Electronic Supplementary Information (ESI)

Cu-Catalyzed arylation of amino group in the indazole ring: Regioselective synthesis of pyrazolo-carbazoles

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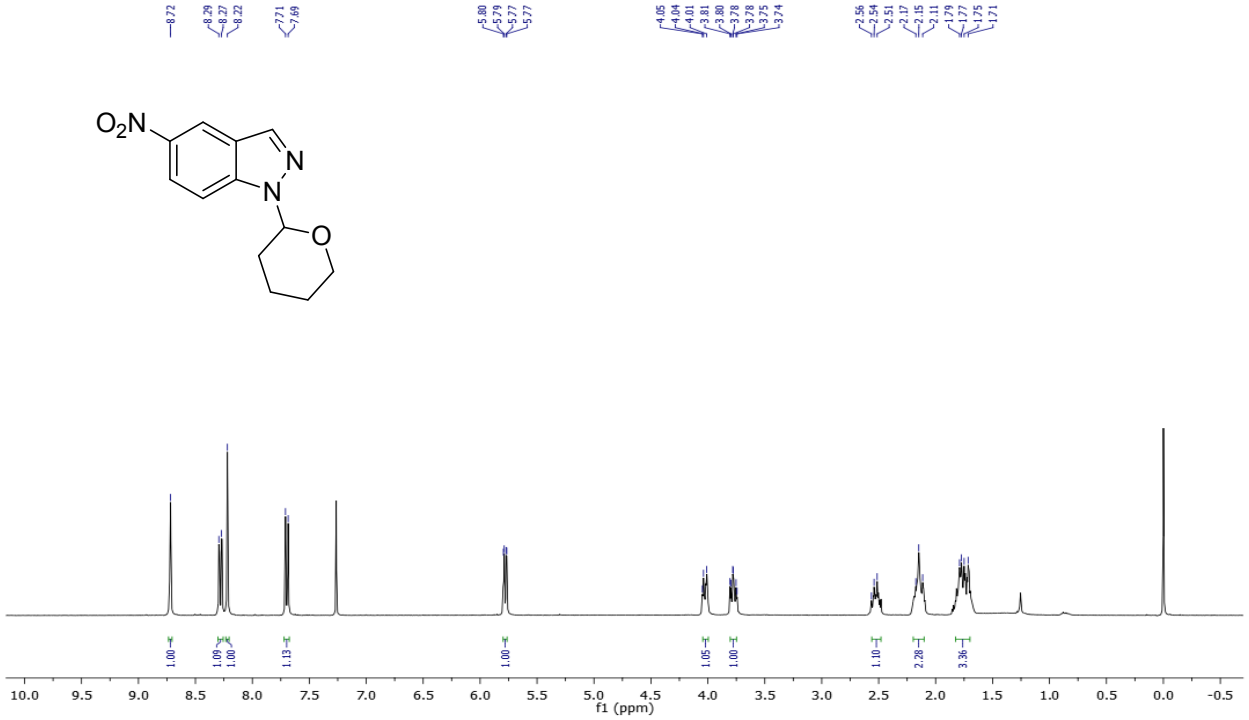
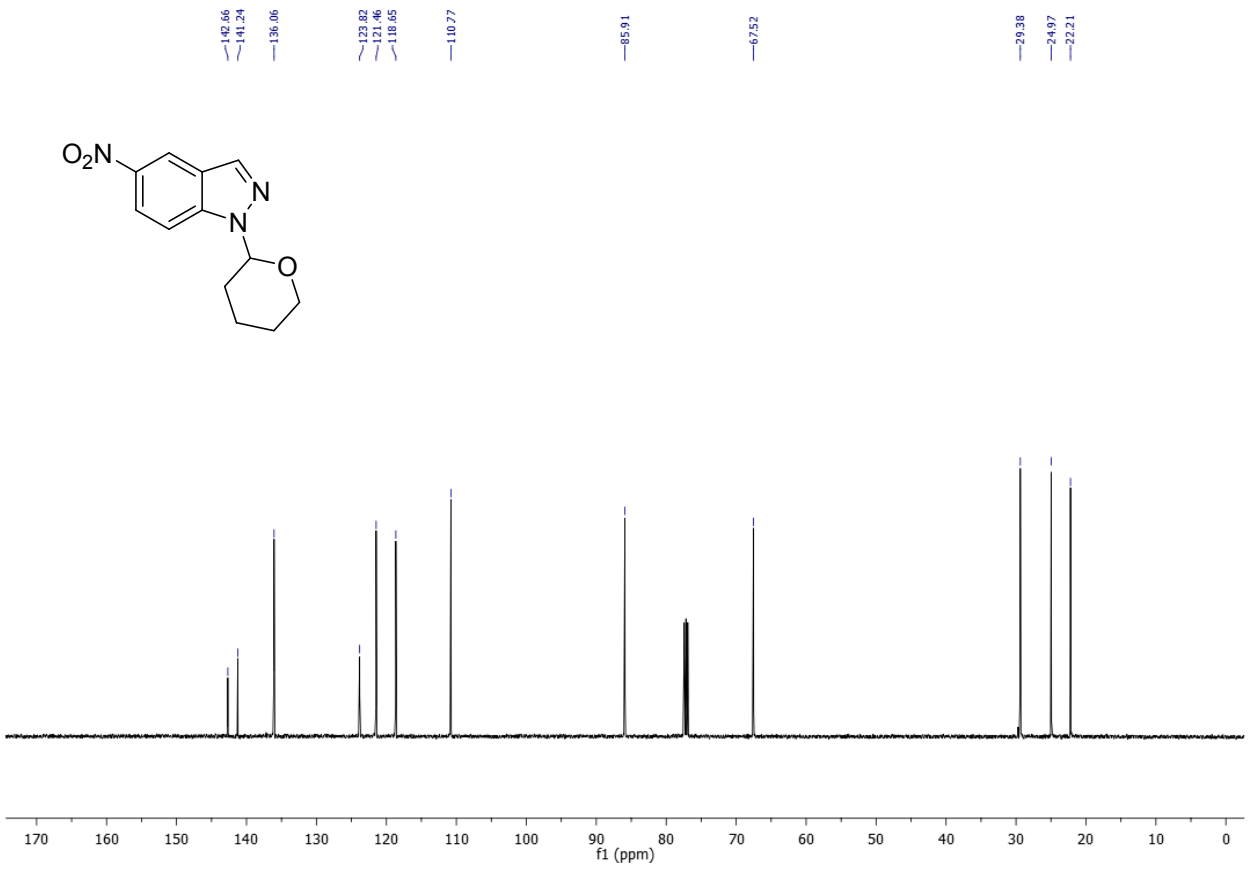
Table of Contents

^{1}H and ^{13}C NMR spectra of compounds:

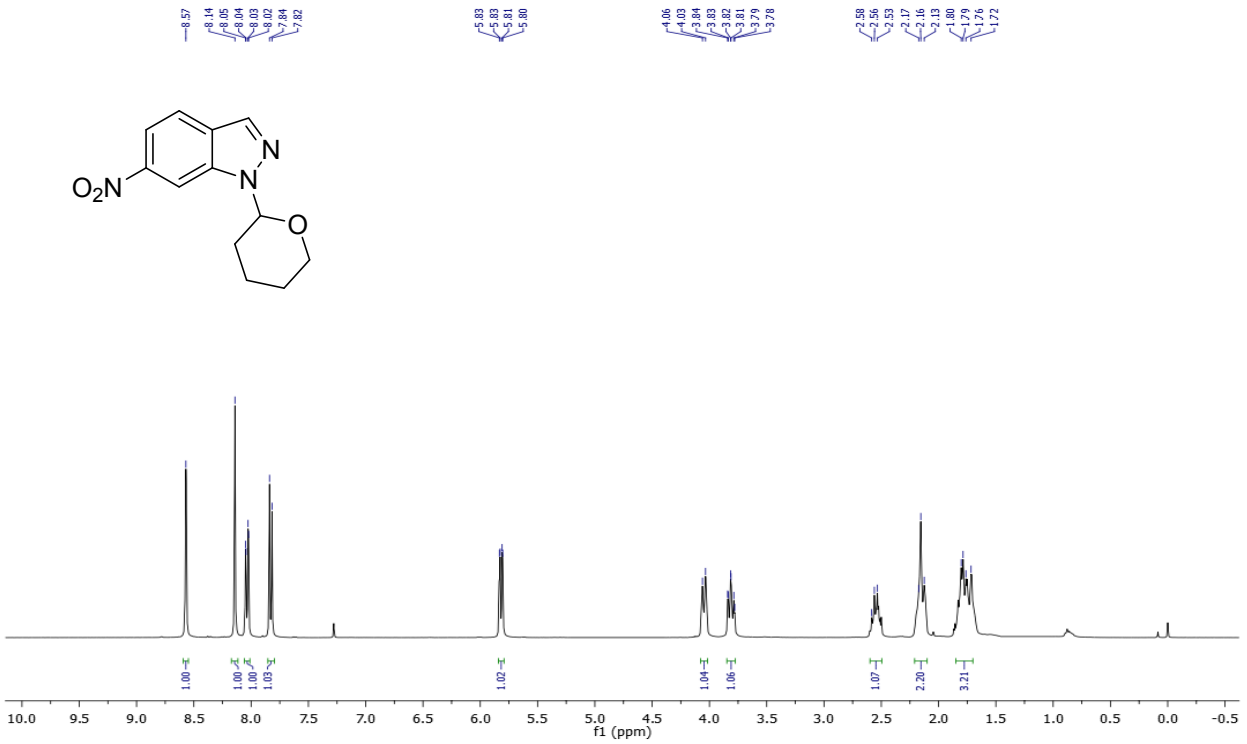
5-Nitro-1-(tetrahydro-2*H*- pyran-2-yl)-1*H*-indazole: ^{1}H-NMR spectrum



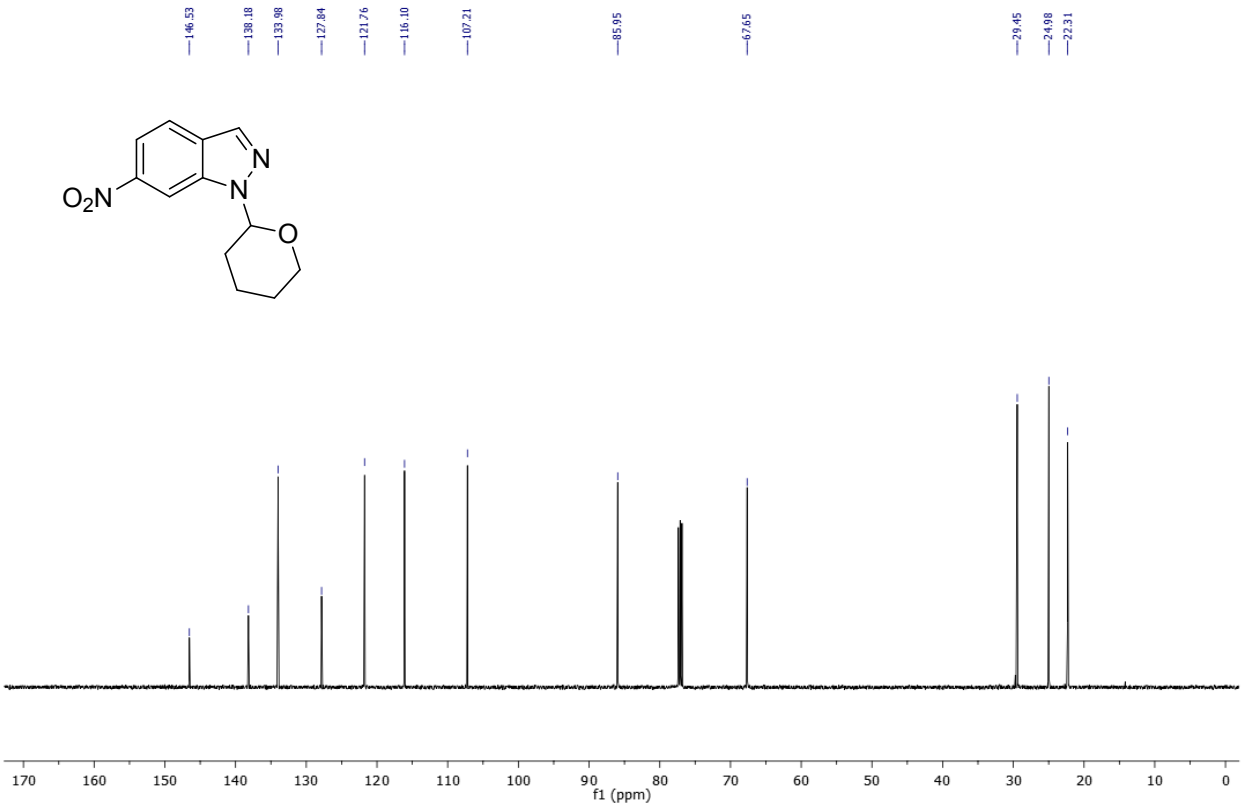
5-Nitro-1-(tetrahydro-2*H*- pyran-2-yl)-1*H*-indazole: ^{13}C-NMR spectrum



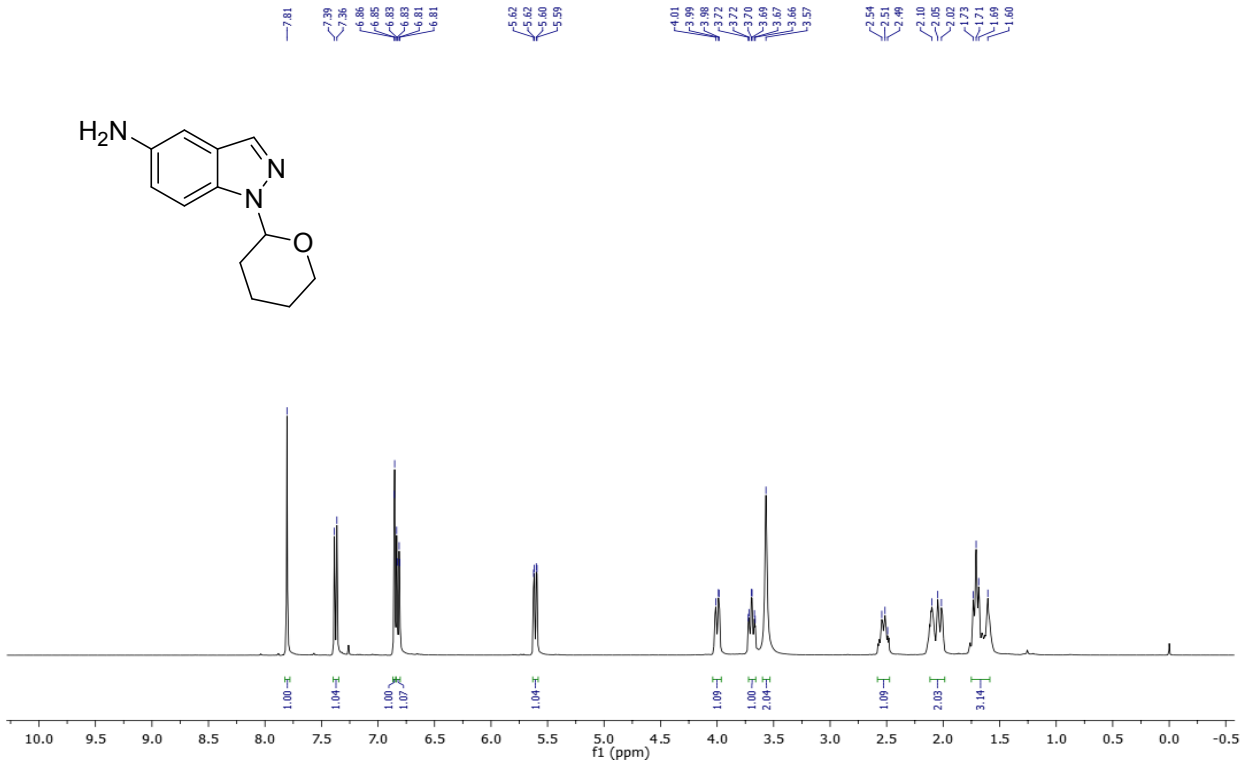
6-Nitro-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazole: ^{1}H-NMR spectrum



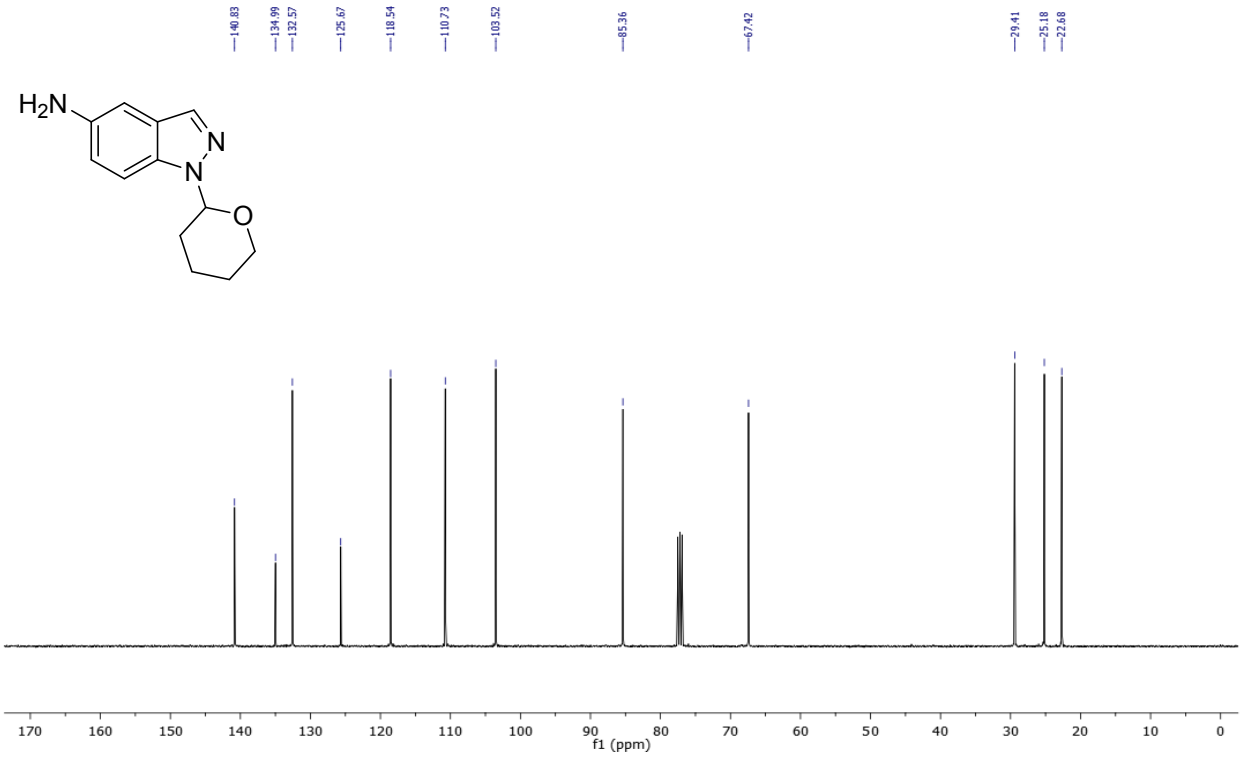
6-Nitro-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazole: ^{13}C-NMR spectrum



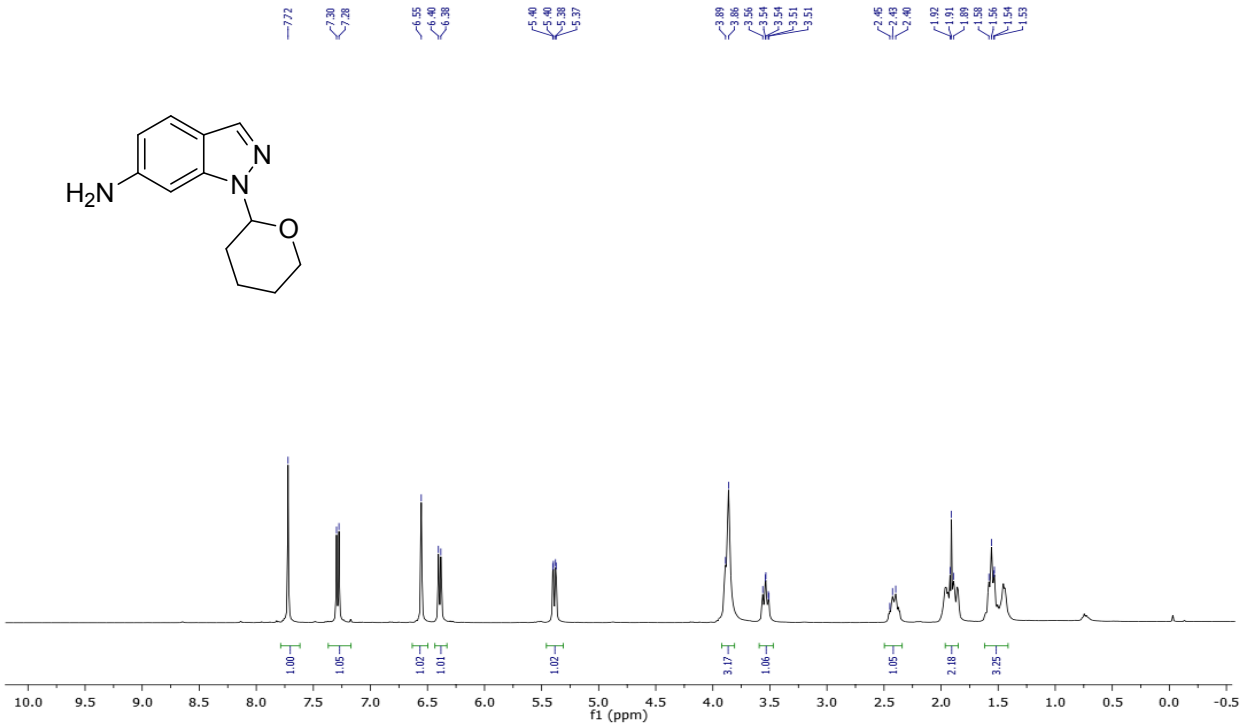
1-(Tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-5-amine: ^{1}H-NMR spectrum



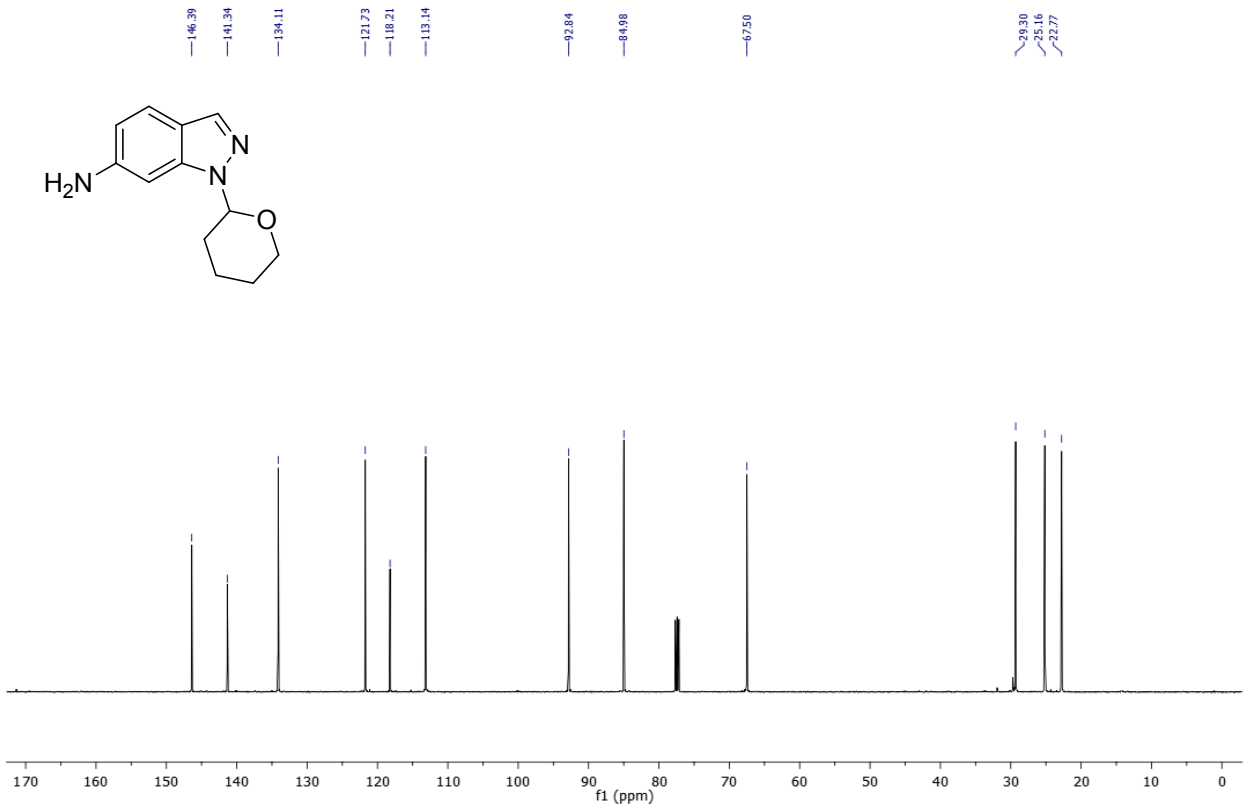
1-(Tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-5-amine: ^{13}C-NMR spectrum



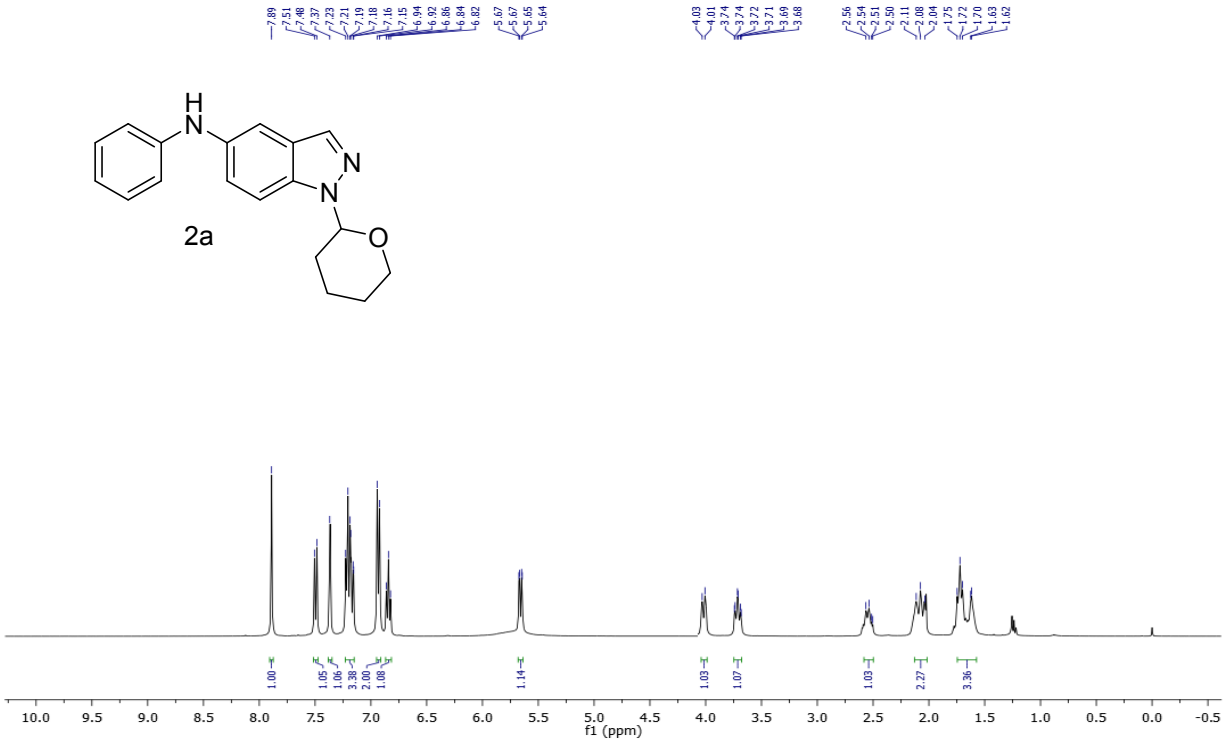
1-(Tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-6-amine: ^{1}H-NMR spectrum



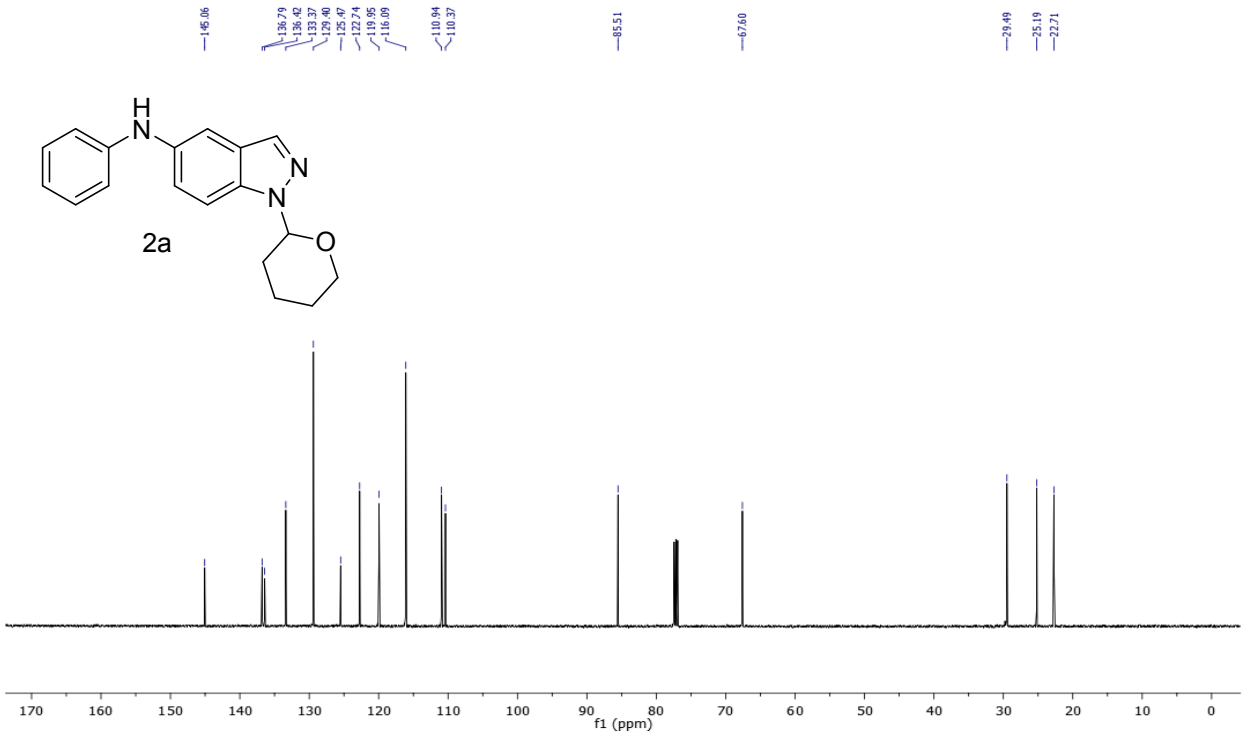
1-(Tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-6-amine: ^{13}C-NMR spectrum



