Supporting Information

An efficient one-pot synthesis of *N*,*N*′-disubstituted urea and carbamates from *N*-Acylbenzotriazoles

Anoop Shyam Singh,[a] Dhananjay Kumar,[b] Nidhi Mishra,[a] Vinod K. Tiwari*[a]

[a]*Department of Chemistry, Centre of Advanced Study, Banaras Hindu University, Varanasi-221005, India*

[b]*Department of Chemistry, University of Delhi, New Delhi-110007, India*

**Corresponding author: E-mail: tiwari_chem@yahoo.co.in; Tel.: +91-542-6702466; fax: +91-542-236817*

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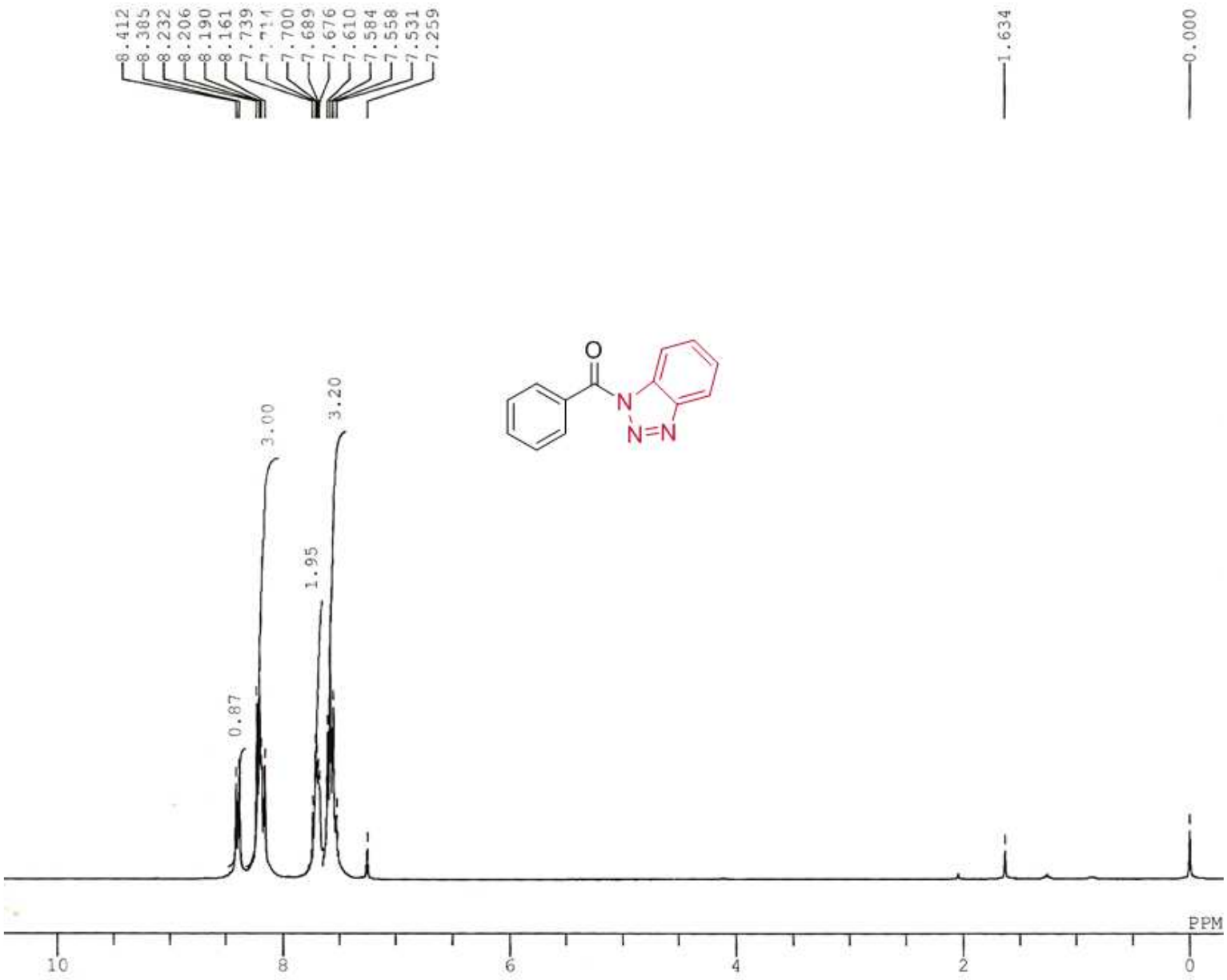
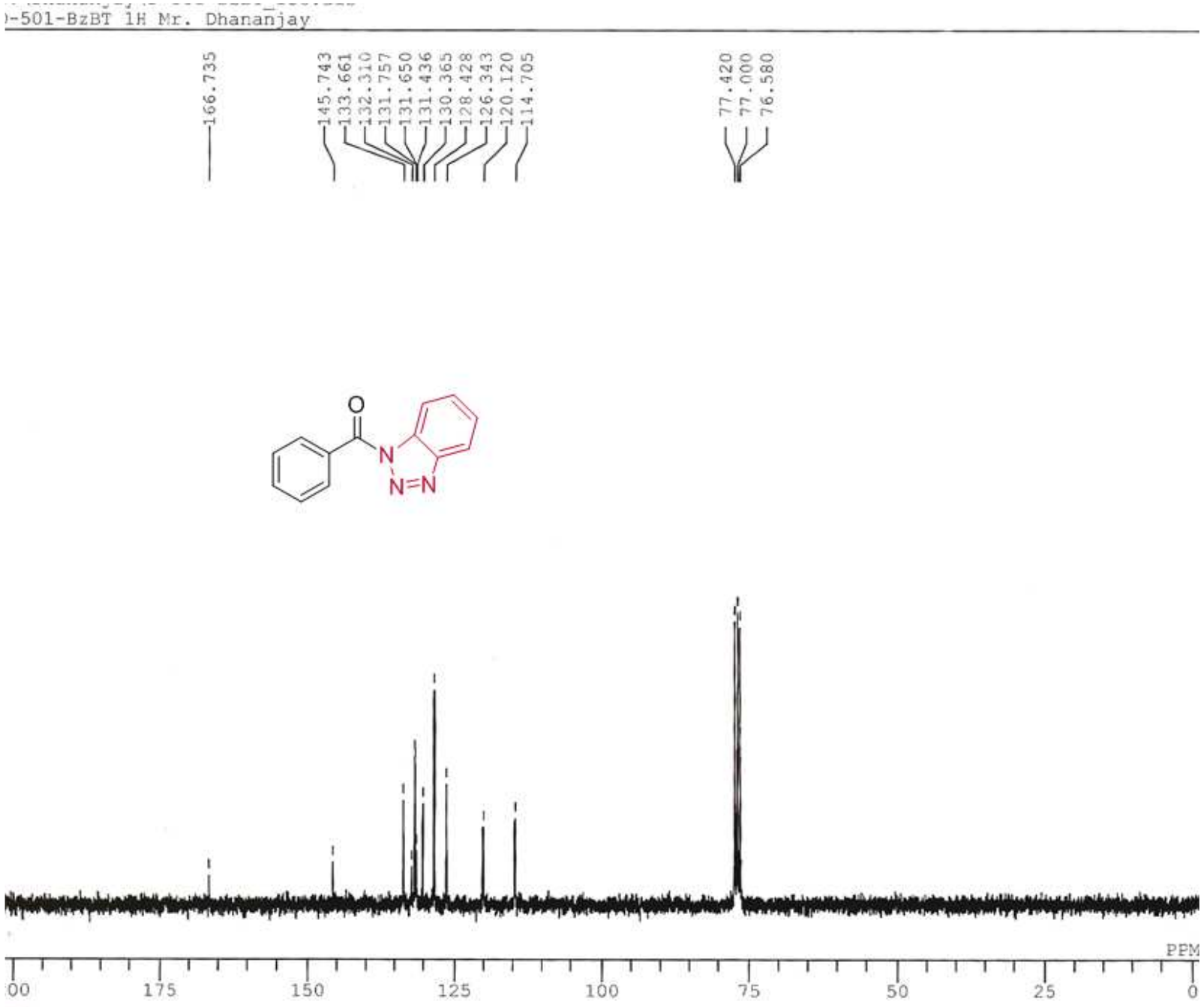
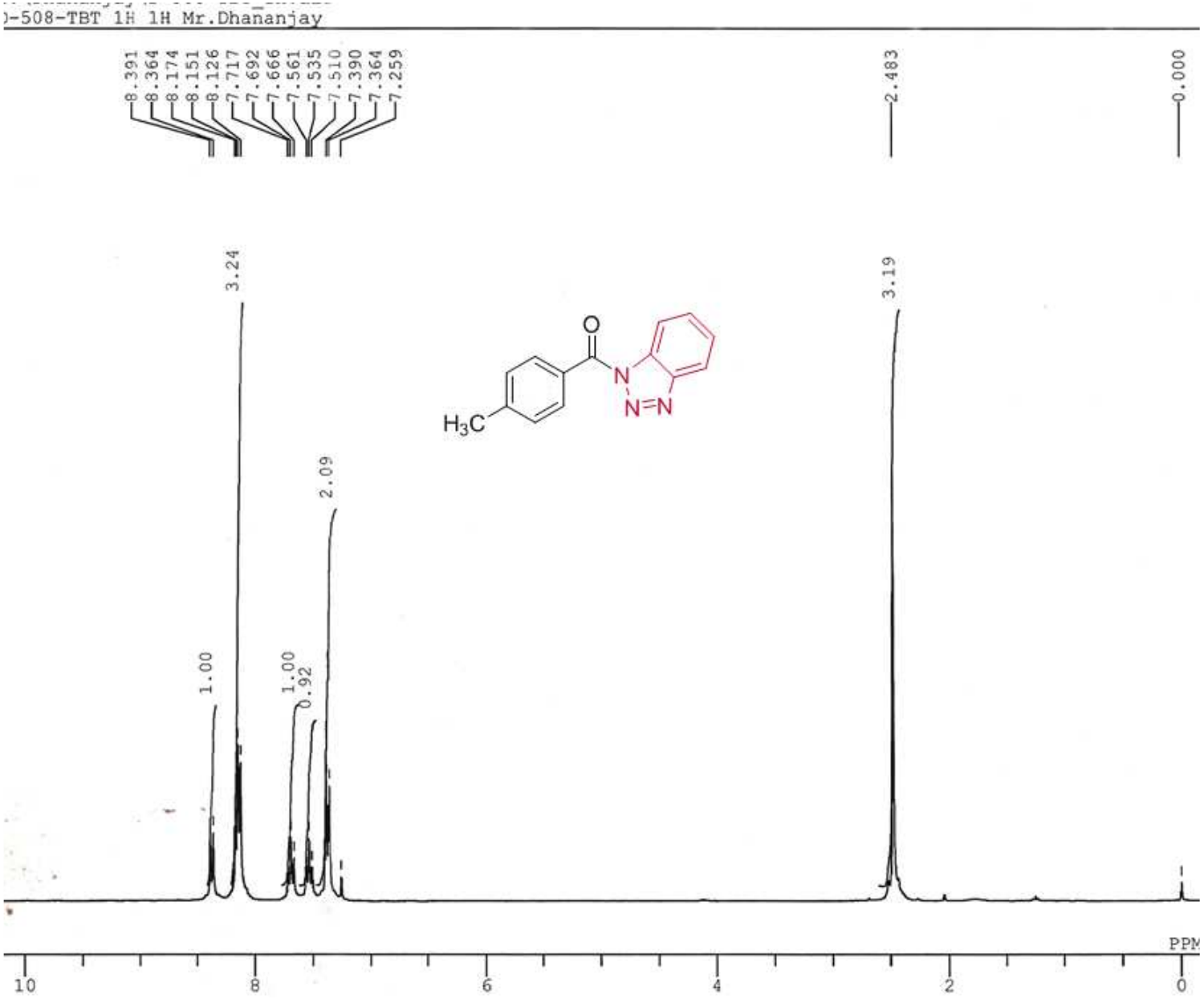
1. ^{1}H and ^{13}C NMR Spectrum of Aryl/alkyl-carbonylbenzotriazole (RCOBt, **2a-p**).



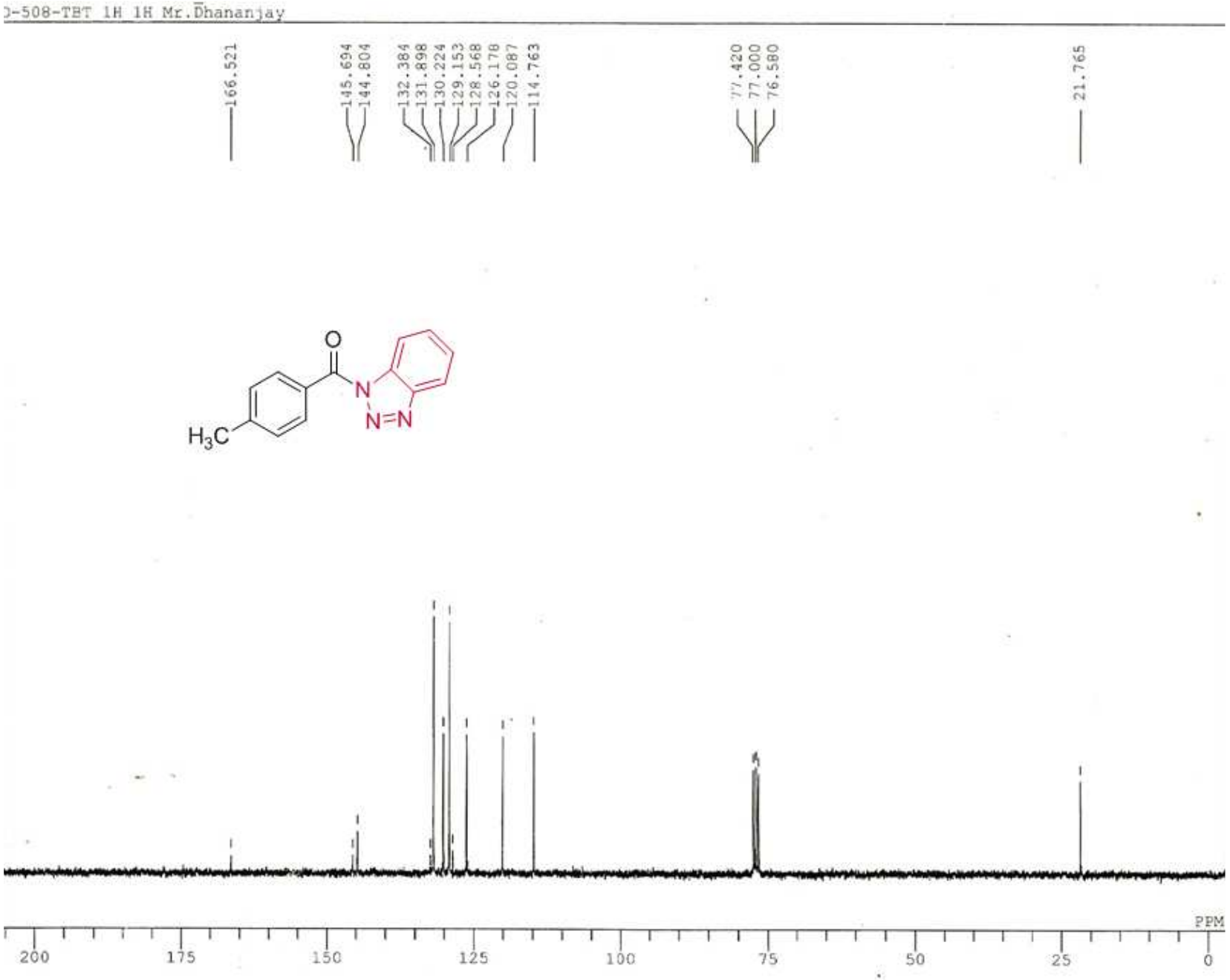
Spectrum 1: 300 MHz ^{1}H NMR of compound **2a**



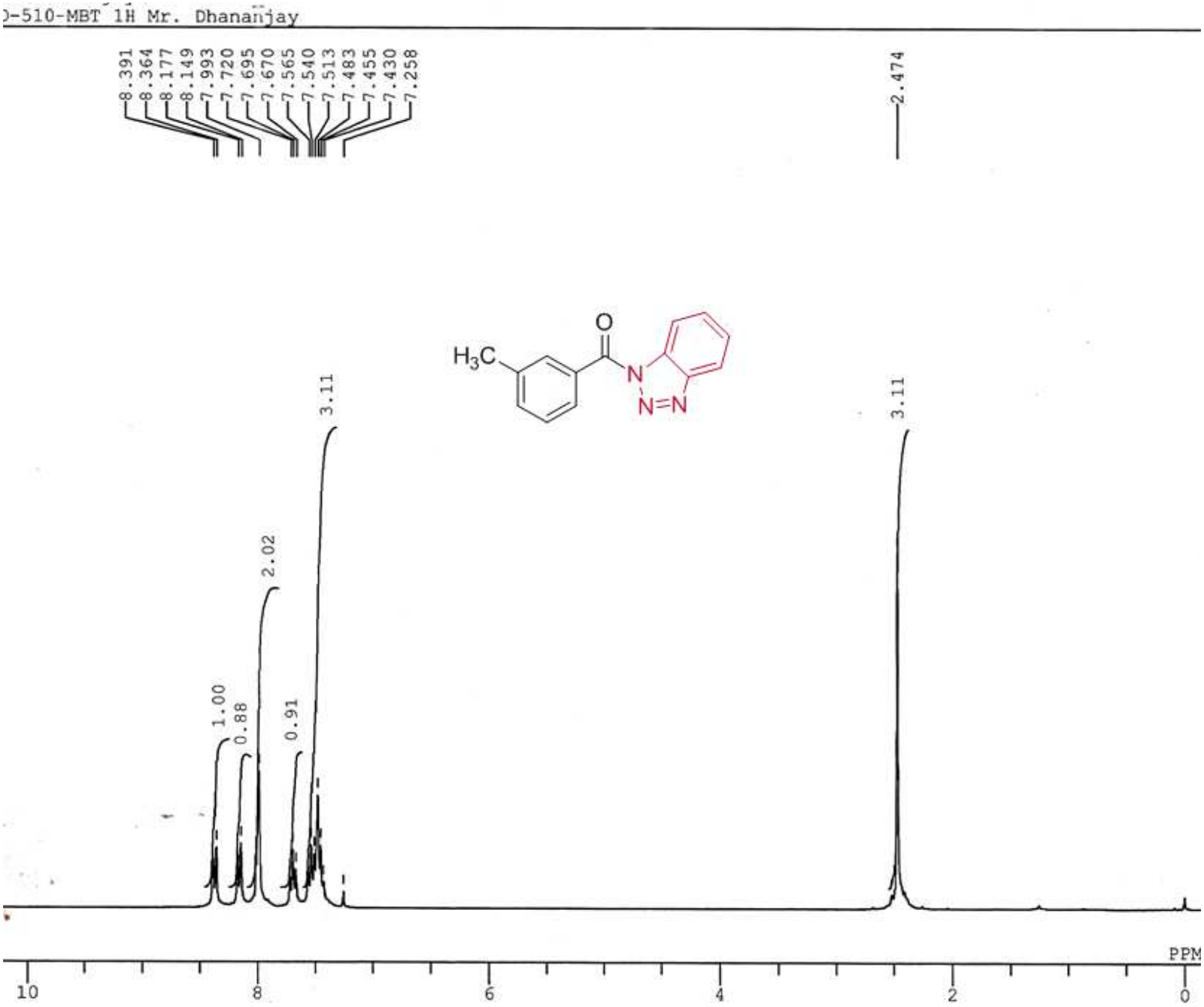
Spectrum 2: 75 MHz ^{13}C NMR of compound **2a**



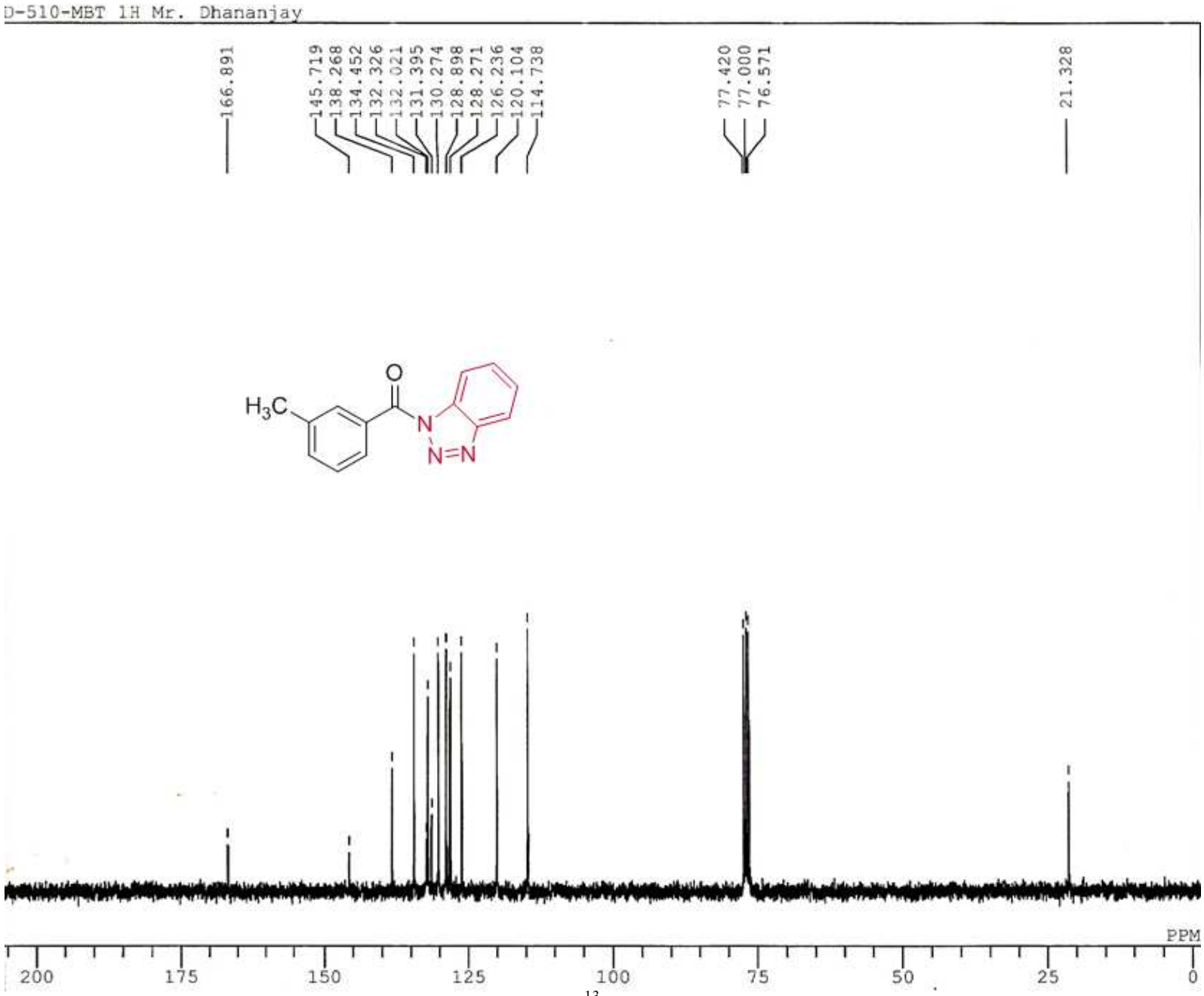
Spectrum 3: 300 MHz ^{1}H NMR of compound **2b**



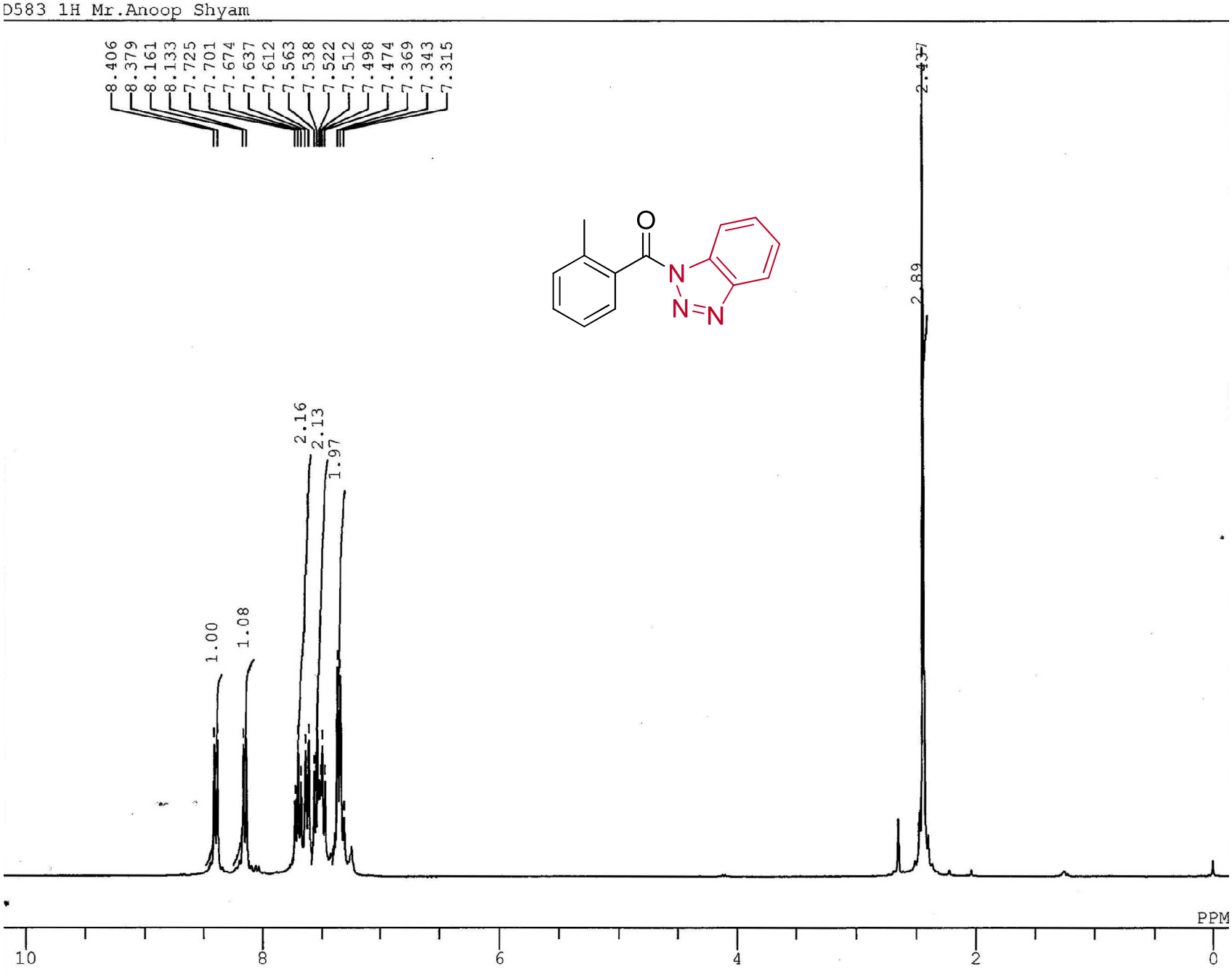
Spectrum 4: 75 MHz ^{13}C NMR of compound **2b**



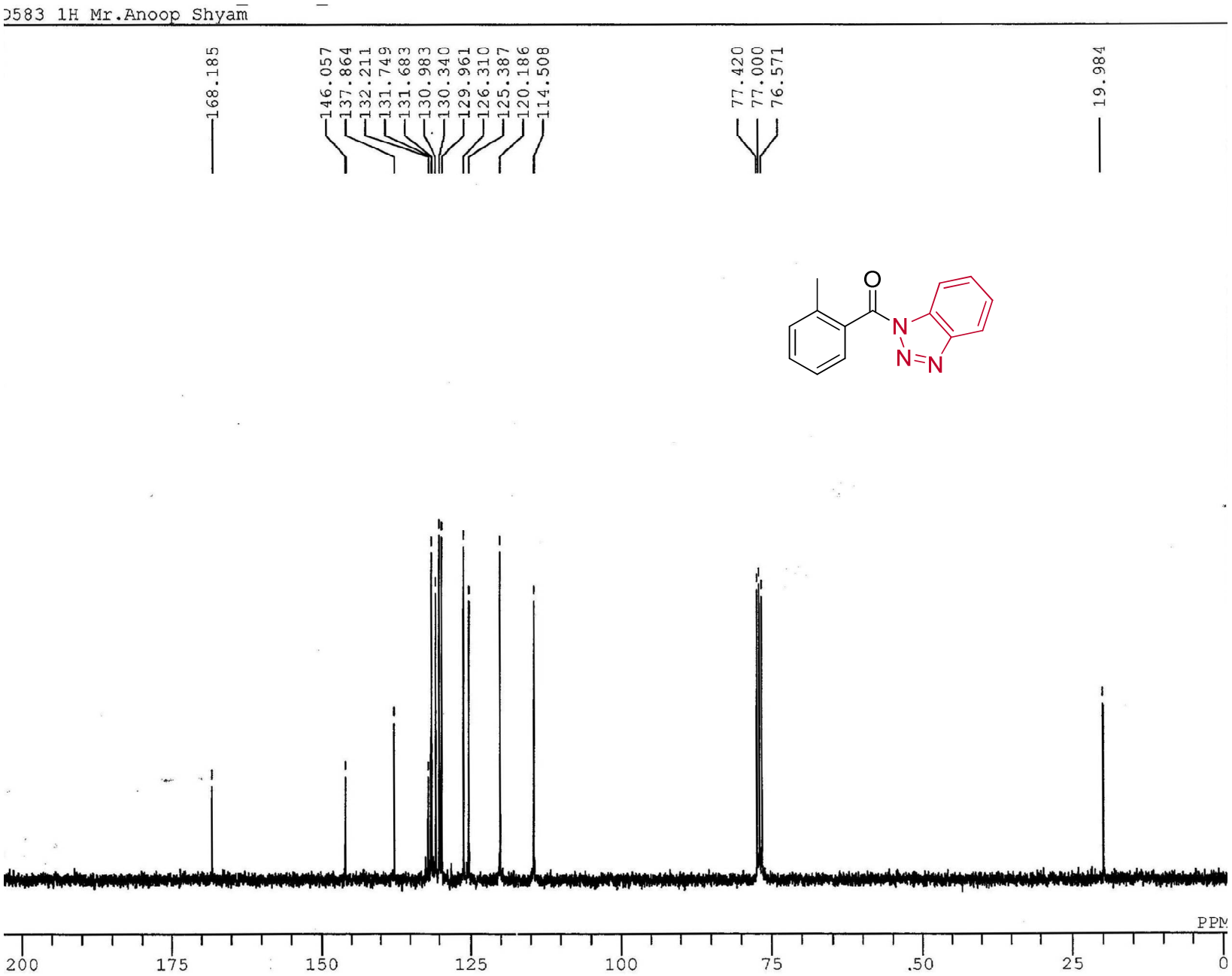
Spectrum 5: 300 MHz ^{1}H NMR of compound **2c**



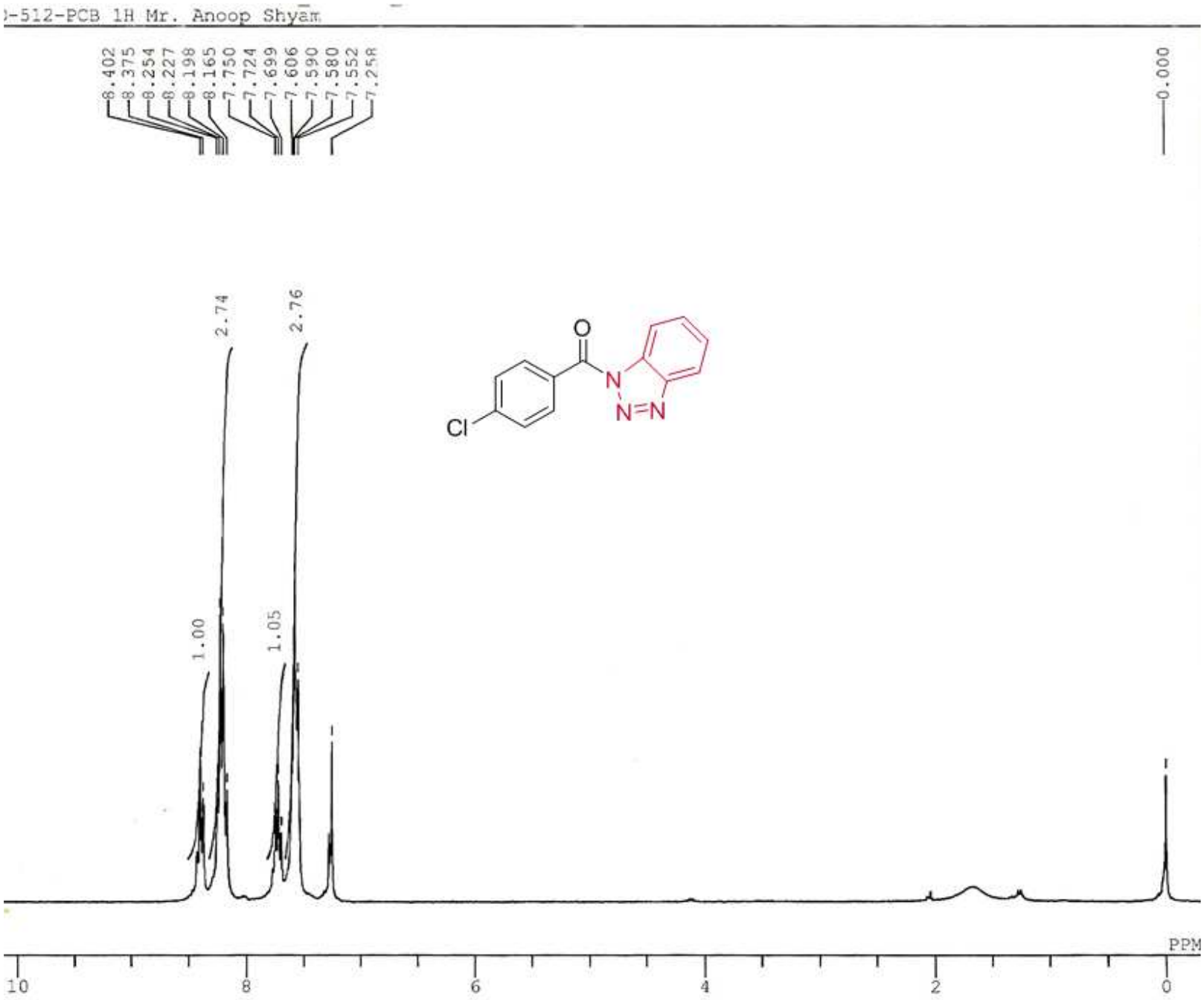
Spectrum 6: 75 MHz ^{13}C NMR of compound **2c**



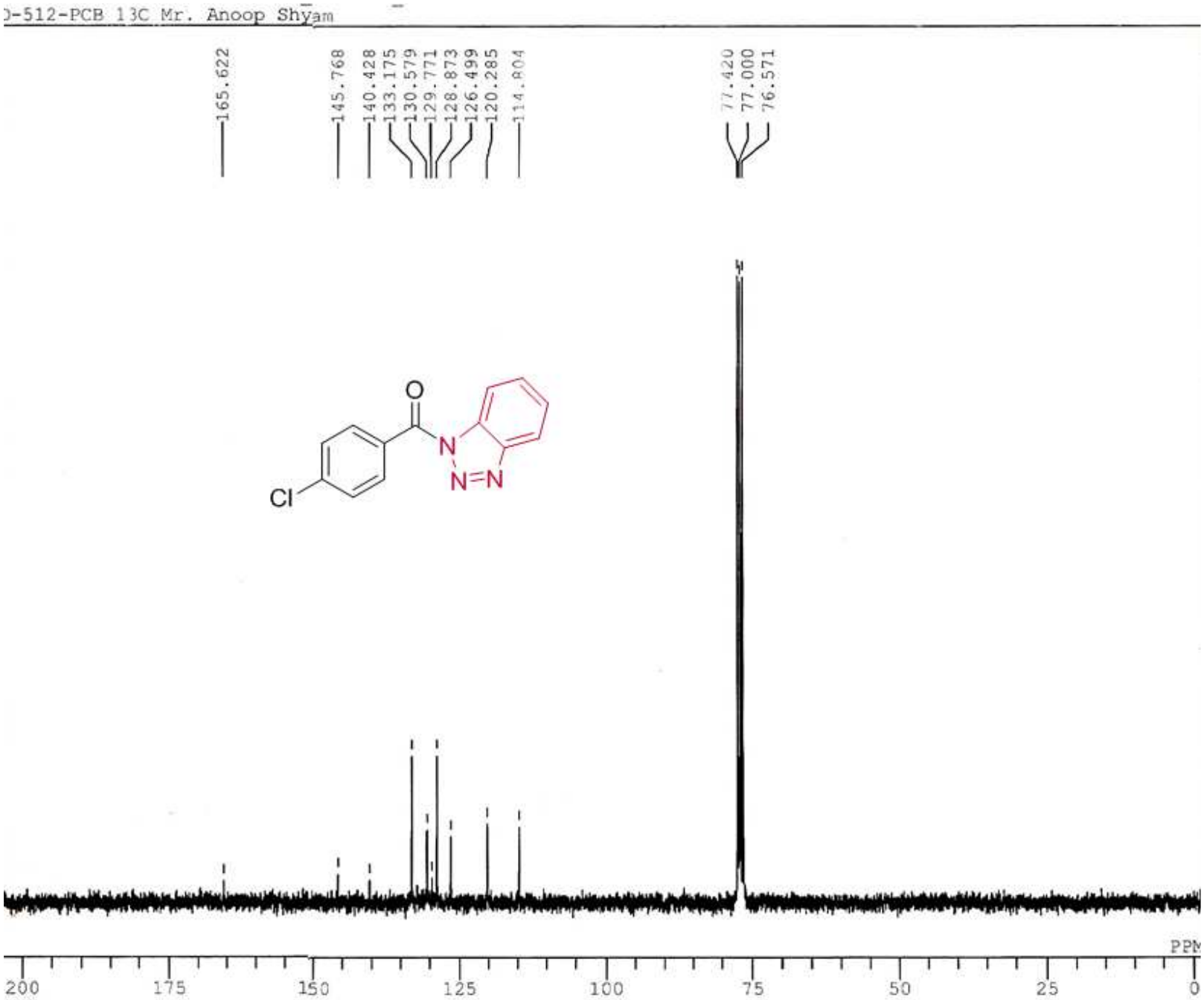
Spectrum 7: 300 MHz ^{1}H NMR of compound **2d**



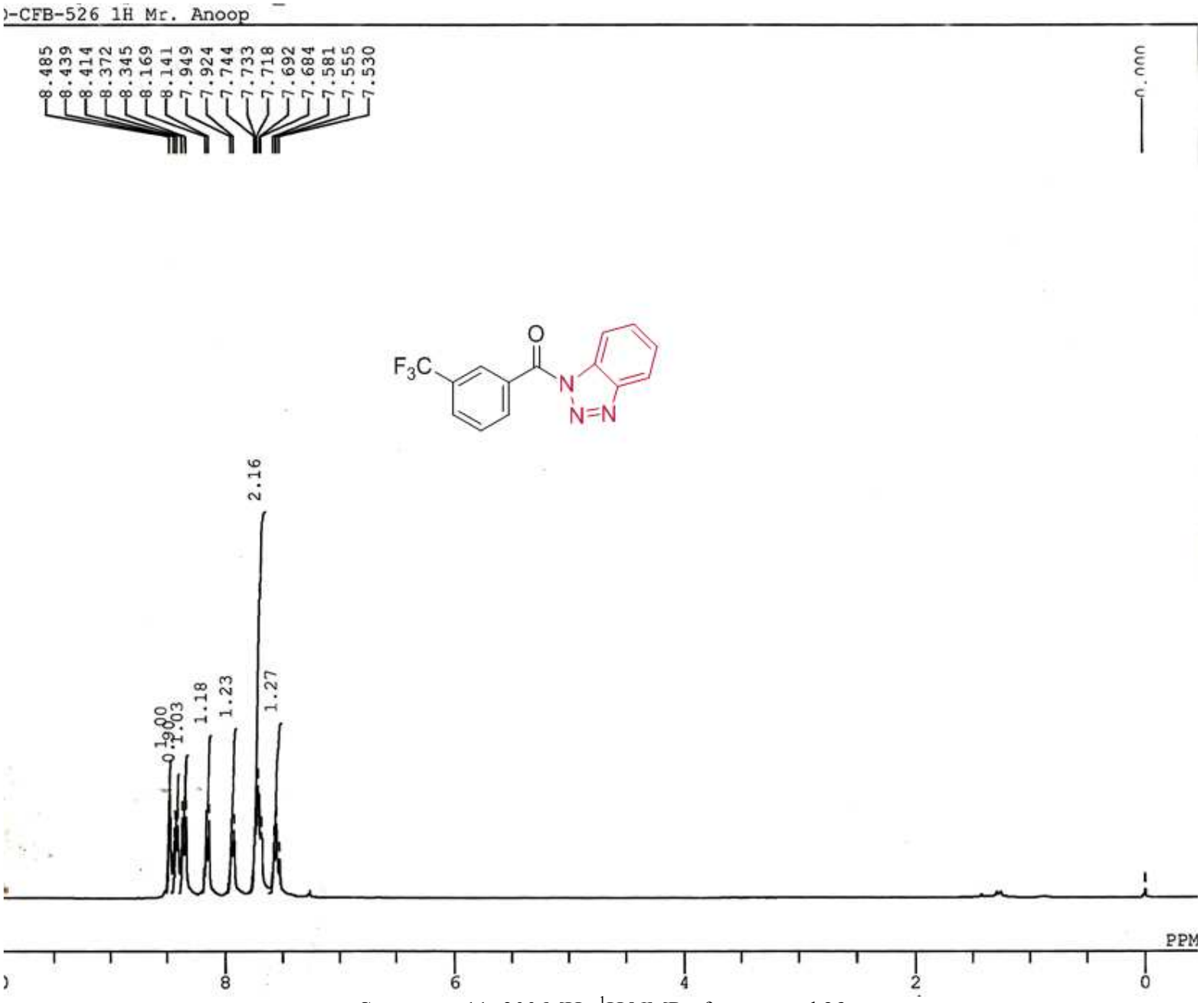
Spectrum 8: 75 MHz ^{13}C NMR of compound **2d**



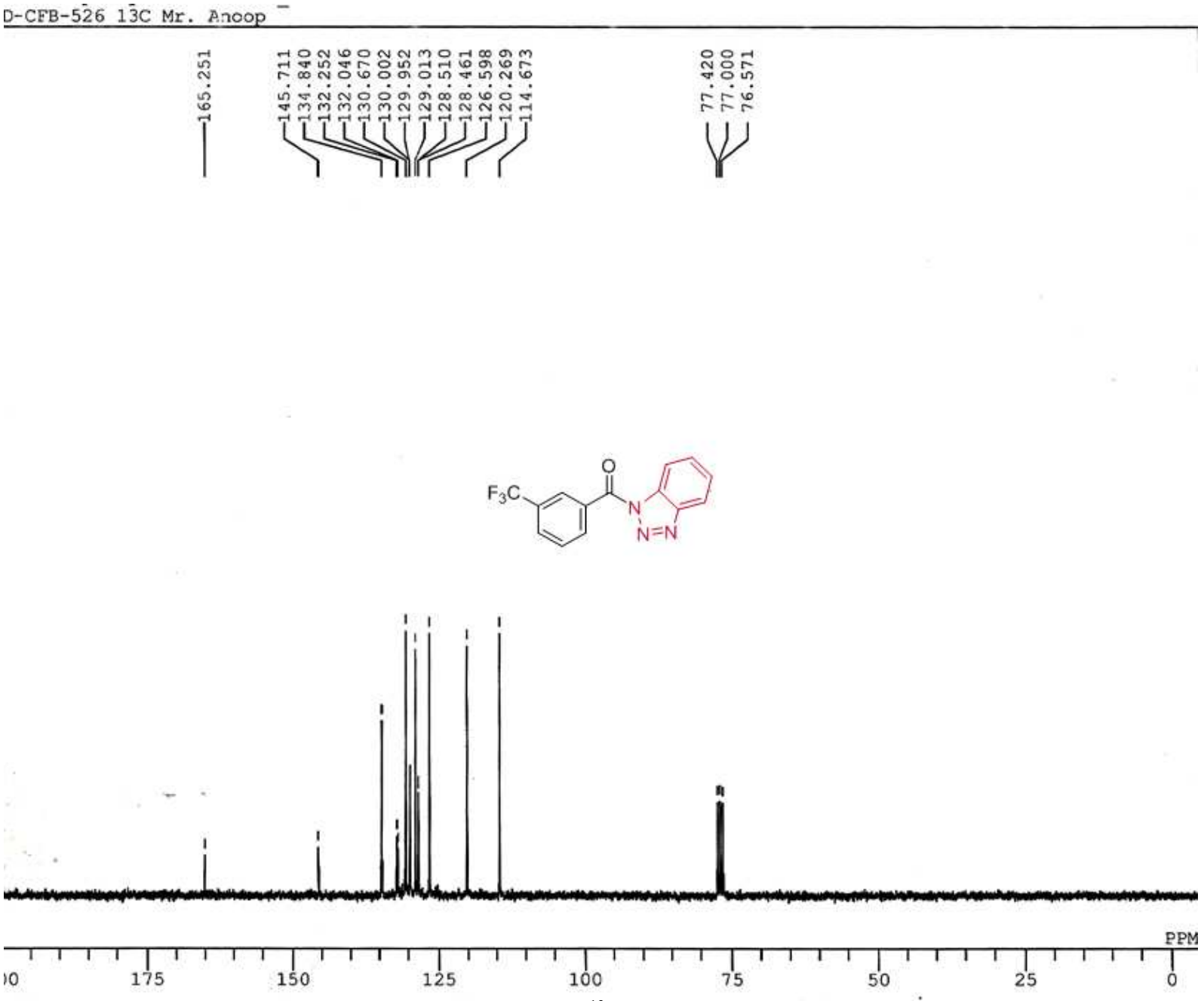
Spectrum 9: 300 MHz ^{1}H NMR of compound **2e**



