Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

ESI

Structure-Property Studies of P-Triarylamine-Substituted Dithieno[3,2-*b*:2',3'-*d*]phospholes

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Content

A. NMR Spectra

A.1 Proton and carbon spectra

Figure S1. Proton NMR spectrum of compound **3a**.

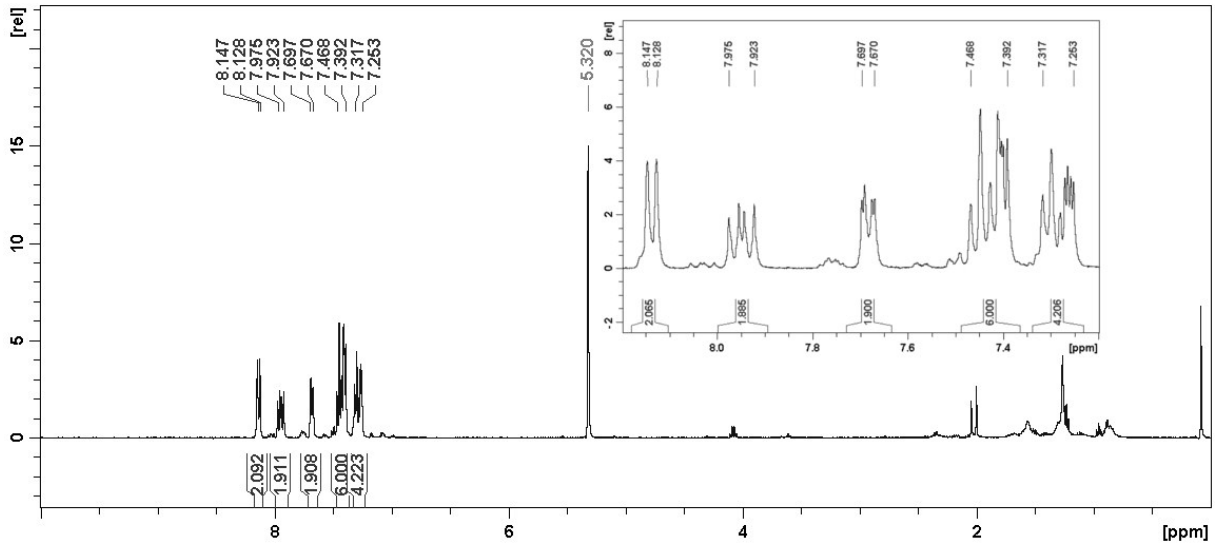


Figure S2. Carbon NMR spectrum of compound **3a**.

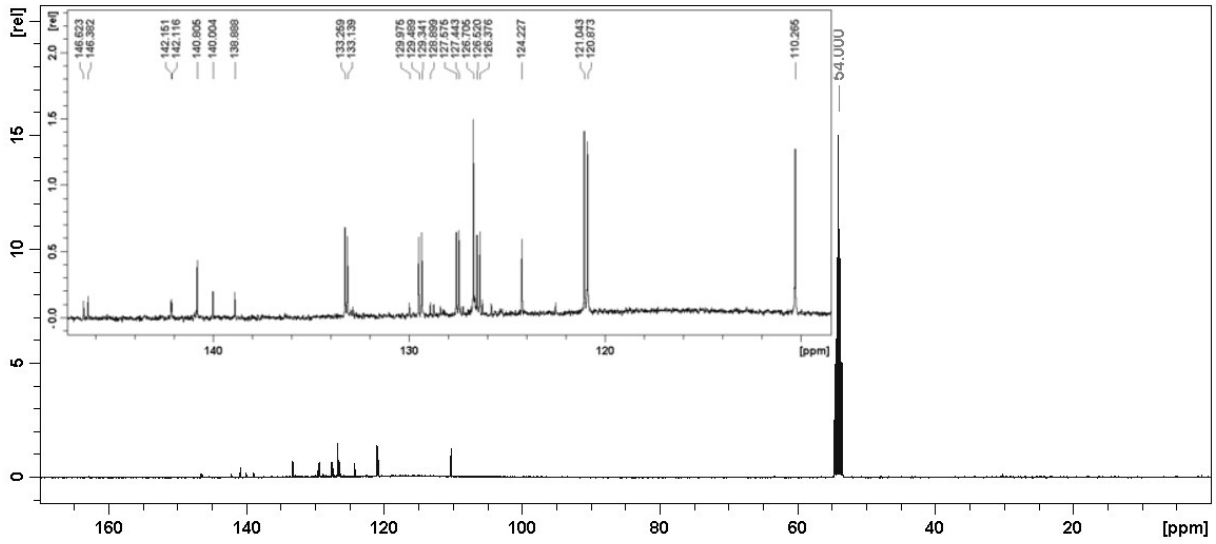


Figure S3. Proton NMR spectrum of compound **3ai**.

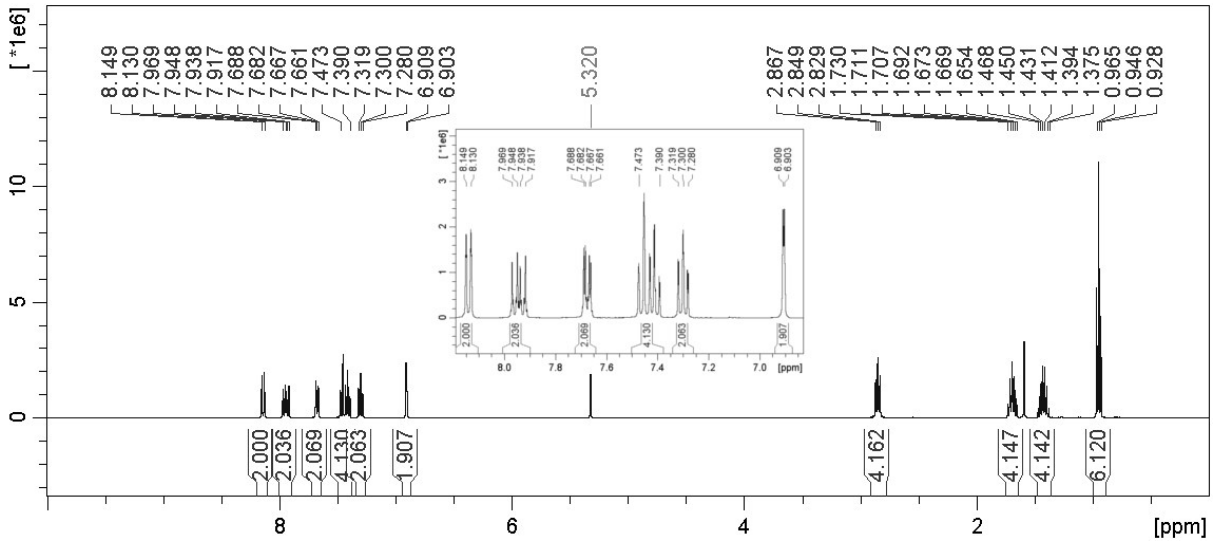


Figure S4. Carbon NMR spectrum of compound **3ai**.

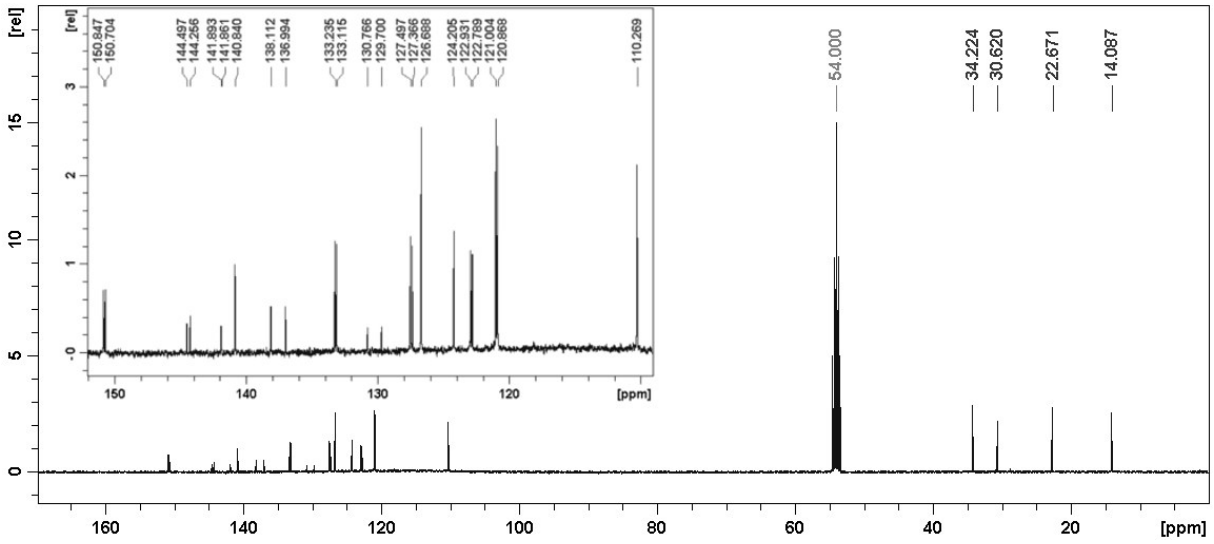


Figure S5. Proton NMR spectrum of compound **3b**.

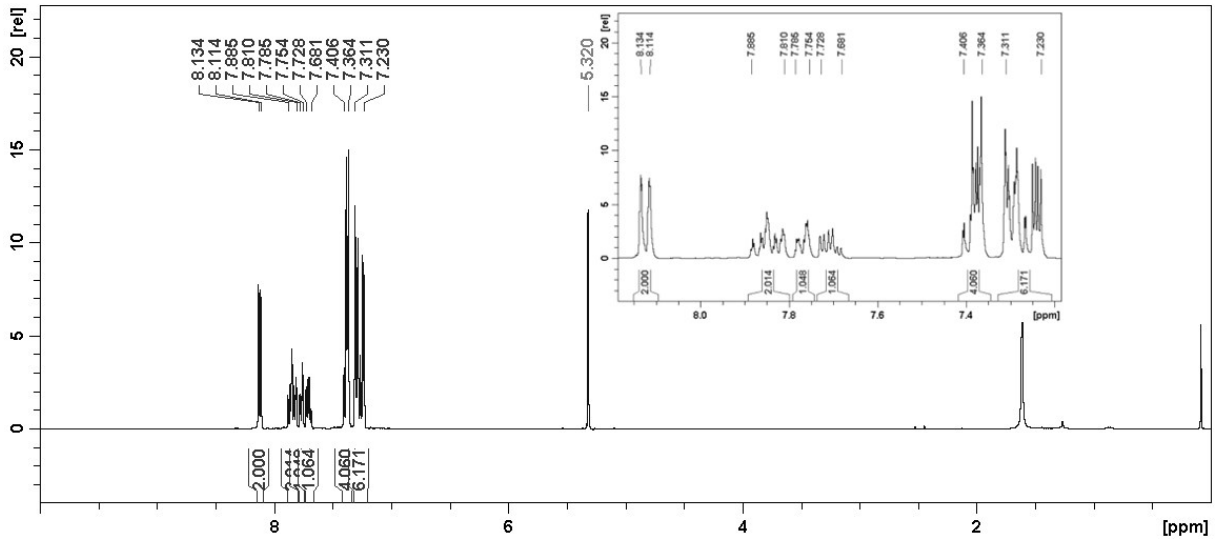


Figure S6. Carbon NMR spectrum of compound **3b**.

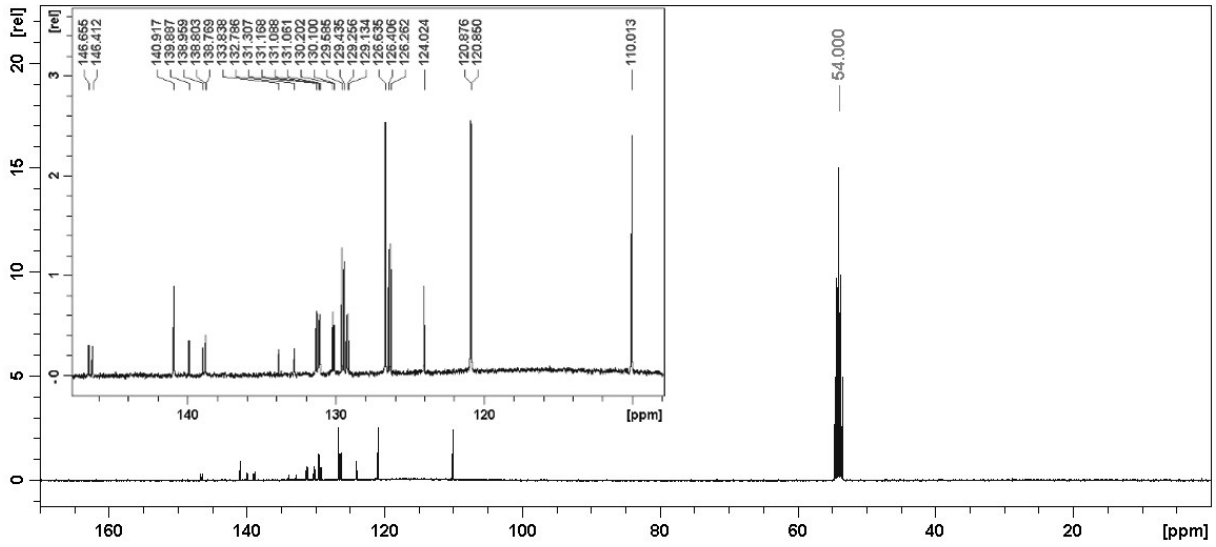


Figure S7. Proton NMR spectrum of compound **3bi**.

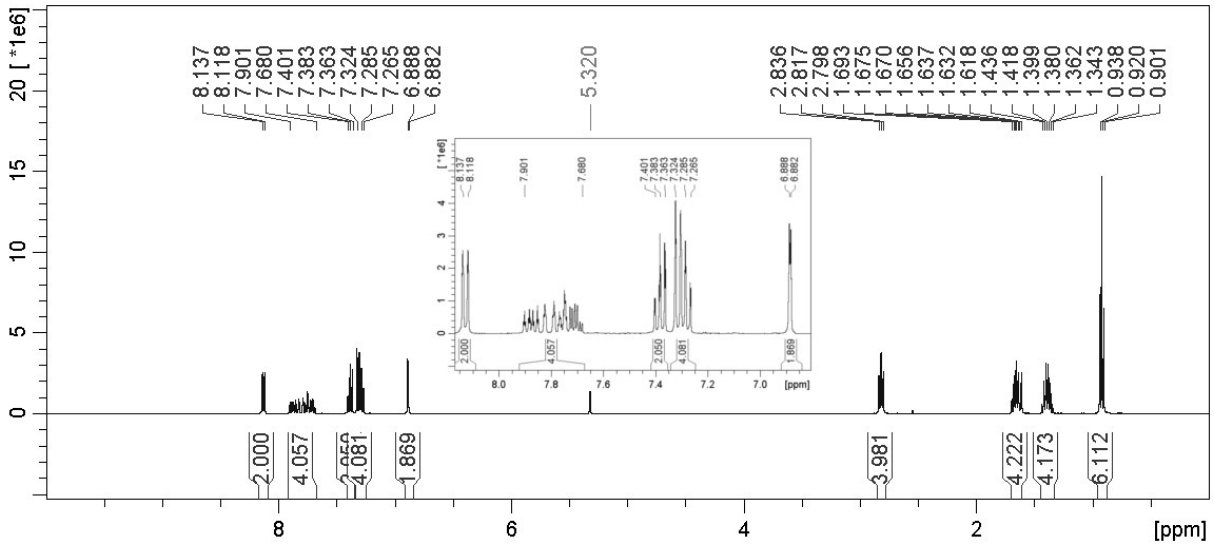


Figure S8. Carbon NMR spectrum of compound **3bi**.

