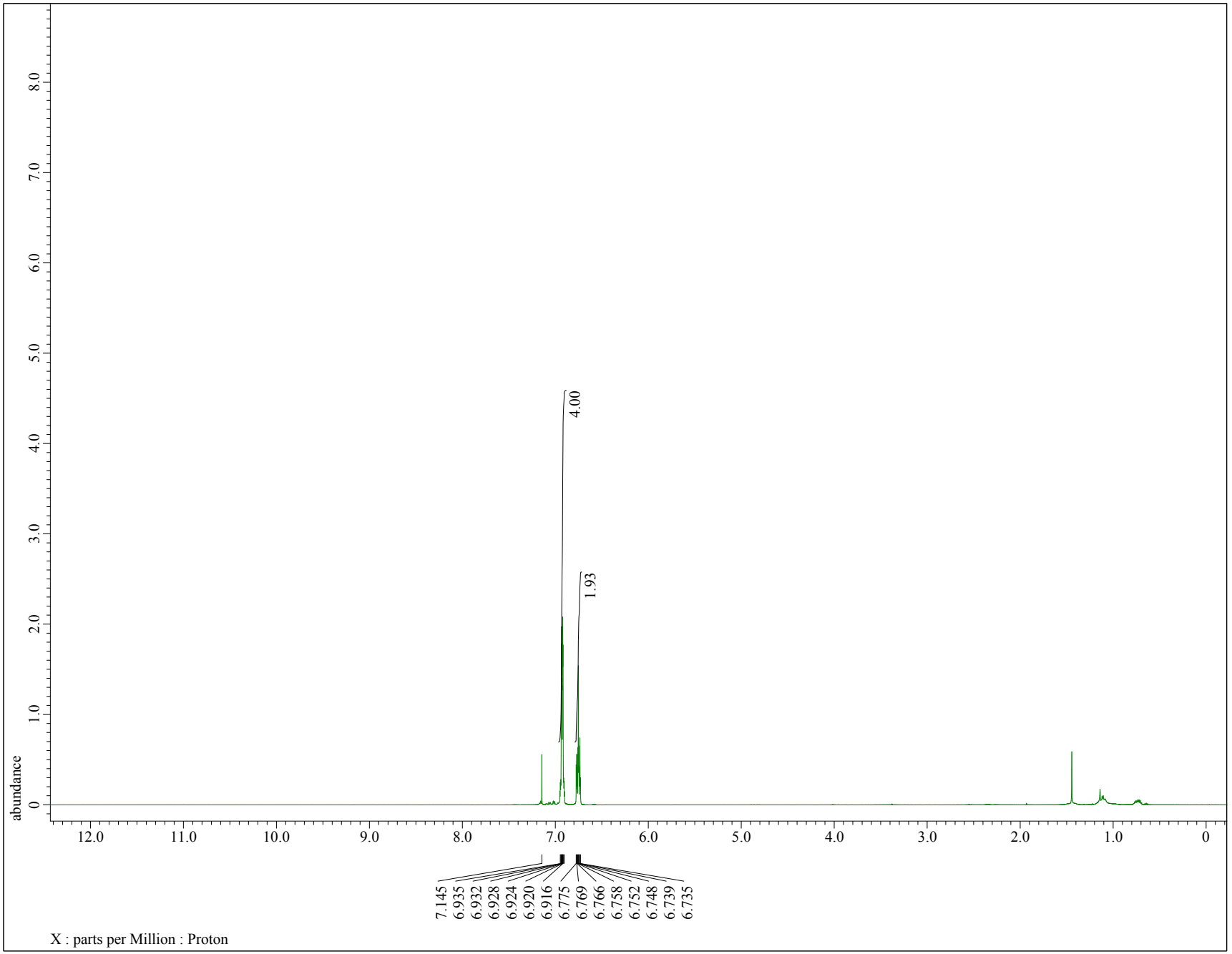

Figure S13: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2g**

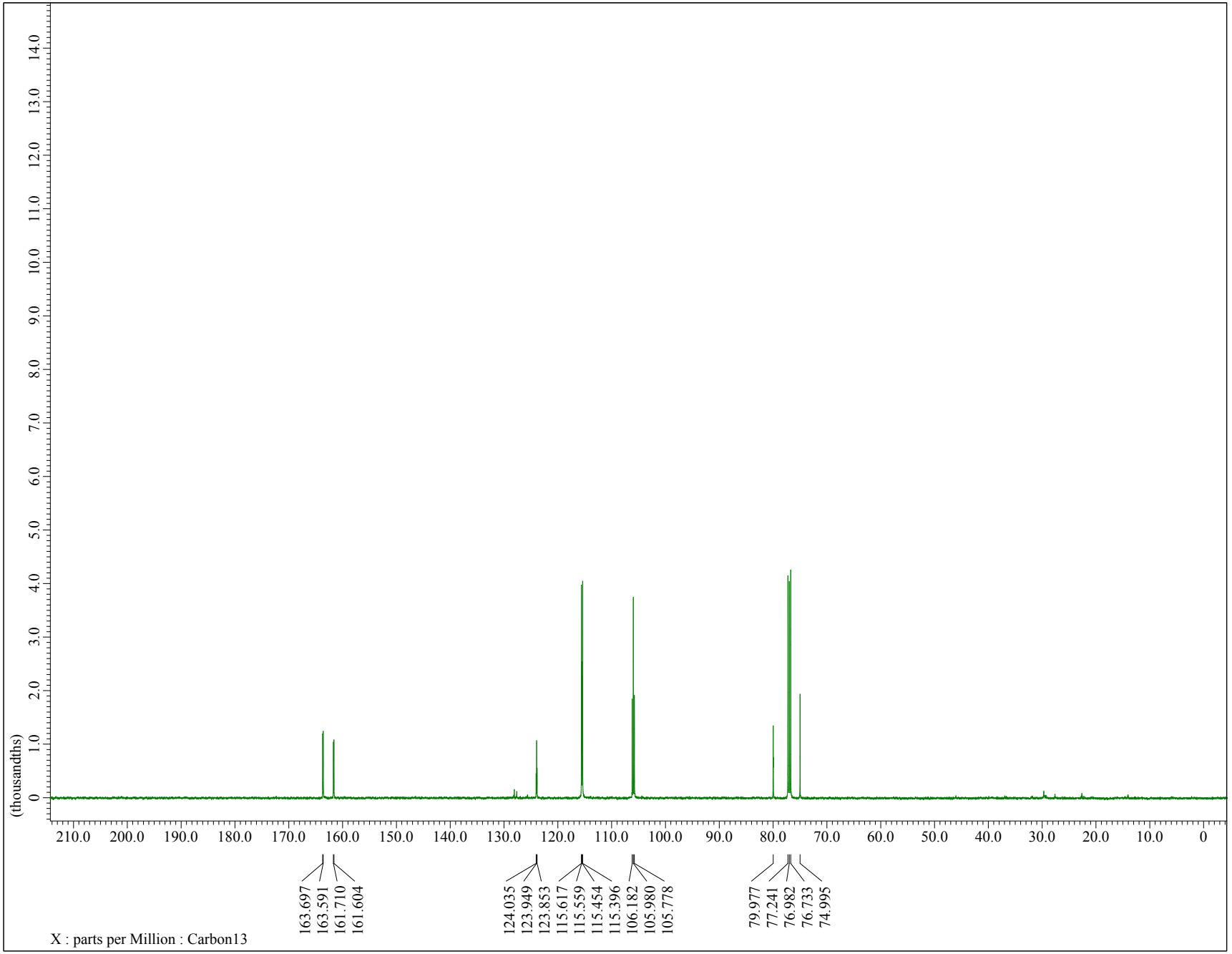

Figure S14: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2g**

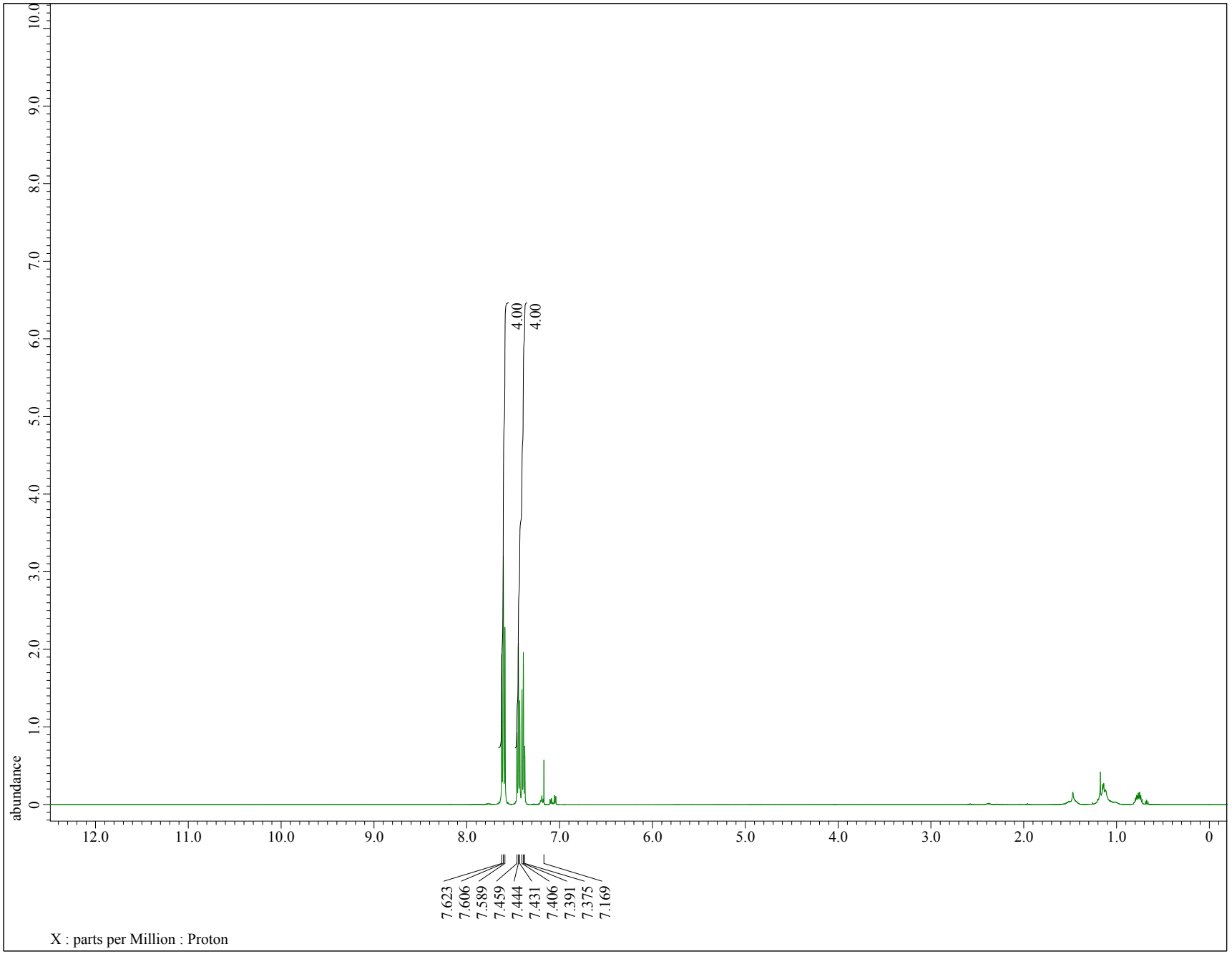

Figure S15: ^{1}HNMR (500 MHz, $CDCl_3$) of compound **2h**

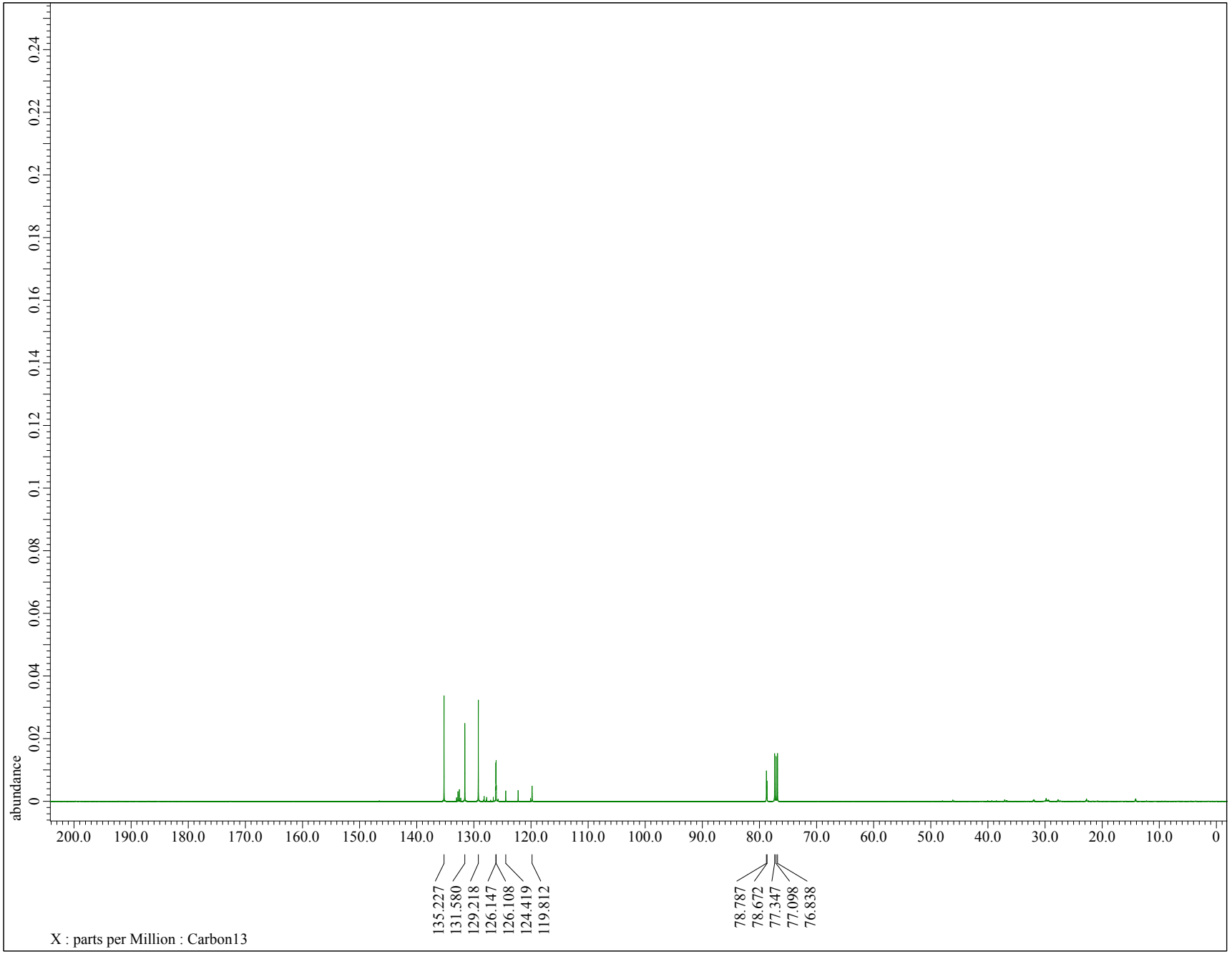

Figure S16: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2h**

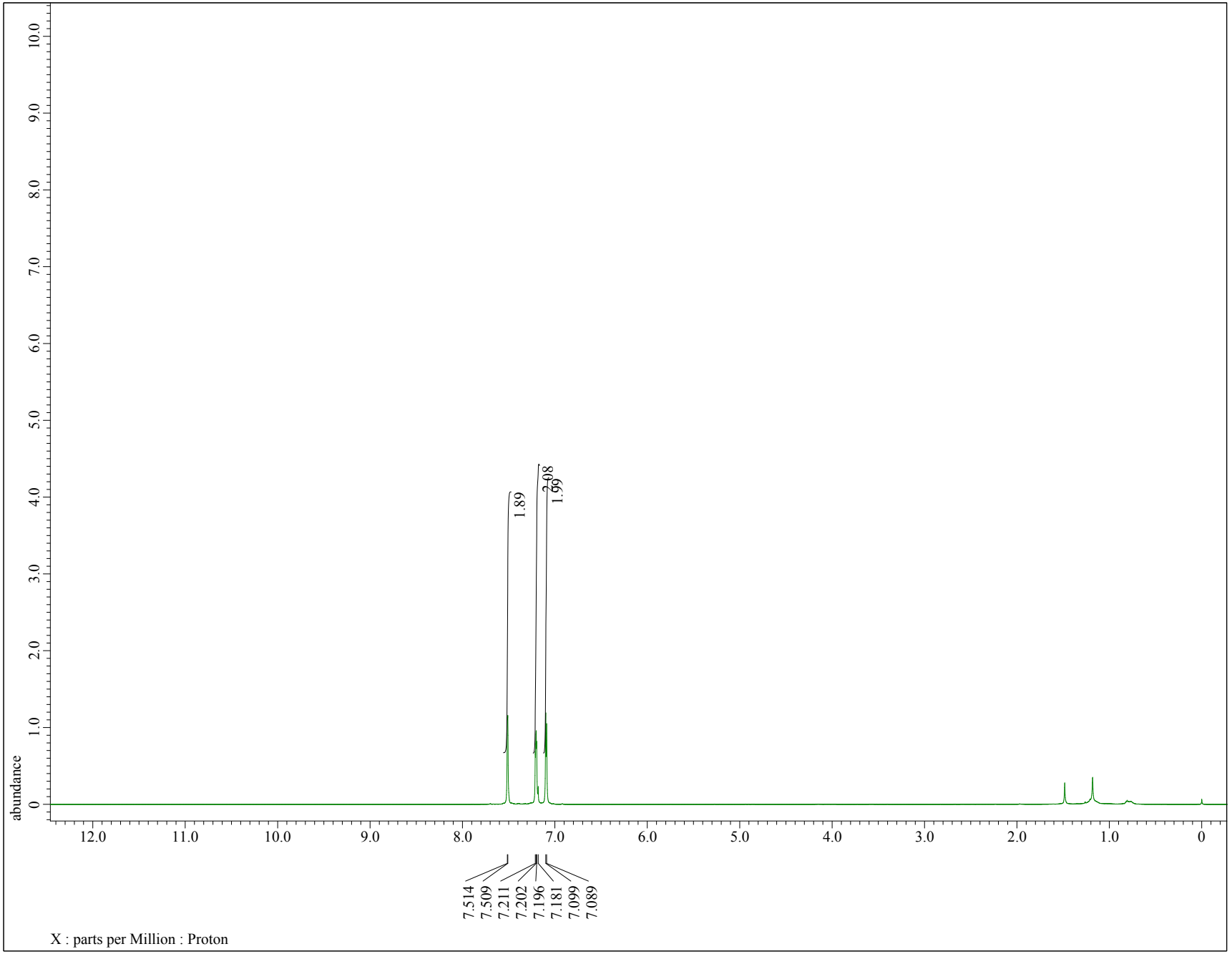

Figure S17: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2i**

