Electronic Supplementary Information

Understanding the Crystalline Formation of Triazenes N-Oxides and the Role of the Halogen···π Interactions

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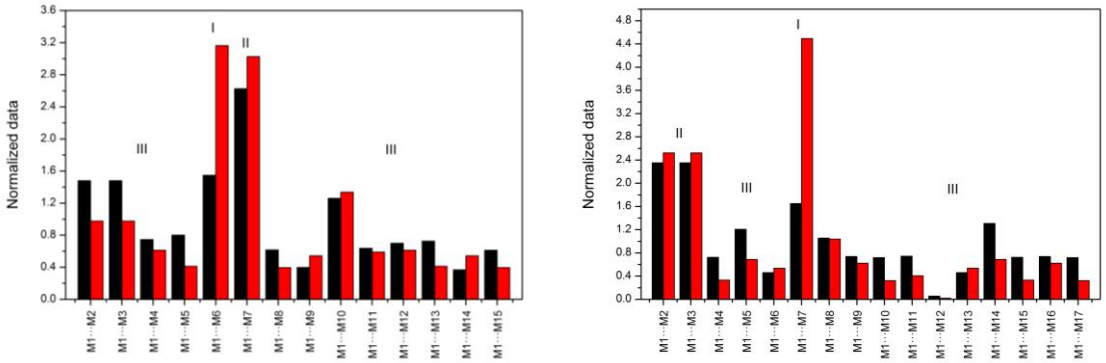
Table S1. Bonds lengths (Å) and bonds angles (°) selected for compounds **1-5**. Standard deviation between parentheses.

Atoms	Compound				
	1	**2**	**3**	**4**	**5**
	Bond length (Å)				
N11–N12	1.284(2)	1.284(3)	1.273(3)	1.285(10)	1.280(2)
N12–N13	1.322(2)	1.328(3)	1.325(3)	1.328(8)	1.323(2)
N11–O	1.291(2)	1.296(2)	1.292(2)	1.331(10)	1.294(2)
C24–X	1.362(2)	1.750(3)	1.899(3)	2.123(10)	–
N13–H1A	0.86	0.86	0.86	0.86	0.86
N11–O	1.291(2)	1.296(2)	1.292(2)	1.303(9)	1.294(2)
	Bond angle (°)				
N11–N12–N13	111.87(15)	112.11(19)	111.98(19)	112,1(7)	112.13(18)
N12–N11–O	122.55(16)	122.5(2)	123.4(2)	121.3(8)	123.29(18)
N12–N13–H1A	120.8	120.04	119.87	120.91	120.21

Topological and Energetic Results



3 **4**

Figure S1. Topological and energetic normalized data of each dimer from the supramolecular cluster of compounds **3** and **4**.

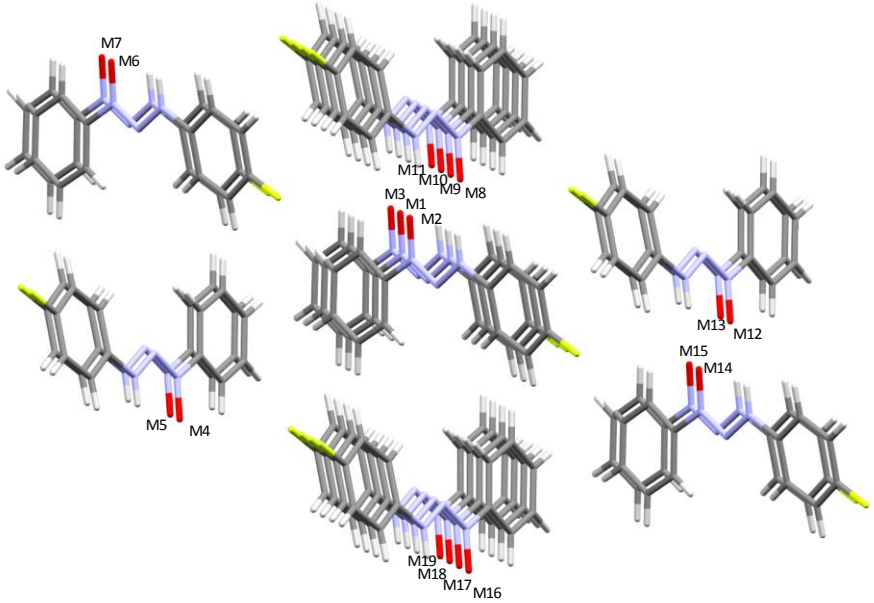


Figure S2. Supramolecular cluster of the compound **1**.

Table S2. Topological and energetic data of each dimer from the supramolecular cluster of compound **1**.

Dimer	Symmetry code	$C_{M1\cdots MN}$ (Å)	$G_{M1\cdots MN}$ (kcal mol^{-1})	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1	x,y,z	-	-	-	-
M1⋯M2	x,1+y,z	47.71	-9.78	2.95	2.99
M1⋯M3	x,-1+y,z	47.71	-9.78	2.95	2.99
M1⋯M4	2-x,1/2+y,1-z	12.46	-2.09	0.77	0.64
M1⋯M5	2-x,-1/2+y,1-z	12.46	-2.09	0.77	0.64
M1⋯M6	1+x,-1+y,z	11.23	-1.42	0.69	0.43
M1⋯M7	1+x,-2+y,z	5.09	-0.55	0.31	0.17
M1⋯M8	2-x,1.5+y,2-z	7.56	-0.86	0.47	0.26
M1⋯M9	2-x,1/2+y,2-z	15.59	-8.86	0.96	2.71
M1⋯M10	2-x,-1/2+y,2-z	15.59	-8.86	0.96	2.71
M1⋯M11	2-x,-1.5+y,2-z	7.56	-0.86	0.47	0.26
M1⋯M12	1-x,1/2+y,2-z	15.67	-2.70	0.97	0.83
M1⋯M13	1-x,-1/2+y,2-z	15.67	-2.70	0.97	0.83
M1⋯M14	-1+x,2+y,z	5.09	-0.55	0.31	0.17
M1⋯M15	-1+x,1+y,z	11.23	-1.42	0.69	0.43
M1⋯M16	1-x,1.5+y,1-z	13.45	-1.29	0.83	0.39
M1⋯M17	1-x,1/2+y,1-z	16.67	-1.87	1.03	0.57
M1⋯M18	1-x,-1/2+y,1-z	16.67	-1.87	1.03	0.57
M1⋯M19	1-x,-1.5+y,1-z	13.45	-1.29	0.83	0.39
Total		290.86	-58.85	18.00	18.00

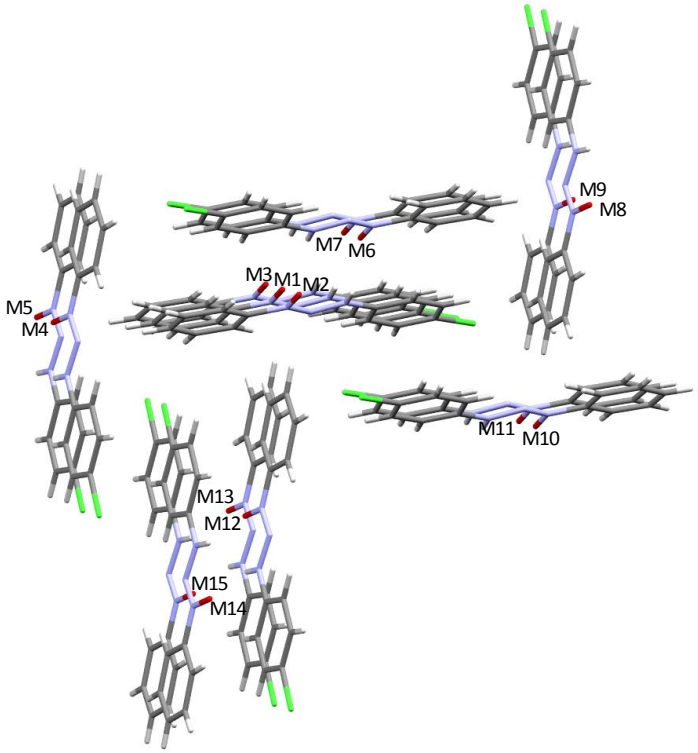


Figure S3. Supramolecular cluster of the compound **2**.

Table S3. Topological and energetic data of each dimer from the supramolecular cluster of compound **2**.

