

## *Supplementary Information*

### **An experimental and theoretical study on the regioselective synthesis of a new class of spiropyrrolothiazoles with quinoxalines motifs via 1,3-dipolar cycloaddition reaction. An evaluation of DFT methods**

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**Table S1.** Calculated electronic activation energies  $E_a$ , reaction Gibbs free energies  $\Delta G$ , reaction enthalpies  $\Delta H$ , reaction energies  $\Delta E_{rxn}$ , activation Gibbs free energies  $\Delta G^\ddagger$ , activation enthalpies  $\Delta H^\ddagger$  and Average Bond Index Changes ( $\delta B_{av}$ ), Synchronicities (Sy) and charge transfer (CT) of possible pathways of 1,3-DC of nitrostyrene **4a** and azomethine ylide **7** Indicated in Scheme 3 at B3LYP/6-31G(d,p), all energies are in kcal/mol.

Structure	$\Delta G^\ddagger$	$E_a$	$\Delta H^\ddagger$	$\Delta E_{rxn}$	$\Delta H$	$\Delta G$	$\delta B_{av}$	Sy	CT
<b>TS endo-5a</b>	21.40	6.53	6.10	-26.13	-26.77	-11.59	0.34	0.79	0.20
<b>TS exo-5a</b>	22.66	8.54	8.34	-19.36	-20.11	-4.32	0.29	0.67	0.16
<b>TS endo-6a</b>	19.63	4.88	4.55	-24.11	-24.75	-9.66	0.21	0.37	0.26
<b>TS exo-6a</b>	24.85	10.26	9.88	-23.68	-24.46	-8.71	0.25	0.53	0.24

**Table S2.** Nucleus-independent chemical shifts (NICS, ppm/mol) at B3LYP/6-31G(d,p)

Structure	<i>endo-5a</i>	<i>exo-5a</i>	<i>endo-6a</i>	<i>exo-6a</i>
TS	-13.74	-13.20	-14.00	-13.07
product	-6.83	-2.85	-3.75	-6.60

Cartesian coordinates of **TS endo-5a** at B3LYP/6-31G(d,p)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-2.543111	-2.767224	0.910038
2	1	-3.363064	-2.072938	1.098677
3	1	-2.171489	-3.195214	1.841101
4	6	-2.439601	-3.176216	-1.688839
5	1	-3.266750	-2.748498	-2.267143
6	1	-1.892397	-3.869121	-2.333426
7	6	-1.530471	-2.106159	-1.149528
8	1	-0.618983	-1.859708	-1.681100
9	6	-2.230813	-0.076638	-1.440180
10	1	-1.922465	0.063806	-2.467378
11	6	-1.688700	0.673549	-0.378853
12	1	-2.341671	0.796374	0.477625
13	6	-0.645616	1.684707	-0.534168
14	6	-0.438982	2.608277	0.511249
15	1	-1.055344	2.541475	1.403125
16	6	0.531651	3.601141	0.412213
17	1	0.668267	4.302637	1.229941
18	6	1.324924	3.695668	-0.732557
19	6	1.136552	2.786542	-1.776941
20	1	1.750636	2.851014	-2.670351
21	6	0.167104	1.793169	-1.681296
22	1	0.045489	1.092960	-2.501043
23	6	-0.641559	-1.127749	0.808221
24	6	-0.679464	-0.735155	2.229134
25	6	-1.718454	-0.708494	3.169666
26	1	-2.715752	-1.053302	2.924266
27	6	-1.467817	-0.204686	4.447634
28	1	-2.273277	-0.190096	5.175880
29	6	-0.205663	0.289222	4.803710
30	1	-0.040924	0.676368	5.804423
31	6	0.832679	0.291901	3.873653
32	1	1.816617	0.676465	4.122193
33	6	0.592230	-0.216899	2.599441
34	6	1.489131	-0.338571	1.457070
35	6	0.741647	-0.914763	0.363411
36	6	2.619735	-0.890609	-0.911648
37	6	3.290389	-1.162645	-2.128055
38	1	2.718633	-1.608610	-2.935781
39	6	4.629949	-0.866890	-2.266364
40	1	5.137404	-1.080088	-3.202426
41	6	5.352781	-0.286396	-1.196671
42	1	6.407029	-0.059522	-1.323100
43	6	4.726994	-0.011012	0.000185
44	1	5.257860	0.431606	0.836748
45	6	3.352948	-0.305148	0.174763
46	7	-1.441514	-2.077731	0.205343
47	7	-3.642794	-0.386874	-1.392814
48	7	2.760836	-0.031732	1.379918
49	7	1.284024	-1.183631	-0.802744
50	8	-4.230693	-0.399872	-0.301190
51	8	-4.188003	-0.672715	-2.467976
52	1	2.082057	4.469826	-0.811798
53	16	-3.067630	-4.105455	-0.222751

Cartesian coordinates of **Ts exo-5a** at B3LYP/6-31G(d,p)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-1.911614	-0.514521	2.591076
2	1	-2.713571	-0.162327	1.944789
3	1	-1.778757	0.173170	3.430413
4	6	-0.698478	-2.870795	2.628450
5	1	-0.823677	-3.850664	2.162333
6	1	-0.030037	-2.976269	3.490141
7	6	-0.170181	-1.871708	1.644298
8	1	0.877407	-1.920985	1.359452
9	6	-0.877284	-2.303155	-0.261490
10	6	-0.973359	-1.132225	-1.023104
11	6	-0.186048	0.431468	1.064192
12	6	-0.760181	1.773474	0.911429
13	6	-2.000986	2.341202	1.242759
14	1	-2.773648	1.782659	1.752611
15	6	-2.259614	3.674336	0.917072
16	1	-3.222191	4.100660	1.183505
17	6	-1.311940	4.466222	0.259235
18	1	-1.540989	5.500101	0.020497
19	6	-0.074180	3.923769	-0.085166
20	1	0.683846	4.512766	-0.591619
21	6	0.192867	2.598713	0.241203
22	6	1.401793	1.820125	0.018360
23	6	1.180189	0.493797	0.549676
24	6	3.313638	-0.060582	-0.004196
25	6	4.372114	-0.999821	-0.054376
26	1	4.193060	-1.988420	0.355129
27	6	5.579262	-0.656795	-0.624786
28	1	6.384460	-1.384266	-0.663721
29	6	5.779381	0.635248	-1.167492
30	1	6.736914	0.887025	-1.613214
31	6	4.766976	1.570665	-1.134506
32	1	4.893496	2.567864	-1.543606
33	6	3.515872	1.250215	-0.555876
34	7	-0.644028	-0.607451	1.837078
35	7	2.529927	2.203284	-0.525957
36	7	2.121520	-0.428431	0.558223
37	1	-1.760155	-2.849897	0.046341
38	1	-0.100577	-0.863559	-1.606953
39	7	0.177951	-3.262280	-0.606371
40	8	0.033229	-4.407776	-0.157943
41	8	1.145740	-2.894826	-1.269425
42	6	-2.208047	-0.422466	-1.303031
43	6	-2.180461	0.671370	-2.196739
44	6	-3.459519	-0.785188	-0.752444
45	6	-3.341150	1.361783	-2.529680
46	1	-1.231262	0.970127	-2.632375
47	6	-4.617265	-0.090315	-1.087430
48	1	-3.530989	-1.627177	-0.070119
49	6	-4.568360	0.985038	-1.979670
50	1	-3.288194	2.195736	-3.223361
51	1	-5.567134	-0.396456	-0.658075
52	1	-5.475568	1.520250	-2.242770
53	16	-2.335484	-2.212252	3.151557

Cartesian coordinates of **TS endo-6a** at B3LYP/6-31G(d,p)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	0.363166	-2.538377	2.321063
2	1	0.687534	-3.271858	1.583268
3	1	-0.584449	-2.829094	2.773720
4	6	2.304933	-0.801077	2.772974
5	1	3.308609	-0.995761	2.383457
6	1	2.381219	0.009065	3.503857
7	6	1.338212	-0.454005	1.671520
8	1	1.183356	0.589139	1.423786
9	6	2.182855	-0.890762	-0.231403
10	6	1.099522	-1.029171	-1.098882
11	6	-0.831342	-0.946132	0.828124
12	6	-1.937662	-1.832771	0.454095
13	6	-2.077416	-3.227589	0.469220
14	1	-1.281065	-3.876707	0.805067
15	6	-3.259681	-3.795342	-0.011948
16	1	-3.365350	-4.875768	-0.001173
17	6	-4.296011	-3.006046	-0.521845
18	1	-5.202417	-3.477324	-0.888846
19	6	-4.157285	-1.618306	-0.581840
20	1	-4.935546	-0.987037	-0.998049
21	6	-2.986163	-1.045338	-0.101826
22	6	-2.573694	0.351640	-0.081734
23	6	-1.237893	0.416099	0.472522
24	6	-1.273449	2.677288	0.247799
25	6	-0.654152	3.941763	0.393676
26	1	0.341432	3.973724	0.825050
27	6	-1.310979	5.087911	-0.002842
28	1	-0.830653	6.054783	0.113354
29	6	-2.608798	5.015914	-0.561710
30	1	-3.110826	5.927823	-0.870157
31	6	-3.237253	3.797664	-0.715246
32	1	-4.232228	3.715142	-1.140319
33	6	-2.591767	2.604047	-0.315021
34	7	0.210056	-1.222841	1.657161
35	7	-3.243315	1.406823	-0.471892
36	7	-0.593764	1.551095	0.637336
37	1	0.733728	-0.268581	-1.771758
38	1	2.613912	-1.837218	0.085917
39	7	0.555183	-2.308198	-1.371355
40	8	0.918413	-3.290870	-0.682187
41	8	-0.268727	-2.398791	-2.293286
42	6	3.145090	0.232661	-0.351843
43	6	4.505369	-0.004850	-0.093147
44	6	2.751773	1.533440	-0.712386
45	6	5.446565	1.018864	-0.203978
46	1	4.829165	-1.007385	0.174393
47	6	3.693173	2.553509	-0.826272
48	1	1.702107	1.749634	-0.884281
49	6	5.044418	2.302203	-0.573153
50	1	6.493998	0.810069	-0.006779
51	1	3.370108	3.550946	-1.110230
52	1	5.774940	3.100712	-0.661169
53	16	1.624730	-2.290492	3.624579

Cartesian coordinates of **Ts exo-6a** at B3LYP/6-31G(d,p)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-1.507827	1.669304	2.218358
2	1	-2.091048	2.194381	1.459891
3	1	-0.876547	2.369980	2.764826
4	6	-2.418870	-0.799461	2.439982
5	1	-3.355910	-1.049798	1.935268
6	1	-2.180946	-1.594593	3.151831
7	6	-1.292489	-0.590156	1.459769
8	1	-0.621630	-1.420378	1.264334
9	6	-1.917023	-0.537844	-0.537700
10	6	-0.769837	-0.110009	-1.216907
11	6	0.491360	0.897002	0.947636
12	6	1.017645	2.213790	0.565477
13	6	0.423630	3.479657	0.460973
14	1	-0.615638	3.645500	0.718775
15	6	1.186830	4.555492	0.001941
16	1	0.725787	5.535673	-0.074907
17	6	2.527832	4.391654	-0.366096
18	1	3.096366	5.244535	-0.723523
19	6	3.131704	3.136154	-0.280806
20	1	4.167117	2.983897	-0.567386
21	6	2.381096	2.061795	0.183089
22	6	2.762287	0.666373	0.376254
23	6	1.603905	-0.049946	0.851478
24	6	2.852494	-1.929399	1.037754
25	6	2.981834	-3.298770	1.371527
26	1	2.100118	-3.817655	1.732548
27	6	4.193169	-3.938905	1.223504
28	1	4.284219	-4.990791	1.477129
29	6	5.323239	-3.238063	0.737381
30	1	6.268981	-3.759536	0.624871
31	6	5.229085	-1.903533	0.405674
32	1	6.079509	-1.343829	0.030292
33	6	3.999619	-1.216678	0.547088
34	7	-0.668918	0.625223	1.600623
35	7	3.940304	0.114643	0.227887
36	7	1.636828	-1.318406	1.192369
37	1	-2.049498	-1.616748	-0.538089
38	1	-0.626696	0.848087	-1.691022
39	7	0.224388	-1.052908	-1.575959
40	8	0.121481	-2.223896	-1.160532
41	8	1.173104	-0.649946	-2.271031
42	6	-3.175037	0.245632	-0.587366
43	6	-4.400376	-0.415989	-0.392976
44	6	-3.208709	1.628708	-0.848339
45	6	-5.610982	0.275197	-0.440464
46	1	-4.401989	-1.490522	-0.228664
47	6	-4.417751	2.318905	-0.896856
48	1	-2.283910	2.169249	-1.027612
49	6	-5.625141	1.647250	-0.688437
50	1	-6.542897	-0.262139	-0.291564
51	1	-4.418588	3.384839	-1.105808
52	1	-6.565757	2.187835	-0.727657
53	16	-2.611872	0.780508	3.377080

