Asymmetric Redox-Annulation of Cyclic Amines

YoungKu Kang,[†] Weijie Chen,[†] Martin Breugst,[‡,*] and Daniel Seidel[†,*]

[†] *Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08854,United States*
[‡] *Department für Chemie, Universität zu Köln, Greinstraße 4, 50931 Köln, Germany*

Supporting Information

Table of Contents

Part I: Computational Studies

1. Computational Details……S-2
2. Graphical Representations of the Calculated Transition States……S-3
3. Schematic Overview of All Calculated Pathways……S-4
4. Coordinates and Calculated Energies for the Starting Materials……S-5
5. Coordinates and Calculated Energies for the Products……S-7
6. Coordinates and Calculated Energies for the Intermediates and Transition States of the Uncatalyzed Reaction……S-11
7. Coordinates and Calculated Energies for the Intermediates and Transition States of the Catalyzed Reaction……S-17
8. References……S-31

Part II: Experimental Part

Additional Experiments Regarding the Regioselectivity of the Asymmetric Redox-Annulation……S-32
Crystal Structures for Compounds 6c, 7c and 8c……S-33
2D-NMR Analysis……S-36
HPLC Profiles……S-40
Copies of NMR Spectra……S-47

Part I: Computational Studies

1 Computational Details

For the computational investigations, the conformational space for each structure was explored using the OPLS-2005 force field[1] and a modified Monte Carlo search algorithm implemented in MacroModel 10.6.[2] An energy cut-off of 20 kcal mol^{-1} was employed for the conformational analysis, and structures with heavy-atom root-mean-square deviations (RMSD) less than 2 Å after the initial force field optimizations were considered to be the same conformer. The remaining structures were subsequently optimized with the dispersion-corrected M06-L functional[3] with Grimme's dispersion-correction D3[4] and the double-ζ basis set 6-31+G(d,p). Solvation by toluene was taken into account by using the integral equation formalism polarizable continuum model (IEFPCM)[5] for all calculations. Vibrational analysis verified that each structure was a minimum or transition state. Following the intrinsic reaction coordinates (IRC) confirmed that all transition states connected the corresponding reactants and products on the potential energy surface. Thermal corrections were obtained from unscaled harmonic vibrational frequencies at the same level of theory for a standard state of 1 mol L^{-1} and 298.15 K. Entropic contributions to the reported free energies were derived from partition functions evaluated with the quasiharmonic approximation by Truhlar and coworkers.[6] Electronic energies were subsequently obtained from single point calculations of the M06-L-D3 geometries employing the meta-hybrid M06-2X functional,[7] Grimme's dispersion-correction D3 (zero-damping), the large quadruple-ζ basis set def2-QZVP,[8] and IEFPCM for toluene, a level expected to give accurate energies.[9] An ultrafine grid was used throughout this study for numerical integration of the density. All density functional theory calculations were performed with Gaussian 09.[10]

2 Graphical Representations of the Calculated Transition States

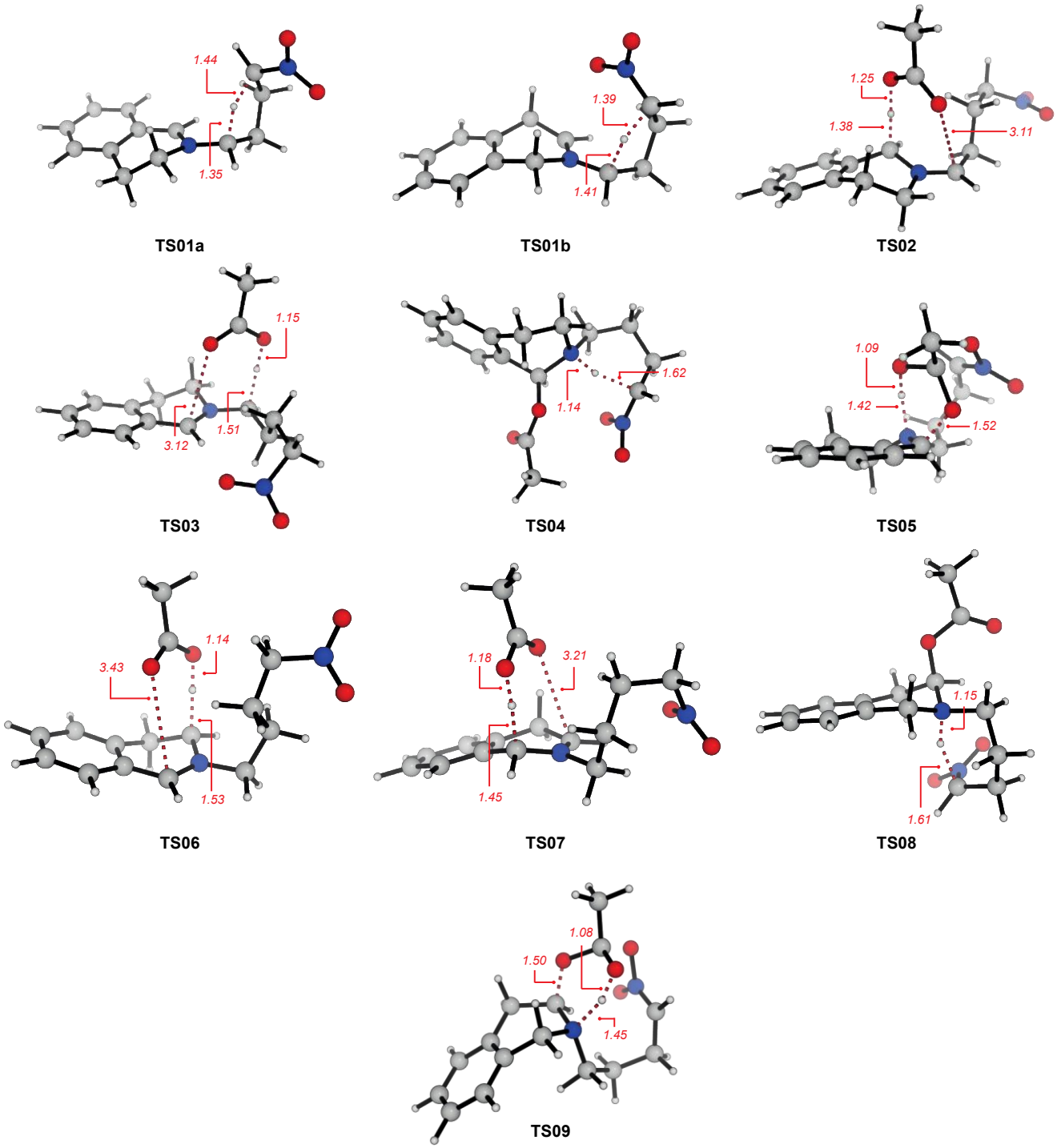
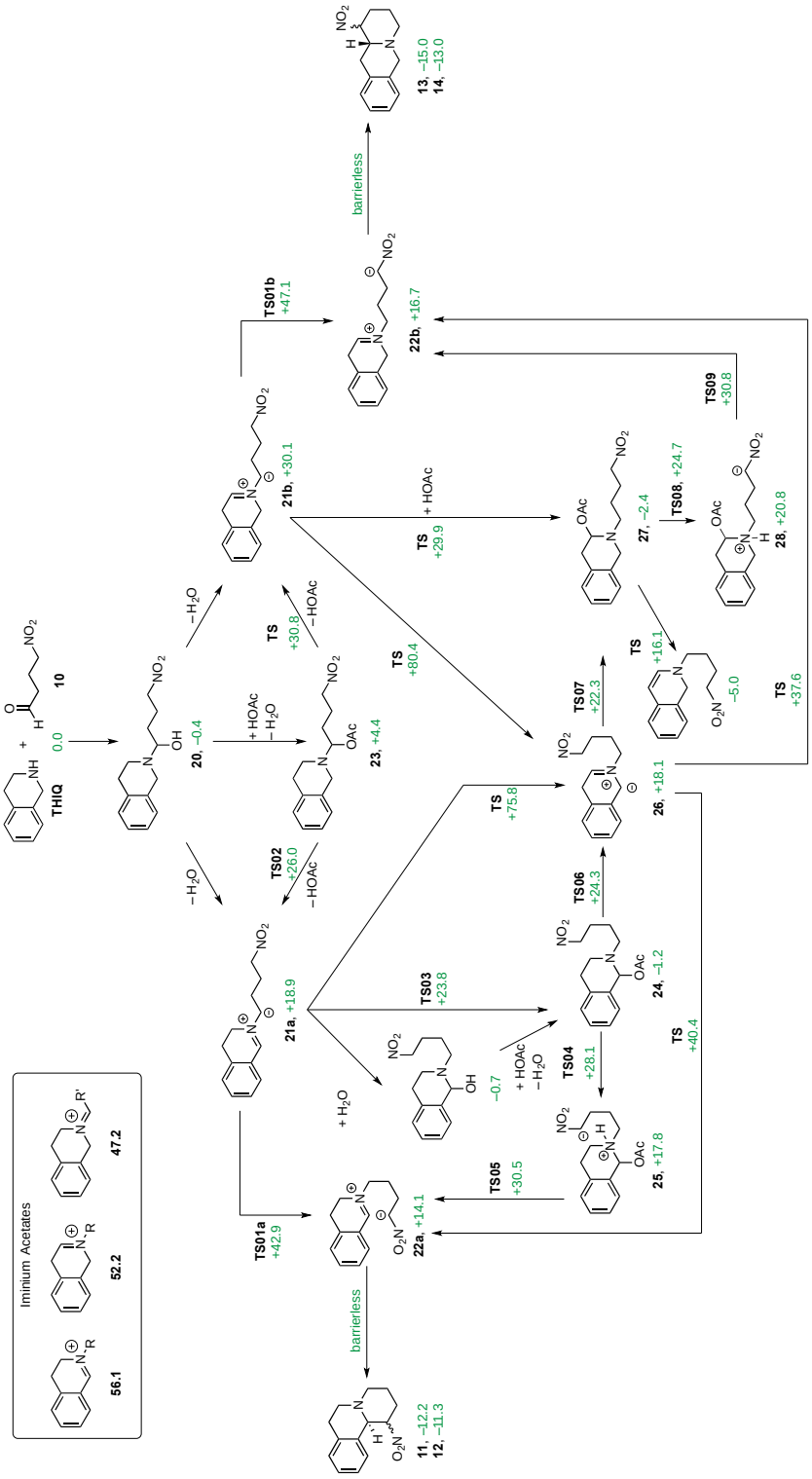


Figure S1. Graphical representation of the calculated transition states and selected bond lengths [in Å, M06-2X-D3/def2-QZVP/IEFPCM//M06-L-D3/6-31+G(d,p)/IEFPCM(toluene)].

3 Schematic Overview of All Calculated Pathways



Scheme S1. Overview about the most important pathways analyzed in redox-annulation reactions [in kcal mol^{-1}, M06-2X-D3/def2-QZVP/IEFPCM//M06-L-D3/6-31+G(d,p)/IEFPCM(toluene)].

4 Coordinates and Calculated Energies for the Starting Materials

4.1 Tetrahydroisoquinoline (THIQ)

SCF energy:	–404.337930 hartree
Zero-point correction:	+0.182575 hartree
Enthalpy correction:	+0.191319 hartree
Free energy correction:	+0.150162 hartree
Quasiharmonic free energy correction:	+0.150166 hartree

Cartesian Coordinates

C	2.55286	0.70273	-0.01907
C	1.34392	1.38973	-0.04921
C	2.55265	-0.69193	0.03042
C	1.34240	-1.37702	0.04964
C	0.12243	-0.69313	0.01502
C	0.12048	0.70943	-0.03250
C	-1.18055	1.46970	-0.07593
C	-2.36365	0.60521	0.34422
H	-1.35088	1.83904	-1.09829
H	-1.11085	2.36684	0.55218
N	-2.37113	-0.70391	-0.30565
H	-3.31011	1.11343	0.13385
H	-2.33417	0.42821	1.42763
C	-1.17935	-1.46179	0.05799
H	1.33654	-2.46549	0.08810
H	3.49099	1.25071	-0.03162
H	3.49052	-1.24022	0.05166
H	1.33936	2.47809	-0.08250
H	-1.11566	-2.34405	-0.58873
H	-1.32916	-1.85194	1.07639
H	-2.37579	-0.56485	-1.31253

4.2 4-Nitrobutyraldehyde (10)

SCF energy:	–436.993135 hartree
Zero-point correction:	+0.116927 hartree
Enthalpy correction:	+0.126154 hartree
Free energy correction:	+0.082284 hartree
Quasiharmonic free energy correction:	+0.084098 hartree

Cartesian Coordinates

C	2.12003	-0.43658	0.40151
O	2.39360	-0.52788	-0.77817
C	1.10587	0.51299	0.96554
C	0.32405	1.29776	-0.07489
H	0.45258	-0.05240	1.64442
H	1.65105	1.19565	1.63167
C	-0.56473	0.43639	-0.96032
H	1.01772	1.81742	-0.74292
H	-0.28779	2.06159	0.41379
N	-1.55106	-0.30391	-0.09970
H	0.00174	-0.32005	-1.50118

H	-1.15616	1.04727	-1.64237
O	-1.29824	-1.47582	0.17437
O	-2.51729	0.32680	0.32265
H	2.64238	-1.07033	1.15265

4.3 Acetic Acid

SCF energy:	–229.112050 hartree
Zero-point correction:	+0.061927 hartree
Enthalpy correction:	+0.067449 hartree
Free energy correction:	+0.034631 hartree
Quasiharmonic free energy correction:	+0.035068 hartree

Cartesian Coordinates

C	1.38675	-0.10636	0.00000
C	-0.08862	0.12396	0.00000
H	1.67529	-0.69006	0.87720
H	1.91410	0.84505	0.00013
H	1.67530	-0.68981	-0.87736
O	-0.64631	1.20199	0.00000
O	-0.77105	-1.04548	0.00000
H	-1.71464	-0.82291	-0.00001

4.4 Water

SCF energy:	–76.439399 hartree
Zero-point correction:	+0.021648 hartree
Enthalpy correction:	+0.025428 hartree
Free energy correction:	+0.004006 hartree
Quasiharmonic free energy correction:	+0.004006 hartree

Cartesian Coordinates

O	0.00000	0.00000	0.11771
H	0.00000	0.76000	-0.47085
H	0.00000	-0.76000	-0.47085

5 Coordinates and Calculated Energies for the Products

5.1 Product 11

SCF energy:	–764.920237 hartree
Zero-point correction:	+0.278524 hartree
Enthalpy correction:	+0.292980 hartree
Free energy correction:	+0.238514 hartree
Quasiharmonic free energy correction:	+0.239443 hartree

Cartesian Coordinates

C	3.78740	0.10412	-0.00288
C	3.09483	-1.04408	0.36327
C	3.10008	1.16725	-0.58735
C	1.72755	1.07254	-0.78461
C	1.02015	-0.07234	-0.39767
C	1.71336	-1.15228	0.16891
C	1.00331	-2.43443	0.50500
C	-0.50204	-2.26542	0.56129
H	1.37555	-2.83701	1.45406
H	1.24832	-3.18092	-0.26210
N	-0.95036	-1.51122	-0.60744
C	-0.47465	-0.13557	-0.60380
H	1.19483	1.89714	-1.25324
H	4.85966	0.16766	0.15956
H	3.62992	2.06485	-0.89175
H	3.62909	-1.88308	0.80521
C	-2.38610	-1.59897	-0.85721
C	-3.22410	-0.82312	0.15179
C	-2.77069	0.62963	0.18450
H	-3.12906	-1.27410	1.14851
H	-4.28433	-0.87769	-0.11492
C	-1.27399	0.70107	0.45482
H	-2.96803	1.10566	-0.78388
H	-3.31296	1.20255	0.94383
N	-0.81669	2.12713	0.41108
O	-1.10935	2.78133	-0.59372
O	-0.13987	2.54778	1.34782
H	-2.66018	-2.65894	-0.87384
H	-2.56949	-1.20076	-1.86501
H	-0.79342	-1.79050	1.51721
H	-1.00078	-3.23985	0.53855
H	-0.72608	0.30578	-1.58066
H	-1.02049	0.36450	1.46374

5.2 Product 12

SCF energy:	–764.918742 hartree
Zero-point correction:	+0.278012 hartree
Enthalpy correction:	+0.292426 hartree
Free energy correction:	+0.237739 hartree
Quasiharmonic free energy correction:	+0.239291 hartree

Cartesian Coordinates

C	-3.86543	-0.53526	-0.10945
C	-3.23875	0.53901	0.51138
C	-3.12590	-1.37337	-0.94437
C	-1.77017	-1.13359	-1.13218
C	-1.12835	-0.07240	-0.48618
C	-1.87364	0.78504	0.33140
C	-1.20142	1.96151	0.97650
C	0.00987	2.38836	0.17337
H	-0.87731	1.70018	1.99280
H	-1.90839	2.79270	1.07412
N	0.92284	1.26157	0.03519
C	0.34491	0.16111	-0.73579
H	-1.20114	-1.78720	-1.79152
H	-4.92613	-0.71171	0.04450
H	-3.60426	-2.20781	-1.44896
H	-3.81231	1.21001	1.14793
C	2.20076	1.65598	-0.55282
C	3.21039	0.52438	-0.46117
C	2.65328	-0.77214	-1.04034
H	3.47777	0.36801	0.58831
H	4.12821	0.80309	-0.98836
C	1.25407	-1.06069	-0.53005
H	2.56602	-0.68795	-2.13140
H	3.31819	-1.61428	-0.83722
N	1.27620	-1.45313	0.95508
O	0.19617	-1.54620	1.52631
O	2.36457	-1.68349	1.47524
H	2.56513	2.53648	-0.01341
H	2.05952	1.95978	-1.61255
H	0.55193	3.19272	0.68126
H	-0.30421	2.78333	-0.81453
H	0.44542	0.37883	-1.82507
H	0.82465	-1.94535	-1.01204

5.3 Product 13

SCF energy:	–764.923818 hartree
Zero-point correction:	+0.277841 hartree
Enthalpy correction:	+0.292579 hartree
Free energy correction:	+0.236619 hartree
Quasiharmonic free energy correction:	+0.238482 hartree

Cartesian Coordinates

C	-4.08136	-1.28998	-0.10942
C	-2.73957	-1.62967	-0.24070
C	-4.43888	0.03951	0.12057
C	-3.44936	1.01135	0.21714
C	-2.09839	0.67423	0.08534
C	-1.73878	-0.65658	-0.14539
C	-0.29489	-1.02049	-0.32161
C	0.67662	0.04789	0.17067
H	-0.09710	-1.20184	-1.38814
H	-0.08359	-1.96842	0.18834
N	0.26008	1.36906	-0.30764

C	-1.04443	1.72788	0.24589
H	-3.72257	2.04967	0.39622
H	-4.84633	-2.05750	-0.18462
H	-5.48441	0.31608	0.22190
H	-2.45491	-2.66481	-0.41906
C	1.21090	2.41704	0.06659
C	2.60037	2.15006	-0.47299
C	3.10245	0.80604	0.03064
H	3.27821	2.94893	-0.15829
H	2.57971	2.15864	-1.56952
C	2.08424	-0.24659	-0.36351
H	4.08460	0.55885	-0.38442
H	3.19598	0.81794	1.12338
N	2.51710	-1.59959	0.15922
O	2.73048	-2.48897	-0.66119
O	2.62340	-1.72304	1.37782
H	1.25828	2.51355	1.17256
H	0.81986	3.36654	-0.31484
H	0.72852	0.03247	1.28036
H	-1.36505	2.65990	-0.23527
H	-0.94194	1.96626	1.32740
H	2.04580	-0.37060	-1.44953

5.4 Product 14

SCF energy:	–764.921521 hartree
Zero-point correction:	+0.278430 hartree
Enthalpy correction:	+0.292955 hartree
Free energy correction:	+0.237485 hartree
Quasiharmonic free energy correction:	+0.239385 hartree

Cartesian Coordinates

C	-3.74984	-1.43092	-0.74790
C	-2.37045	-1.60011	-0.79429
C	-4.28926	-0.32844	-0.08396
C	-3.43952	0.58802	0.52598
C	-2.05158	0.42224	0.48658
C	-1.50782	-0.68405	-0.18156
C	-0.01575	-0.87753	-0.27168
C	0.75830	0.06065	0.66229
H	0.29801	-0.72757	-1.31439
H	0.23896	-1.91948	-0.04098
N	0.22701	1.42771	0.68825
C	-1.14178	1.40269	1.18861
H	-3.85365	1.45249	1.04251
H	-4.40236	-2.15442	-1.22836
H	-5.36526	-0.18320	-0.04682
H	-1.94576	-2.45820	-1.31219
C	0.35019	2.09973	-0.60727
C	1.81820	2.23535	-0.97294
C	2.50492	0.87337	-0.99940
H	2.30723	2.88432	-0.23592
H	1.92034	2.72050	-1.94834
C	2.24978	0.16525	0.31402
H	2.11776	0.27037	-1.82747

H	3.58084	0.97304	-1.16860
N	2.83123	-1.23942	0.33031
O	3.24641	-1.71912	-0.72028
O	2.82010	-1.82051	1.41380
H	-0.11388	3.08666	-0.50899
H	-0.19756	1.57326	-1.41381
H	0.68088	-0.32344	1.68763
H	-1.10041	1.15985	2.26067
H	-1.55082	2.41752	1.12180
H	2.75350	0.66976	1.14430

6 Coordinates and Calculated Energies for the Intermediates and Transition States of the Uncatalyzed Reaction

6.1 Hemiaminal 20

SCF energy:	–841.356794 hartree
Zero-point correction:	+0.304126 hartree
Enthalpy correction:	+0.321268 hartree
Free energy correction:	+0.258999 hartree
Quasiharmonic free energy correction:	+0.262352 hartree

Cartesian Coordinates

C	5.31126	0.61652	0.07469
C	4.17240	1.39502	0.25051
C	5.17993	-0.74621	-0.19592
C	3.91192	-1.30981	-0.28490
C	2.76253	-0.53266	-0.10602
C	2.89200	0.83685	0.16340
C	1.66451	1.68359	0.35997
C	0.41951	1.00020	-0.17433
H	1.79701	2.65783	-0.12535
H	1.52742	1.88858	1.43015
N	0.34893	-0.35981	0.36311
H	-0.47268	1.56074	0.12016
H	0.44107	0.98683	-1.28102
C	1.40688	-1.17102	-0.23339
H	3.80422	-2.37290	-0.49380
H	6.29651	1.06895	0.14523
H	6.06168	-1.36560	-0.33431
H	4.26919	2.45958	0.45661
H	1.19465	-1.36572	-1.30318
H	1.40984	-2.14968	0.26292
C	-0.94543	-0.99641	0.21519
C	-1.97140	-0.38391	1.16284
H	-0.80010	-2.04976	0.49058
O	-1.40781	-1.05991	-1.13961
C	-3.34797	-1.04115	1.15244
H	-2.07213	0.69244	0.97652
H	-1.56000	-0.46529	2.17365
C	-4.19527	-0.82911	-0.09984
H	-3.91834	-0.68247	2.01553
H	-3.25078	-2.12656	1.27321
N	-4.28486	0.64064	-0.39780
H	-5.21978	-1.16666	0.05480
H	-3.75203	-1.29306	-0.97918
H	-1.79187	-0.19964	-1.36875
O	-3.42636	1.12537	-1.14287
O	-5.16305	1.28768	0.16015

6.2 Azomethine Ylide 21a

SCF energy:	–764.863375 hartree
Zero-point correction:	+0.273552 hartree

Enthalpy correction: +0.290090 hartree
Free energy correction: +0.228123 hartree
Quasiharmonic free energy correction: +0.232133 hartree

Cartesian Coordinates

C	-5.42968	-0.84406	0.11887
C	-4.83248	0.41060	0.26972
C	-4.61910	-1.96085	-0.09877
C	-3.23905	-1.82747	-0.17981
C	-2.62478	-0.56455	-0.04022
C	-3.45345	0.55948	0.20275
C	-2.74931	1.86342	0.43371
C	-1.50690	1.95787	-0.42674
H	-2.45785	1.95275	1.49055
H	-3.40043	2.71590	0.21628
N	-0.61004	0.79789	-0.20183
H	-1.77152	1.94874	-1.49022
H	-0.93105	2.86151	-0.22165
C	-1.20532	-0.41833	-0.10305
H	-2.61607	-2.70141	-0.35874
H	-6.50909	-0.94762	0.17357
H	-5.06904	-2.94373	-0.21316
H	-5.44963	1.28863	0.45409
C	0.70591	1.02973	-0.21177
C	1.66043	-0.09010	-0.08832
C	3.10760	0.38564	-0.06054
H	1.51935	-0.81382	-0.91442
H	1.43449	-0.67537	0.82327
C	4.05072	-0.78112	0.07871
H	3.25839	1.08339	0.76943
H	3.33931	0.93977	-0.97588
N	5.50547	-0.38120	0.10157
H	3.97541	-1.49614	-0.74535
H	3.90571	-1.34346	1.00531
O	6.31874	-1.29420	0.21769
O	5.78719	0.80898	0.00465
H	-0.55297	-1.28195	-0.11333
H	1.02199	2.05621	-0.34405

6.3 Azomethine Ylide 21b

SCF energy: –764.845286 hartree
Zero-point correction: +0.273004 hartree
Enthalpy correction: +0.289574 hartree
Free energy correction: +0.227165 hartree
Quasiharmonic free energy correction: +0.231872 hartree

Cartesian Coordinates

C	4.85666	0.75582	-1.00661
C	3.88386	1.46238	-0.29980
C	4.77591	-0.63198	-1.11074
C	3.72023	-1.31306	-0.50647
C	2.75332	-0.60660	0.20753

C	2.83060	0.78651	0.31416
C	1.72808	1.46210	1.07972
C	0.42089	0.77977	0.84807
H	1.64326	2.51170	0.78027
H	2.00772	1.49212	2.15212
N	0.34632	-0.56270	0.79390
C	1.63270	-1.29207	0.92378
H	3.64676	-2.39521	-0.59079
H	5.67362	1.29001	-1.48352
H	5.52803	-1.18254	-1.66810
H	3.94035	2.54640	-0.22703
C	-0.75854	-1.32635	0.68924
C	-2.08613	-0.68535	0.58268
C	-2.34621	-0.03037	-0.78620
H	-2.19843	0.08565	1.36827
H	-2.86450	-1.43072	0.77775
C	-3.51595	0.92642	-0.77863
H	-2.50388	-0.80306	-1.54361
H	-1.46734	0.54535	-1.10048
N	-4.80417	0.23173	-0.40286
H	-3.71203	1.34707	-1.76852
H	-3.40694	1.73934	-0.05873
O	-5.54576	0.79634	0.39780
O	-5.03737	-0.84988	-0.93723
H	-0.60148	-2.39117	0.59703
H	-0.51083	1.32871	0.84550
H	1.47895	-2.30882	0.55817
H	1.84431	-1.35316	1.99940

6.4 Transition State TS01a

SCF energy:	–764.823102 hartree
Zero-point correction:	+0.270371 hartree
Enthalpy correction:	+0.285674 hartree
Free energy correction:	+0.227573 hartree
Quasiharmonic free energy correction:	+0.230006 hartree
Imaginary Frequency:	1375.3 *i*cm^{-1}

Cartesian Coordinates

C	-4.76847	-0.62787	-0.64088
C	-4.15099	0.62105	-0.53901
C	-4.06138	-1.78626	-0.31229
C	-2.74031	-1.69922	0.10522
C	-2.10567	-0.44639	0.19216
C	-2.83011	0.72554	-0.12295
C	-2.12558	2.03194	0.08917
C	-0.64605	1.90815	-0.20717
H	-2.26085	2.35555	1.13103
H	-2.55068	2.82112	-0.53722
N	-0.03782	0.77516	0.52683
H	-0.09767	2.80881	0.07225
H	-0.46882	1.72524	-1.27448
C	-0.74509	-0.34457	0.62818
H	-2.18226	-2.59767	0.35720

H	-5.80018	-0.69542	-0.97221
H	-4.54212	-2.75694	-0.38578
H	-4.70678	1.52425	-0.78032
C	1.33415	0.87965	0.79212
C	1.96718	-0.16252	1.68432
C	2.47698	-1.31834	0.78607
H	1.29012	-0.50859	2.47524
H	2.82418	0.30445	2.17470
C	2.76778	-0.75423	-0.58112
H	1.71535	-2.09936	0.67490
H	3.35904	-1.78900	1.22991
N	4.05307	-0.21350	-0.78399
H	1.97561	0.41303	-0.29812
H	2.41961	-1.26770	-1.47243
O	4.46668	-0.05042	-1.95449
O	4.69802	0.16980	0.22234
H	-0.24200	-1.20471	1.05581
H	1.60842	1.91873	0.96397

6.5 Transition State TS01b

SCF energy:	–764.816277 hartree
Zero-point correction:	+0.269856 hartree
Enthalpy correction:	+0.285111 hartree
Free energy correction:	+0.227399 hartree
Quasiharmonic free energy correction:	+0.229949 hartree
Imaginary Frequency:	1366.9 *i*cm^{-1}

Cartesian Coordinates

C	4.57022	-0.50321	-0.34104
C	3.44355	-0.71550	-1.13262
C	4.43784	0.06669	0.92457
C	3.17713	0.42279	1.39761
C	2.04721	0.19639	0.61187
C	2.17775	-0.37572	-0.65697
C	0.92436	-0.56736	-1.46085
C	-0.08279	0.47899	-1.17128
H	0.45151	-1.53768	-1.21694
H	1.13371	-0.59877	-2.53317
N	-0.23794	0.96779	0.03313
C	0.67214	0.51160	1.10826
H	3.06887	0.87554	2.38051
H	5.55269	-0.77523	-0.71540
H	5.31566	0.24087	1.53941
H	3.54496	-1.14907	-2.12473
C	-1.36960	1.68510	0.48880
C	-2.38968	2.07660	-0.54168
C	-3.27265	0.82782	-0.82741
H	-1.96711	2.50298	-1.46077
H	-3.00513	2.86562	-0.09827
C	-3.33241	0.00535	0.43925
H	-2.83669	0.21244	-1.62046
H	-4.26965	1.13004	-1.16188
N	-2.92444	-1.34264	0.38452

H	-4.21322	0.09283	1.06962
H	-2.24000	0.69266	0.97563
O	-2.03256	-1.68892	-0.43737
O	-3.39437	-2.14841	1.22090
H	-1.08287	2.41679	1.24268
H	-0.79568	0.78389	-1.92617
H	0.19592	-0.37523	1.54967
H	0.68069	1.28759	1.87749

6.6 Zwitterion 22a

SCF energy: –764.874916 hartree
Zero-point correction: +0.275710 hartree
Enthalpy correction: +0.291015 hartree
Free energy correction: +0.234745 hartree
Quasiharmonic free energy correction: +0.235936 hartree

Cartesian Coordinates

C	3.99802	0.07944	-0.23090
C	3.01598	-0.34612	-1.12754
C	3.67424	0.34424	1.10020
C	2.36605	0.17717	1.53547
C	1.38160	-0.26106	0.64065
C	1.70304	-0.51764	-0.70661
C	0.57796	-0.87862	-1.62935
C	-0.46777	-1.71860	-0.92256
H	0.94170	-1.42239	-2.50586
H	0.12417	0.05776	-1.98440
N	-0.85086	-1.13436	0.37380
C	0.02802	-0.46470	1.09408
H	2.09329	0.39002	2.56589
H	5.01946	0.21116	-0.57593
H	4.43875	0.68480	1.79127
H	3.27246	-0.53321	-2.16739
C	-2.14813	-1.51382	0.93669
C	-3.34539	-0.93109	0.20167
C	-3.33450	0.60089	0.14264
H	-4.24331	-1.29158	0.71884
H	-3.39963	-1.34205	-0.81489
C	-2.28636	1.15364	-0.75179
H	-3.20393	1.00714	1.15126
H	-4.31916	0.92990	-0.21370
N	-1.14574	1.68484	-0.30573
O	-0.27728	2.17049	-1.10551
O	-0.87864	1.63853	0.96829
H	-2.14919	-1.18150	1.97903
H	-2.19887	-2.61039	0.93484
H	-2.42388	1.22890	-1.82478
H	-0.23601	-0.25273	2.12232
H	-0.09614	-2.73523	-0.72396
H	-1.37277	-1.80855	-1.52723

6.7 Zwitterion 22b

SCF energy:	–764.869977 hartree
Zero-point correction:	+0.275010 hartree
Enthalpy correction:	+0.290413 hartree
Free energy correction:	+0.233802 hartree
Quasiharmonic free energy correction:	+0.235158 hartree

Cartesian Coordinates

C	-4.33364	0.30762	-0.20448
C	-3.23639	0.97472	-0.74425
C	-4.14138	-0.80303	0.61640
C	-2.85034	-1.24444	0.89573
C	-1.75043	-0.56889	0.36719
C	-1.94086	0.54626	-0.45481
C	-0.72148	1.24038	-0.99022
C	0.39314	0.28829	-1.23034
H	-0.34119	1.96560	-0.25191
H	-0.93213	1.79985	-1.90486
N	0.54641	-0.77022	-0.48398
C	-0.34494	-0.98205	0.68002
H	-2.69471	-2.11497	1.52908
H	-5.33910	0.65087	-0.42967
H	-4.99542	-1.32947	1.03192
H	-3.38342	1.83710	-1.39020
C	1.61116	-1.76179	-0.76139
C	2.98060	-1.14952	-1.00759
C	3.64482	-0.58496	0.26035
H	2.90587	-0.36678	-1.76750
H	3.61589	-1.93203	-1.43779
C	2.73171	0.13297	1.18712
H	4.48190	0.05141	-0.05847
H	4.08848	-1.41267	0.82589
N	2.01527	1.18314	0.79468
O	2.14883	1.61507	-0.42491
O	1.11248	1.70636	1.54285
H	1.01751	0.36903	-2.11114
H	0.05718	-0.38413	1.50988
H	-0.28776	-2.03888	0.94998
H	1.29018	-2.35447	-1.62578
H	1.64038	-2.42850	0.10480
H	2.60217	-0.14712	2.22501

7 Coordinates and Calculated Energies for the Intermediates and Transition States of the Catalyzed Reaction

7.1 Acetylated Hemiaminal 23

SCF energy:	–994.023095 hartree
Zero-point correction:	+0.340494 hartree
Enthalpy correction:	+0.361408 hartree
Free energy correction:	+0.288510 hartree
Quasiharmonic free energy correction:	+0.294750 hartree

Cartesian Coordinates

C	5.19952	-1.50014	0.09796
C	4.45873	-0.74629	1.00130
C	4.60089	-1.95298	-1.07846
C	3.27014	-1.64290	-1.33454
C	2.52223	-0.88060	-0.43144
C	3.11868	-0.42688	0.75337
C	2.32991	0.39609	1.73577
C	0.83578	0.26977	1.50590
H	2.61486	1.45240	1.64177
H	2.58022	0.10034	2.76096
N	0.56274	0.50038	0.08793
H	0.28940	1.01612	2.08965
H	0.48368	-0.72950	1.82647
C	1.07837	-0.58304	-0.73542
H	2.79779	-1.99216	-2.25109
H	6.23815	-1.73735	0.31026
H	5.16924	-2.54253	-1.79207
H	4.92029	-0.39605	1.92269
H	0.96829	-0.29756	-1.79072
H	0.48711	-1.51436	-0.60853
C	-0.80626	0.83106	-0.22488
C	-1.87677	-0.06435	0.37658
H	-0.89625	0.81730	-1.32166
O	-1.09869	2.15788	0.26775
C	-3.26964	0.26724	-0.13905
H	-1.84729	0.02809	1.46907
H	-1.61981	-1.10312	0.13296
C	-4.34588	-0.62817	0.41855
H	-3.29096	0.22057	-1.23342
H	-3.52754	1.29467	0.13843
N	-4.21281	-2.06860	-0.03342
H	-5.34607	-0.34022	0.08322
H	-4.35945	-0.67694	1.50891
C	-0.56007	3.25937	-0.32588
O	-4.76790	-2.91669	0.65820
O	-3.58966	-2.29760	-1.06631
C	0.16880	3.08204	-1.62342
H	0.55365	4.04762	-1.94492
H	-0.50319	2.69503	-2.39574
H	0.98994	2.36964	-1.51215
O	-0.73102	4.32942	0.21614

7.2 Transition State TS02

SCF energy:	–993.980516 hartree
Zero-point correction:	+0.333549 hartree
Enthalpy correction:	+0.355139 hartree
Free energy correction:	+0.280771 hartree
Quasiharmonic free energy correction:	+0.286603 hartree
Imaginary Frequency:	1295.2 *i*cm^{-1}

Cartesian Coordinates

C	-4.98555	-1.31784	-0.69737
C	-4.54094	-0.38616	0.24231
C	-4.05708	-2.05487	-1.43150
C	-2.69171	-1.87156	-1.22276
C	-2.24049	-0.93971	-0.28191
C	-3.17914	-0.18367	0.44252
C	-2.60076	0.81298	1.39922
C	-1.43952	0.20014	2.15786
H	-3.34435	1.16354	2.12057
H	-2.23305	1.69618	0.86018
N	-0.40989	-0.35208	1.24047
H	-1.78480	-0.63663	2.77537
H	-0.94194	0.93202	2.79576
C	-0.81209	-0.63073	-0.09897
H	-1.96901	-2.45349	-1.79099
H	-6.04976	-1.46692	-0.85452
H	-4.39677	-2.78220	-2.16366
H	-5.25805	0.19676	0.81702
H	-0.57078	0.55384	-0.76289
H	-0.12932	-1.34061	-0.57056
C	0.81400	-0.43294	1.67880
C	1.93584	-0.97754	0.88092
H	0.98911	-0.03517	2.67325
O	0.26790	2.42471	0.59088
C	2.49154	0.03621	-0.13171
H	1.60953	-1.88200	0.34696
H	2.73218	-1.27824	1.56789
C	3.55953	-0.54893	-1.01822
H	2.87429	0.91462	0.39365
H	1.68870	0.39470	-0.78459
N	4.81178	-0.95118	-0.26670
H	3.91663	0.17110	-1.75948
H	3.25026	-1.45068	-1.55056
C	0.01996	2.56441	-0.61418
O	5.54119	-1.77365	-0.81250
O	5.03410	-0.41902	0.81690
C	0.14351	3.90348	-1.29955
H	0.80748	3.82800	-2.16458
H	0.52104	4.65967	-0.61130
H	-0.83206	4.21583	-1.68191
O	-0.36759	1.60334	-1.40837

7.3 Transition State 03

SCF energy:	–993.984724 hartree
Zero-point correction:	+0.333745 hartree
Enthalpy correction:	+0.355224 hartree
Free energy correction:	+0.280993 hartree
Quasiharmonic free energy correction:	+0.287269 hartree
Imaginary Frequency:	707.4 *i*cm^{-1}

Cartesian Coordinates

C	4.36905	-1.62869	-0.98008
C	4.25915	-0.69029	0.04857
C	3.22338	-2.22869	-1.50543
C	1.97067	-1.88521	-1.01269
C	1.85309	-0.92866	0.00888
C	3.01289	-0.33769	0.55170
C	2.81046	0.59918	1.70494
C	1.51537	1.36833	1.55193
H	3.64009	1.30635	1.79533
H	2.78634	0.02580	2.64301
N	0.36673	0.47135	1.30724
H	1.55239	2.04270	0.68652
H	1.28198	1.96262	2.43743
C	0.56122	-0.57500	0.52890
H	1.07092	-2.34119	-1.41927
H	5.34840	-1.89287	-1.36815
H	3.30904	-2.96142	-2.30222
H	5.15319	-0.23289	0.46686
C	-0.88314	0.99850	1.67673
C	-2.07052	0.10189	1.45211
O	-0.04619	1.84383	-1.35177
C	-2.61932	0.14982	0.02095
H	-1.83043	-0.94284	1.72129
H	-2.86378	0.40924	2.14278
C	-3.70611	-0.85921	-0.24041
H	-1.81748	0.03717	-0.71582
H	-3.04812	1.14046	-0.16580
N	-3.21022	-2.29171	-0.23427
H	-4.15459	-0.74717	-1.23161
H	-4.51288	-0.84553	0.49556
O	-2.01924	-2.49868	-0.45922
O	-4.04666	-3.16603	-0.03329
H	-0.30800	-1.15874	0.24804
H	-1.03103	2.21651	0.79470
H	-0.80956	1.42875	2.67801
C	-0.63645	2.88473	-1.06138
C	-0.81522	4.01774	-2.03756
H	-0.30166	3.80335	-2.97426
H	-0.43604	4.95013	-1.61229
H	-1.87936	4.17326	-2.23472
O	-1.17693	3.12692	0.11437

7.4 Acetylated Hemiaminal 24

SCF energy:	–994.032938 hartree
Zero-point correction:	+0.341345 hartree
Enthalpy correction:	+0.362243 hartree
Free energy correction:	+0.289766 hartree
Quasiharmonic free energy correction:	+0.295584 hartree

Cartesian Coordinates

C	4.18136	-2.16378	-0.70910
C	3.21931	-2.50280	0.23645
C	4.04417	-0.99140	-1.45438
C	2.94295	-0.17097	-1.24242
C	1.97401	-0.51132	-0.29367
C	2.10621	-1.68482	0.45845
C	1.05000	-2.05816	1.46041
C	0.19100	-0.86940	1.84785
H	1.51080	-2.50107	2.35017
H	0.40565	-2.83668	1.02786
N	-0.25756	-0.18429	0.63472
H	0.74202	-0.18584	2.51641
H	-0.69885	-1.20193	2.39149
C	0.80728	0.40750	-0.09033
H	2.82306	0.74700	-1.81491
H	5.03968	-2.81144	-0.86422
H	4.79087	-0.72181	-2.19532
H	3.32868	-3.41483	0.81990
C	-1.41265	0.68836	0.83280
C	-2.08212	1.08786	-0.47753
O	1.33709	1.60356	0.65685
C	-2.33779	-0.08322	-1.42189
H	-3.02784	1.58582	-0.22966
H	-1.48394	1.84000	-1.00370
C	-3.03179	-1.26377	-0.76928
H	-1.38926	-0.47022	-1.81070
H	-2.92305	0.24976	-2.28401
N	-4.36214	-0.84107	-0.19797
H	-2.46202	-1.68214	0.06170
H	-3.26456	-2.04537	-1.49520
O	-5.19071	-0.39334	-0.98623
O	-4.52973	-0.94613	1.01552
H	0.44528	0.80928	-1.04062
H	-1.14914	1.59309	1.40850
H	-2.12086	0.12881	1.45515
C	1.21536	2.81126	0.07751
C	1.67009	3.89326	1.00862
H	2.64718	3.65305	1.43201
H	0.97011	3.97264	1.84501
H	1.71059	4.84643	0.48455
O	0.78575	2.99734	-1.04772

7.5 Transition State TS04

SCF energy:	–993.984958 hartree
Zero-point correction:	+0.338025 hartree
Enthalpy correction:	+0.357655 hartree
Free energy correction:	+0.290625 hartree
Quasiharmonic free energy correction:	+0.293419 hartree
Imaginary Frequency:	643.8 *i*cm^{-1}

Cartesian Coordinates

C	2.37642	-0.63251	0.82918
C	1.38058	-1.11481	1.84082
C	1.85099	-0.03157	-0.32275
C	0.36841	0.15304	-0.38625
N	-0.37766	-1.06748	0.04148
C	0.27772	-1.87859	1.12753
C	-0.79029	-1.92504	-1.12266
C	-1.99822	-2.75395	-0.72938
H	0.07211	-2.52851	-1.42770
H	-1.05784	-1.24052	-1.93216
C	-3.22795	-1.88063	-0.44948
H	-1.75628	-3.37825	0.14125
H	-2.21030	-3.44990	-1.54696
C	-3.01046	-0.75611	0.54361
H	-4.03579	-2.52724	-0.08792
H	-3.56288	-1.44566	-1.39844
N	-3.01397	0.53989	0.04748
H	-3.50856	-0.80365	1.50704
O	-2.57516	0.74106	-1.12747
O	-3.32958	1.50135	0.79597
C	2.68984	0.40705	-1.34502
C	4.06845	0.24755	-1.21862
C	4.59824	-0.34781	-0.07469
C	3.75527	-0.79273	0.94407
H	4.16973	-1.26699	1.83065
H	5.67285	-0.47171	0.02339
H	2.26159	0.88730	-2.22067
H	4.72812	0.59081	-2.00960
H	0.95104	-0.27457	2.39860
H	1.84487	-1.78024	2.57367
H	0.69125	-2.77855	0.66000
H	-0.51674	-2.18454	1.81477
O	-0.07616	1.16753	0.52892
H	0.01727	0.41938	-1.38609
C	-0.08975	2.43655	0.00635
C	-0.73095	3.38608	0.95268
H	-0.50004	4.41020	0.66559
H	-0.42060	3.19238	1.98073
H	-1.81208	3.21441	0.90201
O	0.35587	2.68695	-1.09129
H	-1.39590	-0.76515	0.46771

7.6 Ammonium Nitronate 25

SCF energy:	–994.004084 hartree
Zero-point correction:	+0.341243 hartree
Enthalpy correction:	+0.360827 hartree
Free energy correction:	+0.294723 hartree
Quasiharmonic free energy correction:	+0.297040 hartree

Cartesian Coordinates

C	2.66135	-0.85995	-0.29497
C	1.90572	-2.04361	-0.84623
C	2.02302	0.36770	-0.05760
C	0.58892	0.55688	-0.46017
N	-0.15828	-0.74719	-0.43120
C	0.52515	-1.68569	-1.36456
C	-0.34293	-1.28785	0.95773
C	-1.16325	-2.56212	0.95939
H	-0.86078	-0.49670	1.50468
H	0.64159	-1.42769	1.41373
C	-2.50740	-2.43862	0.21536
H	-1.34539	-2.81120	2.01047
H	-0.58410	-3.40033	0.54923
C	-3.36462	-1.30068	0.63951
H	-3.05486	-3.37552	0.36888
H	-2.32687	-2.36905	-0.86600
N	-3.35253	-0.12287	0.02600
H	-4.07296	-1.37214	1.45420
O	-4.12171	0.83057	0.36451
O	-2.52378	0.09990	-0.98875
C	2.73522	1.43792	0.48805
C	4.08136	1.29786	0.80589
C	4.72263	0.08090	0.57731
C	4.01407	-0.98557	0.03437
H	4.51301	-1.93623	-0.14049
H	5.77409	-0.03696	0.82173
H	2.22265	2.37882	0.66551
H	4.62745	2.13427	1.23097
H	1.82150	-2.81293	-0.06611
H	2.47350	-2.51365	-1.65534
H	0.57316	-1.17582	-2.33108
H	-0.11031	-2.56470	-1.49024
O	-0.10452	1.44512	0.37765
H	0.50765	0.92039	-1.49341
C	-0.79617	2.47395	-0.26299
C	-1.80506	3.05422	0.64948
H	-1.46984	3.03651	1.68718
H	-2.70289	2.41766	0.57029
H	-2.05990	4.06521	0.33618
O	-0.56019	2.78581	-1.40433
H	-1.17754	-0.49280	-0.77014

7.7 Transition State TS05

SCF energy:	–993.984186 hartree
Zero-point correction:	+0.339626 hartree
Enthalpy correction:	+0.357693 hartree
Free energy correction:	+0.296554 hartree
Quasiharmonic free energy correction: +	0.297459 hartree
Imaginary Frequency:	125.9 *i*cm^{-1}

Cartesian Coordinates

C	-2.66350	0.39796	0.49789
C	-2.19619	1.20206	1.67904
C	-1.73628	-0.22006	-0.35035
C	-0.25760	-0.08829	-0.13616
N	0.15480	0.90373	0.86850
C	-0.75911	0.87665	2.03662
C	0.31188	2.28227	0.33006
C	1.18712	2.46529	-0.90683
H	0.70715	2.87693	1.16358
H	-0.67915	2.69667	0.09194
C	2.68755	2.16549	-0.77029
H	1.08245	3.51815	-1.18987
H	0.78359	1.90065	-1.75303
C	2.97402	0.77112	-0.34642
H	3.14040	2.84013	-0.03663
H	3.16327	2.38318	-1.73511
N	2.51715	-0.23434	-1.04889
H	3.43504	0.50853	0.59264
O	2.53776	-1.50254	-0.41672
O	2.02344	-0.20029	-2.20160
C	-2.17820	-0.96845	-1.44741
C	-3.53492	-1.10835	-1.70733
C	-4.46418	-0.48934	-0.86851
C	-4.02819	0.25607	0.22042
H	-4.75222	0.73283	0.87815
H	-5.52804	-0.59161	-1.06327
H	-1.43986	-1.44166	-2.09072
H	-3.86927	-1.69243	-2.55953
H	-2.83575	1.00359	2.54583
H	-2.31229	2.27493	1.47287
H	-0.35918	1.56645	2.78591
H	-0.69088	-0.13480	2.45209
O	0.22313	-1.45325	0.25692
H	0.22687	0.15232	-1.08255
C	1.54552	-1.59488	0.73417
C	1.72466	-3.02593	1.16521
H	1.02845	-3.23470	1.97839
H	2.74486	-3.17041	1.52201
H	1.52806	-3.70480	0.33543
O	1.83939	-0.70192	1.70547
H	1.25754	0.16451	1.42154

7.8 Transition State TS06

SCF energy:	–993.983563 hartree
Zero-point correction:	+0.333592 hartree
Enthalpy correction:	+0.355097 hartree
Free energy correction:	+0.281020 hartree
Quasiharmonic free energy correction:	+0.286969 hartree
Imaginary Frequency:	720.4 *i*cm^{-1}

Cartesian Coordinates

C	4.58859	0.78834	-0.72164
C	3.96130	0.55098	0.50471
C	4.13904	0.14638	-1.87493
C	3.05293	-0.71785	-1.80451
C	2.41226	-0.94638	-0.57856
C	2.88067	-0.31611	0.59416
C	2.21332	-0.67593	1.89811
C	0.73952	-0.91542	1.68016
H	2.71807	-1.56227	2.32802
H	2.34668	0.12890	2.62905
N	0.46742	-1.73430	0.57310
H	0.09309	0.44807	1.44721
H	0.19682	-1.27528	2.55656
C	1.23053	-1.75790	-0.50534
H	2.67391	-1.20032	-2.70241
H	5.43114	1.47190	-0.77363
H	4.62672	0.32925	-2.82763
H	4.32164	1.04638	1.40367
C	-0.82262	-2.44824	0.56301
C	-2.00394	-1.49171	0.57650
O	0.43902	1.57132	-0.67230
C	-2.03632	-0.59918	-0.65641
H	-2.91768	-2.09175	0.64355
H	-1.96326	-0.87521	1.48333
C	-3.01880	0.53610	-0.55265
H	-2.24659	-1.19362	-1.55251
H	-1.05421	-0.13312	-0.80570
N	-4.46697	0.09258	-0.54130
H	-2.95906	1.22424	-1.40090
H	-2.89880	1.12438	0.36082
O	-4.73146	-1.05077	-0.90313
O	-5.29401	0.92720	-0.18543
H	0.86715	-2.31912	-1.35985
H	-0.84008	-3.10319	1.43900
H	-0.83992	-3.07689	-0.33175
C	-0.05179	2.11821	0.31332
C	-0.40300	3.58239	0.34406
H	0.23418	4.09935	1.06662
H	-1.43398	3.72370	0.67896
H	-0.26722	4.03117	-0.63943
O	-0.33629	1.49892	1.44268

7.9 Azomethine Ylide 26

SCF energy: –764.865605 hartree
Zero-point correction: +0.273895 hartree
Enthalpy correction: +0.290201 hartree
Free energy correction: +0.228428 hartree
Quasiharmonic free energy correction: +0.233074 hartree

Cartesian Coordinates

C	3.97582	-1.73937	-0.69782
C	3.54827	-0.53420	-1.25813
C	3.53808	-2.09362	0.58302
C	2.65791	-1.27699	1.27892
C	2.20540	-0.06402	0.71658
C	2.70556	0.31975	-0.55436
C	2.35061	1.71189	-1.01495
C	0.92574	1.97499	-0.68830
H	2.53347	1.84458	-2.08522
H	3.00068	2.44535	-0.49408
N	0.48701	1.57905	0.50717
C	1.19285	0.73895	1.32187
H	2.28817	-1.57842	2.25688
H	4.66271	-2.38184	-1.24074
H	3.87595	-3.02356	1.03318
H	3.91083	-0.23089	-2.23897
C	-0.88600	1.92883	0.91563
C	-1.81089	0.72264	0.89900
C	-1.81548	0.00345	-0.44295
H	-2.81820	1.07756	1.14525
H	-1.52133	0.02179	1.69162
C	-2.73004	-1.19388	-0.47551
H	-0.80602	-0.36036	-0.67184
H	-2.08711	0.69551	-1.24760
N	-4.19327	-0.82627	-0.33983
H	-2.54453	-1.91197	0.32527
H	-2.68133	-1.73057	-1.42688
O	-4.94624	-1.69958	0.08063
O	-4.54096	0.30090	-0.68071
H	0.23412	2.51383	-1.32225
H	-0.83153	2.36624	1.91643
H	-1.23833	2.70578	0.23206
H	0.71681	0.47646	2.25814

7.10 Transition State TS07

SCF energy: –993.987342 hartree
Zero-point correction: +0.334078 hartree
Enthalpy correction: +0.355492 hartree
Free energy correction: +0.281912 hartree
Quasiharmonic free energy correction: +0.287527 hartree

Imaginary Frequency: 812.8 *i*cm^{-1}

Cartesian Coordinates

C	-2.38609	-1.01983	-0.68596
C	-1.14610	-1.22753	-1.51783
C	-2.25525	-0.51926	0.62047
C	-0.92519	-0.24996	1.18173
N	0.11579	-0.98585	0.55325
C	0.05926	-1.41518	-0.67702
C	1.35153	-1.16819	1.33838
C	2.05287	0.15508	1.62890
H	1.98349	-1.87022	0.79029
H	1.06324	-1.65203	2.27626
C	2.53402	0.91126	0.39122
H	2.89223	-0.06202	2.30092
H	1.36791	0.79539	2.19278
C	3.91453	0.51211	-0.10210
H	1.80737	0.82338	-0.42560
H	2.59175	1.98061	0.61828
N	3.93454	-0.94638	-0.47089
O	4.56424	-1.71614	0.25124
O	3.26662	-1.28718	-1.44649
C	-3.41405	-0.27157	1.37063
C	-4.67463	-0.52205	0.83951
C	-4.79978	-1.04049	-0.44942
C	-3.65236	-1.29242	-1.20007
H	-3.73976	-1.69390	-2.20793
H	-5.78095	-1.24325	-0.86839
H	-3.31590	0.11761	2.38201
H	-5.56048	-0.32020	1.43545
H	-0.97152	-0.35663	-2.16743
H	-1.25170	-2.08807	-2.18949
O	-0.17421	1.72453	-1.31260
C	-0.32908	2.58225	-0.43807
C	-0.35465	4.05601	-0.75311
H	-1.31225	4.48626	-0.44880
H	-0.19998	4.22865	-1.81799
H	0.41836	4.57641	-0.18086
O	-0.47157	2.31651	0.83674
H	0.94919	-1.90030	-1.06593
H	-0.63551	1.15489	0.97734
H	-0.85729	-0.37905	2.26490
H	4.68829	0.63494	0.65626
H	4.18038	1.05011	-1.01340

7.11 Acetylated Hemiaminal 27

SCF energy: –994.029360 hartree
Zero-point correction: +0.340531 hartree
Enthalpy correction: +0.361953 hartree
Free energy correction: +0.286299 hartree
Quasiharmonic free energy correction: +0.294070 hartree

Cartesian Coordinates

C	-3.19860	-0.21781	-0.52421
C	-2.25022	0.61332	-1.33796
C	-2.70152	-1.21235	0.32477
C	-1.22455	-1.42164	0.49013
N	-0.41080	-0.75407	-0.52500
C	-0.83051	0.57045	-0.81988
C	1.00610	-0.89014	-0.19567
C	1.94354	-0.30588	-1.24080
H	1.20189	-1.96666	-0.09666
H	1.21207	-0.44676	0.79804
C	3.38728	-0.76648	-1.06336
H	1.91248	0.79151	-1.21693
H	1.59674	-0.60453	-2.23641
C	3.95993	-0.31629	0.25917
H	4.00353	-0.36648	-1.87359
H	3.45059	-1.85732	-1.13847
N	5.42410	-0.64951	0.42266
O	5.97449	-0.20420	1.42617
O	5.96563	-1.34162	-0.43289
C	-3.59413	-1.99721	1.06234
C	-4.96695	-1.80390	0.96094
C	-5.46427	-0.81166	0.11466
C	-4.58137	-0.02732	-0.61895
H	-4.96257	0.75049	-1.27779
H	-6.53510	-0.65015	0.02999
H	-3.20147	-2.76830	1.72274
H	-5.64717	-2.42340	1.53836
H	-2.58157	1.65582	-1.38893
H	-2.22961	0.25155	-2.37393
O	-0.74085	1.39210	0.42125
C	-0.40739	2.68666	0.27005
C	-0.34738	3.38473	1.59367
H	-1.35809	3.48702	1.99756
H	0.08981	4.37460	1.47537
H	0.22650	2.80190	2.31681
O	-0.19541	3.21085	-0.80877
H	-0.15245	1.03144	-1.53888
H	-0.92574	-1.08610	1.50265
H	-0.99059	-2.49311	0.44778
H	3.48474	-0.78578	1.12534
H	3.90226	0.76551	0.40796

7.12 Transition State TS08

SCF energy:	–993.989242 hartree
Zero-point correction:	+0.337915 hartree
Enthalpy correction:	+0.357682 hartree
Free energy correction:	+0.289796 hartree
Quasiharmonic free energy correction:	+0.293282 hartree
Imaginary Frequency:	650.6 *i*cm^{-1}

Cartesian Coordinates

C	-1.92821	-0.25351	-0.59869
C	-0.73257	0.07018	-1.45372
C	-1.84320	-0.22027	0.79931
C	-0.57308	0.18396	1.49256
N	0.60085	0.09293	0.58594
C	0.34408	0.80769	-0.69822
C	1.89616	0.44692	1.25822
C	2.39265	-0.74381	2.06038
H	1.73627	1.34118	1.87194
H	2.59790	0.69470	0.45817
C	2.70166	-1.96601	1.18364
H	1.66016	-1.00669	2.83542
H	3.29352	-0.43070	2.59737
C	1.56930	-2.40932	0.28174
H	2.98426	-2.79557	1.84205
H	3.57283	-1.73523	0.56055
N	1.71517	-2.20571	-1.08093
H	1.04478	-3.33634	0.49070
O	1.03493	-2.87956	-1.90034
O	2.43280	-1.23228	-1.47457
C	-2.96032	-0.54836	1.57346
C	-4.16054	-0.90539	0.97125
C	-4.24880	-0.94345	-0.42066
C	-3.13971	-0.62040	-1.19323
H	-3.20392	-0.65259	-2.27833
H	-5.18025	-1.22666	-0.90172
H	-2.88106	-0.52560	2.65839
H	-5.02049	-1.16006	1.58326
H	-1.02322	0.67579	-2.31696
H	-0.28957	-0.84877	-1.86245
O	-0.12815	2.12673	-0.39642
C	0.78602	3.14624	-0.41621
C	0.10384	4.44895	-0.16314
H	-0.53551	4.69740	-1.01400
H	0.84318	5.23539	-0.02725
H	-0.54525	4.38250	0.71230
O	1.96581	2.97895	-0.62348
H	0.75163	-1.02390	0.37438
H	1.29117	0.85264	-1.23763
H	-0.37003	-0.47119	2.34518
H	-0.62534	1.21197	1.87193

7.13 Ammonium Nitronate 28

SCF energy:	–993.997999 hartree
Zero-point correction:	+0.340571 hartree
Enthalpy correction:	+0.360672 hartree
Free energy correction:	+0.292637 hartree
Quasiharmonic free energy correction:	+0.295775 hartree

Cartesian Coordinates

C	-2.43966	0.25424	-0.82201
C	-1.58827	1.20539	-1.61060
C	-1.83723	-0.96354	-0.48186
C	-0.49578	-1.23944	-1.07429
N	0.45601	-0.07267	-0.94490
C	-0.21814	1.28379	-0.96562
C	1.57884	-0.17146	-1.94595
C	2.88882	0.30311	-1.34556
H	1.63812	-1.22325	-2.24100
H	1.28307	0.41108	-2.82538
C	3.64991	-0.77395	-0.53469
H	2.69393	1.18183	-0.72243
H	3.53045	0.65409	-2.16043
C	2.86666	-1.86221	0.11936
H	4.26805	-0.24646	0.20497
H	4.35204	-1.27737	-1.20854
N	1.97215	-1.64202	1.07610
H	3.09992	-2.90820	-0.03597
O	1.37644	-2.56575	1.70678
O	1.62846	-0.37902	1.33023
C	-2.50143	-1.87461	0.33533
C	-3.78470	-1.58052	0.79312
C	-4.39096	-0.37366	0.44780
C	-3.71366	0.55085	-0.34727
H	-4.17280	1.50564	-0.59294
H	-5.38745	-0.14302	0.81303
H	-2.01140	-2.80261	0.61842
H	-4.30567	-2.28803	1.43090
H	-1.45883	0.87064	-2.65008
H	-2.01866	2.20879	-1.65002
O	-0.39378	1.67305	0.38406
C	0.62180	2.39650	0.96865
C	0.43325	2.44268	2.44055
H	-0.61923	2.54910	2.70534
H	1.02972	3.24367	2.87283
H	0.77632	1.48026	2.83499
O	1.52608	2.88445	0.32915
H	0.91047	-0.13929	0.05414
H	0.46844	1.97308	-1.46554
H	0.00154	-2.09659	-0.61336
H	-0.58946	-1.43541	-2.15073

7.14 Transition State TS09

SCF energy:	–993.983492 hartree
Zero-point correction:	+0.339488 hartree
Enthalpy correction:	+0.357516 hartree
Free energy correction:	+0.296398 hartree
Quasiharmonic free energy correction:	+0.297263 hartree
Imaginary Frequency:	81.6 *i*cm^{-1}

Cartesian Coordinates

C	-2.43687	-0.57500	0.69620
C	-1.13596	-1.05254	1.26979
C	-2.48987	-0.34261	-0.68563
C	-1.18991	-0.46331	-1.41953
N	-0.10138	0.22562	-0.67164
C	0.10842	-0.41401	0.64005
C	-0.37195	1.69489	-0.62304
C	0.56494	2.57996	0.18989
H	-0.37519	2.01788	-1.67235
H	-1.39146	1.85601	-0.24503
C	2.00148	2.74822	-0.32296
H	0.59203	2.26192	1.23649
H	0.09611	3.56979	0.20280
C	2.73095	1.46048	-0.43342
H	2.52666	3.43443	0.35382
H	1.99564	3.22078	-1.31035
N	2.85244	0.69111	0.61835
H	3.07189	1.03229	-1.36308
O	3.27862	-0.63748	0.36922
O	2.60466	0.97881	1.81272
C	-3.68278	0.05775	-1.28352
C	-4.83519	0.20942	-0.51317
C	-4.78468	-0.01496	0.86177
C	-3.58704	-0.39830	1.46467
H	-3.54535	-0.56790	2.53845
H	-5.67705	0.11498	1.46726
H	-3.70799	0.25403	-2.35363
H	-5.76588	0.51514	-0.98220
H	-1.04545	-2.13138	1.08937
H	-1.10909	-0.92432	2.35502
O	1.06606	-1.56116	0.51465
C	2.20275	-1.45692	-0.31394
C	2.85397	-2.81394	-0.37085
H	2.15663	-3.51753	-0.82717
H	3.11593	-3.15699	0.63000
H	3.75392	-2.75610	-0.98395
O	1.90507	-0.95925	-1.53711
H	1.07751	-0.29324	-1.33347
H	0.56488	0.31438	1.30940
H	-0.87433	-1.50944	-1.52698
H	-1.24175	-0.03404	-2.42489

8 References

1 Banks, J. L.; Beard, H. S.; Cao, Y.; Cho, A. E.; Damm, W.; Farid, R.; Felts, A. K.; Halgren, T. A.; Mainz, D. T.; Maple, J. R.; Murphy, R.; Philipp, D. M.; Repasky, M. P.; Zhang, L. Y.; Berne, B. J.; Friesner, R. A.; Gallicchio, E.; Levy, R. M. *J. Comput. Chem.* **2005**, *26*, 1752–1780.

2 MacroModel, V. 10.6, Schrödinger, LLC, New York, NY, **2014**.

3 Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101.

4 Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

5 Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032–3041.

6 Ribeiro, R. F.; Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2011**, *115*, 14556–14562.

7 Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

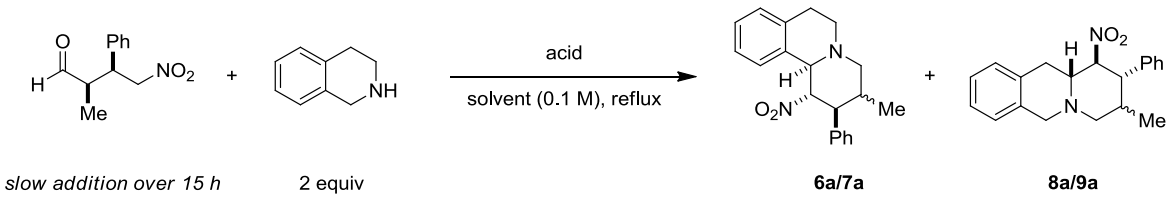
8 Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

9 Goerigk, L.; Grimme, S. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670–6688.

10 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

Part II: Experimental Part

Table S1. Additional experiments regarding the regioselectivity of the asymmetric redox-annulation.

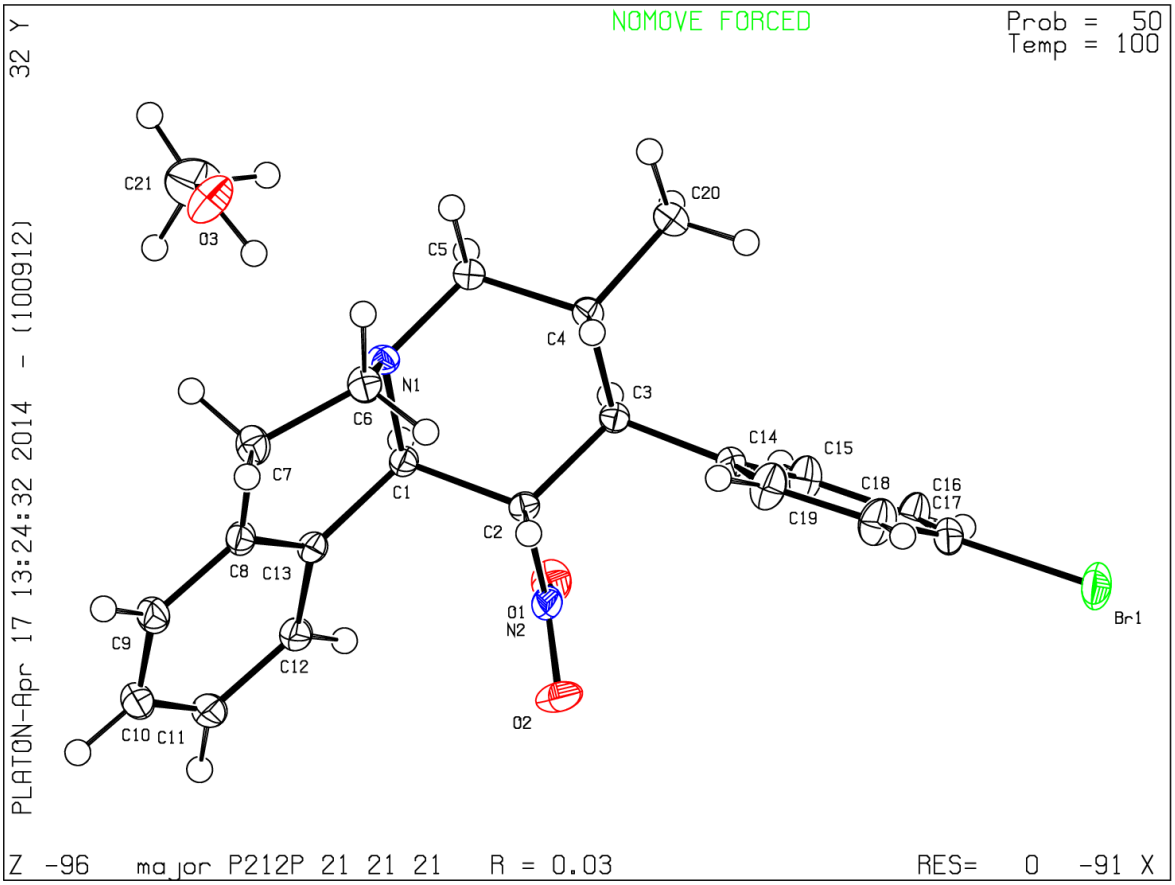


entry	acid (equiv)	solvent	ratio of **6a**/**7a** and **8a**/**9a**[c]	yield of **6a**/**7a** (%)[b]	yield of **8a**/**9a** (%)[b]	dr of **8a**/**9a**[c]
1	AcOH (10)	toluene	5:1	55	14	1:1
2	2-EHA (10)	toluene	1:1.4	ND	40	1:1
3	2-EHA (5)	toluene	1:2.4	ND	41	1:1
4	2-EHA (2.5)	toluene	1:1.5	ND	ND	1.4:1
5	2-EHA (5)	xylenes	1:8.5	ND	58	1.4:1
6	2-EHA (10)	xylenes	1:8.6	ND	62	1.2:1
7[a]	2-EHA (10)	xylenes	1.2:1	ND	ND	1:1

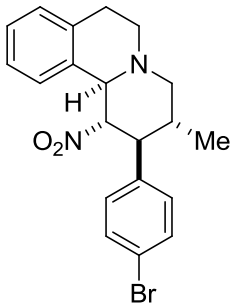
[a] Addition of aldehyde over 2 min. [b] Isolated yield of both diastereomers. [c] Regioisomeric and diastereomeric ratios were determined by ^{1}H NMR of crude reaction mixtures. ND: not determined.

Crystal Structure for Compound 6c

Compound **6c** was recrystallized from methanol and dichloromethane.



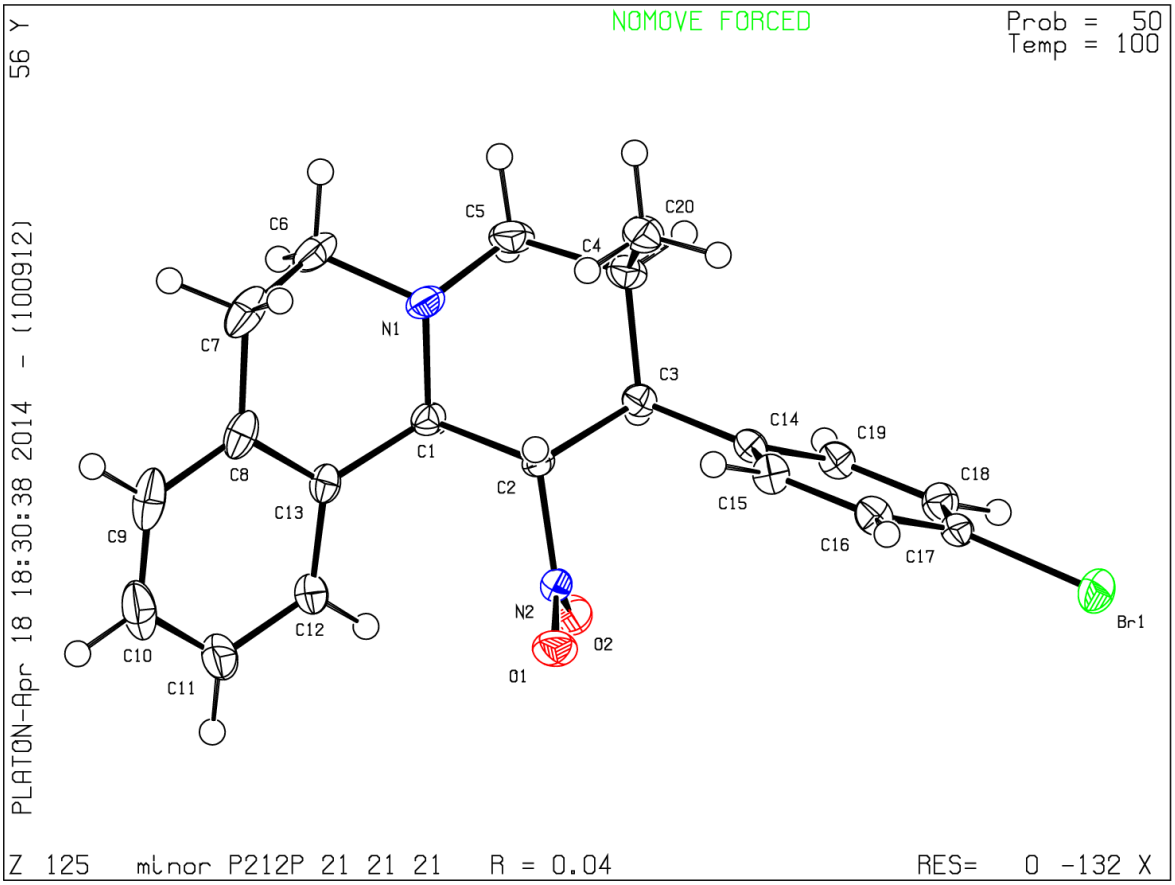
≡



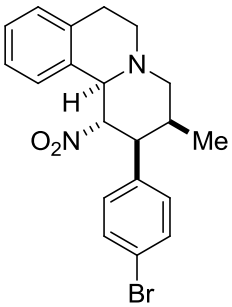
The ellipsoid contour probability level for the thermal ellipsoid plot is 50%.

Crystal Structure for Compound 7c

Compound **7c** was recrystallized from dichloromethane and pentane.



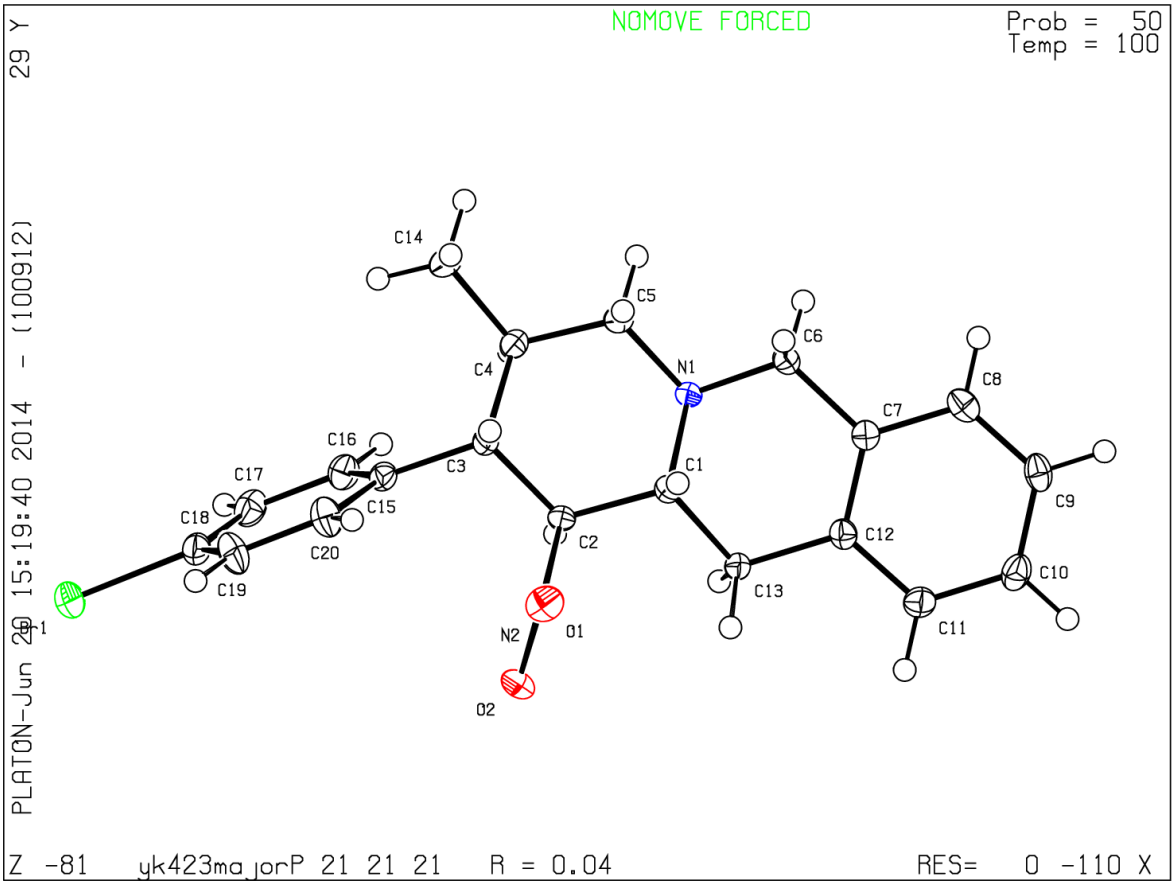
≡

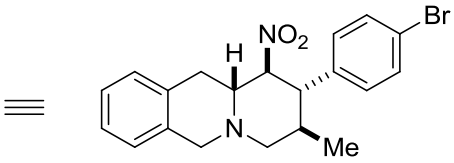


The ellipsoid contour probability level for the thermal ellipsoid plot is 50%.

Crystal Structure for Compound 8c

Compound **8c** was recrystallized from dichloromethane and pentane.

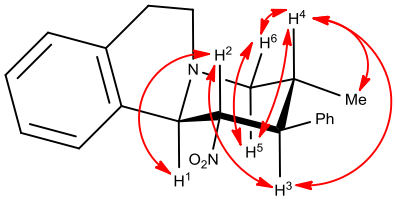




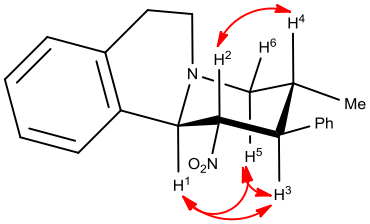
The ellipsoid contour probability level for the thermal ellipsoid plot is 50%.