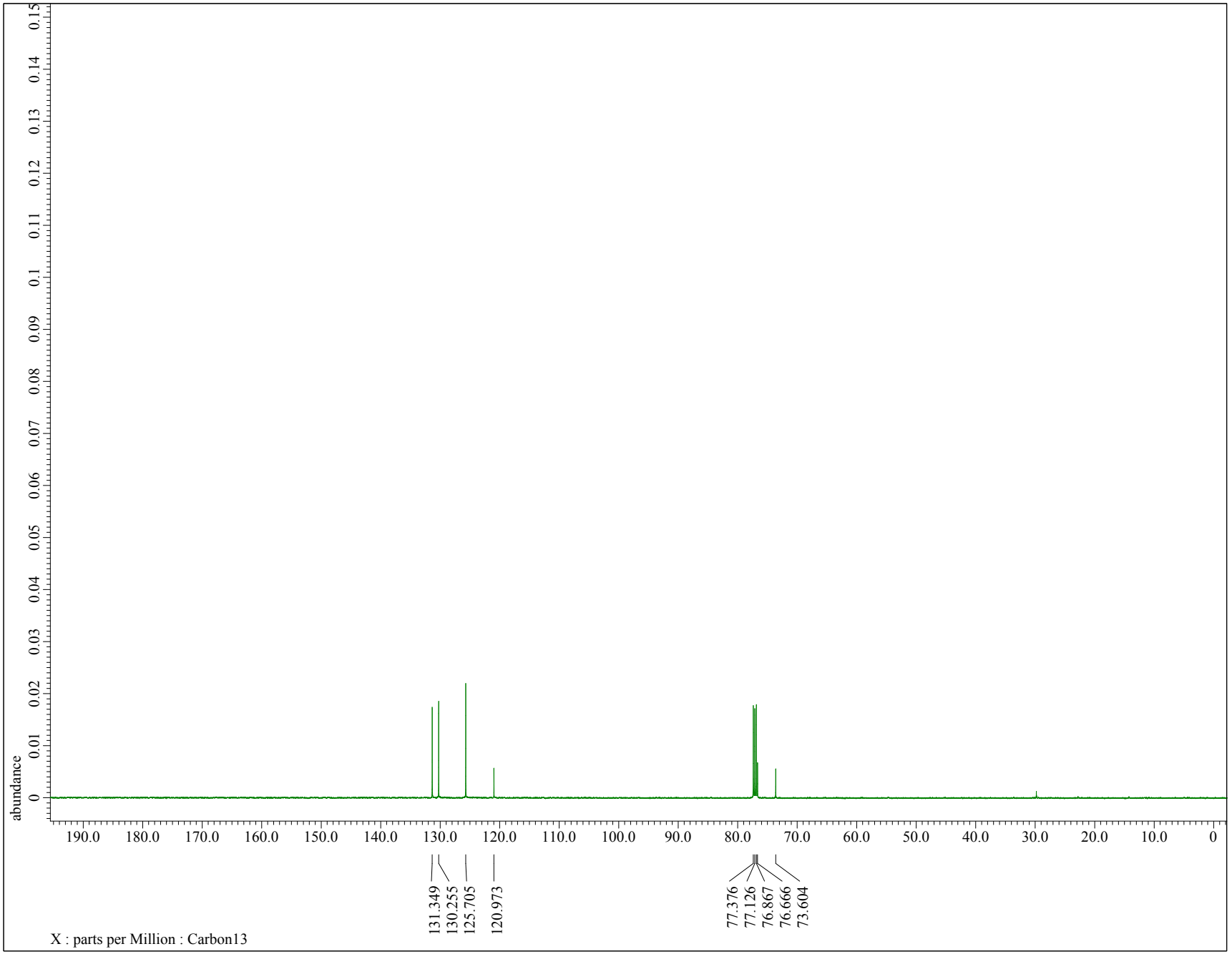

Figure S18: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2i**

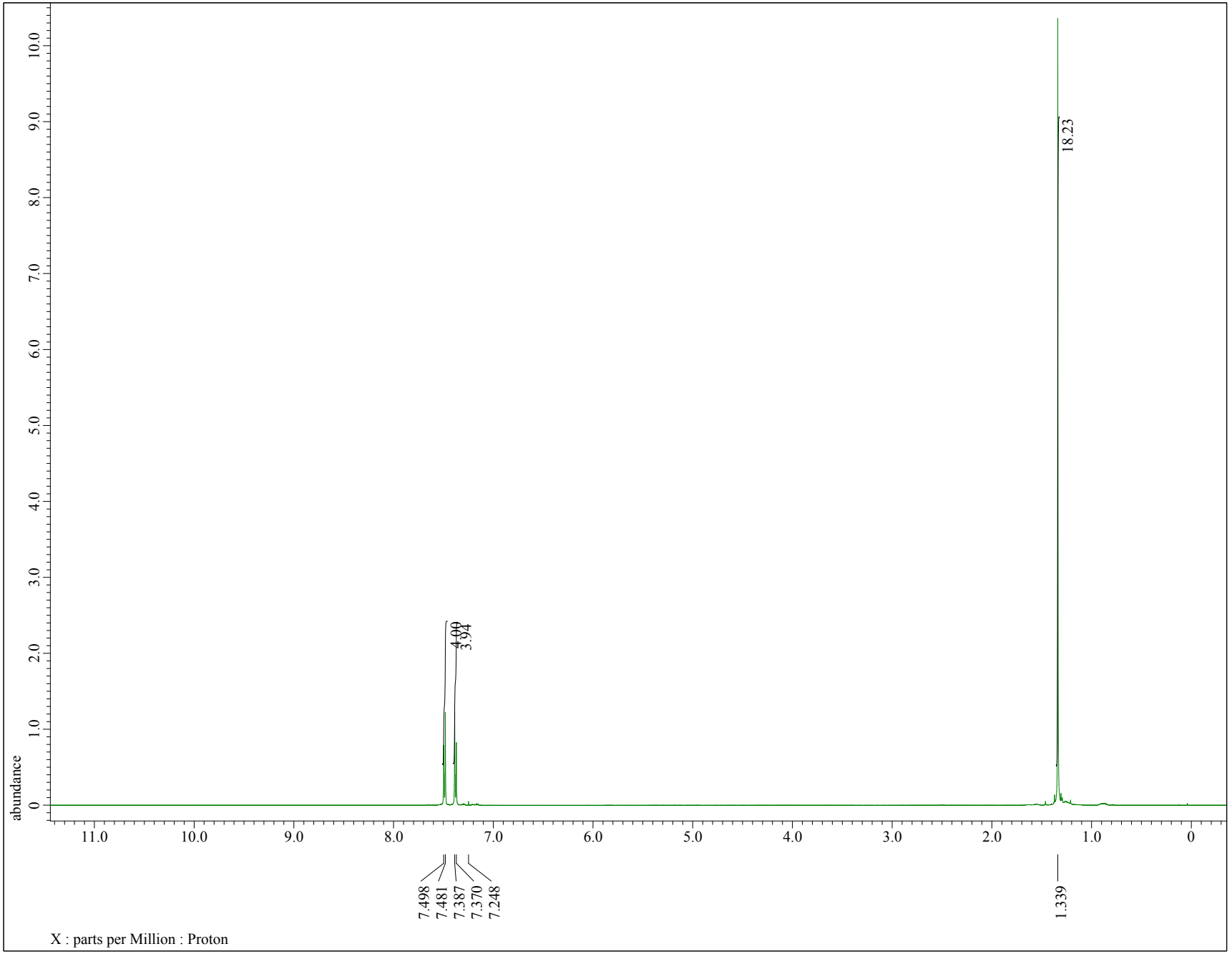

Figure S19: ^{1}HNMR (500 MHz, $CDCl_3$) of compound **2j**

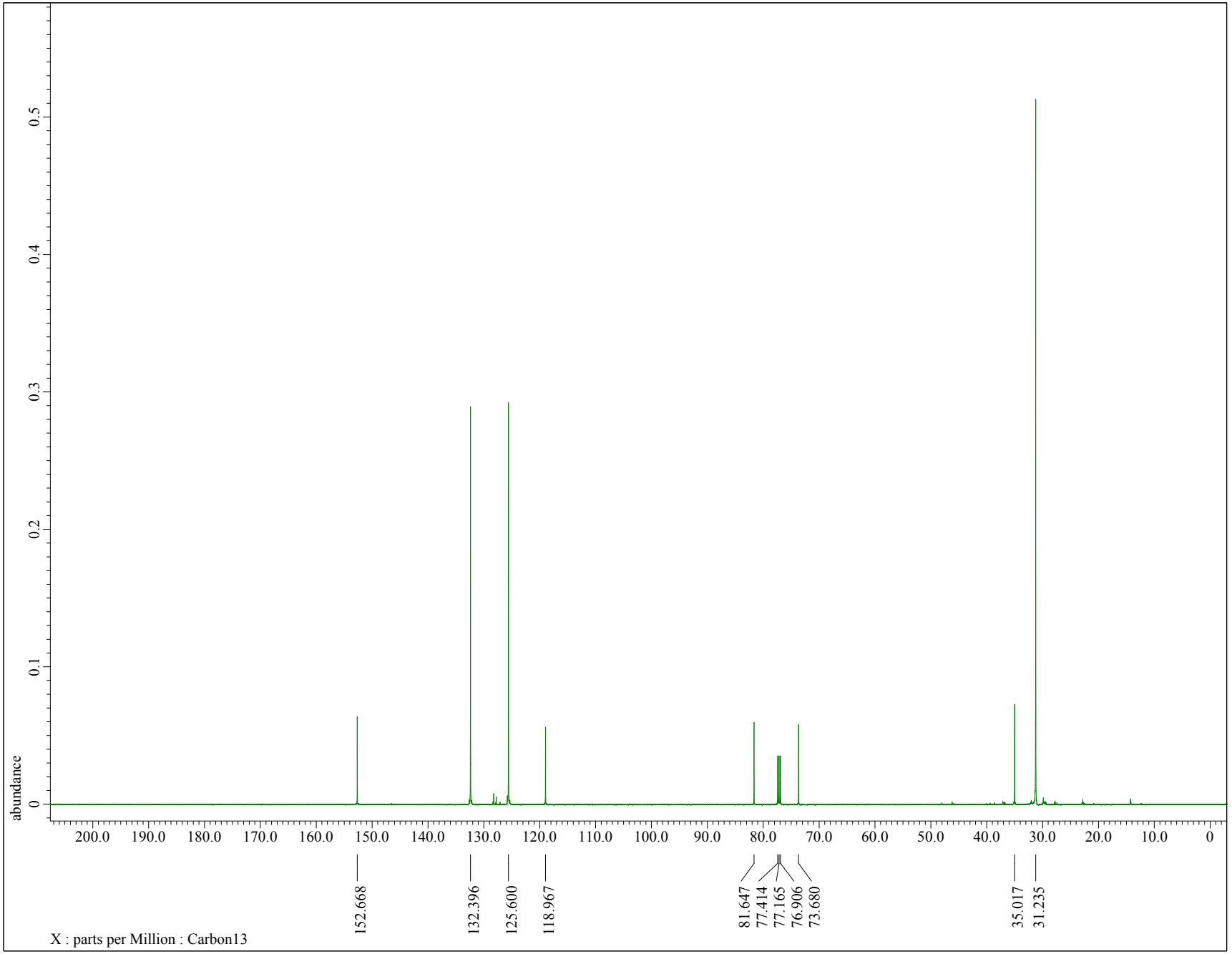

Figure S20: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2j**

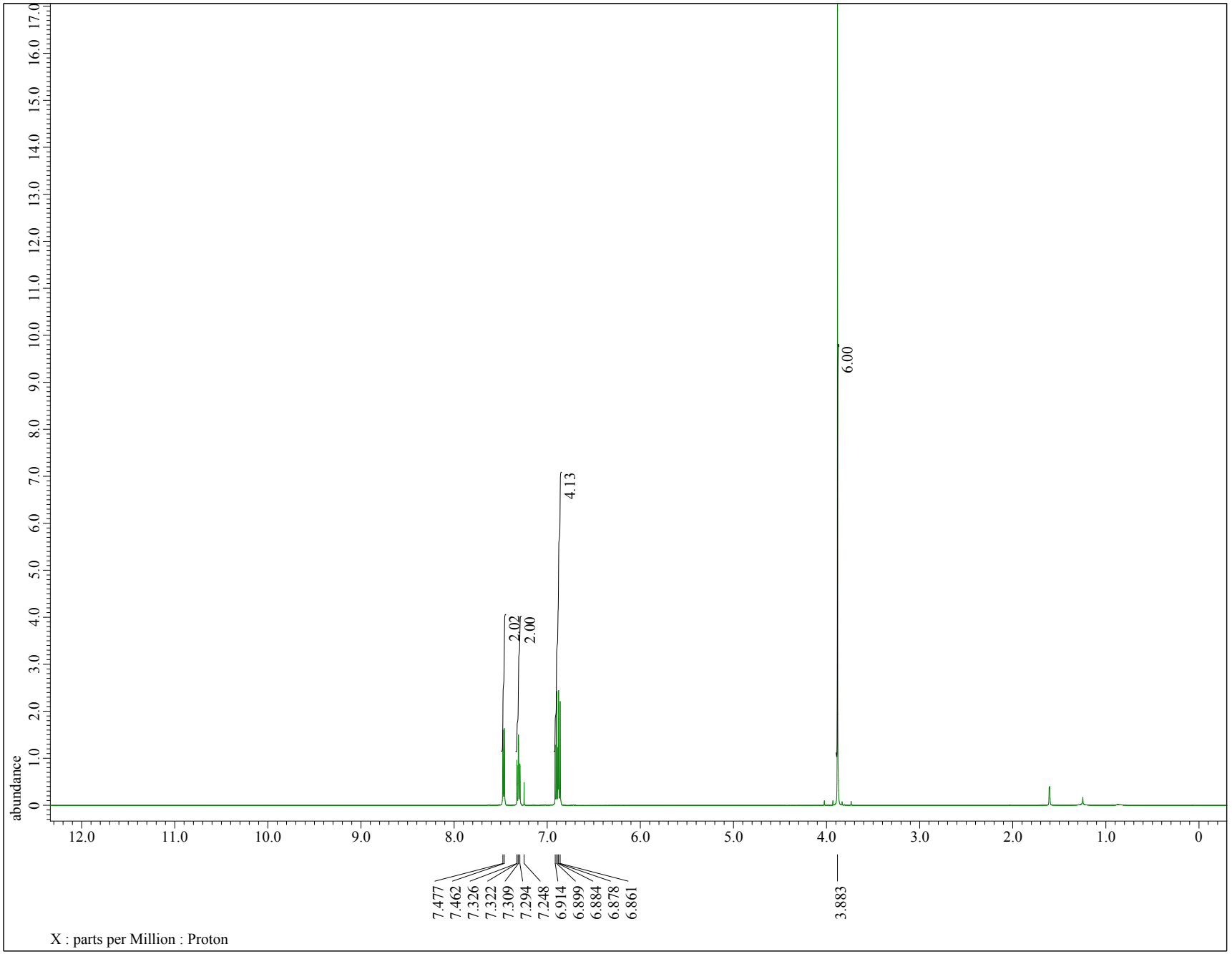

Figure S21: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2k**

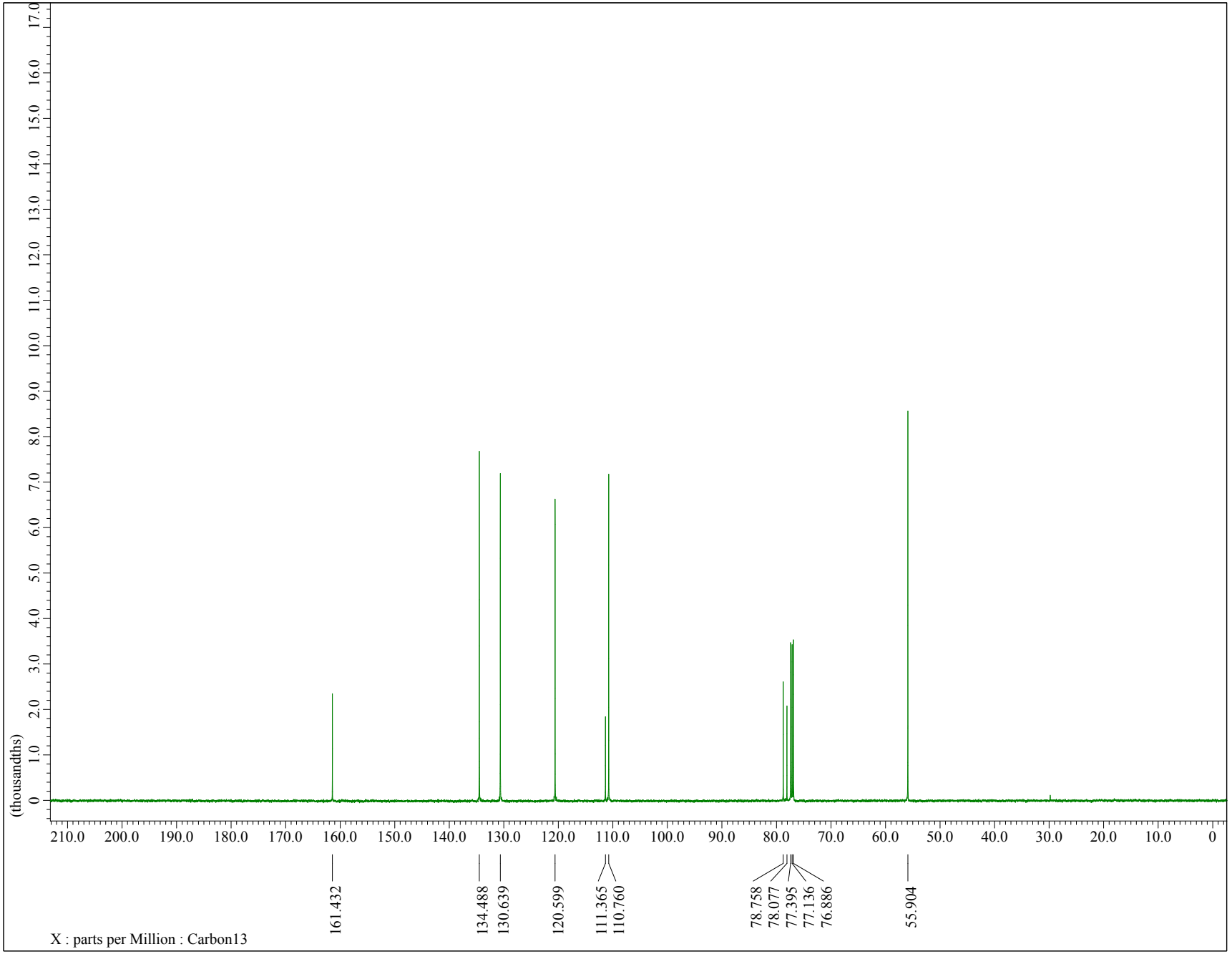

Figure S22: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2k**

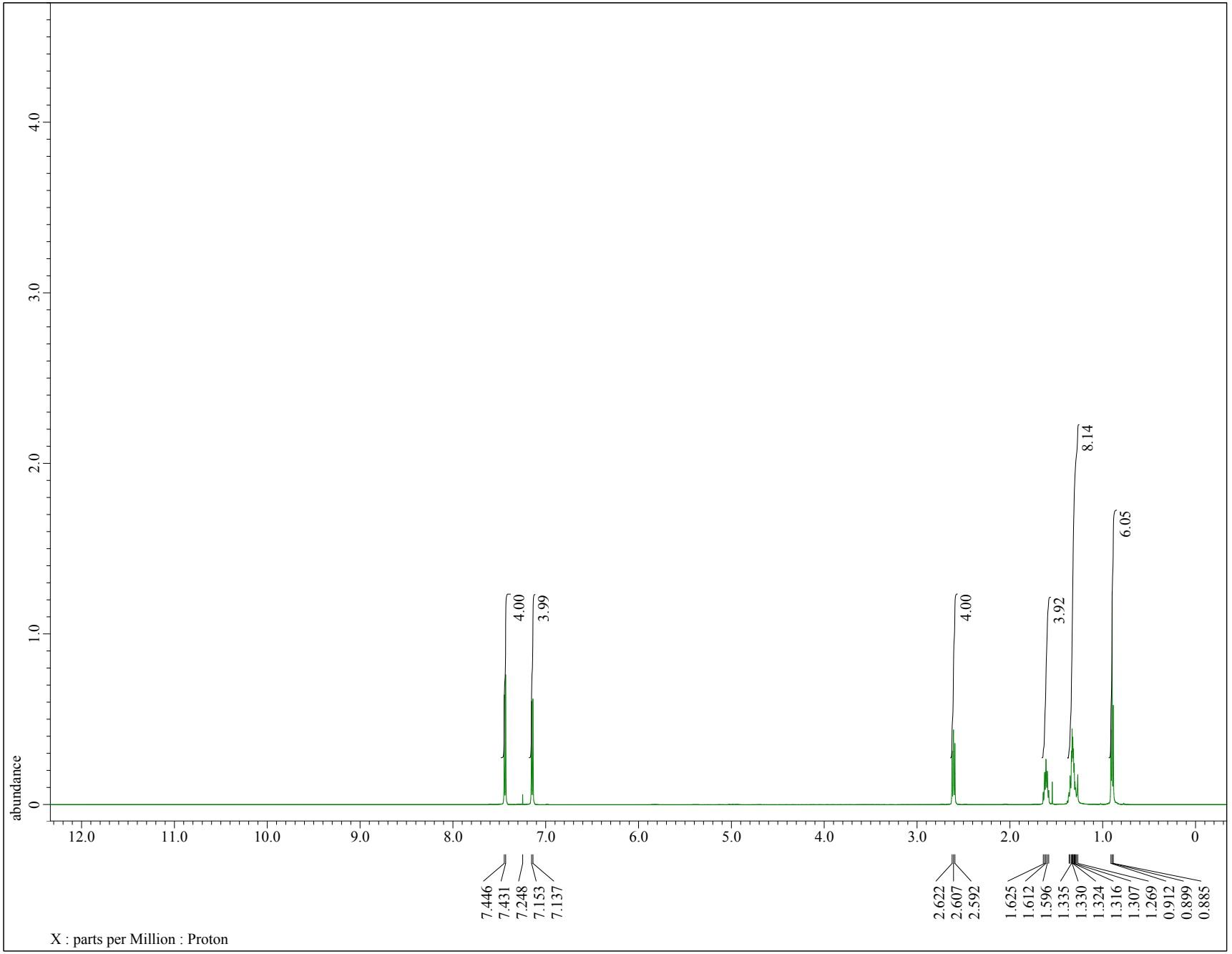