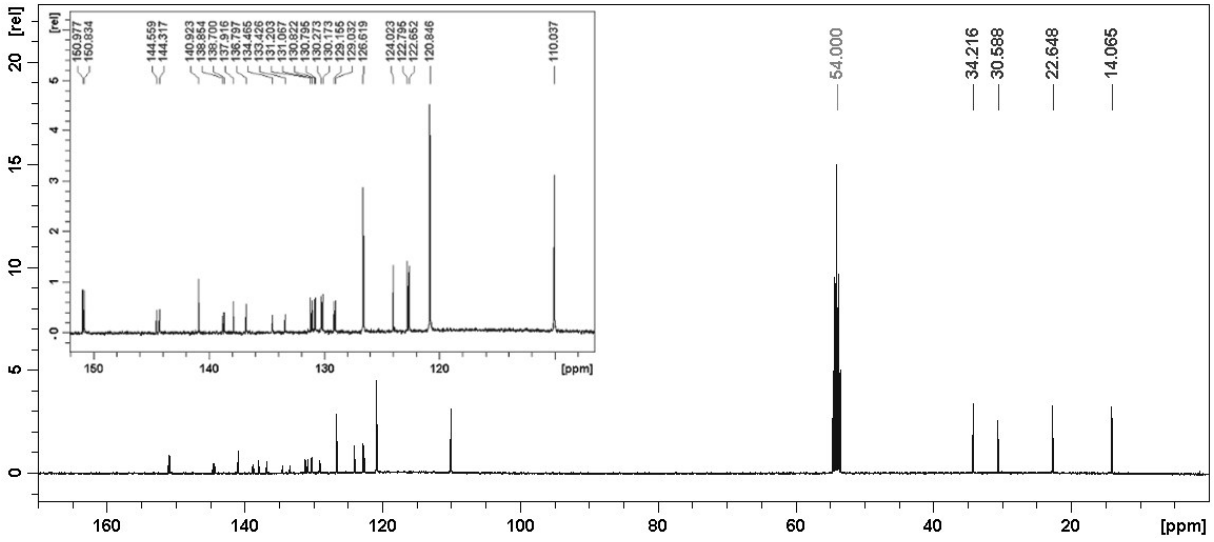


Figure S9. Proton NMR spectrum of compound **3c**.

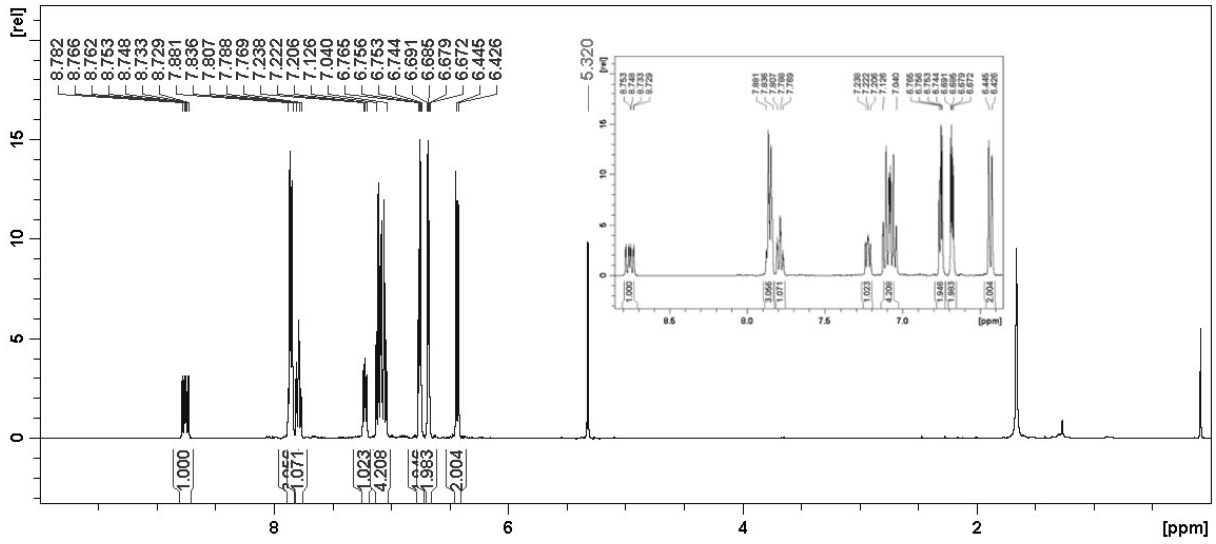


Figure S10. Carbon NMR spectrum of compound **3c**.

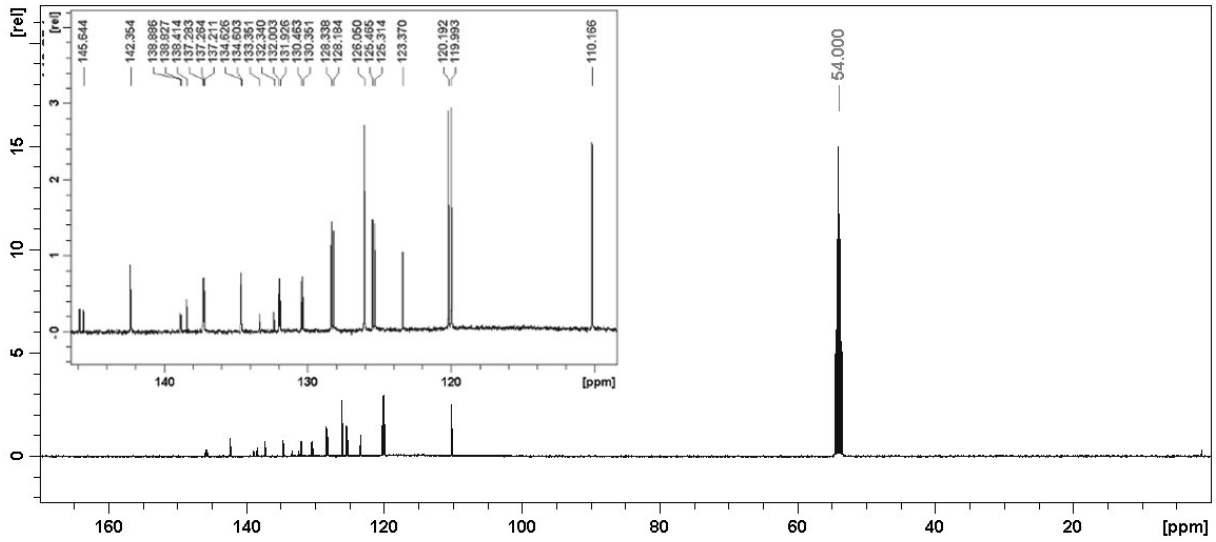


Figure S11. Proton NMR spectrum of compound **3ci**.

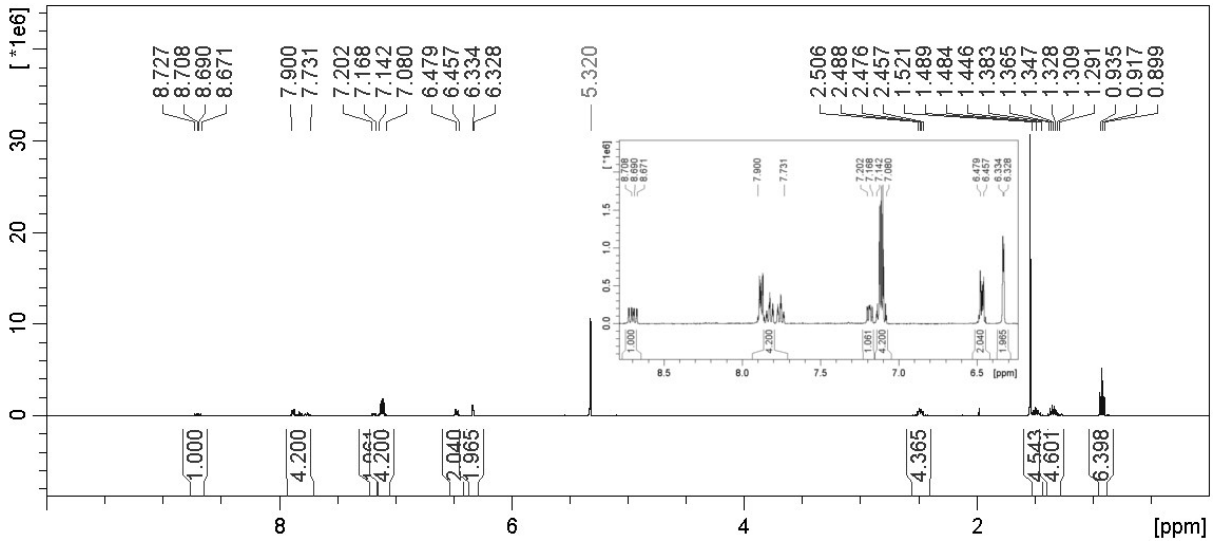


Figure S12. Carbon NMR spectrum of compound **3ci**.

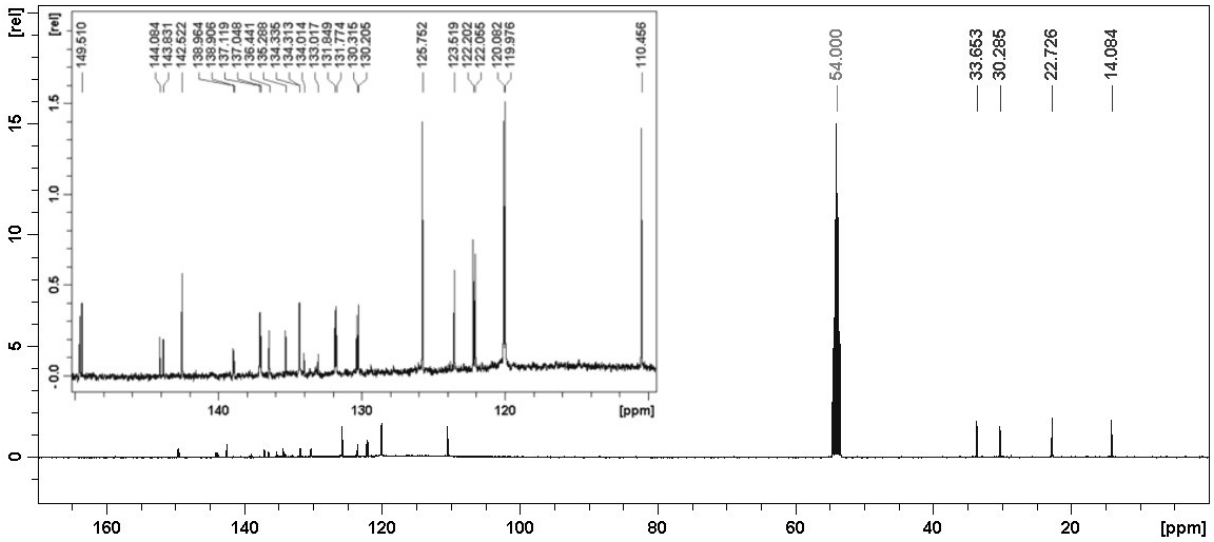


Figure S13. Proton NMR spectrum of compound **3d**.

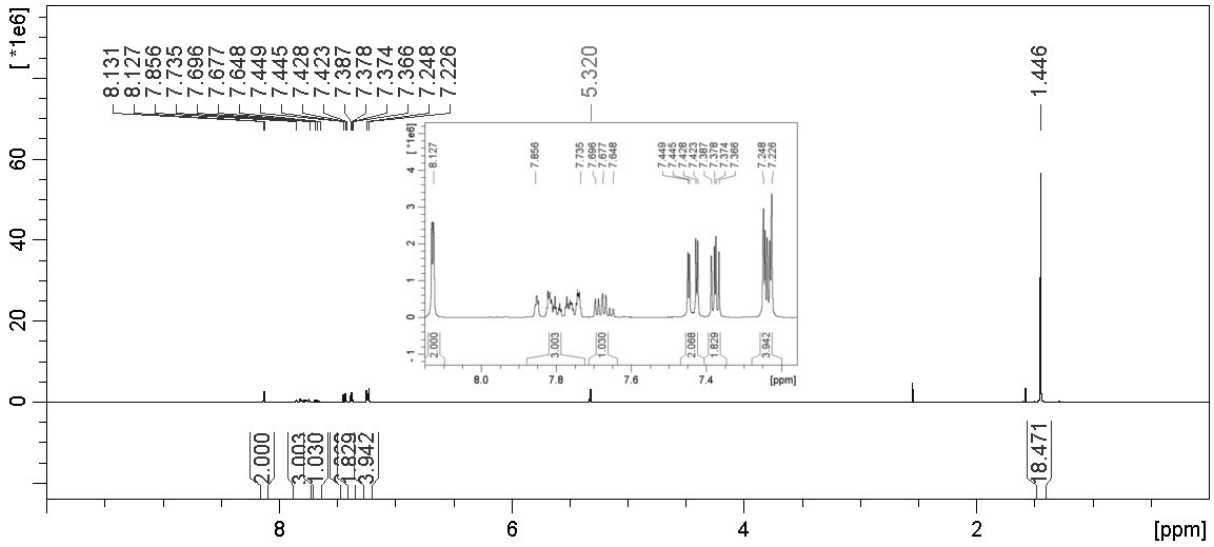


Figure S14. Carbon NMR spectrum of compound **3d**.

