Supporting Information for

Potassium tert-butoxide Mediated Stereoselective/Direct Mannich Reaction of α-Substituted-γ-Lactams with in situ Generated Aryl N-silyl imines

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Computational Details

All density functional theory (DFT) calculations were carried out using *Gaussian 16*.[1] Previous DFT calculations indicated that the dissociation of KO^{t}Bu tetramer to dimer is slightly endergonic by 8.9 kcal/mol, whereas the dissociation of KO^{t}Bu tetramer to monomer is highly endergonic by 27.6 kcal/mol.[2] Therefore, we surmised that KO^{t}Bu dimer is likely the active catalyst under the reaction conditions. In our calculations, dimeric potassium *tert*-butoxide was used as the base, in which one toluene solvent molecule was added to bind to each K to account for explicit solvent effects. Conformational analysis was carried out for transition states using the CREST/xTB[3] package at the GFN2-xTB[4] level of theory. During the TS conformational sampling, forming C–C bond distances and distances between oxygen atom of the enolate and potassium atoms were constrained. Low-energy conformers from CREST conformational search were then fully optimized at the M06-2X/6-31G(d)[5] level of theory. Vibrational frequency calculations were performed at the M06-2X/6-31G(d) level of theory to confirm whether the optimized structure is a local minimum or a transition state. Single point energies and natural population analysis (NPA) charges were calculated at the M06-2X/6-311G++(d,p) level of theory using SMD[6] solvation model and toluene as solvent.

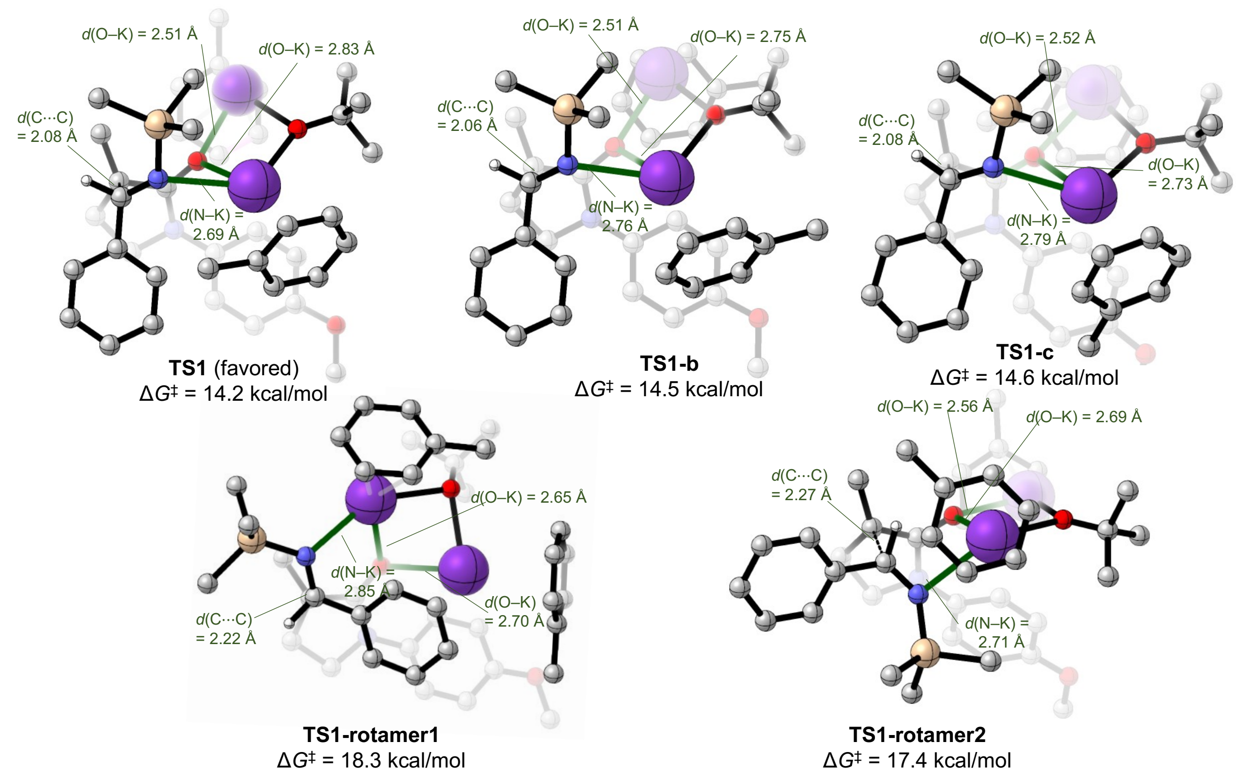


Figure S1. Optimized structures of representative low-energy conformers of **TS1** that lead to the major diastereomeric product **4a**. Gibbs free energies are with respect to lactam **2a**, $[KO^tBu]_2$, and imine **3b**. The three lowest-energy conformers (**TS1**, **TS1-b**, and **TS1-c**) and two other representative rotamers about the forming C–C bonds (**TS1-rotamer1** and **TS1-rotamer2**) are shown.

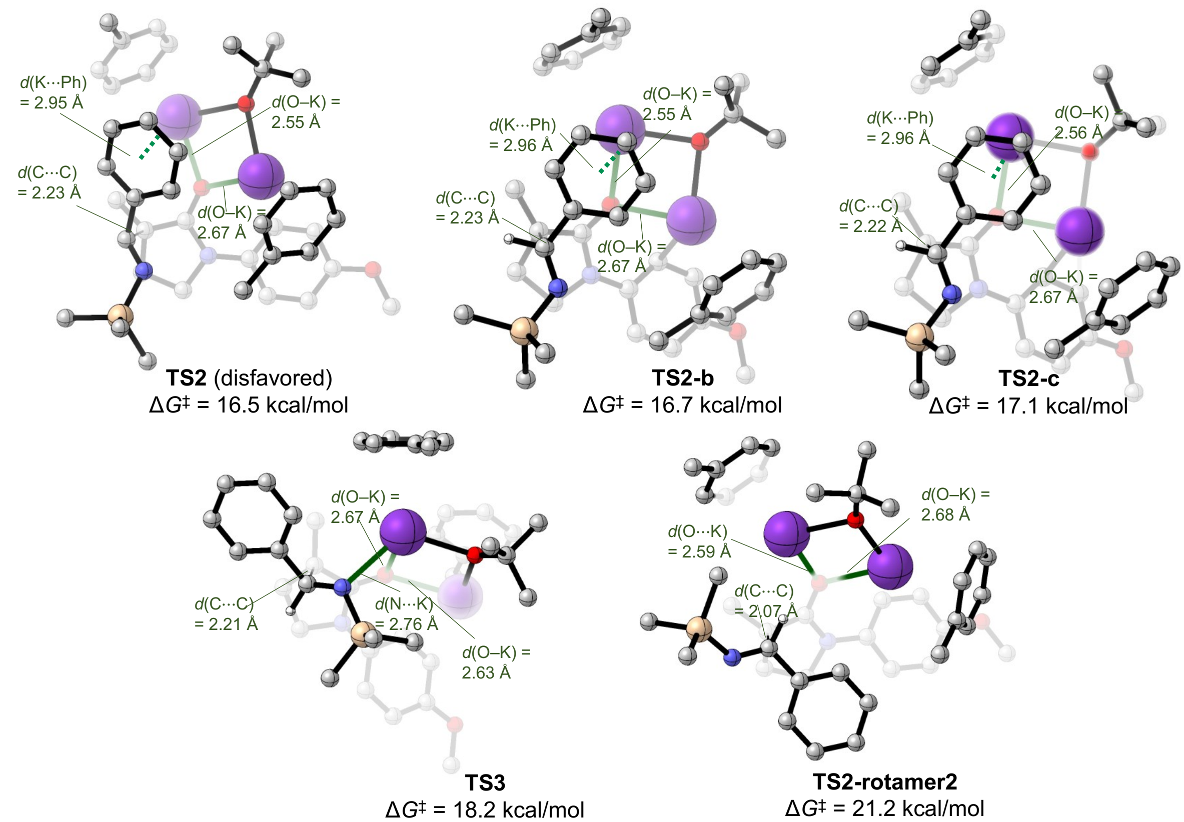


Figure S2. Optimized structures of representative low-energy conformers of **TS2** that lead to the minor diastereomeric product **4a-ent.** Gibbs free energies are with respect to lactam **2a**, [KO*ᵗ*Bu]$_2$, and imine **3b**. The three lowest-energy conformers (**TS2**, **TS2-b**, and **TS2-c**) and two other representative rotamers about the forming C–C bonds (**TS3** and **TS2-rotamer2**) are shown.

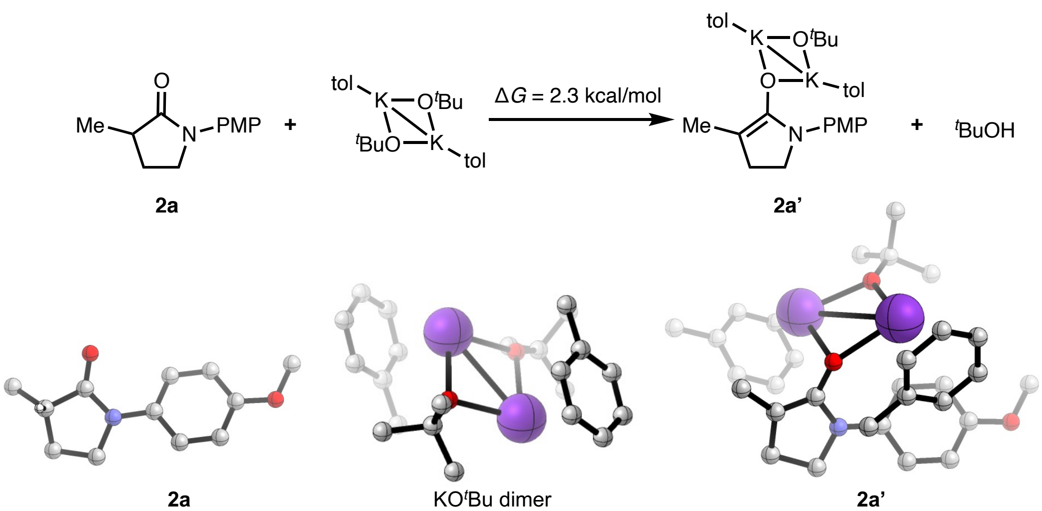


Figure S3. Computed Gibbs free energy of the deprotonation of lactam **2a** with [KO^{t}Bu]$_2$ to give potassium enolate **2a'.**

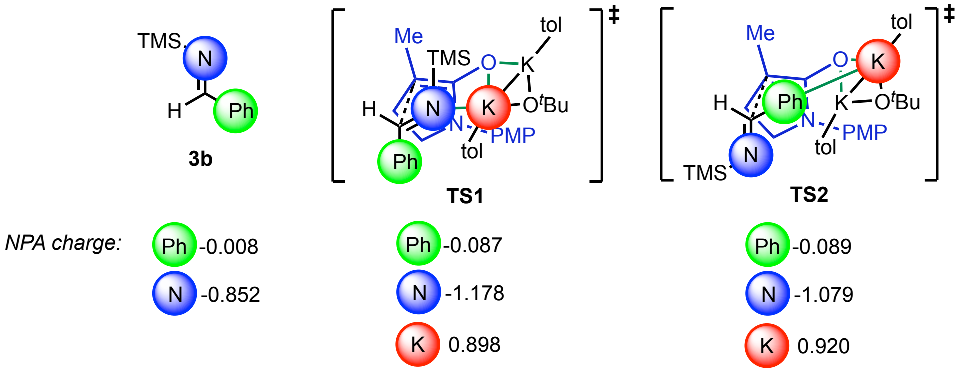


Figure S4. Computed NPA charges for **TS1**, **3b**, and **TS2**. The imine N becomes more negatively charged in the TS, promoting the N–K interaction in **TS1**, whereas a much smaller increase of negative charge was observed for the Ph group on the imine.

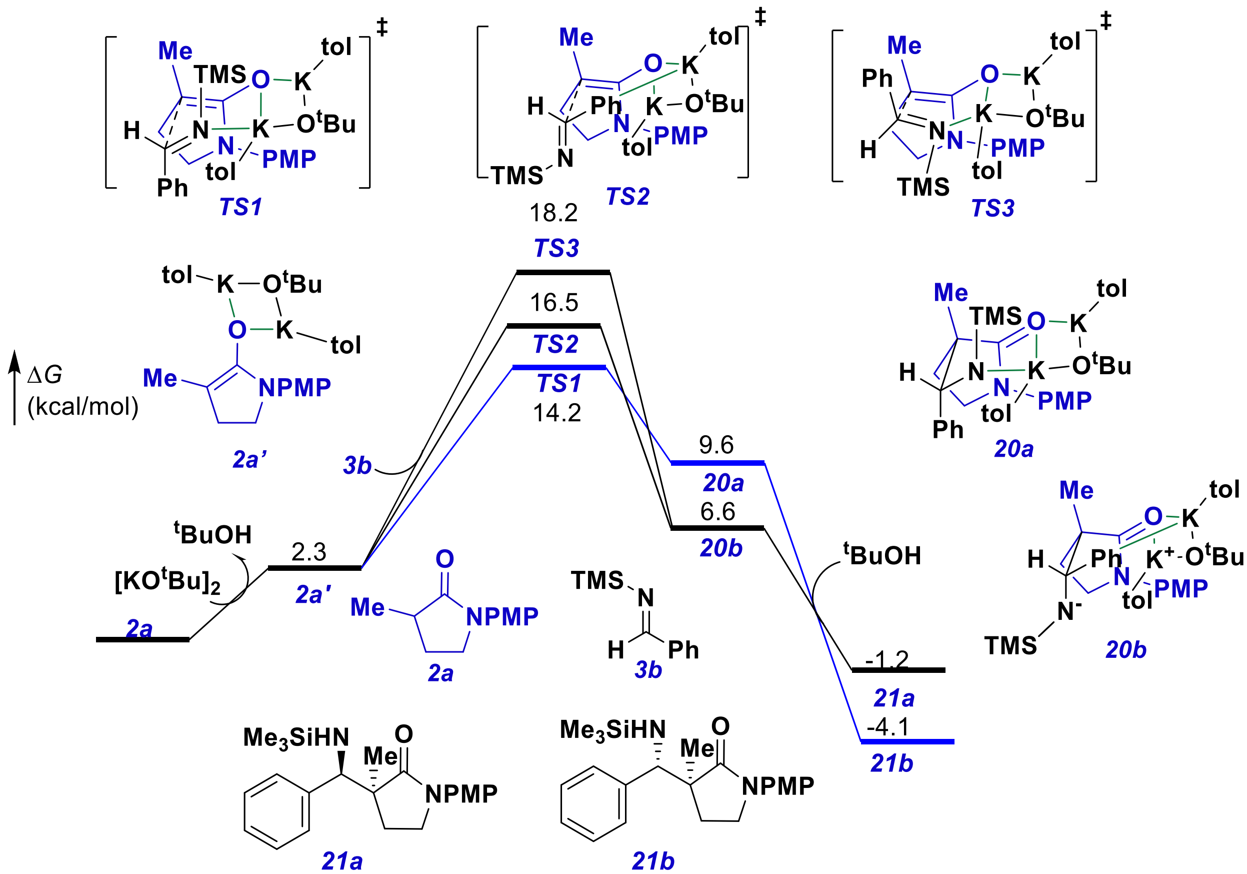


Figure S5. Calculated reaction energy profiles of the imine addition pathways involving **2a** and **3b**.

Cartesian Coordinates and Energies of All Optimized Structures and Imaginary Frequencies of Transition States

	M06-2X/6-31G(d) (gas)			**M06-2X/6-311++G(d,p)/SMD(toluene) //M06-2X/6-31G(d)**			**Imaginary frequency (cm^{-1})**
Compound	**E (a.u.)**	**H (a.u.)**	**G (a.u.)**	**E (a.u.)**	**H (a.u.)**	**G (a.u.)**	
2a	-671.23376	-670.9625	-671.0177	-671.4360	-671.1648	-671.2200	
KO*t*-Bu dimer	-2208.6855	-2208.1371	-2208.2373	-2209.0839	-2208.5356	-2208.6357	
2a'	-2646.3614	-2645.6881	-2645.8074	-2646.8772	-2646.2038	-2646.3231	
***t*-BuOH**	-233.5506	-233.4054	-233.4418	-233.6377	-233.4925	-233.5289	
20a	-3380.5264	-3379.6083	-3379.7570	-3381.1942	-3380.2760	-3380.4247	
20b	-3380.5290	-3379.6111	-3379.7607	-3381.1980	-3380.2802	-3380.4297	
21a	-1405.4094	-1404.8929	-1404.9807	-1405.7685	-1405.2520	-1405.3399	
21b	-1405.4021	-1404.8856	-1404.9749	-1405.7625	-1405.2460	-1405.3353	
3b	-734.1366	-733.8949	-733.9516	-734.2983	-734.0566	-734.1133	
TS1	-3380.5195	-3379.6031	-3379.7511	-3381.1859	-3380.2695	-3380.4175	-258
TS1-b	-3380.5211	-3379.6046	-3379.7503	-3381.1879	-3380.2714	-3380.4170	-265
TS1-c	-3380.5191	-3379.6028	-3379.7503	-3381.1856	-3380.2693	-3380.4168	-260
TS1-rotamer1	-3380.5186	-3379.6028	-3379.7478	-3381.1818	-3380.2660	-3380.4110	-178
TS1-rotamer2	-3380.5069	-3379.5910	-3379.7435	-3381.1758	-3380.2599	-3380.4124	-167
TS2	-3380.5093	-3379.5937	-3379.7452	-3381.1780	-3380.2624	-3380.4138	-194
TS2-b	-3380.5093	-3379.5936	-3379.7449	-3381.1779	-3380.2623	-3380.4135	-191
TS2-c	-3380.5090	-3379.5933	-3379.7439	-3381.1780	-3380.2622	-3380.4128	-196
TS3	-3380.5099	-3379.5942	-3379.7430	-3381.1780	-3380.2623	-3380.4112	-221
TS2-rotamer2	-3380.5001	-3379.5841	-3379.7349	-3381.1715	-3380.2555	-3380.4063	-257

Cartesian Coordinates:

2a

C	-1.0651	0.9094	-0.0929
C	-0.5310	0.2657	1.1852
O	-1.7034	1.9415	-0.1440
C	0.5519	-0.6795	0.6651
H	1.4970	-0.1330	0.5715
H	0.7208	-1.5482	1.3048
C	0.0459	-1.0703	-0.7272
H	0.8568	-1.2766	-1.4316
H	-0.6070	-1.9536	-0.6880
N	-0.7047	0.1071	-1.1556
C	-0.0922	1.3062	2.2032
H	-0.9114	2.0009	2.4025
H	0.2116	0.8348	3.1420
H	0.7537	1.8849	1.8181
C	-1.1322	0.2632	-2.4938
C	-1.0584	-0.8275	-3.3723
C	-1.6141	1.4821	-2.9785
C	-1.4533	-0.7015	-4.6939
H	-0.6985	-1.7898	-3.0251
C	-2.0163	1.6054	-4.3065
H	-1.6840	2.3312	-2.3137
C	-1.9374	0.5165	-5.1741
H	-1.3986	-1.5430	-5.3763
H	-2.3864	2.5651	-4.6476
O	-2.3015	0.5402	-6.4856
C	-2.7957	1.7574	-6.9953
H	-2.0456	2.5548	-6.9240
H	-3.0305	1.5748	-8.0439
H	-3.7048	2.0720	-6.4681
H	-1.3644	-0.3228	1.5962

KOt-Bu dimer

K	0.3226	3.3884	0.5853
K	-0.6717	0.3096	-0.8138
O	-1.7717	2.0664	0.6342
O	1.3808	1.7738	-0.9721
C	-3.0017	1.7968	1.1859
C	-3.7383	0.7027	0.3764
H	-3.1759	-0.2422	0.4213
H	-4.7496	0.4963	0.7473
H	-3.8165	1.0154	-0.6736
C	-2.8616	1.2996	2.6389
H	-2.3249	2.0513	3.2299
H	-3.8286	1.1054	3.1198
H	-2.2760	0.3735	2.6576
C	-3.8915	3.0561	1.2007
H	-4.0253	3.4314	0.1791
H	-4.8829	2.8725	1.6331
H	-3.3976	3.8370	1.7917
C	2.2489	1.6155	-2.0256
C	3.6670	1.2721	-1.5276
H	4.3946	1.1776	-2.3431
H	4.0103	2.0566	-0.8426
H	3.6488	0.3270	-0.9717
C	2.3286	2.9039	-2.8682
H	3.0310	2.8281	-3.7077
H	1.3337	3.1337	-3.2687
H	2.6398	3.7384	-2.2271
C	1.7836	0.4744	-2.9623
H	1.7139	-0.4661	-2.3981
H	0.7919	0.7126	-3.3738
H	2.4609	0.3080	-3.8088
C	0.0848	-1.0463	1.9399
C	1.3137	-0.9372	1.2827
C	1.5523	-1.7747	0.1847
C	0.5863	-2.6783	-0.2538
C	-0.6432	-2.7665	0.4042
C	-0.8872	-1.9505	1.5083
H	-0.1212	-0.4013	2.7897
H	2.5036	-1.7047	-0.3371
H	0.7936	-3.3166	-1.1081
H	-1.3958	-3.4731	0.0677
H	-1.8369	-2.0102	2.0326
C	0.8639	6.2940	-0.9635
C	0.4463	6.8015	0.2656
C	-0.8457	6.5228	0.7187
C	-1.6987	5.7269	-0.0421
C	-1.2812	5.1880	-1.2668
C	0.0028	5.4996	-1.7230
H	1.8614	6.5107	-1.3344
H	1.1131	7.4203	0.8586
H	-1.1879	6.9254	1.6678
H	-2.6931	5.4917	0.3252
H	0.3456	5.0922	-2.6691
C	2.3193	0.1108	1.6743
H	2.2783	0.9101	0.9192
H	2.0993	0.5203	2.6649
H	3.3366	-0.2930	1.6847
C	-2.1583	4.2045	-1.9956
H	-3.1753	4.5901	-2.1202
H	-1.7525	3.9642	-2.9823
H	-2.2164	3.2882	-1.3887

2a'

K	-0.6232	3.6995	-1.2400
K	0.9879	0.5343	0.0379
O	0.3071	1.5704	-2.1180
C	0.3084	0.9650	-3.3503
C	1.3650	1.6016	-4.2736
H	1.4102	1.1317	-5.2639
H	1.1400	2.6671	-4.4076
H	2.3526	1.5250	-3.8046
C	-1.0758	1.0964	-4.0204
H	-1.1185	0.6454	-5.0198

H	-1.8311	0.6136	-3.3885
H	-1.3363	2.1603	-4.1167
C	0.6201	-0.5420	-3.2148
H	1.6134	-0.6777	-2.7629
H	-0.1260	-1.0027	-2.5541
H	0.6106	-1.0775	-4.1722
C	-0.9390	1.9015	1.9529
C	-0.4327	1.6019	3.1860
O	-0.4063	2.4755	0.9396
C	-1.4816	0.9323	4.0317
H	-1.3469	-0.1617	4.1261
H	-1.5350	1.3212	5.0560
C	-2.7724	1.2523	3.2566
H	-3.5334	0.4663	3.3138
H	-3.2116	2.1863	3.6480
N	-2.3141	1.4334	1.8858
C	0.9641	1.8934	3.6199
H	1.4734	2.4799	2.8455
H	1.0066	2.4740	4.5525
H	1.5675	0.9857	3.8016
C	-3.1953	1.7945	0.8707
C	-4.5241	2.1677	1.1469
C	-2.8102	1.7290	-0.4806
C	-5.4020	2.5209	0.1285
H	-4.8791	2.1878	2.1720
C	-3.6803	2.1144	-1.4981
H	-1.8185	1.3773	-0.7574
C	-4.9815	2.5276	-1.2009
H	-6.4249	2.8088	0.3505
H	-3.3332	2.0518	-2.5242
O	-5.8976	2.9325	-2.1313
C	-5.5114	2.8510	-3.4828
H	-5.2572	1.8221	-3.7671
H	-6.3680	3.1881	-4.0667
H	-4.6501	3.4988	-3.6961
C	-0.6665	-1.5683	1.5935
C	0.4991	-1.5557	2.3612
C	1.6889	-2.1085	1.8759
C	1.6879	-2.6666	0.5904
C	0.5265	-2.6872	-0.1804
C	-0.6562	-2.1377	0.3202
H	-1.5688	-1.0962	1.9735
H	0.4854	-1.0930	3.3448
H	2.6060	-3.0944	0.1941
H	0.5471	-3.1191	-1.1764
H	-1.5578	-2.1362	-0.2852
C	2.9335	-2.1286	2.7282
H	2.9693	-3.0405	3.3343
H	3.8391	-2.1059	2.1152
H	2.9585	-1.2768	3.4136
C	-3.0391	5.7940	-1.2717
C	-3.0251	5.2696	0.0218
C	-1.9748	5.5468	0.9030
C	-0.9339	6.3707	0.4522
C	-0.9419	6.8995	-0.8380
C	-1.9963	6.6106	-1.7093
H	-3.8694	5.5559	-1.9316
H	-3.8329	4.6186	0.3449
H	-0.1074	6.5950	1.1227
H	-0.1283	7.5413	-1.1642
H	-2.0059	7.0262	-2.7126
C	-1.9571	4.9685	2.2929
H	-0.9993	4.4855	2.5071
H	-2.1307	5.7499	3.0413
H	-2.7366	4.2085	2.4011

t-BuOH

O	1.0016	1.9025	-1.3929
C	2.0915	2.0588	-2.2994
C	3.2821	2.6831	-1.5709
H	4.1195	2.8573	-2.2541
H	2.9882	3.6368	-1.1234
H	3.6346	2.0209	-0.7707
C	1.5721	2.9938	-3.3843
H	2.3429	3.1795	-4.1381
H	0.6993	2.5509	-3.8722
H	1.2722	3.9481	-2.9422
C	2.4690	0.7002	-2.8906
H	2.8142	0.0196	-2.1027
H	1.5991	0.2497	-3.3770
H	3.2740	0.7963	-3.6261
H	1.2953	1.3123	-0.6833

20a

C	0.8503	1.1782	1.0836
C	0.3253	2.1101	2.1320
C	-1.2863	2.2542	1.8382
H	-1.6201	2.7496	2.7762
O	0.7846	-0.0466	1.1171
Si	-2.7258	0.0674	2.6748
N	-1.9218	1.0265	1.5535
C	1.1633	3.3717	1.8777
H	0.6437	4.2970	2.1367
H	2.0825	3.3254	2.4753
C	1.5095	3.3234	0.3793
H	0.8159	3.9287	-0.2109
H	2.5315	3.6563	0.1676
N	1.3807	1.8999	0.0408
C	0.5014	1.5412	3.5304
H	-0.0885	0.6283	3.6377
H	1.5516	1.3027	3.7421
H	0.1577	2.2634	4.2791
K	-1.3502	-0.9612	-0.3322
K	1.2928	-2.2770	2.1668
C	-1.5007	3.2840	0.7294
C	-1.5018	2.9019	-0.6146
C	-1.6621	4.6402	1.0234
C	-1.5936	3.8464	-1.6318
H	-1.4178	1.8453	-0.8527

C	-1.7722	5.5935	0.0116
H	-1.7006	4.9539	2.0649
C	-1.7231	5.2012	-1.3230
H	-1.5577	3.5299	-2.6718
H	-1.8982	6.6418	0.2669
H	-1.8004	5.9399	-2.1152
C	1.4816	1.4308	-1.2912
C	1.5638	2.3625	-2.3286
C	1.4420	0.0591	-1.6252
C	1.5568	1.9664	-3.6660
H	1.6035	3.4229	-2.1090
C	1.4301	-0.3270	-2.9564
H	1.3950	-0.7173	-0.8672
C	1.4703	0.6147	-3.9878
H	1.6080	2.7276	-4.4358
H	1.3818	-1.3810	-3.2125
C	-4.3168	-0.6467	1.9207
H	-5.0077	0.1546	1.6360
H	-4.1022	-1.2300	1.0145
H	-4.8334	-1.3160	2.6191
C	-3.1957	0.9150	4.3078
H	-3.8213	1.7959	4.1236
H	-3.7607	0.2337	4.9539
H	-2.3148	1.2485	4.8688
C	-1.7924	-1.5412	3.1918
H	-2.4363	-2.1863	3.8027
H	-1.4902	-2.1319	2.3136
H	-0.8986	-1.3166	3.7904
O	0.2447	-2.8725	0.0282
C	0.3436	-4.1044	-0.5678
C	1.2669	-5.0380	0.2502
H	1.3857	-6.0335	-0.1946
H	2.2640	-4.5830	0.3345
H	0.8549	-5.1712	1.2610
C	-1.0424	-4.7723	-0.6744
H	-1.0100	-5.7704	-1.1294
H	-1.4840	-4.8563	0.3257
H	-1.7012	-4.1385	-1.2820
C	0.9323	-3.9678	-1.9855
H	0.2684	-3.3329	-2.5864
H	1.9099	-3.4724	-1.9256
H	1.0555	-4.9282	-2.5020
O	1.4060	0.1179	-5.2547
C	1.4511	1.0469	-6.3142
H	0.6055	1.7448	-6.2691
H	2.3885	1.6166	-6.3049
H	1.3904	0.4641	-7.2329
C	3.8310	-0.6889	0.9354
C	3.8501	-0.1993	2.2412
C	4.1462	-1.0481	3.3069
C	4.4412	-2.4006	3.0881
C	4.4102	-2.8814	1.7740
C	4.1069	-2.0354	0.7049
H	3.5779	-0.0308	0.1099
H	3.6200	0.8466	2.4270
H	4.1586	-0.6574	4.3220
H	4.6254	-3.9307	1.5852
H	4.0686	-2.4323	-0.3052
C	4.8181	-3.3055	4.2350
H	5.9006	-3.2847	4.4010
H	4.3376	-2.9921	5.1662
H	4.5371	-4.3430	4.0339
C	-2.4676	-1.9884	-3.3248
C	-3.5615	-2.2055	-2.4856
C	-4.1834	-1.1308	-1.8519
C	-3.7241	0.1811	-2.0304
C	-2.6382	0.3839	-2.8928
C	-2.0141	-0.6864	-3.5365
H	-1.9794	-2.8258	-3.8139
H	-3.9296	-3.2144	-2.3233
H	-5.0354	-1.3069	-1.1999
H	-2.2738	1.3949	-3.0592
H	-1.1710	-0.5049	-4.1978
C	-4.3410	1.3186	-1.2597
H	-5.4027	1.1327	-1.0726
H	-3.8341	1.4273	-0.2886
H	-4.2364	2.2669	-1.7941

20b

C	-0.5033	-1.1172	1.7183
C	-0.0509	-2.5573	1.6321
C	-0.1065	-2.9856	0.1049
H	0.2608	-4.0388	0.1447
O	0.1890	-0.1370	1.4104
Si	-2.0485	-3.8707	-1.5478
N	-1.4250	-2.8267	-0.3769
C	-1.1587	-3.3095	2.3912
H	-1.3878	-4.2635	1.9106
H	-0.8498	-3.4911	3.4272
C	-2.3761	-2.3791	2.3600
H	-3.0065	-2.6188	1.5015
H	-2.9536	-2.3815	3.2908
N	-1.7800	-1.0494	2.1725
C	1.3218	-2.7376	2.2747
H	2.0886	-2.1407	1.7732
H	1.3067	-2.4478	3.3317
H	1.6265	-3.7888	2.2142
K	-0.6011	1.7441	-0.3062
K	2.6080	0.2509	0.4403
C	0.9518	-2.2448	-0.7430
C	0.5462	-1.1744	-1.5505
C	2.2882	-2.6515	-0.8228
C	1.4416	-0.5059	-2.3796
H	-0.5168	-0.9389	-1.5321
C	3.1928	-2.0018	-1.6703
H	2.6208	-3.5087	-0.2396
C	2.7769	-0.9186	-2.4440
H	1.1035	0.3306	-2.9876
H	4.2202	-2.3521	-1.7374
H	3.4746	-0.4147	-3.1069
C	-2.5581	0.1268	2.2203

C	-3.9400	0.0511	2.0500
C	-1.9833	1.3833	2.4862
C	-4.7387	1.1937	2.1040
H	-4.4082	-0.9087	1.8613
C	-2.7709	2.5236	2.5122
H	-0.9196	1.4565	2.6783
C	-4.1547	2.4419	2.3149
H	-5.8089	1.0906	1.9661
H	-2.3341	3.4971	2.7130
C	-3.8929	-4.1867	-1.2276
H	-4.4496	-3.2507	-1.0997
H	-4.3649	-4.7455	-2.0444
H	-4.0181	-4.7693	-0.3069
C	-1.2063	-5.5794	-1.5710
H	-1.7095	-6.2552	-2.2720
H	-0.1559	-5.5106	-1.8796
H	-1.2292	-6.0512	-0.5809
C	-1.9273	-3.2523	-3.3506
H	-0.8868	-3.0126	-3.6040
H	-2.2829	-4.0024	-4.0676
H	-2.5229	-2.3443	-3.5073
O	1.7527	2.4385	-0.3357
C	2.4529	3.4167	-0.9946
C	3.1378	4.3636	0.0101
H	3.8223	3.7842	0.6435
H	3.7070	5.1675	-0.4733
H	2.3803	4.8119	0.6624
C	3.5407	2.7935	-1.8978
H	3.0705	2.1180	-2.6226
H	4.1307	3.5389	-2.4462
H	4.2333	2.2012	-1.2817
C	1.5103	4.2477	-1.8913
H	2.0209	5.0525	-2.4349
H	1.0325	3.5845	-2.6252
H	0.7222	4.6963	-1.2718
O	-4.8321	3.6190	2.3457
C	-6.2297	3.5676	2.1579
H	-6.4845	3.1521	1.1747
H	-6.7147	2.9699	2.9389
H	-6.5818	4.5969	2.2179
C	4.6028	0.0493	3.0059
C	4.7829	-1.1894	2.3900
C	5.3548	-1.2633	1.1190
C	5.7603	-0.1070	0.4429
C	5.5845	1.1292	1.0781
C	5.0088	1.2101	2.3455
H	4.1559	0.1091	3.9934
H	4.4779	-2.0998	2.8977
H	5.4895	-2.2327	0.6453
H	5.8947	2.0390	0.5698
H	4.8731	2.1805	2.8133
C	6.3358	-0.1782	-0.9485
H	5.5746	0.0800	-1.6950
H	7.1635	0.5260	-1.0700
H	6.7017	-1.1831	-1.1757
C	-2.0650	3.2526	-2.6751
C	-1.6581	2.0561	-3.2722
C	-2.2083	0.8420	-2.8635
C	-3.1791	0.7923	-1.8500
C	-3.5781	1.9991	-1.2640
C	-3.0297	3.2186	-1.6691
H	-1.6303	4.1959	-2.9902
H	-0.9099	2.0723	-4.0600
H	-1.8865	-0.0856	-3.3332
H	-4.3270	1.9797	-0.4766
H	-3.3585	4.1396	-1.1951
C	-3.7497	-0.5249	-1.3982
H	-4.0855	-1.1148	-2.2572
H	-2.9925	-1.1300	-0.8704
H	-4.6048	-0.3697	-0.7339

21a

C	0.8641	0.5939	0.5432
C	0.8167	1.1472	1.9671
C	-0.6644	1.5479	2.2791
H	-0.6368	1.9672	3.2967
O	0.4089	-0.4895	0.2071
Si	-3.1774	0.4447	2.8403
N	-1.5196	0.3748	2.2991
C	1.7424	2.3724	1.8891
H	1.4027	3.2019	2.5155
H	2.7455	2.0878	2.2208
C	1.7776	2.7641	0.4054
H	1.0419	3.5452	0.1787
H	2.7637	3.1077	0.0776
N	1.4329	1.5247	-0.2871
C	1.2914	0.0951	2.9661
H	0.6791	-0.8044	2.8954
H	2.3348	-0.1730	2.7720
H	1.2176	0.4861	3.9867
C	-1.1550	2.6552	1.3512
C	-1.5108	2.3722	0.0271
C	-1.2242	3.9755	1.7973
C	-1.8751	3.3953	-0.8406
H	-1.4907	1.3432	-0.3260
C	-1.6070	5.0031	0.9351
H	-0.9738	4.2015	2.8323
C	-1.9205	4.7158	-0.3896
H	-2.1261	3.1619	-1.8709
H	-1.6594	6.0247	1.2996
H	-2.2129	5.5129	-1.0662
C	1.4280	1.4526	-1.7003
C	1.4273	2.6266	-2.4516
C	1.4408	0.2185	-2.3709
C	1.4360	2.5889	-3.8463
H	1.4093	3.5926	-1.9593
C	1.4430	0.1821	-3.7534
H	1.4387	-0.7005	-1.8017
C	1.4415	1.3621	-4.5048
H	1.4363	3.5227	-4.3959
H	1.4527	-0.7644	-4.2835

C	-3.7154	-1.3255	3.1627
H	-3.6242	-1.9365	2.2580
H	-3.0985	-1.7862	3.9400
H	-4.7614	-1.3687	3.4839
C	-4.3734	1.2322	1.6129
H	-4.3404	0.7243	0.6427
H	-5.4030	1.1751	1.9853
H	-4.1322	2.2866	1.4414
C	-3.1924	1.4704	4.4170
H	-4.1873	1.4589	4.8748
H	-2.4771	1.0833	5.1500
H	-2.9409	2.5175	4.2130
O	1.4497	1.2080	-5.8565
C	1.4480	2.3791	-6.6394
H	0.5504	2.9824	-6.4545
H	2.3378	2.9911	-6.4454
H	1.4548	2.0507	-7.6786
H	-1.2728	-0.2945	1.5723

21b

C	-0.5480	-0.8995	1.6442
C	-0.0011	-2.3298	1.6319
C	-0.0931	-2.9212	0.1900
H	0.0973	-3.9944	0.3321
O	0.0537	0.0773	1.2337
Si	-1.9620	-3.7678	-1.7108
N	-1.4540	-2.8083	-0.3289
C	-0.9747	-3.0743	2.5614
H	-1.1594	-4.1001	2.2312
H	-0.5606	-3.1080	3.5742
C	-2.2653	-2.2472	2.5554
H	-2.9851	-2.6402	1.8300
H	-2.7402	-2.1971	3.5407
N	-1.8234	-0.9116	2.1591
C	1.4431	-2.3357	2.1242
H	2.0501	-1.6531	1.5254
H	1.4926	-2.0148	3.1692
H	1.8709	-3.3422	2.0521
C	0.9745	-2.4280	-0.7796
C	0.8786	-1.1870	-1.4169
C	2.0441	-3.2647	-1.1029
C	1.8327	-0.7976	-2.3501
H	0.0582	-0.5177	-1.1782
C	3.0011	-2.8792	-2.0401
H	2.1223	-4.2379	-0.6215
C	2.8955	-1.6425	-2.6676
H	1.7452	0.1699	-2.8350
H	3.8215	-3.5479	-2.2826
H	3.6342	-1.3377	-3.4024
C	-2.7025	0.1949	2.2240
C	-4.0668	-0.0264	2.4137
C	-2.2436	1.5203	2.1239
C	-4.9676	1.0354	2.5005
H	-4.4531	-1.0363	2.4908
C	-3.1391	2.5712	2.2061
H	-1.1910	1.7132	1.9759
C	-4.5061	2.3442	2.3949
H	-6.0190	0.8189	2.6479
H	-2.7949	3.5974	2.1306
C	-3.8307	-3.5944	-1.7957
H	-4.1268	-2.5451	-1.9043
H	-4.2419	-4.1408	-2.6509
H	-4.2998	-3.9817	-0.8859
C	-1.4547	-5.5421	-1.3542
H	-1.9008	-6.2224	-2.0873
H	-0.3680	-5.6689	-1.4114
H	-1.7844	-5.8565	-0.3582
C	-1.2093	-3.2276	-3.3504
H	-0.1203	-3.3448	-3.3468
H	-1.6150	-3.8220	-4.1774
H	-1.4242	-2.1738	-3.5588
O	-5.2927	3.4526	2.4643
C	-6.6740	3.2513	2.6531
H	-7.1107	2.6759	1.8273
H	-6.8769	2.7325	3.5984
H	-7.1254	4.2430	2.6810
H	-1.7641	-1.8374	-0.3602

3b

C	-3.3042	-0.9405	0.6638
H	-3.0568	-1.2307	1.7025
Si	-4.7203	1.1377	1.5926
N	-4.0212	0.0668	0.3818
C	-2.7211	-1.8360	-0.3607
C	-2.9412	-1.6014	-1.7217
C	-1.9443	-2.9255	0.0358
C	-2.3882	-2.4502	-2.6705
H	-3.5489	-0.7474	-2.0044
C	-1.3894	-3.7772	-0.9153
H	-1.7758	-3.1040	1.0956
C	-1.6117	-3.5391	-2.2687
H	-2.5591	-2.2678	-3.7270
H	-0.7860	-4.6235	-0.6021
H	-1.1804	-4.2013	-3.0133
C	-4.2756	0.6134	3.3476
H	-4.6434	-0.3917	3.5801
H	-3.1933	0.6237	3.5160
H	-4.7267	1.3031	4.0693
C	-6.5808	1.0887	1.3589
H	-6.8472	1.3670	0.3348
H	-6.9768	0.0859	1.5477
H	-7.0816	1.7832	2.0419
C	-4.0599	2.8594	1.2491
H	-4.5057	3.5942	1.9279
H	-2.9735	2.8989	1.3759
H	-4.2889	3.1614	0.2227

TS1

C	0.8293	1.1922	1.1914

C	0.4804	2.1196	2.2225
C	-1.5561	2.1840	1.7838
H	-1.7376	2.6247	2.7800
O	0.5957	-0.0283	1.1839
Si	-2.7543	-0.0902	2.6198
N	-2.0657	0.9886	1.4830
C	1.2524	3.3881	1.9252
H	0.7086	4.3102	2.1582
H	2.1877	3.4128	2.5070
C	1.5533	3.2975	0.4173
H	0.8417	3.9021	-0.1543
H	2.5668	3.6248	0.1591
N	1.3948	1.8731	0.1049
C	0.4525	1.6156	3.6371
H	-0.0924	0.6681	3.6872
H	1.4626	1.4453	4.0431
H	-0.0478	2.3286	4.3042
K	-1.3302	-0.9391	-0.4595
K	1.3925	-2.2538	2.0216
C	-1.5595	3.2390	0.7204
C	-1.5253	2.8973	-0.6342
C	-1.5976	4.5944	1.0625
C	-1.4817	3.8791	-1.6177
H	-1.5198	1.8459	-0.9063
C	-1.5592	5.5831	0.0820
H	-1.6576	4.8728	2.1126
C	-1.4907	5.2288	-1.2638
H	-1.4256	3.5930	-2.6654
H	-1.5879	6.6305	0.3681
H	-1.4575	5.9969	-2.0306
C	1.4150	1.4037	-1.2213
C	1.4610	2.3166	-2.2806
C	1.3891	0.0276	-1.5426
C	1.4069	1.8983	-3.6111
H	1.5048	3.3808	-2.0808
C	1.3251	-0.3833	-2.8647
H	1.3813	-0.7336	-0.7702
C	1.3156	0.5426	-3.9109
H	1.4282	2.6483	-4.3936
H	1.2790	-1.4428	-3.1000
C	-4.3256	-0.8127	1.8520
H	-5.0204	-0.0189	1.5565
H	-4.0901	-1.3973	0.9528
H	-4.8435	-1.4833	2.5474
C	-3.2061	0.7025	4.2772
H	-3.8998	1.5386	4.1348
H	-3.6945	-0.0278	4.9320
H	-2.3272	1.0870	4.8060
C	-1.6892	-1.6253	3.0056
H	-2.2740	-2.3381	3.6005
H	-1.3628	-2.1493	2.0961
H	-0.8055	-1.3502	3.5946
O	0.1607	-2.9033	-0.0105
C	0.2514	-4.1644	-0.5434
C	1.1632	-5.0648	0.3248
H	1.2634	-6.0859	-0.0625
H	2.1712	-4.6268	0.3778
H	0.7528	-5.1324	1.3426
C	-1.1411	-4.8222	-0.6197
H	-1.1197	-5.8417	-1.0253
H	-1.5852	-4.8511	0.3824
H	-1.7906	-4.2103	-1.2591
C	0.8474	-4.1073	-1.9633
H	0.1926	-3.5004	-2.6018
H	1.8288	-3.6177	-1.9247
H	0.9650	-5.0950	-2.4269
O	1.2005	0.0262	-5.1703
C	1.1791	0.9440	-6.2393
H	0.3281	1.6325	-6.1567
H	2.1079	1.5260	-6.2846
H	1.0785	0.3518	-7.1486
C	3.8041	-0.4378	0.9475
C	3.7289	-0.0062	2.2719
C	4.0684	-0.8705	3.3121
C	4.4964	-2.1792	3.0504
C	4.5559	-2.6038	1.7178
C	4.2139	-1.7418	0.6734
H	3.5204	0.2319	0.1418
H	3.3843	1.0018	2.4892
H	4.0068	-0.5262	4.3422
H	4.8757	-3.6194	1.4957
H	4.2527	-2.0933	-0.3536
C	4.9156	-3.0951	4.1737
H	5.9869	-2.9893	4.3762
H	4.3824	-2.8618	5.0996
H	4.7310	-4.1438	3.9241
C	-2.4928	-1.9765	-3.3976
C	-3.5835	-2.1769	-2.5495
C	-4.2016	-1.0895	-1.9349
C	-3.7419	0.2181	-2.1423
C	-2.6561	0.4039	-3.0078
C	-2.0362	-0.6800	-3.6342
H	-2.0080	-2.8233	-3.8735
H	-3.9524	-3.1820	-2.3670
H	-5.0529	-1.2513	-1.2781
H	-2.2879	1.4110	-3.1922
H	-1.1931	-0.5144	-4.2997
C	-4.3716	1.3707	-1.4039
H	-5.4499	1.2212	-1.2946
H	-3.9328	1.4552	-0.3995
H	-4.1979	2.3192	-1.9193

TS1-b

C	-0.8778	-0.8109	-1.5205
C	-0.9867	-0.6827	-2.9431
C	0.0624	1.0851	-3.1236
H	0.1727	0.8972	-4.2069
O	0.1310	-1.1564	-0.8805
Si	2.7133	0.6306	-2.8143
N	1.1446	1.1272	-2.3464
C	-2.4679	-0.5830	-3.2443

H	-2.7130	0.1026	-4.0621
H	-2.8701	-1.5692	-3.5242
C	-3.0911	-0.0999	-1.9203
H	-3.3094	0.9734	-1.9522
H	-4.0162	-0.6316	-1.6684
N	-2.0644	-0.3839	-0.9123
C	-0.1495	-1.5972	-3.7918
H	0.8837	-1.6012	-3.4323
H	-0.5175	-2.6345	-3.7788
H	-0.1418	-1.2680	-4.8383
K	1.4542	0.8944	0.3893
K	1.5840	-3.0250	-0.0198
C	-1.0384	2.0717	-2.8694
C	-1.2639	2.6102	-1.5981
C	-1.8728	2.4757	-3.9161
C	-2.3247	3.4807	-1.3705
H	-0.6028	2.3265	-0.7840
C	-2.9336	3.3513	-3.6962
H	-1.6837	2.0941	-4.9174
C	-3.1710	3.8487	-2.4176
H	-2.4986	3.8748	-0.3733
H	-3.5704	3.6491	-4.5241
H	-3.9975	4.5298	-2.2392
C	-2.2274	-0.0021	0.4276
C	-3.3946	0.6700	0.8145
C	-1.2749	-0.2856	1.4355
C	-3.6084	1.0698	2.1350
H	-4.1556	0.9047	0.0797
C	-1.4826	0.1337	2.7406
H	-0.3733	-0.8459	1.2155
C	-2.6437	0.8199	3.1061
H	-4.5263	1.5937	2.3760
H	-0.7336	-0.0767	3.4996
C	3.9485	1.9230	-2.1899
H	4.9741	1.6760	-2.4882
H	3.7035	2.9147	-2.5850
H	3.9383	1.9924	-1.0935
C	2.9502	0.4402	-4.6821
H	2.3148	-0.3468	-5.1025
H	2.7111	1.3740	-5.2030
H	3.9906	0.1864	-4.9138
C	3.2968	-0.9913	-1.9972
H	2.7366	-1.8503	-2.3875
H	4.3581	-1.1582	-2.2205
H	3.1915	-0.9636	-0.9029
O	2.2239	-1.2084	1.5072
C	3.0262	-1.3975	2.6045
C	2.2767	-0.9925	3.8892
H	1.3654	-1.5973	3.9795
H	2.8728	-1.1185	4.8021
H	1.9733	0.0597	3.8119
C	3.4405	-2.8821	2.7361
H	4.0805	-3.0801	3.6046
H	2.5421	-3.5082	2.8293
H	3.9931	-3.1908	1.8371
C	4.3142	-0.5571	2.4855
H	4.8529	-0.8462	1.5752
H	4.0496	0.5036	2.3929
H	4.9889	-0.6712	3.3436
O	-2.7223	1.2228	4.4075
C	-3.8883	1.9131	4.7939
H	-4.0037	2.8481	4.2302
H	-4.7839	1.2959	4.6508
H	-3.7714	2.1415	5.8531
C	-0.0196	-4.8987	2.0345
C	-0.8443	-3.7849	1.8619
C	-1.4810	-3.5703	0.6413
C	-1.3081	-4.4570	-0.4285
C	-0.4677	-5.5611	-0.2489
C	0.1697	-5.7852	0.9740
H	0.4754	-5.0693	2.9855
H	-0.9803	-3.0710	2.6693
H	-2.1105	-2.6942	0.5071
H	-0.3204	-6.2587	-1.0703
H	0.8094	-6.6542	1.0983
C	-2.0331	-4.2217	-1.7282
H	-3.0597	-4.6002	-1.6707
H	-2.0863	-3.1514	-1.9527
H	-1.5382	-4.7266	-2.5626
C	3.1560	3.3600	1.6921
C	2.3902	3.9685	0.6956
C	1.0049	4.0494	0.8298
C	0.3595	3.5197	1.9549
C	1.1370	2.9087	2.9442
C	2.5247	2.8339	2.8193
H	4.2350	3.2933	1.5890
H	2.8695	4.3706	-0.1918
H	0.4136	4.5167	0.0453
H	0.6467	2.4865	3.8186
H	3.1102	2.3558	3.5988
C	-1.1403	3.5744	2.0763
H	-1.6095	2.8283	1.4225
H	-1.4613	3.3559	3.0988
H	-1.5217	4.5601	1.7907

TS1-c

C	-0.8452	-1.5780	1.2830
C	-0.5127	-2.7425	2.0412
C	1.4498	-2.9105	1.3612
H	1.6731	-3.5755	2.2145
O	-0.4818	-0.4108	1.5117
Si	3.0215	-1.0078	2.4727
N	2.0618	-1.7327	1.2568
C	-1.4563	-3.8310	1.5739
H	-1.0085	-4.8303	1.5436
H	-2.3314	-3.8897	2.2395
C	-1.8796	-3.3789	0.1629
H	-1.3069	-3.9116	-0.6032
H	-2.9462	-3.5329	-0.0368
N	-1.5726	-1.9449	0.1412
C	-0.2844	-2.5728	3.5159

H	-1.2184	-2.3766	4.0651
H	0.1676	-3.4713	3.9540
H	0.3947	-1.7333	3.6953
K	1.4119	0.5581	-0.210
K	-0.7911	1.6974	2.8620
C	1.2213	-3.7013	0.1091
C	1.0952	-3.0640	-1.1280
C	1.1343	-5.0958	0.1478
C	0.8476	-3.7899	-2.2871
H	1.1743	-1.9835	-1.1638
C	0.8877	-5.8309	-1.0101
H	1.2623	-5.6078	1.0993
C	0.7348	-5.1801	-2.2324
H	0.7329	-3.2713	-3.2365
H	0.8216	-6.9139	-0.9591
H	0.5432	-5.7510	-3.1359
C	-1.7001	-1.1785	-1.0280
C	-1.9890	-1.8069	-2.2454
C	-1.5606	0.2279	-1.0356
C	-2.0935	-1.0850	-3.4362
H	-2.1137	-2.8829	-2.2848
C	-1.6600	0.9400	-2.2201
H	-1.3437	0.7715	-0.1237
C	-1.9146	0.2958	-3.4332
H	-2.3079	-1.6226	-4.3531
H	-1.5304	2.0189	-2.2154
C	4.5735	-0.3084	1.6442
H	5.1209	-1.0988	1.1198
H	4.3187	0.4623	0.9036
H	5.2487	0.1551	2.3728
C	3.5556	-2.1904	3.8498
H	2.6990	-2.5842	4.4081
H	4.1066	-3.0447	3.4413
H	4.2117	-1.6808	4.5642
C	2.2167	0.5049	3.3065
H	1.8793	1.2481	2.5696
H	1.3639	0.1966	3.9246
H	2.9427	0.9985	3.9647
O	0.3976	2.5688	0.9168
C	0.6654	3.8589	0.5385
C	0.1955	4.8539	1.6225
H	-0.8848	4.7314	1.7847
H	0.7146	4.6342	2.5650
H	0.3830	5.9039	1.3659
C	2.1824	4.0565	0.3297
H	2.5388	3.3655	-0.4474
H	2.4526	5.0769	0.0273
H	2.7116	3.8150	1.2592
C	-0.0647	4.1836	-0.7795
H	0.1174	5.2017	-1.1482
H	0.2591	3.4705	-1.5494
H	-1.1448	4.0484	-0.6352
O	-1.9506	1.0930	-4.5418
C	-2.1245	0.4523	-5.7849
H	-1.3192	-0.2691	-5.9756
H	-3.0902	-0.0653	-5.8367
H	-2.0947	1.2373	-6.5403
C	-3.6361	0.2721	3.1144
C	-3.7811	1.3096	4.0357
C	-3.8272	2.6349	3.5969
C	-3.7370	2.9456	2.2347
C	-3.5821	1.8936	1.3228
C	-3.5347	0.5691	1.7543
H	-3.5916	-0.7598	3.4497
H	-3.8619	1.0898	5.0966
H	-3.9465	3.4391	4.3193
H	-3.4849	2.1144	0.2622
H	-3.3954	-0.2304	1.0319
C	-3.8356	4.3707	1.7531
H	-3.5251	5.0772	2.5278
H	-3.2099	4.5338	0.8711
H	-4.8685	4.6107	1.4777
C	2.8382	-0.5782	-2.7831
C	1.6379	-0.1093	-3.3165
C	1.4462	1.2598	-3.5203
C	2.4435	2.1816	-3.1870
C	3.6280	1.7006	-2.6118
C	3.8300	0.3358	-2.4183
H	2.9925	-1.6413	-2.6253
H	0.8357	-0.8022	-3.5648
H	0.5110	1.6121	-3.9507
H	4.4042	2.4074	-2.3263
H	4.7570	-0.0187	-1.9774
C	2.2759	3.6530	-3.4705
H	2.4987	4.2581	-2.5859
H	2.9573	3.9670	-4.2687
H	1.2551	3.8817	-3.7868

TS1-rotamer1

C	1.3014	1.2550	0.0192
C	1.1234	2.4096	0.8333
C	-0.6491	1.8717	2.0683
H	-0.9925	2.8978	1.8555
O	1.6308	0.1034	0.3812
Si	-0.1336	2.6065	4.6012
N	-0.2714	1.5068	3.2758
C	0.8238	3.5786	-0.0855
H	-0.0488	4.1663	0.2353
H	1.6693	4.2790	-0.1264
C	0.5870	2.9493	-1.4787
H	-0.4604	3.0424	-1.7887
H	1.1978	3.4060	-2.2658
N	0.9643	1.5516	-1.3080
C	2.0990	2.6413	1.9470
H	2.1030	1.8161	2.6654
H	3.1264	2.7747	1.5782
H	1.8329	3.5418	2.5125
K	0.4831	-2.1923	-0.2996
K	1.4046	-0.7790	2.9271
C	-1.3296	0.8520	1.2024
C	-1.5776	-0.4366	1.6906

C	-1.8068	1.1758	-0.0709
C	-2.2366	-1.3873	0.9109
H	-1.2988	-0.6562	2.7170
C	-2.4537	0.2309	-0.8604
H	-1.6792	2.1923	-0.4335
C	-2.6626	-1.0626	-0.3776
H	-2.4254	-2.3809	1.3142
H	-2.8093	0.5023	-1.8504
H	-3.1813	-1.7945	-0.9896
C	0.8642	0.6108	-2.3393
C	-0.1069	0.7296	-3.3362
C	1.7662	-0.4670	-2.4220
C	-0.2286	-0.2228	-4.3494
H	-0.7926	1.5706	-3.3267
C	1.6280	-1.4342	-3.4052
H	2.5689	-0.5356	-1.6978
C	0.6178	-1.3295	-4.3690
H	-0.9978	-0.0927	-5.1022
H	2.3202	-2.2699	-3.4609
C	-1.3995	2.1668	5.9350
H	-2.4041	2.0885	5.5053
H	-1.1728	1.2165	6.4293
H	-1.4255	2.9408	6.7111
C	-0.4891	4.4044	4.1238
H	-1.5345	4.5243	3.8165
H	-0.3243	5.0626	4.9843
H	0.1394	4.7674	3.3037
C	1.5721	2.4896	5.4115
H	1.5474	2.8941	6.4302
H	1.8948	1.4428	5.4816
H	2.3372	3.0354	4.8507
O	1.8839	-2.9433	1.6380
C	3.2186	-3.2289	1.4807
C	4.1010	-2.3336	2.3854
H	5.1667	-2.5867	2.3280
H	3.9997	-1.2801	2.0876
H	3.7846	-2.4422	3.4324
C	3.5132	-4.6983	1.8402
H	4.5714	-4.9651	1.7265
H	3.2155	-4.8886	2.8784
H	2.9193	-5.3575	1.1955
C	3.6653	-2.9789	0.0215
H	3.0771	-3.6132	-0.6571
H	3.4788	-1.9261	-0.2271
H	4.7275	-3.1911	-0.1542
O	0.5429	-2.3453	-5.2775
C	-0.3321	-2.1679	-6.3707
H	-1.3775	-2.1059	-6.0434
H	-0.0780	-1.2627	-6.9349
H	-0.2050	-3.0433	-7.0074
C	0.4759	-1.1864	6.0305
C	-0.7008	-1.4552	5.3332
C	-0.8031	-2.6110	4.5571
C	0.2604	-3.5123	4.4491
C	1.4377	-3.2257	5.1520
C	1.5461	-2.0797	5.9375
H	0.5597	-0.2917	6.6404
H	-1.5336	-0.7594	5.3799
H	-1.7281	-2.8166	4.0214
H	2.2789	-3.9099	5.0727
H	2.4675	-1.8820	6.4786
C	0.1819	-4.7078	3.5420
H	-0.8585	-4.9804	3.3371
H	0.6992	-4.4361	2.6079
H	0.6860	-5.5746	3.9811
C	0.2528	-5.3942	-0.4096
C	-1.0679	-5.0519	-0.1259
C	-1.8423	-4.3953	-1.0830
C	-1.3118	-4.0594	-2.3329
C	0.0129	-4.4195	-2.6126
C	0.7866	-5.0852	-1.6618
H	0.8602	-5.8876	0.3413
H	-1.4944	-5.2957	0.8425
H	-2.8773	-4.1469	-0.8581
H	0.4302	-4.1726	-3.5867
H	1.8115	-5.3590	-1.8950
C	-2.1298	-3.3107	-3.3538
H	-1.9292	-3.6864	-4.3615
H	-3.2011	-3.4099	-3.1561
H	-1.8802	-2.2411	-3.3439

TS1-rotamer2

C	0.6643	0.7051	1.5107
C	0.3573	1.6434	2.5217
C	-1.8131	1.5684	1.8619
H	-1.8461	0.7469	2.6030
O	0.5269	-0.5451	1.5430
Si	-2.6565	1.8929	-0.8195
N	-1.9611	1.2504	0.6039
C	0.9599	2.9655	2.1360
H	0.3203	3.8279	2.3604
H	1.9135	3.1368	2.6607
C	1.1951	2.8227	0.6207
H	0.4478	3.3619	0.0259
H	2.1855	3.1929	0.3341
N	1.0731	1.3879	0.3605
C	0.2915	1.2140	3.9516
H	-0.0132	0.1631	4.0158
H	1.2652	1.3067	4.4572
H	-0.4211	1.8201	4.5270
K	-1.9356	-1.4467	0.9110
K	1.7556	-2.6039	0.6206
C	-2.2160	2.8650	2.4776
C	-2.1310	4.0731	1.7755
C	-2.7204	2.8893	3.7828
C	-2.5395	5.2666	2.3593
H	-1.7286	4.0691	0.7658
C	-3.1343	4.0824	4.3699
H	-2.7983	1.9552	4.3353
C	-3.0456	5.2758	3.6591
H	-2.4622	6.1945	1.8002

H	-3.5305	4.0787	5.3811
H	-3.3680	6.2079	4.1128
C	1.2667	0.8591	-0.9199
C	2.0057	1.5838	-1.8639
C	0.7456	-0.3869	-1.3308
C	2.2444	1.0942	-3.1513
H	2.4026	2.5603	-1.6124
C	0.9996	-0.8814	-2.5990
H	0.1348	-0.9904	-0.6736
C	1.7539	-0.1533	-3.5258
H	2.8134	1.7056	-3.8423
H	0.5847	-1.8398	-2.8979
C	-4.2776	2.8275	-0.5008
H	-4.8215	2.4033	0.3512
H	-4.1024	3.8834	-0.2712
H	-4.9319	2.7791	-1.3793
C	-3.0257	0.3978	-1.9162
H	-3.6937	-0.3214	-1.4250
H	-3.4932	0.6881	-2.8644
H	-2.0896	-0.1233	-2.1557
C	-1.5589	3.0100	-1.8821
H	-2.0812	3.2273	-2.8221
H	-1.3195	3.9724	-1.4164
H	-0.6179	2.5087	-2.1358
O	-0.4998	-3.2900	-0.0247
C	-1.0242	-4.2527	-0.8520
C	0.0820	-4.8753	-1.7315
H	-0.2897	-5.6429	-2.4213
H	0.5692	-4.0895	-2.3221
H	0.8411	-5.3385	-1.0864
C	-1.6770	-5.3810	-0.0287
H	-2.1150	-6.1710	-0.6518
H	-0.9286	-5.8319	0.6331
H	-2.4681	-4.9573	0.6032
C	-2.0975	-3.6438	-1.7805
H	-2.9363	-3.2594	-1.1808
H	-1.6674	-2.8013	-2.3357
H	-2.5085	-4.3629	-2.5001
O	1.9363	-0.7315	-4.7462
C	2.6545	0.0090	-5.7045
H	2.1577	0.9615	-5.9279
H	3.6801	0.2105	-5.3688
H	2.6836	-0.6039	-6.6052
C	4.1621	-0.9990	-0.6385
C	3.9925	-0.3683	0.5956
C	4.3213	-1.0346	1.7751
C	4.8322	-2.3386	1.7492
C	4.9945	-2.9623	0.5066
C	4.6658	-2.2993	-0.6780
H	3.8823	-0.4861	-1.5548
H	3.5741	0.6331	0.6390
H	4.1703	-0.5390	2.7314
H	5.3887	-3.9753	0.4668
H	4.7963	-2.8024	-1.6318
C	5.2250	-3.0374	3.0271
H	6.2349	-2.7424	3.3320
H	4.5475	-2.7797	3.8462
H	5.2210	-4.1240	2.9057
C	-5.1374	-1.9720	0.7146
C	-4.7189	-2.9603	1.6054
C	-4.2424	-2.6054	2.8683
C	-4.1755	-1.2640	3.2628
C	-4.5988	-0.2817	2.3589
C	-5.0765	-0.6311	1.0968
H	-5.5047	-2.2440	-0.2706
H	-4.7606	-4.0064	1.3176
H	-3.9194	-3.3810	3.5586
H	-4.5410	0.7685	2.6401
H	-5.3908	0.1461	0.4064
C	-3.6352	-0.8808	4.6184
H	-3.6779	-1.7228	5.3144
H	-2.5885	-0.5579	4.5496
H	-4.2056	-0.0519	5.0475

TS2

C	-0.4120	-1.1921	1.6241
C	-0.0238	-2.5543	1.6135
C	-0.1427	-3.0419	-0.5600
H	0.3133	-4.0017	-0.2538
O	0.2939	-0.1667	1.4303
Si	-2.3401	-4.3566	-1.3734
N	-1.3650	-2.9815	-1.0166
C	-1.1957	-3.3783	2.0846
H	-1.3581	-4.2790	1.4747
H	-1.0643	-3.7129	3.1241
C	-2.3985	-2.4237	1.9617
H	-3.0013	-2.6588	1.0836
H	-3.0475	-2.4322	2.8459
N	-1.7954	-1.1003	1.8091
C	1.3662	-2.9481	2.0095
H	2.0993	-2.2010	1.6859
H	1.4700	-3.0606	3.1003
H	1.6620	-3.9080	1.5622
K	-0.4534	1.8440	-0.1644
K	2.6751	0.3488	0.6575
C	0.8788	-2.0754	-1.0682
C	0.4763	-0.8726	-1.6635
C	2.2347	-2.4162	-1.1079
C	1.3983	-0.0313	-2.2769
H	-0.5901	-0.6579	-1.6745
C	3.1619	-1.5881	-1.7465
H	2.5582	-3.3613	-0.6779
C	2.7490	-0.3923	-2.3322
H	1.0739	0.9035	-2.7294
H	4.2050	-1.8889	-1.8044
H	3.4636	0.2527	-2.8348
C	-2.5574	0.0576	1.9555
C	-3.9467	0.0020	1.7858
C	-2.0003	1.2890	2.3665
C	-4.7543	1.1244	1.9788
H	-4.4151	-0.9331	1.4974

C	-2.7971	2.4125	2.5183
H	-0.9400	1.3409	2.5836
C	-4.1813	2.3469	2.3208
H	-5.8254	1.0256	1.8417
H	-2.3654	3.3588	2.8315
C	-4.0074	-4.3641	-0.4785
H	-4.5077	-3.3908	-0.5506
H	-4.6664	-5.1065	-0.9435
H	-3.9161	-4.6231	0.5820
C	-1.4811	-6.0051	-1.0093
H	-2.1315	-6.8360	-1.3052
H	-0.5474	-6.1014	-1.5747
H	-1.2422	-6.1373	0.0516
C	-2.7355	-4.3178	-3.2177
H	-1.8164	-4.3426	-3.8122
H	-3.3584	-5.1685	-3.5169
H	-3.2724	-3.3993	-3.4783
O	1.8953	2.5629	-0.1411
C	2.5923	3.6297	-0.6448
C	3.3117	4.3917	0.4860
H	4.0064	3.7106	0.9950
H	3.8771	5.2623	0.1304
H	2.5744	4.7276	1.2235
C	3.6505	3.1533	-1.6638
H	3.1515	2.6337	-2.4909
H	4.2544	3.9700	-2.0793
H	4.3288	2.4383	-1.1751
C	1.6411	4.6074	-1.3684
H	2.1506	5.4851	-1.7857
H	1.1369	4.0786	-2.1887
H	0.8740	4.9556	-0.6640
O	-4.8679	3.5125	2.4893
C	-6.2632	3.4673	2.2990
H	-6.5168	3.1603	1.2758
H	-6.7417	2.7805	3.0081
H	-6.6282	4.4793	2.4735
C	4.7811	-0.0481	3.0660
C	4.8930	-1.2504	2.3678
C	5.4175	-1.2625	1.0739
C	5.8412	-0.0802	0.4571
C	5.7259	1.1196	1.1711
C	5.2006	1.1388	2.4623
H	4.3721	-0.0360	4.0714
H	4.5701	-2.1795	2.8279
H	5.5012	-2.2044	0.5368
H	6.0458	2.0493	0.7064
H	5.1139	2.0819	2.9934
C	6.3851	-0.0810	-0.9489
H	5.6456	0.3216	-1.6517
H	7.2793	0.5442	-1.0249
H	6.6456	-1.0918	-1.2739
C	-1.9544	3.6255	-2.3127
C	-1.4970	2.5681	-3.1031
C	-2.0112	1.2835	-2.9265
C	-2.9903	1.0227	-1.9559
C	-3.4397	2.0930	-1.1742
C	-2.9311	3.3818	-1.3475
H	-1.5490	4.6234	-2.4479
H	-0.7393	2.7473	-3.8610
H	-1.6519	0.4675	-3.5504
H	-4.1934	1.9107	-0.4139
H	-3.2991	4.1902	-0.7212
C	-3.5271	-0.3703	-1.7467
H	-3.7270	-0.8580	-2.7062
H	-2.8084	-1.0107	-1.2137
H	-4.4565	-0.3422	-1.1710

TS2-b

C	-0.4262	-1.1684	1.6274
C	-0.0764	-2.5407	1.6168
C	-0.2349	-3.0325	-0.5571
H	0.1980	-4.0029	-0.2507
O	0.3050	-0.1637	1.4196
Si	-2.4769	-4.2914	-1.3361
N	-1.4600	-2.9409	-0.9999
C	-1.2650	-3.3304	2.1040
H	-1.4597	-4.2281	1.4991
H	-1.1310	-3.6656	3.1431
C	-2.4420	-2.3429	1.9918
H	-3.0591	-2.5612	1.1192
H	-3.0831	-2.3333	2.8818
N	-1.8036	-1.0373	1.8328
C	1.3071	-2.9715	1.9965
H	2.0556	-2.2431	1.6654
H	1.4200	-3.0877	3.0861
H	1.5729	-3.9385	1.5456
K	-0.4173	1.8495	-0.1849
K	2.6860	0.2918	0.6114
C	0.8069	-2.0962	-1.0797
C	0.4312	-0.8861	-1.6778
C	2.1527	-2.4736	-1.1309
C	1.3693	-0.0733	-2.3052
H	-0.6288	-0.6418	-1.6793
C	3.0954	-1.6745	-1.7834
H	2.4549	-3.4248	-0.6989
C	2.7091	-0.4712	-2.3720
H	1.0656	0.8678	-2.7588
H	4.1294	-2.0038	-1.8499
H	3.4358	0.1513	-2.8854
C	-2.5327	0.1419	1.9752
C	-3.9245	0.1233	1.8184
C	-1.9381	1.3612	2.3695
C	-4.6988	1.2698	2.0062
H	-4.4215	-0.8013	1.5440
C	-2.7019	2.5080	2.5162
H	-0.8748	1.3858	2.5767
C	-4.0890	2.4793	2.3305
H	-5.7733	1.1996	1.8790
H	-2.2412	3.4450	2.8160
C	-4.1294	-4.2534	-0.4150
H	-4.6064	-3.2682	-0.4831

H	-4.8140	-4.9807	-0.8667
H	-4.0277	-4.5108	0.6449
C	-1.6546	-5.9600	-0.9800
H	-2.3307	-6.7751	-1.2620
H	-0.7331	-6.0819	-1.5603
H	-1.4016	-6.0946	0.0773
C	-2.8994	-4.2457	-3.1741
H	-1.9905	-4.2977	-3.7824
H	-3.5507	-5.0789	-3.4617
H	-3.4138	-3.3126	-3.4285
O	1.9451	2.5179	-0.1965
C	2.6710	3.5613	-0.7083
C	3.4181	4.3068	0.4156
H	4.0948	3.6078	0.9248
H	4.0074	5.1585	0.0532
H	2.6946	4.6679	1.1549
C	3.7098	3.0492	-1.7299
H	3.1917	2.5396	-2.5514
H	4.3348	3.8459	-2.1531
H	4.3702	2.3178	-1.2408
C	1.7457	4.5634	-1.4319
H	2.2789	5.4242	-1.8549
H	1.2228	4.0462	-2.2478
H	0.9921	4.9363	-0.7257
O	-4.7415	3.6654	2.4918
C	-6.1390	3.6571	2.3133
H	-6.6304	2.9910	3.0333
H	-6.4744	4.6805	2.4800
H	-6.4096	3.3467	1.2954
C	4.8013	-0.1509	3.0059
C	4.8732	-1.3599	2.3141
C	5.3858	-1.3943	1.0159
C	5.8373	-0.2281	0.3883
C	5.7621	0.9787	1.0960
C	5.2489	1.0202	2.3915
H	4.4014	-0.1215	4.0146
H	4.5281	-2.2769	2.7825
H	5.4384	-2.3413	0.4837
H	6.1041	1.8963	0.6230
H	5.1933	1.9683	2.9177
C	6.3687	-0.2522	-1.0222
H	7.2822	0.3430	-1.1084
H	6.5933	-1.2723	-1.3451
H	5.6369	0.1716	-1.7205
C	-1.8809	3.6627	-2.3282
C	-1.4631	2.5892	-3.1190
C	-2.0158	1.3219	-2.9347
C	-2.9957	1.0949	-1.9562
C	-3.4040	2.1804	-1.1733
C	-2.8565	3.4522	-1.3542
H	-1.4452	4.6468	-2.4694
H	-0.7058	2.7424	-3.8830
H	-1.6869	0.4932	-3.5585
H	-4.1562	2.0237	-0.4057
H	-3.1933	4.2732	-0.7267
C	-3.5784	-0.2792	-1.7444
H	-2.8578	-0.9620	-1.2695
H	-4.4697	-0.2257	-1.1131
H	-3.8584	-0.7325	-2.7009

TS2-c

C	0.4527	1.0688	1.6733
C	0.1605	2.4555	1.6732
C	0.3368	2.9683	-0.4860
H	-0.0691	3.9475	-0.1714
O	-0.3207	0.0977	1.4589
Si	2.6195	4.1715	-1.2375
N	1.5607	2.8479	-0.9287
C	1.3791	3.1892	2.1737
H	1.6096	4.0883	1.5837
H	1.2579	3.5116	3.2184
C	2.5150	2.1571	2.0450
H	3.1346	2.3592	1.1704
H	3.1604	2.1127	2.9308
N	1.8233	0.8798	1.8773
C	-1.2063	2.9305	2.0584
H	-1.9768	2.2396	1.7000
H	-1.3230	3.0189	3.1505
H	-1.4310	3.9196	1.6338
K	0.4173	-1.8587	-0.2165
K	-2.7103	-0.3434	0.6486
C	-0.7290	2.0674	-1.0234
C	-0.3793	0.8657	-1.6521
C	-2.0689	2.4666	-1.0530
C	-1.3358	0.0765	-2.2806
H	0.6776	0.6094	-1.6735
C	-3.0309	1.6928	-1.7081
H	-2.3522	3.4142	-0.6007
C	-2.6710	0.4927	-2.3200
H	-1.0516	-0.8606	-2.7533
H	-4.0594	2.0410	-1.7577
H	-3.4143	-0.1112	-2.8337
C	2.5076	-0.3290	1.9948
C	3.8966	-0.3631	1.8176
C	1.8699	-1.5296	2.3787
C	4.6264	-1.5430	1.9739
H	4.4263	0.5454	1.5512
C	2.5885	-2.7089	2.4935
H	0.8083	-1.5159	2.5956
C	3.9728	-2.7325	2.2865
H	5.7010	-1.5140	1.8317
H	2.0943	-3.6320	2.7823
C	4.2619	4.0727	-0.3022
H	4.1559	4.3071	0.7626
H	4.7170	3.0787	-0.3894
H	4.9675	4.7944	-0.7301
C	1.8443	5.8589	-0.8644
H	2.5472	6.6576	-1.1270
H	0.9328	6.0170	-1.4517
H	1.5844	5.9849	0.1924
C	3.0584	4.1386	-3.0721

H	3.5438	3.1924	-3.3350
H	2.1576	4.2294	-3.6877
H	3.7399	4.9535	-3.3418
O	-1.9355	-2.5125	-0.3196
C	-2.7329	-3.4749	-0.8812
C	-4.2239	-3.1664	-0.6151
H	-4.4723	-2.1802	-1.0368
H	-4.9095	-3.9035	-1.0519
H	-4.3986	-3.1312	0.4685
C	-2.5225	-3.5349	-2.4087
H	-1.4634	-3.7352	-2.6178
H	-3.1251	-4.3093	-2.9000
H	-2.7771	-2.5650	-2.8541
C	-2.4124	-4.8619	-0.2891
H	-3.0420	-5.6629	-0.6967
H	-1.3629	-5.1085	-0.4954
H	-2.5423	-4.8303	0.7984
O	4.5791	-3.9462	2.4176
C	5.9730	-3.9914	2.2172
H	6.5020	-3.3590	2.9408
H	6.2686	-5.0305	2.3608
H	6.2408	-3.6742	1.2007
C	-4.7208	0.4225	3.1235
C	-4.6658	1.6224	2.4150
C	-5.2147	1.7054	1.1342
C	-5.8341	0.5987	0.5433
C	-5.8901	-0.5976	1.2693
C	-5.3369	-0.6890	2.5454
H	-4.2922	0.3557	4.1185
H	-4.1937	2.4944	2.8572
H	-5.1656	2.6450	0.5887
H	-6.3666	-1.4675	0.8245
H	-5.3882	-1.6282	3.0883
C	-6.4107	0.6709	-0.8480
H	-7.3872	0.1808	-0.8947
H	-6.5322	1.7069	-1.1754
H	-5.7567	0.1637	-1.5680
C	1.7441	-3.6931	-2.4364
C	1.3809	-2.5772	-3.1948
C	2.0003	-1.3469	-2.9769
C	2.9937	-1.1995	-1.9969
C	3.3507	-2.3280	-1.2503
C	2.7358	-3.5636	-1.4644
H	1.2564	-4.6488	-2.6026
H	0.6115	-2.6675	-3.9565
H	1.7109	-0.4838	-3.5731
H	4.1133	-2.2335	-0.4826
H	3.0314	-4.4194	-0.8633
C	3.6396	0.1393	-1.7450
H	2.9399	0.8476	-1.2758
H	4.5106	0.0306	-1.0928
H	3.9671	0.5937	-2.6858

TS3

C	-0.4738	-1.3733	1.7620
C	-0.2956	-2.7840	1.6837
C	-0.2561	-2.9151	-0.5237
H	-1.3515	-3.0427	-0.5321
O	0.3948	-0.4754	1.6923
Si	-0.6240	-0.6482	-1.8897
N	0.3049	-1.8670	-1.0989
C	-1.6013	-3.4006	2.1407
H	-1.8497	-4.3400	1.6361
H	-1.5843	-3.6159	3.2218
C	-2.6403	-2.3045	1.8368
H	-3.1036	-2.4598	0.8528
H	-3.4397	-2.2394	2.5818
N	-1.8396	-1.0828	1.8520
C	0.9988	-3.3469	2.1996
H	1.8618	-2.9053	1.6865
H	1.1305	-3.1623	3.2785
H	1.0566	-4.4287	2.0351
K	0.7839	2.1324	1.6104
K	2.5205	-0.7141	0.0826
C	0.4455	-4.2347	-0.5322
C	1.8126	-4.3153	-0.8091
C	-0.2534	-5.4229	-0.2947
C	2.4758	-5.5378	-0.7841
H	2.3368	-3.4006	-1.0693
C	0.4053	-6.6488	-0.2696
H	-1.3291	-5.3857	-0.1434
C	1.7779	-6.7107	-0.5004
H	3.5412	-5.5835	-1.0000
H	-0.1559	-7.5594	-0.0817
H	2.2938	-7.6658	-0.4839
C	-2.3838	0.1943	2.0264
C	-3.5726	0.5720	1.4022
C	-1.7669	1.1173	2.8879
C	-4.1110	1.8470	1.5827
H	-4.0832	-0.1315	0.7515
C	-2.2805	2.3936	3.0529
H	-0.8767	0.8097	3.4281
C	-3.4561	2.7741	2.3925
H	-5.0342	2.1025	1.0762
H	-1.8085	3.1071	3.7244
C	-0.4409	1.0623	-1.1033
H	0.6140	1.3130	-0.9220
H	-0.8625	1.8322	-1.7617
H	-0.9968	1.0781	-0.1569
C	-2.4752	-1.0395	-1.9096
H	-3.0322	-0.2340	-2.4010
H	-2.7001	-1.9742	-2.4345
H	-2.8543	-1.1271	-0.8850
C	-0.0115	-0.4941	-3.6673
H	-0.1265	-1.4431	-4.2012
H	-0.5566	0.2801	-4.2191
H	1.0527	-0.2317	-3.6845
O	2.7631	1.7896	0.1760
C	3.4439	2.6200	-0.6796
C	4.6999	3.1943	0.0055
H	5.3437	2.3698	0.3362

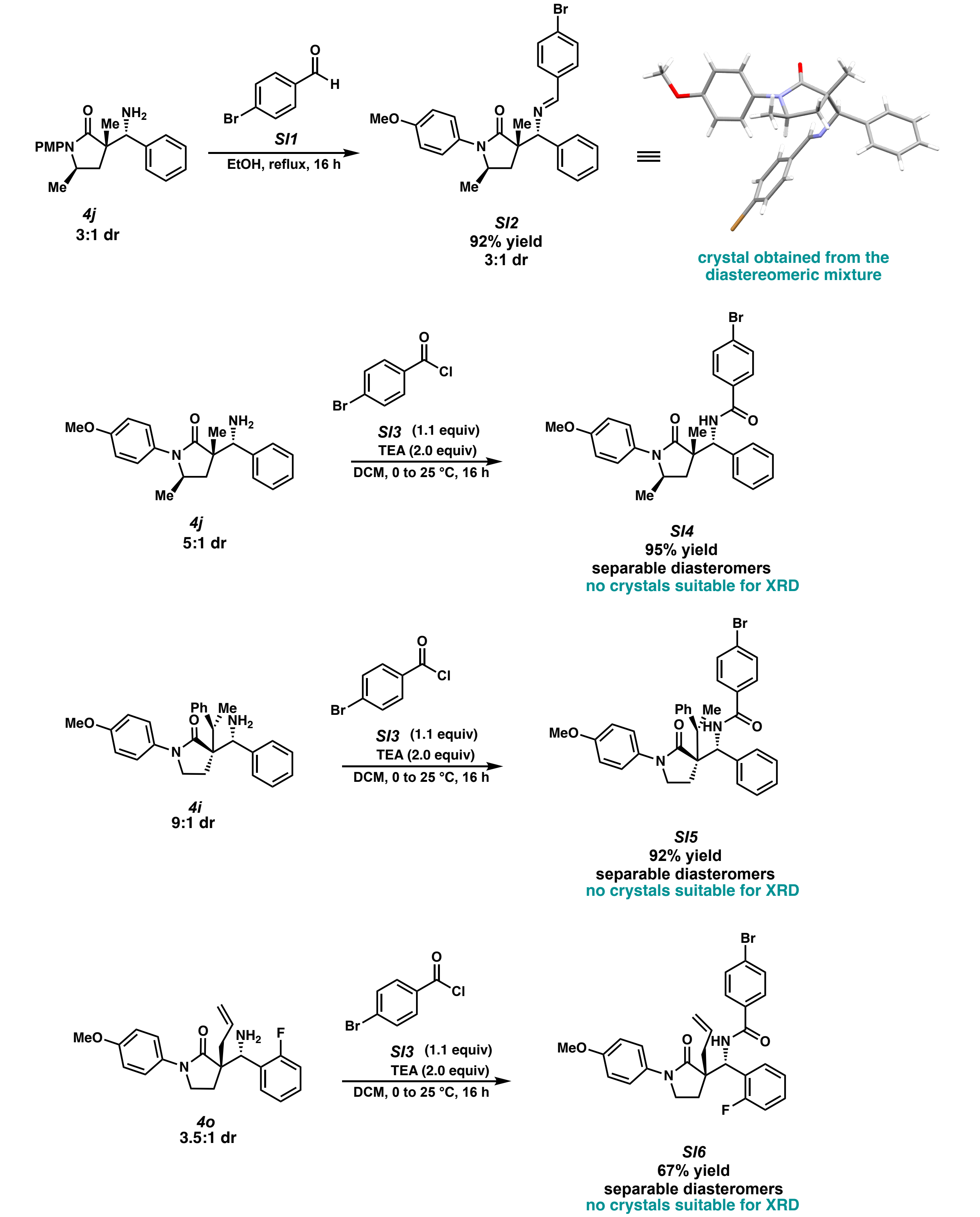
H	5.2859	3.8535	-0.6472
H	4.4018	3.7644	0.8946
C	3.8829	1.8477	-1.9417
H	2.9982	1.4256	-2.4365
H	4.4235	2.4659	-2.6695
H	4.5394	1.0183	-1.6447
C	2.5521	3.8015	-1.1189
H	3.0553	4.4907	-1.8085
H	1.6483	3.4209	-1.6095
H	2.2470	4.3770	-0.2332
O	-3.8827	4.0453	2.6211
C	-5.0656	4.4563	1.9720
H	-4.9594	4.4054	0.8815
H	-5.9221	3.8444	2.2803
H	-5.2330	5.4903	2.2721
C	4.7440	-2.2135	1.9902
C	4.5657	-3.1385	0.9588
C	5.0152	-2.8426	-0.3262
C	5.6493	-1.6258	-0.6100
C	5.8173	-0.7084	0.4313
C	5.3712	-0.9977	1.7222
H	4.3949	-2.4437	2.9929
H	4.0617	-4.0819	1.1499
H	4.8723	-3.5652	-1.1274
H	6.3005	0.2434	0.2280
H	5.5148	-0.2714	2.5174
C	6.1290	-1.3234	-2.0074
H	6.6607	-0.3696	-2.0456
H	6.8037	-2.1073	-2.3655
H	5.2894	-1.2654	-2.7089
C	3.3700	1.8559	3.2649
C	2.6727	0.7150	3.6613
C	1.5770	0.8206	4.5165
C	1.1539	2.0659	4.9970
C	1.8565	3.2056	4.5862
C	2.9561	3.1035	3.7327
H	4.1763	1.7838	2.5433
H	2.9569	-0.2617	3.2783
H	1.0331	-0.0777	4.8012
H	1.5420	4.1822	4.9473
H	3.4818	4.0005	3.4183
C	-0.0033	2.1690	5.9596
H	-0.8444	1.5397	5.6507
H	0.2983	1.8421	6.9605
H	-0.3612	3.1992	6.0422

TS2-rotamer2

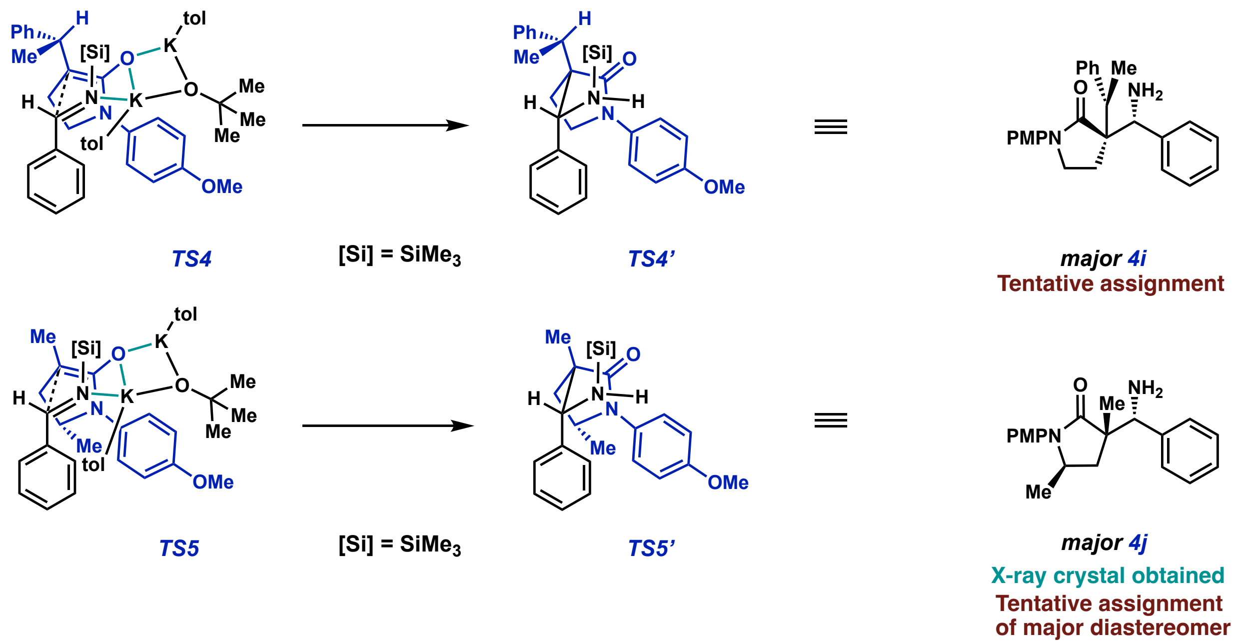
C	-0.6077	-1.1404	1.5287
C	-0.2066	-2.4837	1.2500
C	-0.1056	-2.5539	-0.8244
H	0.4277	-1.5783	-0.8675
O	0.0557	-0.0810	1.3724
Si	2.0872	-3.8894	-1.7256
N	0.4875	-3.6702	-1.1907
C	-1.3243	-3.3887	1.7202
H	-1.5111	-4.2072	1.0129
H	-1.0812	-3.8433	2.6916
C	-2.5424	-2.4565	1.8487
H	-3.1986	-2.5409	0.9750
H	-3.1383	-2.6349	2.7500
N	-1.9441	-1.1207	1.9143
C	1.1835	-2.9401	1.5667
H	1.9553	-2.2863	1.1416
H	1.3635	-3.0120	2.6493
H	1.3321	-3.9307	1.1217
K	-0.6169	2.2487	0.2132
K	2.4031	0.1479	0.2805
C	-1.5622	-2.3849	-1.1393
C	-2.3411	-3.5017	-1.4577
C	-2.1701	-1.1266	-1.1177
C	-3.7071	-3.3686	-1.6862
H	-1.8365	-4.4611	-1.5214
C	-3.5356	-0.9888	-1.3491
H	-1.5577	-0.2532	-0.8951
C	-4.3139	-2.1137	-1.6202
H	-4.3038	-4.2452	-1.9222
H	-3.9945	-0.0042	-1.3046
H	-5.3801	-2.0103	-1.7999
C	-2.7106	0.0304	2.1212
C	-4.0696	0.0501	1.7985
C	-2.1570	1.1721	2.7351
C	-4.8577	1.1761	2.0451
H	-4.5239	-0.8204	1.3373
C	-2.9327	2.2968	2.9639
H	-1.1175	1.1504	3.0424
C	-4.2901	2.3087	2.6217
H	-5.9090	1.1470	1.7824
H	-2.5139	3.1777	3.4422
C	3.0462	-5.1744	-0.7231
H	2.4531	-6.0861	-0.5950
H	3.9769	-5.4501	-1.2328
H	3.3065	-4.8050	0.2754
C	3.1523	-2.3007	-1.6923
H	4.0357	-2.4237	-2.3299
H	2.6027	-1.4292	-2.0728
H	3.5198	-2.0916	-0.6785
C	2.0797	-4.4879	-3.5149
H	1.6216	-3.7416	-4.1727
H	3.0915	-4.6929	-3.8832
H	1.4929	-5.4080	-3.6040
O	1.6569	2.3292	-0.6761
C	2.5620	2.9315	-1.5179
C	3.3572	4.0172	-0.7665
H	3.8939	3.5601	0.0749
H	4.0848	4.5360	-1.4033
H	2.6611	4.7577	-0.3557
C	3.5733	1.9071	-2.0893
H	3.0343	1.0946	-2.5940
H	4.2689	2.3528	-2.8106
H	4.1837	1.4757	-1.2815
C	1.8443	3.5884	-2.7131

H	2.5348	4.0558	-3.4260
H	1.2531	2.8304	-3.2413
H	1.1596	4.3587	-2.3404
O	-4.9593	3.4703	2.8797
C	-6.3224	3.5210	2.5183
H	-6.4516	3.3748	1.4377
H	-6.9053	2.7647	3.0570
H	-6.6737	4.5148	2.7943
C	3.9659	0.4178	3.1059
C	4.0680	-0.9422	2.8182
C	4.8179	-1.3727	1.7214
C	5.4804	-0.4565	0.8973
C	5.3738	0.9078	1.2024
C	4.6239	1.3436	2.2931
H	3.3773	0.7545	3.9534
H	3.5556	-1.6710	3.4386
H	4.8835	-2.4354	1.4980
H	5.8777	1.6359	0.5706
H	4.5459	2.4061	2.5026
C	6.2704	-0.9105	-0.3039
H	5.8418	-0.5066	-1.2285
H	7.3073	-0.5656	-0.2422
H	6.2740	-2.0003	-0.3860
C	-2.2381	5.0709	-0.1813
C	-1.4687	4.9908	-1.3422
C	-1.7374	4.0071	-2.2927
C	-2.7718	3.0823	-2.1037
C	-3.5262	3.1637	-0.9257
C	-3.2696	4.1542	0.0254
H	-2.0425	5.8466	0.5529
H	-0.6602	5.6957	-1.5110
H	-1.1327	3.9526	-3.1938
H	-4.3323	2.4532	-0.7521
H	-3.8754	4.2157	0.9245
C	-3.0462	2.0255	-3.1445
H	-2.8334	2.4049	-4.1475
H	-2.4234	1.1368	-2.9893
H	-4.0896	1.7006	-3.1153

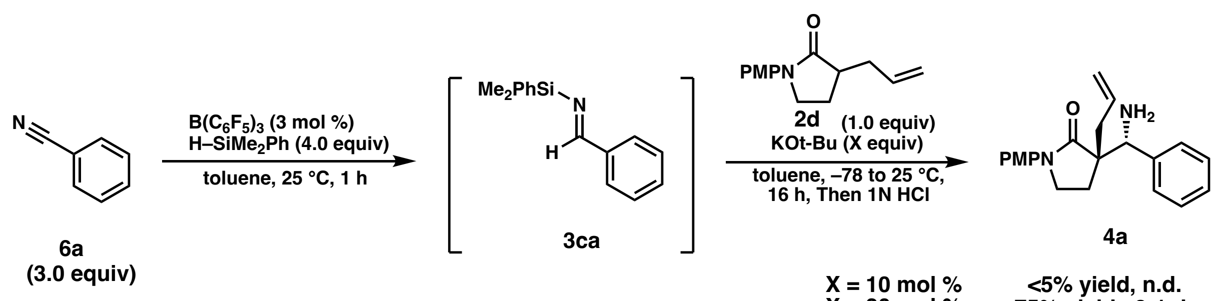
Scheme S1. Derivatization of Mannich Products to Elucidate Relative Stereochemistry



Scheme S2. Extension of Calculated Diastereoselective Transition States to Model the Relative Stereochemistry of Stereotriads

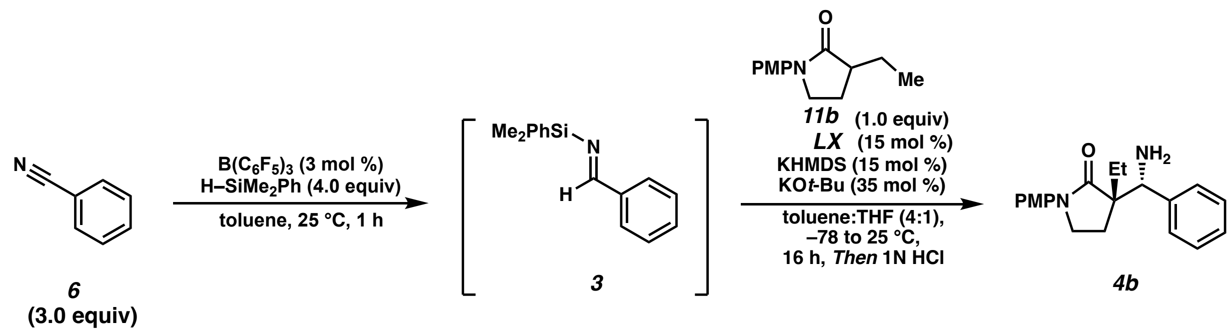


Scheme S3. KO*t*-Bu Loading Screen to Elucidate KO*t*-Bu Catalysis



X = 10 mol %	<5% yield, n.d.
X = 30 mol %	75% yield, 8:1 dr
X = 35 mol %	92% yield, 14:1 dr
X = 40 mol %	92% yield, 15:1 dr
X = 50 mol %	90% yield, 16:1 dr
X = 120 mol %	90% yield, 19:1 dr

Table S1: Precatalyst screen for the asymmetric Mannich reaction



Entry	LX	12b (% yield)	anti:syn	% ee
1	*L1*	95% yield	10:1	60%
2	*L2*	33% yield	10:1	3%
3	*L3*	95% yield	10:1	0%
4	*L4*	92% yield	10:1	0%
5	*L5*	62% yield	10:1	5%
6	*L6*	93% yield	10:1	25%
7	*L7*	94% yield	10:1	13%

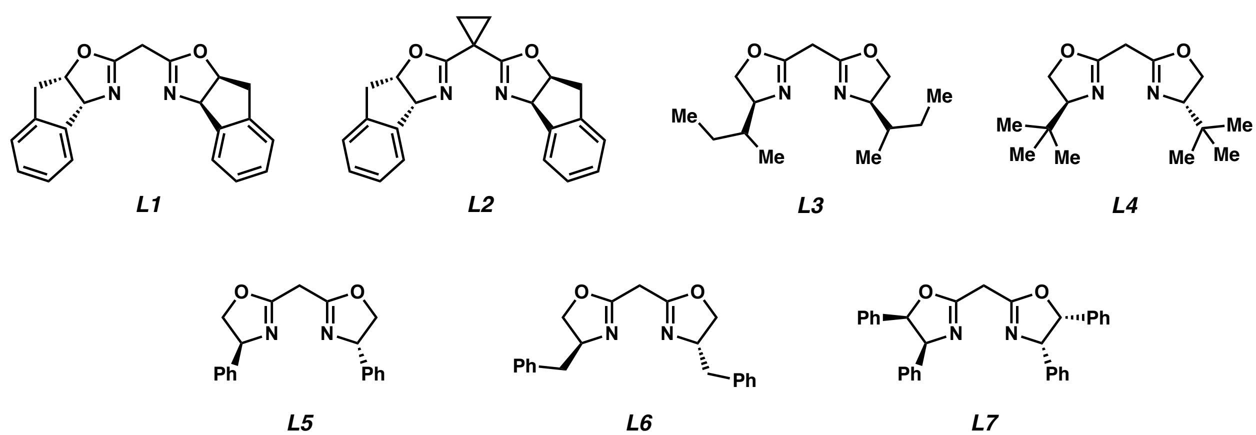
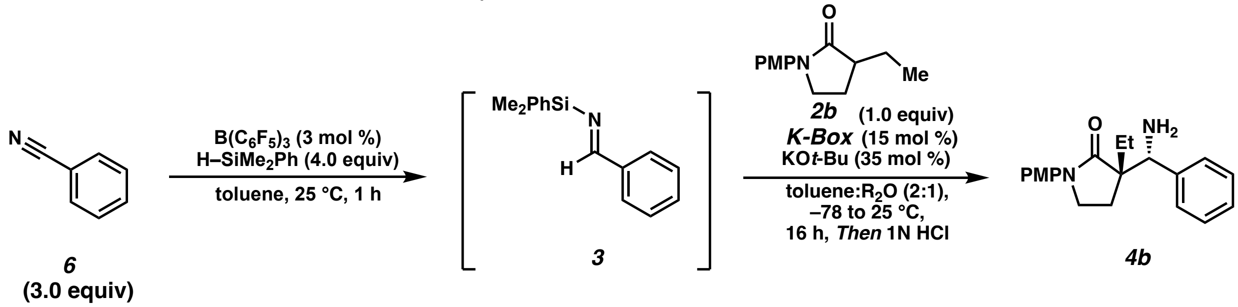


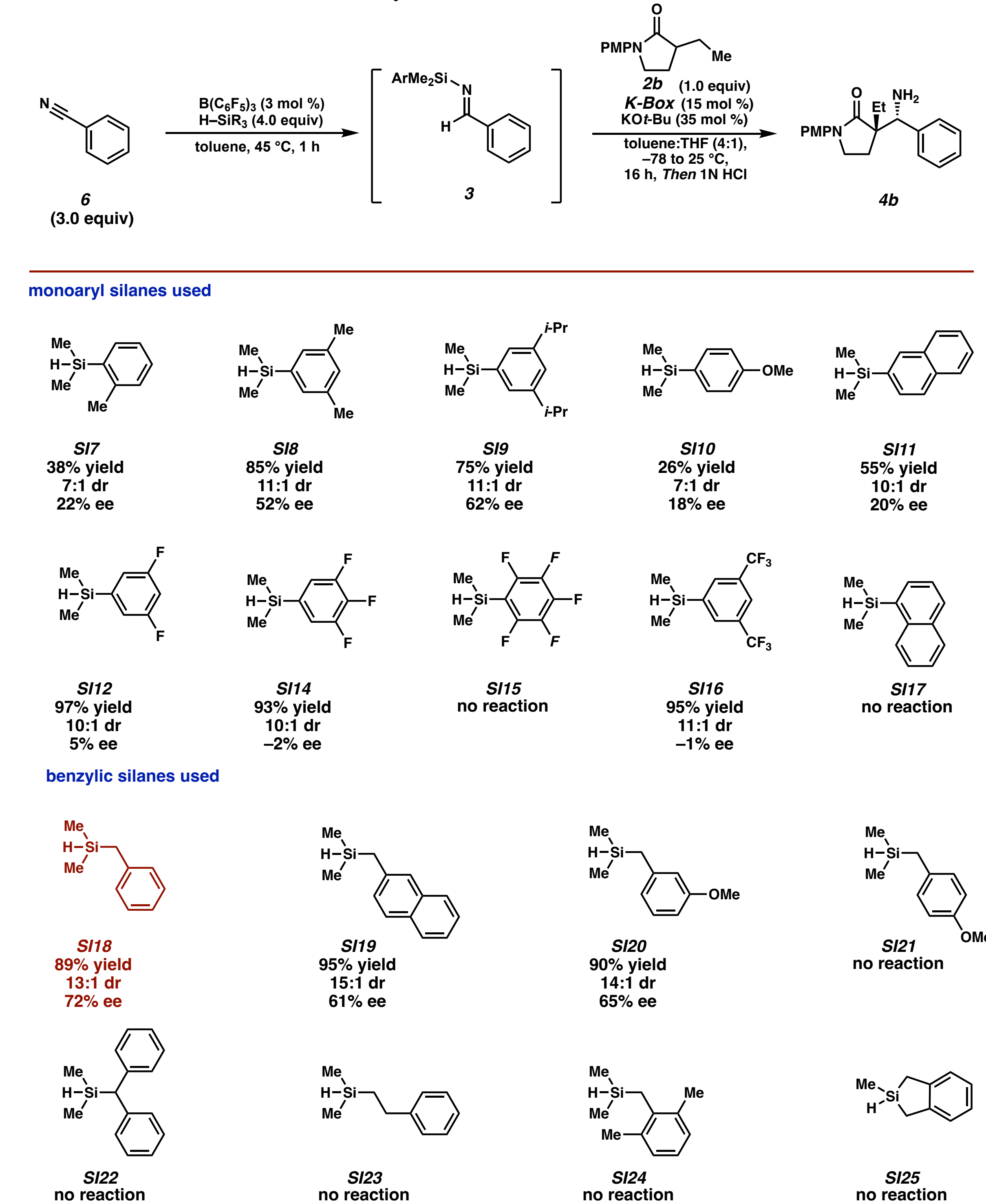
Table S2: Solvent screen for the asymmetric Mannich reaction



Entry	R_2O	*12b (% yield)*	*anti:syn*	*% ee*
1	THF	95% yield	12:1	52%
2	MTBE	85% yield	11:1	20%
3	dioxane	10% yield	9:1	n.d.
4	ether	90% yield	10:1	18%
5	DME	95% yield	11:1	3%
6	2-Me-THF	40% yield	12:1	35%
7	none	65% yield	11:1	18%

note, changing toluene:THF ratio affects ee

Scheme S4: Silane screen for the asymmetric Mannich variation



Silanes were generated from the following procedure: chlorosilane (1.0 equiv) was dissolved in THF (0.2 M) followed by the addition of of magnesium turnings (1.5 equiv) and catalytic iodine as an activator. The aryl/alkyl bromide (1.5 equiv) was then added and the reaction mixture was brought to reflux. Upon complete conversion, the mixture was neutralized with sat'd $NaHCO_3$, and the phases were separated. The aqueous phase was extracted with EtOAc three times and the organics were concentrated via rotary evaporator. The crude mixture was purified via column chromatography to deliver the desired silane. Note: the Grignard formation can be performed without the presence of the chlorosilane; however, this results in lower yield for more unstable Grignard species due to decomposition of the Grignard before chlorosilane addition.

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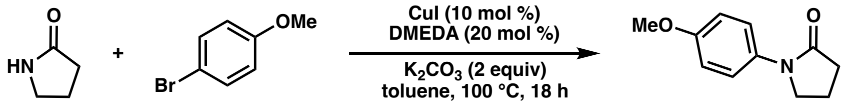
Materials and Methods

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon.[i] Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-MS. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or $KMnO_4$ staining. Silicycle Silia*Flash*® P60 Academic Silica gel (particle size 40–63 µm) was used for flash chromatography. ^1H NMR spectra were recorded on Varian Inova 500 MHz and Bruker 400 MHz spectrometers and are reported relative to residual $CHCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz) and Bruker 400 MHz spectrometers (100 MHz) and are reported relative to $CHCl_3$ (δ 77.16 ppm). Data for ^1H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d = broad doublet. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by use of a Perkin Elmer Spectrum BXII spectrometer or Nicolet 6700 FTIR spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm path-length cell. High resolution mass spectra (HRMS) were obtained from Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or fast atom bombardment (FAB+). Reagents were purchased from commercial sources and used as received unless otherwise stated.

