

Efficient and regioselective synthesis of bicyclic pyrrolidones or bicyclic pyridones by cyclocondensation of heterocyclic ketene aminals with nitro-phenylpropiolate†

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Table S1: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **2a** in THF

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.863151	-1.183853	0.000349
2	6	0	1.483888	-1.343532	0.000216
3	6	0	0.638385	-0.215268	-0.000141
4	6	0	1.198610	1.078561	-0.000363
5	6	0	2.577184	1.243742	-0.000231
6	6	0	3.387573	0.108541	0.000123
7	1	0	3.529621	-2.036319	0.000622
8	1	0	1.050997	-2.337115	0.000387
9	1	0	0.546788	1.944452	-0.000637
10	1	0	3.027163	2.227785	-0.000396
11	6	0	-0.776643	-0.383222	-0.000274
12	6	0	-1.982517	-0.521039	-0.000403
13	6	0	-3.407431	-0.770142	-0.000652
14	8	0	-3.897918	-1.884630	0.000073
15	8	0	-4.102021	0.377651	-0.000386
16	6	0	-5.551966	0.244590	0.000124
17	6	0	-6.134778	1.642603	0.000284
18	1	0	-5.846082	-0.326595	0.885142
19	1	0	-5.846695	-0.326651	-0.884654
20	1	0	-7.226850	1.580348	0.000665
21	1	0	-5.821686	2.198299	0.888445
22	1	0	-5.822302	2.198244	-0.888128
23	7	0	4.846003	0.280278	0.000262
24	8	0	5.292290	1.428669	0.000065
25	8	0	5.546935	-0.732974	0.000565

HF=-780.111286

Zero-point correction=	0.183900 (Hartree/Particle)
Thermal correction to Energy=	0.198847
Thermal correction to Enthalpy=	0.199791
Thermal correction to Gibbs Free Energy=	0.137808
Sum of electronic and zero-point Energies=	-779.927386
Sum of electronic and thermal Energies=	-779.912439
Sum of electronic and thermal Enthalpies=	-779.911495
Sum of electronic and thermal Free Energies=	-779.973477

Table S2: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **2a** in acetonitrile

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.863573	-1.184313	-0.000037
2	6	0	-1.484500	-1.345027	-0.000064
3	6	0	-0.638511	-0.217124	-0.000015
4	6	0	-1.197231	1.077372	0.000061
5	6	0	-2.575626	1.243560	0.000088
6	6	0	-3.386799	0.108728	0.000039
7	1	0	-3.529675	-2.036959	-0.000073
8	1	0	-1.052915	-2.339094	-0.000123
9	1	0	-0.545223	1.943014	0.000098
10	1	0	-3.023640	2.228411	0.000146
11	6	0	0.776473	-0.385968	-0.000041
12	6	0	1.982457	-0.523648	-0.000062
13	6	0	3.407420	-0.770915	-0.000087
14	8	0	3.898722	-1.885844	-0.000102
15	8	0	4.100796	0.376490	-0.000086
16	6	0	5.551933	0.246802	-0.000086
17	6	0	6.131322	1.646061	0.000127
18	1	0	5.847098	-0.322979	-0.885516
19	1	0	5.847081	-0.323247	0.885175
20	1	0	7.223415	1.585427	0.000122
21	1	0	5.817758	2.200969	-0.888364
22	1	0	5.817751	2.200697	0.888785
23	7	0	-4.844170	0.281497	0.000069
24	8	0	-5.291191	1.429972	0.000126
25	8	0	-5.547409	-0.730605	0.000030

HF=-780.1130038

Zero-point correction=	0.183838 (Hartree/Particle)
Thermal correction to Energy=	0.198797
Thermal correction to Enthalpy=	0.199742
Thermal correction to Gibbs Free Energy=	0.137636
Sum of electronic and zero-point Energies=	-779.929165
Sum of electronic and thermal Energies=	-779.914206
Sum of electronic and thermal Enthalpies=	-779.913262
Sum of electronic and thermal Free Energies=	-779.975368

Table S3: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **2a** in dioxane

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.862521	-1.182941	0.000077
2	6	0	-1.482852	-1.340790	-0.000023
3	6	0	-0.637983	-0.212091	-0.000097
4	6	0	-1.201105	1.080421	-0.000071
5	6	0	-2.580065	1.243852	0.000028
6	6	0	-3.389100	0.108163	0.000101
7	1	0	-3.530315	-2.034589	0.000136
8	1	0	-1.047317	-2.333399	-0.000043
9	1	0	-0.549307	1.946558	-0.000128
10	1	0	-3.034236	2.226156	0.000050
11	6	0	0.777100	-0.378448	-0.000193
12	6	0	1.982747	-0.516471	-0.000280
13	6	0	3.407605	-0.768872	-0.000429
14	8	0	3.897323	-1.881859	-0.000223
15	8	0	4.104243	0.380428	-0.000208
16	6	0	5.551199	0.240516	0.000000
17	6	0	6.141048	1.636032	0.000275
18	1	0	5.844595	-0.333218	-0.883986
19	1	0	5.844323	-0.333453	0.883922
20	1	0	7.233096	1.570689	0.000434
21	1	0	5.829843	2.193600	-0.887380
22	1	0	5.829571	2.193364	0.887983
23	7	0	-4.849915	0.278150	0.000207
24	8	0	-5.294050	1.426537	0.000263
25	8	0	-5.545926	-0.737480	0.000322

HF=-780.1071799

Zero-point correction=	0.184028 (Hartree/Particle)
Thermal correction to Energy=	0.198956
Thermal correction to Enthalpy=	0.199900
Thermal correction to Gibbs Free Energy=	0.138086
Sum of electronic and zero-point Energies=	-779.923152
Sum of electronic and thermal Energies=	-779.908224
Sum of electronic and thermal Enthalpies=	-779.907280
Sum of electronic and thermal Free Energies=	-779.969094

Table S4: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **2b** in THF

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.403743	2.347569	-0.000461
2	6	0	1.083317	1.904125	-0.000397
3	6	0	0.791888	0.524340	-0.000148
4	6	0	1.845337	-0.404739	0.000037
5	6	0	3.151172	0.071032	-0.000026
6	6	0	3.454727	1.432206	-0.000273
7	1	0	2.616965	3.410704	-0.000654
8	1	0	0.266474	2.617228	-0.000537
9	1	0	1.653415	-1.469321	0.000230
10	6	0	-0.559967	0.070993	-0.000079
11	6	0	-1.713901	-0.304700	-0.000014
12	6	0	-3.060291	-0.830610	0.000067
13	8	0	-3.322556	-2.019811	-0.000129
14	8	0	-3.969018	0.157621	0.000277
15	6	0	-5.363302	-0.260210	0.000275
16	6	0	-6.211287	0.995099	-0.000002
17	1	0	-5.539563	-0.878131	0.885212
18	1	0	-5.539473	-0.878483	-0.884428
19	1	0	-7.269685	0.718801	0.000038
20	1	0	-6.014045	1.601638	0.888157
21	1	0	-6.014013	1.601267	-0.888408
22	1	0	4.488408	1.752629	-0.000313
23	7	0	4.253660	-0.902238	0.000177
24	8	0	5.405586	-0.467014	0.000144
25	8	0	3.966899	-2.099710	0.000407

HF=-780.1108943

Zero-point correction=	0.184086 (Hartree/Particle)
Thermal correction to Energy=	0.198945
Thermal correction to Enthalpy=	0.199889
Thermal correction to Gibbs Free Energy=	0.138889
Sum of electronic and zero-point Energies=	-779.926809
Sum of electronic and thermal Energies=	-779.911949
Sum of electronic and thermal Enthalpies=	-779.911005
Sum of electronic and thermal Free Energies=	-779.972006

Table S5: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **2b** in acetonitrile

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.406212	2.348476	-0.000497
2	6	0	1.085170	1.906715	-0.000438
3	6	0	0.792380	0.527104	-0.000163
4	6	0	1.844335	-0.403418	0.000053
5	6	0	3.150845	0.070845	-0.000006
6	6	0	3.456030	1.431853	-0.000278
7	1	0	2.620825	3.411194	-0.000711
8	1	0	0.269675	2.621257	-0.000603
9	1	0	1.650646	-1.467594	0.000264
10	6	0	-0.559740	0.074484	-0.000101
11	6	0	-1.713610	-0.301869	-0.000046
12	6	0	-3.059130	-0.829027	0.000019
13	8	0	-3.318792	-2.019684	-0.000077
14	8	0	-3.969187	0.156453	0.000221
15	6	0	-5.364378	-0.261801	0.000278
16	6	0	-6.212310	0.993307	0.000022
17	1	0	-5.539978	-0.878988	0.885713
18	1	0	-5.539955	-0.879352	-0.884903
19	1	0	-7.270342	0.715957	0.000099
20	1	0	-6.015613	1.599608	0.888467
21	1	0	-6.015640	1.599227	-0.888690
22	1	0	4.489623	1.752359	-0.000316
23	7	0	4.250859	-0.903414	0.000226
24	8	0	5.404426	-0.471722	0.000173
25	8	0	3.963544	-2.101270	0.000439

HF=-780.1127108

Zero-point correction=	0.184007 (Hartree/Particle)
Thermal correction to Energy=	0.198880
Thermal correction to Enthalpy=	0.199824
Thermal correction to Gibbs Free Energy=	0.138757
Sum of electronic and zero-point Energies=	-779.928704
Sum of electronic and thermal Energies=	-779.913831
Sum of electronic and thermal Enthalpies=	-779.912887
Sum of electronic and thermal Free Energies=	-779.973954

Table S6: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **2b** in dioxane

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.402007	2.346181	-0.000441
2	6	0	1.082125	1.901408	-0.000387
3	6	0	0.791339	0.521709	-0.000149
4	6	0	1.846574	-0.405869	0.000038
5	6	0	3.151728	0.070862	-0.000014
6	6	0	3.454059	1.431847	-0.000251
7	1	0	2.614048	3.409841	-0.000627
8	1	0	0.263603	2.612811	-0.000529
9	1	0	1.657033	-1.471047	0.000222
10	6	0	-0.560420	0.068348	-0.000093
11	6	0	-1.714498	-0.306017	-0.000042
12	6	0	-3.061811	-0.831657	0.000015
13	8	0	-3.327216	-2.018242	-0.000182
14	8	0	-3.969760	0.160616	0.000262
15	6	0	-5.361012	-0.259315	0.000268
16	6	0	-6.211698	0.994670	0.000028
17	1	0	-5.537383	-0.879144	0.884203
18	1	0	-5.537311	-0.879459	-0.883455
19	1	0	-7.270316	0.718539	0.000077
20	1	0	-6.014361	1.602067	0.887594
21	1	0	-6.014353	1.601733	-0.887763
22	1	0	4.488518	1.750216	-0.000282
23	7	0	4.257715	-0.902350	0.000192
24	8	0	5.406850	-0.461716	0.000169
25	8	0	3.969646	-2.098421	0.000423

HF=-780.1065944

Zero-point correction=	0.184209 (Hartree/Particle)
Thermal correction to Energy=	0.199059
Thermal correction to Enthalpy=	0.200003
Thermal correction to Gibbs Free Energy=	0.139015
Sum of electronic and zero-point Energies=	-779.922385
Sum of electronic and thermal Energies=	-779.907536
Sum of electronic and thermal Enthalpies=	-779.906592
Sum of electronic and thermal Free Energies=	-779.967580

Table S7: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **1d** in THF

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.389903	-0.865883	0.048814
2	6	0	4.821501	0.467319	0.224556
3	6	0	3.852304	1.487062	0.244206
4	6	0	2.501155	1.201624	0.089427
5	6	0	2.039841	-0.147669	-0.094926
6	6	0	3.047532	-1.172171	-0.102706
7	6	0	0.666113	-0.500386	-0.252895
8	6	0	-0.371679	0.554562	-0.356296
9	8	0	0.247503	-1.728812	-0.400843
10	6	0	-1.756100	0.345245	-0.070824
11	7	0	-2.629593	1.369244	-0.190791
12	6	0	-4.063704	1.234428	0.074694
13	6	0	-4.497032	-0.210390	-0.178479
14	6	0	-3.586941	-1.174359	0.586438
15	7	0	-2.184552	-0.863508	0.314034
16	1	0	5.123021	-1.669566	0.033602
17	1	0	5.875104	0.699405	0.343854
18	1	0	4.160625	2.520843	0.383734
19	1	0	1.792978	2.023571	0.121146
20	1	0	2.731301	-2.201780	-0.232649
21	1	0	-0.111846	1.541712	-0.724554
22	1	0	-2.258771	2.279946	-0.421869
23	1	0	-4.276869	1.525275	1.111381
24	1	0	-4.594877	1.926135	-0.583438
25	1	0	-5.533062	-0.343365	0.143023
26	1	0	-4.446197	-0.427518	-1.250798
27	1	0	-3.773559	-1.104229	1.665587
28	1	0	-3.766821	-2.209122	0.286197
29	1	0	-1.459387	-1.587260	0.196766

HF=-650.4867902

Zero-point correction=	0.246195 (Hartree/Particle)
Thermal correction to Energy=	0.168543
Thermal correction to Enthalpy=	0.231687
Thermal correction to Gibbs Free Energy=	0.235187
Sum of electronic and zero-point Energies=	-650.240595
Sum of electronic and thermal Energies=	-650.318247
Sum of electronic and thermal Enthalpies=	-650.255103
Sum of electronic and thermal Free Energies=	-650.251603

Table S8: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **1d** in acetonitrile

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.389972	-0.858728	0.066483
2	6	0	4.813865	0.476070	0.247576
3	6	0	3.839675	1.491633	0.255895
4	6	0	2.491508	1.200522	0.085429
5	6	0	2.037458	-0.150789	-0.104590
6	6	0	3.050249	-1.170688	-0.100801
7	6	0	0.666245	-0.507116	-0.277833
8	6	0	-0.371874	0.546017	-0.385499
9	8	0	0.252903	-1.738164	-0.433892
10	6	0	-1.755053	0.341359	-0.082188
11	7	0	-2.625080	1.365009	-0.202166
12	6	0	-4.058237	1.236980	0.075321
13	6	0	-4.496671	-0.210020	-0.153899
14	6	0	-3.581159	-1.166082	0.614092
15	7	0	-2.180313	-0.862028	0.321250
16	1	0	5.126571	-1.659434	0.059863
17	1	0	5.865009	0.712684	0.379197
18	1	0	4.141690	2.526810	0.398812
19	1	0	1.779167	2.019118	0.108155
20	1	0	2.741199	-2.202169	-0.233920
21	1	0	-0.115771	1.529241	-0.766733
22	1	0	-2.255683	2.271661	-0.451981
23	1	0	-4.261062	1.544046	1.108966
24	1	0	-4.591453	1.920923	-0.588864
25	1	0	-5.529214	-0.336261	0.180704
26	1	0	-4.457979	-0.441677	-1.223624
27	1	0	-3.754115	-1.080243	1.694059
28	1	0	-3.766251	-2.204270	0.329927
29	1	0	-1.463432	-1.590936	0.203073

HF=-650.4882067

Zero-point correction=	0.172694 (Hartree/Particle)
Thermal correction to Energy=	0.193512
Thermal correction to Enthalpy=	0.135783
Thermal correction to Gibbs Free Energy=	0.183652
Sum of electronic and zero-point Energies=	-650.315513
Sum of electronic and thermal Energies=	-650.294695
Sum of electronic and thermal Enthalpies=	-650.352424
Sum of electronic and thermal Free Energies=	-650.304555

Table S9: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **1d** in dioxane

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.119519	0.151575	0.740532
2	6	0	-4.224813	-1.162253	0.242815
3	6	0	-3.141281	-1.696931	-0.481209
4	6	0	-1.989357	-0.955436	-0.698278
5	6	0	-1.860819	0.380350	-0.192423
6	6	0	-2.978394	0.910503	0.533938
7	6	0	-0.695887	1.167019	-0.388620
8	6	0	0.498073	0.688235	-1.146344
9	8	0	-0.494801	2.373948	0.019060
10	6	0	1.640441	0.160168	-0.493765
11	7	0	2.770213	-0.108508	-1.185352
12	6	0	3.976718	-0.676949	-0.580612
13	6	0	4.047834	-0.267461	0.891551
14	6	0	2.735156	-0.613848	1.596149
15	7	0	1.606140	-0.093955	0.824851
16	1	0	-4.950099	0.582794	1.295282
17	1	0	-5.123327	-1.748108	0.408015
18	1	0	-3.206638	-2.706643	-0.880591
19	1	0	-1.174779	-1.397520	-1.265889
20	1	0	-2.908382	1.923722	0.915593
21	1	0	0.605530	0.923990	-2.203284
22	1	0	2.764323	0.099065	-2.173330
23	1	0	3.962105	-1.770066	-0.677703
24	1	0	4.840977	-0.302638	-1.134364
25	1	0	4.876872	-0.785995	1.379846
26	1	0	4.233194	0.809326	0.964331
27	1	0	2.632261	-1.700189	1.711564
28	1	0	2.697538	-0.167701	2.592713
29	1	0	0.745452	0.155783	1.296436

HF=-650.4379818

Zero-point correction=	0.204857 (Hartree/Particle)
Thermal correction to Energy=	0.218452
Thermal correction to Enthalpy=	0.183464
Thermal correction to Gibbs Free Energy=	0.205278
Sum of electronic and zero-point Energies=	-650.233125
Sum of electronic and thermal Energies=	-650.219530
Sum of electronic and thermal Enthalpies=	-650.254518
Sum of electronic and thermal Free Energies=	-650.232704

Table S10: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **7** in acetonitrile

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	5.991319	1.496403	-1.295719
2	6	0	6.377339	0.223305	-1.735799
3	6	0	5.447139	-0.826817	-1.772248
4	6	0	4.164033	-0.539994	-1.362198
5	6	0	3.728993	0.696047	-0.914352
6	6	0	4.682444	1.736661	-0.889963
7	6	0	2.328722	0.974021	-0.487660
8	8	0	1.966270	2.101387	-0.184844
9	6	0	1.832882	-1.368566	0.386643
10	7	0	2.166736	-2.456364	-0.220838
11	6	0	2.664795	-3.556678	0.606594
12	6	0	3.261389	-3.113887	1.950374
13	6	0	2.286305	-2.169979	2.656703
14	7	0	1.909040	-1.113228	1.727160
15	1	0	6.719775	2.301935	-1.272397
16	1	0	7.402815	0.045968	-2.052233
17	1	0	5.734604	-1.817518	-2.114233
18	1	0	4.364563	2.718138	-0.549635
19	1	0	1.838531	-4.264237	0.777670
20	1	0	3.414919	-4.103855	0.022612
21	1	0	3.480634	-3.979620	2.585590
22	1	0	4.205400	-2.584491	1.772807
23	1	0	1.400591	-2.726822	3.001427
24	1	0	2.746765	-1.710861	3.538639
25	1	0	1.391617	-0.309006	2.076546
26	6	0	-0.101654	0.215763	-0.218780
27	6	0	-1.083623	-0.490610	-0.816208
28	1	0	-0.736602	-1.320603	-1.433232
29	6	0	1.342755	-0.207907	-0.492279
30	1	0	1.380631	-0.630689	-1.500445
31	6	0	-0.311269	1.258091	0.843858
32	6	0	-2.555635	-0.442682	-0.706031
33	6	0	-3.235103	-1.678207	-0.671874
34	6	0	-3.319396	0.739053	-0.701435
35	6	0	-4.619683	-1.741574	-0.585971
36	1	0	-2.661554	-2.600584	-0.700479
37	6	0	-4.707848	0.690185	-0.627803
38	1	0	-2.819179	1.694636	-0.775397
39	6	0	-5.340810	-0.548817	-0.561189
40	1	0	-5.145723	-2.687254	-0.544377
41	1	0	-5.305212	1.593646	-0.630873
42	7	0	-6.806868	-0.601159	-0.477957
43	8	0	-7.417929	0.467655	-0.456223
44	8	0	-7.338167	-1.711114	-0.433097
45	8	0	0.139668	1.138811	1.973232
46	8	0	-1.056242	2.297006	0.452792
47	6	0	-1.265279	3.363269	1.422577
48	1	0	-1.343257	2.920040	2.417062

49	1	0	-2.228931	3.793316	1.139194
50	6	0	-0.145463	4.387777	1.345944
51	1	0	-0.353044	5.207925	2.043039
52	1	0	0.812911	3.934838	1.610104
53	1	0	-0.065522	4.801261	0.336066

HF= -1430.5990801

Zero-point correction=	0.419772 (Hartree/Particle)
Thermal correction to Energy=	0.447880
Thermal correction to Enthalpy=	0.448824
Thermal correction to Gibbs Free Energy=	0.355432
Sum of electronic and zero-point Energies=	-1430.179308
Sum of electronic and thermal Energies=	-1430.151200
Sum of electronic and thermal Enthalpies=	-1430.150256
Sum of electronic and thermal Free Energies=	-1430.243648

Table S11: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **7'** in acetonitrile

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.909211	4.895715	0.074064
2	6	0	1.961734	4.958055	1.470210
3	6	0	1.957762	3.782174	2.222343
4	6	0	1.909109	2.543439	1.583875
5	6	0	1.855785	2.470190	0.181518
6	6	0	1.852747	3.662187	-0.564712
7	6	0	1.785892	1.181046	-0.571697
8	8	0	1.661212	1.188383	-1.792205
9	6	0	2.540477	-1.298009	-0.536570
10	7	0	3.386297	-1.971590	0.153306
11	6	0	4.027031	-3.126507	-0.478348
12	6	0	3.278688	-3.678911	-1.701048
13	6	0	2.873852	-2.523689	-2.617056
14	7	0	2.120035	-1.552580	-1.826659
15	1	0	1.910766	5.810142	-0.512460
16	1	0	2.004643	5.921871	1.970243
17	1	0	1.995306	3.827667	3.306931
18	1	0	1.806148	3.592499	-1.646191
19	1	0	5.050834	-2.837969	-0.760146
20	1	0	4.133922	-3.908984	0.283153
21	1	0	3.899862	-4.398722	-2.246183
22	1	0	2.374235	-4.206094	-1.373075
23	1	0	3.770522	-2.063381	-3.061764
24	1	0	2.240073	-2.870727	-3.440477
25	1	0	1.770659	-0.728876	-2.308201
26	6	0	0.461728	-0.565285	0.734958
27	6	0	1.852106	-0.141929	0.208988
28	1	0	2.492115	-0.003178	1.080278
29	6	0	-0.741690	-1.726713	2.677049
30	6	0	-0.741314	-0.251643	-0.096912
31	6	0	-1.104738	-1.059757	-1.184891
32	6	0	-1.508975	0.887327	0.194836
33	6	0	-2.217158	-0.747195	-1.959771
34	1	0	-0.509671	-1.934512	-1.421227
35	6	0	-2.620834	1.214439	-0.574659
36	1	0	-1.234766	1.519298	1.033673
37	6	0	-2.960535	0.387841	-1.643148
38	8	0	-0.638512	-2.105053	3.829355
39	8	0	-1.889124	-1.772333	1.967985
40	6	0	-3.057044	-2.281338	2.657712
41	1	0	-2.751224	-3.109279	3.301611
42	1	0	-3.695677	-2.659253	1.855813
43	6	0	-3.750773	-1.186916	3.454507
44	1	0	-4.672817	-1.578882	3.898939
45	1	0	-3.105304	-0.830906	4.262383
46	1	0	-4.012225	-0.342840	2.808086
47	6	0	0.421084	-1.184827	1.929850
48	1	0	1.350484	-1.340666	2.470313

49	1	0	1.899048	1.642114	2.186903
50	1	0	-3.222908	2.089012	-0.361422
51	8	0	-4.414432	-0.023823	-3.397704
52	8	0	-4.777609	1.729074	-2.153960
53	7	0	-4.137069	0.722535	-2.458639
54	1	0	-2.516022	-1.365027	-2.797581

HF=-1430.5806612

Zero-point correction=	0.433043 (Hartree/Particle)
Thermal correction to Energy=	0.461214
Thermal correction to Enthalpy=	0.462158
Thermal correction to Gibbs Free Energy=	0.368996
Sum of electronic and zero-point Energies=	-1430.147618
Sum of electronic and thermal Energies=	-1430.119447
Sum of electronic and thermal Enthalpies=	-1430.118503
Sum of electronic and thermal Free Energies=	-1430.211665

Table S12: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **5** in acetonitrile

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.381787	4.987820	-0.637261
2	6	0	0.902781	4.734458	-1.909996
3	6	0	0.672695	3.503276	-2.526157
4	6	0	-0.081295	2.526270	-1.877585
5	6	0	-0.608967	2.770905	-0.598255
6	6	0	-0.364860	4.012968	0.014396
7	6	0	-1.418739	1.771383	0.161686
8	8	0	-1.802802	2.032186	1.298599
9	6	0	-3.049189	-0.252256	-0.040574
10	7	0	-3.742393	-0.800052	-0.969734
11	6	0	-4.954158	-1.529366	-0.592522
12	6	0	-5.004052	-1.955442	0.882104
13	6	0	-4.600931	-0.775385	1.766353
14	7	0	-3.296942	-0.287844	1.319251
15	1	0	0.561907	5.944773	-0.155601
16	1	0	1.489065	5.494692	-2.418940
17	1	0	1.080178	3.301858	-3.512576
18	1	0	-0.773731	4.188740	1.003566
19	1	0	-5.822342	-0.897905	-0.833684
20	1	0	-5.032007	-2.409490	-1.242678
21	1	0	-6.005068	-2.310557	1.152407
22	1	0	-4.303680	-2.782518	1.051665
23	1	0	-5.363043	0.017795	1.705475
24	1	0	-4.520044	-1.073389	2.817515
25	1	0	-2.902697	0.507503	1.815203
26	6	0	-0.549181	-0.553923	-0.462736
27	6	0	-1.748068	0.426891	-0.506531
28	1	0	-1.945632	0.620523	-1.561797
29	6	0	0.539136	-2.500305	-1.752643
30	6	0	0.407596	-0.467813	0.680119
31	6	0	-0.009250	-0.691247	2.001939
32	6	0	1.745613	-0.130632	0.444578
33	6	0	0.892014	-0.592546	3.064277
34	1	0	-1.044551	-0.955414	2.190816
35	6	0	2.625528	-0.040683	1.517780
36	1	0	2.109189	0.055136	-0.557440
37	6	0	2.223799	-0.260918	2.834323
38	1	0	0.551132	-0.777536	4.078521
39	8	0	0.587509	-3.065350	-2.829883
40	8	0	1.335165	-2.805279	-0.707001
41	6	0	2.342669	-3.822519	-0.932726
42	1	0	1.906451	-4.620474	-1.538386
43	1	0	2.561156	-4.203172	0.067897
44	6	0	3.584176	-3.239761	-1.592886
45	1	0	4.364469	-4.007187	-1.654690
46	1	0	3.357278	-2.901425	-2.607773
47	1	0	3.976392	-2.394588	-1.017877
48	8	0	4.774650	0.467759	2.215064

49	8	0	4.397511	0.341593	0.072571
50	7	0	4.035224	0.282086	1.249211
51	1	0	2.944593	-0.175067	3.637851
52	6	0	-0.441905	-1.414795	-1.495477
53	1	0	-1.181151	-1.359788	-2.289299
54	1	0	-0.238539	1.572613	-2.369313

HF=-1430.6680813

Zero-point correction=	0.433289 (Hartree/Particle)
Thermal correction to Energy=	0.461300
Thermal correction to Enthalpy=	0.462245
Thermal correction to Gibbs Free Energy=	0.370437
Sum of electronic and zero-point Energies=	-1430.234792
Sum of electronic and thermal Energies=	-1430.206781
Sum of electronic and thermal Enthalpies=	-1430.205836
Sum of electronic and thermal Free Energies=	-1430.297644

Table S13: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for 5' in acetonitrile
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.416083	-2.524176	-1.166822
2	6	0	-6.044759	-1.483793	-1.858459
3	6	0	-5.389255	-0.263550	-2.028709
4	6	0	-4.105823	-0.074481	-1.515236
5	6	0	-3.467843	-1.116499	-0.820830
6	6	0	-4.137471	-2.341625	-0.652626
7	6	0	-2.084217	-1.010465	-0.264464
8	8	0	-1.559276	-1.969308	0.285597
9	6	0	-1.907787	1.461001	0.391682
10	7	0	-2.371002	2.462854	-0.271838
11	6	0	-2.951293	3.567037	0.497134
12	6	0	-3.449289	3.165516	1.893252
13	6	0	-2.360538	2.370667	2.615726
14	7	0	-1.927967	1.281050	1.749104
15	1	0	-5.924469	-3.475040	-1.032220
16	1	0	-7.043690	-1.625693	-2.262855
17	1	0	-5.877593	0.546868	-2.562900
18	1	0	-3.630128	-3.136866	-0.116815
19	1	0	-2.198958	4.366407	0.583117
20	1	0	-3.775967	3.990742	-0.089312
21	1	0	-3.727015	4.049604	2.478458
22	1	0	-4.343951	2.538334	1.796185
23	1	0	-1.516327	3.030620	2.871469
24	1	0	-2.736490	1.943468	3.552030
25	1	0	-1.266827	0.604320	2.127111
26	6	0	0.204176	0.133611	-0.195381
27	6	0	1.038500	0.901588	-0.926834
28	1	0	0.541953	1.588974	-1.612469
29	6	0	-1.300134	0.307200	-0.429118
30	1	0	-1.425131	0.636504	-1.462720
31	6	0	0.630602	-0.738866	0.955874
32	6	0	2.503570	1.088079	-0.904643
33	6	0	2.995473	2.379333	-1.184633
34	6	0	3.435989	0.066058	-0.673252
35	6	0	4.361735	2.655644	-1.191011
36	1	0	2.288041	3.178782	-1.389719
37	6	0	4.794241	0.364270	-0.686350
38	1	0	3.114415	-0.949580	-0.504891
39	6	0	5.285042	1.643791	-0.936969
40	8	0	0.286423	-0.523045	2.107730
41	8	0	1.454749	-1.728611	0.599703
42	6	0	1.921969	-2.626829	1.649318
43	1	0	2.004793	-2.060534	2.578816
44	1	0	2.917085	-2.926873	1.313963
45	6	0	0.981707	-3.811577	1.792198
46	1	0	1.373702	-4.498908	2.550882
47	1	0	-0.014482	-3.481114	2.096499
48	1	0	0.892789	-4.354011	0.845998

49	1	0	-3.620113	0.889148	-1.632223
50	1	0	6.352881	1.822520	-0.937786
51	8	0	6.952452	-0.455824	-0.487249
52	8	0	5.302492	-1.841056	-0.166785
53	7	0	5.753310	-0.725280	-0.429092
54	1	0	4.709303	3.663094	-1.398895

HF= -1430.6543322

Zero-point correction=	0.419772 (Hartree/Particle)
Thermal correction to Energy=	0.447829
Thermal correction to Enthalpy=	0.448773
Thermal correction to Gibbs Free Energy=	0.355705
Sum of electronic and zero-point Energies=	-1430.234560
Sum of electronic and thermal Energies=	-1430.206503
Sum of electronic and thermal Enthalpies=	-1430.205559
Sum of electronic and thermal Free Energies=	-1430.298627

Table S14: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **TS-7** in acetonitrile
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	6.278148	1.444452	-0.608104
2	6	0	6.723065	0.199179	-1.061616
3	6	0	5.799224	-0.798395	-1.379269
4	6	0	4.433509	-0.559221	-1.231139
5	6	0	3.977455	0.688416	-0.777269
6	6	0	4.914959	1.690348	-0.476317
7	6	0	2.524102	1.037229	-0.643437
8	8	0	2.175031	2.203858	-0.600714
9	6	0	1.662317	-1.335447	0.114040
10	7	0	0.979775	-2.371940	-0.358923
11	6	0	0.793024	-3.559757	0.482175
12	6	0	1.996873	-3.756710	1.407275
13	6	0	2.278084	-2.475951	2.196344
14	7	0	2.334970	-1.342369	1.269798
15	1	0	6.995197	2.223294	-0.364004
16	1	0	7.787217	0.008528	-1.171675
17	1	0	6.141772	-1.762280	-1.745302
18	1	0	4.547780	2.655663	-0.143652
19	1	0	-0.129472	-3.450193	1.070353
20	1	0	0.661716	-4.426778	-0.172414
21	1	0	1.811318	-4.583057	2.100545
22	1	0	2.878122	-4.018583	0.809967
23	1	0	1.494310	-2.298183	2.944857
24	1	0	3.235778	-2.540603	2.722005
25	1	0	2.588436	-0.432578	1.638044
26	6	0	0.007167	0.332314	-0.366823
27	6	0	-0.943178	-0.517414	-0.794410
28	1	0	0.049224	-1.911540	-0.851910
29	6	0	1.471730	-0.081127	-0.689550
30	1	0	1.463611	-0.395767	-1.739463
31	6	0	-0.097370	1.304359	0.753472
32	6	0	-2.375601	-0.415968	-0.667742
33	6	0	-3.115398	-1.400692	0.034907
34	6	0	-3.108860	0.601884	-1.329151
35	6	0	-4.497114	-1.355046	0.110622
36	1	0	-2.580916	-2.207411	0.529857
37	6	0	-4.492991	0.641174	-1.282992
38	1	0	-2.564420	1.365772	-1.873996
39	6	0	-5.182863	-0.334710	-0.556728
40	1	0	-5.060461	-2.097962	0.662212
41	1	0	-5.052825	1.422074	-1.783600
42	7	0	-6.634393	-0.290020	-0.493447
43	8	0	-7.215733	0.620196	-1.094479
44	8	0	-7.215348	-1.164019	0.160670
45	8	0	0.697509	1.307779	1.688259
46	8	0	-1.179316	2.094965	0.690463
47	6	0	-1.401260	2.993309	1.804592
48	1	0	-1.110240	2.489170	2.729289

49	1	0	-2.481367	3.158272	1.804819
50	6	0	-0.633718	4.293110	1.616368
51	1	0	-0.859034	4.981524	2.439406
52	1	0	0.443006	4.103314	1.604418
53	1	0	-0.914827	4.776365	0.675223
54	1	0	3.728644	-1.343005	-1.492050

HF=-1430.5064008

Zero-point correction=	0.428472 (Hartree/Particle)
Thermal correction to Energy=	0.456185
Thermal correction to Enthalpy=	0.457129
Thermal correction to Gibbs Free Energy=	0.366225
Sum of electronic and zero-point Energies=	-1430.077929
Sum of electronic and thermal Energies=	-1430.050216
Sum of electronic and thermal Enthalpies=	-1430.049272
Sum of electronic and thermal Free Energies=	-1430.140176

Table S15: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **TS-7'** in acetonitrile
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.155771	4.654326	-1.244656
2	6	0	2.296403	4.161175	-2.545696
3	6	0	1.521323	3.081116	-2.972410
4	6	0	0.603820	2.489924	-2.106118
5	6	0	0.453816	2.982106	-0.796916
6	6	0	1.240393	4.070523	-0.376923
7	6	0	-0.528611	2.428015	0.173582
8	8	0	-0.647664	2.940077	1.291128
9	6	0	-2.599066	0.922808	0.604413
10	7	0	-3.413141	-0.004476	0.131228
11	6	0	-4.541935	-0.560928	0.877055
12	6	0	-4.393249	-0.252039	2.371141
13	6	0	-4.008710	1.215271	2.579586
14	7	0	-2.842217	1.535992	1.756343
15	1	0	2.761327	5.491974	-0.910386
16	1	0	3.012910	4.616484	-3.224137
17	1	0	1.634610	2.691397	-3.979692
18	1	0	1.114761	4.441739	0.634400
19	1	0	-5.478783	-0.151936	0.478412
20	1	0	-4.550858	-1.641252	0.705662
21	1	0	-5.329455	-0.470368	2.893403
22	1	0	-3.614349	-0.892276	2.799821
23	1	0	-4.840927	1.877892	2.307252
24	1	0	-3.753345	1.413673	3.623850
25	1	0	-2.139238	2.229442	2.024264
26	6	0	-0.652766	-0.079942	-0.664848
27	6	0	-1.398160	1.253534	-0.279152
28	1	0	-1.844418	1.569145	-1.226634
29	6	0	-0.913957	-2.117245	-2.072590
30	6	0	0.581886	-0.427755	0.082753
31	6	0	0.751471	-0.115074	1.448598
32	6	0	1.622187	-1.131976	-0.565012
33	6	0	1.893867	-0.490384	2.145264
34	1	0	-0.025794	0.418353	1.985678
35	6	0	2.768486	-1.511905	0.119280
36	1	0	1.515757	-1.377560	-1.615727
37	6	0	2.896043	-1.186342	1.471688
38	8	0	-0.165541	-2.323440	-3.025575
39	8	0	-1.595938	-3.142342	-1.451037
40	6	0	-1.331669	-4.459168	-1.971792
41	1	0	-1.326931	-4.406001	-3.062978
42	1	0	-2.192955	-5.051441	-1.650289
43	6	0	-0.013448	-5.055176	-1.443975
44	1	0	0.763260	-5.065063	-2.213105
45	1	0	0.357000	-4.453351	-0.608519
46	1	0	-0.153764	-6.079075	-1.079125
47	6	0	-1.311108	-0.834193	-1.562266
48	1	0	-3.045735	-0.458447	-0.722614