Dimer	Symmetry code	$C_{M1\cdots MN}$ (Å)	$G_{M1\cdots MN}$ (Kcal mol^{-1})	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1	x,y,z	-	-	-	-
M1···M2	-1+x,y,z	32.52	-4.49	1.48	0.98
M1···M3	1+x,y,z	32.52	-4.49	1.48	0.98
M1···M4	1-x,1/2+y,1/2-z	16.53	-3.18	0.75	0.69
M1···M5	2-x,1/2+y,1/2-z	17.14	-2.04	0.78	0.45
M1···M6	1-x,-y,1-z	33.58	-15.17	1.53	3.31
M1···M7	2-x,-y,1-z	56.22	-13.65	2.56	2.98
M1···M8	x,-1/2-y,1/2+z	13.18	-1.72	0.60	0.38
M1···M9	1+x,-1/2-y,1/2+z	8.40	-1.76	0.38	0.38
M1···M10	2-x,-1-y,1-z	28.66	-6.35	1.30	1.38
M1···M11	3-x,-1-y,1-z	14.00	-2.61	0.64	0.57
M1···M12	1-x,-1/2+y,1/2-z	16.53	-3.18	0.75	0.69
M1···M13	2-x,-1/2+y,1/2-z	17.14	-2.04	0.78	0.45
M1···M14	-1+x,-1/2-y,-1/2+z	8.40	-1.76	0.38	0.38
M1···M15	x,-1/2-y,-1/2+z	13.18	-1.72	0.60	0.38
	Total	308.00	-64.16	14.00	14.00

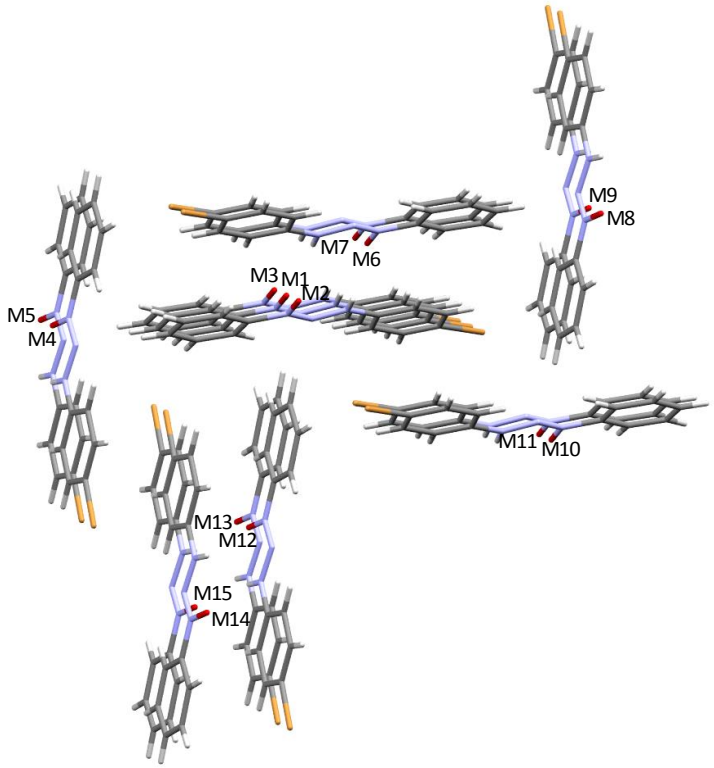


Figure S4. Supramolecular cluster of the compound **3**.

Table S4. Topological and energetic data of each dimer from the supramolecular cluster of compound **3**.

Dimer	Symmetry code	$C_{M1\cdots MN}$ (Å)	$G_{M1\cdots MN}$ (Kcal mol^{-1})	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1	x,y,z	-	-	-	-
M1···M2	-1+x,y,z	32.57	-4.69	1.48	0.98
M1···M3	1+x,y,z	32.57	-4.69	1.48	0.98
M1···M4	1-x,1/2+y,1/2-z	16.43	-2.95	0.75	0.61
M1···M5	2-x,1/2+y,1/2-z	17.60	-1.98	0.80	0.41
M1···M6	1-x,-y,1-z	34.01	-15.20	1.55	3.16
M1···M7	2-x,-y,1-z	57.75	-14.54	2.63	3.03
M1···M8	x,-1/2-y,1/2+z	13.57	-1.91	0.62	0.40
M1···M9	1+x,-1/2-y,1/2+z	8.77	-2.61	0.40	0.54
M1···M10	2-x,-1-y,1-z	27.71	-6.42	1.26	1.34
M1···M11	3-x,-1-y,1-z	14.03	-2.83	0.64	0.59
M1···M12	1-x,-1/2+y,1/2-z	15.39	-2.95	0.70	0.61
M1···M13	2-x,-1/2+y,1/2-z	15.95	-1.98	0.73	0.41
M1···M14	-1+x,-1/2-y,-1/2+z	8.09	-2.61	0.37	0.54
M1···M15	x,-1/2-y,-1/2+z	13.46	-1.91	0.61	0.40
	Total	307.90	-67.26	14.00	14.00

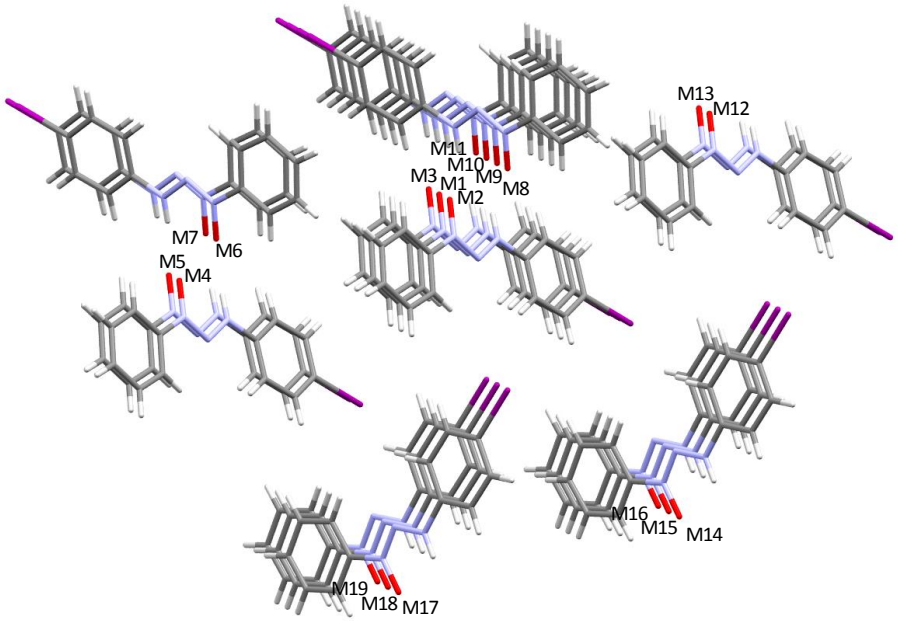


Figure S5. Supramolecular cluster of the compound **4**.

Table S5. Topological and energetic data of each dimer from the supramolecular cluster of compound **4**.

Dimer	Symmetry code	$C_{M1\cdots MN}$ (Å)	$G_{M1\cdots MN}$ (kcal mol^{-1})	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1	x,y,z	-	-	-	-
M1⋯M2	-1+x,y,z	58.61	-11.69	3.27	3.08
M1⋯M3	1+x,y,z	58.61	-11.69	3.27	3.08
M1⋯M4	-2+x,1+y,z	11.77	-1.16	0.66	0.31
M1⋯M5	-1+x,1+y,z	17.42	-3.21	0.97	0.85
M1⋯M6	-1/2+x,1.5-y,2-z	12.16	-1.27	0.68	0.34
M1⋯M7	1/2+x,1.5-y,2-z	12.16	-1.27	0.68	0.34
M1⋯M8	-1.5+x,1/2-y,2-z	8.65	-0.98	0.48	0.26
M1⋯M9	-1/2+x,1/2-y,2-z	18.52	-9.78	1.03	2.58
M1⋯M10	1/2+x,1/2-y,2-z	18.52	-9.78	1.03	2.58
M1⋯M11	1.5+x,1/2-y,2-z	8.65	-0.98	0.48	0.26
M1⋯M12	1+x,-1+y,z	17.42	-3.21	0.97	0.85
M1⋯M13	2+x,-1+y,z	11.77	-1.16	0.66	0.31
M1⋯M14	-1-x,-1/2+y,1.5-z	8.14	-0.67	0.45	0.18
M1⋯M15	-x,-1/2+y,1.5-z	16.49	-2.85	0.92	0.75
M1⋯M16	1-x,-1/2+y,1.5-z	9.35	-2.56	0.52	0.67
M1⋯M17	-1-x,1/2+y,1.5-z	8.14	-0.67	0.45	0.18
M1⋯M18	-x,1/2+y,1.5-z	16.49	-2.85	0.92	0.75
M1⋯M19	1-x,1/2+y,1.5-z	9.35	-2.56	0.52	0.67
Total		322.22	-68.33	18.00	18.00