Cartesian coordinates of **TS endo-5a** at M06-2x/6-31G(d,p)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-2.644149	-2.644298	0.994843
2	1	-3.397917	-1.860634	1.085517
3	1	-2.302232	-2.987767	1.971784
4	6	-2.554542	-3.356205	-1.512088
5	1	-3.326600	-2.872646	-2.124966
6	1	-2.110713	-4.165560	-2.095100
7	6	-1.512118	-2.376048	-1.076429
8	1	-0.607916	-2.195557	-1.641397
9	6	-1.980922	-0.129751	-1.587745
10	1	-1.483622	0.001797	-2.537759
11	6	-1.612565	0.510562	-0.401008
12	1	-2.411815	0.608352	0.330382
13	6	-0.567532	1.546942	-0.328718
14	6	-0.512454	2.362812	0.808343
15	1	-1.273054	2.251250	1.577462
16	6	0.516605	3.283712	0.977614
17	1	0.544769	3.897981	1.871879
18	6	1.512476	3.401559	0.013960
19	6	1.459932	2.608317	-1.132697
20	1	2.233976	2.692178	-1.889470
21	6	0.428244	1.696131	-1.306712
22	1	0.416035	1.070122	-2.193889
23	6	-0.699281	-1.113691	0.735585
24	6	-0.706860	-0.634981	2.135651
25	6	-1.737438	-0.499967	3.071678
26	1	-2.741204	-0.856790	2.874194
27	6	-1.472096	0.133794	4.283599
28	1	-2.270727	0.232478	5.011813
29	6	-0.208339	0.655648	4.575473
30	1	-0.036325	1.148235	5.526557
31	6	0.817150	0.557689	3.642671
32	1	1.802249	0.975280	3.824640
33	6	0.557224	-0.083588	2.438348
34	6	1.433366	-0.262654	1.284950
35	6	0.684850	-0.951815	0.261505
36	6	2.501654	-0.890946	-1.076647
37	6	3.132451	-1.178027	-2.308620
38	1	2.561546	-1.718991	-3.056318
39	6	4.425426	-0.773340	-2.535568
40	1	4.903265	-0.994240	-3.484404
41	6	5.141660	-0.067306	-1.541431
42	1	6.162463	0.244169	-1.736845
43	6	4.552581	0.222786	-0.335247
44	1	5.074599	0.762019	0.448057
45	6	3.222676	-0.180007	-0.074766
46	7	-1.492830	-2.125225	0.234127
47	7	-3.332016	-0.539311	-1.758445
48	7	2.665183	0.128946	1.138372
49	7	1.195265	-1.271654	-0.895463
50	8	-4.054309	-0.682775	-0.769317
51	8	-3.703172	-0.803537	-2.899452
52	1	2.324133	4.108454	0.150633
53	16	-3.262467	-4.047558	0.024373



Cartesian coordinates of **TS exo-5a** at M06-2x/6-31G(d,p)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-2.035167	-0.598716	2.478568
2	1	-2.746912	-0.182436	1.769624
3	1	-1.984970	0.015668	3.381160
4	6	-0.831195	-2.928026	2.590575
5	1	-0.846186	-3.885242	2.063692
6	1	-0.319533	-3.057578	3.549497
7	6	-0.168316	-1.888222	1.748837
8	1	0.895179	-1.946021	1.543140
9	6	-0.698558	-2.225257	-0.322158
10	6	-0.786405	-0.994290	-0.950209
11	6	-0.237309	0.370312	1.085842
12	6	-0.841104	1.692769	0.871369
13	6	-2.101307	2.238998	1.140863
14	1	-2.863183	1.710051	1.696662
15	6	-2.404071	3.519937	0.683841
16	1	-3.387467	3.928758	0.893694
17	6	-1.483356	4.281151	-0.037334
18	1	-1.752439	5.274382	-0.380591
19	6	-0.221341	3.762527	-0.306674
20	1	0.525807	4.324117	-0.858574
21	6	0.084051	2.488328	0.148428
22	6	1.320971	1.732925	-0.019453
23	6	1.139199	0.441967	0.603008
24	6	3.254983	-0.104719	0.029012
25	6	4.316562	-1.037075	-0.007816
26	1	4.153989	-2.004462	0.455278
27	6	5.495904	-0.716390	-0.634608
28	1	6.304809	-1.438950	-0.666686
29	6	5.665042	0.546317	-1.249065
30	1	6.603628	0.781998	-1.739627
31	6	4.646852	1.467894	-1.233150
32	1	4.743199	2.442565	-1.699871
33	6	3.420945	1.163712	-0.599776
34	7	-0.697199	-0.654873	1.861272
35	7	2.420172	2.102255	-0.608538
36	7	2.087538	-0.457883	0.650631
37	1	-1.556792	-2.834459	-0.065523
38	1	0.090243	-0.667243	-1.501346
39	7	0.455447	-3.073650	-0.587105
40	8	0.416576	-4.196519	-0.093931
41	8	1.391031	-2.640662	-1.233848
42	6	-2.038929	-0.282956	-1.197253
43	6	-2.011417	0.893436	-1.963721
44	6	-3.272118	-0.700272	-0.668653
45	6	-3.167733	1.631408	-2.184290
46	1	-1.064681	1.230974	-2.377483
47	6	-4.427243	0.040256	-0.891393
48	1	-3.331631	-1.609939	-0.075074
49	6	-4.382402	1.209434	-1.649735
50	1	-3.117823	2.542160	-2.772625
51	1	-5.370519	-0.304153	-0.478314
52	1	-5.286944	1.782915	-1.823689
53	16	-2.533157	-2.316764	2.827446

Cartesian coordinates of **TS endo-6a** at M06-2x/6-31G(d,p)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	0.410074	-2.584419	2.322433
2	1	0.704003	-3.292501	1.547037
3	1	-0.530324	-2.878314	2.789310
4	6	2.388699	-0.918609	2.740525
5	1	3.339320	-1.148836	2.247968
6	1	2.573872	-0.141550	3.485334
7	6	1.352774	-0.484138	1.746764
8	1	1.228980	0.562080	1.497693
9	6	2.086419	-0.873495	-0.284158
10	6	0.938409	-0.961232	-1.041547
11	6	-0.789988	-0.967874	0.885707
12	6	-1.901908	-1.846582	0.511987
13	6	-2.050570	-3.236730	0.526471
14	1	-1.276069	-3.894255	0.897464
15	6	-3.216294	-3.792976	0.002632
16	1	-3.331909	-4.871768	0.013423
17	6	-4.223270	-3.000855	-0.549872
18	1	-5.116162	-3.467021	-0.952447
19	6	-4.071293	-1.618430	-0.608886
20	1	-4.821955	-0.977345	-1.059442
21	6	-2.916834	-1.059561	-0.085629
22	6	-2.491744	0.336291	-0.073528
23	6	-1.174400	0.393642	0.523952
24	6	-1.163079	2.635277	0.232820
25	6	-0.514949	3.886290	0.351093
26	1	0.469396	3.903136	0.809453
27	6	-1.129533	5.028365	-0.102615
28	1	-0.629641	5.986873	-0.008030
29	6	-2.413028	4.966742	-0.692281
30	1	-2.884181	5.878043	-1.045300
31	6	-3.062571	3.762612	-0.820628
32	1	-4.046640	3.682270	-1.270241
33	6	-2.455076	2.571407	-0.363641
34	7	0.248620	-1.252521	1.707430
35	7	-3.127155	1.383926	-0.510181
36	7	-0.516852	1.512748	0.681330
37	1	0.525751	-0.180395	-1.664153
38	1	2.525836	-1.826590	0.005656
39	7	0.349650	-2.232380	-1.306202
40	8	0.744370	-3.220664	-0.676653
41	8	-0.545580	-2.277869	-2.137480
42	6	3.012522	0.276412	-0.367514
43	6	4.375196	0.073996	-0.121599
44	6	2.569122	1.572540	-0.664823
45	6	5.275690	1.133934	-0.181592
46	1	4.733011	-0.929117	0.097187
47	6	3.469777	2.627806	-0.729672
48	1	1.510217	1.756095	-0.823482
49	6	4.826581	2.414366	-0.487638
50	1	6.329643	0.955182	0.005713
51	1	3.108918	3.624150	-0.965974
52	1	5.526697	3.241814	-0.536390
53	16	1.699141	-2.385700	3.587596

Cartesian coordinates of **TS exo-6a** at M06-2x/6-31G(d,p)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-1.637693	1.576419	2.185216
2	1	-2.019723	2.238873	1.411826
3	1	-1.056550	2.137899	2.919449
4	6	-2.490873	-0.928293	2.384650
5	1	-3.305372	-1.415983	1.840452
6	1	-2.219218	-1.550646	3.241421
7	6	-1.313663	-0.694255	1.492880
8	1	-0.622008	-1.507276	1.291658
9	6	-1.859325	-0.647648	-0.571903
10	6	-0.660024	-0.276421	-1.153942
11	6	0.378607	0.850807	0.950957
12	6	0.855025	2.181308	0.537821
13	6	0.235395	3.431287	0.421440
14	1	-0.795458	3.595922	0.709770
15	6	0.963528	4.508585	-0.079466
16	1	0.478952	5.476169	-0.162761
17	6	2.294445	4.369862	-0.477179
18	1	2.833200	5.227136	-0.866479
19	6	2.925446	3.133925	-0.373896
20	1	3.958054	2.989800	-0.674841
21	6	2.207678	2.060845	0.131380
22	6	2.644075	0.684875	0.352460
23	6	1.525871	-0.052360	0.885205
24	6	2.831583	-1.880228	1.049103
25	6	3.004916	-3.242699	1.383833
26	1	2.147682	-3.775157	1.781687
27	6	4.217974	-3.854230	1.187676
28	1	4.343556	-4.902184	1.439764
29	6	5.309456	-3.130724	0.651306
30	1	6.261185	-3.629663	0.501195
31	6	5.168392	-1.806878	0.317148
32	1	5.984626	-1.226393	-0.099728
33	6	3.929618	-1.151193	0.505014
34	7	-0.772900	0.542305	1.595176
35	7	3.825612	0.172253	0.170210
36	7	1.607786	-1.303013	1.254167
37	1	-2.060772	-1.715083	-0.529688
38	1	-0.436587	0.644408	-1.670682
39	7	0.335868	-1.277036	-1.354518
40	8	0.144309	-2.400289	-0.892317
41	8	1.363405	-0.943122	-1.934916
42	6	-3.030635	0.247784	-0.600236
43	6	-4.313189	-0.281169	-0.409769
44	6	-2.902129	1.629176	-0.803135
45	6	-5.431623	0.545098	-0.393027
46	1	-4.431804	-1.355588	-0.291561
47	6	-4.019807	2.455395	-0.783093
48	1	-1.918104	2.063125	-0.969002
49	6	-5.288309	1.917792	-0.571111
50	1	-6.416682	0.114720	-0.244552
51	1	-3.901227	3.523179	-0.940597
52	1	-6.159295	2.564297	-0.555916
53	16	-3.045227	0.715652	2.957359

