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ACCESSORY PUBLICATION

S_N2 Substitution Reactions at the Amide Nitrogen in the Anomeric Mutagens, *N*-Acyloxy-*N*-alkoxyamides

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Supplementary DFT Computational Data: Structures and Energies

Calculations carried out using Spartan 04 for macintosh
Geometries were optimized at AM1, HF/6-31G*/3-21G and HF/6-31G(d) levels
Frequency calculations at HF/6-31G* verified minima (all positive eigenvalues) and the transition state (one negative eigenvalue).
Energies were calculated by DFT on the stationary points from HF/6-31G*.

Cartesian coordinates for transition state for reaction of ammonia with N-acetoxy-N-methoxyacetamide

H	1.663016	-1.825474	1.577856
C	0.764666	-2.056100	1.015790
H	0.718879	-3.117995	0.821113
C	0.798194	-1.365299	-0.315469
H	-0.099206	-1.729176	1.569811
O	0.881775	-1.877846	-1.371699
N	0.870391	0.136835	-0.311247
O	1.191372	0.574077	0.848744
N	2.447115	0.287169	-1.297553
O	-1.332403	-0.462999	0.167623
C	0.865499	1.968051	1.026162
H	1.633006	2.565279	0.548757
H	0.893568	2.117895	2.093377
H	-0.114601	2.138694	0.605967
C	-2.124447	0.445769	-0.198507
O	-1.854072	1.630631	-0.346356

C	-3.559758	-0.010339	-0.442682
H	-3.978838	-0.385233	0.486656
H	-3.570239	-0.831400	-1.152064
H	-4.170819	0.803552	-0.810092
H	2.316276	-0.322545	-2.084947
H	3.308754	0.074998	-0.823795
H	2.451872	1.241456	-1.607444

Imaginary frequency 446.7cm^{-1} corresponds to $N^1N^2O^3$ stretch

Energy:	HF/6-31G(d)	-604.484561 au	-115.19 kJmol^{-1}
	B3LYP/6-31G(d)//HF/6-31G(d)	-607.996238 au	

Electrostatic Group Charges:

NH_3	+0.4
N	-0.09
OCH_3	+0.17
OAc	-0.77
CH_3CO	+0.3

Cartesian coordinates for N-acetoxy-N-methoxyacetamide

C	1.260004	-0.123876	1.149298
O	0.851706	-0.557041	2.172708
C	2.702492	0.205553	0.872271
N	0.392048	0.024404	0.041532
H	3.294297	-0.174788	1.691720
H	2.827782	1.278729	0.795260
H	3.031861	-0.234721	-0.060582
O	-0.900679	0.207263	0.463823
O	0.739679	1.068776	-0.758996
C	-1.767563	-0.765054	0.097350
O	-1.511539	-1.630739	-0.660448
C	-3.078156	-0.545720	0.797544
C	0.602116	0.729601	-2.123727
H	-2.933030	-0.662289	1.865156
H	-3.797784	-1.266818	0.440098
H	-3.434089	0.461804	0.618590
H	1.203904	-0.136776	-2.362318
H	0.949089	1.592945	-2.672296
H	-0.432139	0.528749	-2.366983

Energy:	HF/6-31G(d)	-548.3834875 au	-17.02 kJmol^{-1}
	B3LYP/6-31G(d)//HF/6-31G(d)	-551.497474 au	

Electrostatic Group Charges:

N	+0.22
OCH_3	+0.03
OAc	-0.04
CH_3CO	0.23

Cartesian coordinates for Ammonia

H	-0.931597	0.000000	-0.092570

N	0.000000	0.000000	0.277710
H	0.465798	-0.806787	-0.092571
H	0.465798	0.806787	-0.092571

Energy:	HF/6-31G(d)	-56.1843562 au	-28.12 kJmol^{-1}
	B3LYP/6-31G(d)//HF/6-31G(d)	-56.5472397au	

Cartesian coordinates for N-ammonium-N-methoxyacetamide

H	1.172855	2.721849	-0.859750
C	1.122558	1.659770	-0.675712
C	-0.207264	1.361632	-0.060515
H	1.916550	1.363594	-0.001911
H	1.241197	1.116078	-1.604829
O	-1.029652	2.135447	0.294160
N	-0.542882	-0.040336	0.046665
O	0.485130	-0.822240	0.471525
N	-1.616476	-0.205866	0.969849
C	0.716221	-1.943477	-0.390496
H	0.946850	-1.602720	-1.387802
H	-0.147544	-2.594005	-0.402556
H	1.560922	-2.452876	0.043215
H	-2.179534	0.642855	0.939529
H	-1.262444	-0.335657	1.911917
H	-2.176486	-1.004049	0.706710

Energy:	HF/631G(d)	-377.1392218	-268.53 kJmol^{-1}
	B3LYP/6-31G(d)//HF/6-31G(d)	-379.3433782	

Cartesian coordinates for acetate

C	0.082077	0.000000	-0.897205
C	-0.039357	0.000000	0.651982
H	0.932092	0.000000	1.137179
H	-0.602549	-0.873396	0.976526
H	-0.602549	0.873396	0.976526
O	1.229227	0.000000	-1.350112
O	-0.998943	0.000000	-1.494894

Energy:	HF/631G(d)	-227.2250684	-298.61 kJmol^{-1}
	B3LYP/6-31G(d)//HF/6-31G(d)	-228.4958189	

E_A (kJmol^{-1}):

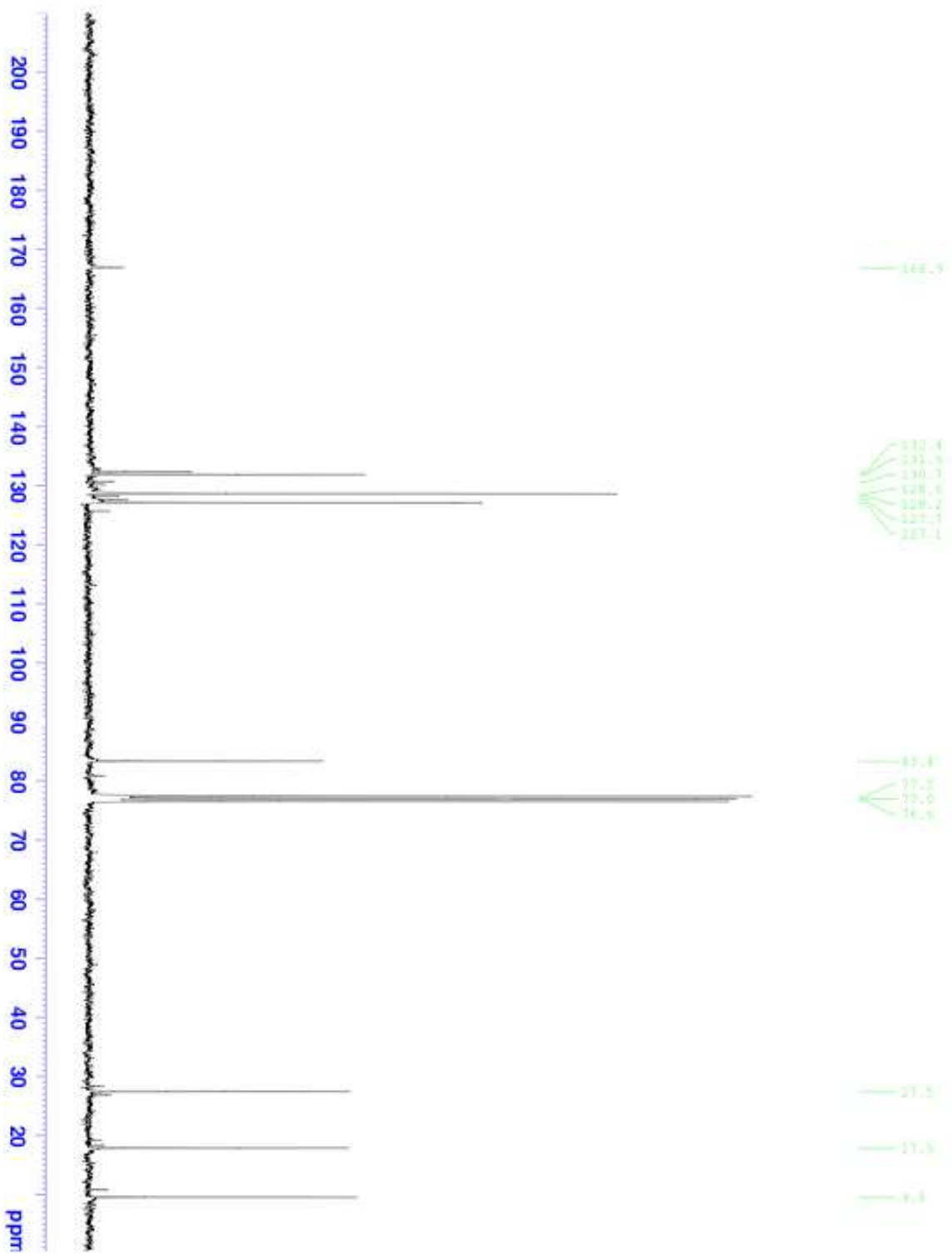
	No solvation	Aqueou solvation
HF/6-31G(d)	218.92	148.79
B3LYP/6-31G(d)	127.42	57.30

ΔE_{react} (kJmol^{-1}):

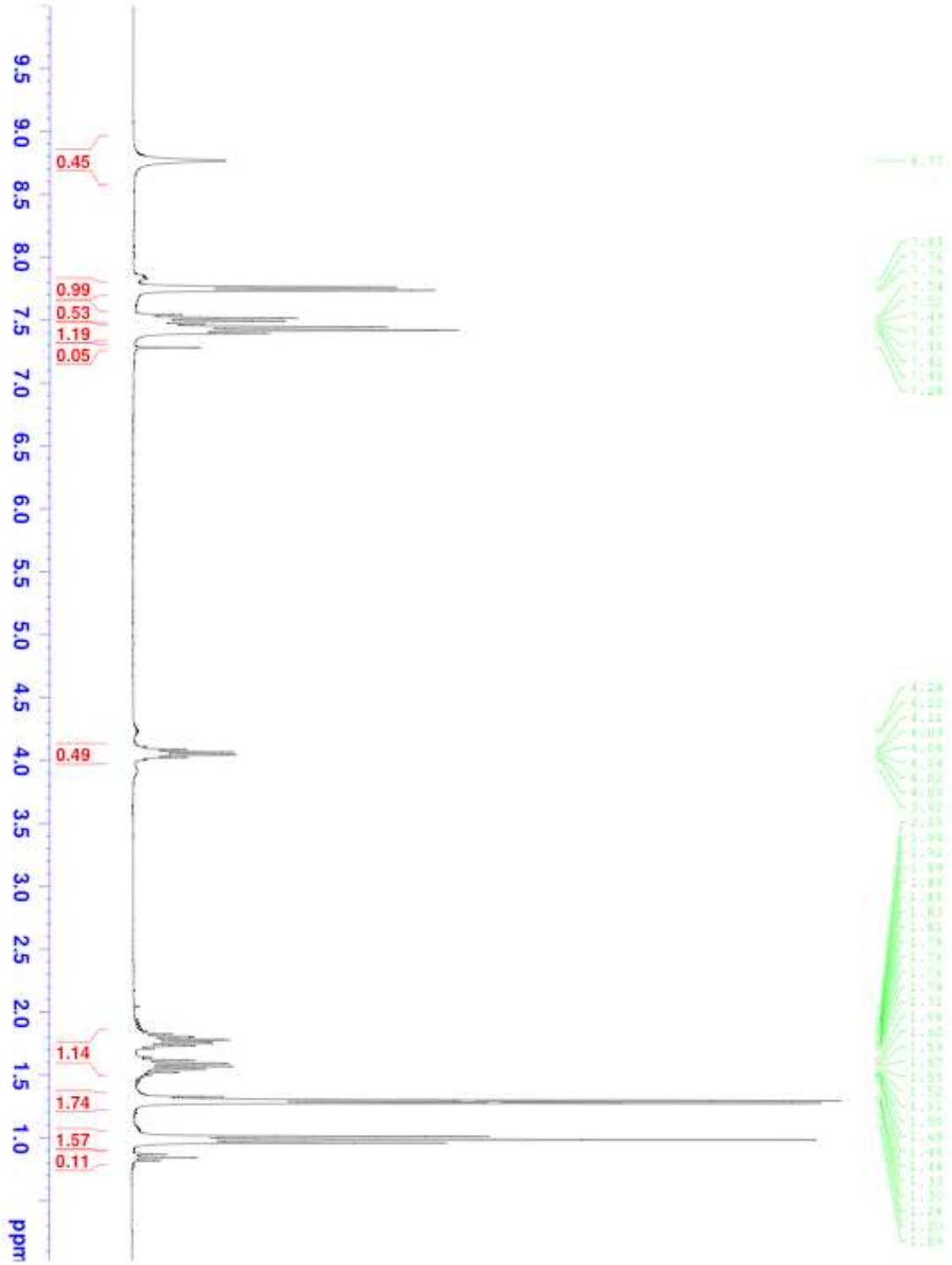
	No solvation	Aqueou solvation
HF/6-31G(d)	535.06	12.44
B3LYP/6-31G(d)	540.22	17.60