List of Abbreviations:

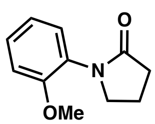
TLC – thin-layer chromatography
DMEDA – dimethyl ethylene diamine
Boc_2O – Di-tert-butyl dicarbonate
LiHMDS – lithium bis(trimethylsilyl)amide
THF – tetrahydrofuran
DMF – dimethylformamide
EtOAc – ethyl acetate
OMP – *ortho*-methoxyphenyl
PMP – *para*-methoxyphenyl
DCM – dichloromethane
KO*t*-Bu – potassium *tert*-butoxide
DMAP – 4-dimethylaminopyridine
TEA – triethyl amine
MeI – methyl iodide
n-BuLi – *n*-butyl lithium
BzCl – benzoyl chloride

General Procedure 1: Synthesis of *N*-Substituted-γ-Lactam Starting Materials



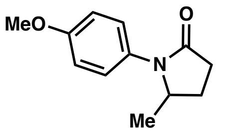
SI7

1-(4-methoxyphenyl)pyrrolidin-2-one (SI7):[7] To a solution of CuI (1.52 g, 8 mmol, 0.1 equiv) in toluene (80 mL 1.0 M) was added DMEDA (1.68 mL, 16 mmol, 0.2 equiv), 4-bromoanisole (10.84 mL, 80 mmol, 1.0 equiv), 2-pyrollidinone (8.2 g, 96 mmol, 1.2 equiv), and K_2CO_3 (22.1 g, 160 mmol, 2.0 equiv). The resultant suspension was heated to 100 °C and allowed to stir for 18 hours. The reaction was cooled to ambient temperature, diluted with EtOAc (100 mL) and filtered through a plug of silica. The filter was concentrated by rotary evaporation. The crude product was the purified by flash column chromatography (80% EtOAc in hexanes) to afford the desired *N*-arylated product **SI7** as a colorless solid (13.1 g, 69 mmol, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.43 (m, 2H), 6.96 – 6.86 (m, 2H), 3.85 – 3.81 (m, 2H), 3.80 (s, 3H), 2.60 (dd, *J* = 8.5, 7.7 Hz, 2H), 2.22 – 2.10 (m, 2H). All characterization data match those reported.[7]



SI8

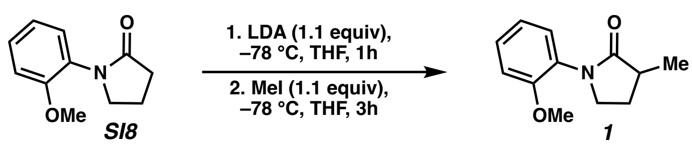
1-(2-methoxyphenyl)pyrrolidin-2-one (SI8):[7] To a solution of CuI (1.52 g, 8 mmol, 0.1 equiv) in toluene (80 mL 1.0 M) was added DMEDA (1.68 mL, 16 mmol, 0.2 equiv), 2-bromoanisole (10.84 mL, 80 mmol, 1.0 equiv), 2-pyrollidinone (8.2 g, 96 mmol, 1.2 equiv), and K_2CO_3 (22.1 g, 160 mmol, 2.0 equiv). The resultant suspension was heated to 100 °C and allowed to stir for 18 hours. The reaction was cooled to ambient temperature, diluted with EtOAc (100 mL) and filtered through a plug of silica. The filter was concentrated via rotary evaporation. The crude product was the purified by flash column chromatography (70% EtOAc in hexanes) to afford the desired *N*-arylated product **SI8** as a pale-yellow oil (13.6 g, 70.4 mmol, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.02 – 6.93 (m, 2H), 3.84 (s, 3H), 3.76 (dd, *J* = 7.3, 6.7 Hz, 2H), 2.56 (dd, *J* = 8.6, 7.6 Hz, 2H), 2.30 – 2.12 (m, 2H). All characterization data match those reported.[7]



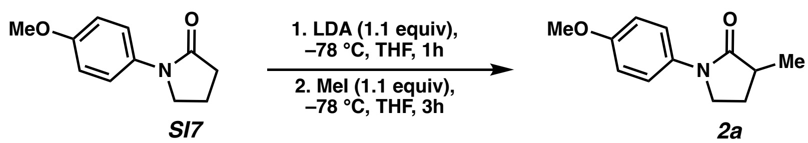
SI9

1-(4-methoxyphenyl)-5-methylpyrrolidin-2-one (SI9): To a solution of CuI (1.52 g, 8 mmol, 0.1 equiv) in toluene (80 mL 1.0 M) was added DMEDA (1.68 mL, 16 mmol, 0.2 equiv), 4-bromoanisole (10.84 mL, 80 mmol, 1.0 equiv), 5-methylpyrrolidin-2-one (9.6 g, 96 mmol, 1.2 equiv), and K_2CO_3 (22.1 g, 160 mmol, 2.0 equiv). The resultant suspension was heated to 100 °C and allowed to stir for 18 hours. The reaction was cooled to ambient temperature, diluted with EtOAc (100 mL) and filtered through a plug of silica. The filter was concentrated via rotary evaporation. The crude product was the purified by flash column chromatography (90% EtOAc in hexanes) to afford the desired *N*-arylated product **SI9** as a pale-yellow oil (14.1 g, 68.8 mmol, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 0.4H)*, 7.26 – 7.21 (m, 1.6H), 7.02 – 6.95 (m, 0.4H)*, 6.96 – 6.88 (m, 1.6H)*, 4.25 – 4.13 (m, 1H), 3.83 (s, 0.6H)*, 3.81 (s, 2.4H)*, 2.67 – 2.49 (m, 2H), 2.37 (dddd, *J* = 13.2, 9.3, 7.4, 6.0 Hz, 1H), 1.75 (dddd, *J* = 12.5, 9.5, 7.4, 5.9 Hz, 1H), 1.18 (d, *J* = 6.3 Hz, 2.4H), 1.08 (d, *J* = 6.3 Hz, 0.4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.11,* 174.35, 157.69, 155.30,* 132.23,* 130.38, 130.19,* 128.88,* 126.12, 120.81,* 114.35, 111.95,* 56.14, 55.86,* 55.64,* 55.46, 31.17, 30.93,* 27.74,* 26.86, 20.36,* 20.30; IR (Neat Film, NaCl) 2968, 2836, 1693, 1513, 1462, 1392, 1286, 1248, 1180, 1033, 831 cm^{-1}; (MM:ESI$^+$) *m/z* calc'd for $C_{12}H_{16}NO_2$ [M+H]$^+$: 206.1181, found 206.1166. Rotomeric peaks (approx. 4:1) denoted with*

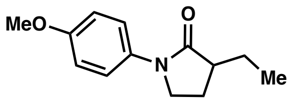
Synthesis of Mannich Donors: Experimental Procedures and Spectroscopic Data



1-(2-methoxyphenyl)-3-methylpyrrolidin-2-one (1): To a solution of *i*-Pr_2NH (710 µL, 5.5 mmol, 1.1 equiv) in THF (15 mL) was added *n*-BuLi (2.50 M in hexanes, 2 mL, 5.5 mmol, 1.1 equiv) dropwise at –78 °C. The resulting mixture was stirred at –78 °C for 20 min. A solution of 1-(4-methoxyphenyl)-3-methylpyrrolidin-2-one **SI8** (950 mg, 5 mmol, 1.0 equiv) in THF (10 mL) was added dropwise to the reaction mixture at –78 °C. The resulting mixture was stirred for 30 min at –78 °C, then MeI (345 µL, 5.5 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred for 3 hours at –78 °C. The reaction mixture was allowed to warm to ambient temperature overnight, diluted with EtOAc and then quenched with a saturated aqueous NH_4Cl solution. The aqueous layer was extracted three times with EtOAc, and the resulting organic layers were dried over Na_2SO_4 and concentrated by rotary evaporation. The resulting crude oil was purified from column chromatography (55% EtOAc in hexanes) to afford **1** as an off-yellow solid. (965 mg, 4.7 mmol, 94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.03 – 6.94 (m, 2H), 3.83 (s, 3H), 3.78 – 3.62 (m, 2H), 2.66 (tq, *J* = 8.6, 7.1 Hz, 1H), 2.39 (dddd, *J* = 12.2, 8.4, 7.2, 3.6 Hz, 1H), 1.81 (dq, *J* = 12.4, 8.5 Hz, 1H), 1.31 (d, *J* = 7.1 Hz, 3H). All characterization data match those reported.[7]

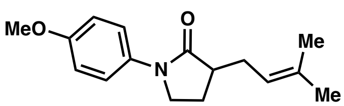


1-(4-methoxyphenyl)-3-methylpyrrolidin-2-one (2a): To a solution of *i*-Pr_2NH (710 μL, 5.5 mmol, 1.1 equiv) in THF (15 mL) was added *n*-BuLi (2.50 M in hexanes, 2 mL, 5.5 mmol, 1.1 equiv) dropwise at –78 °C. The resulting mixture was stirred at –78 °C for 20 min. A solution of 1-(4-methoxyphenyl)-3-methylpyrrolidin-2-one **SI7** (950 mg, 5 mmol, 1.0 equiv) in THF (10 mL) was added dropwise to the reaction mixture at –78 °C. The resulting mixture was stirred for 30 min at –78 °C, then MeI (345 μL, 5.5 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred for 3 h at –78 °C. The reaction mixture was allowed to warm to ambient temperature overnight, diluted with EtOAc and then quenched with a saturated aqueous NH_4Cl solution. The aqueous layer was extracted three times with EtOAc, and the resulting organic layers were dried over Na_2SO_4 and concentrated by rotary evaporation. The crude oil was purified by column chromatography (50% EtOAc in hexanes) to afford **2a** as a colorless solid (970 mg, 4.73 mmol, 95% yield); ^{1}H NMR 400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 9.1 Hz, 2H), 6.90 (d, *J* = 9.1 Hz, 2H), 3.80 (s, 3H), 3.78 – 3.68 (m, 1H), 2.74 – 2.57 (m, 1H), 2.36 (dddd, *J* = 12.3, 8.5, 6.7, 3.6 Hz, 1H), 1.76 (ddt, *J* = 12.5, 9.4, 8.6 Hz, 1H) 1.30 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.43, 156.51, 133.08, 121.57, 114.11, 55.59, 47.06, 38.17, 27.21, 16.42; All characterization data match those reported.[7]



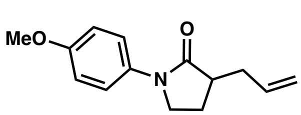
2b

3-ethyl-1-(4-methoxyphenyl)pyrrolidin-2-one (2b): Compound **2b** was prepared from iodoethane using General Procedure 2. The resulting crude oil was purified by column chromatography (50% EtOAc in hexanes) to afford **2b** as a colorless solid (710 mg, 3.3 mmol, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.41 (m, 2H), 7.08 – 6.74 (m, 2H), 3.81 (s, 3H), 3.78 – 3.69 (m, 2H), 2.54 (qd, J = 9.0, 4.3 Hz, 1H), 2.32 (dddd, J = 12.6, 8.7, 6.9, 3.9 Hz, 1H), 1.98 (dqd, J = 13.7, 7.5, 4.2 Hz, 1H), 1.81 (dq, J = 12.6, 8.7 Hz, 1H), 1.51 (ddt, J = 13.7, 9.0, 7.3 Hz, 1H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.80, 156.54, 133.07, 121.66, 114.14, 55.63, 47.31, 44.75, 24.42, 24.38, 11.63. All characterization data match those reported.[8]



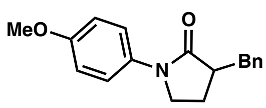
2c

1-(4-methoxyphenyl)-3-(3-methylbut-2-en-1-yl)pyrrolidin-2-one (2c): Compound **2c** was prepared from prenyl chloride using General Procedure 2. The resulting crude oil was purified by column chromatography (50% EtOAc in hexanes) to afford **2c** as on off-brown amorphous solid. (1.15 g, 4.5 mmol, 45% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.43 (m, 2H), 7.04 – 6.80 (m, 2H), 5.16 (tp, J = 7.2, 1.4 Hz, 1H), 3.80 (s, 3H), 3.73 (ddd, J = 8.5, 5.5, 2.7 Hz, 2H), 2.66 (td, J = 8.8, 4.3 Hz, 1H), 2.63 – 2.53 (m, 1H), 2.32 – 2.21 (m, 2H), 1.82 (dq, J = 12.7, 8.5 Hz, 1H), 1.73 (d, J = 1.5 Hz, 3H), 1.66 (d, J = 1.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.51, 156.53, 134.09, 133.06, 121.61, 121.09, 114.11, 55.60, 47.31, 43.66, 29.61, 26.00, 24.23, 18.09**;** IR (Neat Film, NaCl) 2954, 1680, 1519, 1253, 1225, 1031, 916, 825, 715 cm^{-1}; (MM:ESI$^+$) *m/z* calc'd for $C_{16}H_{22}NO_2$ [M+H]$^+$: 260.1651, found 260.1660.



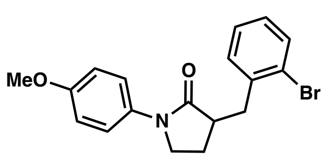
2d

3-allyl-1-(4-methoxyphenyl)pyrrolidin-2-one (2d): Compound **2d** was prepared from allyl bromide using General Procedure 2. The resulting crude oil was purified by column chromatography (50% EtOAc in hexanes) to afford **2d** as an off-yellow amorphous solid. (1.18 g, 4.75 mmol, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.47 (m, 2H), 7.00 – 6.84 (m, 2H), 5.91 – 5.79 (m, 1H), 5.18 – 5.12 (m, 1H), 5.09 (ddt, *J* = 10.1, 2.0, 1.1 Hz, 1H), 3.81 (s, 3H), 3.80 – 3.62 (m, 2H), 2.77 – 2.63 (m, 2H), 2.35 – 2.22 (m, 2H), 1.87 (dq, *J* = 12.8, 8.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.07, 156.63, 135.64, 132.94, 121.70, 117.20, 114.16, 55.63, 47.29, 42.85, 35.64, 24.13; IR (Neat Film, NaCl) 2954, 1680, 1519, 1253, 1225, 1031, 916, 825, 715 cm^{-1}; (MM:ESI$^+$) *m/z* calc'd for $C_{14}H_{18}NO_2$ [M+H]$^+$: 232.1338, found 232.1358.



2e

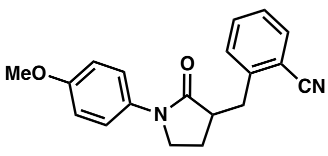
3-benzyl-1-(4-methoxyphenyl)pyrrolidin-2-one (2e): Compound **2e** was prepared from bromobenzene using General Procedure 2. The resulting crude oil was purified by column chromatography (50% EtOAc in hexanes) to afford **2e** as a colorless solid (1.32 g, 4.75 mmol, 95 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.40 (m, 2H), 7.42 – 7.28 (m, 2H), 7.26 – 7.18 (m, 3H), 7.04 – 6.70 (m, 2H), 3.81 (s, 3H), 3.68 (dt, *J* = 9.5, 7.7 Hz, 1H), 3.56 (ddd, *J* = 9.5, 8.6, 3.5 Hz, 1H), 3.31 (dd, *J* = 13.6, 4.0 Hz, 1H), 2.92 (dtd, *J* = 9.4, 8.6, 4.0 Hz, 1H), 2.80 (dd, *J* = 13.6, 9.4 Hz, 1H), 2.17 (dddd, *J* = 12.7, 8.6, 7.7, 3.5 Hz, 1H), 1.86 (dtd, *J* = 12.7, 8.6, 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.94, 156.68, 139.46, 132.88, 129.23, 128.64, 126.53, 121.80, 114.16, 55.62, 47.26, 45.06, 37.24, 24.31. All characterization data match those reported.[8]



2f

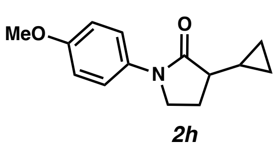
3-(2-bromobenzyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (2f): Compound **2f** was prepared from 1-bromo-2-(bromomethyl)benzene using General Procedure 2. The resulting crude oil was purified by column chromatography (55% EtOAc in hexanes) to afford **2f** as a yellow amorphous solid. (1.36 g, 3.73 mmol, 98% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.35 – 7.30 (m, 1H), 7.30 – 7.22 (m, 1H), 7.13 – 7.07 (m, 1H), 6.98 –

6.87 (m, 2H), 3.81 (s, 3H), 3.75 – 3.63 (m, 2H), 3.50 (dd, *J* = 13.7, 4.4 Hz, 1H), 3.04 (tdd, *J* = 9.3, 8.3, 4.3 Hz, 1H), 2.93 (dd, *J* = 13.7, 9.5 Hz, 1H), 2.16 (dddd, *J* = 12.7, 8.4, 6.8, 3.6 Hz, 1H), 1.92 (ddt, *J* = 12.7, 9.5, 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.64, 156.65, 139.13, 133.09, 132.91, 131.27, 128.25, 127.68, 125.03, 121.64, 114.16, 55.62, 47.21, 44.00, 36.82, 24.45; IR (Neat Film, NaCl) 2952, 1692, 1512, 1469, 1441, 1397, 1248, 1181, 1025, 830, 751 cm^{-1}; (MM:ESI$^+$) *m/z* calc'd for $C_{18}H_{19}BrNO_2$ $[M+H]^+$: 360.0599, found 360.0613.



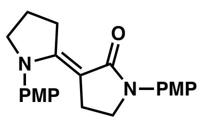
2g

2-((1-(4-methoxyphenyl)-2-oxopyrrolidin-3-yl)methyl)benzonitrile (2g): Compound **2g** was prepared from 2-(bromomethyl)benzonitrile using General Procedure 2. The resulting crude oil was purified by column chromatography (50% EtOAc in hexanes) to afford **2g** as an off-brown amorphous solid. (660 mg, 2.13 mmol, 97% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (ddd, *J* = 7.7, 1.4, 0.6 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.52 – 7.46 (m, 3H), 7.35 (td, *J* = 7.5, 1.4 Hz, 1H), 6.95 – 6.85 (m, 2H), 3.81 (s, 3H), 3.78 – 3.61 (m, 2H), 3.47 (dd, *J* = 14.0, 5.0 Hz, 1H), 3.14 (dd, *J* = 14.0, 8.6 Hz, 1H), 3.00 (dtd, *J* = 9.4, 8.5, 5.0 Hz, 1H), 2.23 (dddd, *J* = 12.7, 8.4, 7.1, 3.3 Hz, 1H), 1.93 (ddt, *J* = 12.7, 9.4, 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.93, 156.80, 143.65, 133.18, 132.93, 132.65, 130.51, 127.22, 121.81, 118.44, 114.20, 113.25, 55.62, 47.17, 44.96, 35.16, 24.28; IR (Neat Film, NaCl) 2942, 2223, 1692, 1513, 1486, 1397, 1285, 1248, 1181, 1034, 831, 762 cm^{-1}; (MM:ESI$^+$) *m/z* calc'd for $C_{19}H_{19}N_2O_2$ $[M+H]^+$: 307.1447, found 307.1453.



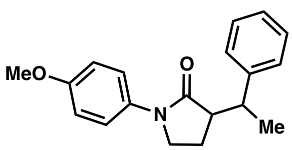
2h

3-cyclopropyl-1-(4-methoxyphenyl)pyrrolidin-2-one (2h): Compound **2h** was prepared from bromocyclopropane using General Procedure 2. The resulting crude oil was purified by column chromatography (50% EtOAc in hexanes) to afford **2h** as a yellow crystalline solid. (150 mg, 0.65 mmol, 30% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 6.94 – 6.88 (m, 2H), 3.80 (s, 3H), 3.78 – 3.71 (m, 2H), 2.32 – 2.15 (m, 2H), 1.95 – 1.82 (m, 1H), 1.08 – 0.98 (m, 1H), 0.71 – 0.63 (m, 1H), 0.55 – 0.42 (m, 2H), 0.32 – 0.23 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.12, 156.47, 133.06, 121.48, 114.07, 55.59, 47.09, 46.82, 24.54, 12.48, 3.52, 1.89; IR (Neat Film, NaCl) 3077, 3003, 2954, 2838, 1681, 1512, 1384, 1286, 1245, 1180, 1032, 824, 704 cm^{-1}; (MM:ESI^+) *m/z* calc'd for $C_{14}H_{18}NO_2$ $[M+H]^+$: 232.1338, found 232.1349.



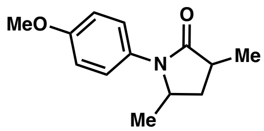
SI10

Inseparable from lactam dimerization impurity **(*E*)-1,1'-bis(4-methoxyphenyl)-1,3,4,4',5,5'-hexahydro-[2,3'-bipyrrolylidene]-2'(1'*H*)-one (SI4)** (20 % yield with **2h**); ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.21 – 7.15 (m, 2H), 7.11 – 7.03 (m, 2H), 6.92 – 6.86 (m, 2H), 3.83 (s, 3H), 3.78 (s, 3H), 3.70 – 3.64 (m, 2H), 3.53 (dd, *J* = 7.8, 6.8 Hz, 2H), 3.36 (tt, *J* = 7.6, 1.8 Hz, 2H), 2.13 – 1.99 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.26, 157.15, 155.40, 153.40, 137.99, 136.65, 134.63, 129.15, 128.34, 127.03, 125.41, 120.55, 113.91, 94.96, 56.86, 46.00, 31.65, 24.26, 22.69, 21.58.



2i

1-(4-methoxyphenyl)-3-(1-phenylethyl)pyrrolidin-2-one (2i): Compound **2i** was prepared from (1-bromoethyl)benzene using General Procedure 2. The resulting crude oil was purified by column chromatography (45% EtOAc in hexanes) to afford **2i** as an off-yellow amorphous solid. (570 mg, 1.93 mmol, 88% yield, 9:1 dr); 1H NMR (400 MHz, CDCl3) δ 7.35 (d, *J* = 9.2 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.25 – 7.15 (m, 1H), 6.87 (d, *J* = 9.2 Hz, 2H), 3.79 (s, 3H), 3.53 – 3.42 (m, 2H), 3.09 (ddd, *J* = 9.4, 8.4, 5.4 Hz, 1H), 2.82 (ddd, *J* = 9.2, 6.7, 5.5 Hz, 1H), 2.08 (dddd, *J* = 12.8, 9.1, 8.4, 5.5 Hz, 1H), 1.80 (dddd, *J* = 12.8, 8.4, 6.7, 5.8 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.98, 156.71, 143.15, 132.71, 128.38, 128.15, 126.74, 122.16, 114.09, 55.60, 49.75, 47.39, 39.89, 21.16, 19.53; IR (Neat Film, NaCl) 2959, 1681, 1512, 1452, 1396, 1294, 1247, 1034, 831, 701 cm^{-1}; (MM:ESI^+) *m/z* calc'd for $C_{19}H_{22}NO_2$ $[M+H]^+$: 296.1651, found 296.1667.

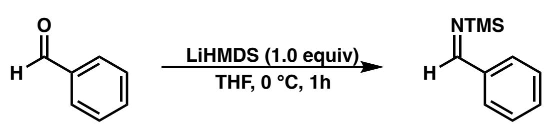


2j

1-(4-methoxyphenyl)-3,5-dimethylpyrrolidin-2-one (2j): Compound **2j** was prepared from lactam **SI3** and methyl iodide using General Procedure 2. The resulting crude oil was purified by column chromatography (70% EtOAc in hexanes) to afford **2j** as an off-brown amorphous solid. (1.035 g, 4.7 mmol, 94% yield, 5:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 6.96 – 6.87 (m, 2H), 4.17 (pd, *J* = 6.4, 4.5 Hz, 1H), 3.80 (s, 3H), 2.74 (ddt, *J* = 15.7, 8.6, 7.1 Hz, 1H), 2.05 – 1.94 (m, 2H), 1.27 (d, *J* = 7.2 Hz, 3H), 1.18 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.55, 157.38, 131.00, 125.31, 114.36, 55.55, 54.06, 36.27, 35.32, 19.70, 16.41; IR (Neat Film, NaCl) 2966, 1693, 1513, 1461, 1392, 1295, 1247, 1181, 1034, 830 cm^{-1}; (MM:ESI$^+$) *m/z* calc'd for $C_{13}H_{18}NO_2$ $[M+H]^+$: 220.1338, found 220.1330.

Synthesis of Isolated Mannich Acceptors: Experimental Procedures and Spectroscopic Data

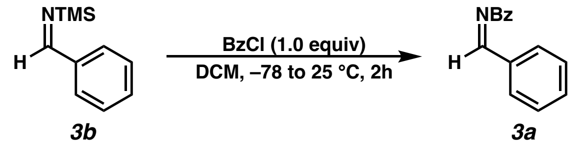
Procedure 3: Synthesis of *N*-trimethylsilyl



SI11 ***3b***

1-phenyl-*N*-(trimethylsilyl)methanimine (3b): *N*-TMS imine **3b** was prepared from a previously reported procedure.[3] To a solution of benzaldehyde **SI11** (5.2 mL, 50 mmol, 1.0 equiv) in THF (50 mL) was added LiHMDS (8.35 g, 50 mmol, 1.0 equiv) at 0 °C under a positive stream of N_2. The reaction mixture was stirred at 0 °C for 1 hour. The solvent was removed by rotary evaporation and the crude oil was purified by vacuum distillation (77 °C, 0.8 torr: Lit = 45 °C at 0.15 torr) to afford imine **3b** as a pale-yellow oil (5.5 g, 31.0 mmol, 62% yield), which was stored under argon at –20 °C. All characterization data match those reported.

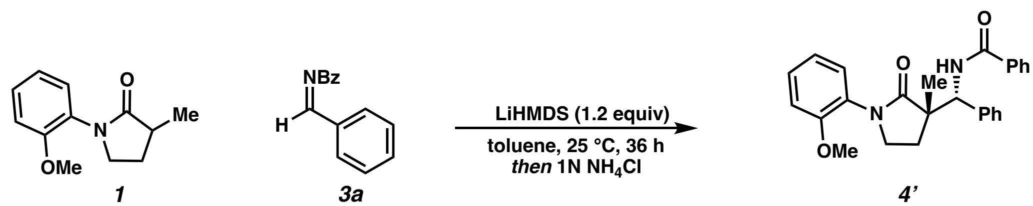
Procedure 4: Synthesis of *N*-Bz benzaldimine



***N*-benzylidenebenzamide (3a):** *N*-Bz imine **3a** was prepared from a previously reported procedure.[3] To a solution of *N*-TMS imine **3a** (177.3 mg, 1.0 mmol, 1.0 equiv) in DCM (2 mL) was added BzCl in one portion at –78 °C. Let warm up to ambient temperature and stir for 2 hours. The solvent and TMSCl were removed *in vacuo* to afford the *N*-Bz imine **3a**. The crude product was used directly without further purification.

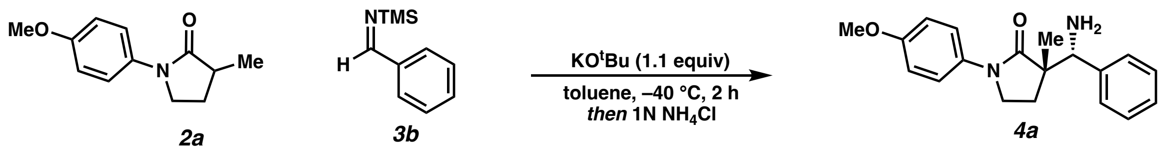
Diastereoselective Mannich Reaction: Experimental Procedures and Spectroscopic Data

General Procedure 5: Indirect Mannich Reaction with Isolated *N*-Bz benzaldimine

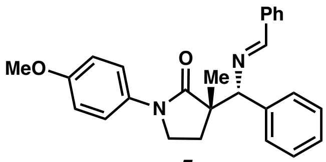


***N*-((*R**)-((*S**)-1-(2-methoxyphenyl)-3-methyl-2-oxopyrrolidin-3-yl)(phenyl)methyl)benzamide (4'):** To a solution of *N*-OMP lactam **1** (42 mg, 0.2 mmol, 1.0 equiv) in toluene (2 mL) was added LiHMDS (40.2 mg, 0.24 mmol, 1.2 equiv) at 25 °C. A solution of *N*-benzoyl imine **3a** (42.4 mg, 0.2 mmol, 1.0 equiv) in toluene (1 mL) was added to the reaction mixture, and the reaction was stirred at 25 °C for 36 hours. The reaction was quenched with saturated NH_4Cl (10 mL) and the aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over Na_2SO_4, and the solvent was removed via rotary evaporator. The crude mixture was purified directly from column chromatography (80% EtOAc in hexanes) to afford Mannich product **4'** as a pale-yellow oil. (56 mg, 0.14 mmol, 70% yield, 2:1 dr). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 5.8 Hz, 1H), 7.88 – 7.79 (m, 2H), 7.56 – 7.49 (m, 2H), 7.49 – 7.44 (m, 1H), 7.43 – 7.38 (m, 2H), 7.38 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.20 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.99 (td, *J* = 7.6, 1.2 Hz, 1H), 6.94 (d, *J* = 1.2 Hz, 1H), 5.22 (d, *J* = 5.8 Hz, 1H), 3.79 – 3.72 (m, 1H), 3.70 (s, 3H), 3.69 – 3.62 (m, 1H), 2.49 (ddd, *J* = 13.0, 7.8, 5.2 Hz, 1H), 1.94 (ddd, *J* = 13.0, 8.1, 6.3 Hz, 1H), 1.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.75, 167.35, 154.82, 138.75, 134.54, 131.43, 129.26, 128.69, 128.59, 128.53, 128.39, 128.13, 127.52, 127.17, 120.96, 111.99, 58.73, 55.58, 47.15, 46.94, 32.08, 19.94; IR (Neat Film, NaCl) 3325, 2930, 1667, 1504, 1416, 1303, 1122, 1046, 1026, 914, 782, 728 cm^{-1}; (MM:ESI$^+$) *m/z* calc'd for $C_{26}H_{27}N_2O_3$ $[M+H]^+$: 415.2016, found 415.2023.

General Procedure 5: Indirect Mannich Reaction with Isolated *N*-TMS benzaldimine

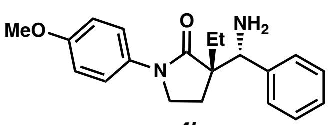


(*S)-3-((*R**)-amino(phenyl)methyl)-1-(4-methoxyphenyl)-3-methylpyrrolidin-2-one (4a):** To a solution of *N*-PMP lactam **2a** (42 mg, 0.2 mmol, 1.0 equiv) in toluene (2 mL) was added potassium *tert*-butoxide (27 mg, 0.22 mmol, 1.1 equiv) at –40 °C. A solution of *N*-TMS imine **3b** (35.4 mg, 0.2 mmol, 1.0 equiv) in toluene (1 mL) was added to the reaction mixture. The reaction mixture was stirred at –40 °C for 2 hours. The reaction was allowed to warm to ambient temperature and loaded directly onto a silica gel column. The crude mixture was purified directly from column chromatography (80% EtOAc in hexanes, 1% TEA) to afford Mannich product **4a** as a pale-yellow oil. (56 mg, 0.18 mmol, 90% yield, >20:1). This procedure was scaled up to 1 mmol of *N*-PMP lactam **2a** to afford Mannich product **4a** as a pale-yellow oil (255 mg, 0.82 mmol, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.47 (m, 2H), 7.42 – 7.28 (m, 5H), 6.94 – 6.88 (m, 2H), 4.29 (s, 1H), 3.81 (s, 3H), 3.63 (dt, *J* = 9.4, 7.9 Hz, 1H), 3.47 (td, *J* = 9.2, 3.1 Hz, 1H), 2.71 (ddd, *J* = 12.5, 9.1, 8.1 Hz, 1H), 2.11 – 1.85 (br, 2H, NH_2), 1.50 (ddd, *J* = 12.5, 7.7, 3.1 Hz, 1H), 1.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.40, 156.72, 142.11, 132.84, 128.25, 128.01, 127.65, 121.91, 114.12, 60.64, 55.60, 50.89, 45.91, 26.19, 22.24; IR (Neat Film, NaCl) 3367, 2955, 1681, 1513, 1455, 1402, 1296, 1249, 1088, 833, 707 cm^{-1}; (MM:ESI$^+$) *m/z* calc'd for $C_{19}H_{23}N_2O_2$ $[M+H]^+$: 311.1760, found 311.1747.



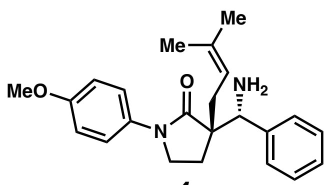
5

(*S)-3-((*R**)-(((*E*)-benzylidene)amino)(phenyl)methyl)-1-(2-methoxyphenyl)-3-methylpyrrolidin-2-one (5):** An isolable imine transfer product **5** was also observed and purified from via column from the above procedure (40% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.77 – 7.66 (m, 2H), 7.55 (dt, *J* = 6.7, 1.6 Hz, 2H), 7.40 – 7.33 (m, 5H), 7.33 – 7.28 (m, 3H), 6.81 – 6.72 (m, 2H), 4.71 (s, 1H), 3.88 – 3.80 (m, 1H), 3.75 (s, 3H), 3.74 – 3.65 (m, 1H), 3.12 (ddd, *J* = 12.7, 8.8, 6.0 Hz, 1H), 1.75 – 1.66 (m, 1H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.95, 161.84, 156.70, 140.85, 136.52, 132.85, 130.70, 128.80, 128.52, 128.49, 128.18, 127.49, 122.42, 114.01, 78.79, 55.58, 51.71, 46.78, 26.37, 22.53; IR (Neat Film, NaCl) 2958, 1682, 1512, 1453, 1402, 1289, 1249, 1180, 1089, 1030, 829, 755, 702, 637 cm^{-1}; (MM:ESI$^+$) *m/z* calc'd for $C_{26}H_{27}N_2O_2$ $[M+H]^+$: 399.2067, found 399.2074. Structure and relative configuration was confirmed via X-ray crystallography. Crystals were obtained from slow evaporation of a solution of **5** in $CDCl_3$. CCDC 2253012



4b

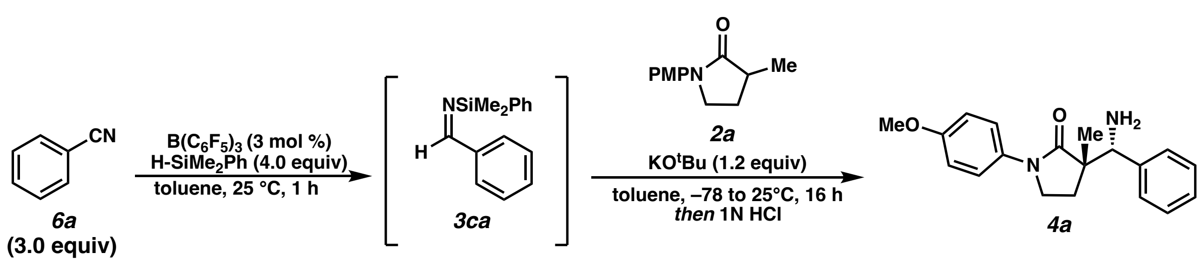
(*S)-3-((*R**)-amino(phenyl)methyl)-3-ethyl-1-(4-methoxyphenyl)pyrrolidin-2-one (4b):** Compound **4b** was prepared from *N*-PMP lactam **2b** using General procedure 5. The crude reaction mixture was purified directly from column chromatography (80% EtOAc in hexanes, 1% TEA) to afford Mannich product **4b** as a pale-yellow oil (52 mg, 0.16 mmol, 80% yield, 13:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.28 (m, 3H), 6.95 – 6.86 (m, 2H), 4.26 (s, 1H), 3.81 (s, 3H), 3.51 (td, *J* = 9.1, 6.1 Hz, 1H), 3.24 (td, *J* = 9.4, 4.7 Hz, 1H), 2.55 (ddd, *J* = 13.0, 9.5, 6.1 Hz, 1H), 1.89 – 1.74 (m, 3H, overlap NH_2), 1.71 (ddd, *J* = 13.4, 8.9, 4.7 Hz, 1H), 1.54 (dq, *J* = 13.6, 7.5 Hz, 1H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.58, 156.84, 142.61, 132.63, 128.30, 127.99, 127.67, 122.22, 114.14, 60.19, 55.62, 54.63, 46.75, 29.73, 24.10, 8.92; IR (Neat Film, NaCl) 3314, 2965, 1681, 1513, 1455, 1404, 1296, 1249, 1034, 833, 721 cm^{-1}; (MM:ESI$^+$) $C_{20}H_{25}N_2O_2$ *m/z* calc'd for $[M+H]^+$: 325.1916, found 325.1931.



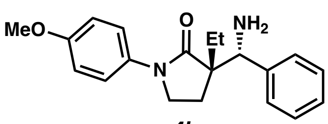
4c

(*S*)-3-((*R*)-amino(phenyl)methyl)-1-(4-methoxyphenyl)-3-(3-methylbut-2-en-1-yl)pyrrolidin-2-one (4c): Compound **4c** was prepared from *N*-PMP lactam **2c** using General Procedure 5. The crude reaction mixture was purified directly from column chromatography (65% EtOAc in hexanes, 1% TEA) to afford Mannich product **4c** as a pale-yellow oil (70 mg, 0.192 mmol, 96% yield, 7:1 dr) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.38 – 7.27 (m, 5H), 6.94 – 6.86 (m, 2H), 5.17 (dddd, *J* = 6.9, 5.4, 2.8, 1.4 Hz, 1H), 4.24 (s, 1H), 3.81 (s, 3H), 3.43 (td, *J* = 8.9, 6.2 Hz, 1H), 3.14 (td, *J* = 9.2, 4.6 Hz, 1H), 2.54 – 2.41 (m, 2H), 2.25 (dd, *J* = 14.2, 8.3 Hz, 1H), 2.08 – 1.79 (br, 2H, NH_2), 1.77 – 1.68 (m, 1H)*, 1.68 (s, 3H), 1.57 – 1.56 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.45, 156.80, 142.57, 135.13, 132.68, 128.29, 127.98, 127.64, 122.28, 119.07, 114.11, 60.48, 55.59, 54.46, 46.71, 35.26, 26.21, 24.50, 18.17; IR (Neat Film, NaCl) 3234, 2930, 1681, 1513, 1453, 1402, 1293, 1250, 1033, 827, 703 cm^{-1}; (MM:ESI$^+$) $C_{23}H_{29}N_2O_2$ *m/z* calc'd for $[M+H]^+$: 365.2229, found 365.2240.

General Procedure 6: Direct Mannich Reaction Using *In-Situ* Generated *N*-SiMe$_2$Ph Benzaldimine Mannich Acceptor

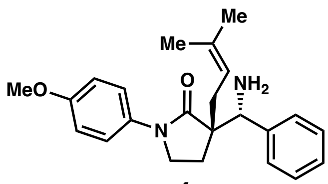


(*S)-3-((*R**)-amino(phenyl)methyl)-1-(4-methoxyphenyl)-3-methylpyrrolidin-2-one (4a):** $B(C_6F_5)_3$ (4 mg, 0.009 mmol, 0.06 equiv) was added to a solution of H-SiMe$_2$Ph (112 μL, 0.8 mmol, 4.0 equiv) in toluene (1 mL). Benzonitrile **6a** (55 μL, 0.6 mmol, 3.0 equiv) was added to the reaction mixture and stirred at ambient temperature for 1 hour. Meanwhile, *N*-PMP lactam **2a** (42 mg, 0.2 mmol, 1.0 equiv) was added to a solution of potassium *tert*-butoxide (28 mg, 0.24 mmol, 1.2 equiv) in toluene (2 mL) and cooled to –78 °C. After 1 hour, the yellow imine mixture **3ca** was added to the cooled reaction mixture at –78 °C dropwise. The reaction mixture was stirred at –78 °C for 2 hours and allowed to warm to ambient temperature overnight. The reaction was quenched with 1 N HCl (4 mL) and diluted with EtOAc (10 mL) and stirred vigorously for 1 hour at ambient temperature. The aqueous layer was separated and extracted with EtOAc (2 x 4 mL) The combined organic layer can be purified to recover any unreacted lactam or aryl nitrile. The aqueous layer was basified with a saturated solution of $NaHCO_3$ (6 mL) and diluted with EtOAc (10 mL). The biphasic mixture was stirred vigorously for 1 hour at ambient temperature. The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated by rotary evaporation. The crude oil was purified by column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4a** as a pale-yellow oil (60 mg, 0.194 mmol, 97% yield, 20:1 dr); The characterization data matches the data acquired from the product obtained using General Procedure 5.



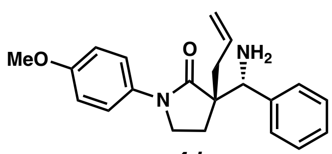
4b

(*S)-3-((*R**)-amino(phenyl)methyl)-3-ethyl-1-(4-methoxyphenyl)pyrrolidin-2-one (4b):** Compound **4b** was prepared from *N*-PMP lactam **2b** using General procedure 6. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4b** as a pale-yellow oil (55 mg, 0.17 mmol, 85% yield, 14:1 dr); The characterization data matches the data acquired from the product obtained using General Procedure 5.



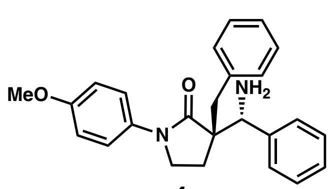
4c

(*S)-3-((*R**)-amino(phenyl)methyl)-1-(4-methoxyphenyl)-3-(3-methylbut-2-en-1-yl)pyrrolidin-2-one (4c):** Compound **4c** was prepared from *N*-PMP lactam **2c** using General Procedure 6. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4c** as a pale-yellow oil (66 mg, 0.18 mmol, 90% yield, 10:1 dr); The characterization data matches the data acquired from the product obtained using General Procedure 5.



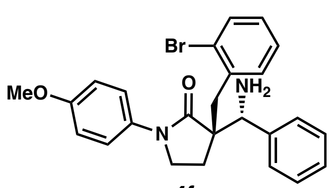
4d

(*S)-3-allyl-3-((*R**)-amino(phenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4d):** Compound **4d** was prepared from *N*-PMP lactam **2d** using General Procedure 6. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4d** as a pale-yellow oil (60 mg, 0.18 mmol, 90% yield, 19:1 dr). On a 1 mmol scale, Mannich product **4d** was isolated as a pale-yellow oil (289 mg, 0.86 mmol, 86% yield, 14:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.39 – 7.34 (m, 2H), 7.34 – 7.29 (m, 3H), 6.96 – 6.87 (m, 2H), 5.79 (dddd, *J* = 16.7, 10.1, 8.4, 6.5 Hz, 1H), 5.17 – 5.05 (m, 2H), 4.25 (s, 1H), 3.81 (s, 3H), 3.47 (td, *J* = 9.0, 6.2 Hz, 1H), 3.21 (td, *J* = 9.4, 4.6 Hz, 1H), 2.63 – 2.47 (m, 2H), 2.19 (ddt, *J* = 13.5, 8.3, 0.9 Hz, 1H), 2.05-1.80 (br, 2H, NH_2) 1.77 (ddd, *J* = 13.2, 8.8, 4.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.06, 156.89, 142.34, 133.77, 132.54, 128.37, 128.01, 127.77, 122.31, 118.96, 114.14, 60.53, 55.62, 54.21, 46.68, 41.47, 24.04; IR (Neat Film, NaCl) 3054, 2917, 1681, 1512, 1454, 1401, 1295, 1248, 1036, 827, 703 cm^{-1}; (MM:ESI^{+}) $C_{21}H_{25}N_2O_2$ *m/z* calc'd for $[M+H]^{+}$: 337.1916, found 337.1930.



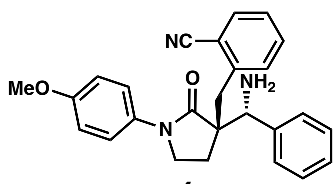
4e

(*S)-3-((*R**)-amino(phenyl)methyl)-3-benzyl-1-(4-methoxyphenyl)pyrrolidin-2-one (4e):** Compound **4e** was prepared from *N*-PMP lactam **2e** using General Procedure 6. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4e** as a yellow oil (65 mg, 0.172 mmol, 86% yield, 7:1 dr); ^{1}H NMR (400 MHz, C_6D_6) δ 7.48 – 7.41 (m, 2H), 7.31 – 7.25 (m, 2H), 7.16 – 7.11 (m, 3H), 7.10 – 7.05 (m, 2H), 6.98 – 6.94 (m, 3H), 6.80 – 6.73 (m, 2H), 4.38 (s, 1H), 3.28 (s, 3H), 3.27 – 3.23 (m, 1H), 2.71 – 2.59 (m, 1H), 2.57 – 2.47 (m, 2H), 2.12 (td, J = 8.4, 7.3 Hz, 1H), 1.43 (ddd, J = 12.5, 8.3, 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.90, 156.82, 142.08, 137.28, 132.18, 129.98, 128.33, 128.15, 128.09, 127.75, 126.73, 122.55, 113.90, 60.74, 55.81, 55.45, 46.35, 42.84, 22.90; IR (Neat Film, NaCl) 3254, 2923, 1676, 1513, 1405, 1295, 1248, 1035, 823, 702 cm^{-1}; (MM:ESI$^+$) $C_{25}H_{27}N_2O_2$ *m/z* calc'd for [M+H]$^+$: 387.2073, found 387.2064



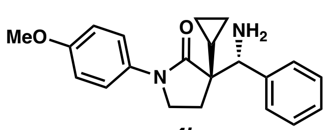
4f

(*S)-3-((*R**)-amino(phenyl)methyl)-3-(2-bromobenzyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4f):** Compound **4f** was prepared from *N*-PMP lactam **2f** using a slightly modified General Procedure 6 that involves adding 0.5 mL of Et_2O to the reaction mixture to ensure solubility of *N*-PMP lactam **2f**. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4f** as a yellow oil (36 mg, 0.077 mmol, 39% yield, 8.5:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 7.7, 1.6 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.39 – 7.32 (m, 3H), 7.30 – 7.21 (m, 3H), 7.13 – 6.99 (m, 2H), 6.91 – 6.83 (m, 2H), 4.39 (s, 1H), 3.80 (s, 3H), 3.29 (d, J = 13.4 Hz, 1H), 3.18 (d, J = 13.4 Hz, 1H), 3.03 – 2.88 (m, 1H), 2.57 – 2.45 (m, 2H), 2.41 – 2.08 (br, NH_2, 2H), 2.08 – 1.87 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.99, 156.95, 141.99, 137.66, 132.95, 132.25, 131.93, 128.48, 128.20, 127.98, 127.53, 125.93, 122.39, 114.06, 61.57, 56.30, 55.59, 46.69, 40.57, 22.45; IR (Neat Film, NaCl) 3216, 2923, 1681, 1512, 1295, 1249, 1036, 823, 744 cm^{-1}; (MM:ESI$^+$) $C_{25}H_{26}BrN_2O_2$ *m/z* calc'd for [M+H]$^+$: 465.1178, found 465.1179



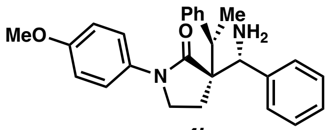
4g

2-(((*S)-3-((*R**)-amino(phenyl)methyl)-1-(4-methoxyphenyl)-2-oxopyrrolidin-3-yl)methyl)benzonitrile (4g):** Compound **4g** was prepared from *N*-PMP lactam **2g** using a slightly modified General Procedure 6 that involves adding 0.5 mL of Et_2O to the reaction mixture to ensure solubility of *N*-PMP lactam **2g**. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4g** as a yellow oil (40 mg, 0.1 mmol, 50% yield, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 1H), 7.51 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.47 – 7.29 (m, 6H), 7.24 – 7.15 (m, 2H), 6.90 – 6.83 (m, 2H), 4.32 (s, 1H), 3.80 (s, 3H), 3.46 (d, *J* = 13.4 Hz, 1H), 3.11 (d, *J* = 13.5 Hz, 1H), 2.92 – 2.82 (m, 1H), 2.63 – 2.48 (m, 2H), 2.02 – 1.86 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.20, 157.03, 142.11, 141.98, 132.84, 132.79, 132.04, 131.41, 128.66, 128.18, 127.96, 127.49, 122.31, 118.36, 114.10, 61.81, 56.06, 55.59, 46.36, 40.07, 23.40; IR (Neat Film, NaCl) 3254, 2923, 2250, 1681, 1512, 1295, 1249, 1034, 823, 701 cm^{-1}; (MM:ESI$^+$) $C_{26}H_{26}N_3O_2$ *m/z* calc'd for $[M+H]^+$: 412.2025, found 412.2012.



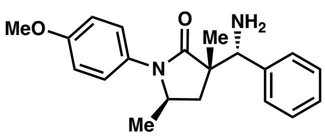
4h

(*S)-3-((*R**)-amino(phenyl)methyl)-3-cyclopropyl-1-(4-methoxyphenyl)pyrrolidin-2-one (4h):** Compound **4h** was prepared from *N*-PMP lactam **2h** using General Procedure 6. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4h** as a pale-yellow oil (58 mg, 0.172 mmol, 86% yield, 8.5:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.43 (m, 4H), 7.40 – 7.28 (m, 3H), 6.98 – 6.87 (m, 2H), 4.51 (s, 1H), 3.81 (s, 3H), 3.76 – 3.62 (m, 1H), 3.53 (td, *J* = 9.2, 2.1 Hz, 1H), 2.77 (dt, *J* = 12.4, 9.2 Hz, 1H), 2.09 –1.84 (br, 2H, NH_2), 1.51 (ddd, *J* = 12.4, 7.4, 2.1 Hz, 1H), 0.68 (tdd, *J* = 6.9, 5.2, 2.4 Hz, 2H), 0.49 – 0.38 (m, 2H), 0.05 – -0.03 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.67, 156.79, 142.22, 132.58, 128.13, 128.07, 127.54, 122.04, 114.17, 59.81, 55.63, 54.46, 46.38, 24.85, 16.53, 2.26, 0.30; IR (Neat Film, NaCl) 3254, 2930, 1681, 1512, 1452, 1401, 1297, 1248, 1180, 1034, 833, 702, 680 cm^{-1}; (MM:ESI$^+$) $C_{21}H_{25}N_2O_2$ *m/z* calc'd for $[M+H]^+$: 337.1916, found 337.1913.



4i

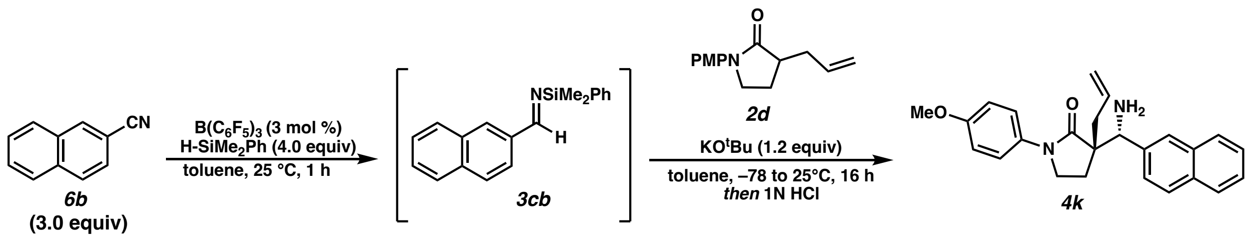
(3*S)-3-((*R**)-amino(phenyl)methyl)-1-(4-methoxyphenyl)-3-(1-phenylethyl)pyrrolidin-2-one (4i):** Compound **4i** was prepared from *N*-PMP lactam **2i** using a slightly modified General Procedure 6 that involves adding 0.5 mL of Et_2O to the reaction mixture to ensure solubility of *N*-PMP lactam **2i**. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4i** as a yellow oil (30 mg, 0.075 mmol, 37% yield, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.39 – 7.34 (m, 3H), 7.30 – 7.22 (m, 4H), 7.22 – 7.15 (m, 1H), 6.83 (d, *J* = 9.3 Hz, 2H), 6.80 – 6.74 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 1H), 4.04 (s, 1H), 3.76 (s, 3H), 3.01 – 2.57 (br, NH_2, 2H), 2.47 – 2.37 (m, 1H), 2.29 – 2.19 (m, 1H), 2.18 – 2.09 (m, 1H), 1.79 (ddd, *J* = 13.5, 9.1, 4.5 Hz, 1H), 1.54 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.45, 157.08, 144.21, 142.93, 131.83, 129.56, 128.44, 128.34, 128.00, 127.61, 126.69, 123.25, 113.95, 61.54, 56.59, 55.55, 46.16, 40.41, 22.19, 14.53; IR (Neat Film, NaCl) 2964, 1673, 1512, 1295, 1248, 1034, 703 cm^{-1}; (MM:ESI$^+$) $C_{26}H_{29}N_2O_2$ *m/z* calc'd for $[M+H]^+$: 401.2229, found 401.2209.



4j

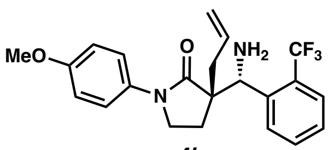
(3*S,5*R**)-3-((*R**)-amino(phenyl)methyl)-1-(4-methoxyphenyl)-3,5-dimethylpyrrolidin-2-one (4j):** Compound **4j** was prepared from *N*-PMP lactam **2j** using General Procedure 6. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4j** as a yellow oil (70 mg, 0.195 mmol, 95% yield, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 7.13 – 7.05 (m, 2H), 7.00 – 6.87 (m, 2H), 4.09 (s, 1H), 3.82 (s, 3H), 3.40 (dp, *J* = 8.2, 6.3 Hz, 1H), 2.69 (dd, *J* = 13.2, 8.2 Hz, 1H), 1.84 (br, 4H*, NH_2), 1.40 (s, 3H), 1.33 (dd, *J* = 13.2, 6.2 Hz, 1H), 1.01 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.31, 157.78, 142.61, 130.30, 128.39, 127.94, 127.76, 126.03, 114.36, 62.63, 55.61, 52.99, 49.59, 37.26, 25.63, 21.36; IR (Neat Film, NaCl) 3374, 2967, 2932, 1682, 1514, 1455, 1394, 1296, 1248, 1181, 1134, 1032, 829, 800, 763, 706 cm^{-1}; (MM:ESI^{+}) $C_{20}H_{25}N_2O_2$ *m/z* calc'd for $[M+H]^{+}$: 325.1916, found 325.1909.

General Procedure 7: Direct Mannich Reaction Using *In-Situ* Generated *N*-SiMe₂Ph Aryl Imine Mannich Acceptor.



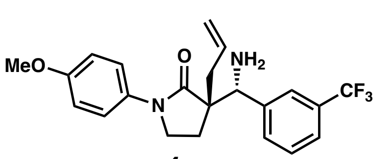
(*S)-3-allyl-3-((*R**)-amino(naphthalen-2-yl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4k):** $B(C_6F_5)_3$ (4 mg, 0.009 mmol, 0.06 equiv) was added to a solution of H-SiMe$_2$Ph (112 μL, 0.8 mmol, 4.0 equiv) in toluene (1 mL). 2-napthonitrile **6b** (55 μL, 0.6 mmol, 3.0 equiv) was added to the reaction mixture and stirred at ambient temperature for 1 hour. Meanwhile, *N*-PMP lactam **2d** (42 mg, 0.2 mmol, 1.0 equiv) was added to a solution of potassium *tert*-butoxide (28 mg, 0.24 mmol, 1.2 equiv) in toluene (2 mL) and cooled to –78 °C. After 1 hour, the yellow imine mixture **3cb** was added to the cooled reaction mixture at –78 °C dropwise. The reaction mixture was stirred at –78 °C for 2 hours and allowed to warm to ambient temperature overnight. The reaction was quenched with 1 N HCl (4 mL) and diluted with EtOAc (10 mL) and stirred vigorously for 1 hour at ambient temperature. The aqueous layer was separated and extracted with EtOAc (2 x 4 mL) The combined organic layer can be purified to recover any unreacted lactam or aryl nitrile. The aqueous layer was basified with a saturated solution of $NaHCO_3$ (6 mL) and diluted with EtOAc (10 mL). The biphasic mixture was stirred vigorously for 1 hour at ambient temperature. The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated by rotary evaporation. The crude oil was purified by column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4k** as a yellow powder (75 mg, 0.194 mmol, 97% yield, 10:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.76 (m, 4H), 7.62 – 7.49 (m, 3H), 7.47 – 7.39 (m, 2H), 6.96 – 6.85 (m, 2H), 5.81 (dddd, *J* = 16.7, 10.1, 8.4, 6.4 Hz, 1H), 5.16 – 5.05 (m, 2H), 4.43 (s, 1H), 3.82 (s, 3H), 3.48 (td, *J* = 9.0, 6.4 Hz, 1H), 3.25 (qd, *J* = 9.4, 4.1 Hz, 1H), 2.75 – 2.58 (m, 2H), 2.22 (dd, *J* = 13.5, 8.4 Hz, 1H), 1.78 (ddd, *J* = 13.1, 8.8, 4.4 Hz, 1H) (C_6H_6 present); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101

MHz, $CDCl_3$) δ 176.14, 156.93, 139.90, 133.74, 133.27, 133.09, 128.48, 128.10, 127.97, 127.75, 126.92, 126.32, 126.10, 126.06, 122.38, 119.04, 114.16, 60.66, 55.64, 54.38, 46.78, 41.58, 24.05; IR (Neat Film, NaCl) 3054, 2923, 1681, 1512, 1455, 1296, 1249, 1035, 922, 826, 753 cm^{-1}; (MM:ESI$^+$) $C_{25}H_{27}N_2O_2$ *m/z* calc'd for $[M+H]^+$: 387.2073, found 387.2070.



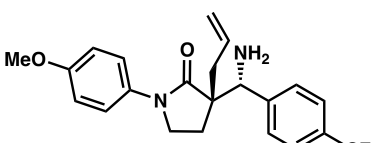
4l

(*S)-3-allyl-3-((*R**)-amino(2-(trifluoromethyl)phenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4l):** Compound **4l** was prepared from 2-(trifluoromethyl)benzonitrile **6c** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4l** as a pale-yellow oil (40 mg, 0.10 mmol, 50% yield, 20:1 dr); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 2H), 7.63 – 7.45 (m, 1H), 7.48 – 7.41 (m, 2H), 7.41 – 7.32 (m, 1H), 6.96 – 6.86 (m, 2H), 5.81 (dddd, *J* = 17.0, 10.1, 8.5, 6.3 Hz, 1H), 5.25 – 5.16 (m, 1H), 5.14 (dddd, *J* = 10.1, 2.0, 1.2, 0.6 Hz, 1H), 4.67 – 4.54 (m, 1H), 3.82 (s, 3H), 3.50 – 3.44 (m, 1H), 3.03 (td, *J* = 9.3, 4.8 Hz, 1H), 2.71 (ddt, *J* = 13.6, 6.3, 1.4 Hz, 1H), 2.42 (dd, *J* = 13.6, 8.6 Hz, 1H), 2.22 (ddd, *J* = 13.2, 9.2, 6.1 Hz, 1H), 2.04 (ddd, *J* = 13.4, 8.8, 4.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.33, 156.99, 143.34, 133.32, 132.43 (d, *J* = 2.2 Hz), 132.38, 128.57, 128.53 (q, *J* = 29.3 Hz), 127.46, 126.01 (q, *J* = 6.0 Hz), 125.87 (q, *J* = 274.0 Hz), 122.17, 119.40, 114.20, 55.64, 55.26 (d, *J* = 2.5 Hz), 53.22, 46.39, 41.14, 25.08; ^{19}F NMR (282 MHz, $CDCl_3$) δ –56.68; IR (Neat Film, NaCl) 2924, 1684, 1511, 1405, 1308, 1249, 1158, 1121, 1036, 772 cm^{-1}; (MM:ESI$^+$) $C_{22}H_{24}F_3N_2O_2$ *m/z* calc'd for $[M+H]^+$: 405.1790, found 405.1789.



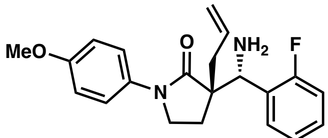
4m

(*S)-3-allyl-3-((*S**)-amino(3-(trifluoromethyl)phenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4m):** Compound **4m** was prepared from 3-(trifluoromethyl)benzonitrile **6d** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4m** as a pale-yellow oil (30 mg, 0.75 mmol, 38% yield, 7:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.63 – 7.50 (m, 3H), 7.46 (d, *J* = 9.1 Hz, 2H), 6.97 – 6.87 (m, 2H), 5.93 – 5.71 (m, 1H), 5.22 – 5.06 (m, 2H), 4.36 (s, 1H), 3.82 (s, 3H), 3.55 (ddd, *J* = 9.4, 8.7, 6.7 Hz, 1H), 3.32 (td, *J* = 9.5, 4.0 Hz, 1H), 2.62 – 2.49 (m, 2H), 2.13 (dd, *J* = 13.6, 8.2 Hz, 1H), 1.79 – 1.55 (br, NH_2, 2H), 1.73 (ddd, *J* = 12.8, 8.7, 4.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.63, 157.04, 143.17, 133.30, 132.34, 131.58, 130.97 (q, *J* = 32.8 Hz), 128.84, 124.73 (m), 122.30, 119.34, 114.21, 59.96, 55.64, 54.15, 46.66, 41.31, 23.68 (not identified, $J^1_{C\text{–}F}$) ; ^{19}F NMR (282 MHz, $CDCl_3$) –62.54; IR (Neat Film, NaCl) 2923, 1681, 1512, 1422, 1328, 1249, 1163, 1122, 1073, 833 cm^{-1}; (MM:ESI$^+$) $C_{22}H_{24}F_3N_2O_2$ *m/z* calc'd for $[M+H]^+$: 405.1790, found 405.1773.



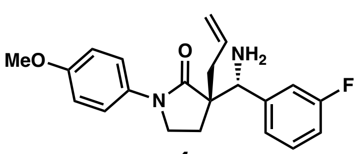
4n

(*S)-3-allyl-3-((*R**)-amino(4-(trifluoromethyl)phenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4n):** Compound **4n** was prepared from 4-(trifluoromethyl)benzonitrile **6e** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4n** as a pale-yellow oil (57 mg, 0.14 mmol, 70% yield, 17:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.39 (m, 2H), 6.95 – 6.87 (m, 2H), 5.79 (dddd, *J* = 16.8, 10.1, 8.3, 6.6 Hz, 1H), 5.19 – 5.07 (m, 2H), 4.35 (s, 1H), 3.82 (s, 3H), 3.58 – 3.47 (m, 1H), 3.40 – 3.27 (m, 1H), 2.63 – 2.48 (m, 2H), 2.12 (ddt, *J* = 13.5, 8.3, 1.0 Hz, 1H), 1.95 – 1.68 (br, NH_2, 2H*), 1.73 (ddd, *J* = 12.8, 8.6, 4.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.66, 157.03, 146.36, 136.18 (d, *J* = 30.9 Hz), 133.32, 132.36, 130.43–125.2 (m), 128.46, 125.30 (q, *J* = 3.9 Hz), 122.28, 119.30, 114.23, 60.02, 55.64, 54.22, 46.67, 41.38, 23.63; ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.48; IR (Neat Film, NaCl) 2923, 1681, 1512, 1405, 1325, 1250, 1165, 1122, 1068, 833 cm^{-1}; (MM:ESI$^+$) $C_{22}H_{24}F_3N_2O_2$ *m/z* calc'd for $[M+H]^+$: 405.1790, found 405.1790.



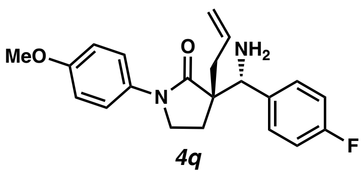
4o

(*S)-3-allyl-3-((*S**)-amino(2-fluorophenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4o):** Compound **4o** was prepared from 2-fluorobenzonitrile **6f** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4o** as a pale-yellow oil (68 mg, 0.194 mmol, 97% yield, 3.5:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 2.7H), 7.30 – 7.22 (m, 1.3H), 7.18 – 6.98 (m, 2H), 6.92 – 6.86 (m, 2H), 5.87 – 5.73 (m, 1H), 5.16 (dtd, *J* = 16.9, 1.8, 1.0 Hz, 1H), 5.12 – 5.06 (m, 1H), 4.66 (s, 0.78H), 4.62 (s, 0.22H), 3.81 (s, 2.34H), 3.80 (s, 0.66H), 3.55 (dd, *J* = 7.9, 6.4 Hz, 0.44H), 3.47 (td, *J* = 9.1, 5.6 Hz, 0.78H), 3.13 (td, *J* = 9.3, 5.1 Hz, 0.78H), 2.95 (ddt, *J* = 13.6, 5.8, 1.5 Hz, 0.22H), 2.69 (ddq, *J* = 13.5, 6.3, 1.3 Hz, 0.78H), 2.43 (ddd, *J* = 13.1, 9.2, 5.7 Hz, 0.78H), 2.31 – 2.15 (m, 1.22H), 2.03 – 1.93 (m, 0.22H), 1.93 – 1.84 (m, 1H), 1.83 – 1.72 (br, NH_2, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) (minor diastereomer denoted with*, overlap**) δ 175.80,* 175.75, 160.70 (d, *J* = 244.1 Hz),* 160.30 (d, *J* = 244.9 Hz), 156.92, 156.89,* 134.36,* 133.57, 132.54,* 132.39, 130.54 (d, *J* = 4.0 Hz),* 129.74 (d, *J* = 13.5 Hz), 129.08 (d, *J* = 8.9 Hz),* 129.04 (d, *J* = 8.5 Hz), 128.90 (d, *J* = 4.0 Hz), 128.47,* 124.48 (d, *J* = 3.5 Hz), 124.20 (d, *J* = 3.4 Hz),* 122.32,* 122.29, 119.12,** 115.44 (d, *J* = 23.5 Hz),** 114.14,** 55.61,** 54.23, 53.86,* 53.47,* 52.49, 46.63, 46.55,* 41.01, 37.11,* 25.57 (d, *J*= 2.1 Hz),* 24.09 (d, *J* = 2.2 Hz) ^{19}F NMR (282 MHz, $CDCl_3$) δ –115.83 (m); IR (Neat Film, NaCl) 2923, 1681, 1512, 1487, 1455, 1403, 1296, 1249, 1182, 1100, 1035, 923, 826, 761 cm^{-1}; (MM:ESI$^+$) $C_{21}H_{24}FN_2O_2$ *m/z* calc'd for $[M+H]^+$: 355.1822, found 355.1812.



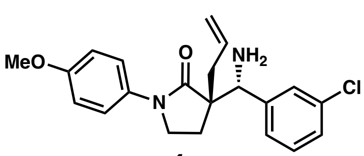
4p

(*S)-3-allyl-3-((*R**)-amino(3-fluorophenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4p):** Compound **4p** was prepared from 3-fluorobenzonitrile **6g** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4p** as a pale-yellow oil (65 mg, 0.186 mmol, 93% yield, 20:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.33 – 7.23 (m, 1H), 7.16 – 7.10 (m, 2H), 6.99 (tdd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 6.95 – 6.87 (m, 2H), 5.78 (dddd, *J* = 16.8, 10.1, 8.3, 6.5 Hz, 1H), 5.18 – 5.06 (m, 2H), 4.28 (s, 1H), 3.81 (s, 3H), 3.53 (ddd, *J* = 9.3, 8.7, 6.6 Hz, 1H), 3.34 (td, *J* = 9.4, 4.1 Hz, 1H), 2.62 – 2.50 (m, 1H), 2.14 (ddt, *J* = 13.6, 8.3, 1.0 Hz, 2H), 1.86 – 1.77 (br, NH_2, 2H), 1.77 – 1.69 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.82, 162.85 (d, *J* = 246.1 Hz), 156.99, 144.90 (d, *J* = 6.6 Hz), 133.47, 132.41, 129.77 (d, *J* = 8.2 Hz), 123.87 (d, *J* = 2.8 Hz), 122.35, 119.17, 114.88 (d, *J* = 20.92 Hz), 114.67 (d, *J* = 20.46 Hz), 114.19, 59.96 (d, *J* = 1.7 Hz), 55.62, 54.20, 46.73, 41.42, 23.72; ^{19}F NMR (282 MHz, $CDCl_3$) δ –112.81 - –112.94 (m); IR (Neat Film, NaCl) 2909, 1681, 1613, 1588, 1513, 1487, 1404, 1296, 1249, 1181, 1101, 1036, 922, 834, 793 cm^{-1}; (MM:ESI$^+$) $C_{21}H_{24}FN_2O_2$ *m/z* calc'd for $[M+H]^+$: 355.1822, found 355.1819.



4q

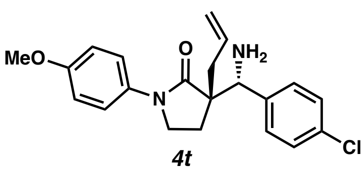
(*S)-3-allyl-3-((*R**)-amino(4-fluorophenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4q):** Compound **4q** was prepared from 4-fluorobenzonitrile **6h** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4q** as a pale-yellow oil (67 mg, 0.190 mmol, 95% yield, 10:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.37 – 7.31 (m, 2H), 7.06 – 6.97 (m, 2H), 6.94 – 6.87 (m, 2H), 5.78 (dddd, *J* = 16.7, 10.1, 8.3, 6.5 Hz, 1H), 5.17 – 5.06 (m, 2H), 4.25 (s, 1H), 3.81 (s, 3H), 3.50 (td, *J* = 8.9, 6.4 Hz, 1H), 3.26 (td, *J* = 9.4, 4.4 Hz, 1H), 2.58 – 2.45 (m, 2H), 2.21 – 2.10 (m, 1H), 2.11 – 1.94 (br, NH_2, 2H), 1.74 (ddd, *J* = 13.0, 8.8, 4.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.91, 162.39 (d, *J* = 245.9 Hz), 156.95, 137.99 (d, *J* = 3.2 Hz), 133.56, 132.43, 129.49 (d, *J* = 7.9 Hz), 122.27, 119.09, 115.20 (d, *J* = 21.1 Hz), 114.18, 59.75, 55.62, 54.19, 46.65, 41.43, 23.85; ^{19}F NMR (282 MHz, $CDCl_3$) δ –114.82 (tt, *J* = 8.5, 5.3 Hz); IR (Neat Film, NaCl) 2909, 1681, 1603, 1512, 1403, 1295, 1249, 1181, 1035, 833 cm^{-1}; (MM:ESI$^+$) $C_{21}H_{24}FN_2O_2$ *m/z* calc'd for $[M+H]^+$: 355.1822, found 355.1829.



4s

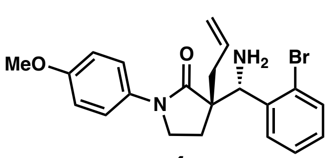
(*S)-3-allyl-3-((*R**)-amino(3-chlorophenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4s):** Compound **4s** was prepared from 3-chlorobenzonitrile **6j** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4s** as a pale-yellow (72 mg, 0.195 mmol, 97% yield, 20:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.39 (ddd, *J* = 2.2, 1.5, 0.9 Hz, 1H), 7.28 – 7.22 (m, 3H), 6.92

– 6.87 (m, 2H), 5.77 (dddd, *J* = 16.8, 10.1, 8.3, 6.5 Hz, 1H), 5.18 – 5.05 (m, 2H), 4.23 (s, 1H), 3.80 (s, 3H), 3.56 – 3.47 (m, 1H), 3.29 (td, *J* = 9.4, 4.2 Hz, 1H), 2.52 (ddd, *J* = 13.0, 9.4, 6.6 Hz, 2H), 2.14 (ddt, *J* = 13.5, 8.3, 1.0 Hz, 1H), 1.75 (ddd, *J* = 13.0, 8.7, 4.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.75, 156.99, 144.45, 134.33, 133.44, 132.36, 129.60, 128.06, 127.95, 126.36, 122.39, 119.19, 114.18, 60.03, 55.61, 54.13, 46.71, 41.37, 23.79; IR (Neat Film, NaCl) 2891, 1681, 1512, 1486, 1430, 1404, 1296, 1249, 1180, 1100, 1035, 826, 790 cm^{-1}; (MM:ESI$^+$) $C_{21}H_{24}ClN_2O_2$ *m/z* calc'd for $[M+H]^+$: 371.1526, found 371.1547.



4t

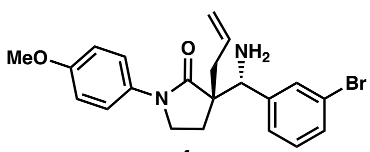
(*S)-3-allyl-3-((*R**)-amino(4-chlorophenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4t):** Compound **4t** was prepared from 4-chlorobenzonitrile **6k** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4t** as a pale-yellow oil (70 mg, 0.190 mmol, 95% yield, 20:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.35 – 7.31 (m, 2H), 7.31 – 7.28 (m, 2H), 6.95 – 6.88 (m, 2H), 5.78 (dddd, *J* = 16.8, 10.1, 8.3, 6.5 Hz, 1H), 5.16 – 5.06 (m, 2H), 4.25 (s, 1H), 3.82 (s, 3H), 3.57 – 3.48 (m, 1H), 3.32 (td, *J* = 9.4, 4.2 Hz, 1H), 2.52 (ddd, *J* = 12.9, 9.6, 6.6 Hz, 2H), 2.18 – 2.08 (m, 1H), 1.72 (ddd, *J* = 12.9, 8.7, 4.2 Hz, 1H), 1.61 (br, NH_2, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.85, 156.98, 140.80, 133.53, 133.50, 132.44, 129.39, 128.52, 122.28, 119.15, 114.21, 59.80, 55.64, 54.21, 46.69, 41.43, 23.71; IR (Neat Film, NaCl) 2908, 1681, 1512, 1403, 1295, 1249, 1179, 1090, 1035, 922, 833 cm^{-1}; (MM:ESI$^+$) $C_{21}H_{24}ClN_2O_2$ *m/z* calc'd for $[M+H]^+$: 371.1526, found 371.1523.



4u

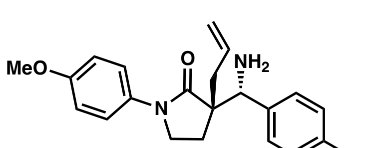
(*S)-3-allyl-3-((*S**)-amino(2-bromophenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4u):** Compound **4u** was prepared from 2-bromobenzonitrile **6l** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4u** as a pale-yellow oil (29 mg, 0.07 mmol, 35% yield, 7:1 dr); ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 1H), 7.43 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.21 (td, *J* = 7.5, 1.5 Hz, 1H), 7.14 – 7.10 (m, 1H), 6.92 – 6.87 (m, 2H), 5.92 – 5.78 (m, 1H), 5.25 – 5.18 (m, 1H), 5.18 – 5.13 (m, 1H), 4.79 (s, 1H), 3.81 (s, 3H), 3.40 (td, *J* = 9.2, 4.9 Hz, 1H), 2.87 (td, *J* = 9.1, 6.0 Hz, 1H), 2.77 (ddt, *J* = 13.7, 6.2, 1.5 Hz, 1H), 2.52 – 2.38 (m, 1H), 2.04 – 1.95 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.78, 156.92, 142.69, 133.62, 133.05, 132.32, 129.02, 128.96, 127.95, 122.30, 122.18, 119.23, 114.14, 58.11, 55.62, 53.98, 46.53, 40.88, 24.72; IR (Neat Film, NaCl) 2923, 1683, 1511, 1296, 1248, 1024, 822, 760 cm^{-1}; (MM:ESI$^+$) $C_{21}H_{24}BrN_2O_2$ *m/z* calc'd for $[M+H]^+$: 415.1021, found 415.1027.



4v

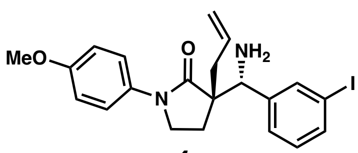
(*S)-3-allyl-3-((*R**)-amino(3-bromophenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4v):** Compound **4v** was prepared from 3-bromobenzonitrile **6m** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4v** as a pale-yellow oil (45 mg, 0.108 mmol, 55% yield, 20:1 dr); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, *J* = 1.9 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.29 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.96 – 6.87 (m, 2H), 5.79 (dddd, *J* = 16.8, 10.1, 8.3, 6.5 Hz, 1H), 5.19 – 5.06 (m, 2H), 4.22 (s, 1H), 3.81 (s, 3H), 3.56 – 3.49 (m, 1H), 3.29 (td, *J* = 9.4, 4.3 Hz, 1H), 2.60 – 2.45 (m, 2H), 2.16 (ddt, *J* = 13.5, 8.3, 1.0 Hz, 1H), 1.76 (ddd, *J* = 13.0, 8.7, 4.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.60, 156.88, 144.63, 133.33, 132.25, 130.84, 130.79, 129.79, 126.71, 122.48, 122.27, 119.09, 114.07, 59.92, 55.51, 54.00, 46.58, 41.24, 23.71; IR (Neat Film, NaCl) 2950, 1681, 1512, 1429, 1403, 1295, 1249, 1180, 1101, 1035, 923, 833, 792 cm^{-1}; (MM:ESI$^+$) $C_{21}H_{24}BrN_2O_2$ *m/z* calc'd for $[M+H]^+$: 415.1021, found 415.1036.



4w

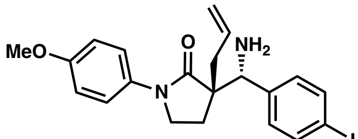
(*S)-3-allyl-3-((*R**)-amino(4-bromophenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4w):** Compound **4w** was prepared from 4-bromobenzonitrile **6n** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford

Mannich product **4w** as a pale-yellow oil (79 mg, 0.190 mmol, 95% yield, 20:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 4H), 7.36 – 7.23 (m, 2H), 6.99 – 6.87 (m, 2H), 5.79 (dddd, J = 16.7, 10.1, 8.3, 6.5 Hz, 1H), 5.20 – 5.07 (m, 2H), 4.26 (s, 1H), 3.83 (s, 3H), 3.54 (ddd, J = 9.3, 8.7, 6.6 Hz, 1H), 3.35 (td, J = 9.4, 4.1 Hz, 1H), 2.61 – 2.49 (m, 2H), 2.14 (ddt, J = 13.5, 8.3, 1.0 Hz, 1H), 1.74 (td, J = 8.8, 4.4 Hz, 1H), 1.69 (br, NH_2, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.81, 156.97, 141.30, 133.47, 132.42, 131.46, 129.75, 122.27, 121.63, 119.16, 114.20, 59.84, 55.63, 54.16, 46.68, 41.41, 23.66; IR (Neat Film, NaCl) 2923, 1681, 1512, 1486, 1404, 1295, 1249, 1178, 1073, 1010, 825 cm^{-1}; (MM:ESI^{+}) $C_{21}H_{24}BrN_2O_2$ *m/z* calc'd for $[M+H]^{+}$: 415.1021, found 415.1015. Relative configuration was determined via X-ray diffraction. Crystals were obtained via a slow evaporation of a solution of **4w** in toluene. CCDC 2253010



4y

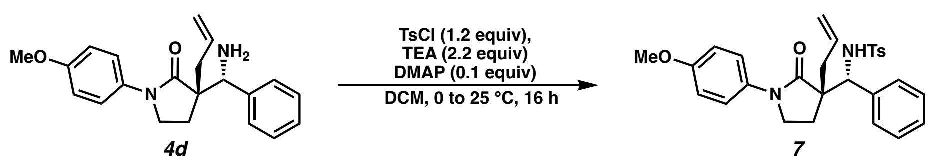
(*S)-3-allyl-3-((*R**)-amino(3-iodophenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4y):** Compound **4y** was prepared from 3-iodobenzonitrile **6p** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4y** as a pale-yellow oil (30 mg, 0.065 mmol, 32% yield, 10:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (t, J = 1.8 Hz, 1H), 7.63 (ddd, J = 7.9, 1.8, 1.0 Hz, 1H), 7.56 – 7.38 (m, 2H), 7.32 (d, J = 1.5 Hz, 1H), 7.05 (t, J = 7.8 Hz, 1H), 7.01 – 6.78 (m, 2H), 5.79 (dddd, J = 16.8, 10.1, 8.2, 6.5 Hz, 1H), 5.24 – 5.03 (m, 2H), 4.18 (s, 1H), 3.81 (s, 3H), 3.57 – 3.46 (m, 1H), 3.32 – 3.21 (m, 1H), 2.61 – 2.43 (m, 2H), 2.17 (ddt, J = 13.5, 8.3, 1.0 Hz, 1H), 1.77 (td, J = 8.7, 4.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.72, 157.01, 144.81, 136.88, 133.46, 132.36, 130.10, 127.44, 122.40, 119.22, 114.21, 94.47, 59.99, 55.64, 54.07, 46.69, 41.33, 23.91; IR (Neat Film, NaCl) 2932, 1681, 1563, 1512, 1429, 1403, 1296, 1248, 1180, 1100, 1035, 922, 832, 791, 701 cm^{-1}; (MM:ESI^{+}) $C_{21}H_{24}IN_2O_2$ *m/z* calc'd for $[M+H]^{+}$: 463.0883, found 463.0892.



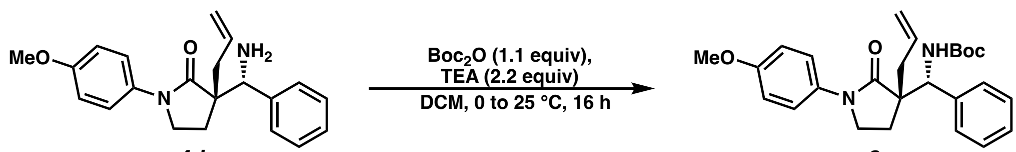
4z

(*S)-3-allyl-3-((*R**)-amino(4-iodophenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4z):** Compound **4z** was prepared from 4-iodobenzonitrile **6q** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4z** as a pale-yellow oil (65 mg, 0.14 mmol, 70% yield, 9:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.54 (m, 2H), 7.53 – 7.39 (m, 2H), 7.16 – 7.07 (m, 2H), 6.97 – 6.85 (m, 2H), 5.77 (dddd, *J* = 16.7, 10.1, 8.3, 6.5 Hz, 1H), 5.17 – 5.06 (m, 2H), 4.24 (s, 1H), 3.81 (s, 3H), 3.52 (ddd, *J* = 9.4, 8.7, 6.7 Hz, 1H), 3.32 (dt, *J* = 9.5, 4.7 Hz, 1H), 2.57 – 2.46 (m, 2H), 2.43 – 2.17 (br, NH_2, 2H), 2.13 (ddt, *J* = 13.5, 8.3, 0.9 Hz, 1H), 1.73 (ddd, *J* = 12.9, 8.7, 4.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.77, 157.01, 141.68, 137.47, 133.39, 132.37, 130.05, 122.32, 119.25, 114.21, 93.30, 59.90, 55.64, 54.06, 46.71, 41.38, 23.68; IR (Neat Film, NaCl) 2923, 1681, 1511, 1484, 1403, 1295, 1249, 1180, 1035, 1005, 921, 823 cm^{-1}; (MM:ESI$^+$) $C_{21}H_{24}IN_2O_2$ *m/z* calc'd for $[M+H]^+$: 463.0883, found 463.0876.

Product Derivatizations: *N*-Protection Followed by Lactam *N*-PMP Deprotection.

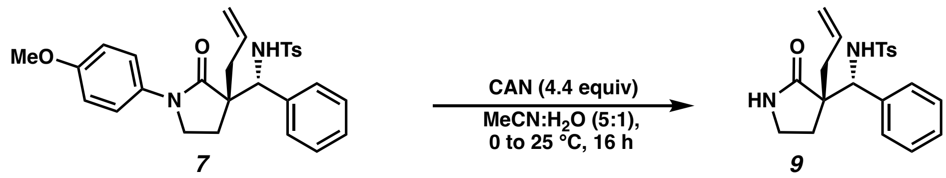


***N*-((*R**)-((*S**)-3-allyl-1-(4-methoxyphenyl)-2-oxopyrrolidin-3-yl)(phenyl)methyl)-4-methylbenzenesulfonamide (7):** Allyl Mannich product **4d** (23 mg, 0.067 mmol, 1.0 equiv) was dissolved in DCM (2 mL) and cooled to 0 °C. TEA (21 μL, 0.147 mmol, 2.2 equiv) was added to the reaction mixture followed by DMAP (0.7 mg, 0.006 mmol, 0.1 equiv) and TsCl (15 mg, 0.08 mmol, 1.2 equivs) and then stirred at 0 °C for 1 h. The reaction mixture was allowed to warm to 25 °C over the next 15 h. The reaction mixture was diluted with DCM (10 mL) and washed with NH_4Cl (10 mL). The organic layer was separated, and the aqueous layer was extracted with DCM (3 x 10 mL). The organic layers were combined, washed with $NaHCO_3$ (10 mL), dried over Na_2SO_4 and concentrated by rotary evaporation. The crude oil was purified by column chromatography (60% EtOAc in Hexanes, 1% TEA) to afford *N*-tosylated product **7** as a pale-yellow oil (32 mg, 0.63 mmol, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.18 – 7.13 (m, 2H), 7.10 (ddt, *J* = 7.7, 6.6, 1.6 Hz, 1H), 7.02 – 6.93 (m, 4H), 6.91 – 6.84 (m, 3H), 6.86 – 6.81 (m, 2H), 5.97 – 5.82 (m, 1H), 5.35 – 5.20 (m, 2H), 4.52 (d, *J* = 8.9 Hz, 1H), 3.78 (s, 3H), 3.23 (td, *J* = 9.4, 3.8 Hz, 1H), 2.74 (ddd, *J* = 6.9, 3.6, 2.4 Hz, 2H), 2.40 – 2.32 (m, 1H), 2.24 (s, 3H), 2.10 (ddd, *J* = 13.5, 9.3, 6.9 Hz, 1H), 1.81 (ddd, *J* = 13.5, 8.7, 3.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.42, 157.31, 142.24, 138.49, 137.10, 132.51, 131.51, 128.93, 128.23, 128.21, 127.79, 126.75, 122.54, 120.40, 114.17, 62.29, 55.61, 51.51, 46.35, 40.28, 25.80, 21.44; IR (Neat Film, NaCl) 3386, 2923, 1667, 1513, 1404, 1323, 1301, 1249, 1160, 1090, 831, 702, 667 cm^{-1}; (MM:ESI$^+$) : $C_{28}H_{31}N_2O_4S$ *m/z* calc'd for [M+H]$^+$: 491.2005, found 491.1993.

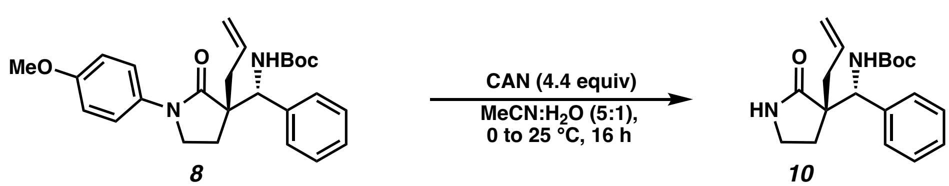


4d   *8*

tert-butyl-((*R)-((*S**)-3-allyl-1-(4-methoxyphenyl)-2-oxopyrrolidin-3-yl)(phenyl)methyl)carbamate (8):** Allyl Mannich product **4d** (23 mg, 0.067 mmol, 1.0 equiv) was dissolved in DCM (2 mL) and cooled to 0 °C. Boc_2O (15 mg, 0.074 mmol, 1.1 equiv) was added to the reaction mixture followed by TEA (21 μL, 0.147 mmol, 2.2 equiv) and stirred at 0 °C for 1 h. The reaction mixture was allowed to warm to 25 °C over the next 15 h. The reaction mixture was diluted with DCM (10 mL) and washed with NH_4Cl (10 mL). The organic layer was separated, and the aqueous layer was extracted with DCM (3 x 10 mL). The organic layers were combined, washed with $NaHCO_3$ (10 mL), dried over Na_2SO_4 and concentrated by rotary evaporation. The crude oil was purified by column chromatography (50% EtOAc in Hexanes, 1% TEA) to afford carbamate product **8** as a pale-yellow oil (28 mg, 0.64 mmol, 96% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 7H), 6.97 – 6.83 (m, 2H), 6.81 (d, *J* = 8.7 Hz, 1H), 5.91 – 5.79 (m, 1H), 5.32 – 5.18 (m, 2H), 4.65 (d, *J* = 8.9 Hz, 1H), 3.80 (s, 3H), 3.20 (td, *J* = 9.3, 2.9 Hz, 1H), 2.66 (dd, *J* = 7.6, 3.5 Hz, 2H), 2.25 (q, *J* = 8.5 Hz, 1H), 2.13 (ddd, *J* = 13.5, 9.4, 7.9 Hz, 1H), 1.91 (ddd, *J* = 13.4, 8.3, 2.9 Hz, 1H), 1.38 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.58, 157.15, 155.40, 140.03, 133.15, 131.82, 128.45, 127.96, 127.88, 122.42, 119.92, 114.12, 79.29, 59.63, 55.61, 51.34, 46.22, 40.61, 28.53, 26.25; IR (Neat Film, NaCl) 3392, 2978, 1712, 1670, 1512, 1456, 1366, 1295, 1249, 1169, 1036, 831, 702 cm^{-1}; (MM:ESI$^+$) : $C_{26}H_{33}N_2O_4$ *m/z* calc'd for [M+H]$^+$: 437.2440, found 437.2453.

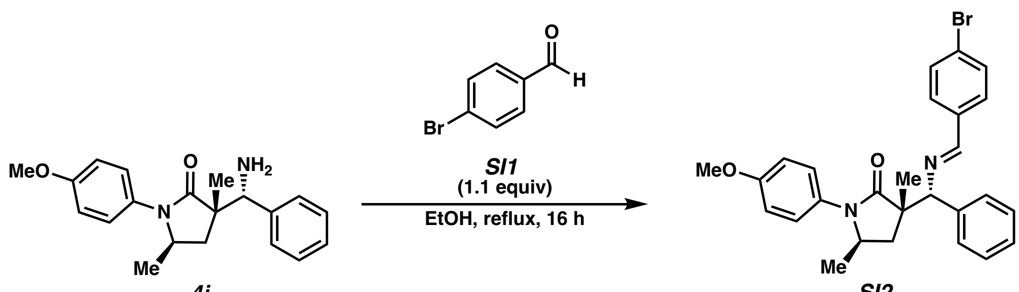


N-((R*)-((S*)-3-allyl-2-oxopyrrolidin-3-yl)(phenyl)methyl)-4-methylbenzenesulfonamide (9): *N*-Ts protected allyl Mannich product **7** (20 mg, 0.04 mmol, 1.0 equiv) was dissolved in a 5:1 mixture of MeCN:H_2O (3.5 mL) and cooled to 0 °C. CAN (88 mg, 0.18 mmol, 4.5 equiv) was added to the reaction mixture and stirred at 0 °C for 1 h and allowed to warm to 25 °C overnight. The reaction mixture was diluted with EtOAc (10 mL) and washed with sat'd $NaHCO_3$ (10 mL) and brine (10 mL). The aqueous layers were combined and extracted with EtOAc (3 x 10mL). The organic layers were combined, dried with Na_2SO_4, concentrated by rotary evaporator, and purified via column chromatography (85% EtOAc in hexanes) to afford *N*-H lactam product **9** as an orange-yellow amorphous solid (13 mg, 0.034 mmol, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 5H), 7.05 – 6.98 (m, 4H), 6.90 (d, *J* = 8.0 Hz, 1H), 5.94 – 5.80 (m, 1H), 5.64 (s, 1H), 5.28 – 5.20 (m, 2H), 4.46 (s, 1H), 2.96 (td, *J* = 9.0, 4.9 Hz, 1H), 2.71 – 2.57 (m, 2H), 2.26 (s, 3H), 2.17 (td, *J* = 9.1, 5.6 Hz, 1H), 2.11 – 2.01 (m, H), 1.80 (ddd, *J* = 13.6, 8.8, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.89, 142.26, 138.41, 137.16, 132.50, 128.94, 128.28, 128.24, 127.67, 126.78, 120.29, 61.93, 49.50, 39.65, 39.27, 28.09, 21.45; IR (Neat Film, NaCl) 3265, 2923, 2853, 1682, 1513, 1456, 1326, 1249, 1160, 1089, 924, 801, 723, 703 cm^{-1}; (MM:ESI$^+$) : $C_{21}H_{25}N_2O_3S$ *m/z* calc'd for $[M+H]^+$:385.1586, found 385.1562.



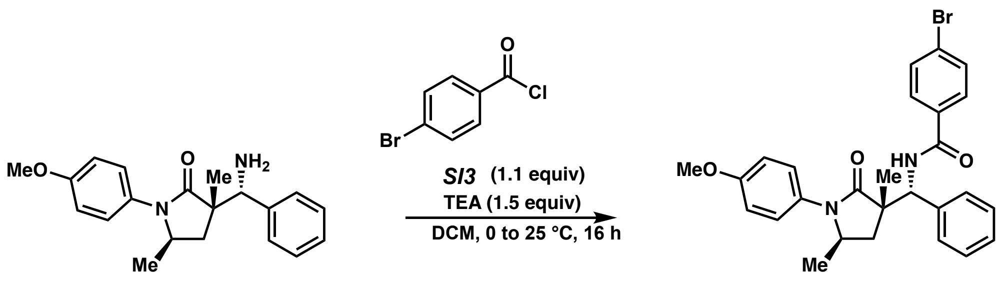
***tert*-butyl ((R*)-((S*)-3-allyl-2-oxopyrrolidin-3-yl)(phenyl)methyl)carbamate (10):** *N*-Boc protected allyl Mannich product **4d** (20 mg, 0.04 mmol, 1.0 equiv) was dissolved in a 5:1 mixture of MeCN:H_2O (3.5 mL) and cooled to 0 °C. CAN (88 mg, 0.18 mmol, 4.5 equiv) was added to the reaction mixture and stirred at 0 °C for 1 h and allowed to warm to 25 °C overnight. The reaction mixture was diluted with EtOAc (10 mL) and washed with sat'd $NaHCO_3$ (10 mL) and brine (10 mL). The aqueous layers were combined and extracted with EtOAc (3 x 10mL). The organic layers were combined, dried with Na_2SO_4, concentrated by rotary evaporator, and purified via column chromatography (80% EtOAc in hexanes) to afford *N*-H lactam product **10** as an orange-yellow crystal (11 mg, 0.033 mmol, 83% yield);); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.20 (m, 5H), 6.78 (d, *J* = 9.0 Hz, 1H), 5.93 – 5.72 (m, 1H), 5.50 (s, 1H), 5.25 – 5.16 (m, 2H), 4.62 (d, *J* = 9.0 Hz, 1H), 3.47 – 3.23 (m, 1H), 2.92 (td, *J* = 8.6, 3.5 Hz, 1H), 2.64 – 2.45 (m, 2H), 2.18 – 1.99 (m, 1H), 1.98 – 1.88 (m, 1H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.06, 155.40, 140.00, 133.08, 128.44, 128.11, 127.78, 119.83, 79.35, 59.13, 49.24, 40.03, 39.18, 28.71, 28.55; IR (Neat Film, NaCl) 3264, 2924, 1694, 1494, 1363, 1325, 1248, 1172, 1161, 918, 778, 703 cm^{-1}; (MM:ESI$^+$) : $C_{19}H_{27}N_2O_3$ *m/z* calc'd for $[M+H]^+$: 331.2022, found 331.2015.

Product Derivatizations: *N*-Functionalization via Imine Formation or *N*-acylation



(3*S*,5*R*)-3-((*R*)-(((*E*)-4-bromobenzylidene)amino)(phenyl)methyl)-1-(4-methoxyphenyl)-3,5-dimethylpyrrolidin-2-one (SI2): Dimethyl Mannich product **4j** (35 mg, 0.108 mmol, 1.0 equiv) was dissolved in ethanol. *Para*-bromo benzaldehyde **SI1** (20 mg, 0.108 mmol, 1.0 equiv) was added to the reaction mixture and the solution was heated to reflux for 16 hours. The reaction was cooled to ambient temperatures and concentrated via rotary evaporator. The crude reaction mixture was then purified via column chromatography (40% EtOAc in hexanes) to afford the *p*-Br imine product **SI2** (48.7 mg, 0.99 mmol, 92% yield) as a yellow crystalline solid. The diastereomeric mixture could not be separated. Crystals suitable for X-ray diffraction were obtained via a vapor diffusion of DCM/hexanes to afford clear crystals. CCDC 2253013. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 0.29H), 8.20 (s, 0.71H), 7.70 – 7.65 (m, 0.58H), 7.65 – 7.59 (m, 1.52H), 7.58 – 7.49 (m, 4H)*, 7.42 – 7.34 (m, 2H), 7.34 (s, 1H), 7.01 – 6.94 (m, 0.58H), 6.86 – 6.80 (m, 2H), 6.76 – 6.69 (m, 1.52H), 4.71 (s, 0.29H), 4.62 (s, 0.71H), 4.25 – 4.15 (m, 0.71H), 4.15 – 4.05 (m, 0.29H), 3.77 (s, 0.87H), 3.75 (s, 2.12H), 3.20 (dd, *J* = 13.3, 7.6 Hz, 0.71H), 2.81 (dd, *J* = 12.6, 8.2 Hz, 0.29H), 1.88 (dd, *J* = 12.6, 7.3 Hz, 0.29H), 1.32 – 1.25 (m, 0.71H)*, 1.24 (s, 2.21H), 1.19 (d, *J* = 6.1 Hz, 0.88H), 1.16 (s, 0.88H), 1.09 (d, *J* = 6.3 Hz, 2.21H). (2.5:1 dr); ^{13}C NMR (101 MHz, $CDCl_3$) δ

177.63, 177.09,* 160.72,* 160.34, **157.80,*** 140.64,* 140.41, 135.57,* 135.35, 131.91, 131.87,* 130.37,* 130.34, 129.92, 129.85,* 128.84, 128.64,* 128.25,* 128.17, 127.63, 127.52,* 126.62, 126.46,* 125.25, 125.11,* 114.29, 114.21,* 79.77, 77.36,* 55.56,* 55.53, 54.02, 52.25,* 51.43, 51.25,* 36.36, 34.98,* 24.43, 22.38,* 21.59, 21.08.* Carbon signals of the minor diastereomer are denoted with*, overlap of both diastereomers are bolded; IR (Neat Film, NaCl) 3264, 2922, 2853, 1691, 1494, 1454, 1377, 1319, 1242, 1150, 910, 768, 702 cm^{-1}; (MM:ESI^{+}) : $C_{27}H_{28}BrN_2O_2$ *m/z* calc'd for $[M+H]^{+}$: 491.1329, found 491.1329.



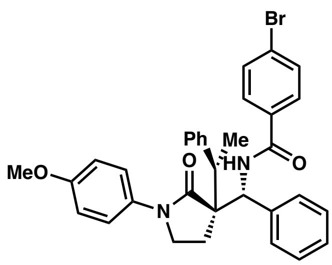
4j
5:1 dr

SI4
95% yield

4-bromo-*N*-((*R*)-((3*S*,5*R*)-1-(4-methoxyphenyl)-3,5-dimethyl-2-oxopyrrolidin-3-yl)(phenyl)methyl)benzamide (SI4): Dimethyl Mannich product **4j** (25 mg, 0.077 mmol, 1.0 equiv) was dissolved in DCM (5 mL) and cooled to 0 °C. TEA (21 µL, 0.15 mmol, 2.0 equiv) and *para*-bromo-benzoyl chloride **SI3** (18.5 mg, 0.11 mmol, 1.1 equiv) were added sequentially to the reaction mixture and stirred at 0 °C for 1 h and allowed to warm to 25 °C overnight. The reaction was diluted with DCM (10 mL) and washed with sat'd $NaHCO_3$ (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The organic layers were combined, dried over Na_2SO_4, concentrated by rotary evaporator and purified via column chromatography (60% EtOAc in hexanes) to afford benzoyl product **SI4** as a colorless amorphous solid (37 mg, 0.073 mmol, 95% yield) separable diastereomers

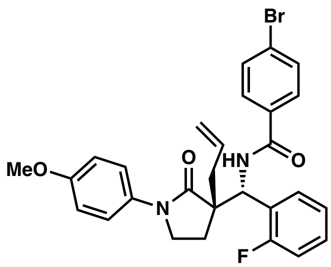
Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 8.1 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.57 – 7.49 (m, 2H), 7.41 – 7.29 (m, 5H), 6.96 – 6.87 (m, 4H), 5.05 (d, J = 8.1 Hz, 1H), 3.82 (s, 3H), 2.57 (ddt, J = 14.0, 7.8, 6.2 Hz, 1H), 2.45 (dd, J = 13.5, 7.6 Hz, 1H), 1.67 – 1.58 (m, 4H), 0.90 (d, J = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.50, 165.22, 158.36, 139.60, 132.95, 131.82, 129.20, 128.89, 128.71, 128.33, 127.96, 126.34, 126.20, 114.61, 60.94, 55.63, 53.08, 47.44, 39.82, 25.95, 20.96; IR (Neat Film, NaCl) 3362, 2931, 1666, 1588, 1510, 1479, 1455, 1327, 1291, 1248, 1180, 1133, 1028, 1010, 828, 751, 705 cm^{-1}; (MM:ESI$^+$) : $C_{27}H_{28}BrN_2O_3$ *m/z* calc'd for $[M+H]^+$: 507.1278, found 507.1291.

Minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, *J* = 8.5 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.57 – 7.50 (m, 2H), 7.50 – 7.43 (m, 2H), 7.43 – 7.33 (m, 2H), 7.33 – 7.28 (m, 1H), 7.15 – 7.04 (m, 2H), 7.01 – 6.93 (m, 2H), 5.14 (d, *J* = 8.5 Hz, 1H), 4.08 – 3.99 (m, 1H), 3.82 (s, 3H), 2.17 – 2.06 (m, 1H), 1.67 – 1.55 (m, 4H), 0.63 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.68, 165.33, 158.69, 140.02, 133.14, 131.81, 129.28, 128.95, 128.75, 128.55, 128.13, 126.99, 126.25, 114.74, 60.59, 55.67, 53.32, 47.33, 37.76, 23.96, 20.20.



SI5

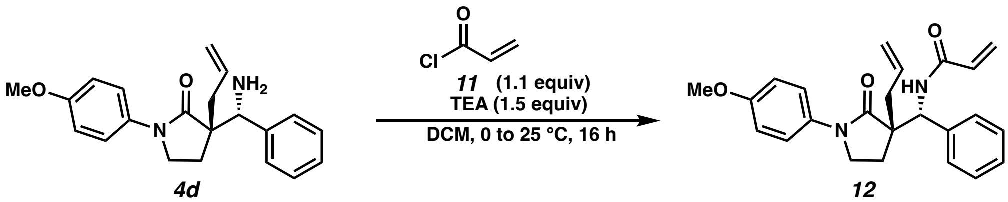
4-bromo-*N*-((1*R*)-((3*S*)-1-(4-methoxyphenyl)-2-oxo-3-(1-phenylethyl)pyrrolidin-3-yl)(phenyl)methyl)benzamide (SI5): Benzyl Mannich product **4i** (8 mg, 0.02 mmol, 1.0 equiv) was dissolved in DCM (2 mL) and cooled to 0 °C. TEA (3.2 µL, 0.04 mmol, 2.0 equiv) and *para*-bromo-benzoyl chloride **SI3** (4.8 mg, 0.022 mmol, 1.1 equiv) were added sequentially to the reaction mixture and stirred at 0 °C for 1 h and allowed to warm to 25 °C overnight. The reaction was diluted with DCM (4 mL) and washed with sat'd $NaHCO_3$ (4 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 5 mL). The organic layers were combined, dried over Na_2SO_4, concentrated by rotary evaporator and purified via column chromatography (60% EtOAc in hexanes) to afford benzoyl product **SI4** as a colorless amorphous solid (10.7 mg, 0.0184 mmol, 92% yield single diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (d, *J* = 8.6 Hz, 1H), 7.89 – 7.78 (m, 2H), 7.61 – 7.56 (m, 2H), 7.47 – 7.43 (m, 2H), 7.41 – 7.38 (m, 2H), 7.34 – 7.27 (m, 5H), 7.26 – 7.21 (m, 1H), 6.82 (s, 4H), 5.42 (d, *J* = 8.6 Hz, 1H), 3.87 – 3.79 (m, 1H), 3.78 (s, 3H), 2.43 (ddd, *J* = 7.9, 6.0, 1.6 Hz, 2H), 2.21 (ddd, *J* = 13.5, 8.1, 6.5 Hz, 1H), 1.91 (ddd, *J* = 13.6, 8.6, 6.3 Hz, 1H), 1.51 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.57, 164.92, 157.80, 141.84, 139.55, 133.04, 131.92, 130.98, 129.16, 129.00, 128.71, 128.69, 128.27, 128.19, 127.19, 126.42, 123.87, 114.29, 57.55, 55.85, 55.60, 47.07, 41.55, 21.42, 14.73; IR (Neat Film, NaCl) 3362, 2958, 1731, 1666, 1589, 1512, 1478, 1409, 1329, 1292, 1250, 1180, 1151, 1032, 1009, 828, 753, 735, 702 cm^{-1}; (MM:ESI$^+$) : $C_{33}H_{32}BrN_2O_3$ *m/z* calc'd for $[M+H]^+$: 583.1591, found 583.1617.



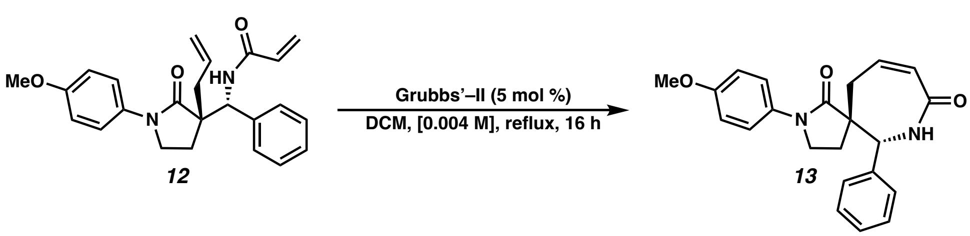
SI6

***N*-((*S*)-((*S*)-3-allyl-1-(4-methoxyphenyl)-2-oxopyrrolidin-3-yl)(2-fluorophenyl)methyl)-4-bromobenzamide (SI6):** *Ortho*-fluoro-Mannich product **4o** (14 mg, 0.04 mmol, 1.0 equiv) was dissolved in DCM (2 mL) and cooled to 0 °C. TEA (6.5 µL, 0.08 mmol, 2.0 equiv) and *para*-bromo-benzoyl chloride **SI3** (9.6 mg, 0.044 mmol, 1.1 equiv) were added sequentially to the reaction mixture and stirred at 0 °C for 1 h and allowed to warm to 25 °C overnight. The reaction was diluted with DCM (8 mL) and washed with sat'd $NaHCO_3$ (8 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The organic layers were combined, dried over Na_2SO_4, concentrated by rotary evaporator and purified via column chromatography (60% EtOAc in hexanes) to afford benzoyl product **SI6** as a colorless amorphous solid (14.4 mg, 0.0367 mmol, 67% yield, single diastereomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.1 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.51 – 7.43 (m, 2H), 7.26 – 7.12 (m, 1H), 7.06 – 6.98 (m, 4H), 6.94 (td, *J* = 7.6, 1.2 Hz, 1H), 6.89 – 6.79 (m, 2H), 5.80 (dddd, *J* = 16.8, 10.4, 8.3, 6.5 Hz, 1H), 5.60 (d, *J* = 8.1 Hz, 1H), 5.22 – 5.12 (m, 2H), 3.74 (s, 3H), 3.33 (td, *J* = 9.4, 4.0 Hz, 1H), 2.73 – 2.64 (m, 1H), 2.64 – 2.50 (m, 2H), 2.15 (ddd, *J* = 13.8, 9.3, 6.9 Hz, 1H), 1.97 – 1.87 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.13, 164.94, 160.55 (d, *J* = 244.1 Hz), 157.52, 132.67, 132.23, 131.80, 131.79 (d, *J* = 23.0 Hz), 131.18, 129.67 (d, *J* = 8.2 Hz), 128.78, 128.40, 126.76 (d, *J* = 13.6 Hz), 126.37, 124.52 (d, *J* = 3.4 Hz), 122.91, 120.43, 115.58 (d, *J* = 22.6 Hz), 114.27, 55.52, 51.11, 46.95, 40.69, 25.12; IR (Neat Film, NaCl) 3361, 2922, 1681, 1666, 1512, 1481, 1329, 1292, 1251, 753, 702 cm^{-1}; (MM:ESI$^+$) : $C_{28}H_{27}BrFN_2O_3$ *m/z* calc'd for $[M+H]^+$: 537.1184, found 537.1200.

Product Derivatizations: Acrylamide Formation Followed by Ring Closing Metathesis



***N*-((*R**)-((*S**)-3-allyl-1-(4-methoxyphenyl)-2-oxopyrrolidin-3-yl)(phenyl)methyl)acrylamide (12):** Allyl Mannich product **4d** (27 mg, 0.08 mmol, 1.0 equiv) was dissolved in DCM (5 mL) and cooled to 0 °C. TEA (21 µL, 0.15 mmol, 2.0 equiv) and acryloyl chloride **11** (10 µL, 0.11 mmol, 1.4 equiv) were added sequentially to the reaction mixture and stirred at 0 °C for 1 h and allowed to warm to 25 °C overnight. The reaction was diluted with DCM (10 mL) and washed with sat'd $NaHCO_3$ (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The organic layers were combined, dried over Na_2SO_4, concentrated by rotary evaporator and purified via column chromatography (60% EtOAc in hexanes) to afford acrylamide product **12** as a yellow oil (28 mg, 0.072 mmol, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.20 – 7.16 (m, 3H), 7.17 – 7.11 (m, 2H), 6.90 – 6.73 (m, 2H), 6.18 (dd, *J* = 17.1, 1.9 Hz, 1H), 6.13 – 6.01 (m, 1H), 5.77 (dddd, *J* = 16.2, 10.8, 8.2, 6.6 Hz, 1H), 5.55 (dd, *J* = 9.8, 1.9 Hz, 1H), 5.20 – 5.07 (m, 2H), 5.00 (d, *J* = 8.6 Hz, 1H), 3.73 (s, 3H), 3.18 (td, *J* = 9.5, 3.4 Hz, 1H), 2.66 – 2.56 (m, 1H), 2.52 (ddt, *J* = 13.8, 8.2, 1.0 Hz, 1H), 2.33 (ddd, *J* = 9.5, 8.7, 7.4 Hz, 1H), 2.07 (ddd, *J* = 13.4, 9.4, 7.4 Hz, 1H), 1.86 (ddd, *J* = 13.5, 8.6, 3.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.03, 164.75, 157.42, 139.30, 132.74, 131.55, 131.19, 128.61, 128.13, 126.50, 122.72, 120.24, 114.26, 58.14, 55.63, 51.07, 46.58, 40.73, 29.85, 25.99; IR (Neat Film, NaCl) 3350, 2922, 1674, 1634, 1513, 1404, 1298, 1249, 1182, 1034, 922, 830, 800, 704 cm^{-1}; (MM:ESI$^+$) : $C_{24}H_{27}N_2O_3$ *m/z* calc'd for $[M+H]^+$ 391.2022, found 391.2037.

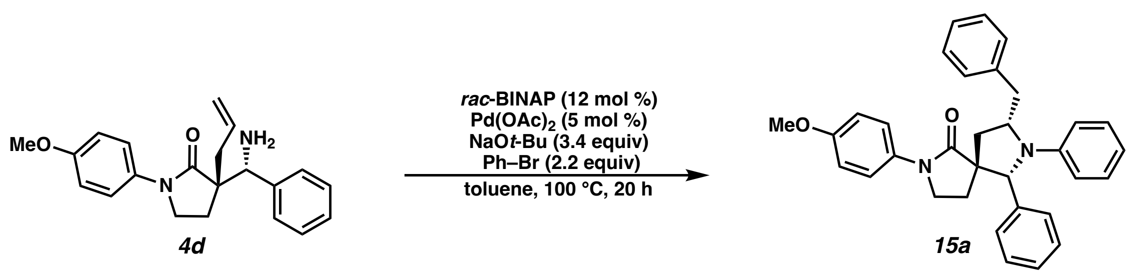


(5*S,6*R**)-2-(4-methoxyphenyl)-6-phenyl-2,7-diazaspiro[4.6]undec-9-ene-1,8-dione (13):** Acrylamide product **12** (15 mg, 0.04 mmol, 1.0 equiv) was dissolved in DCM (8 mL). The resulting solution was sparged with argon for 10 minutes. The Grubbs' second generation catalyst (2 mg, 0.002 mmol, 5 mol %) was added to the reaction mixture under a positive pressure of argon.

The reaction was bubbled with argon for 5 minutes and heated to 40 °C for 16 h. The crude reaction mixture was concentrated by rotary evaporation and purified directly via column chromatography (90% EtOAc in hexanes with 1% Et_3N) in order afford ε-lactam **13** as a brown amorphous solid (11 mg, 0.03 mmol, 75% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.34 – 7.28 (m, 3H), 7.17 – 7.10 (m, 2H), 6.84 – 6.75 (m, 2H), 6.57 (ddd, *J* = 11.0, 8.3, 5.8 Hz, 1H), 6.25 – 6.16 (m, 2H), 4.48 (d, *J* = 5.6 Hz, 1H), 3.78 (s, 3H), 3.43 – 3.24 (m, 3H), 2.74 (dt, *J* = 9.7, 7.9 Hz, 1H), 2.28 (dd, *J* = 14.2, 8.2 Hz, 1H), 2.25 – 2.11 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.52, 170.30, 157.02, 136.78, 136.20, 131.93, 129.16, 129.13, 128.90, 128.29, 122.33, 114.07, 64.64, 58.77, 45.98, 45.36, 36.29, 30.39; IR (Neat Film, NaCl) 2922, 1661, 1512, 1401, 1298, 1247, 1032, 825, 701 cm^{-1}; (MM:ESI$^+$) : $C_{22}H_{23}N_2O_3$ *m/z* calc'd for $[M+H]^+$ 363.1709, found 363.1710.
Et_3N•HCl Present (1:1 ratio)

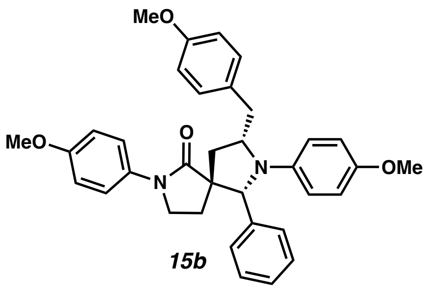
Product Derivatizations: C–N Cross-Coupling Reactions

General Procedure 8: Wolfe-type two-step, one-pot carboamination spirocyclization



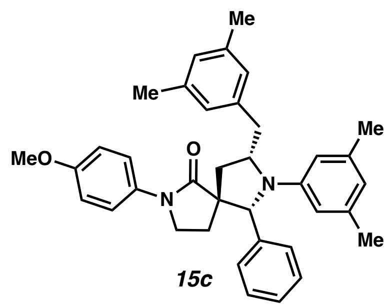
(5*R,6*R**,8*R**)-8-benzyl-2-(4-methoxyphenyl)-6,7-diphenyl-2,7-diazaspiro[4.4]nonan-1-one (15a):** $Pd(OAc)_2$ (0.6 mg, 0.0027 mmol, 5 mol %) and *rac*-BINAP (4 mg, 0.0065 mmol, 12 mol %) were dissolved in toluene (1.0 mL) and stirred for 10 minutes at 25 °C. Meanwhile, allyl Mannich product **4d** (18 mg, 0.054 mmol, 1.0 equiv) was added to a solution of bromobenzene (12 µL, 0.12 mmol, 2.2 equiv) and NaO*t*-Bu (17 mg, 0.18 mmol, 3.4 equiv) in toluene (1.0 mL). The metal-ligand complex solution was added to the reaction mixture. The resulting solution was sparged with argon for 5 minutes, then heated to 100 °C for 20 h. The reaction mixture was cooled to 25 °C, diluted with DCM, then filtered through a pad of celite. The celite was washed with copious amounts of toluene, and the resulting filtrate was concentrated via rotary evaporation and purified via column chromatography (50% EtOAc in hexanes) to afford the spirocyclic pyrrolidine product **15** as a red-orange amorphous solid (21.7 mg, 0.044 mmol, 82% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 7H), 7.26 – 7.20 (m, 5H), 7.12 – 7.05 (m, 2H), 7.02 – 6.96 (m, 1H) 6.86 (d, *J* = 9.1 Hz, 2H), 6.75 – 6.70 (m, 2H), 4.66 (s, 1H), 4.12 – 4.05 (m, 1H), 3.96 (td, *J* =

10.2, 6.2 Hz, 1H), 3.80 (s, 3H), 3.79 – 3.77 (m, 1H), 3.75 (qd, *J* = 3.2, 1.7 Hz, 1H), 2.99 (dd, *J* = 13.3, 10.0 Hz, 1H), 2.67 (dd, *J* = 12.9, 9.8 Hz, 1H), 2.17 (dd, *J* = 12.5, 6.1 Hz, 1H), 2.05 – 1.97 (m, 1H), 1.93 (dd, *J* = 13.0, 6.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.87, 156.46, 147.67, 140.78, 138.93, 132.62, 129.32, 129.15, 128.64, 128.50, 127.68, 126.56, 121.45, 117.78, 114.03, 113.85, 75.32, 60.14, 56.43, 55.46, 45.43, 40.52, 39.16, 33.61; IR (Neat Film, NaCl) 2931, 1693, 1605, 1512, 1464, 1390, 1301, 1248, 1179, 1100, 1033, 901, 834, 741, 704 cm^{-1}; (MM:ESI$^+$) : $C_{33}H_{33}N_2O_2$ *m/z* calc'd for [M+H]$^+$ 489.2542, found 489.2549.