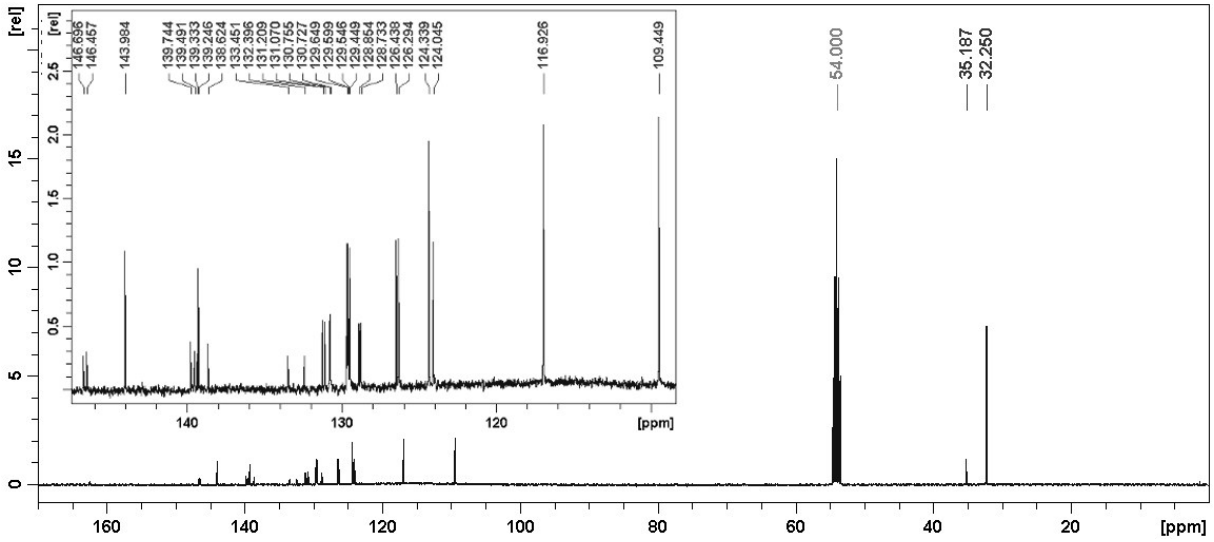


Figure S15. Proton NMR spectrum of compound **3di**.

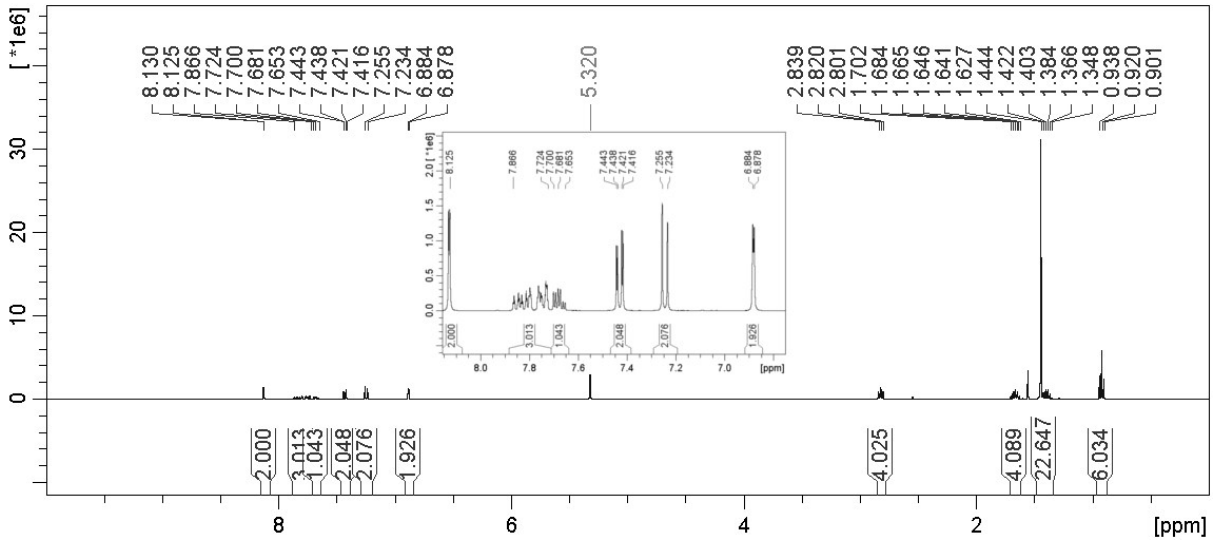


Figure S16. Carbon NMR spectrum of compound **3di**.

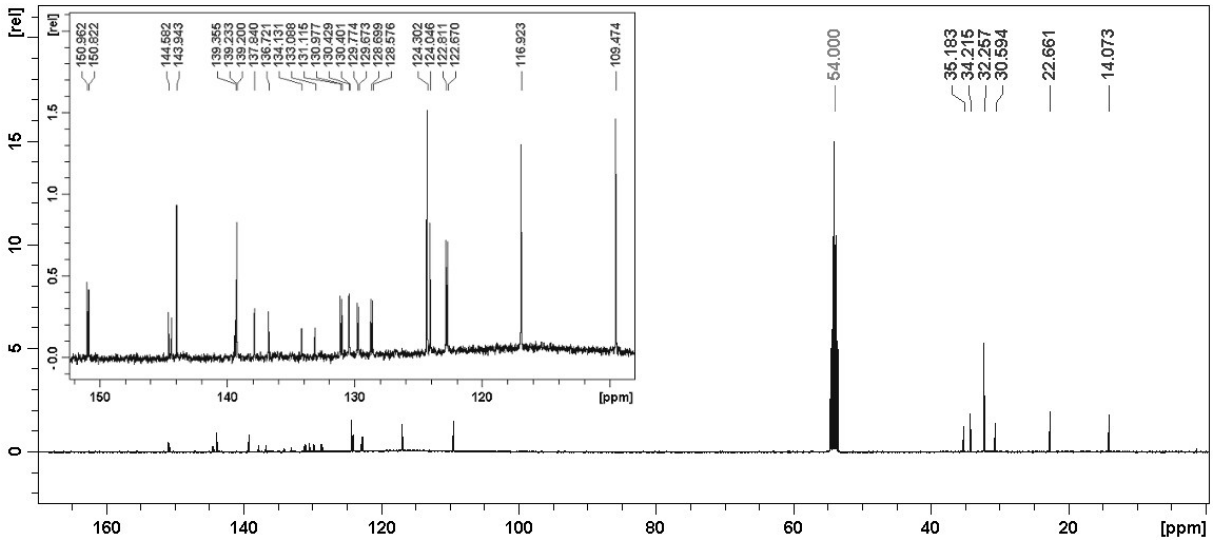


Figure S17. Proton NMR spectrum of compound **3e**.

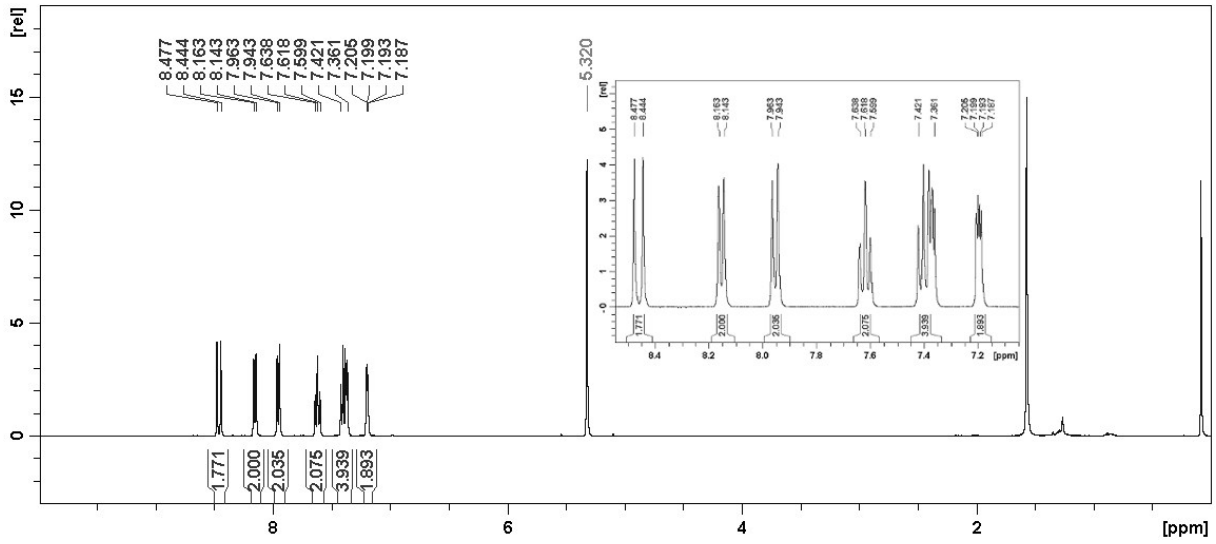


Figure S18. Carbon NMR spectrum of compound **3e**.

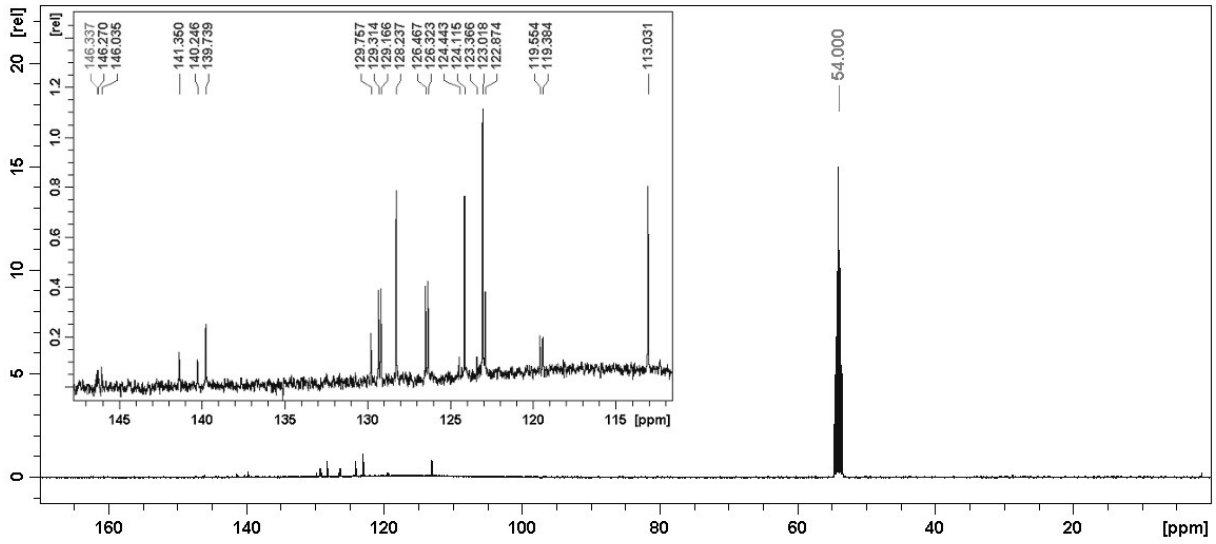


Figure S19. Proton NMR spectrum of compound **3ei**.

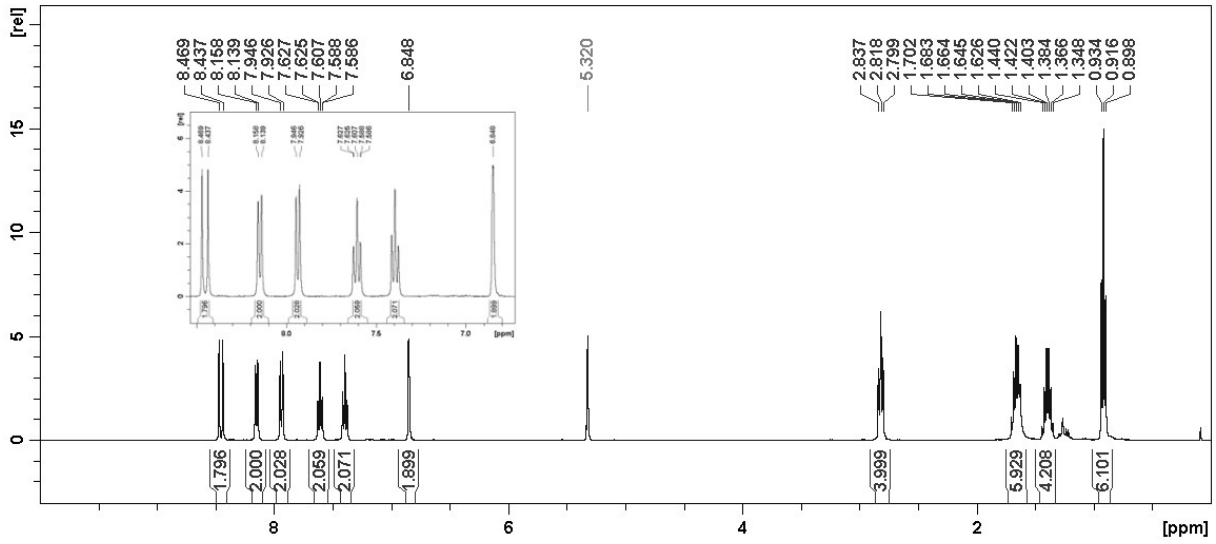
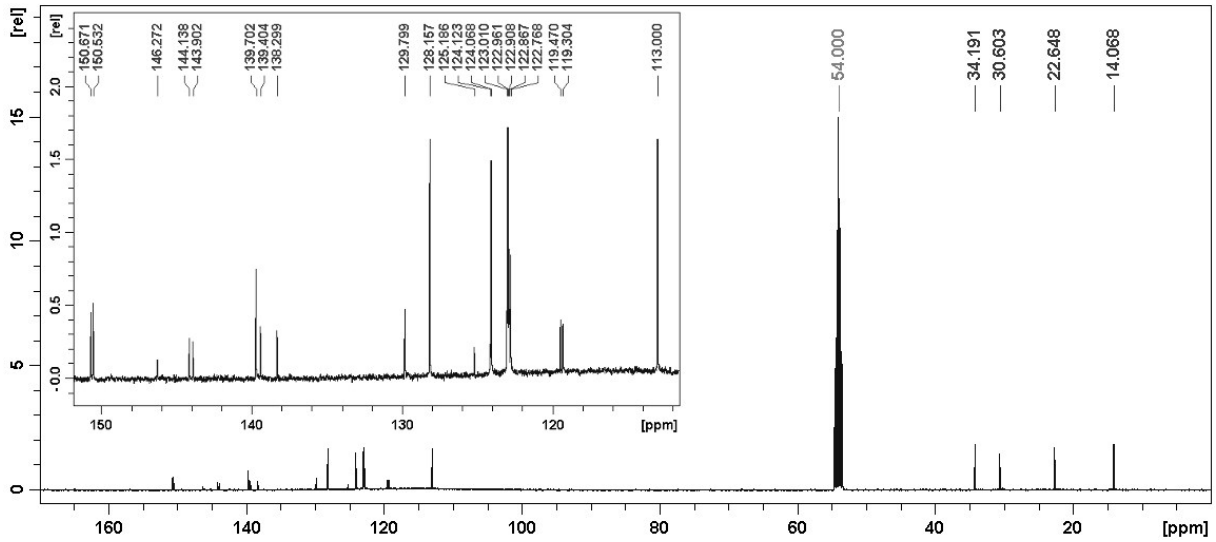


Figure S20. Carbon NMR spectrum of compound **3ei**.