Nuclear Magnetic Resonance Spectra

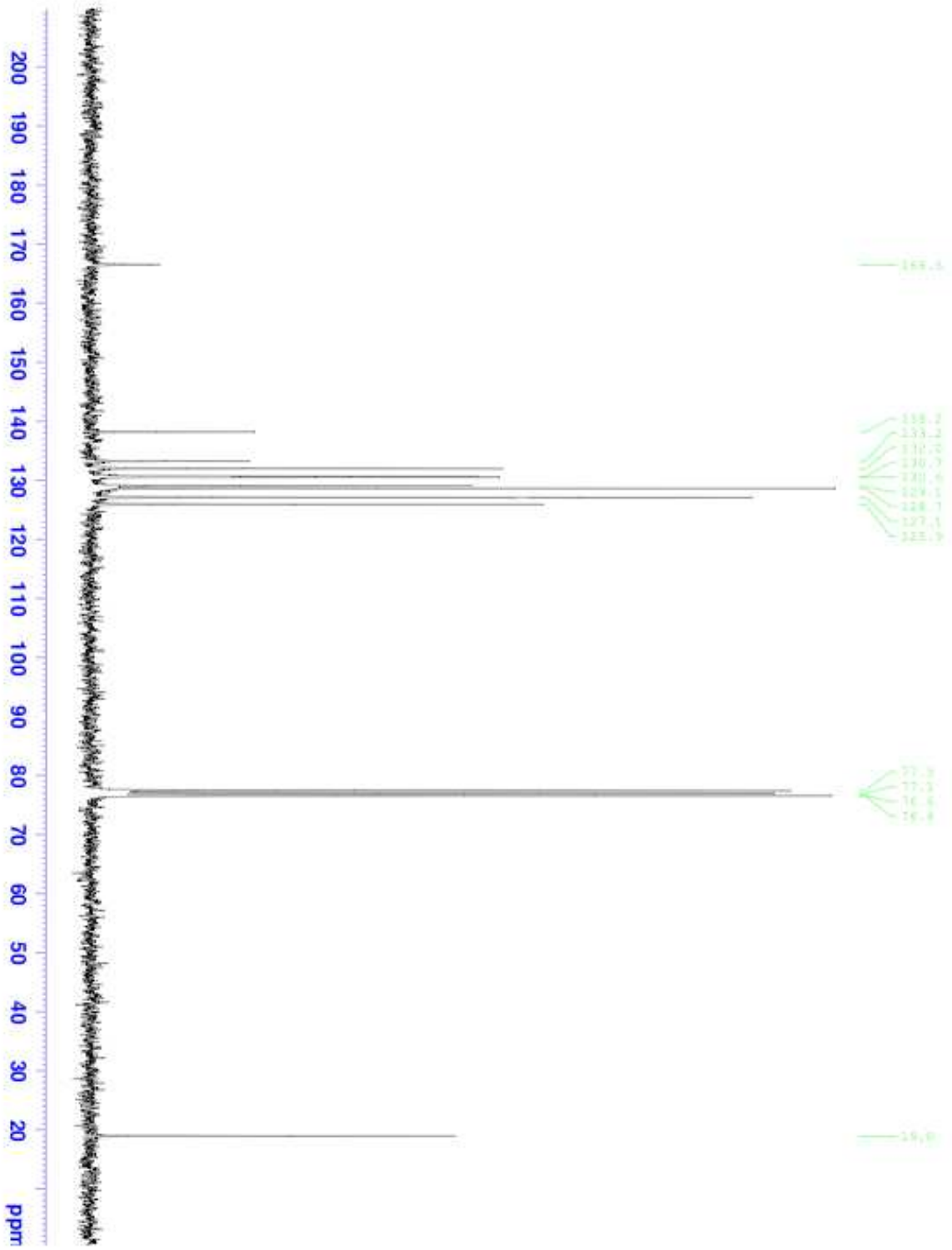
^{13}C NMR *N*-(2-Butoxy)benzamide



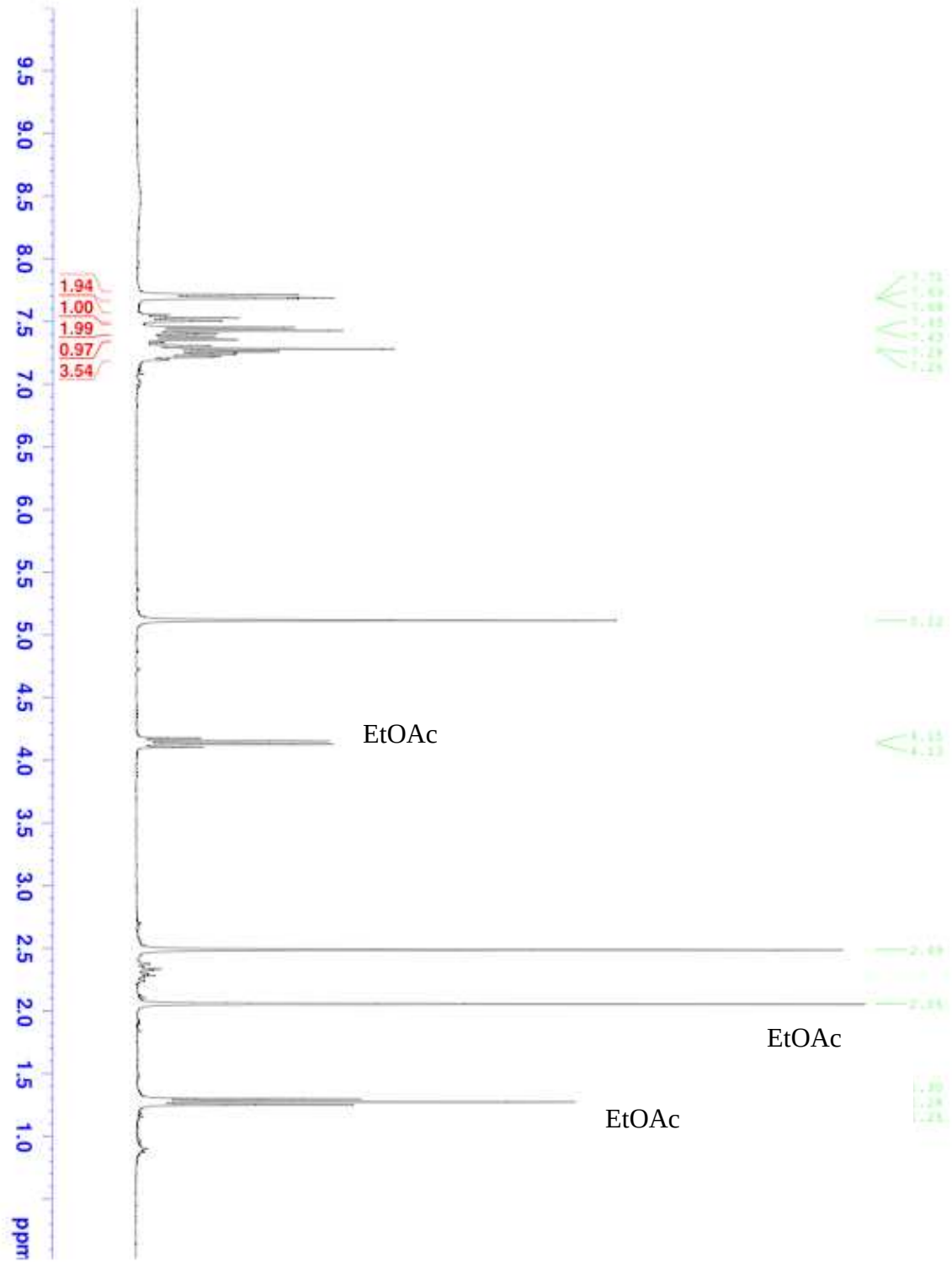
^{1}H NMR *N*-(2-Butoxy)benzamide



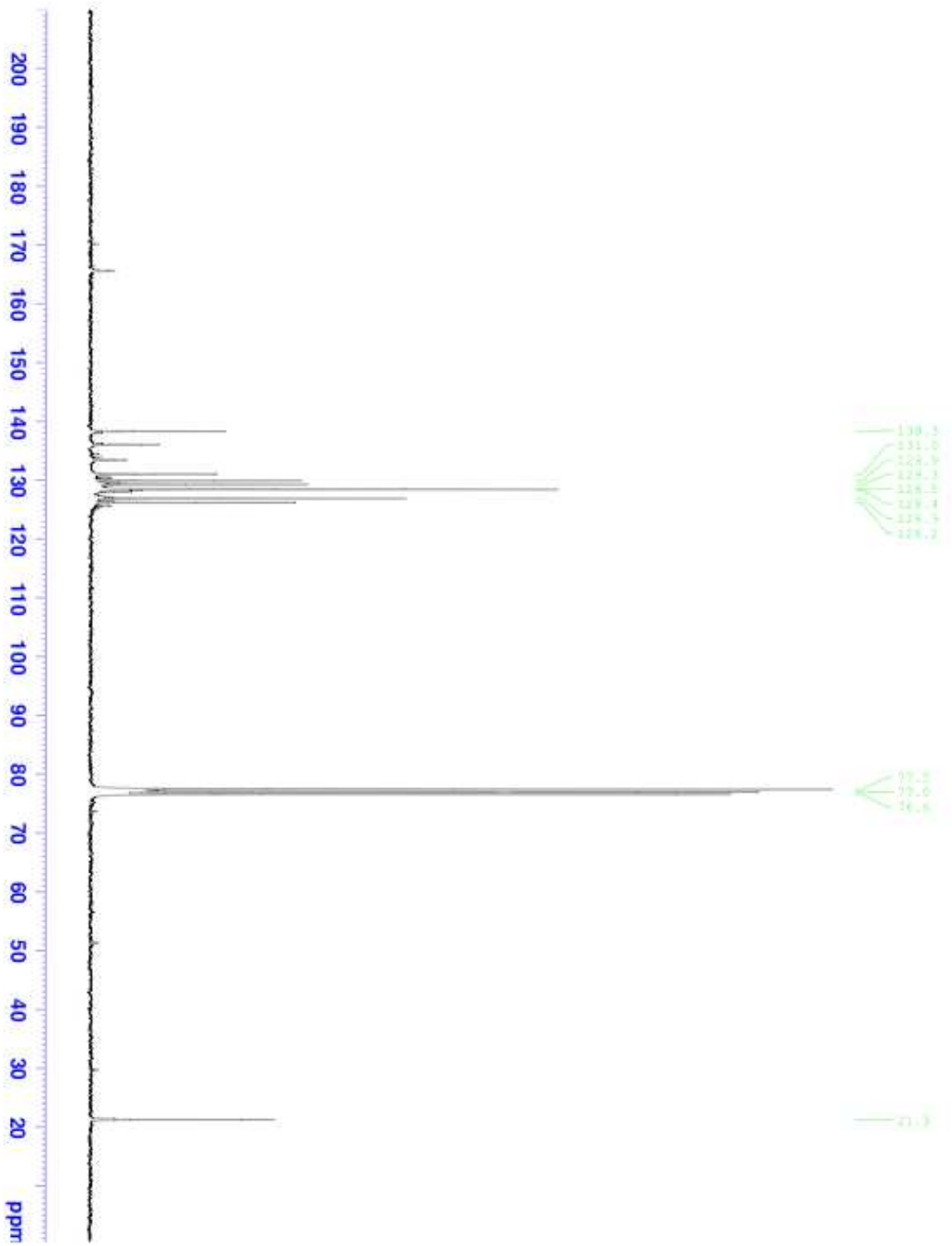
^{13}C NMR *N*-(2-Methylbenzyloxy)benzamide



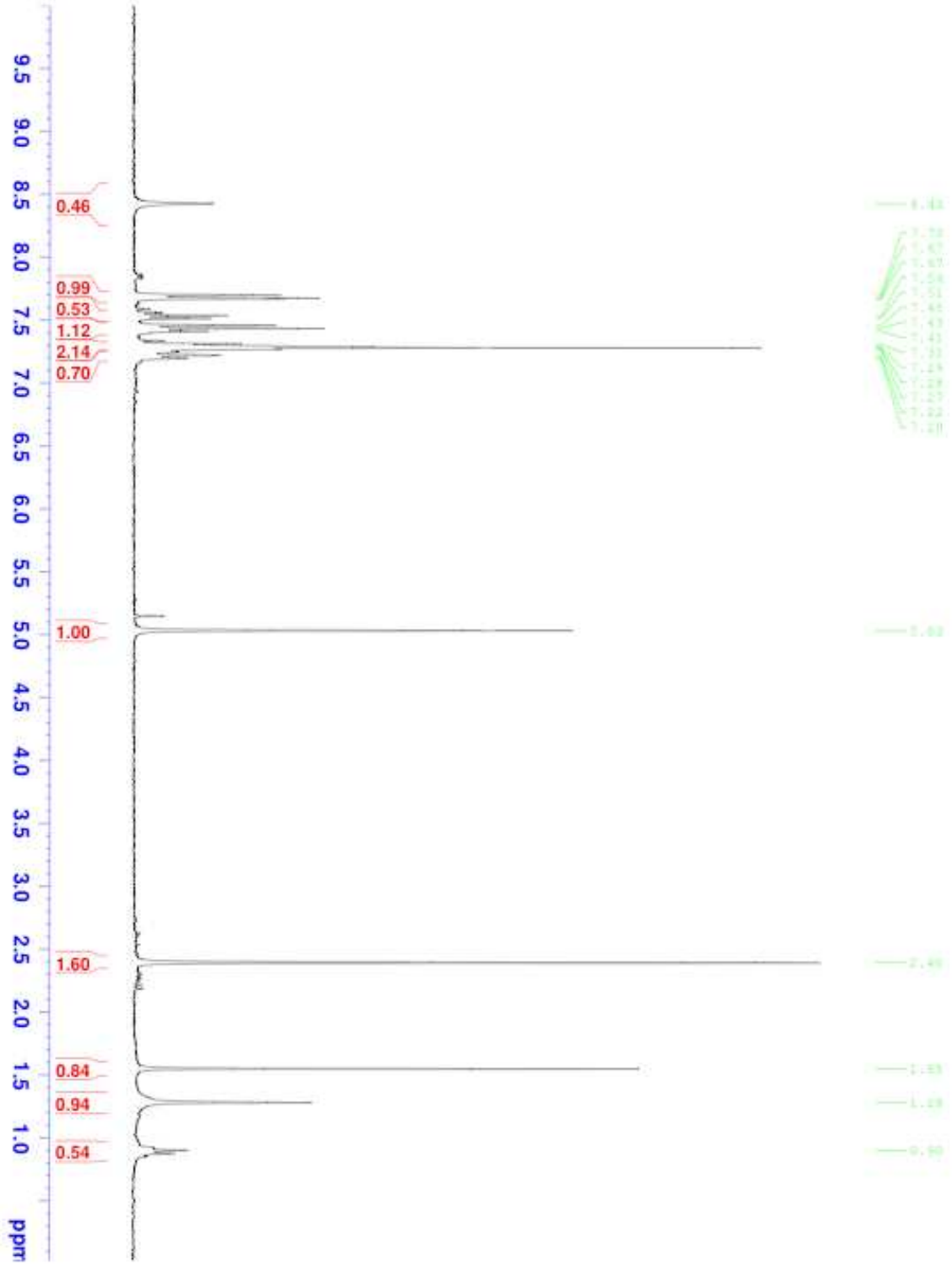
^{1}H NMR *N*-(2-Methylbenzyloxy)benzamide



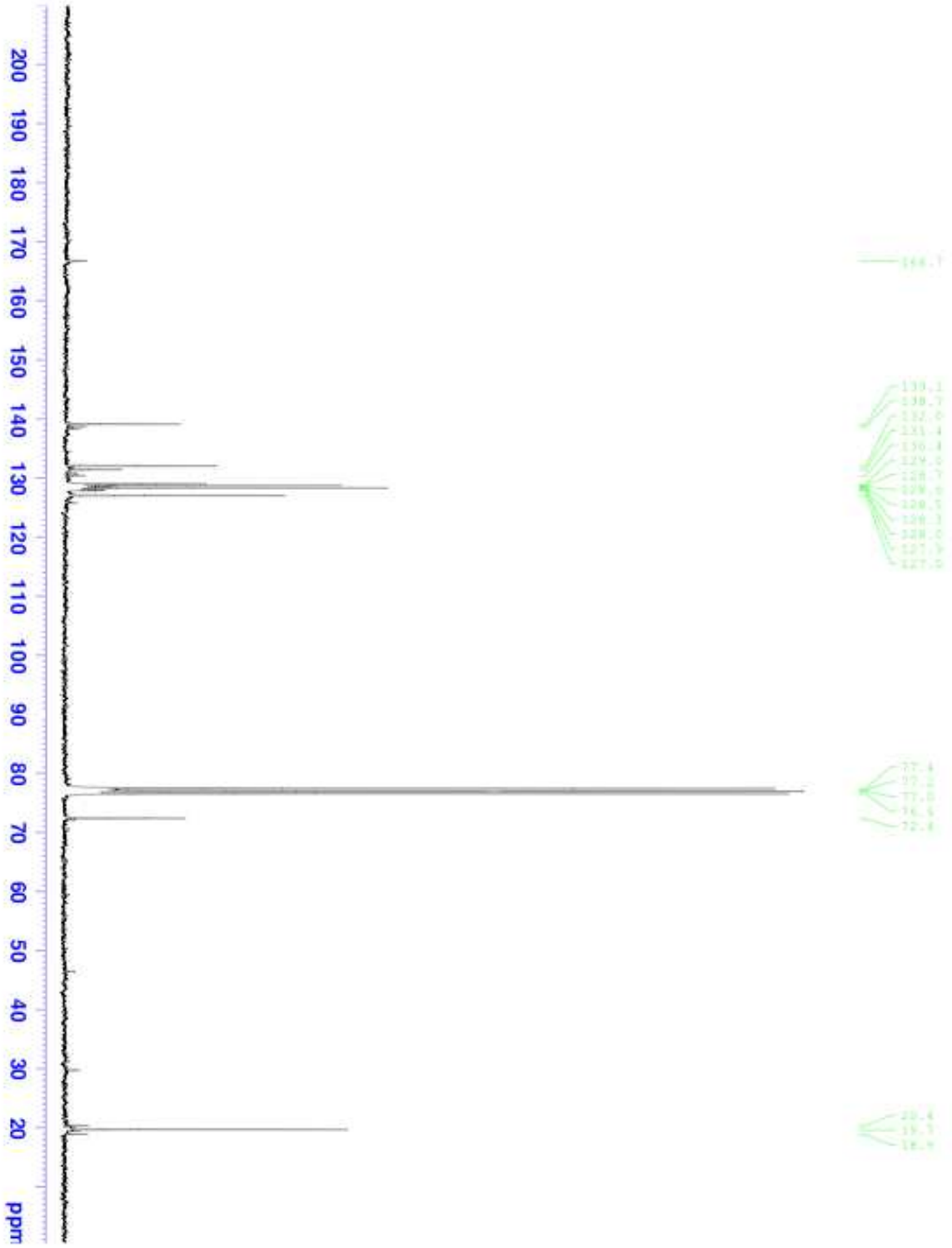
^{13}C NMR *N*-(3-Methylbenzyloxy)benzamide



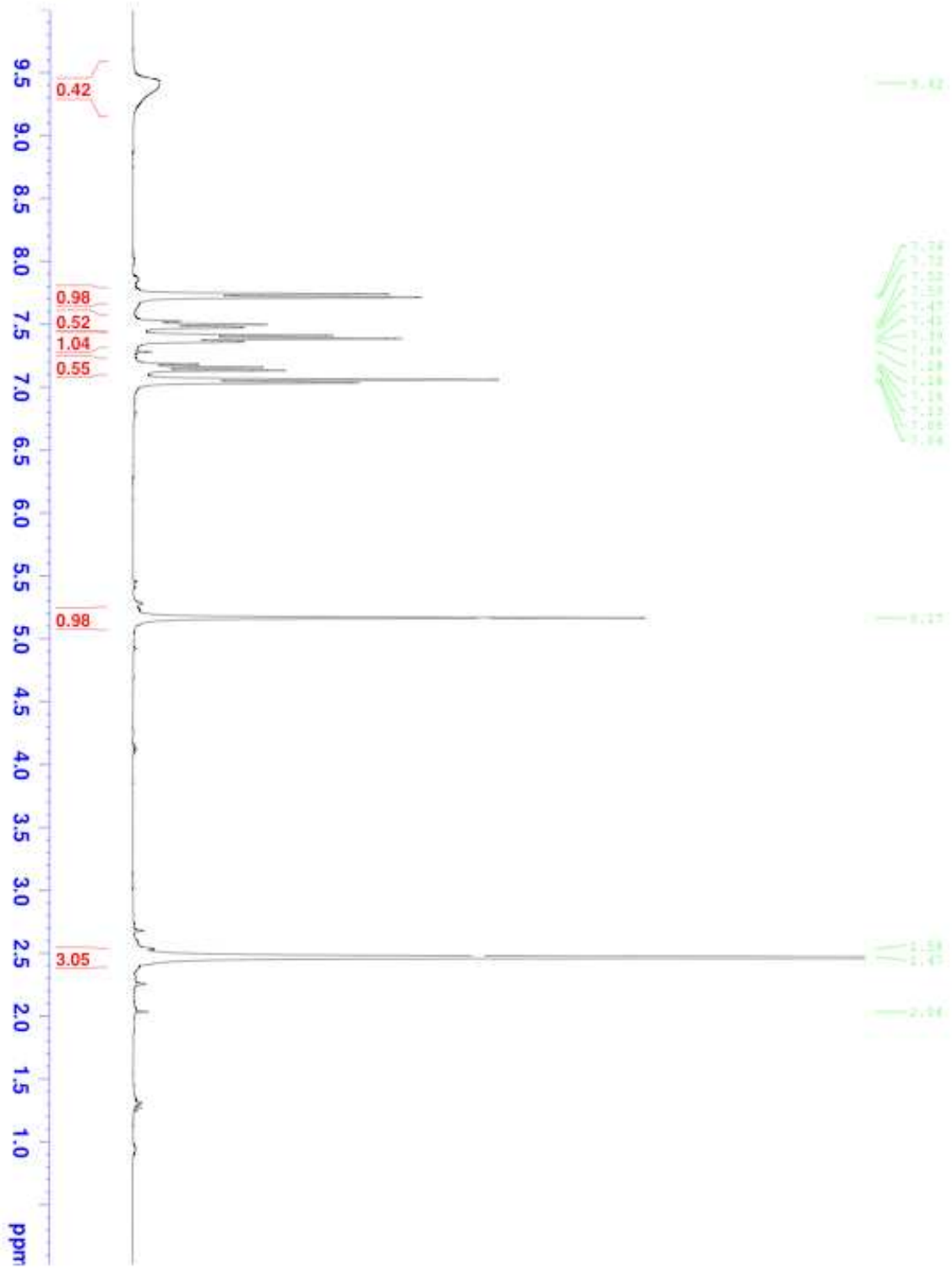
^{1}H NMR *N*-(3-Methylbenzyloxy)benzamide