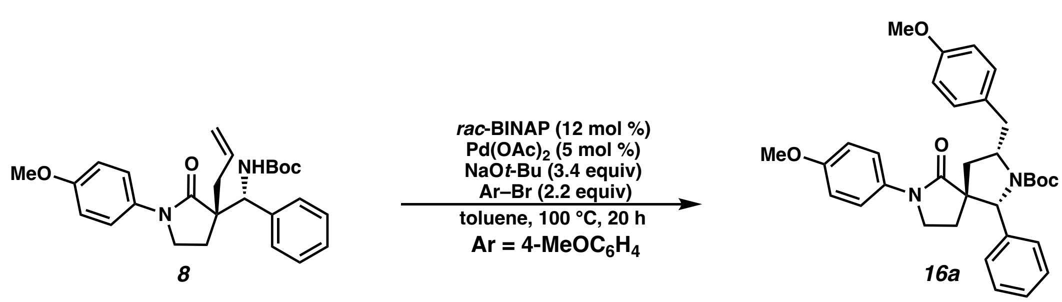
15b

(5*R*,6*R*,8*S*)-8-(4-methoxybenzyl)-2,7-bis(4-methoxyphenyl)-6-phenyl-2,7-diazaspiro[4.4]nonan-1-one (15b): Spirocycle **15b** was synthesized using General Procedure **8** with 4-bromoanisole (28 µL, 0.22 mmol, 2.2 equiv) and allyl Mannich product **4d** (33.6 mg, 0.1 mmol, 1.0 equiv). The crude oil was isolated via column chromatography (50% EtOAc in hexanes) as a yellow amorphous solid (25 mg, 0.046 mmol, 46% yield, 4:1 dr). Note: the major diastereomer coelutes with the retro-Mannich product **2d** after column chromatography as a 2:1 mixture of **15b**:**2d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.81 (m, 2H), 7.61 – 7.57 (m, 2H), 7.50 – 7.47 (m, 2H), 7.42 – 7.37 (m, 3H), 7.32 (ddd, *J* = 8.7, 5.7, 2.6 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 9.2 Hz, 2H), 6.88 (d, *J* = 6.8 Hz, 2H), 4.66 (s, 1H)*, 3.91 – 3.86 (m, 2H), 3.84 (m, 6H), 3.82 (s, 3H), 3.80 – 3.75 (m, 2H), 3.44 (d, *J* = 16.2 Hz, 1H), 2.85 (d, *J* = 16.2 Hz, 1H), 2.65 – 2.58 (m, 1H), 2.16 (ddd, *J* = 13.3, 6.7, 3.2 Hz, 1H), 2.05 – 1.93 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ **175.10,** 174.58, 173.60, 158.76, **158.73**, 158.47, 157.00, 156.64, 149.66, **135.62,** 134.57, 133.40, **132.92,** 132.84, 132.56, 132.48, 132.34, 131.33, 130.68, 130.39, 129.26, 128.81, 128.65, 128.61, 126.70, **121.72,** 121.63, 121.57, **117.20**, 114.33, **114.15,** 113.79, 113.01, 60.98, 55.67, **55.62**, 55.58, 55.44, 55.40, **47.30**, 46.47, 44.06, **42.85**, **35.63,** 30.38, **24.12;** IR (Neat Film, NaCl) 2928, 1692, 1602, 1510, 1475, 1445, 1384, 1301, 1249, 1171, 1115, 1033, 909, 827, 741, 730, 701 cm^{-1}; (MM:ESI$^+$) : $C_{35}H_{37}N_2O_4$ *m/z* calc'd for [M+H]$^+$ 549.2748, found 549.2749. (Bold is compound **2d**)



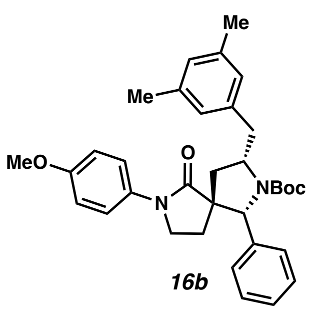
15c

(5*R*,6*R*,8*S*)-8-(3,5-dimethylbenzyl)-7-(3,5-dimethylphenyl)-2-(4-methoxyphenyl)-6-phenyl-2,7-diazaspiro[4.4]nonan-1-one (15c): Spirocycle **15c** was synthesized using General Procedure **8** with 3,5-dimethyl bromobenzene (30 µL, 0.22 mmol, 2.2 equiv) and allyl Mannich product **4d** (33.6 mg, 0.1 mmol, 1.0 equiv). The crude oil was isolated via column chromatography (50% EtOAc in hexanes) as a yellow amorphous solid (43 mg, 0.079 mmol, 79% yield, 9:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 2H), 7.30 (ddd, *J* = 6.1, 3.2, 1.5 Hz, 3H), 7.23 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.02 (s, 2H), 6.93 (s, 1H), 6.87 (d, *J* = 9.2 Hz, 2H), 6.48 (s, 1H), 6.36 (s, 2H), 4.65 (s, 1H), 4.10 – 4.02 (m, 1H), 3.98 (dt, *J* = 10.1, 5.0 Hz, 1H), 3.80 (d, *J* = 0.9 Hz, 3H), 3.79 – 3.74 (m, 1H), 3.67 (dd, *J* = 13.1, 2.6 Hz, 1H), 2.85 (dd, *J* = 13.1, 10.0 Hz, 1H), 2.70 – 2.60 (m, 1H), 2.36 (s, 6H), 2.26 (s, 6H), 2.18 – 2.09 (m, 1H), 2.04 – 1.97 (m, 1H), 1.97 – 1.90 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.96, 156.42, 147.85, 140.95, 139.04, 138.69, 138.12, 132.73, 128.42, 128.14, 127.56, 127.02, 126.58, 121.36, 119.77, 114.03, 111.77, 74.91, 60.11, 56.50, 55.46, 45.42, 40.69, 39.25, 33.46, 21.84, 21.38; IR (Neat Film, NaCl) 2928, 1692, 1602, 1510, 1475, 1445, 1384, 1301, 1249, 1171, 1115, 1033, 909, 827, 741, 730, 701 cm^{-1}; (MM:ESI^{+}) : $C_{37}H_{41}N_2O_2$ *m/z* calc'd for $[M+H]^{+}$ 545.3163, found 545.3173.



8 *16a*

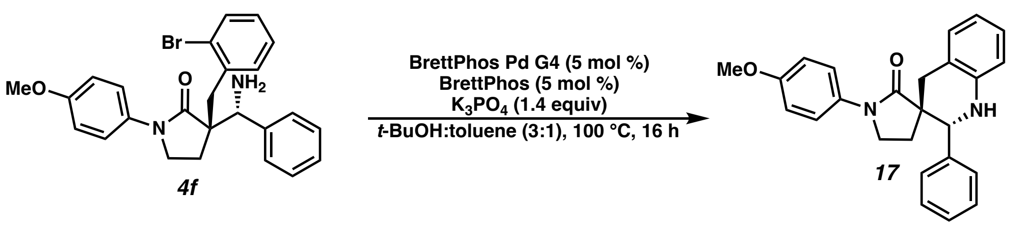
tert-**butyl (1*R*,3*S*,5*R*)-3-(4-methoxybenzyl)-7-(4-methoxyphenyl)-6-oxo-1-phenyl-2,7-diazaspiro[4.4]nonane-2-carboxylate (16a):** $Pd(OAc)_2$ (0.6 mg, 0.0027 mmol, 5 mol %) and *rac*-BINAP (4 mg, 0.0065 mmol, 12 mol %) were dissolved in toluene (1.0 mL) and stirred for 10 minutes at 25 °C. Meanwhile, allyl Mannich product **8** (23.5 mg, 0.054 mmol, 1.0 equiv) was added to a solution of bromobenzene (12 µL, 0.12 mmol, 2.2 equiv) and NaO*t*-Bu (17 mg, 0.18 mmol, 3.4 equiv) in toluene (1.0 mL). The metal-ligand complex solution was added to the reaction mixture. The resulting solution was sparged with argon for 5 minutes, then heated to 100 °C for 20 h. The reaction mixture was cooled to 25 °C, diluted with DCM, then filtered through a pad of celite. The celite was washed with copious amounts of toluene, and the resulting filtrate was concentrated via rotary evaporation and purified via column chromatography (50% EtOAc in hexanes) to afford the spirocyclic pyrrolidine product **16a** as a yellow amorphous solid (24.1 mg, 0.044 mmol, 76% yield, 5:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 7.25 – 7.20 (m, 5H), 7.09 (d, *J* = 7.2 Hz, 2H), 6.88 – 6.84 (m, 2H), 6.84 – 6.79 (m, 2H), 4.96 (br, 1H), 4.23 – 3.98 (m, 1H), 3.84 (dd, *J* = 6.1, 5.1 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.75 – 3.69 (m, 2H), 3.11 (br, 1H), 2.49 (dd, *J* = 13.3, 9.1 Hz, 1H), 2.29 (dd, *J* = 12.5, 6.1 Hz, 1H), 2.15 – 1.98 (m, 1H), 1.76 (dd, *J* = 13.3, 7.0 Hz, 1H), 1.55 – 1.13 (br, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.96, 158.23, 156.62, 155.18, 139.85, 132.37, 130.99, 130.60, 128.04, 127.41, 126.44, 121.92, 114.00, 113.88, 80.20, 70.83, 60.24, 55.61, 55.44, 55.27, 45.65, 38.45, 34.00, 29.72, 28.38; IR (Neat Film, NaCl) 2935, 1693, 1611, 1512, 1454, 1384, 1298, 1248, 1177, 1144, 1111, 1032, 910, 828, 730, 700 cm^{-1}; (MM:ESI^{+}) : $C_{33}H_{39}N_2O_5$ *m/z* calc'd for $[M+H]^{+}$ 543.2853, found 543.2866.



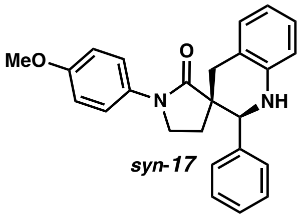
16b

***tert*-butyl (1*R*,3*S*,5*R*)-3-(3,5-dimethylbenzyl)-7-(4-methoxyphenyl)-6-oxo-1-phenyl-2,7-diazaspiro[4.4]nonane-2-carboxylate (16b):** Spirocycle **16b** was synthesized using General Procedure **9** with 3,5-dimethyl bromobenzene (30 µL, 0.22 mmol, 2.2 equiv) and allyl Mannich product **8** (23.5 mg, 0.054 mmol, 1.0 equiv). The crude oil was isolated via column chromatography (50% EtOAc in hexanes) as a yellow amorphous solid (25.4 mg, 0.047 mmol, 87% yield, 10:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 5H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.98 (s, 2H), 6.89 – 6.87 (m, 1H), 6.85 – 6.80 (m, 2H), 4.95 (s, 1H), 4.08 (d, *J* = 13.2 Hz, 1H), 4.02 – 3.88 (m, 1H), 3.84 – 3.79 (m, 1H), 3.78 (s, 3H), 3.76 – 3.70 (m, 2H), 3.04 (s, 1H), 2.51 (dd, *J* = 13.3, 9.2 Hz, 1H), 2.30 (s, 6H), 2.11 – 2.01 (m, 1H), 1.78 (dd, *J* = 13.3, 7.0 Hz, 1H), 1.52 –

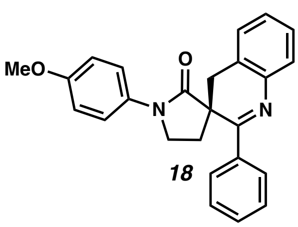
1.18 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.01, 172.04, 156.73, 155.33, 138.93, 138.06, 132.53, 129.85, 128.18, 128.11, 127.54, 126.58, 122.00, 114.13, 80.34, 71.08, 60.26, 55.76, 55.57, 45.76, 38.59, 34.09, 29.71, 28.51, 21.40; IR (Neat Film, NaCl) 2927, 1691, 1604, 1511, 1455, 1381, 1248, 1172, 1142, 1115, 1033, 909, 828, 730, 697 cm^{-1}; (MM:ESI$^+$) : $C_{34}H_{41}N_2O_4$ *m/z* calc'd for $[M+H]^+$ 541.3061, found 541.3072.



(2'*R,3*S**)-1-(4-methoxyphenyl)-2'-phenyl-1',4'-dihydro-2'*H*-spiro[pyrrolidine-3,3'-quinolin]-2-one (17):** BrettPhos Pd G4 (2.5 mg, 0.0025 mmol, 5 mol %) was added to a flame dried vial charged with BrettPhos (1.5 mg, 0.0025 mmol, 5 mol %) and K_3PO_4 (15 mg, 0.07 mmol, 1.4 equiv). The *ortho*-Br benzyl Mannich product **4f** (23 mg, 0.05 mmol, 1.0 equiv, 5:1 dr) was dissolved in a mixture of *t*-BuOH:toluene (0.6 mL:0.2mL) and added to the reaction mixture. The reaction was then heated to 100 °C for 16 h. After the stirring period, the reaction was then cooled to 25 °C, diluted with DCM and filtered through a pad of celite. The celite pad was washed with copious amounts of DCM. The filtrate was concentrated via rotary evaporation and purified via column chromatography (50% EtOAc in hexanes) to afford spirocyclic tetrahydroquinoline **17** as a pale-yellow solid (15.5 mg, 0.04 mmol, 80% yield, 4:1 dr); Note: The major diastereomer was observed to be unstable to silica gel chromatography or when dissolved in $CDCl_3$, as there was an identified product **18** assigned as the dihydroquinoline observed arising from the NMR sample of the *trans* diastereomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.35 – 7.30 (m, 3H), 7.28 – 7.23 (m, 2H), 7.11 – 7.06 (m, 2H), 6.85 – 6.81 (m, 2H), 6.74 (td, J = 7.4, 1.2 Hz, 1H), 6.66 – 6.62 (m, 1H), 4.36 (s, 1H), 3.84 (s, 1H), 3.79 (s, 3H), 3.39 (td, J = 9.4, 1.7 Hz, 1H), 3.18 (d, J = 16.7 Hz, 1H), 2.92 (d, J = 16.6 Hz, 1H), 2.73 (td, J = 9.5, 7.4 Hz, 1H), 2.22 (ddd, J = 13.3, 7.3, 1.8 Hz, 1H), 2.11 – 1.99 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.56, 156.38, 143.70, 140.25, 132.82, 129.39, 128.60, 128.51, 128.08, 127.10, 121.35, 117.94, 113.89, 62.61, 55.56, 46.43, 45.00, 36.43, 30.94; IR (Neat Film, NaCl) 2931, 1690, 1587, 1559, 1512, 1454, 1427, 1399, 1297, 1250, 1181, 1120, 1084, 1033, 909, 829, 768, 730, 692 cm^{-1}; (MM:ESI^{+}) : $C_{25}H_{25}N_2O_2$ *m/z* calc'd for $[M+H]^{+}$ 385.1911, found 385.1906.

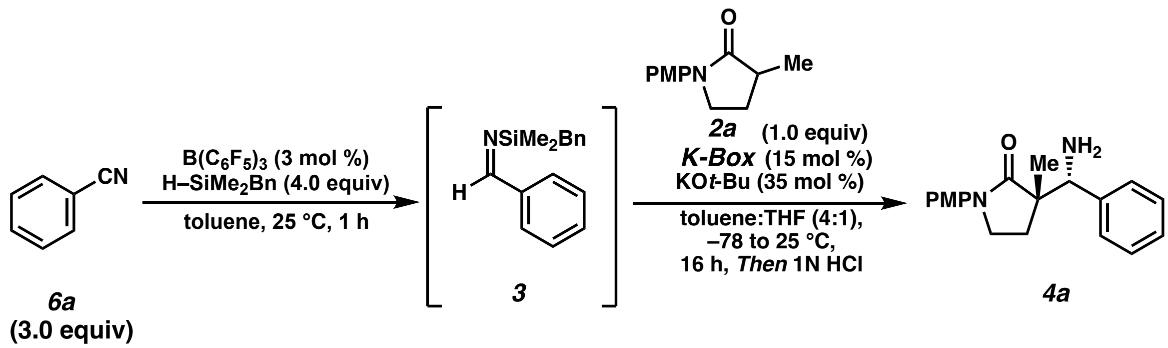


(2'*S*,3*S*)-1-(4-methoxyphenyl)-2'-phenyl-1',4'-dihydro-2'*H*-spiro[pyrrolidine-3,3'-quinolin]-2-one (syn-17): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.35 – 7.27 (m, 3H), 7.20 – 7.12 (m, 2H), 7.08 (dd, *J* = 7.4, 0.9 Hz, 2H), 6.85 – 6.79 (m, 2H), 6.72 (td, *J* = 7.4, 1.2 Hz, 1H), 6.65 (d, *J* = 1.2 Hz, 1H), 4.77 (s, 1H), 4.18 (s, 1H), 3.78 (s, 3H), 3.66 (dd, *J* = 16.6, 8.5 Hz, 1H), 3.35 (td, *J* = 9.6, 3.0 Hz, 1H), 2.66 (d, *J* = 16.1 Hz, 1H), 2.63 – 2.57 (m, 1H), 2.43 (ddd, *J* = 13.5, 8.6, 3.0 Hz, 1H), 1.79 (ddd, *J* = 13.6, 9.7, 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.10, 156.90, 143.71, 139.32, 132.30, 129.94, 128.55, 128.49, 127.51, 127.32, 122.57, 117.88, 114.04, 114.01, 59.43, 55.57, 48.29, 46.35, 38.73, 24.70. IR (Neat Film, NaCl) 2931, 1690, 1587, 1559, 1512, 1454, 1427, 1399, 1297, 1250, 1181, 1120, 1084, 1033, 909, 829, 768, 730, 692 cm^{-1}; (MM:ESI^{+}) : $C_{25}H_{25}N_2O_2$ *m/z* calc'd for $[M+H]^{+}$ 385.1911, found 385.1906.



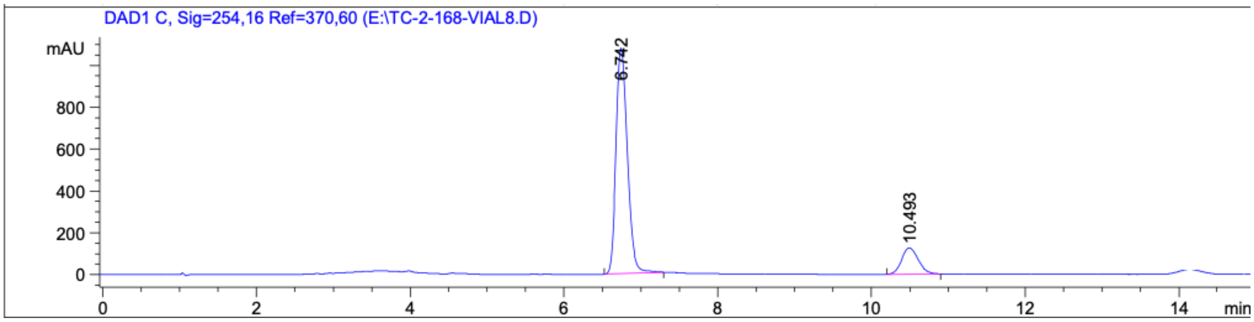
(*S*)-1-(4-methoxyphenyl)-2'-phenyl-4'*H*-spiro[pyrrolidine-3,3'-quinolin]-2-one (18): ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.96, 157.21, 153.58, 146.38, 145.78, 132.17, 128.63, 128.52, 128.27, 128.08, 127.81, 122.11, 119.84, 114.33, 113.95, 55.65, 45.83, 34.53, 30.95, 28.41; (MM:ESI^{+}) : $C_{25}H_{23}N_2O_2$ *m/z* calc'd for $[M+H]^{+}$ 383.1754, found 383.1763.

General Procedure 9: Asymmetric Mannich reaction variation using K-Box catalyst



(*S)-3-((*R**)-amino(phenyl)methyl)-1-(4-methoxyphenyl)-3-methylpyrrolidin-2-one (4a):** $B(C_6F_5)_3$ (4 mg, 0.009 mmol, 0.06 equiv) was added to a solution of H-$SiMe_2Ph$ (112 µL, 0.8 mmol, 4.0 equiv) in toluene (1 mL). Benzonitrile **6a** (55 µL, 0.6 mmol, 3.0 equiv) was added to the reaction mixture and stirred at ambient temperature for 1 hour. Meanwhile, a vial containing bis((3a*R*,8a*S*)-3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazol-2-yl)methane (**L1**, 9.9 mg, 0.03 mmol, 0.15 equiv) and KHMDS (6 mg, 0.03 mmol, 0.15 equiv) cooled to 0 °C and dissolved in THF (0.75 mL). This mixture was allowed to stir for 30 minutes. Meanwhile, *N*-PMP lactam **2a** (42 mg, 0.2 mmol, 1.0 equiv) was added to a solution of potassium *tert*-butoxide (7 mg, 0.07 mmol, 0.35 equiv) in toluene (2 mL) and cooled to –78 °C. After the K-Box catalyst generation, that mixture was added to the lactam mixture at –78 °C and allowed to stir for 15 minutes. After the 1 hr hydrosilylation, the yellow imine mixture **3a** was added to the cooled reaction mixture at –78 °C dropwise. The reaction mixture was stirred at –78 °C for 2 hours and allowed to warm to ambient temperature overnight. The reaction was quenched with 1 N HCl (4 mL) and diluted with EtOAc (10 mL) and stirred vigorously for 1 hour at ambient temperature. The aqueous layer was separated and extracted with EtOAc (2 x 4 mL) The combined organic layer can be purified to recover any unreacted lactam or aryl nitrile. The aqueous layer was basified with a saturated solution of $NaHCO_3$ (6 mL) and diluted with EtOAc (10 mL). The biphasic mixture was stirred vigorously for 1 hour at ambient temperature. The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated by rotary evaporation. The crude oil was purified by column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4a** as a pale-yellow oil (59 mg, 0.193 mmol, 96% yield, 15:1 dr, 71% ee); The characterization data matches the data acquired from the product obtained using General Procedure 5.

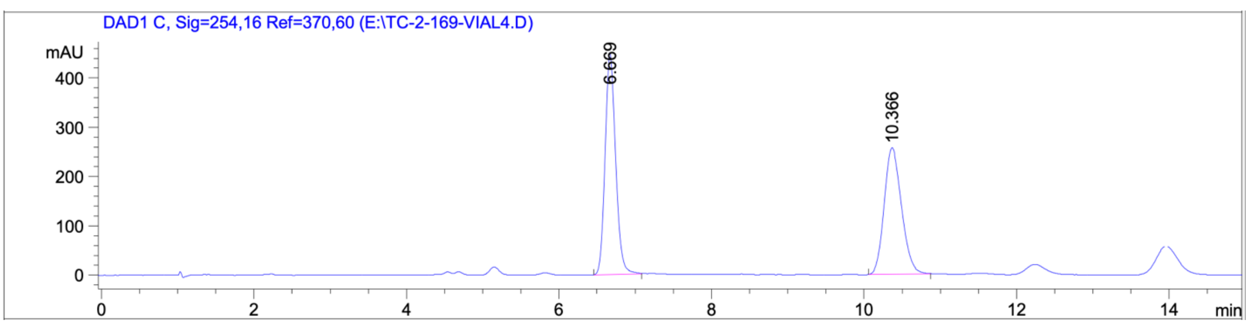
Chiral SFC Separation: 15% MeOH, 2.5 mL/min, Ad-H column, l = 254 nm, t_R (min): major = 6.742 (area: 85.4 %), minor = 10.493 (area: 14.6%), 71% enantiomeric excess.



Signal 2: DAD1 C, Sig=254,16 Ref=370,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.742	BB	0.1595	1.10366e4	1077.60669	85.3901
2	10.493	BB	0.2335	1888.31653	125.52642	14.6099

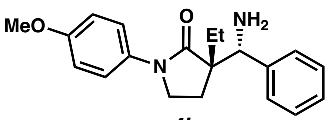
Totals : 1.29249e4 1203.13311



Signal 2: DAD1 C, Sig=254,16 Ref=370,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.669	BB	0.1513	4368.49756	449.97144	51.8515
2	10.366	BB	0.2462	4056.52686	256.88638	48.1485

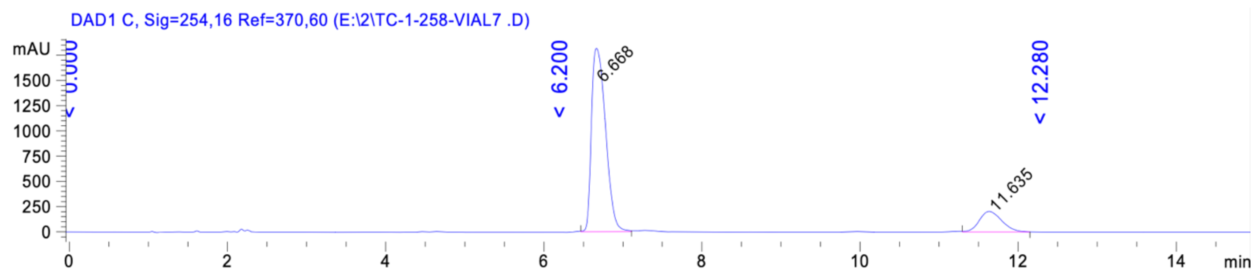
Totals : 8425.02441 706.85782

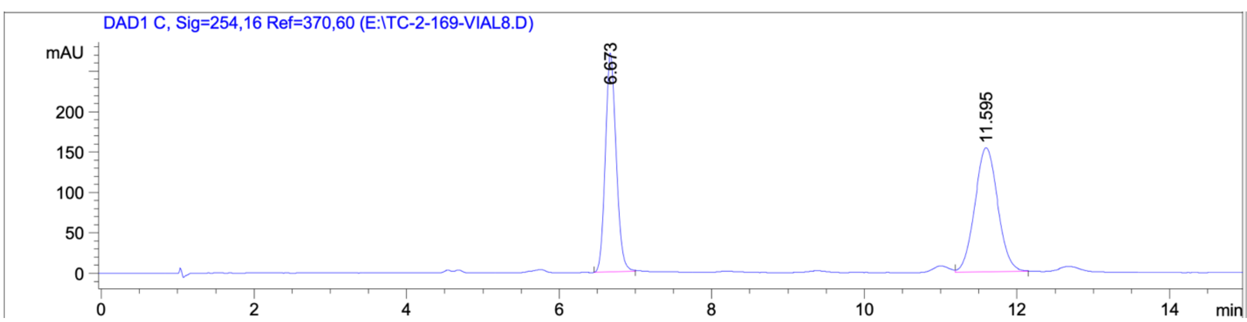


4b

(*S)-3-((*R**)-amino(phenyl)methyl)-3-ethyl-1-(4-methoxyphenyl)pyrrolidin-2-one (4b):** Compound **4b** was prepared from *N*-PMP lactam **2b** using General procedure 6. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4b** as a pale-yellow oil (59 mg, 0.18 mmol, 90% yield, 13:1 dr, 72% ee); The characterization data matches the data acquired from the product obtained using General Procedure 5.

Chiral SFC Separation: 15% MeOH, 2.5 mL/min, Ad-H column, l = 254 nm, t_R (min): major = 6.668 (area: 84.8 %), minor = 11.635 (area: 15.2%), 71% enantiomeric excess



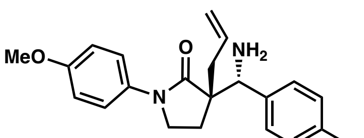


Signal 2: DAD1 C, Sig=254,16 Ref=370,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.668	BB	0.2007	2.25236e4	1816.11169	84.7938
2	11.635	BB	0.3064	4039.20508	204.50429	15.2062
Totals :				2.65628e4	2020.61598	

Signal 1: DAD1 A, Sig=210,16 Ref=370,60

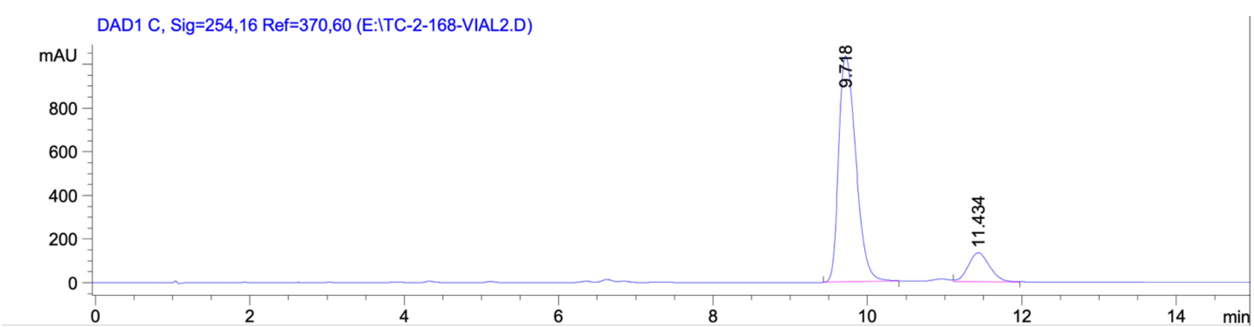
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.673	BB	0.1570	2561.90527	251.17792	45.2068
2	11.594	VB	0.3240	3105.17358	146.09259	54.7932
Totals :				5667.07886	397.27051	



4w

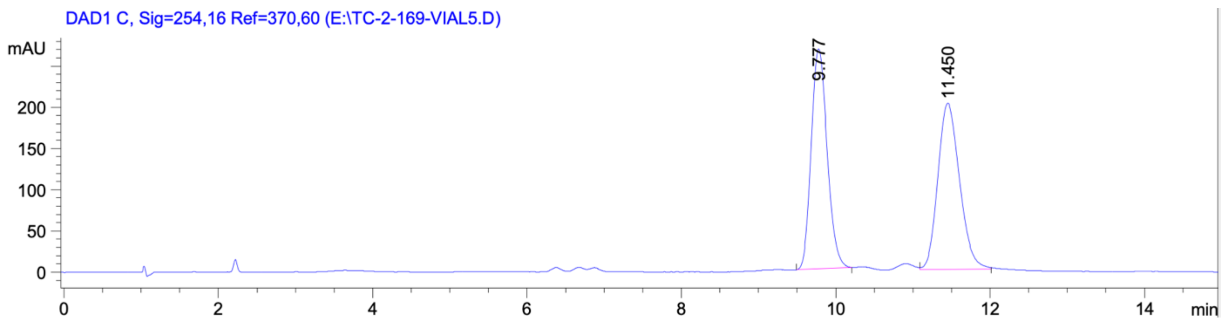
(*S)-3-allyl-3-((*R**)-amino(4-bromophenyl)methyl)-1-(4-methoxyphenyl)pyrrolidin-2-one (4w):** Compound **4w** was prepared from 4-bromobenzonitrile **6n** using General Procedure 7. The crude oil was purified from column chromatography (3% MeOH in EtOAc, 1% TEA) to afford Mannich product **4w** as a pale-yellow oil (77 mg, 0.188 mmol, 94% yield, 12:1 dr, 72% ee). The characterization data matches the data acquired from the product obtained using General Procedure 6.

Chiral SFC Separation: 15% MeOH, 2.5 mL/min, Ad-H column, l = 254 nm, t_R (min): major = 9.718 (area: 86.4%), minor = 11.434 (area: 13.6 %), 72% enantiomeric excess



Signal 2: DAD1 C, Sig=254,16 Ref=370,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.718	BB	0.2401	1.59876e4	1035.56470	86.3745
2	11.434	VB	0.2963	2522.04712	132.35289	13.6255
Totals :				1.85097e4	1167.91759	



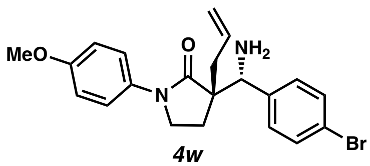
Signal 2: DAD1 C, Sig=254,16 Ref=370,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.777	BB	0.2230	3819.15820	266.85037	49.2843
2	11.450	VB	0.3033	3930.07300	201.68221	50.7157
Totals :				7749.23120	468.53258	

References:

(7) Hayashi, M.; Bachman, S.; Hashimoto, S.; Eichman, C. C.; Stoltz, B. M. Ni-Catalyzed Enantioselective C-Acylation of α-Substituted Lactams. *J. Am. Chem. Soc.* **2016**, *138* (29), 8997–9000.

(8) Jette, C. I.; Geibel, I.; Bachman, S.; Hayashi, M.; Sakurai, S.; Shimizu, H.; Morgan, J. B.; Stoltz, B. M. Palladium-Catalyzed Construction of Quaternary Stereocenters by Enantioselective Arylation of γ-Lactams with Aryl Chlorides and Bromides. *Angew. Chem. Int. Ed.* **2019**, *58* (13), 4297–4301.



4w

The crystal structure of **4w** was registered in the Cambridge crystallographic data center and can be found as CCDC# 2253010

Experimental details for **4w**

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS KAPPA APEX II diffractometer coupled to an PHOTON 100 CMOS detector with graphite monochromated Mo K_α radiation (λ = 0.71073 Å) for the structure of compound D21009. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2017 using established refinement techniques. All non-hydrogen atoms were refined anisotropically. Unless otherwise noted, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).
Compound D21009 crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. The coordinates for the hydrogen atoms bound to N2 were located in the difference Fourier synthesis and refined semi-freely with the help of a restraint on the N-H distance (0.91(4) Å).

Table 1. Crystal data and structure refinement for D21009.

Identification code	D21009	
Empirical formula	C21 H23 Br N2 O2	
Formula weight	415.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.430(3) Å	a= 90°.
	b = 9.489(2) Å	b= 93.651(18)°.
	c = 21.189(5) Å	g = 90°.
Volume	1892.2(9) Å^3	
Z	4	
Density (calculated)	1.458 Mg/m^3	

Absorption coefficient	2.190 mm^{-1}
F(000)	856
Crystal size	0.500 x 0.300 x 0.300 mm^3
Theta range for data collection	1.926 to 36.430°.
Index ranges	-15<=h<=15, -15<=k<=15, -35<=l<=35
Reflections collected	53031
Independent reflections	9140 [R(int) = 0.0291]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7471 and 0.5241
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9140 / 2 / 242
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0267, wR2 = 0.0680
R indices (all data)	R1 = 0.0342, wR2 = 0.0710
Extinction coefficient	n/a
Largest diff. peak and hole	0.656 and -0.498 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for D21009. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	8230(1)	6655(1)	5441(1)	14(1)
C(1)	8442(1)	7918(1)	5154(1)	13(1)
O(1)	8819(1)	9011(1)	5422(1)	17(1)
C(2)	8070(1)	7776(1)	4446(1)	12(1)
C(5)	6679(1)	8602(1)	4295(1)	16(1)
C(6)	5492(1)	8192(1)	4695(1)	18(1)
C(7)	4282(1)	7615(1)	4474(1)	22(1)
C(8)	9294(1)	8437(1)	4089(1)	12(1)
N(2)	10651(1)	7820(1)	4338(1)	17(1)
C(3)	7908(1)	6181(1)	4351(1)	16(1)
C(4)	7639(1)	5576(1)	5003(1)	16(1)
C(11)	8328(1)	6449(1)	6104(1)	13(1)
C(12)	7326(1)	5631(1)	6388(1)	16(1)
C(13)	7406(1)	5413(1)	7040(1)	17(1)
C(14)	8500(1)	6034(1)	7412(1)	15(1)
O(2)	8695(1)	5880(1)	8053(1)	19(1)
C(17)	7799(1)	4889(1)	8345(1)	21(1)
C(15)	9514(1)	6853(1)	7129(1)	16(1)
C(16)	9437(1)	7054(1)	6480(1)	16(1)
C(21)	9093(1)	8247(1)	3379(1)	12(1)
C(22)	9536(1)	7023(1)	3080(1)	15(1)
C(23)	9351(1)	6867(1)	2427(1)	15(1)
C(24)	8731(1)	7954(1)	2070(1)	14(1)
Br(1)	8522(1)	7739(1)	1178(1)	19(1)
C(25)	8286(1)	9187(1)	2350(1)	16(1)
C(26)	8473(1)	9320(1)	3003(1)	15(1)

Table 3. Bond lengths [Å] and angles [°] for D21009.

N(1)-C(1)	1.3643(11)
N(1)-C(11)	1.4161(12)
N(1)-C(4)	1.4671(12)
C(1)-O(1)	1.2236(10)
C(1)-C(2)	1.5262(13)
C(2)-C(3)	1.5333(12)
C(2)-C(5)	1.5441(13)
C(2)-C(8)	1.5522(12)
C(5)-C(6)	1.4984(13)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7)	1.3239(14)
C(6)-H(6)	0.9500
C(7)-H(7A)	0.9500
C(7)-H(7B)	0.9500
C(8)-N(2)	1.4736(12)
C(8)-C(21)	1.5133(12)
C(8)-H(8)	1.0000
N(2)-H(2N1)	0.892(13)
N(2)-H(2N2)	0.909(14)
C(3)-C(4)	1.5319(13)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(11)-C(12)	1.3890(12)
C(11)-C(16)	1.3969(13)
C(12)-C(13)	1.3948(13)
C(12)-H(12)	0.9500
C(13)-C(14)	1.3896(14)
C(13)-H(13)	0.9500
C(14)-O(2)	1.3658(11)
C(14)-C(15)	1.3956(13)
O(2)-C(17)	1.4311(13)

C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(15)-C(16)	1.3860(13)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(21)-C(26)	1.3978(12)
C(21)-C(22)	1.4005(12)
C(22)-C(23)	1.3903(13)
C(22)-H(22)	0.9500
C(23)-C(24)	1.3864(13)
C(23)-H(23)	0.9500
C(24)-C(25)	1.3891(12)
C(24)-Br(1)	1.8983(10)
C(25)-C(26)	1.3912(13)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500

C(1)-N(1)-C(11)	124.10(7)
C(1)-N(1)-C(4)	113.08(7)
C(11)-N(1)-C(4)	121.98(7)
O(1)-C(1)-N(1)	125.77(8)
O(1)-C(1)-C(2)	124.93(8)
N(1)-C(1)-C(2)	109.24(7)
C(1)-C(2)-C(3)	103.31(7)
C(1)-C(2)-C(5)	107.31(7)
C(3)-C(2)-C(5)	113.44(7)
C(1)-C(2)-C(8)	108.23(7)
C(3)-C(2)-C(8)	114.00(7)
C(5)-C(2)-C(8)	110.02(7)
C(6)-C(5)-C(2)	113.98(8)
C(6)-C(5)-H(5A)	108.8
C(2)-C(5)-H(5A)	108.8
C(6)-C(5)-H(5B)	108.8
C(2)-C(5)-H(5B)	108.8
H(5A)-C(5)-H(5B)	107.7

C(7)-C(6)-C(5)	124.43(9)
C(7)-C(6)-H(6)	117.8
C(5)-C(6)-H(6)	117.8
C(6)-C(7)-H(7A)	120.0
C(6)-C(7)-H(7B)	120.0
H(7A)-C(7)-H(7B)	120.0
N(2)-C(8)-C(21)	111.07(7)
N(2)-C(8)-C(2)	108.67(7)
C(21)-C(8)-C(2)	112.68(7)
N(2)-C(8)-H(8)	108.1
C(21)-C(8)-H(8)	108.1
C(2)-C(8)-H(8)	108.1
C(8)-N(2)-H(2N1)	110.0(10)
C(8)-N(2)-H(2N2)	112.8(11)
H(2N1)-N(2)-H(2N2)	100.0(14)
C(4)-C(3)-C(2)	105.86(7)
C(4)-C(3)-H(3A)	110.6
C(2)-C(3)-H(3A)	110.6
C(4)-C(3)-H(3B)	110.6
C(2)-C(3)-H(3B)	110.6
H(3A)-C(3)-H(3B)	108.7
N(1)-C(4)-C(3)	103.35(7)
N(1)-C(4)-H(4A)	111.1
C(3)-C(4)-H(4A)	111.1
N(1)-C(4)-H(4B)	111.1
C(3)-C(4)-H(4B)	111.1
H(4A)-C(4)-H(4B)	109.1
C(12)-C(11)-C(16)	119.25(8)
C(12)-C(11)-N(1)	120.15(8)
C(16)-C(11)-N(1)	120.60(8)
C(11)-C(12)-C(13)	121.04(8)
C(11)-C(12)-H(12)	119.5
C(13)-C(12)-H(12)	119.5
C(14)-C(13)-C(12)	119.40(8)
C(14)-C(13)-H(13)	120.3
C(12)-C(13)-H(13)	120.3

O(2)-C(14)-C(13)	124.54(8)
O(2)-C(14)-C(15)	115.67(8)
C(13)-C(14)-C(15)	119.77(8)
C(14)-O(2)-C(17)	117.01(8)
O(2)-C(17)-H(17A)	109.5
O(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
O(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(15)-C(14)	120.58(8)
C(16)-C(15)-H(15)	119.7
C(14)-C(15)-H(15)	119.7
C(15)-C(16)-C(11)	119.95(8)
C(15)-C(16)-H(16)	120.0
C(11)-C(16)-H(16)	120.0
C(26)-C(21)-C(22)	118.13(8)
C(26)-C(21)-C(8)	120.03(7)
C(22)-C(21)-C(8)	121.83(8)
C(23)-C(22)-C(21)	121.14(8)
C(23)-C(22)-H(22)	119.4
C(21)-C(22)-H(22)	119.4
C(24)-C(23)-C(22)	119.08(8)
C(24)-C(23)-H(23)	120.5
C(22)-C(23)-H(23)	120.5
C(23)-C(24)-C(25)	121.45(8)
C(23)-C(24)-Br(1)	118.52(6)
C(25)-C(24)-Br(1)	120.03(7)
C(24)-C(25)-C(26)	118.61(8)
C(24)-C(25)-H(25)	120.7
C(26)-C(25)-H(25)	120.7
C(25)-C(26)-C(21)	121.58(8)
C(25)-C(26)-H(26)	119.2
C(21)-C(26)-H(26)	119.2

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for D21009. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	19(1)	12(1)	11(1)	0(1)	-1(1)	-4(1)
C(1)	14(1)	12(1)	12(1)	0(1)	1(1)	-3(1)
O(1)	23(1)	13(1)	15(1)	-3(1)	2(1)	-6(1)
C(2)	14(1)	11(1)	12(1)	0(1)	1(1)	-3(1)
C(5)	13(1)	19(1)	16(1)	3(1)	2(1)	-2(1)
C(6)	14(1)	23(1)	16(1)	3(1)	2(1)	-2(1)
C(7)	15(1)	27(1)	24(1)	7(1)	0(1)	-4(1)
C(8)	12(1)	12(1)	13(1)	0(1)	1(1)	-2(1)
N(2)	14(1)	20(1)	17(1)	0(1)	-1(1)	0(1)
C(3)	24(1)	13(1)	13(1)	-1(1)	1(1)	-6(1)
C(4)	22(1)	12(1)	14(1)	0(1)	-1(1)	-6(1)
C(11)	15(1)	14(1)	12(1)	1(1)	0(1)	-1(1)
C(12)	16(1)	19(1)	14(1)	1(1)	0(1)	-5(1)
C(13)	17(1)	20(1)	14(1)	1(1)	3(1)	-3(1)
C(14)	16(1)	15(1)	12(1)	1(1)	1(1)	2(1)
O(2)	25(1)	20(1)	11(1)	1(1)	1(1)	-1(1)
C(17)	25(1)	24(1)	15(1)	3(1)	7(1)	1(1)
C(15)	16(1)	18(1)	14(1)	1(1)	-2(1)	-2(1)
C(16)	15(1)	18(1)	14(1)	2(1)	-1(1)	-4(1)
C(21)	12(1)	11(1)	13(1)	0(1)	2(1)	-1(1)
C(22)	17(1)	12(1)	15(1)	1(1)	3(1)	2(1)
C(23)	17(1)	13(1)	15(1)	0(1)	4(1)	3(1)
C(24)	16(1)	14(1)	12(1)	0(1)	3(1)	1(1)
Br(1)	28(1)	18(1)	12(1)	0(1)	3(1)	4(1)
C(25)	22(1)	14(1)	14(1)	2(1)	3(1)	4(1)
C(26)	19(1)	12(1)	14(1)	0(1)	3(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for D21009.

	x	y	z	U(eq)
H(5A)	6873	9621	4354	19
H(5B)	6368	8452	3845	19
H(6)	5616	8357	5137	21
H(7A)	4123	7435	4034	26
H(7B)	3573	7380	4755	26
H(8)	9320	9471	4180	15
H(2N1)	11033(16)	8353(16)	4651(7)	25
H(2N2)	11345(16)	7879(17)	4060(8)	25
H(3A)	7099	5970	4045	20
H(3B)	8783	5774	4192	20
H(4A)	6610	5442	5051	19
H(4B)	8132	4663	5073	19
H(12)	6573	5214	6133	20
H(13)	6719	4844	7228	21
H(17A)	6805	5182	8275	32
H(17B)	8056	4852	8800	32
H(17C)	7923	3954	8160	32
H(15)	10262	7275	7384	19
H(16)	10139	7602	6291	19
H(22)	9970	6286	3326	17
H(23)	9646	6028	2229	18
H(25)	7863	9925	2100	19
H(26)	8171	10159	3199	18

Table 6. Torsion angles [°] for D21009.

C(11)-N(1)-C(1)-O(1)	4.40(14)
C(4)-N(1)-C(1)-O(1)	174.10(9)
C(11)-N(1)-C(1)-C(2)	-173.11(8)
C(4)-N(1)-C(1)-C(2)	-3.42(10)
O(1)-C(1)-C(2)-C(3)	171.34(9)
N(1)-C(1)-C(2)-C(3)	-11.12(9)
O(1)-C(1)-C(2)-C(5)	-68.54(11)
N(1)-C(1)-C(2)-C(5)	109.00(8)
O(1)-C(1)-C(2)-C(8)	50.15(11)
N(1)-C(1)-C(2)-C(8)	-132.31(7)
C(1)-C(2)-C(5)-C(6)	-53.25(10)
C(3)-C(2)-C(5)-C(6)	60.20(10)
C(8)-C(2)-C(5)-C(6)	-170.78(8)
C(2)-C(5)-C(6)-C(7)	-116.39(11)
C(1)-C(2)-C(8)-N(2)	51.73(9)
C(3)-C(2)-C(8)-N(2)	-62.58(9)
C(5)-C(2)-C(8)-N(2)	168.70(7)
C(1)-C(2)-C(8)-C(21)	175.27(7)
C(3)-C(2)-C(8)-C(21)	60.95(10)
C(5)-C(2)-C(8)-C(21)	-67.77(9)
C(1)-C(2)-C(3)-C(4)	20.57(9)
C(5)-C(2)-C(3)-C(4)	-95.27(9)
C(8)-C(2)-C(3)-C(4)	137.77(8)
C(1)-N(1)-C(4)-C(3)	16.44(10)
C(11)-N(1)-C(4)-C(3)	-173.62(8)
C(2)-C(3)-C(4)-N(1)	-22.45(10)
C(1)-N(1)-C(11)-C(12)	137.17(9)
C(4)-N(1)-C(11)-C(12)	-31.65(13)
C(1)-N(1)-C(11)-C(16)	-43.40(13)
C(4)-N(1)-C(11)-C(16)	147.79(9)
C(16)-C(11)-C(12)-C(13)	0.39(14)
N(1)-C(11)-C(12)-C(13)	179.83(9)
C(11)-C(12)-C(13)-C(14)	0.55(15)
C(12)-C(13)-C(14)-O(2)	-179.15(9)

C(12)-C(13)-C(14)-C(15)	-0.80(14)
C(13)-C(14)-O(2)-C(17)	7.12(13)
C(15)-C(14)-O(2)-C(17)	-171.29(8)
O(2)-C(14)-C(15)-C(16)	178.62(8)
C(13)-C(14)-C(15)-C(16)	0.13(14)
C(14)-C(15)-C(16)-C(11)	0.81(14)
C(12)-C(11)-C(16)-C(15)	-1.06(14)
N(1)-C(11)-C(16)-C(15)	179.49(9)
N(2)-C(8)-C(21)-C(26)	-141.92(8)
C(2)-C(8)-C(21)-C(26)	95.89(9)
N(2)-C(8)-C(21)-C(22)	36.94(11)
C(2)-C(8)-C(21)-C(22)	-85.25(10)
C(26)-C(21)-C(22)-C(23)	-0.73(13)
C(8)-C(21)-C(22)-C(23)	-179.61(8)
C(21)-C(22)-C(23)-C(24)	0.71(13)
C(22)-C(23)-C(24)-C(25)	-0.30(14)
C(22)-C(23)-C(24)-Br(1)	178.74(7)
C(23)-C(24)-C(25)-C(26)	-0.06(14)
Br(1)-C(24)-C(25)-C(26)	-179.09(7)
C(24)-C(25)-C(26)-C(21)	0.03(14)
C(22)-C(21)-C(26)-C(25)	0.35(13)
C(8)-C(21)-C(26)-C(25)	179.25(8)

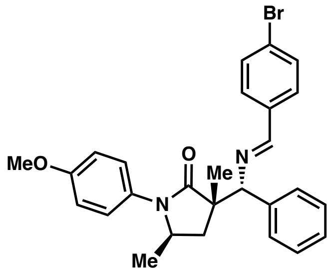
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for D21009 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(8)-H(8)...O(1)#1	1.00	2.38	3.1416(12)	132.1
N(2)-H(2N1)...O(1)#1	0.892(13)	2.511(16)	3.0855(13)	122.6(13)
C(17)-H(17B)...O(1)#2	0.98	2.62	3.2190(14)	119.7
C(23)-H(23)...O(2)#3	0.95	2.49	3.3858(13)	157.1

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,-z+1 #2 -x+3/2,y-1/2,-z+3/2 #3 -x+2,-y+1,-z+1



SI2

The crystal structure of **SI2** was registered in the Cambridge crystallographic data center and can be found as CCDC 2253013

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON II CPAD detector with Cu K_α radiation (λ = 1.54178 Å) from an IμS micro-source for the structure of compound V20240. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2017 using established refinement techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups).

Compound V20240 crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the asymmetric unit. The crystal is not stable at lower temperatures and the data was collected at 200K.

Table 8. Crystal data and structure refinement for V20240.

Identification code	V20240	
Empirical formula	C27 H27 Br N2 O2	
Formula weight	491.41	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.8500(11) Å	a= 90°.
	b = 49.858(4) Å	b= 90.083(7)°.
	c = 8.0771(10) Å	g = 90°.
Volume	4772.1(8) Å^3	
Z	8	
Density (calculated)	1.368 Mg/m^3	
Absorption coefficient	2.548 mm^{-1}	
F(000)	2032	
Crystal size	0.300 x 0.250 x 0.050 mm^3	

Theta range for data collection	3.546 to 74.545°.
Index ranges	-14<=h<=14, -62<=k<=62, -9<=l<=10
Reflections collected	75046
Independent reflections	9652 [R(int) = 0.0709]
Completeness to theta = 67.679°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7538 and 0.4919
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9652 / 0 / 583
Goodness-of-fit on F^2	1.149
Final R indices [I>2sigma(I)]	R1 = 0.0679, wR2 = 0.1654
R indices (all data)	R1 = 0.0732, wR2 = 0.1686
Extinction coefficient	n/a
Largest diff. peak and hole	1.211 and -0.757 e.Å^{-3}

Table 9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for V20240. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	3314(3)	1358(1)	2404(4)	33(1)
C(11)	3013(3)	1088(1)	1978(5)	31(1)
C(12)	2057(3)	1035(1)	1048(5)	34(1)
C(13)	1748(3)	771(1)	684(5)	34(1)
C(14)	2413(3)	562(1)	1246(5)	33(1)
O(2)	2215(2)	295(1)	957(4)	42(1)
C(17)	1255(5)	225(1)	23(8)	64(2)
C(15)	3362(3)	617(1)	2186(5)	38(1)
C(16)	3664(3)	877(1)	2558(5)	37(1)
C(1)	2622(3)	1522(1)	3282(5)	33(1)
O(1)	1619(2)	1488(1)	3541(4)	40(1)
C(2)	3329(3)	1753(1)	3990(5)	34(1)
C(5)	2701(4)	2018(1)	3839(6)	46(1)
C(6)	3497(3)	1678(1)	5860(5)	31(1)
C(21)	4009(3)	1902(1)	6899(5)	32(1)
C(22)	5144(3)	1968(1)	6879(5)	37(1)
C(23)	5558(4)	2170(1)	7894(6)	44(1)
C(24)	4857(4)	2306(1)	8962(5)	48(1)
C(25)	3728(4)	2240(1)	9013(6)	52(1)
C(26)	3306(4)	2041(1)	7989(6)	43(1)
N(2)	4233(3)	1440(1)	5976(4)	30(1)
C(7)	3812(3)	1236(1)	6687(4)	31(1)
C(31)	4457(3)	986(1)	6876(4)	30(1)
C(32)	5529(3)	955(1)	6229(5)	34(1)
C(33)	6128(3)	719(1)	6433(5)	37(1)
C(34)	5633(3)	511(1)	7316(5)	33(1)
Br(1)	6462(1)	190(1)	7684(1)	47(1)
C(35)	4570(4)	534(1)	7954(5)	39(1)
C(36)	3973(4)	771(1)	7725(5)	39(1)
C(3)	4401(3)	1742(1)	2950(5)	36(1)
C(4)	4490(3)	1455(1)	2267(5)	34(1)

C(8)	4896(4)	1443(1)	485(5)	44(1)
N(201)	9412(3)	1360(1)	-2554(4)	35(1)
C(211)	9711(3)	1091(1)	-2970(5)	34(1)
C(212)	9050(3)	879(1)	-2431(5)	38(1)
C(213)	9334(3)	618(1)	-2792(5)	38(1)
C(214)	10298(3)	566(1)	-3726(5)	35(1)
O(202)	10490(3)	299(1)	-4048(4)	45(1)
C(217)	11414(5)	233(1)	-5088(7)	62(1)
C(215)	10976(3)	774(1)	-4267(5)	37(1)
C(216)	10669(3)	1039(1)	-3895(5)	36(1)
C(201)	10110(3)	1527(1)	-1683(5)	33(1)
O(201)	11119(2)	1493(1)	-1448(4)	39(1)
C(202)	9405(3)	1757(1)	-978(5)	34(1)
C(205)	10040(4)	2023(1)	-1132(6)	47(1)
C(206)	9246(3)	1683(1)	894(5)	32(1)
C(221)	8727(3)	1907(1)	1943(5)	35(1)
C(222)	7591(3)	1969(1)	1908(5)	39(1)
C(223)	7156(4)	2169(1)	2921(6)	46(1)
C(224)	7863(4)	2308(1)	3990(6)	50(1)
C(225)	8990(4)	2244(1)	4048(6)	53(1)
C(226)	9424(4)	2045(1)	3030(6)	46(1)
N(202)	8528(3)	1444(1)	1018(4)	32(1)
C(207)	8962(3)	1240(1)	1713(4)	32(1)
C(231)	8320(3)	989(1)	1888(4)	31(1)
C(232)	8844(4)	767(1)	2627(5)	42(1)
C(233)	8246(4)	528(1)	2840(6)	46(1)
C(234)	7158(4)	511(1)	2269(5)	38(1)
Br(2)	6311(1)	193(1)	2601(1)	61(1)
C(235)	6628(4)	726(1)	1500(5)	42(1)
C(236)	7225(3)	962(1)	1317(5)	39(1)
C(203)	8322(3)	1744(1)	-2017(5)	38(1)
C(204)	8239(3)	1458(1)	-2693(5)	36(1)
C(208)	7826(4)	1444(1)	-4468(5)	46(1)

Table 10. Bond lengths [Å] and angles [°] for V20240.

N(1)-C(1)	1.358(5)
N(1)-C(11)	1.434(5)
N(1)-C(4)	1.479(5)
C(11)-C(12)	1.384(5)
C(11)-C(16)	1.384(5)
C(12)-C(13)	1.397(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.383(5)
C(13)-H(13)	0.9500
C(14)-O(2)	1.375(4)
C(14)-C(15)	1.382(5)
O(2)-C(17)	1.406(5)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(15)-C(16)	1.380(5)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(1)-O(1)	1.219(5)
C(1)-C(2)	1.535(5)
C(2)-C(5)	1.522(5)
C(2)-C(3)	1.525(6)
C(2)-C(6)	1.568(5)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-N(2)	1.476(4)
C(6)-C(21)	1.523(5)
C(6)-H(6)	1.0000
C(21)-C(22)	1.385(5)
C(21)-C(26)	1.395(6)
C(22)-C(23)	1.388(5)
C(22)-H(22)	0.9500
C(23)-C(24)	1.378(7)

C(23)-H(23)	0.9500
C(24)-C(25)	1.378(7)
C(24)-H(24)	0.9500
C(25)-C(26)	1.388(6)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
N(2)-C(7)	1.272(5)
C(7)-C(31)	1.470(5)
C(7)-H(7)	0.9500
C(31)-C(32)	1.383(5)
C(31)-C(36)	1.394(5)
C(32)-C(33)	1.385(5)
C(32)-H(32)	0.9500
C(33)-C(34)	1.388(5)
C(33)-H(33)	0.9500
C(34)-C(35)	1.367(6)
C(34)-Br(1)	1.901(4)
C(35)-C(36)	1.390(6)
C(35)-H(35)	0.9500
C(36)-H(36)	0.9500
C(3)-C(4)	1.538(5)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(8)	1.519(6)
C(4)-H(4)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
N(201)-C(201)	1.368(5)
N(201)-C(211)	1.425(5)
N(201)-C(204)	1.476(5)
C(211)-C(216)	1.384(5)
C(211)-C(212)	1.387(5)
C(212)-C(213)	1.377(6)
C(212)-H(212)	0.9500
C(213)-C(214)	1.395(6)

C(213)-H(213)	0.9500
C(214)-O(202)	1.376(5)
C(214)-C(215)	1.385(6)
O(202)-C(217)	1.419(5)
C(217)-H(21A)	0.9800
C(217)-H(21B)	0.9800
C(217)-H(21C)	0.9800
C(215)-C(216)	1.403(5)
C(215)-H(215)	0.9500
C(216)-H(216)	0.9500
C(201)-O(201)	1.222(5)
C(201)-C(202)	1.531(5)
C(202)-C(205)	1.530(5)
C(202)-C(203)	1.534(5)
C(202)-C(206)	1.568(5)
C(205)-H(20A)	0.9800
C(205)-H(20B)	0.9800
C(205)-H(20C)	0.9800
C(206)-N(202)	1.470(5)
C(206)-C(221)	1.528(5)
C(206)-H(206)	1.0000
C(221)-C(222)	1.382(6)
C(221)-C(226)	1.387(6)
C(222)-C(223)	1.389(6)
C(222)-H(222)	0.9500
C(223)-C(224)	1.390(7)
C(223)-H(223)	0.9500
C(224)-C(225)	1.374(7)
C(224)-H(224)	0.9500
C(225)-C(226)	1.389(7)
C(225)-H(225)	0.9500
C(226)-H(226)	0.9500
N(202)-C(207)	1.270(5)
C(207)-C(231)	1.472(5)
C(207)-H(207)	0.9500
C(231)-C(236)	1.383(5)

C(231)-C(232)	1.400(5)
C(232)-C(233)	1.396(6)
C(232)-H(232)	0.9500
C(233)-C(234)	1.371(6)
C(233)-H(233)	0.9500
C(234)-C(235)	1.385(6)
C(234)-Br(2)	1.897(4)
C(235)-C(236)	1.385(6)
C(235)-H(235)	0.9500
C(236)-H(236)	0.9500
C(203)-C(204)	1.533(5)
C(203)-H(20D)	0.9900
C(203)-H(20E)	0.9900
C(204)-C(208)	1.516(6)
C(204)-H(204)	1.0000
C(208)-H(20F)	0.9800
C(208)-H(20G)	0.9800
C(208)-H(20H)	0.9800

C(1)-N(1)-C(11)	122.7(3)
C(1)-N(1)-C(4)	114.4(3)
C(11)-N(1)-C(4)	121.4(3)
C(12)-C(11)-C(16)	119.6(3)
C(12)-C(11)-N(1)	120.7(3)
C(16)-C(11)-N(1)	119.6(3)
C(11)-C(12)-C(13)	120.5(3)
C(11)-C(12)-H(12)	119.8
C(13)-C(12)-H(12)	119.8
C(14)-C(13)-C(12)	119.5(3)
C(14)-C(13)-H(13)	120.3
C(12)-C(13)-H(13)	120.3
O(2)-C(14)-C(15)	115.0(3)
O(2)-C(14)-C(13)	125.3(3)
C(15)-C(14)-C(13)	119.6(3)
C(14)-O(2)-C(17)	117.9(3)
O(2)-C(17)-H(17A)	109.5

O(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
O(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(15)-C(14)	121.0(3)
C(16)-C(15)-H(15)	119.5
C(14)-C(15)-H(15)	119.5
C(15)-C(16)-C(11)	119.7(3)
C(15)-C(16)-H(16)	120.1
C(11)-C(16)-H(16)	120.1
O(1)-C(1)-N(1)	126.5(3)
O(1)-C(1)-C(2)	125.0(4)
N(1)-C(1)-C(2)	108.5(3)
C(5)-C(2)-C(3)	113.3(3)
C(5)-C(2)-C(1)	110.8(3)
C(3)-C(2)-C(1)	102.8(3)
C(5)-C(2)-C(6)	110.2(3)
C(3)-C(2)-C(6)	114.7(3)
C(1)-C(2)-C(6)	104.4(3)
C(2)-C(5)-H(5A)	109.5
C(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(2)-C(6)-C(21)	108.6(3)
N(2)-C(6)-C(2)	109.1(3)
C(21)-C(6)-C(2)	114.0(3)
N(2)-C(6)-H(6)	108.3
C(21)-C(6)-H(6)	108.3
C(2)-C(6)-H(6)	108.3
C(22)-C(21)-C(26)	118.2(4)
C(22)-C(21)-C(6)	123.6(3)
C(26)-C(21)-C(6)	118.2(3)
C(21)-C(22)-C(23)	120.5(4)

C(21)-C(22)-H(22)	119.8
C(23)-C(22)-H(22)	119.8
C(24)-C(23)-C(22)	121.0(4)
C(24)-C(23)-H(23)	119.5
C(22)-C(23)-H(23)	119.5
C(23)-C(24)-C(25)	119.2(4)
C(23)-C(24)-H(24)	120.4
C(25)-C(24)-H(24)	120.4
C(24)-C(25)-C(26)	120.1(4)
C(24)-C(25)-H(25)	119.9
C(26)-C(25)-H(25)	119.9
C(25)-C(26)-C(21)	121.0(4)
C(25)-C(26)-H(26)	119.5
C(21)-C(26)-H(26)	119.5
C(7)-N(2)-C(6)	116.2(3)
N(2)-C(7)-C(31)	121.5(3)
N(2)-C(7)-H(7)	119.2
C(31)-C(7)-H(7)	119.2
C(32)-C(31)-C(36)	118.6(3)
C(32)-C(31)-C(7)	122.1(3)
C(36)-C(31)-C(7)	119.2(3)
C(31)-C(32)-C(33)	121.4(3)
C(31)-C(32)-H(32)	119.3
C(33)-C(32)-H(32)	119.3
C(32)-C(33)-C(34)	118.6(4)
C(32)-C(33)-H(33)	120.7
C(34)-C(33)-H(33)	120.7
C(35)-C(34)-C(33)	121.4(3)
C(35)-C(34)-Br(1)	119.2(3)
C(33)-C(34)-Br(1)	119.3(3)
C(34)-C(35)-C(36)	119.4(3)
C(34)-C(35)-H(35)	120.3
C(36)-C(35)-H(35)	120.3
C(35)-C(36)-C(31)	120.6(4)
C(35)-C(36)-H(36)	119.7
C(31)-C(36)-H(36)	119.7

C(2)-C(3)-C(4)	106.8(3)
C(2)-C(3)-H(3A)	110.4
C(4)-C(3)-H(3A)	110.4
C(2)-C(3)-H(3B)	110.4
C(4)-C(3)-H(3B)	110.4
H(3A)-C(3)-H(3B)	108.6
N(1)-C(4)-C(8)	111.0(3)
N(1)-C(4)-C(3)	102.2(3)
C(8)-C(4)-C(3)	113.5(3)
N(1)-C(4)-H(4)	110.0
C(8)-C(4)-H(4)	110.0
C(3)-C(4)-H(4)	110.0
C(4)-C(8)-H(8A)	109.5
C(4)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(4)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(201)-N(201)-C(211)	122.8(3)
C(201)-N(201)-C(204)	114.0(3)
C(211)-N(201)-C(204)	121.8(3)
C(216)-C(211)-C(212)	119.3(4)
C(216)-C(211)-N(201)	120.6(3)
C(212)-C(211)-N(201)	120.1(3)
C(213)-C(212)-C(211)	121.2(4)
C(213)-C(212)-H(212)	119.4
C(211)-C(212)-H(212)	119.4
C(212)-C(213)-C(214)	119.4(4)
C(212)-C(213)-H(213)	120.3
C(214)-C(213)-H(213)	120.3
O(202)-C(214)-C(215)	124.8(4)
O(202)-C(214)-C(213)	114.8(3)
C(215)-C(214)-C(213)	120.5(4)
C(214)-O(202)-C(217)	117.6(3)
O(202)-C(217)-H(21A)	109.5
O(202)-C(217)-H(21B)	109.5

H(21A)-C(217)-H(21B)	109.5
O(202)-C(217)-H(21C)	109.5
H(21A)-C(217)-H(21C)	109.5
H(21B)-C(217)-H(21C)	109.5
C(214)-C(215)-C(216)	119.2(4)
C(214)-C(215)-H(215)	120.4
C(216)-C(215)-H(215)	120.4
C(211)-C(216)-C(215)	120.4(4)
C(211)-C(216)-H(216)	119.8
C(215)-C(216)-H(216)	119.8
O(201)-C(201)-N(201)	126.0(3)
O(201)-C(201)-C(202)	125.5(3)
N(201)-C(201)-C(202)	108.5(3)
C(205)-C(202)-C(201)	110.6(3)
C(205)-C(202)-C(203)	113.8(3)
C(201)-C(202)-C(203)	102.8(3)
C(205)-C(202)-C(206)	110.0(3)
C(201)-C(202)-C(206)	104.4(3)
C(203)-C(202)-C(206)	114.5(3)
C(202)-C(205)-H(20A)	109.5
C(202)-C(205)-H(20B)	109.5
H(20A)-C(205)-H(20B)	109.5
C(202)-C(205)-H(20C)	109.5
H(20A)-C(205)-H(20C)	109.5
H(20B)-C(205)-H(20C)	109.5
N(202)-C(206)-C(221)	108.7(3)
N(202)-C(206)-C(202)	109.0(3)
C(221)-C(206)-C(202)	114.4(3)
N(202)-C(206)-H(206)	108.2
C(221)-C(206)-H(206)	108.2
C(202)-C(206)-H(206)	108.2
C(222)-C(221)-C(226)	118.7(4)
C(222)-C(221)-C(206)	123.0(3)
C(226)-C(221)-C(206)	118.2(4)
C(221)-C(222)-C(223)	120.8(4)
C(221)-C(222)-H(222)	119.6

C(223)-C(222)-H(222)	119.6
C(222)-C(223)-C(224)	120.1(4)
C(222)-C(223)-H(223)	120.0
C(224)-C(223)-H(223)	120.0
C(225)-C(224)-C(223)	119.3(4)
C(225)-C(224)-H(224)	120.3
C(223)-C(224)-H(224)	120.3
C(224)-C(225)-C(226)	120.5(4)
C(224)-C(225)-H(225)	119.7
C(226)-C(225)-H(225)	119.7
C(221)-C(226)-C(225)	120.6(4)
C(221)-C(226)-H(226)	119.7
C(225)-C(226)-H(226)	119.7
C(207)-N(202)-C(206)	116.6(3)
N(202)-C(207)-C(231)	121.0(3)
N(202)-C(207)-H(207)	119.5
C(231)-C(207)-H(207)	119.5
C(236)-C(231)-C(232)	118.9(3)
C(236)-C(231)-C(207)	122.2(3)
C(232)-C(231)-C(207)	118.9(3)
C(233)-C(232)-C(231)	120.0(4)
C(233)-C(232)-H(232)	120.0
C(231)-C(232)-H(232)	120.0
C(234)-C(233)-C(232)	119.2(4)
C(234)-C(233)-H(233)	120.4
C(232)-C(233)-H(233)	120.4
C(233)-C(234)-C(235)	122.0(4)
C(233)-C(234)-Br(2)	120.1(3)
C(235)-C(234)-Br(2)	117.9(3)
C(234)-C(235)-C(236)	118.2(4)
C(234)-C(235)-H(235)	120.9
C(236)-C(235)-H(235)	120.9
C(231)-C(236)-C(235)	121.7(4)
C(231)-C(236)-H(236)	119.2
C(235)-C(236)-H(236)	119.2
C(204)-C(203)-C(202)	106.7(3)

C(204)-C(203)-H(20D)	110.4
C(202)-C(203)-H(20D)	110.4
C(204)-C(203)-H(20E)	110.4
C(202)-C(203)-H(20E)	110.4
H(20D)-C(203)-H(20E)	108.6
N(201)-C(204)-C(208)	111.1(3)
N(201)-C(204)-C(203)	102.8(3)
C(208)-C(204)-C(203)	113.6(3)
N(201)-C(204)-H(204)	109.7
C(208)-C(204)-H(204)	109.7
C(203)-C(204)-H(204)	109.7
C(204)-C(208)-H(20F)	109.5
C(204)-C(208)-H(20G)	109.5
H(20F)-C(208)-H(20G)	109.5
C(204)-C(208)-H(20H)	109.5
H(20F)-C(208)-H(20H)	109.5
H(20G)-C(208)-H(20H)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 11. Anisotropic displacement parameters ($Å^2$x 10^3) for V20240. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	28(2)	30(2)	41(2)	1(1)	-4(1)	-3(1)
C(11)	28(2)	32(2)	34(2)	2(1)	-2(1)	-2(1)
C(12)	31(2)	32(2)	39(2)	0(2)	-6(2)	3(1)
C(13)	28(2)	38(2)	37(2)	-1(2)	-7(2)	-5(2)
C(14)	35(2)	28(2)	36(2)	0(1)	0(2)	-4(1)
O(2)	48(2)	29(1)	50(2)	-3(1)	-13(1)	-4(1)
C(17)	65(3)	40(2)	87(4)	-14(2)	-34(3)	-7(2)
C(15)	39(2)	31(2)	45(2)	6(2)	-11(2)	5(2)
C(16)	30(2)	38(2)	42(2)	0(2)	-13(2)	-2(2)
C(1)	28(2)	31(2)	40(2)	6(2)	-7(2)	-1(1)
O(1)	28(1)	38(1)	53(2)	-1(1)	-5(1)	-1(1)
C(2)	30(2)	27(2)	45(2)	5(2)	-8(2)	-2(1)
C(5)	48(2)	32(2)	60(3)	6(2)	-15(2)	3(2)
C(6)	24(2)	28(2)	41(2)	1(1)	-2(1)	-2(1)
C(21)	31(2)	27(2)	37(2)	2(1)	0(2)	0(1)
C(22)	33(2)	34(2)	44(2)	-4(2)	-4(2)	1(2)
C(23)	39(2)	40(2)	51(2)	-4(2)	-10(2)	-7(2)
C(24)	64(3)	36(2)	44(2)	-4(2)	-7(2)	-6(2)
C(25)	65(3)	39(2)	53(3)	-9(2)	10(2)	5(2)
C(26)	41(2)	38(2)	51(2)	-3(2)	7(2)	2(2)
N(2)	29(2)	29(1)	33(2)	1(1)	-5(1)	0(1)
C(7)	31(2)	30(2)	31(2)	0(1)	-3(1)	-2(1)
C(31)	31(2)	30(2)	28(2)	2(1)	-2(1)	-1(1)
C(32)	32(2)	34(2)	38(2)	6(2)	1(2)	-2(1)
C(33)	30(2)	40(2)	40(2)	3(2)	5(2)	2(2)
C(34)	39(2)	28(2)	32(2)	0(1)	-6(2)	3(1)
Br(1)	49(1)	31(1)	61(1)	4(1)	-1(1)	7(1)
C(35)	47(2)	28(2)	42(2)	6(2)	10(2)	-4(2)
C(36)	40(2)	32(2)	47(2)	5(2)	12(2)	-1(2)
C(3)	39(2)	33(2)	36(2)	4(2)	-2(2)	-8(2)
C(4)	28(2)	36(2)	37(2)	6(2)	-5(2)	-4(1)

C(8)	44(2)	49(2)	39(2)	2(2)	-4(2)	-4(2)
N(201)	28(2)	34(2)	42(2)	-1(1)	3(1)	4(1)
C(211)	31(2)	33(2)	37(2)	2(2)	-2(2)	2(1)
C(212)	32(2)	42(2)	41(2)	-2(2)	9(2)	1(2)
C(213)	36(2)	39(2)	40(2)	0(2)	2(2)	-5(2)
C(214)	35(2)	35(2)	35(2)	-1(2)	-2(2)	3(2)
O(202)	54(2)	33(1)	49(2)	-2(1)	10(1)	1(1)
C(217)	80(4)	40(2)	65(3)	-4(2)	24(3)	11(2)
C(215)	31(2)	39(2)	40(2)	-2(2)	3(2)	5(2)
C(216)	30(2)	36(2)	44(2)	2(2)	2(2)	-1(2)
C(201)	32(2)	32(2)	35(2)	6(1)	4(2)	2(1)
O(201)	27(1)	40(1)	51(2)	0(1)	3(1)	4(1)
C(202)	31(2)	28(2)	43(2)	3(2)	1(2)	3(1)
C(205)	47(3)	32(2)	63(3)	5(2)	11(2)	-1(2)
C(206)	24(2)	31(2)	41(2)	-1(1)	-2(1)	2(1)
C(221)	38(2)	29(2)	38(2)	1(1)	0(2)	-1(2)
C(222)	34(2)	36(2)	48(2)	-4(2)	2(2)	-1(2)
C(223)	46(2)	39(2)	52(2)	-2(2)	8(2)	8(2)
C(224)	71(3)	32(2)	47(2)	-5(2)	2(2)	5(2)
C(225)	69(3)	37(2)	54(3)	-8(2)	-15(2)	-5(2)
C(226)	45(2)	40(2)	54(3)	-2(2)	-9(2)	-4(2)
N(202)	30(2)	30(2)	36(2)	2(1)	-1(1)	0(1)
C(207)	31(2)	33(2)	31(2)	1(1)	0(1)	1(1)
C(231)	33(2)	32(2)	30(2)	2(1)	-2(1)	0(1)
C(232)	39(2)	42(2)	45(2)	10(2)	-13(2)	-3(2)
C(233)	53(3)	34(2)	51(2)	10(2)	-11(2)	-1(2)
C(234)	43(2)	36(2)	35(2)	-1(2)	2(2)	-11(2)
Br(2)	68(1)	43(1)	70(1)	5(1)	-3(1)	-21(1)
C(235)	35(2)	46(2)	45(2)	1(2)	-3(2)	-7(2)
C(236)	31(2)	39(2)	47(2)	7(2)	-2(2)	4(2)
C(203)	36(2)	37(2)	40(2)	5(2)	2(2)	8(2)
C(204)	29(2)	40(2)	38(2)	4(2)	3(2)	5(2)
C(208)	43(2)	54(3)	41(2)	1(2)	-4(2)	2(2)

Table 12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for V20240.

	x	y	z	U(eq)
H(12)	1608	1180	654	41
H(13)	1086	736	56	41
H(17A)	576	289	588	96
H(17B)	1218	30	-93	96
H(17C)	1304	308	-1075	96
H(15)	3812	473	2581	46
H(16)	4316	912	3210	44
H(5A)	2499	2049	2677	69
H(5B)	3186	2164	4231	69
H(5C)	2014	2012	4510	69
H(6)	2744	1631	6336	37
H(22)	5643	1874	6164	44
H(23)	6337	2215	7853	52
H(24)	5148	2444	9656	57
H(25)	3238	2332	9751	63
H(26)	2525	1998	8029	52
H(7)	3064	1245	7104	37
H(32)	5861	1099	5632	41
H(33)	6862	699	5978	44
H(35)	4241	389	8549	47
H(36)	3229	787	8150	47
H(3A)	5069	1785	3638	43
H(3B)	4359	1873	2030	43
H(4)	4995	1345	2991	41
H(8A)	4855	1257	86	66
H(8B)	5678	1506	428	66
H(8C)	4416	1557	-207	66
H(212)	8390	915	-1801	46
H(213)	8876	474	-2408	46
H(21A)	11324	323	-6158	92

H(21B)	11438	38	-5258	92
H(21C)	12118	292	-4566	92
H(215)	11641	738	-4882	45
H(216)	11120	1183	-4281	44
H(20A)	10261	2051	-2288	71
H(20B)	10717	2018	-433	71
H(20C)	9550	2170	-774	71
H(206)	10003	1639	1367	38
H(222)	7102	1874	1182	47
H(223)	6373	2210	2883	55
H(224)	7570	2447	4675	60
H(225)	9475	2337	4790	64
H(226)	10206	2003	3078	55
H(207)	9711	1250	2127	38
H(232)	9607	779	2983	51
H(233)	8589	379	3374	56
H(235)	5874	710	1107	50
H(236)	6874	1111	786	47
H(20D)	7656	1786	-1323	45
H(20E)	8355	1875	-2938	45
H(204)	7736	1348	-1966	43
H(20F)	8316	1553	-5174	69
H(20G)	7051	1512	-4530	69
H(20H)	7842	1257	-4848	69

Table 13. Torsion angles [°] for V20240.

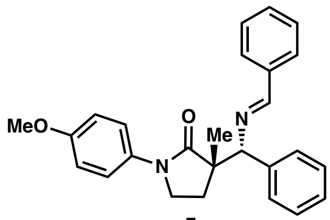
C(1)-N(1)-C(11)-C(12)	59.0(5)
C(4)-N(1)-C(11)-C(12)	-135.8(4)
C(1)-N(1)-C(11)-C(16)	-118.5(4)
C(4)-N(1)-C(11)-C(16)	46.7(5)
C(16)-C(11)-C(12)-C(13)	-0.3(6)
N(1)-C(11)-C(12)-C(13)	-177.8(4)
C(11)-C(12)-C(13)-C(14)	-0.7(6)
C(12)-C(13)-C(14)-O(2)	-179.0(4)
C(12)-C(13)-C(14)-C(15)	1.2(6)
C(15)-C(14)-O(2)-C(17)	179.3(4)
C(13)-C(14)-O(2)-C(17)	-0.4(6)
O(2)-C(14)-C(15)-C(16)	179.5(4)
C(13)-C(14)-C(15)-C(16)	-0.7(6)
C(14)-C(15)-C(16)-C(11)	-0.3(7)
C(12)-C(11)-C(16)-C(15)	0.8(6)
N(1)-C(11)-C(16)-C(15)	178.4(4)
C(11)-N(1)-C(1)-O(1)	-15.1(6)
C(4)-N(1)-C(1)-O(1)	178.7(4)
C(11)-N(1)-C(1)-C(2)	161.8(3)
C(4)-N(1)-C(1)-C(2)	-4.4(4)
O(1)-C(1)-C(2)-C(5)	-44.6(5)
N(1)-C(1)-C(2)-C(5)	138.5(4)
O(1)-C(1)-C(2)-C(3)	-166.0(4)
N(1)-C(1)-C(2)-C(3)	17.1(4)
O(1)-C(1)-C(2)-C(6)	74.0(4)
N(1)-C(1)-C(2)-C(6)	-102.9(3)
C(5)-C(2)-C(6)-N(2)	-172.7(3)
C(3)-C(2)-C(6)-N(2)	-43.4(4)
C(1)-C(2)-C(6)-N(2)	68.3(3)
C(5)-C(2)-C(6)-C(21)	-51.1(4)
C(3)-C(2)-C(6)-C(21)	78.2(4)
C(1)-C(2)-C(6)-C(21)	-170.1(3)
N(2)-C(6)-C(21)-C(22)	44.8(5)
C(2)-C(6)-C(21)-C(22)	-77.0(4)

N(2)-C(6)-C(21)-C(26)	-132.1(4)
C(2)-C(6)-C(21)-C(26)	106.0(4)
C(26)-C(21)-C(22)-C(23)	-1.3(6)
C(6)-C(21)-C(22)-C(23)	-178.2(4)
C(21)-C(22)-C(23)-C(24)	1.1(6)
C(22)-C(23)-C(24)-C(25)	-0.2(7)
C(23)-C(24)-C(25)-C(26)	-0.5(7)
C(24)-C(25)-C(26)-C(21)	0.3(7)
C(22)-C(21)-C(26)-C(25)	0.6(6)
C(6)-C(21)-C(26)-C(25)	177.7(4)
C(21)-C(6)-N(2)-C(7)	114.6(3)
C(2)-C(6)-N(2)-C(7)	-120.6(3)
C(6)-N(2)-C(7)-C(31)	179.7(3)
N(2)-C(7)-C(31)-C(32)	-3.1(5)
N(2)-C(7)-C(31)-C(36)	177.4(4)
C(36)-C(31)-C(32)-C(33)	-1.1(6)
C(7)-C(31)-C(32)-C(33)	179.4(4)
C(31)-C(32)-C(33)-C(34)	-0.4(6)
C(32)-C(33)-C(34)-C(35)	1.1(6)
C(32)-C(33)-C(34)-Br(1)	-177.6(3)
C(33)-C(34)-C(35)-C(36)	-0.4(6)
Br(1)-C(34)-C(35)-C(36)	178.3(3)
C(34)-C(35)-C(36)-C(31)	-1.0(6)
C(32)-C(31)-C(36)-C(35)	1.8(6)
C(7)-C(31)-C(36)-C(35)	-178.7(4)
C(5)-C(2)-C(3)-C(4)	-142.7(3)
C(1)-C(2)-C(3)-C(4)	-23.0(4)
C(6)-C(2)-C(3)-C(4)	89.6(4)
C(1)-N(1)-C(4)-C(8)	-131.4(3)
C(11)-N(1)-C(4)-C(8)	62.2(4)
C(1)-N(1)-C(4)-C(3)	-10.2(4)
C(11)-N(1)-C(4)-C(3)	-176.5(3)
C(2)-C(3)-C(4)-N(1)	20.5(4)
C(2)-C(3)-C(4)-C(8)	140.1(3)
C(201)-N(201)-C(211)-C(216)	-58.4(5)
C(204)-N(201)-C(211)-C(216)	135.8(4)

C(201)-N(201)-C(211)-C(212)	120.8(4)
C(204)-N(201)-C(211)-C(212)	-44.9(5)
C(216)-C(211)-C(212)-C(213)	0.4(6)
N(201)-C(211)-C(212)-C(213)	-178.8(4)
C(211)-C(212)-C(213)-C(214)	-0.5(6)
C(212)-C(213)-C(214)-O(202)	-178.6(4)
C(212)-C(213)-C(214)-C(215)	0.9(6)
C(215)-C(214)-O(202)-C(217)	-3.7(6)
C(213)-C(214)-O(202)-C(217)	175.8(4)
O(202)-C(214)-C(215)-C(216)	178.1(4)
C(213)-C(214)-C(215)-C(216)	-1.4(6)
C(212)-C(211)-C(216)-C(215)	-0.8(6)
N(201)-C(211)-C(216)-C(215)	178.4(4)
C(214)-C(215)-C(216)-C(211)	1.3(6)
C(211)-N(201)-C(201)-O(201)	15.6(6)
C(204)-N(201)-C(201)-O(201)	-177.6(4)
C(211)-N(201)-C(201)-C(202)	-161.7(3)
C(204)-N(201)-C(201)-C(202)	5.1(4)
O(201)-C(201)-C(202)-C(205)	43.5(5)
N(201)-C(201)-C(202)-C(205)	-139.1(3)
O(201)-C(201)-C(202)-C(203)	165.4(4)
N(201)-C(201)-C(202)-C(203)	-17.3(4)
O(201)-C(201)-C(202)-C(206)	-74.8(4)
N(201)-C(201)-C(202)-C(206)	102.6(3)
C(205)-C(202)-C(206)-N(202)	173.8(3)
C(201)-C(202)-C(206)-N(202)	-67.5(3)
C(203)-C(202)-C(206)-N(202)	44.1(4)
C(205)-C(202)-C(206)-C(221)	51.8(4)
C(201)-C(202)-C(206)-C(221)	170.5(3)
C(203)-C(202)-C(206)-C(221)	-77.8(4)
N(202)-C(206)-C(221)-C(222)	-45.7(5)
C(202)-C(206)-C(221)-C(222)	76.5(5)
N(202)-C(206)-C(221)-C(226)	131.4(4)
C(202)-C(206)-C(221)-C(226)	-106.4(4)
C(226)-C(221)-C(222)-C(223)	1.0(6)
C(206)-C(221)-C(222)-C(223)	178.1(4)

C(221)-C(222)-C(223)-C(224)	-0.2(7)
C(222)-C(223)-C(224)-C(225)	-0.9(7)
C(223)-C(224)-C(225)-C(226)	1.1(7)
C(222)-C(221)-C(226)-C(225)	-0.8(6)
C(206)-C(221)-C(226)-C(225)	-178.0(4)
C(224)-C(225)-C(226)-C(221)	-0.2(7)
C(221)-C(206)-N(202)-C(207)	-114.9(4)
C(202)-C(206)-N(202)-C(207)	119.7(3)
C(206)-N(202)-C(207)-C(231)	-179.4(3)
N(202)-C(207)-C(231)-C(236)	-0.3(6)
N(202)-C(207)-C(231)-C(232)	178.4(4)
C(236)-C(231)-C(232)-C(233)	-2.7(6)
C(207)-C(231)-C(232)-C(233)	178.6(4)
C(231)-C(232)-C(233)-C(234)	2.1(7)
C(232)-C(233)-C(234)-C(235)	-0.6(7)
C(232)-C(233)-C(234)-Br(2)	-178.1(3)
C(233)-C(234)-C(235)-C(236)	-0.3(7)
Br(2)-C(234)-C(235)-C(236)	177.3(3)
C(232)-C(231)-C(236)-C(235)	1.8(6)
C(207)-C(231)-C(236)-C(235)	-179.5(4)
C(234)-C(235)-C(236)-C(231)	-0.3(6)
C(205)-C(202)-C(203)-C(204)	142.4(3)
C(201)-C(202)-C(203)-C(204)	22.7(4)
C(206)-C(202)-C(203)-C(204)	-89.9(4)
C(201)-N(201)-C(204)-C(208)	131.3(4)
C(211)-N(201)-C(204)-C(208)	-61.8(5)
C(201)-N(201)-C(204)-C(203)	9.5(4)
C(211)-N(201)-C(204)-C(203)	176.4(3)
C(202)-C(203)-C(204)-N(201)	-20.0(4)
C(202)-C(203)-C(204)-C(208)	-140.1(3)

Symmetry transformations used to generate equivalent atoms:



5

The crystal structure of **5** was registered in the Cambridge crystallographic data center and can be found as CCDC 2253012

X-Ray Structure Determination

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS KAPPA APEX II diffractometer coupled to an PHOTON 100 CMOS detector with graphite monochromated Mo K_α radiation (λ = 0.71073 Å) for the structure of compound D19141. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2017 using established refinement techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups).

Compound D19141 crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit.

Table 14. Crystal data and structure refinement for D19141.

Identification code	D19141	
Empirical formula	C26 H26 N2 O2	
Formula weight	398.49	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 19.640(5) Å	a= 90°.
	b = 6.1440(16) Å	b= 94.127(6)°.
	c = 17.135(5) Å	g = 90°.
Volume	2062.3(9) $Å^3$	
Z	4	
Density (calculated)	1.283 Mg/m^3	
Absorption coefficient	0.081 mm^{-1}	
F(000)	848	
Crystal size	0.300 x 0.300 x 0.200 mm^3	
Theta range for data collection	2.079 to 35.630°.	
Index ranges	-31<=h<=31, -10<=k<=9, -27<=l<=27	

Reflections collected	110686
Independent reflections	9463 [R(int) = 0.0390]
Completeness to theta = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7471 and 0.7041
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9463 / 0 / 273
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.1106
R indices (all data)	R1 = 0.0501, wR2 = 0.1175
Extinction coefficient	n/a
Largest diff. peak and hole	0.569 and -0.261 e.Å^{-3}

Table 15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for D19141. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	8328(1)	3132(1)	6113(1)	12(1)
C(1)	8676(1)	3351(1)	6862(1)	12(1)
C(2)	9154(1)	1784(1)	7114(1)	15(1)
C(3)	9517(1)	1929(1)	7843(1)	15(1)
C(4)	9401(1)	3674(1)	8328(1)	13(1)
O(1)	9723(1)	3979(1)	9059(1)	17(1)
C(7)	10207(1)	2372(1)	9326(1)	18(1)
C(5)	8928(1)	5261(1)	8079(1)	16(1)
C(6)	8563(1)	5110(1)	7359(1)	15(1)
C(8)	7960(1)	4706(1)	5707(1)	11(1)
O(2)	7793(1)	6481(1)	5955(1)	16(1)
C(9)	7834(1)	3953(1)	4858(1)	11(1)
C(10)	7920(1)	1487(1)	4926(1)	14(1)
C(11)	8439(1)	1213(1)	5628(1)	14(1)
C(12)	8412(1)	4983(1)	4425(1)	16(1)
C(13)	7134(1)	4755(1)	4502(1)	11(1)
C(21)	7033(1)	4224(1)	3637(1)	12(1)
C(22)	6815(1)	2168(1)	3376(1)	15(1)
C(23)	6738(1)	1711(1)	2578(1)	18(1)
C(24)	6876(1)	3300(1)	2033(1)	18(1)
C(25)	7093(1)	5351(1)	2286(1)	18(1)
C(26)	7169(1)	5804(1)	3086(1)	15(1)
N(2)	6588(1)	3781(1)	4924(1)	13(1)
C(14)	6227(1)	5086(1)	5297(1)	14(1)
C(31)	5657(1)	4350(1)	5743(1)	15(1)
C(32)	5370(1)	5814(1)	6247(1)	21(1)
C(33)	4830(1)	5180(2)	6680(1)	26(1)
C(34)	4574(1)	3086(2)	6606(1)	27(1)
C(35)	4854(1)	1613(2)	6101(1)	25(1)
C(36)	5396(1)	2241(1)	5672(1)	19(1)

Table 16. Bond lengths [Å] and angles [°] for D19141.

N(1)-C(8)	1.3677(9)
N(1)-C(1)	1.4158(9)
N(1)-C(11)	1.4682(9)
C(1)-C(2)	1.3926(9)
C(1)-C(6)	1.4031(10)
C(2)-C(3)	1.3955(10)
C(2)-H(2)	0.9500
C(3)-C(4)	1.3859(10)
C(3)-H(3)	0.9500
C(4)-O(1)	1.3737(9)
C(4)-C(5)	1.3934(10)
O(1)-C(7)	1.4236(9)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(5)-C(6)	1.3859(10)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(8)-O(2)	1.2236(8)
C(8)-C(9)	1.5301(9)
C(9)-C(10)	1.5282(10)
C(9)-C(12)	1.5363(9)
C(9)-C(13)	1.5449(9)
C(10)-C(11)	1.5291(10)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-N(2)	1.4624(9)
C(13)-C(21)	1.5160(10)
C(13)-H(13)	1.0000

C(21)-C(26)	1.3939(10)
C(21)-C(22)	1.3973(10)
C(22)-C(23)	1.3930(10)
C(22)-H(22)	0.9500
C(23)-C(24)	1.3919(11)
C(23)-H(23)	0.9500
C(24)-C(25)	1.3901(11)
C(24)-H(24)	0.9500
C(25)-C(26)	1.3945(10)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
N(2)-C(14)	1.2735(9)
C(14)-C(31)	1.4707(10)
C(14)-H(14)	0.9500
C(31)-C(32)	1.3943(10)
C(31)-C(36)	1.3955(12)
C(32)-C(33)	1.3922(12)
C(32)-H(32)	0.9500
C(33)-C(34)	1.3836(15)
C(33)-H(33)	0.9500
C(34)-C(35)	1.3917(13)
C(34)-H(34)	0.9500
C(35)-C(36)	1.3901(11)
C(35)-H(35)	0.9500
C(36)-H(36)	0.9500

C(8)-N(1)-C(1)	126.65(6)
C(8)-N(1)-C(11)	112.01(5)
C(1)-N(1)-C(11)	120.53(5)
C(2)-C(1)-C(6)	118.47(6)
C(2)-C(1)-N(1)	119.08(6)
C(6)-C(1)-N(1)	122.44(6)
C(1)-C(2)-C(3)	121.57(6)
C(1)-C(2)-H(2)	119.2
C(3)-C(2)-H(2)	119.2
C(4)-C(3)-C(2)	119.43(6)

C(4)-C(3)-H(3)	120.3
C(2)-C(3)-H(3)	120.3
O(1)-C(4)-C(3)	124.65(6)
O(1)-C(4)-C(5)	115.86(6)
C(3)-C(4)-C(5)	119.49(6)
C(4)-O(1)-C(7)	116.77(6)
O(1)-C(7)-H(7A)	109.5
O(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
O(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(6)-C(5)-C(4)	121.14(6)
C(6)-C(5)-H(5)	119.4
C(4)-C(5)-H(5)	119.4
C(5)-C(6)-C(1)	119.89(6)
C(5)-C(6)-H(6)	120.1
C(1)-C(6)-H(6)	120.1
O(2)-C(8)-N(1)	126.75(6)
O(2)-C(8)-C(9)	124.83(6)
N(1)-C(8)-C(9)	108.26(5)
C(10)-C(9)-C(8)	102.55(5)
C(10)-C(9)-C(12)	111.35(5)
C(8)-C(9)-C(12)	105.12(5)
C(10)-C(9)-C(13)	115.92(5)
C(8)-C(9)-C(13)	110.89(5)
C(12)-C(9)-C(13)	110.24(5)
C(9)-C(10)-C(11)	103.49(5)
C(9)-C(10)-H(10A)	111.1
C(11)-C(10)-H(10A)	111.1
C(9)-C(10)-H(10B)	111.1
C(11)-C(10)-H(10B)	111.1
H(10A)-C(10)-H(10B)	109.0
N(1)-C(11)-C(10)	103.82(5)
N(1)-C(11)-H(11A)	111.0
C(10)-C(11)-H(11A)	111.0

N(1)-C(11)-H(11B)	111.0
C(10)-C(11)-H(11B)	111.0
H(11A)-C(11)-H(11B)	109.0
C(9)-C(12)-H(12A)	109.5
C(9)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(9)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
N(2)-C(13)-C(21)	110.25(5)
N(2)-C(13)-C(9)	109.73(5)
C(21)-C(13)-C(9)	111.51(5)
N(2)-C(13)-H(13)	108.4
C(21)-C(13)-H(13)	108.4
C(9)-C(13)-H(13)	108.4
C(26)-C(21)-C(22)	118.76(6)
C(26)-C(21)-C(13)	119.69(6)
C(22)-C(21)-C(13)	121.54(6)
C(23)-C(22)-C(21)	120.38(6)
C(23)-C(22)-H(22)	119.8
C(21)-C(22)-H(22)	119.8
C(24)-C(23)-C(22)	120.35(7)
C(24)-C(23)-H(23)	119.8
C(22)-C(23)-H(23)	119.8
C(25)-C(24)-C(23)	119.72(7)
C(25)-C(24)-H(24)	120.1
C(23)-C(24)-H(24)	120.1
C(24)-C(25)-C(26)	119.77(7)
C(24)-C(25)-H(25)	120.1
C(26)-C(25)-H(25)	120.1
C(21)-C(26)-C(25)	121.01(7)
C(21)-C(26)-H(26)	119.5
C(25)-C(26)-H(26)	119.5
C(14)-N(2)-C(13)	116.44(6)
N(2)-C(14)-C(31)	122.70(7)
N(2)-C(14)-H(14)	118.6

C(31)-C(14)-H(14)	118.6
C(32)-C(31)-C(36)	119.38(7)
C(32)-C(31)-C(14)	118.70(7)
C(36)-C(31)-C(14)	121.92(6)
C(33)-C(32)-C(31)	120.41(8)
C(33)-C(32)-H(32)	119.8
C(31)-C(32)-H(32)	119.8
C(34)-C(33)-C(32)	119.82(8)
C(34)-C(33)-H(33)	120.1
C(32)-C(33)-H(33)	120.1
C(33)-C(34)-C(35)	120.28(8)
C(33)-C(34)-H(34)	119.9
C(35)-C(34)-H(34)	119.9
C(36)-C(35)-C(34)	119.98(9)
C(36)-C(35)-H(35)	120.0
C(34)-C(35)-H(35)	120.0
C(35)-C(36)-C(31)	120.13(7)
C(35)-C(36)-H(36)	119.9
C(31)-C(36)-H(36)	119.9

Symmetry transformations used to generate equivalent atoms:

Table 17. Anisotropic displacement parameters ($Å^2$x 10^3) for D19141. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	14(1)	10(1)	11(1)	-1(1)	0(1)	2(1)
C(1)	12(1)	12(1)	11(1)	0(1)	1(1)	1(1)
C(2)	18(1)	14(1)	14(1)	-2(1)	-1(1)	4(1)
C(3)	17(1)	16(1)	14(1)	0(1)	-1(1)	4(1)
C(4)	14(1)	16(1)	10(1)	1(1)	1(1)	0(1)
O(1)	20(1)	21(1)	11(1)	0(1)	-2(1)	4(1)
C(7)	18(1)	19(1)	15(1)	5(1)	-2(1)	-1(1)
C(5)	18(1)	18(1)	11(1)	-2(1)	1(1)	5(1)
C(6)	16(1)	16(1)	12(1)	-2(1)	1(1)	5(1)
C(8)	12(1)	10(1)	11(1)	0(1)	1(1)	0(1)
O(2)	22(1)	11(1)	14(1)	-2(1)	-1(1)	4(1)
C(9)	12(1)	11(1)	10(1)	-1(1)	1(1)	0(1)
C(10)	16(1)	11(1)	14(1)	-3(1)	-2(1)	2(1)
C(11)	16(1)	10(1)	15(1)	-2(1)	-1(1)	3(1)
C(12)	14(1)	19(1)	15(1)	1(1)	3(1)	-2(1)
C(13)	13(1)	11(1)	11(1)	0(1)	1(1)	0(1)
C(21)	12(1)	13(1)	11(1)	0(1)	1(1)	0(1)
C(22)	16(1)	14(1)	14(1)	-1(1)	0(1)	-1(1)
C(23)	19(1)	19(1)	16(1)	-4(1)	-1(1)	-2(1)
C(24)	16(1)	26(1)	12(1)	-3(1)	0(1)	-1(1)
C(25)	18(1)	24(1)	12(1)	3(1)	1(1)	-3(1)
C(26)	17(1)	16(1)	13(1)	2(1)	1(1)	-2(1)
N(2)	12(1)	15(1)	12(1)	1(1)	2(1)	1(1)
C(14)	14(1)	16(1)	13(1)	1(1)	1(1)	3(1)
C(31)	13(1)	21(1)	12(1)	2(1)	1(1)	5(1)
C(32)	18(1)	28(1)	18(1)	-2(1)	3(1)	8(1)
C(33)	18(1)	43(1)	18(1)	-1(1)	5(1)	11(1)
C(34)	16(1)	44(1)	22(1)	10(1)	6(1)	7(1)
C(35)	16(1)	30(1)	28(1)	9(1)	6(1)	2(1)
C(36)	16(1)	22(1)	20(1)	3(1)	4(1)	2(1)

Table 18. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for D19141.

	x	y	z	U(eq)
H(2)	9236	588	6782	19
H(3)	9841	842	8004	19
H(7A)	9986	942	9321	26
H(7B)	10386	2723	9860	26
H(7C)	10584	2344	8980	26
H(5)	8854	6468	8409	19
H(6)	8237	6196	7201	18
H(10A)	8095	869	4446	17
H(10B)	7482	773	5022	17
H(11A)	8355	-146	5916	17
H(11B)	8911	1187	5460	17
H(12A)	8854	4512	4670	24
H(12B)	8379	6573	4452	24
H(12C)	8372	4522	3876	24
H(13)	7113	6372	4565	14
H(22)	6719	1074	3745	18
H(23)	6590	307	2406	21
H(24)	6822	2984	1489	22
H(25)	7189	6441	1917	22
H(26)	7315	7209	3256	18
H(14)	6329	6596	5287	17
H(32)	5544	7254	6296	25
H(33)	4638	6181	7024	31
H(34)	4206	2651	6901	32
H(35)	4676	179	6050	29
H(36)	5589	1232	5330	23

Table 19. Torsion angles [°] for D19141.

C(8)-N(1)-C(1)-C(2)	-165.03(6)
C(11)-N(1)-C(1)-C(2)	3.74(9)
C(8)-N(1)-C(1)-C(6)	14.04(10)
C(11)-N(1)-C(1)-C(6)	-177.19(6)
C(6)-C(1)-C(2)-C(3)	0.16(11)
N(1)-C(1)-C(2)-C(3)	179.27(6)
C(1)-C(2)-C(3)-C(4)	-0.12(11)
C(2)-C(3)-C(4)-O(1)	179.43(7)
C(2)-C(3)-C(4)-C(5)	-0.44(10)
C(3)-C(4)-O(1)-C(7)	-0.06(10)
C(5)-C(4)-O(1)-C(7)	179.81(6)
O(1)-C(4)-C(5)-C(6)	-178.90(6)
C(3)-C(4)-C(5)-C(6)	0.98(11)
C(4)-C(5)-C(6)-C(1)	-0.94(11)
C(2)-C(1)-C(6)-C(5)	0.37(10)
N(1)-C(1)-C(6)-C(5)	-178.71(6)
C(1)-N(1)-C(8)-O(2)	-9.85(11)
C(11)-N(1)-C(8)-O(2)	-179.43(6)
C(1)-N(1)-C(8)-C(9)	165.62(6)
C(11)-N(1)-C(8)-C(9)	-3.95(7)
O(2)-C(8)-C(9)-C(10)	-162.44(6)
N(1)-C(8)-C(9)-C(10)	21.98(7)
O(2)-C(8)-C(9)-C(12)	81.04(8)
N(1)-C(8)-C(9)-C(12)	-94.54(6)
O(2)-C(8)-C(9)-C(13)	-38.09(9)
N(1)-C(8)-C(9)-C(13)	146.33(5)
C(8)-C(9)-C(10)-C(11)	-30.46(6)
C(12)-C(9)-C(10)-C(11)	81.50(7)
C(13)-C(9)-C(10)-C(11)	-151.42(5)
C(8)-N(1)-C(11)-C(10)	-15.83(7)
C(1)-N(1)-C(11)-C(10)	173.87(6)
C(9)-C(10)-C(11)-N(1)	28.62(7)
C(10)-C(9)-C(13)-N(2)	52.92(7)
C(8)-C(9)-C(13)-N(2)	-63.45(7)

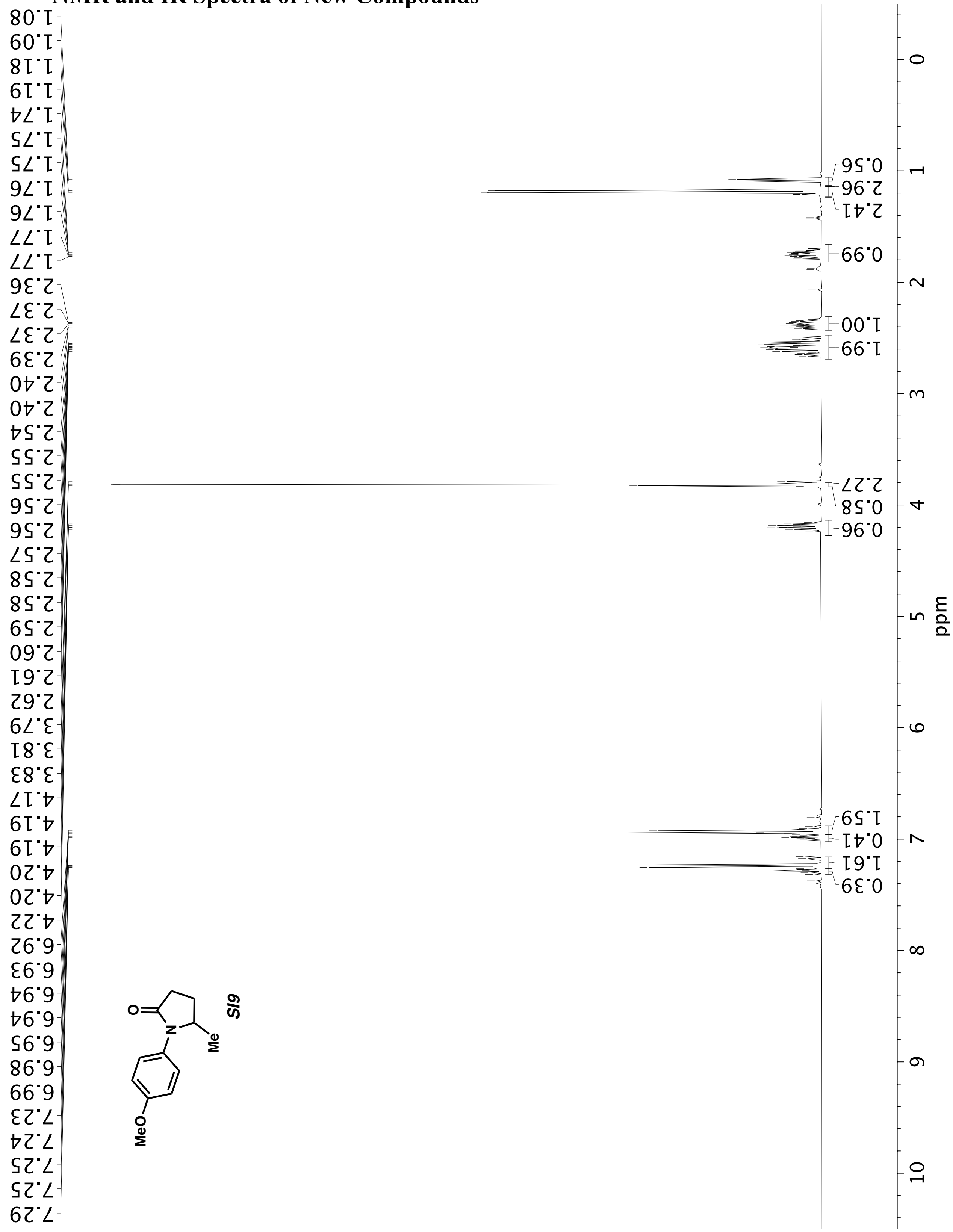
C(12)-C(9)-C(13)-N(2)	-179.44(5)
C(10)-C(9)-C(13)-C(21)	-69.53(7)
C(8)-C(9)-C(13)-C(21)	174.11(5)
C(12)-C(9)-C(13)-C(21)	58.11(7)
N(2)-C(13)-C(21)-C(26)	140.78(6)
C(9)-C(13)-C(21)-C(26)	-97.07(7)
N(2)-C(13)-C(21)-C(22)	-40.19(8)
C(9)-C(13)-C(21)-C(22)	81.96(8)
C(26)-C(21)-C(22)-C(23)	0.15(10)
C(13)-C(21)-C(22)-C(23)	-178.88(6)
C(21)-C(22)-C(23)-C(24)	-0.10(11)
C(22)-C(23)-C(24)-C(25)	0.13(11)
C(23)-C(24)-C(25)-C(26)	-0.21(11)
C(22)-C(21)-C(26)-C(25)	-0.23(10)
C(13)-C(21)-C(26)-C(25)	178.82(6)
C(24)-C(25)-C(26)-C(21)	0.26(11)
C(21)-C(13)-N(2)-C(14)	-121.09(6)
C(9)-C(13)-N(2)-C(14)	115.72(6)
C(13)-N(2)-C(14)-C(31)	179.47(6)
N(2)-C(14)-C(31)-C(32)	168.35(7)
N(2)-C(14)-C(31)-C(36)	-11.84(10)
C(36)-C(31)-C(32)-C(33)	0.23(11)
C(14)-C(31)-C(32)-C(33)	-179.96(7)
C(31)-C(32)-C(33)-C(34)	-0.27(12)
C(32)-C(33)-C(34)-C(35)	-0.03(12)
C(33)-C(34)-C(35)-C(36)	0.36(12)
C(34)-C(35)-C(36)-C(31)	-0.40(12)
C(32)-C(31)-C(36)-C(35)	0.11(11)
C(14)-C(31)-C(36)-C(35)	-179.70(7)

Symmetry transformations used to generate equivalent atoms:

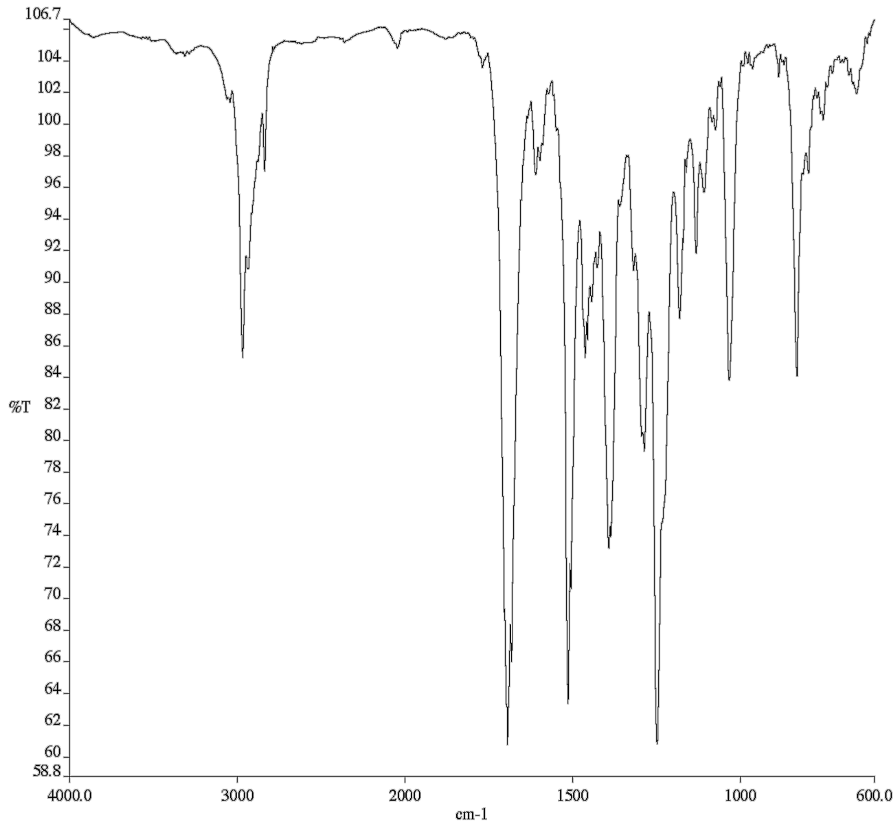
References:

1) Sheldrick, G. M. *Acta Cryst.* **1990**, A46, 467-473.
2) Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3-8.
3) Müller, P. *Crystallography Reviews* **2009**, *15*, 57-83.

