Electronic Supplementary Material (ESI) for RSC Advances.

Experimental and theoretical approving of anomeric based oxidation in the preparation of 2-sbstituted benz-(imida, oxa and othia)-zoles using [2,6-DMPy-NO_2]$C(NO_2)_3$ as a novel nano molten salt catalyst

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Fig S1. The IR spectrum of 2-(1-phenylprop-1-en-2-yl)-1H-benzo[d]imidazole (Table 3, entry 2)

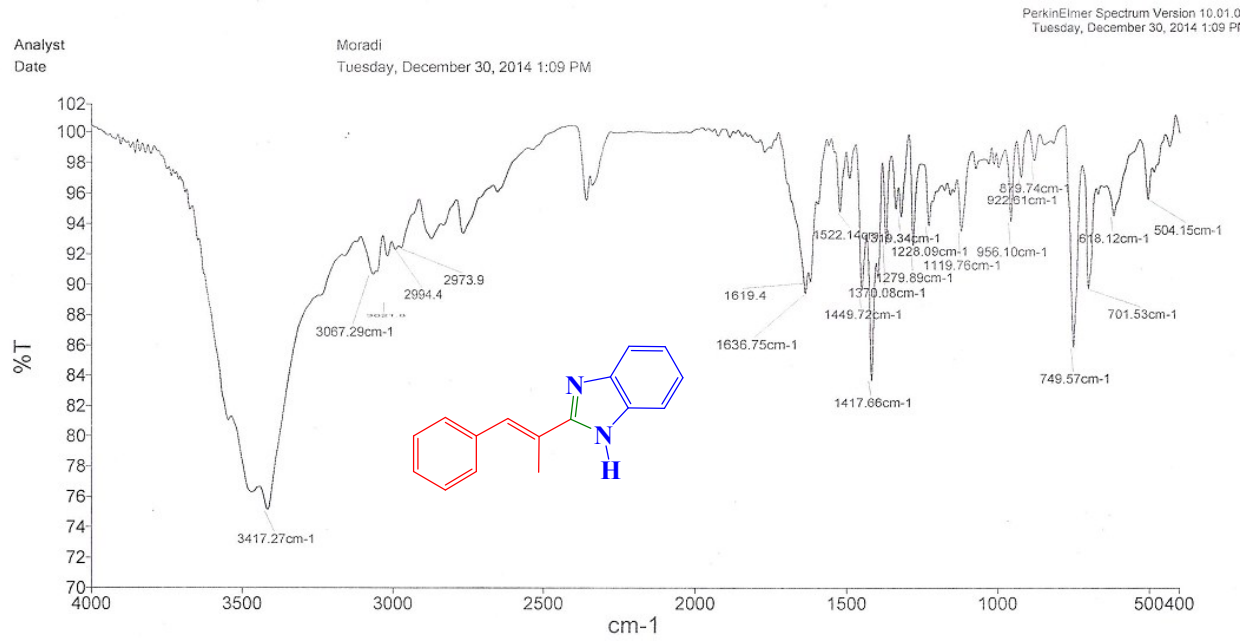


Fig S2. The ^{1}H NMR spectrum of 2-(1-phenylprop-1-en-2-yl)-1H-benzo[d]imidazole (Table 3, entry 2)

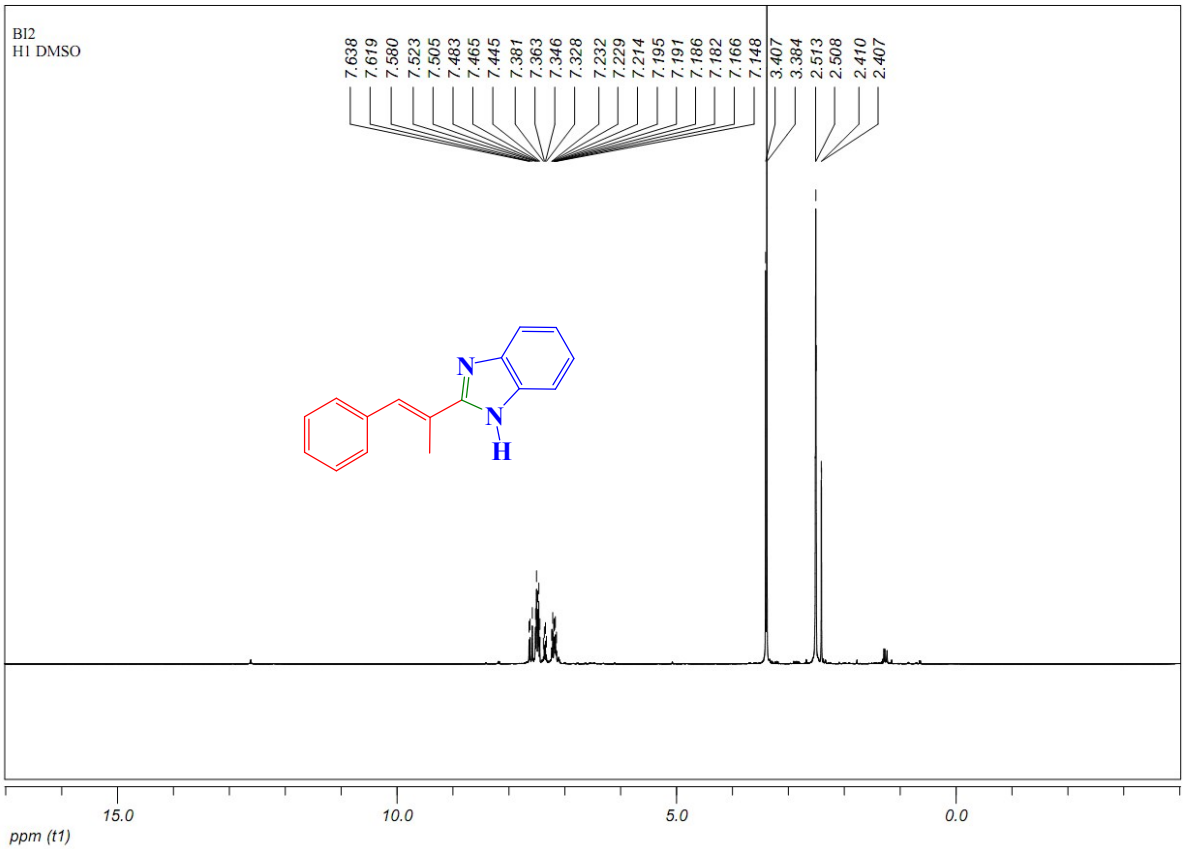


Fig S3. The ^{1}H NMR spectrum of 2-(1-phenylprop-1-en-2-yl)-1H-benzo[d]imidazole (Table 3, entry 2)

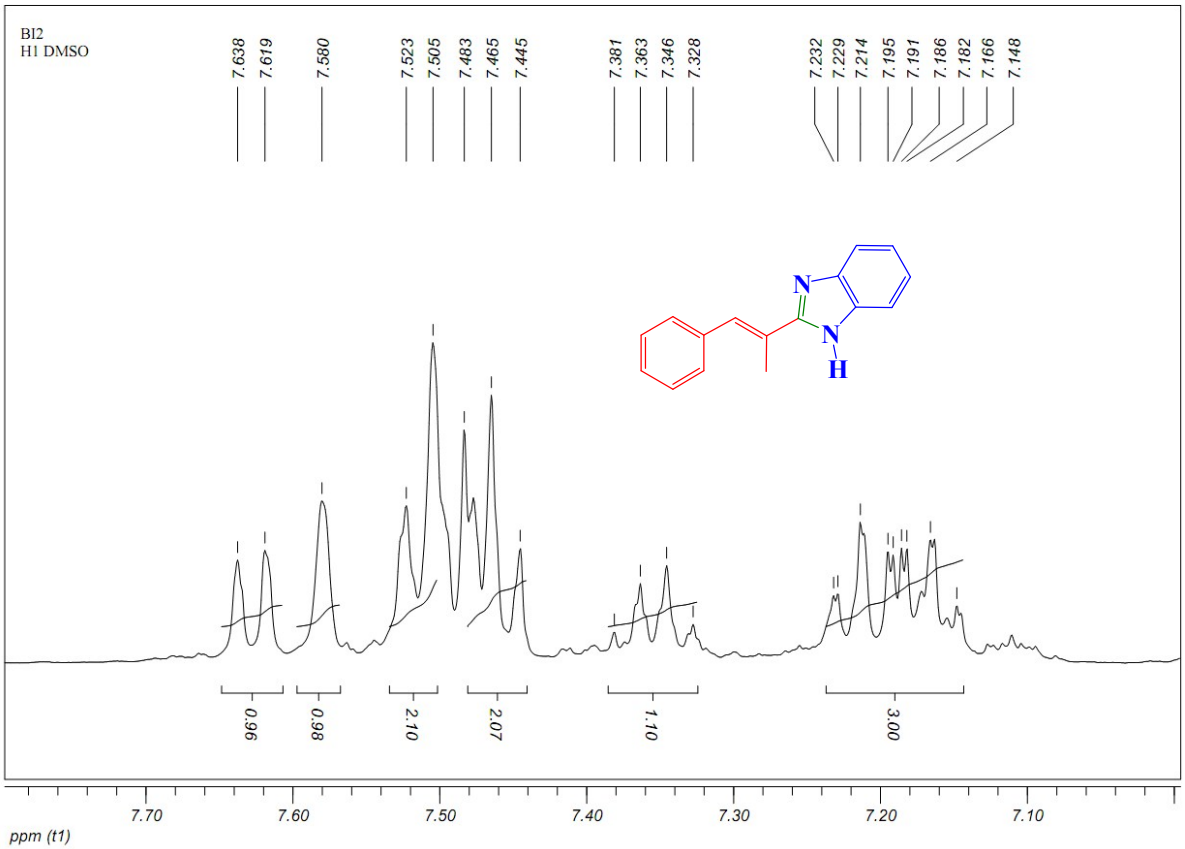


Fig S4. The ^{1}H NMR spectrum of 2-(1-phenylprop-1-en-2-yl)-1H-benzo[d]imidazole (Table 3, entry 2)

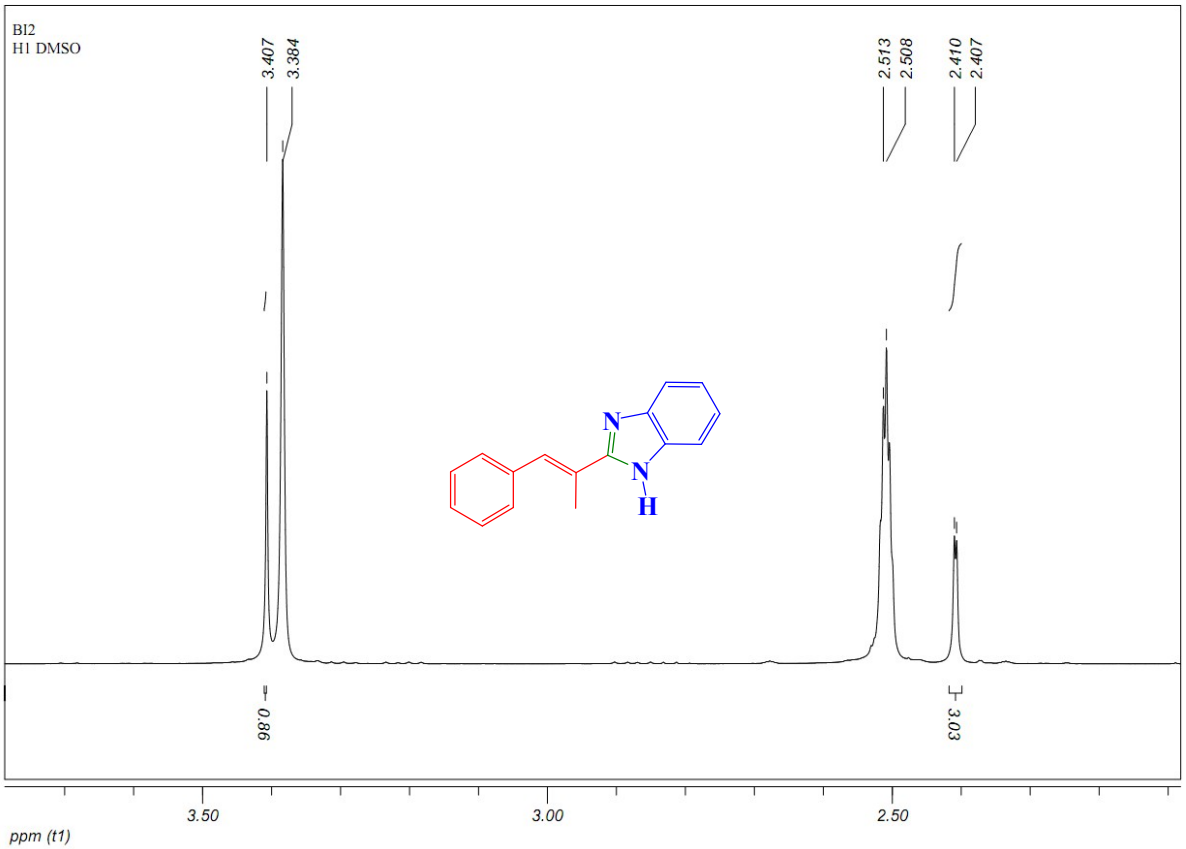


Fig S5. The ^{13}C NMR spectrum of 2-(1-phenylprop-1-en-2-yl)-1H-benzo[d]imidazole (Table 3, entry 2)

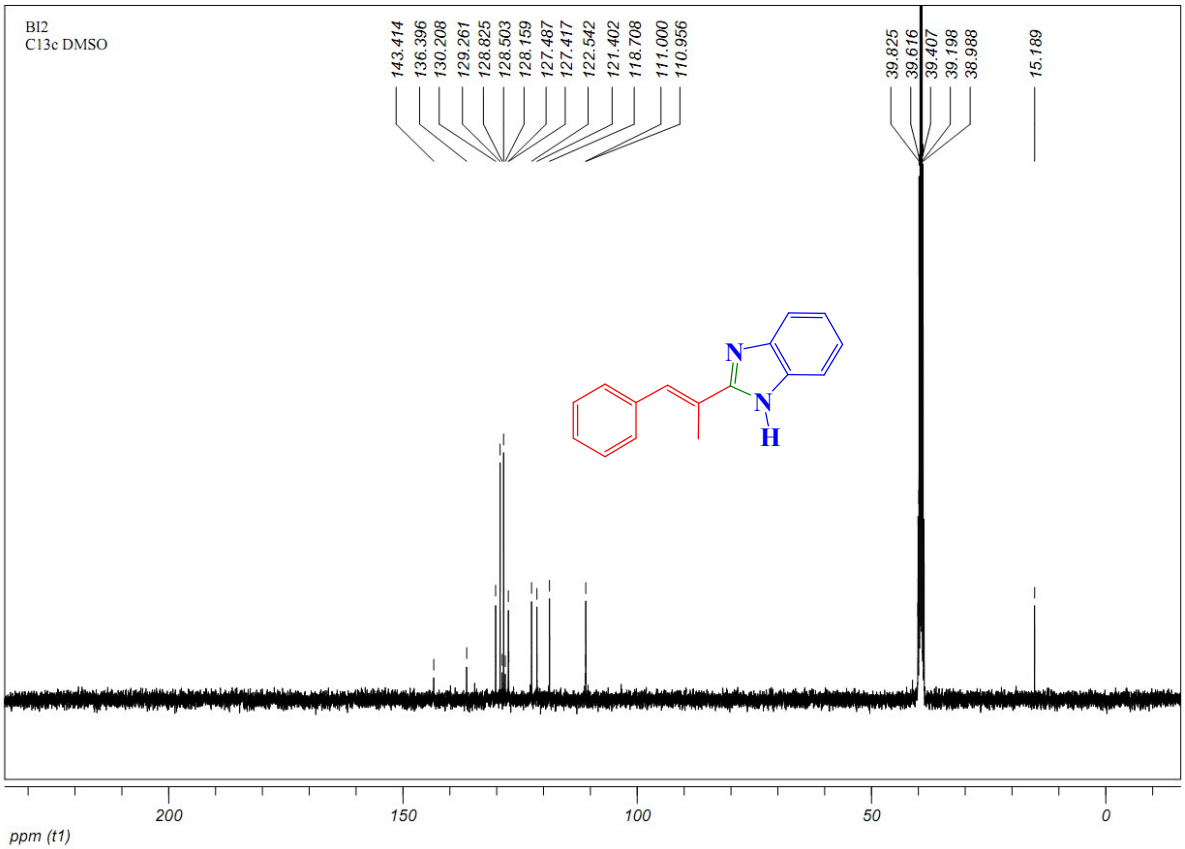


Fig S6. The ^{13}C NMR spectrum of 2-(1-phenylprop-1-en-2-yl)-1H-benzo[d]imidazole (Table 3, entry 2)

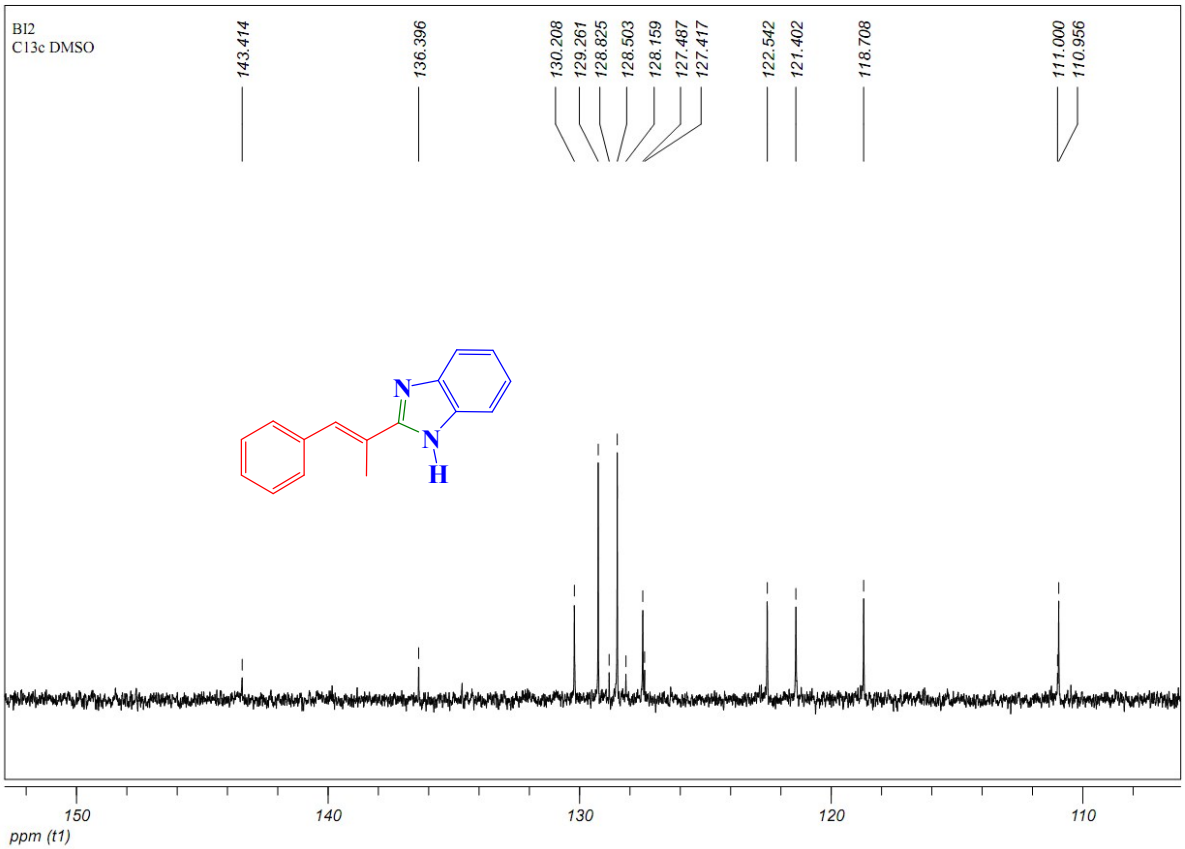


Fig S7. The ^{13}C NMR spectrum of 2-(1-phenylprop-1-en-2-yl)-1H-benzo[d]imidazole (Table 3, entry 2)

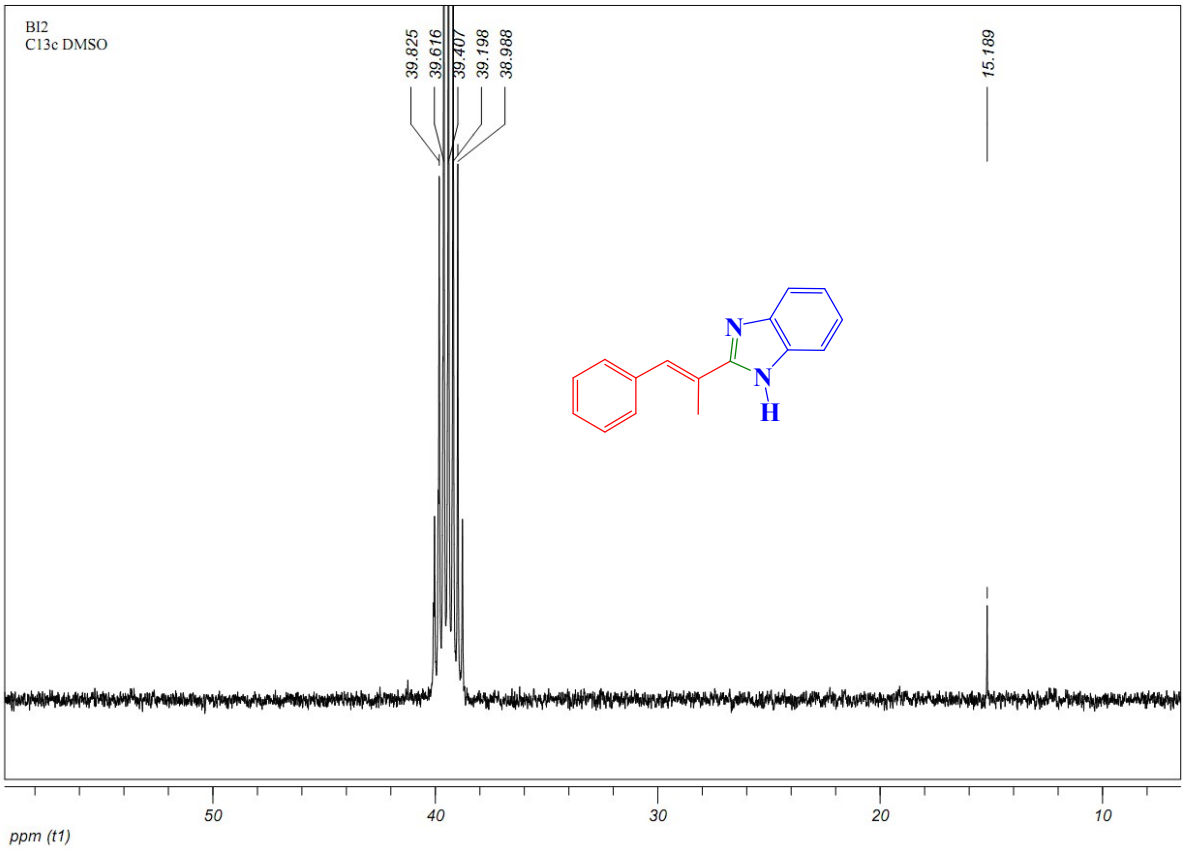


Fig S8. The Mass spectrum of 2-(1-phenylprop-1-en-2-yl)-1H-benzo[d]imidazole (Table 3, entry 2)