2D-NMR Analysis for Compound 6a, Selected Interactions

Gcosy



Noesy

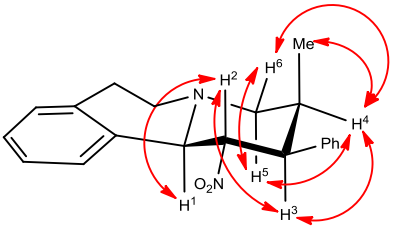


^{1}H NMR shifts

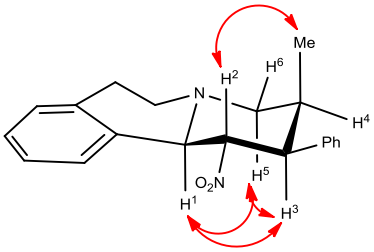
Proton	Chemical shift
H^1	4.39
H^2	4.97
H^3	3.11
H^4	2.30–2.23
H^5, H^6	3.00–2.92
Me	0.73

2D-NMR Analysis for Compound 7a, Selected Interactions

Gcosy



Noesy

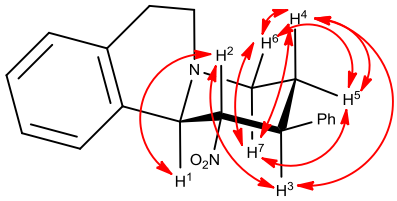


^{1}H NMR shifts

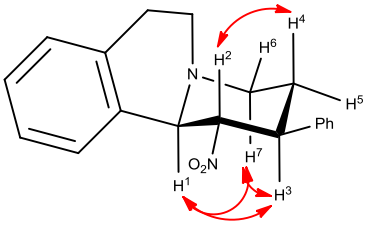
Proton	Chemical shift
H^1	4.20
H^2	5.09
H^3	3.82
H^4	2.18–2.09
H^5	3.25
H^6	2.98
Me	0.95

2D-NMR Analysis for Compound 6k, Selected Interactions

Gcosy



Noesy

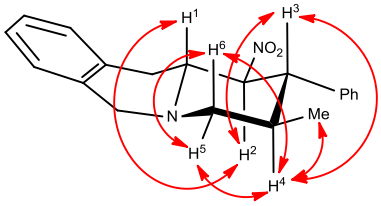


^{1}H NMR shifts

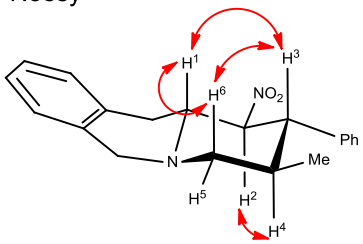
Proton	Chemical shift
H^1	4.37
H^2	4.97
H^3	3.56
H^4	2.17–2.09
H^5	1.83–1.77
H^6,H^7	3.38–3.22

2D-NMR Analysis for Compound 8a, Selected Interactions

Gcosy



Noesy

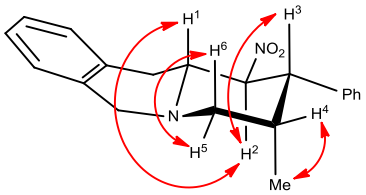


^{1}H NMR shifts

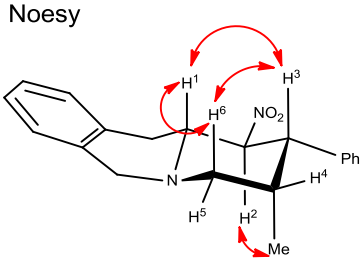
Proton	Chemical shift
H^1, H^3, H^5, H^6	3.01–2.77
H^2	4.66
H^4	2.26–2.13
Me	0.78

2D-NMR Analysis for Compound 9a, Selected Interactions

Gcosy



Noesy

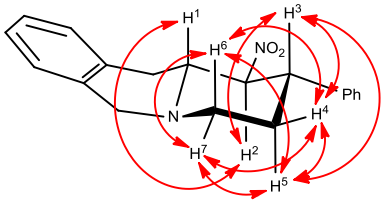


^{1}H NMR shifts

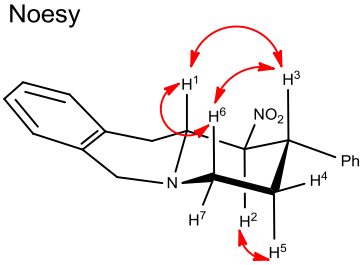
Proton	Chemical shift
H^1	2.92–2.82
H^2	5.09
H^3	3.65
H^4	2.31–2.14
H^5	3.16–3.02
H^6	2.70
Me	1.00

2D-NMR Analysis for Compound 8k, Selected Interactions

Gcosy



Noesy

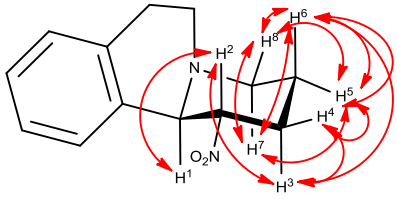


^{1}H NMR shifts

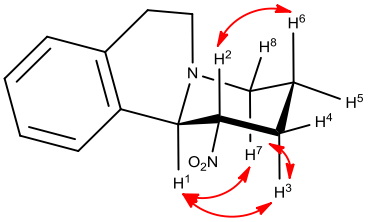
Proton	Chemical shift
H^1	3.02–2.91
H^2	4.62
H^3	3.30
H^4, H^5	2.16–1.95
H^6	2.49
H^7	3.23

2D-NMR Analysis for Compound 11, Selected Interactions

Gcosy



Noesy

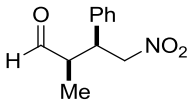


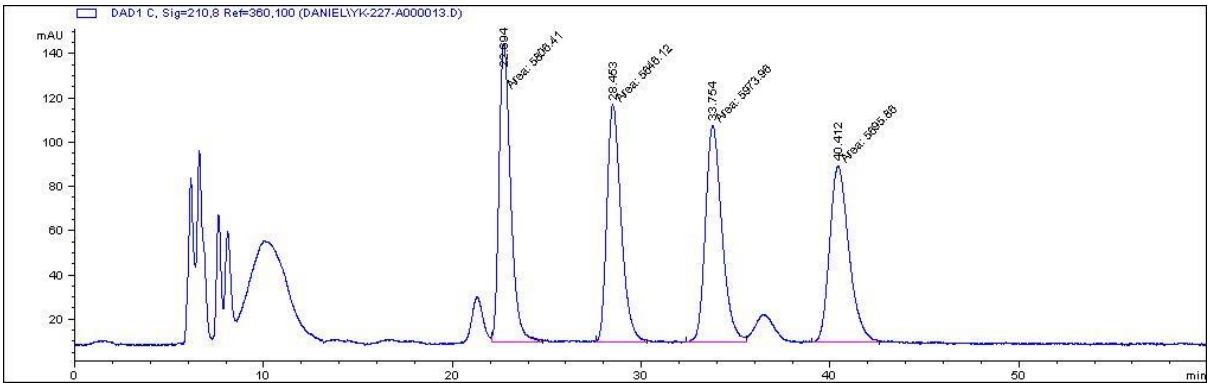
$J_{H1,H2}$ = 9.3 Hz

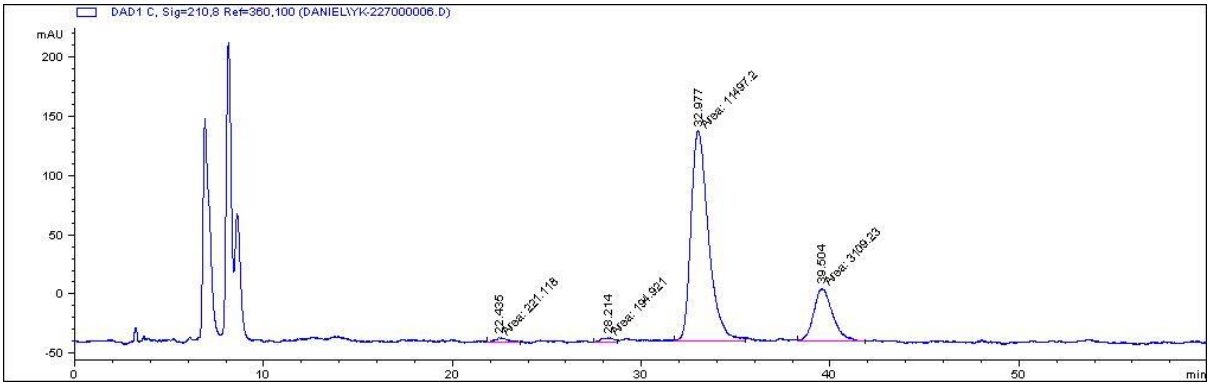
^{1}H NMR shifts

Proton	Chemical shift
H^1	4.20
H^2	4.74–4.62
H^3, H^4	2.30–2.23
H^5	1.72–1.61
H^6	1.94
H^7, H^8	3.04–2.93

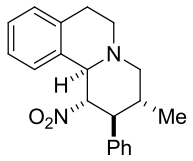
HPLC Profile of 5a

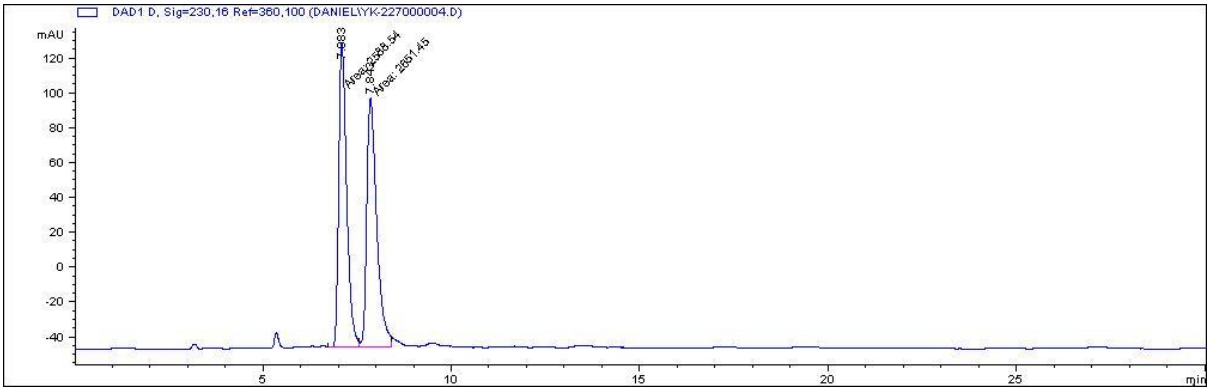


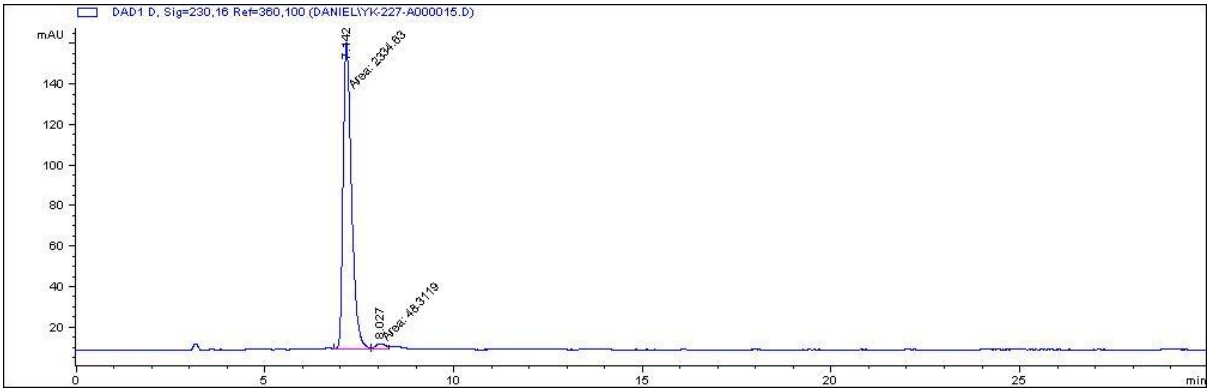




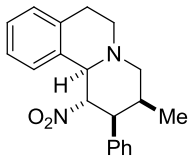
HPLC Profile of 6a

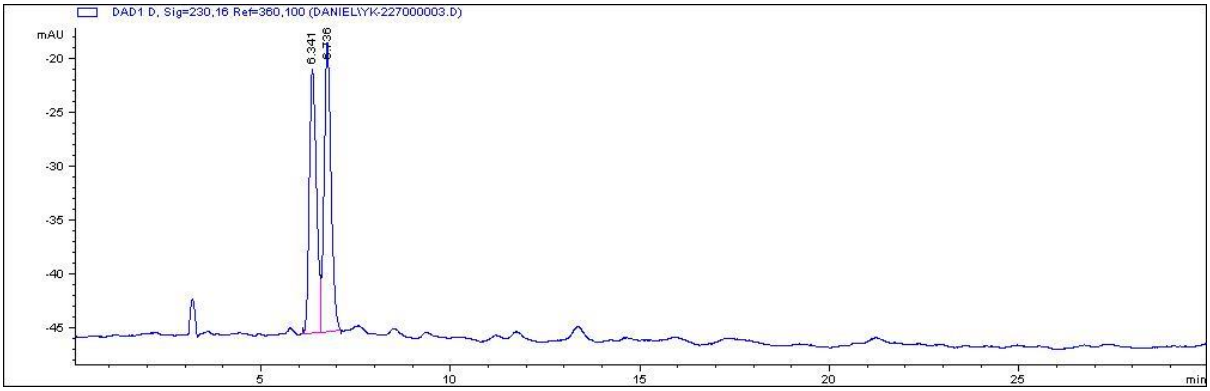


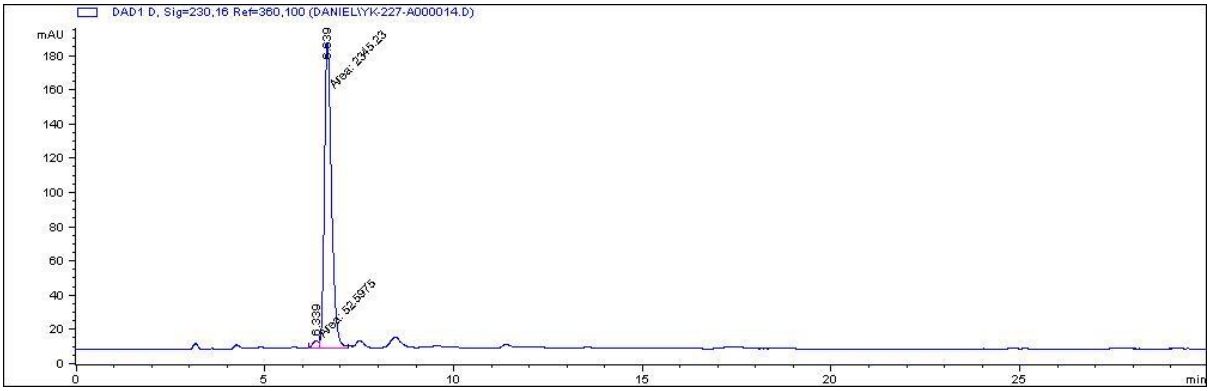




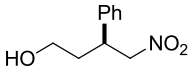
HPLC Profile of 7a

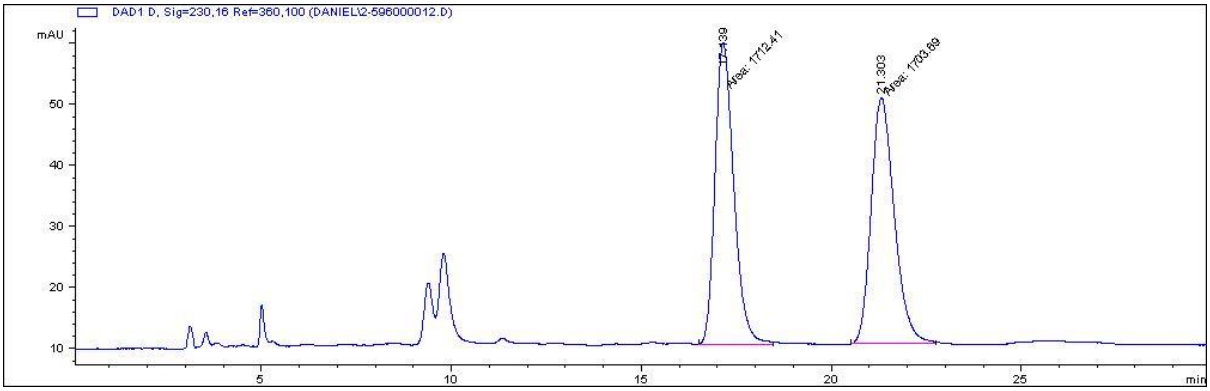


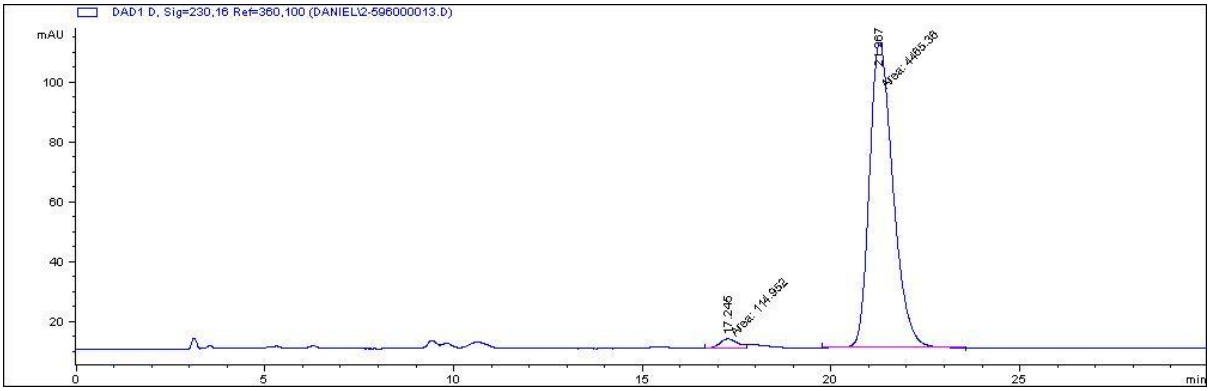




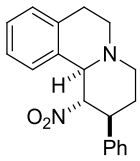
HPLC Profile of 5k (Product was reduced to the corresponding alcohol using $NaBH_4$ for HPLC analysis)