Figure S23: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2l**

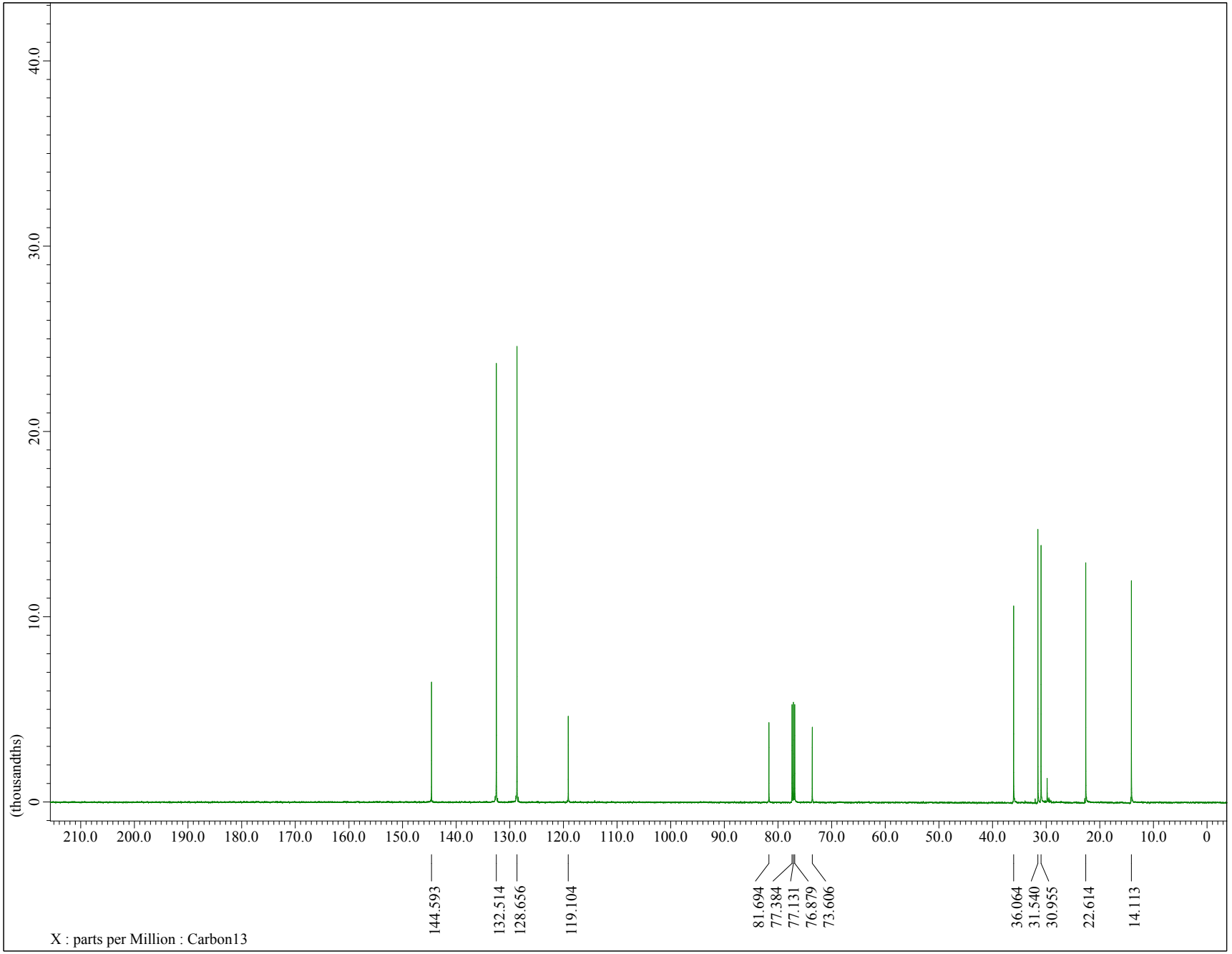

Figure S24: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2l**

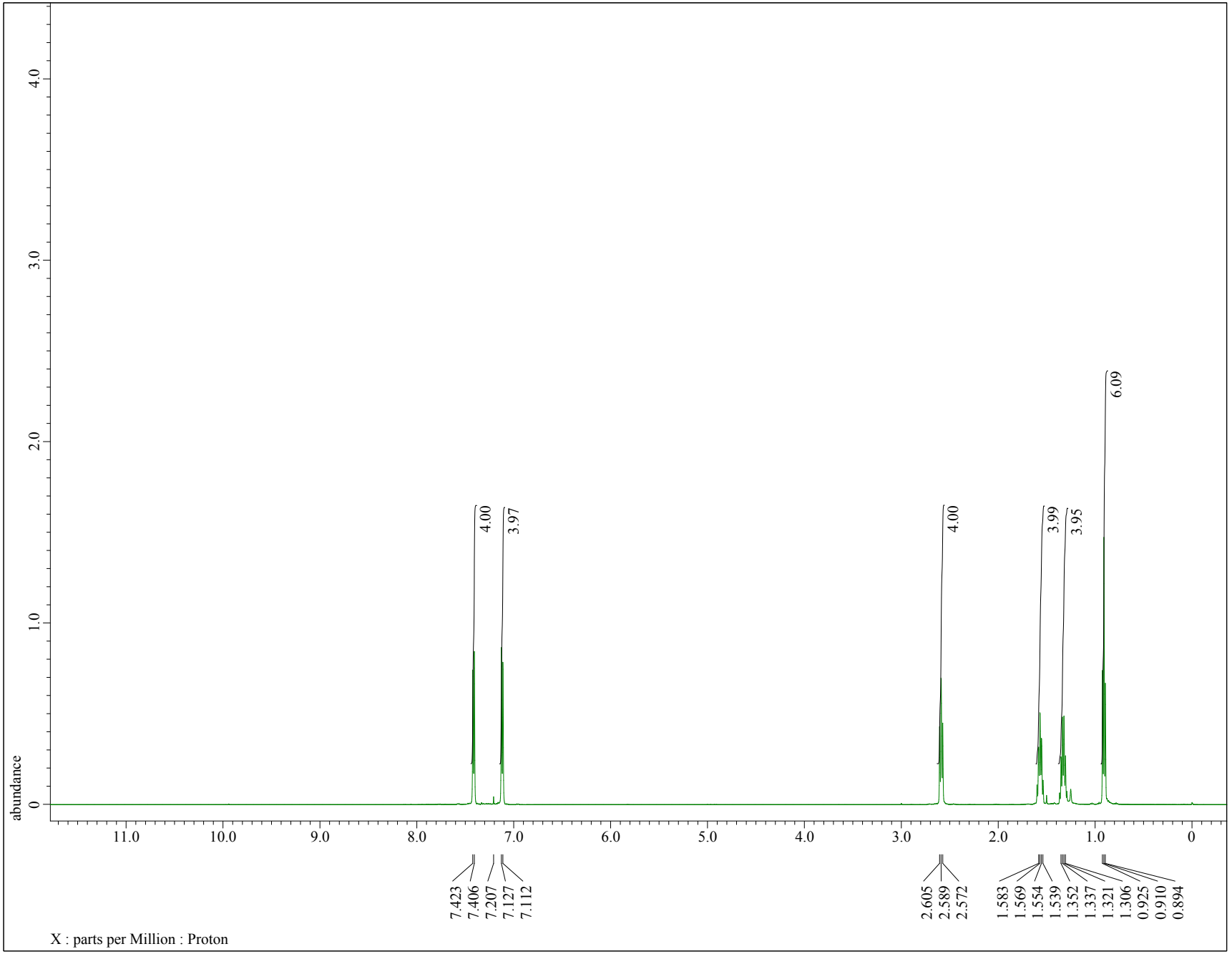

Figure S25: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2m**

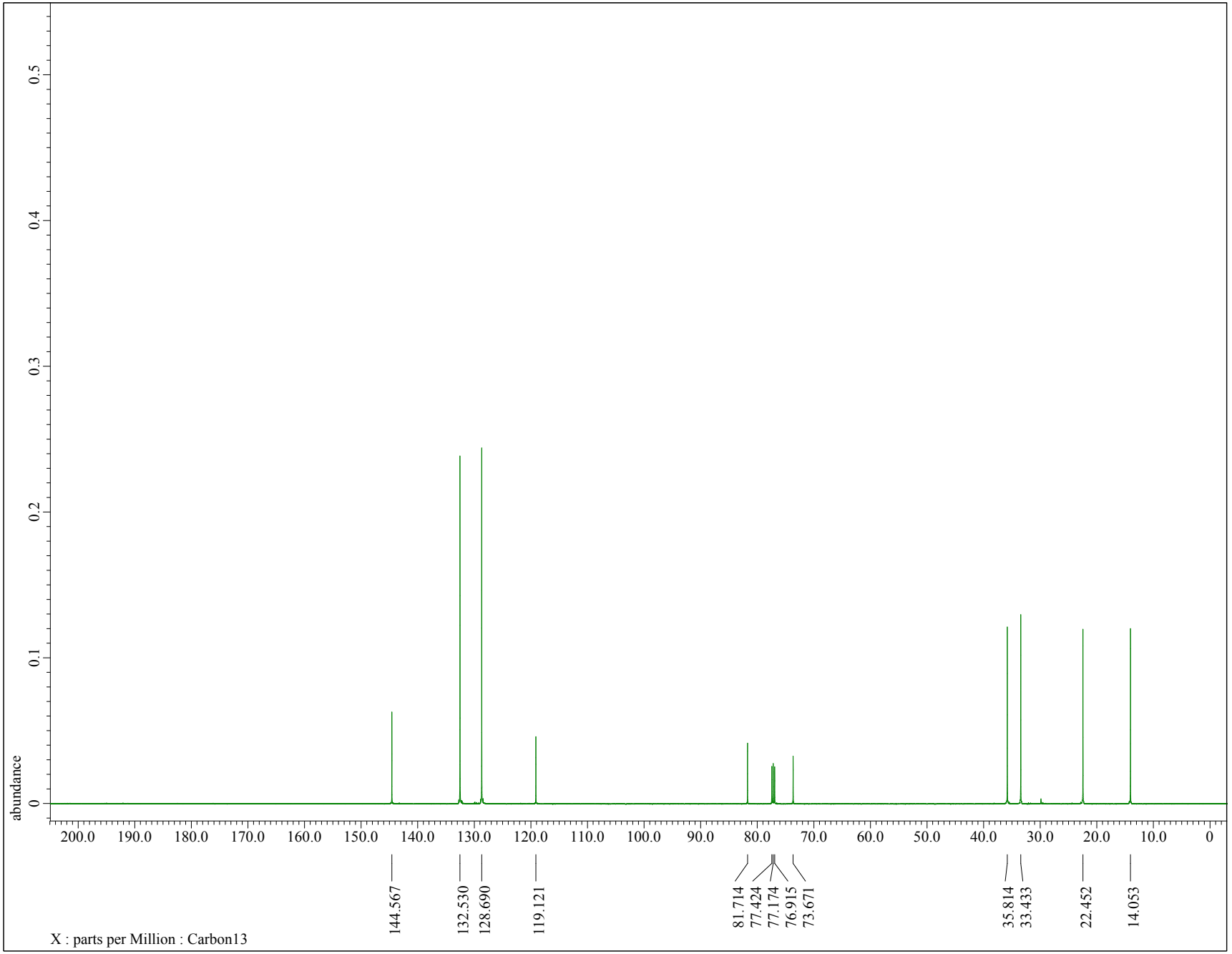

Figure S26: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2m**

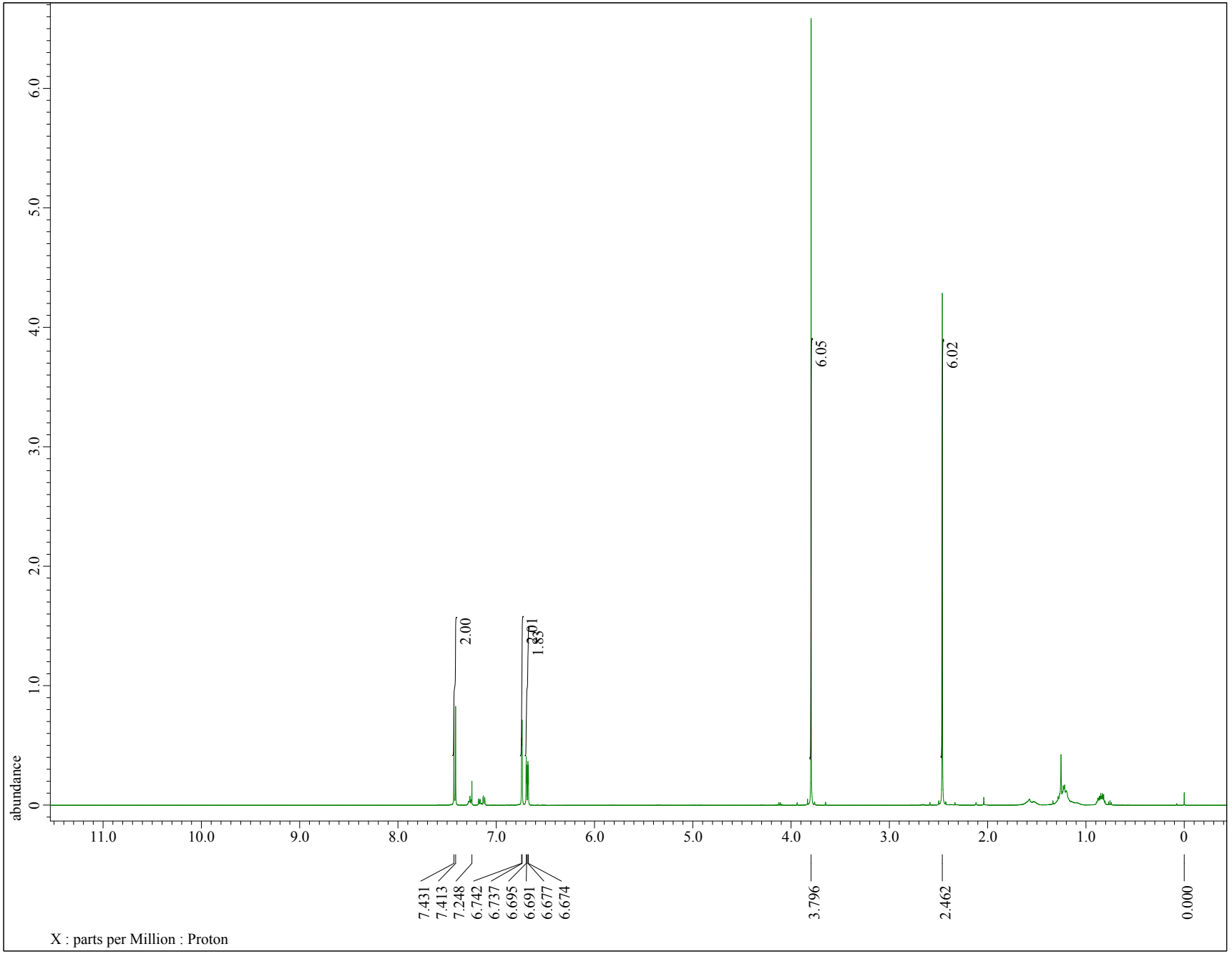

Figure S27: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2n**

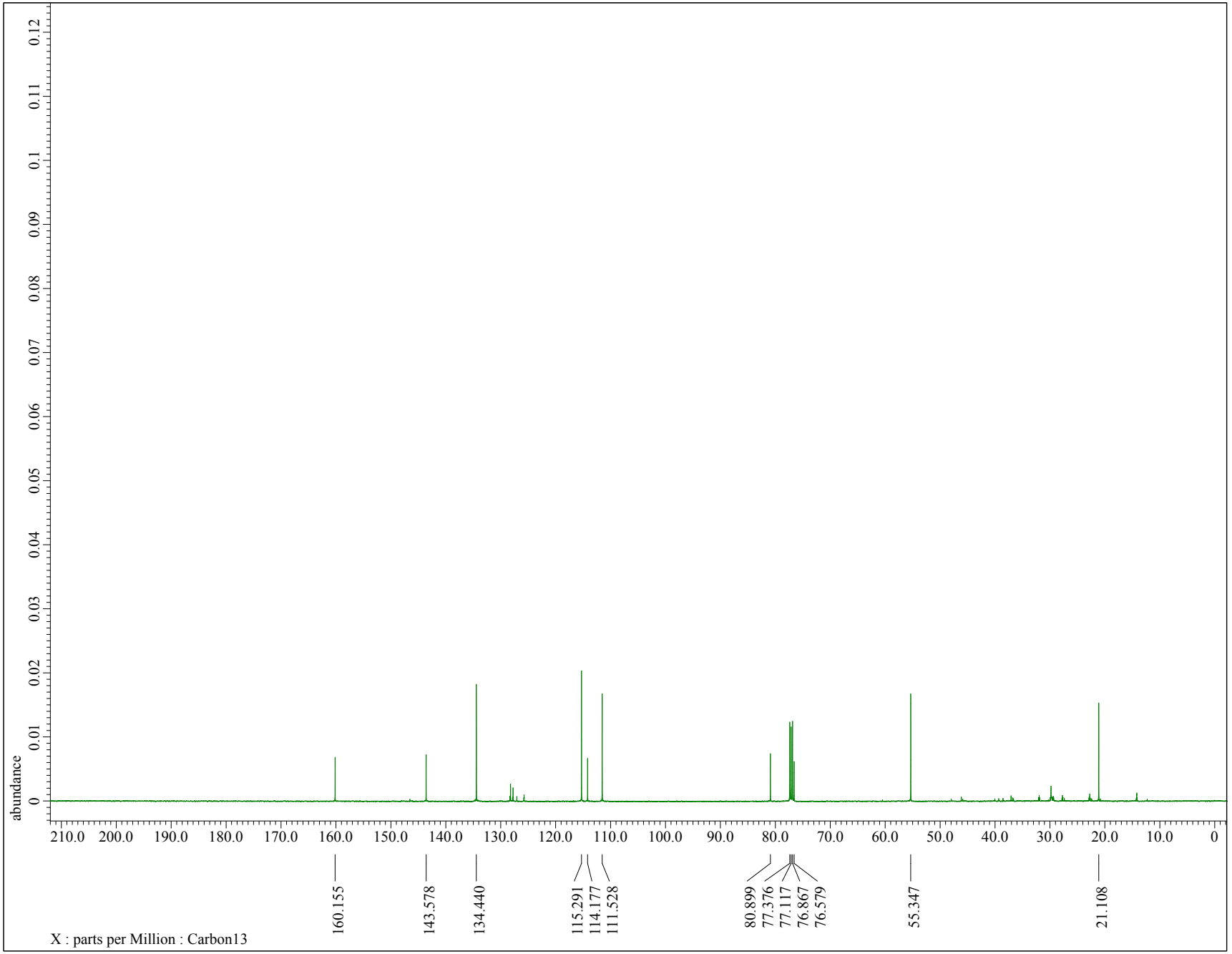