A.2 Assignment of NMR signals and 1D NOE difference spectra of 3c and 3ci

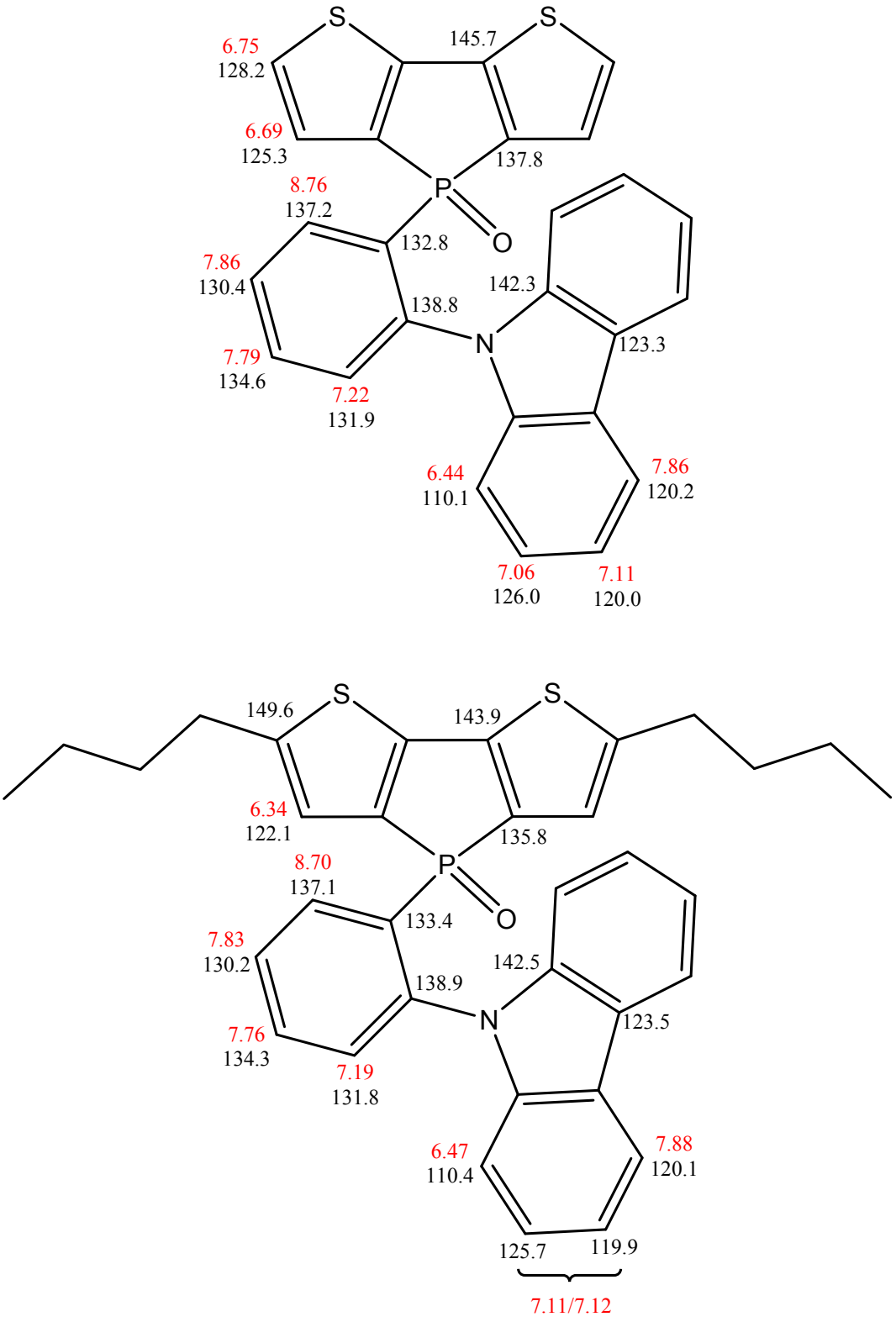


Figure S21. Assignment of proton (red) and carbon (black) NMR signals of **3c** (top) and **3ci** (bottom).

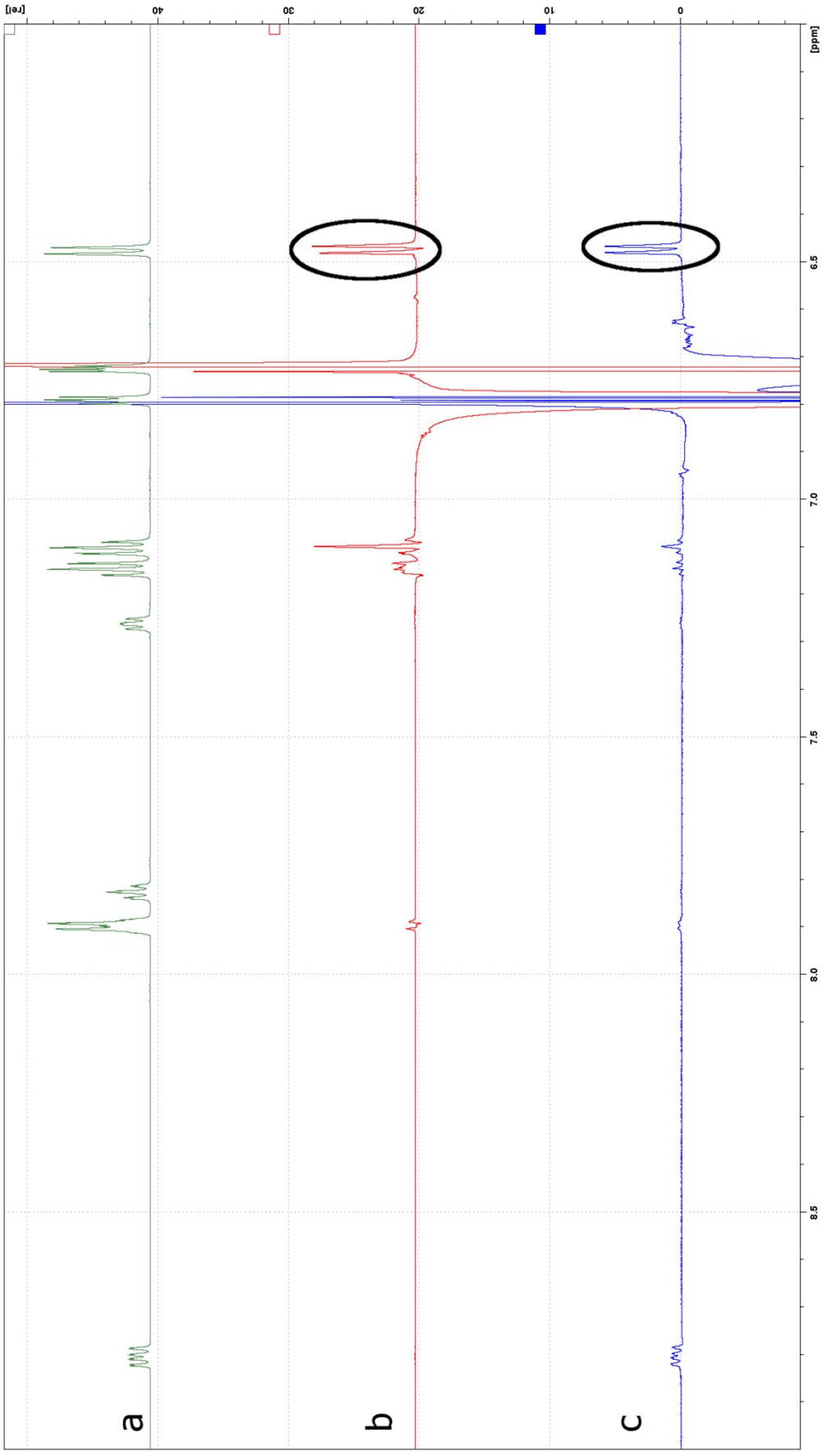


Figure S22. ^{1}H NMR (a) and 1D NOE difference spectrum of compound **3c** obtained upon irradiation of the thiophene α (b) and β (c) protons.

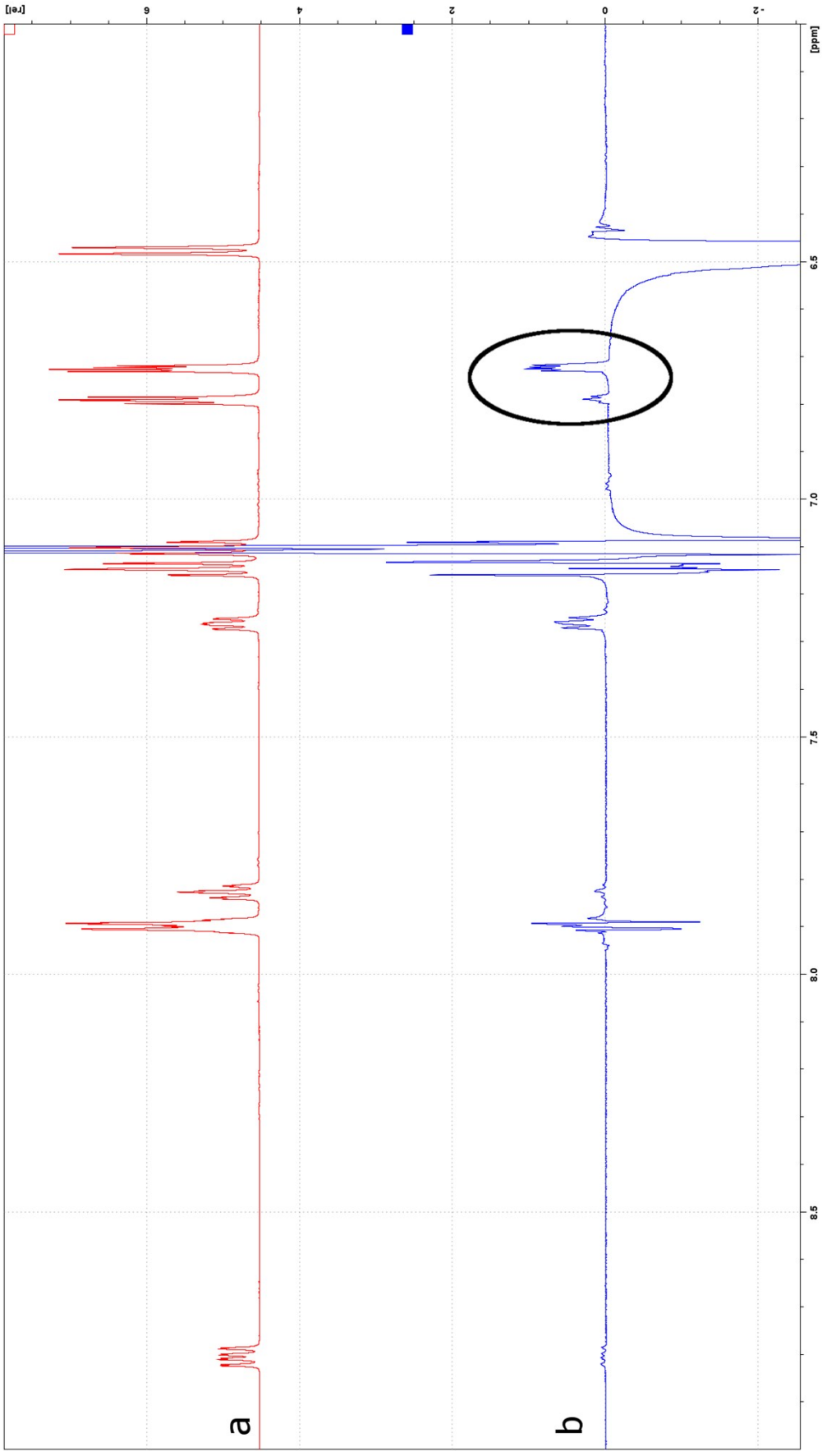


Figure S23. ^{1}H NMR (a) and 1D NOE difference spectrum of compound **3c** obtained upon irradiation of the carbazole 1 proton (b).

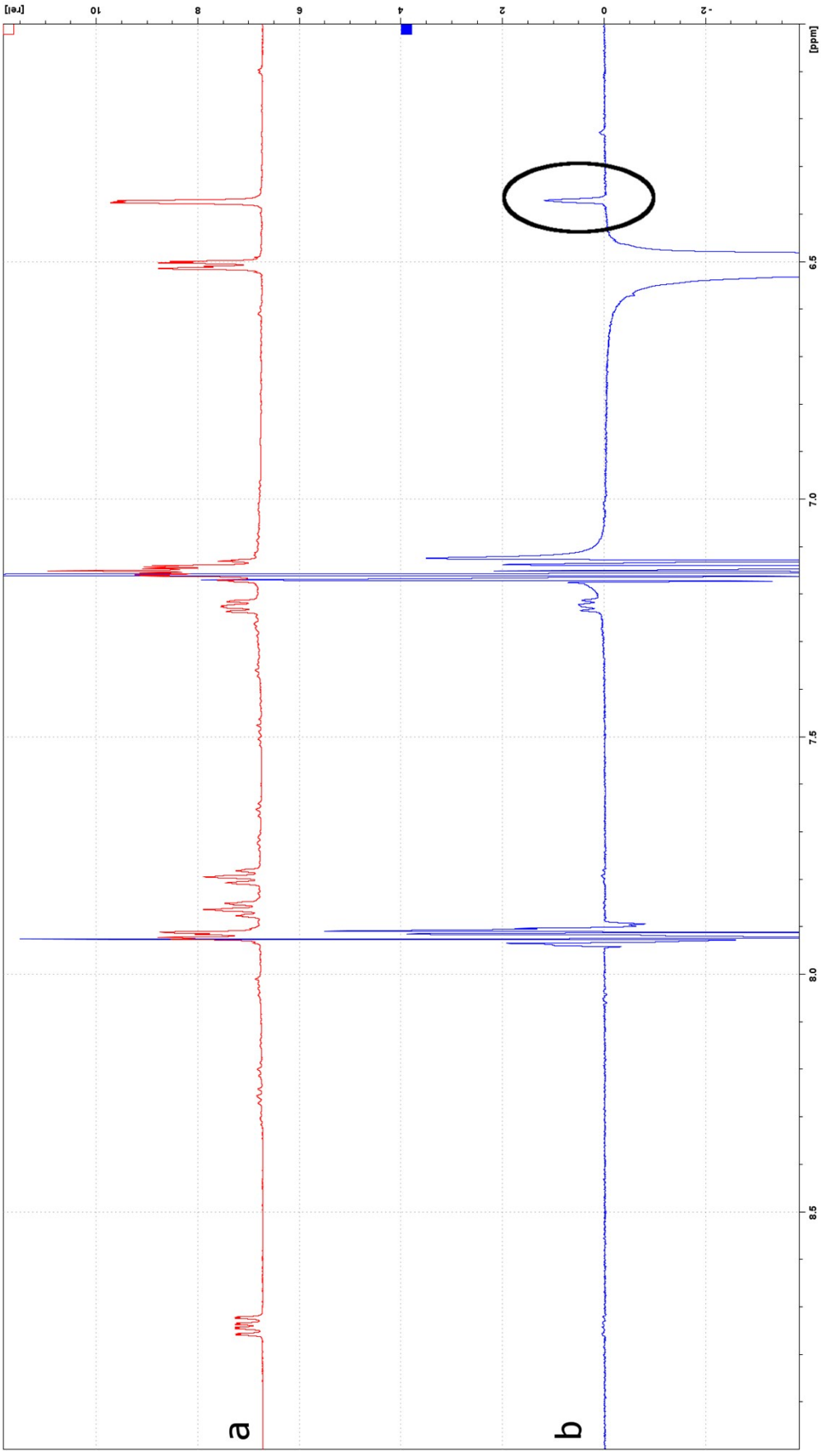


Figure S24. ^{1}H NMR (a) and 1D NOE difference spectrum of compound **3ci** obtained upon irradiation of the thiophene β (b) proton.