Cartesian coordinates of **TS endo-5a** at wB97xD/6-31G(d,p)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-2.592326	-2.692043	0.967262
2	1	-3.384526	-1.945856	1.044512
3	1	-2.242008	-3.008737	1.949471
4	6	-2.482000	-3.386181	-1.534187
5	1	-3.276669	-2.903744	-2.122281
6	1	-2.022785	-4.162519	-2.149073
7	6	-1.479438	-2.377793	-1.093235
8	1	-0.614727	-2.099436	-1.679038
9	6	-2.077996	-0.038326	-1.557393
10	1	-1.613214	0.081157	-2.524214
11	6	-1.642565	0.555894	-0.372813
12	1	-2.412068	0.647133	0.388599
13	6	-0.594921	1.594288	-0.324490
14	6	-0.516672	2.412973	0.807726
15	1	-1.251538	2.296817	1.599230
16	6	0.501085	3.350616	0.941417
17	1	0.547976	3.968236	1.832459
18	6	1.461589	3.483571	-0.054605
19	6	1.387835	2.684103	-1.193783
20	1	2.136569	2.776350	-1.973884
21	6	0.368190	1.752720	-1.330284
22	1	0.342458	1.119961	-2.211173
23	6	-0.699894	-1.074538	0.706086
24	6	-0.702249	-0.628184	2.117382
25	6	-1.738741	-0.492952	3.042744
26	1	-2.746991	-0.822163	2.820985
27	6	-1.475594	0.107577	4.271401
28	1	-2.279173	0.205540	4.994212
29	6	-0.205601	0.598050	4.584412
30	1	-0.032430	1.068772	5.546295
31	6	0.826692	0.499511	3.659826
32	1	1.815615	0.895928	3.863331
33	6	0.569066	-0.110401	2.440013
34	6	1.448950	-0.289131	1.291073
35	6	0.690077	-0.927146	0.248776
36	6	2.517823	-0.899028	-1.075468
37	6	3.147253	-1.179290	-2.308671
38	1	2.564988	-1.680181	-3.075013
39	6	4.455769	-0.818078	-2.515602
40	1	4.933219	-1.032855	-3.466014
41	6	5.187957	-0.164276	-1.499060
42	1	6.221754	0.112412	-1.677650
43	6	4.599957	0.117501	-0.291103
44	1	5.137507	0.617877	0.507072
45	6	3.254114	-0.240488	-0.051107
46	7	-1.469310	-2.113008	0.206266
47	7	-3.411124	-0.496220	-1.656002
48	7	2.696868	0.057699	1.164123
49	7	1.199992	-1.239631	-0.910711
50	8	-4.109841	-0.585380	-0.636590
51	8	-3.816906	-0.837336	-2.772480
52	1	2.263834	4.206271	0.052578
53	16	-3.131266	-4.129687	0.002185

Cartesian coordinates of **TS exo-5a** at wB97xD/6-31G(d,p)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-2.170295	1.255426	-1.846520
2	1	-2.839880	0.689277	-1.202869
3	1	-2.232929	0.889129	-2.874013
4	6	-0.875694	3.502478	-1.422468
5	1	-0.821758	4.269340	-0.646589
6	1	-0.417775	3.894349	-2.336300
7	6	-0.198442	2.255248	-0.963502
8	1	0.880594	2.224702	-0.852220
9	6	-0.527224	2.002670	1.170574
10	6	-0.577841	0.645765	1.435866
11	6	-0.284220	-0.097621	-0.989002
12	6	-0.909502	-1.421072	-1.104147
13	6	-2.212851	-1.852103	-1.367913
14	1	-3.008799	-1.169783	-1.630427
15	6	-2.514928	-3.208672	-1.288215
16	1	-3.532198	-3.529119	-1.488515
17	6	-1.549006	-4.155767	-0.950235
18	1	-1.815082	-5.205855	-0.892270
19	6	-0.245096	-3.749352	-0.690529
20	1	0.532536	-4.458748	-0.427887
21	6	0.059898	-2.399514	-0.772268
22	6	1.335529	-1.732850	-0.543131
23	6	1.131566	-0.318044	-0.723142
24	6	3.326936	0.028146	-0.312746
25	6	4.425753	0.903436	-0.161826
26	1	4.251818	1.964344	-0.303038
27	6	5.661545	0.408085	0.172912
28	1	6.499884	1.086466	0.293560
29	6	5.851782	-0.978179	0.369229
30	1	6.835515	-1.352623	0.632782
31	6	4.799891	-1.849978	0.231937
32	1	4.917252	-2.918071	0.379694
33	6	3.516129	-1.368370	-0.109416
34	7	-0.784502	1.114374	-1.372094
35	7	2.484773	-2.263401	-0.241041
36	7	2.104779	0.552498	-0.633303
37	1	-1.399511	2.643859	1.183134
38	1	0.345463	0.182744	1.766680
39	7	0.651467	2.757140	1.564676
40	8	0.561949	3.980792	1.472351
41	8	1.656777	2.169405	1.931734
42	6	-1.807636	-0.121611	1.609053
43	6	-1.715020	-1.466569	1.997773
44	6	-3.085801	0.413332	1.380014
45	6	-2.851947	-2.250608	2.143229
46	1	-0.734766	-1.900501	2.171009
47	6	-4.221616	-0.373196	1.526053
48	1	-3.199655	1.453854	1.087424
49	6	-4.111686	-1.708505	1.908694
50	1	-2.749800	-3.291355	2.432612
51	1	-5.199711	0.063611	1.349492
52	1	-5.001530	-2.318883	2.022420
53	16	-2.609777	3.017623	-1.707917

Cartesian coordinates of **TS endo-6a** at wB97xD/6-31G(d,p)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	0.416049	-2.598857	2.299352
2	1	0.679677	-3.299199	1.506603
3	1	-0.508765	-2.893984	2.794638
4	6	2.371729	-0.900410	2.754466
5	1	3.346180	-1.053889	2.280384
6	1	2.492810	-0.139936	3.529992
7	6	1.342394	-0.486586	1.749607
8	1	1.206028	0.558334	1.502081
9	6	2.101491	-0.877103	-0.299881
10	6	0.962034	-0.991270	-1.062542
11	6	-0.796863	-0.978197	0.883388
12	6	-1.915662	-1.850496	0.510891
13	6	-2.081255	-3.237110	0.535909
14	1	-1.311796	-3.901577	0.903302
15	6	-3.257165	-3.785304	0.028896
16	1	-3.384305	-4.862676	0.049861
17	6	-4.260232	-2.986319	-0.518080
18	1	-5.162543	-3.444538	-0.908581
19	6	-4.092743	-1.607039	-0.586826
20	1	-4.842696	-0.962073	-1.031914
21	6	-2.927927	-1.056800	-0.078680
22	6	-2.491628	0.333771	-0.070699
23	6	-1.177749	0.382300	0.525414
24	6	-1.154036	2.626181	0.240321
25	6	-0.500051	3.872877	0.362488
26	1	0.480577	3.887856	0.827417
27	6	-1.103269	5.017209	-0.099609
28	1	-0.598321	5.972819	-0.002775
29	6	-2.380352	4.961531	-0.700854
30	1	-2.842420	5.873882	-1.063080
31	6	-3.036326	3.761665	-0.830489
32	1	-4.016099	3.689722	-1.290097
33	6	-2.440802	2.568806	-0.364193
34	7	0.243955	-1.262306	1.703896
35	7	-3.119277	1.385298	-0.510101
36	7	-0.517185	1.499407	0.689635
37	1	0.534925	-0.214280	-1.678668
38	1	2.553624	-1.820158	-0.001842
39	7	0.408055	-2.272609	-1.345090
40	8	0.824252	-3.264132	-0.729177
41	8	-0.474098	-2.329450	-2.195184
42	6	3.011246	0.285938	-0.375809
43	6	4.374332	0.095884	-0.125243
44	6	2.558689	1.578428	-0.671177
45	6	5.264948	1.163882	-0.176459
46	1	4.742446	-0.903470	0.092081
47	6	3.448462	2.642777	-0.724475
48	1	1.500560	1.755153	-0.832339
49	6	4.805129	2.441362	-0.476959
50	1	6.319792	0.994175	0.014100
51	1	3.077612	3.636707	-0.954902
52	1	5.498254	3.275329	-0.516369
53	16	1.750000	-2.437259	3.522751

Cartesian coordinates of **TS exo-6a** at wB97xD/6-31G(d,p)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-1.604038	1.561495	2.201772
2	1	-2.152336	2.093037	1.424464
3	1	-0.990250	2.251817	2.780653
4	6	-2.474633	-0.909839	2.413608
5	1	-3.369435	-1.193717	1.851626
6	1	-2.259793	-1.688436	3.149153
7	6	-1.306602	-0.691852	1.501125
8	1	-0.633252	-1.512357	1.278098
9	6	-1.868201	-0.600021	-0.606830
10	6	-0.675843	-0.208390	-1.184095
11	6	0.403375	0.829936	0.945050
12	6	0.881001	2.157176	0.537484
13	6	0.240555	3.390853	0.394638
14	1	-0.803354	3.527958	0.650573
15	6	0.960979	4.475457	-0.100336
16	1	0.463912	5.434263	-0.207585
17	6	2.301853	4.351235	-0.467011
18	1	2.835906	5.212013	-0.854968
19	6	2.949124	3.125920	-0.342509
20	1	3.988229	2.998393	-0.626307
21	6	2.239088	2.045514	0.157057
22	6	2.672712	0.669659	0.381585
23	6	1.545967	-0.073494	0.879069
24	6	2.846887	-1.904130	1.057018
25	6	3.014919	-3.268774	1.383646
26	1	2.151561	-3.809037	1.755944
27	6	4.233610	-3.875583	1.212729
28	1	4.355282	-4.925794	1.457402
29	6	5.335780	-3.145921	0.711005
30	1	6.291875	-3.641884	0.579600
31	6	5.200570	-1.819533	0.386501
32	1	6.027621	-1.236372	-0.003651
33	6	3.956648	-1.168533	0.549751
34	7	-0.741243	0.532569	1.603566
35	7	3.858132	0.157341	0.222504
36	7	1.617311	-1.330205	1.230902
37	1	-2.055486	-1.669315	-0.580459
38	1	-0.465944	0.736245	-1.660627
39	7	0.313555	-1.193102	-1.465718
40	8	0.145175	-2.341108	-1.049651
41	8	1.311539	-0.827951	-2.085073
42	6	-3.054211	0.277569	-0.617326
43	6	-4.321695	-0.272450	-0.392636
44	6	-2.962544	1.659361	-0.840202
45	6	-5.457447	0.530302	-0.364411
46	1	-4.419092	-1.346384	-0.257025
47	6	-4.096602	2.461080	-0.813057
48	1	-1.995622	2.116622	-1.030204
49	6	-5.348858	1.901421	-0.568175
50	1	-6.429015	0.080297	-0.188438
51	1	-4.002125	3.528250	-0.987901
52	1	-6.233067	2.529672	-0.545521
53	16	-2.754438	0.670093	3.289101

## Experimental section

**General procedure for preparation of spiropyrrothiazole 5(a–n):** A mixture of ninhydrin **1** (0.178 g, 1 mmol), 1,2-phenylenediamine **2** (0.108 g, 1 mmol), thiazolidin-4-carboxylic acid **3** (0.133 g, 1 mmol) and trans- $\beta$ -nitrostyrene **4a** (0.149 g, 1 mmol) was heated under reflux for about 5 h (the progress of the reaction was monitored by TLC). After completion, the reaction mixture was filtered and the precipitated solid was washed with 3 mL cold ethanol (70%) to afford pure product **5a-n**.