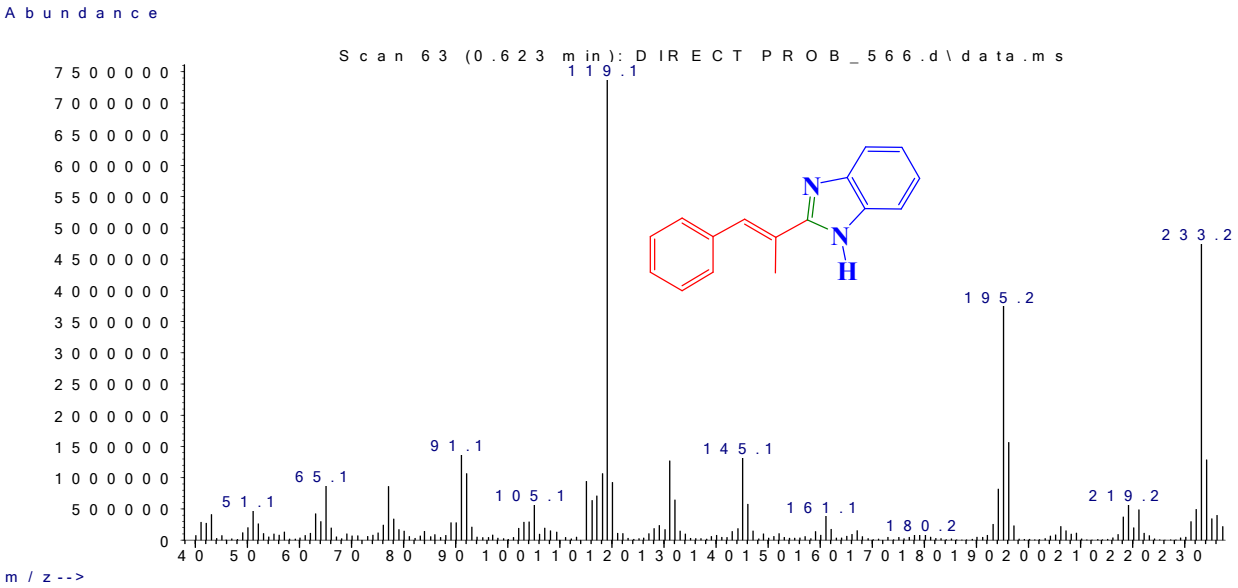


Fig S9. The IR spectrum of 2-([1,1'-biphenyl]-4-yl)-1H-benzo[d]imidazole (Table 3, entry 3)

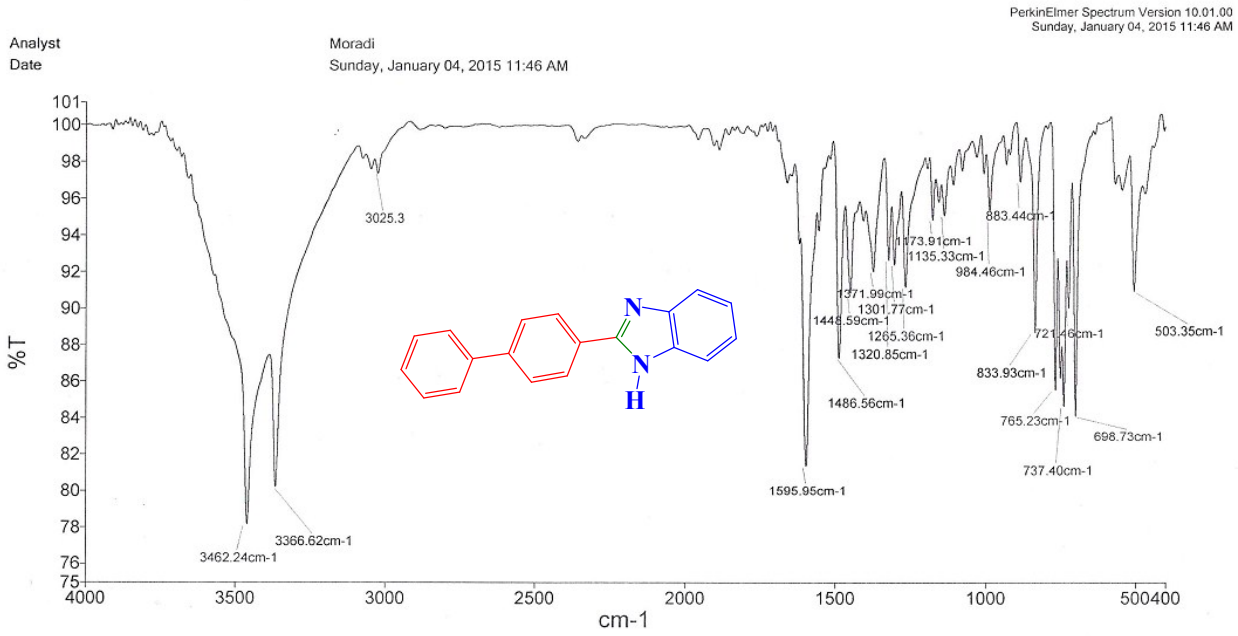


Fig S10. The ^{1}H NMR spectrum of 2-([1,1'-biphenyl]-4-yl)-1H-benzo[d]imidazole (Table 3, entry 3)

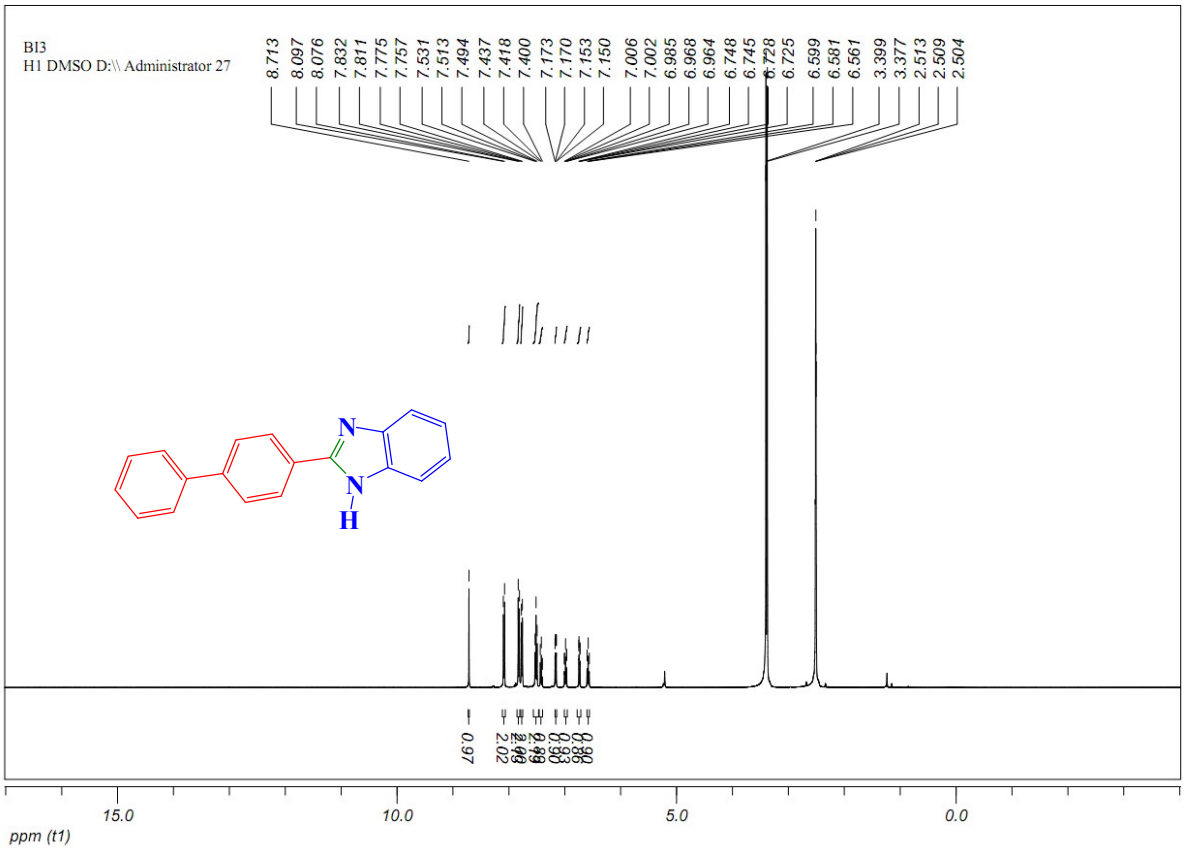


Fig S11. The ^{1}H NMR spectrum of 2-([1,1'-biphenyl]-4-yl)-1H-benzo[d]imidazole (Table 3, entry 3)

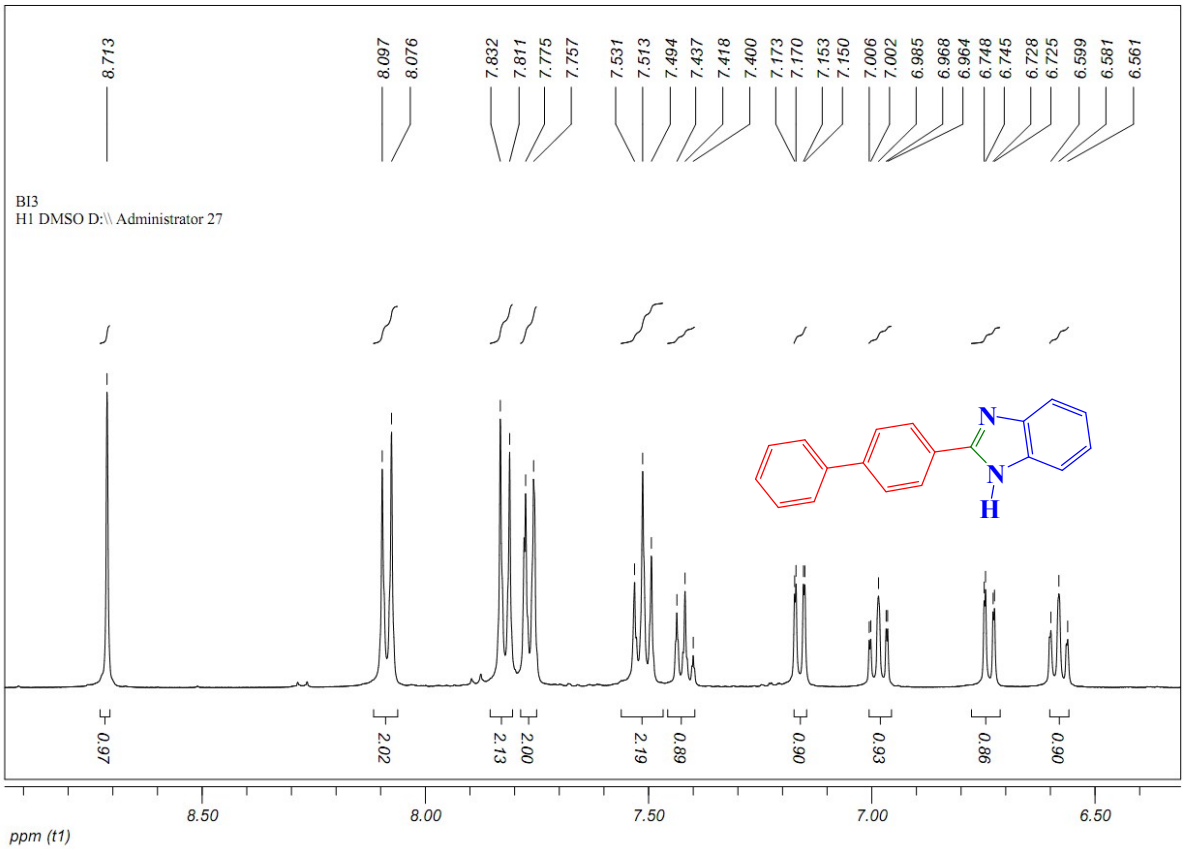


Fig S12. The ^{13}C NMR spectrum of 2-([1,1'-biphenyl]-4-yl)-1H-benzo[d]imidazole (Table 3, entry 3)

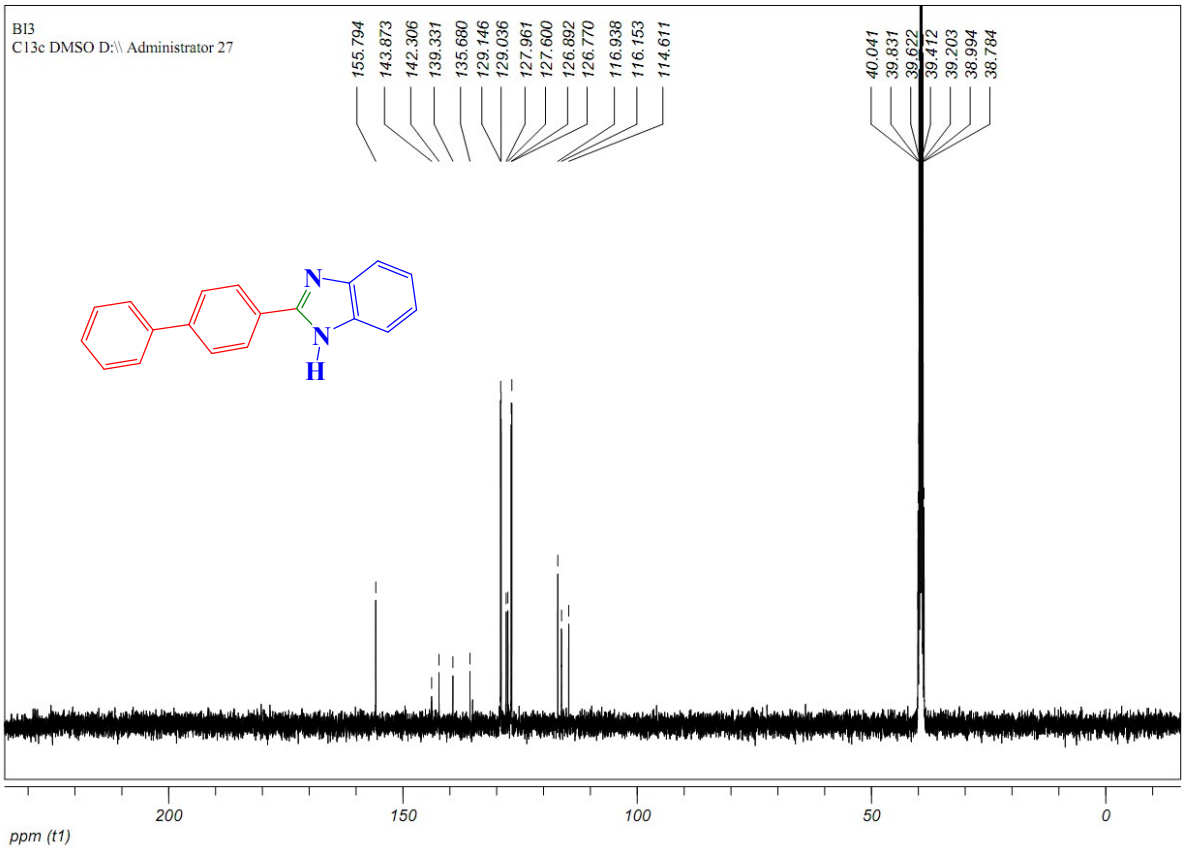


Fig S13. The ^{13}C NMR spectrum of 2-([1,1'-biphenyl]-4-yl)-1H-benzo[d]imidazole (Table 3, entry 3)

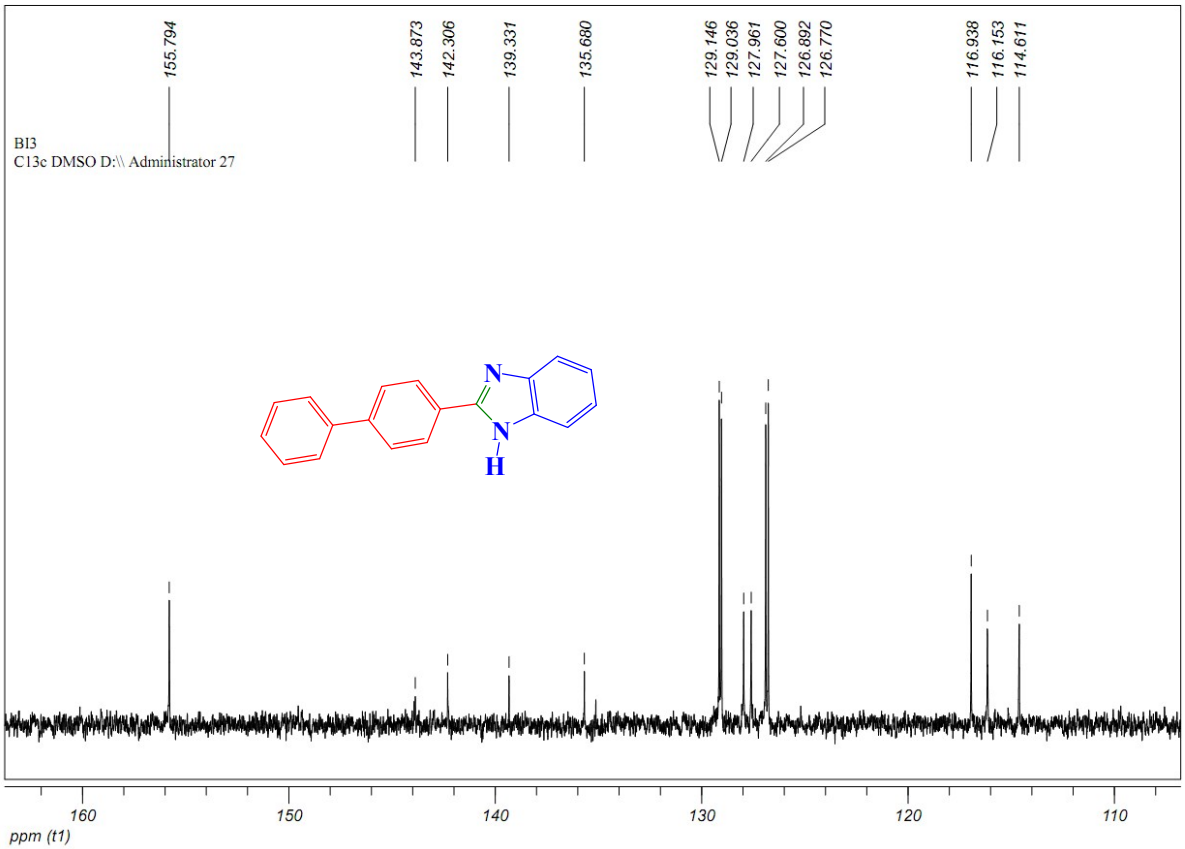


Fig S14. The Mass spectrum of 2-([1,1'-biphenyl]-4-yl)-1H-benzo[d]imidazole (Table 3, entry 3)

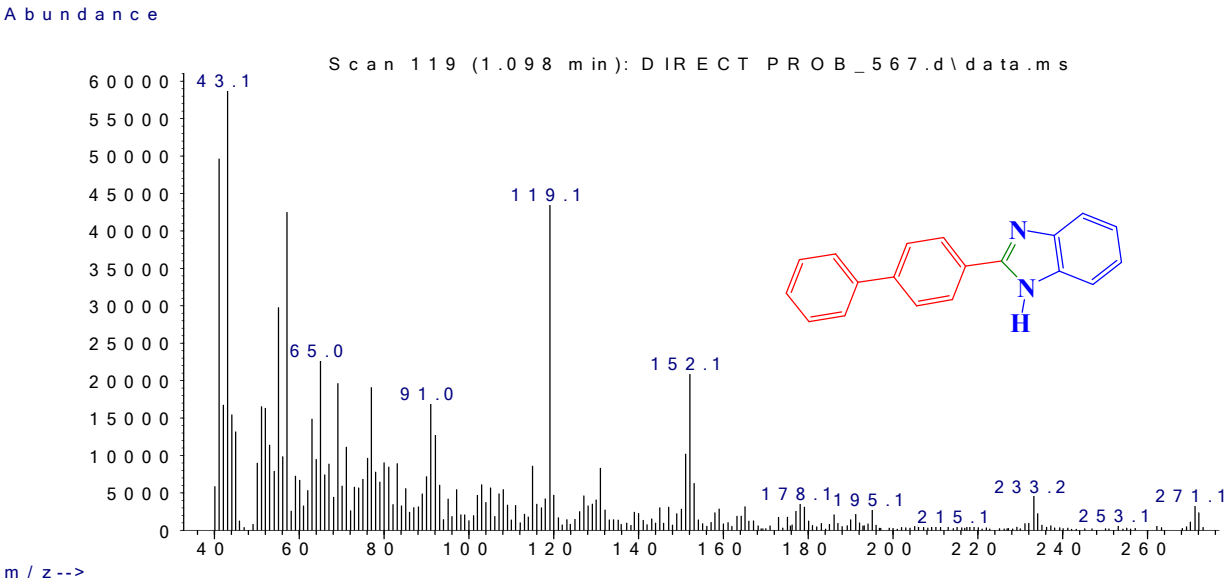


Fig S15. The IR spectrum of 4-(1H-benzo[d]imidazol-2-yl)-2-ethoxyphenol (Table 3, entry 5)