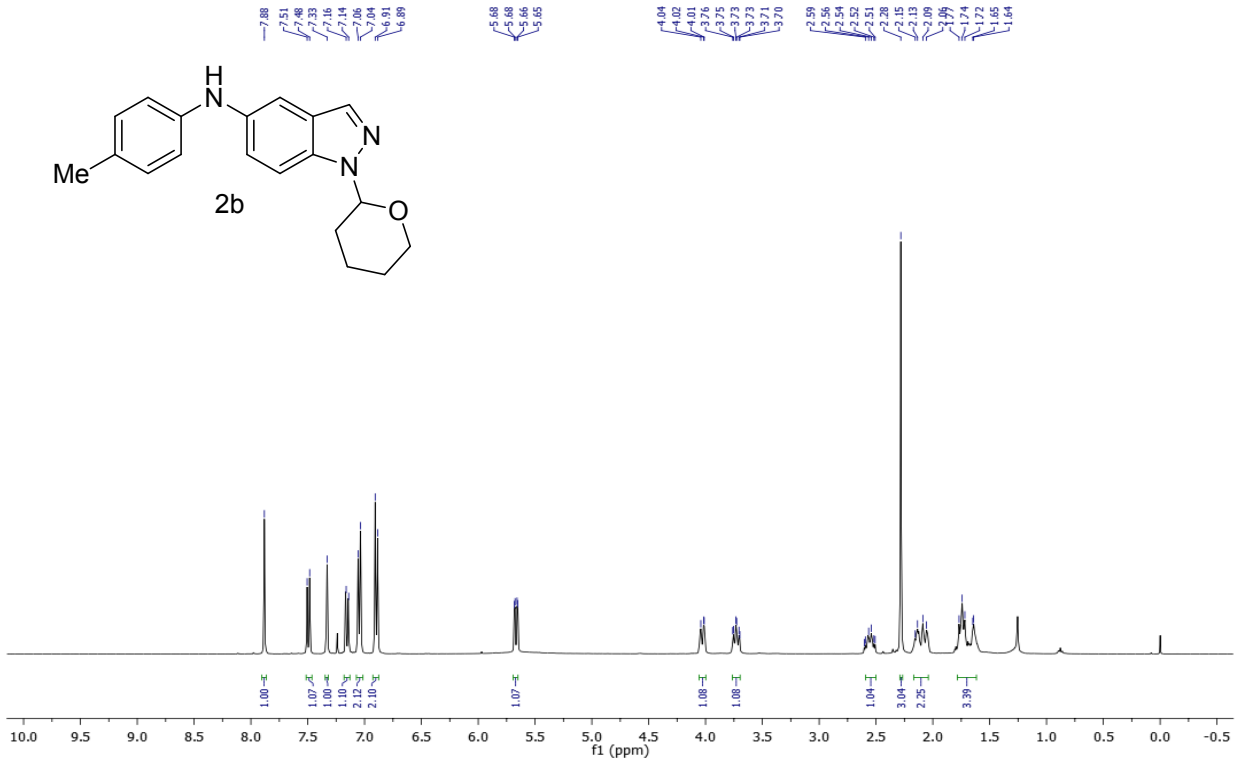
_N_-Phenyl-1-(tetrahydro-2_H_-pyran-2-yl)-1_H_-indazol-5-amine: ^{1}H-NMR spectrum



N-Phenyl-1-(tetrahydro-2_H_-pyran-2-yl)-1_H_-indazol-5-amine: ^{13}C-NMR spectrum



1-(Tetrahydro-2*H*-pyran-2-yl)-*N*-(p-tolyl)-1*H*-indazol-5-amine: ^{1}H-NMR spectrum



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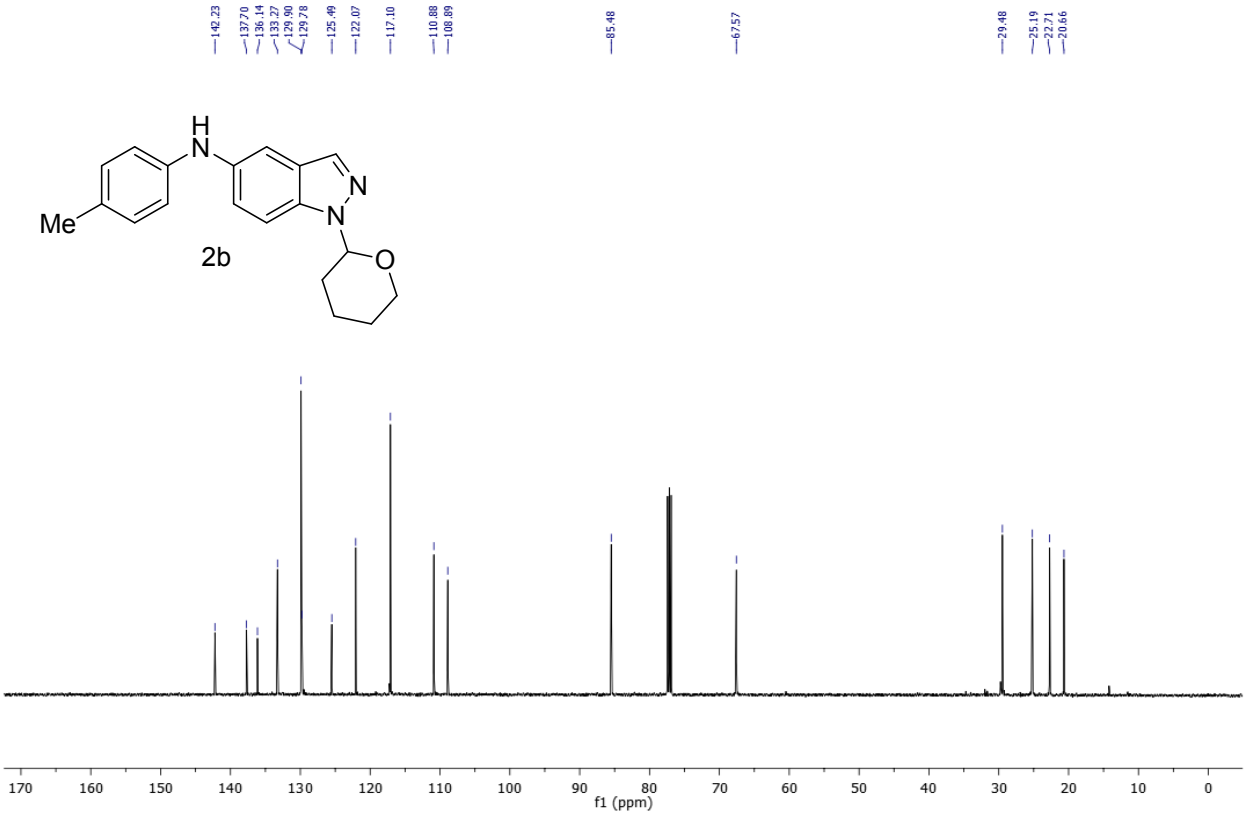
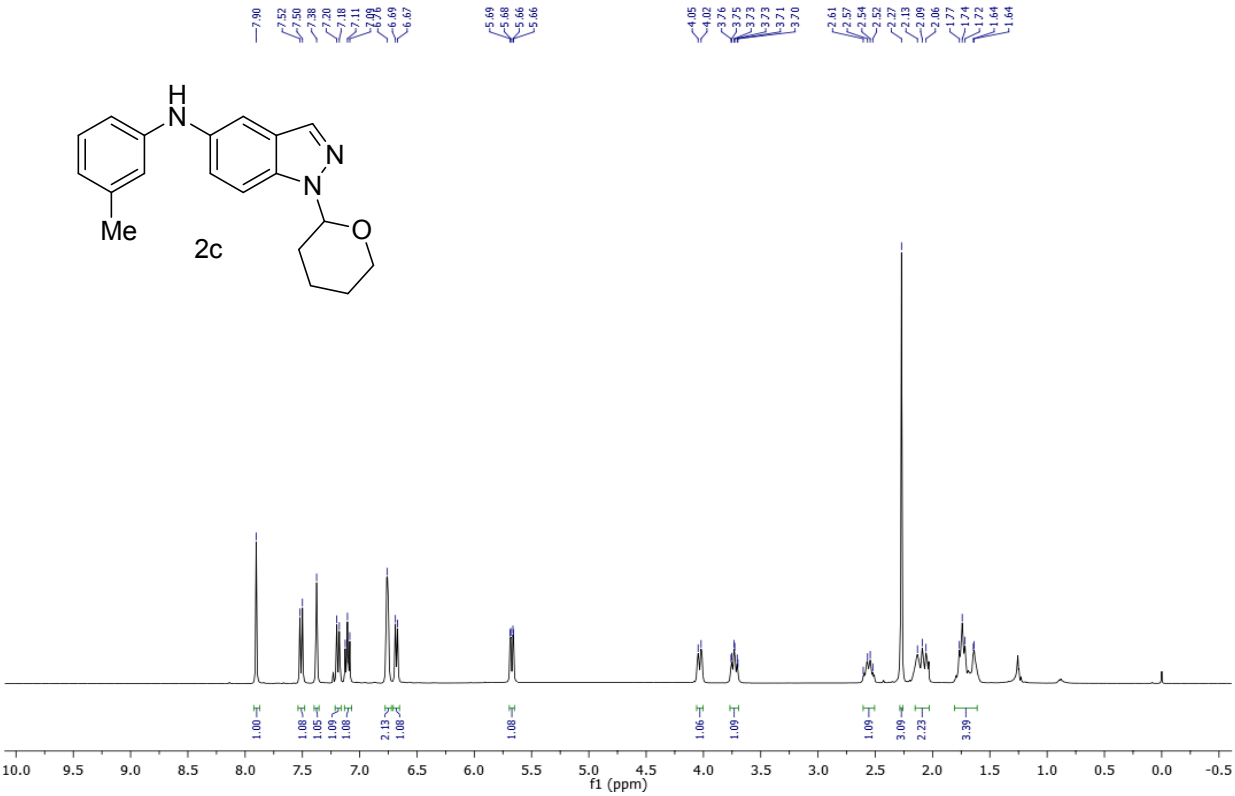


1-(Tetrahydro-2*H*-pyran-2-yl)-*N*-(m-tolyl)-1*H*-indazol-5-amine: ^{1}H-NMR spectrum



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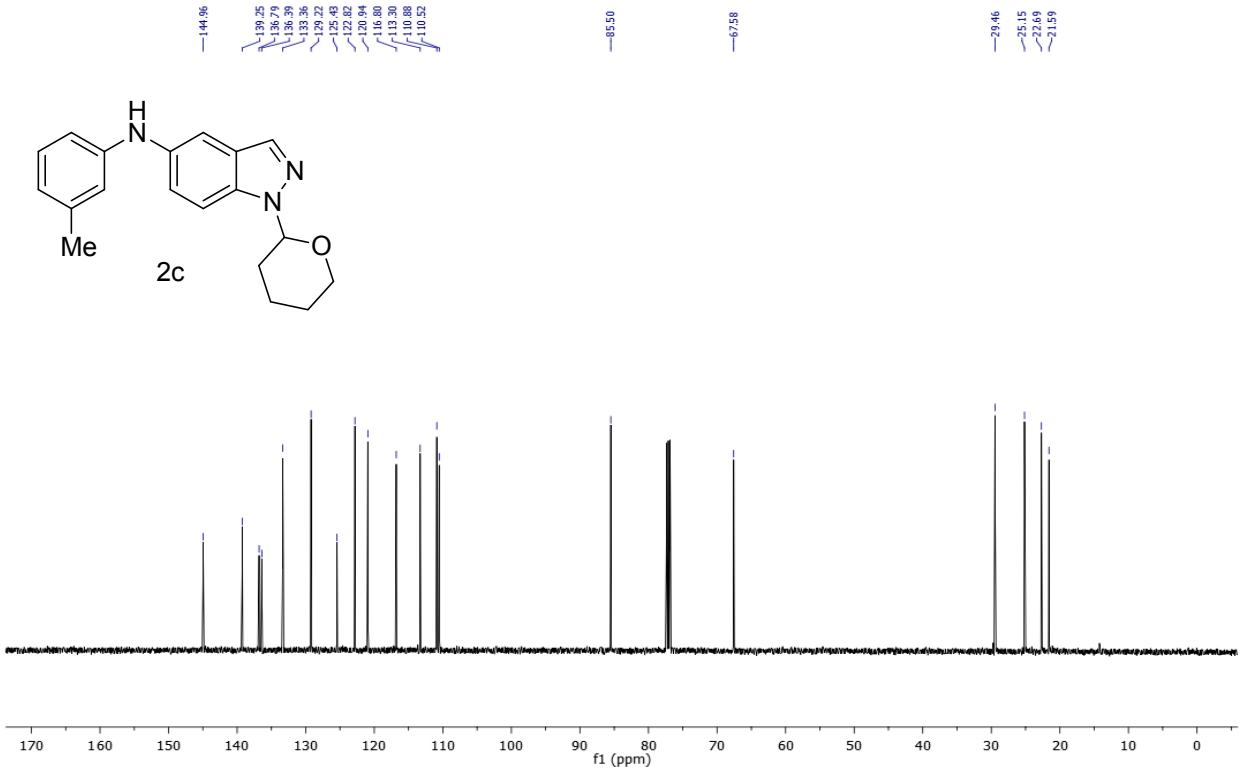
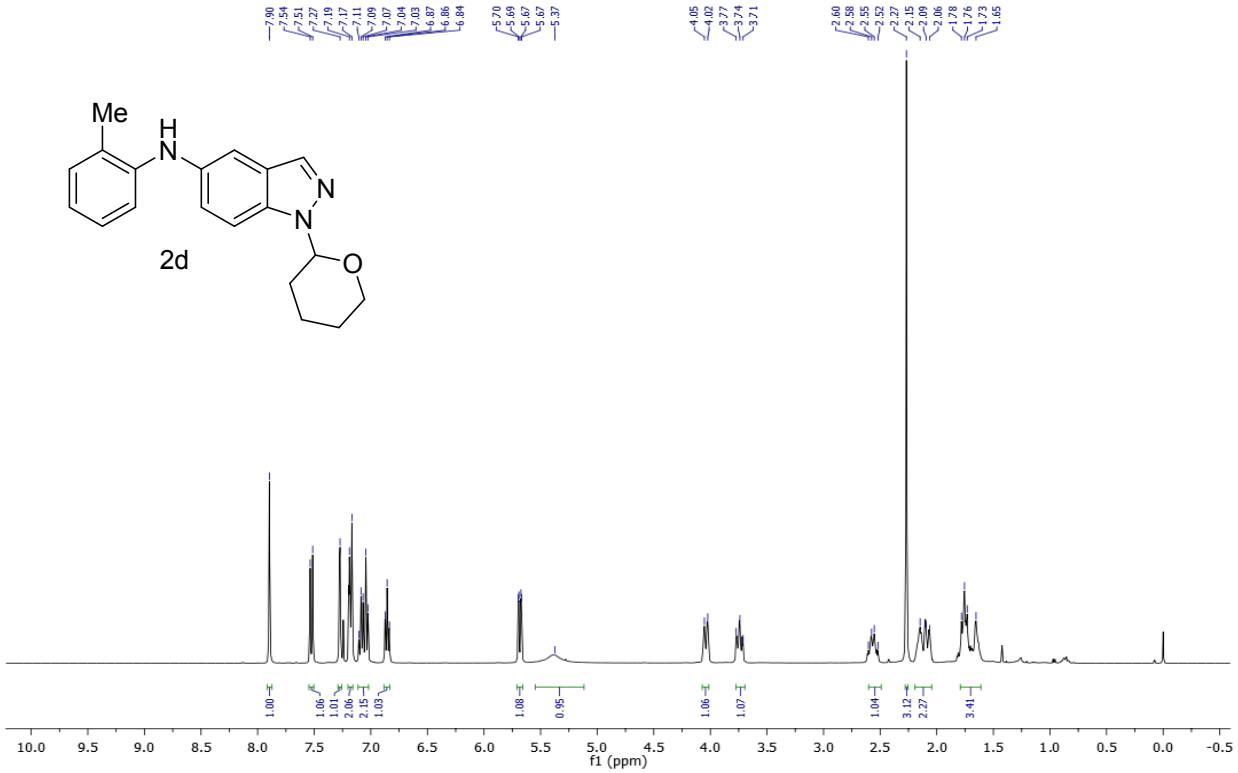


1-(Tetrahydro-2H-pyran-2-yl)-N-(o-tolyl)-1H-indazol-5-amine: ^{1}H-NMR spectrum



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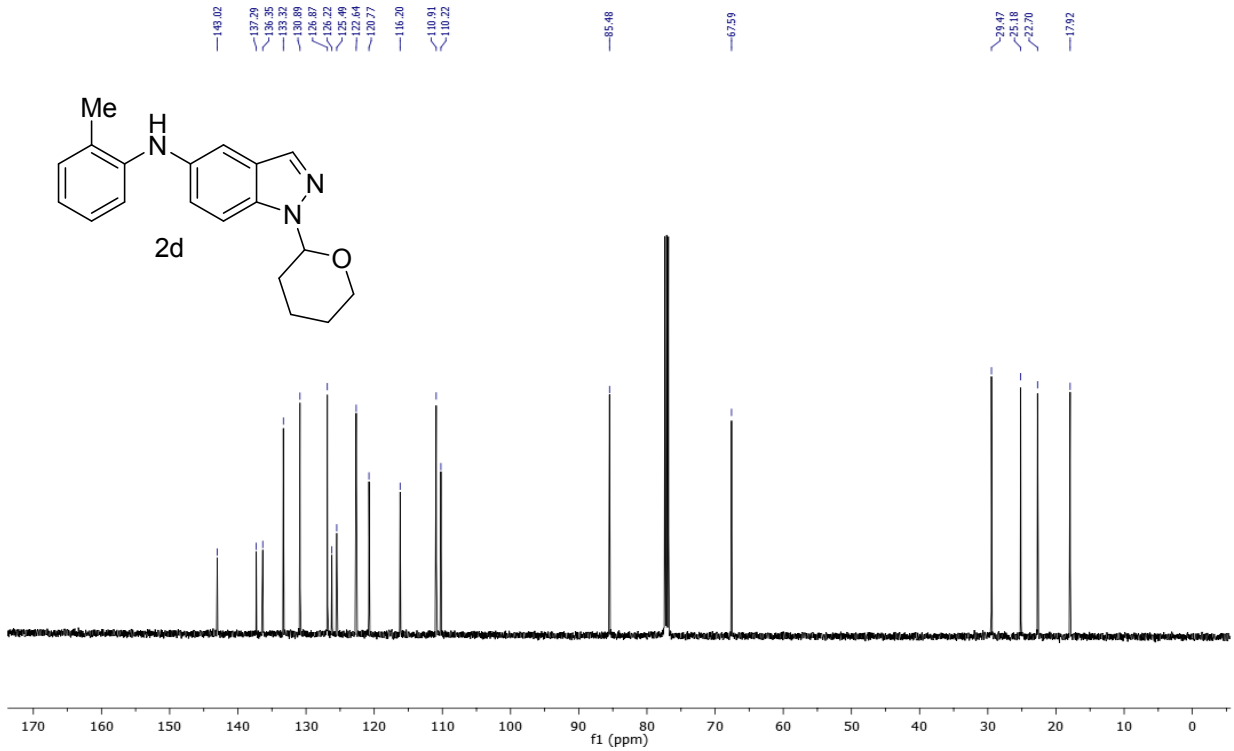
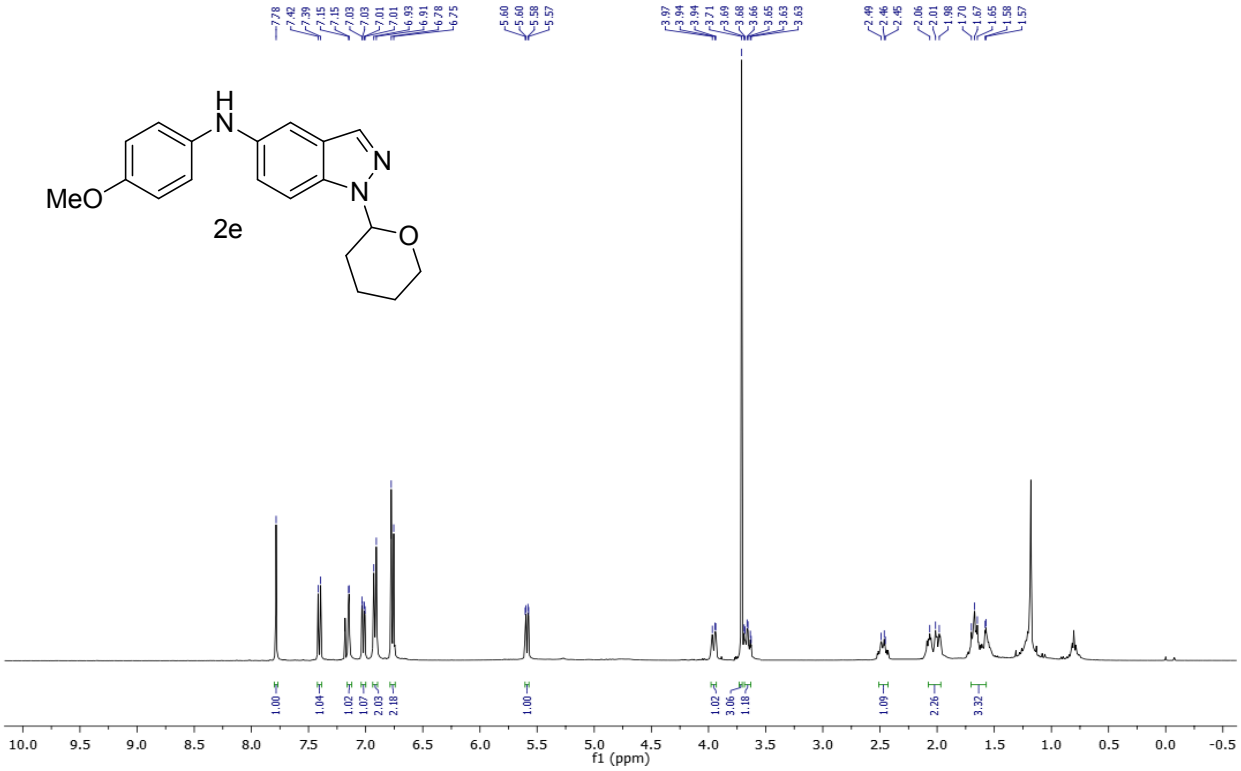


***N*-(4-Methoxyphenyl)-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-5-amine: ^{1}H-NMR spectrum**



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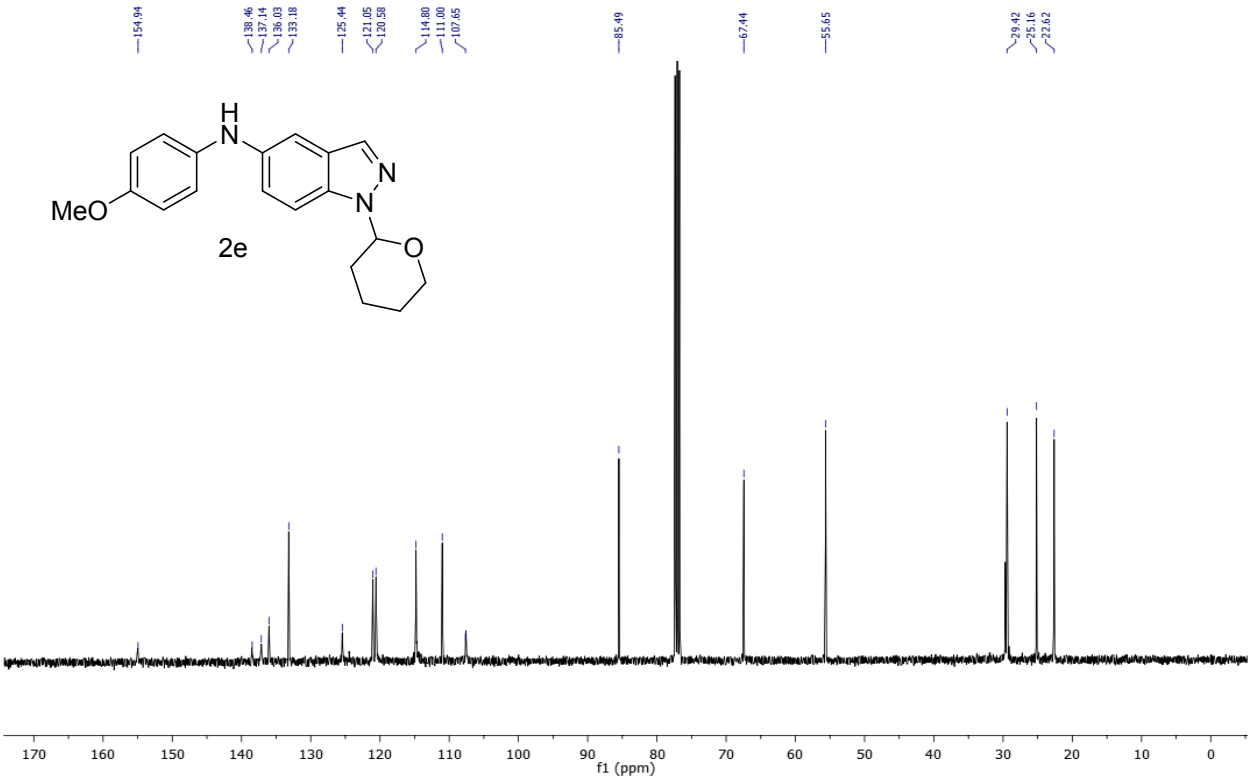
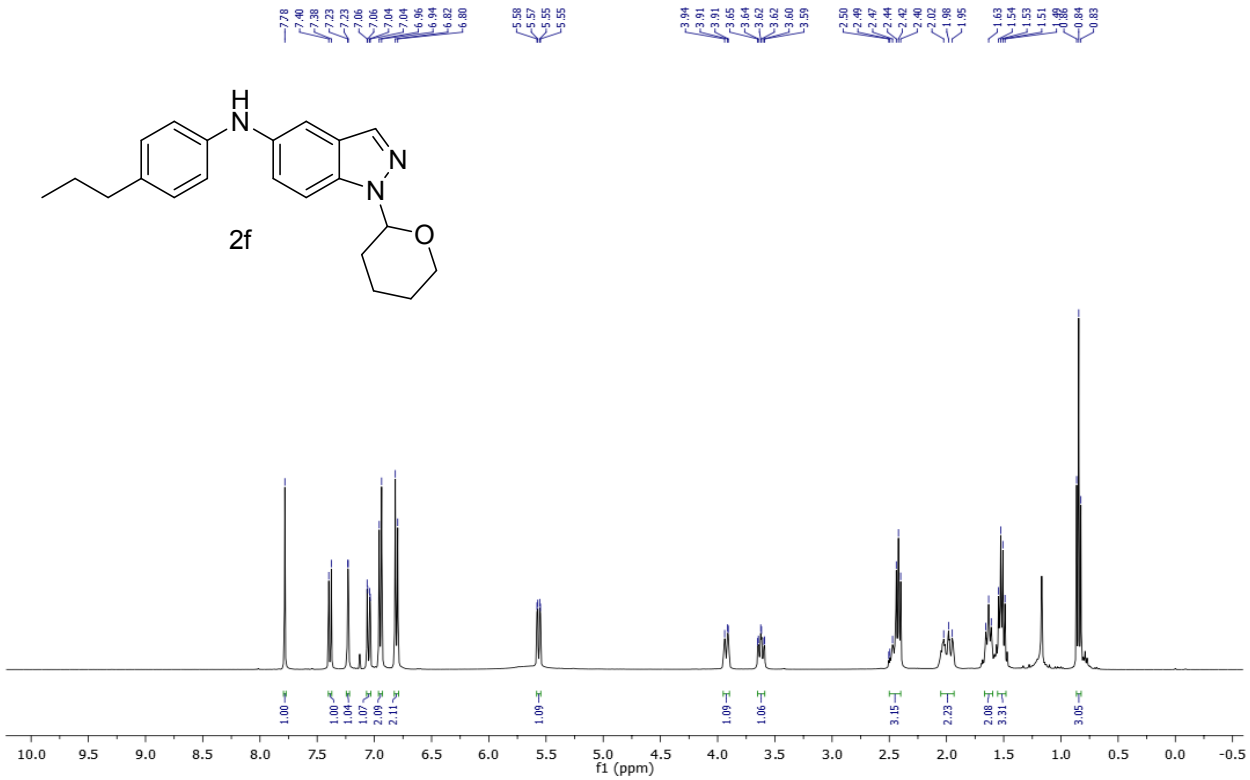
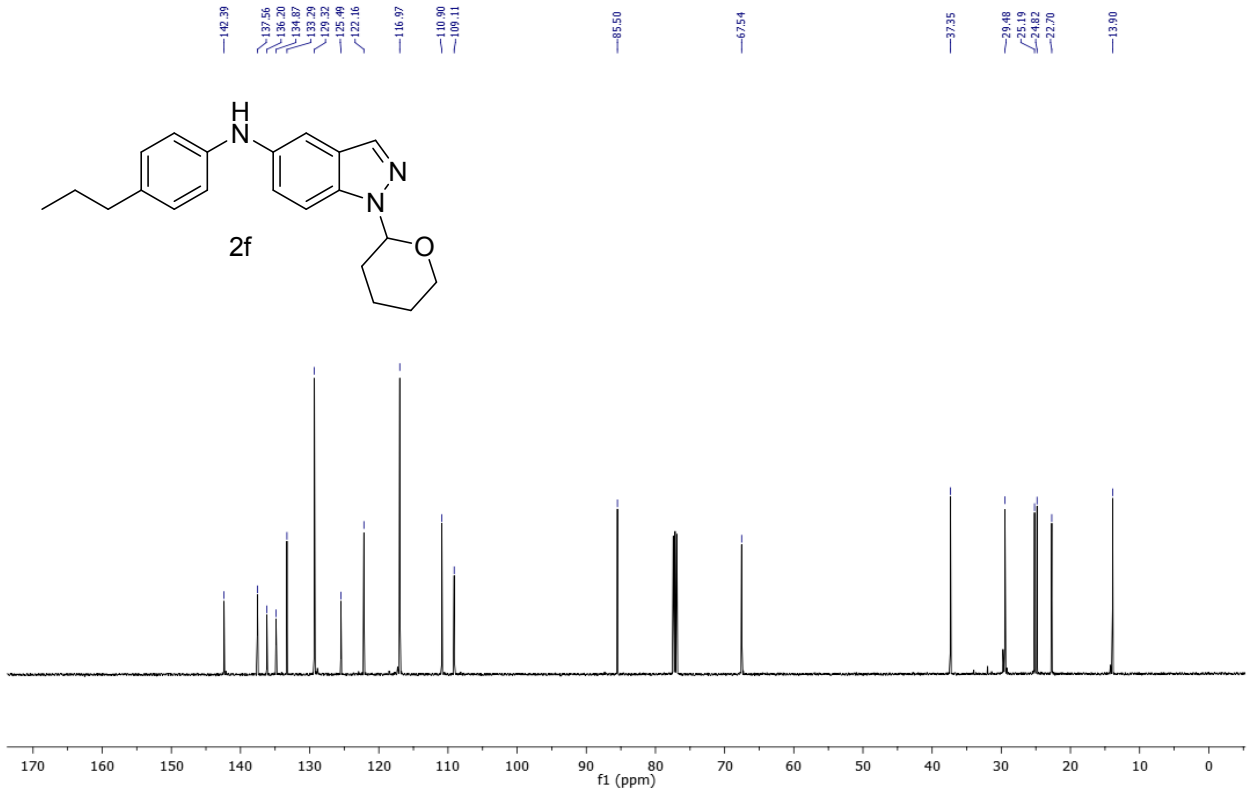