Spectrum 10: 75 MHz ^{13}C NMR of compound **2e**

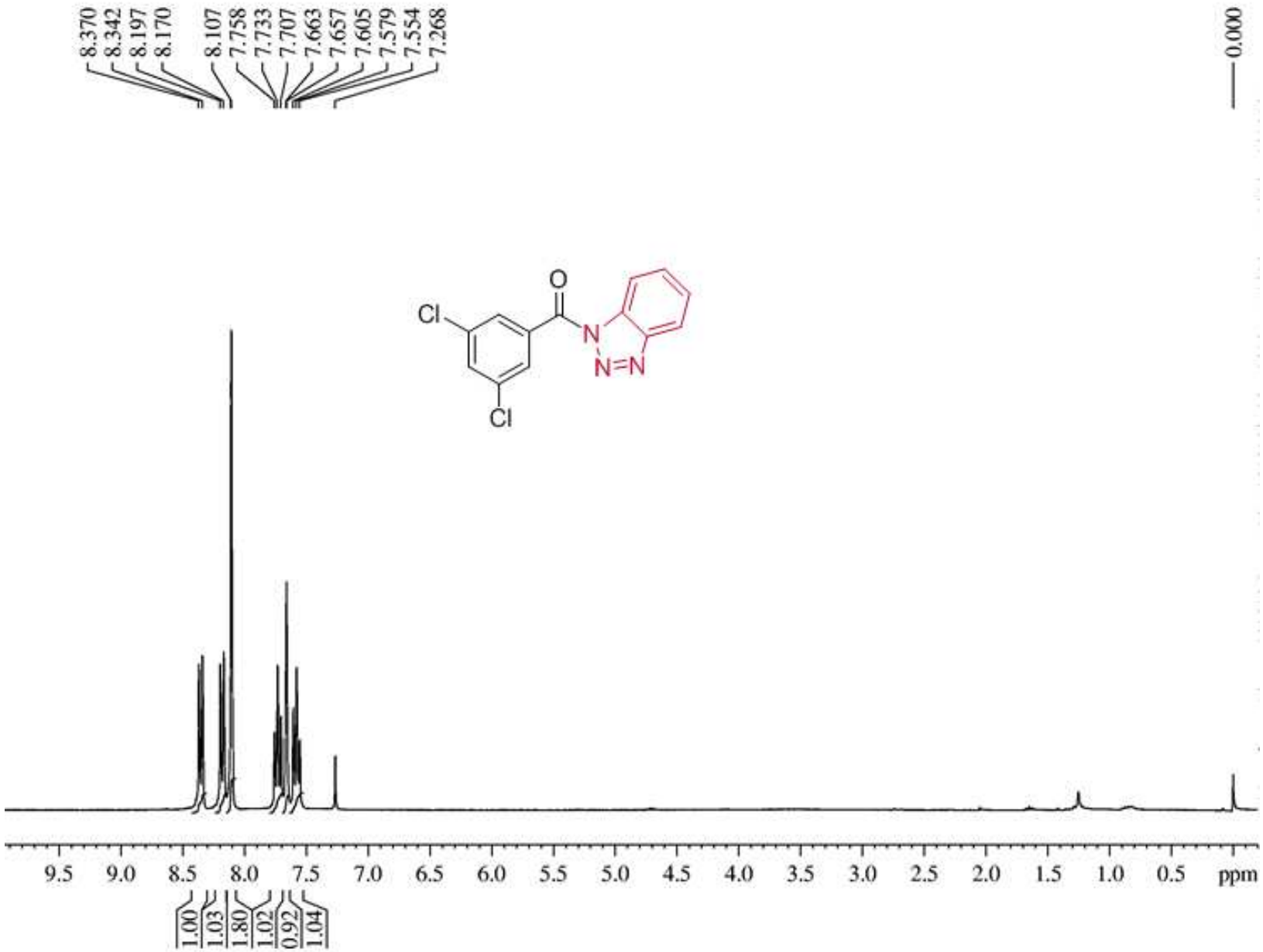


Spectrum 11: 300 MHz ^{1}H NMR of compound **2f**

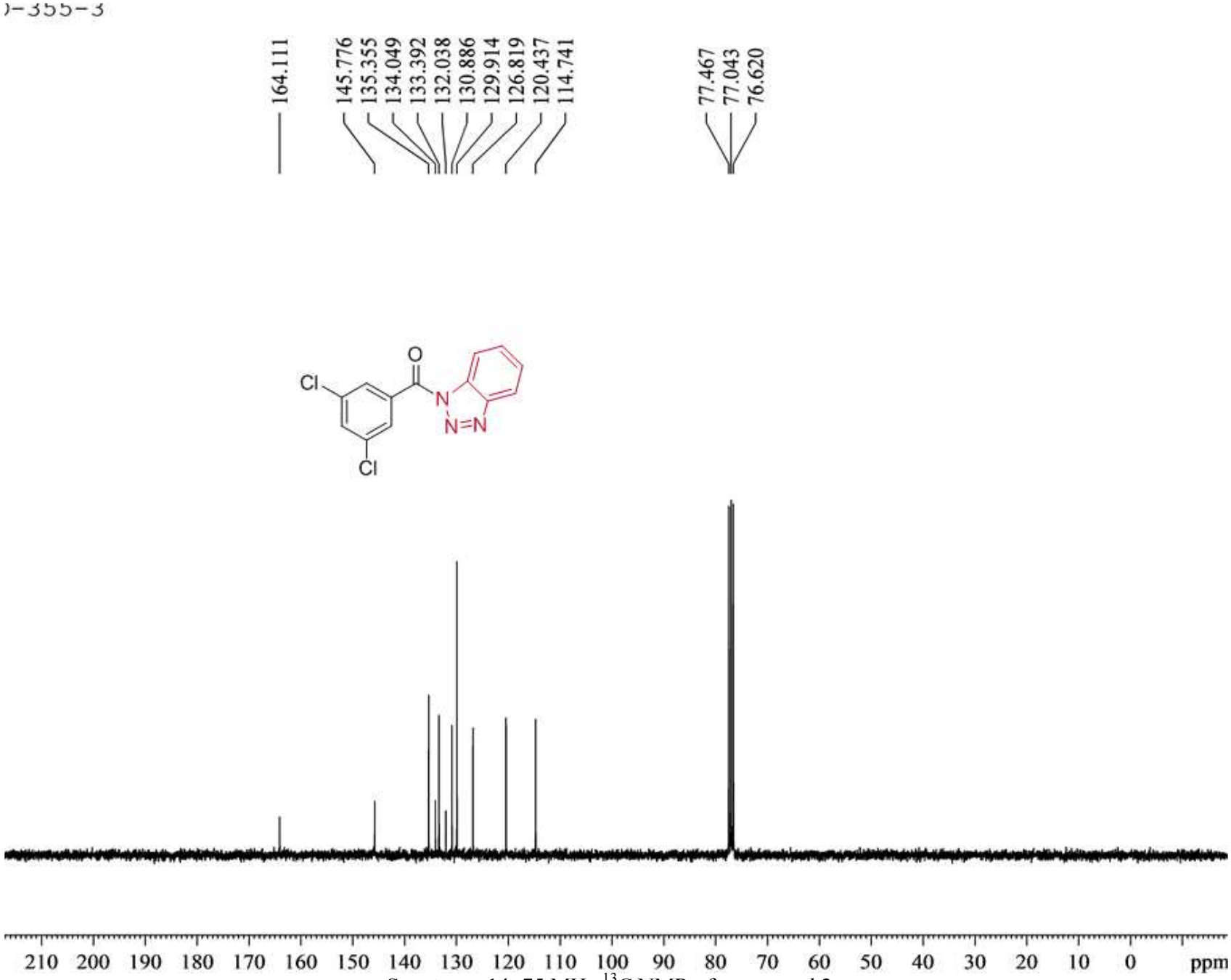


Spectrum 12: 75 MHz ^{13}C NMR of compound **2f**

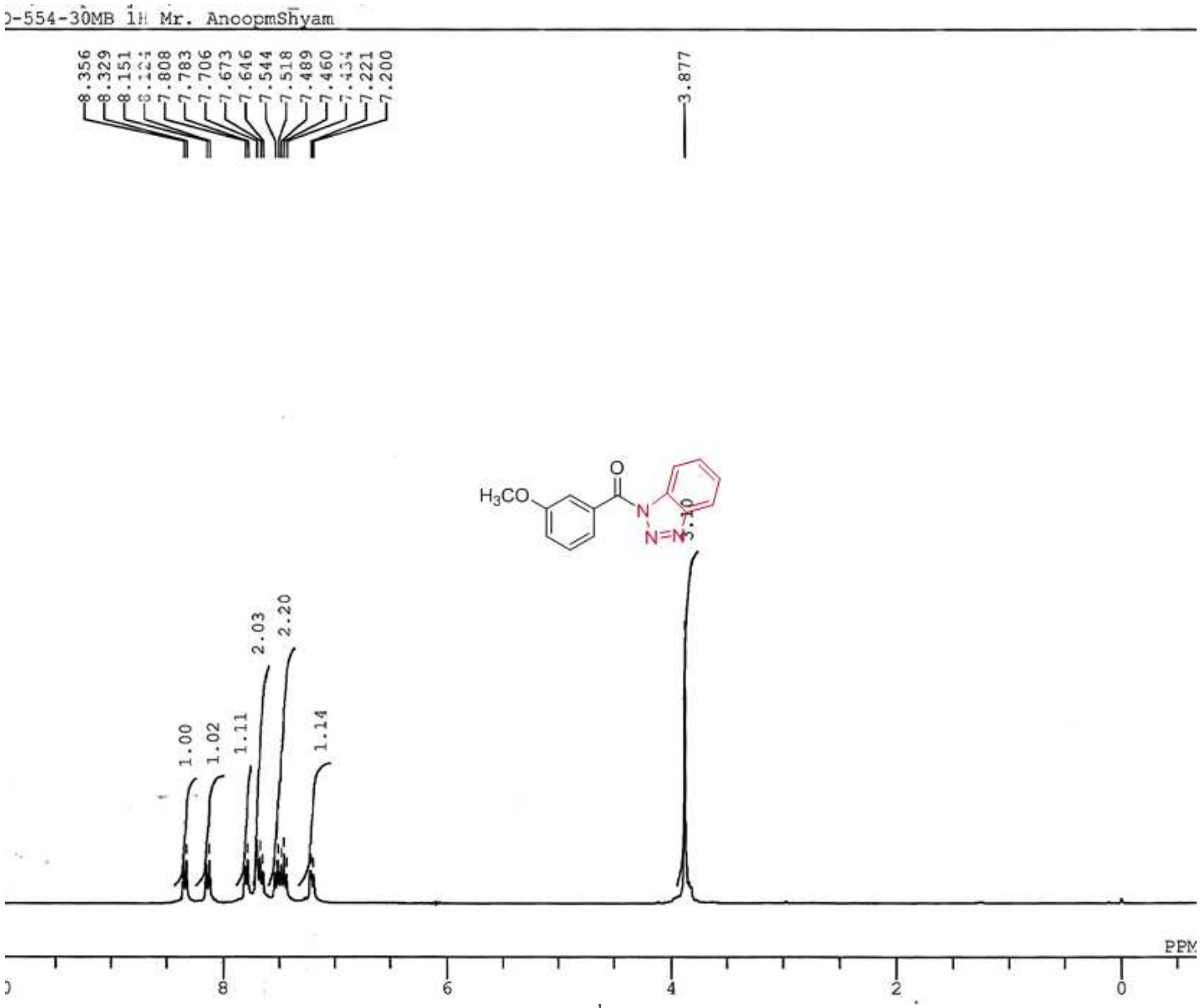
D-355-3



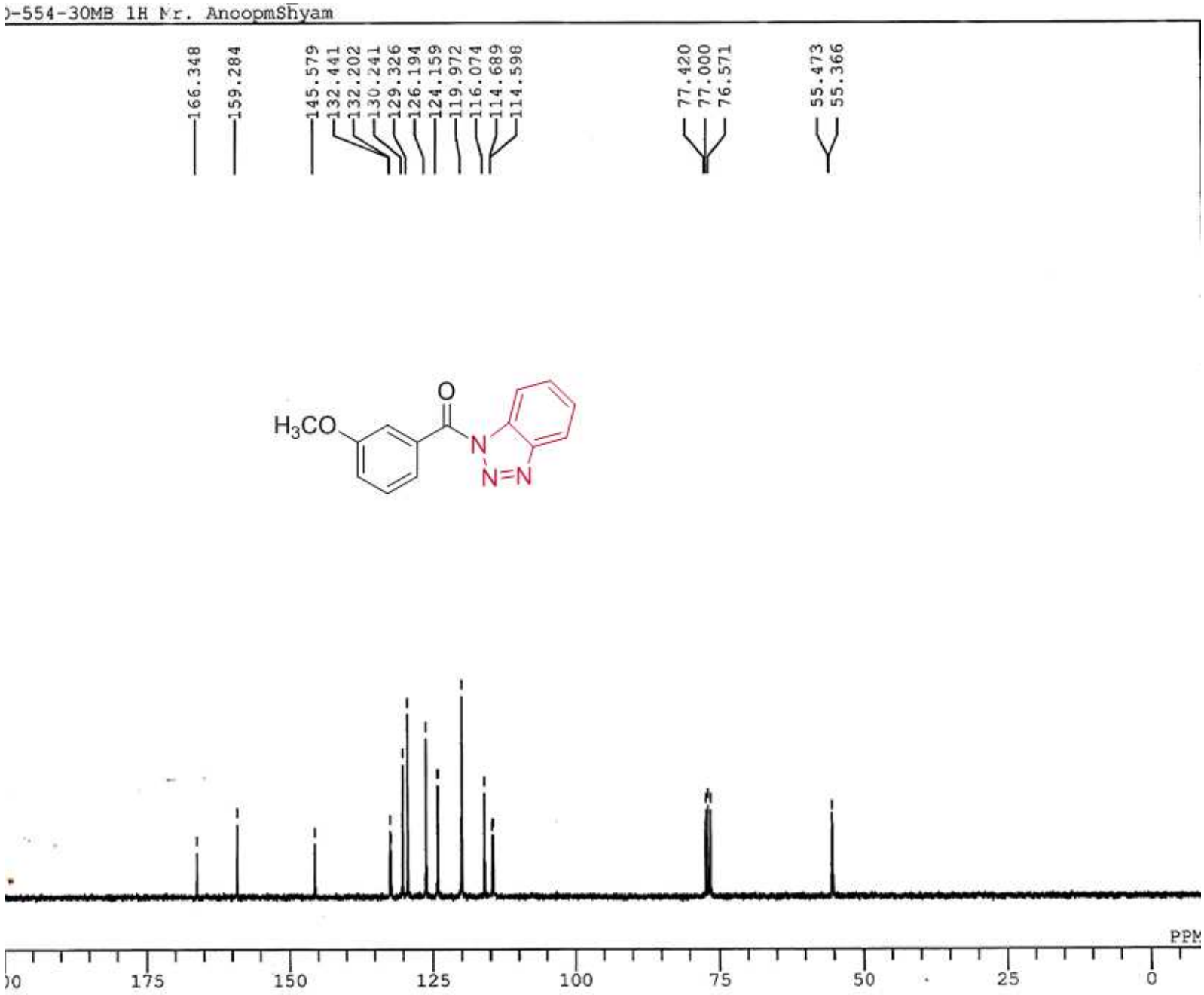
Spectrum 13: 300 MHz ^{1}H NMR of compound **2g**



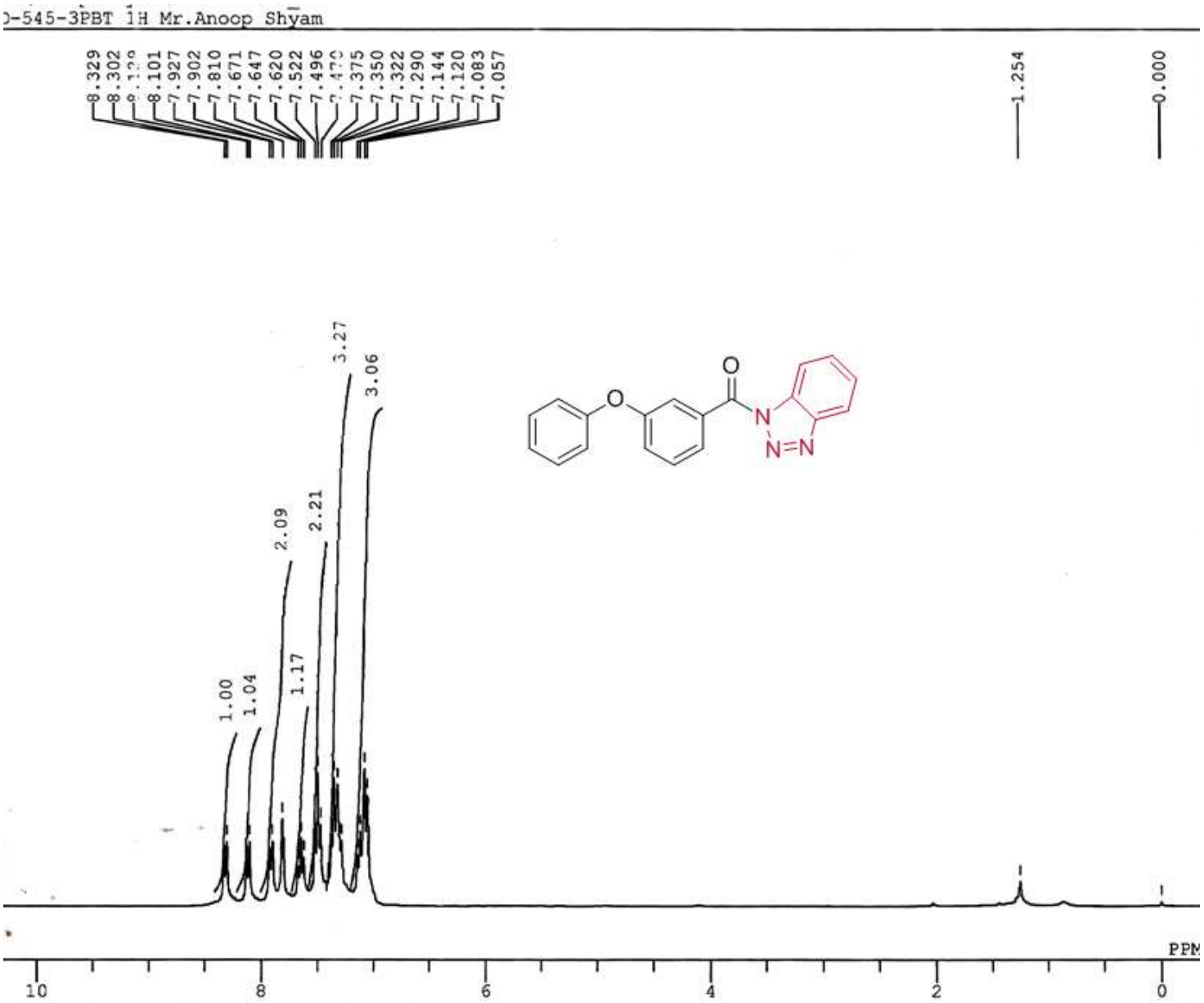
Spectrum 14: 75 MHz ^{13}C NMR of compound **2g**



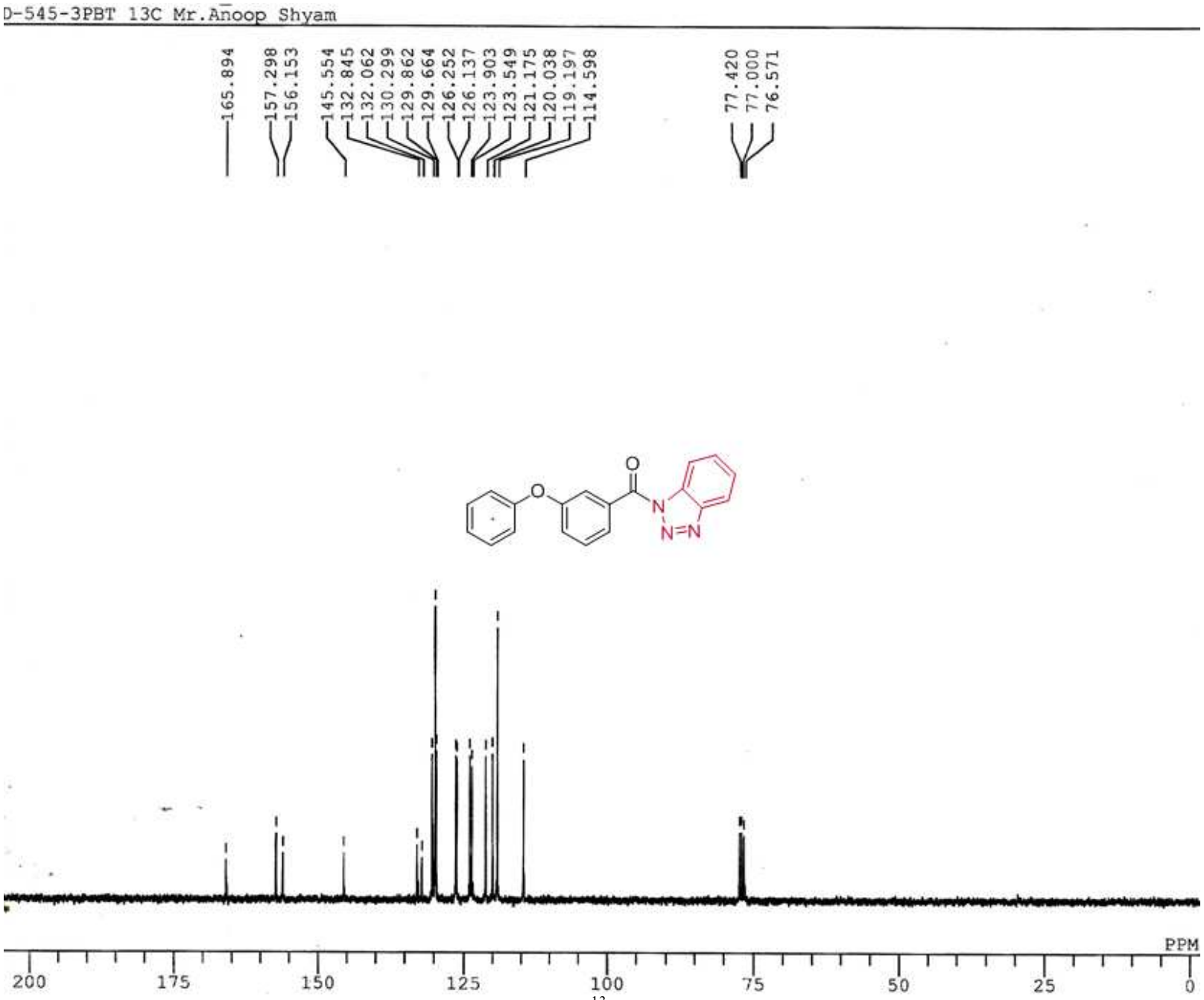
Spectrum 15: 300 MHz ^{1}H NMR of compound **2h**



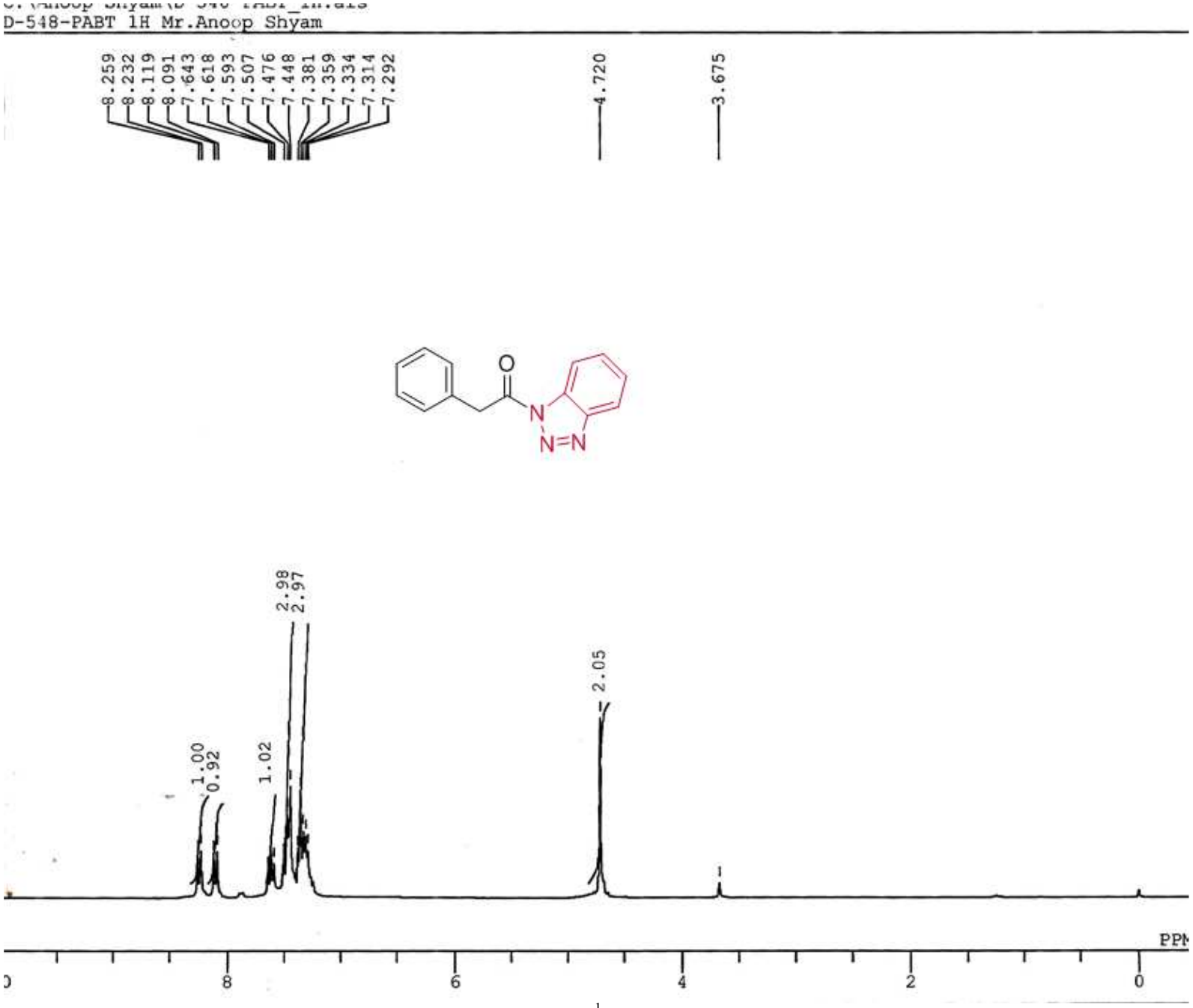
Spectrum 16: 75 MHz ^{13}C NMR of compound **2h**



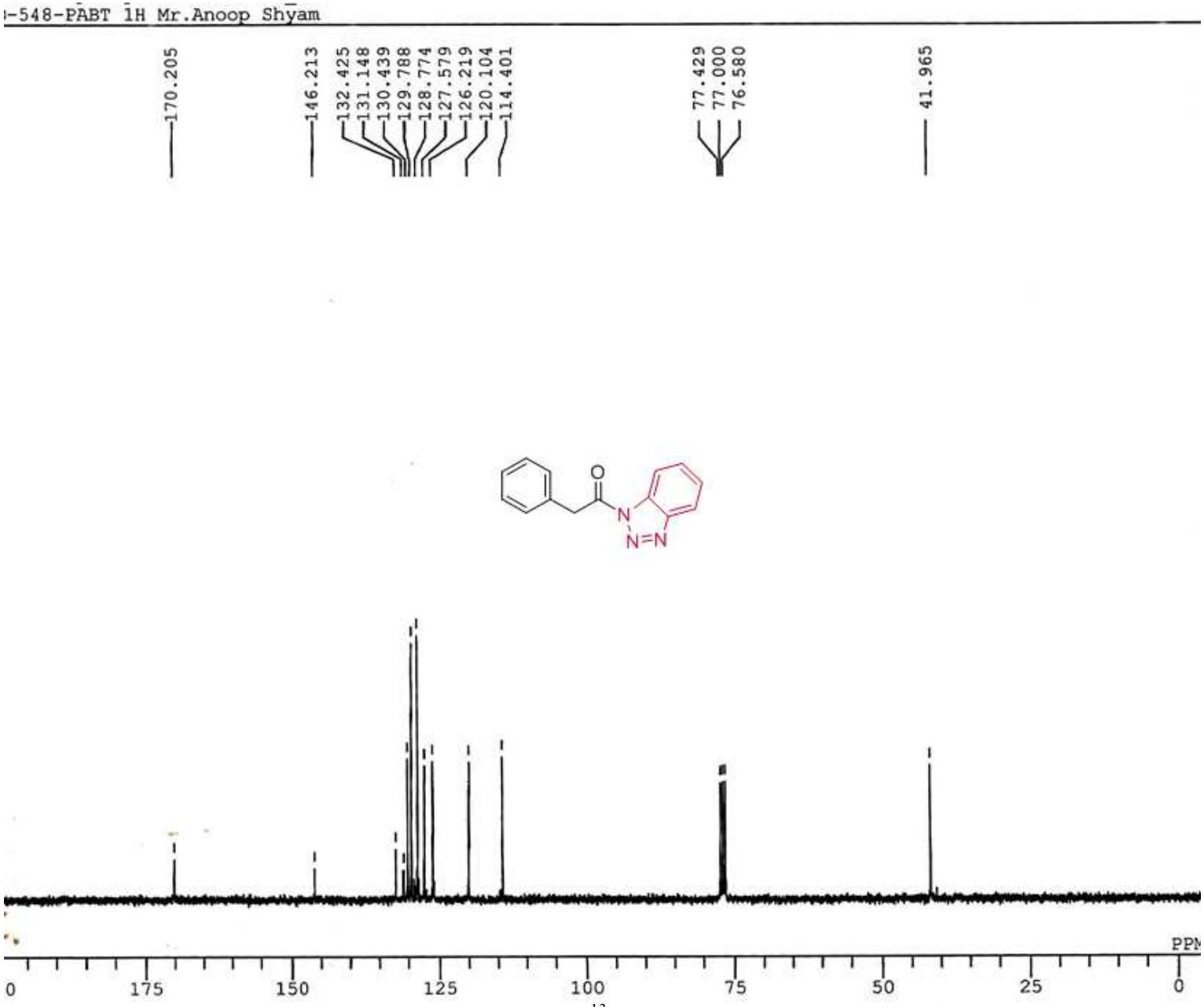
Spectrum 17: 300 MHz ^{1}H NMR of compound **2i**



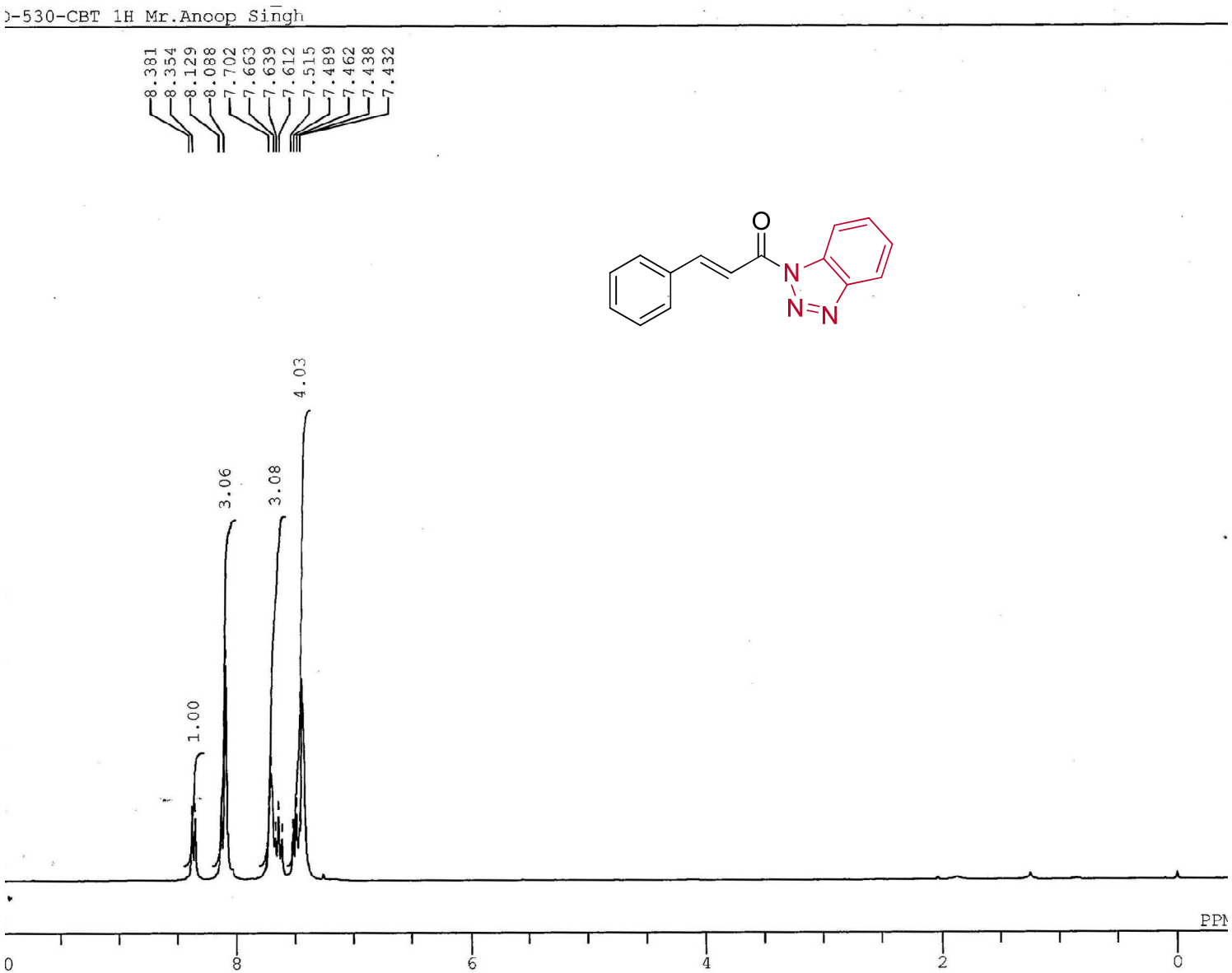
Spectrum 18: 75 MHz ^{13}C NMR of compound **2i**



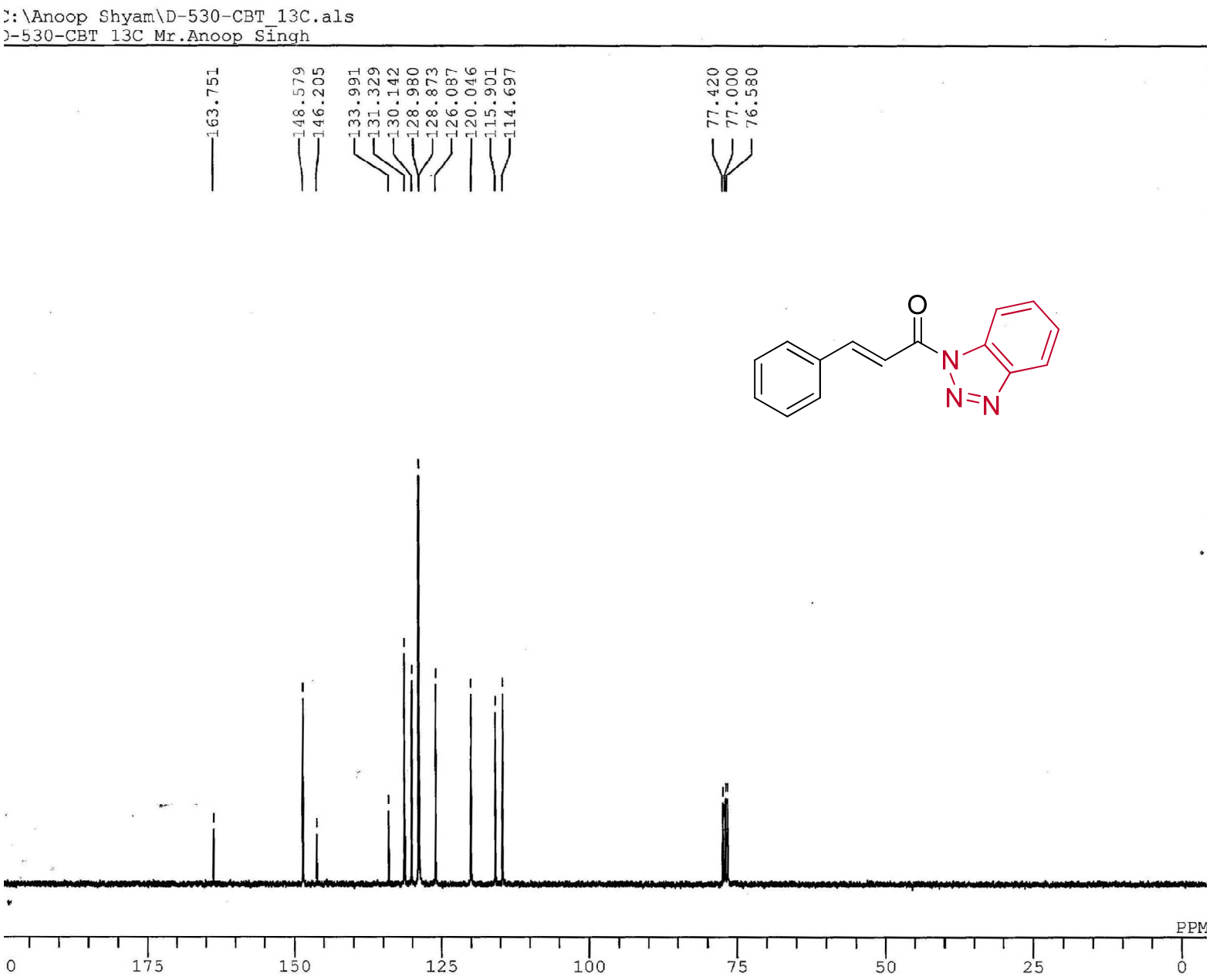
Spectrum 19: 300 MHz ^{1}H NMR of compound **2j**



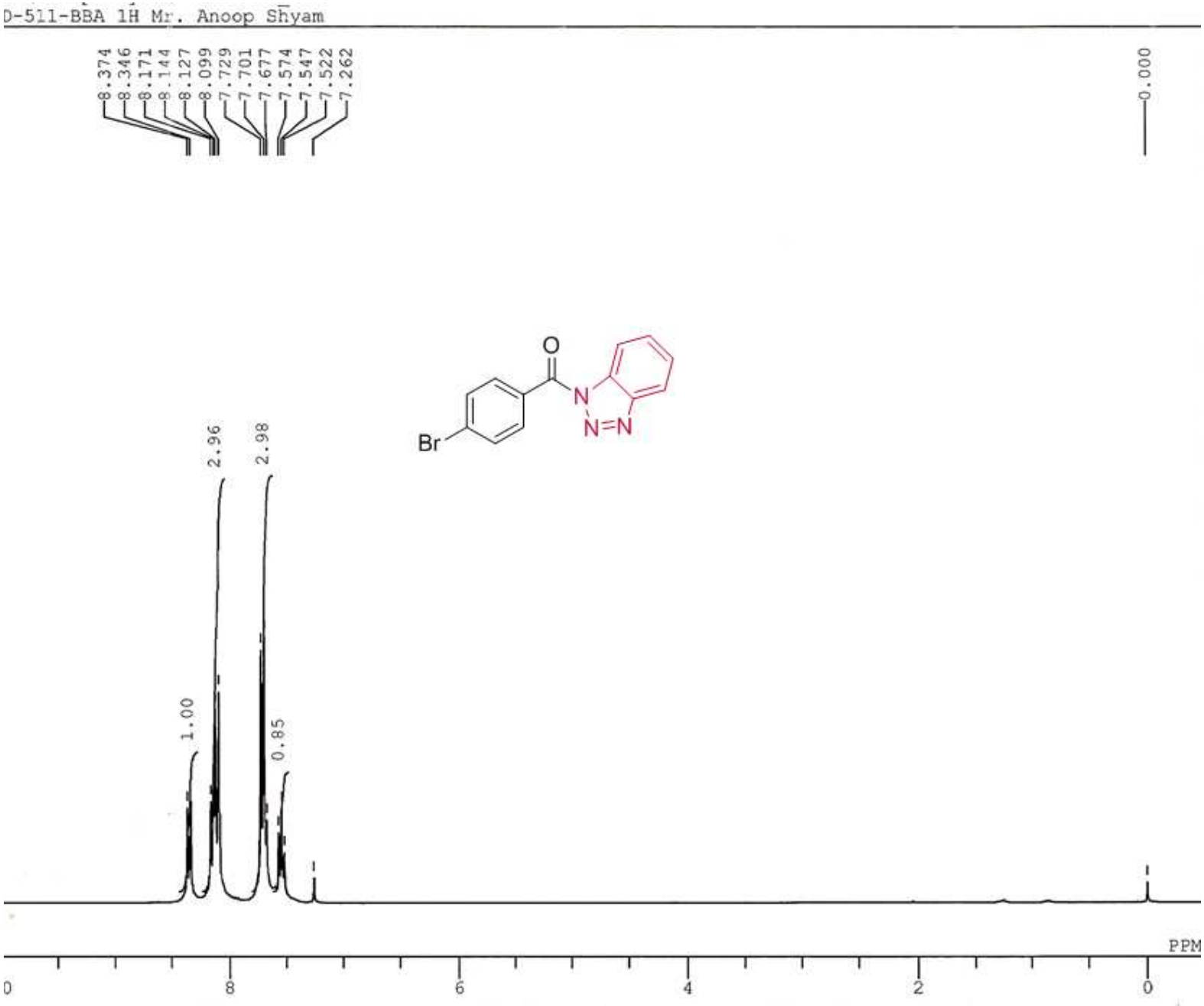
Spectrum 20: 75 MHz ^{13}C NMR of compound **2j**



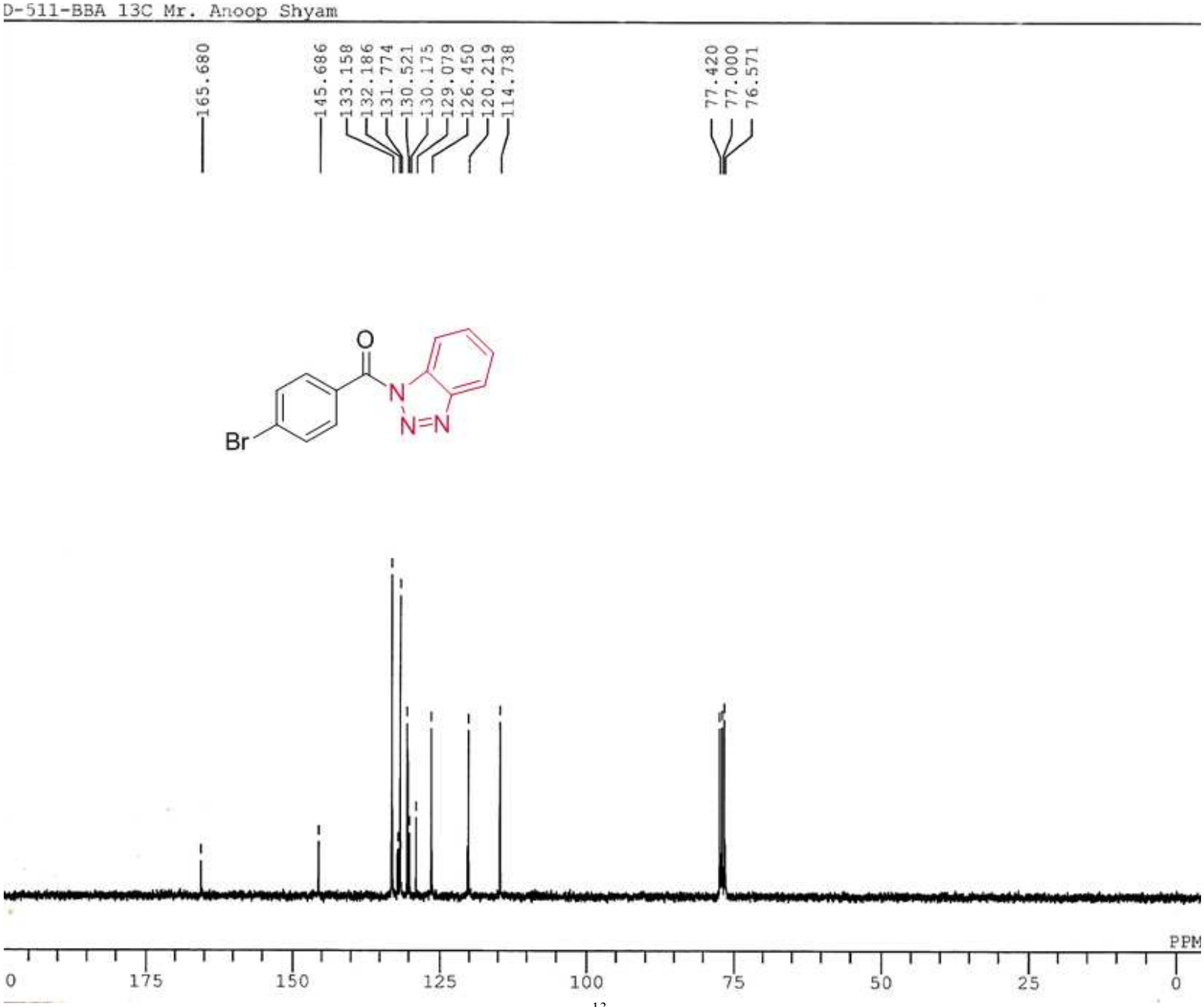
Spectrum 21: 300 MHz ^{1}H NMR of compound **2k**



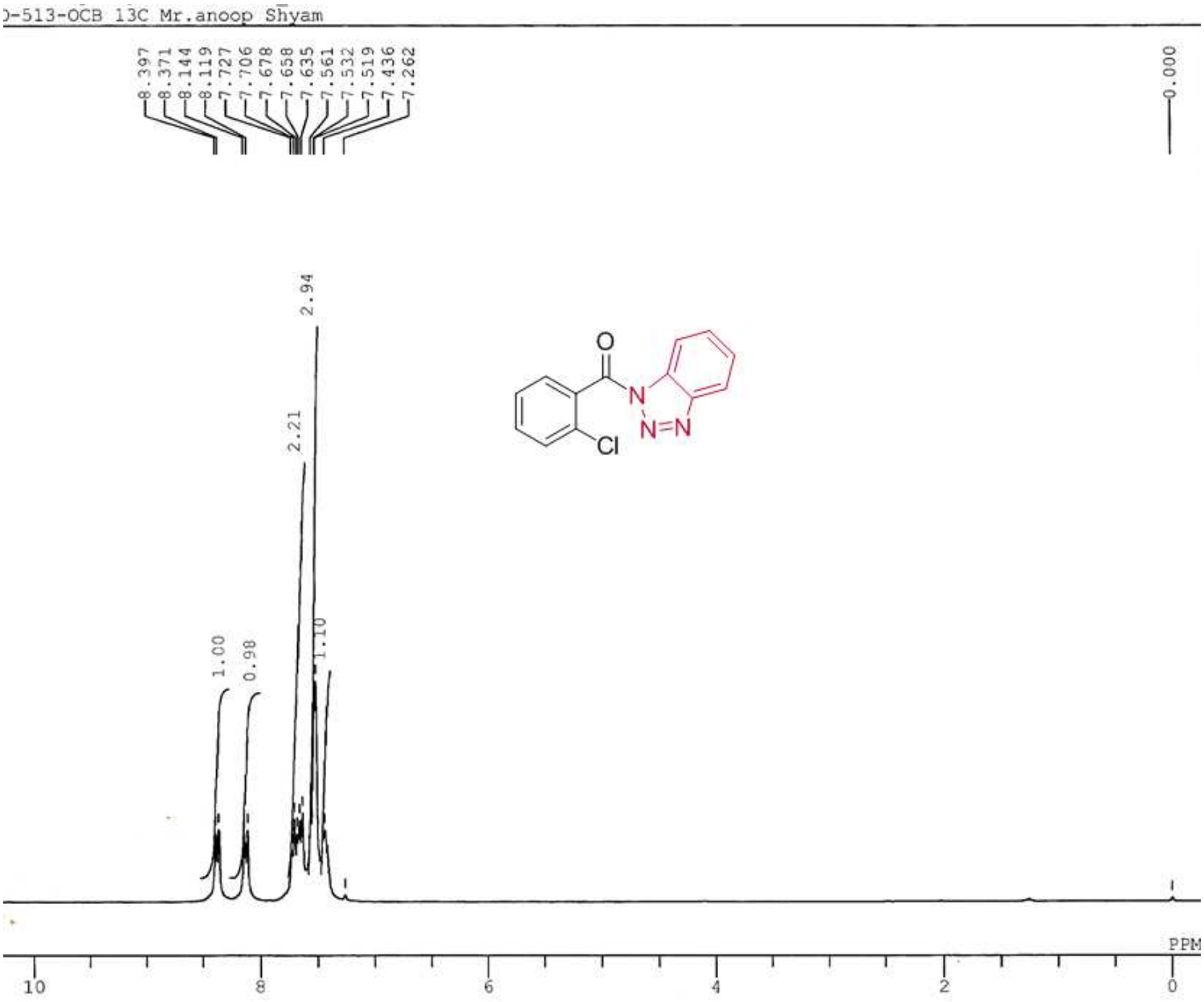
Spectrum 22: 75 MHz ^{13}C NMR of compound **2k**



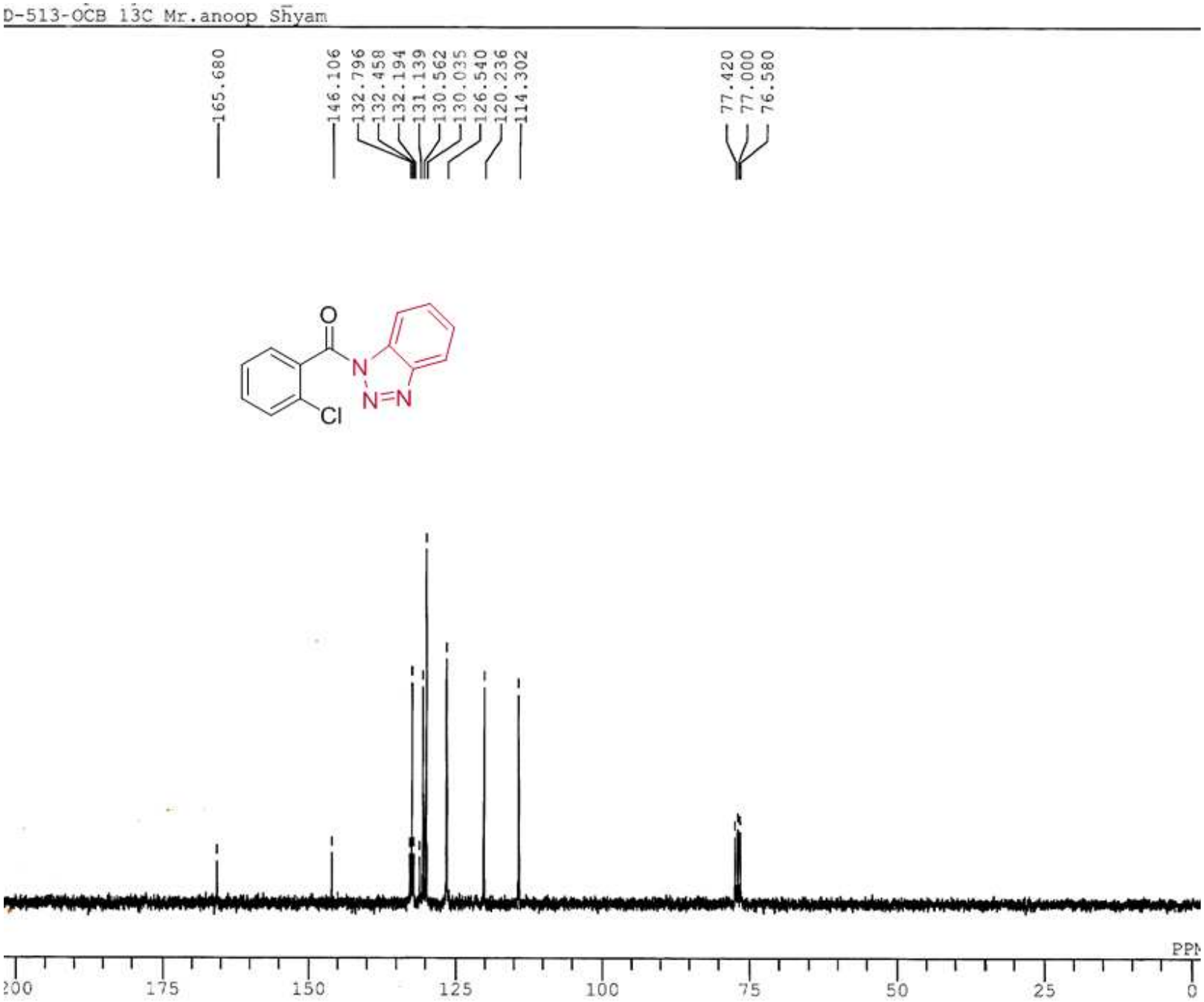
Spectrum 23: 300 MHz ^{1}H NMR of compound **2l**