Figure S28: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2n**

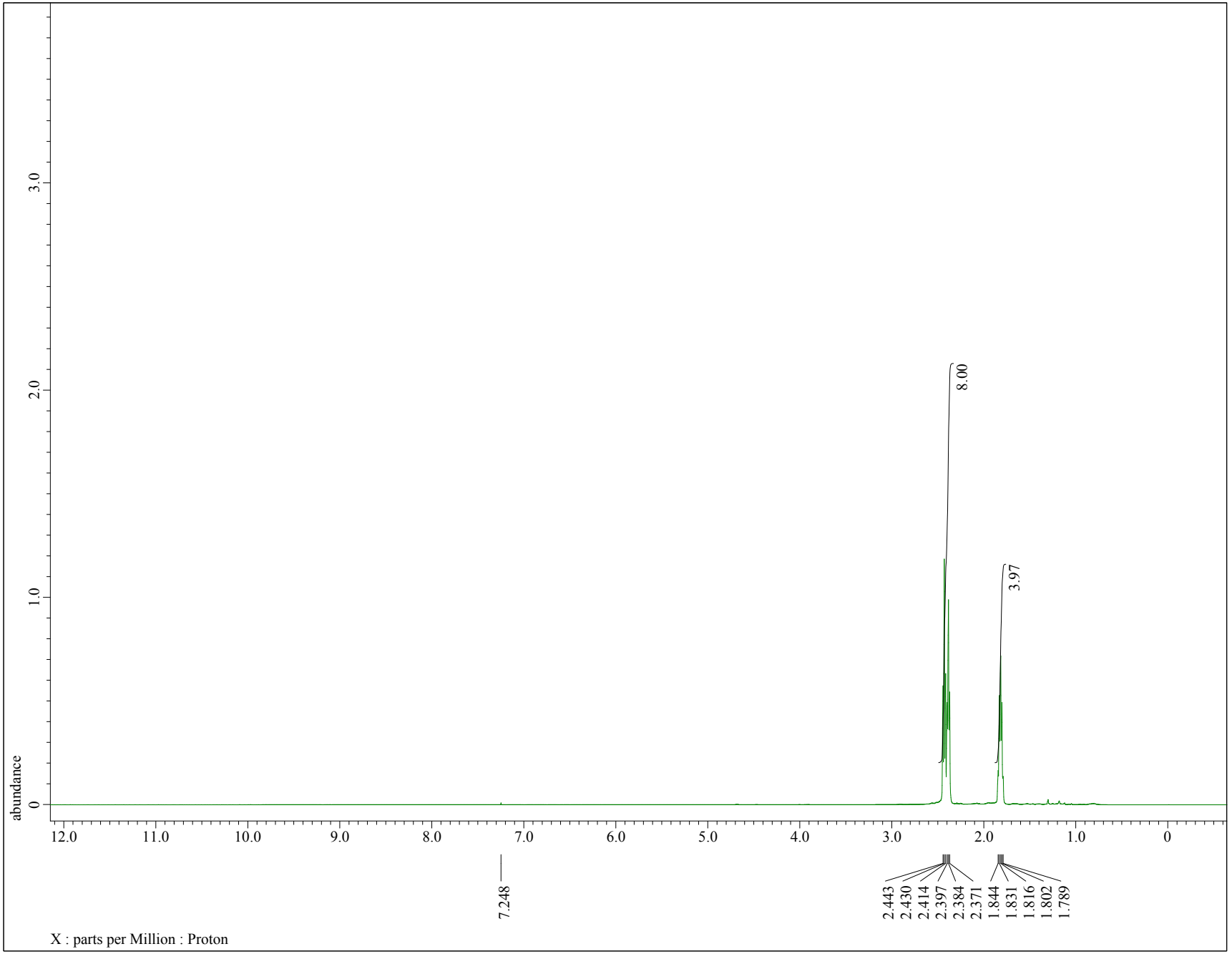

Figure S29: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2o**

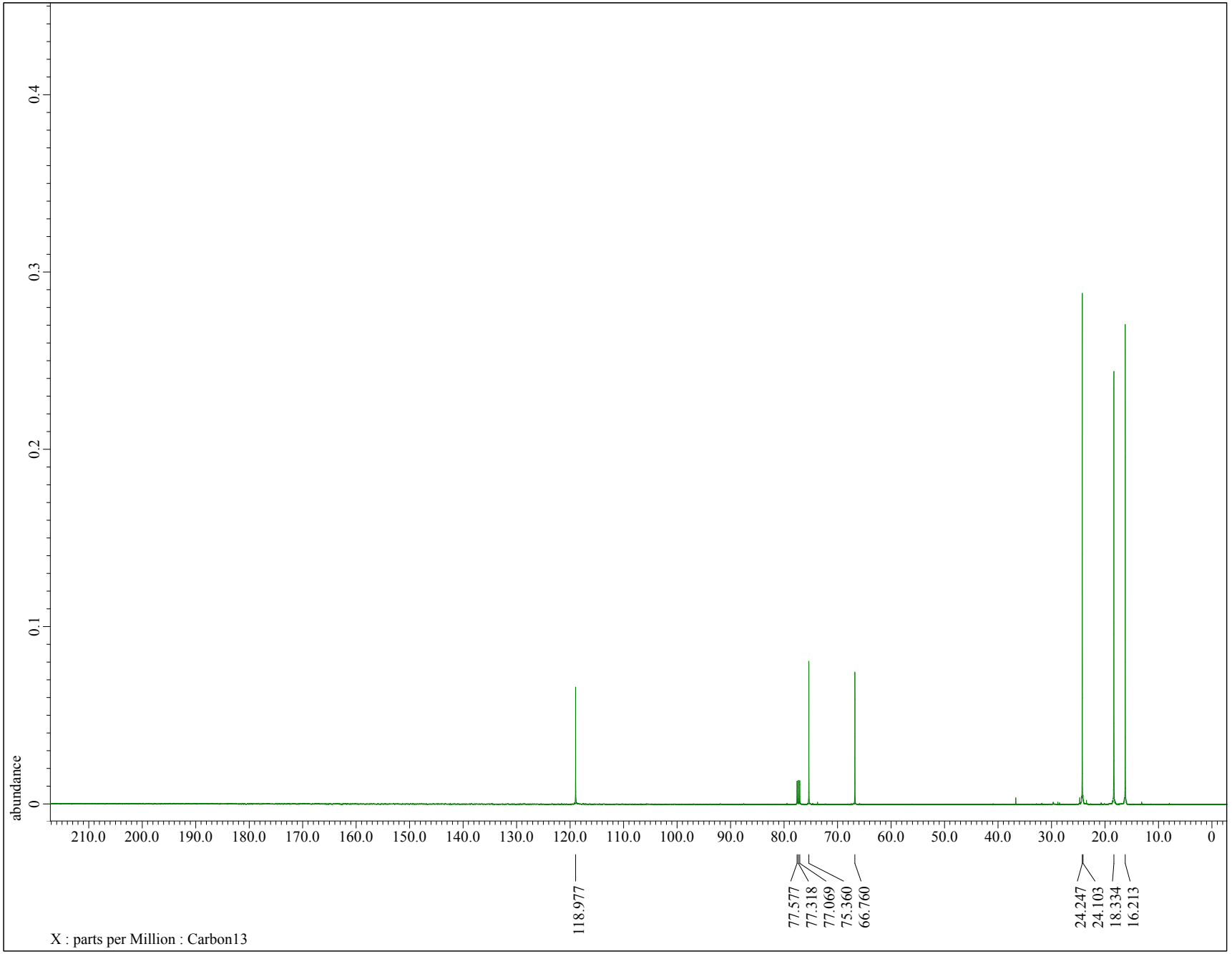

Figure S30: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2o**

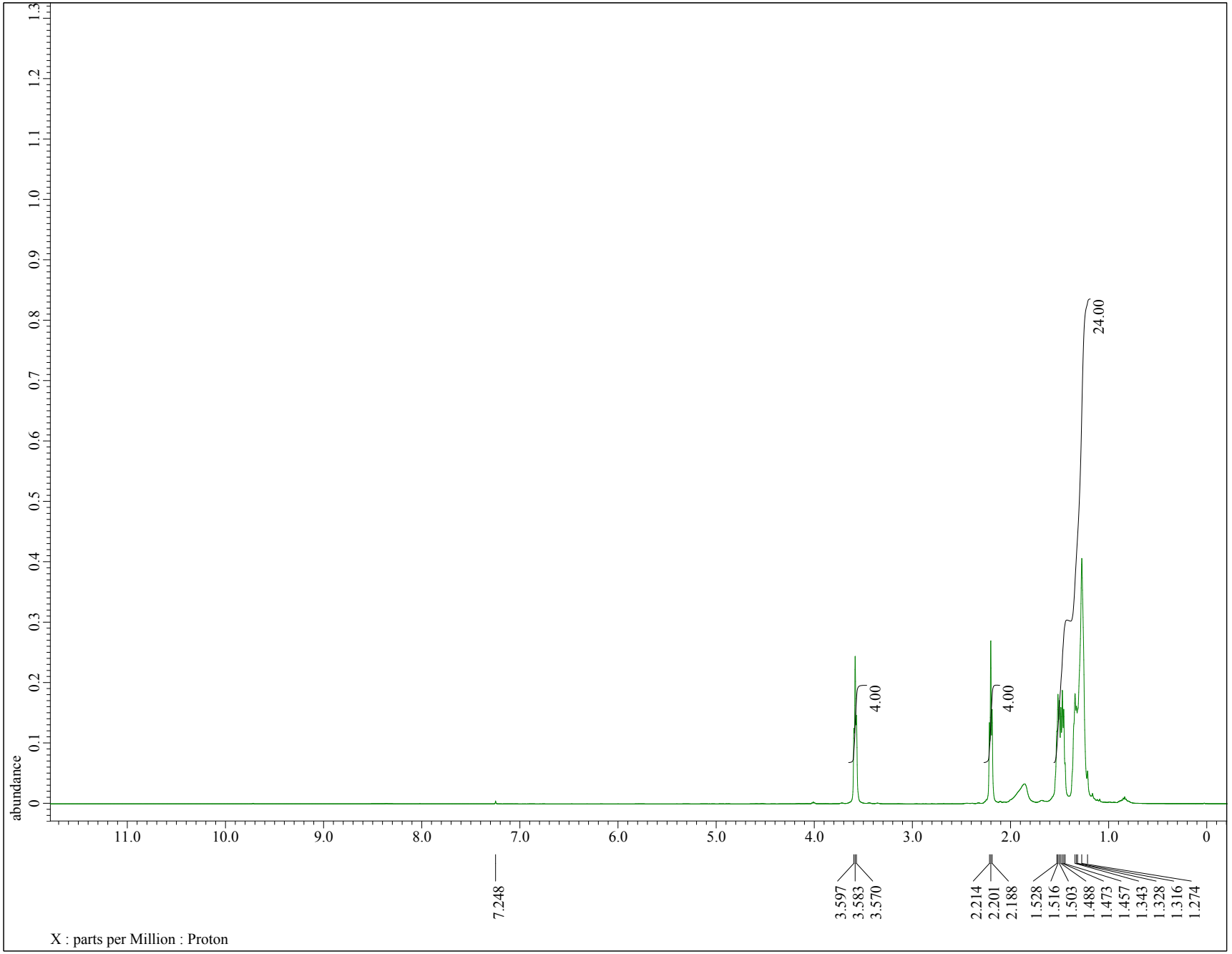

Figure S31: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2p**

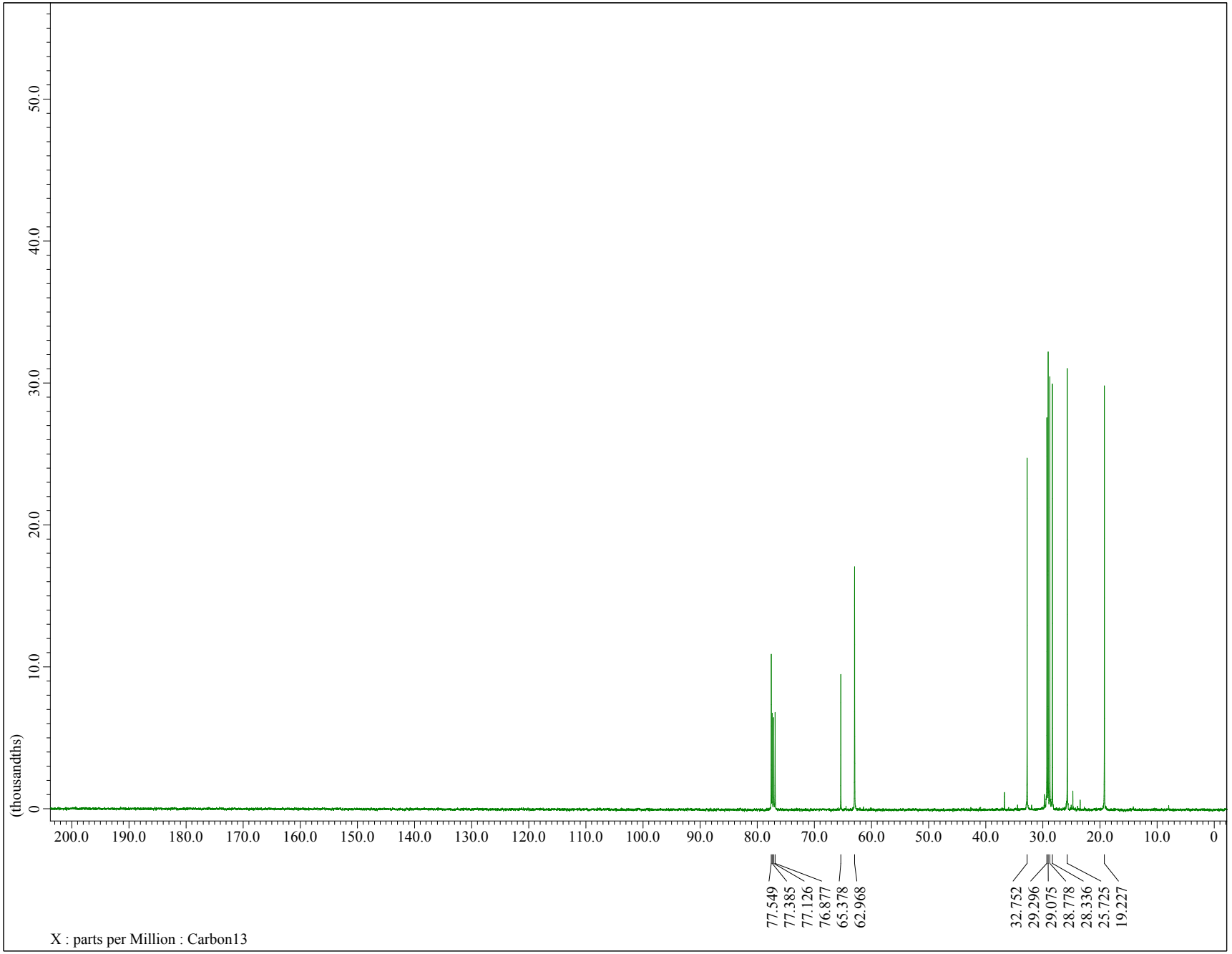

Figure S32: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2p**

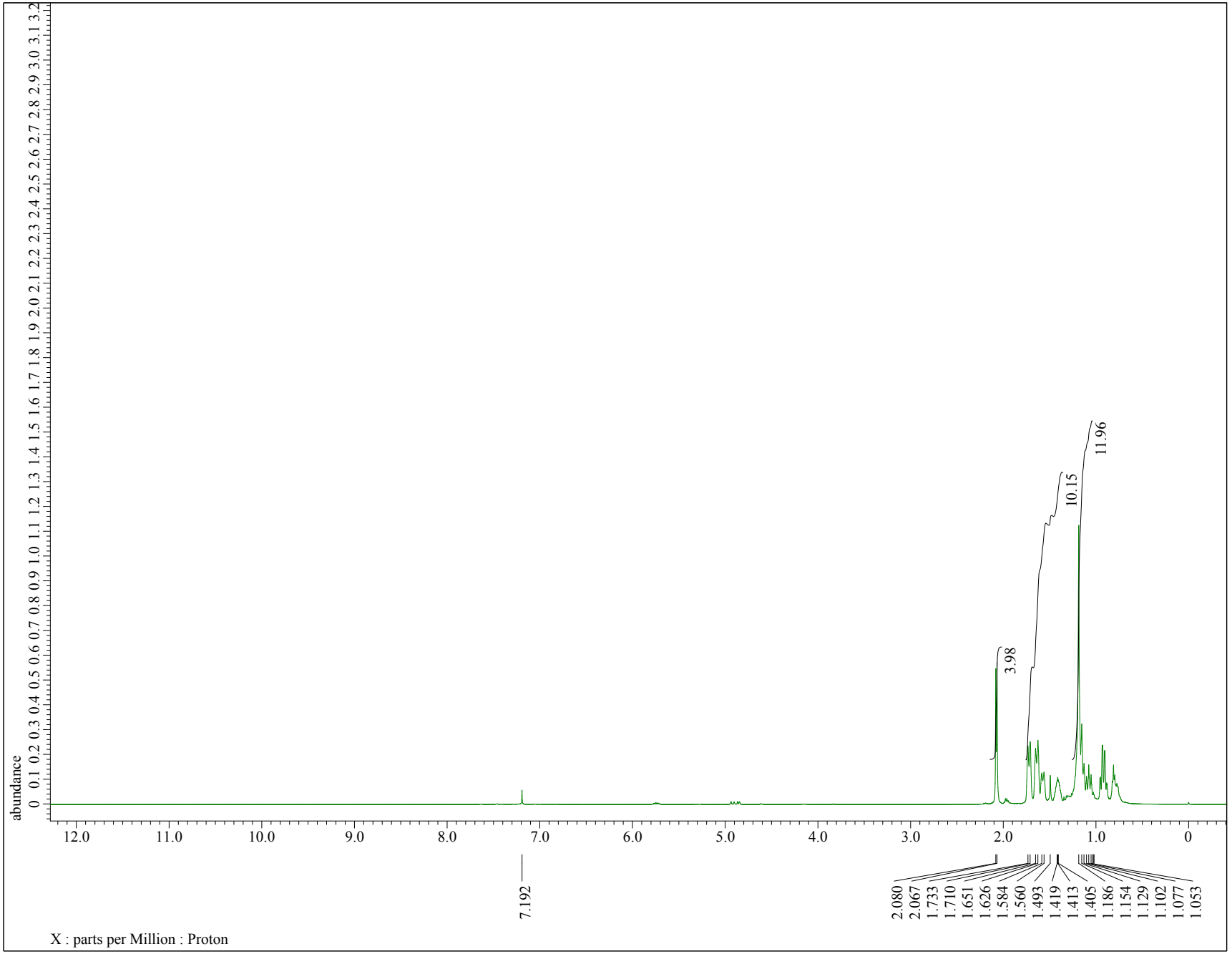