***N*-(4-Propylphenyl)-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-5-amine: ^{1}H-NMR spectrum**



***N*-(4-Propylphenyl)-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-5-amine: ^{13}C-NMR spectrum**



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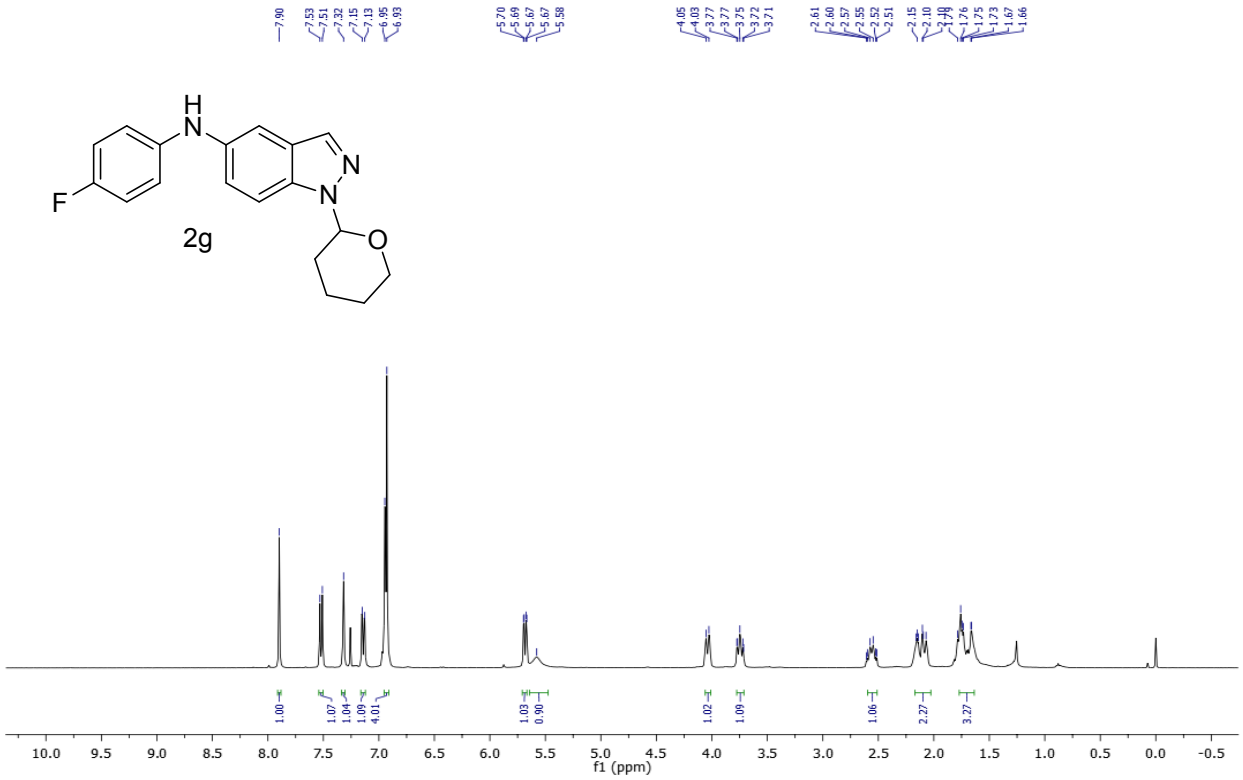
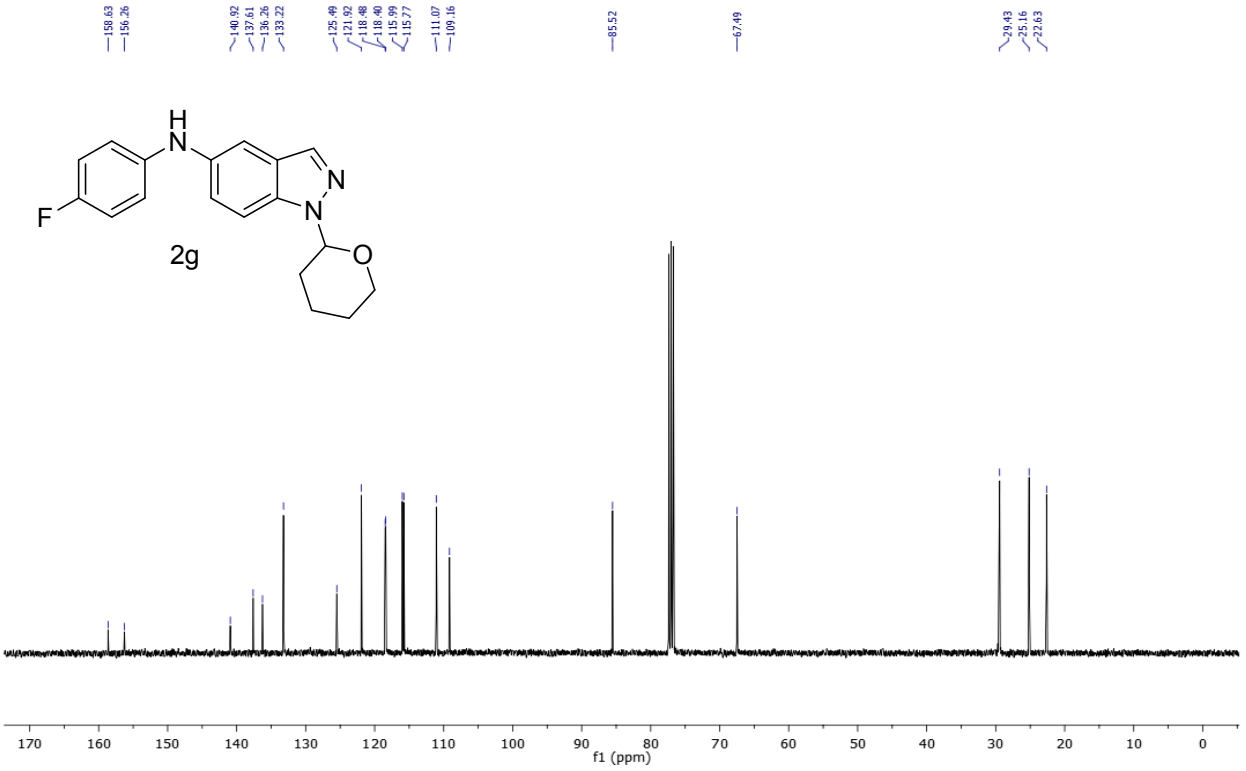
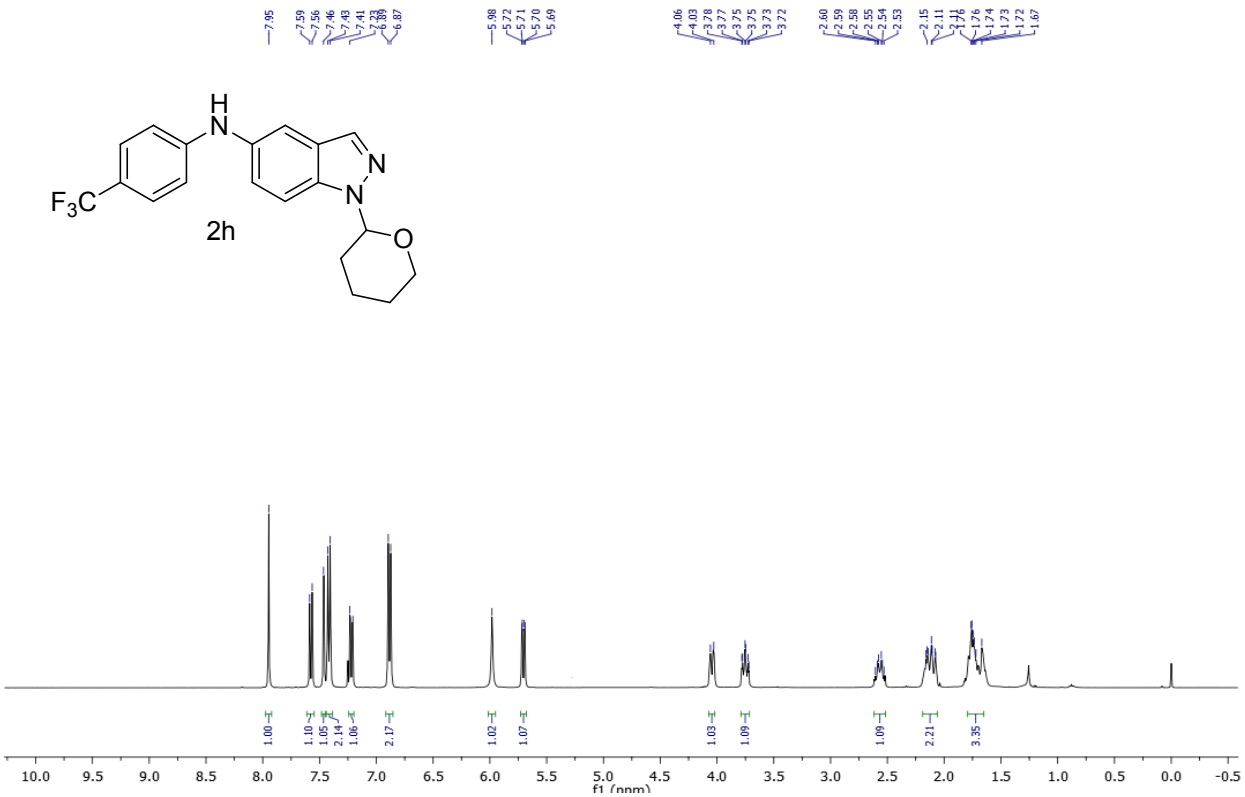


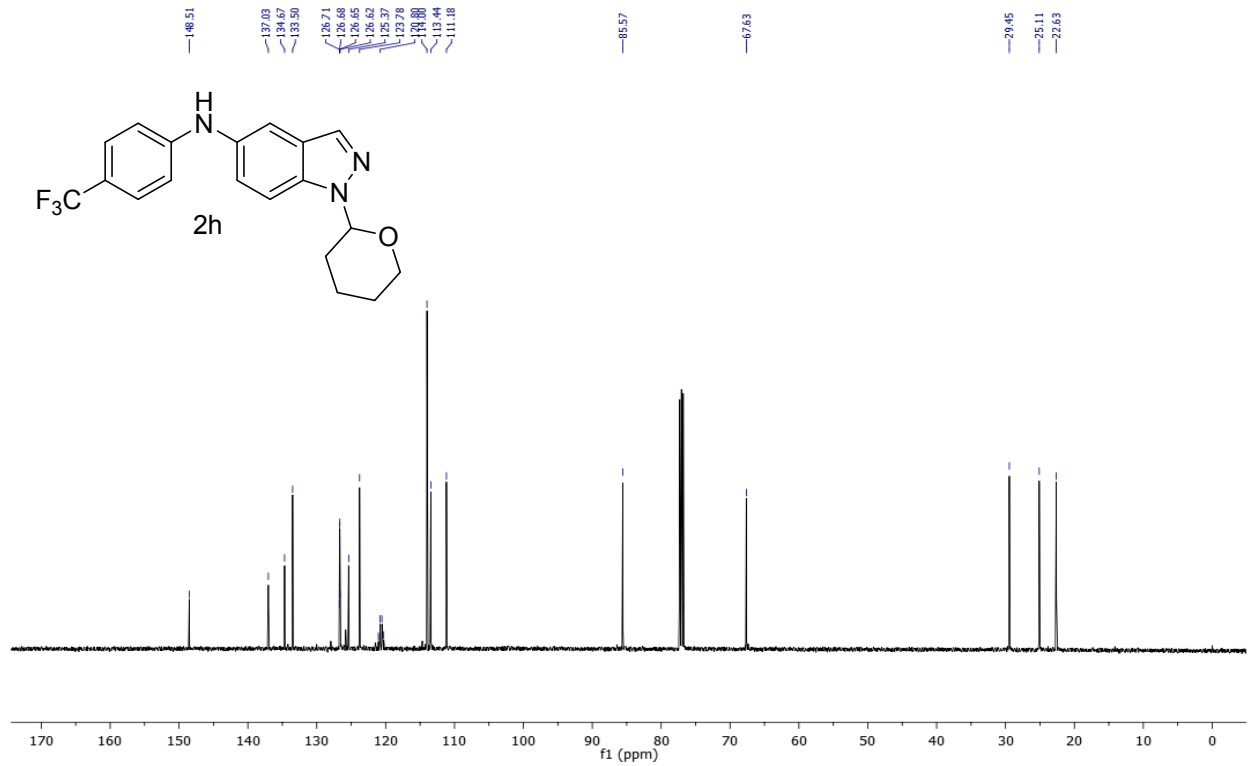
***N*-(4-Fluorophenyl)-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-5-amine: ^{13}C-NMR spectrum**



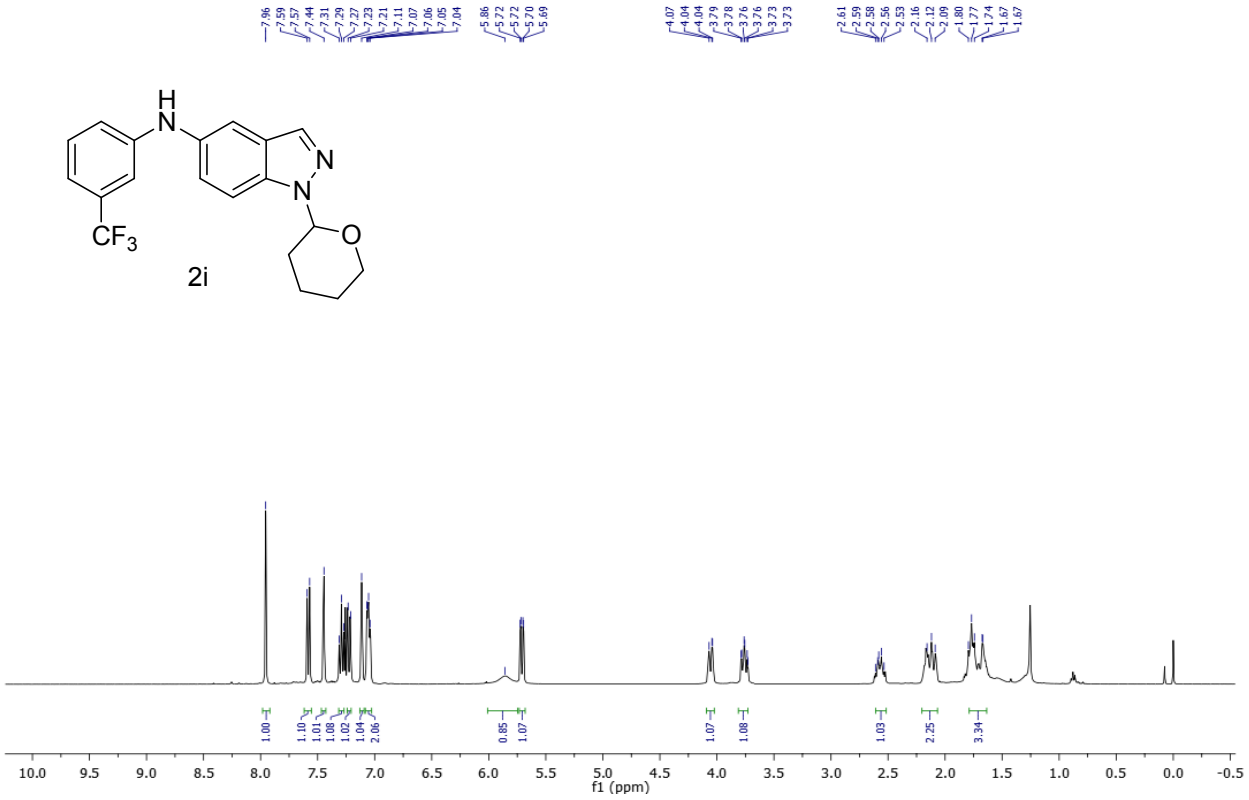
1-(Tetrahydro-2*H*-pyran-2-yl)-*N*-(4-(trifluoromethyl) phenyl)-1*H*-indazol-5-amine: ^{1}H-NMR spectrum



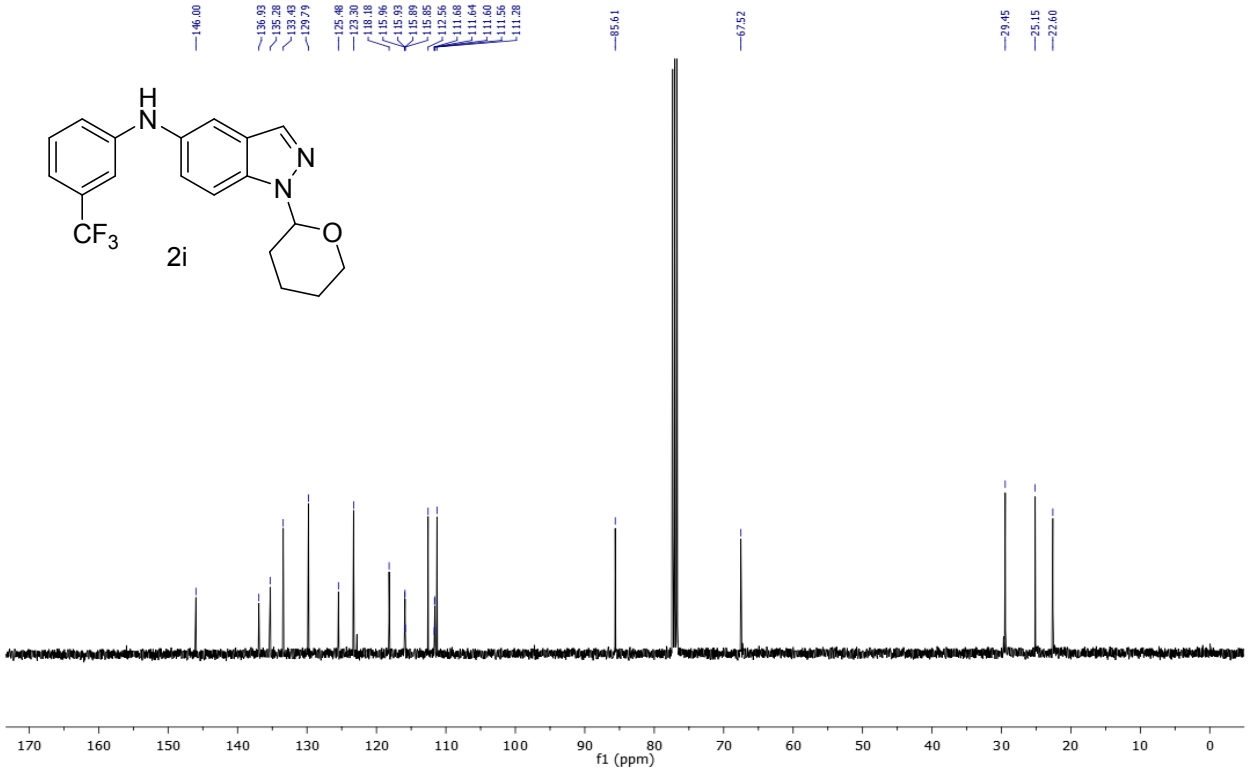
1-(Tetrahydro-2*H*-pyran-2-yl)-*N*-(4-(trifluoromethyl) phenyl)-1*H*-indazol-5-amine: ^{13}C-NMR spectrum



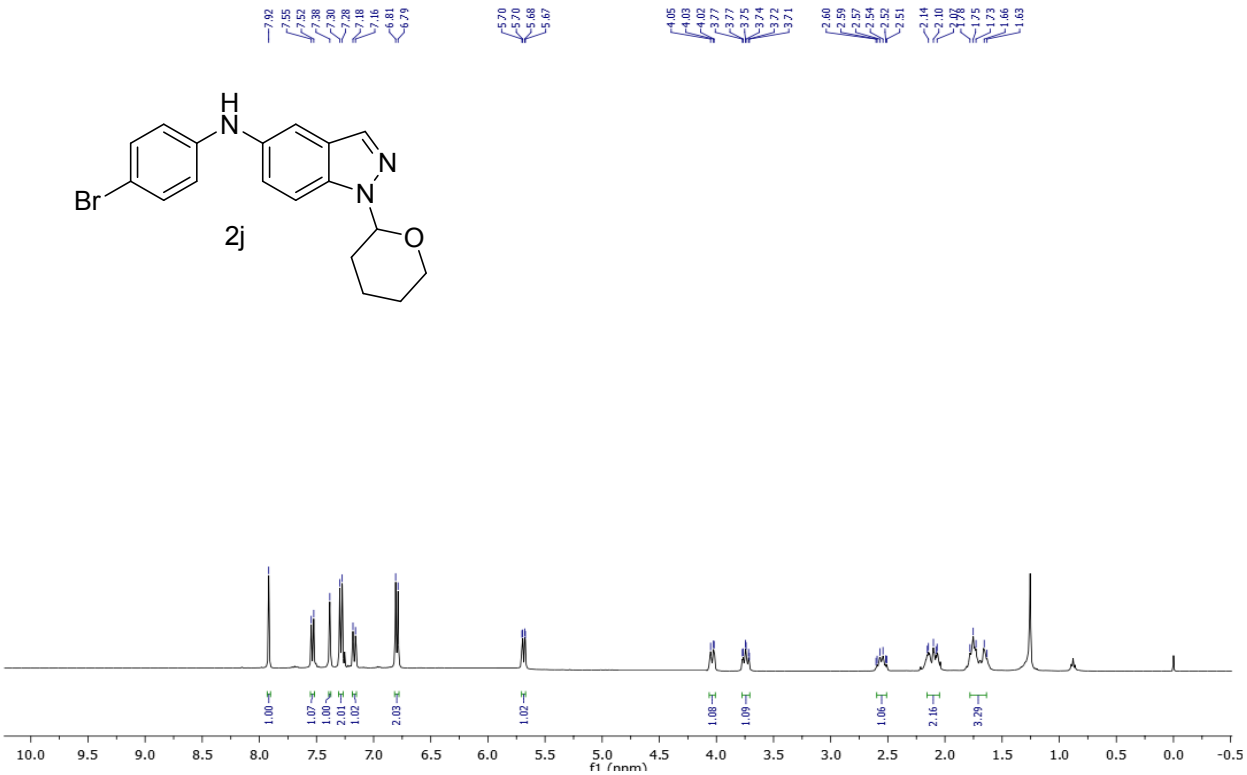
1-(Tetrahydro-2*H*-pyran-2-yl)-*N*-(3-(trifluoromethyl) phenyl)-1*H*-indazol-5-amine: ^{1}H-NMR spectrum



1-(Tetrahydro-2*H*-pyran-2-yl)-*N*-(3-(trifluoromethyl) phenyl)-1*H*-indazol-5-amine: ^{13}C-NMR spectrum



***N*-(4-Bromophenyl)-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-5-amine: ^{1}H-NMR spectrum**



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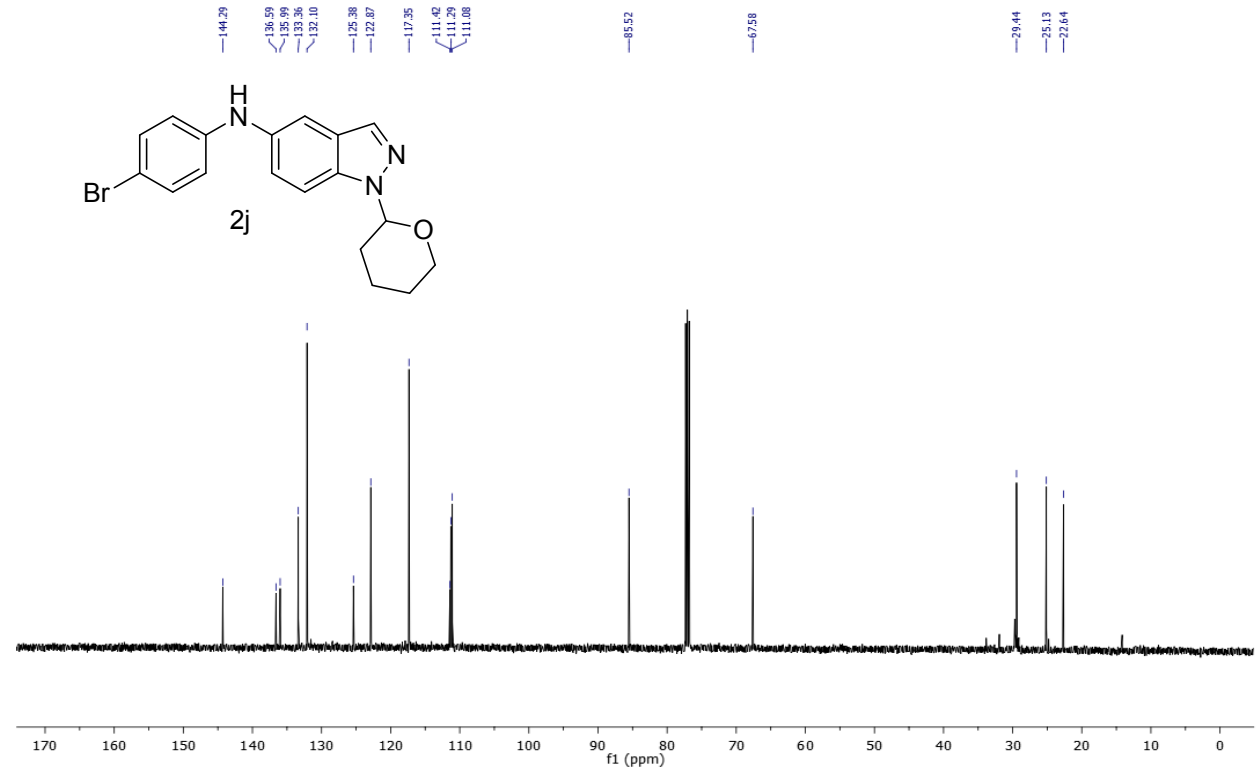

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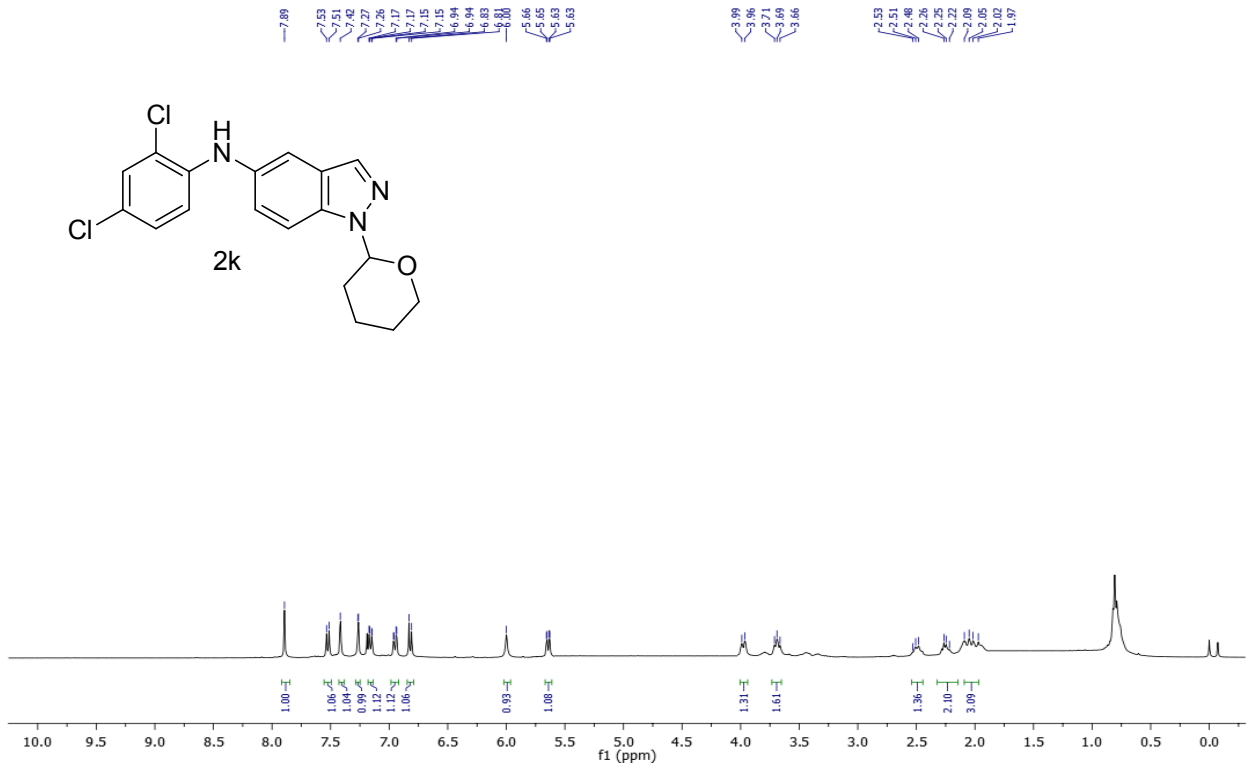