49	1	0	0.032902	1.631970	-2.444828
50	1	0	3.569553	-2.045407	-0.377801
51	8	0	4.186914	-1.271420	3.389322
52	8	0	4.974622	-2.193912	1.577857
53	7	0	4.103713	-1.577813	2.196420
54	1	0	2.020115	-0.257544	3.195550

HF=-1430.4964404

Zero-point correction=	0.436872 (Hartree/Particle)
Thermal correction to Energy=	0.441682
Thermal correction to Enthalpy=	0.453571
Thermal correction to Gibbs Free Energy=	0.373289
Sum of electronic and zero-point Energies=	-1430.059568
Sum of electronic and thermal Energies=	-1430.054758
Sum of electronic and thermal Enthalpies=	-1430.042869
Sum of electronic and thermal Free Energies=	-1430.123151

Table S16: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for **TS-5** in acetonitrile
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.165339	5.067004	-0.592655
2	6	0	1.850912	4.602692	-1.719518
3	6	0	1.547581	3.349825	-2.256349
4	6	0	0.558532	2.558901	-1.675096
5	6	0	-0.138145	3.019929	-0.543591
6	6	0	0.178724	4.281229	-0.008436
7	6	0	-1.219267	2.239470	0.118408
8	8	0	-1.791064	2.696388	1.113239
9	6	0	-2.945942	0.321509	-0.065886
10	7	0	-3.372025	-0.689478	-0.803496
11	6	0	-4.518540	-1.519154	-0.422864
12	6	0	-4.869715	-1.325495	1.057158
13	6	0	-4.887360	0.165829	1.402470
14	7	0	-3.617890	0.764249	0.992995
15	1	0	1.403767	6.039761	-0.171799
16	1	0	2.624586	5.214781	-2.175153
17	1	0	2.085967	2.982782	-3.125044
18	1	0	-0.363403	4.624107	0.866232
19	1	0	-5.371802	-1.265428	-1.064086
20	1	0	-4.251606	-2.560781	-0.624690
21	1	0	-5.843192	-1.774283	1.277769
22	1	0	-4.120426	-1.827261	1.679780
23	1	0	-5.719105	0.672749	0.894449
24	1	0	-5.007143	0.323519	2.477865
25	1	0	-3.227604	1.598721	1.435126
26	6	0	-0.523037	-0.264139	-0.451401
27	6	0	-1.611325	0.900472	-0.496968
28	1	0	-1.723965	1.098719	-1.565779
29	6	0	0.033588	-2.464623	-1.459340
30	6	0	0.578733	-0.154572	0.544835
31	6	0	0.348748	0.235457	1.878001
32	6	0	1.892900	-0.496083	0.176619
33	6	0	1.381753	0.278452	2.815896
34	1	0	-0.656507	0.495167	2.195165
35	6	0	2.905616	-0.442724	1.129173
36	1	0	2.119939	-0.808016	-0.835563
37	6	0	2.680597	-0.063325	2.452058
38	1	0	1.169604	0.576566	3.838813
39	8	0	0.992650	-2.576183	-2.215005
40	8	0	-0.476000	-3.536790	-0.763991
41	6	0	0.221052	-4.783005	-0.962601
42	1	0	0.439763	-4.890911	-2.027662
43	1	0	-0.504766	-5.546364	-0.669003
44	6	0	1.506743	-4.880125	-0.124835
45	1	0	1.559675	-5.829175	0.420415
46	1	0	2.401583	-4.782579	-0.744609
47	1	0	1.522209	-4.072761	0.613956
48	8	0	5.133883	-0.865940	1.609239

49	8	0	4.504365	-0.948554	-0.474748
50	7	0	4.281840	-0.779146	0.722310
51	1	0	3.503954	-0.039207	3.154340
52	6	0	-0.770997	-1.280629	-1.285322
53	1	0	-2.549770	-1.109027	-1.352147
54	1	0	0.355154	1.576804	-2.089445

HF=-1430.5904383

Zero-point correction=	0.445721 (Hartree/Particle)
Thermal correction to Energy=	0.448923
Thermal correction to Enthalpy=	0.453970
Thermal correction to Gibbs Free Energy=	0.375238
Sum of electronic and zero-point Energies=	-1430.144717
Sum of electronic and thermal Energies=	-1430.141515
Sum of electronic and thermal Enthalpies=	-1430.136468
Sum of electronic and thermal Free Energies=	-1430.215200

Table S17: Cartesian coordinates and energy of B3LYP/6-31++G(d,p) optimized conformation for TS-5' in acetonitrile
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.803078	-2.234841	-0.707100
2	6	0	-6.404068	-1.116695	-1.292676
3	6	0	-5.630373	-0.002698	-1.623860
4	6	0	-4.260994	0.001044	-1.360544
5	6	0	-3.648831	-1.117281	-0.773244
6	6	0	-4.434403	-2.237959	-0.456968
7	6	0	-2.175238	-1.205033	-0.500819
8	8	0	-1.654205	-2.283994	-0.279874
9	6	0	-1.745353	1.329447	0.038718
10	7	0	-1.271964	2.428769	-0.547792
11	6	0	-1.299307	3.705182	0.176517
12	6	0	-2.514982	3.764686	1.104143
13	6	0	-2.547960	2.535800	2.014947
14	7	0	-2.409400	1.326274	1.199599
15	1	0	-6.402456	-3.104331	-0.451770
16	1	0	-7.471917	-1.115621	-1.494360
17	1	0	-6.092516	0.862824	-2.090550
18	1	0	-3.945155	-3.101179	-0.017892
19	1	0	-0.370154	3.818141	0.753385
20	1	0	-1.330934	4.516122	-0.557624
21	1	0	-2.483022	4.674005	1.712493
22	1	0	-3.432270	3.800728	0.504672
23	1	0	-1.734886	2.575439	2.752443
24	1	0	-3.494141	2.476775	2.561711
25	1	0	-2.422271	0.428346	1.675042
26	6	0	0.180321	-0.056604	-0.205128
27	6	0	1.000586	0.871436	-0.737959
28	1	0	-0.298403	2.124652	-0.998166
29	6	0	-1.314388	0.060795	-0.628243
30	1	0	-1.299113	0.269141	-1.703515
31	6	0	0.360450	-0.842050	1.042058
32	6	0	2.434372	0.995545	-0.551455
33	6	0	2.999428	2.224554	-0.137519
34	6	0	3.329664	-0.047735	-0.873553
35	6	0	4.375156	2.394029	-0.000122
36	1	0	2.332043	3.054976	0.080159
37	6	0	4.700404	0.159477	-0.768094
38	1	0	2.957519	-1.009253	-1.199670
39	6	0	5.253618	1.361509	-0.325002
40	8	0	-0.488995	-0.869279	1.931139
41	8	0	1.557126	-1.440057	1.147913
42	6	0	1.827404	-2.164355	2.372205
43	1	0	1.377634	-1.625940	3.209851
44	1	0	2.915855	-2.139369	2.464715
45	6	0	1.304980	-3.590272	2.283023
46	1	0	1.564701	-4.140441	3.195220
47	1	0	0.217245	-3.593010	2.170937
48	1	0	1.746936	-4.110873	1.427663

49	1	0	-3.673863	0.872986	-1.633028
50	1	0	6.328053	1.470570	-0.255413
51	8	0	6.821380	-0.756004	-0.984492
52	8	0	5.116327	-1.995283	-1.528289
53	7	0	5.610349	-0.944016	-1.119522
54	1	0	4.770720	3.347172	0.340567

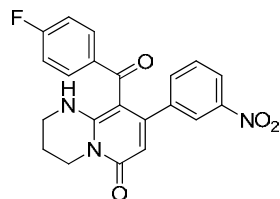
HF=-1430.5754383

Zero-point correction=	0.429619 (Hartree/Particle)
Thermal correction to Energy=	0.457089
Thermal correction to Enthalpy=	0.458033
Thermal correction to Gibbs Free Energy=	0.368095
Sum of electronic and zero-point Energies=	-1430.145819
Sum of electronic and thermal Energies=	-1430.118349
Sum of electronic and thermal Enthalpies=	-1430.117405
Sum of electronic and thermal Free Energies=	-1430.207343

Procedures and spectral data

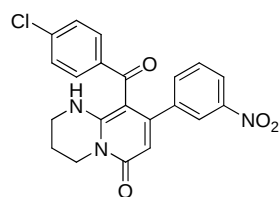
General Preparation of 3 or 4: To a solution of Heterocyclic ketene amins (HKAs) **1** (1 mmol) in CH₃CN (25 mL) was added 0.219g of ethyl 3-(p-nitrophenyl) propiolate **2a** or ethyl 3-(m-nitrophenyl)propiolate **2b** (1 mmol) at rt. The resulting mixture was refluxed for 6h and then quenched with H₂O. The mixture was extracted with EtOAc and combined organic layer was dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Purification by silica gel column chromatography (PE : EtOAc = 1 : 1) provided analytically pure product 3 or 4 in 70~91% yield.

9-(4-Fluorobenzoyl)-8-(3-nitrophenyl)-3,4-dihydro-1H-pyrido[1,2-a]pyrimidin-6(2H)-one (3c)



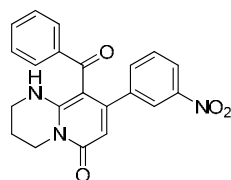
Yellow solid; mp: 228.3-230.0°C. IR (KBr): 3061, 2876, 1664, 1575, 1342, 852, 717cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 1.99-2.04 (m, 2H, CH₂), 3.48-3.53 (m, 2H, CH₂), 3.97-4.02 (m, 2H, CH₂), 5.64-5.68 (m, 1H, CH), 6.83 (t, *J* = 8.53 Hz, 2H, PhH), 7.22 (t, *J* = 6.65 Hz, 2H, PhH), 7.36 (t, *J* = 7.88 Hz, 1H, PhH), 7.53 (d, *J* = 7.45 Hz, 1H, PhH), 7.74-7.78 (m, 1H, PhH), 7.89 (d, *J* = 7.95 Hz, 1H, PhH), 10.26 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 19.0, 39.7, 39.9, 96.8, 106.1, 114.7-114.8 (d, *J* = 21.25 Hz), 122.6, 123.3, 130.1, 131.5, 134.9, 139.0, 142.5, 147.2, 152.1, 154.3, 160.5, 162.2-164.2 (d, *J* = 247.5Hz), 192.3. HR-TOFMS calcd for C₂₁H₁₆N₃O₄F [M⁺], 393.1131; found, 393.1125.

9-(4-Chlorobenzoyl)-8-(3-nitrophenyl)-3,4-dihydro-1H-pyrido[1,2-a]pyrimidin-6(2H)-one(3b)



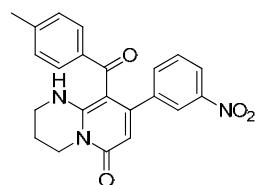
Yellow solid; mp: 262.9-264.1°C. IR (KBr): 3073, 1662, 1569, 1473, 1335, 846, 719 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 2.03-2.08 (m, 2H, CH₂), 3.49-3.53 (m, 2H, CH₂), 3.98-4.02 (m, 2H, CH₂), 5.64-5.67 (m, 1H, CH), 7.06 (d, *J* = 8.05 Hz, 2H, PhH), 7.15 (d, *J* = 8.05 Hz, 2H, PhH), 7.36 (t, *J* = 7.83 Hz, 1H, PhH), 7.52 (d, *J* = 7.25 Hz, 1H, PhH), 7.74-7.76 (m, 1H, PhH), 7.90 (d, *J* = 7.5 Hz, 1H, PhH), 10.30 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 19.0, 39.8, 39.9, 96.9, 106.3, 122.6, 123.4, 127.9, 130.1, 130.6, 135.0, 135.2, 141.3, 142.4, 147.2, 152.1, 154.4, 160.4, 192.3. HR-TOFMS calcd for C₂₁H₁₆N₃O₄Cl [M⁺], 409.0830; found, 409.0829.

9-Benzoyl-8-(3-nitrophenyl)-3,4-dihydro-1H-pyrido[1,2-a]pyrimidin-6(2H)-one (3d)



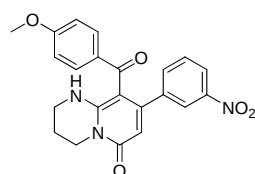
Yellow solid; mp: 246.6-247.2°C. IR (KBr): 3083, 1665, 1569, 1476, 1341, 838, 700cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 1.99-2.05 (m, 2H, CH₂), 3.44-3.46 (m, 2H, CH₂), 3.99-4.03 (m, 2H, CH₂), 5.64-5.66 (m, 1H, CH), 7.01 (d, *J* = 6.55 Hz, 2H, PhH), 7.08 (d, *J* = 6.25 Hz, 1H, PhH), 7.15 (d, *J* = 6.5 Hz, 2H, PhH), 7.32 (t, *J* = 7.25 Hz, 1H, PhH), 7.53 (d, *J* = 6.85 Hz, 1H, PhH), 7.74-7.76 (m, 1H, PhH), 7.83 (d, *J* = 7.25 Hz, 1H, PhH), 10.31 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 19.0, 39.8, 39.9, 96.9, 106.0, 122.5, 123.4, 127.9, 128.8, 129.9, 130.6, 134.9, 142.5, 147.1, 152.3, 154.3, 160.5, 193.8. HR-TOFMS calcd for C₂₁H₁₈N₃O₄ [(M+H)⁺], 376.1297; found, 376.1297.

9-(4-Methylbenzoyl)-8-(3-nitrophenyl)-3,4-dihydro-1H-pyrido[1,2-a]pyrimidin-6(2H)-one(3e)



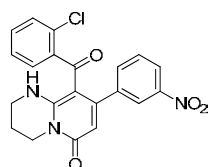
Yellow solid; mp: 297.2-298.8°C. IR (KBr):3084, 1668, 1569, 1476, 1338, 837, 704 cm⁻¹. ¹H NMR(500 MHz, DMSO-*d*₆): δ = 2.03-2.05 (m, 2H, CH₂), 2.08 (s, 3H, CH₃), 3.48-3.51 (m, 2H, CH₂), 3.98-4.02 (m, 2H, CH₂), 5.64-5.66 (m, 1H, CH), 6.82 (d, *J* = 7.6Hz, 2H, PhH), 7.05 (d, *J* = 7.7Hz, 2H, PhH), 7.34 (t, *J* = 7.9Hz, 1H, PhH), 7.53 (d, *J* = 7.6Hz, 1H, PhH), 7.72-7.74 (m, 1H, PhH), 7.86 (d, *J* = 7.6Hz, 1H, PhH), 10.16 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 19.1, 21.1, 39.8, 39.9, 97.0, 105.7, 122.4, 123.3, 128.3, 128.9, 129.9, 134.8, 139.8, 140.6, 142.5, 147.1, 152.3, 154.1, 160.5, 193.8. HR-TOFMS calcd for C₂₂H₁₉N₃O₄ [M⁺], 389.1384; found, 389.1376.

9-(4-Methoxybenzoyl)-8-(3-nitrophenyl)-3,4-dihydro-1H-pyrido[1,2-a]pyrimidin-6(2H)-one (3f)



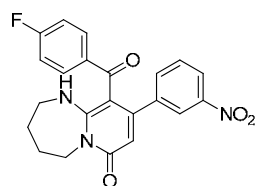
Yellow solid; mp: 254.2-255.8°C. IR (KBr):3239, 1662, 1570, 1341, 839, 700cm⁻¹. ¹H NMR(500 MHz, DMSO-*d*₆): δ = 2.00-2.04 (m, 2H, CH₂), 3.47-3.49 (m, 2H, CH₂), 3.61 (s, 3H, OCH₃), 3.98-4.01 (m, 2H, CH₂), 5.64-5.66 (m, 1H, CH), 6.56 (d, *J* = 8.4Hz, 2H, PhH), 7.16 (d, *J* = 8.4Hz, 2H, PhH), 7.36 (t, *J* = 7.93Hz, 1H, PhH), 7.54 (d, *J* = 7.4Hz, 1H, PhH), 7.77-7.79 (m, 1H, PhH), 7.88 (d, *J* = 8.05Hz, 1H, PhH), 9.98 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 19.1, 39.8, 39.9, 55.6, 96.9, 105.3, 113.2, 122.5, 123.3, 129.9, 131.1, 134.8, 142.6, 147.2, 152.2, 153.8, 160.5, 161.4, 193.0. HR-TOFMS calcd for C₂₂H₁₉N₃O₅ [M⁺], 405.1331; found, 405.1325.

9-(2-Chlorobenzoyl)-8-(3-nitrophenyl)-3,4-dihydro-1H-pyrido[1,2-a]pyrimidin-6(2H)-one(3g)



Yellow solid; mp: 207.6-209.4°C. IR (KBr): 3202, 2935, 1642, 1570, 1491, 1443, 1234, 821, 765 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 2.07-2.09(m, 2H, CH₂), 3.56-3.58 (m, 2H, CH₂), 4.00-4.02 (m, 2H, CH₂), 5.51-5.53 (m, 1H, CH), 6.91 (d, *J* = 2.15 Hz, 1H, PhH), 6.95 (t, *J* = 4.33 Hz, 1H, PhH), 6.99 (t, *J* = 4.4 Hz, 1H, PhH), 7.05 (d, *J* = 3.7 Hz, 1H, PhH), 7.33 (t, *J* = 7.7 Hz, 1H, PhH), 7.45 (d, *J* = 5.1 Hz, 1H, PhH), 7.74-7.76 (m, 1H, PhH), 7.86 (d, *J* = 7.95Hz, 1H, PhH), 11.06 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 18.8, 39.8, 40.0, 98.2, 107.4, 122.6, 126.7, 129.6, 129.7, 130.2, 130.5, 141.8, 146.9, 152.6, 155.0, 160.2, 190.0. HR-TOFMS calcd for C₂₁H₁₆N₃O₄Cl [M⁺], 409.0834; found, 409.0829.

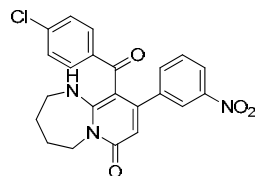
10-(4-Fluorobenzoyl)-9-(3-nitrophenyl)-2,3,4,5-tetrahydropyrido[1,2-a][1,3]diazepin-7(1H)-one(3h)



Yellow solid; mp: 297.7-300.1°C. IR (KBr): 3298, 3077, 1671, 1599, 1528, 1345, 801, 709 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 1.85-1.89 (m, 4H, 2CH₂), 3.44-3.47 (m, 2H, CH₂), 4.27-4.30 (m, 2H, CH₂), 5.92-5.94 (m, 1H, CH), 6.91 (t, *J* = 8.15 Hz, 2H, PhH), 7.35

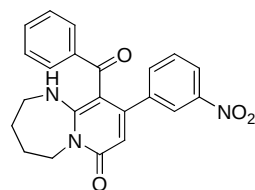
(d, $J = 5.7$ Hz, 2H, PhH), 7.40 (t, $J = 7.83$ Hz, 1H, PhH), 7.55 (d, $J = 7.2$ Hz, 1H, PhH), 7.78-7.80 (m, 1H, PhH), 7.94 (d, $J = 7.65$ Hz, 1H, PhH), 8.97 (br, 1H, NH). ^{13}C NMR (125 MHz, DMSO- d_6): $\delta = 24.2, 25.2, 44.7, 45.5, 101.9, 109.9, 114.9-115.1$ (d, $J = 21.25$ Hz), 122.9-123.1 (d, $J = 20$ Hz), 124.5, 130.2, 131.8, 134.8, 138.2, 141.9, 147.4, 151.7, 158.2, 161.8-162.7 (d, $J = 117.5$ Hz), 164.7, 193.5. HR-TOFMS calcd for $\text{C}_{22}\text{H}_{19}\text{FN}_3\text{O}_4$ [(M+H) $^+$], 408.1360; found, 408.1347.

10-(4-Chlorobenzoyl)-9-(3-nitrophenyl)-2, 3, 4, 5-tetrahydropyrido[1, 2-a][1, 3] diazepin-7(1H)-one(3i)



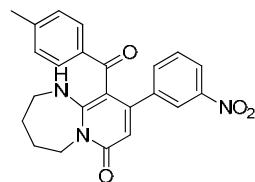
Yellow solid; mp: 196.8-197.6°C. IR (KBr): 3226, 2922, 1668, 1566, 1463, 1336, 797, 705 cm^{-1} . ^1H NMR (500 MHz, DMSO- d_6): $\delta = 1.86-1.88$ (m, 4H, 2CH $_2$), 3.46-3.49 (m, 2H, CH $_2$), 4.27-4.30 (m, 2H, CH $_2$), 5.90-5.92 (m, 1H, CH), 7.14 (d, $J = 8.4$ Hz, 2H, PhH), 7.27 (d, $J = 8.4$ Hz, 2H, PhH), 7.40 (t, $J = 7.98$ Hz, 1H, PhH), 7.54 (d, $J = 7.7$ Hz, 1H, PhH), 7.77-7.79 (m, 1H, PhH), 7.94 (d, $J = 8.0$ Hz, 1H, PhH), 9.10 (br, 1H, NH). ^{13}C NMR (125 MHz, DMSO- d_6): $\delta = 24.2, 25.1, 44.7, 45.4, 101.7, 109.9, 122.9, 123.1, 128.1, 130.2, 130.8, 134.8, 136.0, 140.4, 141.9, 147.3, 151.7, 158.3, 161.8, 193.5$. HR-TOFMS calcd for $\text{C}_{22}\text{H}_{19}\text{ClN}_3\text{O}_4$ [(M+H) $^+$], 424.1064; found, 424.1054.

10-Benzoyl-9-(3-nitrophenyl)-2,3,4,5-tetrahydropyrido[1,2-a][1,3]diazepin-7(1H)- one(3j)



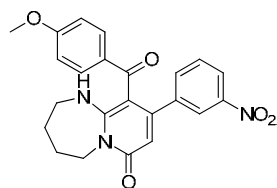
Yellow solid; mp: 238.4-242.8°C. IR (KBr): 3305, 3069, 1668, 1596, 1529, 1346, 749, 699 cm^{-1} . ^1H NMR (500 MHz, DMSO- d_6): $\delta = 1.85-1.89$ (m, 4H, 2CH $_2$), 3.44-3.48 (m, 2H, CH $_2$), 4.28-4.31 (m, 2H, CH $_2$), 5.89-5.91 (m, 1H, CH), 7.07 (t, $J = 7.18$ Hz, 2H, PhH), 7.17 (t, $J = 6.88$ Hz, 1H, PhH), 7.26 (d, $J = 7.25$ Hz, 1H, PhH), 7.29-7.31 (m, 1H, PhH), 7.35 (t, $J = 7.80$ Hz, 1H, PhH), 7.53 (d, $J = 7.40$ Hz, 1H, PhH), 7.77-7.79 (m, 1H, PhH), 7.87 (d, $J = 7.75$ Hz, 1H, PhH), 9.00 (br, 1H, NH). ^{13}C NMR (125 MHz, DMSO- d_6): $\delta = 24.3, 25.3, 44.7, 45.5, 102.0, 109.8, 122.8, 123.1, 128.0, 129.0, 130.1, 131.4, 134.7, 141.6, 141.9, 147.3, 151.8, 158.2, 161.8, 195.0$. HR-TOFMS calcd for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_4$ [M $^+$], 389.1379; found, 389.1376.

10-(4-Methylbenzoyl)-9-(3-nitrophenyl)-2,3,4,5-tetrahydropyrido[1,2-a][1,3]diazepin-7(1H)-one(3k)



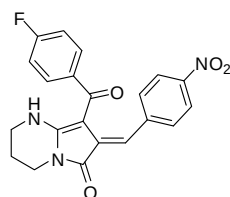
Yellow solid; mp: 215.2-215.7°C. IR (KBr): 3304, 1665, 1605, 1526, 1355, 787, 744 cm^{-1} . ^1H NMR (500 MHz, DMSO- d_6): $\delta = 1.84-1.88$ (m, 4H, 2CH $_2$), 2.12 (s, 3H, CH $_3$), 3.20-3.25 (m, 2H, CH $_2$), 4.23-4.29 (m, 2H, CH $_2$), 5.89-5.92 (m, 1H, CH), 6.89 (d, $J = 5.75$ Hz, 2H, PhH), 7.17 (d, $J = 6.3$ Hz, 2H, PhH), 7.37 (d, $J = 7.05$ Hz, 1H, PhH), 7.52 (d, $J = 6.25$ Hz, 1H, PhH), 7.75-7.77 (m, 1H, PhH), 7.89 (d, $J = 6.75$ Hz, 1H, PhH), 8.69 (br, 1H, NH). ^{13}C NMR (125 MHz, DMSO- d_6): $\delta = 21.2, 24.4, 25.4, 44.7, 45.6, 102.4, 109.7, 122.7, 123.1, 128.6, 129.2, 130.1, 134.6, 138.8, 141.7, 141.9, 147.3, 151.7, 157.8, 161.8, 194.8$. HR-TOFMS calcd for $\text{C}_{23}\text{H}_{22}\text{N}_3\text{O}_4$ [(M+H) $^+$], 404.1610; found, 404.1609.

10-(4-Methoxybenzoyl)-9-(3-nitrophenyl)-2,3,4,5-tetrahydropyrido[1,2-a][1,3]diazepin-7(1H)-one(3l)



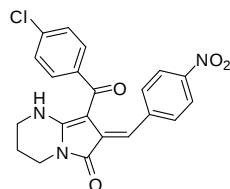
Yellow solid; mp: 196.5-198.4°C. IR (KBr): 3307, 2940, 1664, 1603, 1526, 1354, 845, 738 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 1.81-1.86 (m, 4H, 2CH₂), 3.52-3.55 (m, 2H, CH₂), 3.64 (s, 3H, OCH₃), 4.26-4.30 (m, 2H, CH₂), 5.93-5.95 (m, 1H, CH), 6.64 (d, *J* = 8.3 Hz, 2H, PhH), 7.29 (d, *J* = 8.3 Hz, 1H, PhH), 7.34-7.36 (m, 1H, PhH), 7.40 (t, *J* = 7.85 Hz, 1H, PhH), 7.56 (d, *J* = 7.4 Hz, 1H, PhH), 7.80-7.82 (m, 1H, PhH), 7.92 (d, *J* = 7.9 Hz, 1H, PhH), 8.47 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 24.4, 25.5, 44.7, 45.7, 55.7, 102.5, 109.6, 113.4, 122.9, 130.0, 130.1, 131.5, 133.7, 134.6, 141.8, 147.3, 151.5, 157.5, 161.8, 162.1, 193.9. HR-TOFMS calcd for C₂₃H₂₂N₃O₅ [(M+H)⁺], 420.1559; found, 420.1551.

9-(4-Fluorobenzoyl)-8-(4-nitrophenyl)-3,4-dihydro-1H-pyrido[1,2-a]pyrimidin-6(2H)-one(4c)



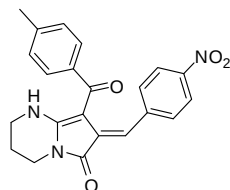
Red solid; mp: 236.6-237.6°C. IR(KBr): 3129, 1727, 1637, 1593, 1510, 1335, 855, 766 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 2.00-2.04 (m, 2H, CH₂), 3.50-3.54 (m, 2H, CH₂), 3.67-3.71 (m, 2H, CH₂), 6.72 (t, *J* = 8.5 Hz, 2H, PhH), 6.86-6.88 (m, 1H, CH), 7.13 (d, *J* = 8.3 Hz, 2H, PhH), 7.37 (t, *J* = 6.63 Hz, 2H, PhH), 7.70 (d, *J* = 8.1 Hz, 2H, PhH), 9.97 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 19.6, 37.2, 39.6, 89.7, 114.5-114.7 (d, *J* = 21.25 Hz), 118.5, 122.6, 129.2, 129.7, 130.5, 130.9, 138.4, 144.1, 145.0, 159.8, 168.2, 183.9. HR-TOFMS calcd for C₂₁H₁₇N₃O₄F [(M+H)⁺], 394.1205; found, 394.1203.

9-(4-Chlorobenzoyl)-8-(4-nitrophenyl)-3,4-dihydro-1H-pyrido[1,2-a]pyrimidin-6(2H)-one(4a)



Red solid; mp: 234.8-236.4°C. IR(KBr): 3225, 1728, 1640, 1589, 1513, 1335, 847, 770cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 2.00-2.04 (m, 2H, CH₂), 3.49-3.54 (m, 2H, CH₂), 3.70-3.71 (m, 2H, CH₂), 6.89-6.91 (m, 1H, CH), 6.93 (d, *J* = 8.1 Hz, 2H, PhH), 7.10 (d, *J* = 8.25 Hz, 2H, PhH), 7.29 (d, *J* = 8.15 Hz, 2H, PhH), 7.70 (d, *J* = 8.3 Hz, 2H, PhH), 10.06 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 19.5, 37.4, 39.8, 89.9, 118.7, 122.6, 127.8, 129.7, 129.8, 131.0, 135.3, 140.6, 144.2, 145.1, 159.9, 168.1, 183.7. HR-TOFMS calcd for C₂₁H₁₆N₃O₄Cl[M⁺], 409.0833; found, 409.0829.

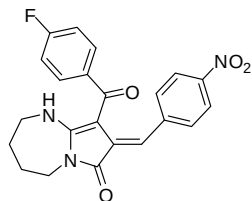
9-(4-Methylbenzoyl)-8-(4-nitrophenyl)-3,4-dihydro-1H-pyrido[1,2-a]pyrimidin-6(2H)-one(4e)



Red solid; mp: 230.1-231.1 . IR (KBr): 3418, 1723, 1641, 1594, 1515, 1334, 839, 756 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 1.93-1.97 (m, 2H, CH₂), 2.03 (s, 3H, CH₃), 3.58-3.60 (m, 2H, CH₂), 3.68-3.70 (m, 2H, CH₂), 6.67 (d, *J* = 7.7 Hz, 2H, PhH), 6.87-6.89 (m, 1H, CH), 7.05 (d, *J* = 8.4 Hz, 2H, PhH), 7.17 (d, *J* = 7.75 Hz, 2H, PhH), 7.63 (d, *J* = 6.7 Hz, 2H, PhH), 10.07 (br, 1H, NH). ¹³C NMR

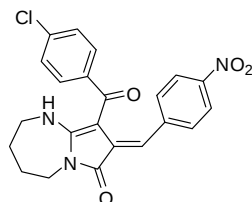
(125 MHz, DMSO-*d*₆): δ = 19.6, 20.8, 37.3, 39.5, 89.9, 118.4, 122.4, 128.0, 128.2, 129.5, 130.9, 139.3, 140.3, 144.2, 144.9, 159.8, 168.2, 185.3. HR-TOFMS calcd for C₂₂H₂₀N₃O₄ [(M+H)⁺], 390.1443; found, 390.1454.

10-(4-Fluorobenzoyl)-9-(4-nitrophenyl)-2,3,4,5-tetrahydropyrido[1,2-a][1,3]diazepin-7(1H)-one(4h)



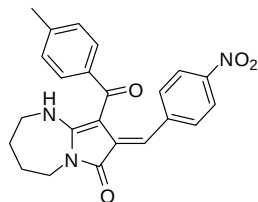
Red solid; mp: 220.0-222.3 °C. IR (KBr): 3417, 1719, 1592, 1544, 1503, 1338, 846, 773 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 1.96-2.00 (m, 4H, 2CH₂), 3.74-3.77 (m, 2H, CH₂), 3.98-4.01 (m, 2H, CH₂), 6.73 (t, *J* = 8.5 Hz, 2H, PhH), 6.87-6.90 (m, 1H, CH), 7.15 (d, *J* = 8.3 Hz, 2H, PhH), 7.39 (t, *J* = 6.48 Hz, 2H, PhH), 7.73 (d, *J* = 8.25 Hz, 2H, PhH), 10.50 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 24.5, 26.4, 39.9, 42.3, 90.9, 114.5-114.7 (d, *J* = 21.25 Hz), 119.2, 122.7, 129.1, 129.8, 130.7, 138.2, 144.0, 145.1, 162.5, 165.0, 169.0, 184.5. HR-TOFMS calcd for C₂₂H₁₉FN₃O₄ [(M+H)⁺], 408.1360; found, 408.1360.

10-(4-Chlorobenzoyl)-9-(4-nitrophenyl)-2,3,4,5-tetrahydropyrido[1,2-a][1,3]diazepin-7(1H)-one(4i)



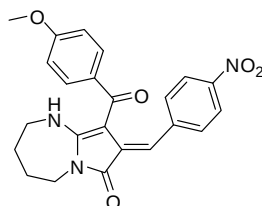
Red solid; mp: 204.6-206.8 °C. IR (KBr): 3067, 2928, 1726, 1626, 1499, 1331, 827, 767 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 2.00-2.04 (m, 4H, 2CH₂), 3.78-3.82 (m, 2H, CH₂), 4.02-4.05 (m, 2H, CH₂), 6.93-6.95 (m, 1H, CH), 6.97 (d, *J* = 8.3 Hz, 2H, PhH), 7.14 (d, *J* = 8.5 Hz, 2H, PhH), 7.33 (d, *J* = 8.35 Hz, 2H, PhH), 7.75 (d, *J* = 8.55 Hz, 2H, PhH), 10.65 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 24.5, 26.4, 40.3, 42.3, 91.0, 119.5, 122.7, 127.9, 129.8, 130.0, 130.1, 135.4, 140.4, 144.1, 145.2, 165.2, 169.0, 184.3. HR-TOFMS calcd for C₂₂H₁₉ClN₃O₄ [(M+H)⁺], 424.1064; found, 424.1062.

10-(4-Methylbenzoyl)-9-(4-nitrophenyl)-2,3,4,5-tetrahydropyrido[1,2-a][1,3]diazepin-7(1H)-one(4k)



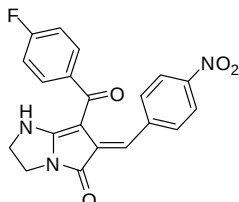
Red solid; mp: 215.7-216.4 °C. IR (KBr): 3072, 1662, 1569, 1473, 1335, 846, 719 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 1.94-1.98 (m, 4H, 2CH₂), 1.97 (s, 3H, CH₃), 3.74-3.76 (m, 2H, CH₂), 3.97-4.00 (m, 2H, CH₂), 6.67 (d, *J* = 7.55 Hz, 2H, PhH), 6.88-6.90 (m, 1H, CH), 7.05 (d, *J* = 8.3 Hz, 2H, PhH), 7.18 (d, *J* = 7.55 Hz, 2H, PhH), 7.63 (t, *J* = 8.23 Hz, 2H, PhH), 10.65 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 20.8, 24.5, 26.5, 39.9, 42.3, 91.1, 119.2, 122.4, 127.5, 128.2, 129.3, 130.9, 139.0, 140.4, 144.1, 145.0, 165.1, 169.1, 185.8. HR-TOFMS calcd for C₂₃H₂₂N₃O₄ [(M+H)⁺], 404.1610; found, 404.1613.