Figure S33: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2q**

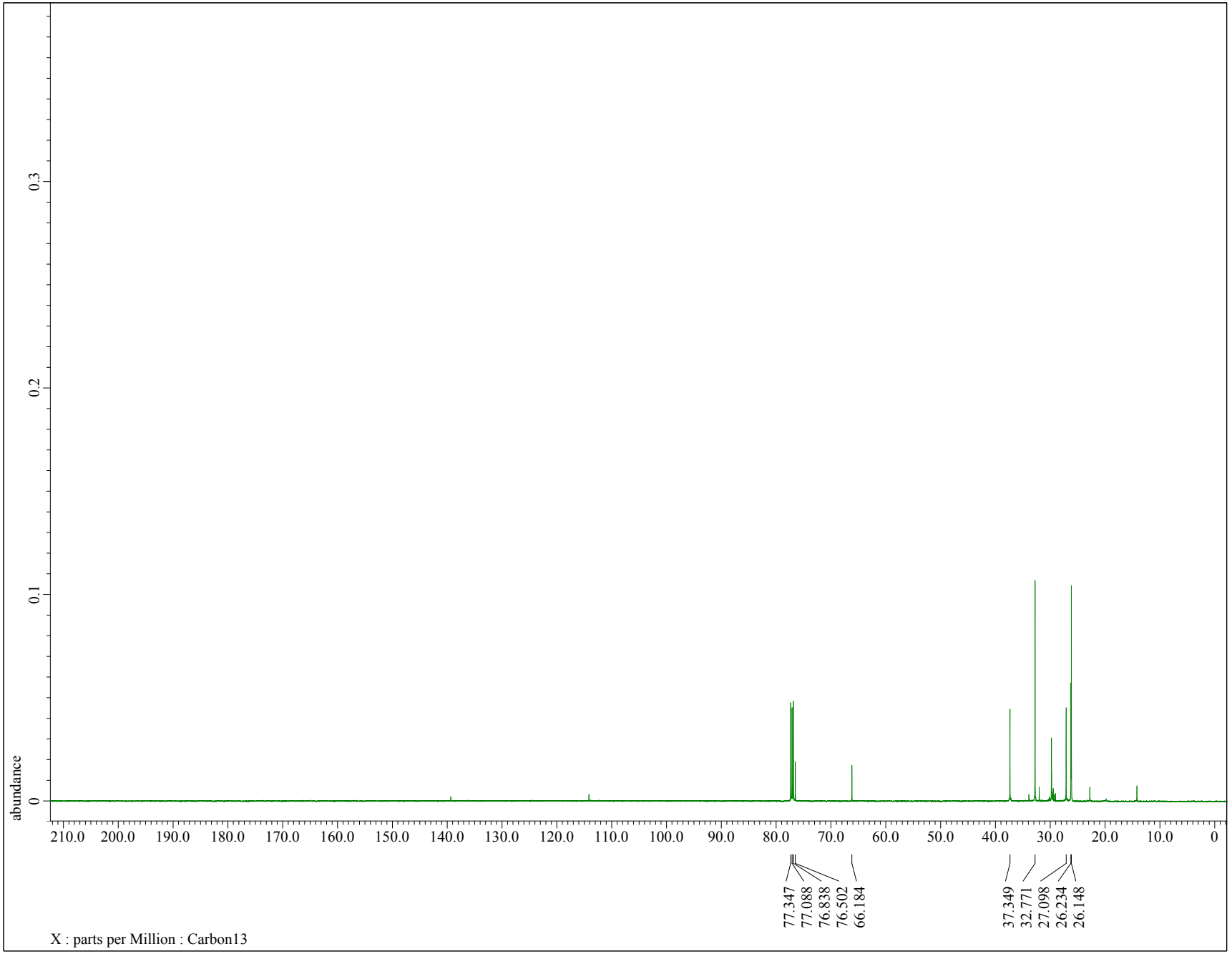

Figure 34: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2q**

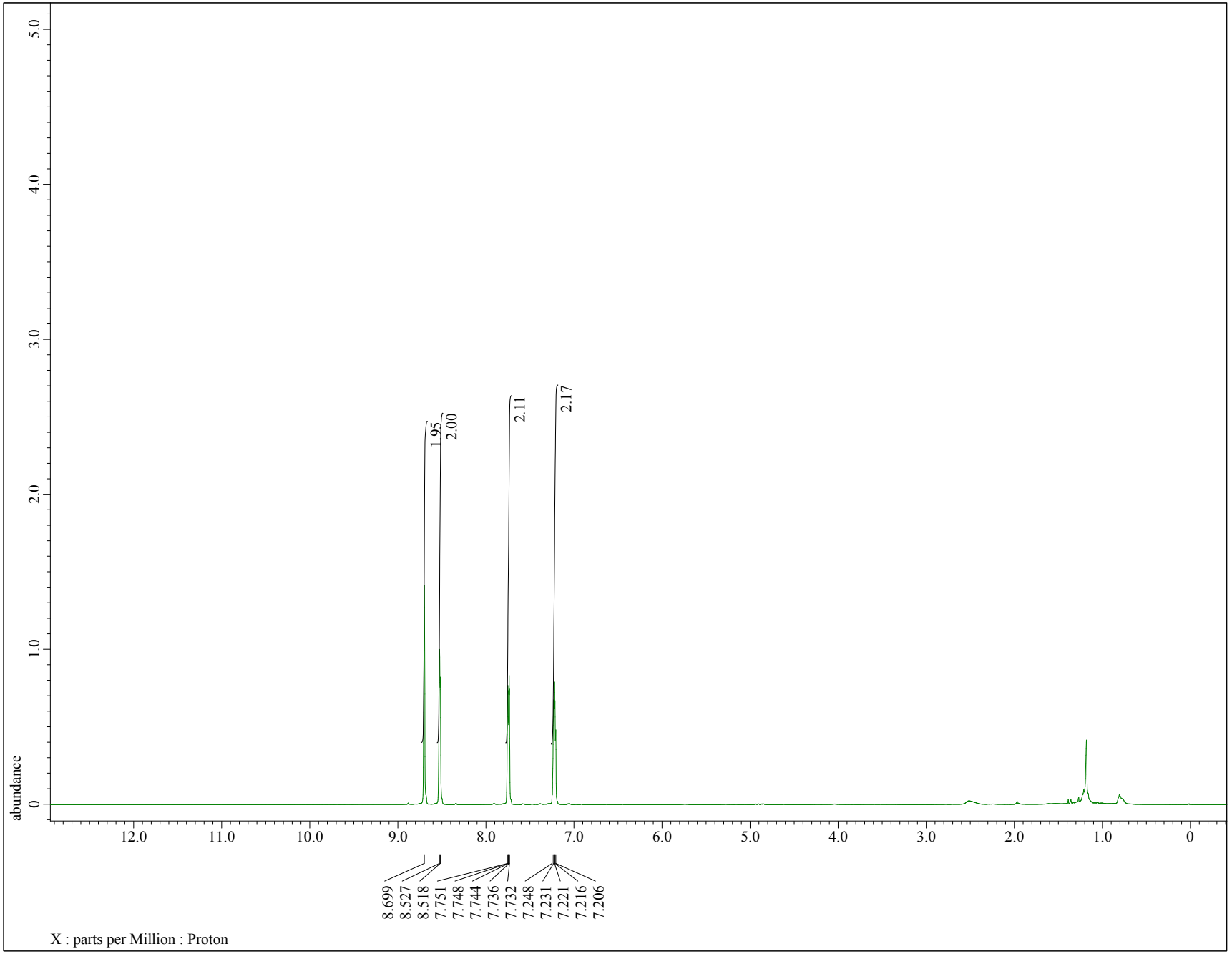

Figure S35: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2r**

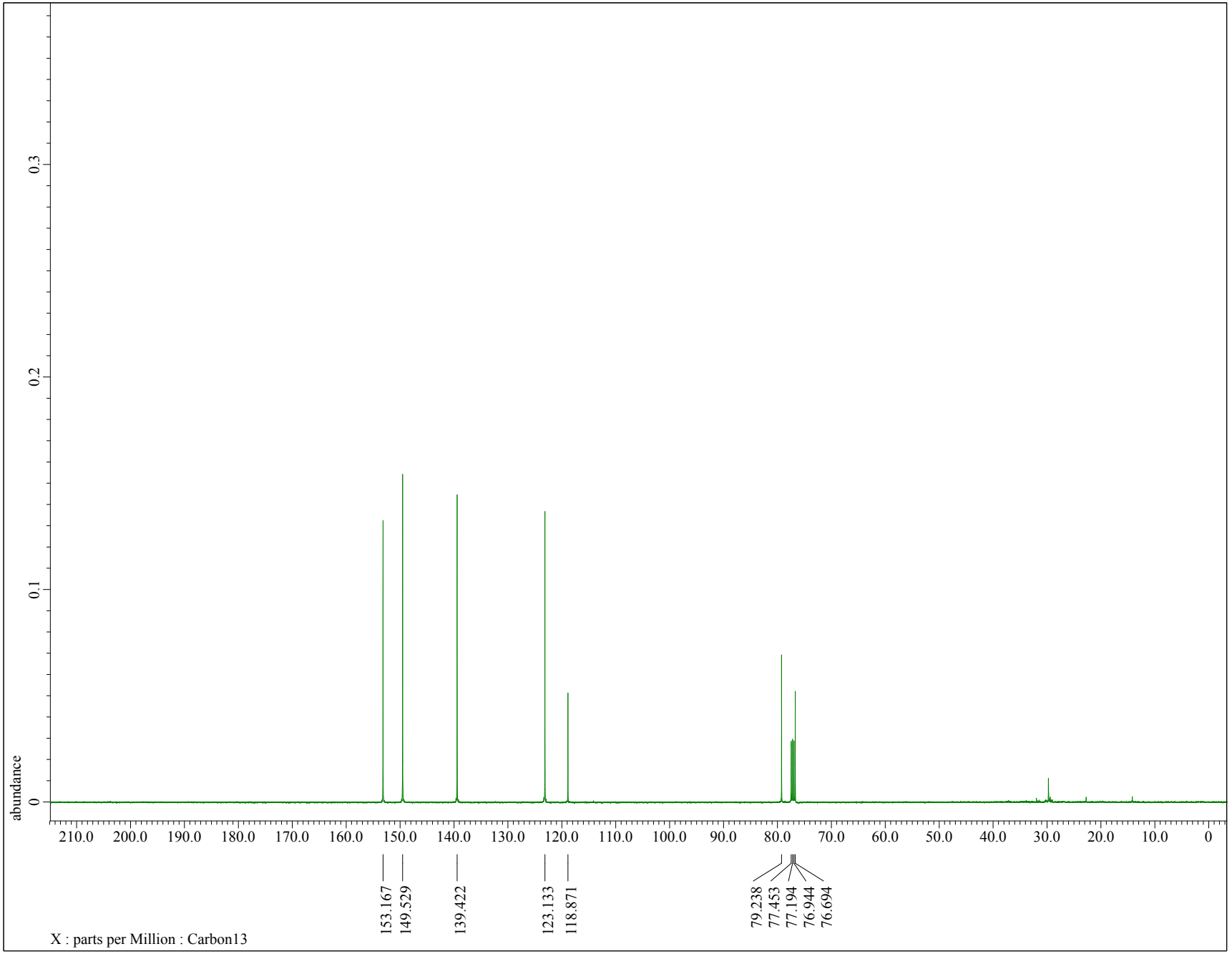

Figure S36: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2r**

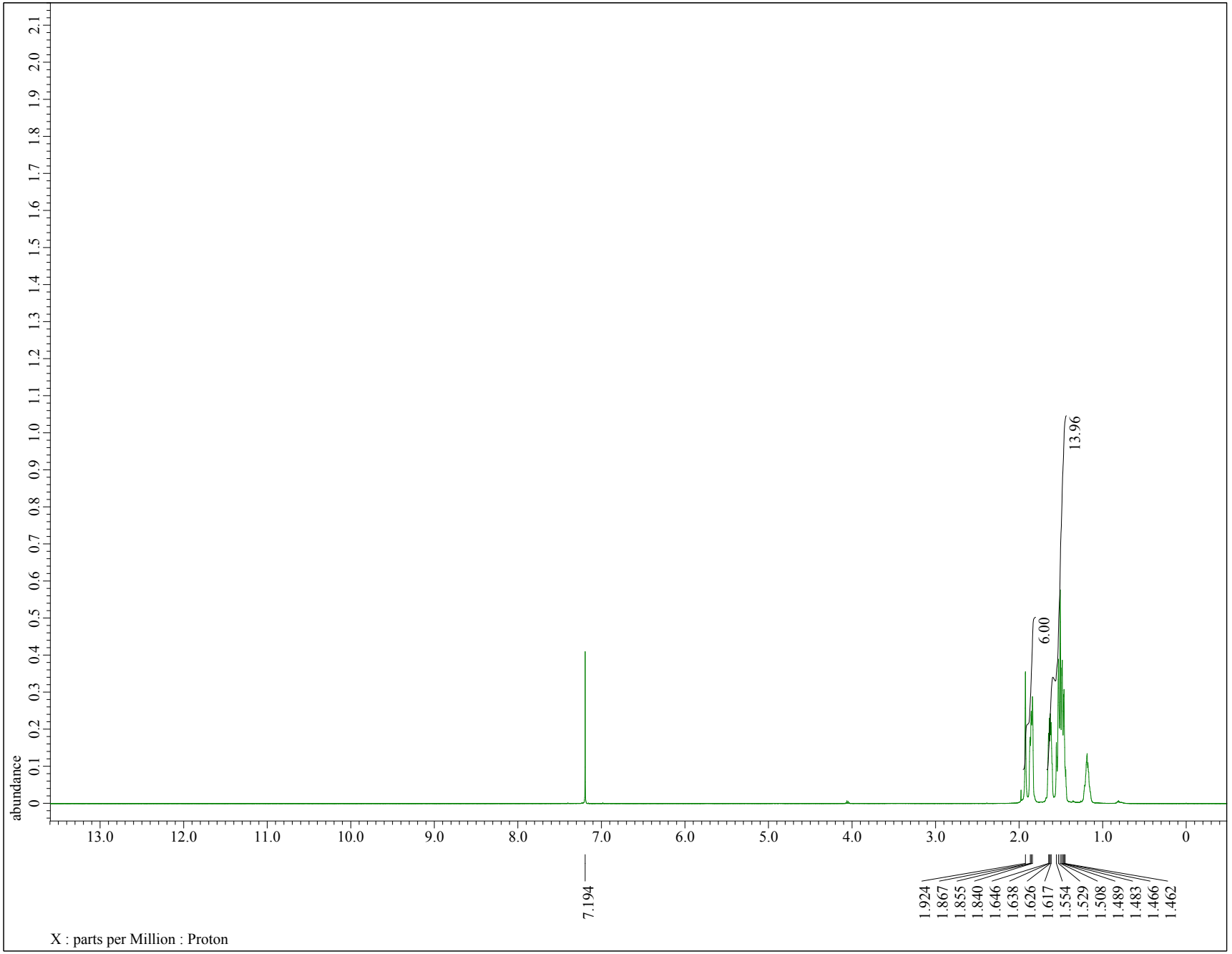

Figure S37: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2s**

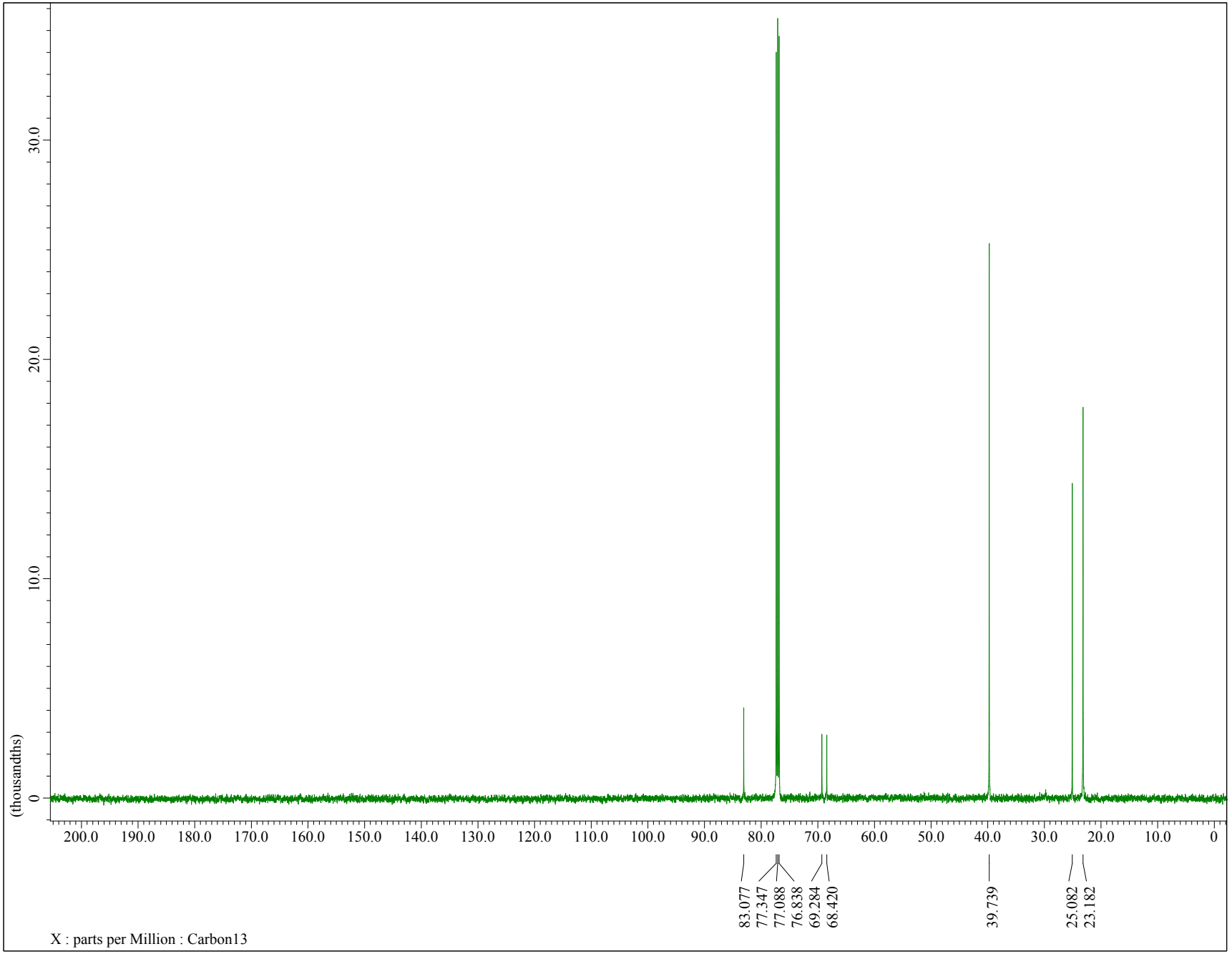