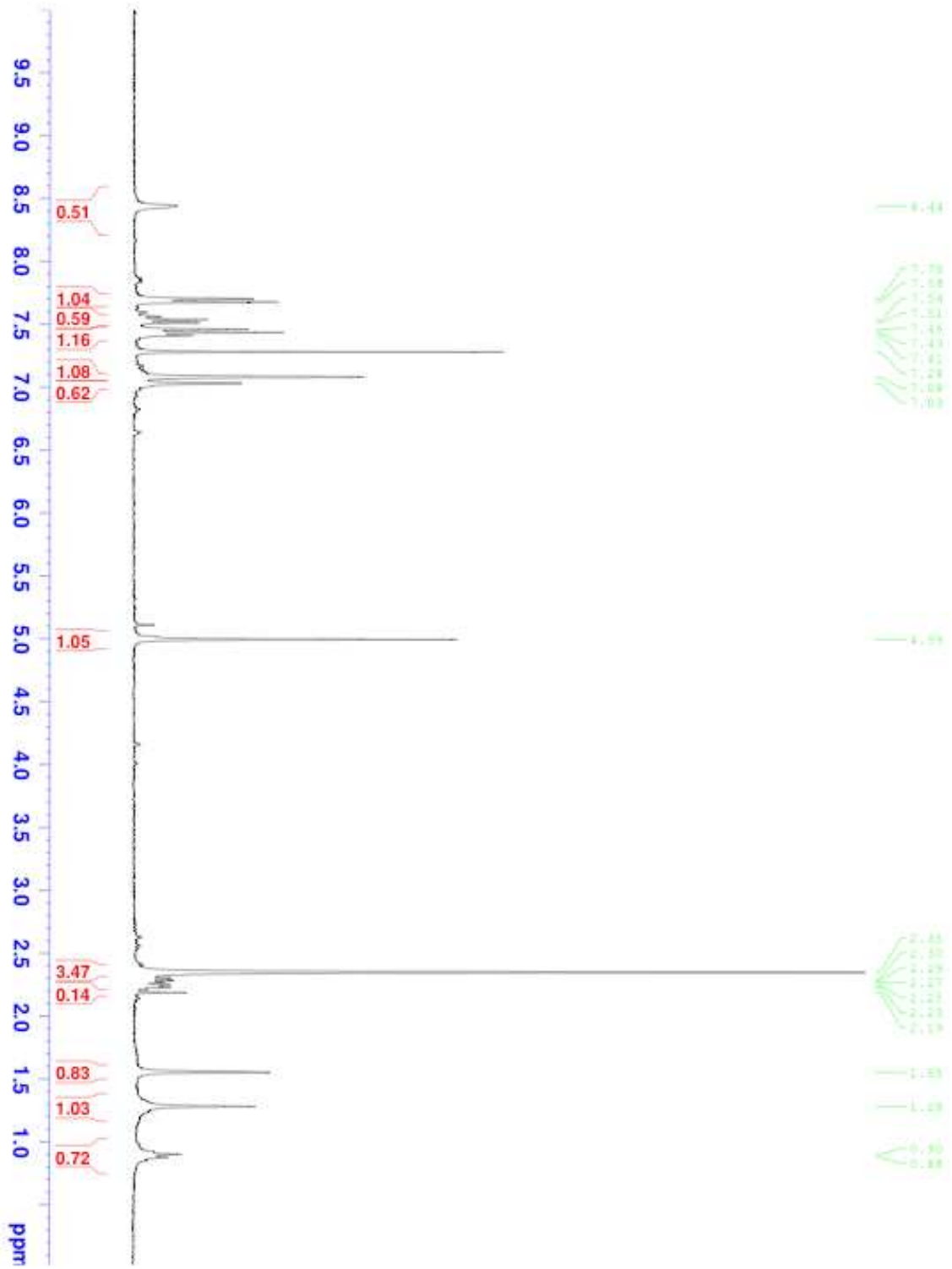
^{13}C NMR *N*-(2,6-Dimebenzyloxy)benzamide



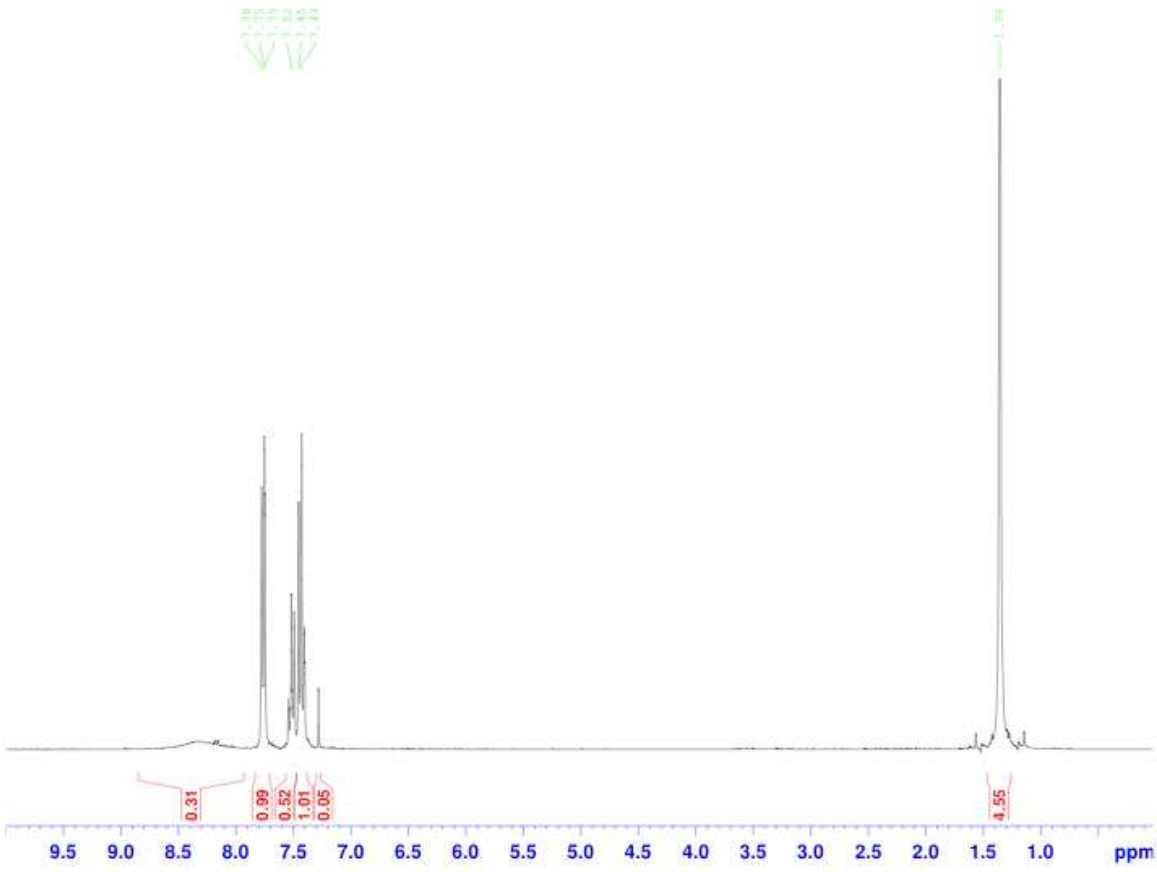
^{1}H NMR *N*-(2,6-Dimebenzyloxy)benzamide



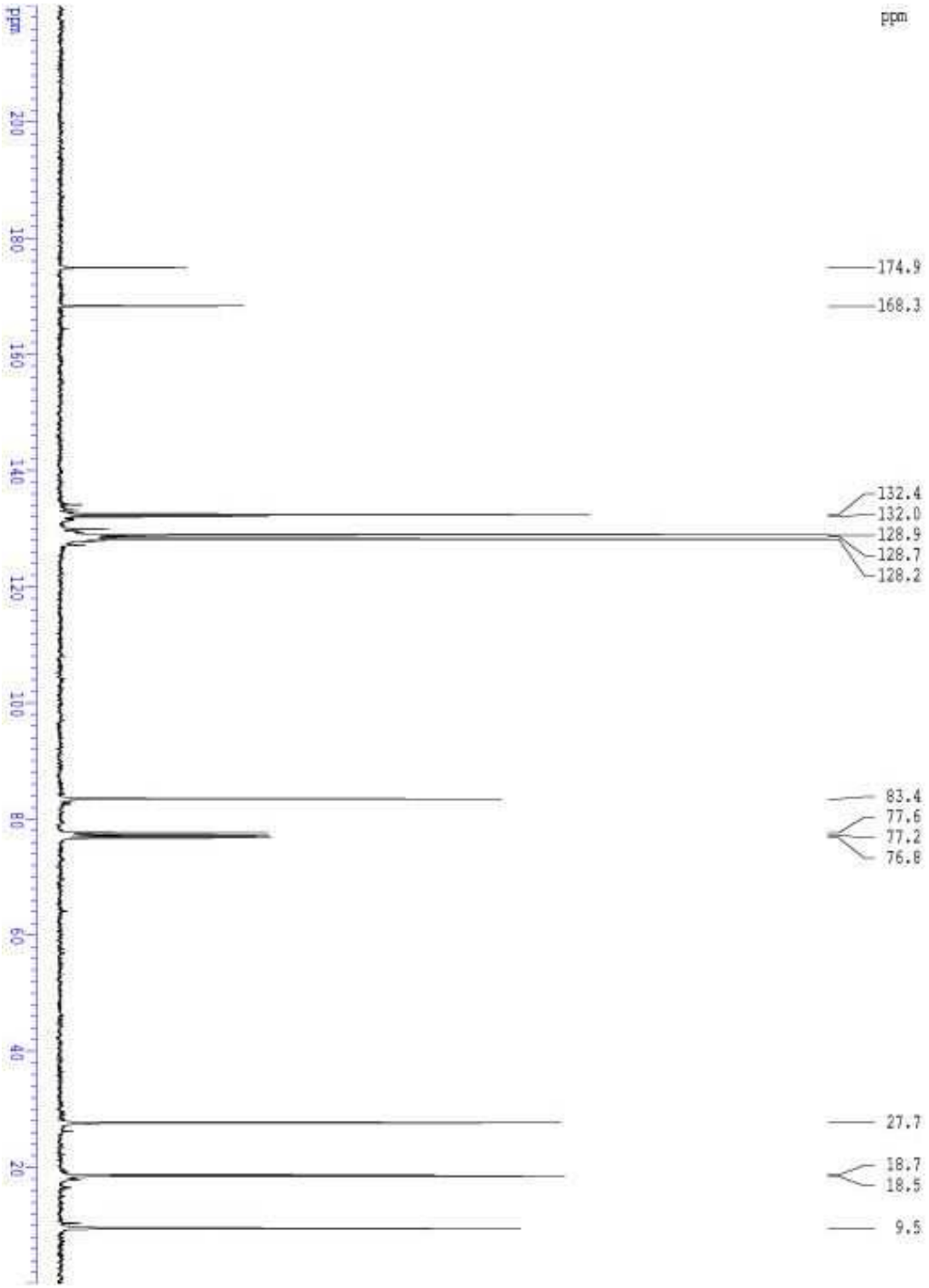
^{1}H NMR *N*-(3,5-Dimethylbenzyloxy)benzamide



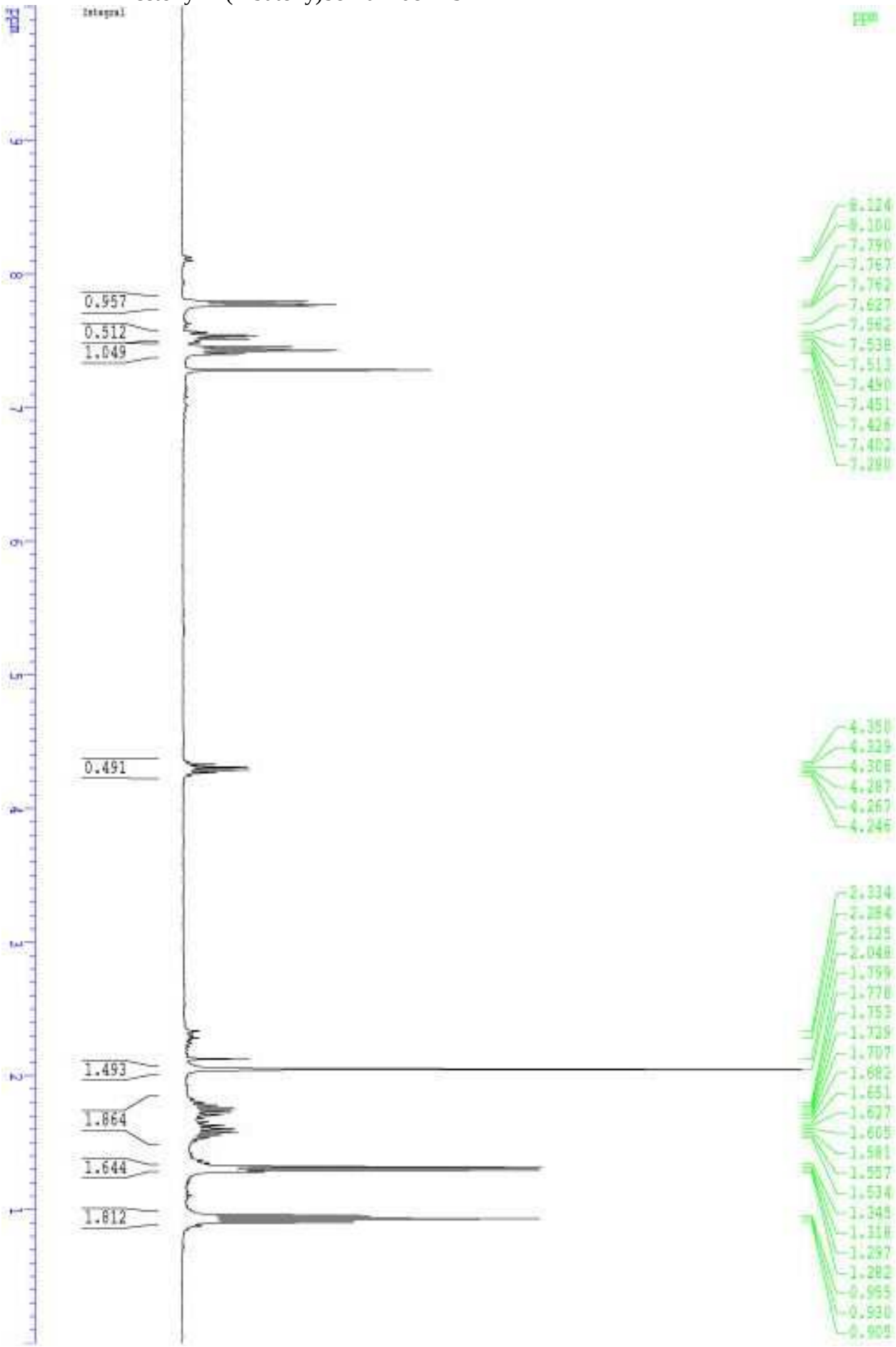
^{1}H NMR *N*-tert-Butoxybenzamide



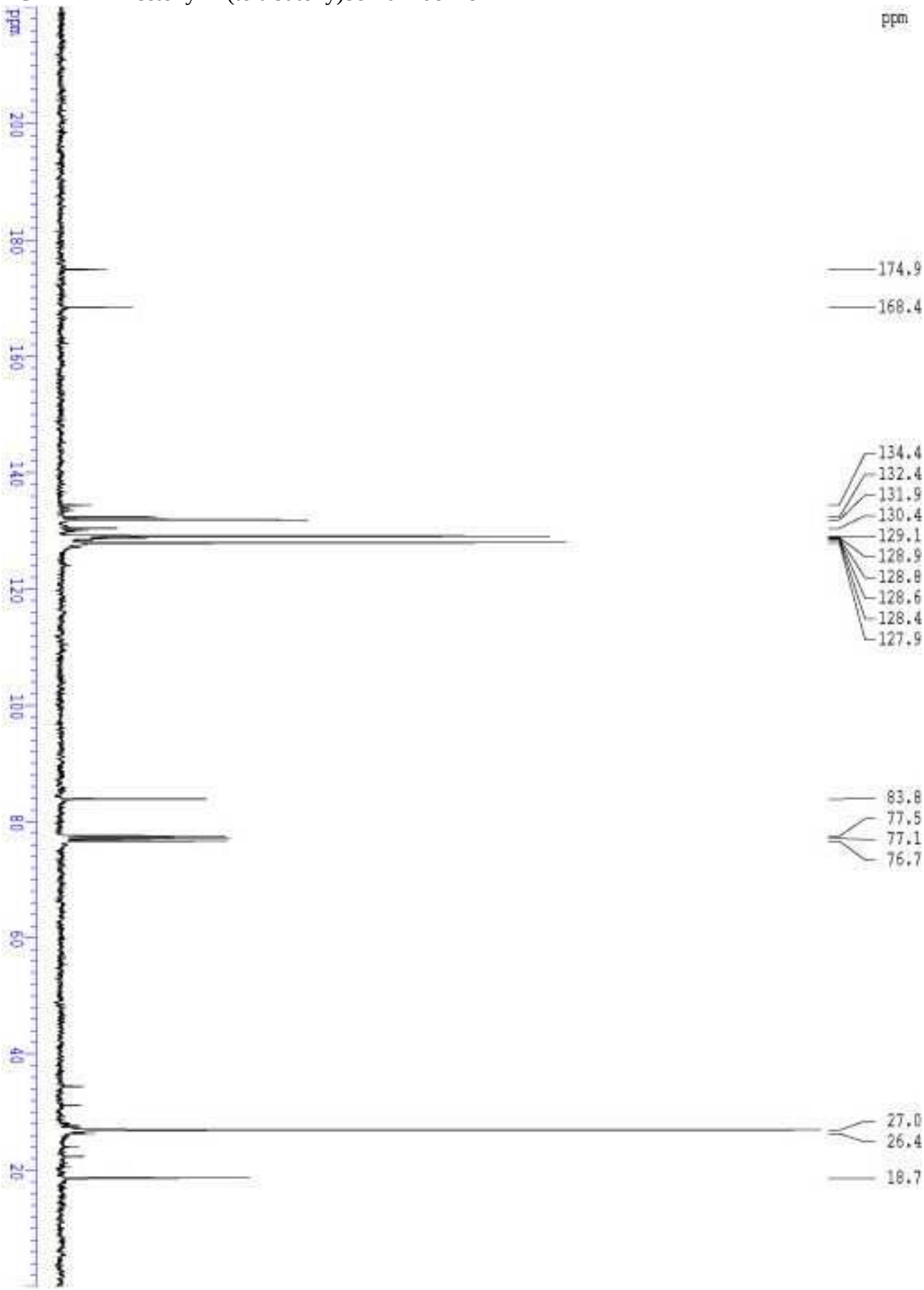
^{13}C NMR *N*-Acetoxy-*N*-(2-butoxy)benzamide**11b**