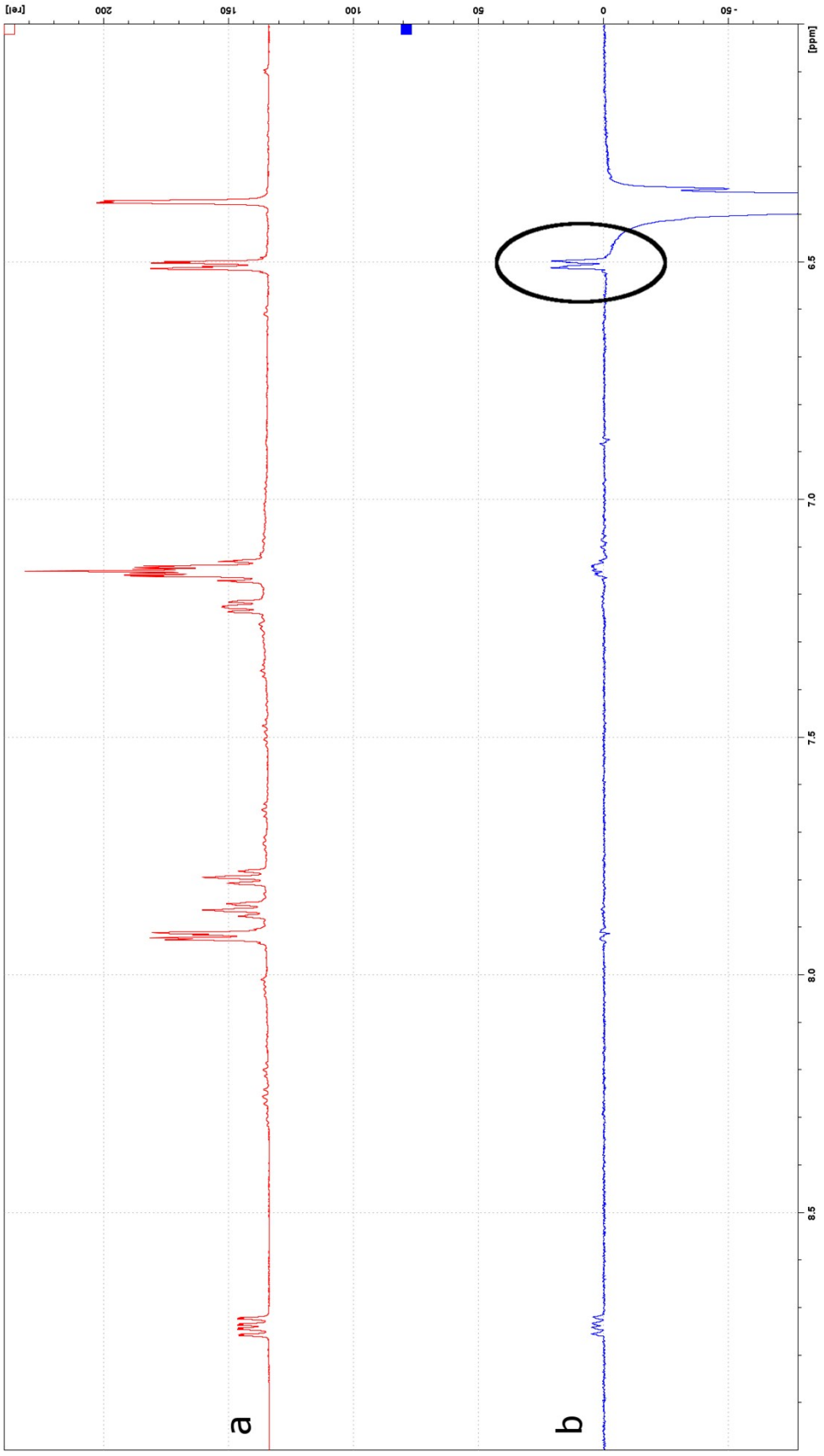


Figure S25. ^{1}H NMR (a) and 1D NOE difference spectrum of compound **3ci** obtained upon irradiation of the carbazole 1 proton (b).

B. Theoretical Data (B3LYP/6-31G+(d); Gaussian09)[S1]

Figure S26. Frontier orbitals for the *para*- and *meta*-functionalized species.

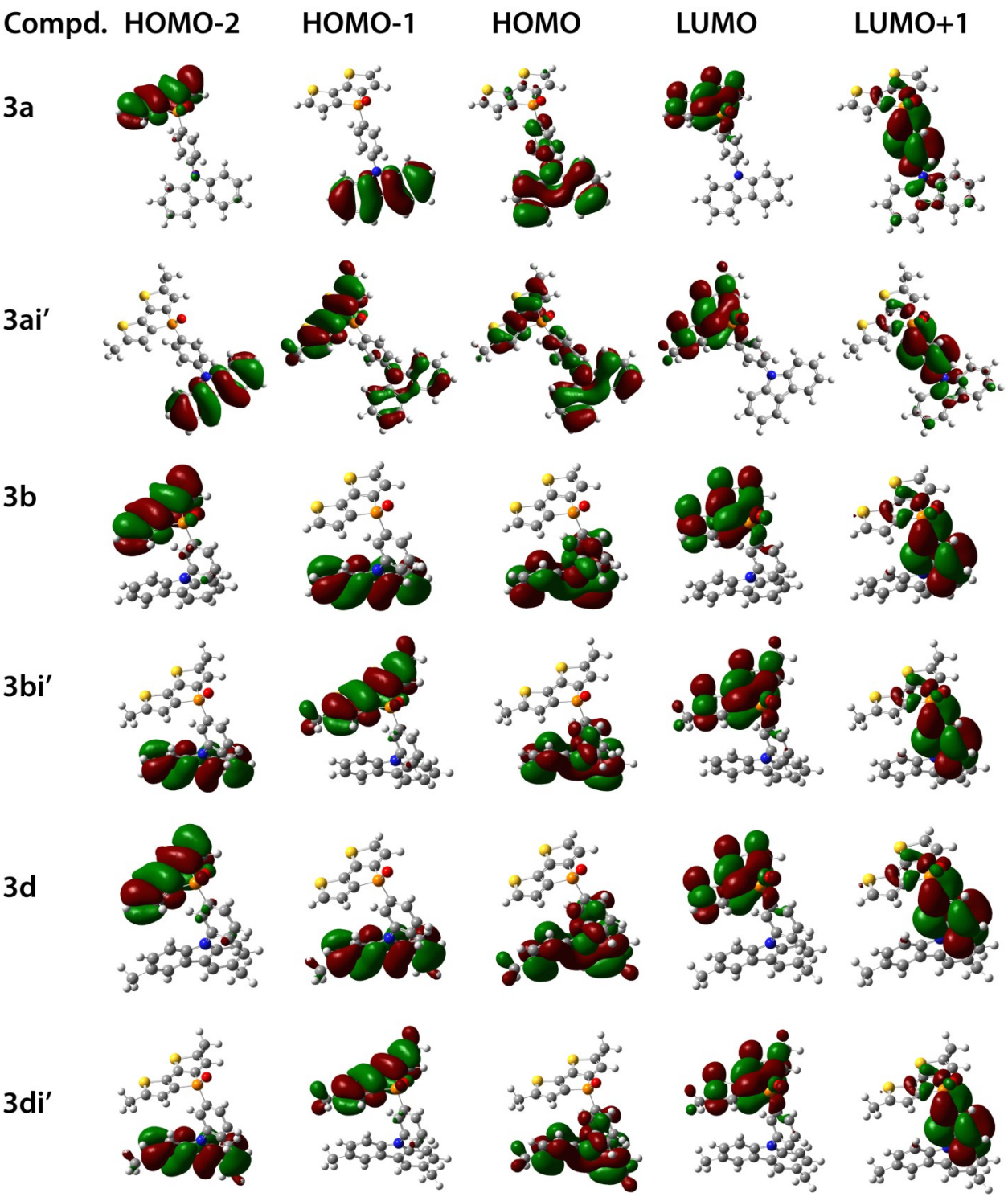


Figure S27. Frontier orbitals for the *ortho*-functionalized species.

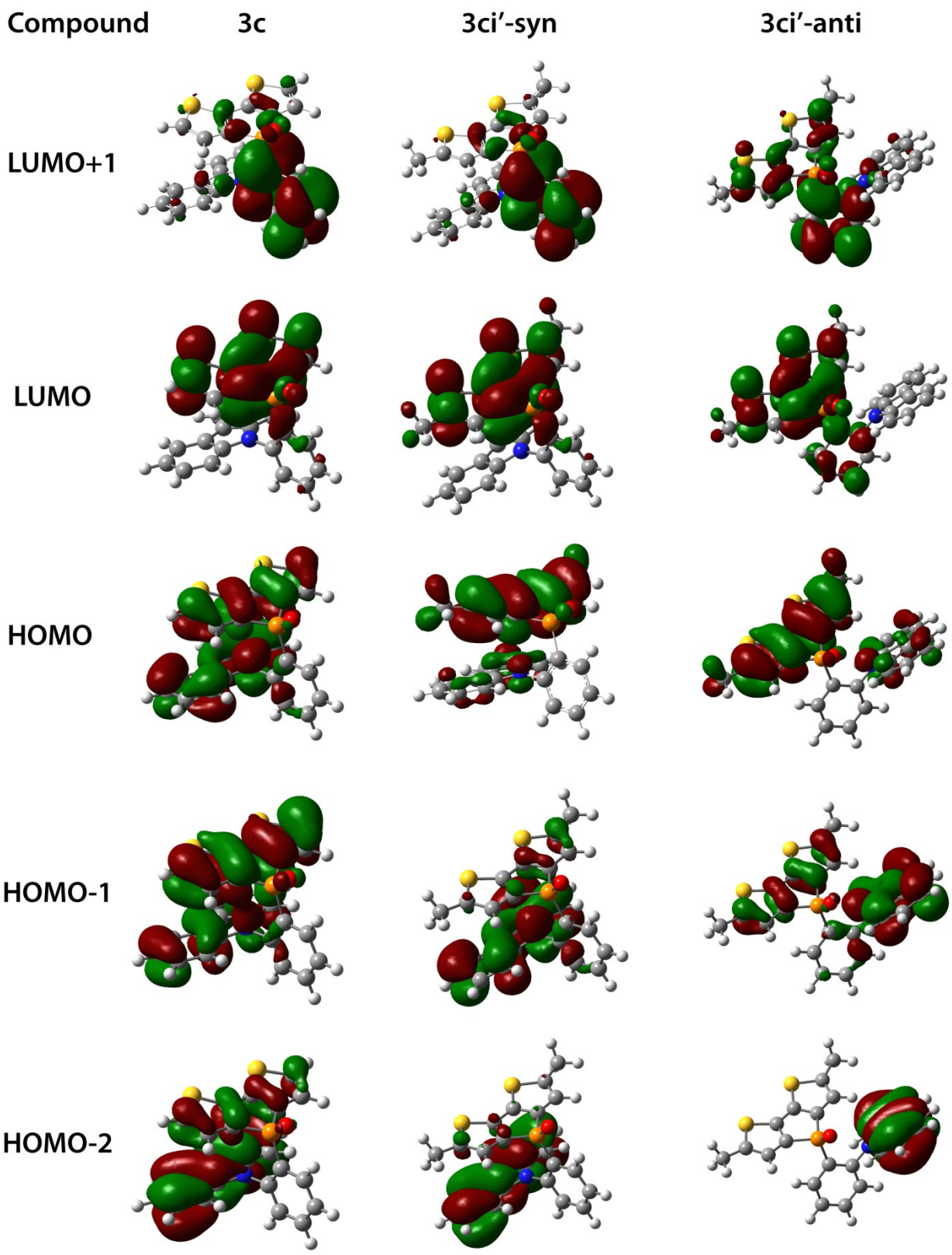


Figure S28. Frontier orbitals for the indolocarbazole-functionalized species.

