Acceptorless Dehydrogenative Condensation: Synthesis of Indoles and Quinolines from Diols and Anilines.

Electronic Supplementary Information

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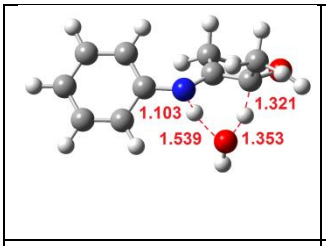
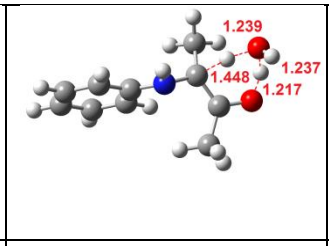
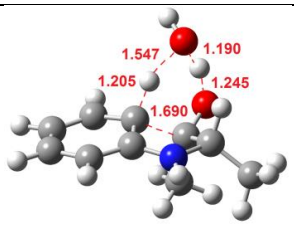
Optimized Geometries



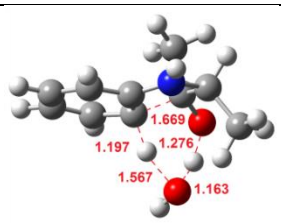
TS1a



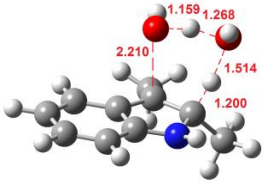
TS2a



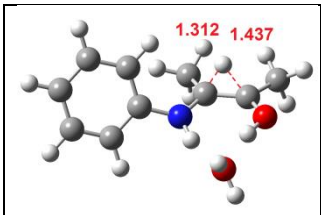
TS3a1



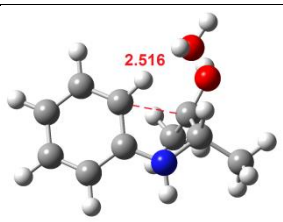
TS3a2



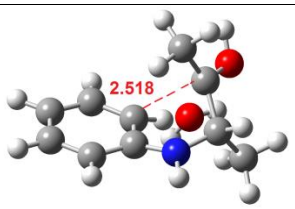
TS4a1



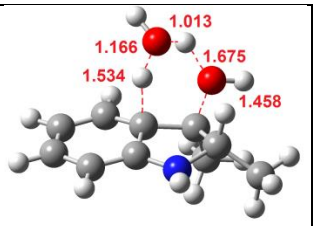
TS1b



TS3b1



TS3b2



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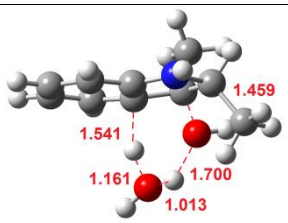
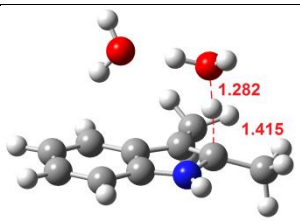


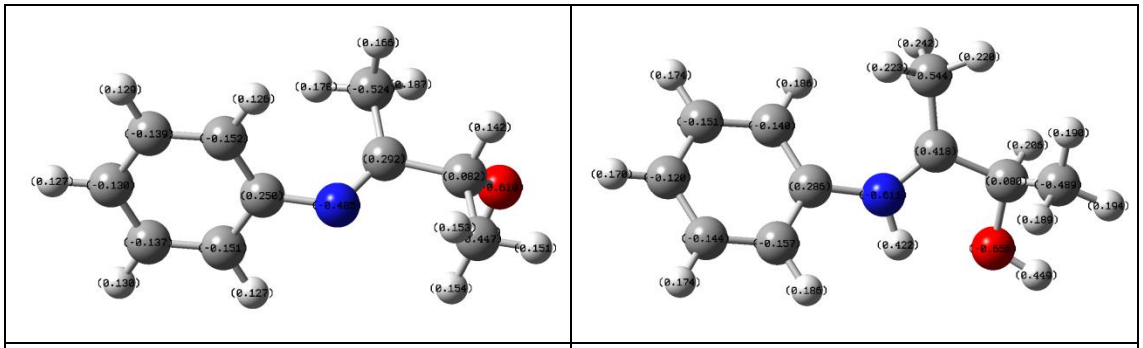
TS4b2



TS5b

Figure S1. Geometries at B3LYP/6-31G* level of TSs involved in the transformation imine **Ia** into indole **II** catalysed with H_2O.

Figure S2. Geometries at B3LYP/6-31G* level of TSs involved in the transformation imine **Ia** into indole **II** catalysed with H_2O and TsOH.



Ia	Ib

Figure S3. Mulliken atomic charges.

IRCs

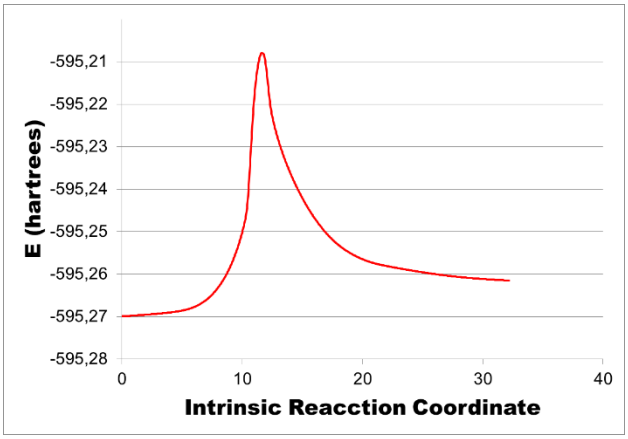


Figure S4. Energy profile (IRC, *E*) corresponding to the transition structure **TS1a** in **gas-phase**

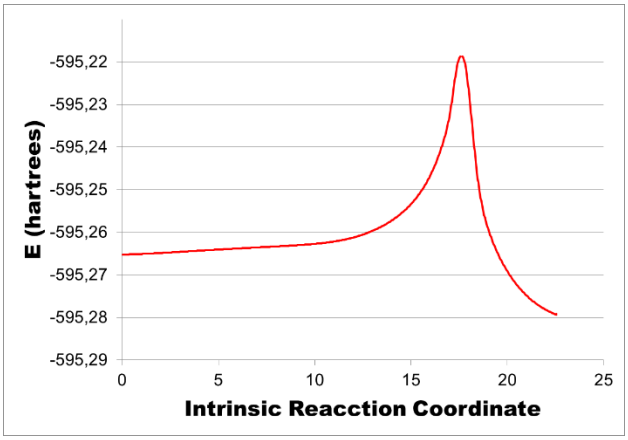


Figure S5. Energy profile (IRC, *E*) corresponding to the transition structure **TS2a** in **gas-phase**

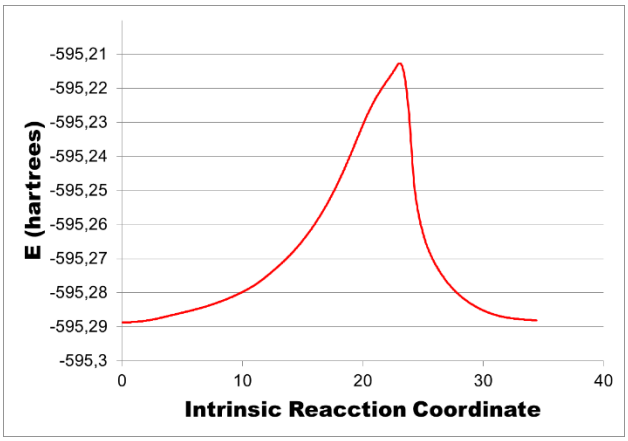


Figure S6. Energy profile (IRC, *E*) corresponding to the transition structure **TS3a1** in **gas-phase**

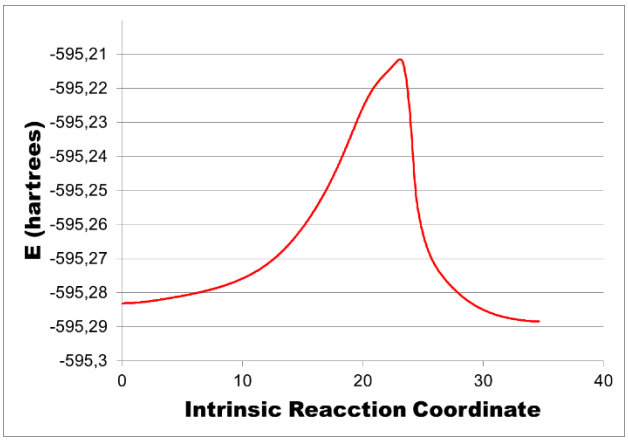


Figure S7. Energy profile (IRC, *E*) corresponding to the transition structure **TS3a2** in **gas-phase**

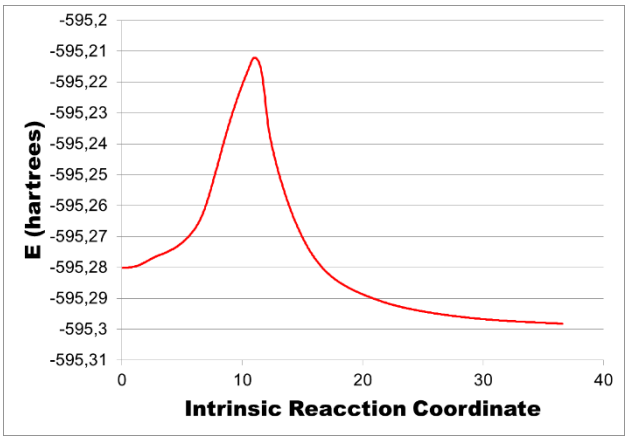


Figure S8. Energy profile (IRC, *E*) corresponding to the transition structure **TS4a1** in **gas-phase**

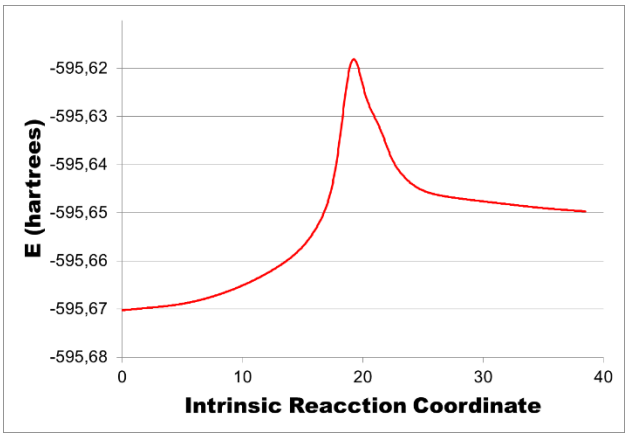


Figure S9. Energy profile (IRC, *E*) corresponding to the transition structure **TS1b** in **gas-phase**

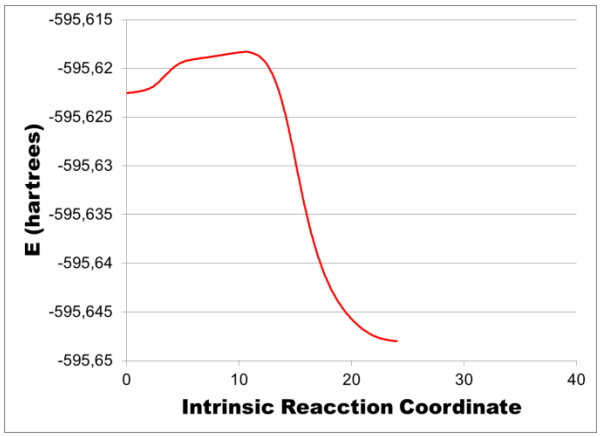


Figure S10. Energy profile (IRC, *E*) corresponding to the transition structure **TS3b1** in **gas-phase**

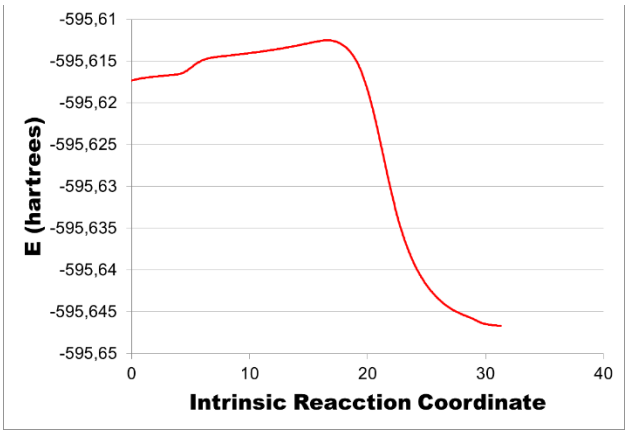


Figure S11. Energy profile (IRC, *E*) corresponding to the transition structure **TS3b2** in **gas-phase**

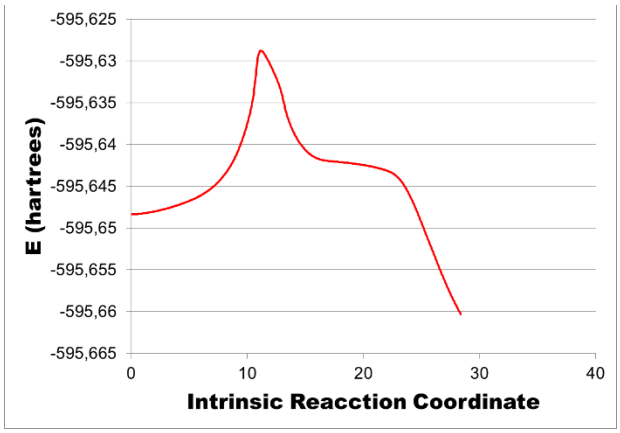


Figure S12. Energy profile (IRC, *E*) corresponding to the transition structure **TS4b1** in **gas-phase**

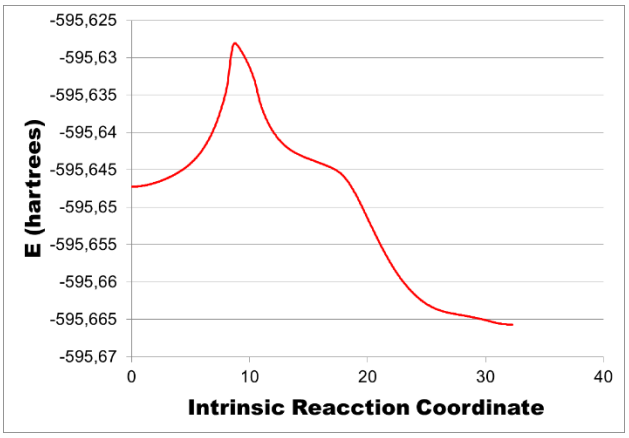


Figure S13. Energy profile (IRC, *E*) corresponding to the transition structure **TS4b2** in **gas-phase**

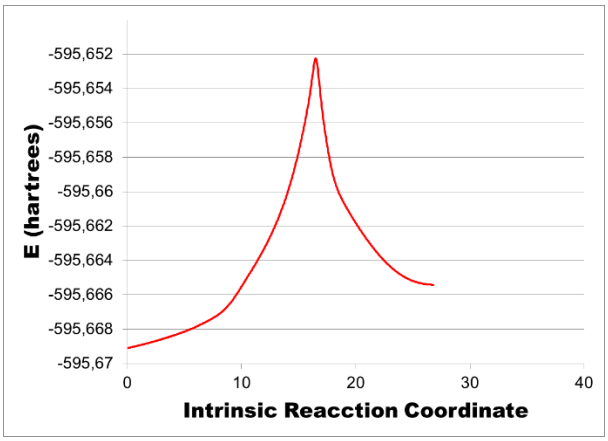


Figure S14. Energy profile (IRC, *E*) corresponding to the transition structure **TS5b** in **gas-phase**

Figure S15. Mechanism for the transformation of the imine **Ia** into indole **II** catalysed with H_2O at B3LYP level (See Table S1)

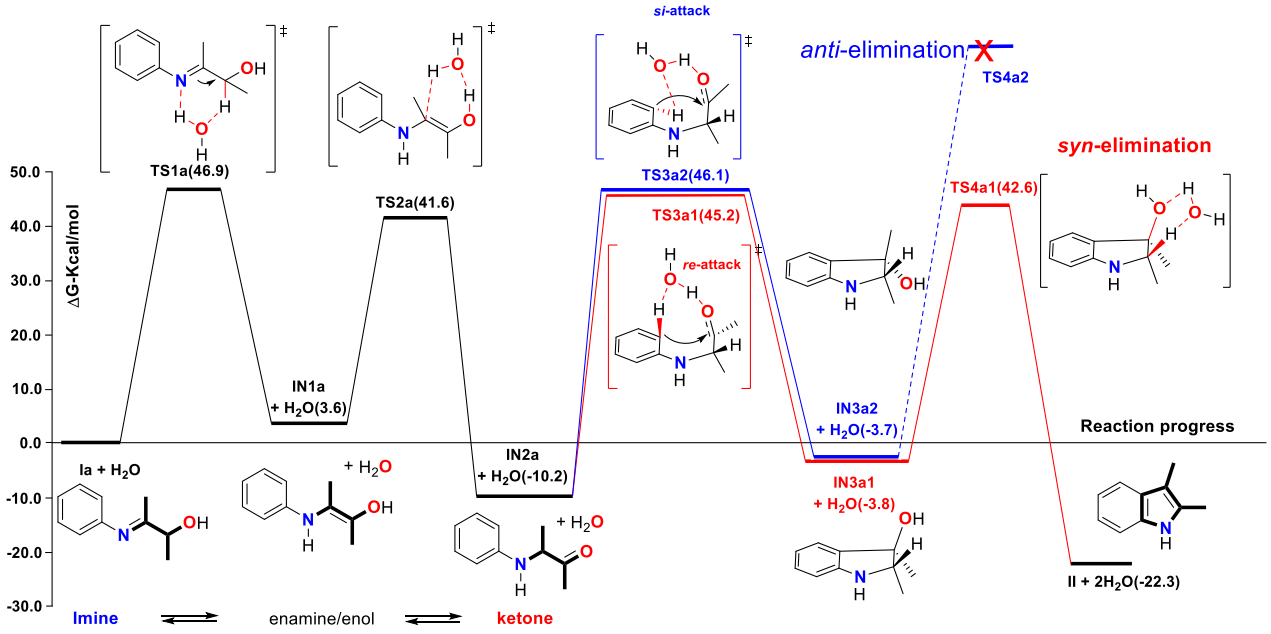


Figure S16. Mechanism for the transformation of the imine **Ia** into indole **II** catalysed with H_2O and p-TSA at B3LYP level (See Table S2)

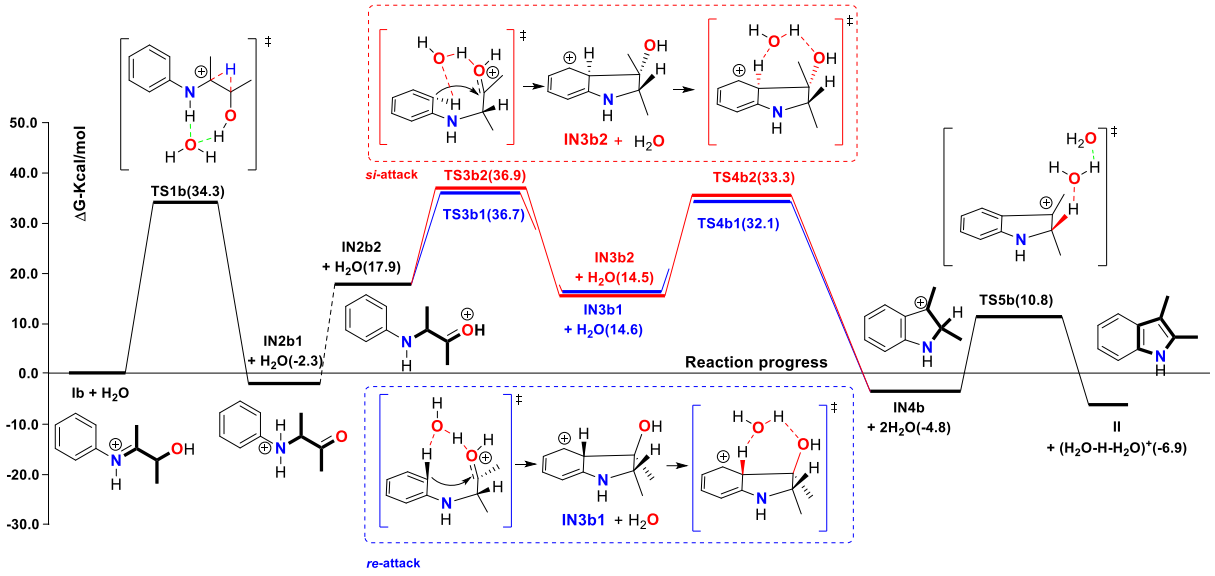
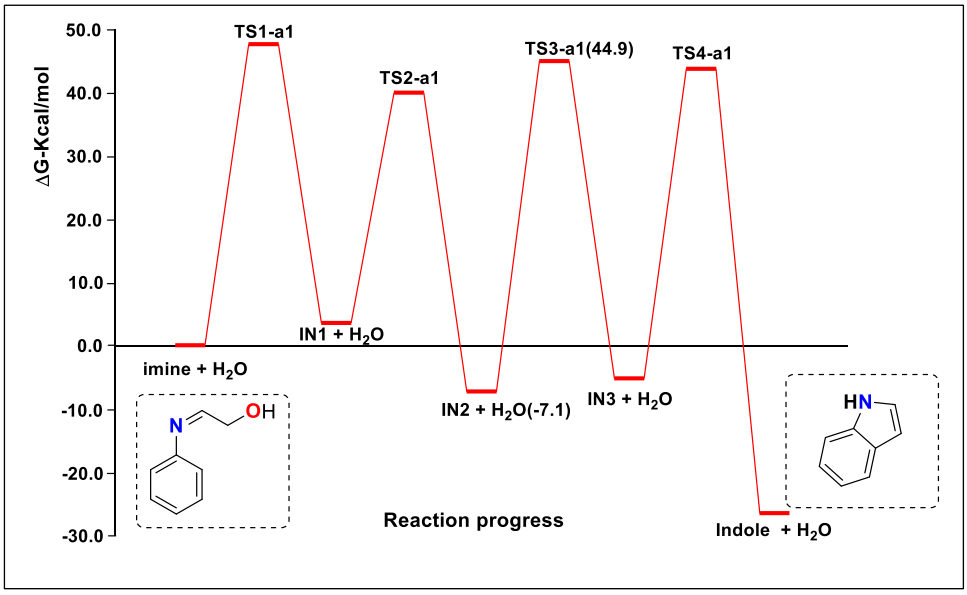


Figure S17. Transformation of imine (from aniline and 1,2-Ethyleneglycol) into indole catalysed with H_2O. Free energy profile (ΔG) at B3LYP/6-31G* level in 1,2-Ethyleneglycol as solvent.(See Table S3)



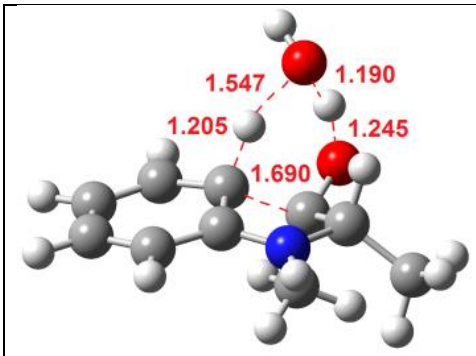
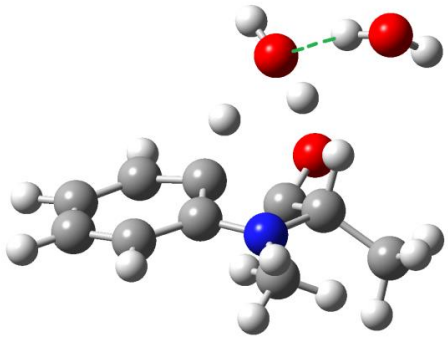
	
TS3a1	**TS3a1-1H2O**
ΔG=36.9 kcal/mol relative to **Ia** + **H_2O** (see Table S4)	G=-671,505922 au ΔG=22.4 kcal/mol relative to **Ia** + **$2H_2O$** (see Table S4)

Figure S18. Comparison of the energy of **TS3a1** with **TS3a1-1H2O** (with the additional water molecule) at B3LYP-D3/6-31G* level. **TS3a1-1H2O** has been calculated keeping the core of the transition state frozen.

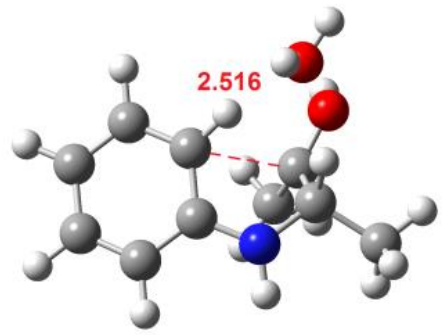
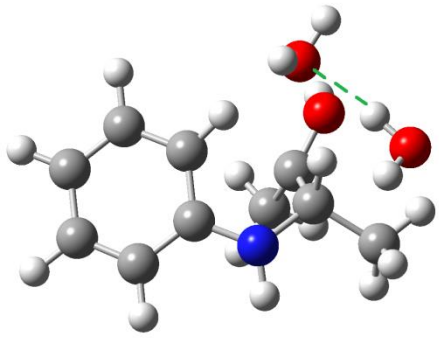
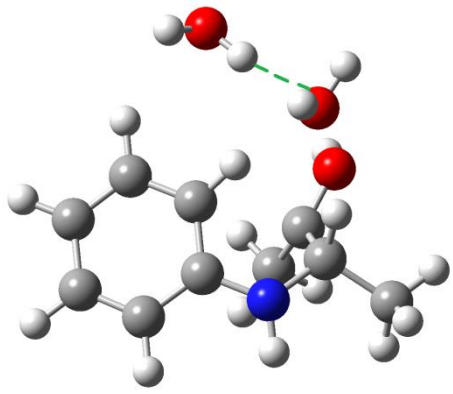
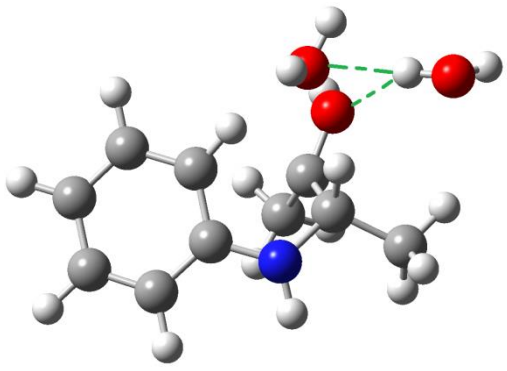
	
TS3b1	**TS3b1-1H2O-1**
ΔG=24.8 kcal/mol relative to **Ib** + **H_2O** (see Table S5)	G=-671,946571 au ΔG=20.7 kcal/mol relative to **Ib** + **$2H_2O$** (see Table S5)
	
TS3b1-1H2O-2	**TS3b1-1H2O-3**
G=--671,950031 au ΔG=18.5 kcal/mol relative to **Ib** + **$2H_2O$** (see Table S5)	G=-671,947817 au ΔG=19.9 kcal/mol relative to **Ib** + **$2H_2O$** (see Table S5)

Figure S19. Comparison of the energy of **TS3b1** with **TS3b1-1H2O-1,2,3** (with the additional water molecule) at B3LYP-D3/6-31G* level. **TS3b1-1H2O** has been calculated keeping the core of the transition state frozen. Note: Observe the calculated energy difference depending on the location and orientation of the additional water molecule.