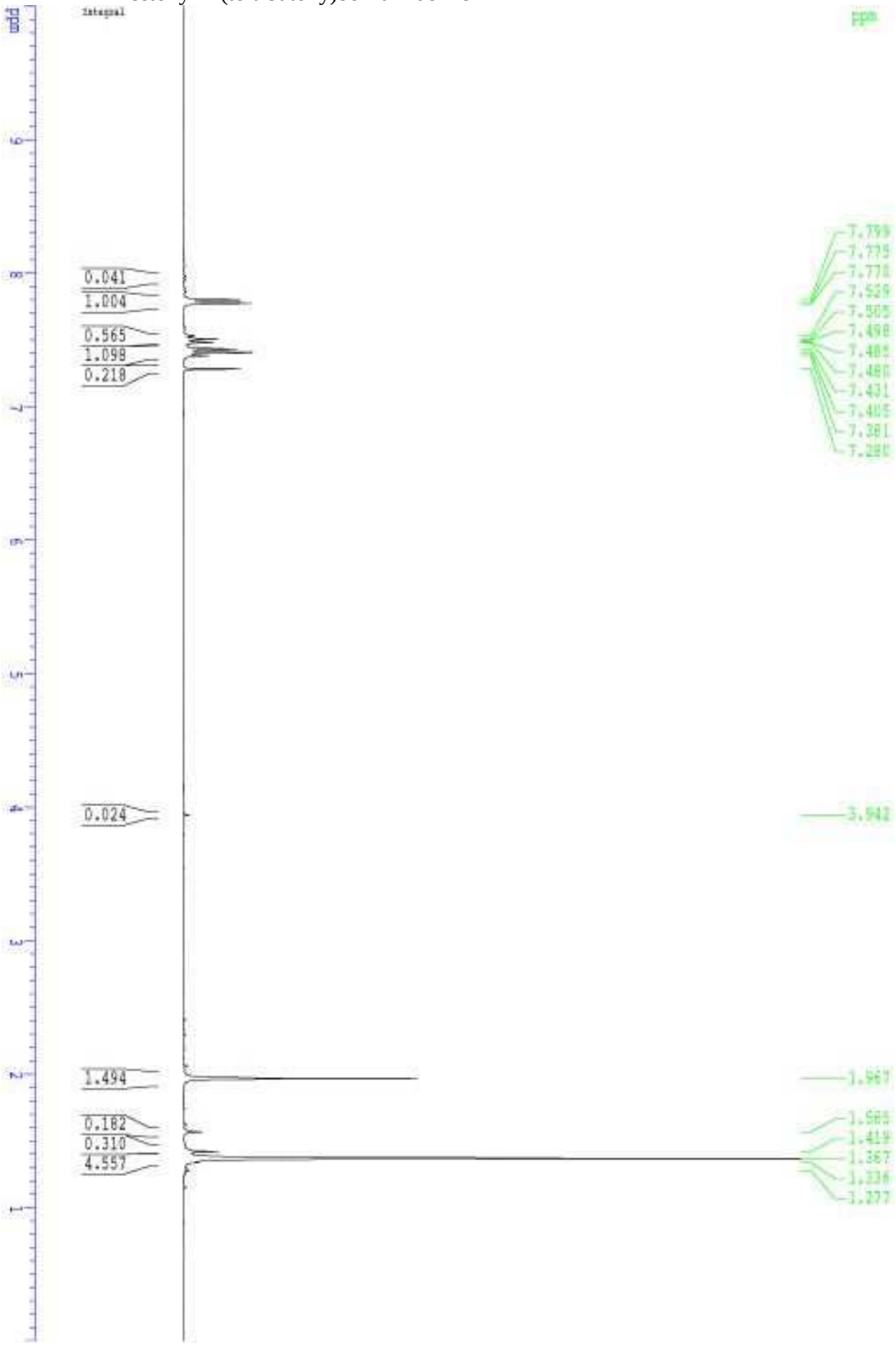
^{1}H NMR *N*-Acetoxy-*N*-(2-butoxy)benzamide **11b**



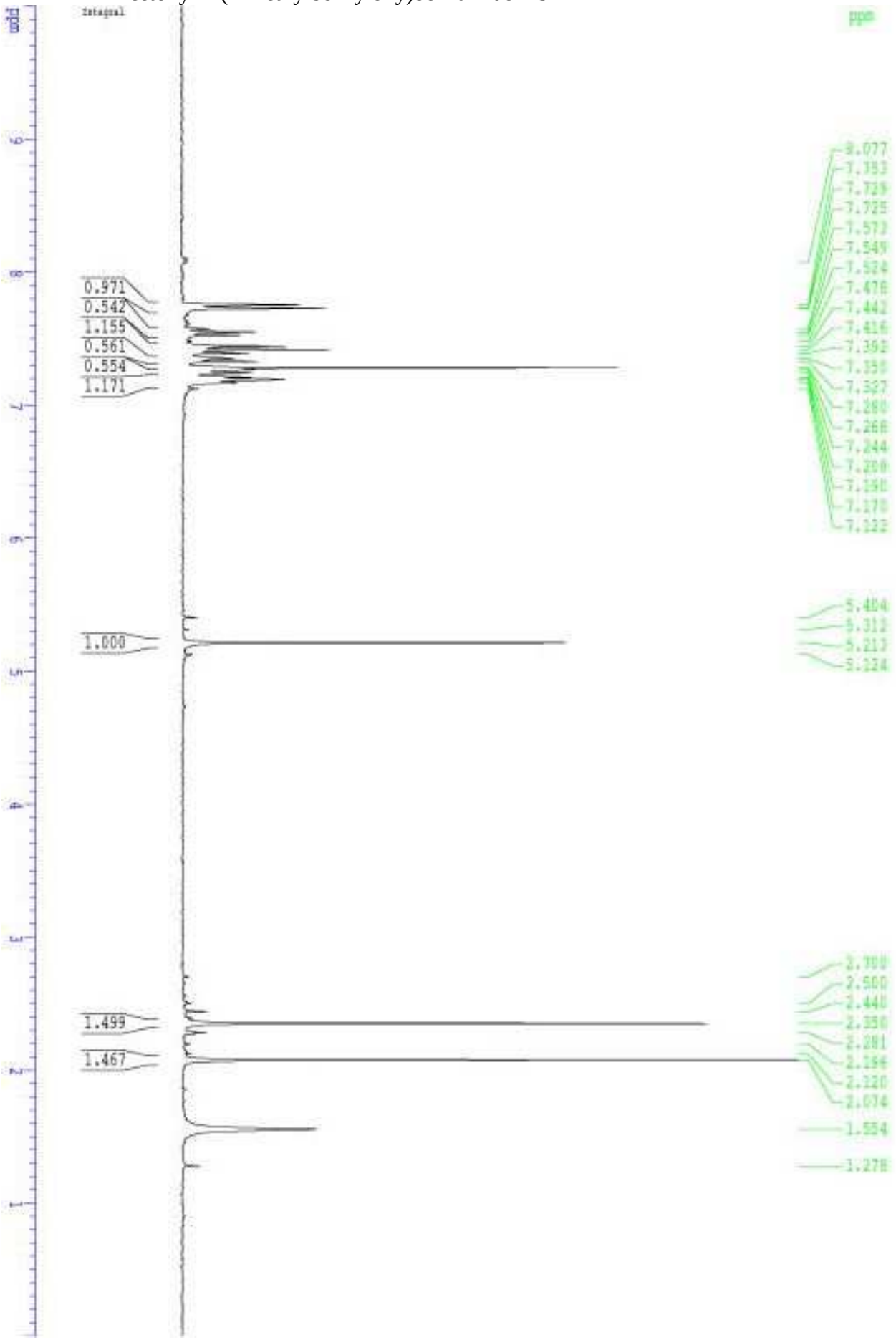
^{13}C NMR *N*-Acetoxy-*N*-(tert-butoxy)benzamide**11c**



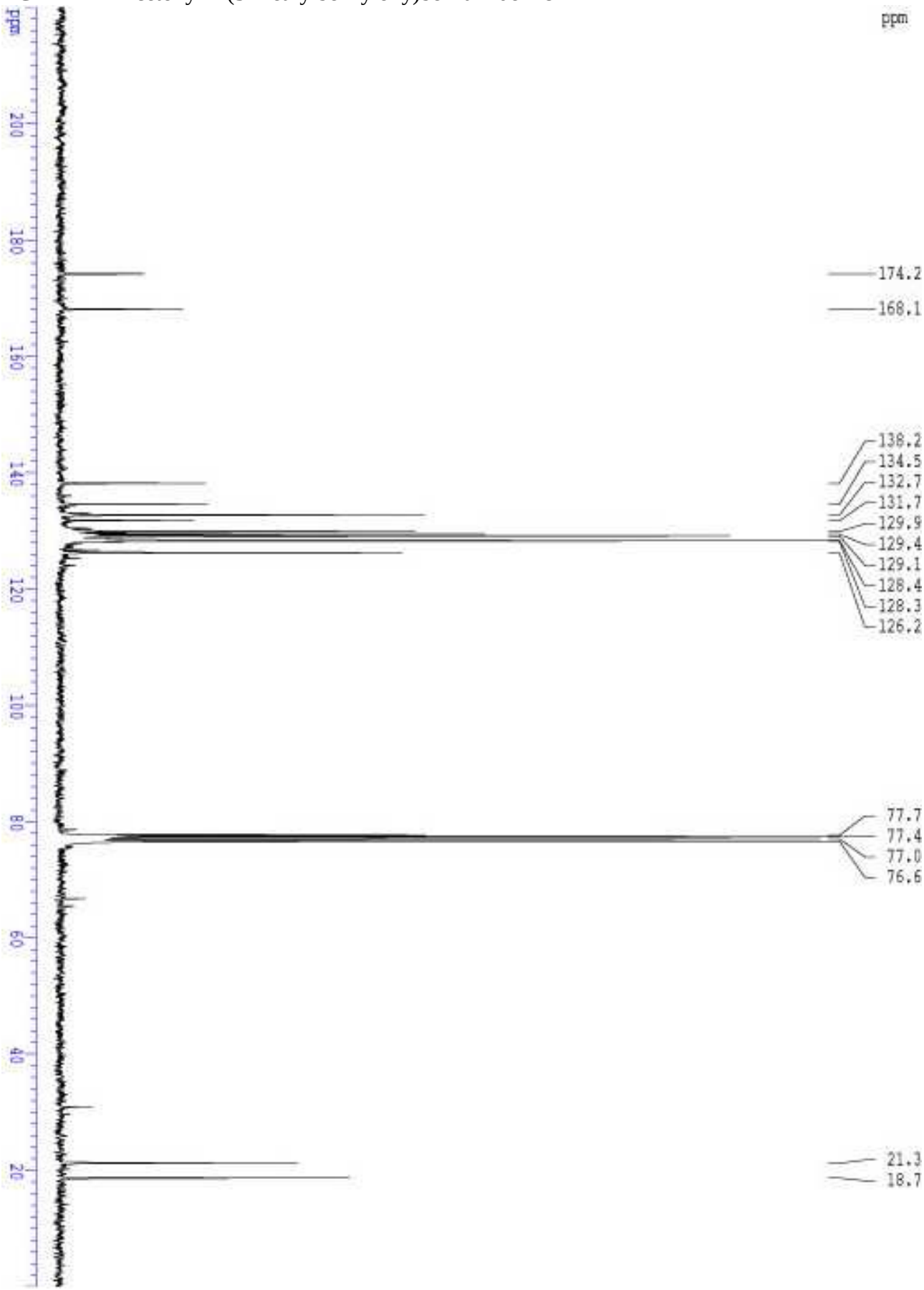
^{1}H NMR *N*-Acetoxy-*N*-(tert-butoxy)benzamide**11c**



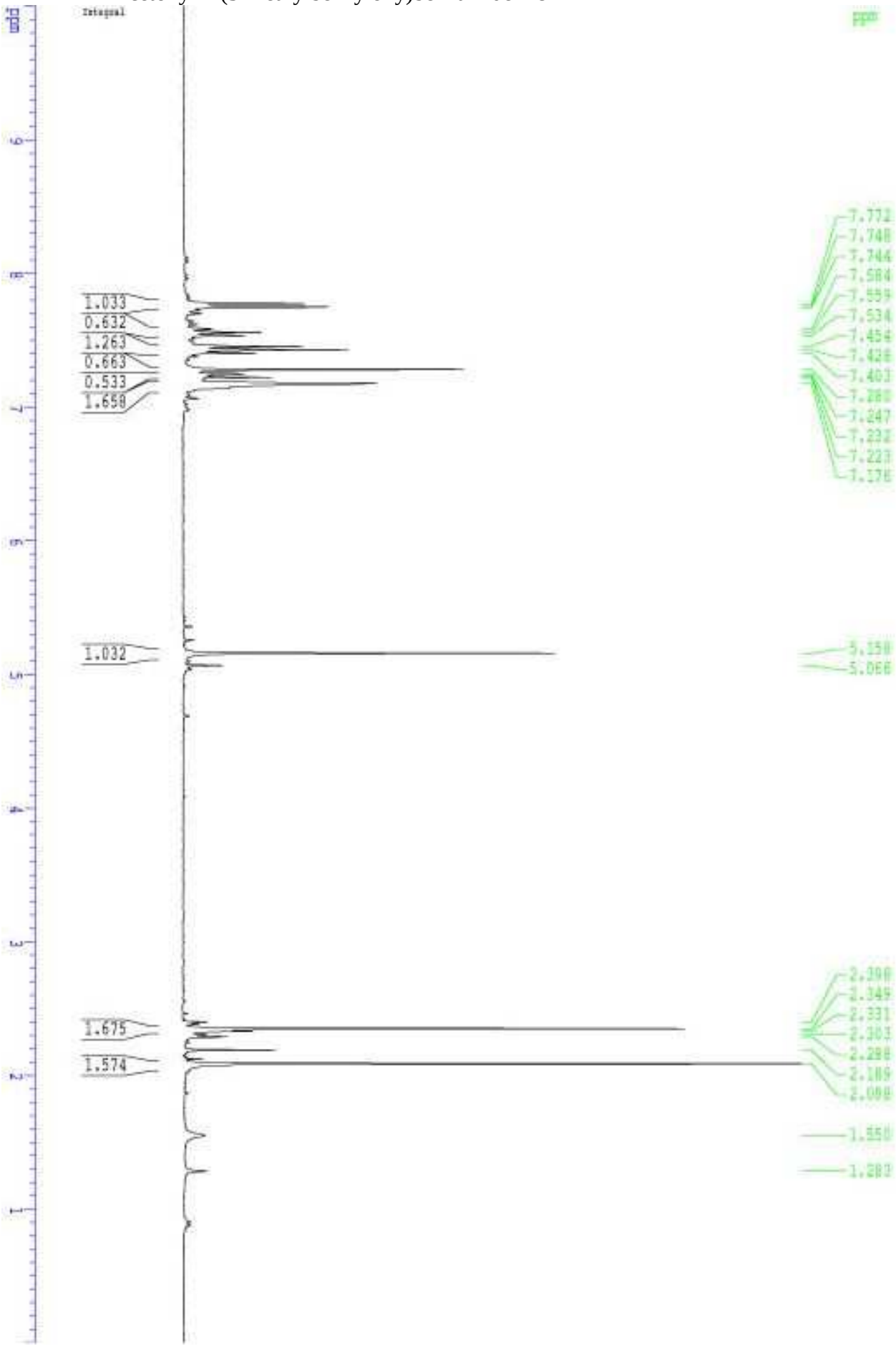
^{1}H NMR *N*-Acetoxy-*N*-(2-methylbenzyloxy)benzamide**12b**