Figure S38: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2s**

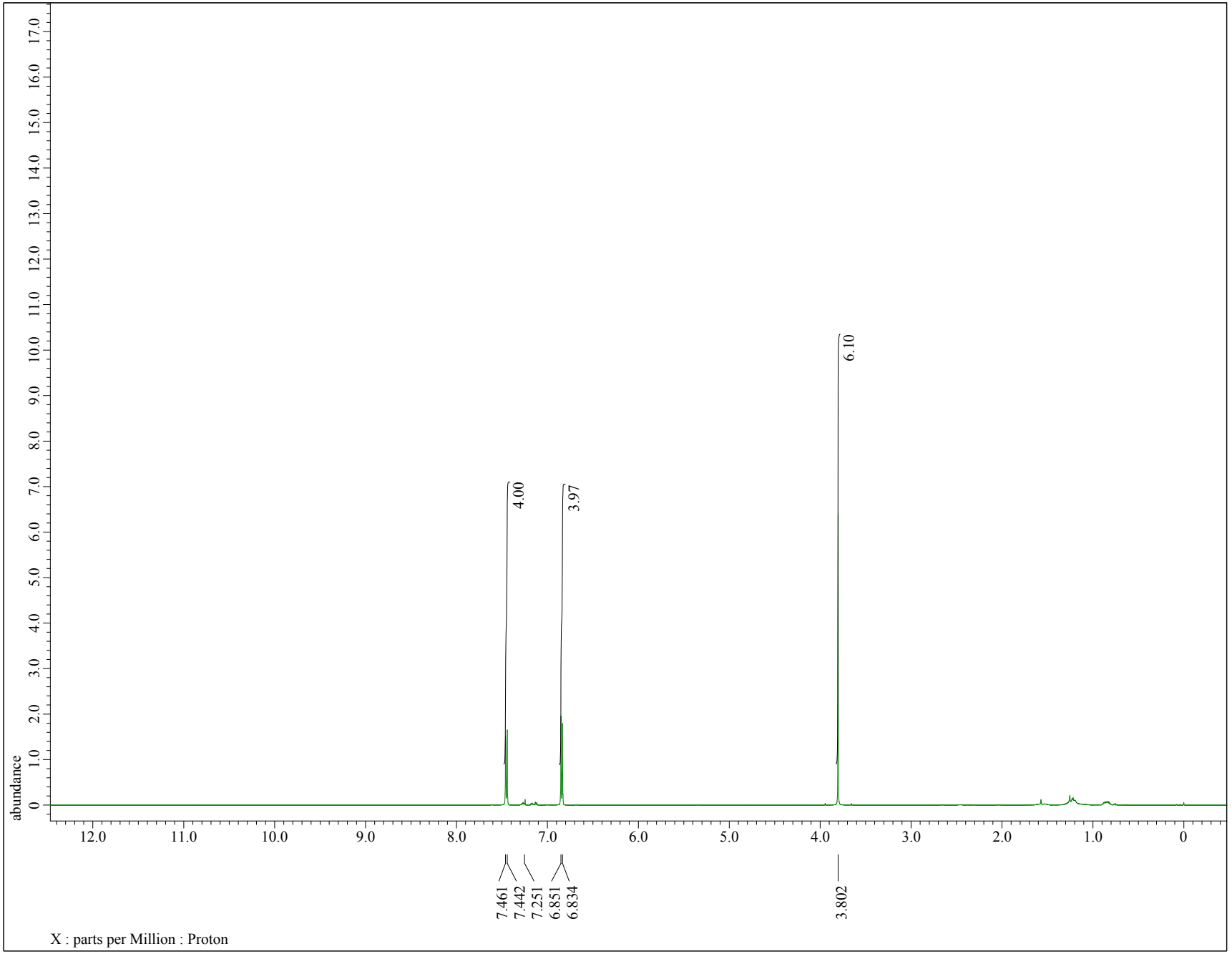

Figure S39: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2t**

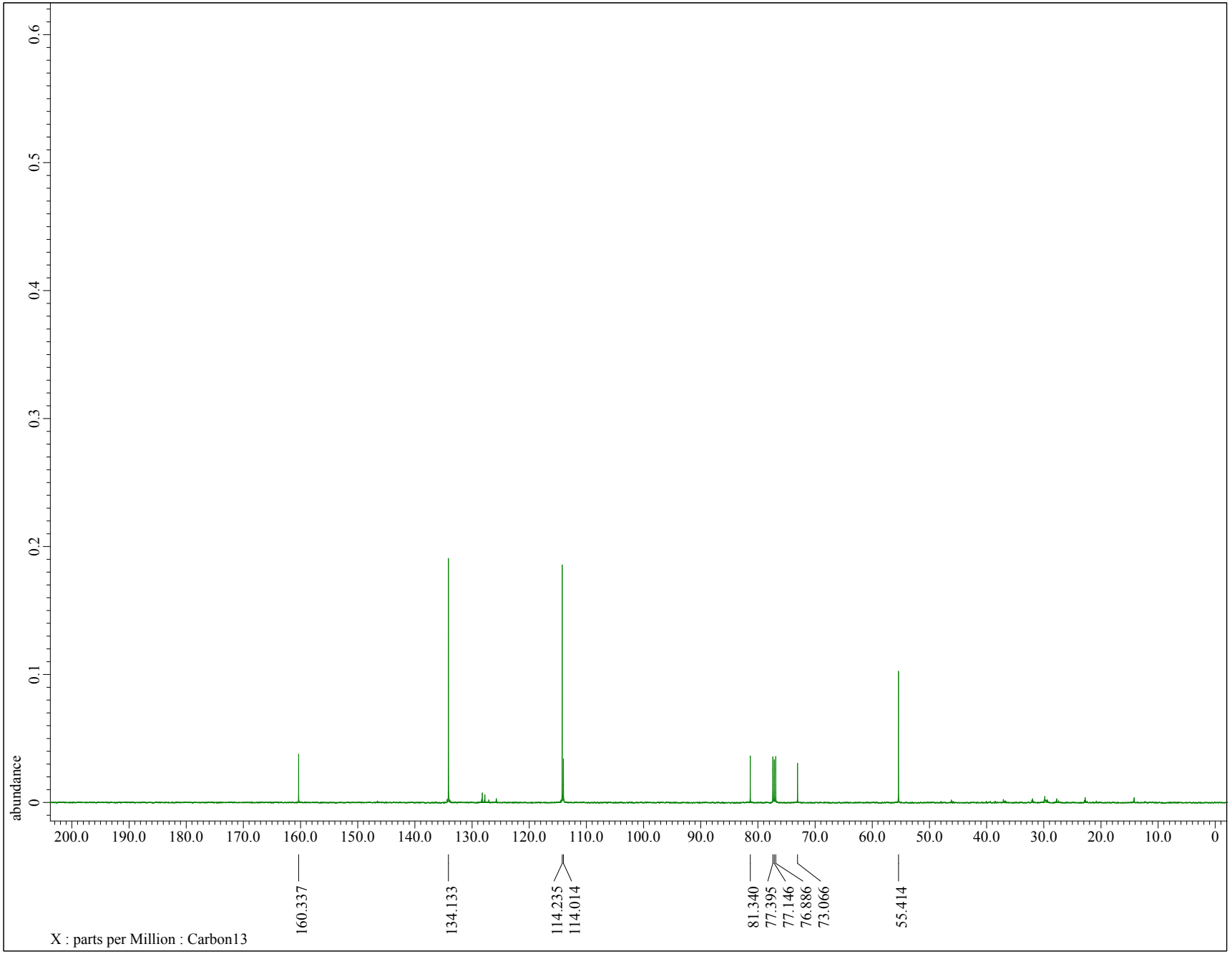

Figure S40: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2t**

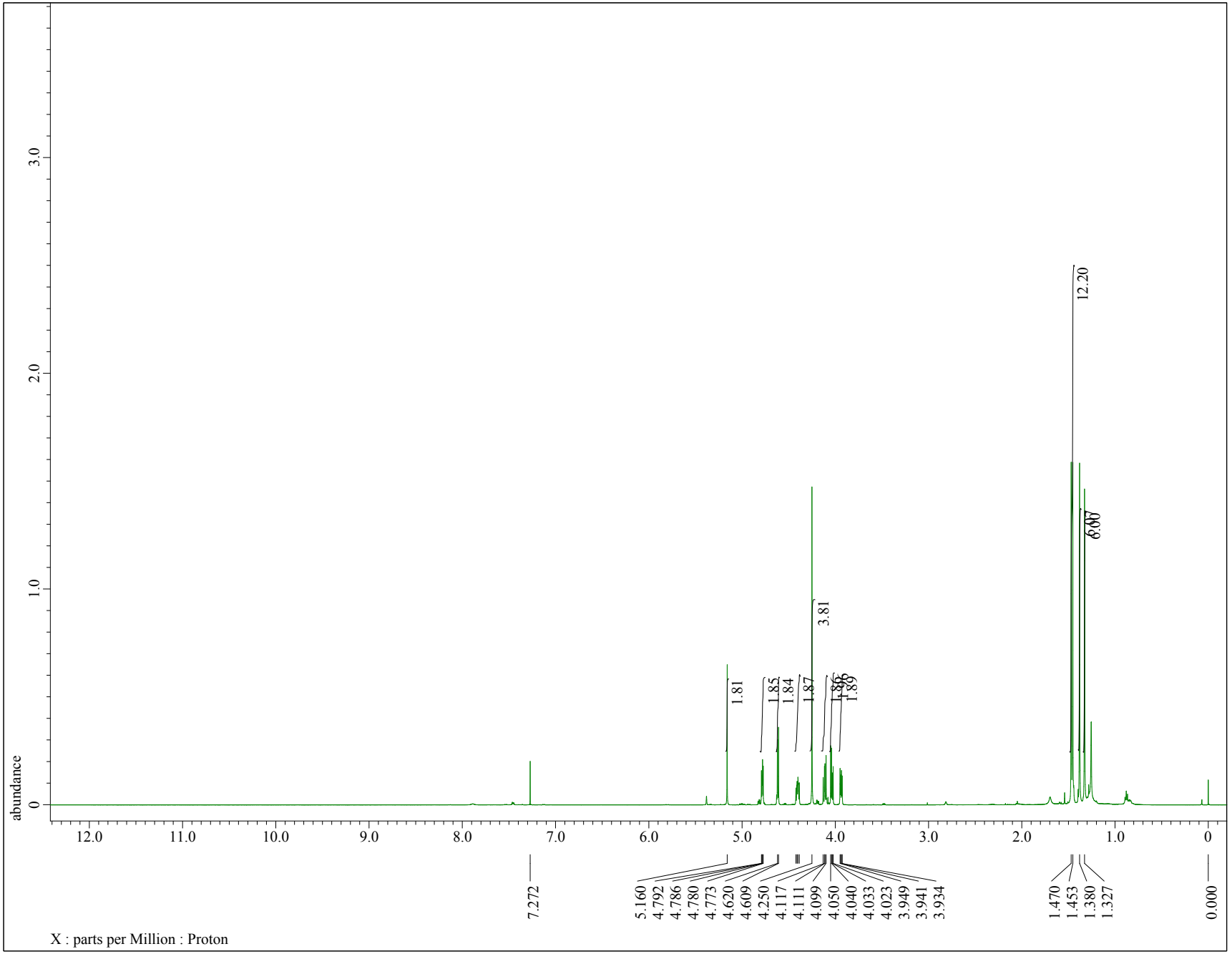

Figure S41: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2u**

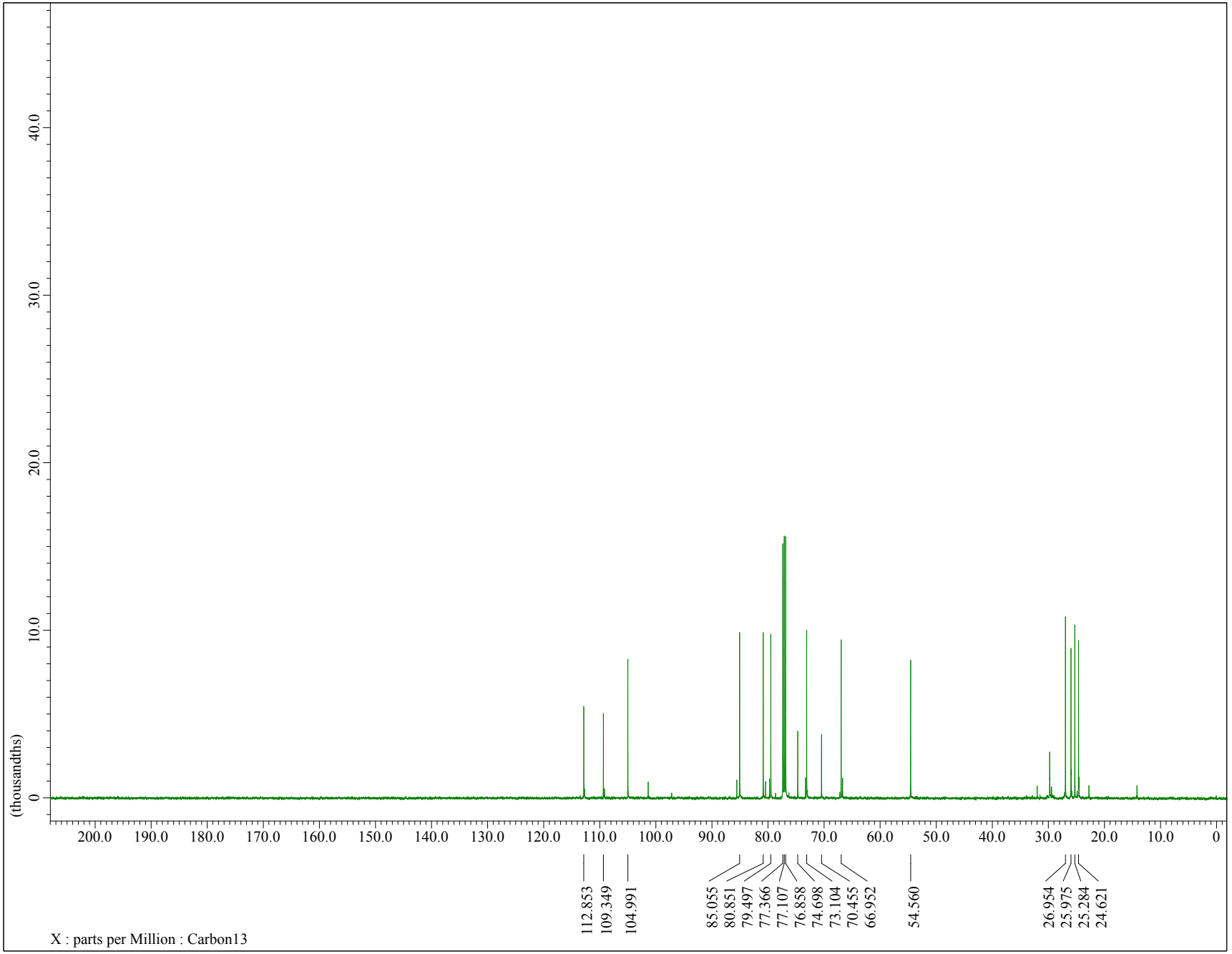

Figure S42: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2u**

2. ^{1}H and ^{13}C NMR Spectrum of Unsymmetric dialkyne (**3a-e**).