10-(4-Methoxybenzoyl)-9-(4-nitrophenyl)-2,3,4,5-tetrahydropyrido[1,2-a][1,3]diazepin-7(1H)-one(4l)



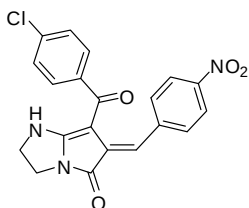
Red solid; mp: 192.2-194.3°C. IR (KBr): 3429, 2923, 1724, 1587, 1331, 838, 769 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 1.95-1.98 (m, 4H, 2CH₂), 3.50-3.53 (m, 2H, CH₂), 3.71-3.73 (m, 2H, CH₂), 3.88 (s, 3H, OCH₃), 6.41 (d, *J* = 4.23 Hz, 2H, PhH), 6.88-6.90 (m, 1H, CH), 7.08 (d, *J* = 4.23 Hz, 2H, PhH), 7.26 (d, *J* = 4.23 Hz, 2H, PhH), 7.66 (t, *J* = 6.85 Hz, 2H, PhH), 10.56 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 24.6, 26.5, 39.8, 42.3, 55.7, 91.0, 113.5, 119.0, 122.4, 129.7, 130.0, 131.0, 134.2, 144.0, 145.0, 161.4, 165.0, 169.2, 185.3. HR-TOFMS calcd for C₂₂H₁₉N₃O₄ [(M+H)⁺], 389.1376; found, 389.1372.

8-(4-Fluorobenzoyl)-7-(4-nitrophenyl)-2,3-dihydroimidazo[1,2-a]pyridin-5(1H)-one (4m)



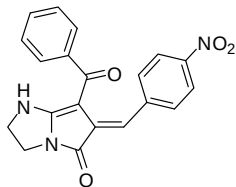
Red solid; mp: 253.8-255.7°C. IR (KBr): 3292, 1701, 1589, 1497, 1336, 845, 772 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 3.63-3.67 (m, 2H, CH₂), 3.92-3.96 (m, 2H, CH₂), 7.00 (t, *J* = 8.58 Hz, 2H, PhH), 7.13-7.17 (m, 2H, PhH), 7.35-7.37 (m, 1H, PhH), 7.78 (d, *J* = 8.35 Hz, 2H, PhH), 8.20 (d, *J* = 8.25 Hz, 2H, PhH), 9.82 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 42.4, 44.1, 85.0, 114.4-114.5 (d, *J* = 20 Hz), 123.8, 129.1, 130.7, 133.9, 136.2, 140.3, 143.0, 147.0, 163.2, 164.1, 168.6, 184.9. HR-TOFMS calcd for C₂₀H₁₄N₃O₄F [M⁺], 379.0949; found, 379.0968.

8-(4-Chlorobenzoyl)-7-(4-nitrophenyl)-2,3-dihydroimidazo[1,2-a]pyridin-5(1H)-one (4n)



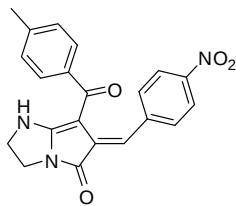
Red solid; mp: 264.2-265.4°C. IR (KBr): 3303, 2921, 1670, 1581, 1496, 1336, 823, 764 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 3.63-3.67 (m, 2H, CH₂), 3.90-3.96 (m, 2H, CH₂), 7.10 (d, *J* = 8.3 Hz, 2H, PhH), 7.24 (d, *J* = 8.3 Hz, 2H, PhH), 7.36-7.38 (m, 1H, PhH), 7.77 (d, *J* = 8.7 Hz, 2H, PhH), 8.20 (d, *J* = 8.75 Hz, 2H, PhH), 9.81 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 42.4, 44.1, 85.0, 123.8, 127.7, 128.6, 130.7, 133.2, 133.7, 136.5, 142.6, 142.9, 147.0, 164.1, 168.5, 184.7. HR-TOFMS calcd for C₂₀H₁₅N₃O₄Cl [(M+H)⁺], 396.0751; found, 396.0770.

8-Benzoyl-7-(4-nitrophenyl)-2,3-dihydroimidazo[1,2-a]pyridin-5(1H)-one (4o)



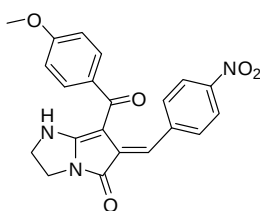
Red solid; mp: 258.4-260.0°C. IR (KBr): 3453, 3283, 1700, 1588, 1526, 1245, 751, 704 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 3.63-3.66 (m, 2H, CH₂), 3.88-3.92 (m, 2H, CH₂), 7.11 (d, *J* = 7.2 Hz, 2H, PhH), 7.15 (d, *J* = 7.2 Hz, 2H, PhH), 7.33-7.35 (m, 1H, PhH), 7.78 (d, *J* = 8.8 Hz, 2H, PhH), 8.20 (d, *J* = 8.75 Hz, 2H, PhH), 9.87 (br, 1H, NH). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 42.3, 44.1, 85.0, 123.8, 126.8, 127.6, 128.6, 130.7, 134.0, 136.0, 143.1, 143.9, 146.9, 164.0, 168.6, 186.2. HR-TOFMS calcd for C₂₀H₁₅N₃O₄ [M⁺], 361.1060; found, 361.1063.

8-(4-Methylbenzoyl)-7-(4-nitrophenyl)-2,3-dihydroimidazo[1,2-a]pyridin-5(1H)-one (4p)



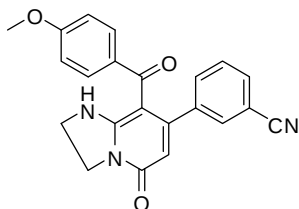
Red solid; mp: 241.2-243.2°C. IR (KBr): 3304, 2922, 1706, 1577, 1507, 1337, 764 cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ = 2.22 (s, 3H, CH_3), 3.61-3.66 (m, 2H, CH_2), 3.86-3.94 (m, 2H, CH_2), 6.97 (d, J = 7.7 Hz, 2H, PhH), 7.04 (d, J = 7.75 Hz, 2H, PhH), 7.33-7.35 (m, 1H, PhH), 7.80 (d, J = 8.5 Hz, 2H, PhH), 8.20 (d, J = 8.5 Hz, 2H, PhH), 9.87 (br, 1H, NH). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$): δ = 21.18, 42.3, 44.1, 85.0, 123.8, 126.9, 128.1, 130.7, 134.2, 135.7, 138.0, 141.2, 143.1, 146.9, 164.0, 168.6, 186.3. HR-TOFMS calcd for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_4$ [M^+], 375.1227; found, 375.1219.

8-(4-Methoxybenzoyl)-7-(4-nitrophenyl)-2,3-dihydroimidazo[1,2-a]pyridin-5(1H)-one (4q)



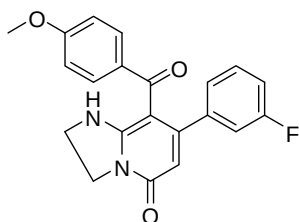
Red solid; mp: 222.0-225.4°C. IR (KBr): 3303, 1703, 1584, 1512, 1246, 842, 774 cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ = 3.54-3.58 (m, 2H, CH_2), 3.70 (s, 3H, OCH_3), 3.91-3.95 (m, 2H, CH_2), 6.74 (d, J = 8.15 Hz, 2H, PhH), 7.15 (d, J = 8.15 Hz, 2H, PhH), 7.34-7.37 (m, 1H, PhH), 7.81 (d, J = 8.4 Hz, 2H, PhH), 8.20 (d, J = 8.35 Hz, 2H, PhH), 9.90 (br, 1H, NH). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$): δ = 42.3, 44.1, 55.4, 85.0, 112.9, 123.8, 128.6, 130.6, 134.4, 135.3, 136.5, 143.1, 146.9, 159.8, 164.0, 168.8, 185.9. HR-TOFMS calcd for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_5$ [M^+], 391.1158; found, 391.1168.

3-(8-(4-methoxybenzoyl)-5-oxo-1,2,3,5-tetrahydroimidazo[1,2-a]pyridin-7-yl)benzonitrile



Red solid; mp: 216.4-218.2°C. ^1H NMR (500 MHz, $\text{CDCl}_3+\text{DMSO}-d_6$): δ = 3.65 (s, 3H, CH_3), 3.90 (t, J = 9.5 Hz, 2H, CH_2), 4.19 (t, J = 9.5 Hz, 2H, CH_2), 5.60 (d, J = 1.05 Hz, 1H, PhH), 6.49 (d, J = 8.55 Hz, 2H, PhH), 7.17-7.14 (m, 3H, PhH), 7.32-7.29 (m, 3H, PhH), 7.83 (d, J = 5.10 Hz, 2H, PhH), 8.42 (br, 1H, NH). ^{13}C NMR (125 MHz, $\text{CDCl}_3+\text{DMSO}-d_6$): δ = 42.8, 43.6, 55.3, 96.3, 107.9, 111.6, 112.8, 118.1, 128.9, 130.7, 131.1, 131.7, 132.5, 132.9, 141.1, 152.8, 156.9, 159.8, 161.4, 191.7. HR-TOFMS calcd for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_3$ [M^+], 371.1270; found, 371.1275.

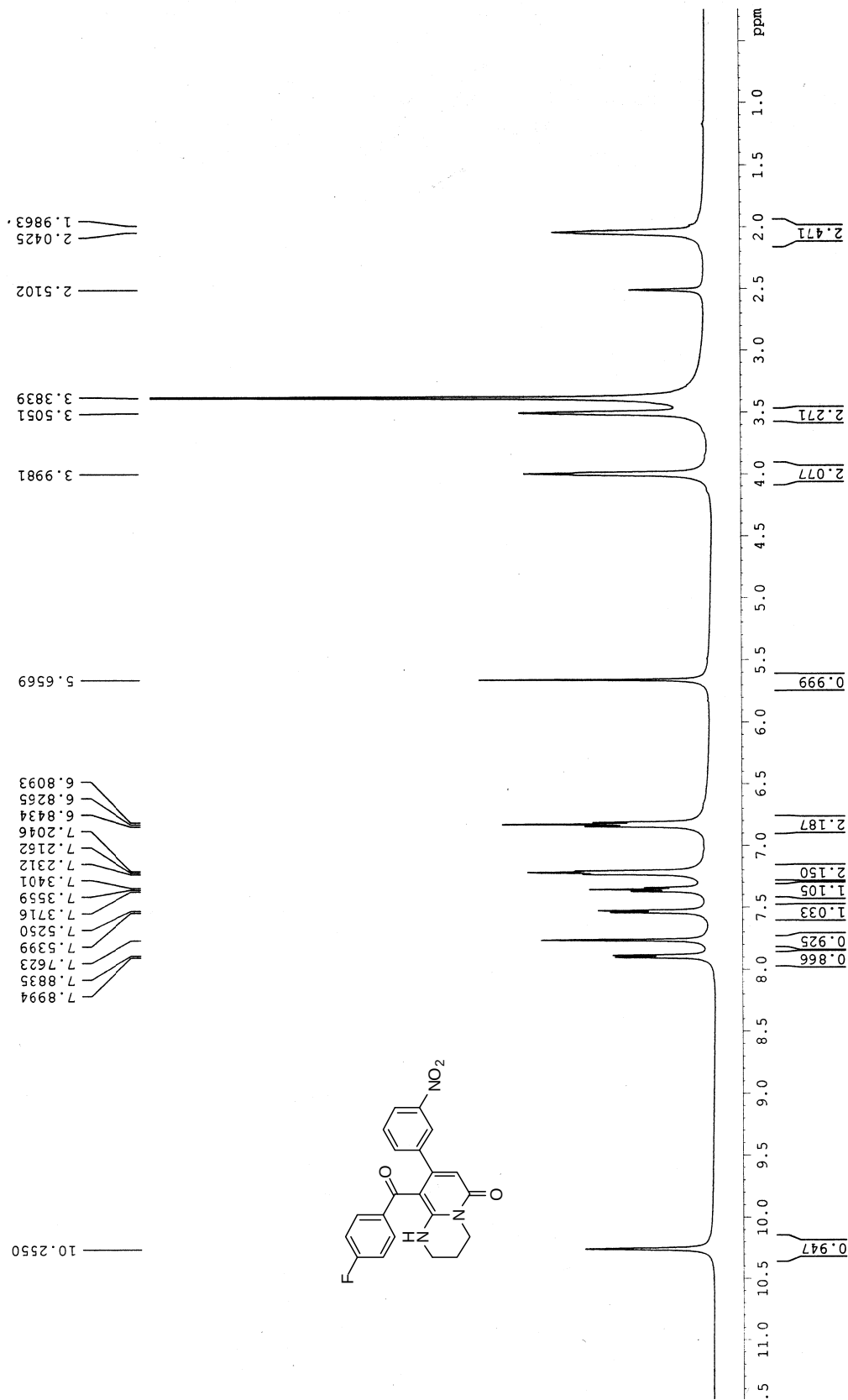
7-(3-fluorophenyl)-8-(4-methoxybenzoyl)-2,3-dihydroimidazo[1,2-a]pyridin-5(1H)-one



Red solid; mp: 208.3-209.9°C. ^1H NMR (500 MHz, $\text{CDCl}_3+\text{DMSO}-d_6$): δ = 3.65 (s, 3H, CH_3), 3.70 (s, 3H, OCH_3), 3.91-3.95 (m, 2H, CH_2), 6.74 (d, J = 8.15 Hz, 2H, PhH), 7.15 (d, J = 8.15 Hz, 2H, PhH), 7.34-7.37 (m, 1H, PhH), 7.81 (d, J = 8.4 Hz, 2H, PhH), 8.20 (d,

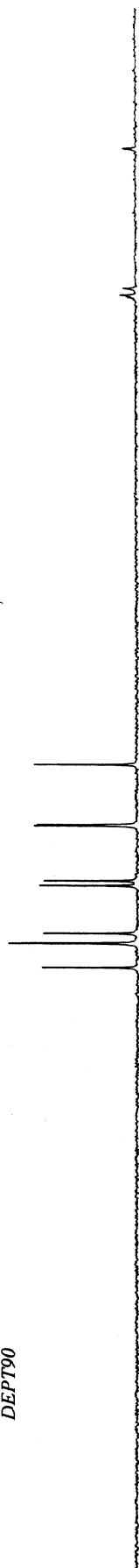
$J = 8.35$ Hz, 2H, PhH), 9.90 (br, 1H, NH). ^{13}C NMR (125 MHz, $\text{CDCl}_3 + \text{DMSO}-d_6$): $\delta = 43.11, 43.71, 55.57, 96.09, 107.61, 113.15, 122.62, 123.30, 129.92, 130.87, 133.30, 134.75, 141.68, 147.23, 152.60, 152.62, 156.78, 159.71, 161.47, 191.42$. HR-TOFMS calcd for $\text{C}_{21}\text{H}_{17}\text{FN}_2\text{O}_3[\text{M}^+]$, 364.1223; found, 364.1223.