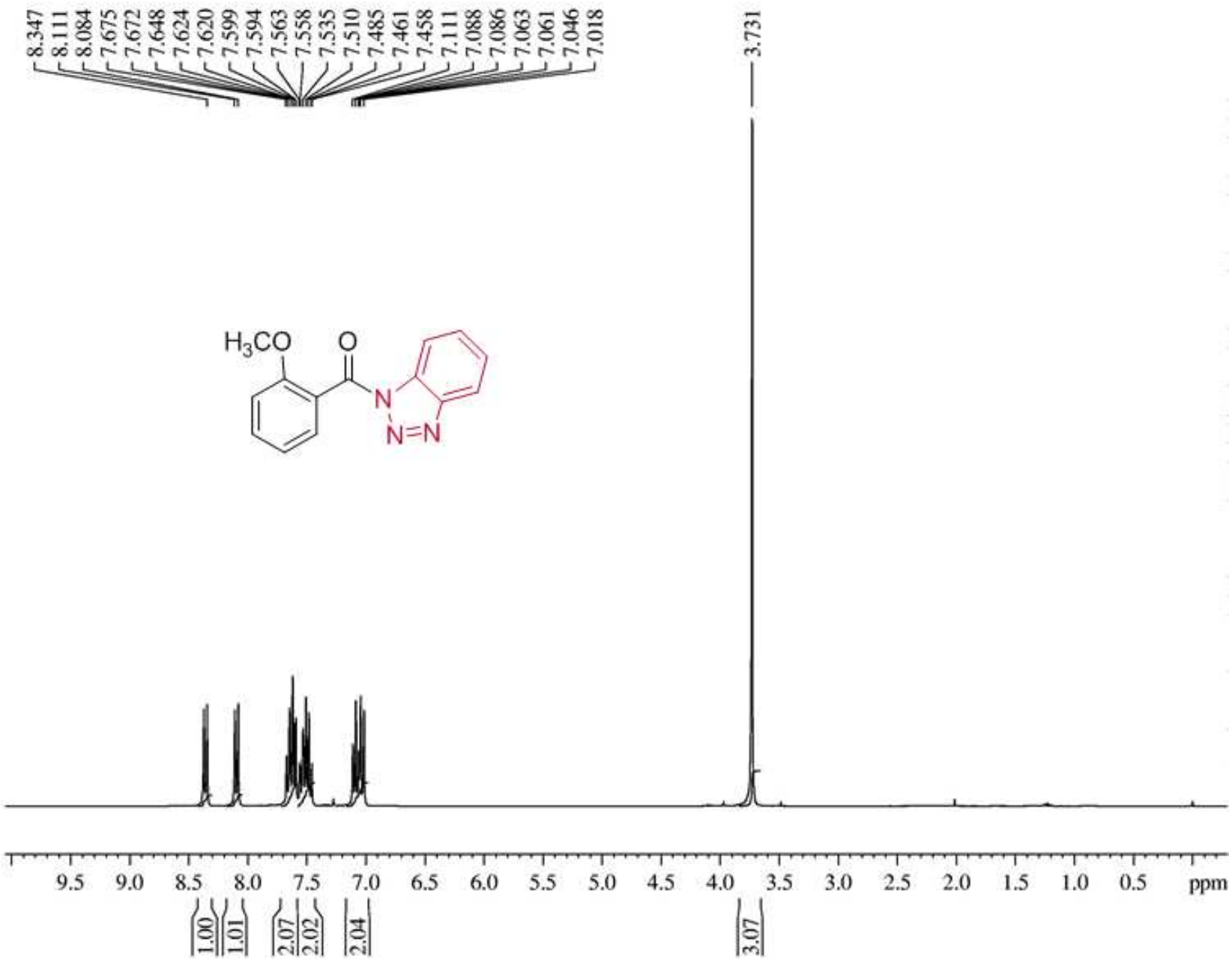
Spectrum 24: 75 MHz ^{13}C NMR of compound **2l**



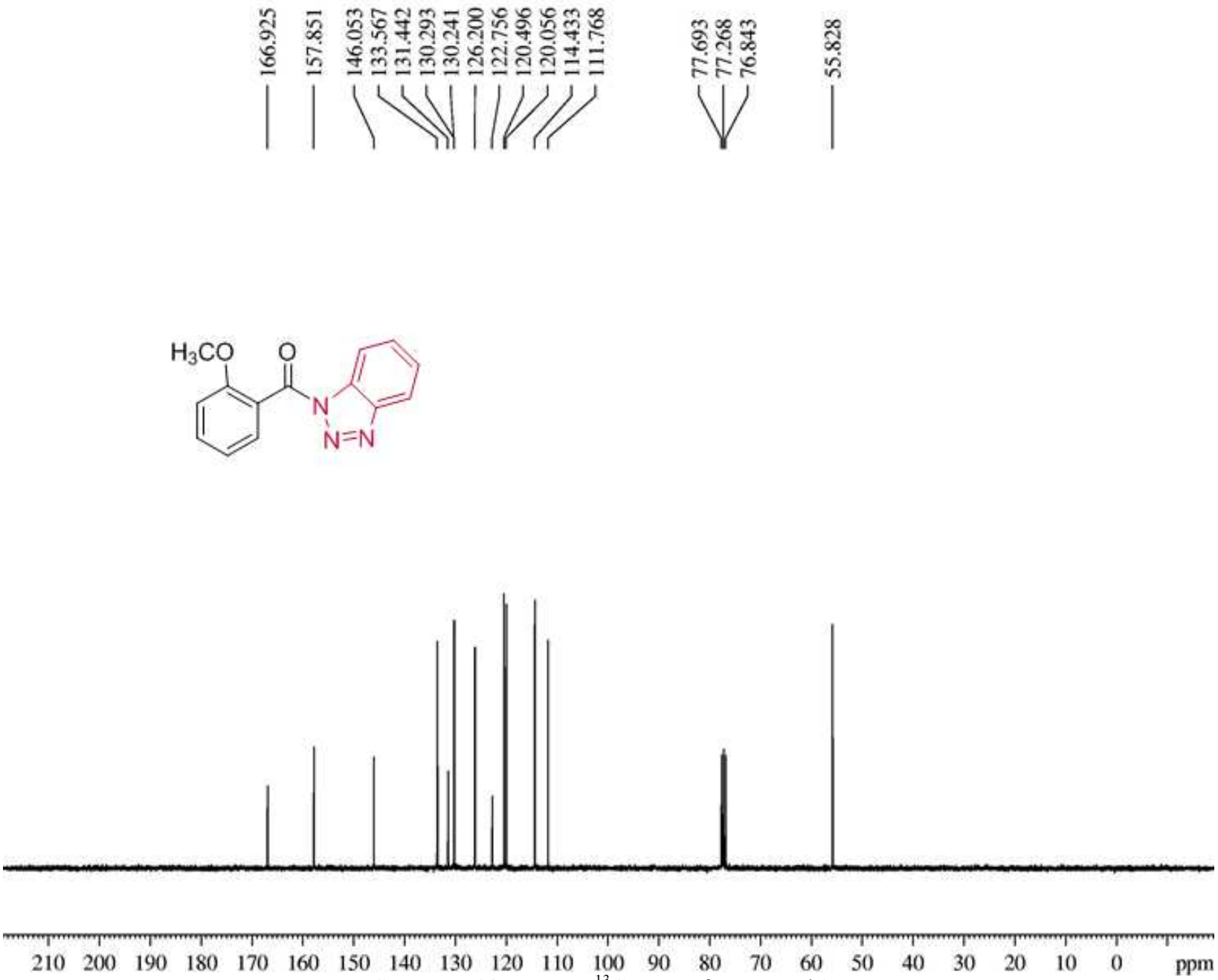
Spectrum 25: 300 MHz ^{1}H NMR of compound **2m**



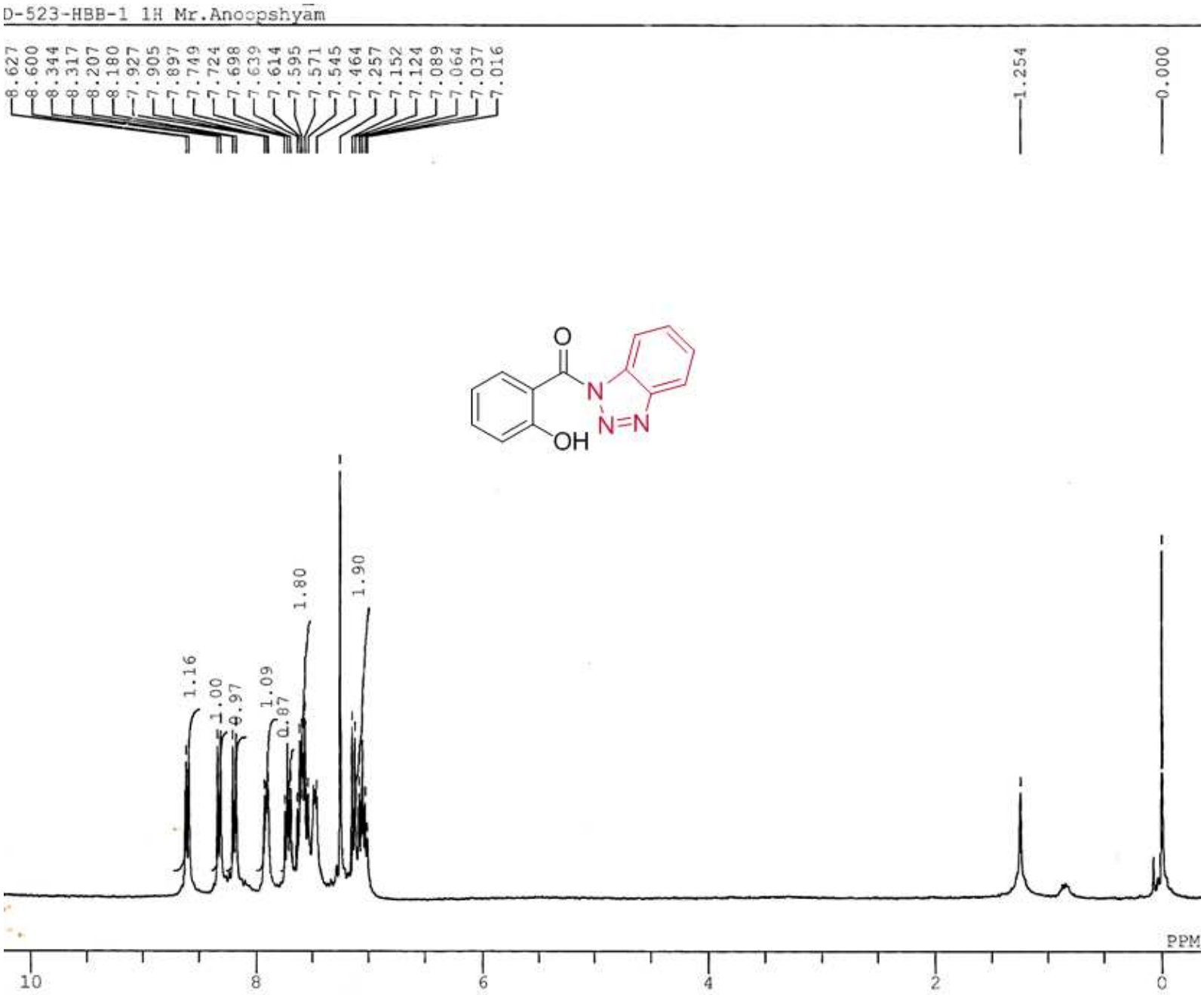
Spectrum 26: 75 MHz ^{13}C NMR of compound **2m**



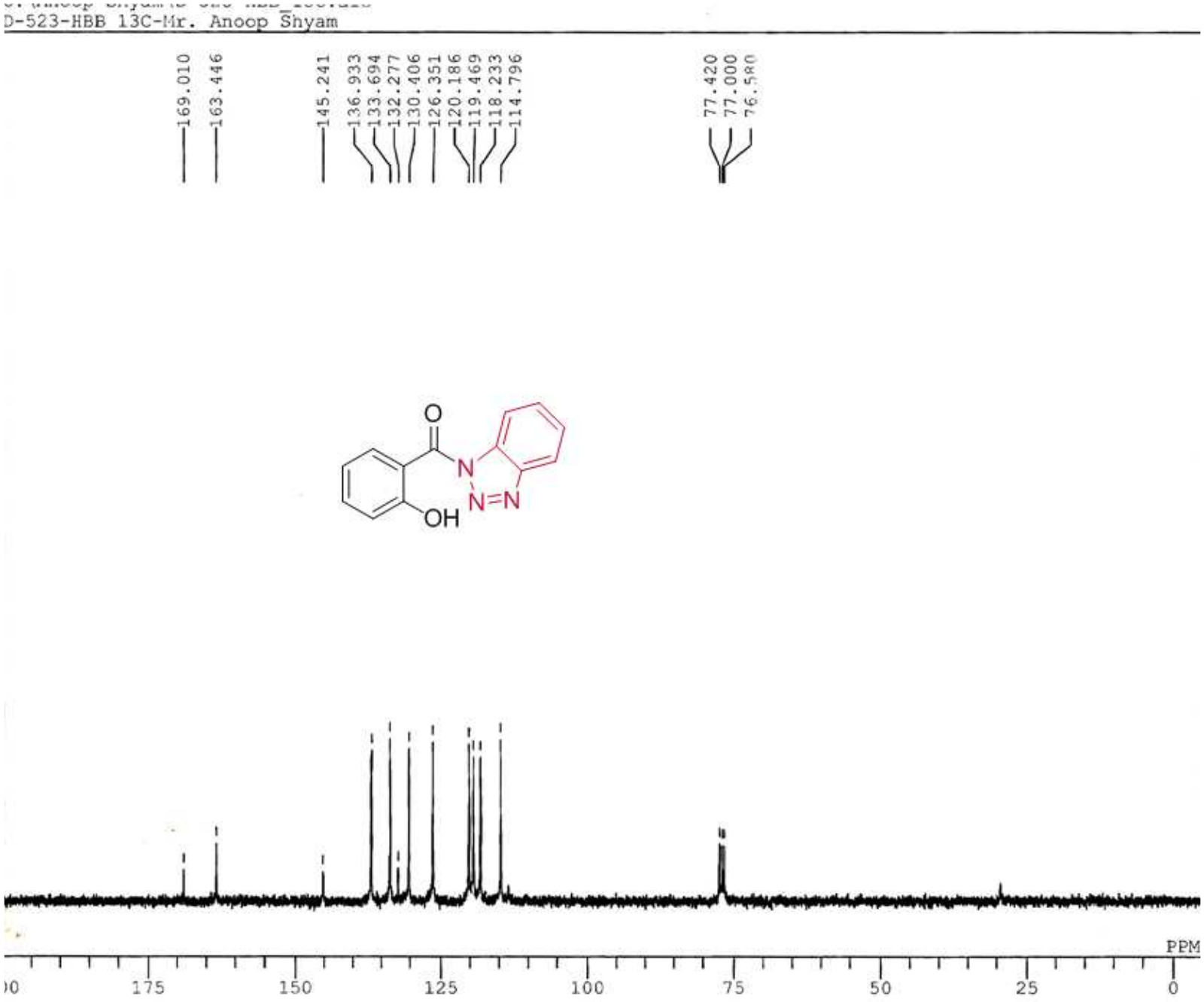
Spectrum 27: 300 MHz ^{1}H NMR of compound **2n**



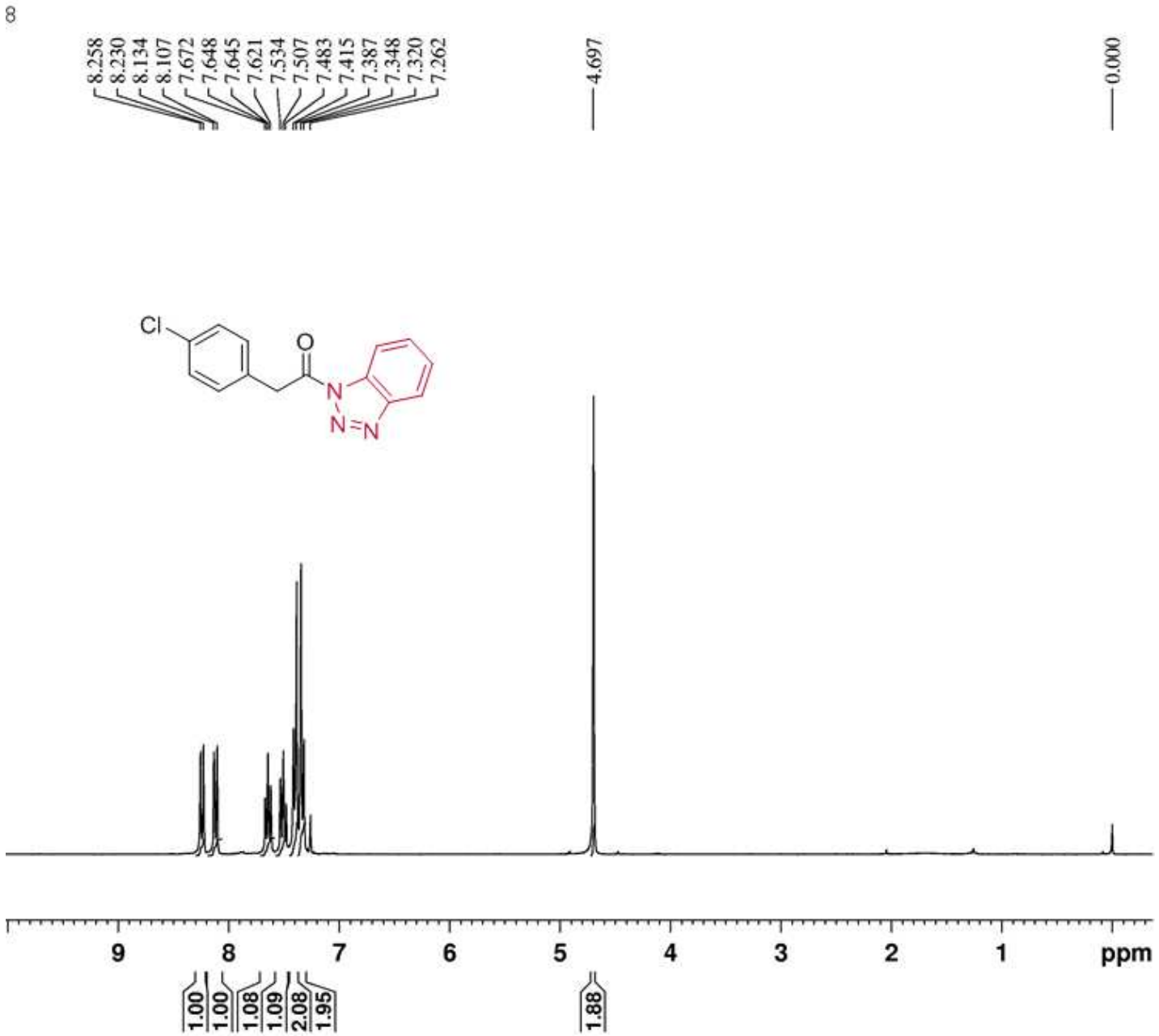
Spectrum 28: 75 MHz ^{13}C NMR of compound **2n**



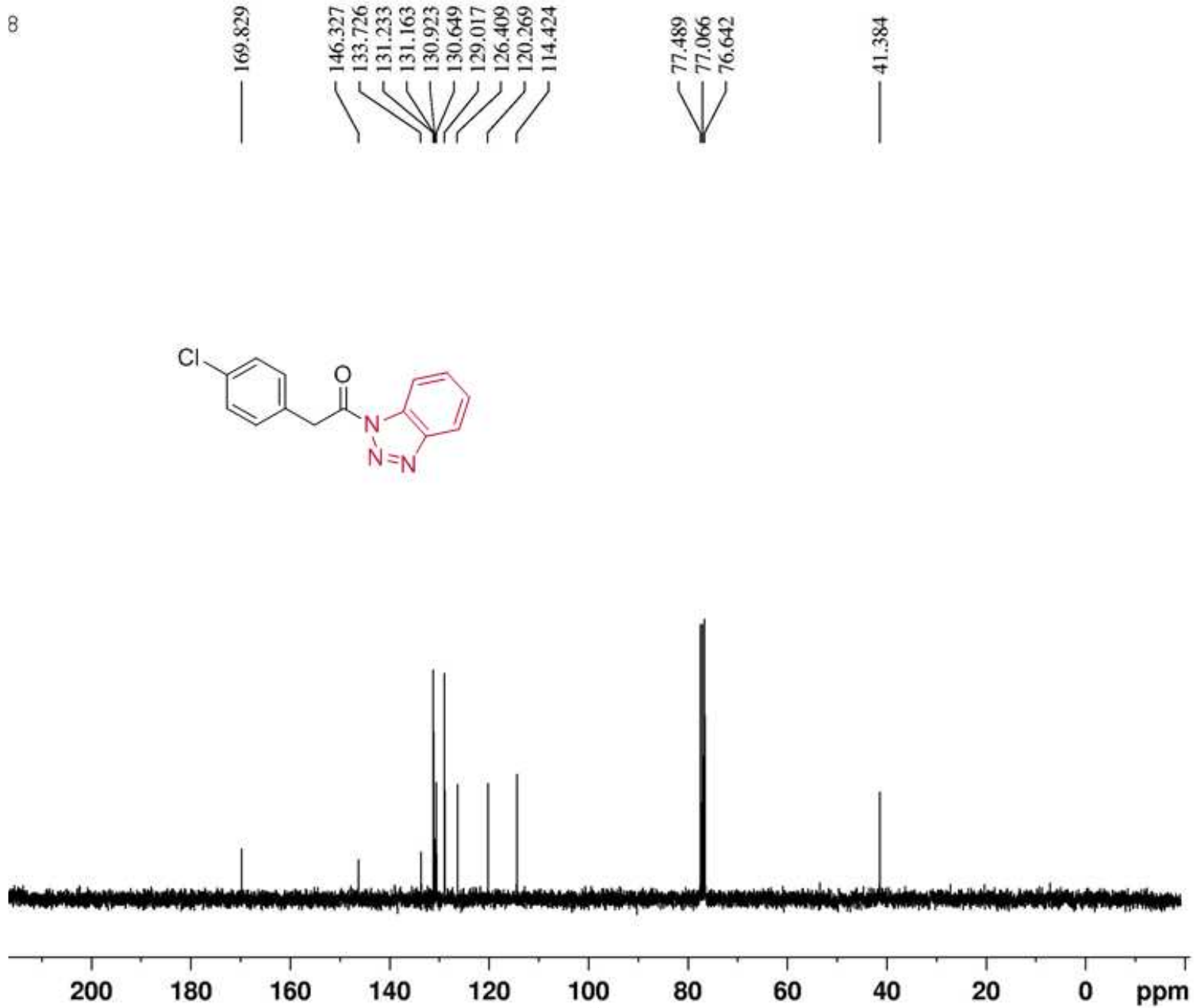
Spectrum 29: 300 MHz ^{1}H NMR of compound **2o**



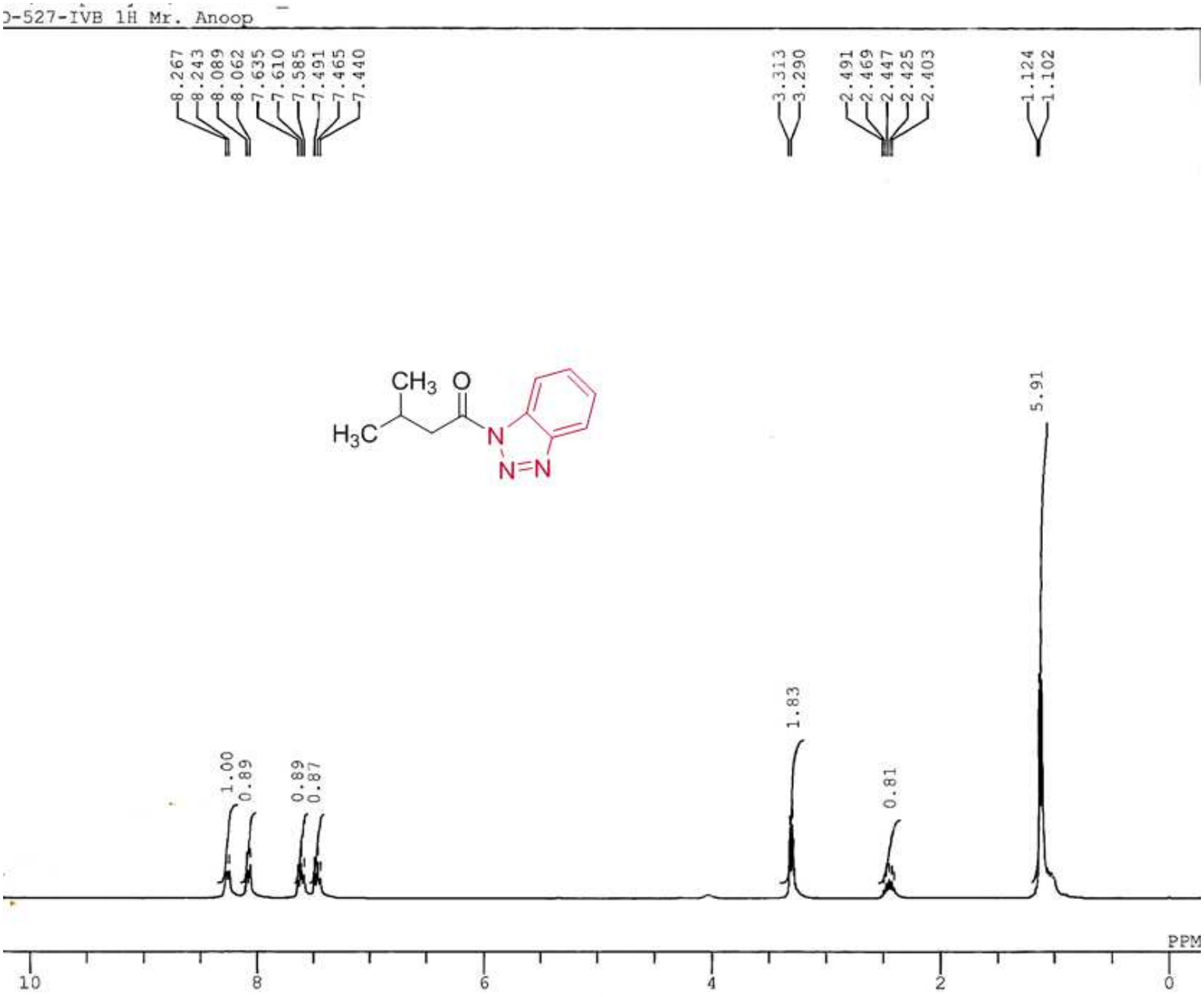
Spectrum 30: 75 MHz ^{13}C NMR of compound **2o**



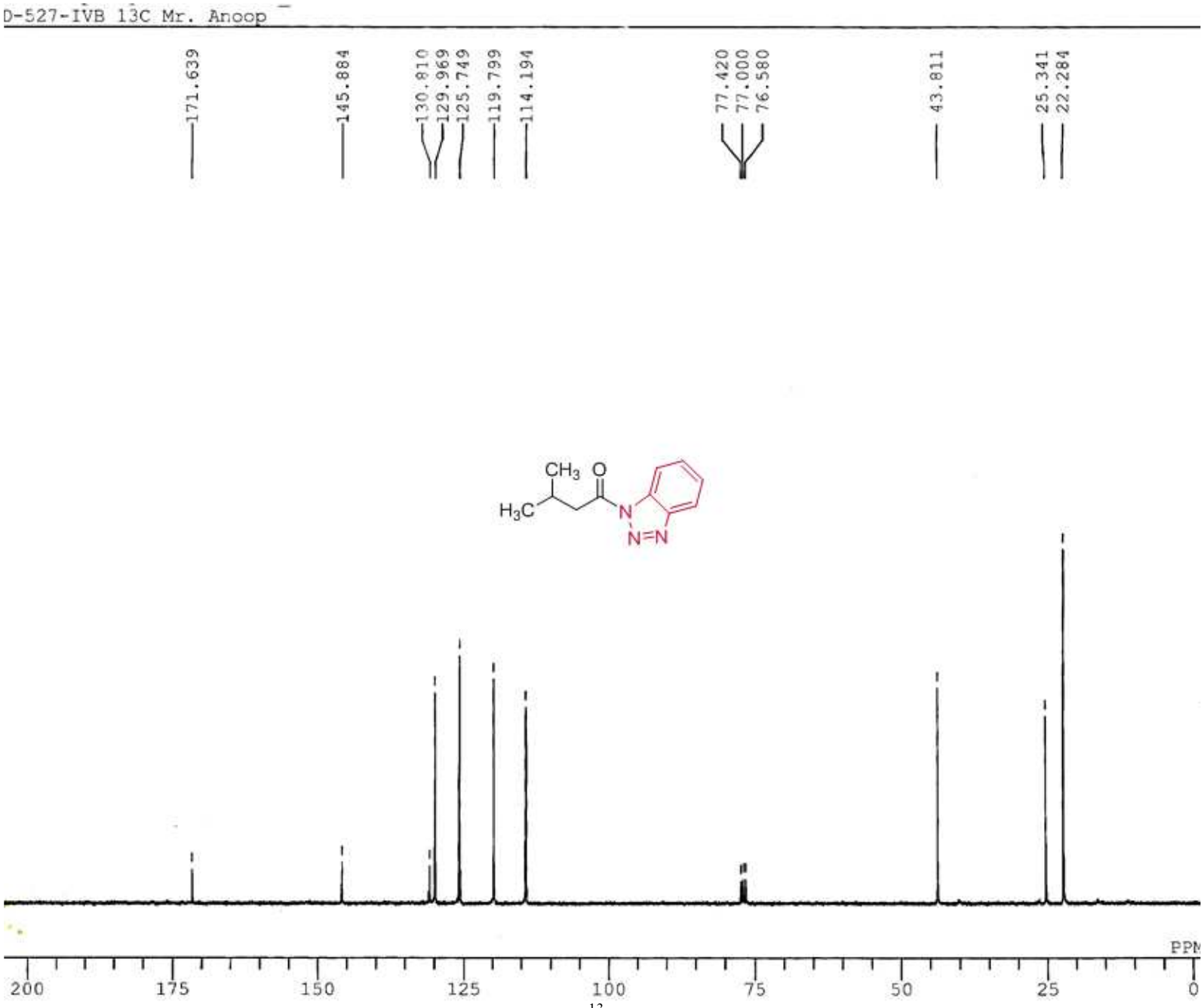
Spectrum 31: 300 MHz ^{1}H NMR of compound **2p**



Spectrum 32: 75 MHz ^{13}C NMR of compound **2p**

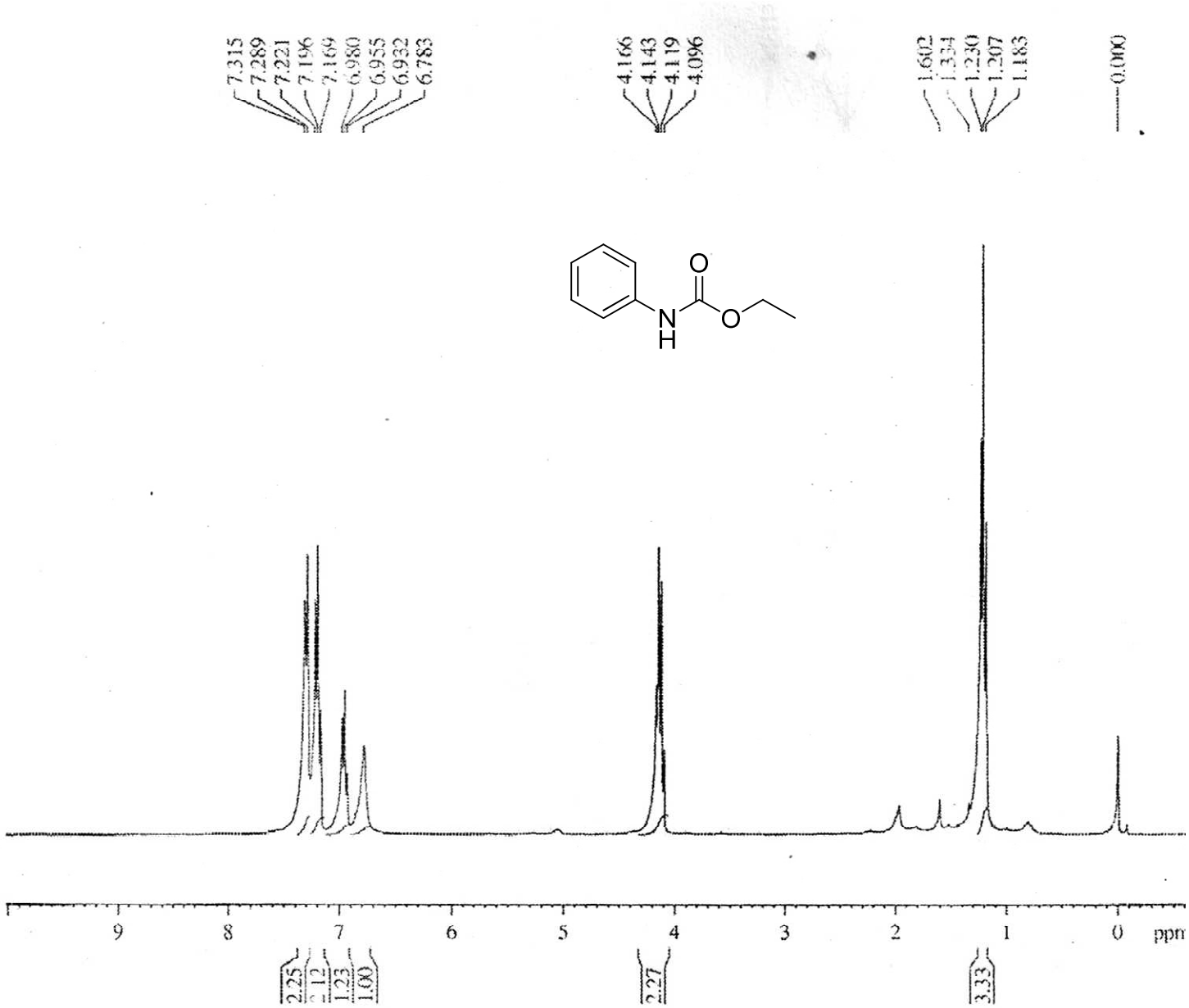


Spectrum 33: 300 MHz ^{1}H NMR of compound **2q**

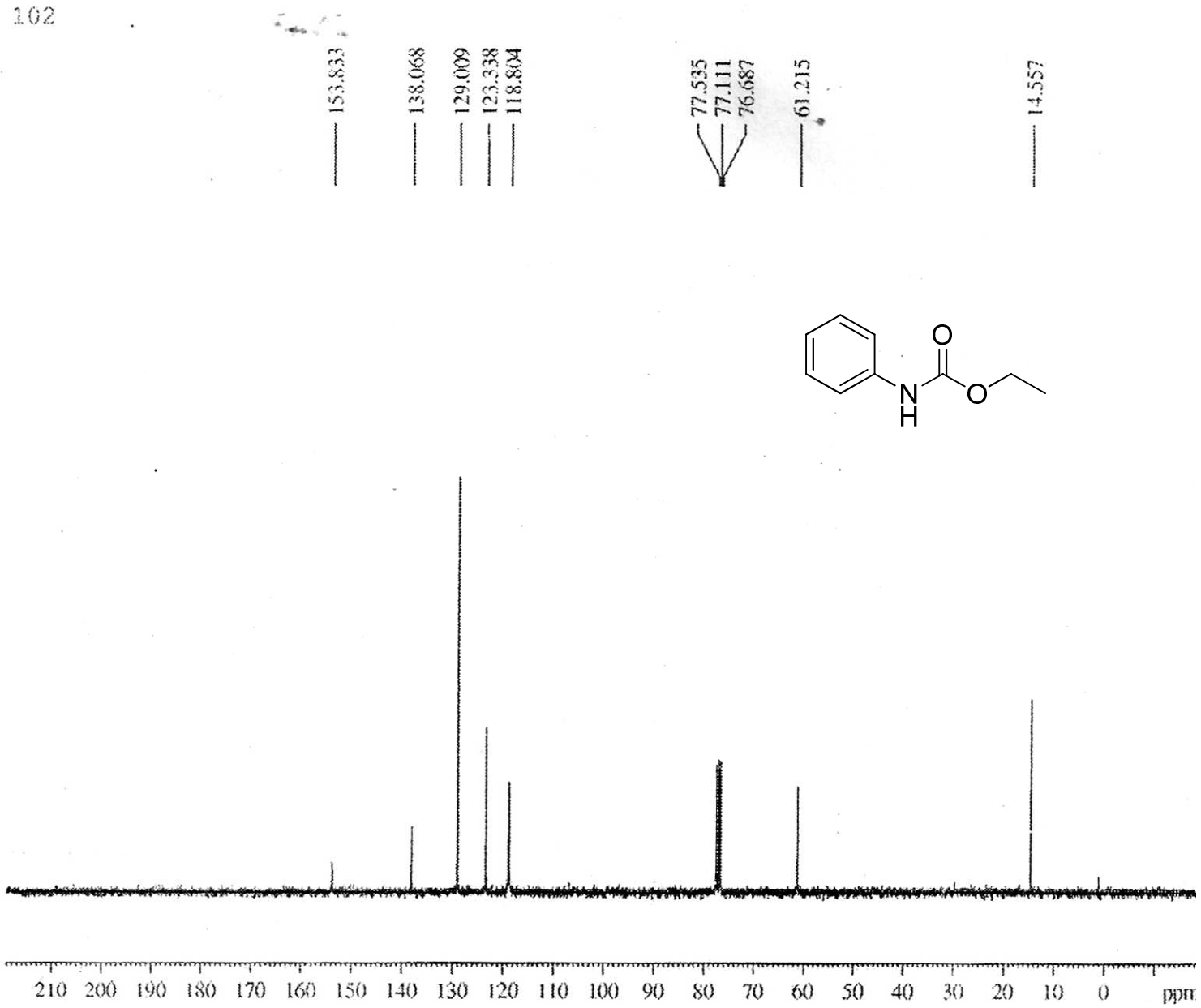


Spectrum 34: 75 MHz ^{13}C NMR of compound **2q**

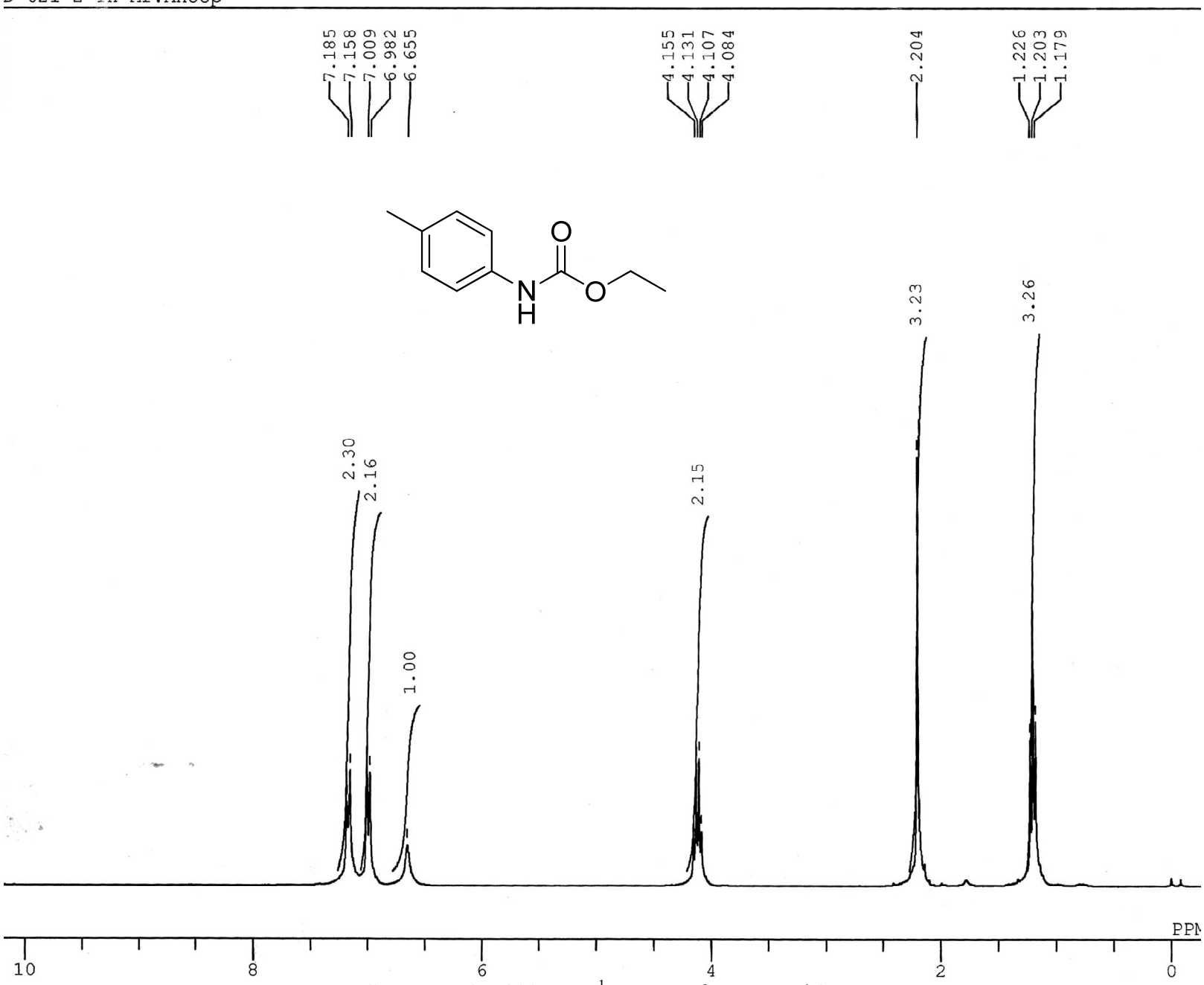
2. ^{1}H and ^{13}C NMR spectrum of Carbamates (**3a-t**).



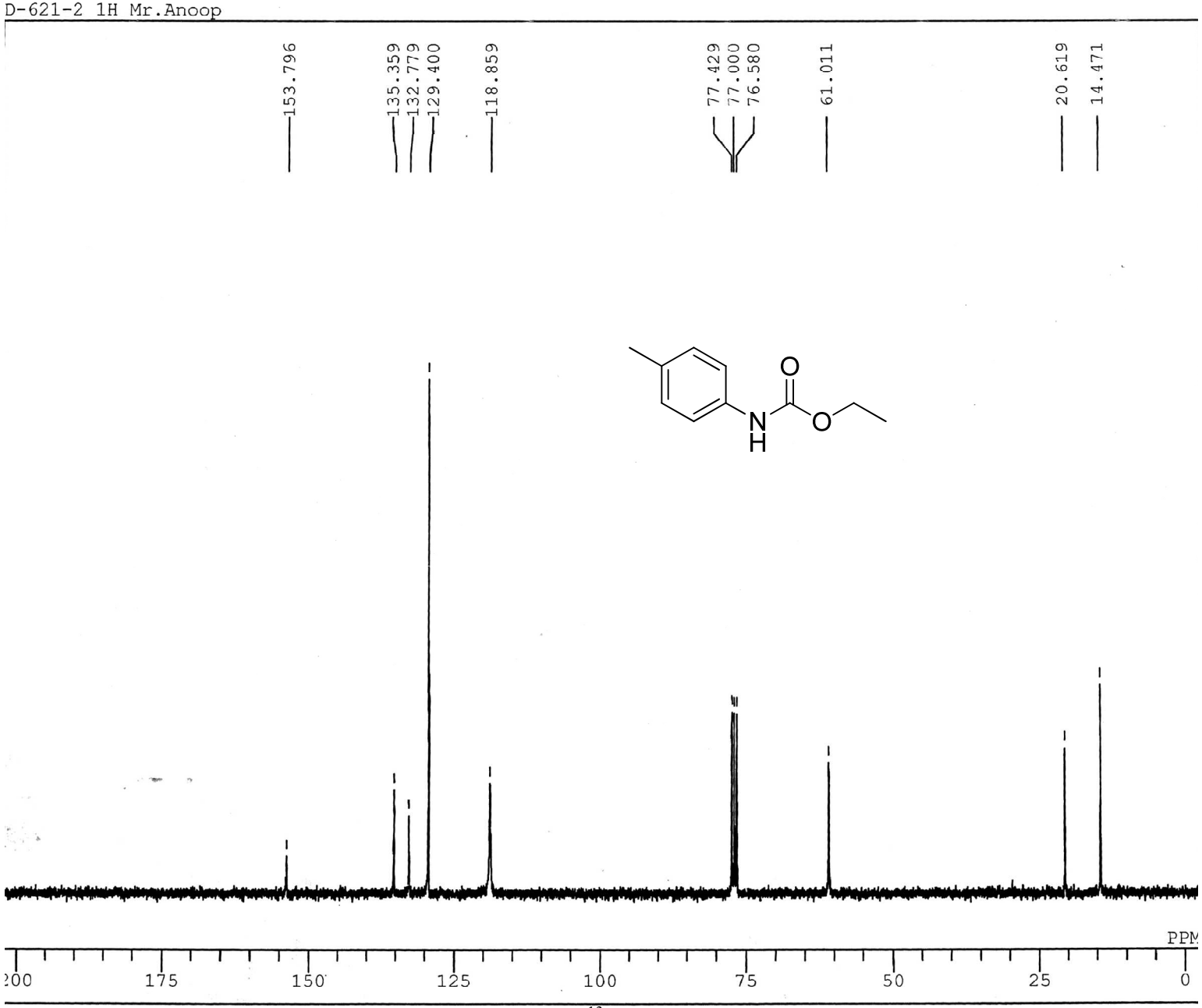
Spectrum 35: 300 MHz ^{1}H NMR of compound **3a**



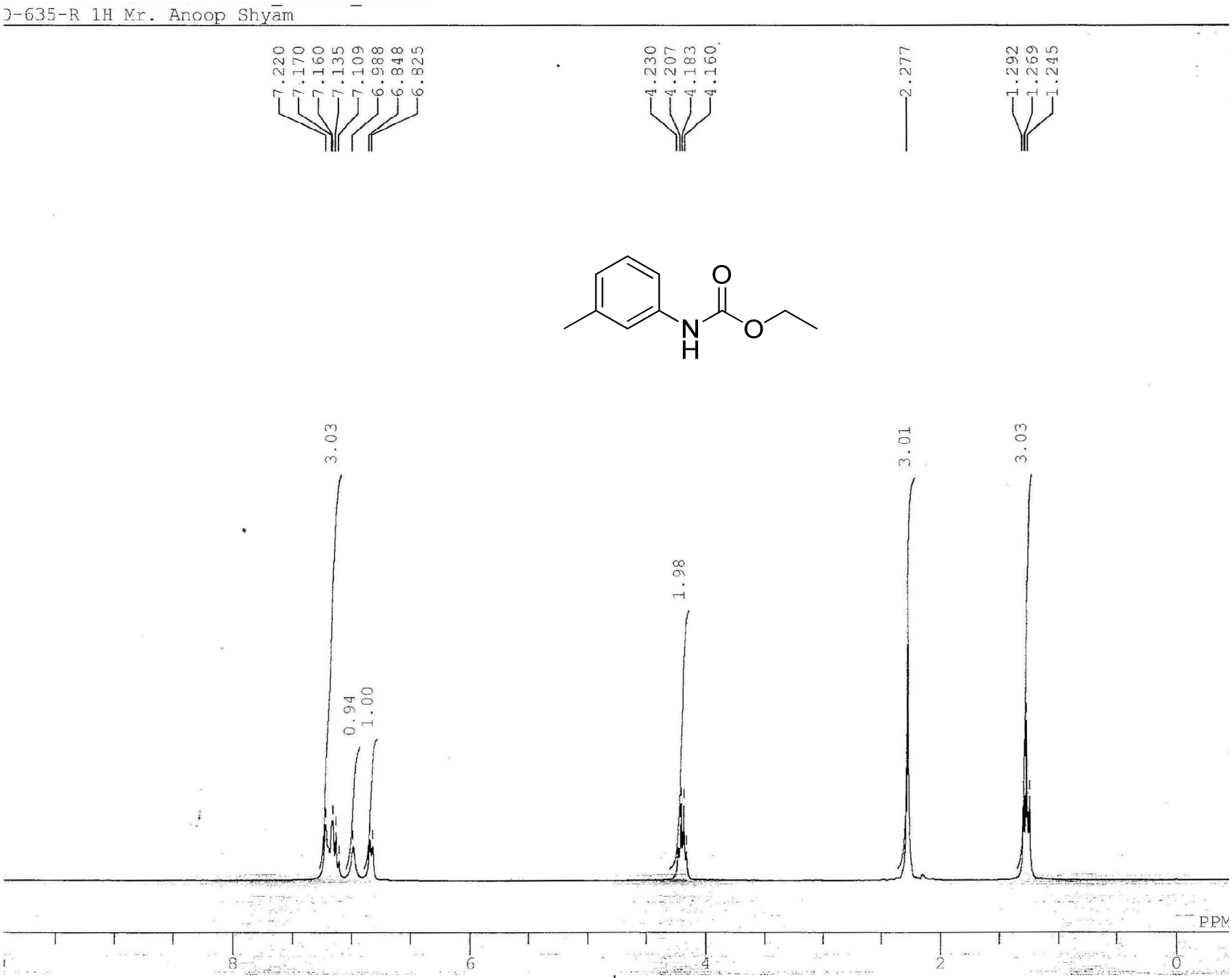
Spectrum 36: 75 MHz ^{13}C NMR of compound **3a**