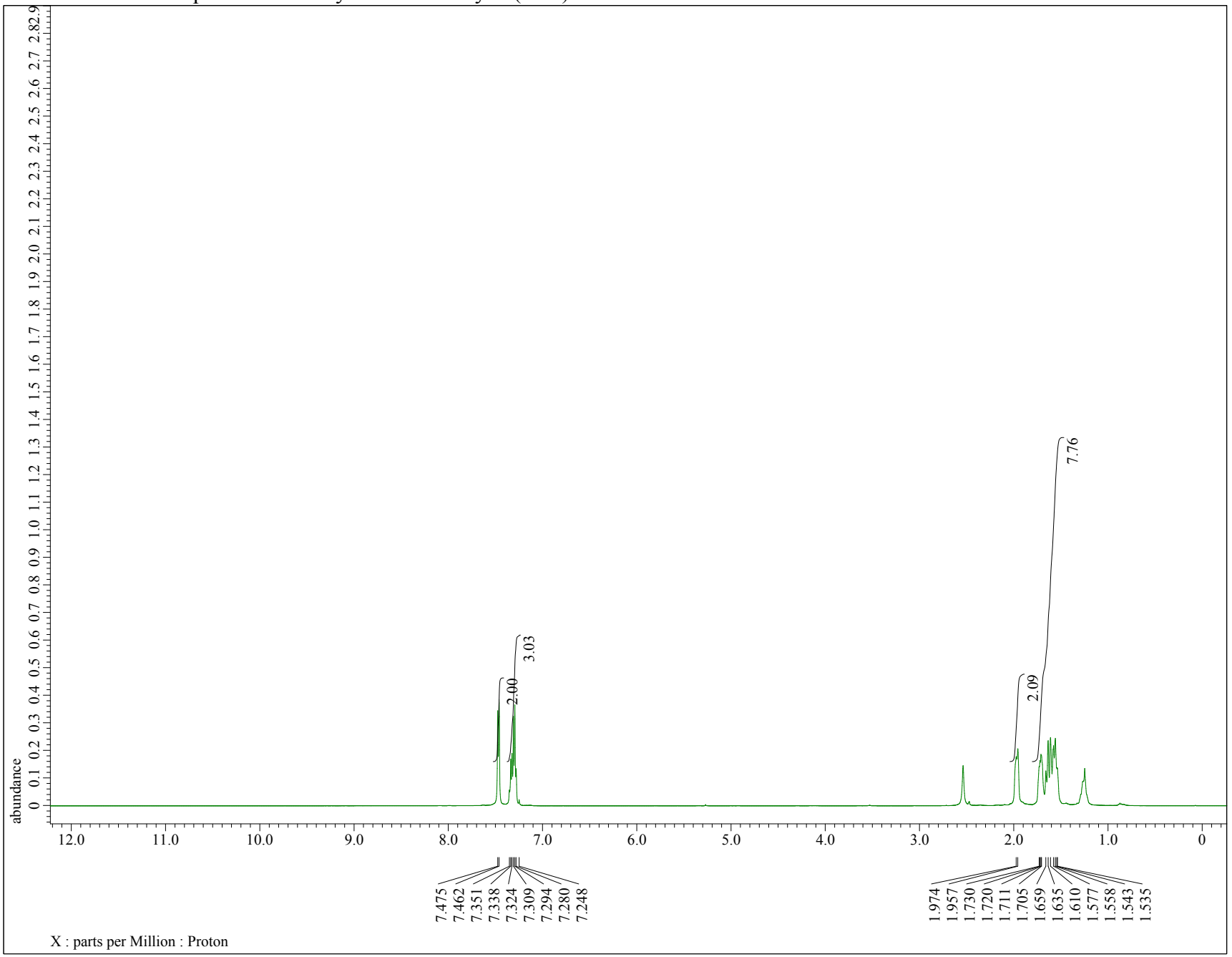

Figure S43: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **3a**

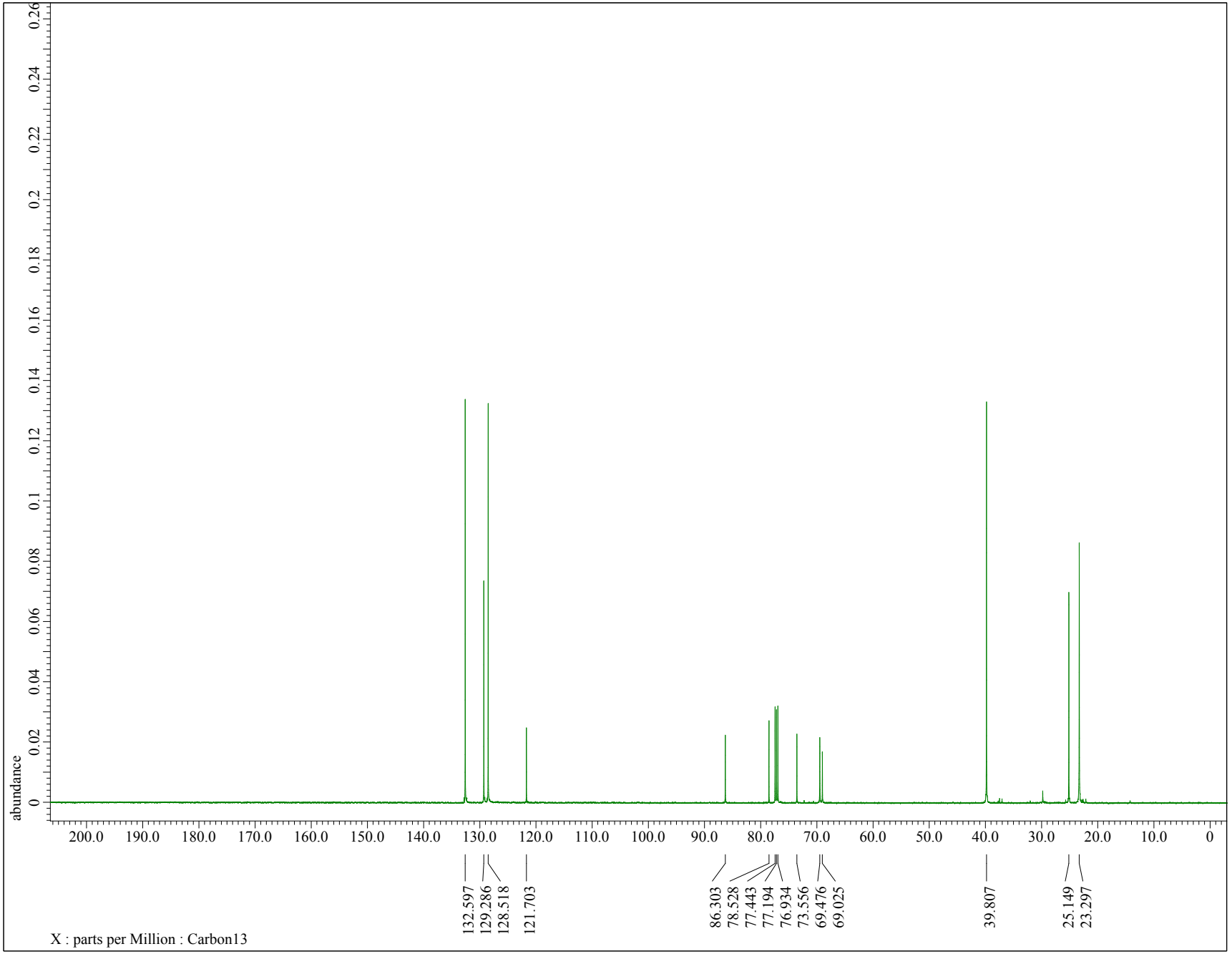

Figure S44: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **3a**

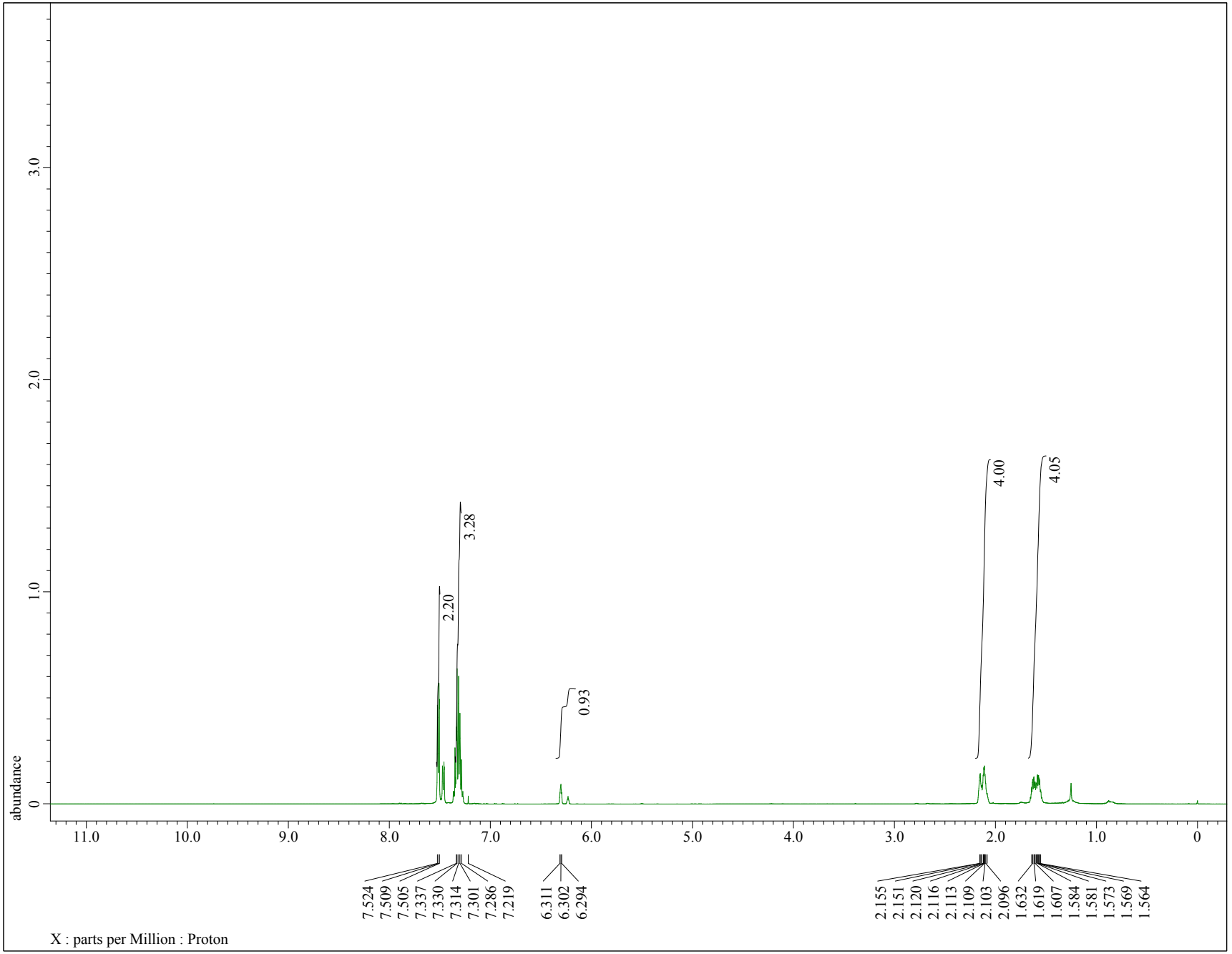

Figure S45: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **3b**

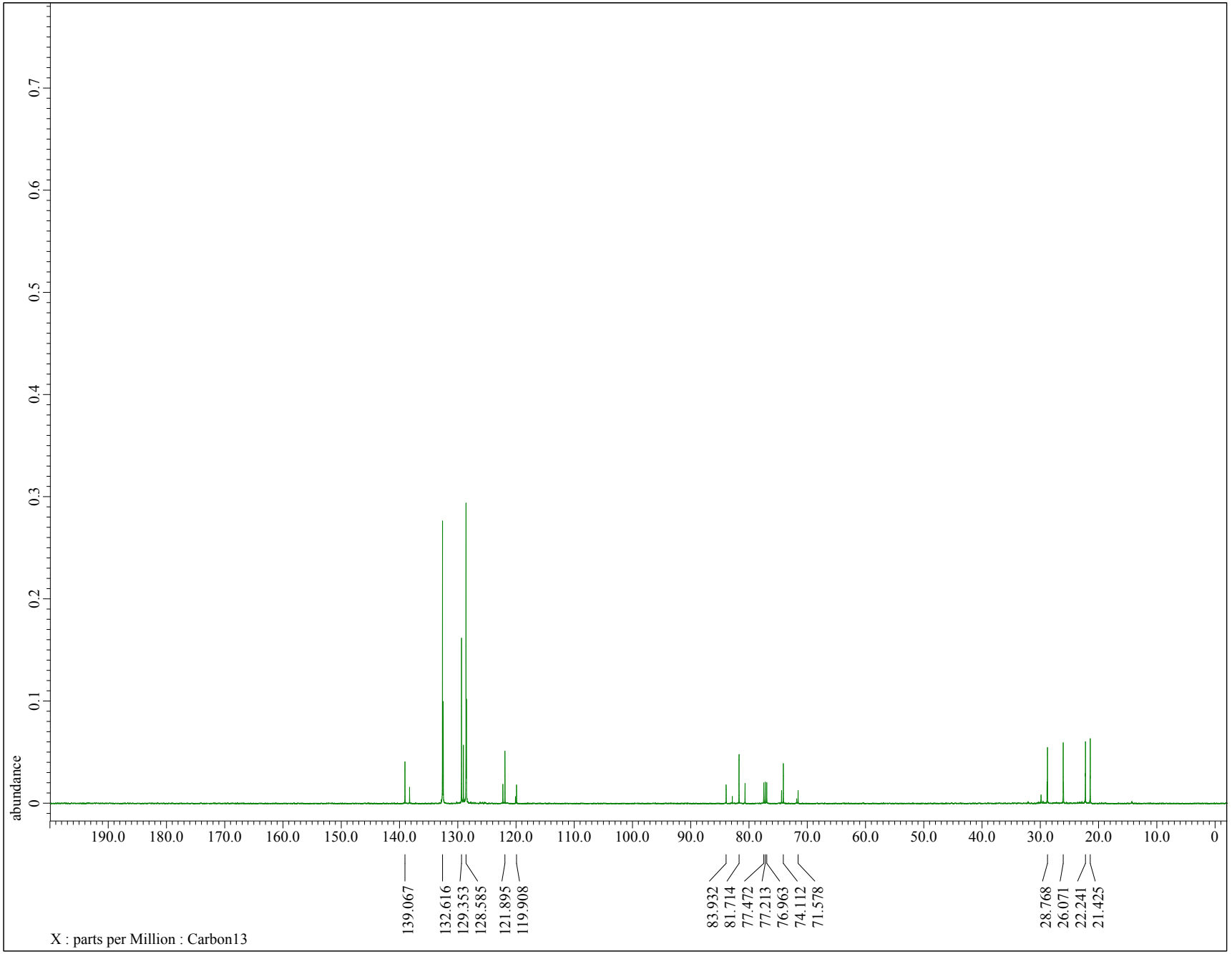

Figure S46: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **3b**

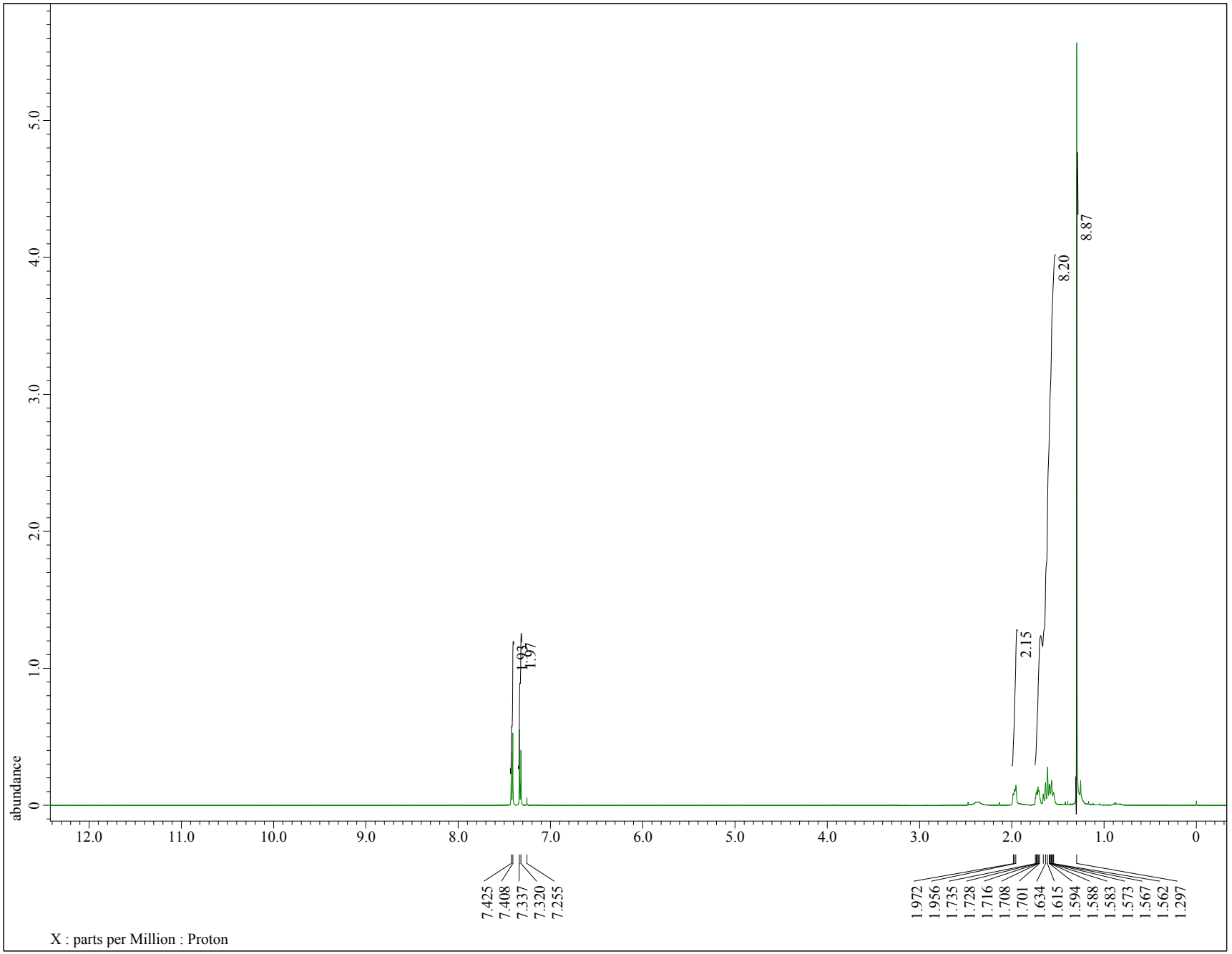

Figure S47: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **3c**

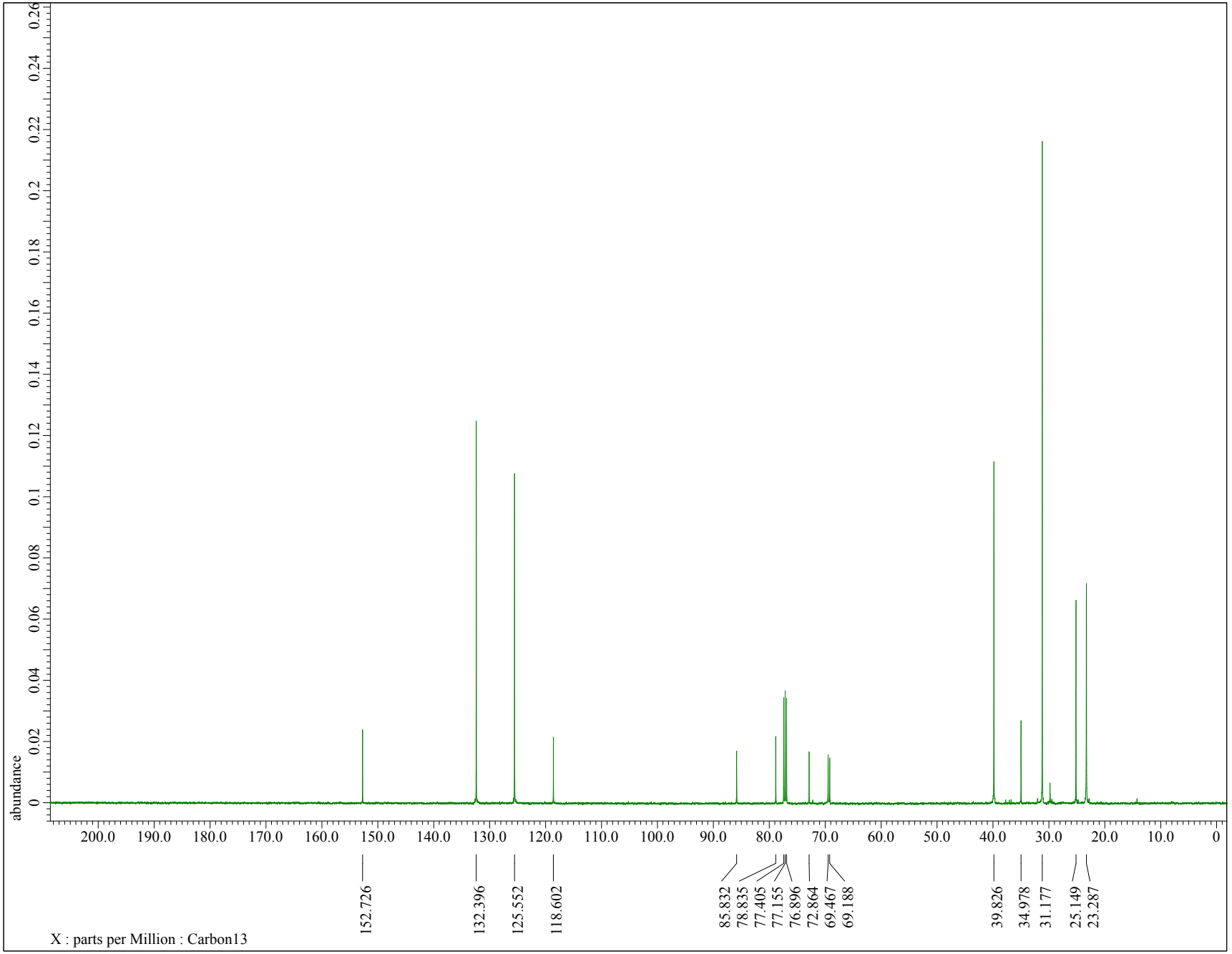

Figure S48: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **3c**

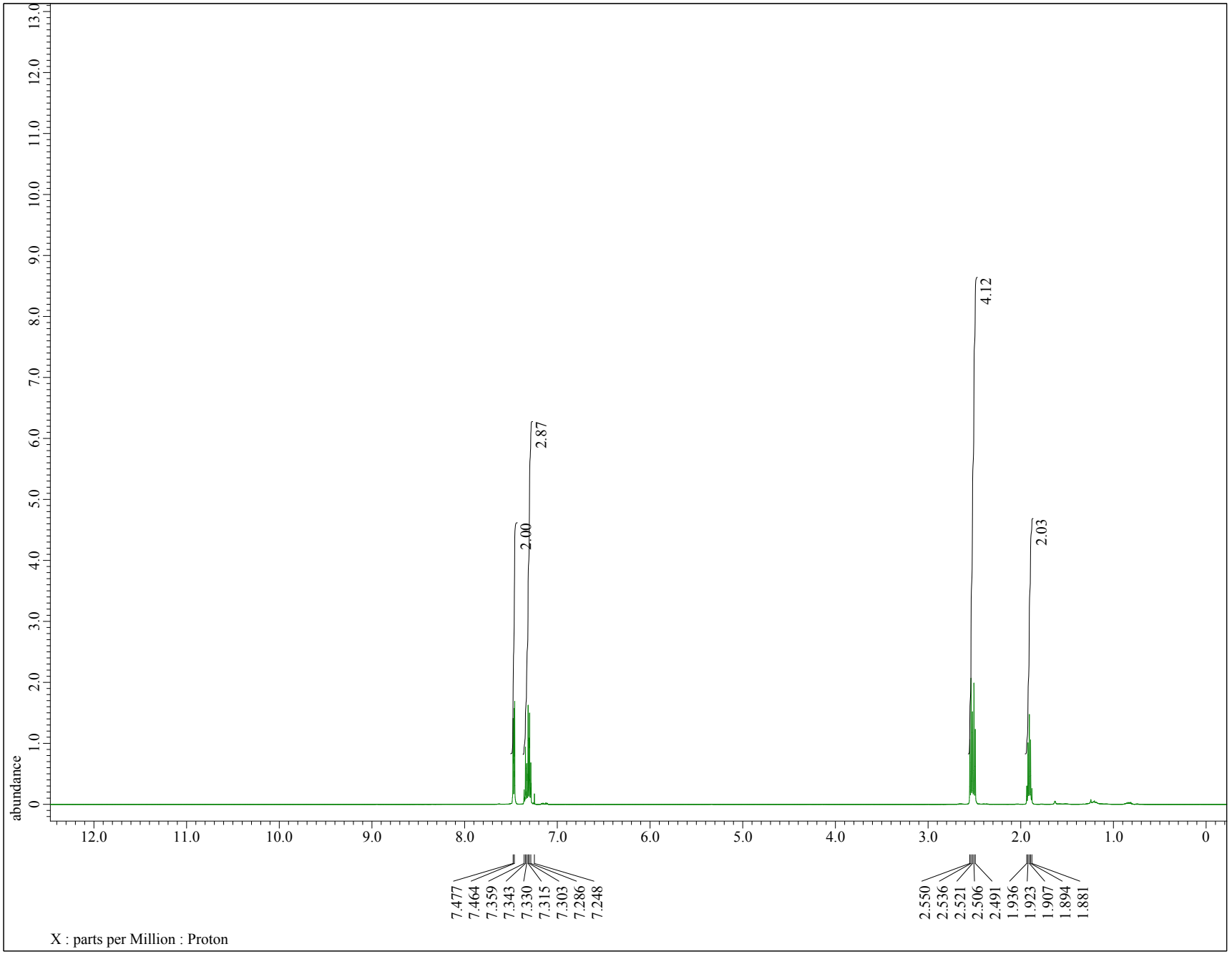

Figure S49: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **3d**

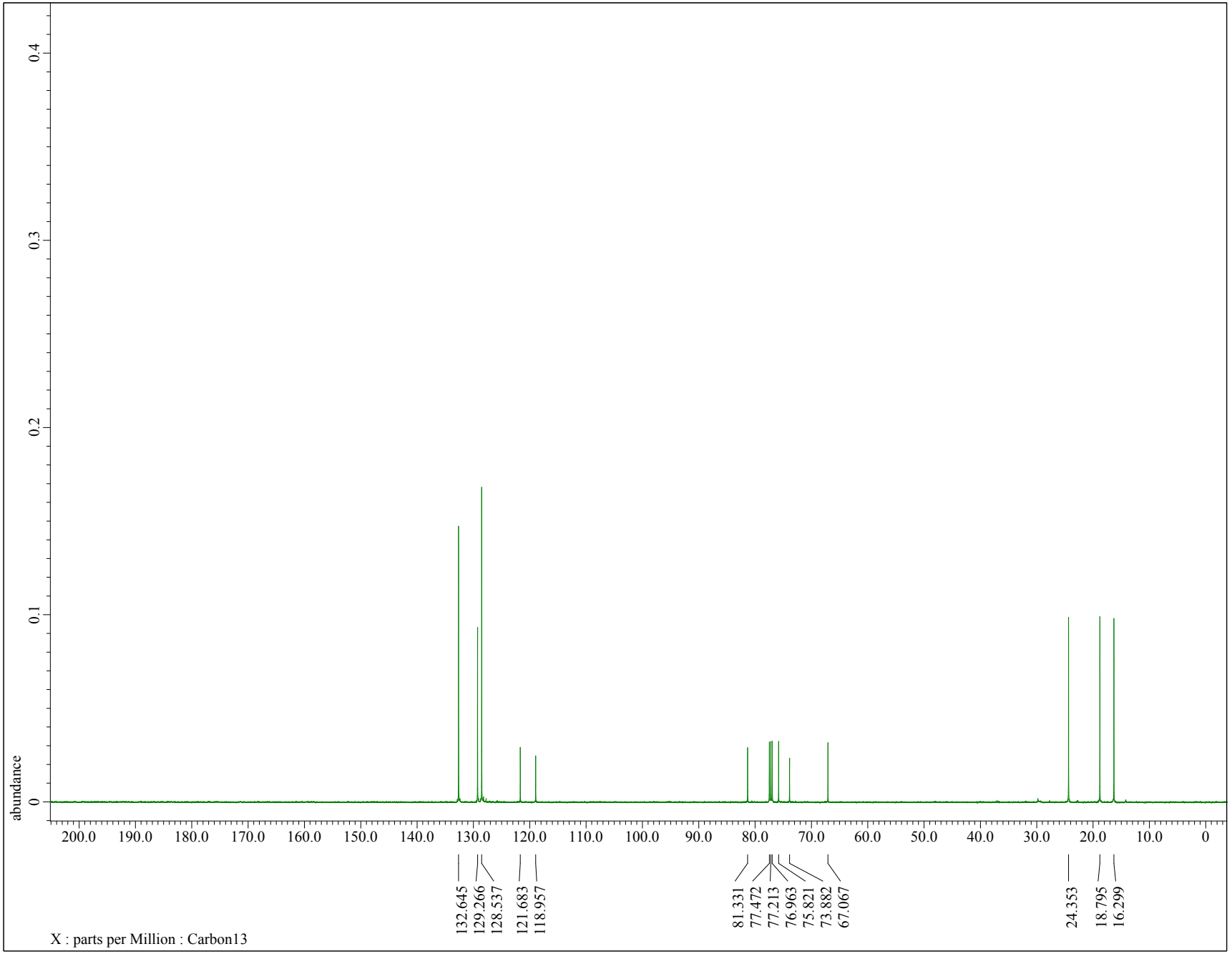

Figure S50: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **3d**

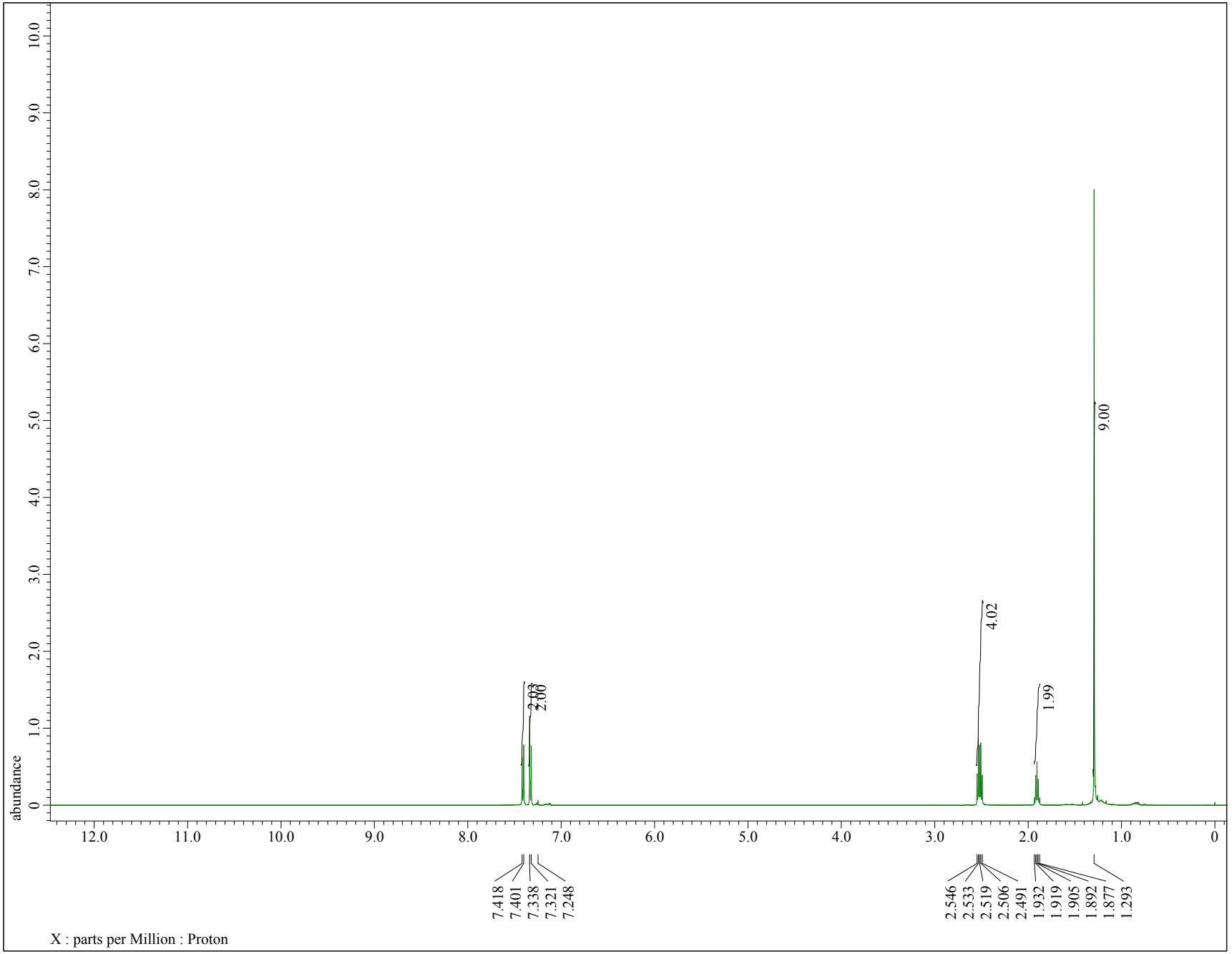

Figure S51: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **3e**

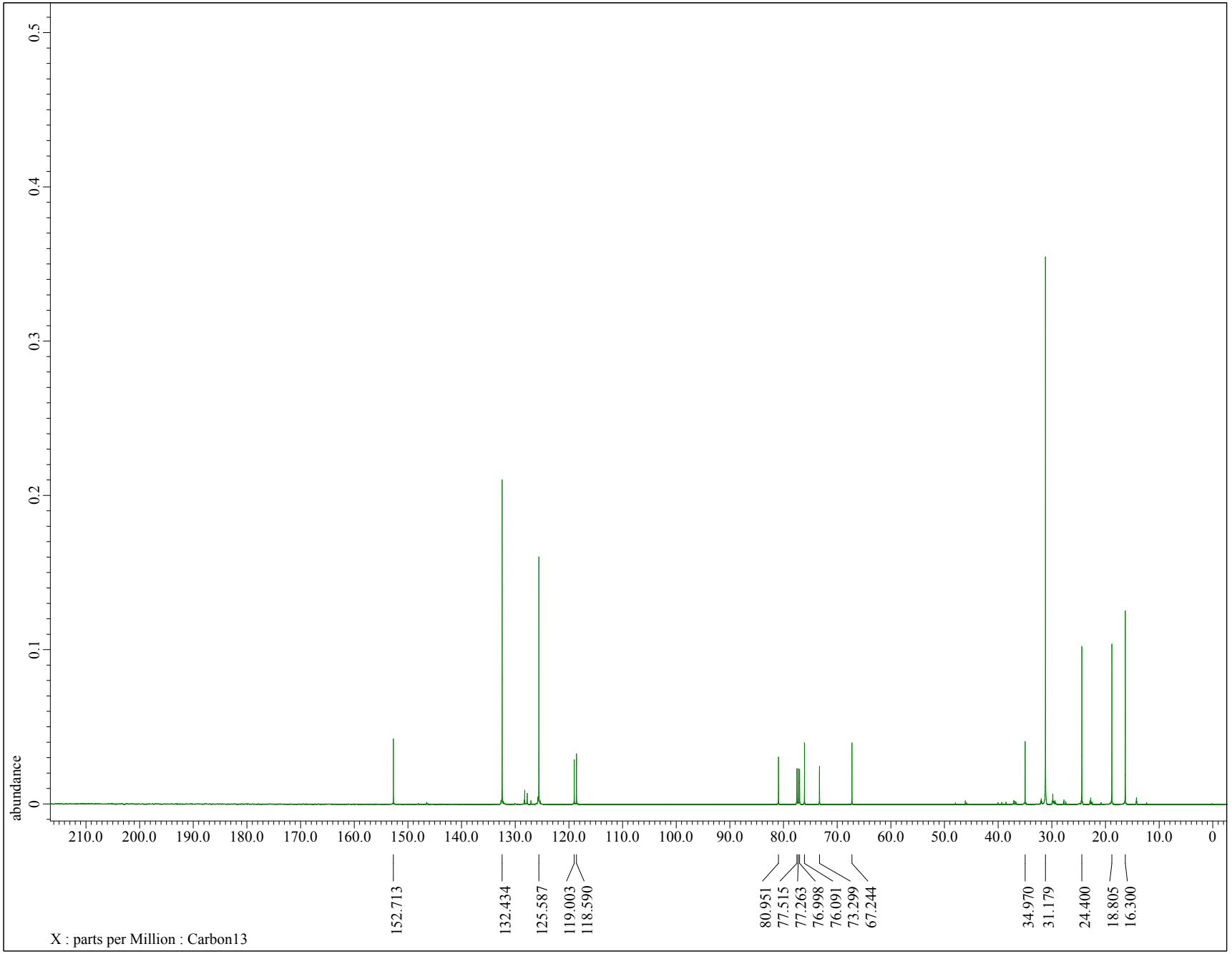

Figure S52: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **3e**

3. Single Crystal X-Ray data and structure of compounds 2a.

Data Collection and Refinement

Data of compound **2a** (**Figure S53)** was collected on Bruker Apex II CCD-Diffractometer using graphite monochromated Mo*K*α radiation (λ = 0.71073 Å). The structures were solved by the Patterson method as the compound is containing Iodine (I^{131}), the heavy metal and then refined on F^2 by the full matrix least-squares technique with the SHELX-86 set of software using the WinGX (version 2014.1) program package. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms using SHELX default parameters. The process has been validated through the IUCR site (International Union of Crystallography) and no A level error was found. Hence the cystal solved is validated. Further information on the crystal structure (excluding structure factors) has been given in table 1(Supporting Information) and also deposited in the Cambridge Crystallographic Data Centre as supplementary publication number 1856228. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk) or via internet.

Table S1. Crystallographic refinement data for compound **2a**

Compound 2a	