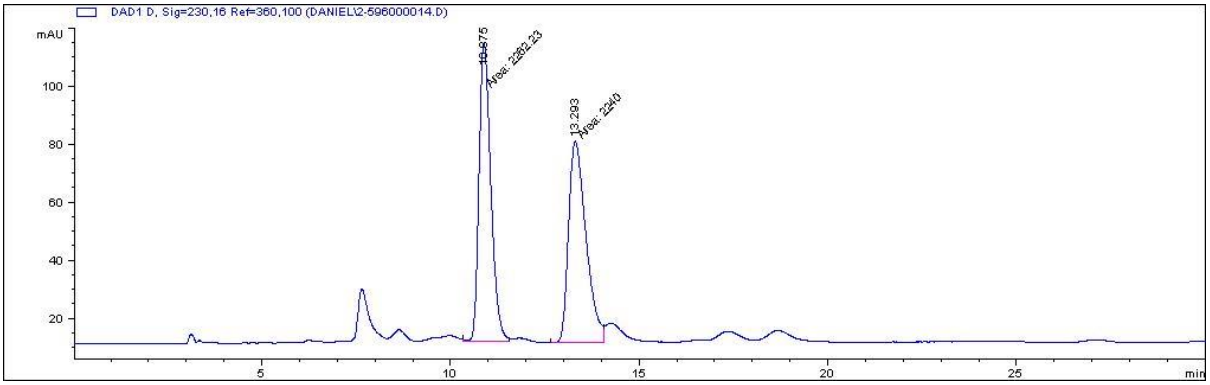


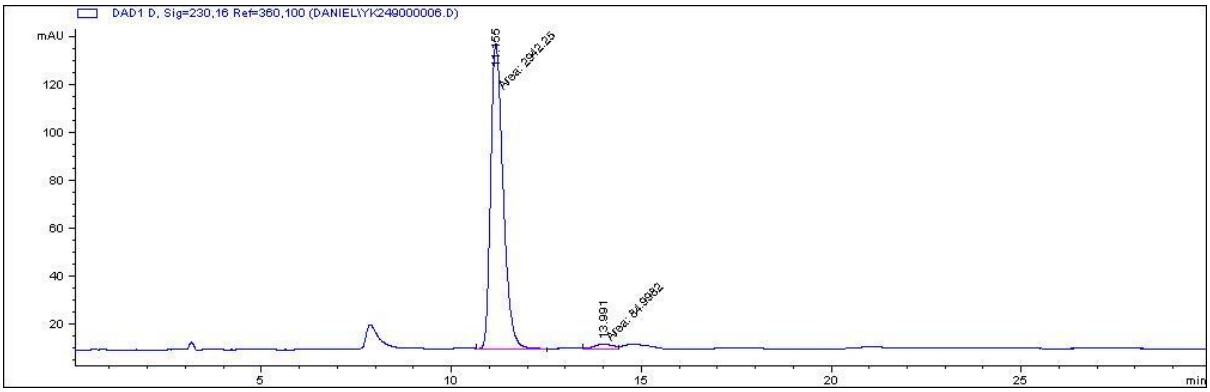




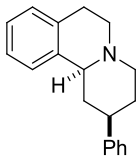
HPLC Profile of 6k

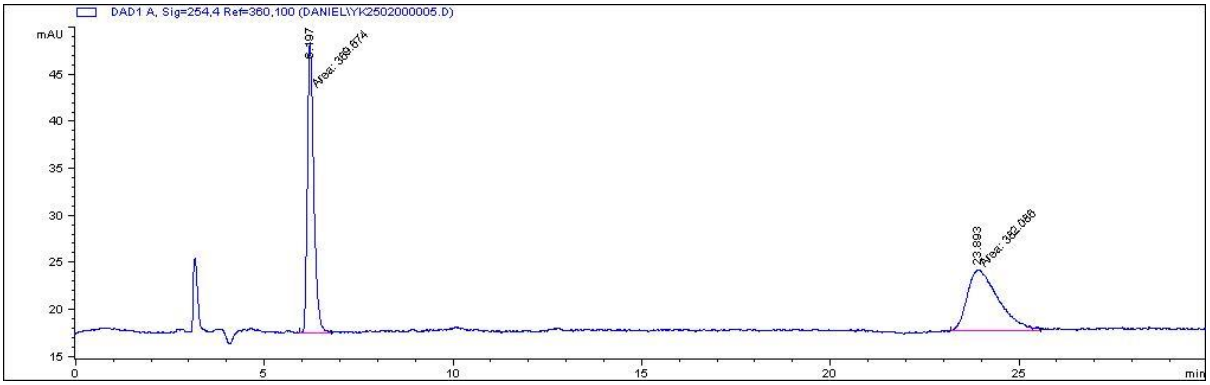


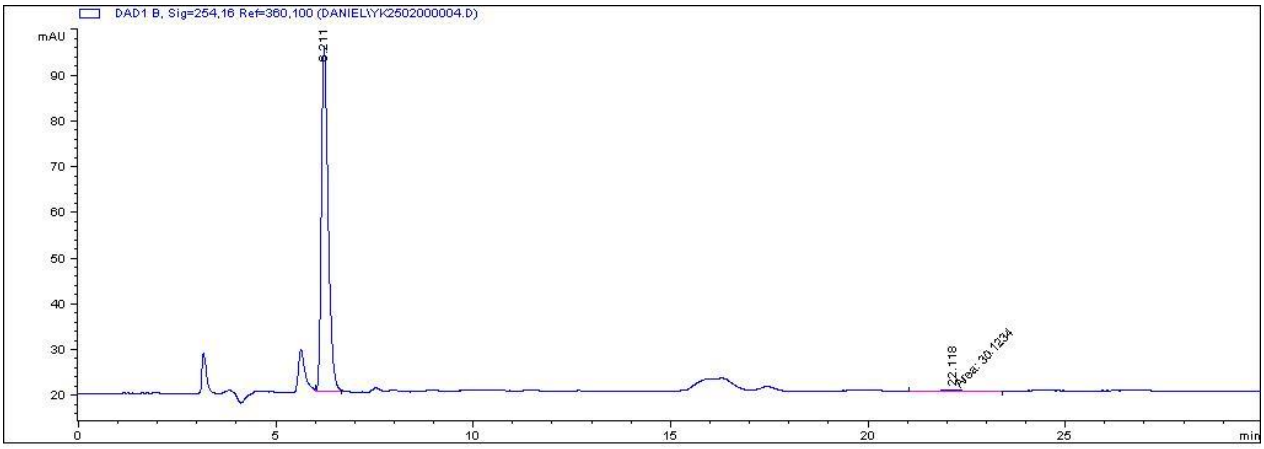




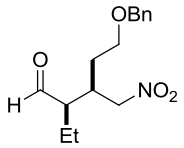
HPLC Profile of 16

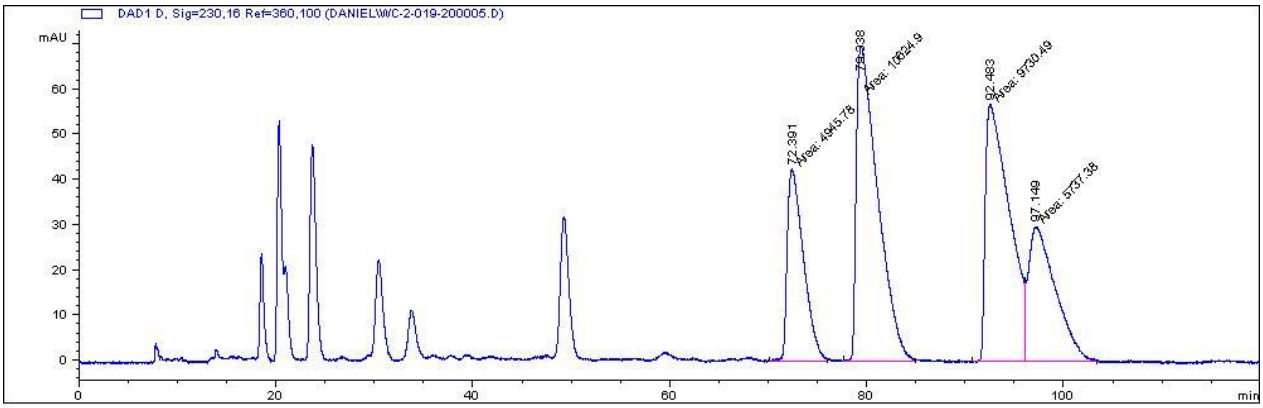


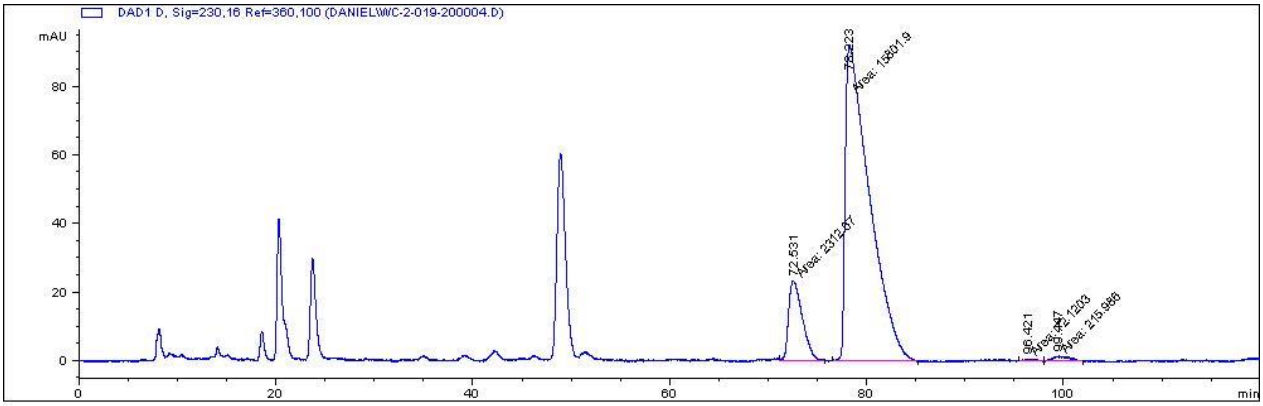




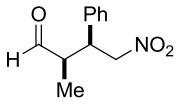
HPLC Profile of 18

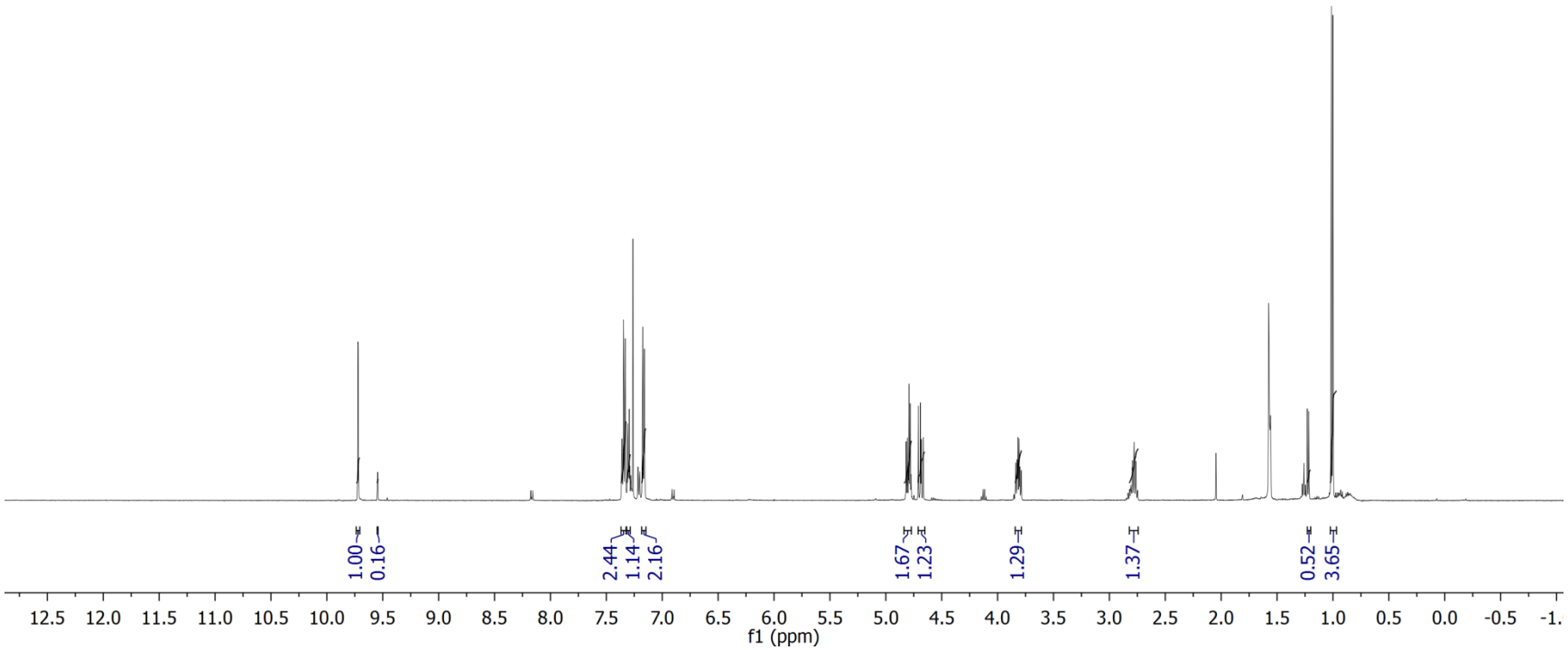




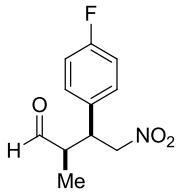


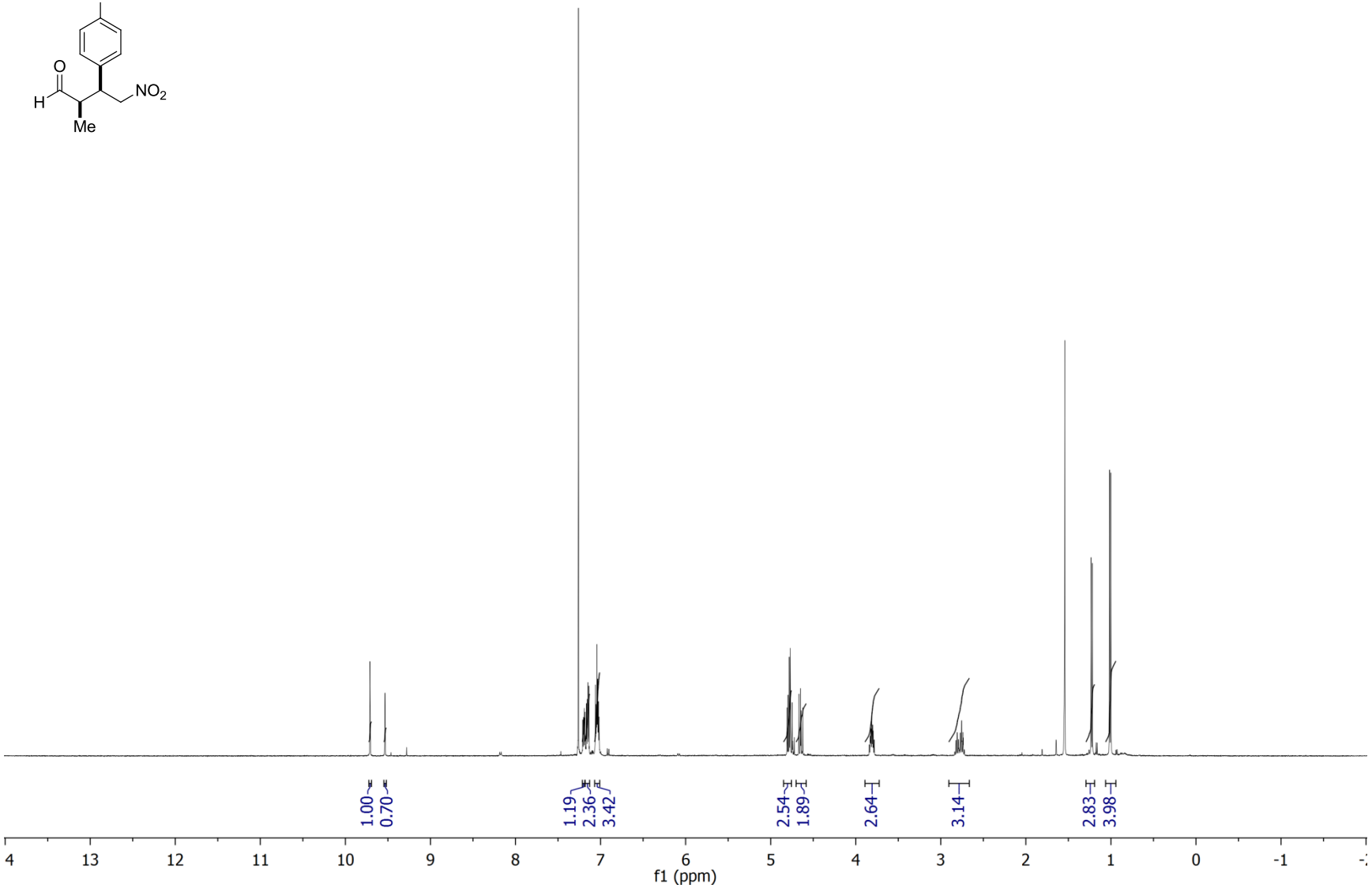
^{1}H NMR of **5a** in $CDCl_3$



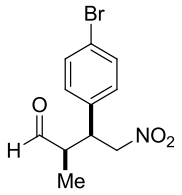


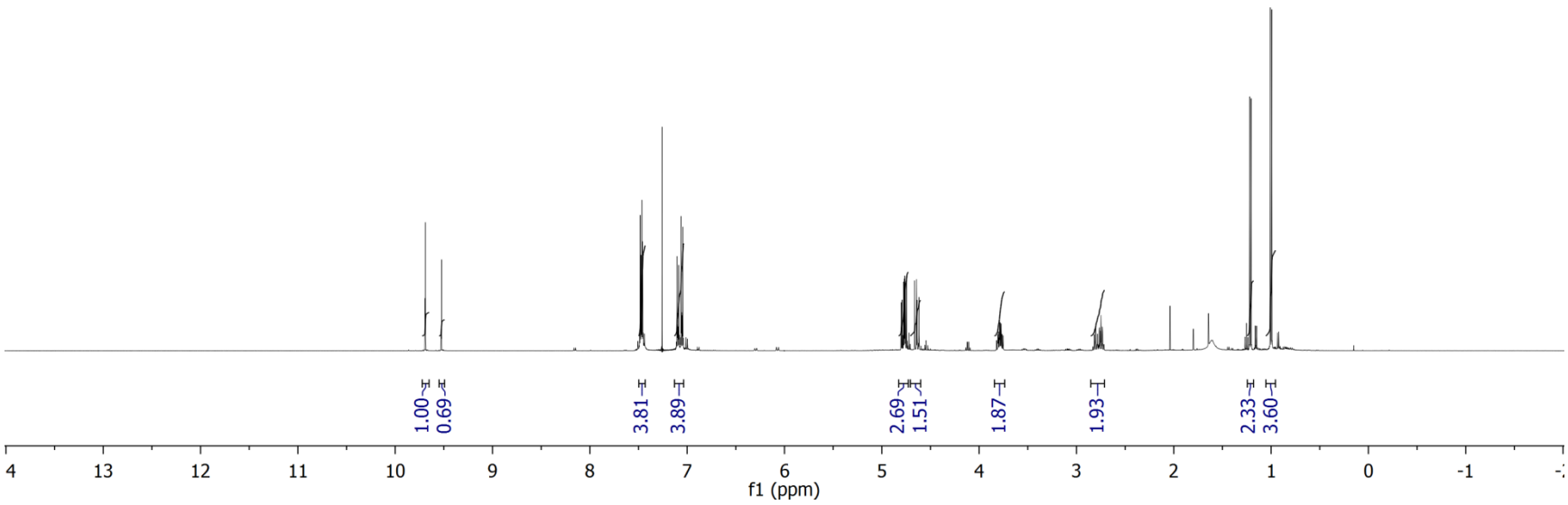
^{1}H NMR of **5b** in $CDCl_3$



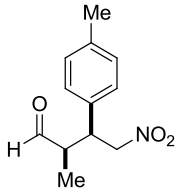


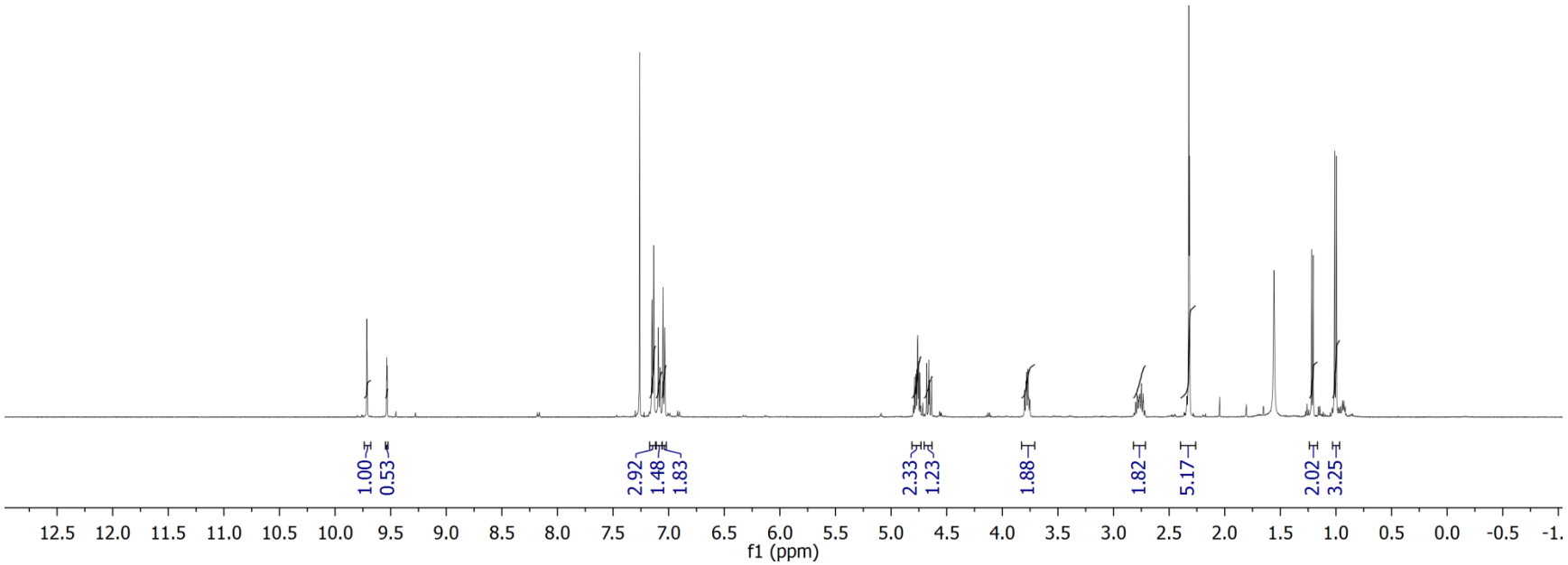
^{1}H NMR of **5c** in $CDCl_3$



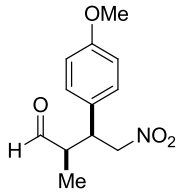


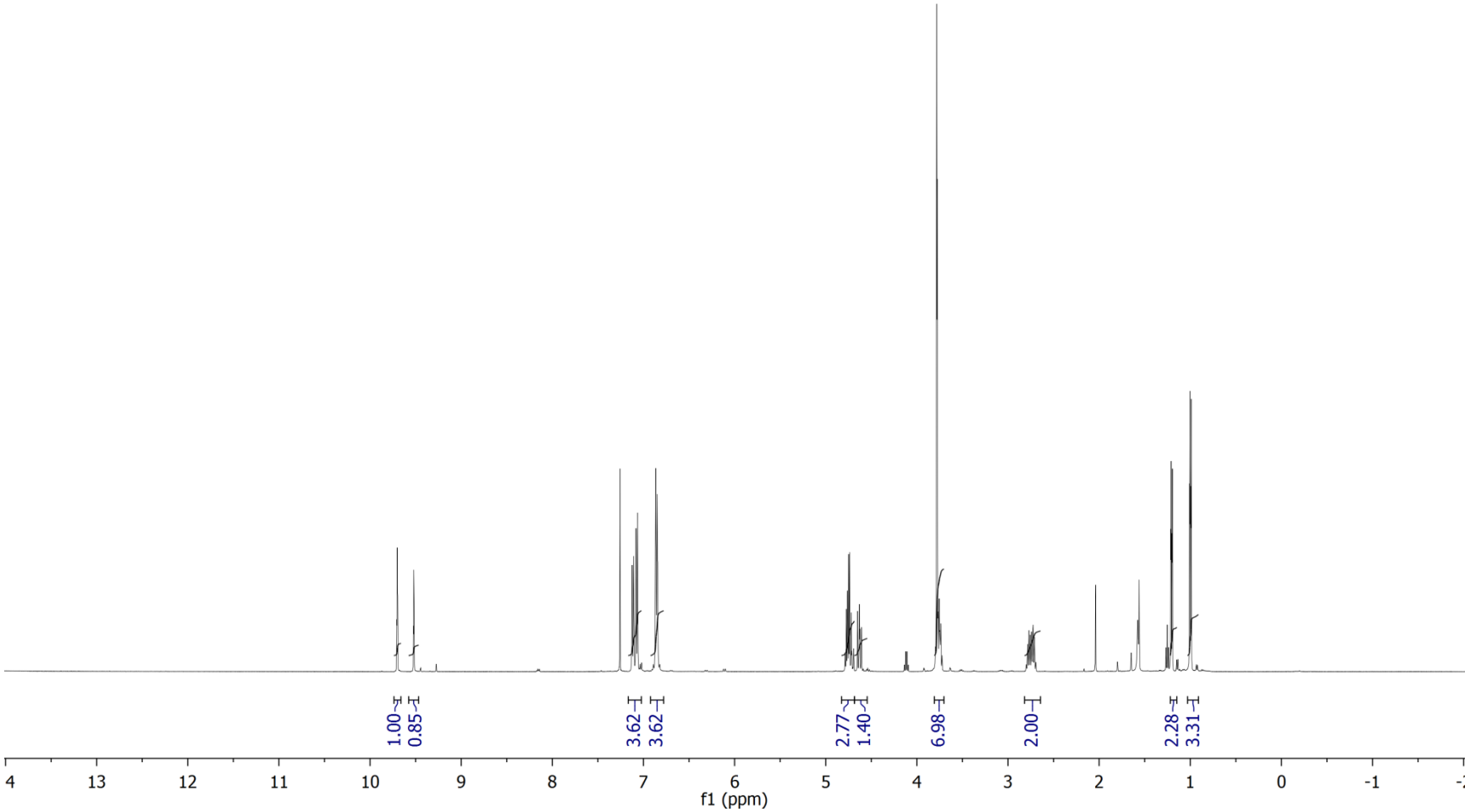
^{1}H NMR of **5d** in $CDCl_3$



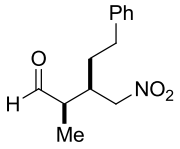


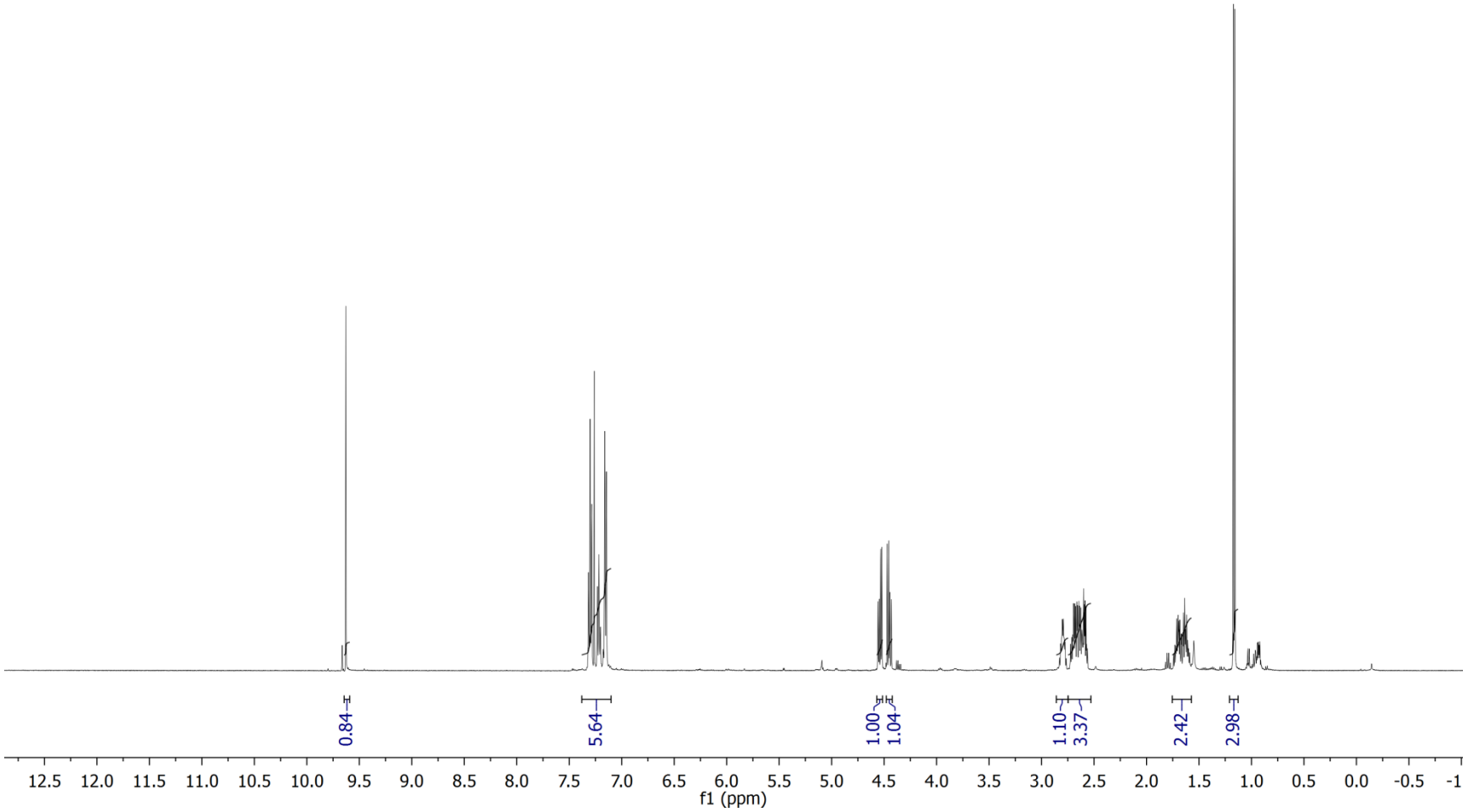
^{1}H NMR of **5e** in $CDCl_3$



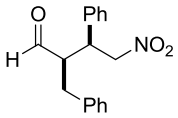


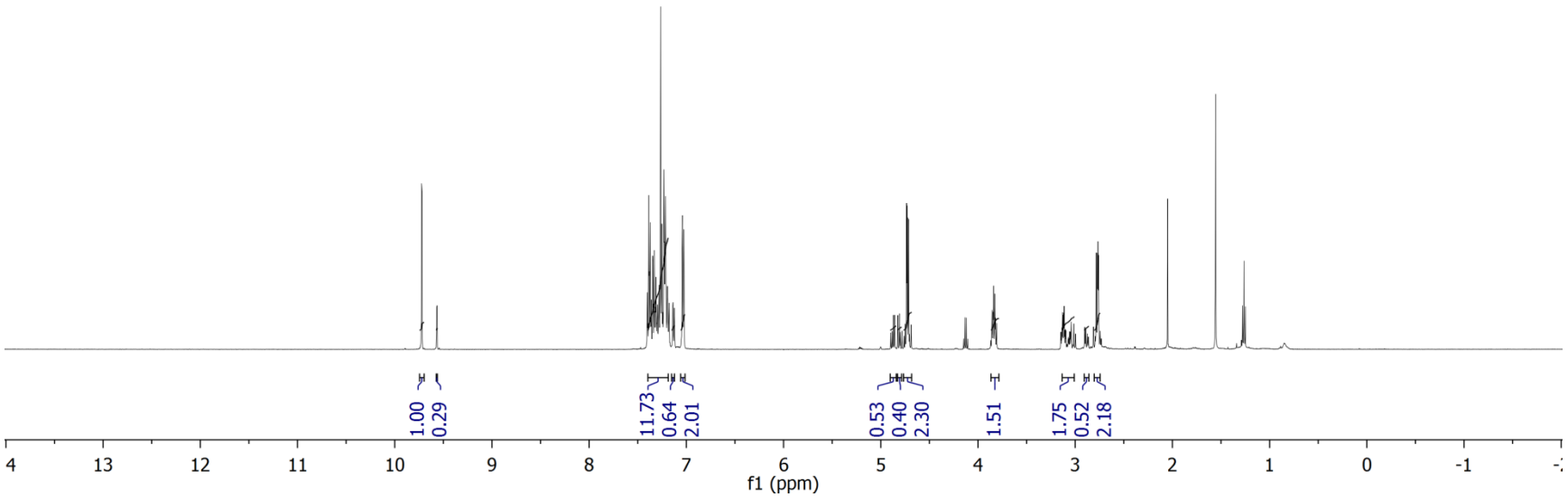
^{1}H NMR of **5f** in $CDCl_3$



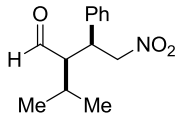


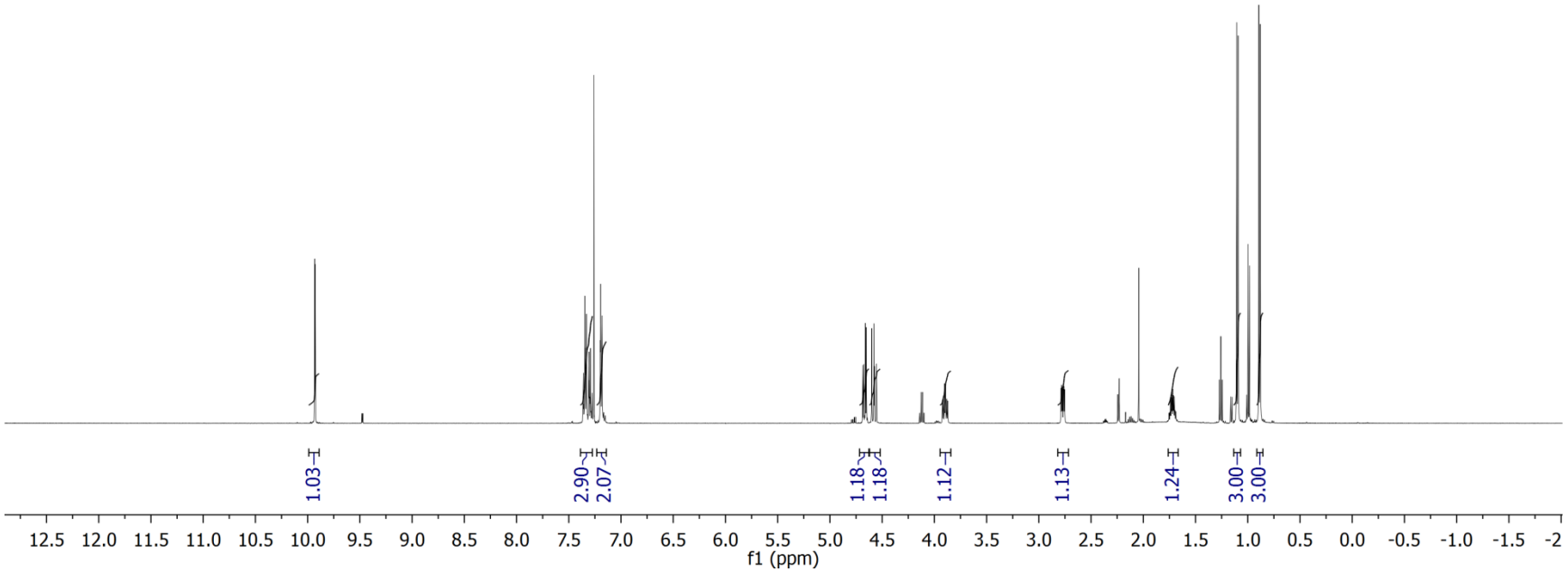
^{1}H NMR of **5g** in $CDCl_3$



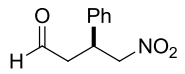


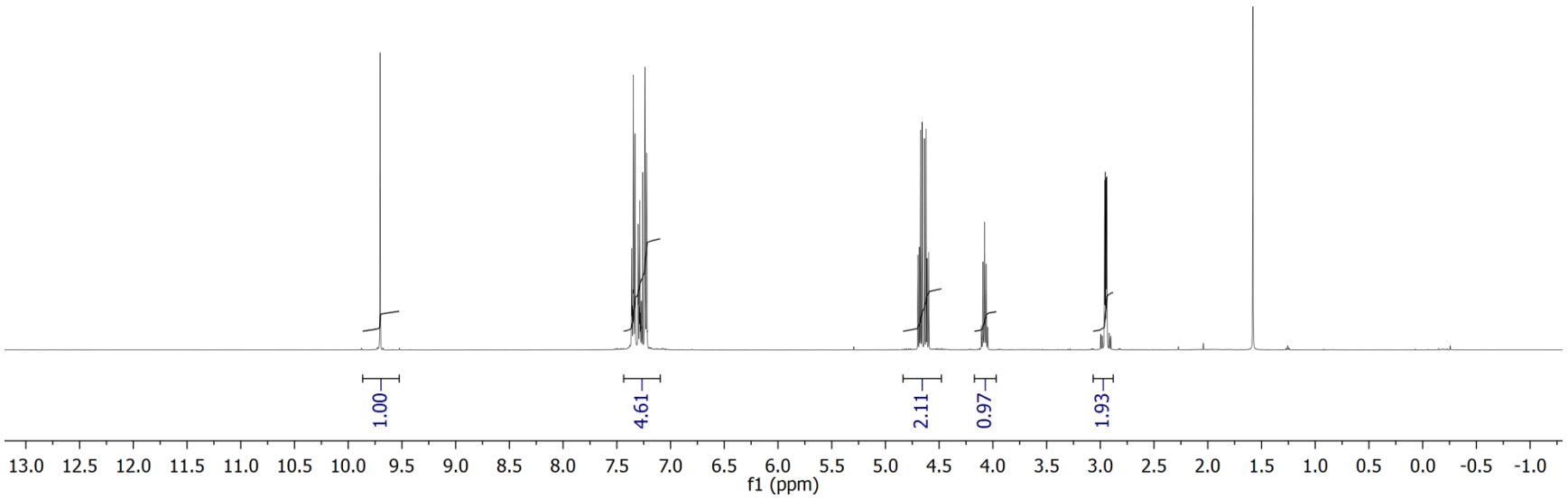
^{1}H NMR of **5h** in $CDCl_3$



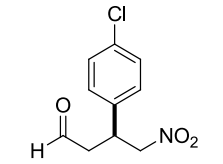


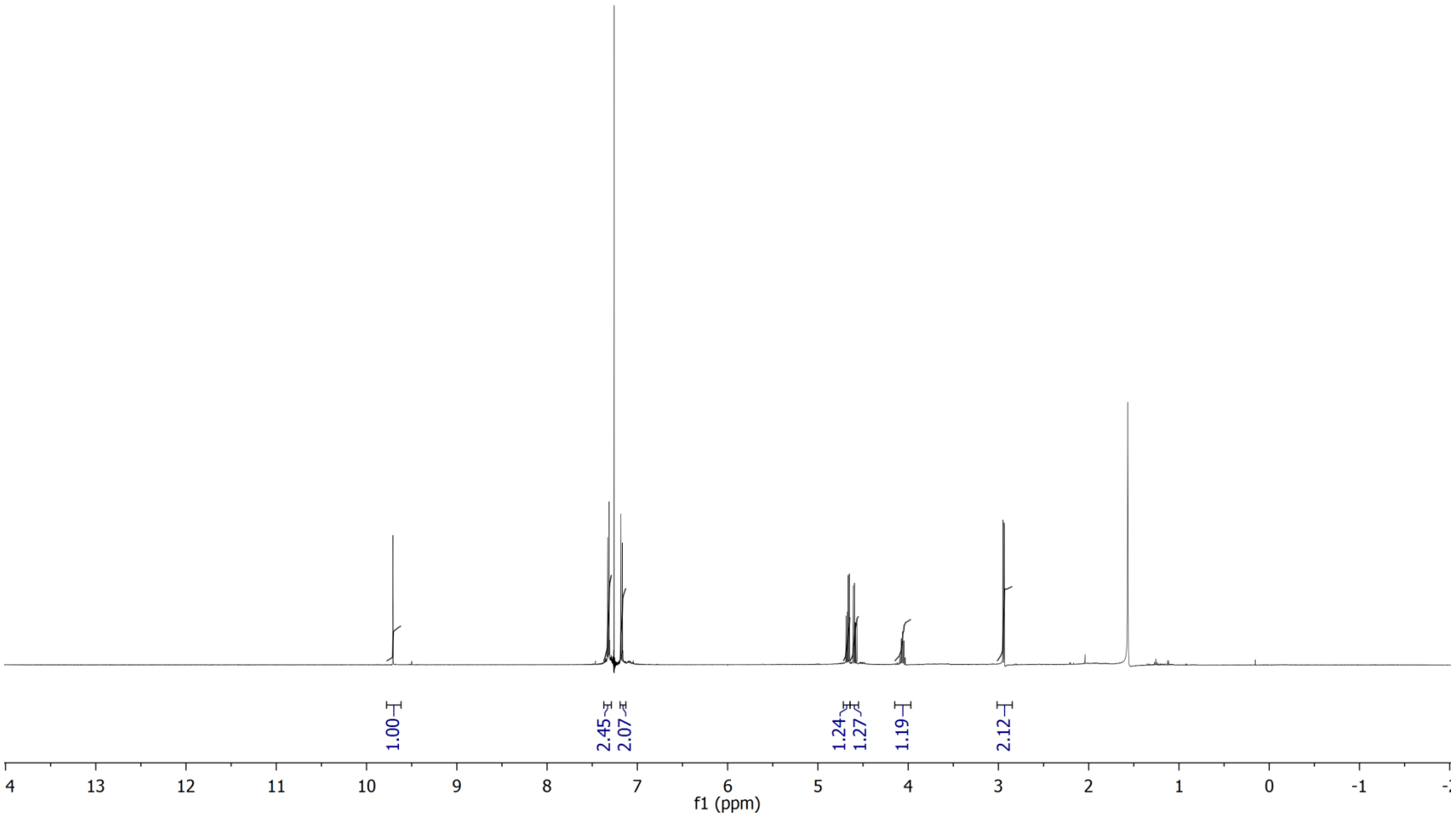
^{1}H NMR of **5k** in $CDCl_3$



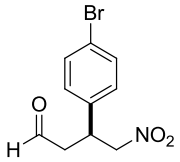


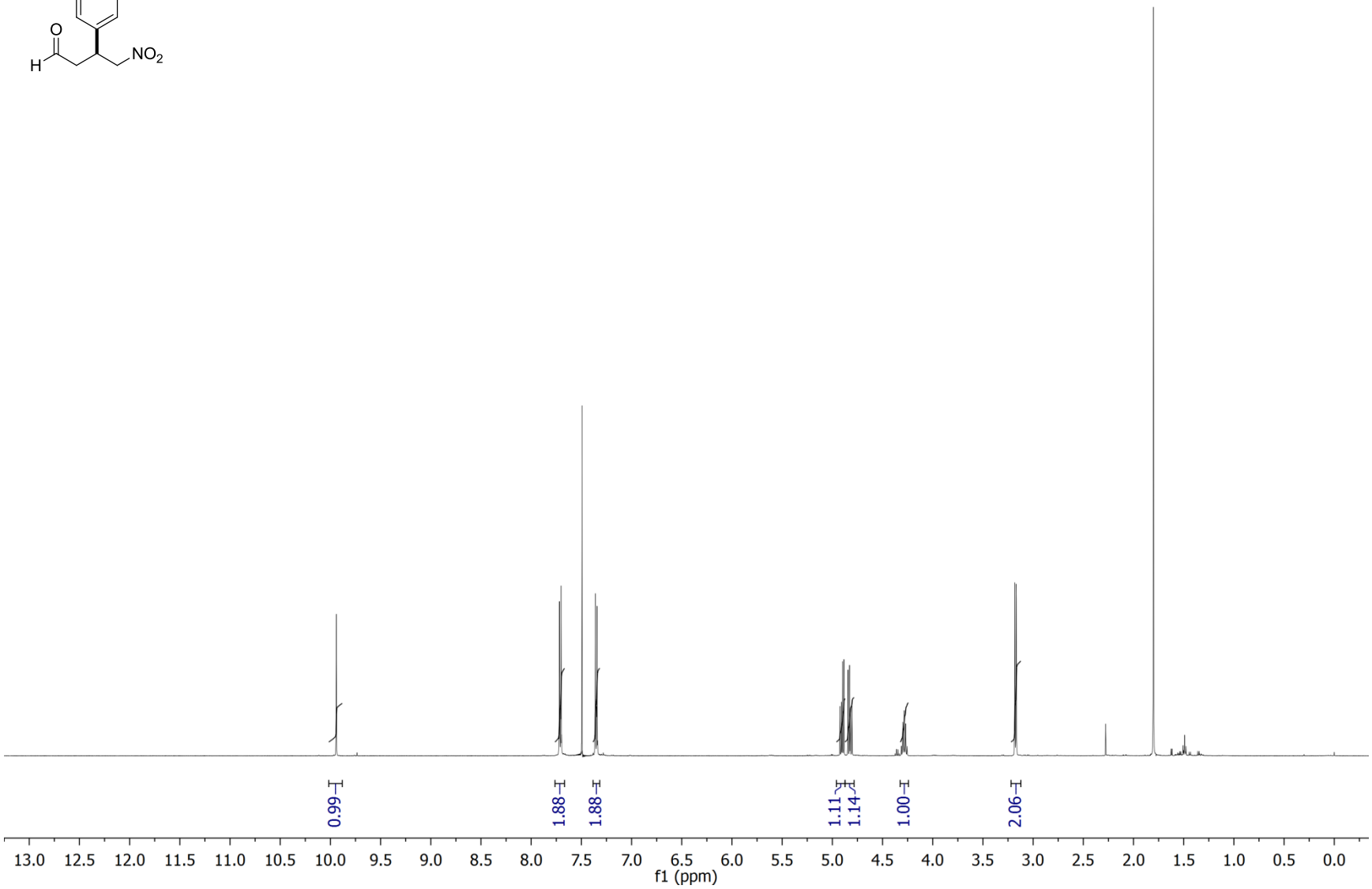
^{1}H NMR of **5l** in $CDCl_3$



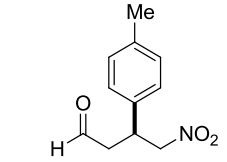


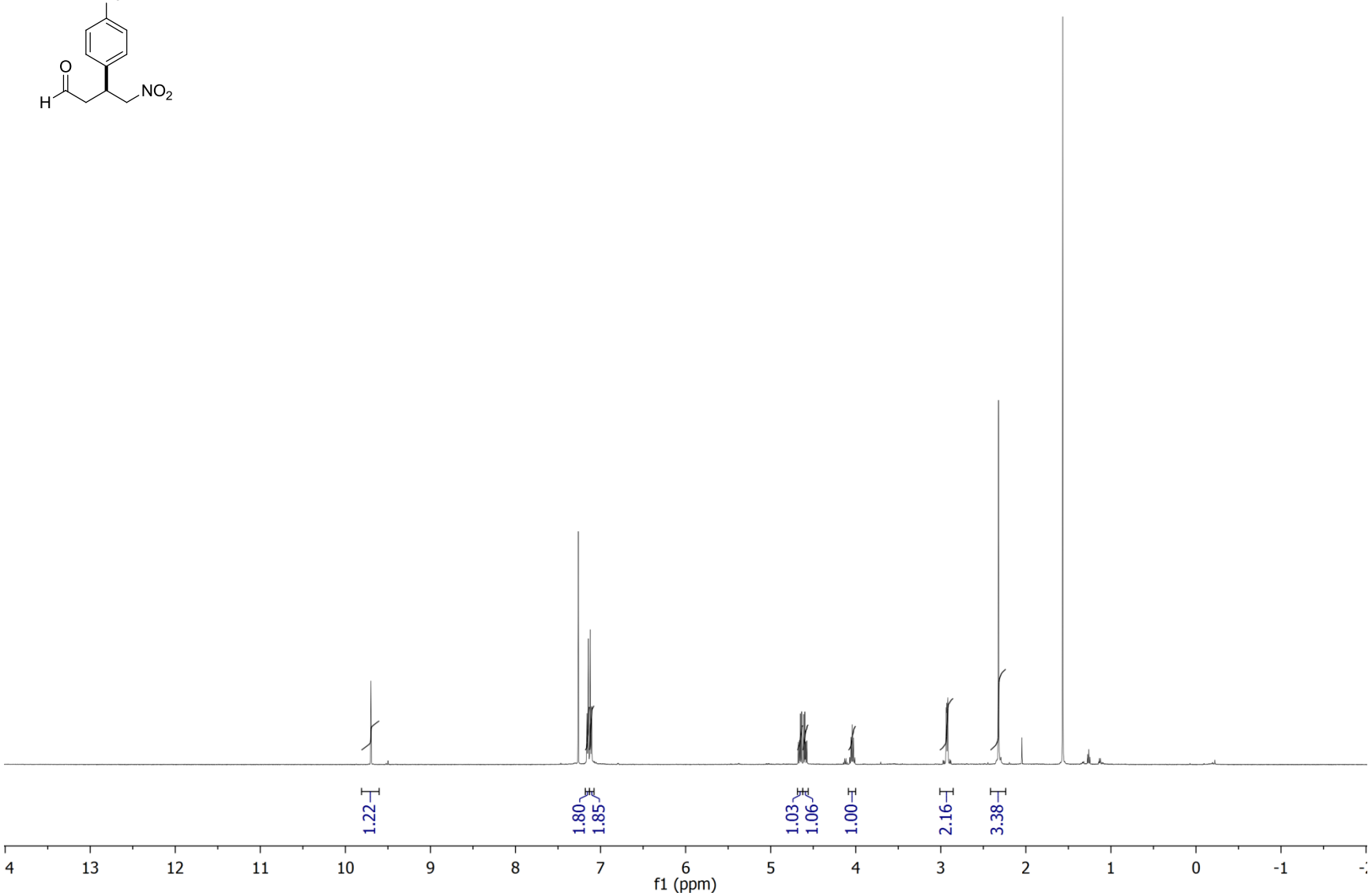
^{1}H NMR of **5m** in $CDCl_3$



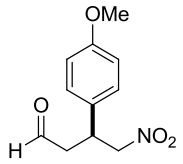


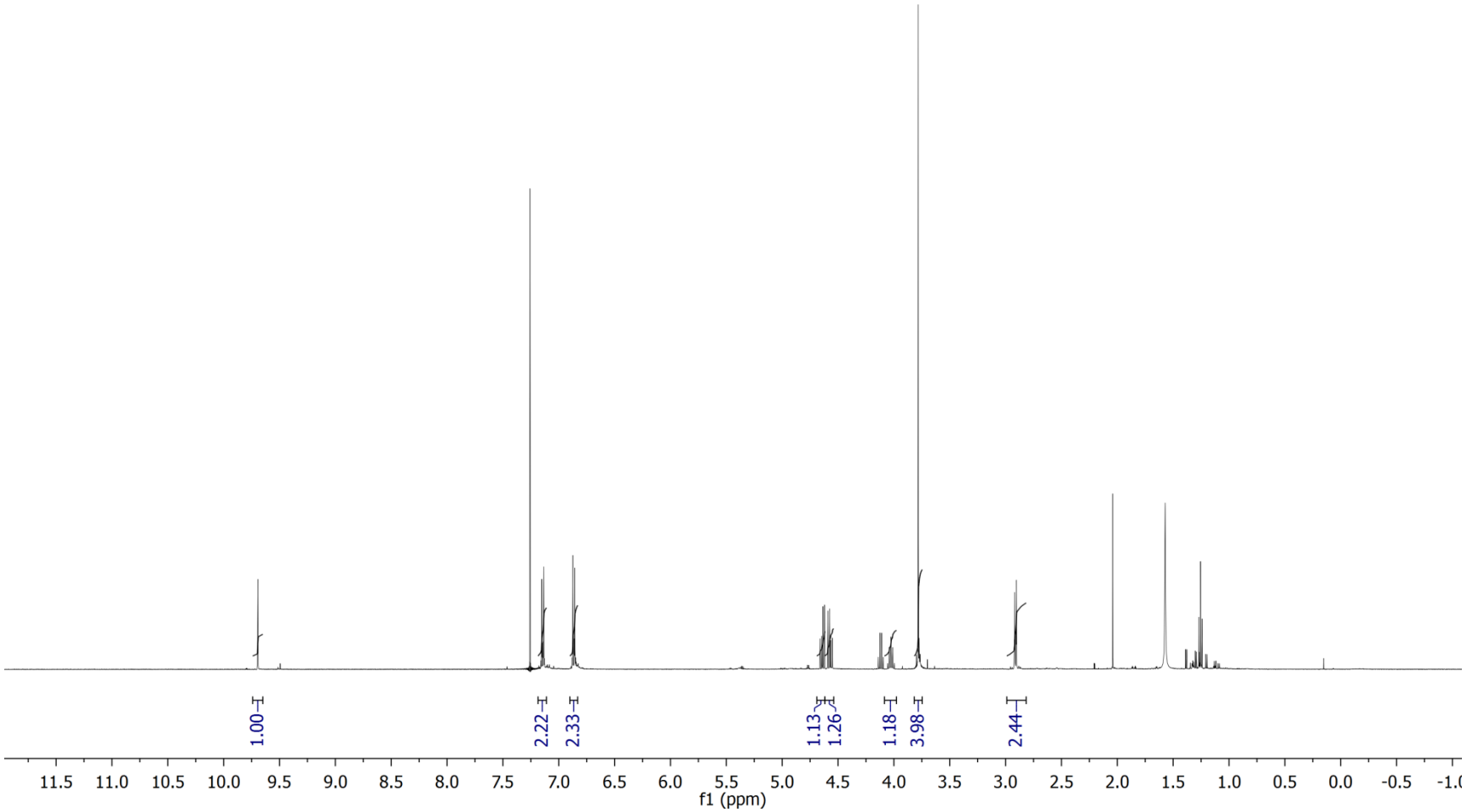
^{1}H NMR of **5n** in $CDCl_3$



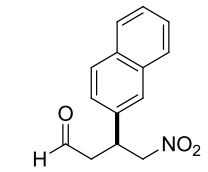


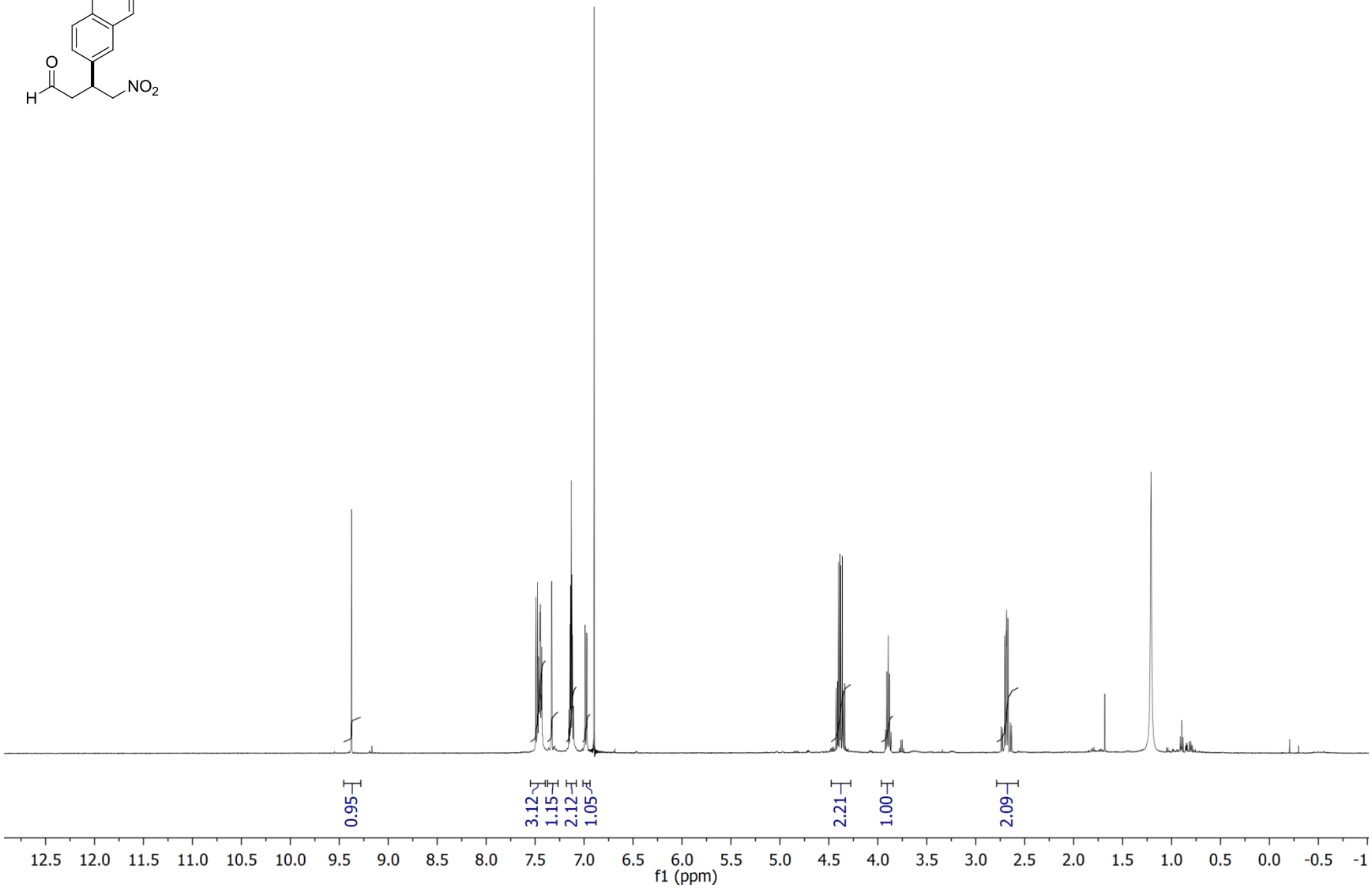
^{1}H NMR of **5o** in $CDCl_3$



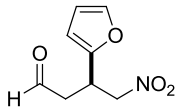


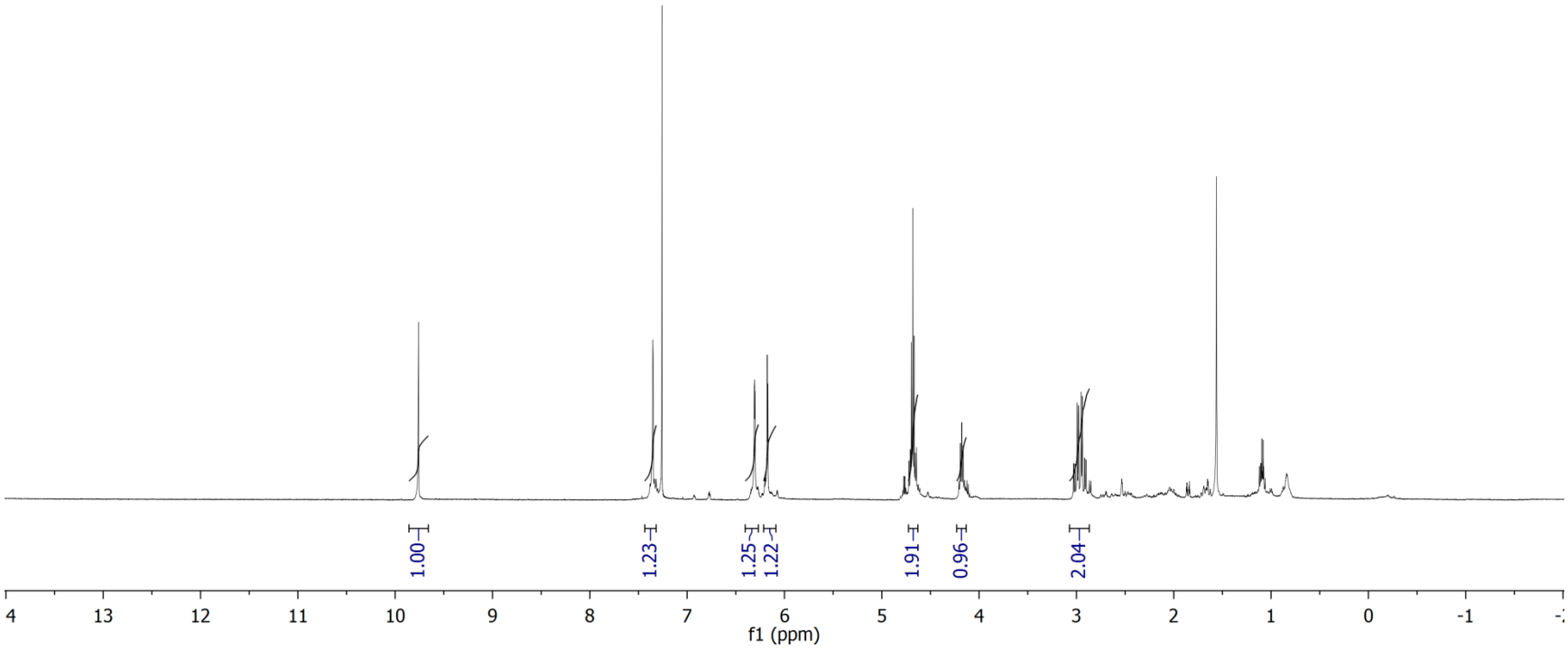
^{1}H NMR of **5p** in $CDCl_3$



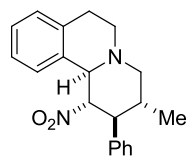


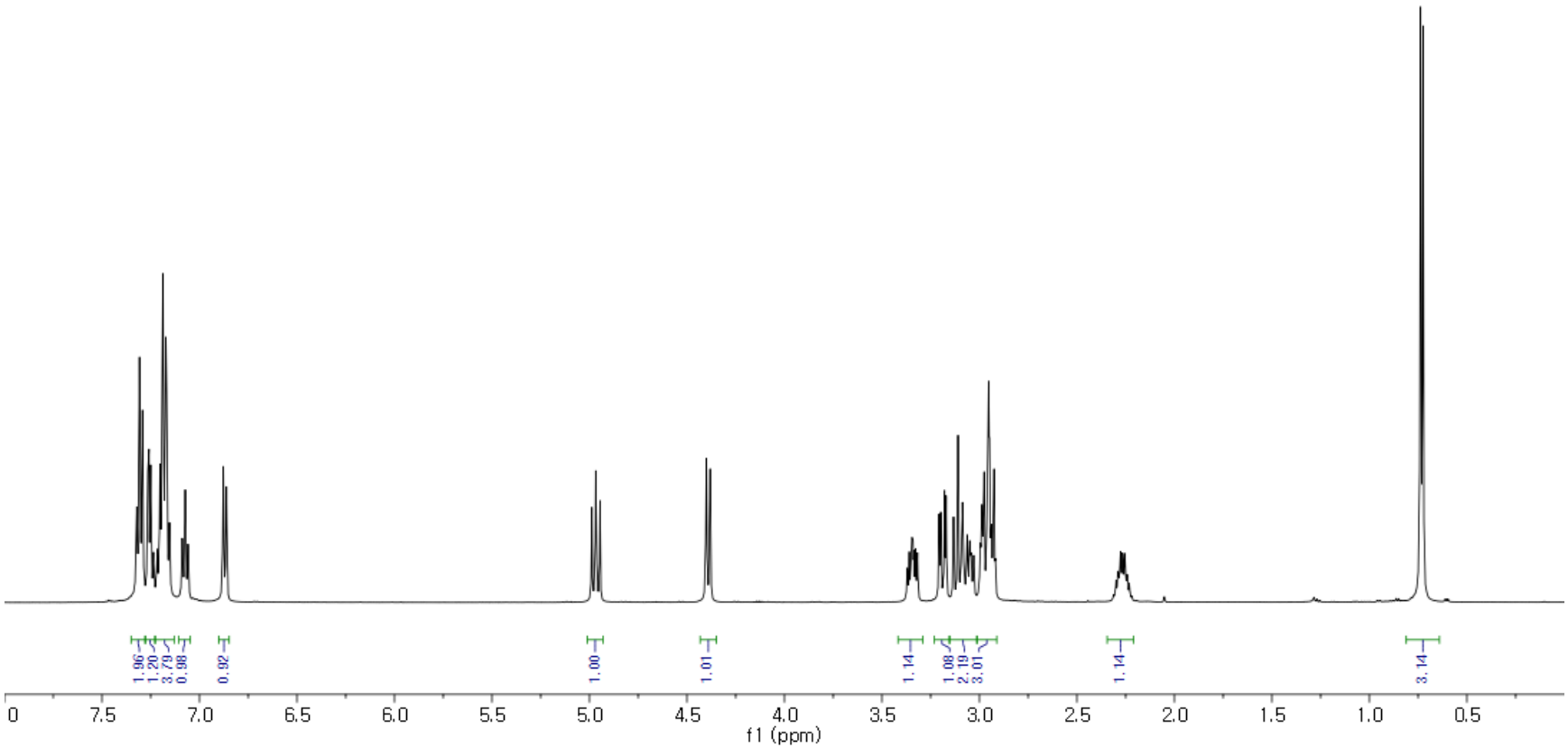
^{1}H NMR of **5q** in $CDCl_3$



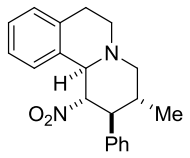


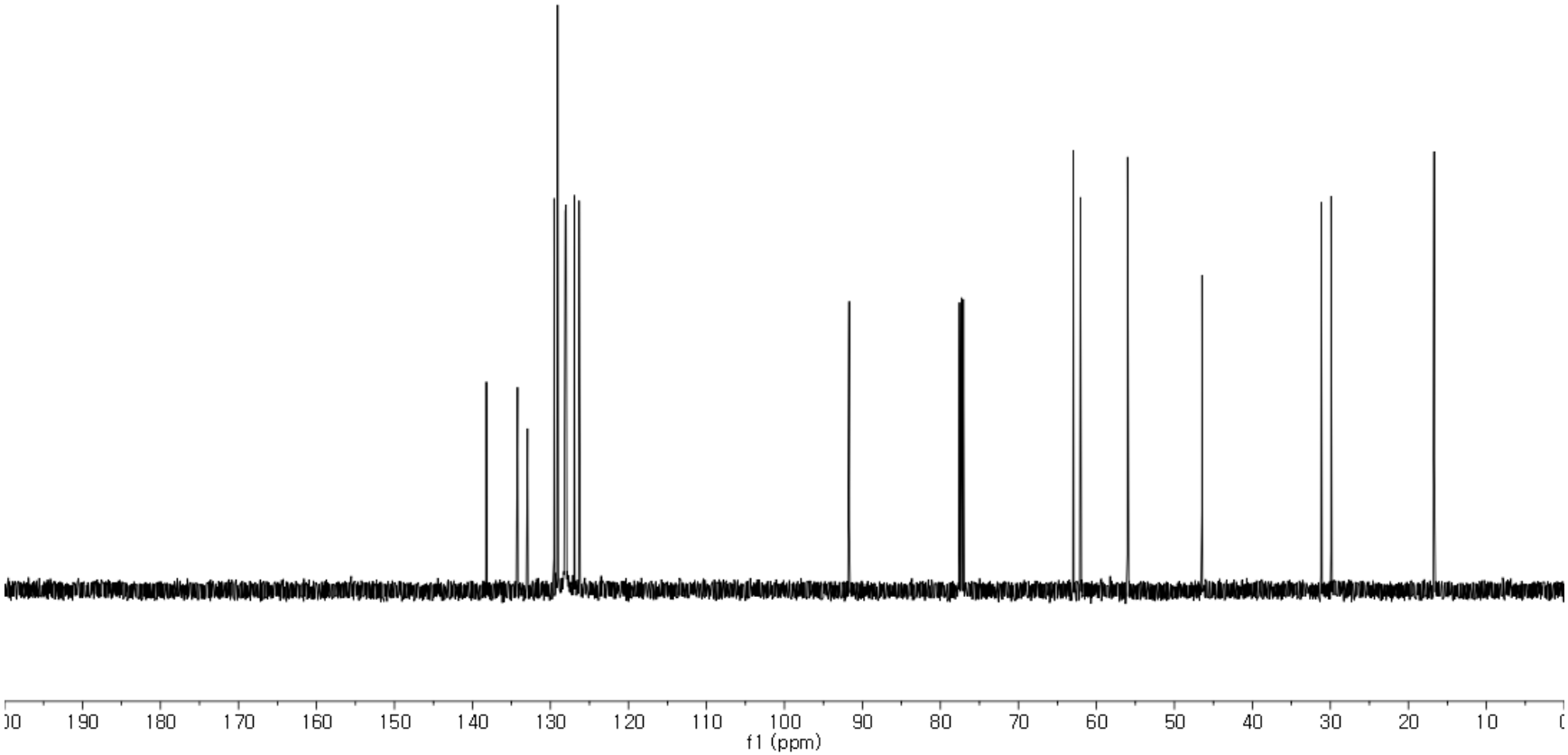
^{1}H NMR of **6a** in $CDCl_3$



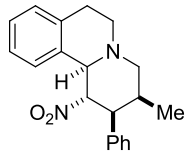


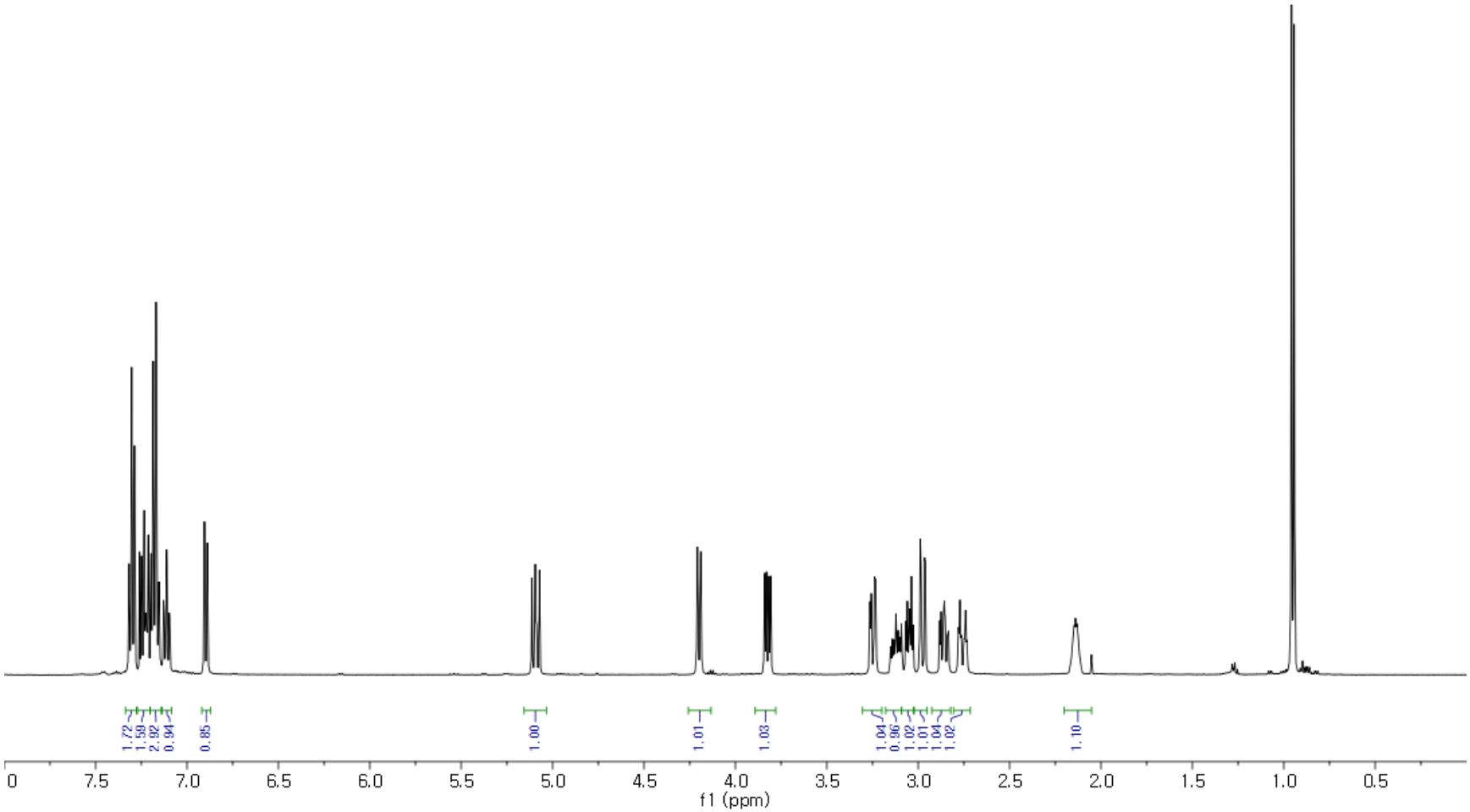
^{13}C NMR of **6a** in $CDCl_3$



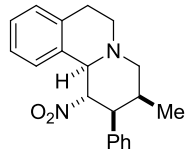


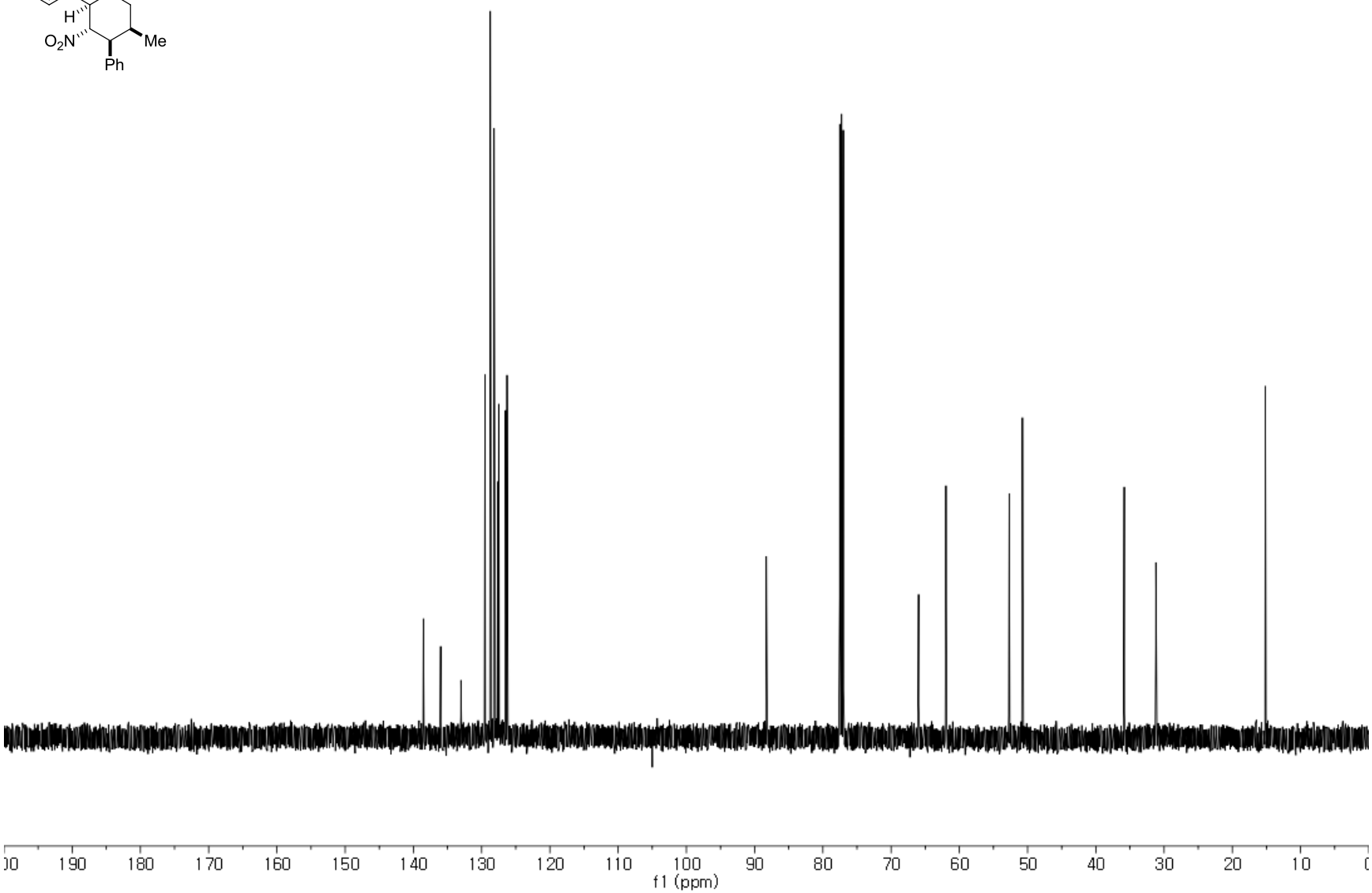
^{1}H NMR of **7a** in $CDCl_3$



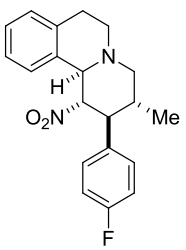