Table S1. Transformation of imine **Ia** into indole **II** catalysed with H_2O. B3LYP/6-31G* total energies (*E*, au) in gas phase. B3LYP/6-31G* total energies (*E*,*H* and *G* in au), *S* (Cal/Mol-Kelvin) and ΔG (kcal/mol) in N,N-dimethylacetamide (423.15 K). (see Figure S15)

	B3LYP/6-31G*	B3LYP/6-31G*. solvent = N,N-dimethylacetamide				
	E	*E*	*H*	*S*	*G*	*ΔG*
Ia	-518.848375	-518.855583	-518.620440	131.006	-518.708782	
H_2O	-76.408954	-76.416124	-76.389571	47.956	-76.421910	
IN1a	-518.843929	-518.851236	-518.615990	129.161	-518.703087	
IN2a	-518.865575	-518.873927	-518.638518	128.325	-518.725052	
IN3a1	-518.863570	-518.871222	-518.635259	117.961	-518.714804	
IN3a2	-518.863550	-518.870937	-518.634922	118.233	-518.714651	
II	-442.456083	-442.462727	-442.257025	113.309	-442.333434	
$2H_2O$	-152.830336	-152.839557	-152.784484	71.647	-152.832798	
Ia + **H_2O**	-595.257329	-595.271707	-595.010011	178.962	-595.130692	0.0
TS1a	-595.207924	-595.219697	-594.962219	138.955	-595.055921	46.9
IN1a + **H_20**	-595.252883	-595.267360	-595.005561	177.117	-595.124997	3.6
TS2a	-595.218671	-595.228612	-594.972407	136.518	-595.064465	41.6
IN2a + **H_20**	-595.274529	-595.290051	-595.028089	176.281	-595.146962	-10.2
TS3a1	-595.212638	-595.228712	-594.971903	128.680	-595.058676	45.2
IN3a1 + **H_20**	-595.272524	-595.287346	-595.024830	165.917	-595.136714	-3.8
TS4a1	-595.212157	-595.228105	-594.971620	135.148	-595.062754	42.6
II + **$2H_2O$**	-595.286419	-595.302285	-595.041509	184.956	-595.166232	-22.3
TS3a2	-595.211452	-595.228037	-594.971062	127.737	-595.057200	46.1
IN3a2 + **H_20**	-595.272504	-595.287061	-595.024493	166.189	-595.136561	-3.7

Table S2. Transformation of imine **Ib** into indole **II** catalysed with H_2O and TsOH. B3LYP/6-31G* total energies (*E*, au) in gas phase. B3LYP/6-31G* total energies (*E*,*H* and *G* in au), *S* (Cal/Mol-Kelvin) and ΔG (kcal/mol) in N,N-dimethylacetamide (423.15 K). (see Figure S16)

	B3LYP/6-31G*	B3LYP/6-31G*. solvent = N,N-dimethylacetamide				
	E	*E*	*H*	*S*	*G*	*ΔG*
Ib	-519.240394	-519.310435	-519.062613	124.831	-519.146791	
H_2O	-76.4089536	-76.416124	-76.389571	47.956	-76.421910	
IN2b1	-519.238769	-519.315732	-519.065048	126.719	-519.150498	
IN2b2	-519.208780	-519.283405	-519.034287	124.454	-519.118210	
IN3b1	-519.219915	-519.291836	-519.044441	117.291	-519.123534	
IN3b2	-519.219715	-519.291677	-519.042864	119.843	-519.123678	
IN4b	-442.816429	-442.886055	-442.667451	112.759	-442.743488	
II	-442.456083	-442.462727	-442.257025	113.309	-442.333434	
$2H_2O$	-152.830336	-152.839557	-152.784484	71.647	-152.832798	
$(H_2O\text{-}H\text{-}H_2O)^+$	-153.163083	-153.264847	-153.199040	70.041	-153.246271	
Ib + **H_2O**	-595.649348	-595.726559	-595.452184	172.787	-595.568701	0.0
TS1b	-595.618084	-595.690297	-595.416648	144.315	-595.513964	34.3
IN2b1 + **H_20**	-595.647722	-595.731856	-595.454619	174.675	-595.572408	-2.3
IN2b2 + **H_20**	-595.617734	-595.699529	-595.423858	172.410	-595.540120	17.9
TS3b1	-595.618277	-595.691076	-595.417336	137.824	-595.510275	36.7
IN3b1 + **H_20**	-595.628868	-595.707960	-595.434012	165.247	-595.545444	14.6
TS4b1	-595.628773	-595.701134	-595.428722	131.649	-595.517497	32.1
TS3b2	-595.612475	-595.685669	-595.411275	146.349	-595.509963	36.9
IN3b2 + **H_20**	-595.628669	-595.707801	-595.432435	167.799	-595.545588	14.5
TS4b2	-595.628033	-595.700619	-595.427712	130.478	-595.515697	33.3
IN4b + **$2H_20$**	-595.646765	-595.725612	-595.446593	184.406	-595.576286	-4.8
TS5b	-595.652245	-595.723360	-595.451968	147.619	-595.551513	10.8
II + **$(H_2O\text{-}H\text{-}H_2O)^+$**	-595.619166	-595.727575	-595.456065	183.350	-595.579705	-6.9

Table S3. Transformation of imine into indole catalysed with H_2O. B3LYP/6-31G* total energies (*E*, au) in gas phase. B3LYP/6-31G* total energies (*E*,*H* and *G* in au), *S* (Cal/Mol-Kelvin) and ΔG (kcal/mol) in 1,2-Ethyleneglycol (423.15 K). (see Figure S17)

	B3LYP/6-31G*	B3LYP/6-31G*. solvent = 1.2-Ethanediol				
	E	*E*	*H*	*S*	*G*	*ΔG*
imine	-440.210750	-440.218655	-440.045121	113.810	-440.121866	
H_2O	-76.408954	-76.416149	-76.389596	49.333	-76.422863	
IN1	-440.204747	-440.213484	-440.039680	113.058	-440.115919	
IN2	-440.222967	-440.231728	-440.058285	110.965	-440.133112	
IN3	-440.228071	-440.236193	-440.061358	101.598	-440.129869	
indole	-363.816693	-363.823780	-363.679597	90.996	-363.740959	
imine + H_2O	-516.619704	-516.634803	-516.434717	163.143	-516.544729	0.0
TS1-a1	-516.571441	-516.583557	-516.389997	116.999	-516.468893	47.6
IN1-a + H_2O	-516.613701	-516.629632	-516.429276	162.391	-516.538782	3.7
TS2-a1	-516.584425	-516.595025	-516.400621	118.586	-516.480588	40.2
IN2-a + H_20	-516.631921	-516.647876	-516.447881	160.298	-516.555975	-7.1
TS3-a1	-516.576555	-516.593679	-516.398099	111.375	-516.473203	44.9
IN3-a + H_2O	-516.637025	-516.652342	-516.450954	150.931	-516.552732	-5.0
TS4-a1	-516.576639	-516.591277	-516.396870	115.460	-516.474728	43.9
indole + $2H_2O$	-516.634601	-516.656077	-516.458789	189.662	-516.586685	-26.3

Table S4. Transformation of imine **Ia** into indole **II** catalysed with H_2O. B3LYP-D3/6-31G* total energies (*E*,*H* and *G* in au), *S* (Cal/Mol-Kelvin) and ΔG (kcal/mol) in N,N-dimethylacetamide (423.15 K). (see Figure 3)

	B3LYP-D3/6-31G*. solvent = N,N-dimethylacetamide				
	E	*H*	*S*	*G*	*ΔG*
Ia	-518.875610	-518.641732	122.184	-518.724125	
H_2O	-76.416132	-76.389581	47.956	-76.421920	
IN1a	-518.871034	-518.635770	129.507	-518.723100	
IN2a	-518.895468	-518.659908	128.379	-518.746478	
IN3a1	-518.894121	-518.657993	117.493	-518.737222	
IN3a2	-518.894233	-518.658064	117.668	-518.737411	
II	-442.477989	-442.272308	113.846	-442.349078	
$2H_2O$	-152.841023	-152.785963	71.638	-152.834271	
Ia + **H_2O**	-595.291742	-595.031313	170.140	-595.146045	0.0
TS1a	-595.244944	-594.987332	137.982	-595.080378	41.2
IN1a + **H_20**	-595.287166	-595.025351	177.463000	-595.145020	0.6
TS2a	-595.254635	-594.998491	136.631	-595.090625	34.8
IN2a + **H_20**	-595.311600	-595.049489	176.335000	-595.168398	-14.0
TS3a1	-595.257420	-595.000581	128.546	-595.087264	36.9
IN3a1 + **H_20**	-595.310253	-595.047574	165.449000	-595.159142	-8.2
TS4a1	-595.255044	-594.998531	135.452	-595.089871	35.2
II + **$2H_2O$**	-595.319012	-595.058271	185.484000	-595.183349	-23.4
TS3a2	-595.257453	-595.000418	127.454	-595.086364	37.5
IN3a2 + **H_20**	-595.310365	-595.047645	165.624000	-595.159331	-8.3

Table S5. Transformation of imine **Ib** into indole **II** catalysed with H_2O and TsOH. B3LYP-D3/6-31G* total energies (*E*,*H* and *G* in au), *S* (Cal/Mol-Kelvin) and ΔG (kcal/mol) in N,N-dimethylacetamide (423.15 K). (see Figure 4)

	B3LYP-D3/6-31G*. solvent = N,N-dimethylacetamide				
	E	*H*	*S*	*G*	*ΔG*
Ib	-519.323855	-519.075701	120.330	-519.156843	
H_2O	-76.416132	-76.389581	47.956	-76.421920	
IN2b1	-519.338080	-519.087497	127.258	-519.173311	
IN2b2	-519.305482	-519.057868	119.620	-519.138531	
IN3b1	-519.316937	-519.069388	116.822	-519.148165	
IN3b2	-519.316965	-519.067938	119.127	-519.148269	
IN4b	-442.903663	-442.684749	111.898	-442.760206	
II	-442.477989	-442.272308	113.846	-442.349078	
$2H_2O$	-152.841023	-152.785963	71.638	-152.834271	
$(H_2O\text{-}H\text{-}H_2O)^+$	-153.266166	-153.200410	70.130	-153.247700	
Ib + **H_2O**	-595.739987	-595.465282	168.286	-595.578763	0.0
TS1b	-595.714745	-595.441070	143.954	-595.538143	25.5
IN2b1 + **H_20**	-595.754212	-595.477078	175.214	-595.595231	-10.3
IN2b2 + **H_20**	-595.721614	-595.447449	167.576	-595.560451	11.5
TS3b1	-595.718688	-595.443416	142.172	-595.539287	24.8
IN3b1 + **H_20**	-595.733069	-595.458969	164.778	-595.570085	5.4
TS4b1	-595.731548	-595.458661	130.146	-595.546422	20.3
TS3b2	-595.713637	-595.438810	148.795	-595.539147	24.9
IN3b2 + **H_20**	-595.733097	-595.457519	167.083	-595.570189	5.4
TS4b2	-595.731286	-595.458278	130.229	-595.546096	20.5
IN4b + **$2H_20$**	-595.744685	-595.463911	183.536	-595.594477	-9.9
TS5b	-595.750459	-595.479076	150.281	-595.580415	-1.0
II + **$(H_2O\text{-}H\text{-}H_2O)^+$**	-595.744155	-595.472718	183.976	-595.596778	-11.3

Z-matrix (Transformation of imine **Ia** into indole **II** catalysed with H_2O.Solvent: N,N-dimethylacetamide)

Ia 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.044910	-1.113454	0.662842
2	6	0	1.662173	-1.218256	0.531850
3	6	0	0.939861	-0.240483	-0.171225
4	6	0	1.637818	0.819989	-0.771943
5	6	0	3.025232	0.906129	-0.654494
6	6	0	3.735157	-0.053154	0.069103
7	1	0	3.588319	-1.870702	1.222322
8	1	0	1.122865	-2.051609	0.972583
9	1	0	1.087615	1.559400	-1.347038
10	1	0	3.551309	1.729580	-1.130599
11	1	0	4.815172	0.017908	0.161619
12	7	0	-0.447604	-0.414817	-0.345828
13	6	0	-1.314509	0.436114	0.051906
14	6	0	-2.792370	0.129376	-0.206144
15	1	0	-3.280178	1.058042	-0.528880
16	8	0	-3.421115	-0.167495	1.051635
17	1	0	-3.042721	-1.008198	1.358306
18	6	0	-1.058761	1.702083	0.839551
19	1	0	-0.058105	1.722225	1.275708
20	1	0	-1.167503	2.582624	0.192418
21	1	0	-1.810218	1.787900	1.631061
22	6	0	-3.043977	-0.963508	-1.236862
23	1	0	-2.646336	-0.680401	-2.216662
24	1	0	-2.550404	-1.895390	-0.944551
25	1	0	-4.120875	-1.136728	-1.326072

IN1a 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.364422	-0.486933	0.563337
2	6	0	2.077405	-0.713549	1.042814
3	6	0	0.954959	-0.259503	0.326094
4	6	0	1.163008	0.429958	-0.881524
5	6	0	2.457322	0.658154	-1.346546
6	6	0	3.568429	0.204495	-0.633514
7	1	0	4.215125	-0.849758	1.135101
8	1	0	1.931766	-1.249163	1.979452
9	1	0	0.304856	0.769420	-1.453675
10	1	0	2.594804	1.194546	-2.282418
11	1	0	4.573808	0.384907	-1.002523
12	7	0	-0.334291	-0.538350	0.796672
13	6	0	-1.456548	0.288919	0.465972
14	6	0	-2.498013	-0.259971	-0.195138
15	8	0	-3.655806	0.416116	-0.480372
16	1	0	-3.613254	1.305232	-0.095771
17	1	0	-0.340886	-0.898409	1.745500
18	6	0	-1.411239	1.722751	0.951199
19	1	0	-2.120915	2.386061	0.439091
20	1	0	-1.608932	1.800093	2.030320
21	1	0	-0.415643	2.144806	0.774332
22	6	0	-2.572023	-1.665922	-0.706054
23	1	0	-1.622571	-2.181661	-0.565128
24	1	0	-3.365303	-2.218357	-0.186695
25	1	0	-2.832693	-1.658586	-1.771151

IN2a 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.276175	0.673197	0.342999
2	6	0	-2.002620	1.225679	0.416608
3	6	0	-0.873649	0.488570	0.008486
4	6	0	-1.064851	-0.817970	-0.476456
5	6	0	-2.349832	-1.360557	-0.542243
6	6	0	-3.463318	-0.626839	-0.136912
7	1	0	-4.130523	1.264819	0.662328
8	1	0	-1.868643	2.237010	0.796225
9	1	0	-0.219241	-1.414326	-0.803399
10	1	0	-2.473165	-2.372070	-0.920913
11	1	0	-4.459038	-1.056501	-0.192893
12	7	0	0.395695	1.061150	0.130820
13	6	0	1.555791	0.523781	-0.560322
14	6	0	2.155707	-0.716163	0.140499
15	8	0	2.741041	-1.549079	-0.525381
16	1	0	0.381907	2.070610	0.200501
17	6	0	2.017853	-0.824462	1.644902
18	1	0	2.270247	0.119979	2.139161
19	1	0	0.974422	-1.041312	1.902233
20	1	0	2.659169	-1.629503	2.009242
21	6	0	2.649967	1.598847	-0.651868
22	1	0	3.531734	1.194520	-1.155539
23	1	0	2.290417	2.460243	-1.226756
24	1	0	2.946345	1.948094	0.344205
25	1	0	1.304933	0.198529	-1.581242

IN3a1 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.069547	0.536231	0.046693
2	6	0	-2.005013	1.444271	0.071759
3	6	0	-0.706062	0.935484	0.029322
4	6	0	-0.478951	-0.448125	-0.036573
5	6	0	-1.540695	-1.341664	-0.054055
6	6	0	-2.850007	-0.843168	-0.018459
7	1	0	-4.087771	0.916371	0.072185
8	1	0	-2.187956	2.514963	0.116878
9	1	0	-1.352480	-2.411266	-0.111243
10	1	0	-3.694021	-1.526424	-0.043930
11	7	0	0.512413	1.627816	0.069186
12	6	0	1.552190	0.715706	-0.449514
13	6	0	1.020621	-0.702361	-0.035163
14	8	0	1.446619	-1.709500	-0.951975
15	1	0	0.510247	2.560234	-0.331590
16	1	0	1.004060	-1.530518	-1.797933
17	6	0	1.507555	-1.167251	1.339625
18	1	0	1.003051	-2.100036	1.608477
19	1	0	2.586428	-1.352372	1.323295
20	1	0	1.284900	-0.416403	2.103692
21	6	0	2.953850	1.093237	0.006866
22	1	0	3.676580	0.350474	-0.348344
23	1	0	3.246478	2.067004	-0.404075
24	1	0	3.015252	1.156492	1.097157
25	1	0	1.531740	0.718609	-1.556081

IN3a2 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.998253	0.376528	-0.100384
2	6	0	-2.014275	1.294485	0.283034
3	6	0	-0.688544	0.857816	0.328597
4	6	0	-0.359689	-0.466209	0.001782
5	6	0	-1.342741	-1.370985	-0.374529
6	6	0	-2.676354	-0.943701	-0.429941
7	1	0	-4.034195	0.703132	-0.146823
8	1	0	-2.276437	2.319822	0.531479
9	1	0	-1.074089	-2.392696	-0.632978
10	1	0	-3.458559	-1.635503	-0.728675
11	7	0	0.456191	1.570276	0.702454
12	6	0	1.645785	0.834798	0.216945
13	1	0	2.452655	0.924557	0.953432
14	6	0	1.137632	-0.660296	0.162730
15	8	0	1.730443	-1.427501	-0.884358
16	1	0	0.448292	2.566897	0.512874
17	1	0	1.339873	-1.126528	-1.720204
18	6	0	1.488272	-1.397767	1.458222
19	1	0	1.028179	-2.390484	1.465159
20	1	0	2.575043	-1.516795	1.535246
21	1	0	1.130868	-0.835917	2.326722
22	6	0	2.144099	1.360404	-1.132855
23	1	0	2.458374	2.407036	-1.041877
24	1	0	3.002208	0.779386	-1.483690
25	1	0	1.355312	1.314733	-1.894595

II 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.898352	-0.541796	0.000965
2	6	0	-1.820665	-1.422375	-0.000409
3	6	0	-0.536354	-0.871294	-0.001071
4	6	0	-0.310898	0.531905	-0.001102
5	6	0	-1.419217	1.395015	-0.000204
6	6	0	-2.699833	0.853101	0.001151
7	1	0	-3.910235	-0.938064	0.002008
8	1	0	-1.974508	-2.498717	-0.000744
9	1	0	-1.278212	2.473097	-0.000023
10	1	0	-3.563349	1.512942	0.002604
11	7	0	0.703149	-1.475593	-0.001538
12	6	0	1.701439	-0.506554	-0.000356
13	6	0	1.117051	0.740604	-0.000762
14	1	0	0.868472	-2.470110	0.001141
15	6	0	3.138648	-0.918904	0.001767
16	1	0	3.388519	-1.518549	0.887784
17	1	0	3.390594	-1.521192	-0.881861
18	1	0	3.793169	-0.044155	0.001229
19	6	0	1.799036	2.076055	-0.000241
20	1	0	1.516893	2.673429	0.877070
21	1	0	2.888732	1.978373	0.010835
22	1	0	1.532752	2.667563	-0.887700

TS1a1 imaginary frequencies = -1417.7198

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.371409	1.080553	-0.332240
2	6	0	1.984676	1.198618	-0.318862
3	6	0	1.187718	0.114002	0.082817
4	6	0	1.803482	-1.074482	0.503248
5	6	0	3.193657	-1.183402	0.480690
6	6	0	3.983829	-0.112741	0.059863
7	1	0	3.976235	1.925774	-0.649063
8	1	0	1.503849	2.126277	-0.616621
9	1	0	1.200199	-1.896870	0.873113
10	1	0	3.659713	-2.108449	0.809180
11	1	0	5.066231	-0.201852	0.050243
12	7	0	-0.207412	0.304143	0.107847
13	6	0	-1.181093	-0.554921	-0.194556
14	6	0	-2.520867	-0.047655	0.020308
15	1	0	-2.325640	1.199163	-0.369596
16	8	0	-3.496199	-0.873699	-0.613366
17	1	0	-4.243033	-0.297868	-0.831998
18	1	0	-0.604933	1.332663	0.109106
19	8	0	-1.675275	2.379528	-0.245734
20	1	0	-1.483638	2.668488	-1.154379
21	6	0	-0.941573	-1.869787	-0.871301
22	1	0	0.046881	-1.935281	-1.330122
23	1	0	-1.054761	-2.696014	-0.156744
24	1	0	-1.723999	-2.007138	-1.621574
25	6	0	-2.906851	0.242385	1.482495
26	1	0	-3.809913	0.861954	1.512904
27	1	0	-3.112332	-0.693740	2.017407
28	1	0	-2.117512	0.791835	2.001244

TS2a1 imaginary frequencies = -1913.1188

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.629898	-0.679610	-0.578579
2	6	0	-2.321183	-0.998399	-0.925874
3	6	0	-1.232758	-0.337805	-0.323157
4	6	0	-1.505501	0.648397	0.643252
5	6	0	-2.822406	0.955295	0.986704
6	6	0	-3.895375	0.299475	0.382993
7	1	0	-4.449852	-1.206018	-1.061066
8	1	0	-2.128781	-1.764661	-1.675013
9	1	0	-0.686274	1.174762	1.122906
10	1	0	-3.005719	1.719693	1.737938
11	1	0	-4.917750	0.543590	0.655767
12	7	0	0.068777	-0.635043	-0.738785
13	6	0	1.251853	-0.407661	0.058431
14	6	0	1.919323	0.838676	-0.153376
15	1	0	2.464139	-1.113479	-0.302122
16	8	0	3.115219	1.002938	0.305611
17	1	0	0.116384	-1.455871	-1.329079
18	1	0	4.151326	-1.310357	-0.894017
19	8	0	3.663352	-1.300934	-0.052917
20	1	0	3.593748	-0.115477	0.292128
21	6	0	1.401490	1.923927	-1.059907
22	1	0	1.752926	1.744281	-2.084462
23	1	0	0.312236	1.969970	-1.081090
24	1	0	1.823711	2.879445	-0.735952
25	6	0	1.253428	-1.024750	1.471711
26	1	0	0.317419	-0.788659	1.990267
27	1	0	1.348617	-2.115128	1.432592
28	1	0	2.084035	-0.638098	2.067962

TS3a1 1 imaginary frequencies = -1103.3972

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.108180	-0.630850	-0.046822
2	6	0	2.087777	-1.394673	-0.577350
3	6	0	0.775829	-0.871593	-0.519840
4	6	0	0.513922	0.483391	-0.085293
5	6	0	1.614223	1.175735	0.540505
6	6	0	2.879951	0.646051	0.540637
7	1	0	4.119656	-1.030238	-0.054835
8	1	0	2.276475	-2.390685	-0.969053
9	1	0	0.112352	1.182297	-0.981174
10	1	0	1.423532	2.166846	0.946886
11	1	0	3.716191	1.192704	0.965972
12	7	0	-0.369519	-1.533659	-0.736918
13	6	0	-1.563415	-0.726645	-0.449309
14	6	0	-1.041534	0.386009	0.567512
15	8	0	-1.722503	1.530728	0.493941
16	1	0	-0.406474	-2.485832	-1.075258
17	8	0	-0.915856	2.089691	-1.696392
18	1	0	-1.466061	1.946756	-0.650896
19	1	0	-0.552793	2.990759	-1.689586
20	6	0	-0.931133	-0.114074	2.014945
21	1	0	-0.439232	0.653003	2.619367
22	1	0	-1.936298	-0.262966	2.423115
23	1	0	-0.368227	-1.050479	2.104670
24	1	0	-1.847764	-0.171520	-1.352424
25	6	0	-2.741240	-1.564640	0.025382
26	1	0	-3.560536	-0.894749	0.304719
27	1	0	-3.108272	-2.225705	-0.769815
28	1	0	-2.484411	-2.180191	0.894149

TS3a2 1 imaginary frequencies = -956.4678

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.121730	0.343597	-0.284019
2	6	0	-2.170534	1.328516	-0.451081
3	6	0	-0.814296	0.972234	-0.257387
4	6	0	-0.404820	-0.406838	-0.099727
5	6	0	-1.464406	-1.354743	0.170495
6	6	0	-2.782819	-0.998175	0.058304
7	1	0	-4.171611	0.606734	-0.389869
8	1	0	-2.455487	2.357908	-0.651037
9	1	0	0.143078	-0.830926	-1.076162
10	1	0	-1.179446	-2.383583	0.380079
11	1	0	-3.575243	-1.725288	0.207133
12	7	0	0.218343	1.805734	-0.096449
13	6	0	1.477449	1.147424	0.298929
14	1	0	1.887137	1.695520	1.157910
15	6	0	1.013914	-0.316091	0.774652
16	8	0	1.872599	-1.298376	0.491667
17	1	0	0.129146	2.808809	-0.193029
18	8	0	1.297546	-1.573280	-1.831168
19	1	0	1.735569	-1.532016	-0.754914
20	1	0	0.982333	-2.484109	-1.951035
21	6	0	0.664205	-0.286380	2.272956
22	1	0	0.242247	-1.250141	2.572786
23	1	0	1.587670	-0.131841	2.842818
24	1	0	-0.047079	0.508747	2.529948
25	6	0	2.515758	1.127978	-0.819378
26	1	0	3.390638	0.571419	-0.471708
27	1	0	2.140642	0.628440	-1.715909

28	1	0	2.824520	2.148315	-1.078334

TS4a1 1 imaginary frequencies = -930.2046

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.291804	-0.473701	0.368687
2	6	0	-2.261988	-1.401337	0.395434
3	6	0	-0.978175	-0.962023	0.023989
4	6	0	-0.742184	0.397364	-0.315701
5	6	0	-1.809015	1.314306	-0.336436
6	6	0	-3.078104	0.874595	-0.002525
7	1	0	-4.295241	-0.792298	0.639415
8	1	0	-2.442798	-2.434833	0.676770
9	1	0	1.703153	2.342077	1.135162
10	1	0	-1.631370	2.355592	-0.589115
11	1	0	-3.915122	1.566041	-0.005804
12	7	0	0.177356	-1.675489	-0.112281
13	6	0	1.294020	-0.766323	-0.379124
14	6	0	0.660140	0.552109	-0.553640
15	8	0	1.168036	1.559534	1.347047
16	1	0	0.331863	-2.524552	0.415738
17	1	0	1.955721	-0.670797	0.617558
18	8	0	2.726439	-0.212465	1.837663
19	1	0	1.941392	0.775311	1.708119
20	1	0	2.373021	-0.729134	2.580785
21	6	0	2.244192	-1.266535	-1.470339
22	1	0	3.085135	-0.576274	-1.584845
23	1	0	2.661154	-2.237733	-1.184224
24	1	0	1.741188	-1.380526	-2.437862
25	6	0	1.267928	1.646493	-1.373876
26	1	0	2.336847	1.754053	-1.173943
27	1	0	1.151549	1.411065	-2.441881
28	1	0	0.776149	2.604192	-1.186392

Z-matrix (Transformation of imine **Ib** into indole **II** catalysed with H_2O and TsOH. Solvent: N,N-dimethylacetamide)

Ib 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.077712	-1.234806	0.513333
2	6	0	-1.694641	-1.300669	0.370915
3	6	0	-1.004474	-0.184086	-0.115925
4	6	0	-1.682104	0.978439	-0.498525
5	6	0	-3.068264	1.025556	-0.356899
6	6	0	-3.764565	-0.071968	0.153797
7	1	0	-3.617892	-2.092699	0.900382
8	1	0	-1.154419	-2.201309	0.650280
9	1	0	-1.154385	1.815467	-0.940445
10	1	0	-3.603997	1.919219	-0.660292
11	1	0	-4.843875	-0.026398	0.259315
12	7	0	0.416011	-0.320891	-0.256225
13	6	0	1.389284	0.516250	-0.057737
14	6	0	2.785496	-0.017495	-0.318533
15	1	0	3.278567	0.707843	-0.986670
16	8	0	2.621055	-1.265852	-0.967781
17	1	0	3.456548	-1.758642	-0.957296
18	1	0	0.749540	-1.244744	-0.558176
19	6	0	1.202444	1.921099	0.397841
20	1	0	0.307956	2.032149	1.015913
21	1	0	2.079422	2.262600	0.951986
22	1	0	1.097125	2.582855	-0.472470
23	6	0	3.596189	-0.144581	0.983780
24	1	0	3.115464	-0.850231	1.668101
25	1	0	4.597841	-0.515498	0.742590
26	1	0	3.721670	0.816007	1.490324

IN2b1 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.378245	0.690636	-2.829646
2	6	0	-1.140874	-0.253773	-1.829076
3	6	0	-1.307309	0.131129	-0.501991
4	6	0	-1.705131	1.416413	-0.140905
5	6	0	-1.938469	2.348297	-1.152562
6	6	0	-1.773765	1.986345	-2.492227
7	1	0	-1.259171	0.407489	-3.870421
8	1	0	-0.842977	-1.266881	-2.086994
9	1	0	-1.840578	1.692001	0.902192
10	1	0	-2.254610	3.353174	-0.891843
11	1	0	-1.960743	2.715001	-3.274555
12	7	0	-1.068441	-0.867429	0.564172
13	6	0	0.248958	-0.827875	1.349251
14	1	0	0.116438	-0.116365	2.169361
15	6	0	0.422352	-2.273437	1.880040
16	8	0	-0.205729	-3.157395	1.324656
17	1	0	-1.839387	-0.828028	1.240371
18	6	0	1.347123	-2.503855	3.039584
19	1	0	1.676668	-3.545069	3.046148
20	1	0	2.209023	-1.830233	3.030777
21	1	0	0.793077	-2.313579	3.970215
22	6	0	1.427743	-0.419824	0.463186
23	1	0	2.343308	-0.428461	1.060754
24	1	0	1.560175	-1.114122	-0.372519
25	1	0	1.292306	0.590237	0.070337
26	1	0	-1.100337	-1.841092	0.200495

IN2b2 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.289735	-0.207052	-0.537556
2	6	0	2.043672	0.218636	-0.995016
3	6	0	0.980863	0.295271	-0.092843
4	6	0	1.137517	-0.042637	1.249930
5	6	0	2.388967	-0.472767	1.693902
6	6	0	3.461322	-0.556004	0.804297
7	1	0	4.123436	-0.267444	-1.229839
8	1	0	1.904527	0.495317	-2.036952
9	1	0	0.311491	0.039042	1.949525
10	1	0	2.523134	-0.735590	2.738282
11	1	0	4.432163	-0.889764	1.156775
12	7	0	-0.297687	0.772090	-0.598813
13	6	0	-1.639456	0.323897	-0.076987
14	6	0	-1.331589	-0.199473	-1.424289
15	8	0	-0.930717	-1.485452	-1.424071
16	1	0	-0.290811	1.735200	-0.934855
17	6	0	-1.835609	0.386552	-2.714483
18	1	0	-2.762961	-0.126683	-2.991271
19	1	0	-2.049176	1.454918	-2.640160
20	1	0	-1.107183	0.235594	-3.519331
21	1	0	-0.543905	-1.734698	-2.282110
22	6	0	-2.669630	1.381931	0.230778
23	1	0	-3.648362	0.905194	0.345377
24	1	0	-2.427164	1.883799	1.172287
25	1	0	-2.752673	2.137842	-0.555546
26	1	0	-1.509150	-0.429566	0.696189

IN3b1 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.108231	0.437107	-0.145576
2	6	0	2.151684	1.399465	0.064124
3	6	0	0.806442	0.962685	0.124223
4	6	0	0.445545	-0.483017	0.215746
5	6	0	1.542353	-1.424254	-0.131990
6	6	0	2.809210	-0.971033	-0.279618
7	1	0	4.144647	0.748823	-0.245531
8	1	0	2.403935	2.454466	0.100465
9	1	0	0.199427	-0.677046	1.278628
10	1	0	1.312117	-2.485309	-0.171046
11	1	0	3.626999	-1.655414	-0.479581
12	7	0	-0.296213	1.679758	0.037110
13	6	0	-1.529392	0.862144	-0.009405
14	6	0	-0.972791	-0.527133	-0.493356
15	8	0	-1.789907	-1.522356	0.063363
16	1	0	-0.307632	2.694464	0.000124
17	6	0	-0.853927	-0.656543	-2.011630
18	1	0	-0.383112	-1.609706	-2.276907
19	1	0	-1.845242	-0.623986	-2.473276
20	1	0	-0.247248	0.142263	-2.449702
21	1	0	-1.904062	-2.251812	-0.565151
22	6	0	-2.637089	1.510161	-0.824606
23	1	0	-3.493690	0.830964	-0.866741
24	1	0	-2.979534	2.435367	-0.348978
25	1	0	-2.320267	1.739684	-1.846224
26	1	0	-1.874619	0.700545	1.021504

IN3b2 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.959667	0.478754	-0.018792
2	6	0	-1.980362	1.422707	0.170409
3	6	0	-0.638817	0.979639	0.071557
4	6	0	-0.296149	-0.359613	-0.489217
5	6	0	-1.420559	-1.335243	-0.525227
6	6	0	-2.689287	-0.907742	-0.330647
7	1	0	-3.997274	0.777977	0.105017
8	1	0	-2.219018	2.437409	0.472371
9	1	0	-0.038770	-0.184003	-1.553561
10	1	0	-1.194806	-2.358803	-0.809405
11	1	0	-3.528120	-1.590229	-0.417666
12	7	0	0.460576	1.580007	0.477844
13	6	0	1.690153	0.759918	0.326844
14	1	0	2.266816	0.854228	1.252849
15	6	0	1.073555	-0.694274	0.185546
16	8	0	1.778809	-1.509713	-0.717244
17	1	0	0.475529	2.525813	0.847841
18	6	0	0.918636	-1.359116	1.555106
19	1	0	0.420783	-2.328717	1.462170
20	1	0	1.905970	-1.521351	2.004462
21	1	0	0.341358	-0.739856	2.249540
22	6	0	2.534897	1.214545	-0.862882
23	1	0	3.410011	0.567326	-0.958878
24	1	0	1.980084	1.167218	-1.804597
25	1	0	2.882602	2.241720	-0.714166
26	1	0	2.445923	-2.028532	-0.239118

IN4b 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.934877	0.453891	0.427675
2	6	0	1.925850	1.370731	0.615711
3	6	0	0.652731	1.031834	0.105879
4	6	0	0.430309	-0.230755	-0.580505
5	6	0	1.520381	-1.148450	-0.745388
6	6	0	2.743130	-0.800204	-0.247653
7	1	0	3.926523	0.683613	0.807266
8	1	0	2.097801	2.309690	1.130944
9	1	0	1.367059	-2.093836	-1.255092
10	1	0	3.590830	-1.468521	-0.353431
11	7	0	-0.492274	1.718635	0.141836
12	6	0	-1.573203	0.983721	-0.511505
13	6	0	-0.892371	-0.282835	-0.960675
14	1	0	-0.610571	2.631977	0.561458
15	6	0	-1.605917	-1.362869	-1.689919
16	1	0	-0.969848	-2.233778	-1.858977
17	1	0	-2.498275	-1.684770	-1.138612
18	1	0	-1.956265	-0.999543	-2.665858
19	6	0	-2.249284	1.795211	-1.633939
20	1	0	-3.056427	1.209007	-2.081172
21	1	0	-2.686370	2.710641	-1.225232
22	1	0	-1.526398	2.061548	-2.409686
23	1	0	-2.328652	0.722627	0.246736

TS1b 1 imaginary frequencies = -937.5560

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.441039	0.629063	0.731646
2	6	0	2.067578	0.776976	0.919429
3	6	0	1.178360	0.071108	0.102800
4	6	0	1.661233	-0.777305	-0.898866
5	6	0	3.038081	-0.936365	-1.063732
6	6	0	3.929749	-0.232490	-0.253320
7	1	0	4.129603	1.178822	1.366104
8	1	0	1.684413	1.426511	1.701838
9	1	0	0.971753	-1.299044	-1.558030
10	1	0	3.410392	-1.599770	-1.838442
11	1	0	4.999923	-0.352078	-0.389897
12	7	0	-0.228104	0.276681	0.288455
13	6	0	-1.182098	-0.699580	0.199050
14	6	0	-2.547234	-0.352791	-0.122252
15	1	0	-1.602728	-0.965124	-1.015032
16	8	0	-2.934796	0.848128	-0.500078
17	1	0	-2.272732	1.591597	-0.453489
18	1	0	-0.512938	1.249635	0.354482
19	6	0	-0.867369	-2.055010	0.820072
20	1	0	0.201913	-2.251347	0.749901
21	1	0	-1.141664	-2.020327	1.879812
22	1	0	-1.398028	-2.879778	0.344056
23	6	0	-3.703492	-1.299498	0.034139
24	1	0	-4.172235	-1.098247	1.005671
25	1	0	-4.442411	-1.092137	-0.743072
26	1	0	-3.418173	-2.349482	0.001439
27	8	0	-1.339863	2.984786	-0.200617
28	1	0	-0.975969	3.444845	-0.975635
29	1	0	-1.762186	3.671192	0.342878