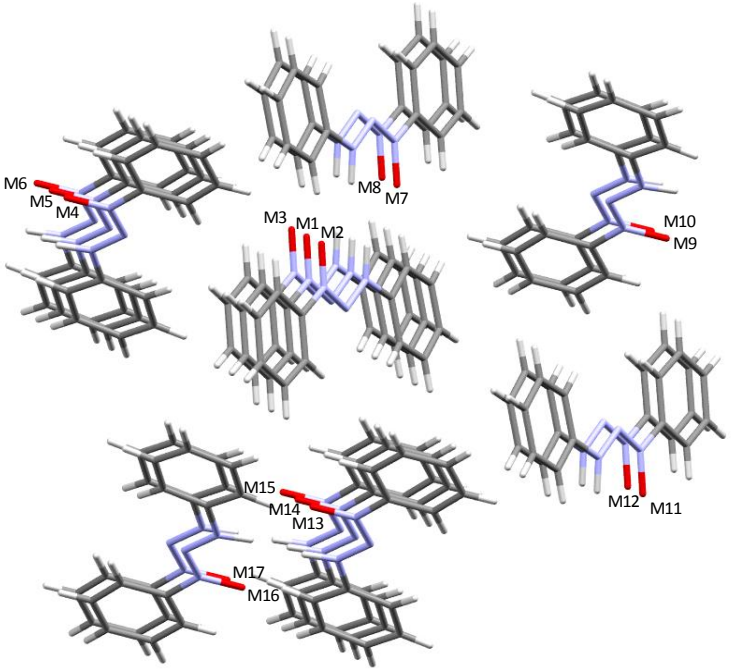


Figure S6. Supramolecular cluster of the compound **5**.

Table S6. Topological and energetic data of each dimer from the supramolecular cluster of compound **5**.

Dimer	Symmetry code	$C_{M1\cdots MN}$ (Å)	$G_{M1\cdots MN}$ (Kcal mol^{-1})	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1	x,y,z	-	-		
M1⋯M2	-1+x,y,z	41.49	-9.44	2.35	2.52
M1⋯M3	1+x,y,z	41.49	-9.44	2.35	2.52
M1⋯M4	-1.5+x,1/2-y,1/2+z	12.75	-1.24	0.72	0.33
M1⋯M5	-1/2+x,1/2-y,1/2+z	21.31	-2.57	1.21	0.69
M1⋯M6	1/2+x,1/2-y,1/2+z	8.12	-2.00	0.46	0.54
M1⋯M7	2-x,-y,2-z	29.10	-16.82	1.65	4.49
M1⋯M8	3-x,-y,2-z	18.62	-3.88	1.06	1.04
M1⋯M9	1.5-x,-1/2+y,1.5-z	13.02	-2.33	0.74	0.62
M1⋯M10	2.5-x,-1/2+y,1.5-z	12.68	-1.21	0.72	0.32
M1⋯M11	3-x,-y,1-z	13.10	-1.52	0.74	0.41
M1⋯M12	4-x,-y,1-z	0.97	-0.07	0.05	0.02
M1⋯M13	-1/2+x,1/2-y,-1/2+z	8.12	-2.00	0.46	0.54
M1⋯M14	1/2+x,1/2-y,-1/2+z	23.06	-2.57	1.31	0.69
M1⋯M15	1.5+x,1/2-y,-1/2+z	12.75	-1.24	0.72	0.33
M1⋯M16	1.5-x,1/2+y,1.5-z	13.02	-2.33	0.74	0.62
M1⋯M17	2.5-x,1/2+y,1.5-z	12.68	-1.21	0.72	0.32
	Total	282.28	-59.89	16.00	16.00

Compound	View Axis		
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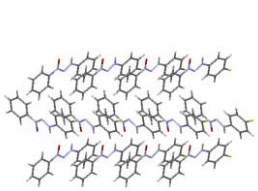
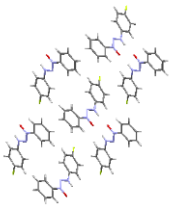
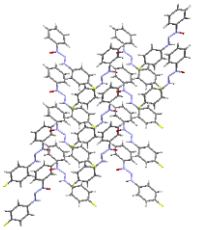
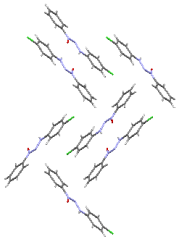
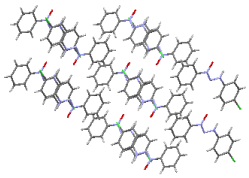
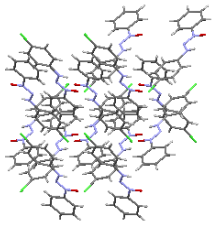
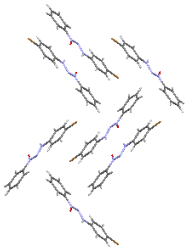
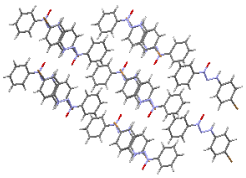
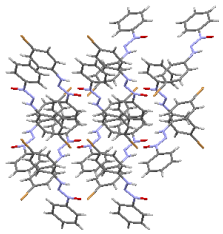
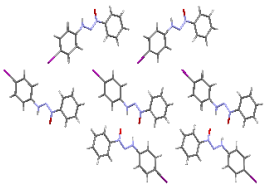
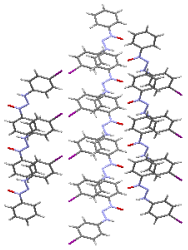
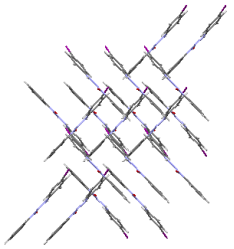
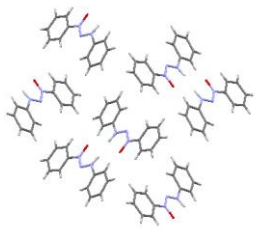
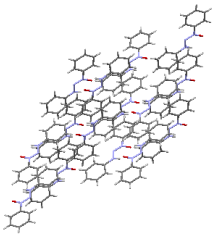
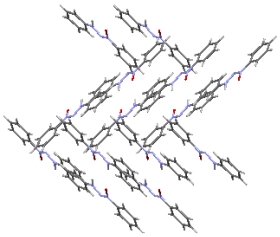
1			
2			
3			
4			
5			

Figure S7. Supramolecular clusters for the studied compounds **1-5**, viewed from different axis.

Crystallization Mechanism

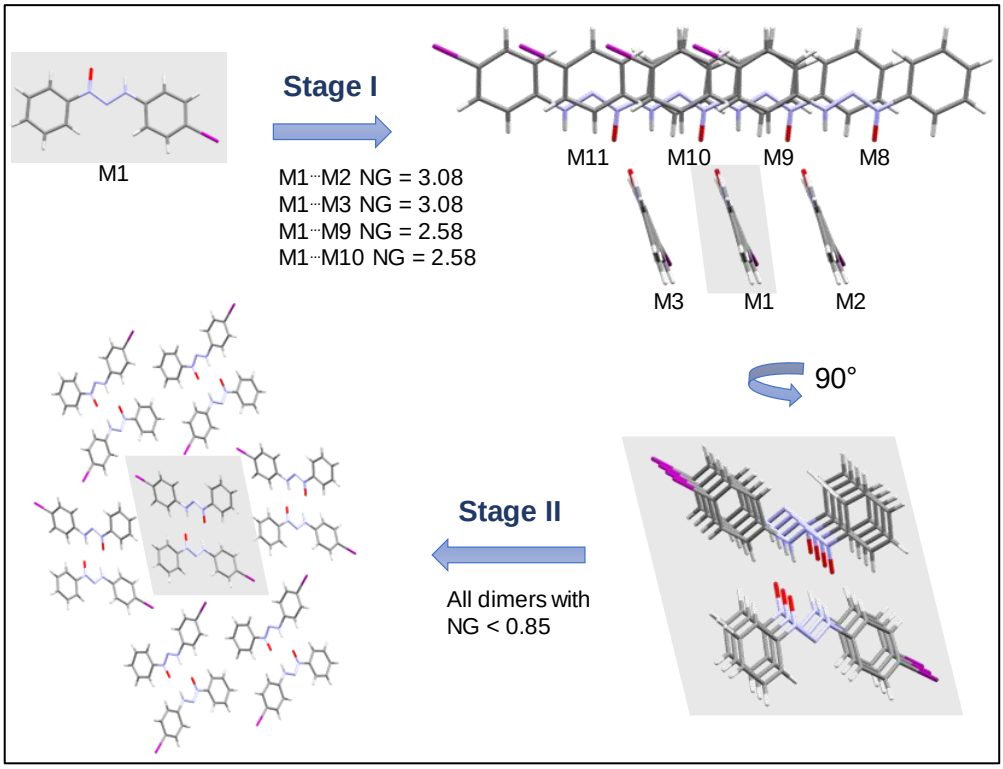


Figure S8. Crystallization mechanism of compound **4**.