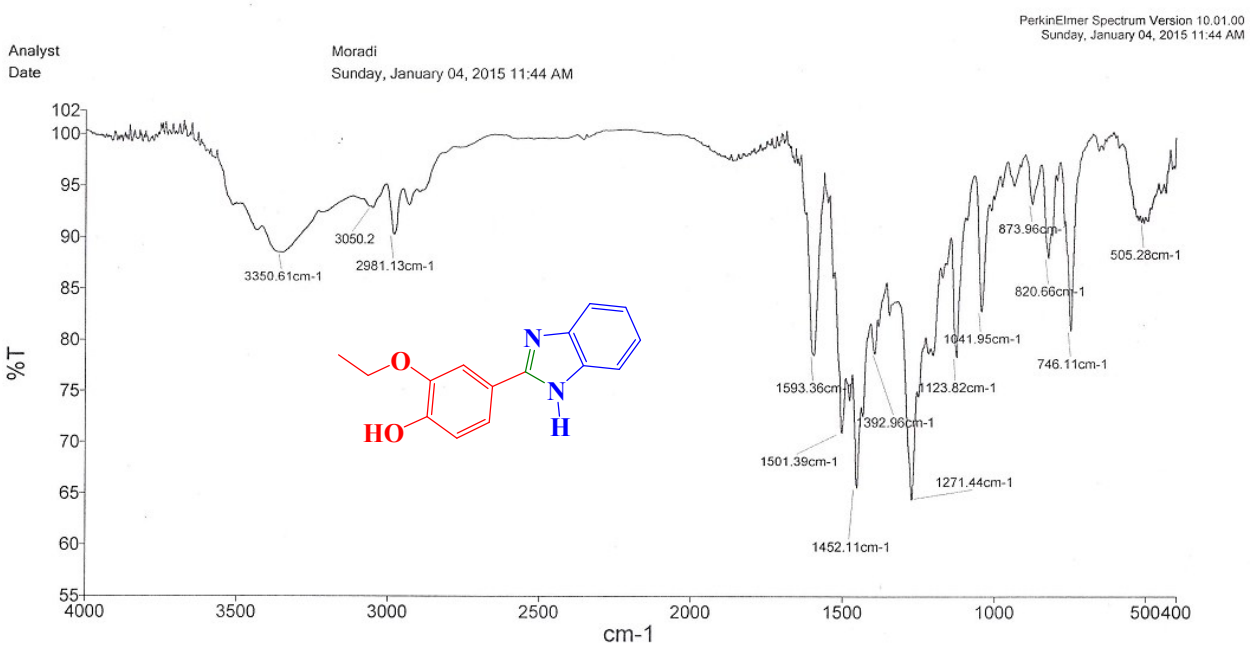


Fig S16. The ^{1}H NMR spectrum of 4-(1H-benzo[d]imidazol-2-yl)-2-ethoxyphenol (Table 3, entry 5)

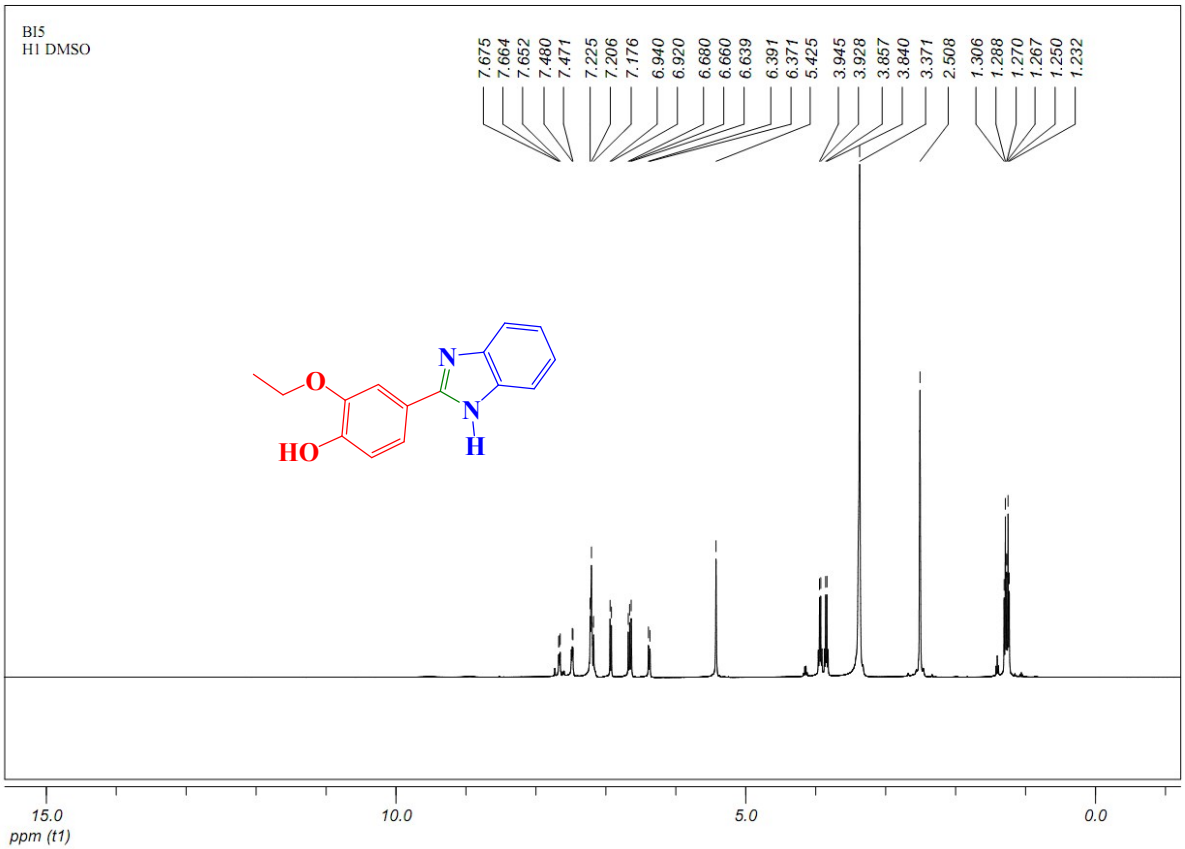


Fig S17. The ^{1}H NMR spectrum of 4-(1H-benzo[d]imidazol-2-yl)-2-ethoxyphenol (Table 3, entry 5)

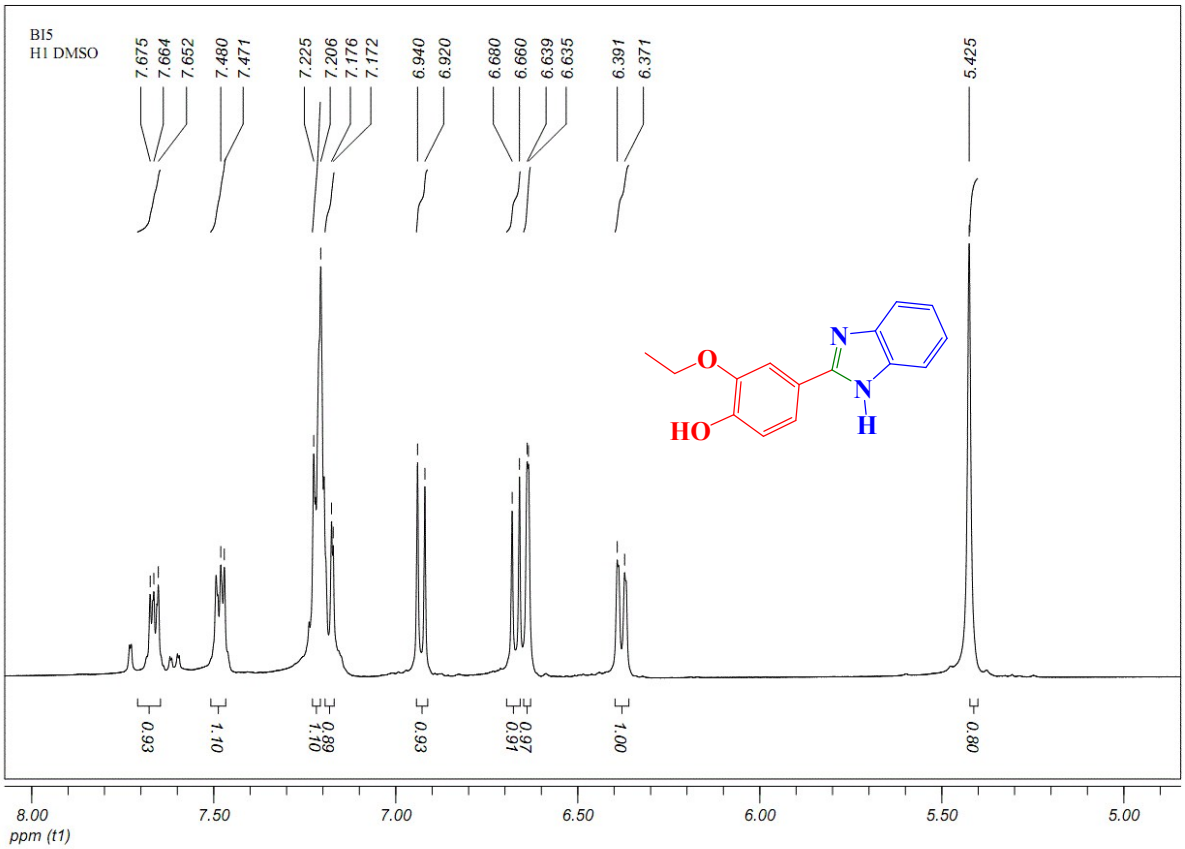


Fig S18. The ^{1}H NMR spectrum of 4-(1H-benzo[d]imidazol-2-yl)-2-ethoxyphenol (Table 3, entry 5)

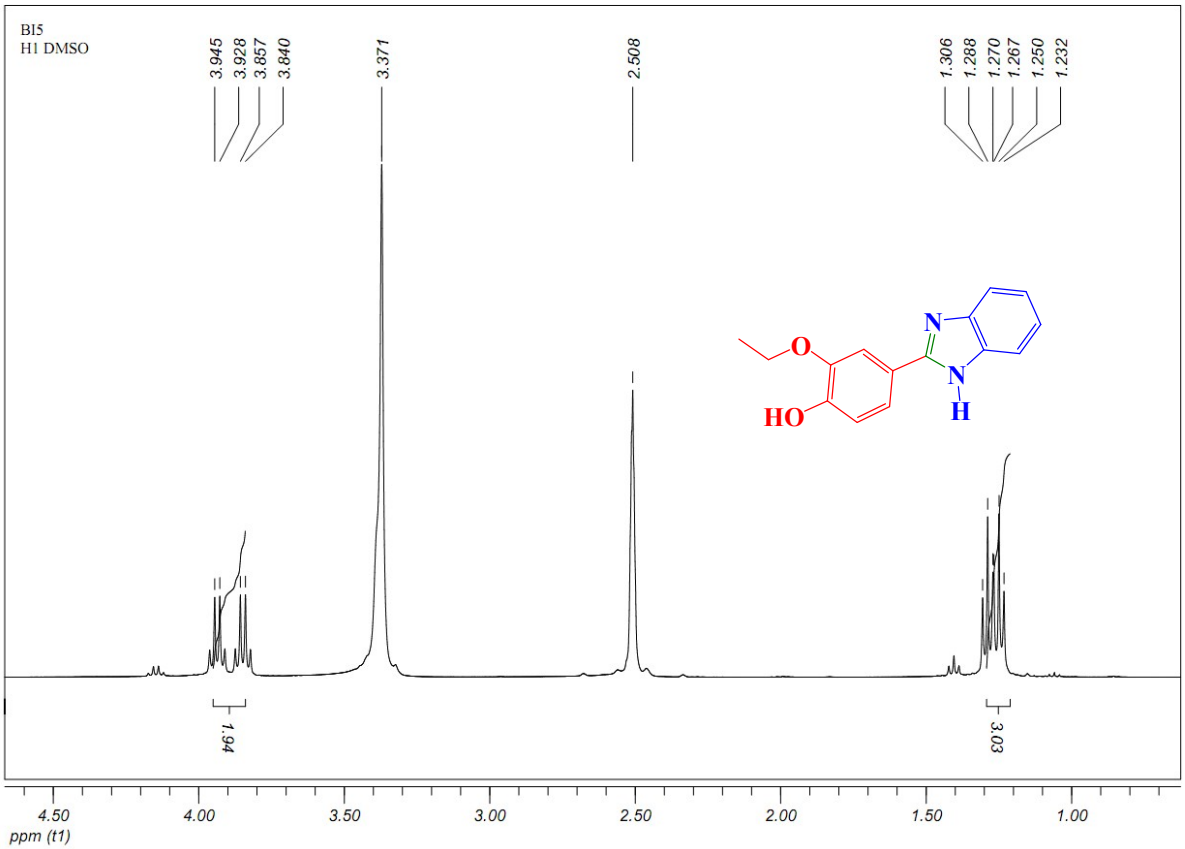


Fig S16. The ^{13}C NMR spectrum of 4-(1H-benzo[d]imidazol-2-yl)-2-ethoxyphenol (Table 3, entry 5)

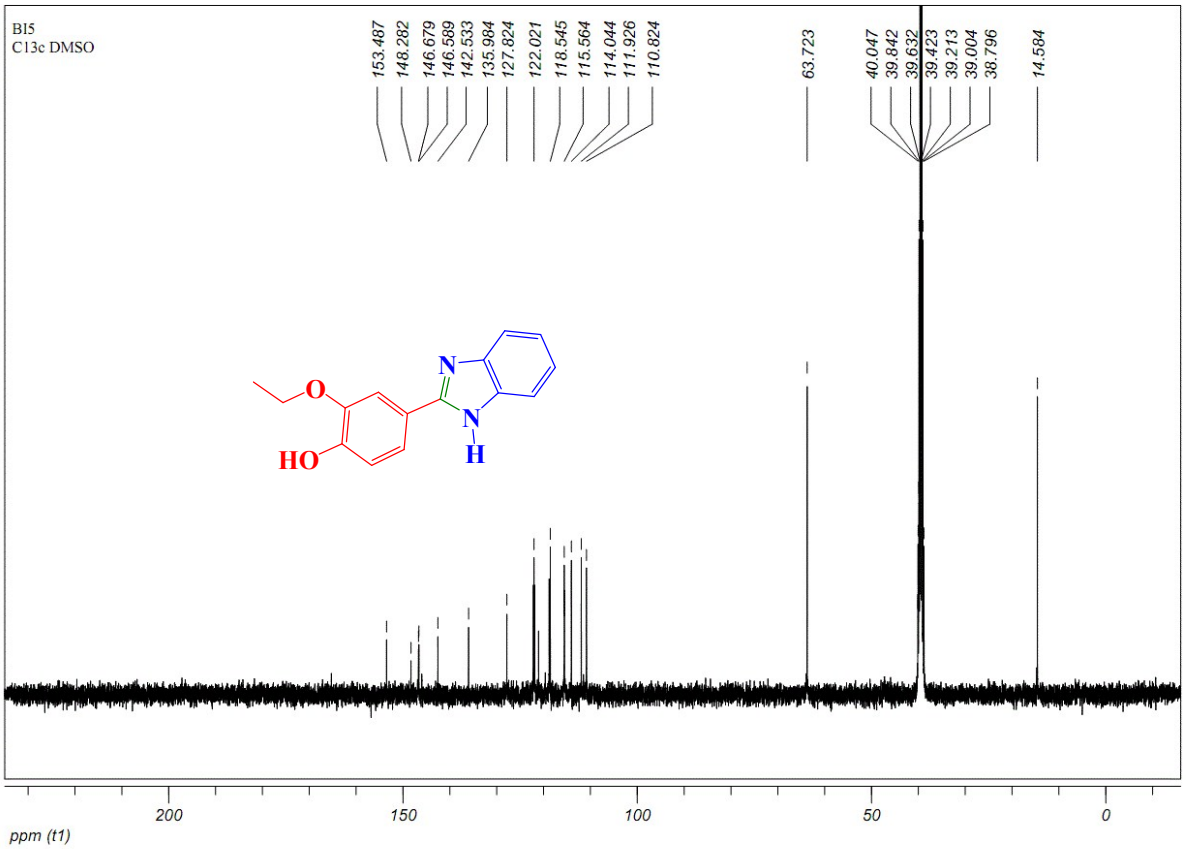


Fig S20. The ^{13}C NMR spectrum of 4-(1H-benzo[d]imidazol-2-yl)-2-ethoxyphenol (Table 3, entry 5)

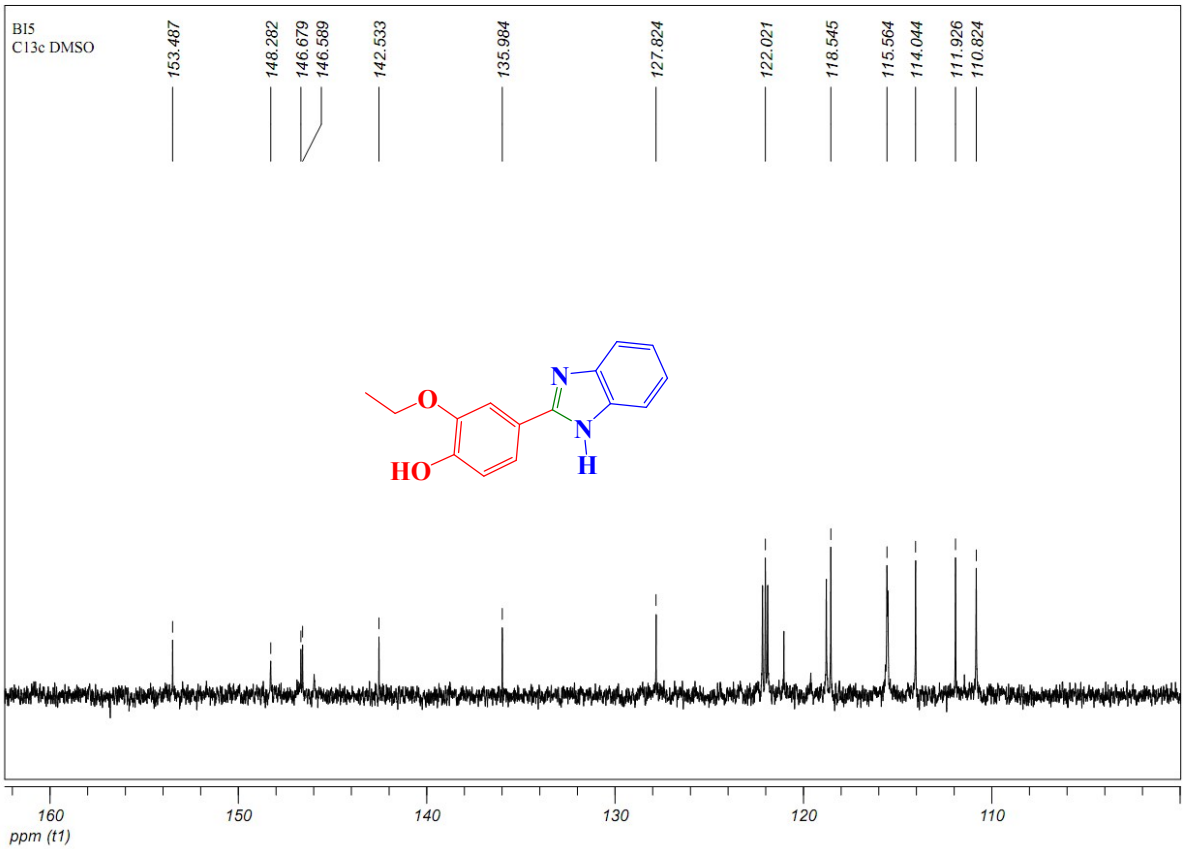


Fig S21. The ^{13}C NMR spectrum of 4-(1H-benzo[d]imidazol-2-yl)-2-ethoxyphenol (Table 3, entry 5)

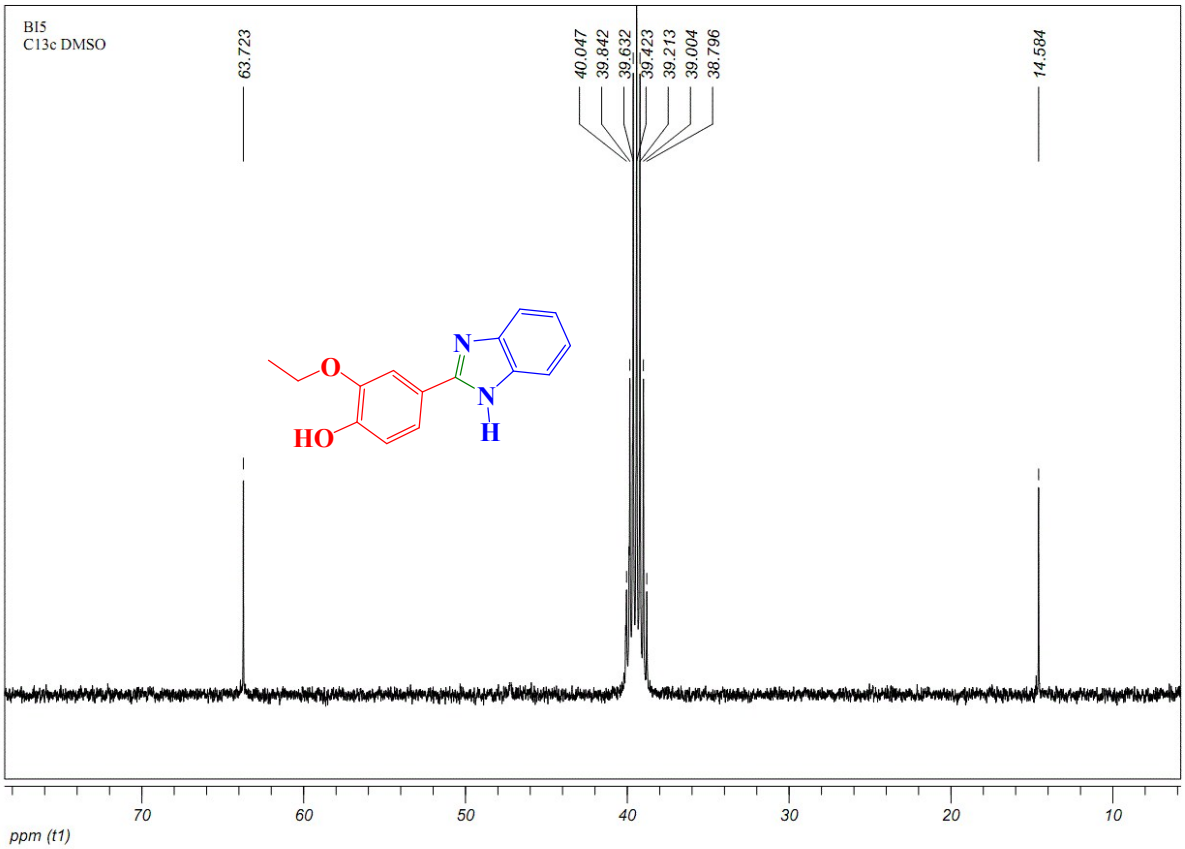


Fig S22. The Mass spectrum of 4-(1H-benzo[d]imidazol-2-yl)-2-ethoxyphenol (Table 3, entry 5)

