Supplementary Information

Conformational Behaviour, Photochemistry and Flash Vacuum Pyrolysis of a 2-(1*H*-Tetrazol-1-yl)thiophene

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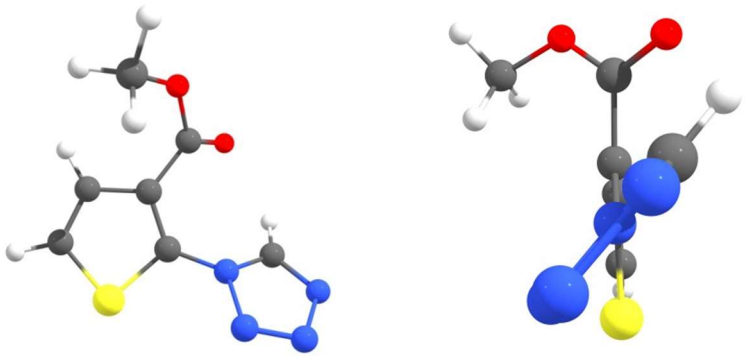
Table of Contents



15-III
Er_{ZPE} = 42.7 kJ mol^{-1}

Figure S1: Optimized structure of the theoretically predicted conformer **15-III** calculated at the B3LYP/6-311++G(d,p) level with relative zero-point-corrected energy [kJ mol^{-1}]. Calculations were carried out in order to find higher energy isomers of compound **15** having *trans* orientation concerning the O=C–O–C(H3) dihedral (~180º). Theoretical calculations allowed us to find a single conformation corresponding to a minimum. As mentioned in the manuscript, its relative energy is above 40 kJ mol^{-1} and therefore not significant from an experimental point of view.

Table S1: Experimental IR spectrum (Ar matrix, 16 K), B3LYP/6-311++G(d,p) calculated vibrational frequencies ($\tilde{\nu}$ [cm^{-1}], absolute IR intensities (A^{th} [km mol^{-1}] for 2-(1*H*-tetrazol-1-yl)thiophene **15**.

Ar matrix [a]			Calculated [b]			
15			**15-I**		**15-II**	
$\tilde{\nu}$	I		$\tilde{\nu}$	A^{th}	$\tilde{\nu}$	A^{th}
704	w	{	704	8.7		
					708	12.5
712	m	{	708	15.8		
					712	13.6
963	br	{	950	15.6		
					950	10.9
983	w				976	6.2
995	w		984	9.6		
995	w				986	13.3
1016	m		1003	25.2		
1076	s	{	1067	17.2		
					1068	9.4
1144	br	{	1136	21.4		
					1136	35.6
1204	m		1193	63.6		
1186	m				1188	13.1
1263	vs		1254	107		
1270	s				1261	98.6
1295	m		1321	23.6		
1300	m				1314	8.7
1405	w				1401	29.6
1408	m		1400	18.2		
1444	m		1443	9.3		
1446	m				1444	14.1
1482	br	{	1478	16.5		
					1476	14.2
1554	m		1546	36.5		
1560	m				1554	15.2
1729	vs		1722	84.2		
1738	s				1732	114.0
2966	br	{	2994	9.9		
					2996	8.8

[a] Only bands in the 3300-600 cm^{-1} region having calculated intensities above 5 km mol^{-1} (for both conformers) are included. Experimental intensities are presented in qualitative terms: vs = very strong, s = strong, m = medium, w = weak and br = broad; [b] Scaled B3LYP/6-311++G(d,p) frequencies.

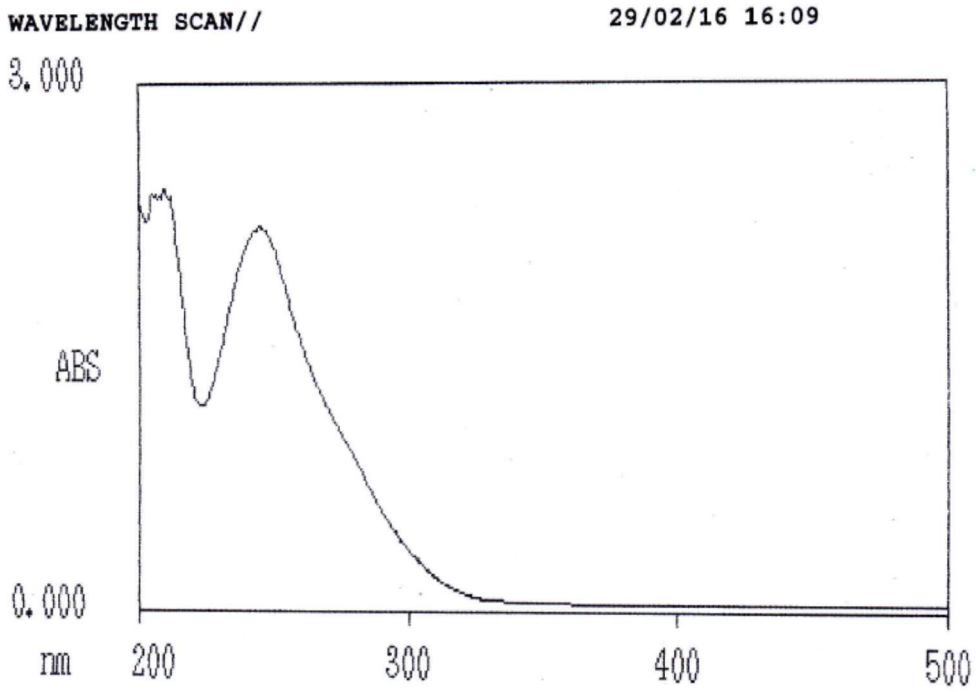


Figure S2: Experimental UV-Vis spectrum of 2-(1*H*-tetrazol-1-yl)thiophene **15** in acetonitrile solution.