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-023 in DMSO
12052101

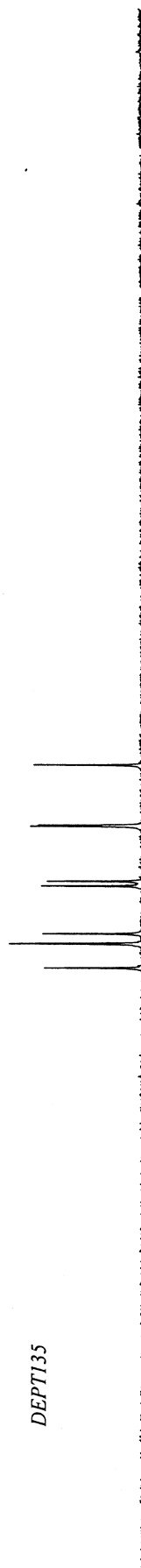


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 3c

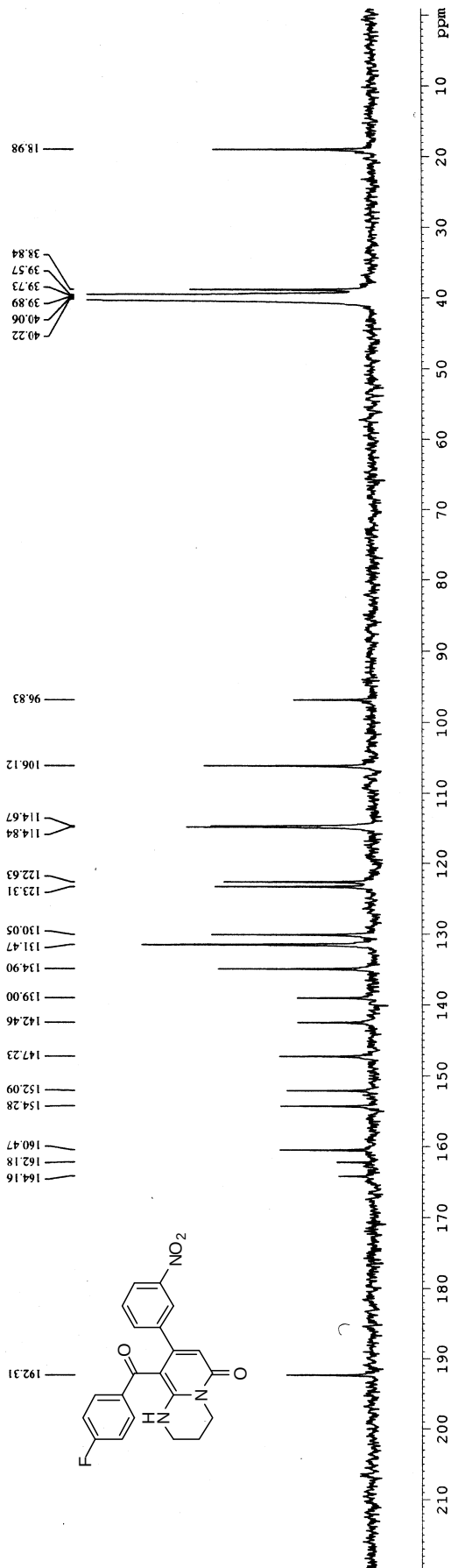
DEPT90



DEPT135

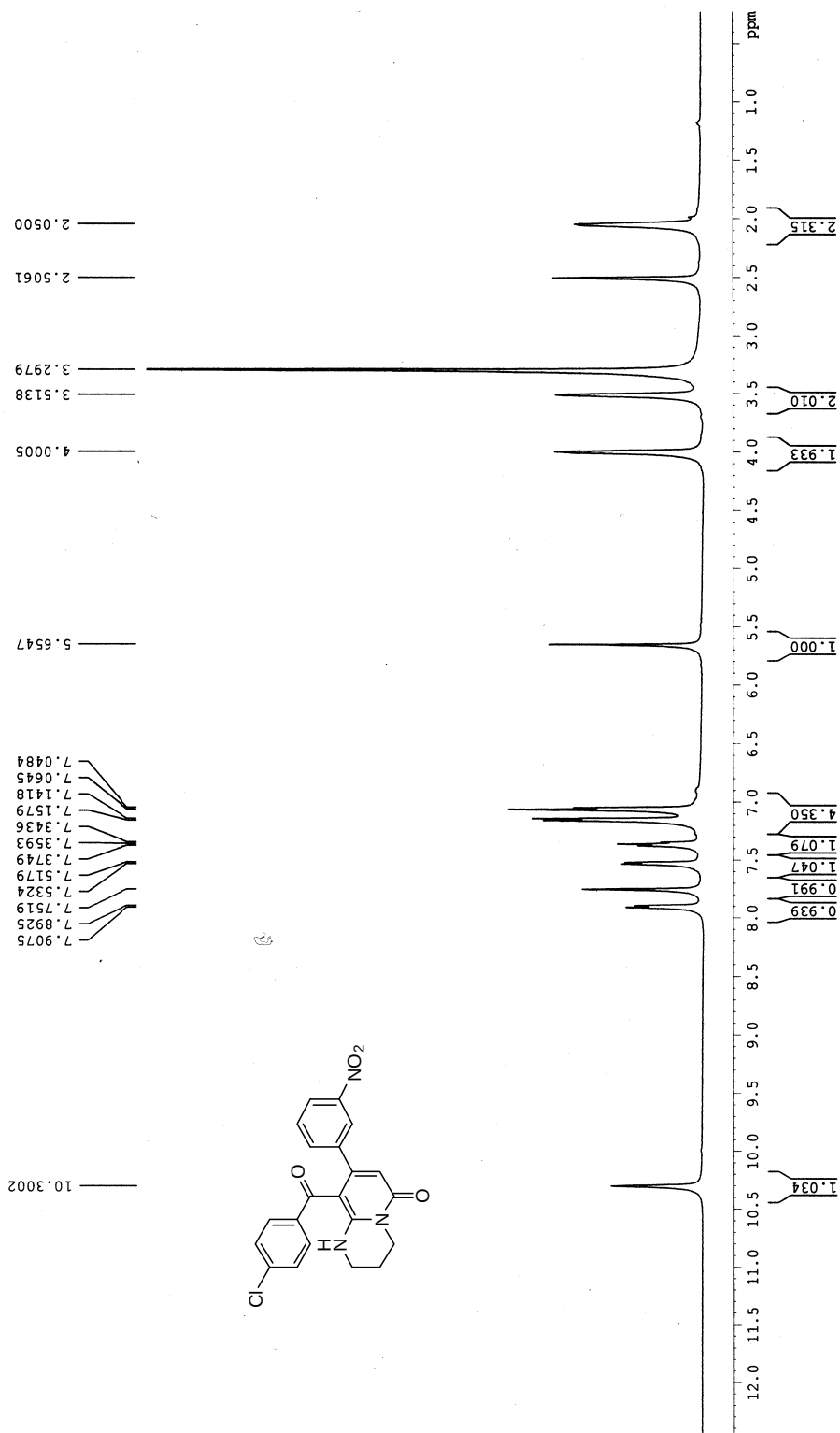


YUNNAN UNIVER. AV. DRX 500
fanjuan fj-023 in DMSO
12052101

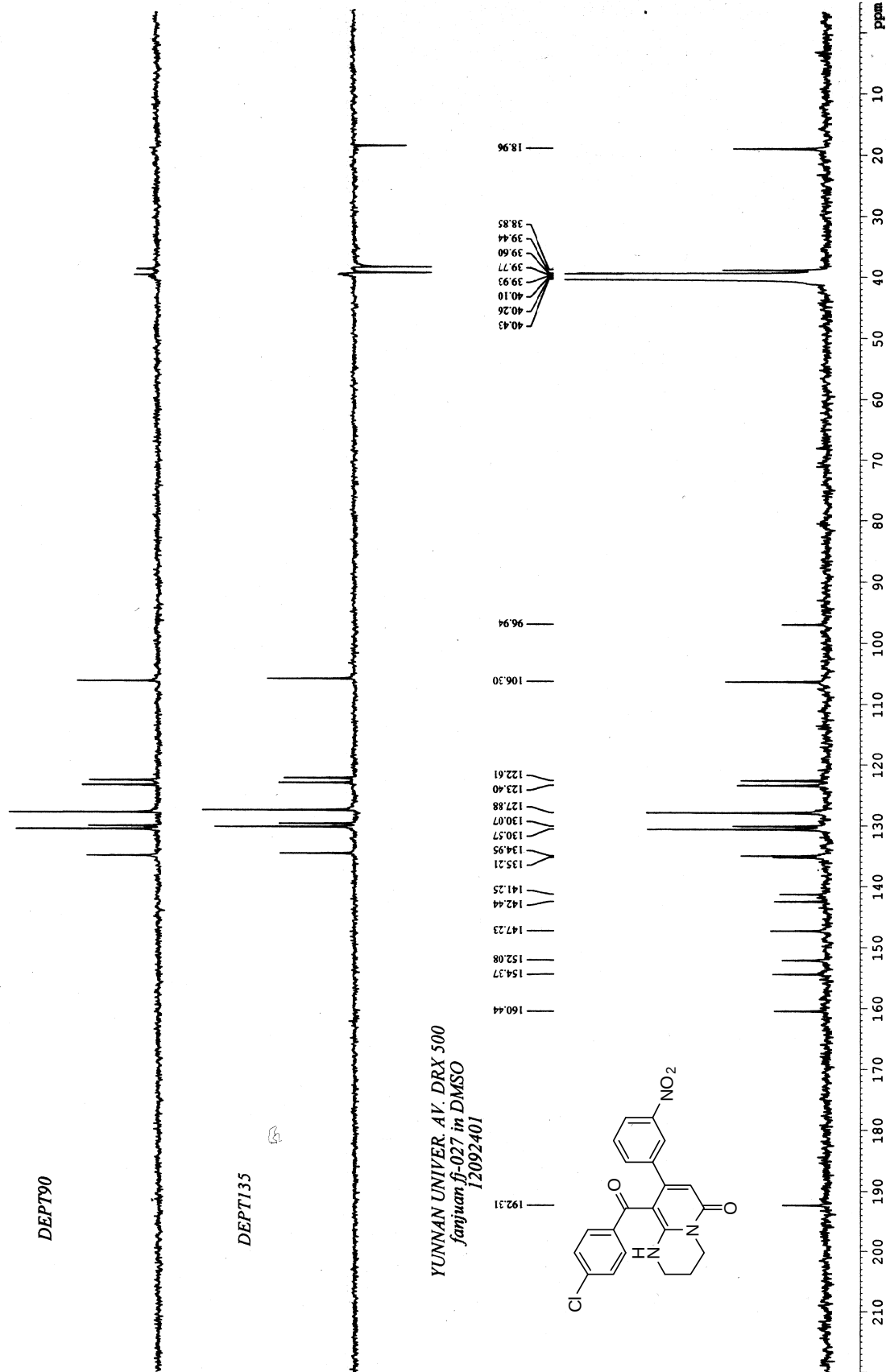


¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 3c

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-027 in DMSO
12092401

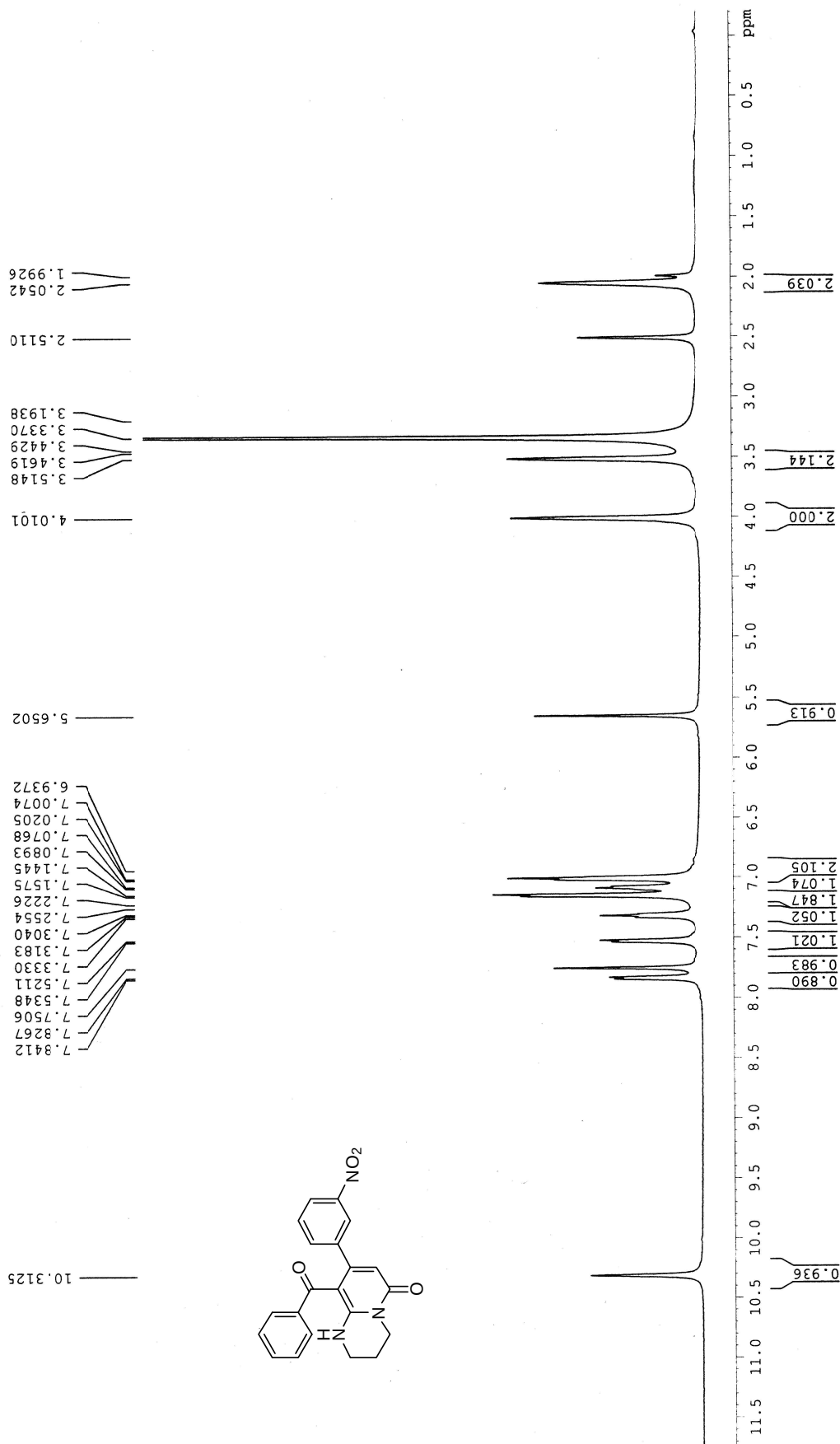


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 3b

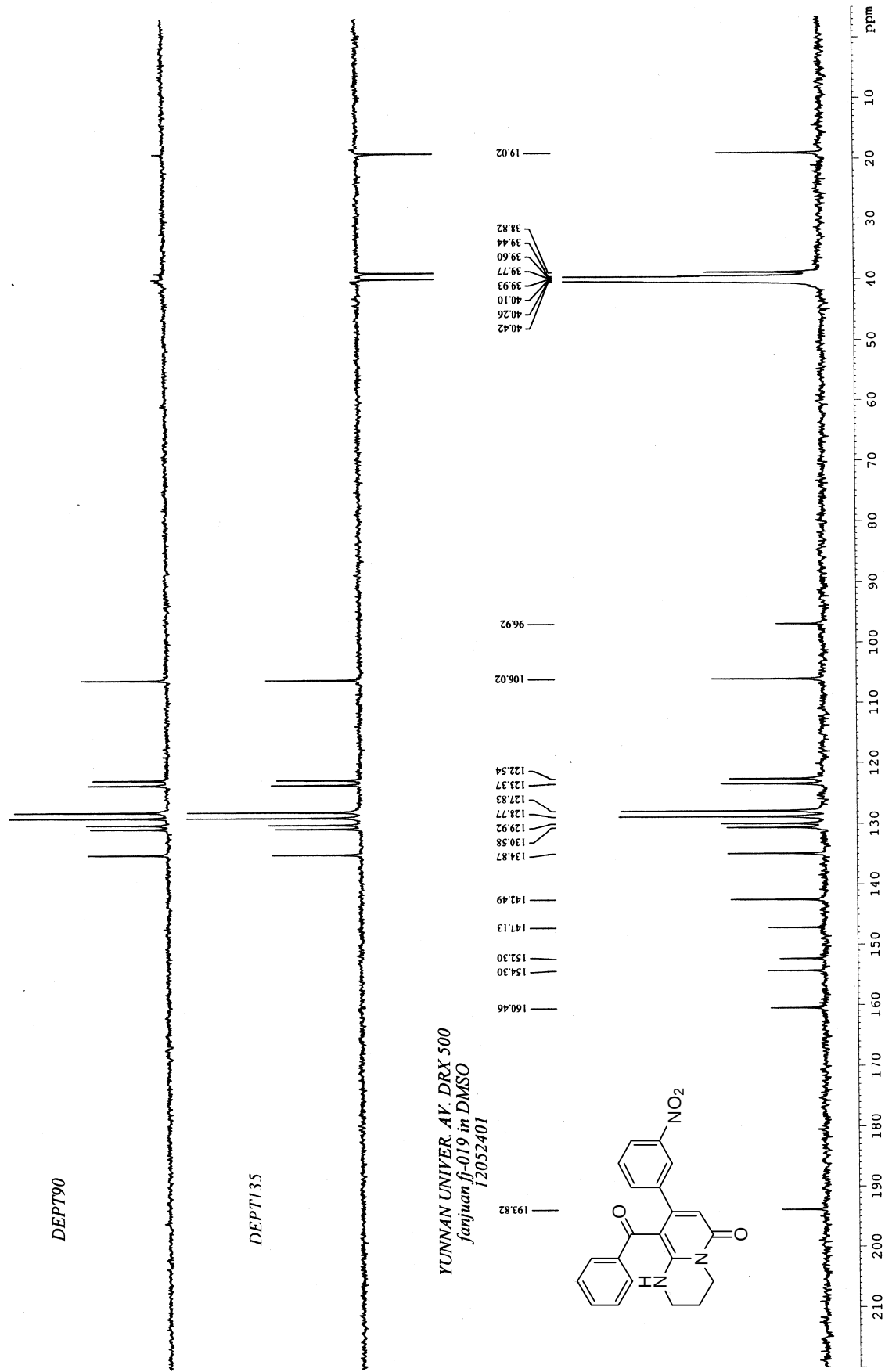


¹³C NMR (125MHz, DMSO-d₆) spectrum of 3b

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-019 in DMSO
12052401

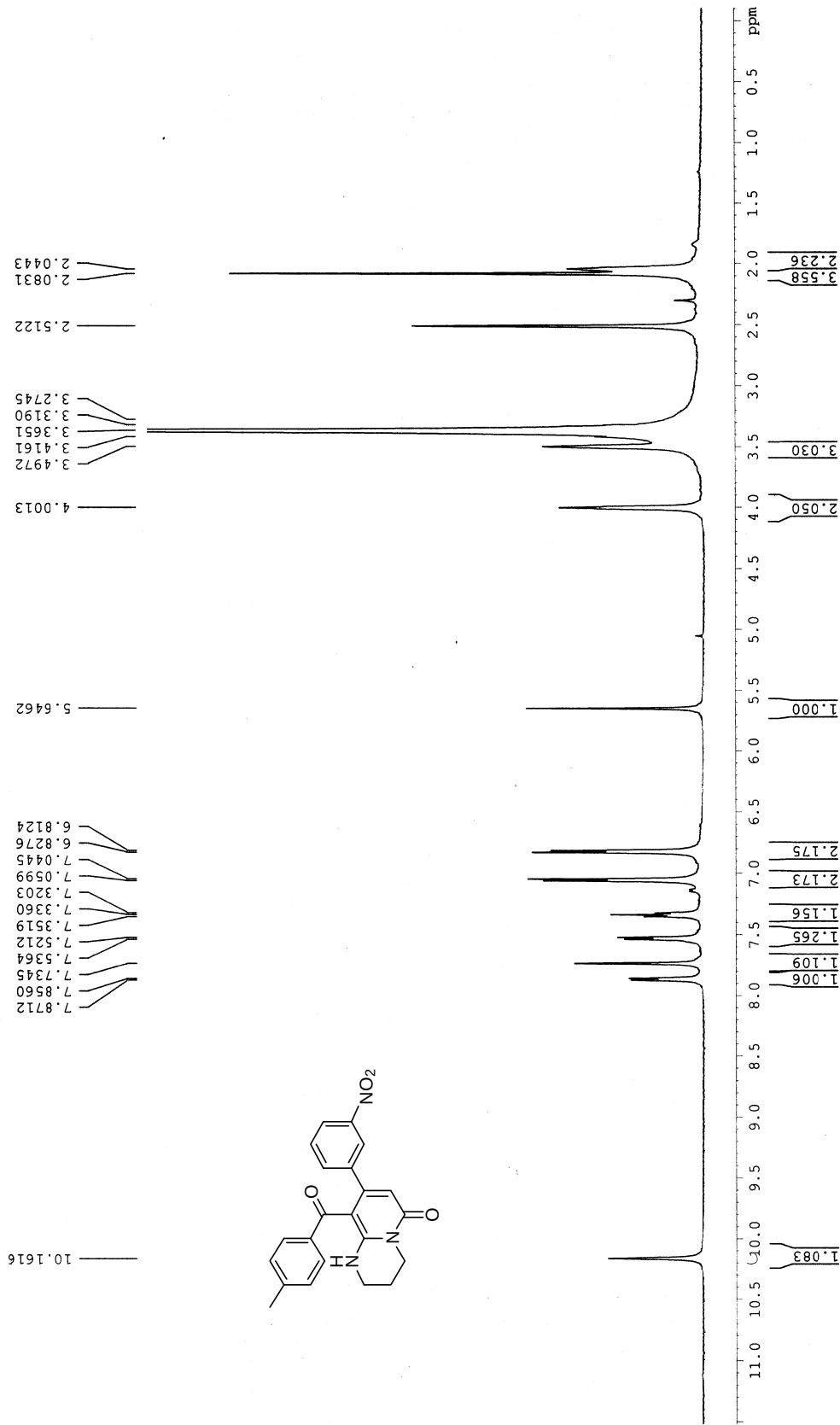


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 3d



¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 3d

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-024 in DMSO
12052402

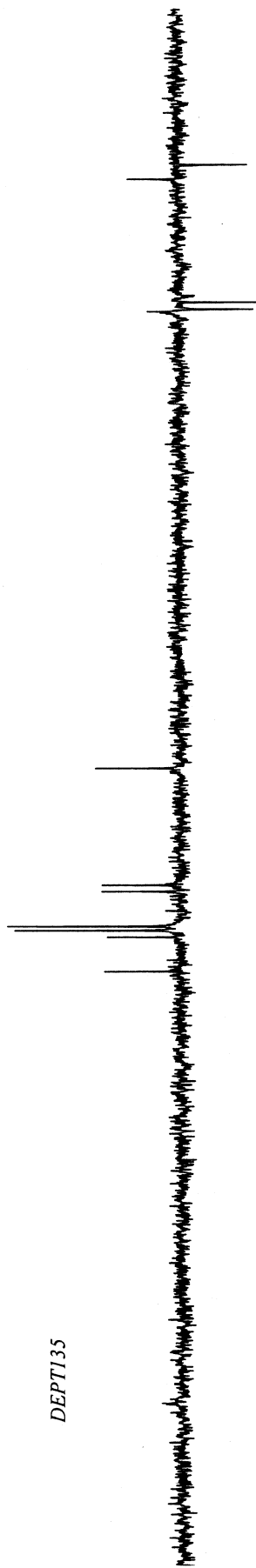


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 3e

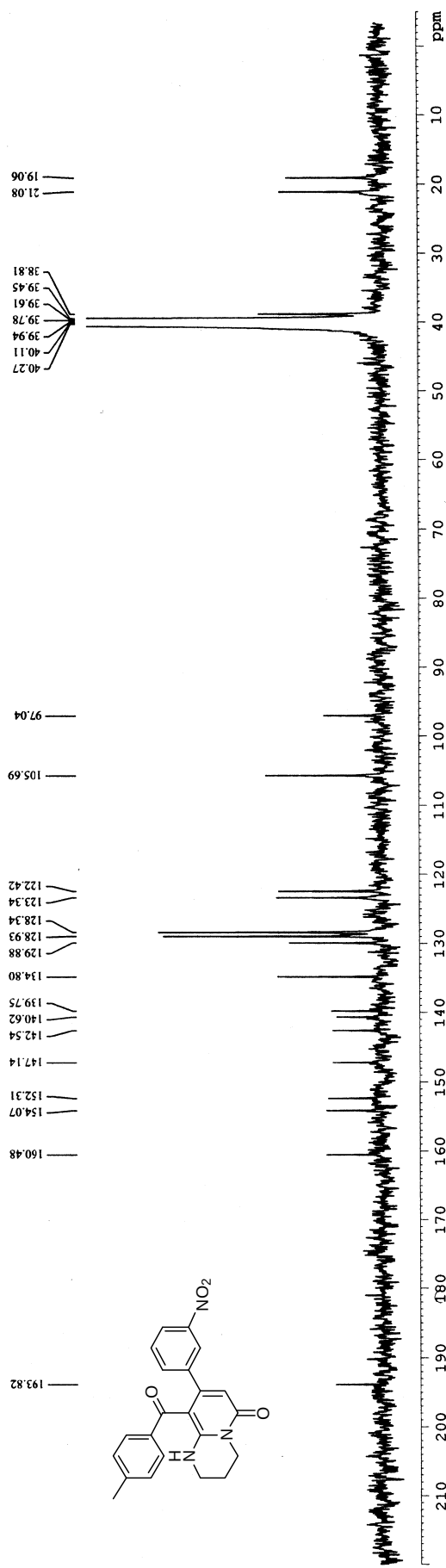
DEPT90



DEPT135

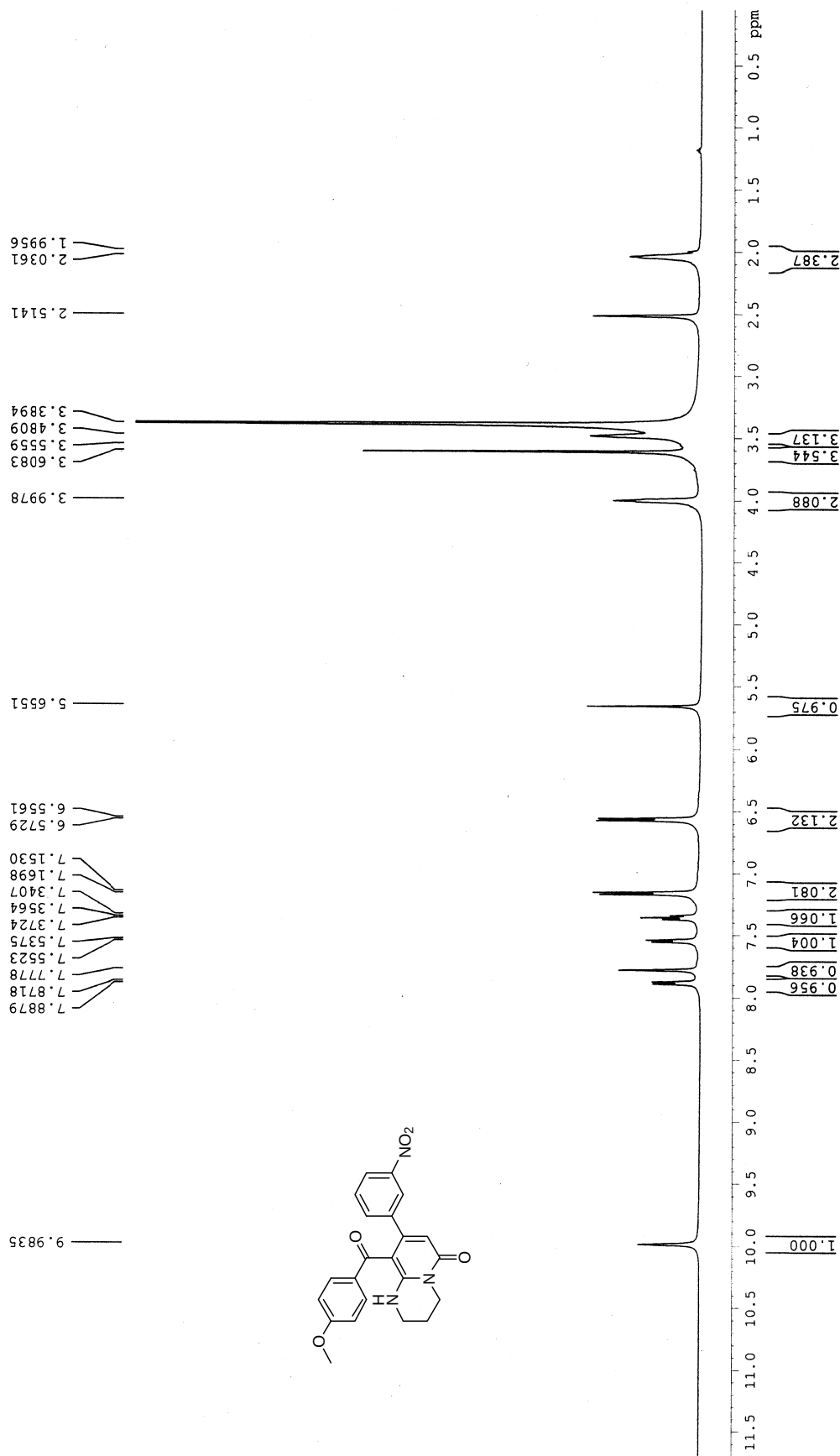


YUNNAN UNIVER. AV. DRX 500
fanyuan fj-024 in DMSO
12052402



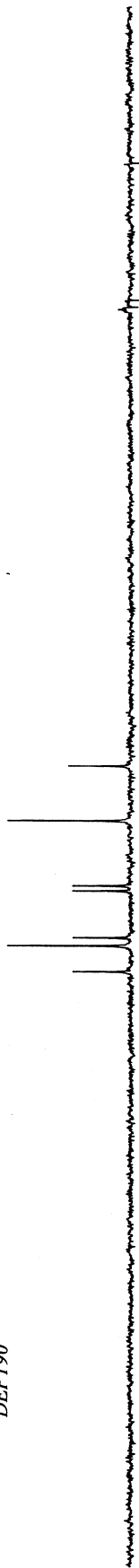
¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 3e

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-026 in DMSO
12052802



¹H NMR (500MHz, DMSO-*d*₆) spectrum of 3f

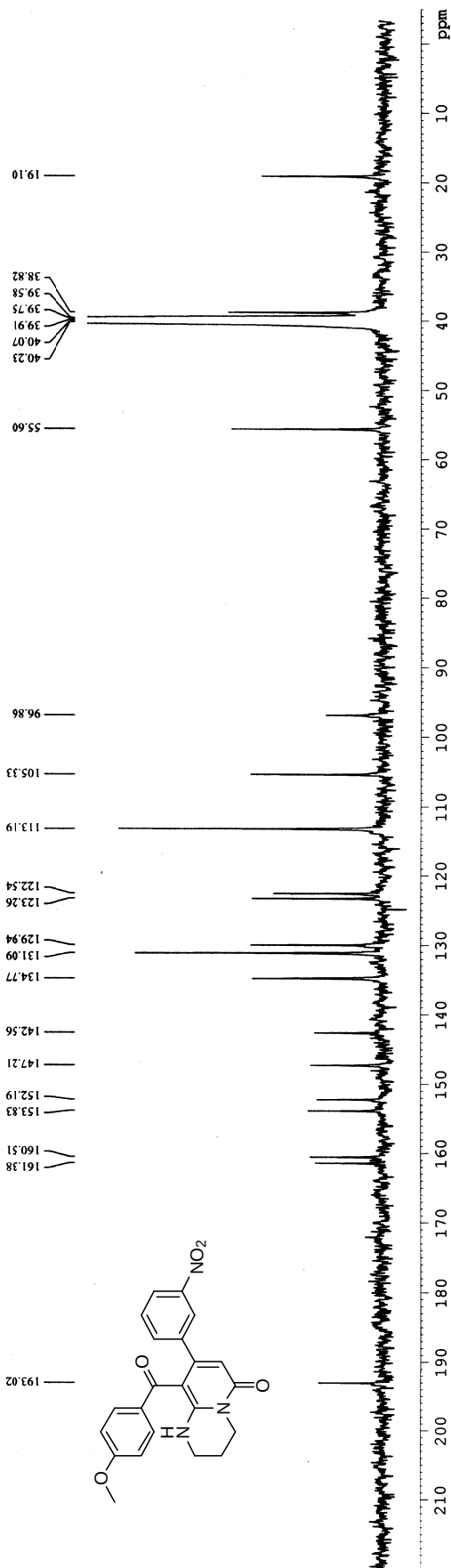
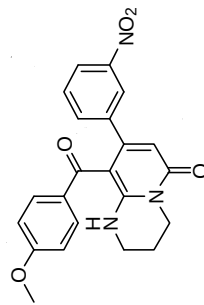
DEPT90



DEPT135

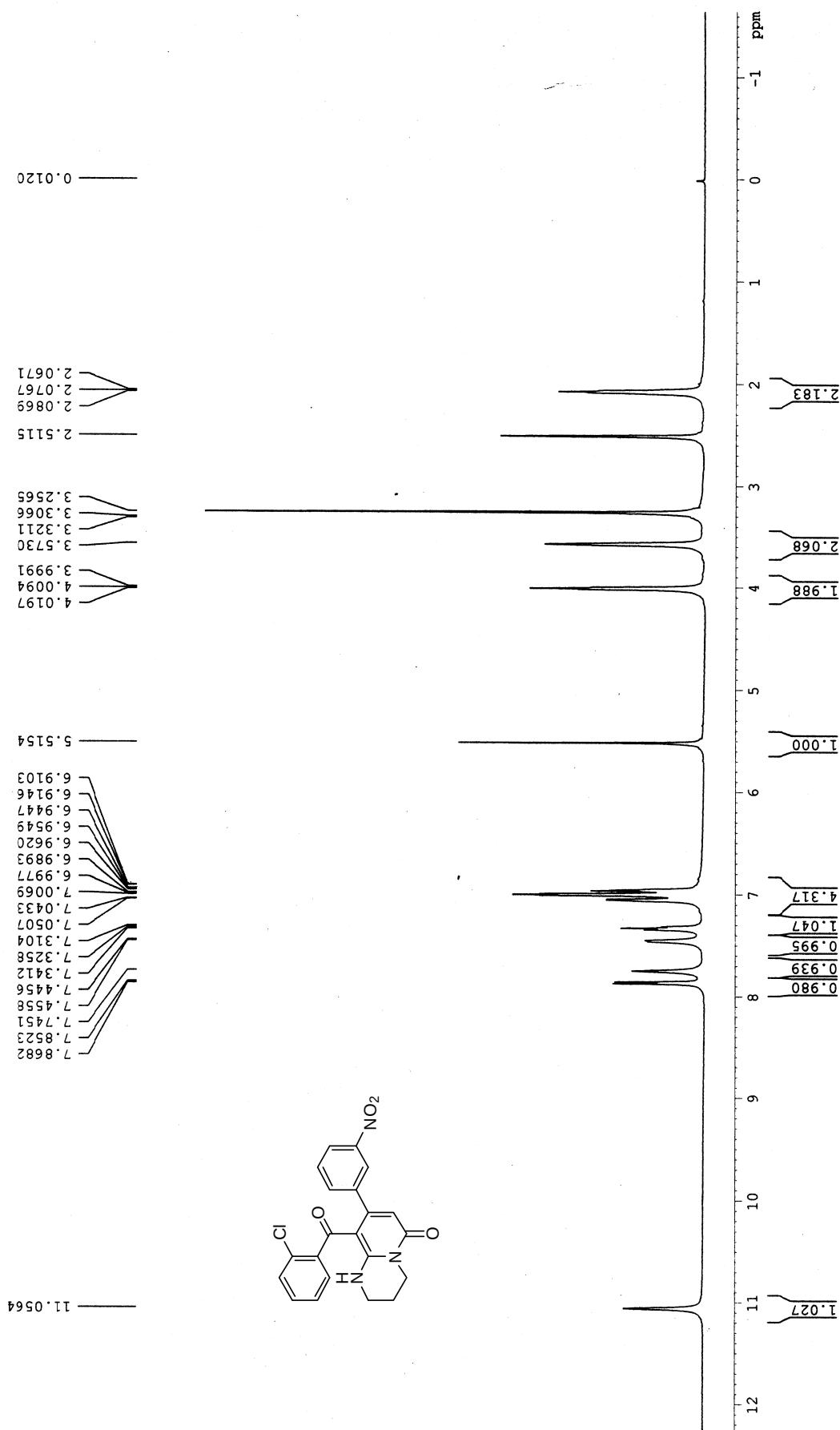


YUNNAN UNIVER. AV. DRX 500
fanjuan fj-026 in DMSO
12052802



¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 3f

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-037 in DMSO
12092403



¹H NMR (500MHz, DMSO-*d*₆) spectrum of 3g

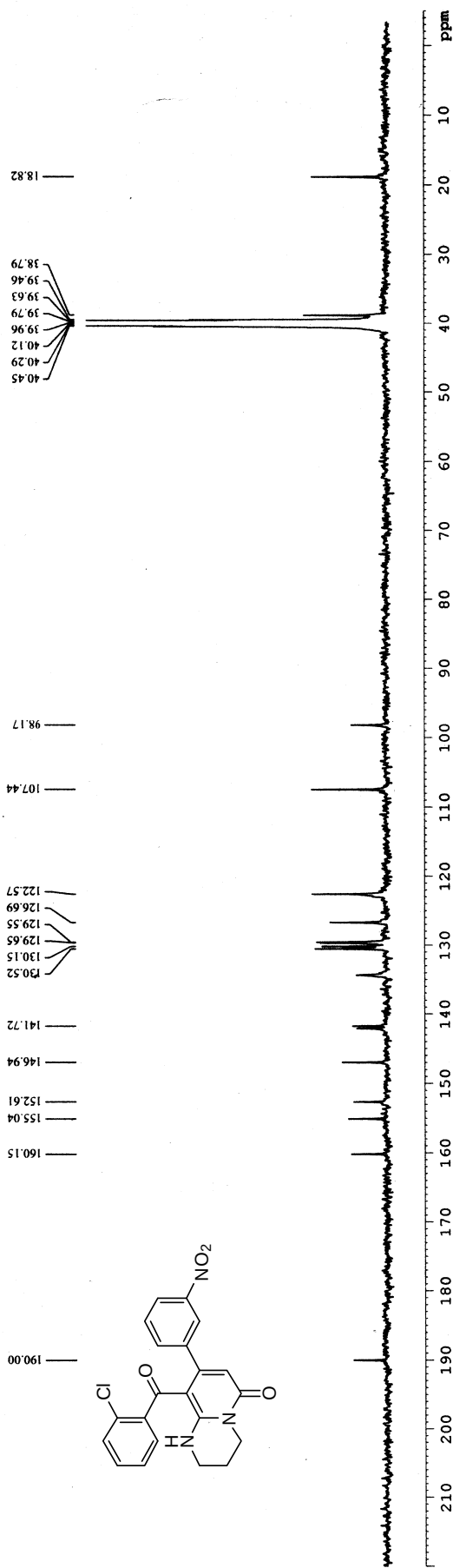
DEPT90



DEPT135

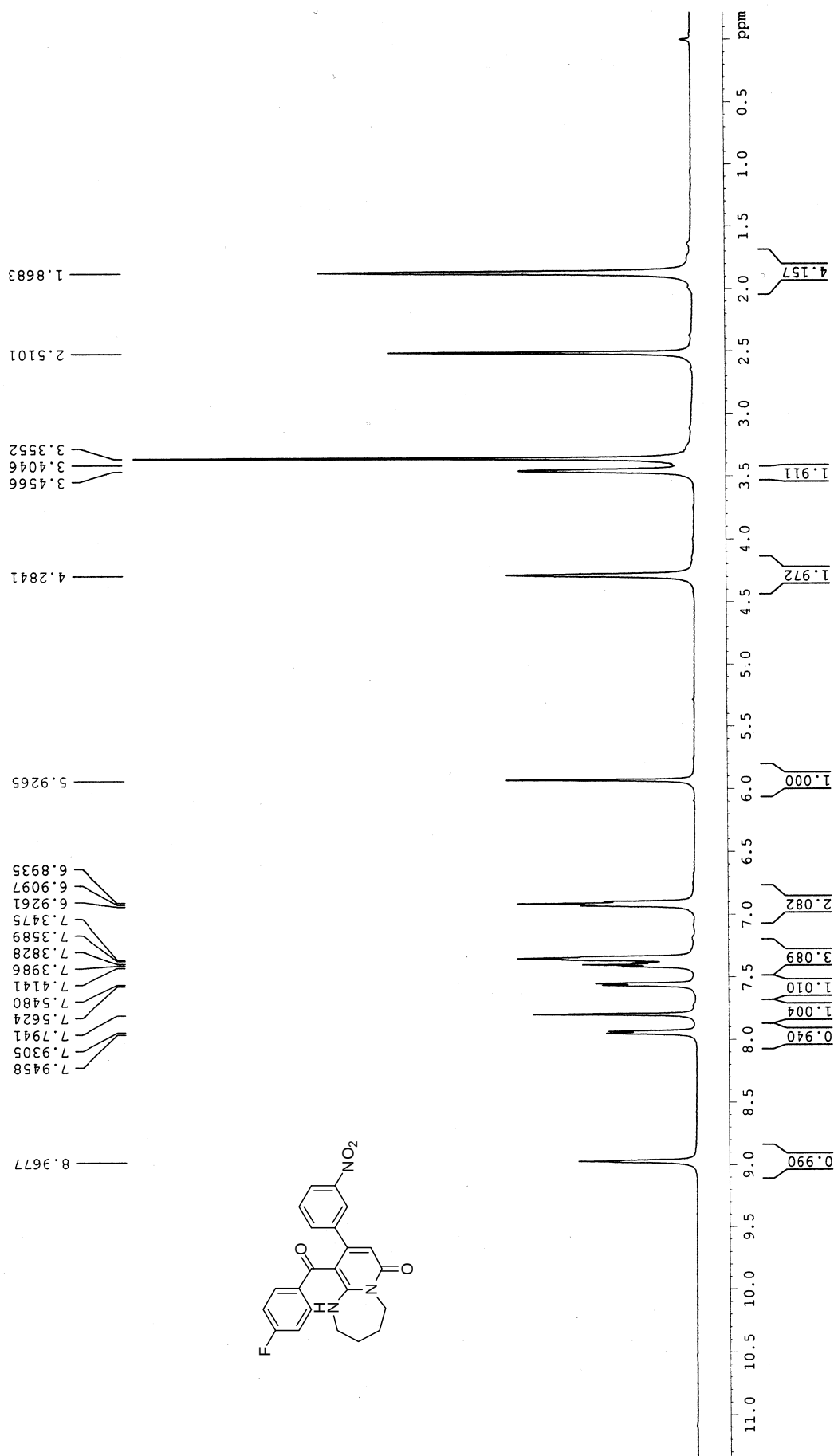


YUNNAN UNIVER. AV. DRX 500
fanjuan fj-037 in DMSO
12092403



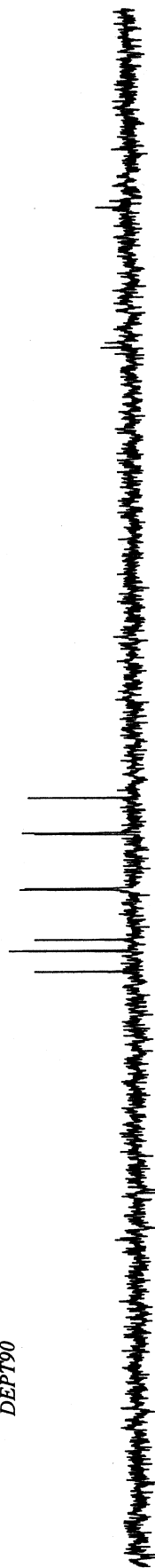
^{13}C NMR (125MHz, DMSO- d_6) spectrum of 3g

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-043 in DMSO
12100903

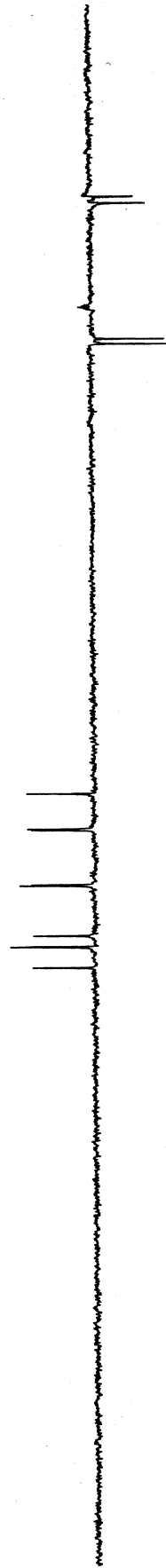


¹H NMR (500MHz, DMSO-d₆) spectrum of 3h

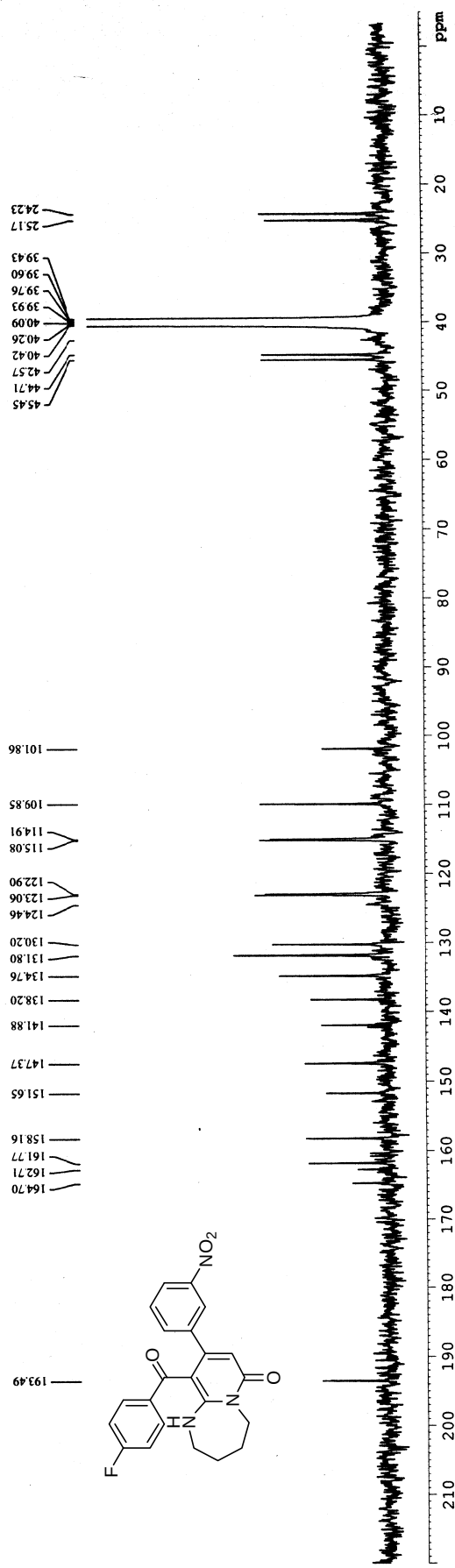
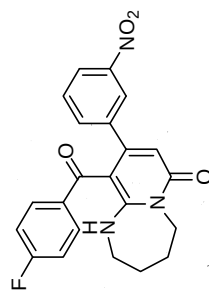
DEPT90



DEPT135

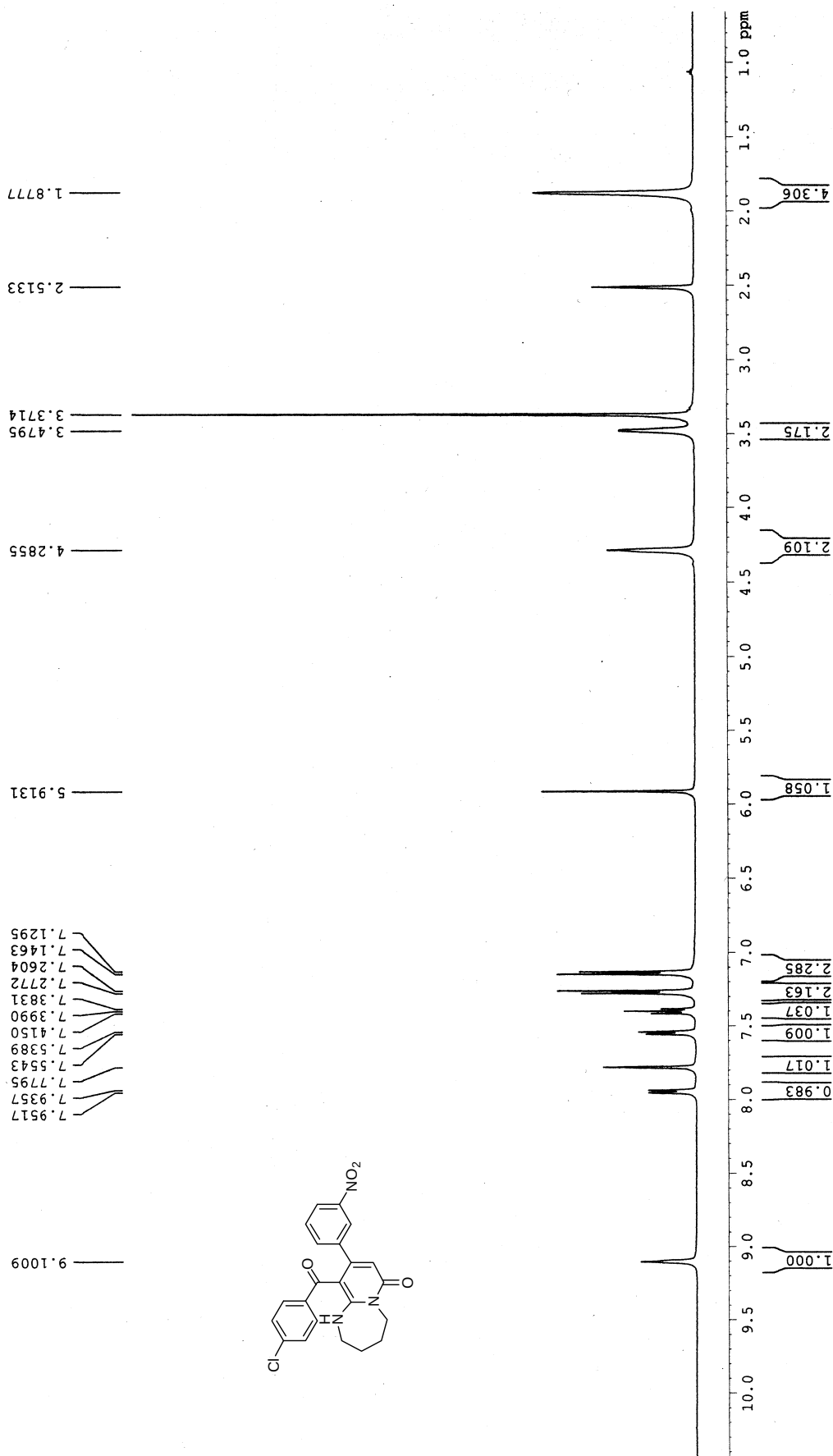


YUNNAN UNIVER. AV. DRX 500
fajuan fj-043 in DMSO
12100903



¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 3h

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-044 in DMSO
12101102

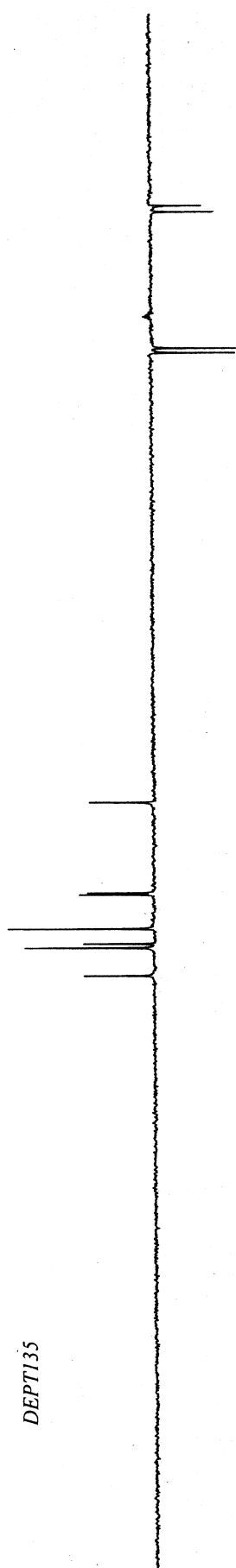


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 3i

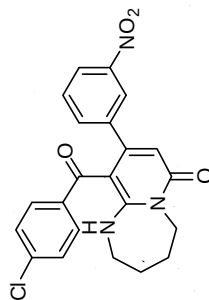
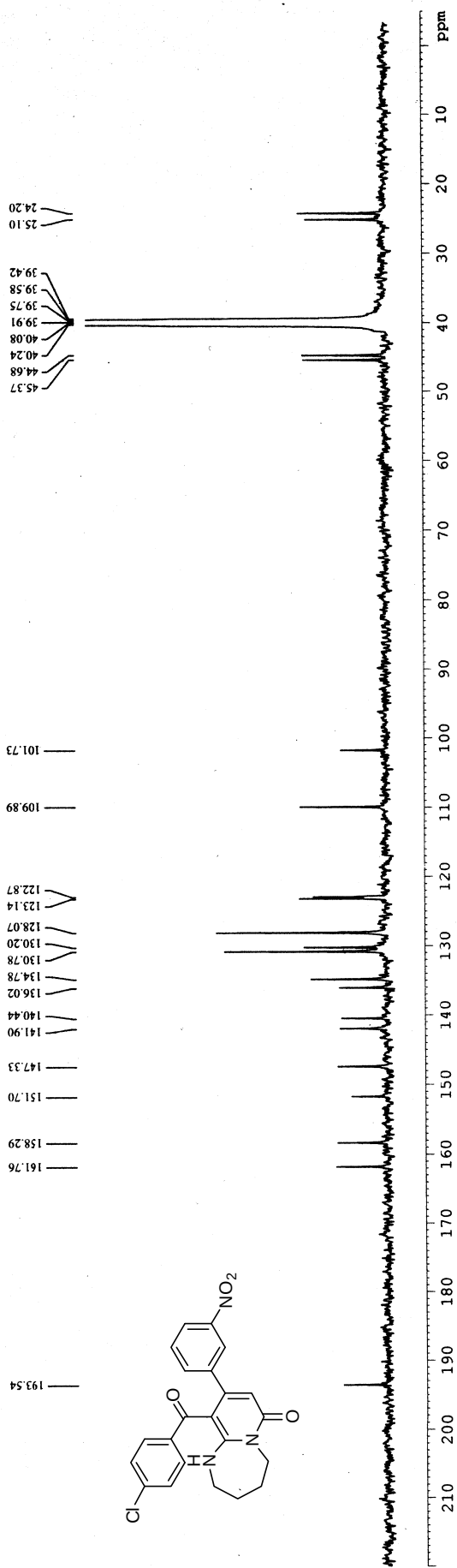
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DEPT135