TS3b1 1 imaginary frequencies = -173.1725

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.151411	0.456744	-0.535768
2	6	0	2.048754	1.291874	-0.435505
3	6	0	0.838996	0.786663	0.077242
4	6	0	0.776703	-0.554577	0.543106
5	6	0	1.915208	-1.381162	0.415187
6	6	0	3.088252	-0.893229	-0.132930
7	1	0	4.076396	0.850836	-0.946965
8	1	0	2.104967	2.322540	-0.776405
9	1	0	-0.018964	-0.871124	1.212873
10	1	0	1.870618	-2.397593	0.796091
11	1	0	3.964467	-1.526895	-0.221640
12	7	0	-0.332737	1.520029	0.033510
13	6	0	-1.558404	0.754393	0.051493
14	6	0	-1.360817	-0.520161	-0.783339
15	8	0	-2.106843	-1.510282	-0.385004
16	1	0	-0.327314	2.387190	-0.487382
17	8	0	-1.587604	-0.911917	2.866576
18	1	0	-2.218315	-1.572625	3.192262
19	1	0	-1.203482	-0.528213	3.670370
20	6	0	-0.832485	-0.538470	-2.177312
21	1	0	-0.367090	-1.501188	-2.412952
22	1	0	-1.682165	-0.395213	-2.864093
23	1	0	-0.108478	0.256680	-2.348103
24	1	0	-2.108429	-2.261323	-1.012505
25	6	0	-2.750894	1.562478	-0.496985
26	1	0	-3.667296	0.967064	-0.477151

27	1	0	-2.903667	2.433243	0.147473
28	1	0	-2.574460	1.912310	-1.520130
29	1	0	-1.800572	0.412331	1.065276

TS3b2 1 imaginary frequencies = -134.1513

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.038117	0.725769	-0.673761
2	6	0	1.909738	1.532181	-0.662196
3	6	0	0.681722	0.998304	-0.226342
4	6	0	0.633713	-0.325209	0.276347
5	6	0	1.789578	-1.133297	0.217618
6	6	0	2.983121	-0.621460	-0.260827
7	1	0	3.977143	1.138748	-1.031013
8	1	0	1.957429	2.552500	-1.033165
9	1	0	-0.163477	-0.657727	0.933881
10	1	0	1.739230	-2.143073	0.614834
11	1	0	3.879022	-1.233064	-0.284673
12	7	0	-0.504349	1.677888	-0.432027
13	6	0	-1.763183	0.991101	-0.230469
14	1	0	-2.512382	1.497043	-0.866626
15	6	0	-1.604626	-0.385718	-0.876304
16	8	0	-2.320237	-1.318590	-0.322488
17	1	0	-0.505151	2.684480	-0.520634
18	8	0	-0.837829	-1.931260	2.597200
19	1	0	-1.605956	-2.352997	3.012591
20	1	0	-0.191613	-1.857363	3.316679
21	6	0	-1.133086	-0.567751	-2.278687
22	1	0	-0.703844	-1.562667	-2.433204
23	1	0	-2.012784	-0.468842	-2.936090
24	1	0	-0.408392	0.194249	-2.559882
25	6	0	-2.326996	0.959673	1.200994
26	1	0	-3.347504	0.564966	1.202253
27	1	0	-1.724956	0.355636	1.883664
28	1	0	-2.362181	1.987083	1.574170
29	1	0	-2.309707	-2.154021	-0.831946

TS4b1 1 imaginary frequencies = -904.3146

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.215333	0.486421	-0.080934
2	6	0	2.222478	1.453824	-0.092825
3	6	0	0.889268	1.027462	-0.246684
4	6	0	0.569693	-0.364938	-0.250924
5	6	0	1.626965	-1.319444	-0.350591
6	6	0	2.934503	-0.895046	-0.217600
7	1	0	4.249849	0.802484	0.019737
8	1	0	2.468722	2.509517	-0.037451
9	1	0	0.358885	-0.596733	1.251014
10	1	0	1.390520	-2.374760	-0.463279
11	1	0	3.749588	-1.610603	-0.230626
12	7	0	-0.224804	1.774209	-0.452475
13	6	0	-1.444594	0.950338	-0.420748
14	6	0	-0.890628	-0.496764	-0.712815
15	8	0	-1.557448	-1.473898	0.139095
16	1	0	-0.260649	2.760469	-0.226349
17	8	0	-0.232846	-0.899776	2.209338
18	1	0	-1.019045	-1.304904	1.716410
19	1	0	0.236666	-1.599195	2.706470
20	6	0	-1.000291	-0.950452	-2.166939
21	1	0	-0.541782	-1.935697	-2.288461
22	1	0	-2.046382	-1.013302	-2.487930
23	1	0	-0.487762	-0.246982	-2.829664
24	1	0	-2.449094	-1.657698	-0.200465
25	6	0	-2.534063	1.488088	-1.341545
26	1	0	-3.424490	0.850625	-1.304946
27	1	0	-2.843591	2.487404	-1.017452
28	1	0	-2.191862	1.557195	-2.377405
29	1	0	-1.833396	0.924471	0.610325

TS4b2 1 imaginary frequencies = -858.1828

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.385708
3	6	0	1.246122	0.000000	2.046120
4	6	0	2.456008	0.137105	1.300945
5	6	0	2.416129	0.023018	-0.121414
6	6	0	1.193200	0.001347	-0.763320
7	1	0	-0.953489	-0.020961	-0.520334
8	1	0	-0.928454	-0.053043	1.945397
9	1	0	2.511231	1.676234	1.244342
10	1	0	3.344493	0.018837	-0.687561
11	1	0	1.140045	-0.031366	-1.846106
12	7	0	1.508619	-0.141875	3.363593
13	6	0	2.945722	-0.099648	3.683114
14	6	0	3.630715	-0.132399	2.251107
15	8	0	4.601963	0.940189	2.067604
16	1	0	0.799405	-0.081123	4.081533
17	8	0	2.958647	2.732498	1.422502
18	1	0	3.864774	2.399639	1.727875
19	1	0	3.054350	3.215403	0.577403
20	6	0	4.325886	-1.467401	1.988365
21	1	0	4.758982	-1.491068	0.984373
22	1	0	5.126889	-1.637304	2.719690
23	1	0	3.613262	-2.292685	2.079674
24	1	0	5.417940	0.742514	2.555918
25	6	0	3.299264	1.102032	4.563210
26	1	0	2.759963	1.033301	5.513768

27	1	0	4.367536	1.117689	4.802737
28	1	0	3.030670	2.051787	4.091413
29	1	0	3.212866	-1.016843	4.221021

TS5b 1 imaginary frequencies = -1182.6449

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.545251	-0.024787	0.900630
2	6	0	1.710570	1.075789	0.838795
3	6	0	0.554044	0.961706	0.044565
4	6	0	0.246645	-0.236567	-0.667865
5	6	0	1.120029	-1.347876	-0.575004
6	6	0	2.254119	-1.231863	0.206920
7	1	0	3.450681	0.030705	1.497399
8	1	0	1.939440	1.989219	1.378713
9	1	0	-2.046475	-0.574123	1.572367
10	1	0	0.909557	-2.264395	-1.118566
11	1	0	2.947064	-2.063824	0.283869
12	7	0	-0.462734	1.843772	-0.162702
13	6	0	-1.483276	1.238234	-0.935578
14	6	0	-0.991814	-0.033959	-1.338984
15	8	0	-0.835524	-1.296039	2.341935
16	1	0	-0.512904	2.780120	0.214287
17	8	0	-2.752570	-0.054470	1.057113
18	1	0	-1.030807	-2.105209	2.841002
19	1	0	-3.156631	0.584479	1.670822
20	6	0	-1.695010	-1.004109	-2.232653
21	1	0	-1.623040	-2.029464	-1.855500
22	1	0	-2.752480	-0.758318	-2.357927
23	1	0	-1.234318	-0.991055	-3.229107
24	1	0	-0.043494	-1.490537	1.810792
25	6	0	-2.496472	2.113095	-1.636745
26	1	0	-3.317064	1.512865	-2.037165
27	1	0	-2.927342	2.850911	-0.951556
28	1	0	-2.033865	2.653531	-2.470036
29	1	0	-2.179537	0.517279	0.063247

Z-matrix (Transformation of **imine** into **indole** catalysed with H_2O . Solvent: 1,2-Ethyleneglycol)

Imine 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.392442
3	6	0	1.211227	0.000000	2.101517
4	6	0	2.421024	0.050731	1.389575
5	6	0	2.413723	0.070774	-0.004888
6	6	0	1.206483	0.035584	-0.704985
7	1	0	-0.944323	-0.015325	-0.537748
8	1	0	-0.929189	-0.011167	1.954265
9	1	0	3.360692	0.107779	1.931917
10	1	0	3.355476	0.120562	-0.545307
11	1	0	1.204457	0.052306	-1.791309
12	7	0	1.143703	0.001073	3.512250
13	6	0	1.987311	-0.672958	4.190570
14	1	0	2.745939	-1.324364	3.729541
15	6	0	1.978930	-0.649725	5.696176
16	1	0	2.884605	-0.150315	6.062526
17	1	0	1.109612	-0.074994	6.043802
18	8	0	2.028320	-1.964410	6.242669
19	1	0	1.202154	-2.409892	5.997259

IN1 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.391182
3	6	0	1.212185	0.000000	2.106390
4	6	0	2.420147	0.002090	1.386924
5	6	0	2.405225	-0.006767	-0.007326
6	6	0	1.201756	-0.008443	-0.713785
7	1	0	-0.949006	0.000471	-0.530477
8	1	0	-0.942119	-0.001726	1.936645
9	1	0	3.363116	0.033649	1.923760
10	1	0	3.350406	-0.004120	-0.544814
11	1	0	1.198313	-0.012911	-1.799758
12	7	0	1.196450	0.021313	3.500930
13	6	0	2.285379	-0.445960	4.271464
14	1	0	2.801806	-1.342855	3.915788
15	6	0	2.661429	0.156322	5.407254
16	1	0	2.193955	1.069366	5.762076
17	8	0	3.617764	-0.282914	6.274419
18	1	0	4.013726	-1.096740	5.921115
19	1	0	0.279471	-0.092885	3.913101

IN2 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.390417
3	6	0	1.210858	0.000000	2.108190
4	6	0	2.418958	0.003018	1.389994
5	6	0	2.404012	-0.000015	-0.006169
6	6	0	1.202699	-0.000169	-0.712968
7	1	0	-0.948724	0.001998	-0.530699

8	1	0	-0.942321	-0.004002	1.935162
9	1	0	3.371533	0.002923	1.909928
10	1	0	3.350237	0.001037	-0.541179
11	1	0	1.200327	-0.000531	-1.798842
12	7	0	1.175764	-0.034273	3.507320
13	6	0	2.338311	0.311963	4.297229
14	1	0	2.887100	1.190845	3.926361
15	6	0	3.318358	-0.852571	4.435117
16	1	0	2.843495	-1.856564	4.366470
17	1	0	1.999091	0.547854	5.314813
18	8	0	4.503848	-0.711449	4.626911
19	1	0	0.292645	0.262170	3.898803

IN3 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.398913
3	6	0	1.231818	0.000000	2.056568
4	6	0	2.432256	0.002814	1.328464
5	6	0	2.422182	-0.005803	-0.059669
6	6	0	1.192492	-0.001518	-0.730895
7	1	0	-0.951013	0.005261	-0.526769
8	1	0	-0.933893	0.004185	1.955254
9	1	0	3.359343	0.000614	-0.611085
10	1	0	1.163995	0.001558	-1.816612
11	7	0	1.487364	-0.035826	3.433310
12	6	0	2.891289	0.357859	3.640939
13	1	0	3.326032	-0.157237	4.502075
14	6	0	3.594166	-0.003897	2.299429
15	1	0	4.045867	-1.001260	2.365565
16	8	0	4.678708	0.851723	1.970064
17	1	0	0.803139	0.413407	4.031261
18	1	0	2.996460	1.444613	3.800947
19	1	0	4.296388	1.711815	1.729201

Indole 0 imaginary frequencies

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.389882
3	6	0	1.240941	0.000000	2.035871
4	6	0	2.472195	-0.000923	1.320837
5	6	0	2.436347	-0.000965	-0.084985
6	6	0	1.206772	-0.000372	-0.730411
7	1	0	-0.946873	0.000480	-0.533097
8	1	0	-0.930518	0.000747	1.952139
9	1	0	3.360710	-0.000671	-0.657233
10	1	0	1.169453	0.000170	-1.816450
11	7	0	1.551543	0.001237	3.381235
12	6	0	2.926473	0.000828	3.533285
13	1	0	3.366544	0.002823	4.520961
14	6	0	3.523613	-0.001000	2.300708
15	1	0	4.588275	0.000444	2.111136
16	1	0	0.882480	0.001269	4.134861

TS1-a1 1 imaginary frequencies = -1564.7877

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.392274
3	6	0	1.214582	0.000000	2.094615
4	6	0	2.425456	0.033516	1.387551
5	6	0	2.413194	0.028719	-0.006166
6	6	0	1.205200	0.008642	-0.706421
7	1	0	-0.945922	-0.004343	-0.534366
8	1	0	-0.933870	-0.004453	1.947557
9	1	0	3.369598	0.089311	1.920895
10	1	0	3.355367	0.056279	-0.546665
11	1	0	1.203091	0.014172	-1.792464
12	7	0	1.156353	-0.018255	3.500653
13	6	0	2.103297	-0.424394	4.320483
14	1	0	2.998564	-0.907046	3.923604
15	6	0	1.864017	-0.374366	5.738258
16	1	0	1.762648	0.655849	6.111495
17	1	0	0.554107	-0.586962	5.735680
18	8	0	2.820282	-1.109594	6.482004
19	1	0	2.340429	-1.794300	6.967932
20	1	0	0.178202	0.048424	4.069483
21	8	0	-0.656716	-0.253235	5.230855
22	1	0	-1.120824	-1.083949	5.030062

TS2-a1 1 imaginary frequencies = -1850.0902

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.390773
3	6	0	1.211103	0.000000	2.109615
4	6	0	2.418510	0.003833	1.389007
5	6	0	2.404143	0.008426	-0.005969
6	6	0	1.202122	0.006911	-0.713651
7	1	0	-0.948904	0.000124	-0.530823
8	1	0	-0.942725	-0.001974	1.935442
9	1	0	3.364208	-0.010226	1.920752
10	1	0	3.350067	0.010707	-0.542176
11	1	0	1.199440	0.010635	-1.799639
12	7	0	1.186580	-0.036510	3.506164
13	6	0	2.291188	0.399003	4.306383
14	1	0	2.865789	1.246084	3.906217
15	6	0	3.058365	-0.611187	4.945907
16	1	0	2.812682	-1.666087	4.759003
17	1	0	2.196108	1.210015	5.544128
18	8	0	3.922325	-0.364277	5.852874
19	1	0	0.272638	0.147314	3.898318
20	1	0	2.368120	1.505996	7.293655
21	8	0	2.832312	1.683109	6.456872
22	1	0	3.584207	0.779201	6.283123

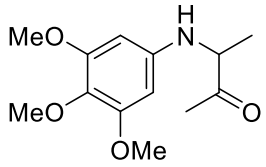
TS3-a1 1 imaginary frequencies = -1097.7126

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.381389
3	6	0	1.251517	0.000000	2.036495
4	6	0	2.489541	0.183476	1.311142
5	6	0	2.412729	0.069473	-0.124369
6	6	0	1.200670	0.004161	-0.765061
7	1	0	-0.953040	-0.033926	-0.522687
8	1	0	-0.927670	-0.065847	1.943513
9	1	0	3.019272	1.240991	1.561084
10	1	0	3.343889	0.111368	-0.685106
11	1	0	1.140677	-0.029812	-1.848627
12	7	0	1.490297	-0.268112	3.329926
13	6	0	2.920795	-0.327989	3.641682
14	1	0	3.120859	-1.101946	4.388557
15	6	0	3.610245	-0.617941	2.253893
16	1	0	3.492154	-1.688476	2.003847
17	8	0	4.859800	-0.185810	2.122411
18	1	0	0.757175	-0.385233	4.015315
19	1	0	3.289951	0.637981	4.006457
20	8	0	4.176884	2.117206	2.082962
21	1	0	4.706001	1.064189	2.153729
22	1	0	4.564846	2.560789	1.310755

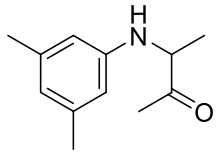
TS4-a1 1 imaginary frequencies = -1155.4253

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.386595
3	6	0	1.246339	0.000000	2.038997
4	6	0	2.457445	0.047644	1.295074
5	6	0	2.424967	0.043464	-0.110917
6	6	0	1.198266	0.012207	-0.751798
7	1	0	-0.950999	-0.013441	-0.526409
8	1	0	-0.929424	-0.016367	1.948734
9	1	0	5.201399	2.031943	1.952080
10	1	0	3.351143	0.087744	-0.676711
11	1	0	1.147366	0.013116	-1.836301
12	7	0	1.529248	-0.077169	3.374677
13	6	0	2.961684	0.105679	3.575395
14	1	0	3.402700	-0.619766	4.265781
15	6	0	3.531420	0.127994	2.234510
16	1	0	4.542902	-0.190417	2.025844
17	8	0	4.231276	2.101467	1.961896
18	1	0	0.869214	0.254476	4.065441
19	1	0	3.193370	1.223316	4.064393
20	8	0	3.657631	2.564936	4.259730
21	1	0	3.992265	2.469804	3.019531
22	1	0	2.865379	3.126908	4.287604

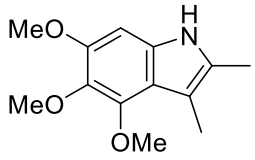
Materials and Measurements. Starting materials, if commercially available, were purchased and used as such. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at 300 and 75 MHz. Chemical shifts are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform. Coupling constants (*J*) are given in Hertz (Hz). Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m). HRMS were recorded using TOF electrospray ionization (ESI-positive). Melting points were recorded on a Cambridge Instruments apparatus and are uncorrected. The solvents used were of spectroscopic or equivalent grade. Water was twice distilled and passed through a Millipore apparatus. All reaction mixtures were filtered through a 0.45 μm PTFE 25 mm syringe filter.



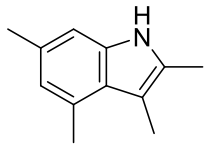
3-((3,4,5-trimethoxyphenyl)amino)butan-2-one (2a)[1] Yield: 37 %, (187 mg), Yellow oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.78 (s, 2H), 4.29 (s, 1H), 4.07 – 3.93 (m, 1H), 3.78 (s, 6H), 3.73 (s, 3H), 2.19 (s, 3H), 1.39 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.55, 154.11, 143.39, 130.46, 90.67, 61.11, 59.14, 56.00, 25.66, 18.07.



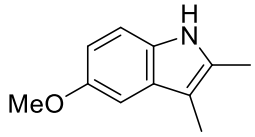
3-((3,5-dimethylphenyl)amino)butan-2-one (2b): Yield: 57 % (218 mg), Yellow oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.42 (dd, *J* = 1.5, 0.7 Hz, 1H), 6.23 (dt, *J* = 1.5, 0.8 Hz, 2H), 4.06 (q, *J* = 7.0 Hz, 1H), 2.26 (s, 6H), 1.42 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.77, 146.67, 139.12, 120.03, 110.97, 58.69, 25.73, 21.52, 18.08. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{12}H_{18}NO$ 192.1383, found 192.1385. IR (ATR): 3307, 2917, 1597, 1035, 1446, 691 cm^{-1}.



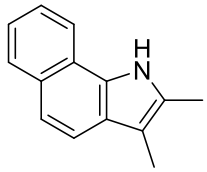
4,5,6-trimethoxy-2,3-dimethyl-1*H*-indole (3a): Yield 99% (470 mg), white solid, m.p.: 73-75 °C.^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.54 (s, 1H), 6.55 (s, 1H), 3.98 (s, 3H), 3.88 (s, 3H), 3.86 (s, 3H), 2.33 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (75 MHZ, $CDCl_3$) δ 150.15, 146.68, 136.60, 132.21, 128.99, 116.50, 106.75, 89.99, 61.87, 61.54, 56.46, 11.36, 10.13. HRMS (ESI-TOF) m/z: [M+ H^+] calcd for $C_{13}H_{18}NO_3$ 236.1281, found 236.1282. IR (ATR): 3342, 2930, 1623, 1459, 1100, 625 cm^{-1}.



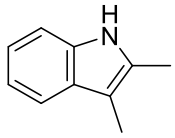
2,3,4,6-tetramethyl-1*H*-indole (3b): Yield 83% (287 mg), white solid, m.p.: 134-135 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.50 (s, 1H), 6.87 (s, 1H), 6.62 (s, 1H), 2.66 (s, 3H), 2.39 (s, 3H), 2.38 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (75 MHZ, $CDCl_3$) δ 135.97, 135.69, 130.67, 129.96, 129.56, 122.60, 108.17, 107.71, 21.54, 20.13, 11.57, 11.55. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{12}H_{16}N$ 174.1277, found 174.1276. IR (ATR): 3376, 2914, 1448, 1250, 1014, 831 cm^{-1}.



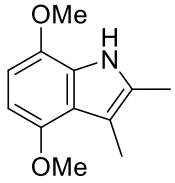
5-methoxy-2,3-dimethyl-1*H*-indole (3c):[2] Yield 30% (107 mg), pink solid, m.p.: 109-110 °. ^{1}H NMR (300 MHz, Chloroform-d) δ 7.57 (s, 1H), 7.14 (dd, J = 8.7, 0.6 Hz, 1H), 6.94 (d, J = 2.5 Hz, 1H), 6.77 (dd, J = 8.7, 2.5 Hz, 1H), 3.87 (s, 3H), 2.34 (d, J = 0.8 Hz, 3H), 2.20 (d, J = 0.7 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 153.97, 131.79, 130.41, 129.97, 110.79, 110.61, 107.13, 100.58, 56.11, 11.78, 8.66. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{11}H_{14}NO$ 176.1070, found 176.1074.



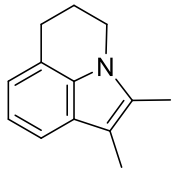
2,3-dimethyl-1*H*-benzo[*g*]indole (3d):[3] Yield 79% (308 mg), yellowish solid, m.p.: 146-148°. ^{1}H NMR (300 MHz, Chloroform-d) δ 8.42 (s, 1H), 7.98 – 7.88 (m, 2H), 7.62 (dd, J = 8.5, 0.7 Hz, 1H), 7.50 (dd, J = 8.4, 0.9 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.41 – 7.35 (m, 1H), 2.47 (d, J = 0.7 Hz, 3H), 2.31 (d, J = 0.8 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 130.10, 129.30, 129.04, 128.96, 125.26, 125.08, 123.23, 121.39, 119.87, 119.22, 118.79, 109.08, 11.80, 8.76. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{14}H_{14}N$ 196.1121, found 196.1123.



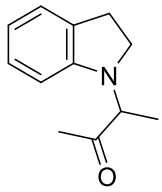
2,3-dimethyl-1*H*-indole (3e):[4] Yield 70% (203 mg), white solid, m.p.: 104-105 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.75 (s, 1H), 7.67 – 7.61 (m, 1H), 7.41 – 7.37 (m, 1H), 7.31 – 7.21 (m, 2H), 2.50 (d, *J* = 0.8 Hz, 3H), 2.39 (d, *J* = 0.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.29, 130.76, 129.53, 120.99, 119.11, 118.05, 110.14, 107.21, 11.63, 8.57. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{10}H_{12}N$ 146.0964, found 146.0958.



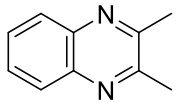
4,7-dimethoxy-2,3-dimethyl-1*H*-indole (3f):[5] Yield 99% (410 mg), pink solid, m.p.: 102-103 °C . ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 6.44 (d, *J* = 8.3 Hz, 1H), 6.34 (d, *J* = 8.3 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 2.40 (d, *J* = 0.7 Hz, 3H), 2.31 (d, *J* = 0.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.04, 140.56, 129.13, 126.77, 120.32, 107.88, 100.73, 98.85, 55.86, 55.77, 11.35, 10.55. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{12}H_{16}NO_2$ 206.1176, found 206.1179.



1,2-dimethyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*] quinoline (3g):[6] Yield 86% (319 mg), yellowish solid, m.p.: 86-87 °C.^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.35 (dd, J = 7.9, 1.0 Hz, 1H), 7.02 (dd, J = 7.9, 7.0 Hz, 1H), 6.88 (dd, J = 7.0, 1.0 Hz, 1H), 4.09 – 3.98 (m, 2H), 3.01 (t, J = 6.2 Hz, 2H), 2.37 (s, 3H), 2.30 (s, 3H), 2.32 – 2.20 (m, 2H). ^{13}C NMR (75 MHz, CDCl3) δ 133.78, 131.42, 126.36, 120.80, 118.77, 117.53, 115.48, 105.87, 41.51, 24.96, 23.15, 9.64, 8.98. HRMS (ESI-TOF) *m/z*: [M+ H^{+}] calcd for $C_{13}H_{16}N$ 186.1277, found 186.1274.

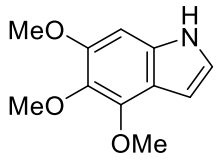


3-(indolin-1-yl)butan-2-one (2d):[7] Yield 80% (303 mg), yellow oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.12 – 7.01 (m, 2H), 6.67 (td, *J* = 7.4, 1.0 Hz, 1H), 6.35 – 6.31 (m, 1H), 4.07 (q, *J* = 7.0 Hz, 1H), 3.53 – 3.33 (m, 2H), 3.07 – 2.96 (m, 2H), 2.22 (s, 3H), 1.29 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.80, 150.49, 130.05, 127.49, 124.86, 118.00, 106.60, 60.96, 48.95, 28.47, 27.38, 11.01. HRMS (ESI-TOF) *m/z*: [M+ H^{+}] calcd for $C_{12}H_{16}NO$ 190.1226, found 190.1226.

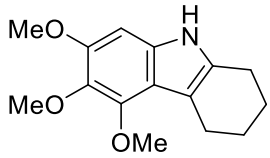


2,3-dimethylquinoxaline (4):[8] Yield 88% (278 mg), white solid, m.p.:

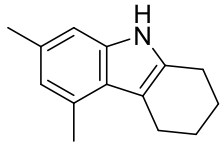
842 mg, 88% yield, oil. 1 H NMR (300 MHz, CDCl3) δ: 8.07 (bs, 1H), 7.04 (dd, J = 3.3, 2.4 Hz, 1H), 6.65 (d, J = 0.8 Hz, 1H), 6.65 (ddd, J = 3.2, 2.2, 0.9 Hz, 1H), 4.11 (s, 3H), 3.88 (s, 6H). 13C NMR (75 MHz, CDCl3) δ: 151.3 (2C, C), 146.1 (1C, C), 132.9 (1C, C), 122.3(1C, CH), 115.1 (1C, C), 100.5 (1C, CH), 89.6 (1C, CH), 61.7 (1C, CH3), 60.8 (1C, CH3), 56.4 (1C, CH3).



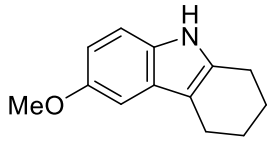
4,5,6-trimethoxy-1*H*-indole (5):[9] 75% yield, 357 mg, oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.07 (bs, 1H), 7.04 (dd, *J* = 3.3, 2.4 Hz, 1H), 6.65 (d, *J* = 0.8 Hz, 1H), 6.65 (ddd, *J* = 3.2, 2.2, 0.9 Hz, 1H), 4.11 (s, 3H), 3.88 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.3 (2C, C), 146.1 (1C, C), 132.9 (1C, C), 122.3(1C, CH), 115.1 (1C, C), 100.5 (1C, CH), 89.6 (1C, CH), 61.7 (1C, CH3), 60.8 (1C, CH3), 56.4 (1C, CH3).



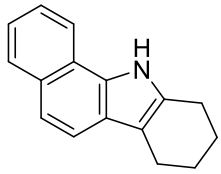
5,6,7-trimethoxy-2,3,4,9-tetrahydro-1*H*-carbazole (7a): Yield 98% (512 mg), oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.60 (s, 1H), 6.57 (s, 1H), 3.98 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H), 2.92 – 2.86 (m, 2H), 2.68 – 2.64 (m, 2H), 1.91 – 1.81 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.18, 146.44, 136.51, 132.56, 132.32, 115.45, 109.48, 90.42, 61.97, 61.56, 56.50, 23.69, 23.35, 23.12, 22.66. HRMS (ESI-TOF) m/z: [M+ H^++ $2H_2O$] calcd for $C_{15}H_{20}NO_5$ 294.1336, found 294.1337. IR (ATR): 2935, 1597, 1463, 1102, 997, 727 cm^{-1}.



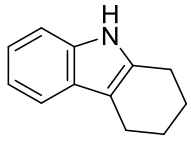
5,7-dimethyl-2,3,4,9-tetrahydro-1*H*-carbazole (7b):[10] Yield 35% (139 mg), white solid, m.p.: 141-142 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.49 (s, 1H), 6.88 (dt, *J* = 1.5, 0.7 Hz, 1H), 6.62 (dt, *J* = 1.6, 0.8 Hz, 1H), 3.04 – 2.92 (m, 2H), 2.69-2.67 (m, 2H), 2.61 (s, 3H), 2.38 (s, 3H), 1.87-1.75 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.23, 132.86, 130.78, 129.85, 124.65, 122.29, 110.44, 108.28, 23.95, 23.73, 23.54, 22.95, 21.61, 19.86. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{14}H_{18}N$ 200.1434, found 200.1426.



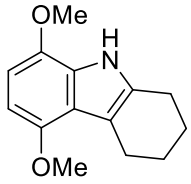
6-methoxy-2,3,4,9-tetrahydro-1*H*-carbazole (7c):[11] Yield 41% (165 mg), pink solid, m.p.: 168-169 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.16 (dd, *J* = 8.7, 0.6 Hz, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.77 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.86 (s, 3H), 2.70-2.68 (m, 4H), 1.98 – 1.80 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.00, 135.24, 130.86, 128.35, 111.07, 110.65, 110.17, 100.43, 56.12, 23.48, 23.45, 23.35, 21.10. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{13}H_{16}NO$ 202.1226, found 202.1222.



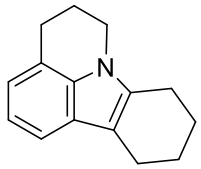
8,9,10,11-tetrahydro-7*H*-benzo[*a*]carbazole (7d):[10] Yield 35% (155 mg), pink-white solid, m.p.: 139-140 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 7.95 – 7.86 (m, 2H), 7.61 (dd, *J* = 8.6, 0.7 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.37 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 2.94 – 2.72 (m, 4H), 1.97.-1.93 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.37, 130.18, 129.79, 129.07, 125.26, 123.46, 123.20, 121.63, 119.95, 119.26, 118.60, 112.13, 23.52, 23.46, 23.46, 21.20. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{16}H_{16}N$ 222.1277, found 222.1273.