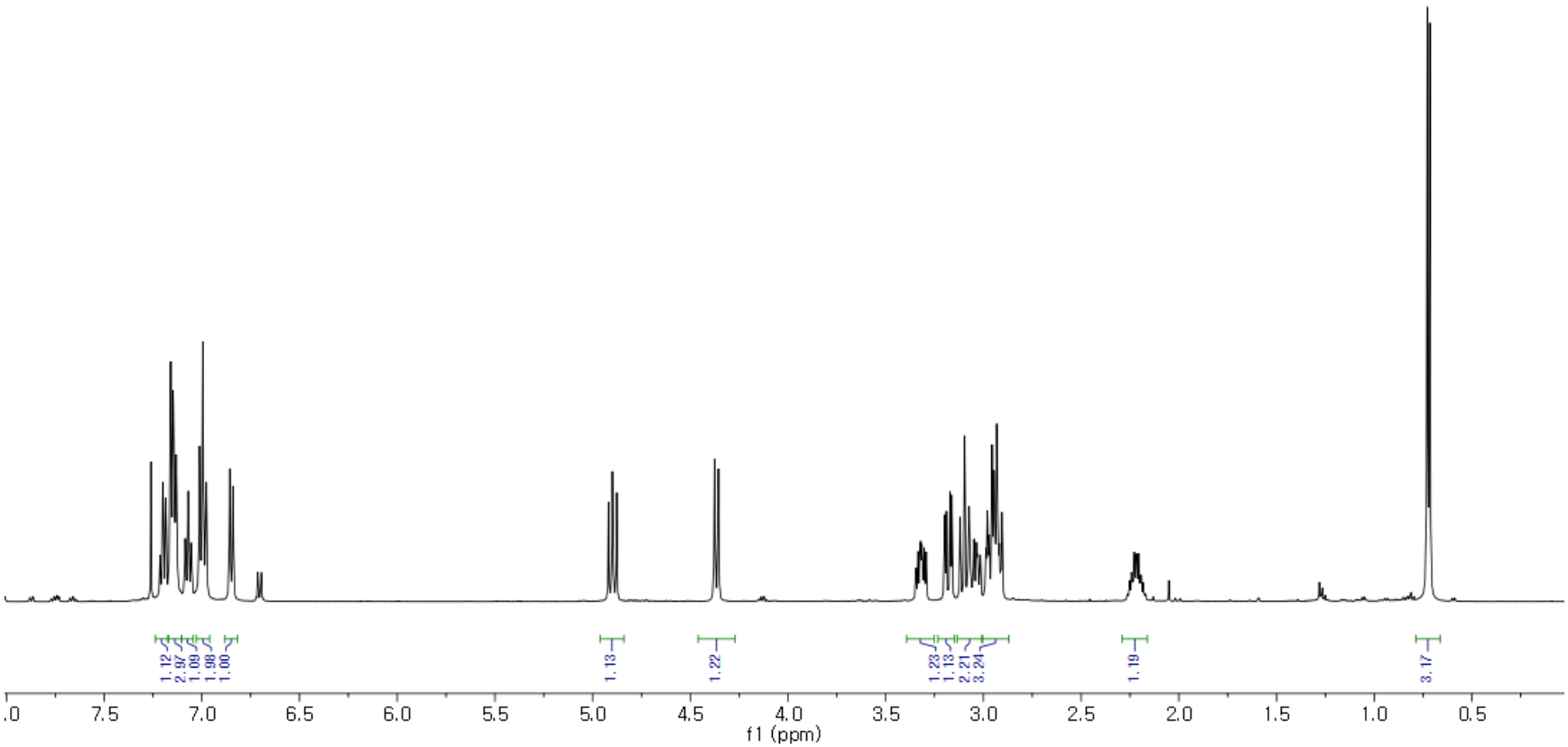
^{13}C NMR of **7a** in $CDCl_3$



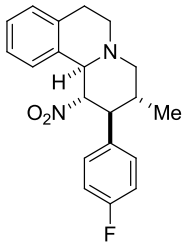


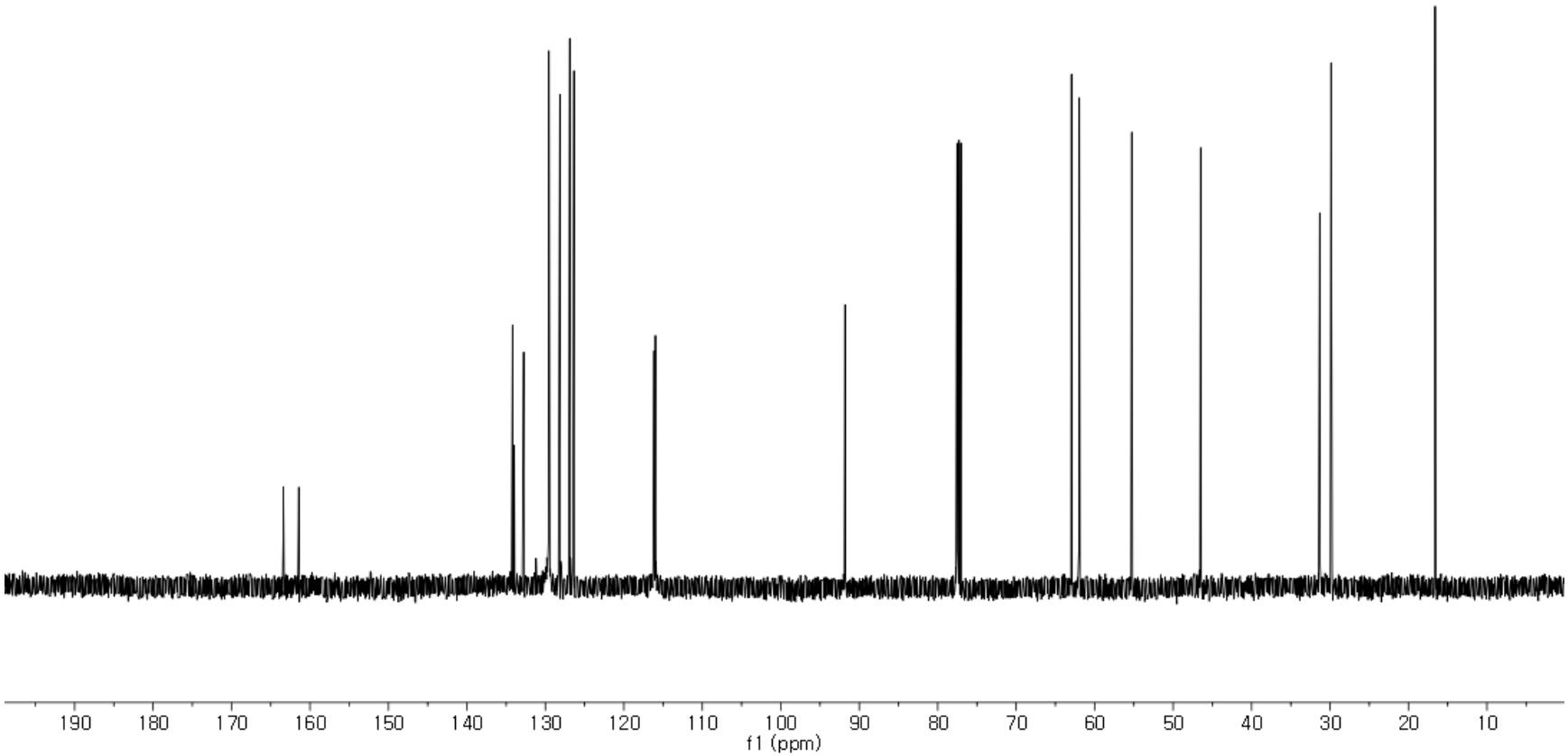
^{1}H NMR of **6b** in $CDCl_3$



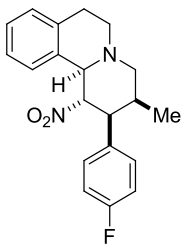


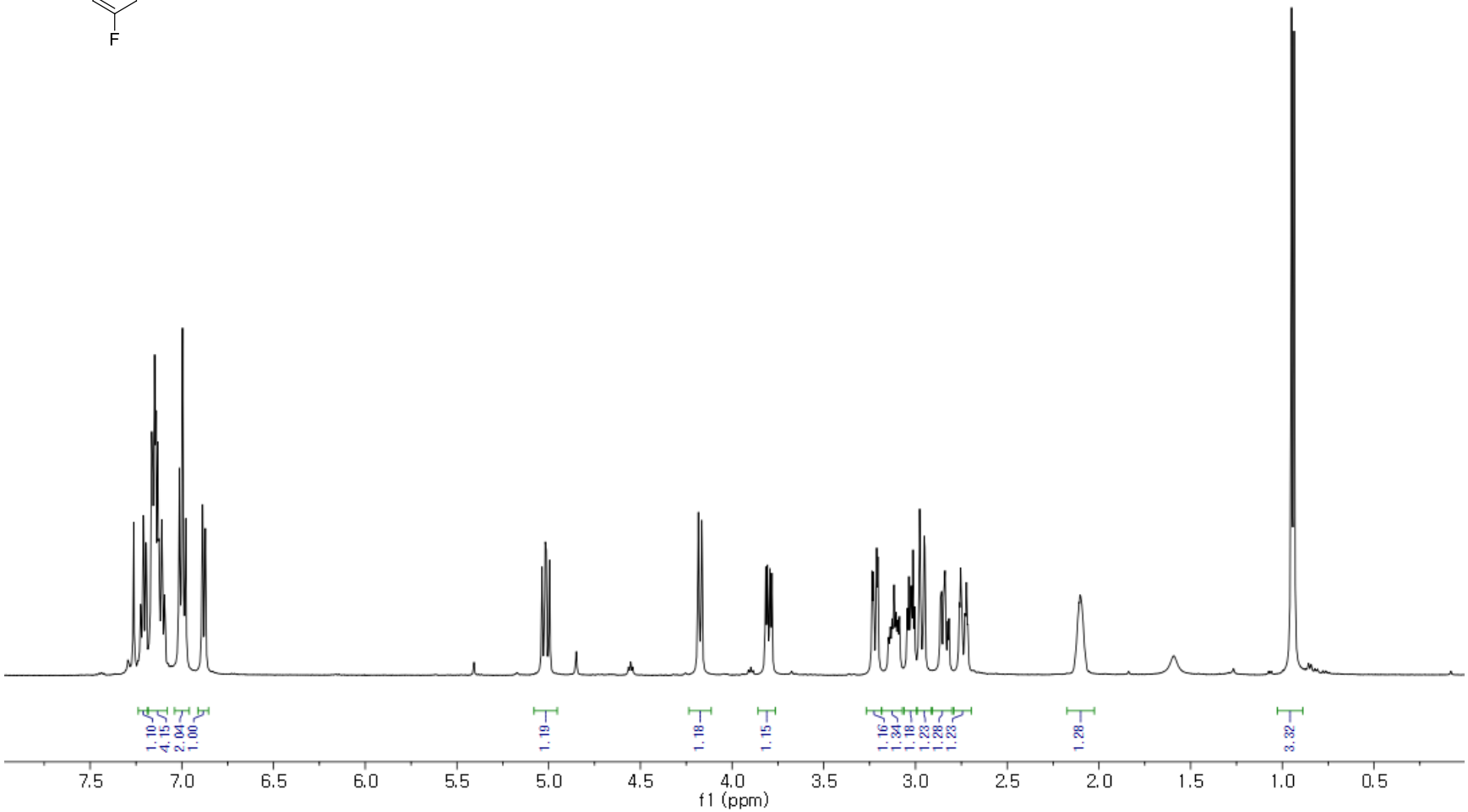
^{13}C NMR of **6b** in $CDCl_3$



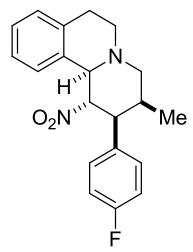


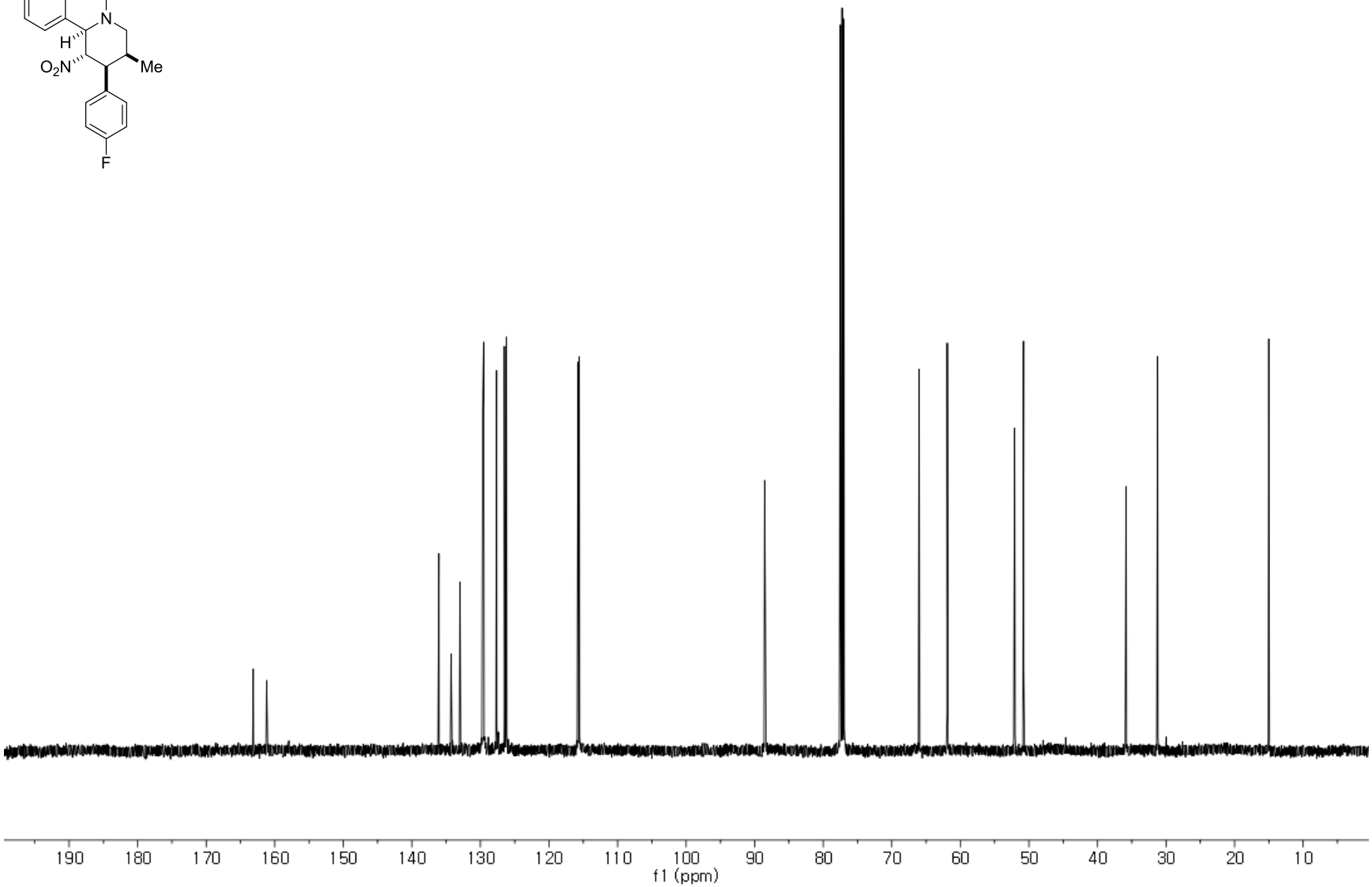
^{1}H NMR of **7b** in $CDCl_3$



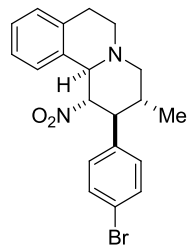


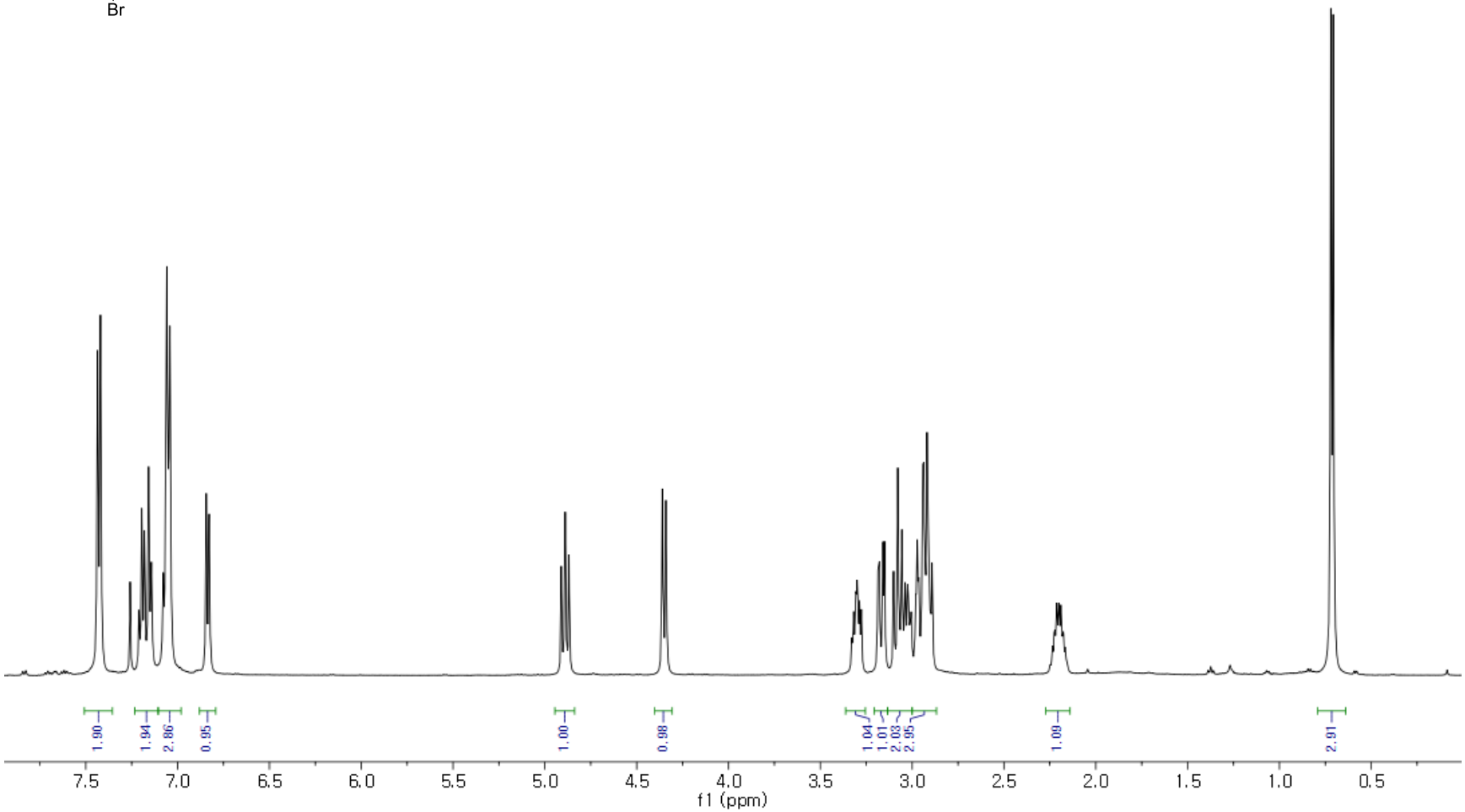
^{13}C NMR of **7b** in $CDCl_3$



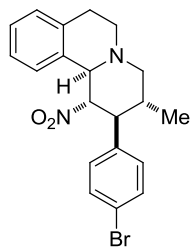


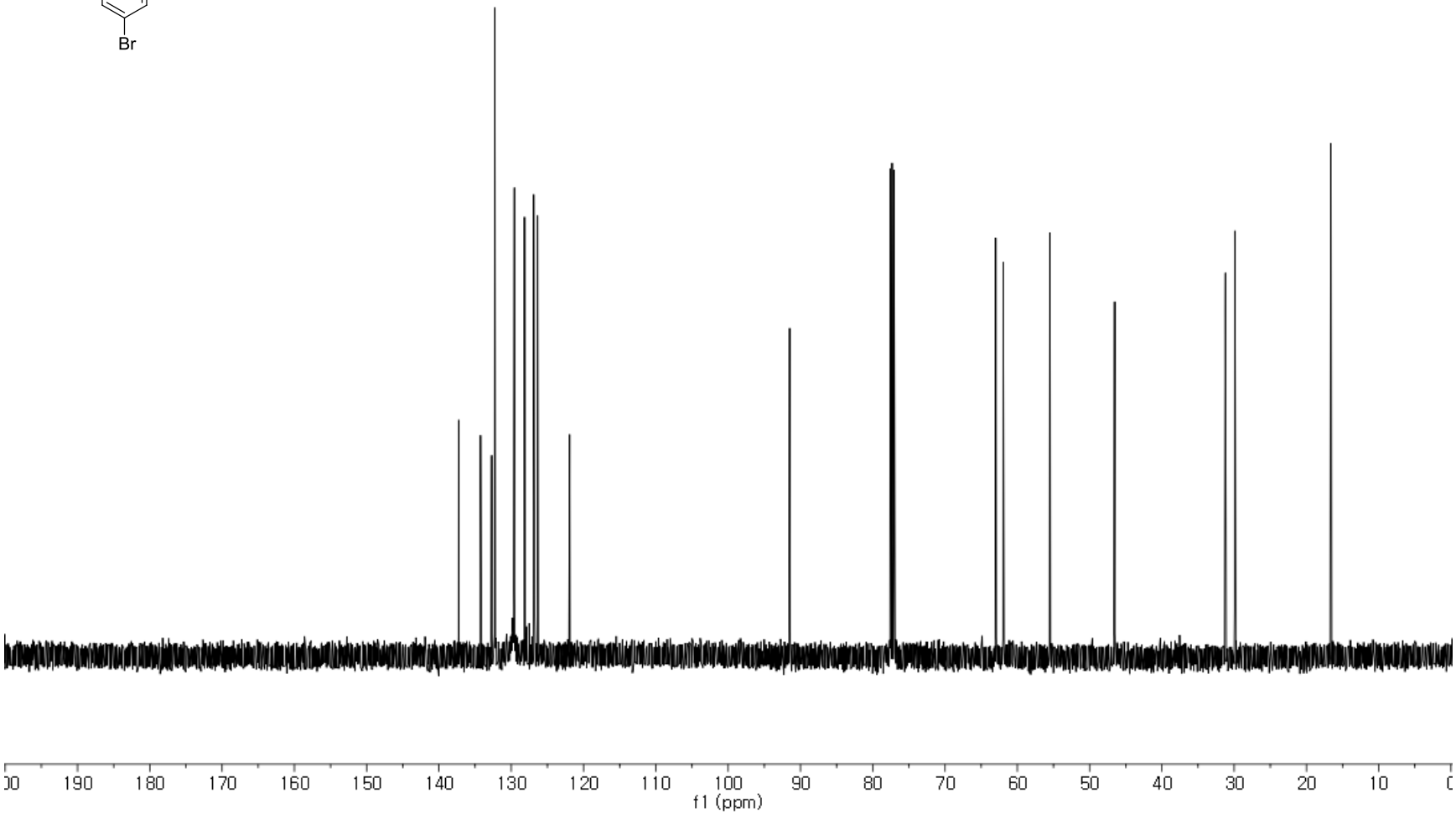
^{1}H NMR of **6c** in $CDCl_3$



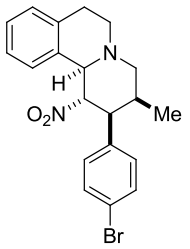


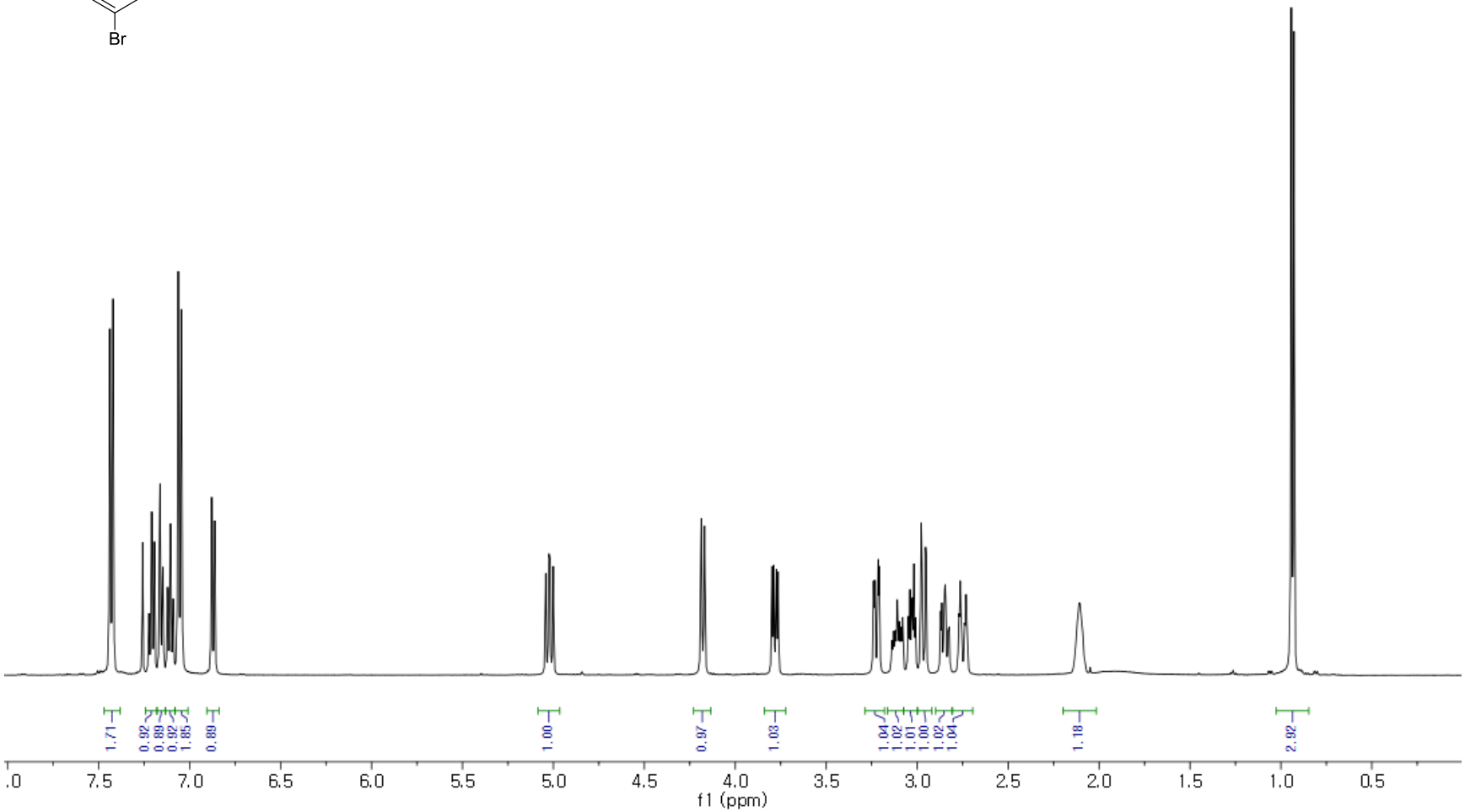
^{13}C NMR of **6c** in $CDCl_3$



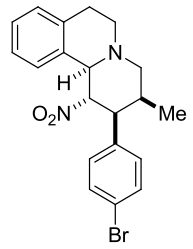


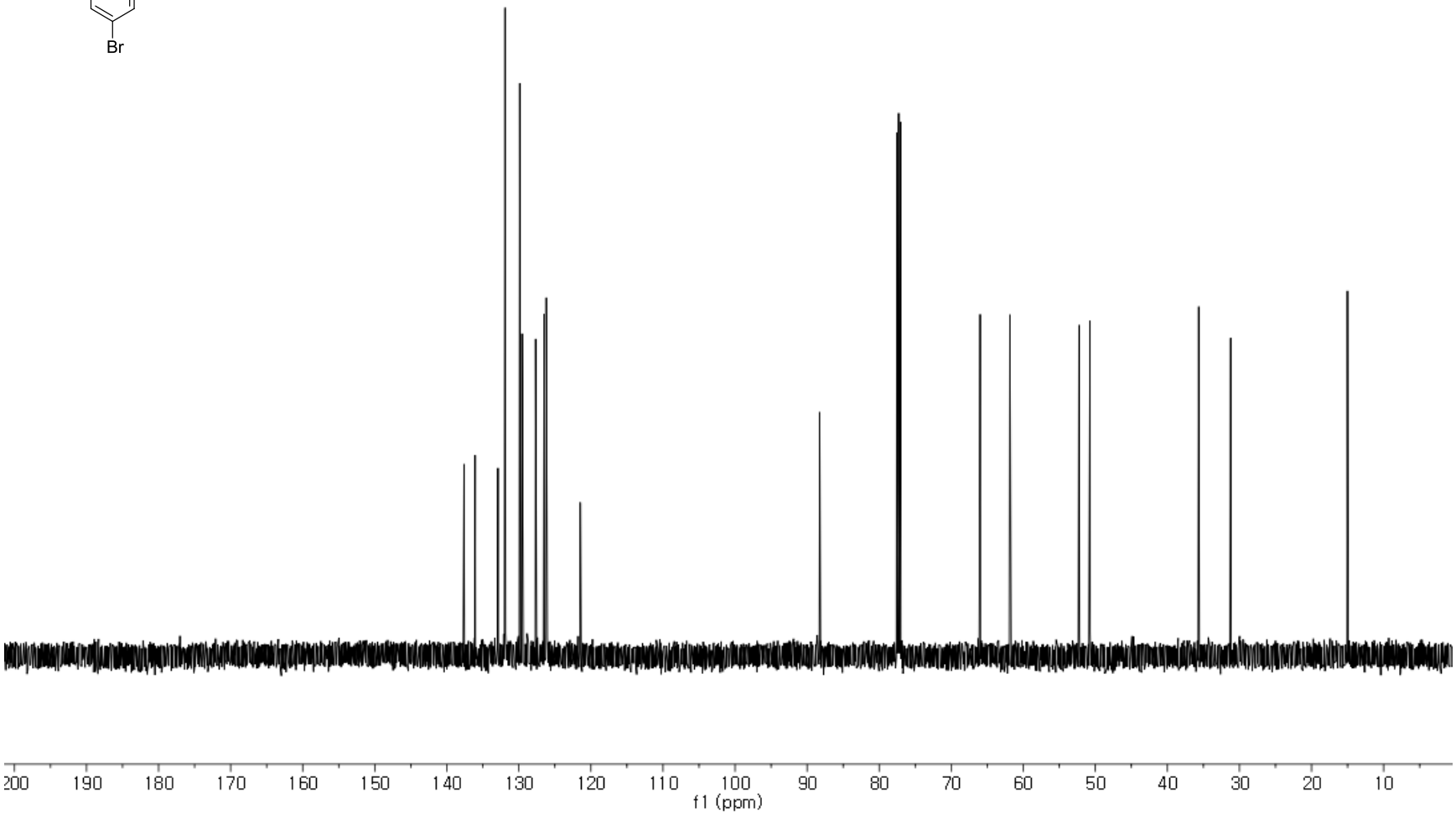
^{1}H NMR of **7c** in $CDCl_3$



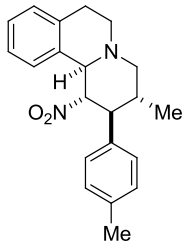


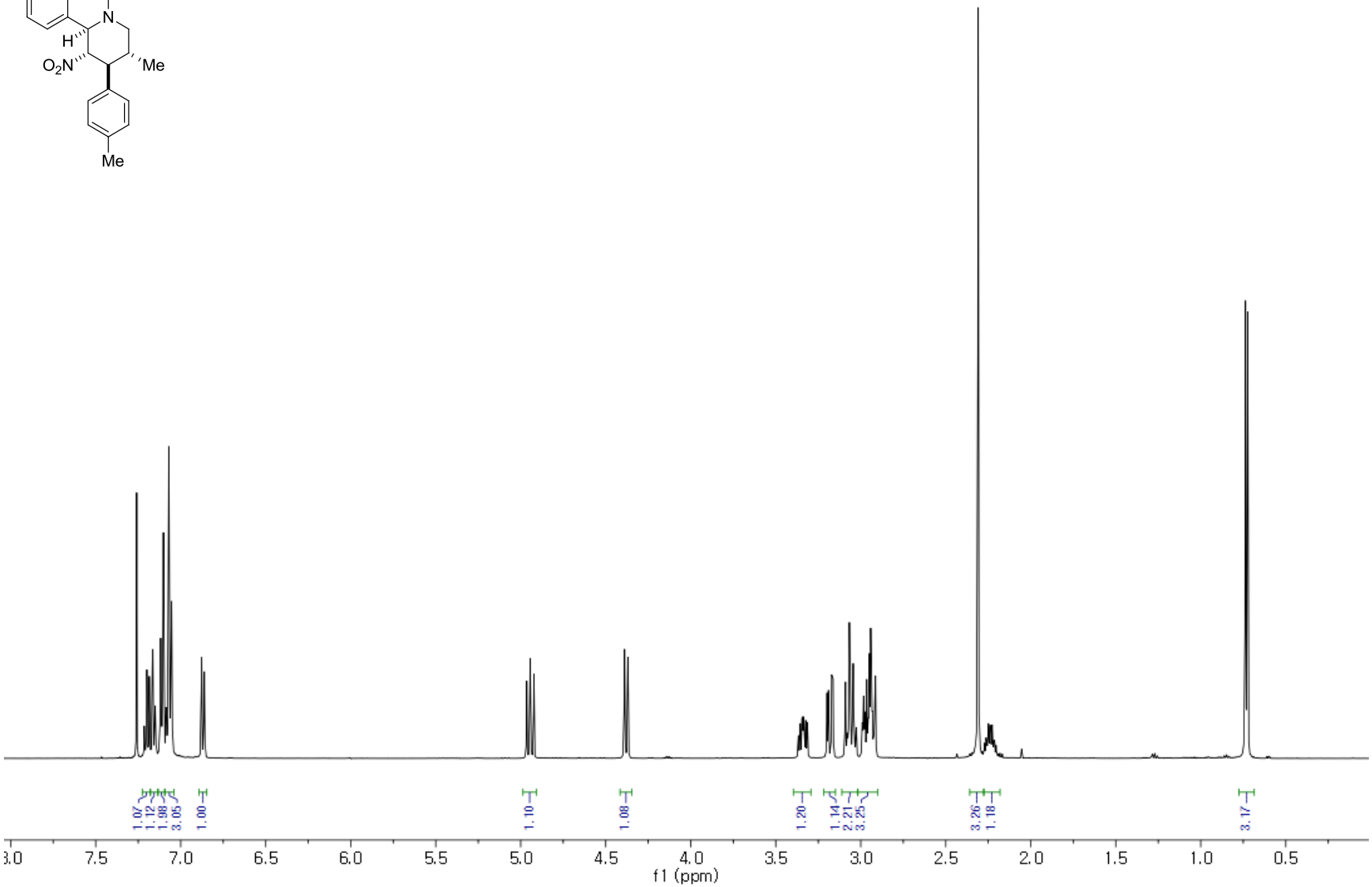
^{13}C NMR of **7c** in $CDCl_3$



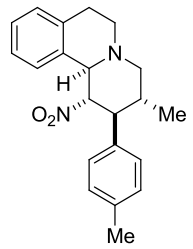


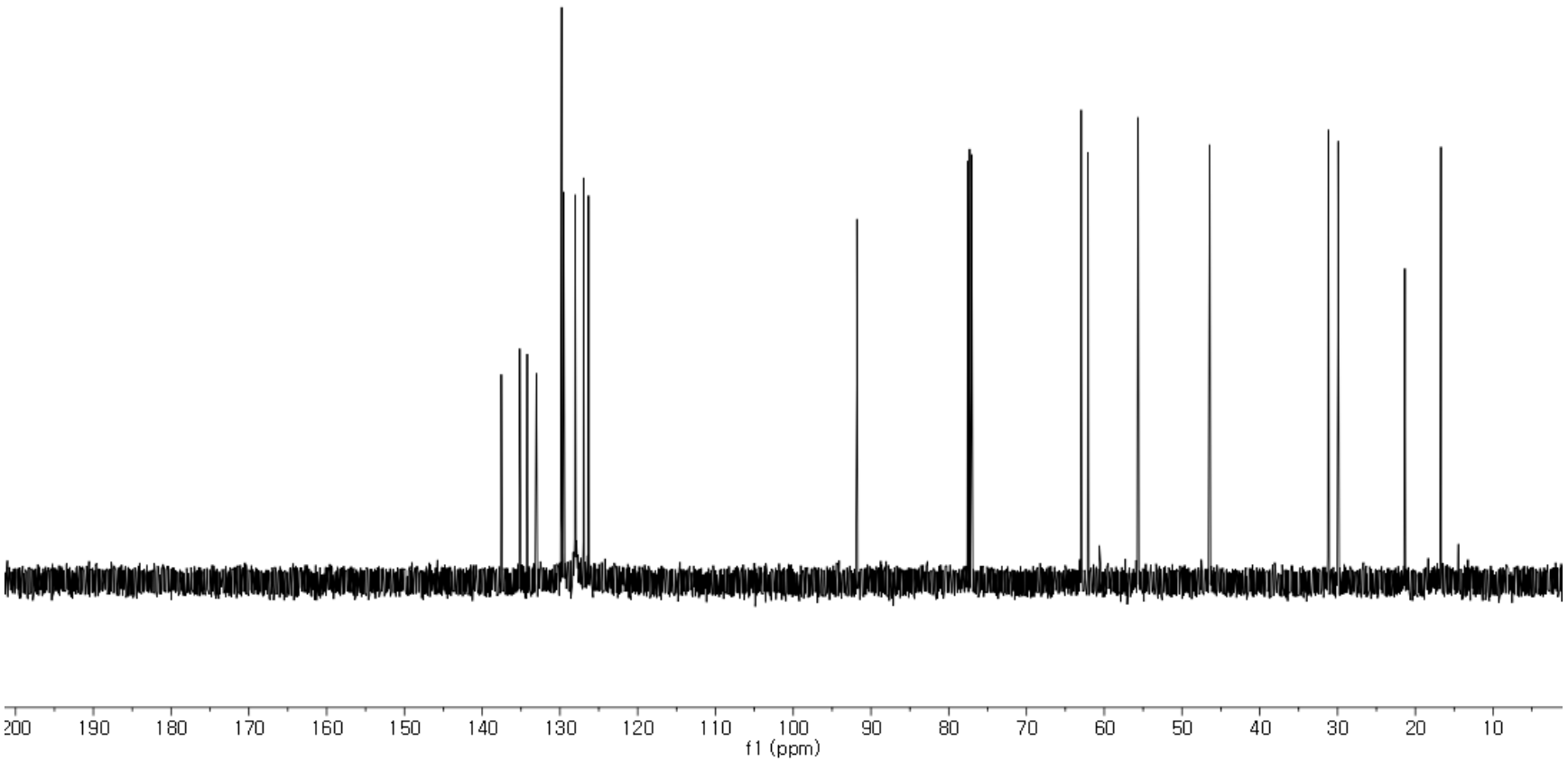
^{1}H NMR of **6d** in $CDCl_3$



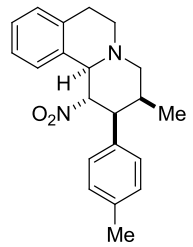


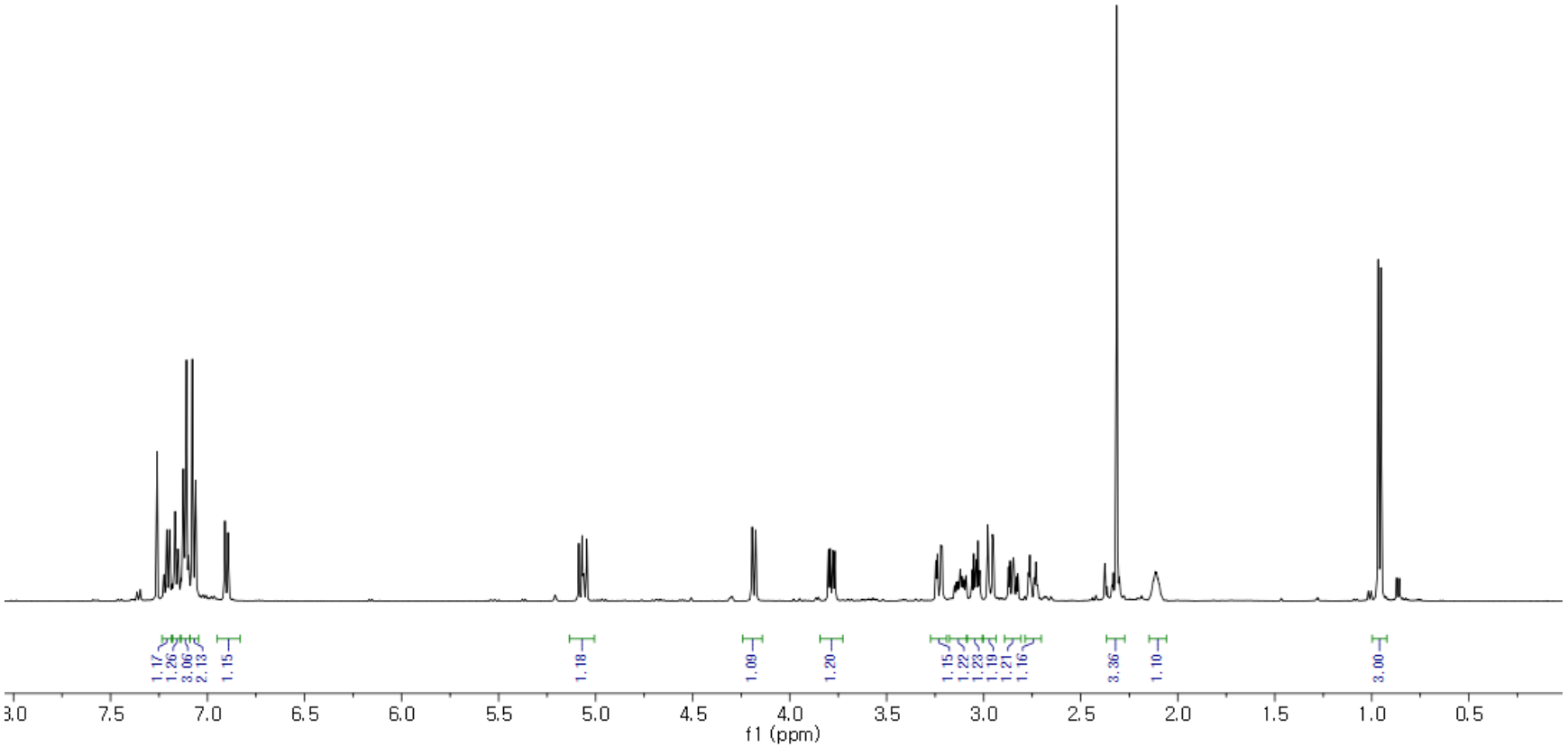
^{13}C NMR of **6d** in $CDCl_3$



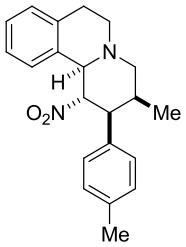


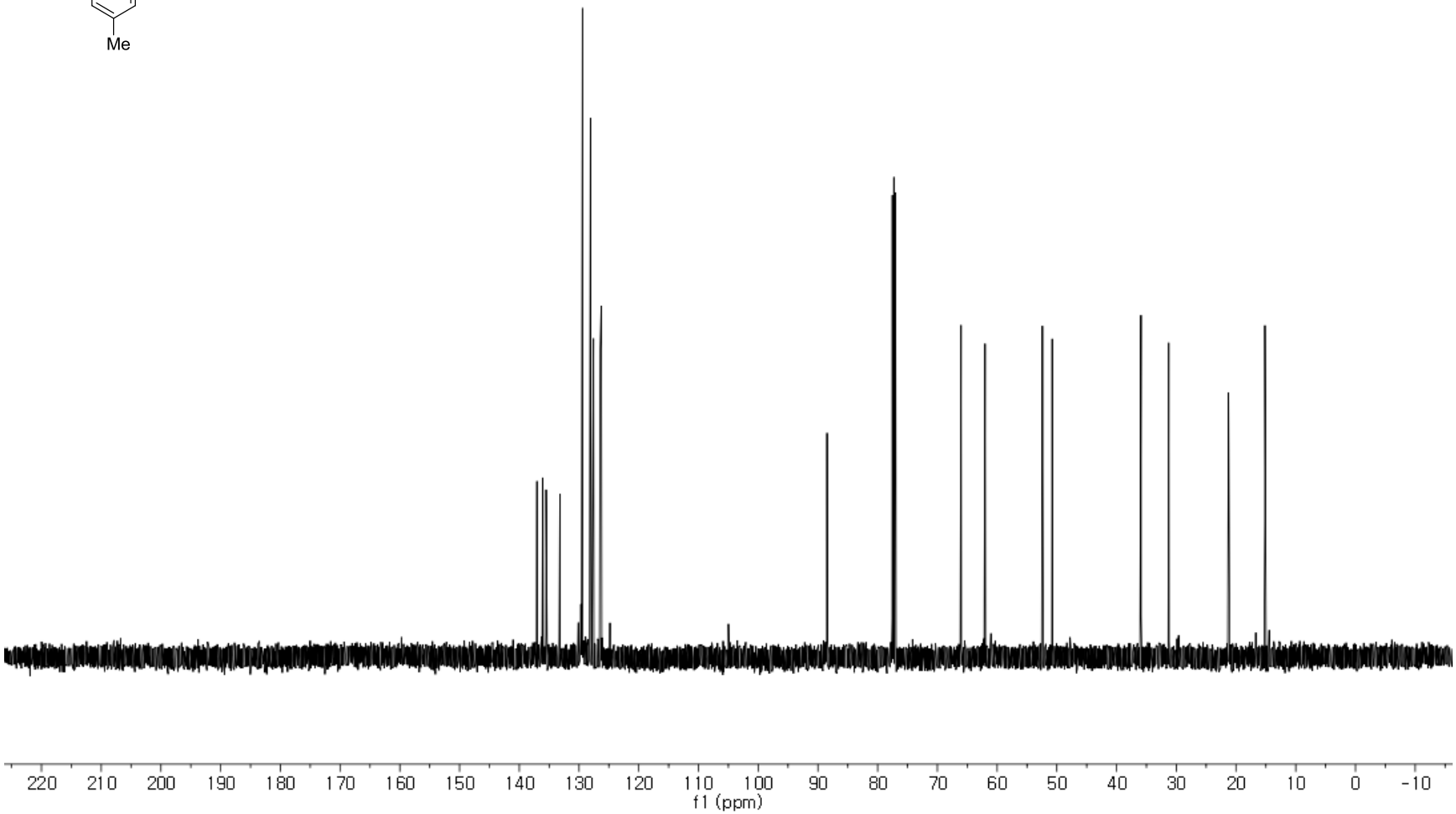
^{1}H NMR of **7d** in $CDCl_3$



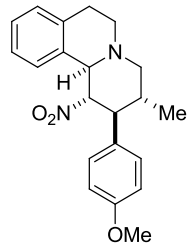


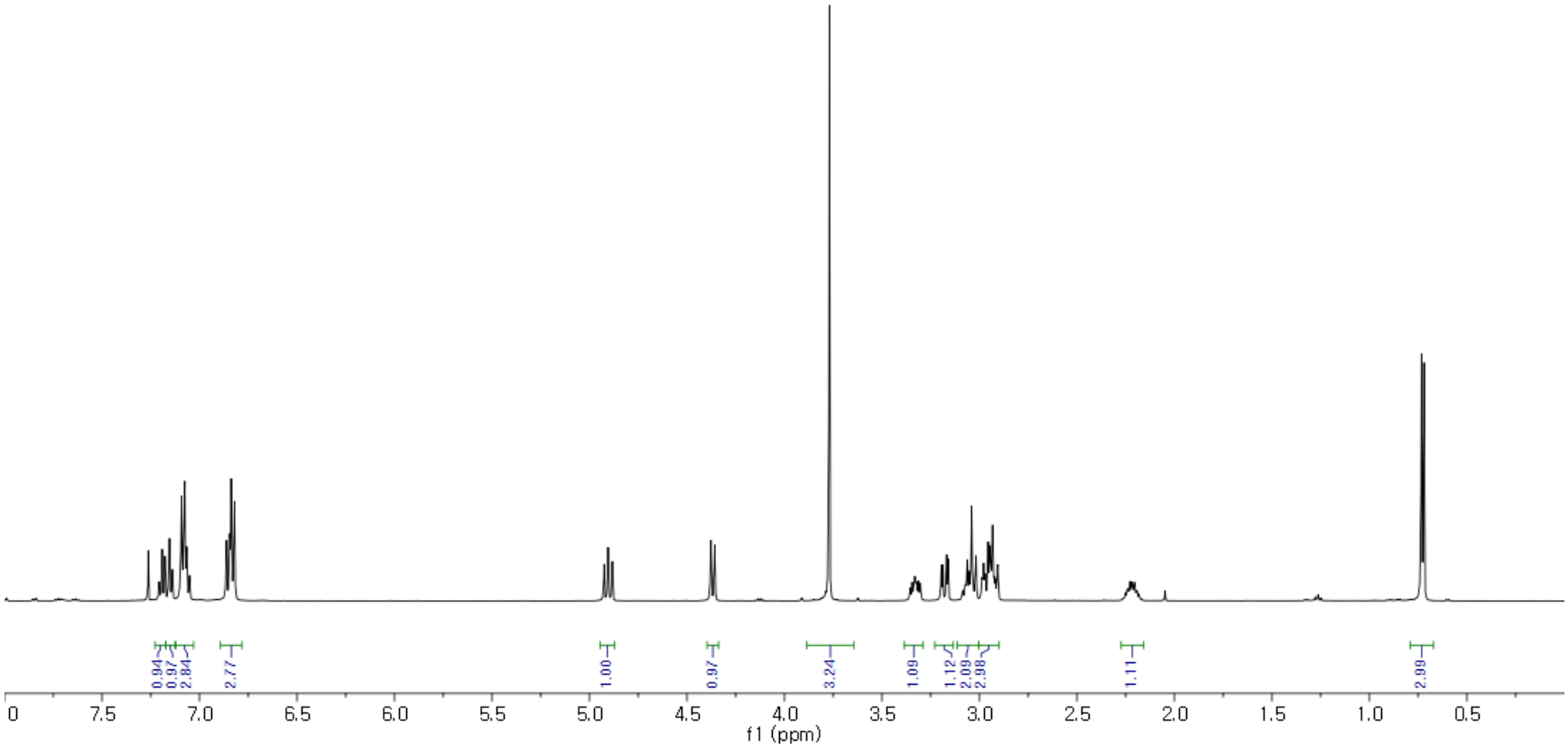
^{13}C NMR of **7d** in $CDCl_3$



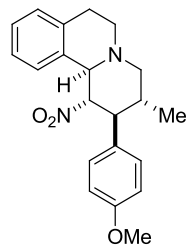


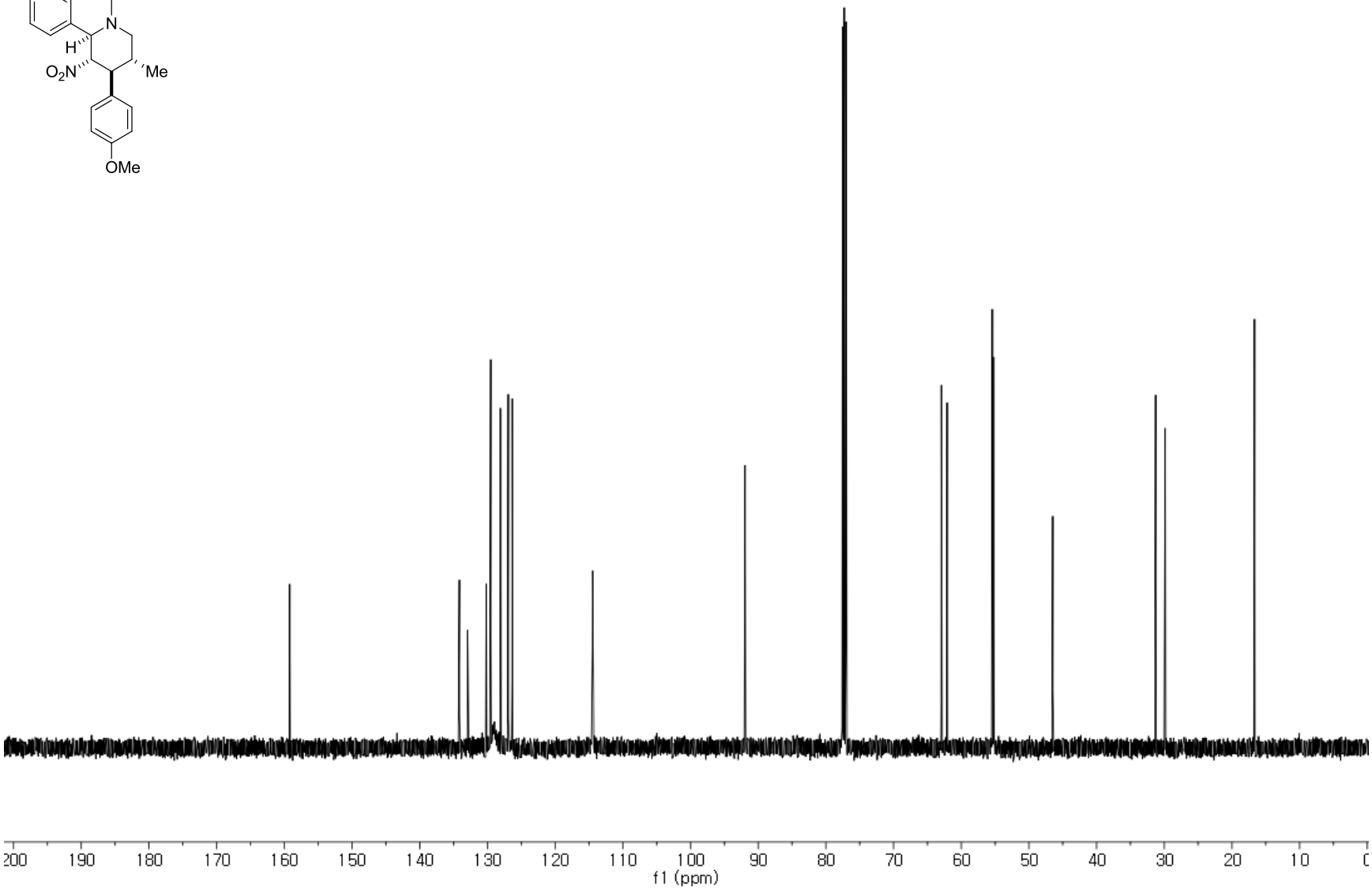
^{1}H NMR of **6e** in $CDCl_3$



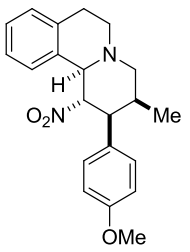


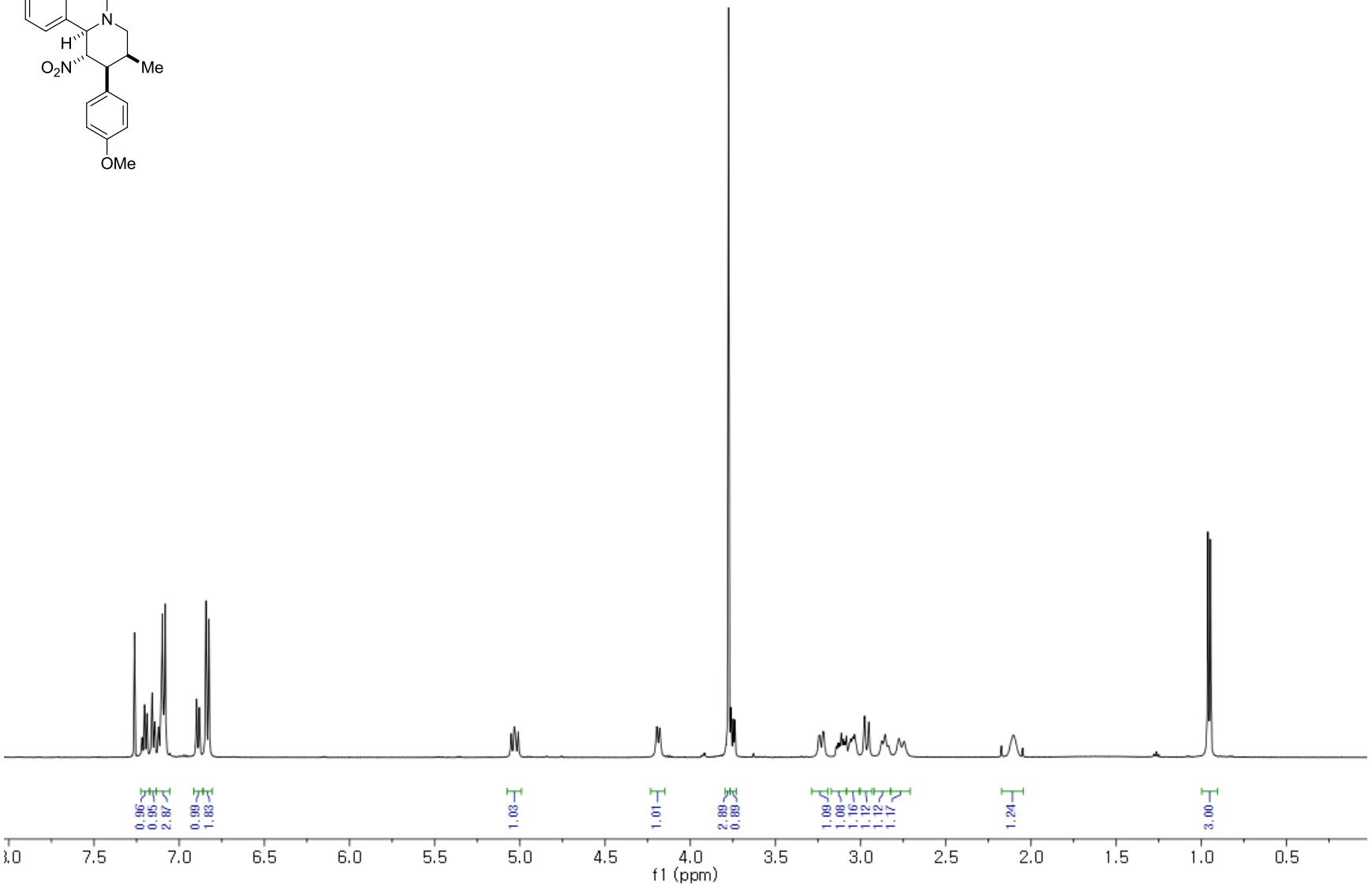
^{13}C NMR of **6e** in $CDCl_3$



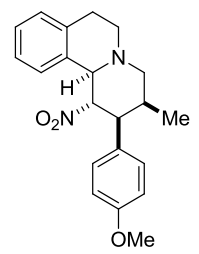


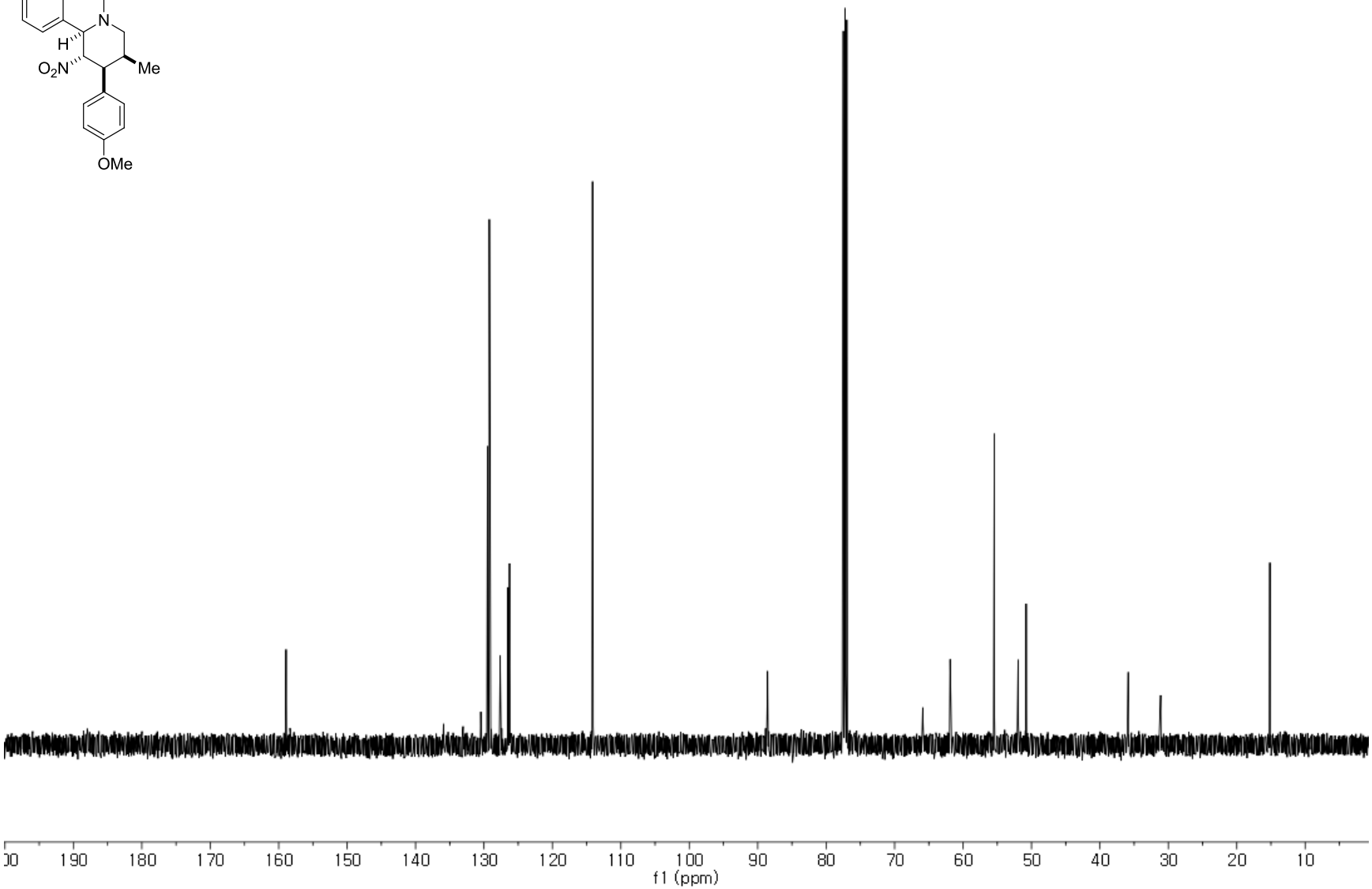
^{1}H NMR of **7e** in $CDCl_3$



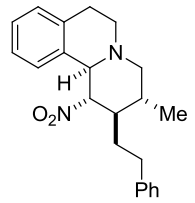


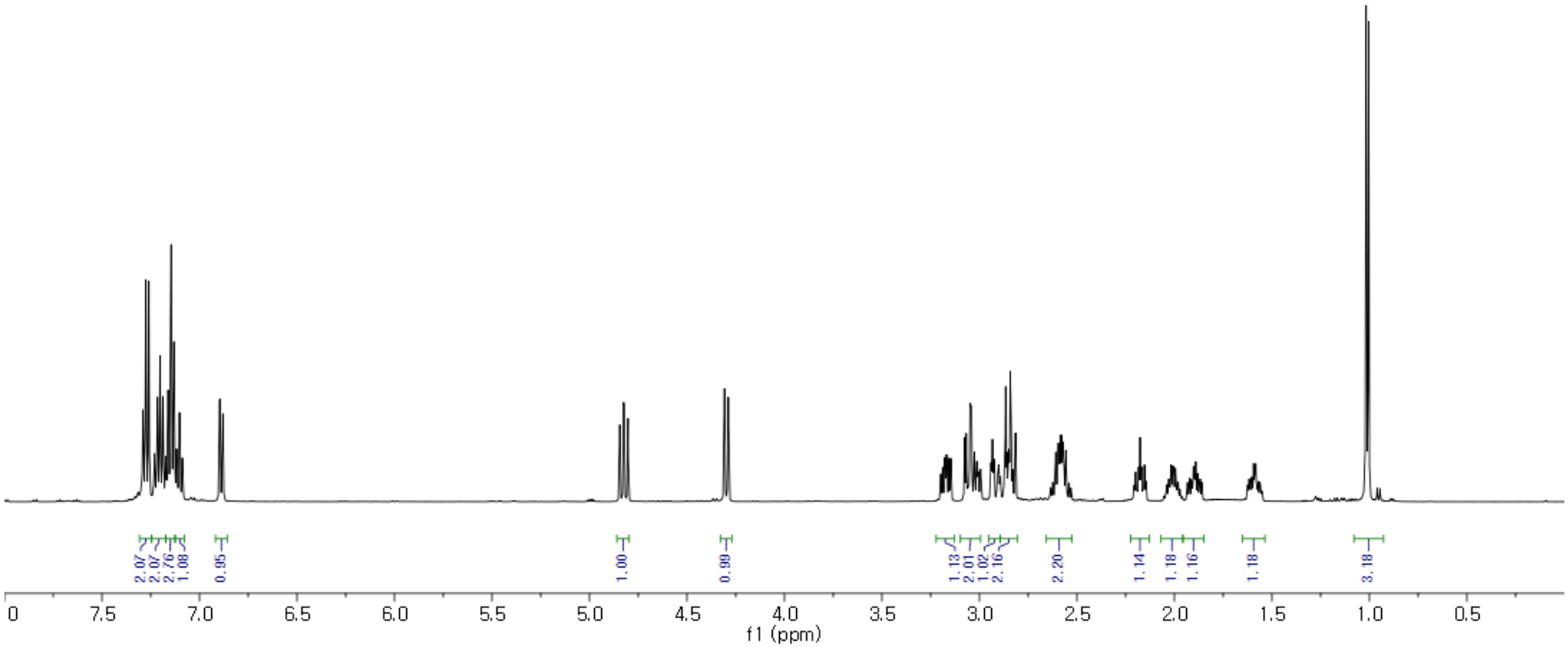
^{13}C NMR of **7e** in $CDCl_3$



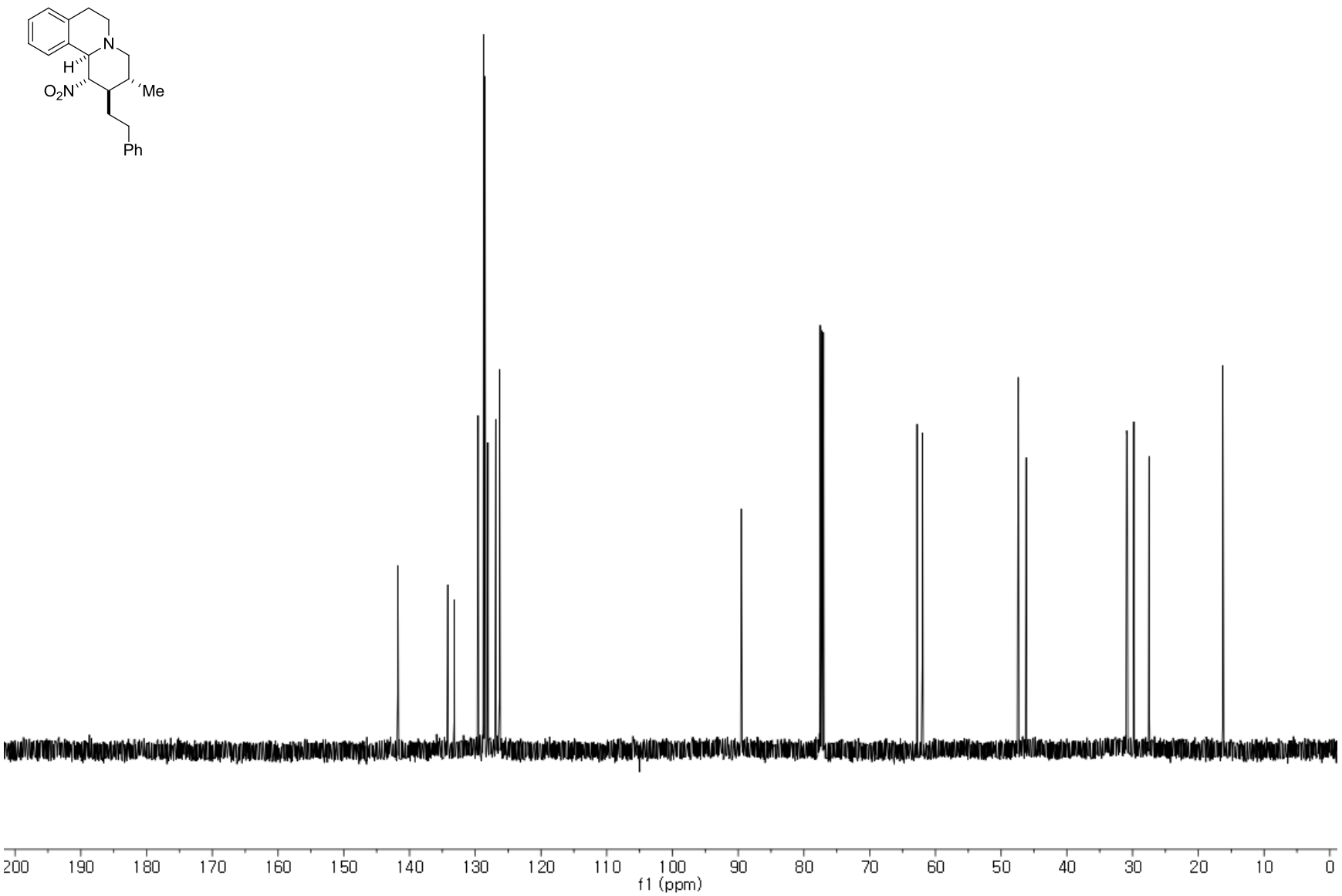


^{1}H NMR of **6f** in $CDCl_3$

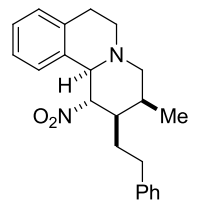


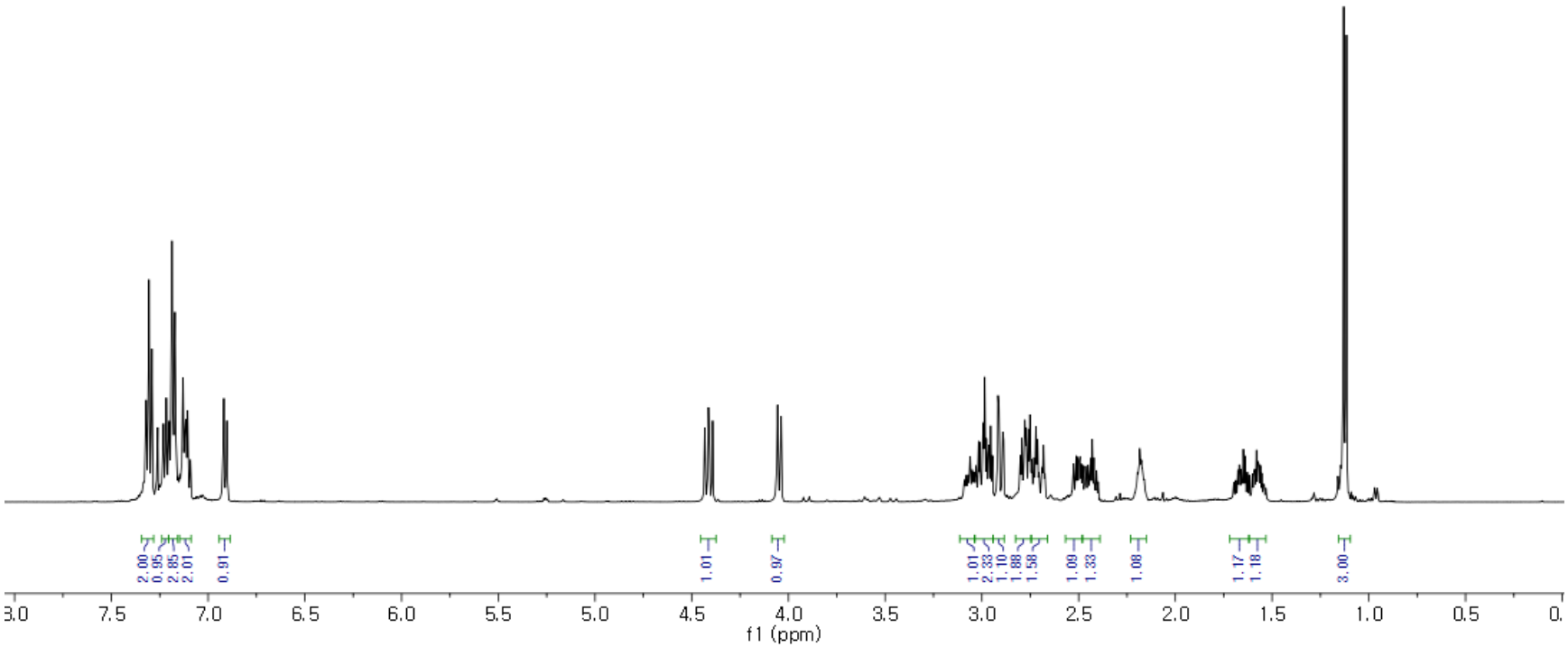


^{13}C NMR of **6f** in $CDCl_3$

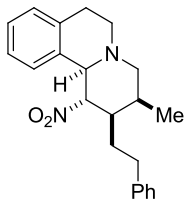


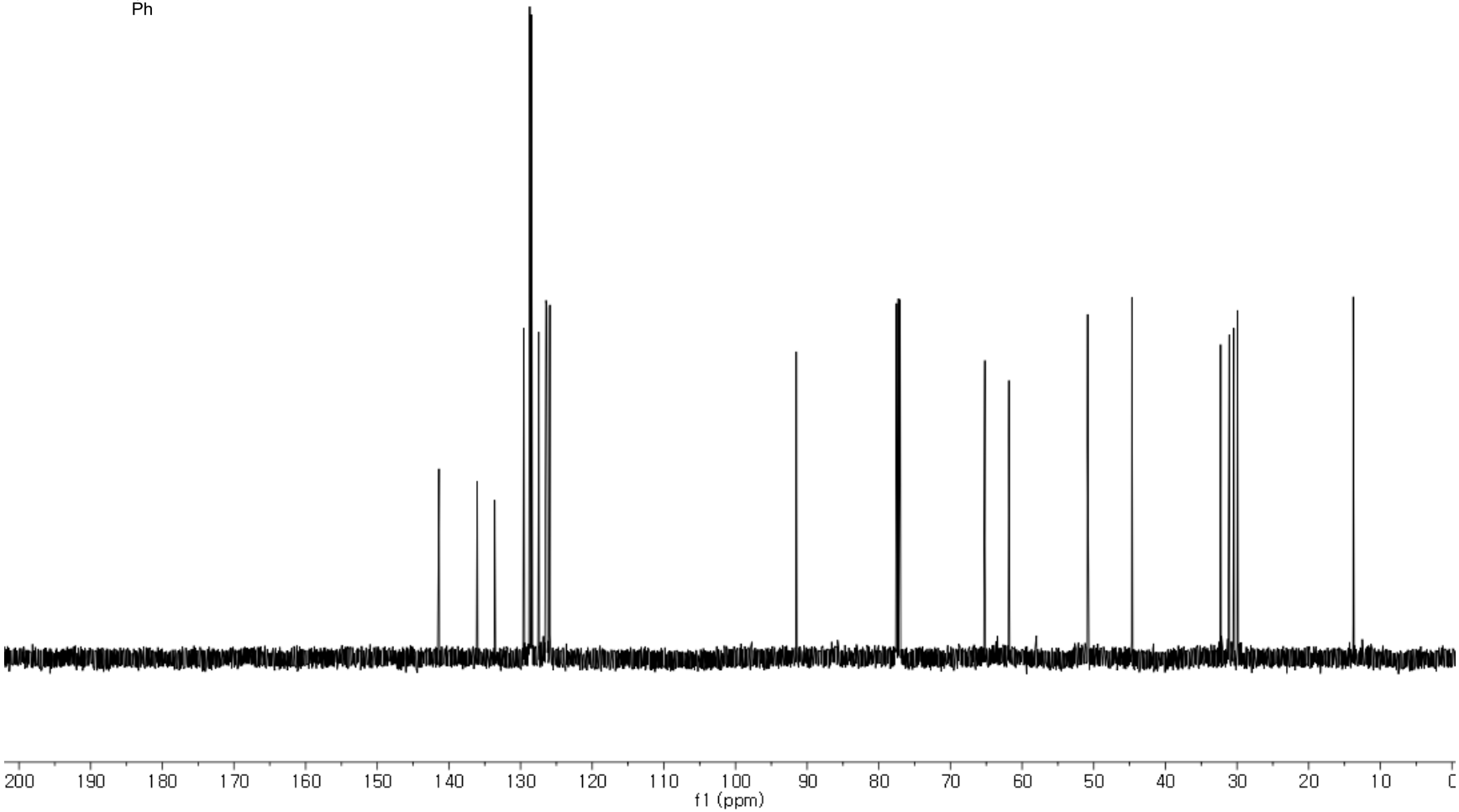
^{1}H NMR of **7f** in $CDCl_3$



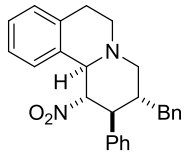


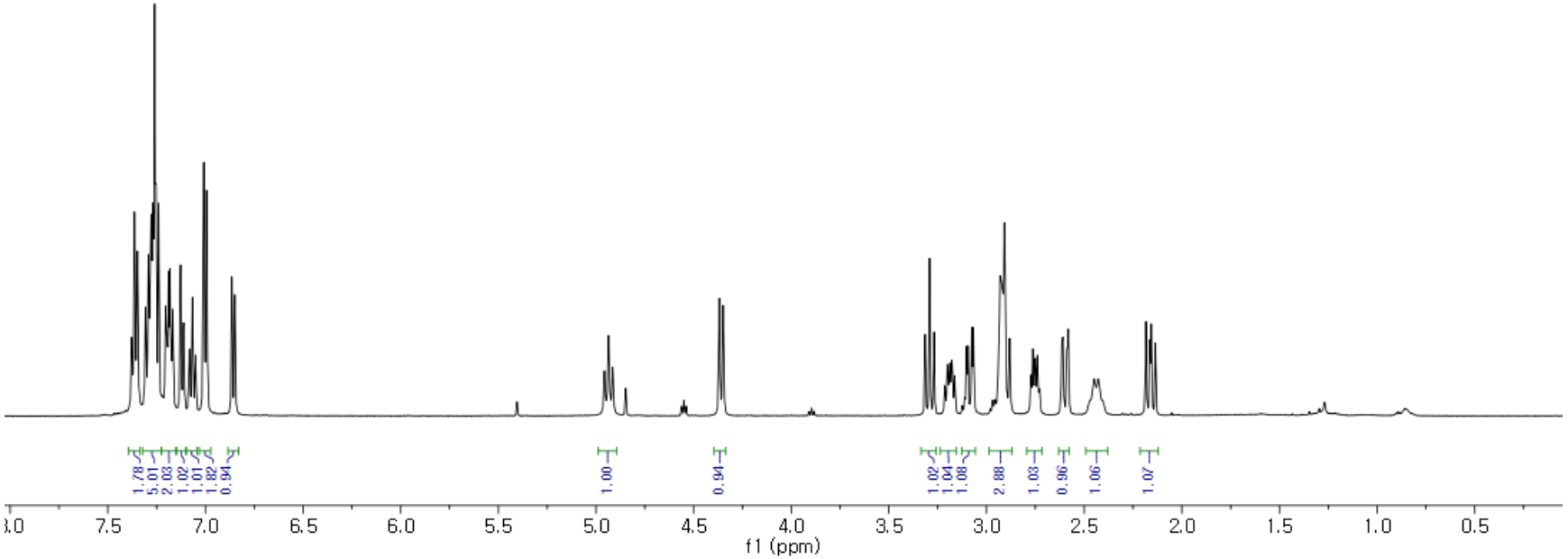
^{13}C NMR of **7f** in $CDCl_3$



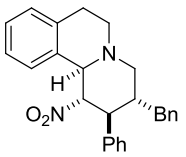


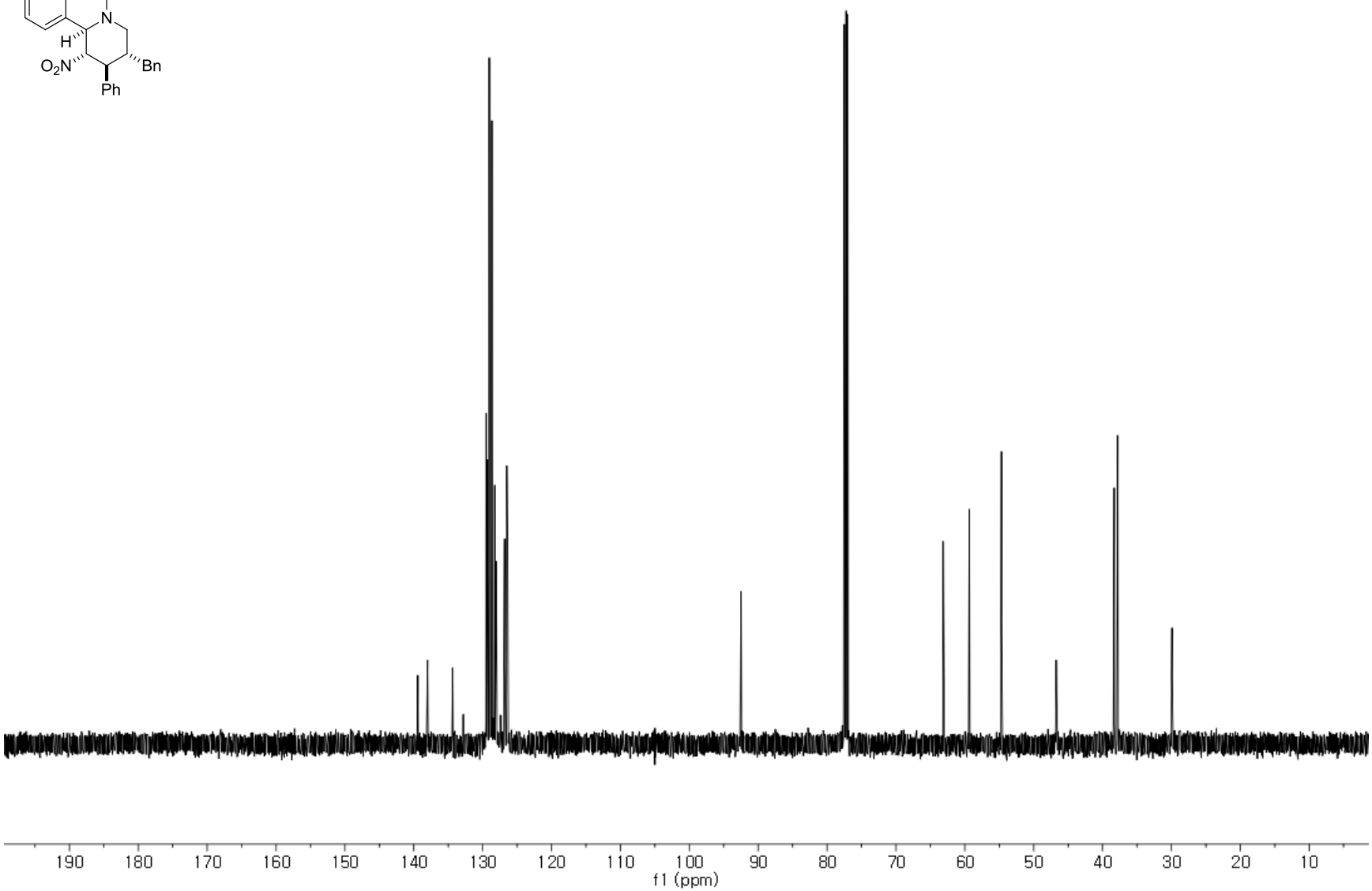
^{1}H NMR of **6g** in $CDCl_3$



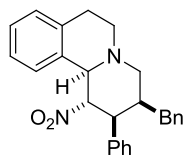


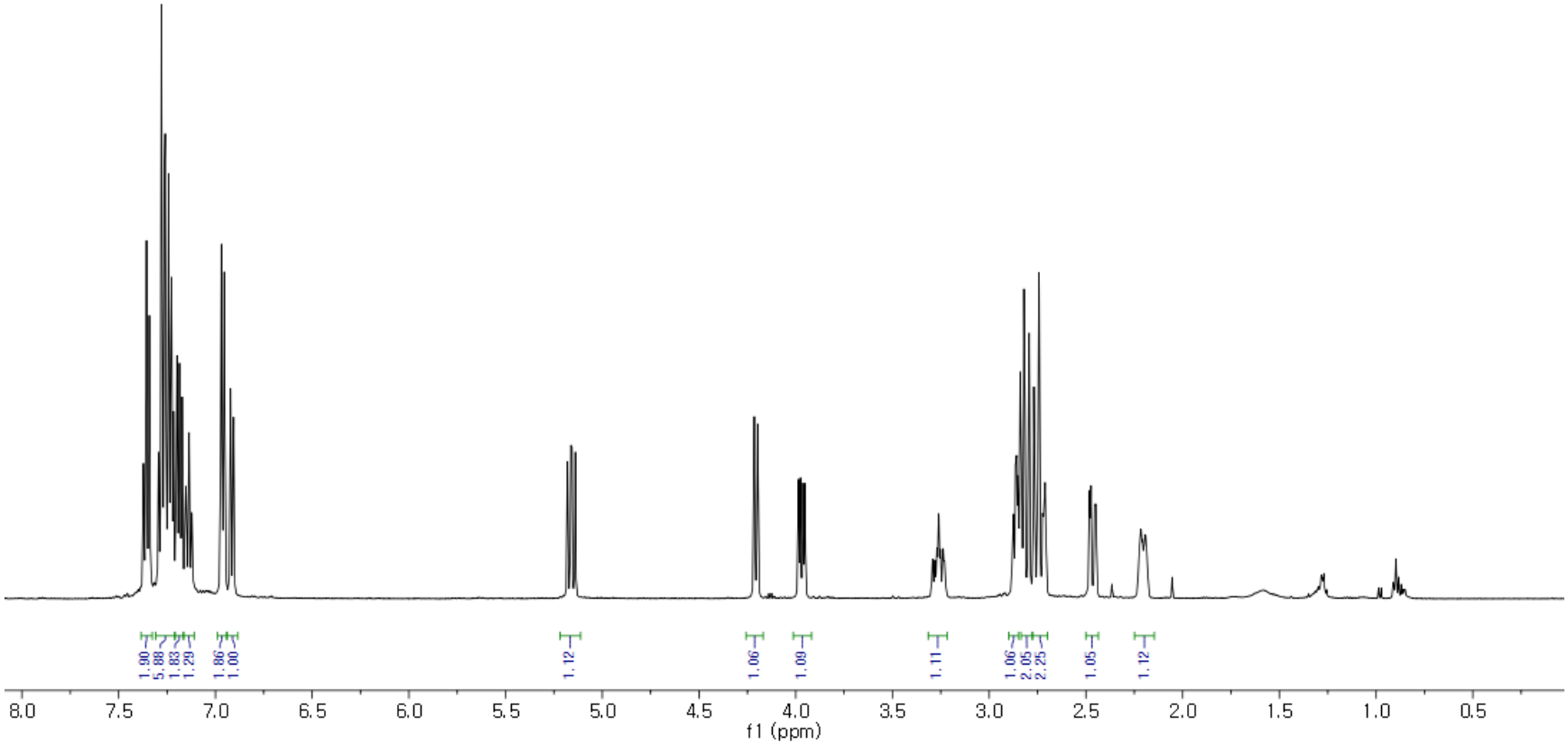
^{13}C NMR of **6g** in $CDCl_3$



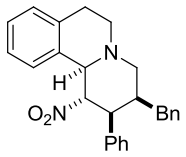