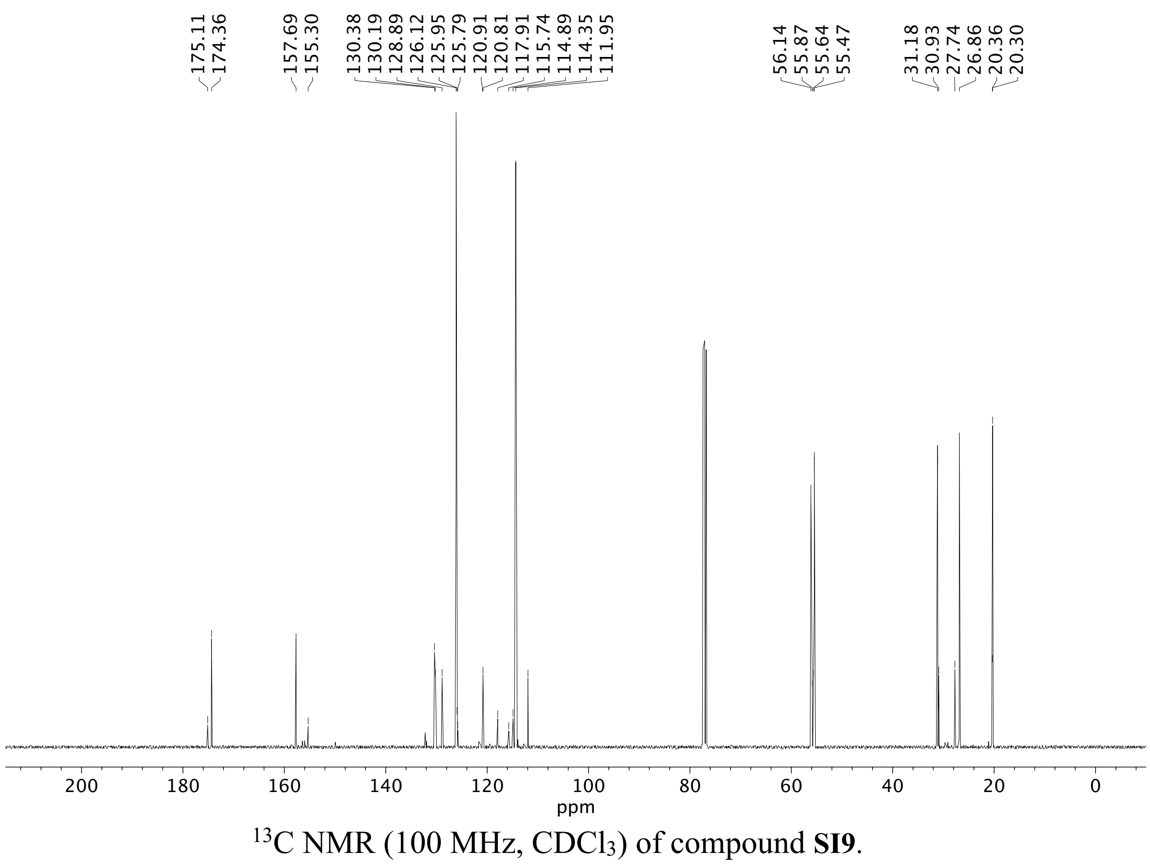
NMR and IR Spectra of New Compounds



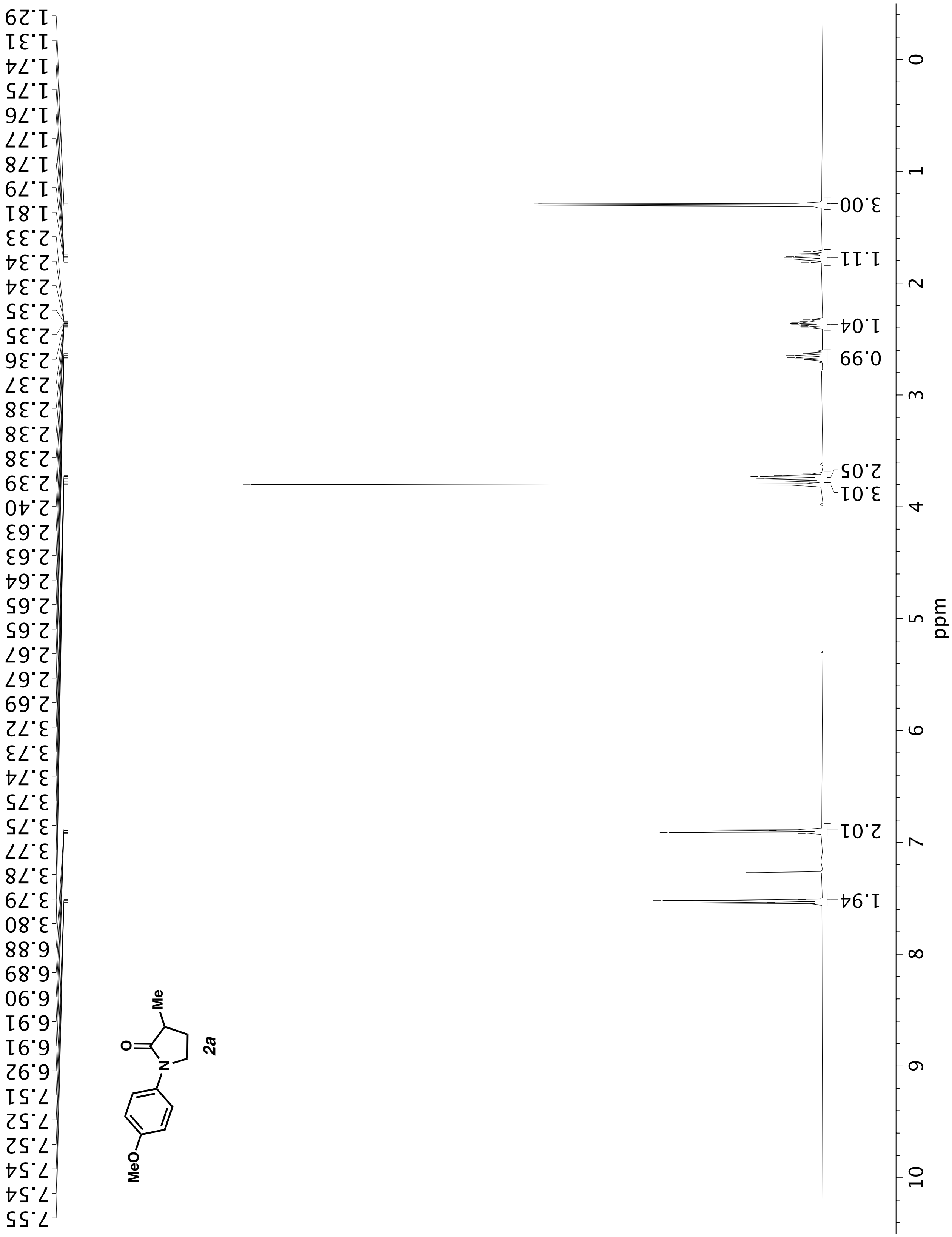
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI9.**



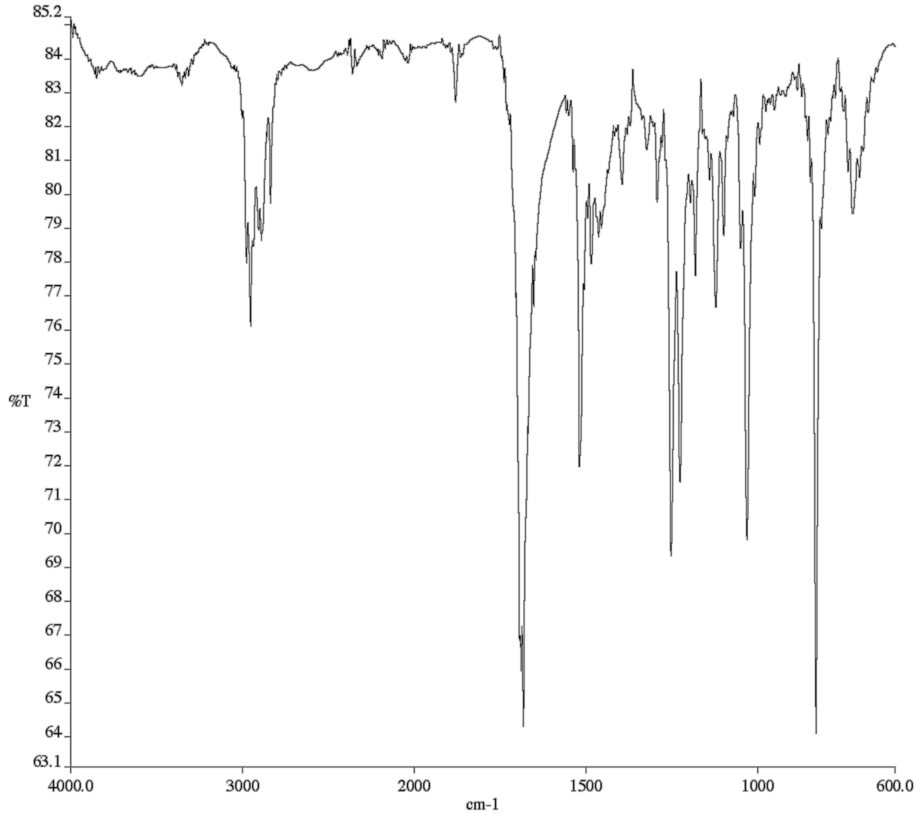
Infrared spectrum (Thin Film, NaCl) of compound **SI9.**



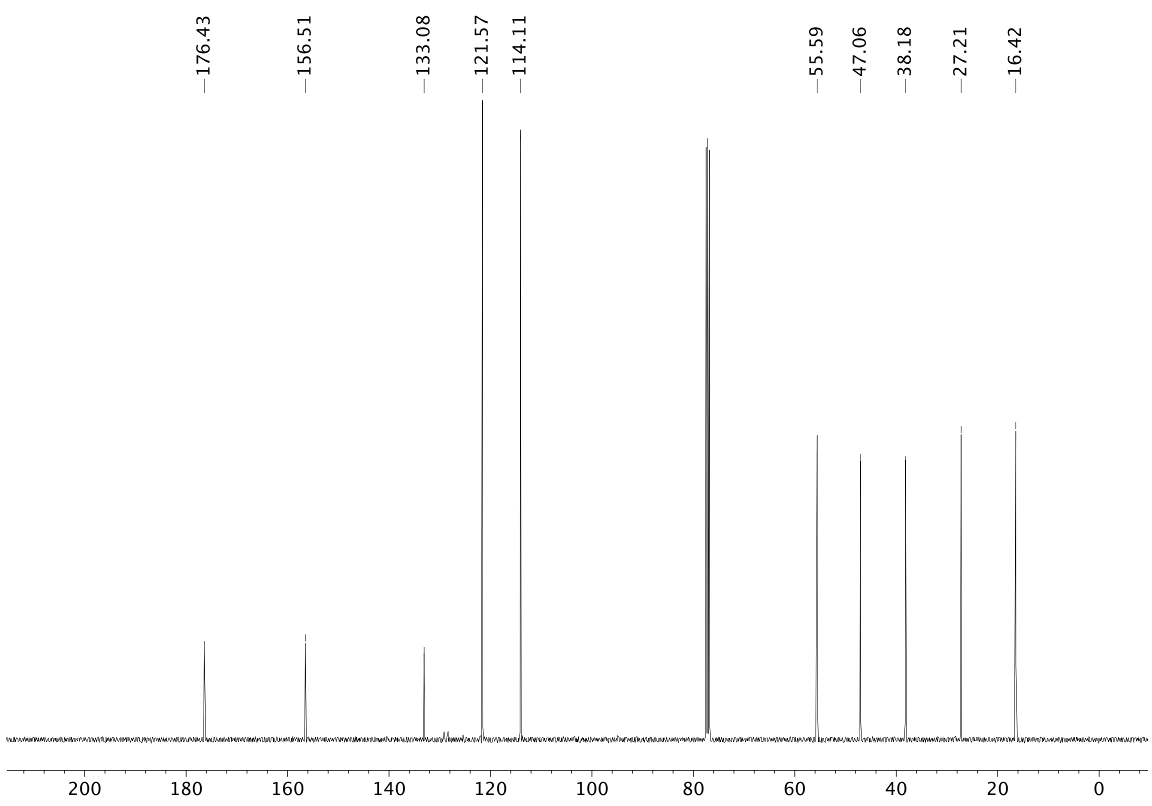
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI9**.



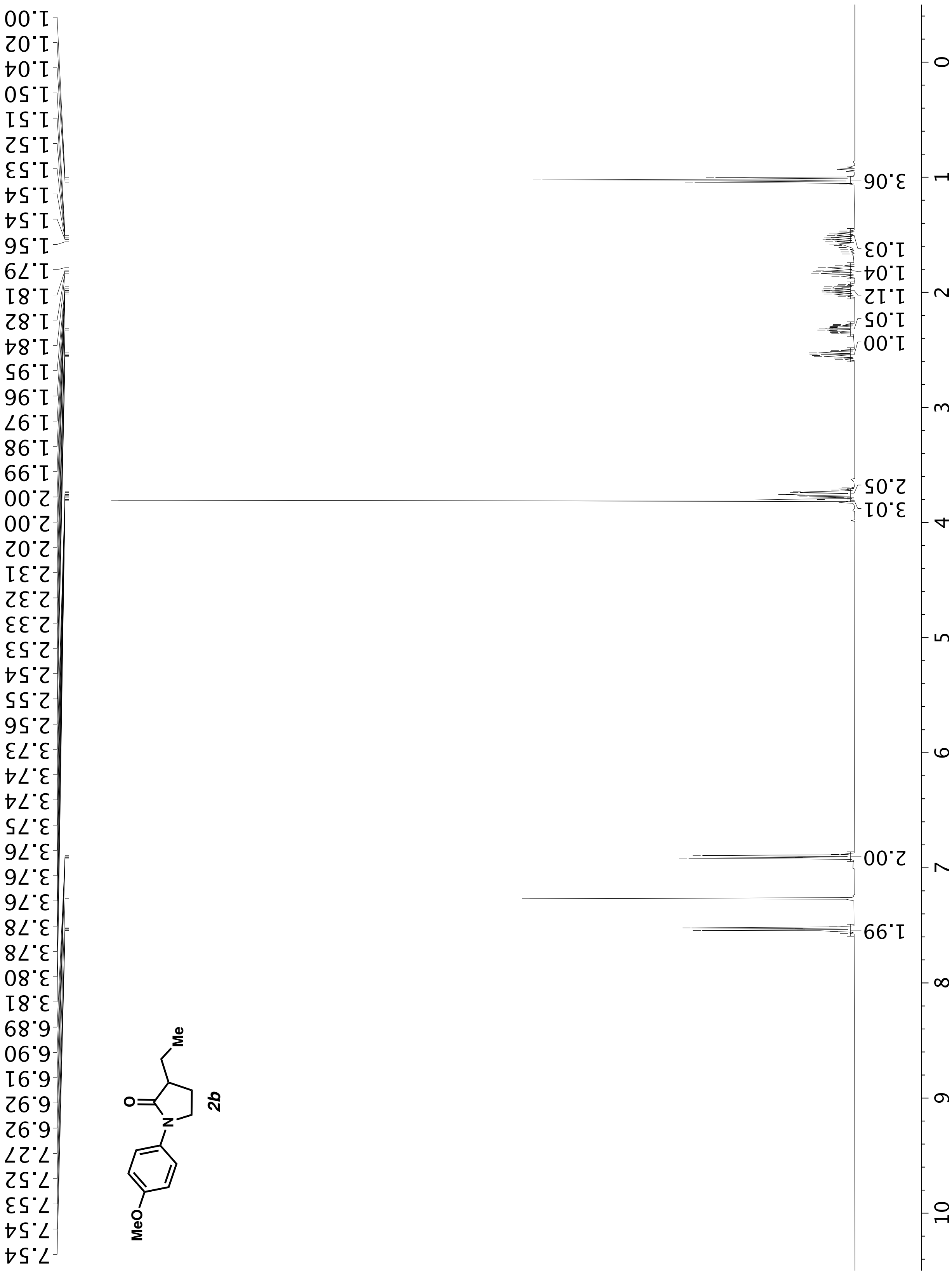
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**.



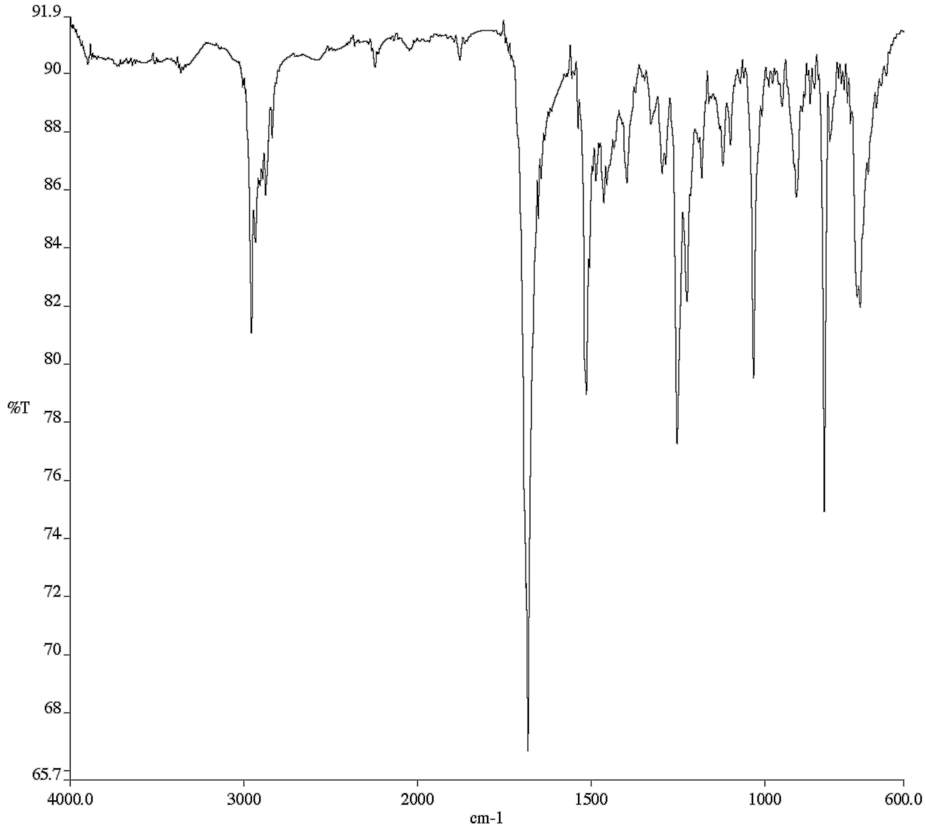
Infrared spectrum (Thin Film, NaCl) of compound **2a**.



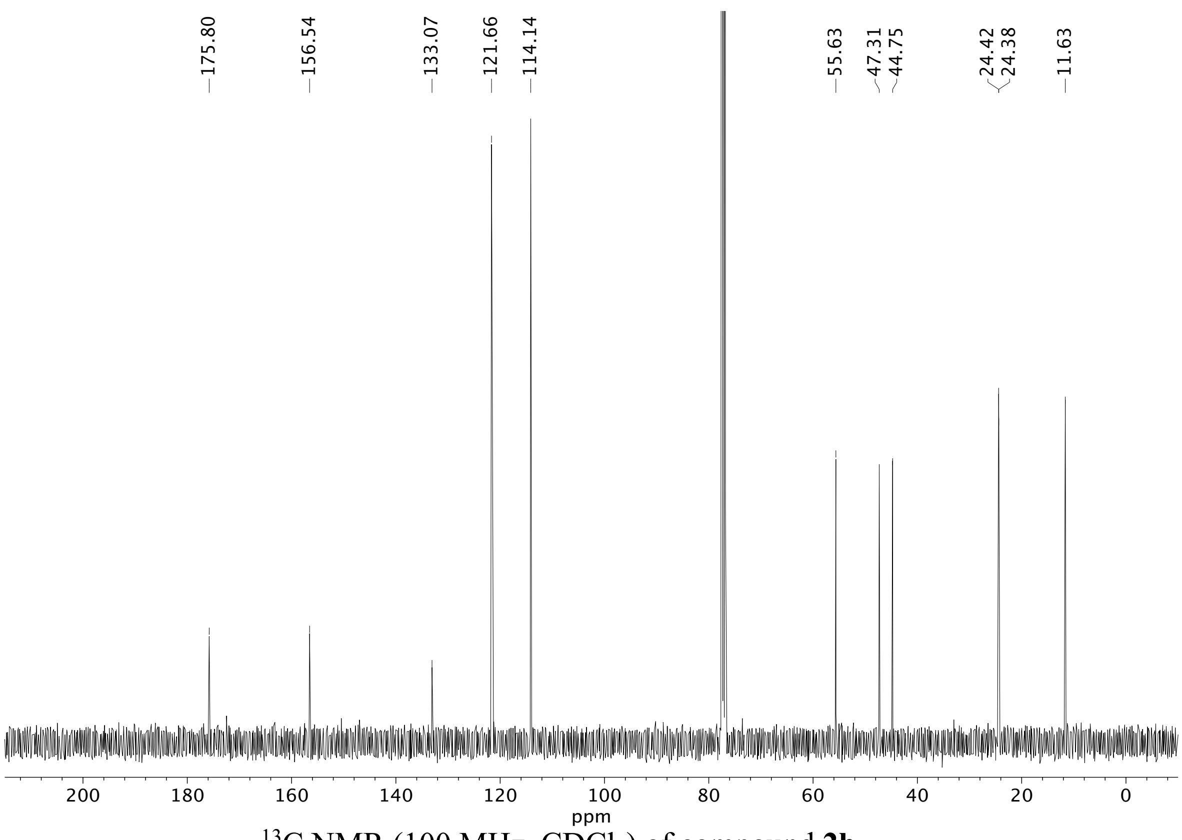
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2a**.



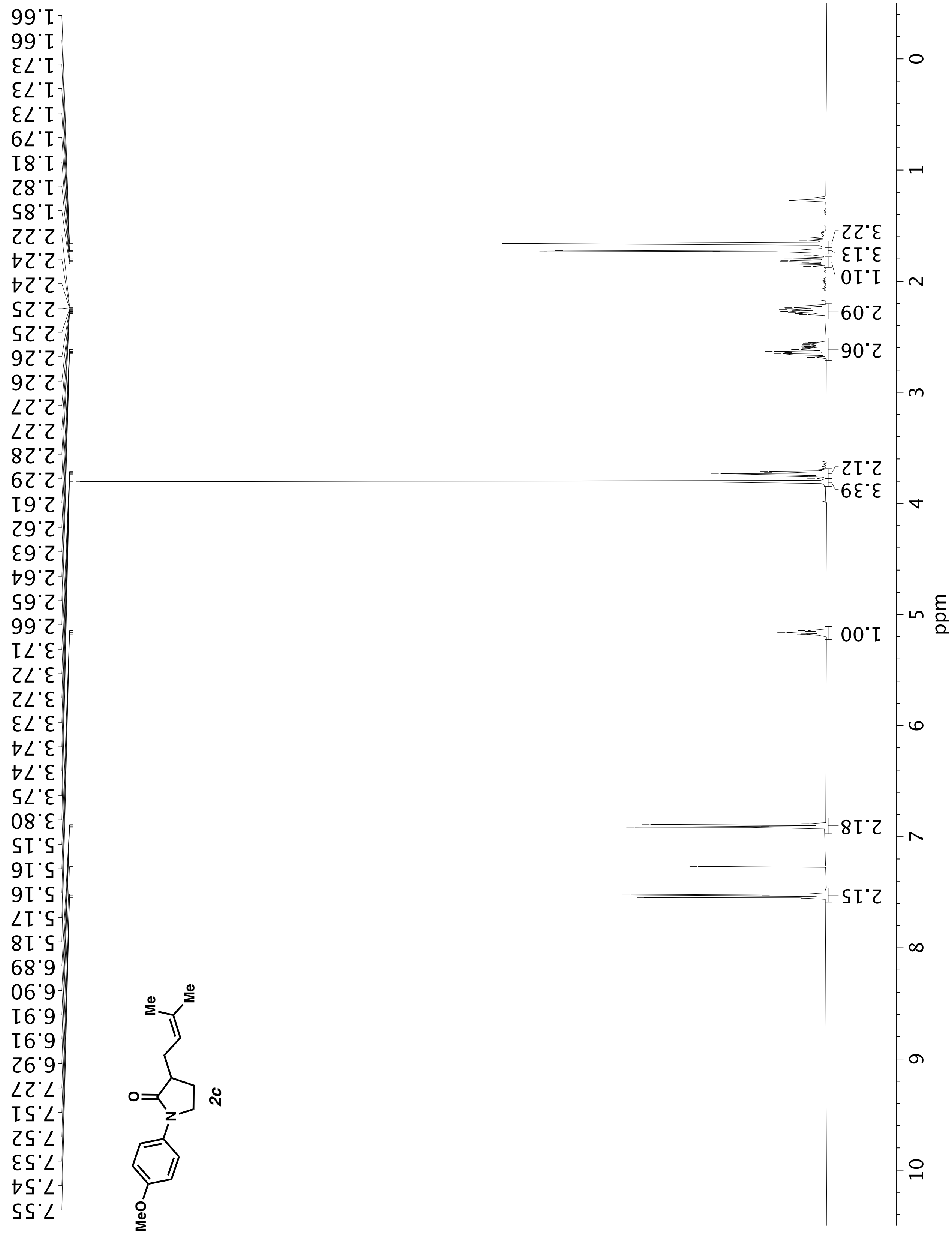
[1]H NMR (400 MHz, $CDCl_3$) of compound **2b**.



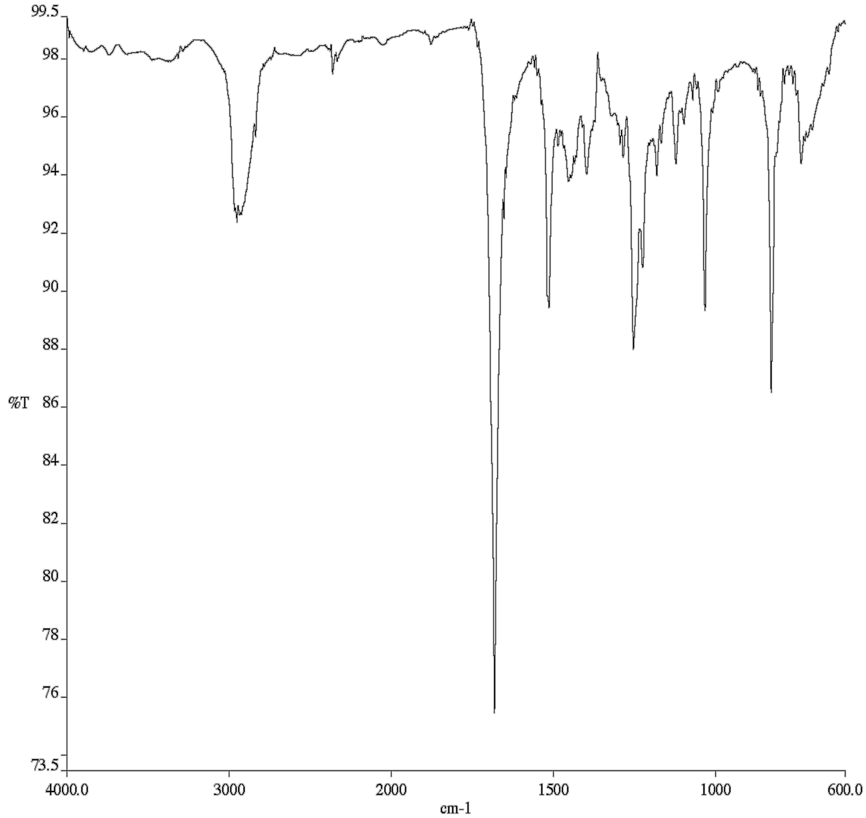
Infrared spectrum (Thin Film, NaCl) of compound **2b**.



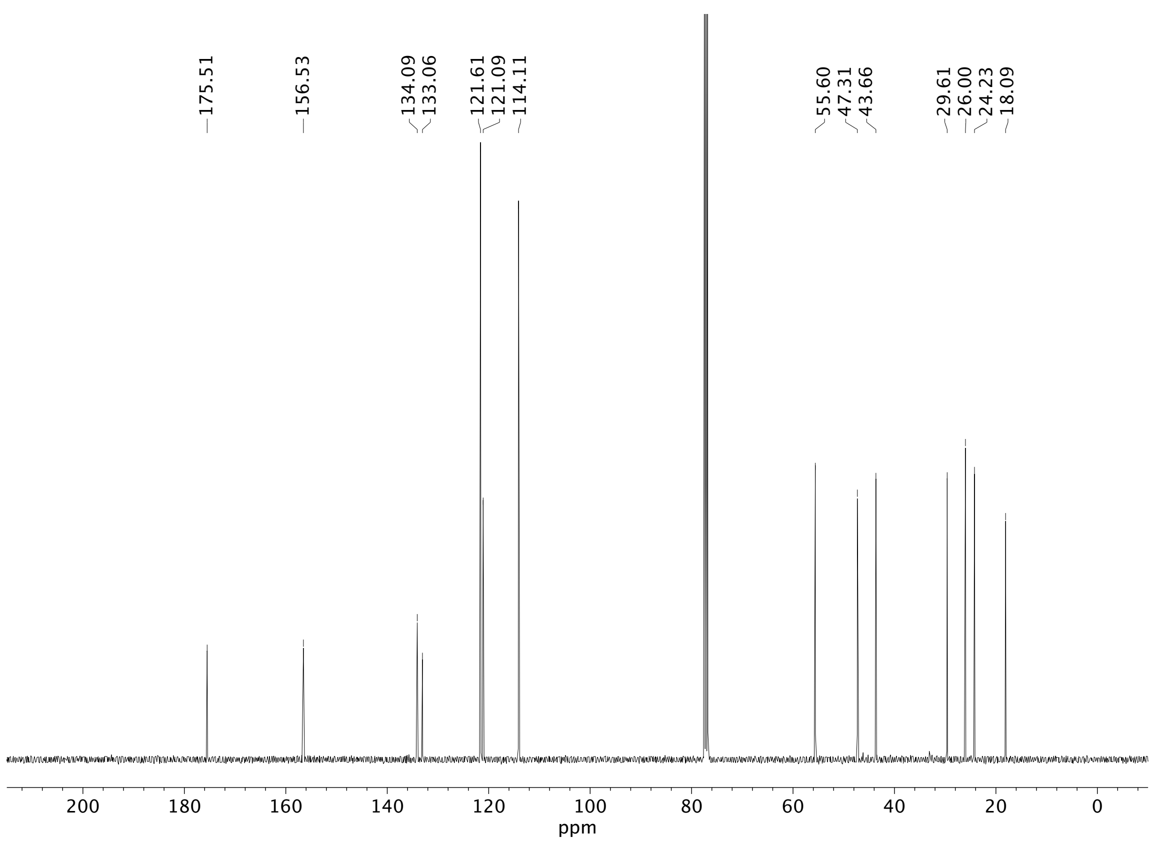
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2b**.



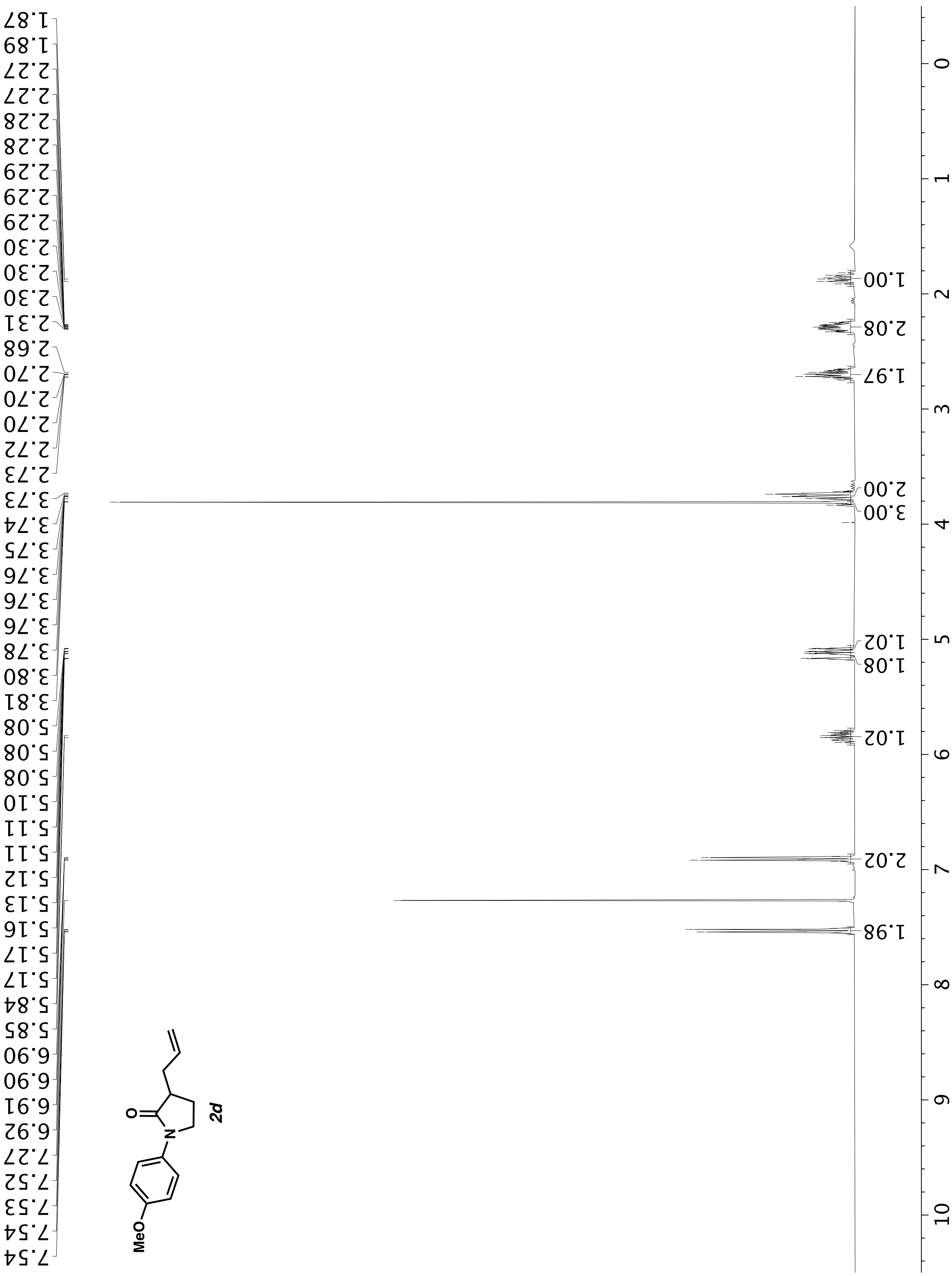
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2c**.



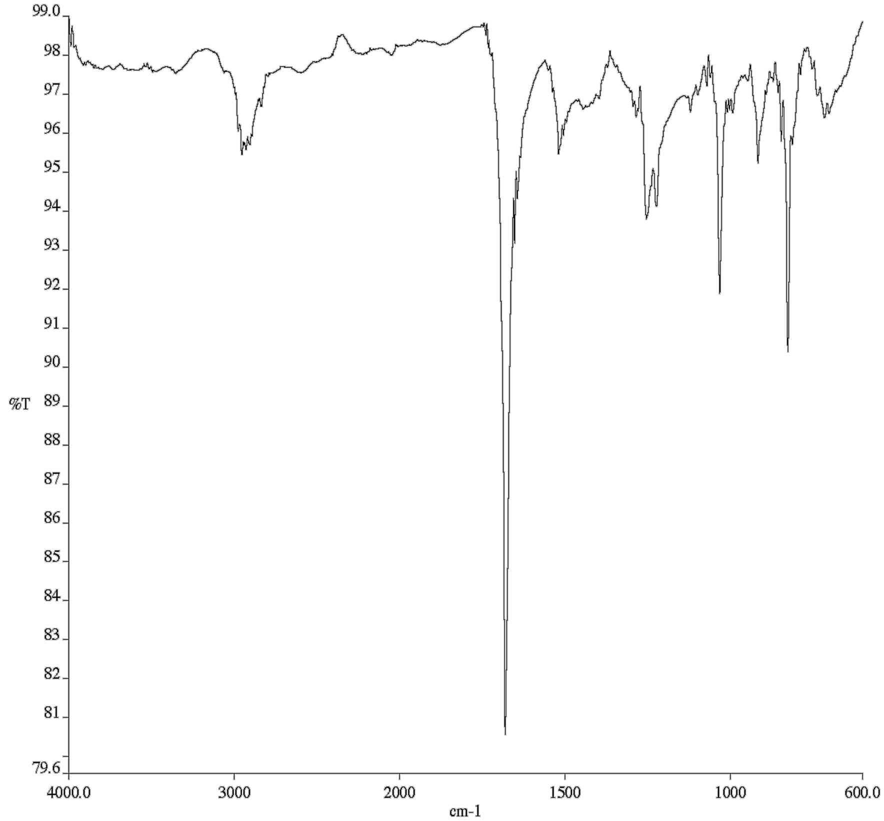
Infrared spectrum (Thin Film, NaCl) of compound **2c**.



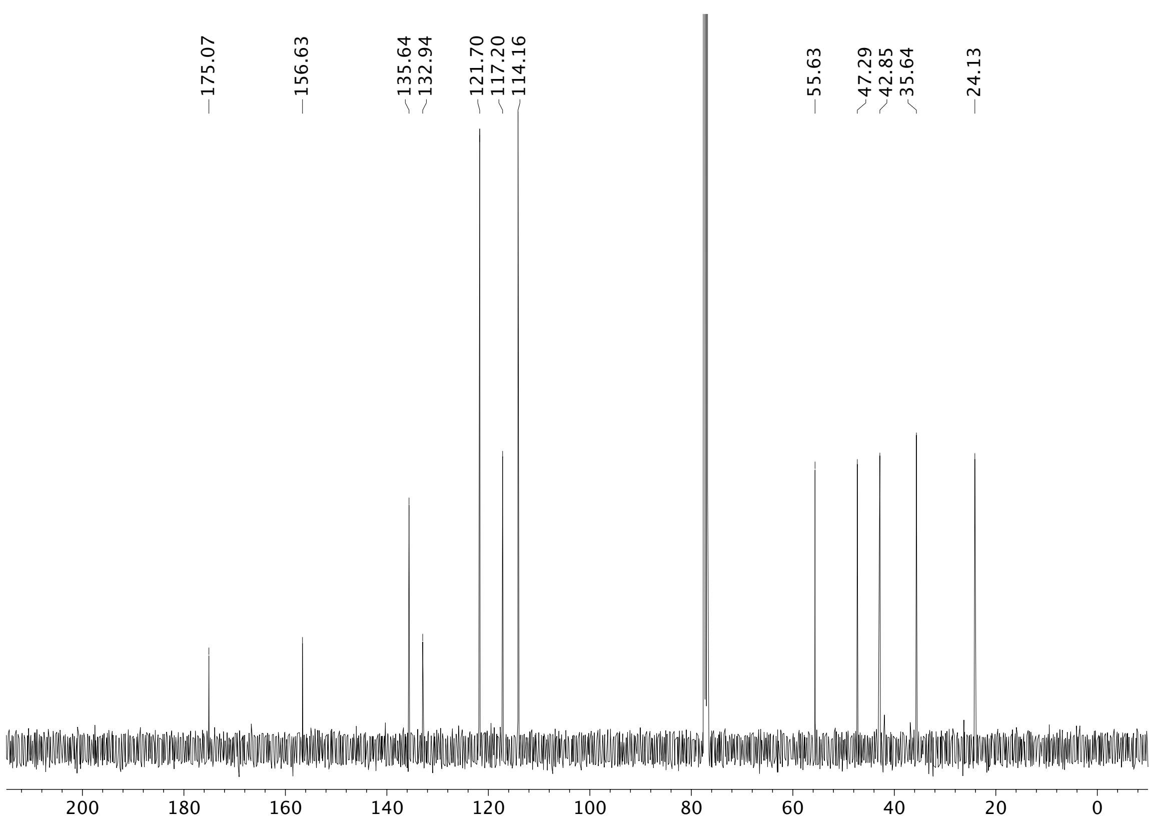
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2c**.



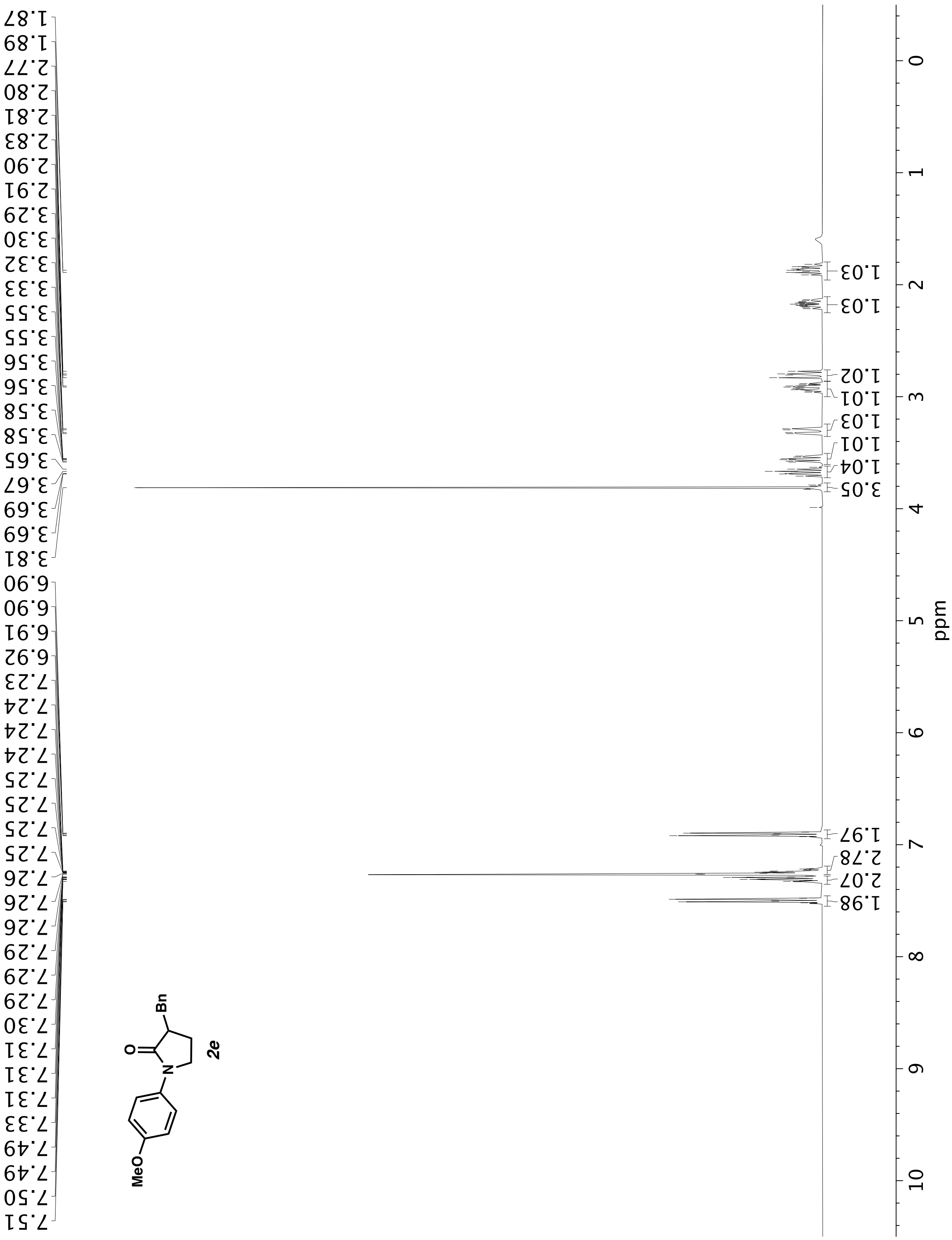
[1]H NMR (400 MHz, $CDCl_3$) of compound **2d**.



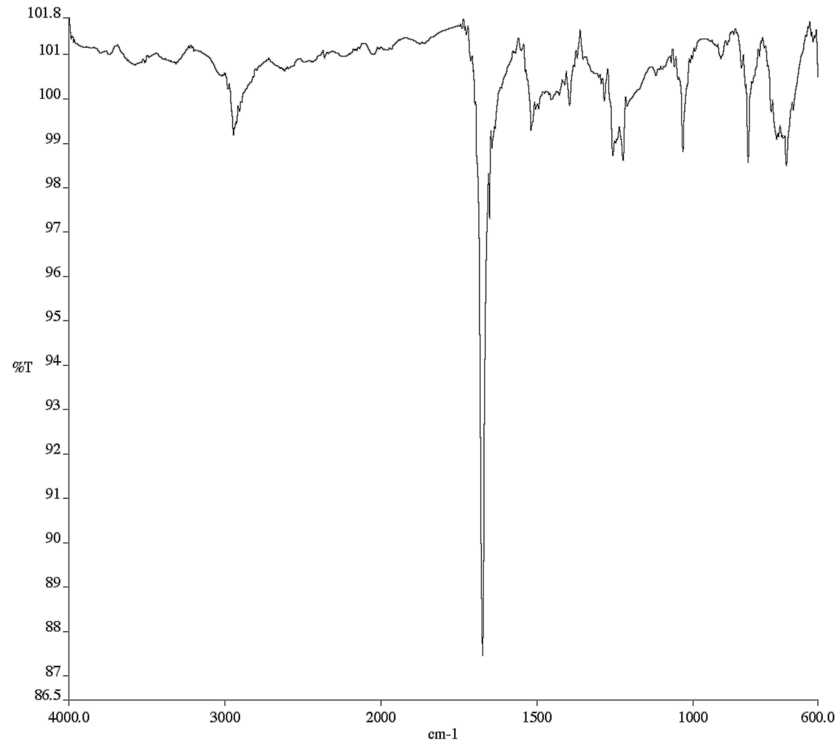
Infrared spectrum (Thin Film, NaCl) of compound **2d**.



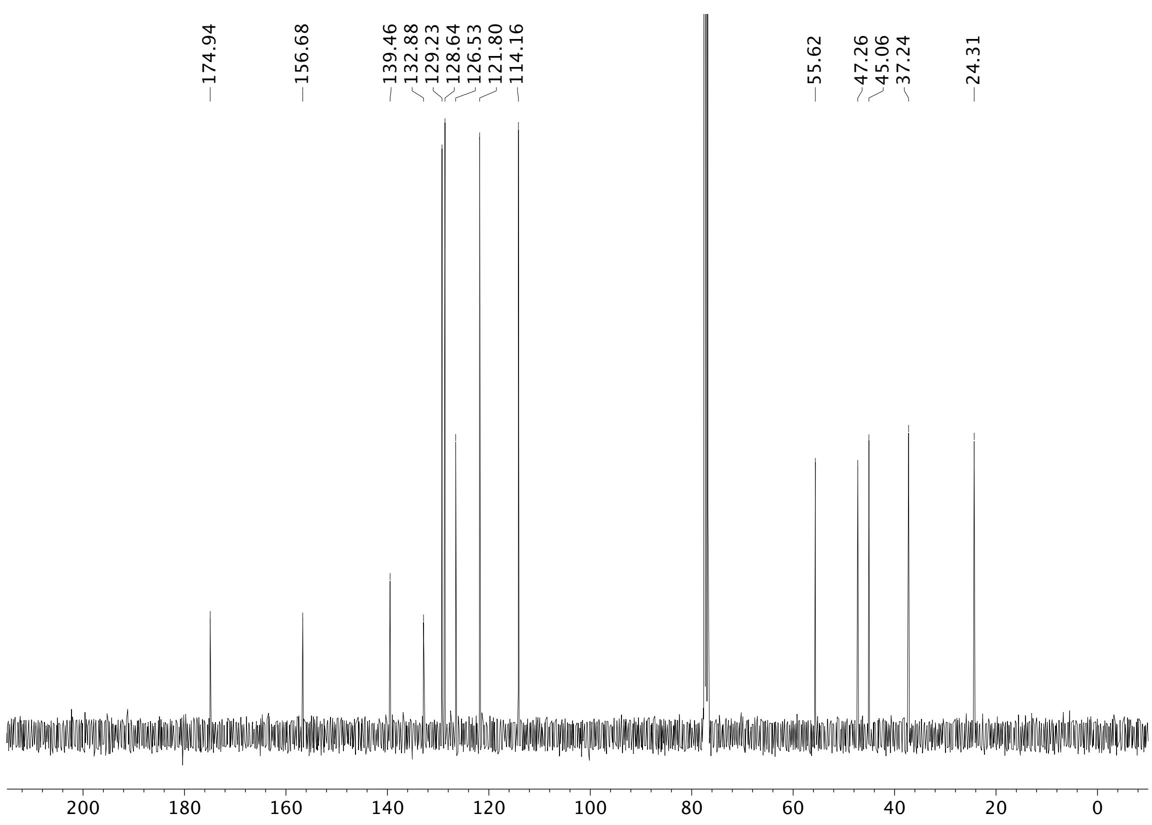
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2d**.



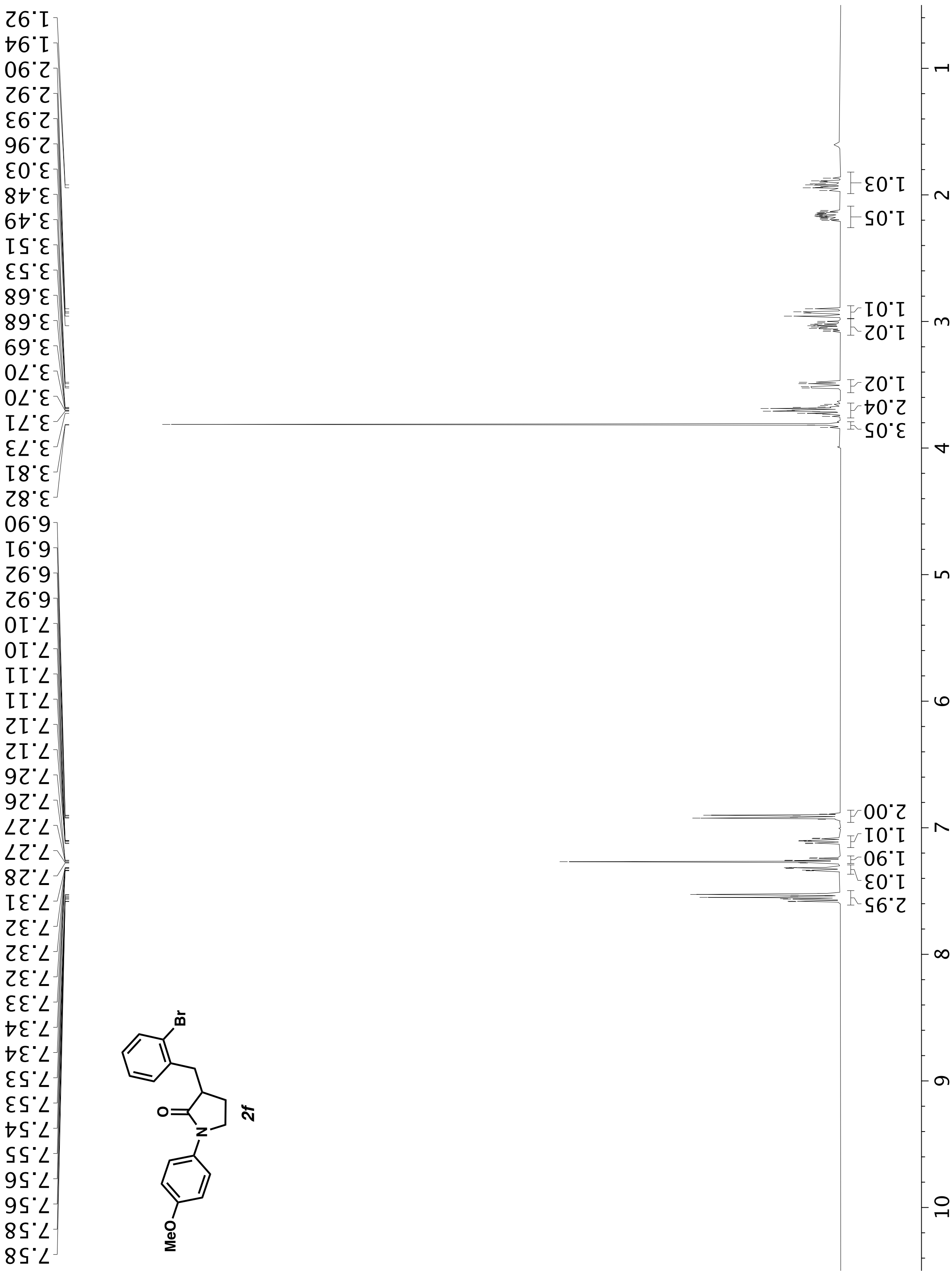
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2e**.



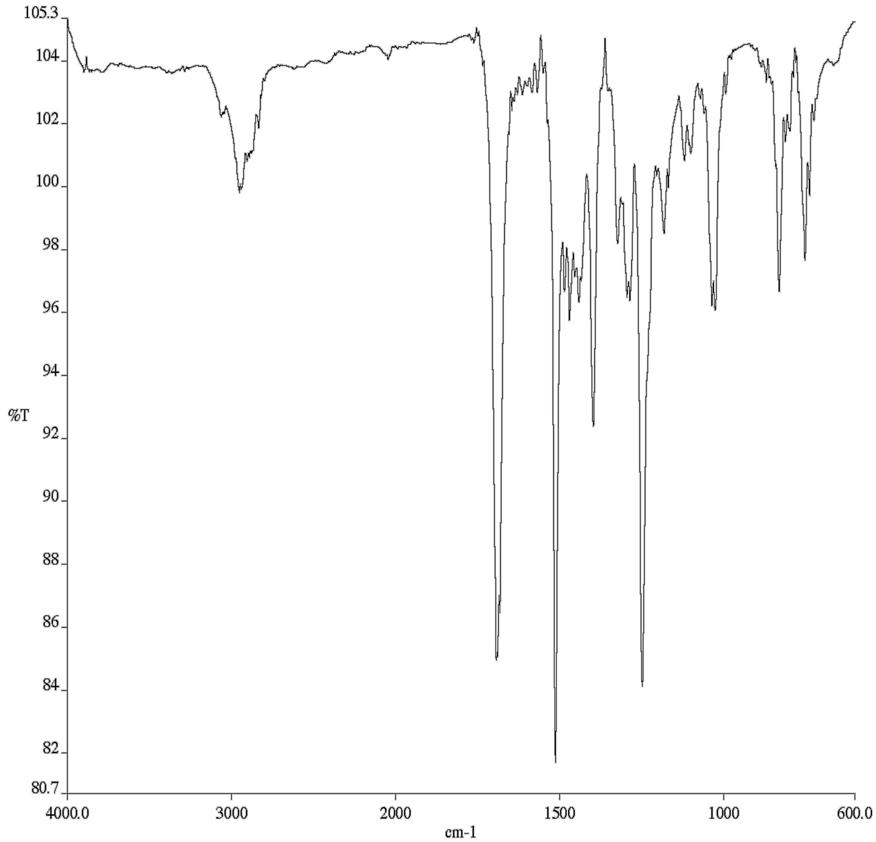
Infrared spectrum (Thin Film, NaCl) of compound **2e**.



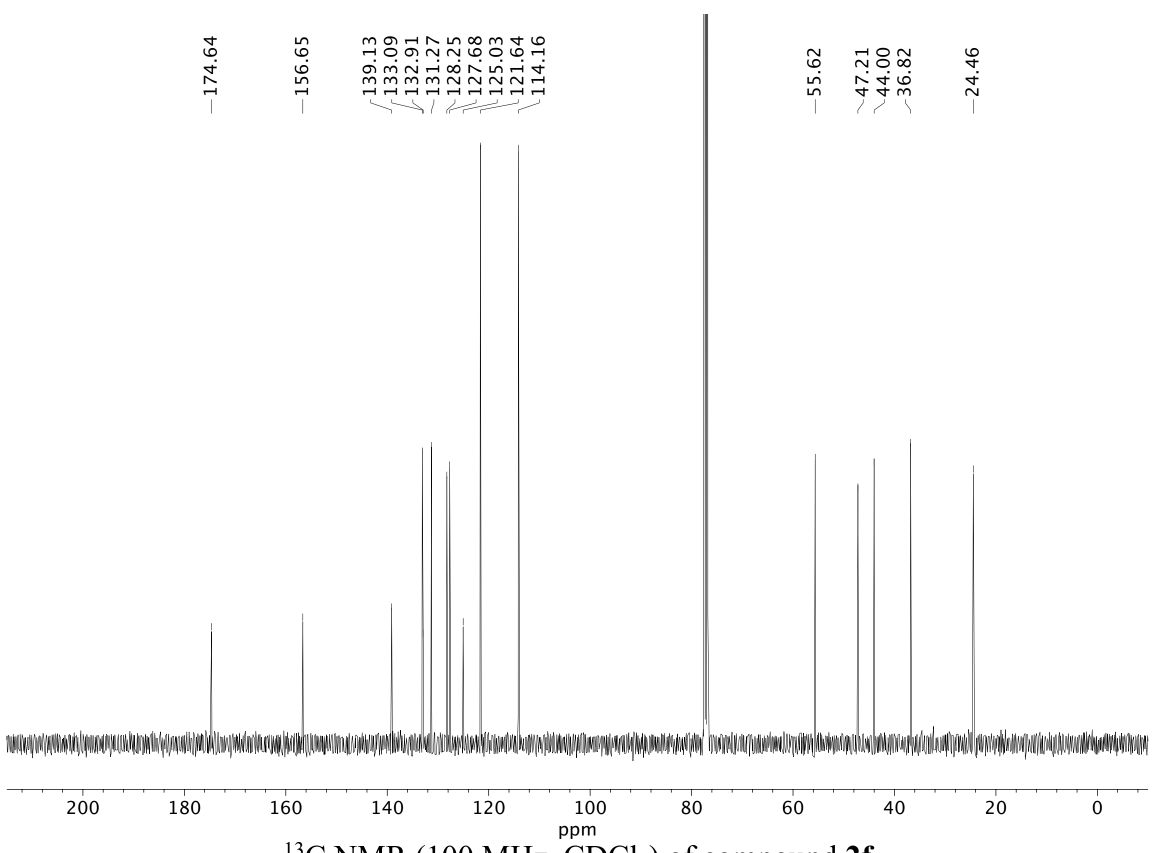
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2e**.



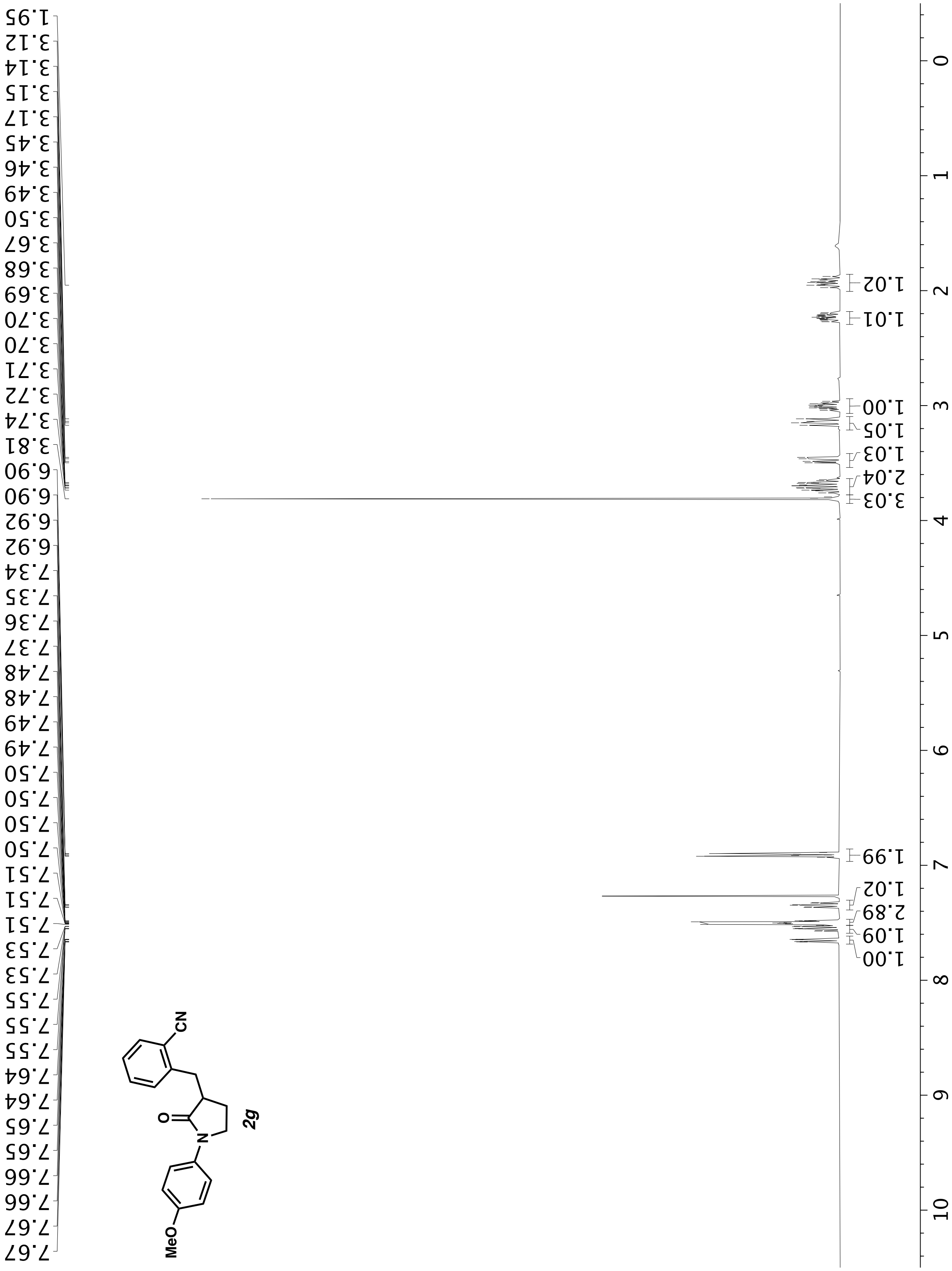
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2f**.



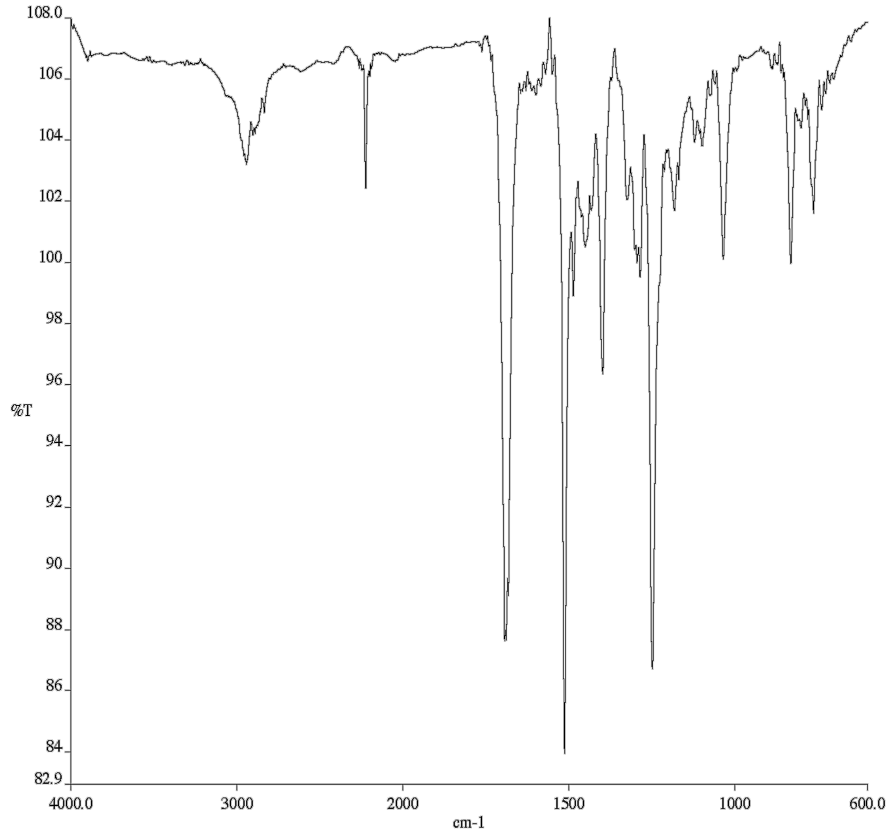
Infrared spectrum (Thin Film, NaCl) of compound **2f**.



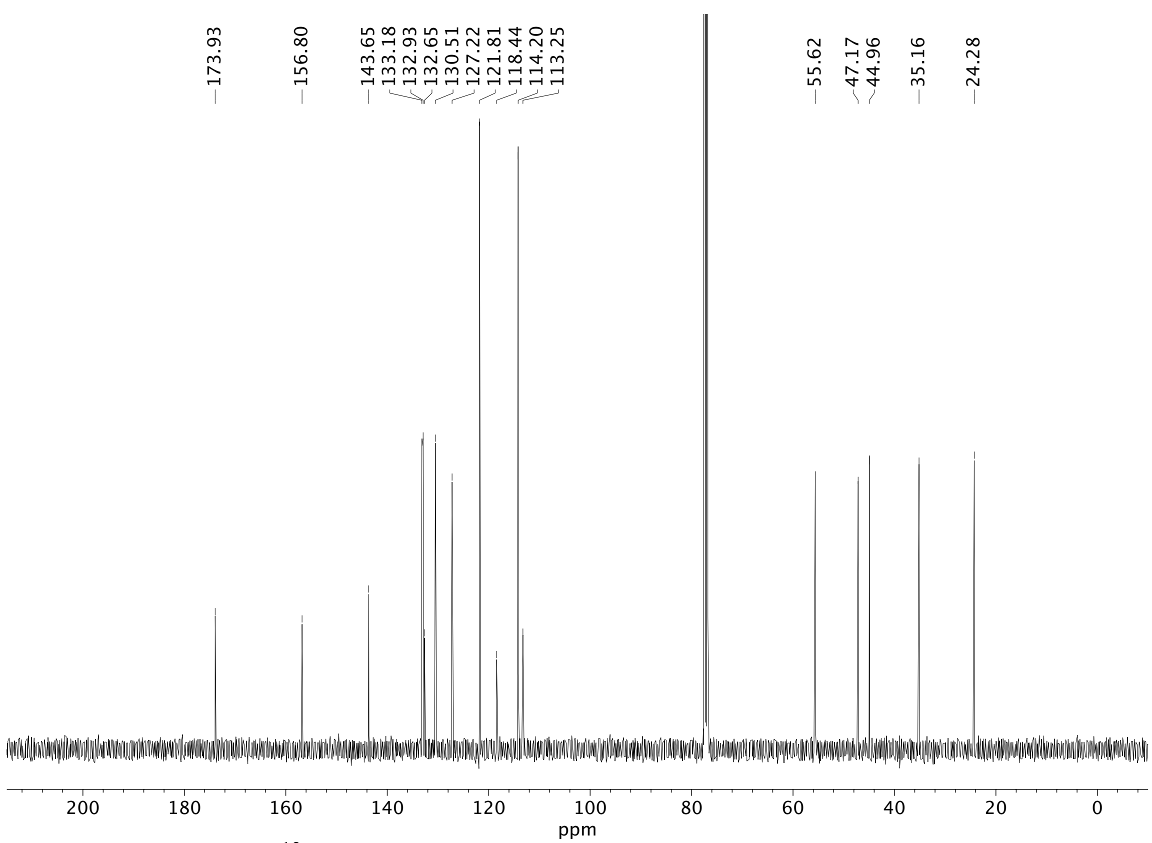
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2f**.



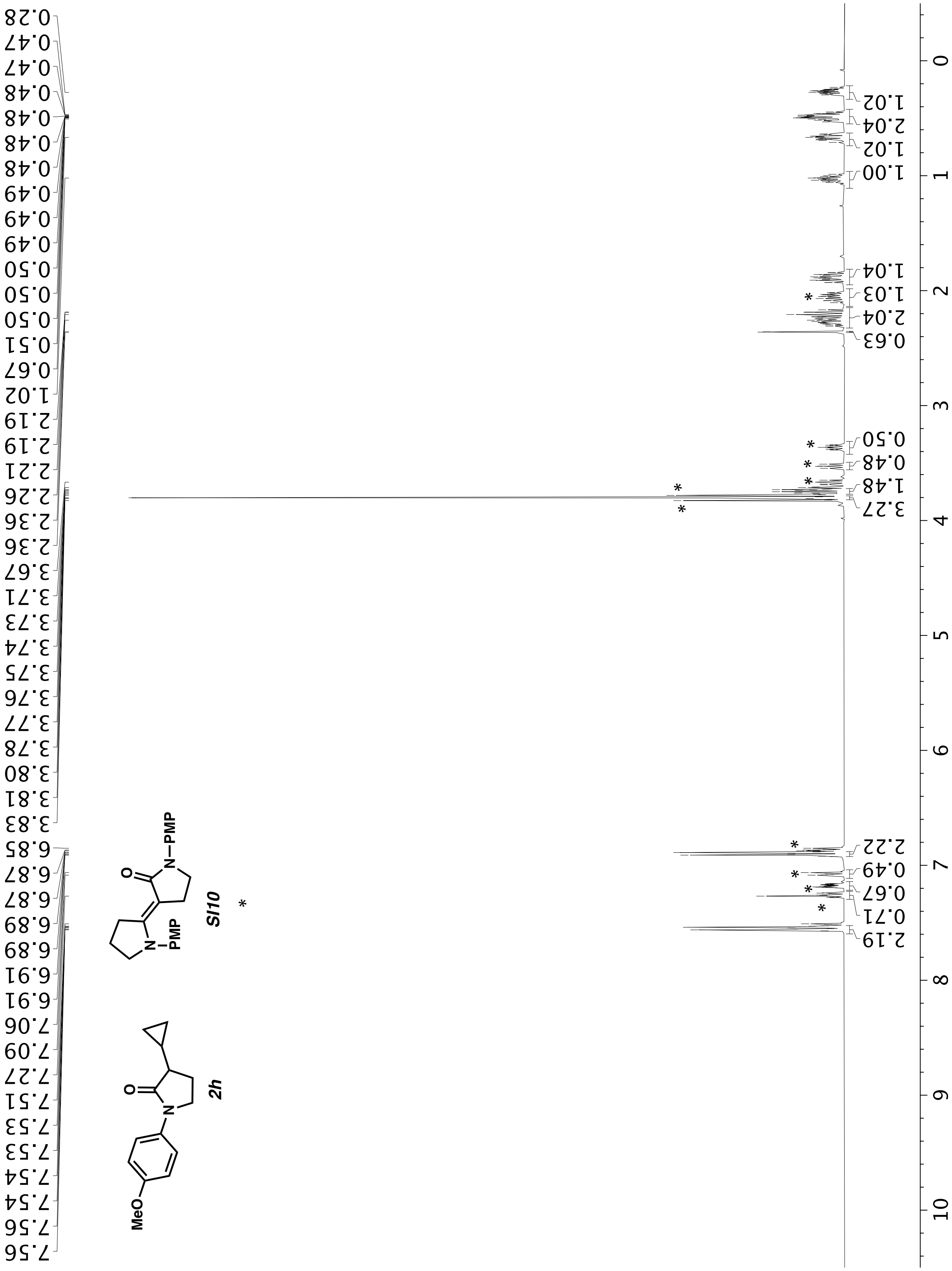
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2g**.



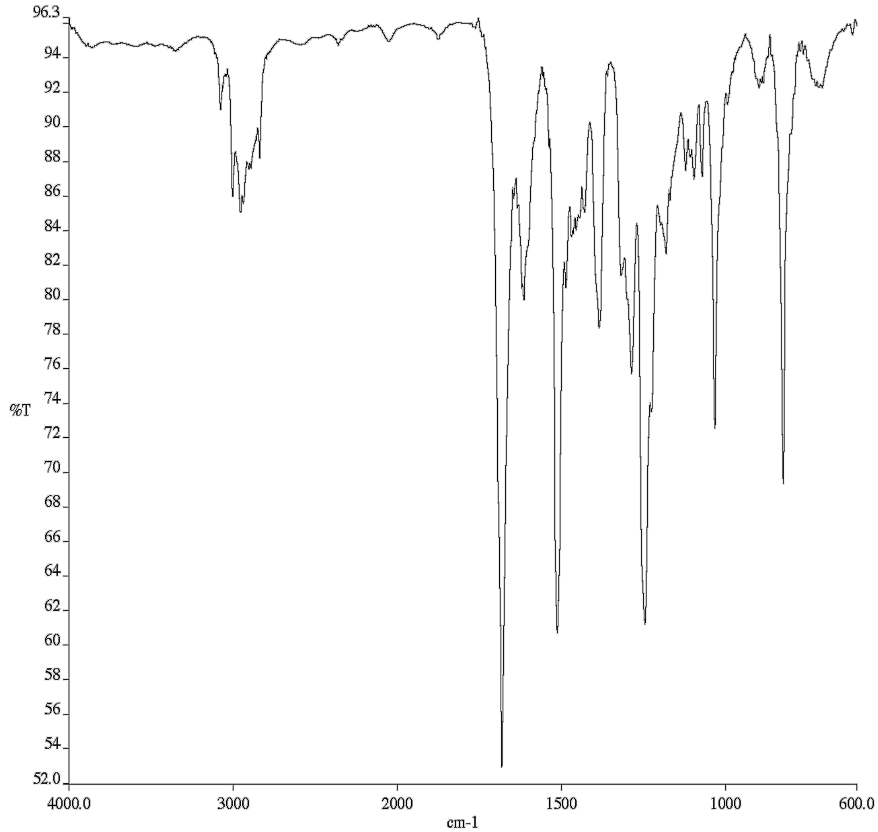
Infrared spectrum (Thin Film, NaCl) of compound **2g**.



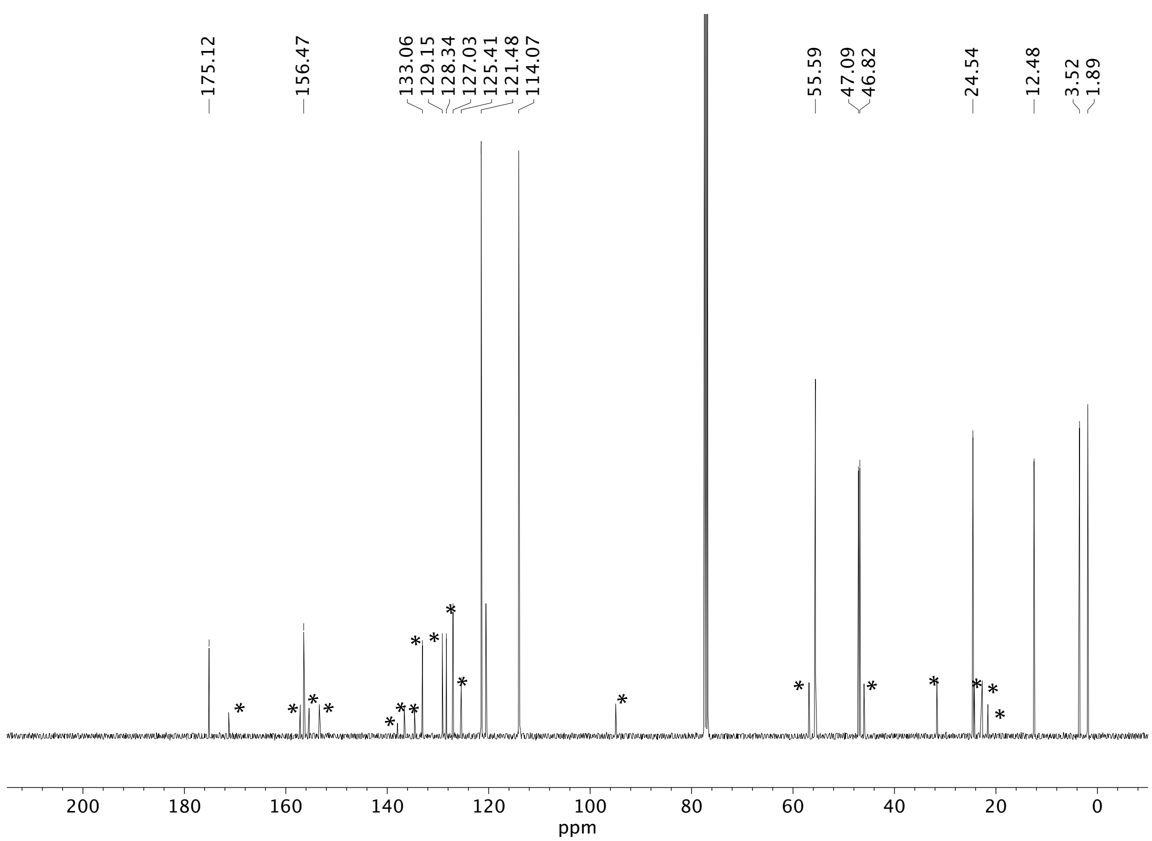
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2g**.



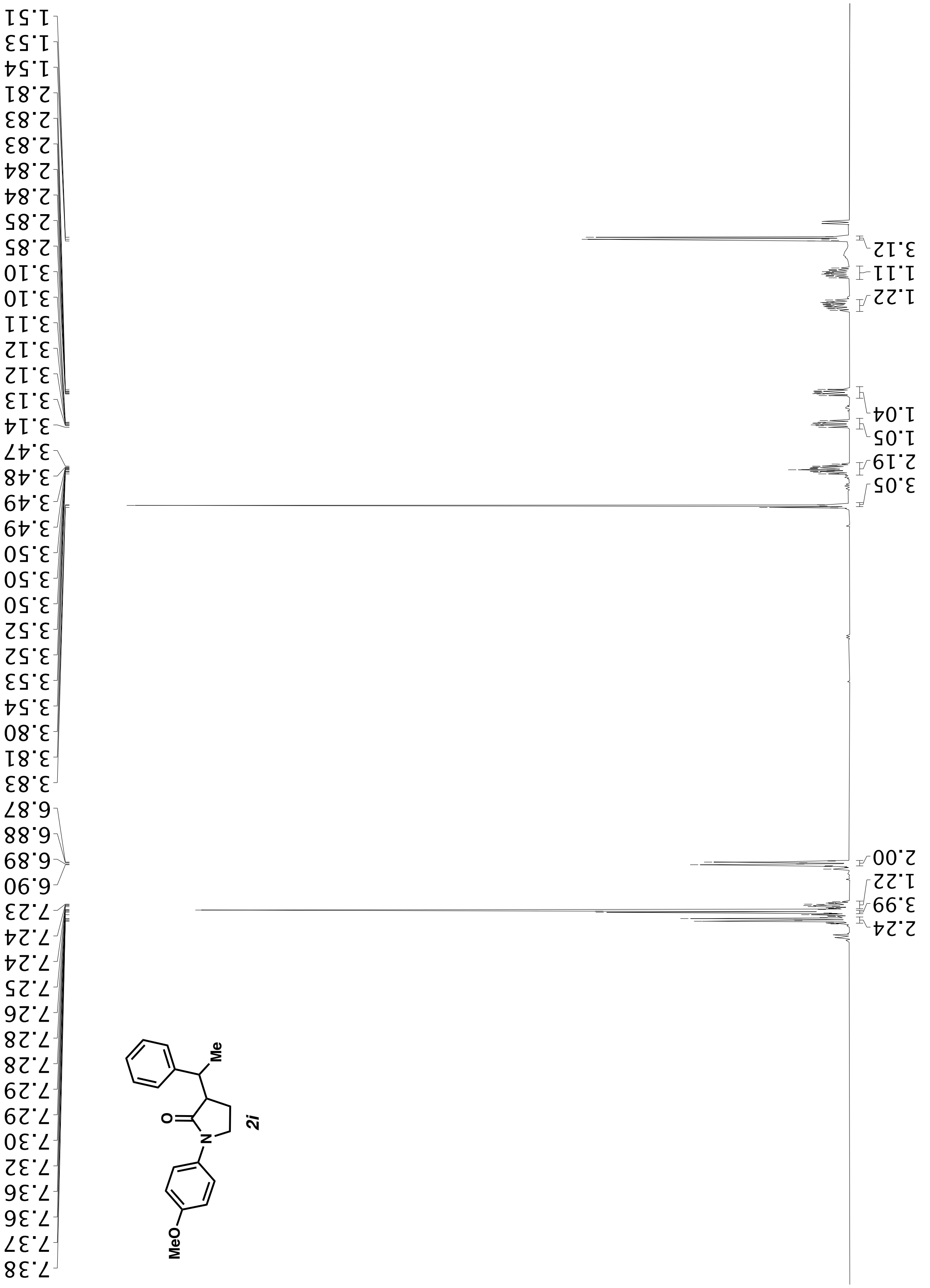
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2h**. (**SI10** impurity)



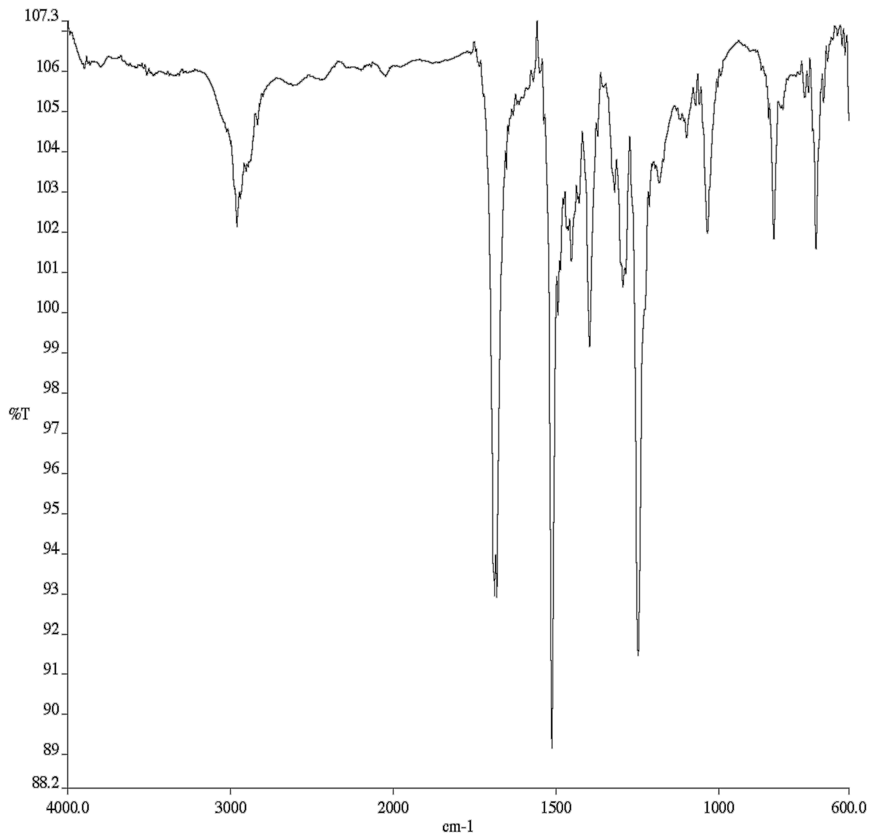
Infrared spectrum (Thin Film, NaCl) of compound **2h**. (**SI10** impurity)



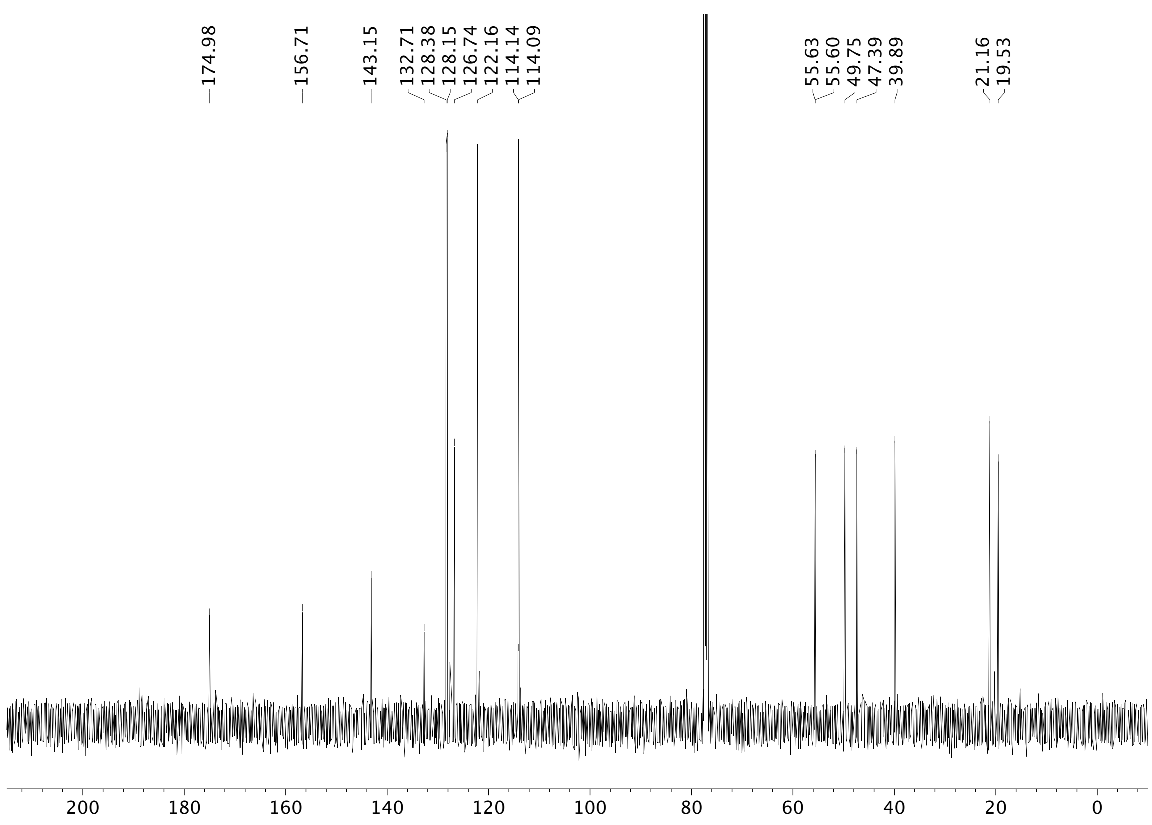
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2h**. (**SI10** impurity)



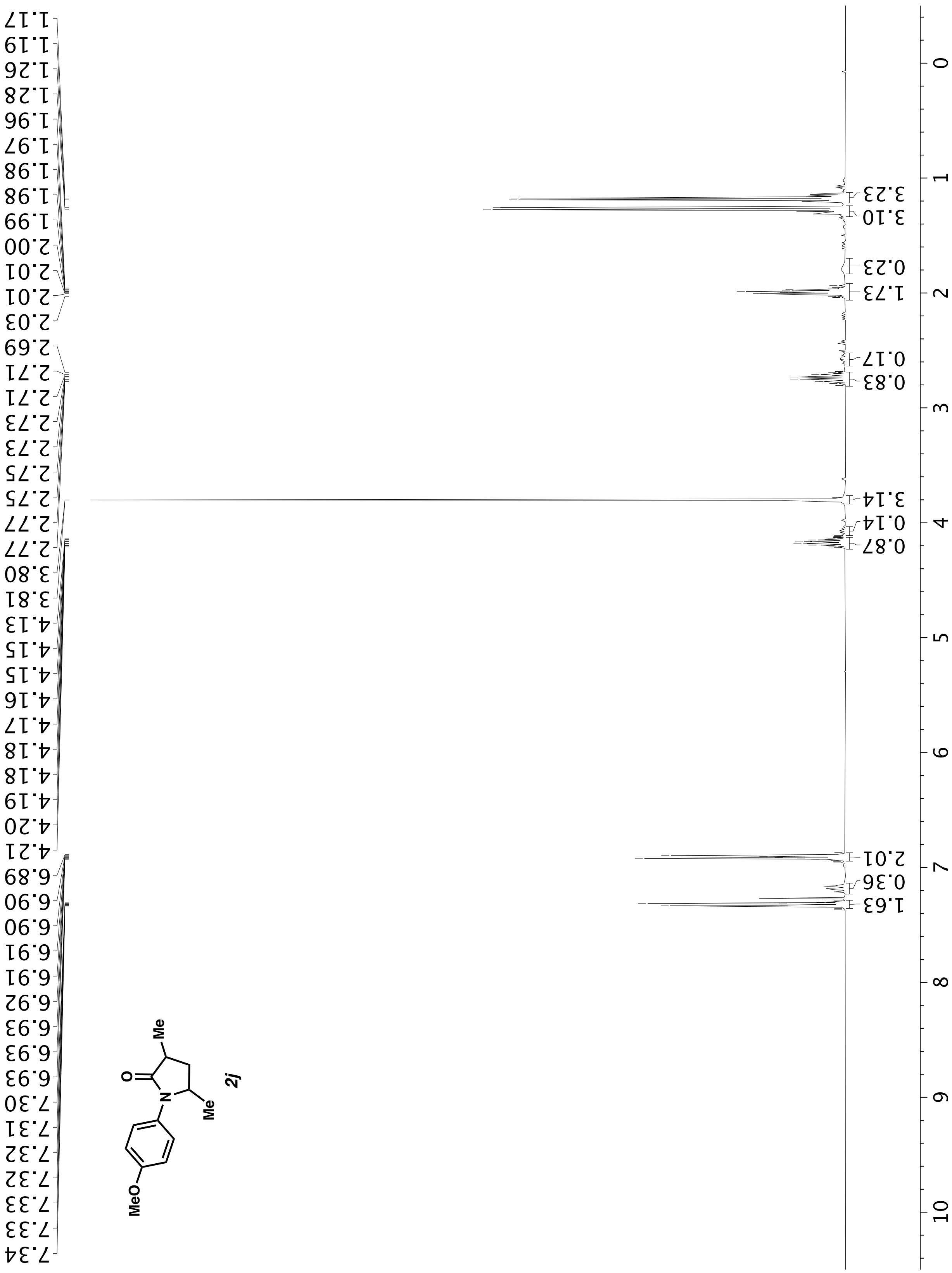
^{1}H NMR (400 MHz, CDCl$_3$) of compound **2i**.



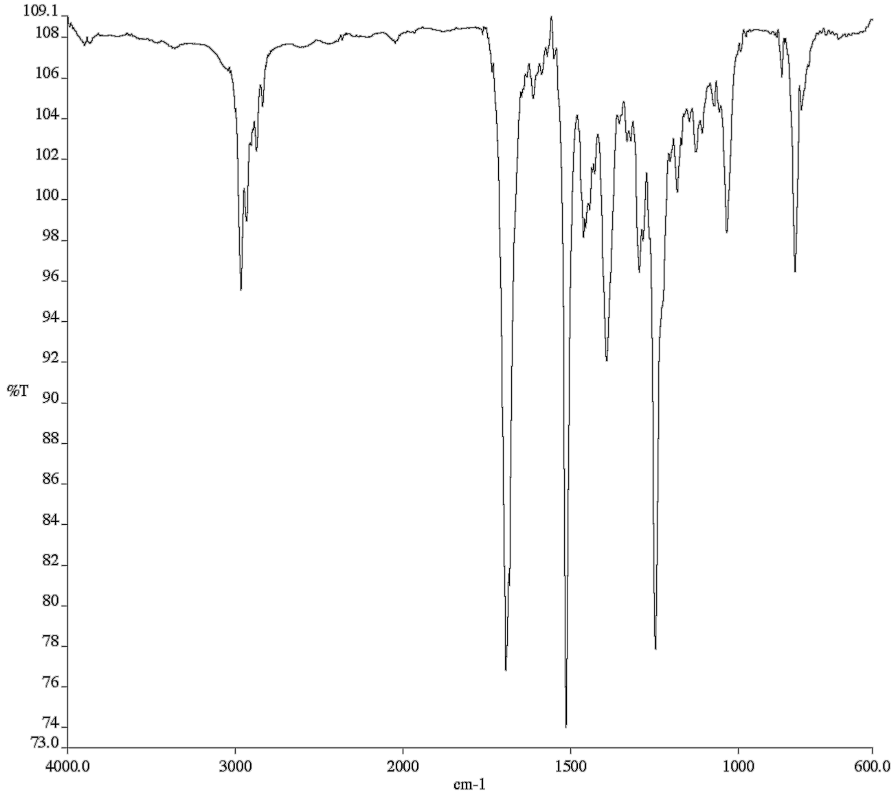
Infrared spectrum (Thin Film, NaCl) of compound **2i**.



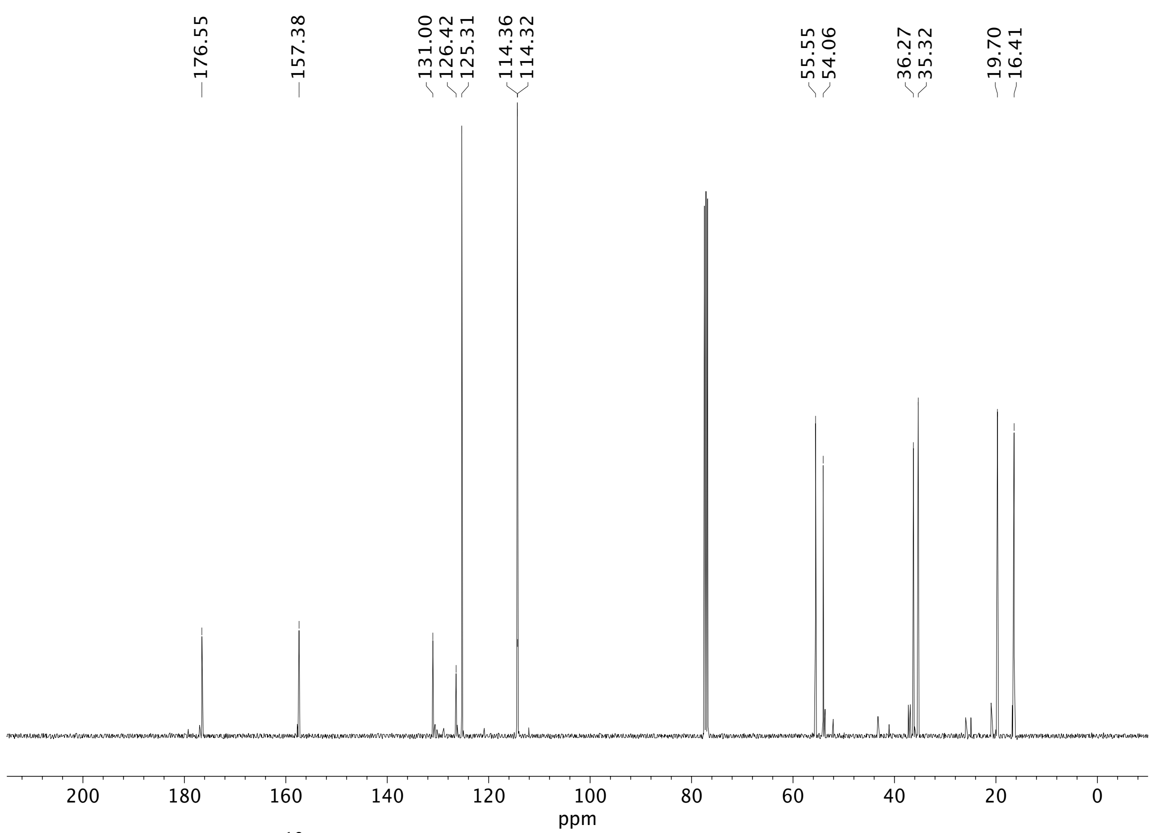
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2i**.



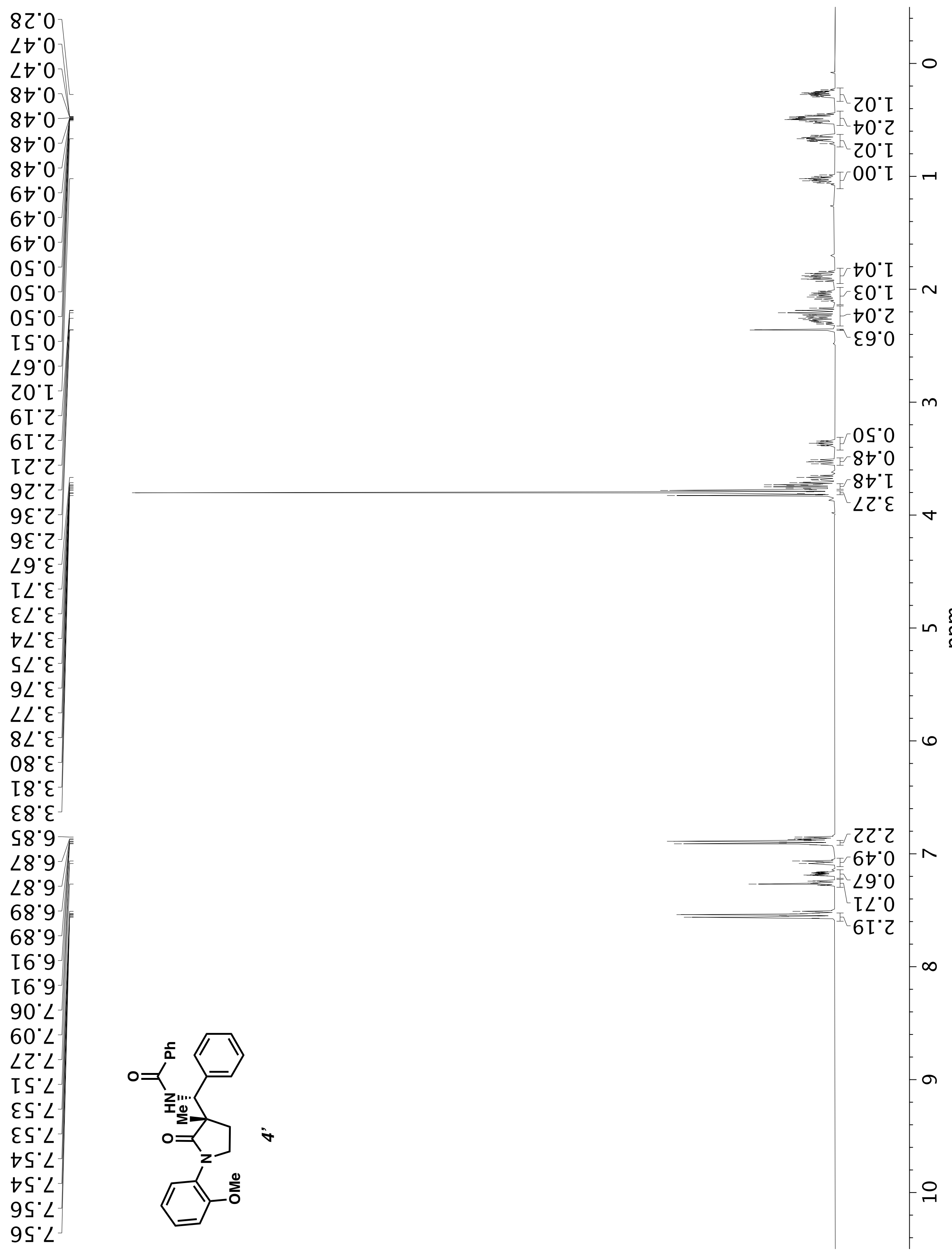
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2j**.



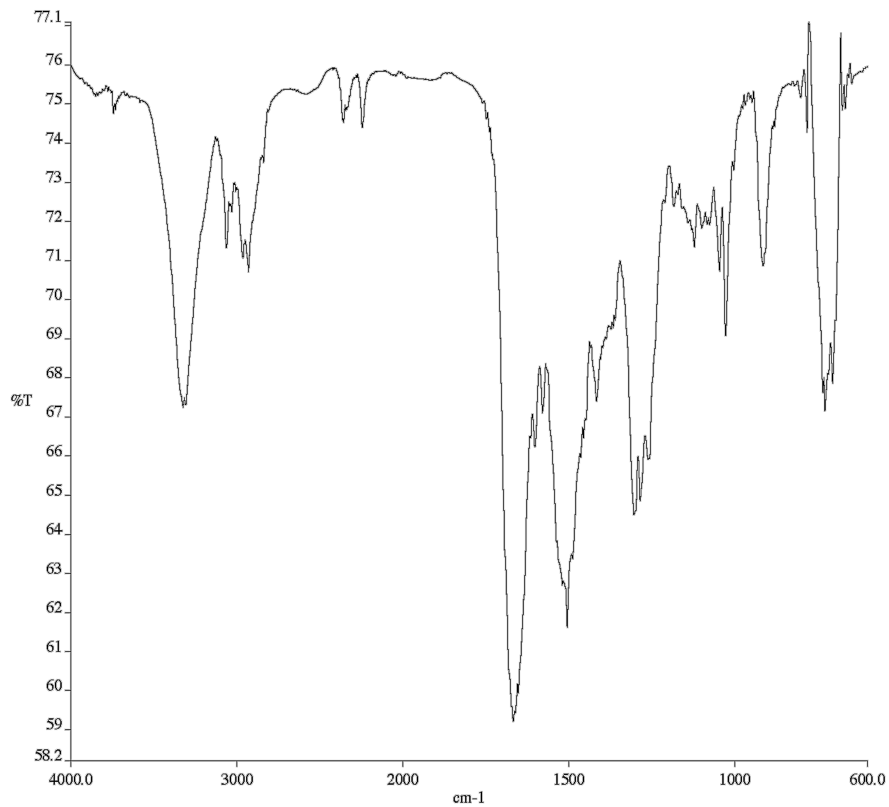
Infrared spectrum (Thin Film, NaCl) of compound **2j**.



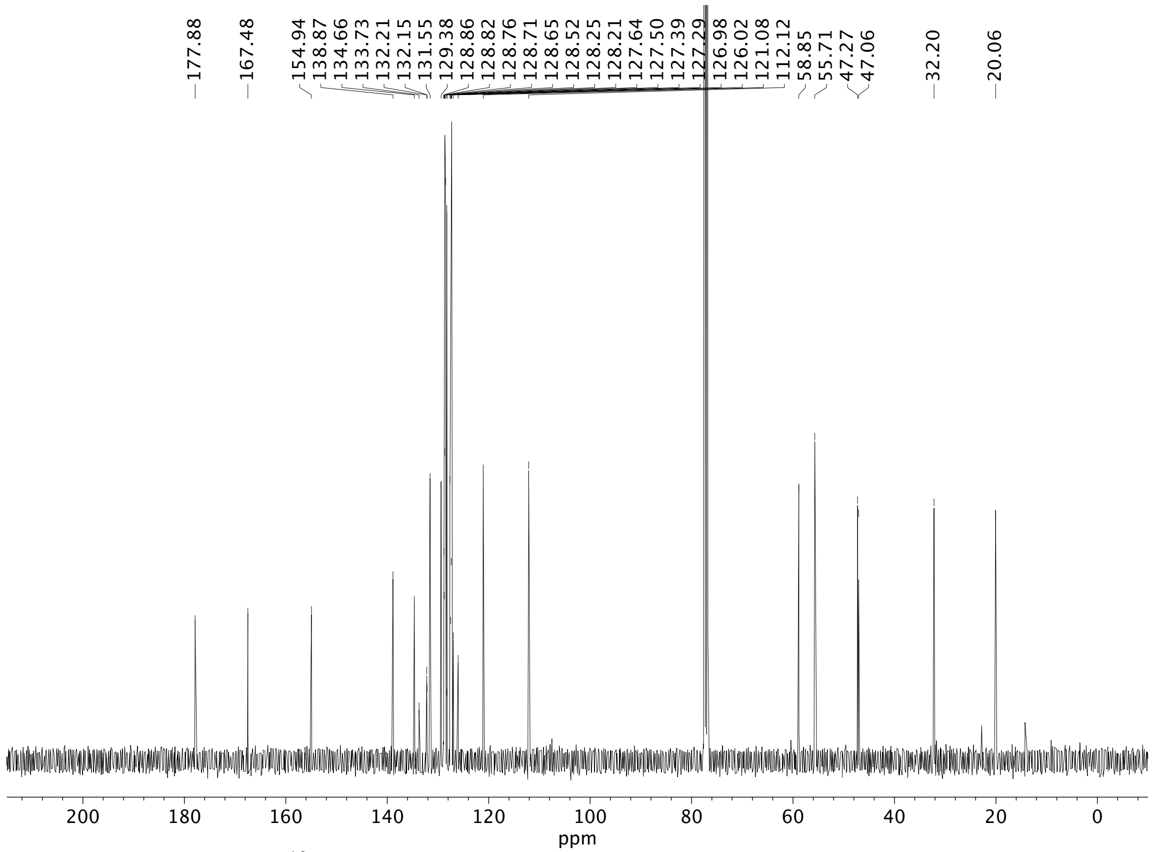
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2j**.



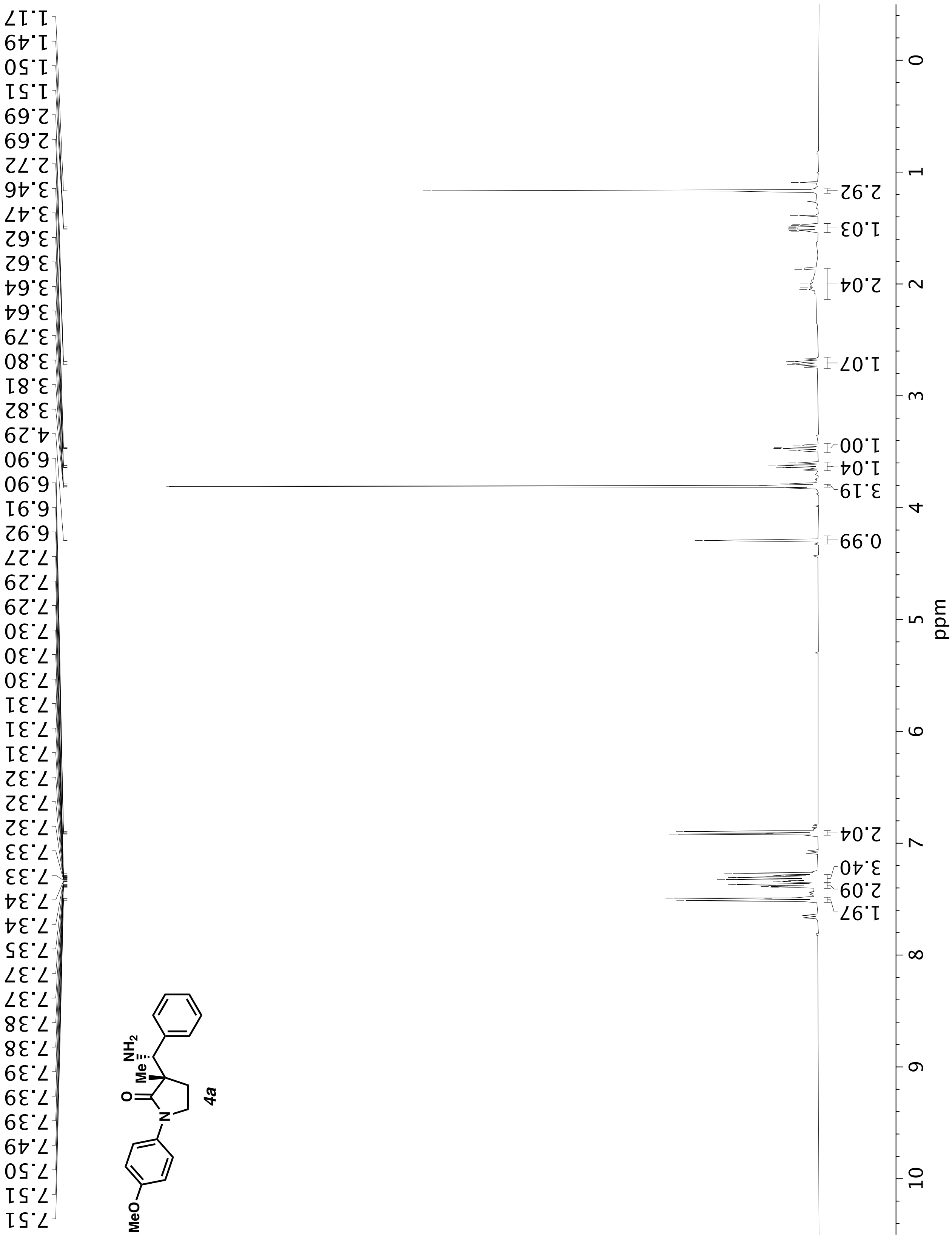
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4’**



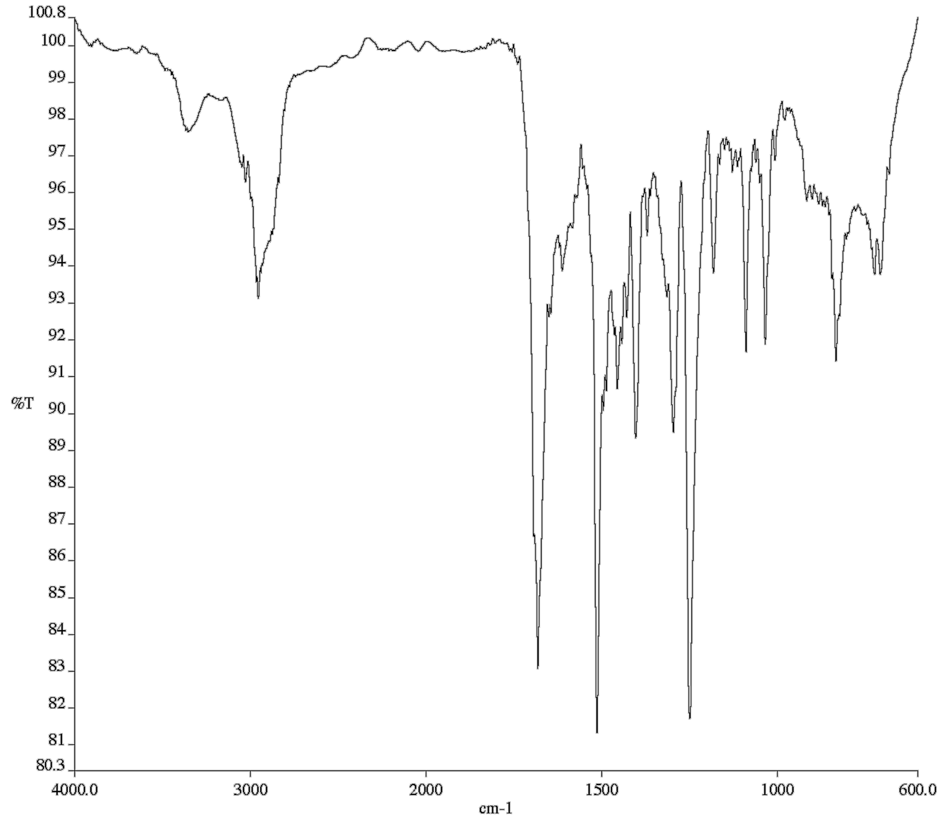
Infrared spectrum (Thin Film, NaCl) of compound **4’**



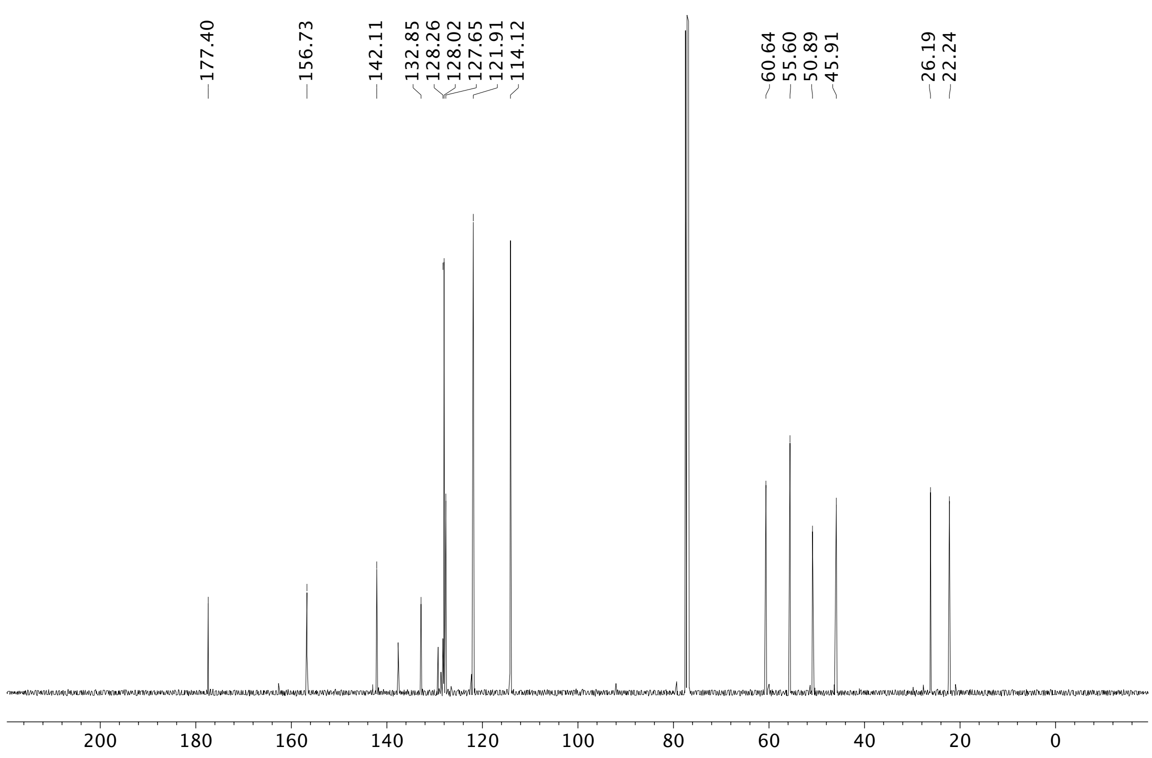
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4’**



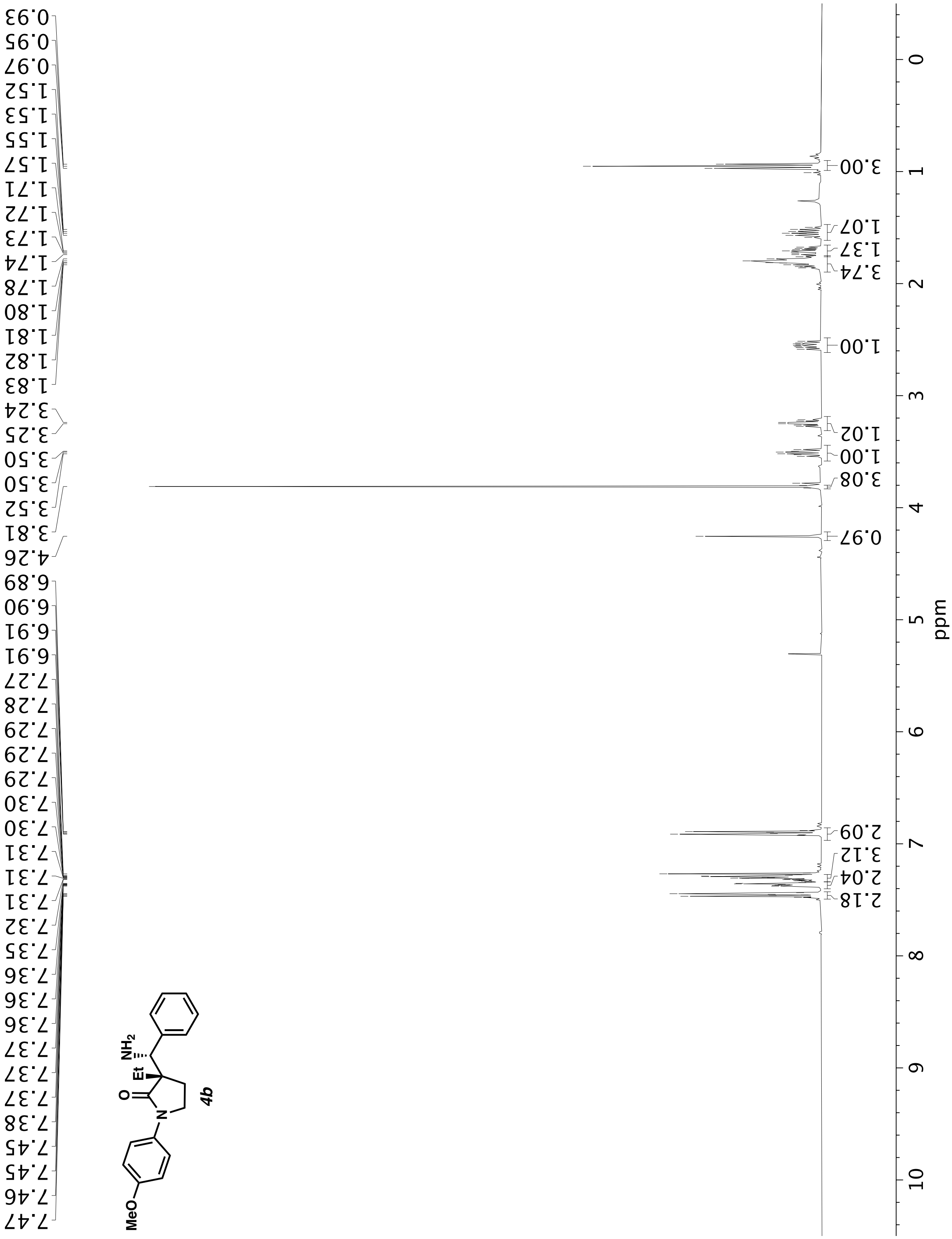
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4a**.