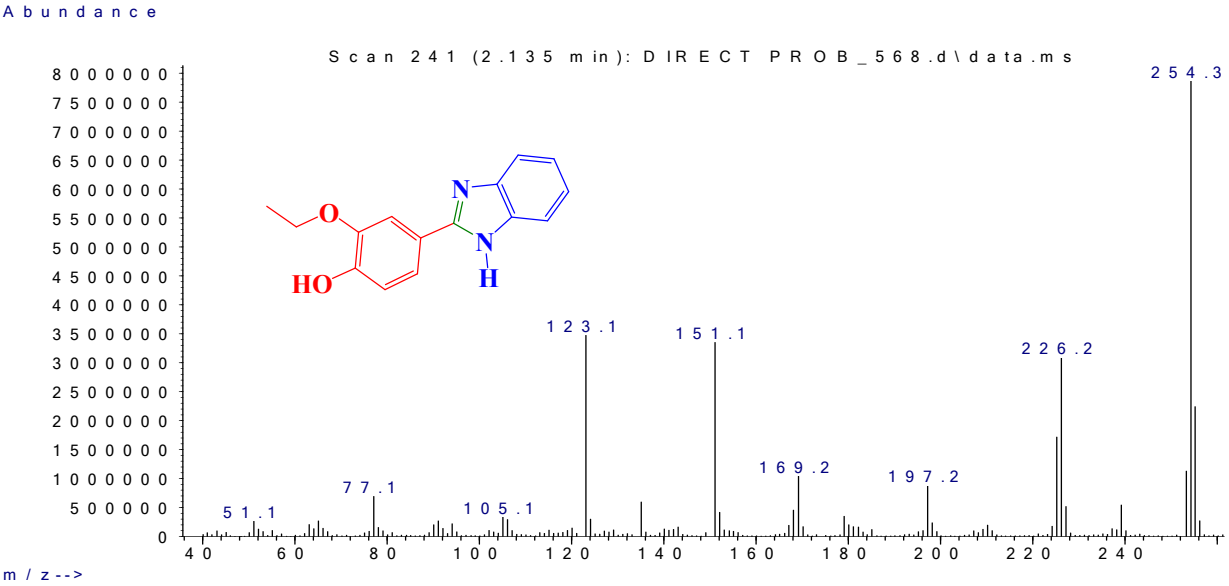


Fig S23. The IR spectrum of 2-(1H-indol-3-yl)-1H-benzo[d]imidazole (Table 3, entry 6)

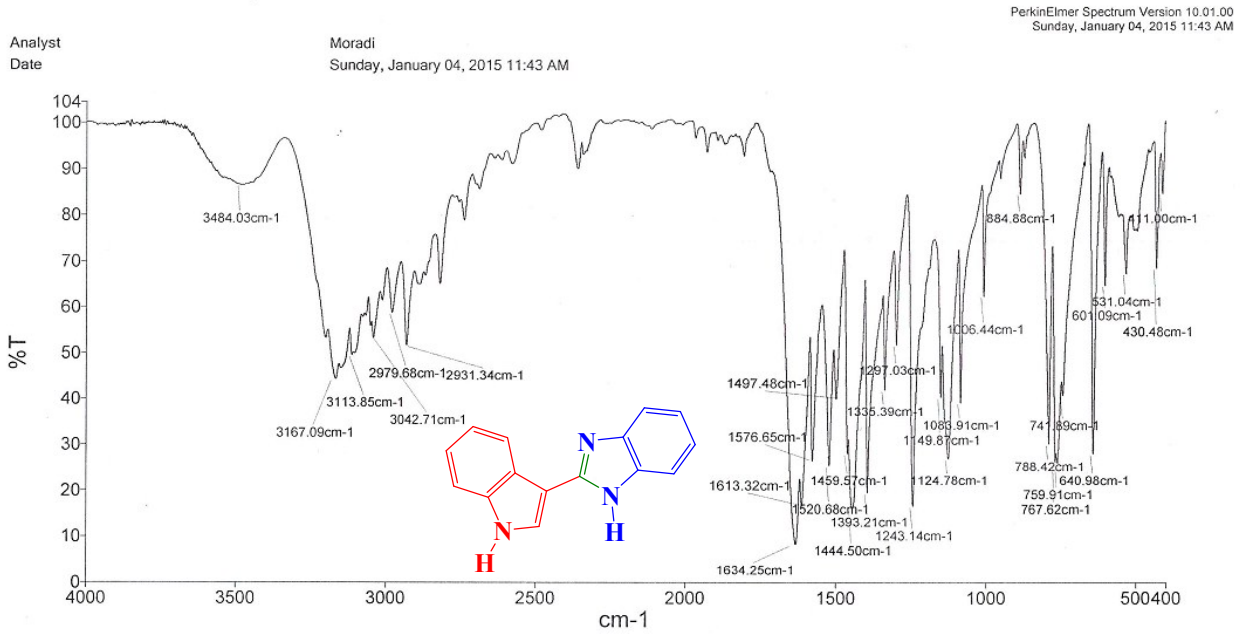


Fig S24. The ^{1}H NMR spectrum of 2-(1H-indol-3-yl)-1H-benzo[d]imidazole (Table 3, entry 6)

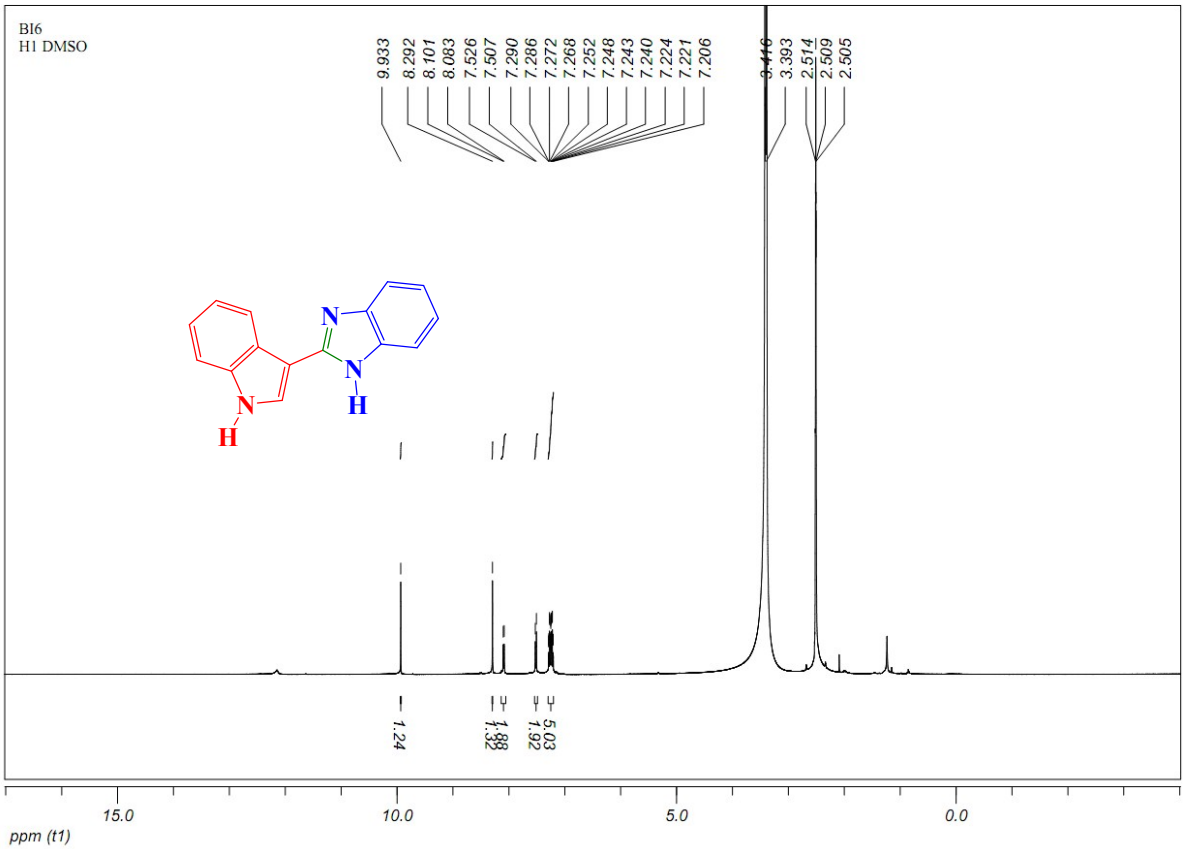


Fig S25. The ^{1}H NMR spectrum of 2-(1H-indol-3-yl)-1H-benzo[d]imidazole (Table 3, entry 6)

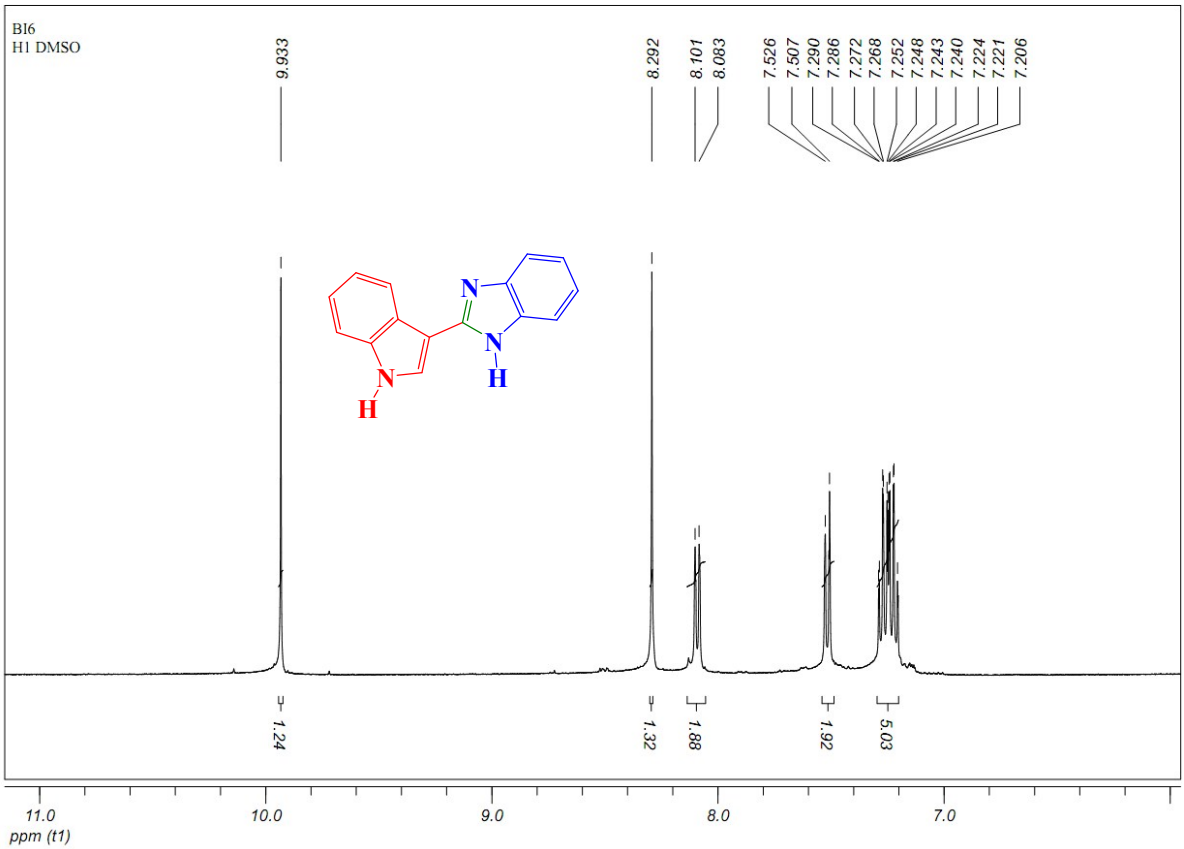


Fig S26. The ^{1}H NMR spectrum of 2-(1H-indol-3-yl)-1H-benzo[d]imidazole (Table 3, entry 6)

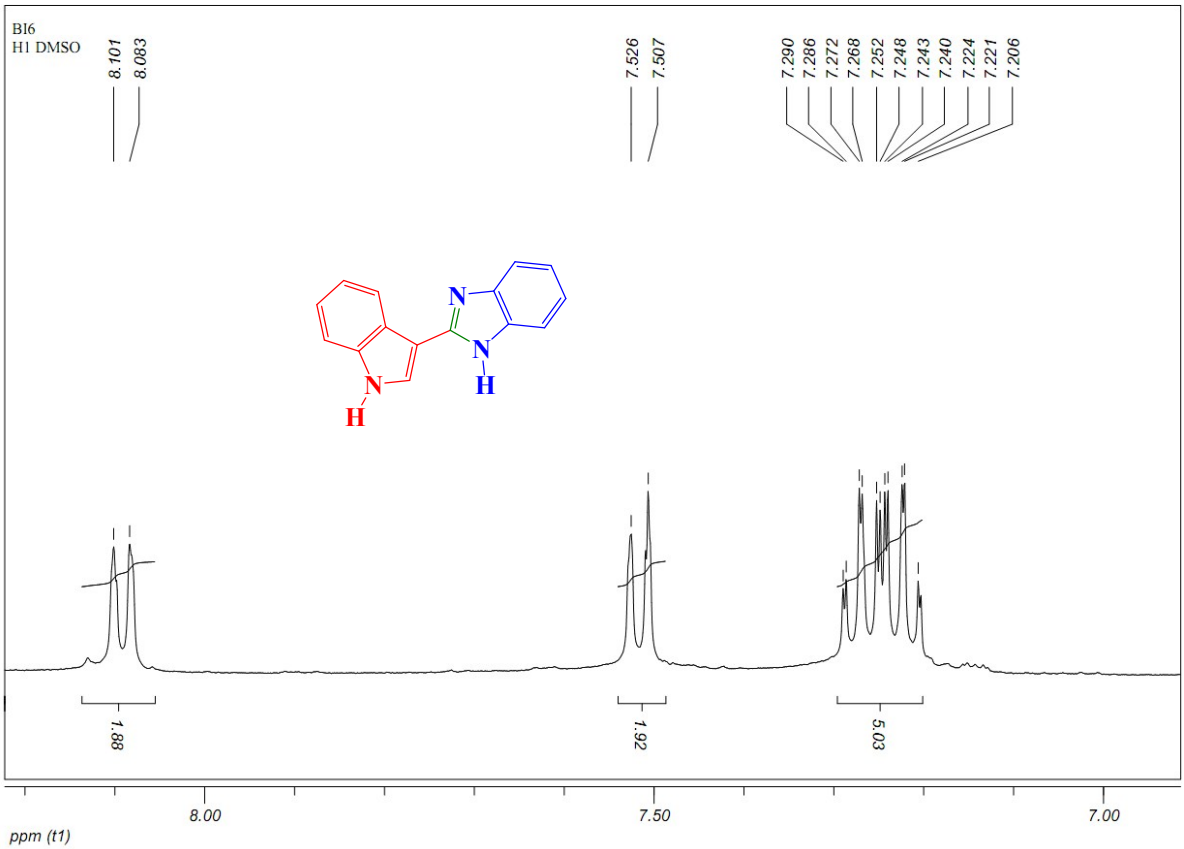


Fig S27. The ^{13}C NMR spectrum of 42-(1H-indol-3-yl)-1H-benzo[d]imidazole (Table 3, entry 6)

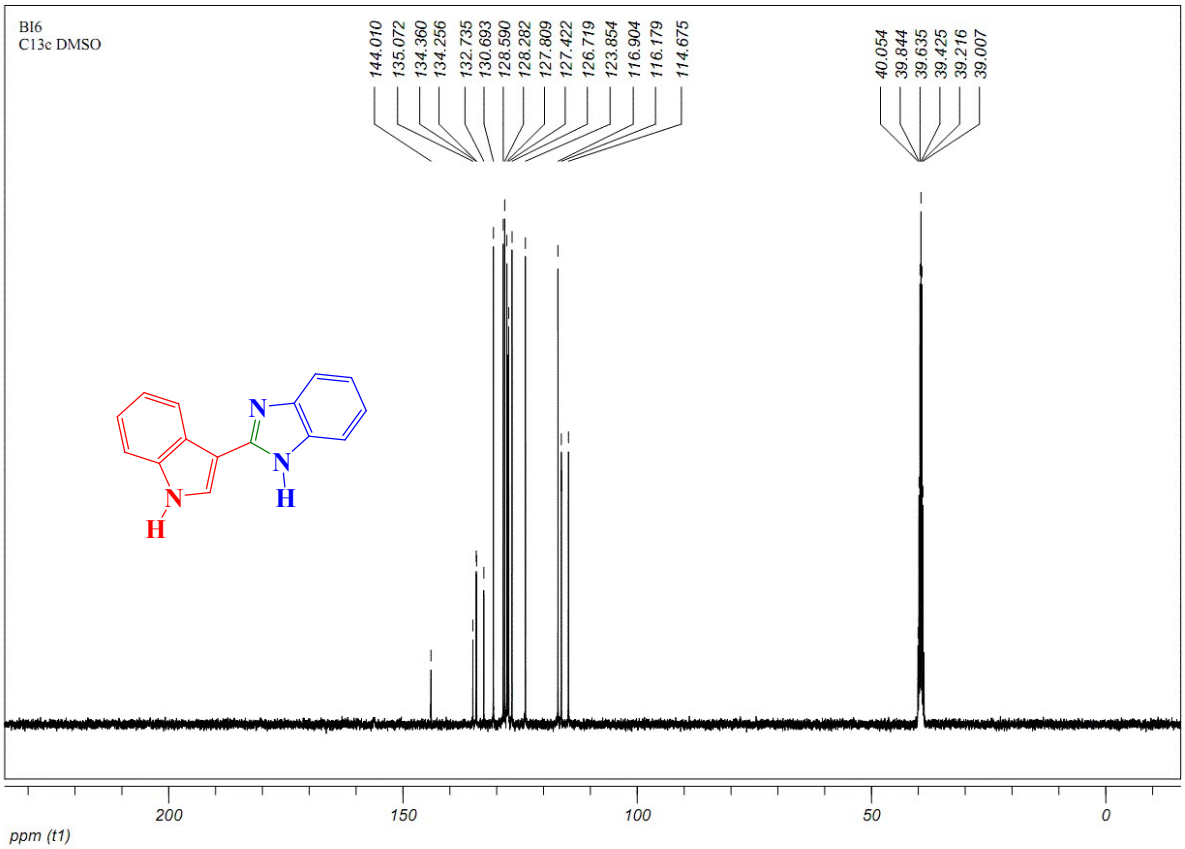


Fig S28. The ^{13}C NMR spectrum of 2-(1H-indol-3-yl)-1H-benzo[d]imidazole (Table 3, entry 6)

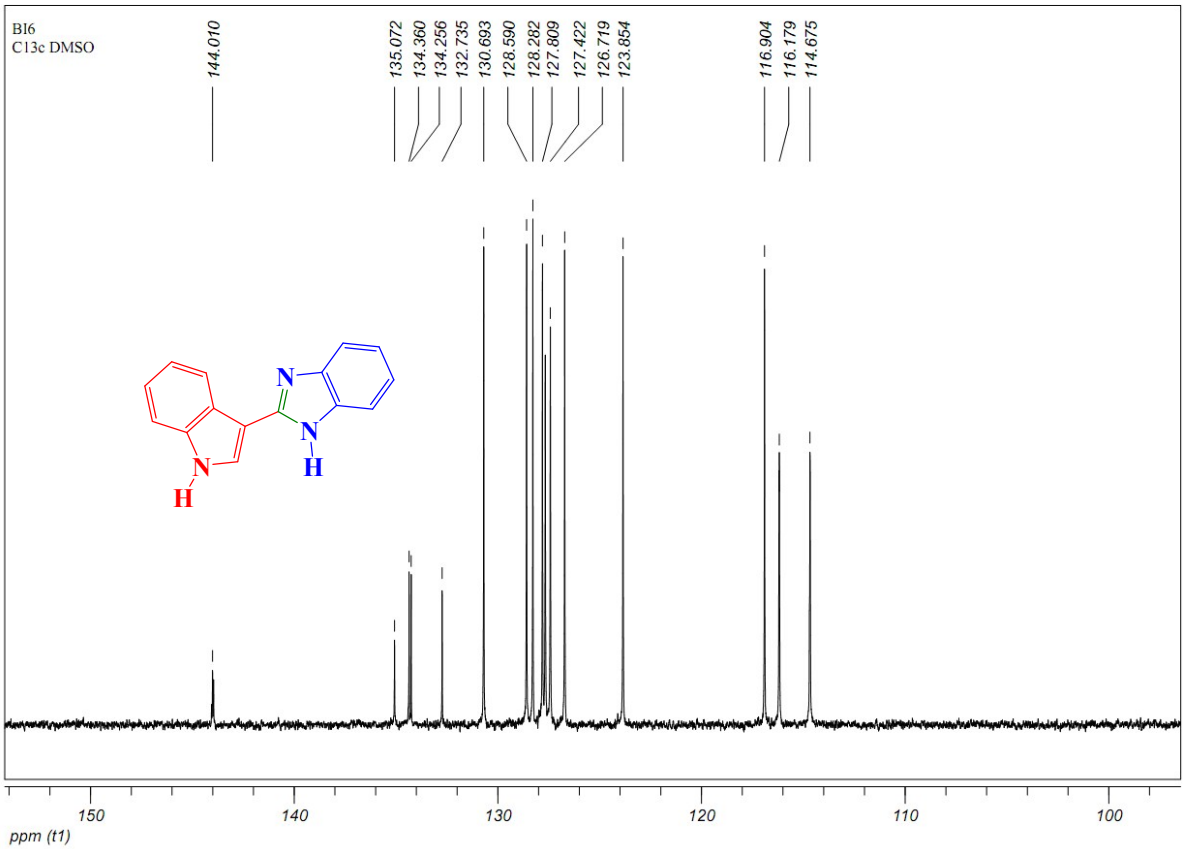


Fig S29. The Mass spectrum of 2-(1H-indol-3-yl)-1H-benzo[d]imidazole (Table 3, entry 6)

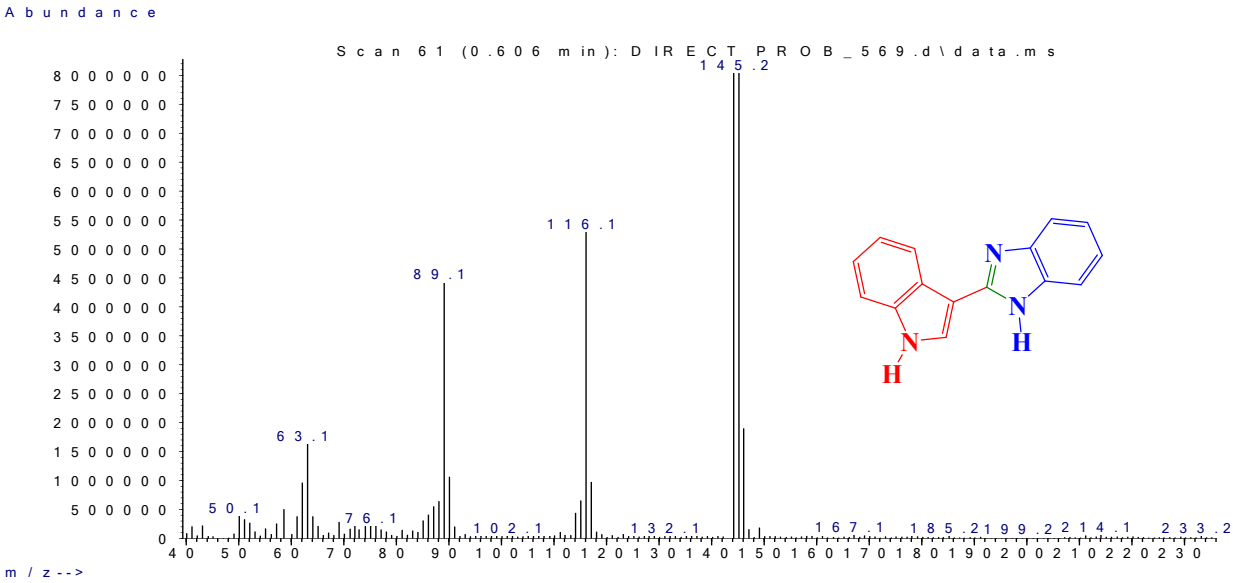


Fig S30. The IR spectrum of 2-(pyridin-4-yl)-1H-benzo[d]imidazole (Table 3, entry 8)