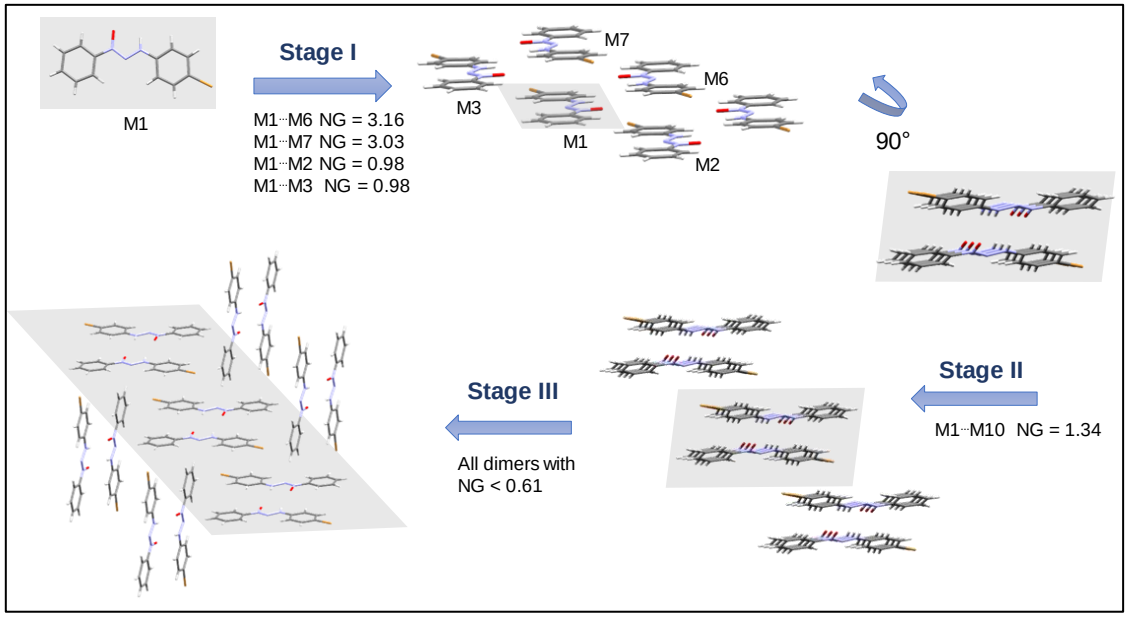


Figure S9. Crystallization mechanism of compound **3**.

Table S7. QTAIM data of H···π and halogen···π interactions for compounds **1-5**.

Compound	Interction	$\nabla^2\rho_b$	Ɛ	V	G	BPL	H
1	F···π	0.018184	0.545958	-0.00224	0.003393	6.312046	0.001153
	H···π	0.017387	0.774596	-0.002941	0.003644	5.443762	0.000703
2	Cl···π	0.018271	0.775426	-0.002862	0.003715	6.536461	0.000853
3	Br···π	0.020241	0.770078	-0.003135	0.004098	6.544656	0.000963
4	I···π	0.016639	0.614798	-0.002113	0.003136	6.910251	0.001023
5	H···π	0.008262	0.472495	-0.001161	0.001614	6.241198	0.000453
	H···π	0.013288	0.831961	-0.002248	0.002785	6.117797	0.000537

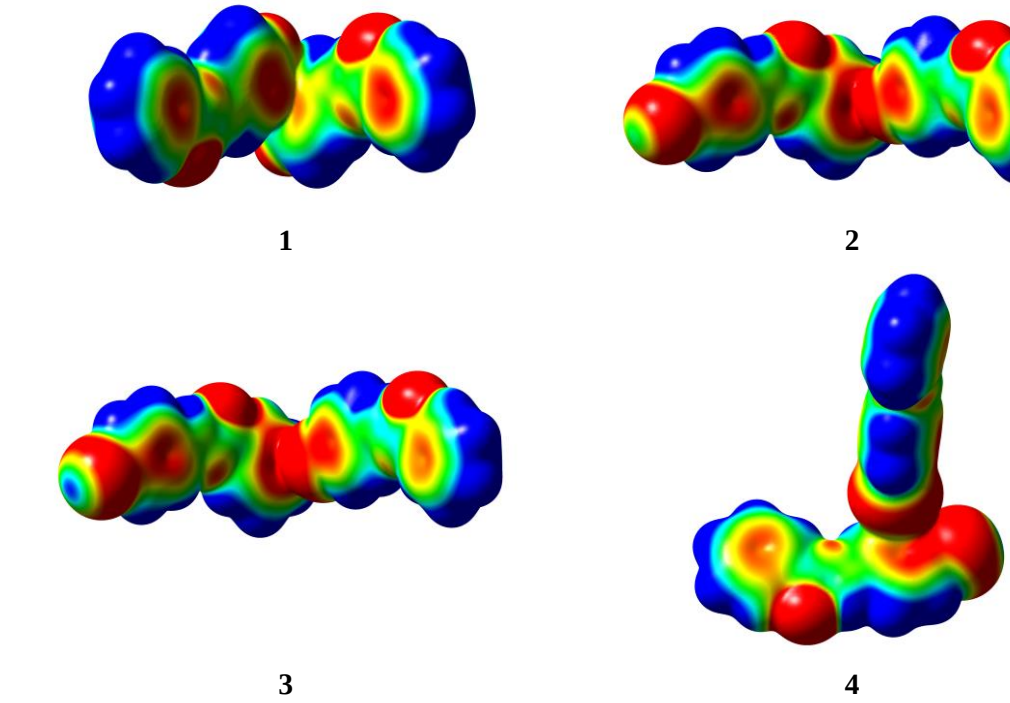


Figure S10. Molecular electrostatic potential of the involved dimers in X···π interactions for compounds **1-4**.

Thermogravimetric Analysis

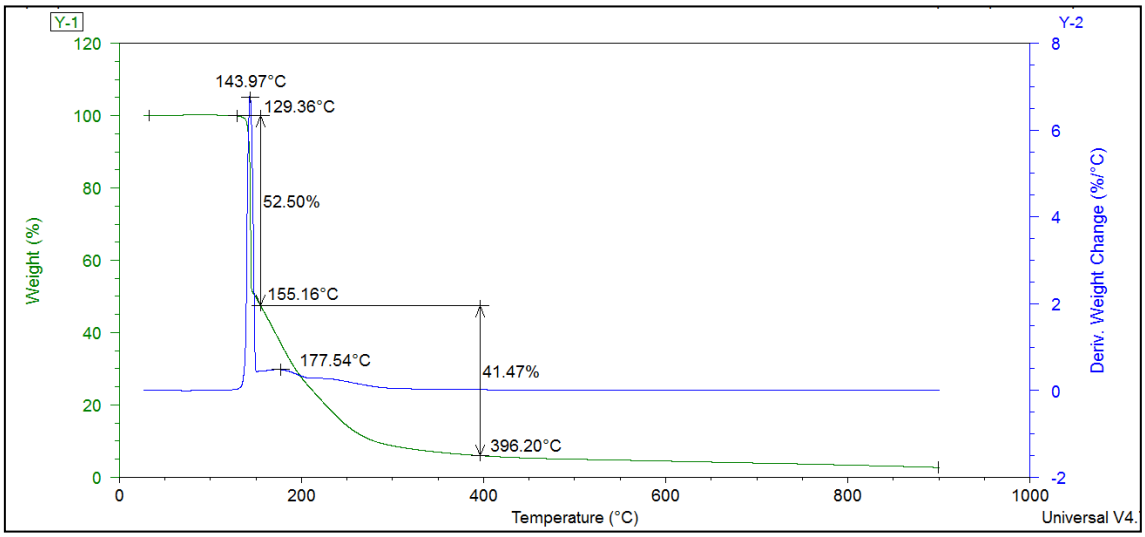


Figure S11. TGA thermogram at heating rate of 10 °C min^{-1} for compound **1**.