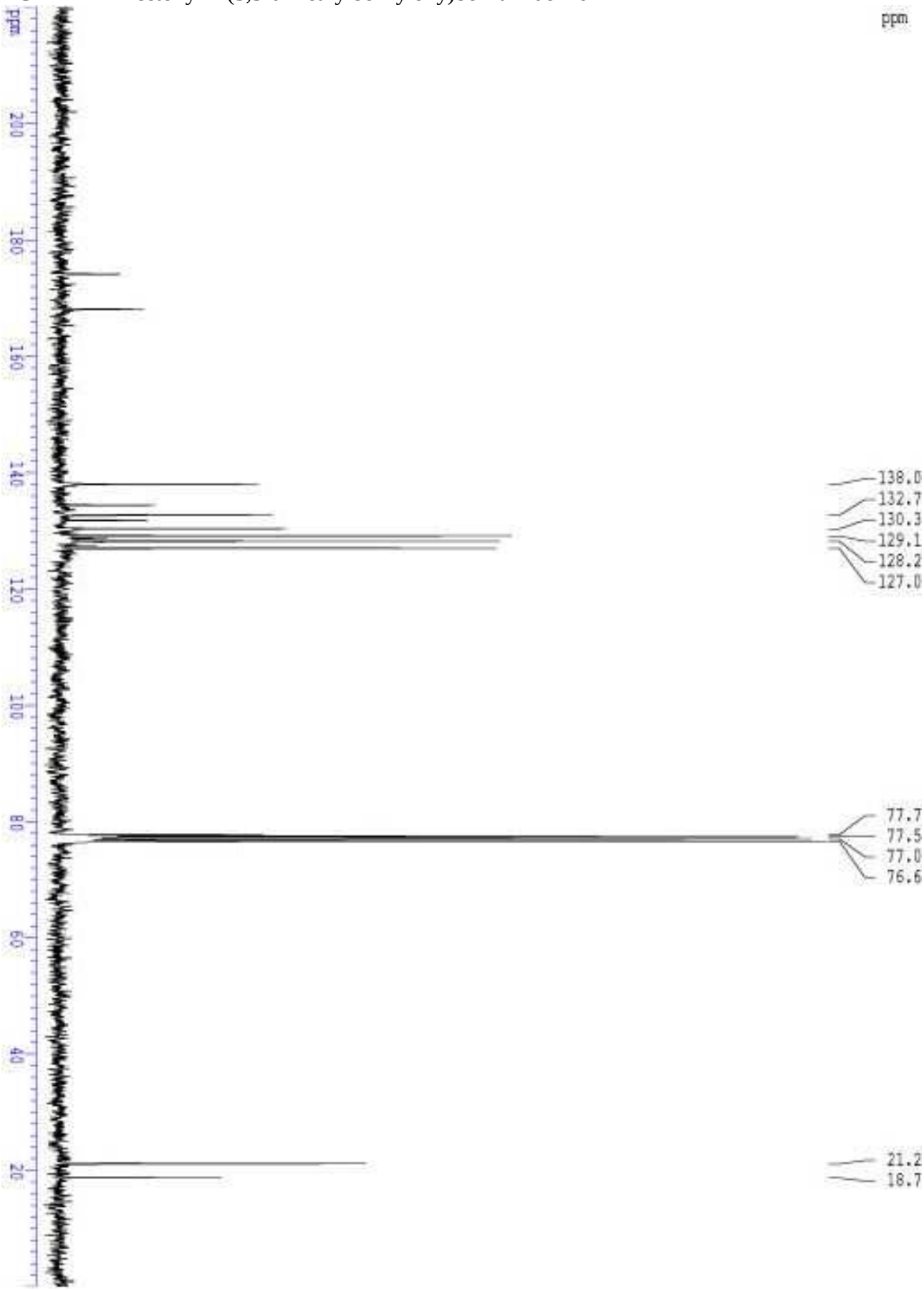
^{13}C NMR *N*-Acetoxy-*N*-(3-methylbenzyloxy)benzamide**12c**



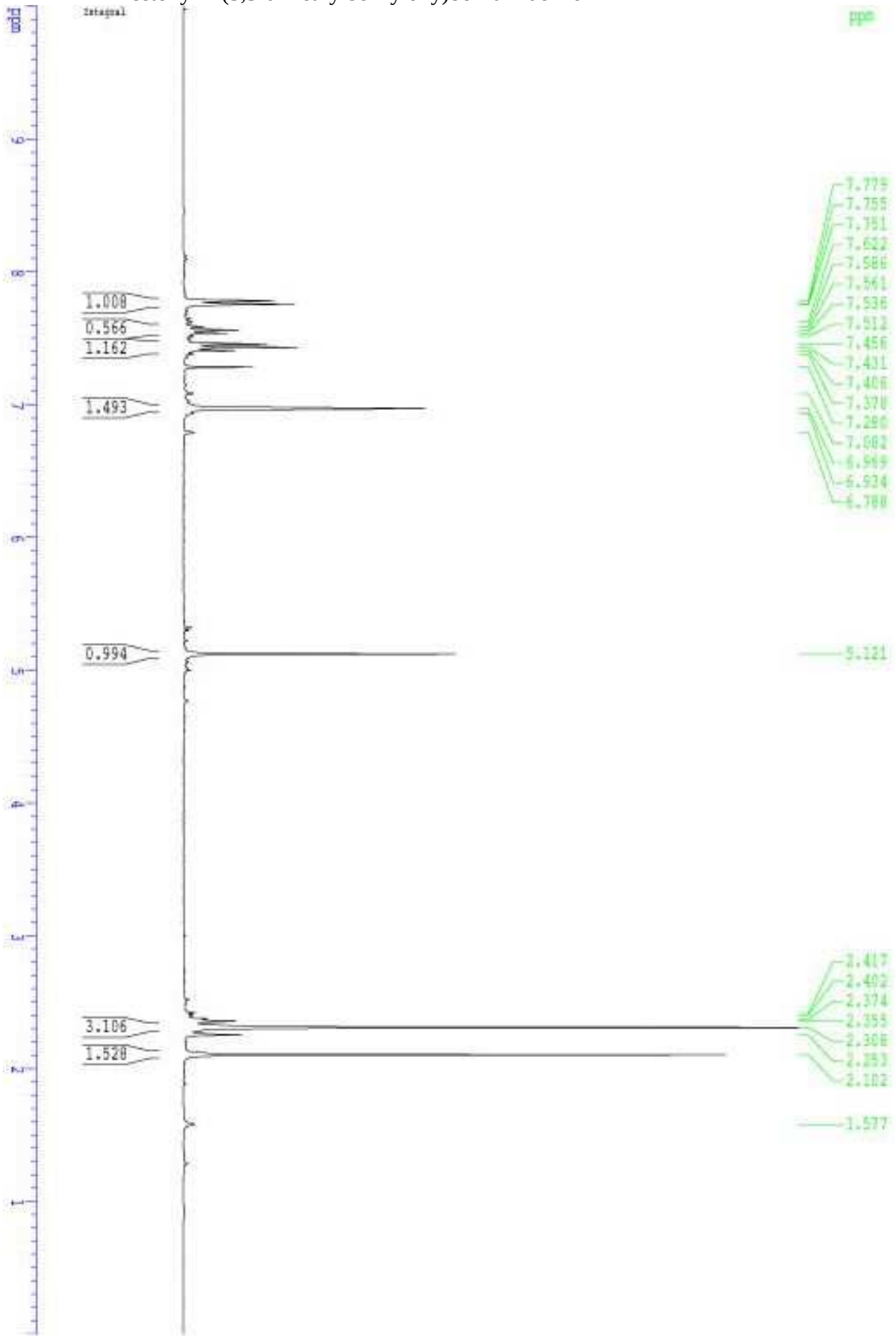
^{1}H NMR *N*-Acetoxy-*N*-(3-methylbenzyloxy)benzamide**12c**



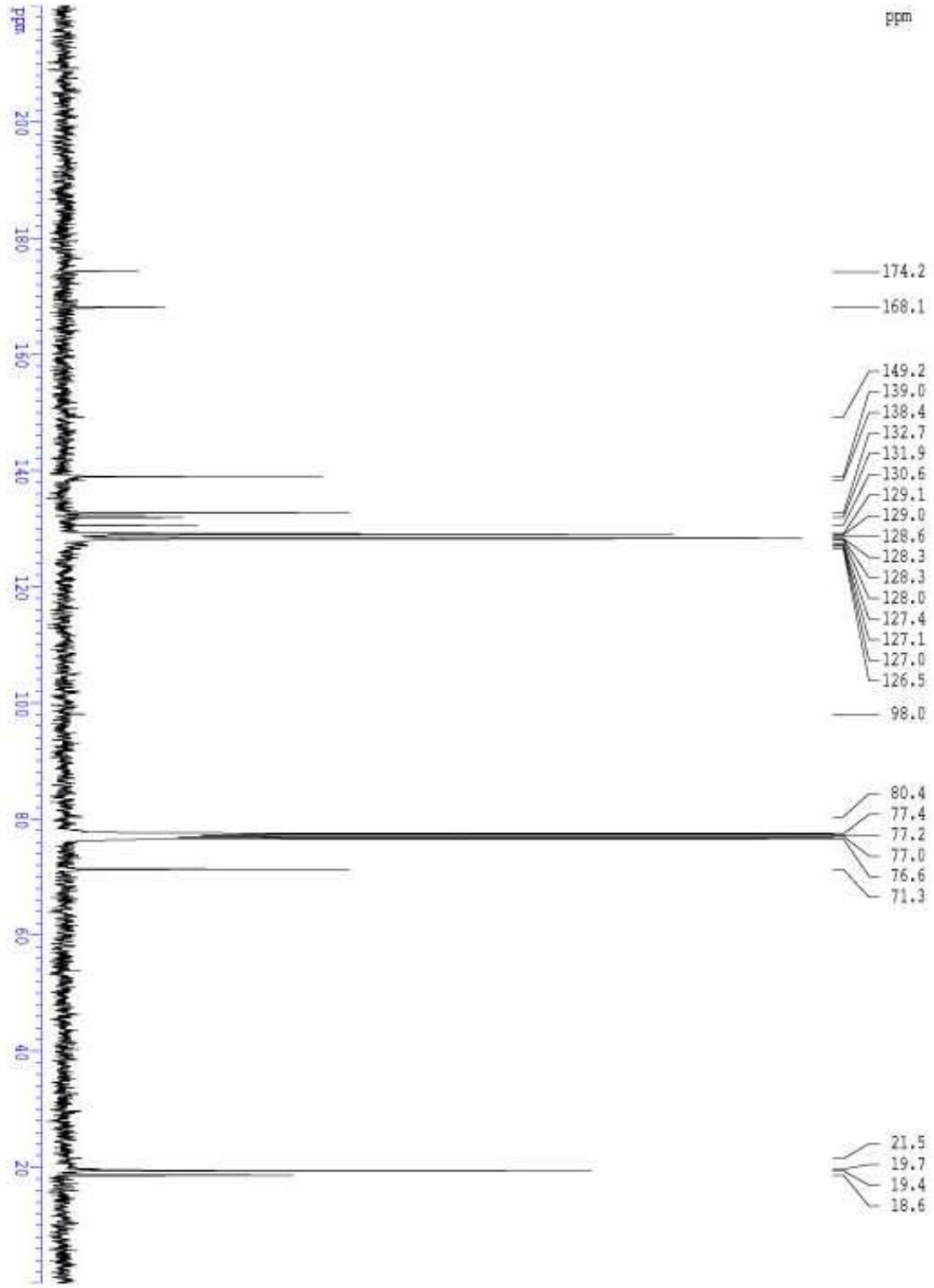
^{13}C NMR *N*-Acetoxy-*N*-(3,5-dimethylbenzyloxy)benzamide**12d**



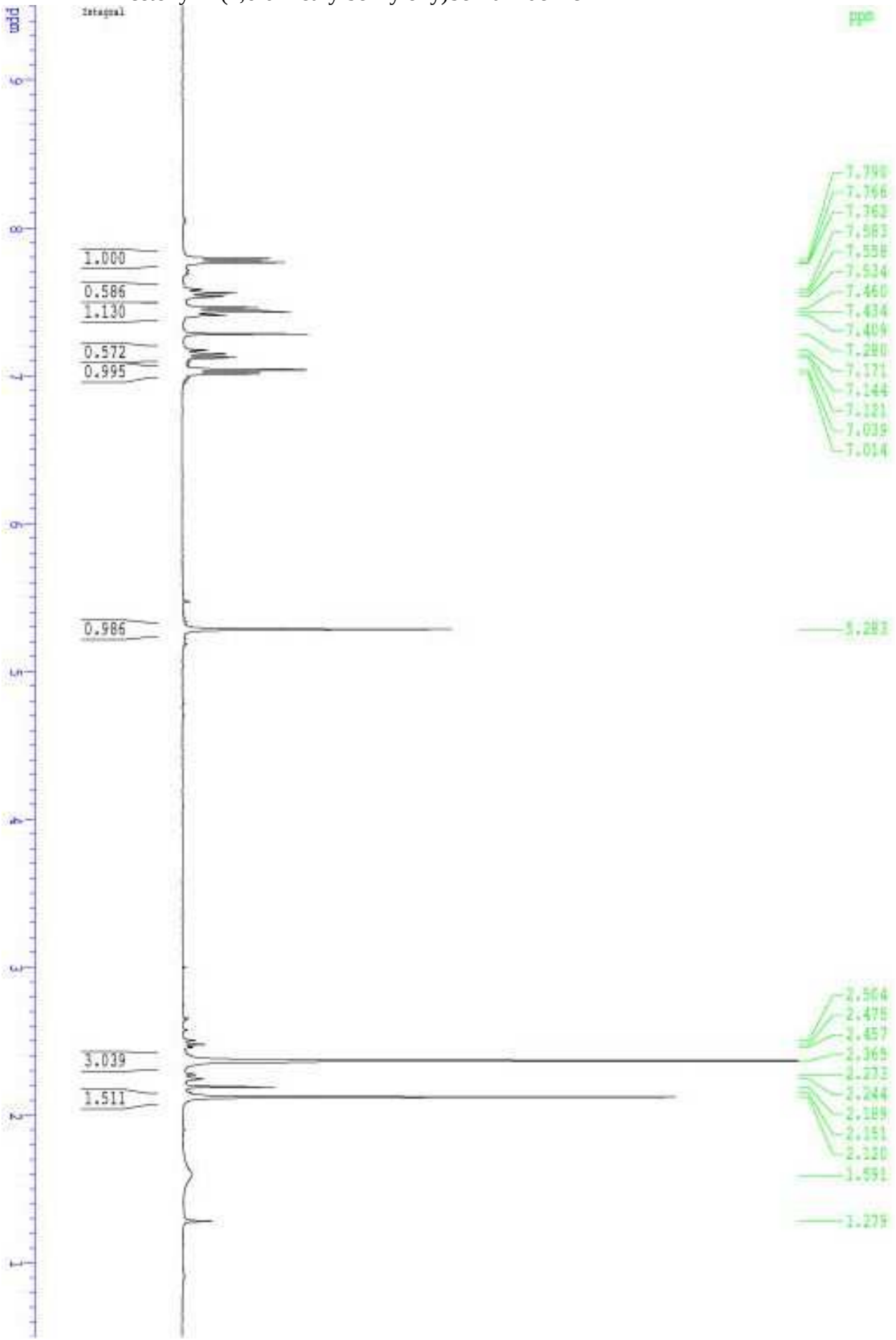
^{1}H NMR *N*-Acetoxy-*N*-(3,5-dimethylbenzyloxy)benzamide**12d**



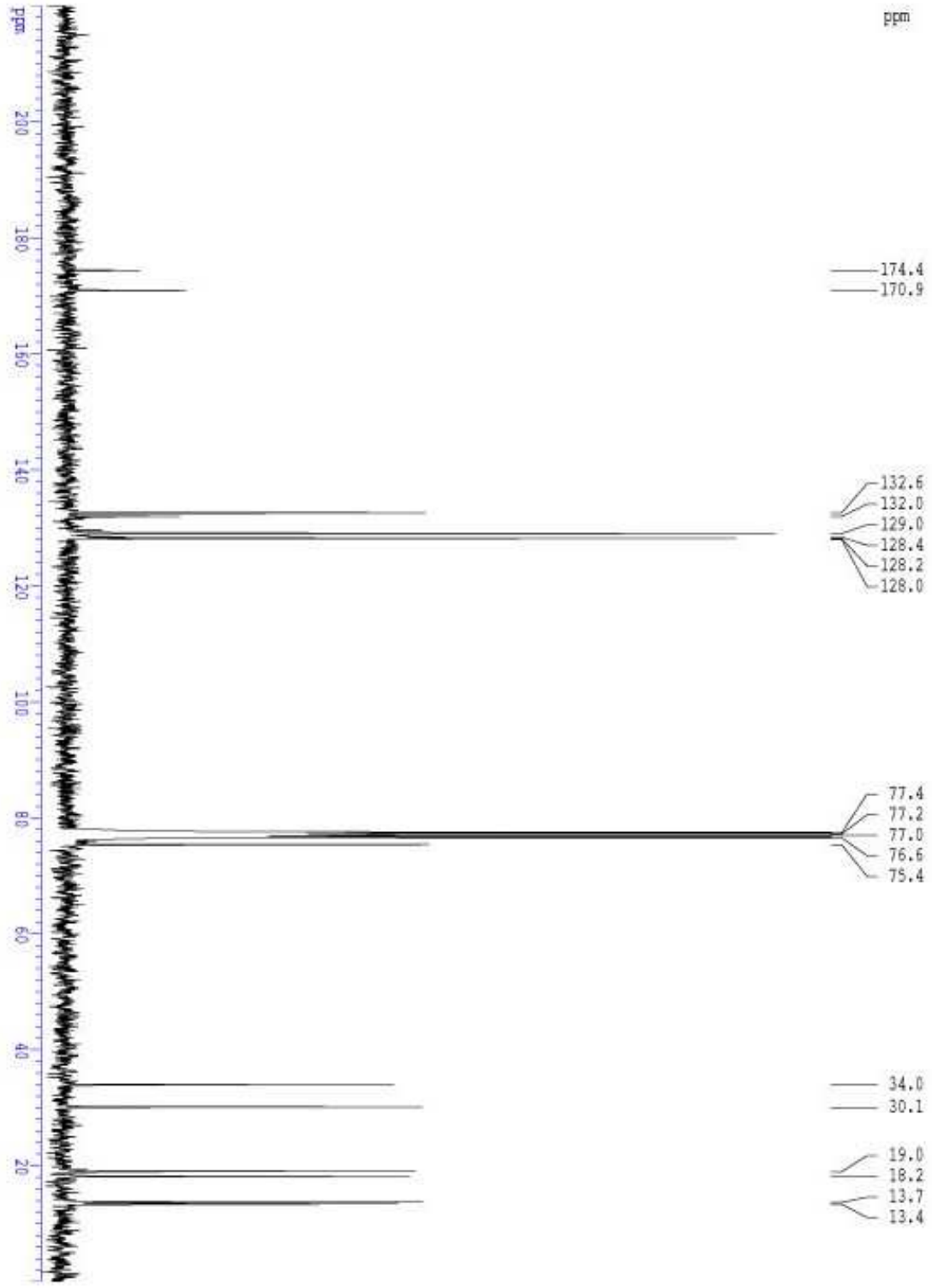
^{13}C NMR *N*-Acetoxy-*N*-(2,6-dimethylbenzyloxy)benzamide**12e**