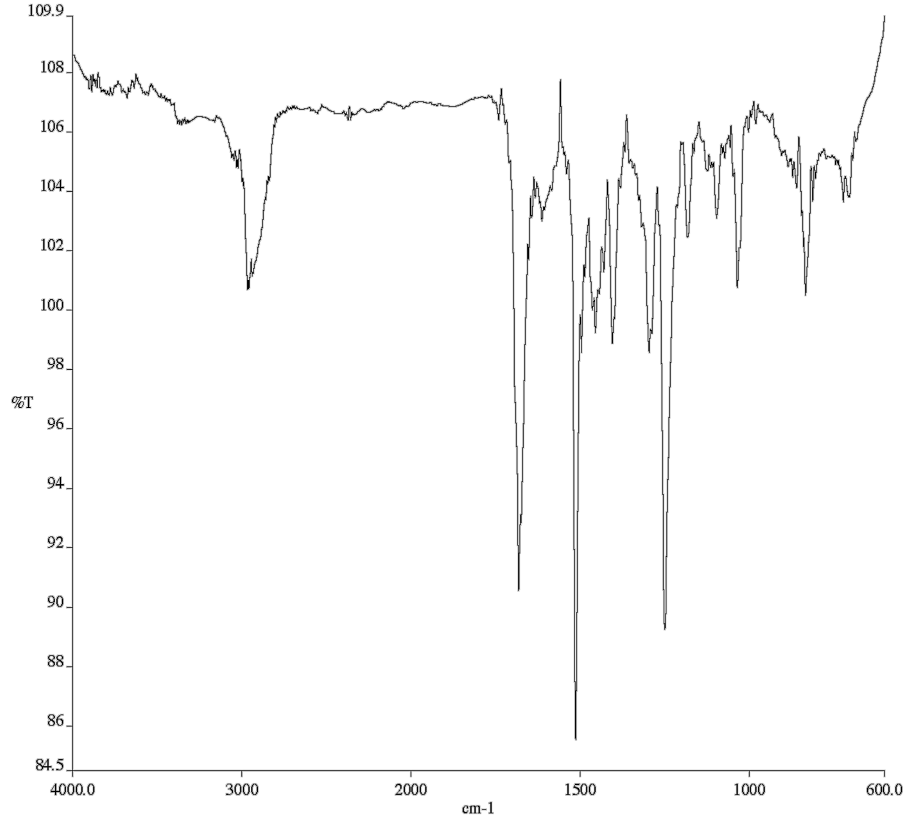
Infrared spectrum (Thin Film, NaCl) of compound **4a**.



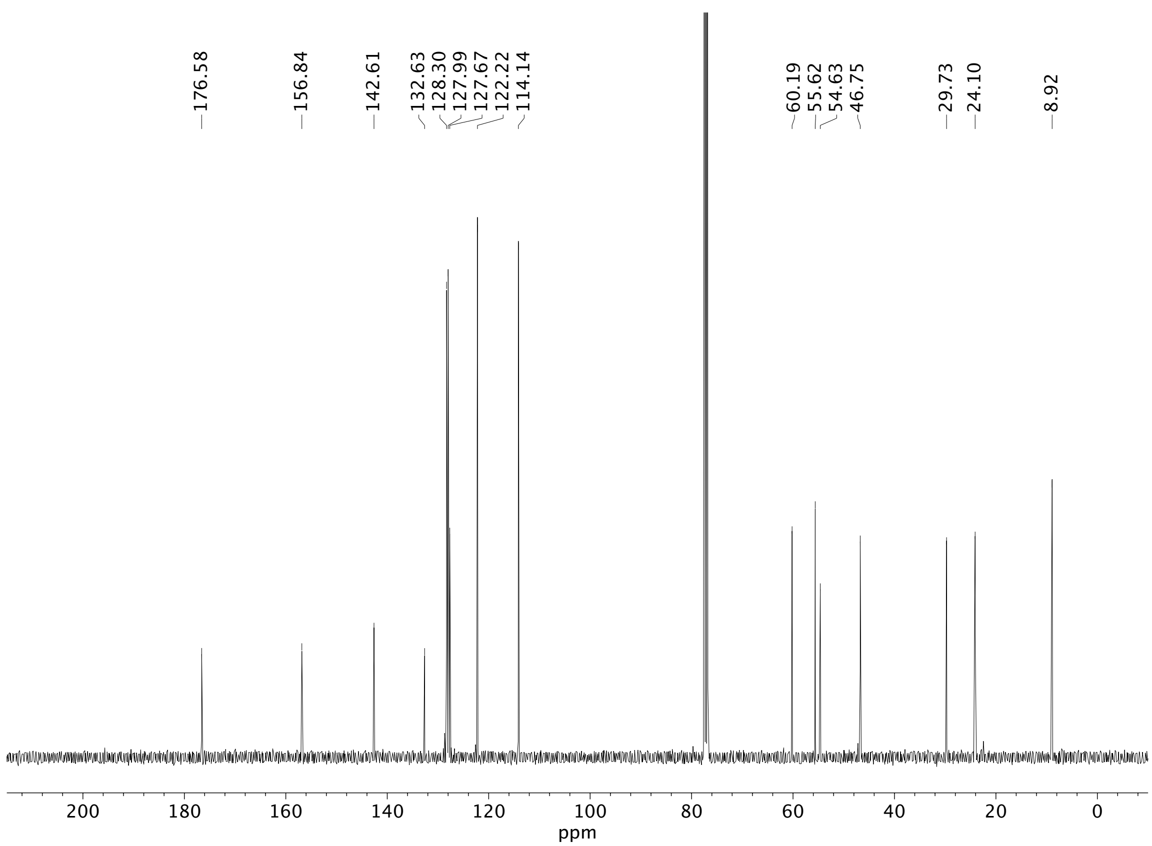
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4a**.



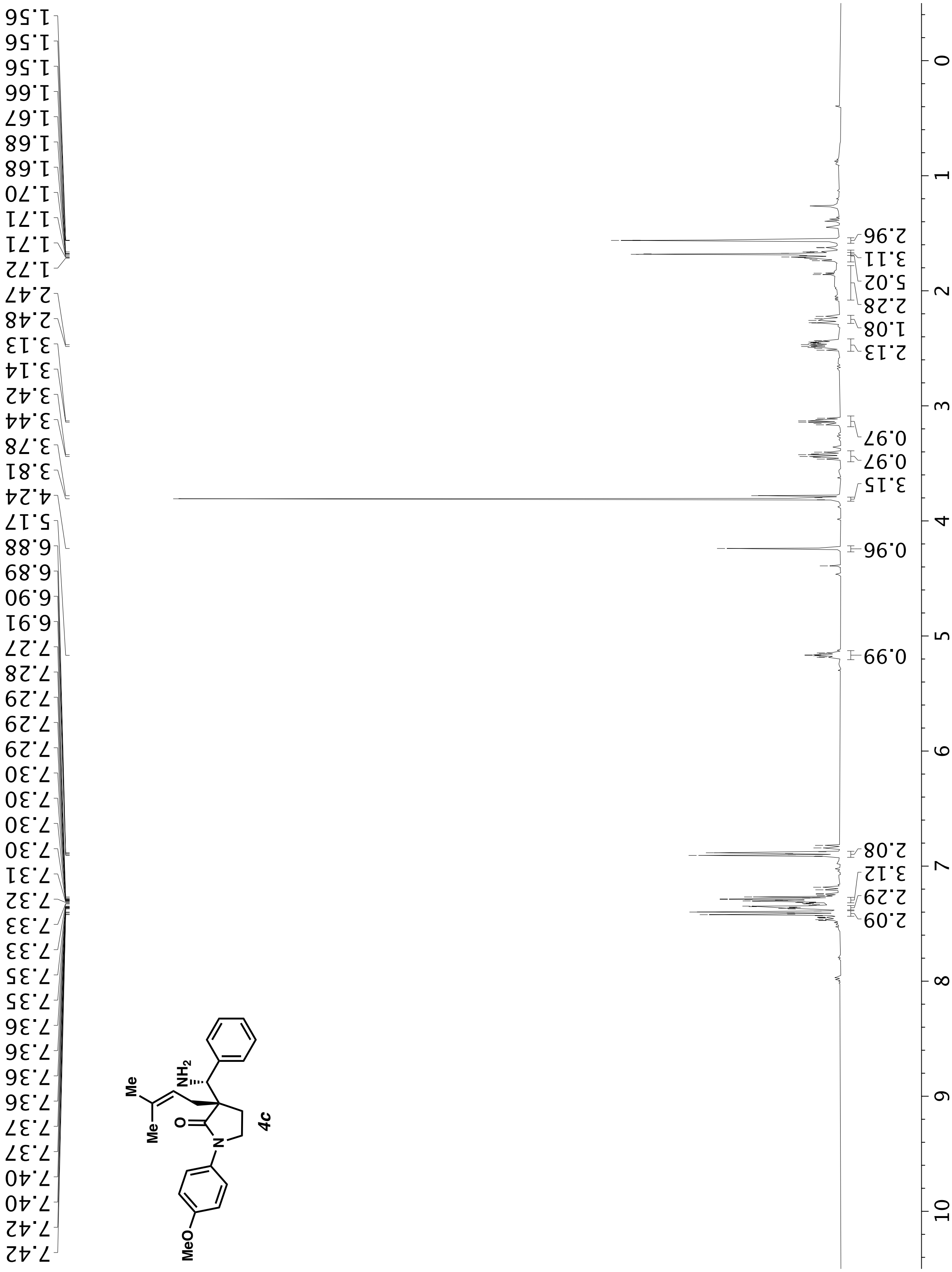
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4b.**



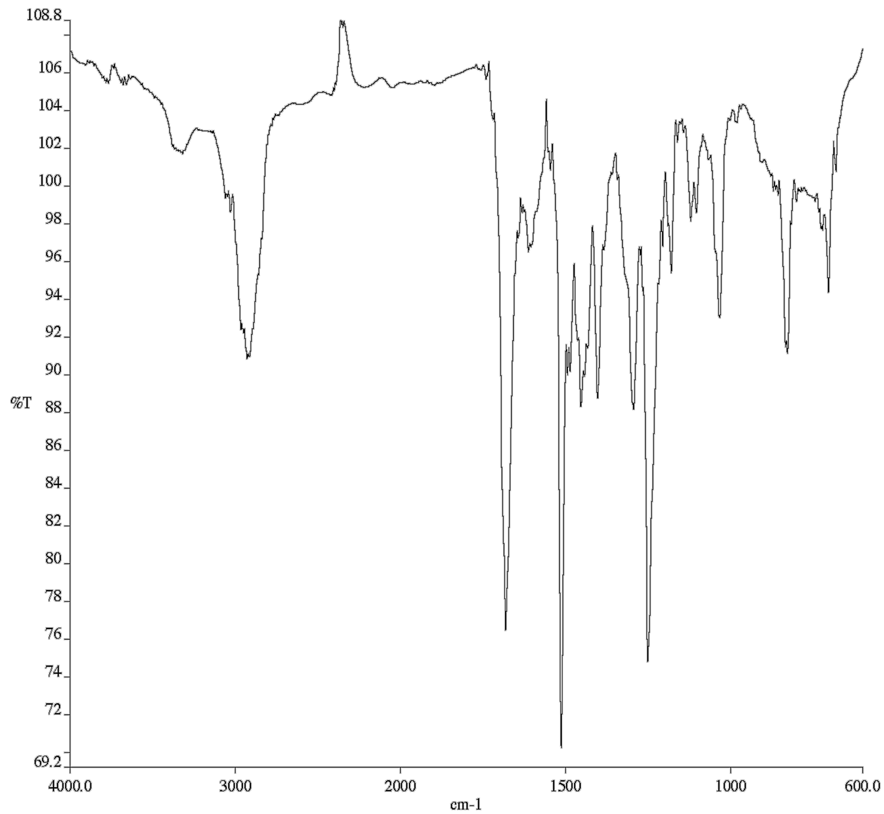
Infrared spectrum (Thin Film, NaCl) of compound **4b**.



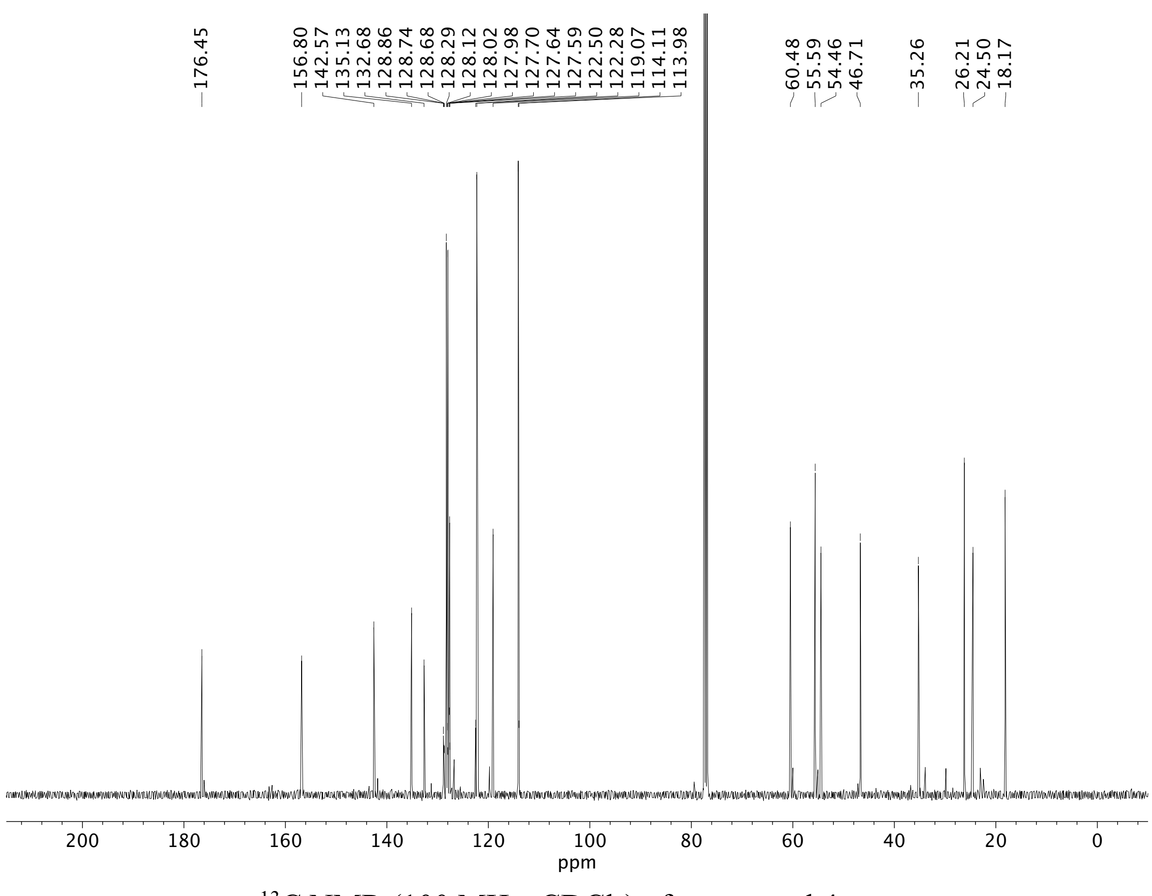
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4b**.



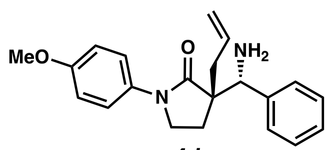
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4c**.



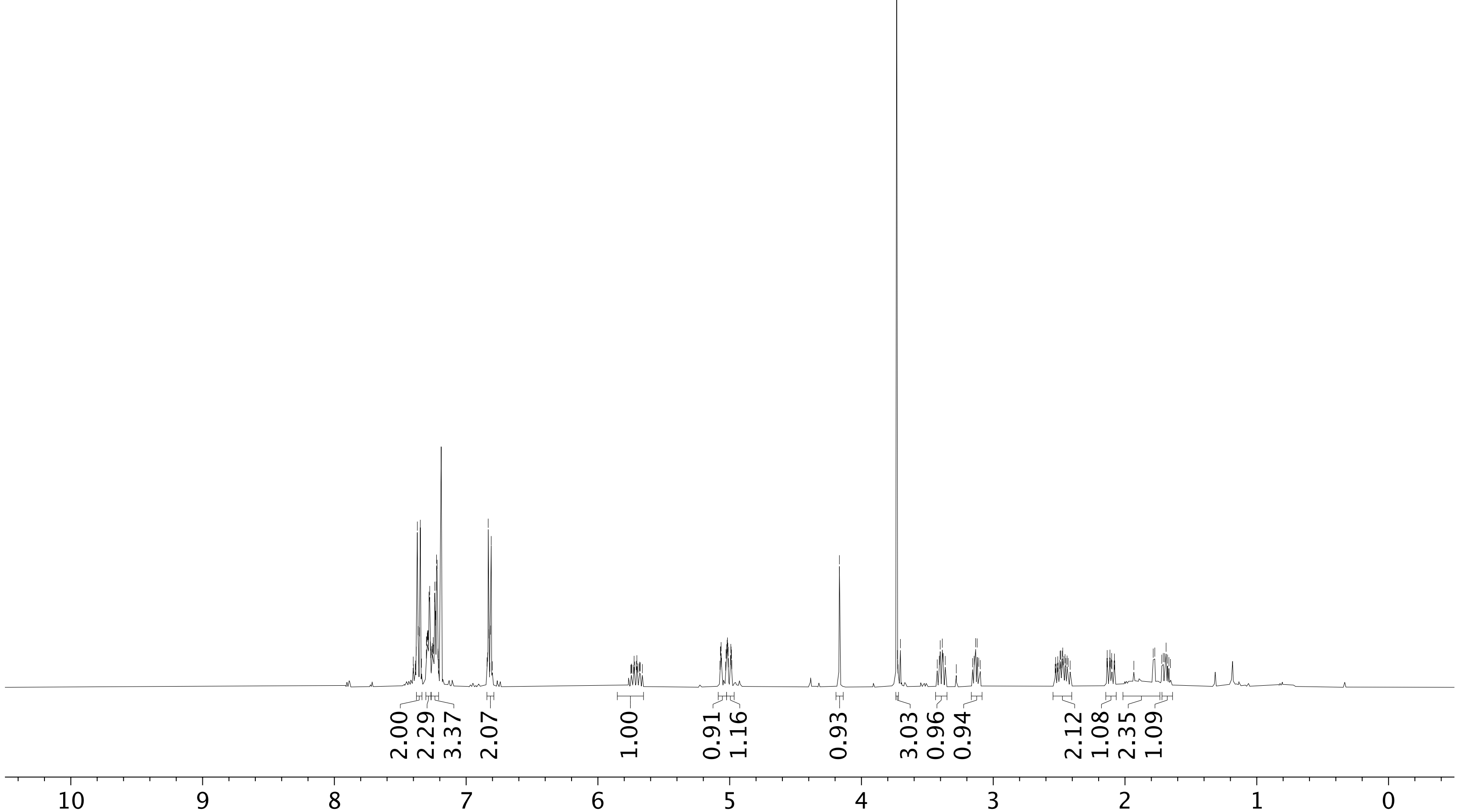
Infrared spectrum (Thin Film, NaCl) of compound **4c**.



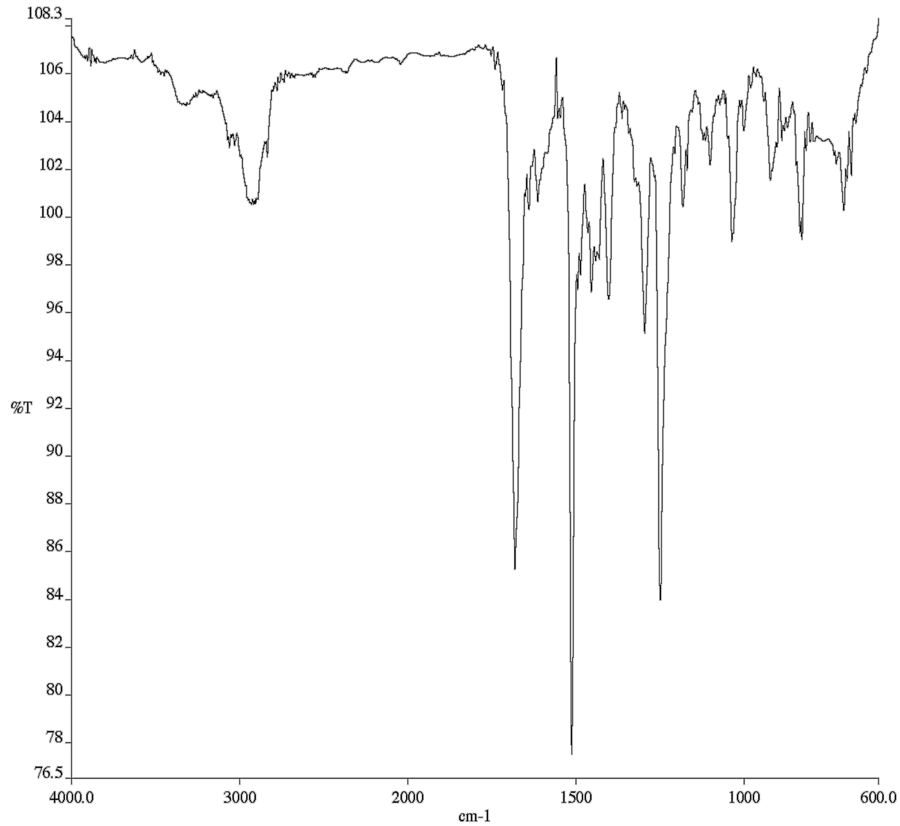
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4c**.



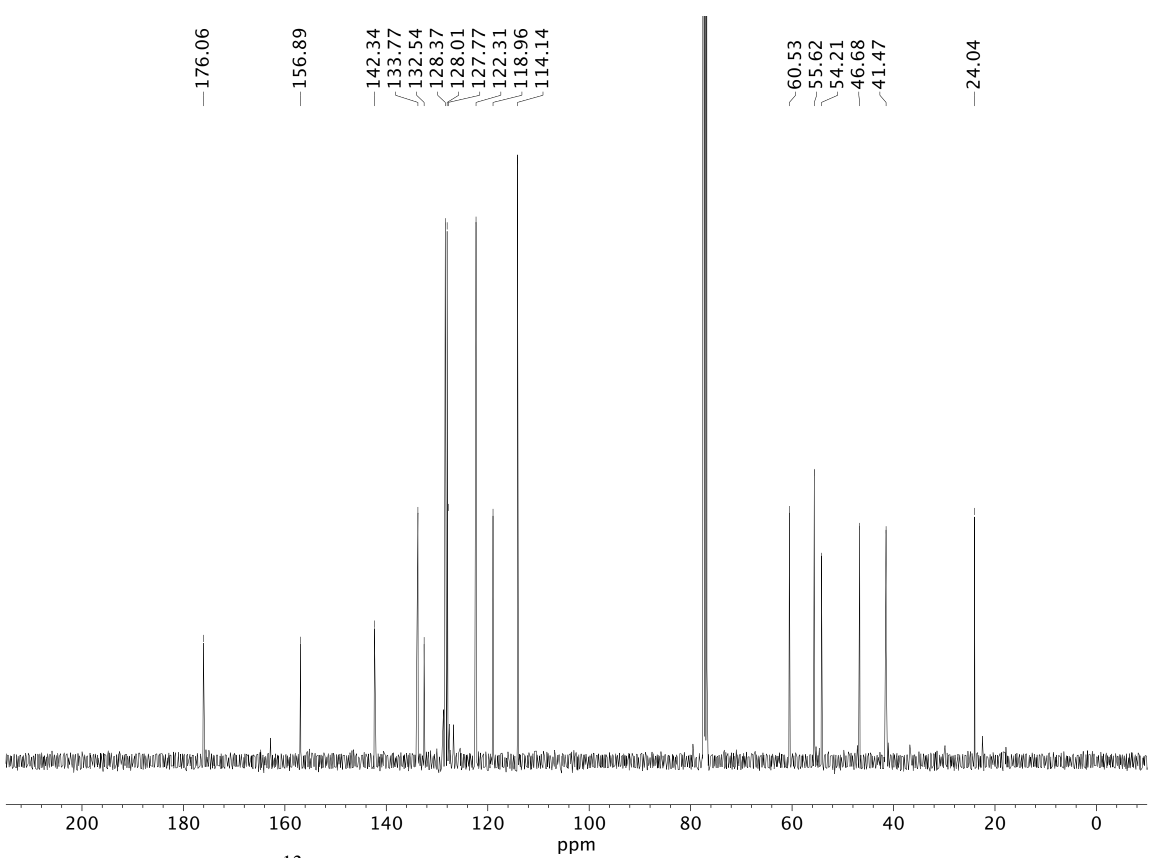
4d



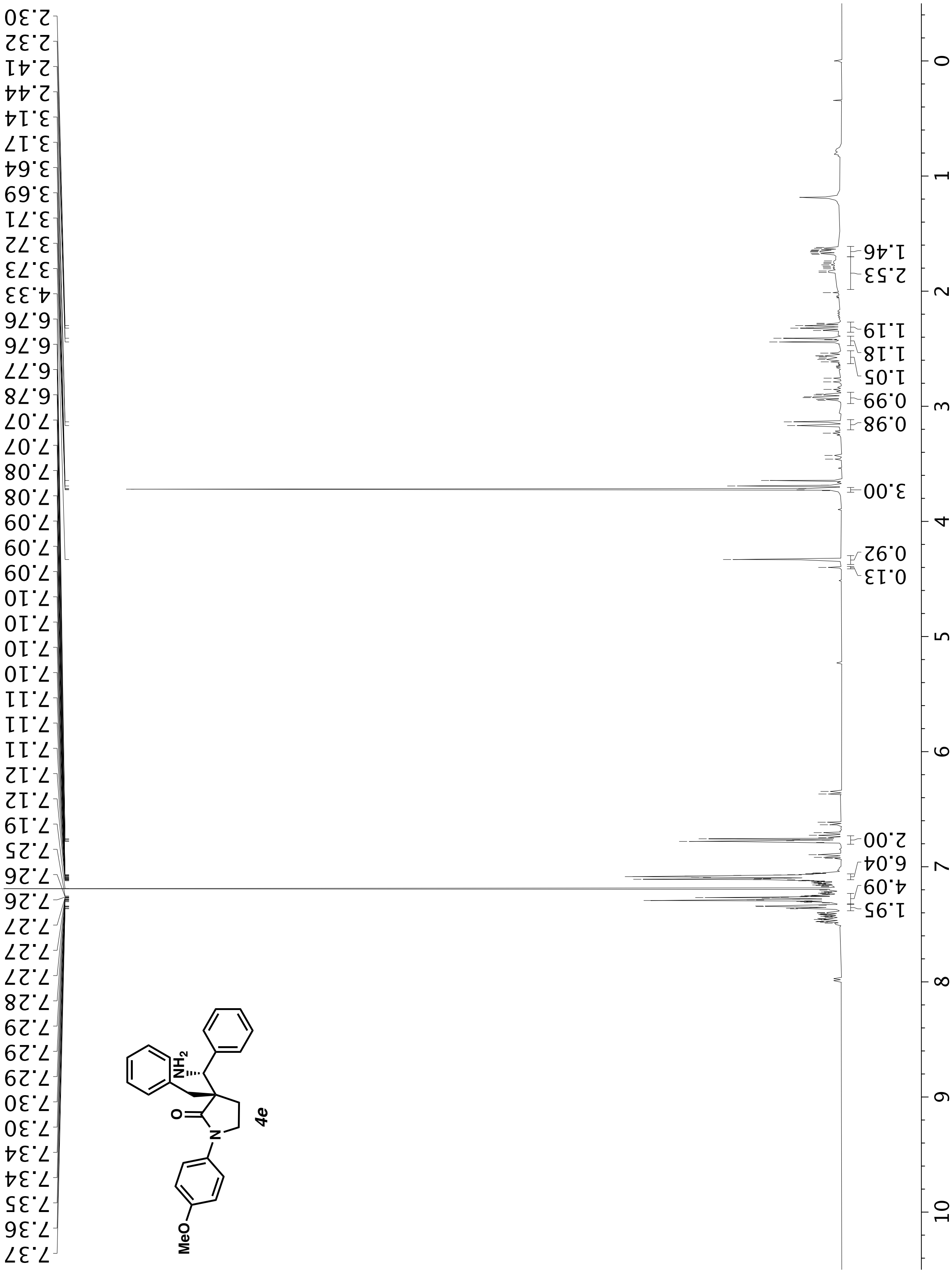
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4d**.



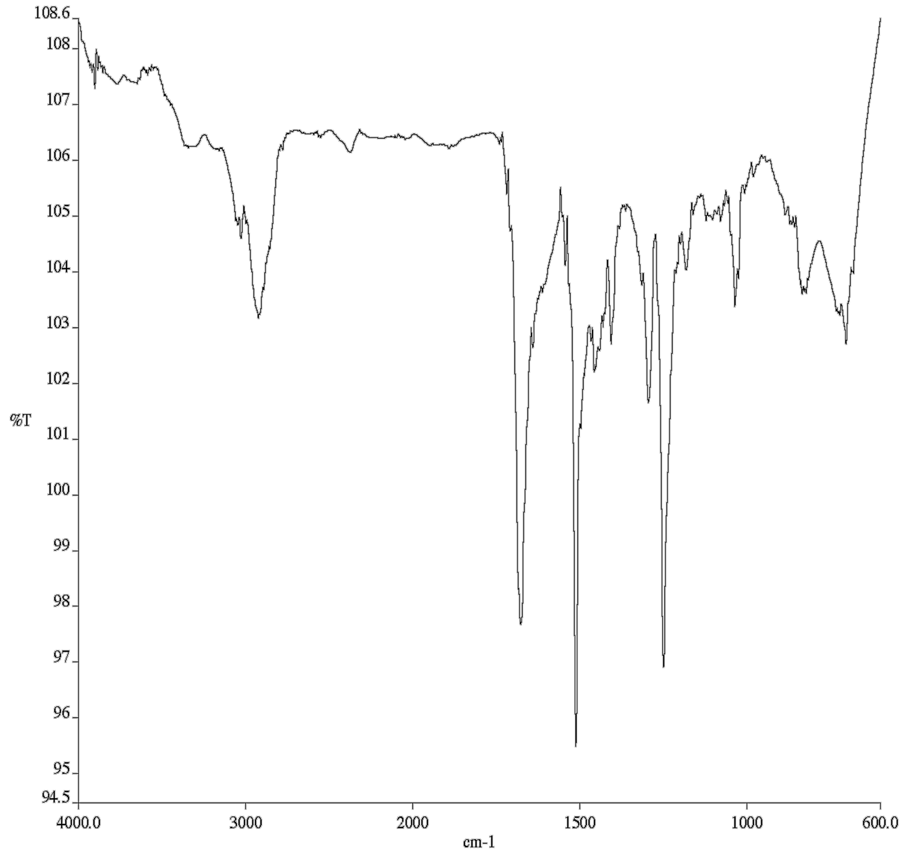
Infrared spectrum (Thin Film, NaCl) of compound **4d**.



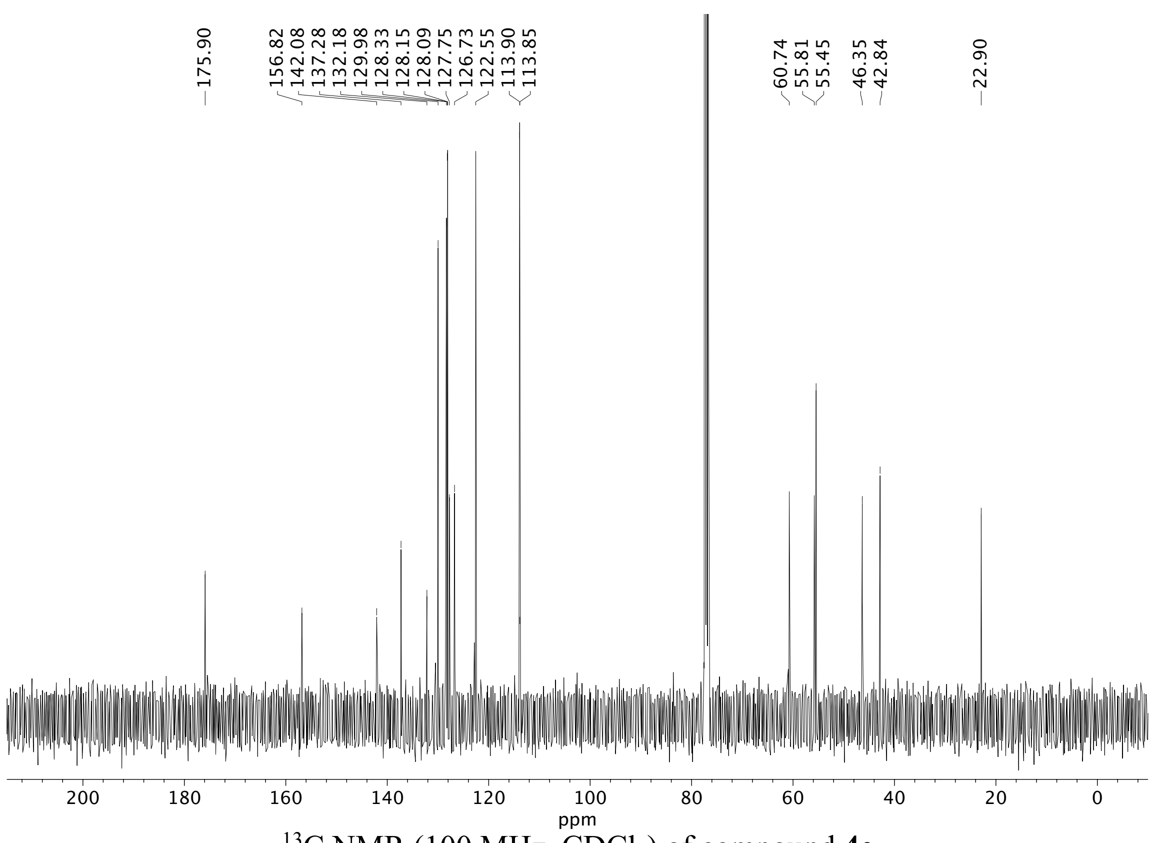
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4d**.



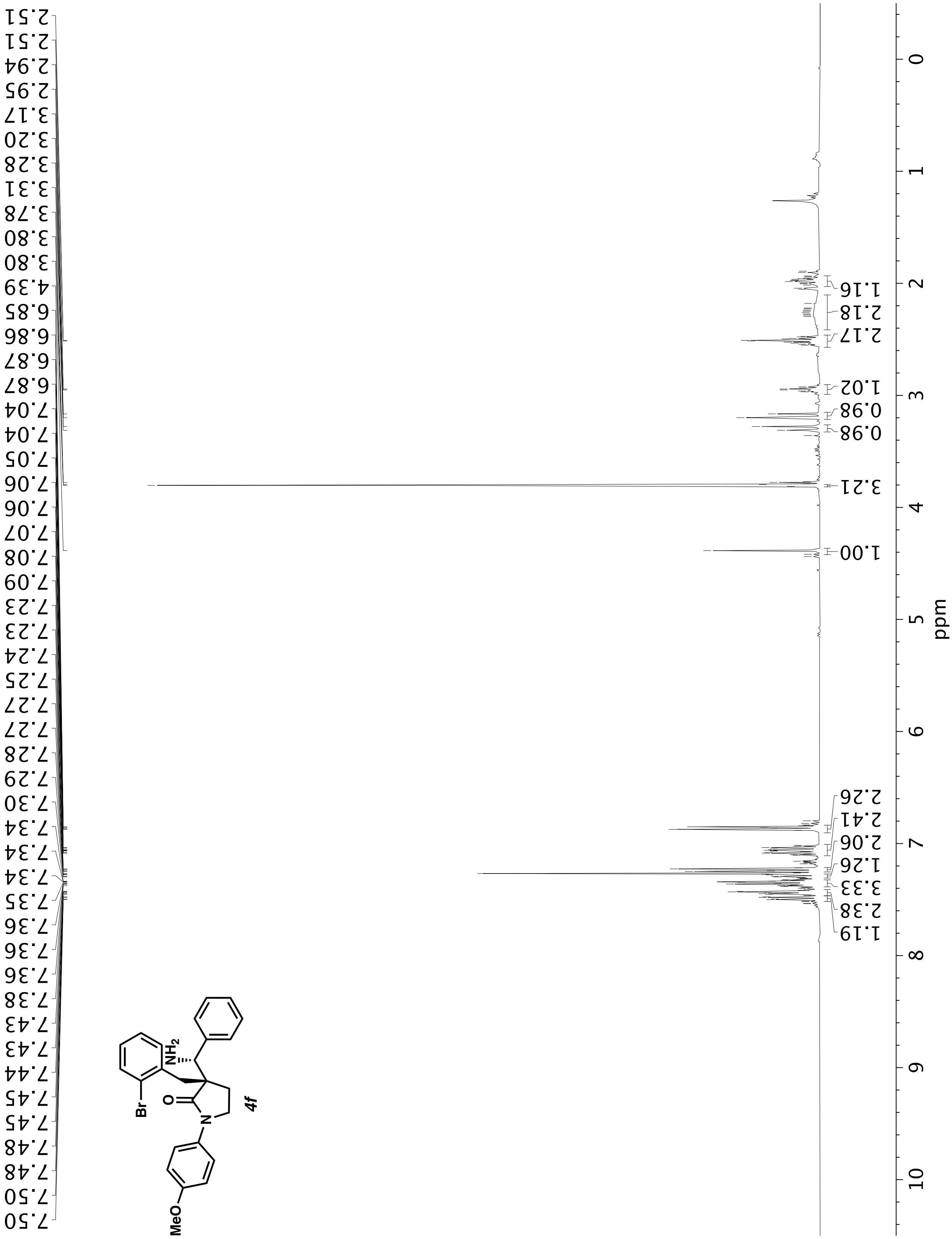
^{1}H NMR (400 MHz, C_6D_6) of compound **4e**.



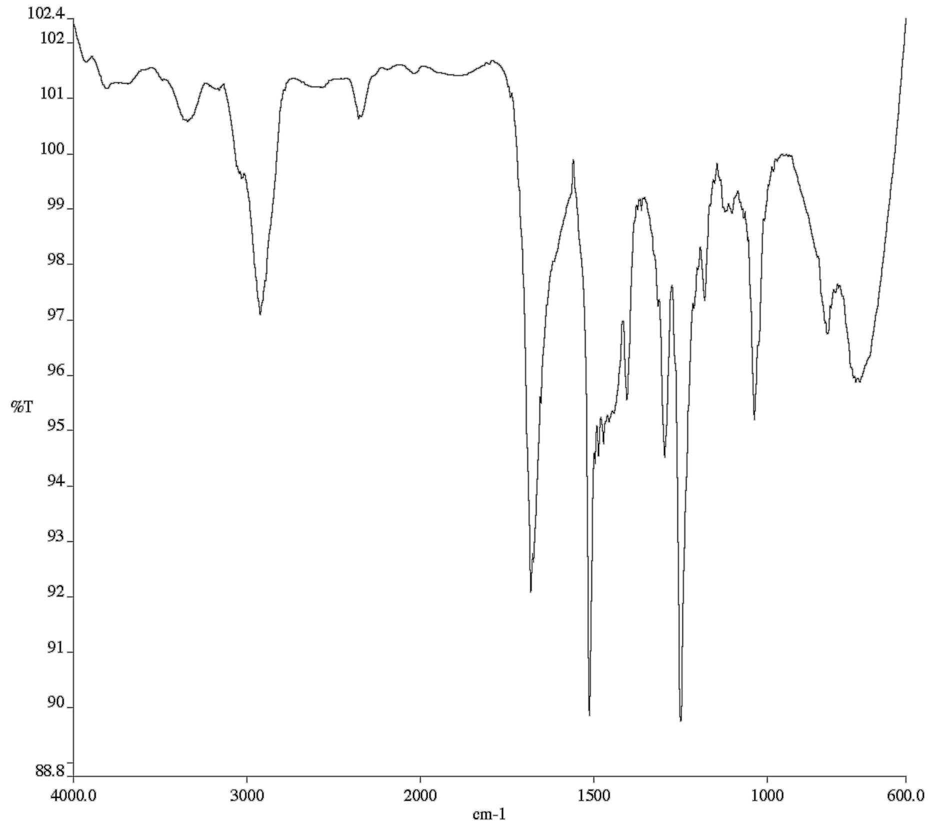
Infrared spectrum (Thin Film, NaCl) of compound **4e**.



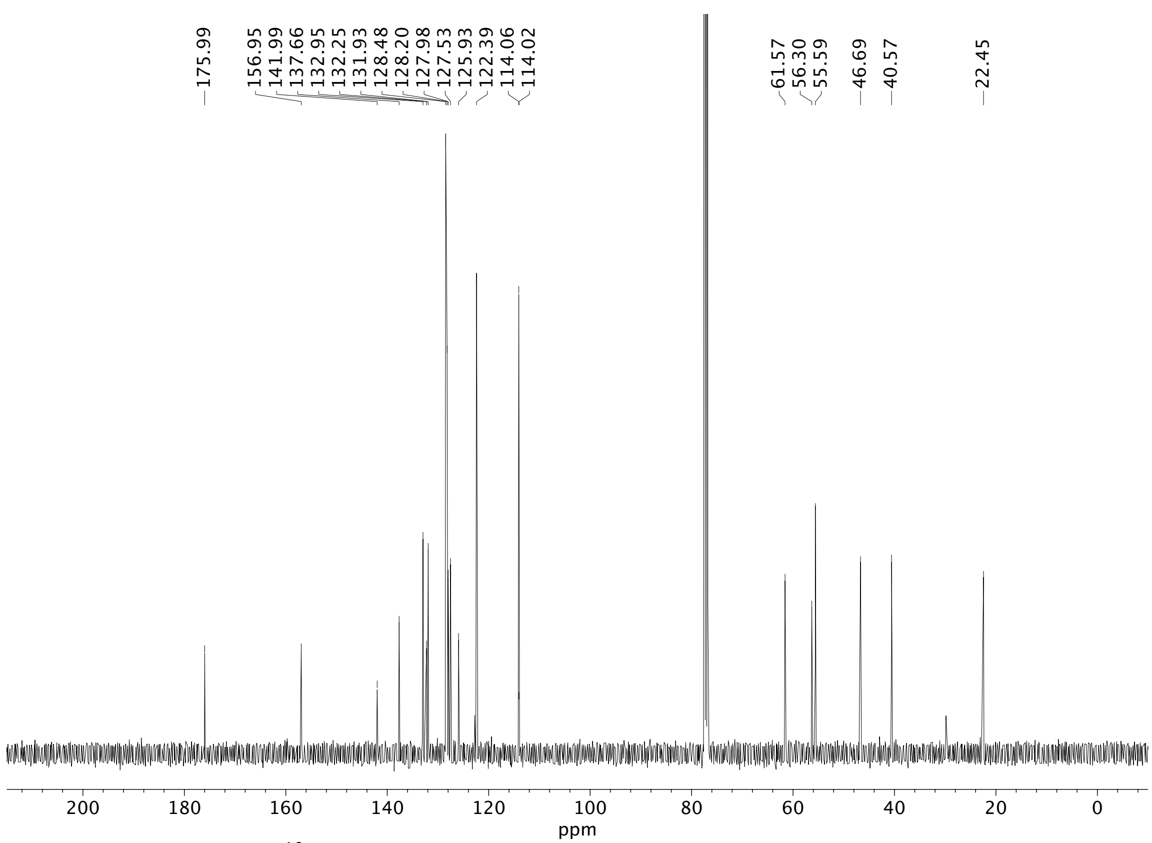
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4e**.



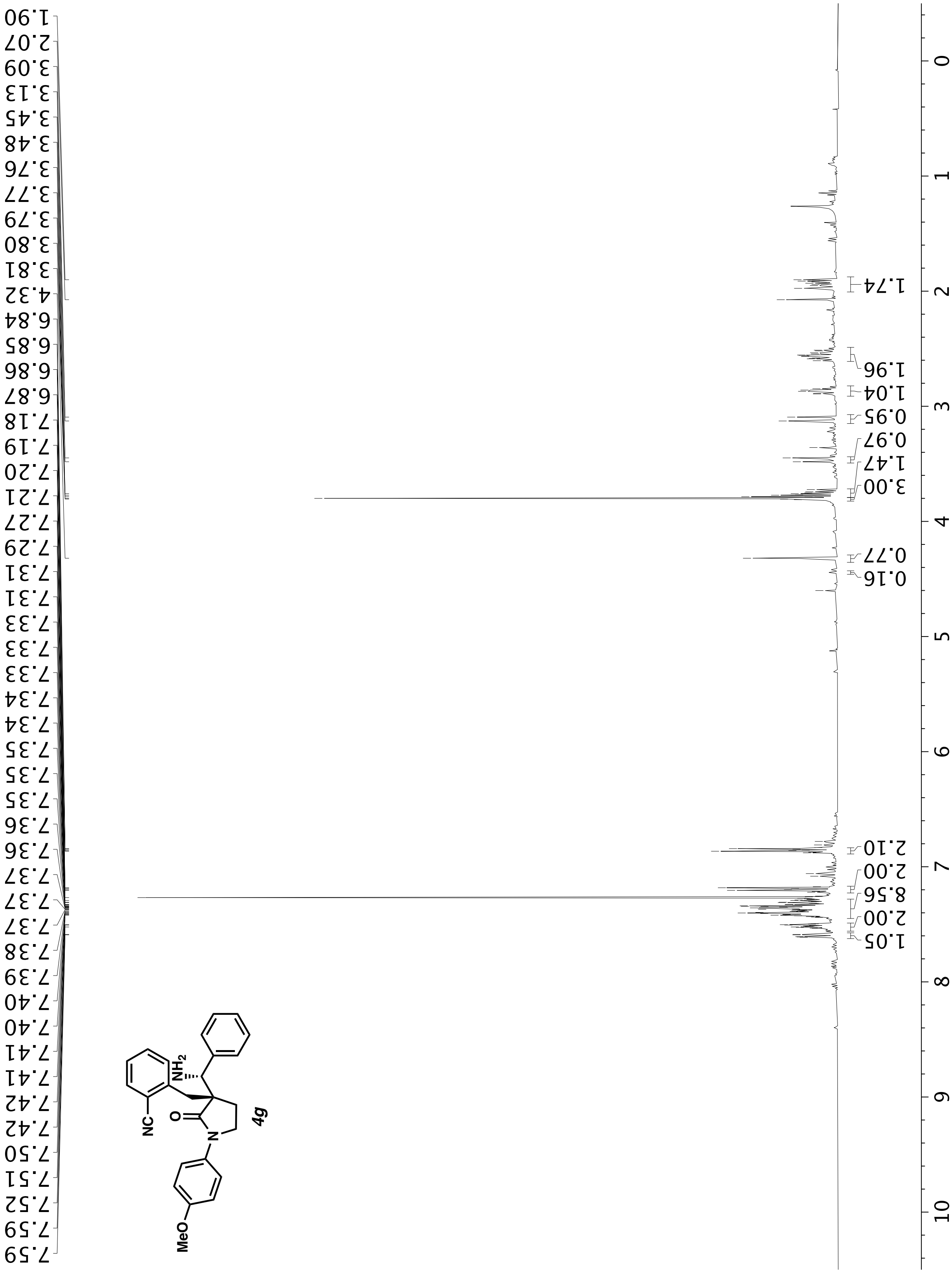
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4f**.



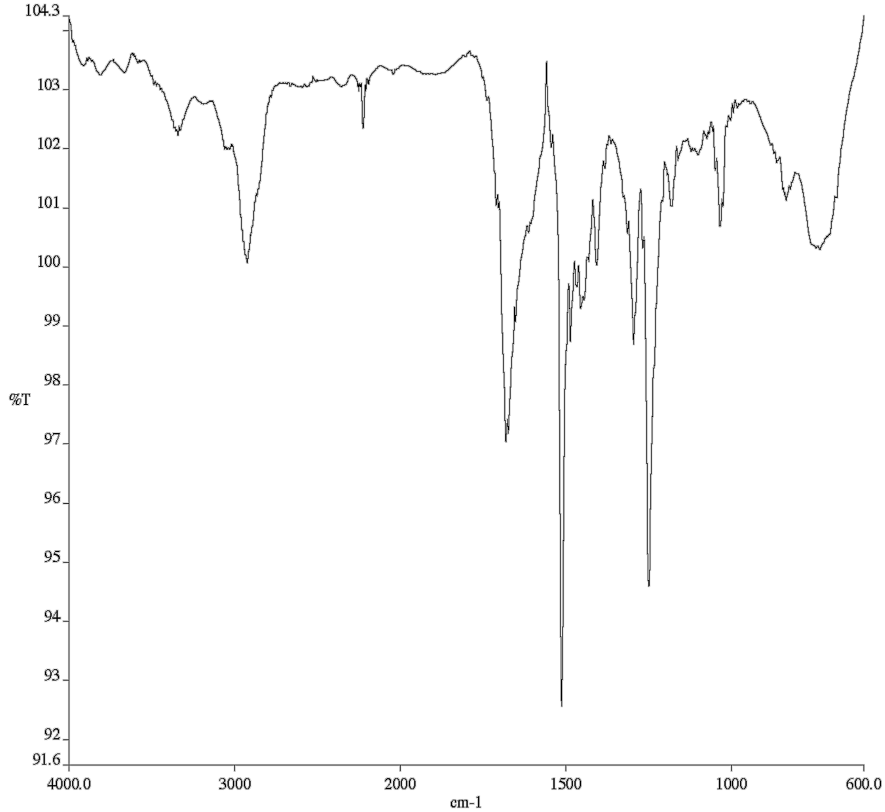
Infrared spectrum (Thin Film, NaCl) of compound **4f**.



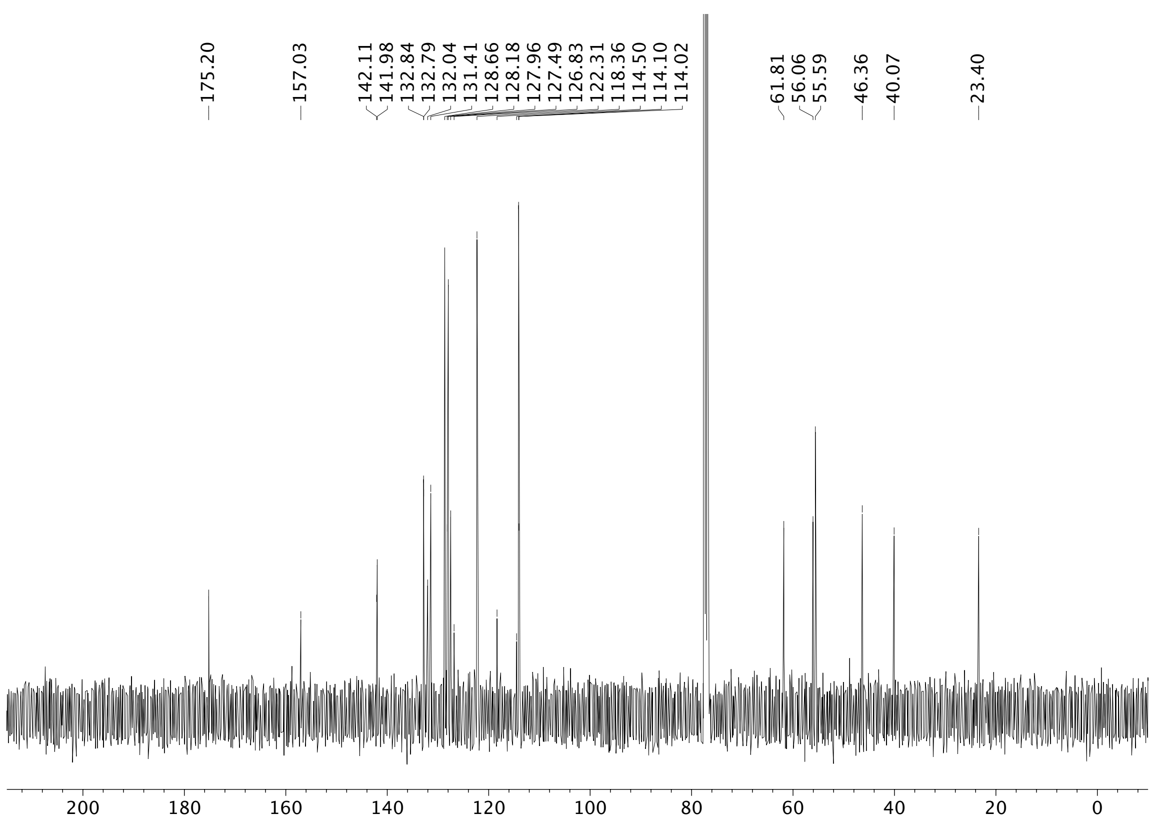
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4f**.



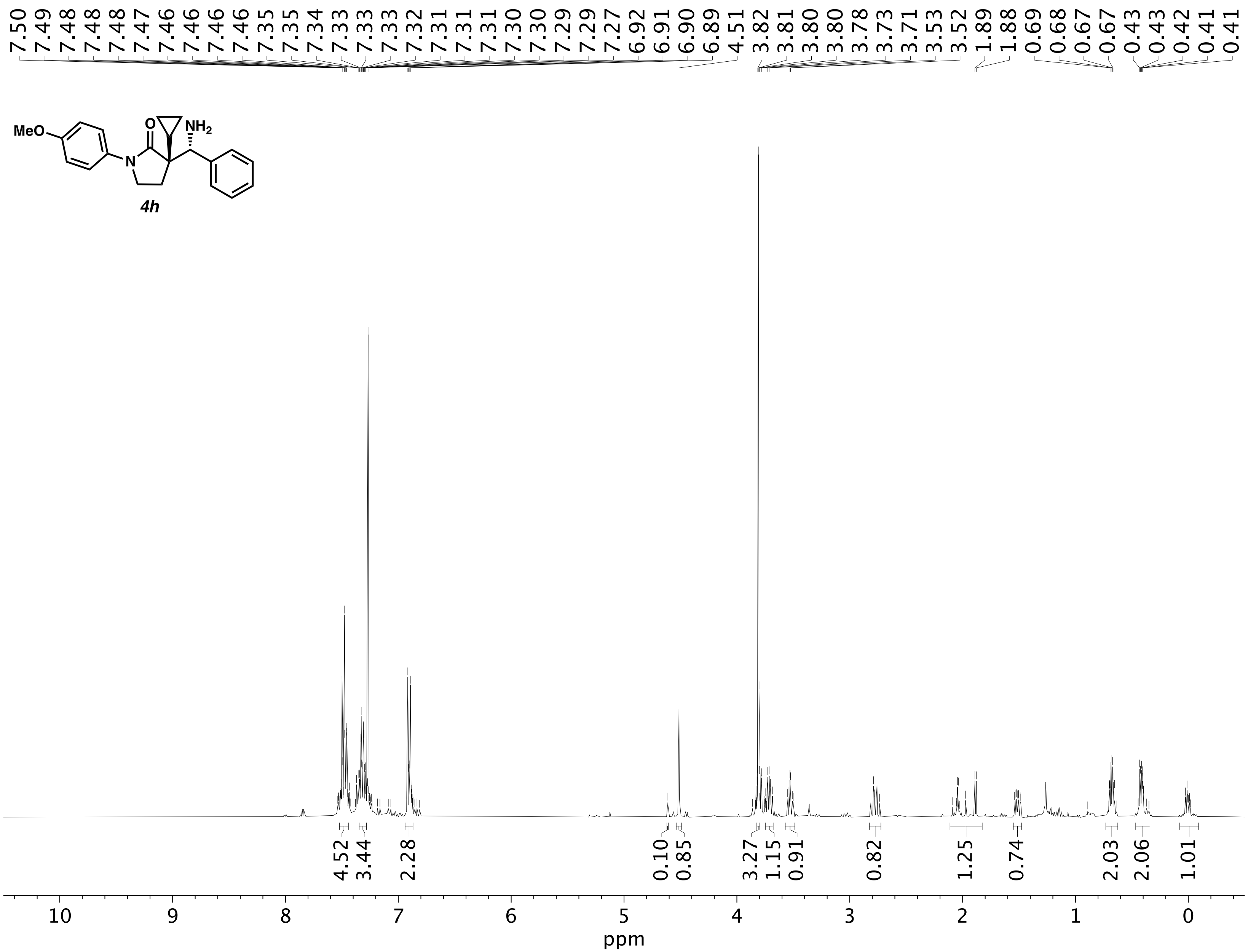
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4g**.



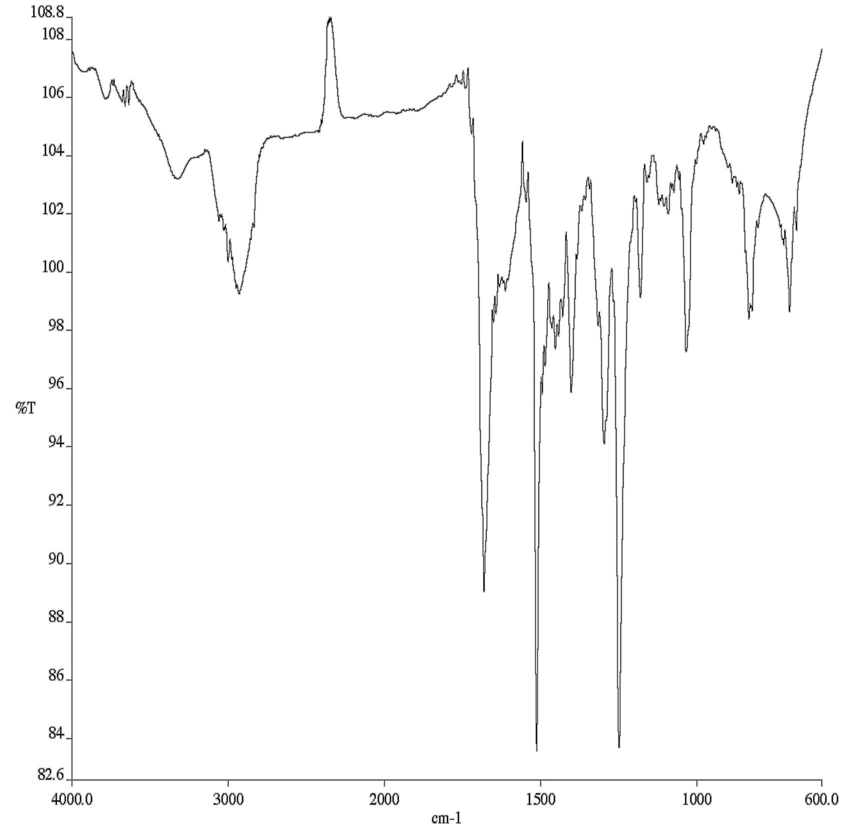
Infrared spectrum (Thin Film, NaCl) of compound **4g**.



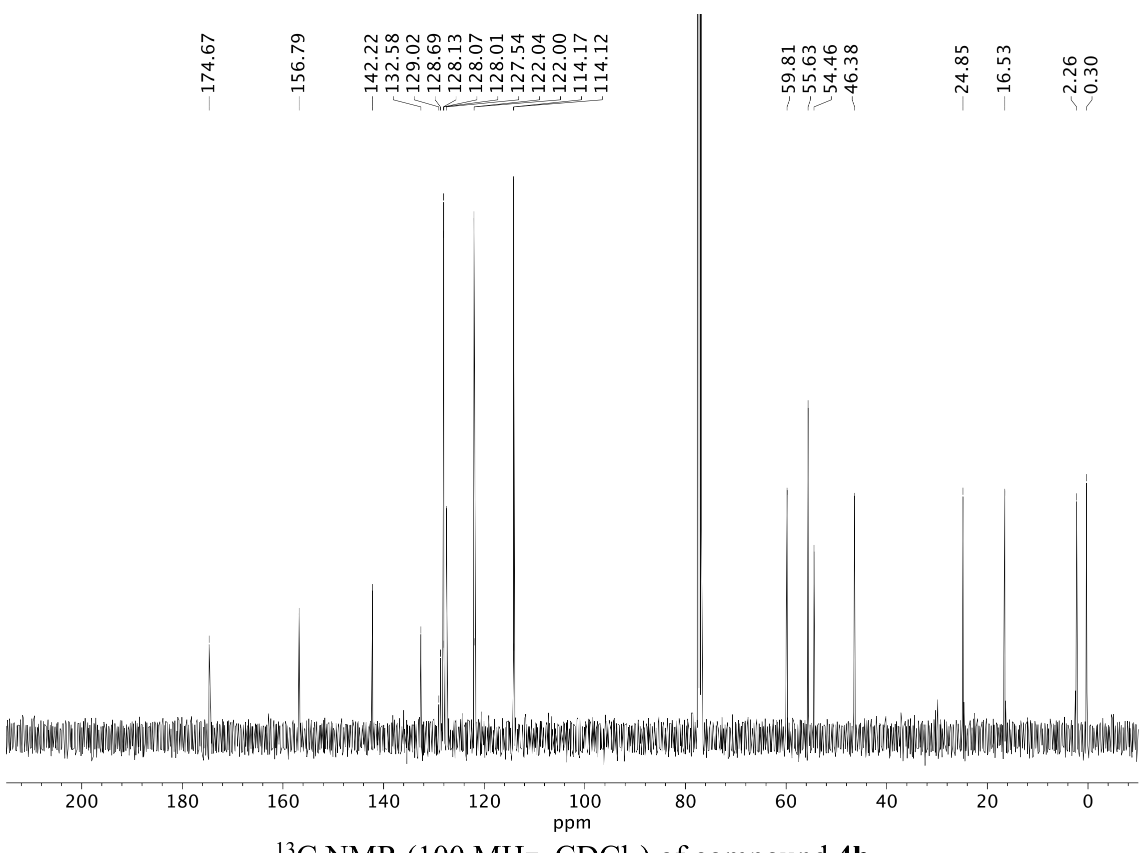
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4g**.



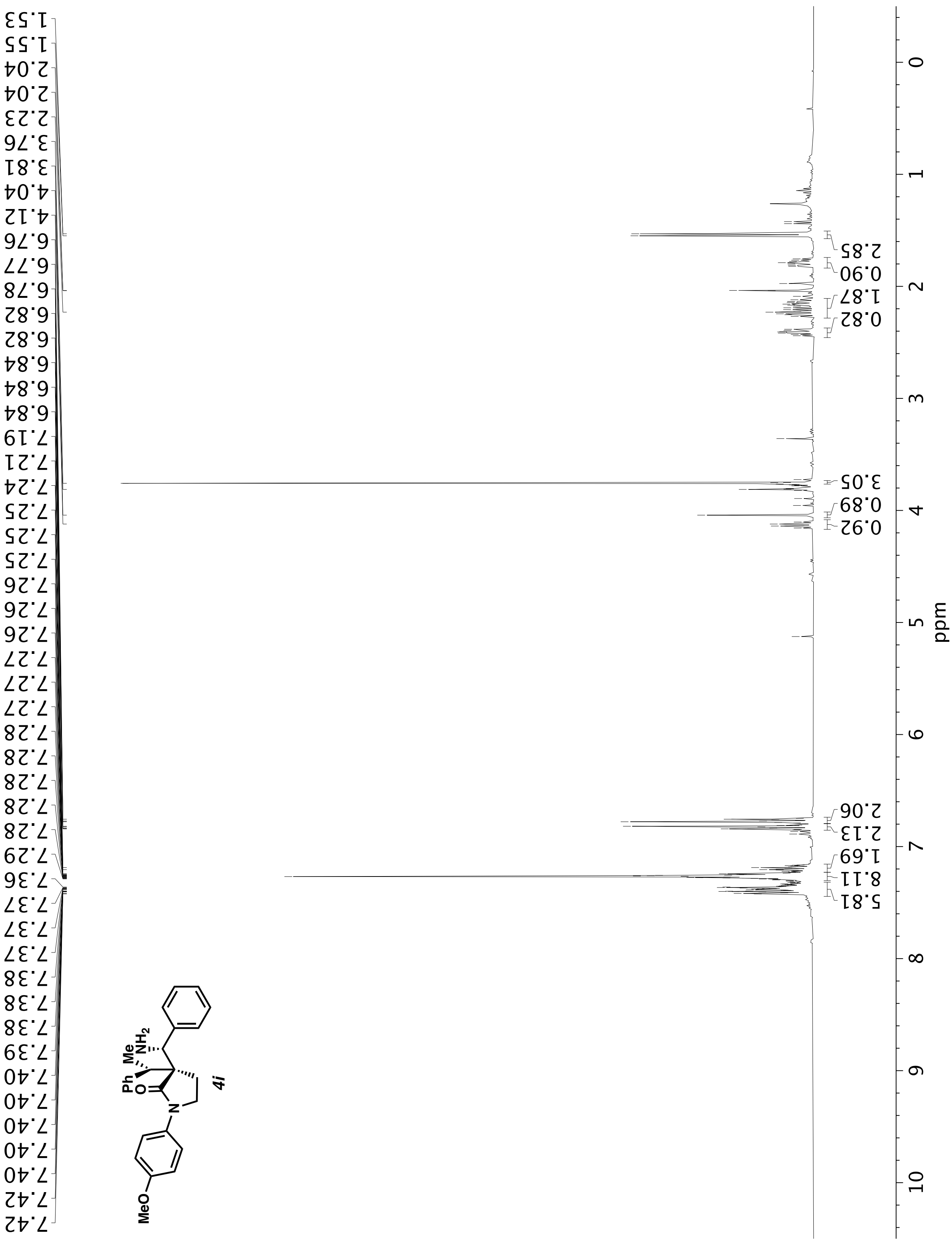
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4h**.



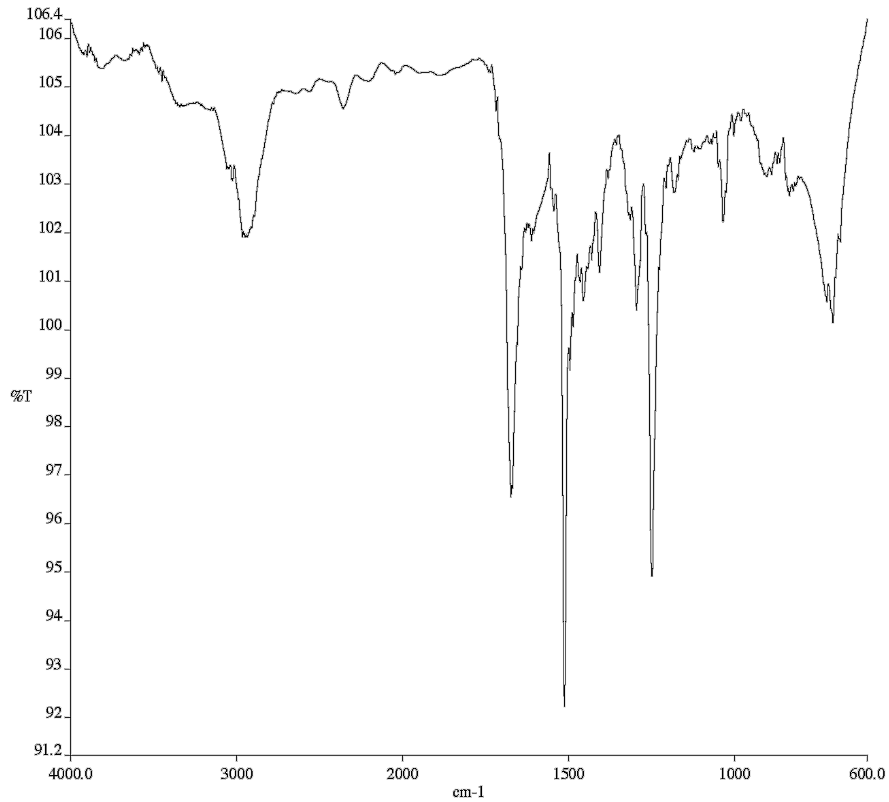
Infrared spectrum (Thin Film, NaCl) of compound **4h**.



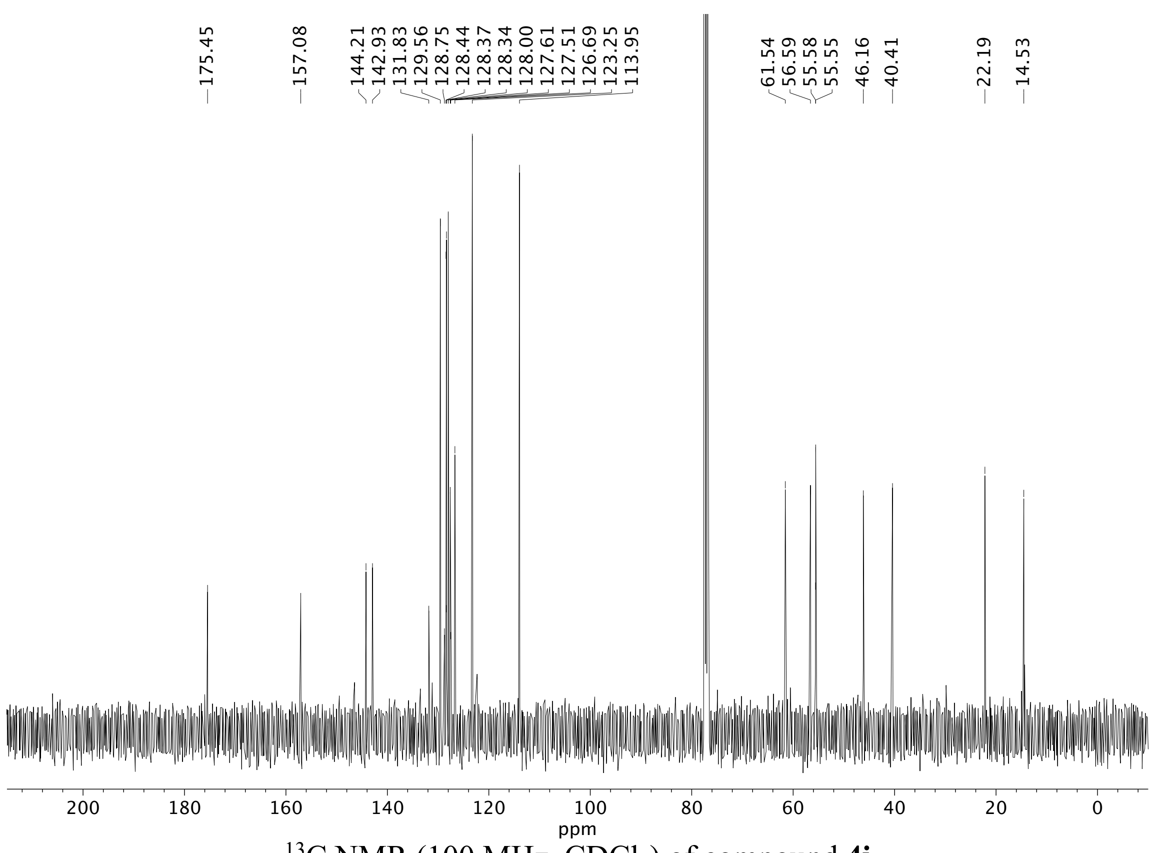
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4h**.



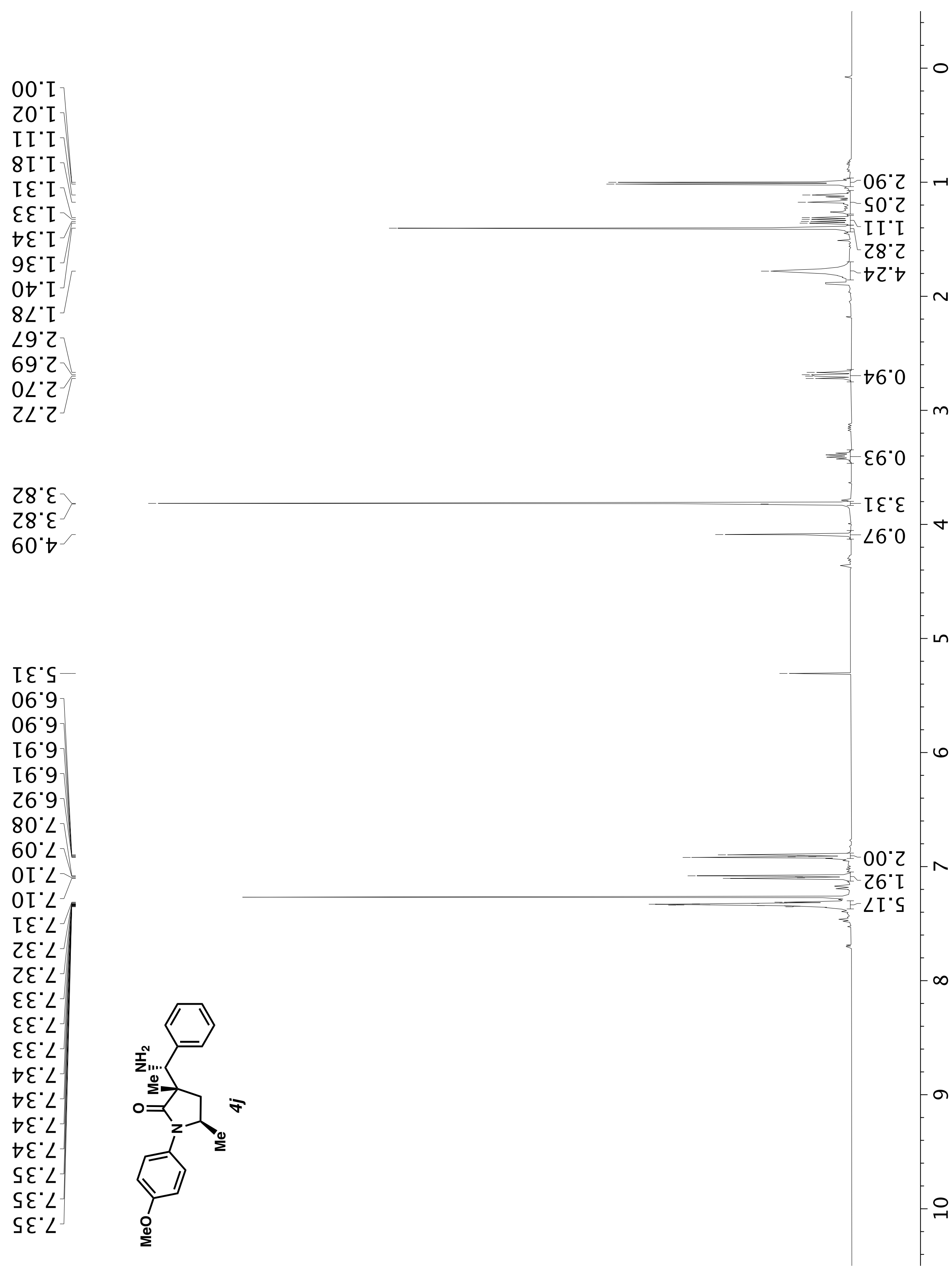
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4i**.



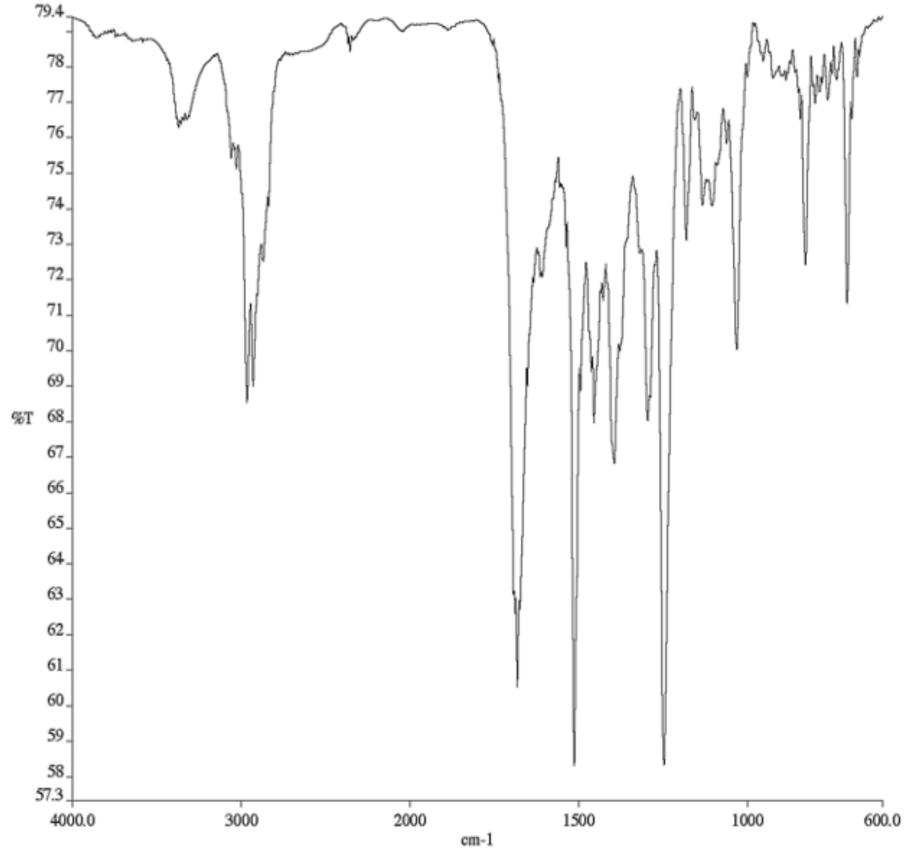
Infrared spectrum (Thin Film, NaCl) of compound **4i**.



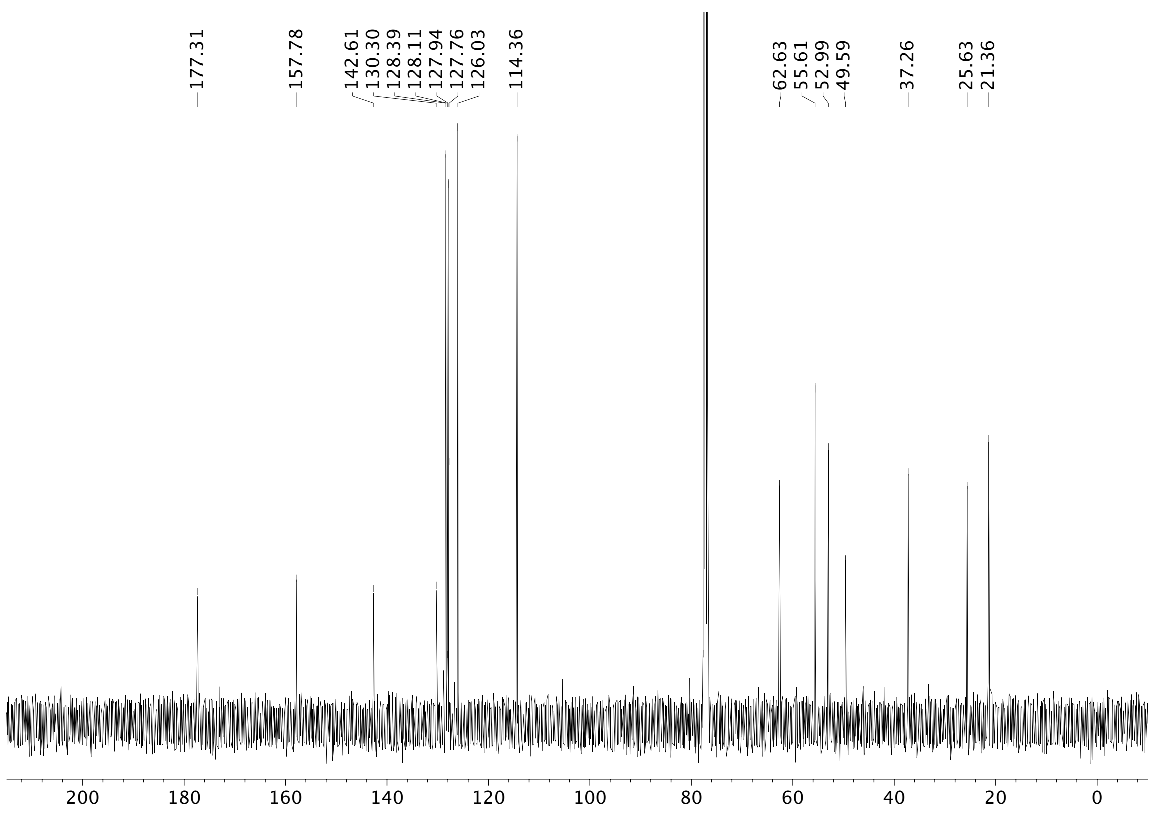
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4i**.



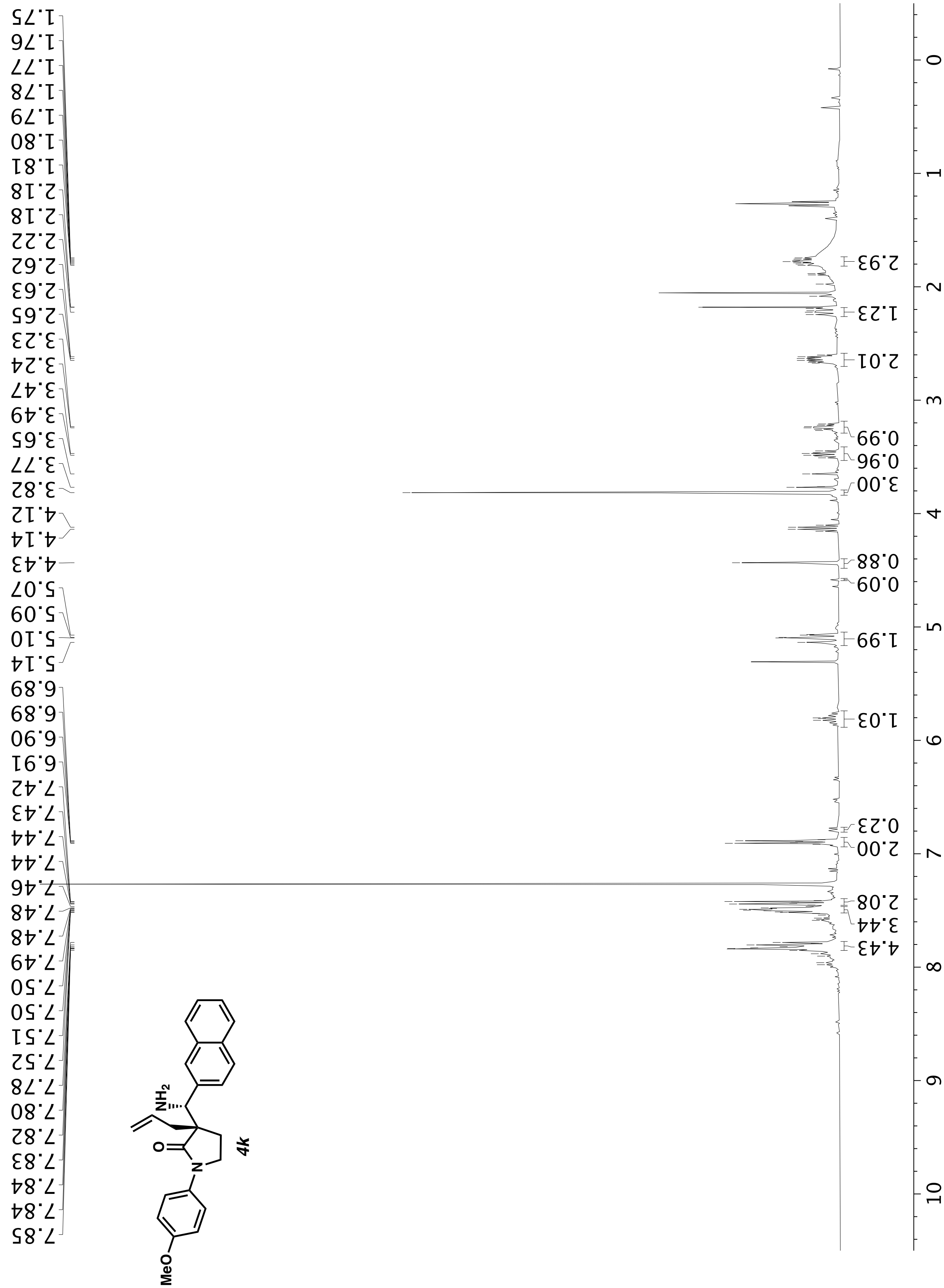
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4j**.



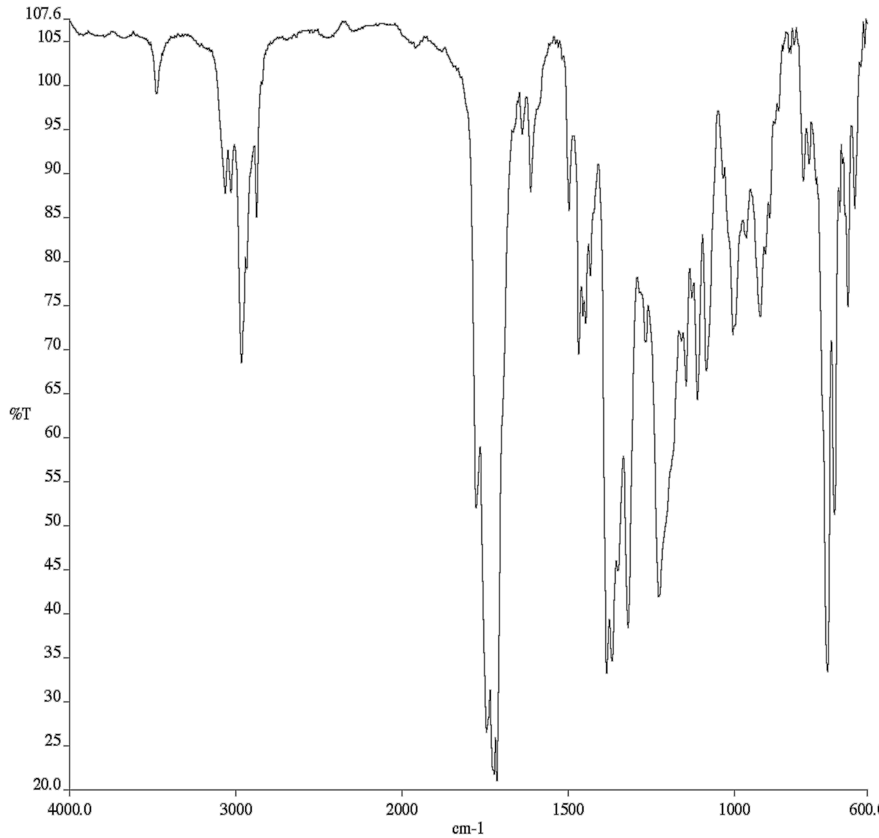
Infrared spectrum (Thin Film, NaCl) of compound **4j**.



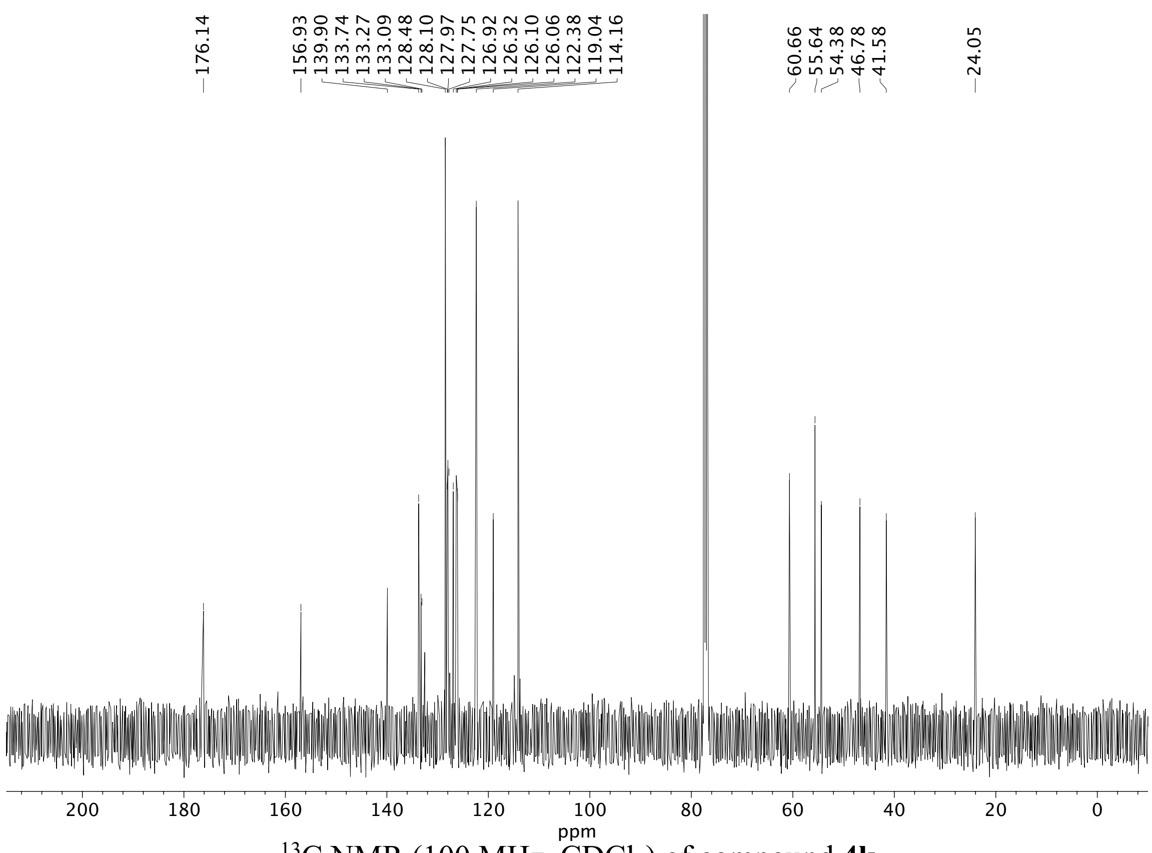
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4j**.



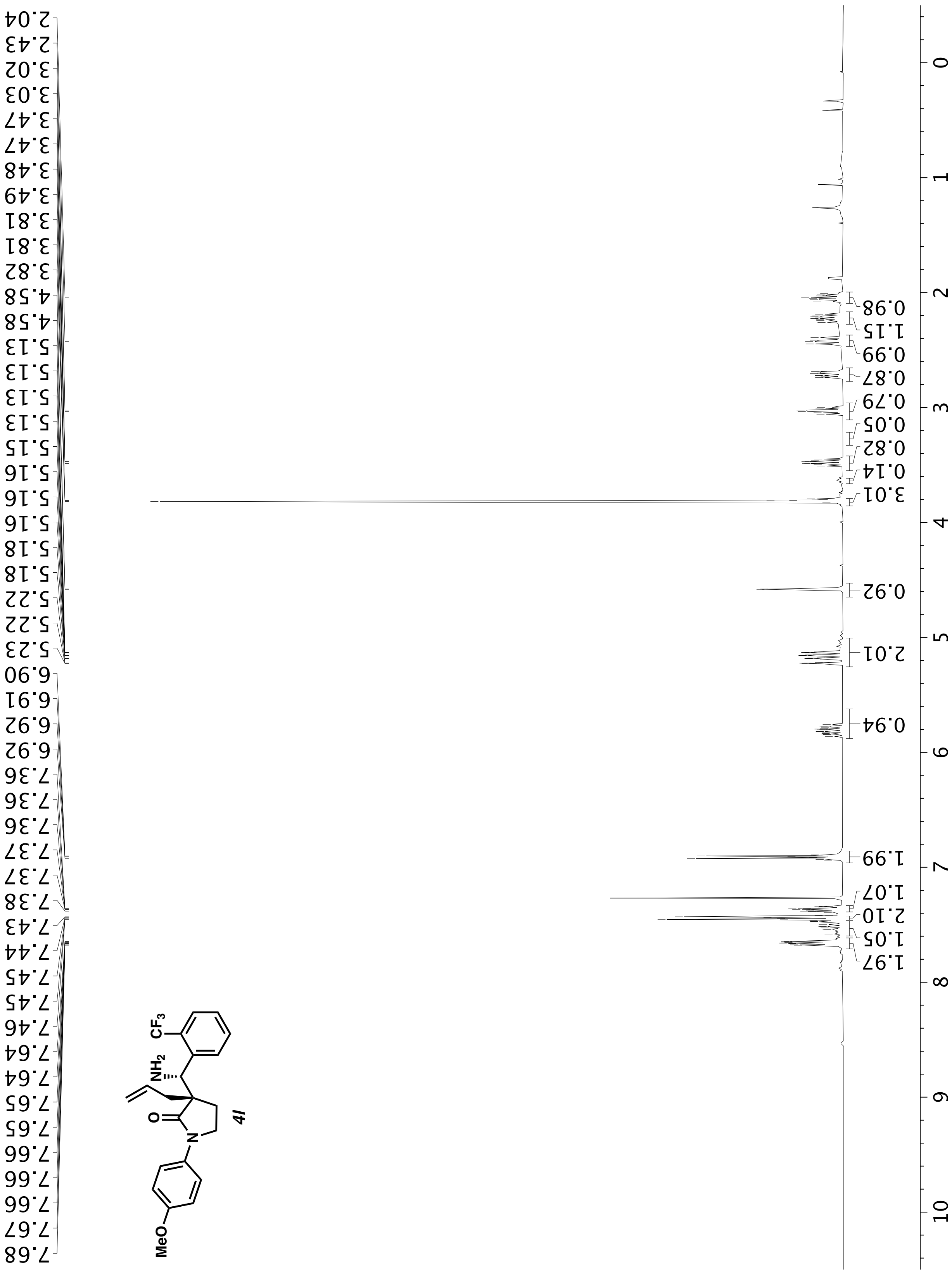
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4k**.



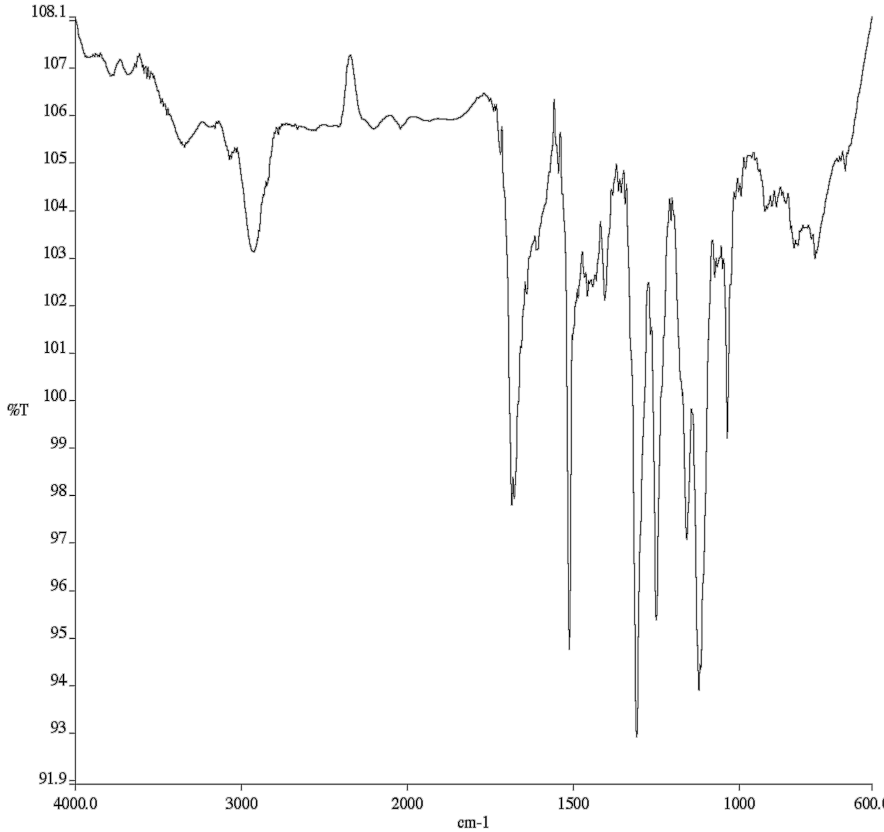
Infrared spectrum (Thin Film, NaCl) of compound **4k**.



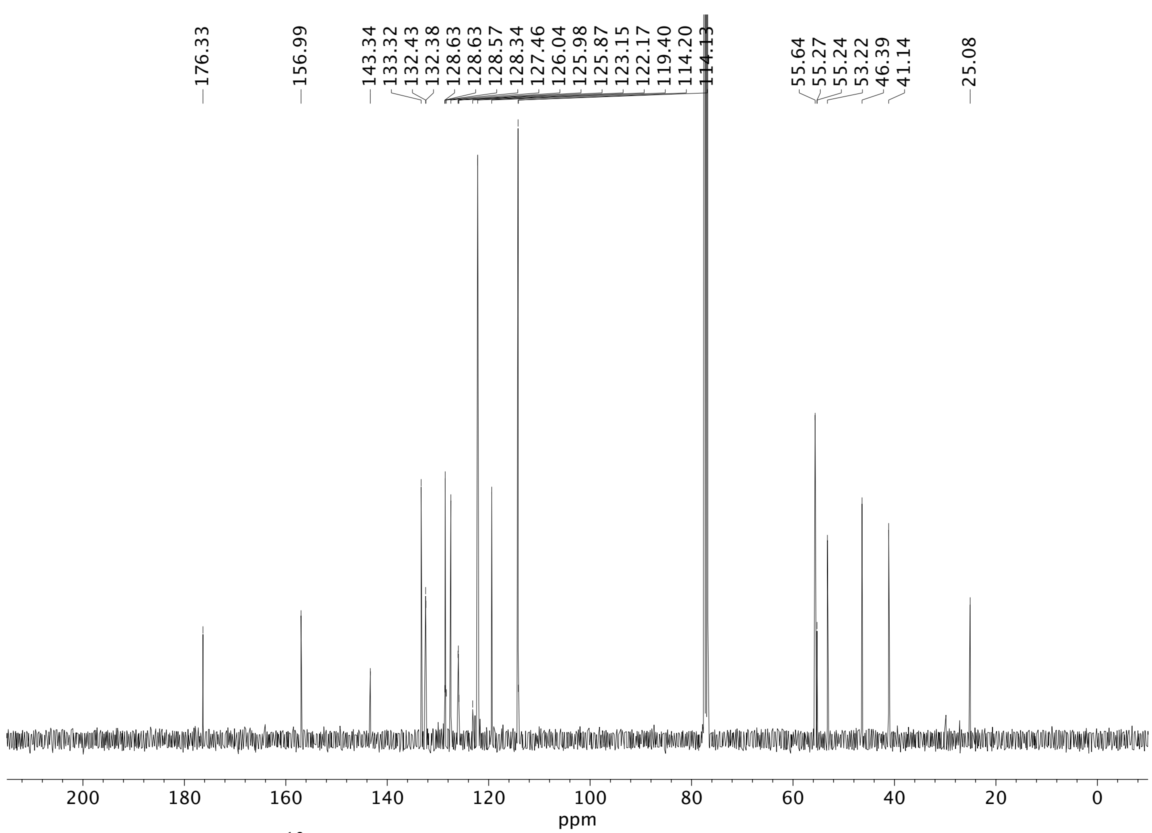
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4k**.



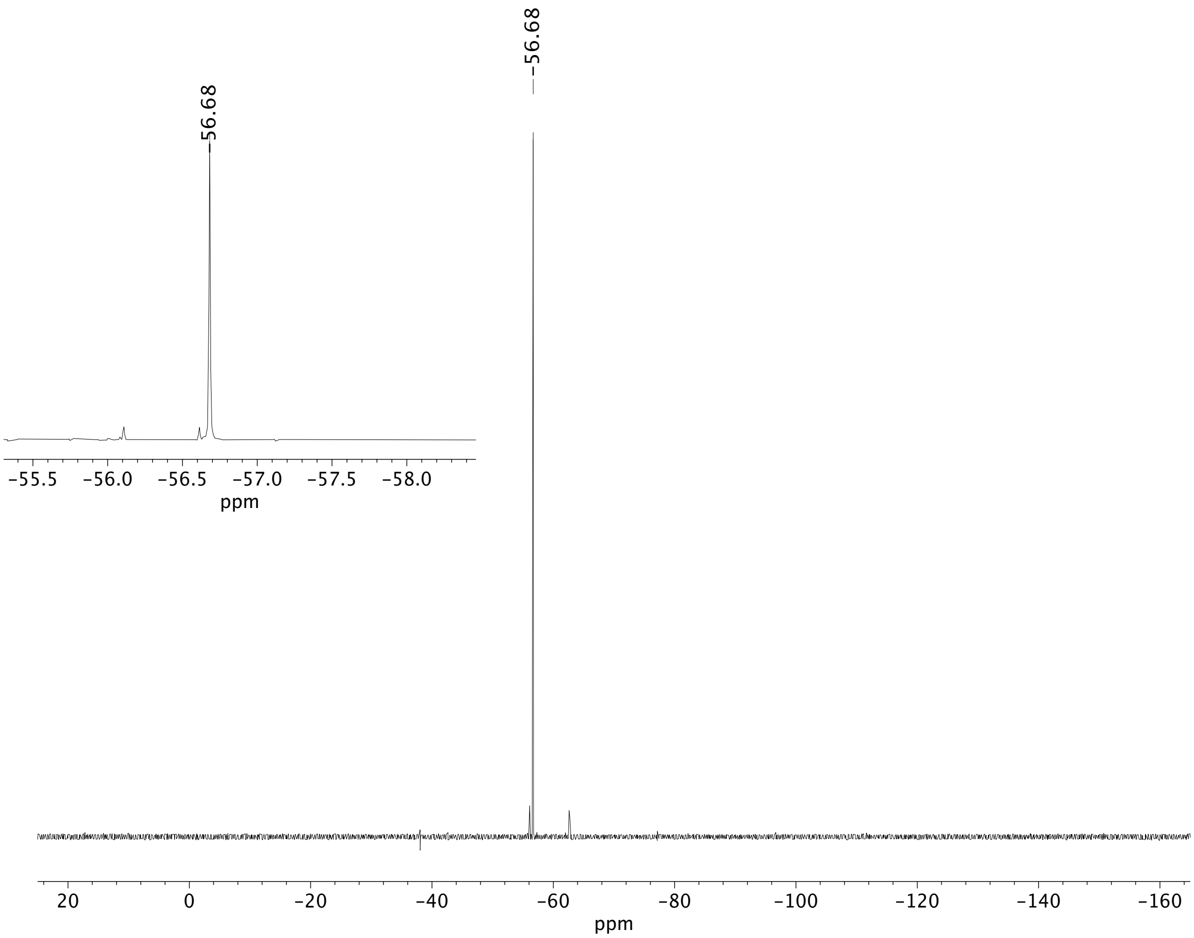
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4l**



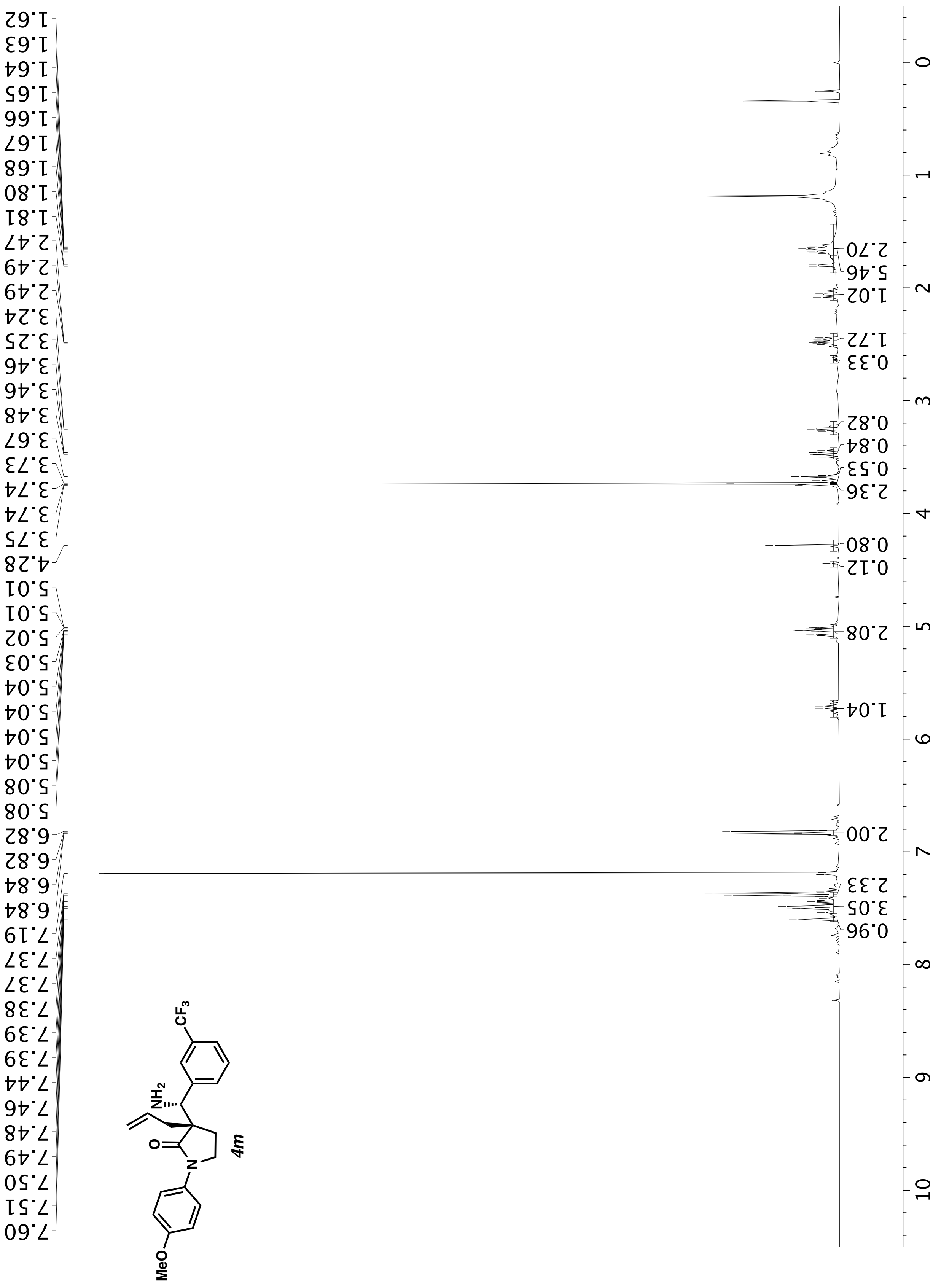
Infrared spectrum (Thin Film, NaCl) of compound **4l**.



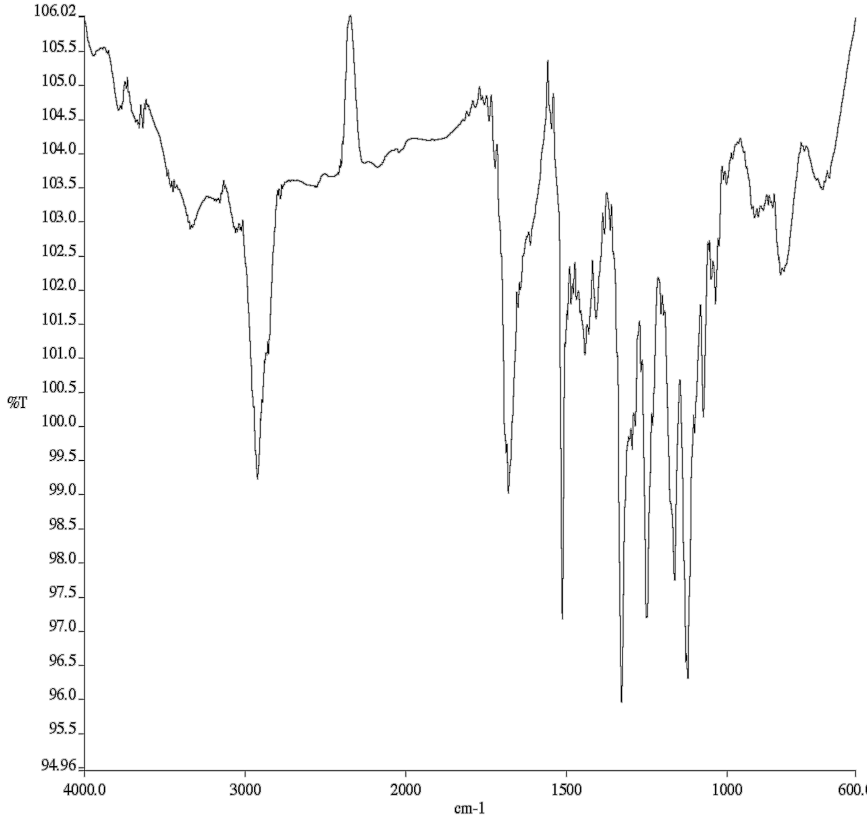
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4l**.