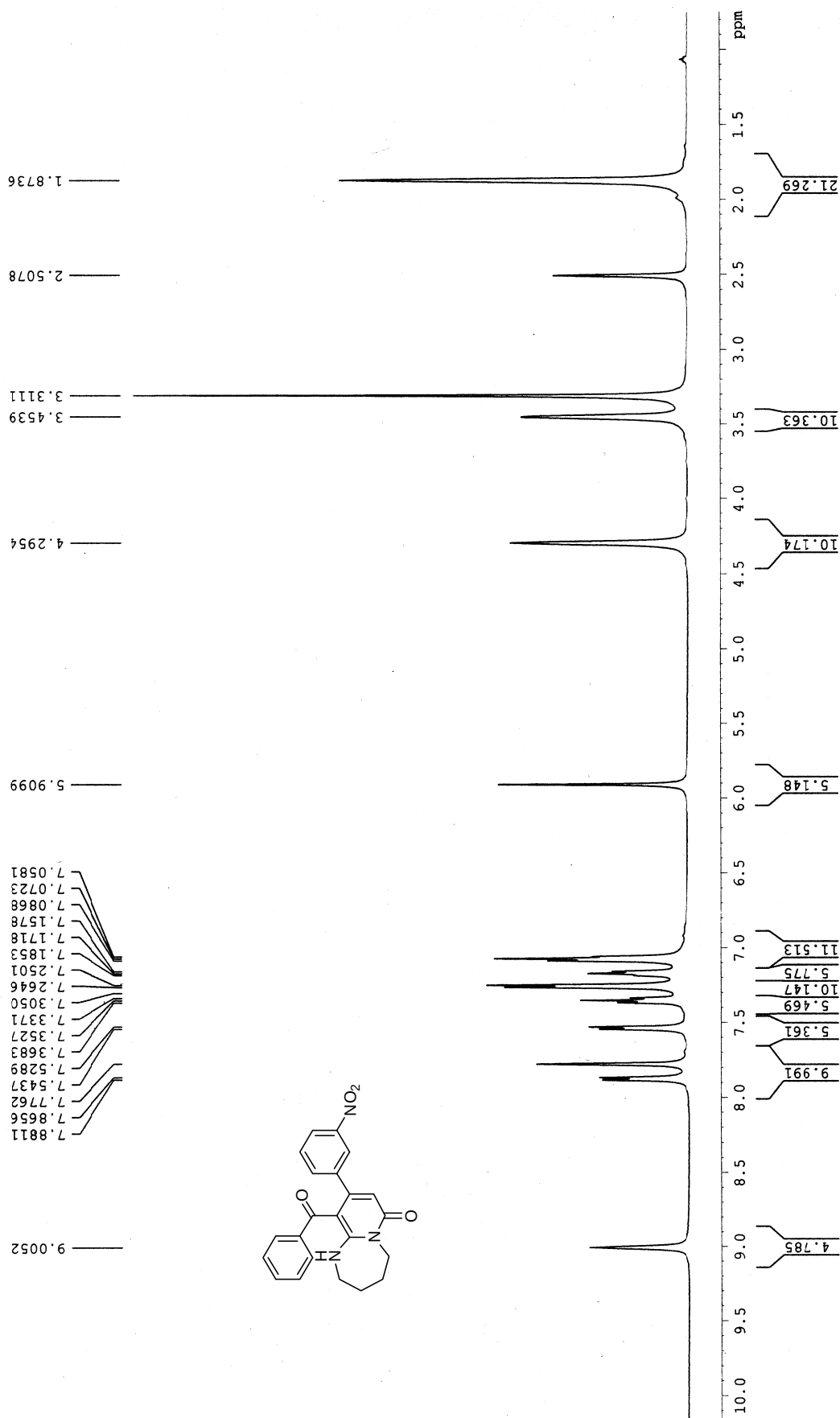


YUNNAN UNIVER. AV. DRX 500
fanjuan fj-044 in DMSO
12101102



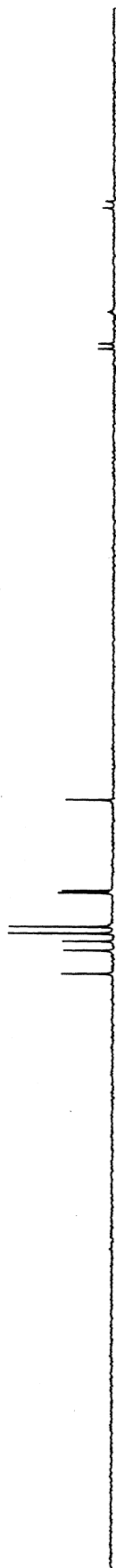
¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 3i

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-033 in DMSO
12101101

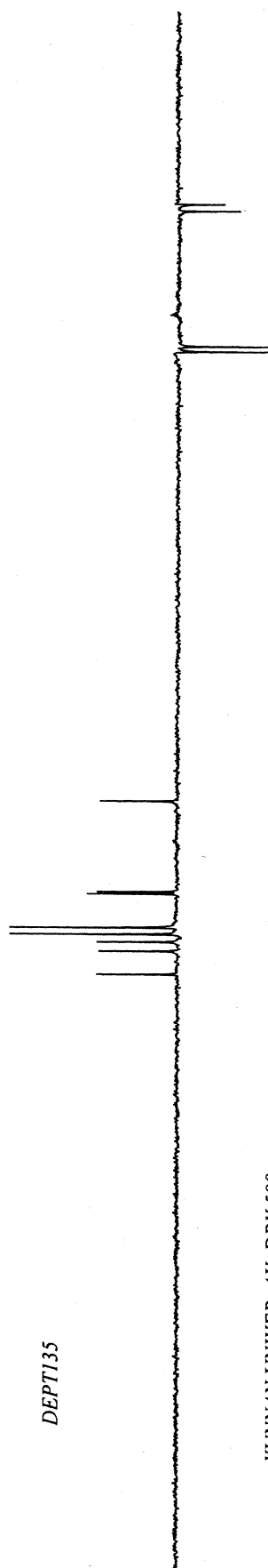


¹H NMR (500MHz, DMSO-d₆) spectrum of 3j

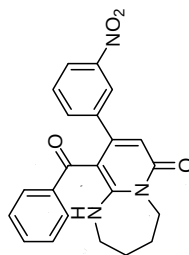
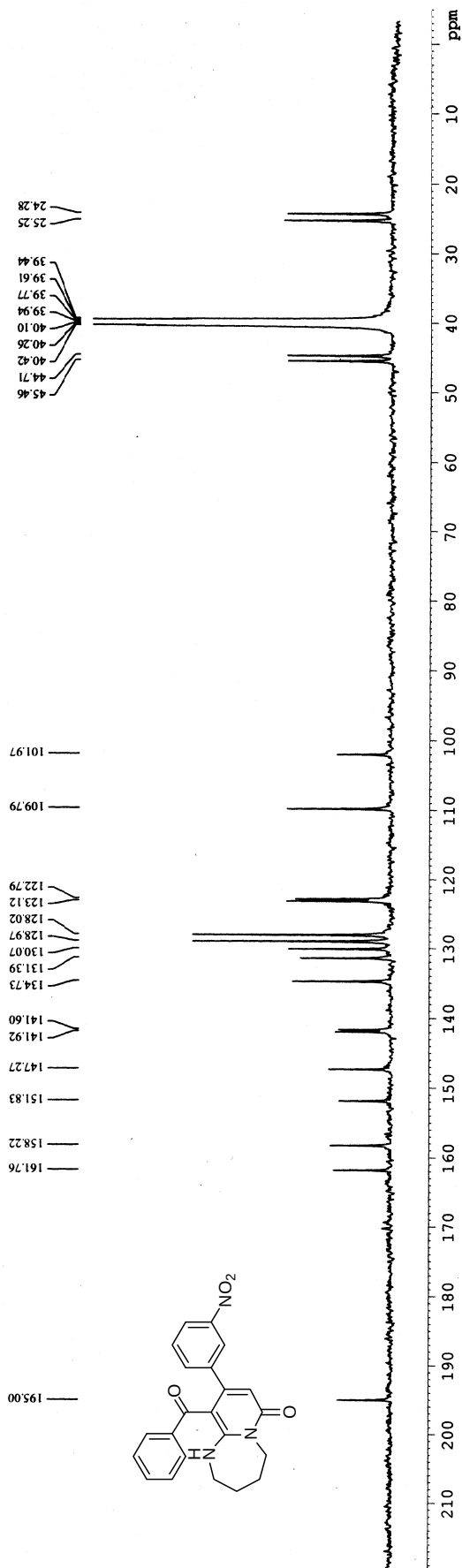
DEPT90



DEPT135

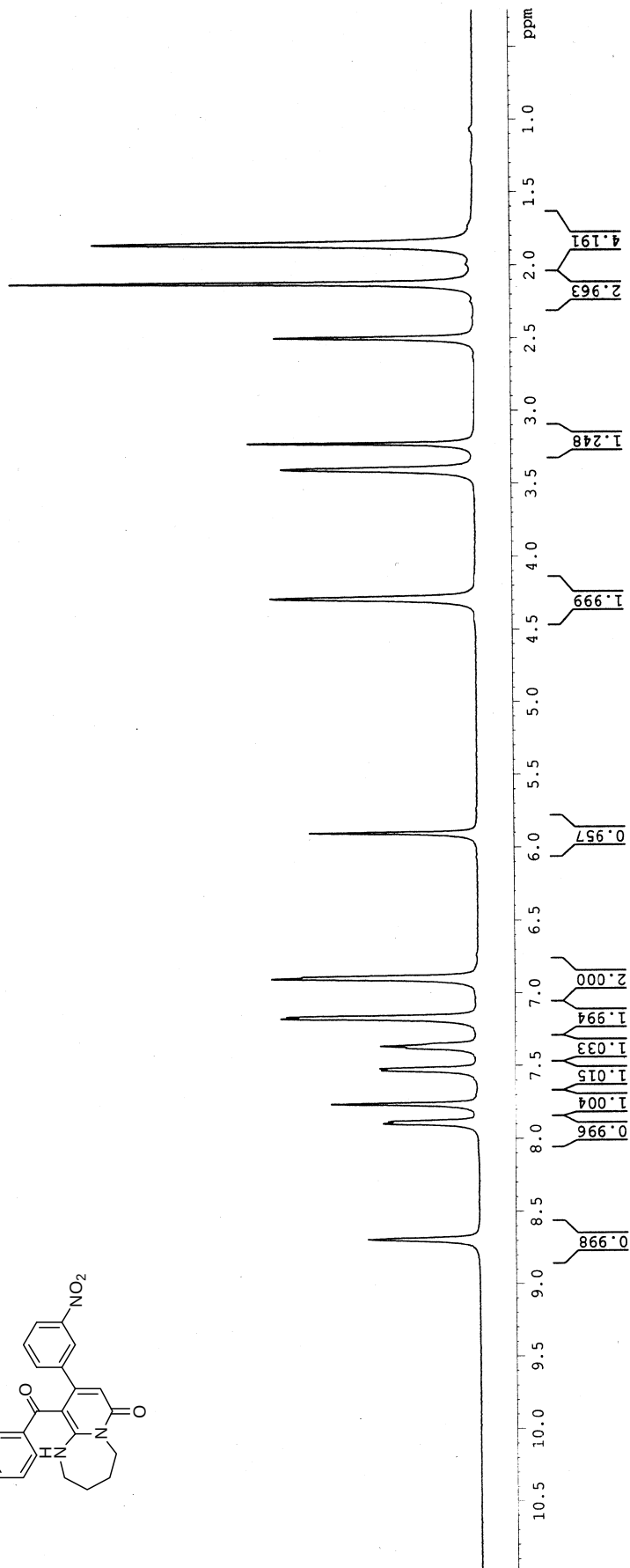
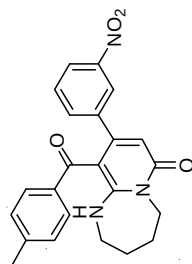


YUNNAN UNIVER. AV. DRX 500
fanjuan fj-033 in DMSO
12101101

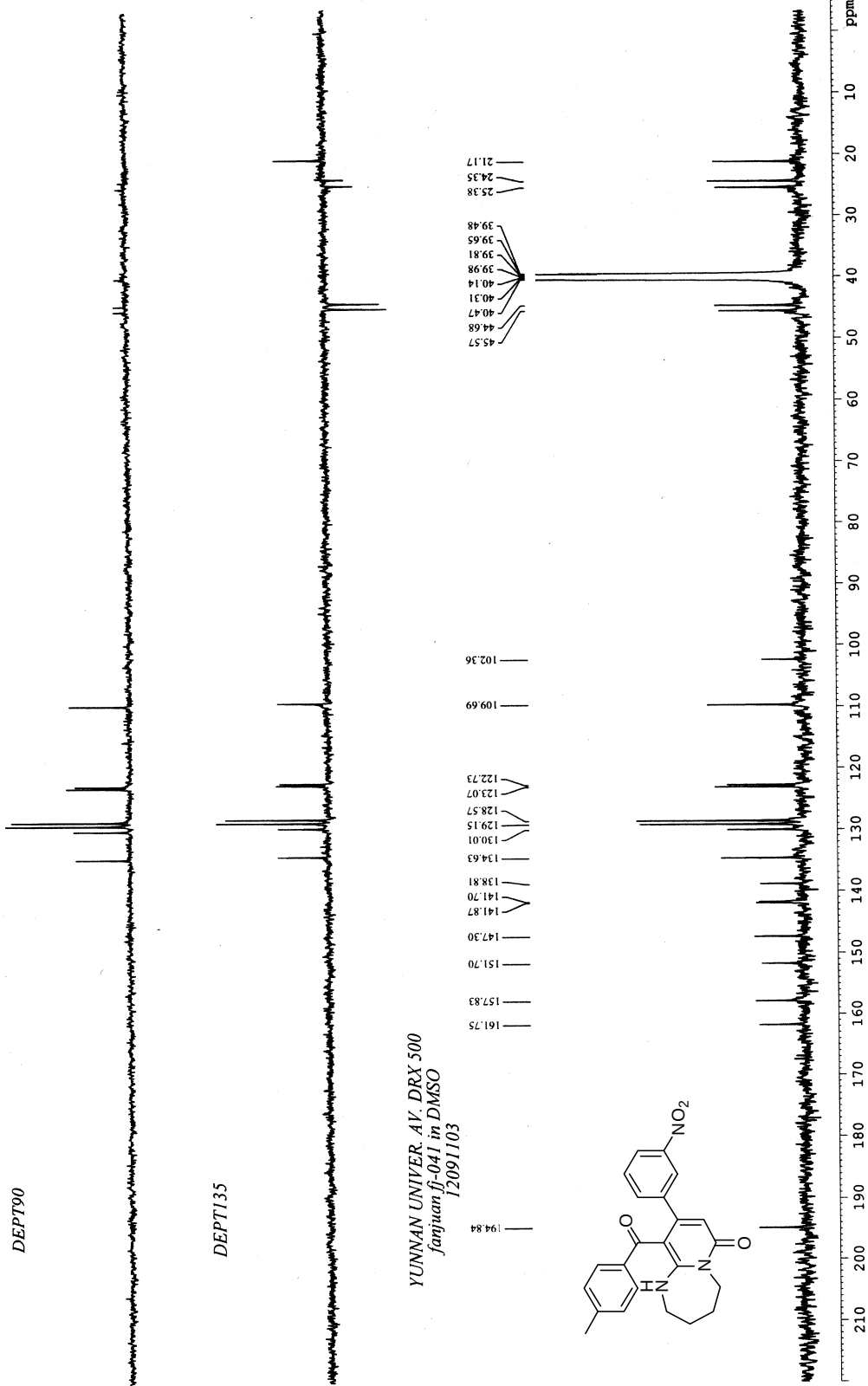


¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 3j

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-041 in DMSO
12091103

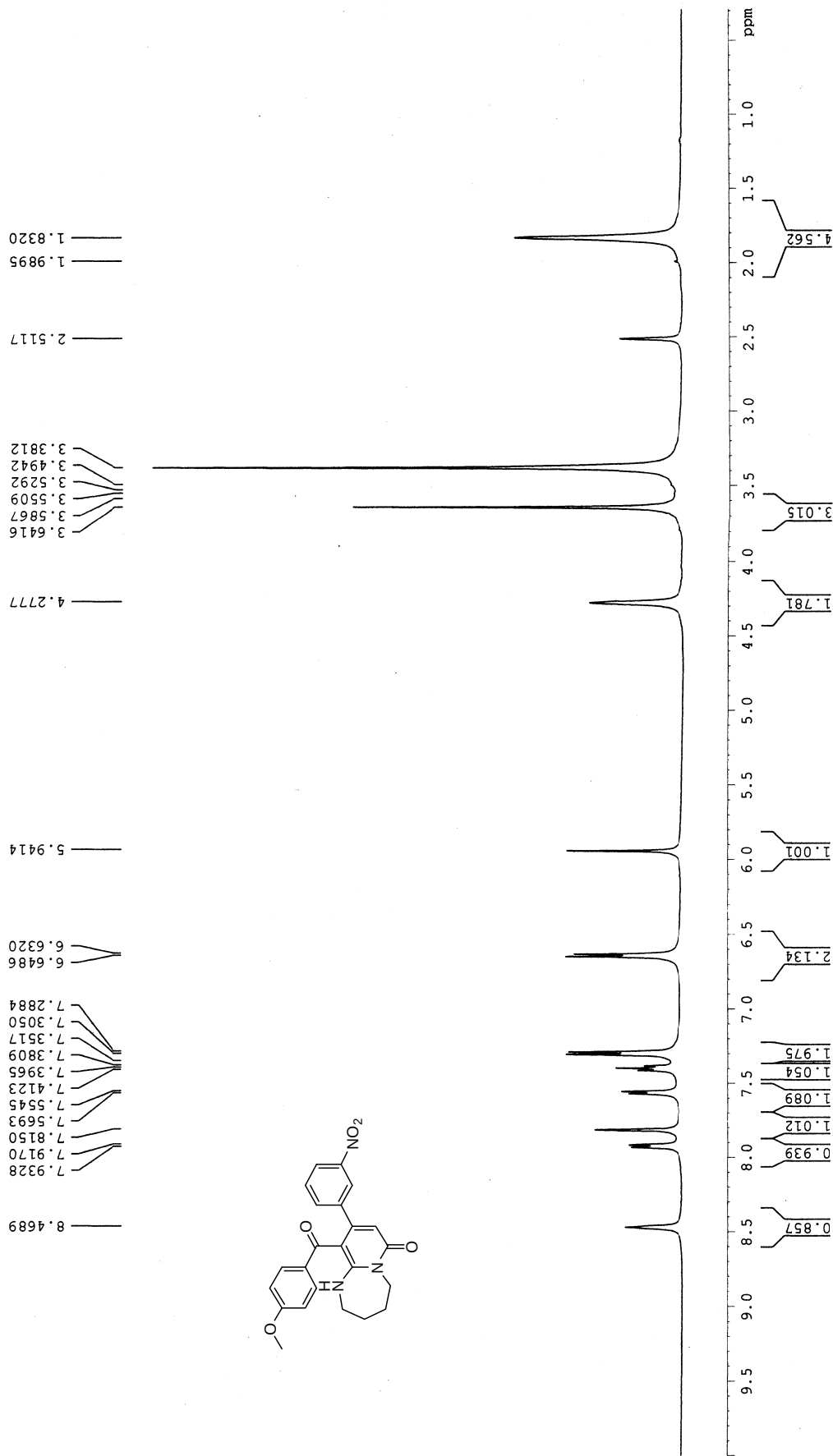


¹H NMR (500 MHz, DMSO-*d*₆) spectrum of 3k



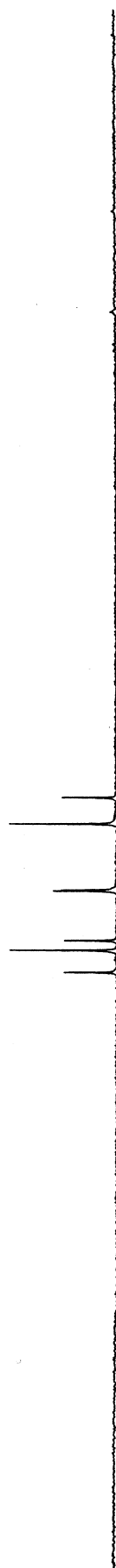
¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 3k

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-036 in DMSO
121022203

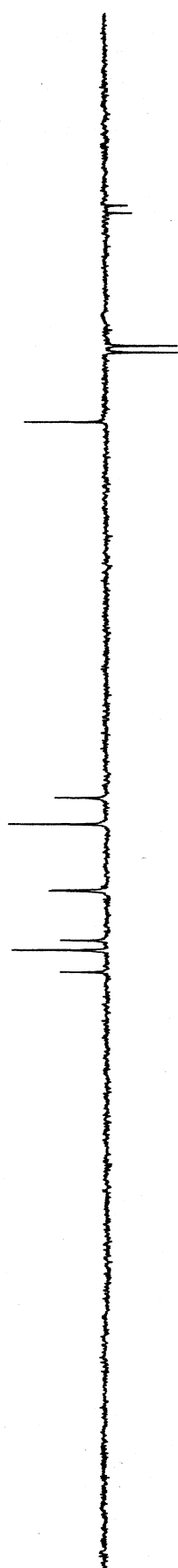


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 3l

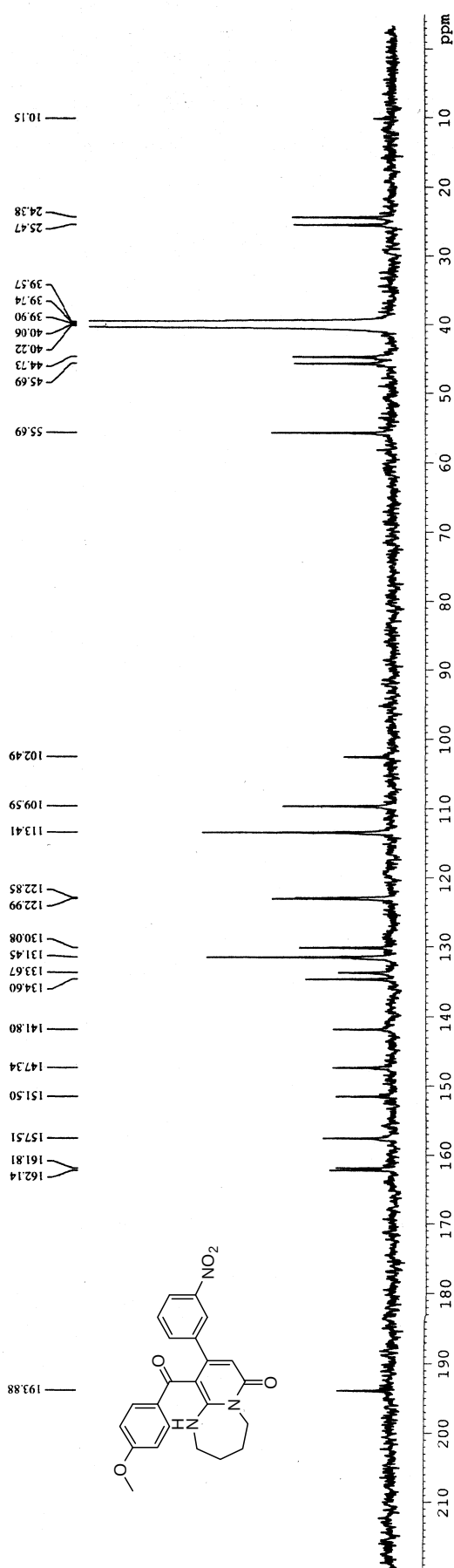
DEPT90



DEPT135

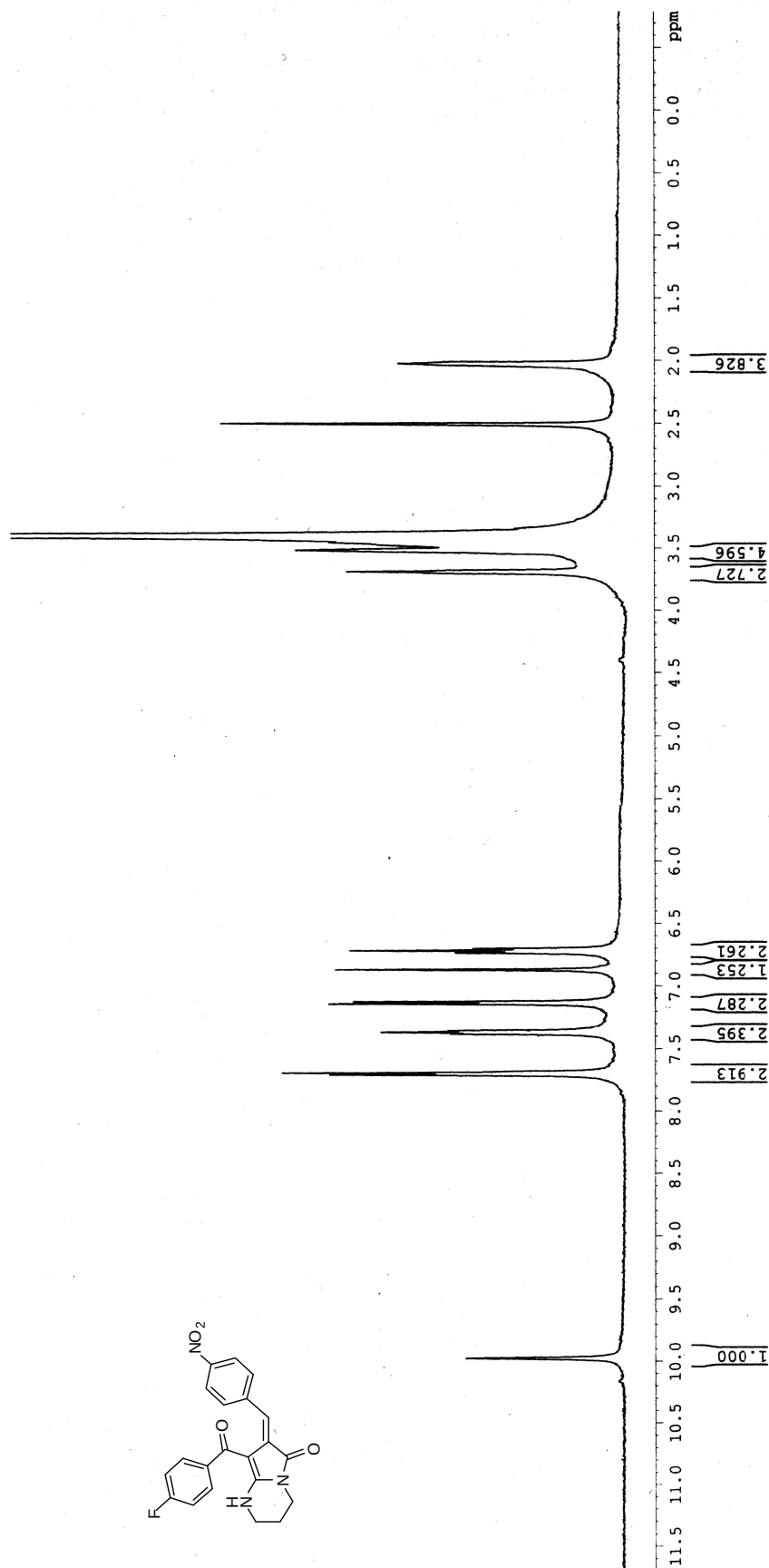
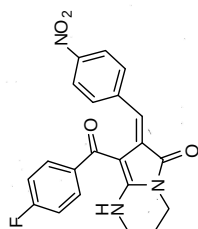


YUNNAN UNIVER. AV. DRX 500
fanjuan fj-036 in DMSO
12102203



¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 3l

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-013 in DMSO
12032601

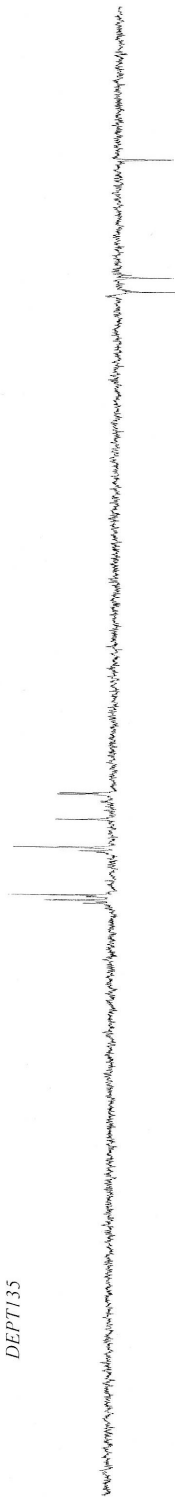


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 4c

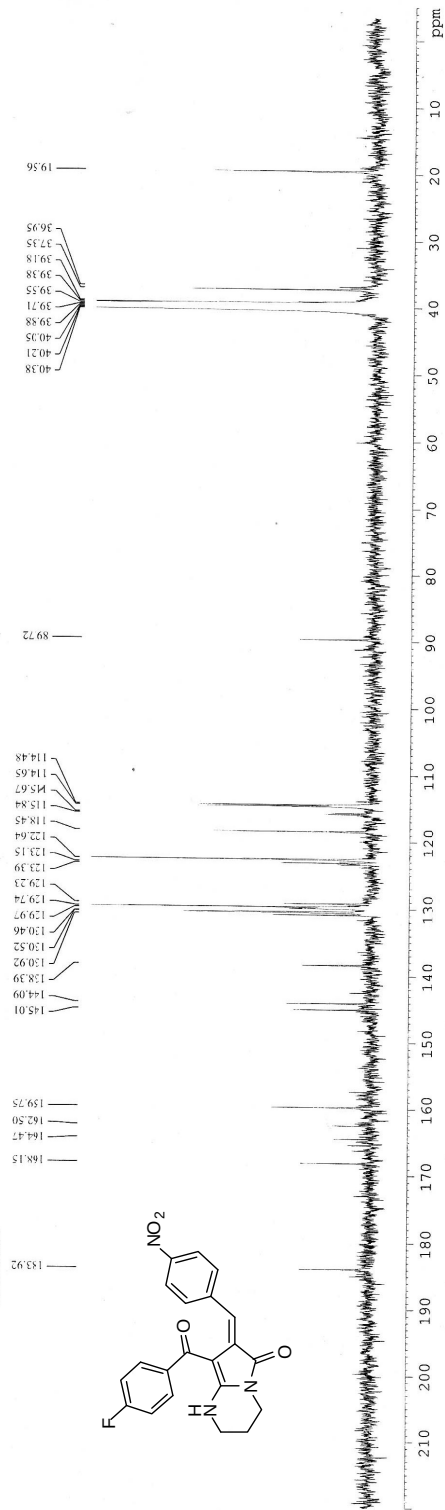
DEPT90



DEPT135

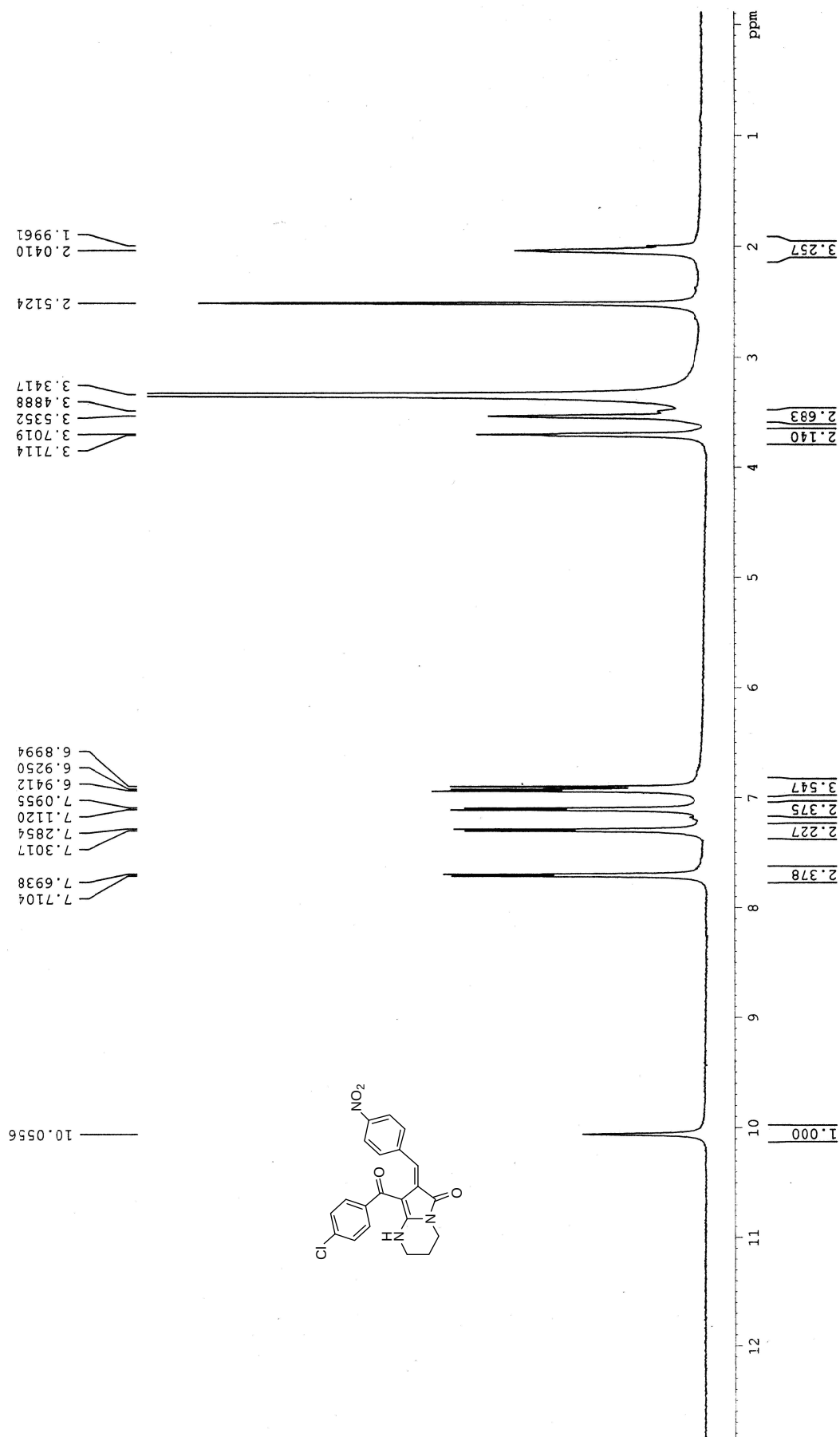


YUNNAN UNIVER. AV. DRX 500
fanjuan fj-013 in DMSO
12032601



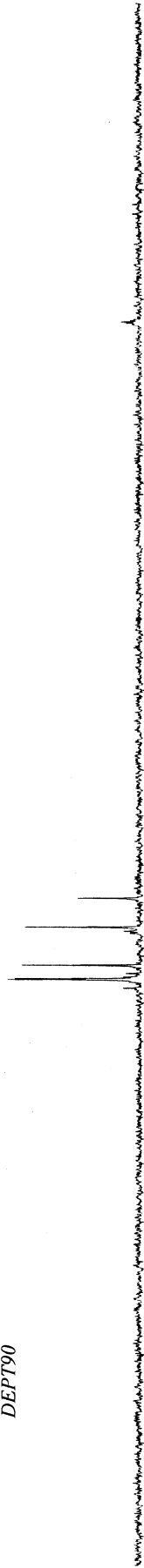
¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 4c

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-009 in DMSO
12030502

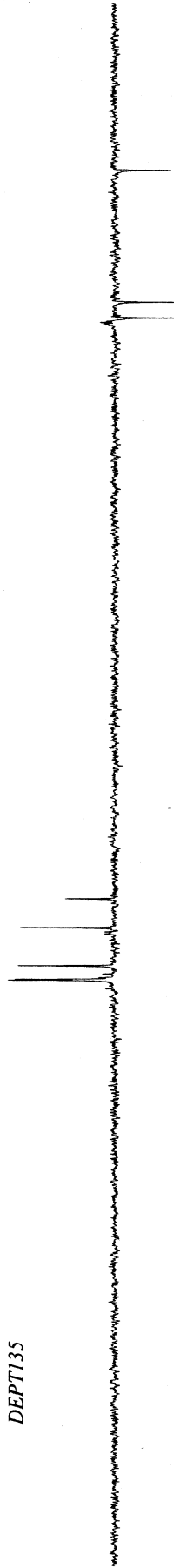


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 4a

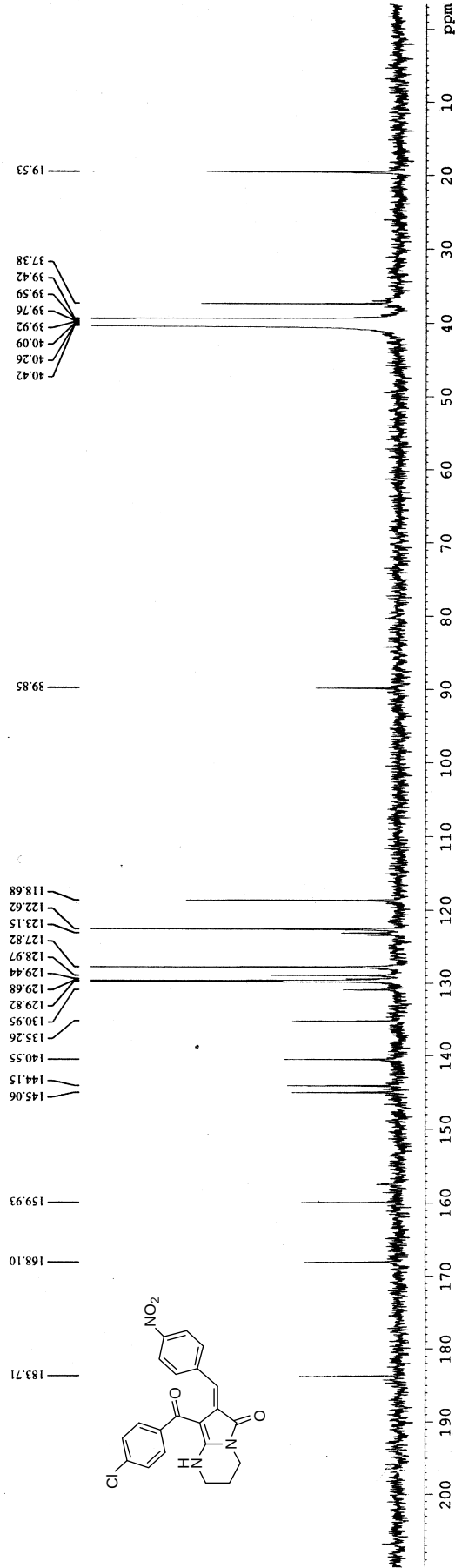
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DEPT135