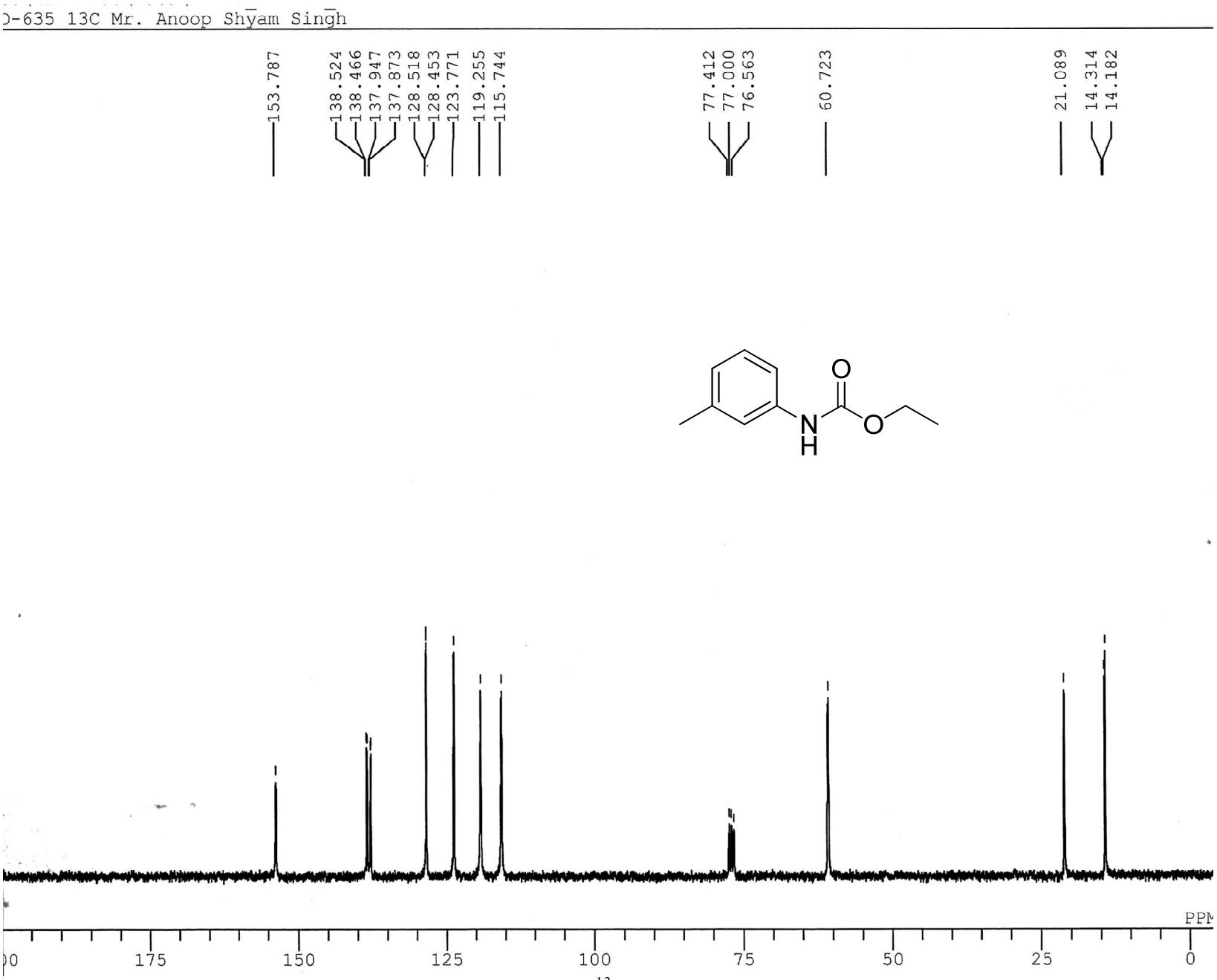
Spectrum 37: 300 MHz ^{1}H NMR of compound **3b**



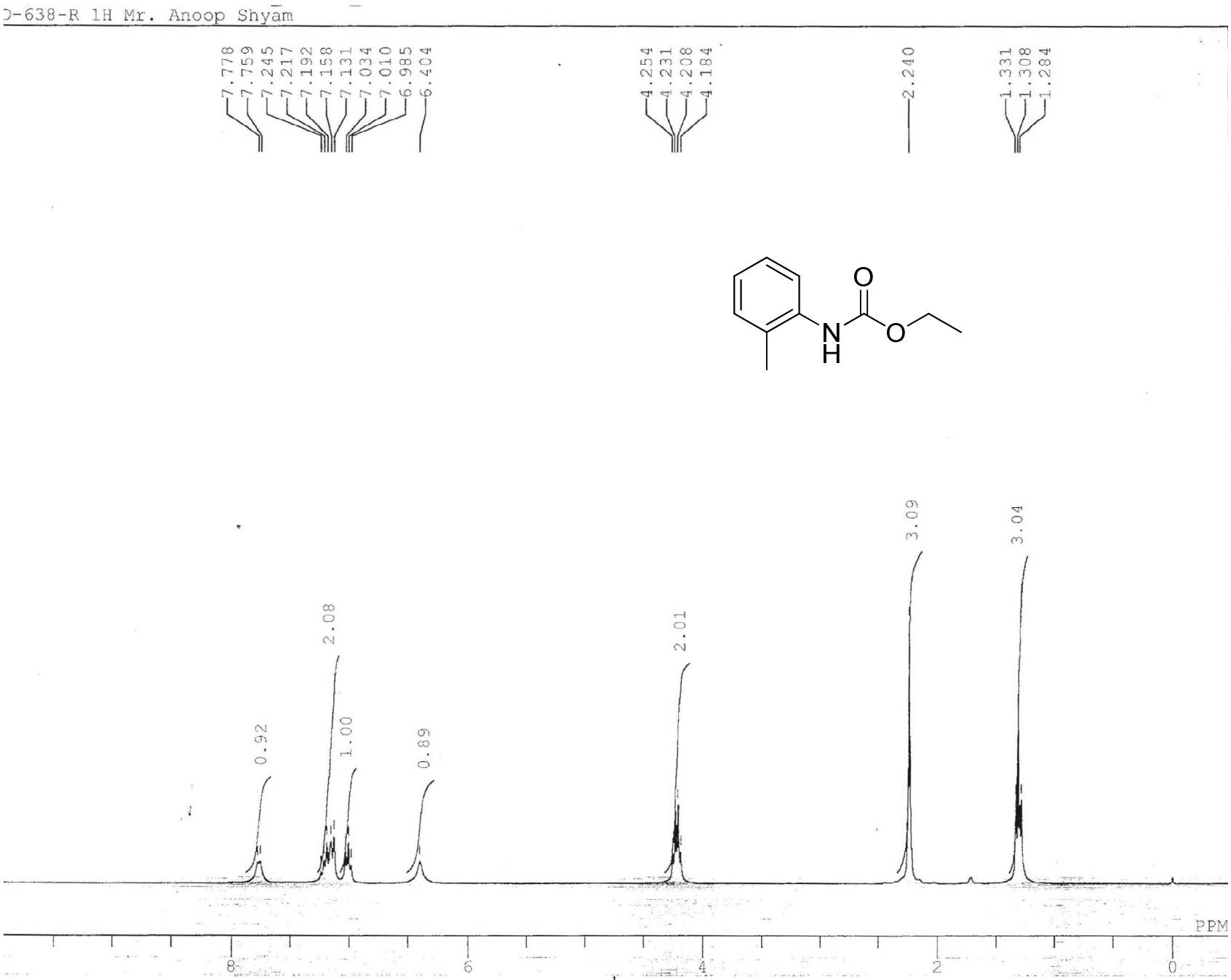
Spectrum 38: 75 MHz ^{13}C NMR of compound **3b**



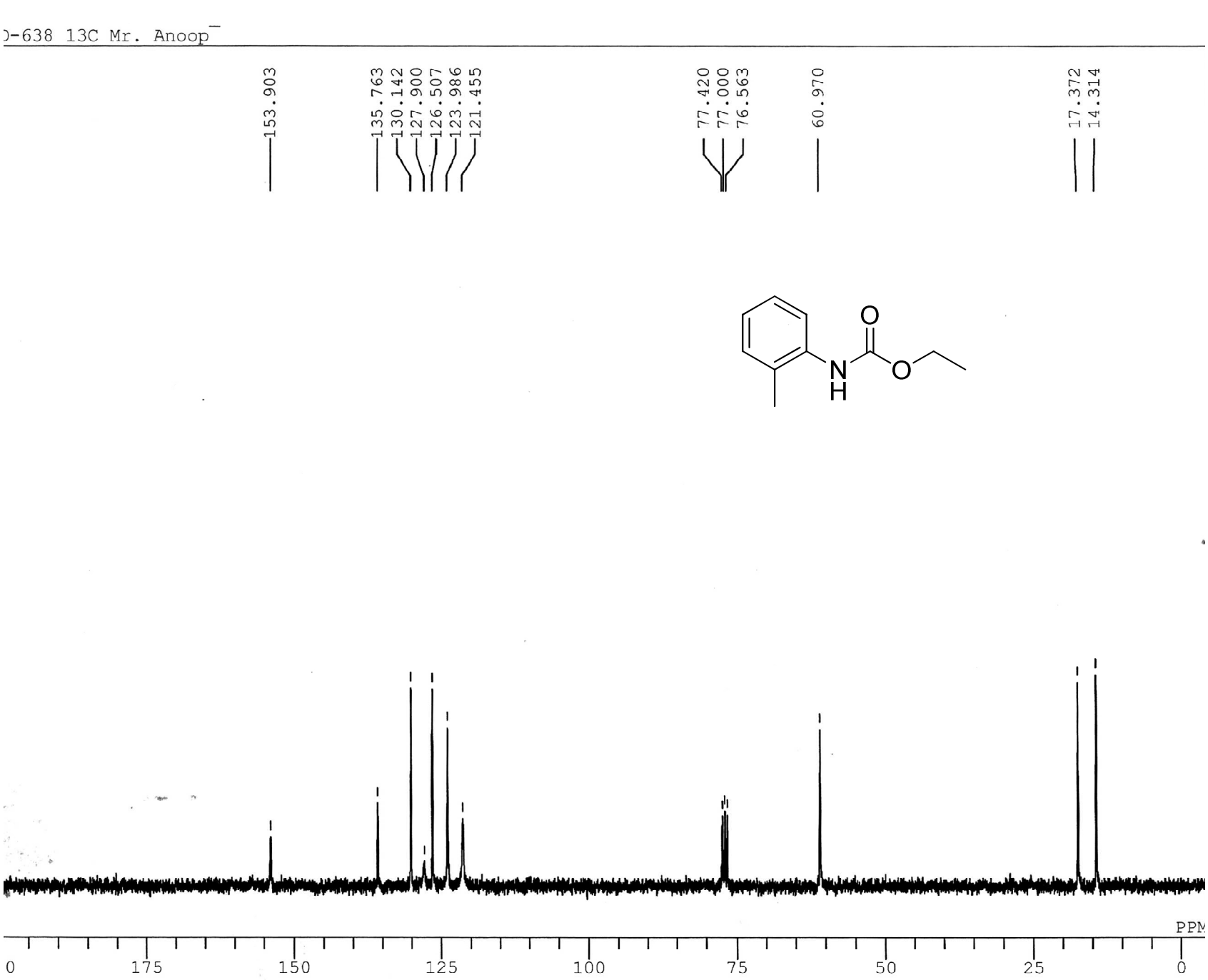
Spectrum 39: 300 MHz ^{1}H NMR of compound **3c**



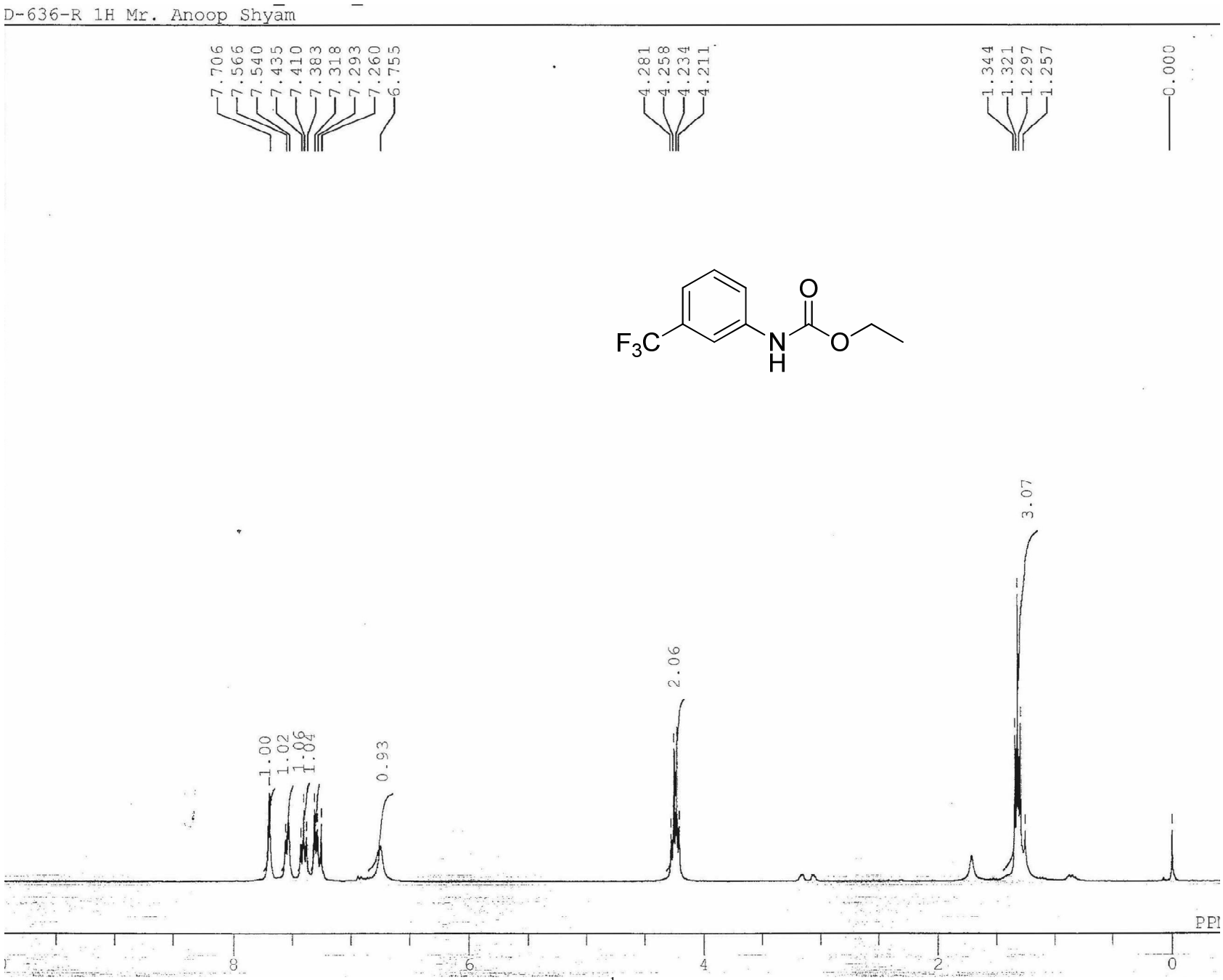
Spectrum 40: 75 MHz ^{13}C NMR of compound **3c**



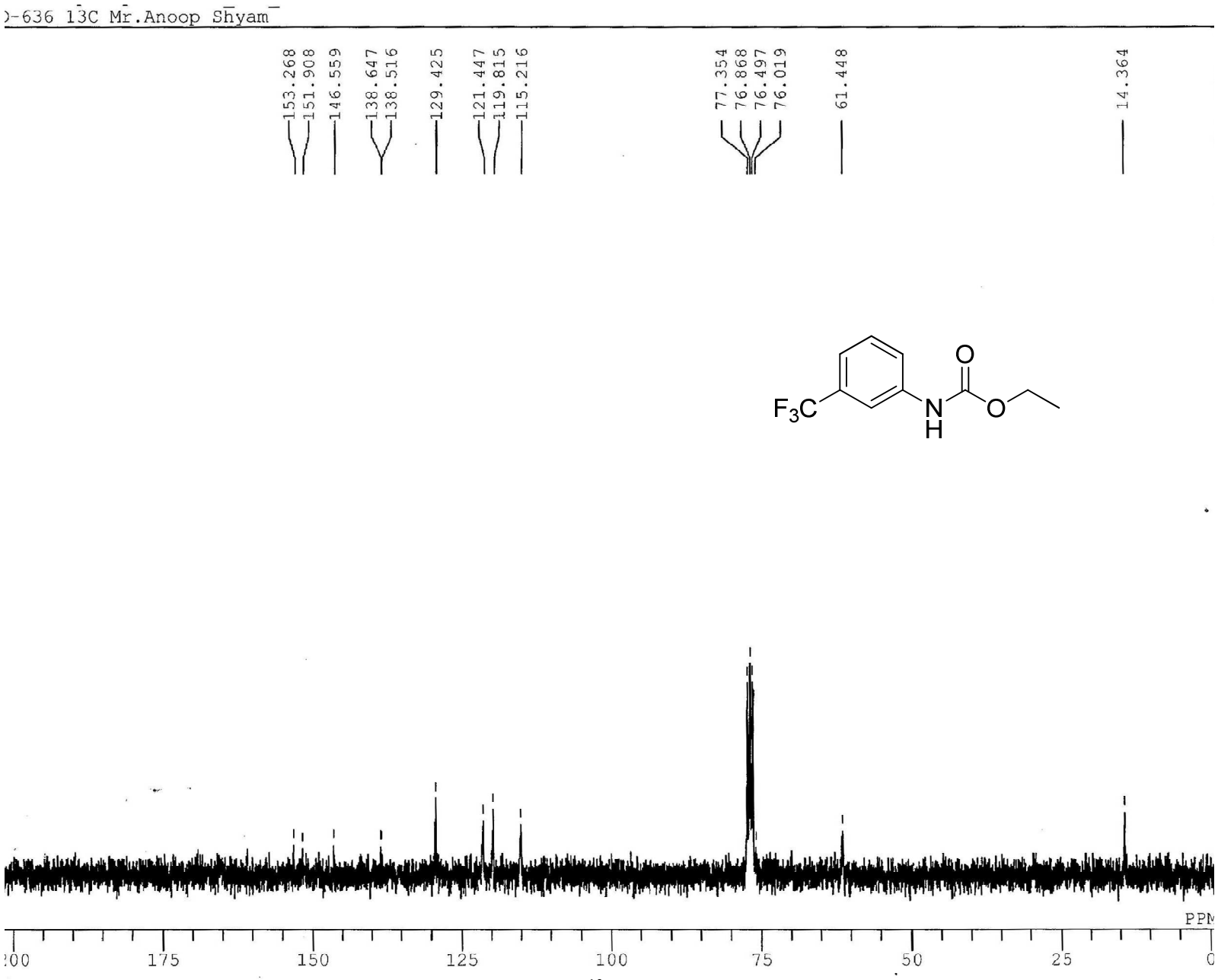
Spectrum 41: 300 MHz ^{1}H NMR of compound **3d**



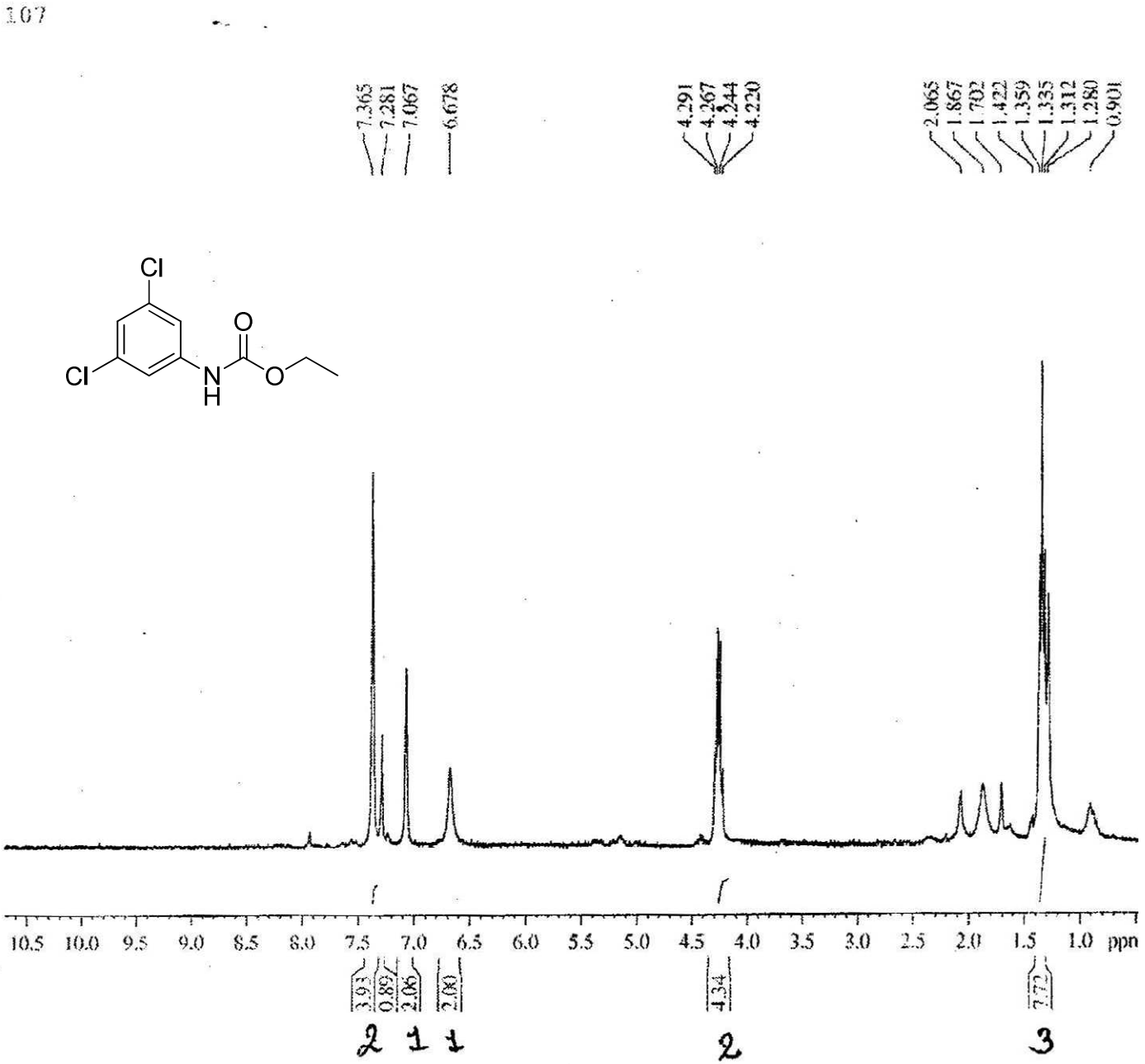
Spectrum 42: 75 MHz ^{13}C NMR of compound **3d**



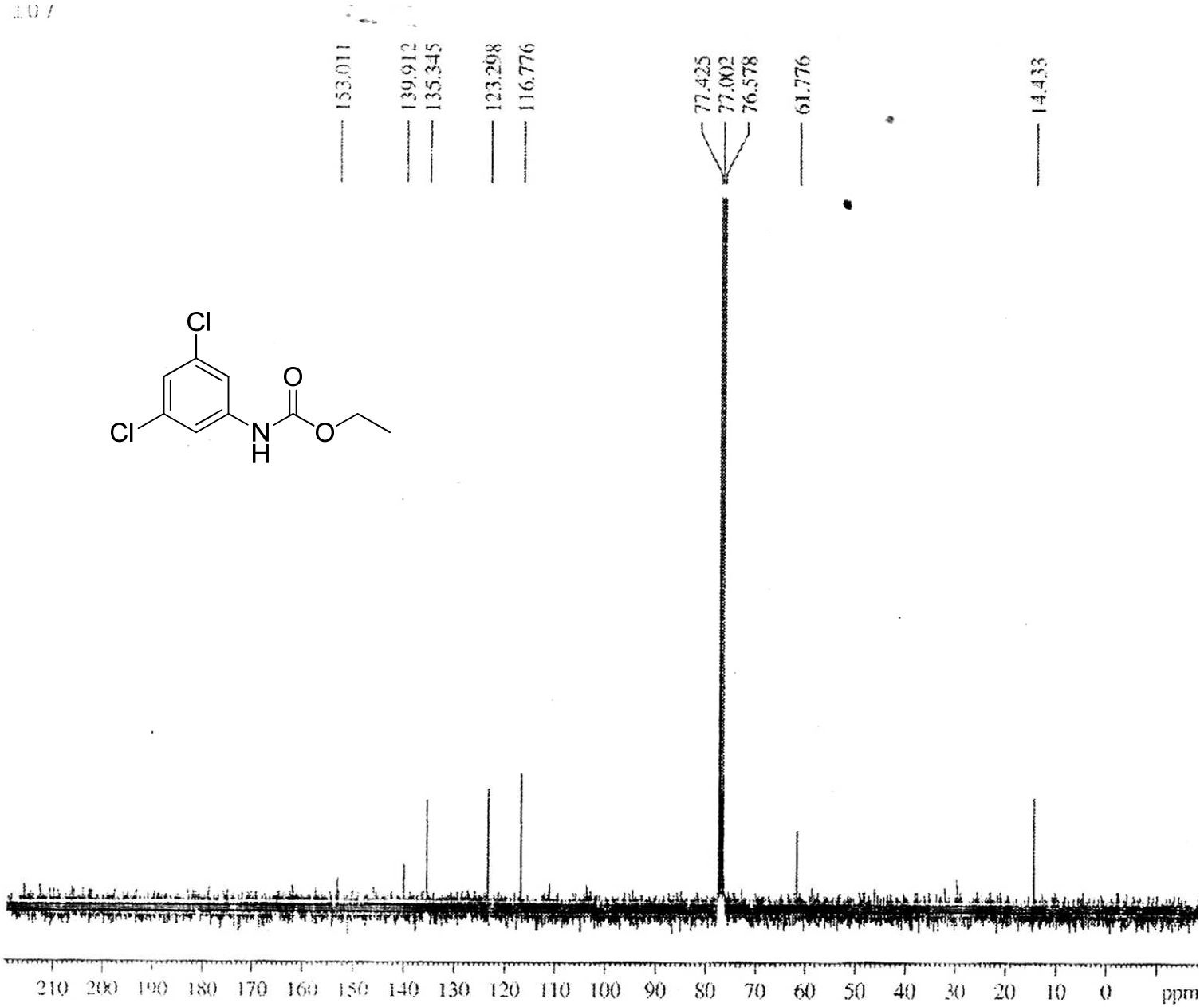
Spectrum 43: 300 MHz ^{1}H NMR of compound **3e**



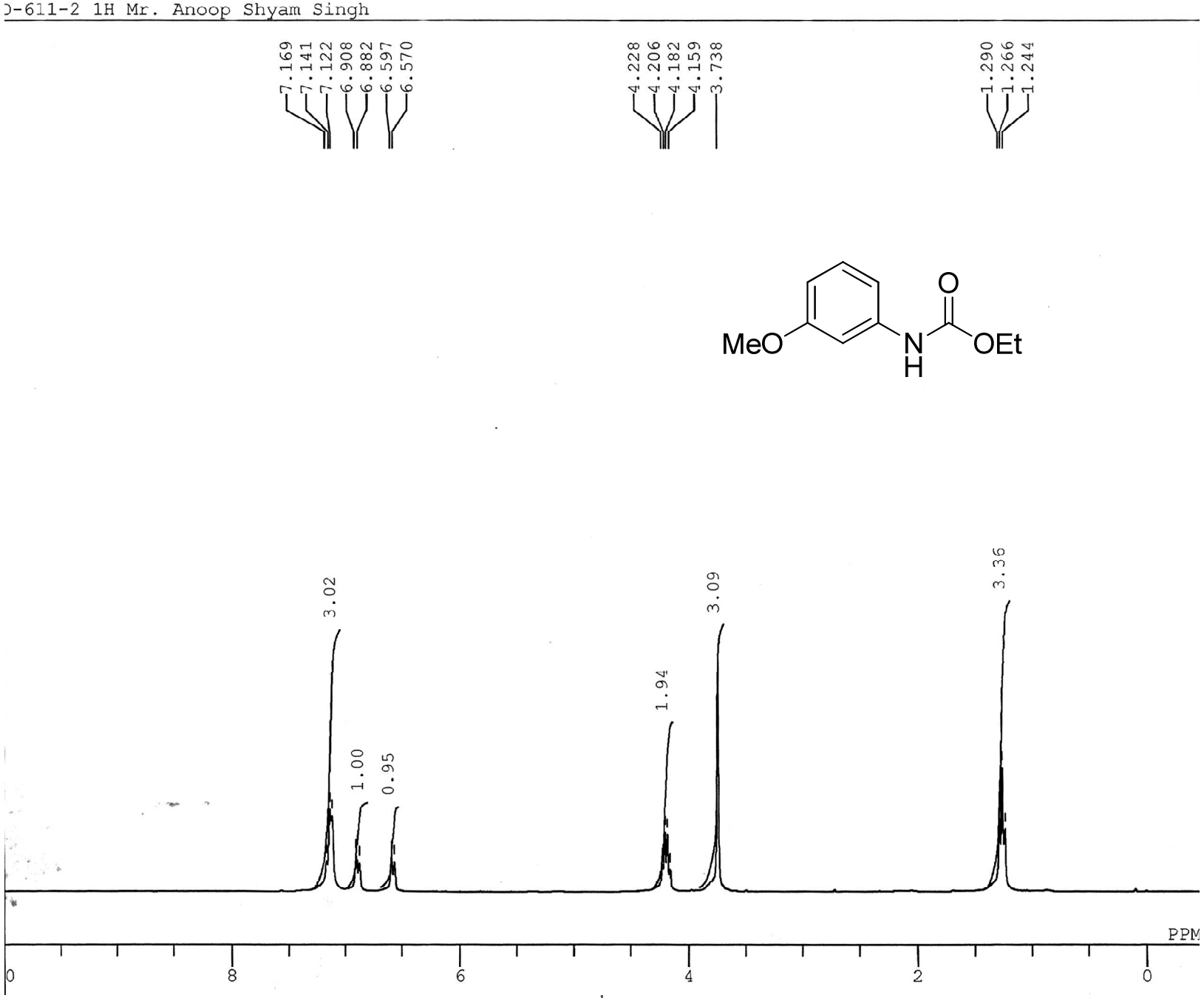
Spectrum 44: 75 MHz ^{13}C NMR of compound **3e**



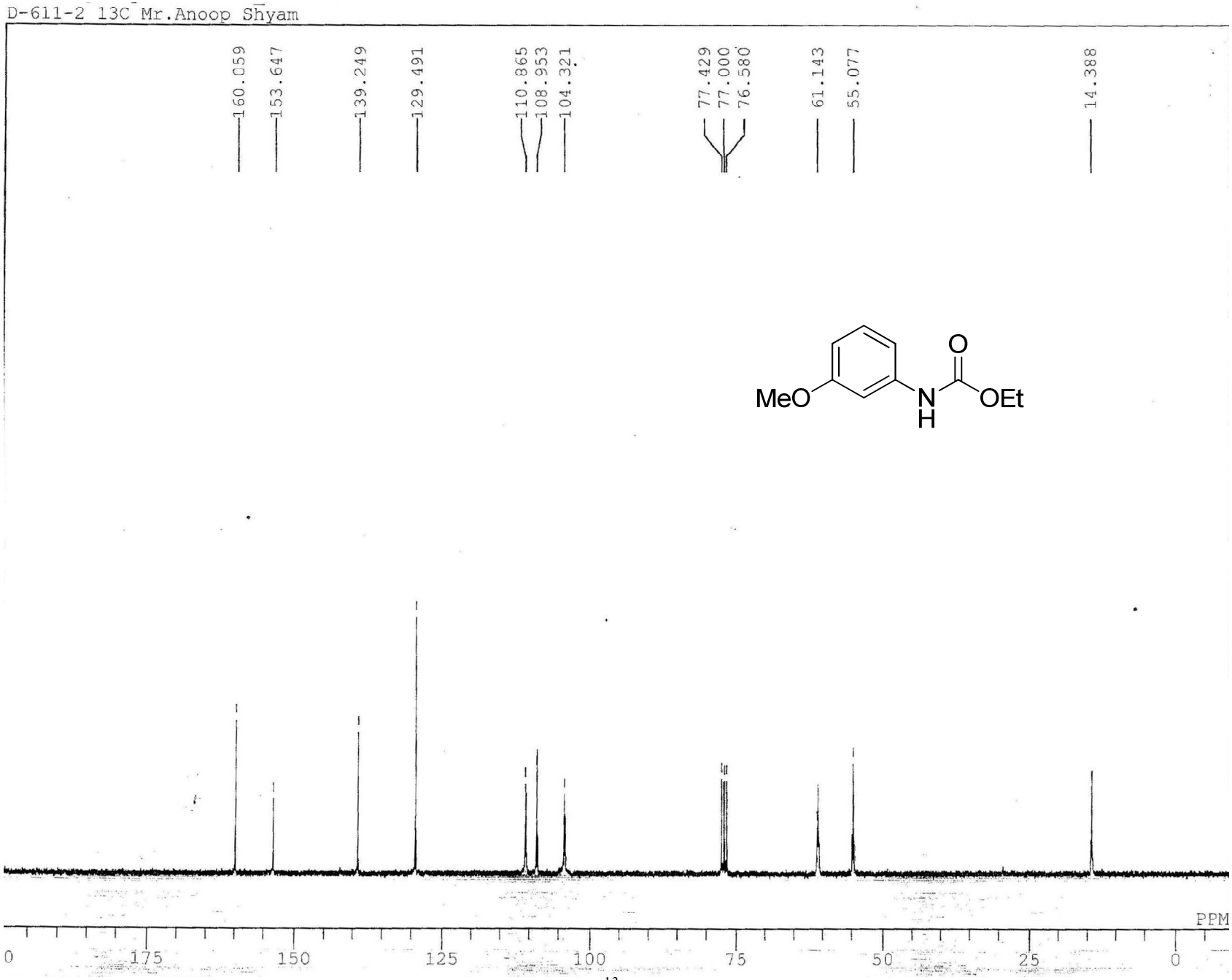
Spectrum 45: 300 MHz ^{1}H NMR of compound **3f**



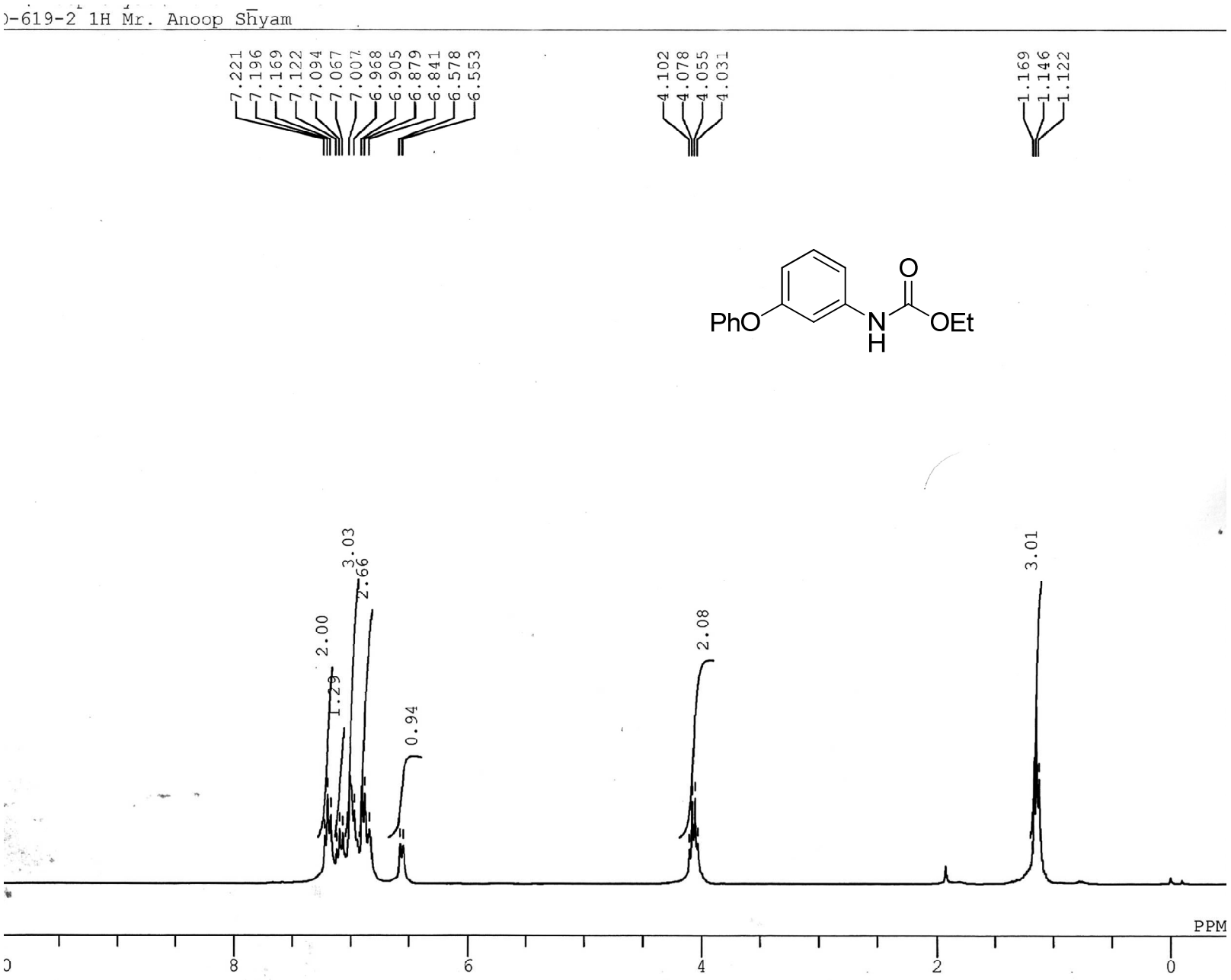
Spectrum 46: 75 MHz ^{13}C NMR of compound **3f**



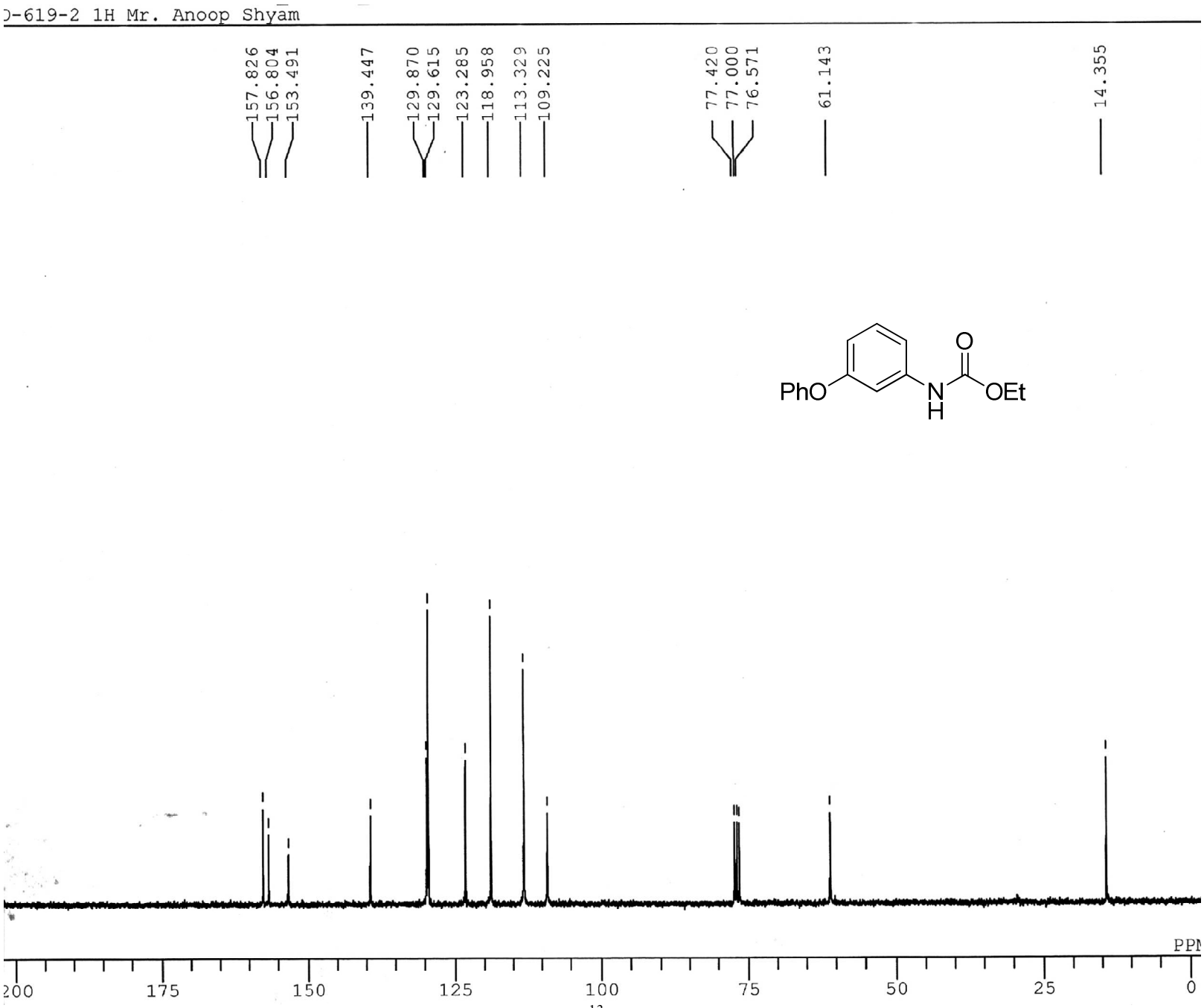
Spectrum 47: 300 MHz ^{1}H NMR of compound **3g**



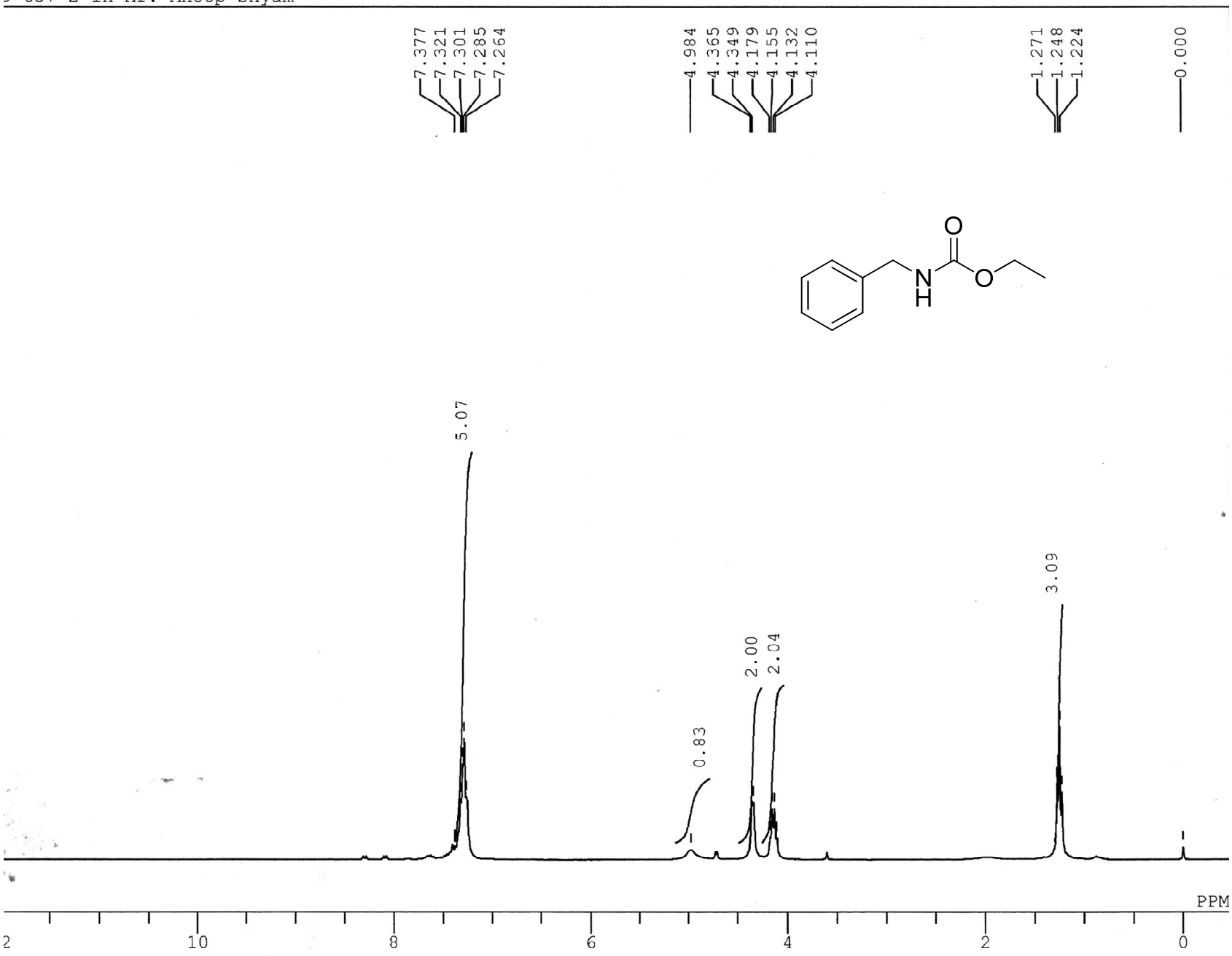
Spectrum 48: 75 MHz ^{13}C NMR of compound **3g**



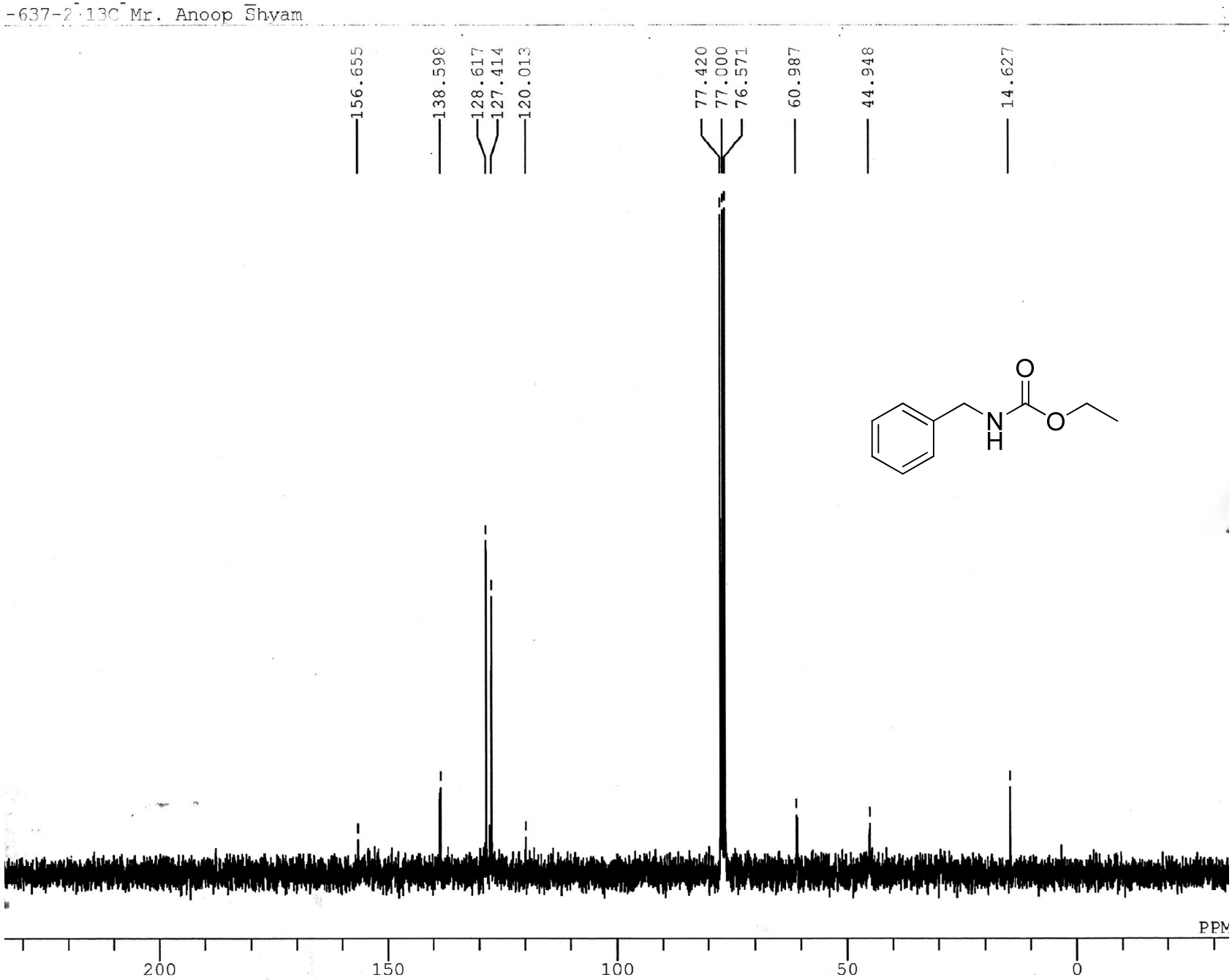
Spectrum 49: 300 MHz ^{1}H NMR of compound **3h**