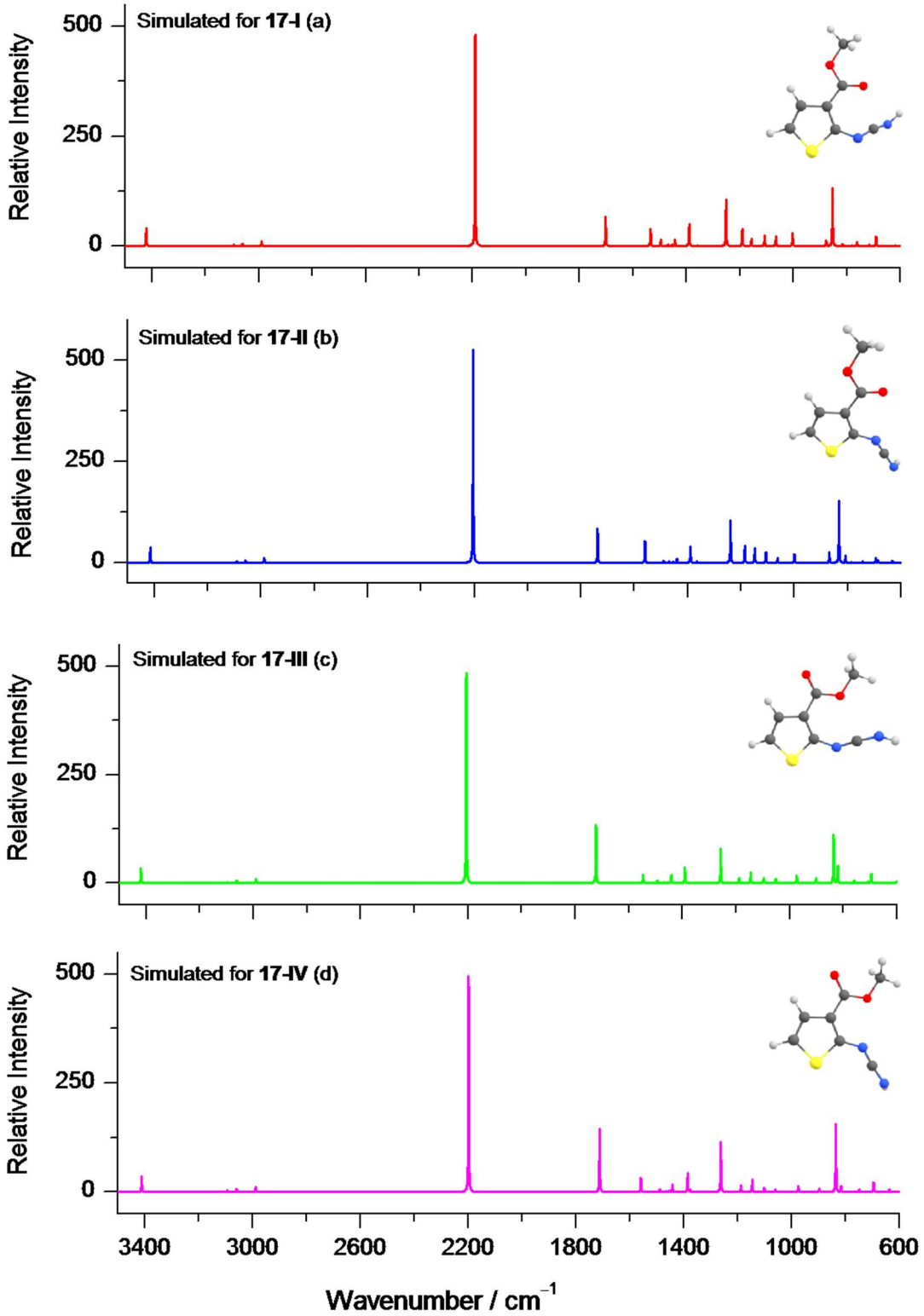


Figure S3: IR spectra of thiophen-2-ylcarbodiimide **17** conformers simulated at the B3LYP/6-311++G(d,p) level: (a) conformer **17-I**; (b) conformer **17-II**; (c) conformer **17-III**; (d) conformer **17-IV**.