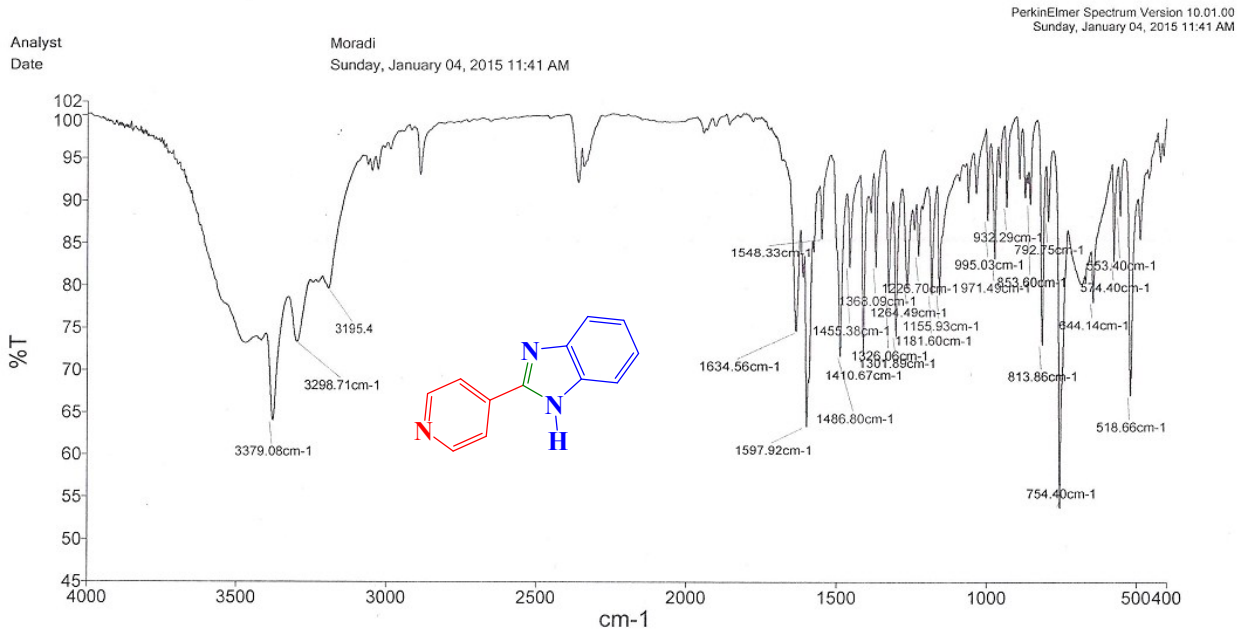


Fig S31. The ^{1}H NMR spectrum of 2-(pyridin-4-yl)-1H-benzo[d]imidazole (Table 3, entry 8)

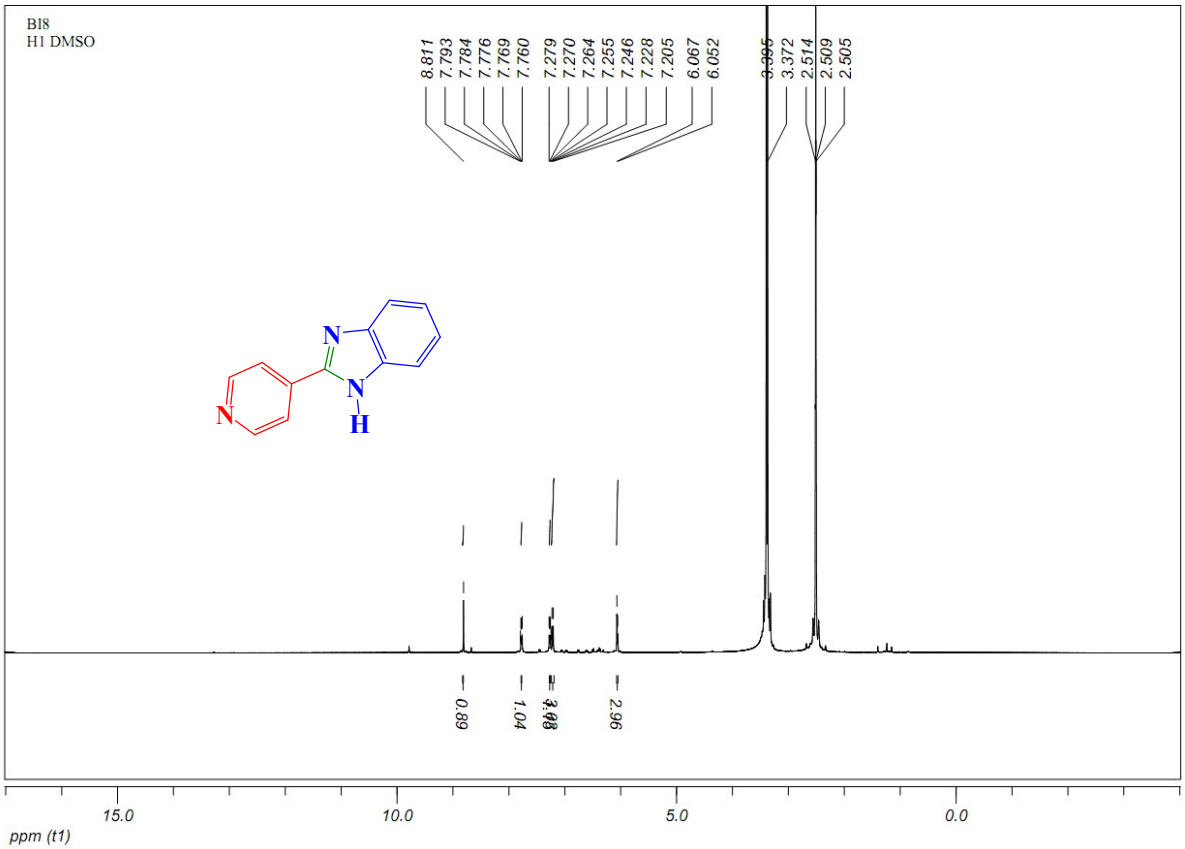


Fig S32. The ^{1}H NMR spectrum of 2-(pyridin-4-yl)-1H-benzo[d]imidazole (Table 3, entry 8)

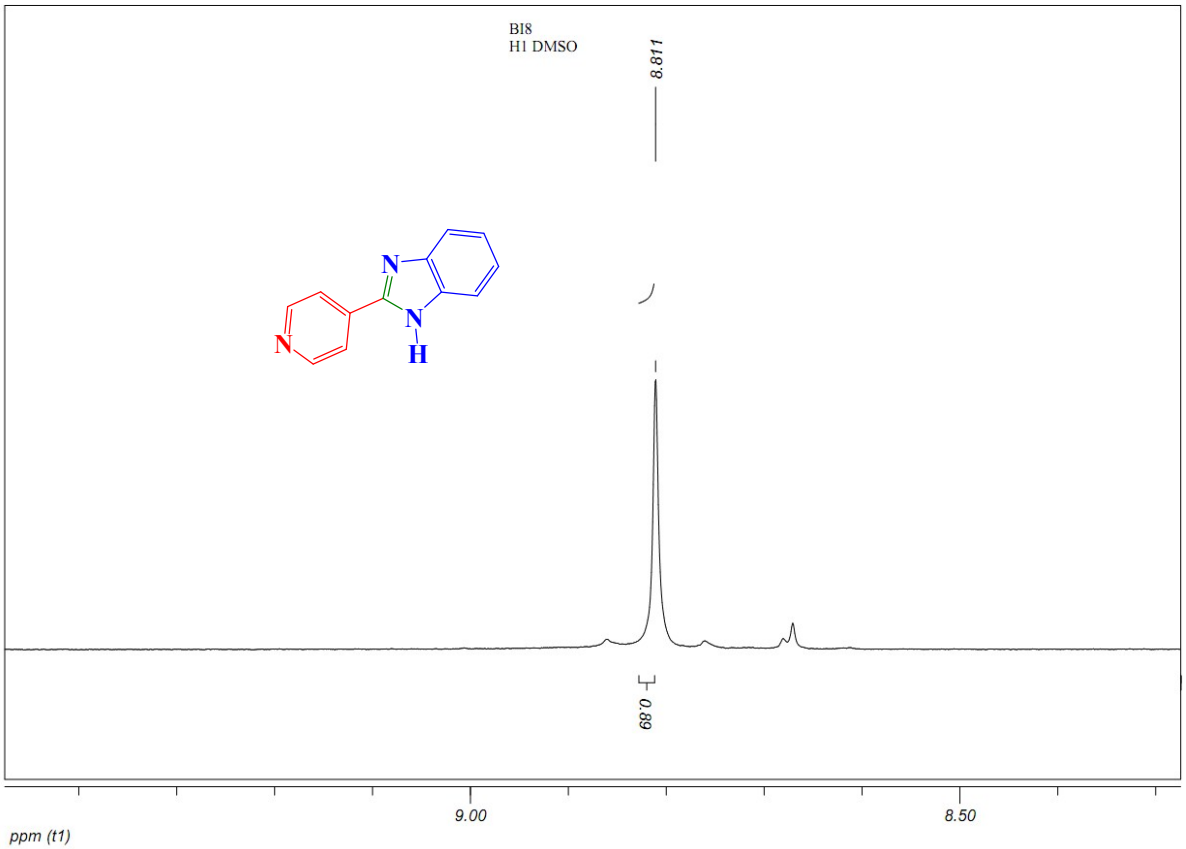


Fig S33. The ^{1}H NMR spectrum of 2-(pyridin-4-yl)-1H-benzo[d]imidazole (Table 3, entry 8)

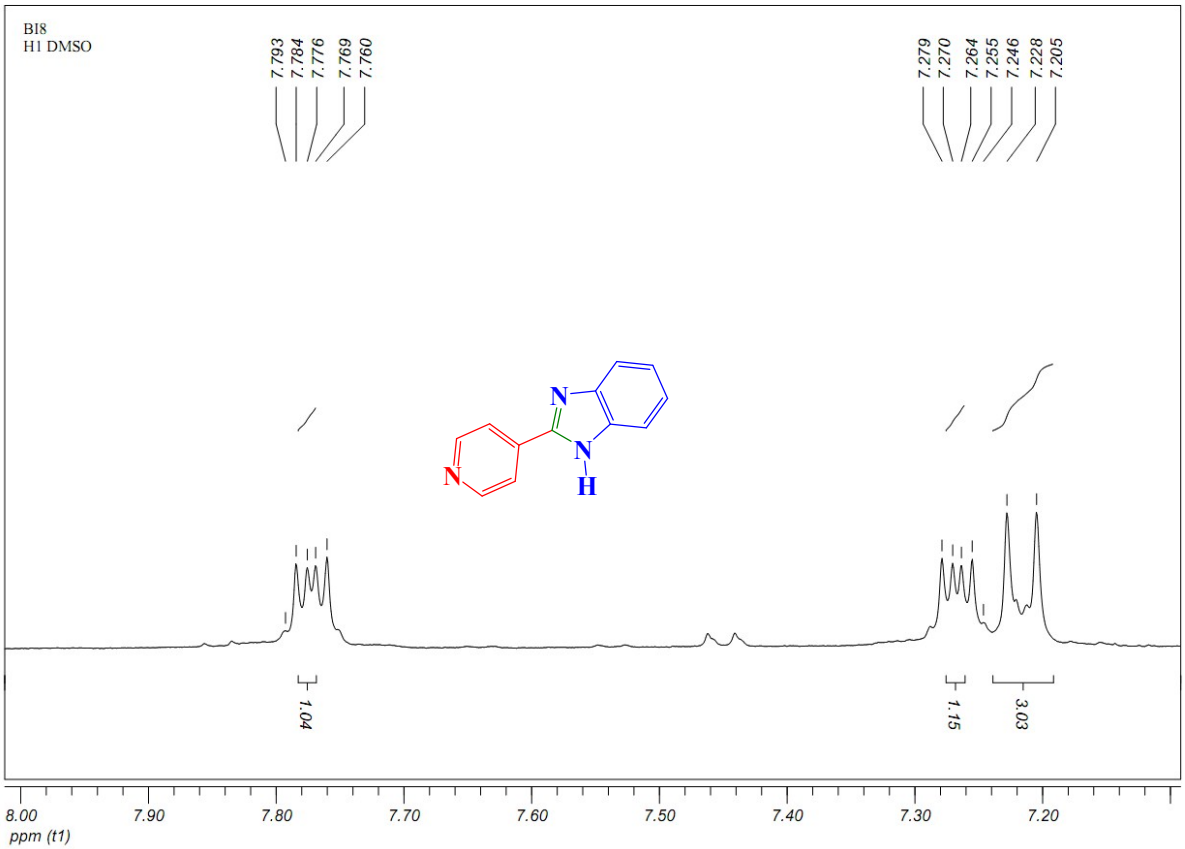


Fig S34. The ^{1}H NMR spectrum of 2-(pyridin-4-yl)-1H-benzo[d]imidazole (Table 3, entry 8)

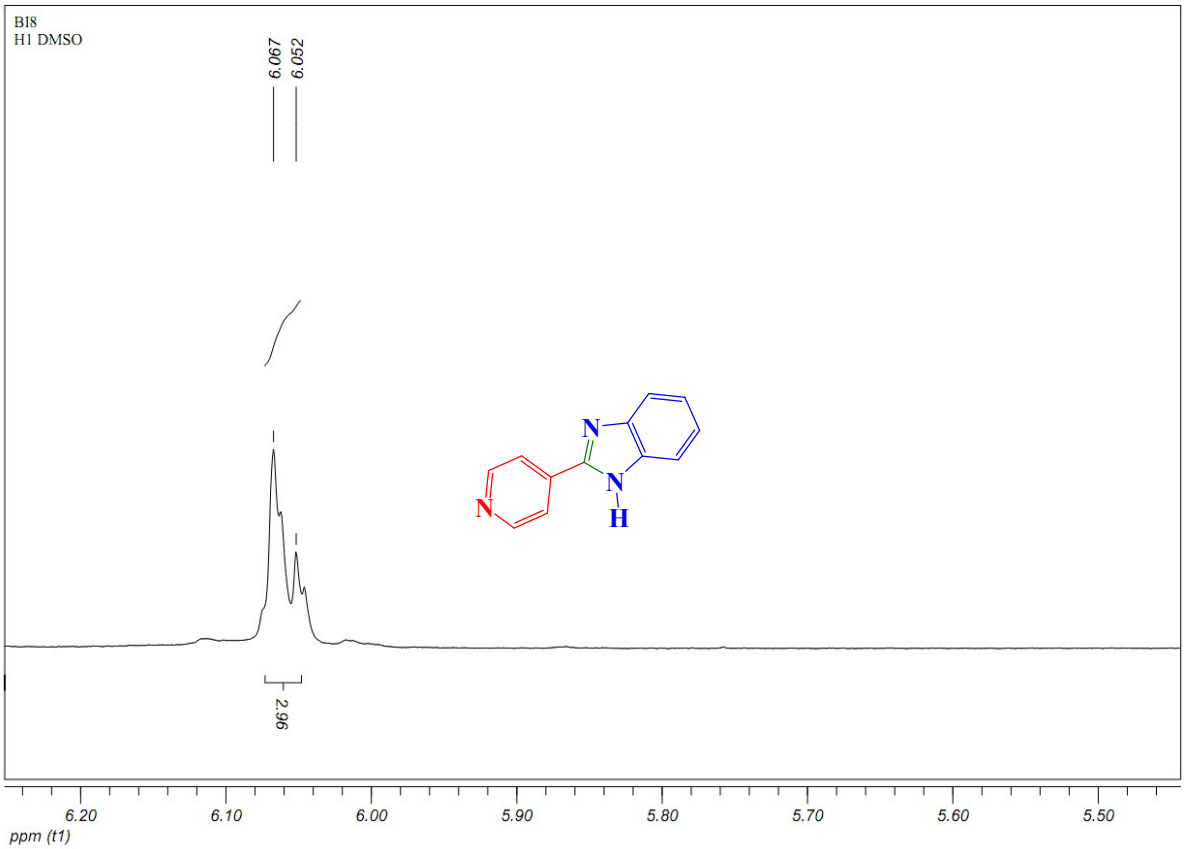


Fig S35. The ^{13}C NMR spectrum of 2-(pyridin-4-yl)-1H-benzo[d]imidazole (Table 3, entry 8)

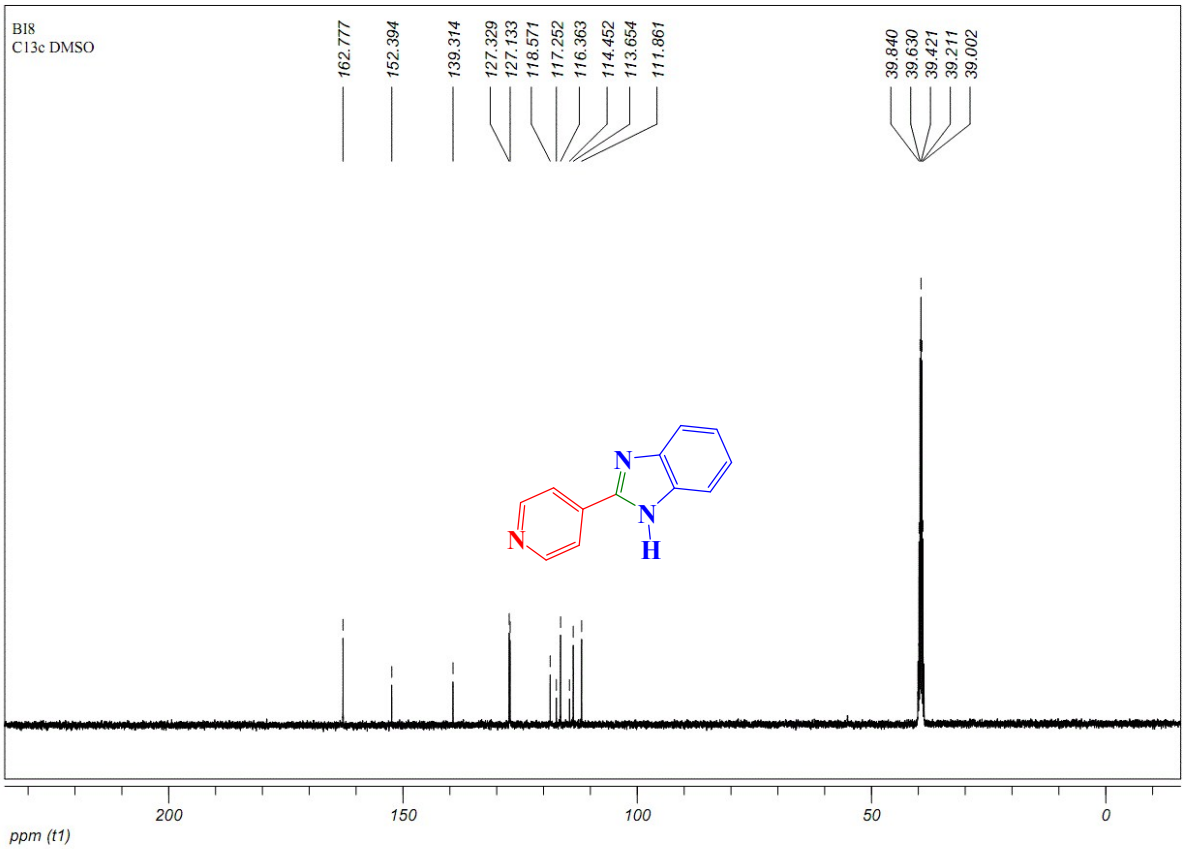


Fig S36. The ^{13}C NMR spectrum of 2-(pyridin-4-yl)-1H-benzo[d]imidazole (Table 3, entry 8)

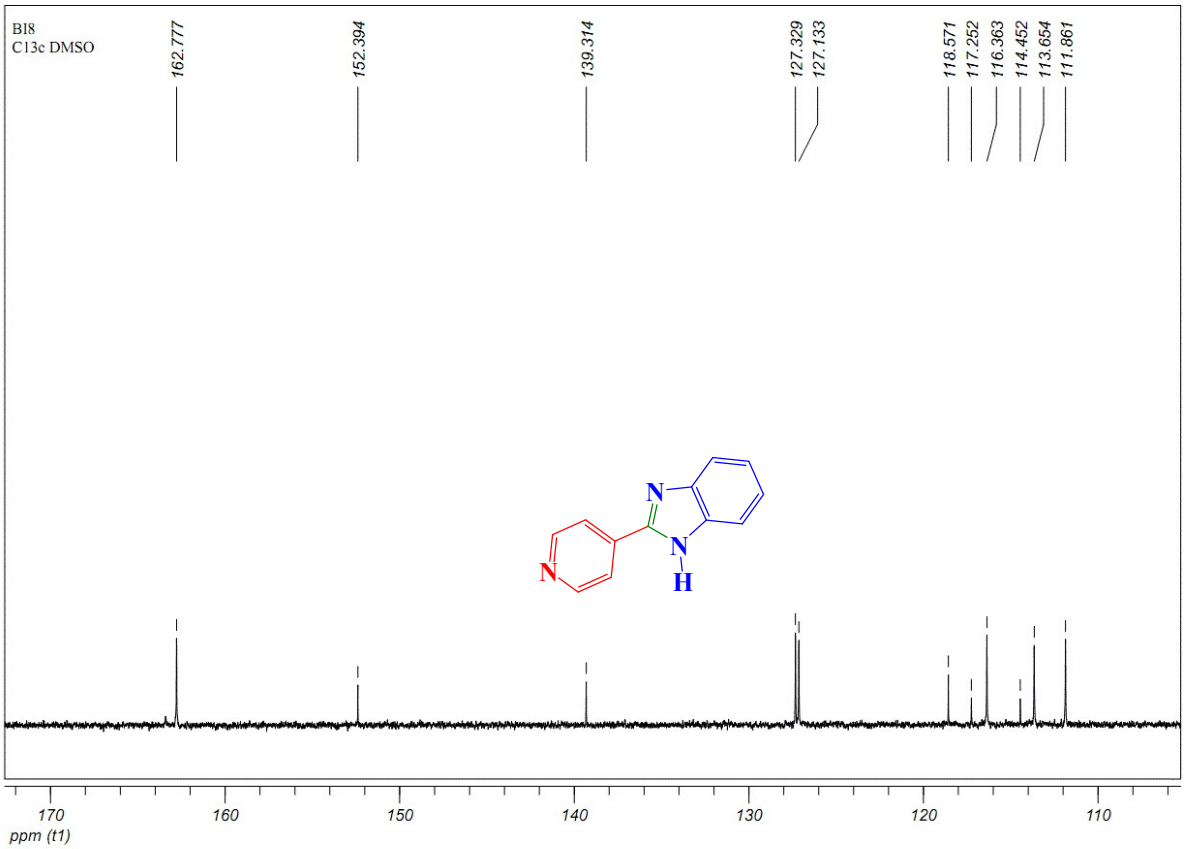


Fig S37. The Mass spectrum of 2-(pyridin-4-yl)-1H-benzo[d]imidazole (Table 3, entry 8)