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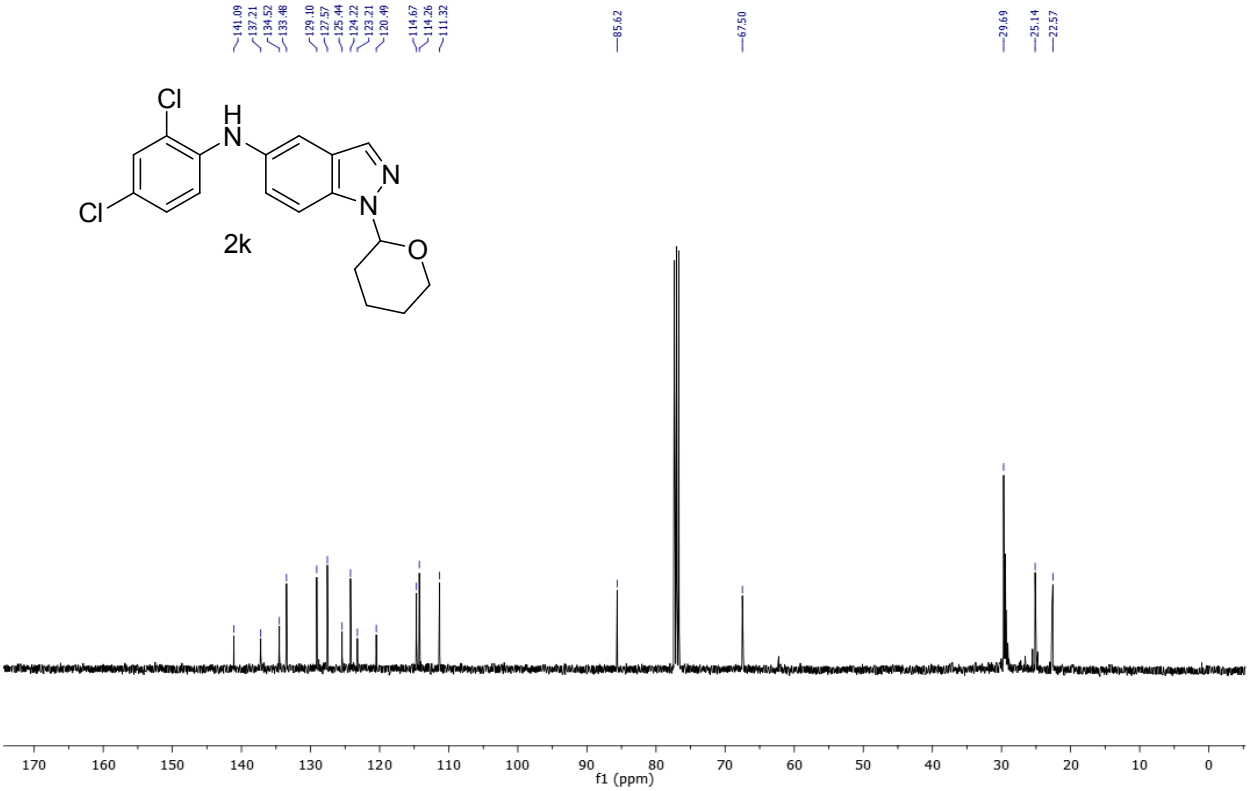

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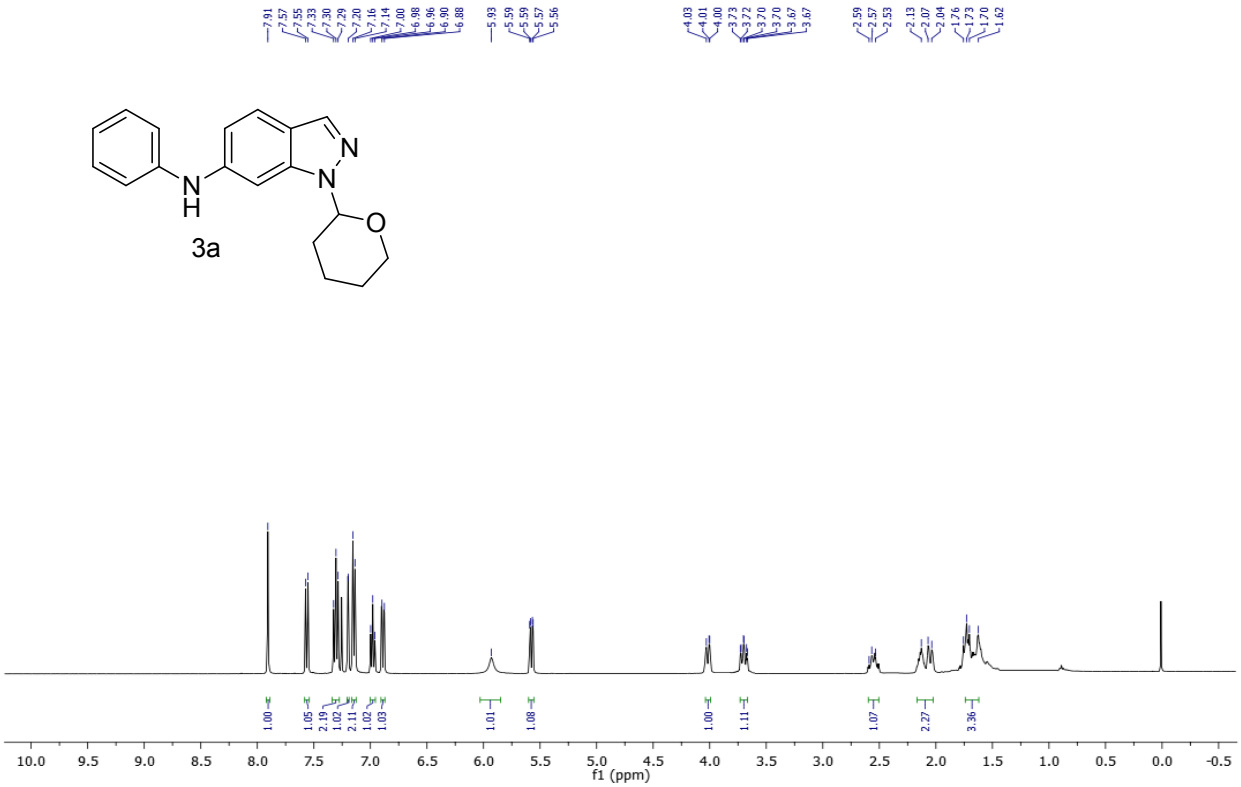

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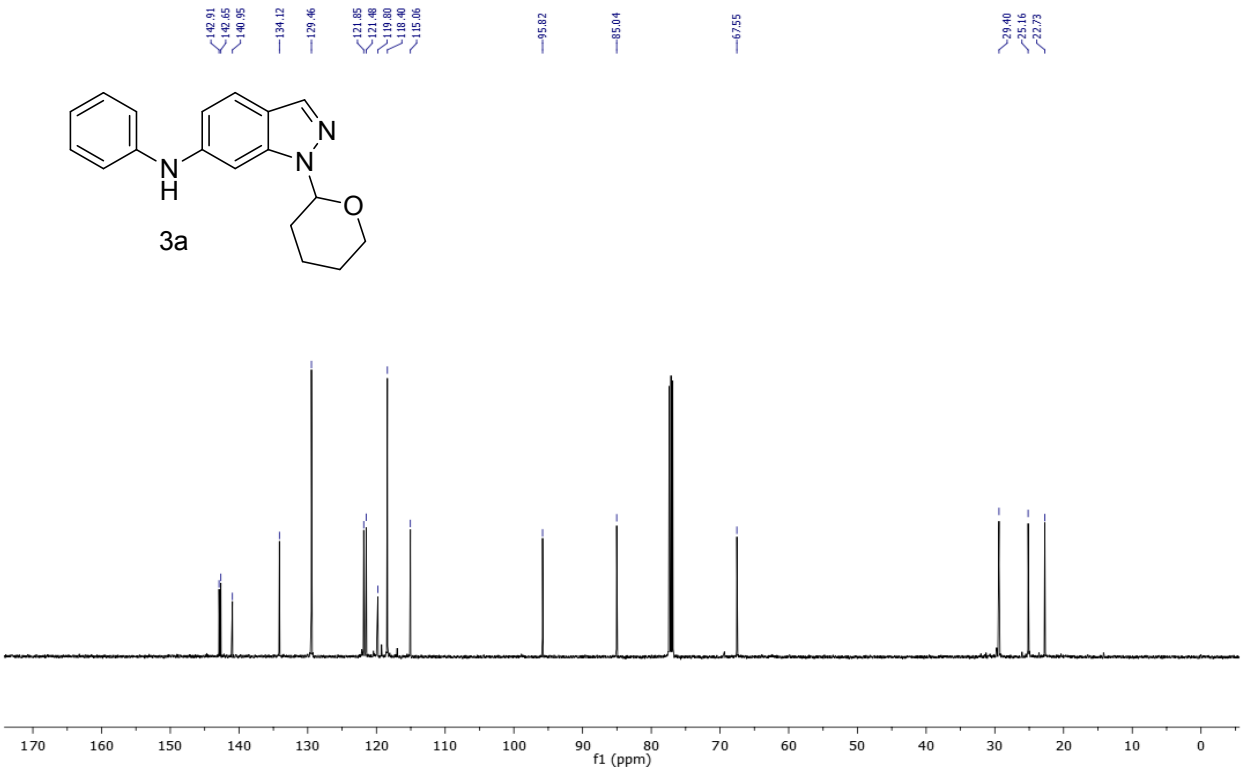
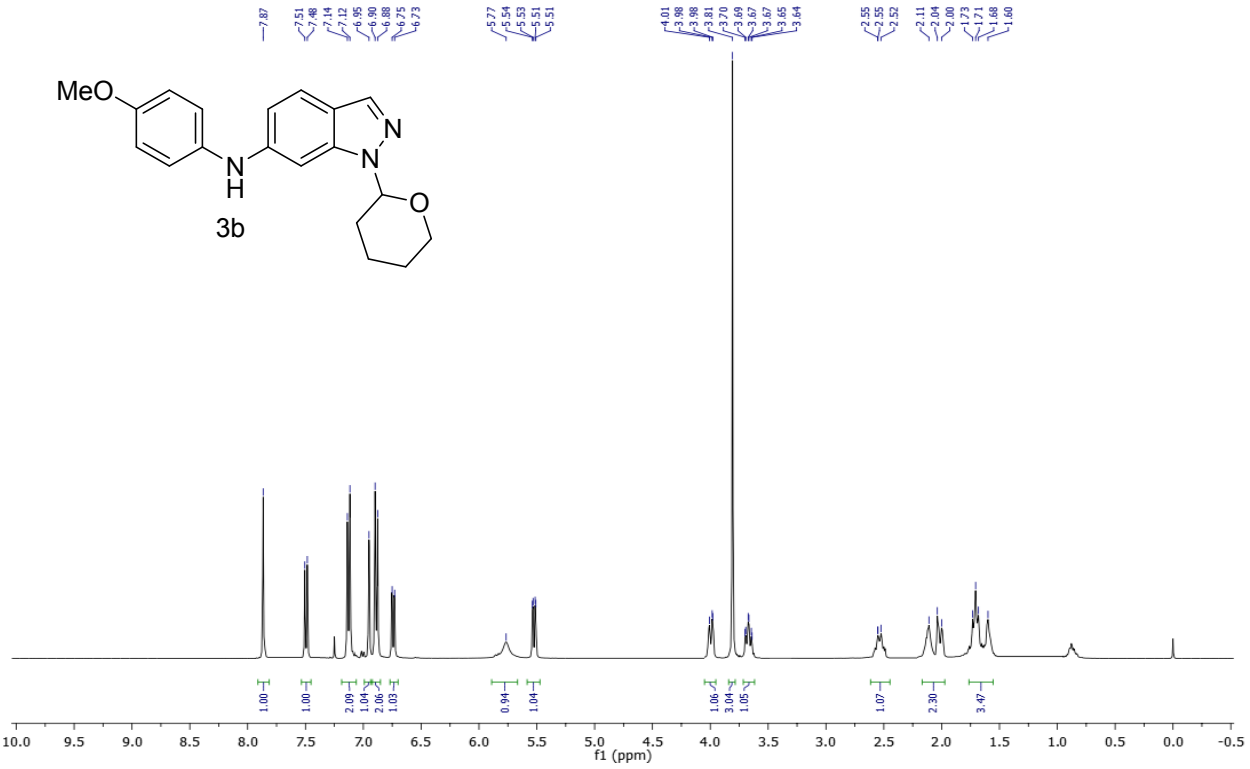
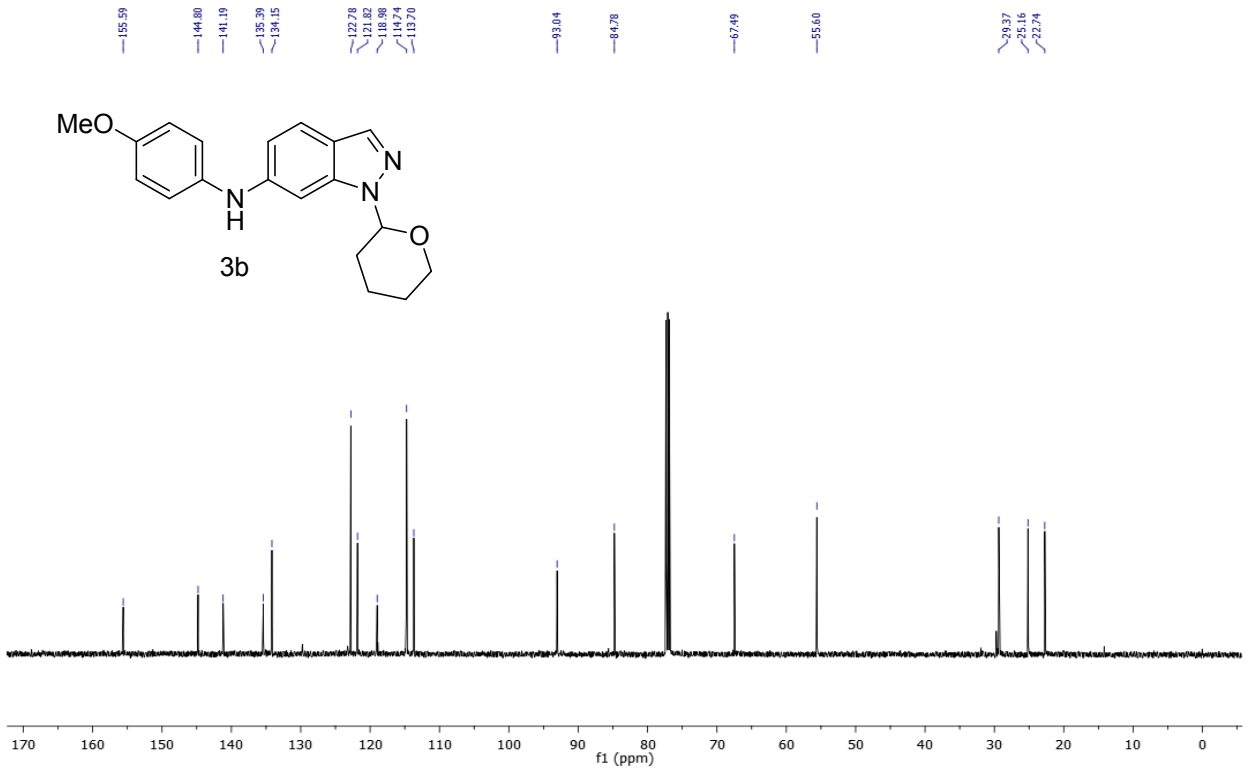


***N*-(4-Methoxyphenyl)-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-6-amine: ^{1}H-NMR spectrum**



***N*-(4-Methoxyphenyl)-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-6-amine: ^{13}C-NMR spectrum**



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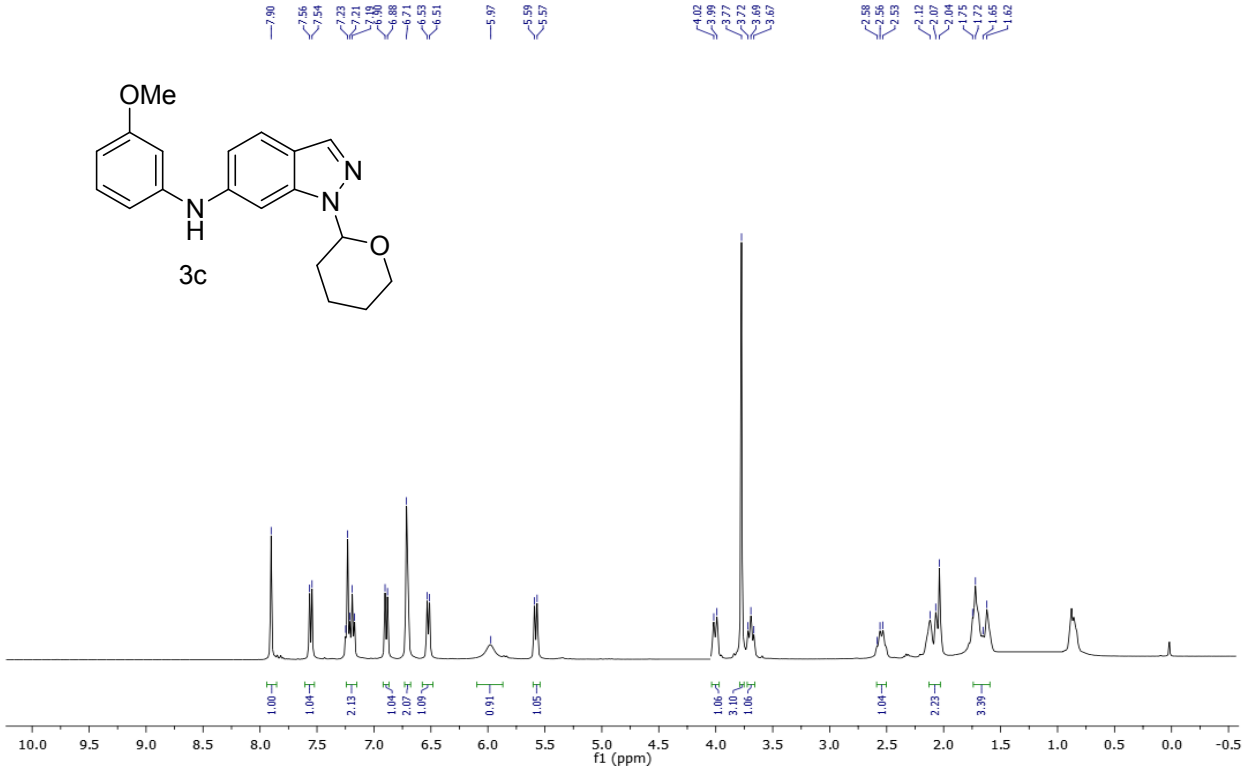
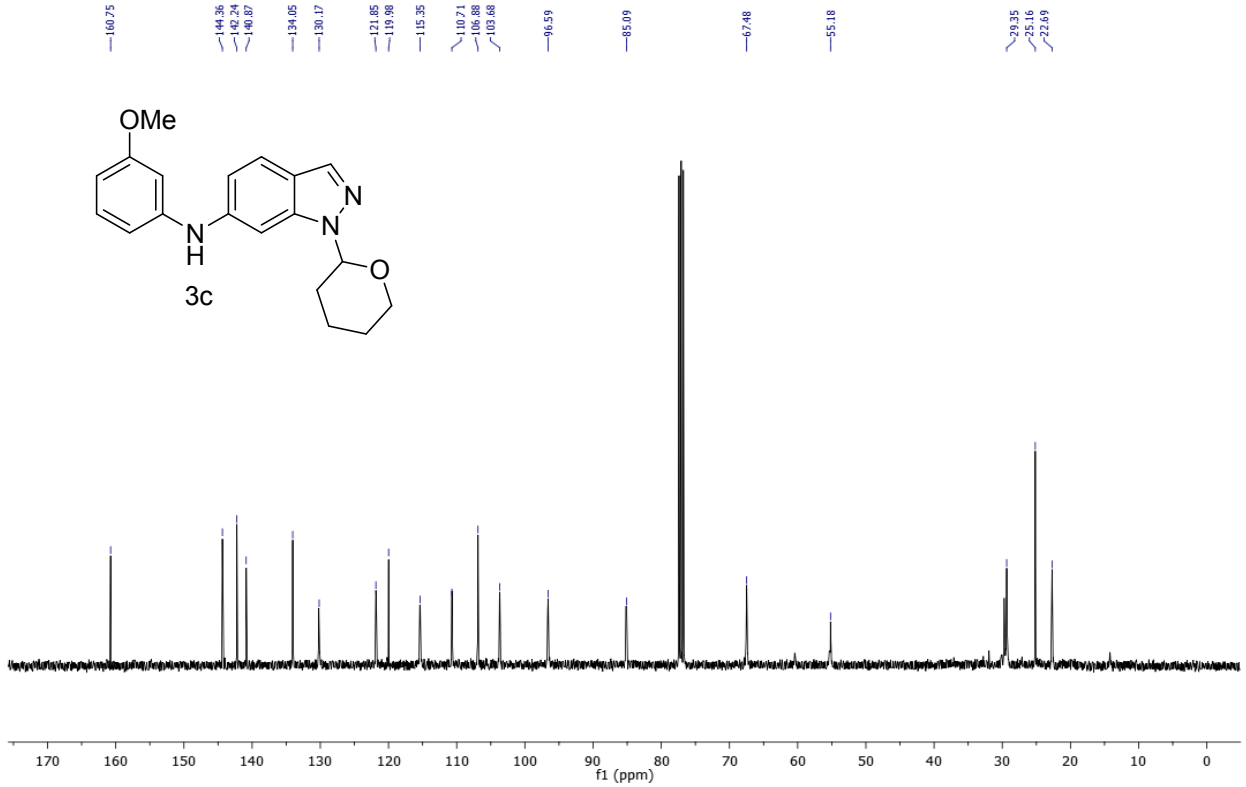


***N*-(3-Methoxyphenyl)-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-6-amine: ^{13}C-NMR spectrum**



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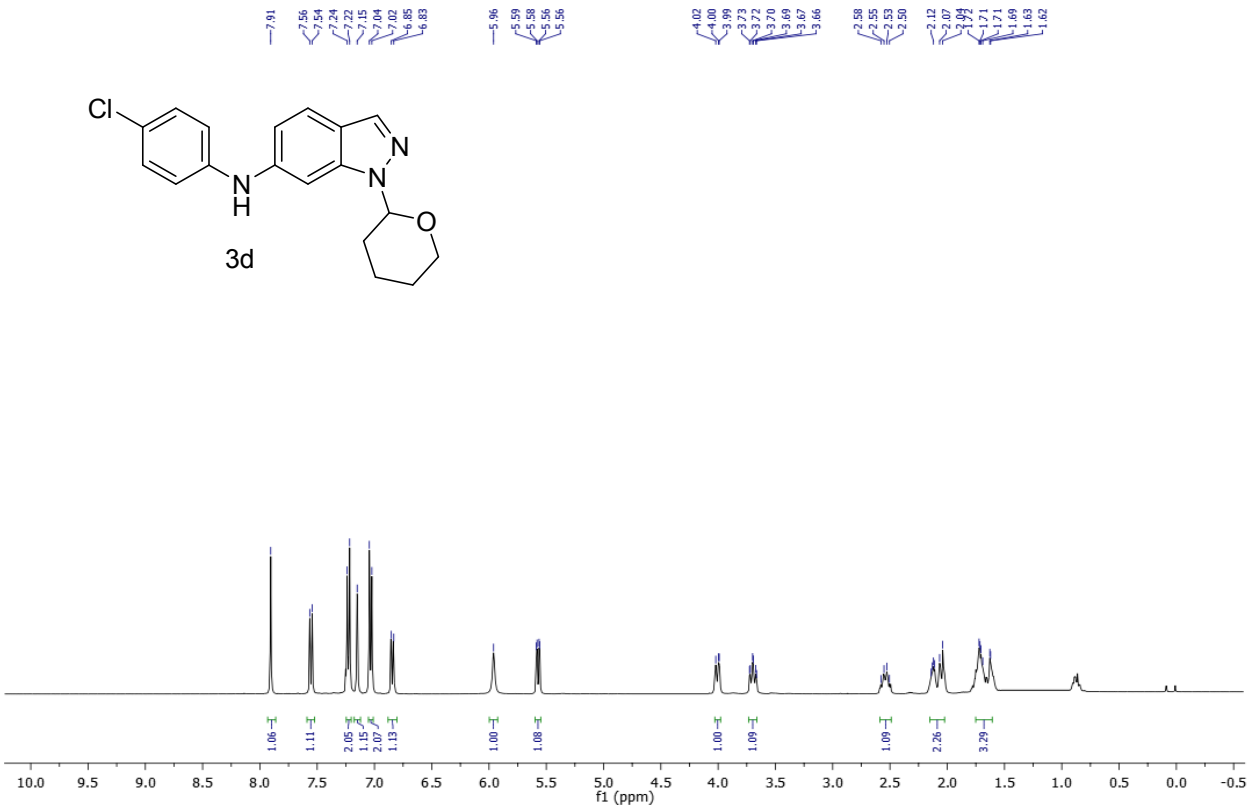

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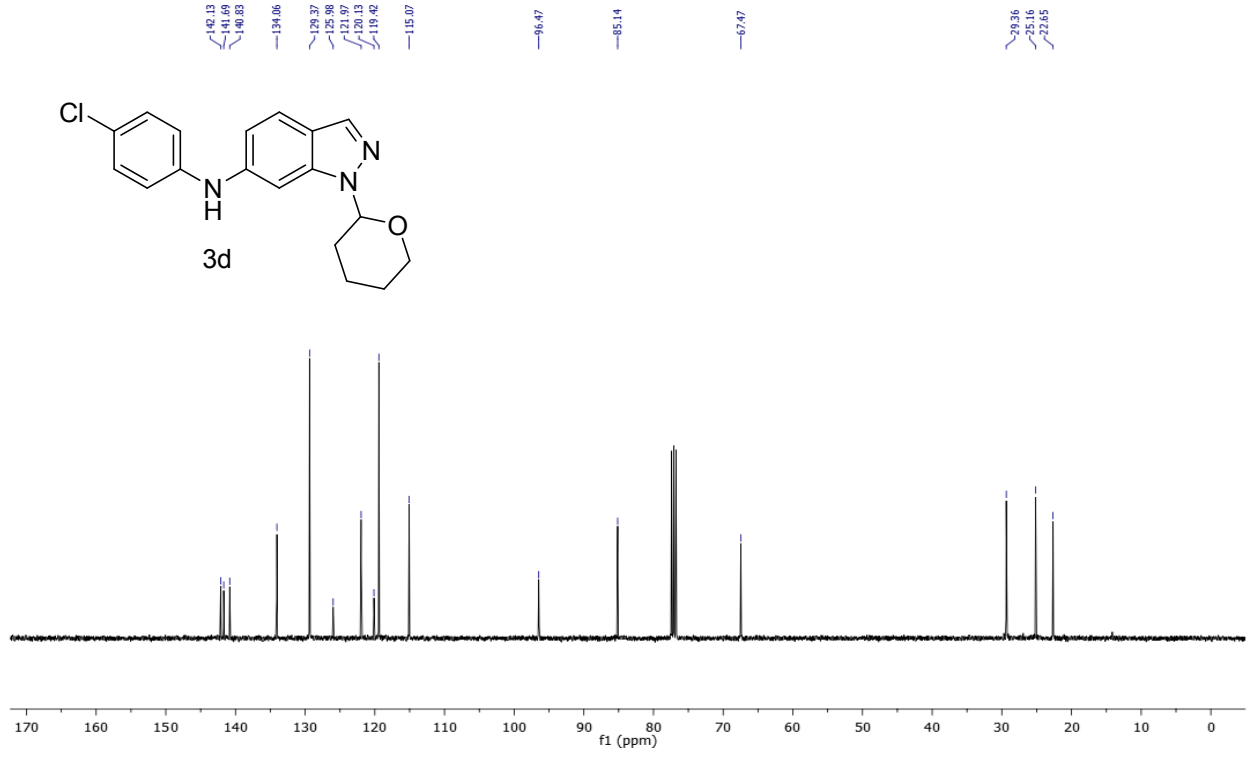

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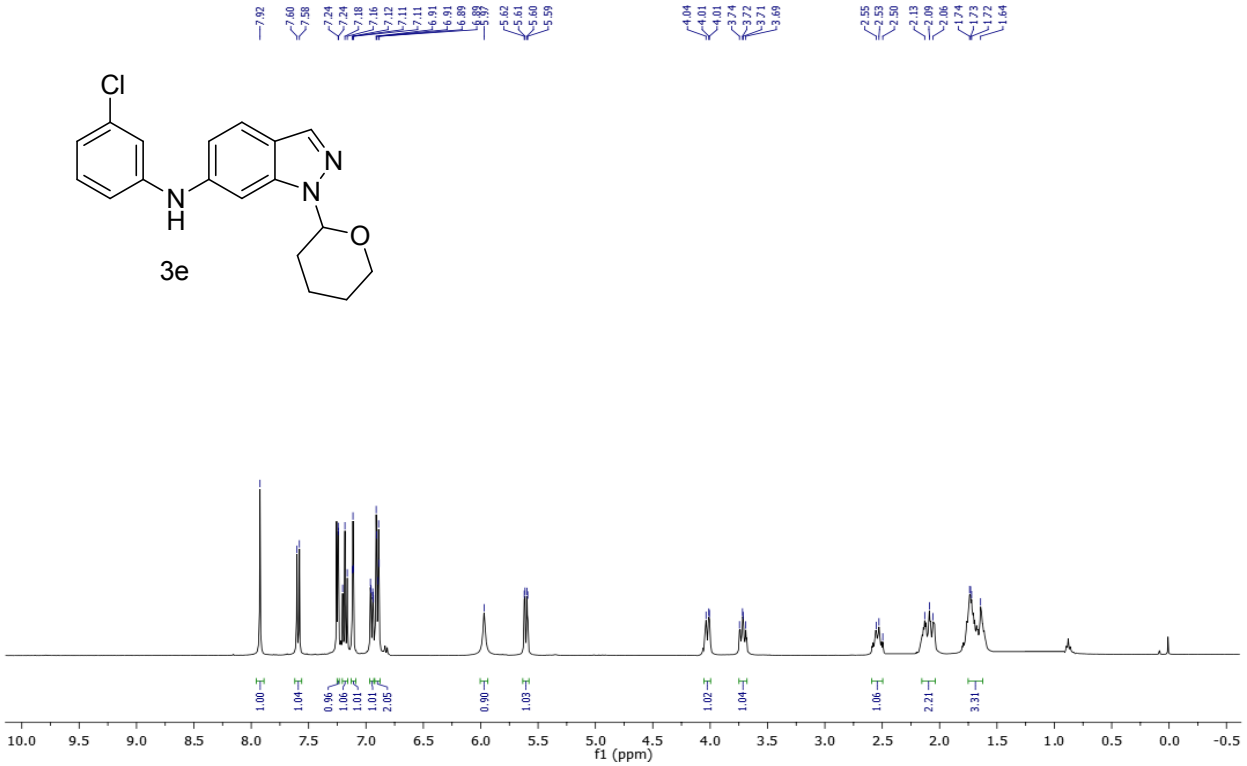