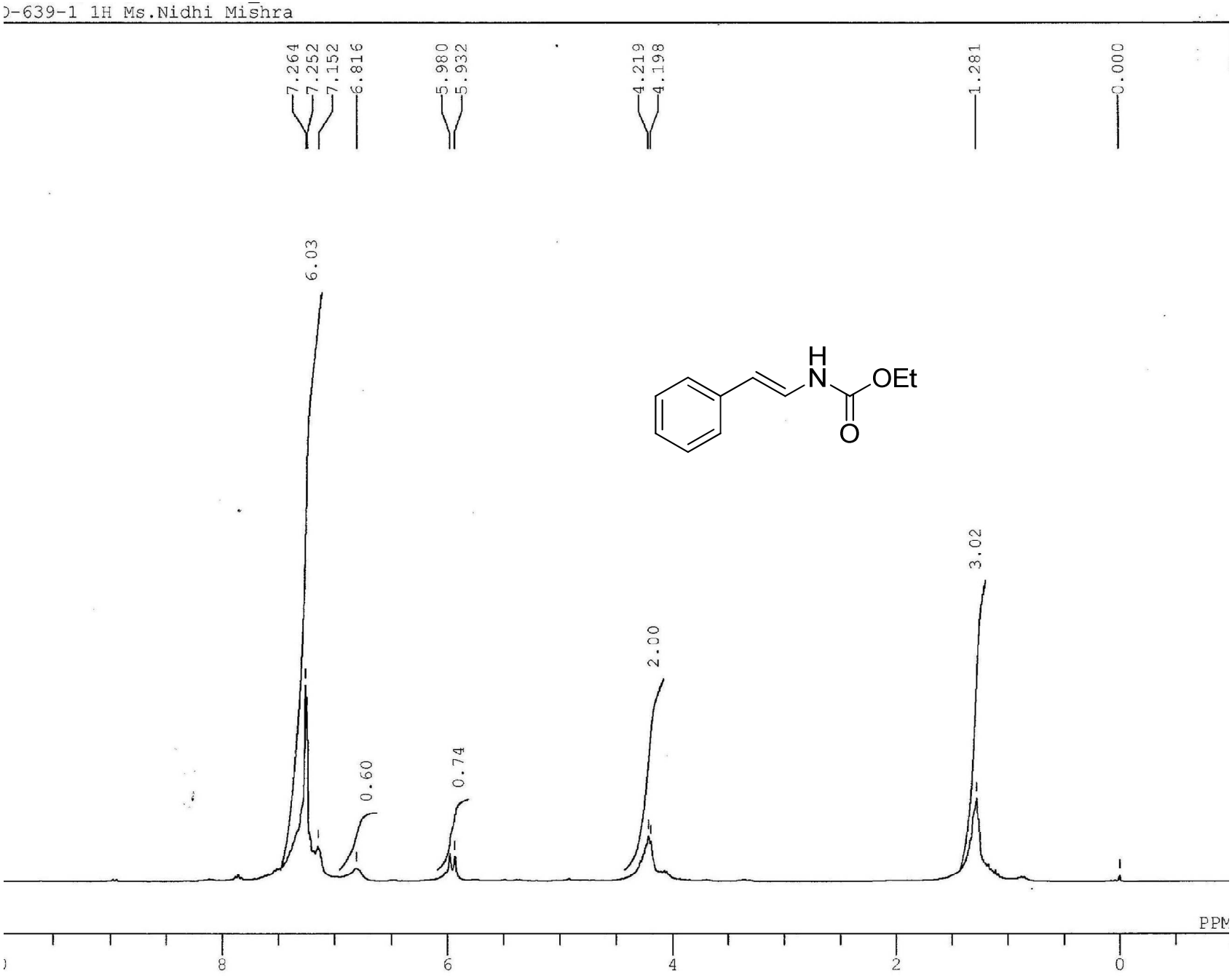
Spectrum 50: 75 MHz ^{13}C NMR of compound **3h**



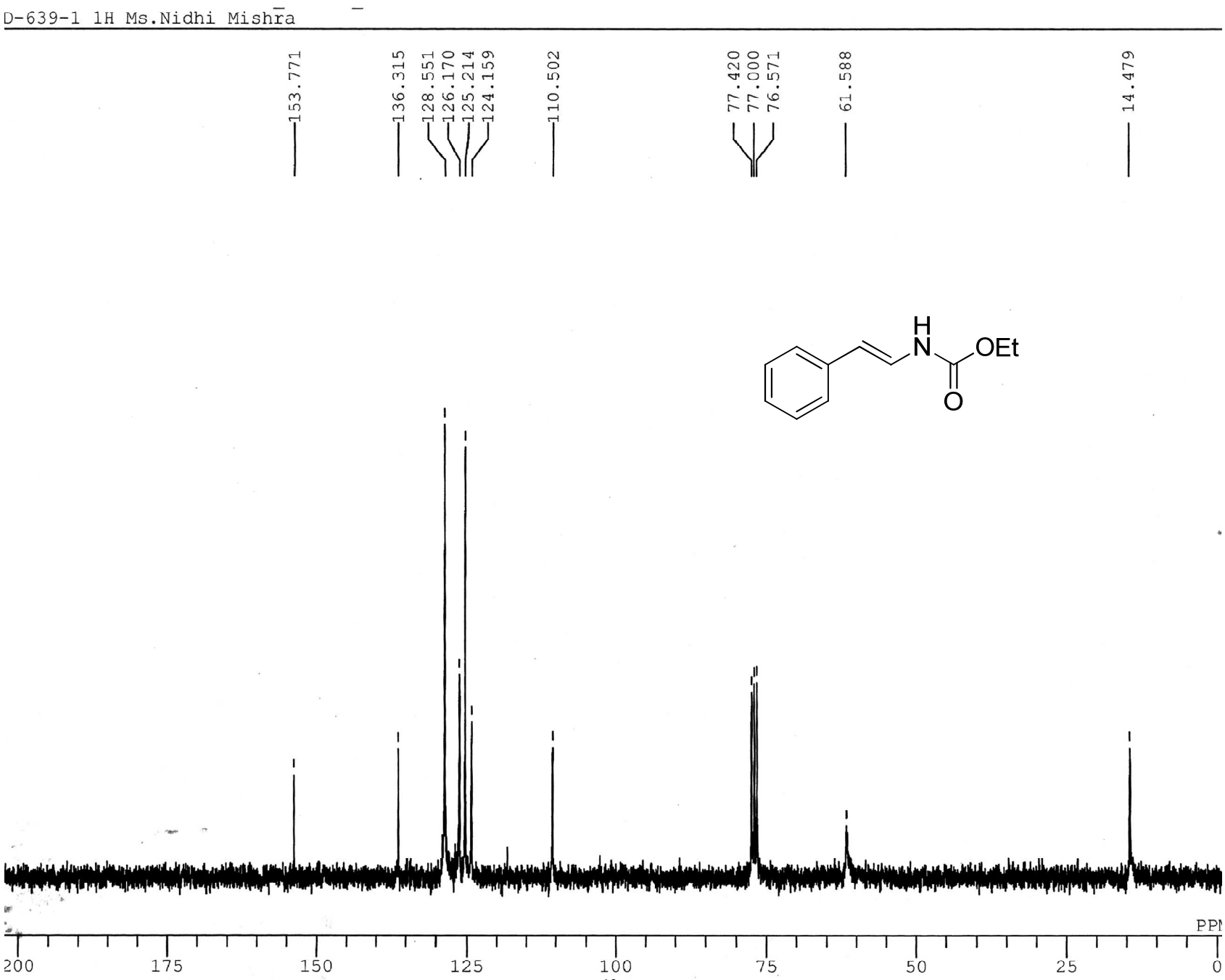
Spectrum 51: 300 MHz ^{1}H NMR of compound **3i**



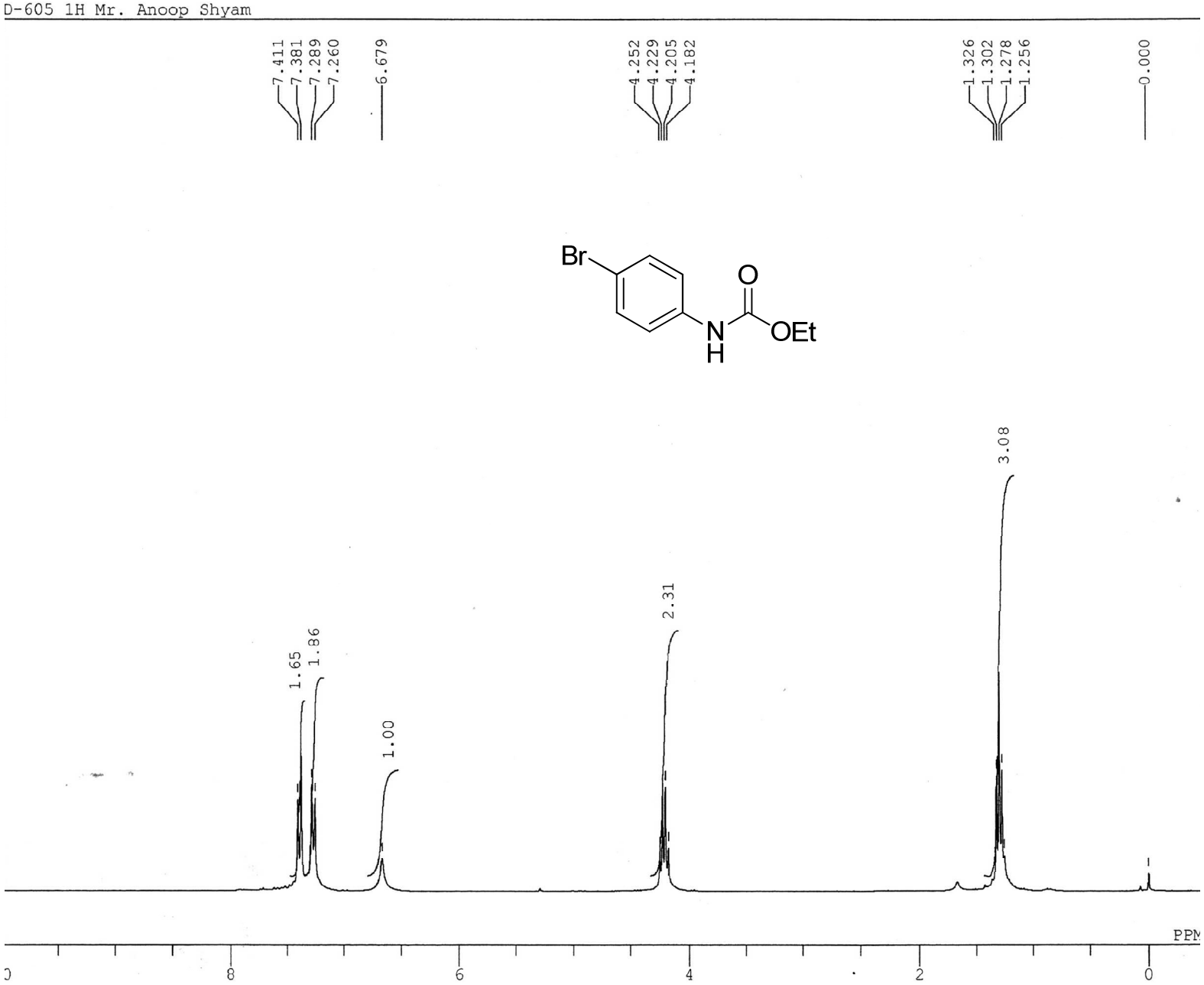
Spectrum 52: 75 MHz ^{13}C NMR of compound **3i**



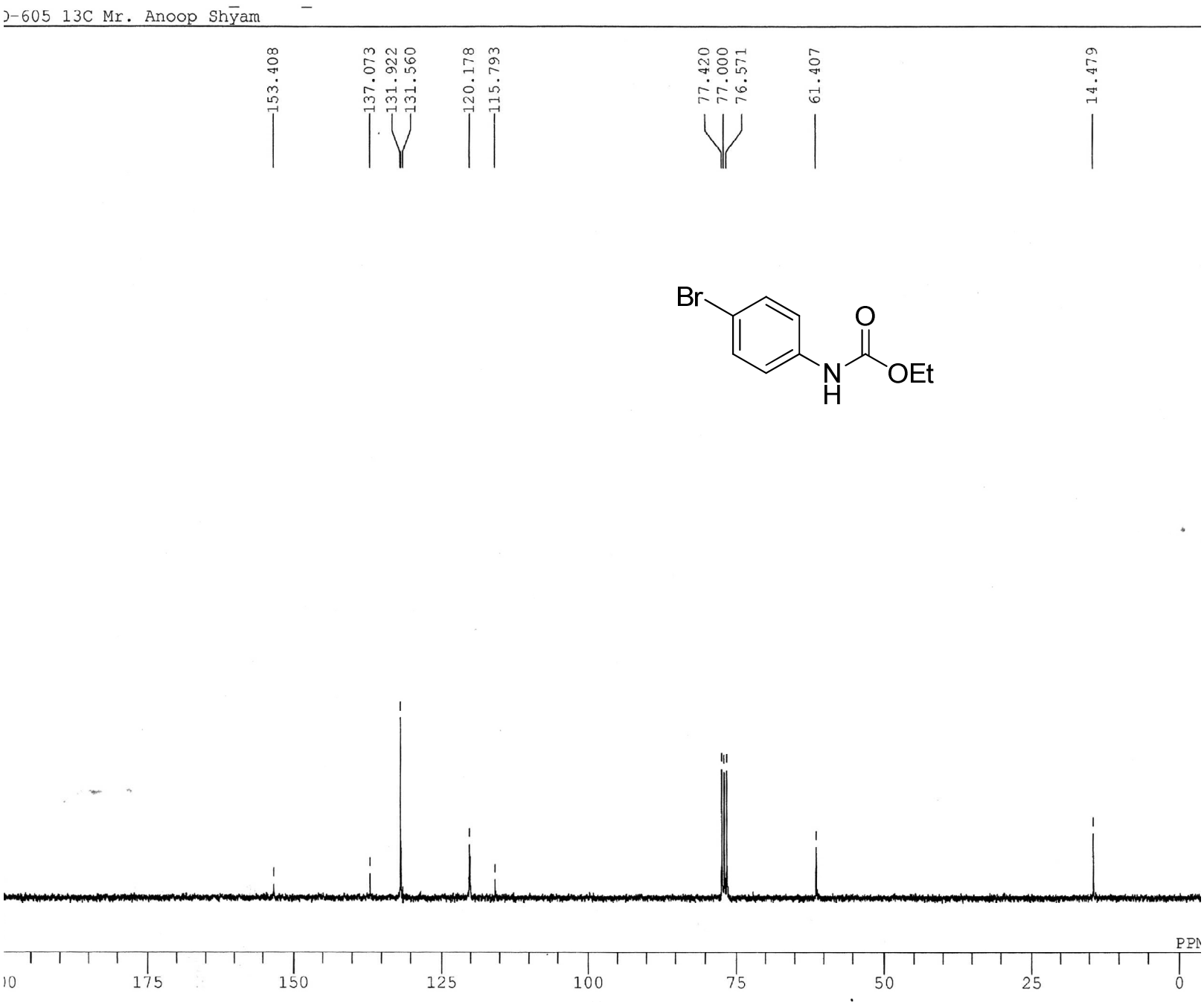
Spectrum 53: 300 MHz ^{1}H NMR of compound **3j**



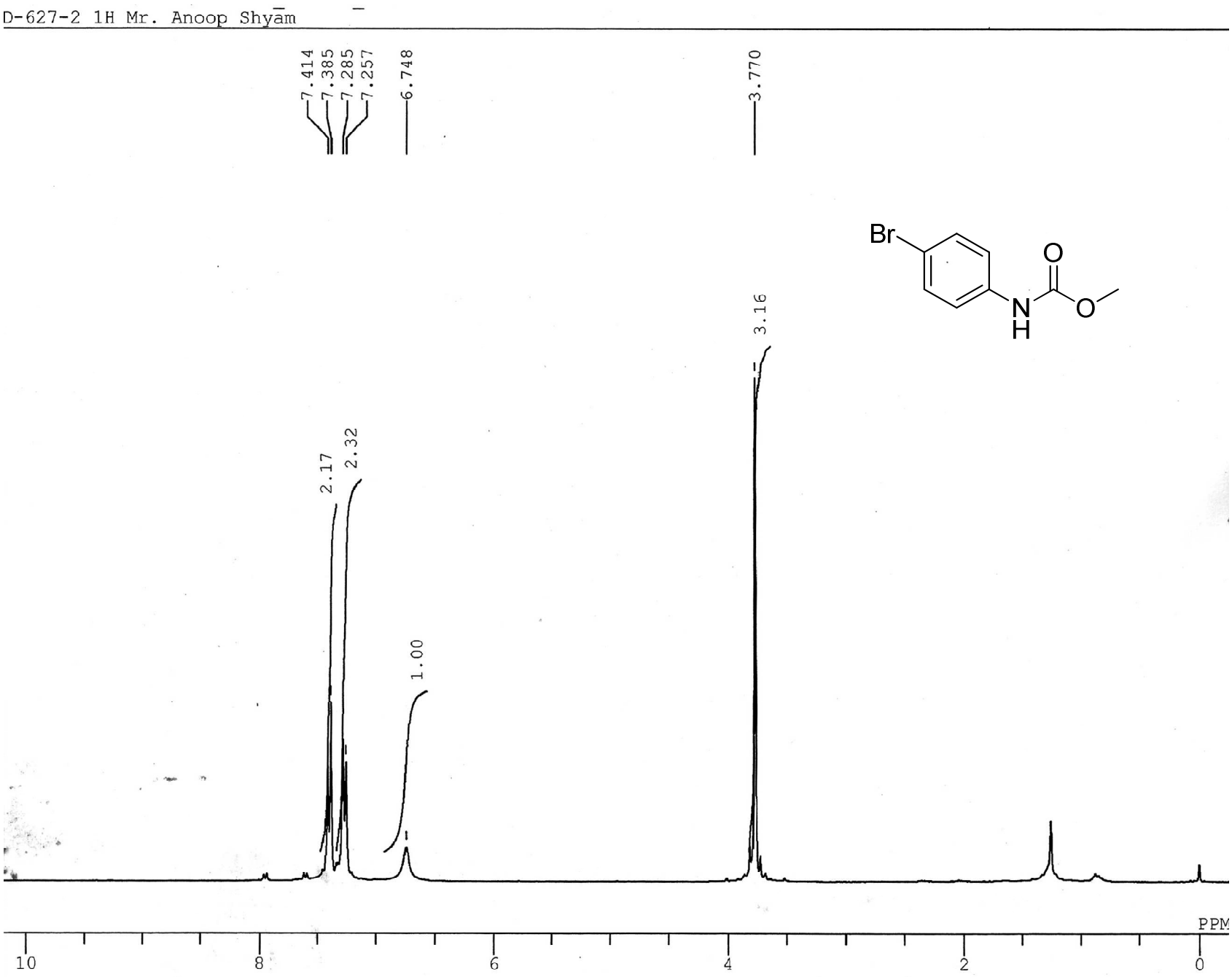
Spectrum 54: 75 MHz ^{13}C NMR of compound **3j**



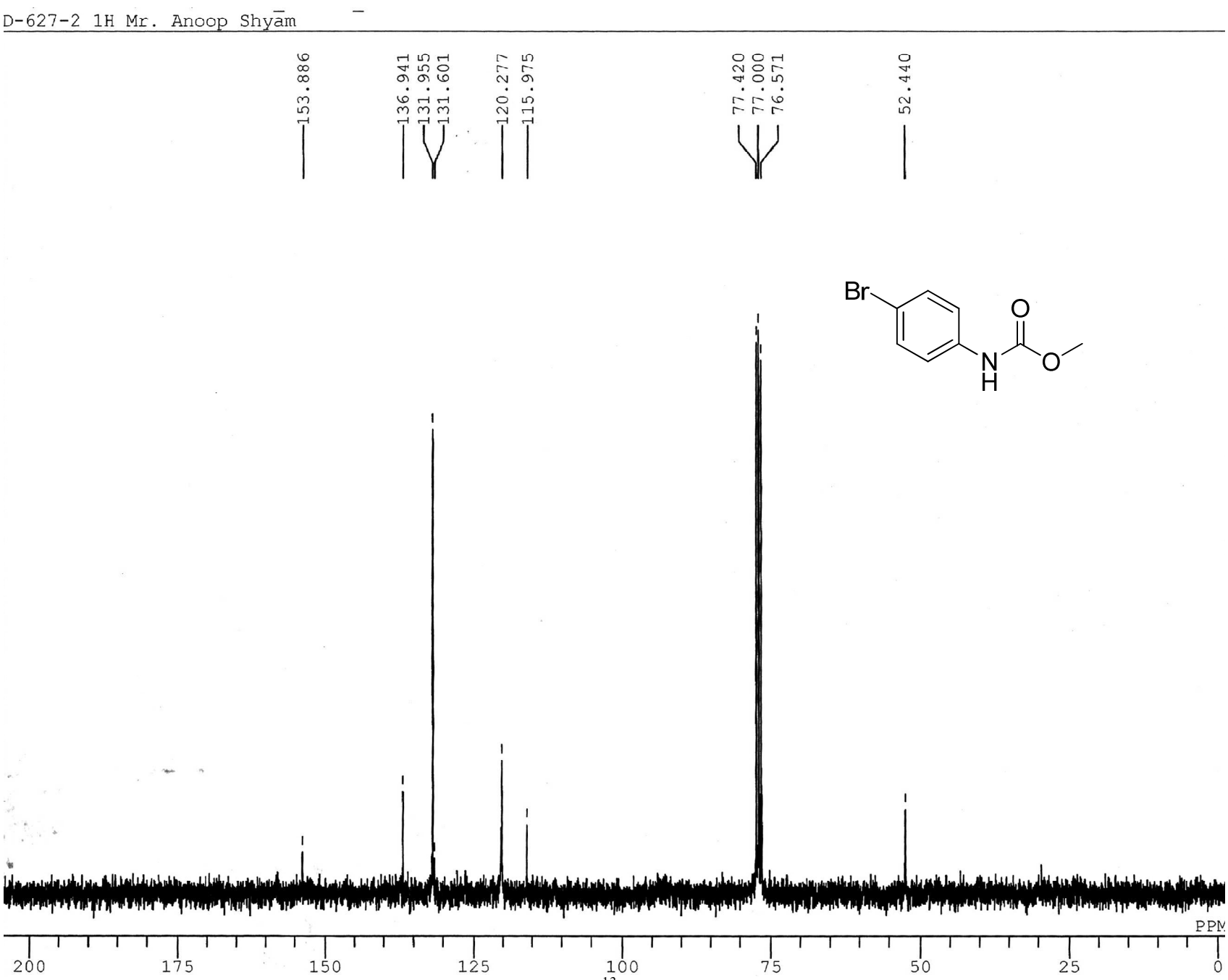
Spectrum 55: 300 MHz ^{1}H NMR of compound **3k**



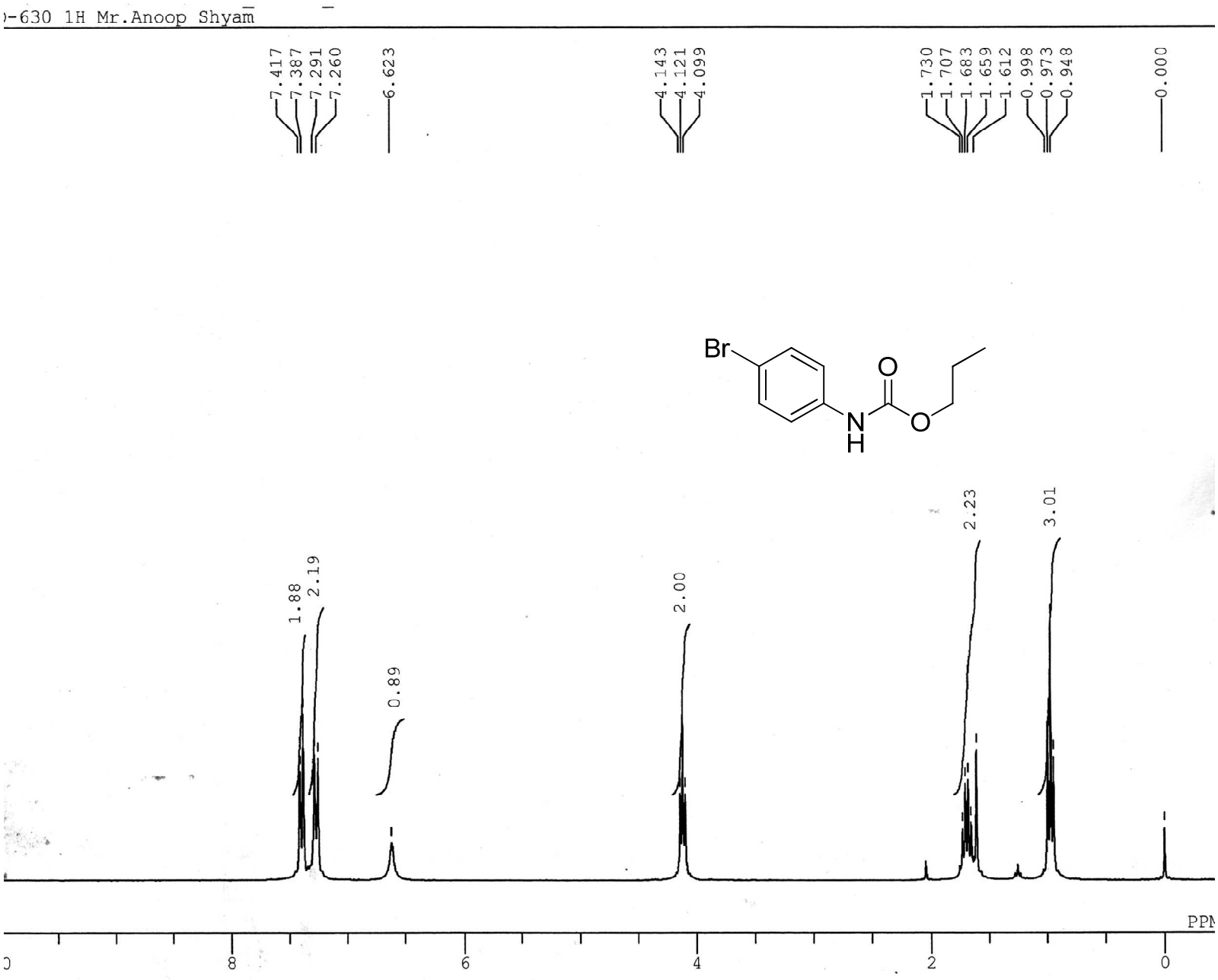
Spectrum 56: 75 MHz ^{13}C NMR of compound **3k**



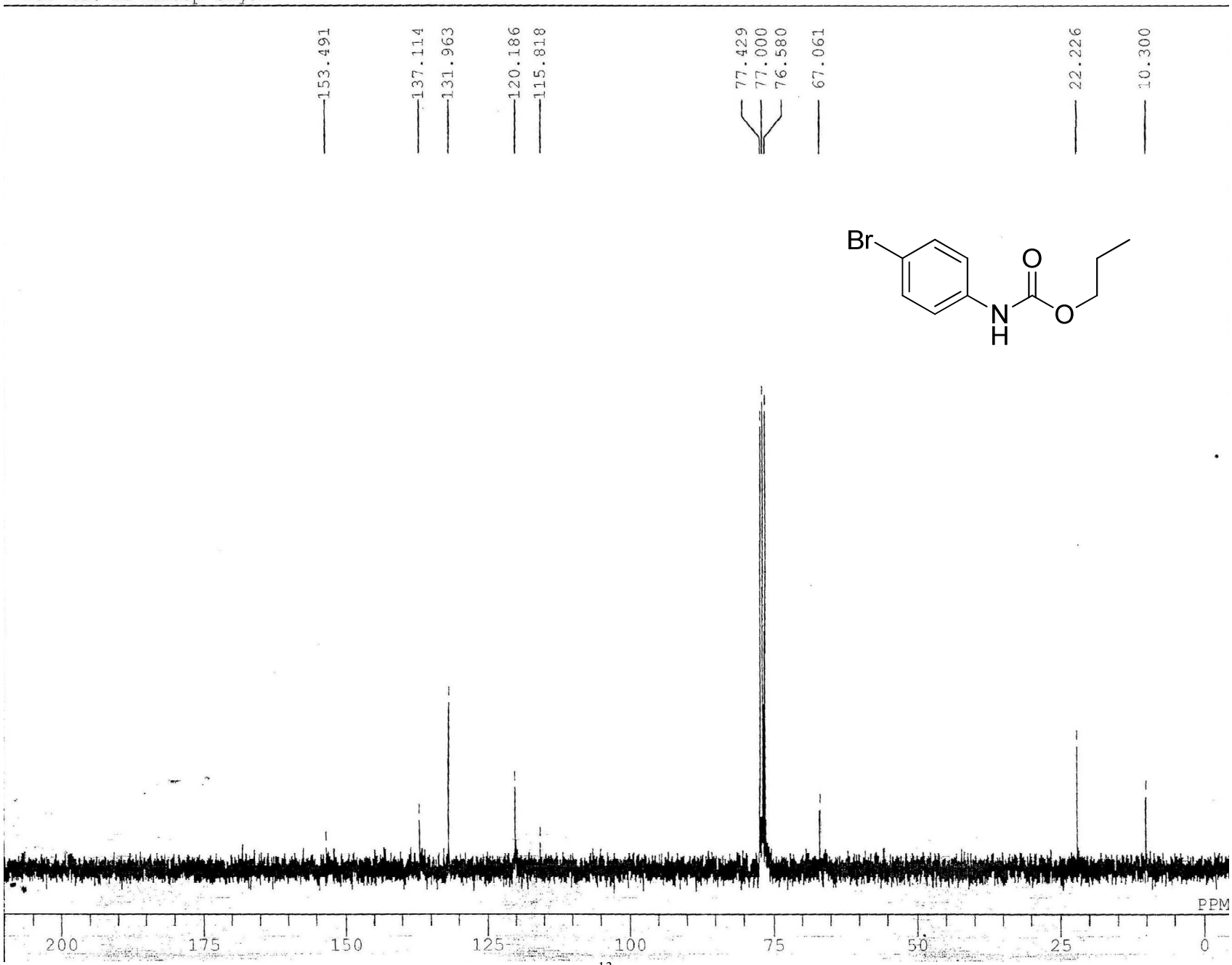
Spectrum 57: 300 MHz ^{1}H NMR of compound **3l**



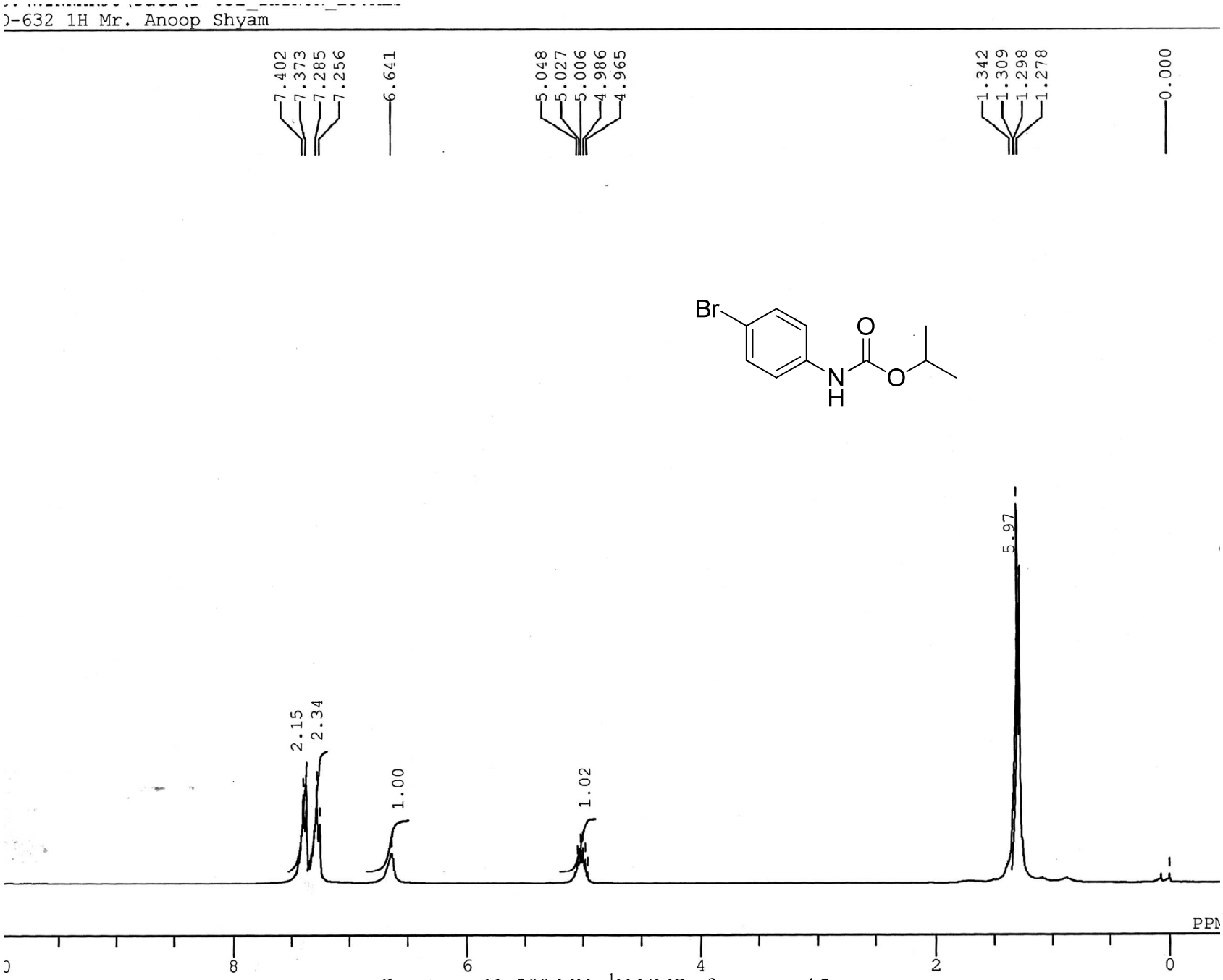
Spectrum 58: 75 MHz ^{13}C NMR of compound **3l**



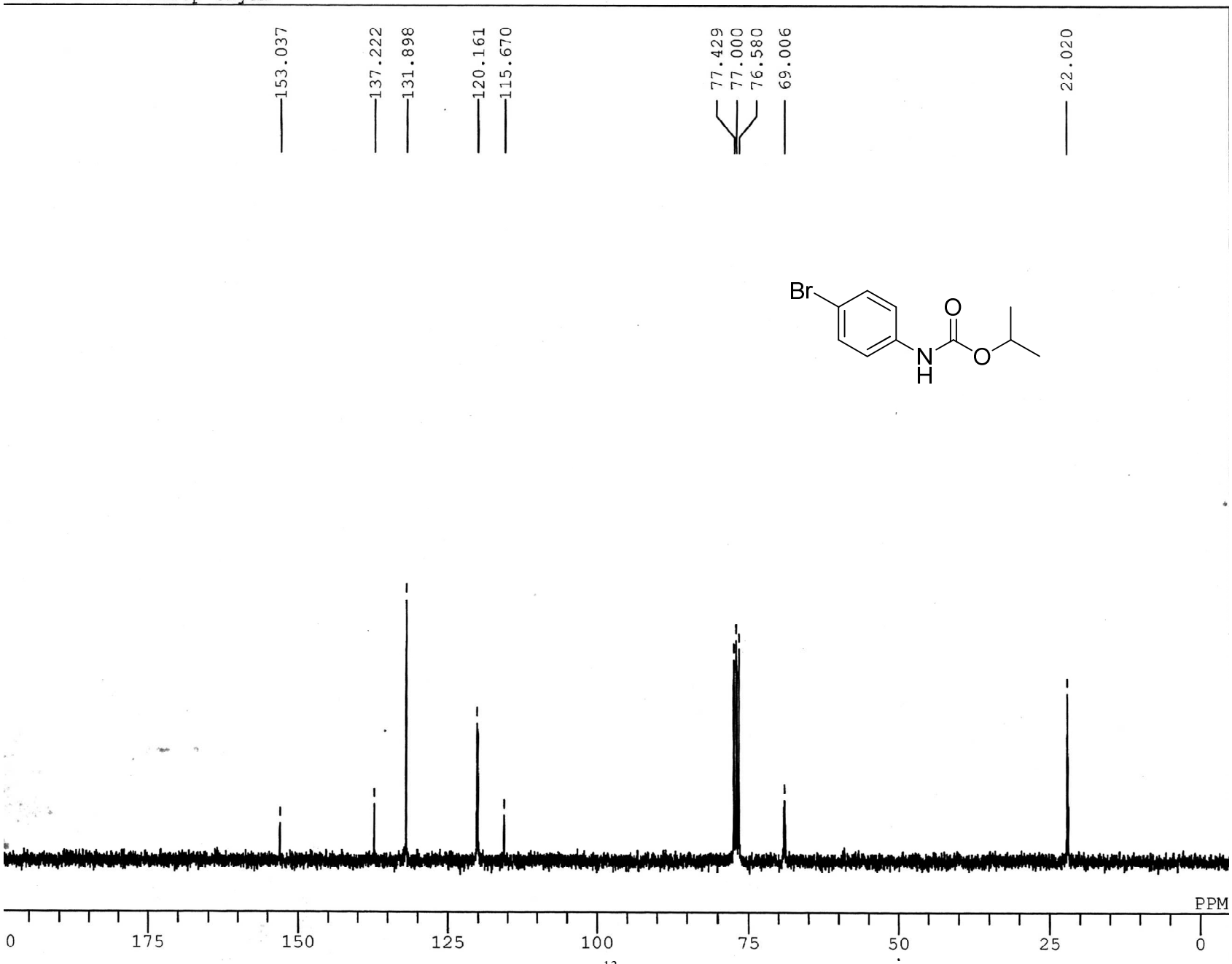
Spectrum 59: 300 MHz ^{1}H NMR of compound **3m**



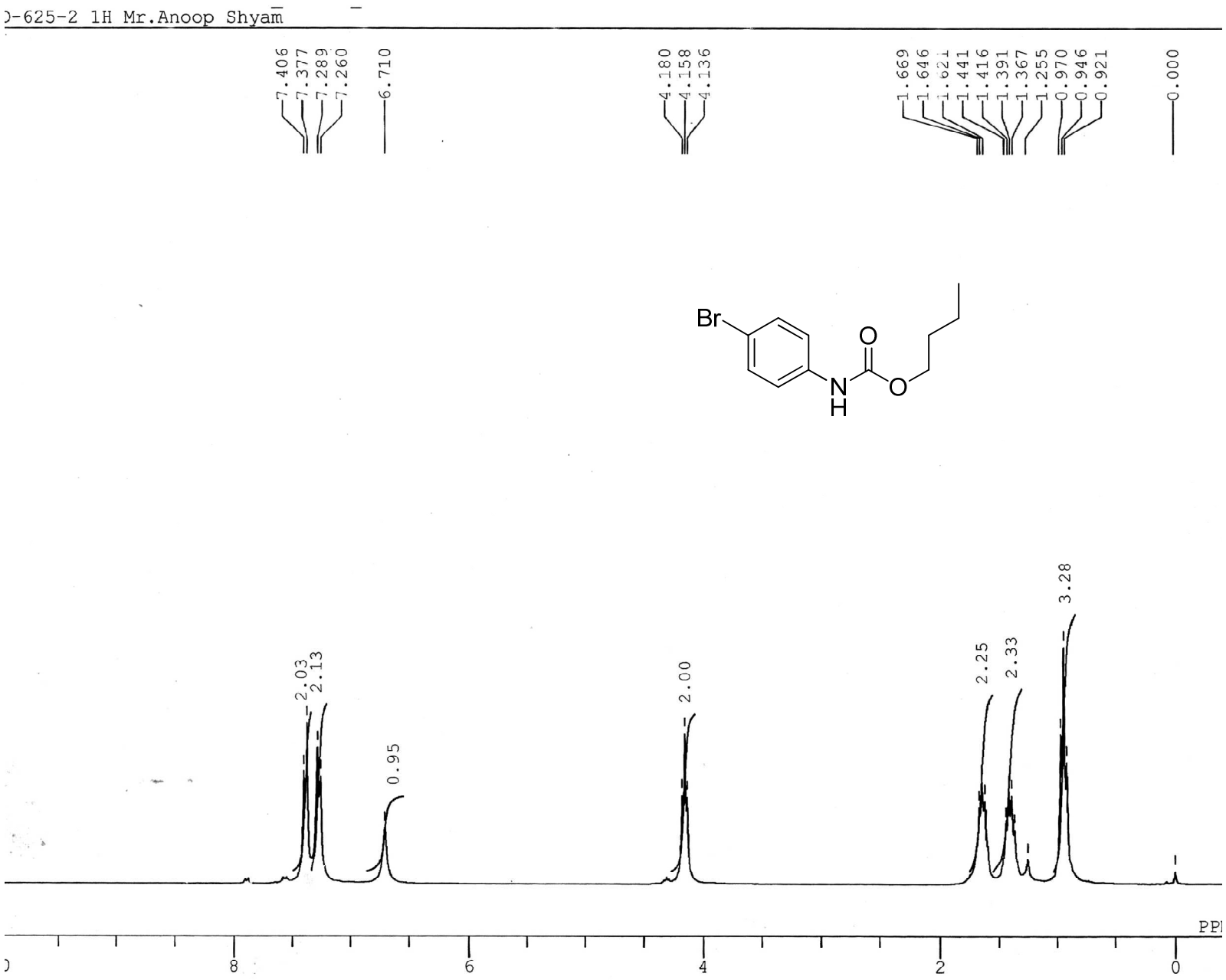
Spectrum 60: 75 MHz ^{13}C NMR of compound **3m**



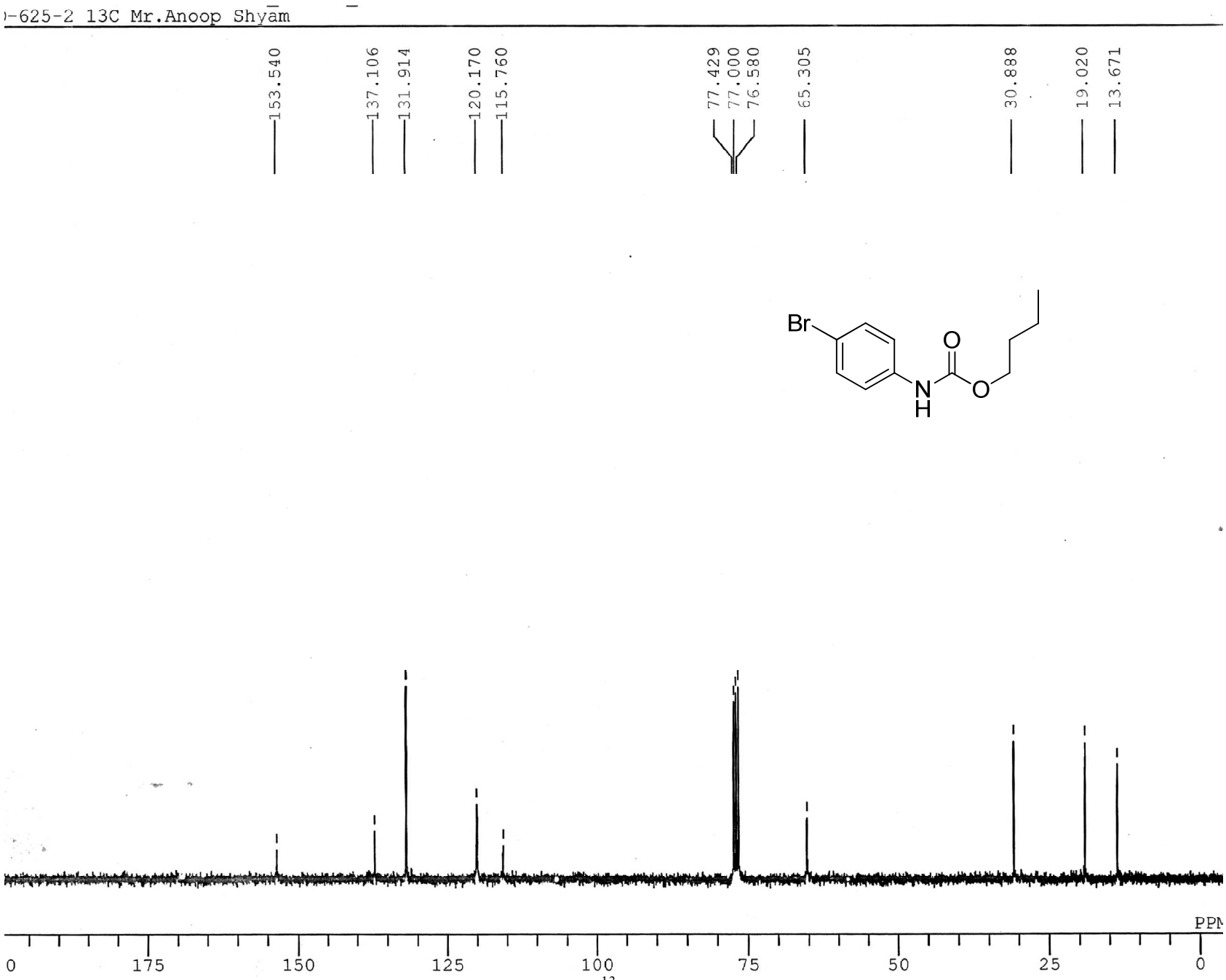
Spectrum 61: 300 MHz ^{1}H NMR of compound **3n**



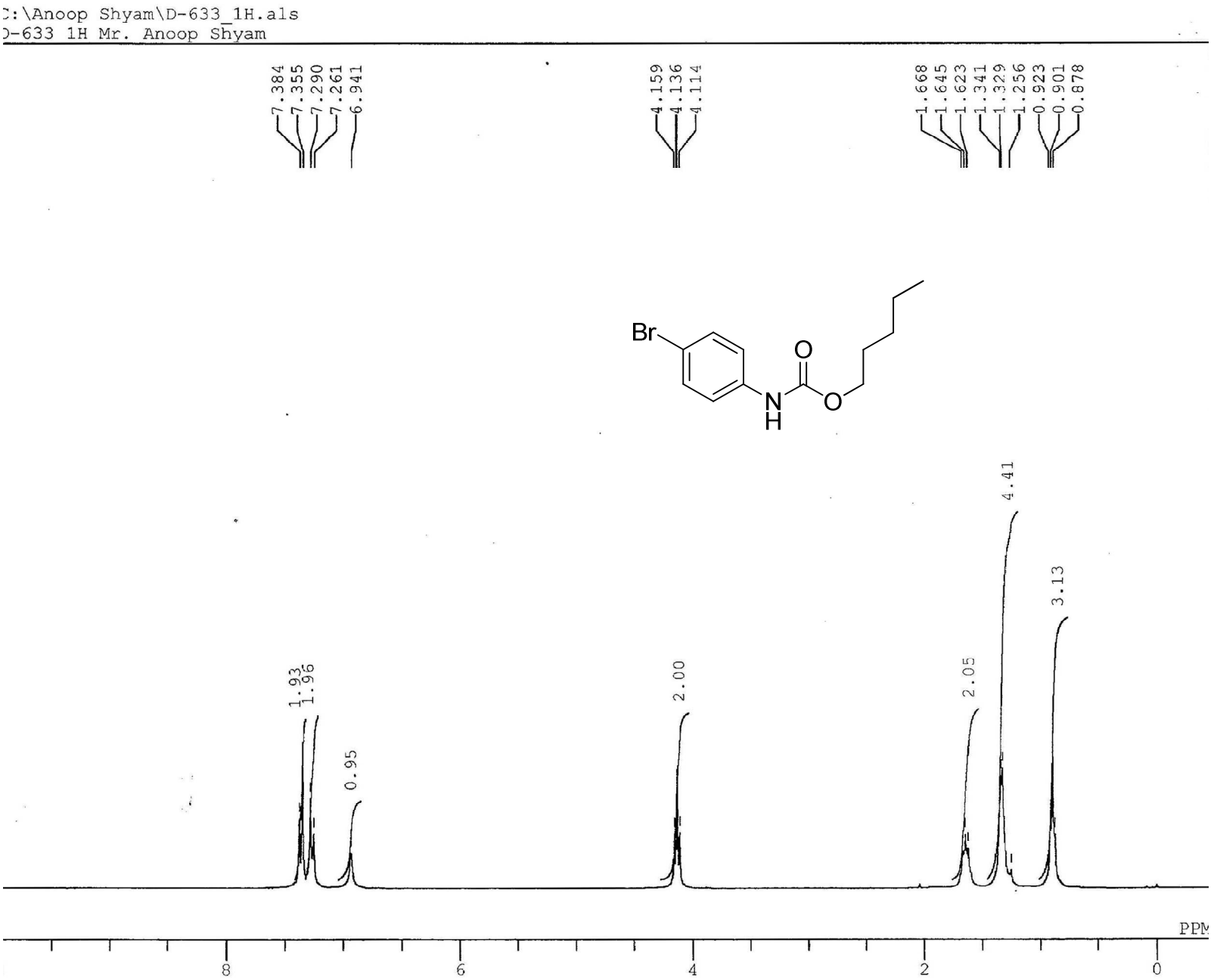
Spectrum 62: 75 MHz ^{13}C NMR of compound **3n**