## Spectroscopic data of synthesized compounds

### 7'-nitro-6'-(phenyl)-3',6',7',7a'-tetrahydro-1'H-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c]thiazole]

#### (5a)

Gray solid (0.38 g, 85%); **mp**: 236-238°C. **IR** (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1548, 1373. **<sup>1</sup>H NMR** (400MHz, CDCl<sub>3</sub>),  $\delta_{\text{H}}$ : 8.16-8.21 (m, 2H, ArH), 8.05 (d, 1H,  $J=7.6$  Hz, ArH), 7.69-8.00 (m, 4H, ArH), 7.65 (td, 1H,  $J=7.6, 0.8$  Hz, ArH), 6.89 (dd, 1H,  $J=11.2, 7.2$  Hz, H<sub>b</sub>), 6.85 (d, 1H,  $J=7.2$  Hz, ArH), 6.79 (t, 2H,  $J=7.2$  Hz, ArH), 6.69 (d, 2H,  $J=7.2$  Hz, ArH), 4.88 (q, 1H,  $J=7.2$  Hz, H<sub>c</sub>), 4.75 (d, 1H,  $J=11.2$  Hz, H<sub>a</sub>), 4.05 (1/2ABq, 1H,  $J=9.6$  Hz, N-CH<sub>f</sub>), 3.91 (1/2ABq, 1H,  $J=9.6$  Hz, N-CH<sub>g</sub>), 3.23 (ABq d, 1H,  $J=10.4$  Hz, H<sub>d</sub>), 3.09 (ABq d, 1H,  $J=10.4$  Hz, H<sub>e</sub>) ppm. **<sup>13</sup>C NMR** (100MHz, CDCl<sub>3</sub>),  $\delta_{\text{C}}$ : 161.8, 152.3, 143.0, 142.3, 141.2, 138.5, 132.1, 131.6, 130.9, 129.9, 129.5, 129.2, 129.1, 128.0, 127.8, 126.1, 122.5, 85.7, 75.3 (spiro carbon), 68.2, 56.5, 54.3, 33.5 ppm. **MS**:  $m/z = 453$  [ $\text{M}^+ + 1$ ]; Anal. Calcd. For C<sub>26</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>S: C, 69.01; H, 4.45; N, 12.38. Found: C, 69.12; H, 4.37; N, 12.45.

### 7'-nitro-6'-(p-tolyl)-3',6',7',7a'-tetrahydro-1'H-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c]thiazole]

#### (5b)

Gray solid (0.33 g, 70%); **mp**: 223-225°C. **IR** (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1547, 1371. **<sup>1</sup>H NMR** (400MHz, CDCl<sub>3</sub>),  $\delta_{\text{H}}$ : 7.70-8.20 (m, 7H, ArH), 7.64 (td, 1H,  $J=7.2, 1.2$  Hz, ArH), 6.86 (dd, 1H,  $J=11.2, 7.2$  Hz, H<sub>b</sub>), 6.56-6.61 (m, 4H, ArH), 4.87 (q, 1H,  $J=7.2$  Hz, H<sub>c</sub>), 4.71 (d, 1H,  $J=11.6$  Hz, H<sub>a</sub>), 4.04 (1/2ABq, 1H,  $J=9.6$  Hz, N-CH<sub>f</sub>), 3.91 (1/2ABq, 1H,  $J=9.6$  Hz, N-CH<sub>g</sub>), 3.22 (ABq d, 1H,  $J=10.4$  Hz, H<sub>d</sub>), 3.08 (ABq d, 1H,  $J=10.4$  Hz, H<sub>e</sub>), 1.99 (s, 3H, Ar-CH<sub>3</sub>) ppm. **<sup>13</sup>C NMR** (100MHz, CDCl<sub>3</sub>),  $\delta_{\text{C}}$ : 162.0, 143.1, 142.3, 141.3, 138.5, 137.5, 132.1, 130.8, 129.9, 129.5, 129.2, 129.0, 128.7, 128.5, 127.7, 126.1, 122.4, 85.9, 75.2 (spiro carbon), 68.1, 56.3, 54.3, 33.4, 20.8 ppm. **MS**:  $m/z = 466$  [ $\text{M}^+$ ]; Anal. Calcd. For C<sub>27</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>S: C, 69.51; H, 4.75; N, 12.01. Found: C, 69.63; H, 4.84; N, 11.91.

### 6'-(4-methoxyphenyl)-7'-nitro-3',6',7',7a'-tetrahydro-1'H-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c]thiazole] (5c)

Cream solid (0.42g, 87%); **mp**: 231-233°C. **IR** (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1543, 1374, 1253, 1029. **<sup>1</sup>H NMR** (400MHz, CDCl<sub>3</sub>),  $\delta_{\text{H}}$ : 7.71-8.19 (m, 7H, ArH), 7.64 (td, 1H,  $J=7.6, 0.8$  Hz, ArH), 6.82 (dd, 1H,  $J=11.2, 7.2$  Hz, H<sub>b</sub>), 6.62 (d, 2H,  $J=8.8$  Hz, ArH), 6.32 (d, 2H,  $J=8.8$  Hz, ArH), 4.86 (q, 1H,  $J=7.2$  Hz, H<sub>c</sub>), 4.69 (d, 1H,  $J=11.2$  Hz, H<sub>a</sub>), 4.04 (1/2ABq, 1H,  $J=9.6$  Hz, N-CH<sub>f</sub>), 3.91 (1/2ABq, 1H,  $J=9.6$  Hz, N-CH<sub>g</sub>), 3.51 (s, 3H, Ar-OCH<sub>3</sub>), 3.21 (ABq d, 1H,



$J=10.4$  Hz,  $H_d$ ), 3.09 (ABq d, 1H,  $J=10.4$  Hz,  $H_e$ ), ppm.  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{C}}$ : 162.0, 158.8, 152.4, 143.2, 142.4, 141.3, 138.5, 132.1, 130.8, 129.9, 129.5, 129.2, 129.1, 129.0, 126.1, 123.5, 122.4, 113.4, 86.1, 75.3 (spiro carbon), 68.1, 56.1, 54.9, 54.2, 33.4 ppm. **MS**:  $m/z = 483$  [ $\text{M}^+ + 1$ ]; Anal. Calcd. For  $\text{C}_{27}\text{H}_{22}\text{N}_4\text{O}_3\text{S}$ : C, 67.20; H, 4.60; N, 11.61. Found: C, 67.32; H, 4.54; N, 11.65.

**4-(7'-nitro-3',6',7',7a'-tetrahydro-1'H-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c]thiazol]-6'-yl)benzotrile (5d)**

Gray solid (0.35g, 75%); **mp**: 246-248°C. **IR** (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 2227, 1546, 1373.  $^1\text{H NMR}$  (400MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{H}}$ : 8.21 (d, 1H,  $J=7.6$  Hz, ArH), 8.14-8.16 (m, 1H, ArH), 8.07 (d, 1H,  $J=7.6$  Hz, ArH), 7.73-8.03 (m, 5H, ArH), 7.11 (d, 2H,  $J=8.4$  Hz, ArH), 6.92 (dd, 1H,  $J=11.2, 7.6$  Hz,  $H_b$ ), 6.83 (d, 2H,  $J=8.4$  Hz, ArH), 4.88 (q, 1H,  $J=7.6$  Hz,  $H_c$ ), 4.76 (d, 1H,  $J=11.2$  Hz,  $H_a$ ), 4.04 (1/2ABq, 1H,  $J=9.6$  Hz, N- $\text{CH}_f$ ), 3.91 (1/2ABq, 1H,  $J=9.6$  Hz, N- $\text{CH}_g$ ), 3.25 (ABq d, 1H,  $J=10.8$  Hz,  $H_d$ ), 3.04 (ABq d, 1H,  $J=10.8$  Hz,  $H_e$ ) ppm.  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{C}}$ : 161.1, 152.0, 142.4, 142.1, 141.1, 138.5, 137.4, 132.3, 131.7, 131.3, 130.3, 129.6, 129.3, 128.5, 126.1, 122.7, 117.9, 111.9, 85.3, 75.2 (spiro carbon), 68.0, 56.1, 54.5, 33.6 ppm. **MS**:  $m/z = 477$  [ $\text{M}^+$ ]; Anal. Calcd. For  $\text{C}_{27}\text{H}_{19}\text{N}_5\text{O}_2\text{S}$ : C, 67.91; H, 4.01; N, 14.67. Found: C, 68.02; H, 4.10; N, 14.60.

**7'-nitro-6'-(2-nitrophenyl)-3',6',7',7a'-tetrahydro-1'H-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c]thiazole] (5e)**

Gray solid (0.44g, 88%); **mp**: 230-232°C. **IR** (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1551, 1370.  $^1\text{H NMR}$  (400MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{H}}$ : 8.19 (d, 1H,  $J=8.4$  Hz, ArH), 7.63-8.05 (m, 7H, ArH), 7.39 (d, 1H,  $J=7.2$  Hz, ArH), 7.31 (d, 1H,  $J=7.6$  Hz, ArH), 6.96-7.03 (m, 2H, ArH), 6.86 (dd, 1H,  $J=10.8, 7.2$  Hz,  $H_b$ ), 5.94 (d, 1H,  $J=10.8$  Hz,  $H_a$ ), 4.92 (q, 1H,  $J=7.2$  Hz,  $H_c$ ), 4.00 (1/2ABq, 1H,  $J=9.6$  Hz, N- $\text{CH}_f$ ), 3.84 (1/2ABq, 1H,  $J=9.6$  Hz, N- $\text{CH}_g$ ), 3.28 (ABq d, 1H,  $J=10.4$  Hz,  $H_d$ ), 3.12 (t, 1H,  $J=10$  Hz,  $H_e$ ) ppm.  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{C}}$ : 161.2, 153.8, 150.3, 143.5, 142.4, 140.9, 140.8, 137.8, 132.7, 131.2, 130.2, 130.1, 129.4, 129.3, 129.2, 128.7, 127.0, 125.8, 124.8, 122.4, 85.9, 75.3 (spiro carbon), 68.1, 53.6, 48.8, 33.4 ppm. **MS**:  $m/z = 451$  [ $\text{M}^+ - \text{NO}_2$ ]; Anal. Calcd. For  $\text{C}_{26}\text{H}_{19}\text{N}_5\text{O}_4\text{S}$ : C, 62.77; H, 3.85; N, 14.08. Found: C, 62.90; H, 3.93; N, 14.00.

**6'-(4-bromophenyl)-7'-nitro-3',6',7',7a'-tetrahydro-1'H-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c]thiazole] (5f)**

Gray solid (0.44g, 83%); **mp**: 256-257°C. **IR** (KBr) ( $\nu_{\text{max}}/\text{cm}^{-1}$ ): 1544, 1374, 1071.  $^1\text{H NMR}$  (400MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{H}}$ : 8.19 (d, 1H,  $J=8$  Hz, ArH), 7.64-8.17 (m, 7H, ArH), 6.94 (d, 2H,  $J=8.8$  Hz, ArH), 6.85 (dd, 1H,  $J=11.2, 7.6$  Hz,  $H_b$ ), 6.59 (d, 2H,  $J=8.4$  Hz, ArH), 4.87 (q, 1H,  $J=7.6$  Hz,  $H_c$ ), 4.69 (d, 1H,  $J=11.2$  Hz,  $H_a$ ), 4.02 (1/2ABq, 1H,  $J=9.6$  Hz, N- $\text{CH}_f$ ), 3.91 (1/2ABq, 1H,  $J=9.6$  Hz, N- $\text{CH}_g$ ), 3.23 (ABq d, 1H,  $J=10.8$  Hz,  $H_d$ ), 3.06 (ABq d, 1H,  $J=10.8$  Hz,  $H_e$ ) ppm.  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{C}}$ : 161.5, 152.2, 142.6, 142.4, 141.2, 138.5, 132.2, 131.2, 131.0, 130.9, 130.1,

129.5, 129.42, 129.41, 129.2, 126.1, 122.6, 122.0, 85.7, 75.1 (spiro carbon), 68.0, 56.0, 54.4, 33.5 ppm. **MS**:  $m/z = 532 [M^+ + 1]$ ; Anal. Calcd. For  $C_{26}H_{19}BrN_4O_2S$ : C, 58.76; H, 3.60; N, 10.54. Found: C, 58.87; H, 3.52; N, 10.61.