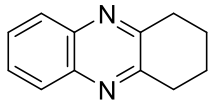
6,7,8,9-tetrahydro-1*H*-carbazole (7e):[12] Yield 45% (154 mg), white solid, m.p.: 117-118 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.66 (s, 1H), 7.49 – 7.44 (m, 1H), 7.28 (dd, *J* = 6.8, 1.7 Hz, 1H), 7.17 – 7.03 (m, 2H), 2.78 – 2.66 (m, 4H), 1.93-1.87 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.76, 134.20, 127.95, 121.12, 119.23, 117.86, 110.44, 110.32, 23.43, 23.39, 23.35, 21.05. HMRS (ESI-TOF) m/z: [M+H^+] calcd for $C_{12}H_{14}N$ 172.1120, found 172.1119.



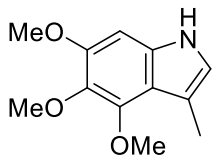
5,8-dimethoxy-2,3,4,9-tetrahydro-1*H*-carbazole (7f):[5] Yield 33% (153 mg), white solid, m.p.: 97-98 °C ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 6.44 (d, *J* = 8.3 Hz, 1H), 6.33 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 2.98 – 2.89 (m, 2H), 2.75 – 2.67 (m, 2H), 1.96 – 1.77 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.97, 140.83, 132.28, 127.12, 119.23, 110.63, 101.06, 98.95, 55.94, 55.88, 23.75, 23.36, 23.10, 23.08. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{14}H_{18}NO_2$ 232.1332, found 232.1332.



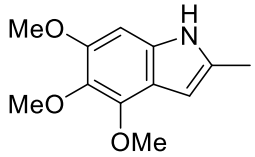
5,6,8,9,10,11-hexahydro-4*H*-pyrido[3,2,1-*jk*]carbazole (7g): Yield 67% (283 mg), white solid, m.p.: 59-60 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.30 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.98 (dd, *J* = 7.9, 7.1 Hz, 1H), 6.85 (dd, *J* = 7.1, 1.1 Hz, 1H), 4.04 – 3.94 (m, 2H), 3.07 – 2.92 (m, 2H), 2.82 – 2.64 (m, 4H), 2.32 – 2.15 (m, 2H), 1.93-1.86 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.53, 134.05, 124.97, 120.99, 118.86, 117.69, 115.38, 108.93, 41.10, 25.09, 23.60, 23.28, 23.05, 21.82, 21.51. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{12}H_{18}N$ 212.1434, found 212.1434. IR (ATR): 2928, 2854, 1477, 1073, 802, 667 cm^{-1}.



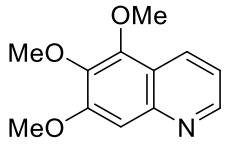
1,2,3,4-tetrahydrophenazine (8):[13] Yield 23% (85 mg), pink solid, m.p.: 93-94 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.02 – 7.91 (m, 2H), 7.69 – 7.61 (m, 2H), 3.18-3.14 (m, 4H), 2.2-1.98 (m, 4). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.28, 141.32, 129.08, 128.45, 33.33, 22.93. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{12}H_{13}N_2$ 185.1073, found 185.1079.



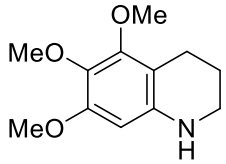
4,5,6-trimethoxy-3-methyl-1*H*-indole (9a):[9] Yield 66% (292 mg), oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 6.54 (d, *J* = 0.9 Hz, 1H), 6.24 (dt, *J* = 2.1, 1.0 Hz, 1H), 4.08 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 2.38 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.21, 145.19, 135.54, 133.11, 115.79, 97.93, 89.55, 61.62, 60.69, 56.44, 13.67. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{12}H_{16}NO_3$ 222.1125, found 222.1127.



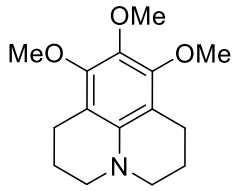
4,5,6-trimethoxy-2-methyl-1*H*-indole (9b): Yield 13% (58 mg), yellowish solid, m.p.: 88-89 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.71 (s, 1H), 6.75 (dq, *J* = 2.3, 1.1 Hz, 1H), 6.61 (s, 1H), 4.00 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 2.43 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.16, 147.37, 136.61, 133.57, 120.29, 115.66, 111.85, 90.20, 61.85, 61.54, 56.37, 11.63. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{12}H_{16}NO_3$ 222.1125, found 222.1125. IR (ATR) : 3340, 2925, 1621, 1439, 1110, 632 cm^{-1}.



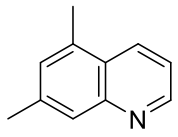
5,6,7-trimethoxyquinoline (10a): Yield 38% (167 mg), oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.77 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.35 (ddd, *J* = 8.3, 1.8, 0.7 Hz, 1H), 7.29 – 7.24 (m, 2H), 4.07 (s, 3H), 4.01 (s, 3H), 3.99 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.98, 149.80, 146.95, 146.16, 140.91, 130.32, 119.43, 118.91, 104.20, 61.66, 61.31, 56.14. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{12}H_{14}NO_3$ 220.1968, found 220.0963. IR (ATR): 2939, 1615, 1477, 1236, 1120, 811 cm^{-1}.



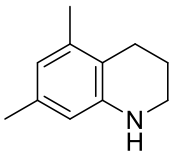
5,6,7-trimethoxy-1,2,3,4-tetrahydroquinoline (10b):[14] Yield 5% (22 mg), yellow oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.87 (s, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.77 (s, 3H), 3.27 – 3.18 (m, 2H), 2.65 (t, *J* = 6.5 Hz, 2H), 1.97 – 1.84 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.23, 152.09, 141.18, 133.99, 107.53, 94.46, 61.25, 60.56, 55.99, 42.06, 22.16, 20.75. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{12}H_{18}NO_3$ 224.1281, found 224.1285.



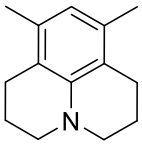
3,4,5-trimethoxyjulolidine (10c): Yield 4% (21 mg), white solid, m.p.: 89-90 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.82 (s, 6H), 3.82 (s, 3H), 3.10 – 2.96 (m, 4H), 2.69 (t, *J* = 6.7 Hz, 4H), 1.97-1.94 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.65, 139.95, 127.87, 111.18, 61.12, 60.51, 50.20, 22.04, 21.52. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{15}H_{22}NO_3$ 264.1594, found 264.1599. IR (ATR): 2922, 1461, 1287, 1091, 1018, 801 cm^{-1}.



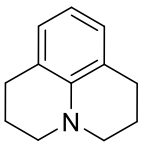
5,7-dimethylquinoline (11a):[15] Yield 62% (21 mg), yellowish oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.86 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.26 (ddd, *J* = 8.5, 1.7, 0.9 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.34 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.22 (s, 1H), 2.64 (d, *J* = 0.8 Hz, 3H), 2.52 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.04, 148.98, 139.45, 134.27, 132.35, 129.50, 126.75, 125.83, 120.01, 21.94, 18.60. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{11}H_{12}N$ 158.0964, found 158.0962.



5,7-dimethyl-1,2,3,4-tetrahydroquinoline (11b):[16] Yield 7% (20 mg), yellow oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.36 (s, 1H), 6.21 (s, 1H), 3.29 – 3.14 (m, 2H), 2.60 (t, *J* = 6.6 Hz, 2H), 2.19 (s, 3H), 2.14 (s, 3H), 2.04 – 1.90 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.00, 137.24, 135.93, 120.18, 117.44, 113.11, 41.80, 23.92, 22.86, 21.10, 19.39. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{11}H_{16}N$ 162.1277, found 162.1279.



3,5-Dimethyljulolidine (11c):[17] Yield 17% (69 mg), yellow solid, m.p.: 70-71 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.38 (s, 1H), 3.13 – 2.99 (m, 4H), 2.63 (t, *J* = 6.8 Hz, 4H), 2.16 – 2.08 (s, 6H), 2.10-2.98 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.87, 133.97, 120.51, 118.51, 50.36, 25.01, 22.57, 19.67. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{14}H_{20}N$ 202.1590, found 264.1583.



Julolidine (12c):[18] Yield 10% (35 mg), white solid, m.p.: 40 - 41 °C. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.78 (dt, *J* = 7.4, 0.9 Hz, 2H), 6.49 (t, *J* = 7.4 Hz, 1H), 3.22 – 3.05 (m, 4H), 2.76 (t, *J* = 6.5 Hz, 4H), 2.08 – 1.90 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.11, 127.06, 121.72, 115.86, 50.20, 27.79, 22.26. HRMS (ESI-TOF) *m/z*: [M+ H^+] calcd for $C_{12}H_{16}N$ 174.12827, found 174.1282.

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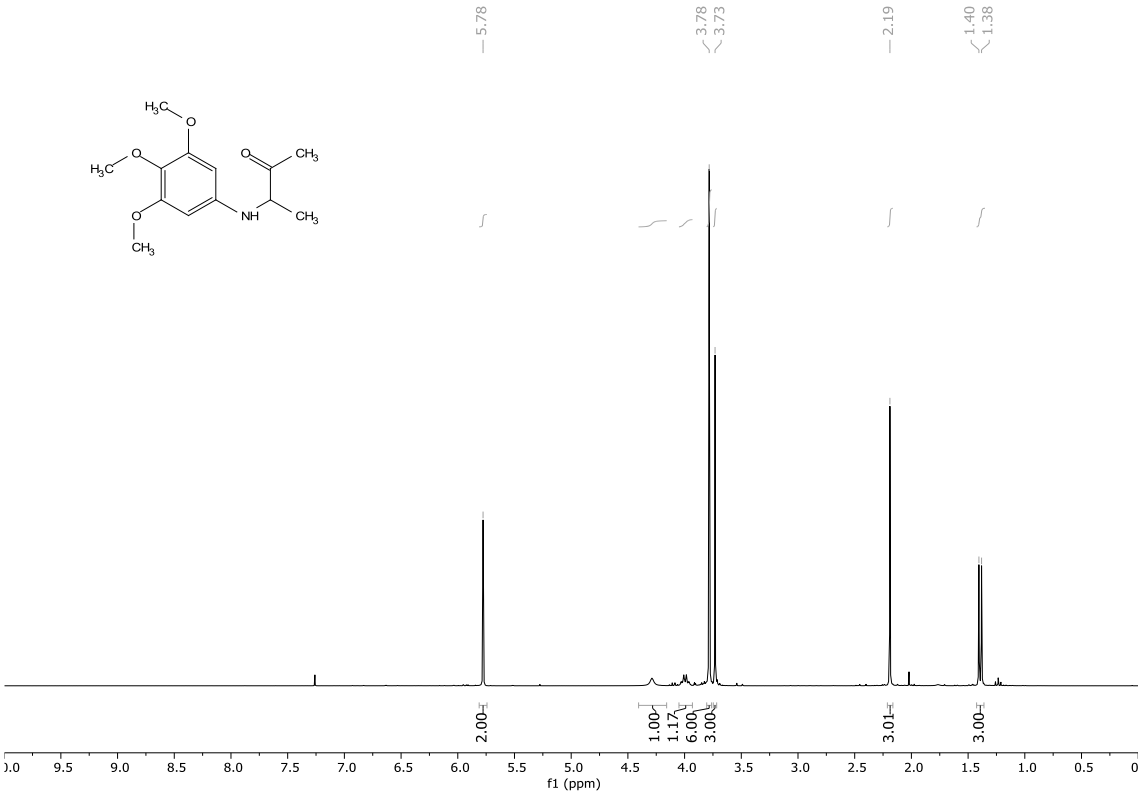
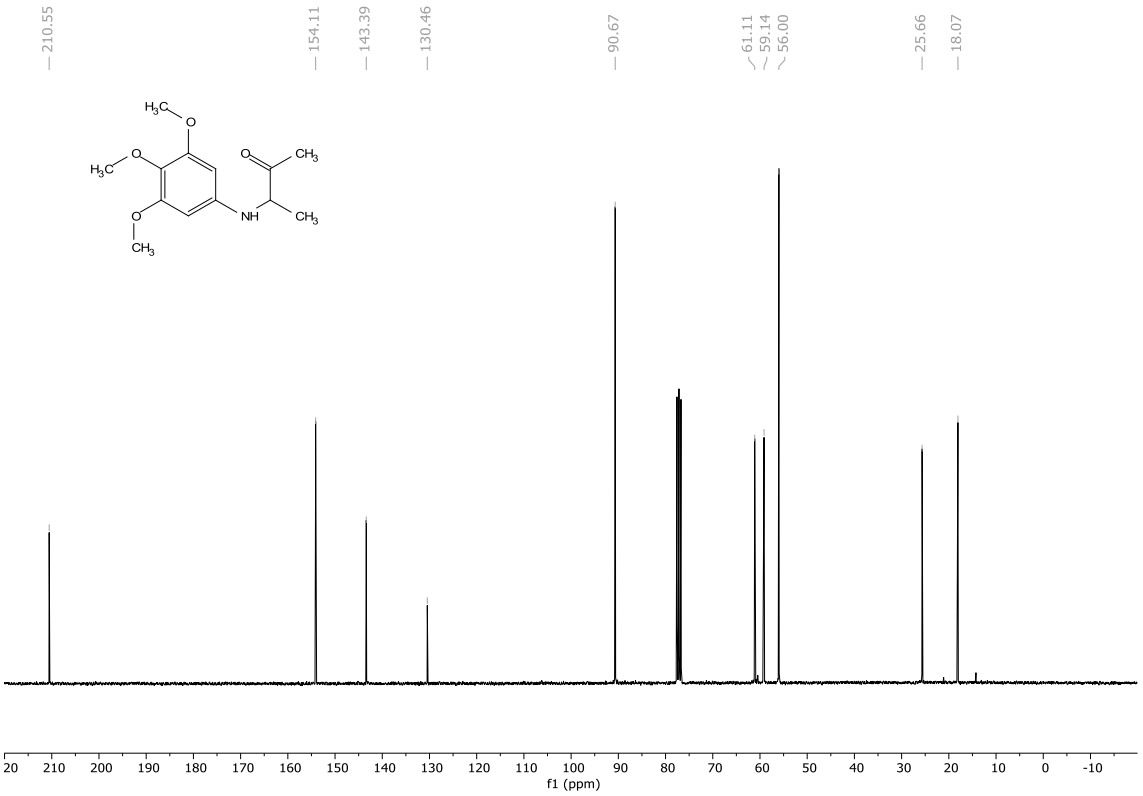
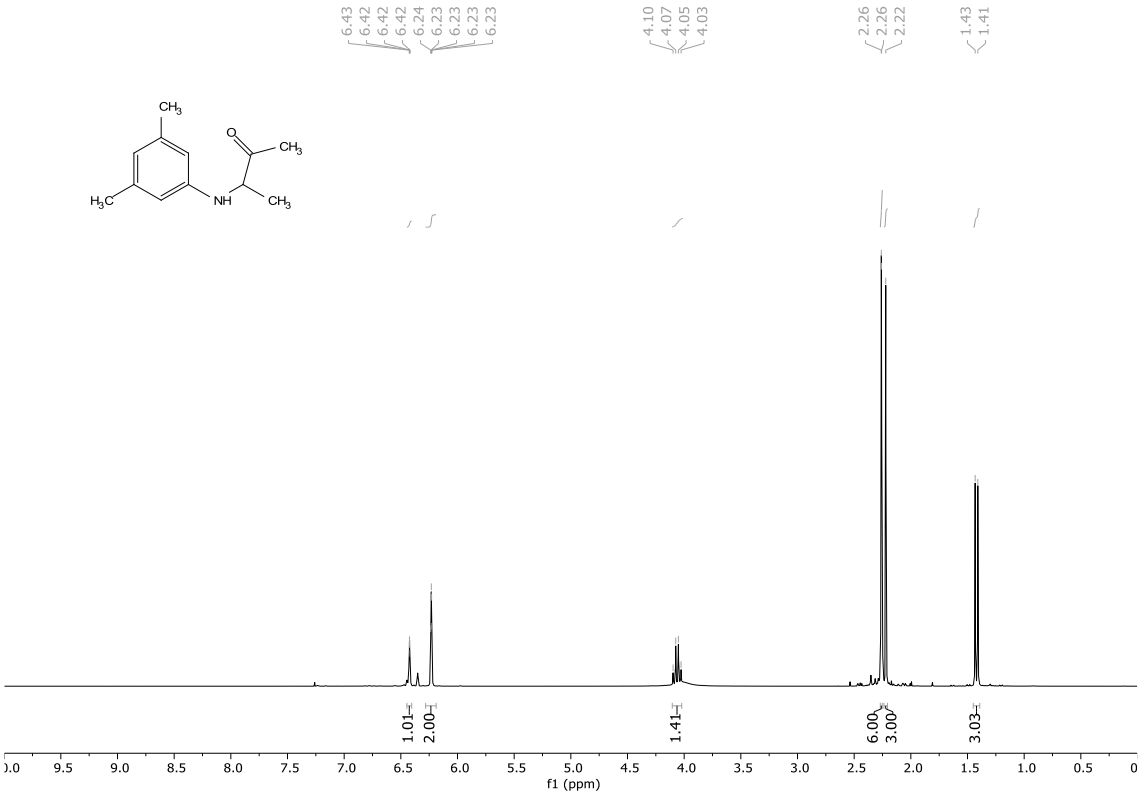
^{1}H- and ^{13}C NMR spectra

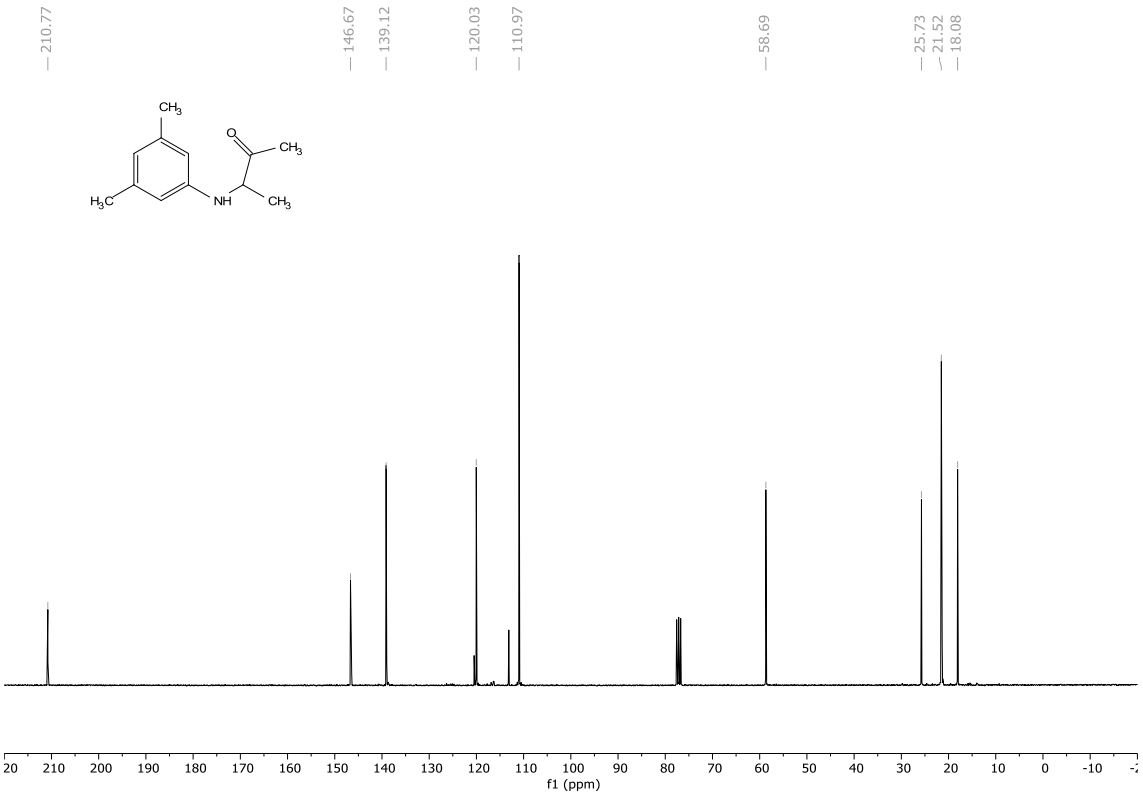
3-((3,4,5-trimethoxyphenyl)amino)butan-2-one (2a)



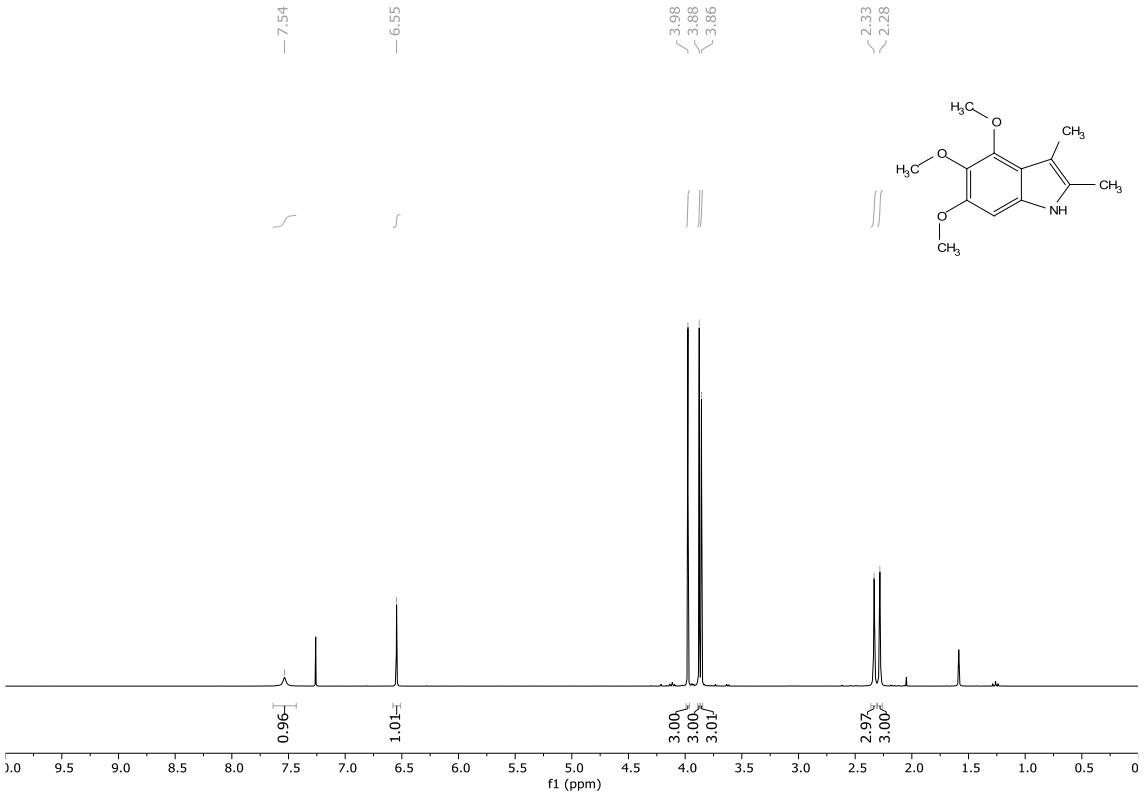


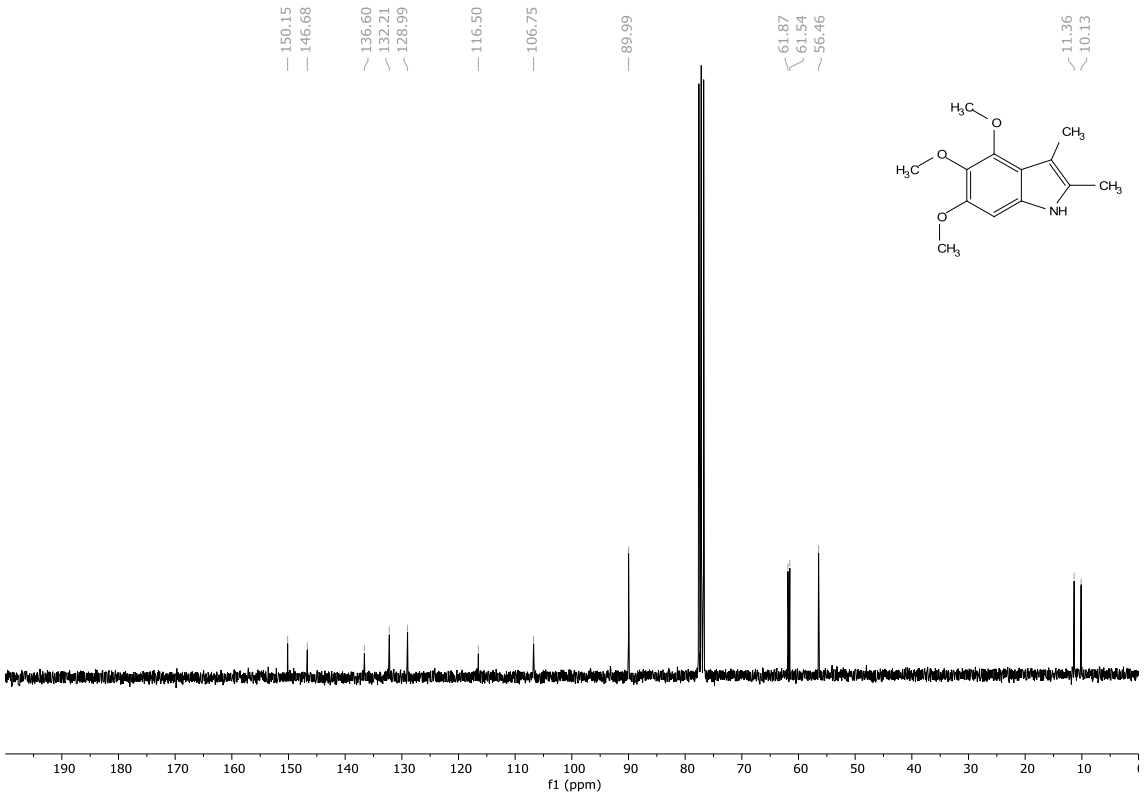
3-((3,5-dimethylphenyl)amino)butan-2-one (2b):



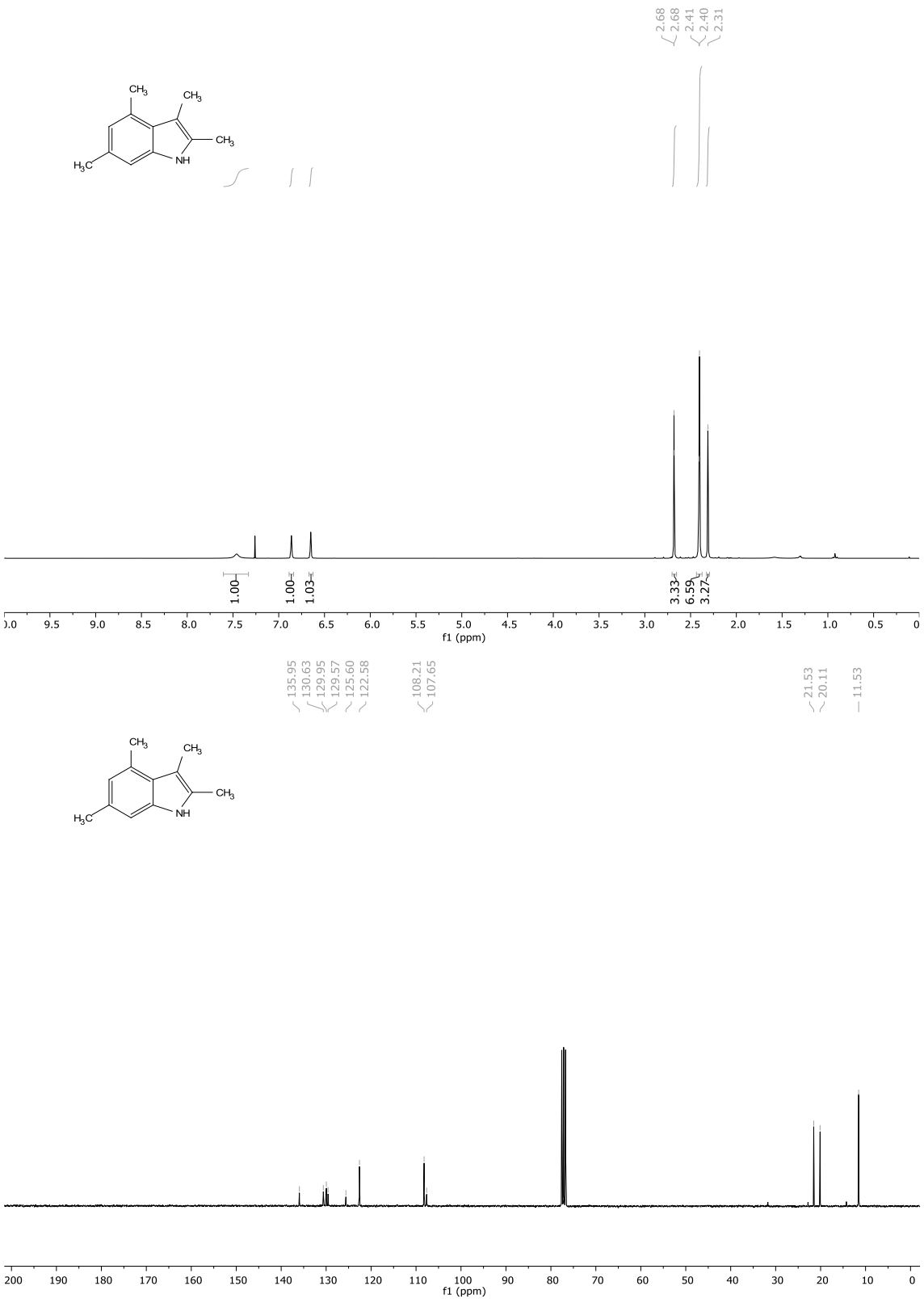


4,5,6-trimethoxy-2,3-dimethyl-1*H*-indole (3a):