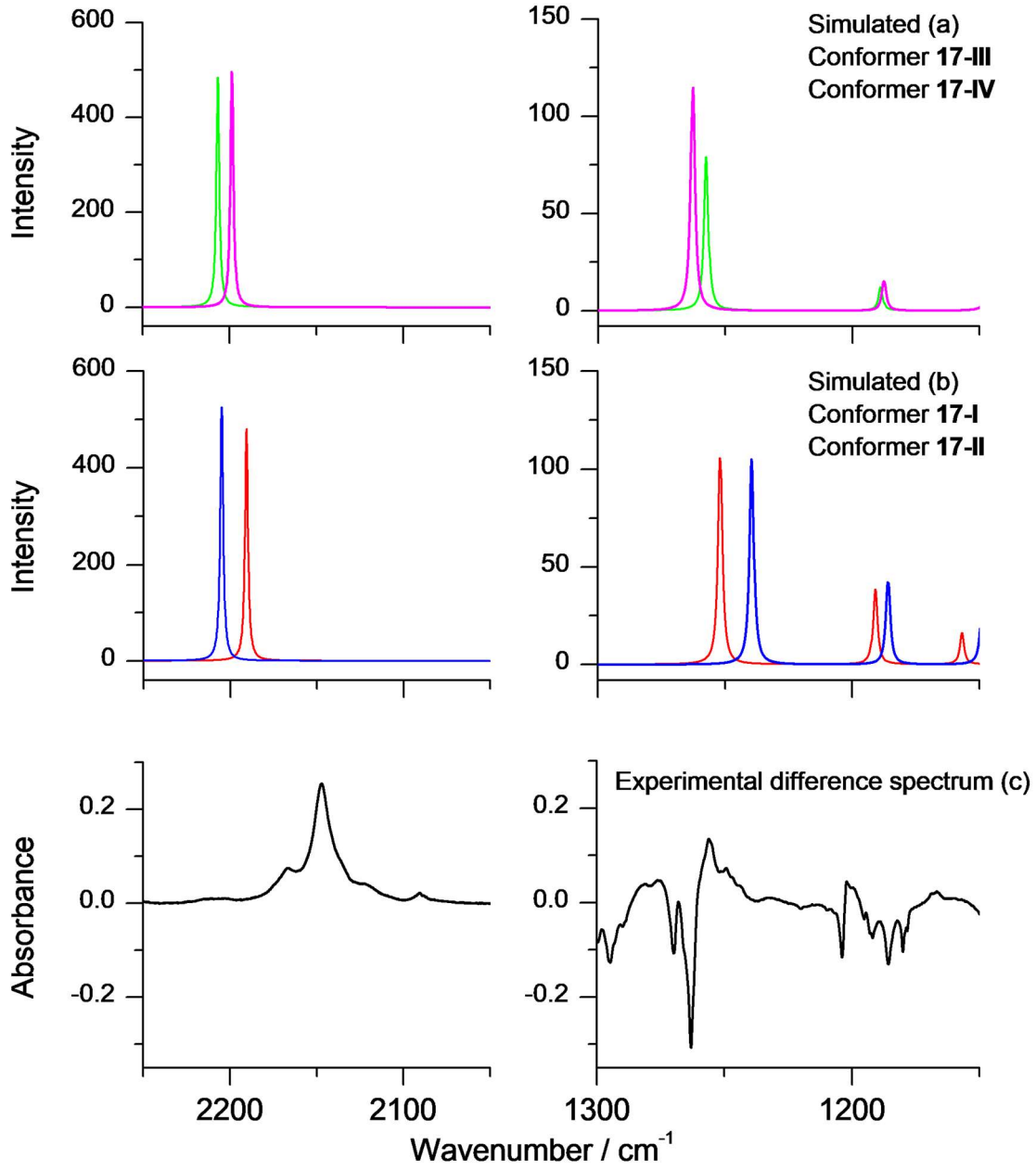


Figure S4: (a) B3LYP/6-311++G(d,p) simulated IR spectra for conformers **17-III** and **17-IV**; (b) B3LYP/6-311++G(d,p) simulated IR spectra for conformers **17-I** and **17-II**. The calculated spectra was simulated using Lorentzian functions centered at the calculated frequency scaled by 0.95, above 3400 cm^{-1}, and 0.98, below 3400 cm^{-1}, and with full-width-at-half-maximum (fwhm) equal to 2 cm^{-1}; (c) Experimental difference IR obtained from the spectrum after irradiation of matrix-isolated tetrazole **15** at 245 nm (~22m min, ~5 mW) "*minus*" the spectrum of the sample before irradiation. The negative bands correspond to tetrazole **15** and positive bands are due to the photoproduct.