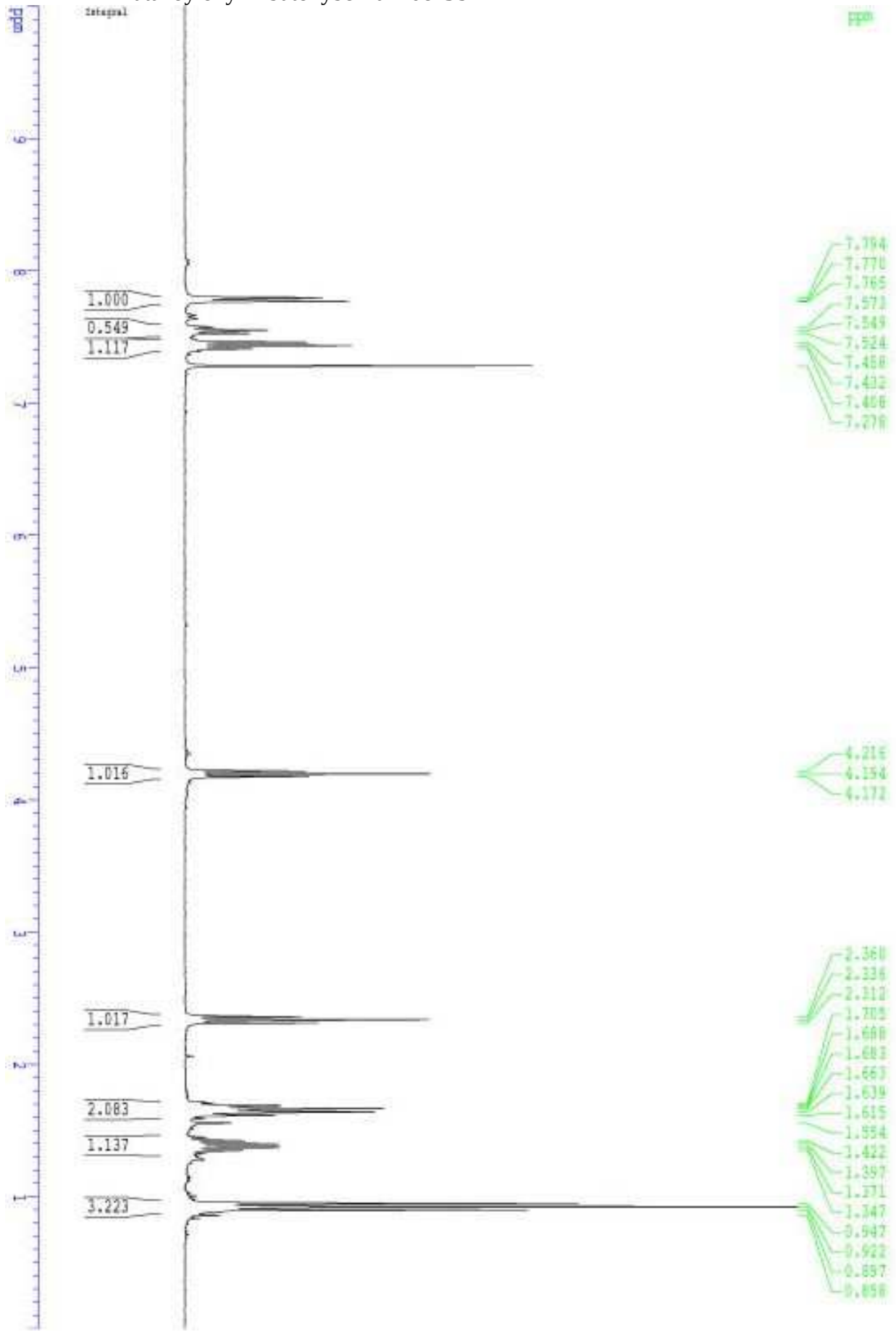
^{1}H NMR *N*-Acetoxy-*N*-(2,6-dimethylbenzyloxy)benzamide**12e**



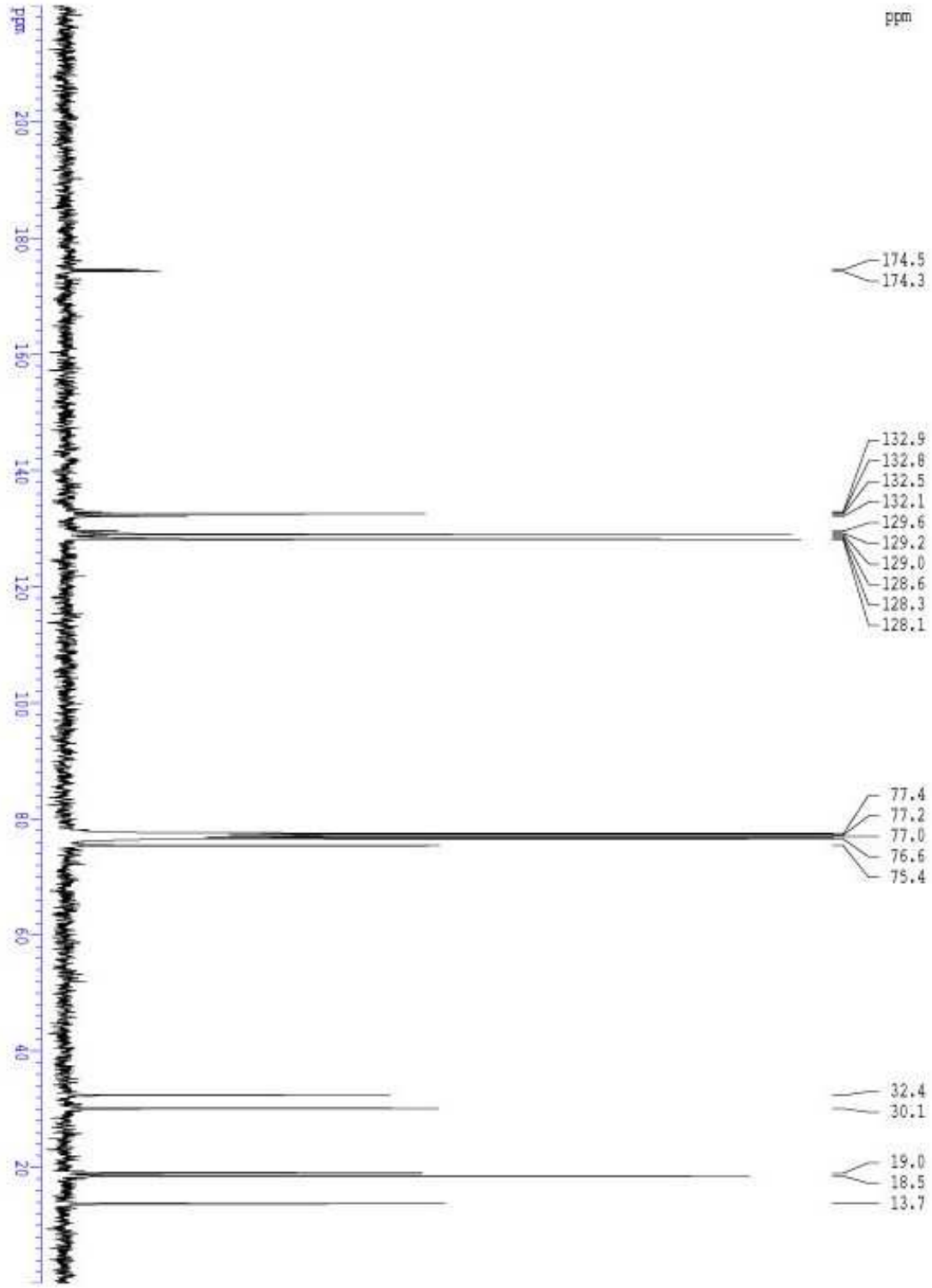
^{13}C NMR *N*-Butanoyloxy-*N*-butoxybenzamide**13b**



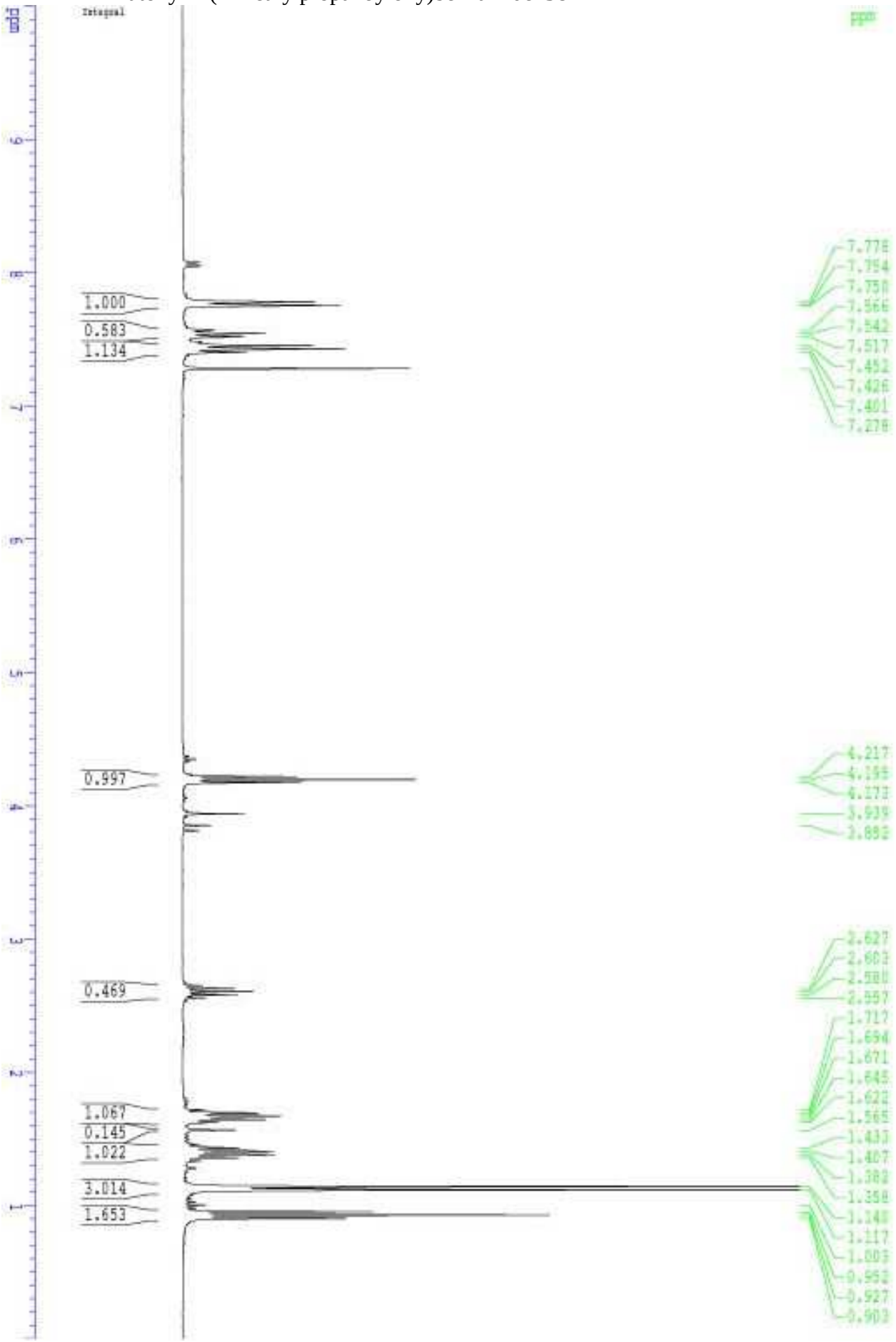
^{1}H NMR *N*-Butanoyloxy-*N*-butoxybenzamide**13b**



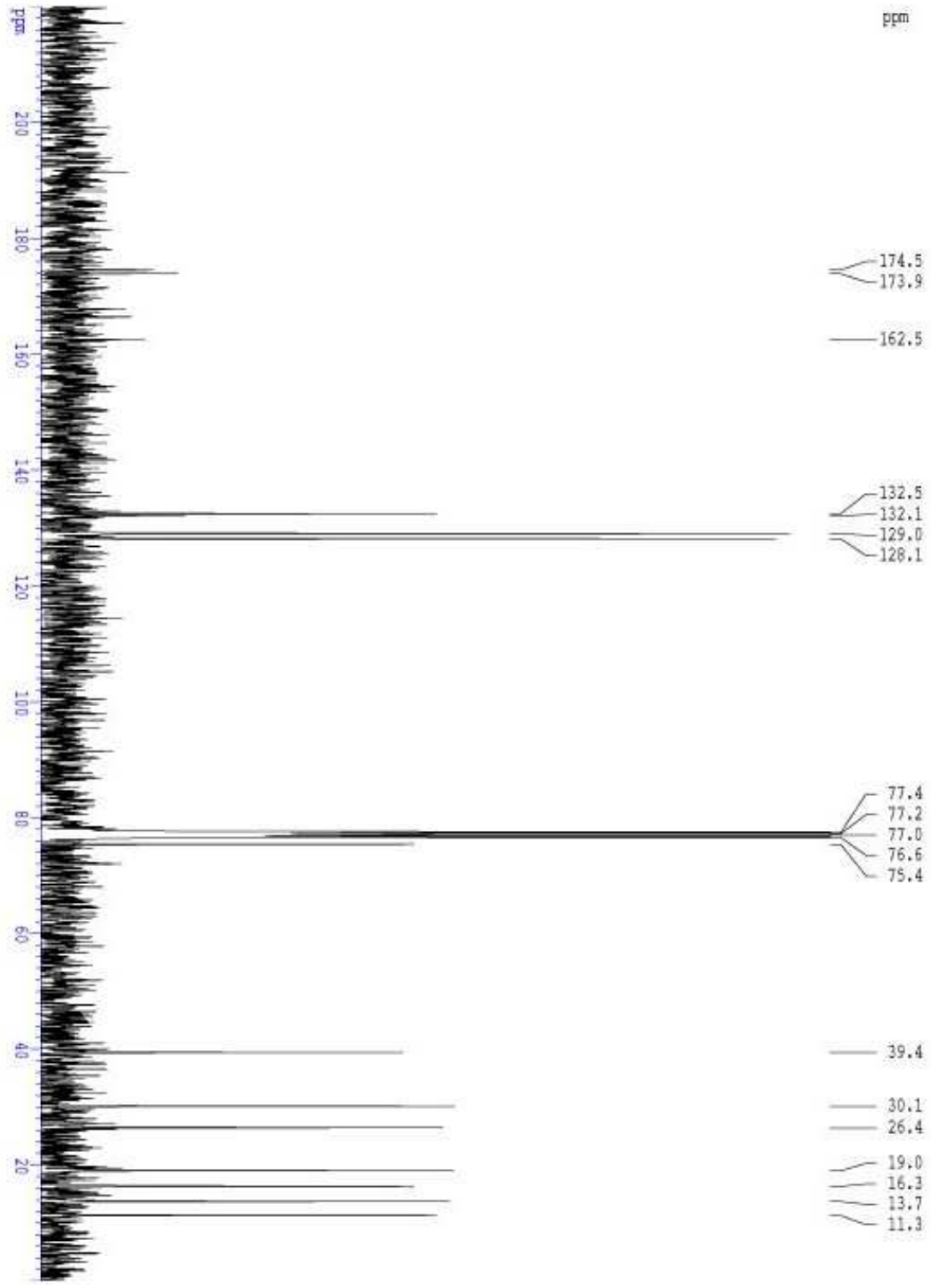
^{13}C NMR *N*-Butoxy-*N*-(2-methylpropanoyloxy)benzamide**13c**



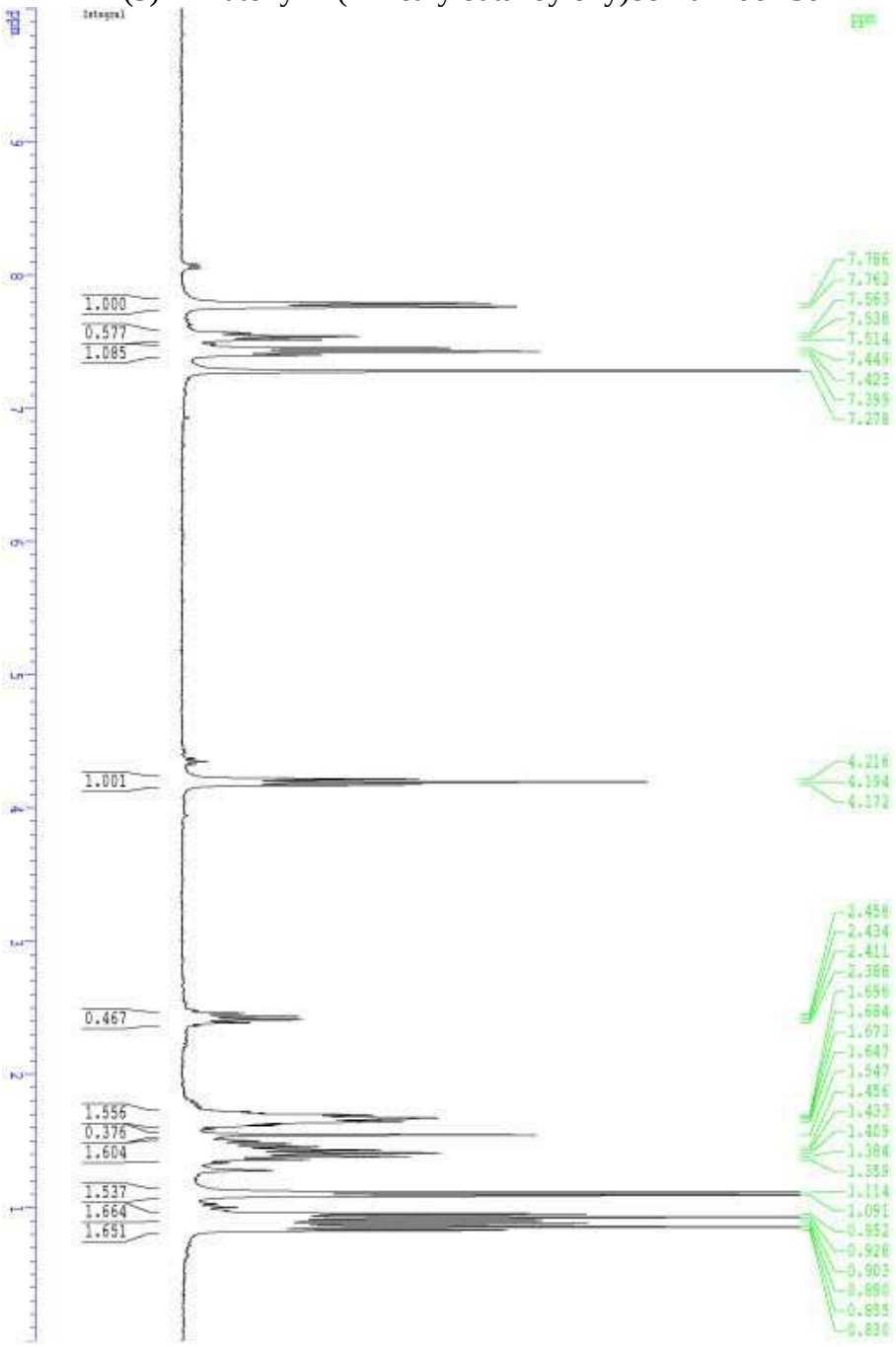
^{1}H NMR *N*-Butoxy-*N*-(2-methylpropanoyloxy)benzamide**13c**