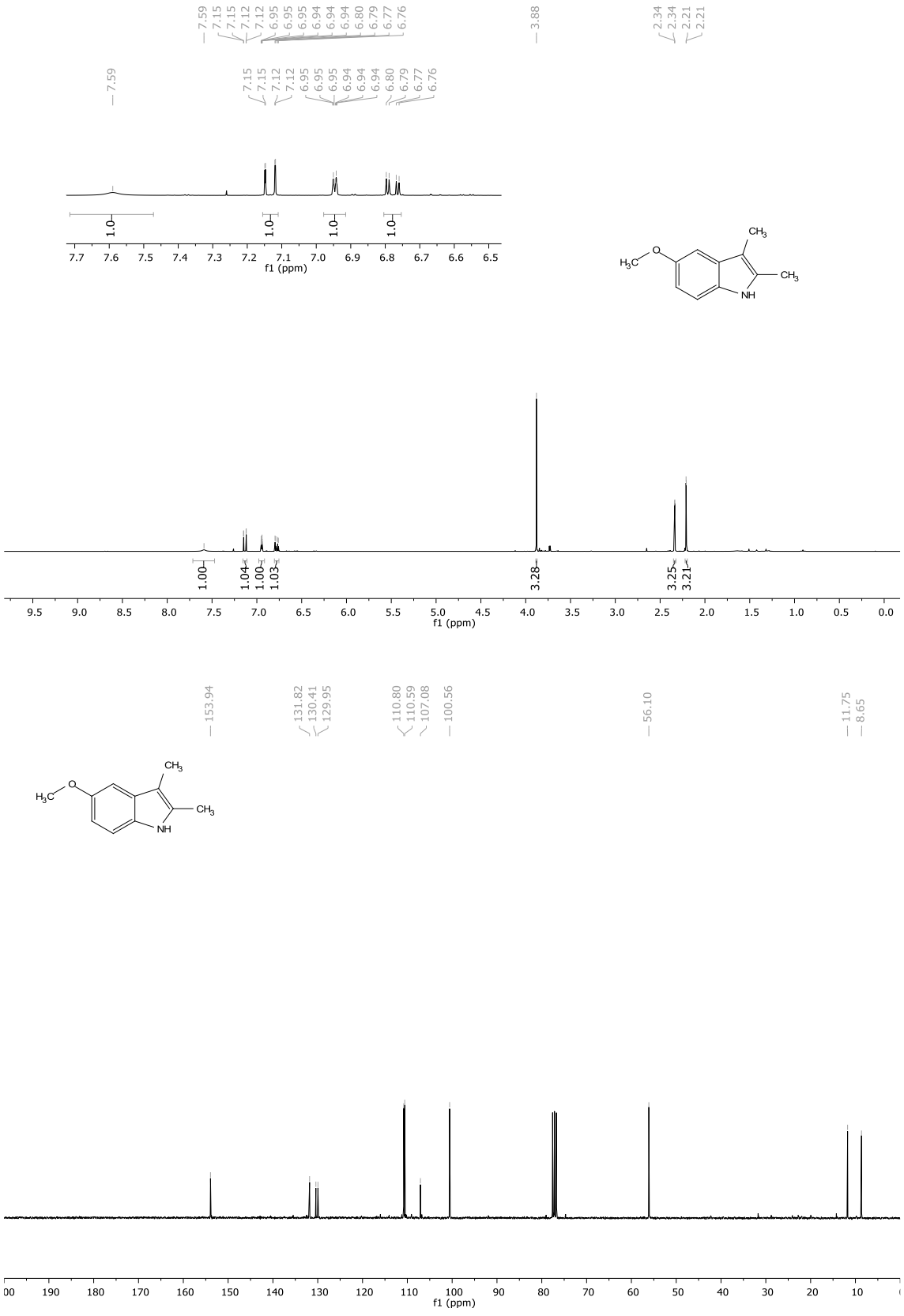




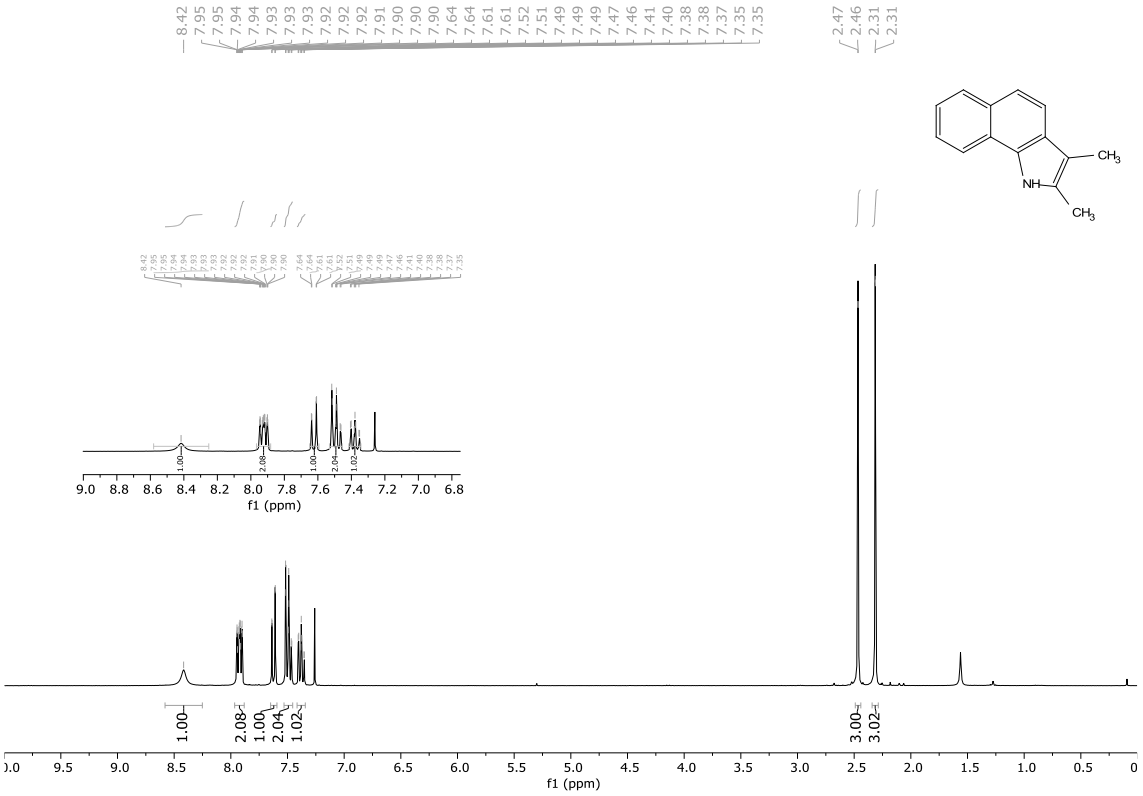
2,3,4,6-tetramethyl-1*H*-indole (3b)

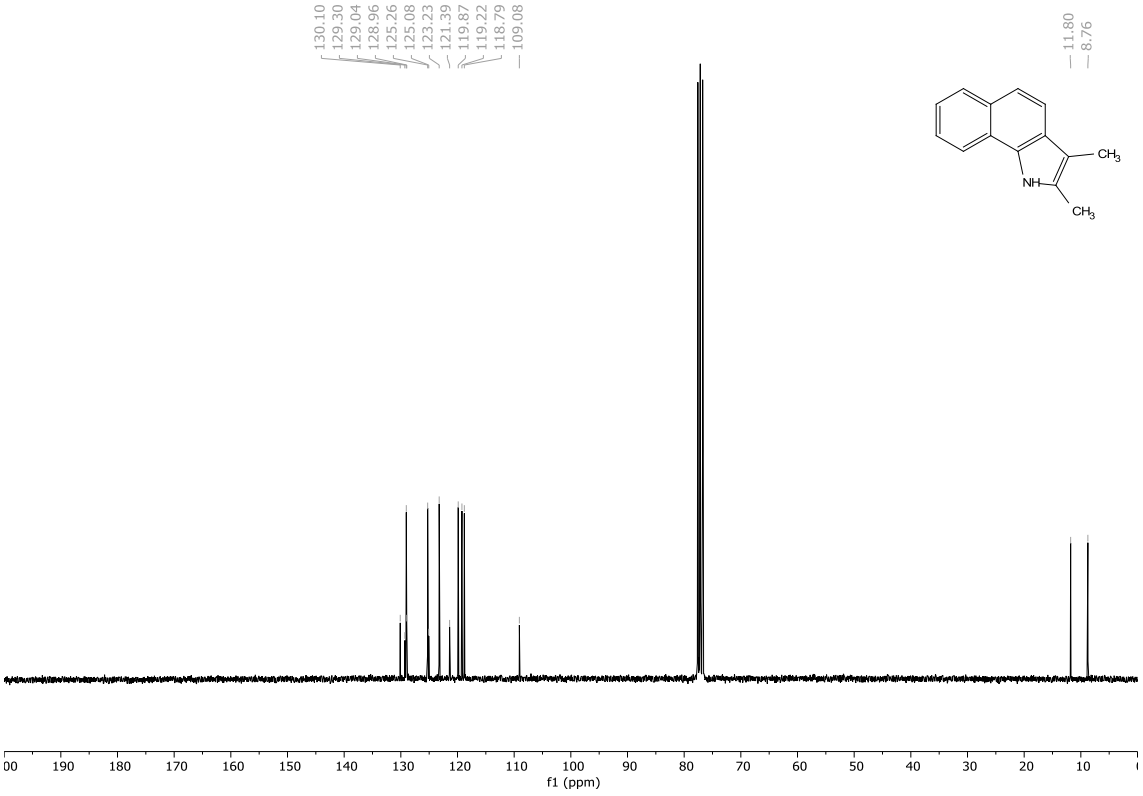


5-methoxy-2,3-dimethyl-1*H*-indole (3c):

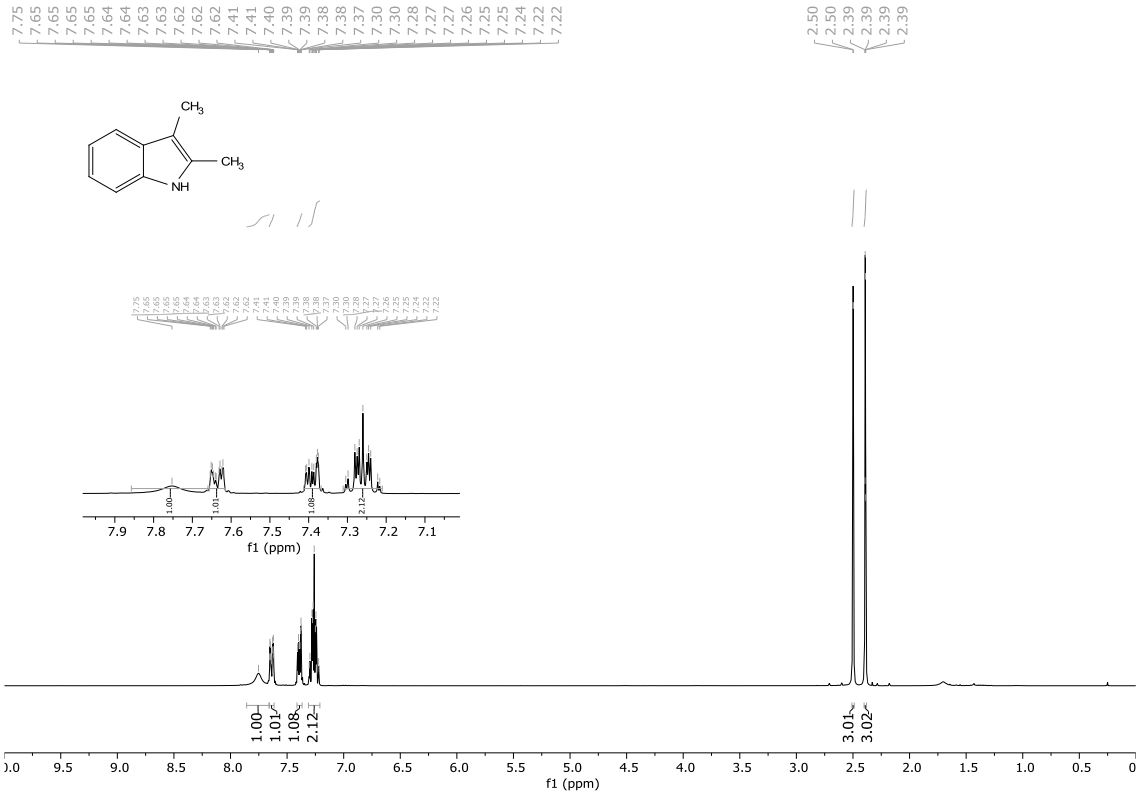


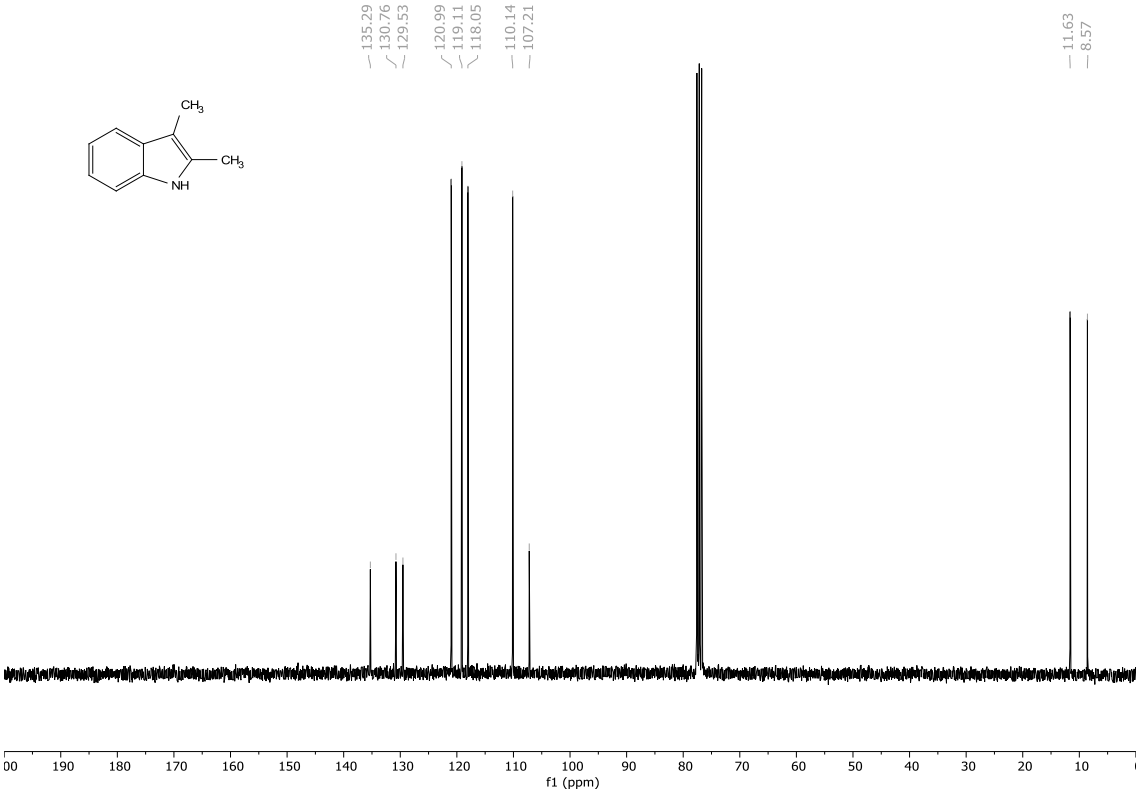
2,3-dimethyl-1*H*-benzo[*g*]indole (3d):



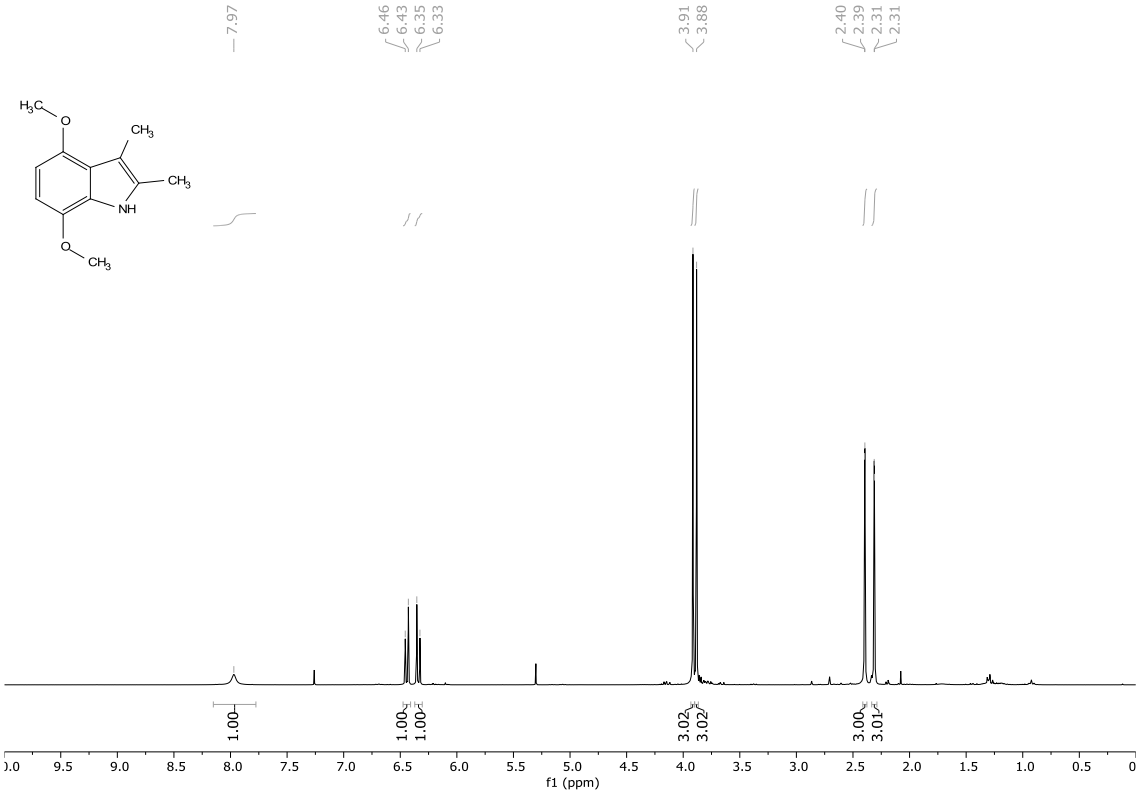


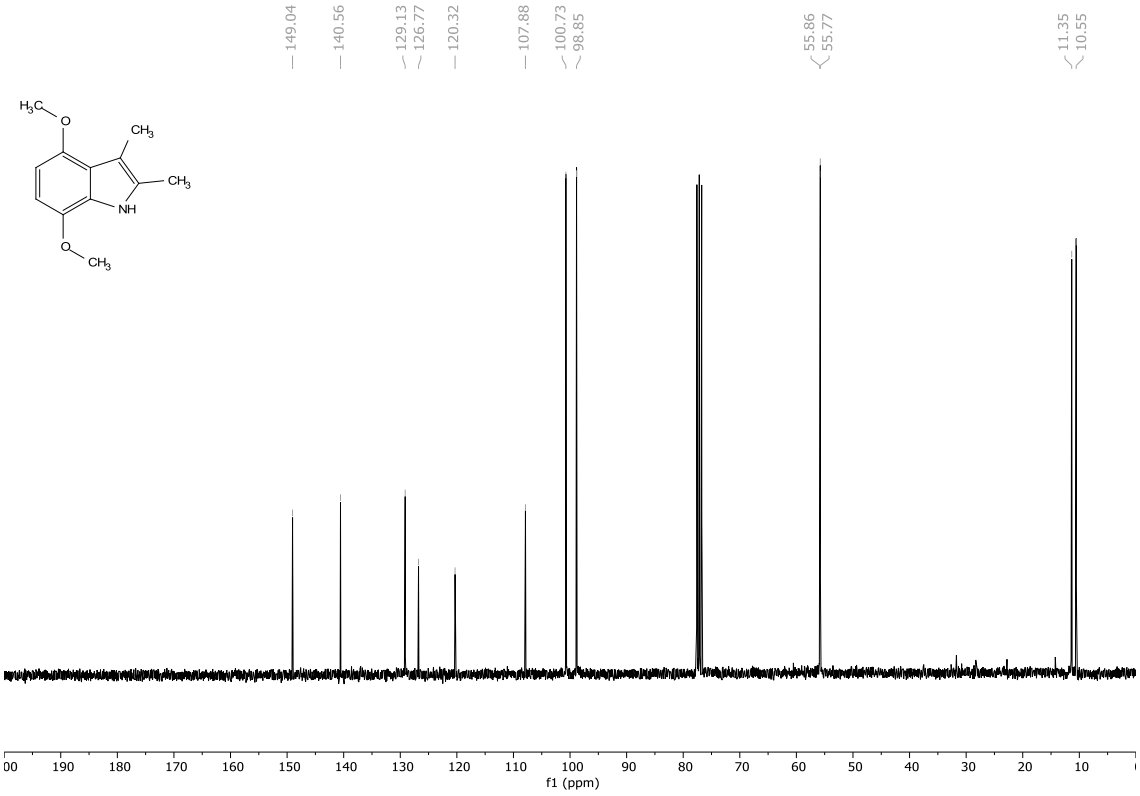
2,3-dimethyl-1*H*-indole (3e):



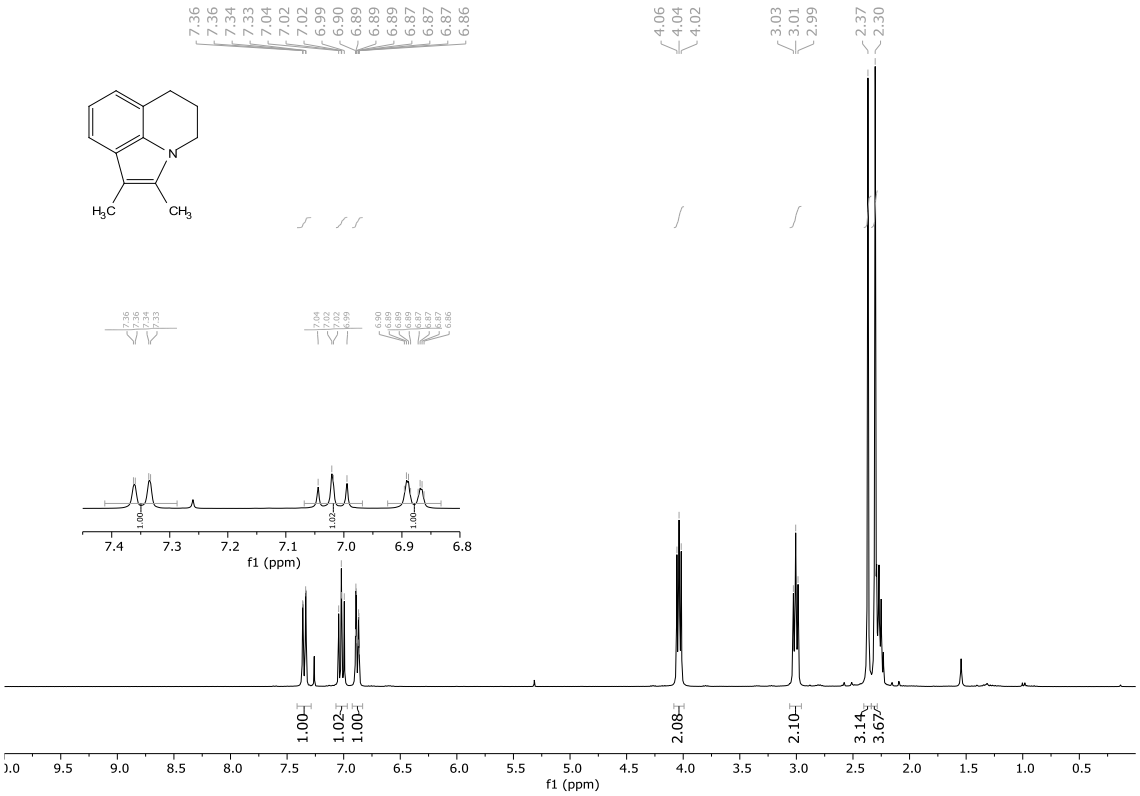


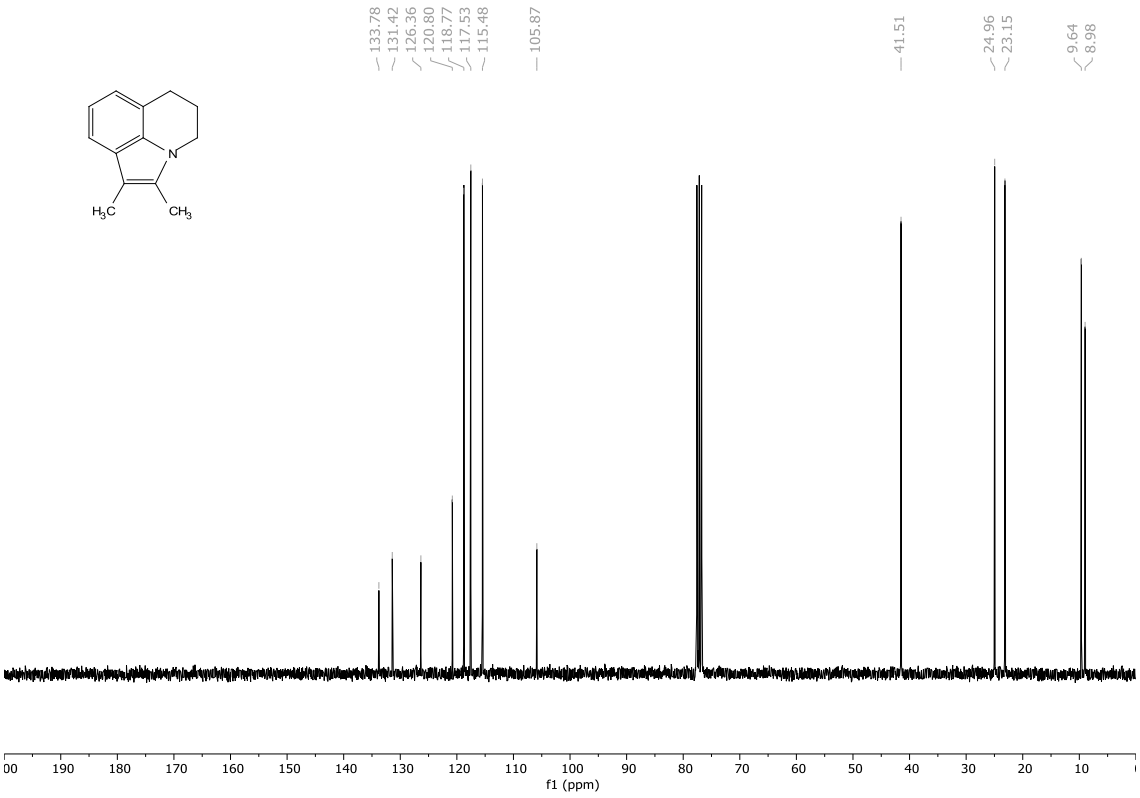
4,7-dimethoxy-2,3-dimethyl-1*H*-indole (3f):



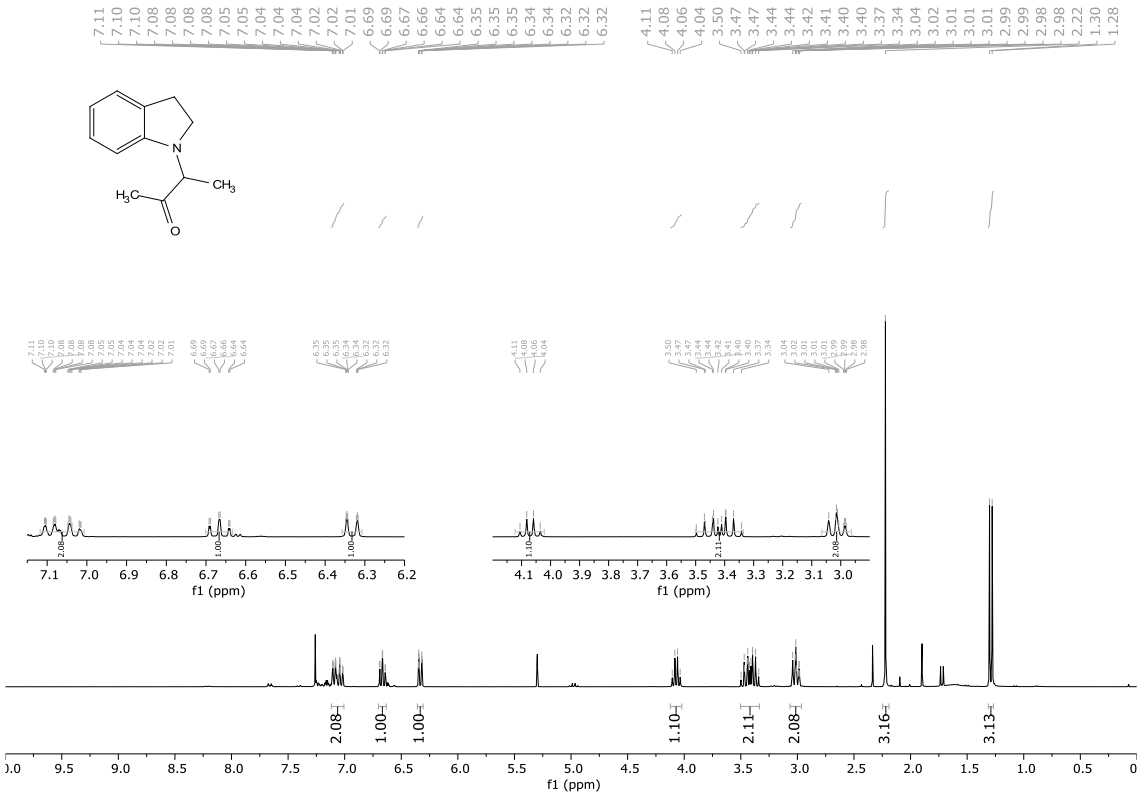


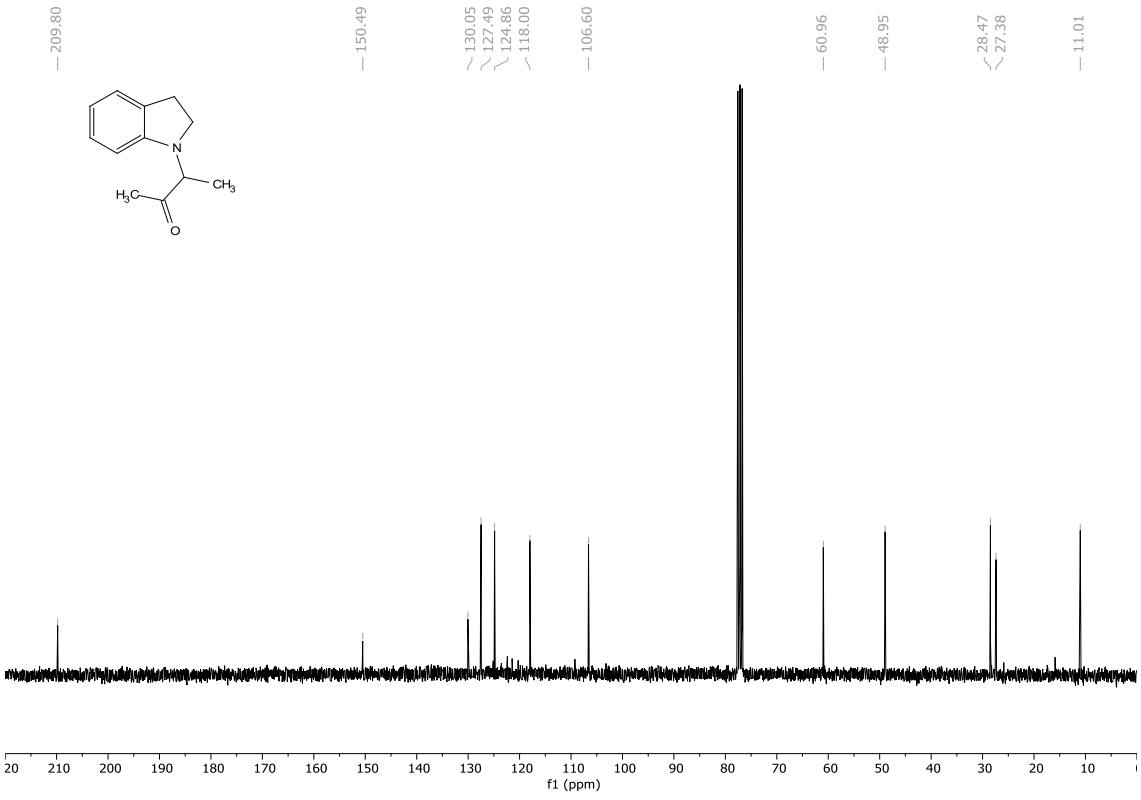
1,2-dimethyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*] quinoline (3g):