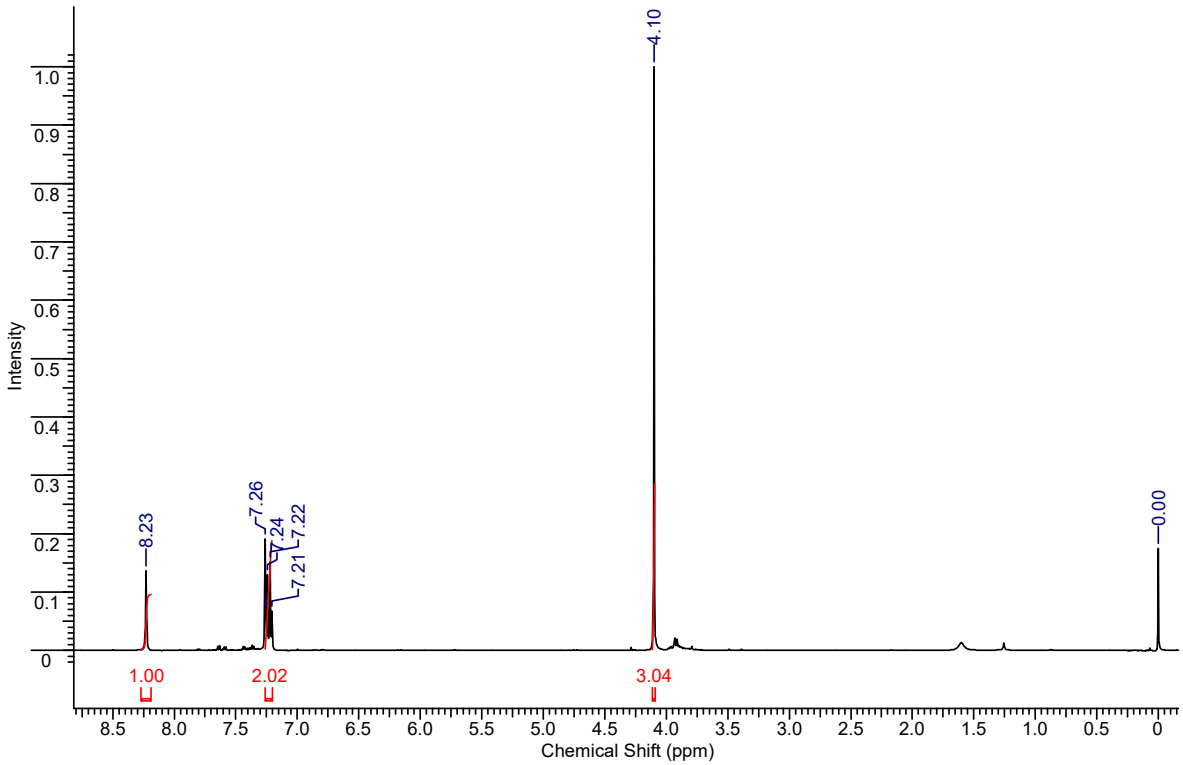


Figure S5: ^{1}H NMR spectrum of compound **18**.

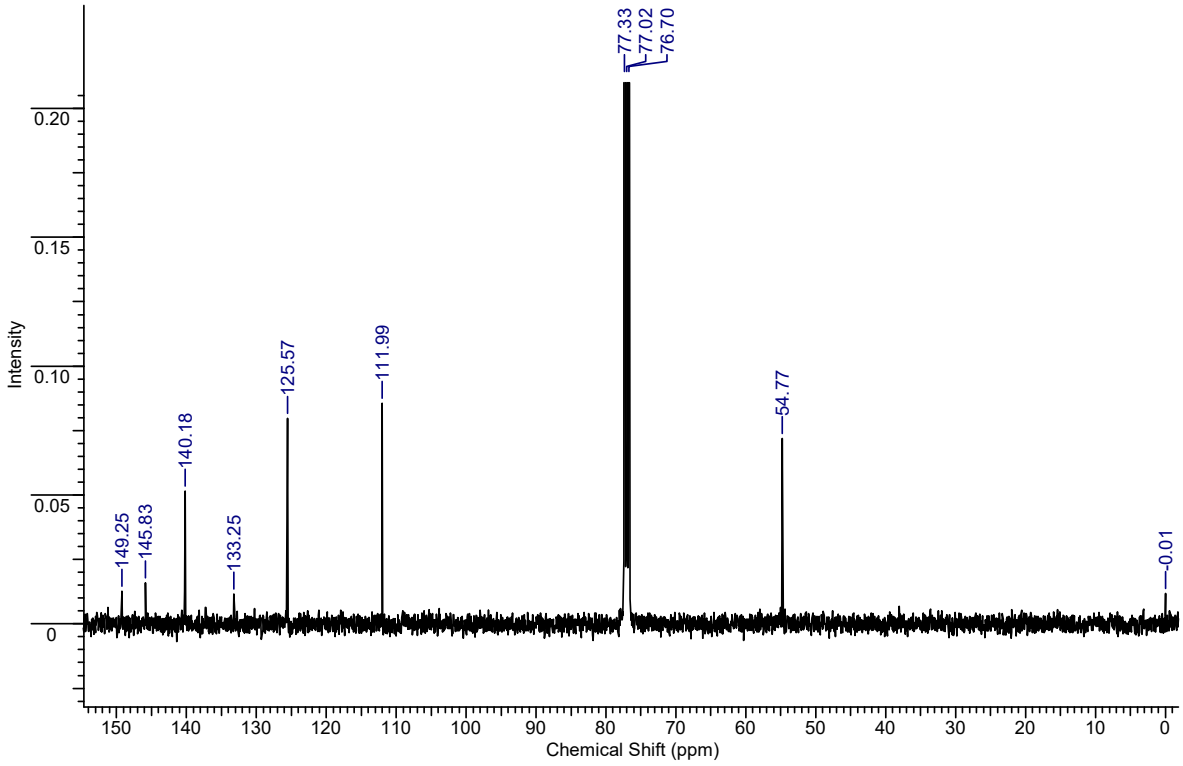


Figure S6: ^{13}C NMR spectrum of compound **18**.