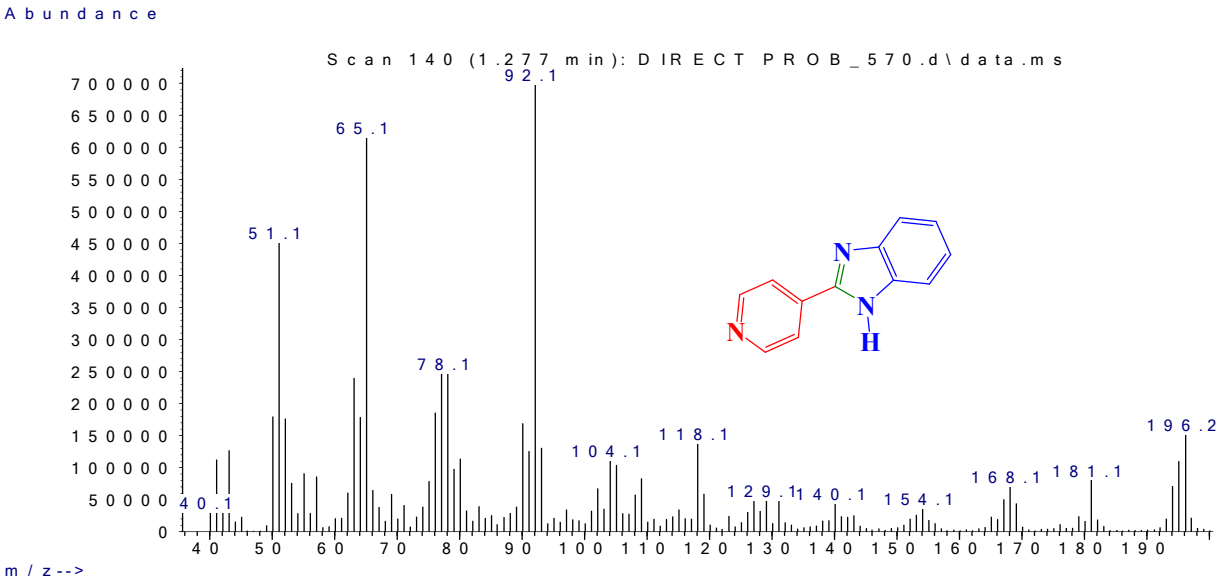


Fig S38. The IR spectrum of 4-(1H-benzo[d]imidazol-2-yl)benzene-1,2-diol (Table 3, entry 9)

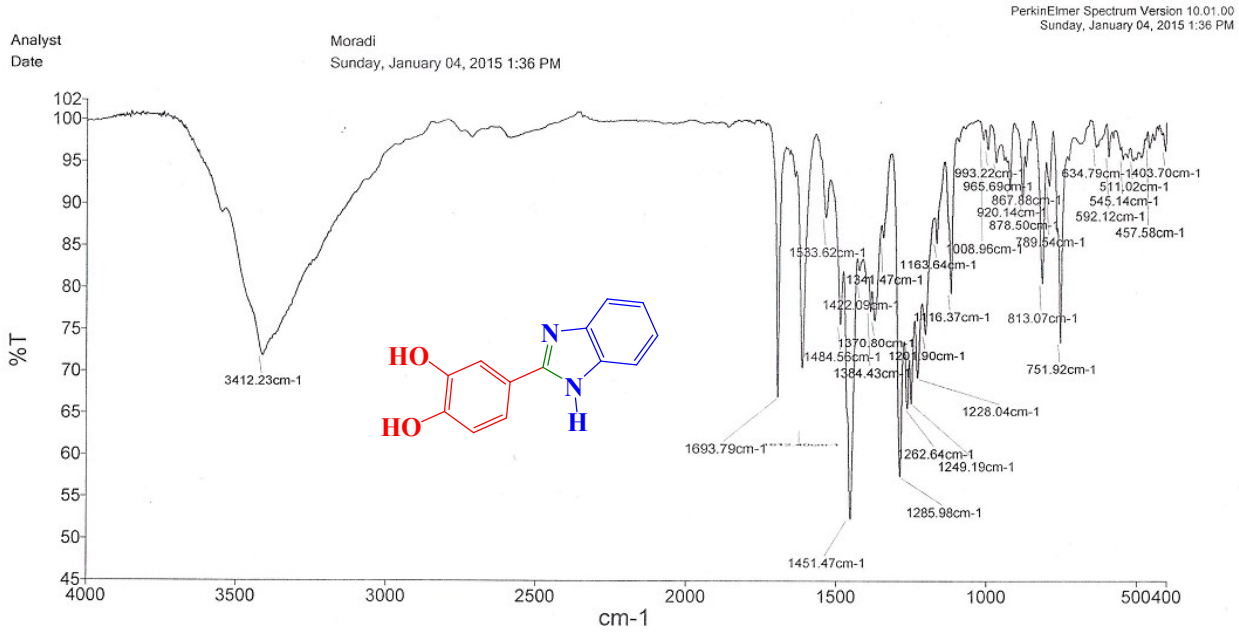


Fig S39. The ^{1}H NMR spectrum of 4-(1H-benzo[d]imidazol-2-yl)benzene-1,2-diol (Table 3, entry 9)

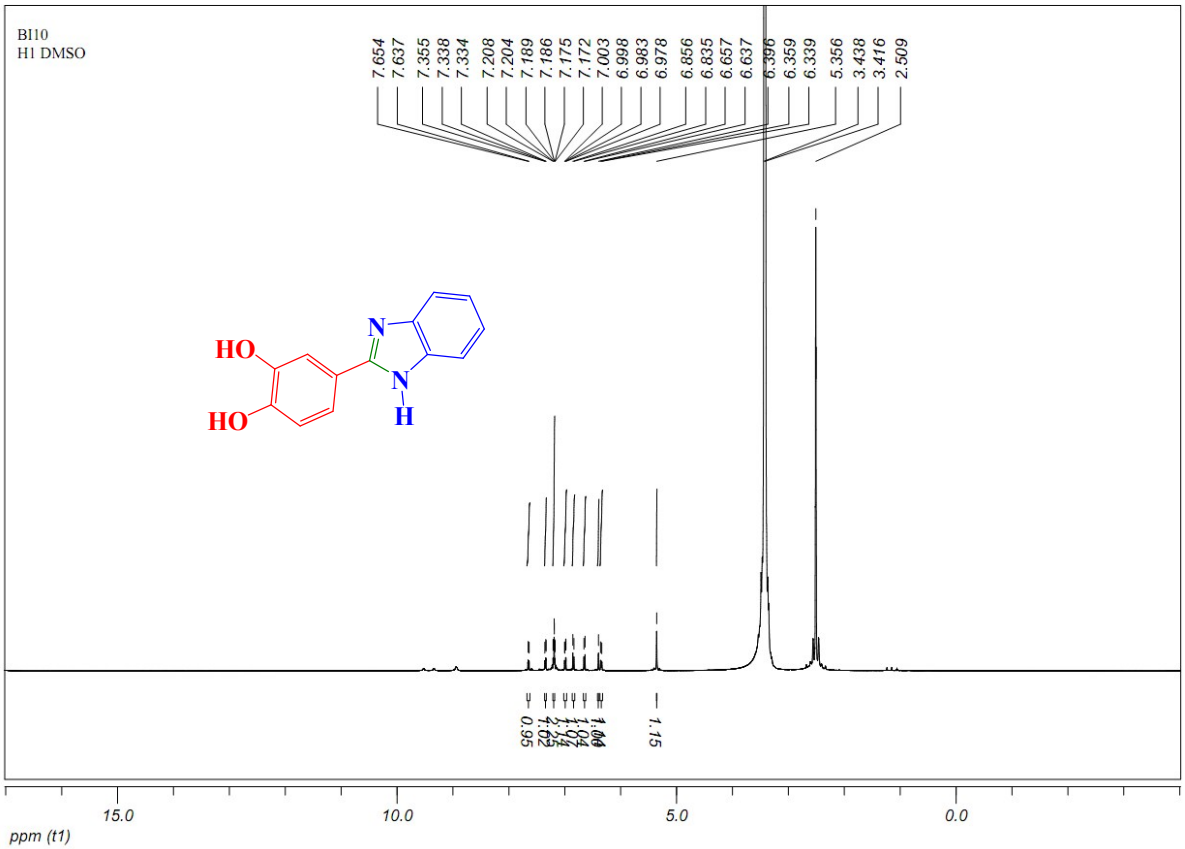


Fig S40. The ^{1}H NMR spectrum of 4-(1H-benzo[d]imidazol-2-yl)benzene-1,2-diol (Table 3, entry 9)

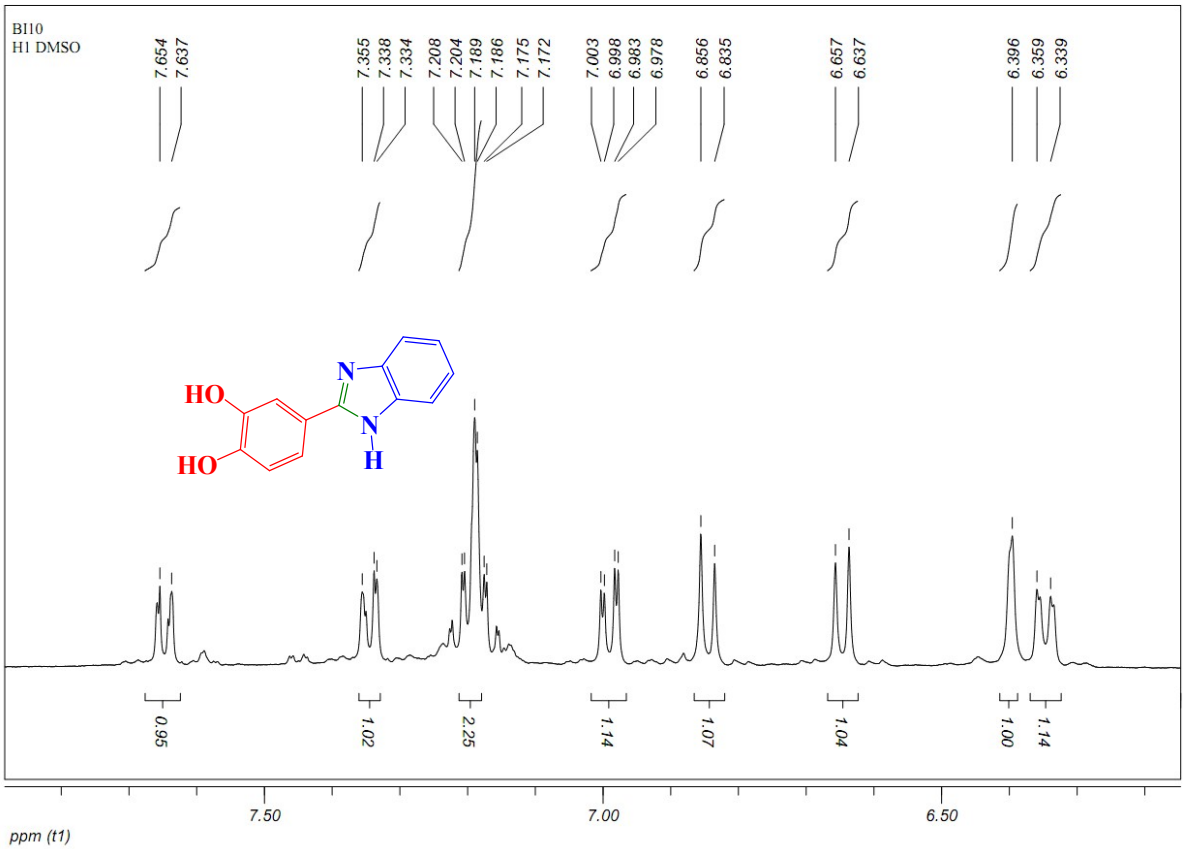


Fig S41. The ^{1}H NMR spectrum of 4-(1H-benzo[d]imidazol-2-yl)benzene-1,2-diol (Table 3, entry 9)

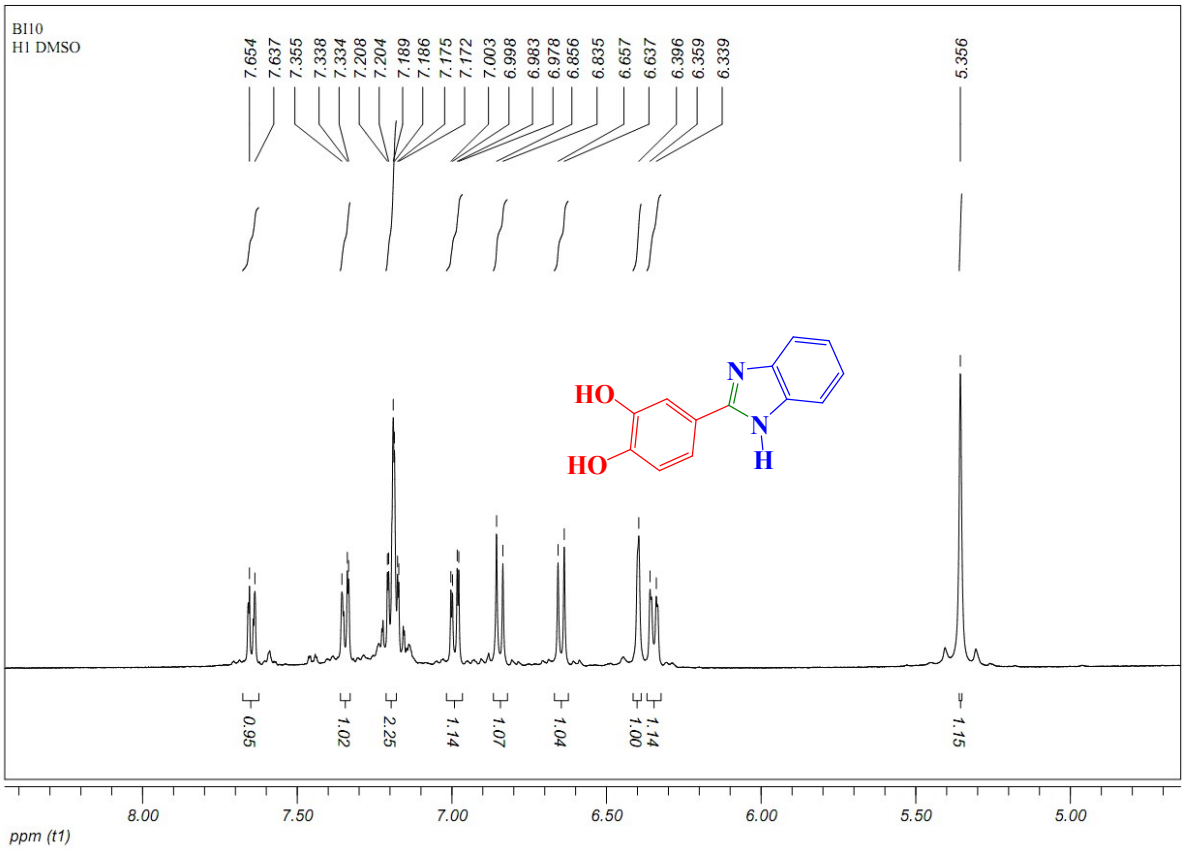


Fig S42. The ^{13}C NMR spectrum of 4-(1H-benzo[d]imidazol-2-yl)benzene-1,2-diol (Table 3, entry 9)

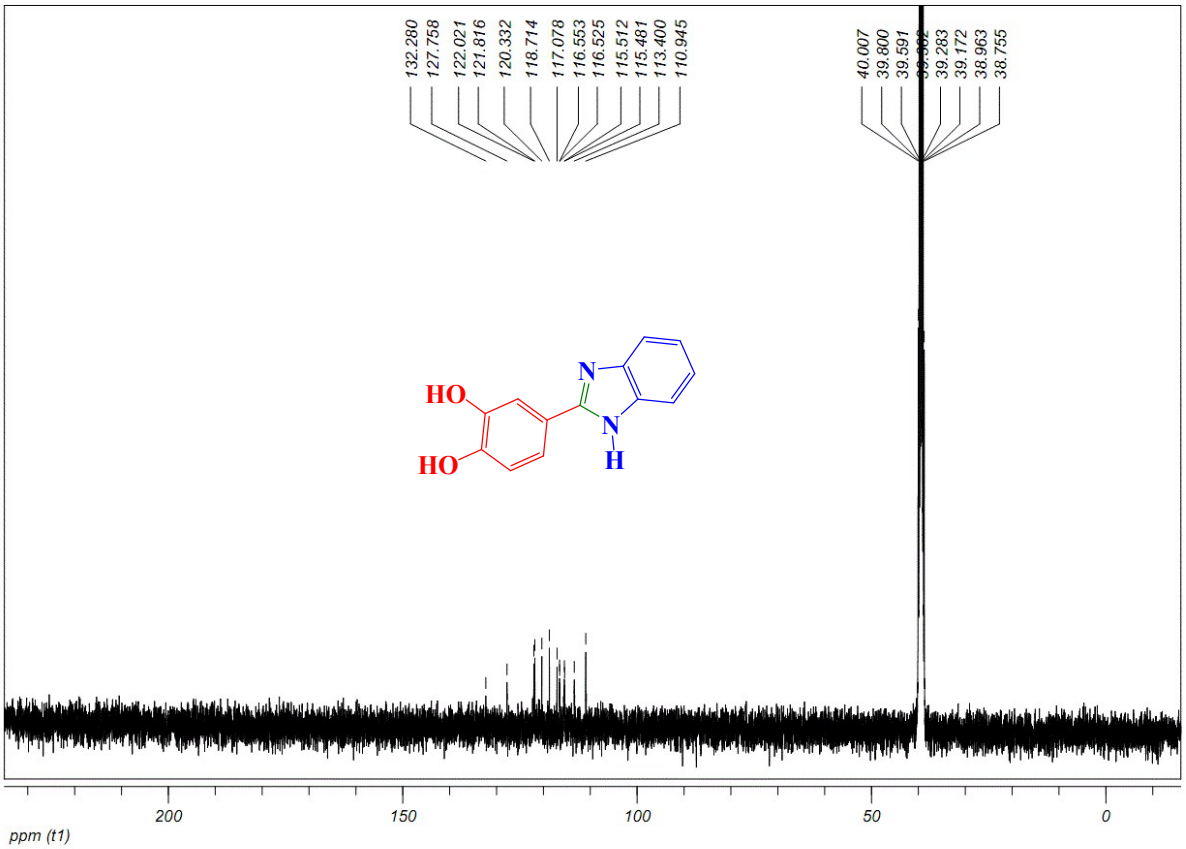


Fig S43. The ^{13}C NMR spectrum of 4-(1H-benzo[d]imidazol-2-yl)benzene-1,2-diol (Table 3, entry 9)

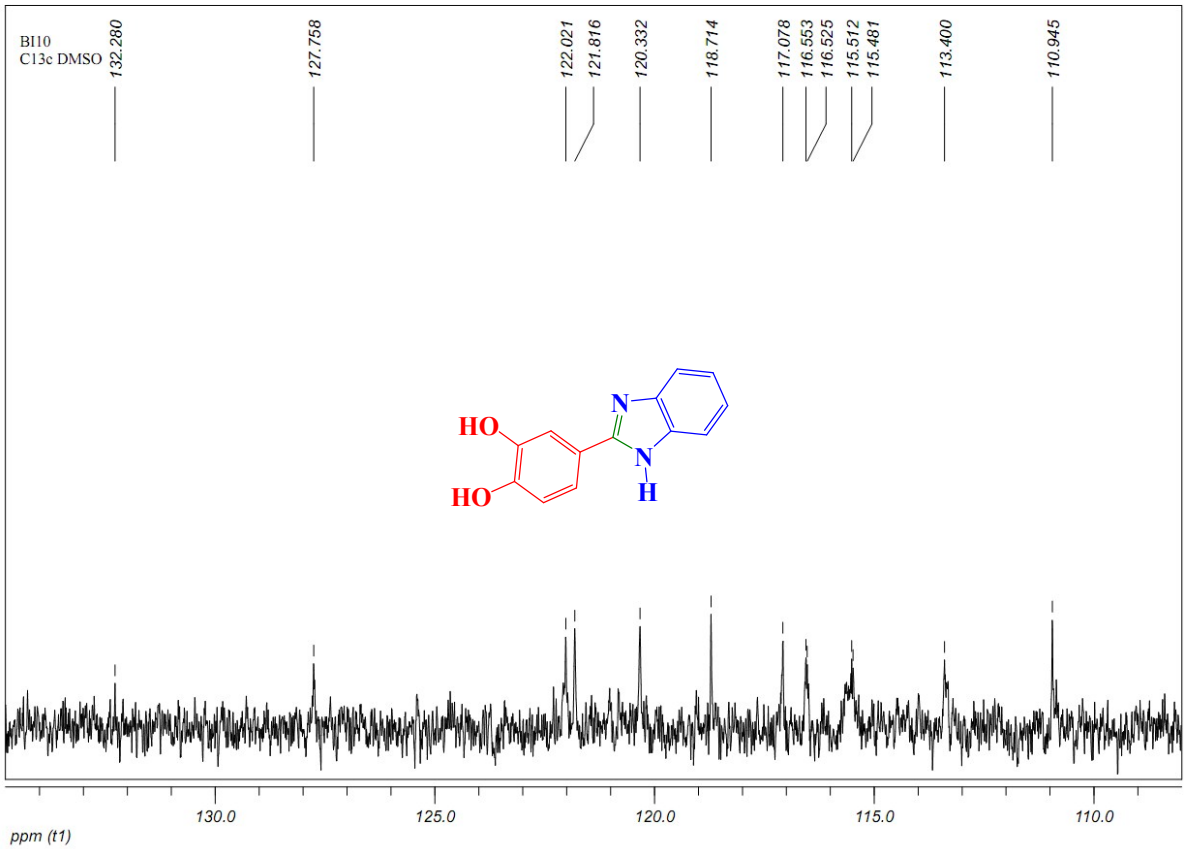


Fig S44. The Mass spectrum of 4-(1H-benzo[d]imidazol-2-yl)benzene-1,2-diol (Table 3, entry 9)