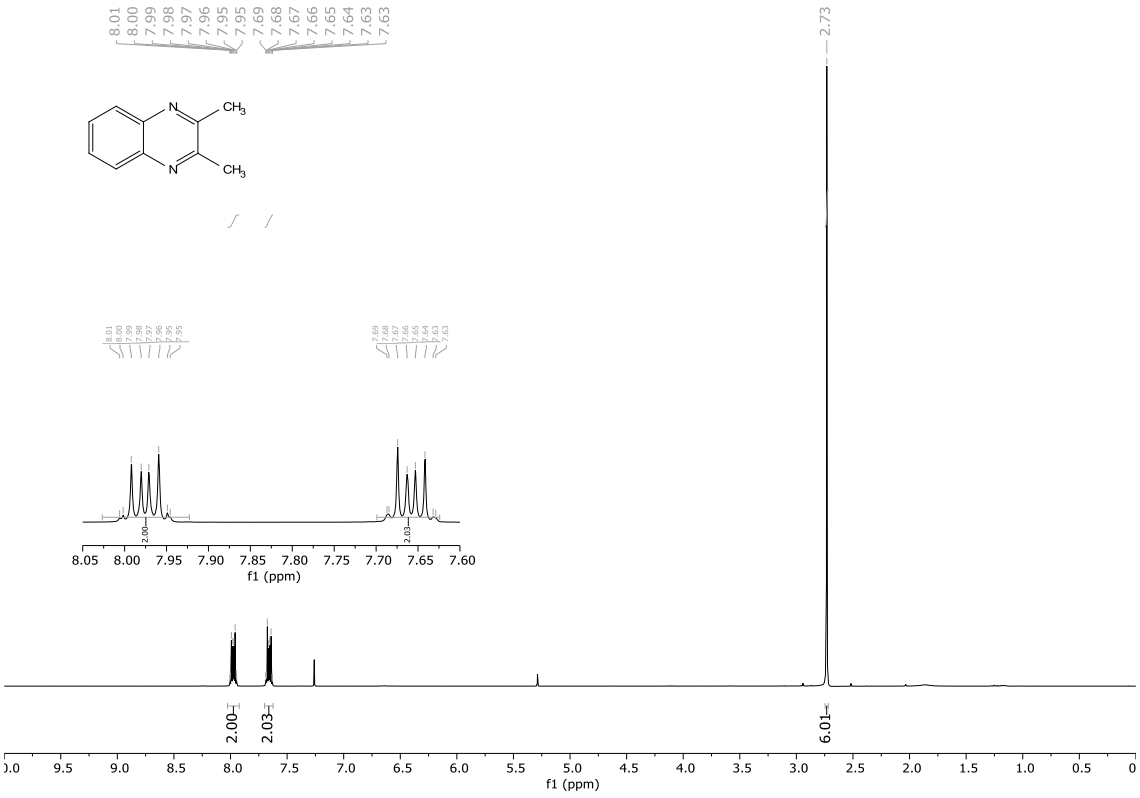


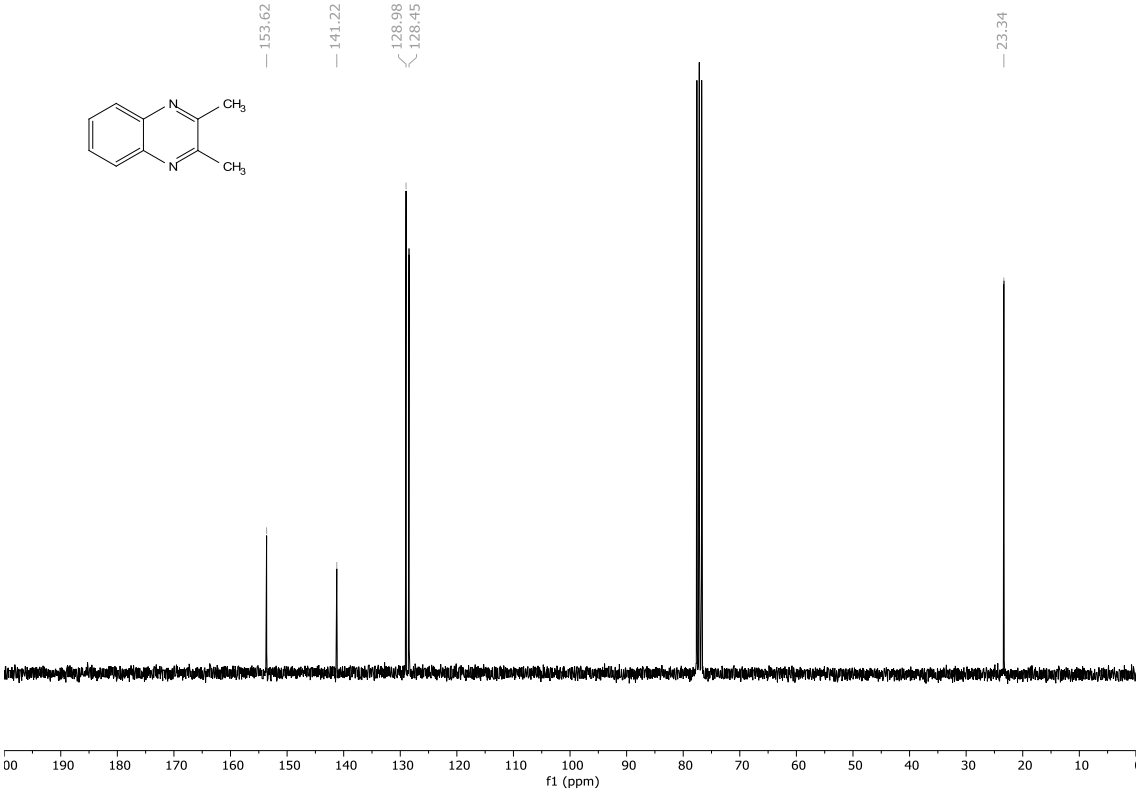
3-(indolin-1-yl)butan-2-one (2d):



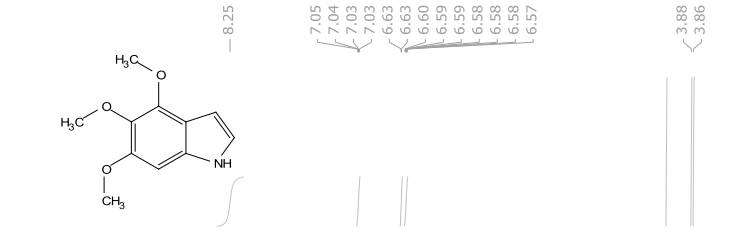


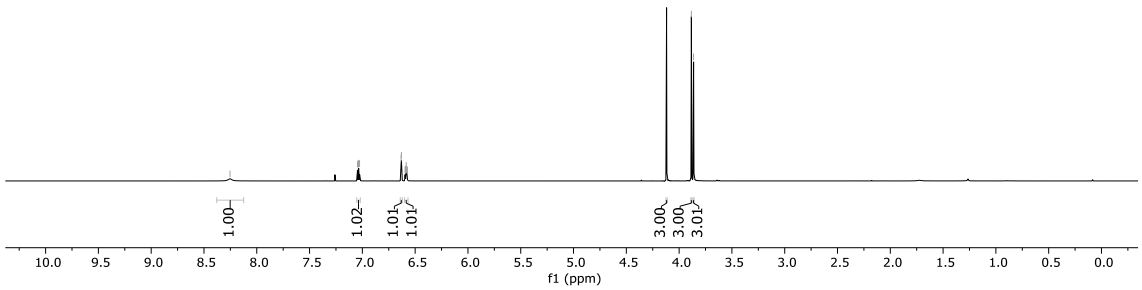
2,3-dimethylquinoxaline (4):

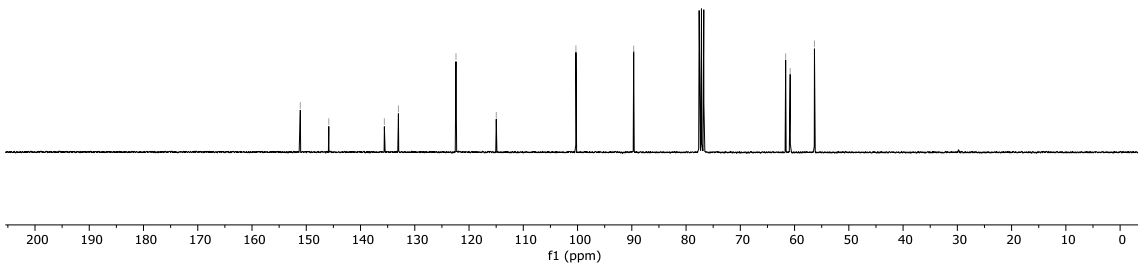




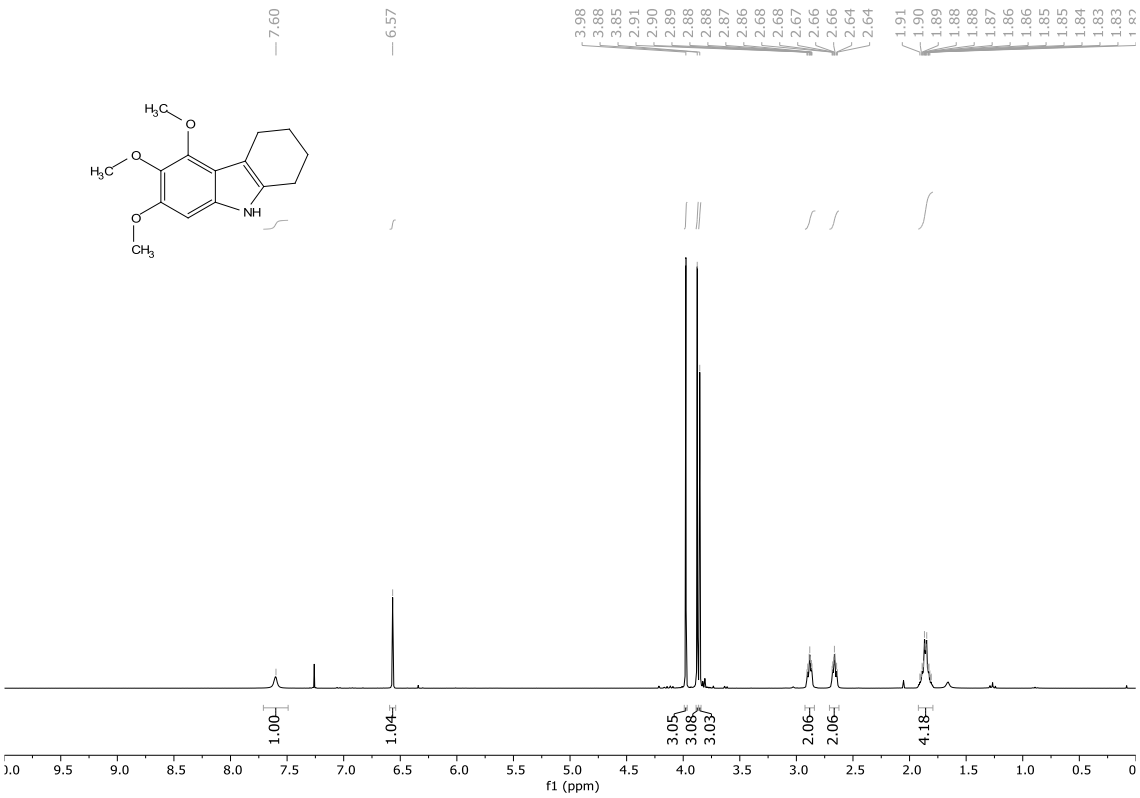
5,6,7-trimethoxy-1*H*-indole (5)

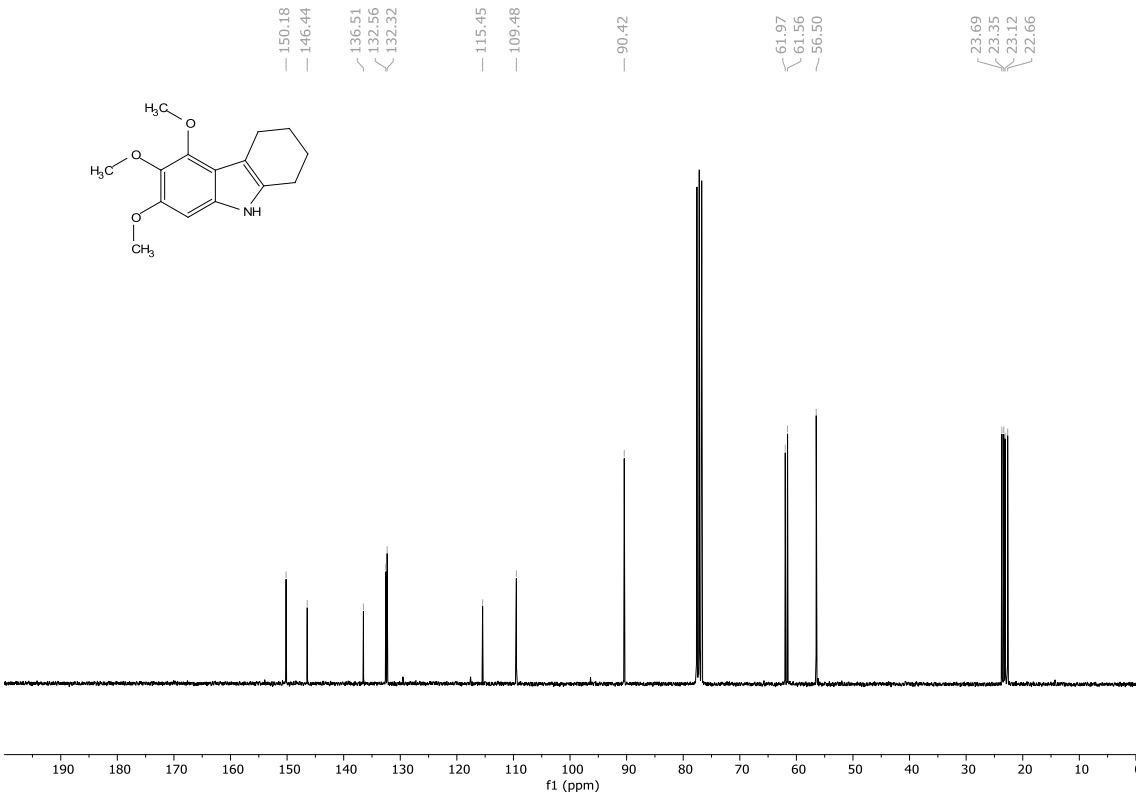




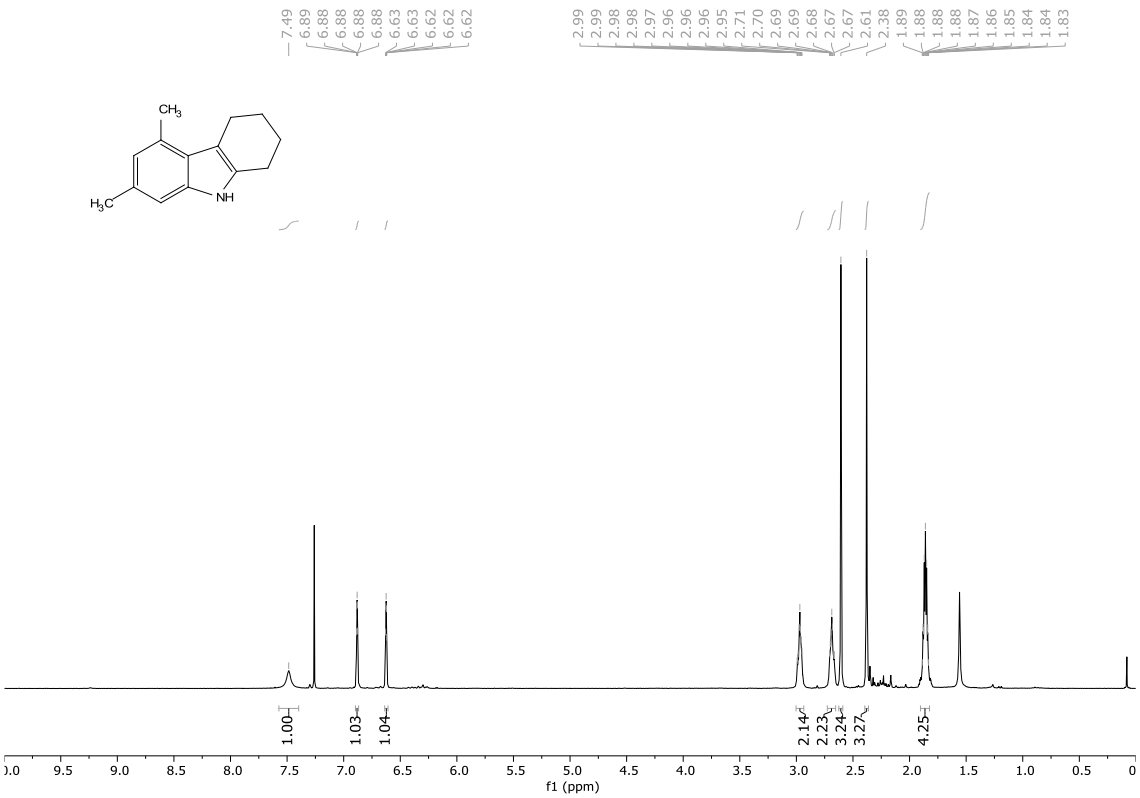


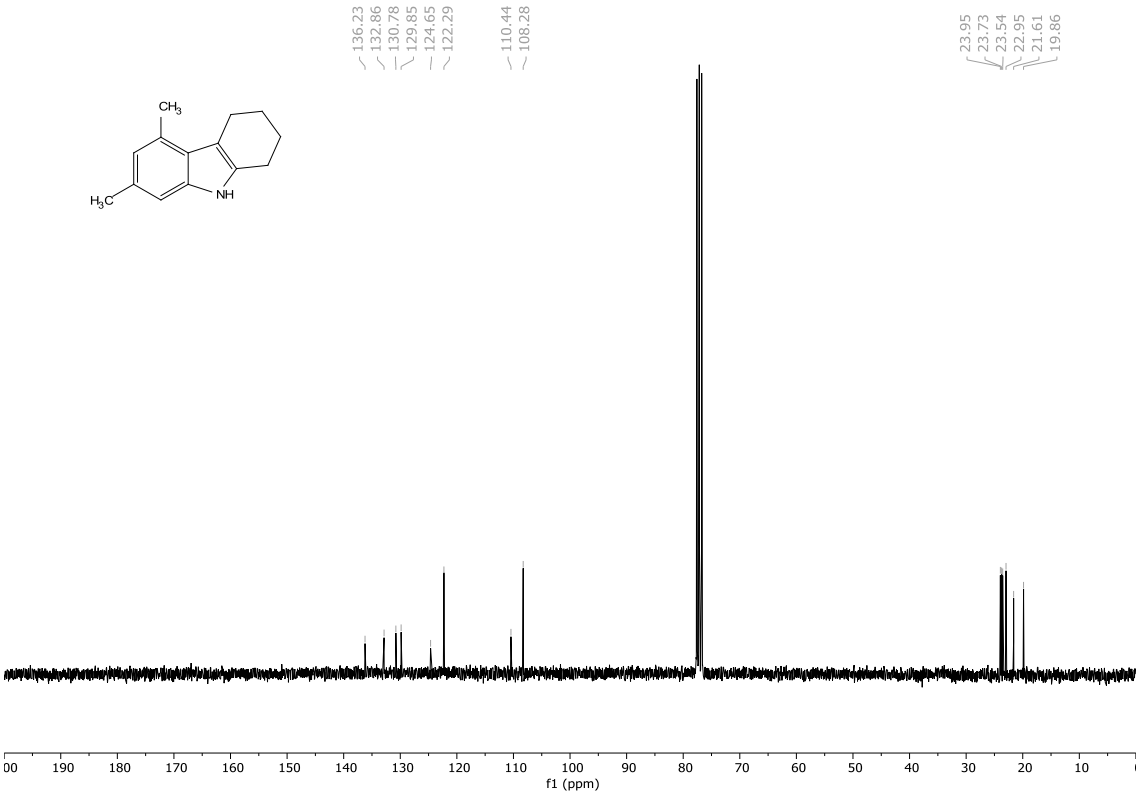
5,6,7-trimethoxy-2,3,4,9-tetrahydro-1*H*-carbazole (7a)



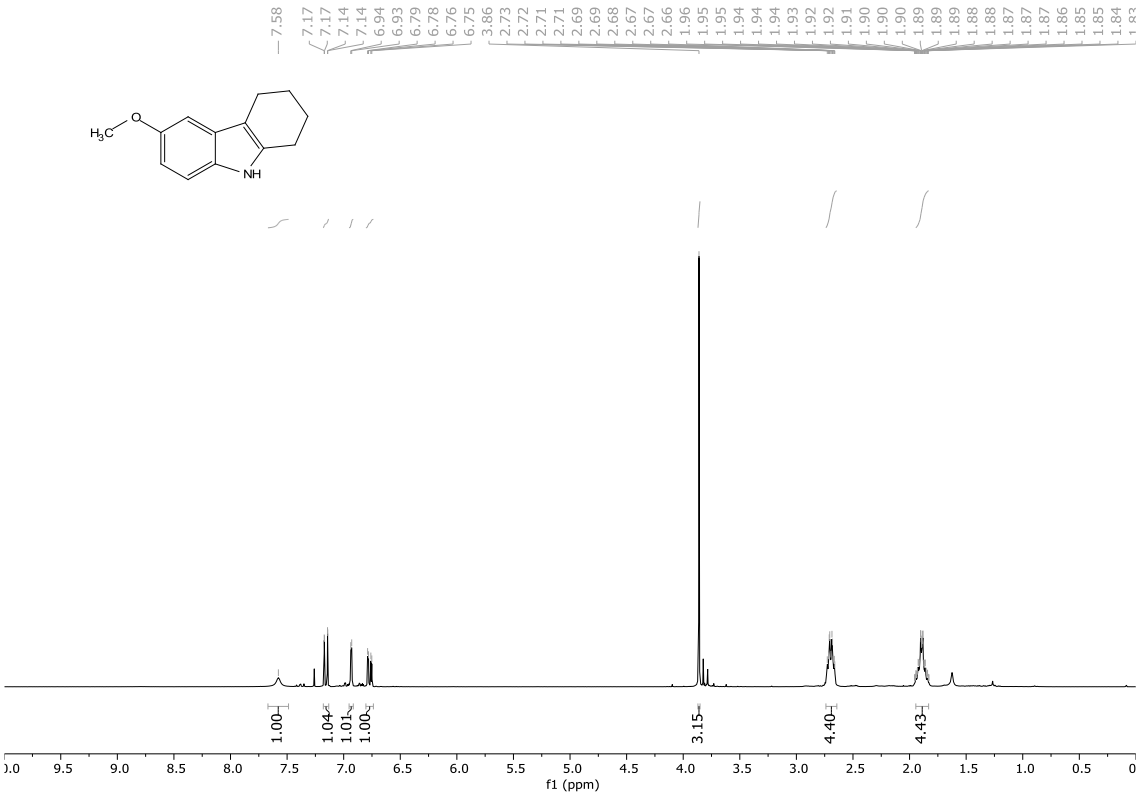


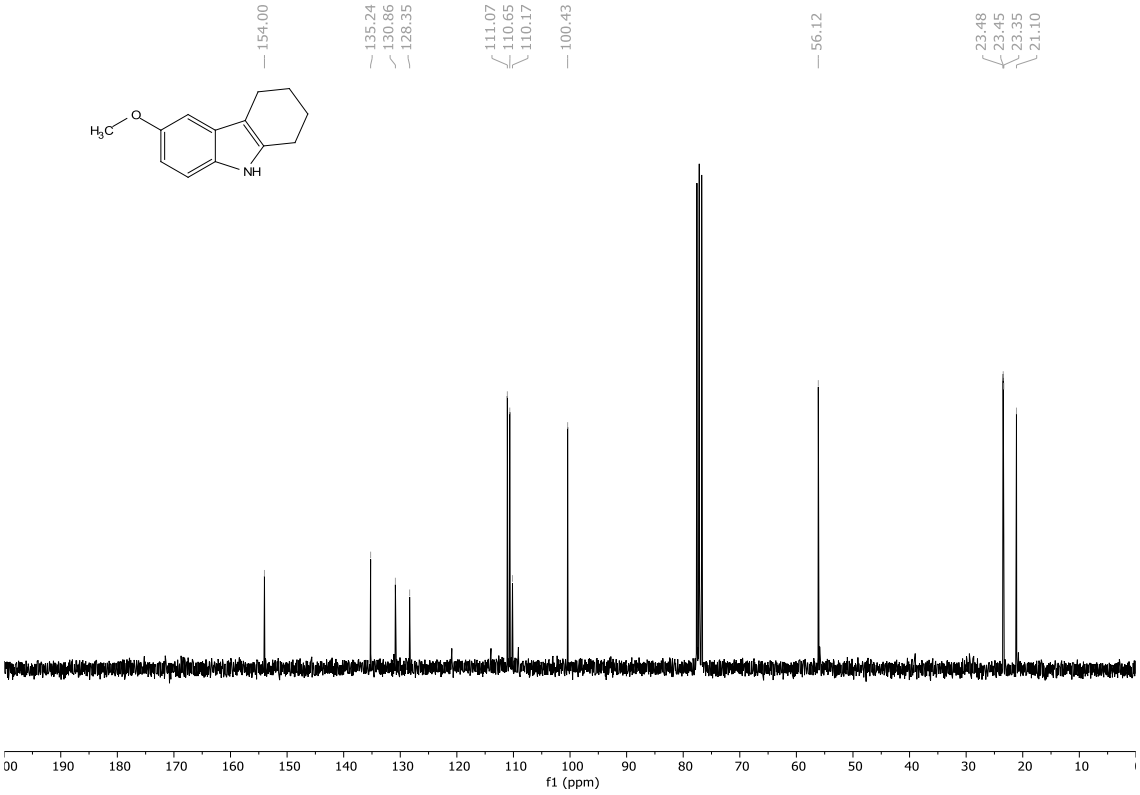
5,7-dimethyl-2,3,4,9-tetrahydro-1*H*-carbazole (7b):



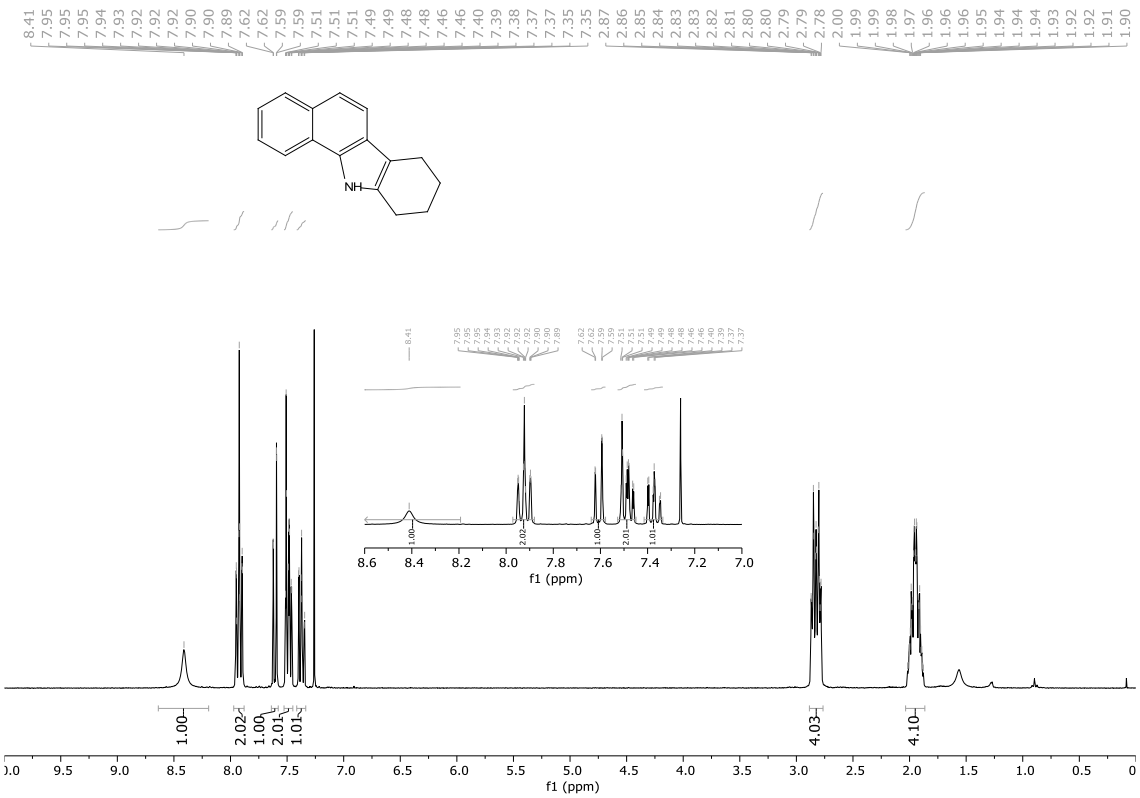


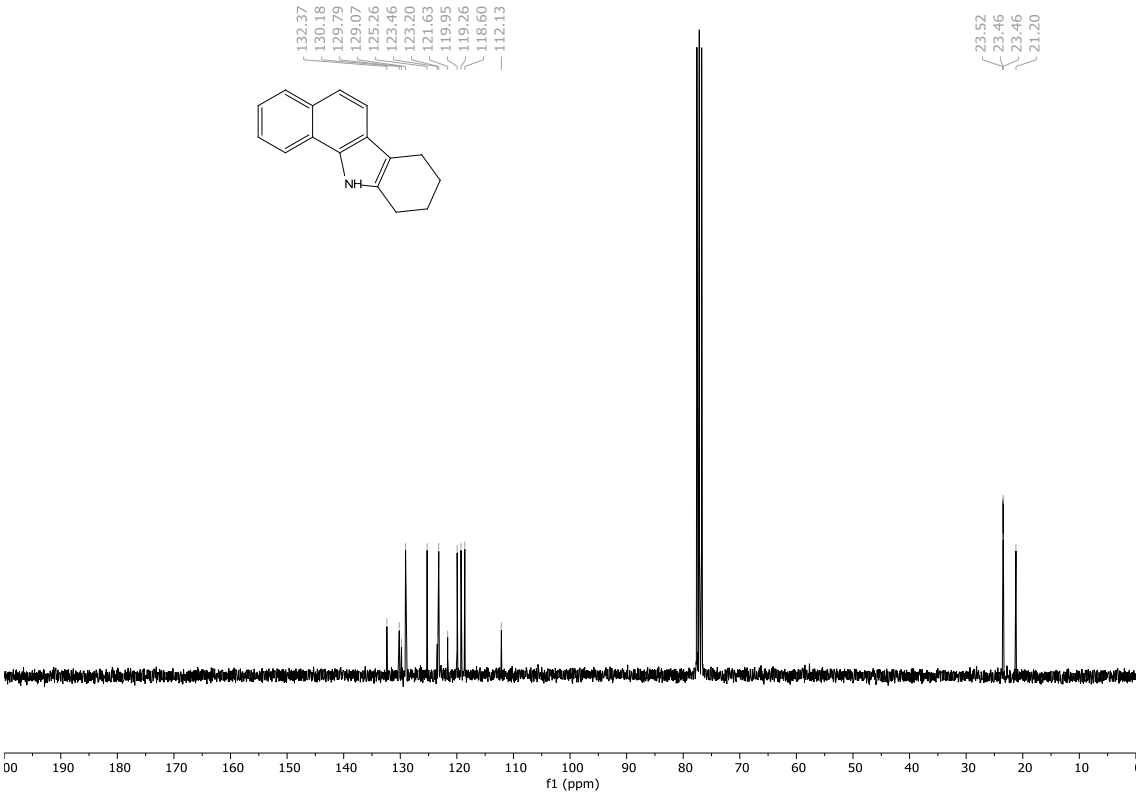
6-methoxy-2,3,4,9-tetrahydro-1*H*-carbazole (7c):