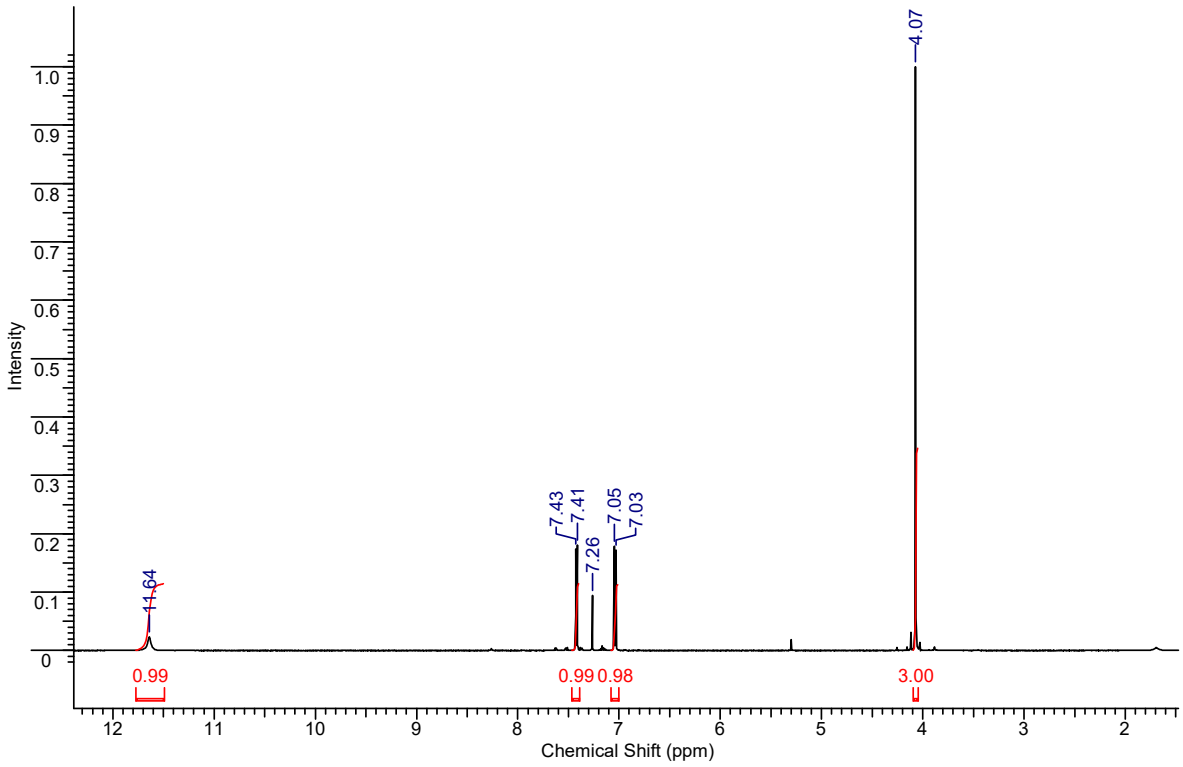


Figure S7: ^{1}H NMR spectrum of compound **19**.