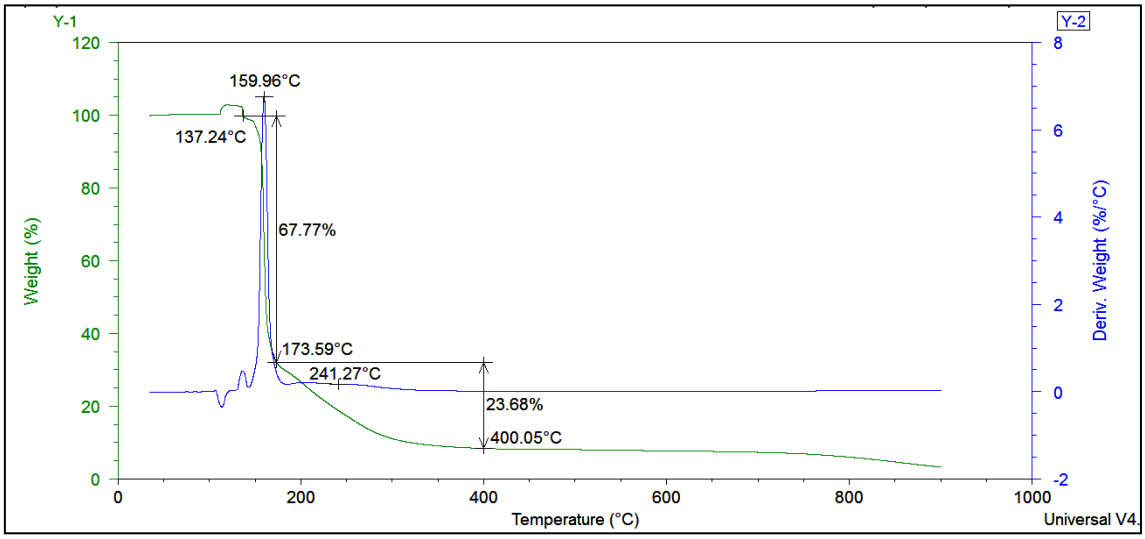


Figure S12. TGA thermogram at heating rate of 10 °C min^{-1} for compound **2**.

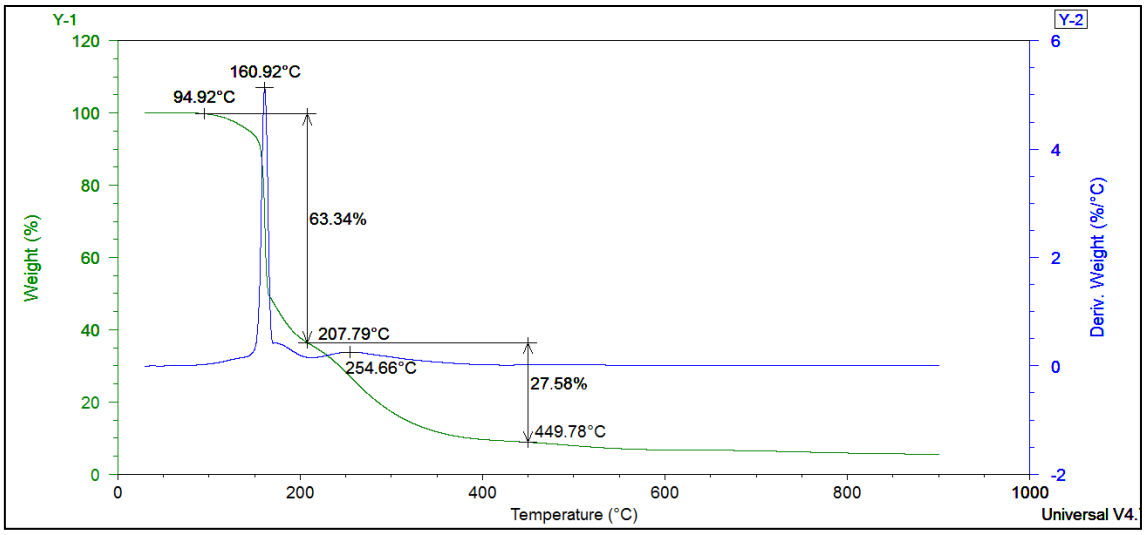


Figure S13. TGA thermogram at heating rate of 10 °C min^{-1} for compound **3**.

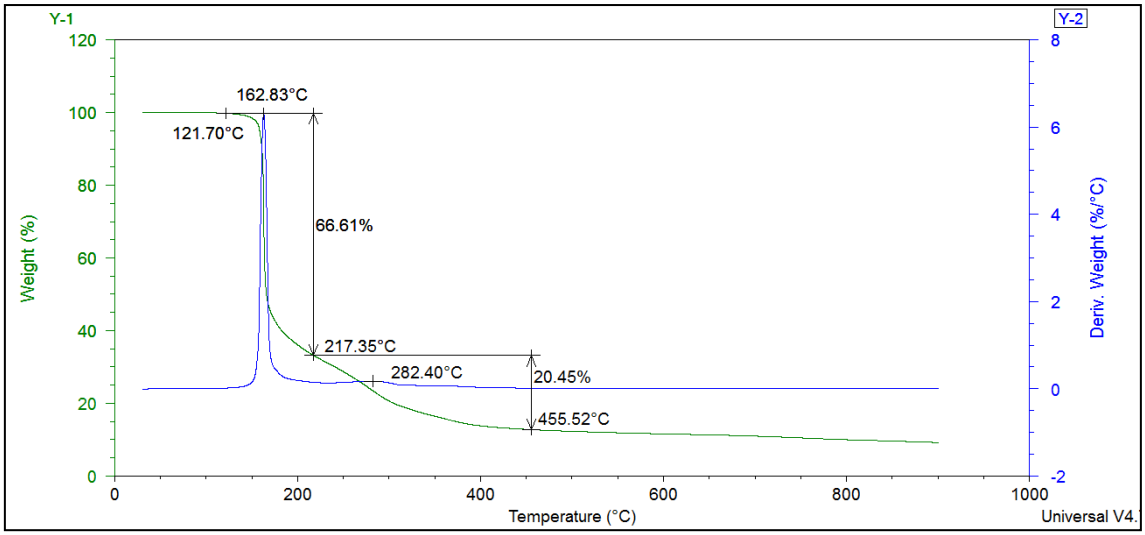


Figure S14. TGA thermogram at heating rate of 10 °C min^{-1} for compound **4**.

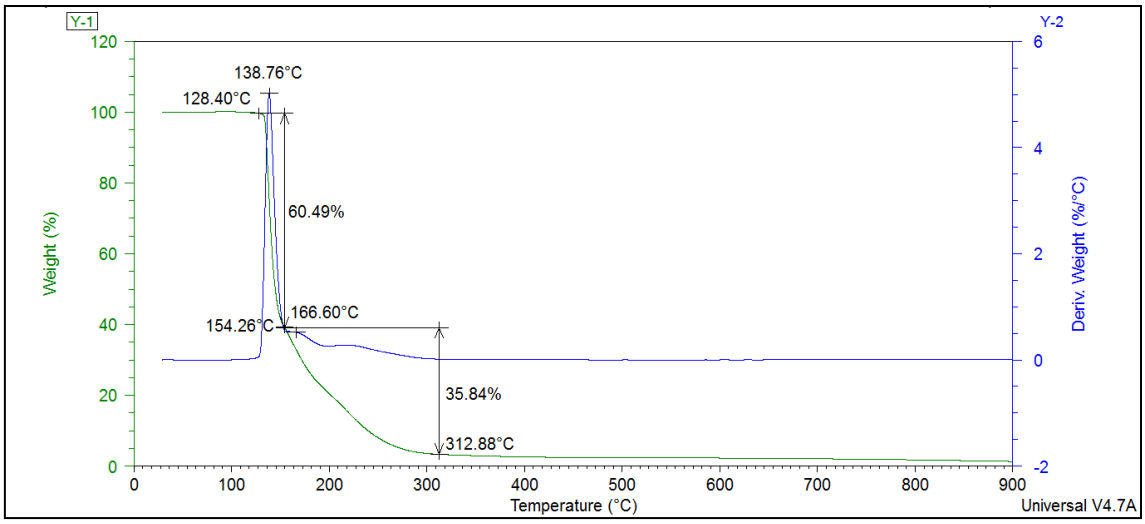


Figure S15. TGA thermogram at heating rate of 10 °C min^{-1} for compound **5**.