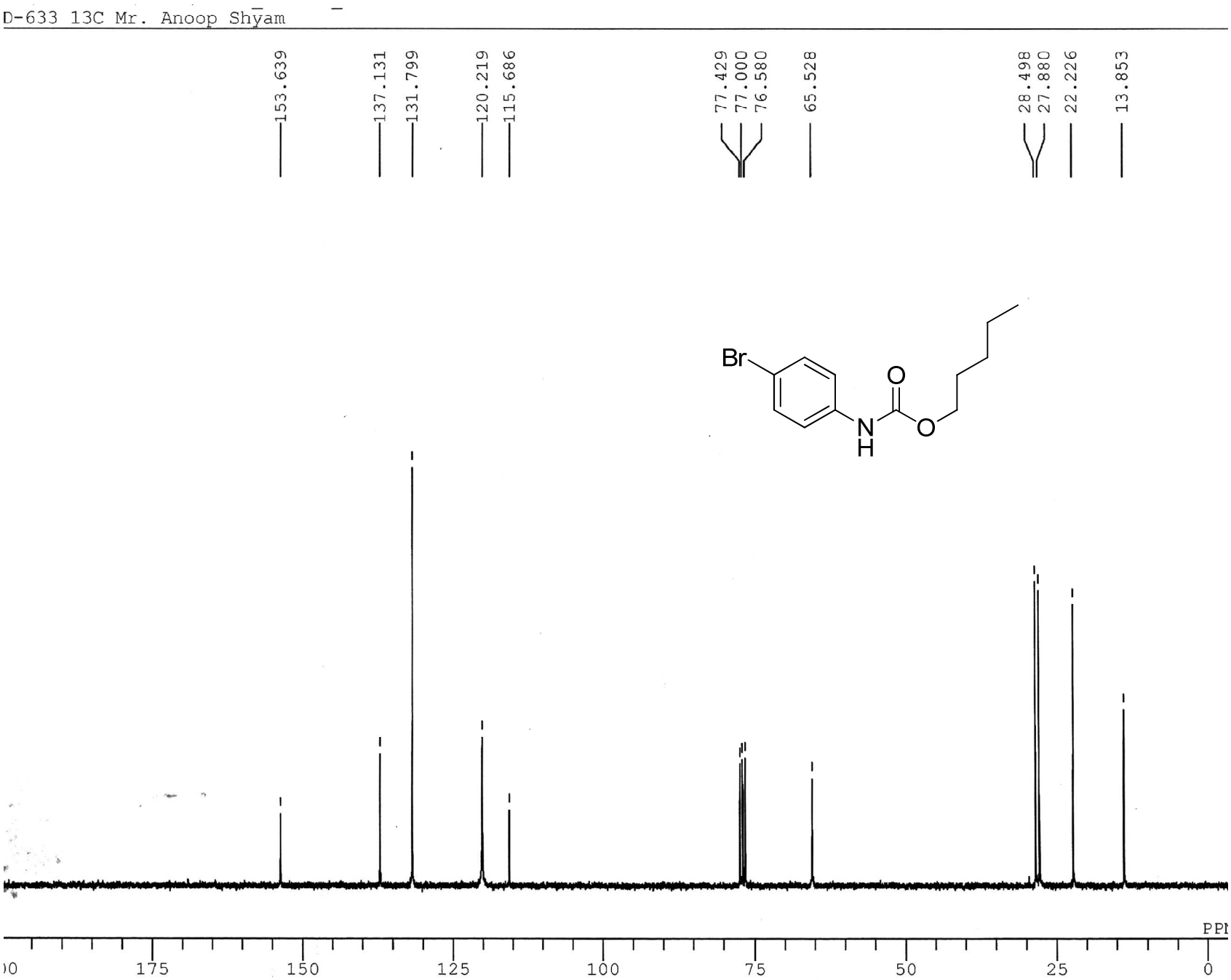
Spectrum 63: 300 MHz ^{1}H NMR of compound **3o**



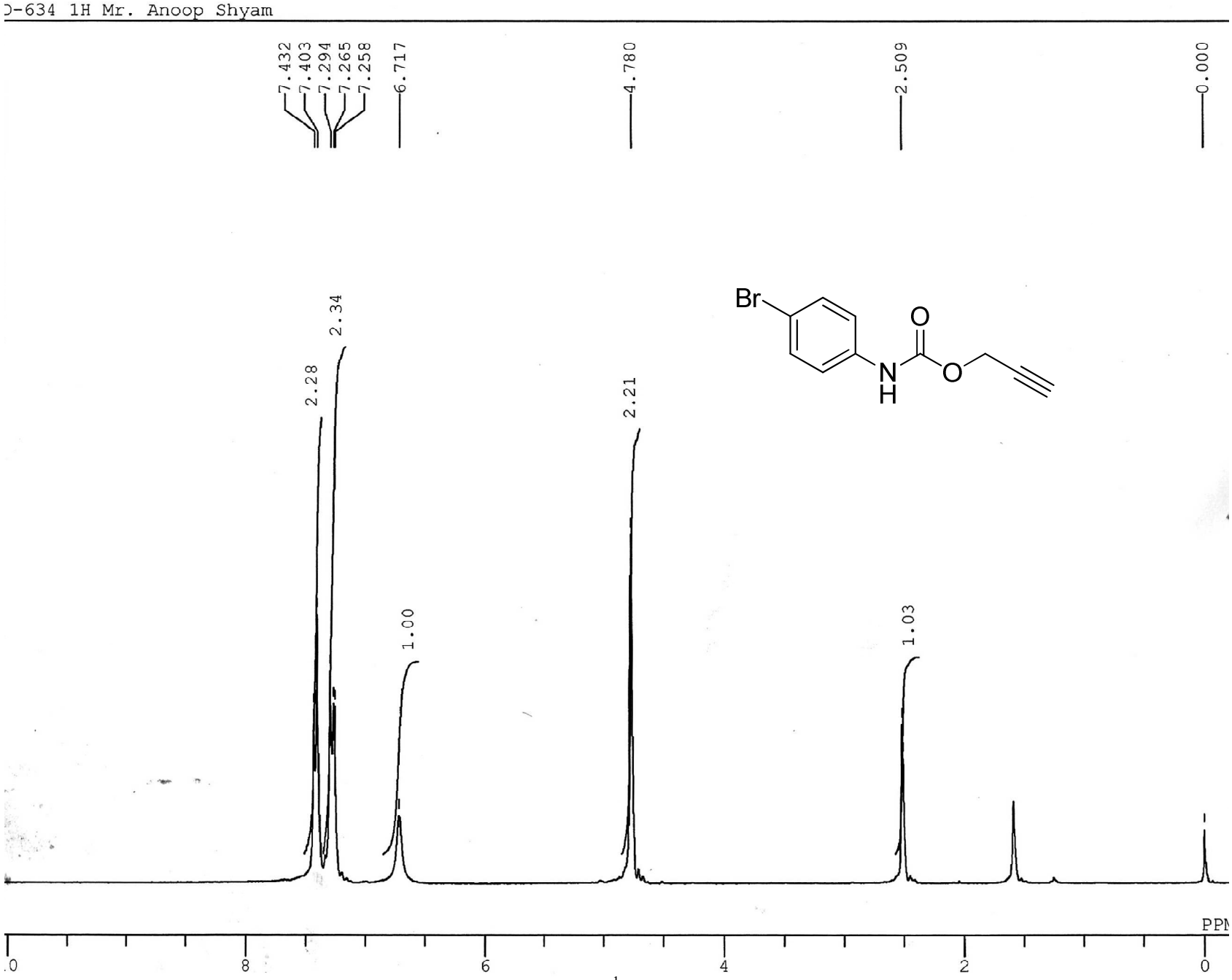
Spectrum 64: 75 MHz ^{13}C NMR of compound **3o**



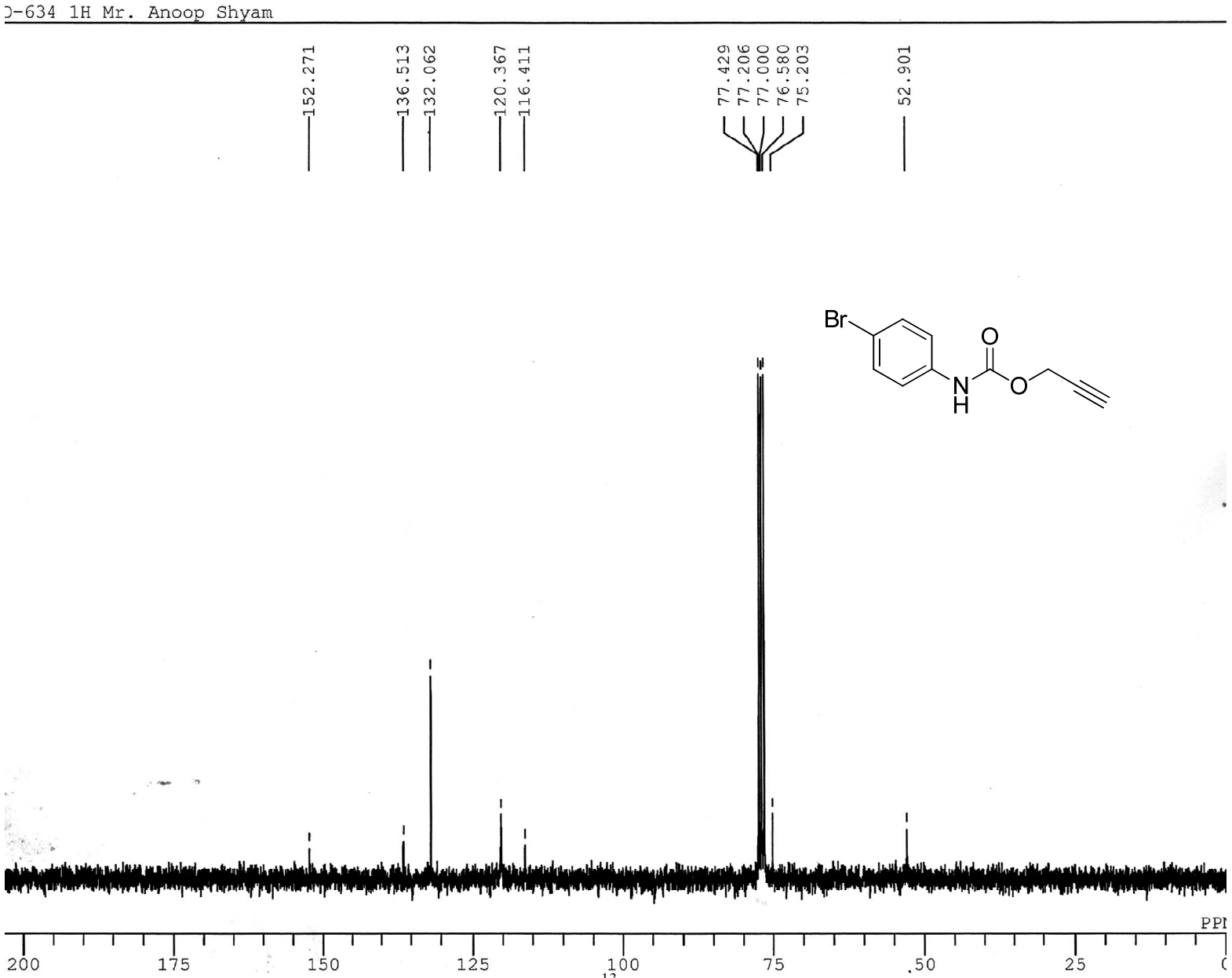
Spectrum 65: 300 MHz ^{1}H NMR of compound **3p**



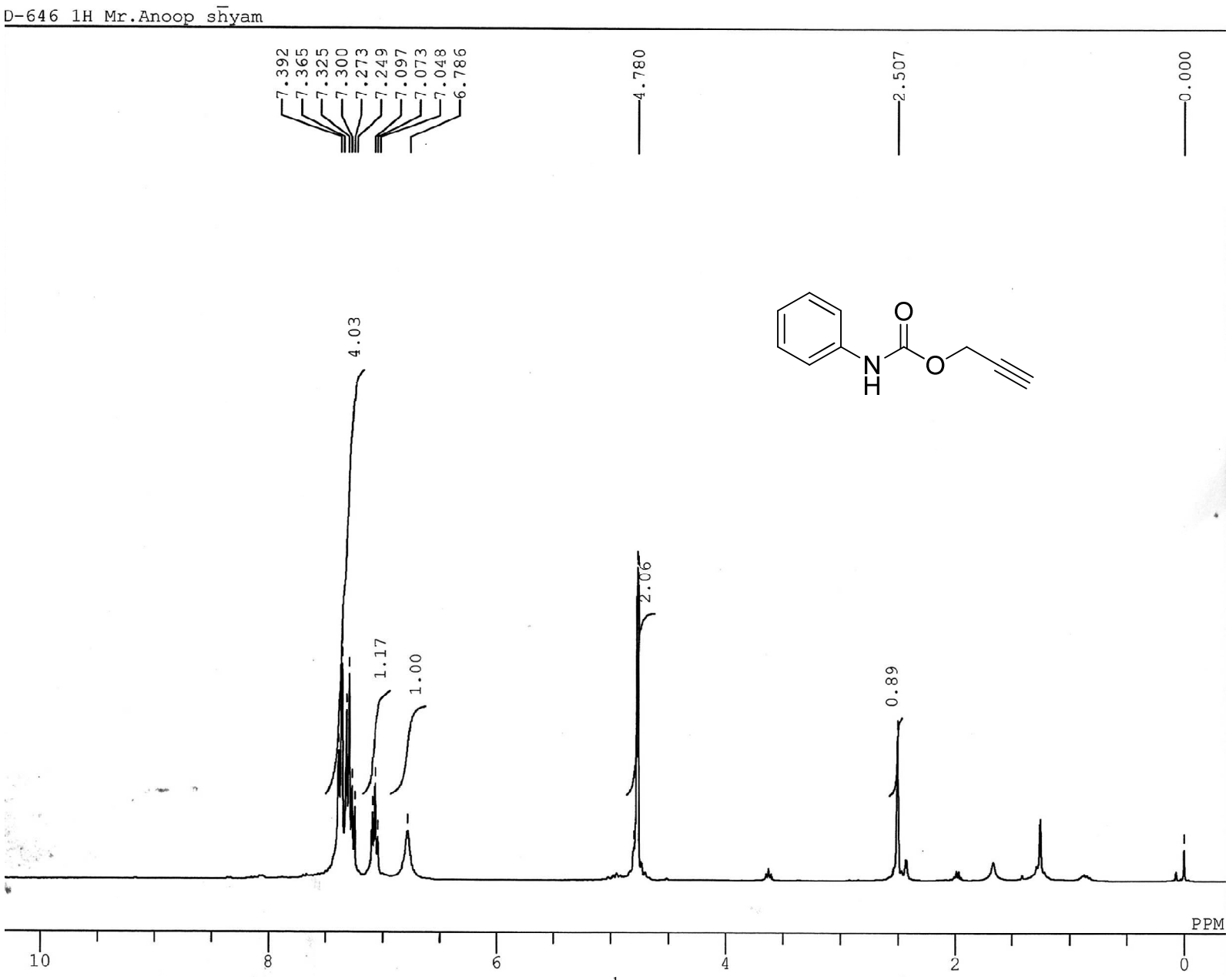
Spectrum 66: 75 MHz ^{13}C NMR of compound **3p**



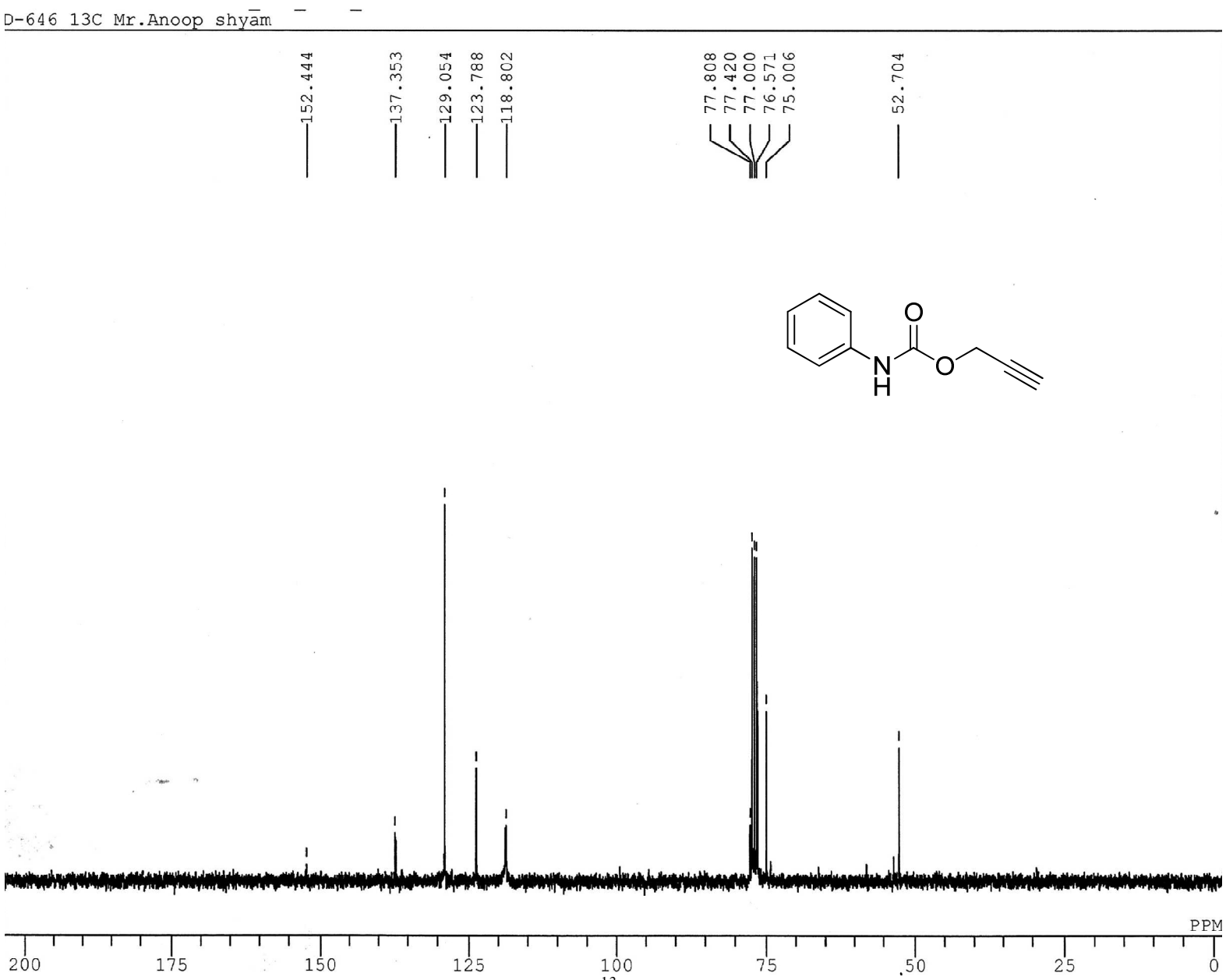
Spectrum 67: 300 MHz ^{1}H NMR of compound **3q**



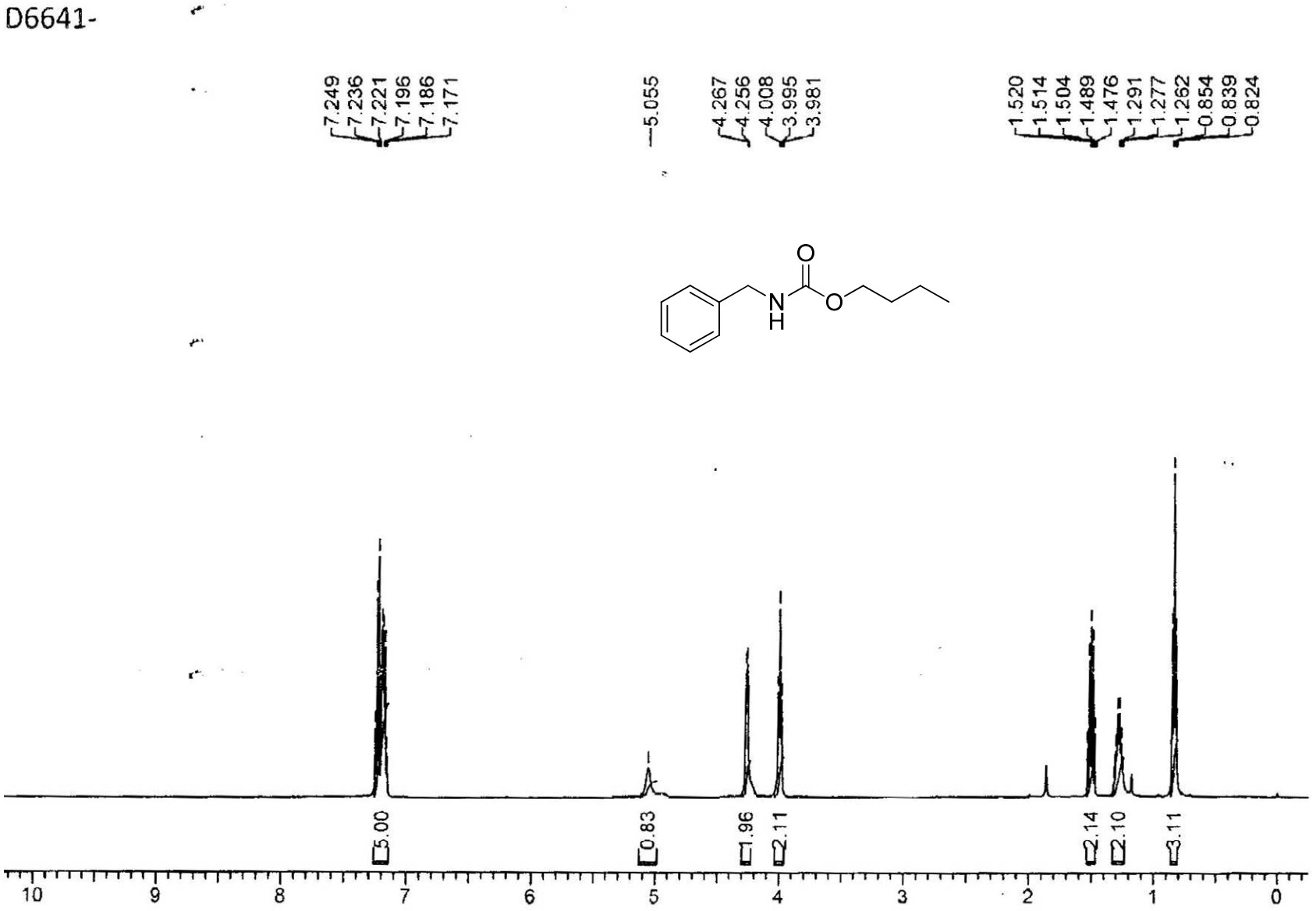
Spectrum 68: 75 MHz ^{13}C NMR of compound **3q**



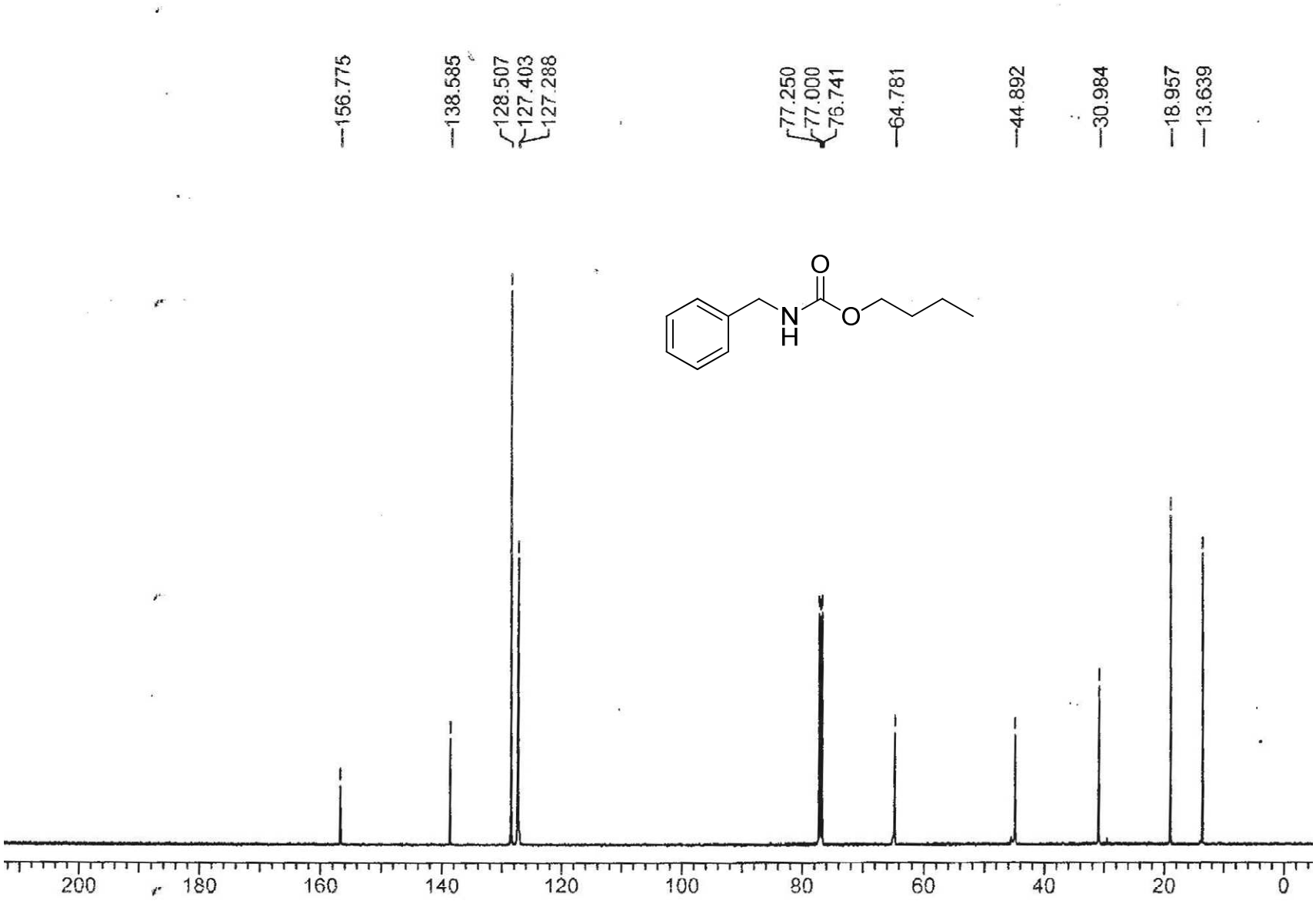
Spectrum 69: 300 MHz ^{1}H NMR of compound **3r**



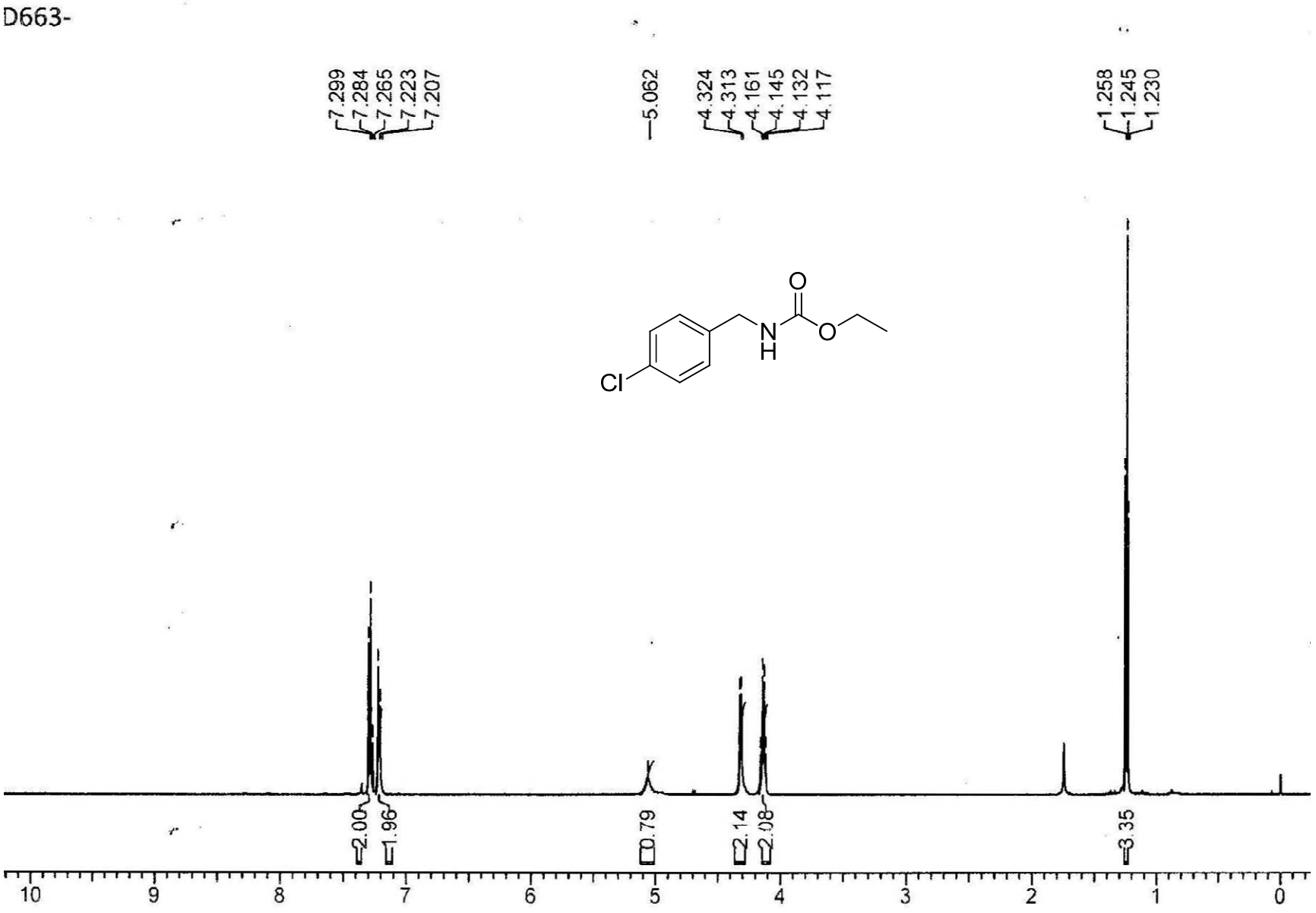
Spectrum 70: 75 MHz ^{13}C NMR of compound **3r**



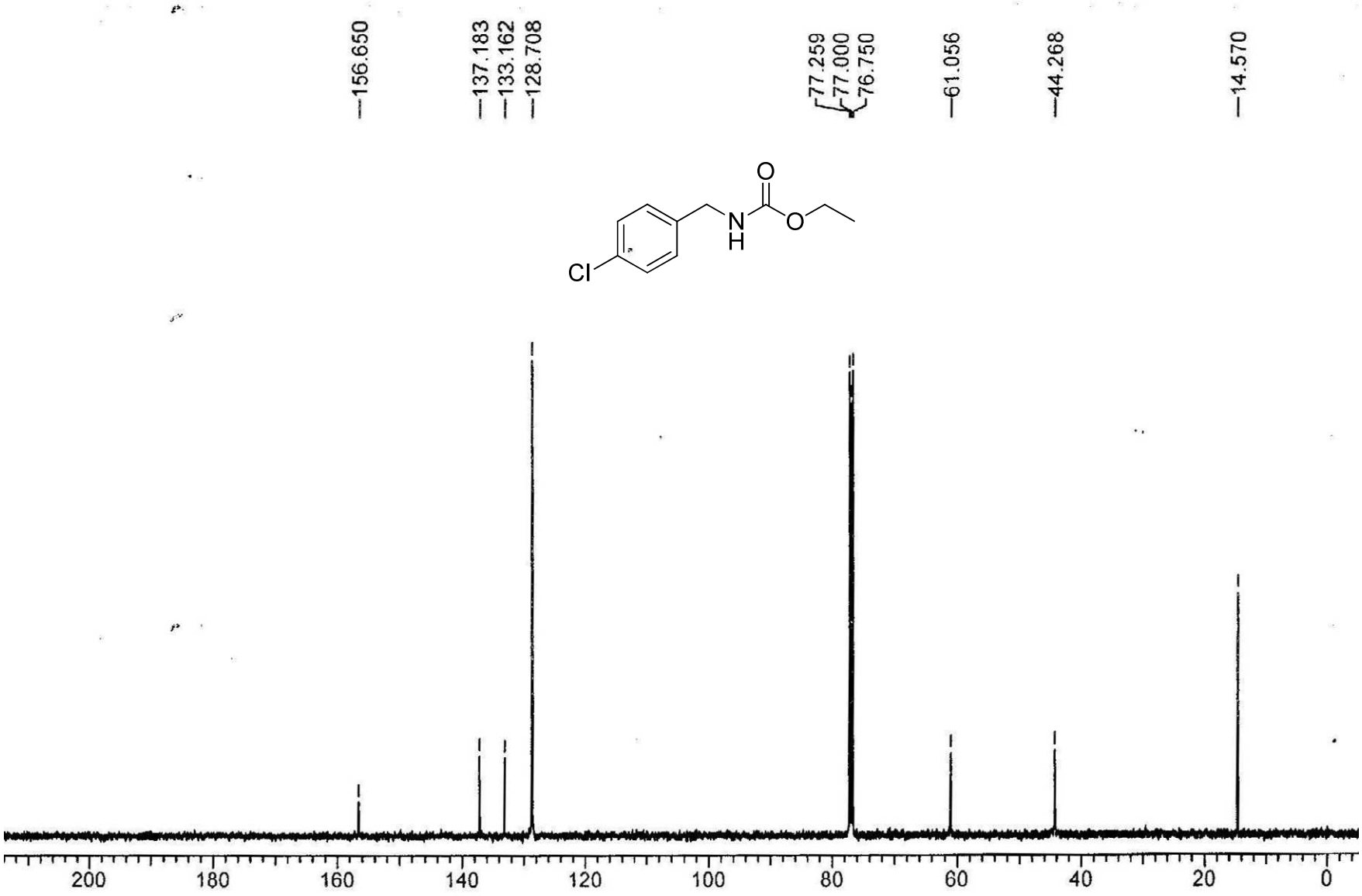
Spectrum 71: 500 MHz ^{1}H NMR of compound **3s**



Spectrum 72: 125 MHz ^{13}C NMR of compound **3s**

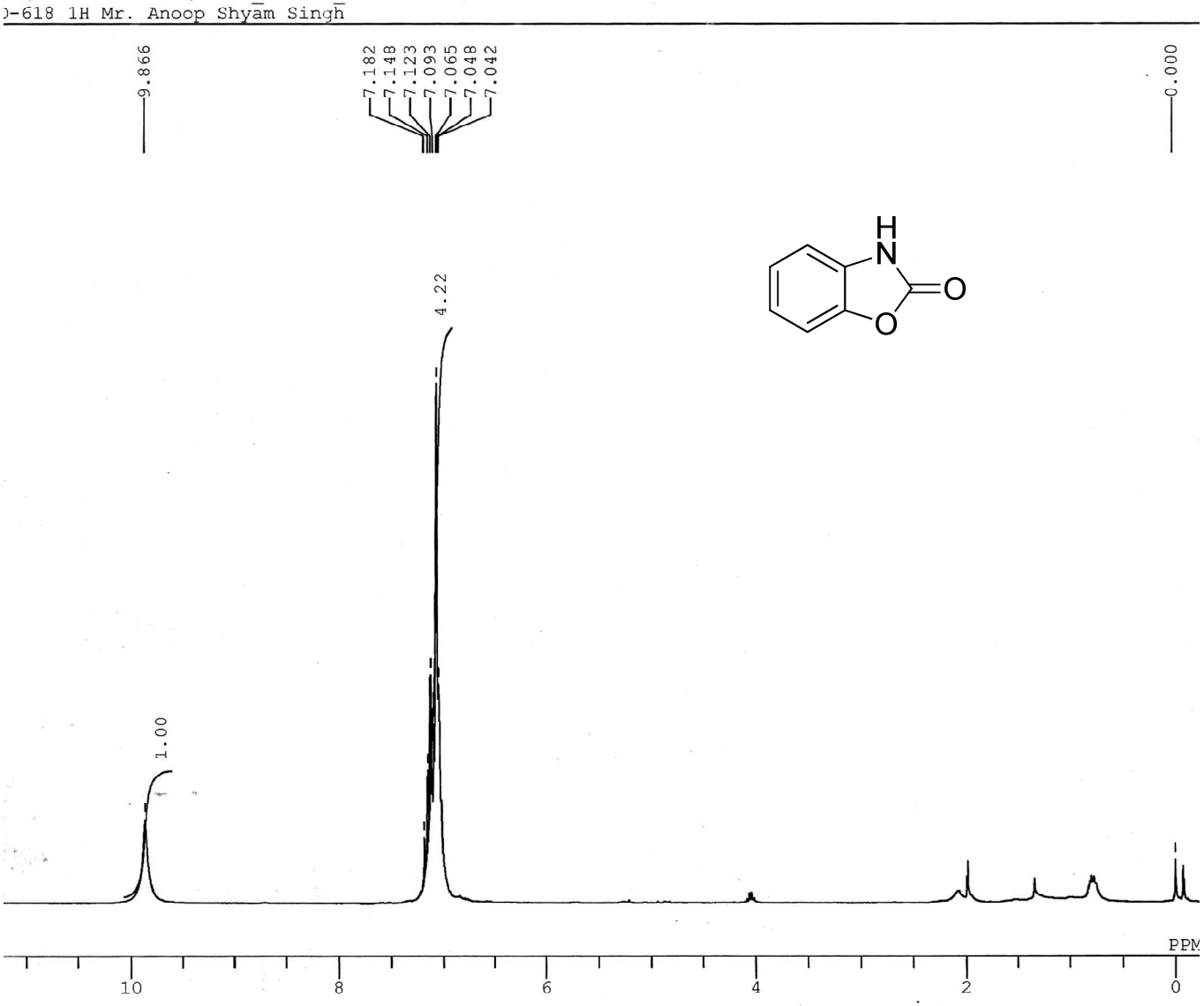


Spectrum 73: 500 MHz ^{1}H NMR of compound **3t**

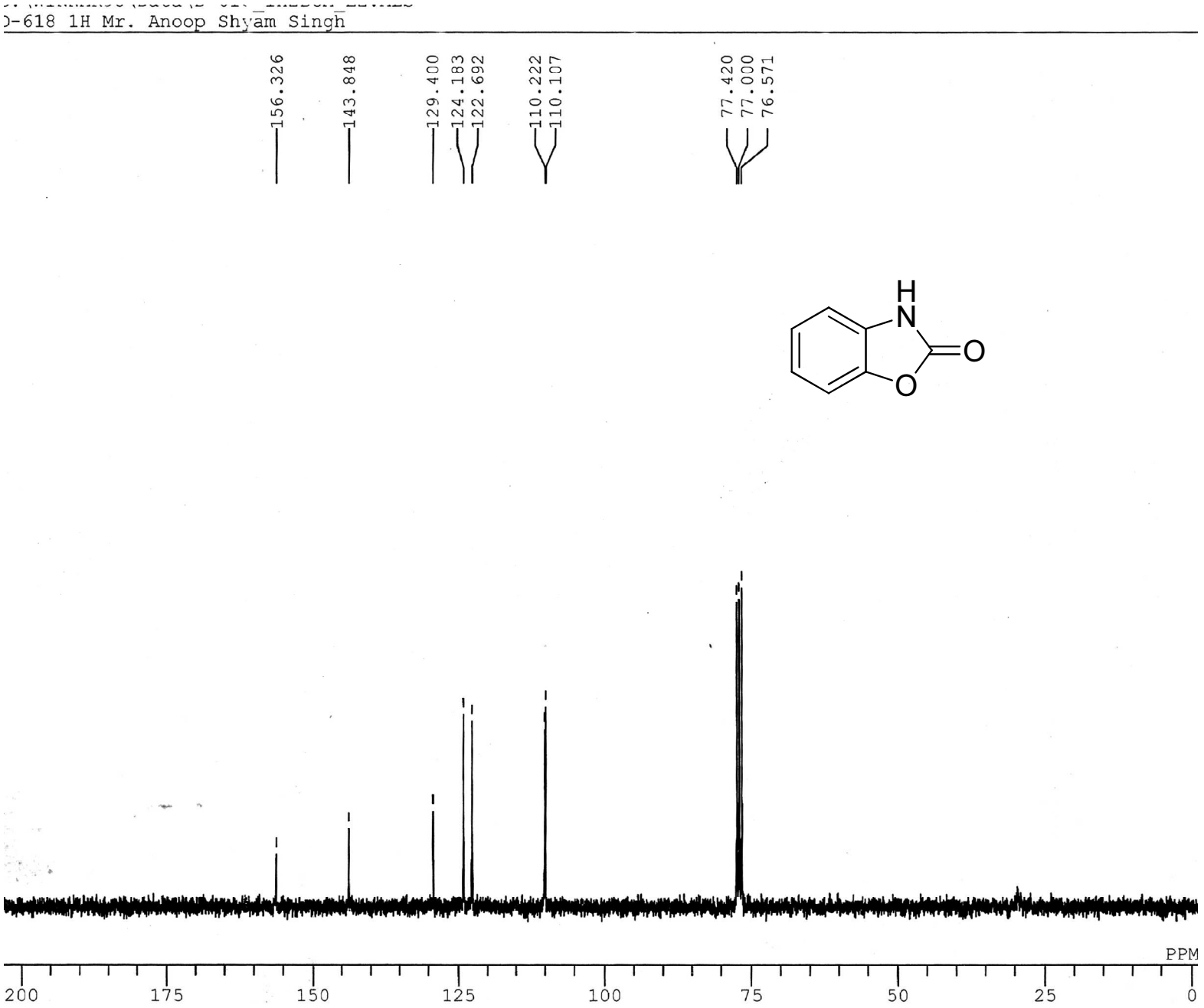


Spectrum 74: 125 MHz ^{13}C NMR of compound **3t**

3. ^{1}H and ^{13}C NMR spectrum of compound **4**

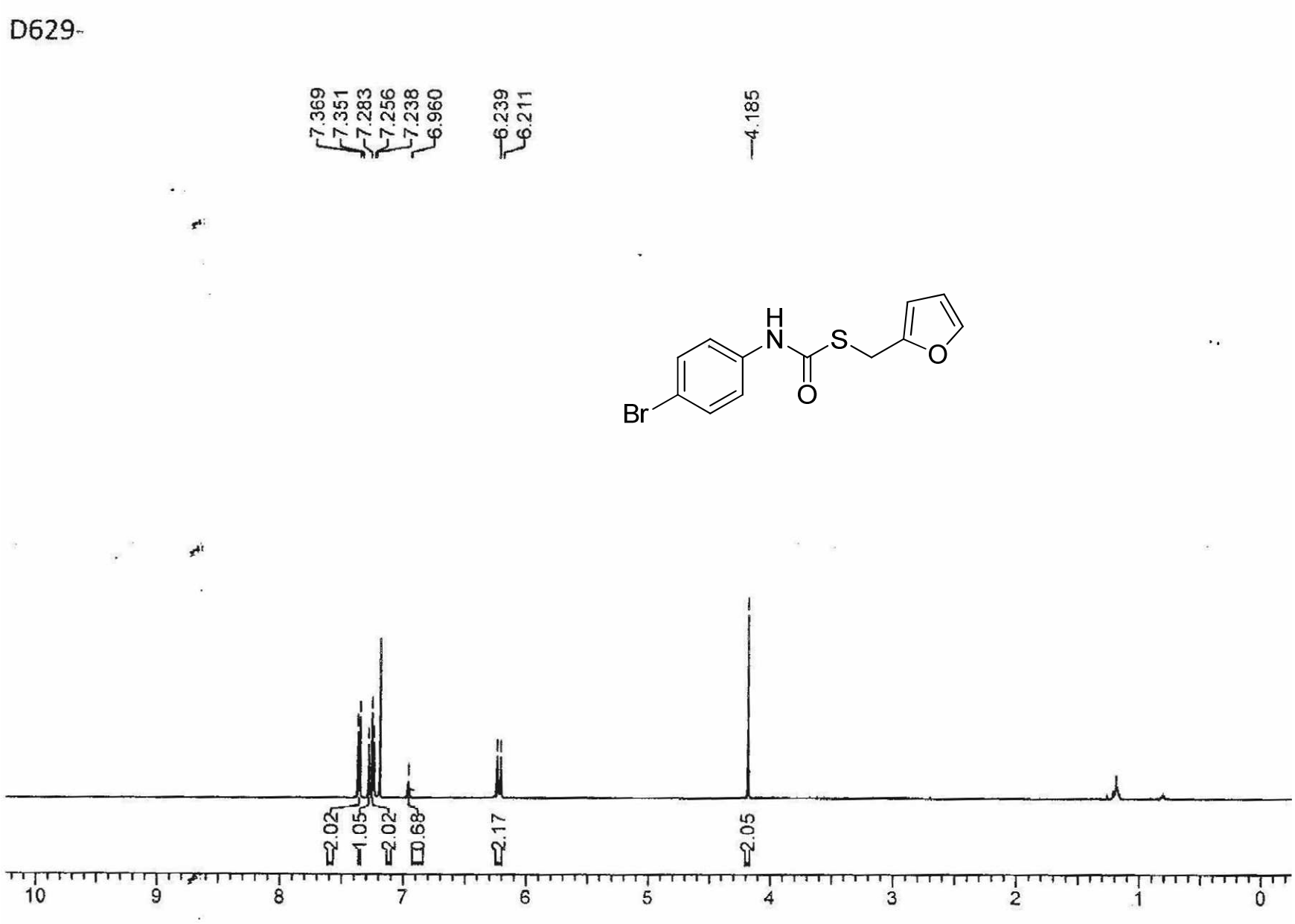


Spectrum 75: 300 MHz ^{1}H NMR of compound **4**

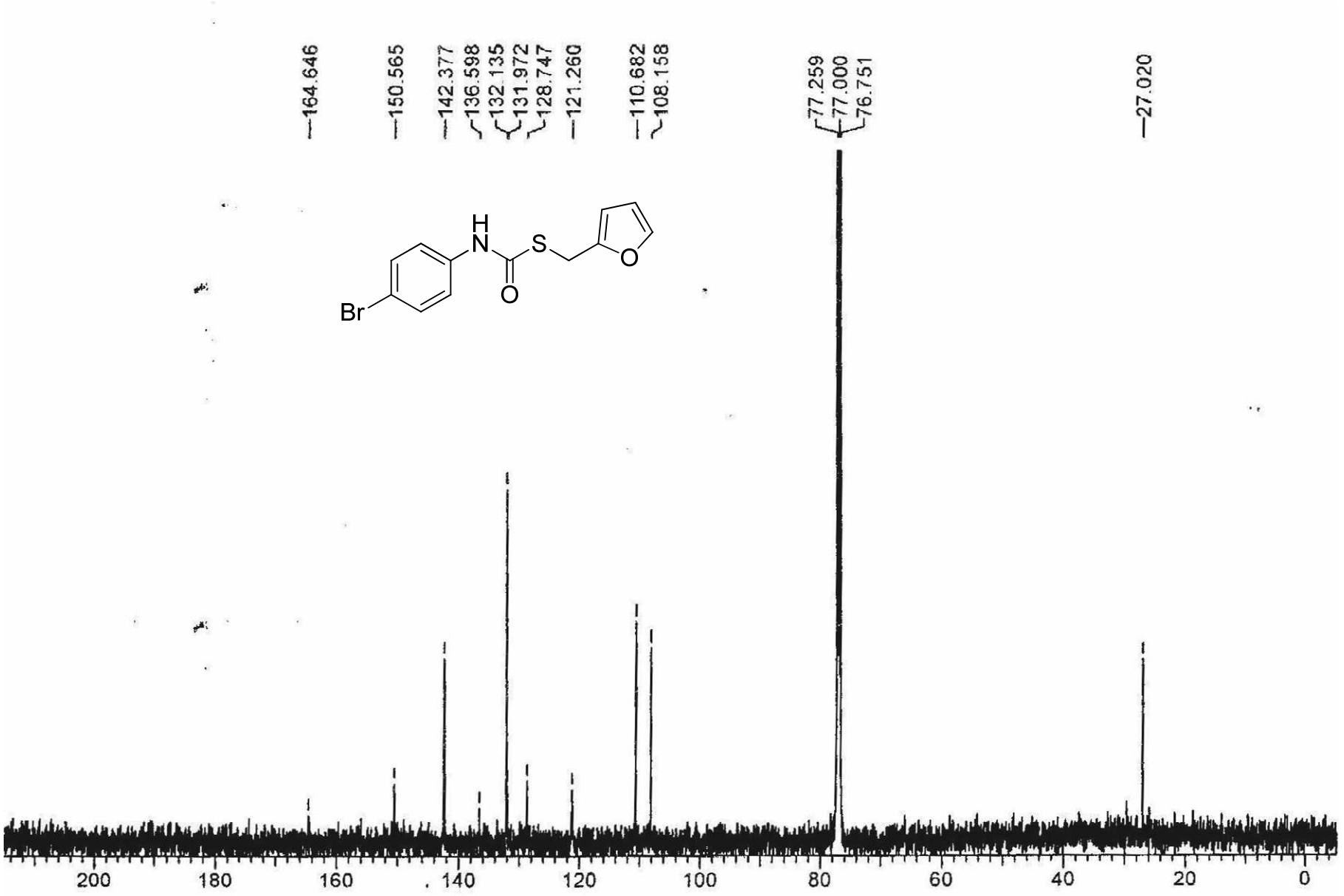


Spectrum 76: 75 MHz ^{13}C NMR of compound **4**

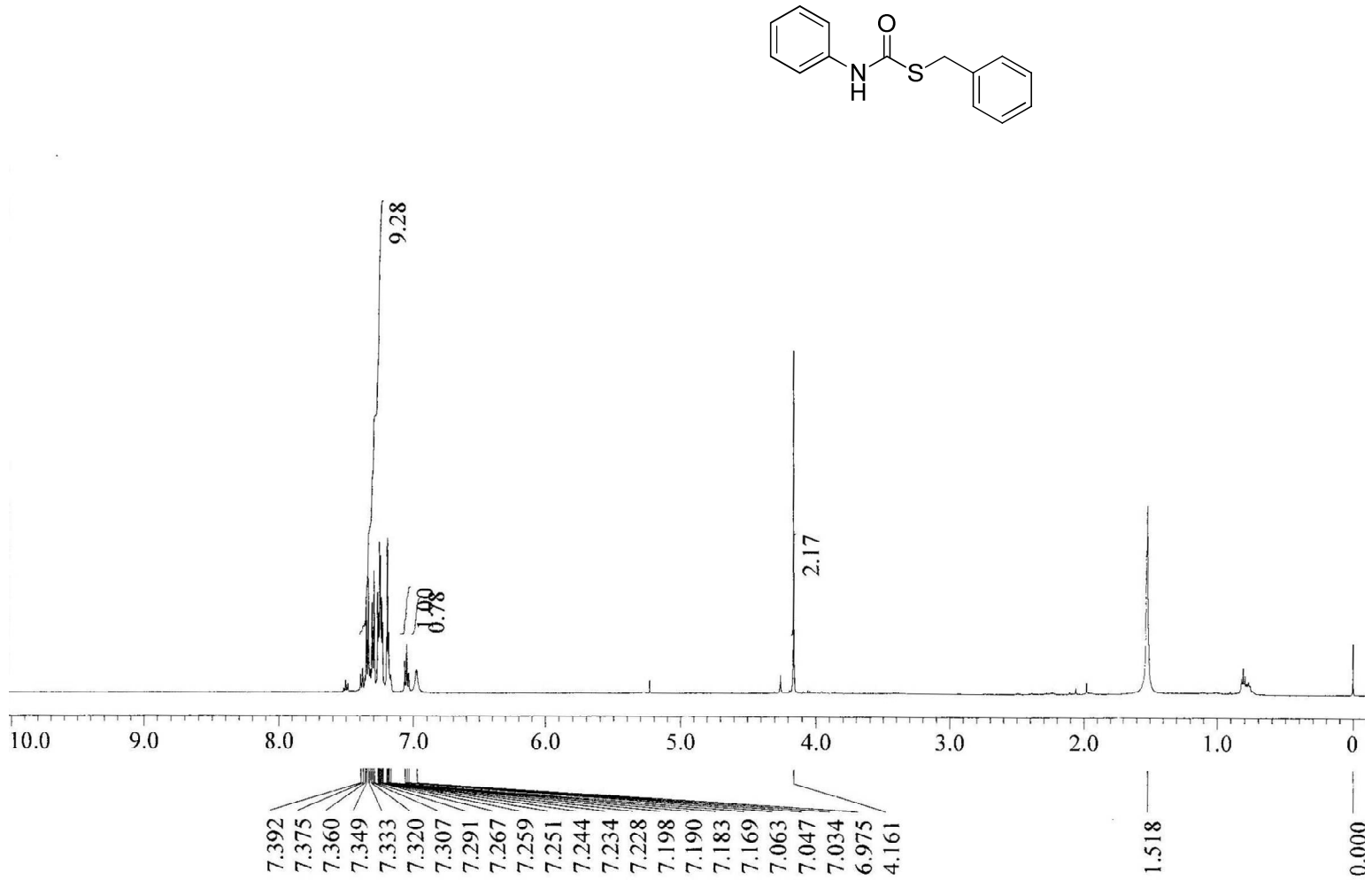
4. ^{1}H and ^{13}C NMR spectrum of thiocarbamates (**5a-g**)