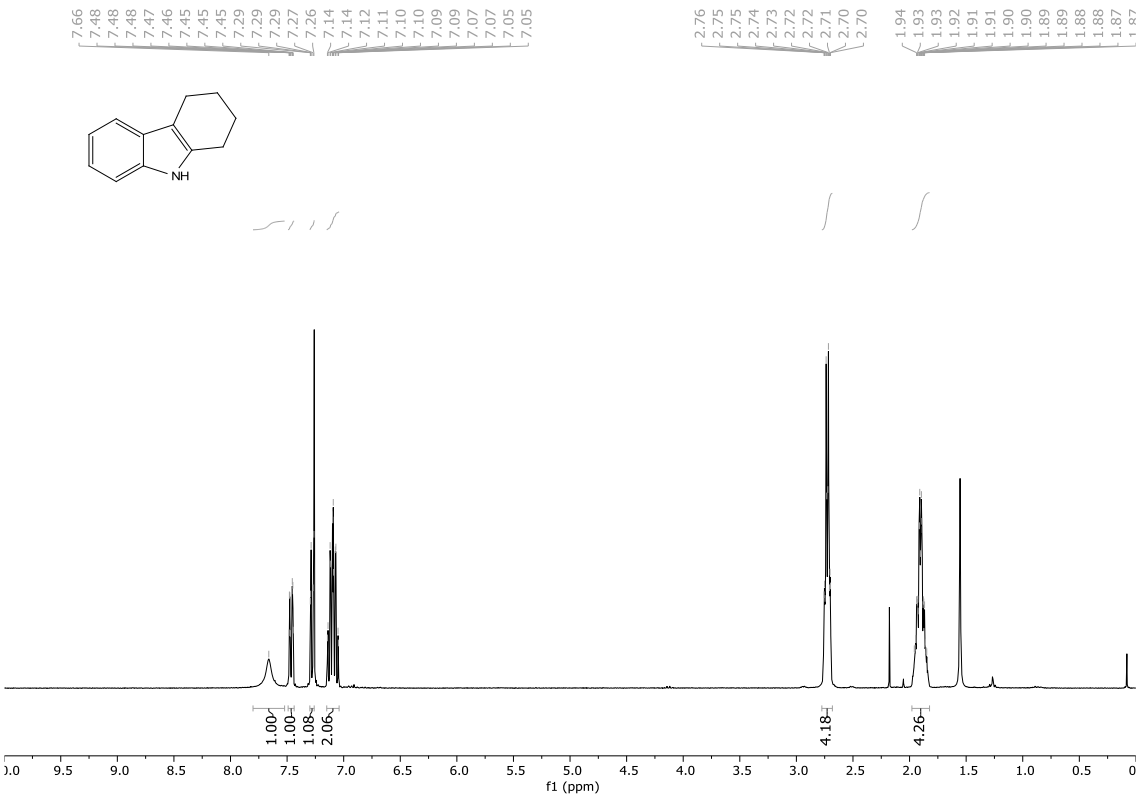


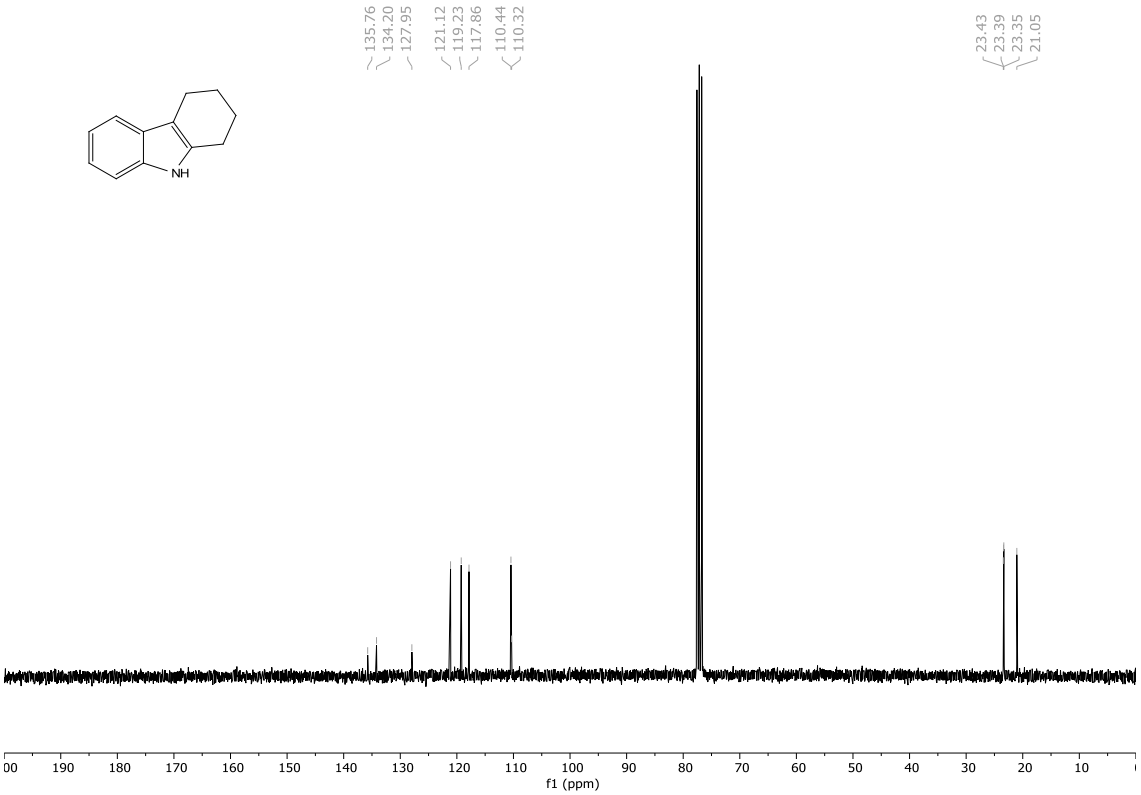
8,9,10,11-tetrahydro-7*H*-benzo[*a*]carbazole (7d):



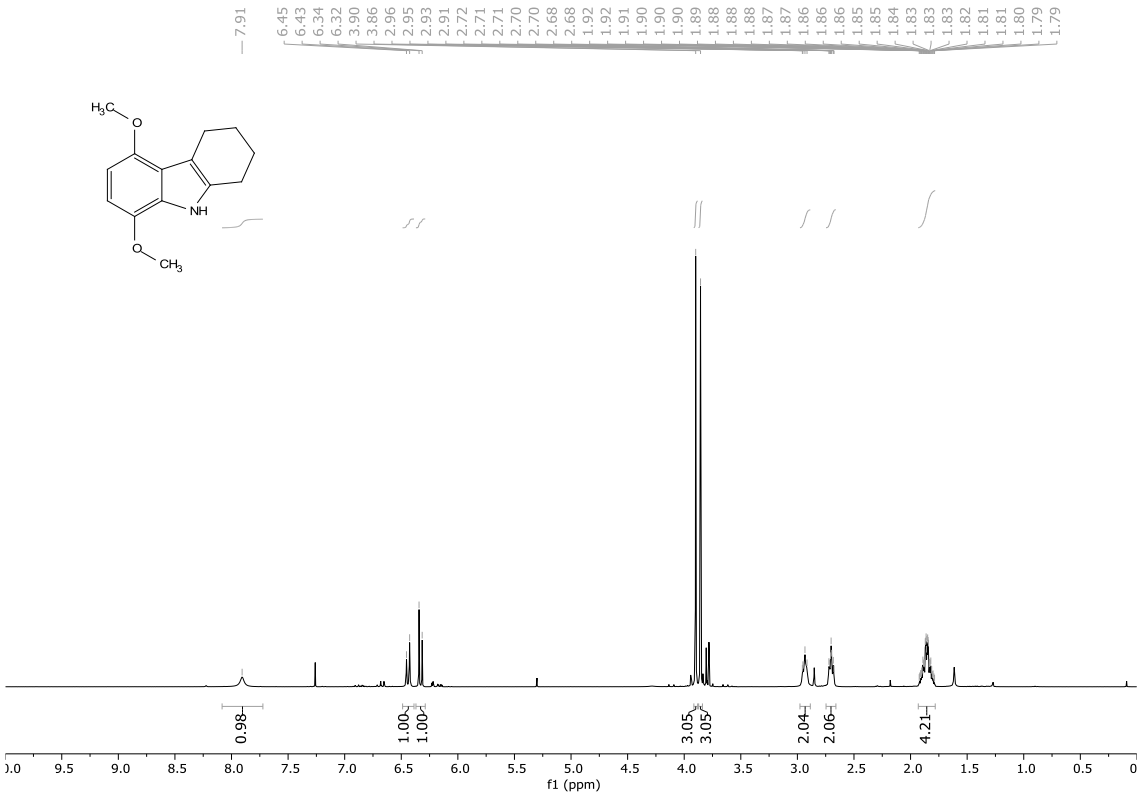


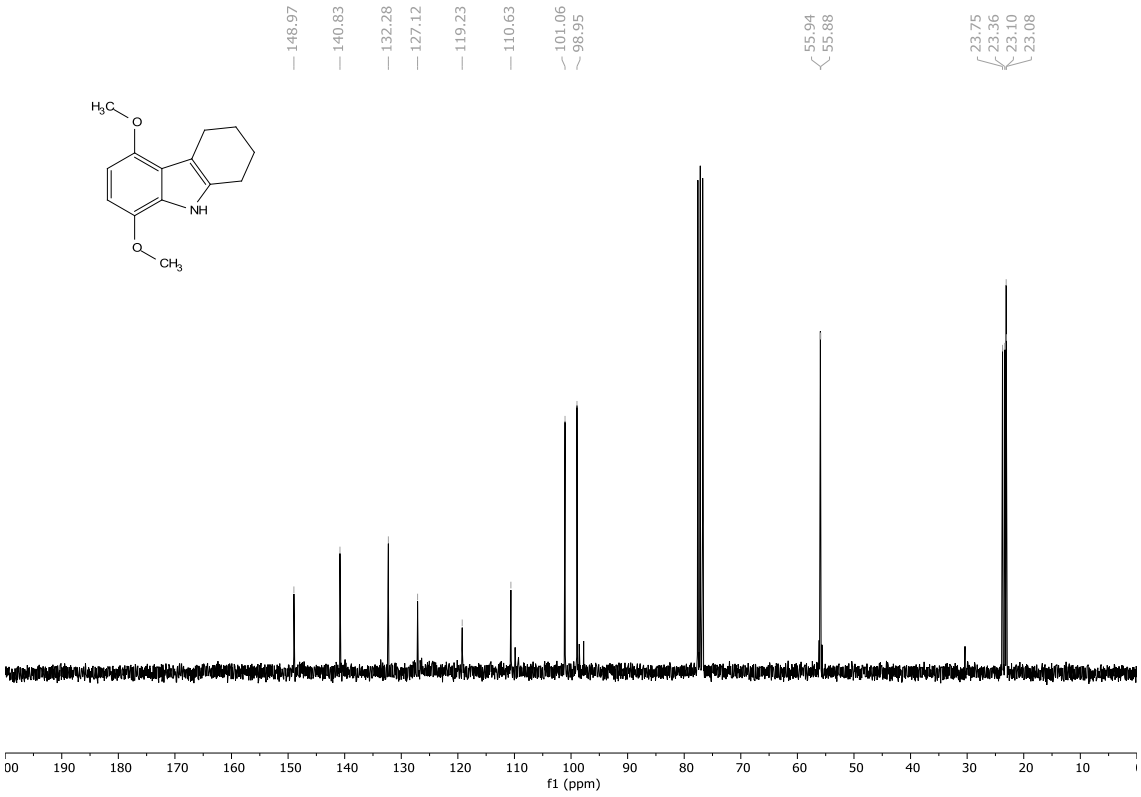
6,7,8,9-tetrahydro-1*H*-carbazole (7e):



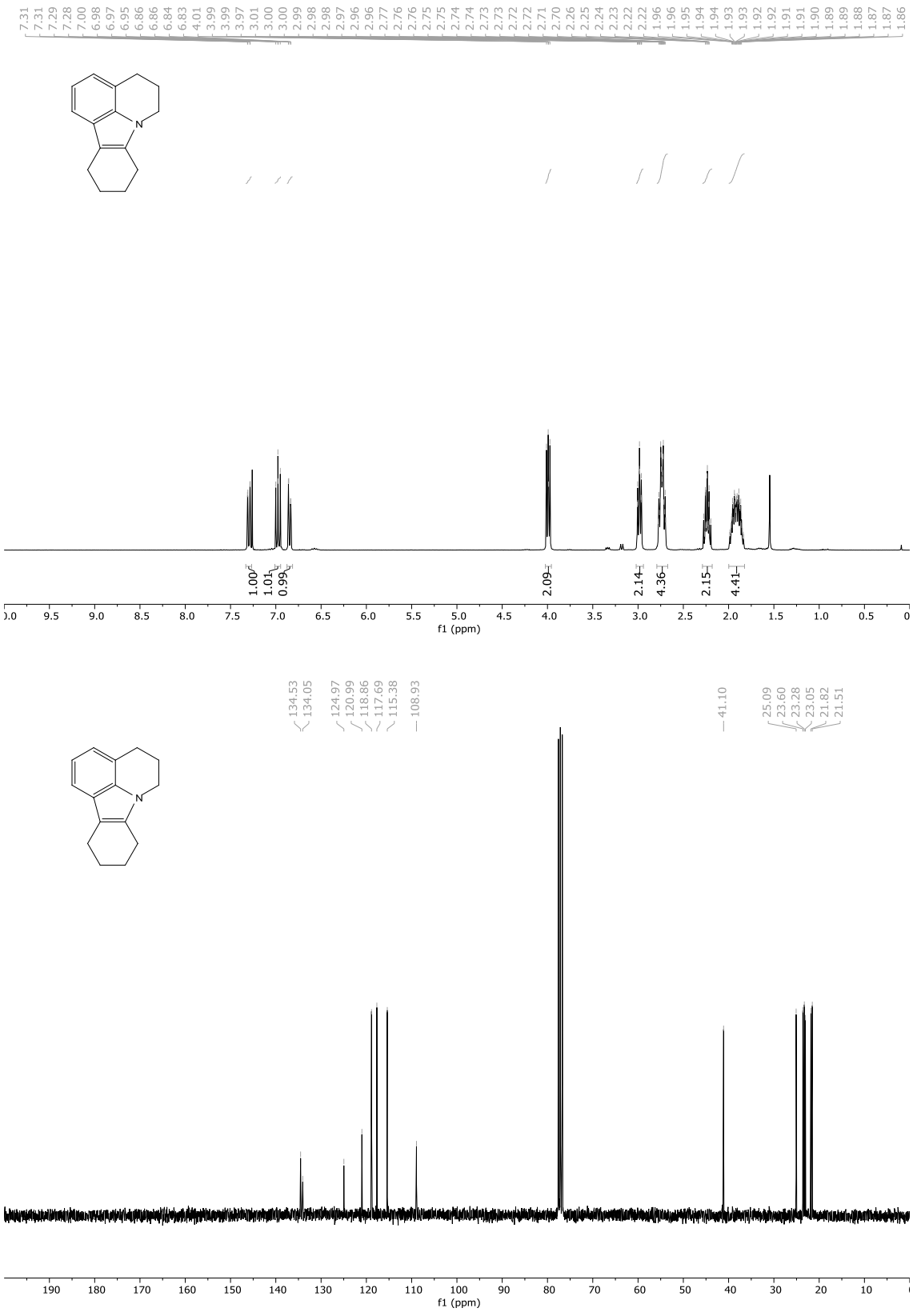


5,8-dimethoxy-2,3,4,9-tetrahydro-1*H*-carbazole (7f):

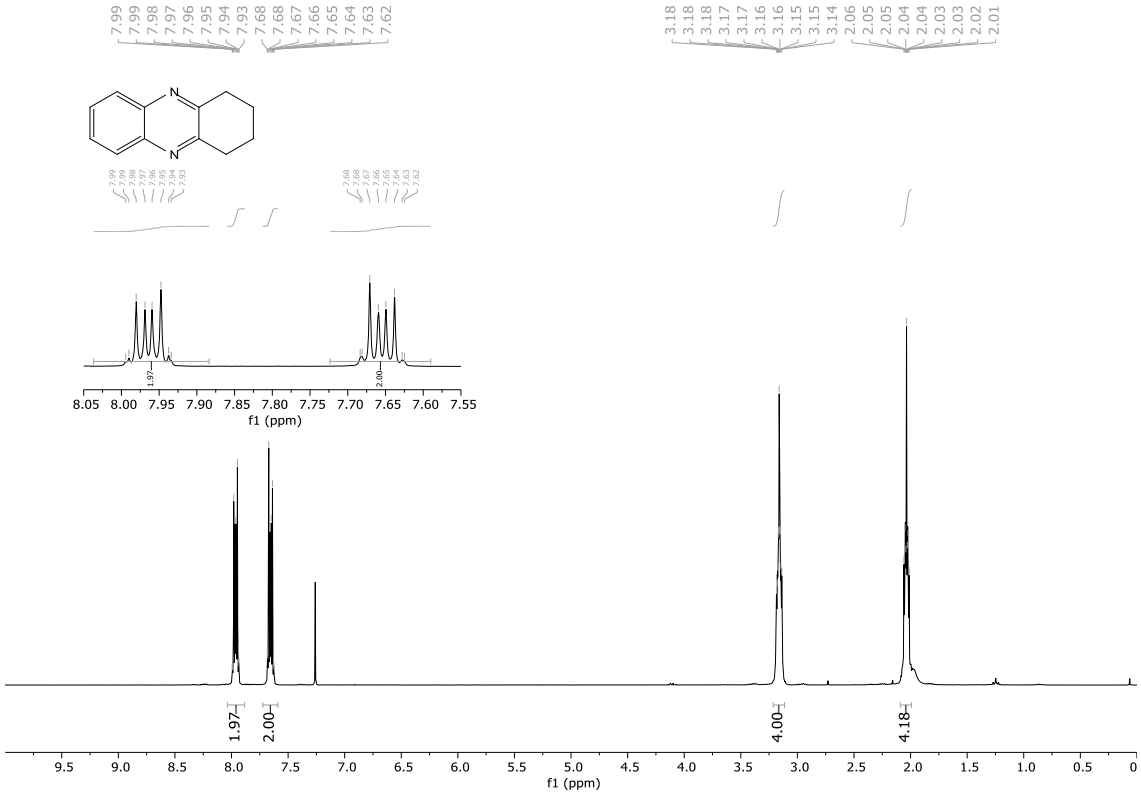


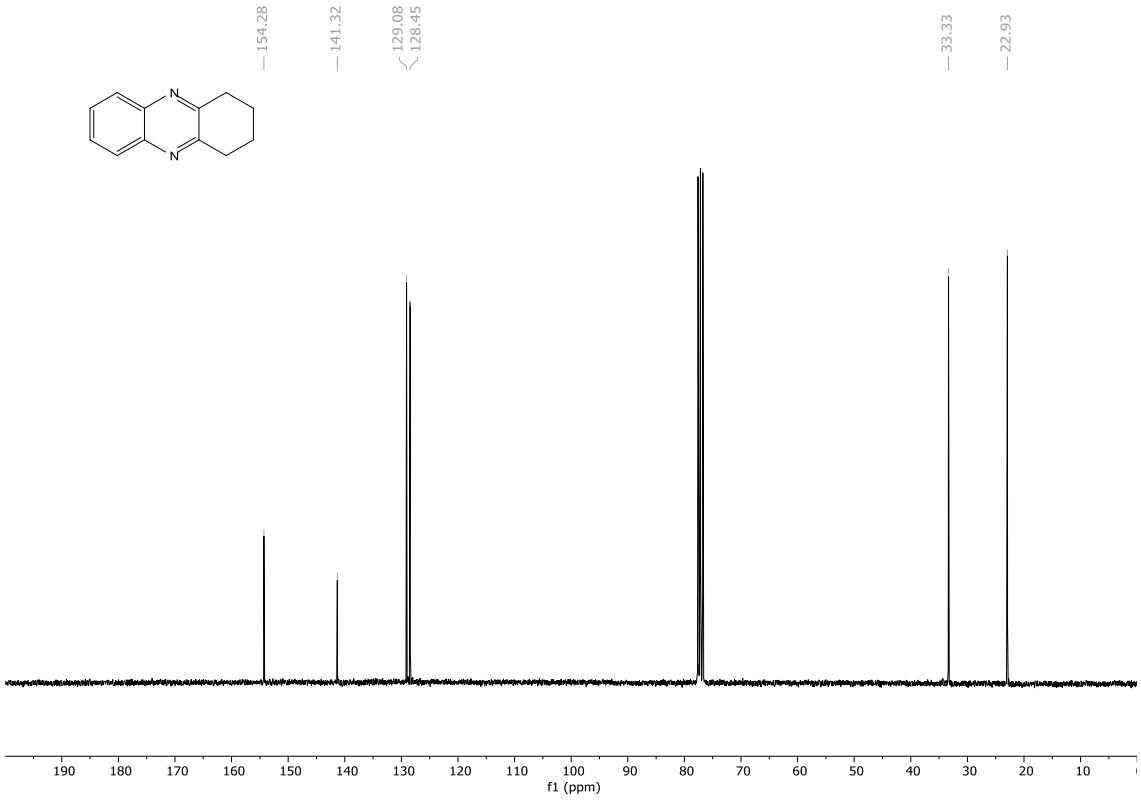


5,6,8,9,10,11-hexahydro-4*H*-pyrido[3,2,1-*jk*]carbazole (7g):

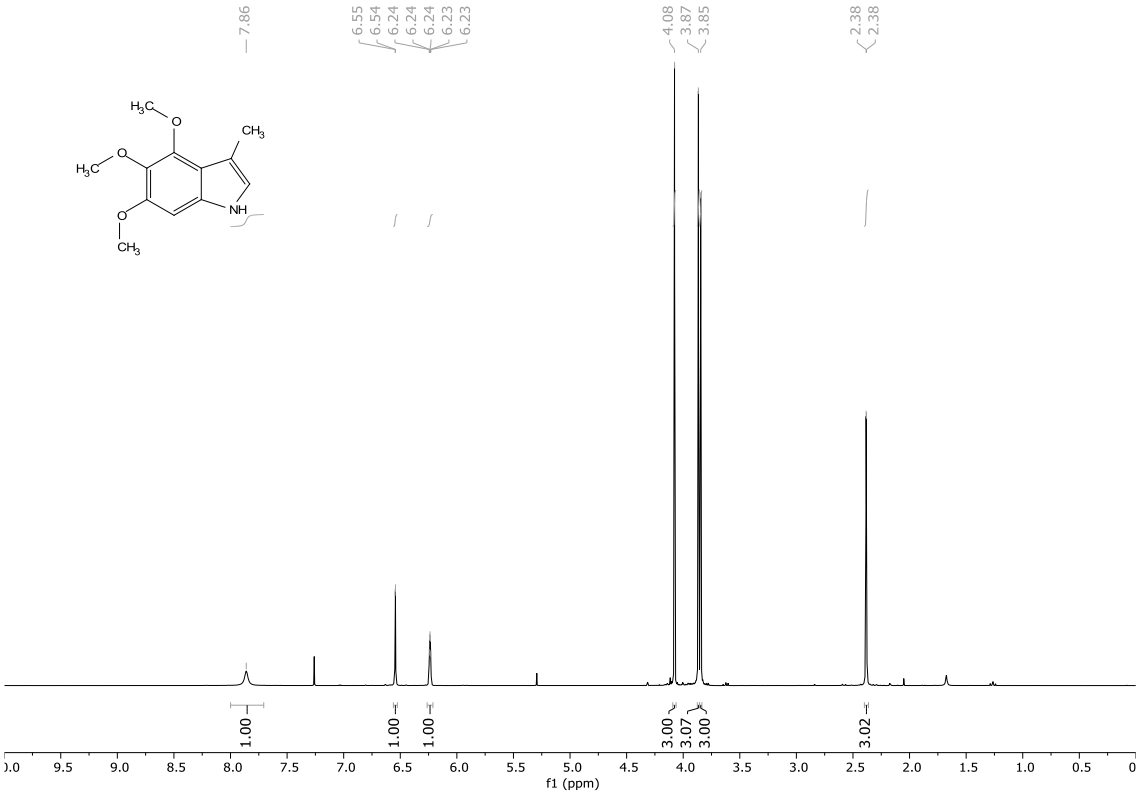


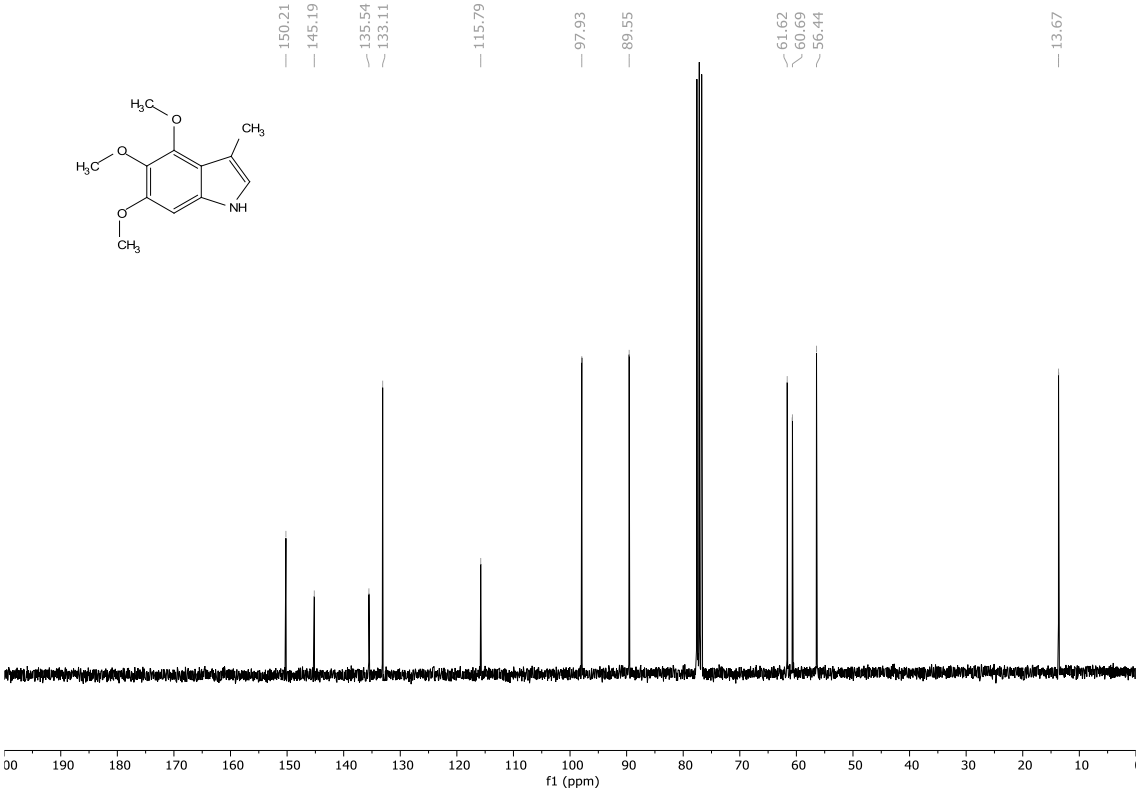
1,2,3,4-tetrahydrophenazine (8):



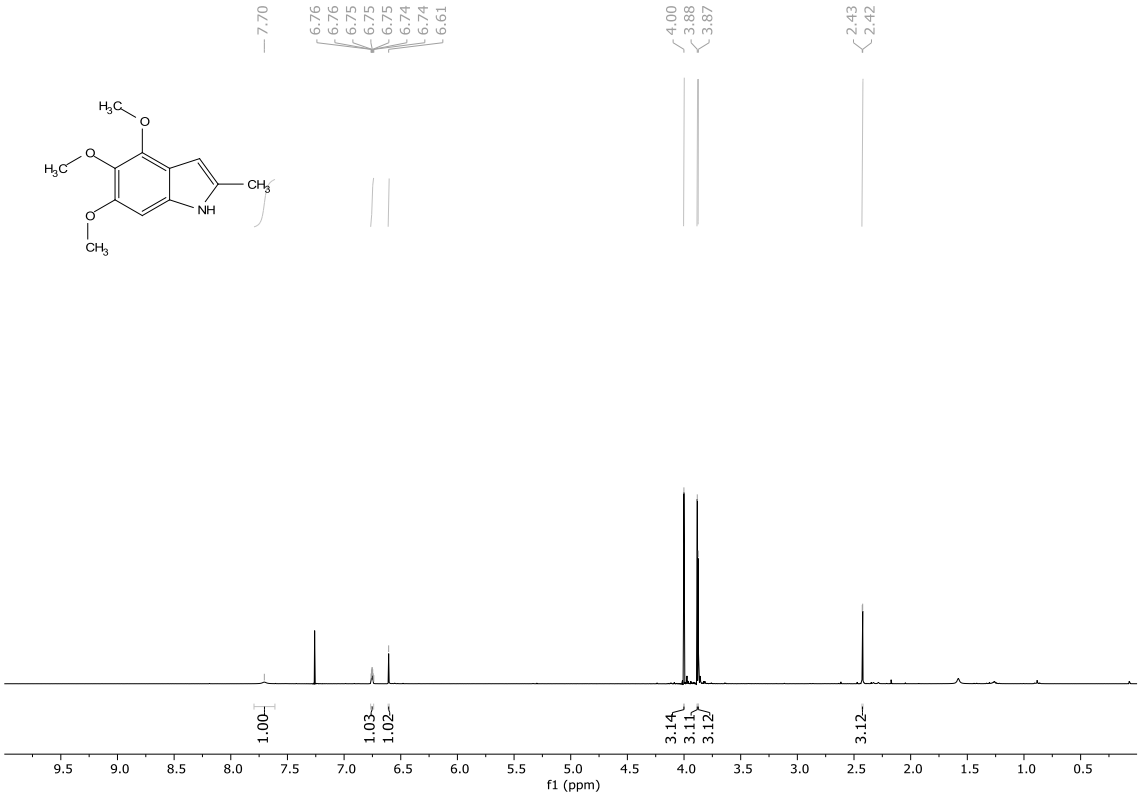


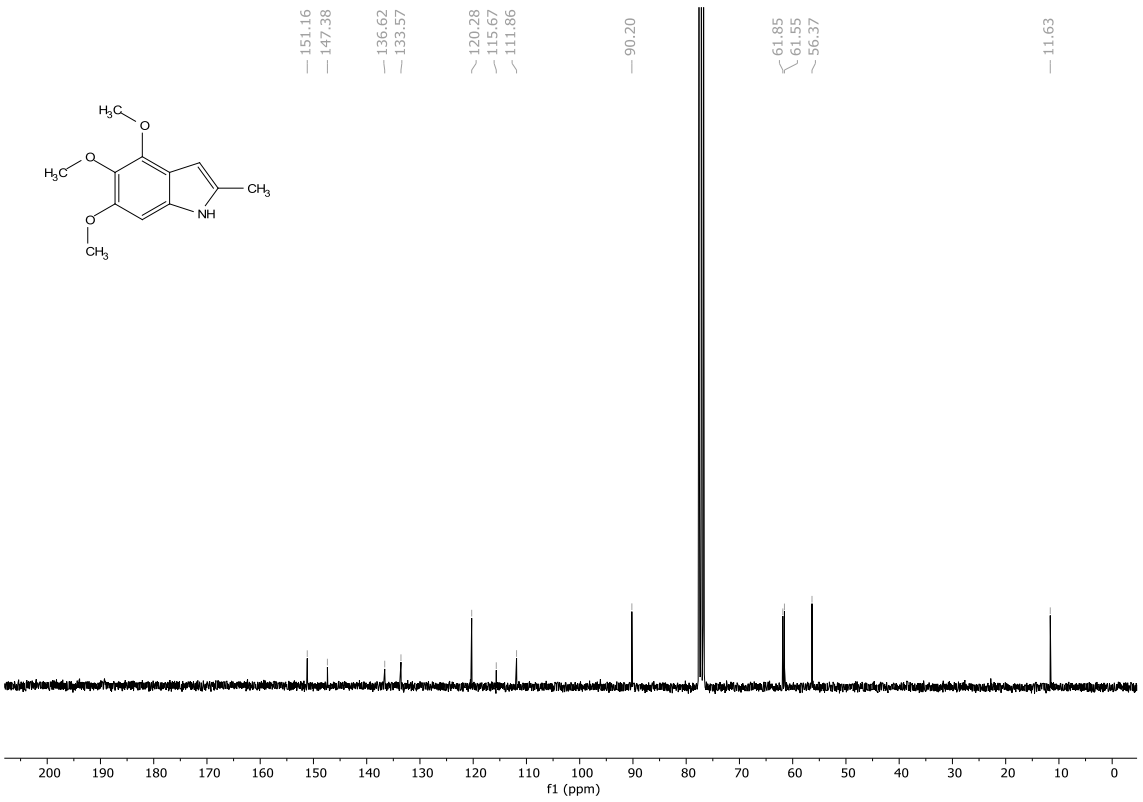
4,5,6-trimethoxy-3-methyl-1*H*-indole (9a)