DSC

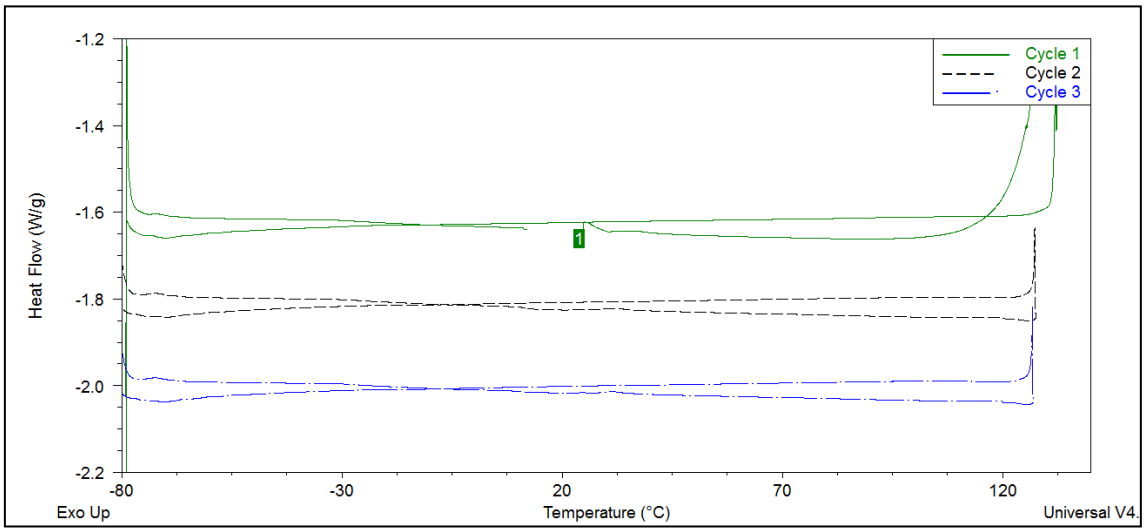


Figure S16. DSC thermogram at heat flow of 10 °C min^{-1} for compound **1**.

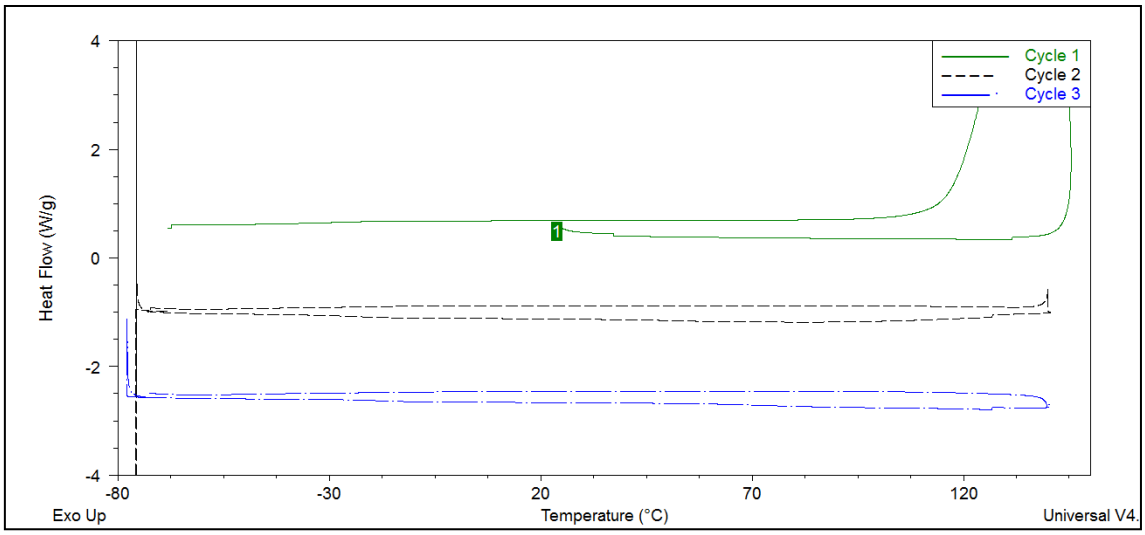


Figure S17. DSC thermogram at heat flow of 10 °C min^{-1} for compound **2**.

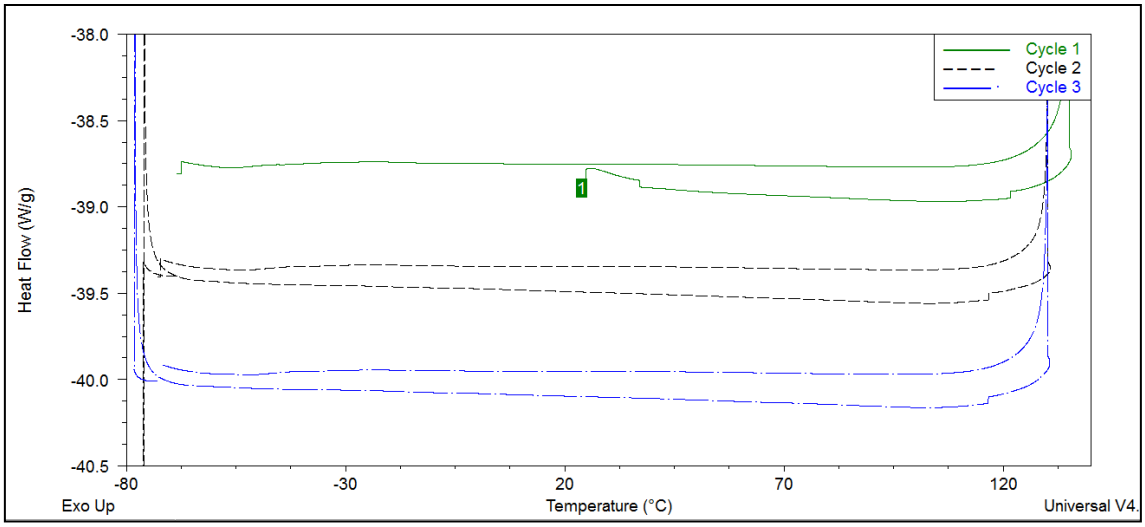


Figure S18. DSC thermogram at heat flow of 10 °C min^{-1} for compound **3**.

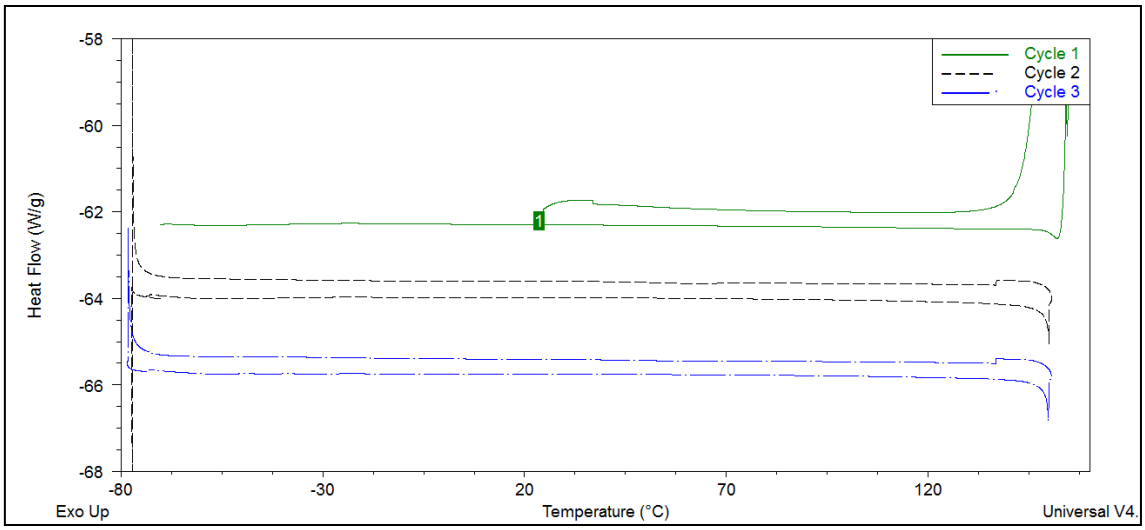


Figure S19. DSC thermogram at heat flow of 10 °C min^{-1} for compound **4**.