**6'-(4-chlorophenyl)-7'-nitro-3',6',7',7a'-tetrahydro-1'H-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c]thiazole] (5g)**

Gray solid (0.45g, 93%); **mp**: 246-248°C. **IR** (KBr) ( $\nu_{max}/cm^{-1}$ ): 1542, 1374, 1098. **<sup>1</sup>H NMR** (400MHz,  $CDCl_3$ ),  $\delta_H$ : 8.19 (d, 1H,  $J=8$  Hz, ArH), 7.73-8.17 (m, 6H, ArH), 7.65 (td, 1H,  $J=7.6, 0.8$  Hz, ArH), 6.85 (dd, 1H,  $J=11.2, 7.2$  Hz,  $H_b$ ), 6.79 (d, 2H,  $J=8.4$  Hz, ArH), 6.65 (d, 2H,  $J=8.4$  Hz, ArH), 4.87 (q, 1H,  $J=7.2$  Hz,  $H_c$ ), 4.71 (d, 1H,  $J=11.2$  Hz,  $H_a$ ), 4.03 (1/2ABq, 1H,  $J=9.6$  Hz, N- $CH_f$ ), 3.91 (1/2ABq, 1H,  $J=9.6$  Hz, N- $CH_g$ ), 3.23 (ABq d, 1H,  $J=10.4$  Hz,  $H_d$ ), 3.06 (ABq d, 1H,  $J=10.4$  Hz,  $H_e$ ) ppm. **<sup>13</sup>C NMR** (100MHz,  $CDCl_3$ ),  $\delta_C$ : 161.5, 152.2, 142.6, 142.4, 141.2, 138.6, 133.8, 132.2, 131.0, 130.4, 130.1, 129.4, 129.2, 129.2, 128.2, 126.1, 122.6, 85.8, 75.1 (spiro carbon), 68.0, 55.9, 54.3, 33.5 ppm. **MS**:  $m/z = 486 [M^+]$ ; Anal. Calcd. For  $C_{26}H_{19}ClN_4O_2S$ : C, 64.13; H, 3.93; N, 11.51. Found: C, 64.26; H, 4.03; N, 11.41.

**6'-(2-methoxyphenyl)-7'-nitro-3',6',7',7a'-tetrahydro-1'H-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c]thiazole] (5h)**

Cream solid (0.41g, 85%); **mp**: 234-236°C. **IR** (KBr) ( $\nu_{max}/cm^{-1}$ ): 1550, 1369, 1251, 1022. **<sup>1</sup>H NMR** (400MHz,  $CDCl_3$ ),  $\delta_H$ : 8.18 (d, 1H,  $J=7.6$  Hz, ArH), 8.15-8.16 (m, 1H, ArH), 8.02 (d, 1H,  $J=7.6$  Hz, ArH), 7.67-7.99 (m, 4H, ArH), 7.58 (t, 1H,  $J=7.2$  Hz, ArH), 6.97 (dd, 1H,  $J=7.6, 1.2$  Hz, ArH), 6.83 (dd, 1H,  $J=11.6, 7.2$  Hz,  $H_b$ ), 6.79 (dd, 1H,  $J=7.6, 1.2$  Hz, ArH), 6.35-6.40 (m, 2H, ArH), 5.39 (d, 1H,  $J=11.2$  Hz,  $H_a$ ), 4.87 (q, 1H,  $J=6.8$  Hz,  $H_c$ ), 4.03 (1/2ABq, 1H,  $J=9.2$  Hz, N- $CH_f$ ), 3.86 (1/2ABq, 1H,  $J=8.8$  Hz, N- $CH_g$ ), 3.22 (ABq d, 1H,  $J=10.4$  Hz,  $H_d$ ), 3.19 (s, 3H, Ar- $OCH_3$ ), 3.11 (t, 1H,  $J=10$  Hz,  $H_e$ ) ppm. **<sup>13</sup>C NMR** (100MHz,  $CDCl_3$ ),  $\delta_C$ : 162.3, 157.3, 152.5, 143.9, 142.2, 141.1, 137.9, 131.3, 130.2, 129.7, 129.5, 129.0, 128.99, 128.97, 128.7, 126.9, 121.8, 120.3, 119.7, 110.4, 86.0, 74.8 (spiro carbon), 68.5, 54.7, 53.6, 49.2, 33.2 ppm. **MS**:  $m/z = 483 [M^+ + 1]$ ; Anal. Calcd. For  $C_{27}H_{22}N_4O_3S$ : C, 67.20; H, 4.60; N, 11.61. Found: C, 67.26; H, 4.67; N, 11.51.

**6'-(4-fluorophenyl)-7'-nitro-3',6',7',7a'-tetrahydro-1'H-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c]thiazole] (5i)**

Cream solid (0.38g, 82%); **mp**: 240-242°C. **IR** (KBr) ( $\nu_{max}/cm^{-1}$ ): 1549, 1374, 1231. **<sup>1</sup>H NMR** (400MHz,  $CDCl_3$ ),  $\delta_H$ : 8.16-8.18 (m, 2H, ArH), 8.07 (d, 1H,  $J=7.6$  Hz, ArH), 7.64-8.02 (m, 5H, ArH), 6.84 (dd, 1H,  $J=11.2, 7.2$  Hz,  $H_b$ ), 6.68 (dd, 2H,  $J=8.8, 5.2$  Hz, ArH), 6.50 (t, 2H,  $J=8.8$  Hz, ArH), 4.87 (q, 1H,  $J=7.2$  Hz,  $H_c$ ), 4.72 (d, 1H,  $J=11.2$  Hz,  $H_a$ ), 4.04 (1/2ABq, 1H,  $J=9.6$  Hz, N- $CH_f$ ), 3.91 (1/2ABq, 1H,  $J=9.6$  Hz, N- $CH_g$ ), 3.22 (ABq d, 1H,  $J=10.8$  Hz,  $H_d$ ), 3.08 (ABq d, 1H,  $J=10.4$  Hz,  $H_e$ ) ppm. **<sup>13</sup>C NMR** (100MHz,  $CDCl_3$ ),  $\delta_C$ : 163.2, 161.7, 160.8, 152.2, 142.8, 142.4, 141.2, 138.5, 132.2, 131.0, 130.1, 129.5, 129.45, 129.40, 129.3, 129.2, 127.6, 127.5, 126.1, 122.6, 115.1, 114.9, 85.9, 75.2 (spiro carbon), 68.1, 55.9, 54.3, 33.5 ppm. **MS**:  $m/z = 471 [M^+ + 1]$ ; Anal. Calcd. For  $C_{26}H_{19}FN_4O_2S$ : C, 66.37; H, 4.07; N, 11.91. Found: C, 66.47; H, 4.18; N, 11.83.

**6'-(3-bromophenyl)-7'-nitro-3',6',7',7a'-tetrahydro-1'H-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c]thiazole] (5j)**

Cream solid (0.39g, 74%); **mp**: 237-238°C. **IR** (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1545, 1371, 1072. **<sup>1</sup>H NMR** (400MHz, CDCl<sub>3</sub>),  $\delta_{\text{H}}$ : 8.17 -8.21 (m, 2H, ArH), 8.07 (d, 1H,  $J=7.6$  Hz, ArH), 7.72 -8.02 (m, 4H, ArH), 7.66 (td, 1H,  $J=7.6, 1.2$  Hz, ArH), 6.97-7.00 (m, 1H, ArH), 6.89 (t, 1H,  $J=1.6$  Hz, ArH), 6.82 (dd, 1H,  $J=11.2, 7.2$  Hz, H<sub>b</sub>), 6.60 -6.68 (m, 2H, ArH), 4.88 (q, 1H,  $J=7.2$  Hz, H<sub>c</sub>), 4.69 (d, 1H,  $J=11.2$  Hz, H<sub>a</sub>), 4.03 (1/2ABq, 1H,  $J=9.6$  Hz, N-CH<sub>f</sub>), 3.91 (1/2ABq, 1H,  $J=9.6$  Hz, N-CH<sub>g</sub>), 3.23 (ABq d, 1H,  $J=10.8$  Hz, H<sub>d</sub>), 3.04 (ABq d, 1H,  $J=10.8$  Hz, H<sub>e</sub>) ppm. **<sup>13</sup>C NMR** (100MHz, CDCl<sub>3</sub>),  $\delta_{\text{C}}$ : 161.4, 152.2, 142.5, 142.4, 141.2, 138.5, 134.1, 132.3, 131.2, 131.1, 130.9, 130.1, 129.4, 129.1, 126.5, 126.0, 122.6, 122.0, 85.6, 75.2 (spiro carbon), 68.1, 56.2, 54.2, 33.5 ppm. **MS**:  $m/z = 531$  [M<sup>+</sup>]; Anal. Calcd. For C<sub>26</sub>H<sub>19</sub>BrN<sub>4</sub>O<sub>2</sub>S: C, 58.76; H, 3.60; N, 10.54. Found: C, 58.89; H, 3.70; N, 10.46.

**6'-(furan-2-yl)-7'-nitro-3',6',7',7a'-tetrahydro-1'H-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c]thiazole] (5k)**

Gray solid (0.35g, 80%); **mp**: 221-222°C. **IR** (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1553, 1372. **<sup>1</sup>H NMR** (400MHz, CDCl<sub>3</sub>),  $\delta_{\text{H}}$ : 7.70 - 8.16 (m, 7H, ArH), 7.66 (td, 1H,  $J=7.6, 1.2$  Hz, ArH), 6.80 (t, 1H,  $J=1.2$  Hz, furan), 6.70 (dd, 1H,  $J=10.4, 7.6$  Hz, H<sub>b</sub>), 5.81 (dd, 1H,  $J=3.2, 1.6$  Hz, furan), 5.54 (d, 1H,  $J=3.6$  Hz, furan), 4.91 (d, 1H,  $J=10.8$  Hz, H<sub>a</sub>), 4.89 (q, 1H,  $J=7.6$  Hz, H<sub>c</sub>), 3.91 (1/2ABq, 1H,  $J=9.2$  Hz, N-CH<sub>f</sub>), 3.86 (1/2ABq, 1H,  $J=9.2$  Hz, N-CH<sub>g</sub>), 3.20 (ABq d, 1H,  $J=10.4$  Hz, H<sub>d</sub>), 2.97 (ABq d, 1H,  $J=10.4$  Hz, H<sub>e</sub>) ppm. **<sup>13</sup>C NMR** (100MHz, CDCl<sub>3</sub>),  $\delta_{\text{C}}$ : 161.5, 152.4, 147.0, 142.9, 142.5, 142.1, 141.3, 138.4, 132.2, 130.9, 129.9, 129.7, 129.2, 129.1, 126.0, 122.5, 110.1, 107.9, 85.6, 73.8 (spiro carbon), 68.0, 53.3, 51.0, 33.1 ppm. **MS**:  $m/z = 443$  [M<sup>+</sup> + 1]; Anal. Calcd. For C<sub>24</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub>S: C, 65.14; H, 4.10; N, 12.66. Found: C, 65.20; H, 4.15; N, 12.61.

**7'-nitro-6'-(thiophen-2-yl)-3',6',7',7a'-tetrahydro-1'H-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c]thiazole] (5l)**

Cream solid (0.38g, 85%); **mp**: 228-230°C. **IR** (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1551, 1372. **<sup>1</sup>H NMR** (400MHz, CDCl<sub>3</sub>),  $\delta_{\text{H}}$ : 7.72-8.19 (m, 7H, ArH), 7.65 (t, 1H,  $J=7.2$  Hz, ArH), 6.75 (dd, 1H,  $J=4.8, 0.8$  Hz, thiophen), 6.70 (dd, 1H,  $J=10.8, 7.6$  Hz, H<sub>b</sub>), 6.49 (t, 1H,  $J=3.6$  Hz, thiophen), 6.45 (d, 1H,  $J=3.2$  Hz, thiophen), 5.04 (d, 1H,  $J=10.8$  Hz, H<sub>a</sub>), 4.90 (q, 1H,  $J=7.6$  Hz, H<sub>c</sub>), 3.94 (t, 2H,  $J=10$  Hz, N-CH<sub>f</sub>H<sub>g</sub>), 3.20 (ABq d, 1H,  $J=10.4$  Hz, H<sub>d</sub>), 3.03 (ABq d, 1H,  $J=10.8$  Hz, H<sub>e</sub>) ppm. **<sup>13</sup>C NMR** (100MHz, CDCl<sub>3</sub>),  $\delta_{\text{C}}$ : 161.6, 152.6, 142.6, 142.5, 141.3, 138.8, 134.6, 132.2, 131.0, 130.0, 129.6, 129.3, 129.2, 126.6, 126.3, 126.0, 125.3, 122.6, 88.0, 74.7 (spiro carbon), 67.8, 53.8, 53.0, 33.3 ppm. **MS**:  $m/z = 458$  [M<sup>+</sup>]; Anal. Calcd. For C<sub>24</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 62.86; H, 3.96; N, 12.22. Found: C, 62.95; H, 4.07; N, 12.14.