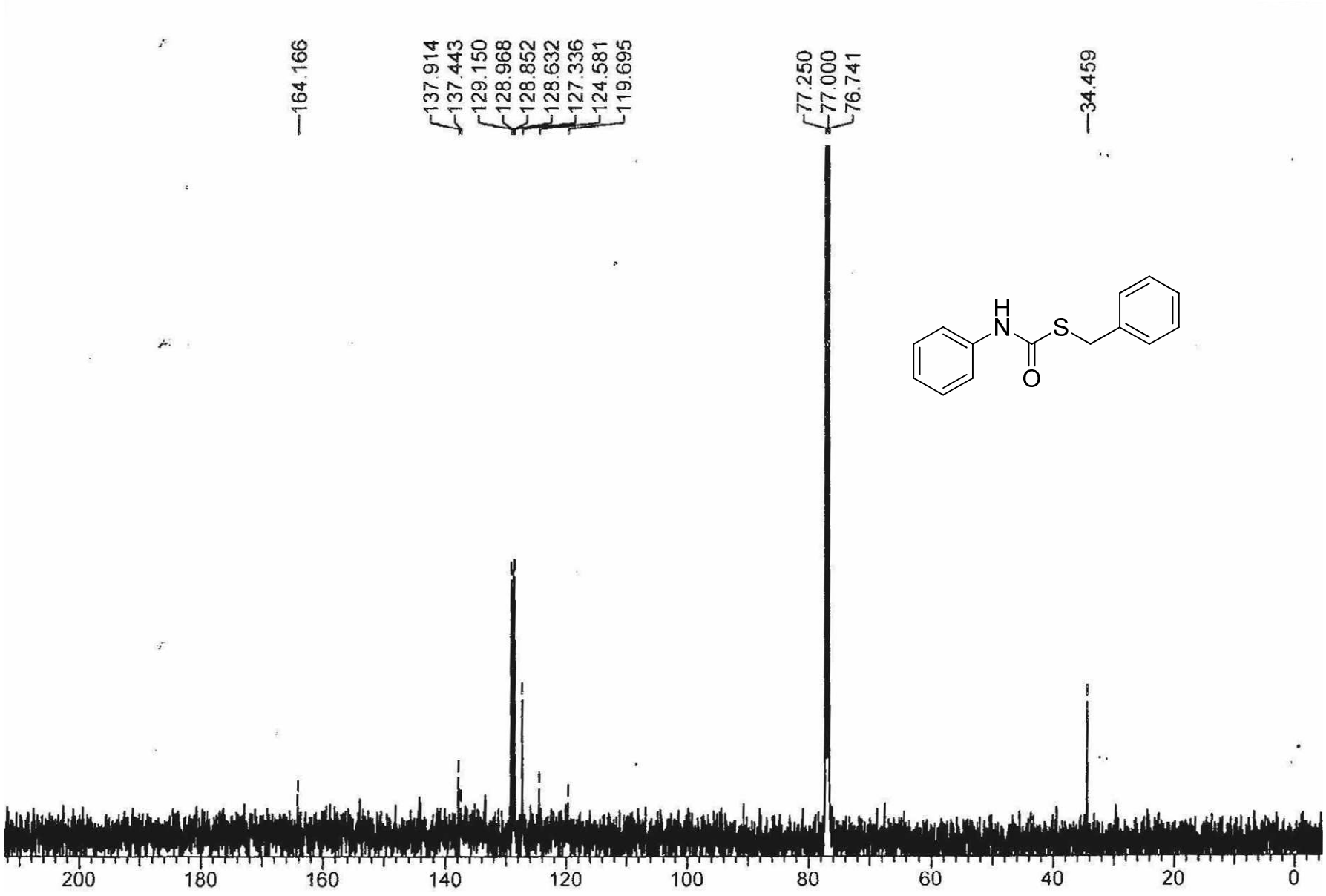
Spectrum 77: 500 MHz ^{1}H NMR of compound **5a**



Spectrum 78: 125 MHz ^{13}C NMR of compound **5a**

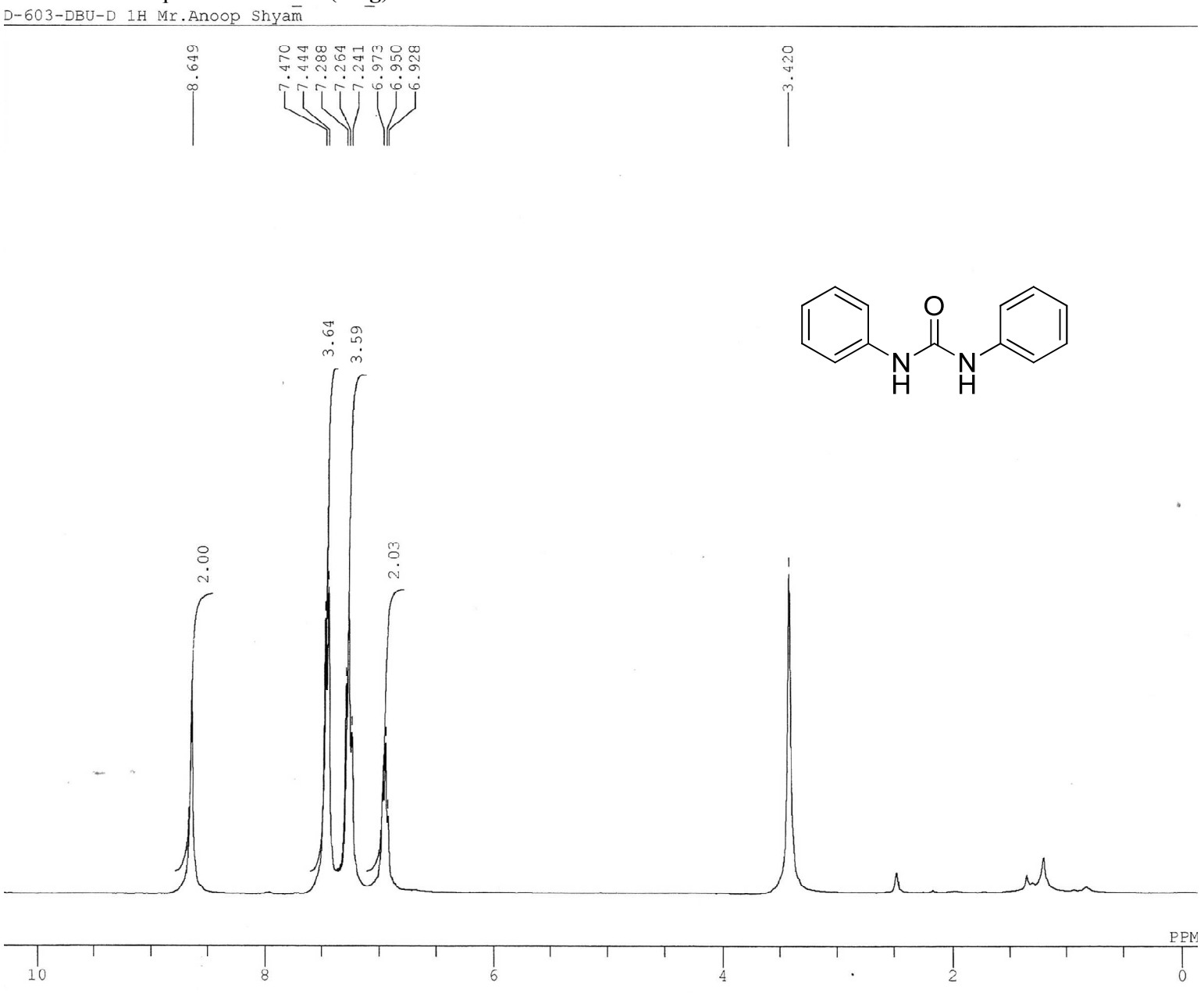


Spectrum 79: 500 MHz ^{1}H NMR of compound **5b**

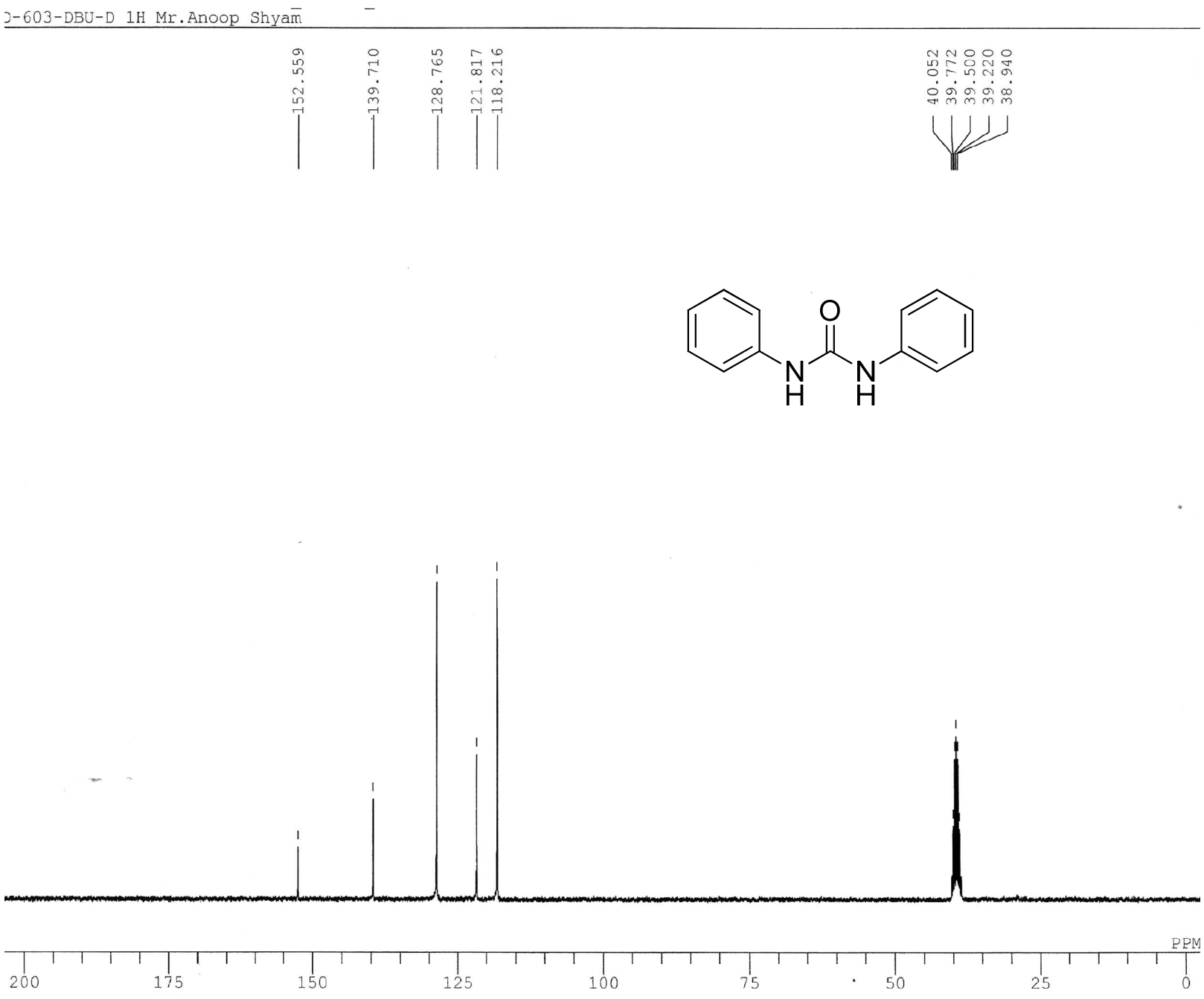


Spectrum 80: 125 MHz ^{13}C NMR of compound **5b**

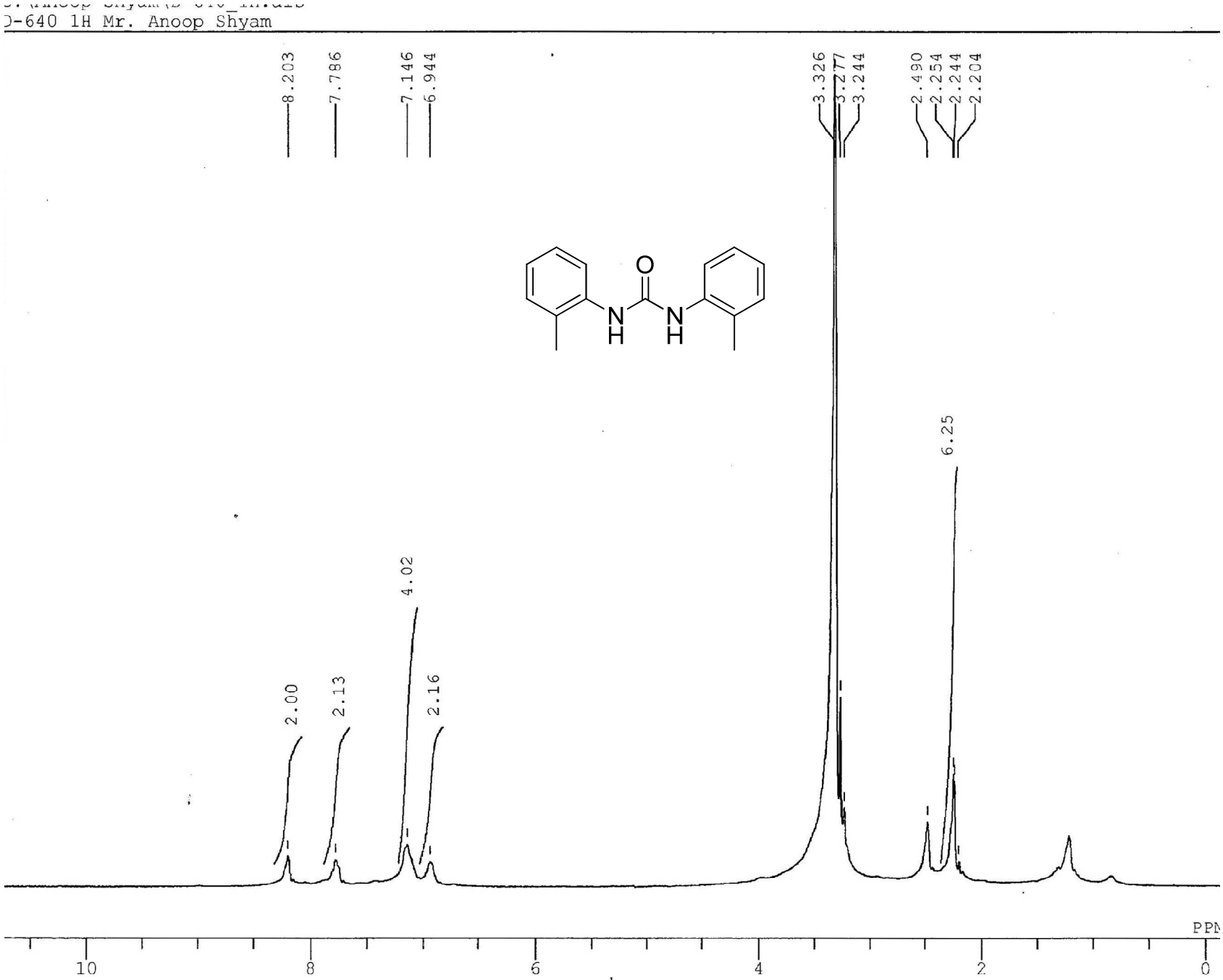
5. ^{1}H and ^{13}C NMR spectrum of urea (**6a-g**)



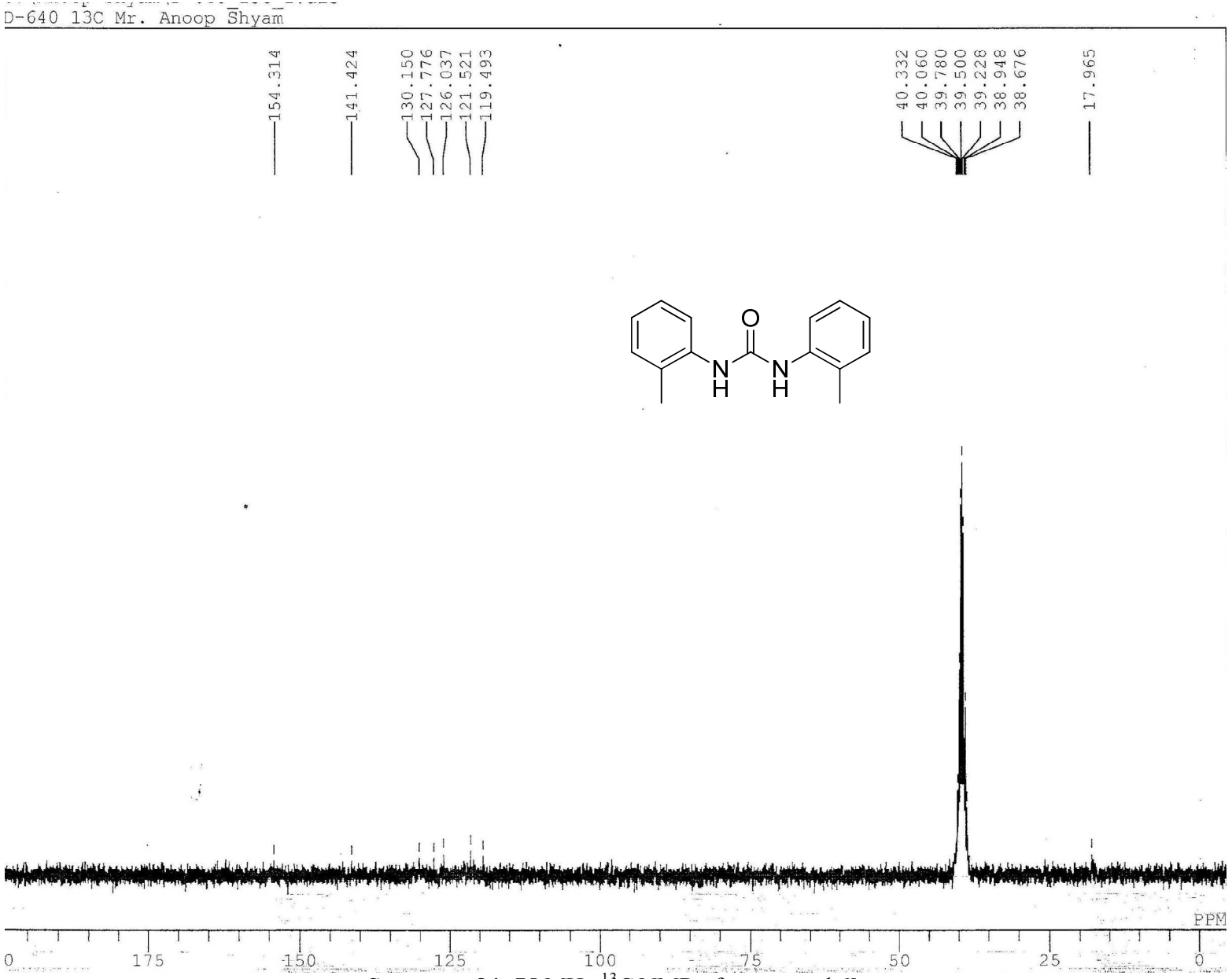
Spectrum 81: 300 MHz ^{1}H NMR of compound **6a**



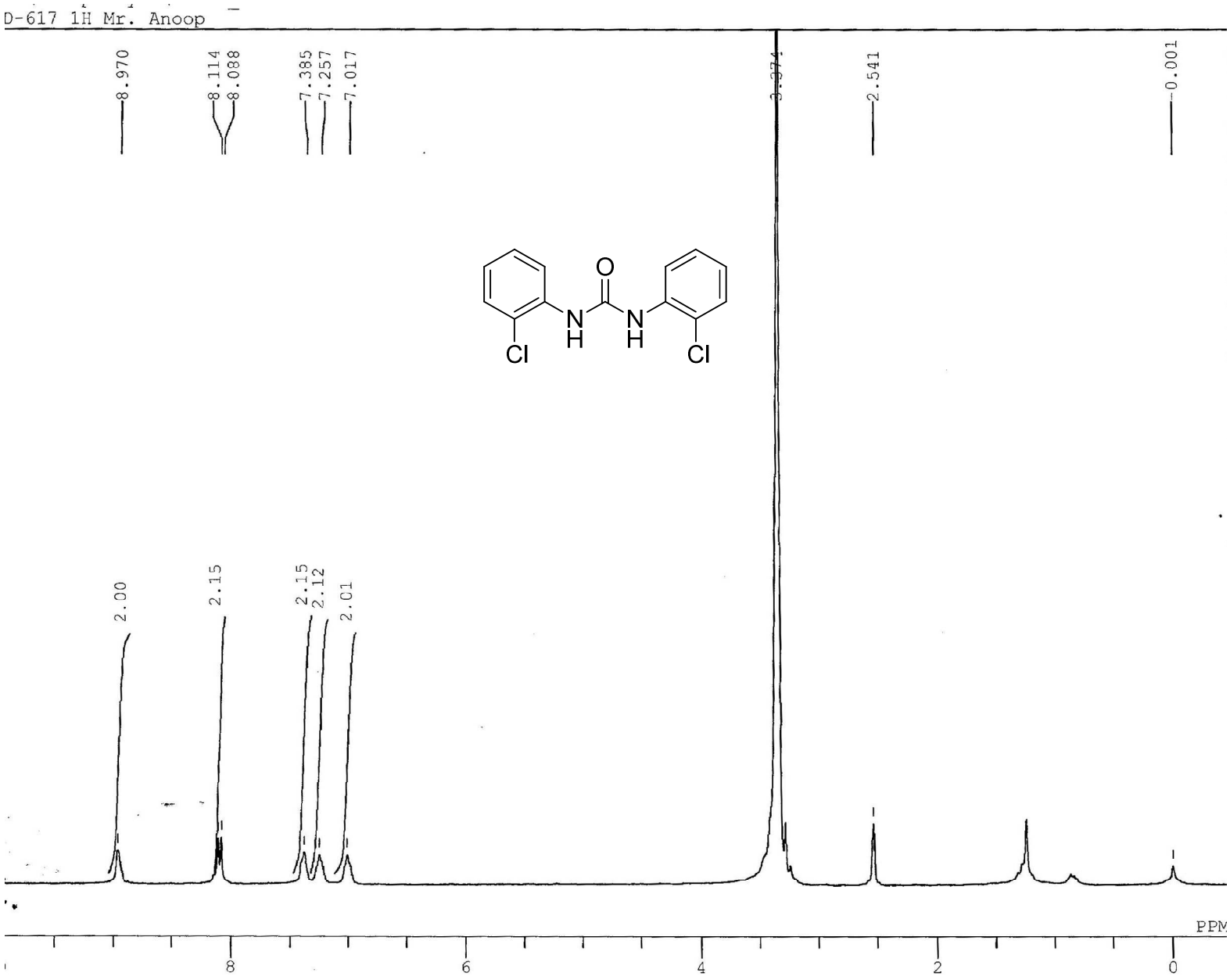
Spectrum 82: 75 MHz ^{13}C NMR of compound **6a**



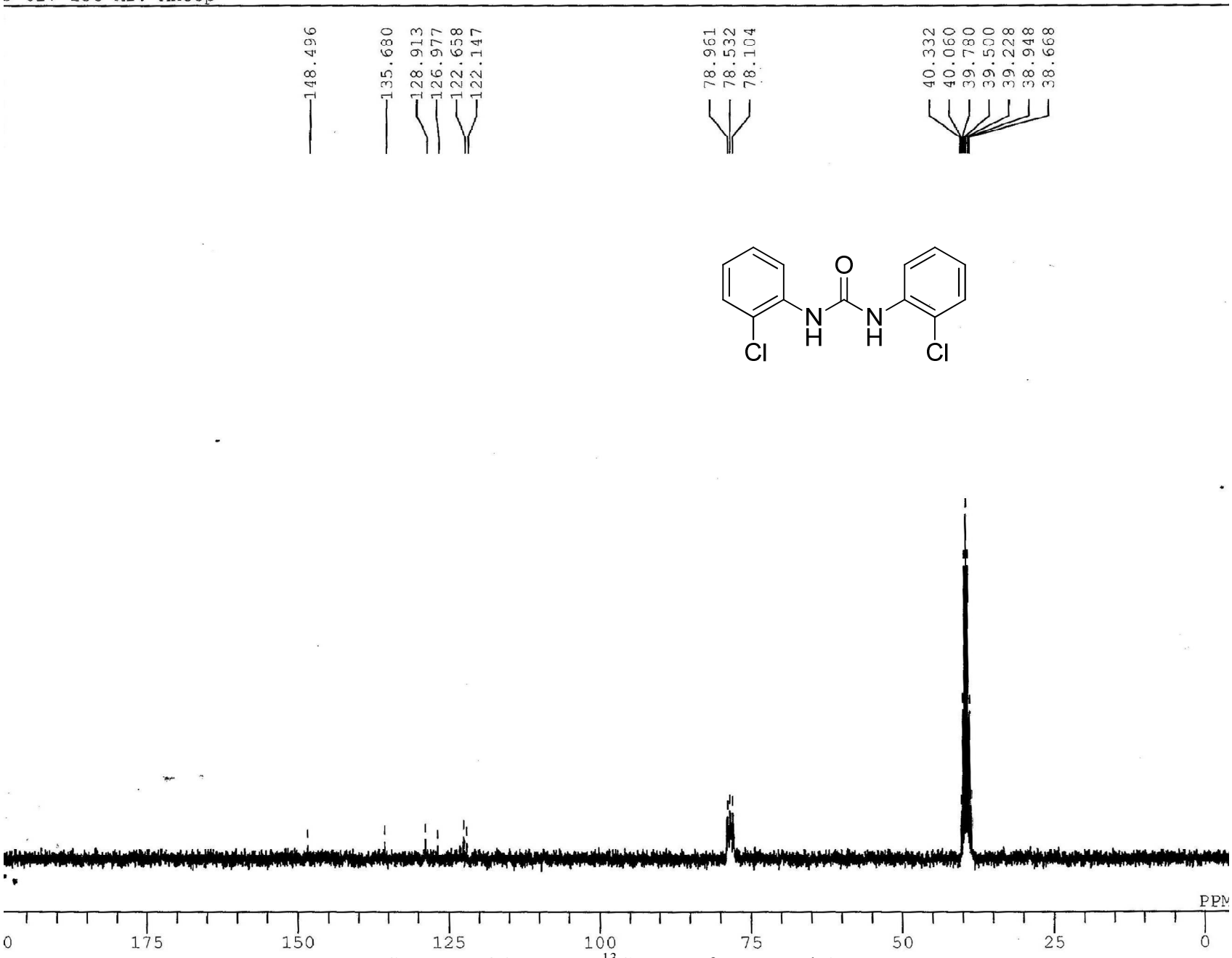
Spectrum 83: 300 MHz ^{1}H NMR of compound **6b**



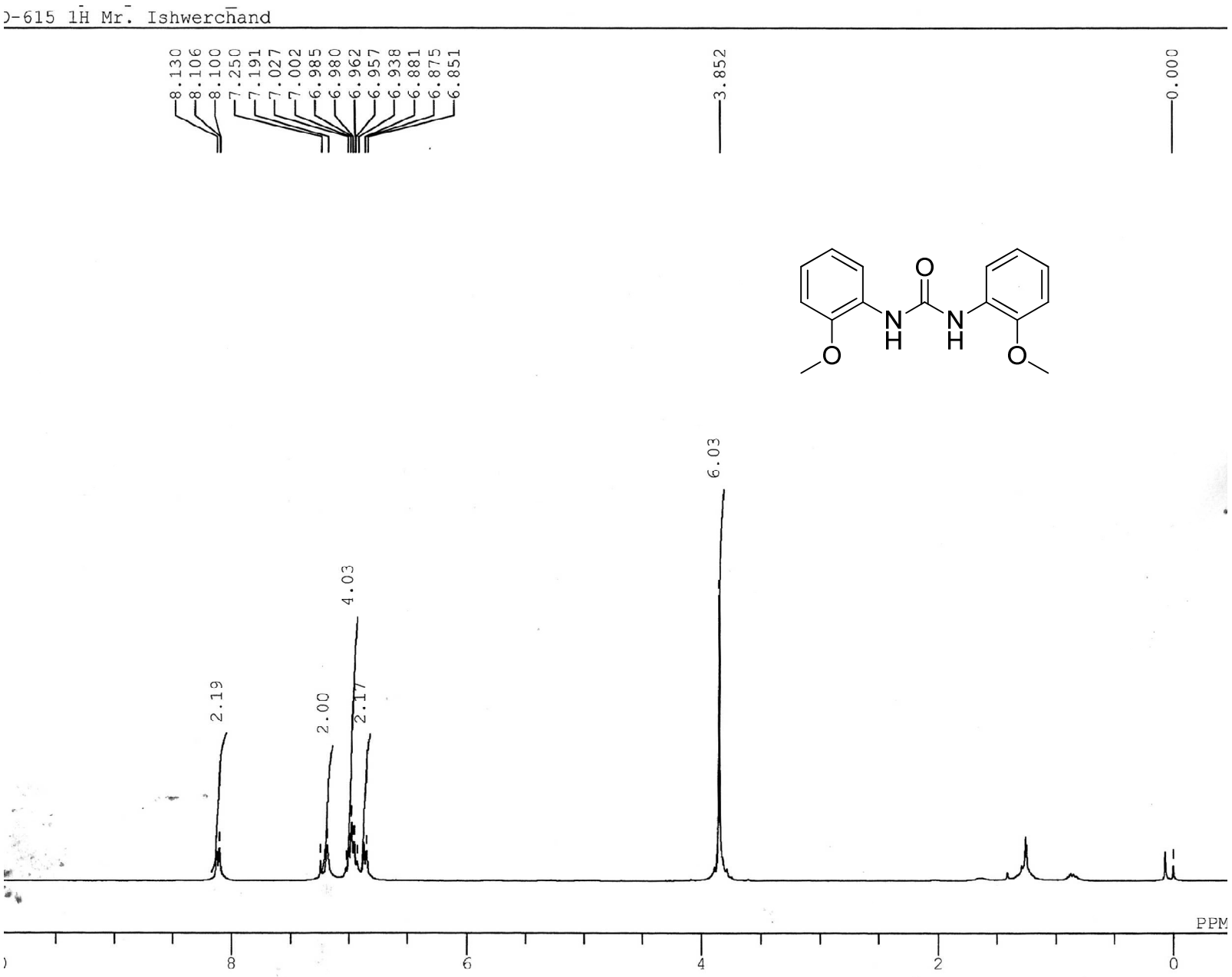
Spectrum 84: 75 MHz ^{13}C NMR of compound **6b**



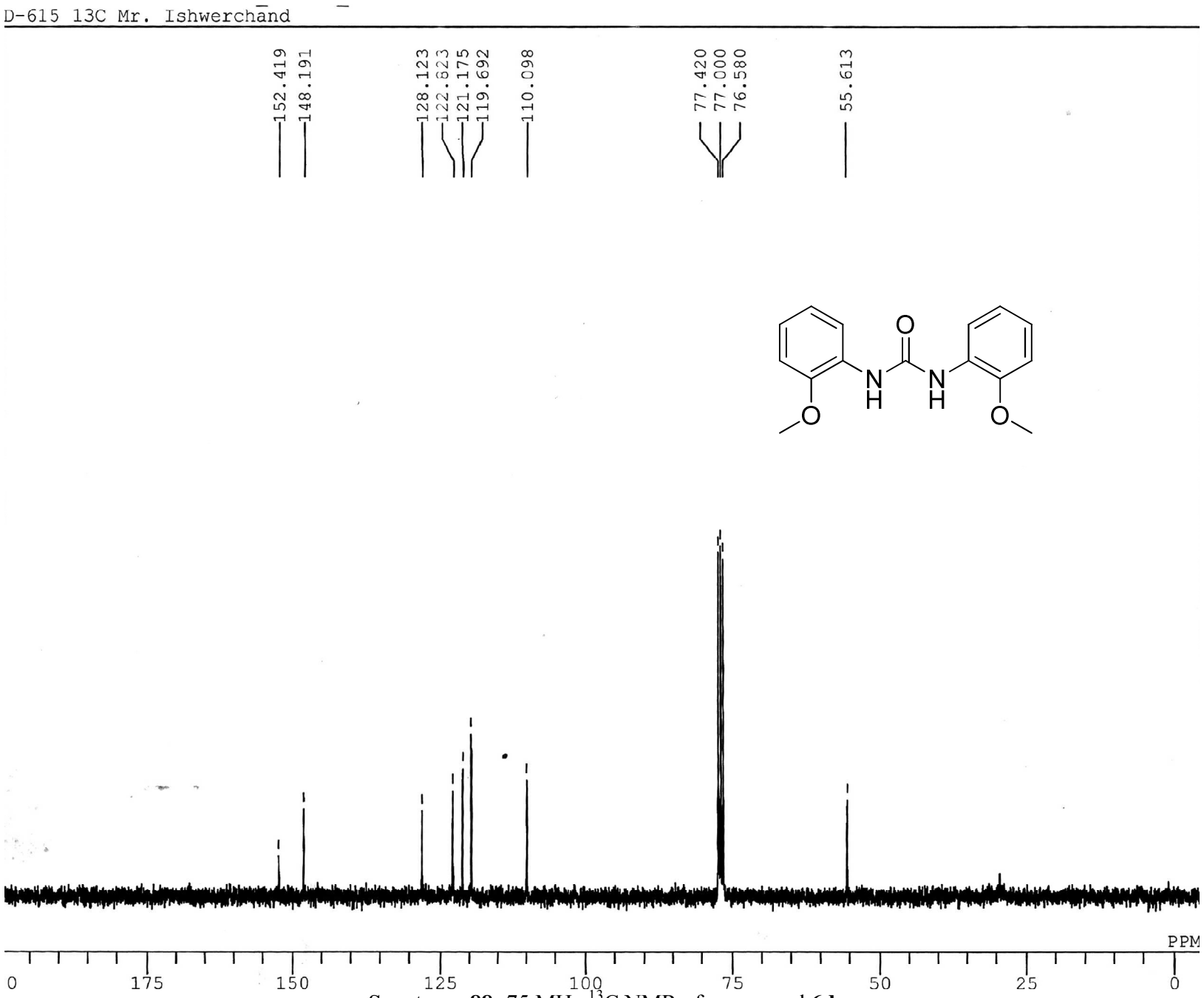
Spectrum 85: 300 MHz ^{1}H NMR of compound **6c**



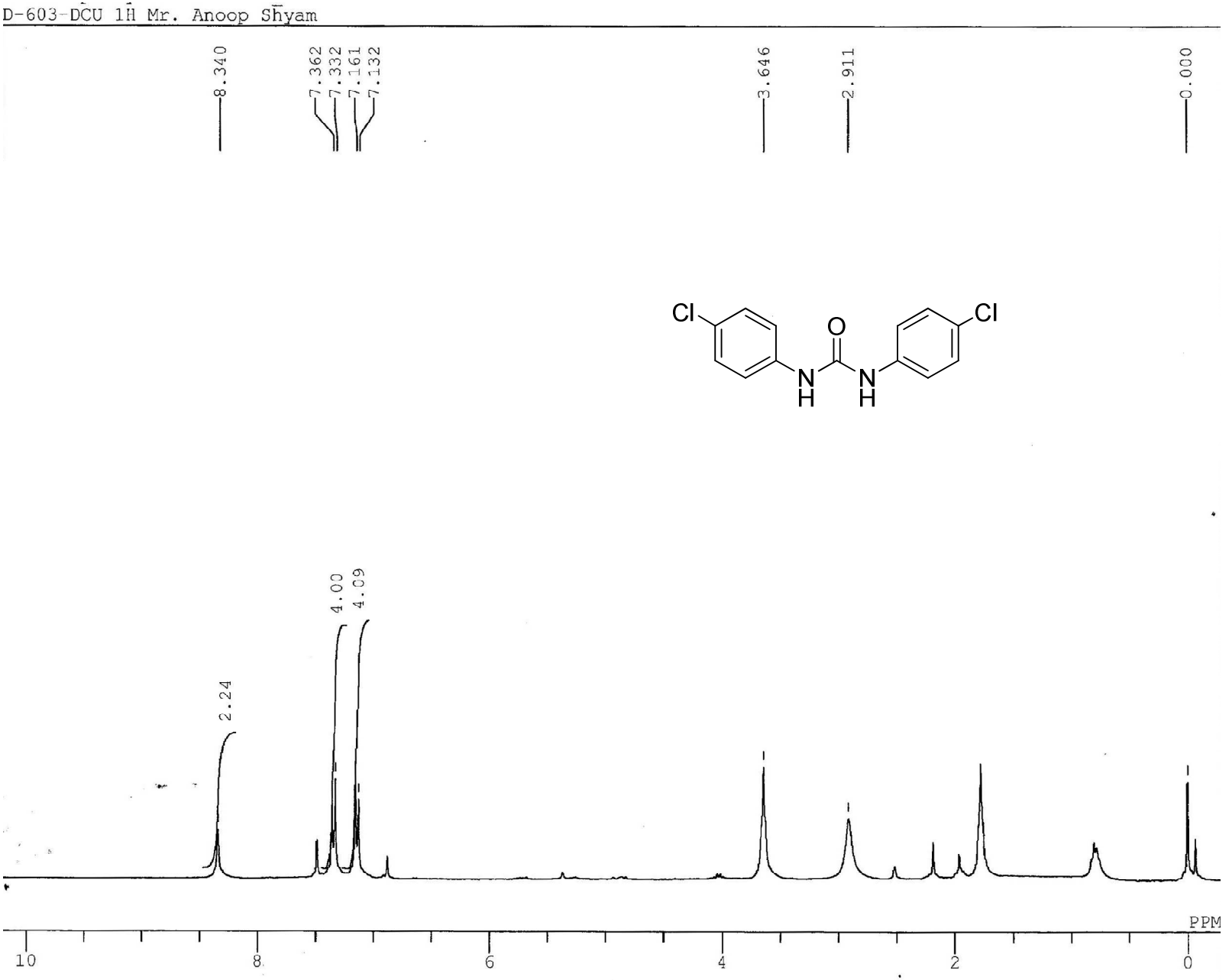
Spectrum 86: 75 MHz ^{13}C NMR of compound **6c**



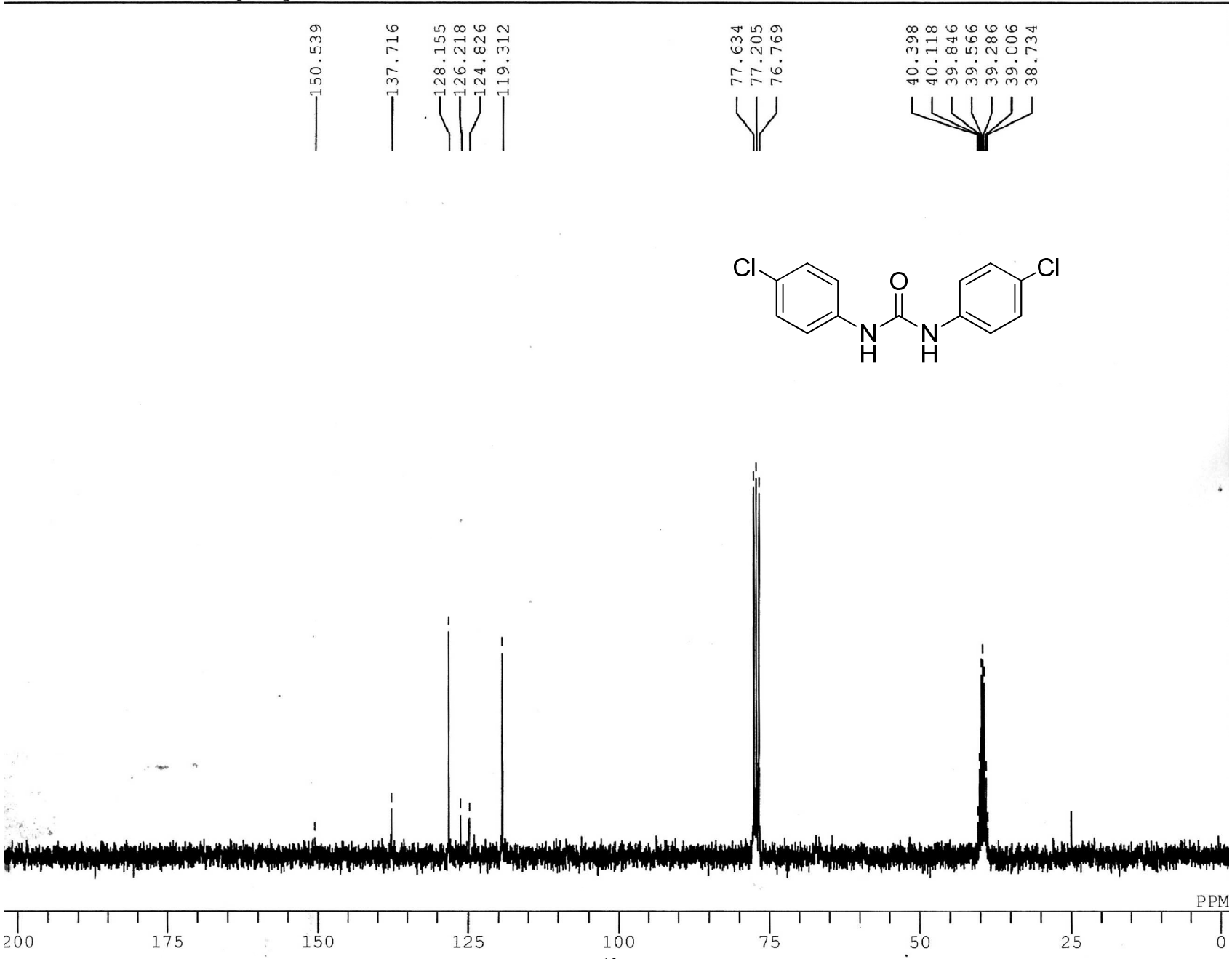
Spectrum 87: 300 MHz ^{1}H NMR of compound **6d**



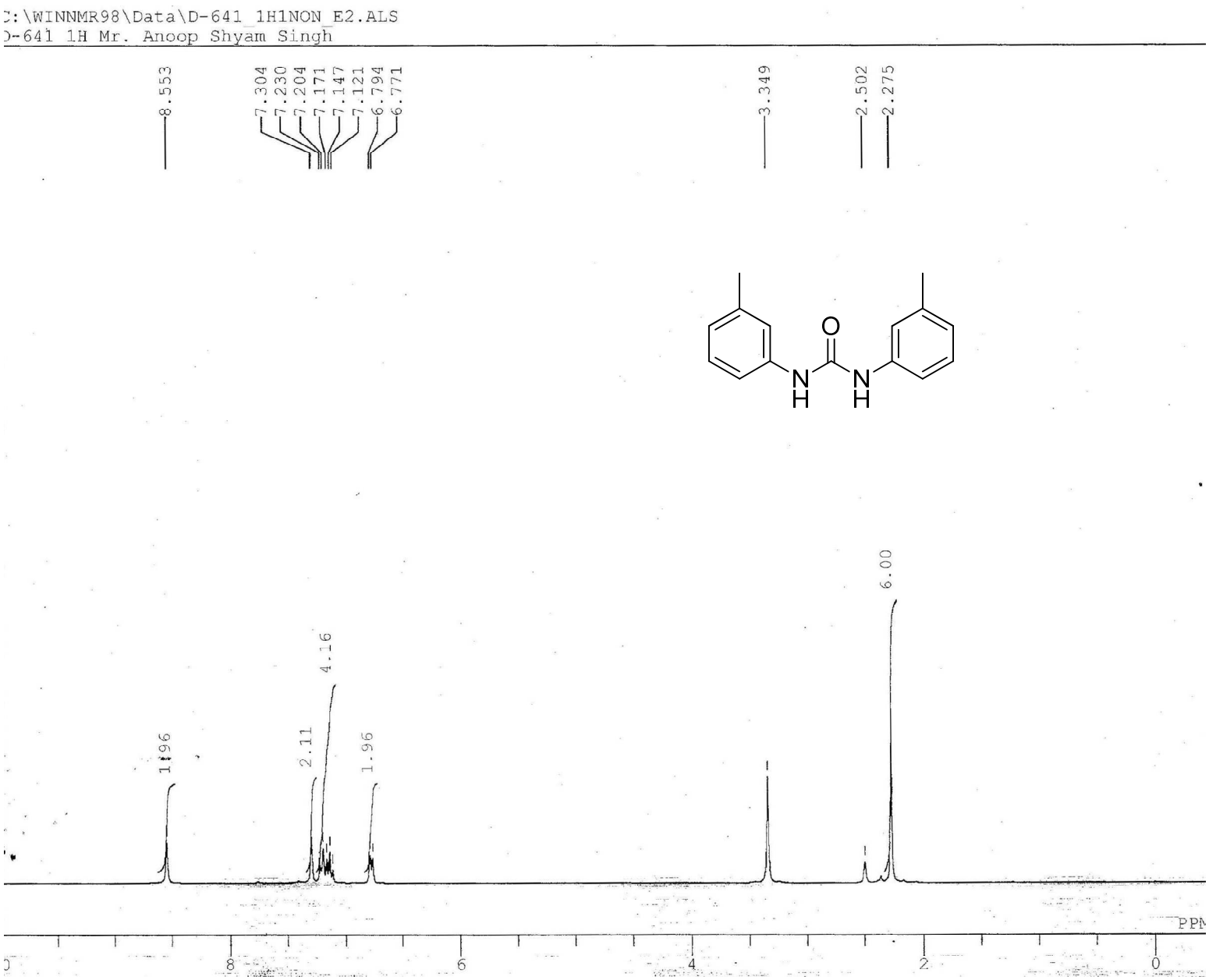
Spectrum 88: 75 MHz ^{13}C NMR of compound **6d**



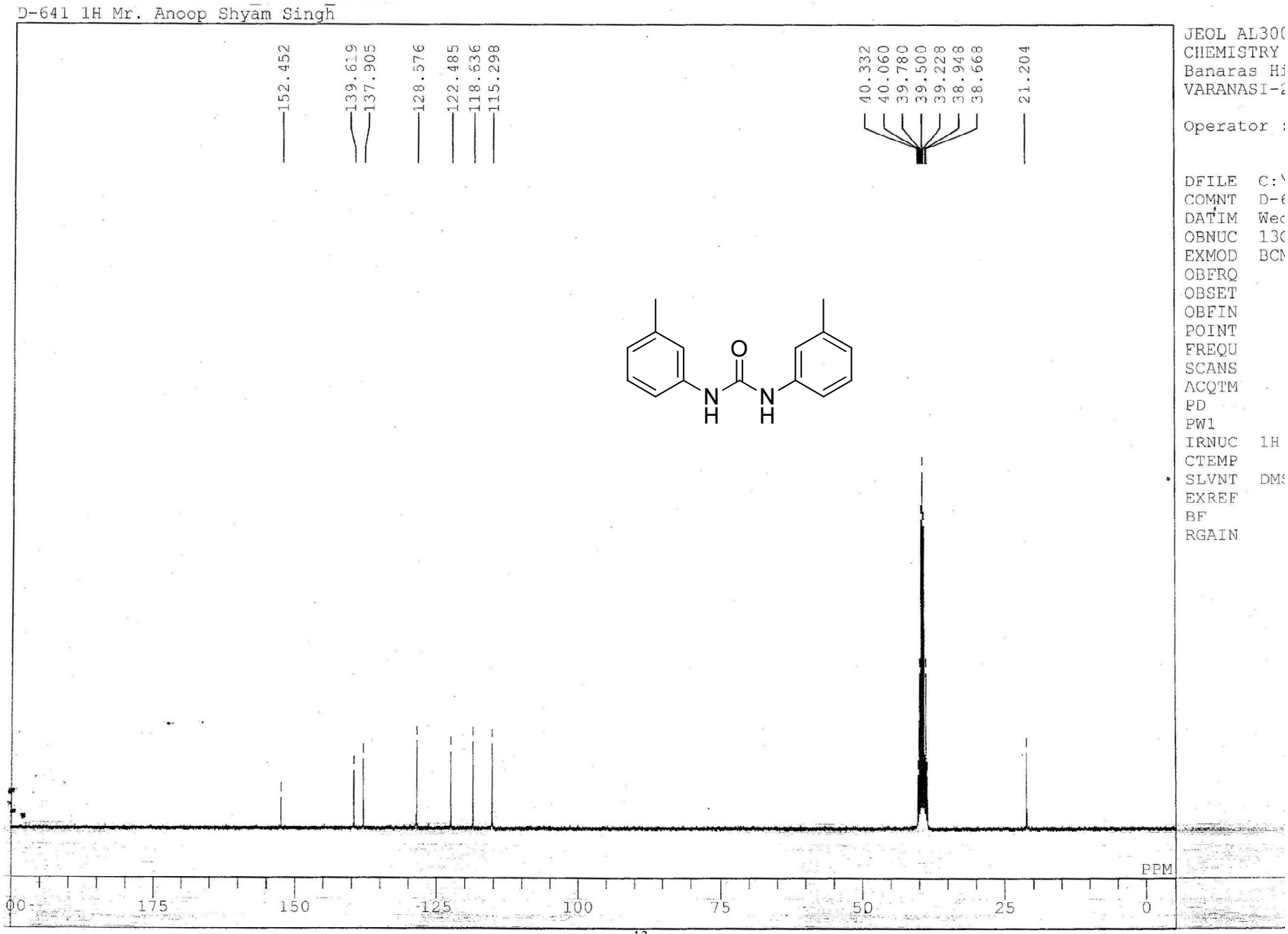
Spectrum 89: 300 MHz ^{1}H NMR of compound **6e**