Infrared Spectra

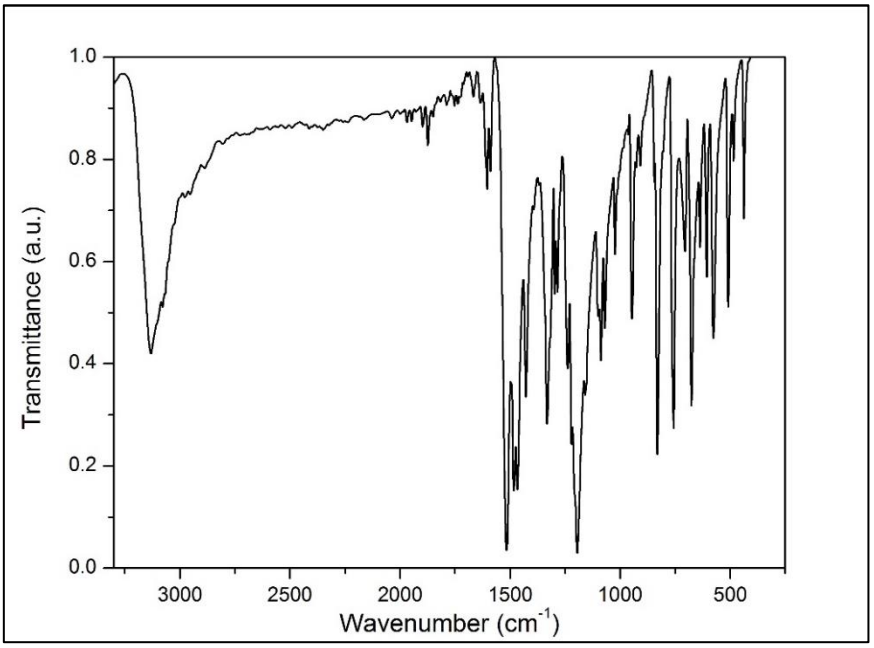


Figure S20. Infrared Spectra of compound **1**.

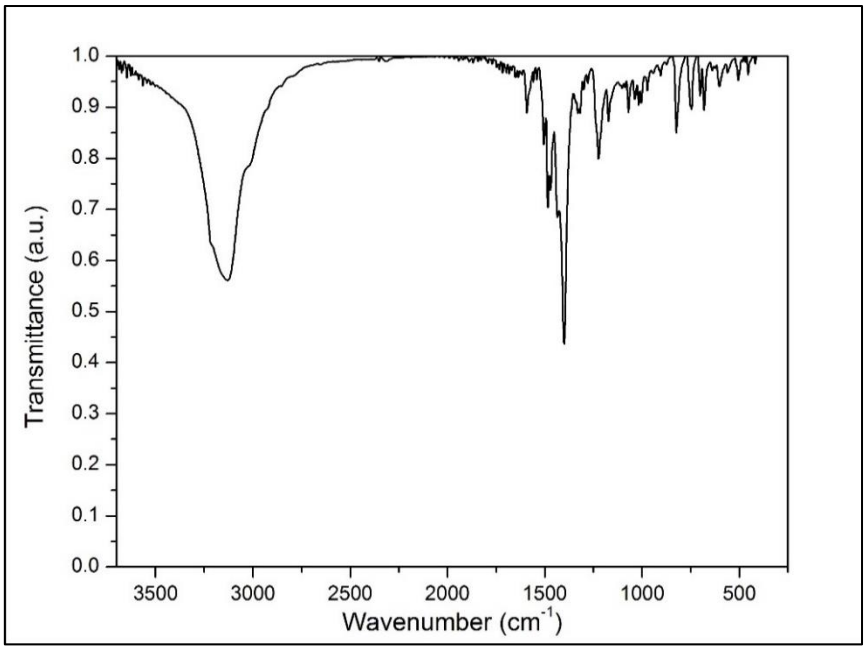


Figure S21. Infrared Spectra of compound **2**.

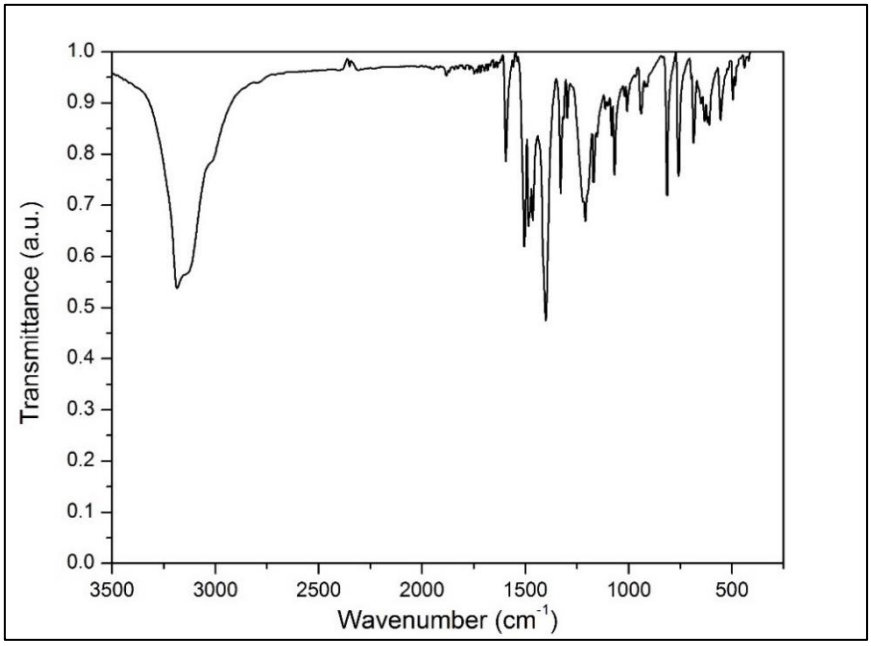


Figure S22. Infrared Spectra of compound **3**.

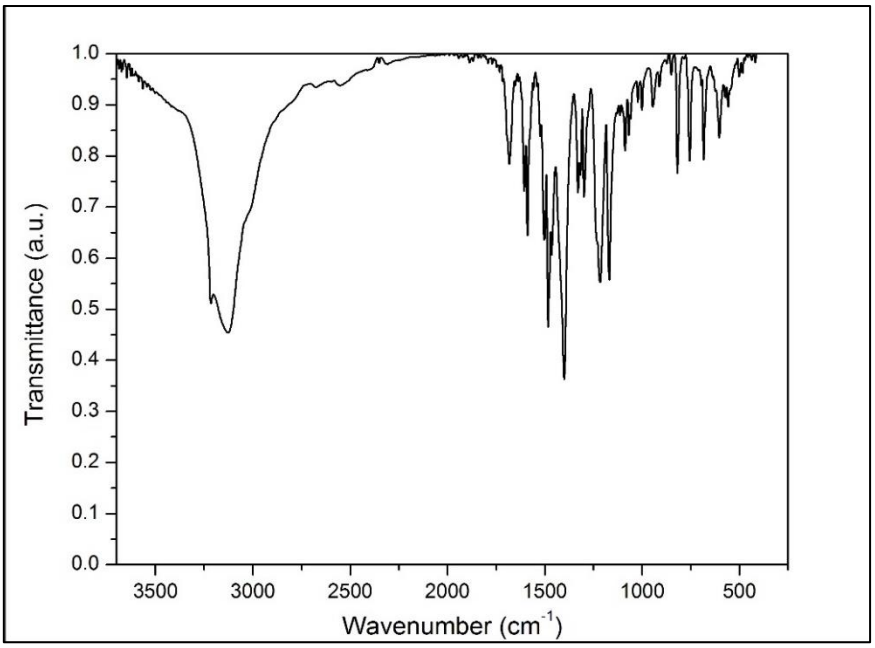


Figure S23. Infrared Spectra of compound **4**.

Raman Spectra

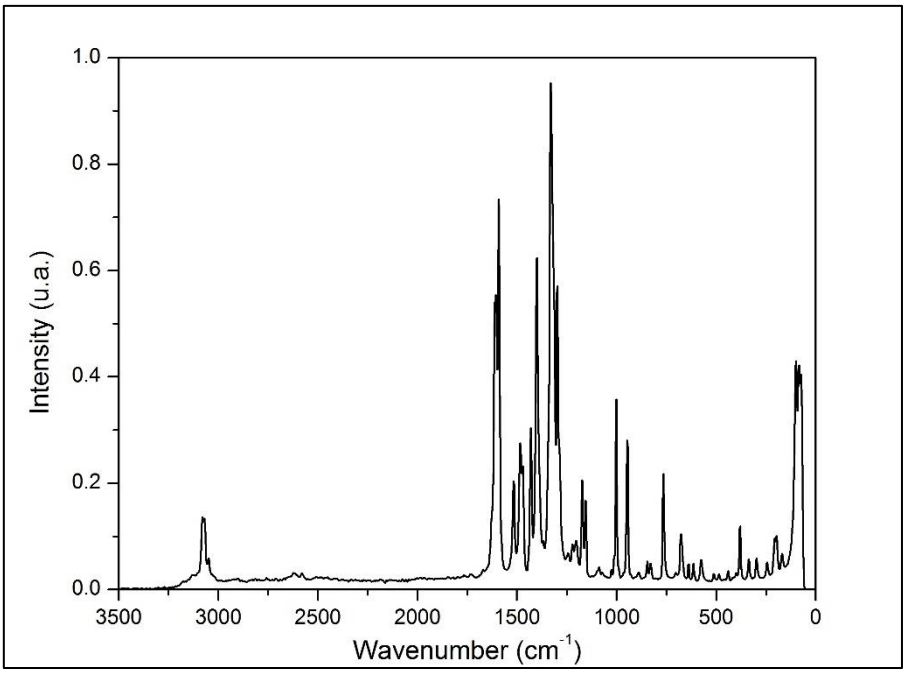


Figure S24. Raman Spectra of compound **1**.