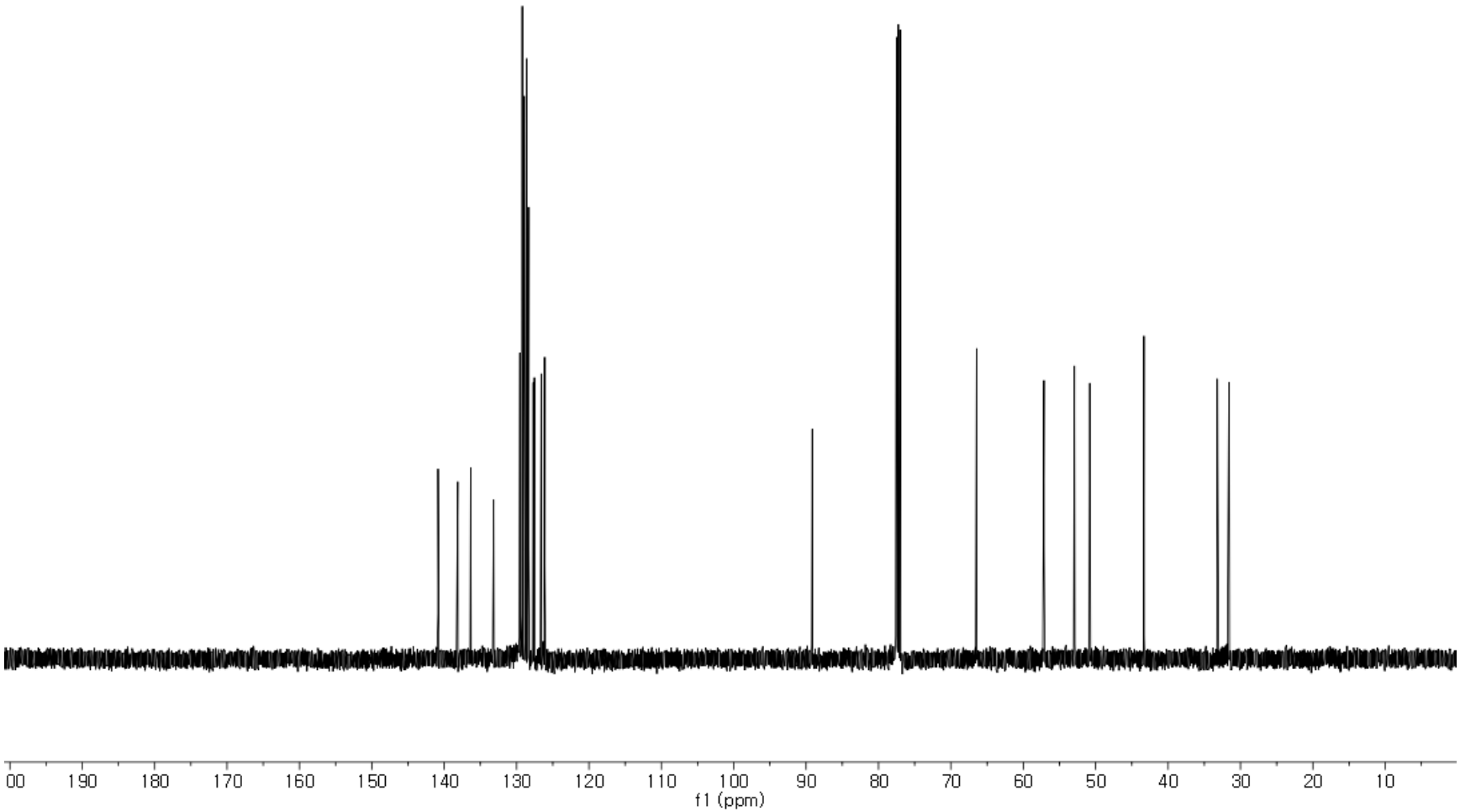
^{1}H NMR of **7g** in $CDCl_3$



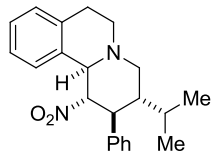


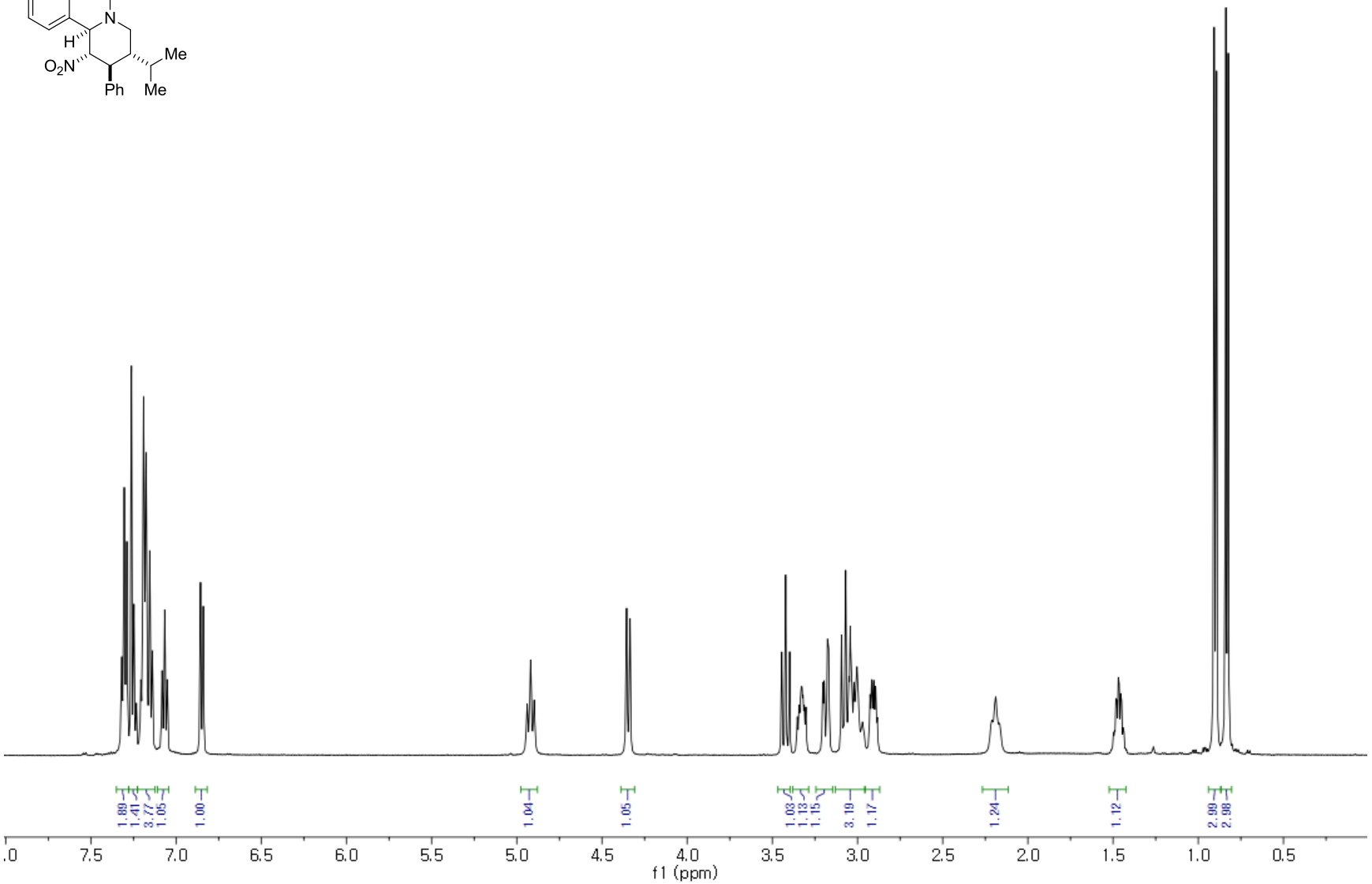
^{13}C NMR of **7g** in $CDCl_3$



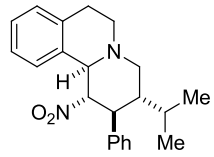


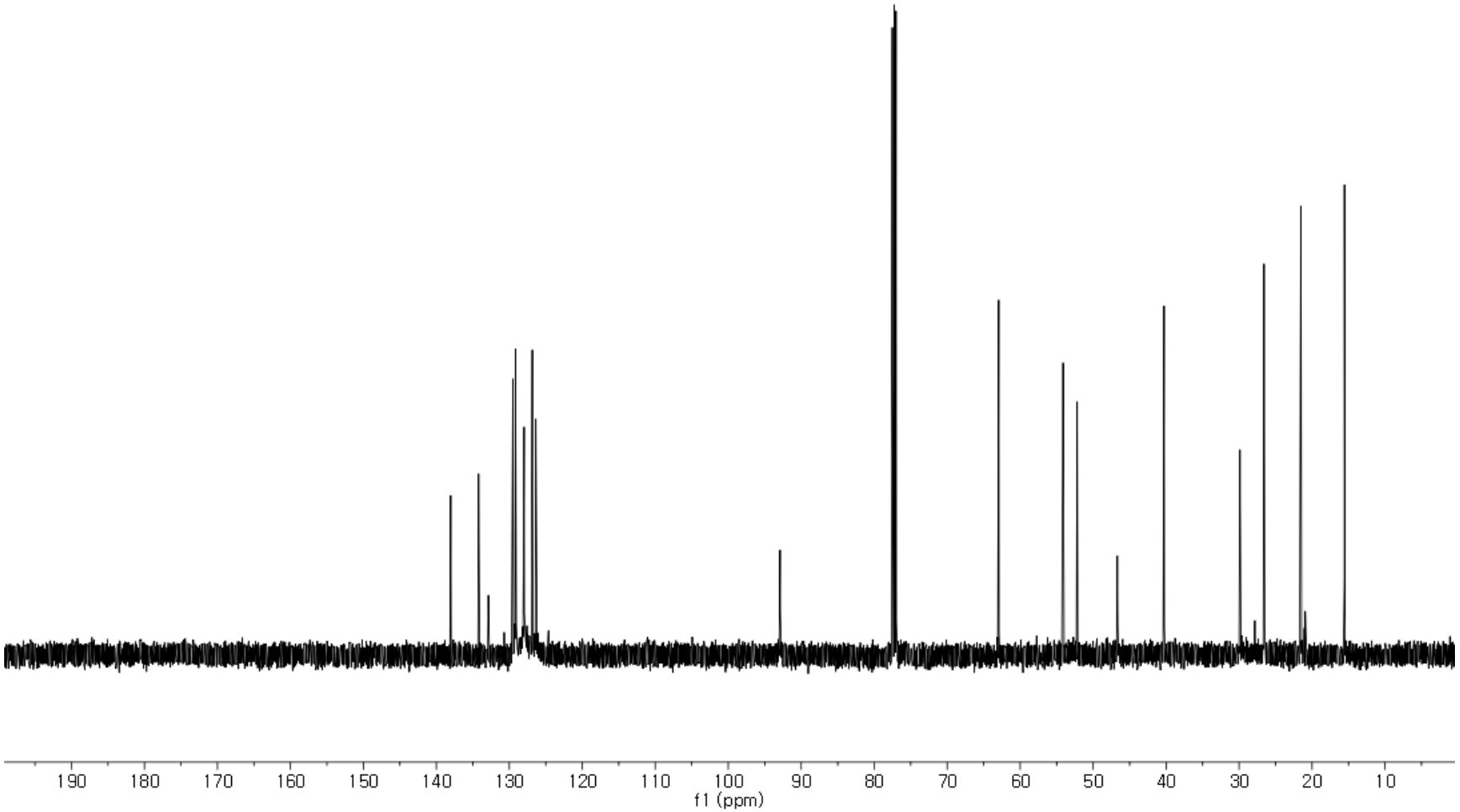
^{1}H NMR of **6h** in $CDCl_3$



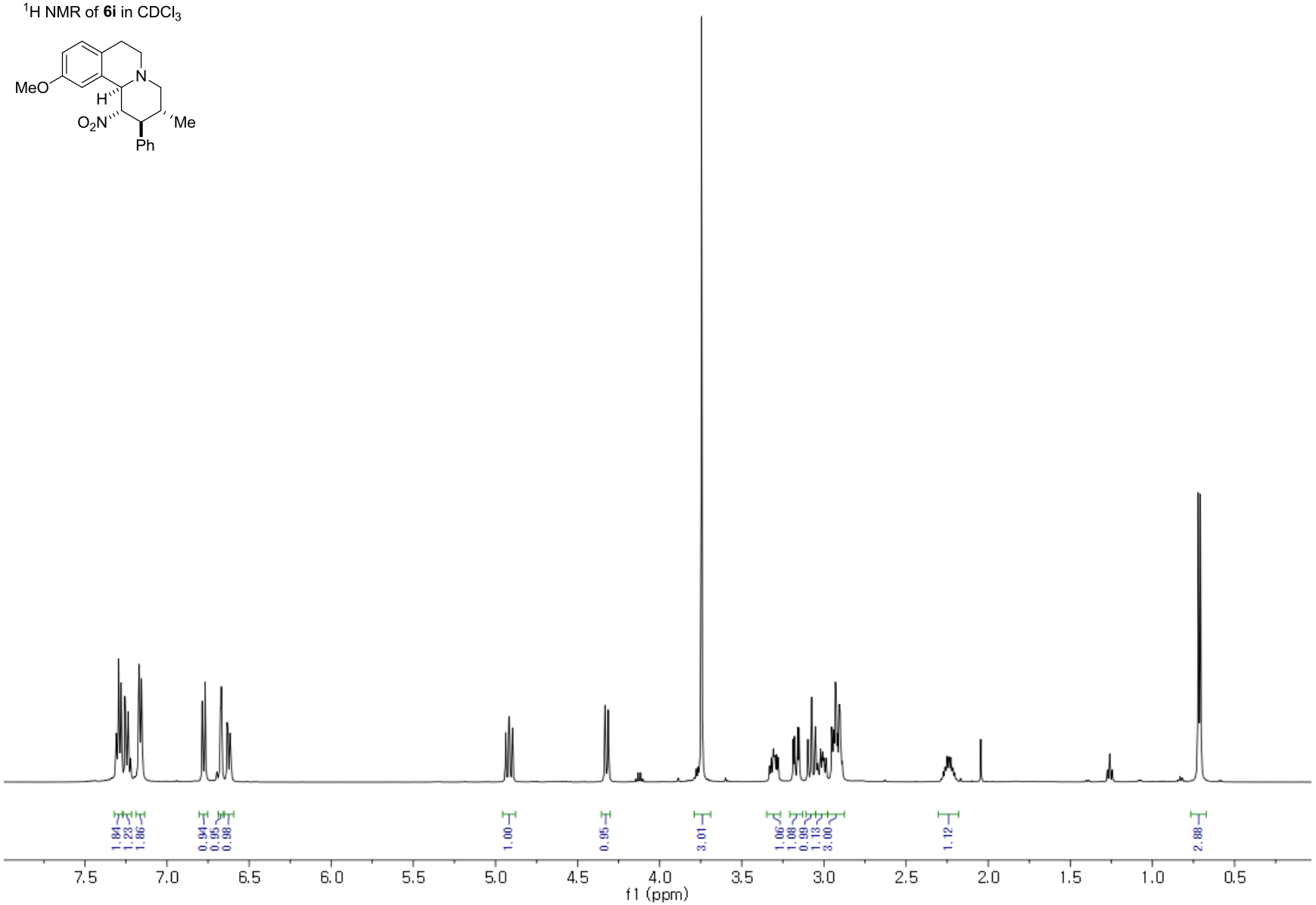


^{13}C NMR of **6h** in $CDCl_3$

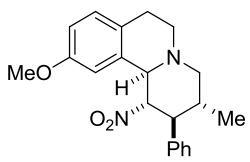


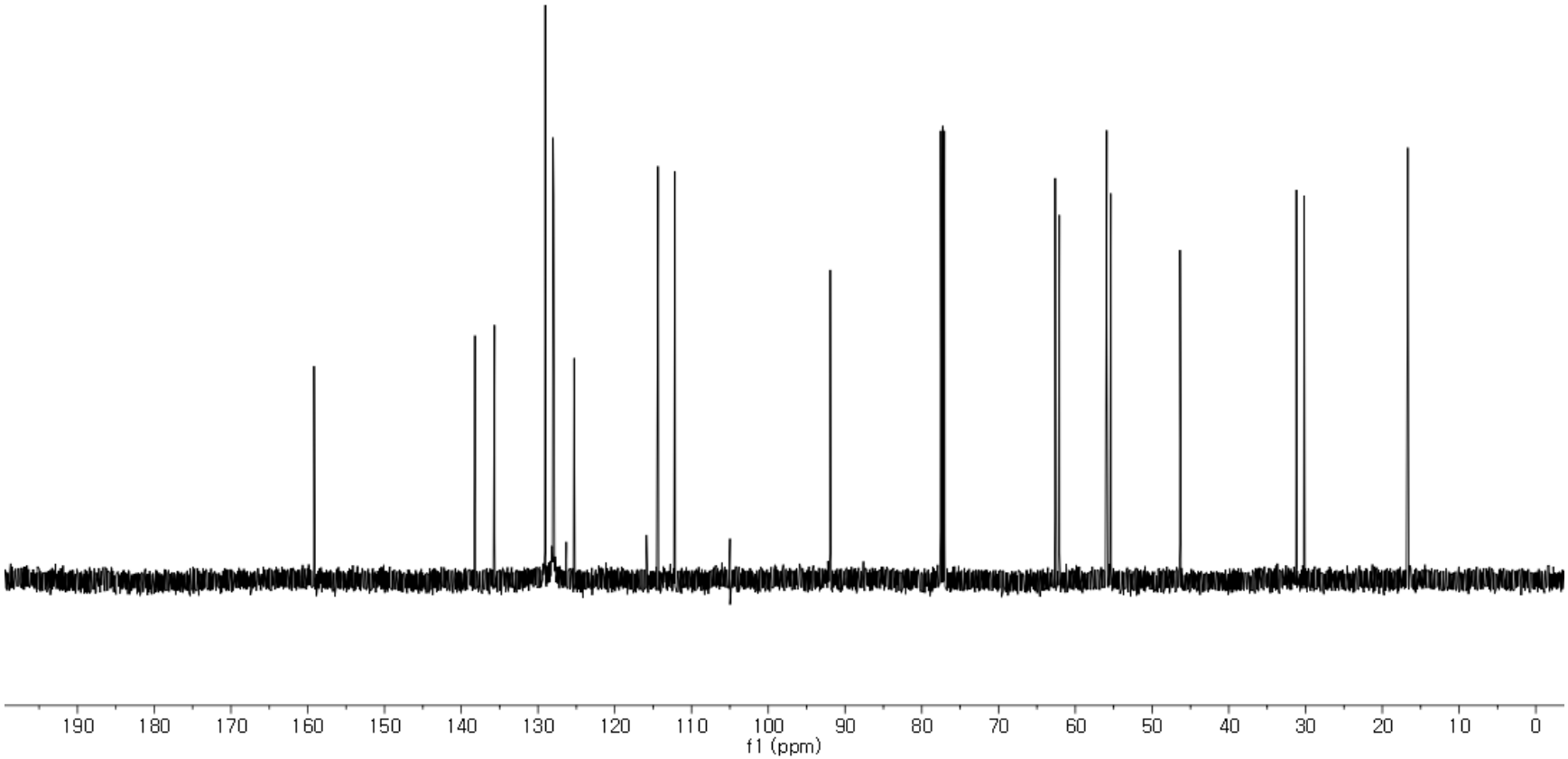


^{1}H NMR of **6i** in $CDCl_3$

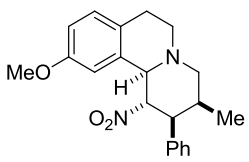


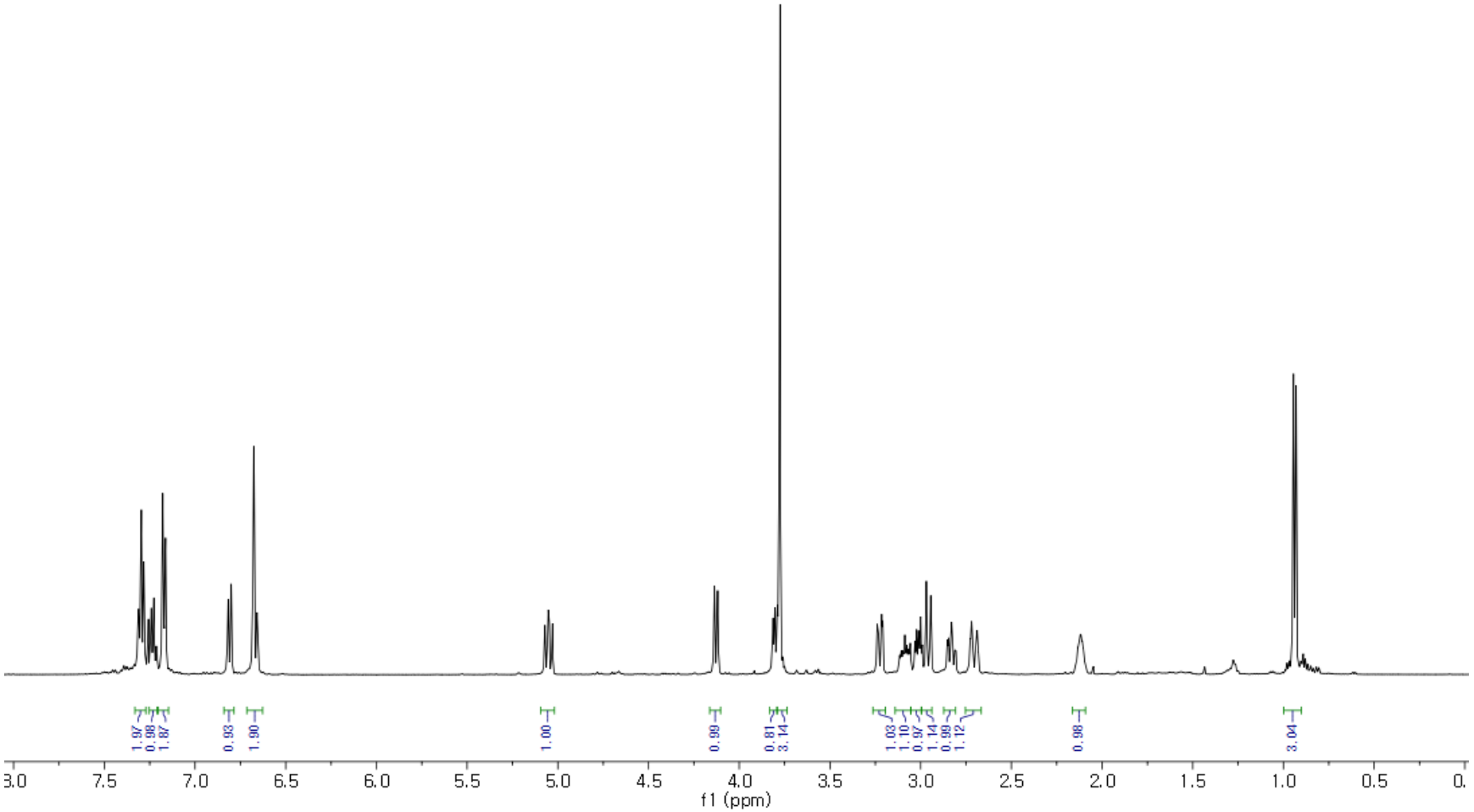
^{13}C NMR of **6i** in $CDCl_3$



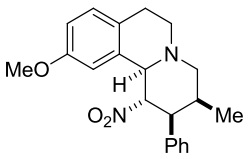


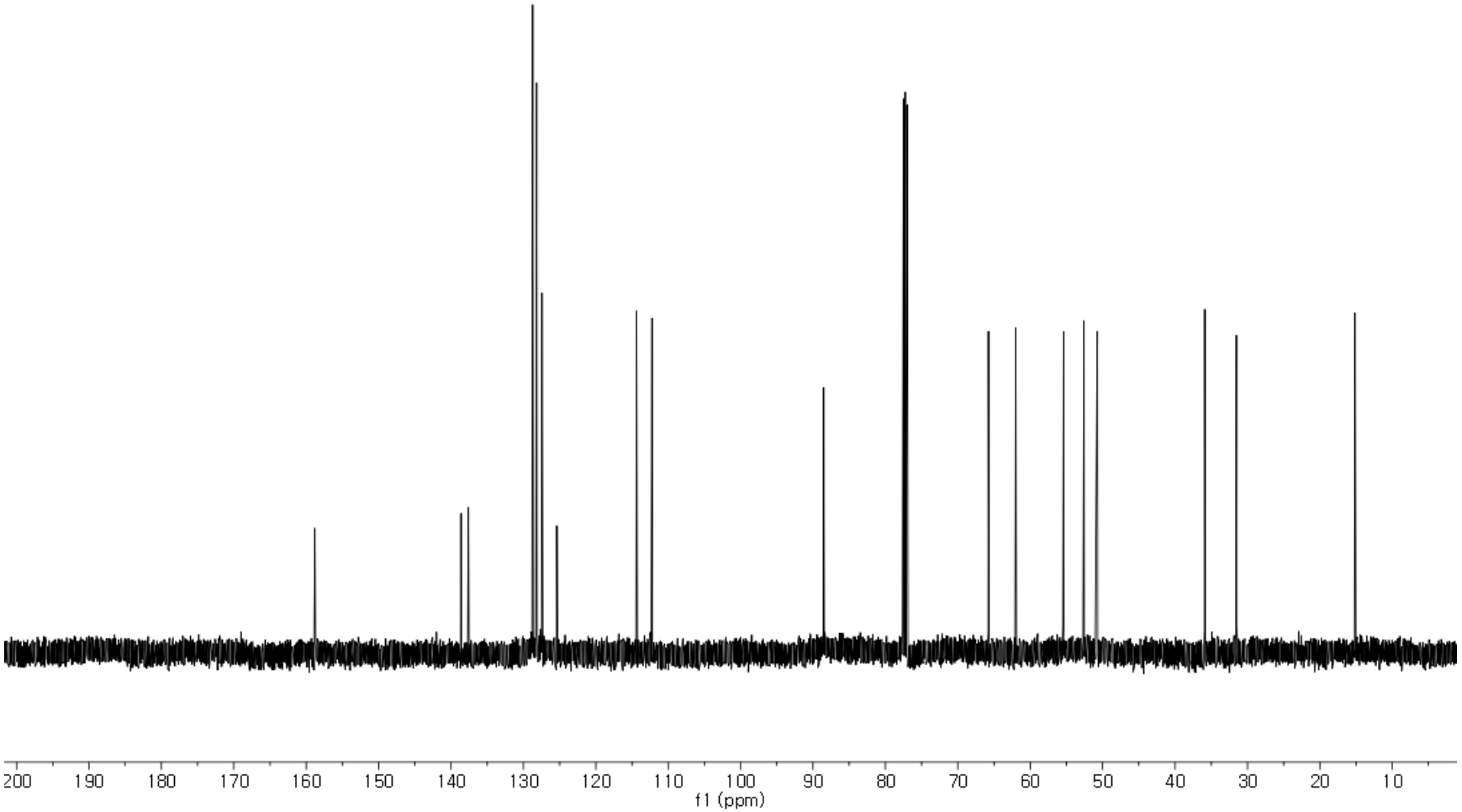
^{1}H NMR of **7i** in $CDCl_3$



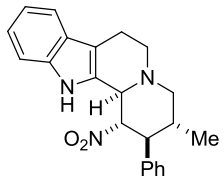


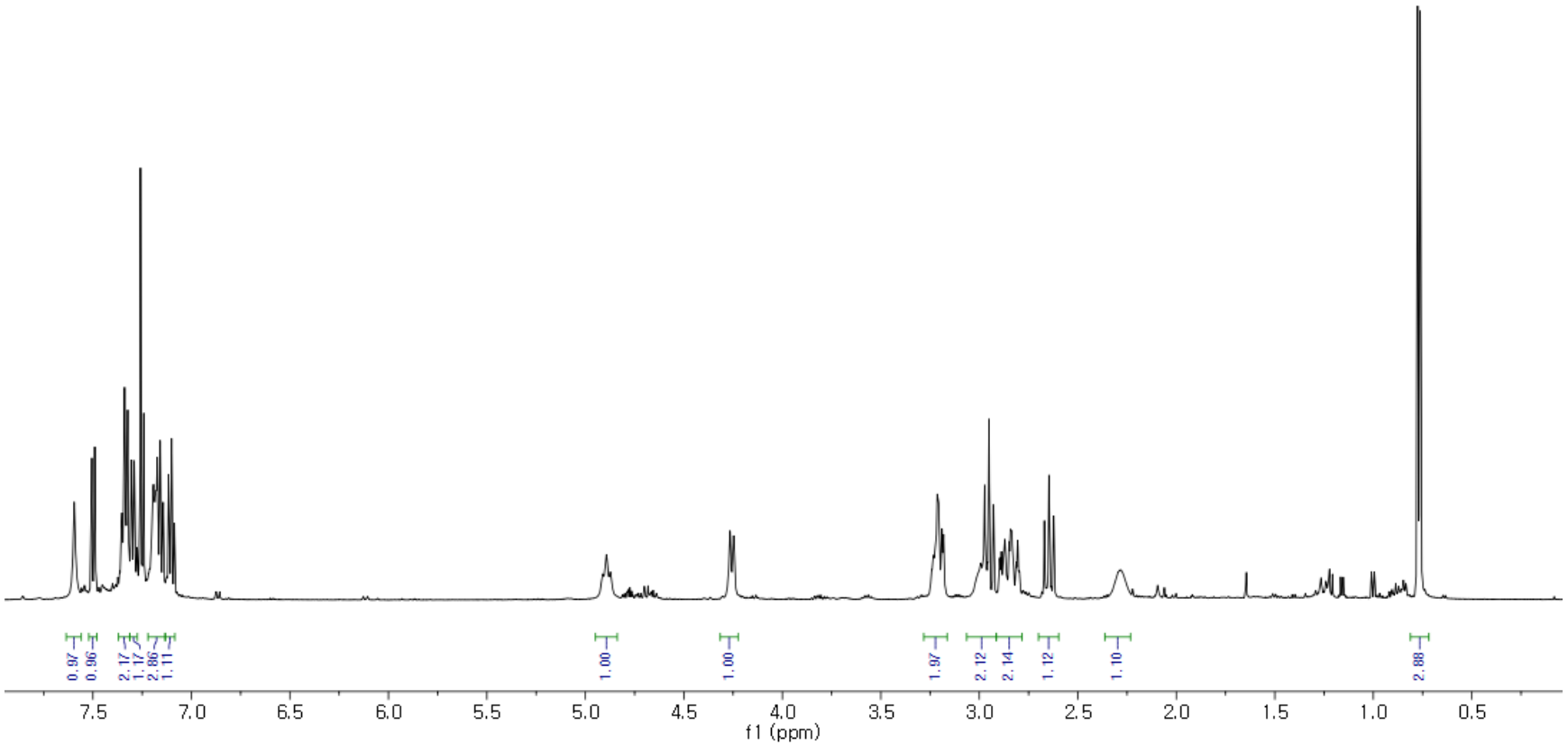
^{13}C NMR of **7i** in $CDCl_3$



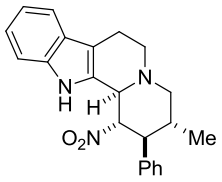


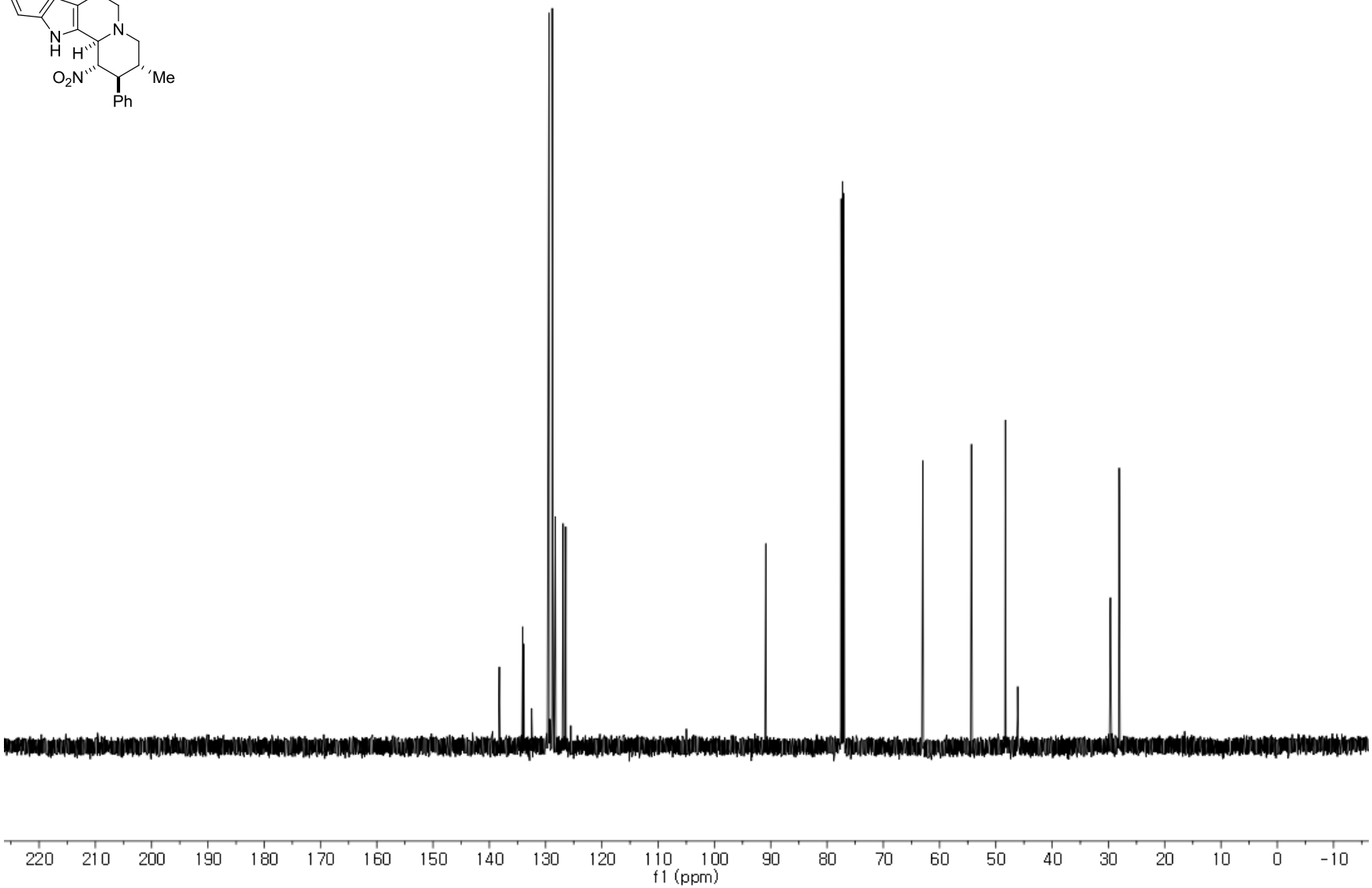
^{1}H NMR of **6j** in $CDCl_3$



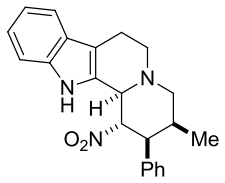


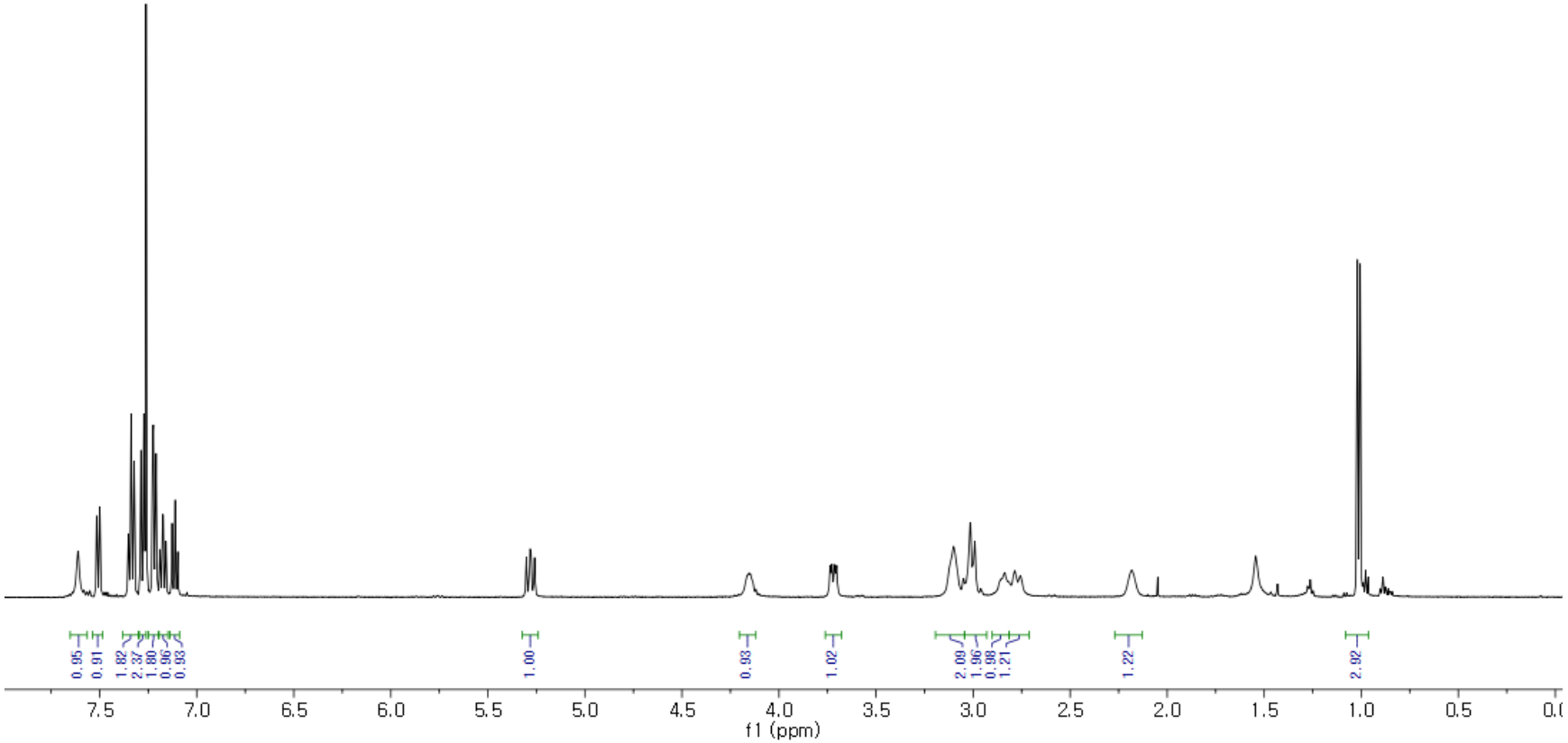
^{13}C NMR of **6j** in $CDCl_3$



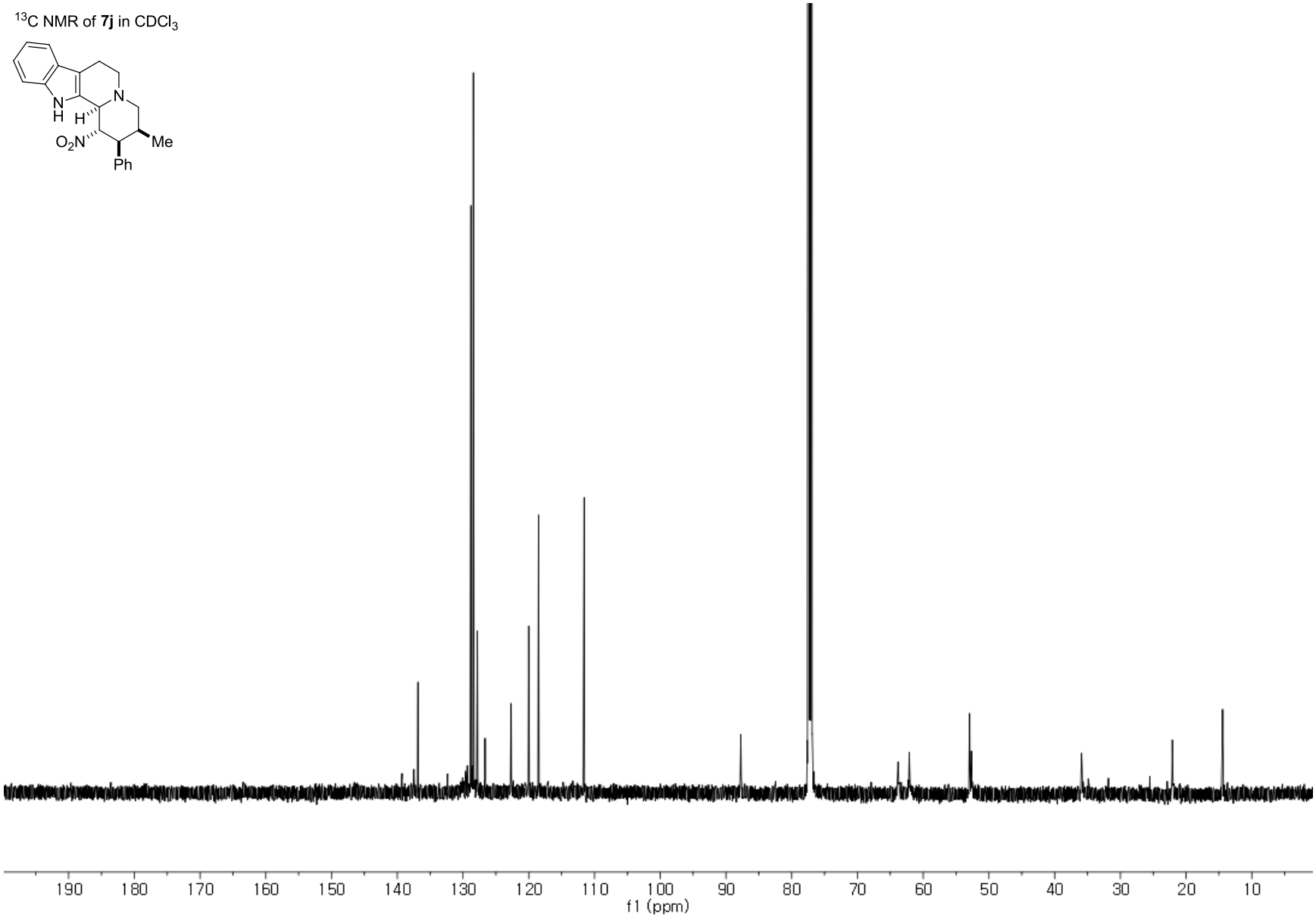


^{1}H NMR of **7j** in $CDCl_3$

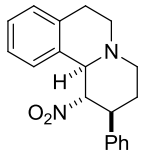


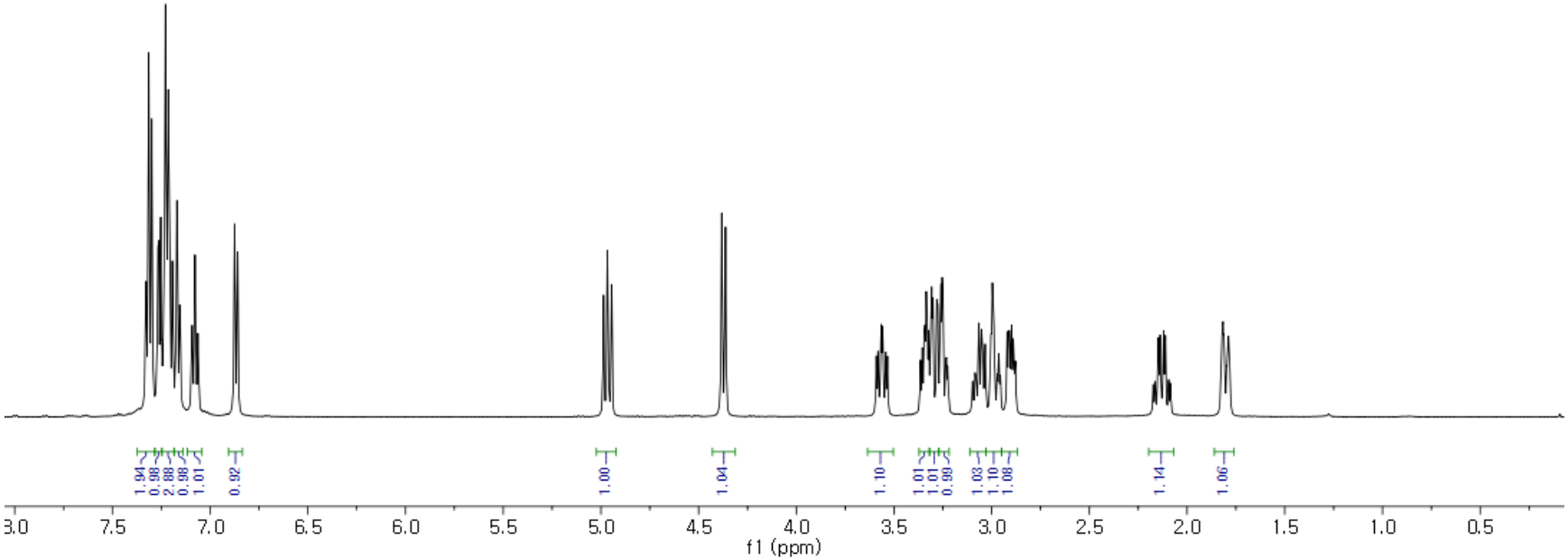


^{13}C NMR of **7j** in $CDCl_3$

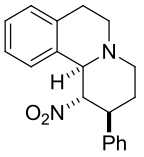


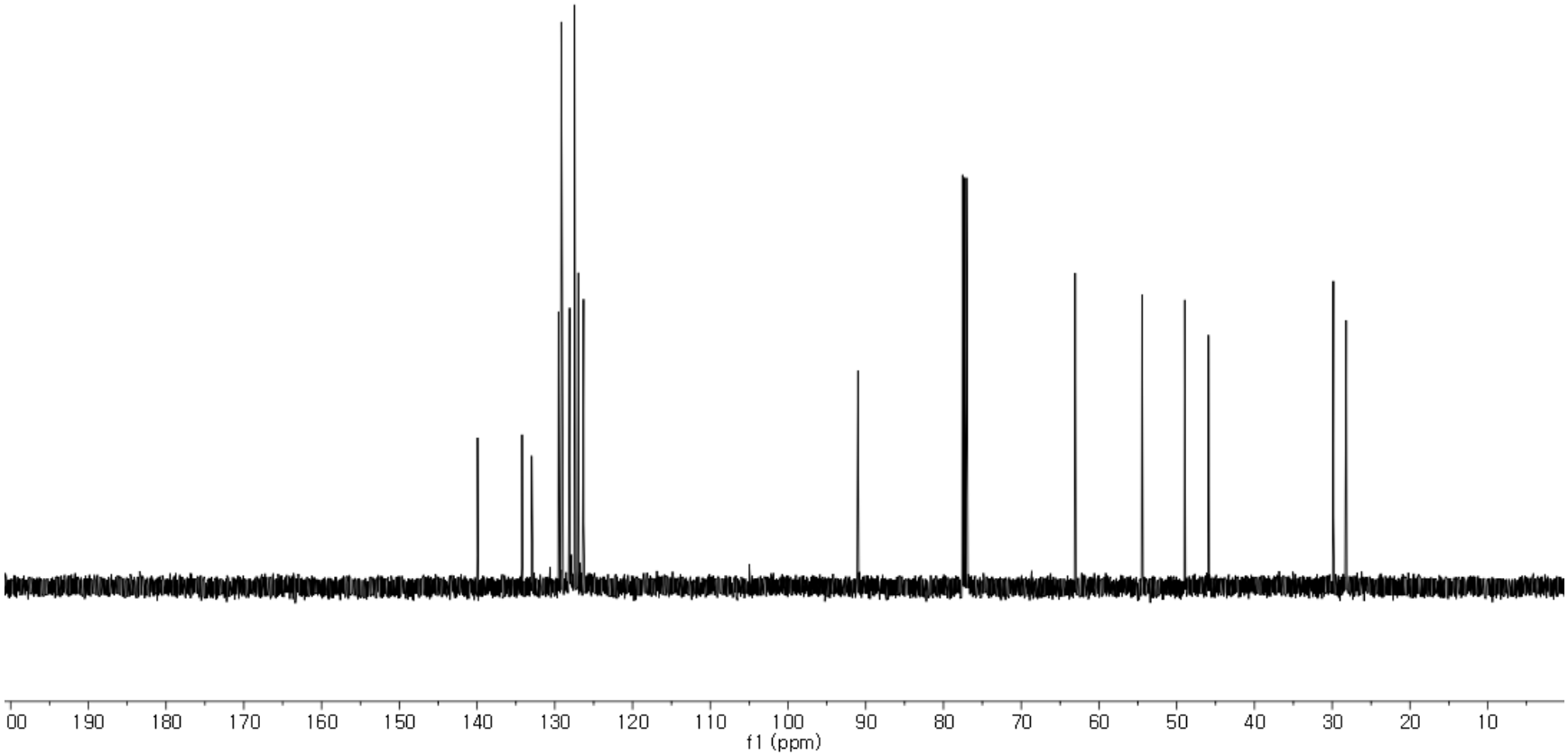
^{1}H NMR of **6k** in $CDCl_3$



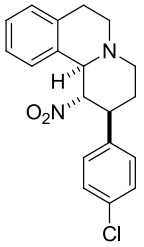


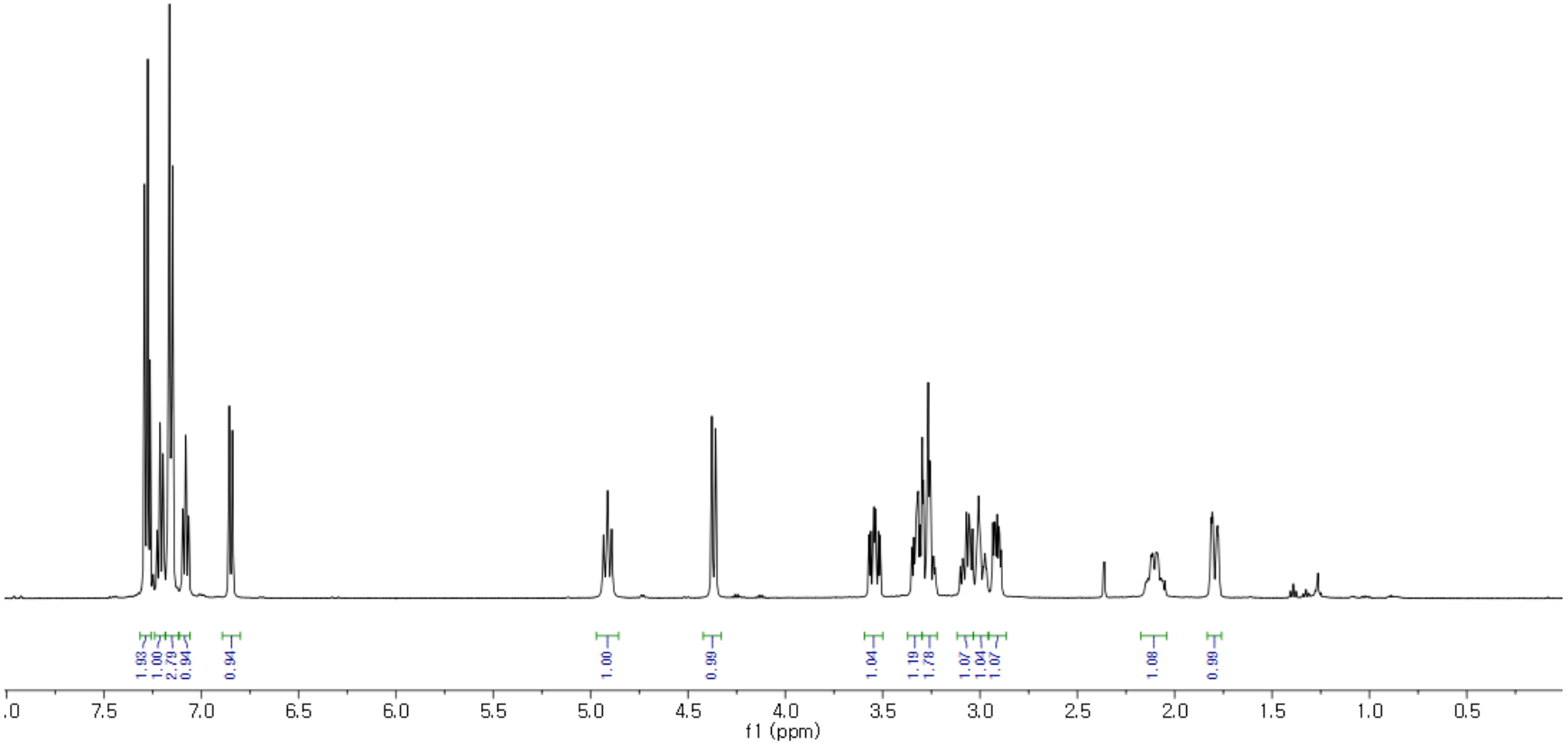
^{13}C NMR of **6k** in $CDCl_3$



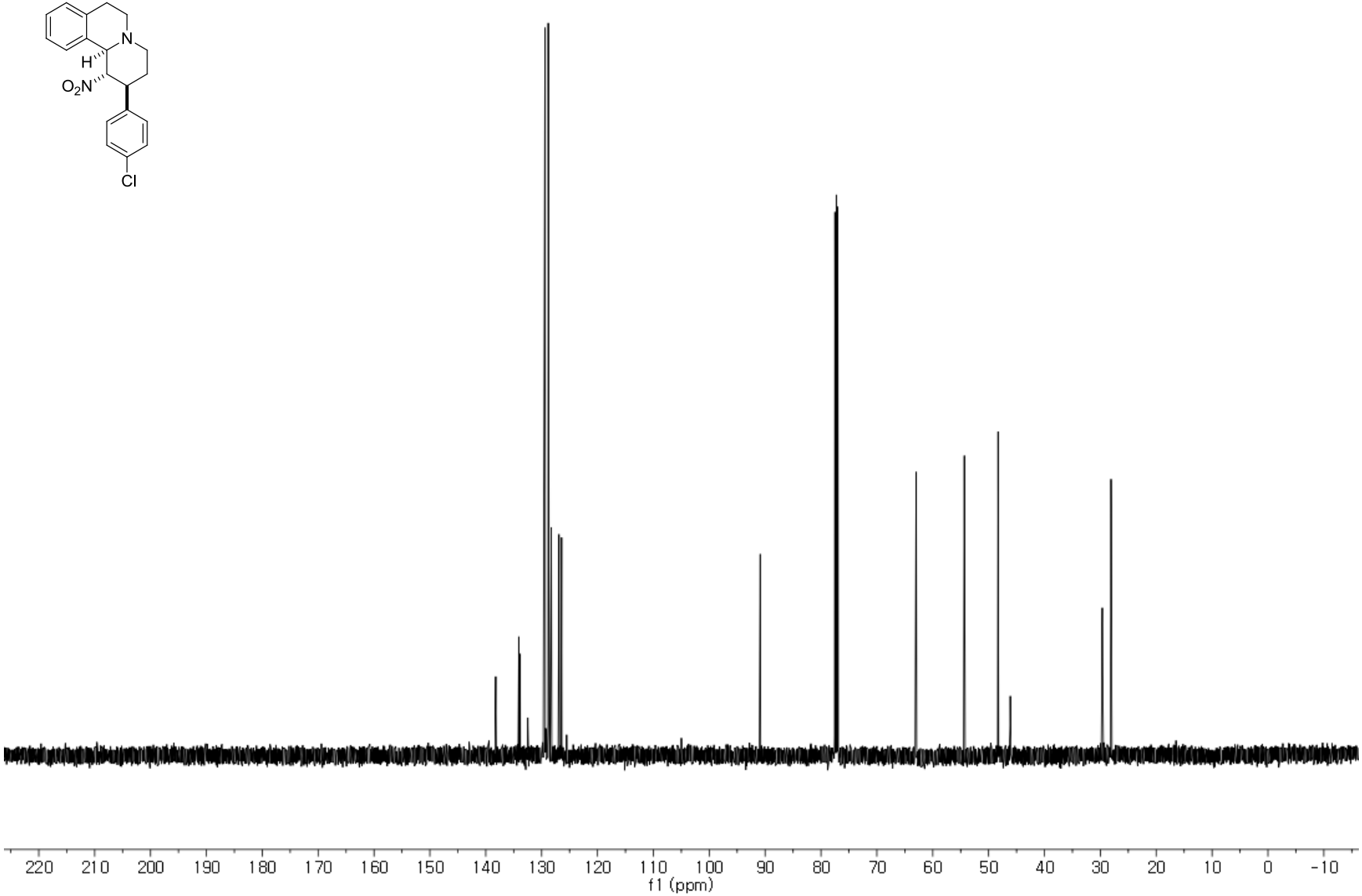


^{1}H NMR of **6l** in $CDCl_3$

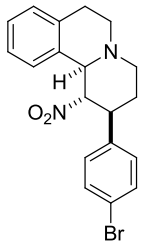


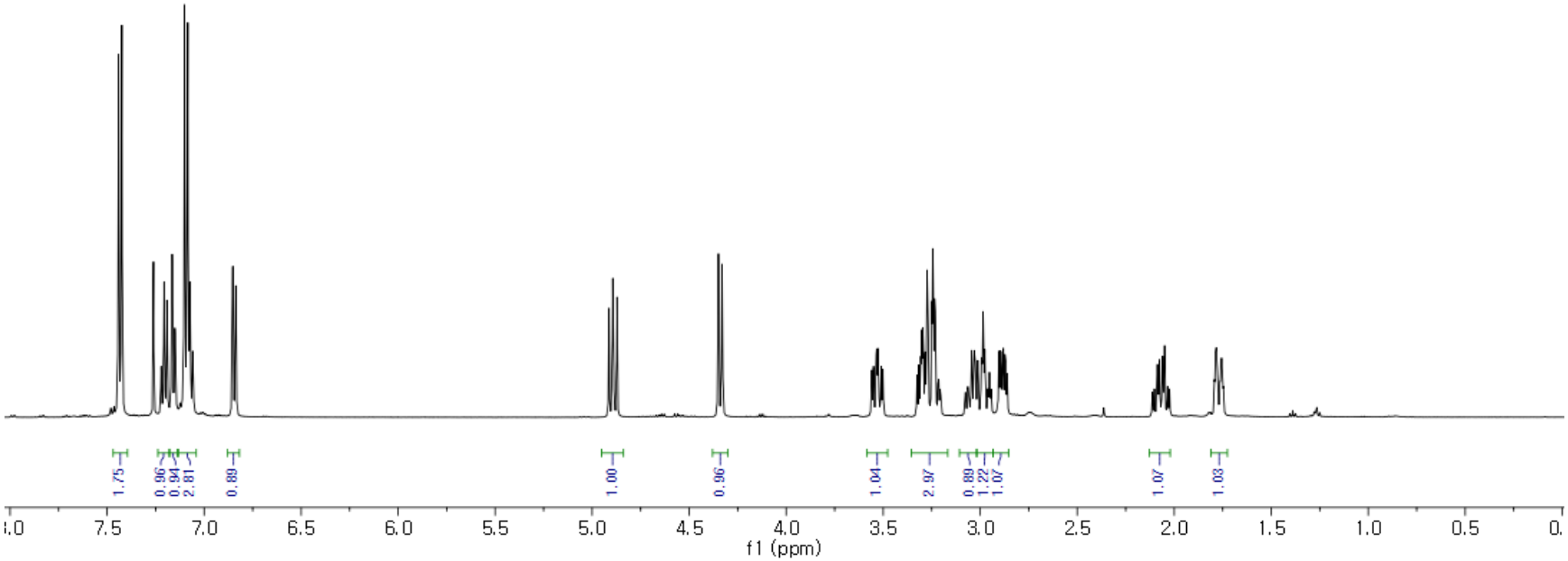


^{13}C NMR of **6l** in $CDCl_3$

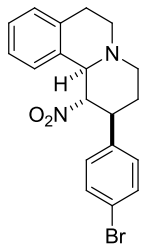


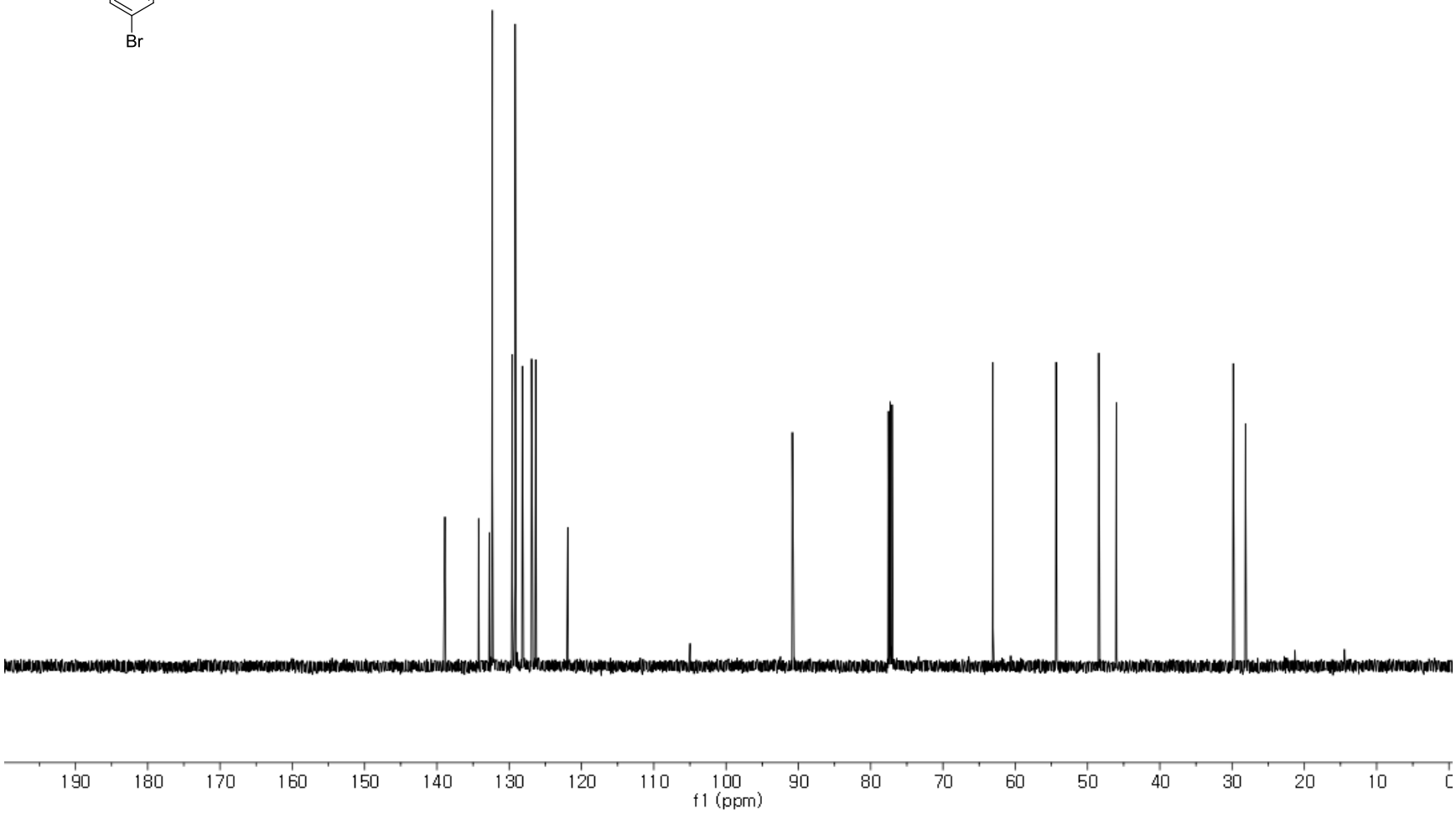
^{1}H NMR of **6m** in $CDCl_3$



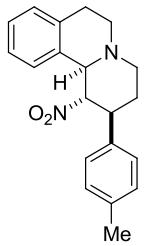


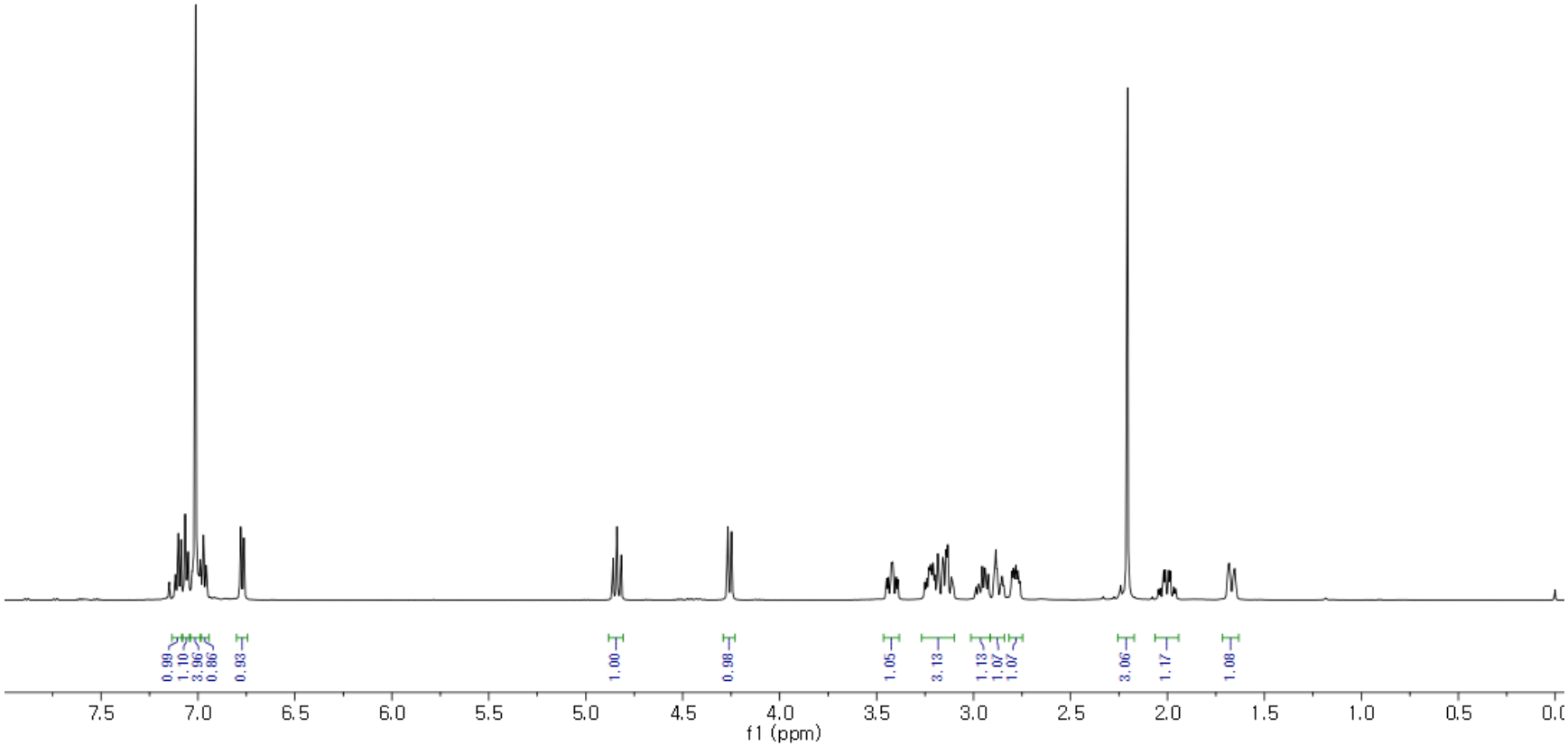
^{13}C NMR of **6m** in $CDCl_3$



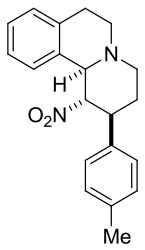


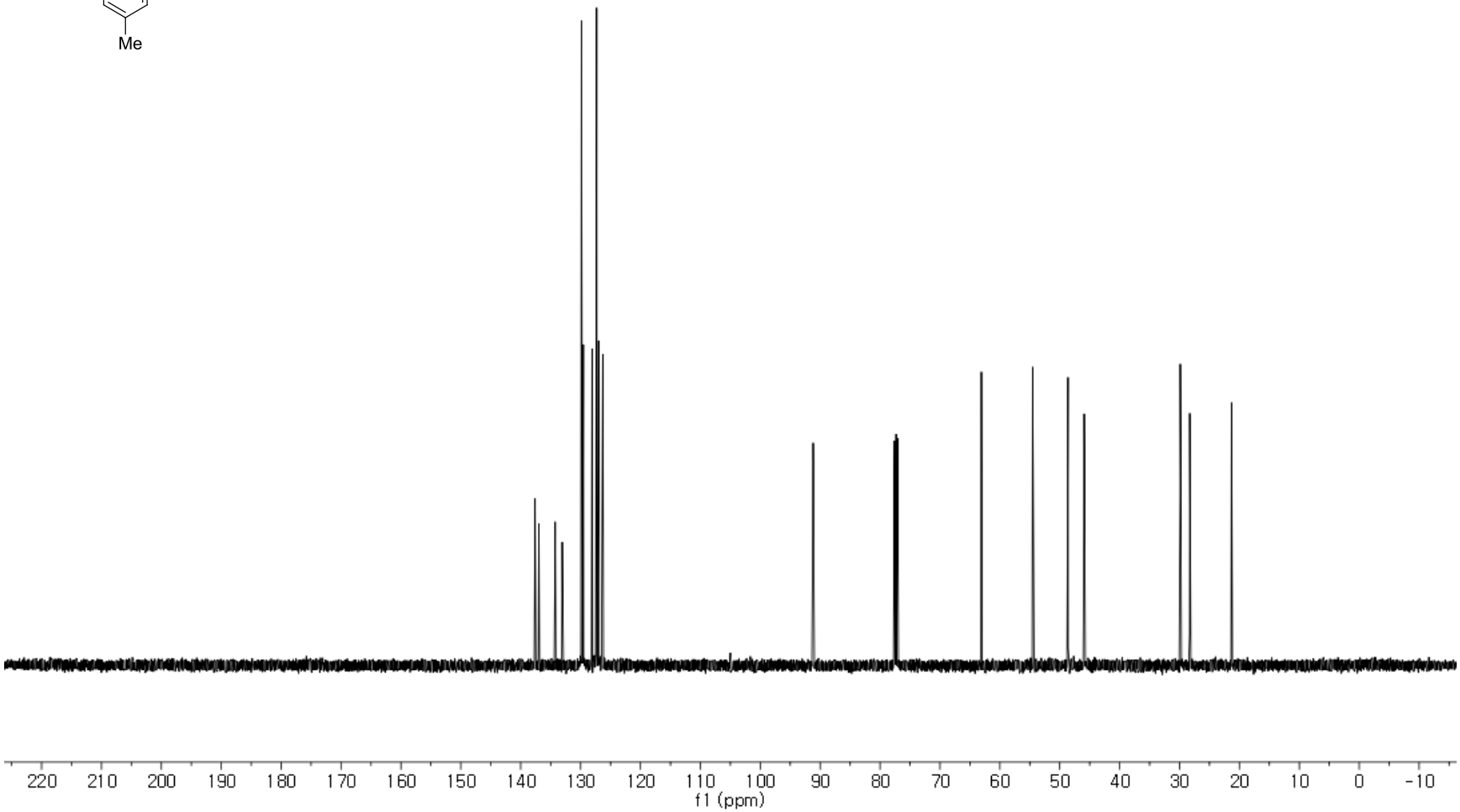
^{1}H NMR of **6n** in $CDCl_3$



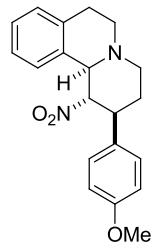


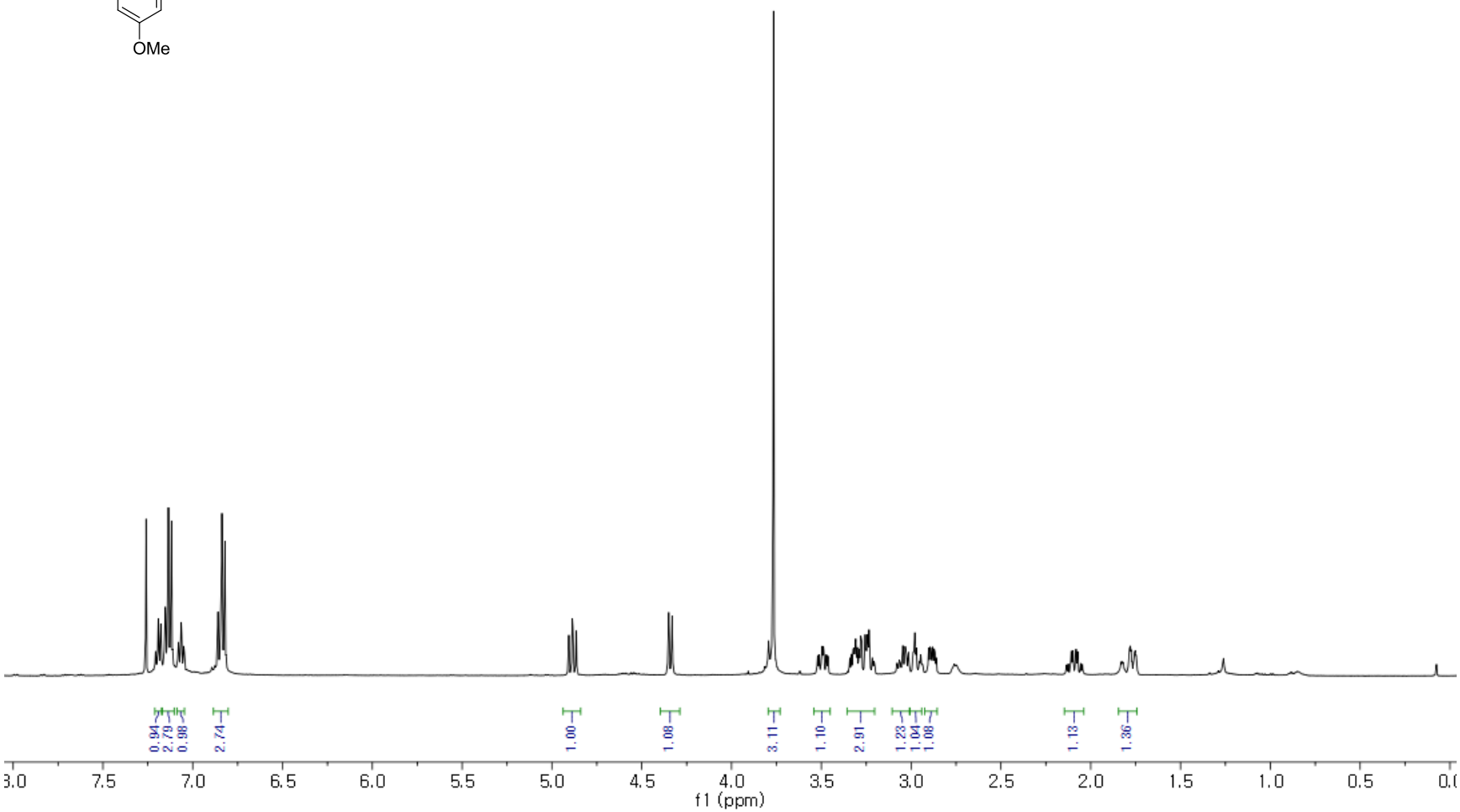
^{13}C NMR of **6n** in $CDCl_3$



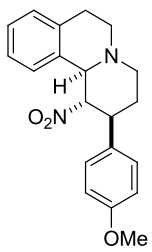


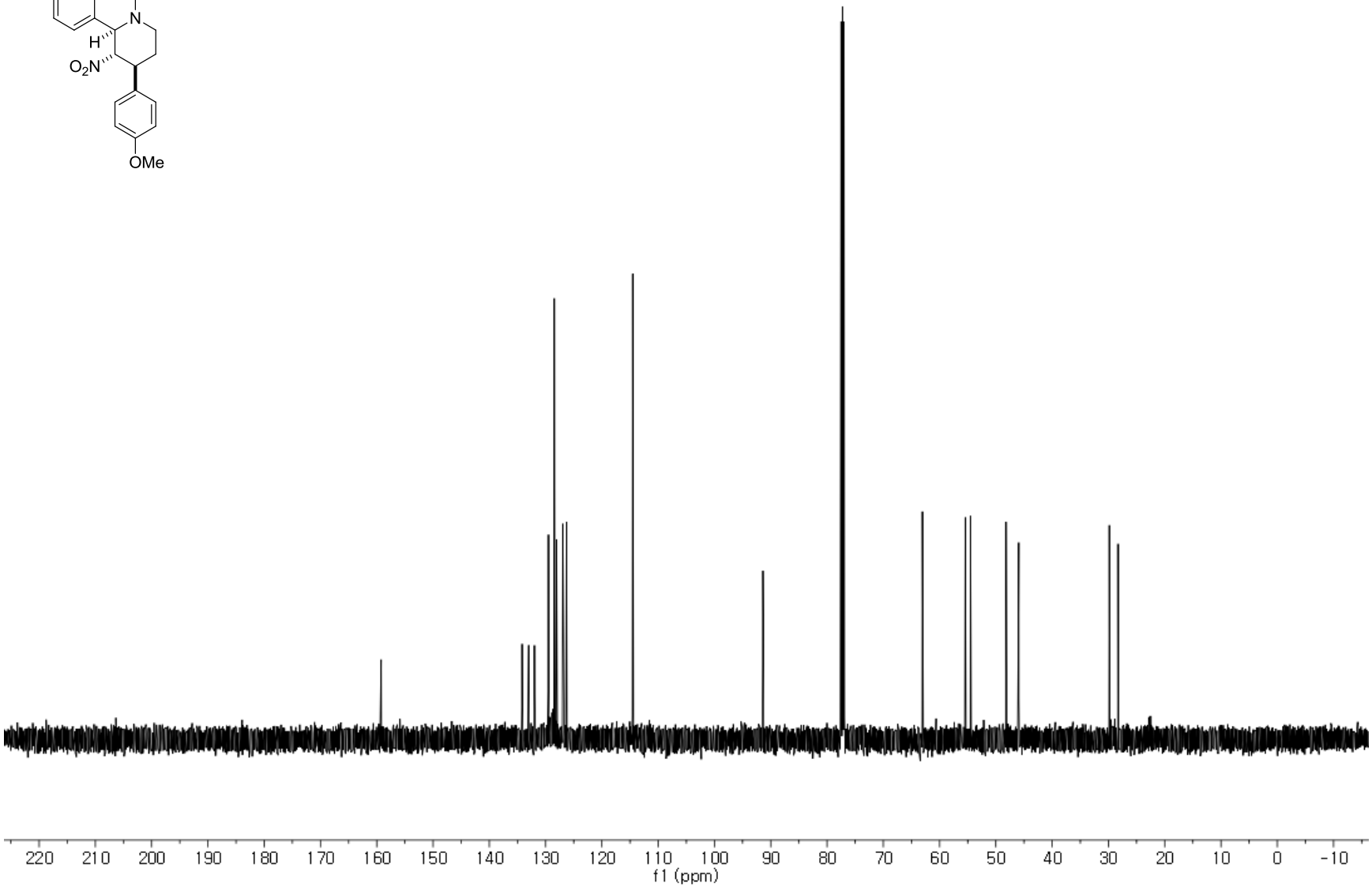
^{1}H NMR of **6o** in $CDCl_3$



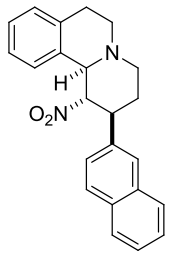


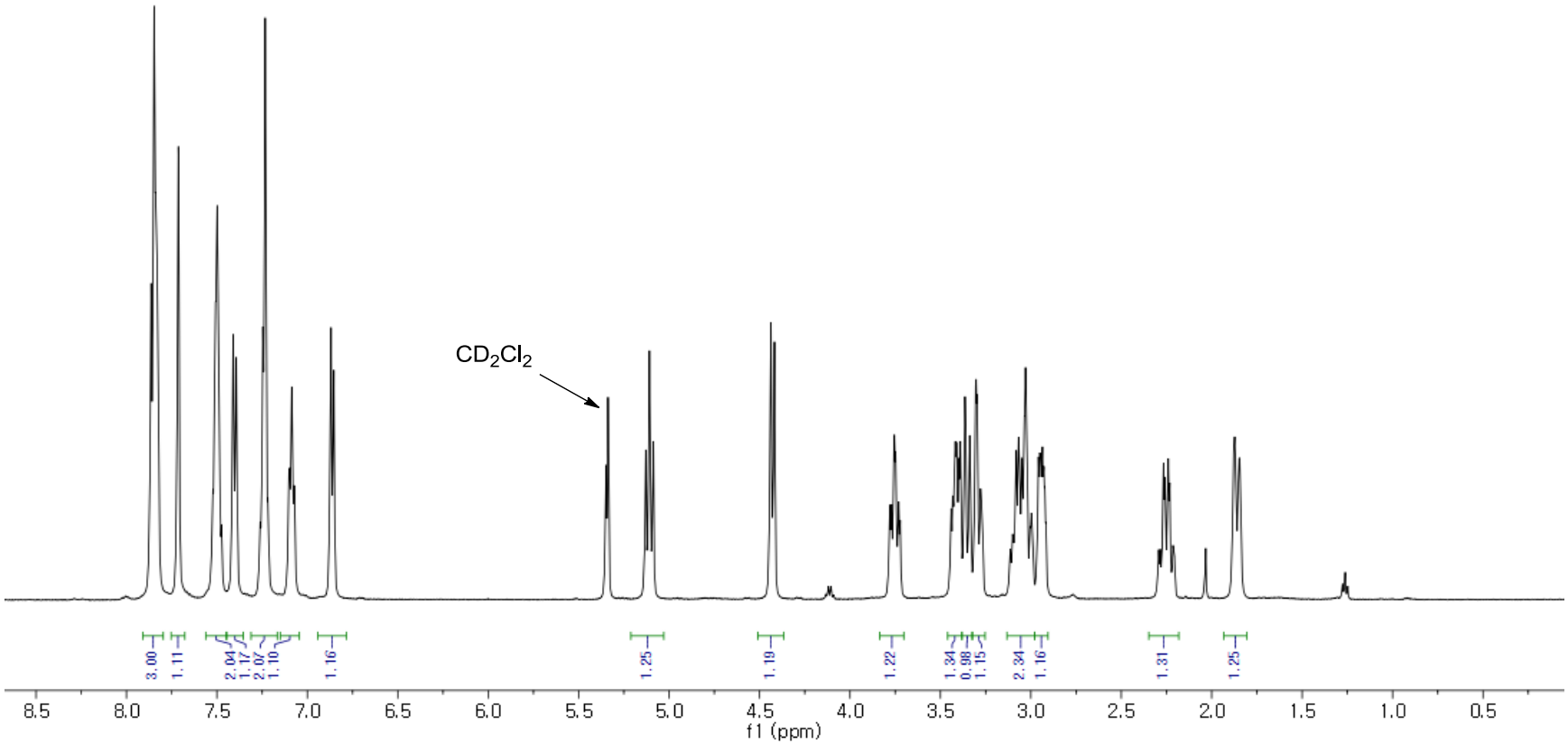
^{13}C NMR of **6o** in $CDCl_3$



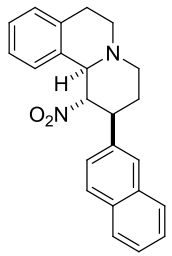


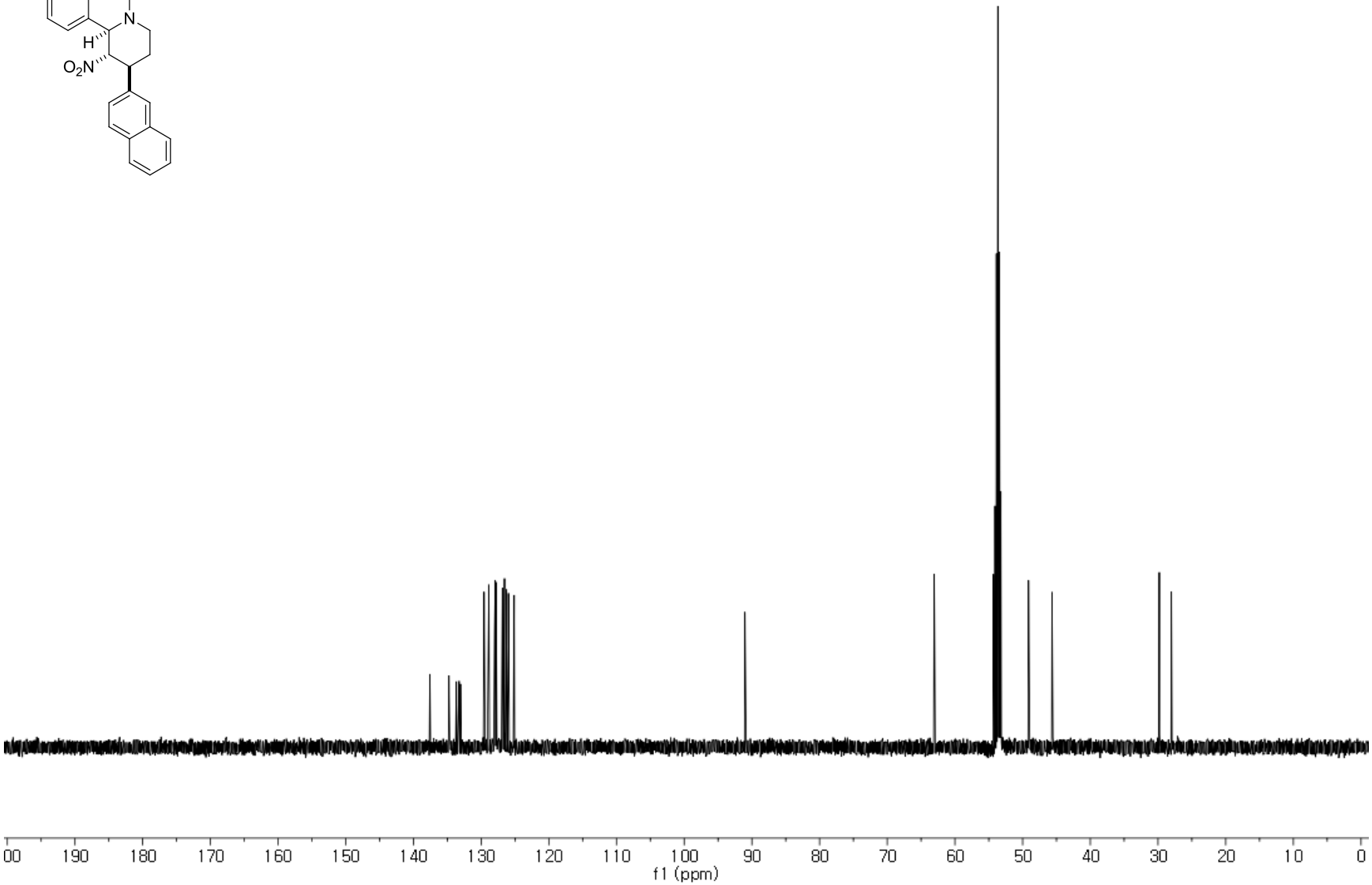
^{1}H NMR of **6p** in CD_2Cl_2



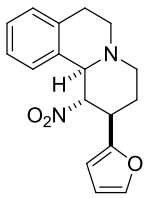


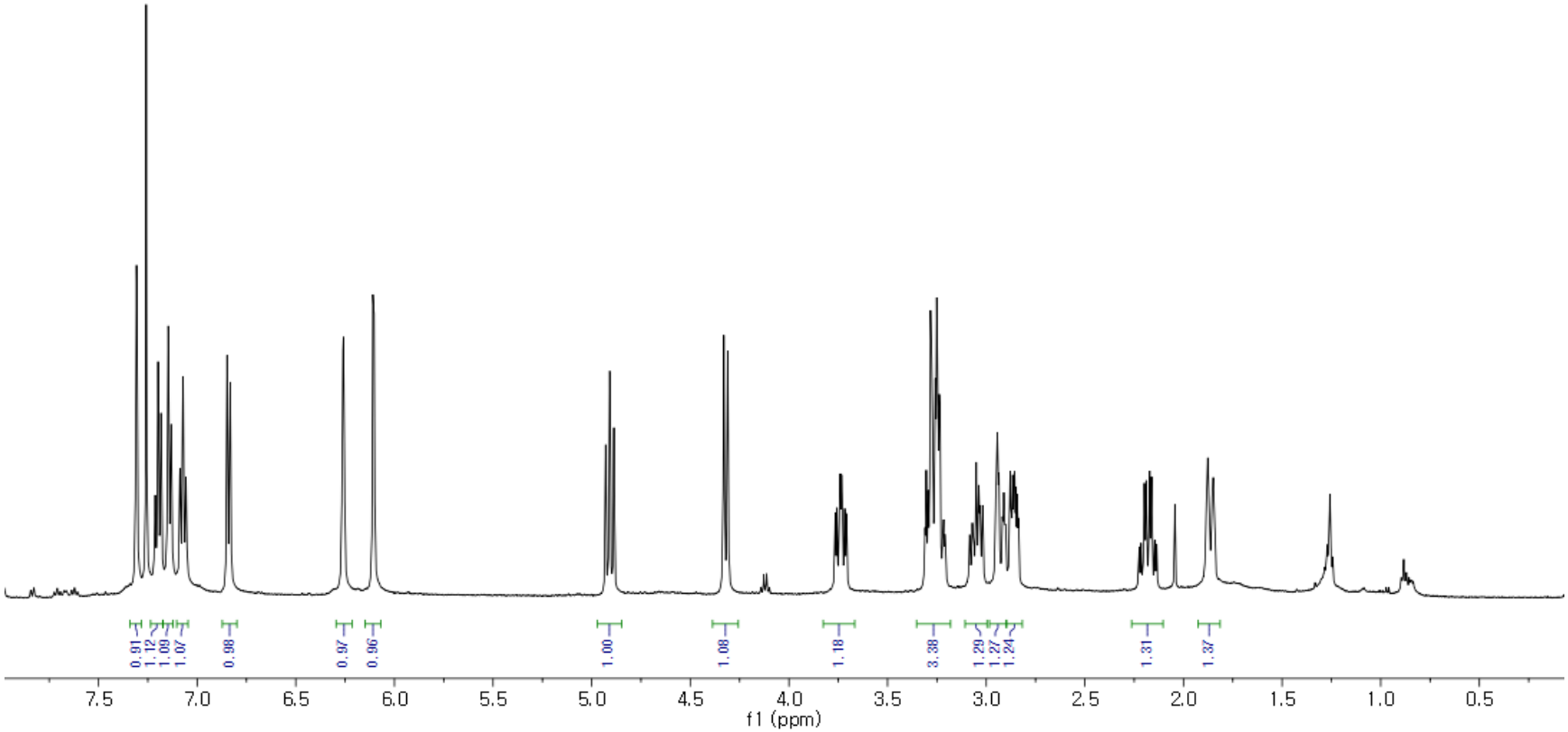