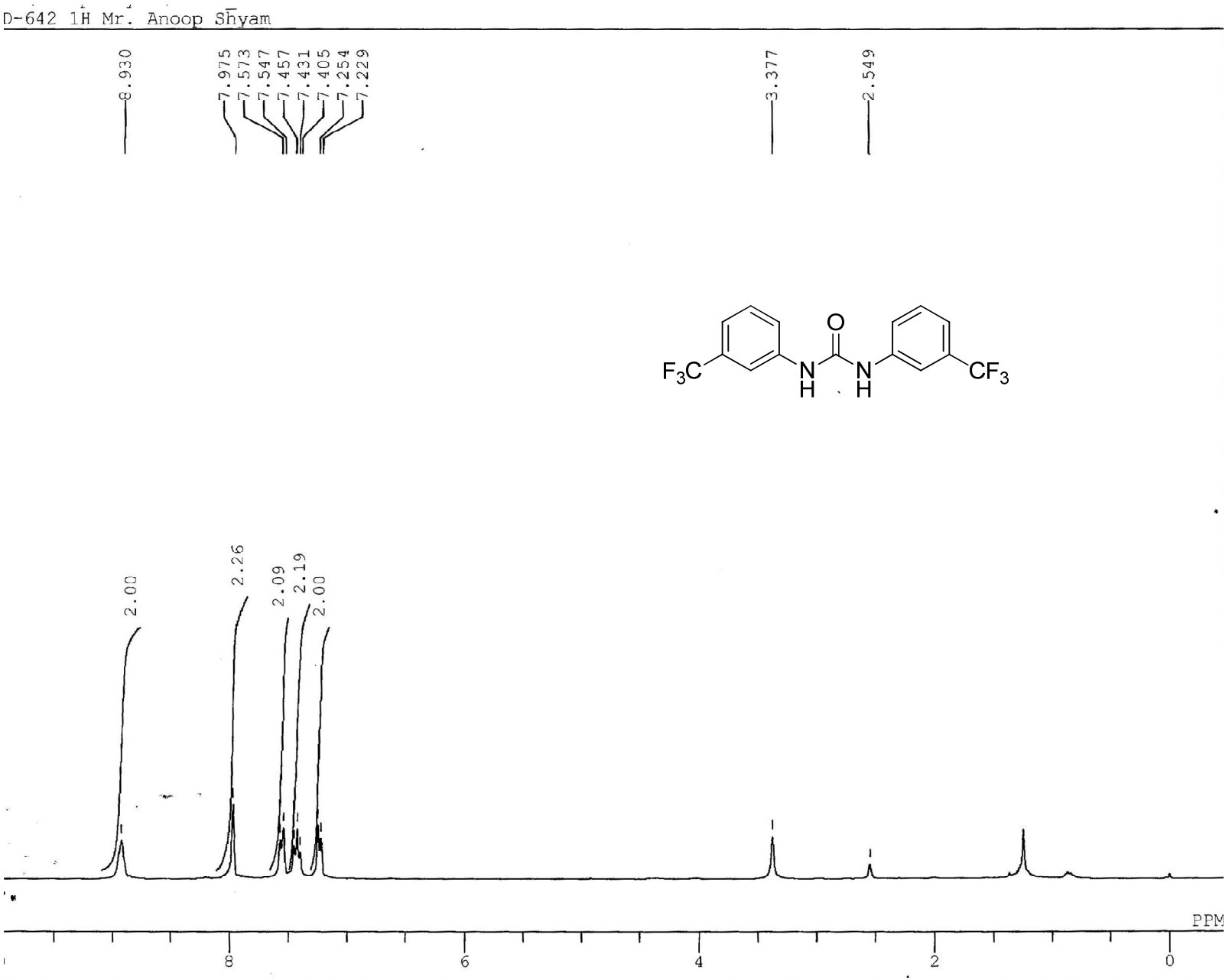
Spectrum 90: 75 MHz ^{13}C NMR of compound **6e**



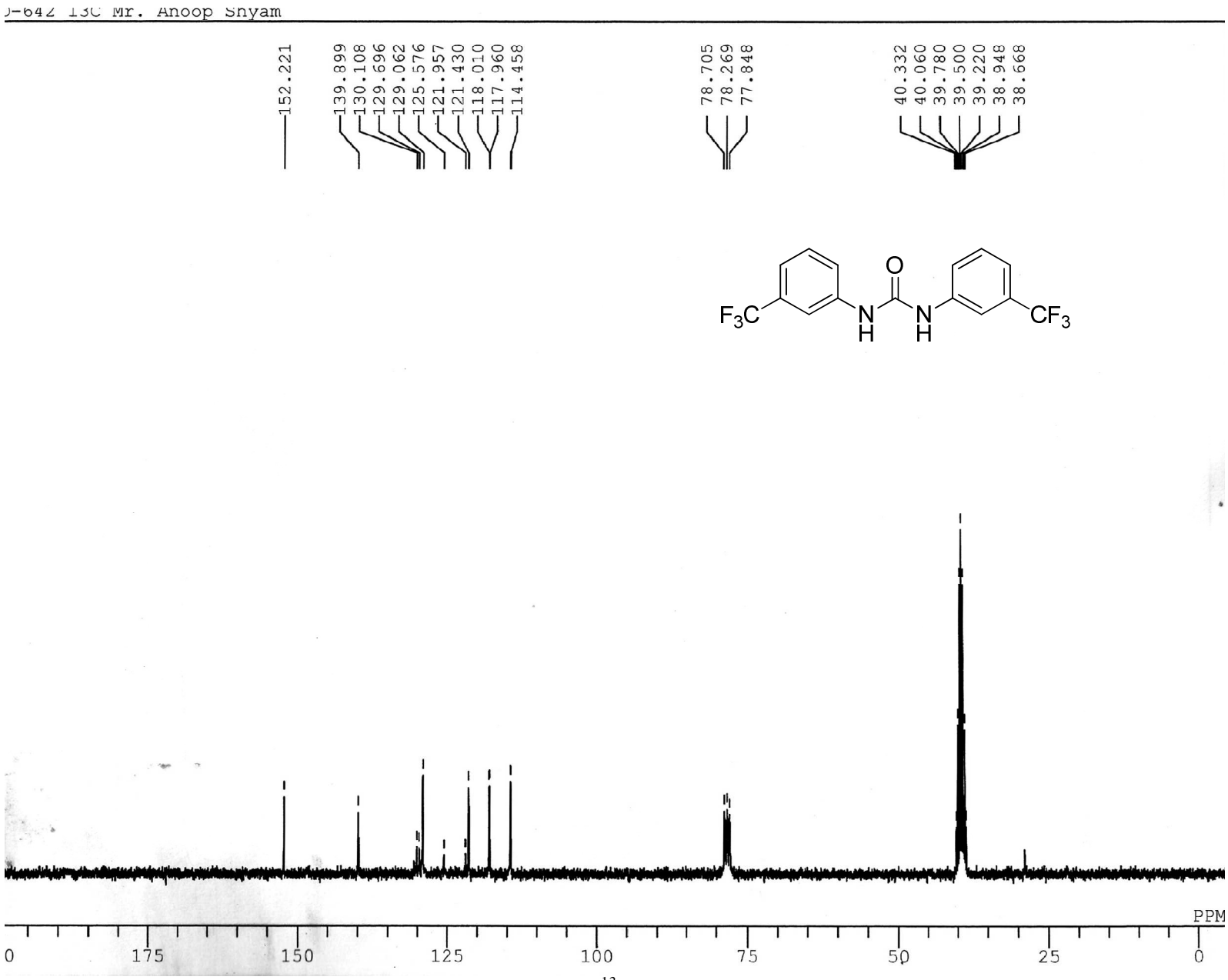
Spectrum 91: 300 MHz ^{1}H NMR of compound **6f**



Spectrum 92: 75 MHz ^{13}C NMR of compound **6f**

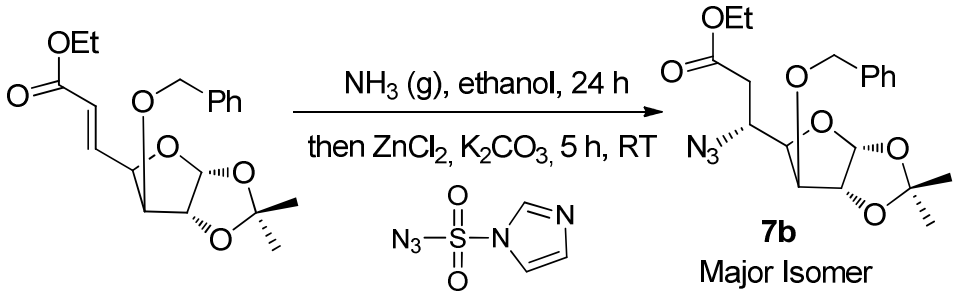


Spectrum 93: 300 MHz ^{1}H NMR of compound **6g**

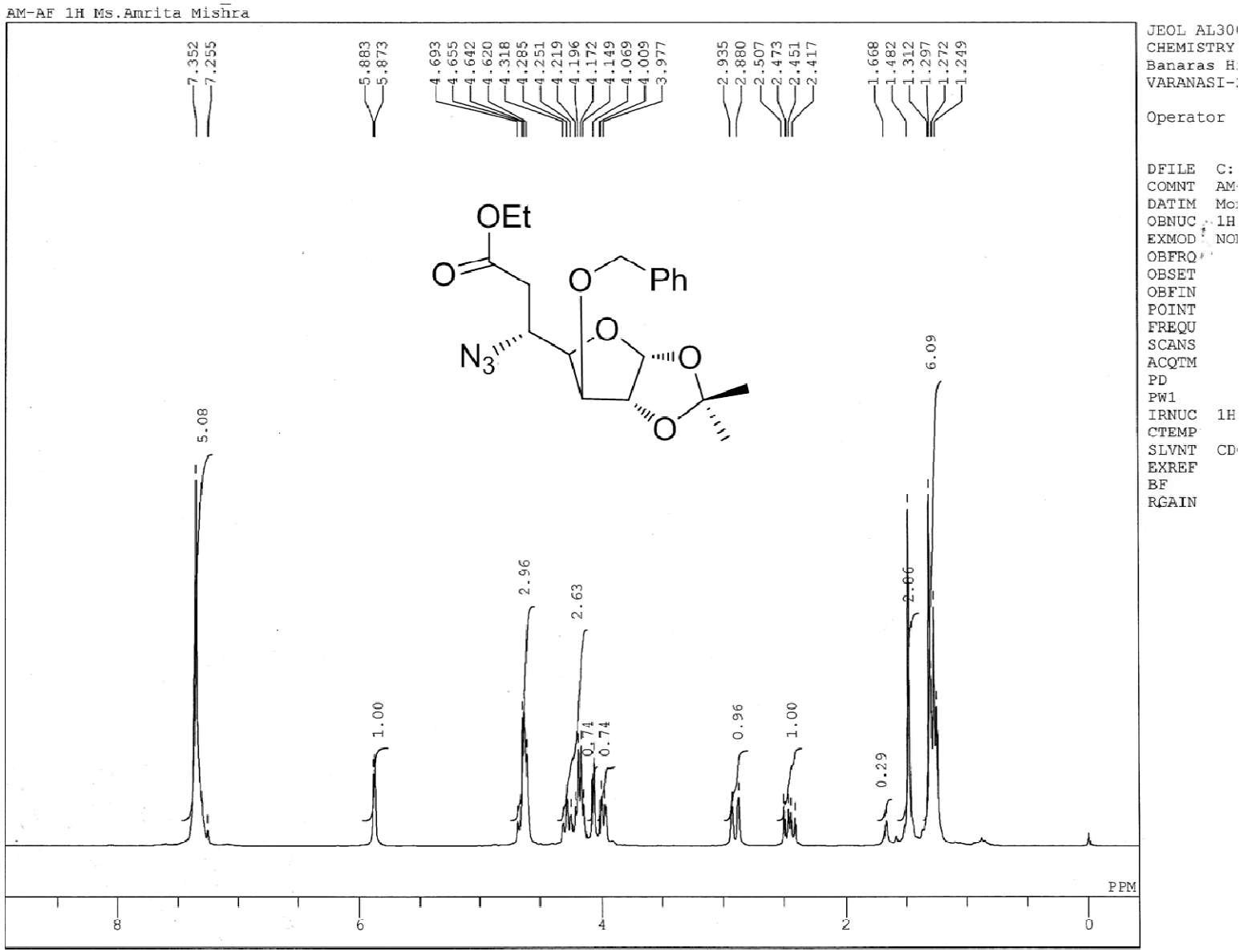


Spectrum 94: 75 MHz ^{13}C NMR of compound **6g**

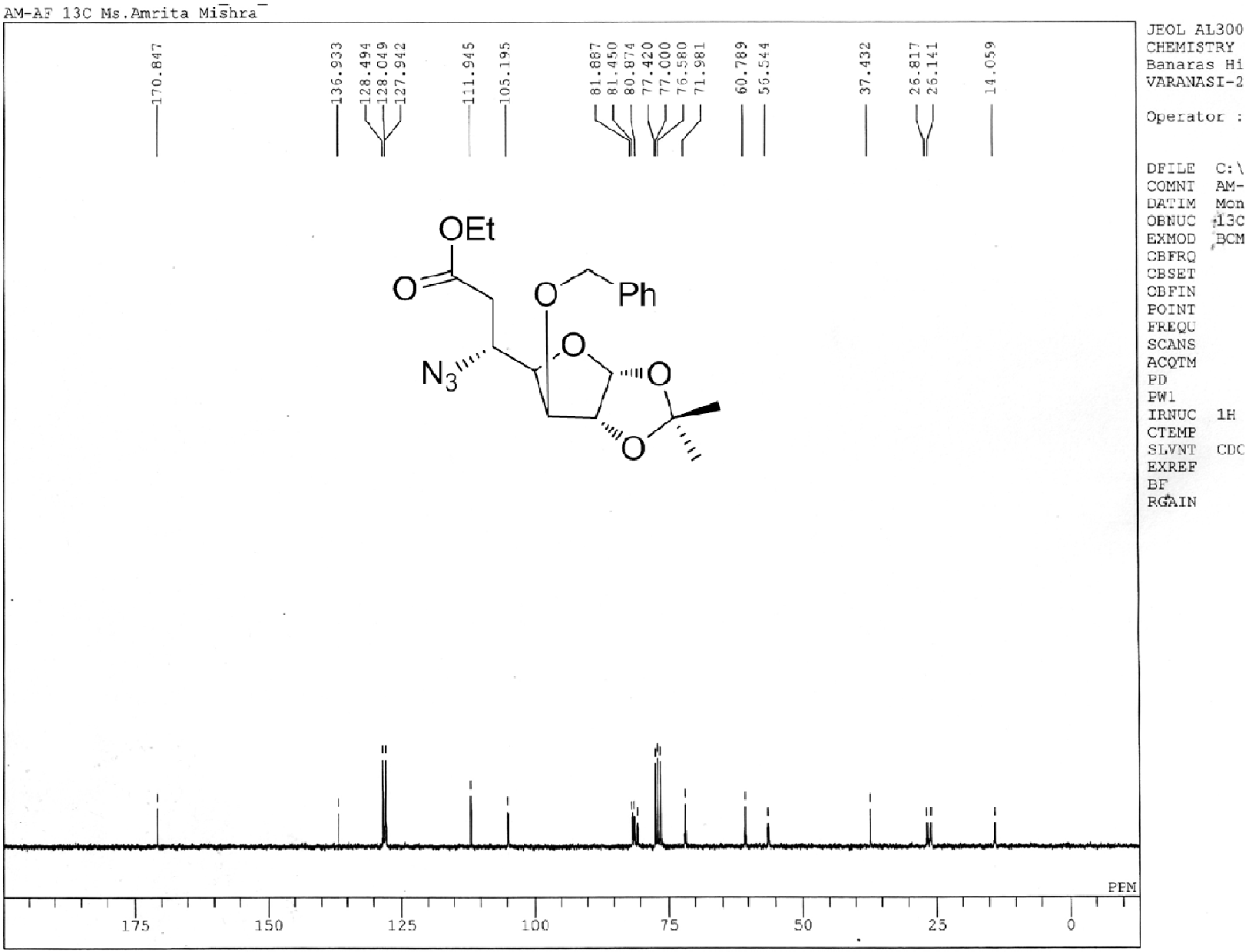
Procedure for the synthesis of glycosyl-*β*-azido ester (7b) (ref. 13f A. Mishra, V. K. Tiwari, *J. Org. Chem*., 2015, **80**, 4869)**:** Ammonia gas was passed for 3 h into a stirring solution of glycosyl-*β*-olefinic ester **(**10.0 g, 0.028 mol in dry ethanol (100 ml). The mixture was stirred at room temperature. After 12 hours a diastereomeric mixture of ethyl-[5-amino-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene]- *α*-D-gluco- and *β*-L-ido-heptofuranurnate **was obtained as** colourless oil (9.42g, 90% yield). To this mixture imidazole-1-sulphonyl azide (5.34g, 0.030 mol), K_2CO_3 (7.12g, 0.050 mol) and $ZnCl_2$ (5 mol%) were added and allowed to stir for 5 hours at room temperature 5 hrs. Purification by flash chromatography afforded glycosyl-*β*-azido ester **7b** as major product. White crystals, mp 82-84°C; yield 60%; R_f= 0.52 (10% ethyl acetate/*n*-hexane); MS: *m/z* 392 $[M+H]^+$; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.35 (m, 5H), 5.87 (d, *J* = 3.0 Hz,1H), 4.69-4.62 (m, 3H), 4.28 (dd, *J* = 9.9, 19.2 Hz, 1H), 4.18 (q, *J* = 6.9 Hz, 2H), 4.06 (m, 1H), 3.99 (d, *J* = 9.6 Hz, 1H), 2.90 (d, *J* = 16.5 Hz, 1H), 2.46 (dd, *J* = 10.2, 16.8 Hz, 1H), 1.48 (s, 3H), 1.31 (s, 3H), 1.27 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 170.8, 136.9, 128.4 (2C), 128.0, 127.9 (2C), 111.9, 105.1, 81.8, 81.4, 80.8, 71.9, 60.7, 56.5, 37.4, 26.8, 26.1, 14.0 ppm; IR (KBr) ν_{max}: 2980, 2933, 2134 (azide- N_3), 2096, 1742 (C=O), 1465, 1399, 1081, 1037, 731 cm^{-1}.



6. ^{1}H and ^{13}C NMR spectrum of glycosyl-β-azido ester **7b**

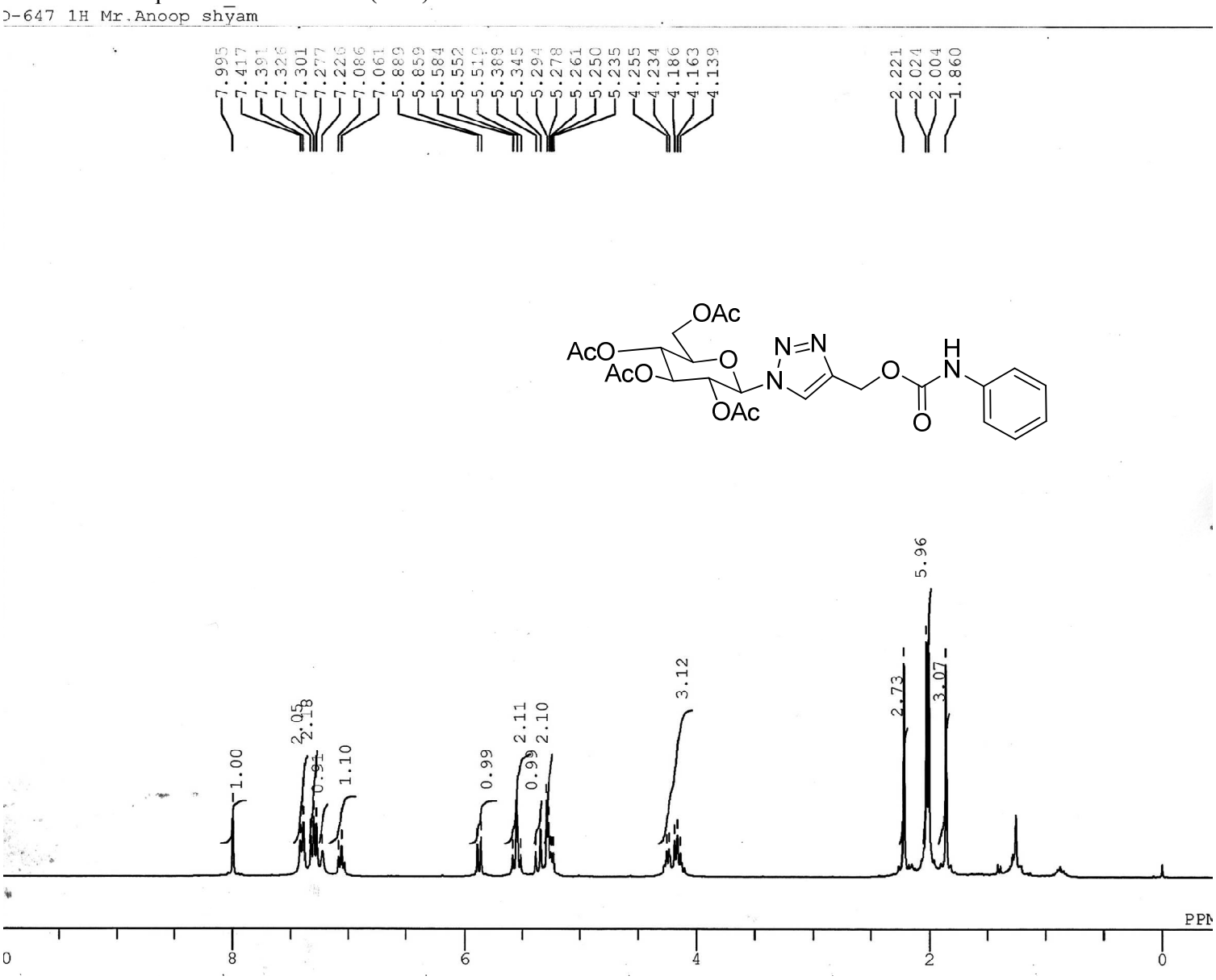


Spectrum 95: 300 MHz ^{1}H NMR of compound **7b**

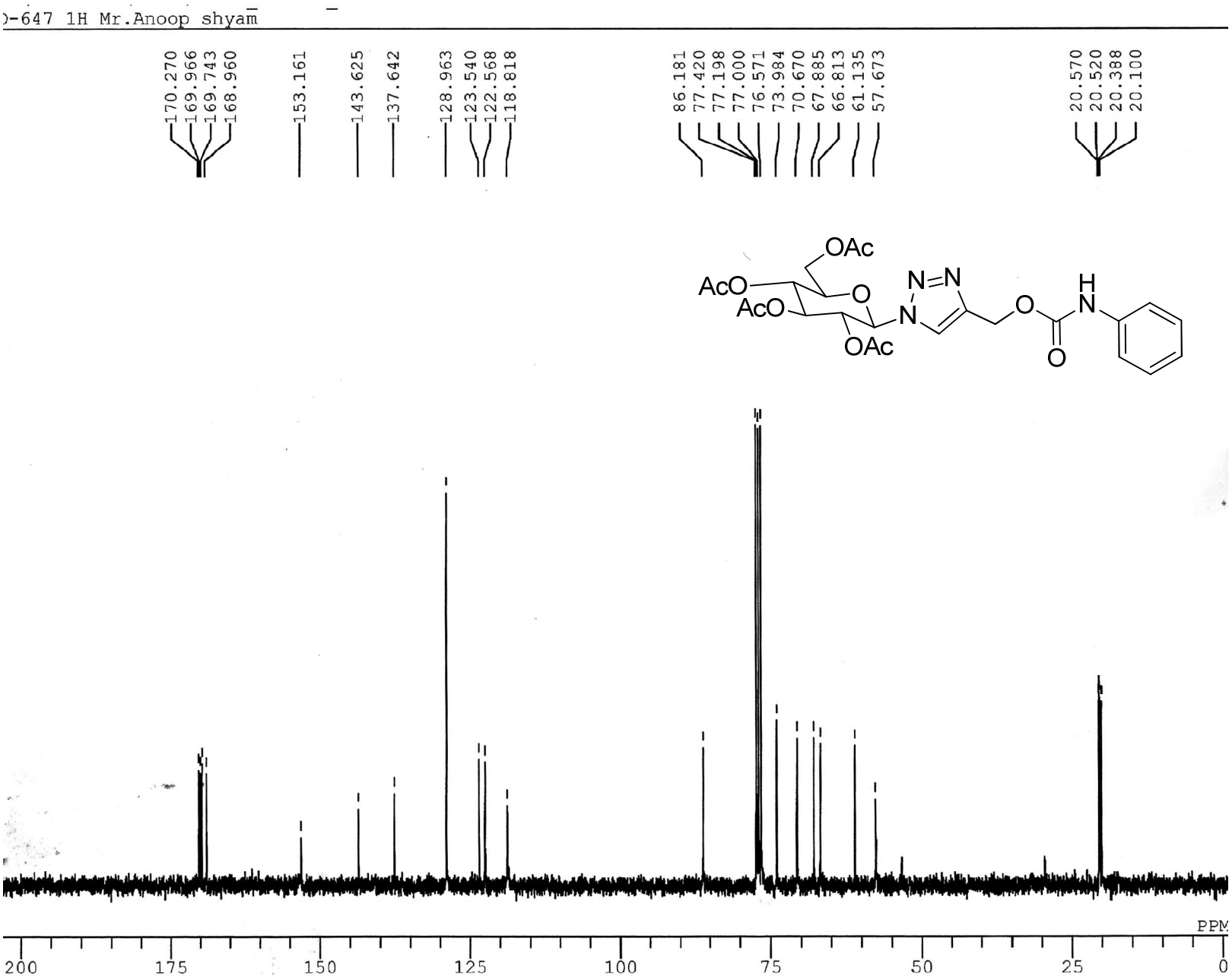


Spectrum 96: 75 MHz ^{13}C NMR of compound **7b**

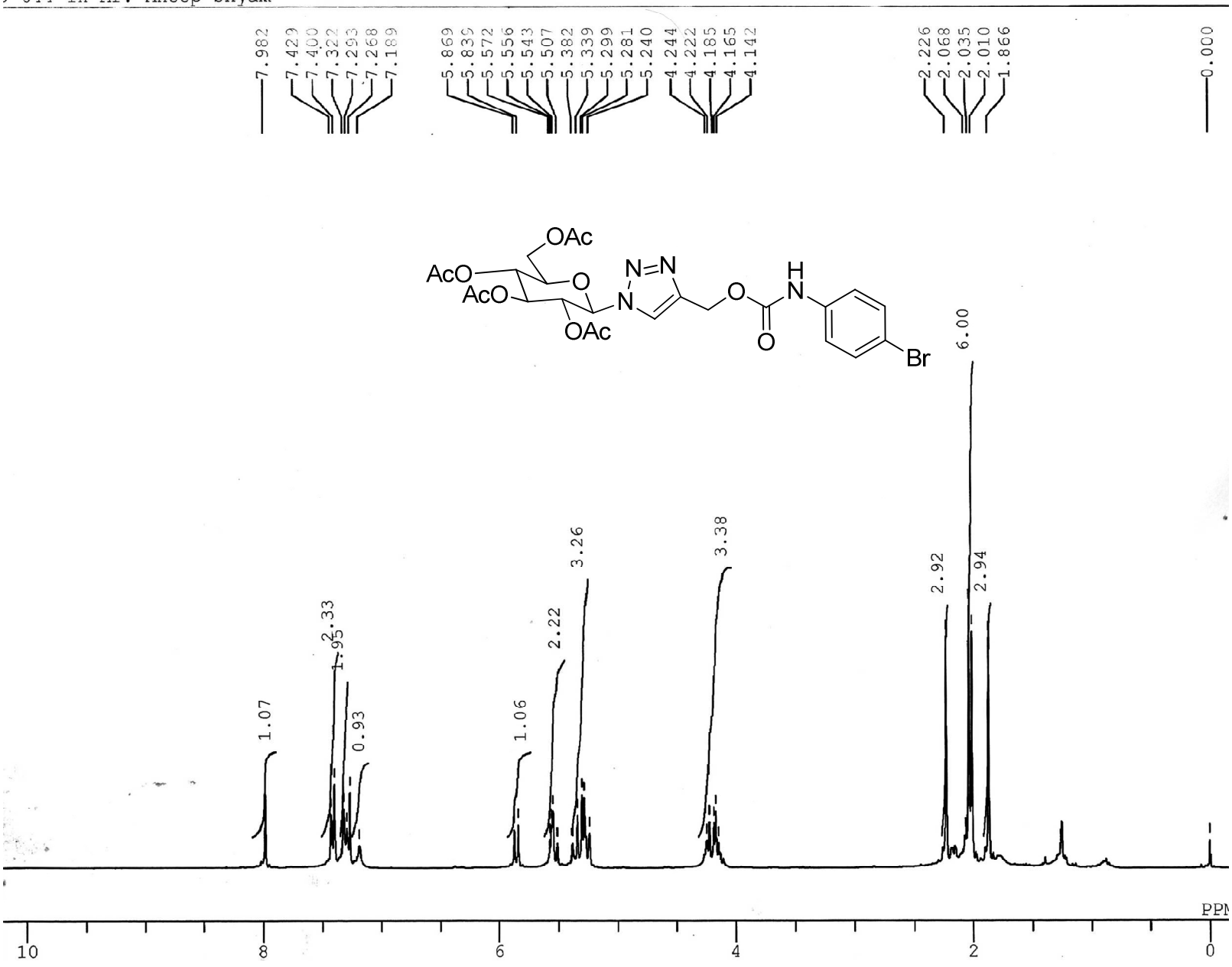
7. ^{1}H and ^{13}C NMR spectrum of triazoles (**8a-c**)



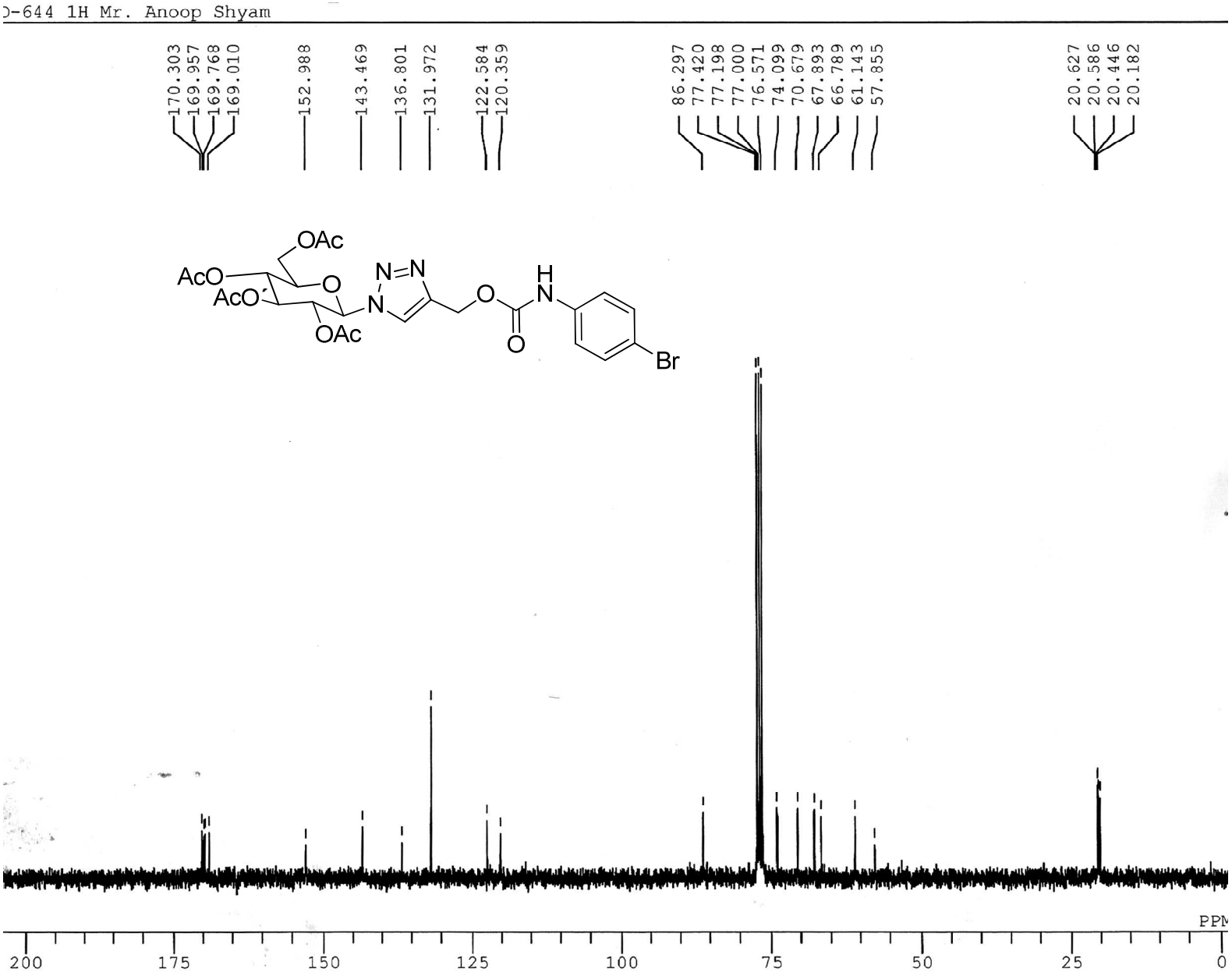
Spectrum 97: 300 MHz ^{1}H NMR of compound **8a**



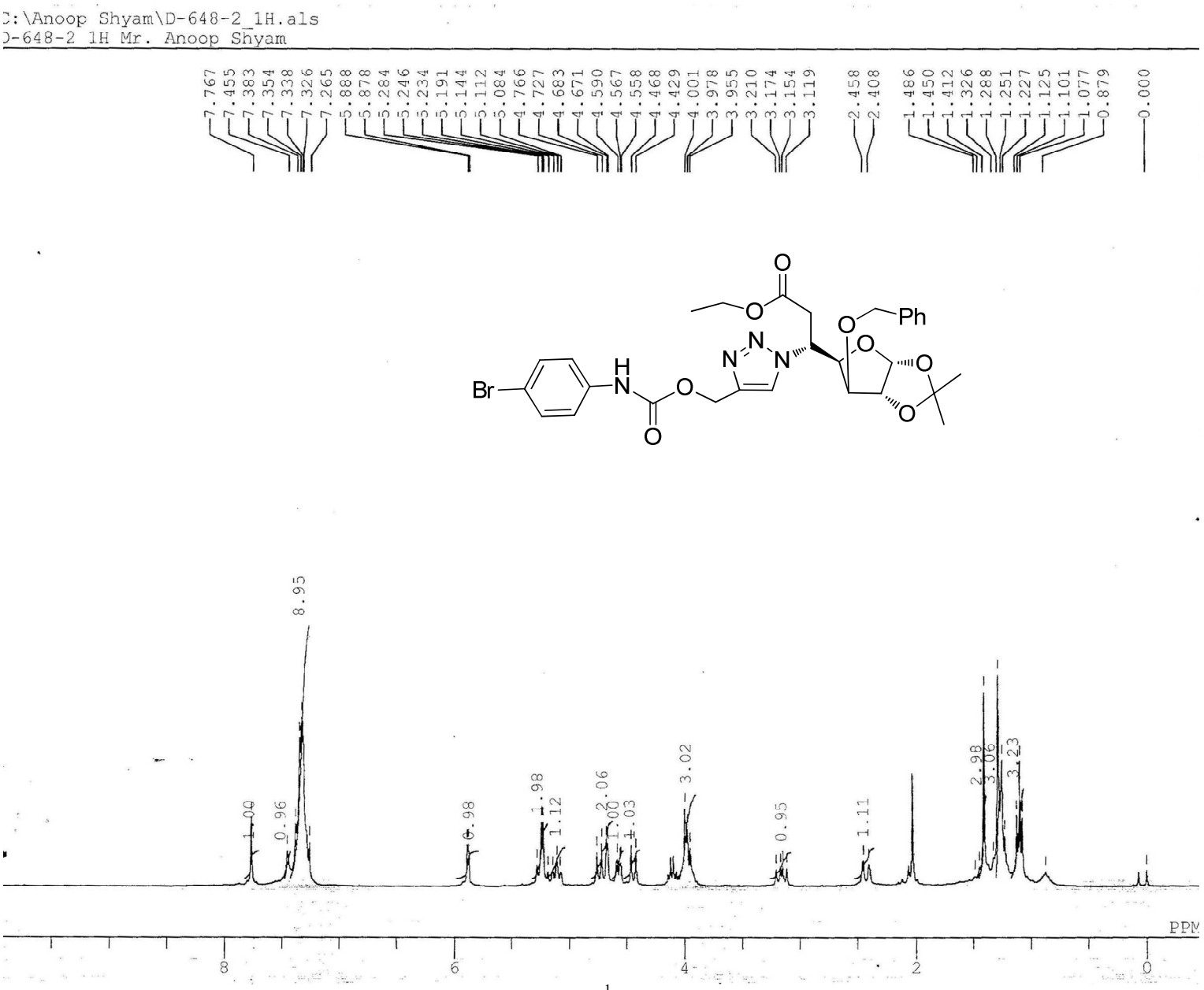
Spectrum 98: 75 MHz ^{13}C NMR of compound **8a**



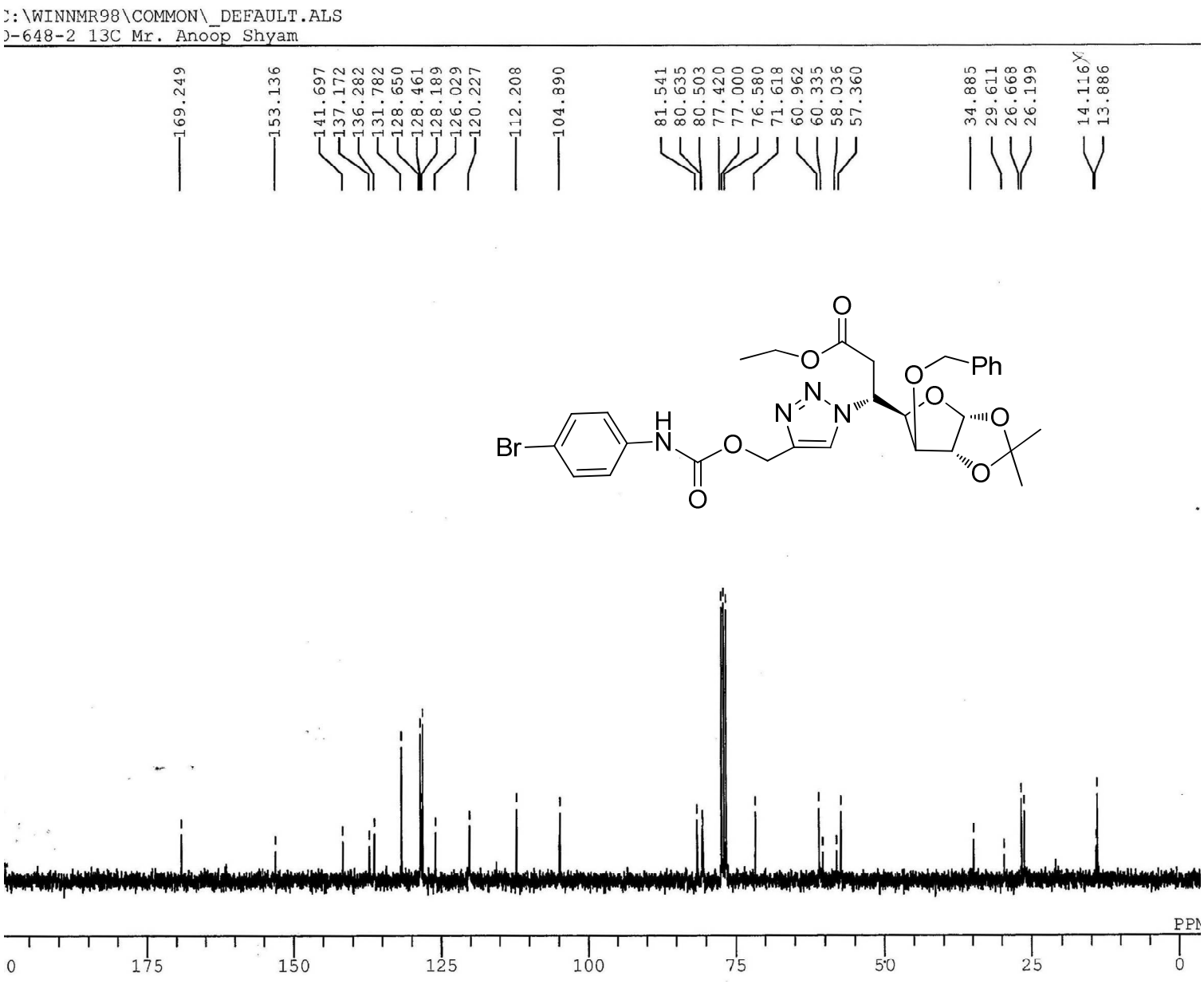
Spectrum 99: 300 MHz ^{1}H NMR of compound **8b**



Spectrum 100: 75 MHz ^{13}C NMR of compound **8b**



Spectrum 101: 300 MHz ^{1}H NMR of compound **8c**



Spectrum 102: 75 MHz ^{13}C NMR of compound **8c**

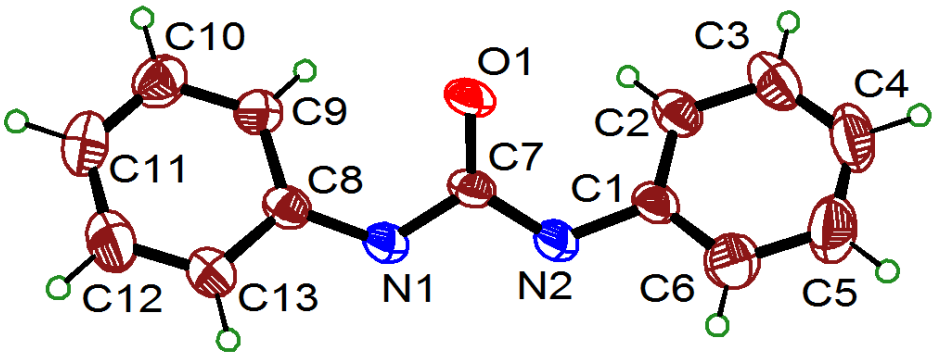
8. Single Crystal X-Ray Experimental details, refinement data and visualized molecular structure of compounds 6a & 4.

Data Collection and Refinement

Single-crystal X-ray data of compound **6a** were collected on Xcalibur Eos (Oxford) CCD-Diffractometer using graphite monochromated Mo*K*\α radiation (λ = 0.71073 Å). The data integration and reduction were processed with CrysAlis Pro software. Data of compound **4** was collected on Bruker SMART CCD-Diffractometer using graphite monochromatedMo*K*α radiation (λ = 0.71073 Å). The structures were solved by the direct method and then refined on F^2 by the full matrix least-squares technique with the SHELX-97 set of software using the WinGX (version 1.80.05) program package. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms using SHELX default parameters. Molecular structures have drawn using ORTEP software. Further information on the crystal structure (excluding structure factors) has been given in table 1-5 (Supporting Information) and also deposited in the Cambridge Crystallographic Data Centre as supplementary publications numbers 1482293 (**6a**) and 1482294 (4). 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.

Procedure for crystallization of compound 6a and 4

For crystallization a mixture of ethyl acetate and hexane (2:8) has been used and kept in dark place at temperature 25 ^{o}C. The single crystal appeared after three days was isolated in its initial state of growth.

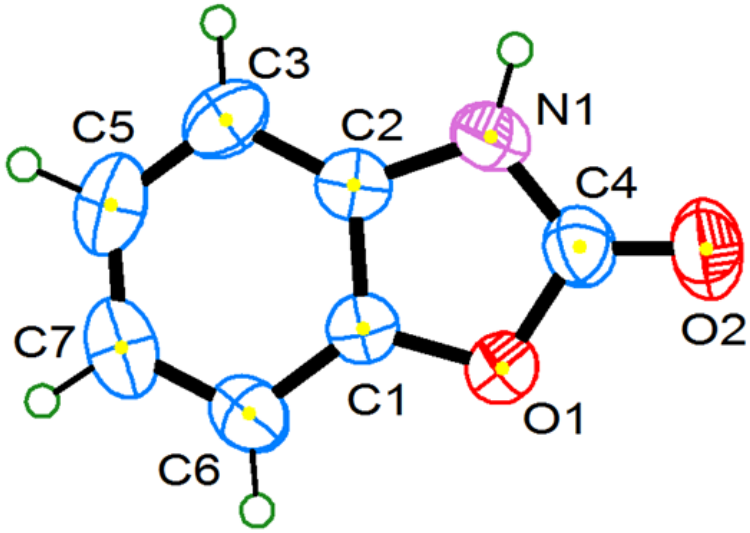


Selected bond length (Å): O1-C7 1.230(3), N1-C8 1.406(4), N1-C7 1.367(4), N1-HN1 0.86(3), N2-C1 1.421(4), N2-C7 1.342(4), N2-HN2 0.87(3); **Selected bond angles:** C8 N1 C7 125.4(3), C8 N1 HN1 116(2), C7 N1 HN1 116(2), N1 C8 C13 118.7(3), N1 C8 C9 123.0(3), C1 N2 C7 126.2(3), C1 N2 HN2 121(2), C7 N2 HN2 113(2), N2 C1 C6 118.7(3), N2 C1 C2 120.9(3), O1 C7 N1 121.6(3), O1 C7 N2 124.0(3), N1 C7 N2 114.4(3)

Figure S1. Molecular structure of compound **6a.** Thermal ellipsoids of carbon, nitrogen, sulfur and oxygen are set at 40 % probability.

Table S1. Crystallographic refinement data for compound **6a**

Compound 6a	
Empirical Formula	C_{13} H_{12} N_2 O
Formula Weight	212.25
Crystal System	Orthorhombic
Space group	P n a 21
a (Å)	9.1004(11)
b (Å)	10.5785(19)
c (Å)	11.775(2)
β (^{o})	90,90,90
V (Å^3)	1133.6(3)
Z	4
Density (calc)	1.244
F(000)	548
μ (mm^{-1})	0.083
Crystal Size [mm]	0.14 x 0.16 x 0.24
Temperature (K)	293
Radiation	0.71073
θ Min-Max [^{o}]	3.41, 28.95
h, k, l	-10:11; -4:13; -6:15
Tot.,UniqData, R(int)	3405, 1805, 0.0286
Obs. data [I > 2.0 σ(I)]	1157
Nref, Npar	3015, 154
R1, wR2, S	0.0481, 0.0991, 1.062
Min. - Max. resd. dens. [e/ Å^3]	-0.129, 0.138
CCDC	1482293



Selected bond length (Å): O1-C1 1.380(2), O1-C4 1.369(2), N1-H1 0.860(1), N1-C2 1.385(2), N1-C4 1.347(2), O2-C4 1.206(2); **Selected bond angles (°):** C1 O1 C4 107.0(1), H1 N1 C2 125.1(1), H1 N1 C4 125.1(1), C2 N1 C4 109.8(1), O1 C1 C2 109.3(1), O1 C1 C6 127.5(1), N1 C2 C1 105.5(1), N1 C2 C3 133.7(1), O1 C4 N1 108.2(1), O1 C4 O2 121.7(1), N1 C4 O2 130.1(2)

Figure S2. Molecular structure of compound **4**. Thermal ellipsoids of carbon, nitrogen and iron are set at 40 % probability.

Table S2. Crystallographic refinement data for compound **4**

Compound 4	
Empirical Formula	$C_7 H_5 N O_2$
Formula Weight	135.12
Crystal System	Orthorhombic
Space group	P 21 21 21
a (Å)	4.4436(14)
b (Å)	6.641(2)
c (Å)	20.957(6)
β (°)	90,90,90
V (Å^3)	618.5(3)
Z	4
Density (calc)	1.451
F(000)	264
μ (mm^{-1})	0.108
Crystal Size [mm]	0.14 x 0.15 x 0.22
Temperature (K)	293
Radiation	0.71073
θ Min-Max [°]	3.22, 24.94
h, k, l	-5:5; -6:89; -16:27
Tot.,UniqData, R(int)	3269, 1471, 0.0267
Obs. data [I > 2.0 σ(I)]	1322
Nref, Npar	1528, 91
R1, wR2, S	0.0386, 0.0969, 1.061
Min. - Max. resd. dens. [e/ Å^3]	-0.258, 0.133
CCDC	1482294