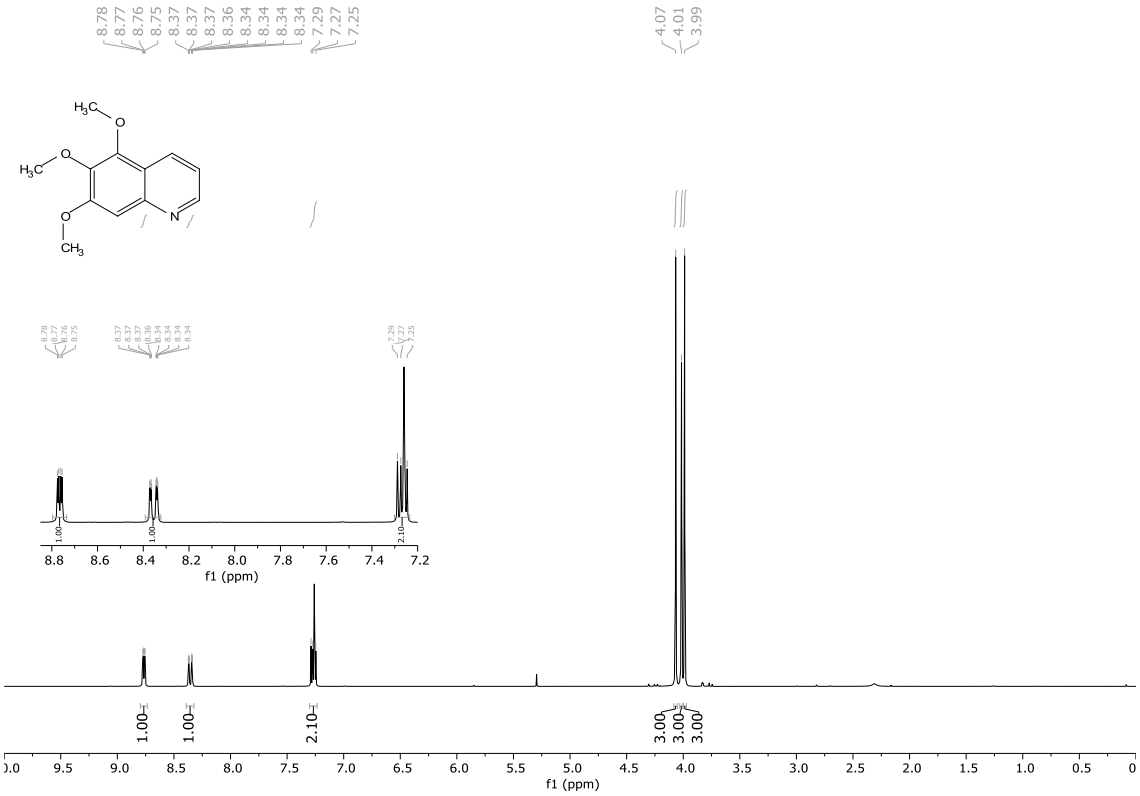


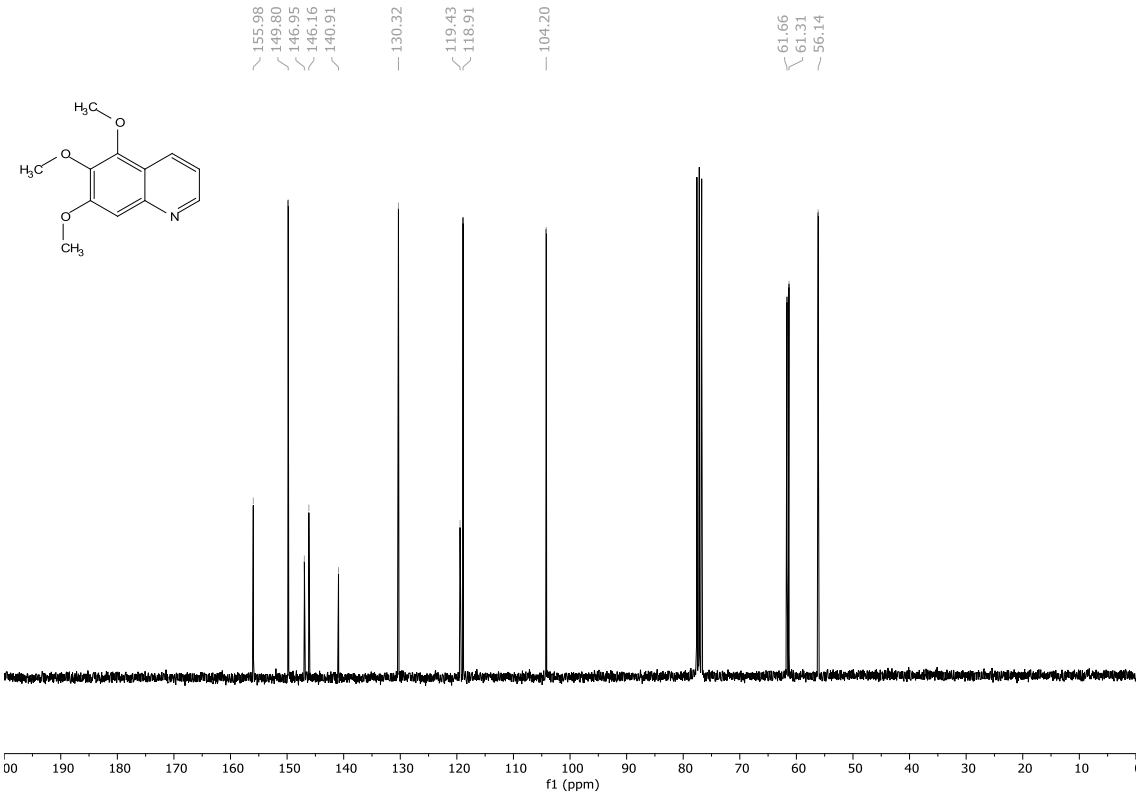
4,5,6-trimethoxy-2-methyl-1*H*-indole (9b)



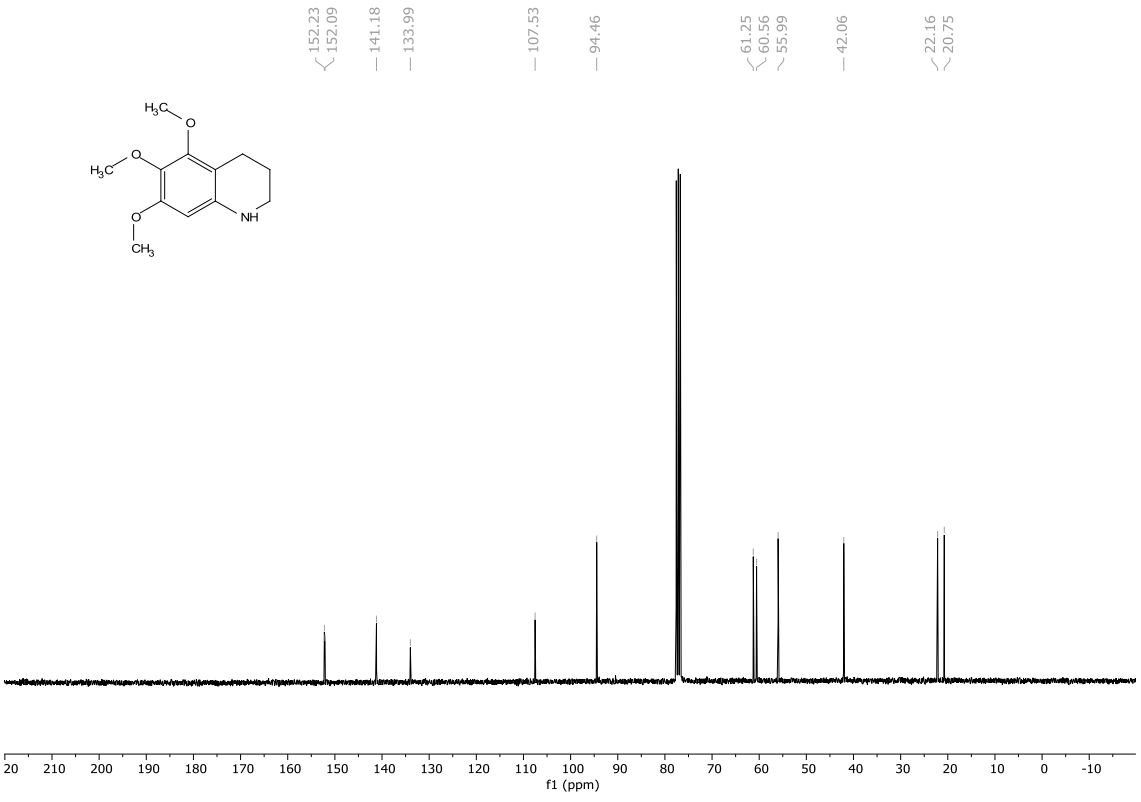


5,6,7-trimethoxyquinoline (10a):

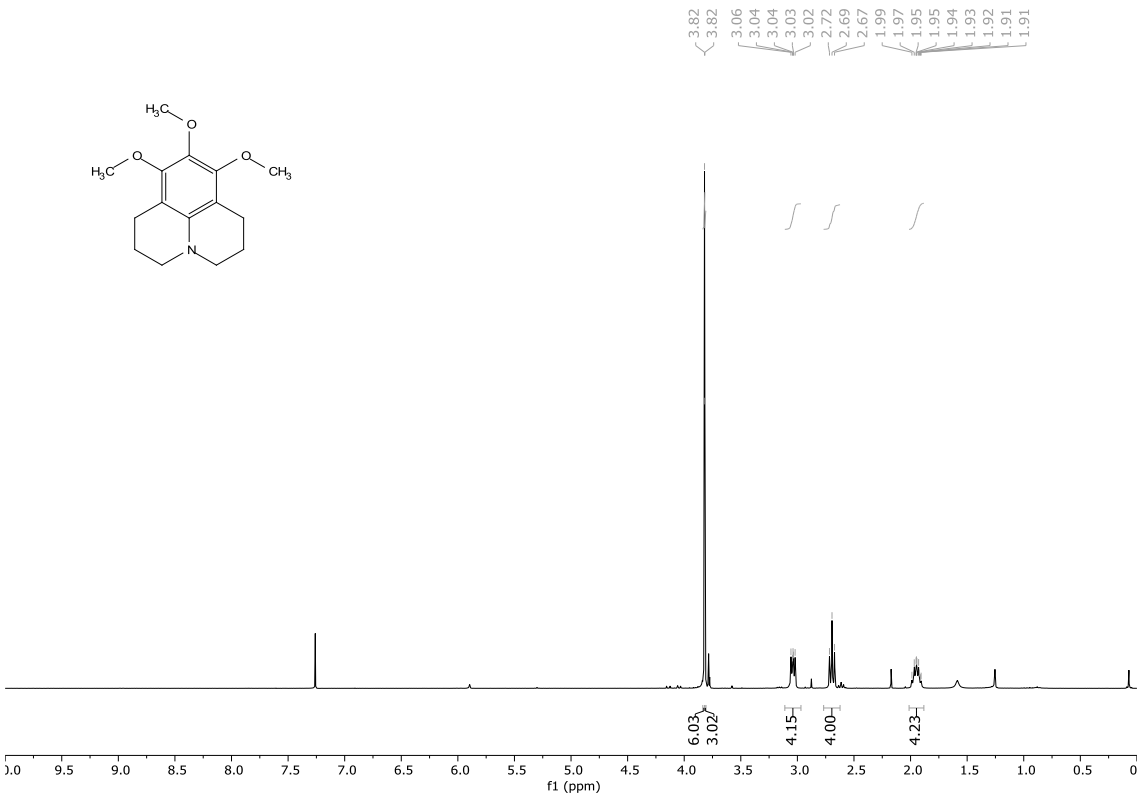


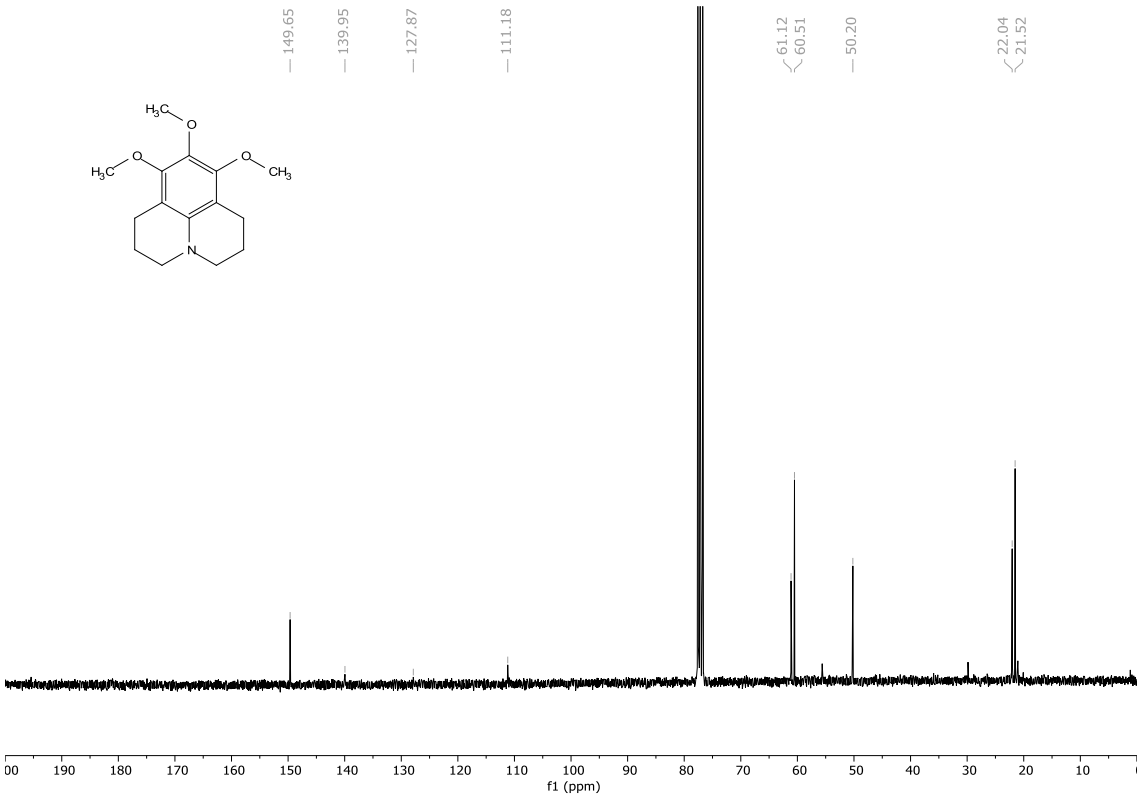


5,6,7-trimethoxy-1,2,3,4-tetrahydroquinoline (10b):

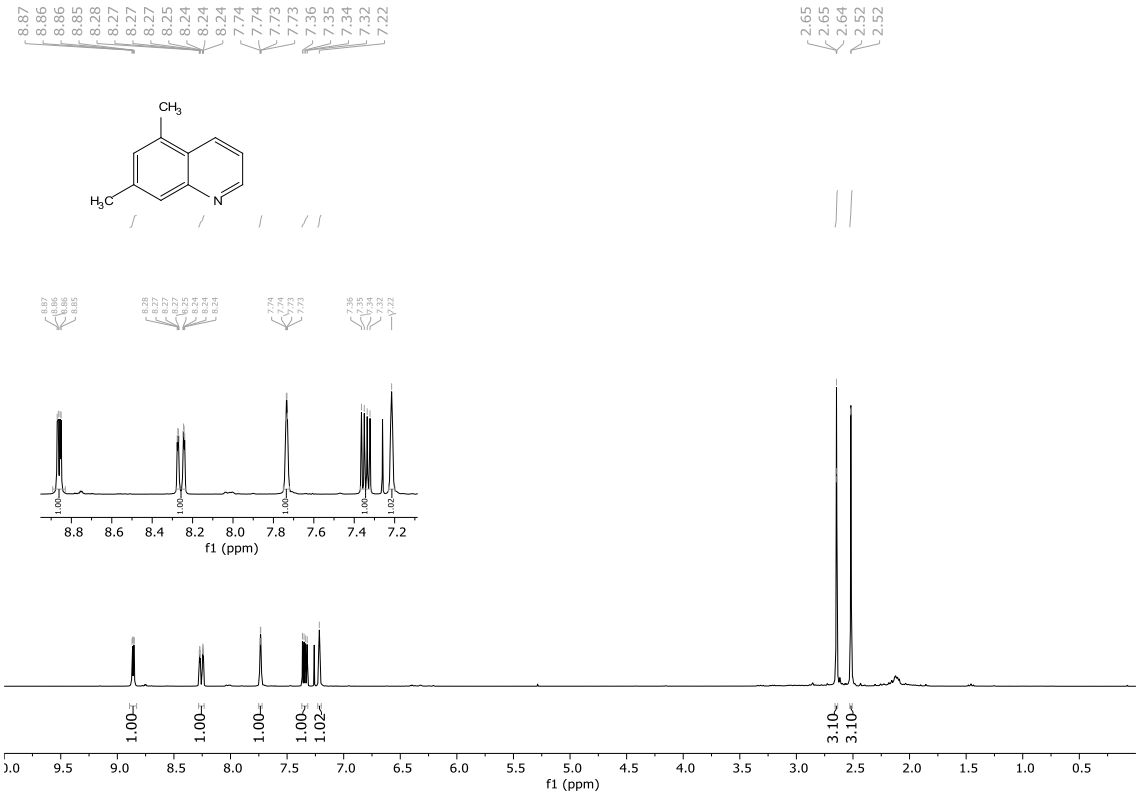


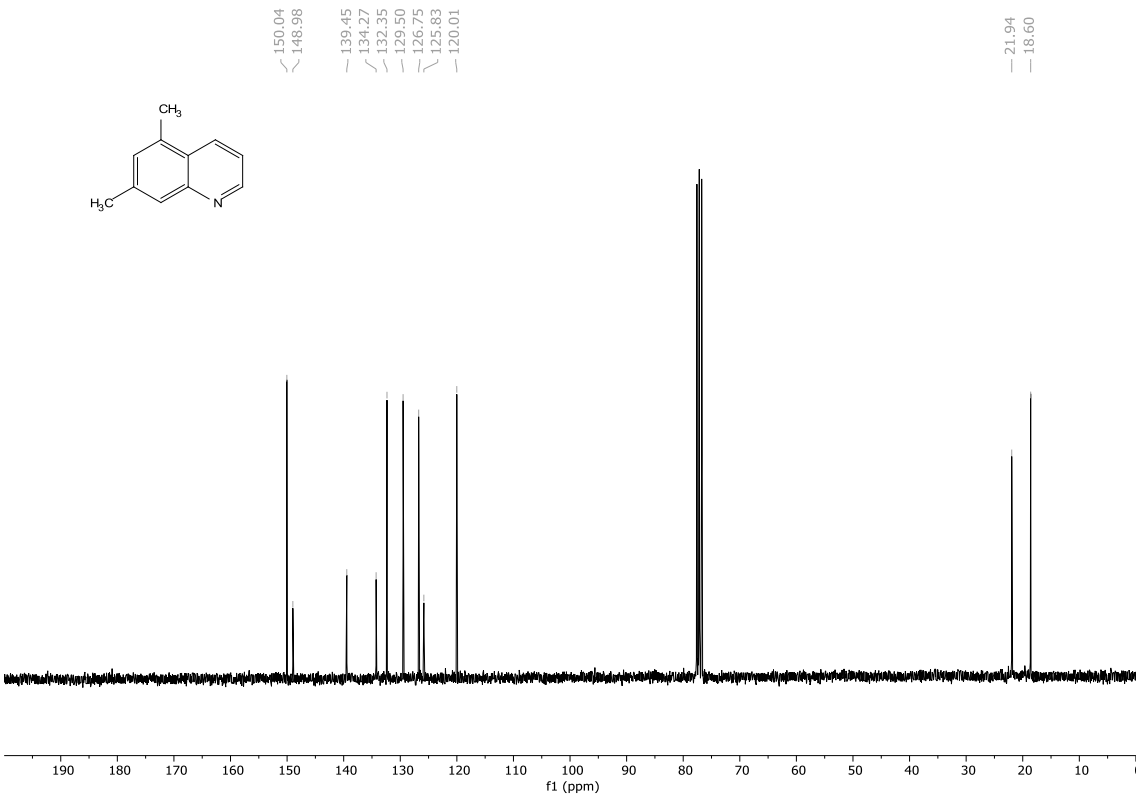
3,4,5-trimethoxyjulolidine (10c):



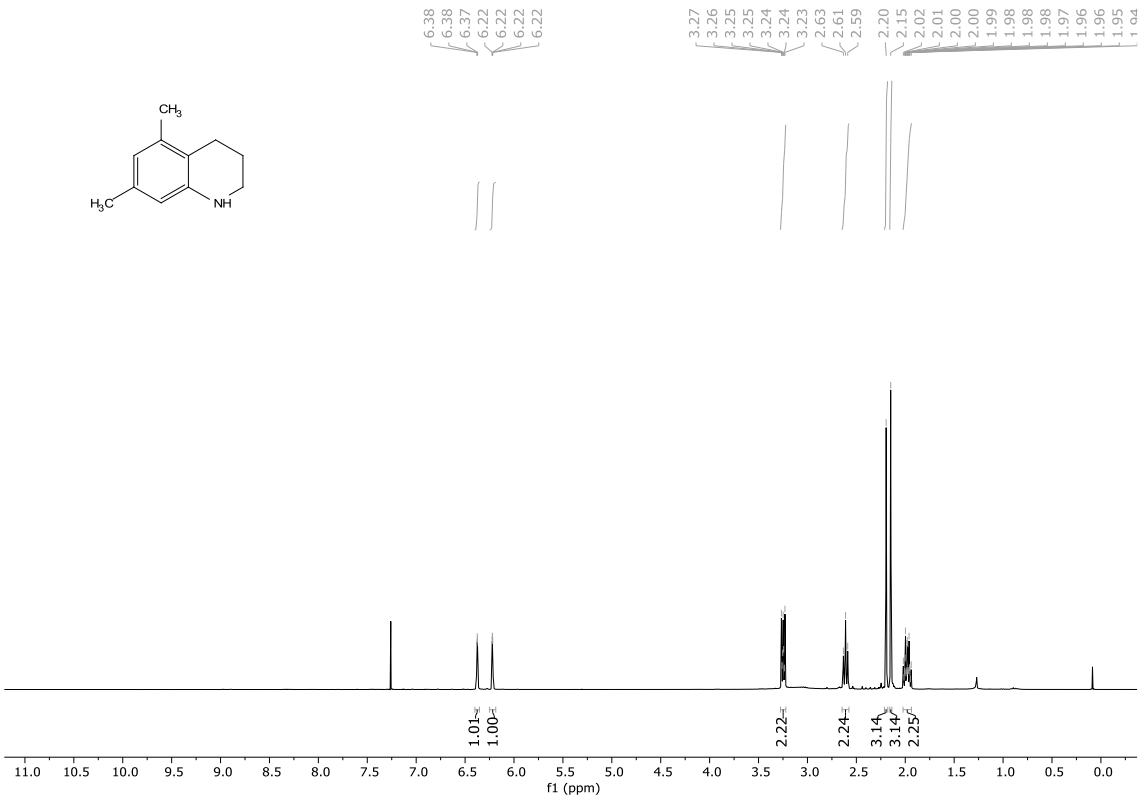


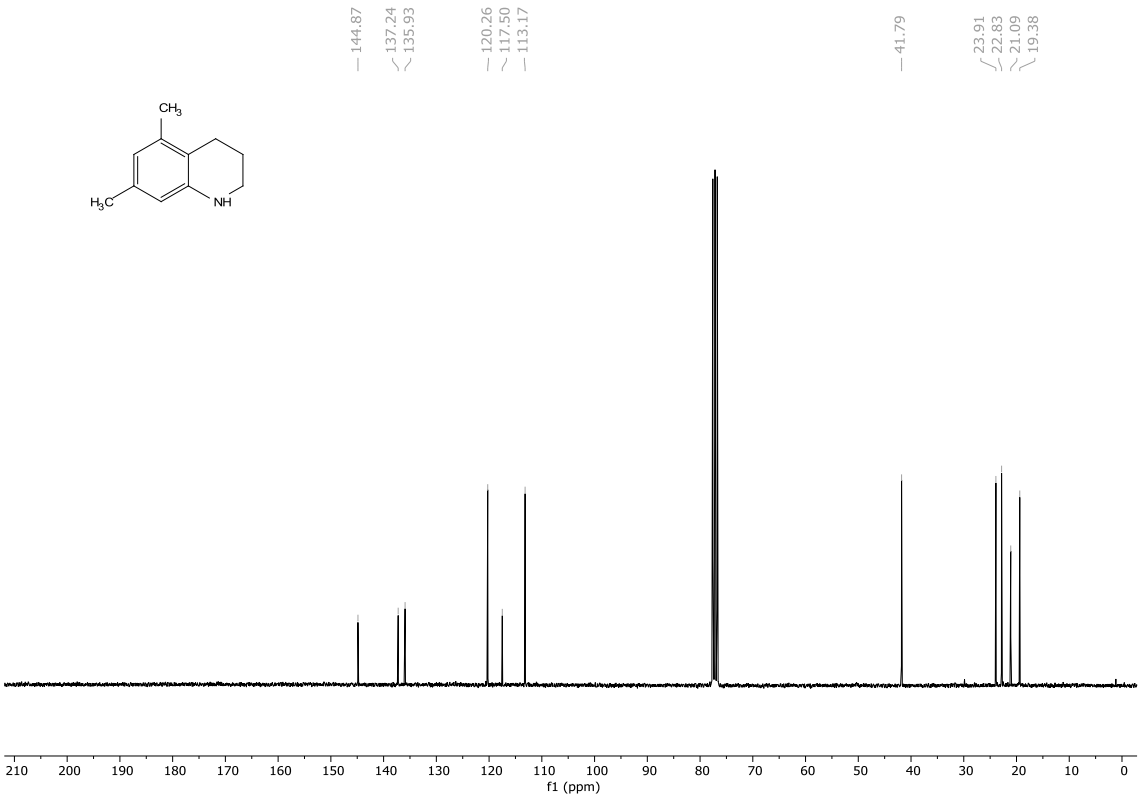
5,7-dimethylquinoline (11a):



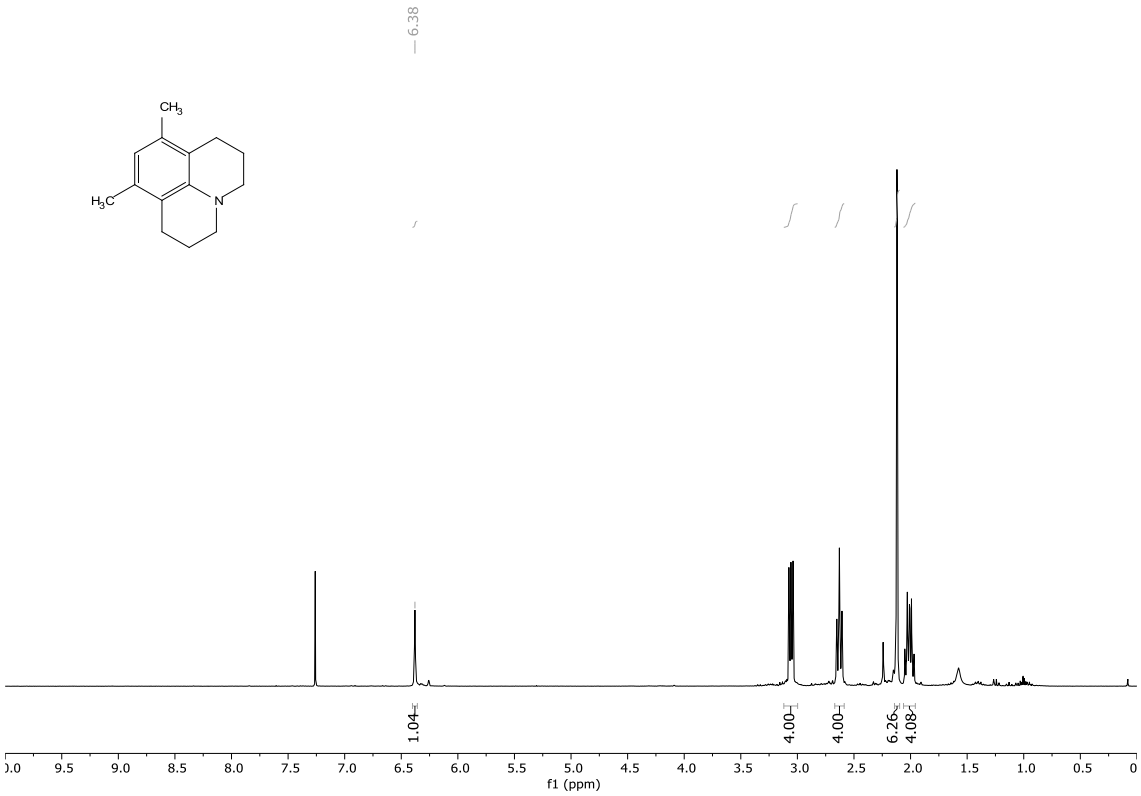


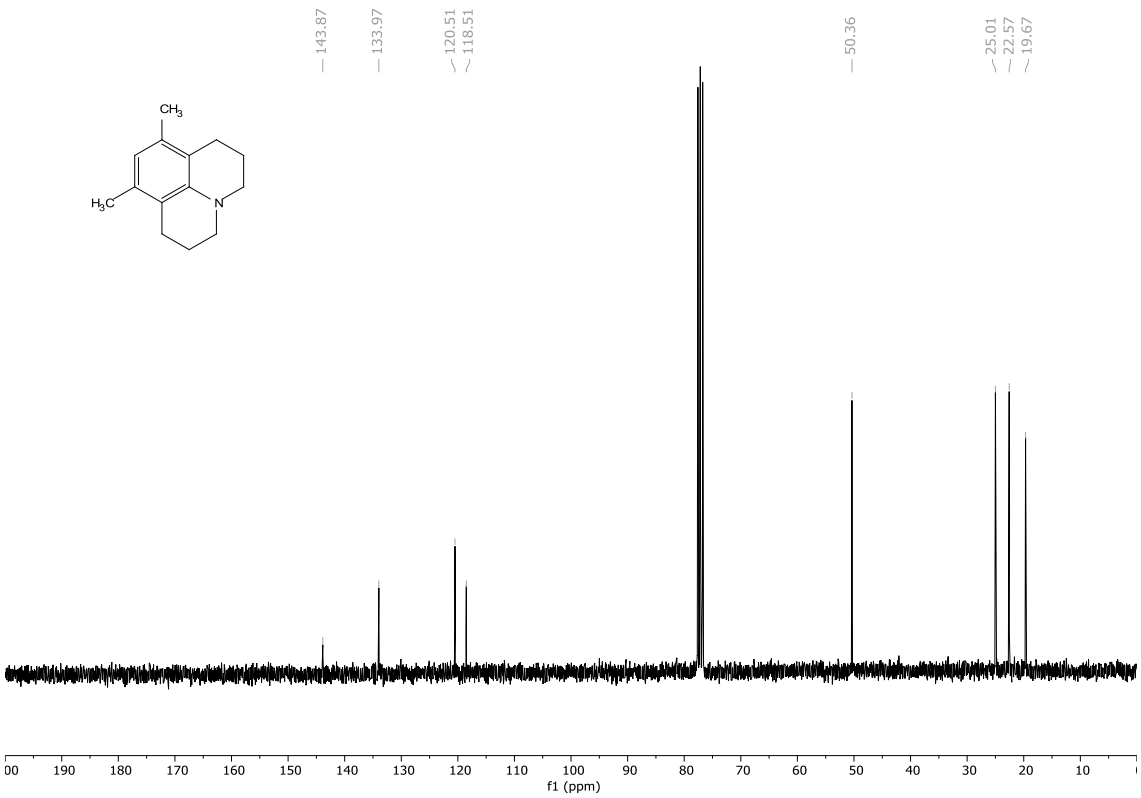
5,7-dimethyl-1,2,3,4-tetrahydroquinoline (11b):





3,5-Dimethyljulolidine (11c):





Julolidine (12c):