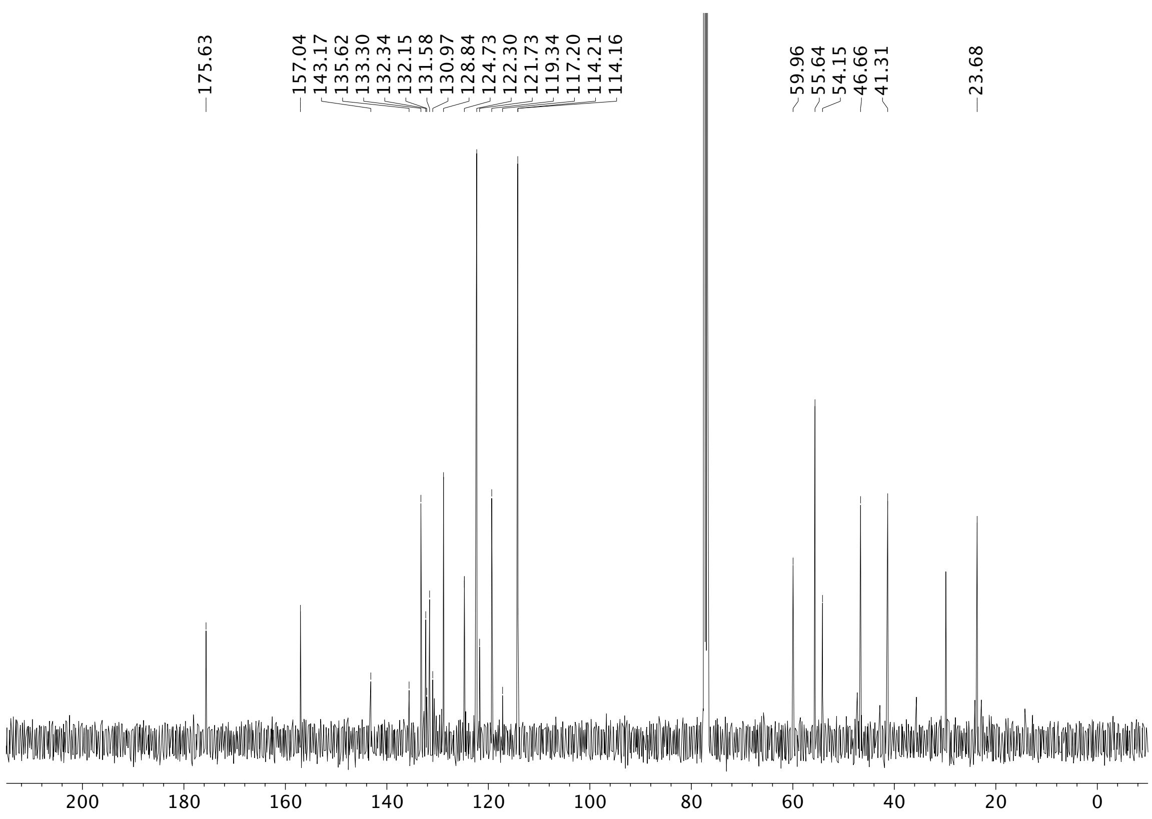
^{19}F NMR (282 MHz, $CDCl_3$) of compound **4l**.



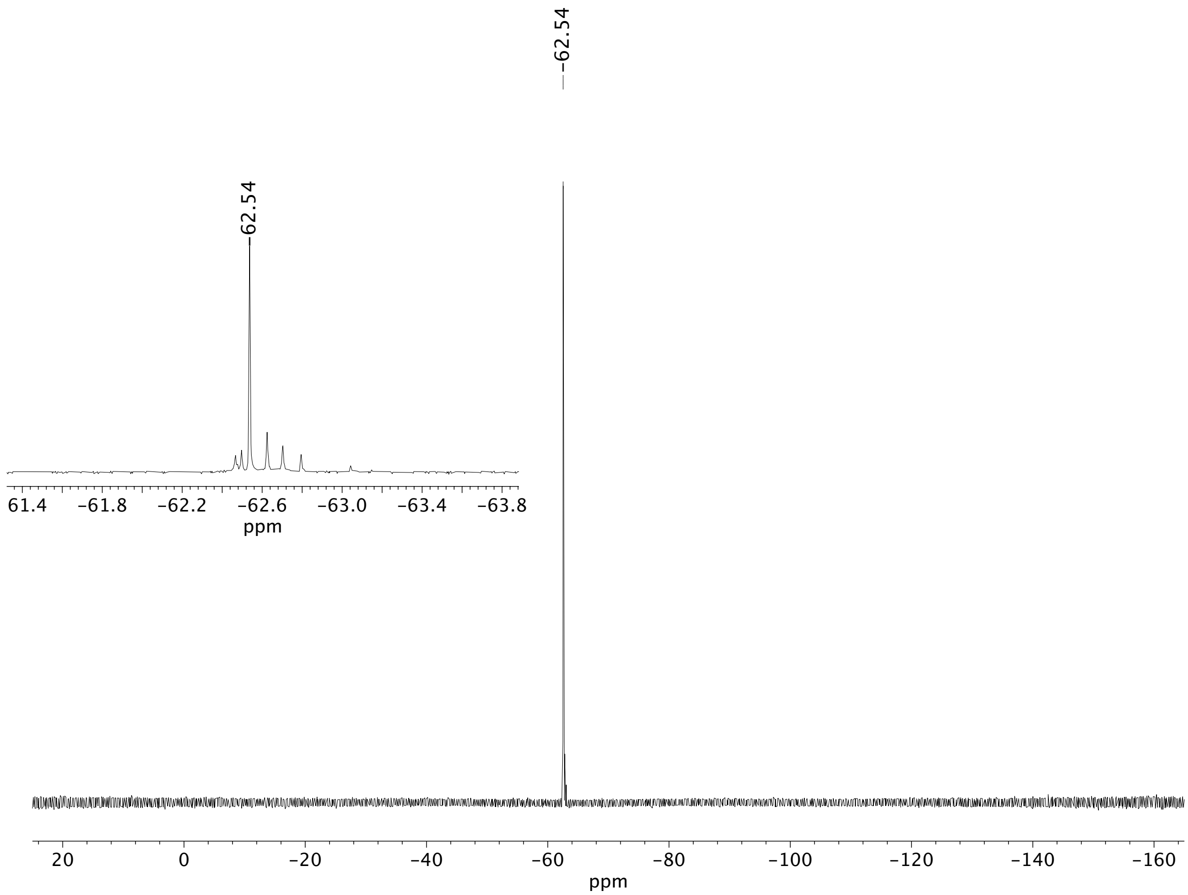
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4m.**



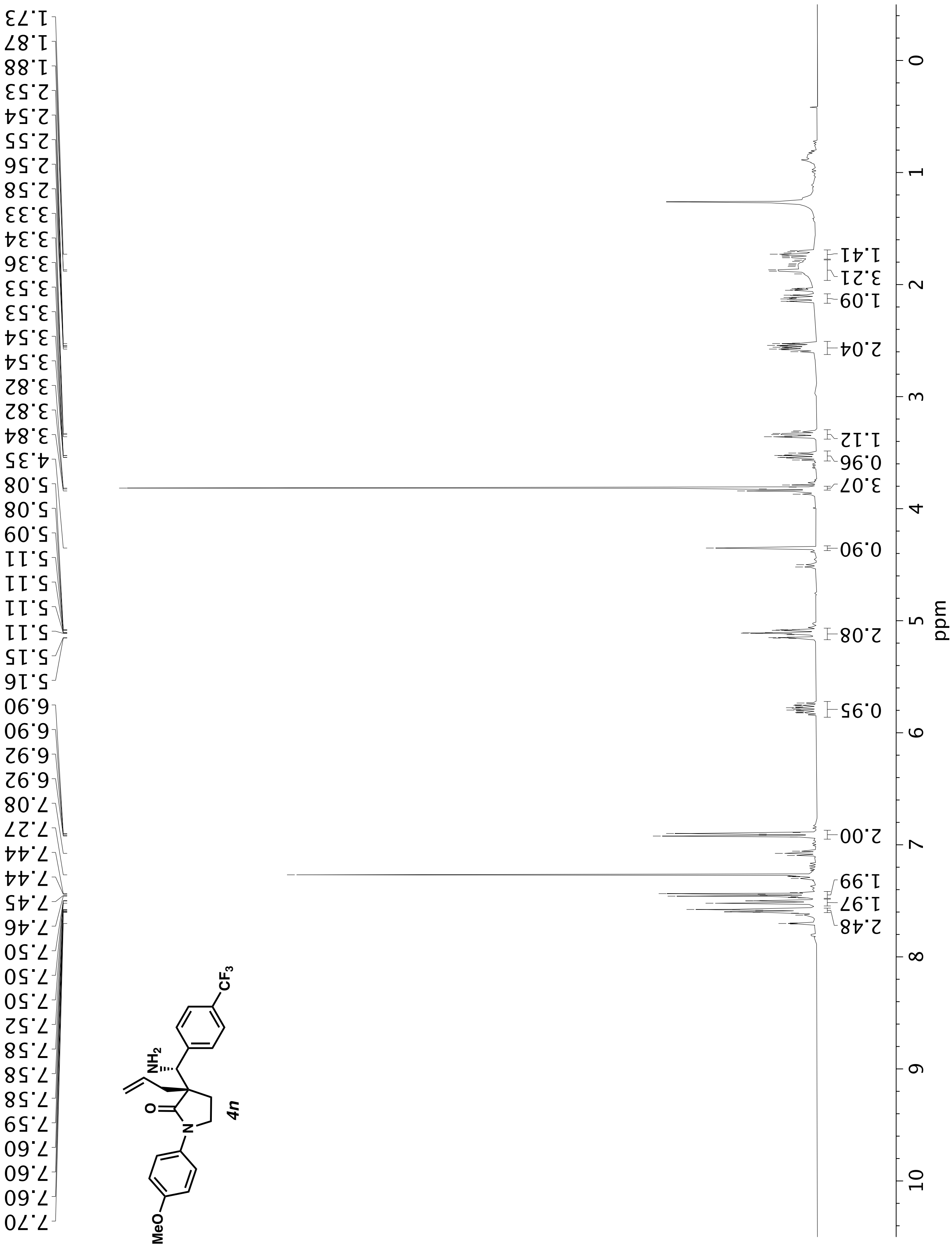
Infrared spectrum (Thin Film, NaCl) of compound **4m**.



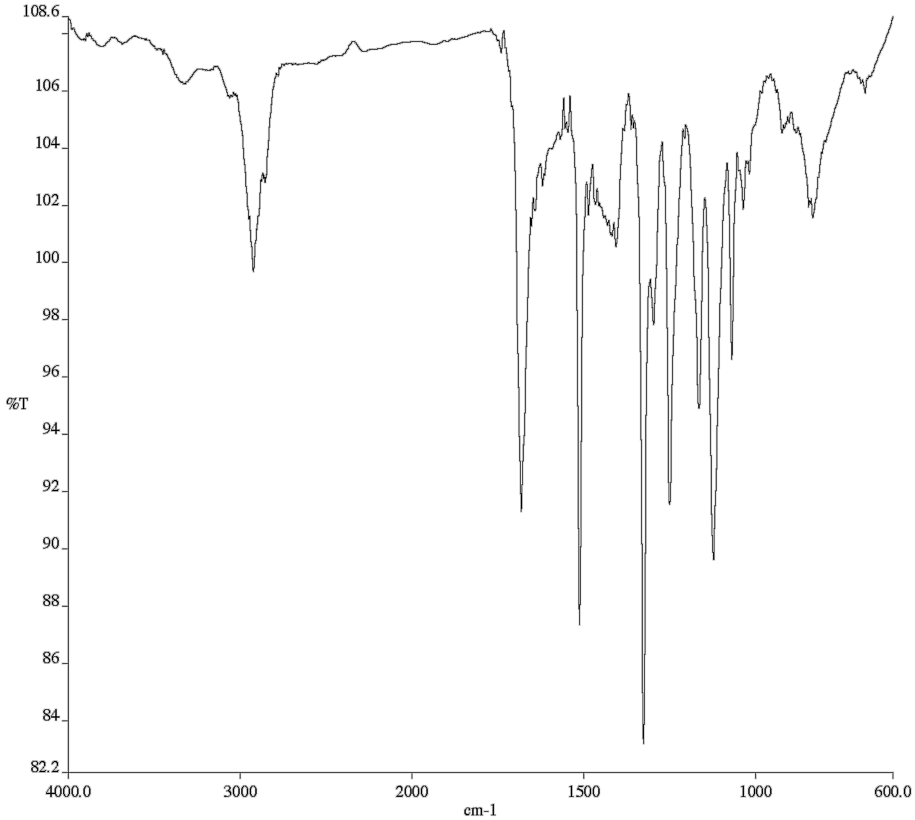
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4m**.



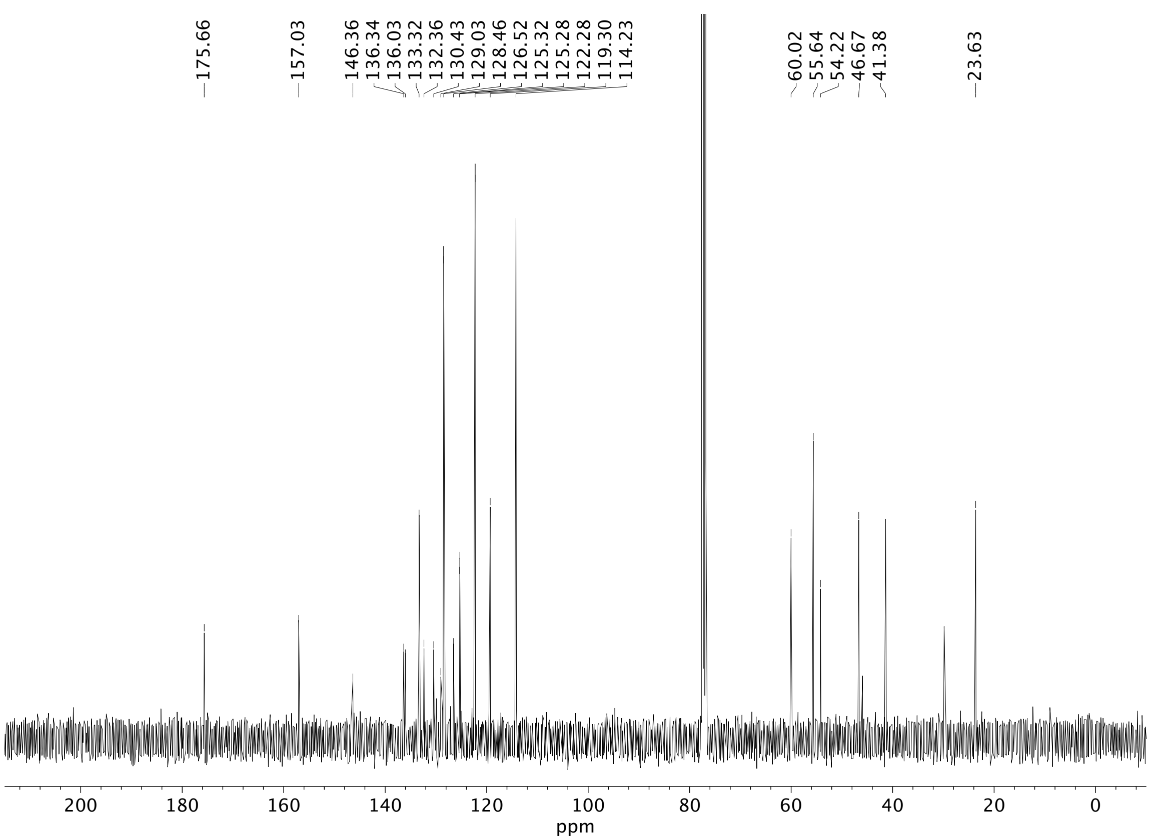
^{19}F NMR (282 MHz, $CDCl_3$) of compound **4m**.



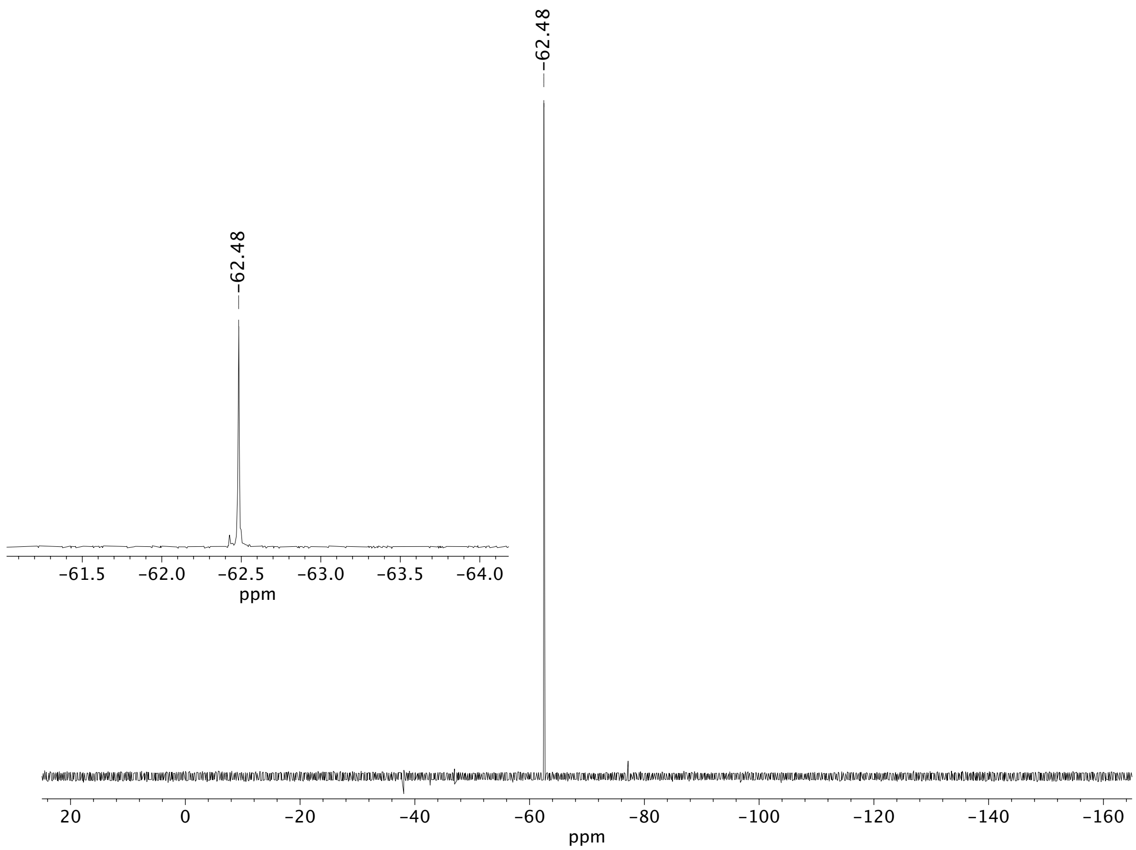
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4n**.



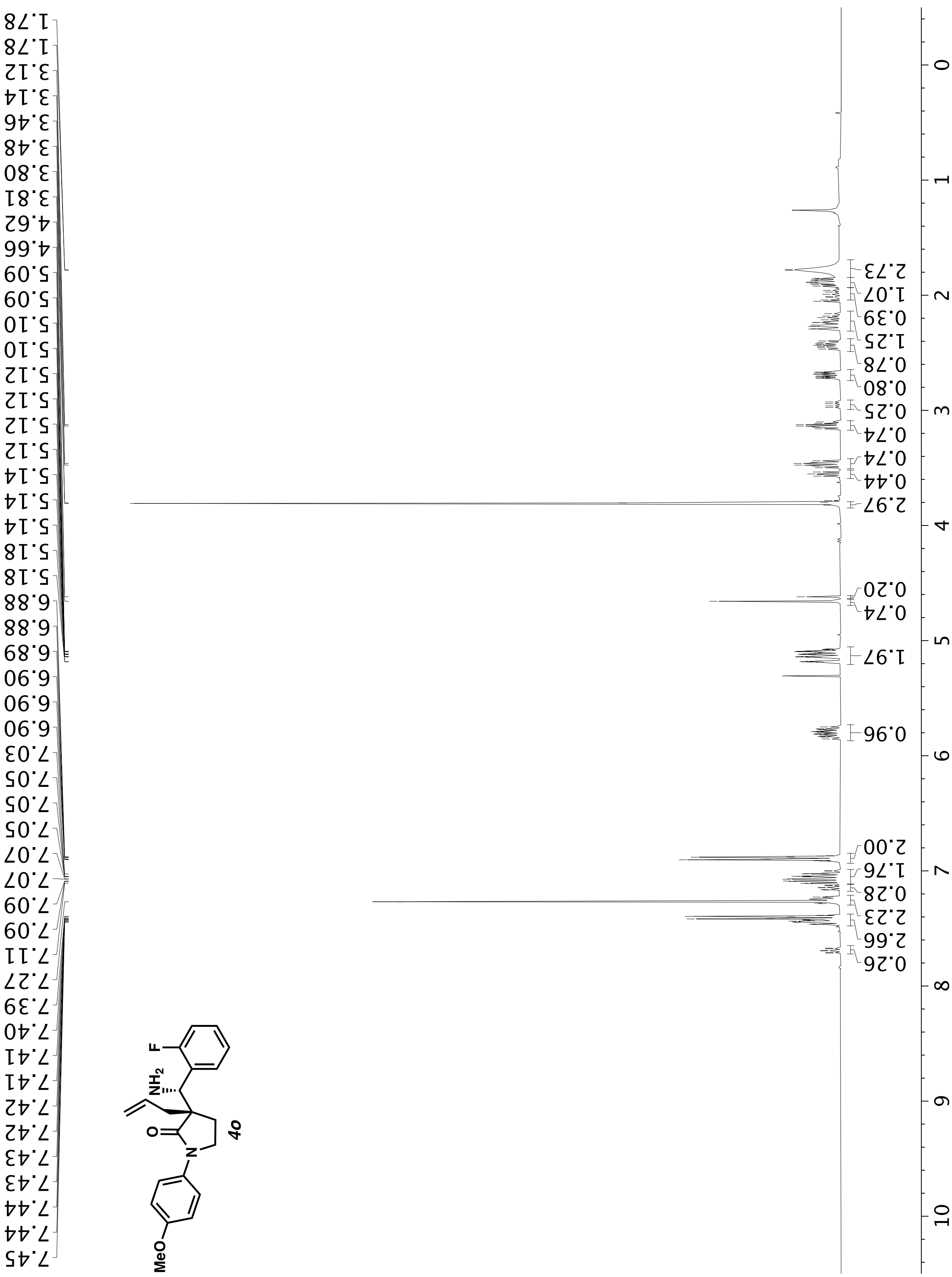
Infrared spectrum (Thin Film, NaCl) of compound **4n**.



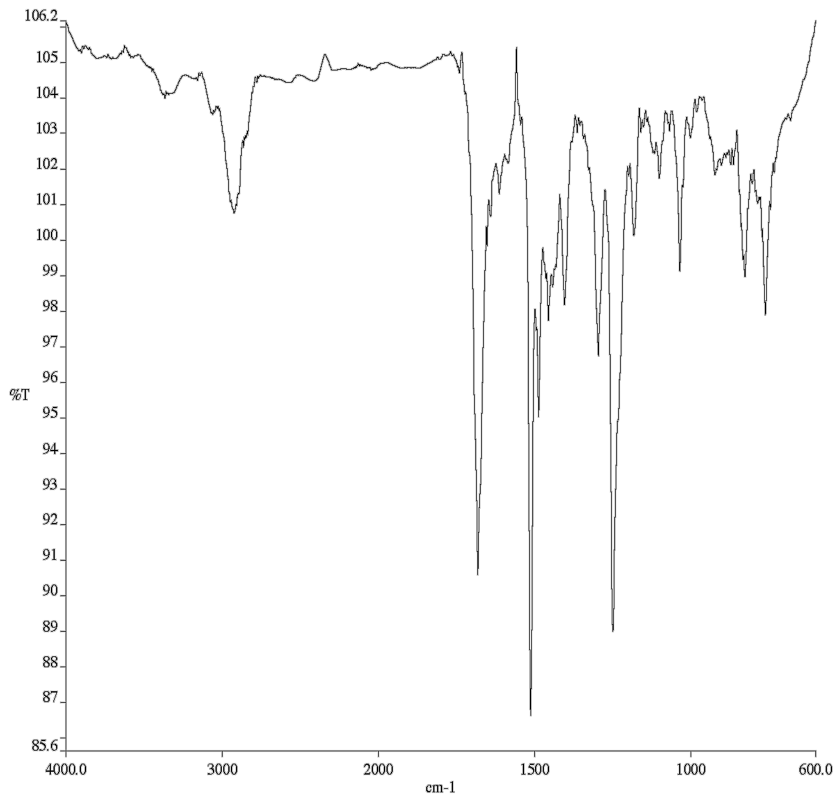
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4n**.



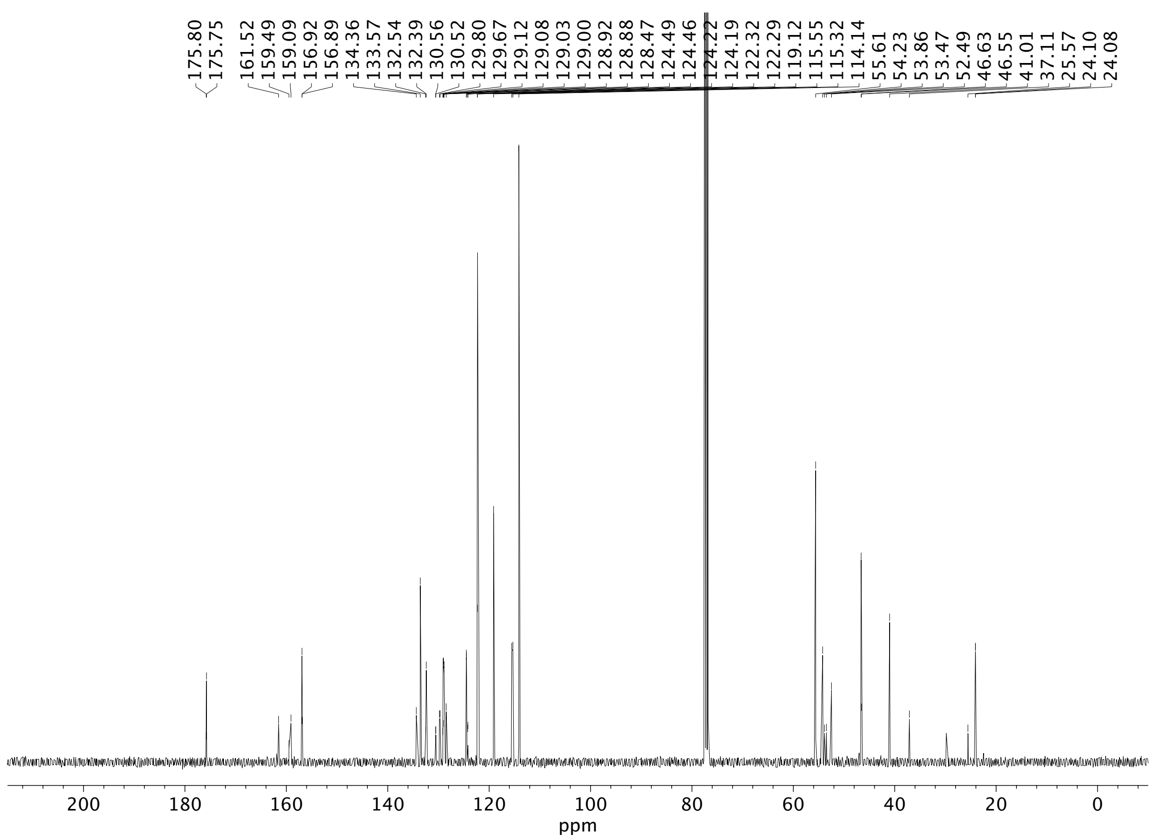
^{19}F NMR (282 MHz, $CDCl_3$) of compound **4n**.



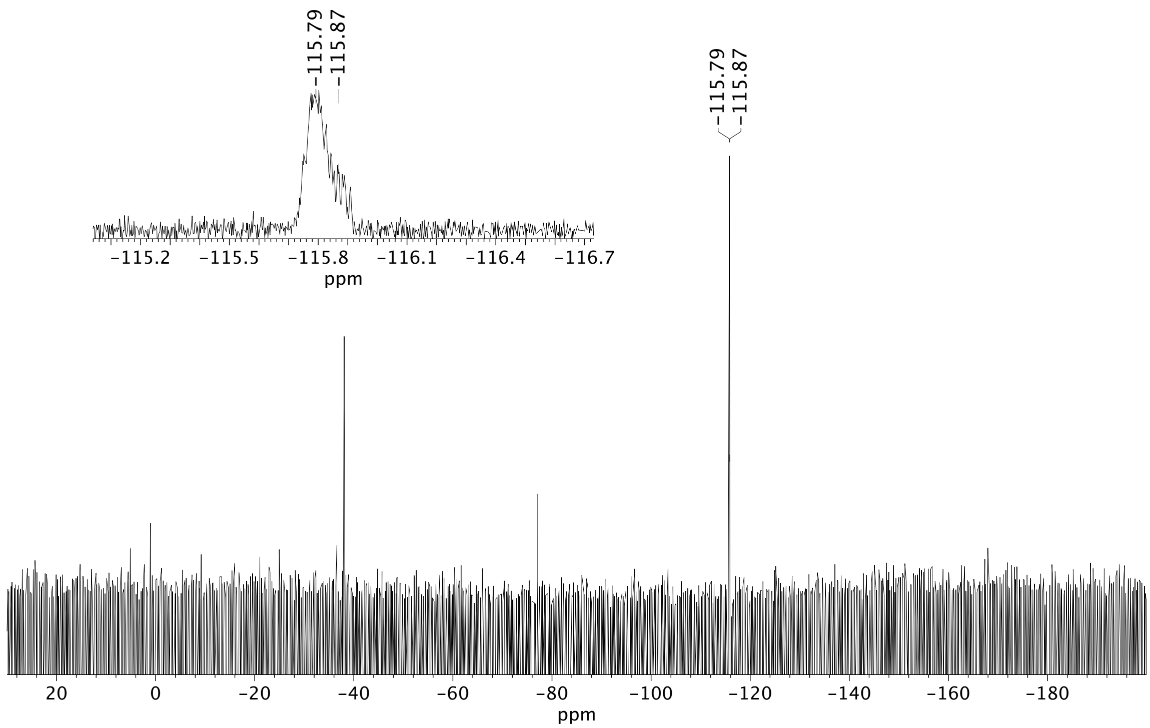
[1]H NMR (400 MHz, $CDCl_3$) of compound **4o**.



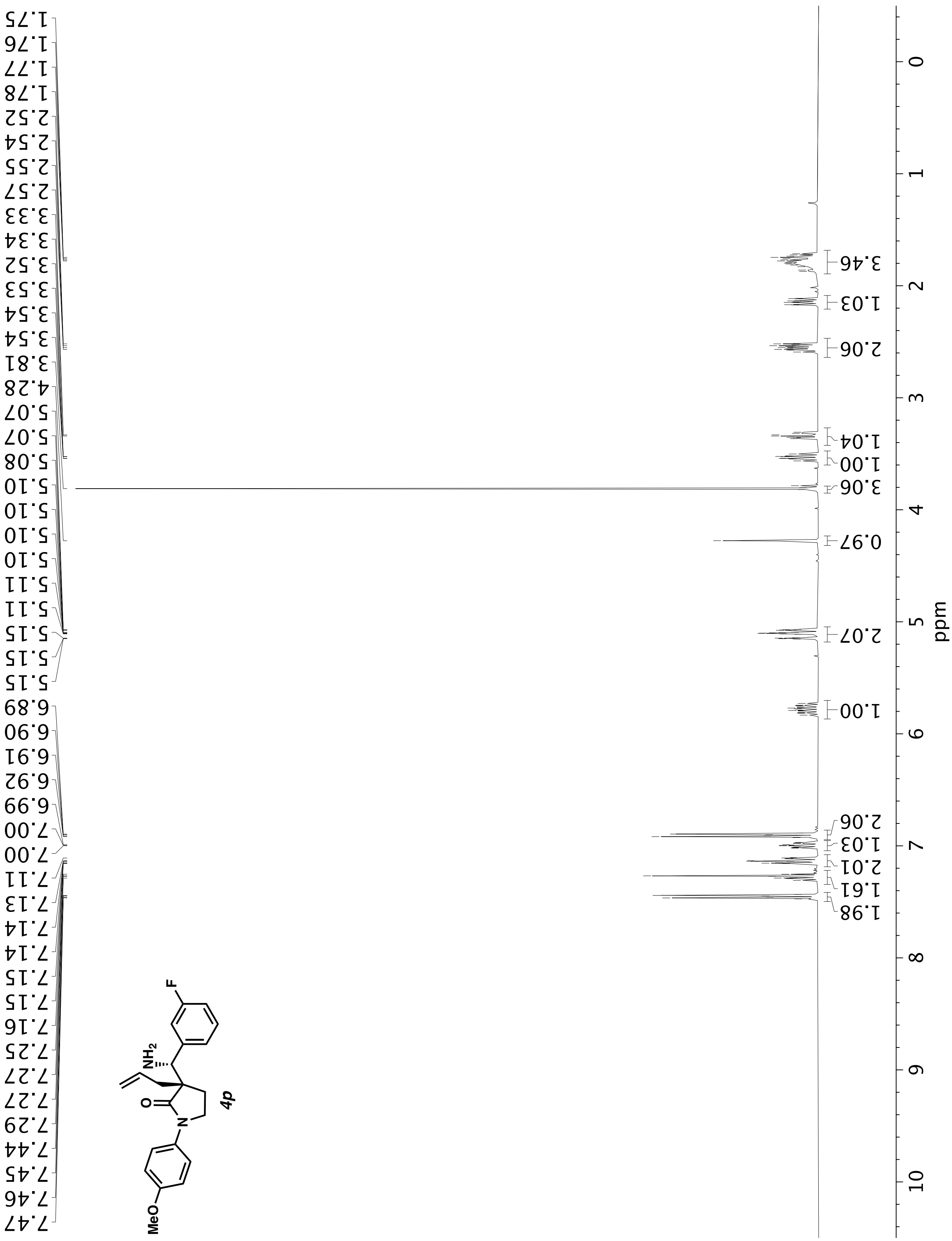
Infrared spectrum (Thin Film, NaCl) of compound **4o**.



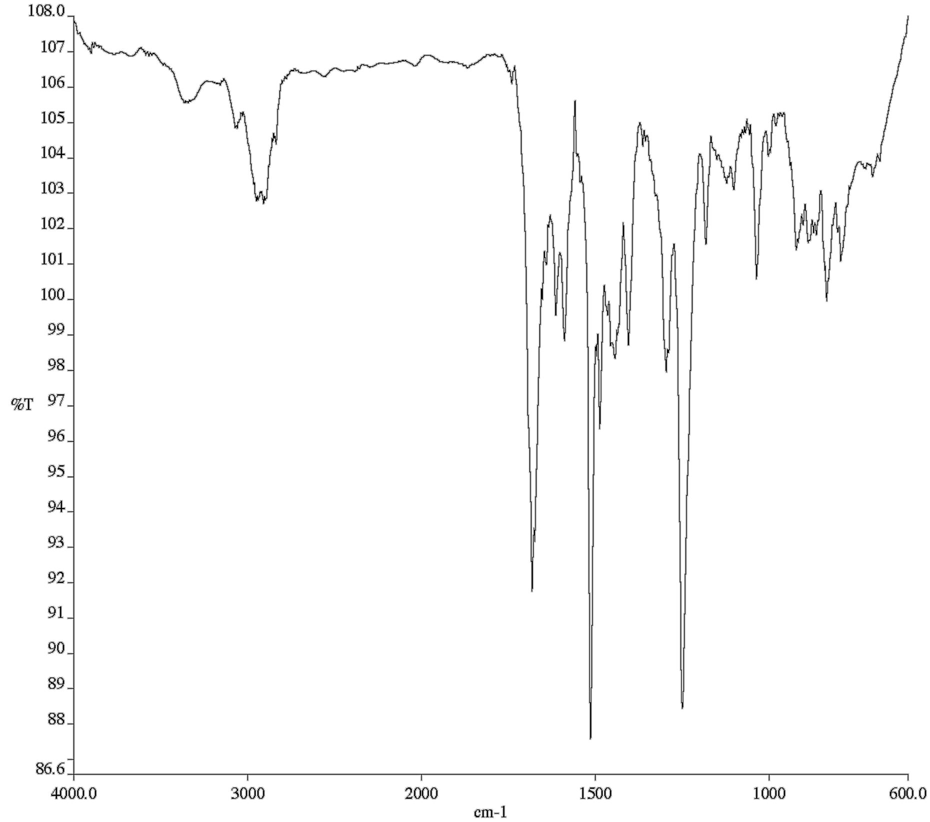
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4o**.



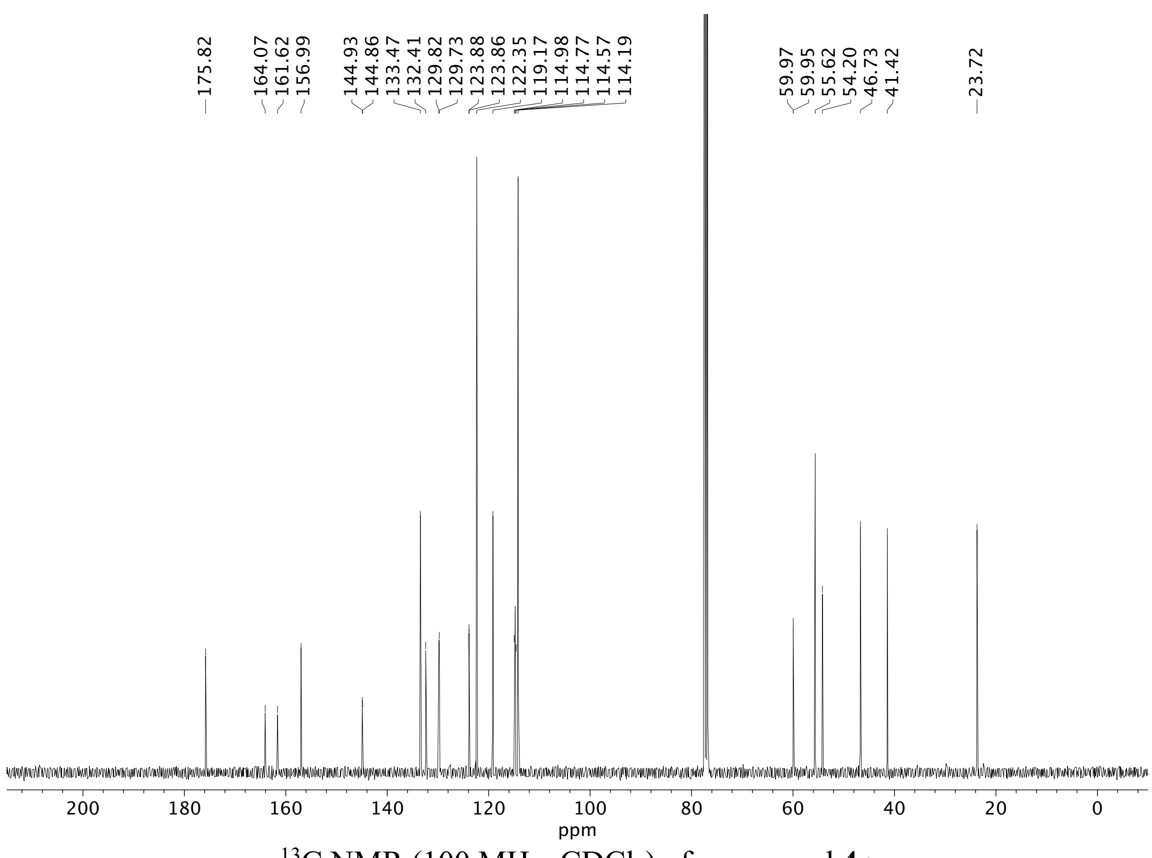
^{19}F NMR (282 MHz, $CDCl_3$) of compound **4o**.



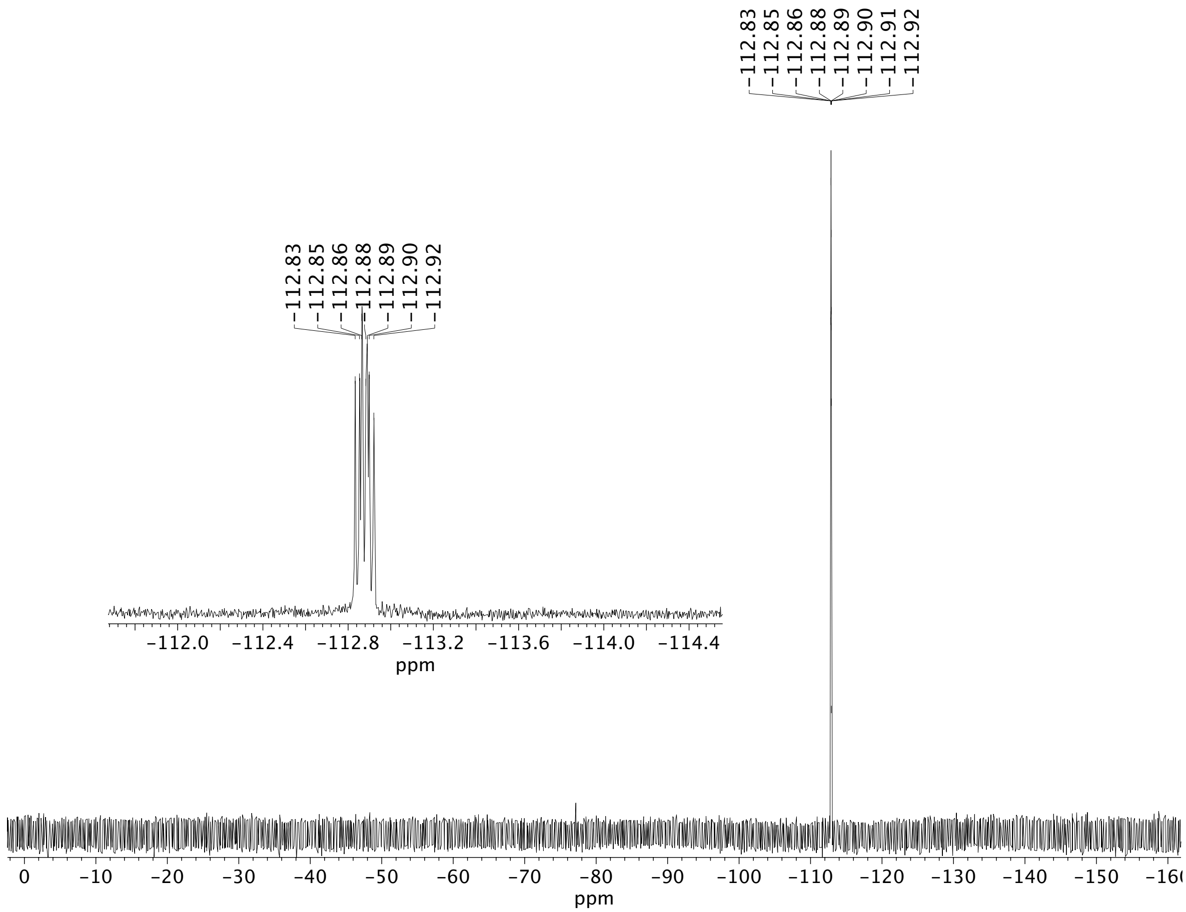
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4p**.



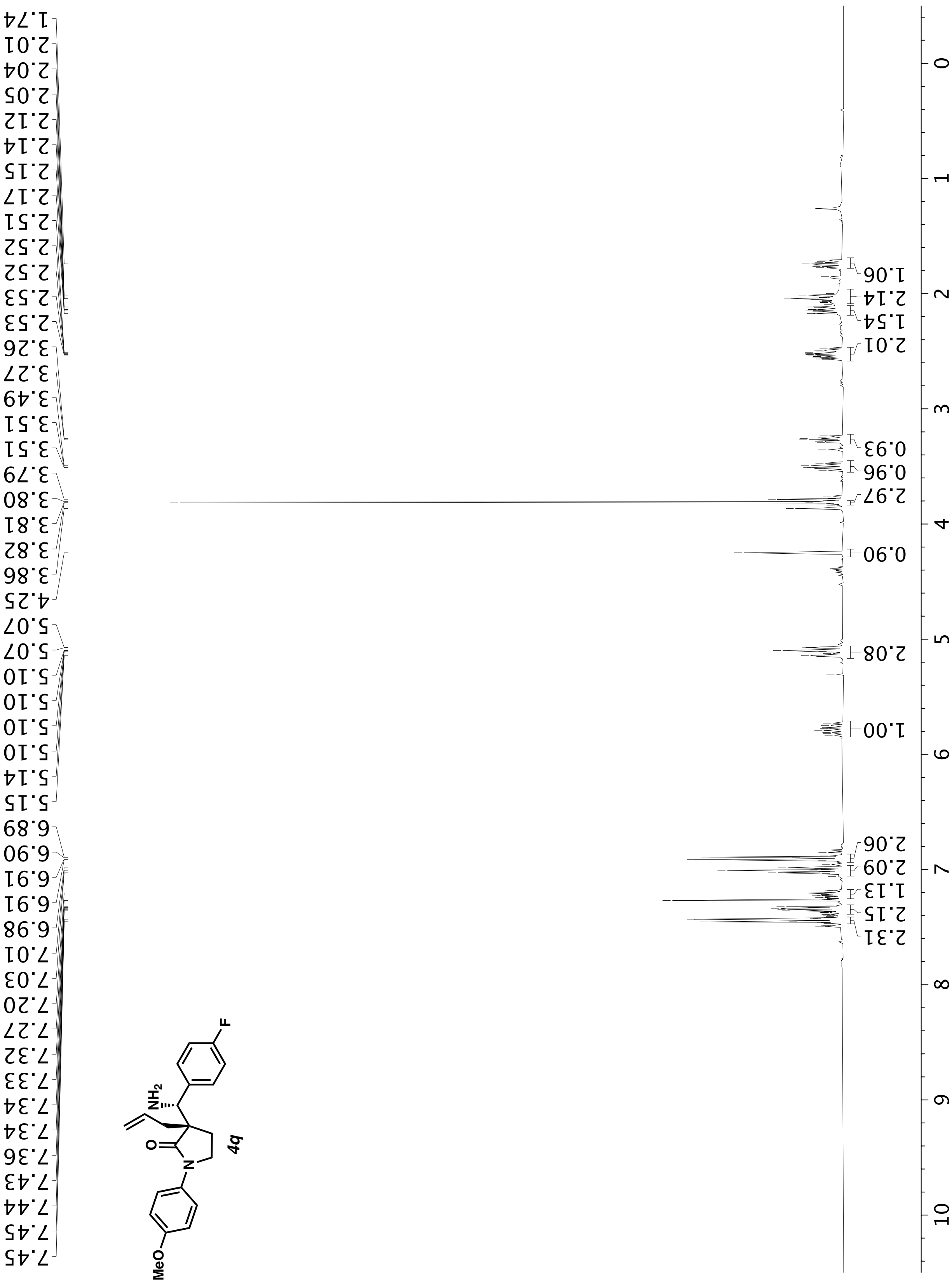
Infrared spectrum (Thin Film, NaCl) of compound **4p**.



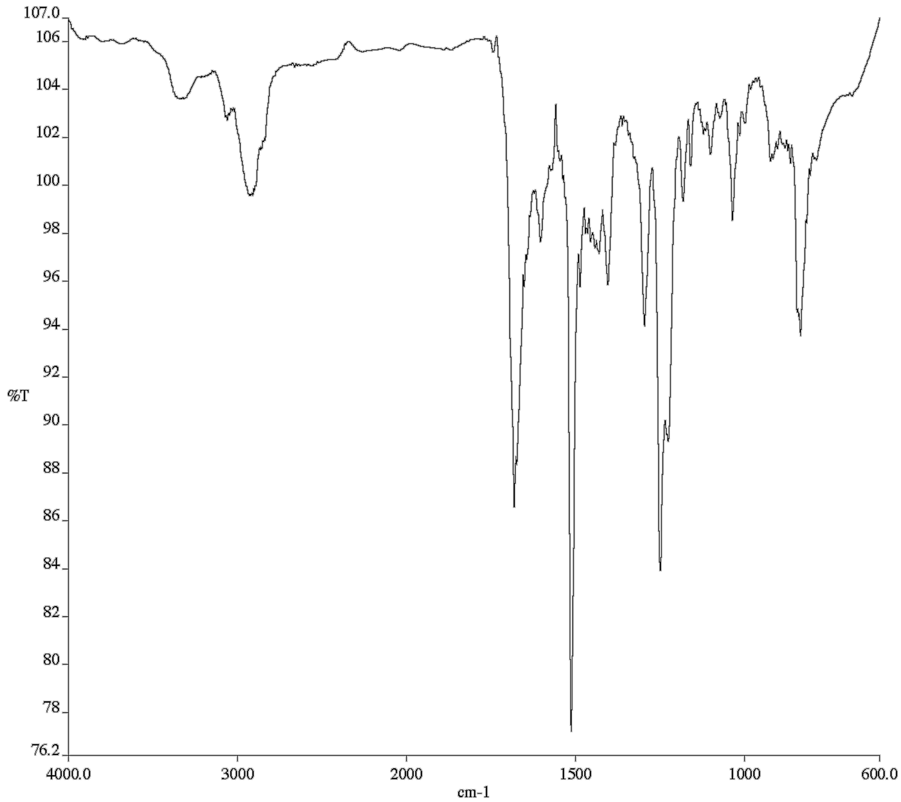
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4p**.



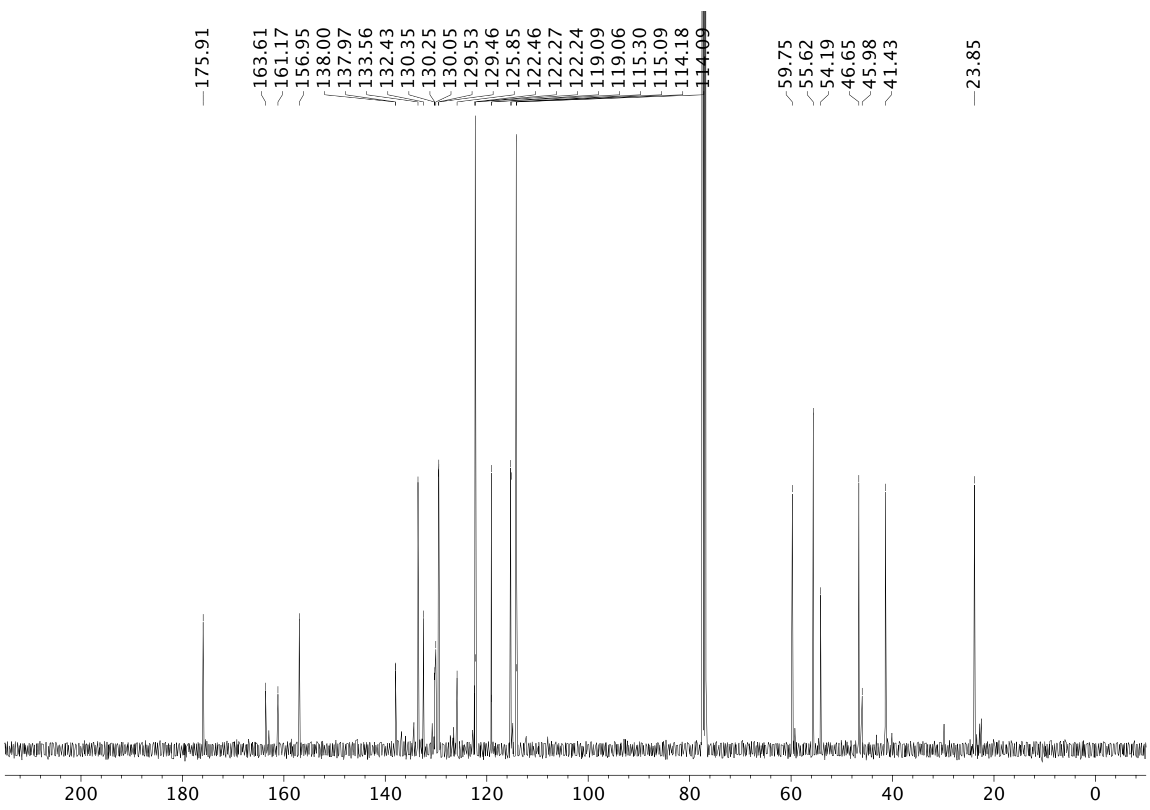
^{19}F NMR (282 MHz, $CDCl_3$) of compound **4p**.



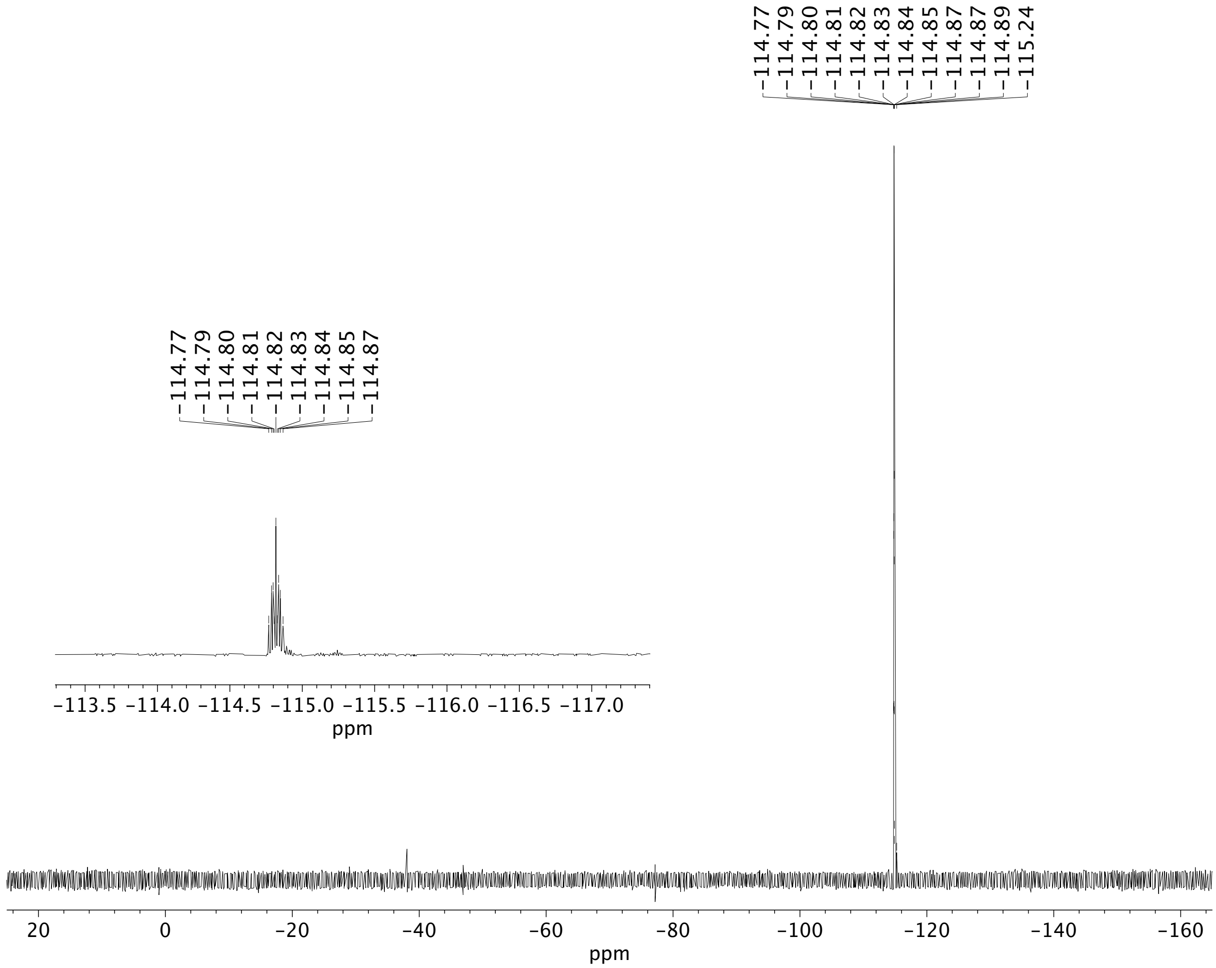
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4q**.



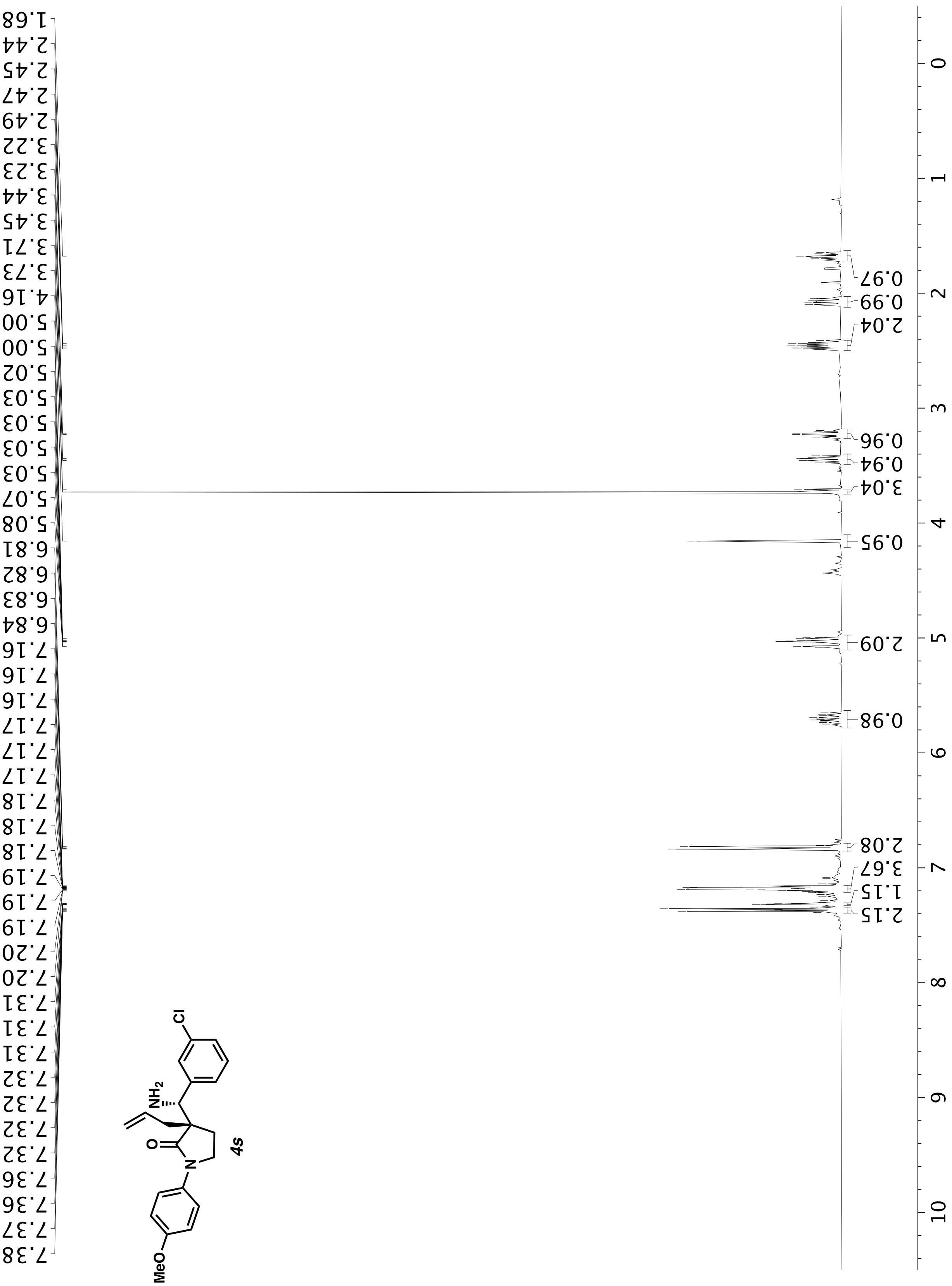
Infrared spectrum (Thin Film, NaCl) of compound **4q**.



^{13}C NMR (100 MHz, $CDCl_3$) of compound **4q**.

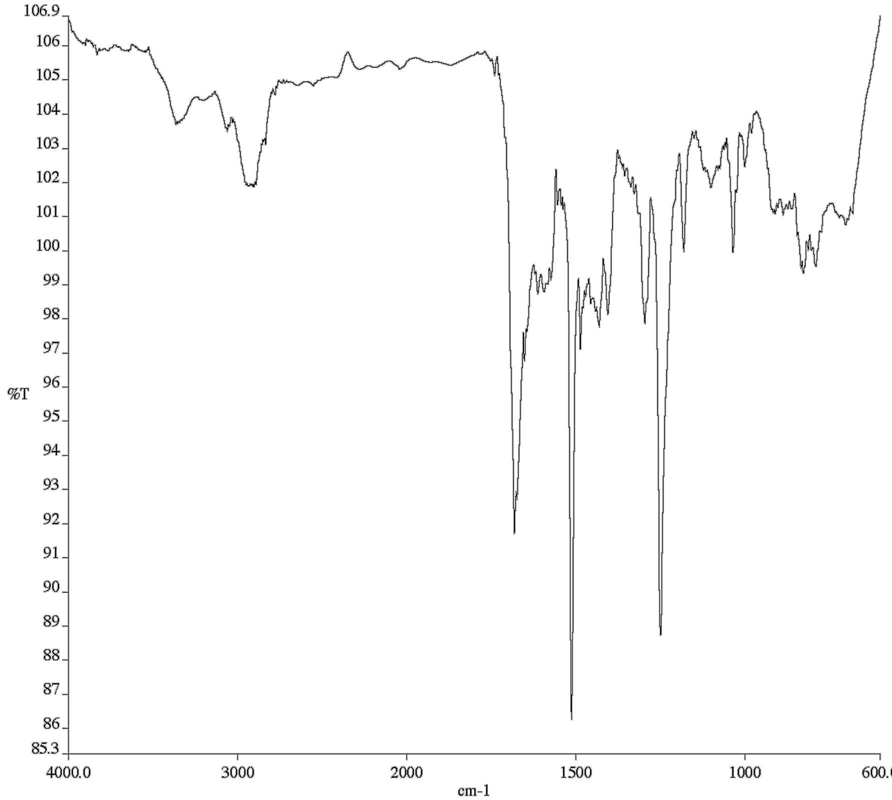


^{19}F NMR (282 MHz, $CDCl_3$) of compound **4q**.

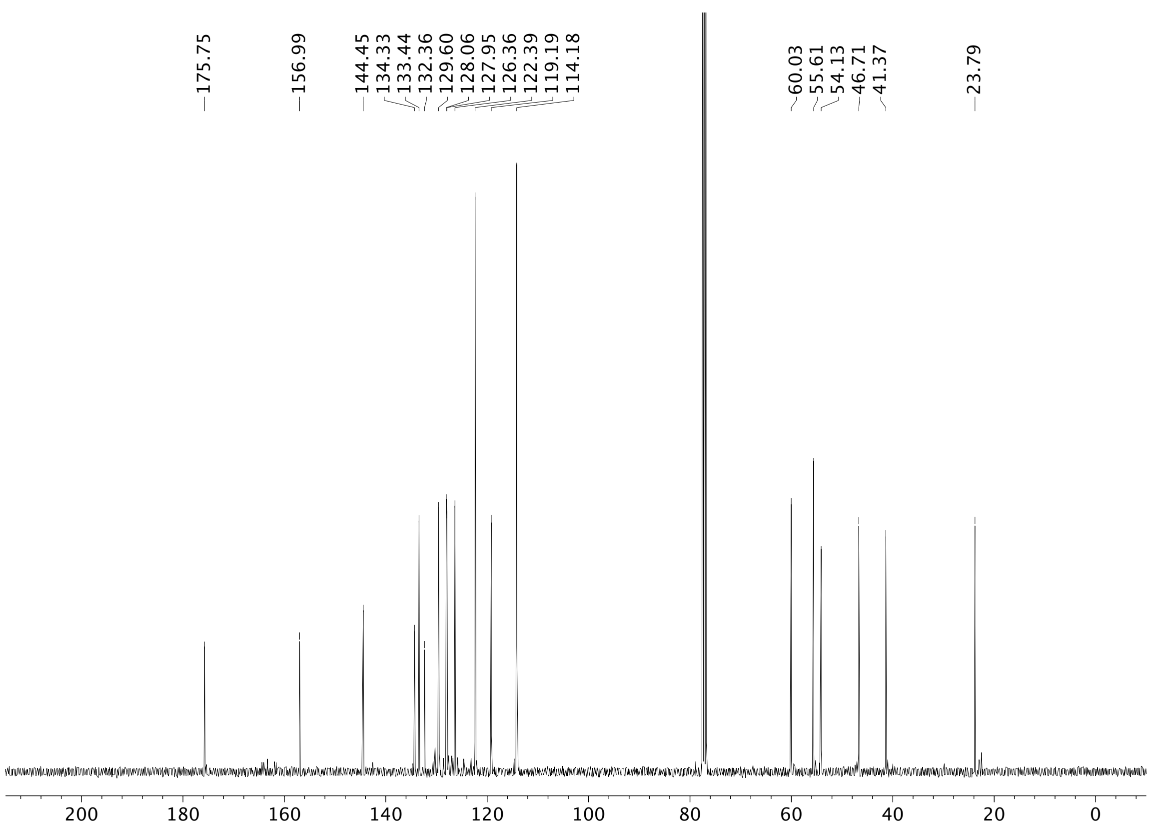


4s

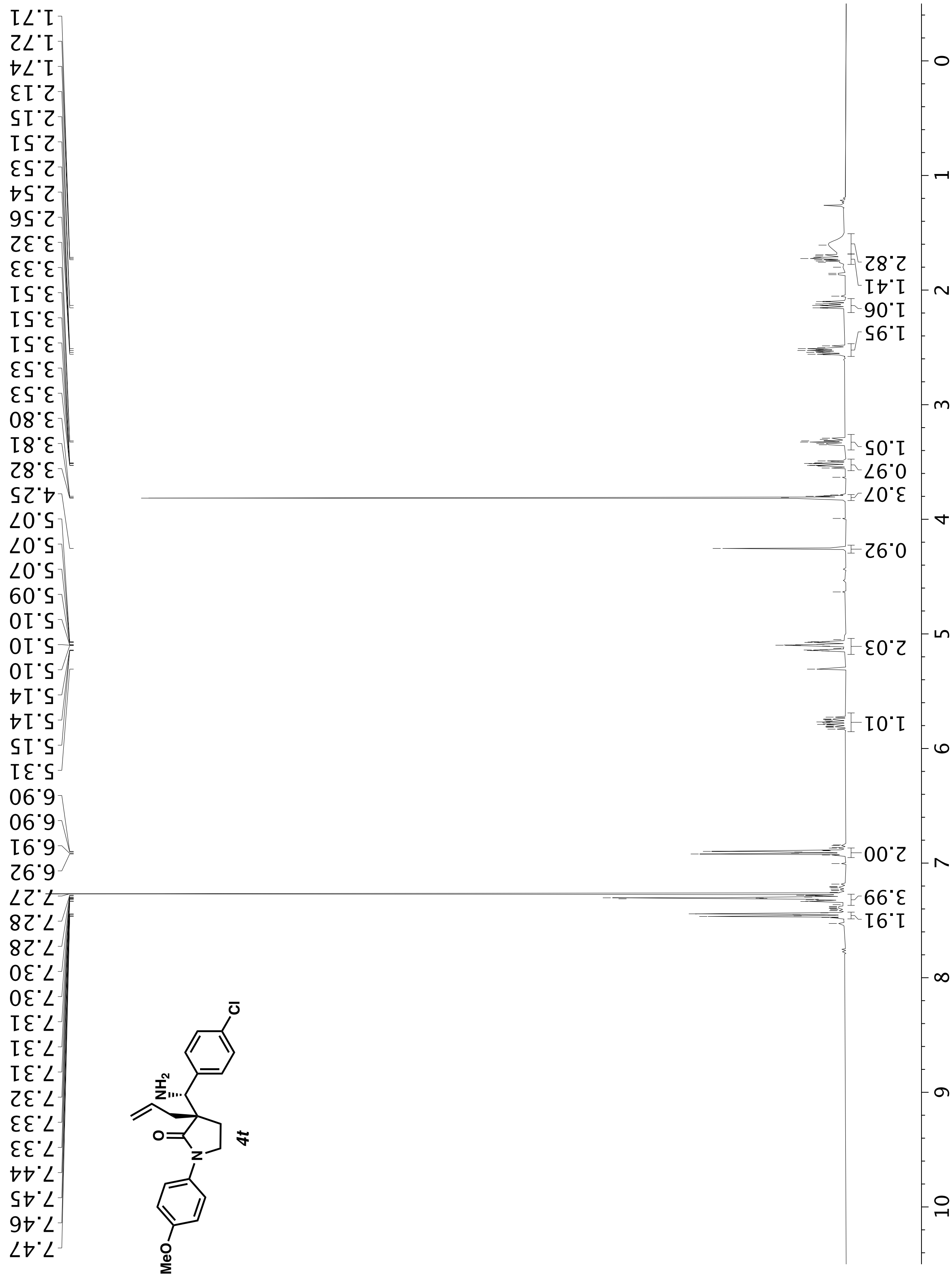
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4s**.



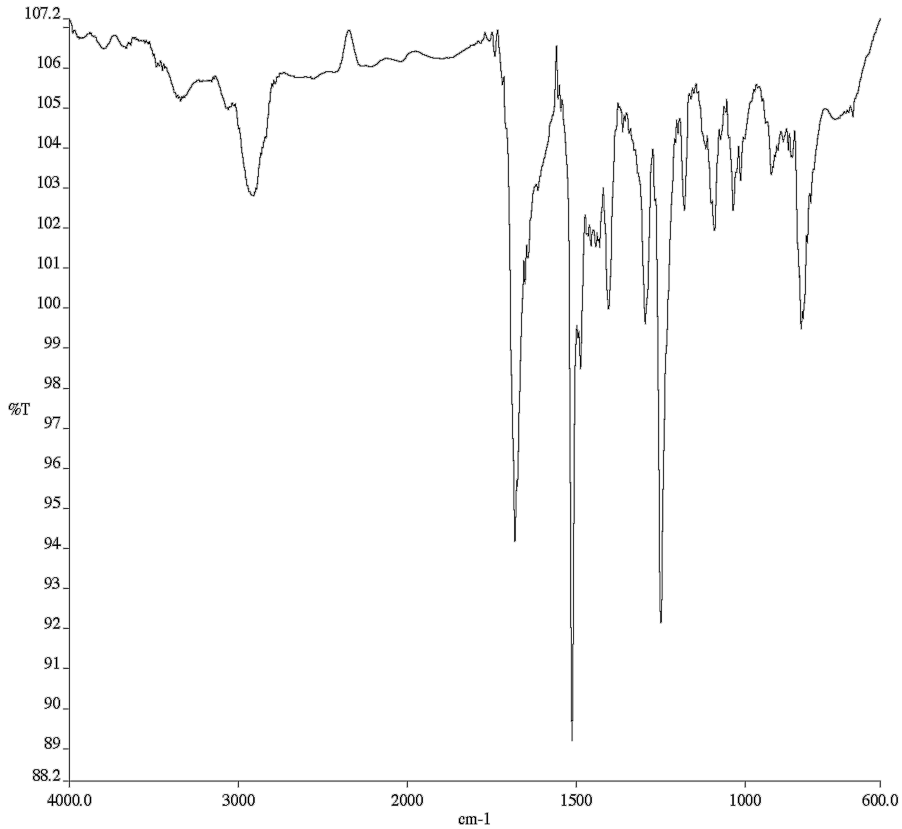
Infrared spectrum (Thin Film, NaCl) of compound **4s**.



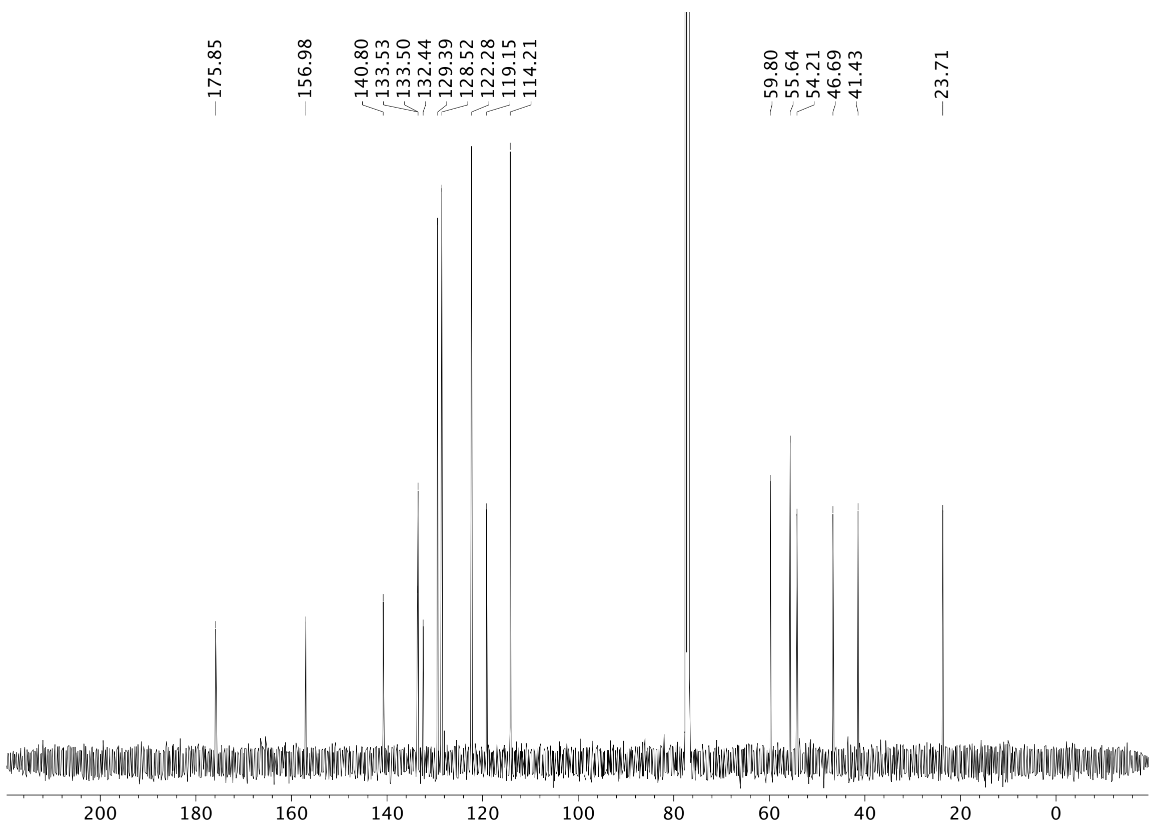
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4s**.



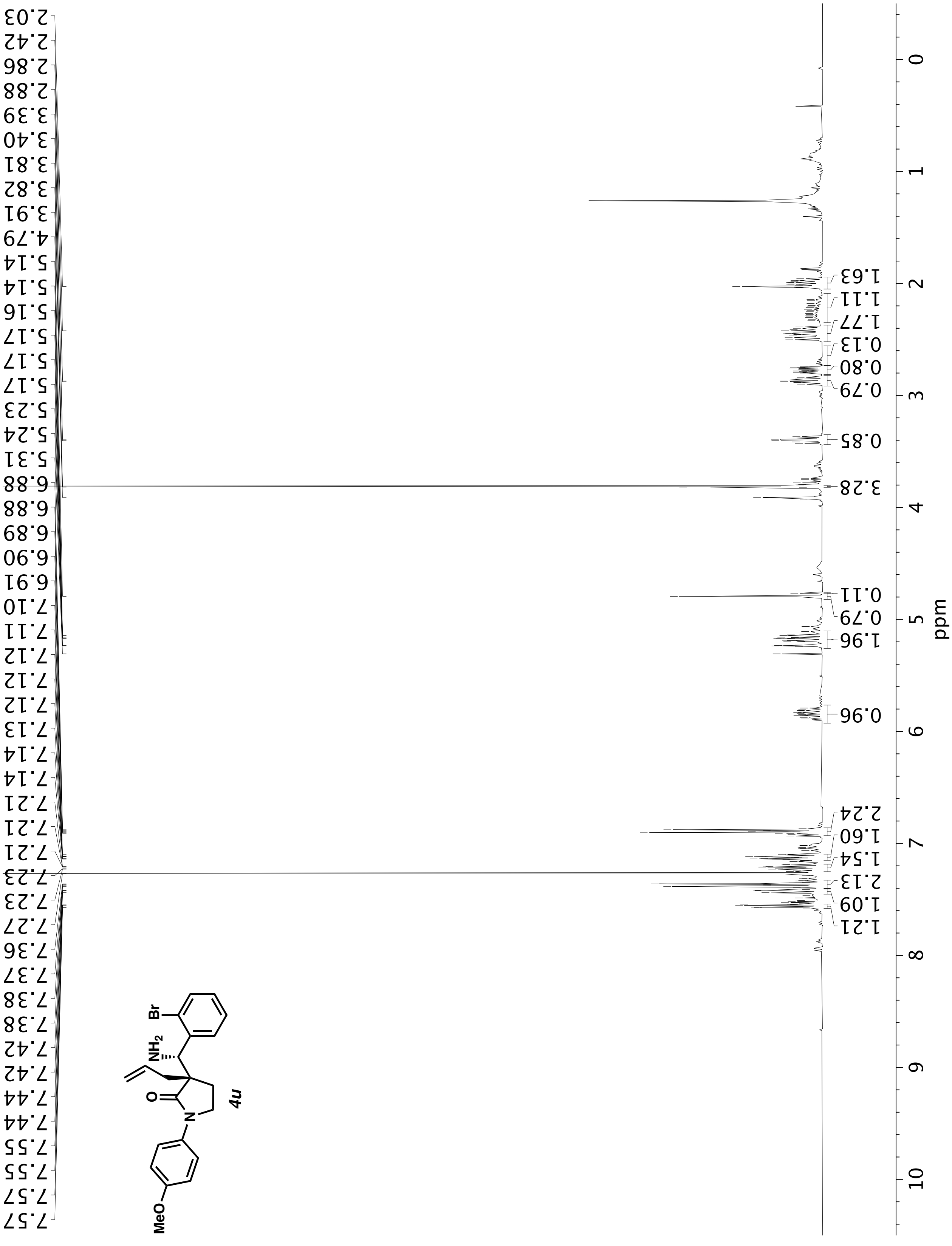
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4t**.



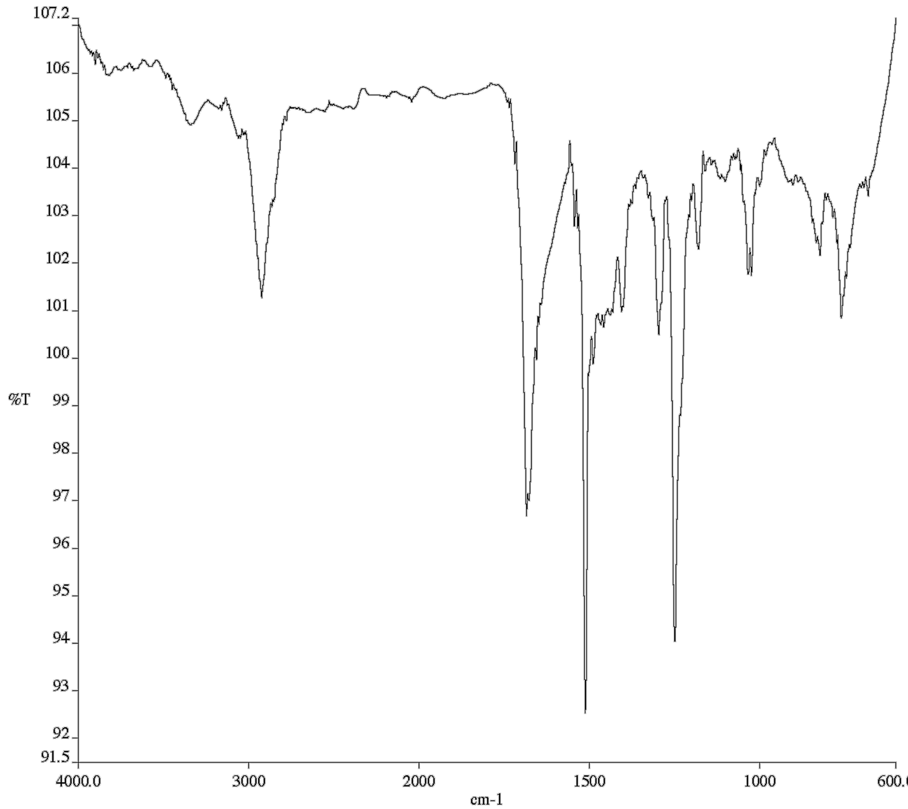
Infrared spectrum (Thin Film, NaCl) of compound **4t**.



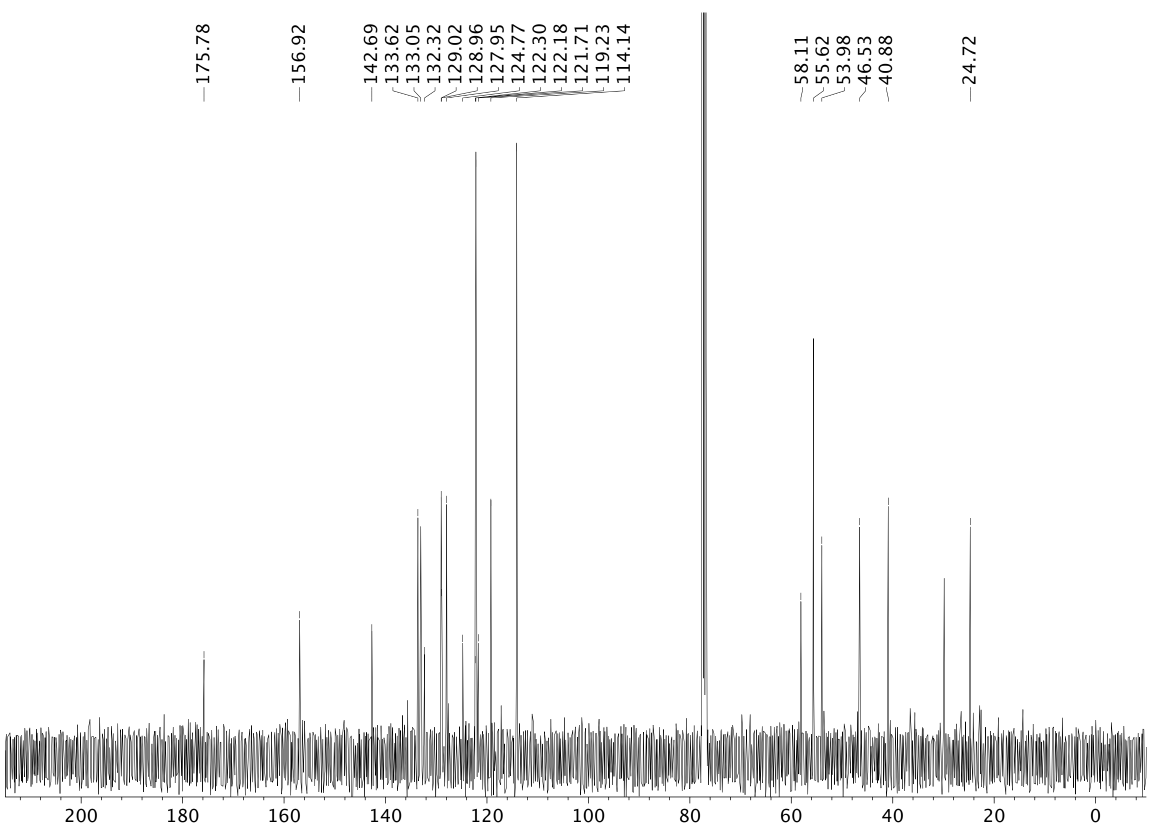
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4t**.



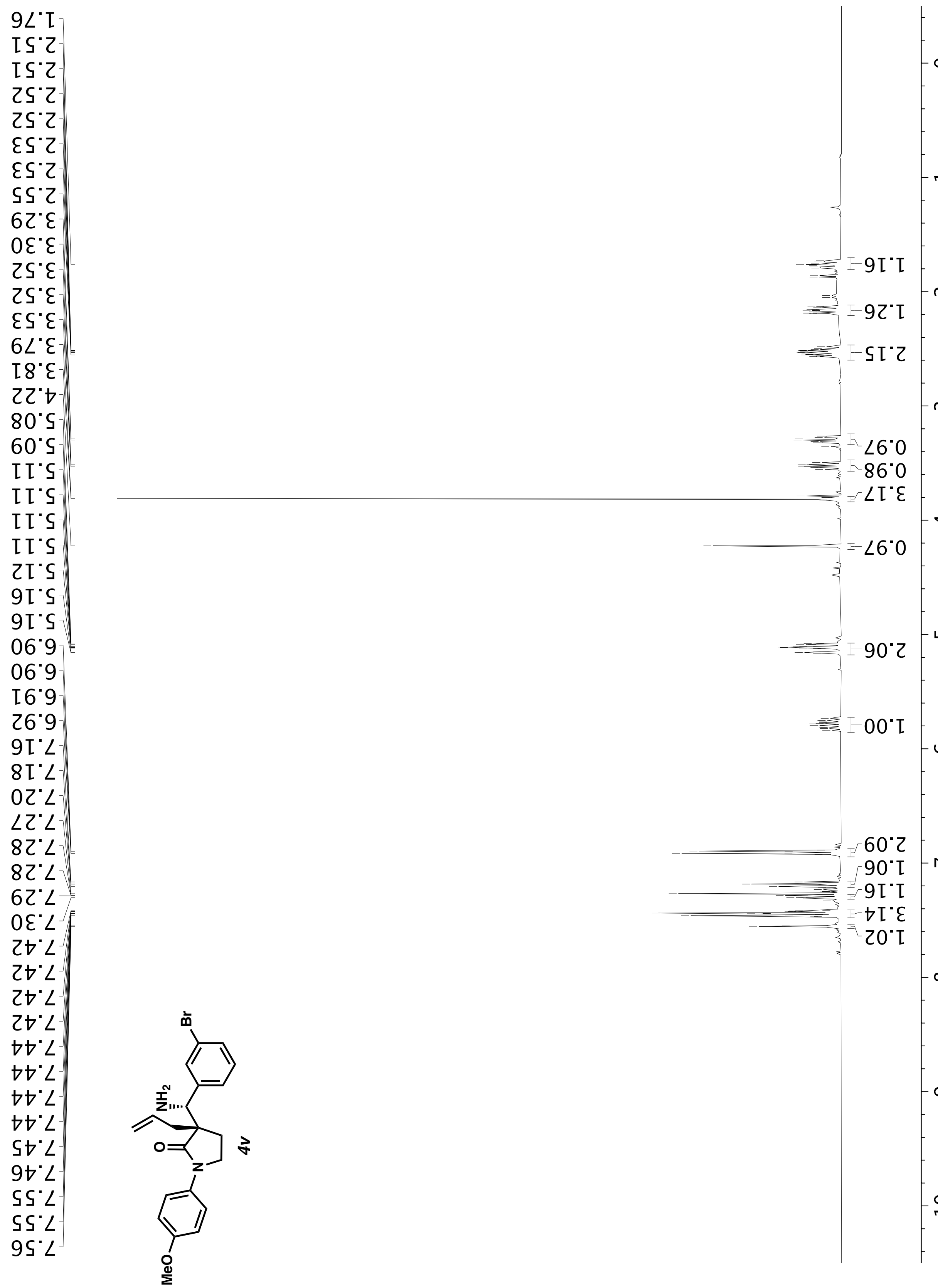
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4u**.



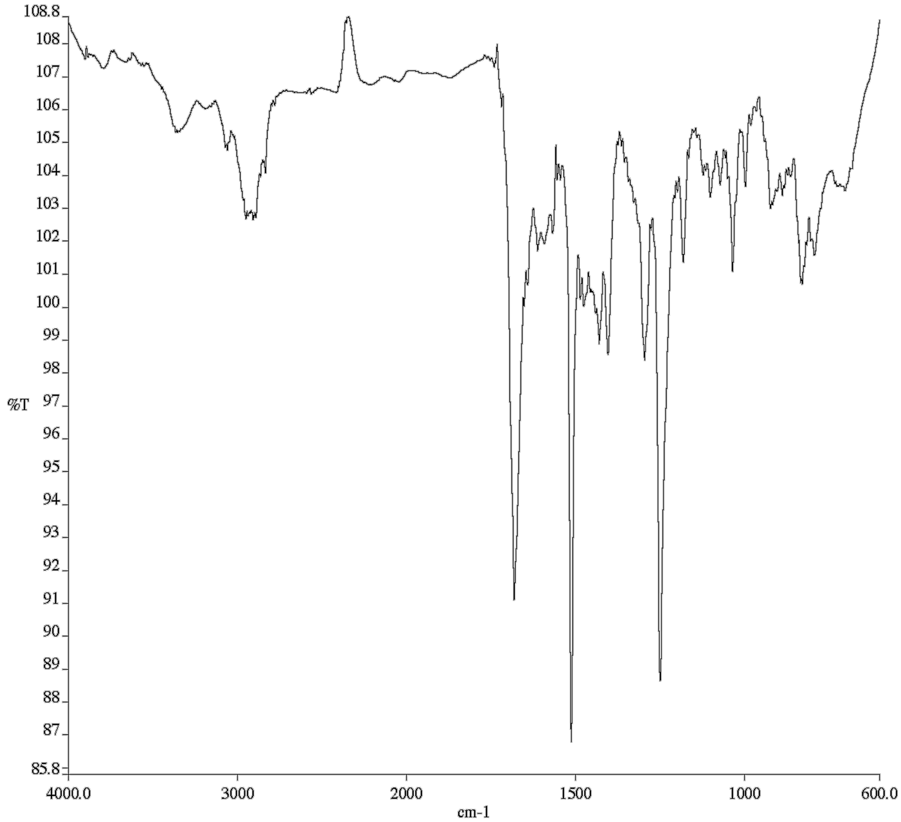
Infrared spectrum (Thin Film, NaCl) of compound **4u**.



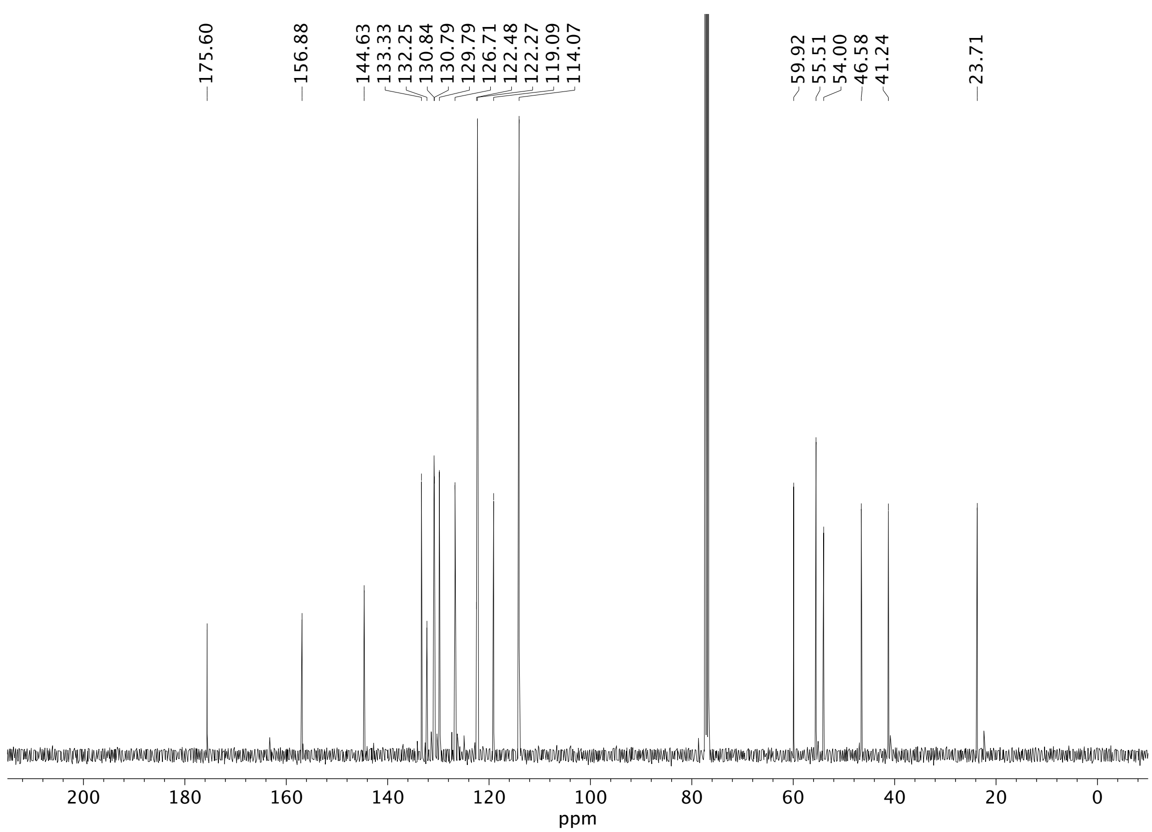
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4u**.



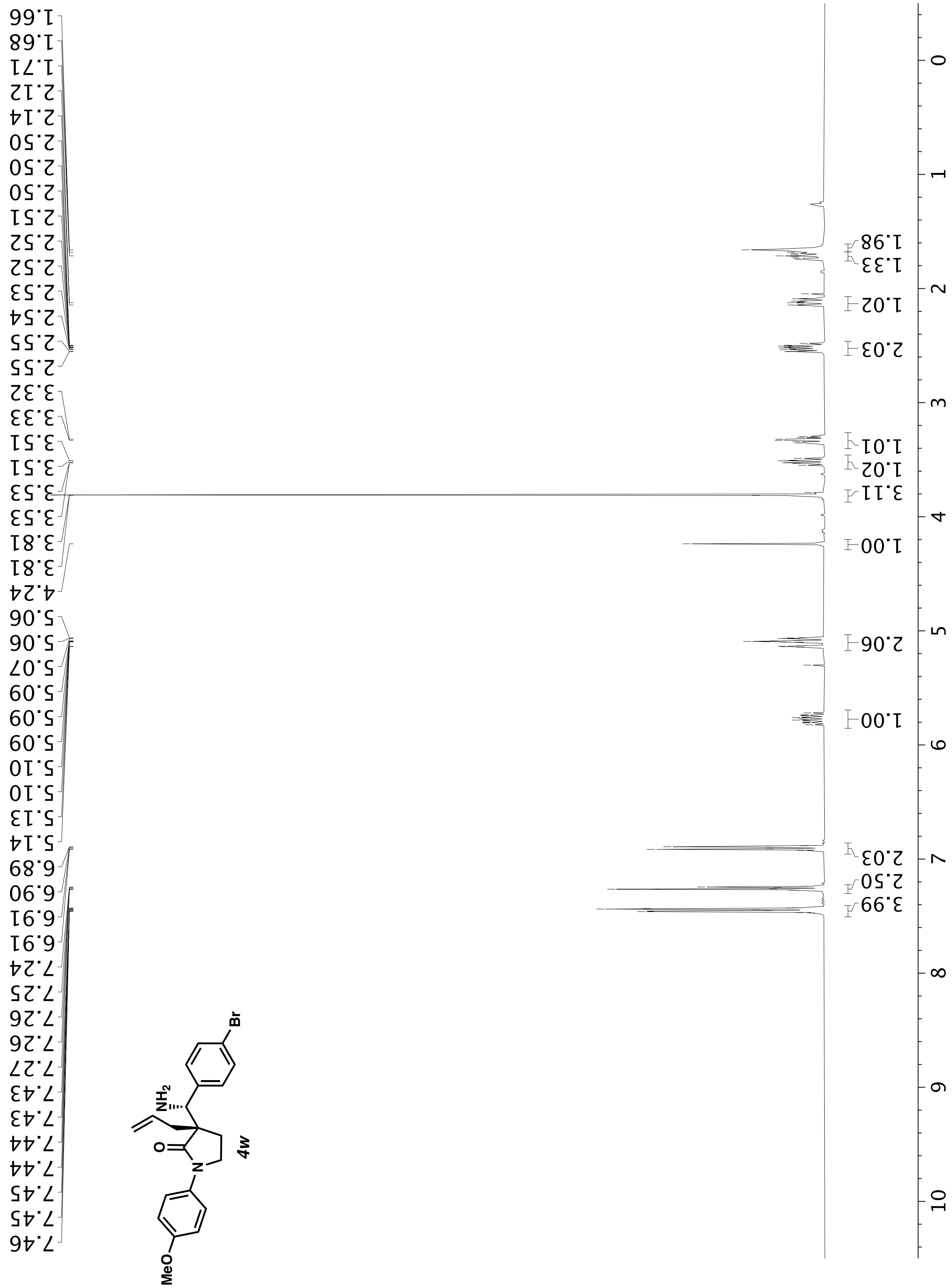
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4v**.



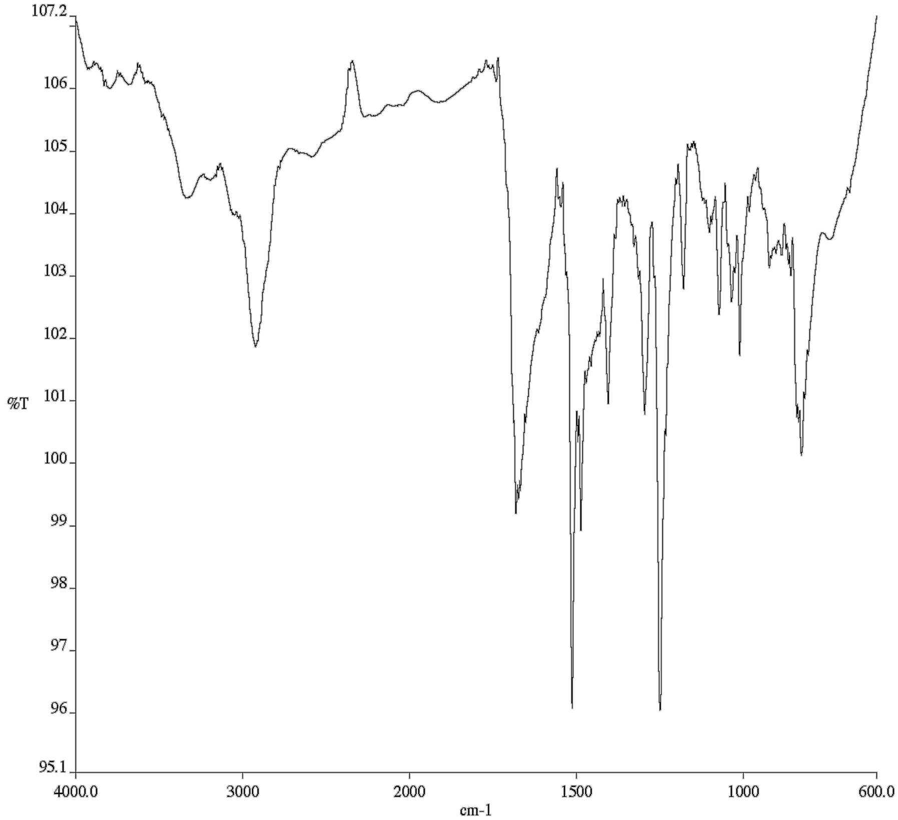
Infrared spectrum (Thin Film, NaCl) of compound **4v**.



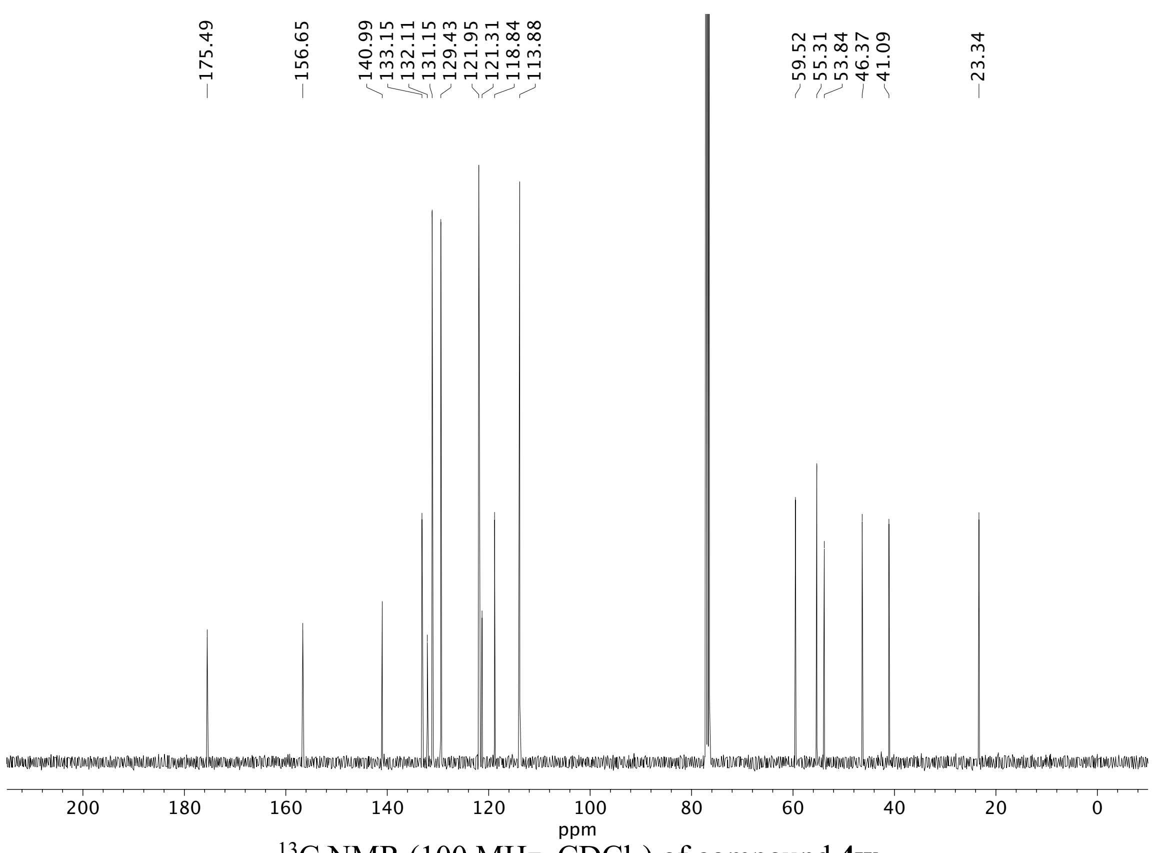
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4v**.



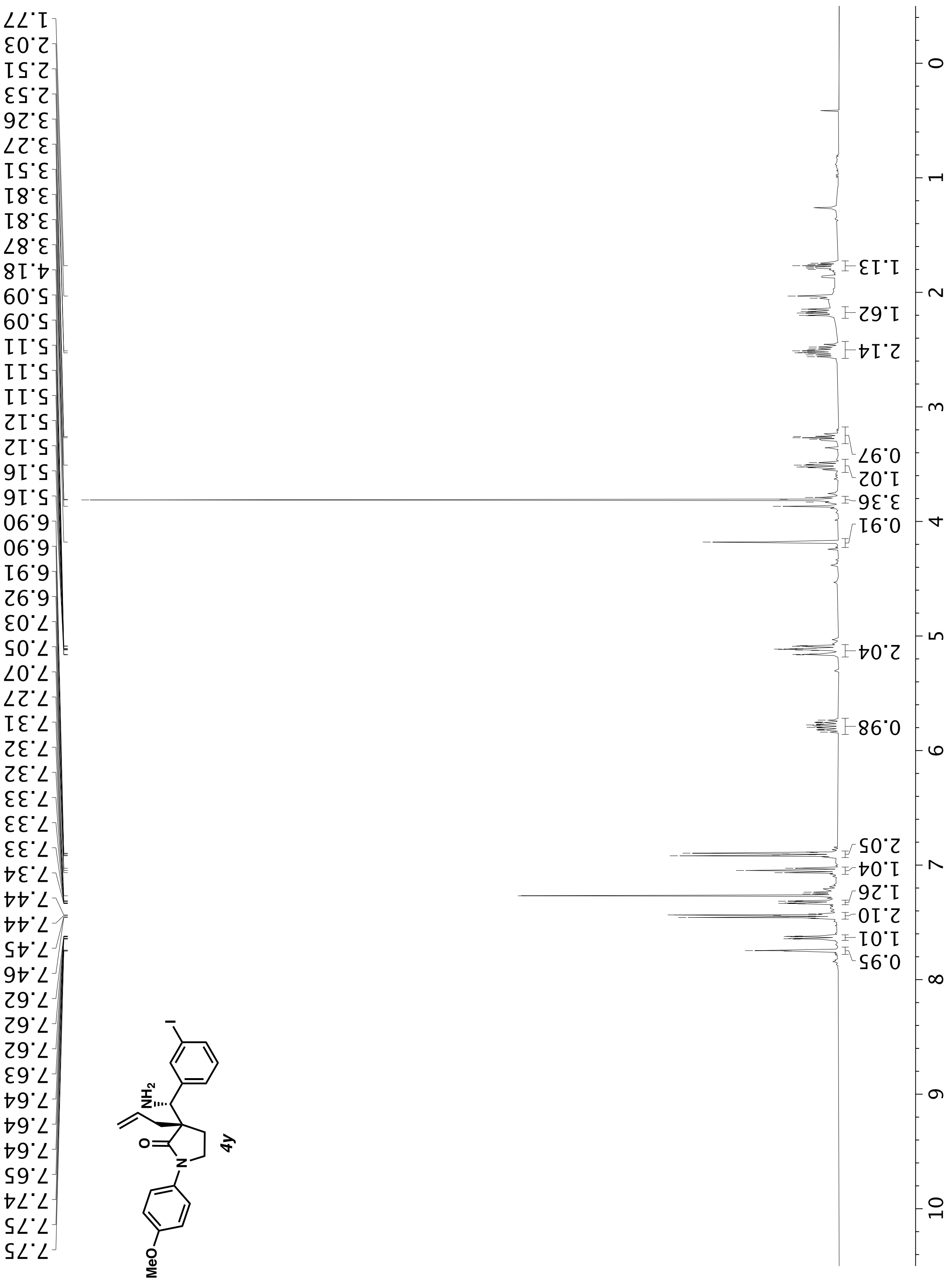
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4w**.



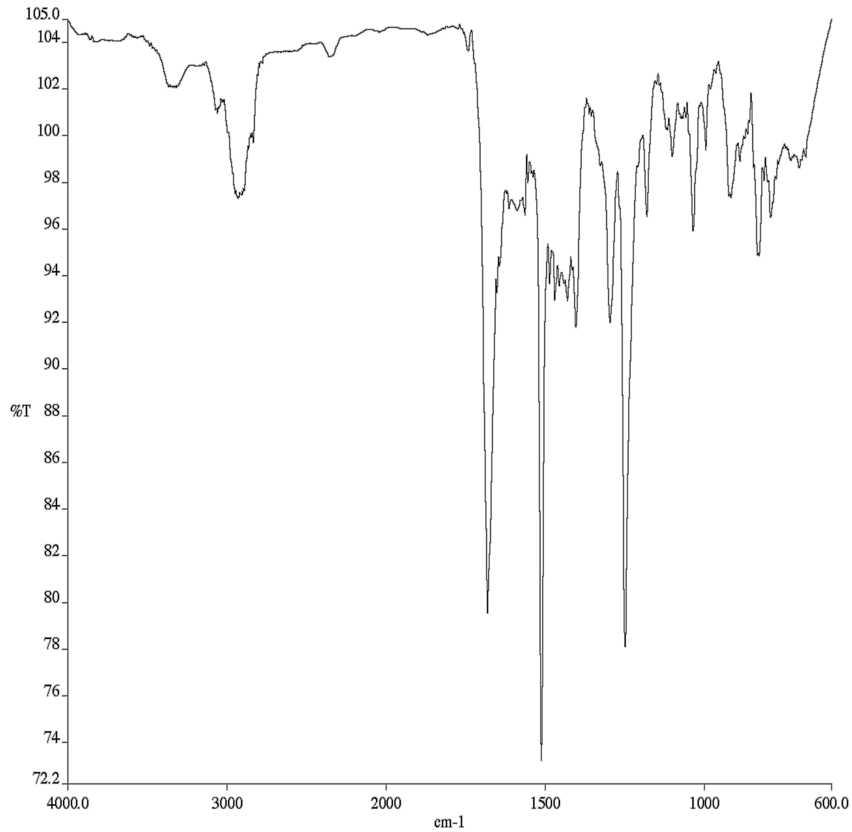
Infrared spectrum (Thin Film, NaCl) of compound **4w**.



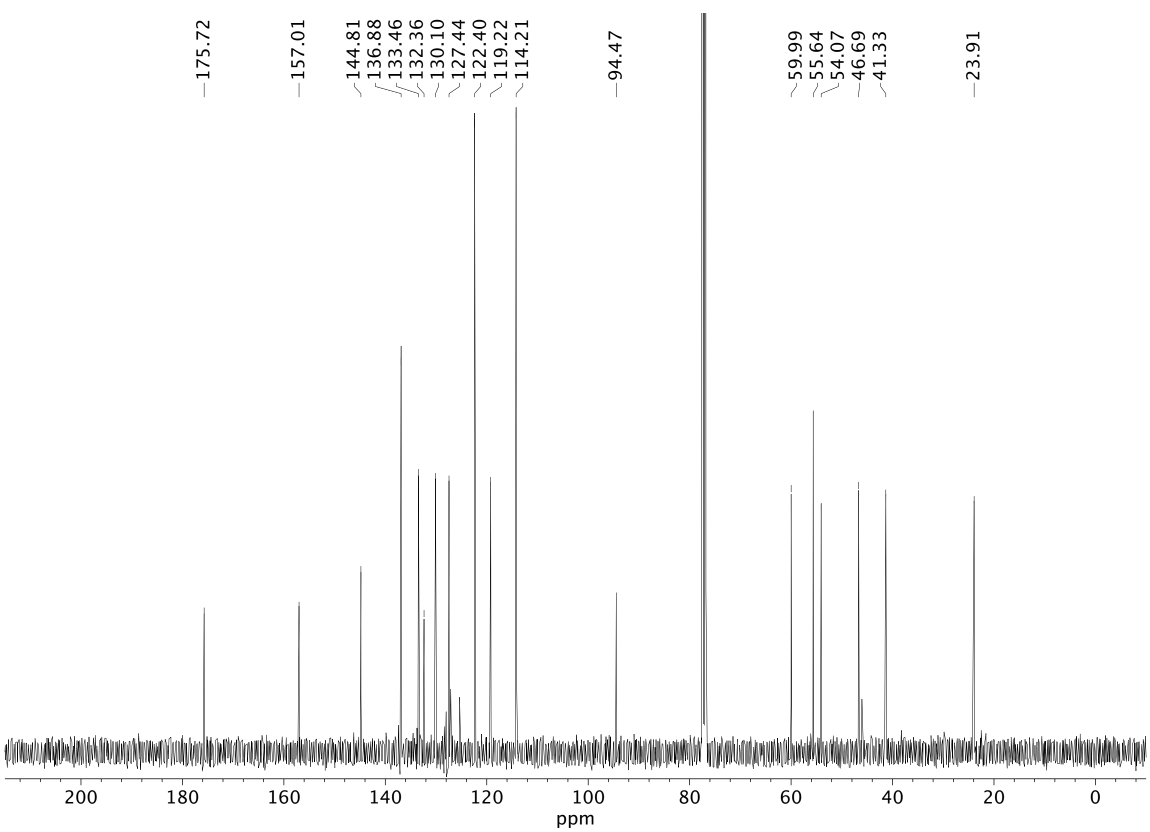
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4w**.