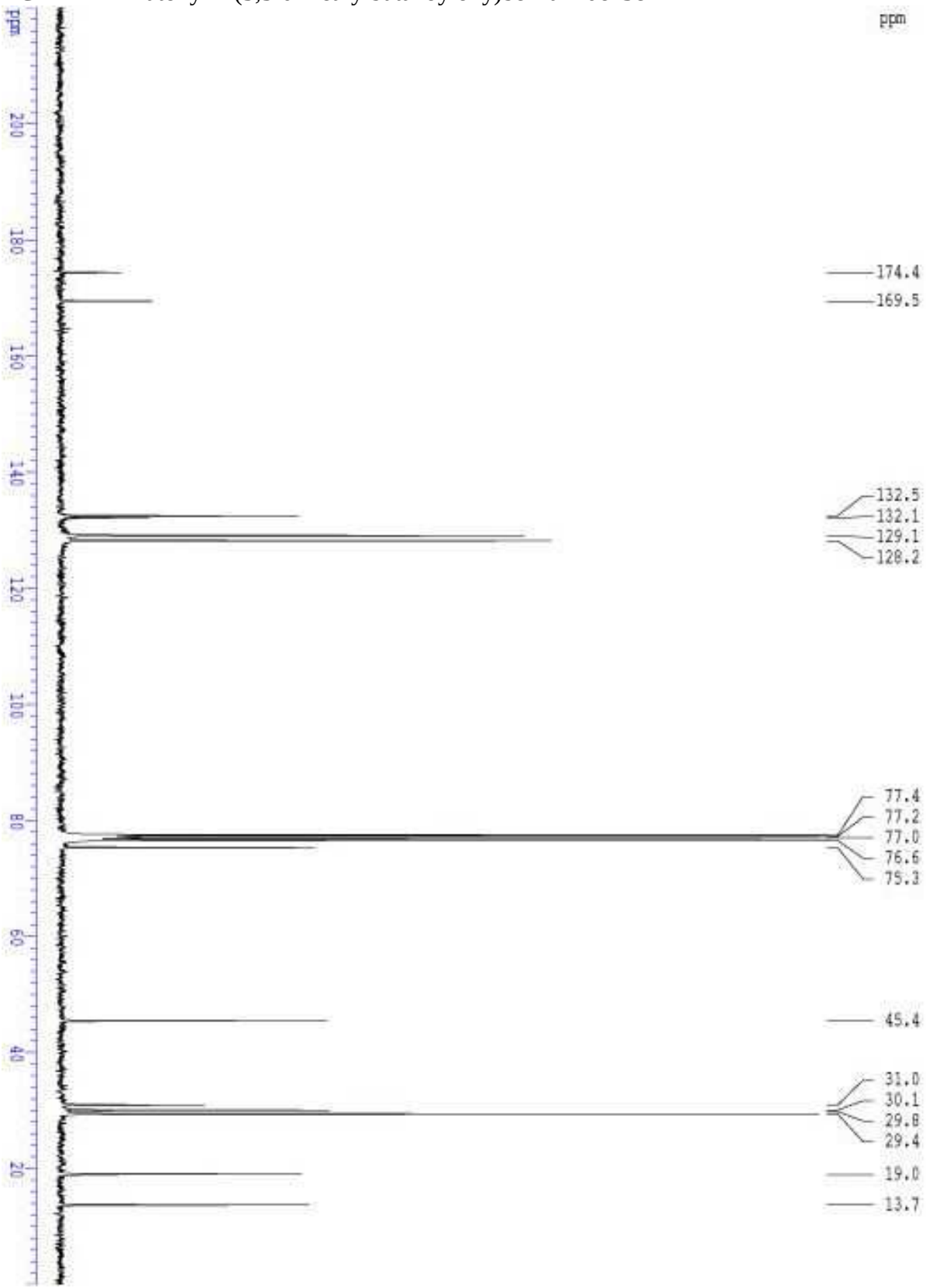
^{13}C NMR (*S*)-*N*-Butoxy-*N*-(2-methylbutanoyloxy)benzamide **13d**



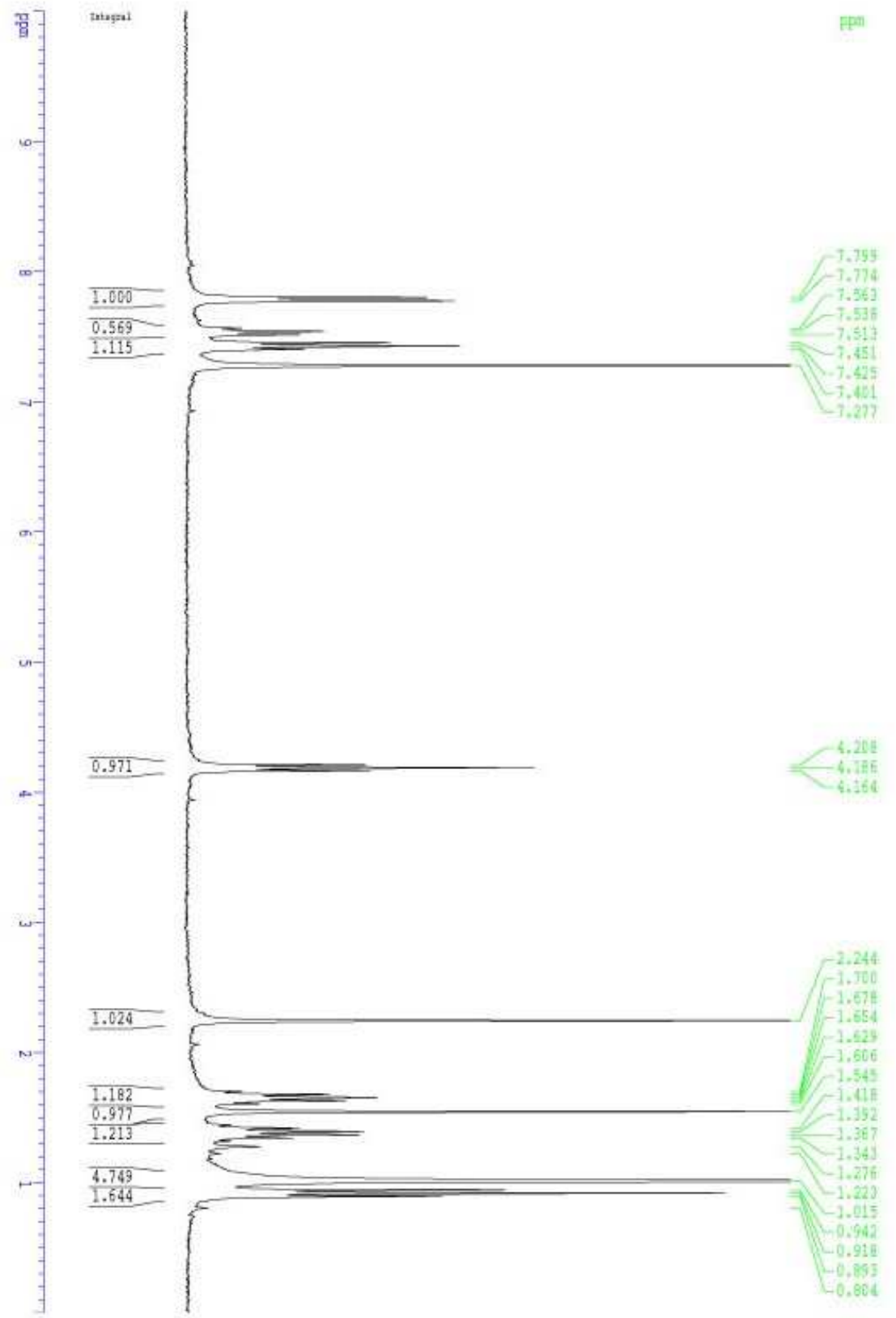
^{1}H NMR (*S*)-*N*-Butoxy-*N*-(2-methylbutanoyloxy)benzamide **13d**



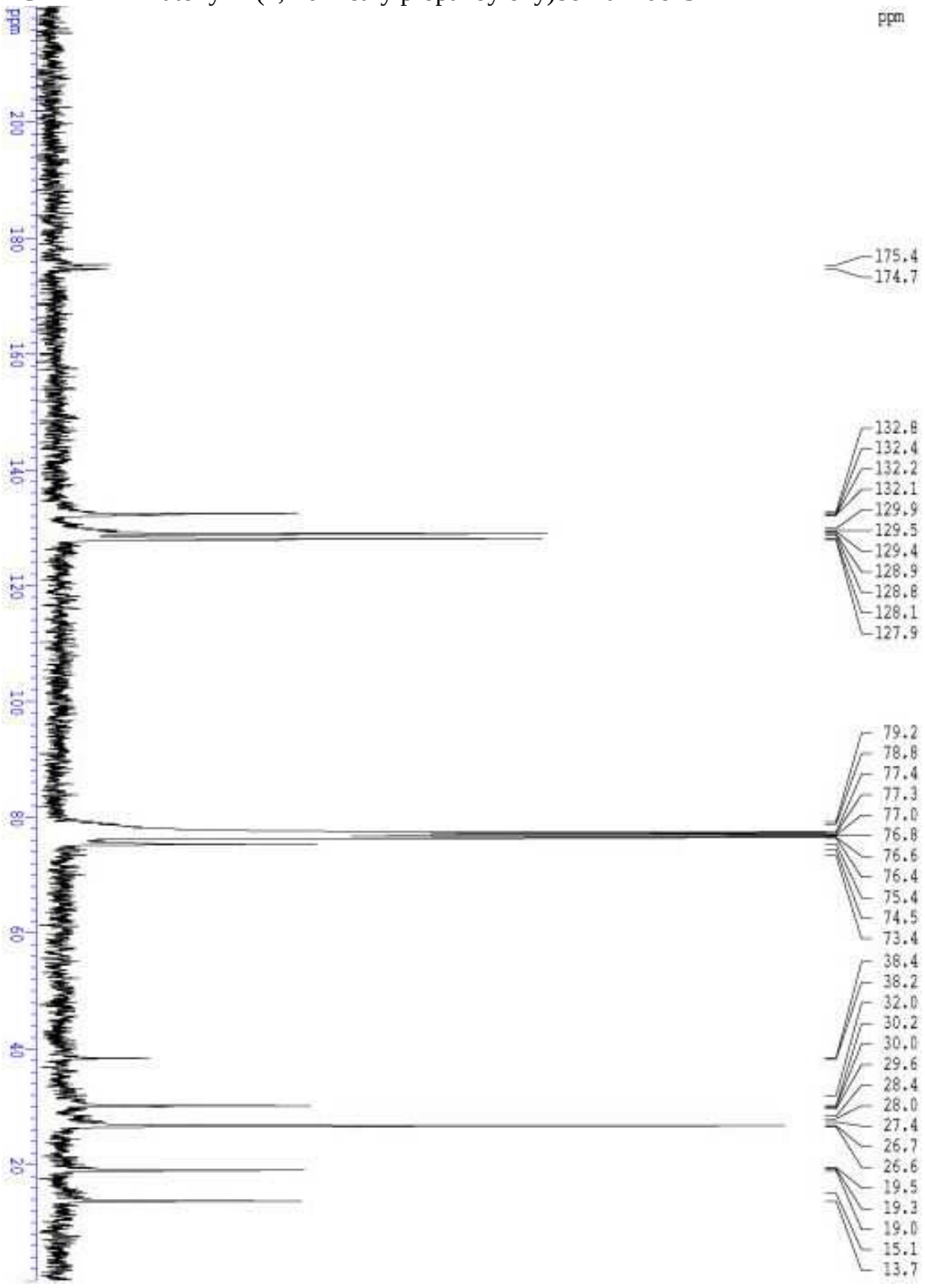
^{13}C NMR *N*-Butoxy-*N*-(3,3-dimethylbutanoyloxy)benzamide**13e**



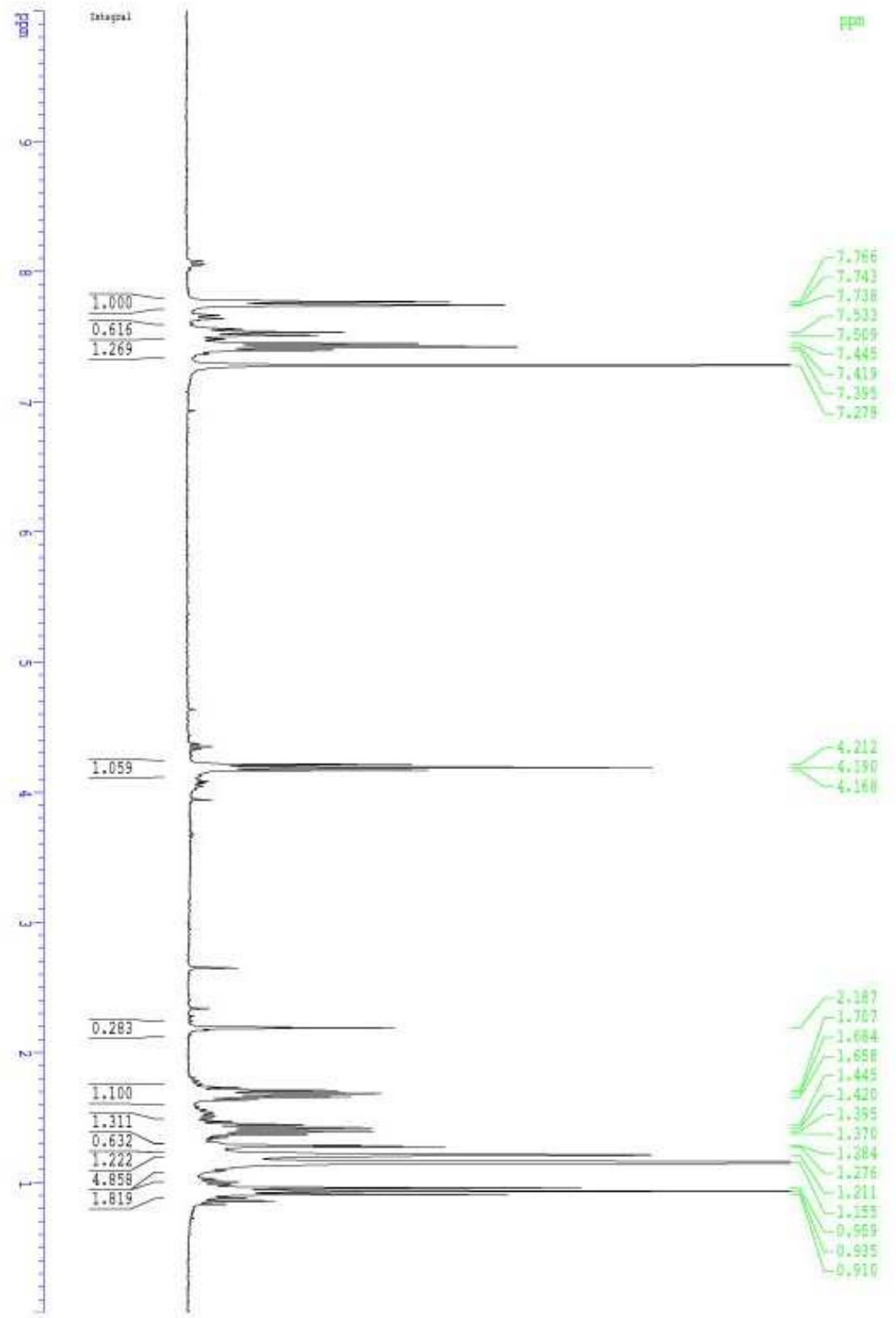
^{1}H NMR *N*-Butoxy-*N*-(3,3-dimethylbutanoyloxy)benzamide**13e**