**6'-(naphthalen-1-yl)-7'-nitro-3',6',7',7a'-tetrahydro-1'H-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c]thiazole] (5m)**

Light green solid (0.36g, 73%); **mp**: 226-228°C. **IR** (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1544, 1374.  **$^1\text{H}$  NMR** (400MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{H}}$ : 8.38 (d, 1H,  $J=7.6$  Hz, ArH), 8.23 (d, 1H,  $J=8$  Hz, ArH), 7.91 (d, 1H,  $J=8$  Hz, ArH), 7.35-7.79 (m, 9H, ArH), 7.23 (t, 1H,  $J=7.2$  Hz, ArH), 7.11 (t, 1H,  $J=7.2$  Hz, ArH), 6.90 (t, 1H,  $J=7.6$  Hz, ArH), 6.81 (dd, 1H,  $J=10, 7.2$  Hz,  $\text{H}_b$ ), 5.83 (d, 1H,  $J=10.4$  Hz,  $\text{H}_a$ ), 5.06 (q, 1H,  $J=6.8$  Hz,  $\text{H}_c$ ), 4.04 (1/2ABq, 1H,  $J=8.8$  Hz, N- $\text{CH}_f$ ), 3.90 (1/2ABq, 1H,  $J=8.8$  Hz, N- $\text{CH}_g$ ), 3.29 (ABq d, 1H,  $J=10.4$  Hz,  $\text{H}_d$ ), 3.17 (t, 1H,  $J=10$  Hz,  $\text{H}_e$ ) ppm.  **$^{13}\text{C}$  NMR** (100MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{C}}$ : 161.7, 152.3, 143.6, 142.1, 141.0, 138.1, 133.4, 132.0, 131.8, 130.7, 129.9, 129.4, 129.2, 129.0, 128.5, 128.4, 128.3, 127.1, 126.1, 125.7, 125.3, 124.0, 122.5, 122.4, 88.0, 75.0 (spiro carbon), 68.5, 52.6, 51.7, 33.0 ppm. **MS**:  $m/z = 502$  [ $\text{M}^+$ ]; Anal. Calcd. For  $\text{C}_{30}\text{H}_{22}\text{N}_4\text{O}_2\text{S}$ : C, 71.69; H, 4.41; N, 11.15. Found: C, 71.79; H, 4.48; N, 11.08.

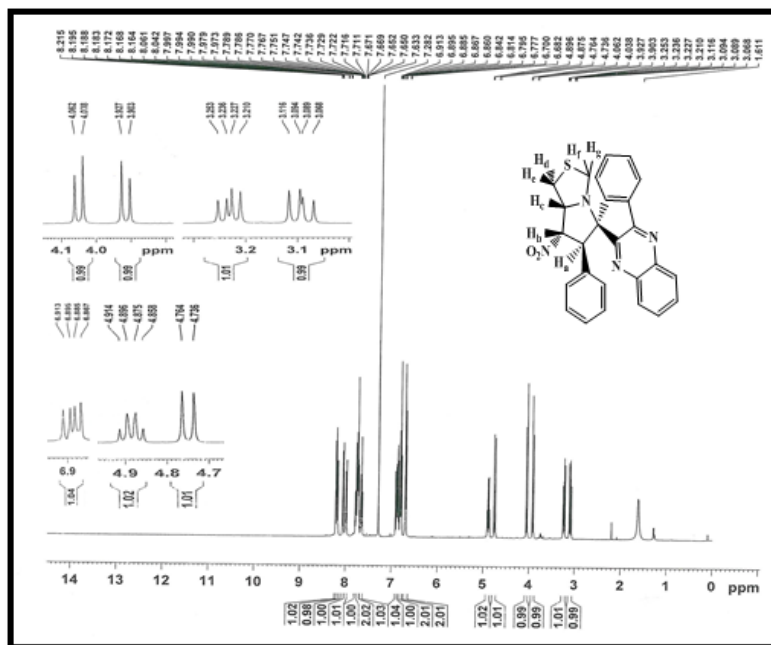


Fig. S1 . <sup>1</sup>H NMR spectrum of **5a** in CDCl<sub>3</sub>

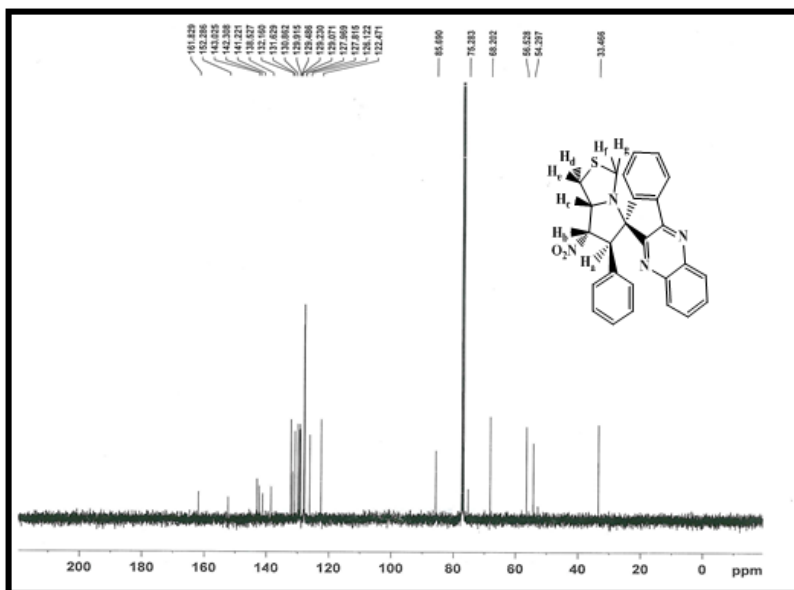


Fig. S2 . <sup>13</sup>C NMR spectrum of **5a** in CDCl<sub>3</sub>

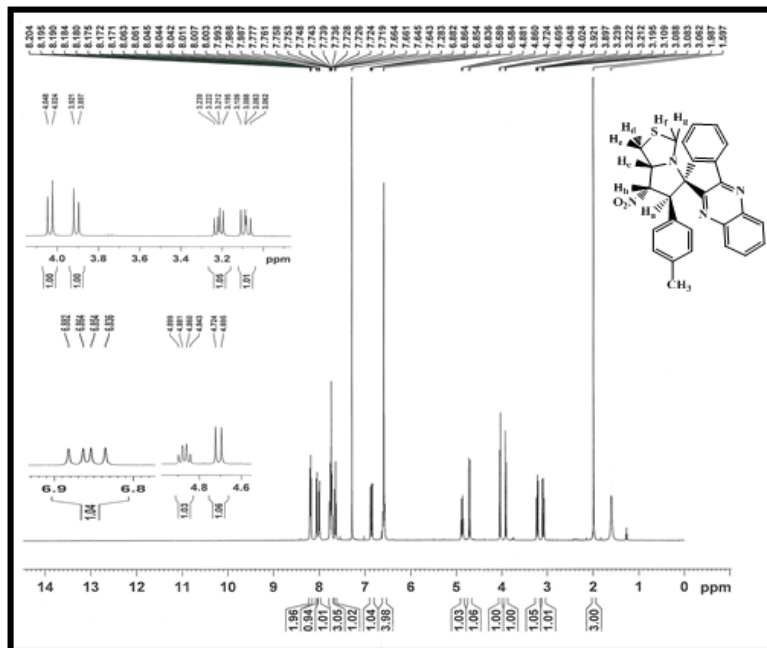


Fig. S3 . <sup>1</sup>H NMR spectrum of **5b** in CDCl<sub>3</sub>.