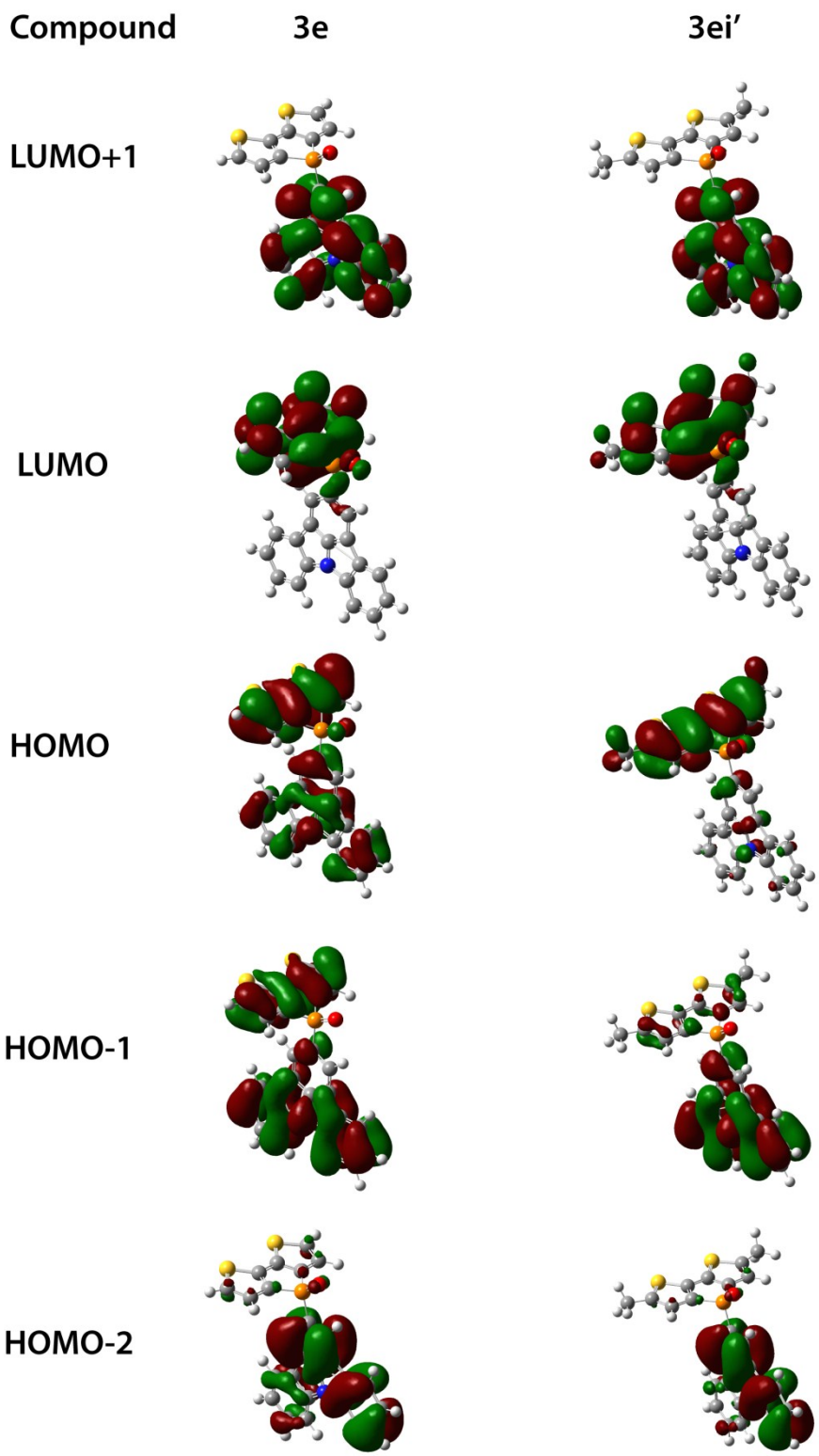


Table S1. Cartesian coordinates for **3a** from DFT calculations

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.382883	-2.581009	-2.066919
2	6	0	3.545569	-2.644026	-0.983359
3	6	0	3.527507	-1.426498	-0.249646
4	6	0	4.354227	-0.458184	-0.791427
5	16	0	5.166805	-1.027467	-2.209475
6	1	0	4.597721	-3.352156	-2.794442
7	1	0	2.975151	-3.528424	-0.722862
8	6	0	4.376865	0.799818	-0.061973
9	6	0	3.568428	0.832247	1.060384
10	16	0	5.225442	2.291424	-0.286023
11	6	0	3.630259	2.072755	1.751891
12	6	0	4.481636	2.959627	1.145291
13	1	0	3.080267	2.300674	2.657969
14	1	0	4.728288	3.967977	1.449495
15	15	0	2.715167	-0.777370	1.259022
16	6	0	0.956742	-0.507908	0.845710
17	6	0	-0.000299	-0.972289	1.756152
18	6	0	0.533633	0.135345	-0.326509
19	6	0	-1.359546	-0.789951	1.506566
20	1	0	0.331985	-1.464938	2.665012
21	6	0	-0.822075	0.304062	-0.588580
22	1	0	1.262675	0.492593	-1.049038
23	6	0	-1.778573	-0.155082	0.330587
24	1	0	-2.099428	-1.125130	2.226284
25	8	0	2.884862	-1.524730	2.547717
26	7	0	-3.159392	0.020507	0.066802
27	6	0	-4.134145	-0.987793	0.090261
28	6	0	-3.784779	1.230815	-0.265497
29	6	0	-5.391826	-0.418122	-0.231212
30	6	0	-5.169951	0.995366	-0.454875
31	6	0	-6.013751	2.063795	-0.779388
32	6	0	-5.474606	3.341048	-0.901989
33	1	0	-6.119303	4.177944	-1.154734
34	6	0	-4.102221	3.559815	-0.694187
35	1	0	-3.701214	4.565801	-0.783239
36	6	0	-3.240330	2.513681	-0.370813
37	6	0	-6.526097	-1.236184	-0.288546
38	6	0	-6.393460	-2.598336	-0.035861
39	1	0	-7.266685	-3.243137	-0.075748
40	6	0	-5.136393	-3.149533	0.264943
41	1	0	-5.050392	-4.216832	0.449775
42	6	0	-3.991819	-2.357395	0.329418
43	1	0	-3.024368	-2.794778	0.551934
44	1	0	-2.184616	2.695068	-0.199397
45	1	0	-7.077472	1.897468	-0.928162
46	1	0	-7.496756	-0.812344	-0.532495
47	1	0	-1.149699	0.775355	-1.509600

Table S2. Cartesian coordinates for **3b** from DFT calculations

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.942852	-1.478503	3.288650
2	6	0	-2.739534	-2.126368	2.097784
3	6	0	-2.830644	-1.243900	0.987088
4	6	0	-3.102935	0.061811	1.356346
5	16	0	-3.250464	0.226201	3.072418
6	1	0	-2.935928	-1.893505	4.287545
7	1	0	-2.540391	-3.189579	2.025285
8	6	0	-3.218485	0.995924	0.247698
9	6	0	-3.039138	0.433371	-1.003781
10	16	0	-3.545454	2.692217	0.148377
11	6	0	-3.164976	1.377616	-2.059084
12	6	0	-3.437399	2.638077	-1.593050
13	1	0	-3.069828	1.140197	-3.112690
14	1	0	-3.592313	3.544637	-2.162552
15	15	0	-2.705390	-1.360056	-0.836292
16	6	0	-0.936268	-1.600699	-1.240583
17	6	0	-0.616383	-2.603678	-2.162513
18	6	0	0.078273	-0.826031	-0.665257
19	6	0	0.718054	-2.818605	-2.514409
20	1	0	-1.414462	-3.200570	-2.592850
21	6	0	1.411477	-1.033838	-1.031156
22	1	0	-0.154898	-0.064434	0.072731
23	6	0	1.728047	-2.032582	-1.964394
24	1	0	0.970746	-3.591827	-3.234552
25	1	0	2.763079	-2.175974	-2.258279
26	8	0	-3.587125	-2.331383	-1.561792
27	7	0	2.438267	-0.235103	-0.464299
28	6	0	3.580133	-0.712769	0.191795
29	6	0	2.490073	1.165365	-0.478608
30	6	0	4.370791	0.390781	0.601139
31	6	0	3.677304	1.587452	0.172021
32	6	0	3.960277	2.954578	0.272425
33	6	0	3.070384	3.873451	-0.275890
34	1	0	3.278404	4.937107	-0.202865
35	6	0	1.904641	3.437093	-0.928215
36	1	0	1.225277	4.169263	-1.356120
37	6	0	1.598299	2.082517	-1.041819
38	6	0	5.564542	0.163734	1.295840
39	6	0	5.947714	-1.144365	1.577303
40	1	0	6.872668	-1.332820	2.114768
41	6	0	5.144520	-2.225908	1.177072
42	1	0	5.455307	-3.239756	1.414395
43	6	0	3.952198	-2.027938	0.483723
44	1	0	3.332878	-2.868579	0.188709
45	1	0	0.698185	1.756731	-1.552657
46	1	0	4.866034	3.292733	0.769083
47	1	0	6.181223	0.999798	1.615371

Table S3. Cartesian coordinates for **3c** from DFT calculations
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.012261	-1.289584	-1.509569
2	6	0	0.646701	-0.045247	-1.997839
3	6	0	-0.277285	-0.120972	-3.074866
4	6	0	-0.607872	-1.418583	-3.377239
5	16	0	0.212979	-2.567800	-2.353909
6	1	0	-0.680495	0.734548	-3.604758
7	1	0	-1.296980	-1.775524	-4.131374
8	6	0	2.023788	-1.262438	-0.465242
9	6	0	2.472030	0.003641	-0.128271
10	16	0	2.846073	-2.491694	0.428599
11	6	0	3.494971	-0.012799	0.858332
12	6	0	3.802749	-1.290750	1.256776
13	1	0	3.991800	0.869099	1.248374
14	1	0	4.537623	-1.606573	1.985906
15	15	0	1.641341	1.248021	-1.177710
16	8	0	2.524637	2.086618	-2.061413
17	6	0	0.625385	2.359834	-0.105935
18	6	0	1.076357	3.692231	-0.102615
19	6	0	-0.487188	2.026597	0.691424
20	6	0	0.452355	4.665993	0.678015
21	1	0	1.919614	3.949519	-0.736812
22	6	0	-1.110983	3.009307	1.470368
23	6	0	-0.644027	4.323757	1.471431
24	1	0	0.821066	5.688145	0.660949
25	1	0	-1.970432	2.725154	2.071529
26	1	0	-1.138556	5.073456	2.083502
27	7	0	-1.044688	0.708071	0.722954
28	6	0	-0.806496	-0.244690	1.722535
29	6	0	-2.219710	0.347316	0.050547
30	6	0	-1.782833	-1.270020	1.628416
31	6	0	-2.686285	-0.891474	0.559393
32	6	0	-1.736134	-2.349527	2.520472
33	6	0	0.188382	-0.264047	2.703471
34	6	0	-0.739674	-2.381748	3.494868
35	1	0	-0.695207	-3.211398	4.195260
36	6	0	0.207271	-1.344431	3.585769
37	1	0	-2.473571	-3.146336	2.460687
38	1	0	0.971284	-1.383551	4.357921
39	1	0	0.924325	0.530559	2.776239
40	6	0	-3.845045	-1.463852	0.018802
41	6	0	-2.900744	1.033264	-0.958379
42	6	0	-4.059057	0.448666	-1.471738
43	1	0	-4.610680	0.962988	-2.254647
44	6	0	-4.525310	-0.790794	-0.995501
45	1	0	-4.216160	-2.415006	0.392720
46	1	0	-5.429421	-1.221694	-1.417284
47	1	0	-2.545082	1.990861	-1.327490

Table S4. Cartesian coordinates for **3d** from DFT calculations
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.155307	-2.851764	-2.718512
2	6	0	1.212314	-2.116525	-2.187941
3	6	0	0.970797	-1.148368	-1.201004
4	6	0	-0.337393	-0.921380	-0.762346
5	6	0	-1.399511	-1.643355	-1.319454
6	6	0	-1.154301	-2.615642	-2.295141
7	6	0	3.224893	-0.929222	-0.116457
8	6	0	4.057888	0.135194	0.303874
9	6	0	3.353502	1.364080	0.003998
10	6	0	2.118731	0.998023	-0.583595
11	7	0	2.044454	-0.400405	-0.656466
12	6	0	3.667720	2.718686	0.169796
13	6	0	2.771661	3.701934	-0.247441
14	6	0	1.555404	3.304379	-0.843729
15	6	0	1.212728	1.967988	-1.022290
16	6	0	3.605959	-2.260893	0.070867
17	6	0	4.840903	-2.506614	0.662376
18	6	0	5.702067	-1.467380	1.076624
19	6	0	5.295395	-0.146007	0.896035
20	6	0	-3.181490	-1.343712	1.008916
21	15	0	-3.139061	-1.367789	-0.822033
22	6	0	-3.414215	0.442605	-0.881620
23	6	0	-3.517748	0.944110	0.403835
24	6	0	-3.389471	-0.050936	1.456718
25	6	0	-3.547960	1.445375	-1.880260
26	6	0	-3.750931	2.688411	-1.338559
27	16	0	-3.782168	2.654104	0.406365
28	16	0	-3.460913	0.026296	3.183722
29	6	0	-3.208300	-1.697079	3.297584
30	6	0	-3.078155	-2.286900	2.067150
31	8	0	-4.086674	-2.269854	-1.553875
32	6	0	3.083086	5.170213	-0.069428
33	6	0	7.037564	-1.795449	1.703944
34	1	0	0.351358	-3.600230	-3.480381
35	1	0	2.226540	-2.274472	-2.538875
36	1	0	-0.514431	-0.186329	0.016156
37	1	0	-1.989617	-3.169957	-2.710268
38	1	0	4.614376	3.005689	0.620651
39	1	0	0.860303	4.070510	-1.178141
40	1	0	0.273024	1.697034	-1.490826
41	1	0	2.961339	-3.080977	-0.225675
42	1	0	5.151942	-3.537327	0.813685
43	1	0	5.939541	0.667303	1.220566
44	1	0	-3.506954	1.261499	-2.947250
45	1	0	-3.894813	3.628822	-1.851913
46	1	0	-3.175694	-2.163466	4.272232
47	1	0	-2.921785	-3.350341	1.931507
48	1	0	3.025809	5.712072	-1.020563
49	1	0	2.375348	5.651444	0.616323
50	1	0	4.087680	5.317345	0.336607
51	1	0	6.922068	-2.440880	2.582393
52	1	0	7.692855	-2.324754	1.001814
53	1	0	7.559875	-0.889528	2.023692

Table S5. Cartesian coordinates for **3e** from DFT calculations
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.387443	1.853667	-0.000230
2	6	0	4.397788	2.809009	-0.000308
3	6	0	5.689167	-0.768221	-0.000015
4	6	0	4.301631	-0.678785	-0.000021
5	7	0	3.459786	0.448830	-0.000128
6	6	0	1.996092	2.221689	-0.000229
7	6	0	1.658622	3.575200	-0.000304
8	6	0	2.672958	4.534343	-0.000382
9	6	0	4.021263	4.154390	-0.000384
10	6	0	6.258049	-2.044084	0.000119
11	6	0	5.462527	-3.197411	0.000245
12	6	0	4.069625	-3.107591	0.000242
13	6	0	3.465304	-1.849993	0.000111
14	6	0	-0.101034	0.493944	-0.000021
15	6	0	1.210023	0.979909	-0.000113
16	6	0	2.178173	-0.014531	-0.000056
17	6	0	2.067986	-1.395970	0.000082
18	6	0	0.746725	-1.861306	0.000168
19	6	0	-0.303467	-0.910373	0.000116
20	6	0	-3.957896	0.121393	3.202719
21	6	0	-2.989918	-0.723946	2.726003
22	6	0	-2.946992	-0.742811	1.305383
23	6	0	-3.887214	0.090743	0.727215
24	16	0	-4.838174	0.911406	1.918408
25	6	0	-3.887276	0.090491	-0.727190
26	6	0	-2.947082	-0.743240	-1.305146
27	6	0	-2.990244	-0.725000	-2.725767
28	6	0	-3.958360	0.120067	-3.202688
29	16	0	-4.838489	0.910560	-1.918589
30	15	0	-1.990693	-1.607684	0.000224
31	8	0	-1.991451	-3.108044	0.000417
32	1	0	5.444037	2.523464	-0.000311
33	1	0	6.311901	0.119714	-0.000114
34	1	0	0.615945	3.878754	-0.000306
35	1	0	2.414219	5.588495	-0.000438
36	1	0	4.792646	4.918431	-0.000445
37	1	0	7.339545	-2.139945	0.000126
38	1	0	5.936619	-4.173840	0.000346
39	1	0	3.460104	-4.006196	0.000339
40	1	0	-0.958960	1.159839	-0.000052
41	1	0	0.485849	-2.914772	0.000272
42	1	0	-4.218884	0.331982	4.230384
43	1	0	-2.343201	-1.308996	3.368949
44	1	0	-2.343583	-1.310276	-3.368563
45	1	0	-4.219487	0.330234	-4.230404