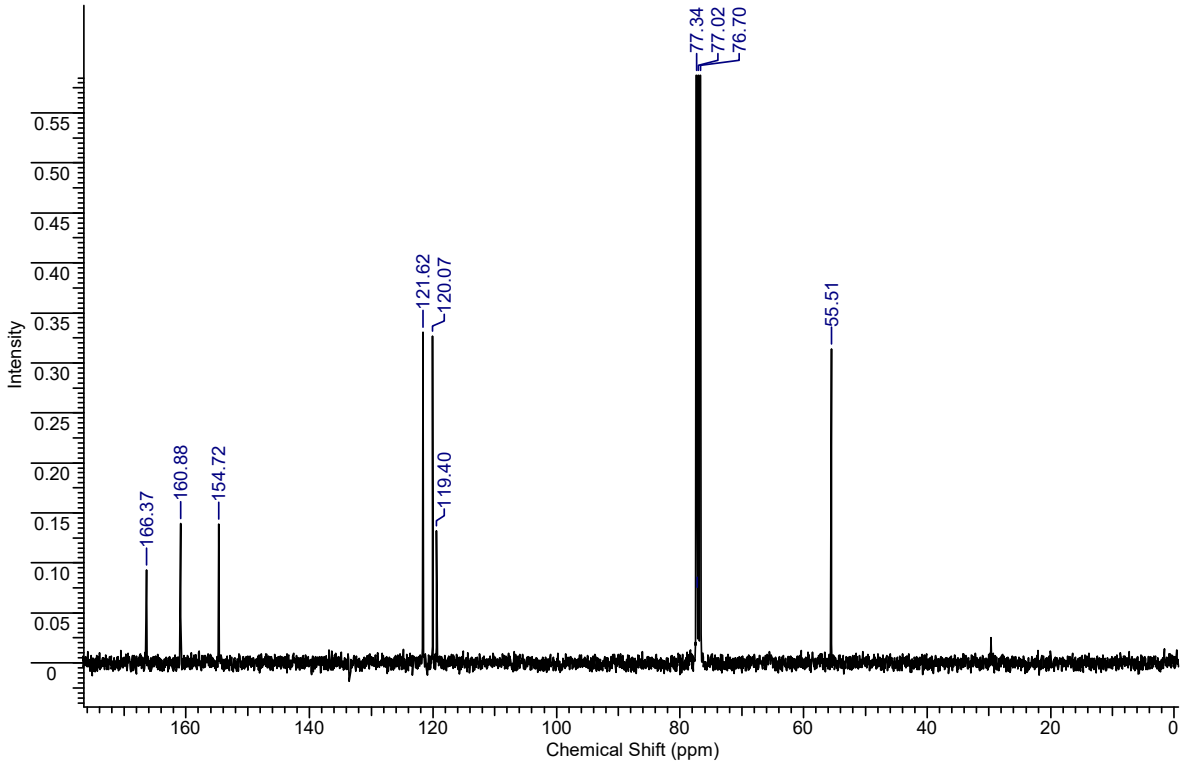


Figure S8: ^{13}C NMR spectrum of compound **19**.

Table S2: Crystallographic data for compounds **15** and **19**.

	15	**19**
Formula	C_7 H_6 N_4 O_2 S	C_7 H_6 N_2 O_2 S
M	210.22	182.20
λ (Å)	0.71073	0.71073
T (K)	293(2)	150(2)
crystal system	Monoclinic	Monoclinic
space group	*P* 2_1/c	*P* 2_1/c
a (Å)	3.9245(5)	8.454(4)
b (Å)	18.054(2)	12.125(6)
c (Å)	12.6455(15)	7.206(3)
α (°)	90	90
β (°)	98.936(8)	91.66(2)
γ (°)	90	90
V (Å^3)	885.09(19)	738.4(6)
Z	4	4
ρ_{calc} (g.cm^{-3})	1.578	1.639
μ (mm^{-1})	0.343	0.390
Crystal size	0.20×0.20×0.30	0.20×0.10×0.08
Crystal colour	Colourless	Colourless
Crystal description	Prism	Plate
θ_{max} (°)	25.681	25.772
total data	5591	2802
unique data	1710	1394
R_{int}	0.0404	0.0492
R [*I*>2σ(*I*)]	0.0347	0.0530
R_w	0.0909	0.1132
Goodness of fit	1.026	1.017
ρ_{min}	-0.230	-0.341
ρ_{max}	0.204	0.420

B3LYP/6-311++G(d,p) calculations

Tetrazole 15:

Conformer 15-I

Energy = -1038.1302489 Ha, ZPE = 0.1359625 Ha

C	-0.492805000	0.594609000	-0.052650000
C	0.890053000	0.555676000	-0.072554000
C	1.449952000	1.874752000	-0.103075000
C	0.511616000	2.857746000	-0.104560000
S	-1.098917000	2.222961000	-0.064286000
H	2.514680000	2.052861000	-0.115211000
H	0.660822000	3.926478000	-0.110873000
N	-1.441676000	-0.438610000	-0.001239000
C	-1.521394000	-1.660963000	-0.589570000
H	-0.728582000	-2.103359000	-1.163099000
N	-2.628194000	-0.231558000	0.657817000
N	-3.338993000	-1.277348000	0.466413000
N	-2.683950000	-2.191907000	-0.305103000
C	1.716612000	-0.670287000	-0.032427000
O	1.311648000	-1.802360000	-0.186118000
O	3.010947000	-0.378750000	0.198750000
C	3.910861000	-1.504254000	0.252650000
H	3.904806000	-2.040542000	-0.696881000
H	4.891670000	-1.077547000	0.448118000
H	3.618841000	-2.184105000	1.053375000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3321	14.4	960	8.9
3251	0.8	915	1.8
3233	1.6	901	9.1
3163	11.7	869	18.2
3131	14.7	836	16.6
3055	31.5	799	2.4
1758	264.9	774	4.7
1578	114.8	723	48.3
1507	53.5	719	24.5
1497	14.1	681	0.2
1483	11.1	656	9.9
1482	8.3	602	2.2
1473	30.0	529	4.7
1429	58.6	518	3.1
1386	15.3	411	1.6
1348	74.1	364	12.6
1279	346.0	334	6.0
1222	14.0	322	0.5
1217	199.9	287	5.2
1195	8.7	207	6.0
1171	1.0	162	5.0
1159	71.1	147	0.3
1117	10.5	134	0.1
1089	54.3	111	0.4
1023	80.8	98	1.7
1005	30.0	45	3.9
970	48.9	34	2.2