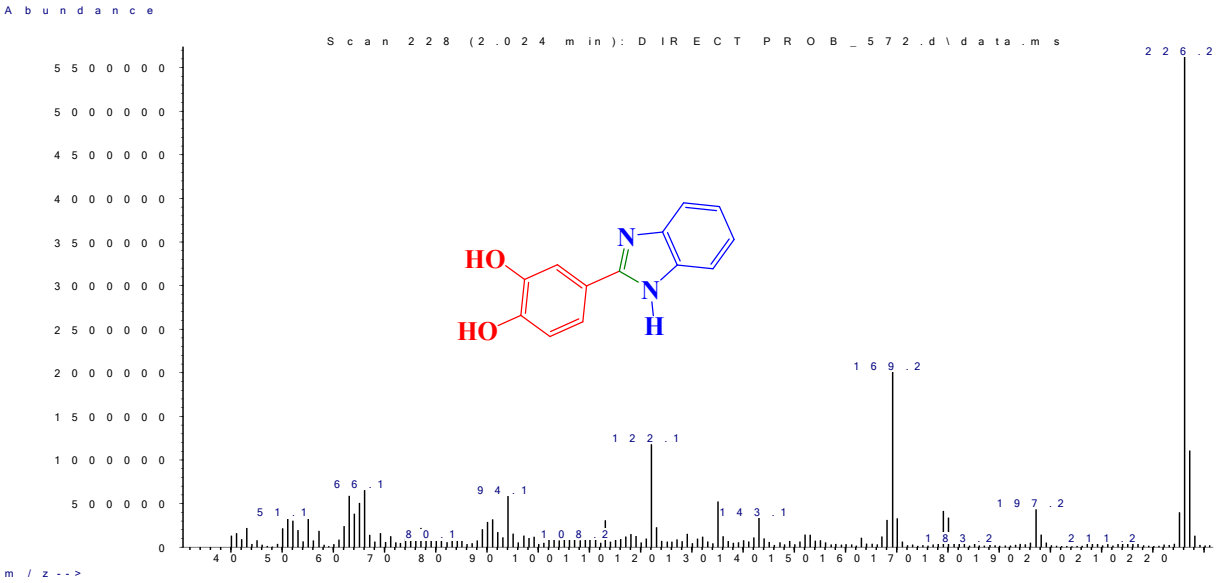


Table S1. Electronic energy, zero point energy and corrected electronic energy at B3LYP/TZVP level of theory

Compounds	Eel	ZPE	E_0
imidazole - conformer a	-612.3043242	0.2210152	-612.083309
imidazole - conformer b	-612.3032782	0.2210562	-612.082222
imidazole - conformer c	-612.3035067	0.2210327	-612.082474
oxazole - conformer d	-632.1763749	0.2083179	-631.968057
oxazole - conformer e	-632.1770962	0.2085502	-631.968546
thiazole - conformer d	-955.1488112	0.2055292	-954.943282
thiazole - conformer e	-955.1477722	0.2056792	-954.942093
2-phenyl benzimidazole	-611.1258177	0.1980097	-610.927808
2-phenyl benzoxazole	-630.9918714	0.1854994	-630.806372
2-phenyl benzothiazole	-953.9596356	0.1821176	-953.777518
H_2	-1.179649	0.010075	-1.169574
$CH(NO_2)_3$	-654.2022471	0.0542011	-654.148046
TS-N	-1266.4597391	0.2674921	-1266.192247
TS-O	-1286.3200136	0.2549566	-1286.065057
TS-S	-1609.2876398	0.2518588	-1609.035781
Intermediate 8 - imidazole	-1265.3277024	0.2537404	-1265.073962
Intermediate 8 - oxazole	-1285.1817145	0.2400655	-1284.941649
Intermediate 8 - thiazole	-1608.1500665	0.2374145	-1607.912652
HNO_3	-280.9952319	0.0261319	-280.969100
TS-NH	-893.251073	0.240758	-893.010315
TS-O	-913.1104628	0.2279628	-912.882500
TS-S	-1236.0765702	0.2249152	-1235.851655
Intermediate 8 - imidazole	-892.1427982	0.2257162	-891.917082

Intermediate 8 - oxazole	-912.0048902	0.2129852	-911.791905
Intermediate 8 - thiazole	-1234.9717652	0.2099572	-1234.761808

Fig. S45. Total Energy along IRC of **TS-N** *via* $CH(NO_2)_3$

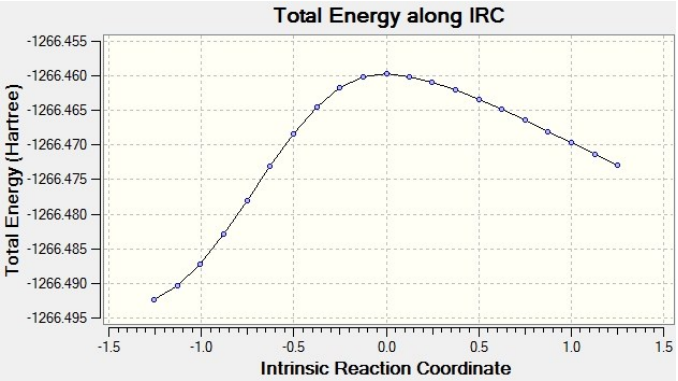


Fig. S46. Total Energy along IRC of **TS-O** *via* $CH(NO_2)_3$

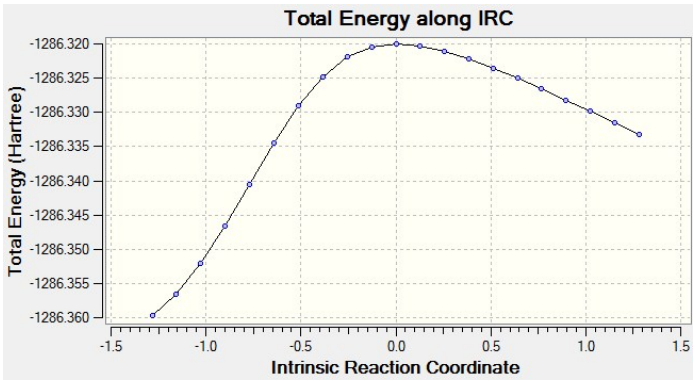


Fig. S47. Total Energy along IRC of **TS-S** *via* $CH(NO_2)_3$

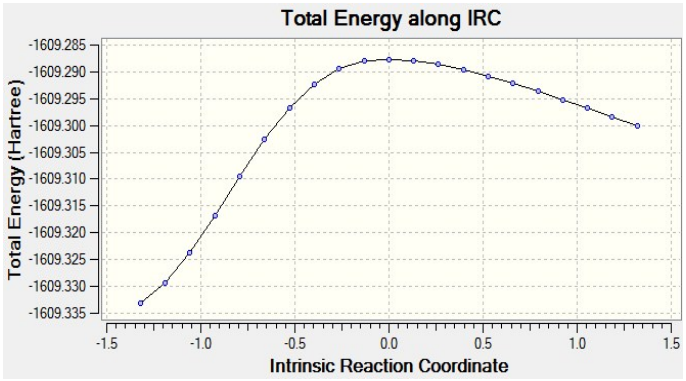


Fig. S48. Total Energy along IRC of **TS-N** *via* HNO_3

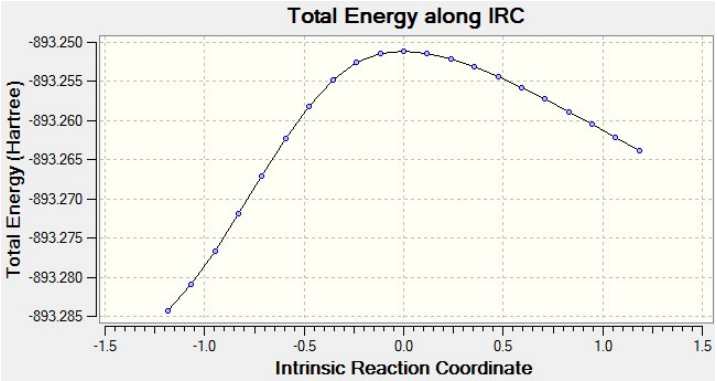
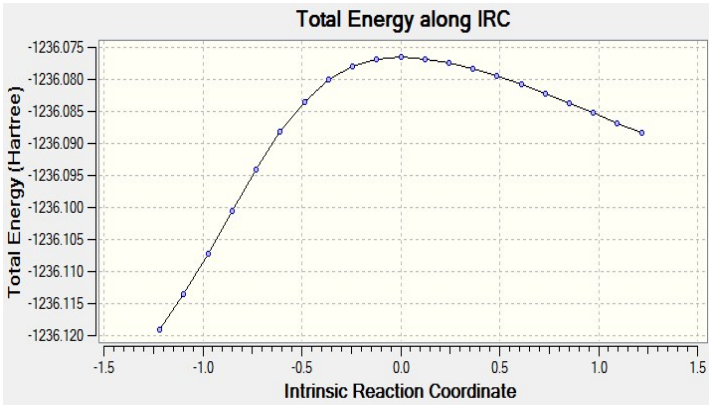


Fig. S49. Total Energy along IRC of **TS-O** *via* HNO_3

Fig. S50. Total Energy along IRC of **TS-S** *via* HNO_3



Cartesian atomic coordinates of calculated structures at B3LYP/TZVP level of theory

"imidazole - conformer a"

C	4.173015000	0.693236000	0.255729000
C	4.173347000	-0.694579000	0.249153000
C	2.980019000	-1.413338000	0.080872000
C	1.808510000	-0.701445000	-0.087727000
C	1.808139000	0.702322000	-0.081075000
C	2.979394000	1.413048000	0.094370000
N	0.476954000	-1.134228000	-0.212311000
C	-0.305829000	0.003009000	-0.728874000
N	0.476483000	1.135600000	-0.201403000
C	-1.748623000	0.000681000	-0.273511000
C	-2.066544000	-0.007500000	1.086130000
C	-3.393349000	-0.008966000	1.493620000
C	-4.418846000	-0.002184000	0.548297000
C	-4.109760000	0.005883000	-0.805989000
C	-2.776744000	0.007308000	-1.212502000
H	5.103275000	1.232104000	0.384456000
H	5.103879000	-1.234206000	0.372604000
H	2.981324000	-2.496709000	0.080739000
H	2.980317000	2.496376000	0.104347000
H	0.312650000	-2.013602000	-0.679370000
H	-0.295543000	0.008583000	-1.835983000
H	0.311411000	2.019571000	-0.659394000
H	-1.265205000	-0.012653000	1.813677000
H	-3.632874000	-0.015306000	2.550180000
H	-5.453372000	-0.003267000	0.869776000
H	-4.901028000	0.011002000	-1.545752000
H	-2.535282000	0.013656000	-2.270245000

"imidazole - conformer b"

C	3.721532000	0.811277000	-0.694034000
C	3.721539000	0.811347000	0.693923000
C	2.681097000	0.203005000	1.412084000
C	1.656714000	-0.392427000	0.701059000
C	1.656706000	-0.392498000	-0.701024000
C	2.681081000	0.202861000	-1.412121000
N	0.526002000	-1.094158000	1.148280000
C	-0.379609000	-1.314445000	0.000076000
N	0.525989000	-1.094276000	-1.148164000
C	-1.618380000	-0.428476000	0.000034000
C	-1.515054000	0.966827000	0.000010000
C	-2.657704000	1.756549000	-0.000036000
C	-3.919974000	1.164895000	-0.000060000

C	-4.032290000	-0.220049000	-0.000036000
C	-2.885017000	-1.010094000	0.000011000
H	4.532342000	1.284050000	-1.233867000
H	4.532355000	1.284175000	1.233699000
H	2.681752000	0.203575000	2.495459000
H	2.681724000	0.203321000	-2.495496000
H	0.077833000	-0.763985000	1.990178000
H	-0.714903000	-2.356170000	0.000130000
H	0.077806000	-0.764174000	-1.990082000
H	-0.537550000	1.434489000	0.000028000
H	-2.565907000	2.835979000	-0.000054000
H	-4.809310000	1.783209000	-0.000096000
H	-5.009806000	-0.686889000	-0.000052000
H	-2.974118000	-2.091162000	0.000031000

“imidazole - conformer c”

C	-4.149481000	0.683046000	-0.086170000
C	-4.088864000	-0.571418000	-0.679743000
C	-2.882289000	-1.284104000	-0.719563000
C	-1.759299000	-0.701361000	-0.167810000
C	-1.816765000	0.571082000	0.416416000
C	-3.006902000	1.276058000	0.466808000
N	-0.439246000	-1.213796000	-0.062815000
C	0.310650000	-0.274084000	0.801786000
N	-0.520638000	0.949595000	0.803869000
C	1.730844000	-0.058008000	0.325388000
C	2.754559000	-0.860985000	0.828546000
C	4.058928000	-0.717132000	0.366352000
C	4.351448000	0.237363000	-0.602517000
C	3.335507000	1.046345000	-1.104410000
C	2.031242000	0.898618000	-0.644989000
H	-5.091453000	1.216275000	-0.051113000
H	-4.982996000	-1.012679000	-1.101583000
H	-2.832734000	-2.271991000	-1.160675000
H	-3.054790000	2.264809000	0.906890000
H	0.017273000	-1.372925000	-0.952351000
H	0.346149000	-0.701835000	1.814828000
H	-0.440050000	1.516517000	1.635518000
H	2.527895000	-1.600964000	1.588227000
H	4.845555000	-1.346158000	0.765046000
H	5.367118000	0.355139000	-0.960277000
H	3.560761000	1.796332000	-1.853077000
H	1.238986000	1.534365000	-1.019374000

“oxazole - conformer d”

C	4.146455000	0.636831000	0.068826000

C	4.050553000	-0.619979000	0.652428000
C	2.822051000	-1.296121000	0.710642000
C	1.729623000	-0.661914000	0.166714000
C	1.811355000	0.604263000	-0.414821000
C	3.019109000	1.274688000	-0.469144000
C	-0.295121000	-0.250845000	-0.765603000
N	0.507112000	0.983946000	-0.775688000
C	-1.714715000	-0.067976000	-0.297364000
C	-2.745002000	-0.757149000	-0.932847000
C	-4.059570000	-0.622154000	-0.495571000
C	-4.348395000	0.205497000	0.583348000
C	-3.321244000	0.898152000	1.221501000
C	-2.010300000	0.763209000	0.783488000
H	5.105121000	1.138569000	0.030226000
H	4.934321000	-1.092121000	1.062132000
H	2.731075000	-2.276481000	1.158895000
H	3.095909000	2.261603000	-0.908371000
H	-0.294961000	-0.735874000	-1.754946000
H	0.400322000	1.550718000	-1.604606000
H	-2.518175000	-1.404085000	-1.773160000
H	-4.854280000	-1.161068000	-0.996715000
H	-5.370413000	0.314222000	0.925663000
H	-3.545410000	1.545018000	2.060981000
H	-1.208583000	1.305934000	1.267308000
O	0.433313000	-1.121633000	0.136603000

“oxazole - conformer e”

C	-4.089771000	-0.458749000	0.652270000
C	-4.072054000	0.776913000	0.014150000
C	-2.892203000	1.290812000	-0.539139000
C	-1.756613000	0.515722000	-0.431093000
C	-1.763516000	-0.726148000	0.204820000
C	-2.926070000	-1.232204000	0.752177000
C	0.289400000	-0.381710000	-0.748145000
N	-0.446678000	-1.263844000	0.170766000
C	1.701742000	-0.101144000	-0.311826000
C	2.729819000	-0.939921000	-0.741419000
C	4.034531000	-0.733644000	-0.306187000
C	4.321765000	0.320590000	0.555208000
C	3.300413000	1.165985000	0.978657000
C	1.994127000	0.955183000	0.550639000
H	-5.015811000	-0.835226000	1.067834000
H	-4.984942000	1.354392000	-0.061069000
H	-2.865572000	2.256021000	-1.027051000
H	-2.935866000	-2.197352000	1.242787000
H	0.282168000	-0.834741000	-1.745772000
H	-0.011679000	-1.318216000	1.085443000
H	2.507751000	-1.755206000	-1.420678000

H	4.826202000	-1.390770000	-0.644633000
H	5.338576000	0.487137000	0.889270000
H	3.521844000	1.994266000	1.640652000
H	1.200532000	1.620488000	0.865032000
O	-0.495734000	0.844501000	-0.858483000

“thiazole - conformer d”

C	-4.138000000	-1.065200000	-0.093334000
C	-4.335616000	0.246568000	0.320442000
C	-3.246686000	1.114511000	0.444282000
C	-1.978329000	0.647043000	0.151603000
C	-1.772728000	-0.678714000	-0.257675000
C	-2.857124000	-1.538388000	-0.384492000
C	0.418742000	0.156565000	-0.689876000
N	-0.426499000	-1.006780000	-0.433796000
C	1.856654000	-0.031100000	-0.283505000
C	2.872093000	0.480987000	-1.091181000
C	4.207792000	0.334238000	-0.728592000
C	4.538929000	-0.332616000	0.445369000
C	3.529564000	-0.849741000	1.254688000
C	2.196545000	-0.697575000	0.895808000
H	-4.984534000	-1.732717000	-0.195918000
H	-5.333216000	0.604603000	0.540112000
H	-3.395599000	2.139697000	0.759375000
H	-2.709114000	-2.564347000	-0.700953000
H	0.380337000	0.458969000	-1.743440000
H	-0.229001000	-1.801796000	-1.025810000
H	2.616359000	0.996112000	-2.010671000
H	4.986645000	0.736896000	-1.364547000
H	5.577599000	-0.451632000	0.728758000
H	3.783661000	-1.370823000	2.169792000
H	1.409035000	-1.095966000	1.522168000
S	-0.429231000	1.525562000	0.278530000

“thiazole - conformer e”

C	-4.092892000	-1.144104000	0.174586000
C	-4.325120000	0.222388000	0.286729000
C	-3.269790000	1.130459000	0.187596000
C	-1.984604000	0.651400000	-0.021040000
C	-1.747999000	-0.727299000	-0.136005000
C	-2.801752000	-1.624985000	-0.046265000
C	0.418991000	0.041663000	-0.727259000
N	-0.391885000	-1.092266000	-0.320760000
C	1.850952000	-0.041423000	-0.273320000
C	2.872916000	-0.111498000	-1.219759000
C	4.202639000	-0.215336000	-0.822297000

C	4.523624000	-0.252395000	0.529599000
C	3.510059000	-0.179393000	1.482154000
C	2.183620000	-0.071567000	1.083950000
H	-4.918498000	-1.841279000	0.242983000
H	-5.331054000	0.590199000	0.446178000
H	-3.452576000	2.193543000	0.279380000
H	-2.615402000	-2.686151000	-0.157260000
H	0.383413000	0.132444000	-1.812773000
H	0.000515000	-1.602828000	0.460626000
H	2.625649000	-0.087604000	-2.274741000
H	4.985215000	-0.268479000	-1.569167000
H	5.557755000	-0.332147000	0.841562000
H	3.754992000	-0.197730000	2.537118000
H	1.402445000	0.017914000	1.829500000
S	-0.480820000	1.603783000	-0.098131000

“2-phenyl benzimidazole”

C	4.178025000	-0.751024000	0.060517000
C	4.214526000	0.648004000	-0.071958000
C	3.050101000	1.401845000	-0.134674000
C	1.847987000	0.704960000	-0.061561000
C	1.792559000	-0.700718000	0.069228000
C	2.976632000	-1.438887000	0.133078000
N	0.526327000	1.102587000	-0.085347000
C	-0.250675000	-0.036808000	0.016585000
N	0.479016000	-1.123616000	0.112771000
C	-1.714929000	-0.007042000	0.011272000
C	-2.437551000	1.182205000	0.163934000
C	-3.827032000	1.172626000	0.147679000
C	-4.515943000	-0.024330000	-0.016776000
C	-3.804841000	-1.213589000	-0.161455000
C	-2.417964000	-1.208100000	-0.148187000
H	5.111081000	-1.298683000	0.106889000
H	5.172865000	1.149386000	-0.125657000
H	3.084662000	2.479729000	-0.235241000
H	2.942943000	-2.515846000	0.235241000
H	0.191551000	2.038578000	-0.235637000
H	-1.925244000	2.124161000	0.321195000
H	-4.371358000	2.100894000	0.270442000
H	-5.598831000	-0.031261000	-0.028621000
H	-4.335186000	-2.149610000	-0.287220000
H	-1.855257000	-2.125003000	-0.259455000

“2-phenyl benzoxazole”

C	4.181118000	-0.650417000	-0.000125000
C	4.133516000	0.751683000	0.000436000

C	2.922710000	1.440925000	0.000619000
C	1.786128000	0.655701000	0.000210000
C	1.805786000	-0.742139000	-0.000378000
C	3.023100000	-1.419179000	-0.000587000
C	-0.236996000	-0.137243000	0.000170000
N	0.494908000	-1.204550000	-0.000488000
C	-1.691584000	-0.049755000	0.000199000
C	-2.344913000	1.187993000	-0.000391000
C	-3.732793000	1.241305000	-0.000513000
C	-4.479816000	0.067236000	-0.000090000
C	-3.832524000	-1.166743000	0.000528000
C	-2.447242000	-1.229126000	0.000673000
H	5.145628000	-1.142446000	-0.000256000
H	5.059633000	1.312418000	0.000646000
H	2.875298000	2.521475000	0.000886000
H	3.056320000	-2.500569000	-0.000976000
H	-1.764415000	2.100516000	-0.000581000
H	-4.232214000	2.202250000	-0.000981000
H	-5.561951000	0.112657000	-0.000200000
H	-4.410738000	-2.082457000	0.000956000
H	-1.932571000	-2.180599000	0.001155000
O	0.472713000	1.048395000	-0.000218000

“2-phenyl benzothiazole”

C	4.097815000	1.153064000	0.000592000
C	4.357220000	-0.224389000	-0.000073000
C	3.320183000	-1.147254000	-0.000535000
C	2.014353000	-0.665623000	-0.000378000
C	1.738782000	0.719044000	0.000342000
C	2.798586000	1.631824000	0.000801000
C	-0.366082000	0.016126000	0.000085000
N	0.401444000	1.055238000	0.000541000
C	-1.832030000	0.073799000	0.000083000
C	-2.619643000	-1.082919000	0.001242000
C	-4.005498000	-0.993825000	0.001208000
C	-4.625908000	0.251414000	0.000051000
C	-3.850030000	1.408454000	-0.001081000
C	-2.465843000	1.324381000	-0.001070000
H	4.926196000	1.850345000	0.000946000
H	5.381293000	-0.576270000	-0.000203000
H	3.526050000	-2.209838000	-0.001056000
H	2.583958000	2.692503000	0.001340000
H	-2.152247000	-2.060282000	0.002253000
H	-4.600957000	-1.898351000	0.002125000
H	-5.706752000	0.320339000	0.000031000
H	-4.327198000	2.380831000	-0.002003000
H	-1.854701000	2.216455000	-0.001947000
S	0.502676000	-1.555435000	-0.000805000