Table S6. Cartesian coordinates for **3ai'** from DFT calculations

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.454600	-0.920553	0.307510
2	6	0	5.697354	-0.421738	-0.157902
3	6	0	5.446227	0.898035	-0.698336
4	6	0	4.059394	1.149482	-0.545014
5	7	0	3.461132	0.039849	0.068289
6	6	0	4.341506	-2.199058	0.860541
7	6	0	5.500073	-2.966077	0.962544
8	6	0	6.742374	-2.480699	0.520907
9	6	0	6.846044	-1.213027	-0.043381
10	6	0	6.265524	1.874716	-1.275865
11	6	0	5.700839	3.079862	-1.682287
12	6	0	4.327560	3.319498	-1.507751
13	6	0	3.489698	2.364365	-0.936068
14	6	0	0.333087	-0.588988	1.976923
15	6	0	1.687071	-0.448728	1.676798
16	6	0	2.085502	-0.092467	0.382494
17	6	0	1.114182	0.129895	-0.605978
18	6	0	-0.236057	0.006947	-0.296150
19	6	0	-0.638880	-0.357163	0.996603
20	6	0	-4.164712	3.115771	0.652860
21	6	0	-3.310099	2.348061	1.404901
22	6	0	-3.250901	0.994029	0.976074
23	6	0	-4.066135	0.735783	-0.108845
24	16	0	-4.918689	2.155207	-0.618745
25	6	0	-4.047476	-0.642198	-0.570439
26	6	0	-3.217263	-1.482540	0.146352
27	6	0	-3.239418	-2.822192	-0.328999
28	6	0	-4.081089	-3.001829	-1.398804
29	16	0	-4.869132	-1.487629	-1.839813
30	15	0	-2.391212	-0.541815	1.482597
31	8	0	-2.534449	-1.013019	2.899325
32	6	0	-4.372952	-4.262077	-2.155009
33	6	0	-4.492766	4.569691	0.807225
34	1	0	3.386011	-2.587321	1.194446
35	1	0	5.437117	-3.961904	1.391183
36	1	0	7.626265	-3.103533	0.617257
37	1	0	7.804540	-0.842532	-0.395385
38	1	0	7.329574	1.694798	-1.399702
39	1	0	6.325593	3.844748	-2.132957
40	1	0	3.906858	4.270411	-1.821107
41	1	0	2.433470	2.563775	-0.794779
42	1	0	0.015101	-0.867416	2.976763
43	1	0	2.437965	-0.600826	2.444651
44	1	0	1.426203	0.382336	-1.613670
45	1	0	-0.977186	0.178926	-1.071434
46	1	0	-2.752084	2.750285	2.243040
47	1	0	-2.664939	-3.634695	0.101591
48	1	0	-3.781649	-5.082209	-1.739323
49	1	0	-5.429739	-4.544733	-2.089756
50	1	0	-4.121019	-4.172155	-3.217746
51	1	0	-5.556444	4.730924	1.015836
52	1	0	-3.922133	4.985664	1.641746
53	1	0	-4.242256	5.145838	-0.090731

Table S7. Cartesian coordinates for **3bi'** from DFT calculations
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.942852	-1.478503	3.288650
2	6	0	-2.739534	-2.126368	2.097784
3	6	0	-2.830644	-1.243900	0.987088
4	6	0	-3.102935	0.061811	1.356346
5	16	0	-3.250464	0.226201	3.072418
6	1	0	-2.935928	-1.893505	4.287545
7	1	0	-2.540391	-3.189579	2.025285
8	6	0	-3.218485	0.995924	0.247698
9	6	0	-3.039138	0.433371	-1.003781
10	16	0	-3.545454	2.692217	0.148377
11	6	0	-3.164976	1.377616	-2.059084
12	6	0	-3.437399	2.638077	-1.593050
13	1	0	-3.069828	1.140197	-3.112690
14	1	0	-3.592313	3.544637	-2.162552
15	15	0	-2.705390	-1.360056	-0.836292
16	6	0	-0.936268	-1.600699	-1.240583
17	6	0	-0.616383	-2.603678	-2.162513
18	6	0	0.078273	-0.826031	-0.665257
19	6	0	0.718054	-2.818605	-2.514409
20	1	0	-1.414462	-3.200570	-2.592850
21	6	0	1.411477	-1.033838	-1.031156
22	1	0	-0.154898	-0.064434	0.072731
23	6	0	1.728047	-2.032582	-1.964394
24	1	0	0.970746	-3.591827	-3.234552
25	1	0	2.763079	-2.175974	-2.258279
26	8	0	-3.587125	-2.331383	-1.561792
27	7	0	2.438267	-0.235103	-0.464299
28	6	0	3.580133	-0.712769	0.191795
29	6	0	2.490073	1.165365	-0.478608
30	6	0	4.370791	0.390781	0.601139
31	6	0	3.677304	1.587452	0.172021
32	6	0	3.960277	2.954578	0.272425
33	6	0	3.070384	3.873451	-0.275890
34	1	0	3.278404	4.937107	-0.202865
35	6	0	1.904641	3.437093	-0.928215
36	1	0	1.225277	4.169263	-1.356120
37	6	0	1.598299	2.082517	-1.041819
38	6	0	5.564542	0.163734	1.295840
39	6	0	5.947714	-1.144365	1.577303
40	1	0	6.872668	-1.332820	2.114768
41	6	0	5.144520	-2.225908	1.177072
42	1	0	5.455307	-3.239756	1.414395
43	6	0	3.952198	-2.027938	0.483723
44	1	0	3.332878	-2.868579	0.188709
45	1	0	0.698185	1.756731	-1.552657
46	1	0	4.866034	3.292733	0.769083
47	1	0	6.181223	0.999798	1.615371

Table S8. Cartesian coordinates for **3ci'-syn** from DFT calculations
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.772486	-2.991562	2.741249
2	6	0	-0.583630	-2.946287	3.058953
3	6	0	-1.455184	-2.216251	2.254163
4	6	0	-0.984929	-1.525613	1.131788
5	6	0	0.385958	-1.559828	0.802328
6	6	0	1.246228	-2.307571	1.623134
7	6	0	0.881788	1.049016	-0.545193
8	15	0	1.049388	-0.765918	-0.721562
9	6	0	2.862517	-0.660663	-0.476316
10	6	0	3.224227	0.656380	-0.272624
11	6	0	2.126114	1.603547	-0.305312
12	6	0	3.981150	-1.539801	-0.519427
13	6	0	5.181710	-0.899604	-0.333269
14	16	0	4.940757	0.831868	-0.111885
15	16	0	2.045382	3.328397	-0.175258
16	6	0	0.306126	3.308165	-0.460046
17	6	0	-0.147832	2.025516	-0.638897
18	8	0	0.566468	-1.420826	-1.981944
19	6	0	6.559494	-1.488348	-0.313747
20	6	0	-0.481122	4.582626	-0.486013
21	6	0	-2.650084	0.306791	0.914718
22	6	0	-3.788667	0.565123	0.111558
23	6	0	-3.800809	-0.439593	-0.933025
24	6	0	-2.663174	-1.258732	-0.733214
25	7	0	-1.932827	-0.769642	0.369651
26	6	0	-4.677799	-0.720508	-1.988359
27	6	0	-4.416122	-1.813452	-2.807499
28	6	0	-3.285812	-2.619347	-2.586621
29	6	0	-2.392625	-2.355626	-1.551564
30	6	0	-2.351767	1.080706	2.038484
31	6	0	-3.211430	2.133157	2.347193
32	6	0	-4.337823	2.413220	1.554783
33	6	0	-4.631191	1.634941	0.437957
34	1	0	1.462638	-3.556874	3.360017
35	1	0	-0.964748	-3.478122	3.925434
36	1	0	-2.514433	-2.169195	2.485466
37	1	0	2.304199	-2.345092	1.390969
38	1	0	3.915181	-2.607717	-0.697170
39	1	0	-1.188493	1.802391	-0.834988
40	1	0	6.498899	-2.566051	-0.487310
41	1	0	7.200338	-1.059744	-1.092453
42	1	0	7.060838	-1.331182	0.648218
43	1	0	-0.182418	5.234465	-1.315155
44	1	0	-1.542494	4.349989	-0.603915
45	1	0	-0.365561	5.154553	0.441455
46	1	0	-5.552660	-0.098902	-2.156827
47	1	0	-5.087866	-2.046199	-3.628158
48	1	0	-3.095606	-3.462778	-3.243512
49	1	0	-1.501211	-2.953948	-1.412987
50	1	0	-1.478777	0.873536	2.648007
51	1	0	-3.002686	2.749574	3.216655
52	1	0	-4.987090	3.241956	1.820416
53	1	0	-5.505814	1.849543	-0.169520

Table S9. Cartesian coordinates for **3ci'-anti** from DFT calculations

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.211620	-1.633500	-1.242343
2	6	0	-0.381959	-0.595140	-1.936917
3	6	0	-1.658241	-0.934803	-2.462845
4	6	0	-2.040101	-2.219993	-2.158596
5	16	0	-0.801032	-3.035476	-1.209993
6	1	0	-2.278177	-0.265713	-3.050669
7	6	0	1.559077	-1.361347	-0.770831
8	6	0	2.043431	-0.107270	-1.092996
9	16	0	2.745139	-2.305612	0.062388
10	6	0	3.386921	0.095676	-0.673425
11	6	0	3.919829	-0.997185	-0.030978
12	1	0	3.954110	1.004865	-0.847481
13	15	0	0.791273	0.796150	-2.066427
14	8	0	1.187799	1.229646	-3.452499
15	6	0	0.216232	2.275428	-1.114655
16	6	0	0.456322	3.492861	-1.776240
17	6	0	-0.396222	2.312198	0.153991
18	6	0	0.108812	4.713927	-1.196943
19	1	0	0.913059	3.457797	-2.760972
20	6	0	-0.743833	3.540740	0.729726
21	6	0	-0.491928	4.739887	0.062759
22	1	0	0.305301	5.639519	-1.731588
23	1	0	-1.217261	3.539214	1.707854
24	1	0	-0.767162	5.684444	0.524672
25	7	0	-0.708953	1.126007	0.894132
26	6	0	0.062752	0.608514	1.942995
27	6	0	-2.000735	0.594778	1.004141
28	6	0	-0.710737	-0.334246	2.668211
29	6	0	-2.030326	-0.342925	2.067945
30	6	0	-0.139055	-0.999895	3.760590
31	6	0	1.374785	0.919618	2.308510
32	6	0	1.173592	-0.703643	4.124237
33	1	0	1.626356	-1.208986	4.973120
34	6	0	1.916862	0.252746	3.407293
35	1	0	-0.715718	-1.728620	4.325123
36	1	0	2.934746	0.479234	3.714462
37	1	0	1.954498	1.652404	1.756208
38	6	0	-3.222023	-1.021444	2.354490
39	6	0	-3.139350	0.887255	0.249001
40	6	0	-4.317651	0.208942	0.562785
41	1	0	-5.219609	0.422328	-0.005392
42	6	0	-4.360637	-0.742042	1.599429
43	1	0	-3.262666	-1.746427	3.163869
44	1	0	-5.293559	-1.254496	1.818970
45	1	0	-3.110850	1.620214	-0.551806
46	6	0	5.295028	-1.162396	0.545055
47	1	0	5.842129	-1.988508	0.073524
48	1	0	5.871524	-0.245425	0.384138
49	1	0	5.267616	-1.357332	1.624652
50	6	0	-3.317111	-2.922259	-2.512488
51	1	0	-3.923053	-2.275821	-3.155768
52	1	0	-3.136168	-3.859247	-3.053711
53	1	0	-3.911774	-3.160416	-1.621476

Table S10. Cartesian coordinates for **3di'** from DFT calculations

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.512388	-1.973145	-3.503781
2	6	0	1.534843	-1.379219	-2.767963
3	6	0	1.246916	-0.746130	-1.549031
4	6	0	-0.071743	-0.706182	-1.085740
5	6	0	-1.099936	-1.279283	-1.843323
6	6	0	-0.807846	-1.921111	-3.051706
7	6	0	3.476841	-0.765507	-0.393648
8	6	0	4.256538	0.160990	0.339649
9	6	0	3.505777	1.397892	0.386648
10	6	0	2.298079	1.173028	-0.316897
11	7	0	2.285315	-0.145467	-0.793095
12	6	0	3.757663	2.656589	0.946572
13	6	0	2.826057	3.684409	0.807343
14	6	0	1.637912	3.432266	0.087661
15	6	0	1.357364	2.194058	-0.480776
16	6	0	3.910750	-2.080272	-0.585939
17	6	0	5.143796	-2.442454	-0.053341
18	6	0	5.952619	-1.537386	0.667768
19	6	0	5.493883	-0.235170	0.862338
20	6	0	-2.904574	-1.695027	0.448350
21	15	0	-2.853827	-1.223348	-1.319146
22	6	0	-3.210693	0.522452	-0.897557
23	6	0	-3.341681	0.653312	0.471630
24	6	0	-3.172913	-0.580819	1.220443
25	6	0	-3.381035	1.751718	-1.591326
26	6	0	-3.642894	2.810566	-0.756804
27	16	0	-3.679627	2.290216	0.926759
28	16	0	-3.253312	-0.976317	2.904729
29	6	0	-2.920194	-2.673632	2.565427
30	6	0	-2.761796	-2.881939	1.217528
31	8	0	-3.752144	-1.936089	-2.285567
32	6	0	3.069882	5.048030	1.412014
33	6	0	7.289341	-1.984992	1.213041
34	6	0	-3.891239	4.243368	-1.118615
35	6	0	-2.845397	-3.673677	3.678792
36	1	0	0.743540	-2.463851	-4.444504
37	1	0	2.556432	-1.389329	-3.132815
38	1	0	-0.283389	-0.232899	-0.132378
39	1	0	-1.616483	-2.367775	-3.620973
40	1	0	4.683152	2.834966	1.488286
41	1	0	0.914756	4.235764	-0.028353
42	1	0	0.438010	2.035224	-1.033486
43	1	0	3.306588	-2.802231	-1.124223
44	1	0	5.495084	-3.461547	-0.195195
45	1	0	6.097047	0.472164	1.425965
46	1	0	-3.325425	1.860409	-2.668754
47	1	0	-2.555798	-3.861304	0.800452
48	1	0	3.012052	5.839859	0.656160
49	1	0	2.326228	5.285640	2.182225
50	1	0	4.057448	5.105673	1.878051
51	1	0	7.188619	-2.874615	1.845391
52	1	0	7.987363	-2.242497	0.407286
53	1	0	7.755982	-1.200439	1.815159
54	1	0	-3.813909	4.364659	-2.202314
55	1	0	-4.890129	4.576689	-0.815117
56	1	0	-3.163587	4.917516	-0.652665
57	1	0	-2.056771	-3.428280	4.399046