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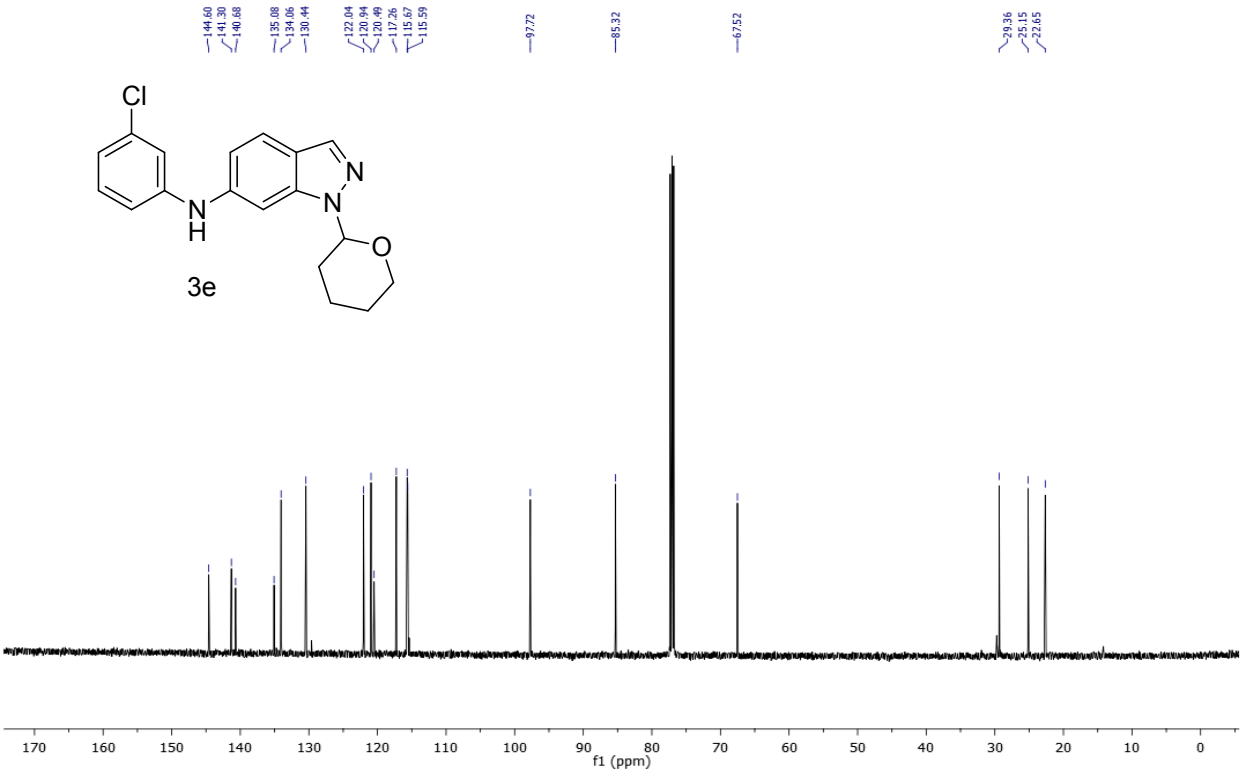
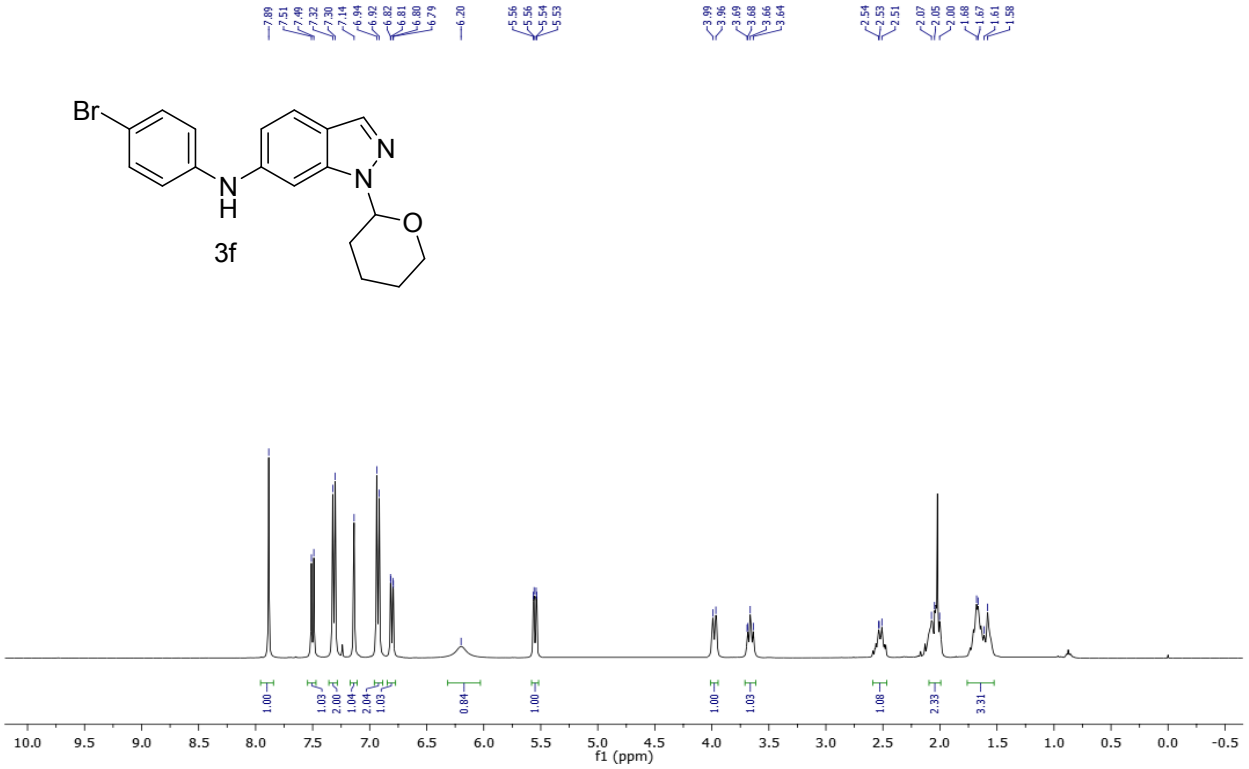
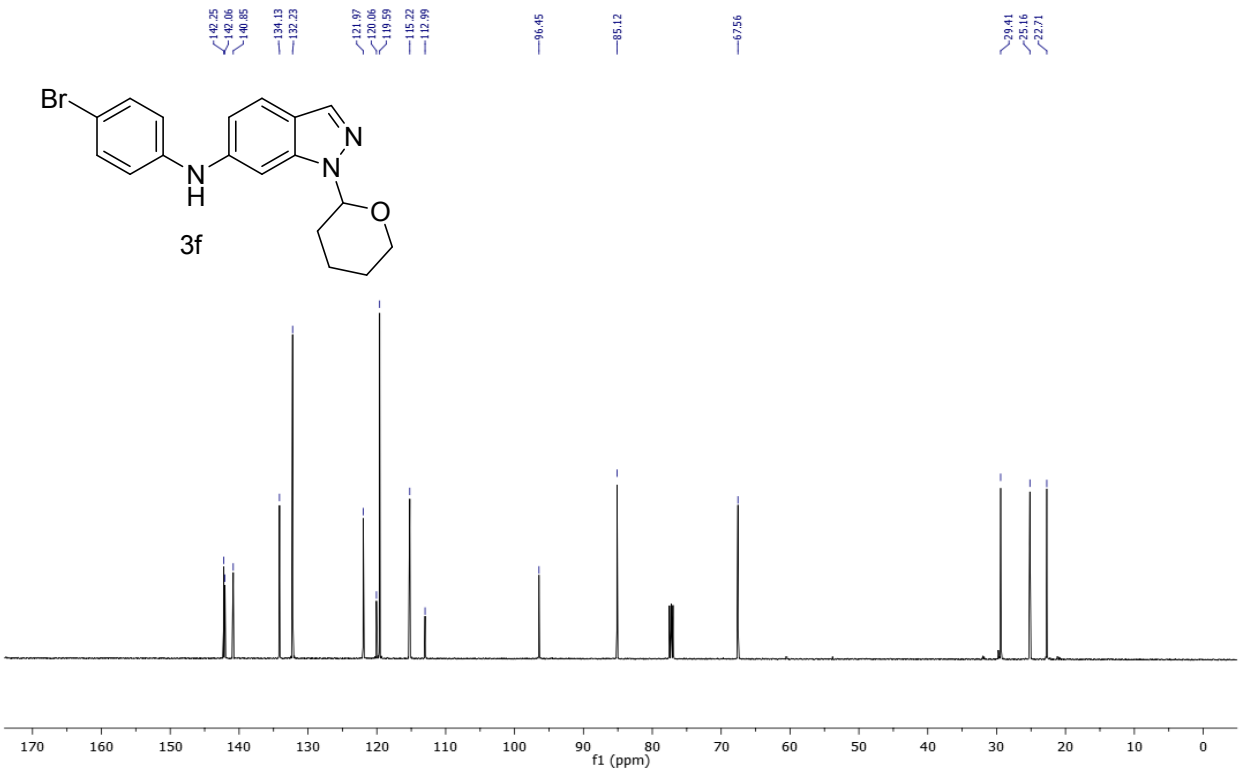


***N*-(4-Bromophenyl)-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-6-amine: ^{1}H-NMR spectrum**



***N*-(4-Bromophenyl)-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-6-amine: ^{13}C-NMR spectrum**



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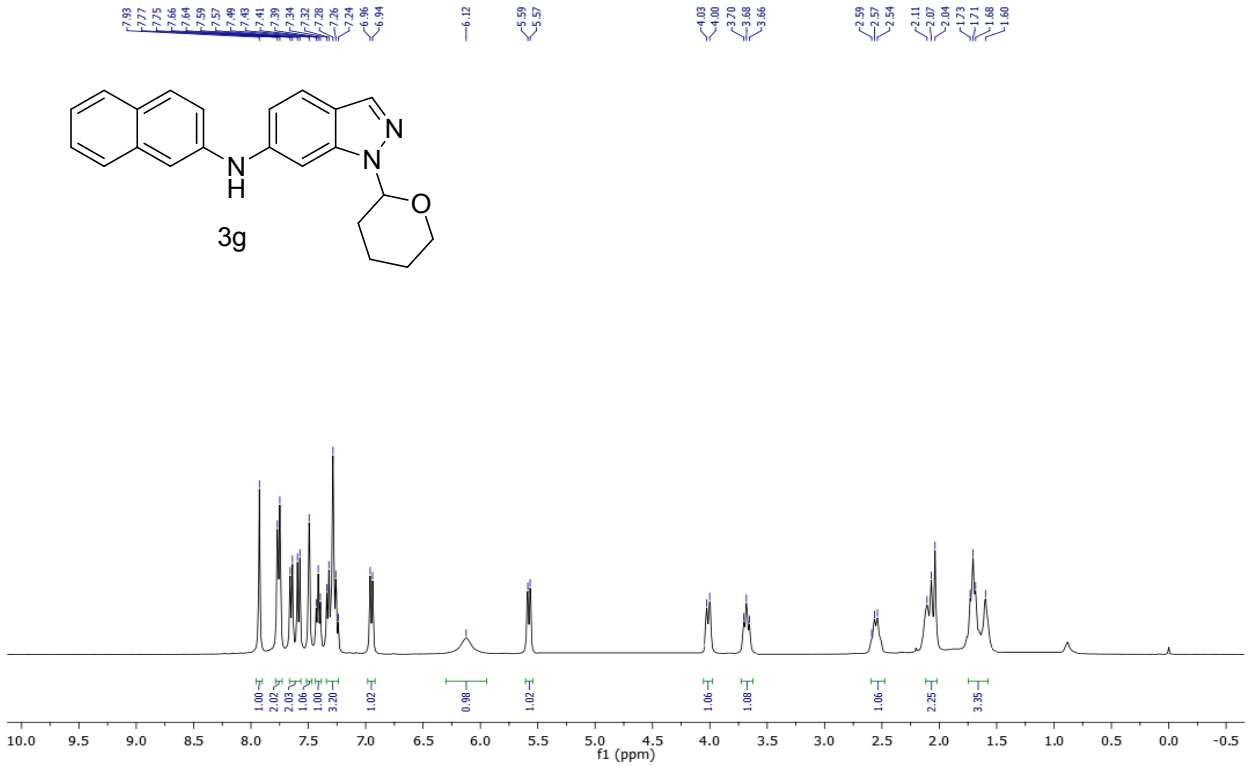
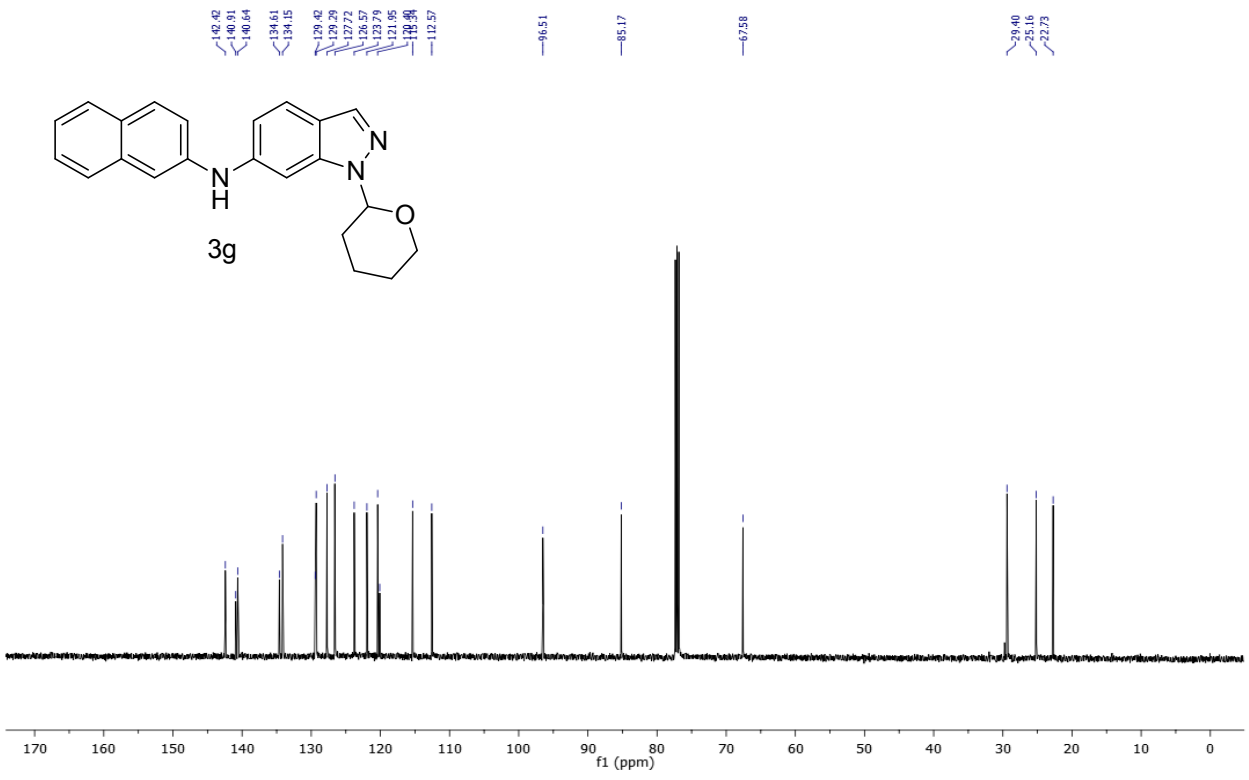
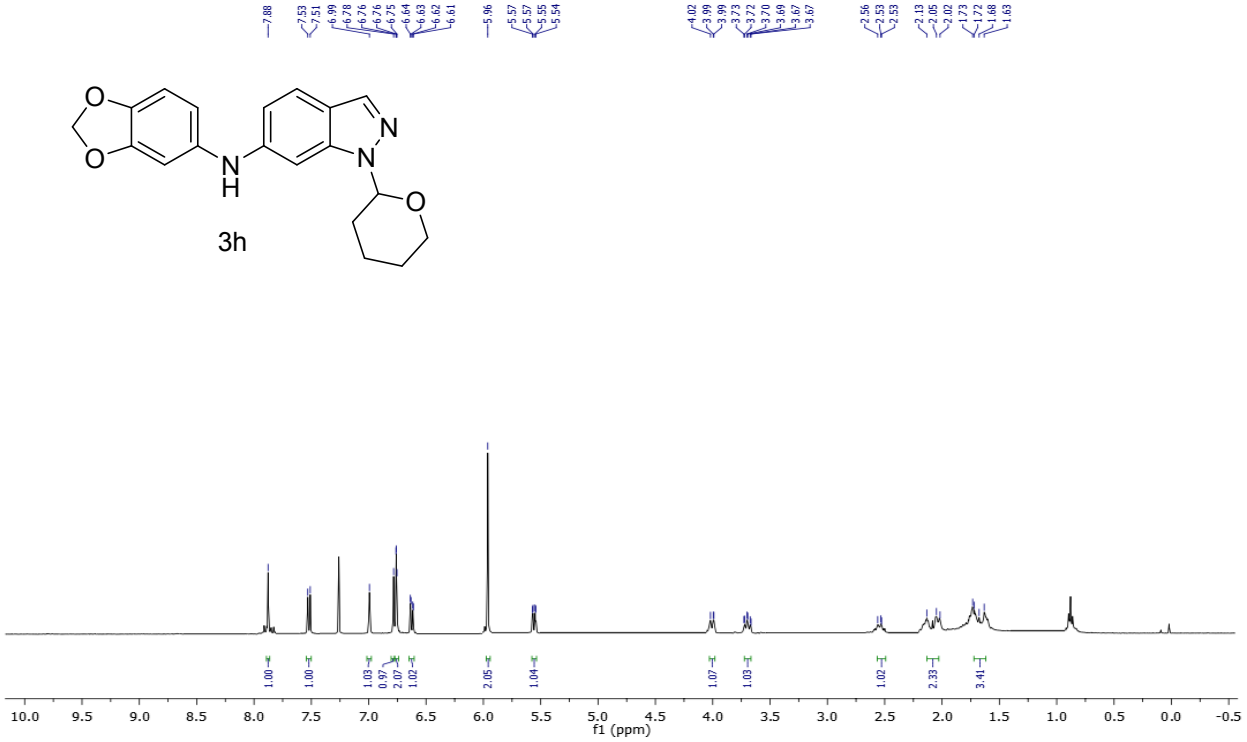


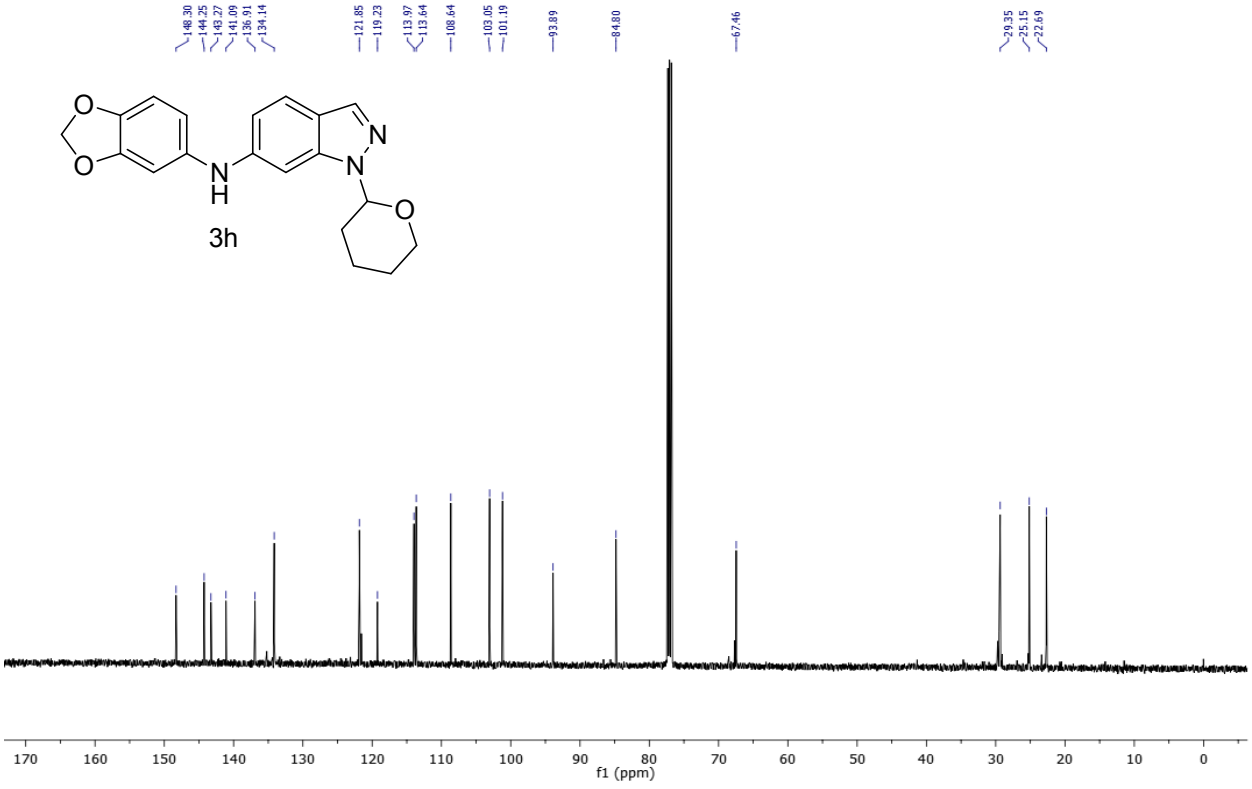
***N*-(Naphthalen-2-yl)-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-6-amine: ^{13}C-NMR spectrum**



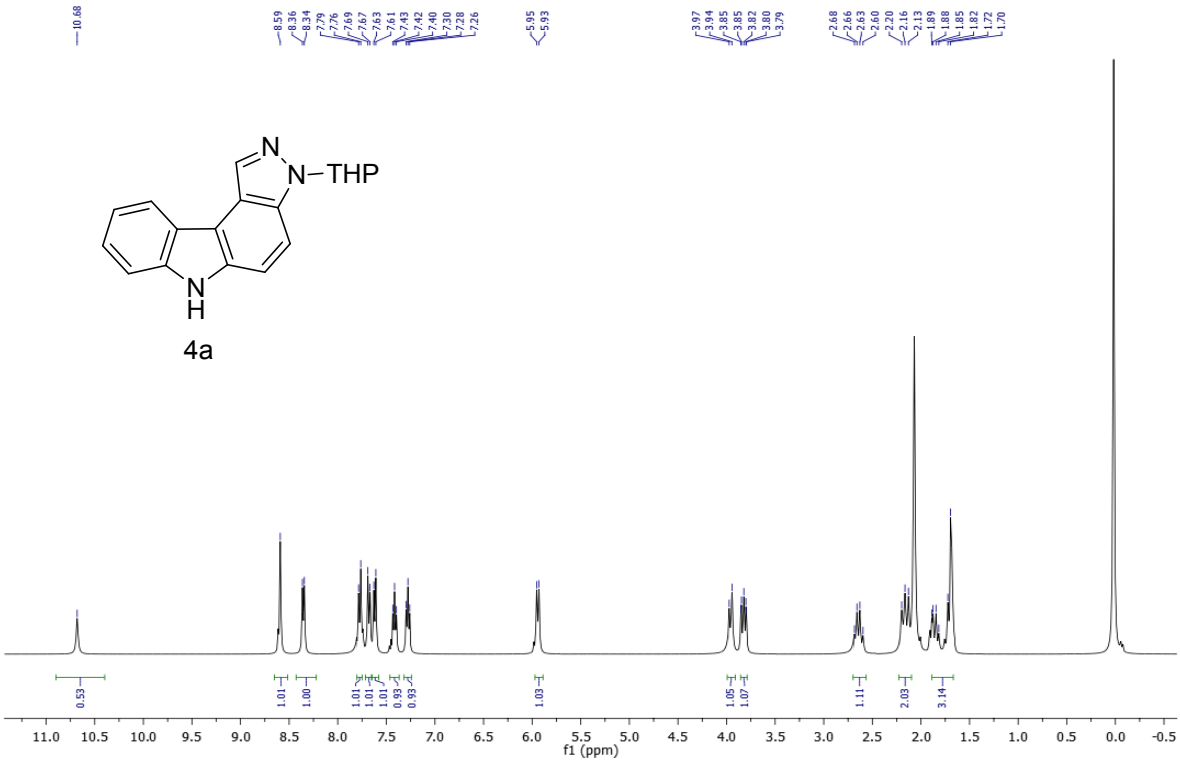
***N*-(Benzo[*d*] [1, 3] dioxol-5-yl)-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-6-amine: ^{1}H-NMR spectrum**



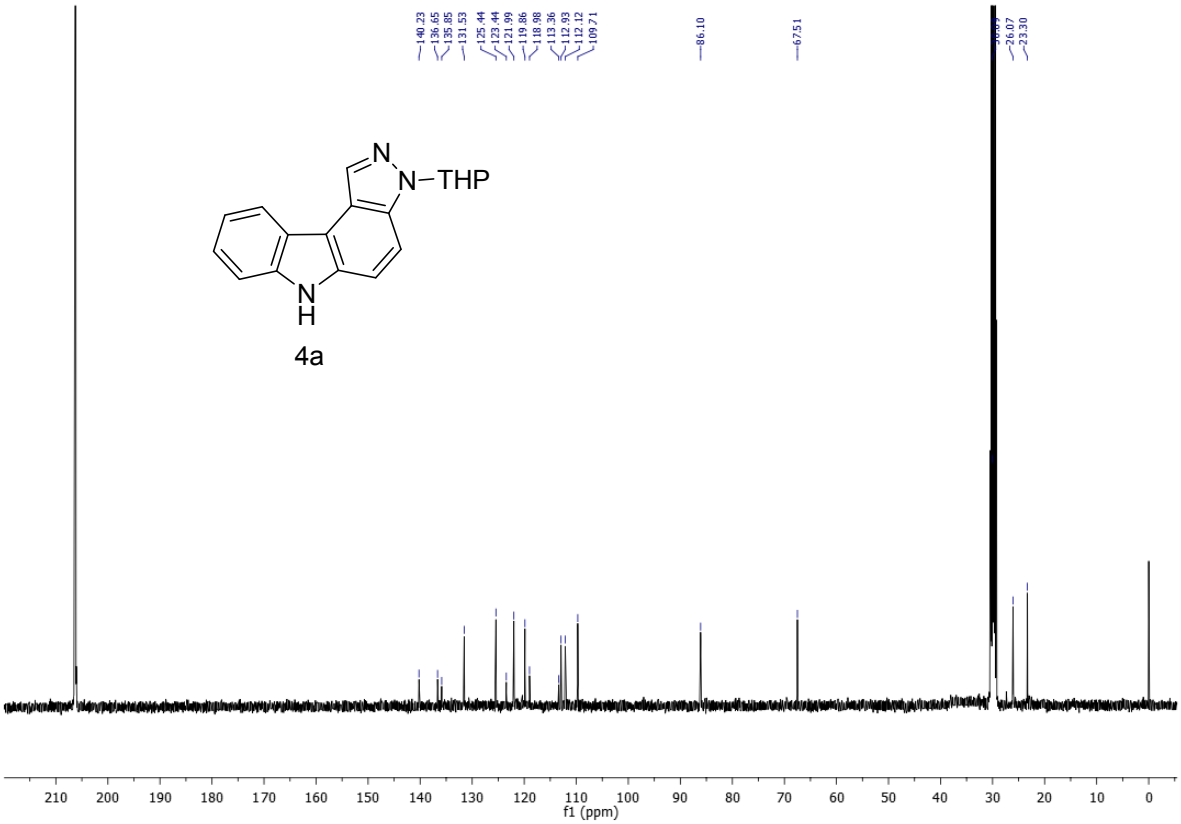
***N*-(Benzo[d] [1, 3] dioxol-5-yl)-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-indazol-6-amine: ^{13}C-NMR spectrum**



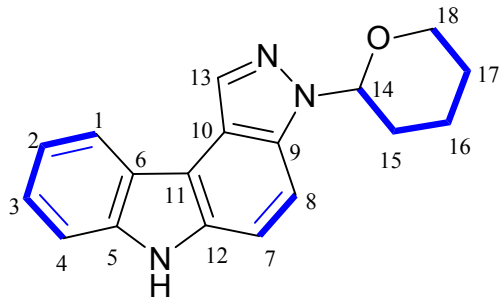
^{1}H, ^{13}C, COSY, HSQC and HMBC spectra of 3-(tetrahydro-2*H*-pyran-2-yl)-3, 6-dihydropyrazolo [3, 4-*c*] Carbazole (4a) .