Empirical Formula	$C_{16}H_{10}$
Formula Weight	202.24
Crystal System	'Monoclinic''
Space group	'*P 2(2)/1*'
a (Å)	6.5476(5)
b (Å)	5.9893(4)
c (Å)	14.4785(12)
α, β, γ (°)	90.00, 103.07, 90.00
V (Å^3)	553.08(7)
Z	4
Density (calc)	1.214

F(000)	212
μ (mm^{-1})	0.069
Crystal Size [mm]	0.40 x 0.36 x 0.29
Temperature (K)	100(2)
Radiation	Mo$K\alpha$ 0.71073
θ Min-Max [°]	5.10, 33.21
h, k, l	-9:10; -9:6; -22:22
Tot.,UniqData, R(int)	16338, 2046, 0.0710
Obs. data [I > 2.0 σ(I)]	0.0685-0.1839
Nref, Npar	2123, 73
R1, *w*R2, S	0.0685(1750), 0.1961(2046), 0.852
CCDC	1856228

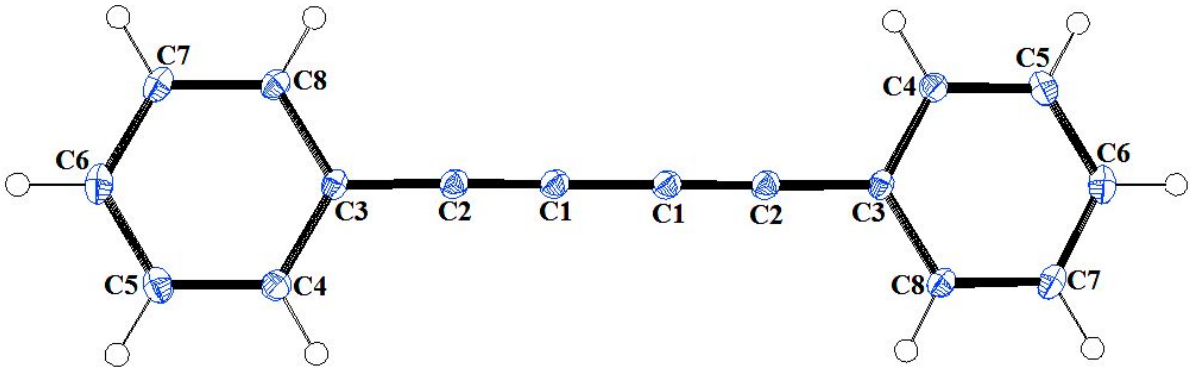

Figure S53. Molecular structure of **2a**. Thermal ellipsoids of carbon is set at 40 % probability.

Bond angles of compound 2a

Number	Atom1	Atom2	Atom3	Angle
1	C2	C1	C1	179.4(1)
2	C1	C2	C3	178.4(1)
3	C2	C3	C4	120.3(1)
4	C2	C3	C8	120.1(1)
5	C4	C3	C8	119.6(1)
6	C3	C4	H4	120.0
7	C3	C4	C5	119.9(1)
8	H4	C4	C5	120.1
9	C4	C5	H5	119.8
10	C4	C5	C6	120.3(1)
11	H5	C5	C6	119.9
12	C5	C6	H6	119.9
13	C5	C6	C7	120.1(1)
14	H6	C6	C7	120.0
15	C6	C7	H7	119.8
16	C6	C7	C8	120.3(1)
17	H7	C7	C8	119.8

18	C3	C8	C7	119.8(1)
19	C3	C8	H8	120.1
20	C7	C8	H8	120.1
21	C1	C1	C2	179.4(1)
22	C1	C2	C3	178.4(1)
23	C2	C3	C4	120.3(1)
24	C2	C3	C8	120.1(1)
25	C4	C3	C8	119.6(1)
26	C3	C4	H4	120.0
27	C3	C4	C5	119.9(1)
28	H4	C4	C5	120.1
29	C4	C5	H5	119.8
30	C4	C5	C6	120.3(1)
31	H5	C5	C6	119.9
32	C5	C6	H6	119.9
33	C5	C6	C7	120.1(1)
34	H6	C6	C7	120.0
35	C6	C7	H7	119.8
36	C6	C7	C8	120.3(1)

37	H7	C7	C8	119.8
38	C3	C8	C7	119.8(1)
39	C3	C8	H8	120.1
40	C7	C8	H8	120.1

Bond lengths of compound 2a

Number	**Atom 1**	**Atom 2**	**Cyclicity**	**Length**
1	C1	C2	acyclic	1.212(2)
2	C1	C1	acyclic	1.367(2)
3	C2	C3	acyclic	1.431(2)
4	C3	C4	cyclic	1.400(2)
5	C3	C8	cyclic	1.404(2)
6	C4	H4	acyclic	0.950 1
7	C4	C5	cyclic	1.392(2)
8	C5	H5	acyclic	0.950 1
9	C5	C6	cyclic	1.389(2)
10	C6	H6	acyclic	0.950 1
11	C6	C7	cyclic	1.389(2)
12	C7	H7	acyclic	0.950 1
13	C7	C8	cyclic	1.391(2)
14	C8	H8	acyclic	0.950 1
15	C1	C2	acyclic	1.212(2)

16	C2	C3	acyclic	1.431(2)
17	C3	C4	cyclic	1.400(2)
18	C3	C8	cyclic	1.404(2)
19	C4	H4	acyclic	0.950 1
20	C4	C5	cyclic	1.392(2)
21	C5	H5	acyclic	0.950 1
22	C5	C6	cyclic	1.389(2)
23	C6	H6	acyclic	0.950 1
24	C6	C7	cyclic	1.389(2)
25	C7	H7	acyclic	0.950 1
26	C7	C8	cyclic	1.391(2)
27	C8	H8	acyclic	0.950 1