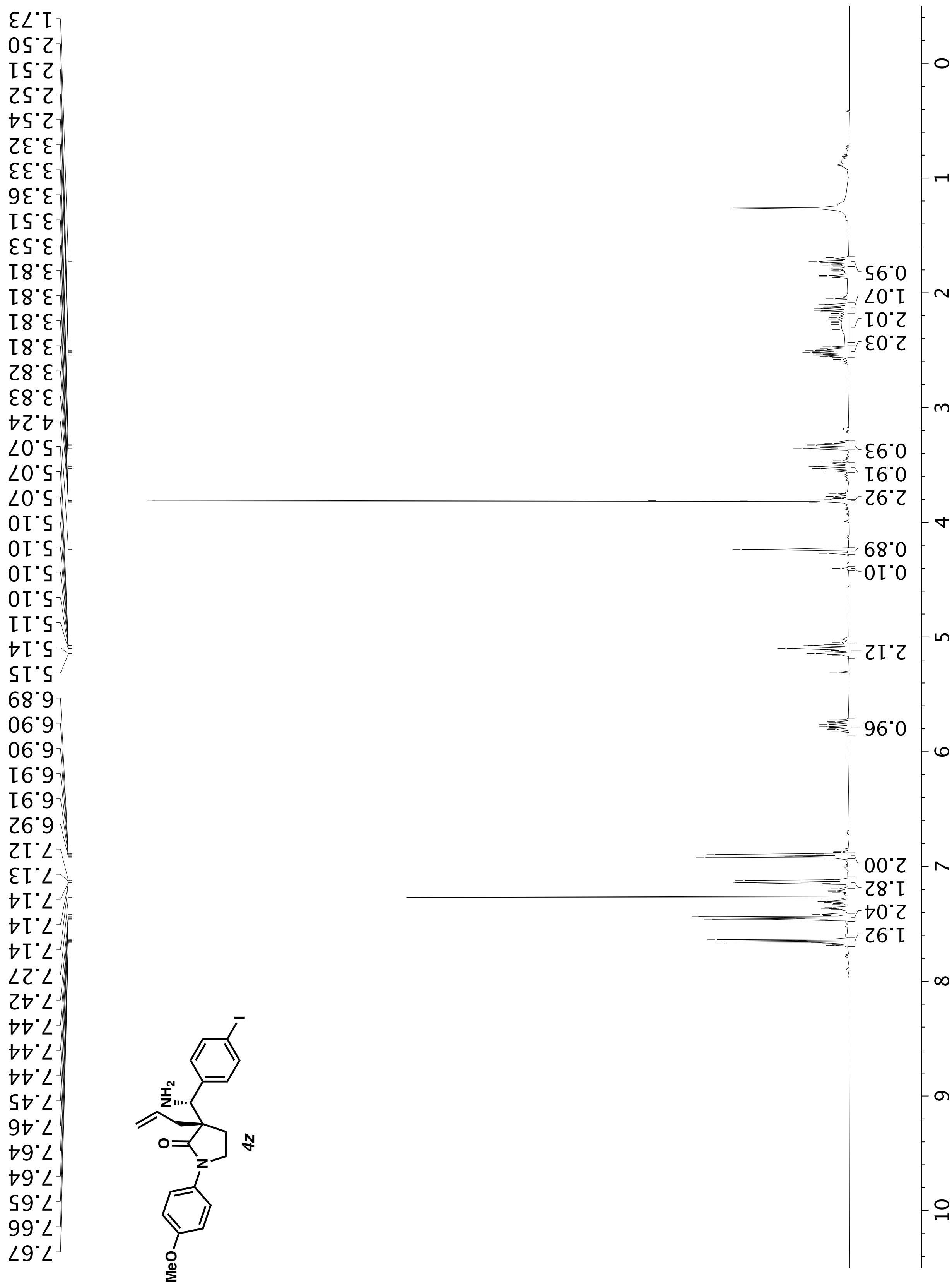
^{1}H NMR (400 MHz, CDCl$_3$) of compound **4y**.



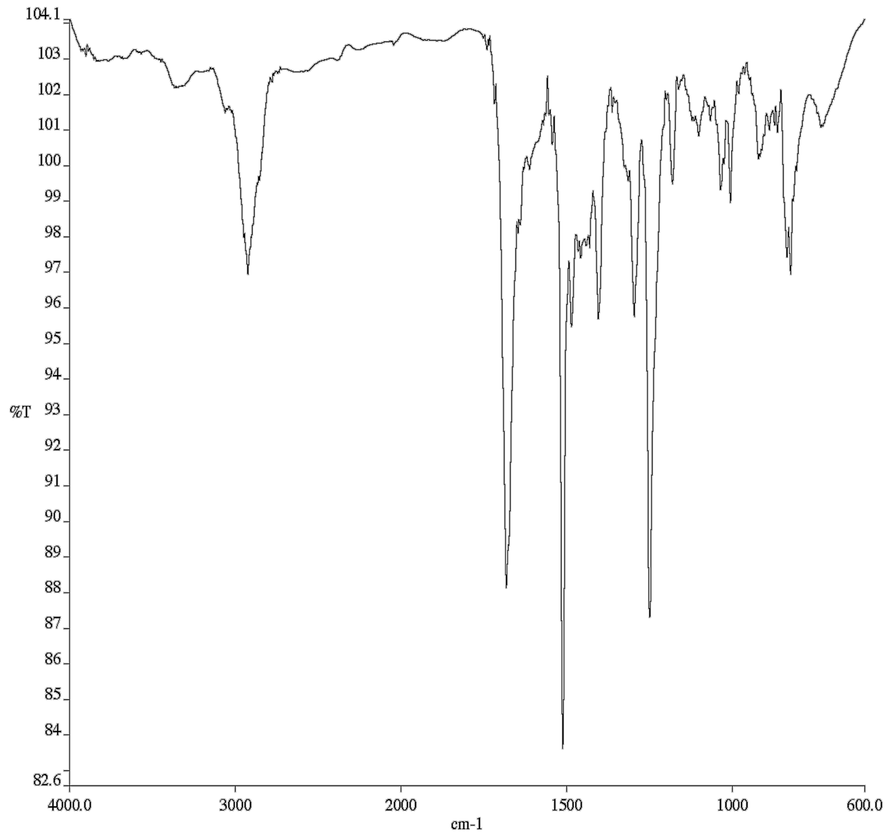
Infrared spectrum (Thin Film, NaCl) of compound **4y**.



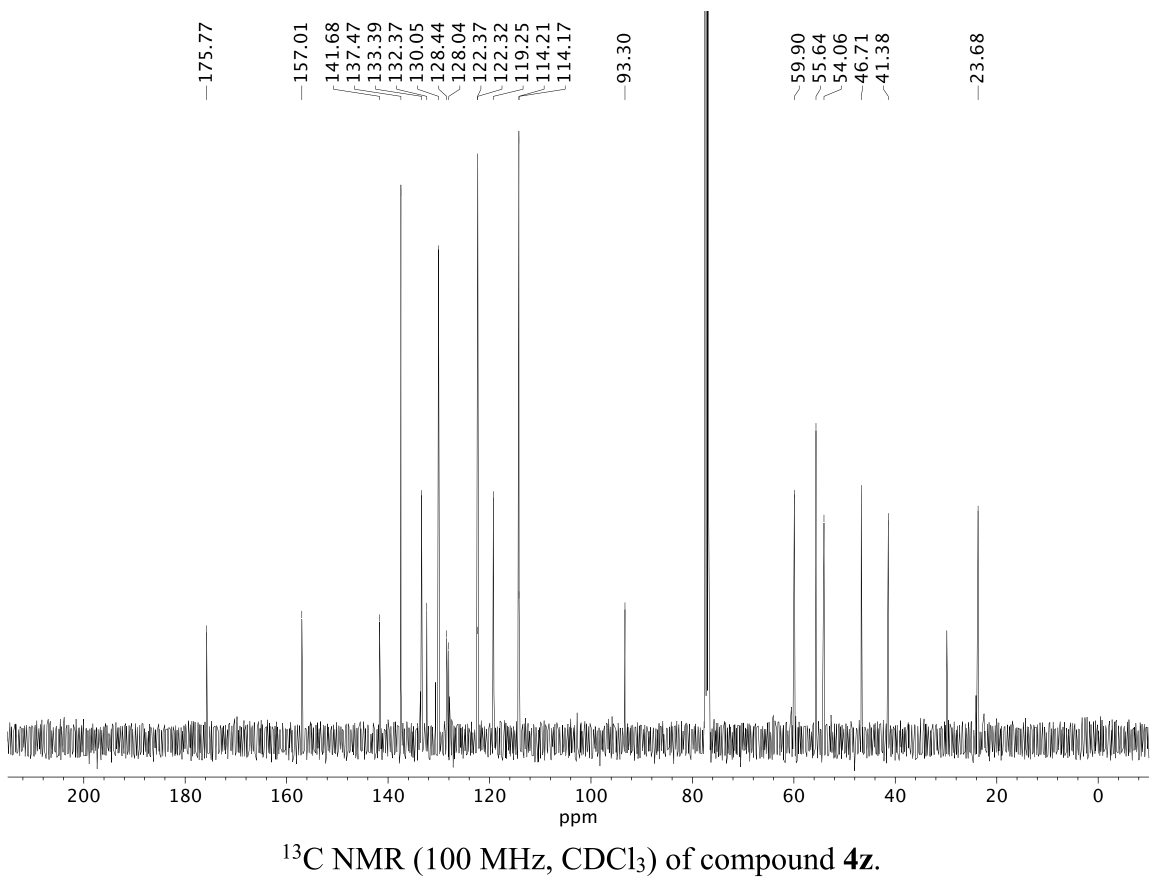
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4y**.



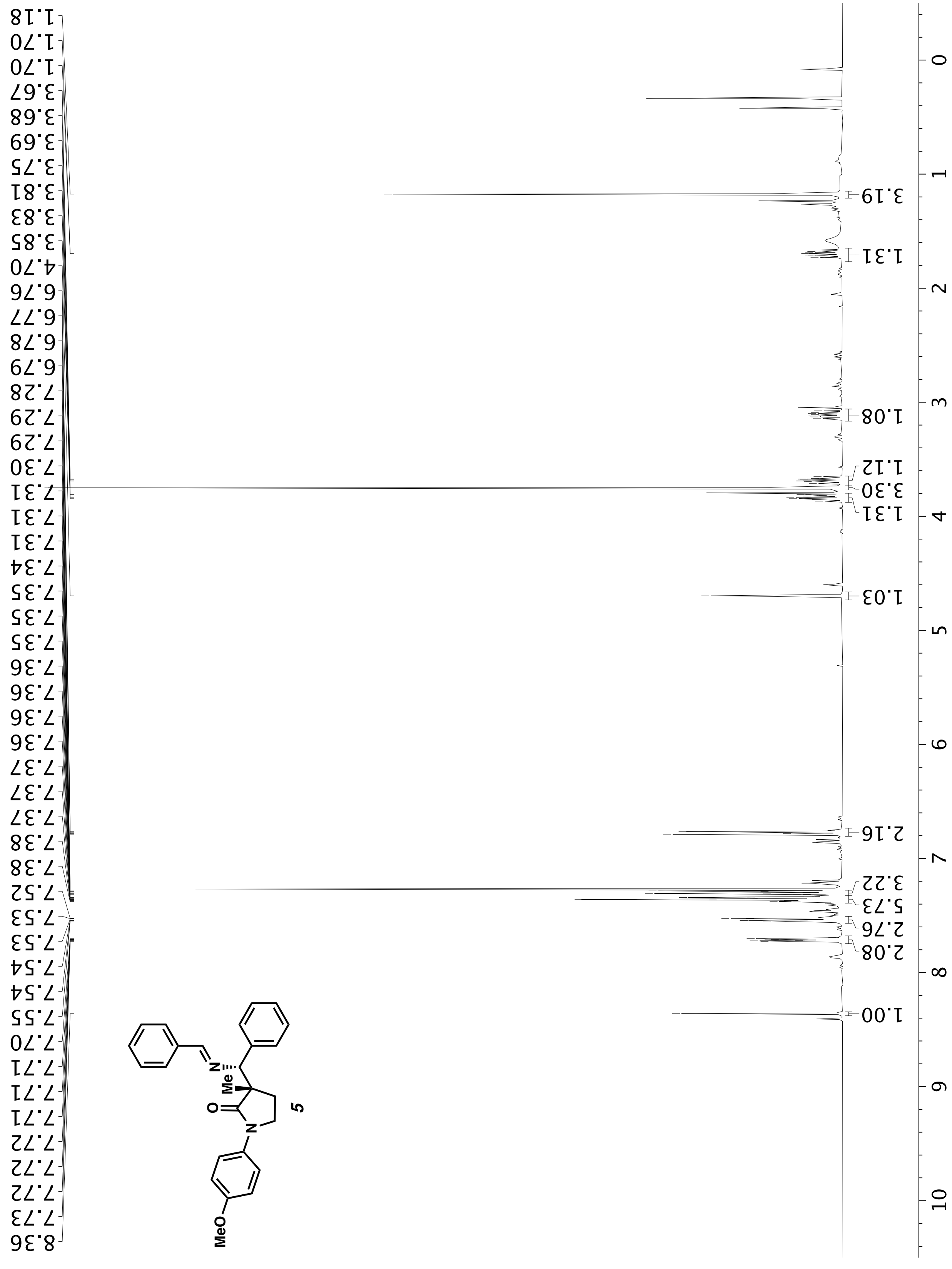
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4z**.



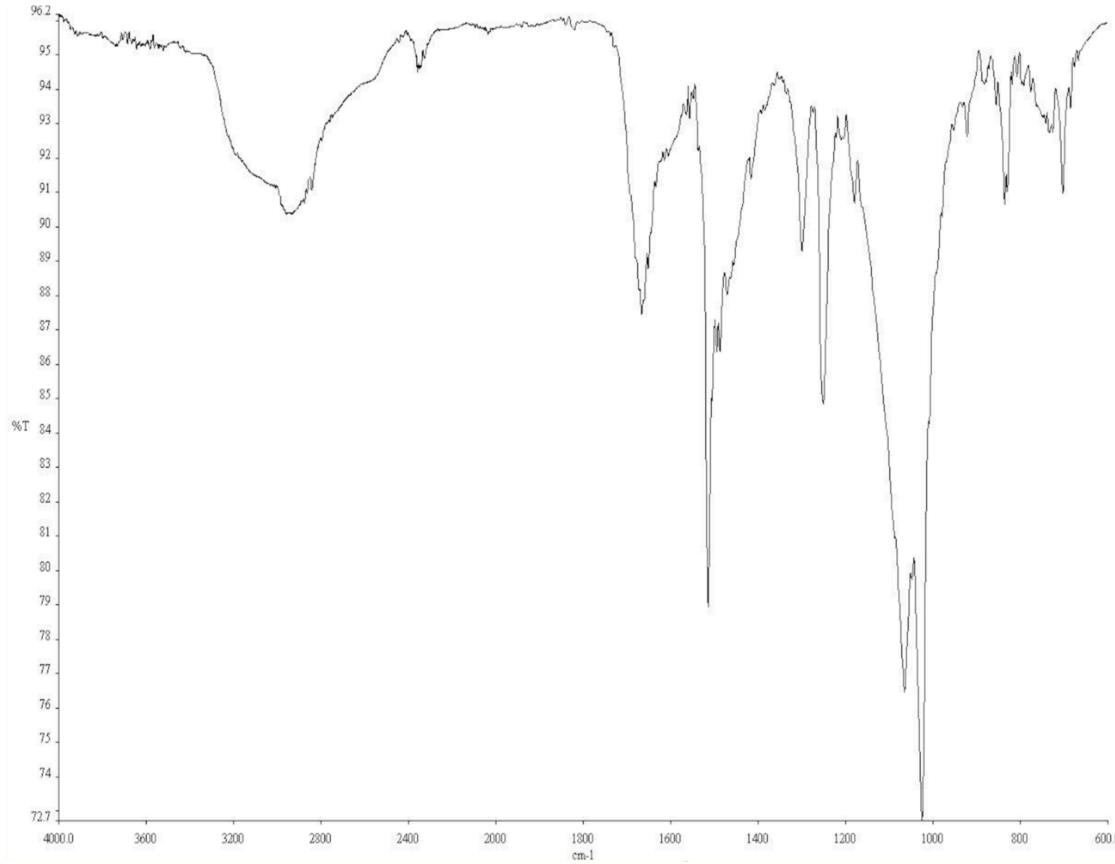
Infrared spectrum (Thin Film, NaCl) of compound **4z**.



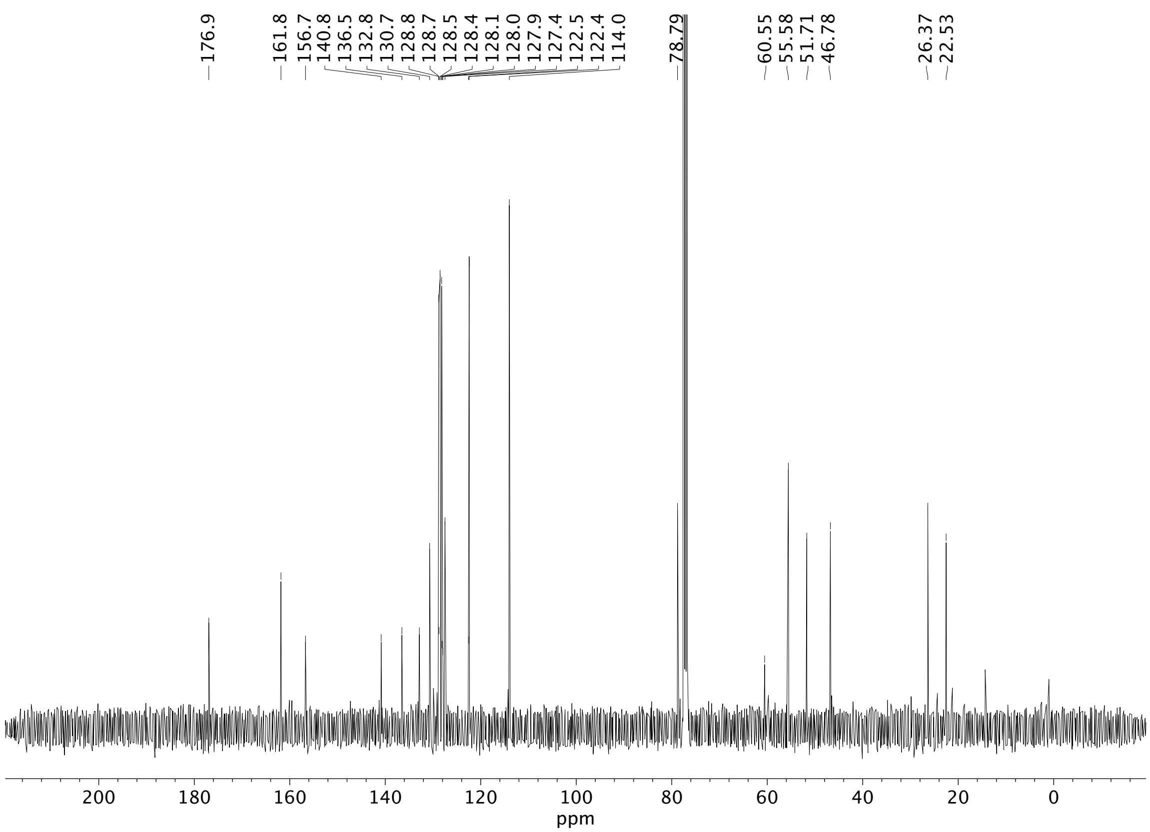
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4z**.



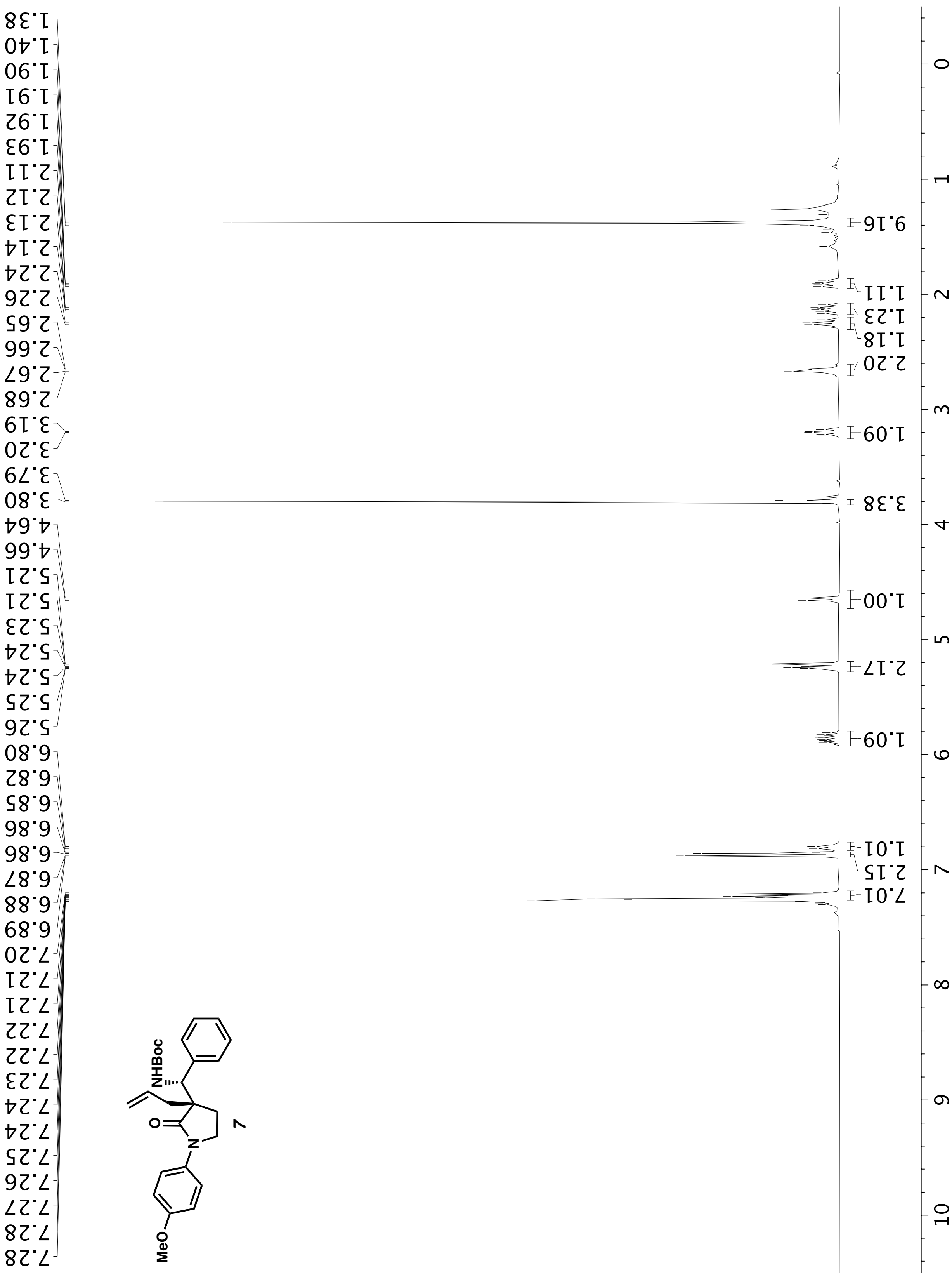
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5**.



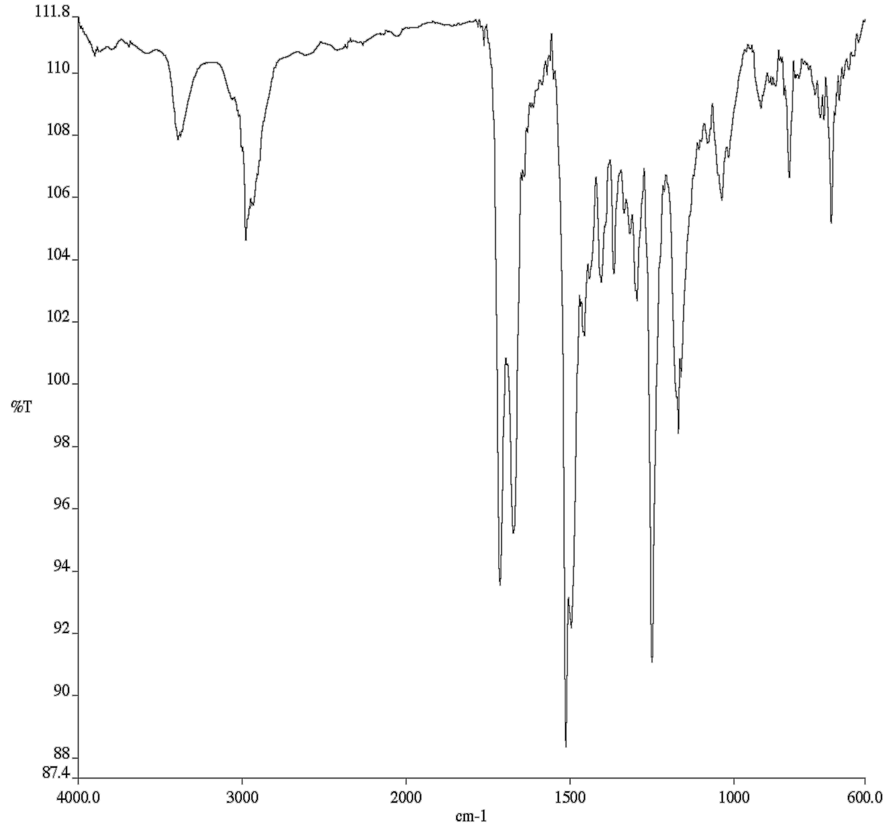
Infrared spectrum (Thin Film, NaCl) of compound **5**.



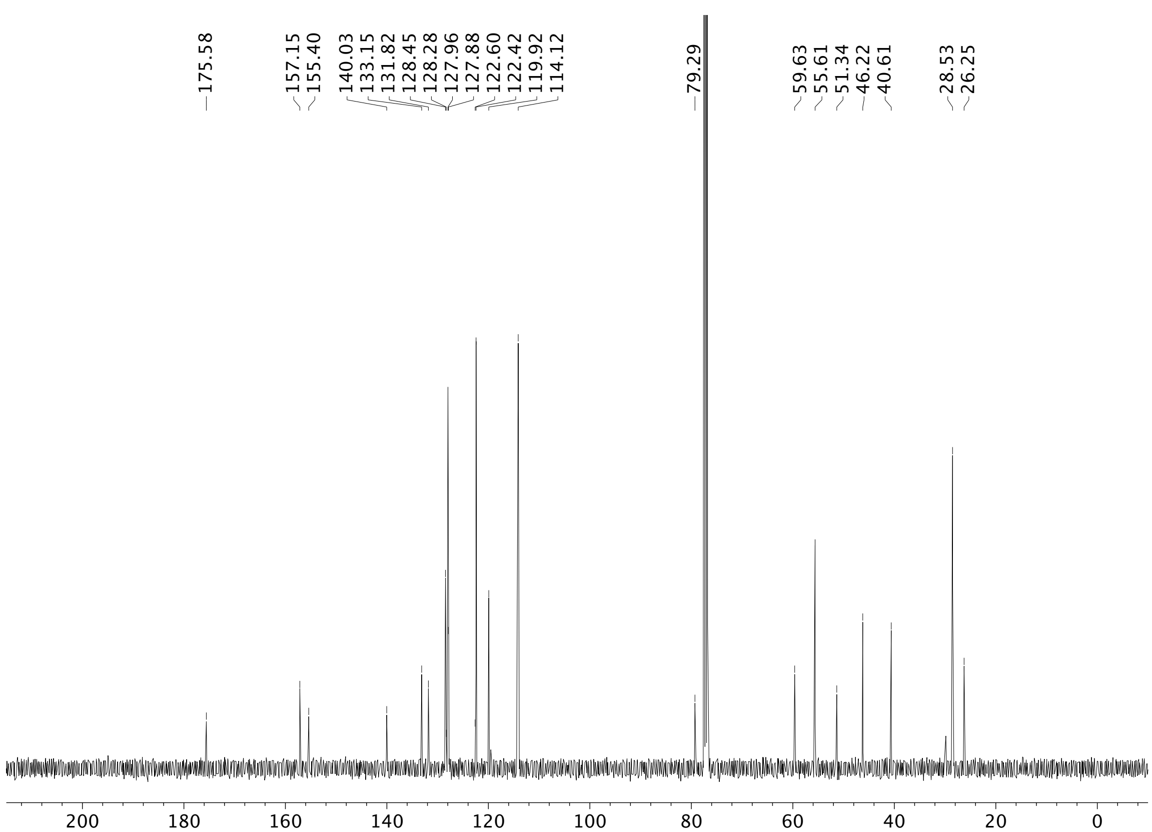
^{13}C NMR (100 MHz, $CDCl_3$) of compound **5**.



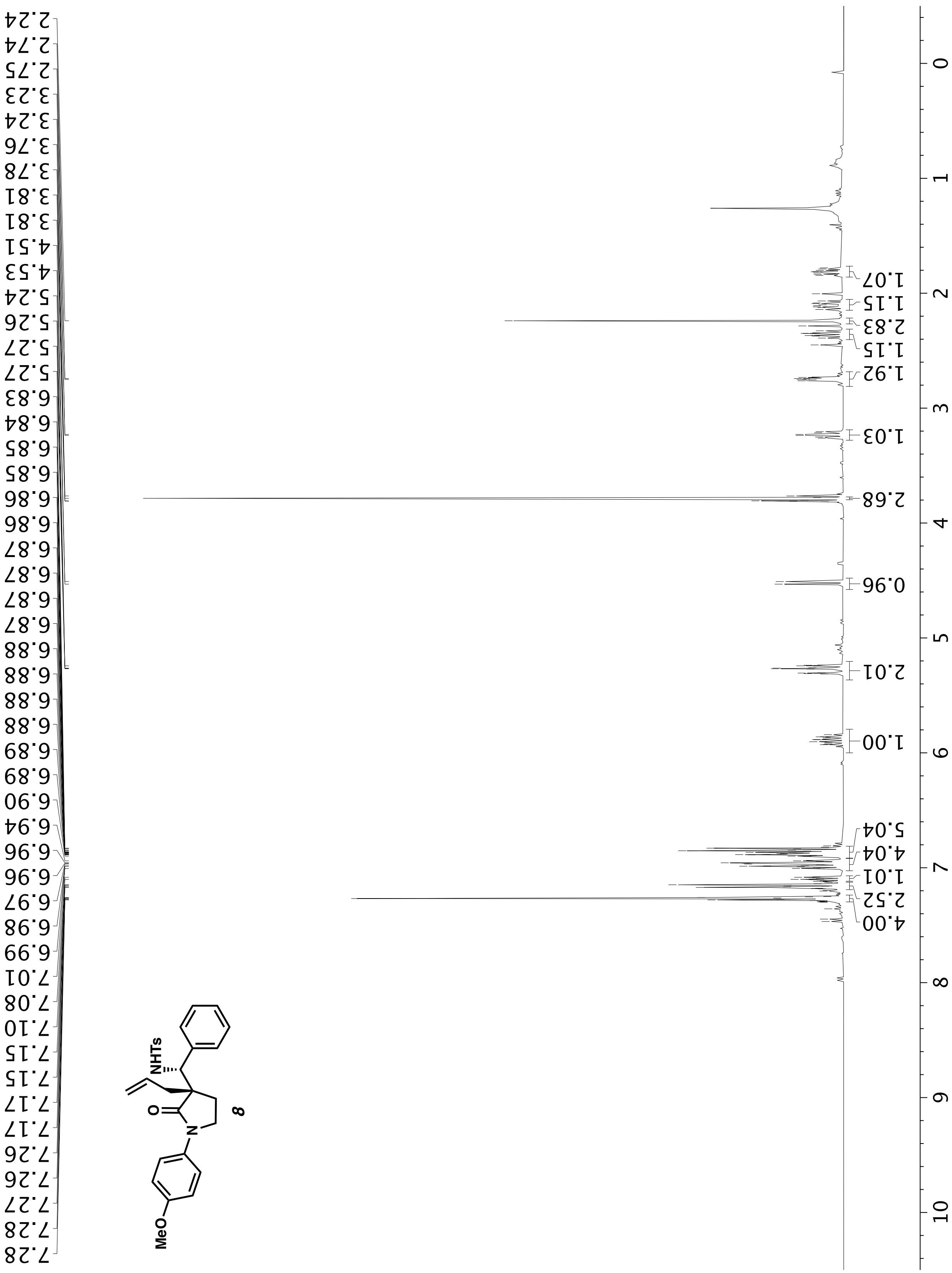
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7**.



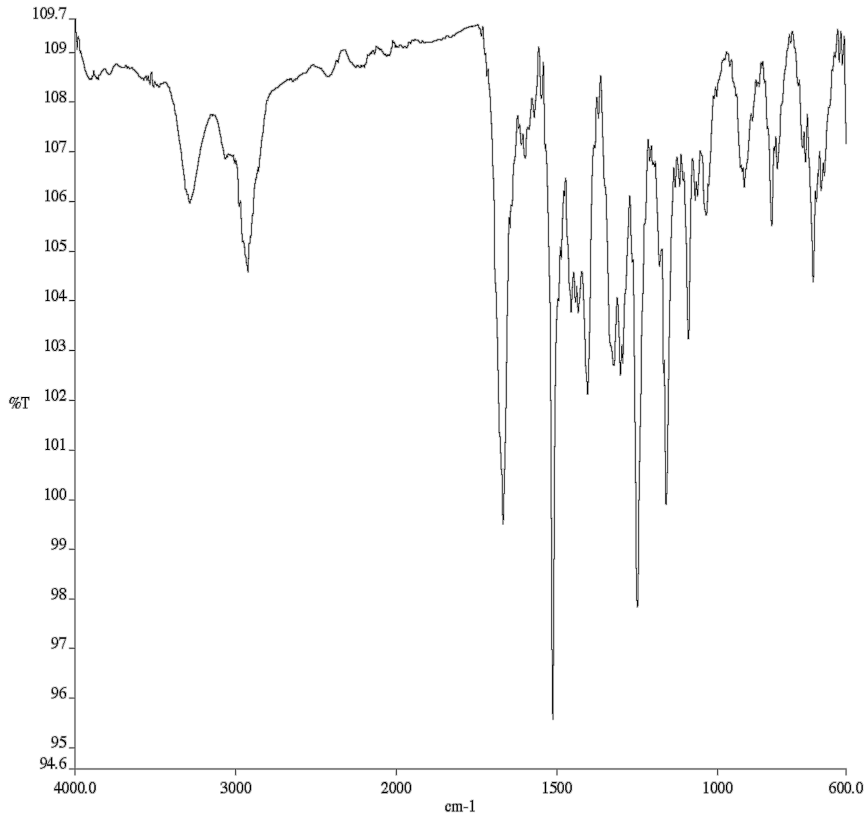
Infrared spectrum (Thin Film, NaCl) of compound **7**.



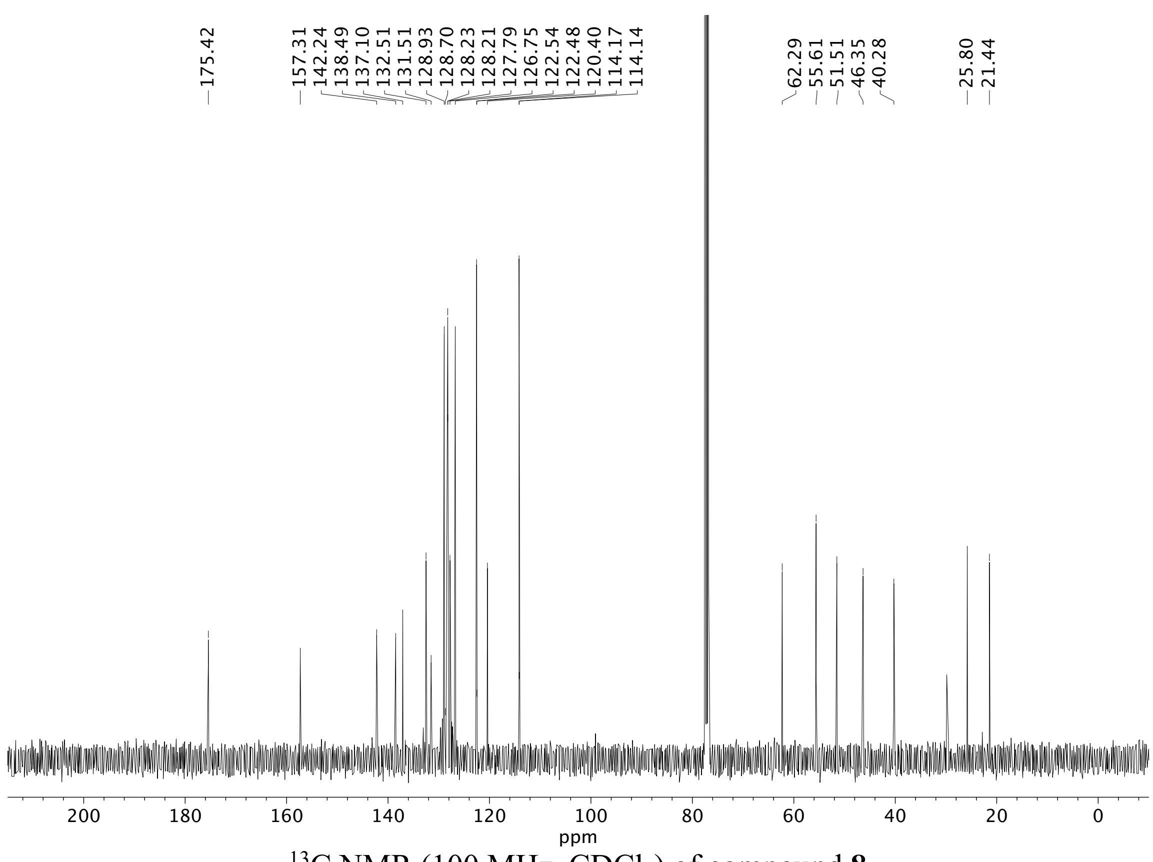
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7**.



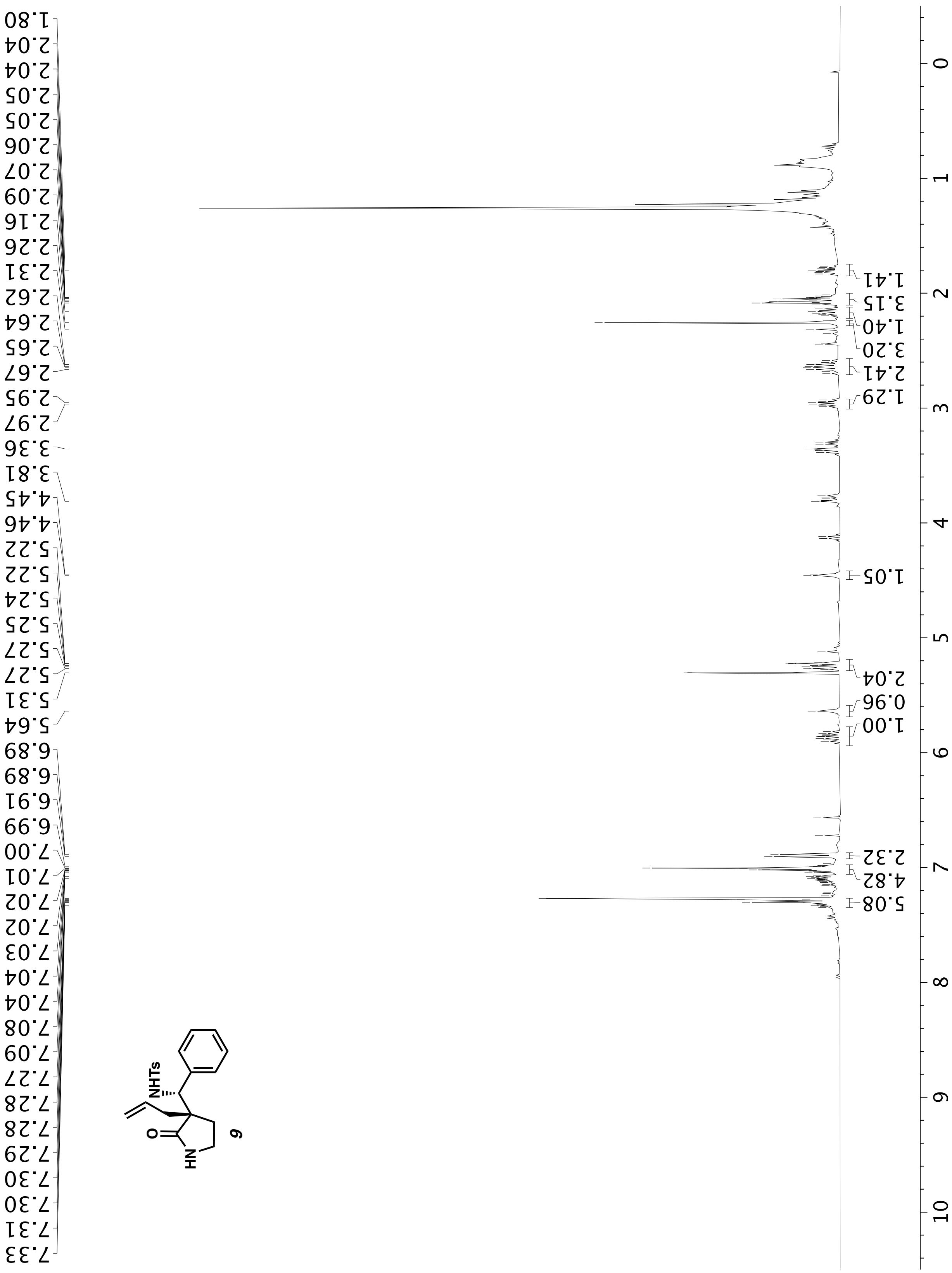
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8**.



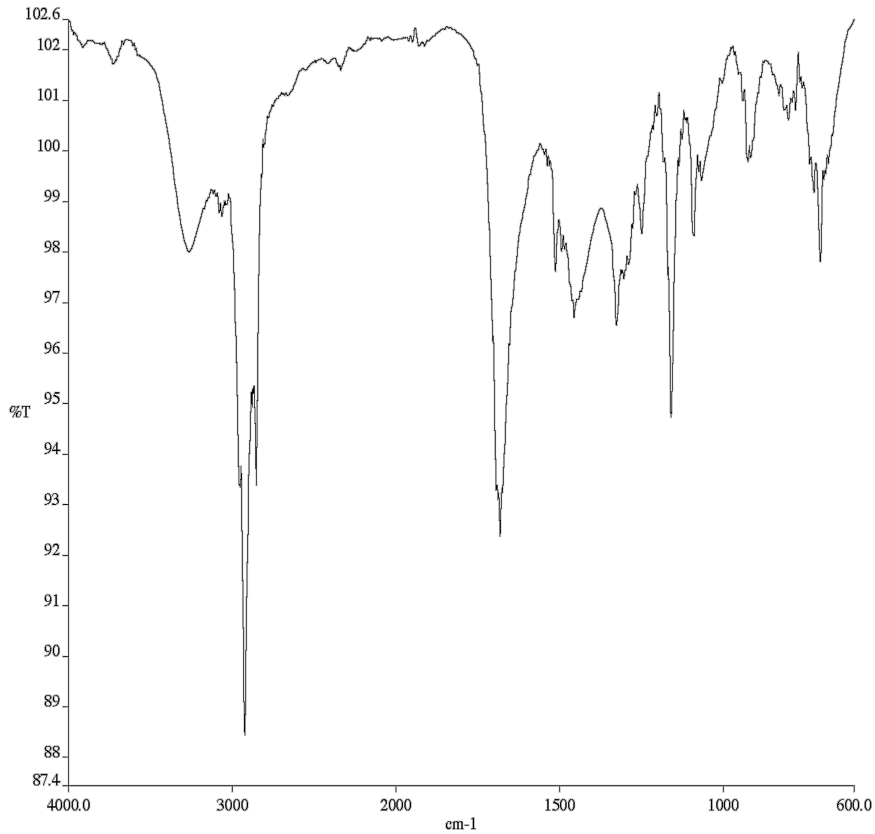
Infrared spectrum (Thin Film, NaCl) of compound **8**.



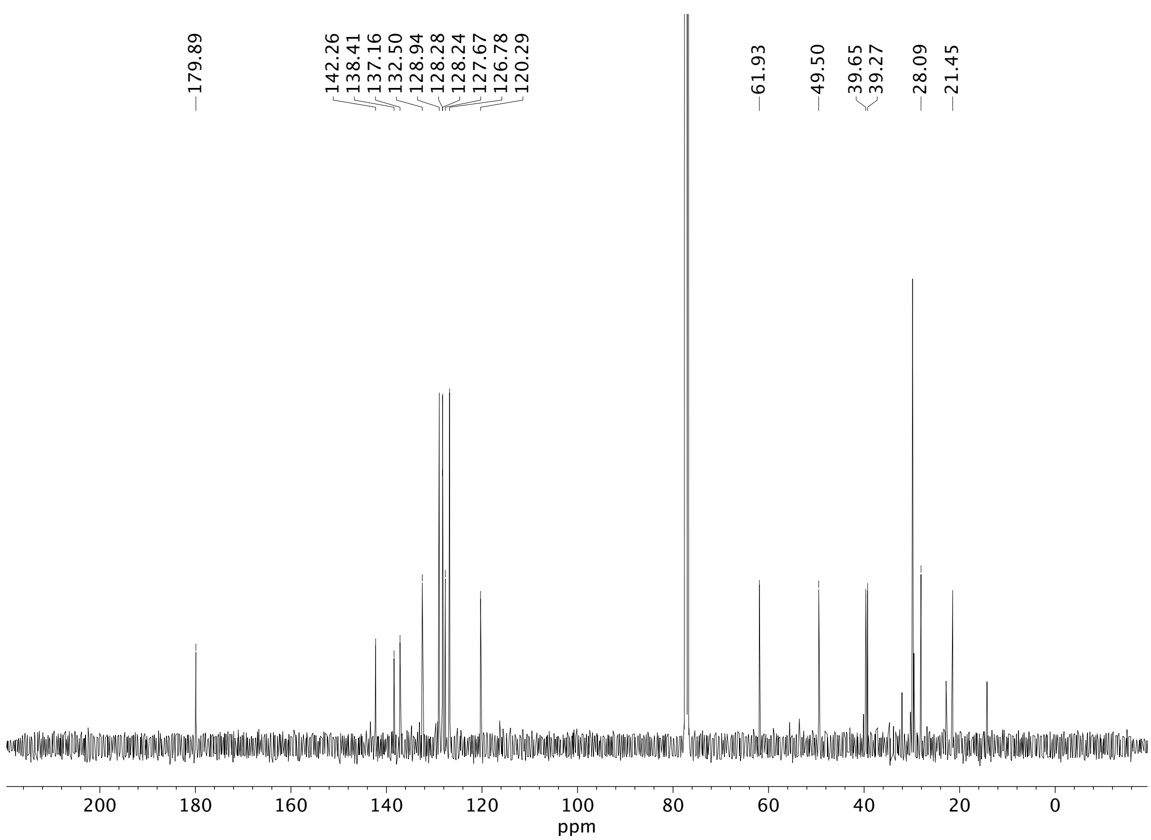
^{13}C NMR (100 MHz, $CDCl_3$) of compound **8**.



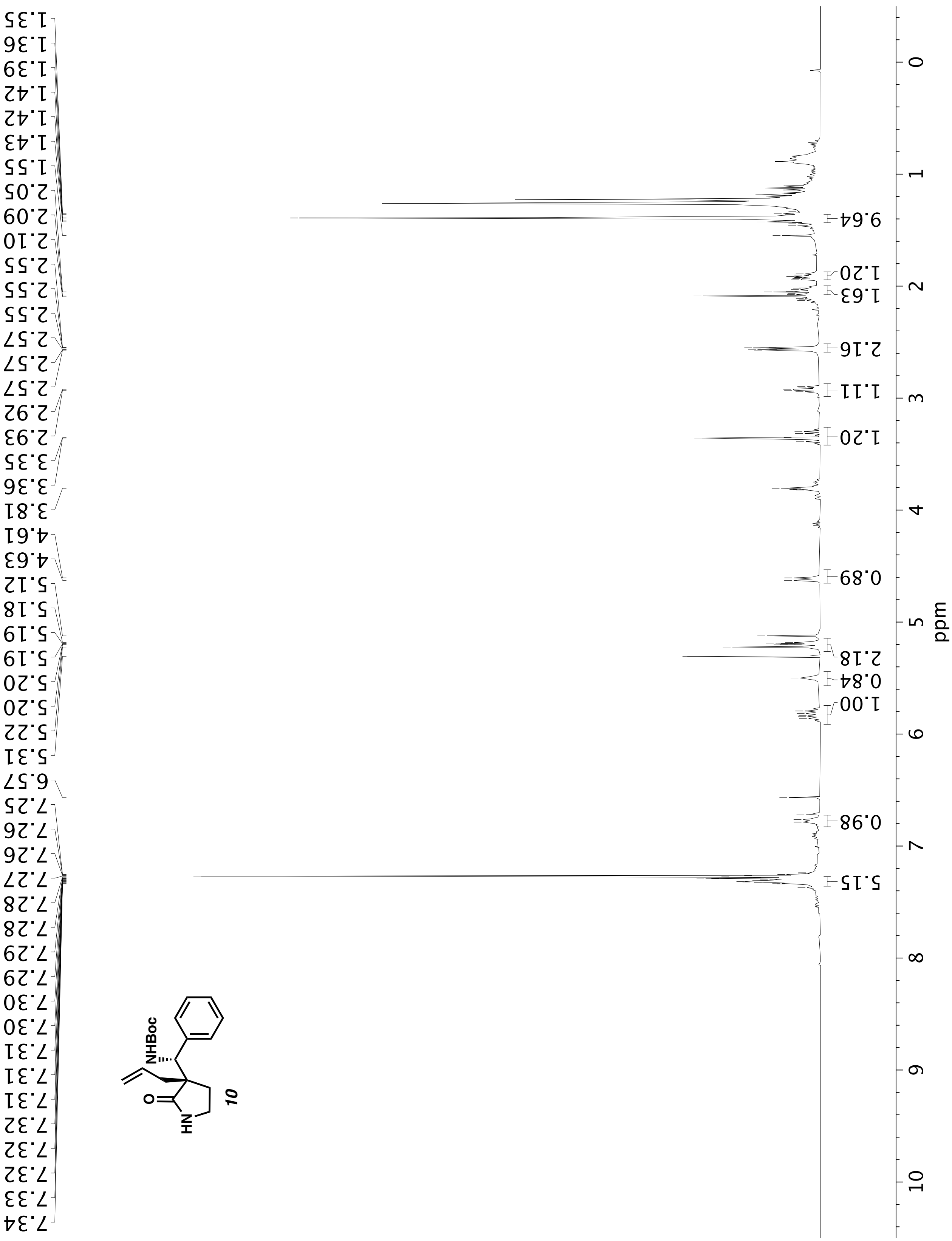
^{1}H NMR (500 MHz, $CDCl_3$) of compound **9**.



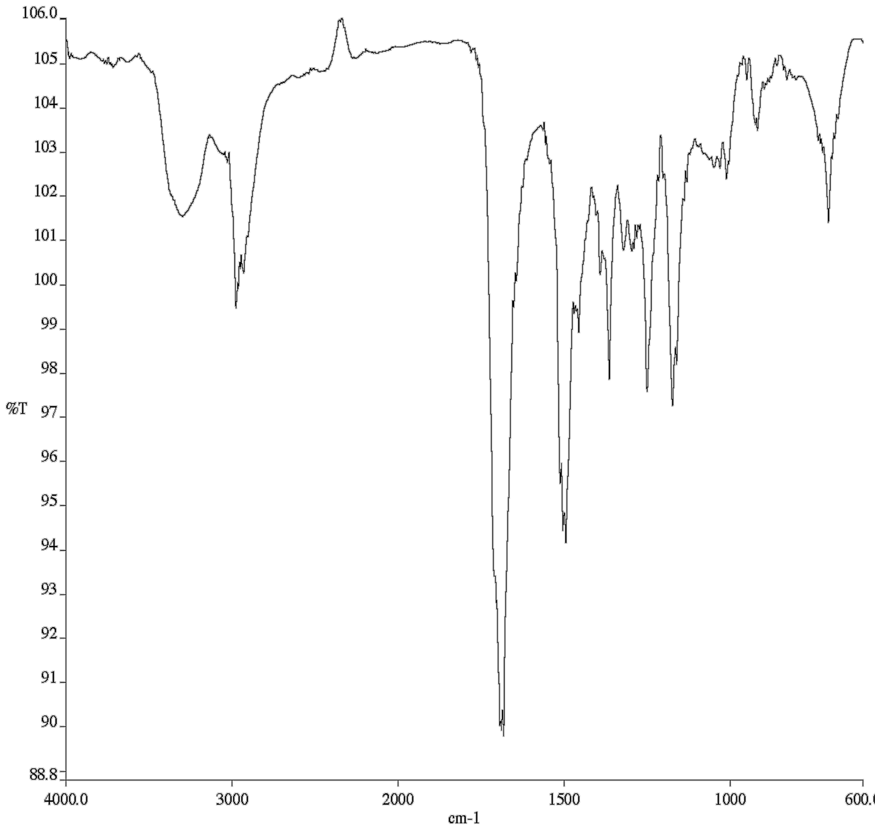
Infrared spectrum (Thin Film, NaCl) of compound **9**.



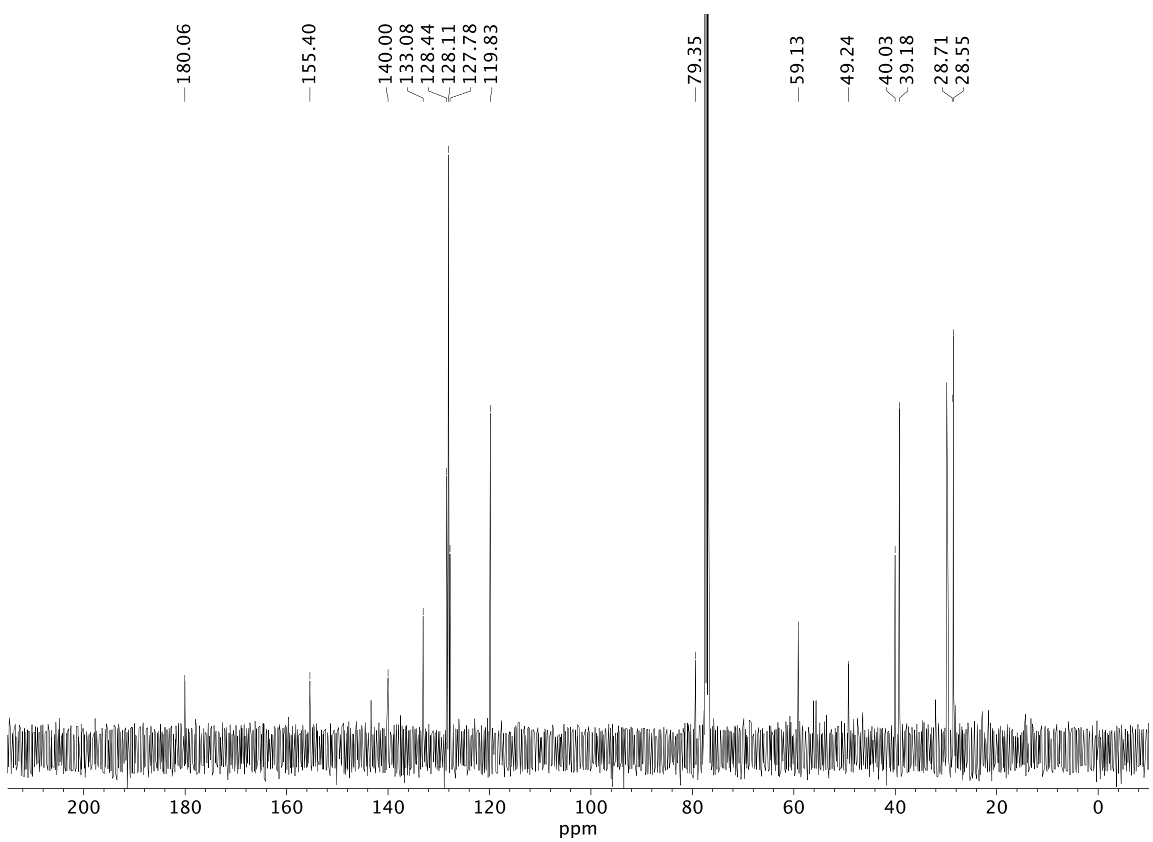
^{13}C NMR (100 MHz, $CDCl_3$) of compound **9**.



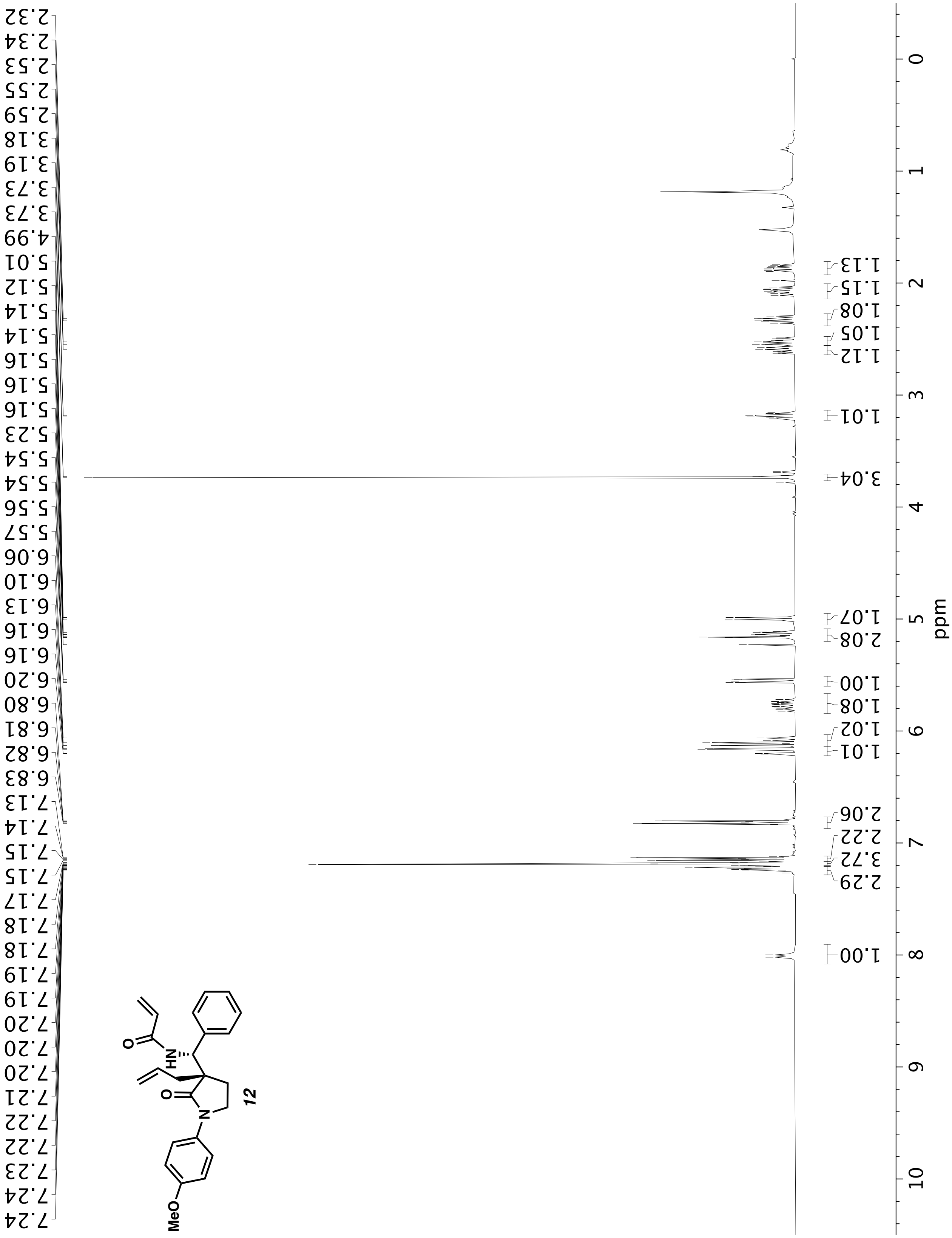
[1]H NMR (400 MHz, $CDCl_3$) of compound **10**.



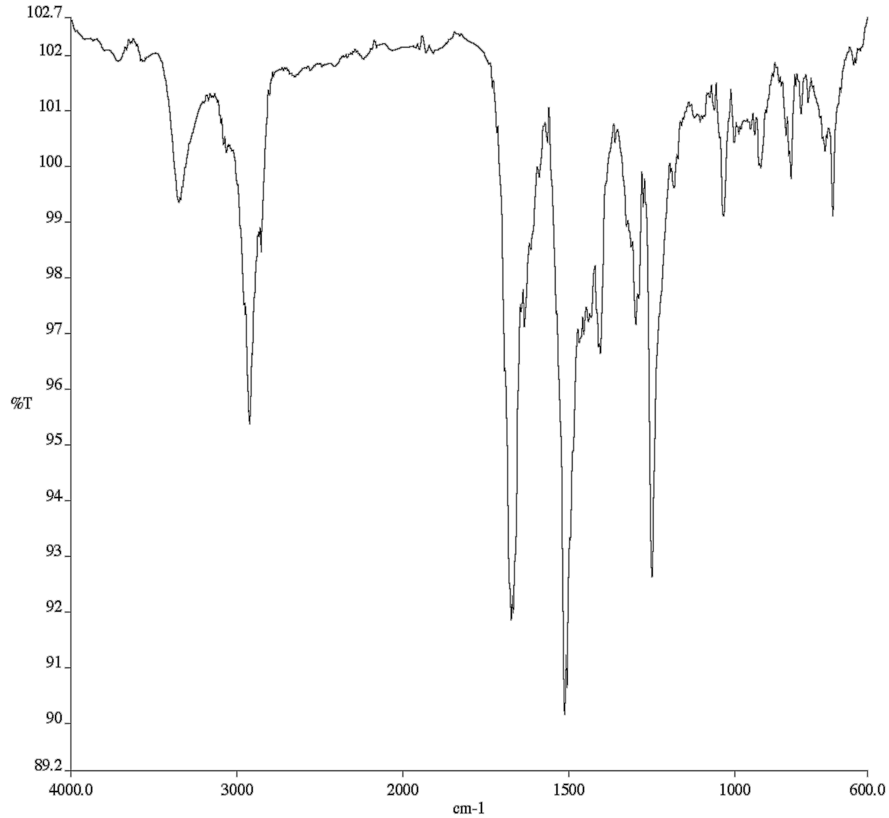
Infrared spectrum (Thin Film, NaCl) of compound **10**.



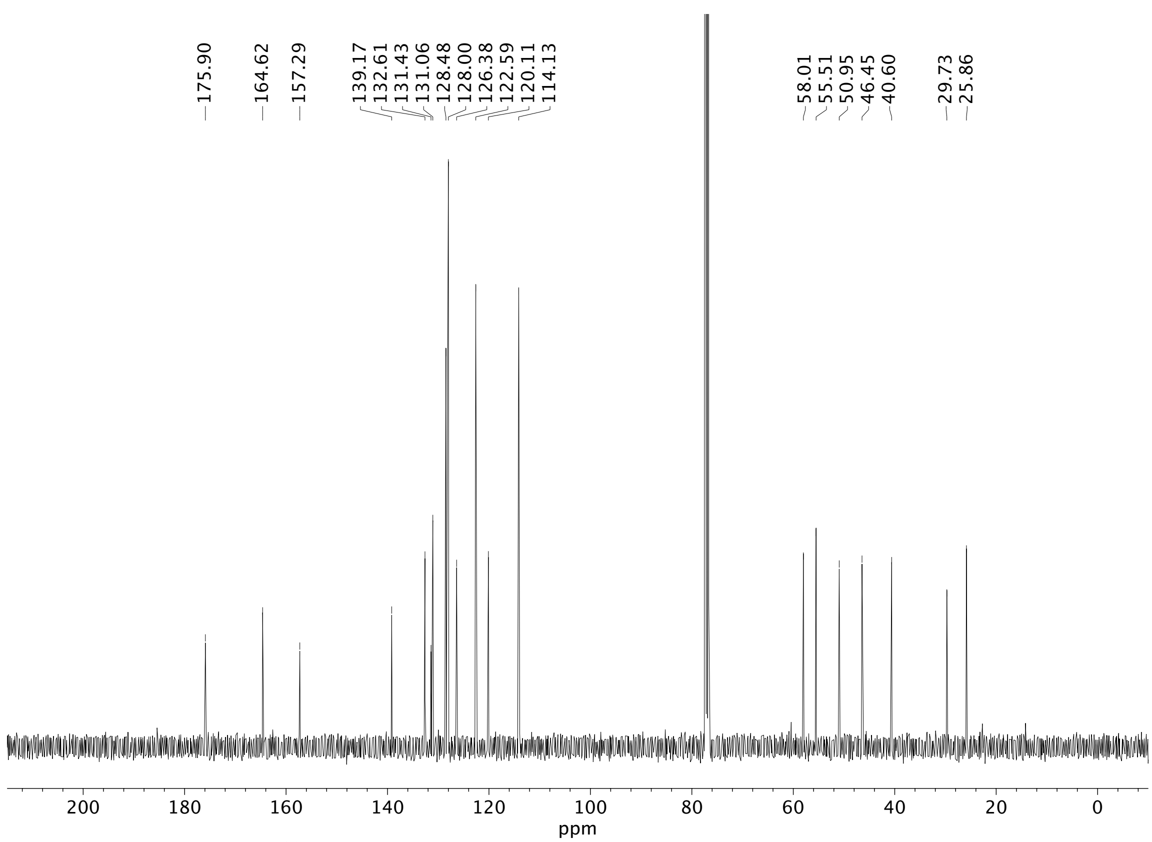
^{13}C NMR (100 MHz, $CDCl_3$) of compound **10**.



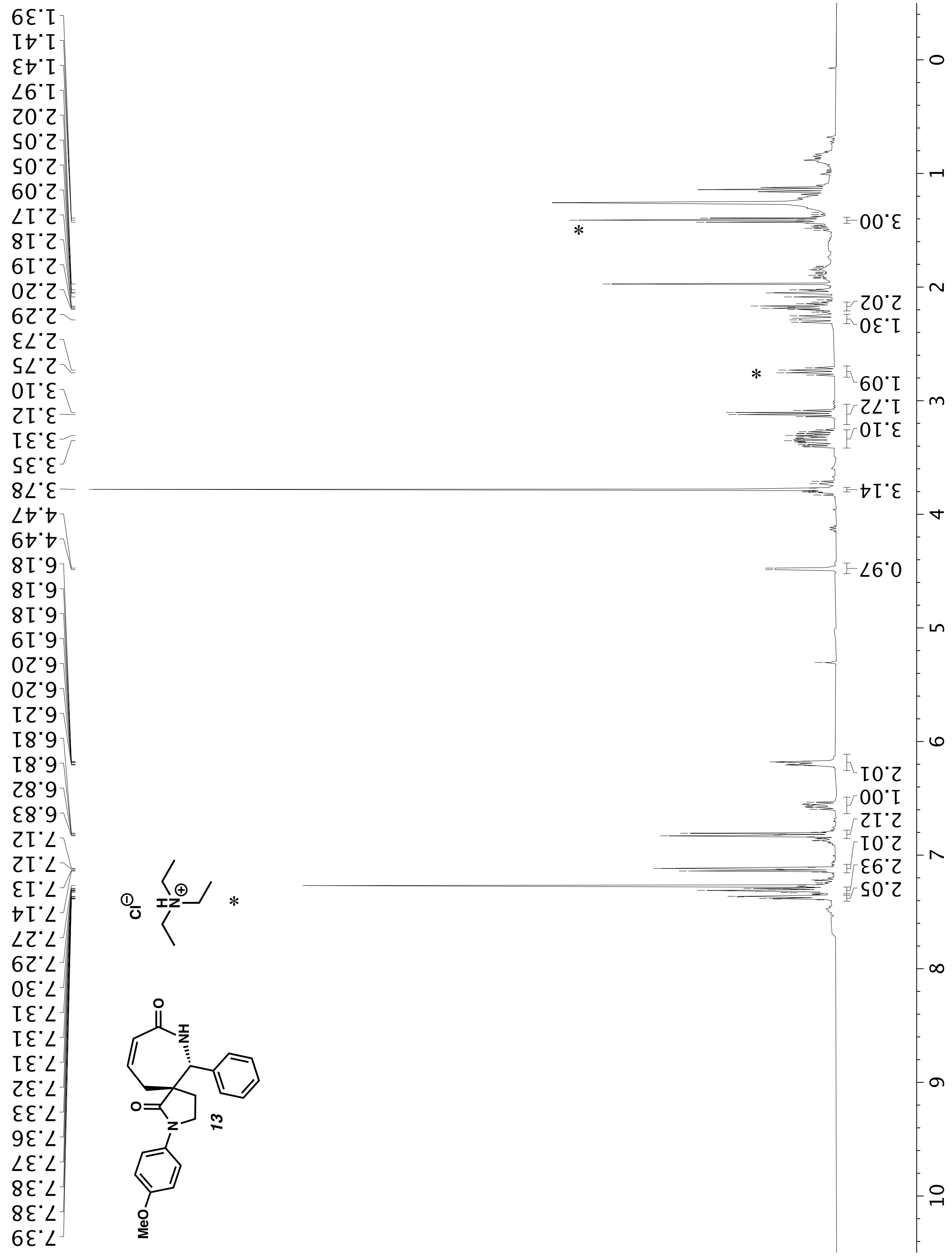
^{1}H NMR (400 MHz, $CDCl_3$) of compound **12**.



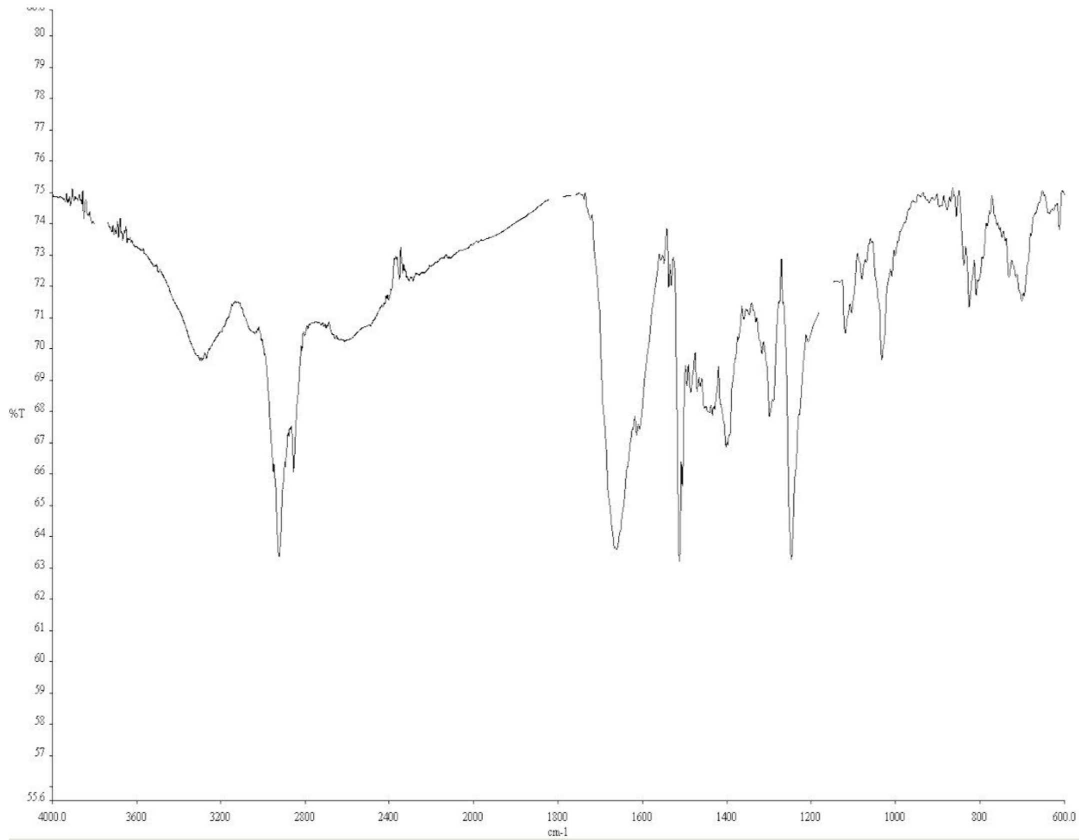
Infrared spectrum (Thin Film, NaCl) of compound **12**.



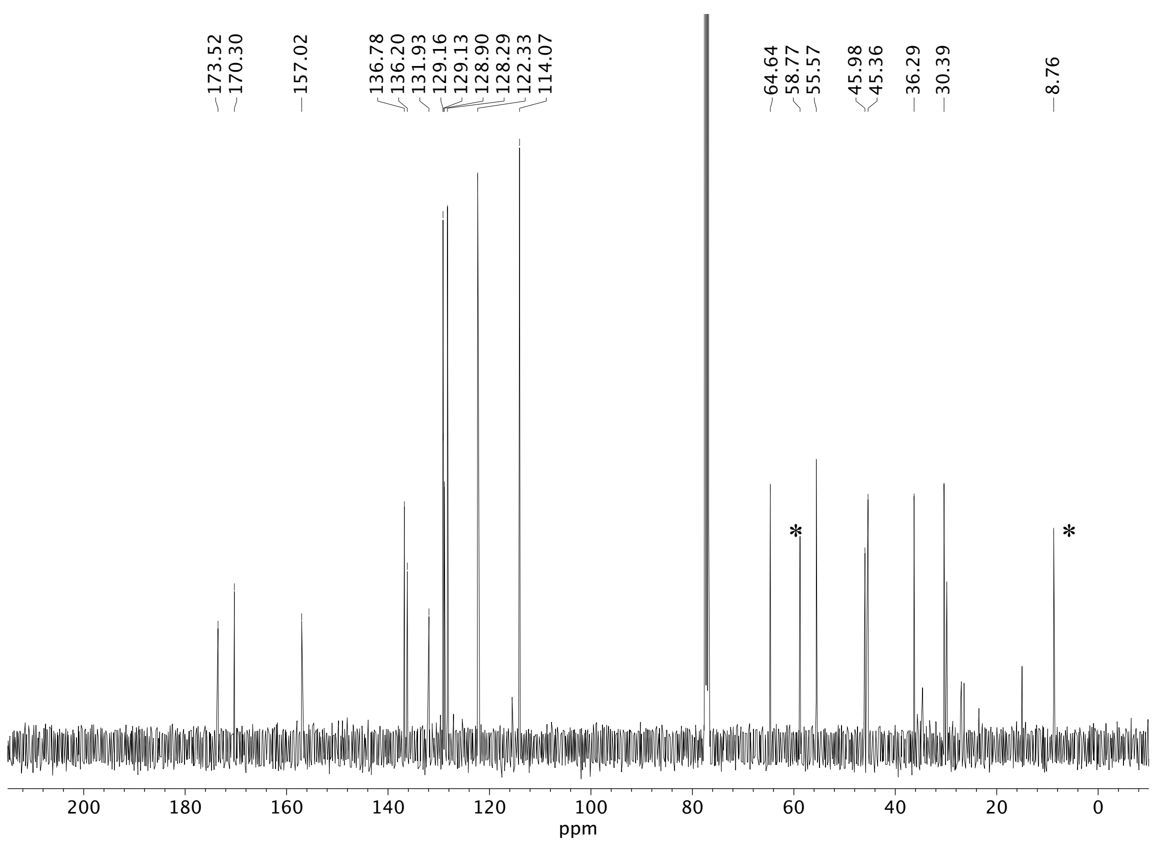
^{13}C NMR (100 MHz, $CDCl_3$) of compound **12**.



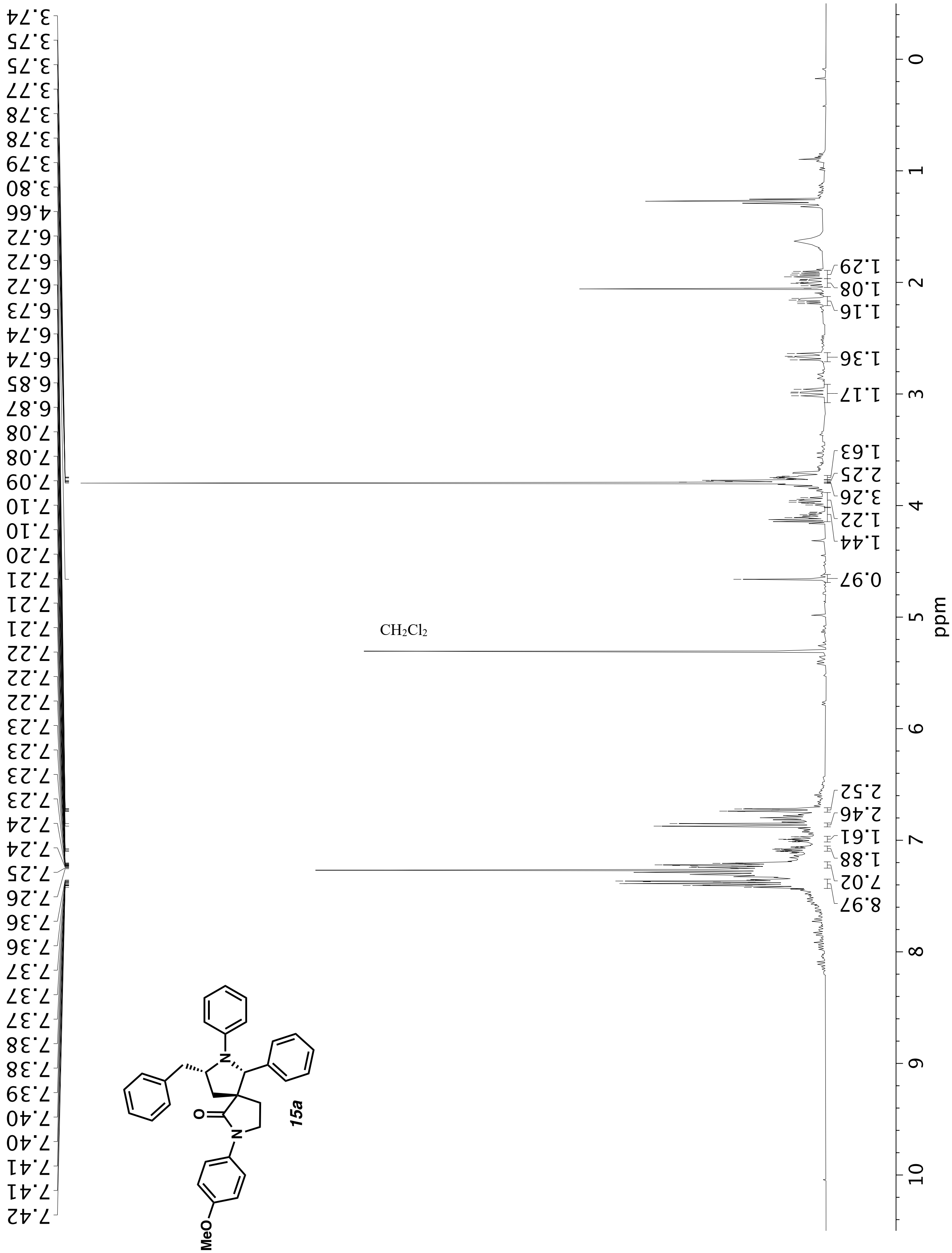
^1H NMR (400 MHz, $CDCl_3$) of compound **13**.



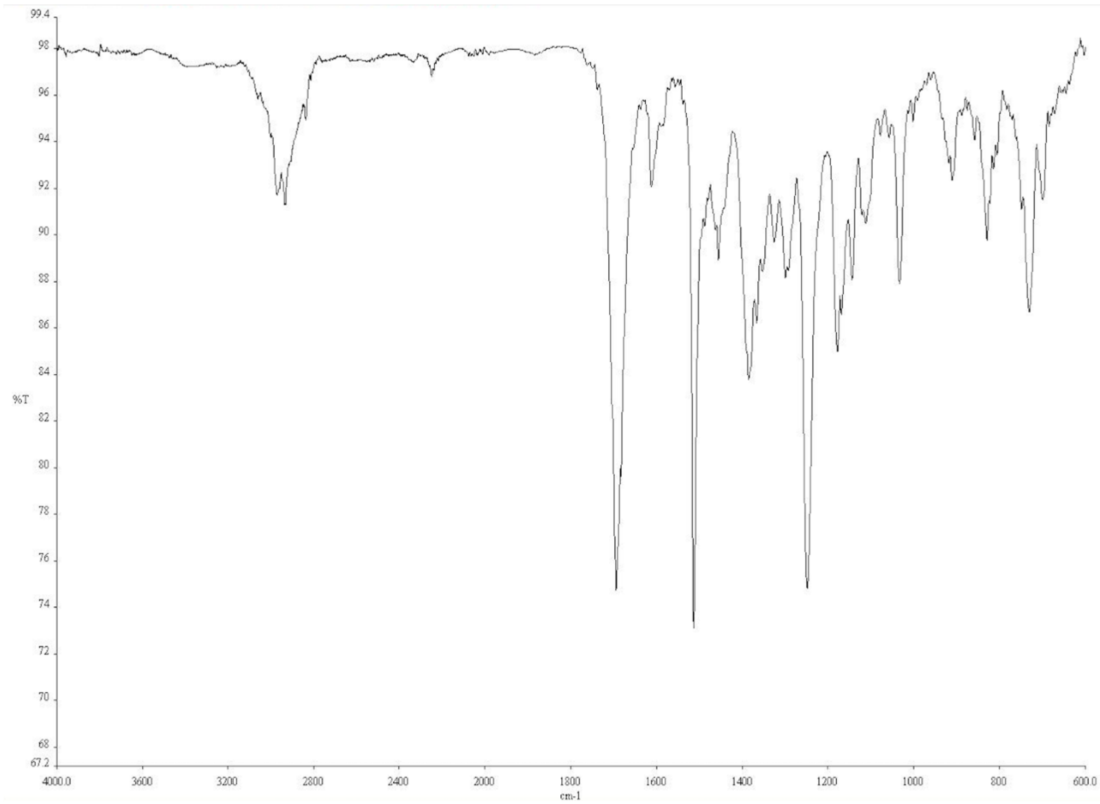
Infrared spectrum (Thin Film, NaCl) of compound **13**.



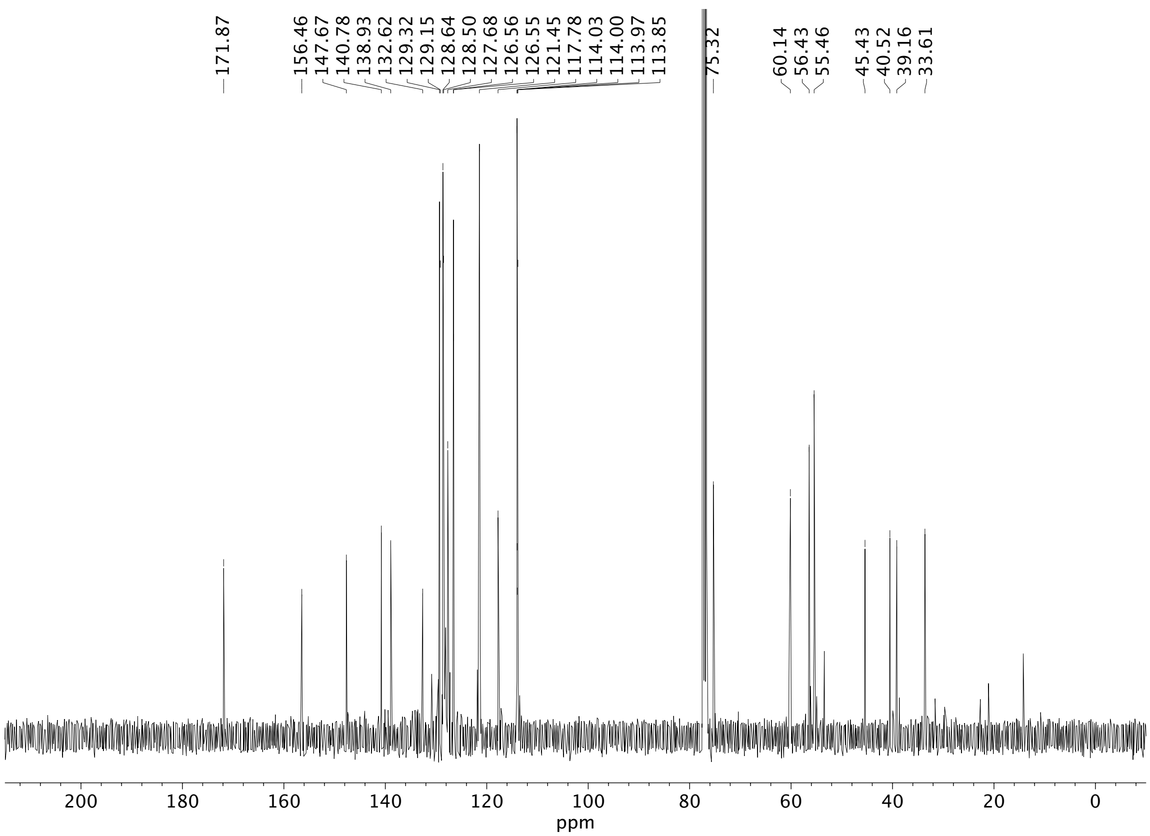
^{13}C NMR (100 MHz, $CDCl_3$) of compound **13**.



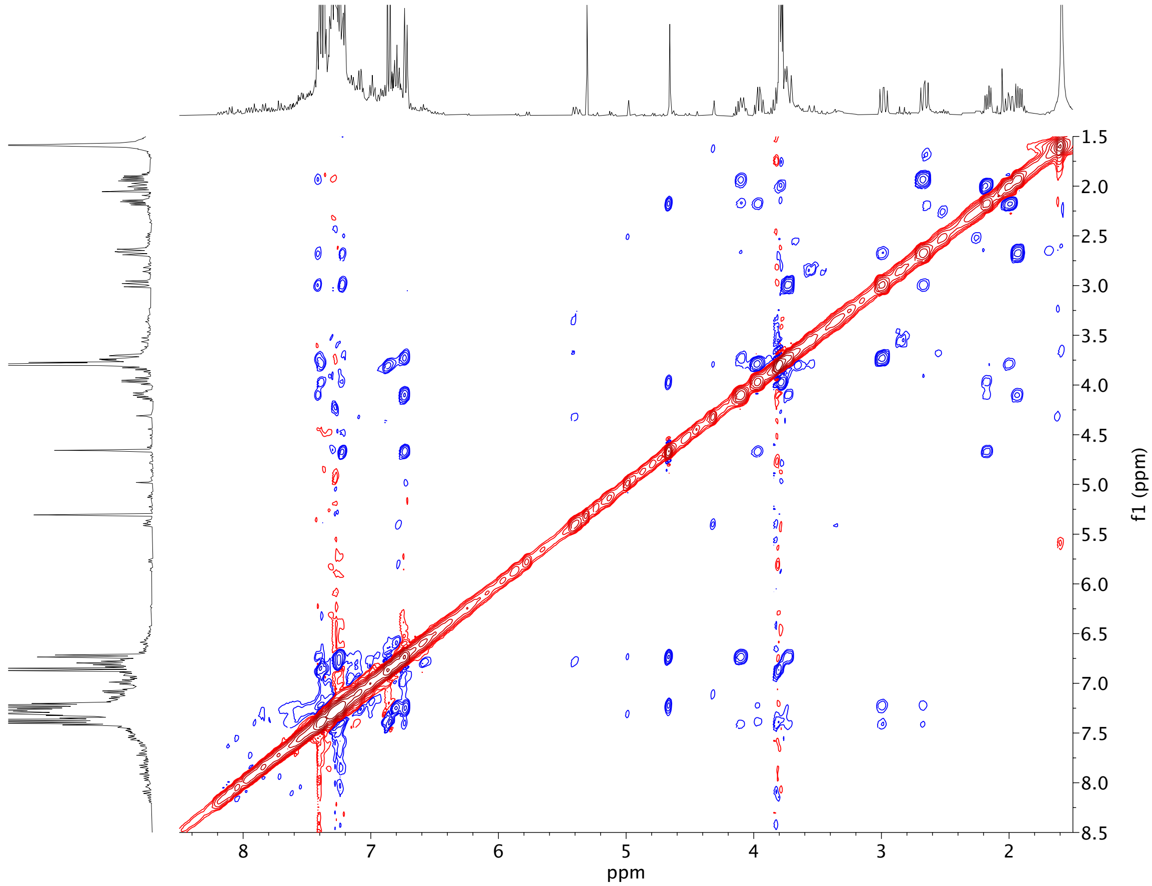
^{1}H NMR (400 MHz, $CDCl_3$) of compound **15a**.



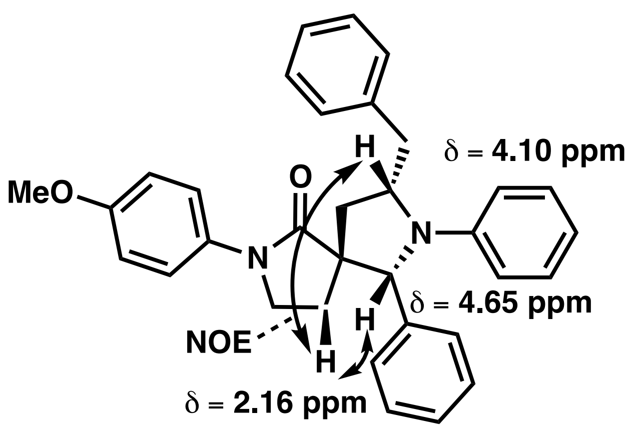
Infrared spectrum (Thin Film, NaCl) of compound **15a**.

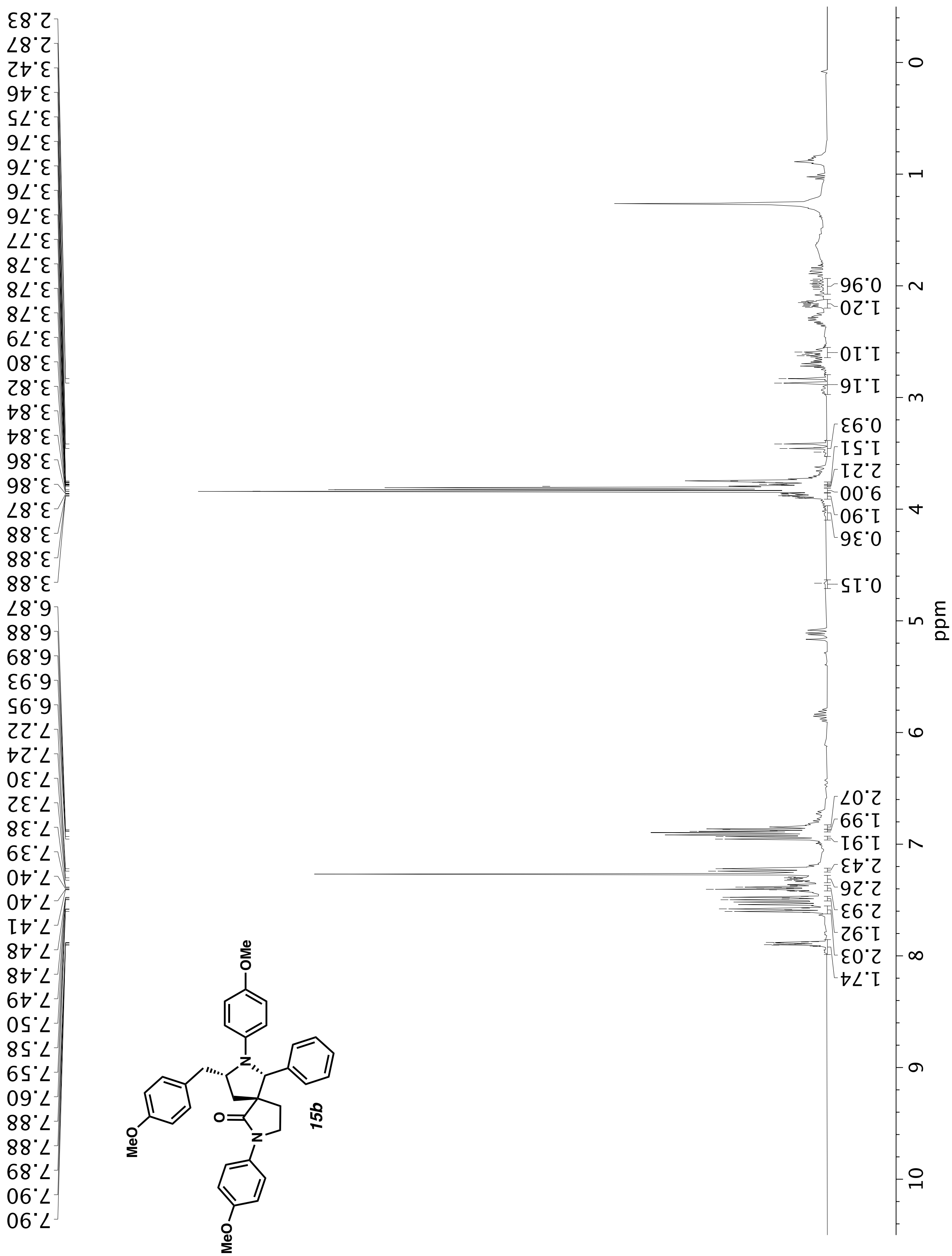


^{13}C NMR (100 MHz, $CDCl_3$) of compound **15a.**

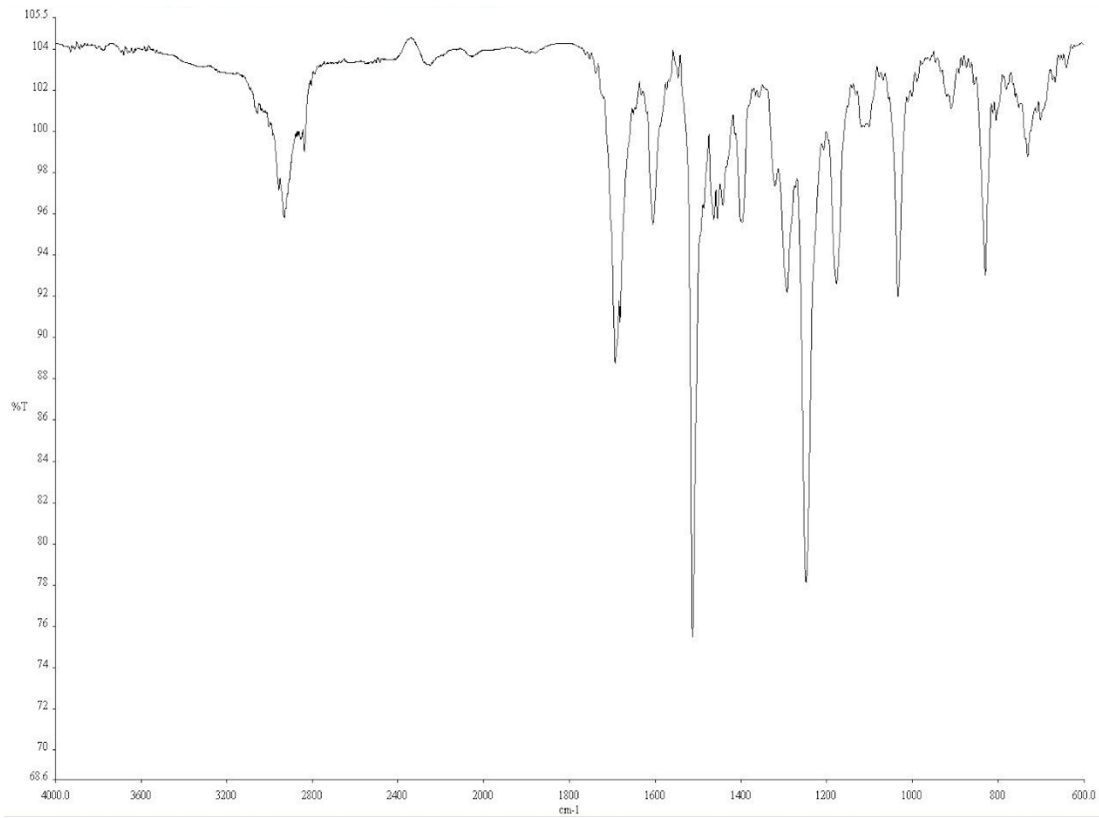


NOESY (400 MHz, $CDCl_3$) of compound **15a.**

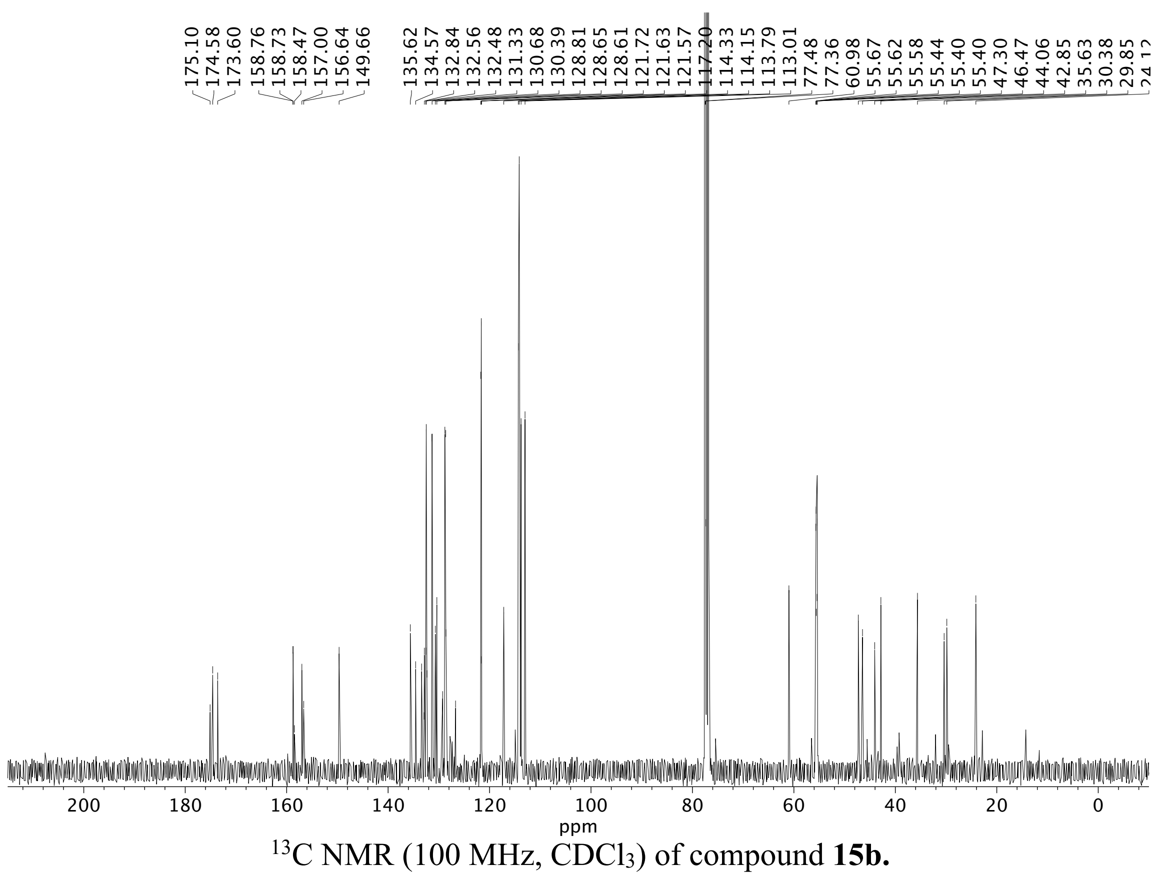




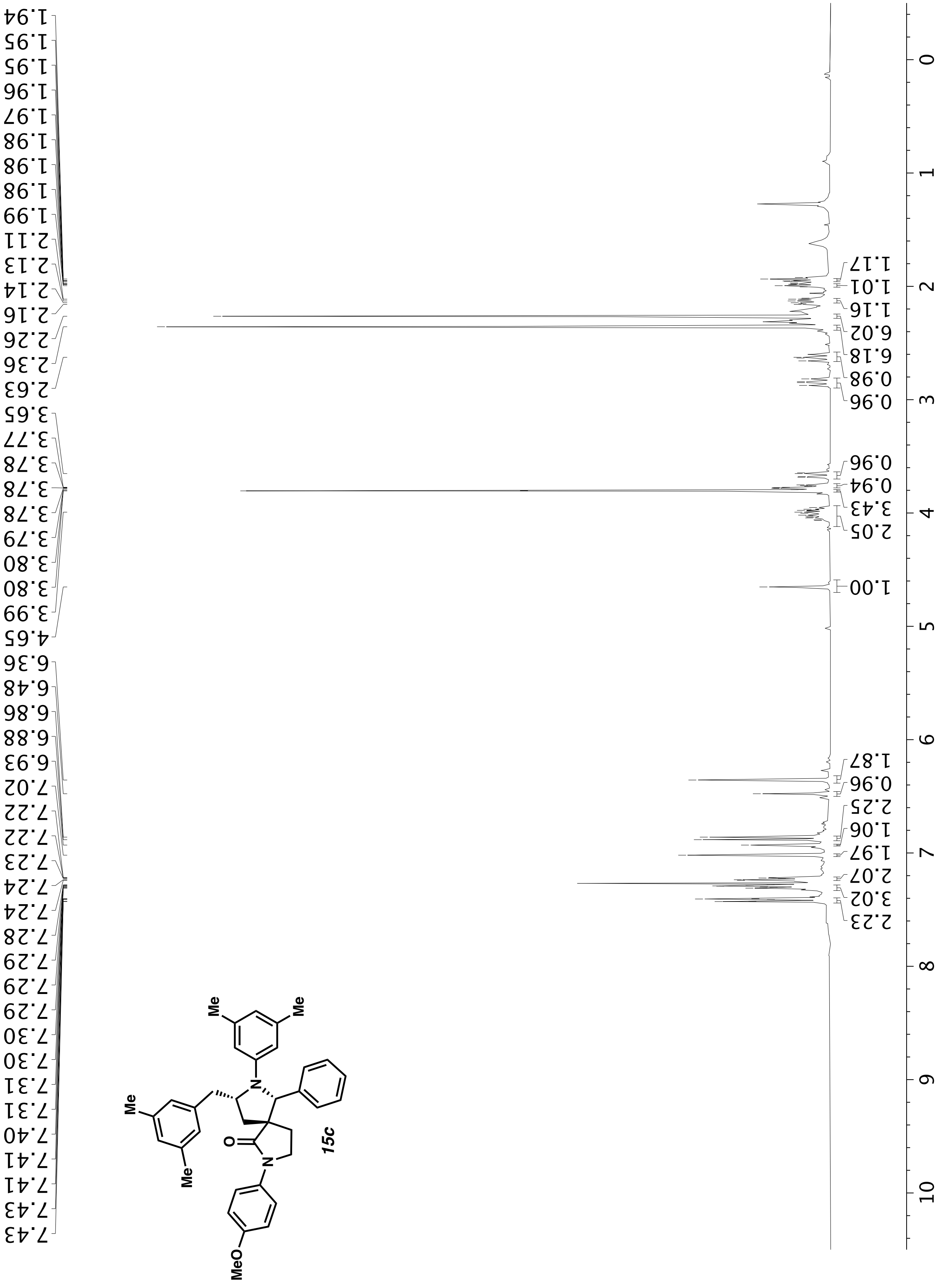
^{1}H NMR (400 MHz, $CDCl_3$) of compound **15b**.



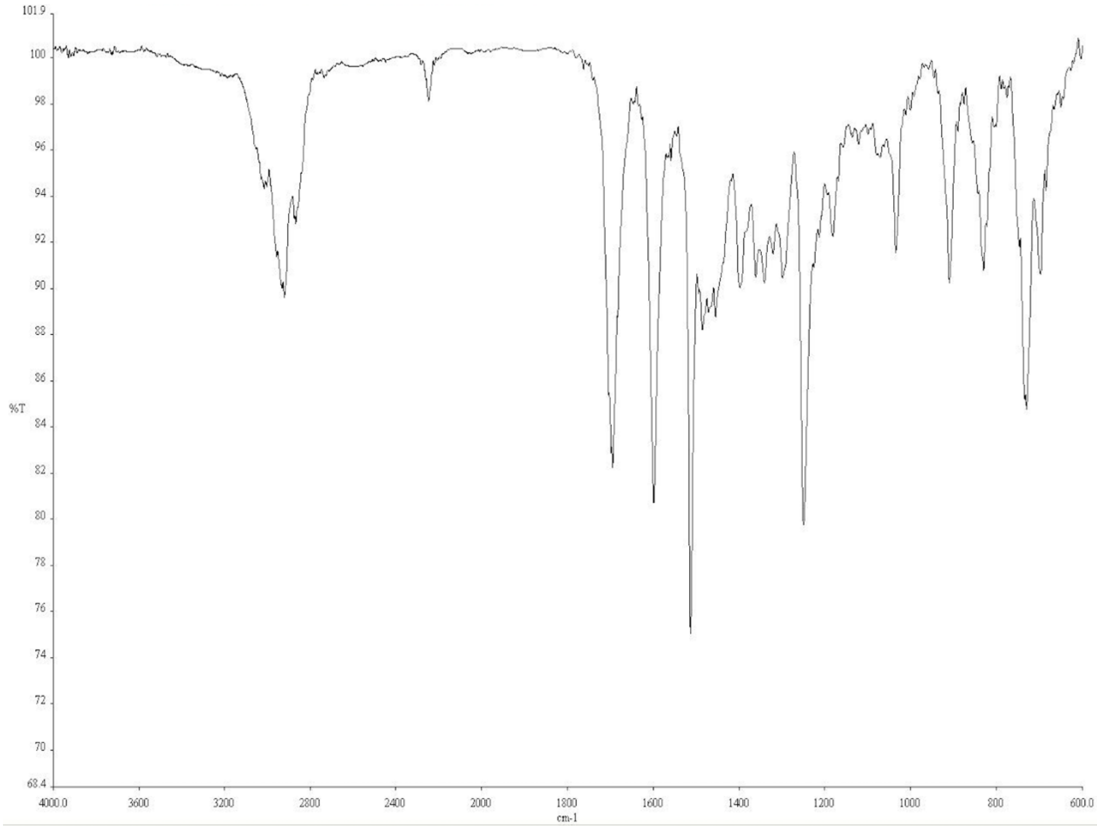
Infrared spectrum (Thin Film, NaCl) of compound **15b**.



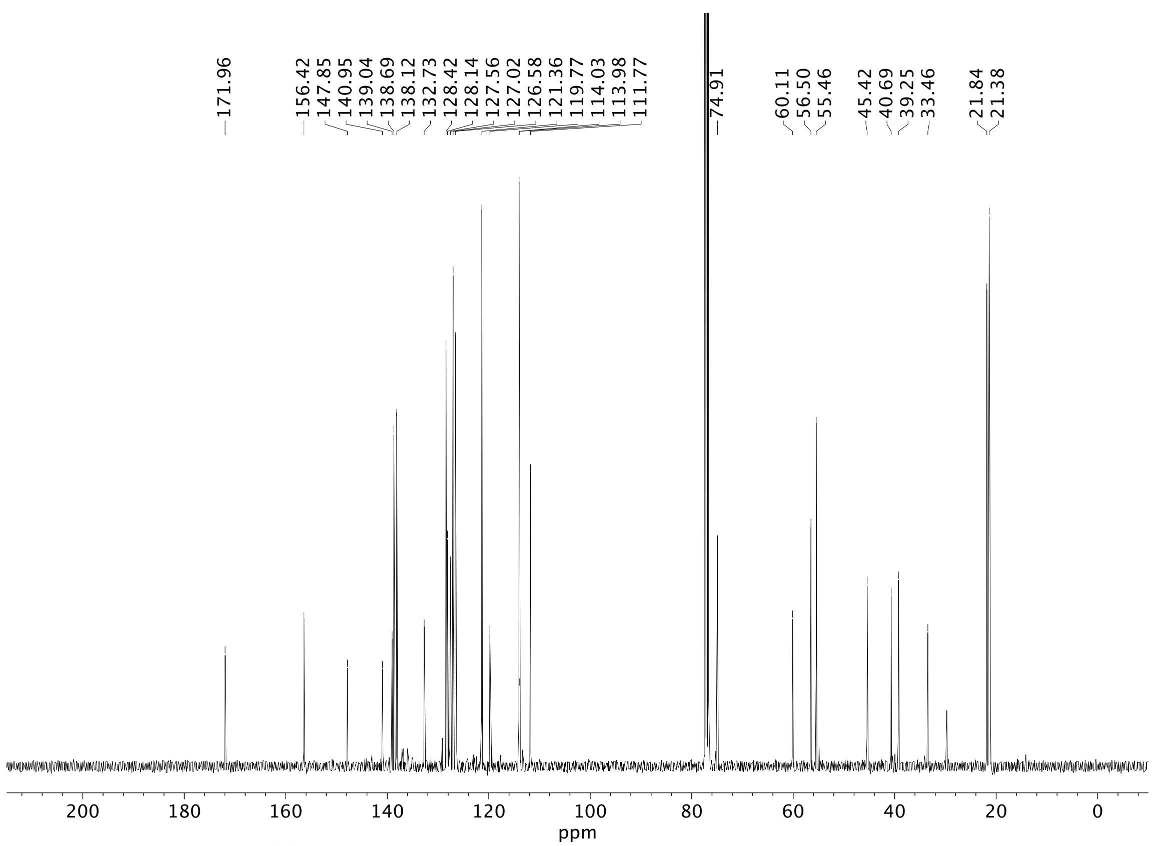
^{13}C NMR (100 MHz, $CDCl_3$) of compound **15b.**



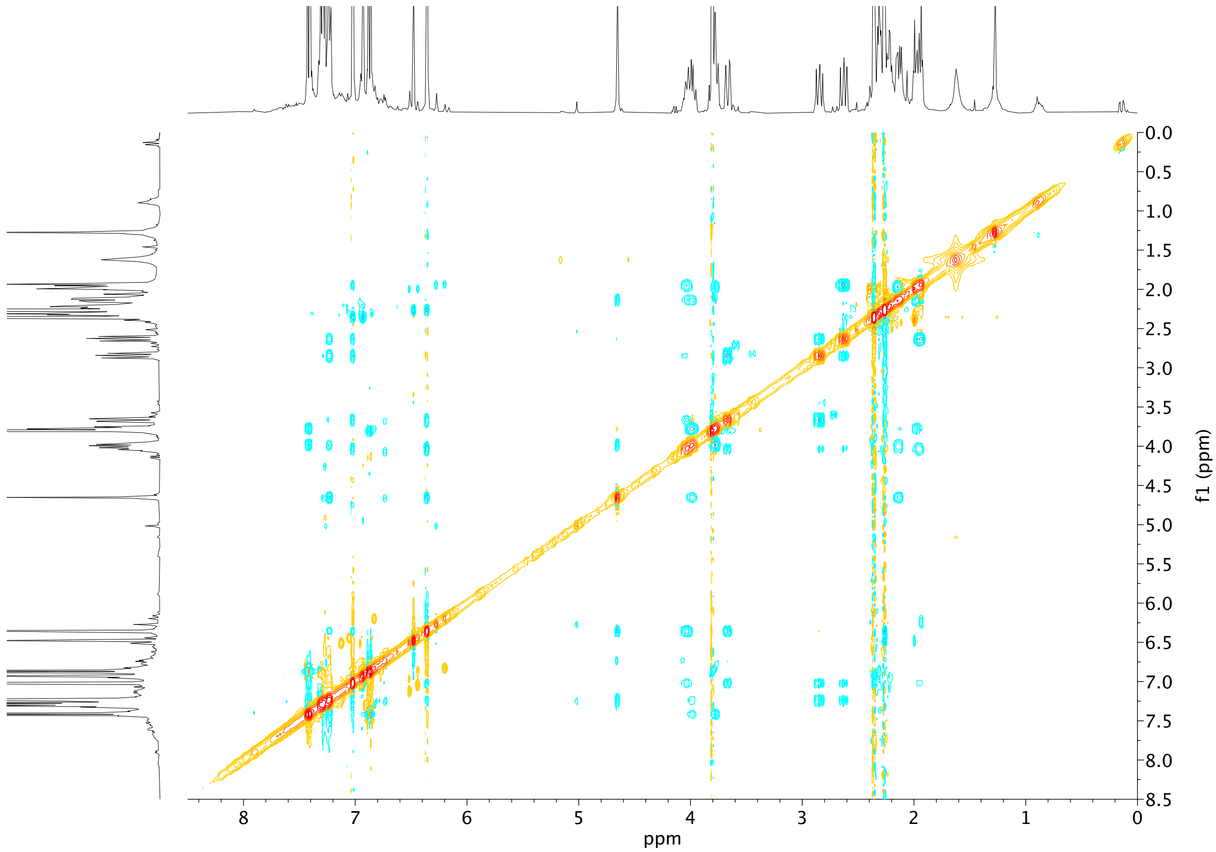
^{1}H NMR (400 MHz, $CDCl_3$) of compound **15c**.