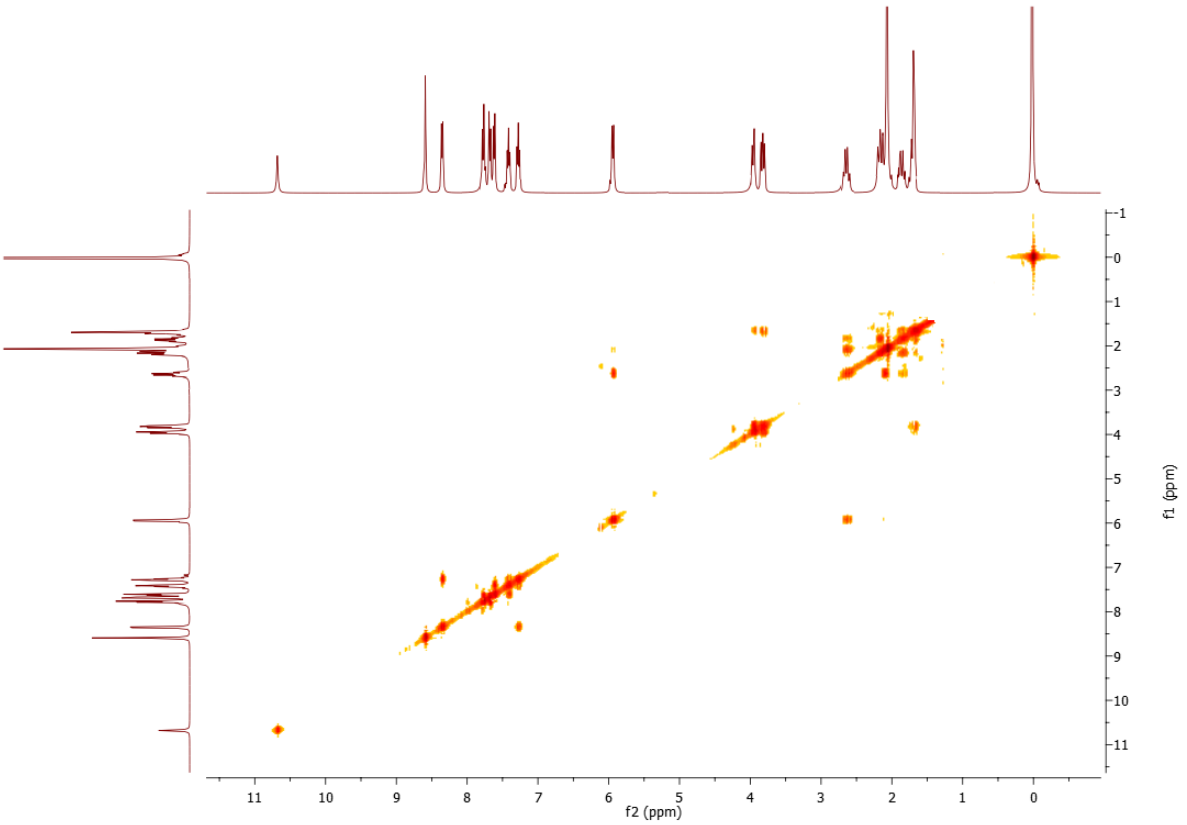
3-(Tetrahydro-2*H*-pyran-2-yl)-3, 6-dihydropyrazolo [3, 4-*c*] Carbazole: ^{13}C-NMR spectrum



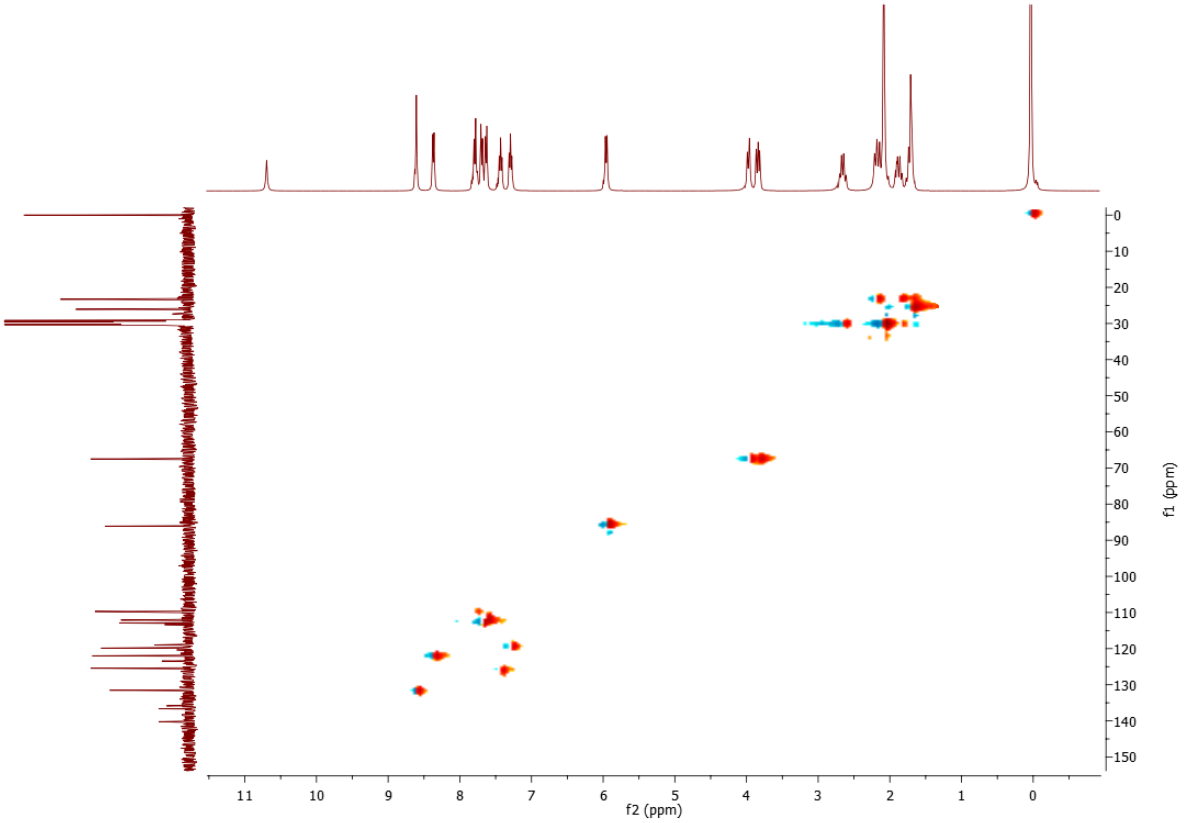
COSY Correlations (bold lines) of 3-(tetrahydro-2*H*-pyran-2-yl)-3, 6-dihydropyrazolo [3, 4-*c*] carbazole (4a)



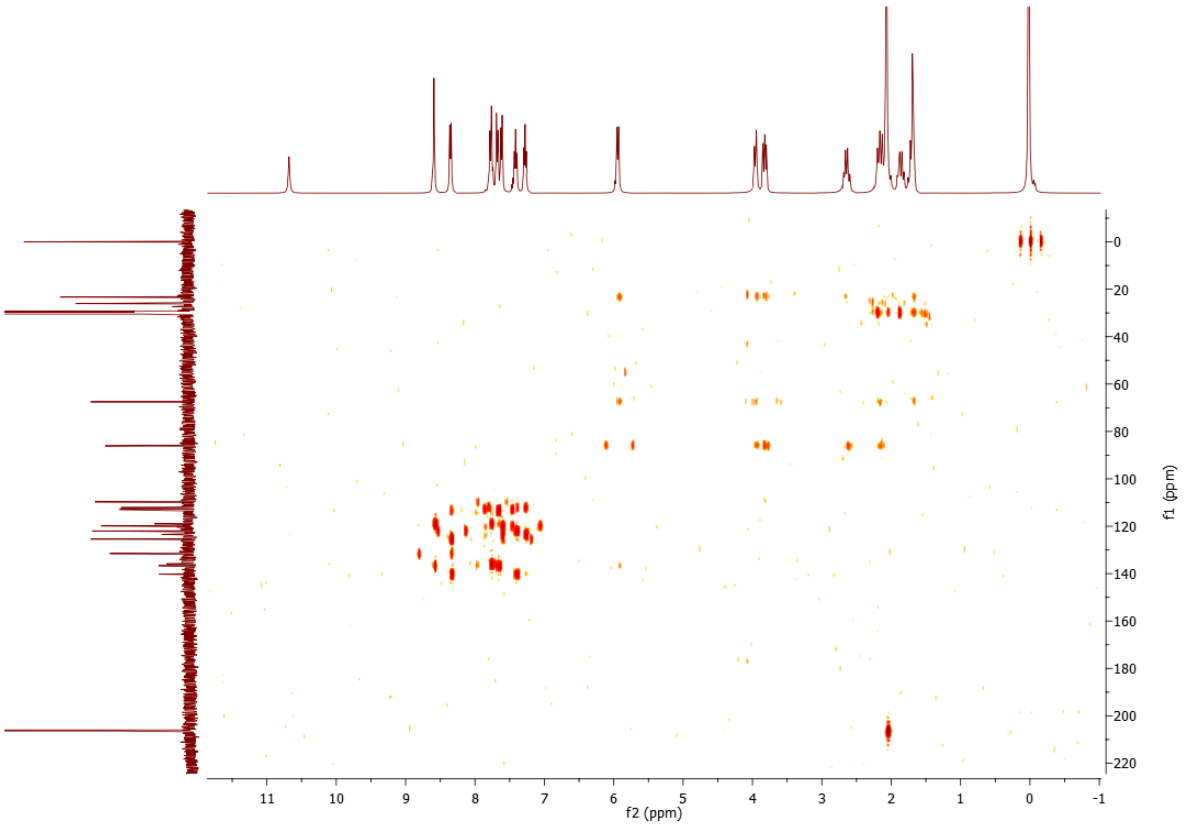
4a



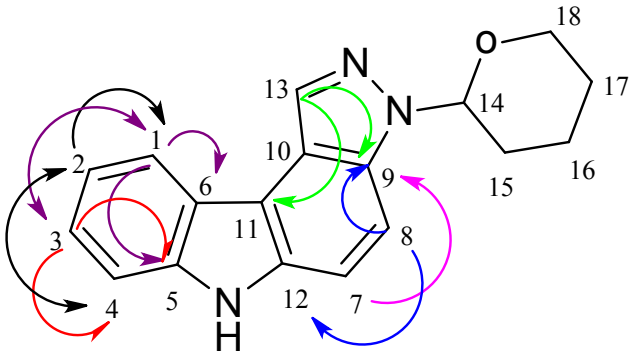
HSQC Spectrum of 3-(tetrahydro-2*H*-pyran-2-yl)-3, 6-dihydropyrazolo [3, 4-*c*] carbazole (4a)



HMBC Spectrum of 3-(tetrahydro-2*H*-pyran-2-yl)-3, 6-dihydropyrazolo [3, 4-*c*] carbazole (4a)

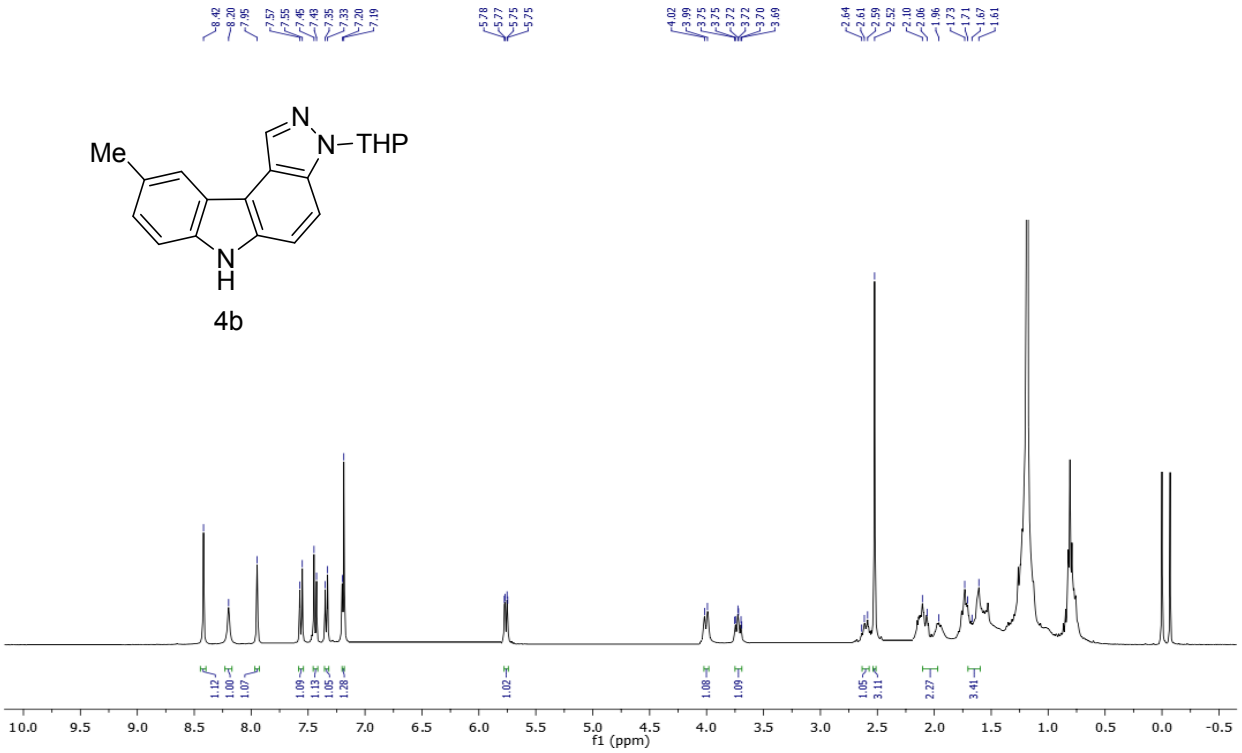


HMBC Correlations of 3-(tetrahydro-2*H*-pyran-2-yl)-3, 6-dihydropyrazolo [3, 4-*c*] carbazole (4a)

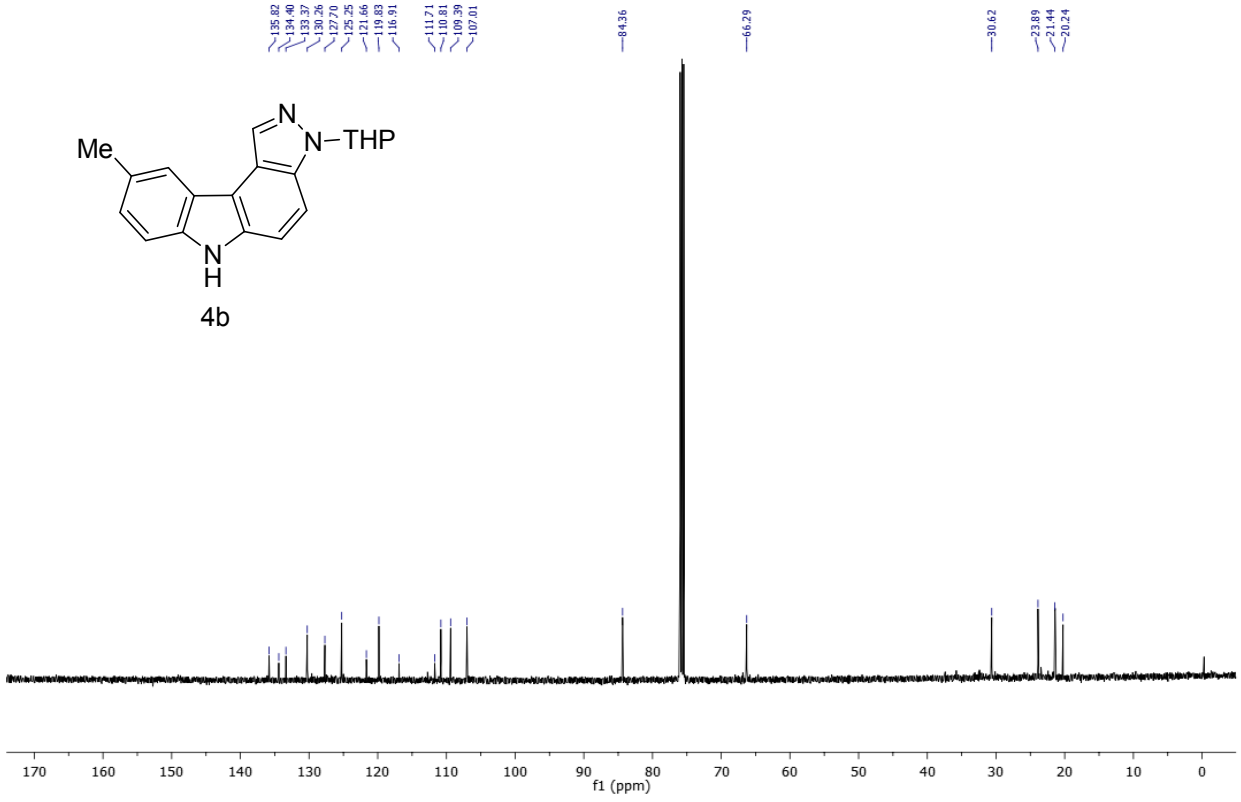


Carbon Number	^{1}H-Value	^{13}C-NMR	HSQC	HMBC Correlations
C_1	8.35 (d)	122	122	C_3 (125.4), C_5 (140.2), C_6 (113.3)
C_2	7.28 (t)	119.8	119.8	C_1 (122), C_4 (112.1)
C_3	7.42 (t)	125.4	125.4	C_1 (122), C_4 (112.1), C_5 (140.2)
C_4	7.62 (d)	112.1	112.1	C_2 (119.8)
C_5	-	140.2	-	-
C_6	-	113.3	-	-
C_7	7.68 (d)	112.9	112.9	C_9 (136.6)
C_8	7.77 (d)	109.7	109.7	C_9 (136.6), C_{12} (135.8)
C_9	-	136.6	-	-
C_{10}	-	123.4	-	-
C_{11}	-	118.9	-	-
C_{12}	-	135.8	-	-
C_{13}	8.59 (s)	131.5	131.5	C_9 (136.6), C_{11} (118.9)
C_{14}	5.94 (d)	86.1	86.1	C_{16} (23.3), C_{18} (67.5), C_9 (136.6)
C_{15}	2.64 (dd)	30.0	30.0	C_{11} (23.3), C_{14} (86.1)
	2.16 (m)			C_{14} (86.1), C_{15} (30.0), C_{18} (67.5)
C_{16}	2.10 (m)	23.3	23.3	C_{17} (26.0)
	1.87 (m)			C_{15} (30.0)
C_{17}	1.65 (m)	26.0	26.0	C_{15} (30.0), C_{16} (23.3), C_{18} (67.5)
C_{18}	3.96 (d)	67.5	67.5	C_{14} (86.1), C_{16} (23.3)
	3.82 (m)			C_{14} (86.1), C_{16} (23.3)

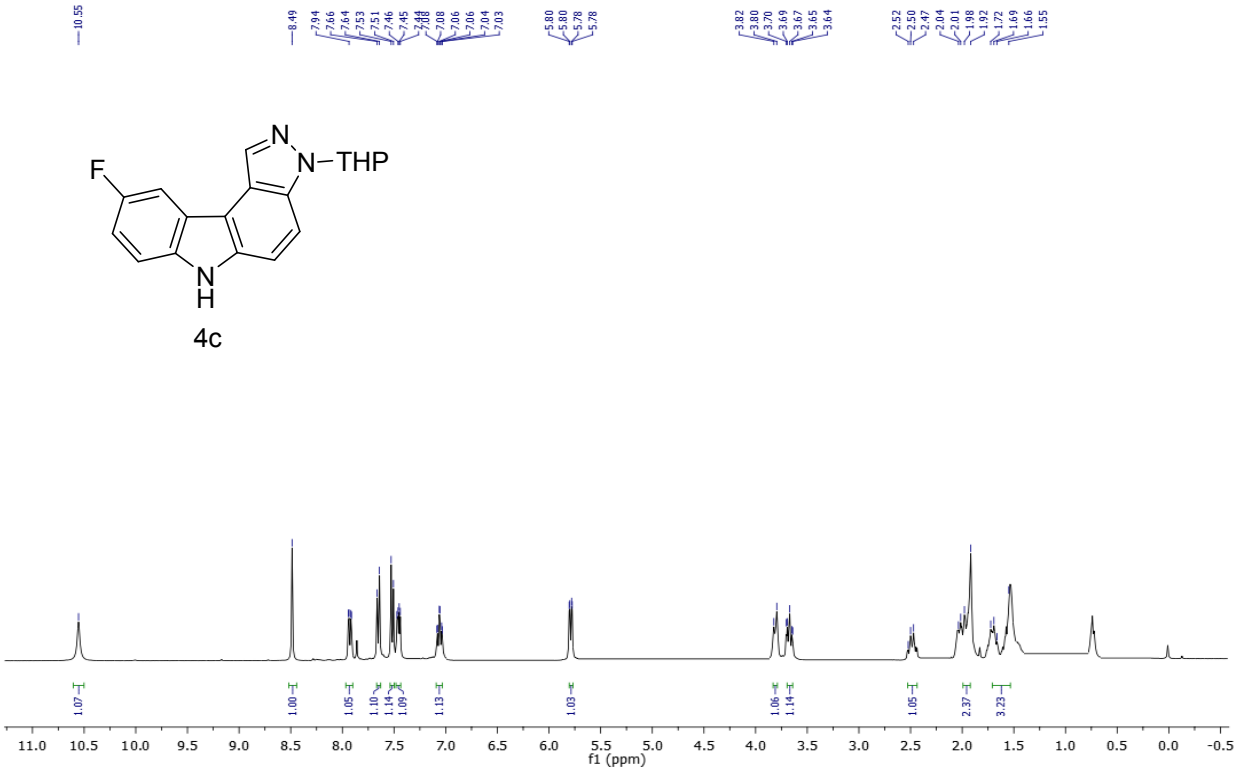
9-Methyl-3-(tetrahydro-2*H*-pyran-2-yl)-3, 6-dihydropyrazolo [3, 4-*c*] carbazole: ^{1}H-NMR spectrum



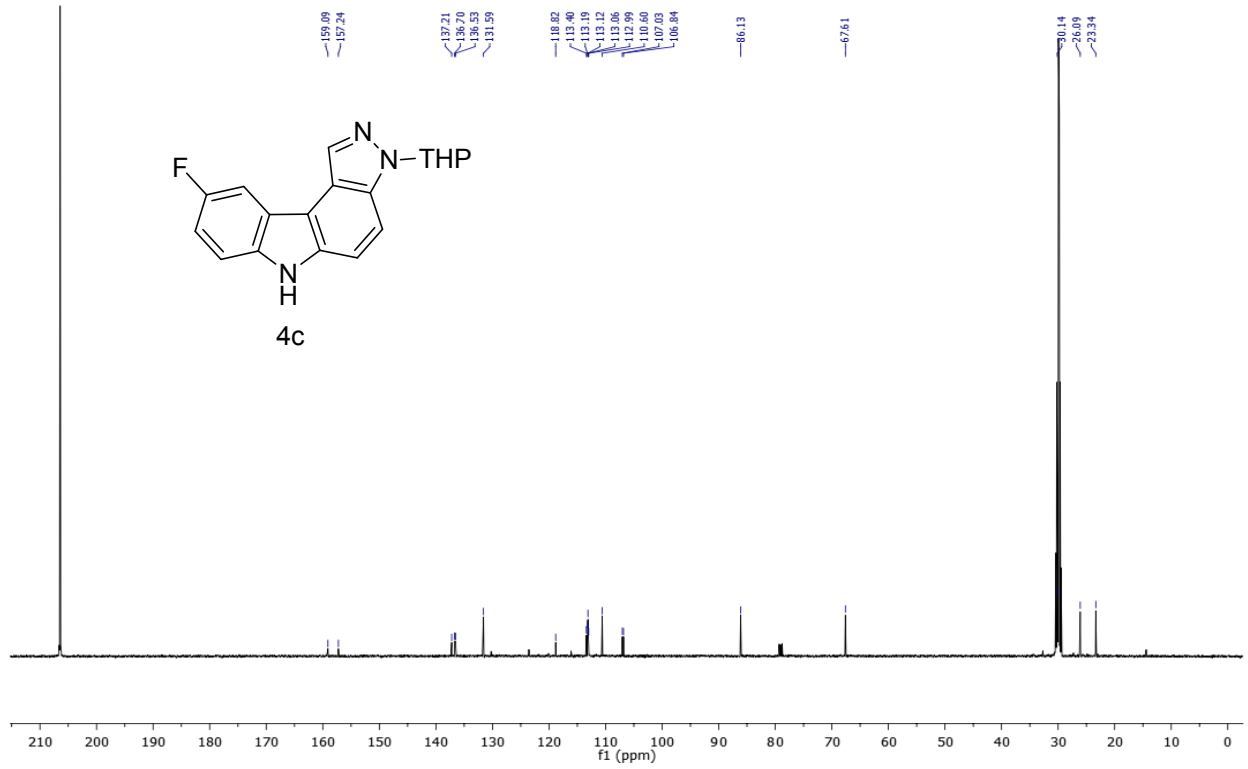
9-Methyl-3-(tetrahydro-2*H*-pyran-2-yl)-3, 6-dihydropyrazolo [3, 4-*c*] carbazole: ^{13}C-NMR spectrum



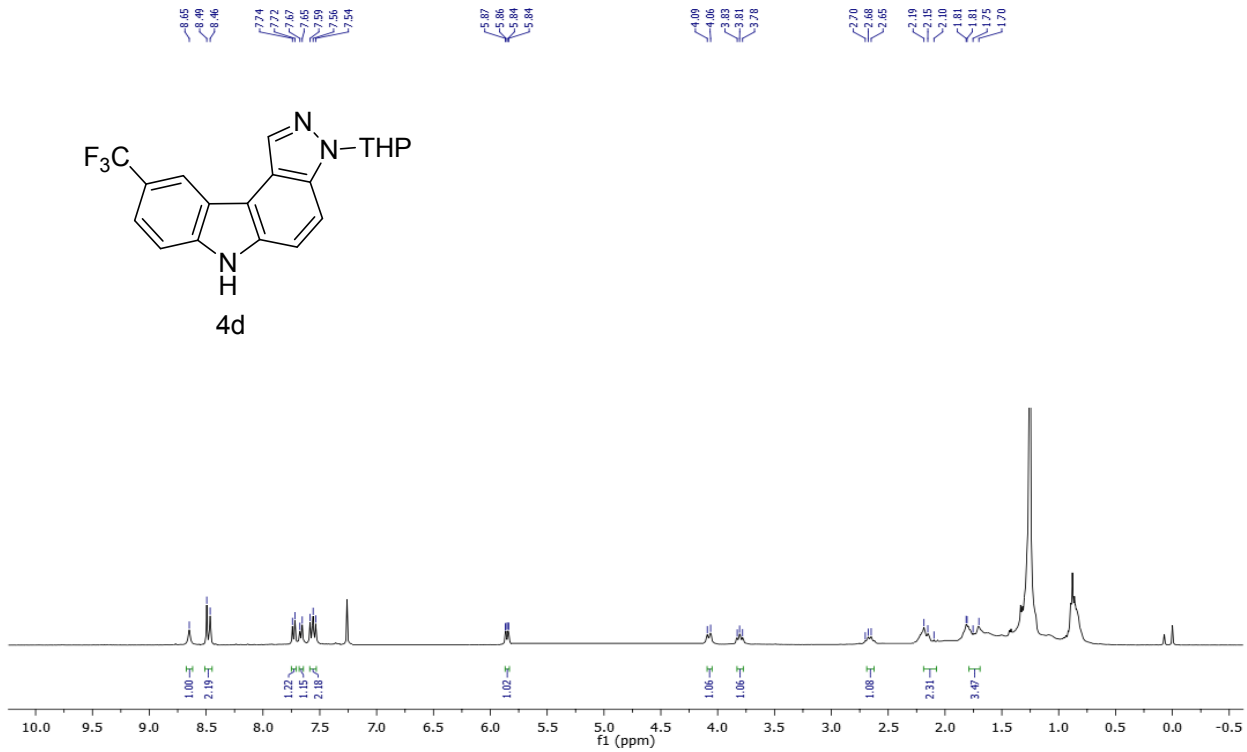
9-Fluoro-3-(tetrahydro-2*H*-pyran-2-yl)-3, 6-dihydropyrazolo [3, 4-*c*] carbazole: ^{1}H-NMR spectrum



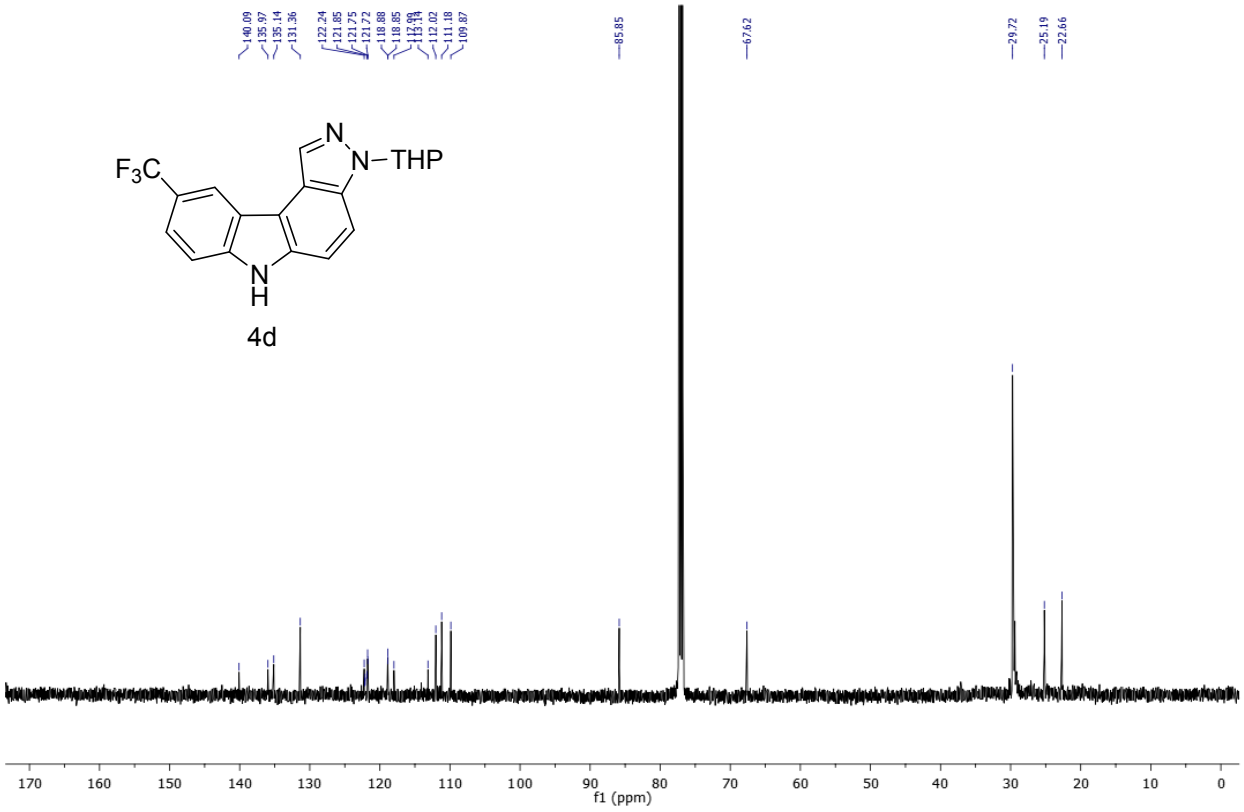
9-Fluoro-3-(tetrahydro-2*H*-pyran-2-yl)-3, 6-dihydropyrazolo [3, 4-*c*] carbazole: ^{13}C-NMR spectrum



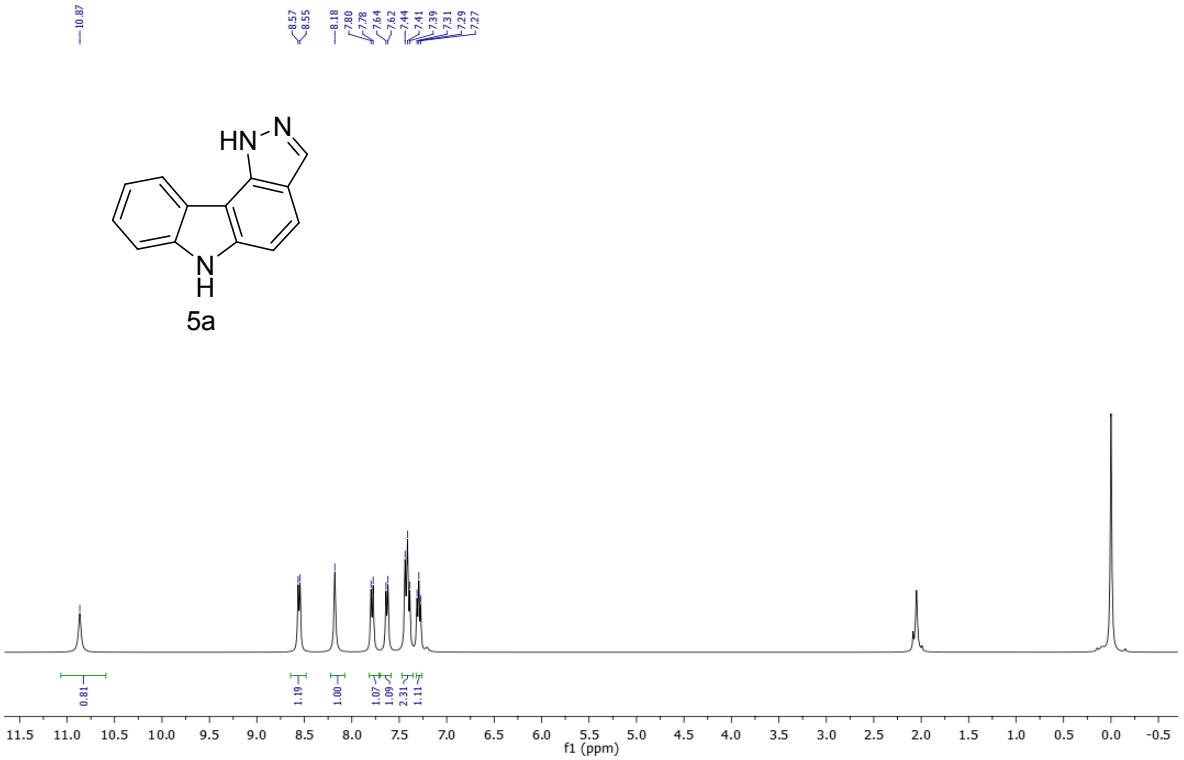
3-(Tetrahydro-2*H*-pyran-2-yl)-9-(trifluoromethyl)-3, 6-dihydropyrazolo [3, 4-*c*] carbazole: ^{1}H-NMR Spectrum