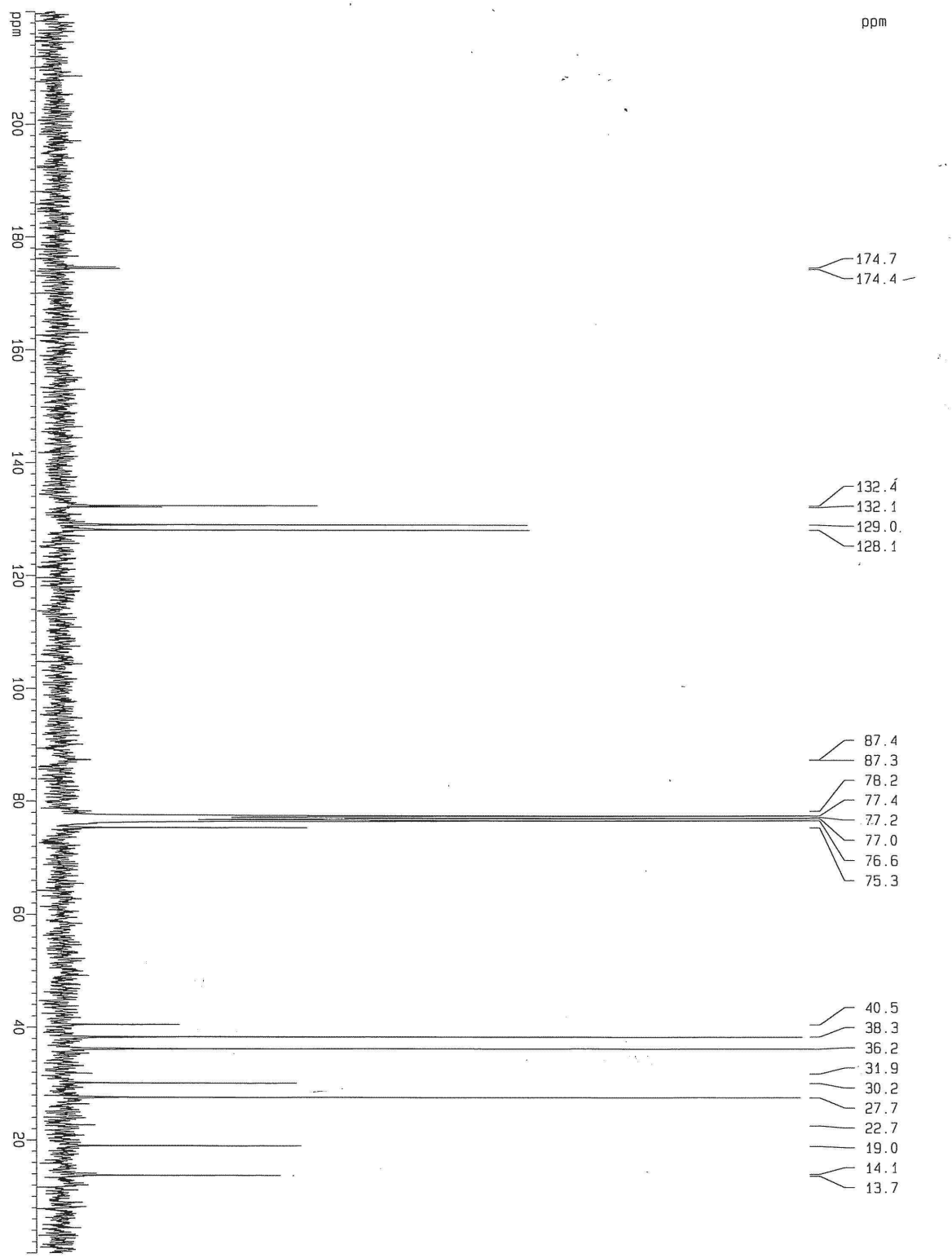
^{13}C NMR *N*-Butoxy-*N*-(2,2-dimethylpropanoyloxy)benzamide**13f**



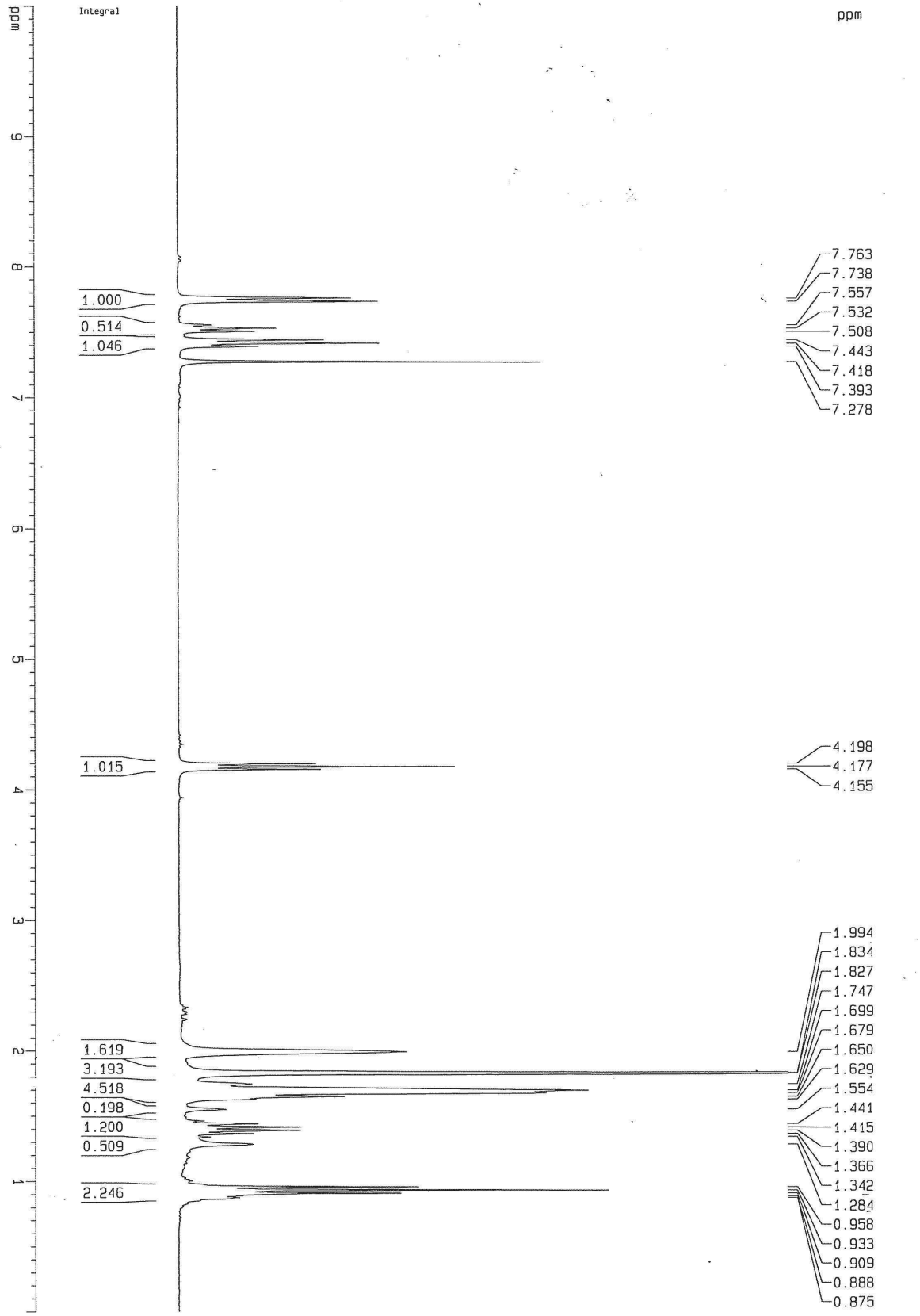
^{1}H NMR *N*-Butoxy-*N*-(2,2-dimethylpropanoyloxy)benzamide**13f**



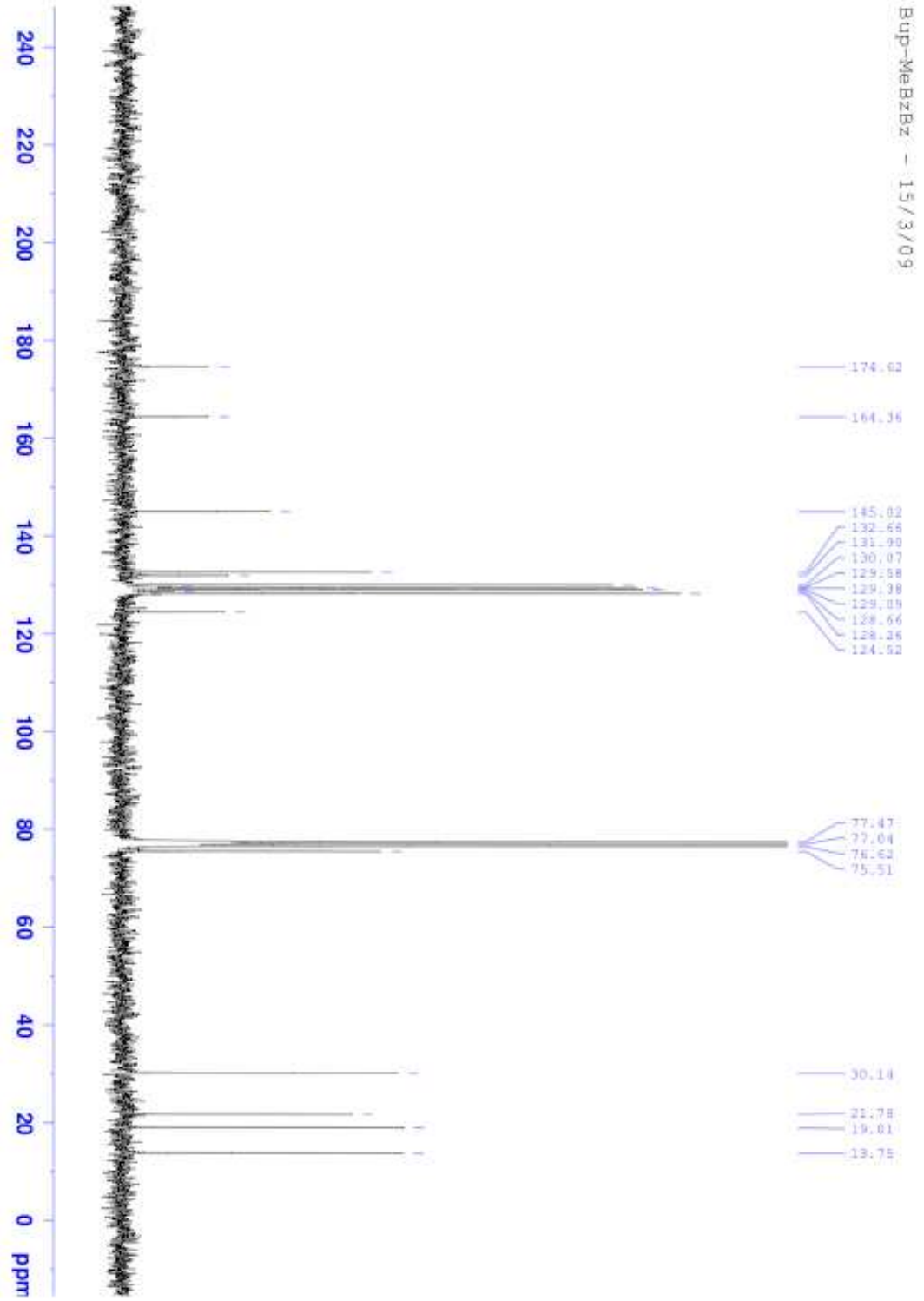
^{13}C NMR *N*-(Adamantane-1-carboxoyloxy)-*N*-butoxybenzamide **13g**



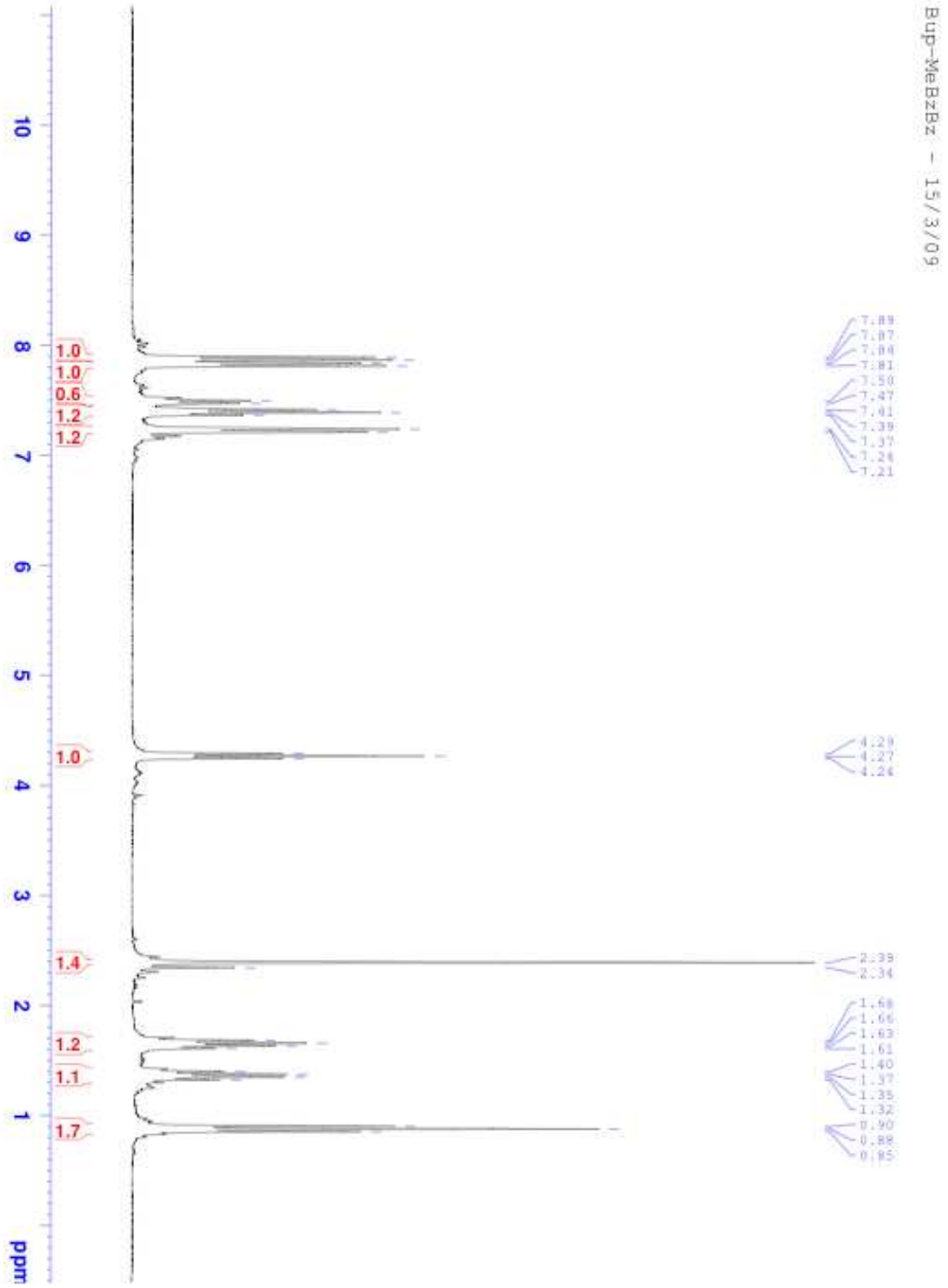
^{1}H NMR *N*-(Adamantane-1-carboxoyloxy)-*N*-butoxybenzamide **13g**



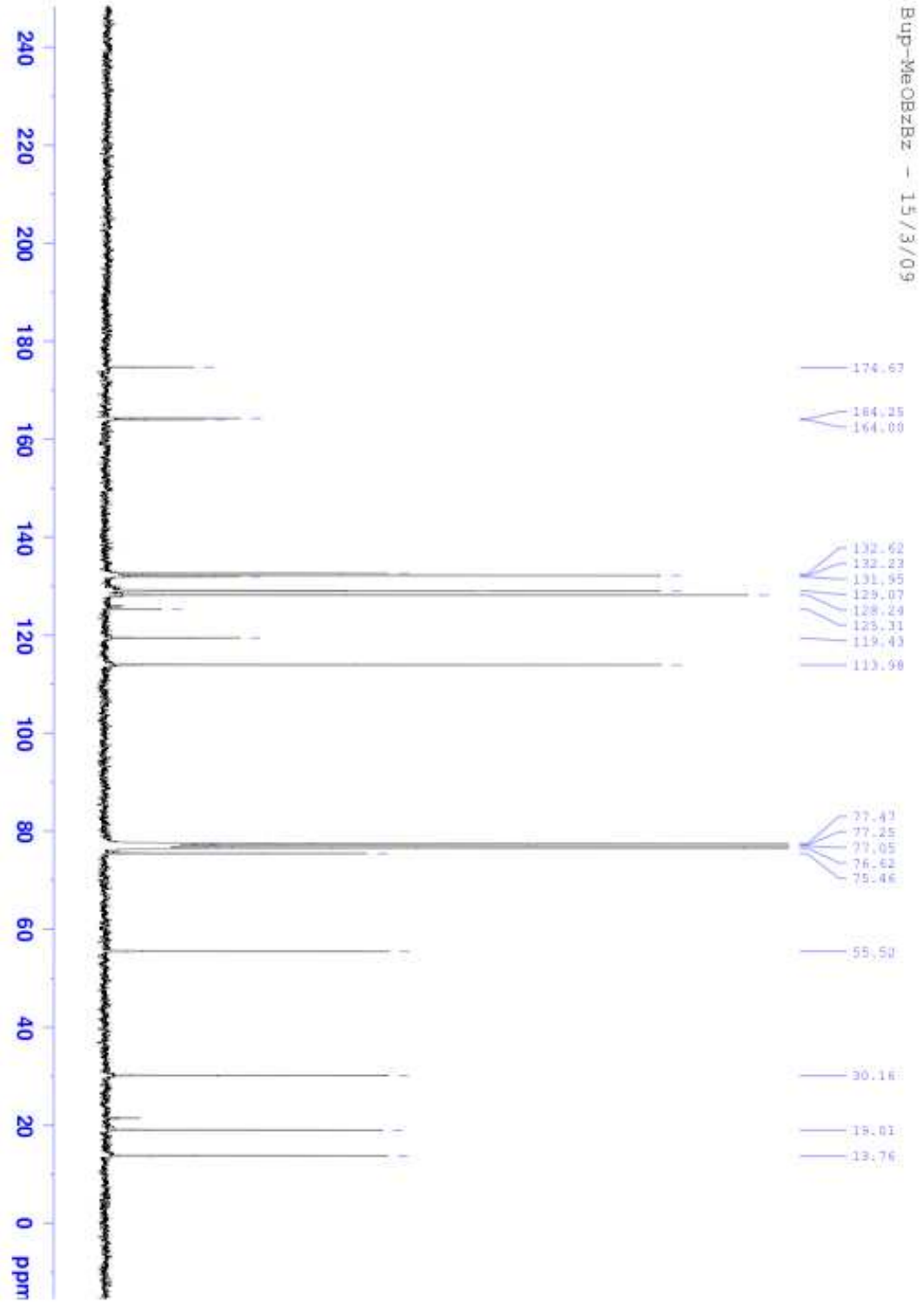
^{13}C NMR *N*-Butoxy-*N*-(4-methylbenzoyloxy)benzamide **14b**



^{1}H NMR *N*-Butoxy-*N*-(4-methylbenzoyloxy)benzamide **14b**



^{13}C NMR *N*-Butoxy-*N*-(4-methoxybenzoyloxy)benzamide**14c**



^{1}H NMR *N*-Butoxy-*N*-(4-methoxybenzoyloxy)benzamide**14c**