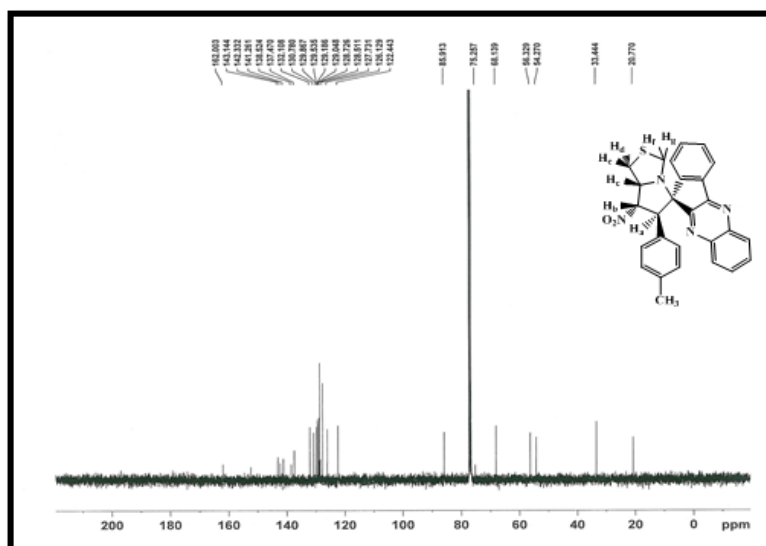


Fig. S4 . <sup>13</sup>C NMR spectrum of **5b** in CDCl<sub>3</sub>

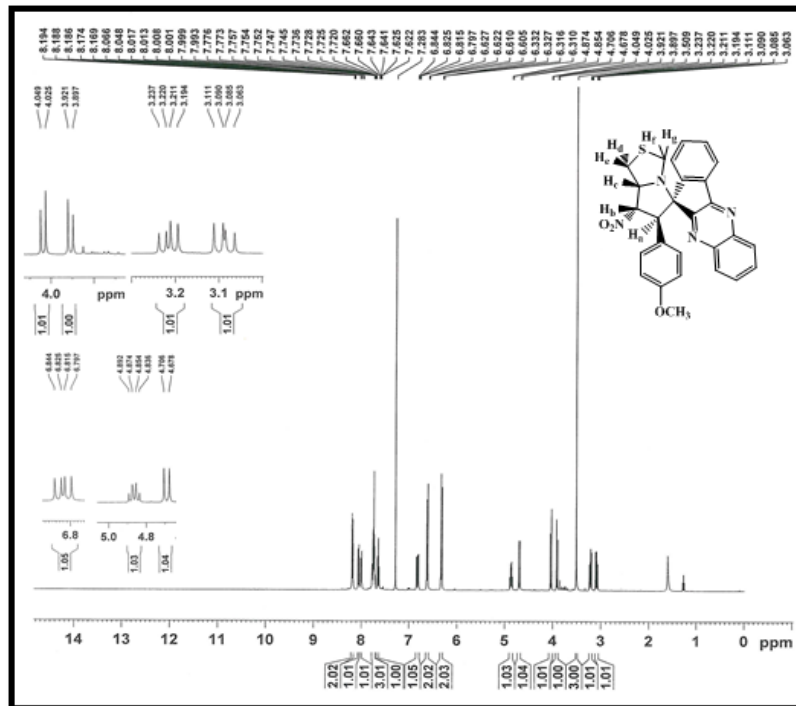


Fig. S5 .  $^1\text{H}$  NMR spectrum of **5c** in  $\text{CDCl}_3$

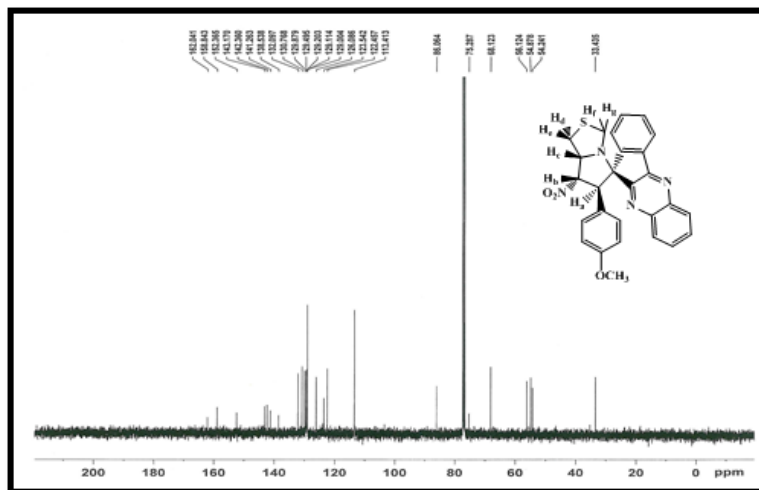


Fig. S6 .  $^{13}\text{C}$  NMR spectrum of **5c** in  $\text{CDCl}_3$







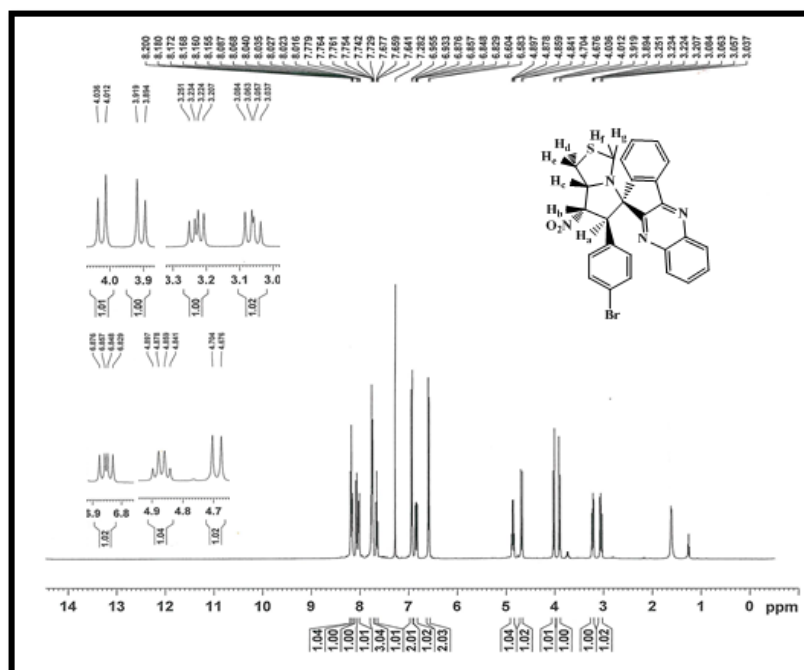


Fig. S11. <sup>1</sup>H NMR spectrum of **5f** in CDCl<sub>3</sub>

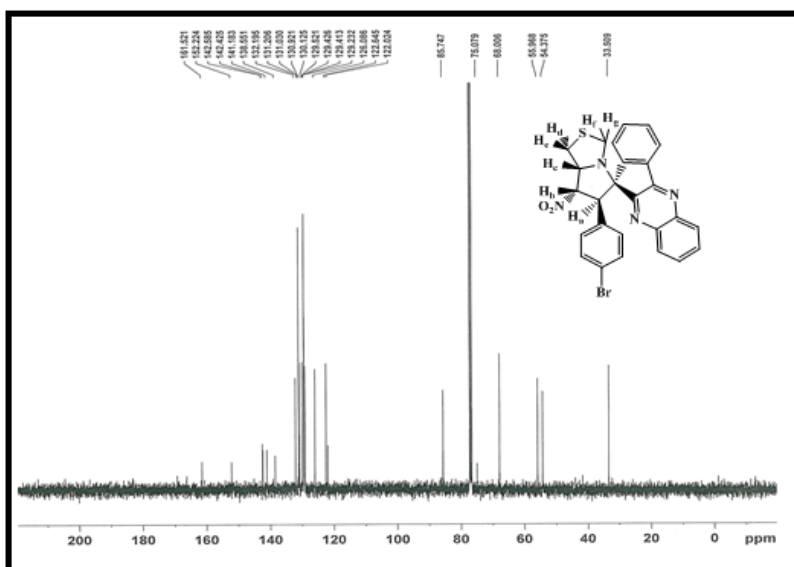


Fig. S12. <sup>13</sup>C NMR spectrum of **5f** in CDCl<sub>3</sub>

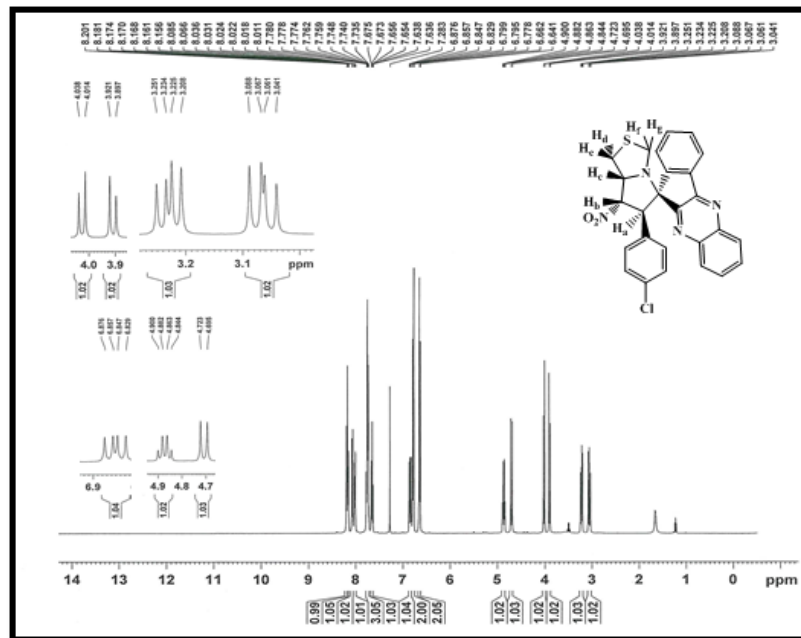


Fig. S13.  $^1H$  NMR spectrum of **5g** in CDCl<sub>3</sub>

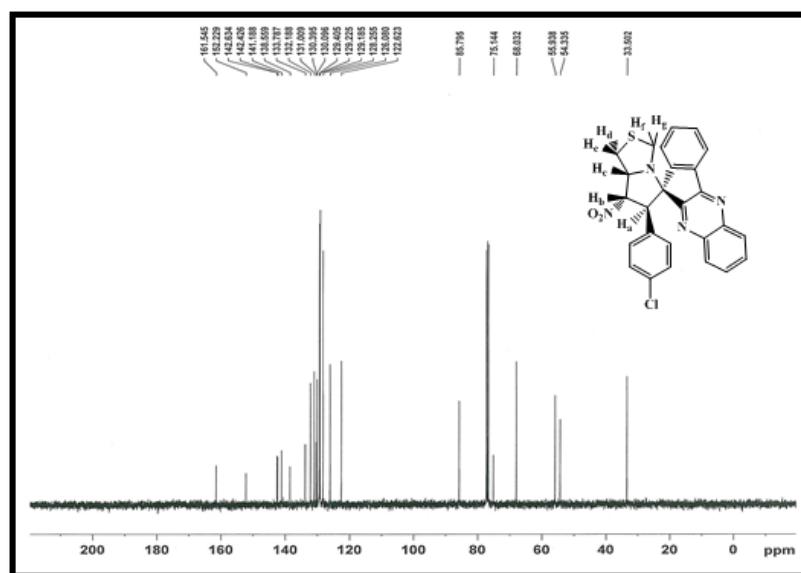


Fig. S14.  $^{13}C$  NMR spectrum of **5g** in CDCl<sub>3</sub>

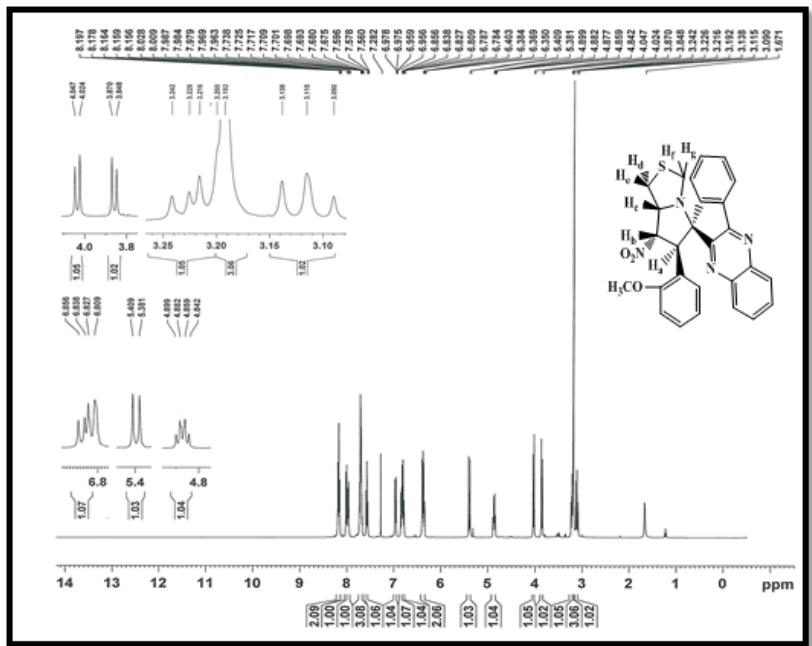


Fig. S15. <sup>1</sup>H NMR spectrum of **5h** in CDCl<sub>3</sub>

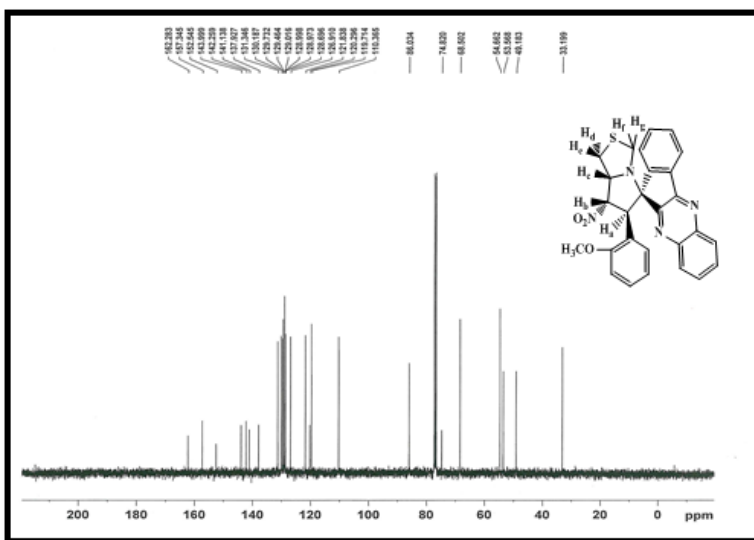