Conformer 15-II

Energy = - 1038.1289100 Ha, ZPE = 0.1358529 Ha

C	0.041841000	-0.831294000	0.043052000
C	1.250906000	-0.165013000	0.029848000
C	2.352190000	-1.077176000	0.042152000
C	1.969280000	-2.382652000	0.054435000
S	0.247333000	-2.555769000	0.060927000
H	3.377975000	-0.738220000	0.025358000
H	2.592698000	-3.263475000	0.044947000
N	-1.266543000	-0.317542000	0.046512000
C	-1.899746000	0.485303000	0.932711000
H	-1.431953000	0.903316000	1.806679000
N	-2.175443000	-0.650135000	-0.922542000
N	-3.268262000	-0.059729000	-0.609096000
N	-3.136800000	0.660358000	0.543694000
C	1.507656000	1.296069000	-0.049188000
O	2.616316000	1.766554000	-0.148788000
O	0.383406000	2.035123000	-0.006504000
C	0.557439000	3.462462000	-0.137995000
H	1.024474000	3.697279000	-1.094633000
H	-0.445549000	3.879134000	-0.087224000
H	1.179183000	3.844000000	0.672310000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3296	3.0	957	3.9
3248	1.3	928	3.5
3227	2.9	922	16.1
3165	7.1	868	11.4
3133	13.2	840	14.0
3057	27.6	803	0.8
1768	370.5	774	10.4
1586	48.1	726	39.0
1506	46.5	723	35.6
1497	6.8	688	4.1
1484	13.2	659	3.8
1484	7.1	606	1.0
1474	44.7	528	3.5
1430	97.8	510	1.0
1402	12.0	402	1.1
1340	27.2	370	11.0
1287	312.1	349	7.1
1220	13.1	318	3.3
1213	41.3	281	1.9
1187	17.4	203	5.2
1171	1.3	155	1.6
1160	111.7	138	0.2
1111	15.8	126	1.1
1091	30.9	100	0.6
1006	45.1	89	0.3
996	19.1	36	3.5
971	34.9	27	7.3

Conformer 15-III

Energy = -1038.1134503 Ha, ZPE = 0.135447 Ha

C	-0.234689000	0.624626000	-0.127802000
C	1.039020000	0.138099000	-0.317290000
C	1.993911000	1.198669000	-0.426967000
C	1.435398000	2.435680000	-0.308576000
S	-0.273126000	2.361724000	-0.053572000
H	3.047326000	1.036888000	-0.608765000
H	1.926739000	3.395661000	-0.349787000
N	-1.436975000	-0.083508000	0.023065000
C	-1.973528000	-1.123168000	-0.668942000
H	-1.462005000	-1.636068000	-1.465098000
N	-2.361452000	0.303338000	0.958585000
N	-3.367402000	-0.476291000	0.816325000
N	-3.162689000	-1.380228000	-0.183525000
C	1.372979000	-1.310781000	-0.483552000
O	0.817420000	-2.012474000	-1.291923000
O	2.357147000	-1.830276000	0.276619000
C	2.841286000	-1.175950000	1.465953000
H	3.652508000	-0.488058000	1.223524000
H	2.041694000	-0.644319000	1.982665000
H	3.220577000	-1.975912000	2.098946000

Carbodiimide 17:

Conformer 17-I

Energy = -928.6456244 Ha, ZPE = 0.1232524 Ha

C	1.090988000	0.301438000	0.105981000
C	0.068683000	-0.631017000	-0.014813000
C	0.572293000	-1.965709000	-0.166069000
C	1.928439000	-2.035884000	-0.153242000
S	2.654885000	-0.469315000	0.055259000
H	-0.074631000	-2.823343000	-0.278410000
H	2.556252000	-2.906990000	-0.257028000
N	1.068522000	1.655183000	0.319642000
C	0.281352000	2.527094000	-0.024404000
N	-0.291814000	3.523723000	-0.412279000
H	-1.189958000	3.786425000	-0.025987000
C	-1.355631000	-0.281427000	0.061057000
O	-1.802265000	0.838905000	0.216095000
O	-2.147788000	-1.370942000	-0.053251000
C	-3.564429000	-1.129470000	0.014181000
H	-4.029082000	-2.106313000	-0.100195000
H	-3.876249000	-0.459349000	-0.788090000
H	-3.831192000	-0.687583000	0.975136000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3602	129.5	871	414.6
3250	0.4	832	10.9
3227	1.5	796	6.4
3156	14.0	777	30.1
3123	18.5	731	11.4
3051	37.1	704	65.9
2235	1516.3	631	8.0
1737	210.5	591	2.5
1566	124.9	559	14.6
1527	45.3	527	53.5
1498	10.2	504	10.6
1483	9.7	432	23.0
1472	45.8	427	34.2
1418	160.8	374	10.0
1385	3.5	333	11.3
1277	333.8	292	4.1
1215	121.6	276	18.7
1181	50.7	189	0.9
1171	0.8	166	1.4
1130	77.5	135	0.4
1087	68.7	109	2.1
1023	94.0	100	3.8
907	1.0	74	4.0
895	39.3	56	0.4