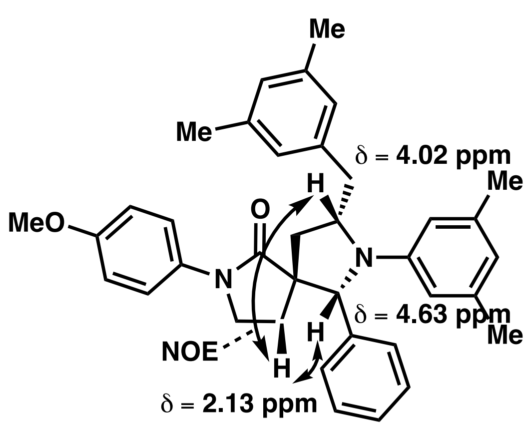
Infrared spectrum (Thin Film, NaCl) of compound **15c**.

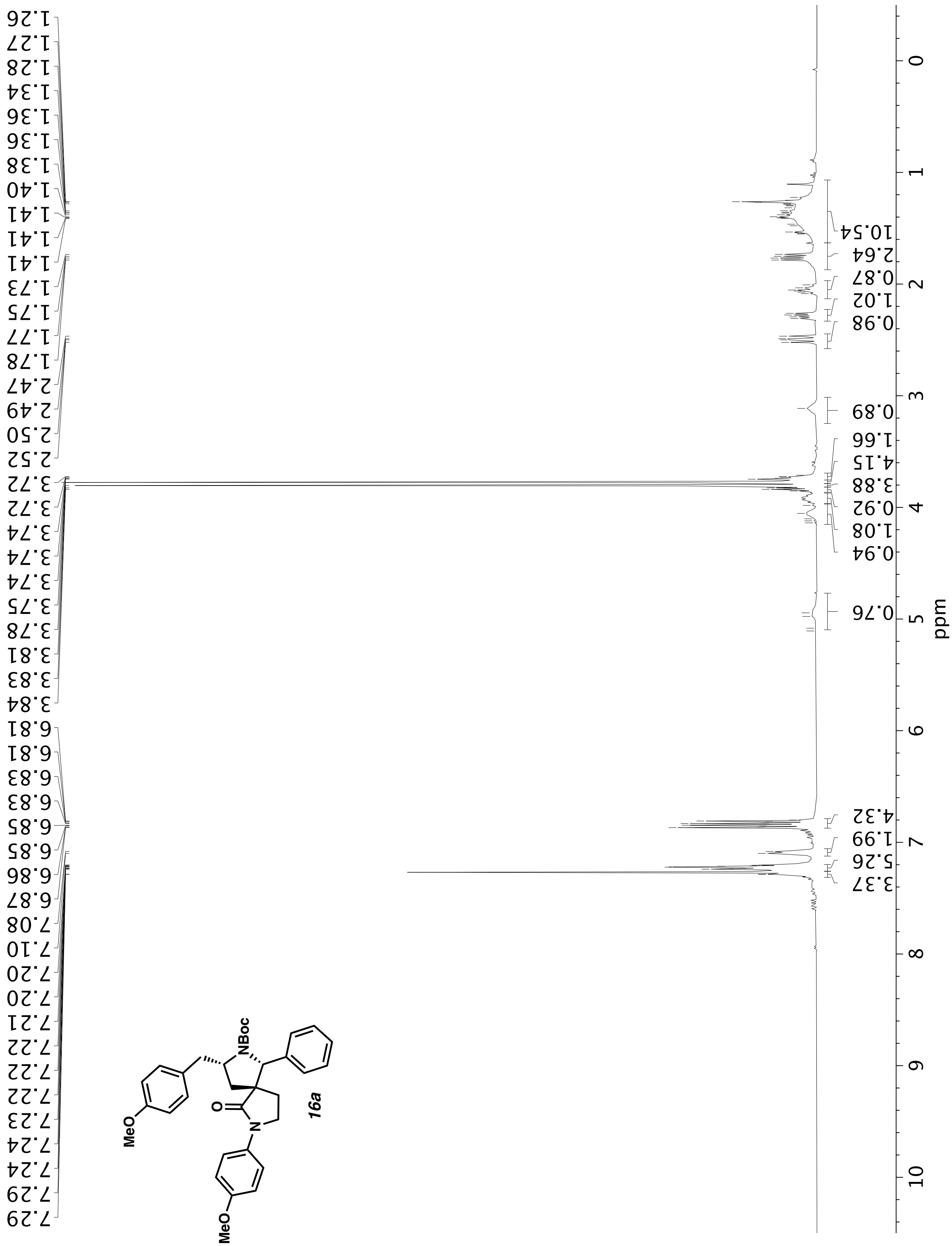


^{13}C NMR (100 MHz, $CDCl_3$) of compound **15c.**

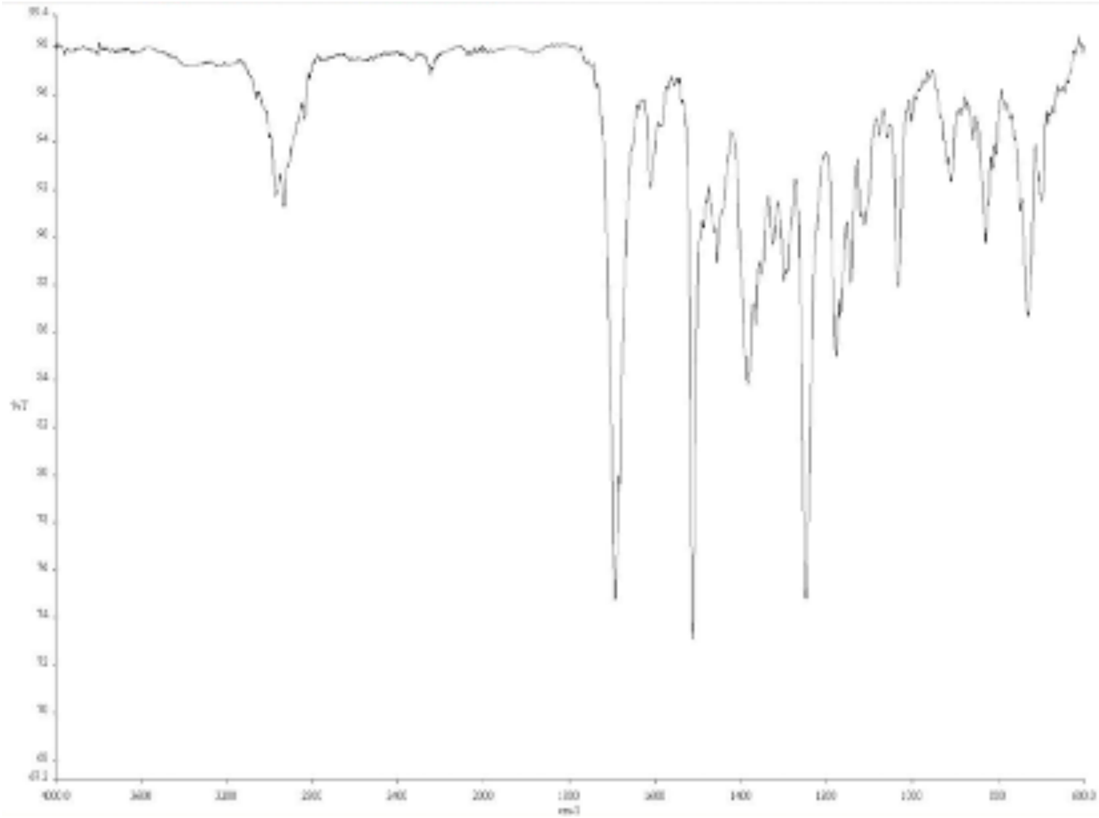


NOESY (400 MHz, $CDCl_3$) of compound **15c.**

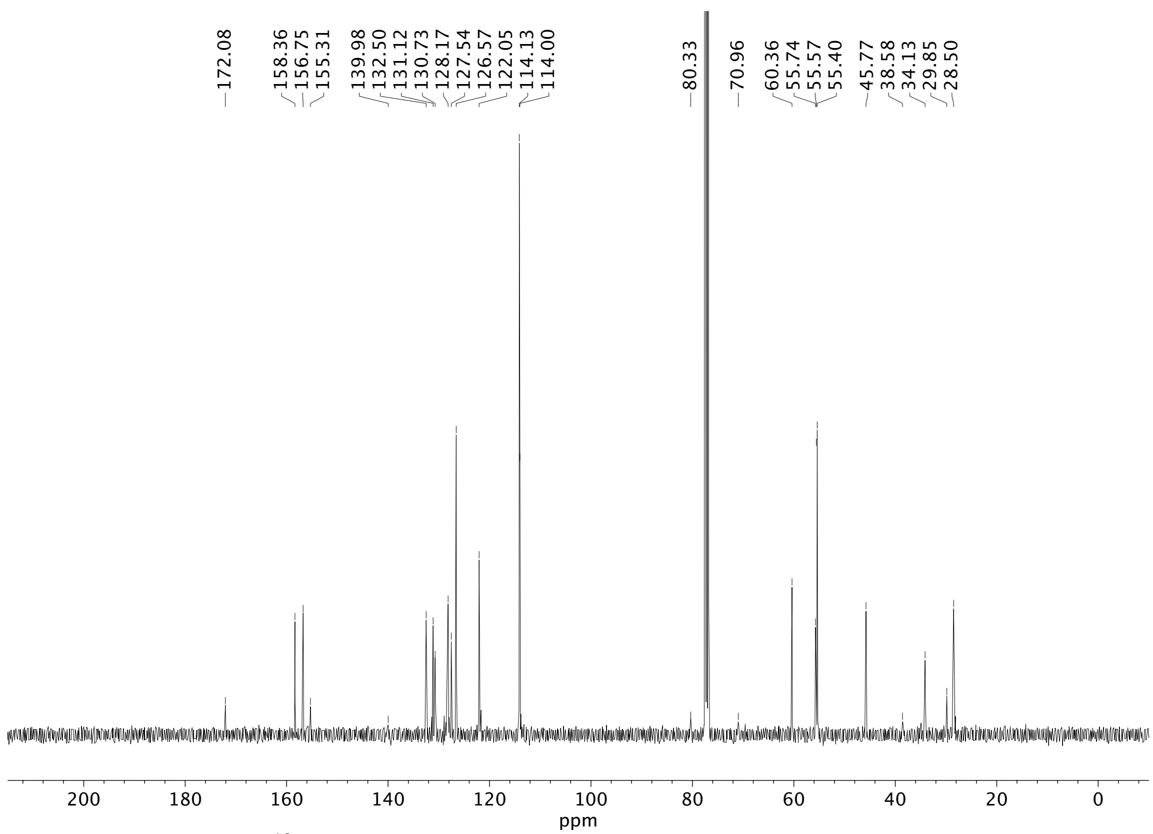




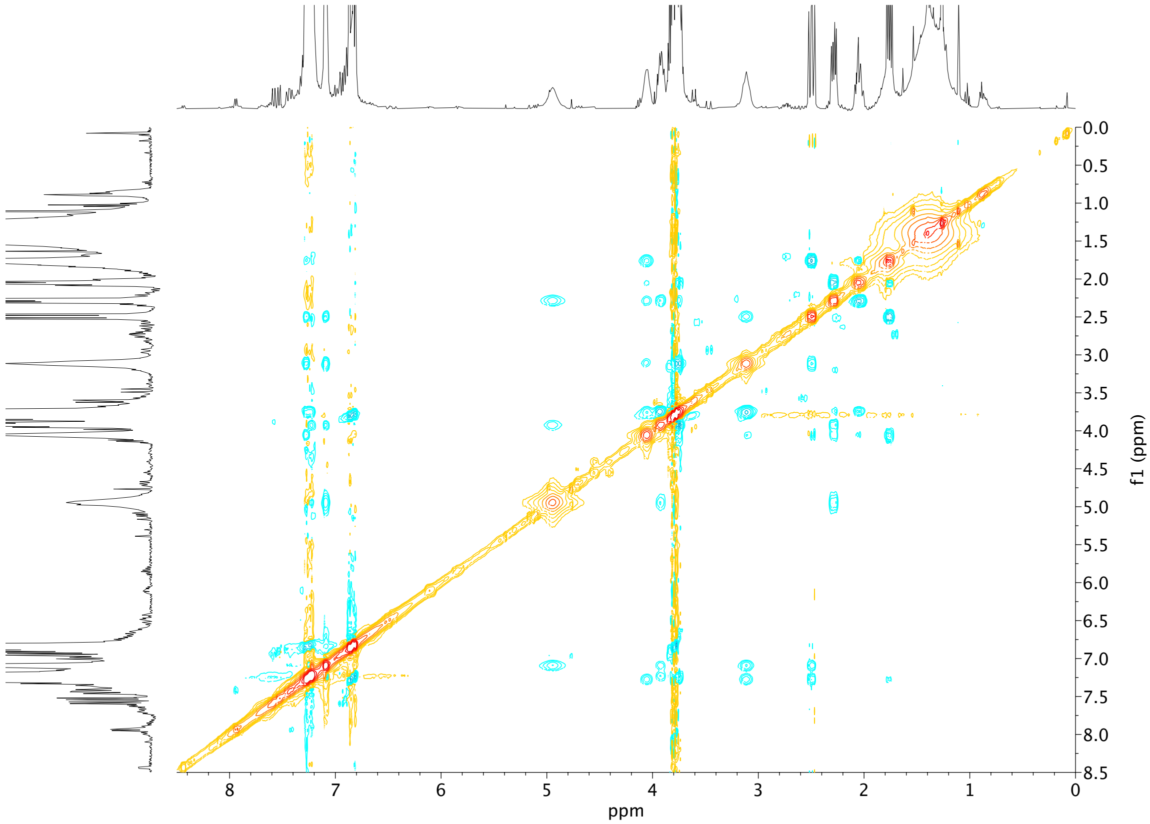
^{1}H NMR (400 MHz, $CDCl_3$) of compound **16a**.



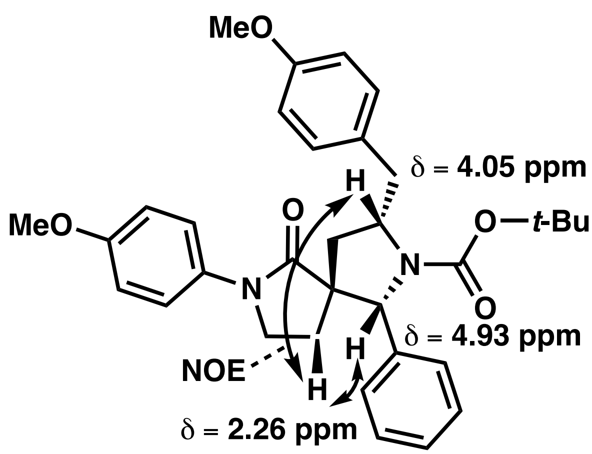
Infrared spectrum (Thin Film, NaCl) of compound **16a**.

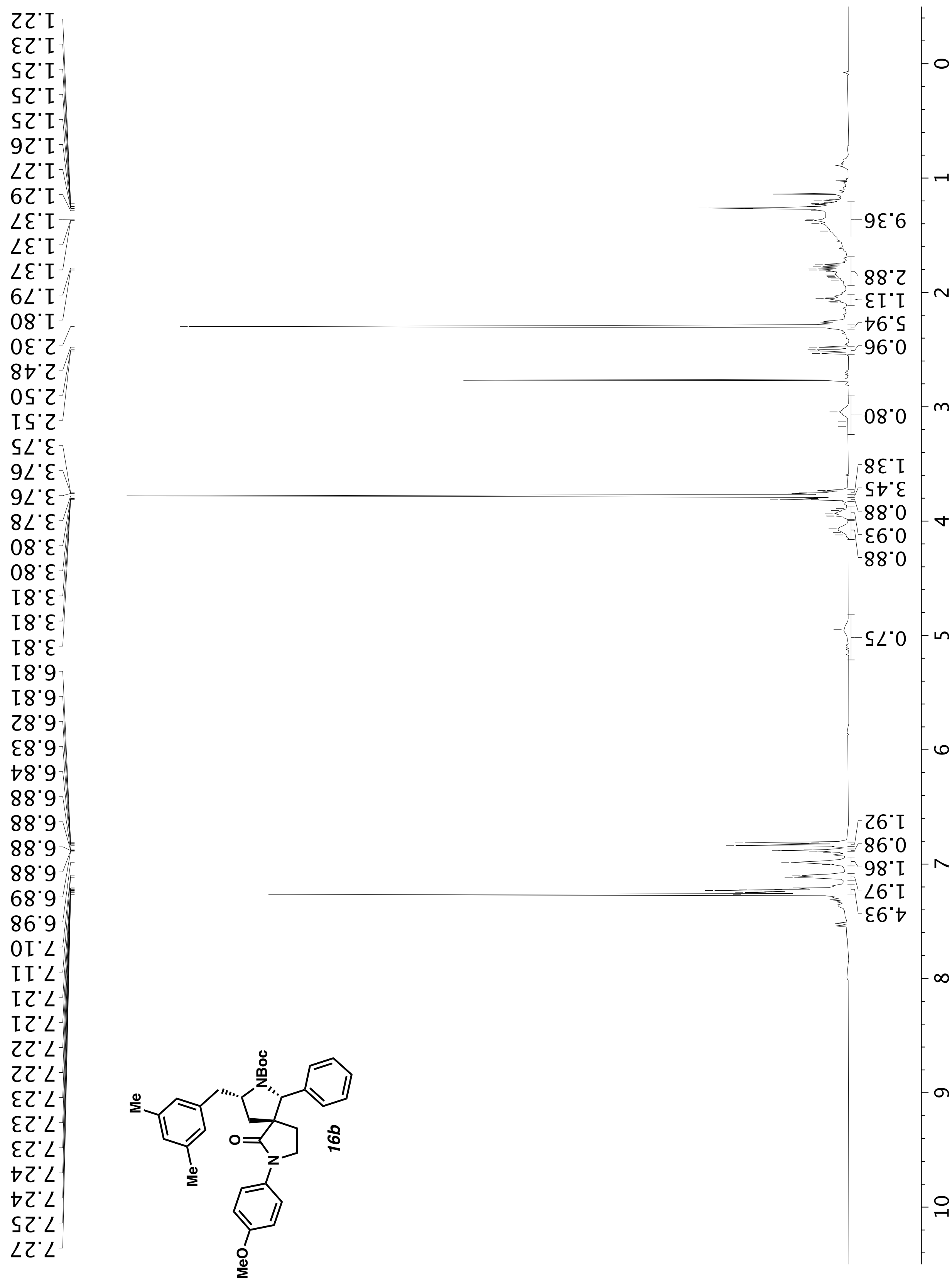


^{13}C NMR (100 MHz, $CDCl_3$) of compound **16a.**

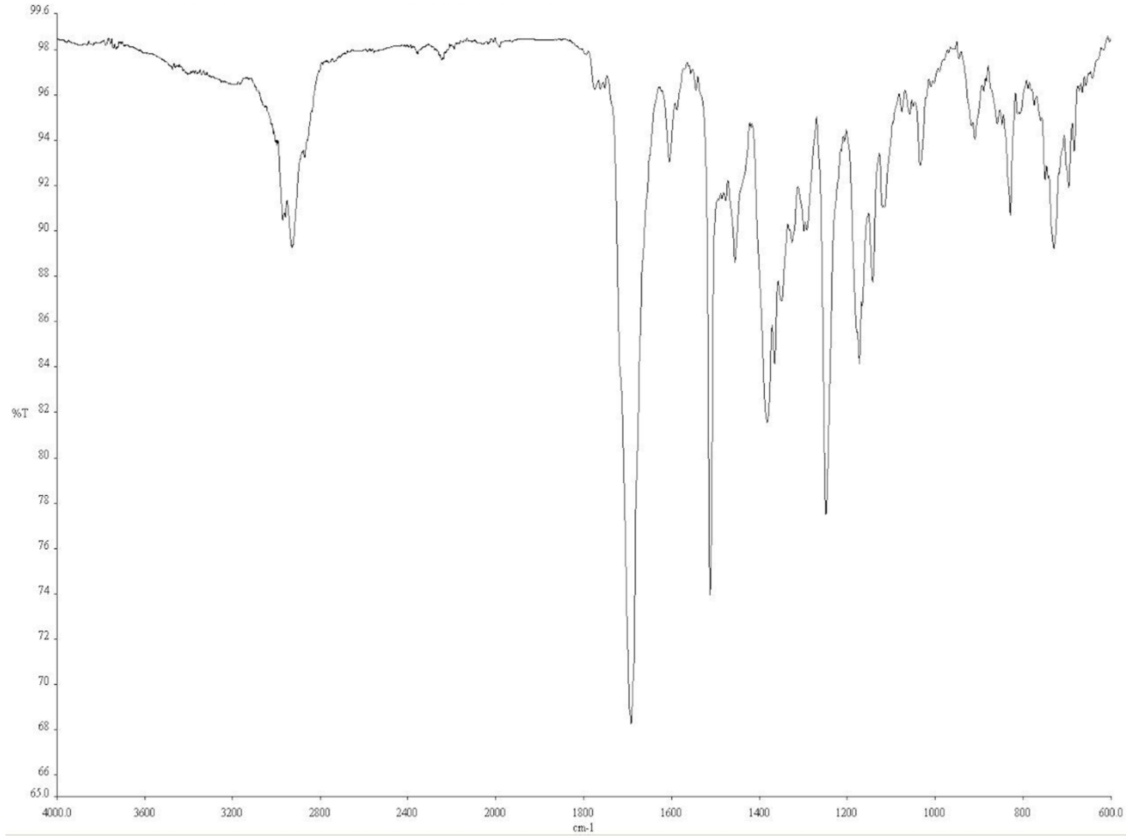


NOESY (400 MHz, $CDCl_3$) of compound **16a.**

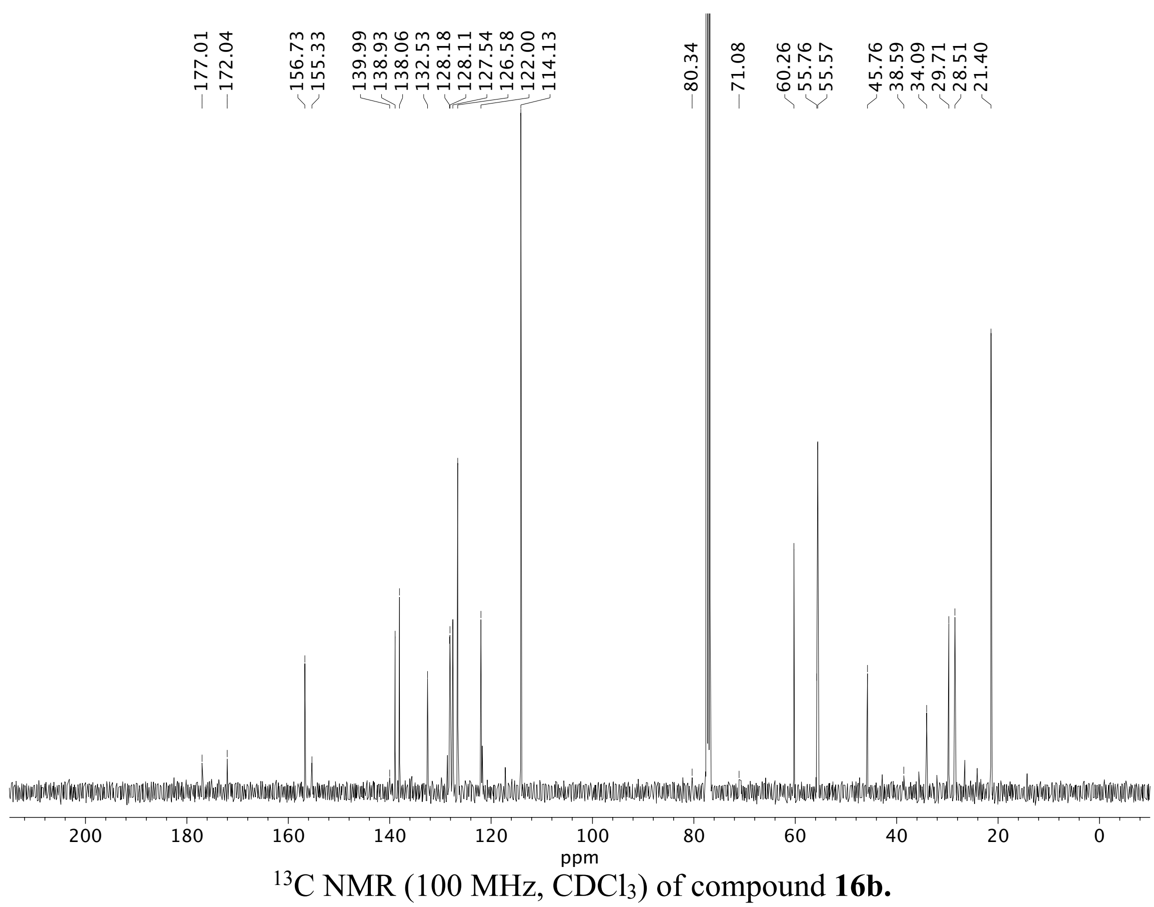




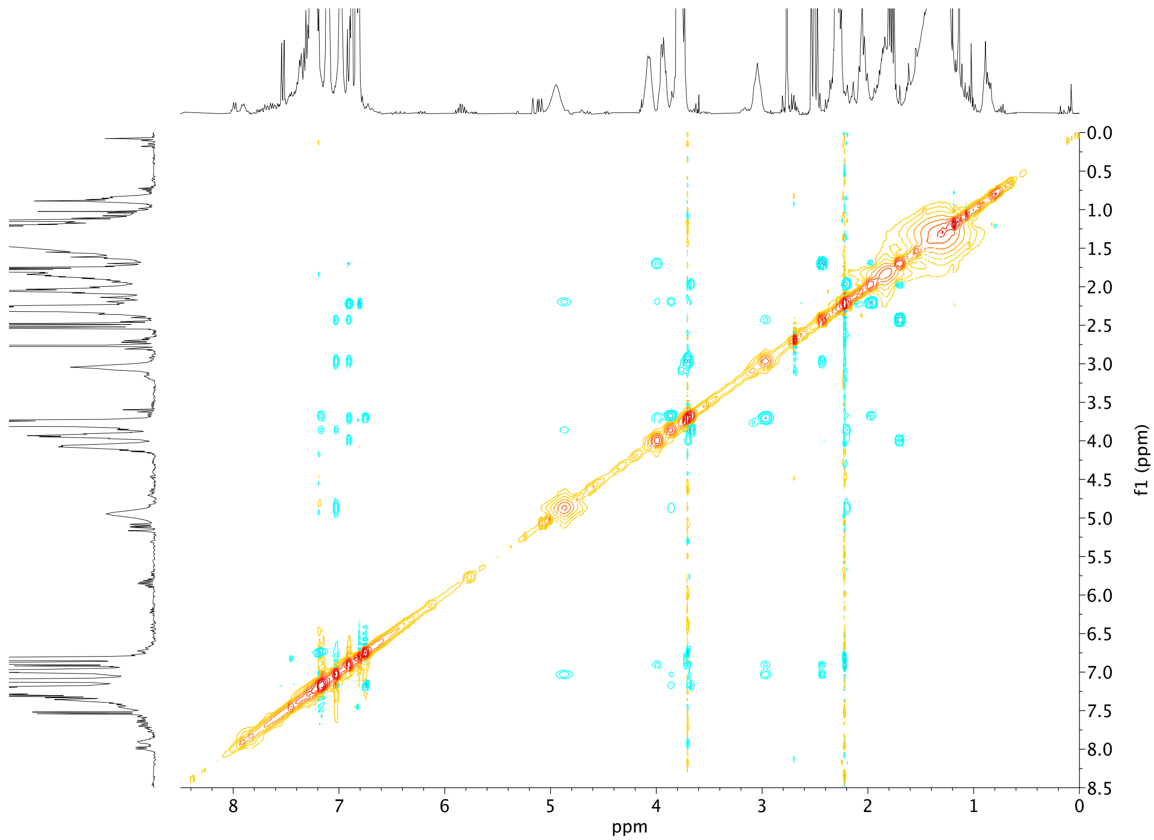
^{1}H NMR (400 MHz, $CDCl_3$) of compound **16b**.



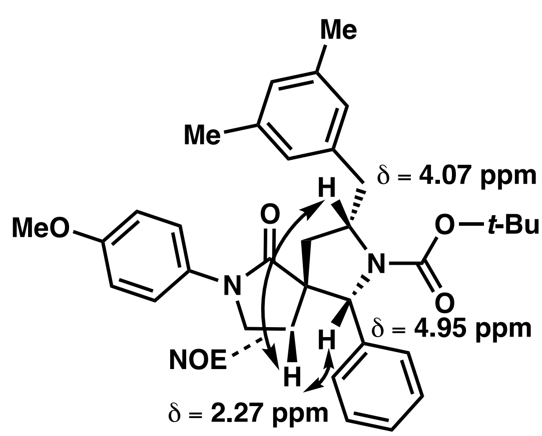
Infrared spectrum (Thin Film, NaCl) of compound **16b**.

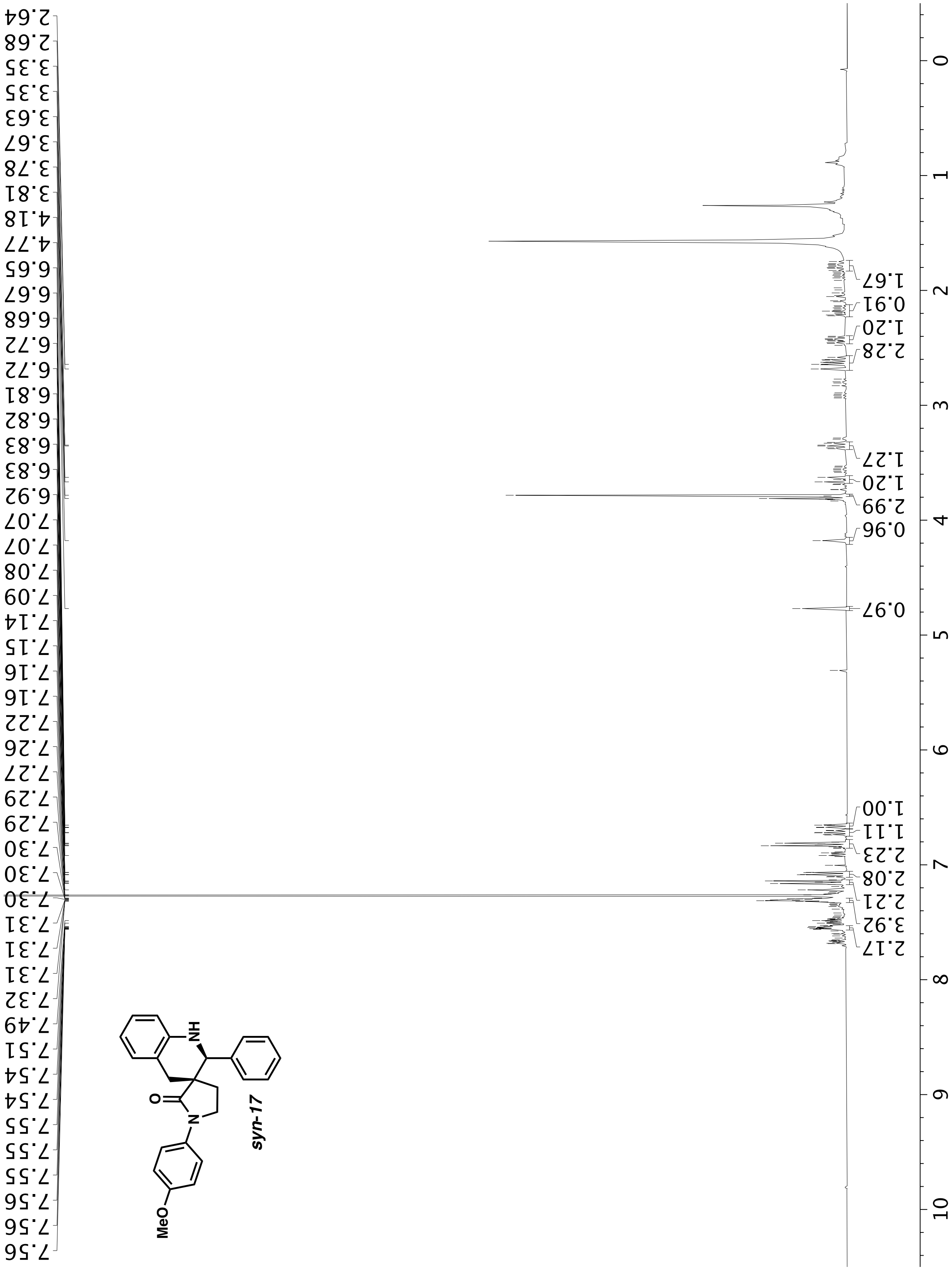


^{13}C NMR (100 MHz, $CDCl_3$) of compound **16b.**

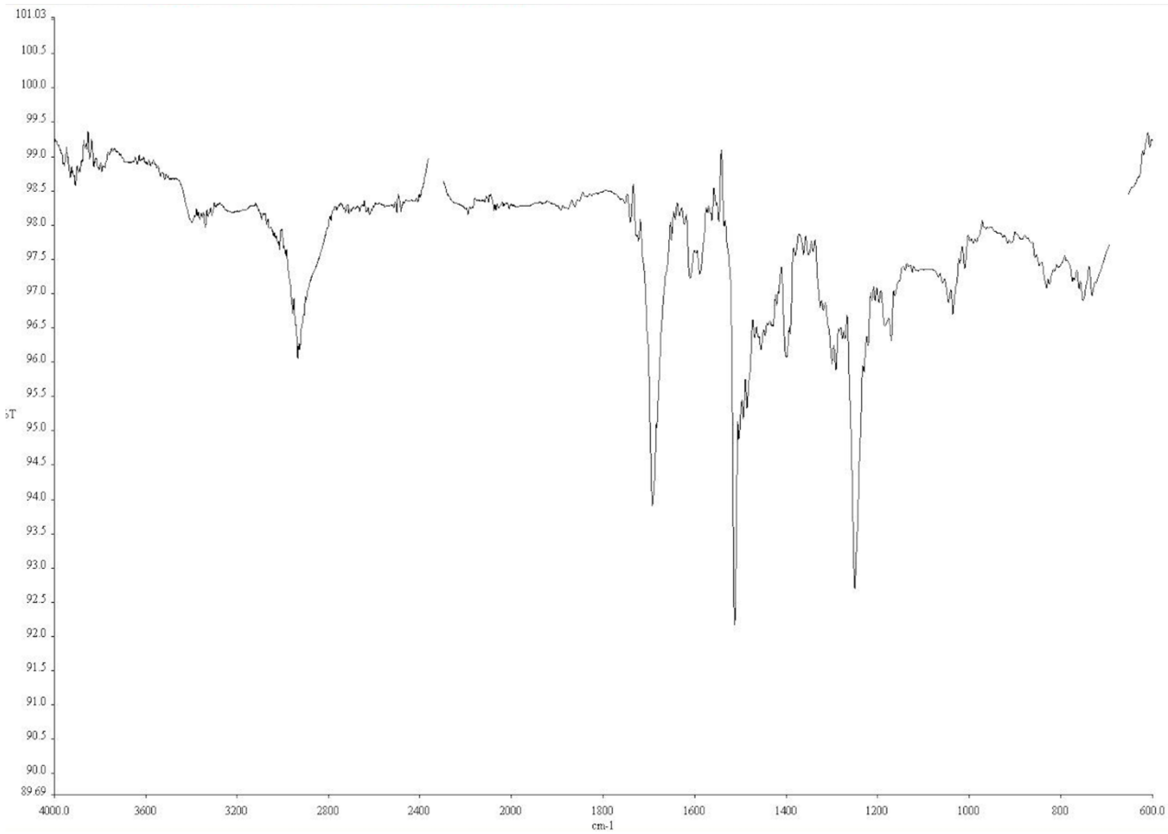


NOESY (400 MHz, $CDCl_3$) of compound **16b.**

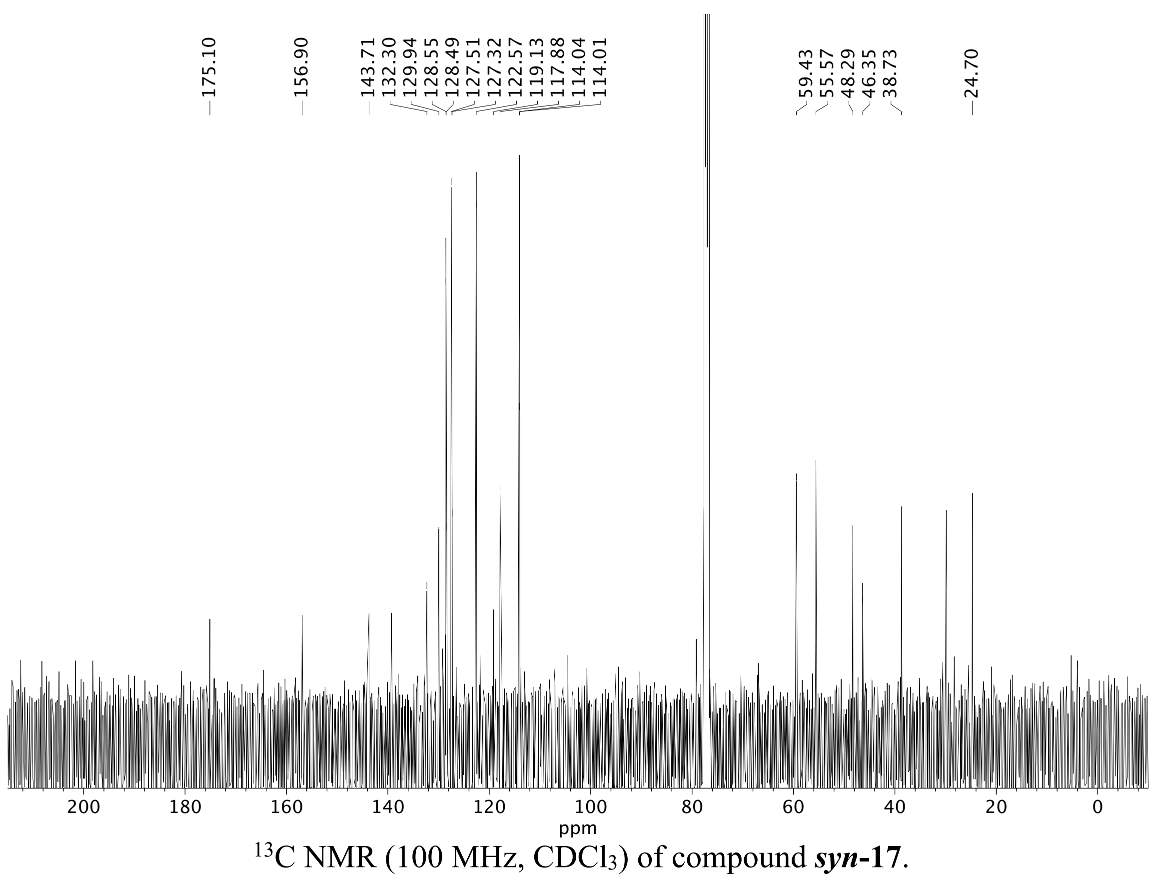




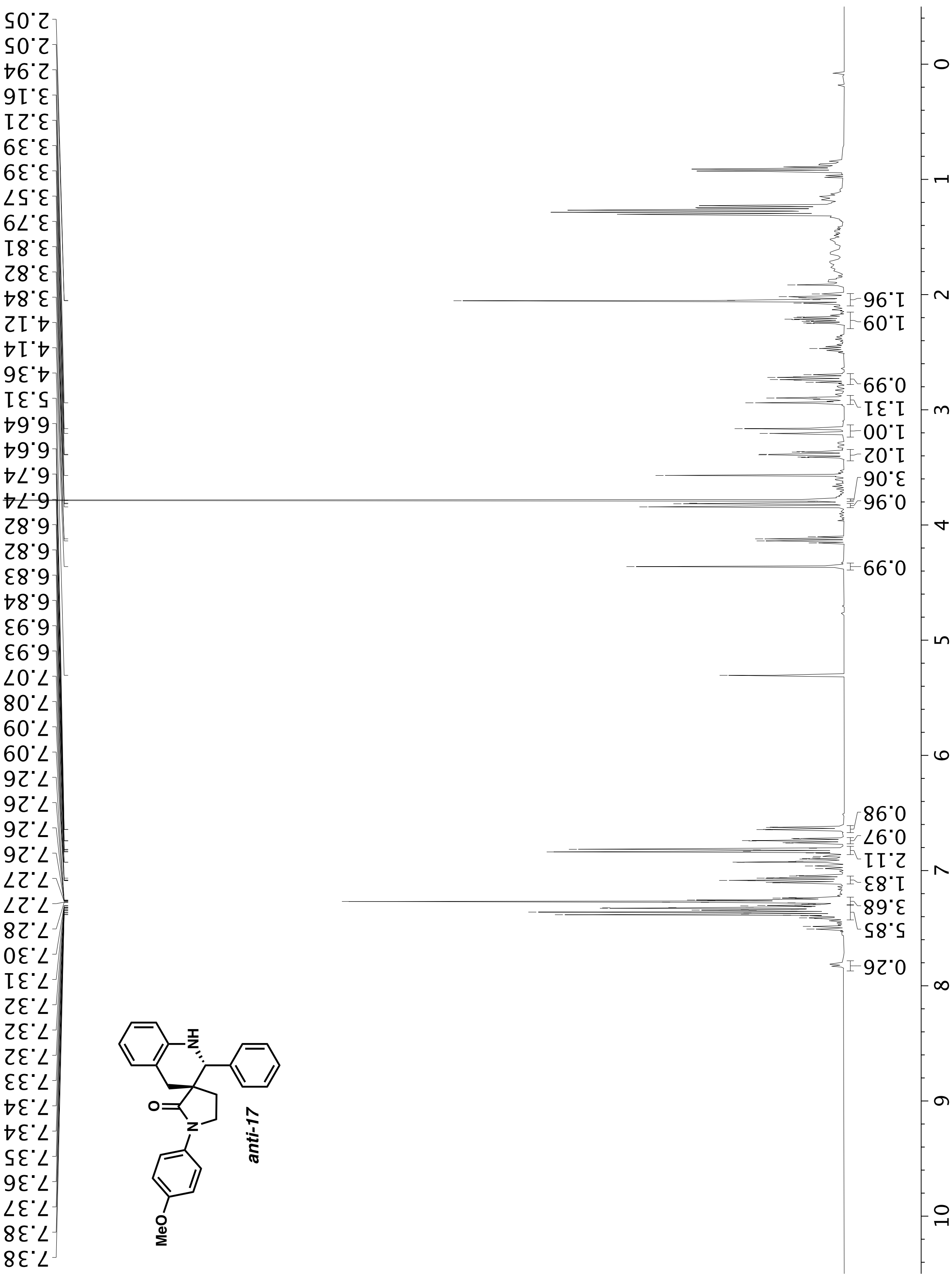
[1]H NMR (400 MHz, $CDCl_3$) of compound ***syn*-17**.



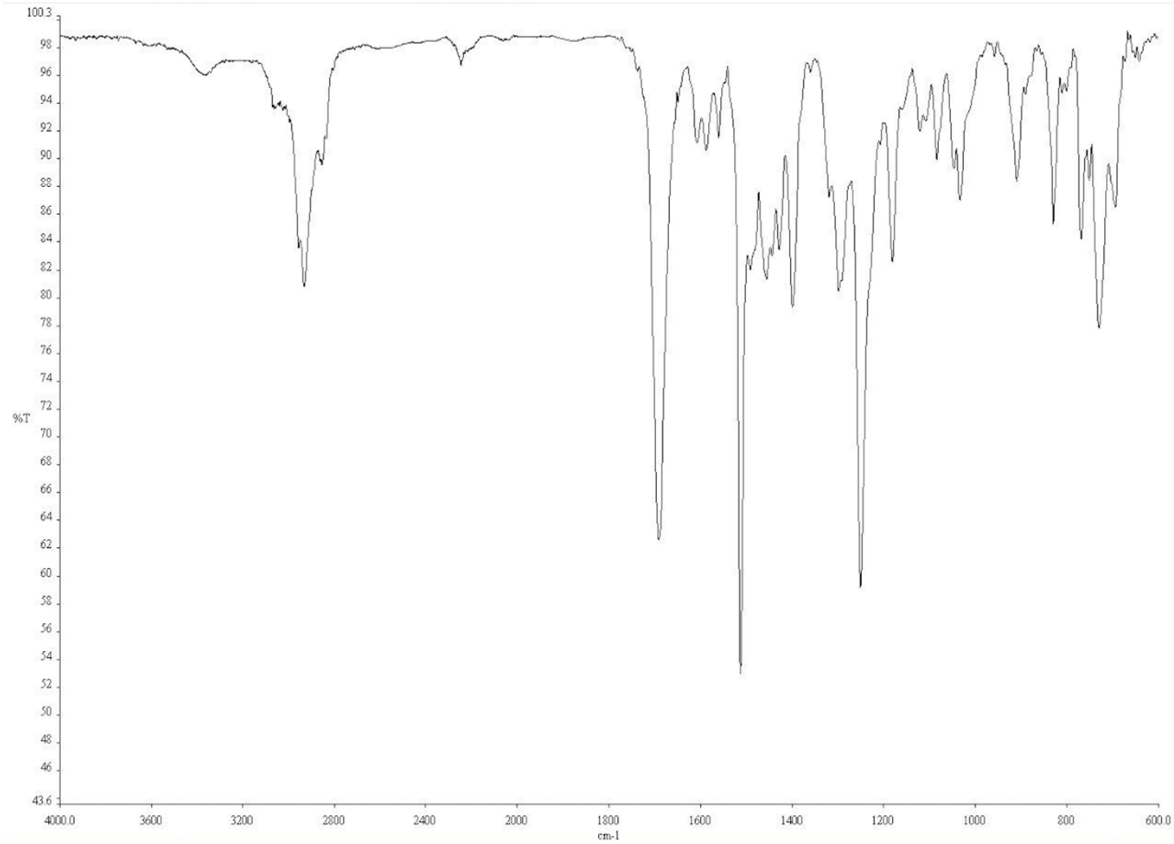
Infrared spectrum (Thin Film, NaCl) of compound ***syn*-17**.



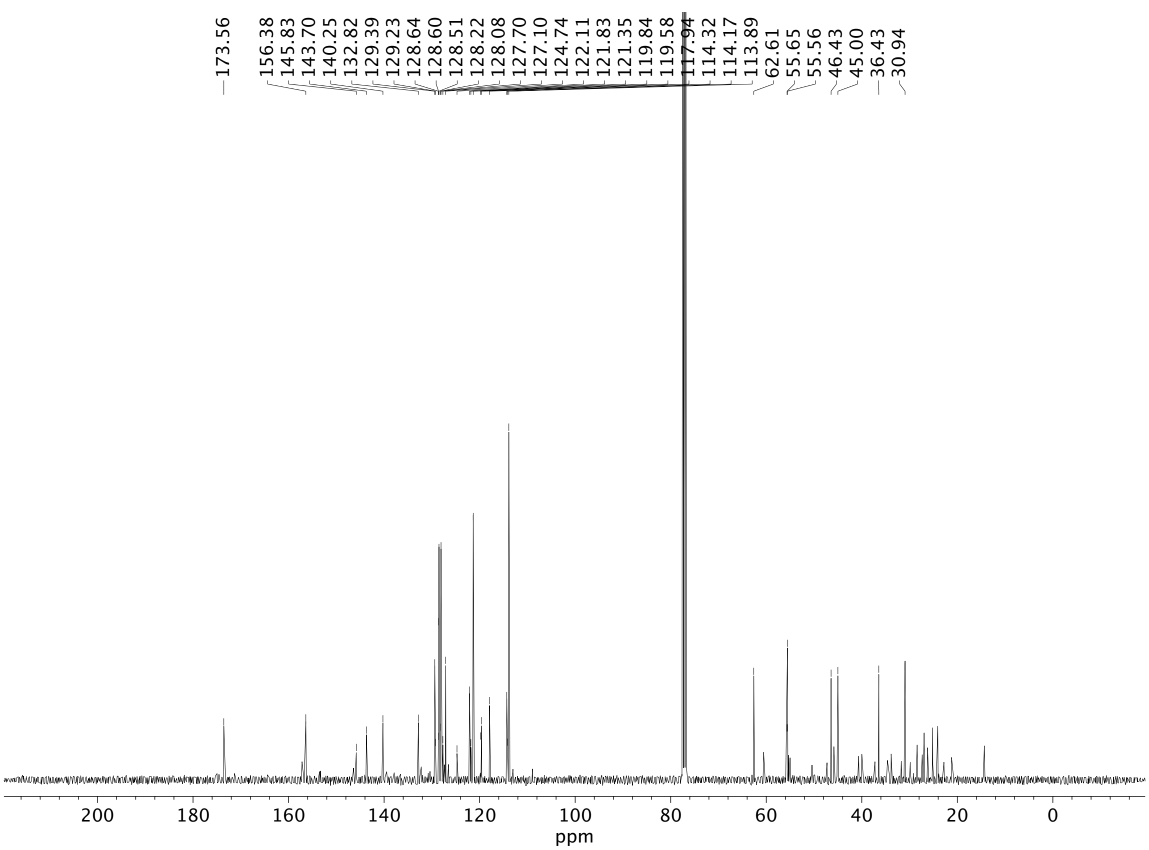
^{13}C NMR (100 MHz, $CDCl_3$) of compound ***syn*-17**.



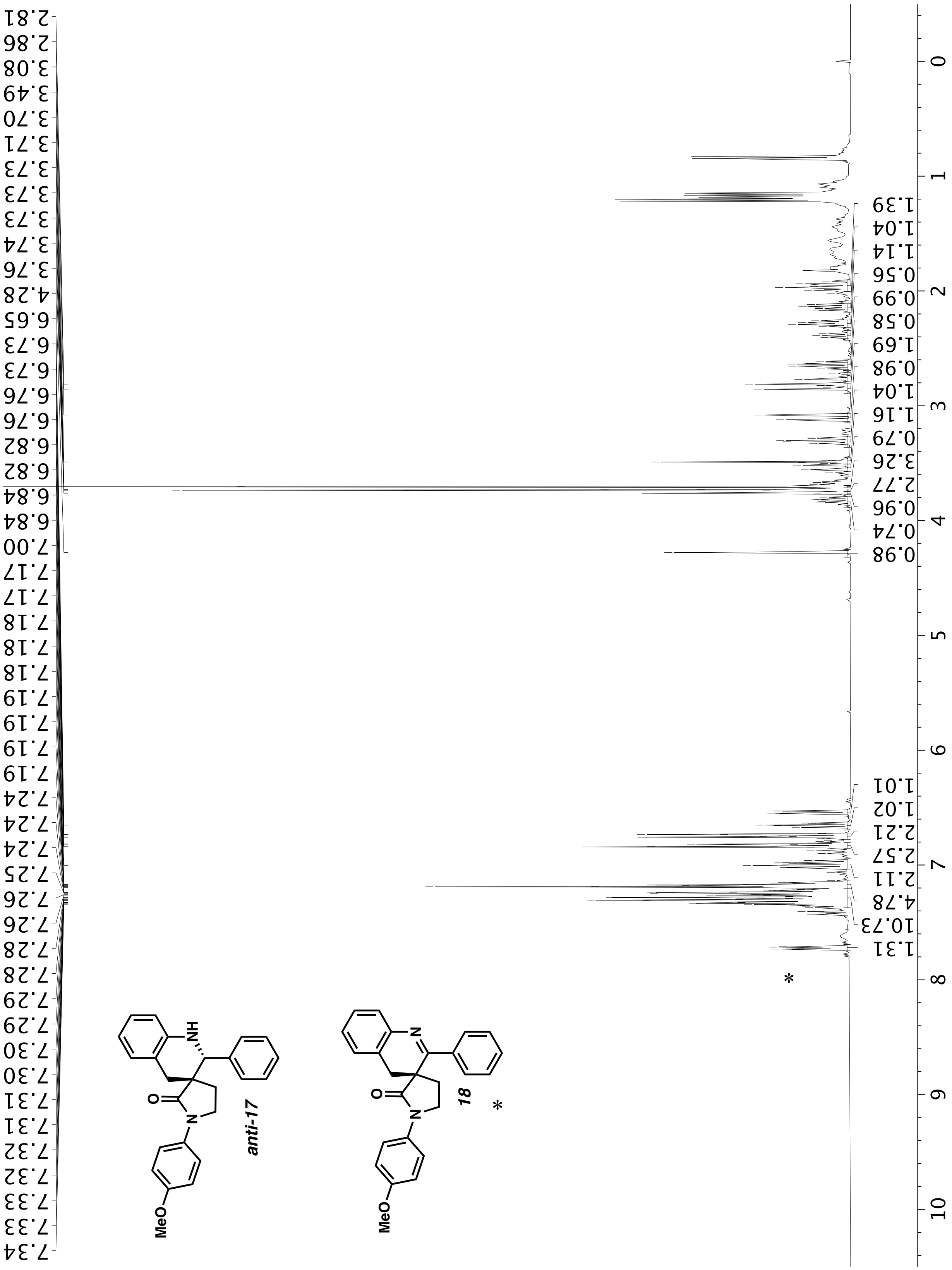
[1]H NMR (400 MHz, $CDCl_3$) of compound ***anti*-17**.



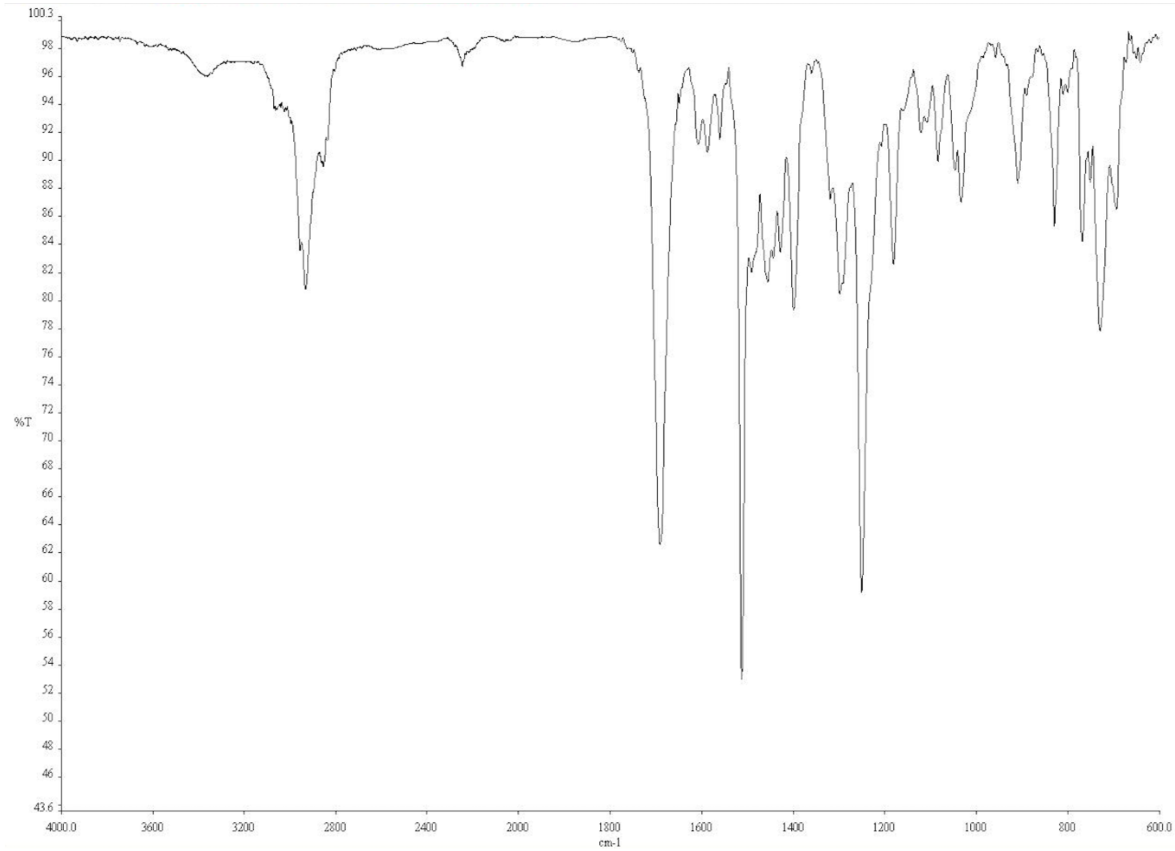
Infrared spectrum (Thin Film, NaCl) of compound ***anti*-17**.



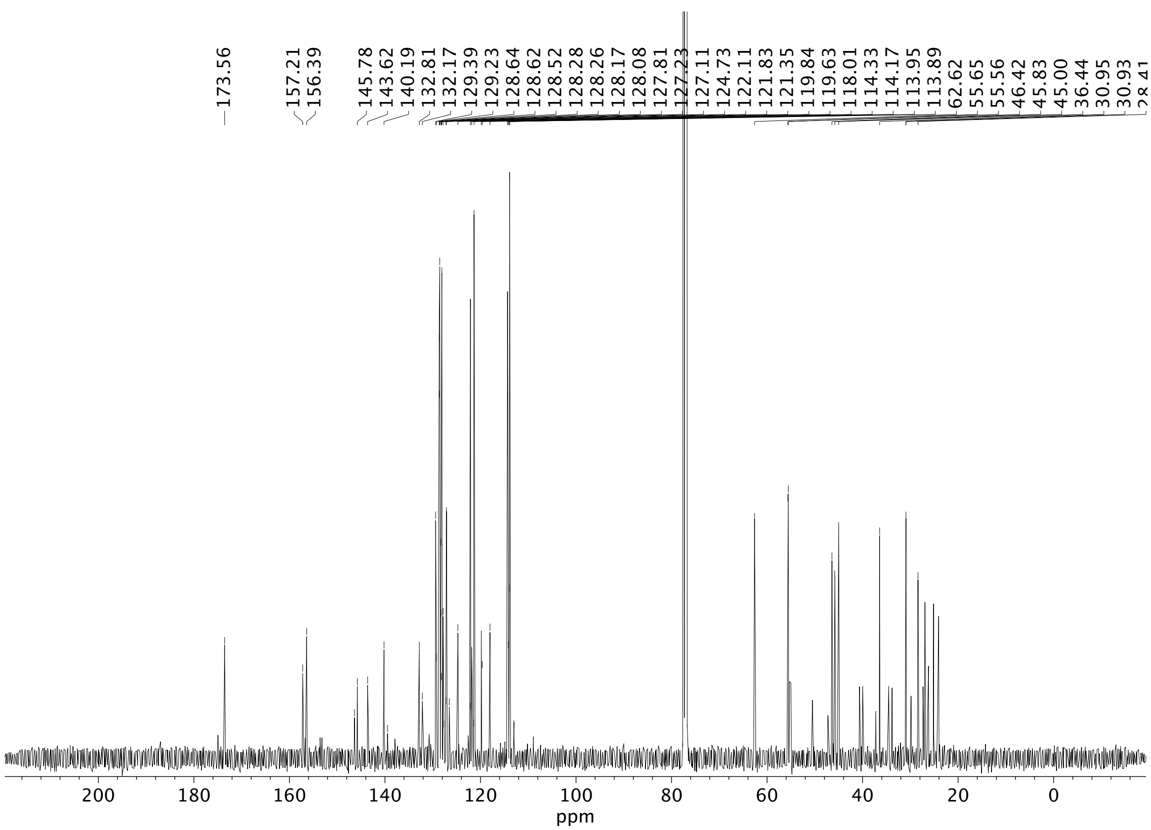
^{13}C NMR (100 MHz, CDCl$_3$) of compound ***anti*-17**.



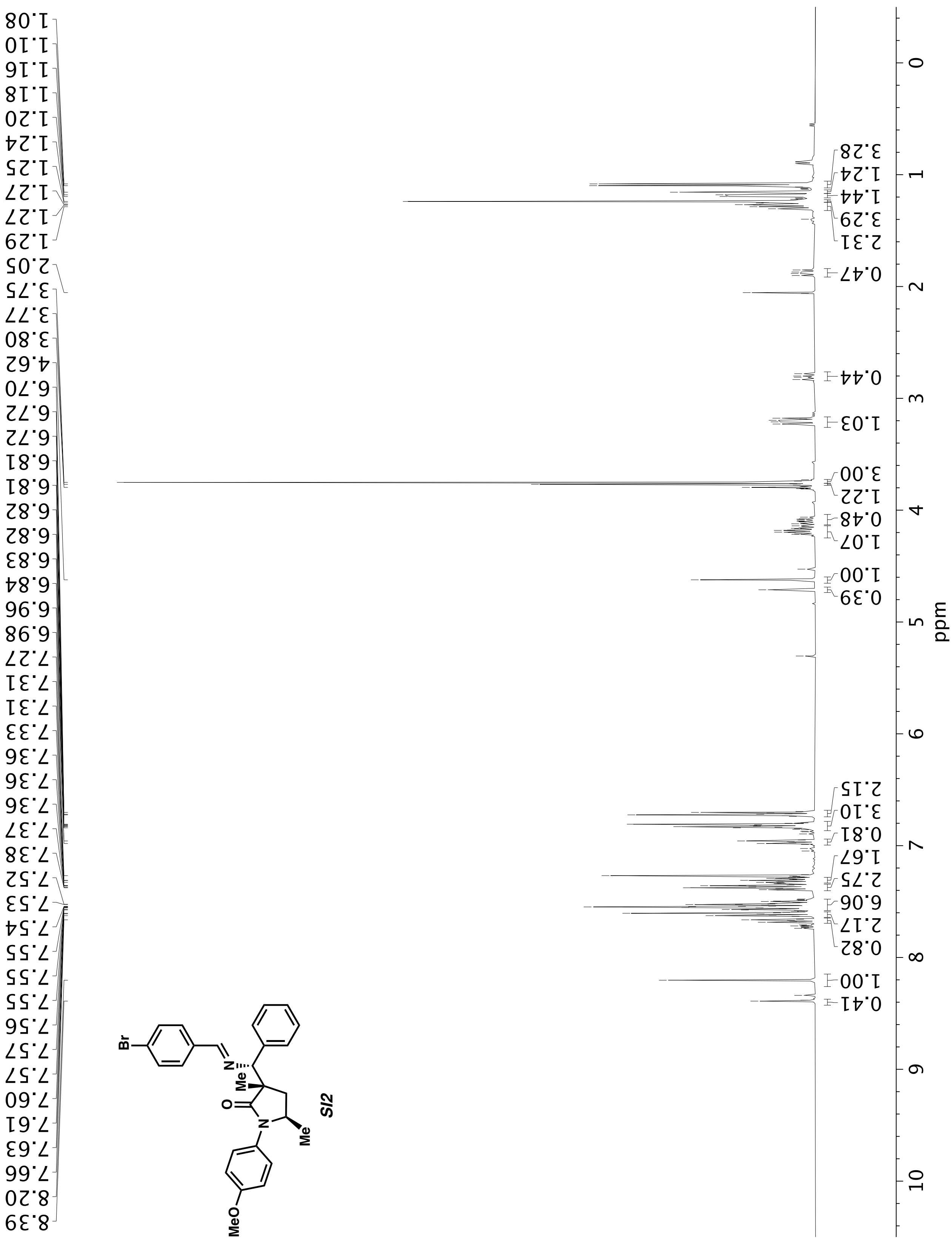
^{1}H NMR (400 MHz, $CDCl_3$) of compound ***anti-17*** and ***18***.



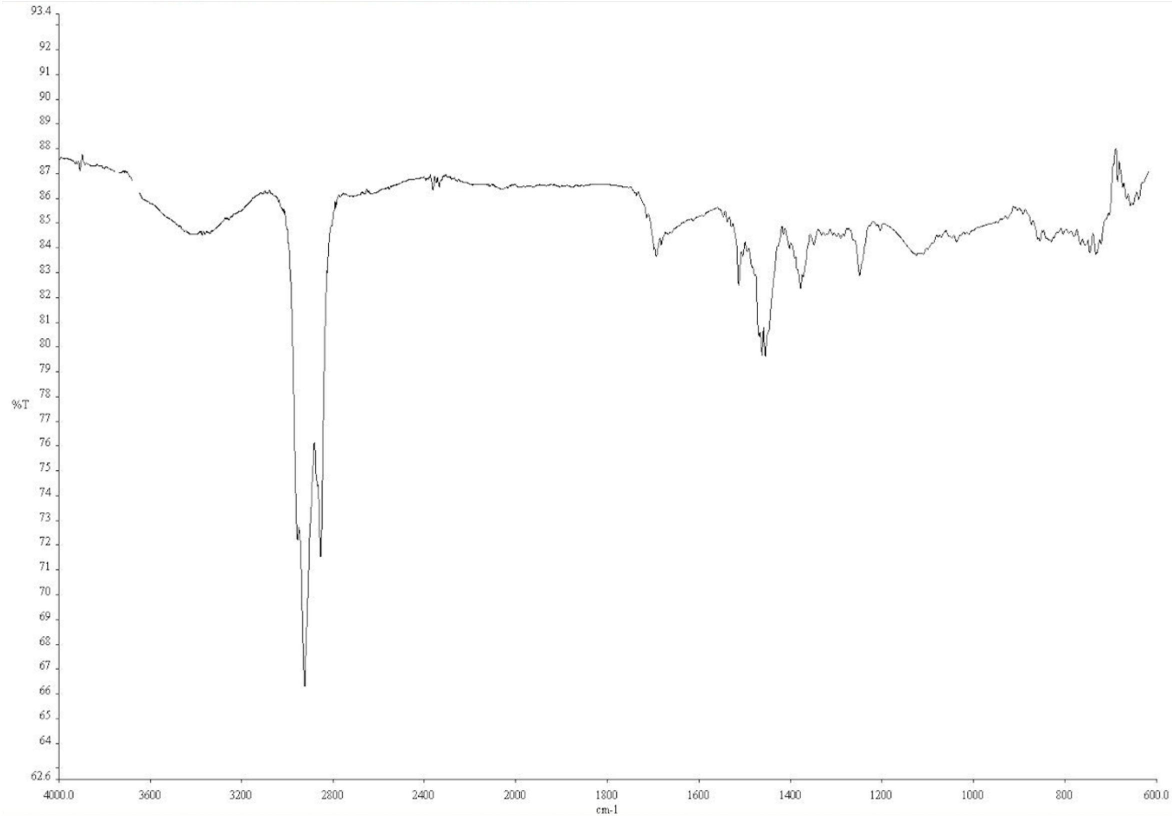
Infrared spectrum (Thin Film, NaCl) of compound ***anti*-17** and ***18***.



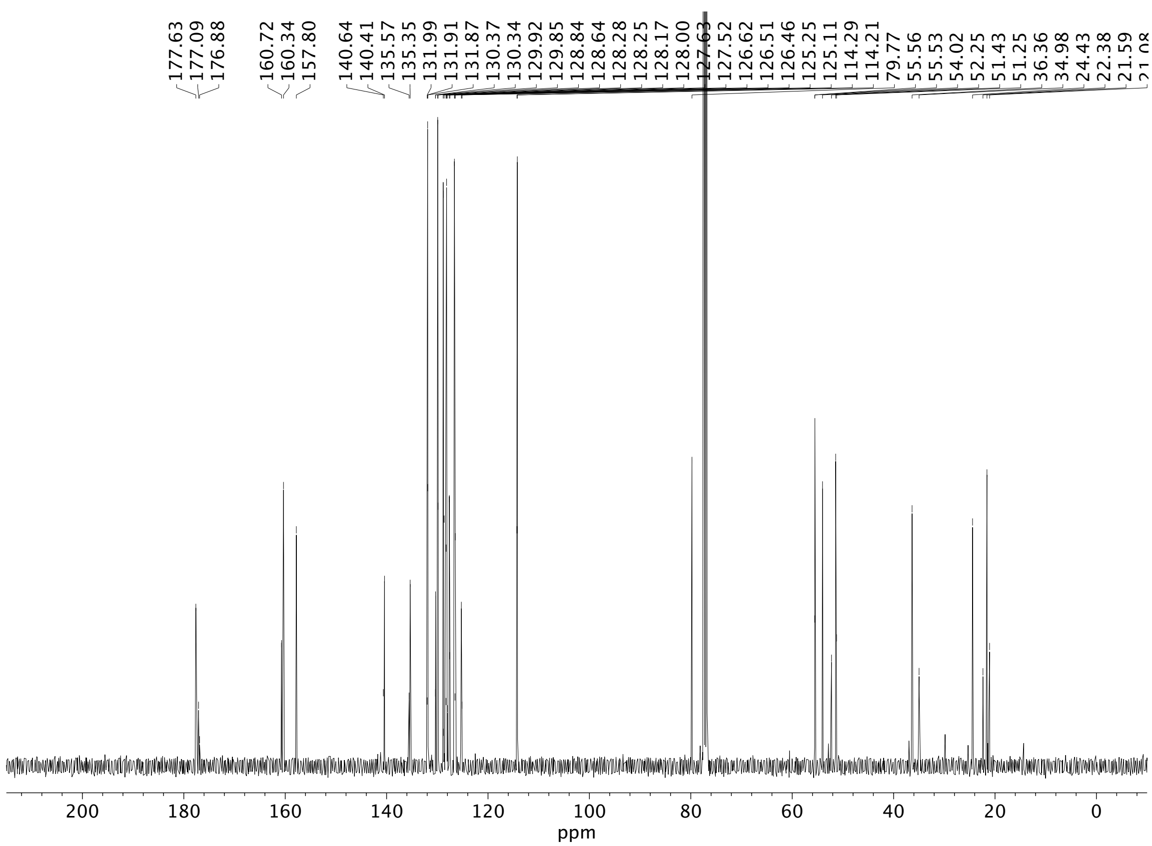
^{13}C NMR (100 MHz, $CDCl_3$) of compound ***anti*-17** and ***18***.



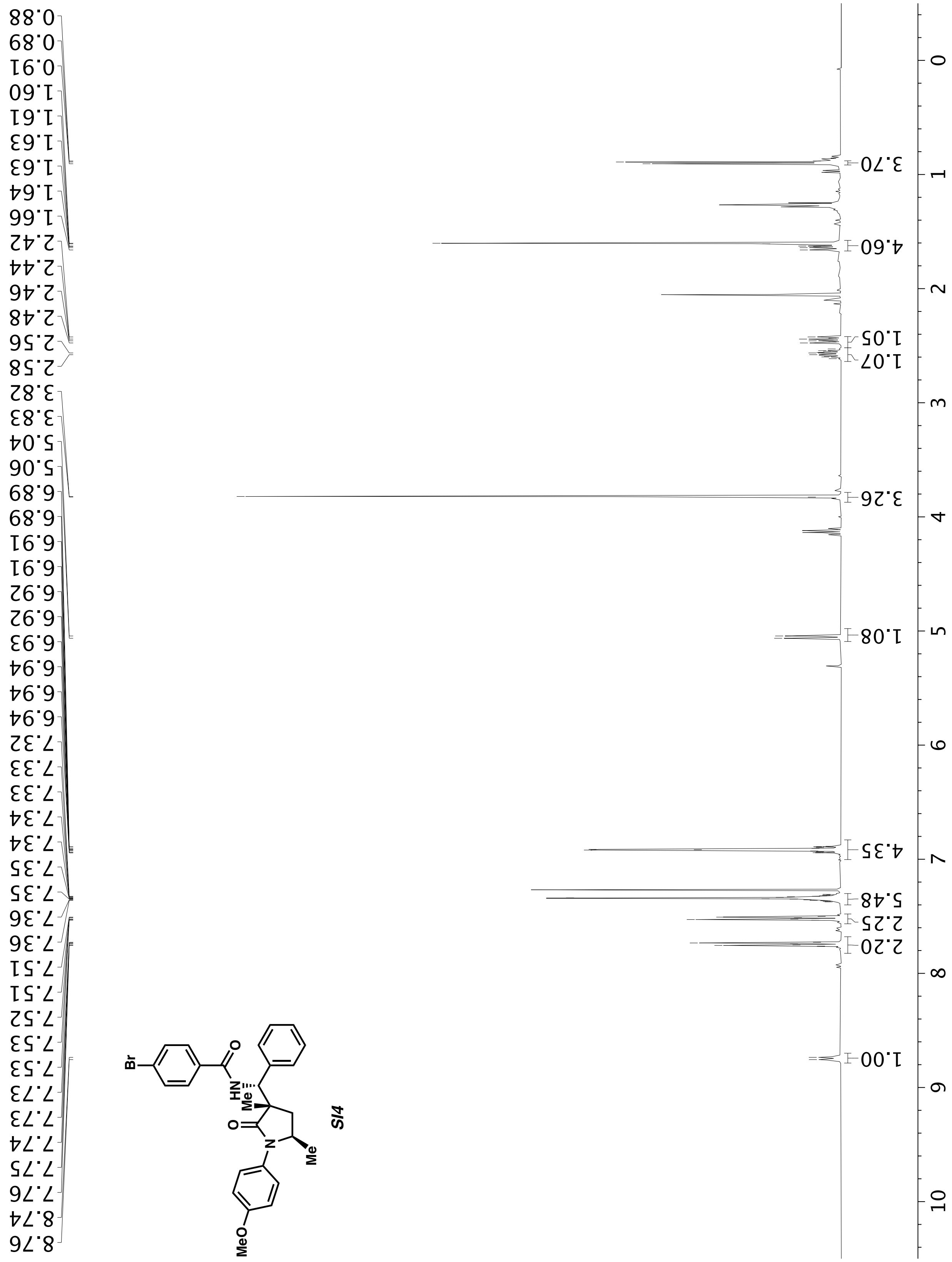
^{1}H NMR (400 MHz, $CDCl_3$) of compound **S12**.



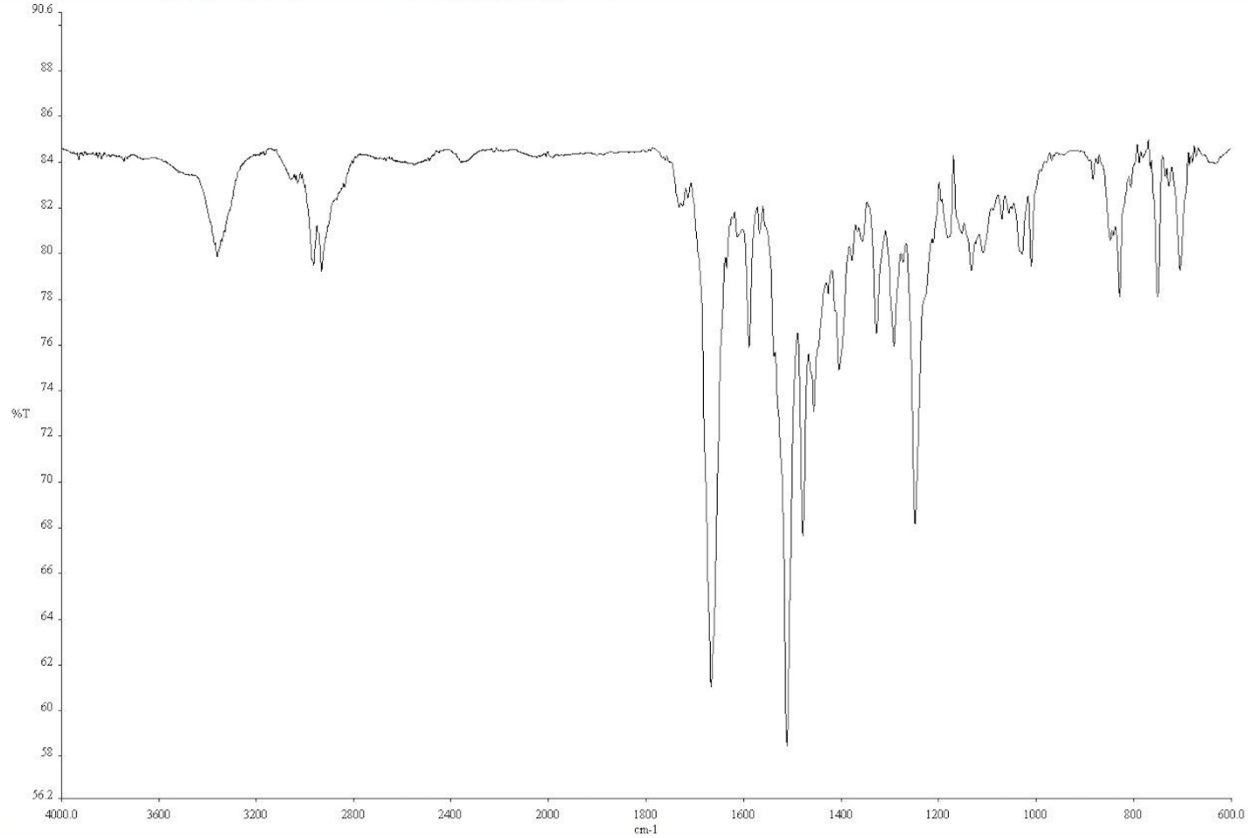
Infrared spectrum (Thin Film, NaCl) of compound **SI2**.



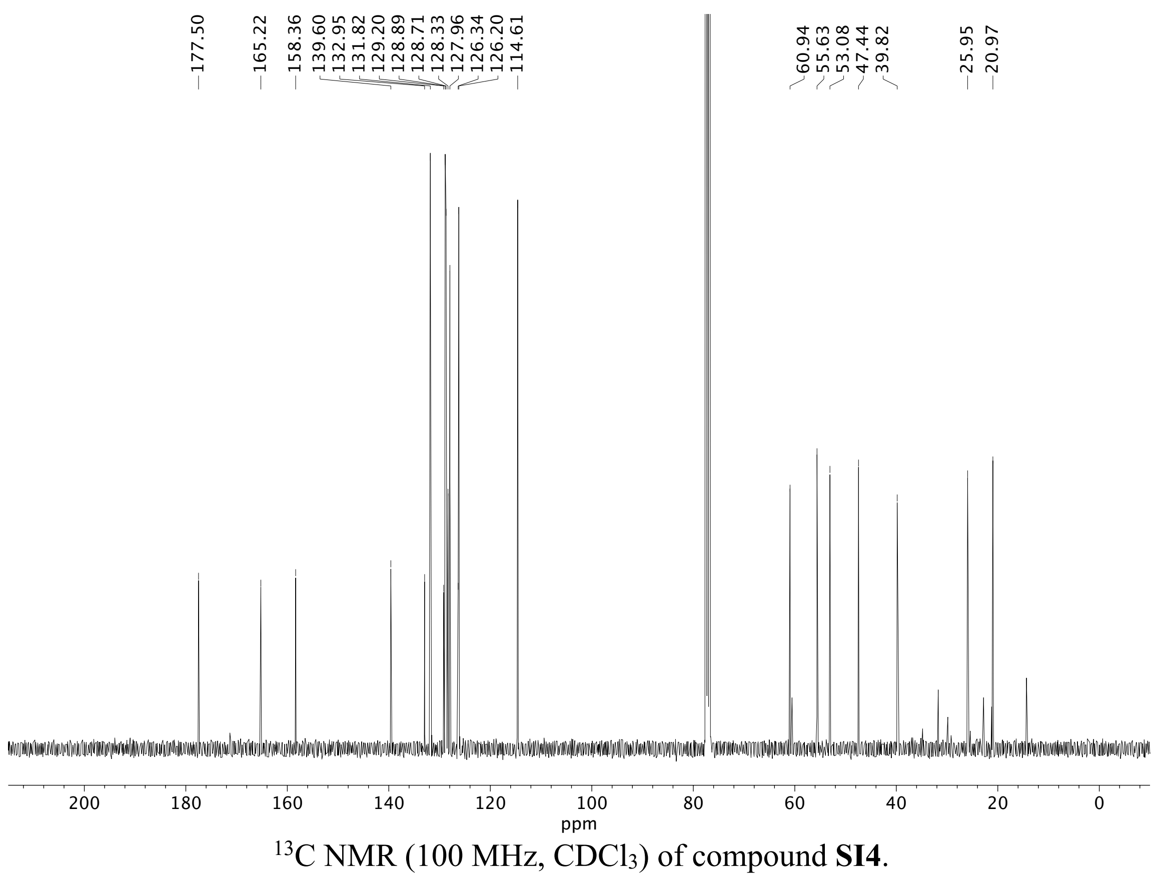
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI2**.



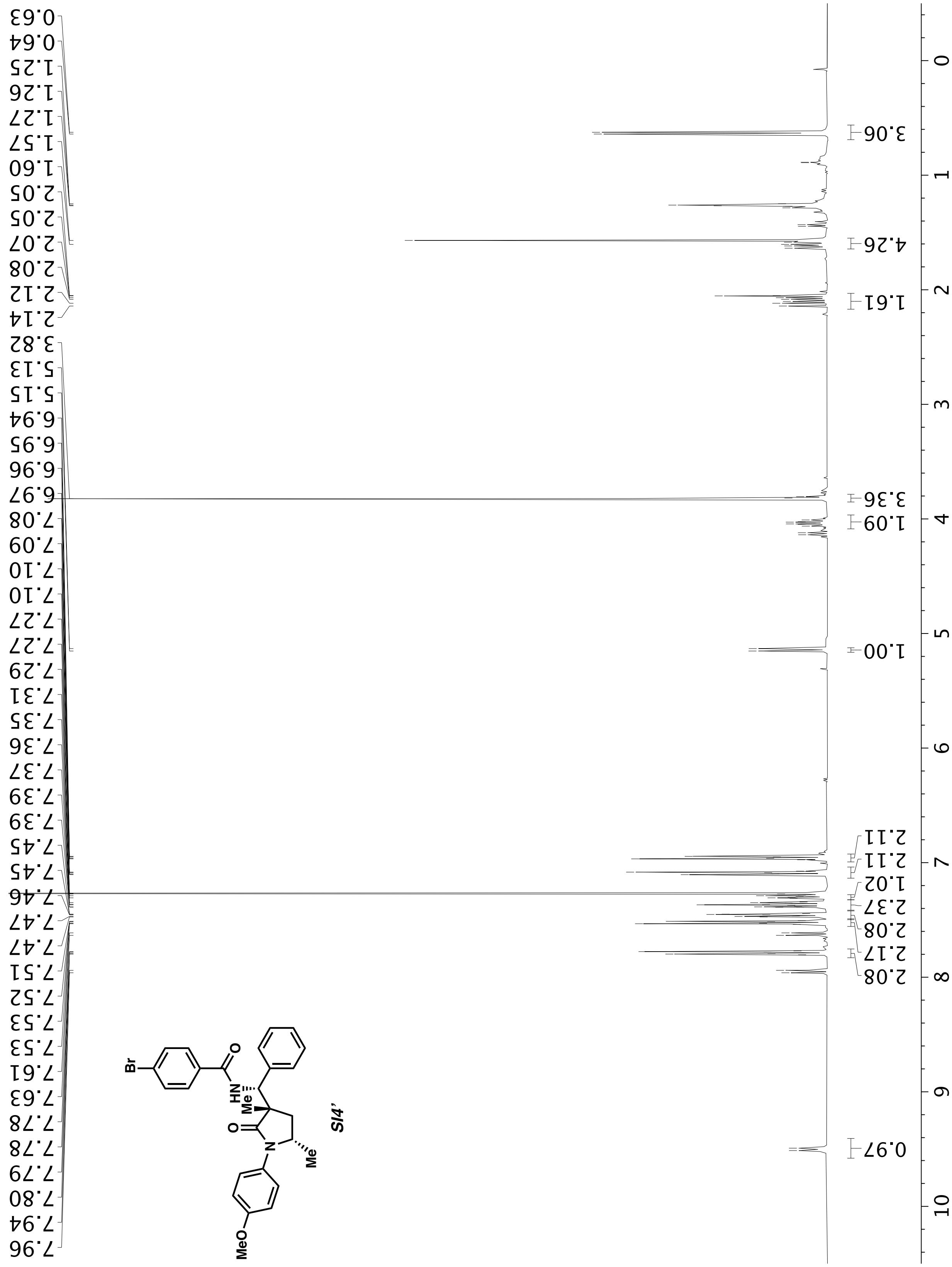
[1]H NMR (400 MHz, $CDCl_3$) of compound **S14**.



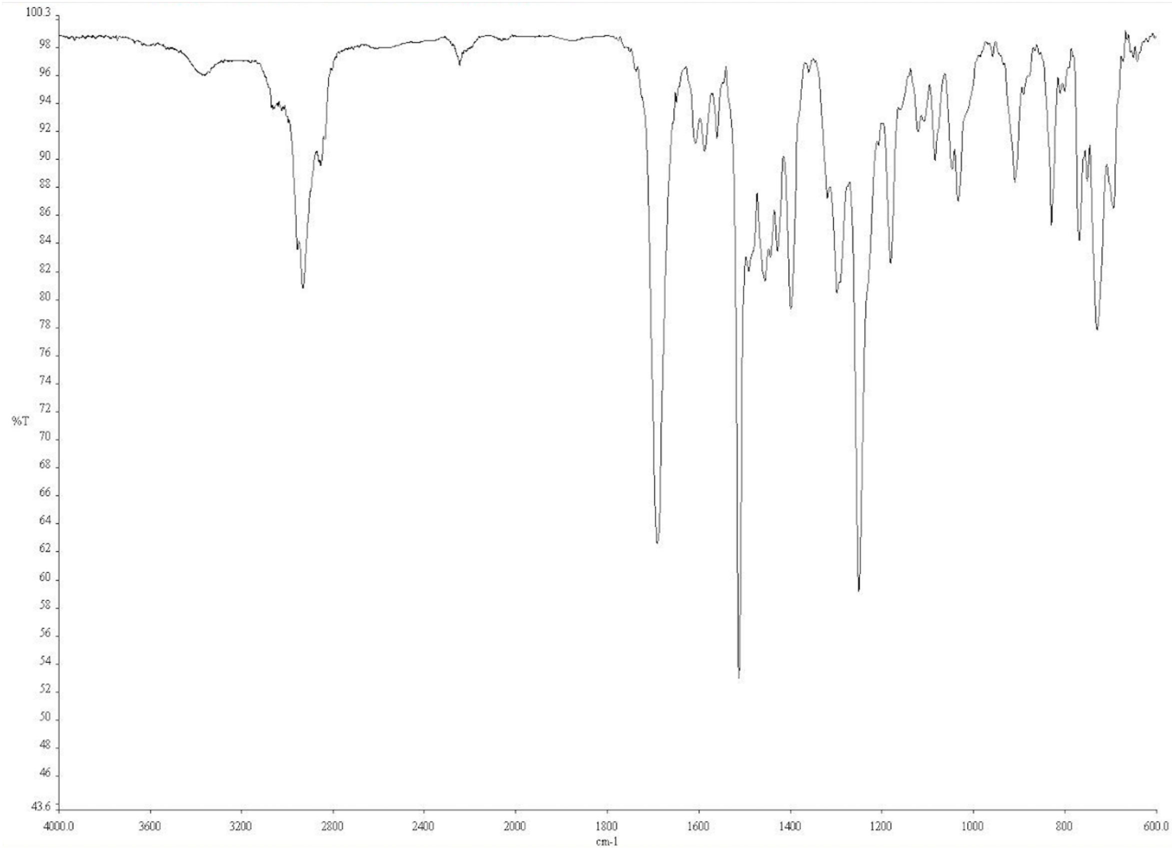
Infrared spectrum (Thin Film, NaCl) of compound **SI4**.



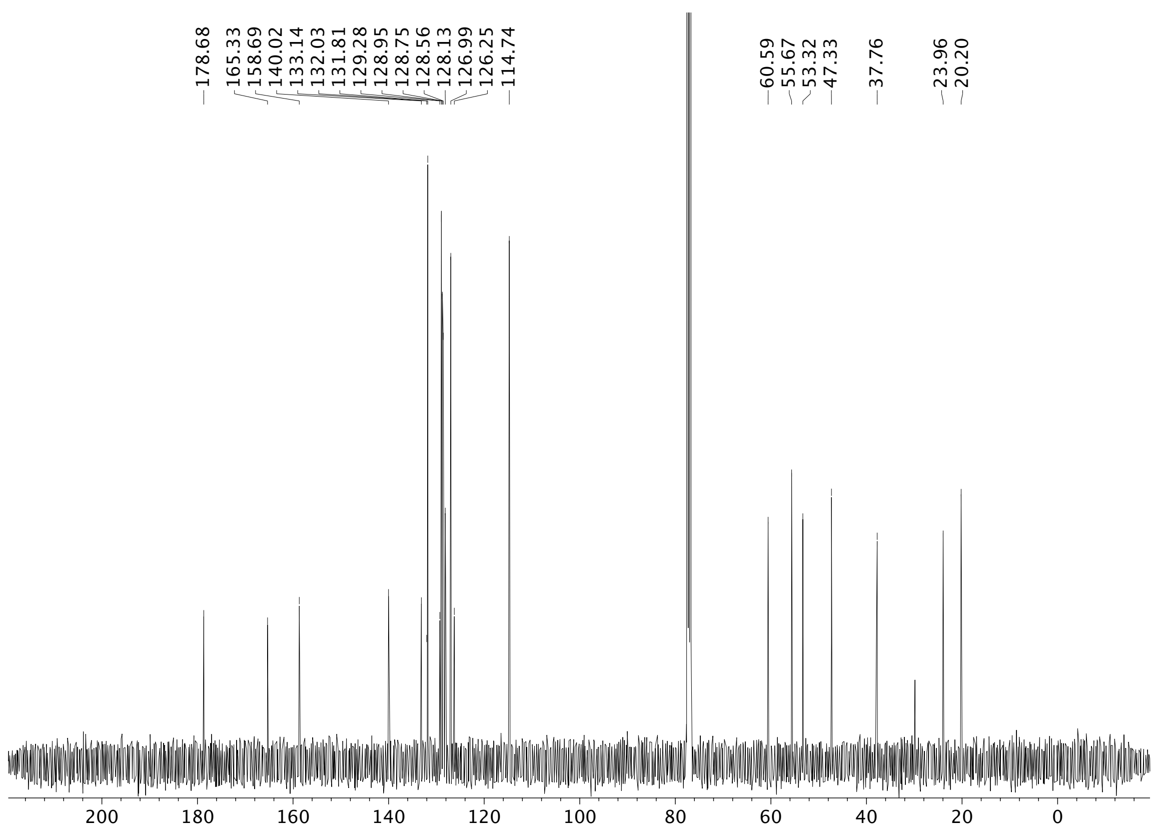
^{13}C NMR (100 MHz, CDCl$_3$) of compound **SI4**.



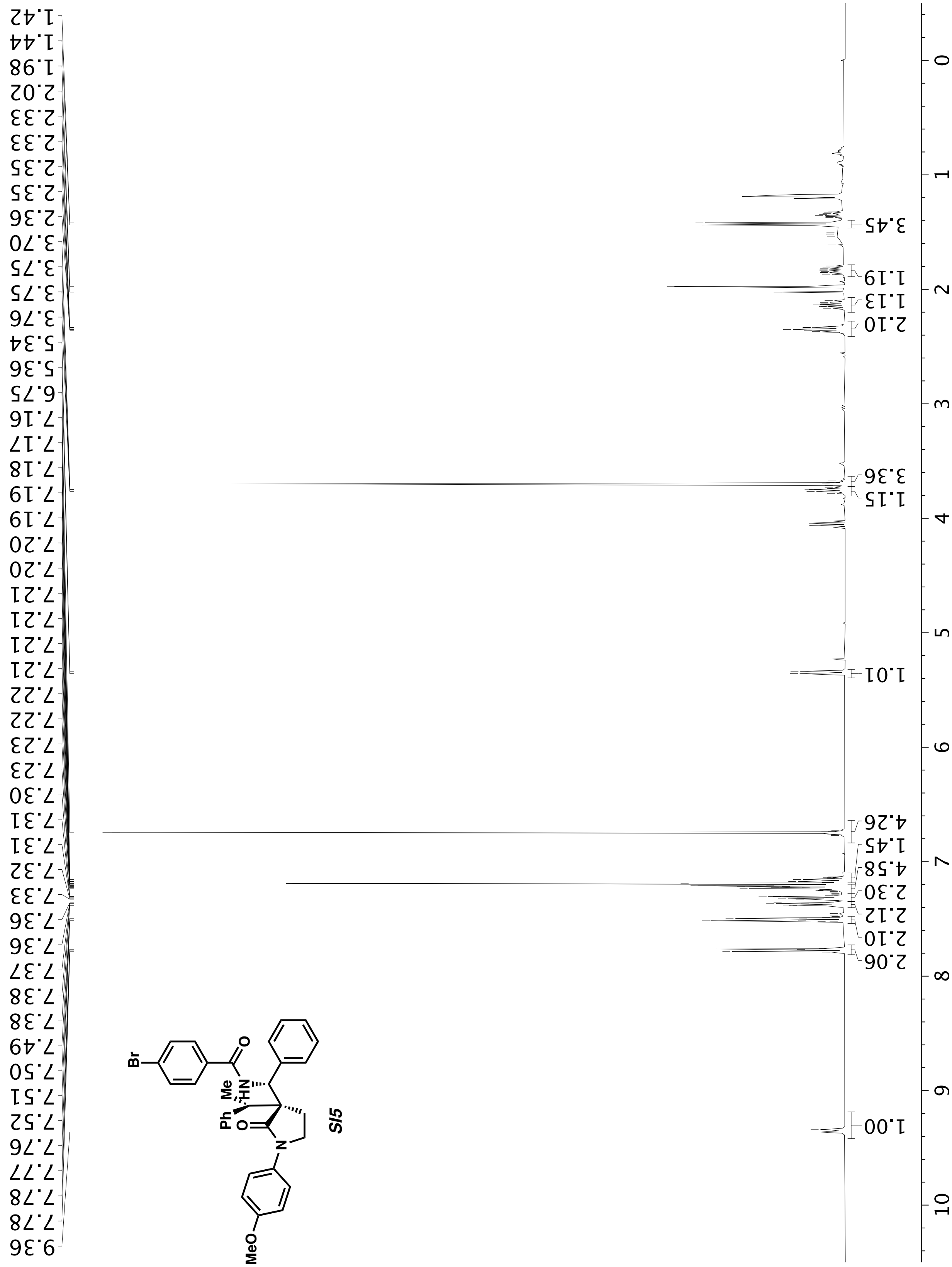
^{1}H NMR (400 MHz, $CDCl_3$) of compound **S14'** .



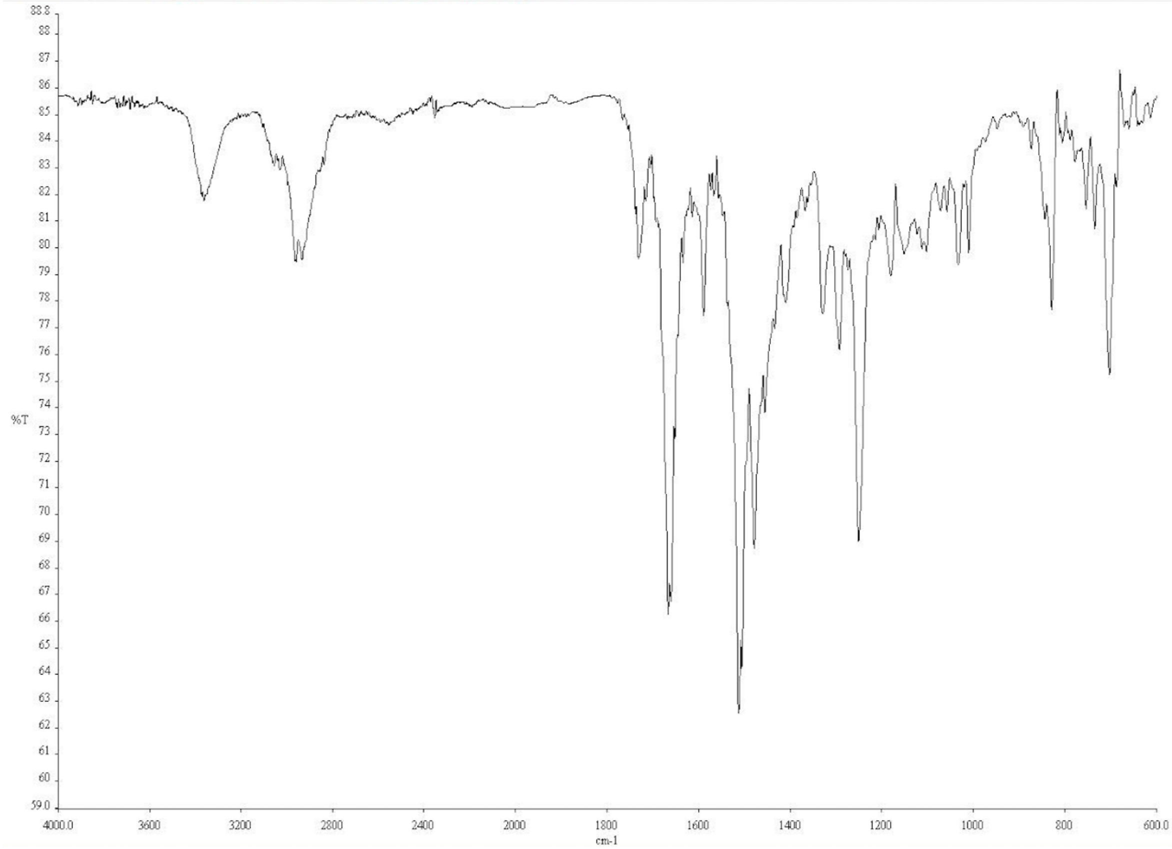
Infrared spectrum (Thin Film, NaCl) of compound **SI4'**.



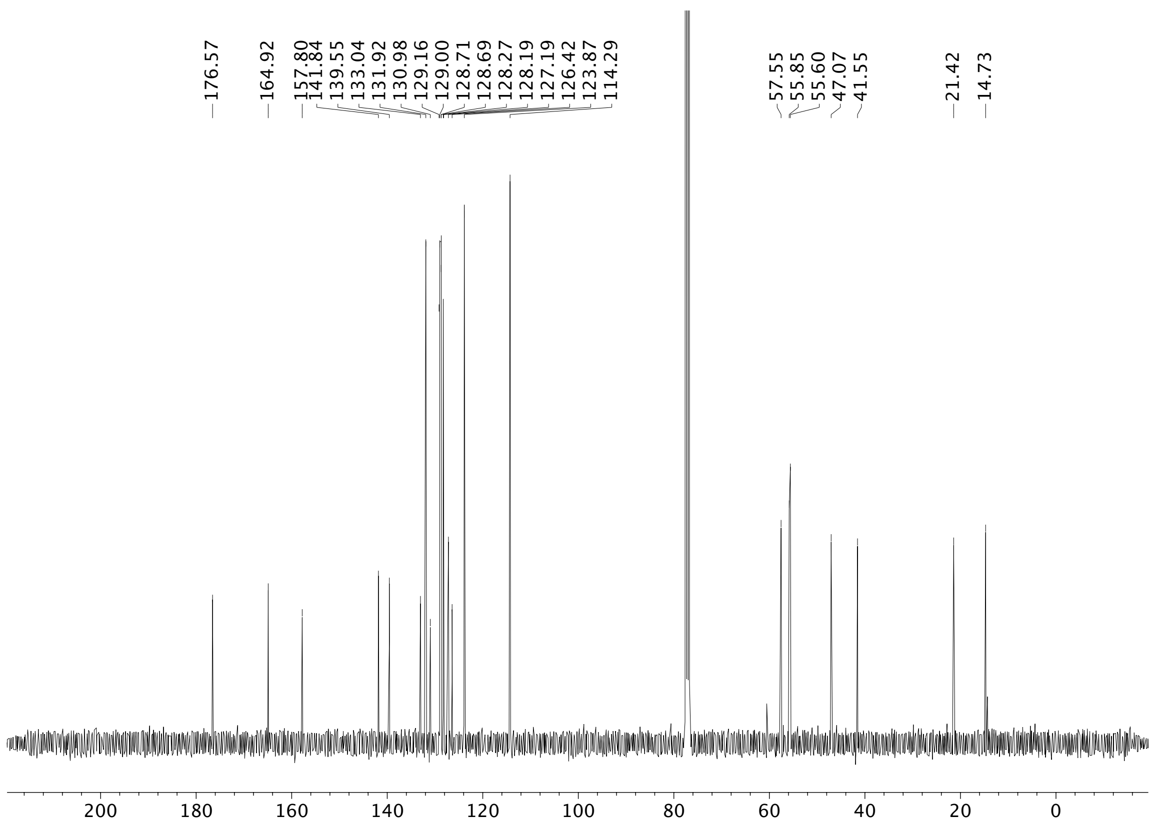
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI4'**.



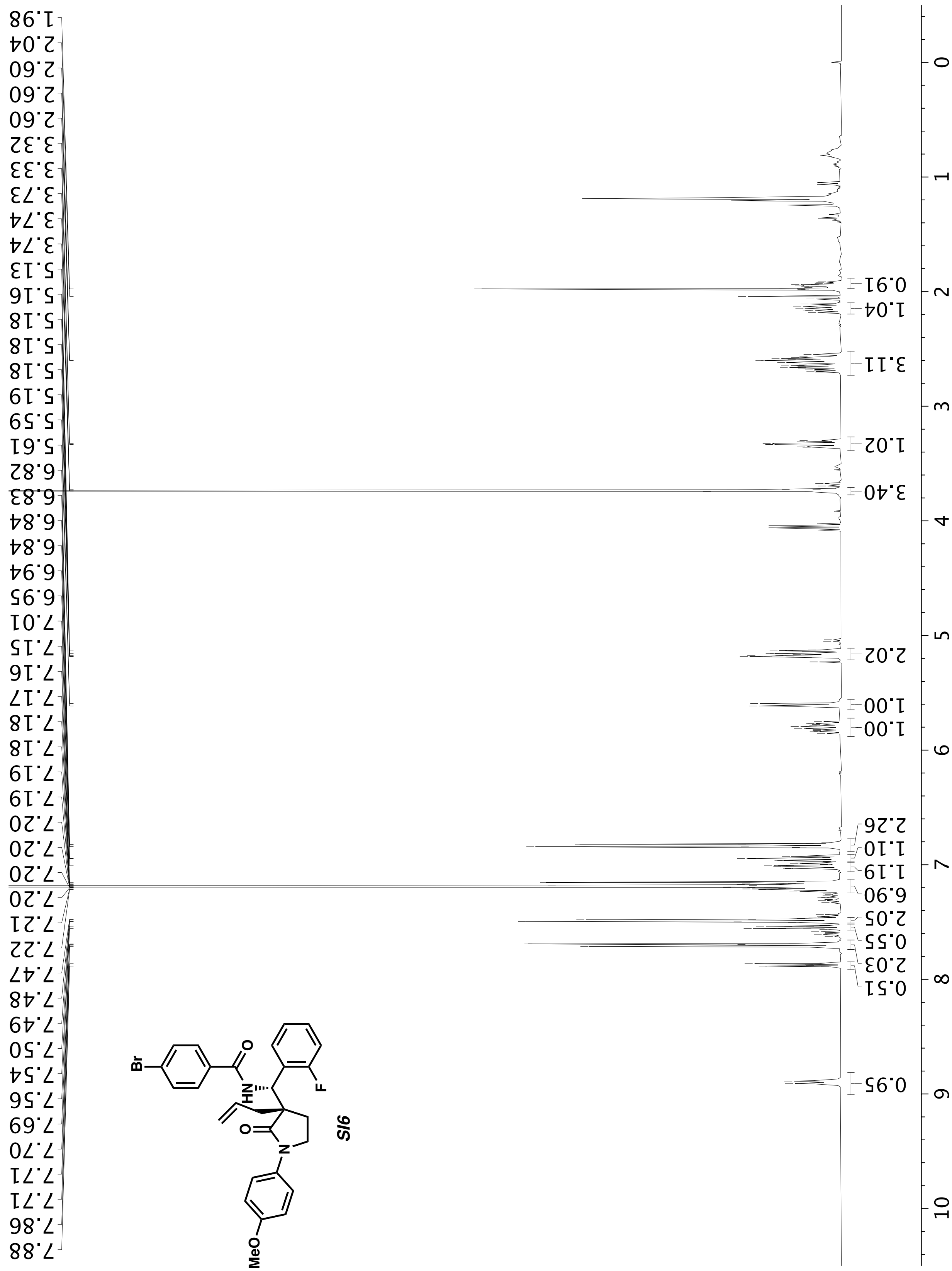
^{1}H NMR (400 MHz, $CDCl_3$) of compound **S15**.



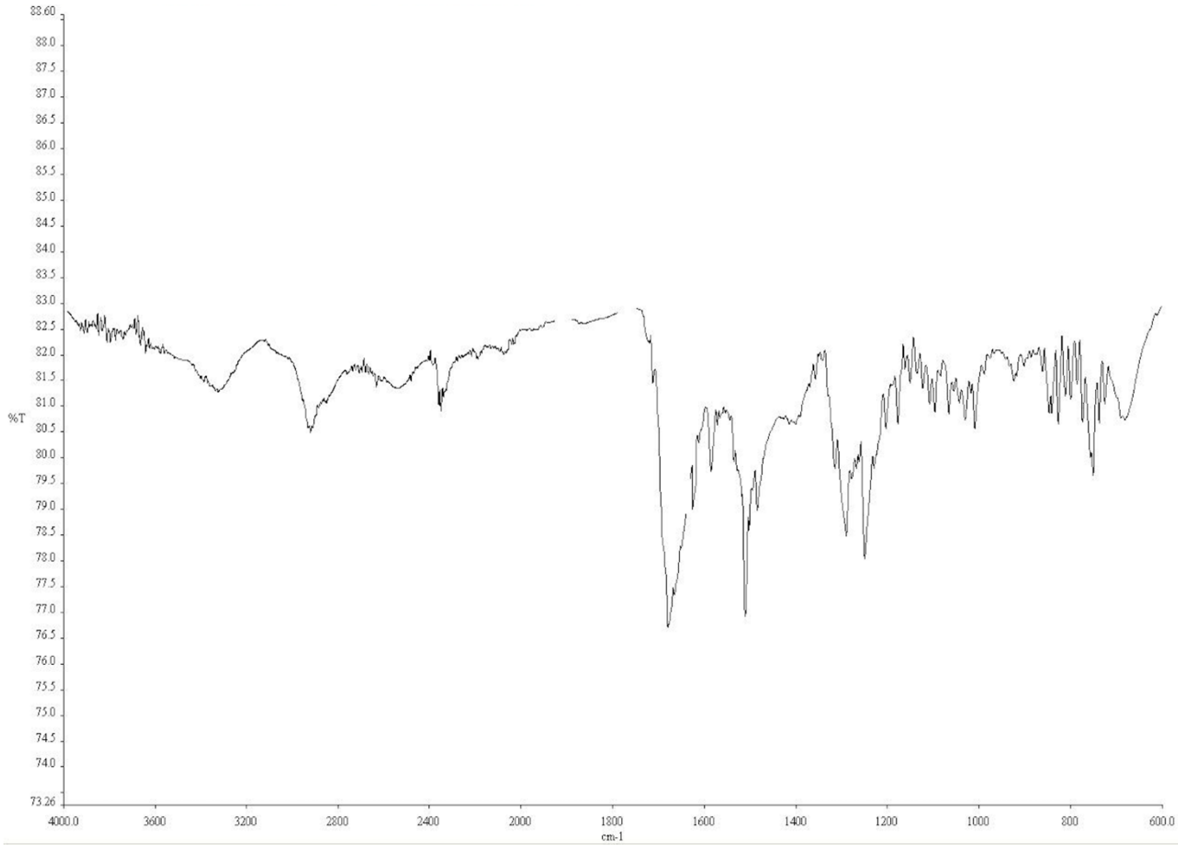
Infrared spectrum (Thin Film, NaCl) of compound **SI5**.



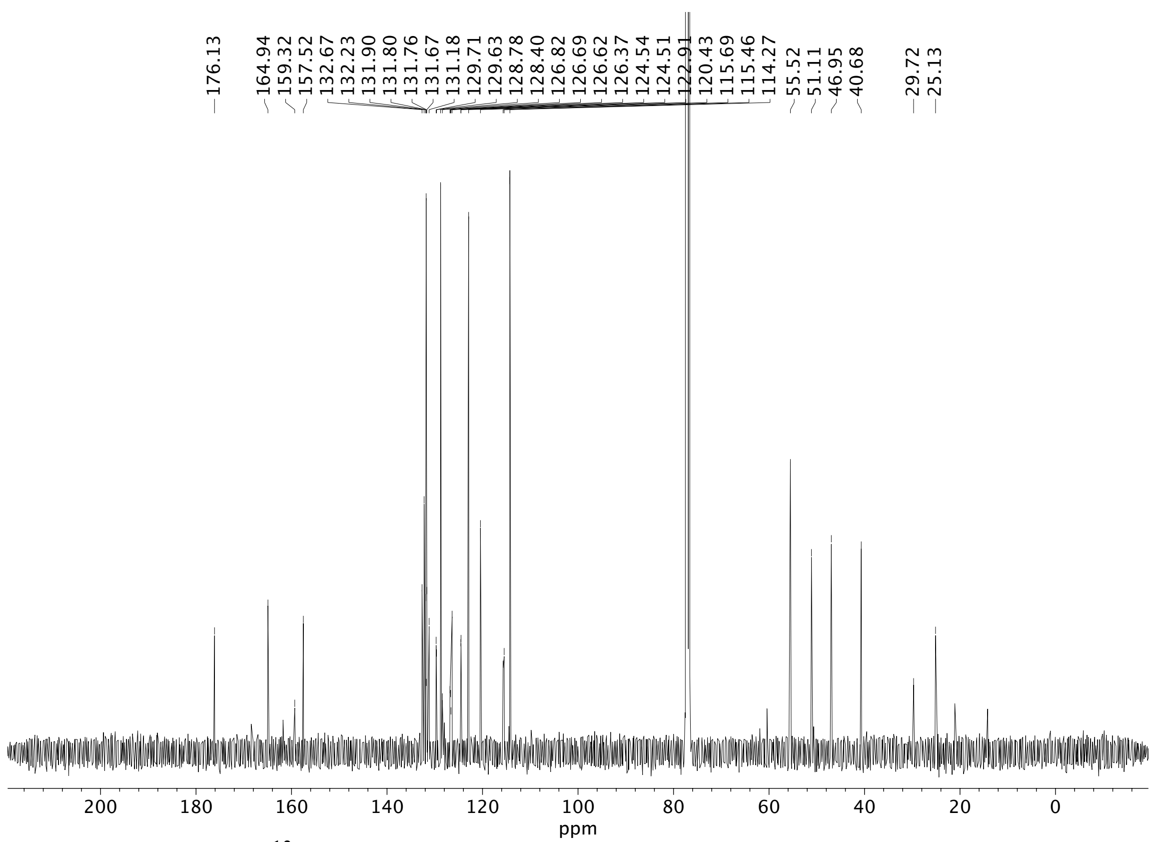
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI5**.



^{1}H NMR (400 MHz, $CDCl_3$) of compound **S16**.



Infrared spectrum (Thin Film, NaCl) of compound **SI6**.



^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI6**.