58	1	0	-3.788263	-3.743054	4.232966
59	1	0	-2.626419	-4.662309	3.266836

Table S11. Cartesian coordinates for **3ei'** from DFT calculations
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.586716	-0.649419	-0.073290
2	6	0	-5.975234	-0.723746	-0.074250
3	6	0	-4.641846	2.812676	0.356091
4	6	0	-3.642923	1.853312	0.232114
5	7	0	-3.731894	0.460169	0.060764
6	6	0	-3.763831	-1.820416	-0.225597
7	6	0	-4.382457	-3.061678	-0.377660
8	6	0	-5.776286	-3.136240	-0.378650
9	6	0	-6.558600	-1.983581	-0.229119
10	6	0	-4.249490	4.144026	0.515335
11	6	0	-2.896828	4.506591	0.549725
12	6	0	-1.893925	3.543396	0.425801
13	6	0	-2.247175	2.203483	0.265359
14	6	0	-1.045569	-1.860935	-0.249548
15	6	0	-2.361440	-1.385174	-0.179949
16	6	0	-2.455448	-0.013591	-0.006621
17	6	0	-1.475664	0.962599	0.107314
18	6	0	-0.170235	0.466098	0.035657
19	6	0	0.015841	-0.929309	-0.139825
20	6	0	3.682759	0.515493	-3.174839
21	6	0	2.711039	-0.380799	-2.803993
22	6	0	2.663718	-0.607357	-1.401300
23	6	0	3.606994	0.123651	-0.705952
24	16	0	4.567192	1.101597	-1.766719
25	6	0	3.602001	-0.086861	0.732252
26	6	0	2.654989	-0.985798	1.182264
27	6	0	2.692133	-1.170539	2.591348
28	6	0	3.660039	-0.418706	3.210270
29	16	0	4.553407	0.545714	2.035467
30	15	0	1.696056	-1.640835	-0.236613
31	8	0	1.674143	-3.126059	-0.452171
32	6	0	4.034155	0.994169	-4.550593
33	6	0	4.000670	-0.353607	4.668048
34	1	0	-6.587927	0.163702	0.041006
35	1	0	-5.691397	2.540704	0.329975
36	1	0	-3.783067	-3.959569	-0.493999
37	1	0	-6.261453	-4.100010	-0.496930
38	1	0	-7.641119	-2.067260	-0.233138
39	1	0	-5.011814	4.910853	0.613809
40	1	0	-2.625739	5.550217	0.674523
41	1	0	-0.847683	3.833142	0.453468
42	1	0	-0.796495	-2.908509	-0.385208
43	1	0	0.695631	1.117388	0.109305
44	1	0	2.059264	-0.862471	-3.524341
45	1	0	2.035786	-1.837730	3.138875
46	1	0	3.920341	2.079645	-4.650743
47	1	0	5.066456	0.745072	-4.821456
48	1	0	3.373629	0.519936	-5.281326
49	1	0	3.333063	-1.013602	5.228288
50	1	0	5.030175	-0.673921	4.864498
51	1	0	3.888006	0.658836	5.072296

Reference for DFT calculations:

S1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Jr. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 09, Revision A.02, Gaussian, Inc.: Wallingford CT, **2009**.

C. Photo-physical Data

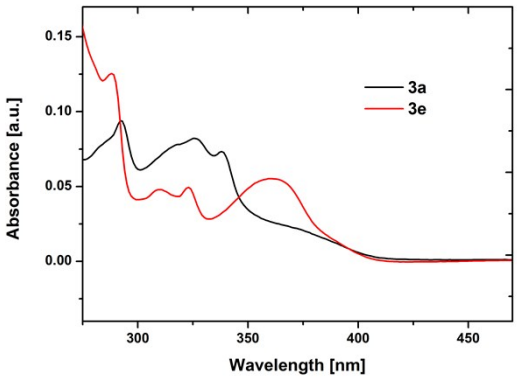


Figure S29. Absorption spectra of **3a** and **3e** recorded from 5 μM solutions in DCM at r.t.

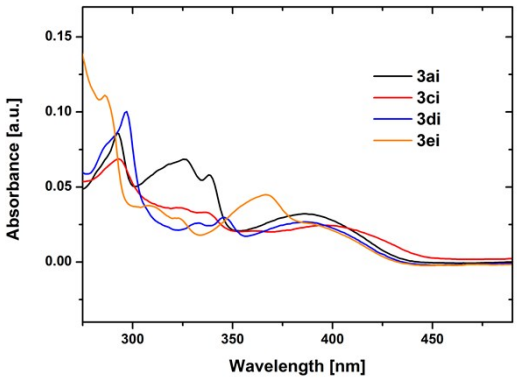


Figure S30. Absorption spectra of **3ai**, **3ci**, **3di** and **3ei** recorded from 5 μM solutions in DCM at r.t.

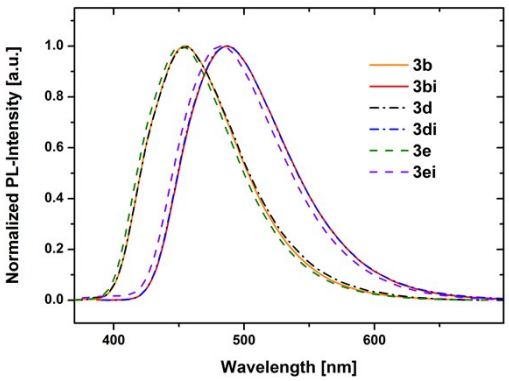


Figure S31. Normalized emission spectra of **3b**, **3bi**, **3d**, **3di**, **3e** and **3ei** recorded from 5 μM solutions in DCM at r.t.

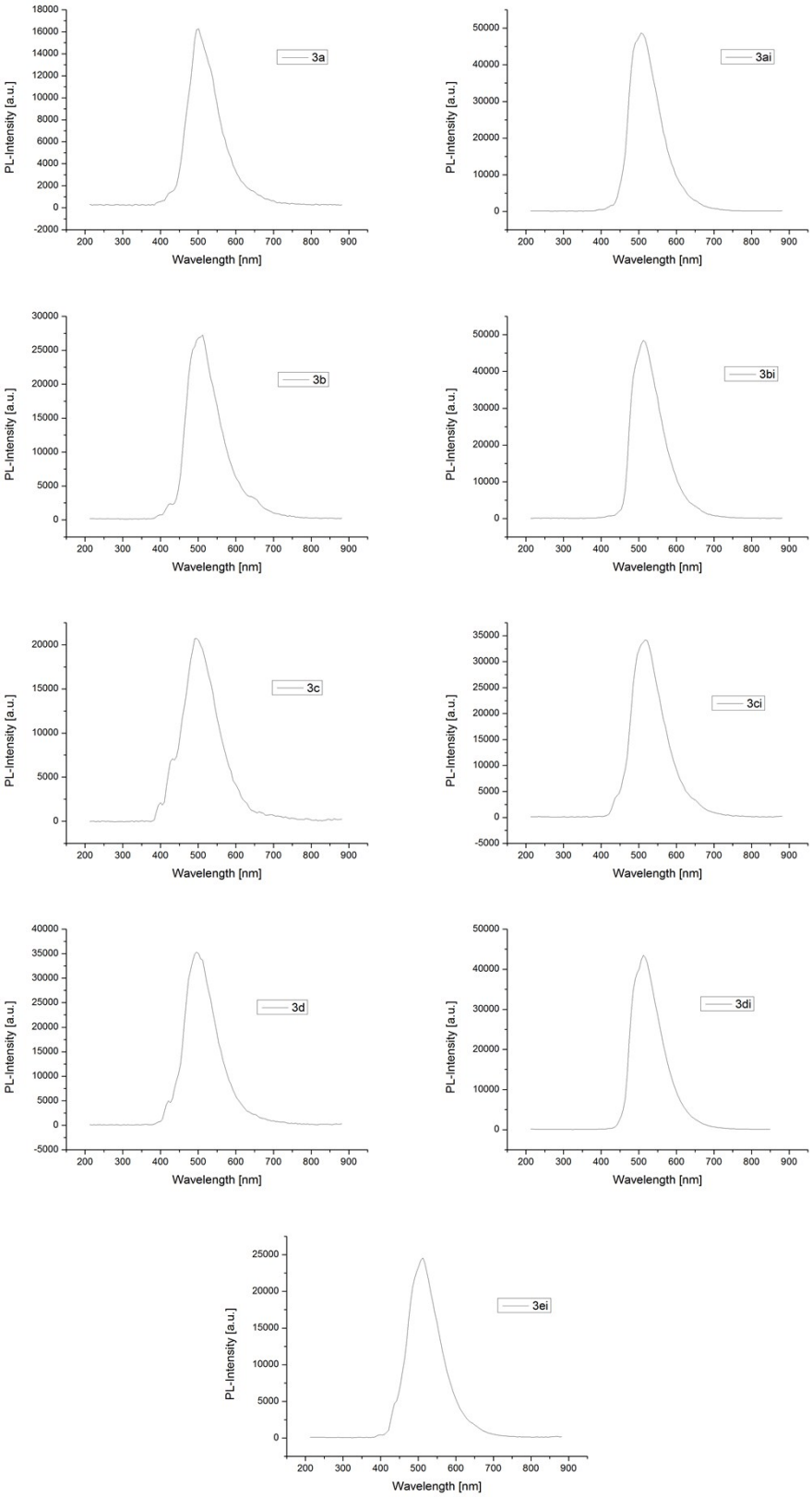


Figure S32. Low temperature phosphorescence spectra of compounds **3a**-**3di** and **3ei**.

D. Crystallography

Table S12. Details on data collection and refinement for **3c**.

formula	$C_{26}H_{16}NOPS_2$
fw	453.5
cryst.size, mm	0.65 x 0.66 x 0.42
color, shape	yellow fragment
crystal system	monoclinic
space group	$P2_1$ (no. 4)
a, Å	8.3295(6)
b, Å	14.1464(10)
c, Å	8.8132(6)
α, deg	90
β, deg	103.1530(19)
γ, deg	90
V, Å^3	1011.24(12)
T, K	100
Z	2
ρ_{calc}, g cm^{-3}	1.4894
μ, mm^{-1} (MoKα)	0.363
F(000)	468
absorption corrections, T_{min}-T_{max}	Multi-scan, 0.79–0.86
θ range, deg	2.37–32.72
no. of rflns measd	82676
R_{int}	0.0407
no. of rflns unique	7360
no. of rflns $I>3\sigma(I)$	7293
no. of params / restraints	281 / 0
R_1 ($I > 3\sigma(I)$) [a]	0.0198
R_1 (all data)	0.0201
wR_2 ($I > 3\sigma(I)$)	0.0272
wR_2 (all data)	0.0273
GooF	1.92
Diff.Four.peaks	-0.20 / 0.28

E. CV Measurements

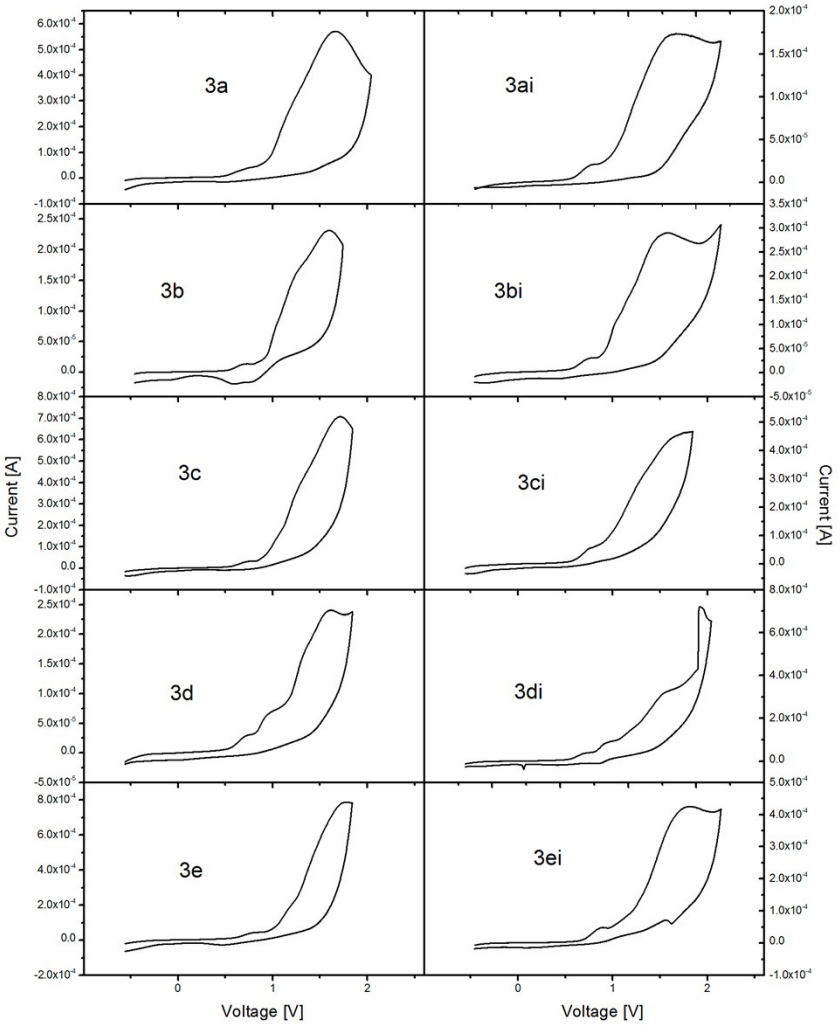


Figure S33. Cyclic voltammograms of compounds **3a(i)**-**3e(i)**.