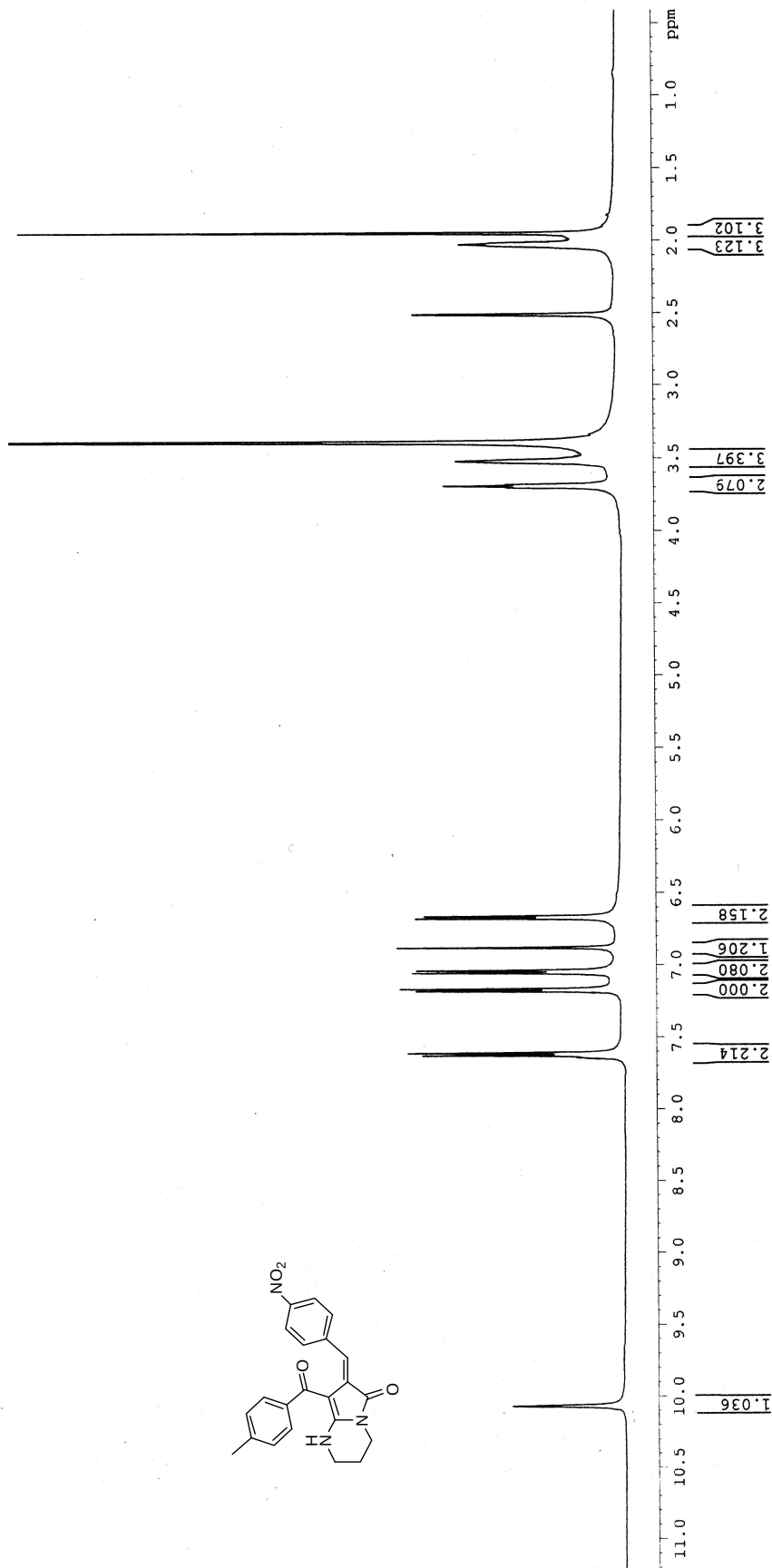
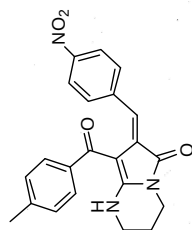


YUNNAN UNIVER. AV. DRX 500
farijuan fj-009 in DMSO
12030502



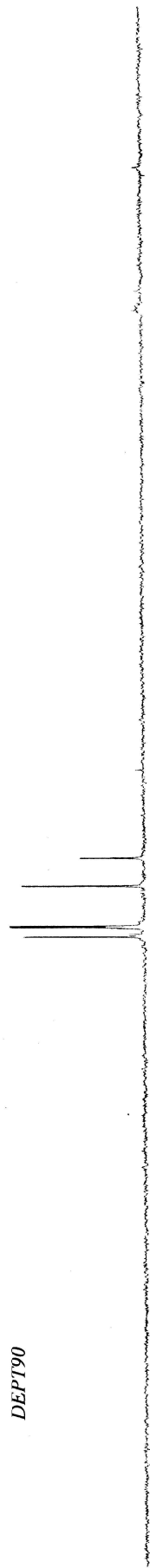
¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 4a

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-010 in DMSO
12030801

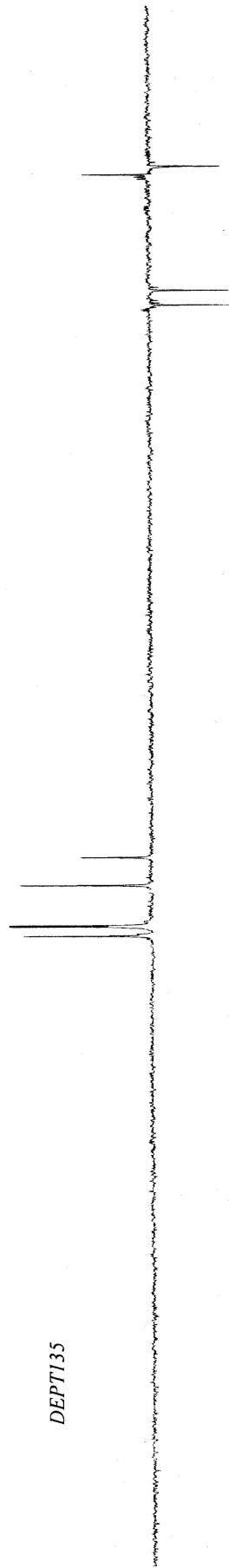


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 4e

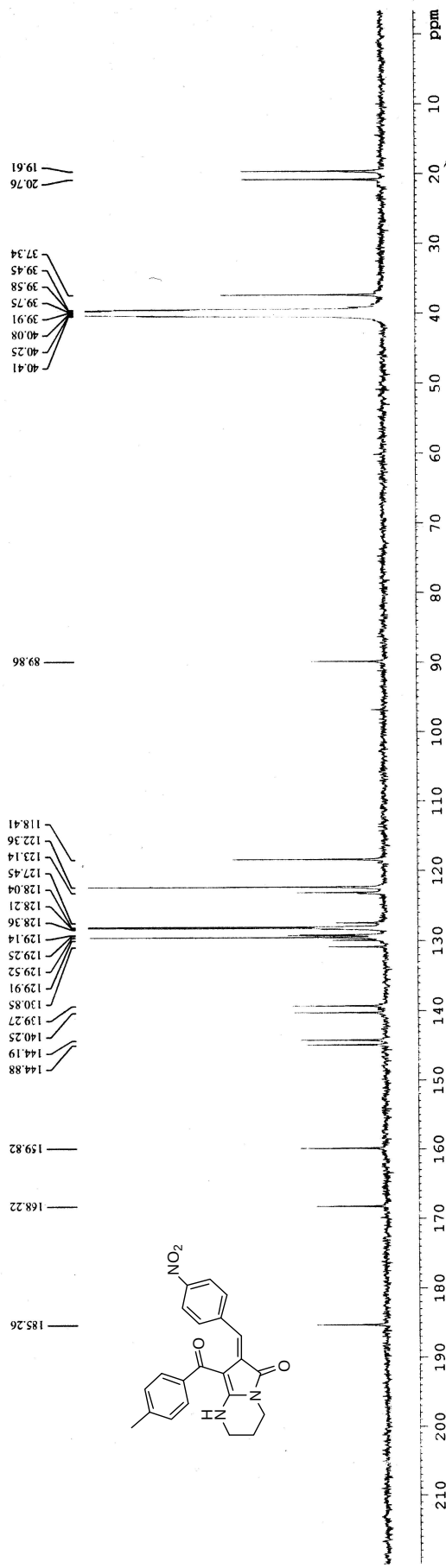
DEPT90



DEPT135

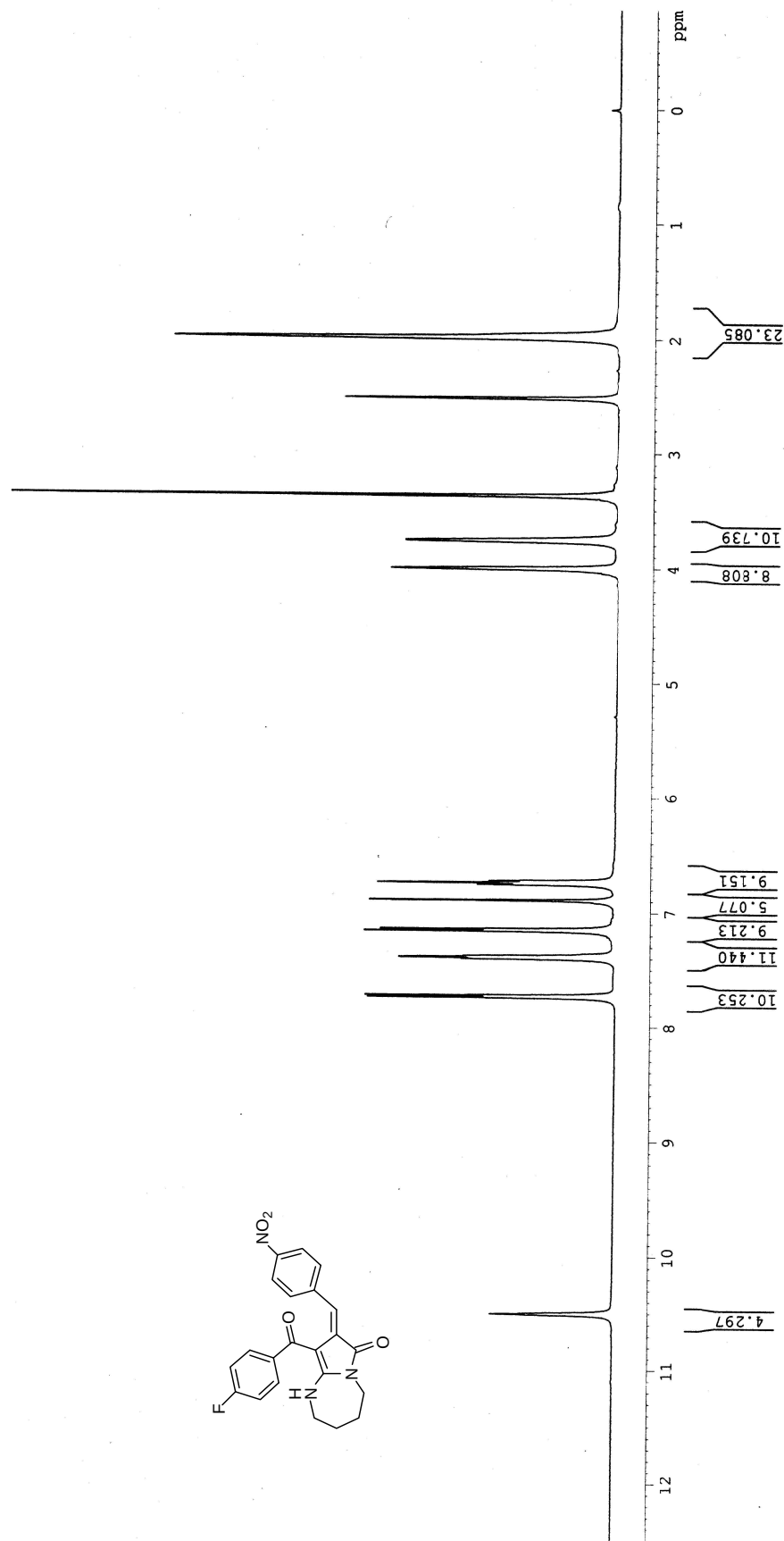
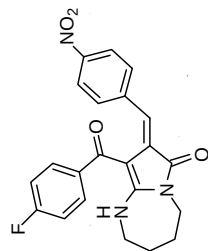


YUNNAN UNIVER. AV. DRX 500
fanjuan fj-010 in DMSO
12030801



¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 4e

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-042 in DMSO
12100902



¹H NMR (500MHz, DMSO-*d*₆) spectrum of 4h

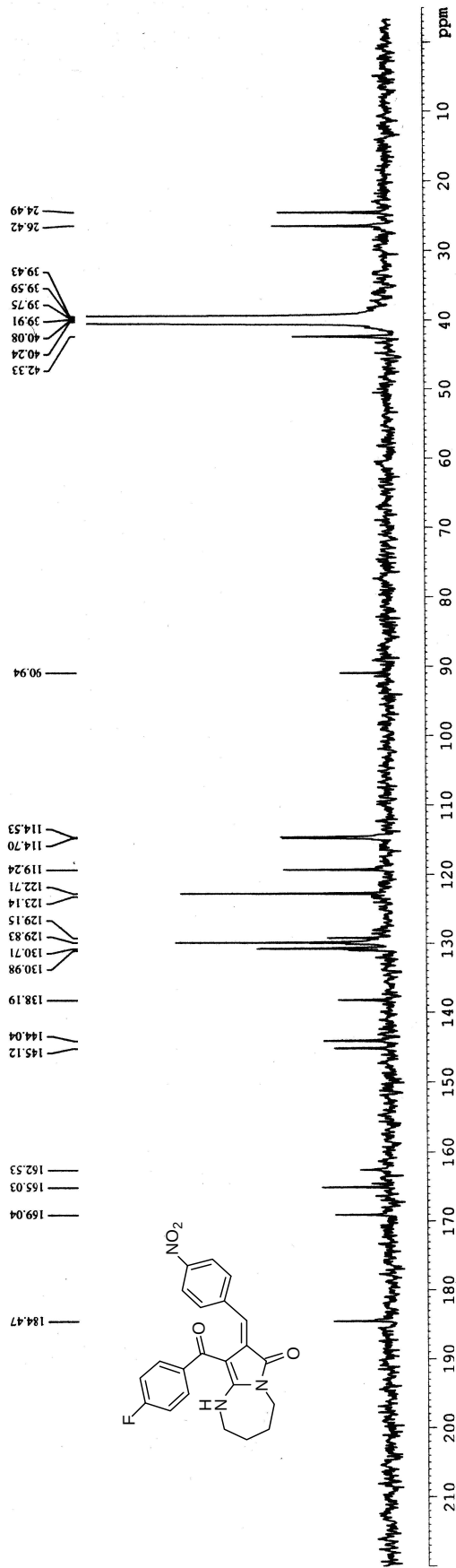
DEPT90



DEPT135

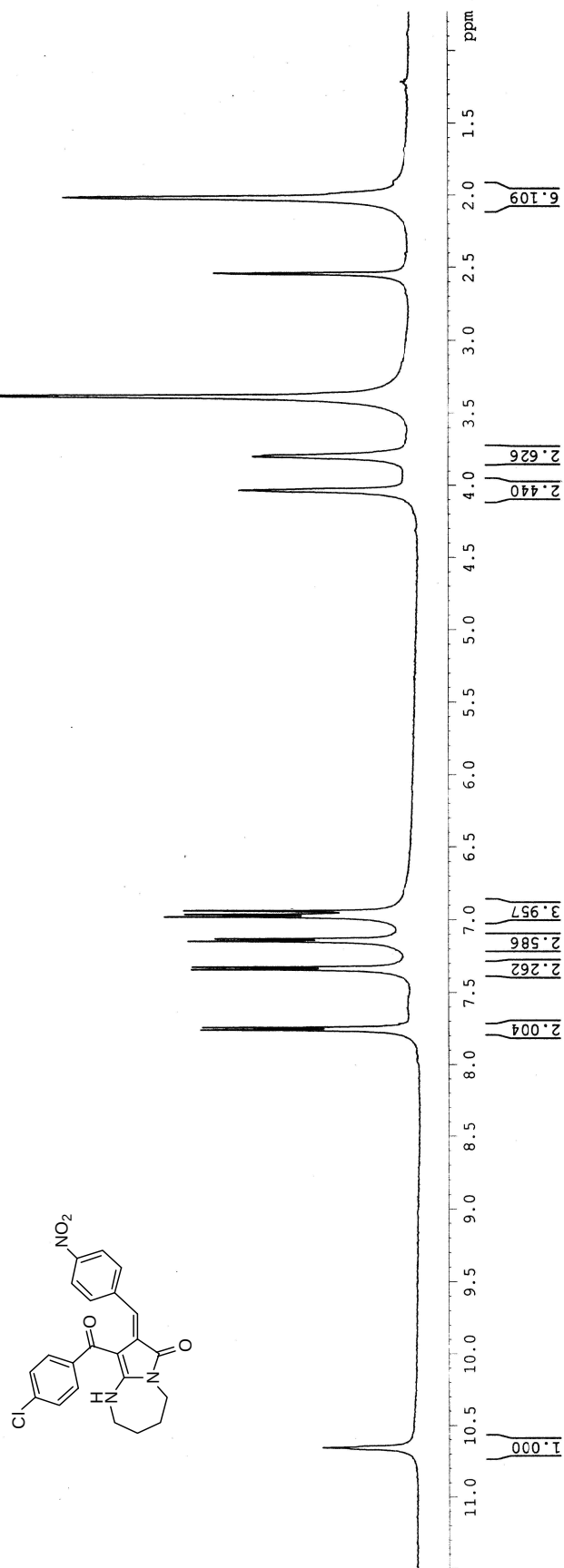


YUNNAN UNIVER. AV. DRX 500
Janjuan ji-042 in DMSO
 12100902



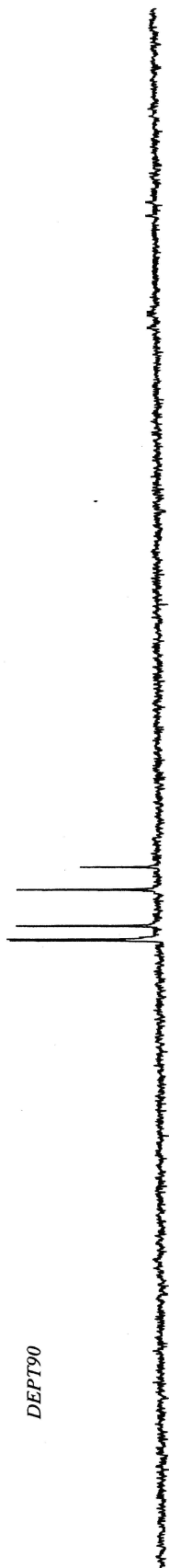
¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 4h

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-022 in DMSO
12051602

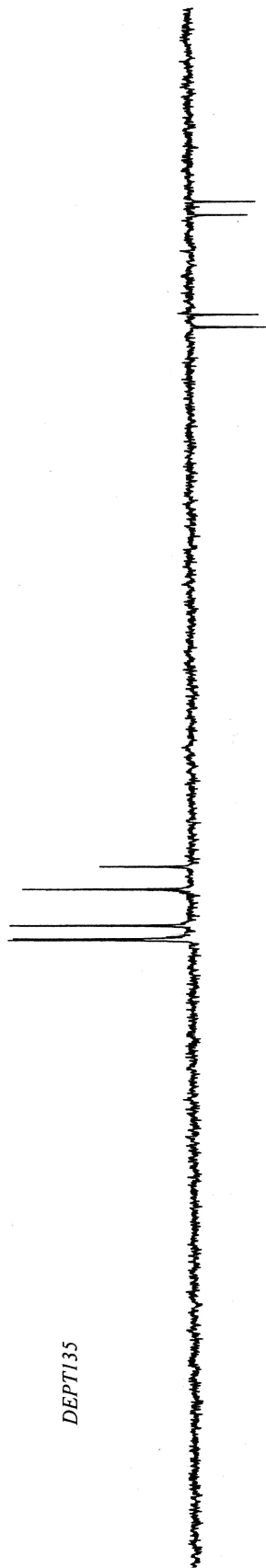


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 4i

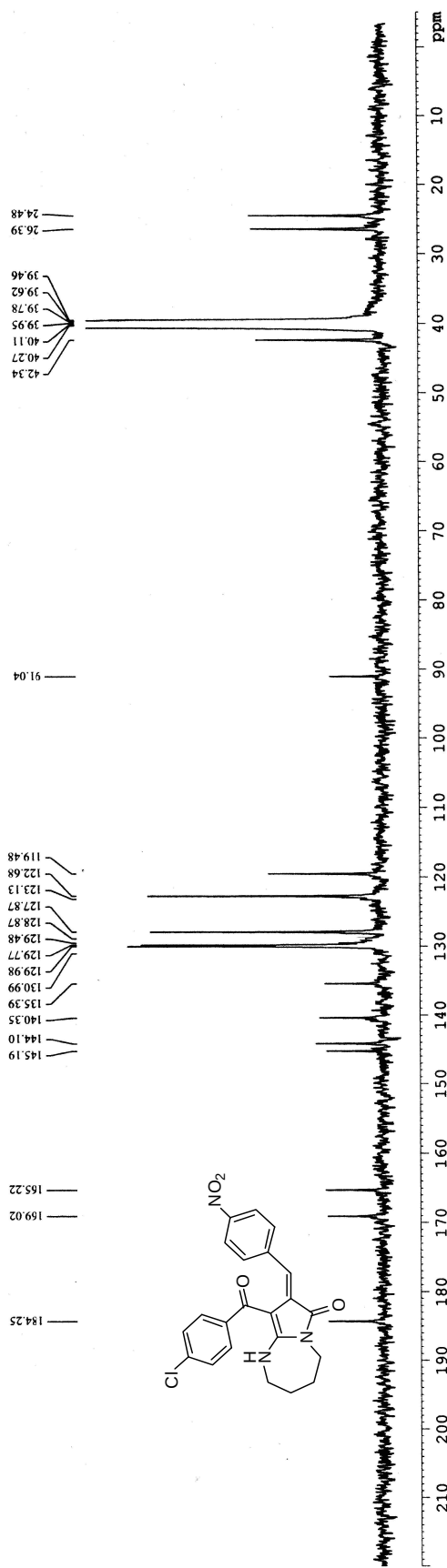
DEPT90



DEPT135

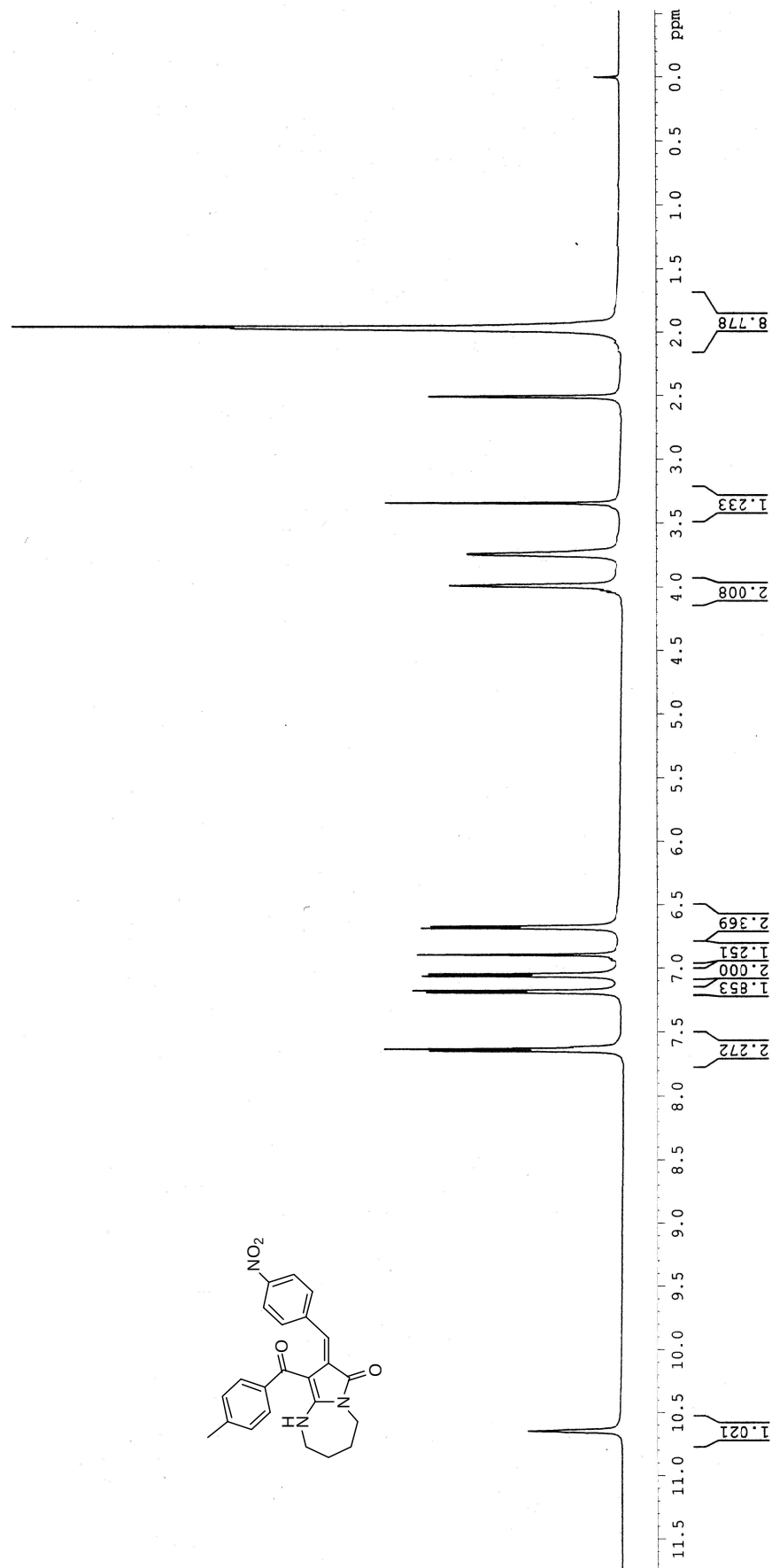
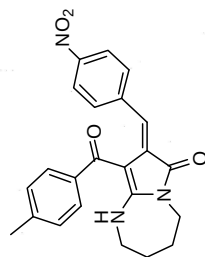


YUNNAN UNIVER. AV. DRX 500
faniuan fi-022 in DMSO



¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 4i

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-040 in DMSO
12091102

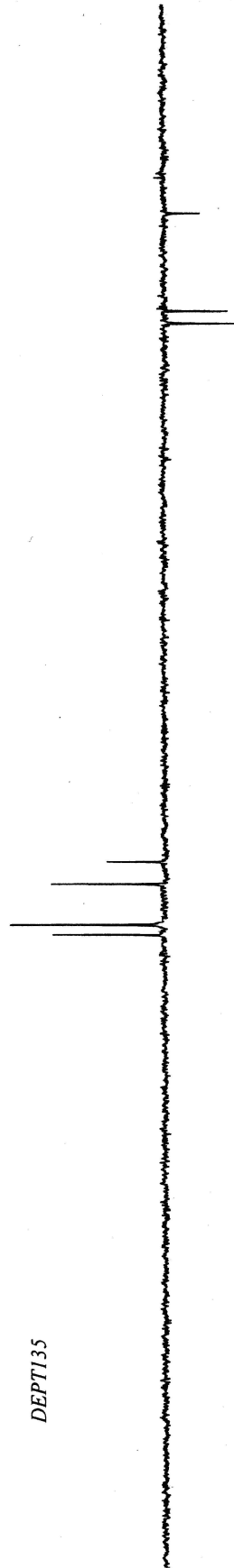


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 4k

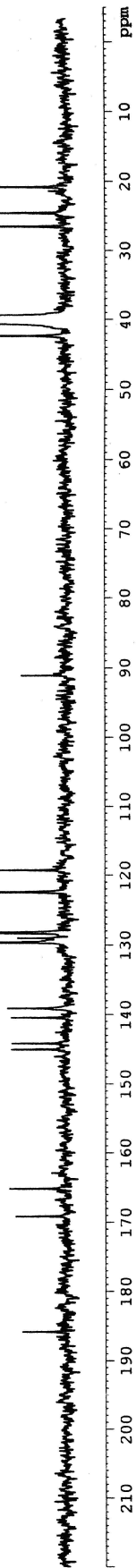
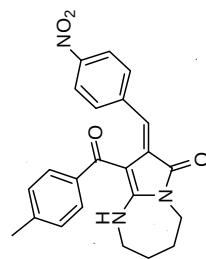
DEPT90