^{13}C NMR of **6p** in CD_2Cl_2



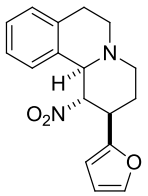


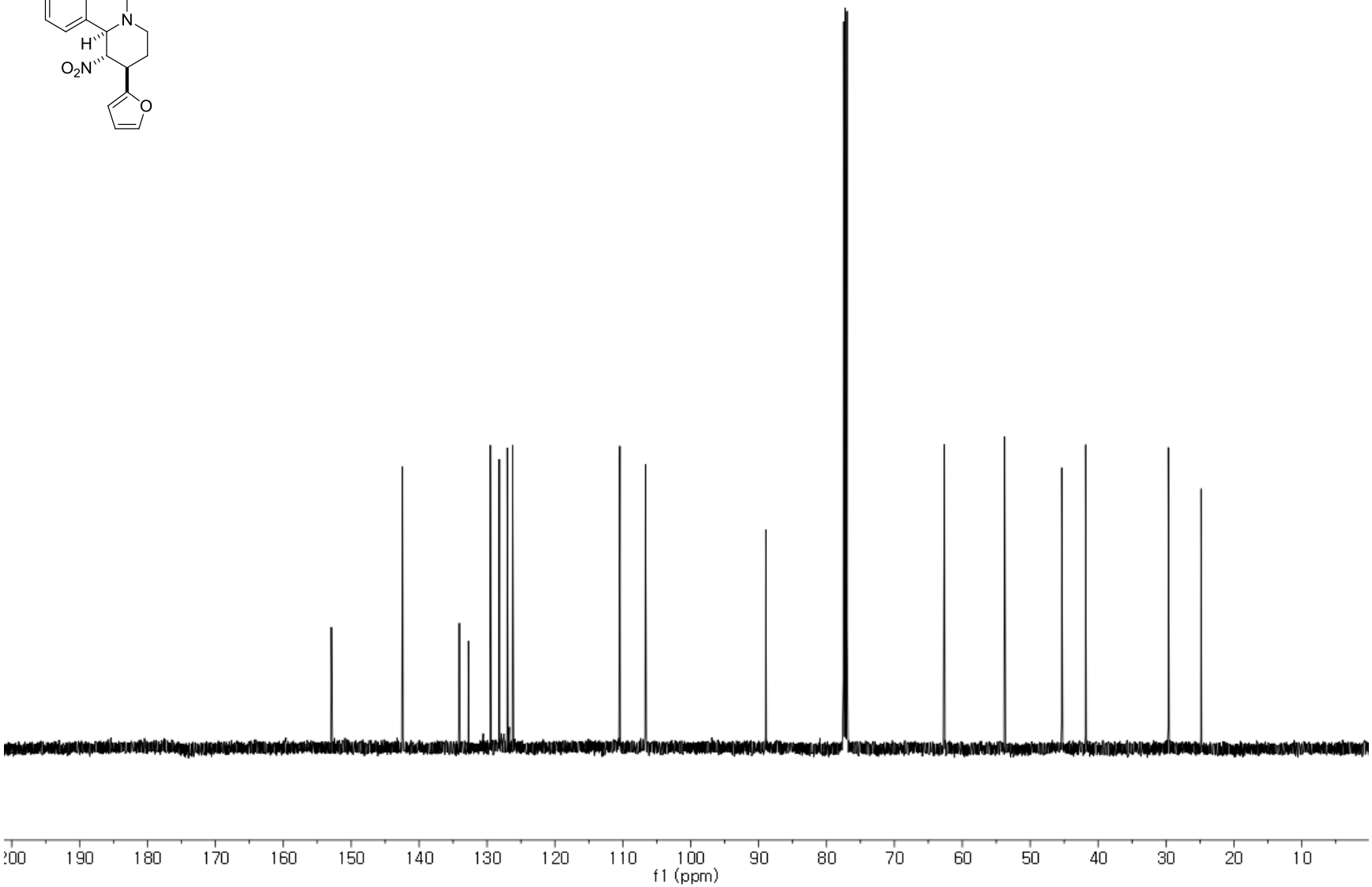
^{1}H NMR of **6q** in $CDCl_3$



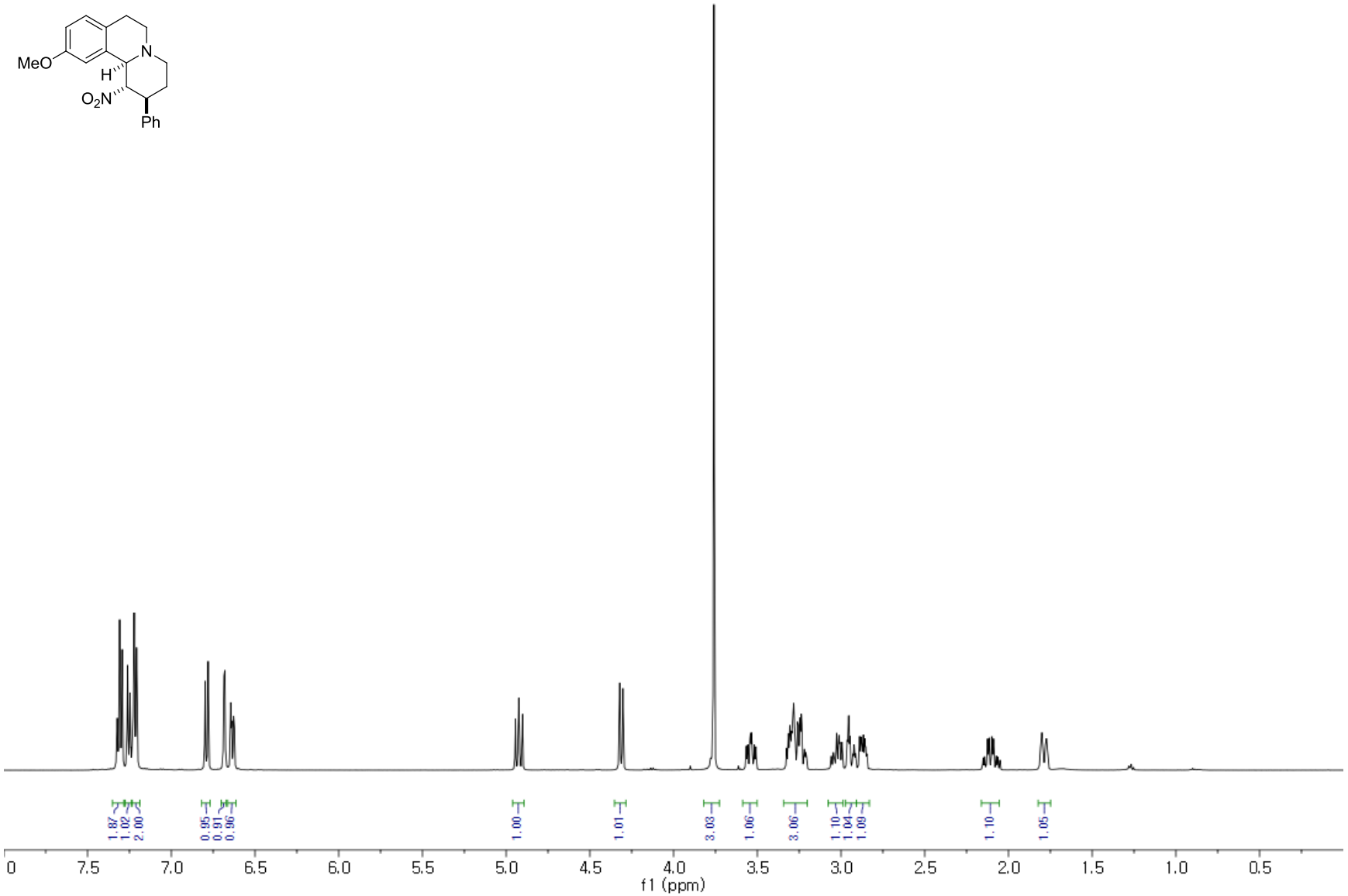


^{13}C NMR of **6q** in $CDCl_3$

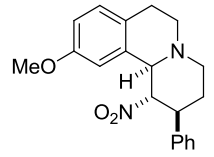


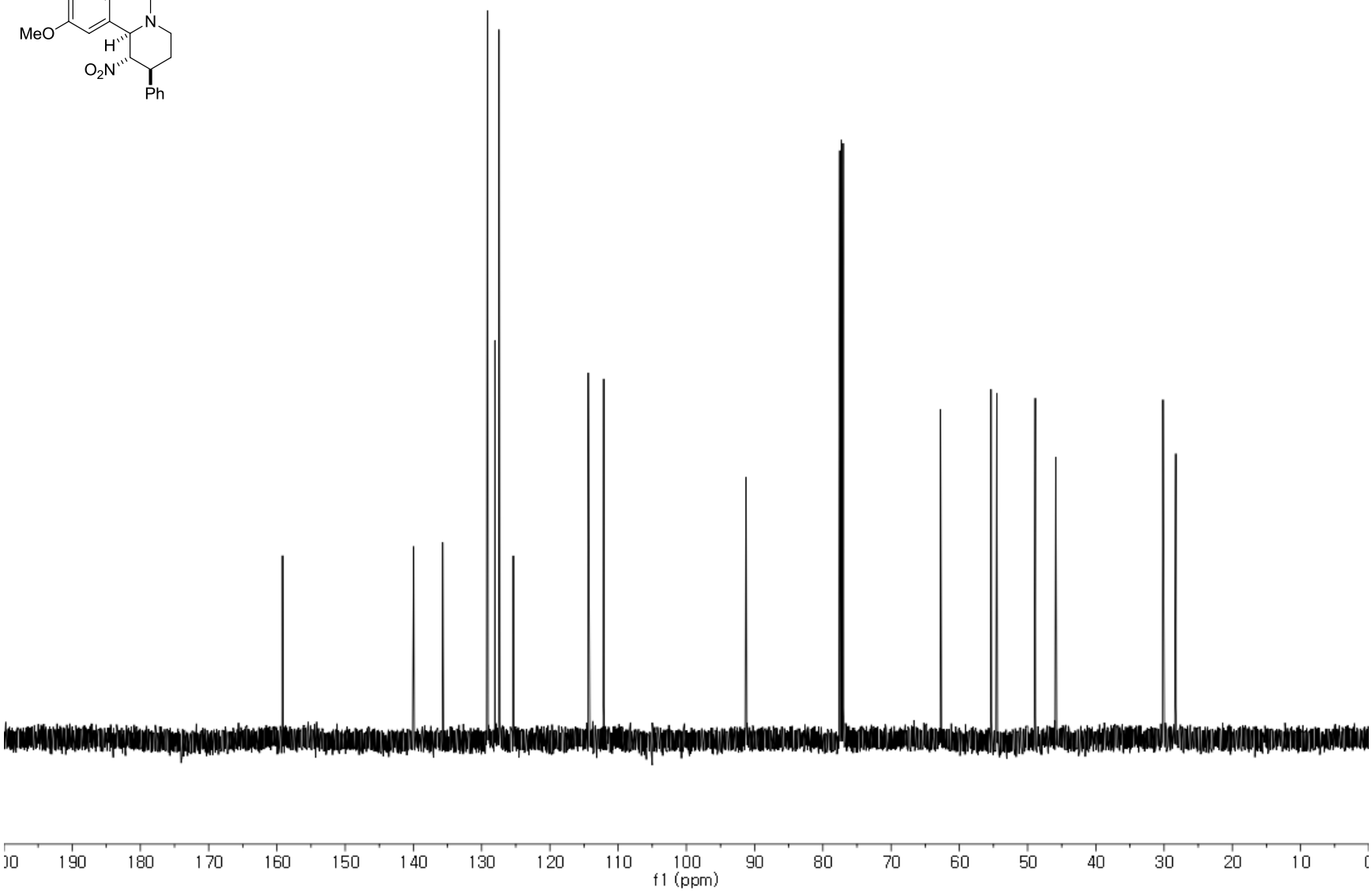


^{1}H NMR of **6r** in $CDCl_3$

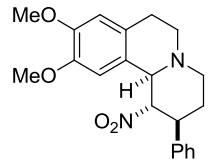


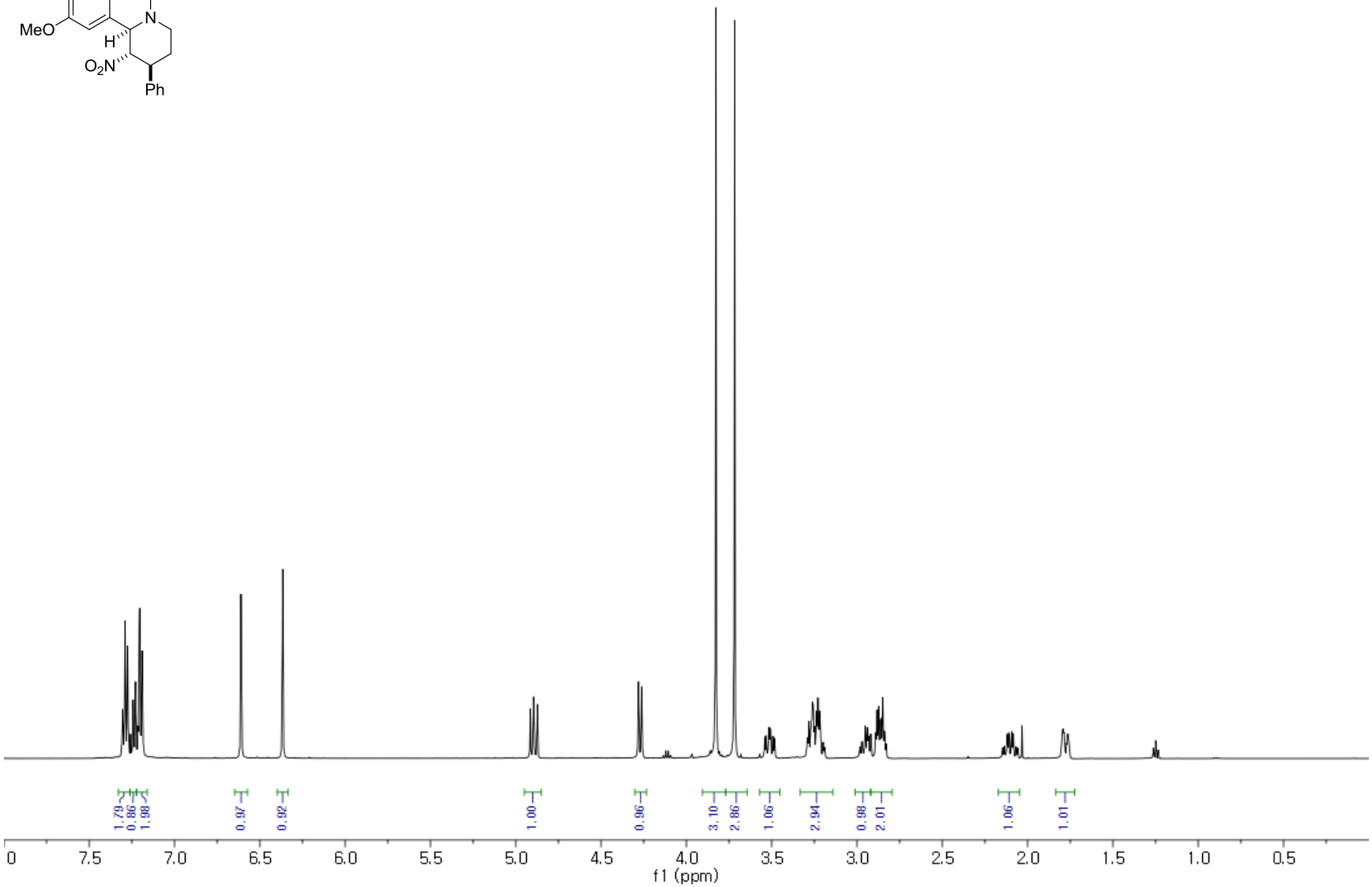
^{13}C NMR of **6r** in $CDCl_3$



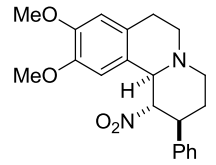


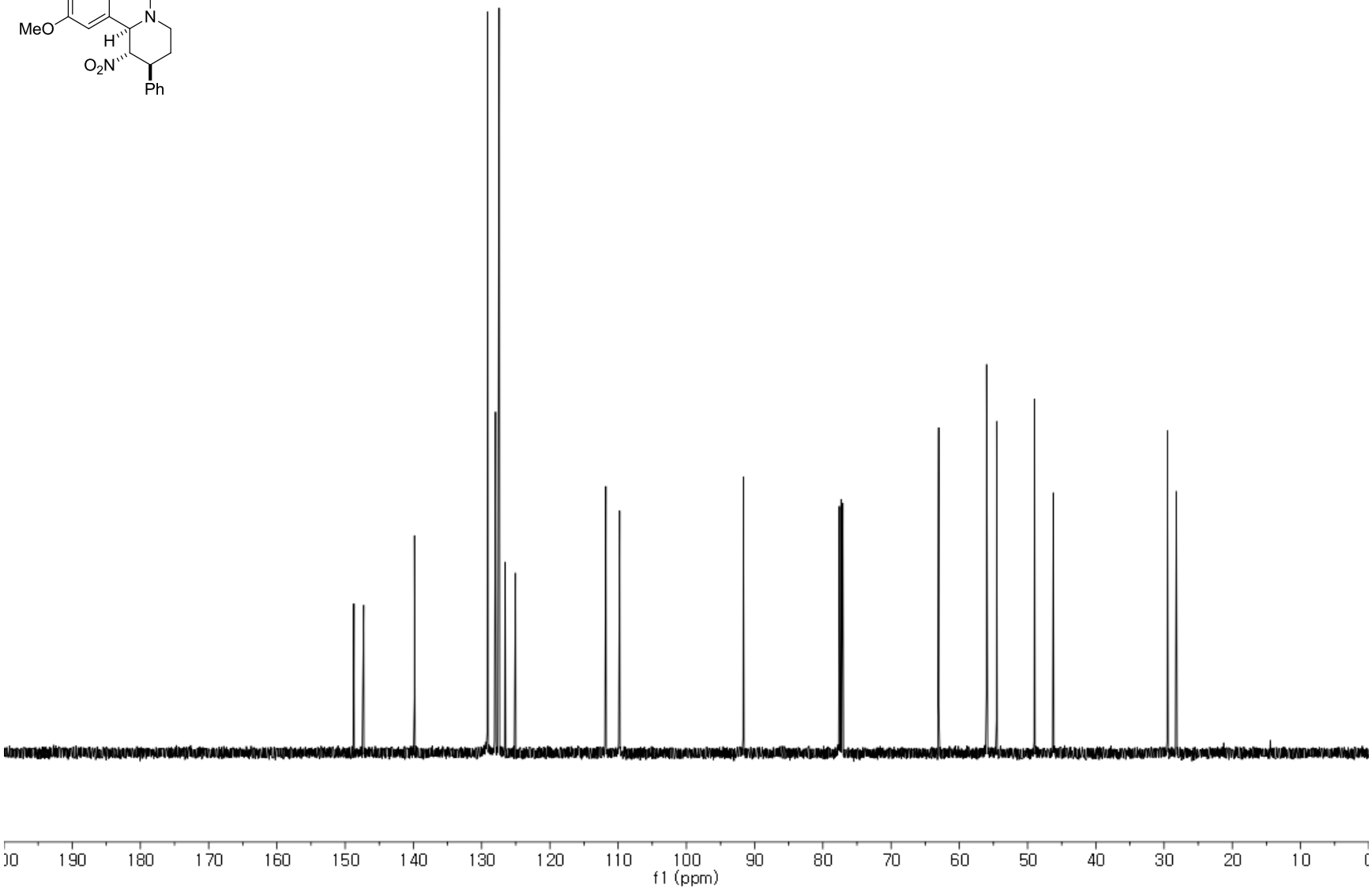
^{1}H NMR of **6s** in $CDCl_3$



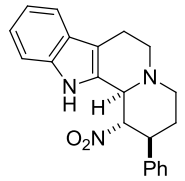


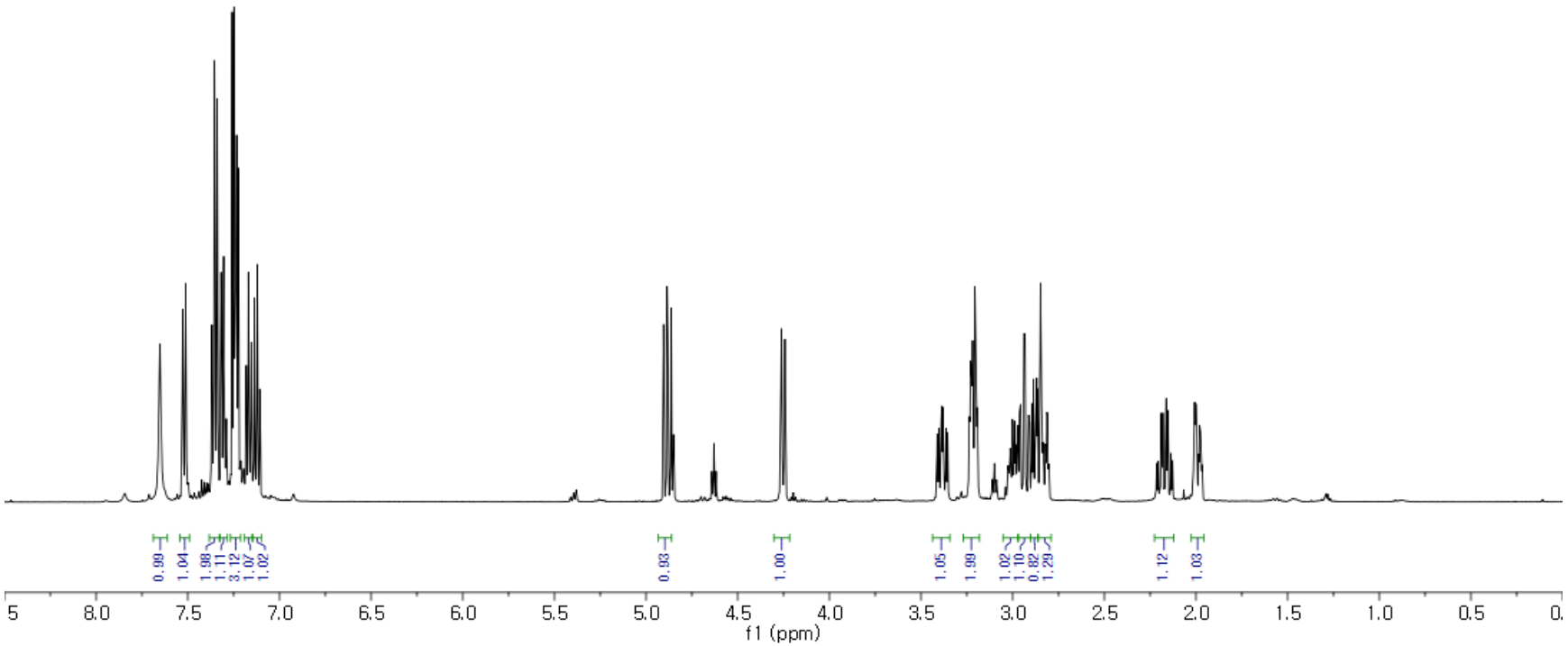
^{13}C NMR of **6s** in $CDCl_3$



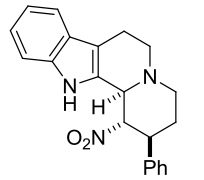


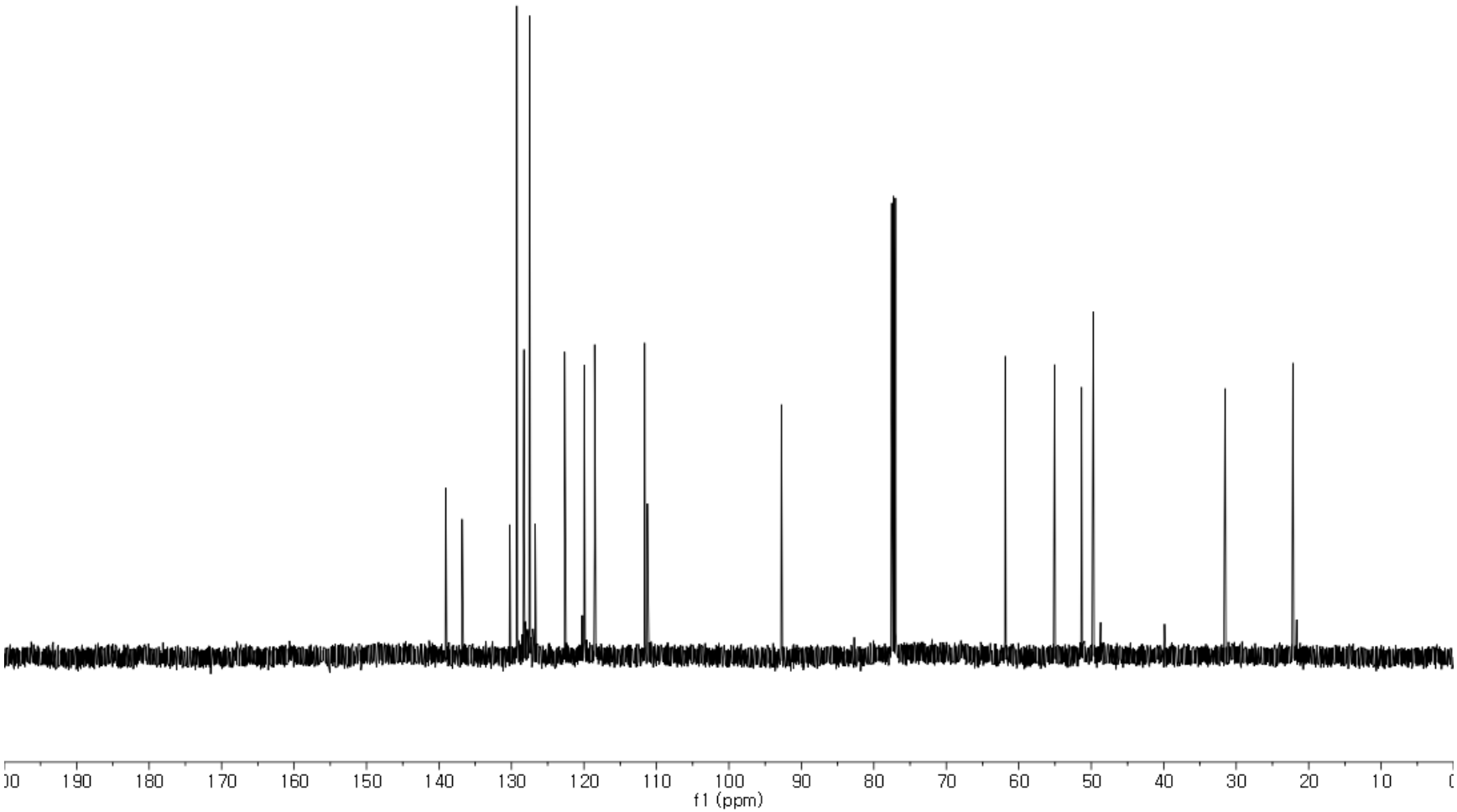
^{1}H NMR of **6t** in $CDCl_3$



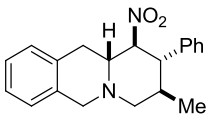


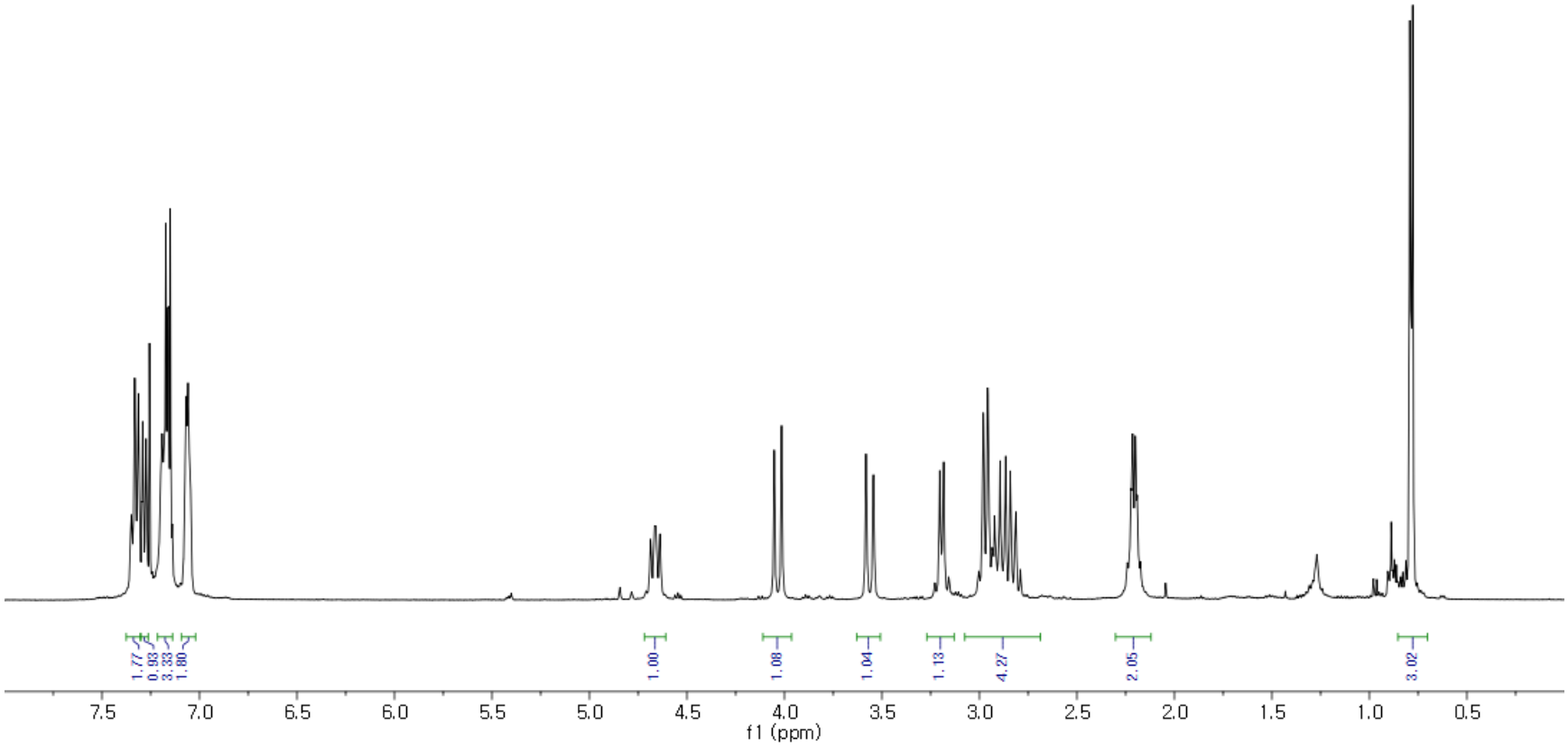
^{13}C NMR of **6t** in $CDCl_3$



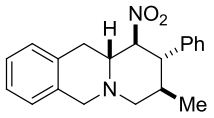


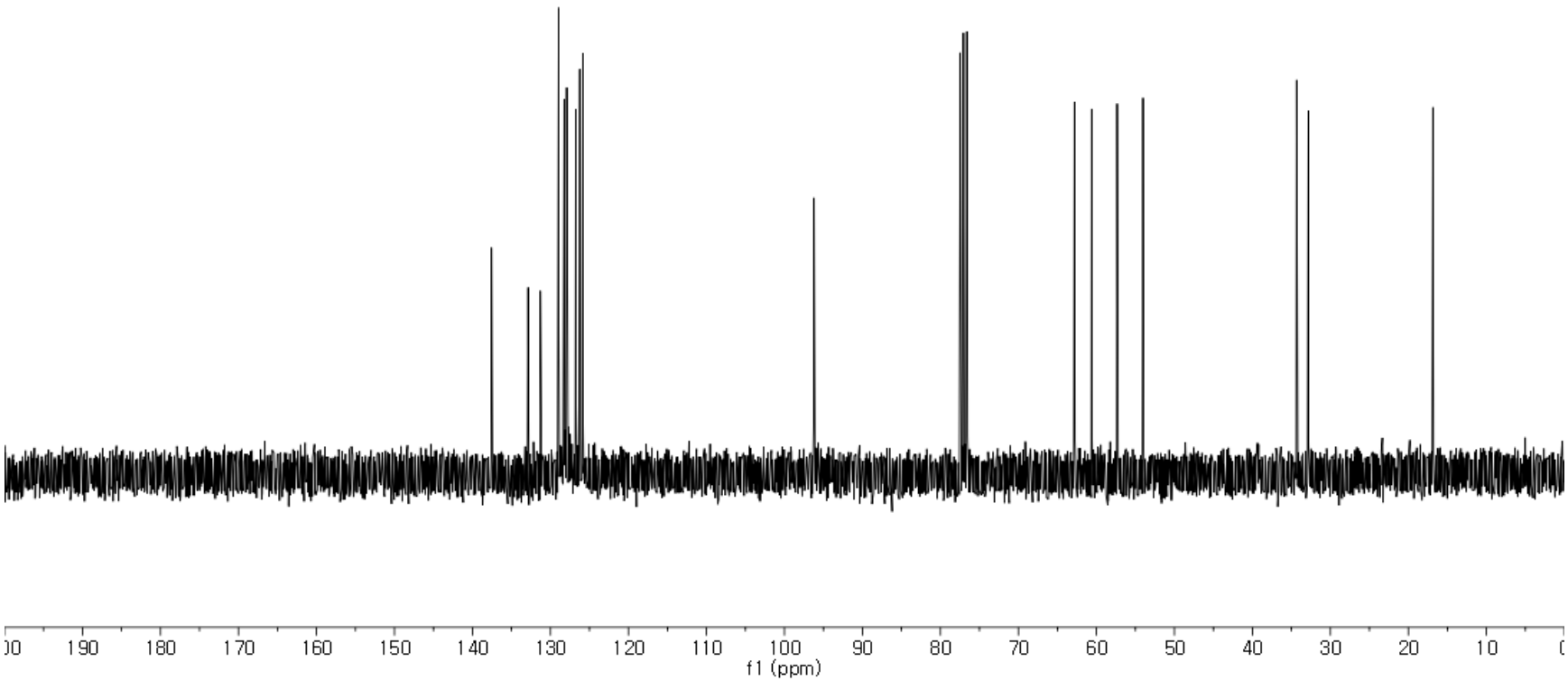
^{1}H NMR of **8a** in $CDCl_3$



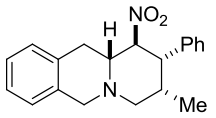


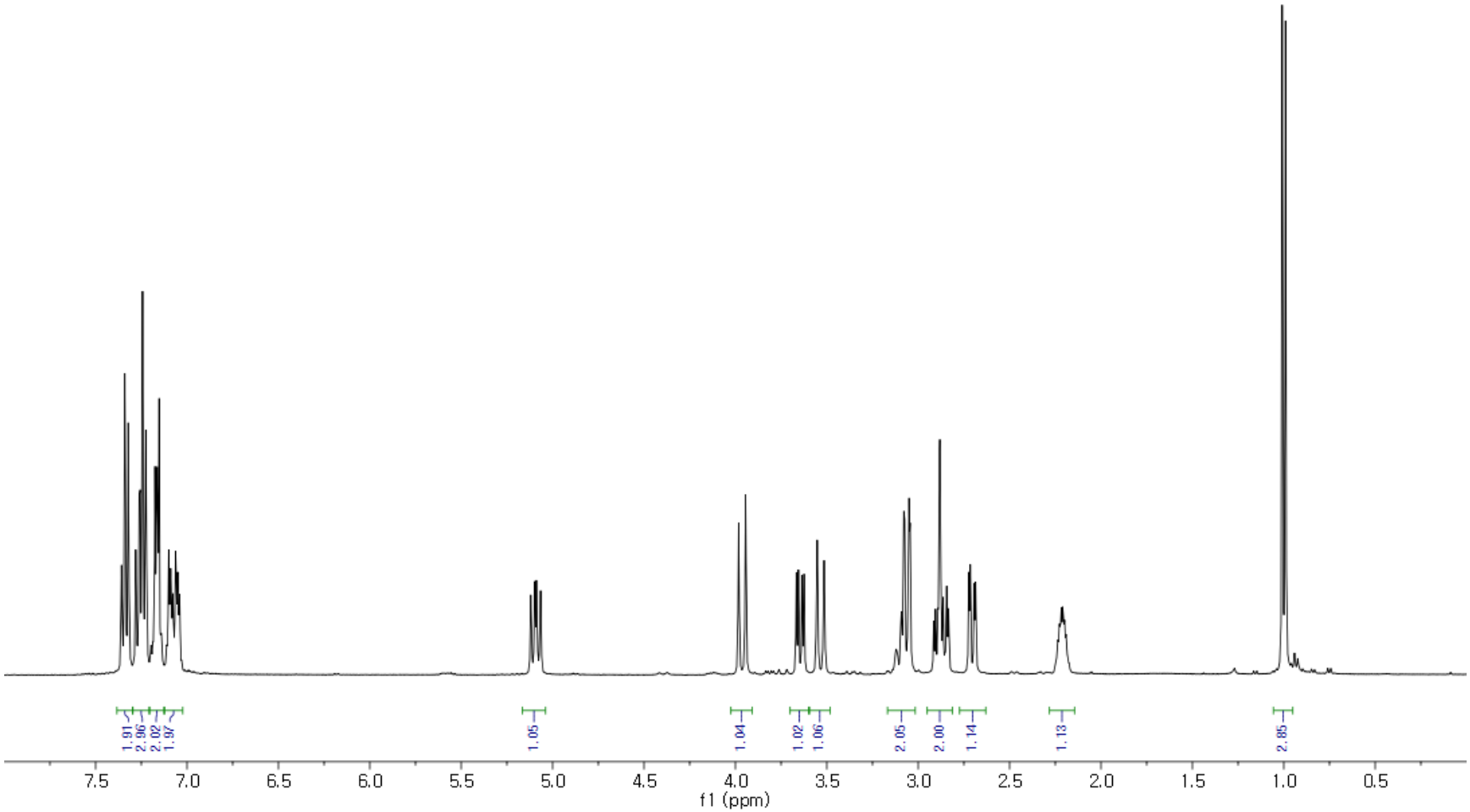
^{13}C NMR of **8a** in $CDCl_3$



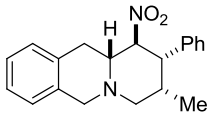


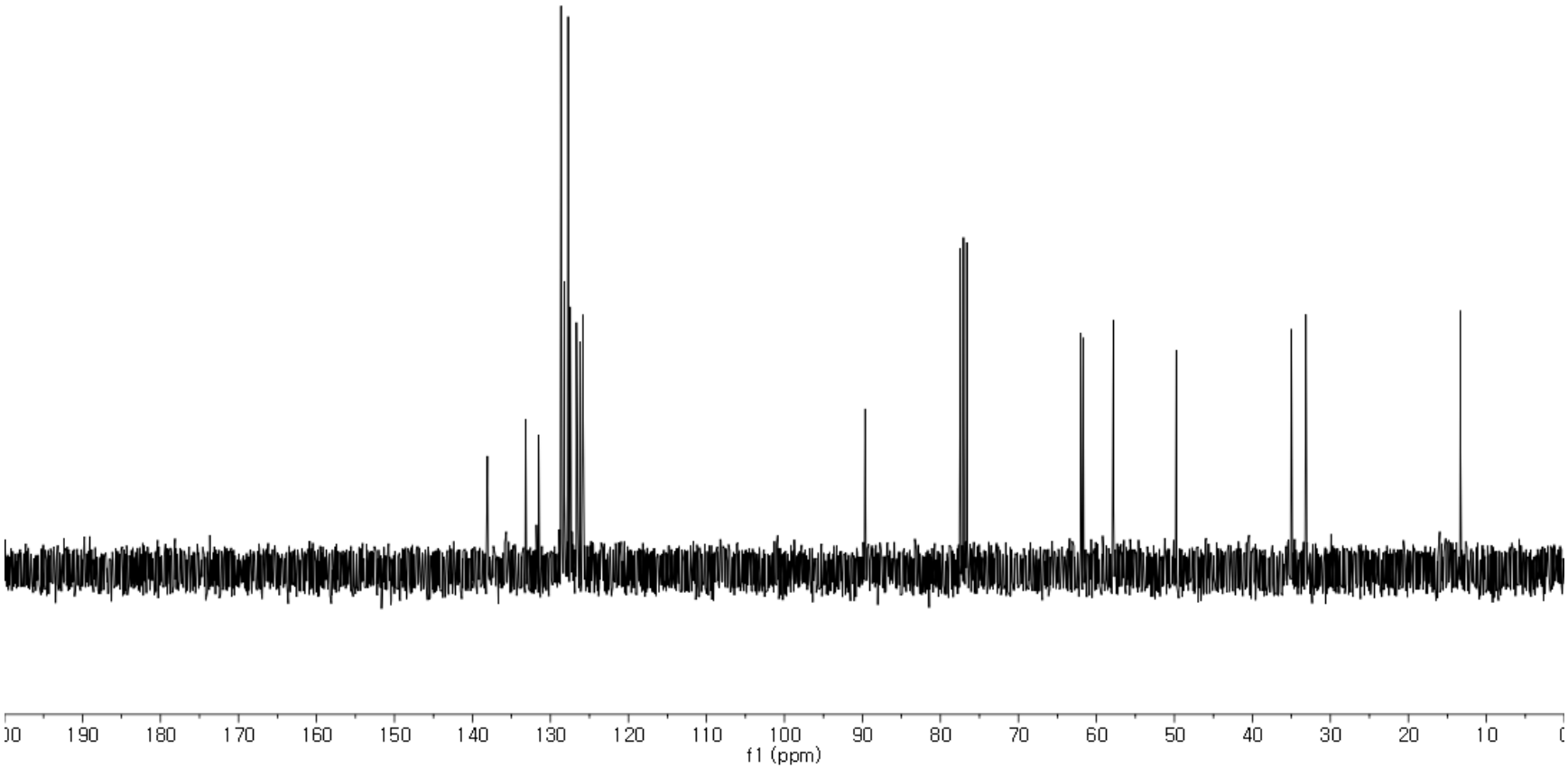
^{1}H NMR of **9a** in $CDCl_3$



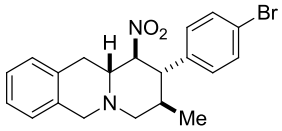


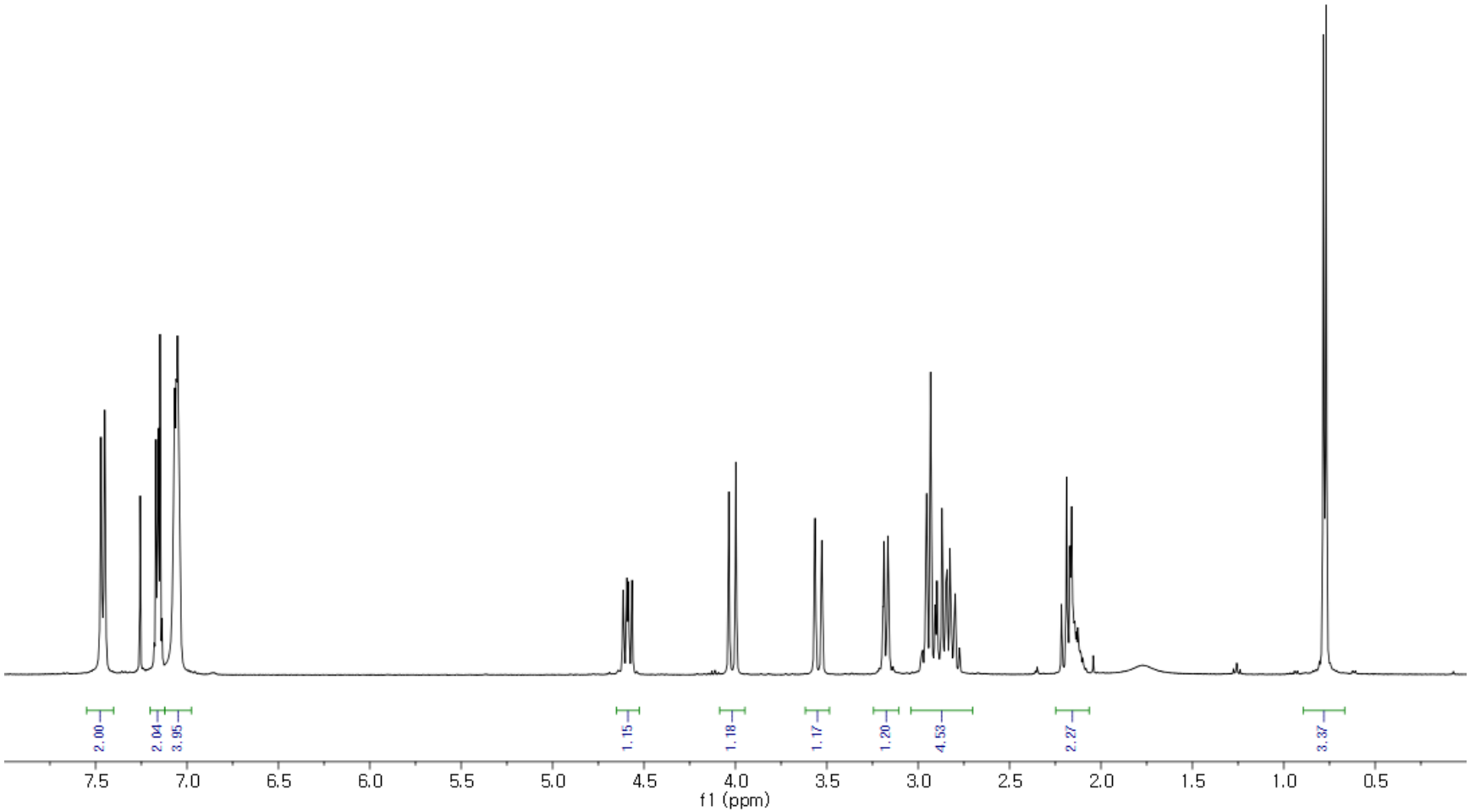
^{13}C NMR of **9a** in $CDCl_3$



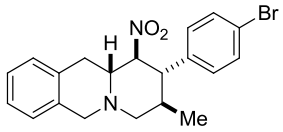


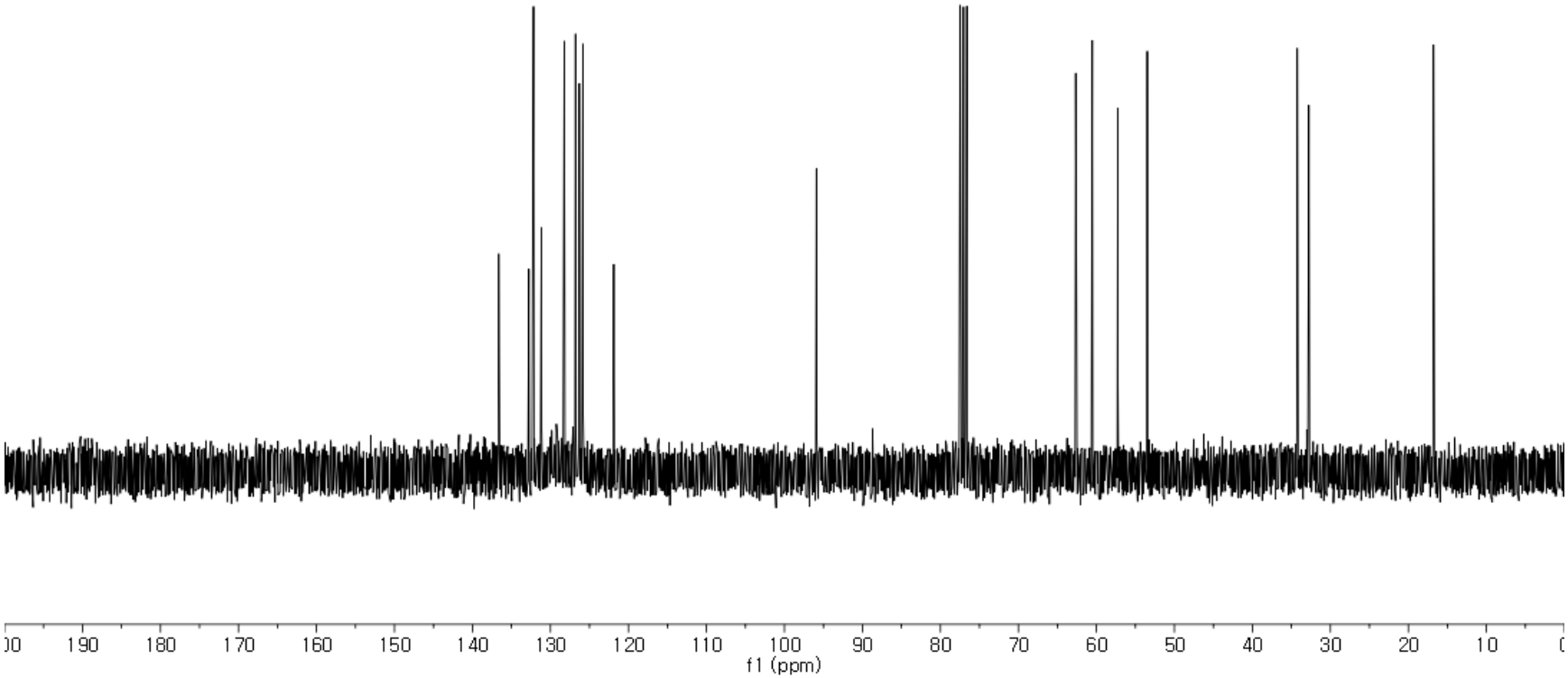
^{1}H NMR of **8c** in $CDCl_3$



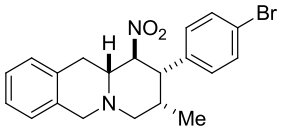


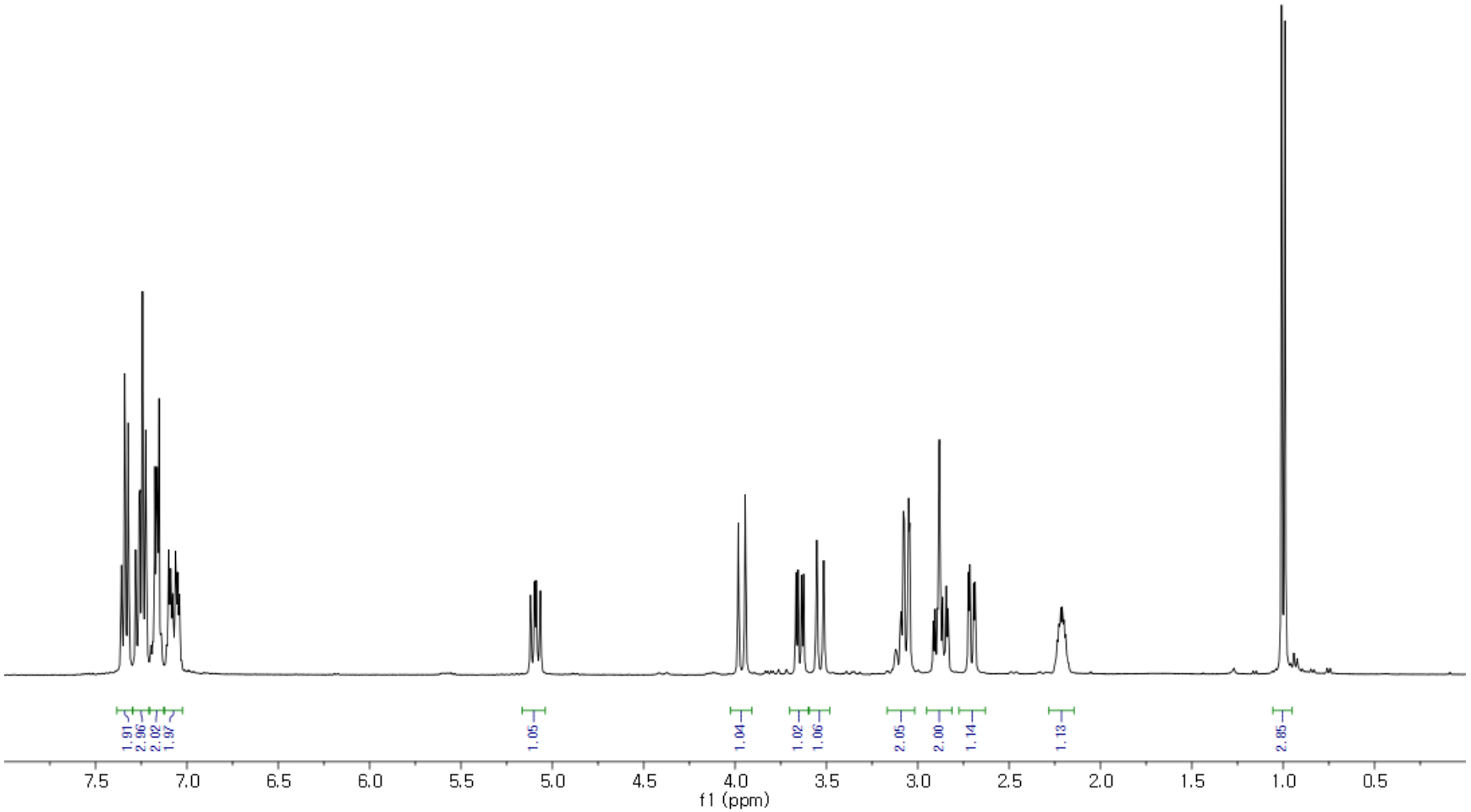
^{13}C NMR of **8c** in $CDCl_3$



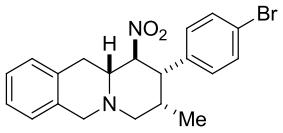


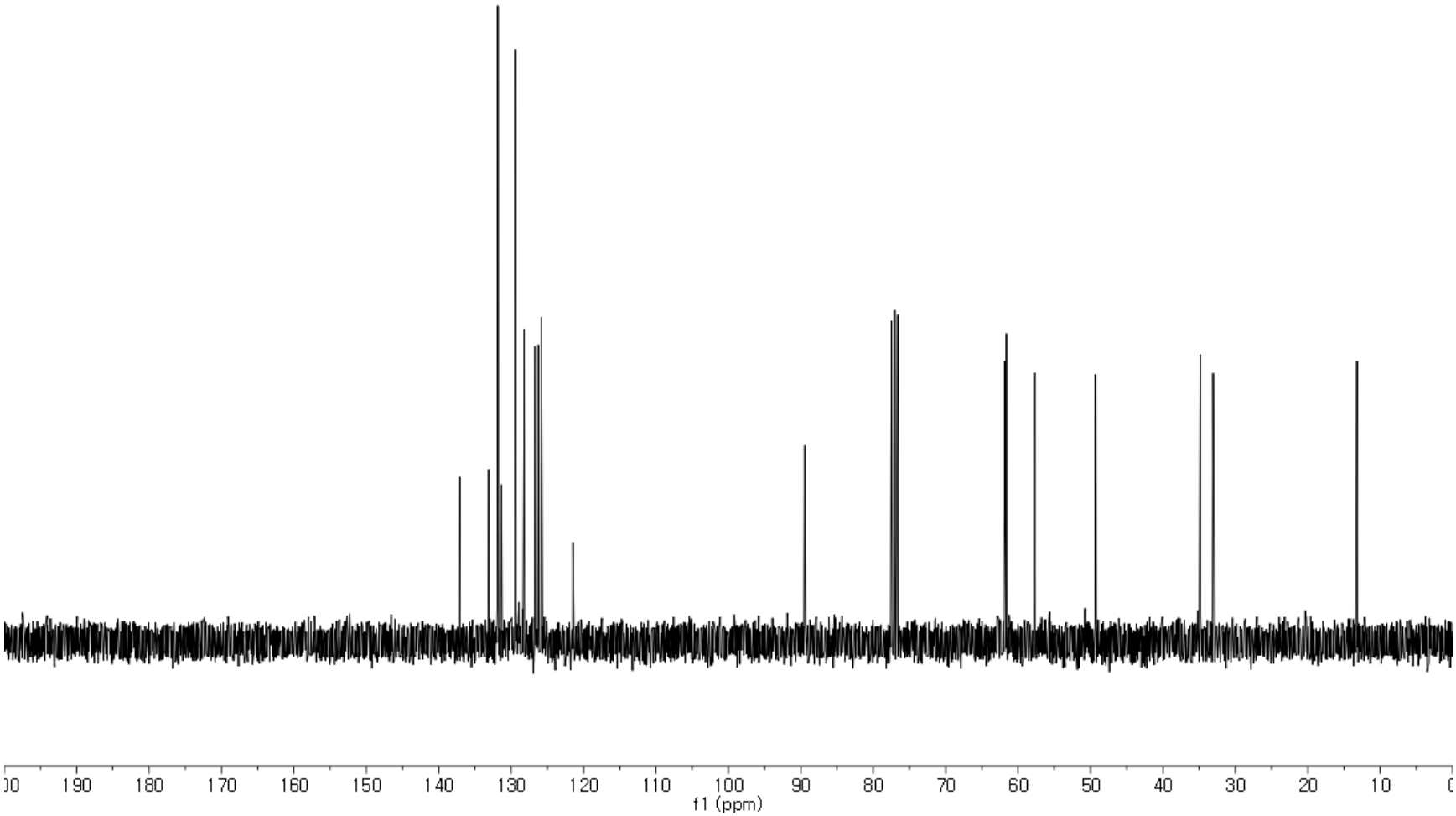
^{1}H NMR of **9c** in $CDCl_3$



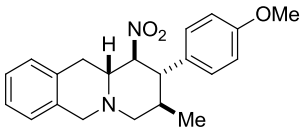


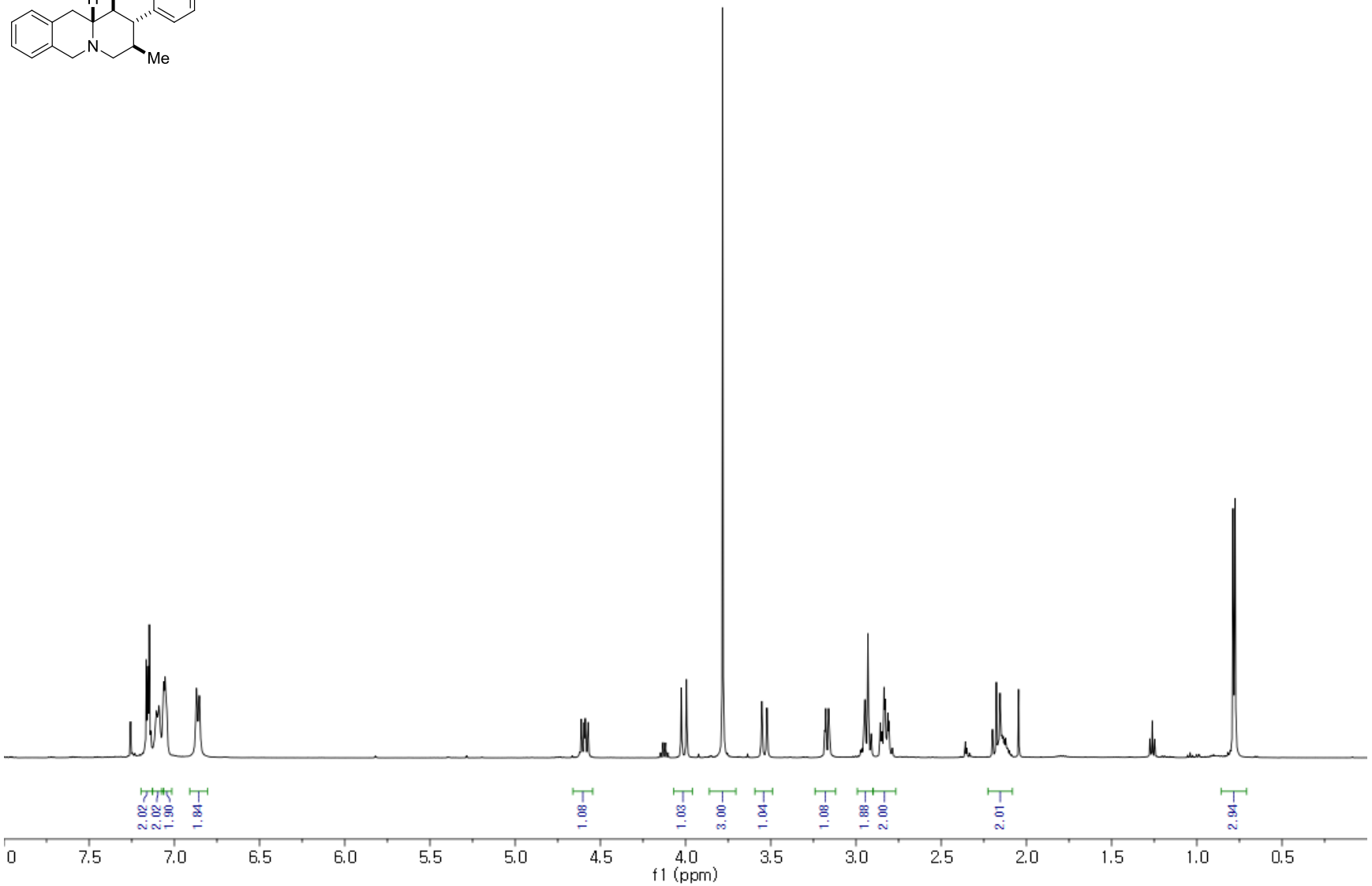
^{13}C NMR of **9c** in $CDCl_3$



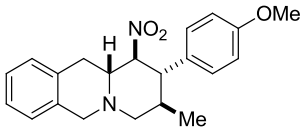


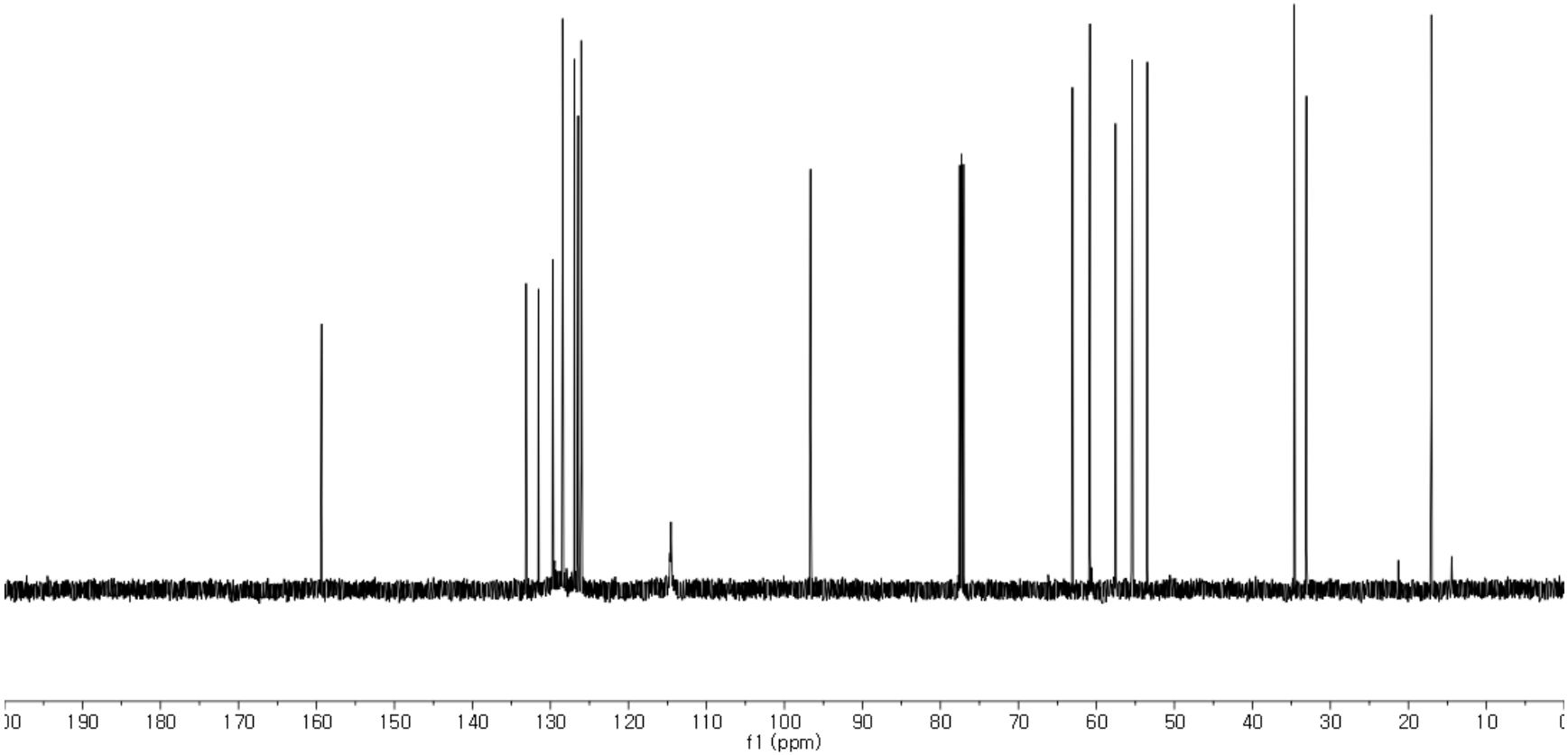
^{1}H NMR of **8e** in $CDCl_3$



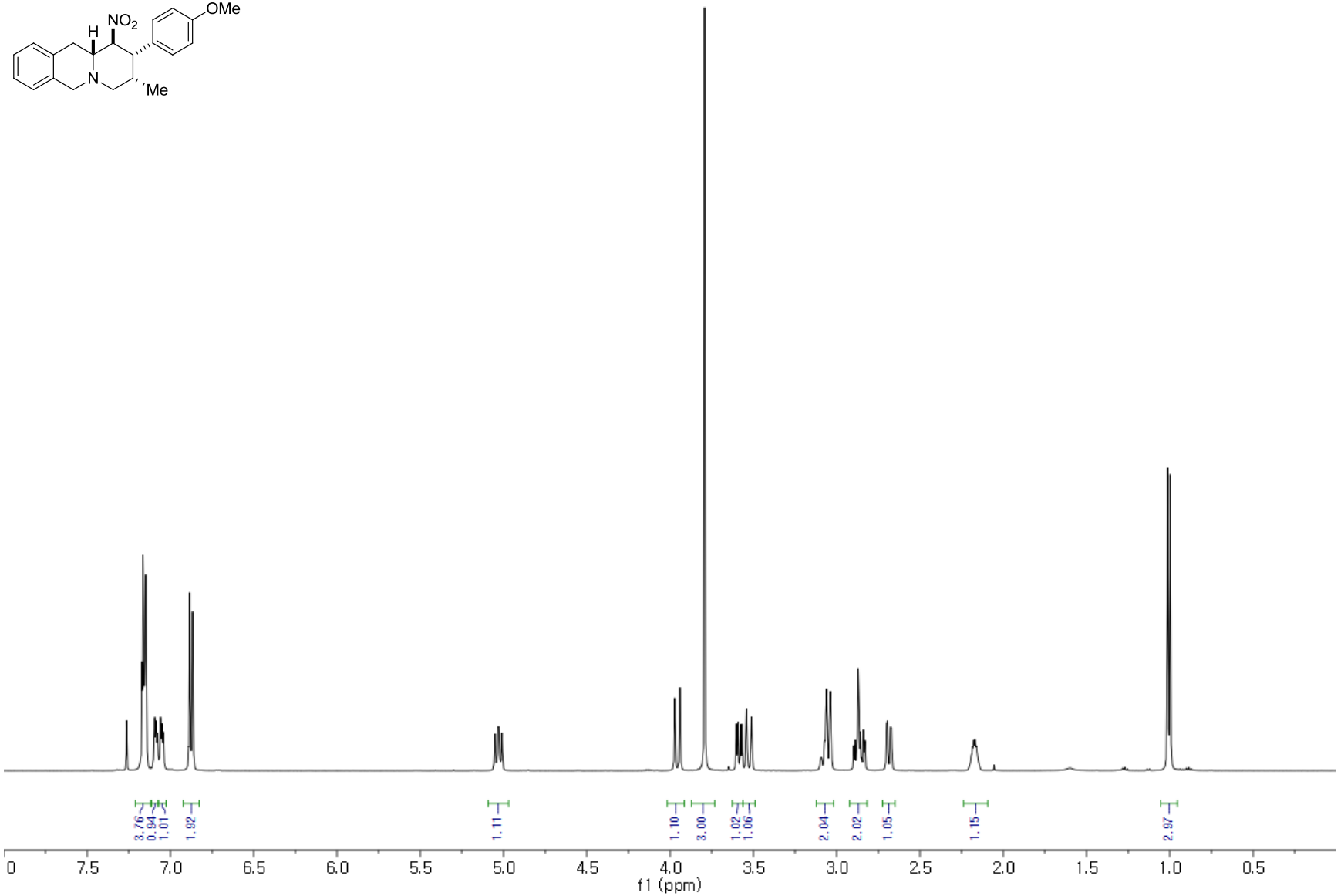


^{13}C NMR of **8e** in $CDCl_3$

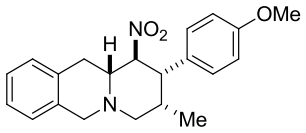


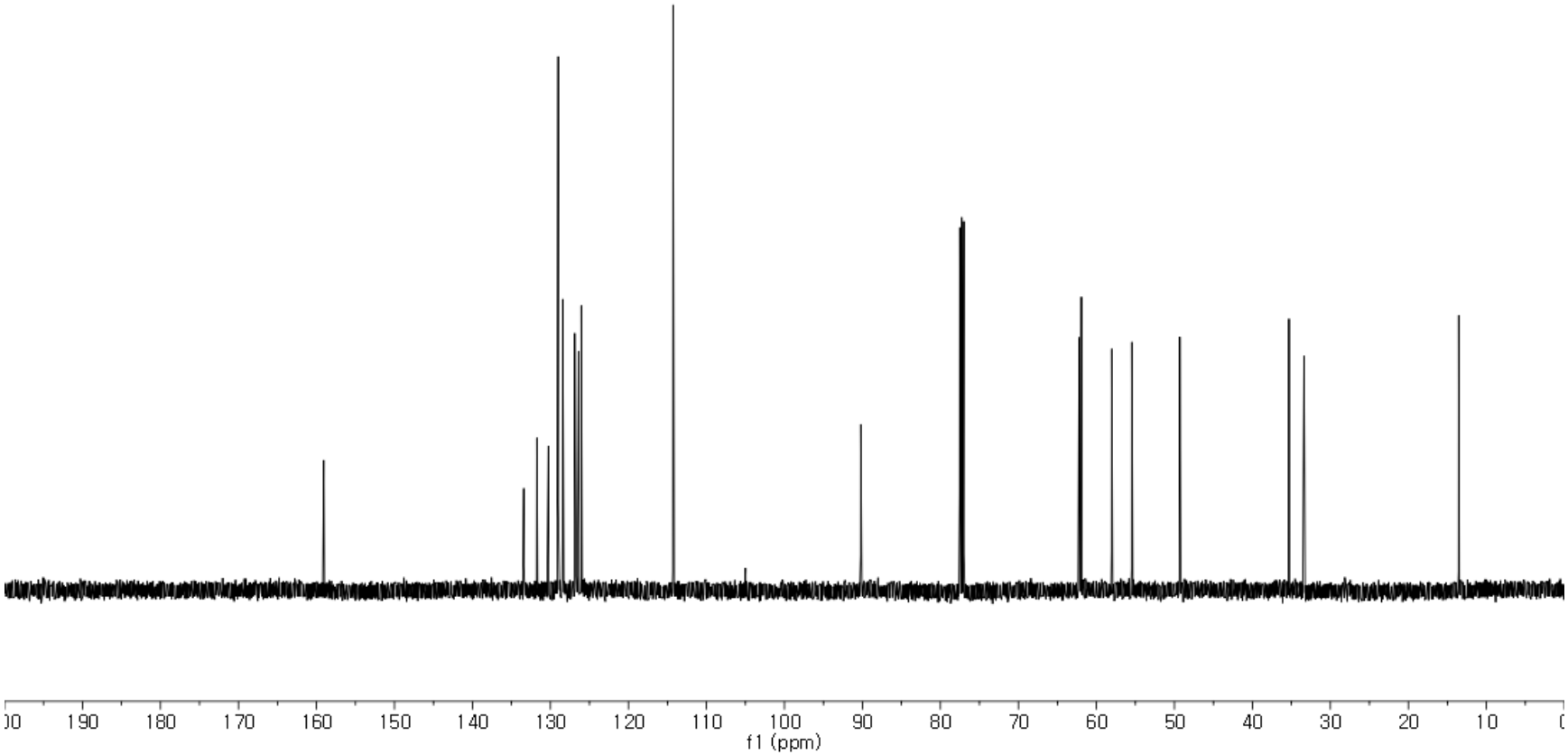


^{1}H NMR of **9e** in $CDCl_3$

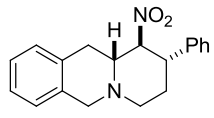


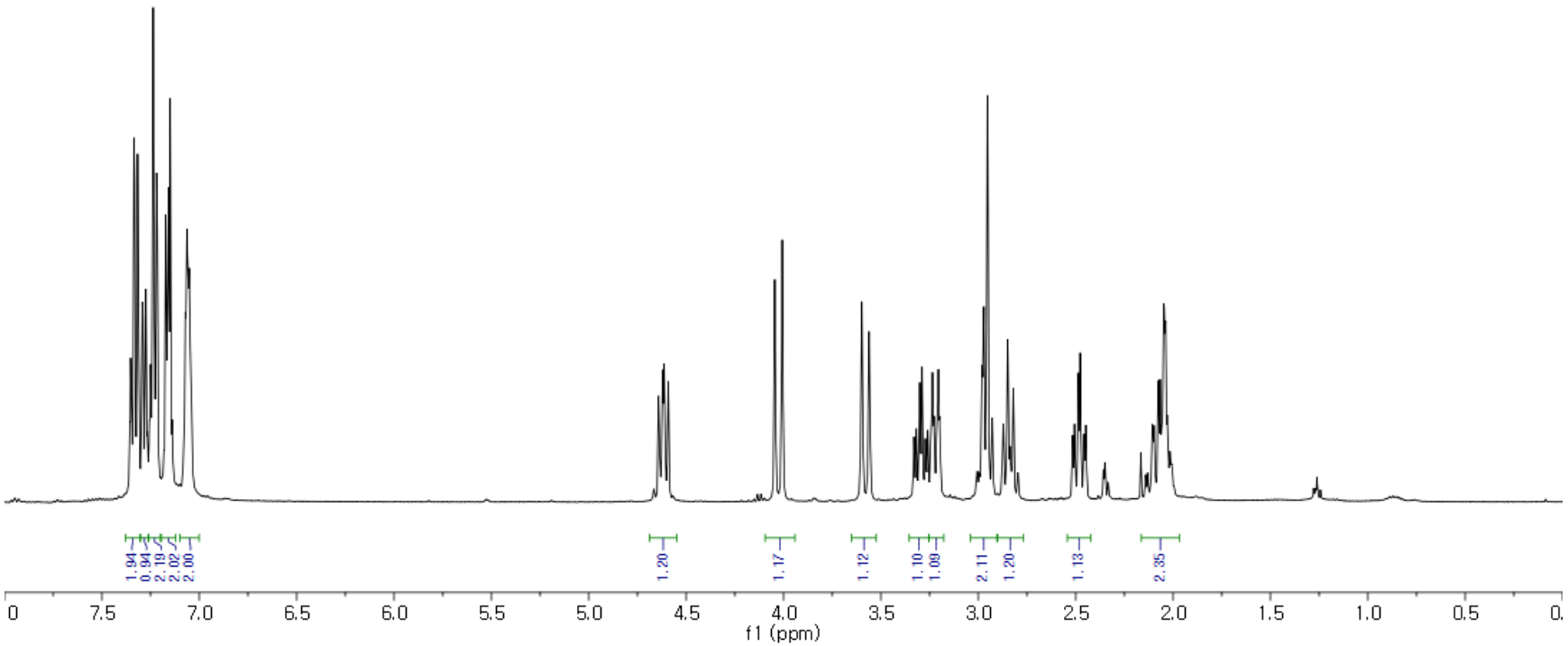
^{13}C NMR of **9e** in $CDCl_3$



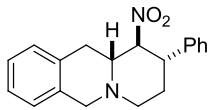


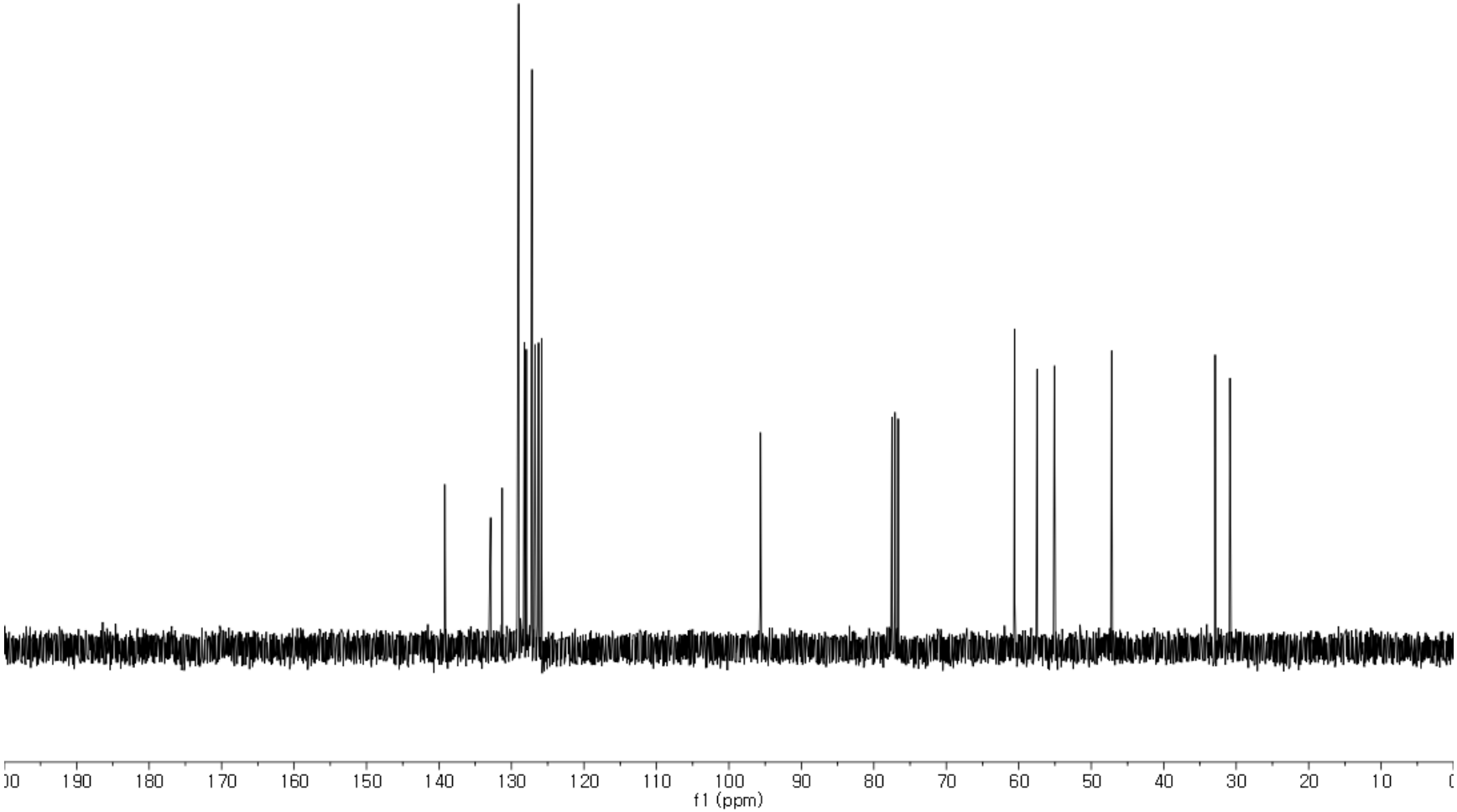
^{1}H NMR of **8k** in $CDCl_3$



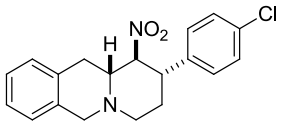


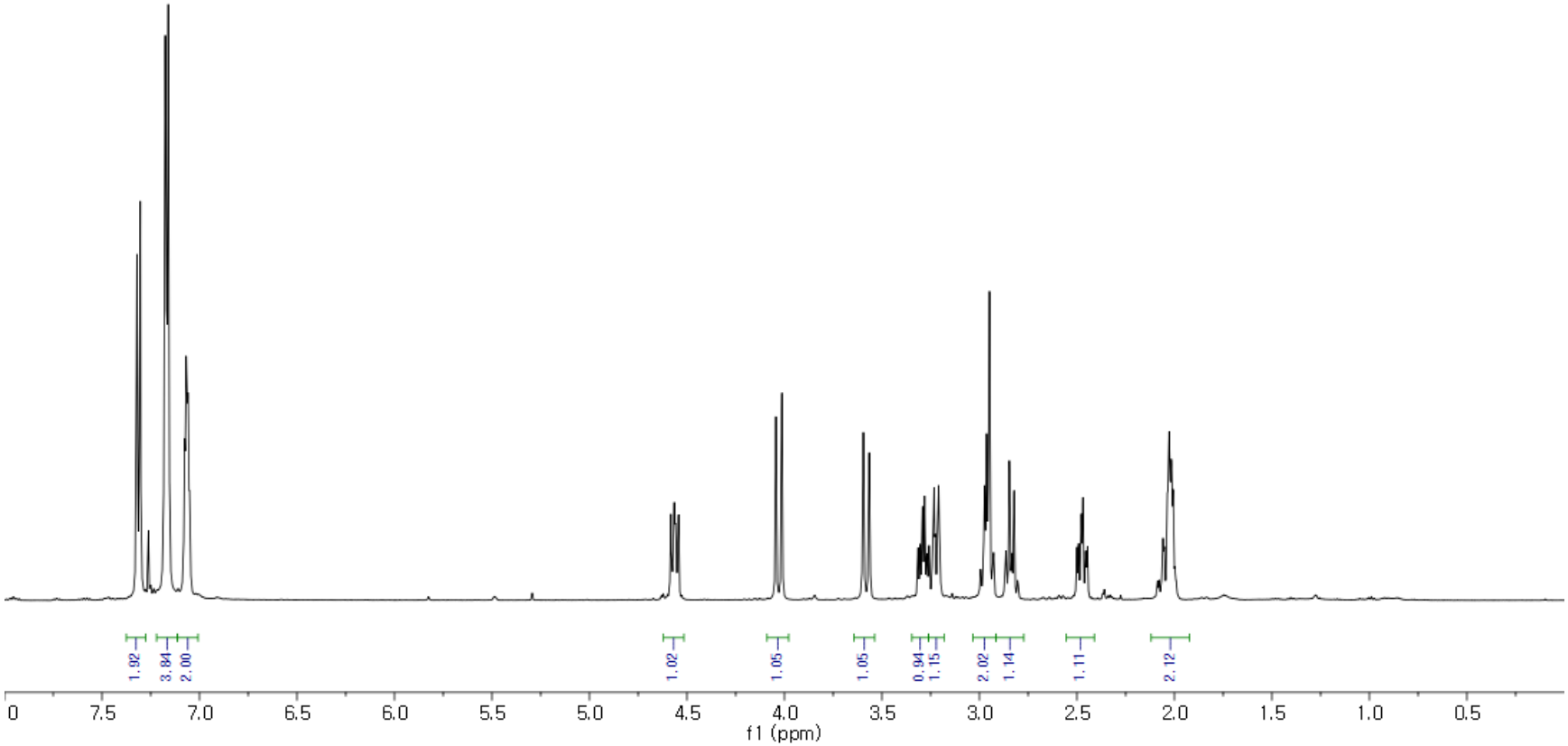
^{13}C NMR of **8k** in $CDCl_3$



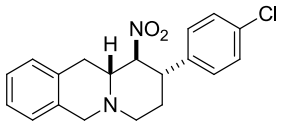


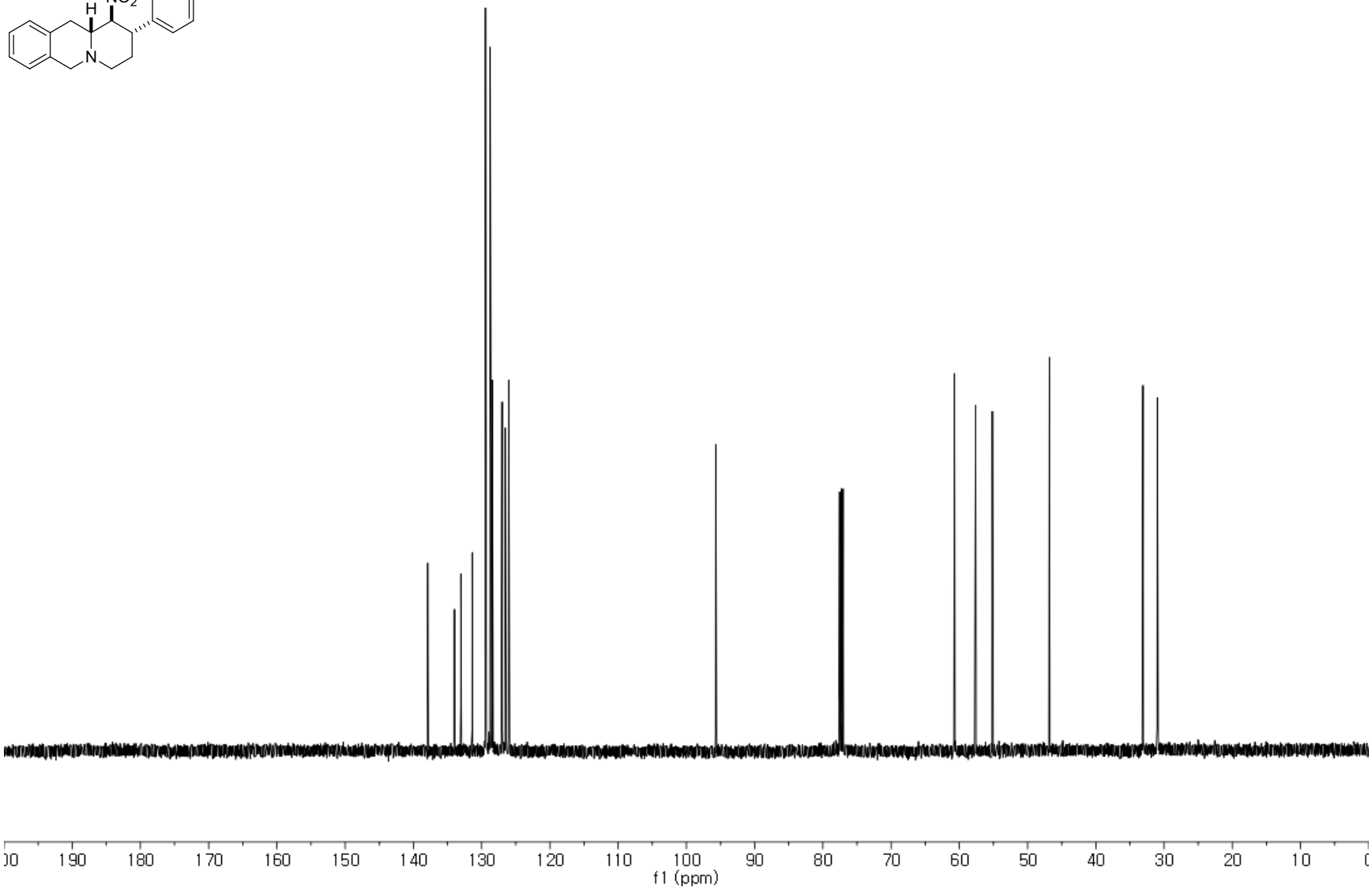
^{1}H NMR of **8l** in $CDCl_3$