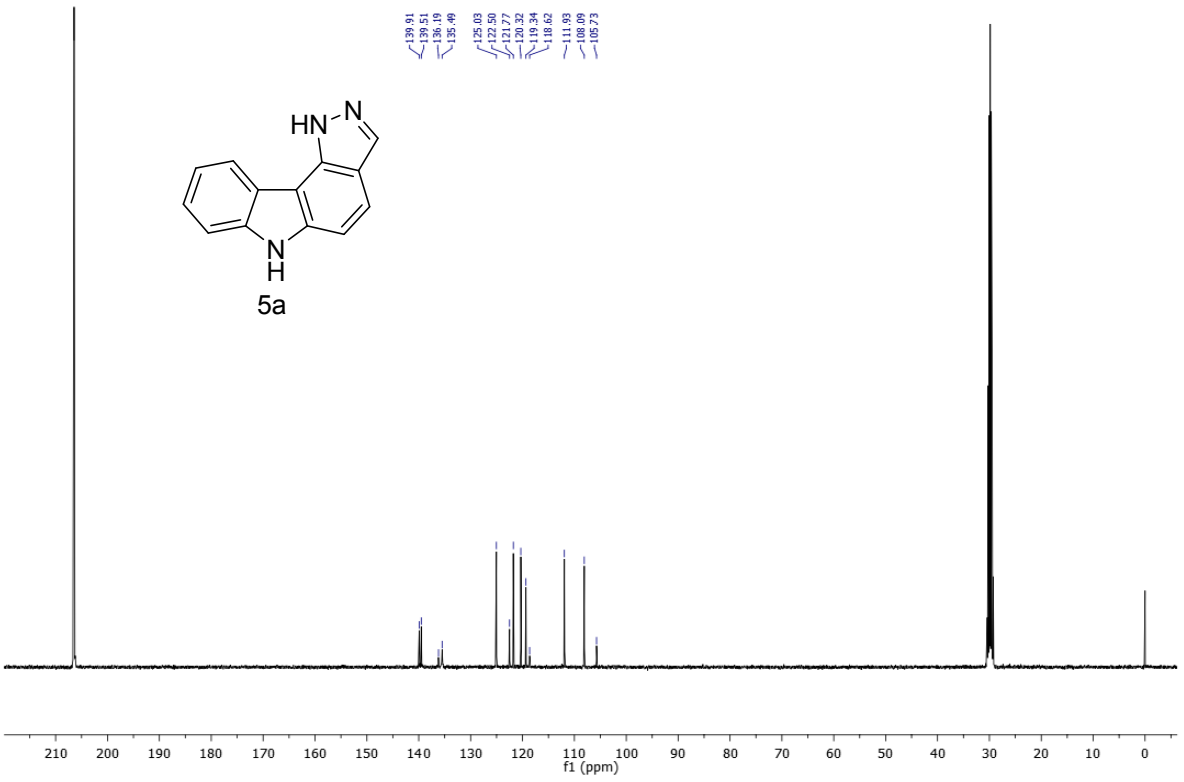
3-(Tetrahydro-2*H*-pyran-2-yl)-9-(trifluoromethyl)-3,6-dihydropyrazolo [3, 4-*c*] carbazole: ^{13}C-NMR Spectrum



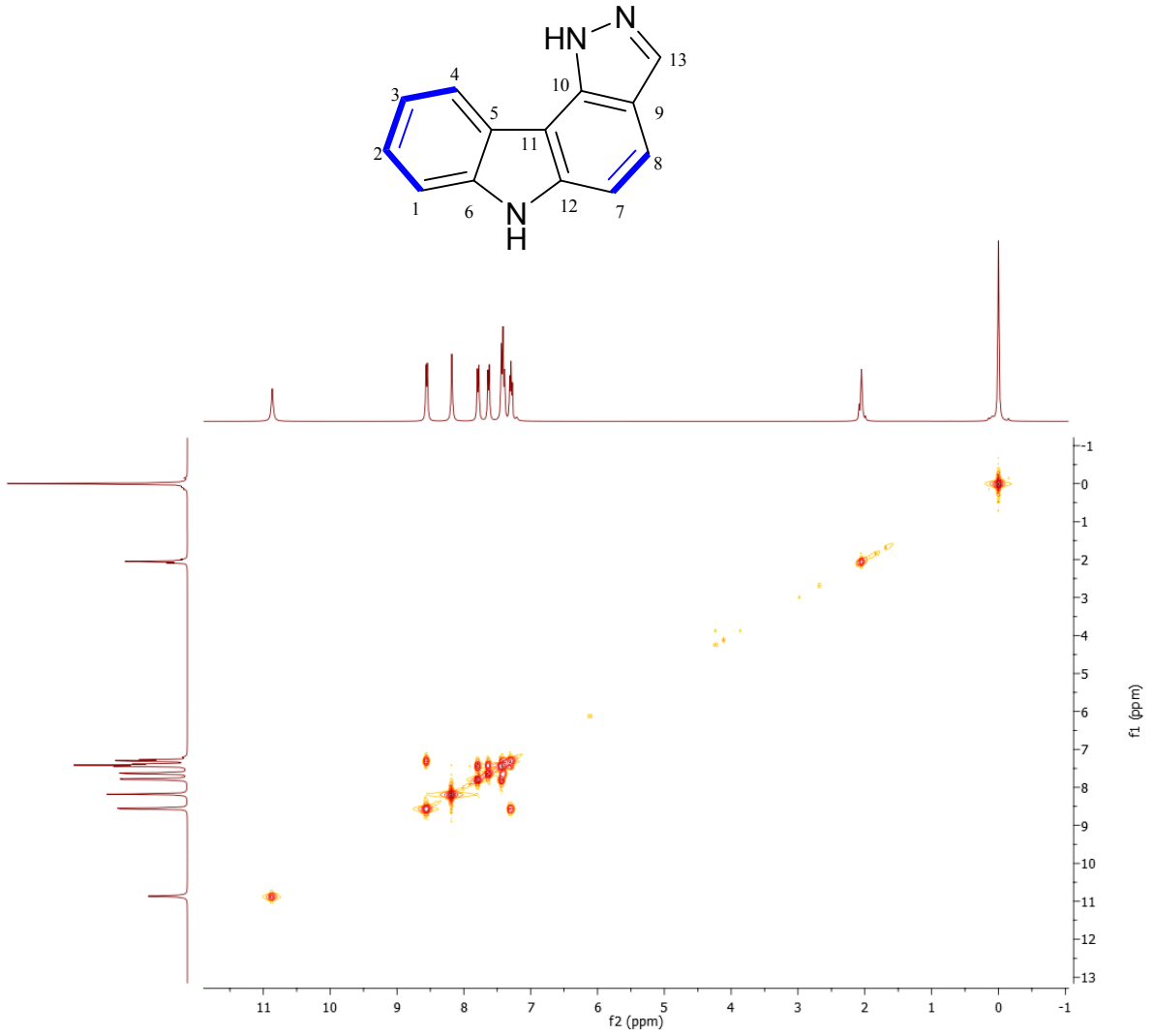
^{1}H, ^{13}C, COSY, HSQC and HMBC spectra of 1, 6-dihydropyrazolo [4, 3-*c*] carbazole (5a)



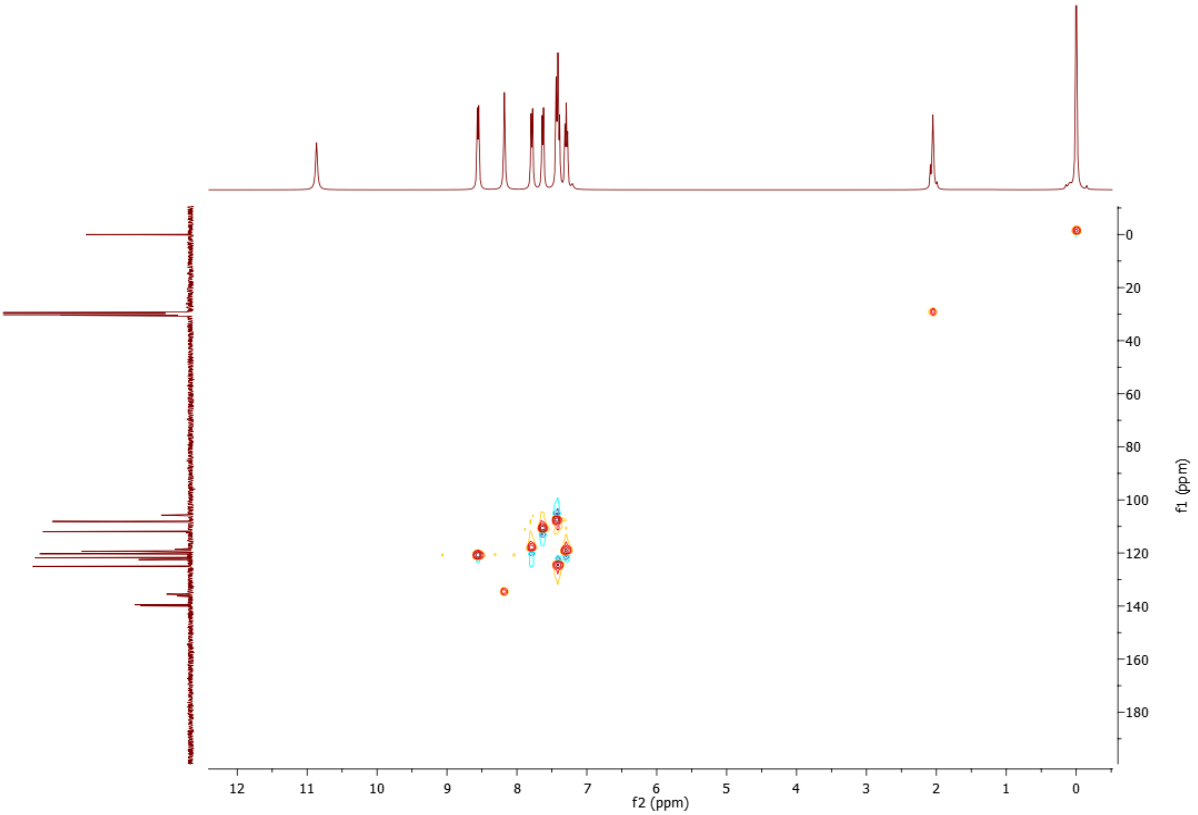
1, 6-Dihydropyrazolo [4, 3-*c*] carbazole: ^{13}C-NMR spectrum



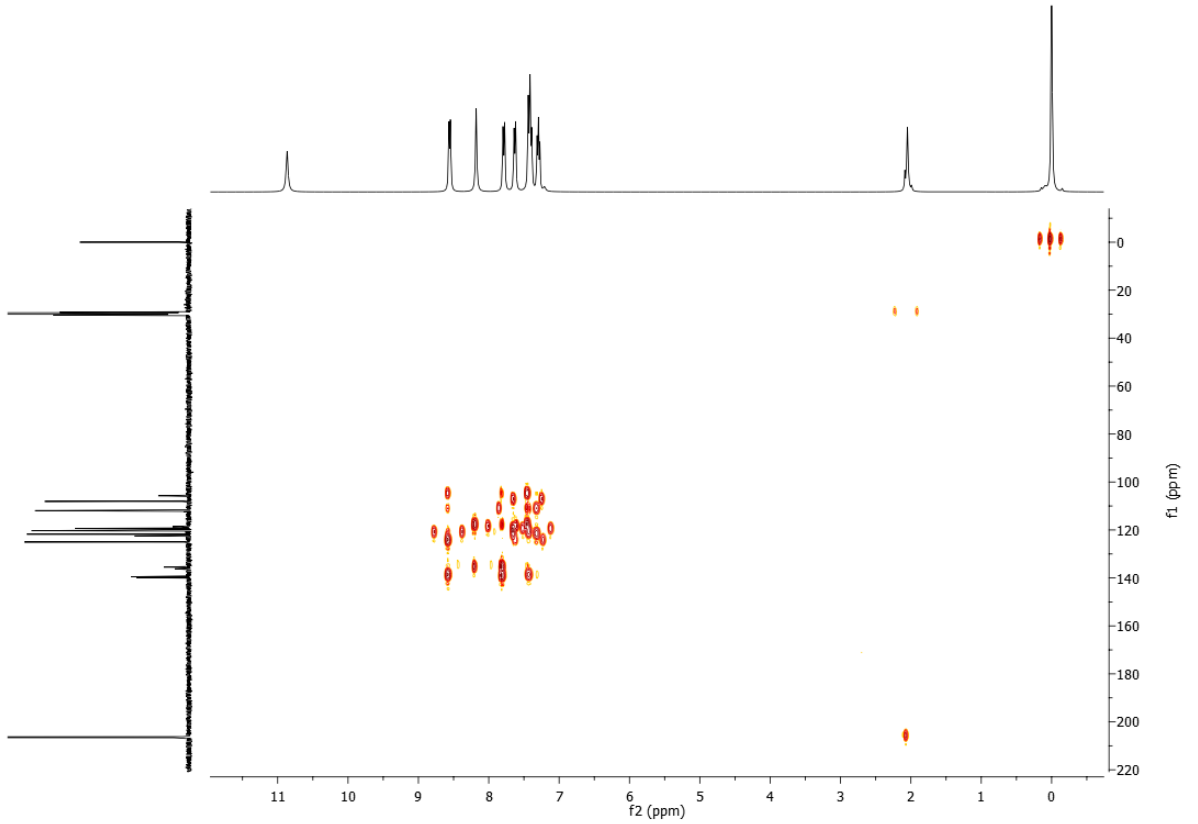
COSY Correlations (bold lines) of 1, 6-dihydropyrazolo [4, 3-*c*] carbazole (5a)



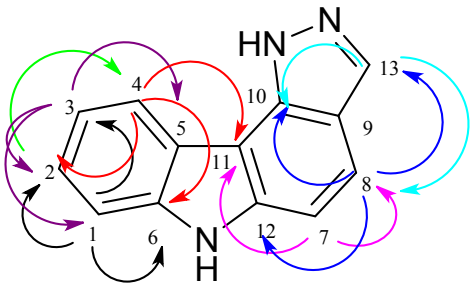
HSQC Spectrum of 1, 6-dihydropyrazolo [4, 3-*c*] carbazole (5a)



HMBC Spectrum of 1, 6-dihydropyrazolo [4, 3-*c*] carbazole (5a)

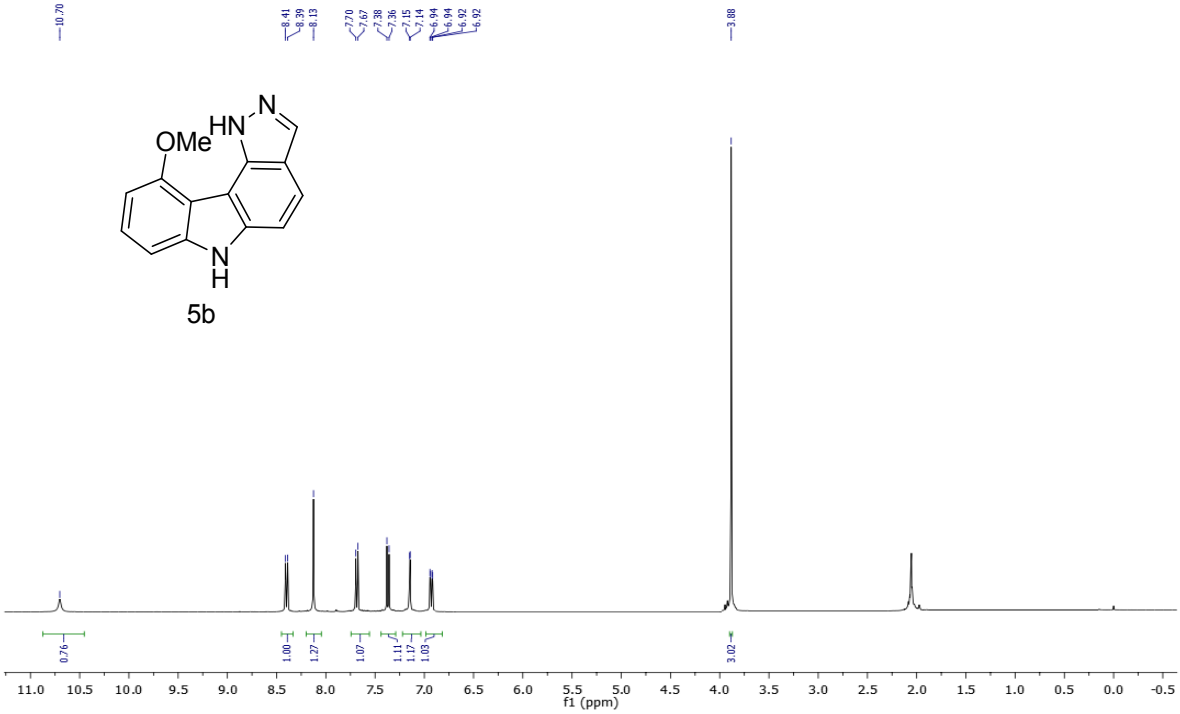


HMBC Correlations of 1, 6-dihydropyrazolo [4, 3-*c*] carbazole (5a)

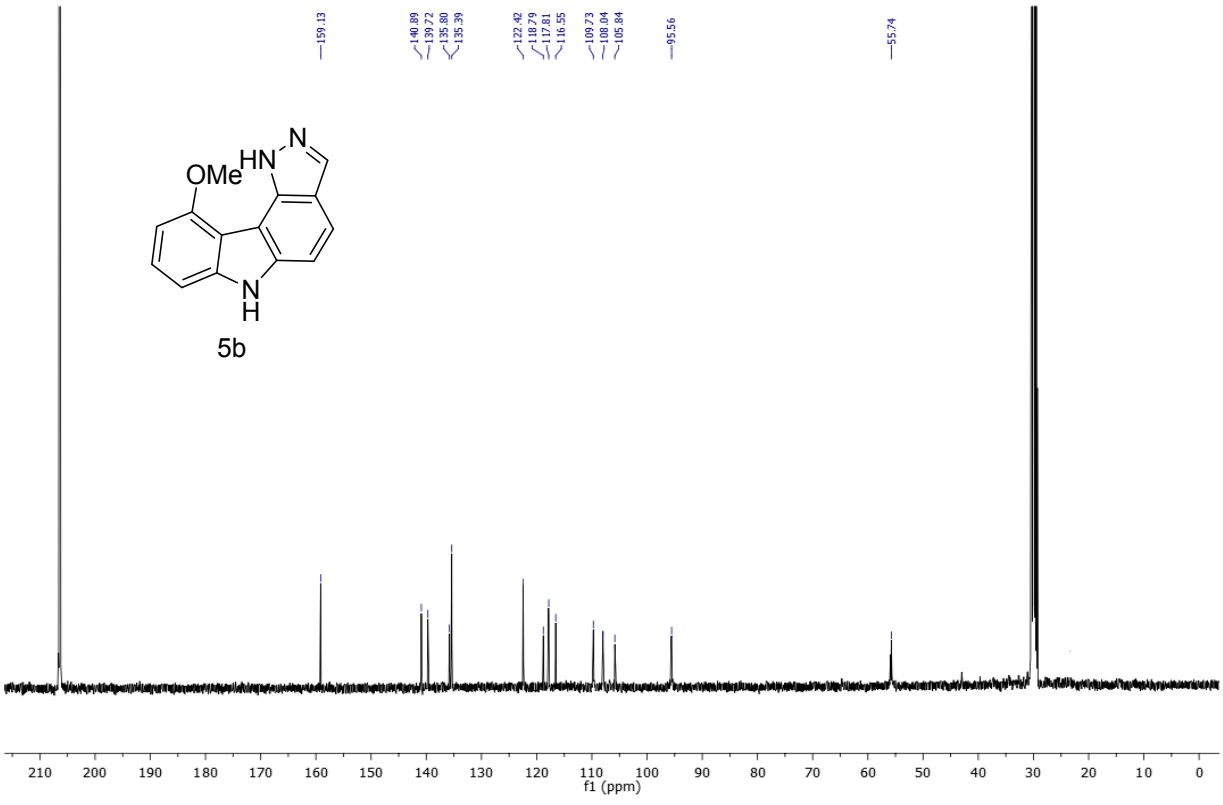


Carbon Number	^{1}H-Value	^{13}C-NMR	HSQC	HMBC Correlations
C_1	7.40 (m)	125.0	125.0	C_2 (111.9), C_3 (119.3), C6 (139.9)
C_2	7.63 (d)	111.9	111.9	C_4 (120.3)
C_3	7.30 (m)	119.3	119.3	C_1 (125.0), C_2 (111.9), C_5 (121.7)
C_4	8.56 (d)	120.3	120.3	C_2 (111.9), C_6 (139.9), C_{11} (105.7)
C_5	-	121.7	-	-
C_6	-	139.9	-	-
C_7	7.43 (m)	108.1	108.1	C_8 (118.6), C_{11} (105.7)
C_8	7.79 (d)	118.6	118.6	C_{10} (136.2), C_{12} (139.5), C_{13} (135.5)
C_9	-	122.5	-	-
C_{10}	-	136.2	-	-
C_{11}	-	105.7	-	-
C_{12}	-	139.5	-	-
C_{13}	8.18 (s)	135.5	135.5	C_8 (118.6), C_{10} (136.2)

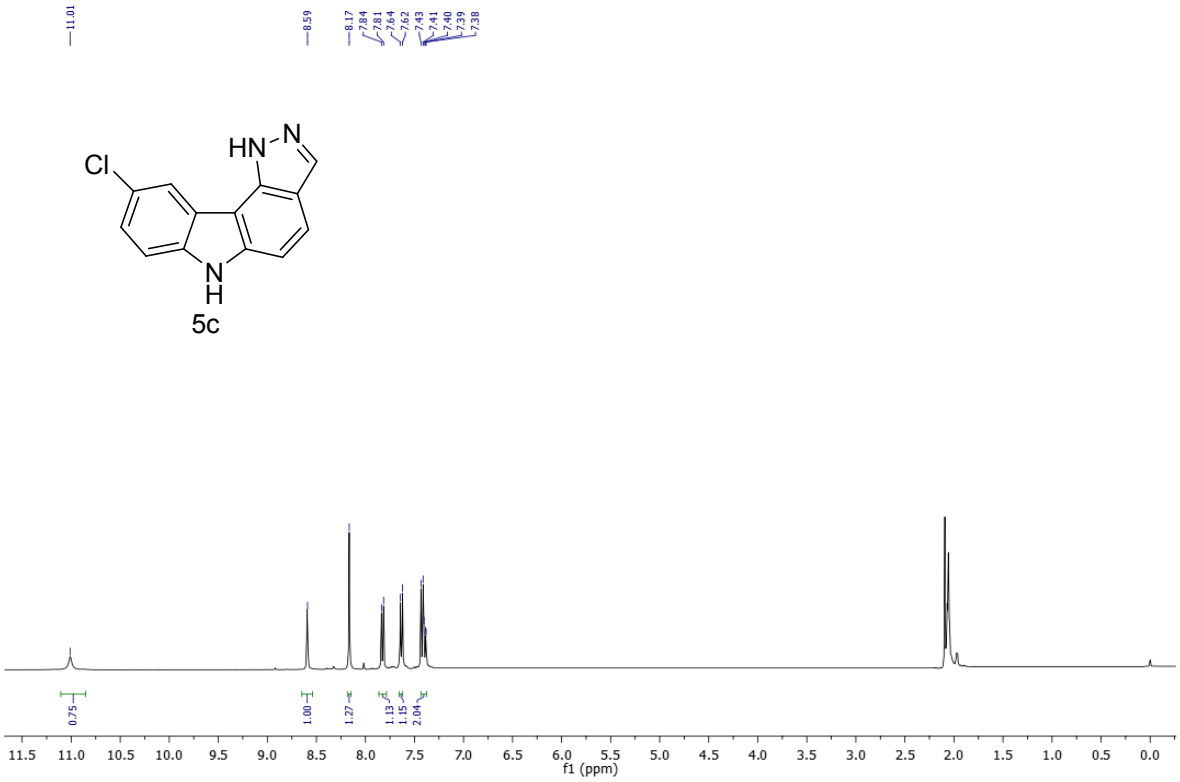
10-Methoxy-1, 6-dihydropyrazolo [4, 3-*c*] carbazole: ^{1}H-NMR Spectrum



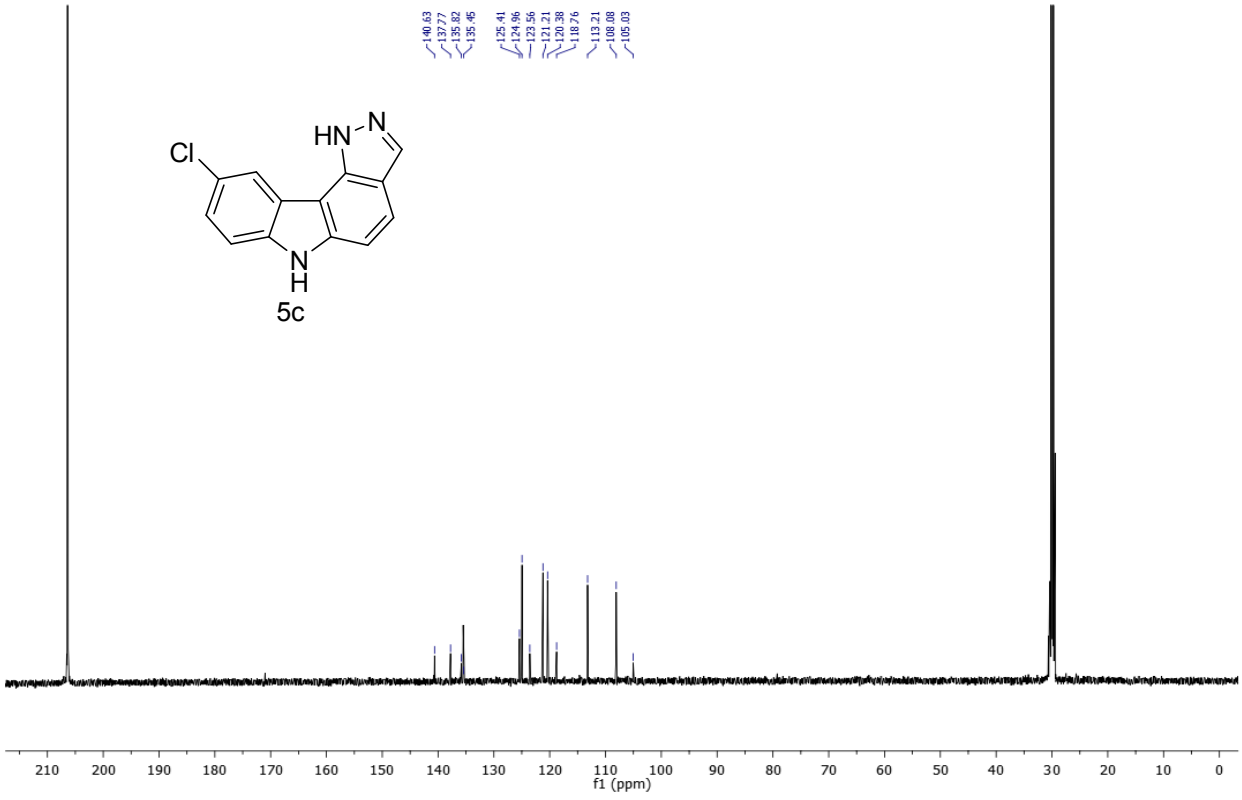
10-Methoxy-1, 6-dihydropyrazolo [4, 3-*c*] carbazole: ^{13}C-NMR Spectrum



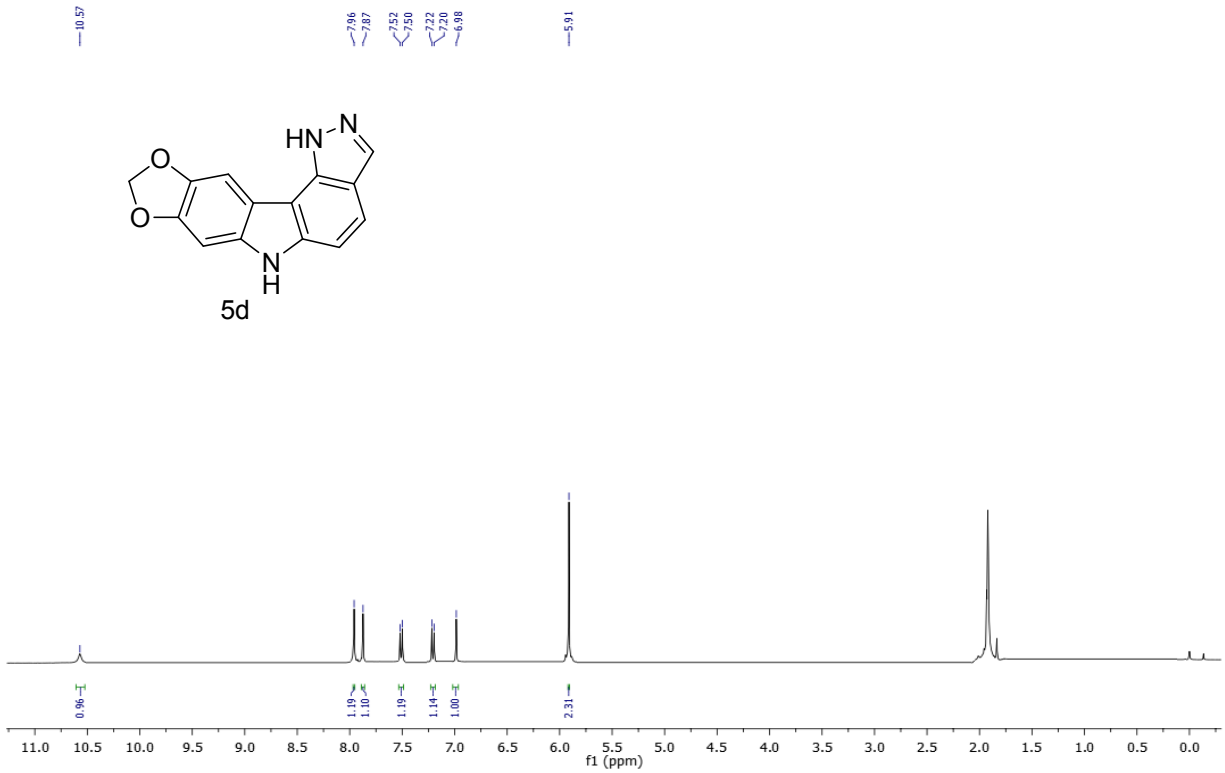
9-Chloro-1, 6-dihydropyrazolo [4, 3-*c*] carbazole: ^{1}H-NMR Spectrum