"H_2"

H	0.000000000	0.000000000	0.371961000
H	0.000000000	0.000000000	-0.371961000

"$CH(NO_2)_3$"

C	-0.115261000	0.020833000	0.695374000
N	-0.967603000	-0.153456000	-0.558497000
O	-2.104061000	0.253121000	-0.429710000
O	-0.449735000	-0.646829000	-1.533171000
N	1.114850000	-0.878564000	0.611653000
O	2.170592000	-0.370380000	0.313758000
O	0.876636000	-2.045097000	0.848062000
N	0.319598000	1.478002000	0.824352000
O	0.262433000	2.176912000	-0.160439000
O	0.700689000	1.770924000	1.938981000
H	-0.699784000	-0.254863000	1.564697000

"TS-N *via* $CH(NO_2)_3$"

C	3.200397000	-3.032188000	0.659231000
C	2.956032000	-3.653074000	-0.569536000
C	1.770996000	-3.439328000	-1.268098000
C	0.844289000	-2.587287000	-0.687546000
C	1.082242000	-1.975192000	0.552745000
C	2.266539000	-2.181814000	1.243835000
N	-0.419641000	-2.167038000	-1.087317000
C	-0.887479000	-1.193705000	-0.234104000
N	-0.054193000	-1.228340000	0.861664000
C	-2.343046000	-0.905451000	-0.129496000
C	-3.037840000	-0.364966000	-1.213161000
C	-4.407977000	-0.158308000	-1.128678000
C	-5.090405000	-0.471936000	0.043837000
C	-4.398502000	-0.996549000	1.129702000
C	-3.028662000	-1.219809000	1.045324000
H	4.140488000	-3.209161000	1.164868000
H	3.708299000	-4.305323000	-0.993523000
H	1.587581000	-3.912670000	-2.223871000
H	2.462231000	-1.689684000	2.186516000
H	-0.877199000	-2.403115000	-1.951706000
H	-0.457254000	0.196692000	-0.935095000
H	-0.055593000	-0.449423000	1.515776000
H	-2.498440000	-0.069363000	-2.105406000
H	-4.939395000	0.267695000	-1.970166000
H	-6.156753000	-0.297164000	0.113176000

H	-4.923857000	-1.235422000	2.045779000
H	-2.493656000	-1.644557000	1.884639000
C	0.825857000	2.001699000	-0.085826000
N	0.138066000	2.430507000	1.142418000
O	-0.198492000	1.520763000	1.907344000
O	-0.103024000	3.609741000	1.316876000
N	0.884198000	3.100792000	-1.089250000
O	1.957634000	3.603800000	-1.363822000
O	-0.199764000	3.395856000	-1.571099000
N	2.122157000	1.362783000	0.154507000
O	2.539656000	1.244370000	1.302092000
O	2.662706000	0.920792000	-0.851142000
H	0.025071000	0.965430000	-0.676492000

"TS-O *via* $CH(NO_2)_3$"

C	-2.920008000	3.222227000	0.721701000
C	-2.543710000	3.871630000	-0.457377000
C	-1.337620000	3.582154000	-1.096714000
C	-0.553961000	2.627397000	-0.489681000
C	-0.909725000	1.980221000	0.688419000
C	-2.109645000	2.261670000	1.323178000
C	1.014069000	1.127415000	-0.073820000
N	0.154249000	1.129302000	0.990543000
C	2.428098000	0.724831000	-0.021218000
C	3.312239000	1.198748000	-0.995834000
C	4.648092000	0.824659000	-0.958321000
C	5.110072000	-0.025412000	0.041685000
C	4.229289000	-0.502519000	1.008400000
C	2.892194000	-0.132957000	0.980803000
H	-3.870641000	3.465299000	1.177668000
H	-3.206190000	4.608496000	-0.891884000
H	-1.036994000	4.068854000	-2.013846000
H	-2.410287000	1.749048000	2.225882000
H	0.467072000	-0.144142000	-0.944231000
H	0.073208000	0.316621000	1.598378000
H	2.953376000	1.857298000	-1.774586000
H	5.328638000	1.196185000	-1.713809000
H	6.151719000	-0.319911000	0.065386000
H	4.582235000	-1.168452000	1.785314000
H	2.218399000	-0.529451000	1.729046000
C	-1.012970000	-1.870405000	-0.202321000
N	-0.409276000	-2.452948000	1.000783000
O	-0.044710000	-1.645142000	1.866528000
O	-0.246714000	-3.655756000	1.070762000
N	-1.155613000	-2.890702000	-1.283788000
O	-2.267057000	-3.285255000	-1.582408000
O	-0.100502000	-3.239567000	-1.788430000
N	-2.249053000	-1.123779000	0.048677000

O	-2.688981000	-1.036597000	1.190240000
O	-2.716175000	-0.574097000	-0.939721000
H	-0.081897000	-0.850446000	-0.737658000
O	0.685480000	2.158855000	-0.893542000

"TS-S *via* $CH(NO_2)_3$"

C	4.097217000	-1.296867000	1.019491000
C	4.323146000	-2.042430000	-0.140078000
C	3.266240000	-2.438639000	-0.951775000
C	1.980808000	-2.081101000	-0.569765000
C	1.753456000	-1.340021000	0.596869000
C	2.813097000	-0.936496000	1.403881000
C	-0.421070000	-1.404385000	-0.223447000
N	0.400722000	-1.093974000	0.812404000
C	-1.879710000	-1.578968000	-0.041202000
C	-2.745432000	-1.459705000	-1.132720000
C	-4.106740000	-1.663932000	-0.967224000
C	-4.619208000	-1.978340000	0.289435000
C	-3.762967000	-2.091788000	1.378485000
C	-2.396084000	-1.898334000	1.217463000
H	4.936931000	-0.984286000	1.626071000
H	5.334799000	-2.306063000	-0.419590000
H	3.442844000	-3.005707000	-1.856114000
H	2.638036000	-0.340426000	2.289203000
H	-0.489647000	0.029297000	-1.033376000
H	0.092671000	-0.375798000	1.470428000
H	-2.353630000	-1.175825000	-2.102049000
H	-4.771145000	-1.561770000	-1.815656000
H	-5.683812000	-2.127408000	0.418572000
H	-4.156215000	-2.334462000	2.357479000
H	-1.732434000	-2.009944000	2.064627000
C	-0.043908000	2.213925000	-0.136674000
N	-0.837700000	2.313668000	1.092239000
O	-0.746114000	1.357838000	1.873333000
O	-1.564425000	3.274060000	1.262262000
N	-0.450640000	3.237226000	-1.137610000
O	0.321234000	4.136009000	-1.417107000
O	-1.563631000	3.064691000	-1.611708000
N	1.399929000	2.155022000	0.085577000
O	1.842872000	2.213902000	1.229036000
O	2.066132000	1.981317000	-0.926758000
H	-0.370292000	0.883463000	-0.782399000
S	0.445257000	-2.450919000	-1.369648000

"Intermediate 8 - imidazole *via* $CH(NO_2)_3$"

C	4.417102000	-0.664885000	-0.165379000

C	4.972650000	0.621804000	-0.067679000
C	4.176932000	1.756885000	-0.015259000
C	2.803389000	1.551458000	-0.067148000
C	2.248857000	0.268719000	-0.172048000
C	3.047003000	-0.870011000	-0.219085000
N	1.721292000	2.425579000	-0.033019000
C	0.565760000	1.728433000	-0.119320000
N	0.867154000	0.432519000	-0.209169000
C	-0.762396000	2.323242000	-0.117831000
C	-1.003291000	3.497672000	0.609845000
C	-2.269366000	4.062427000	0.612241000
C	-3.303448000	3.460319000	-0.100956000
C	-3.068727000	2.293662000	-0.821260000
C	-1.802831000	1.725911000	-0.838221000
H	5.077497000	-1.521402000	-0.198612000
H	6.048772000	0.730301000	-0.029992000
H	4.606030000	2.747066000	0.063545000
H	2.607392000	-1.856655000	-0.289768000
H	1.768240000	3.432012000	-0.034972000
H	0.162021000	-0.353549000	-0.167618000
H	-0.219279000	3.943074000	1.210819000
H	-2.455516000	4.960554000	1.187040000
H	-4.294005000	3.897068000	-0.086955000
H	-3.869269000	1.812971000	-1.367633000
H	-1.634360000	0.829890000	-1.421263000
C	-0.950509000	-1.901278000	0.020656000
N	-2.320850000	-1.576054000	-0.279261000
O	-2.609735000	-1.340833000	-1.453063000
O	-3.099579000	-1.445214000	0.665932000
N	-0.776744000	-2.188270000	1.483170000
O	-0.968778000	-3.316578000	1.890266000
O	-0.439714000	-1.231422000	2.172935000
N	-0.291533000	-2.902495000	-0.787906000
O	-0.790087000	-3.317947000	-1.819167000
O	0.830453000	-3.233812000	-0.370984000

"Intermediate 8 - oxazole *via* $CH(NO_2)_3$"

C	-4.157364000	-1.421162000	-0.184466000
C	-4.030317000	-2.809402000	-0.027578000
C	-2.785387000	-3.428283000	0.043826000
C	-1.702361000	-2.579726000	-0.050234000
C	-1.812483000	-1.204377000	-0.205571000
C	-3.052692000	-0.583203000	-0.277469000
C	0.325459000	-1.750732000	-0.134485000
N	-0.499191000	-0.726917000	-0.257375000
C	1.769417000	-1.769189000	-0.121821000
C	2.440168000	-2.883821000	0.406868000
C	3.824459000	-2.897618000	0.440054000

C	4.547145000	-1.811367000	-0.050570000
C	3.884133000	-0.709934000	-0.584316000
C	2.499018000	-0.684648000	-0.627561000
H	-5.147489000	-0.987641000	-0.234107000
H	-4.923258000	-3.416881000	0.039810000
H	-2.671939000	-4.496354000	0.163871000
H	-3.138227000	0.487228000	-0.403818000
H	-0.226373000	0.315681000	-0.219249000
H	1.875654000	-3.718919000	0.798617000
H	4.342589000	-3.752238000	0.855467000
H	5.629347000	-1.824897000	-0.016998000
H	4.439722000	0.135589000	-0.967447000
H	2.004929000	0.169952000	-1.070166000
C	-0.045191000	2.119520000	0.016374000
N	1.339986000	2.544628000	0.094776000
O	2.007996000	2.471759000	-0.935436000
O	1.788577000	2.850295000	1.196424000
N	-0.721496000	2.320415000	1.346988000
O	-1.197709000	3.406196000	1.610073000
O	-0.744149000	1.336500000	2.078419000
N	-0.853361000	2.709625000	-1.044356000
O	-0.350889000	3.359798000	-1.940843000
O	-2.058129000	2.429524000	-0.970951000
O	-0.354515000	-2.899338000	-0.010750000

"Intermediate 8 - thiazole *via* $CH(NO_2)_3$"

C	4.062496000	-1.417729000	-0.197654000
C	4.910885000	-0.308023000	-0.083324000
C	4.402065000	0.979951000	-0.009077000
C	3.020078000	1.128680000	-0.054664000
C	2.173301000	0.018878000	-0.165444000
C	2.685889000	-1.275300000	-0.240646000
C	0.591653000	1.687924000	-0.098556000
N	0.830899000	0.390883000	-0.184493000
C	-0.722989000	2.305184000	-0.110876000
C	-0.942470000	3.512255000	0.572475000
C	-2.200323000	4.091668000	0.566745000
C	-3.249717000	3.477670000	-0.114407000
C	-3.037197000	2.285305000	-0.799014000
C	-1.779765000	1.701661000	-0.807058000
H	4.489501000	-2.410303000	-0.253638000
H	5.982508000	-0.456280000	-0.051447000
H	5.057509000	1.836027000	0.078449000
H	2.025445000	-2.129093000	-0.330347000
H	0.060922000	-0.330330000	-0.147920000
H	-0.140452000	3.973833000	1.135178000
H	-2.368237000	5.014128000	1.107449000
H	-4.234318000	3.927845000	-0.106915000

H	-3.847663000	1.794871000	-1.320961000
H	-1.628725000	0.790047000	-1.369263000
C	-1.200518000	-1.849373000	0.020676000
N	-2.564691000	-1.394119000	0.095261000
O	-3.161264000	-1.123044000	-0.944091000
O	-3.016836000	-1.198522000	1.225947000
N	-0.749143000	-2.378217000	1.355236000
O	-1.174188000	-3.450621000	1.730524000
O	0.039710000	-1.669211000	1.972772000
N	-0.799375000	-2.746299000	-1.034130000
O	-1.424023000	-2.817384000	-2.078847000
O	0.264638000	-3.353370000	-0.817375000
S	2.067192000	2.609265000	0.003112000

"HNO_3"

N	0.000000000	0.158194000	0.000000000
O	-0.982275000	0.835619000	0.000000000
O	1.168153000	0.470128000	0.000000000
O	-0.264134000	-1.240032000	0.000000000
H	0.626052000	-1.633080000	0.000000000

"TS-N *via* HNO_3"

C	4.383365000	-0.005043000	0.681895000
C	4.518876000	-0.888723000	-0.392545000
C	3.405523000	-1.453394000	-1.011017000
C	2.161455000	-1.097664000	-0.515461000
C	2.024312000	-0.217754000	0.566679000
C	3.131458000	0.344204000	1.182250000
N	0.867138000	-1.477238000	-0.871349000
C	-0.045491000	-0.704008000	-0.194936000
N	0.659001000	-0.115623000	0.834963000
C	-1.460877000	-1.153950000	-0.047241000
C	-2.532511000	-0.262937000	-0.109800000
C	-3.827284000	-0.729262000	0.089373000
C	-4.062449000	-2.077370000	0.338985000
C	-2.995128000	-2.968029000	0.394647000
C	-1.696873000	-2.509917000	0.207281000
H	5.269638000	0.422841000	1.131965000
H	5.507621000	-1.135496000	-0.756762000
H	3.511311000	-2.133184000	-1.846615000
H	3.026658000	1.034514000	2.008508000
H	0.620603000	-1.971348000	-1.712969000
H	-0.302974000	0.574411000	-1.202044000
H	0.260914000	0.681265000	1.315149000
H	-2.365912000	0.783503000	-0.335090000
H	-4.653919000	-0.032066000	0.037513000

H	-5.074394000	-2.434024000	0.486666000
H	-3.170389000	-4.018715000	0.589743000
H	-0.864772000	-3.199585000	0.275427000
O	-0.041843000	2.473280000	-0.039265000
N	-1.011877000	3.376938000	-0.202457000
O	-0.799555000	4.497783000	0.219937000
O	-2.050677000	3.011747000	-0.758639000
H	-0.253879000	1.419951000	-0.836505000

"TS-O *via* HNO_3"

C	4.324600000	-0.253860000	0.639112000
C	4.355917000	-1.226998000	-0.364242000
C	3.181886000	-1.744754000	-0.912804000
C	2.008252000	-1.237404000	-0.402317000
C	1.960306000	-0.279084000	0.602393000
C	3.124247000	0.240073000	1.146221000
O	0.709313000	-1.569492000	-0.756812000
C	-0.111224000	-0.706841000	-0.112671000
N	0.604643000	-0.079417000	0.872050000
C	-1.536878000	-1.068436000	-0.002485000
C	-2.497255000	-0.094839000	0.284487000
C	-3.824685000	-0.469142000	0.439255000
C	-4.201016000	-1.802800000	0.301538000
C	-3.245836000	-2.767398000	-0.001244000
C	-1.913324000	-2.405960000	-0.155216000
H	5.257411000	0.131304000	1.029759000
H	5.310223000	-1.581033000	-0.731199000
H	3.188333000	-2.489350000	-1.696464000
H	3.103202000	0.999414000	1.915682000
H	-0.241612000	0.498771000	-1.253015000
H	0.257494000	0.786059000	1.269113000
H	-2.226927000	0.953832000	0.324356000
H	-4.568551000	0.288362000	0.650170000
H	-5.239435000	-2.087257000	0.418209000
H	-3.536103000	-3.803890000	-0.118209000
H	-1.168106000	-3.154736000	-0.386158000
O	0.249901000	2.437183000	-0.199009000
N	-0.669256000	3.399709000	-0.307679000
O	-0.295664000	4.545378000	-0.138496000
O	-1.829581000	3.060396000	-0.555385000
H	-0.105327000	1.333399000	-0.947390000

"TS-S *via* HNO_3"

C	4.209889000	0.149572000	0.992508000
C	4.544410000	-0.788919000	0.012827000
C	3.556302000	-1.467414000	-0.691954000
C	2.230228000	-1.189911000	-0.389073000

C	1.896095000	-0.257546000	0.598554000
C	2.884231000	0.426789000	1.297774000
S	0.762522000	-1.879359000	-1.103534000
C	-0.237699000	-0.729616000	-0.193301000
N	0.519558000	-0.149793000	0.774230000
C	-1.687971000	-0.996328000	0.015911000
C	-2.609746000	0.052625000	0.078175000
C	-3.946502000	-0.218755000	0.342480000
C	-4.377623000	-1.527744000	0.533124000
C	-3.464173000	-2.573846000	0.460300000
C	-2.123846000	-2.313305000	0.204038000
H	4.995432000	0.677933000	1.516772000
H	5.585250000	-0.984520000	-0.209819000
H	3.815455000	-2.184679000	-1.459542000
H	2.621719000	1.166801000	2.042263000
H	-0.395743000	0.520235000	-1.291820000
H	0.131613000	0.636780000	1.282841000
H	-2.299369000	1.073288000	-0.111875000
H	-4.653023000	0.600526000	0.382442000
H	-5.422506000	-1.732592000	0.730931000
H	-3.791461000	-3.595866000	0.604435000
H	-1.415147000	-3.130429000	0.167354000
O	0.166078000	2.418309000	-0.180729000
N	-0.675289000	3.438825000	-0.330859000
O	-0.264908000	4.546407000	-0.032763000
O	-1.811808000	3.193953000	-0.747646000
H	-0.238928000	1.336086000	-0.980103000

“Intermediate 8 - imidazole *via* HNO_3”

C	-4.279598000	0.169406000	-0.033111000
C	-4.450925000	-1.211459000	0.163552000
C	-3.365979000	-2.072993000	0.244923000
C	-2.103663000	-1.500733000	0.125877000
C	-1.916853000	-0.117978000	-0.064262000
C	-3.019183000	0.734039000	-0.150460000
N	-0.825336000	-2.027960000	0.147148000
C	0.065782000	-0.995040000	-0.007440000
N	-0.559682000	0.158307000	-0.140878000
C	1.515061000	-1.205432000	-0.011303000
C	2.368454000	-0.202178000	0.461938000
C	3.742336000	-0.403654000	0.465782000
C	4.280914000	-1.600997000	0.003382000
C	3.437743000	-2.601637000	-0.470361000
C	2.062924000	-2.406596000	-0.479630000
H	-5.154351000	0.804202000	-0.094115000
H	-5.452634000	-1.612565000	0.251488000
H	-3.502318000	-3.136812000	0.393175000
H	-2.886803000	1.796793000	-0.305422000

H	-0.574651000	-2.979431000	0.358190000
H	-0.062531000	1.678046000	-0.519081000
H	1.951960000	0.722422000	0.839236000
H	4.393666000	0.377639000	0.836975000
H	5.353110000	-1.752971000	0.008602000
H	3.851306000	-3.530189000	-0.843758000
H	1.420708000	-3.178217000	-0.887940000
O	0.054092000	2.619895000	-0.921187000
N	0.691235000	3.411235000	0.002792000
O	0.834114000	4.562123000	-0.321294000
O	1.048911000	2.881922000	1.043219000

"Intermediate 8 - oxazole *via* HNO_3"

C	-4.257667000	-0.120328000	0.008875000
C	-4.304419000	-1.518737000	0.110621000
C	-3.143940000	-2.287747000	0.145990000
C	-1.959130000	-1.581762000	0.077359000
C	-1.886595000	-0.193420000	-0.022460000
C	-3.052423000	0.568012000	-0.059516000
O	-0.672399000	-2.061820000	0.088772000
C	0.124990000	-0.952338000	-0.003246000
N	-0.539509000	0.165689000	-0.072111000
C	1.565549000	-1.164364000	-0.013071000
C	2.435483000	-0.082101000	0.169830000
C	3.807419000	-0.287652000	0.149688000
C	4.324829000	-1.564915000	-0.049574000
C	3.462923000	-2.643895000	-0.225368000
C	2.089171000	-2.449805000	-0.205934000
H	-5.186402000	0.435100000	-0.016990000
H	-5.266004000	-2.013080000	0.161722000
H	-3.167592000	-3.366019000	0.223189000
H	-3.016486000	1.646025000	-0.142955000
H	-0.225532000	1.824839000	-0.394973000
H	2.039085000	0.908511000	0.345371000
H	4.474146000	0.552581000	0.296734000
H	5.396658000	-1.719539000	-0.064269000
H	3.861714000	-3.638807000	-0.378730000
H	1.419439000	-3.287559000	-0.343952000
O	-0.334700000	2.777414000	-0.726985000
N	0.487458000	3.585401000	0.034473000
O	0.407019000	4.759782000	-0.206982000
O	1.199853000	3.033951000	0.855089000

"Intermediate 8 - thiazole *via* HNO_3"

C	-4.146745000	0.737503000	-0.056584000
C	-4.579164000	-0.588813000	0.077378000

C	-3.668573000	-1.632722000	0.151067000
C	-2.312875000	-1.322319000	0.094033000
C	-1.866131000	0.006624000	-0.038995000
C	-2.798585000	1.046246000	-0.115781000
S	-0.926042000	-2.394439000	0.165234000
C	0.138489000	-0.981309000	-0.003949000
N	-0.488515000	0.154381000	-0.090309000
C	1.595155000	-1.145842000	-0.006760000
C	2.411420000	-0.135043000	0.517243000
C	3.791417000	-0.285513000	0.516829000
C	4.373743000	-1.439211000	-0.000269000
C	3.568091000	-2.449104000	-0.518122000
C	2.187443000	-2.306566000	-0.520456000
H	-4.878867000	1.532740000	-0.114462000
H	-5.639218000	-0.804109000	0.121883000
H	-4.005539000	-2.656055000	0.252633000
H	-2.461230000	2.068226000	-0.227292000
H	0.111214000	1.707388000	-0.507578000
H	1.962119000	0.752418000	0.942206000
H	4.412862000	0.499634000	0.928939000
H	5.450815000	-1.551855000	0.001377000
H	4.015472000	-3.346665000	-0.926385000
H	1.569039000	-3.088251000	-0.944589000
O	0.282815000	2.606634000	-0.951375000
N	0.857855000	3.438752000	-0.010643000
O	1.083656000	4.555383000	-0.394671000
O	1.075093000	2.965738000	1.091343000

Fig. S51. The ^{1}H NMR spectrum of DMSO-d_6 with high intensity