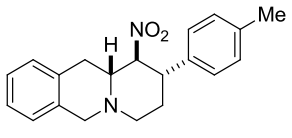


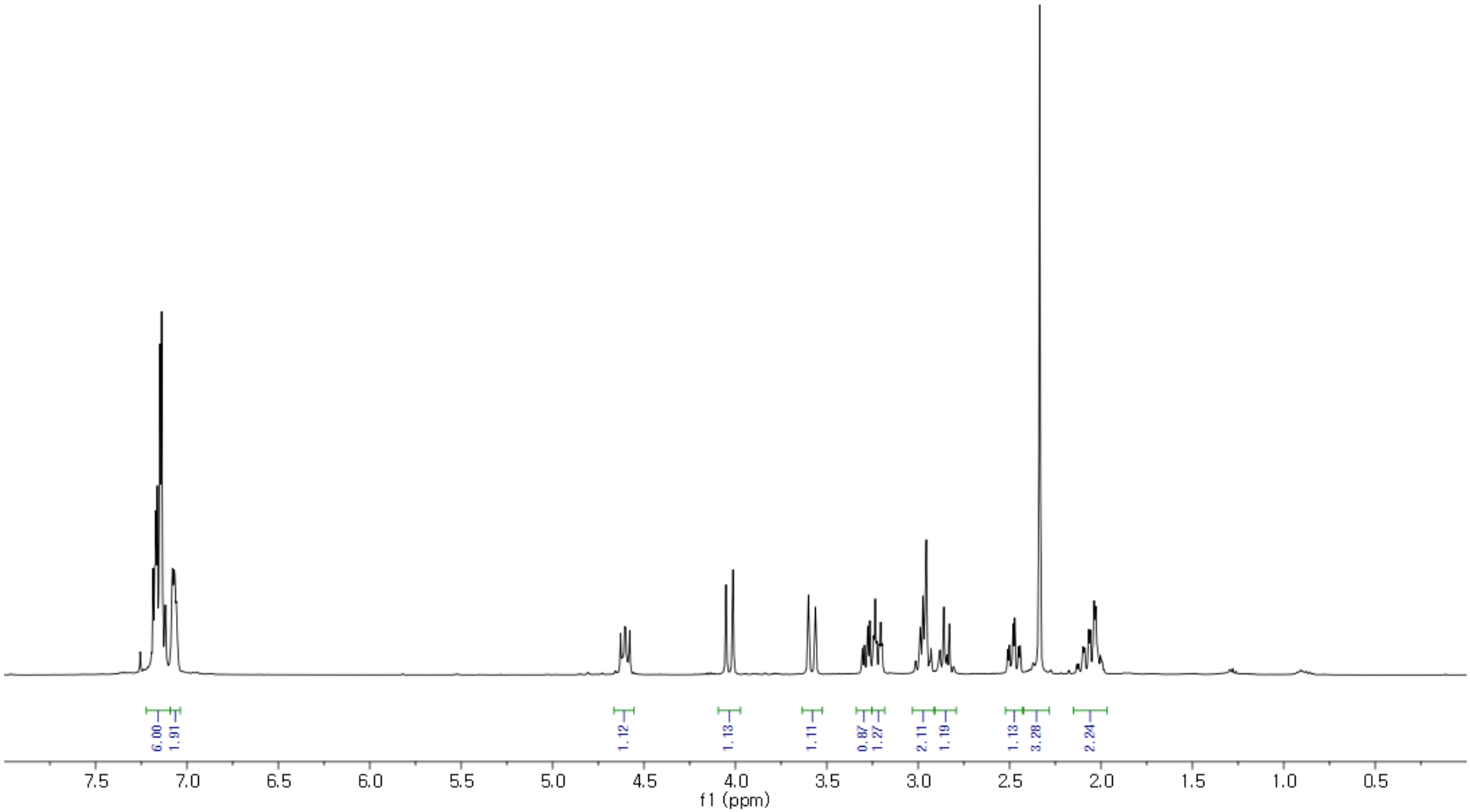
^{13}C NMR of **8l** in $CDCl_3$



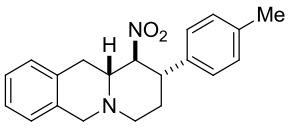


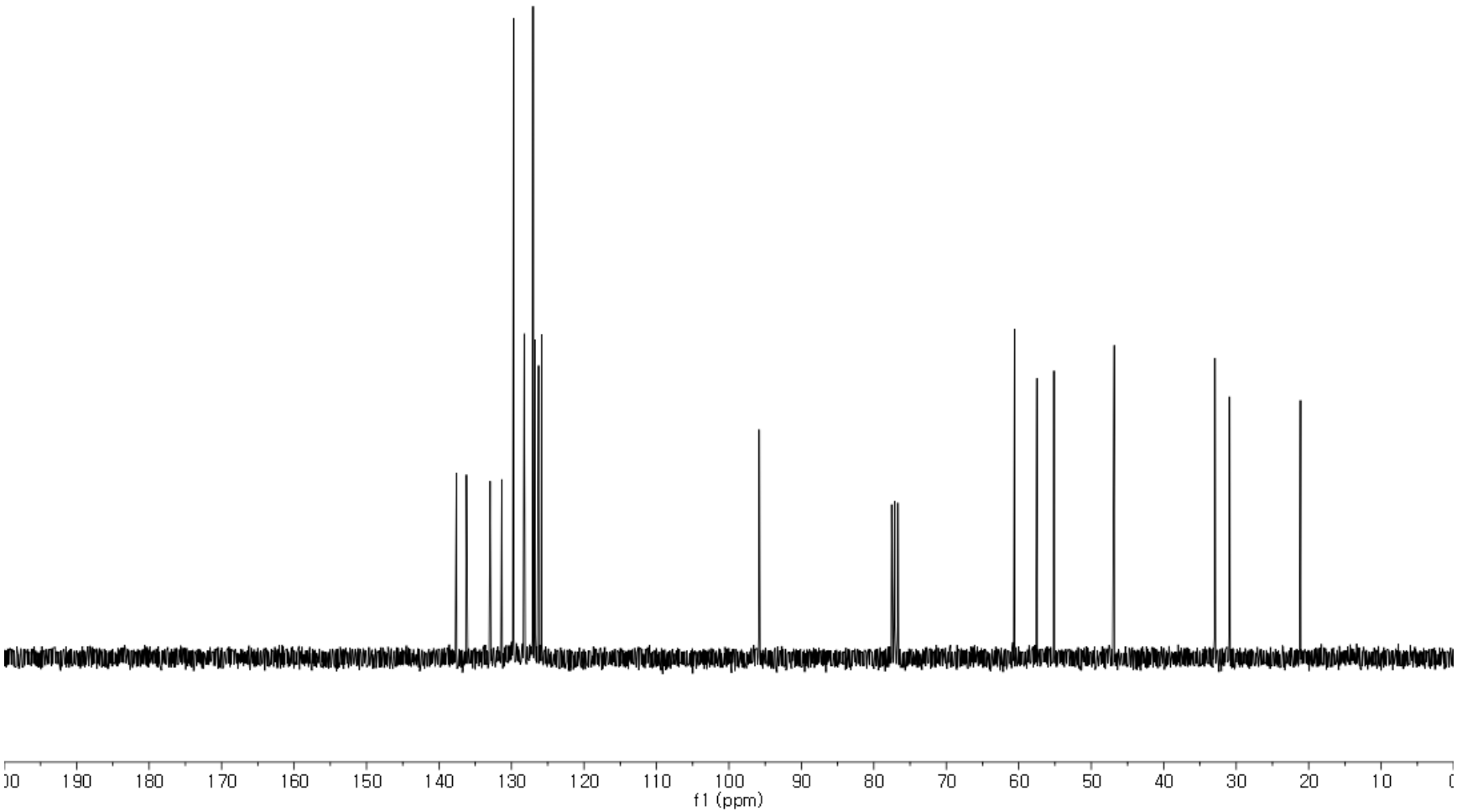
^{1}H NMR of **8n** in $CDCl_3$



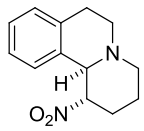


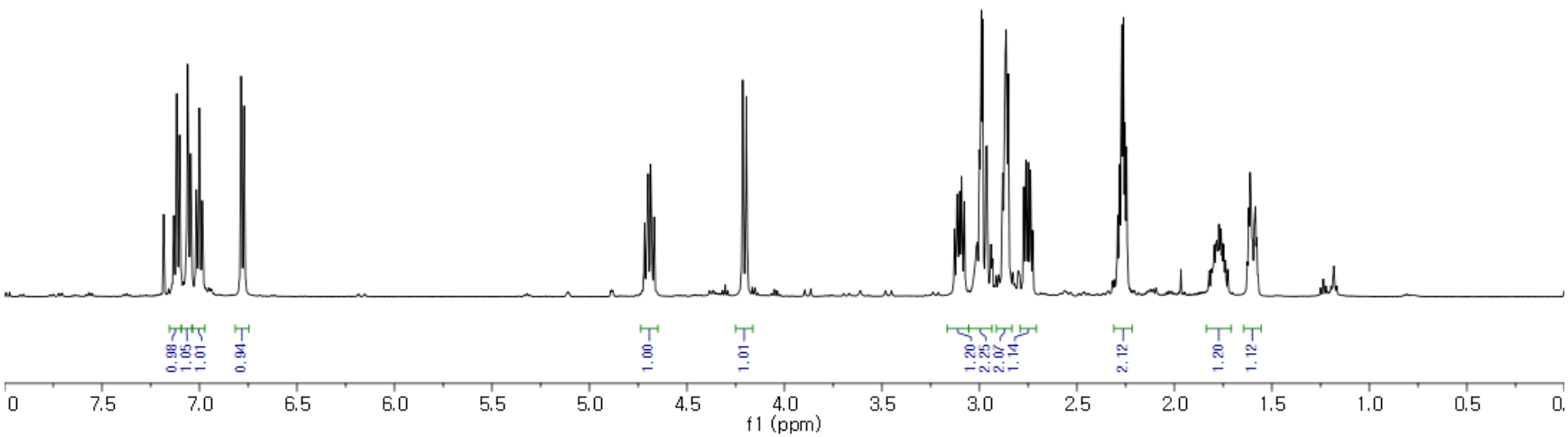
^{13}C NMR of **8n** in $CDCl_3$



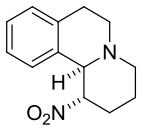


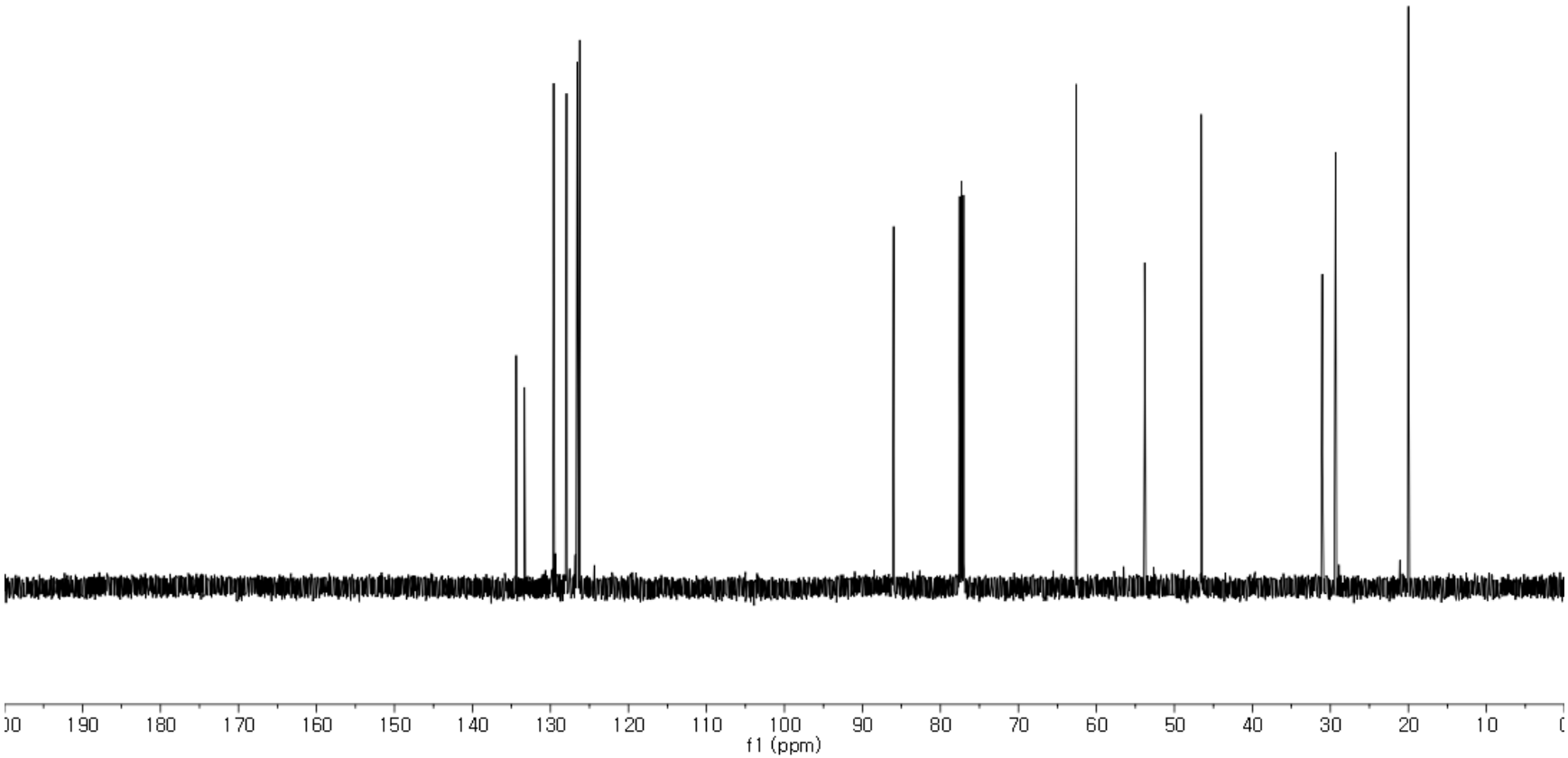
^{1}H NMR of **11** in $CDCl_3$



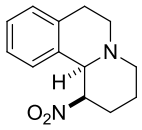


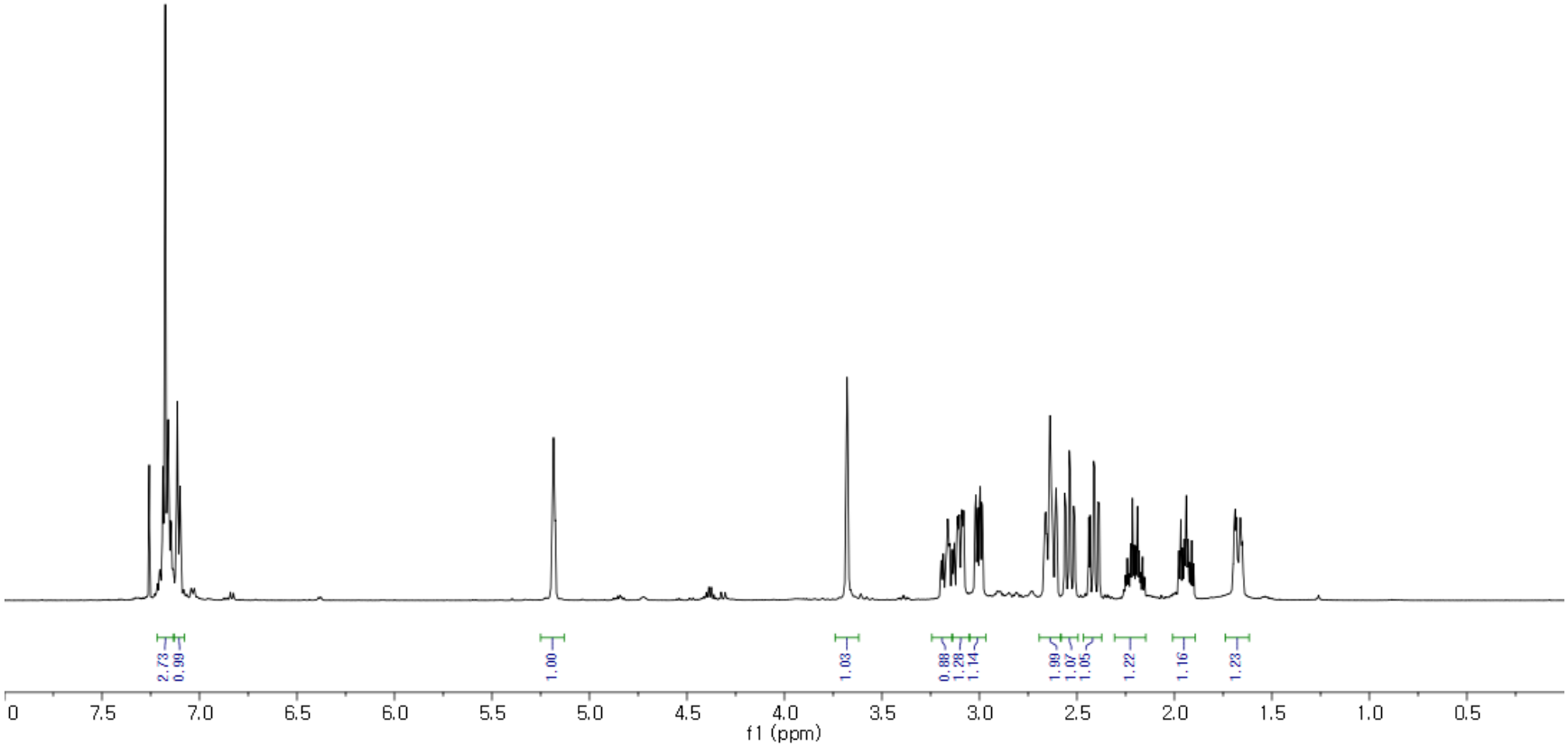
^{13}C NMR of **11** in $CDCl_3$



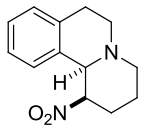


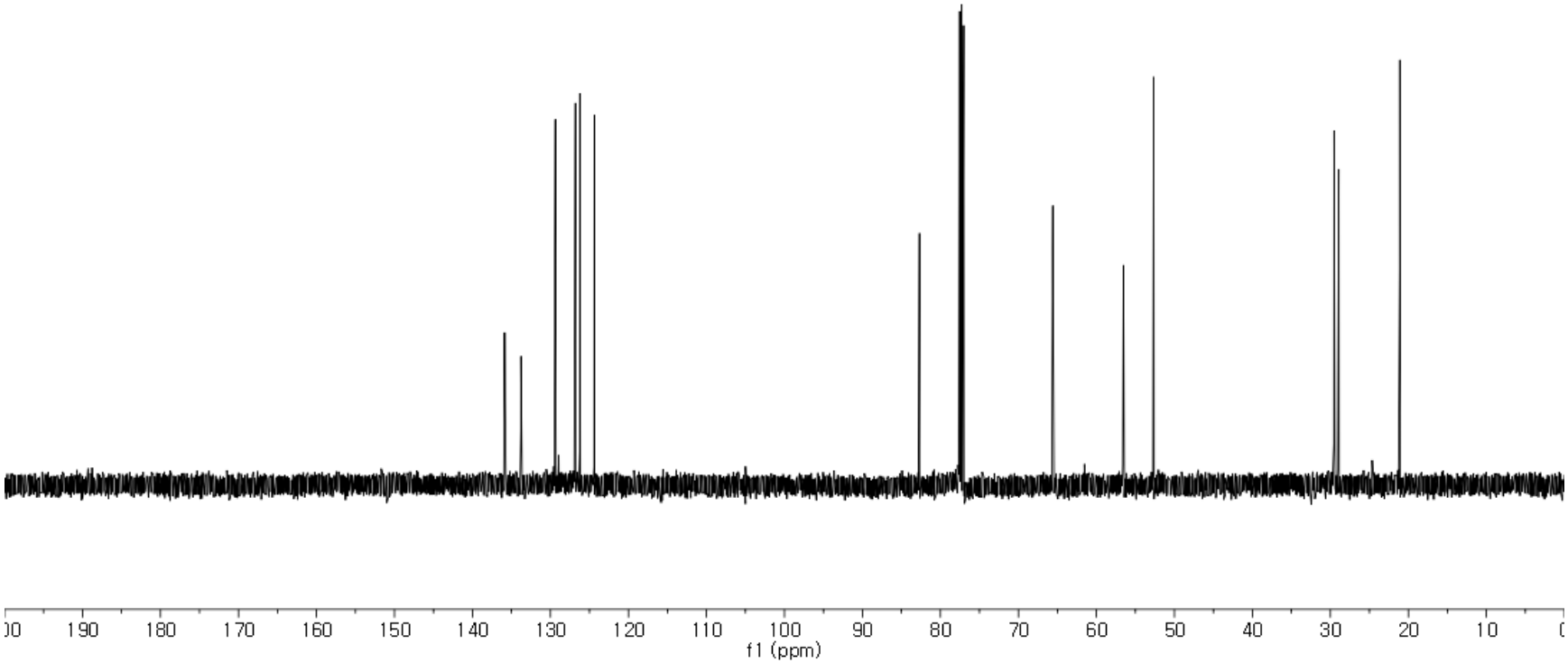
^{1}H NMR of **12** in $CDCl_3$



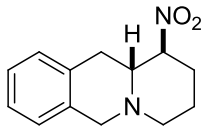


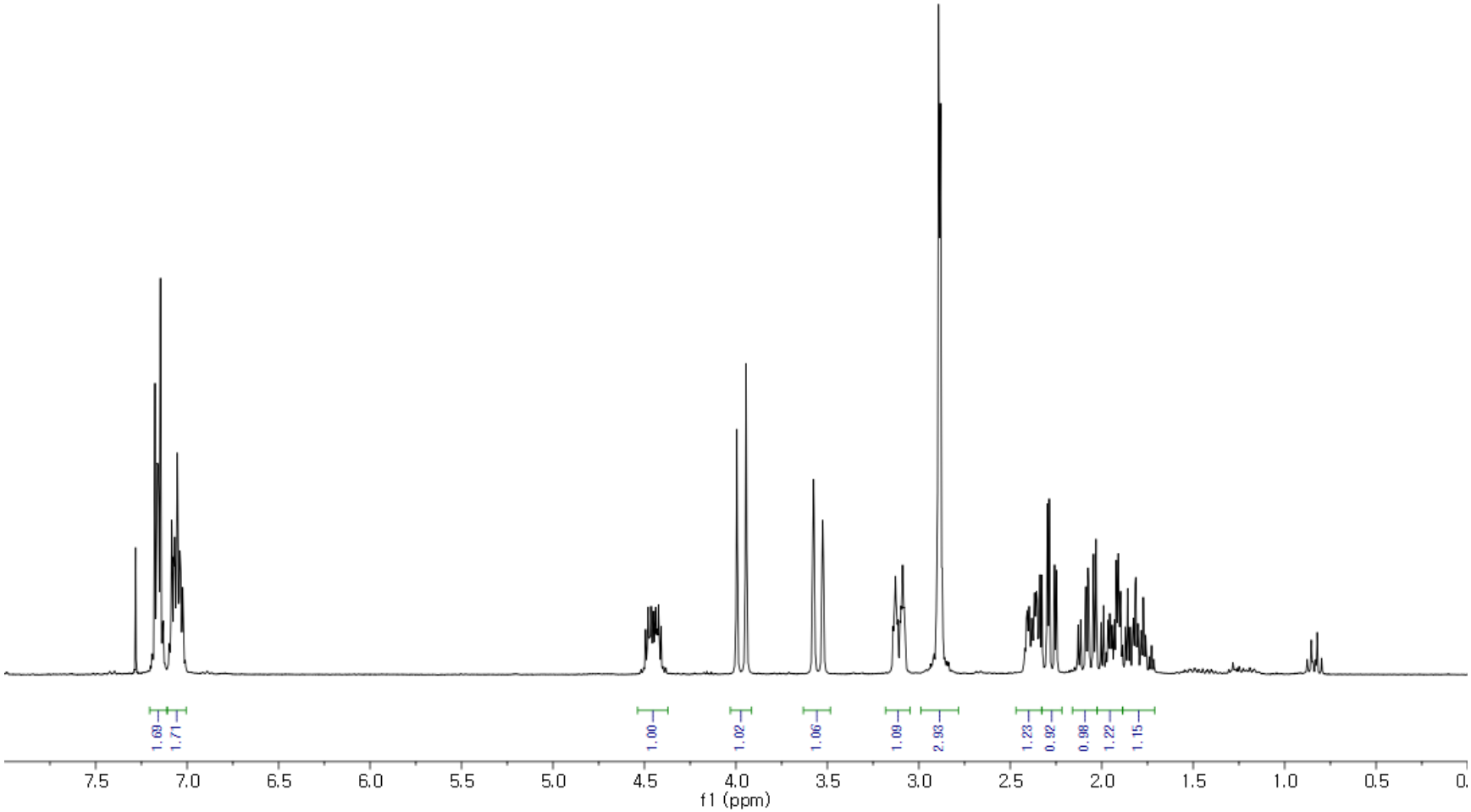
^{13}C NMR of **12** in $CDCl_3$



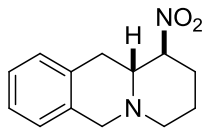


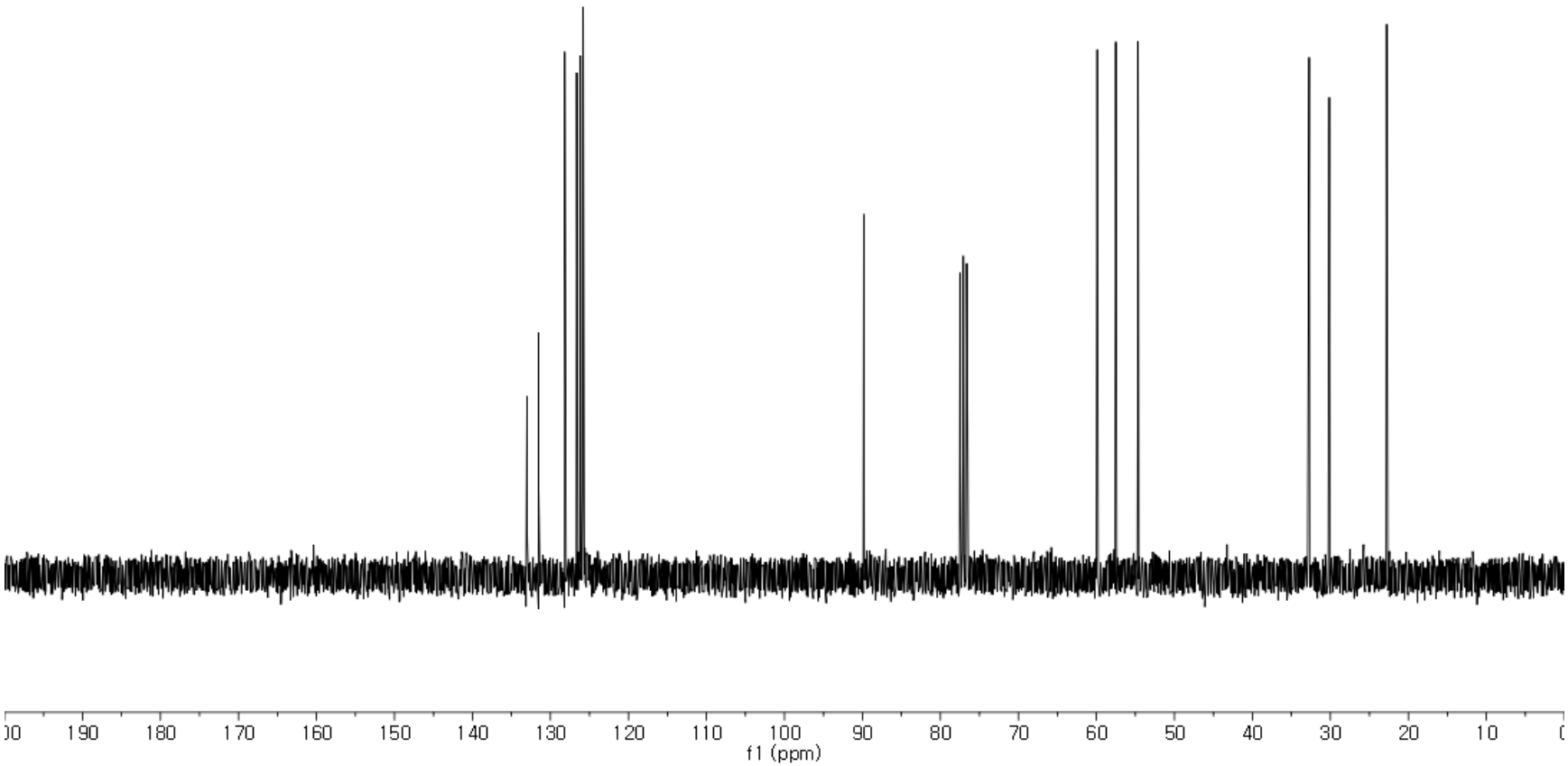
^{1}H NMR of **13** in $CDCl_3$



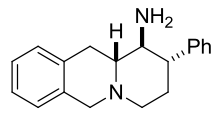


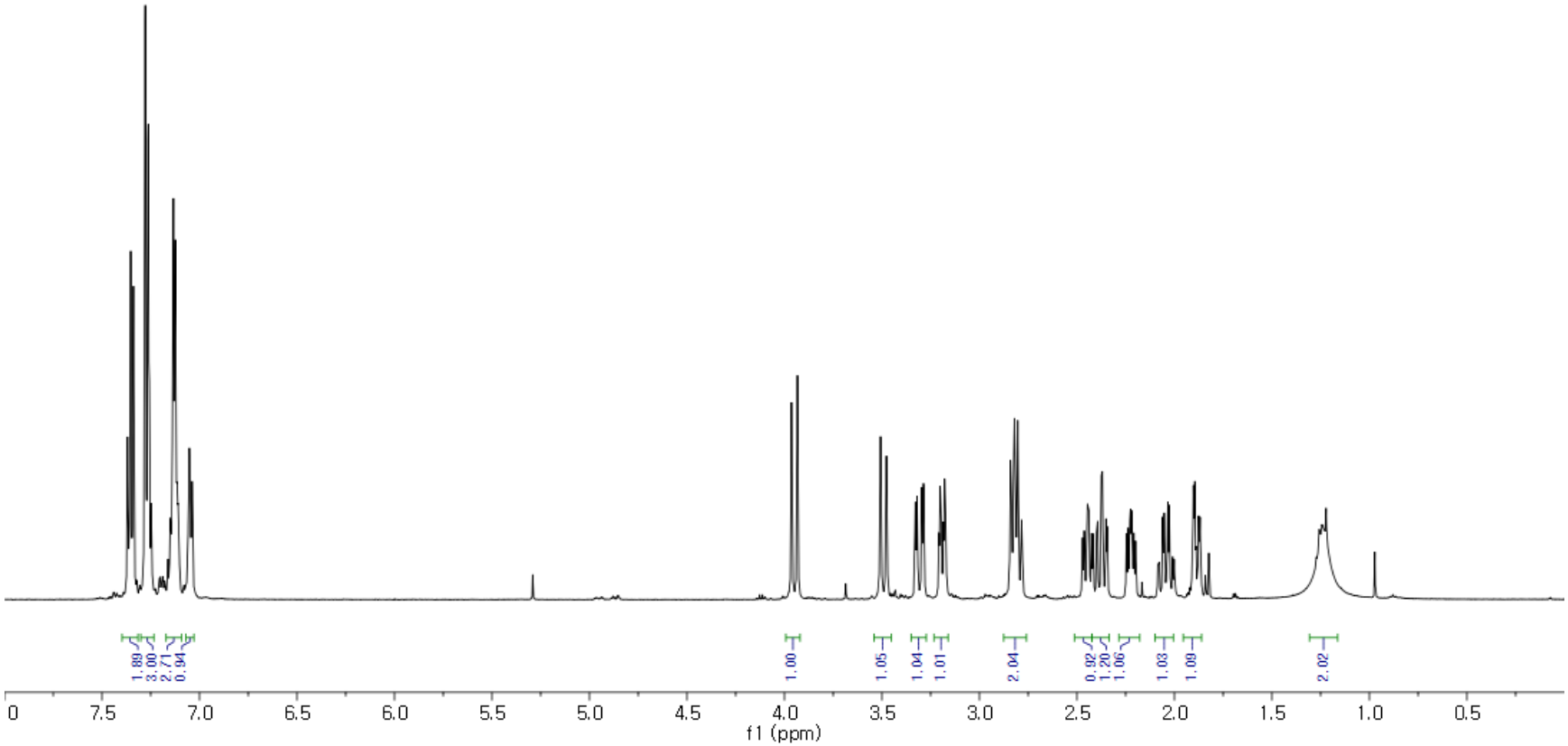
^{13}C NMR of **13** in $CDCl_3$



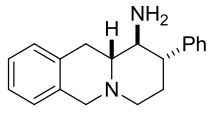


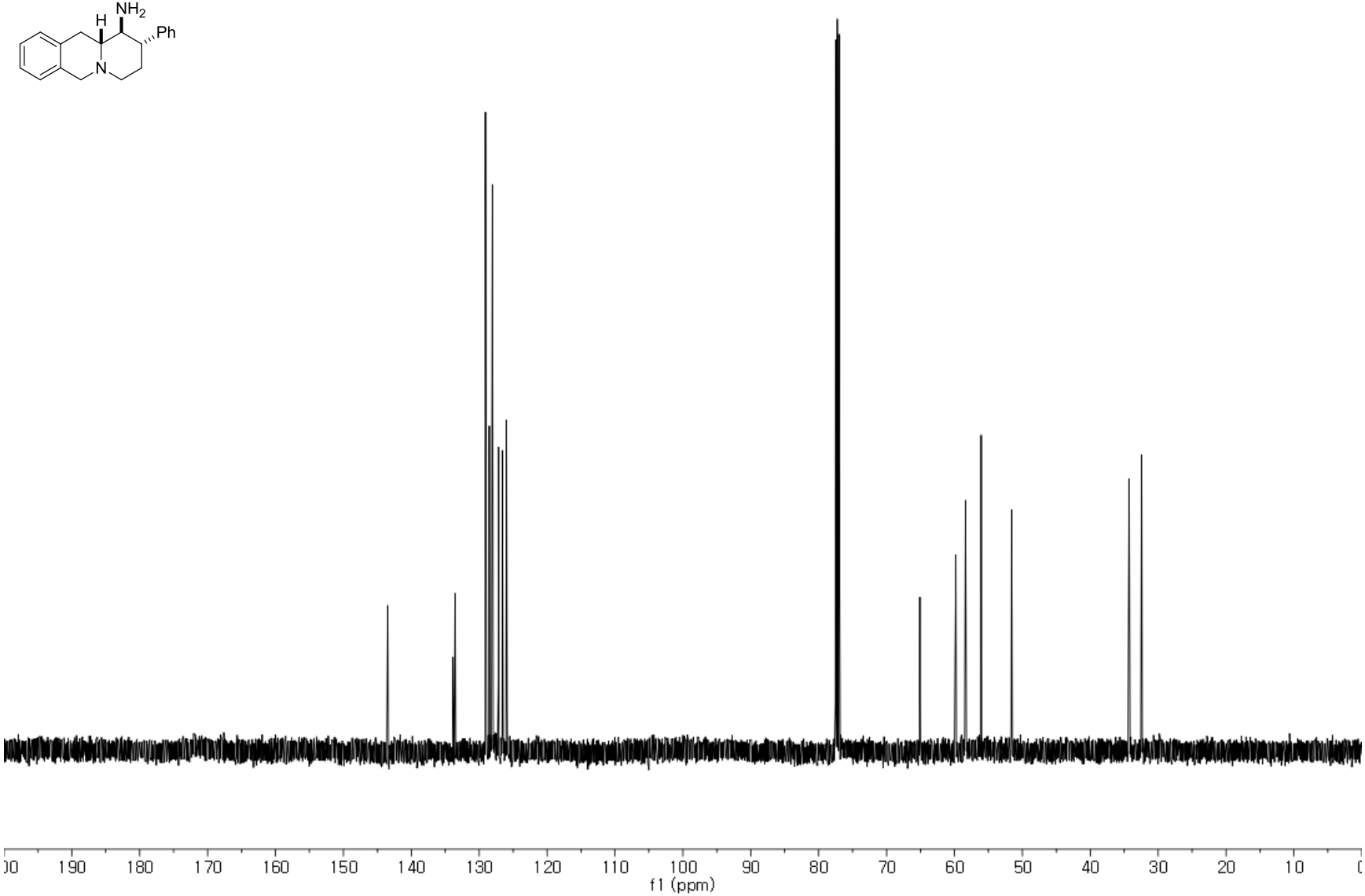
^{1}H NMR of **15** in $CDCl_3$



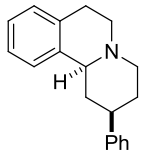


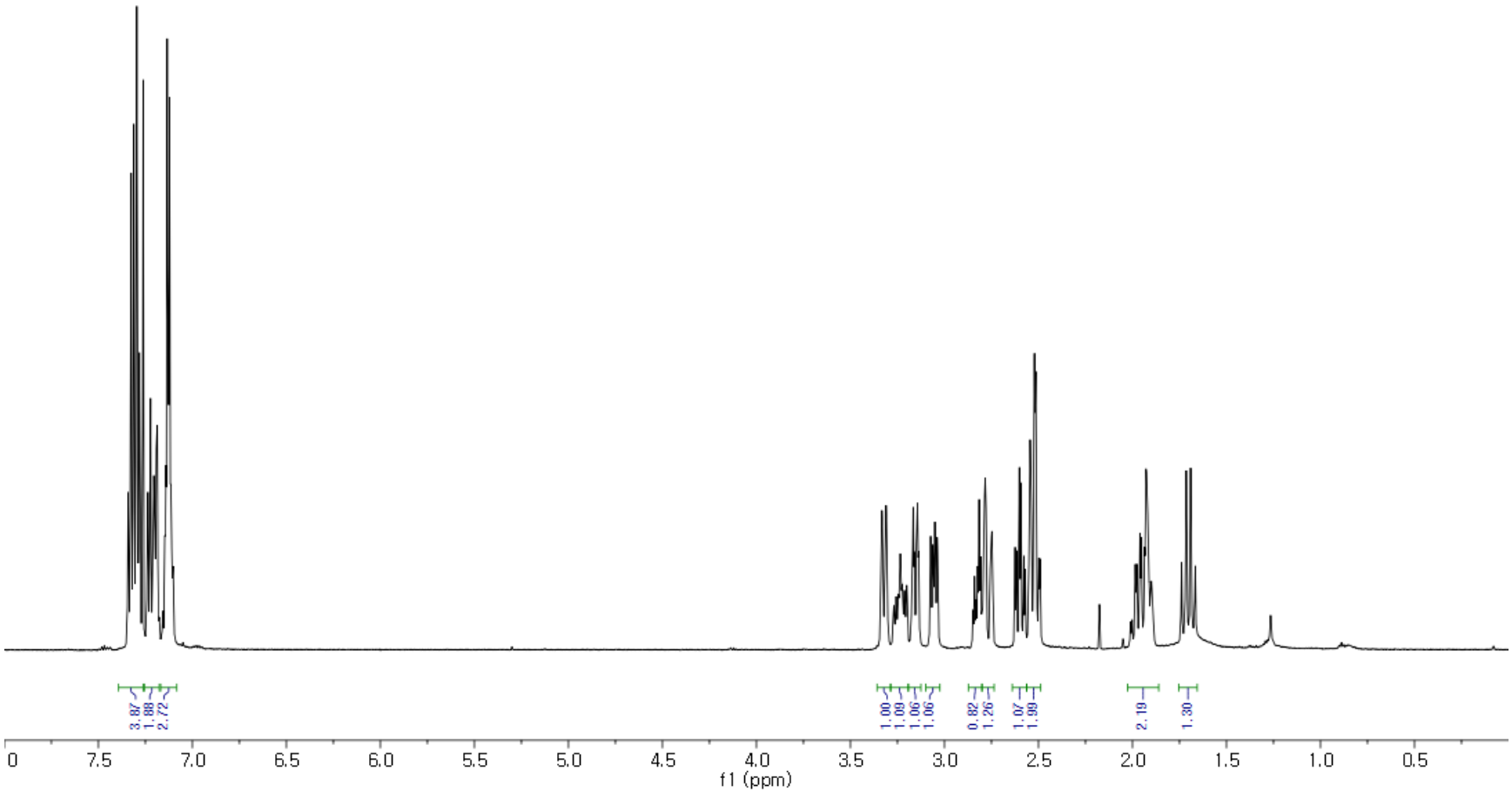
^{13}C NMR of **15** in $CDCl_3$



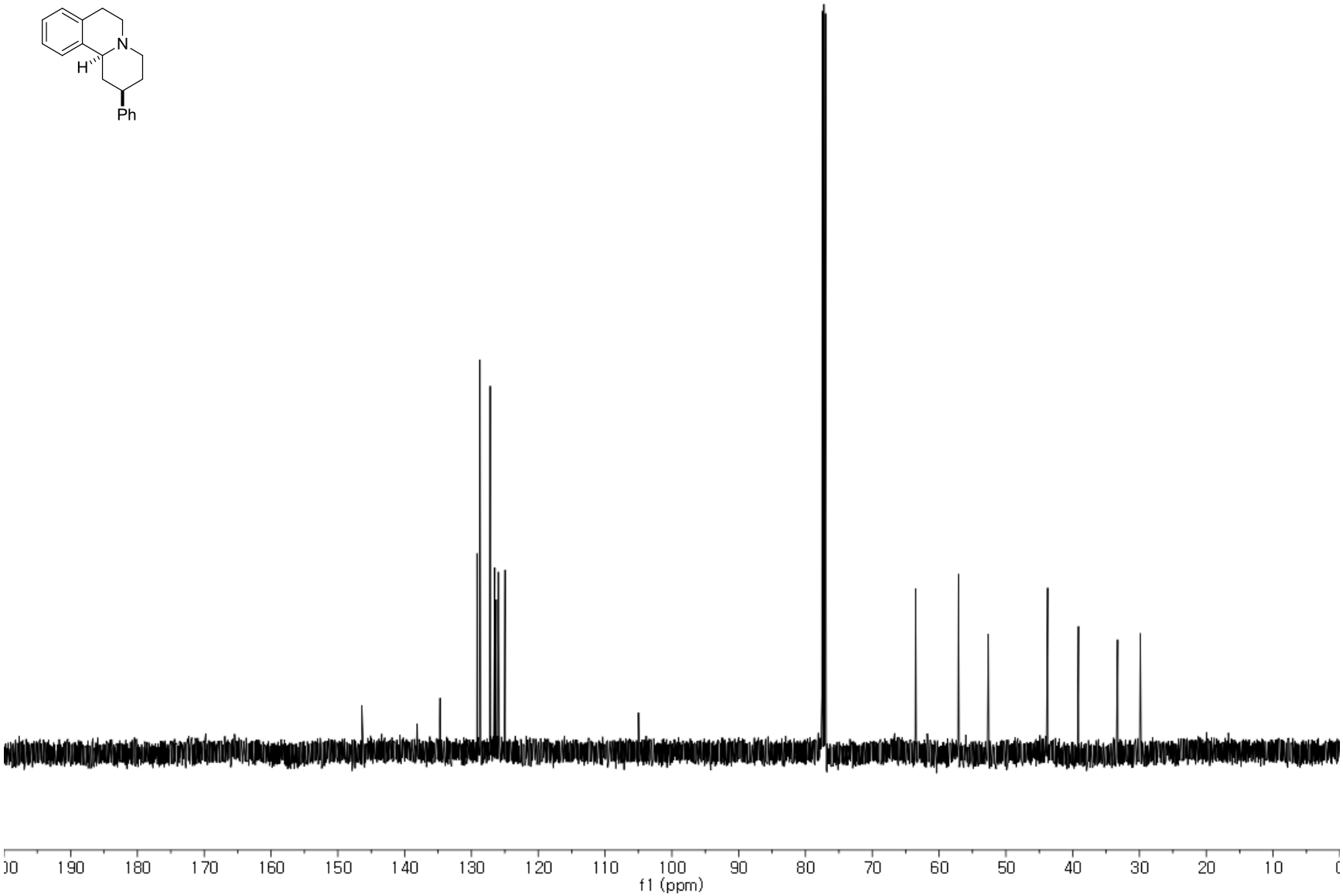


^{1}H NMR of **16** in $CDCl_3$

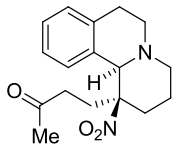


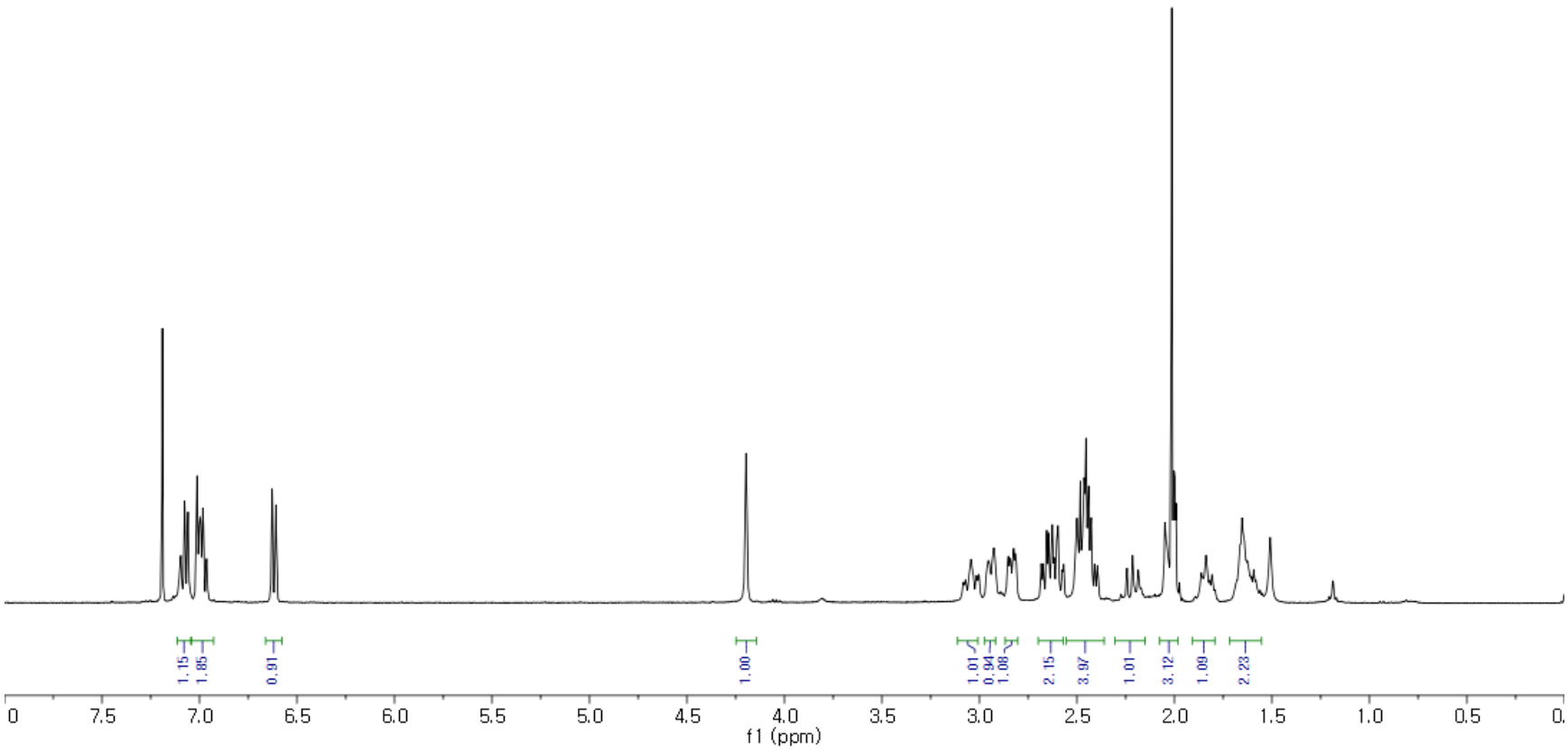


^{13}C NMR of **16** in $CDCl_3$

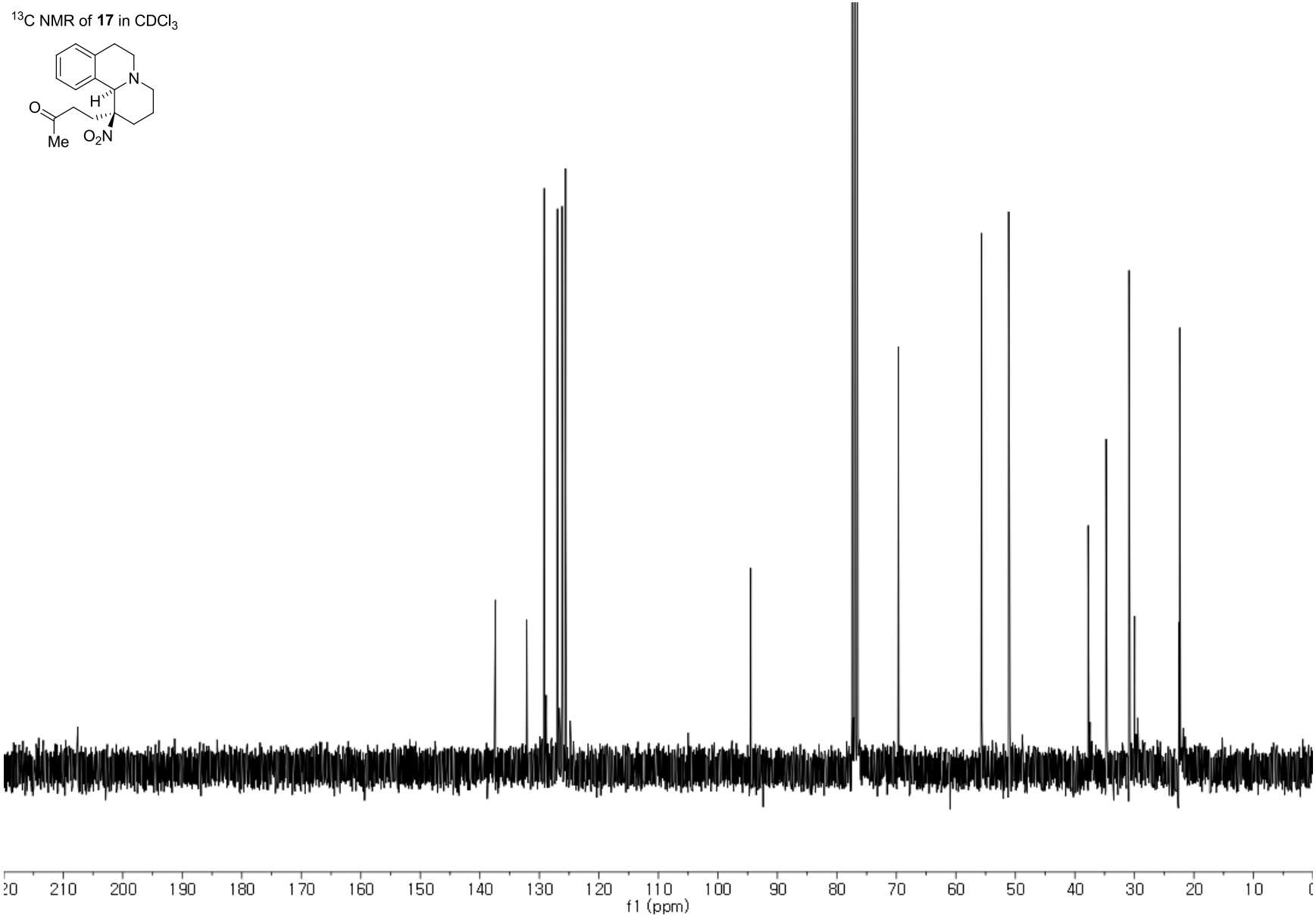


^{1}H NMR of **17** in $CDCl_3$

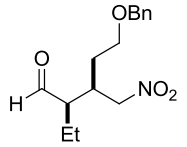


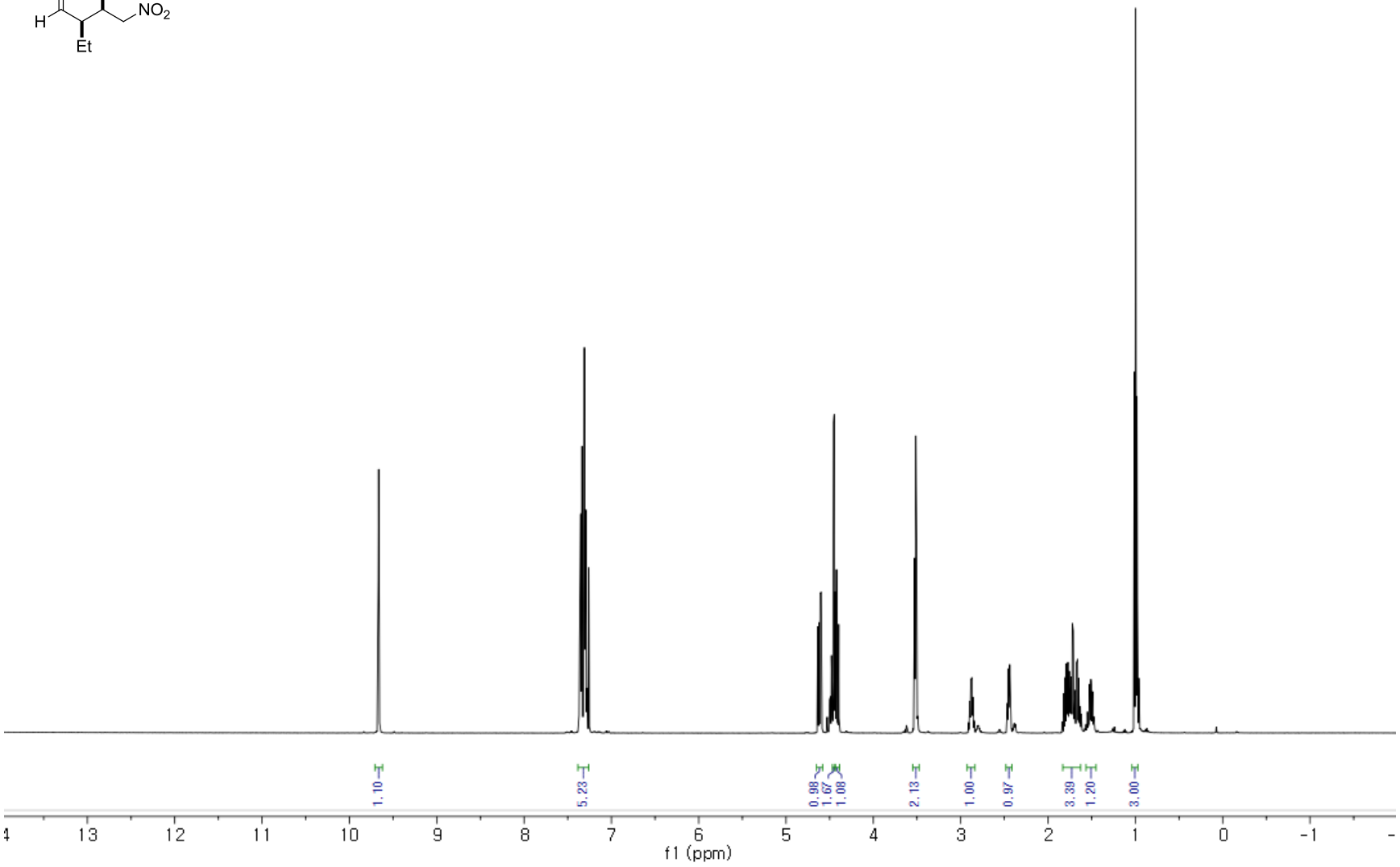


^{13}C NMR of **17** in $CDCl_3$

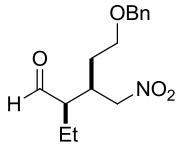


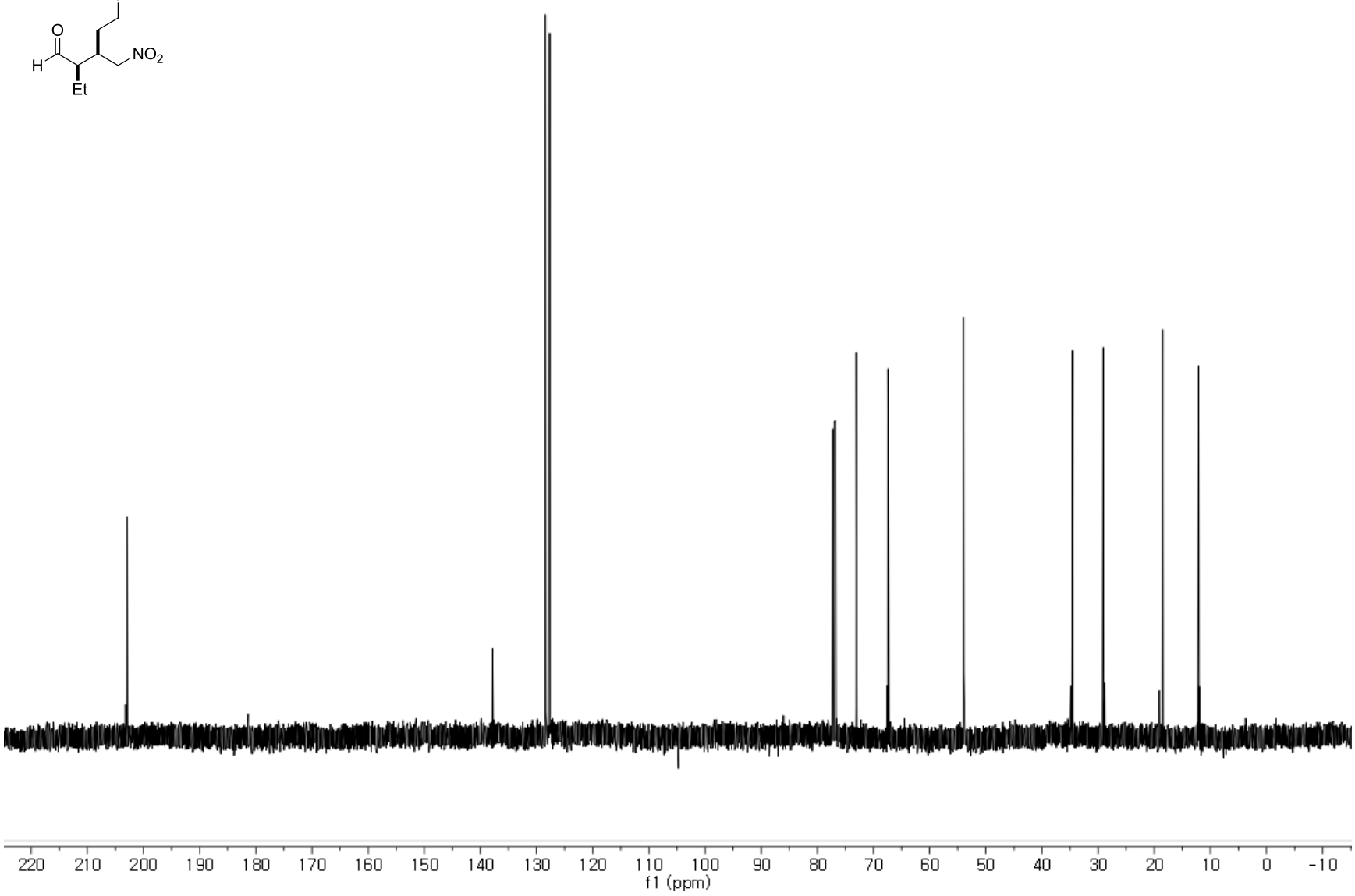
^{1}H NMR of **18** in $CDCl_3$



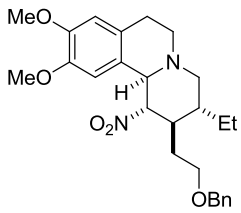


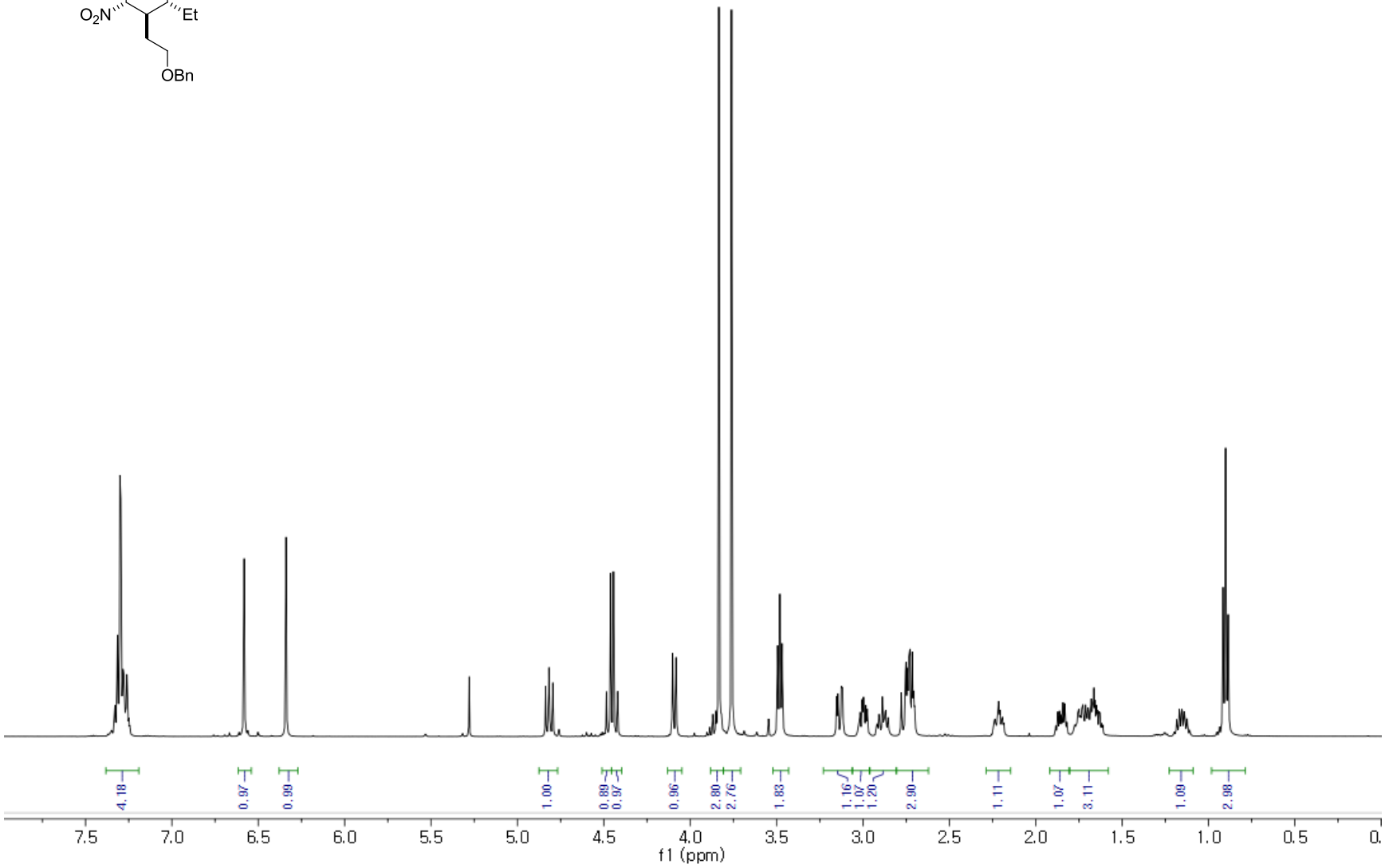
^{13}C NMR of **18** in $CDCl_3$



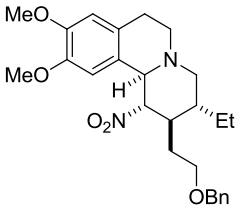


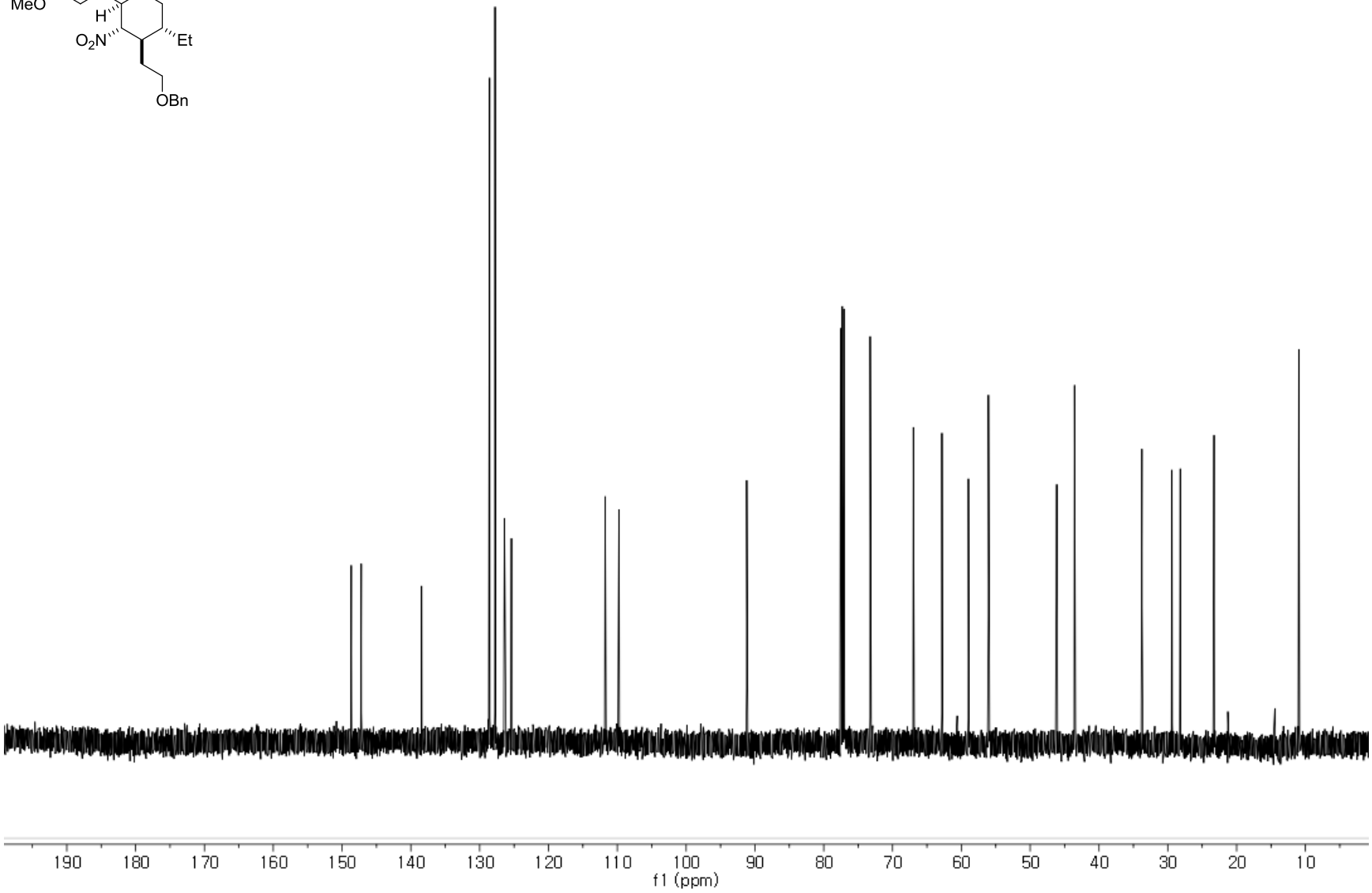
^{1}H NMR of **19** in $CDCl_3$



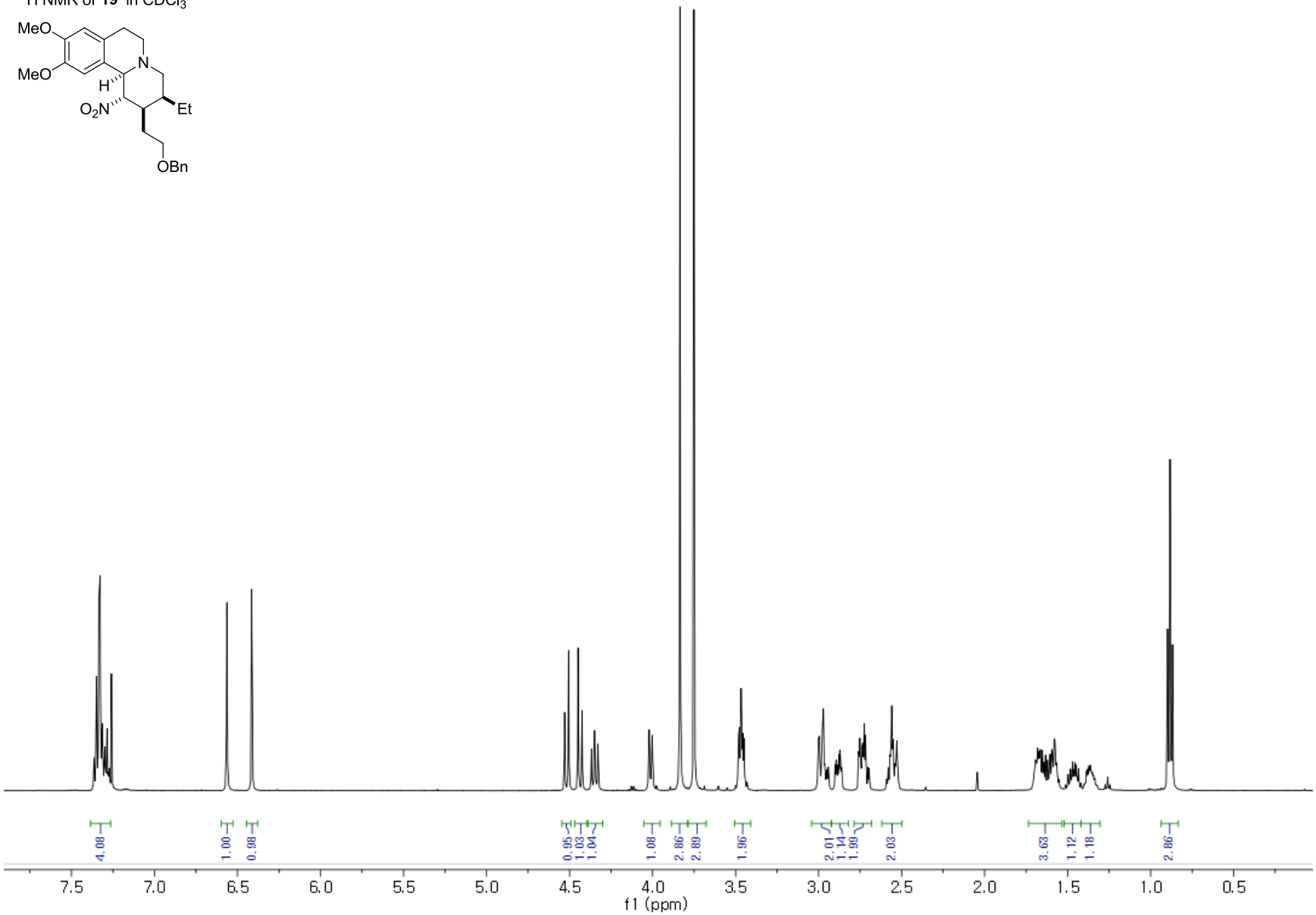


^{13}C NMR of **19** in $CDCl_3$

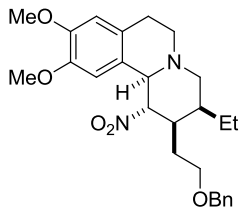


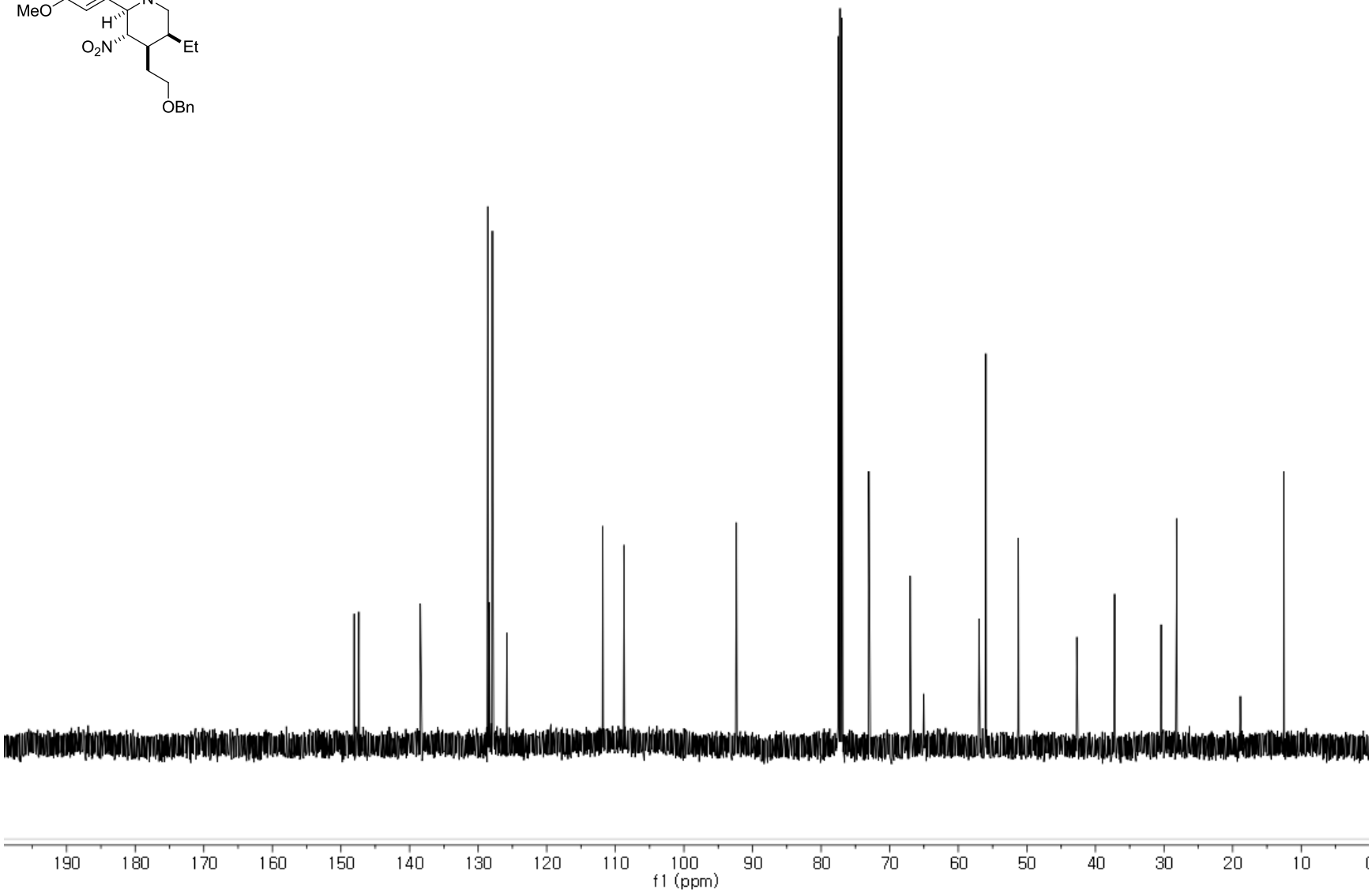


^{1}H NMR of **19'** in $CDCl_3$

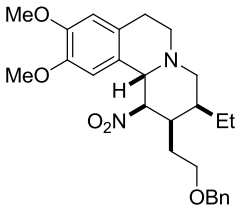


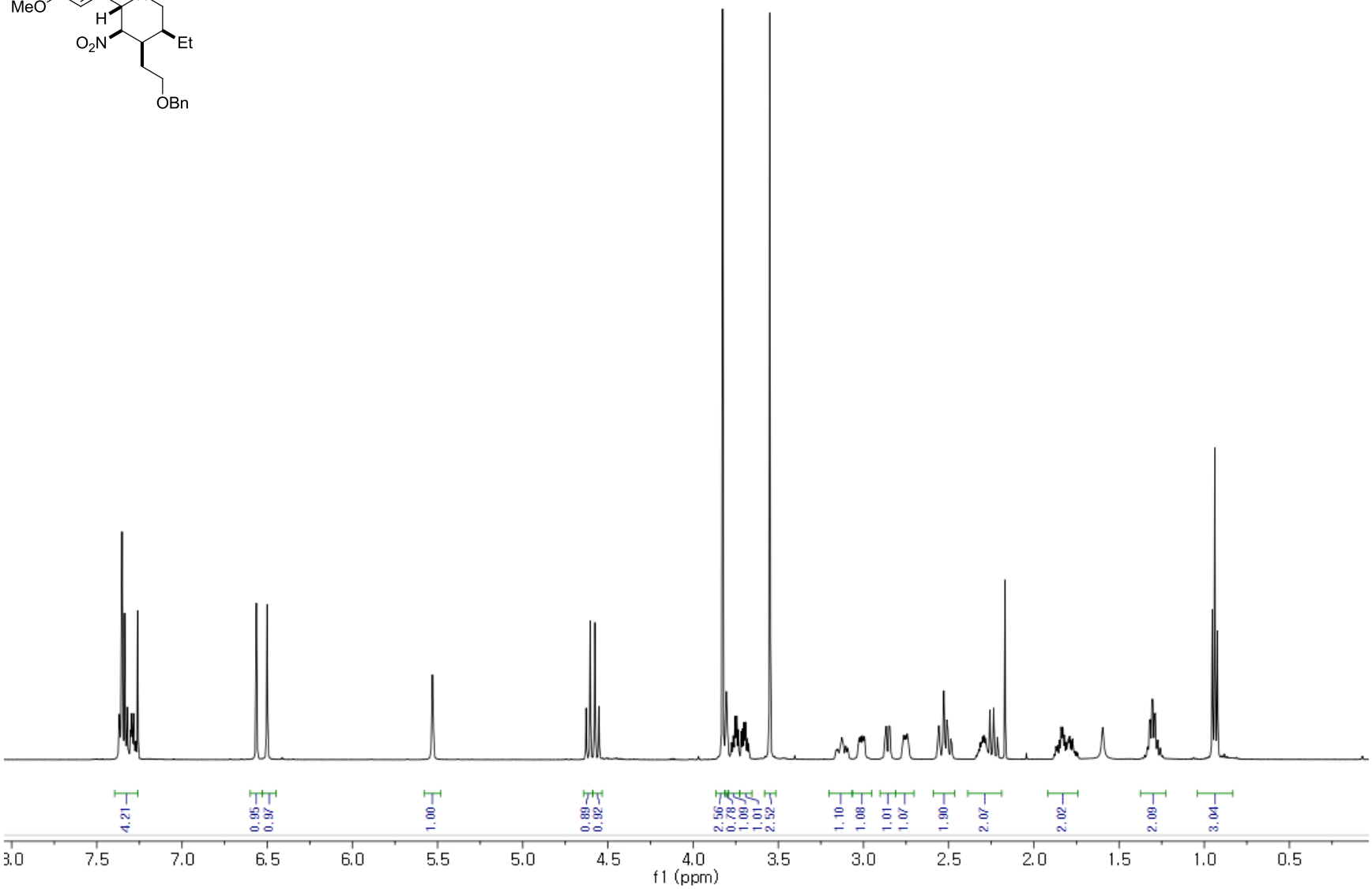
^{13}C NMR of **19'** in $CDCl_3$



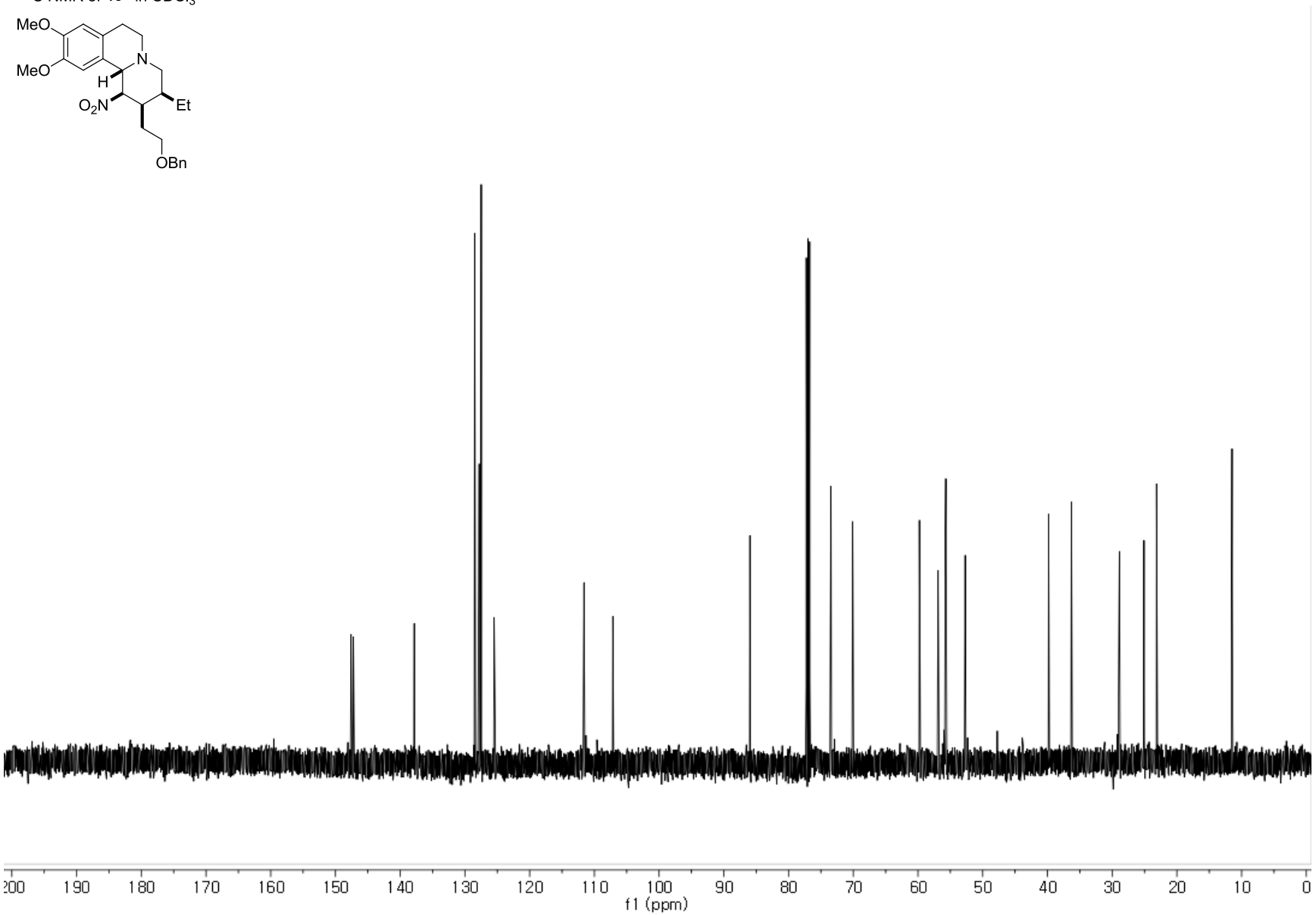


^{1}H NMR of **19"** in $CDCl_3$

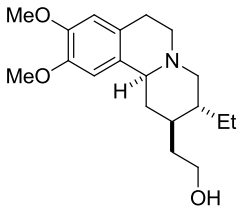


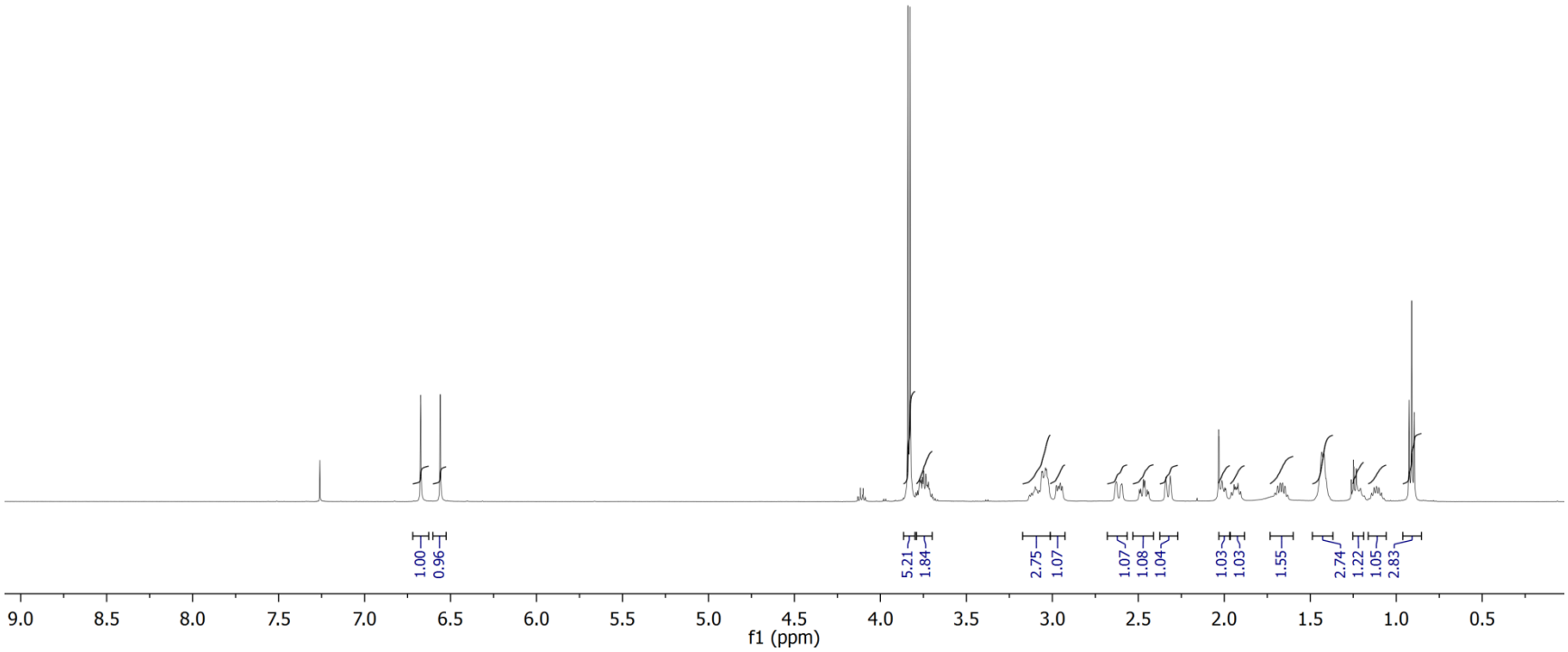


^{13}C NMR of **19"** in $CDCl_3$

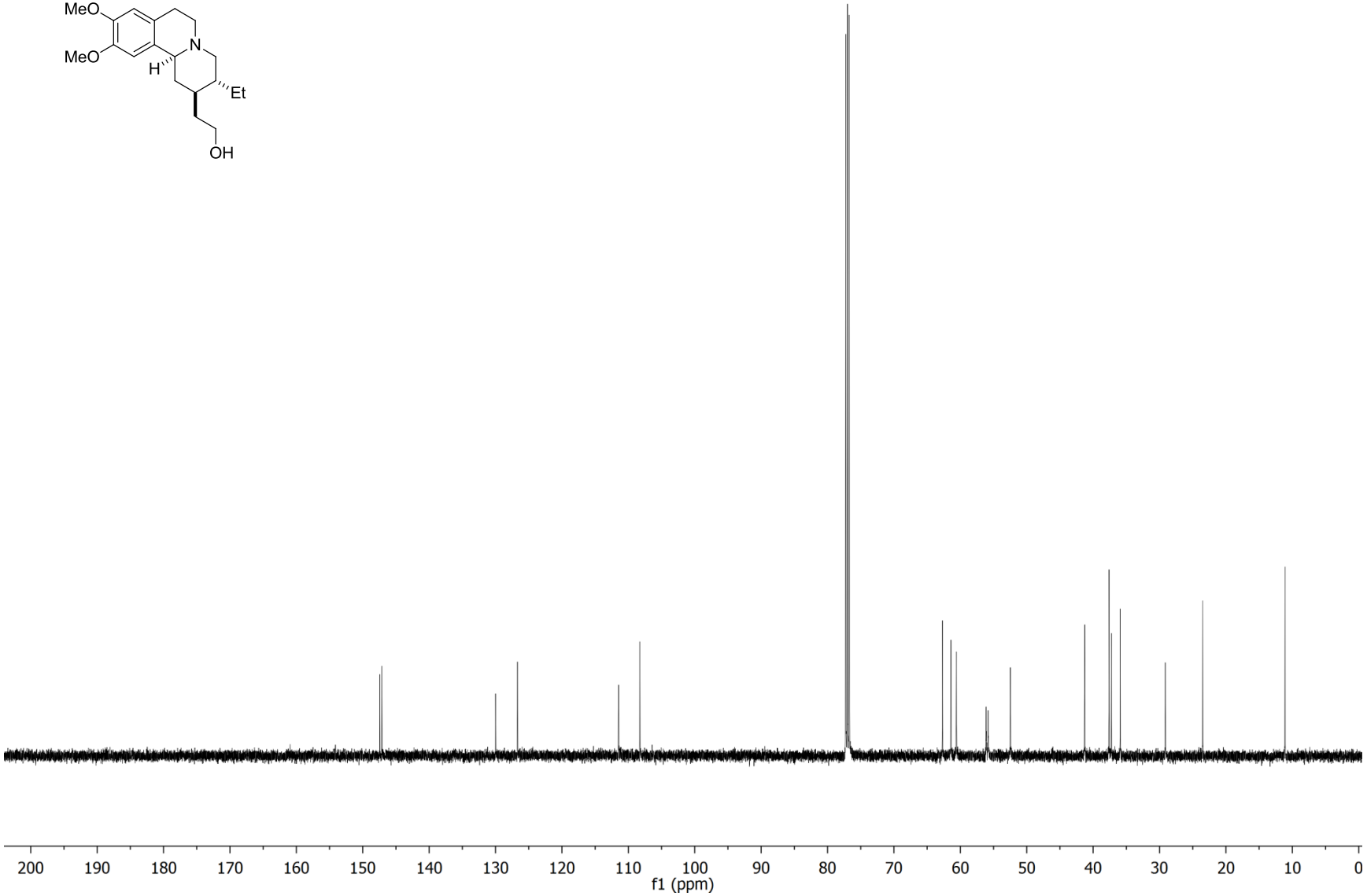


^{1}H NMR of (-)-protoemetinol in $CDCl_3$