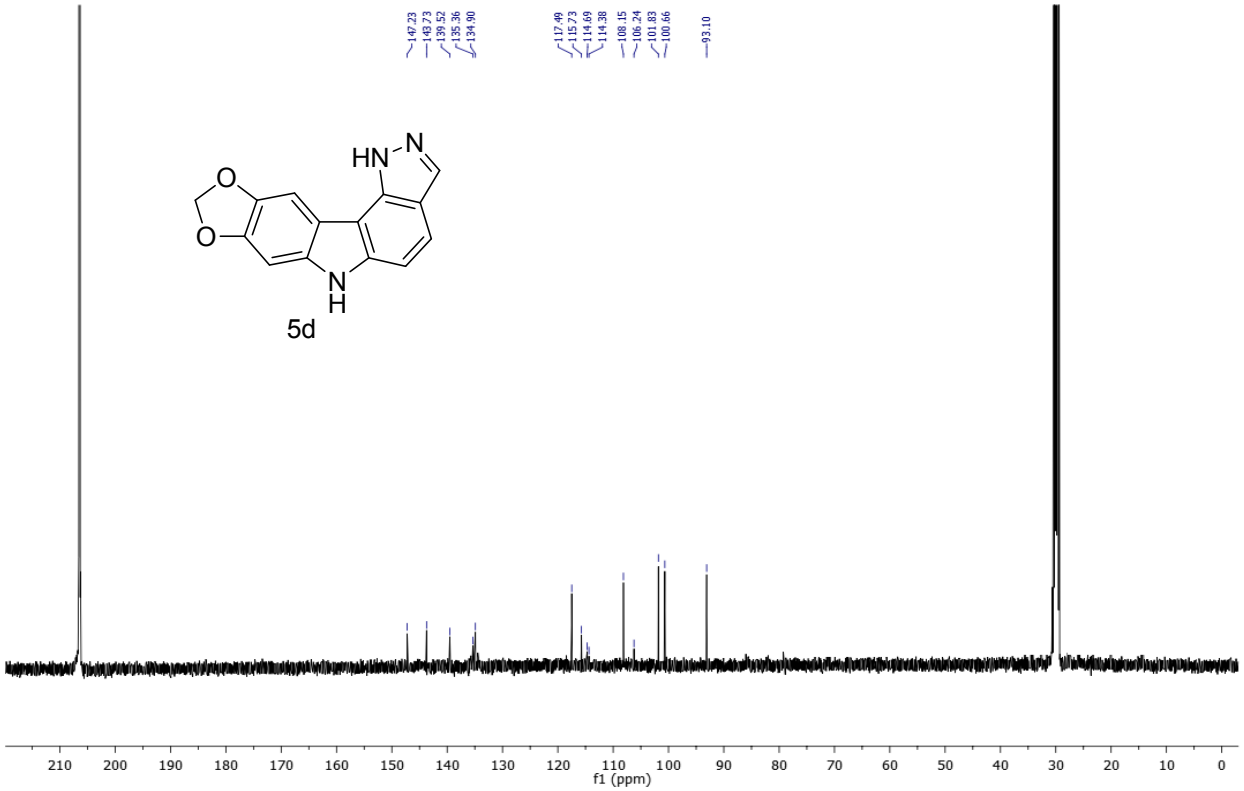
9-Chloro-1, 6-dihydropyrazolo [4, 3-*c*] carbazole: ^{13}C-NMR Spectrum



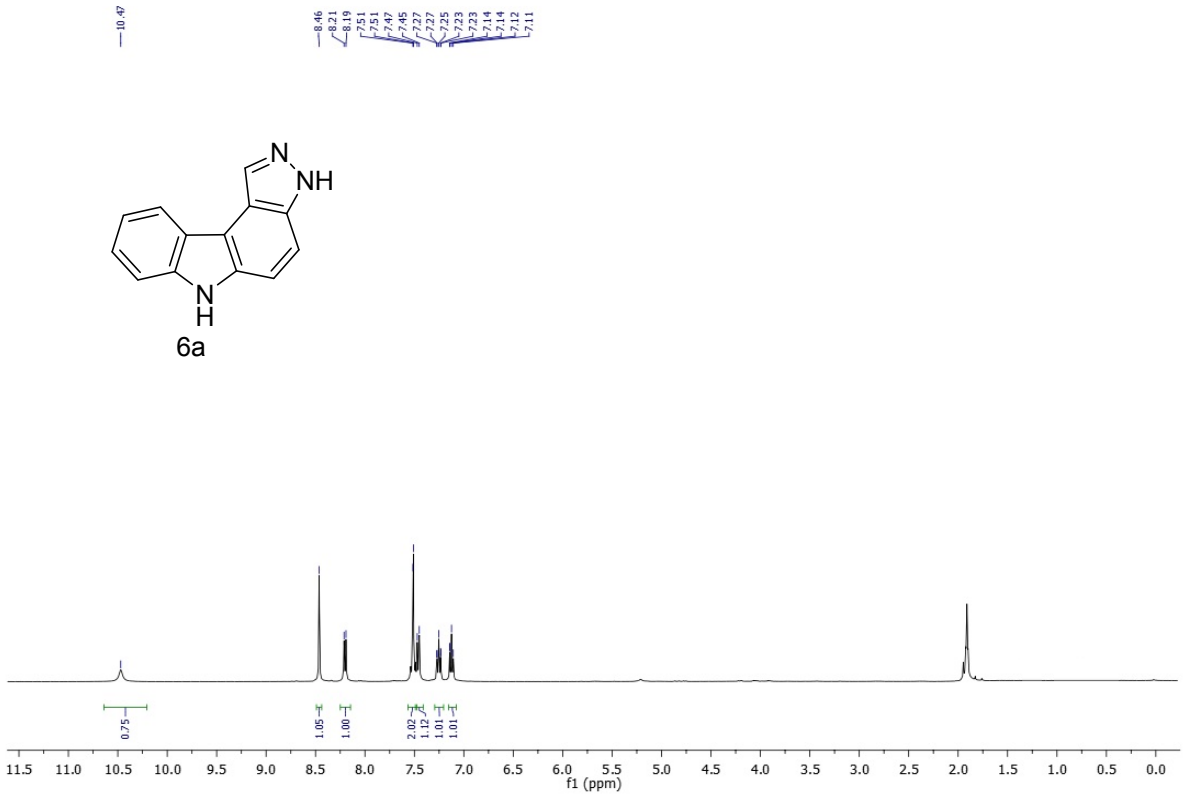
1,6-Dihydro-[1,3]dioxolo[4,5-*b*]Pyrazolo[3,4-*c*]carbazole: ^{1}H-NMR Spectrum



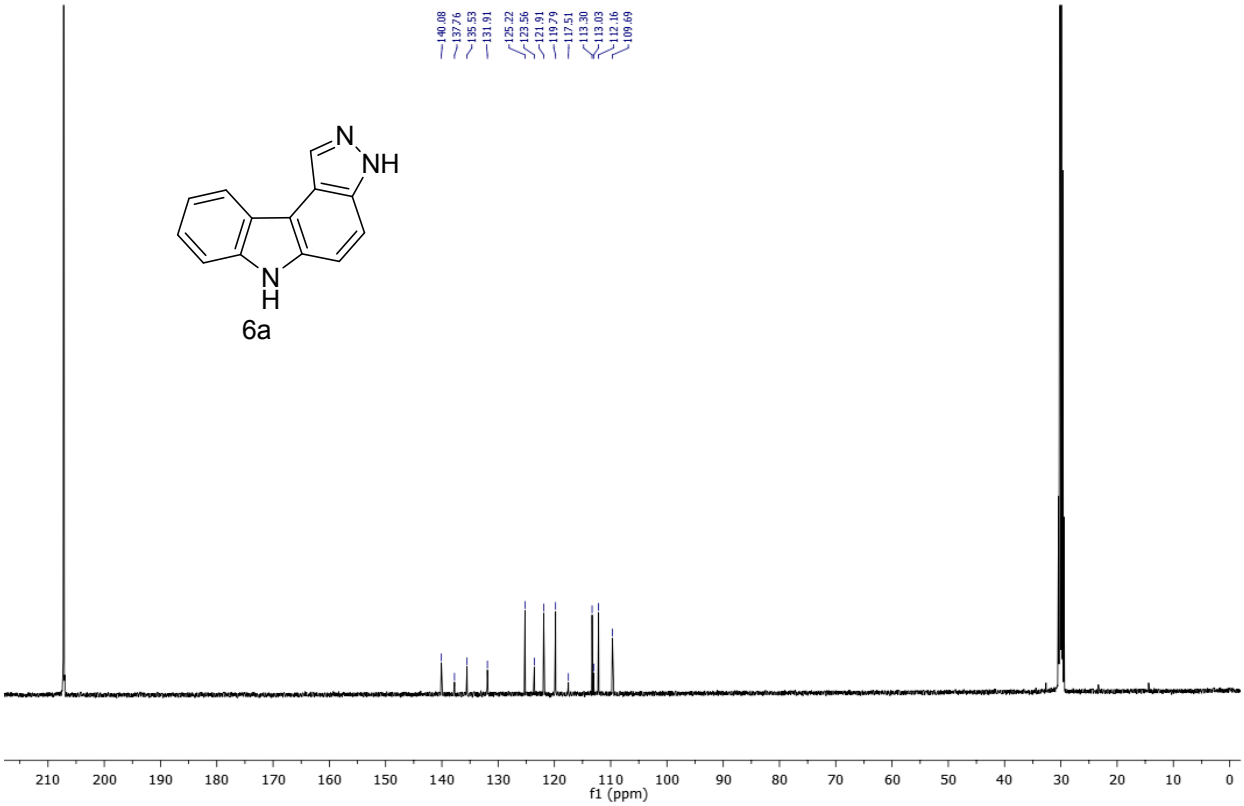
1,6-Dihydro-[1,3]dioxolo[4,5-b]Pyrazolo[3,4-*c*]carbazole: ^{13}C-NMR Spectrum



1, 6-Dihydropyrazolo [3, 4-*c*] carbazole: ^{1}H-NMR Spectrum



1, 6-Dihydropyrazolo [3, 4-*c*] carbazole: ^{13}C-NMR Spectrum



Cartesian coordinates of transition states

CMD transition states in *5*-*N*-aryl-indazole for different sites: **TS-C4**, **TS-C6** and **TS-C2'**

TS-C4 (TS-1 in Fig. 3)

Pd	1.293403	-0.027234	0.020509
H	-0.251456	1.262273	1.355484
C	1.028071	0.800413	2.883550
O	1.805182	0.251290	2.042559
C	1.461528	0.853518	4.330559
O	0.940701	-0.329472	-1.980798
C	0.305168	-1.414039	-2.299758
O	-0.095144	-2.270824	-1.489929
C	0.045208	-1.574145	-3.790857
O	-0.099401	1.310788	2.591129
H	0.706728	-0.942427	-4.386461
H	0.154322	-2.623957	-4.074464
H	-0.991153	-1.281710	-3.993775
H	1.425141	1.888303	4.682542
H	0.754369	0.276989	4.935202
H	2.466765	0.449182	4.451474
P	3.133183	-1.537524	-0.032006
C	4.721290	-0.805259	0.553095
H	4.568385	-0.370823	1.544398
H	5.514345	-1.559564	0.602938
H	5.028872	-0.007378	-0.128886
C	3.564190	-2.290530	-1.653637
H	3.742303	-1.501927	-2.389055
H	4.456872	-2.919085	-1.566334
H	2.725371	-2.900625	-1.997375
C	2.884623	-2.988149	1.074642
H	2.698042	-2.634327	2.091957
H	2.008119	-3.545680	0.733921
H	3.760790	-3.645865	1.073127
C	-0.145721	2.639147	-0.463421
C	-1.169075	3.430669	-1.028272
C	-2.473919	2.931130	-1.199154
C	-2.726019	1.632241	-0.802704
C	-1.705043	0.801438	-0.241059
C	-0.397516	1.308053	0.000486
C	0.988519	3.504707	-0.453059
H	-3.260910	3.531356	-1.647666
H	1.992165	3.295610	-0.108392
H	-1.031139	5.460295	-1.726049
N	-1.973396	-0.528161	0.059064
H	-1.215215	-1.176816	-0.150282
C	-3.214659	-1.124570	0.323097
C	-4.236765	-0.459803	1.025334
C	-3.415671	-2.461835	-0.070137
C	-5.438690	-1.114351	1.300261
H	-4.079547	0.555144	1.375403
C	-4.614743	-3.109333	0.225588
H	-2.624505	-2.976013	-0.609298
C	-5.639485	-2.440290	0.904067
H	-6.216713	-0.585952	1.844986
H	-4.751637	-4.141457	-0.085958
H	-6.574666	-2.945336	1.126586
N	0.703699	4.698333	-0.962409
N	-0.605512	4.649137	-1.306064
H	-3.711945	1.211933	-0.966884

TS-C6

Pd	-1.435408	-0.414769	0.051723
H	0.206125	-0.935350	1.688594
C	-1.283914	-0.534281	3.026782
O	-2.086277	-0.376806	2.054261
C	-1.821793	-0.386194	4.430798
O	-0.954430	-0.460170	-1.943654
C	-0.648430	0.680141	-2.485218
O	-0.663576	1.773924	-1.893276
C	-0.229661	0.585486	-3.944695
O	-0.048948	-0.805387	2.896543
H	-0.647977	-0.300230	-4.426971
H	-0.525764	1.493247	-4.475292
H	0.863030	0.513024	-3.984627
H	-2.904732	-0.261138	4.422305
H	-1.544360	-1.262297	5.023153
H	-1.353515	0.486265	4.897697
P	-3.568202	0.481037	-0.440460
C	-4.955920	-0.378368	0.413848
H	-4.735090	-0.428444	1.482671
H	-5.904068	0.147428	0.257103
H	-5.045041	-1.399383	0.031847
C	-4.091579	0.526775	-2.202288
H	-4.028647	-0.475777	-2.632763
H	-5.118313	0.898160	-2.288116
H	-3.423029	1.186738	-2.759270
C	-3.702409	2.229008	0.115274
H	-3.496834	2.280697	1.187791
H	-2.947769	2.816879	-0.413637
H	-4.699794	2.636151	-0.083950
C	3.051884	-2.218745	-0.491894
C	1.946614	-3.069271	-0.229517
C	0.722510	-2.557479	0.204375
C	0.589810	-1.170822	0.390711
C	1.700847	-0.301151	0.069563
C	2.926359	-0.826829	-0.344439
C	4.094279	-3.111481	-0.895738
H	-0.105545	-3.220710	0.444058
H	3.756588	-0.171011	-0.583516

H	5.108634	-2.880543	-1.191855
H	1.886950	-5.215690	-0.406903
N	1.487214	1.080675	0.186652
H	0.611798	1.400355	-0.221784
C	2.467351	2.075700	0.307144
C	3.610442	1.909785	1.111985
C	2.265268	3.311982	-0.336484
C	4.528414	2.951230	1.252277
H	3.765755	0.974867	1.640380
C	3.182872	4.350581	-0.175740
H	1.387530	3.441509	-0.964293
C	4.325347	4.178869	0.612630
H	5.403551	2.803965	1.879921
H	3.007208	5.296779	-0.680979
H	5.042145	4.986195	0.729302
N	3.684311	-4.371825	-0.884338
N	2.392627	-4.347413	-0.478096

TS-C2'

Pd	1.914939	0.211950	0.175532
C	0.386164	1.533001	0.951927
C	-0.971871	1.083586	1.028939
C	-1.823309	1.611010	2.027103
C	-1.329234	2.504145	2.969726
C	0.011118	2.924267	2.946185
C	0.843057	2.429744	1.949391
H	0.555275	2.144192	-0.276763
H	-1.997291	2.872458	3.744498
H	0.382377	3.627772	3.685467
H	1.873820	2.775908	1.901950
C	1.836575	2.422918	-1.829535
O	2.552261	1.472814	-1.387046
C	2.323907	3.188535	-3.037432
O	1.420926	-1.063119	1.709049
C	0.721766	-2.111635	1.404177
O	0.342830	-2.407338	0.255873
C	0.351754	-2.983695	2.595662
O	0.726564	2.780160	-1.318748
H	1.022750	-2.817753	3.440552
H	-0.666310	-2.724726	2.907891
H	0.352897	-4.035876	2.300711
H	2.414195	4.248223	-2.781219
H	3.283910	2.803436	-3.381754
H	1.580289	3.108252	-3.836180
H	-2.853107	1.277739	2.090816
P	3.557452	-1.313822	-0.624612
C	3.050053	-2.130689	-2.194580
H	2.866910	-1.367843	-2.956242
H	3.822029	-2.821018	-2.552324
H	2.119010	-2.674223	-2.014433
C	4.015220	-2.717243	0.473645
H	3.140343	-3.352257	0.629696
H	4.818071	-3.313365	0.026777
H	4.342052	-2.334238	1.443753
C	5.174536	-0.527544	-1.030368
H	4.998033	0.312361	-1.706631
H	5.632636	-0.140306	-0.115668
H	5.859370	-1.242238	-1.499650
N	-1.404929	0.132388	0.121275
H	-0.684001	-0.506167	-0.203948
C	-5.051075	0.176763	-0.627067
C	-5.254473	-1.204045	-0.869946
C	-4.201614	-2.130487	-0.781892
C	-2.953773	-1.645646	-0.427119
C	-2.725541	-0.259394	-0.176865
C	-3.769402	0.655952	-0.292799
C	-6.340740	0.763064	-0.829595
H	-4.350848	-3.189141	-0.972967
H	-2.111810	-2.326158	-0.332067
H	-3.594327	1.716680	-0.148785
H	-6.633336	1.801438	-0.748784
H	-7.096167	-2.173256	-1.406850
N	-7.243468	-0.148883	-1.157034
N	-6.583758	-1.336081	-1.180454

CMD transition states in 6-*N*-aryl-indazole for different sites: **TS-C5, TS-C7** and **TS- C2'**

TS-C5

Pd	-1.435007	-0.413195	-0.042128
H	0.154390	-1.211120	1.578876
C	-1.420386	-1.127577	2.858579
O	-2.179475	-0.837662	1.883658
C	-2.038407	-1.301980	4.225867
O	-0.840080	-0.014475	-1.965184
C	-0.575693	1.223997	-2.250900
O	-0.677190	2.175544	-1.455440
C	-0.086019	1.441951	-3.675173
O	-0.160489	-1.284146	2.761991
H	-0.456052	0.666983	-4.349527
H	-0.382418	2.433856	-4.023575
H	1.008983	1.397024	-3.673424
P	-3.557795	0.575927	-0.435430
C	-4.975865	-0.433733	0.169480
H	-4.788255	-0.716462	1.208013
H	-5.917984	0.121105	0.101669
H	-5.055150	-1.347496	-0.426574
C	-4.013713	0.979428	-2.171319
H	-3.941172	0.082858	-2.792238
H	-5.034356	1.374082	-2.218626
H	-3.321016	1.729016	-2.559858
C	-3.731627	2.179223	0.450124
H	-3.582396	2.018754	1.521263
H	-2.954193	2.855671	0.086156
H	-4.720393	2.620494	0.283280
C	3.012675	-2.197089	-0.674106
C	1.903594	-3.081948	-0.587602
C	0.680771	-2.577042	-0.130951
C	0.554878	-1.230945	0.248295
C	1.700883	-0.350851	0.096577
C	2.937418	-0.839269	-0.338883
H	-0.172025	-3.244170	-0.022868
H	3.791102	-0.182044	-0.458684
H	4.993427	-2.673872	-1.336499
H	1.899958	-5.292089	-1.118041
N	1.510048	0.992610	0.405646
H	0.589859	1.352362	0.165678
C	2.490880	1.981432	0.597310
C	3.661310	1.740716	1.339643
C	2.254054	3.275571	0.097253
C	4.578740	2.770177	1.555812
H	3.836815	0.758550	1.765888
C	3.171910	4.299745	0.333388
H	1.349795	3.460176	-0.476740
C	4.344224	4.055320	1.055896
H	5.476014	2.567560	2.134763
H	2.971886	5.292894	-0.060074
H	5.060072	4.852840	1.231431
N	3.691110	-4.262874	-1.358554
H	-3.121272	-1.184212	4.182349
H	-1.781836	-2.291124	4.615881
H	-1.609923	-0.561075	4.907909
C	2.416692	-4.345492	-1.028924
N	4.047894	-2.957792	-1.135590

TS-C7

Pd	1.289109	-0.028333	0.010191
H	-0.252687	1.357022	1.328166
C	1.010330	0.870813	2.863654
O	1.766795	0.270942	2.038803
C	1.430512	0.922001	4.314378
O	0.968175	-0.341431	-1.991309
C	0.302165	-1.411080	-2.300932
O	-0.130813	-2.241600	-1.480797
C	0.050703	-1.584473	-3.791296
O	-0.087506	1.434176	2.553130
H	0.758581	-1.008195	-4.389882
H	0.094365	-2.644321	-4.053488
H	-0.961008	-1.226932	-4.013669
P	3.098068	-1.590650	0.017505
C	4.697266	-0.907926	0.633423
H	4.535673	-0.451957	1.613699
H	5.459927	-1.690061	0.716215
H	5.053552	-0.133956	-0.052557
C	3.542763	-2.376555	-1.585113
H	3.764180	-1.602981	-2.324836
H	4.411765	-3.033174	-1.470355
H	2.692599	-2.962542	-1.942879
C	2.773109	-3.019126	1.133121
H	2.578853	-2.647950	2.142868
H	1.882978	-3.546364	0.779418
H	3.622889	-3.710146	1.157110
C	-0.148501	2.628928	-0.540374
C	-1.154914	3.483356	-1.049661
C	-2.472824	2.987547	-1.133578
C	-2.742743	1.694011	-0.729852
C	-1.712427	0.836460	-0.230671
C	-0.377156	1.314755	-0.036154
H	-3.272596	3.604351	-1.535292
H	1.928443	3.057877	-0.344549
H	-0.880737	5.617058	-1.773515
N	-1.981222	-0.483074	0.081020
H	-1.219614	-1.131564	-0.117586
C	-3.226938	-1.087634	0.326604
C	-4.241794	-0.446441	1.058503
C	-3.429626	-2.408268	-0.114462

C	-5.443816	-1.108125	1.315132
H	-4.079792	0.555304	1.442414
C	-4.629006	-3.064340	0.162841
H	-2.641062	-2.902793	-0.675253
C	-5.648187	-2.418114	0.870423
H	-6.218627	-0.598982	1.882086
H	-4.769992	-4.083996	-0.185464
H	-6.583511	-2.929143	1.078362
N	0.812586	4.622446	-1.076747
H	-3.744969	1.298116	-0.844480
C	-0.477852	4.701914	-1.359172
N	0.995597	3.365965	-0.571563
H	1.424528	1.959926	4.658643
H	0.698071	0.373875	4.915502
H	2.419827	0.484297	4.449513

TS- C2'

Pd	1.907608	0.230902	0.167453
C	0.344569	1.507354	0.968528
C	-0.993338	1.013197	1.082741
C	-1.834037	1.507395	2.105002
C	-1.347804	2.421481	3.032654
C	-0.026303	2.891386	2.968124
C	0.795341	2.425167	1.948600
H	0.476449	2.095950	-0.273224
H	-2.005532	2.764267	3.827648
H	0.340214	3.609448	3.695740
H	1.810735	2.809182	1.871642
C	1.723995	2.421172	-1.846167
O	2.485458	1.505673	-1.405950
C	2.165581	3.201437	-3.062069
O	1.482047	-1.057695	1.709557
C	0.806460	-2.124285	1.411368
O	0.409512	-2.417804	0.268859
C	0.490579	-3.018470	2.601254
O	0.604939	2.731360	-1.325081
H	-0.526681	-2.792120	2.940108
H	0.513740	-4.066839	2.294142
H	1.177024	-2.842613	3.431590
H	-2.846351	1.130970	2.201218
P	3.585854	-1.238380	-0.649738
C	3.094743	-2.056878	-2.223550
H	2.882081	-1.293802	-2.977192
H	3.886915	-2.718144	-2.591813
H	2.183345	-2.632809	-2.043619
C	4.088302	-2.634254	0.437641
H	3.234689	-3.298985	0.587475
H	4.910434	-3.200323	-0.013224
H	4.401590	-2.248396	1.411026
C	5.174744	-0.397349	-1.055072
H	4.967202	0.446103	-1.717832
H	5.628056	-0.009961	-0.138085
H	5.876973	-1.084142	-1.539859
N	-1.418465	0.038187	0.190522
H	-0.693313	-0.603010	-0.122540
C	-5.035708	0.081605	-0.585393
C	-5.257905	-1.272631	-0.941636
C	-4.171711	-2.171021	-0.903075
C	-2.931583	-1.707841	-0.505196
C	-2.725722	-0.339827	-0.145997
C	-3.780498	0.574143	-0.196146
H	-4.302976	-3.215345	-1.172160
H	-2.081634	-2.382078	-0.450506
H	-3.626021	1.623928	0.025793
H	-6.478943	1.670141	-0.577132
H	-7.229116	-2.182170	-1.602892
N	-7.228138	-0.149737	-1.149510
C	-6.645955	-1.330890	-1.277102
N	-6.248252	0.701375	-0.728403
H	2.222072	4.264001	-2.807854
H	3.133665	2.850683	-3.420127
H	1.413476	3.093853	-3.849486

Potential energy profile: **TS-2** and **TS-3**

TS--2

N	-0.278144	2.250099	-1.525666
H	-0.201199	3.047273	-2.145790
C	-1.279943	2.422844	-0.557318
C	-1.674663	1.325748	0.249976
C	-1.862250	3.690198	-0.374093
C	-2.531940	1.601927	1.345950
C	-2.738672	3.907870	0.685622
H	-1.583708	4.514713	-1.027373
C	-3.052206	2.870042	1.577644
H	-3.160863	4.898405	0.833982
H	-2.841686	0.775332	1.981333
H	-3.717981	3.050896	2.416447
C	2.404338	0.610355	0.433695
C	3.524857	1.352284	-0.026150
C	3.416487	2.287926	-1.065867
C	2.139922	2.513608	-1.556769
C	1.003092	1.802216	-1.080832
C	1.121329	0.768950	-0.145499
C	2.937769	-0.176849	1.504827
H	4.271710	2.837381	-1.446906
H	1.997057	3.272427	-2.324139
H	2.412583	-0.855570	2.163076
H	5.532579	1.301306	0.739793
N	4.232817	0.035703	1.683778
N	4.589349	0.946928	0.741048
H	-2.282372	0.385368	-0.452137
Pd	-0.421368	-0.467909	0.209552
C	-3.159799	-1.511418	-0.211271
O	-2.159111	-1.809334	0.510759
C	-4.357608	-2.439806	-0.219418
O	-3.226972	-0.459028	-0.925522
H	-5.201323	-1.934218	0.261934
H	-4.653277	-2.652687	-1.250618
H	-4.138891	-3.366358	0.313185
P	0.772493	-2.468280	-0.248362
C	0.977992	-3.636795	1.167091
H	0.006724	-3.781606	1.647792
H	1.362644	-4.604604	0.826691
H	1.670754	-3.218558	1.901916
C	2.432880	-2.457829	-1.050280
H	3.182156	-2.038061	-0.377216
H	2.721893	-3.477686	-1.326207
H	2.394275	-1.837431	-1.949703
C	-0.210648	-3.472610	-1.446389
H	-1.199063	-3.663564	-1.024714
H	-0.331649	-2.915020	-2.379288
H	0.290041	-4.423901	-1.657537

TS-3

N	0.462012	2.168220	-1.824331
H	0.708881	2.836210	-2.541107
C	-0.583632	2.508783	-0.962484
C	-0.678458	1.726518	0.218046
C	-1.394467	3.636657	-1.155014
C	-1.458599	2.237499	1.276631
C	-2.221056	4.071883	-0.119804
H	-1.332759	4.197621	-2.085571
C	-2.220900	3.395499	1.110850
H	-2.832090	4.959636	-0.255891
H	-1.495387	1.703156	2.221119
H	-2.830132	3.762444	1.932682
C	2.213426	0.469898	0.883843
C	3.559688	0.676425	0.485415
C	3.902067	1.246488	-0.756320
C	2.858258	1.667865	-1.566398
C	1.507647	1.512244	-1.161569
C	1.137923	0.843686	0.025800
C	2.322696	-0.159342	2.161602
H	4.934914	1.373271	-1.065224
H	3.075888	2.157440	-2.513074
H	1.527394	-0.486840	2.817040
H	5.335559	0.171658	1.584566
N	3.587550	-0.316682	2.527698
N	4.331199	0.180718	1.505469
Pd	-0.560427	-0.321912	0.092510
P	-2.755568	-1.361522	0.187381
C	-3.336104	-2.160195	-1.382082
H	-2.620600	-2.931824	-1.680598
H	-4.326479	-2.615634	-1.265273
H	-3.379118	-1.410516	-2.177640
C	-4.196740	-0.277011	0.601868
H	-4.260037	0.536299	-0.126589
H	-5.138641	-0.837482	0.604397
H	-4.044201	0.174158	1.586394
C	-2.960200	-2.748380	1.399749
H	-2.204712	-3.512513	1.196486
H	-2.795541	-2.372917	2.414208
H	-3.958485	-3.197969	1.343973
O	0.282518	-2.666334	-0.183005
C	1.245787	-2.914925	-0.898708
O	1.909818	-1.979389	-1.582828
C	1.817712	-4.293773	-1.095623
H	1.956621	-4.498921	-2.160728
H	2.802903	-4.342467	-0.619766
H	1.159138	-5.035945	-0.645333
H	1.535728	-1.097016	-1.360264