DEPT135

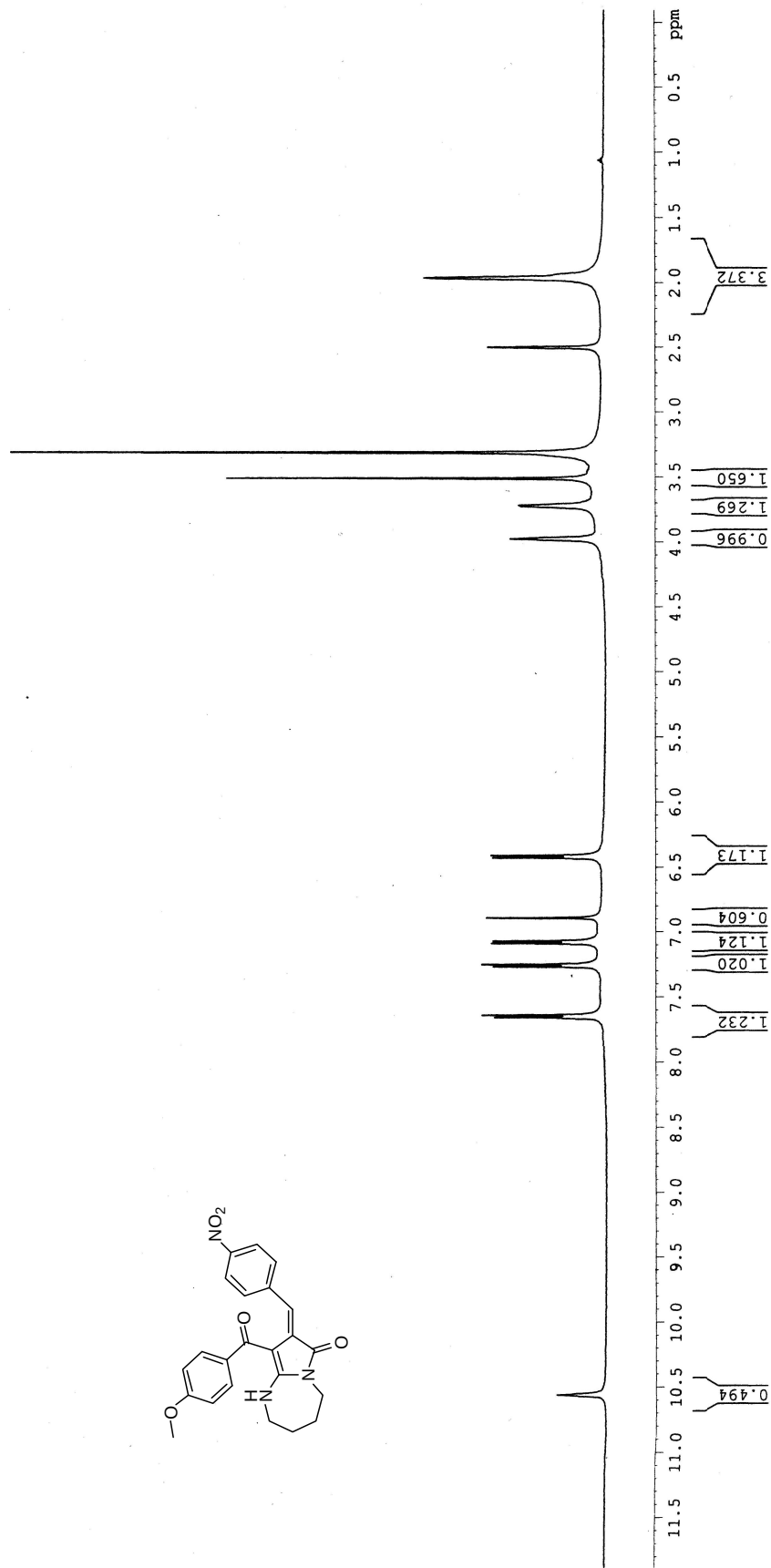


YUNNAN UNIVER. AV. DRX 500
fanjuan fj-040 in DMSO
12091102



¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 4k

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-034 in DMSO
12102202

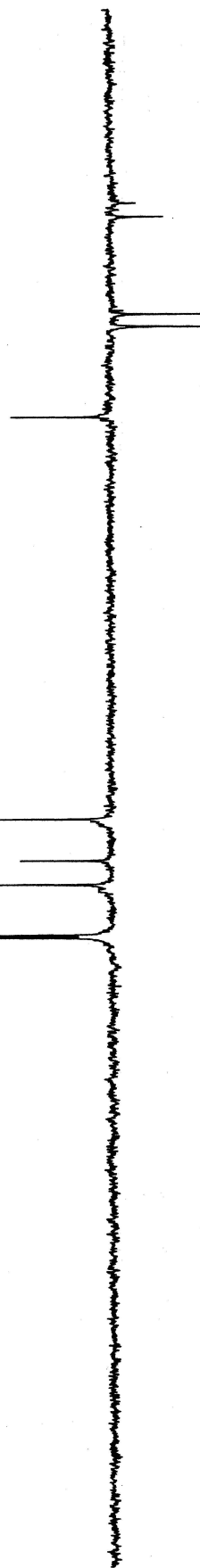


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 4l

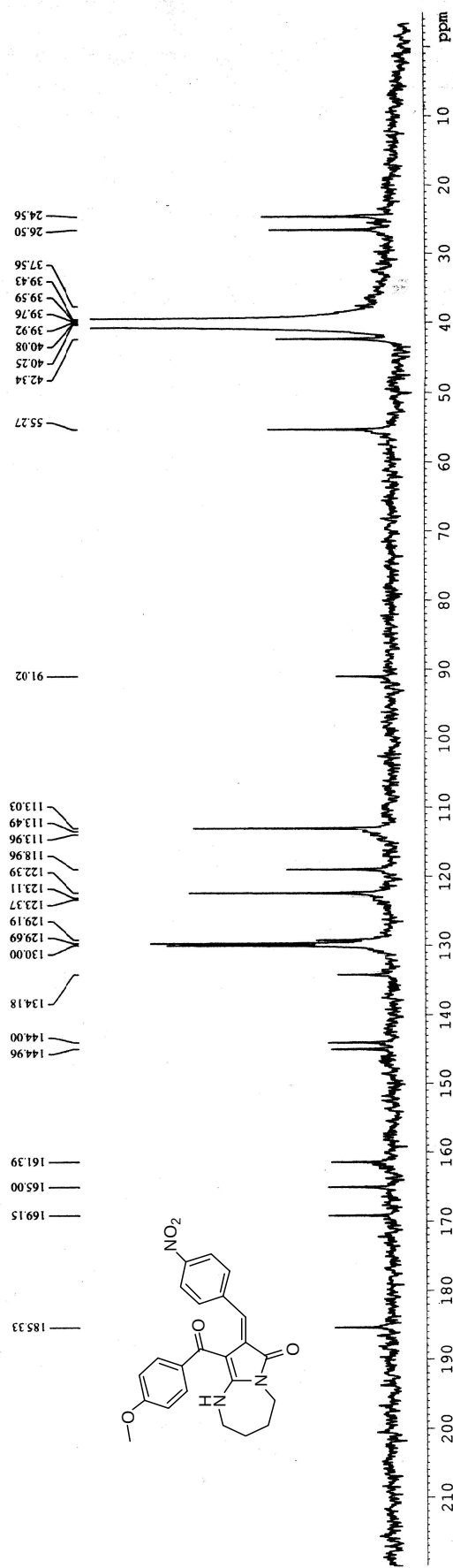
DEPT90



DEPT135

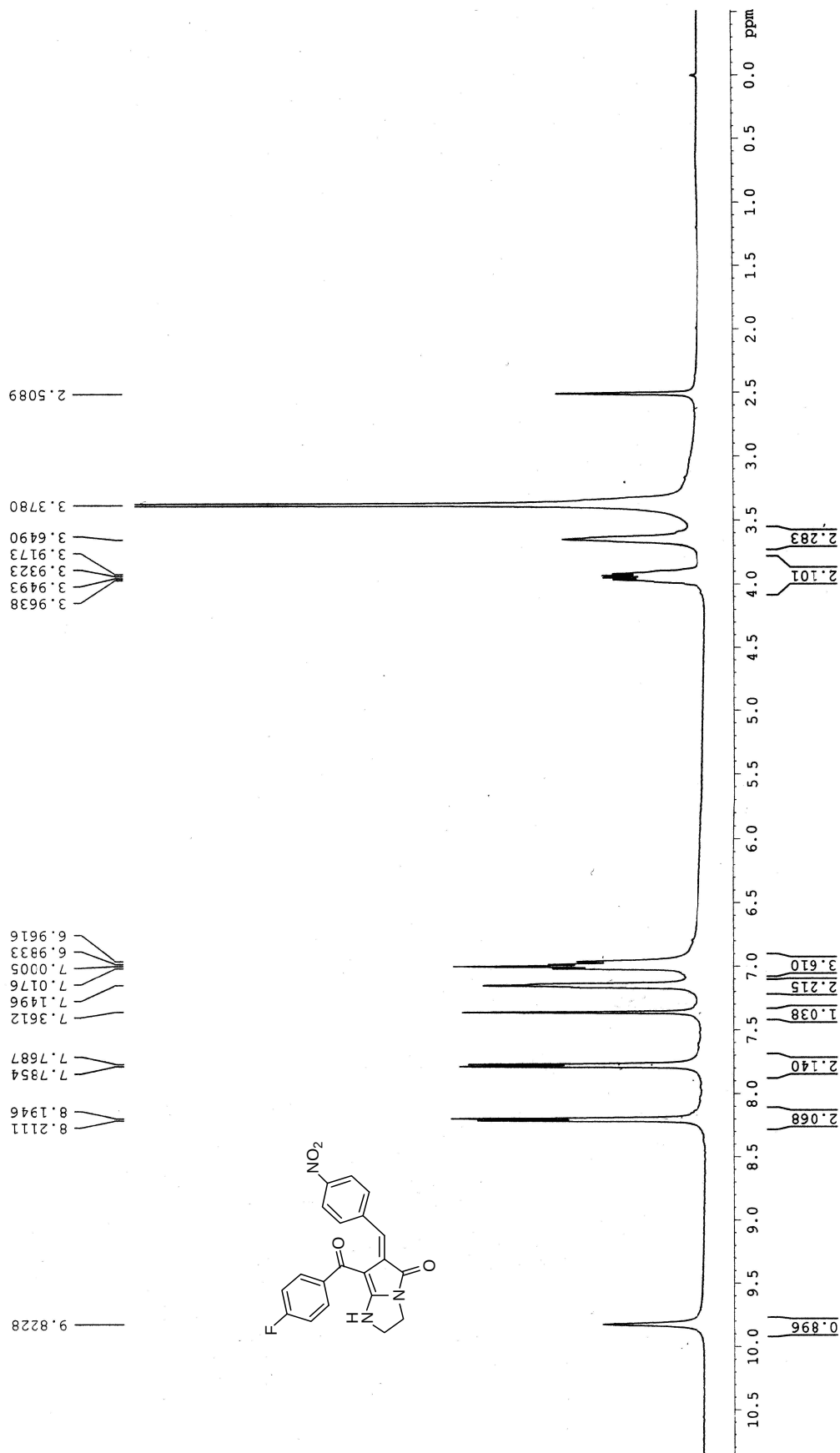


YUNNAN UNIVER. AV. DRX 500
fanjuan fj-034 in DMSO
12102202



¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 4l

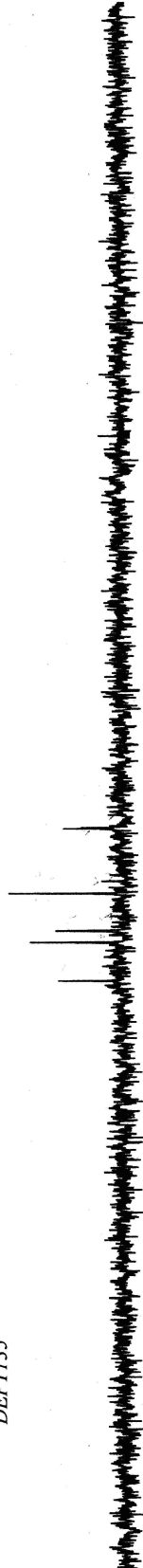
YUNNAN UNIVER. AV. DRX 500
fanjuan fj-028 in DMSO
12082802



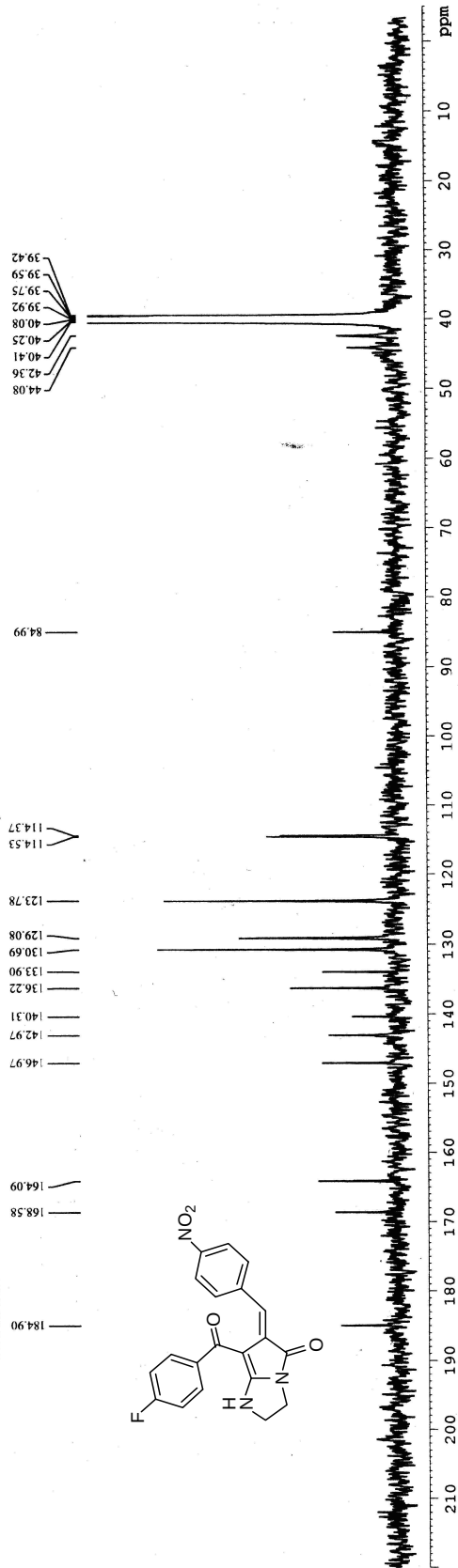
DEPT90



DEPT135

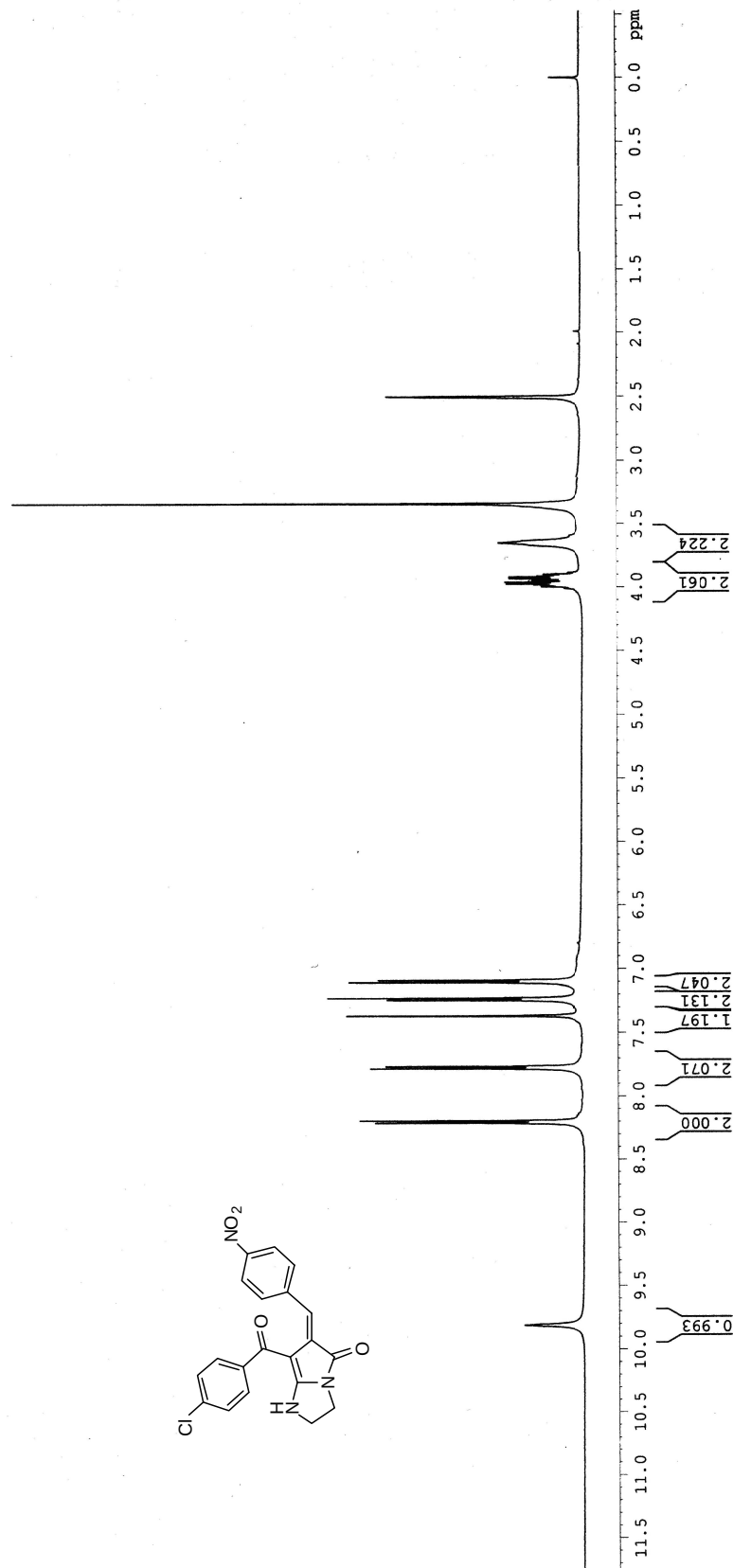
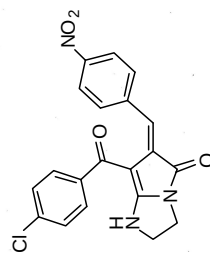


YUNNAN UNIVER. AV. DRX 500
farijuan fj-028 in DMSO
12082802

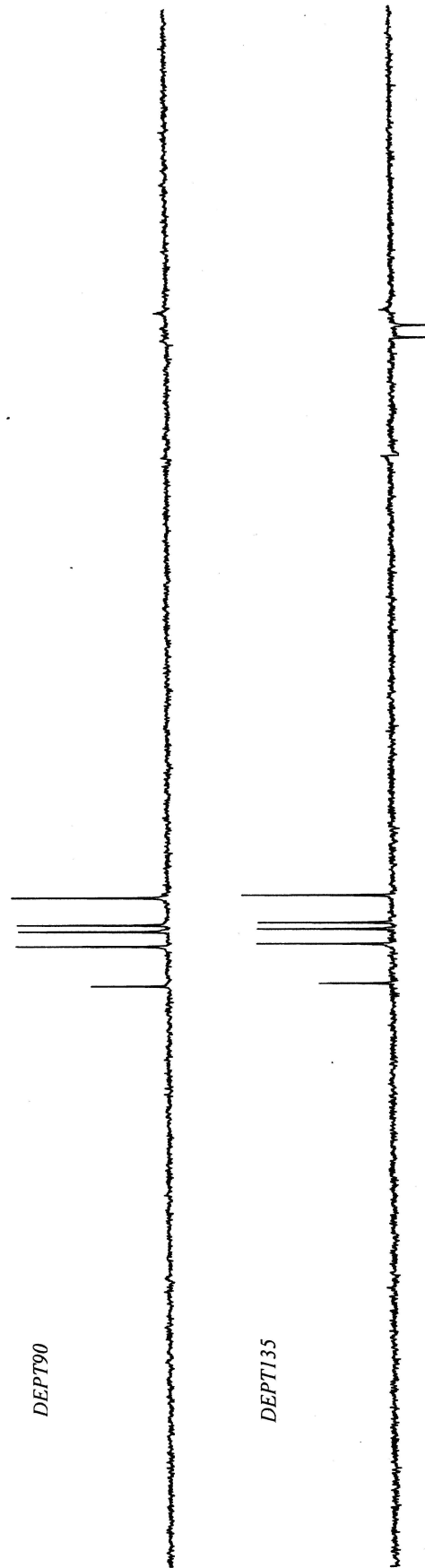


¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 4m

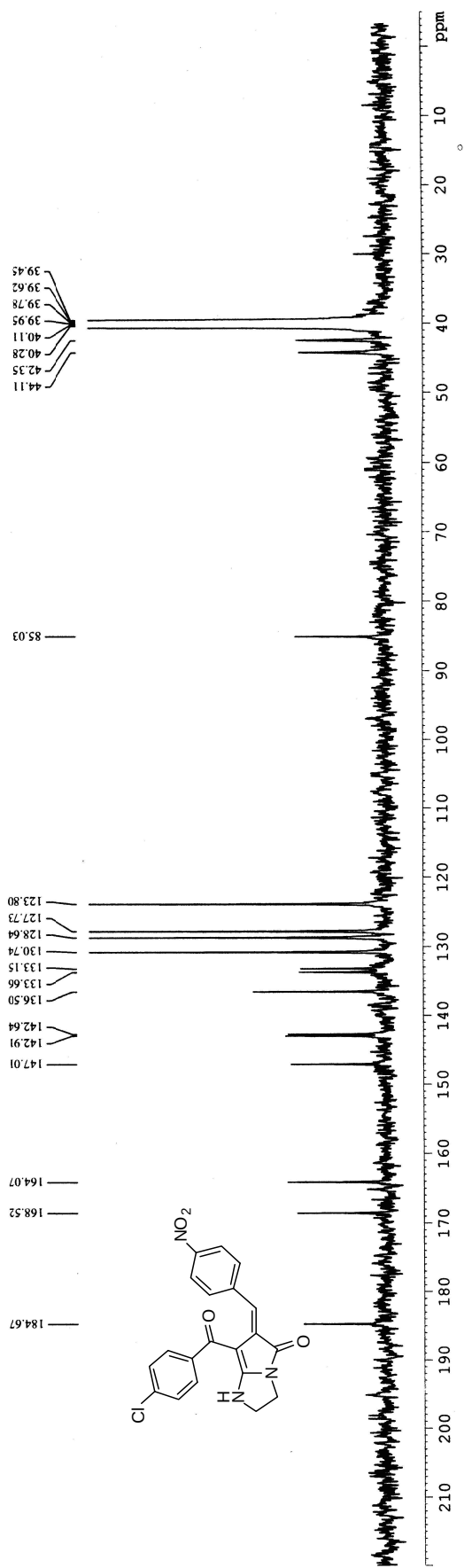
YUNNAN UNIVER. AV. DRX 500
fanjuan fj-029 in DMSO
12091101



¹H NMR (500MHz, DMSO-*d*₆) spectrum of 4n

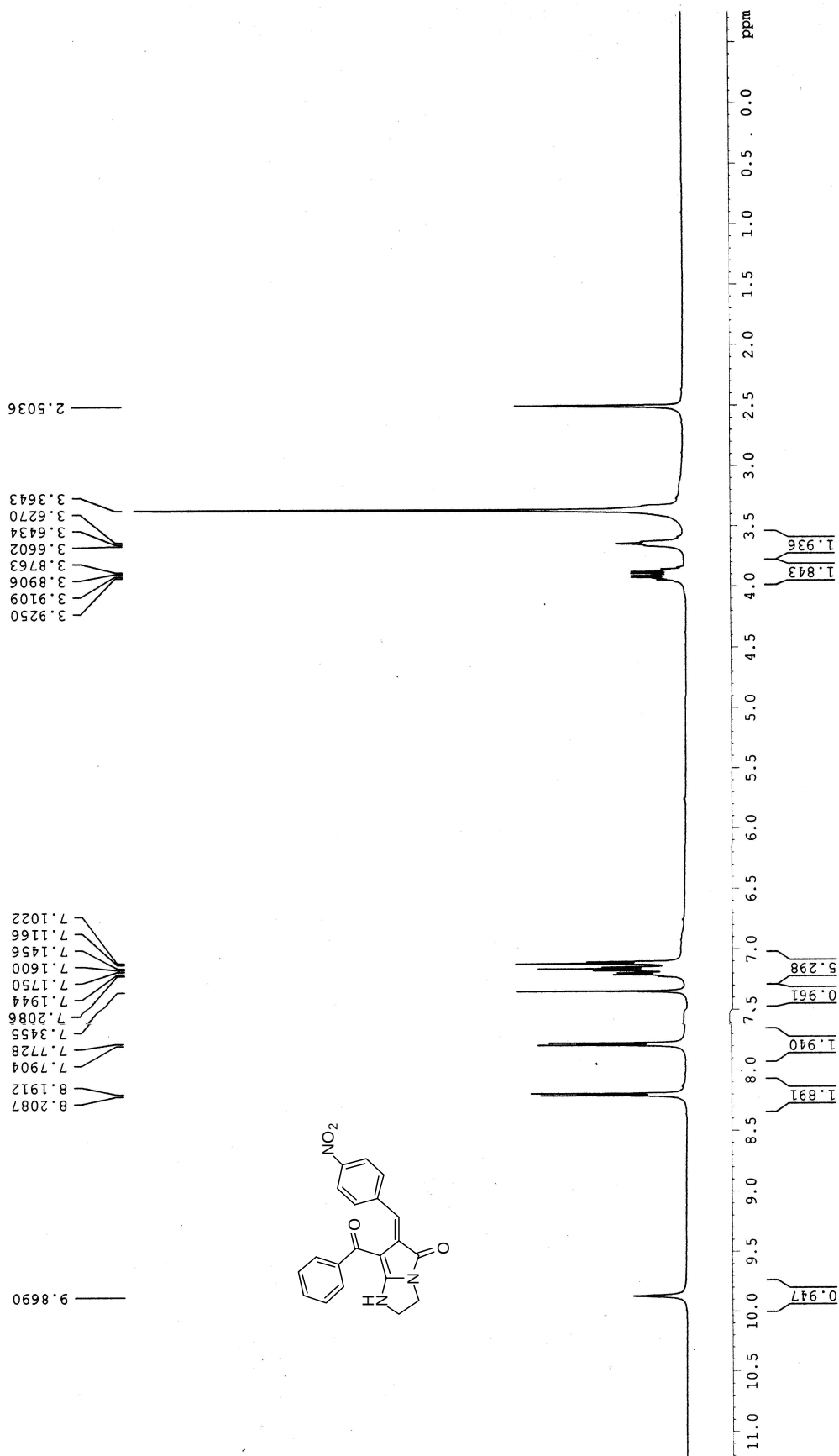


YUNNAN UNIVER. AV. DRX 500
fanjuan fj-029 in DMSO
 12091101



¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 4n

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-030 in DMSO
12102201

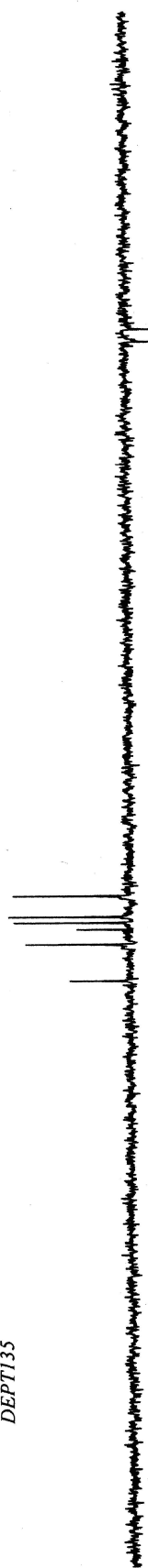


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 40

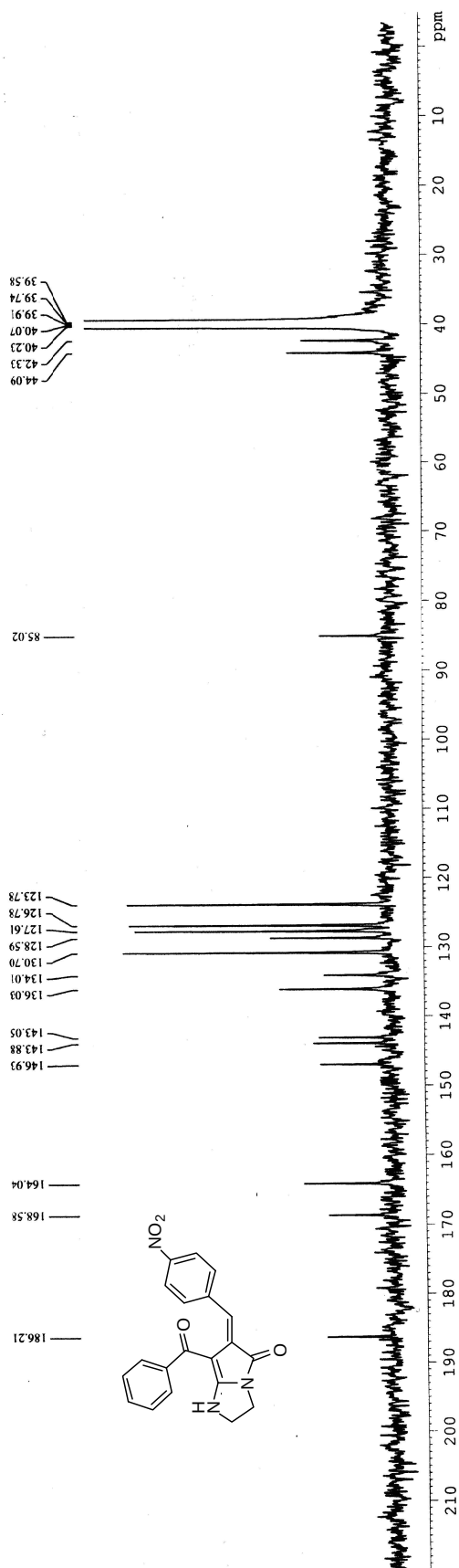
DEPT90



DEPT135

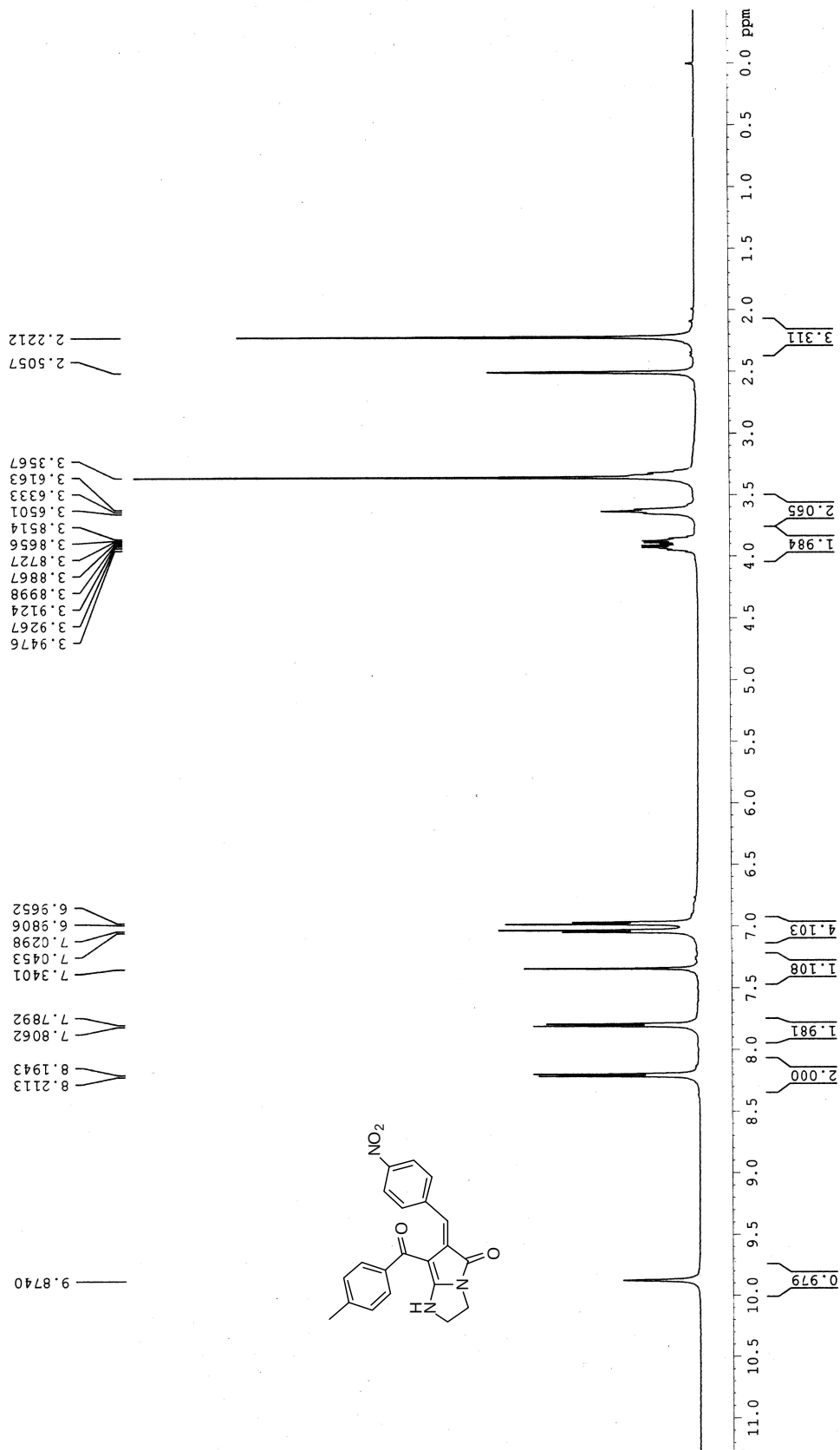


YUNNAN UNIVER. AV. DRX 500
farjuran fj-030 in DMSO
12102201



¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 40

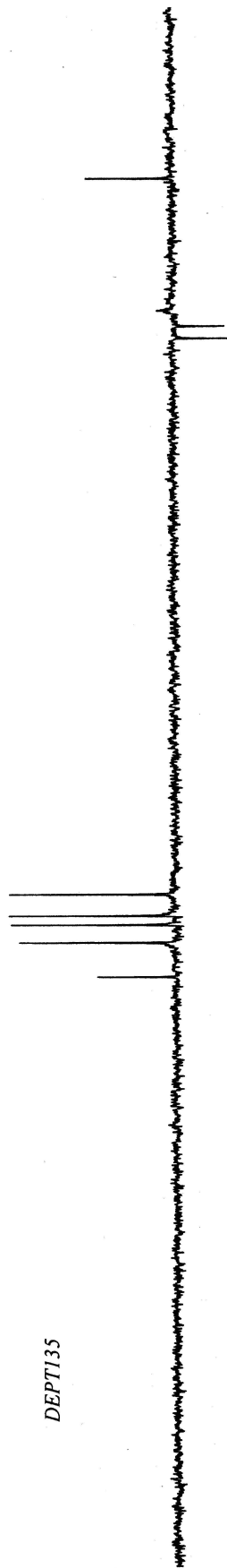
YUNNAN UNIVER. AV. DRX 500
fanjuan fj-031 in DMSO
12100901



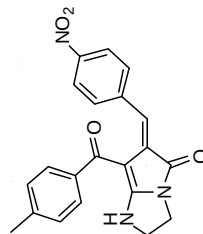
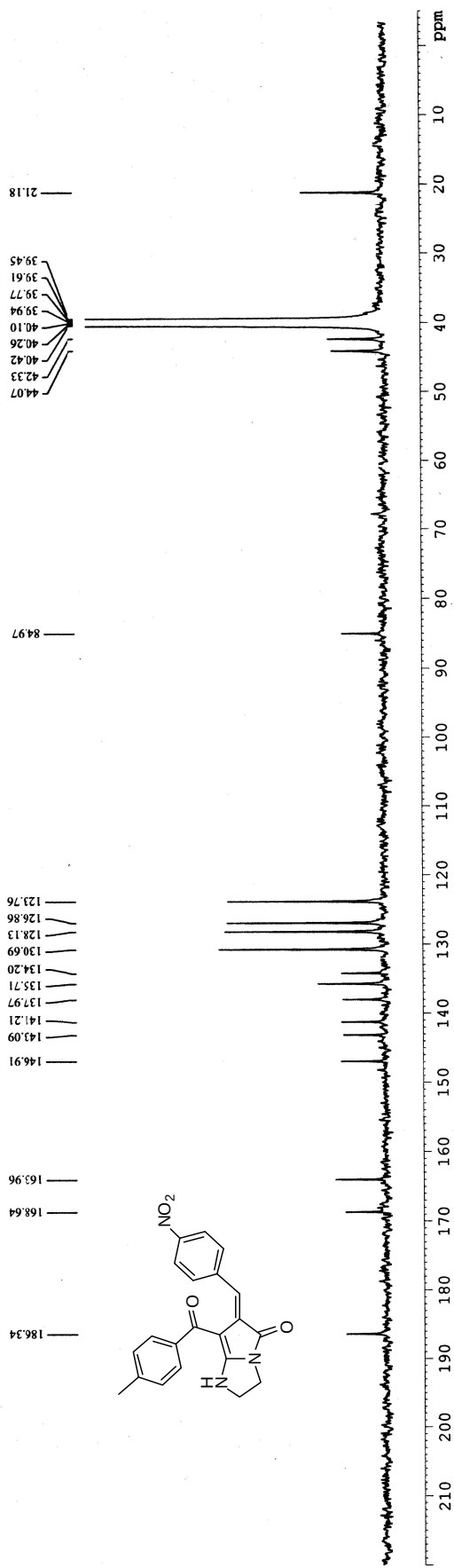
DEPT90