Conformer 17-II

Energy = -928.6408148 Ha, ZPE = 0.1228882 Ha

C	0.816636000	0.117024000	-0.049682000
C	-0.527104000	0.441391000	0.007704000
C	-0.740993000	1.856887000	0.068616000
C	0.409133000	2.580458000	0.058019000
S	1.814624000	1.561812000	-0.031817000
H	-1.726377000	2.295679000	0.118691000
H	0.528925000	3.652231000	0.092910000
N	1.352164000	-1.137449000	-0.150775000
C	2.460377000	-1.615710000	-0.000291000
N	3.547262000	-2.167948000	-0.027986000
H	3.929176000	-2.633893000	0.785382000
C	-1.610868000	-0.564606000	0.020742000
O	-1.474149000	-1.763153000	0.080250000
O	-2.827274000	0.037469000	-0.038263000
C	-3.959761000	-0.848237000	-0.023507000
H	-4.833451000	-0.202431000	-0.080681000
H	-3.975005000	-1.434728000	0.896405000
H	-3.926379000	-1.525835000	-0.877800000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3595	123.4	850	483.3
3249	0.1	825	56.5
3230	1.4	802	7.0
3153	15.8	759	13.2
3120	19.3	708	40.9
3049	40.8	699	21.8
2250	1651.4	645	14.1
1773	272.0	597	13.5
1592	165.1	552	4.5
1520	15.7	546	38.0
1499	11.5	502	8.9
1482	9.2	446	6.4
1470	29.5	408	78.5
1418	126.1	367	5.6
1393	15.3	338	19.1
1265	331.6	272	3.5
1210	133.1	263	17.0
1172	116.3	186	7.3
1171	0.8	151	2.6
1129	85.1	131	0.2
1084	38.7	101	1.4
1020	63.9	79	0.3
911	1.8	39	8.1
887	86.5	35	3.4

Conformer 17-III

Energy = -928.6423357 Ha, ZPE = 0.1229846 Ha

C	0.814572000	0.622060000	-0.046437000
C	0.504764000	-0.730500000	0.021783000
C	1.677343000	-1.549073000	0.083456000
C	2.837792000	-0.842443000	0.059035000
S	2.546740000	0.864303000	-0.048098000
H	1.617622000	-2.626685000	0.141737000
H	3.849946000	-1.214082000	0.096887000
N	0.062613000	1.762145000	-0.141296000
C	-1.082057000	2.127826000	0.049073000
N	-2.196467000	2.620747000	0.062959000
H	-2.571971000	3.057603000	0.894654000
C	-0.828900000	-1.361292000	0.014399000
O	-1.014931000	-2.556550000	0.064693000
O	-1.829014000	-0.457966000	-0.060063000
C	-3.167957000	-0.984923000	-0.100673000
H	-3.814059000	-0.113927000	-0.180918000
H	-3.382586000	-1.546891000	0.809293000
H	-3.291585000	-1.638904000	-0.964583000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3600	109.3	853	346.5
3249	0.3	838	124.9
3222	2.3	800	3.4
3162	7.3	775	17.8
3125	17.5	720	10.8
3052	33.1	710	68.3
2252	1522.8	613	12.4
1758	425.5	595	8.1
1578	60.3	543	21.1
1524	21.4	530	2.1
1498	7.9	500	22.7
1485	8.5	442	2.6
1471	58.3	389	81.5
1419	113.4	356	6.6
1393	2.4	323	1.0
1283	248.7	304	14.1
1213	38.0	258	31.3
1172	1.0	187	5.3
1169	77.6	164	9.8
1120	35.4	136	0.2
1073	31.5	109	0.1
994	53.9	103	1.6
920	35.1	54	9.7
917	2.2	34	3.7

Conformer 17-IV

Energy = -928.6411317 Ha, ZPE = 0.1229499 Ha

C	-0.715039000	-0.083366000	-0.007189000
C	0.476989000	-0.786486000	0.001958000
C	0.270053000	-2.203317000	0.011730000
C	-1.039102000	-2.563980000	0.010448000
S	-2.089162000	-1.179334000	-0.005802000
H	1.095395000	-2.900718000	0.019153000
H	-1.463732000	-3.555906000	0.015064000
N	-0.878481000	1.277567000	-0.025177000
C	-1.844196000	2.017469000	0.018006000
N	-2.732627000	2.844111000	-0.103765000
H	-3.161950000	3.287085000	0.698943000
C	1.858193000	-0.251364000	0.001650000
O	2.840208000	-0.962676000	-0.002978000
O	1.918949000	1.091697000	0.008120000
C	3.241135000	1.658687000	0.000801000
H	3.090932000	2.736003000	0.003631000
H	3.785231000	1.348422000	-0.892340000
H	3.797016000	1.344689000	0.885415000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3591	113.1	853	495.5
3248	0.3	833	44.3
3225	2.3	804	3.9
3156	12.2	764	17.8
3121	19.0	710	67.8
3049	38.2	704	0.9
2244	1568.5	650	22.3
1747	459.2	596	9.8
1591	100.2	548	38.6
1519	19.6	534	5.6
1497	6.1	502	13.7
1482	8.9	457	1.4
1471	57.2	408	68.7
1414	135.5	355	14.8
1405	15.4	346	2.1
1289	361.3	280	4.8
1212	47.5	269	17.7
1169	85.9	180	5.7
1169	4.5	148	3.8
1124	30.8	134	0.0
1082	17.9	101	1.4
995	45.7	76	0.3
924	2.1	43	8.9
915	23.4	32	3.1