Fig. S16. <sup>13</sup>C NMR spectrum of **5h** in CDCl<sub>3</sub>

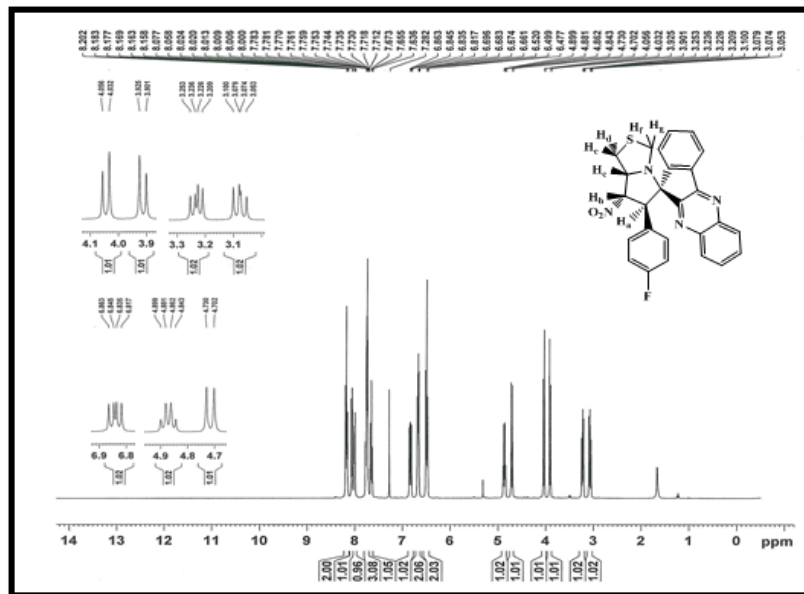


Fig. S17. <sup>1</sup>H NMR spectrum of **5i** in CDCl<sub>3</sub>

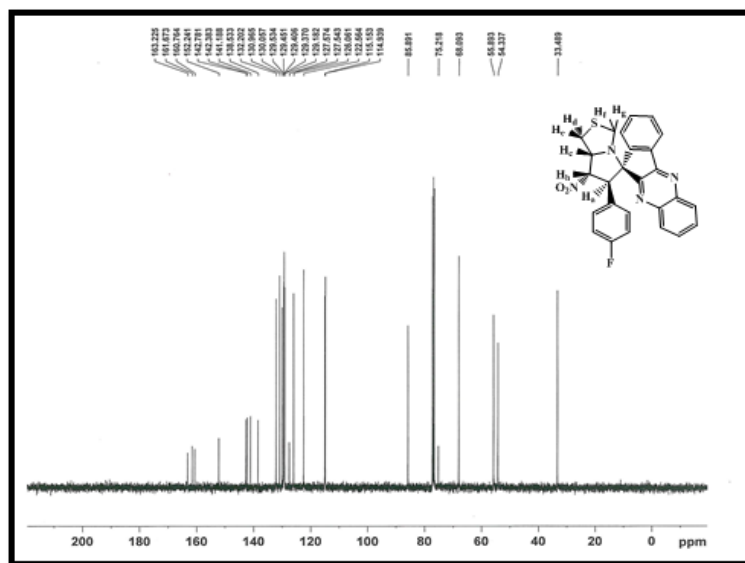


Fig. S18. <sup>13</sup>C NMR spectrum of **5i** in CDCl<sub>3</sub>

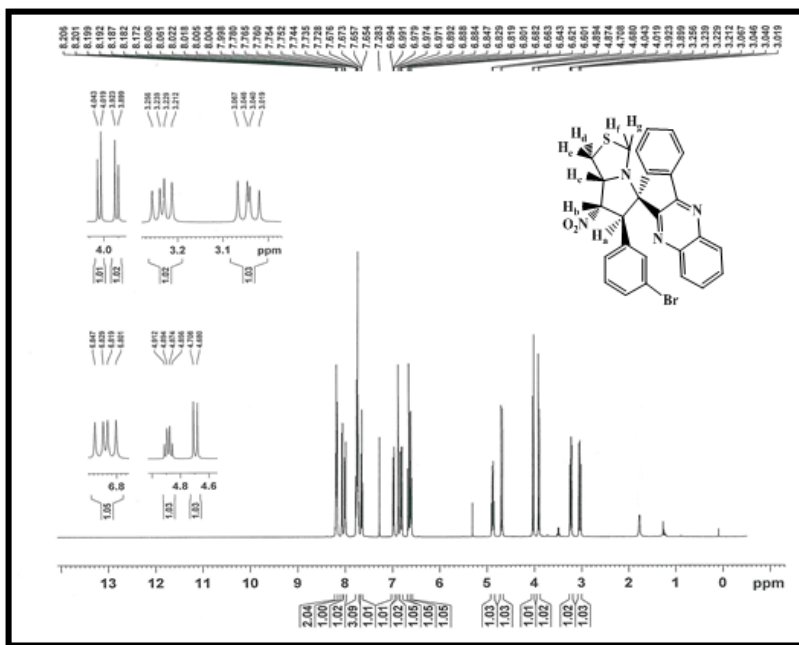


Fig. S19. <sup>1</sup>H NMR spectrum of **5j** in CDCl<sub>3</sub>

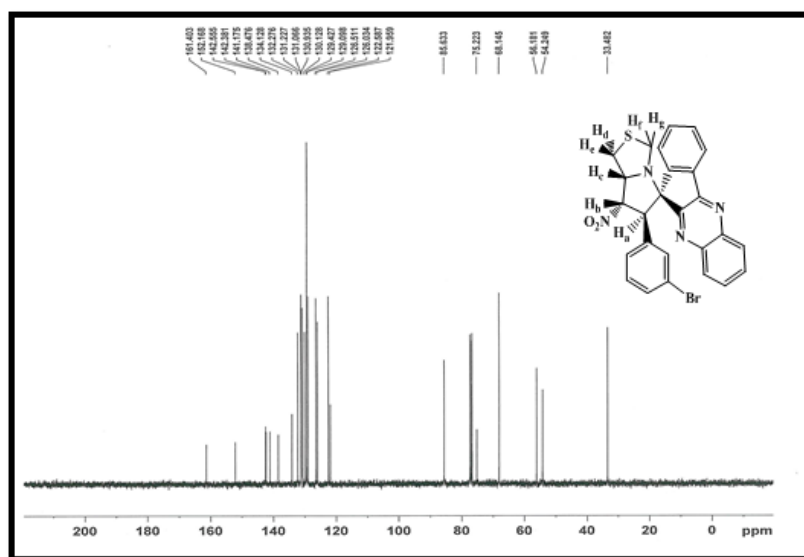


Fig. S20. <sup>13</sup>C NMR spectrum of **5j** in CDCl<sub>3</sub>

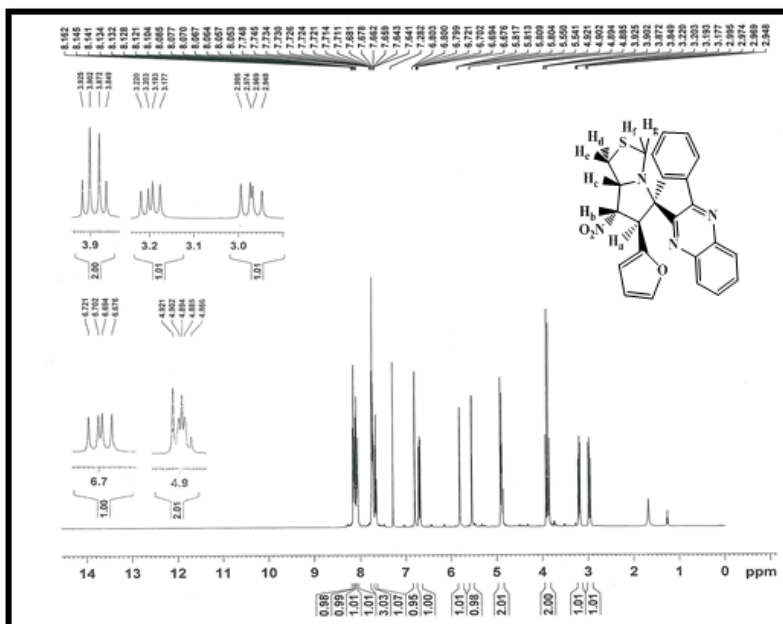


Fig. S21.  $^1H$  NMR spectrum of **5k** in  $CDCl_3$

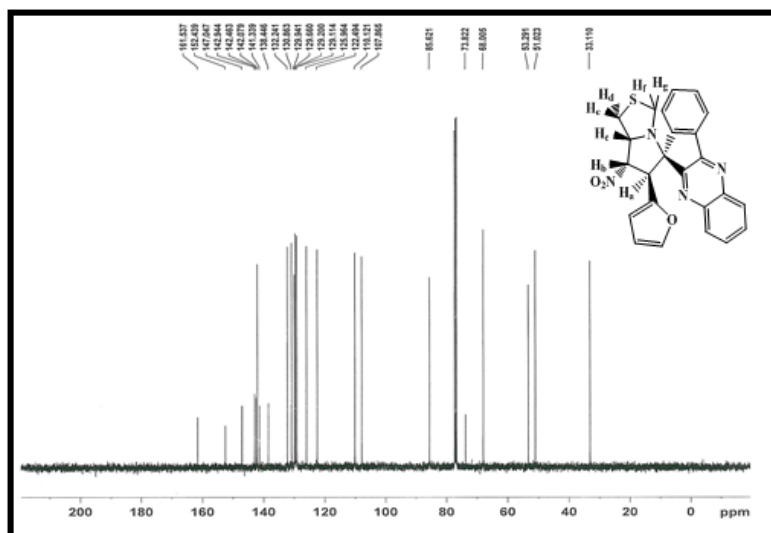
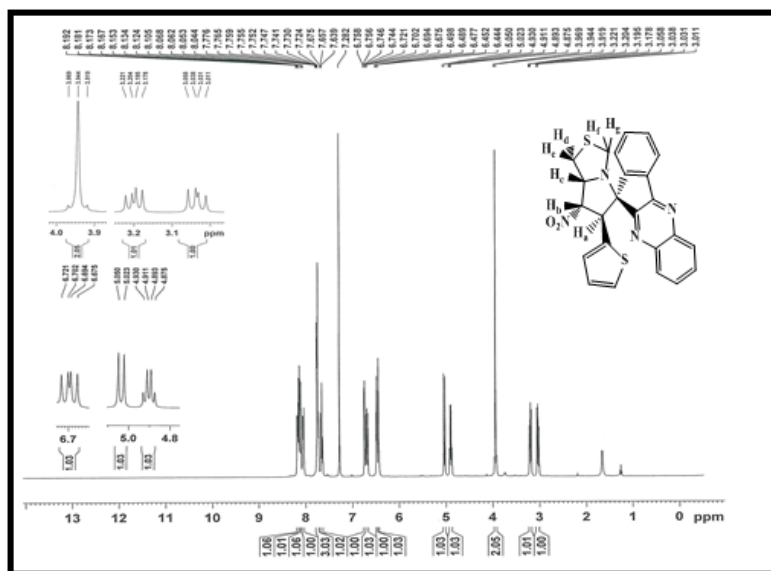


Fig. S22.  $^{13}C$  NMR spectrum of **5k** in  $CDCl_3$





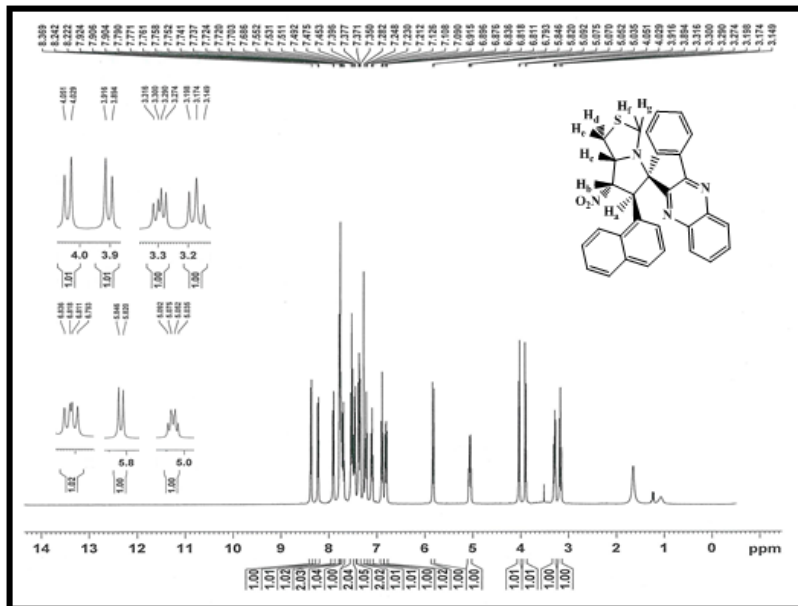


Fig. S25.  $^{13}\text{C}$  NMR spectrum of **5m** in  $\text{CDCl}_3$

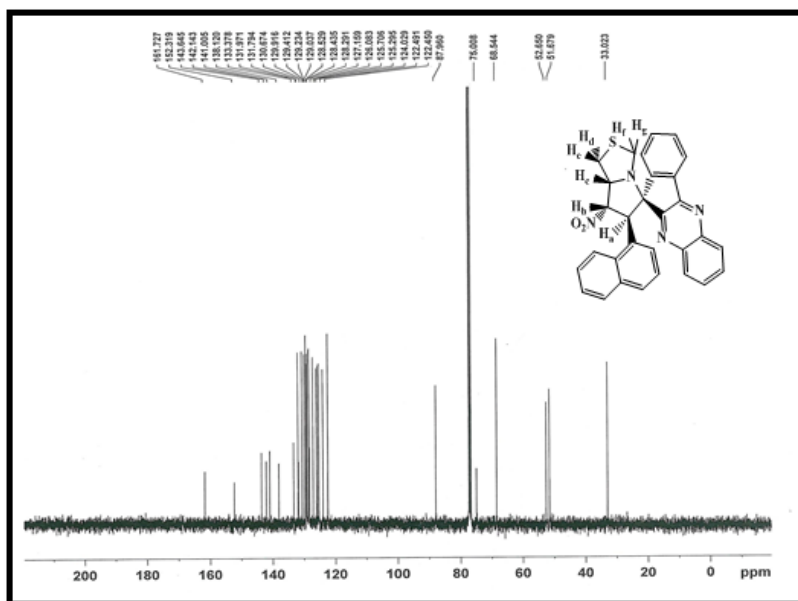


Fig. S26.  $^{13}\text{C}$  NMR spectrum of **5m** in  $\text{CDCl}_3$