DEPT135

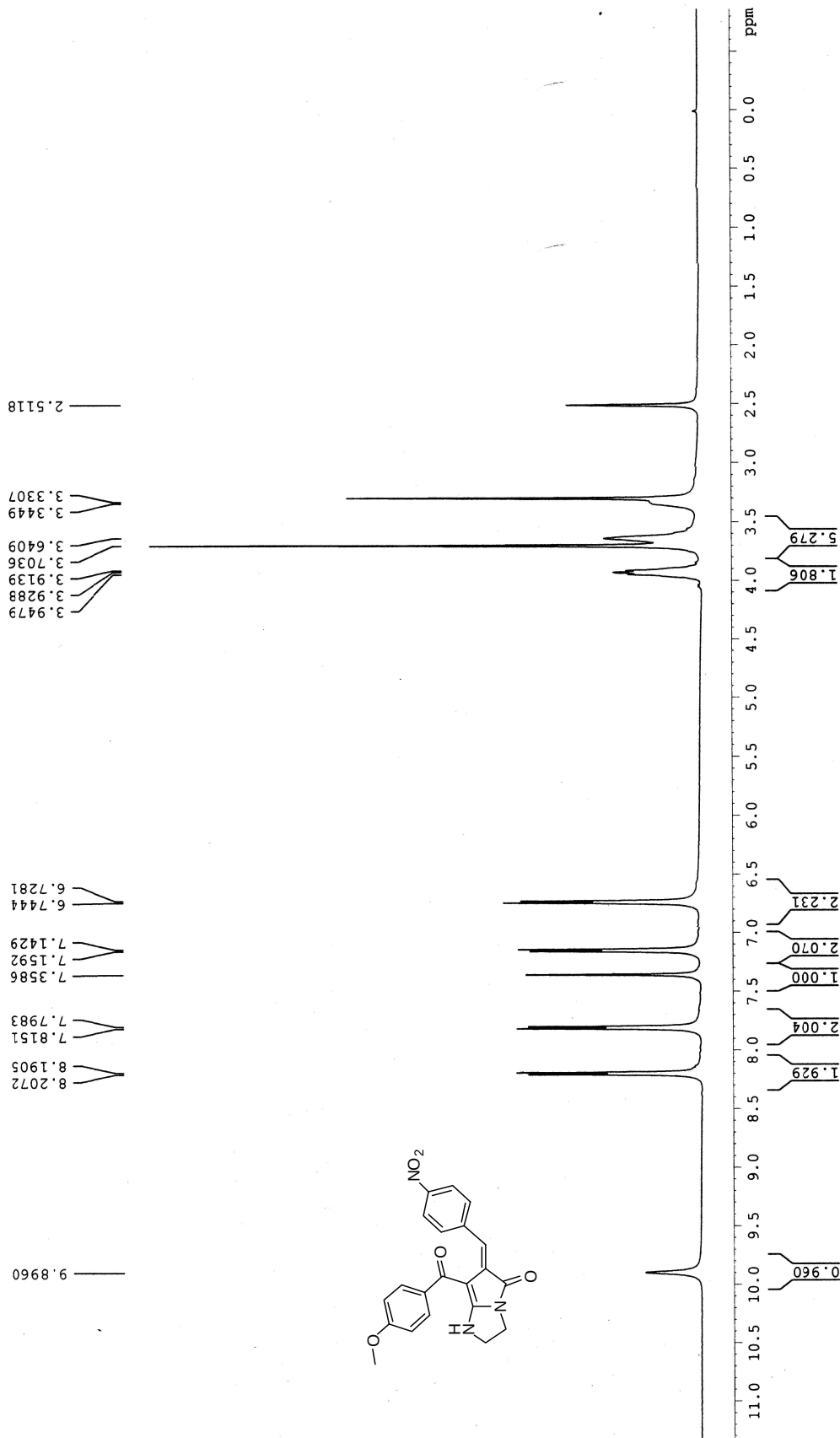


YUNNAN UNIVER. AV. DRX 500
fanjuan fj-031 in DMSO
12100901



¹³C NMR (125MHz, DMSO-*d*₆) spectrum of 4p

YUNNAN UNIVER. AV. DRX 500
fanjuan fj-032 in DMSO
12092402

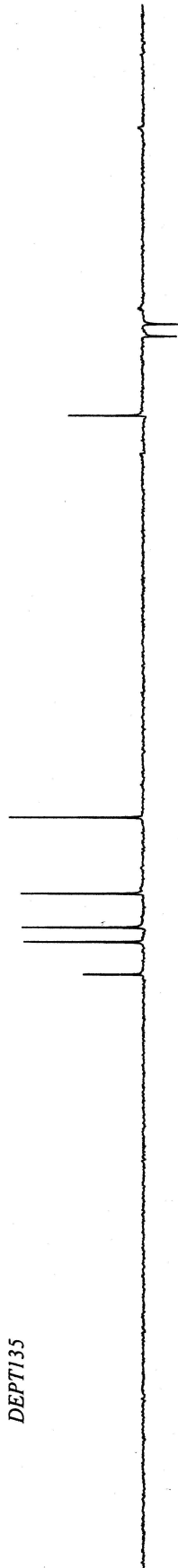


¹H NMR (500MHz, DMSO-*d*₆) spectrum of 4q

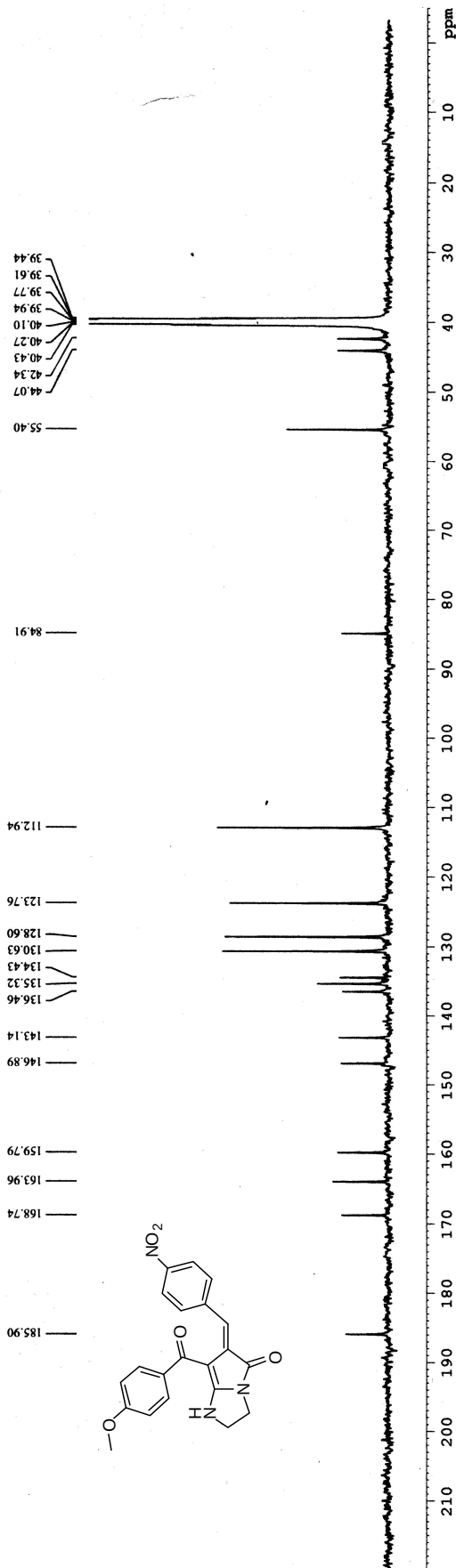
DEPT90



DEPT135

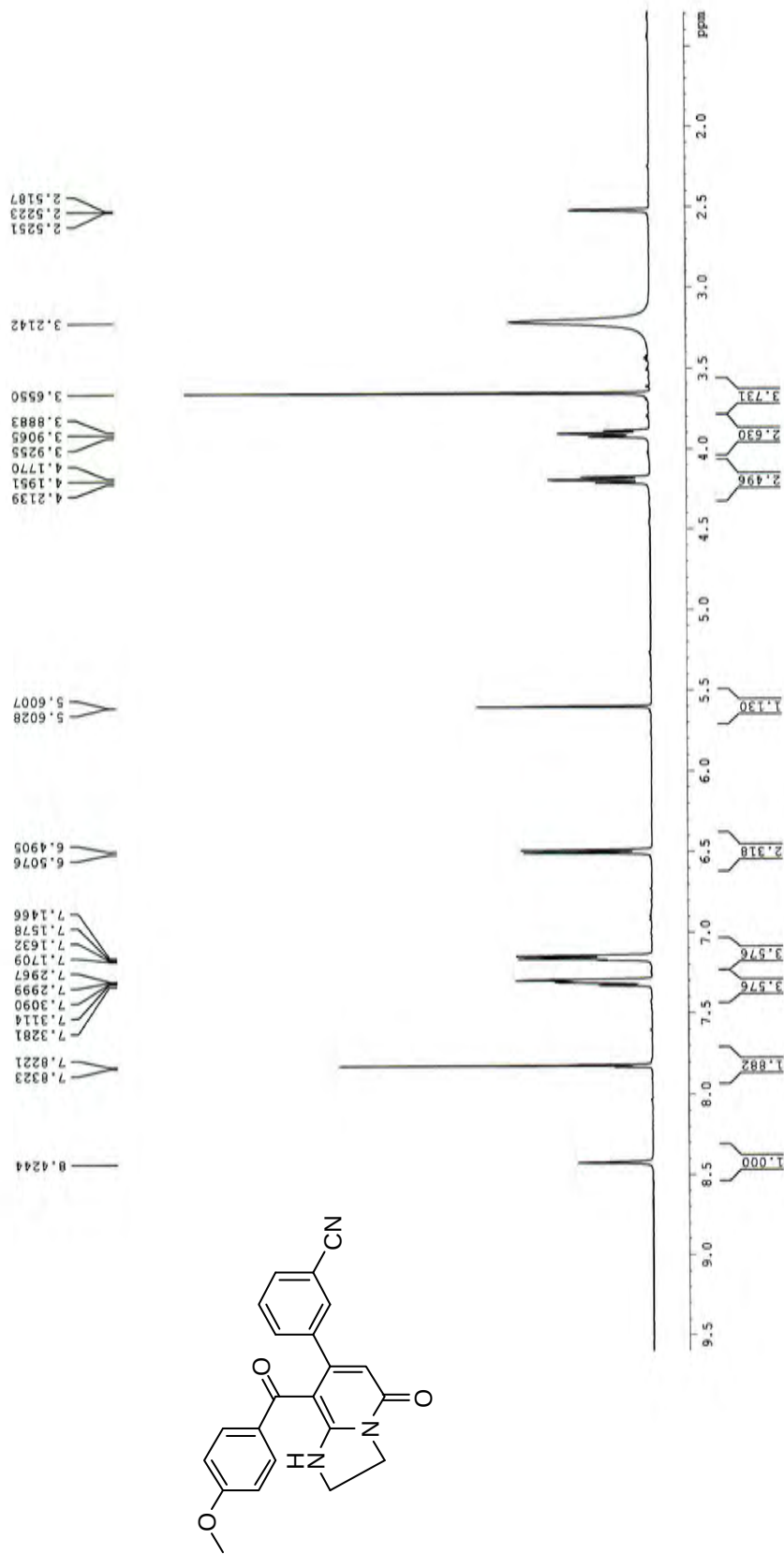


YUNNAN UNIVER. AV. DRX 500
fanjuan fj-032 in DMSO
12092402

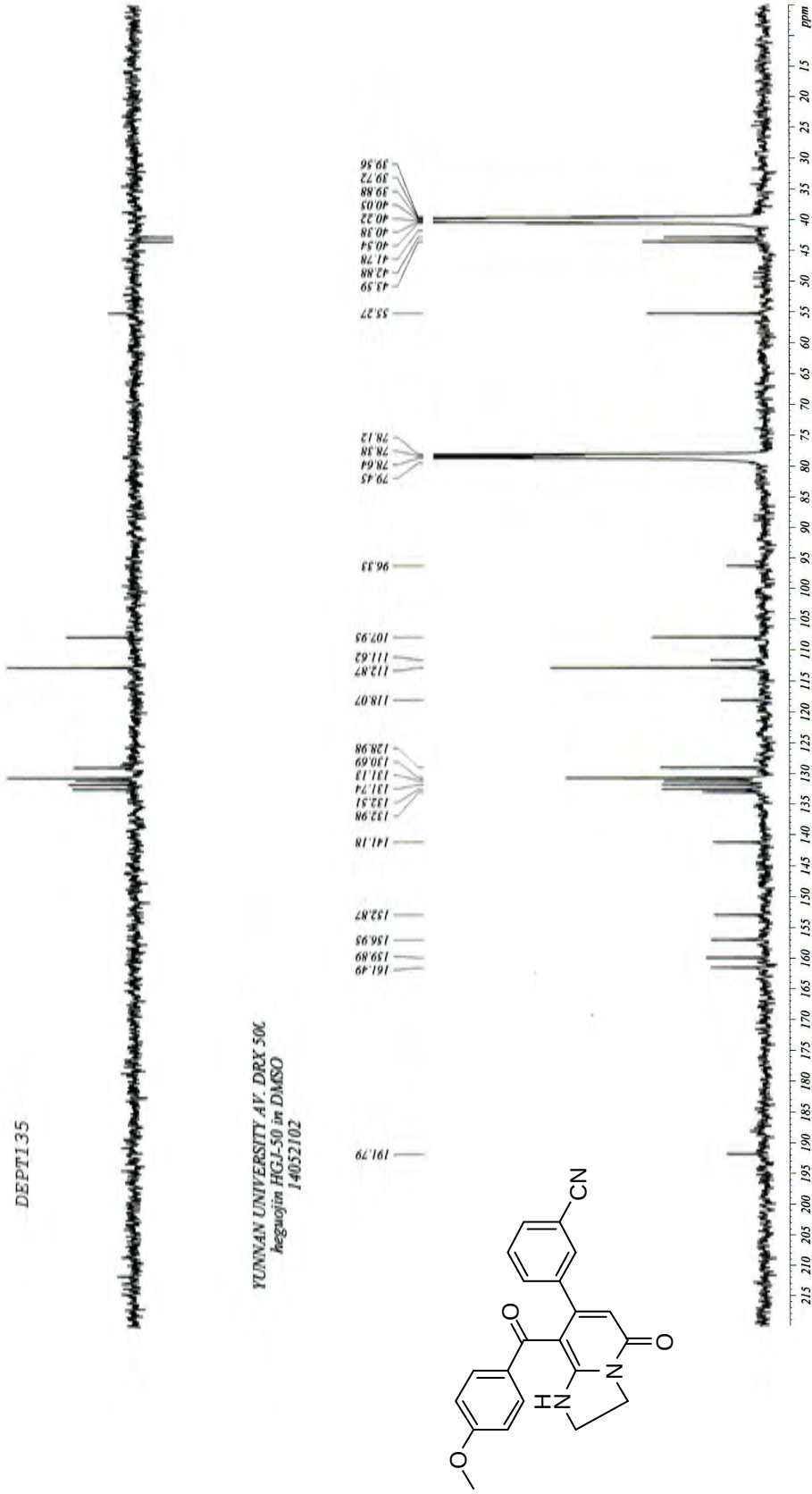


¹³C NMR (125MHz, DMSO-d₆) spectrum of 4q

YUNNAN UNIVERSITY AV. DRX 500
heguojin HGJ-50 in DMSO
14052102

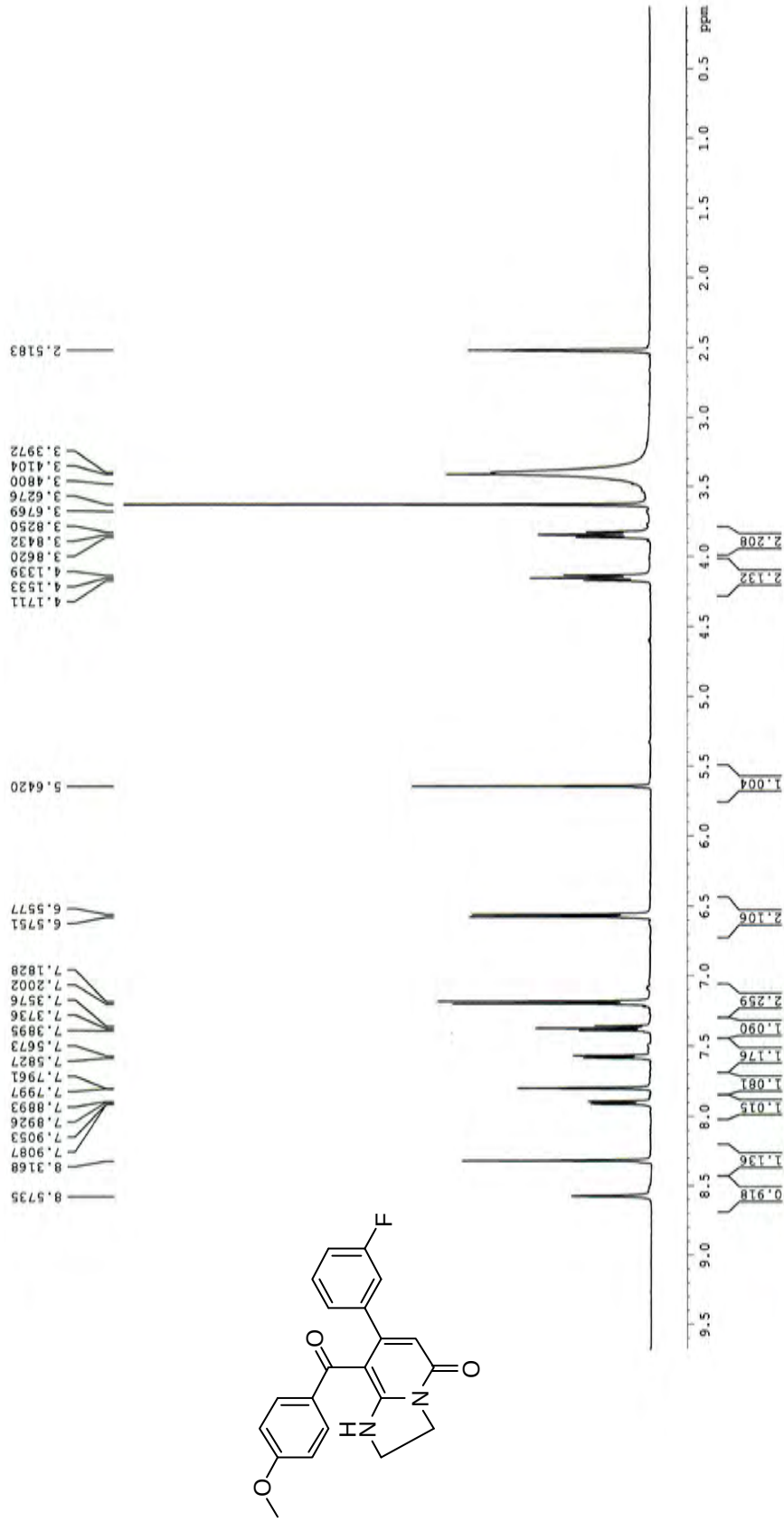


¹H NMR (500 MHz, CDCl₃+DMSO-*d*₆) spectrum of 3r

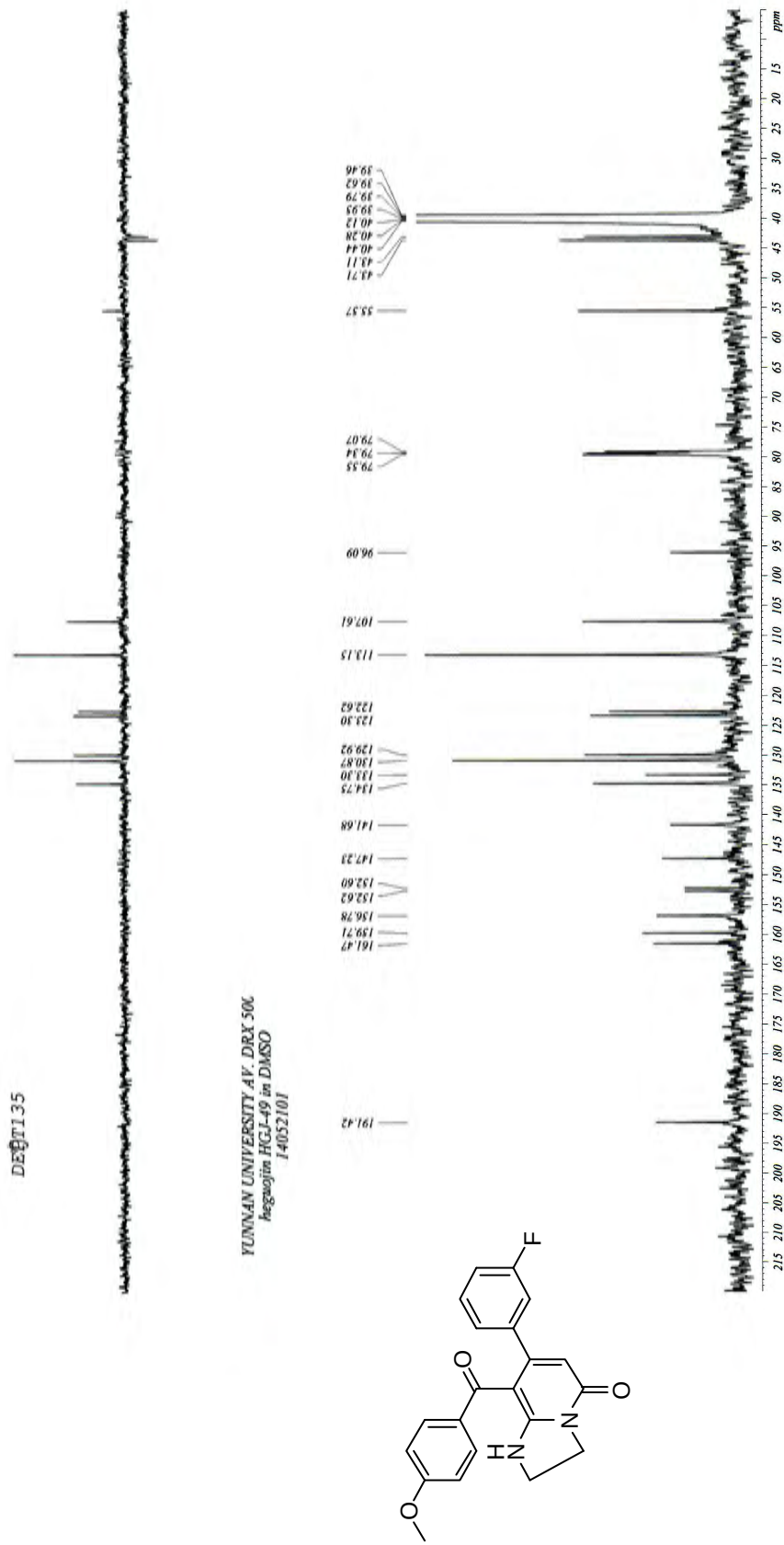


¹³C NMR (125MHz, CDCl₃+DMSO-*d*₆) spectrum of 3r

YUNNAN UNIVERSITY AV. DRX 500
 heguojin HGJ-49 in DMSO
 14052101



¹H NMR (500MHz, CDCl₃+DMSO-*d*₆) spectrum of 3s



CCDC 978904 : X-Ray data for compound **3c**

ORTEP drawing of **3c**

Crystals were obtained by slow diffusion of EtOH/H₂O

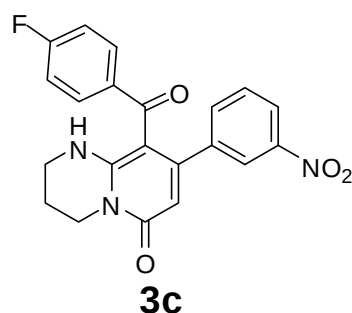
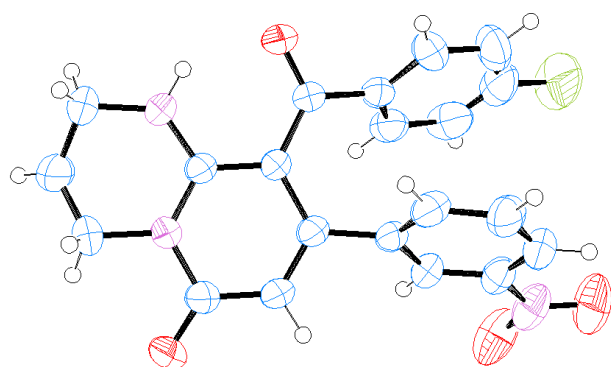


Table. Crystal data and structure refinement for **3c**.

Identification code	120528b
Empirical formula	C ₂₁ H ₁₅ FN ₃ O ₄
Formula weight	392.36
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.9126(11) Å alpha = 67.925(2) deg. b = 9.8932(13) Å beta = 81.427(2) deg. c = 12.7628(17) Å gamma = 86.609(2) deg.
Volume	915.5(2) Å ³
Z, Calculated density	2, 1.423 Mg/m ³
Absorption coefficient	0.107 mm ⁻¹
F(000)	406
Crystal size	0.21 x 0.17 x 0.12 mm
Theta range for data collection	1.74 to 25.00 deg.
Limiting indices	-9<=h<=9, -11<=k<=11, -15<=l<=15
Reflections collected / unique	7312 / 3221 [R(int) = 0.0272]
Completeness to theta = 25.00	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9872 and 0.9778
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3221 / 0 / 263
Goodness-of-fit on F ²	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0619, wR2 = 0.1628
R indices (all data)	R1 = 0.0985, wR2 = 0.1835
Extinction coefficient	0.014(4)
Largest diff. peak and hole	0.544 and -0.356 e.Å ⁻³

Table. Bond lengths [Å] and angles [deg] for **3c**.

F(1)-C(13)	1.370(4)
N(1)-C(4)	1.371(3)
N(1)-C(8)	1.410(3)
N(1)-C(1)	1.468(3)
N(2)-C(4)	1.335(3)
N(2)-C(3)	1.457(3)
N(2)-H(4)	0.8600
N(3)-O(4)	1.219(4)
N(3)-O(3)	1.230(4)

N(3)-C(18)	1.467(4)
O(1)-C(8)	1.237(3)
O(2)-C(9)	1.246(3)
C(1)-C(2)	1.422(5)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-C(3)	1.423(5)
C(2)-H(2)	0.9300
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.419(4)
C(5)-C(6)	1.437(4)
C(5)-C(9)	1.452(4)
C(6)-C(7)	1.357(4)
C(6)-C(16)	1.496(4)
C(7)-C(8)	1.416(4)
C(7)-H(7)	0.9300
C(9)-C(10)	1.499(4)
C(10)-C(15)	1.376(4)
C(10)-C(11)	1.385(4)
C(11)-C(12)	1.386(5)
C(11)-H(11)	0.9300
C(12)-C(13)	1.358(6)
C(12)-H(12)	0.9300
C(13)-C(14)	1.362(6)
C(14)-C(15)	1.381(4)
C(14)-H(14)	0.9300
C(15)-H(15)	0.9300
C(16)-C(17)	1.377(4)
C(16)-C(21)	1.389(4)
C(17)-C(18)	1.374(4)
C(17)-H(17)	0.9300
C(18)-C(19)	1.370(4)
C(19)-C(20)	1.375(5)
C(19)-H(19)	0.9300
C(20)-C(21)	1.392(4)
C(20)-H(20)	0.9300
C(21)-H(21)	0.9300
C(4)-N(1)-C(8)	122.7(2)
C(4)-N(1)-C(1)	120.1(2)
C(8)-N(1)-C(1)	117.0(2)
C(4)-N(2)-C(3)	126.5(2)
C(4)-N(2)-H(4)	116.7
C(3)-N(2)-H(4)	116.7
O(4)-N(3)-O(3)	122.8(3)
O(4)-N(3)-C(18)	119.0(3)
O(3)-N(3)-C(18)	118.2(3)
C(2)-C(1)-N(1)	113.7(3)
C(2)-C(1)-H(1A)	108.8
N(1)-C(1)-H(1A)	108.8
C(2)-C(1)-H(1B)	108.8
N(1)-C(1)-H(1B)	108.8
H(1A)-C(1)-H(1B)	107.7
C(1)-C(2)-C(3)	117.5(4)
C(1)-C(2)-H(2)	121.2
C(3)-C(2)-H(2)	121.2
C(2)-C(3)-N(2)	110.9(3)
C(2)-C(3)-H(3A)	109.4
N(2)-C(3)-H(3A)	109.4
C(2)-C(3)-H(3B)	109.4
N(2)-C(3)-H(3B)	109.4
H(3A)-C(3)-H(3B)	108.0
N(2)-C(4)-N(1)	117.5(2)

N(2)-C(4)-C(5)	121.6(2)
N(1)-C(4)-C(5)	120.8(2)
C(4)-C(5)-C(6)	116.3(2)
C(4)-C(5)-C(9)	119.2(2)
C(6)-C(5)-C(9)	124.5(2)
C(7)-C(6)-C(5)	121.2(3)
C(7)-C(6)-C(16)	115.7(2)
C(5)-C(6)-C(16)	122.9(2)
C(6)-C(7)-C(8)	122.4(3)
C(6)-C(7)-H(7)	118.8
C(8)-C(7)-H(7)	118.8
O(1)-C(8)-N(1)	119.4(3)
O(1)-C(8)-C(7)	124.9(3)
N(1)-C(8)-C(7)	115.7(2)
O(2)-C(9)-C(5)	122.3(3)
O(2)-C(9)-C(10)	116.6(2)
C(5)-C(9)-C(10)	121.0(2)
C(15)-C(10)-C(11)	118.9(3)
C(15)-C(10)-C(9)	118.9(3)
C(11)-C(10)-C(9)	122.2(3)
C(10)-C(11)-C(12)	120.6(3)
C(10)-C(11)-H(11)	119.7
C(12)-C(11)-H(11)	119.7
C(13)-C(12)-C(11)	117.8(4)
C(13)-C(12)-H(12)	121.1
C(11)-C(12)-H(12)	121.1
C(12)-C(13)-C(14)	123.6(3)
C(12)-C(13)-F(1)	118.2(4)
C(14)-C(13)-F(1)	118.1(4)
C(13)-C(14)-C(15)	117.7(4)
C(13)-C(14)-H(14)	121.2
C(15)-C(14)-H(14)	121.2
C(10)-C(15)-C(14)	121.1(3)
C(10)-C(15)-H(15)	119.4
C(14)-C(15)-H(15)	119.4
C(17)-C(16)-C(21)	118.6(3)
C(17)-C(16)-C(6)	120.6(2)
C(21)-C(16)-C(6)	120.7(3)
C(18)-C(17)-C(16)	119.6(3)
C(18)-C(17)-H(17)	120.2
C(16)-C(17)-H(17)	120.2
C(19)-C(18)-C(17)	122.7(3)
C(19)-C(18)-N(3)	119.0(3)
C(17)-C(18)-N(3)	118.3(3)
C(18)-C(19)-C(20)	118.0(3)
C(18)-C(19)-H(19)	121.0
C(20)-C(19)-H(19)	121.0
C(19)-C(20)-C(21)	120.3(3)
C(19)-C(20)-H(20)	119.9
C(21)-C(20)-H(20)	119.9
C(16)-C(21)-C(20)	120.7(3)
C(16)-C(21)-H(21)	119.6
C(20)-C(21)-H(21)	119.6

CCDC 978904 : X-Ray data for compound **4i**

ORTEP drawing of **4i**

Crystals were obtained by slow diffusion of EtOH/H₂O

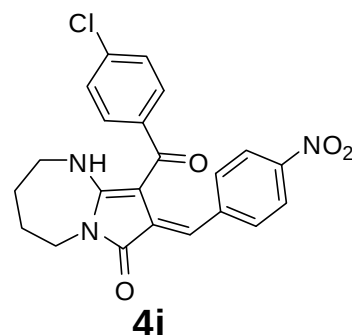
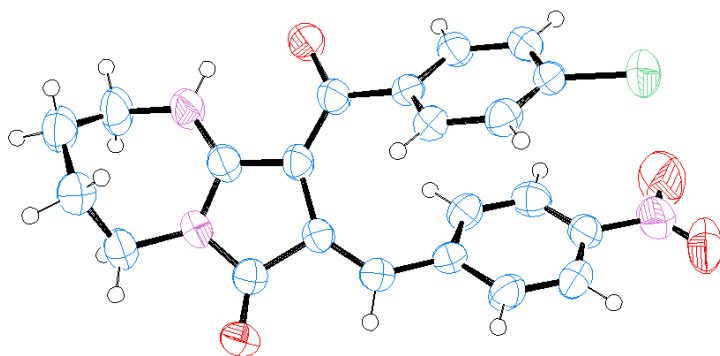


Table . Crystal data and structure refinement for **4i**.

Empirical formula	C ₂₂ H ₁₈ ClN ₃ O ₄
Formula weight	423.84
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.0486(12) Å alpha = 99.276(2) deg. b = 9.6016(13) Å beta = 100.169(2) deg. c = 11.8421(16) Å gamma = 99.535(2) deg.
Volume	979.3(2) Å ³
Z, Calculated density	2, 1.437 Mg/m ³
Absorption coefficient	0.231 mm ⁻¹
F(000)	440
Crystal size	0.22 x 0.12 x 0.10 mm
Theta range for data collection	1.78 to 25.15 deg.
Limiting indices	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -14 ≤ l ≤ 14
Reflections collected / unique	7854 / 3487 [R(int) = 0.0331]
Completeness to theta = 25.15	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9773 and 0.9509
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3487 / 0 / 271
Goodness-of-fit on F ²	1.056
Final R indices [I > 2sigma(I)]	R1 = 0.0489, wR2 = 0.1138
R indices (all data)	R1 = 0.0897, wR2 = 0.1385
Largest diff. peak and hole	0.186 and -0.276 e.Å ⁻³

Table. Bond lengths [Å] and angles [deg] for **4i**.

Cl(1)-C(1)	1.747(3)
N(1)-C(9)	1.311(3)
N(1)-C(10)	1.466(3)
N(1)-H(1)	0.8600
N(2)-C(9)	1.379(3)
N(2)-C(14)	1.400(3)
N(2)-C(13)	1.477(3)
N(3)-O(3)	1.214(3)
N(3)-O(4)	1.220(3)
N(3)-C(20)	1.472(4)
O(1)-C(7)	1.258(3)
O(2)-C(14)	1.208(3)

C(1)-C(2)	1.375(4)
C(1)-C(6)	1.379(4)
C(2)-C(3)	1.384(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.382(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.387(3)
C(4)-C(7)	1.495(3)
C(5)-C(6)	1.380(3)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-C(8)	1.426(3)
C(8)-C(9)	1.430(3)
C(8)-C(15)	1.456(3)
C(10)-C(11)	1.498(4)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(12)	1.512(4)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.499(4)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-C(15)	1.504(4)
C(15)-C(16)	1.343(3)
C(16)-C(17)	1.460(3)
C(16)-H(16)	0.9300
C(17)-C(22)	1.393(4)
C(17)-C(18)	1.400(3)
C(18)-C(19)	1.371(4)
C(18)-H(18)	0.9300
C(19)-C(20)	1.372(4)
C(19)-H(19)	0.9300
C(20)-C(21)	1.376(4)
C(21)-C(22)	1.380(4)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300
C(9)-N(1)-C(10)	125.8(2)
C(9)-N(1)-H(1)	117.1
C(10)-N(1)-H(1)	117.1
C(9)-N(2)-C(14)	109.8(2)
C(9)-N(2)-C(13)	127.3(2)
C(14)-N(2)-C(13)	121.1(2)
O(3)-N(3)-O(4)	123.8(3)
O(3)-N(3)-C(20)	118.7(3)
O(4)-N(3)-C(20)	117.5(3)
C(2)-C(1)-C(6)	121.8(2)
C(2)-C(1)-Cl(1)	119.0(2)
C(6)-C(1)-Cl(1)	119.2(2)
C(1)-C(2)-C(3)	119.0(3)
C(1)-C(2)-H(2)	120.5
C(3)-C(2)-H(2)	120.5
C(4)-C(3)-C(2)	120.5(3)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	118.9(2)
C(3)-C(4)-C(7)	122.4(2)
C(5)-C(4)-C(7)	118.7(2)
C(6)-C(5)-C(4)	121.4(3)
C(6)-C(5)-H(5)	119.3
C(4)-C(5)-H(5)	119.3
C(5)-C(6)-C(1)	118.2(3)

C(5)-C(6)-H(6)	120.9
C(1)-C(6)-H(6)	120.9
O(1)-C(7)-C(8)	122.2(2)
O(1)-C(7)-C(4)	116.9(2)
C(8)-C(7)-C(4)	120.9(2)
C(7)-C(8)-C(9)	119.0(2)
C(7)-C(8)-C(15)	134.7(2)
C(9)-C(8)-C(15)	106.1(2)
N(1)-C(9)-N(2)	123.7(2)
N(1)-C(9)-C(8)	125.4(3)
N(2)-C(9)-C(8)	110.9(2)
N(1)-C(10)-C(11)	114.5(3)
N(1)-C(10)-H(10A)	108.6
C(11)-C(10)-H(10A)	108.6
N(1)-C(10)-H(10B)	108.6
C(11)-C(10)-H(10B)	108.6
H(10A)-C(10)-H(10B)	107.6
C(10)-C(11)-C(12)	114.3(2)
C(10)-C(11)-H(11A)	108.7
C(12)-C(11)-H(11A)	108.7
C(10)-C(11)-H(11B)	108.7
C(12)-C(11)-H(11B)	108.7
H(11A)-C(11)-H(11B)	107.6
C(13)-C(12)-C(11)	115.7(3)
C(13)-C(12)-H(12A)	108.3
C(11)-C(12)-H(12A)	108.3
C(13)-C(12)-H(12B)	108.3
C(11)-C(12)-H(12B)	108.3
H(12A)-C(12)-H(12B)	107.4
N(2)-C(13)-C(12)	112.1(2)
N(2)-C(13)-H(13A)	109.2
C(12)-C(13)-H(13A)	109.2
N(2)-C(13)-H(13B)	109.2
C(12)-C(13)-H(13B)	109.2
H(13A)-C(13)-H(13B)	107.9
O(2)-C(14)-N(2)	123.9(3)
O(2)-C(14)-C(15)	129.4(3)
N(2)-C(14)-C(15)	106.7(2)
C(16)-C(15)-C(8)	138.5(2)
C(16)-C(15)-C(14)	115.2(2)
C(8)-C(15)-C(14)	105.9(2)
C(15)-C(16)-C(17)	132.0(2)
C(15)-C(16)-H(16)	114.0
C(17)-C(16)-H(16)	114.0
C(22)-C(17)-C(18)	117.3(2)
C(22)-C(17)-C(16)	122.2(2)
C(18)-C(17)-C(16)	120.3(2)
C(19)-C(18)-C(17)	122.3(3)
C(19)-C(18)-H(18)	118.9
C(17)-C(18)-H(18)	118.9
C(18)-C(19)-C(20)	118.2(3)
C(18)-C(19)-H(19)	120.9
C(20)-C(19)-H(19)	120.9
C(19)-C(20)-C(21)	122.0(3)
C(19)-C(20)-N(3)	118.3(3)
C(21)-C(20)-N(3)	119.7(3)
C(20)-C(21)-C(22)	119.0(3)
C(20)-C(21)-H(21)	120.5
C(22)-C(21)-H(21)	120.5
C(21)-C(22)-C(17)	121.2(3)
C(21)-C(22)-H(22)	119.4
C(17)-C(22)-H(22)	119.4