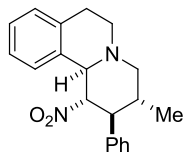


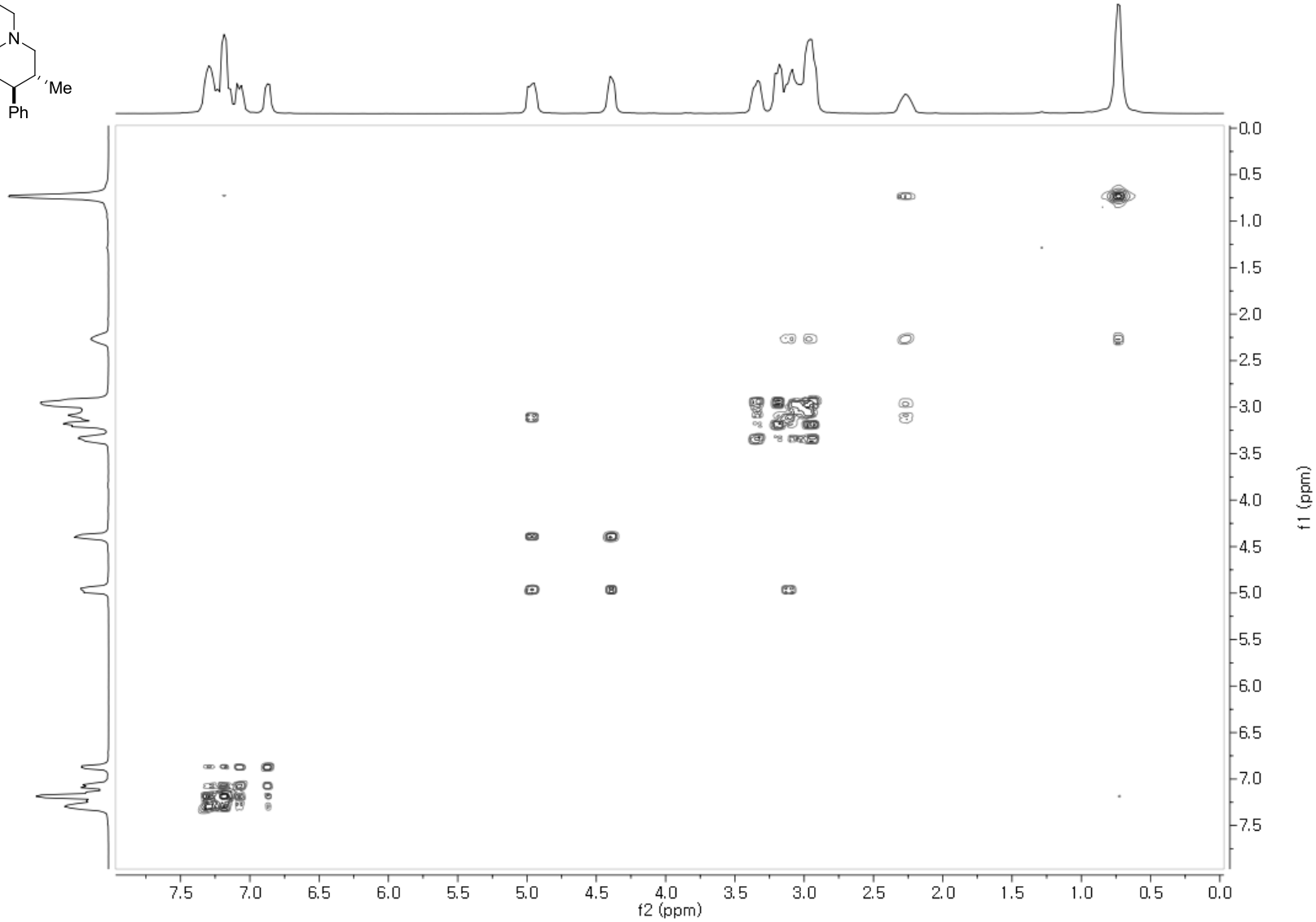


^{13}C NMR of (-)-protoemetinol in $CDCl_3$

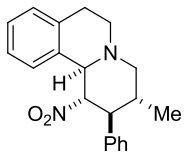


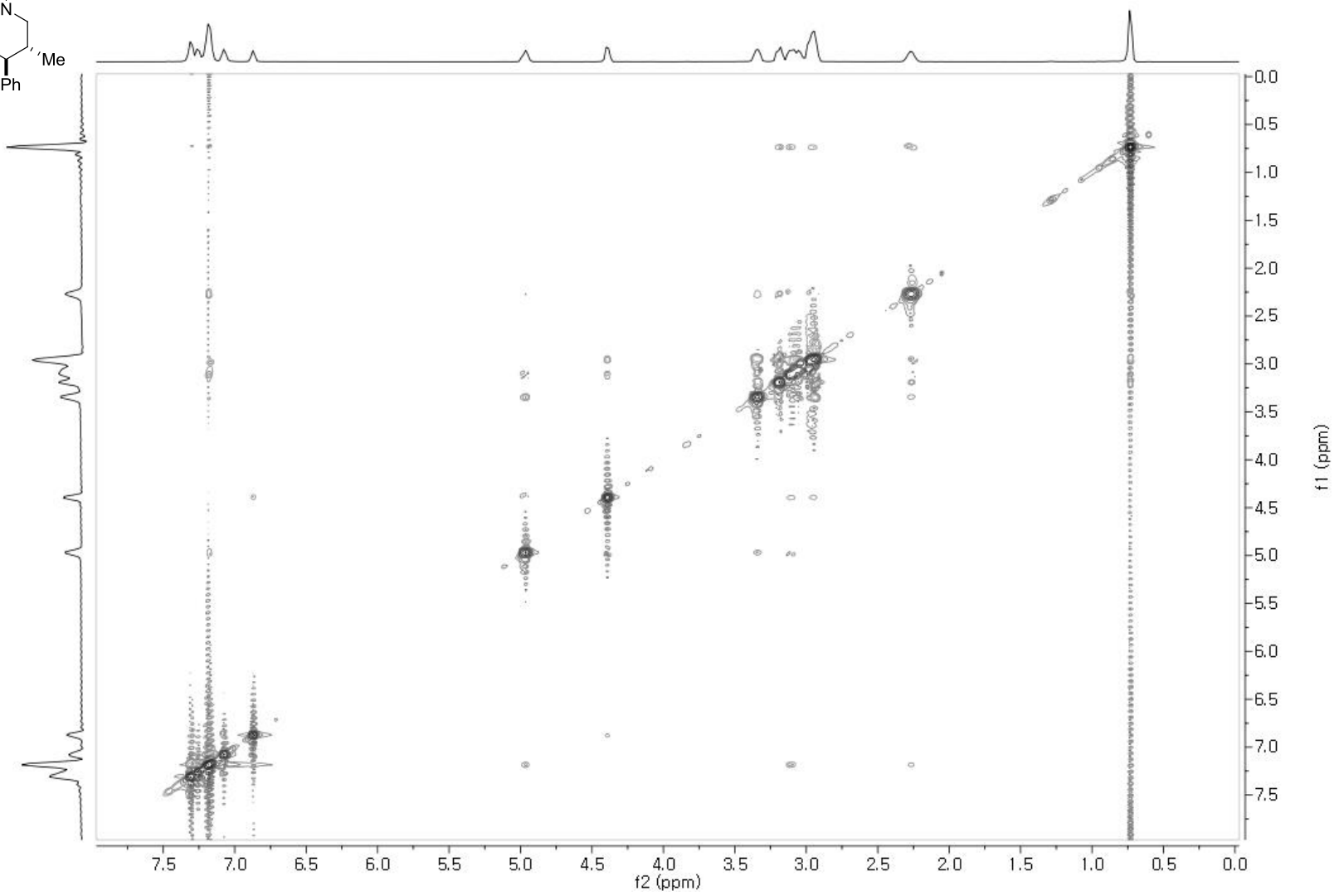
Gcosy of **6a** in $CDCl_3$



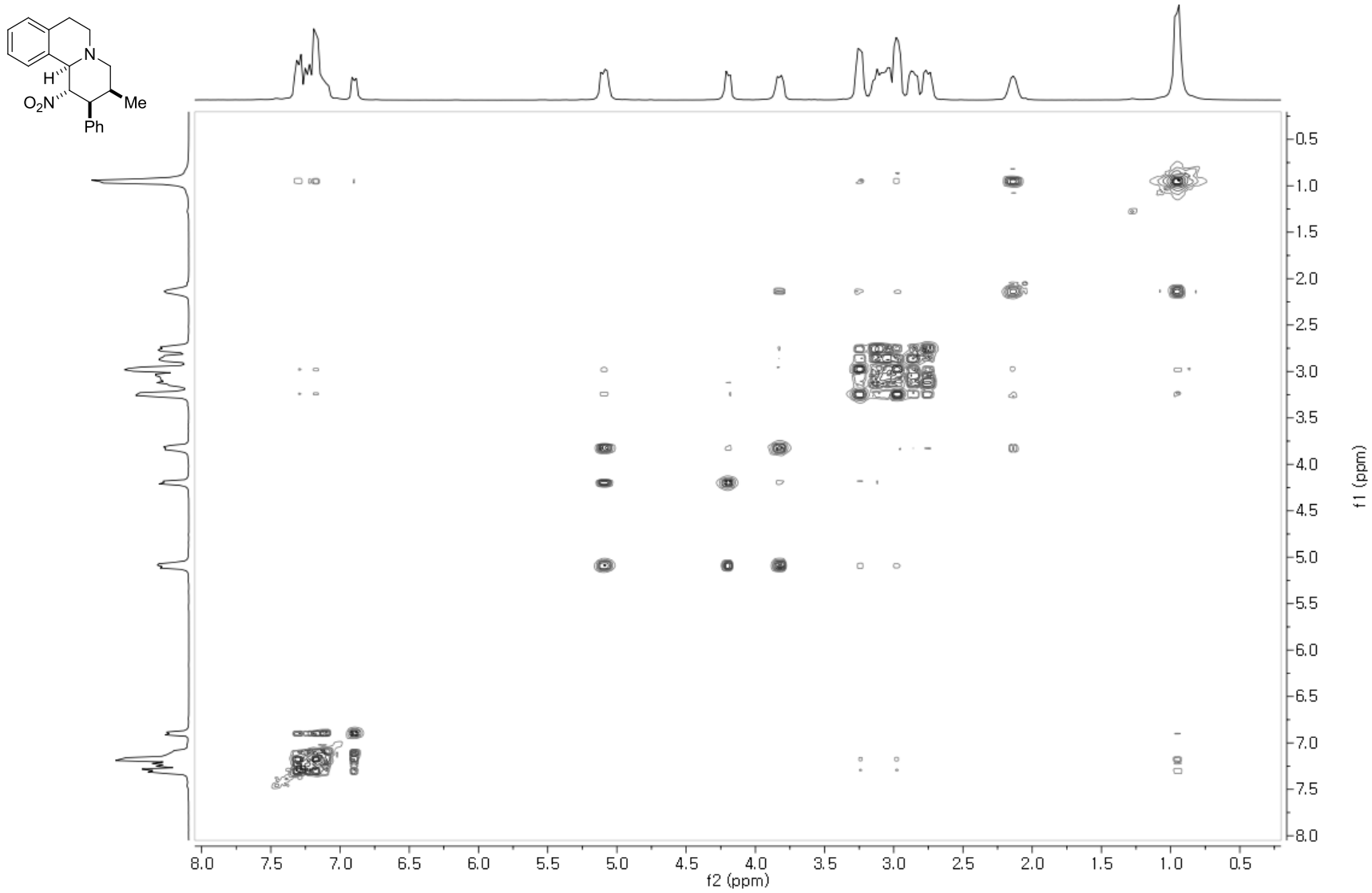


Noesy of **6a** in $CDCl_3$

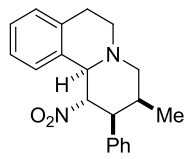


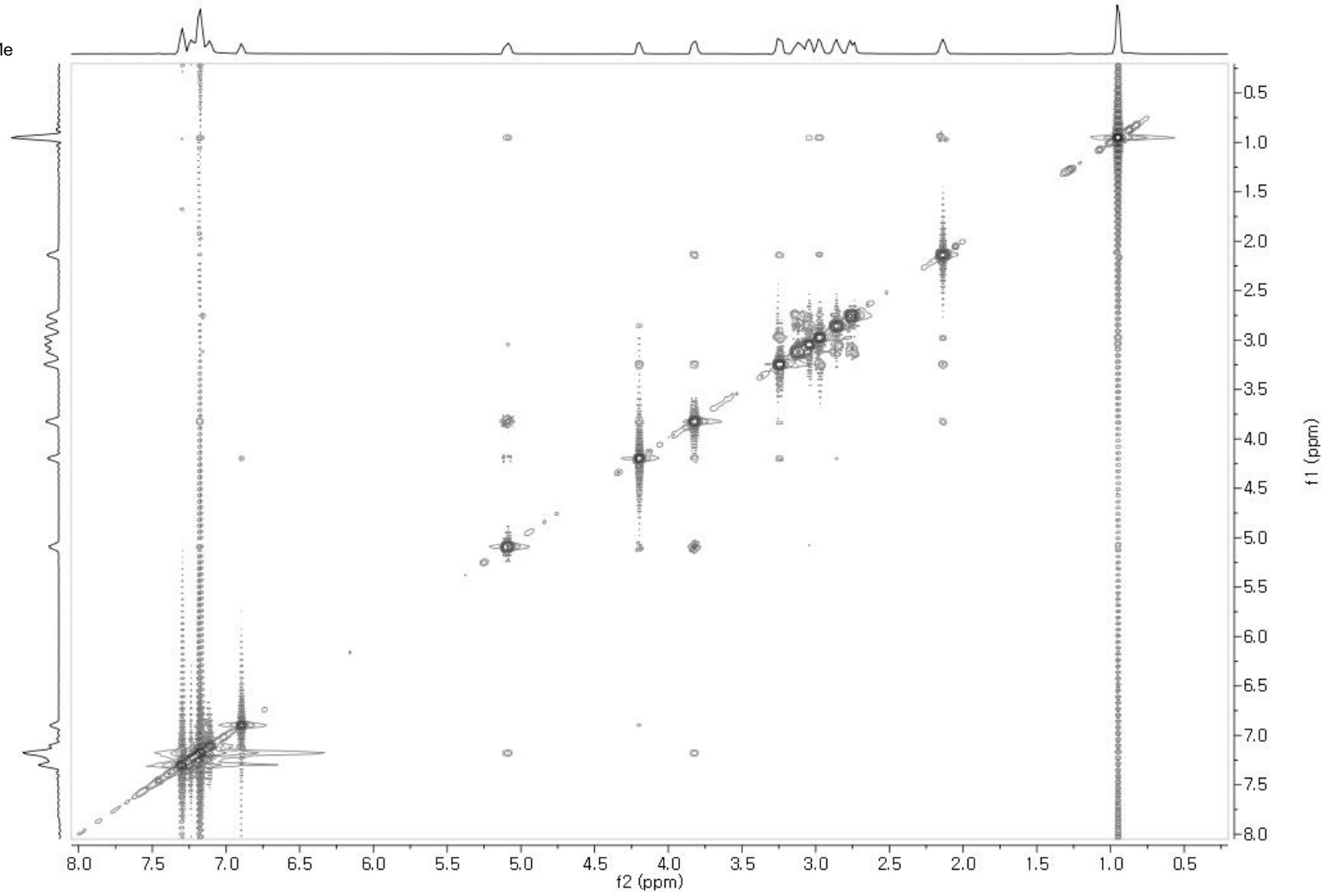


Gcosy of 7**a** in $CDCl_3$

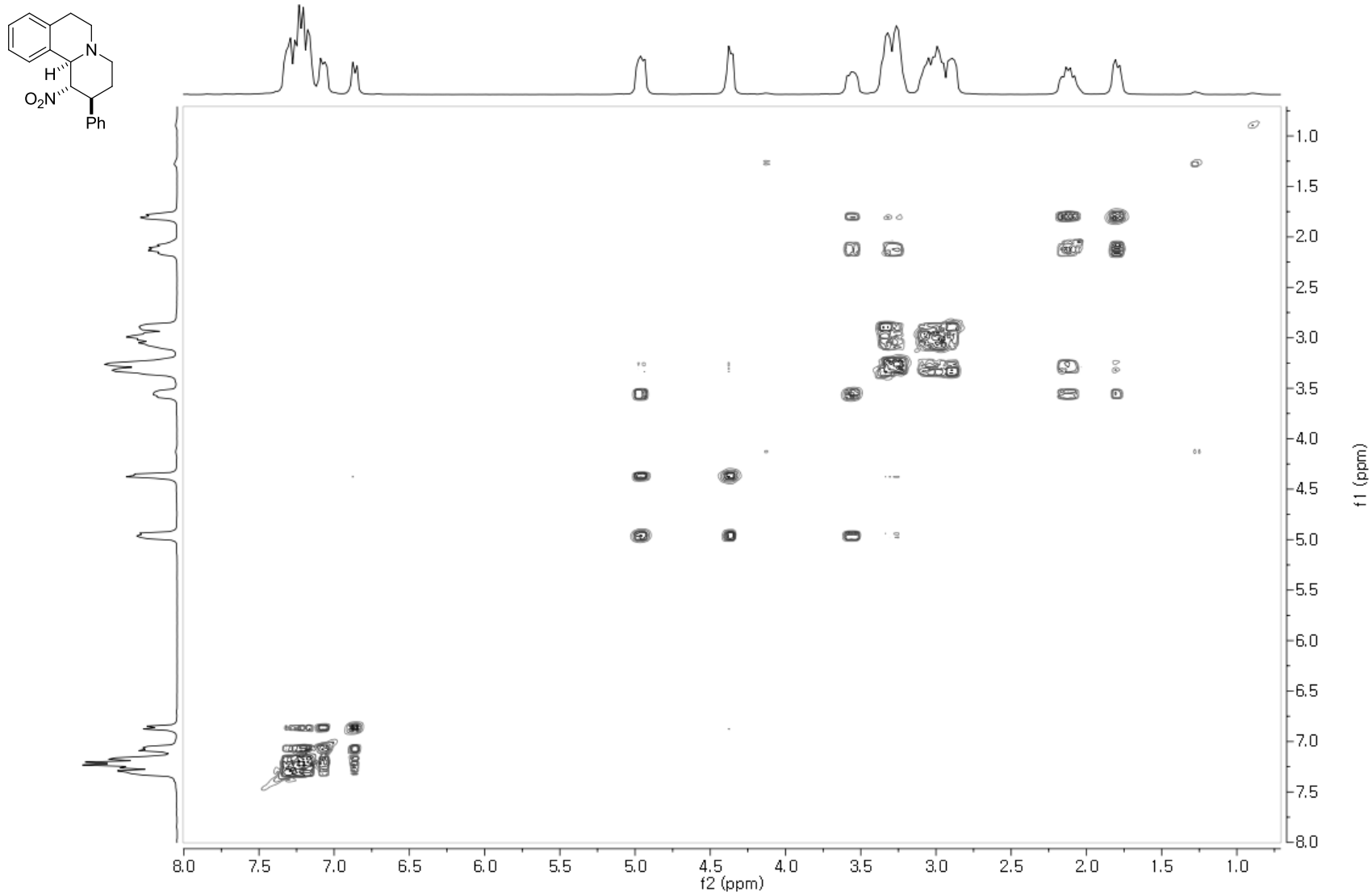


Noesy of 7**a** in $CDCl_3$

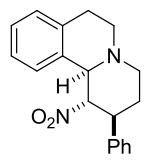


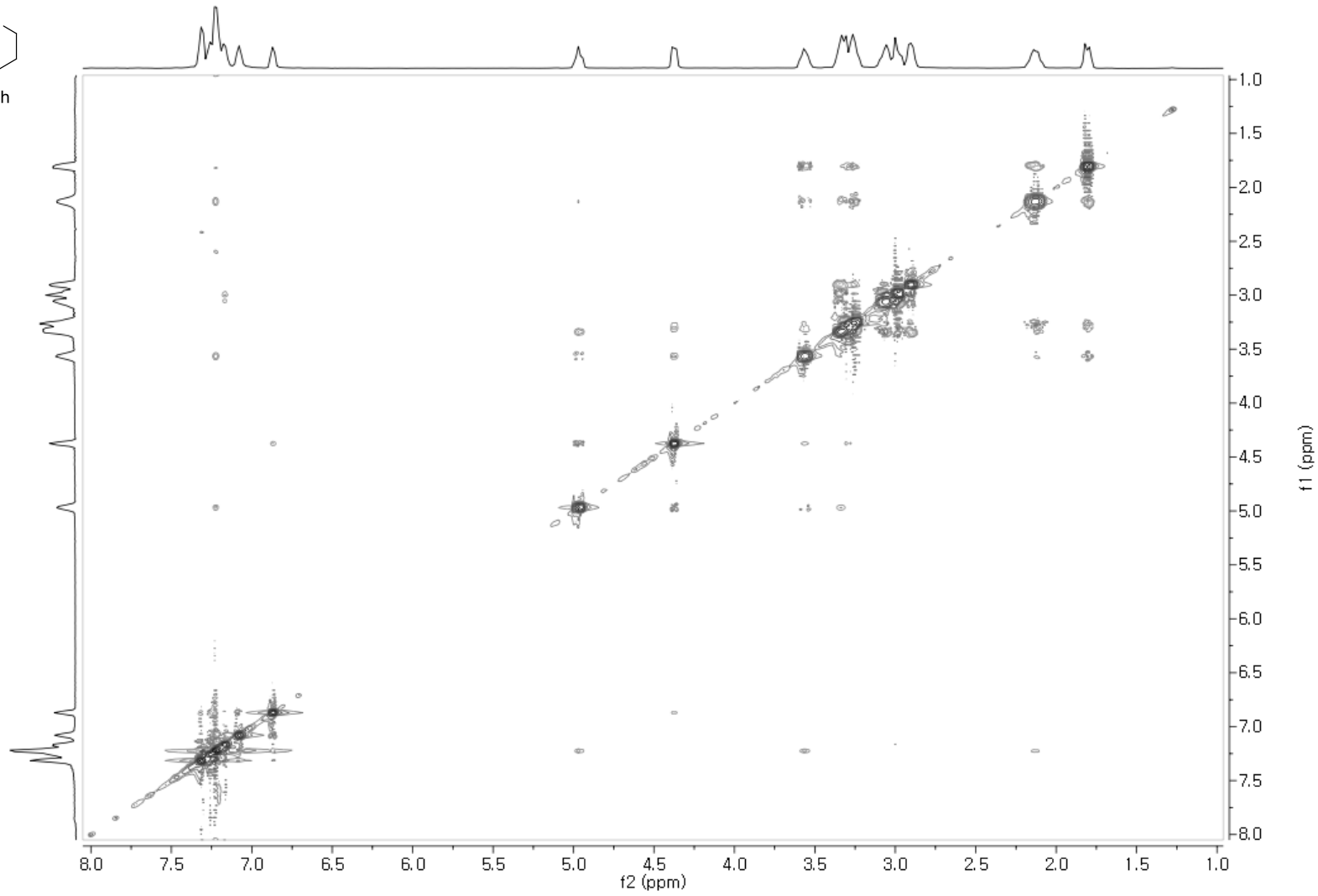


Gcosy of **6k** in $CDCl_3$

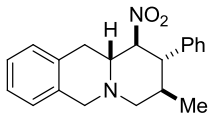


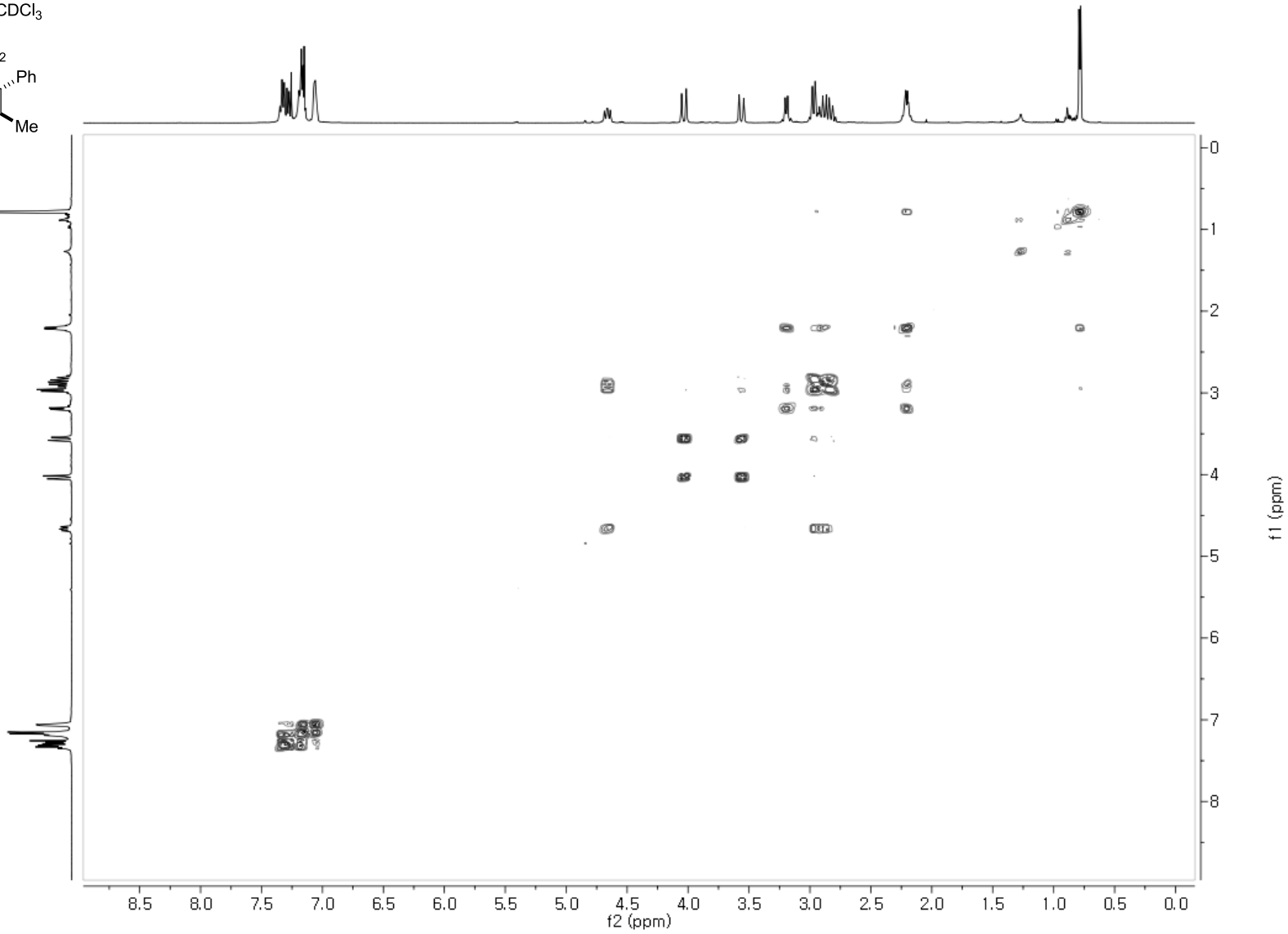
Noesy of **6k** in $CDCl_3$



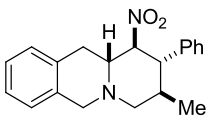


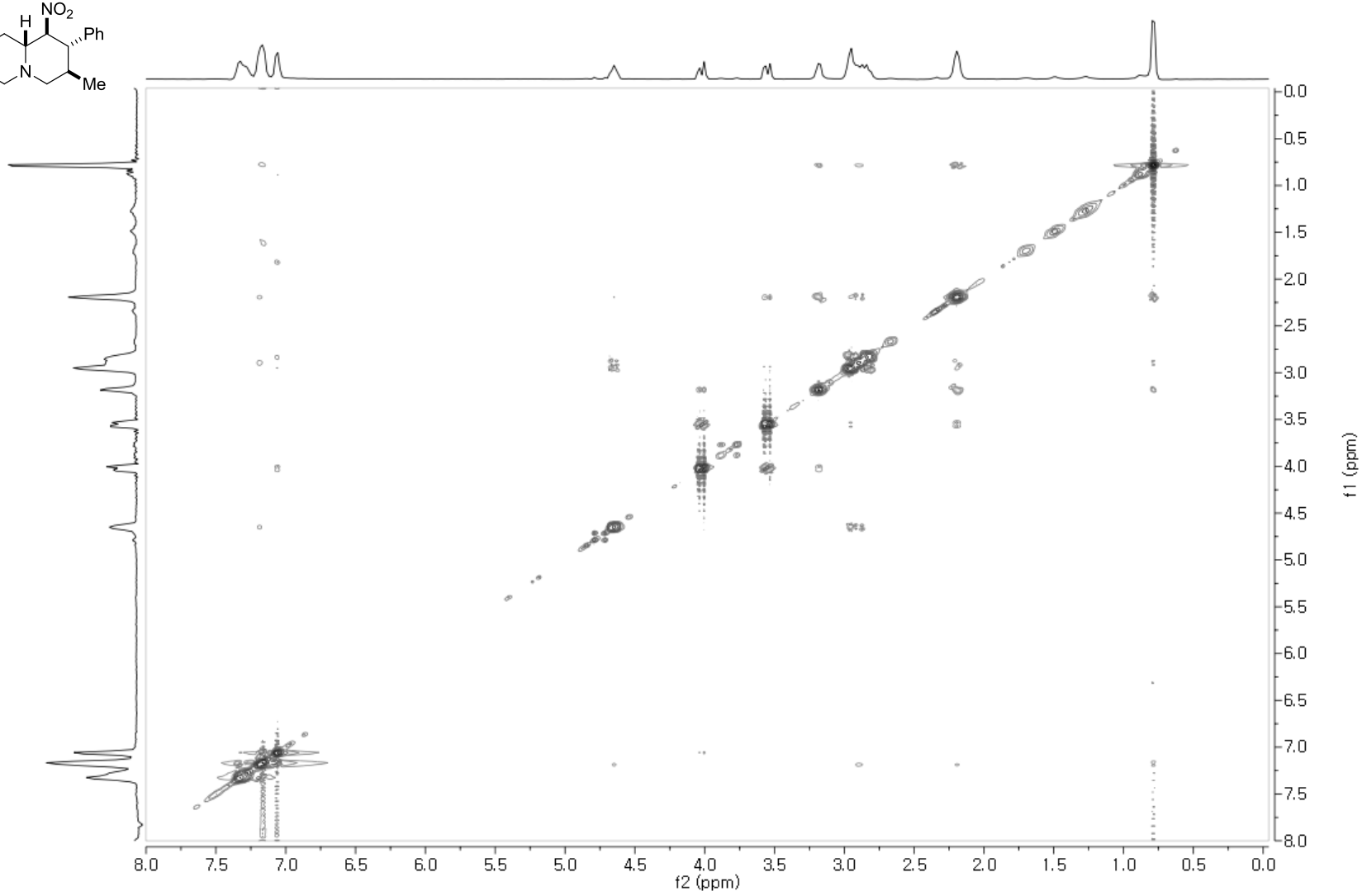
Gcosy of **8a** in $CDCl_3$



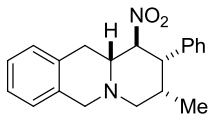


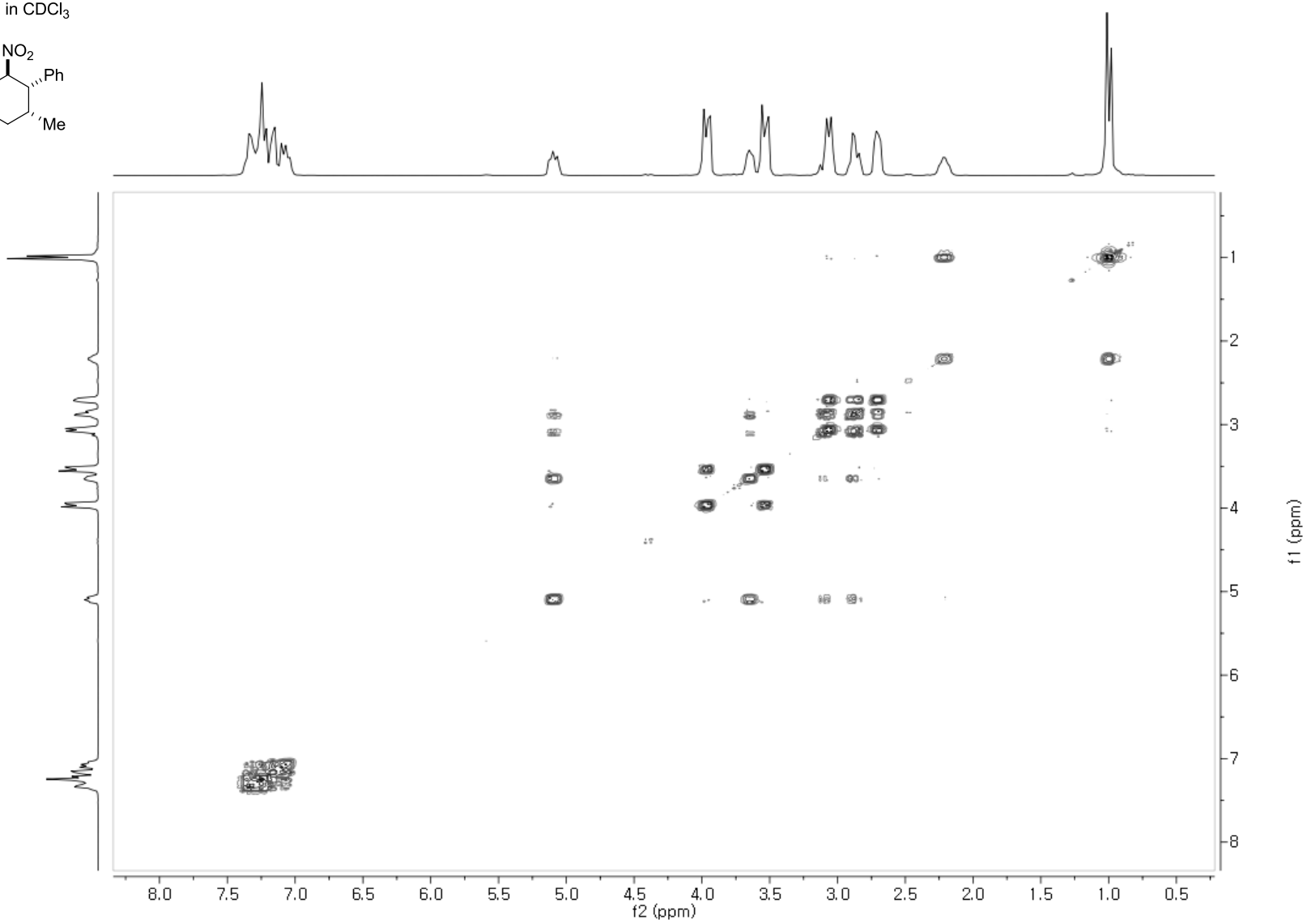
Noesy of **8a** in $CDCl_3$



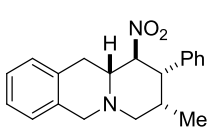


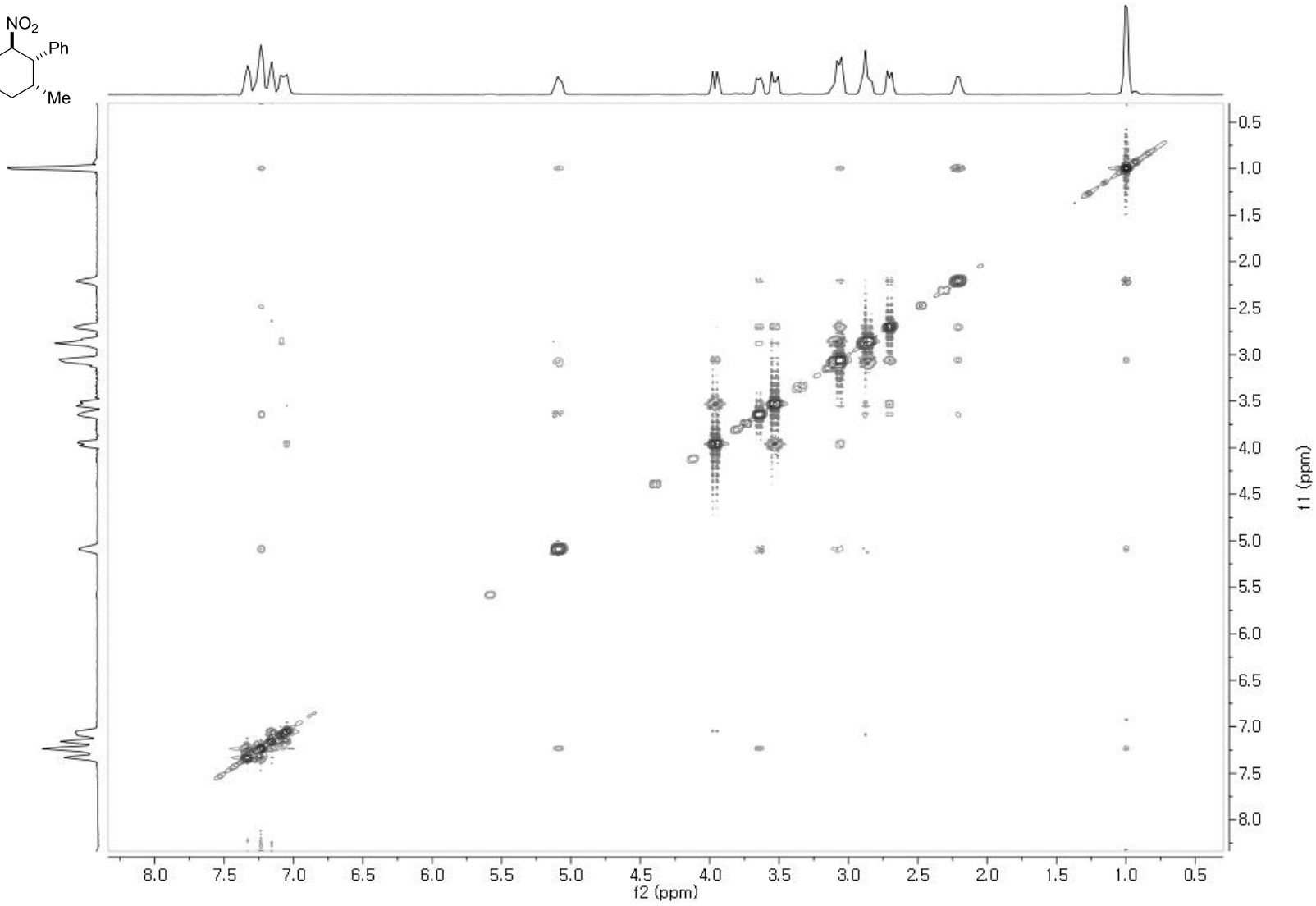
Gcosy of **9a** in $CDCl_3$



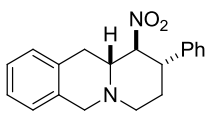


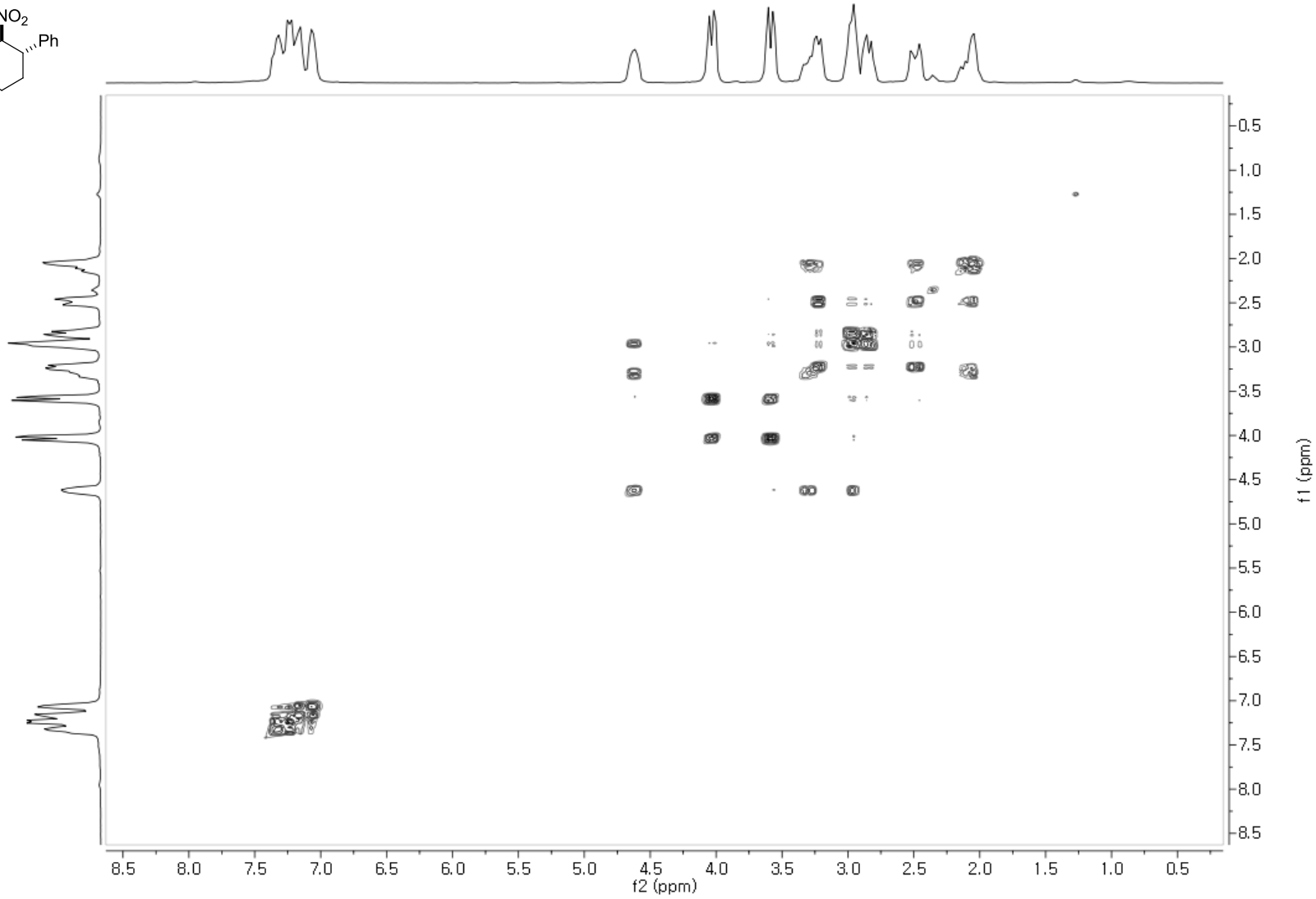
Noesy of **9a** in $CDCl_3$



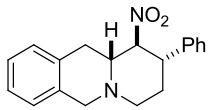


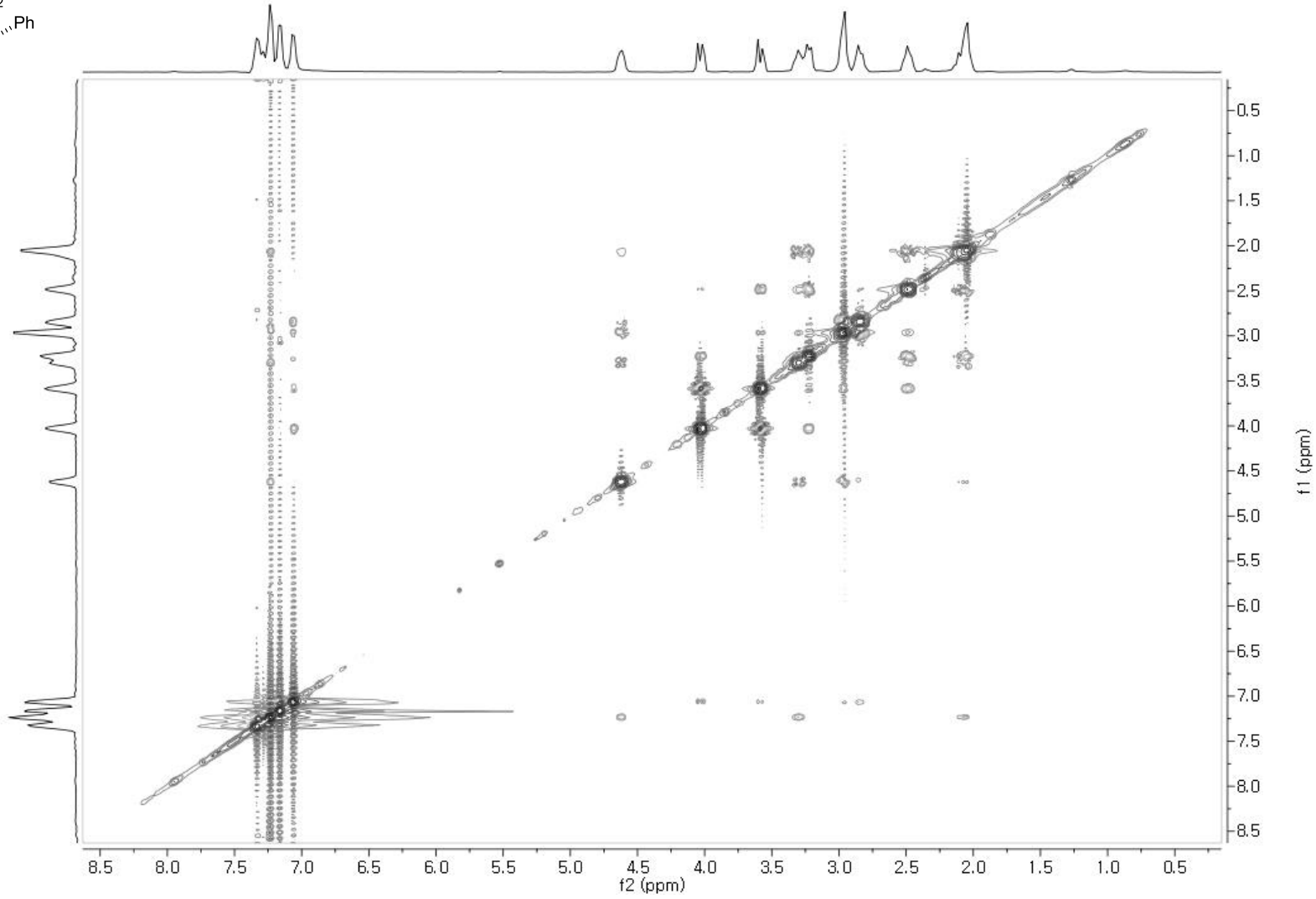
Gcosy of **8k** in $CDCl_3$



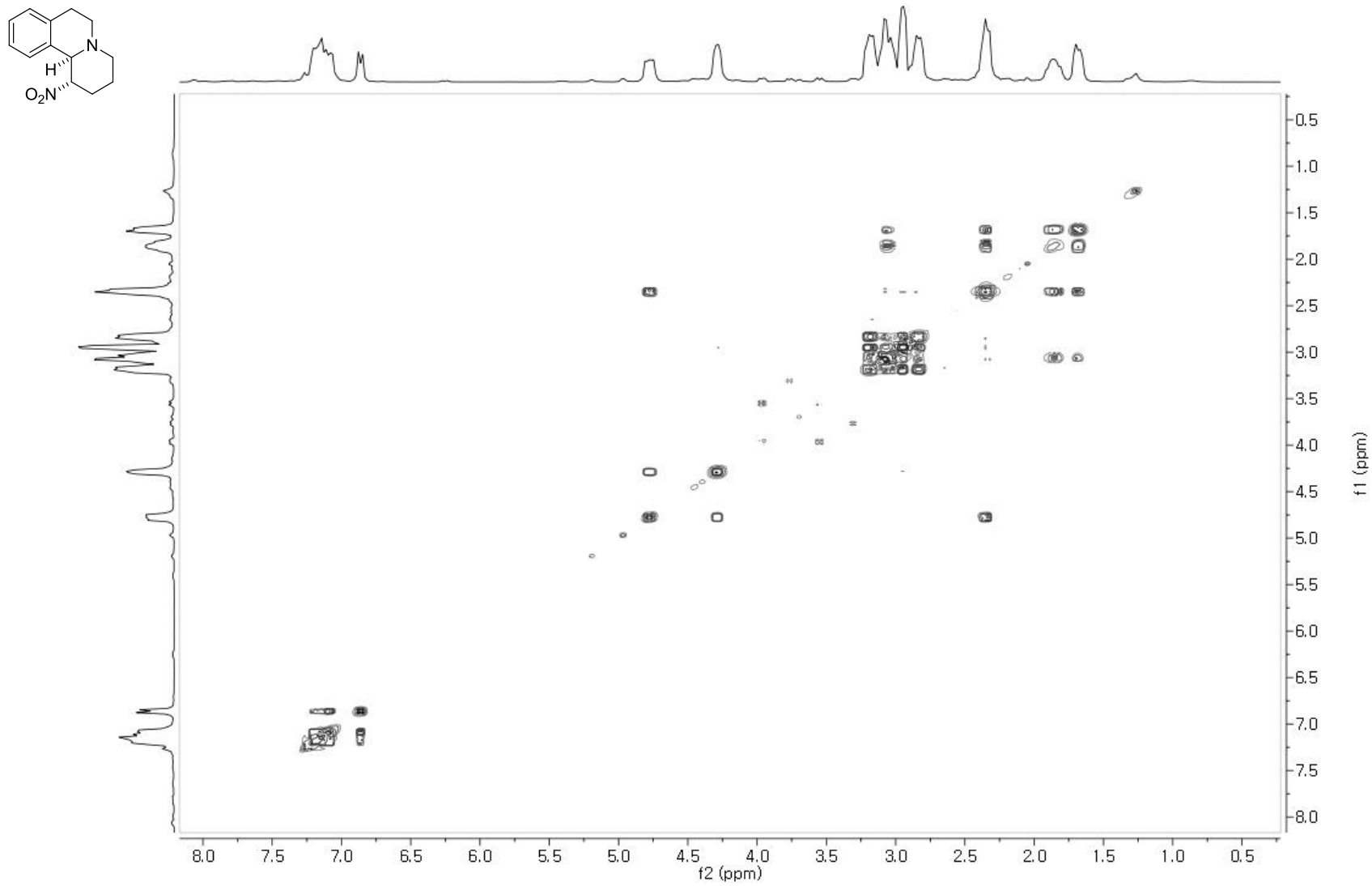


Noesy of **8k** in $CDCl_3$

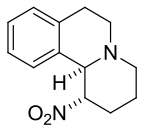


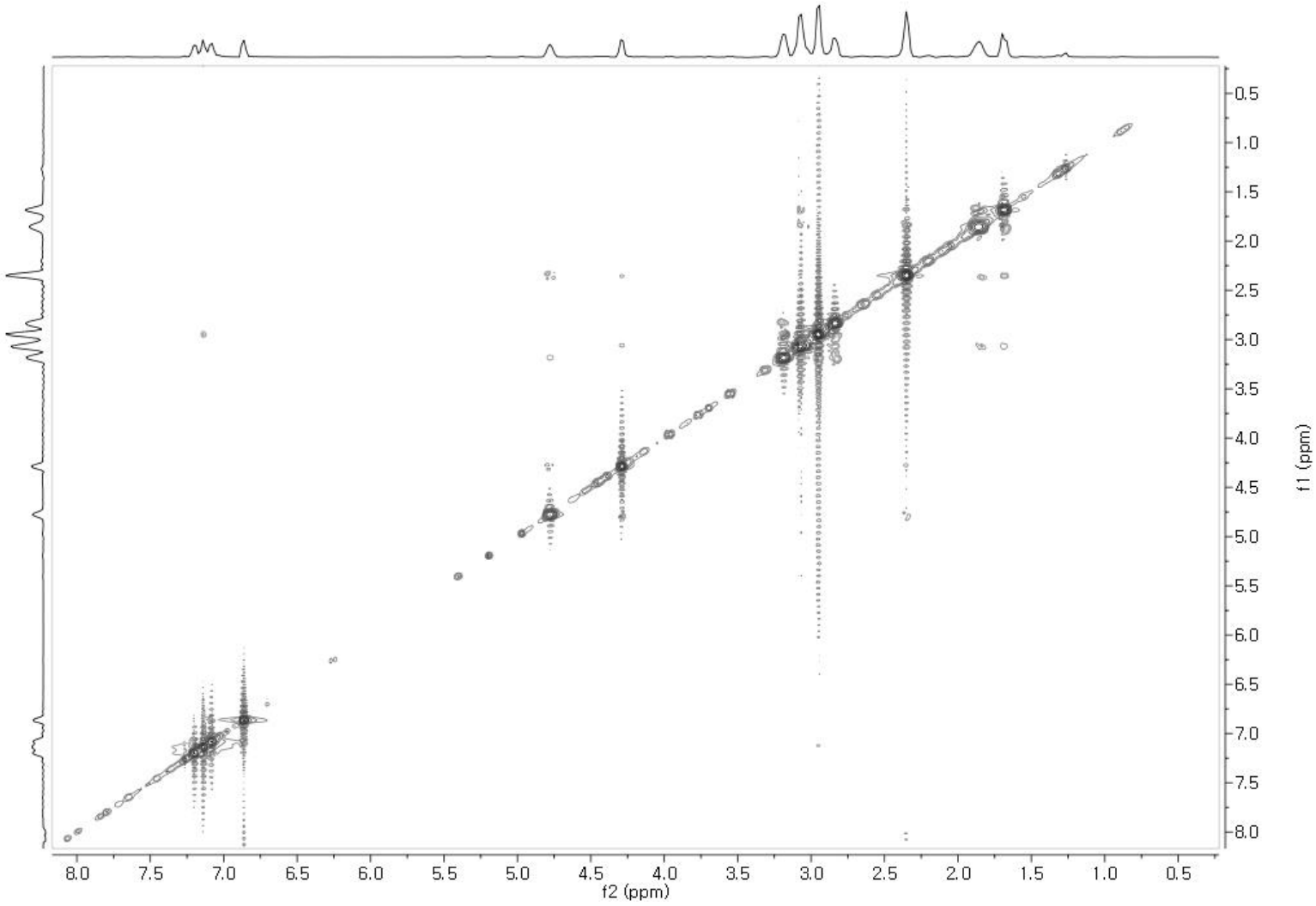


Gcosy of **11** in $CDCl_3$

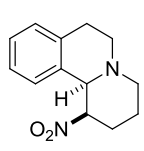


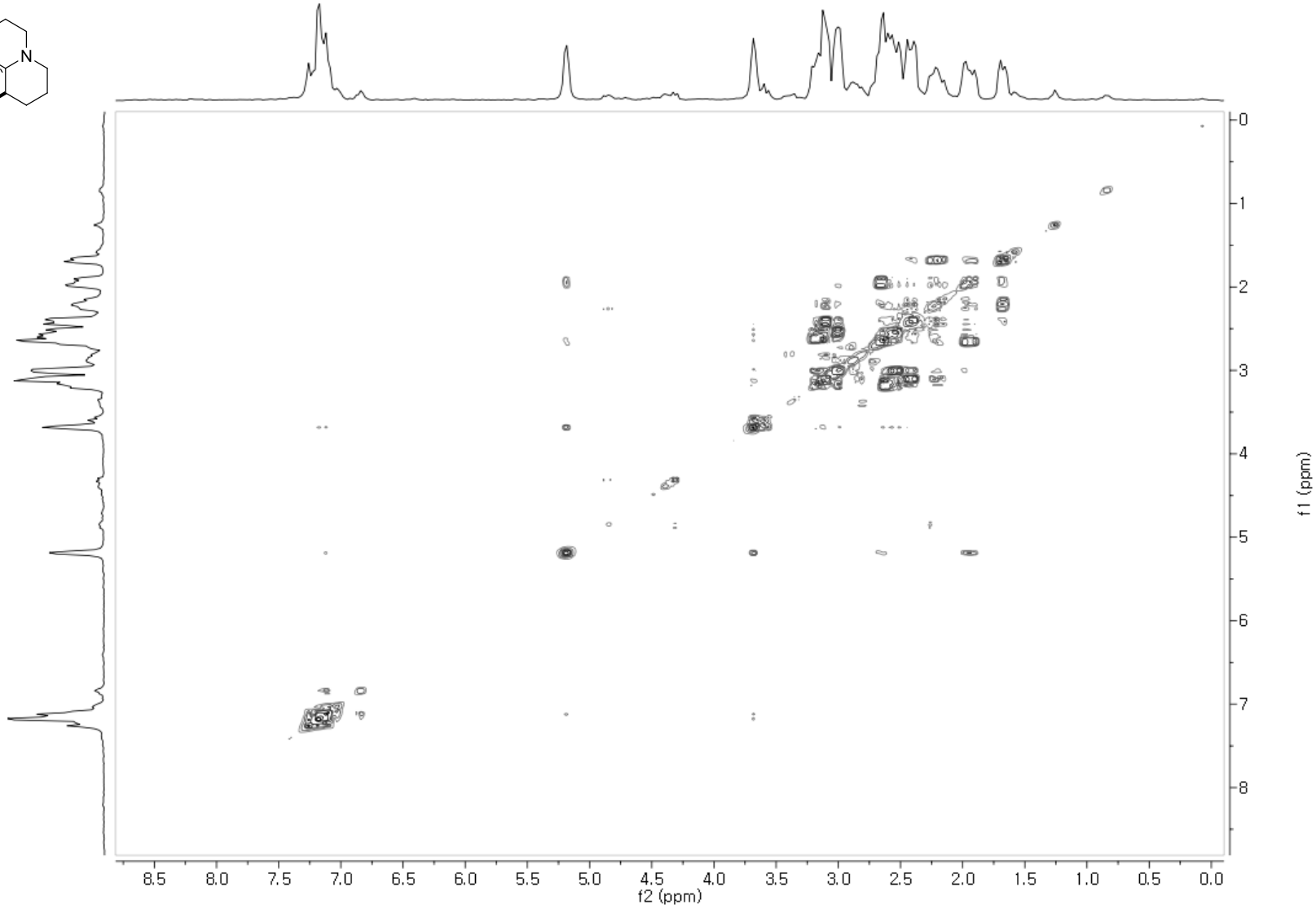
Noesy of **11** in $CDCl_3$



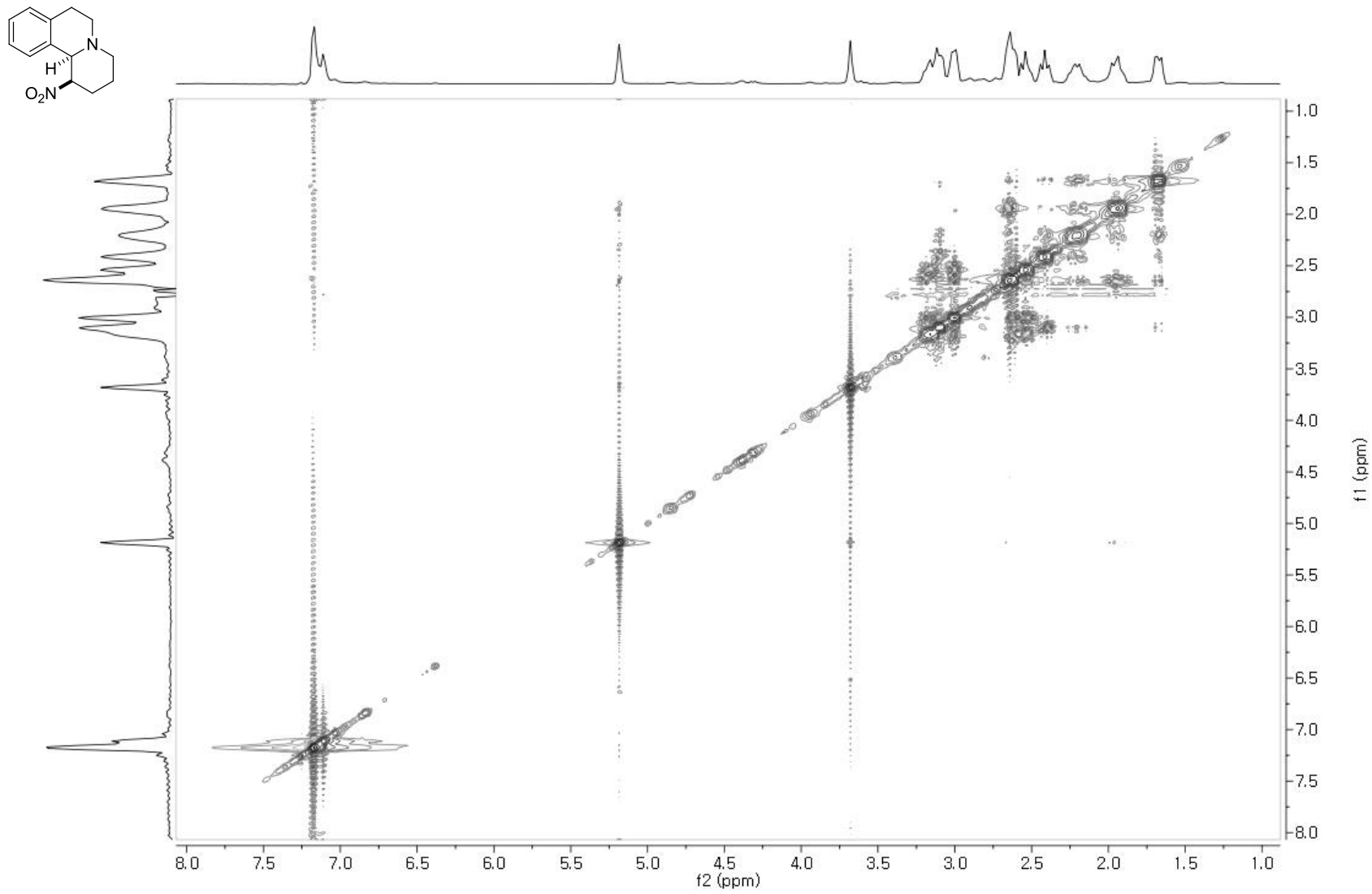


Gcosy of **12** in $CDCl_3$

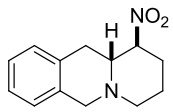


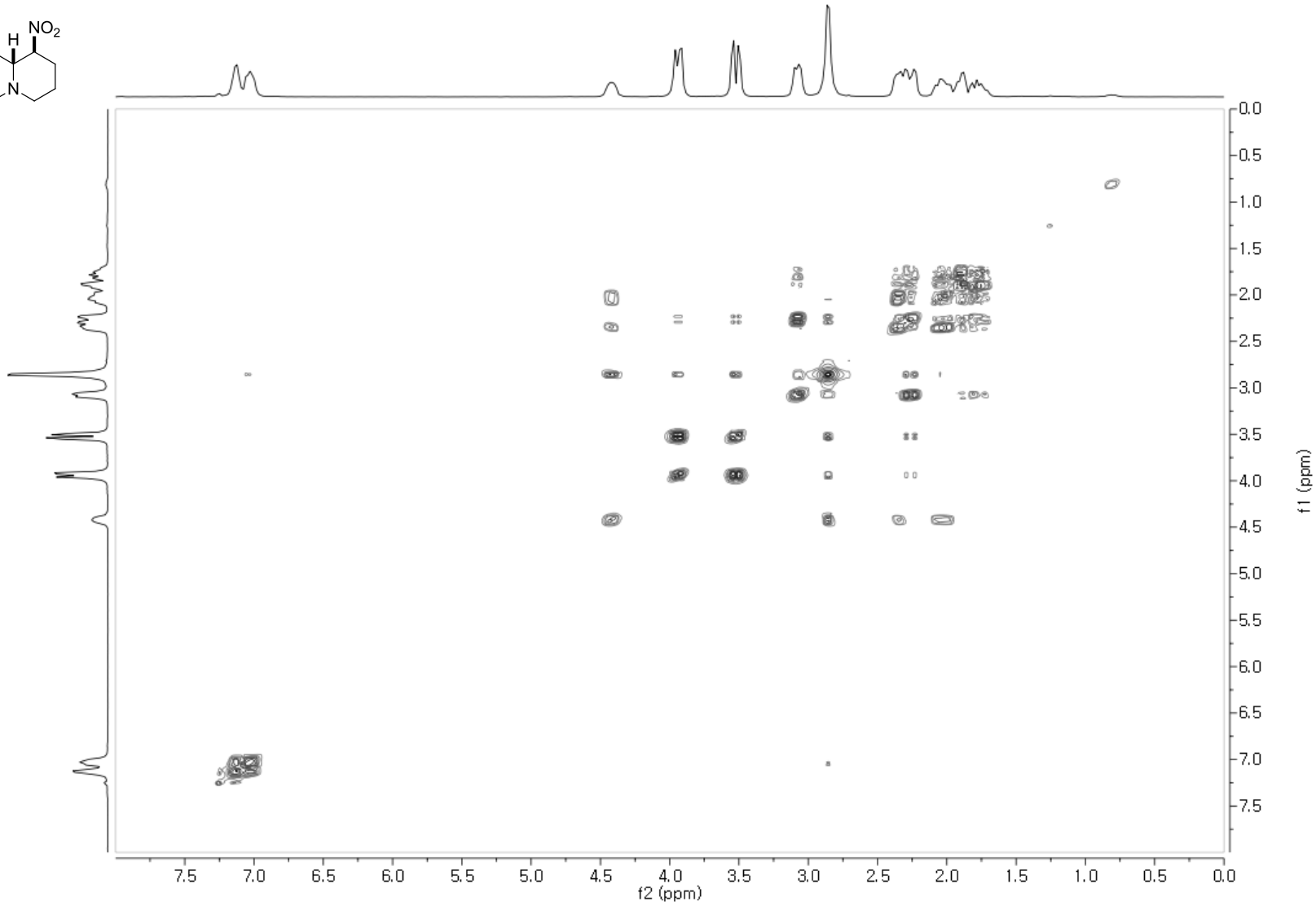


Noesy of **12** in $CDCl_3$

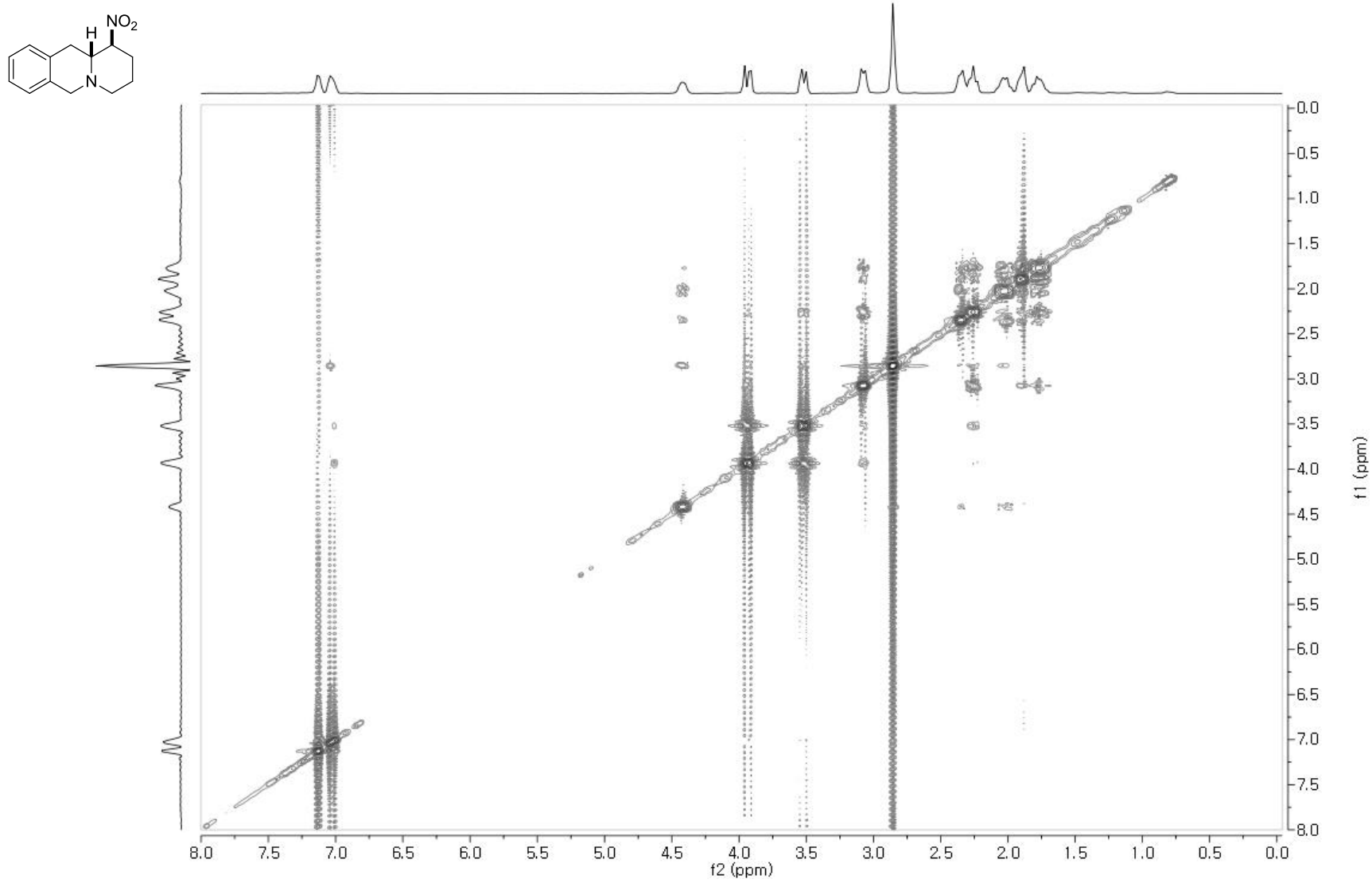


Gcosy of **13** in $CDCl_3$

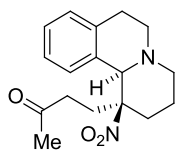


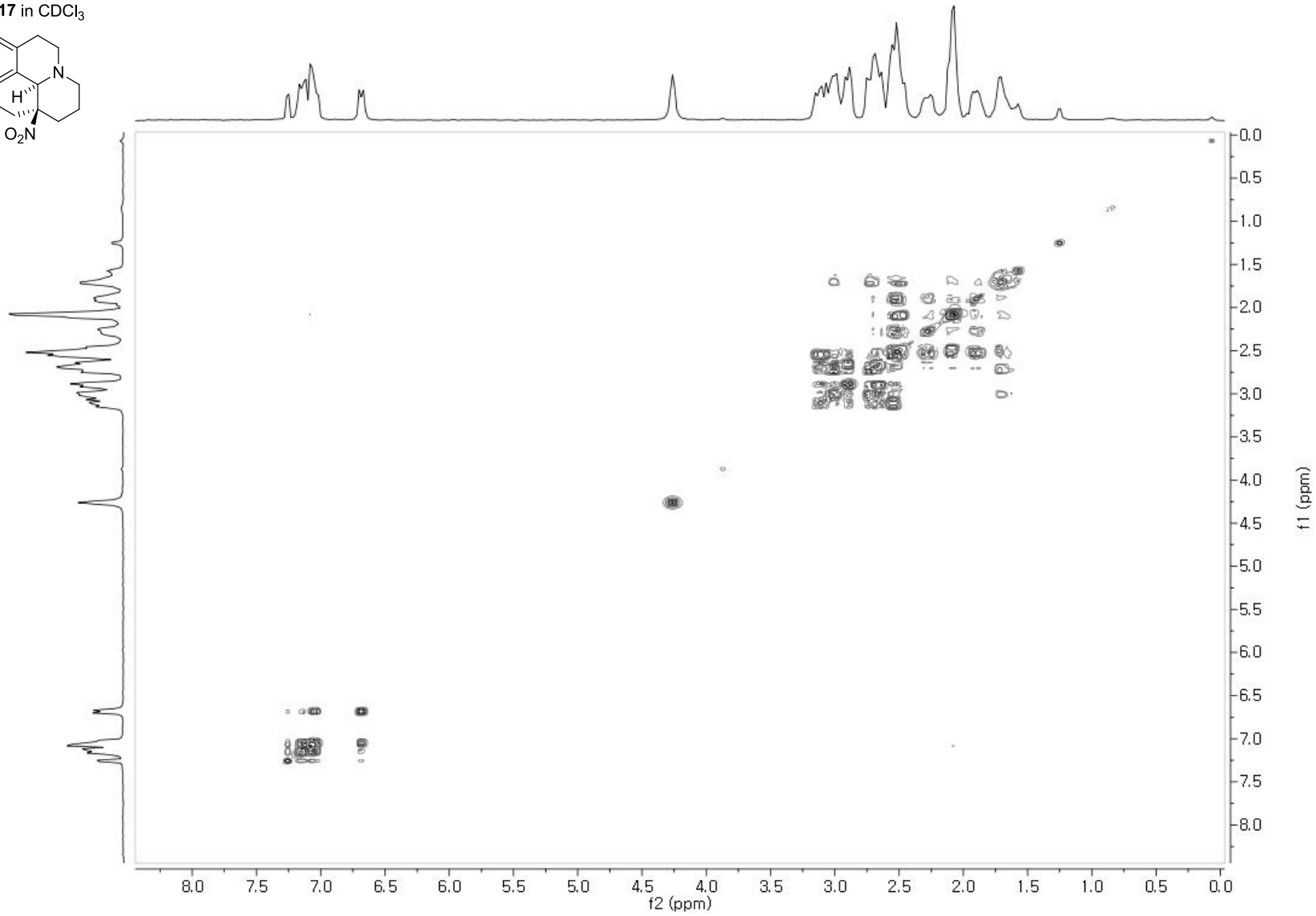


Noesy of **13** in $CDCl_3$

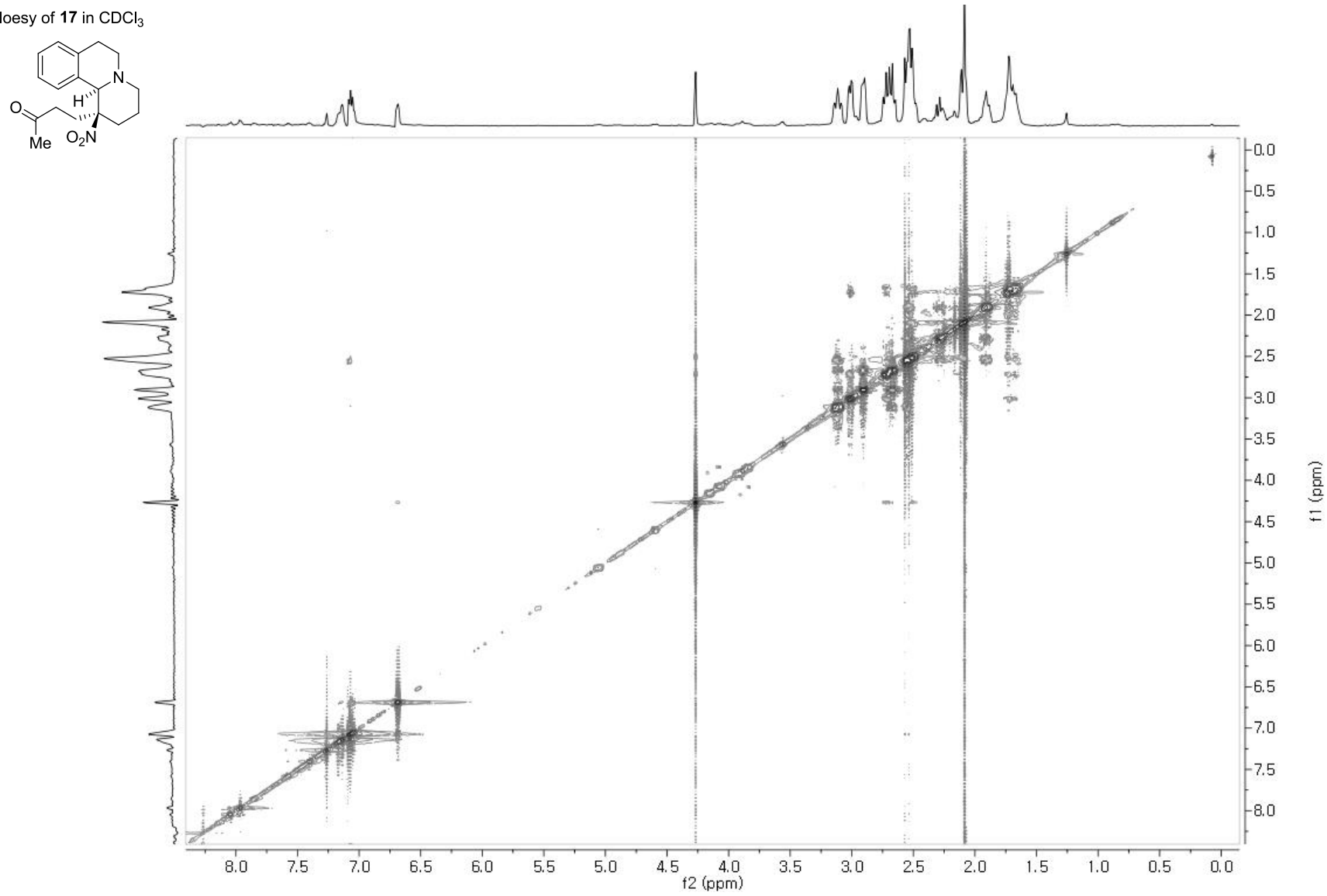


Gcosy of **17** in $CDCl_3$

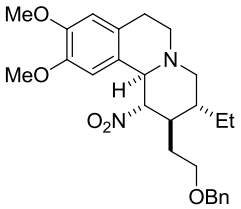


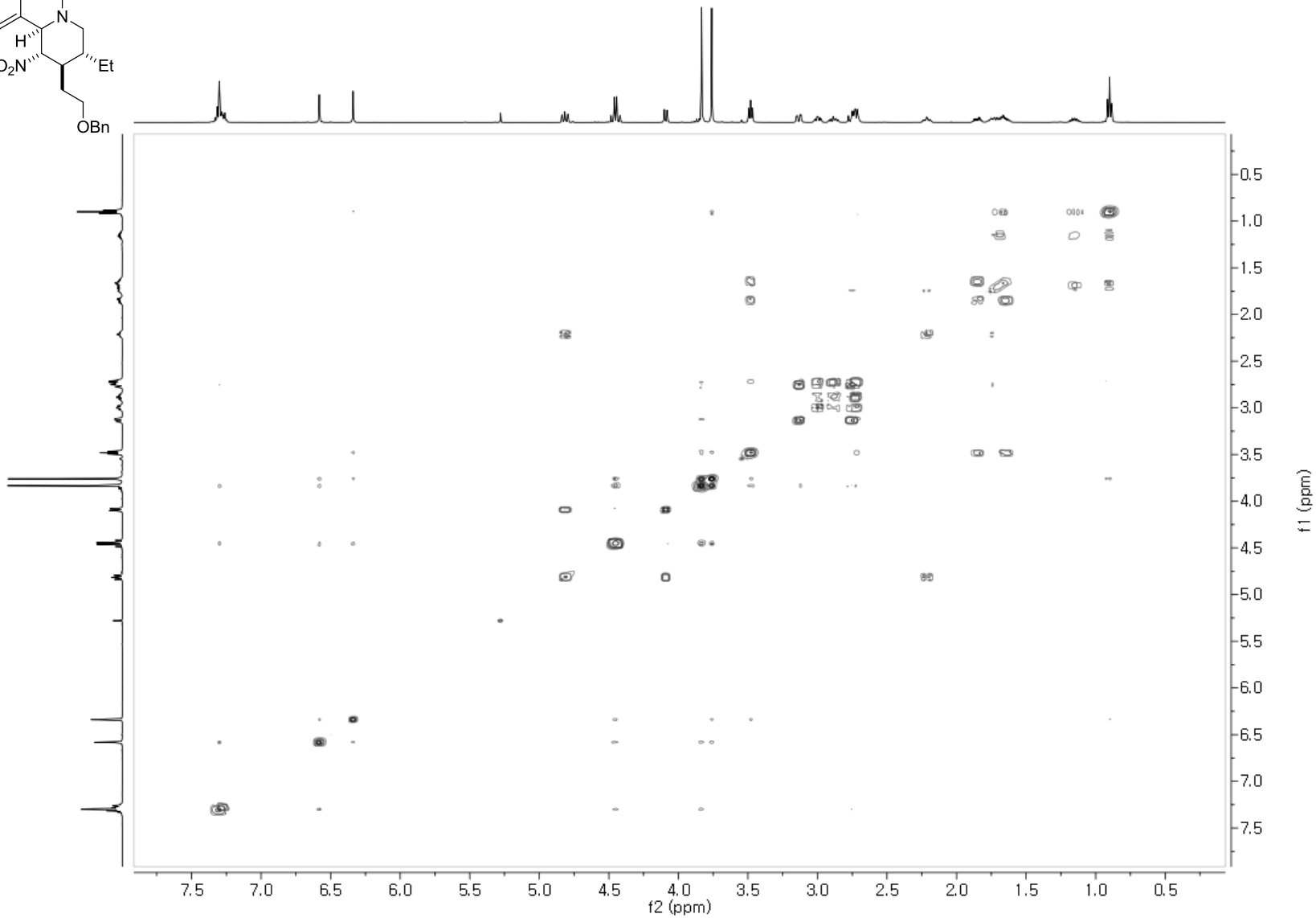


Noesy of **17** in $CDCl_3$

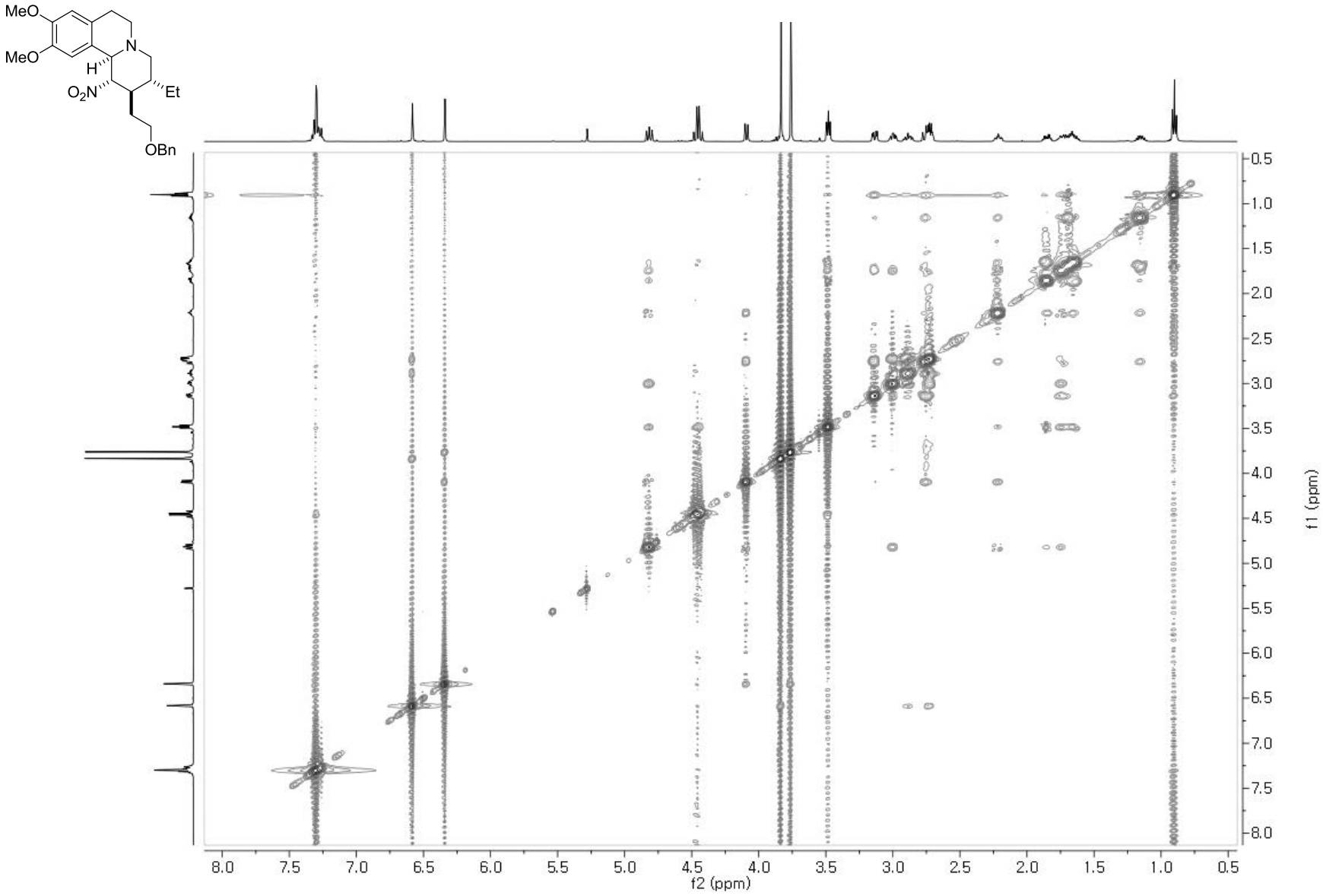


Gcosy of **19** in $CDCl_3$

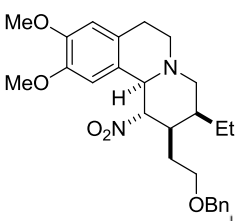


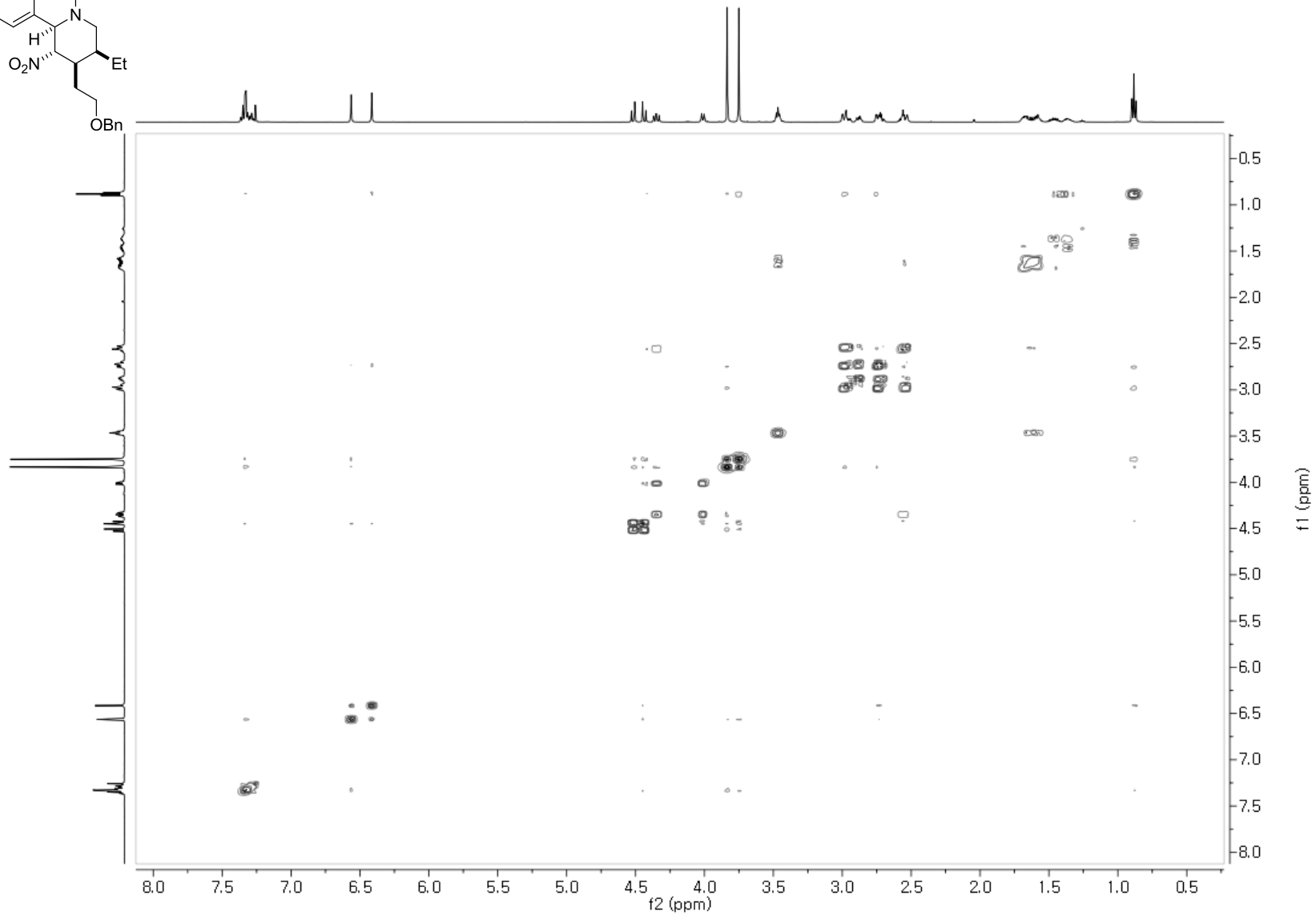


Noesy of **19** in $CDCl_3$

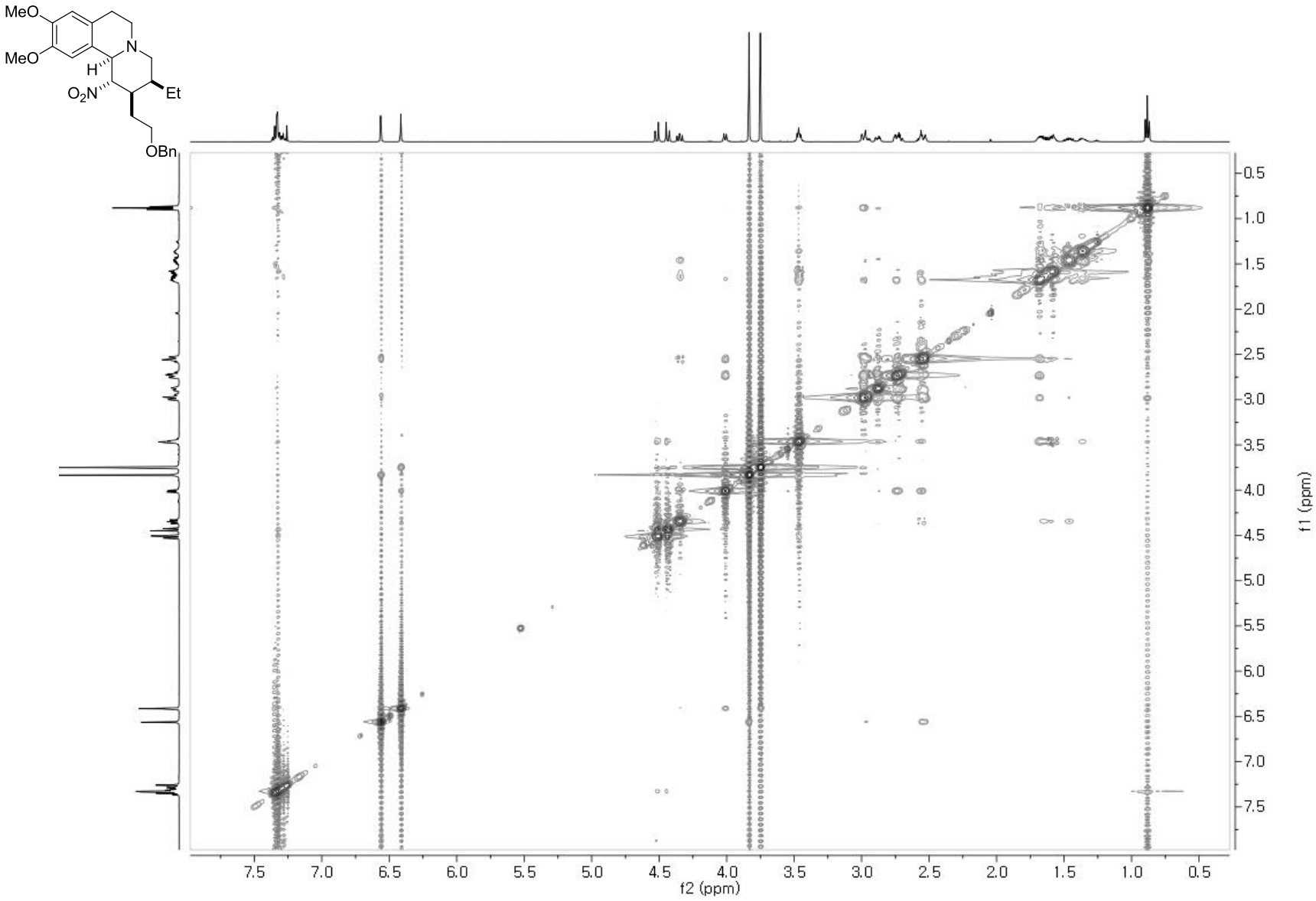


Gcosy of **19'** in $CDCl_3$

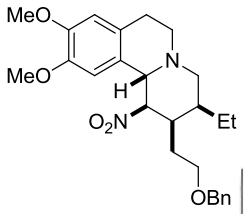


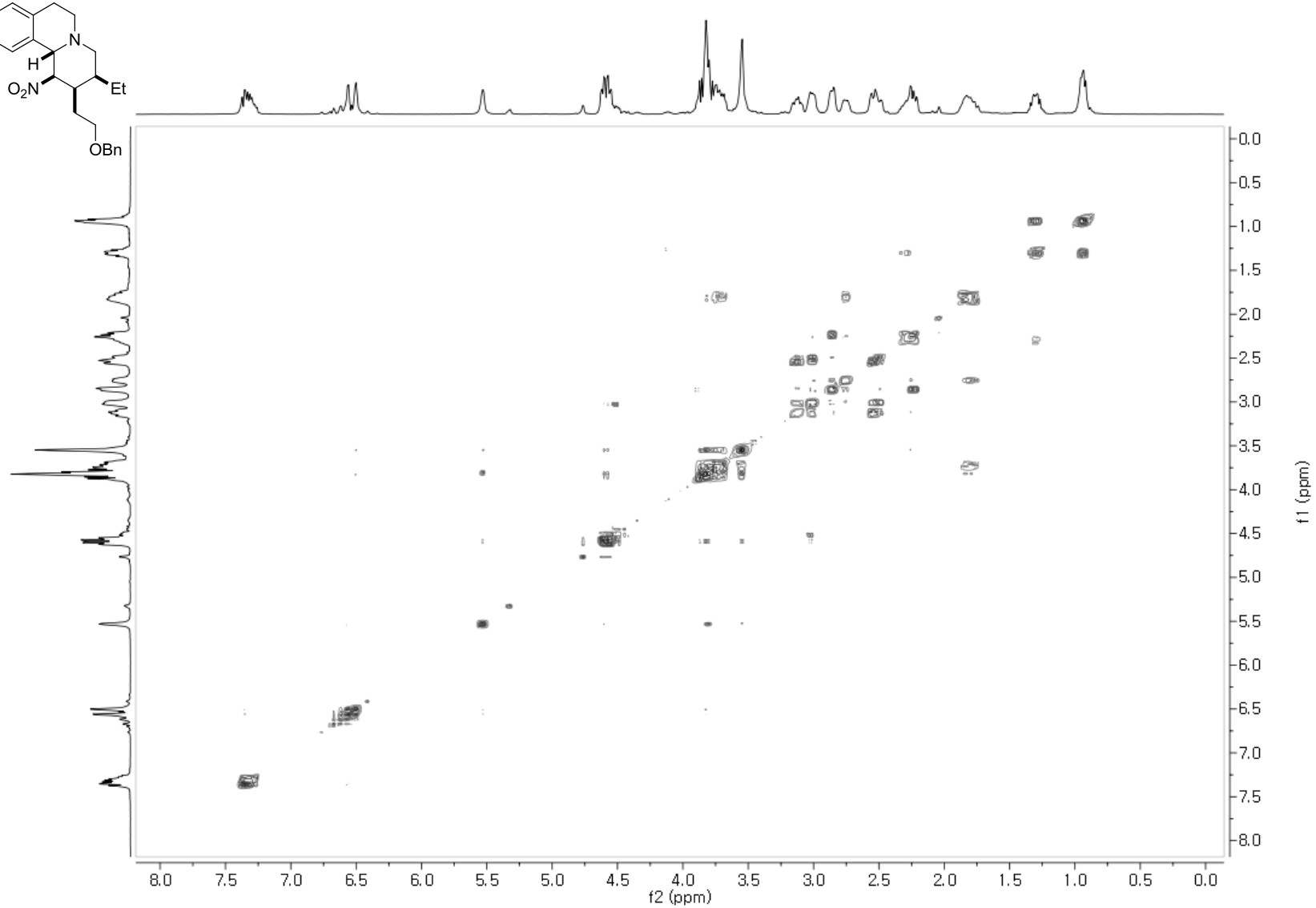
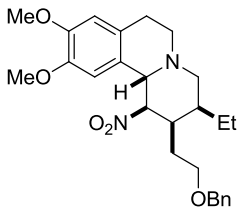
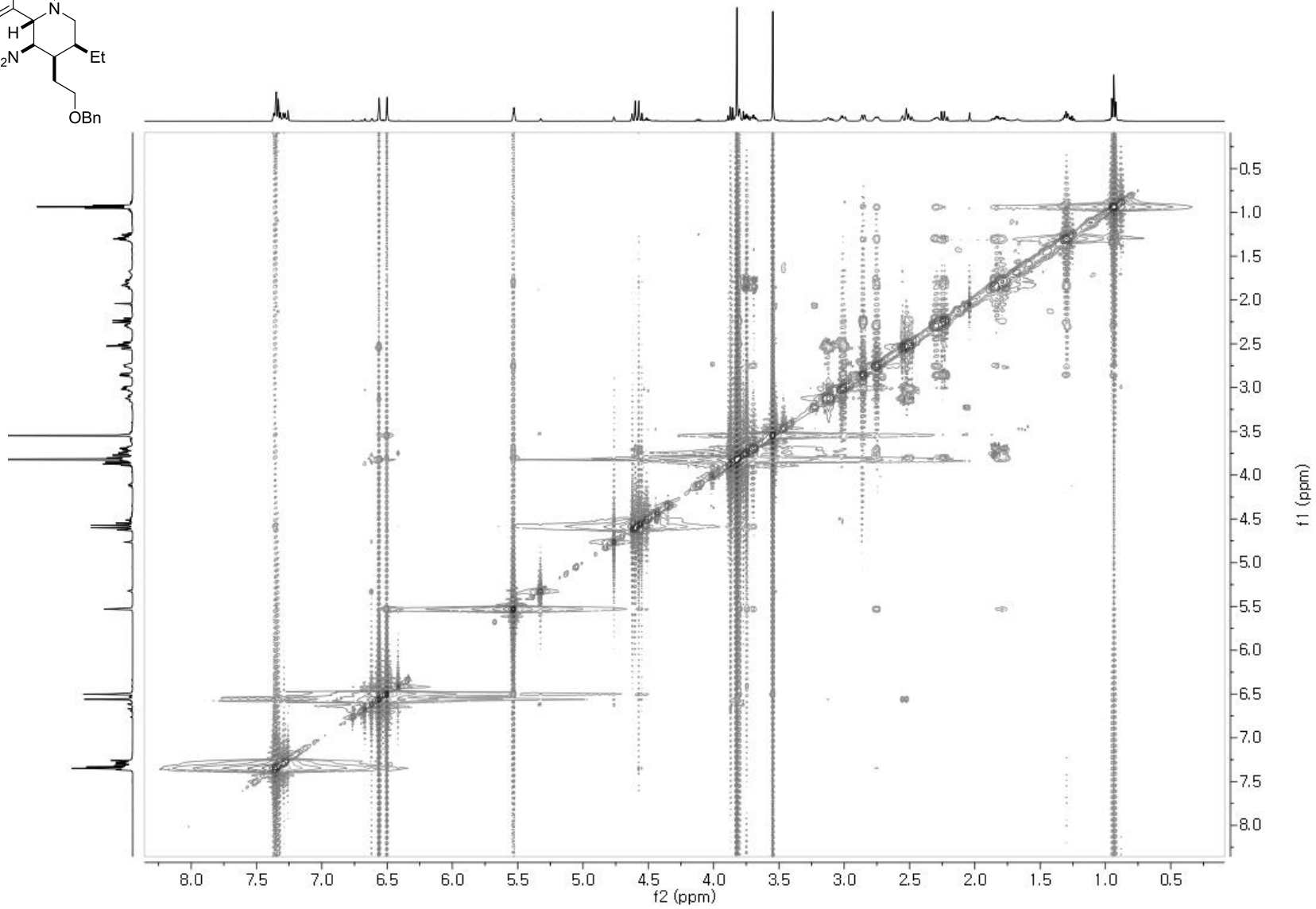


Noesy of **19'** in $CDCl_3$



Gcosy of **19"** in $CDCl_3$





Noesy of **19"** in $CDCl_3$