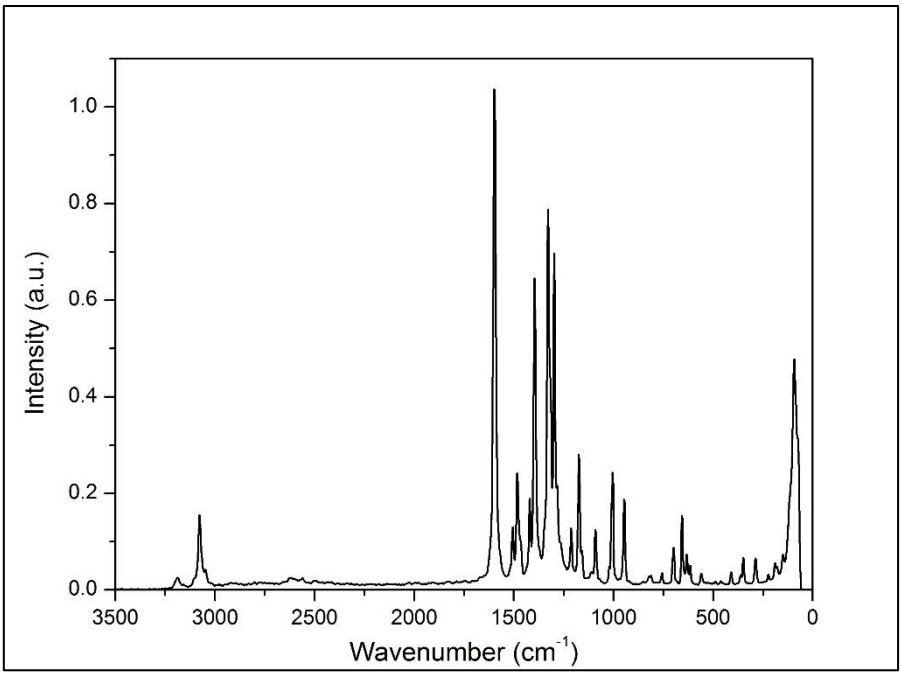


Figure S25. Raman Spectra of compound **2**.

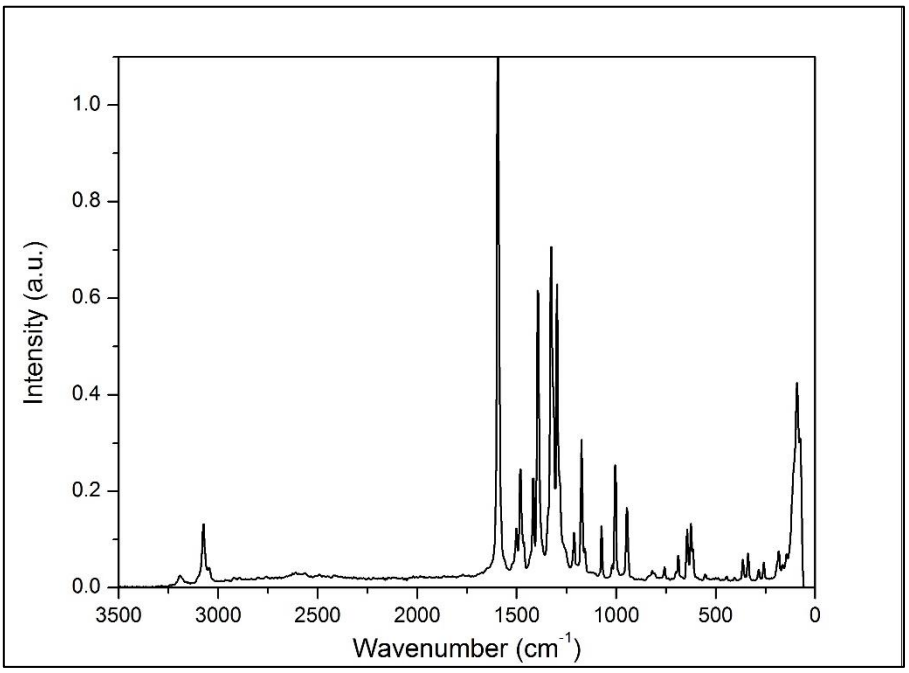


Figure S26. Raman Spectra of compound **3**.

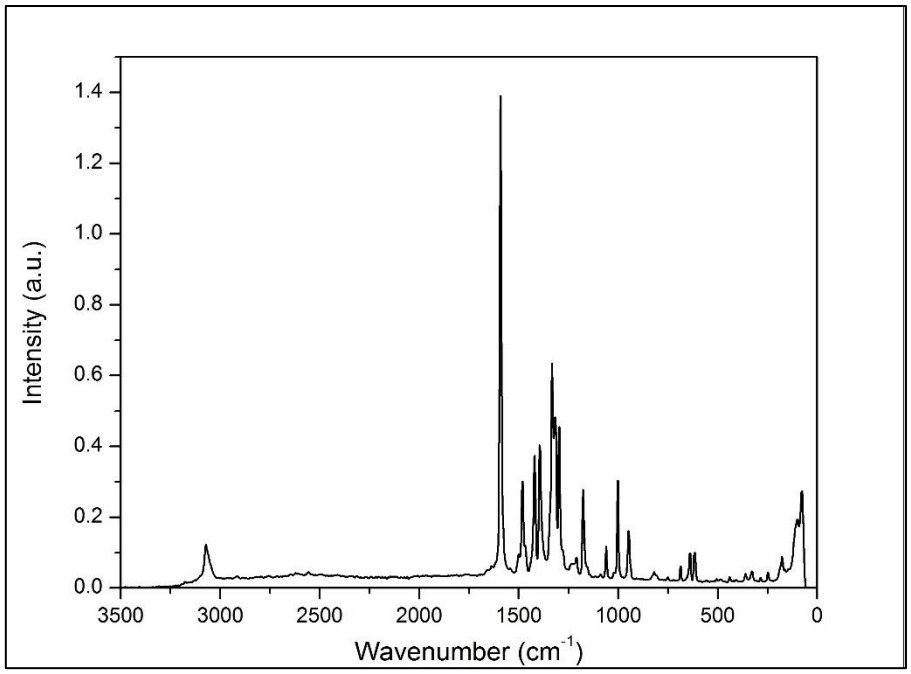
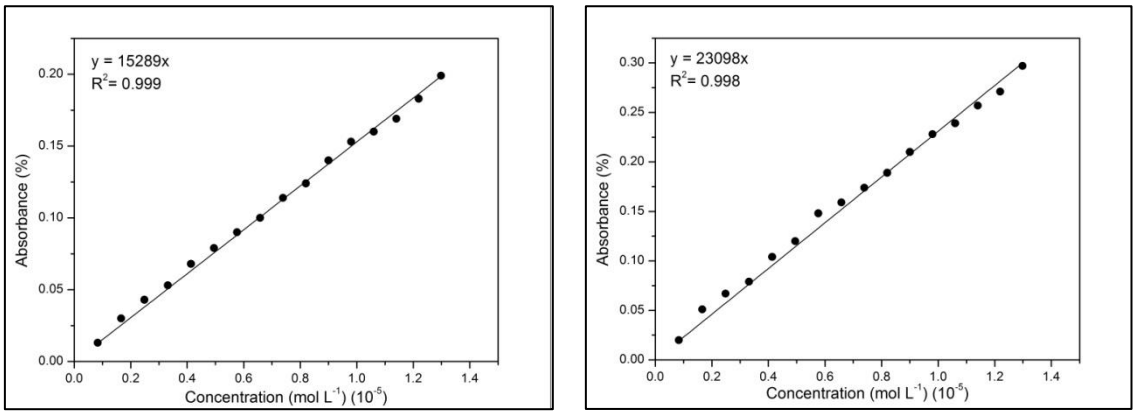


Figure S27. Raman Spectra of compound **4**.

UV-Vis



(a) (b)

Figure S28. (a) Straight lines of absorbance *versus* concentration at (a) 234 nm and (b) 348 nm, for **1** in ethanol at 25 °C.

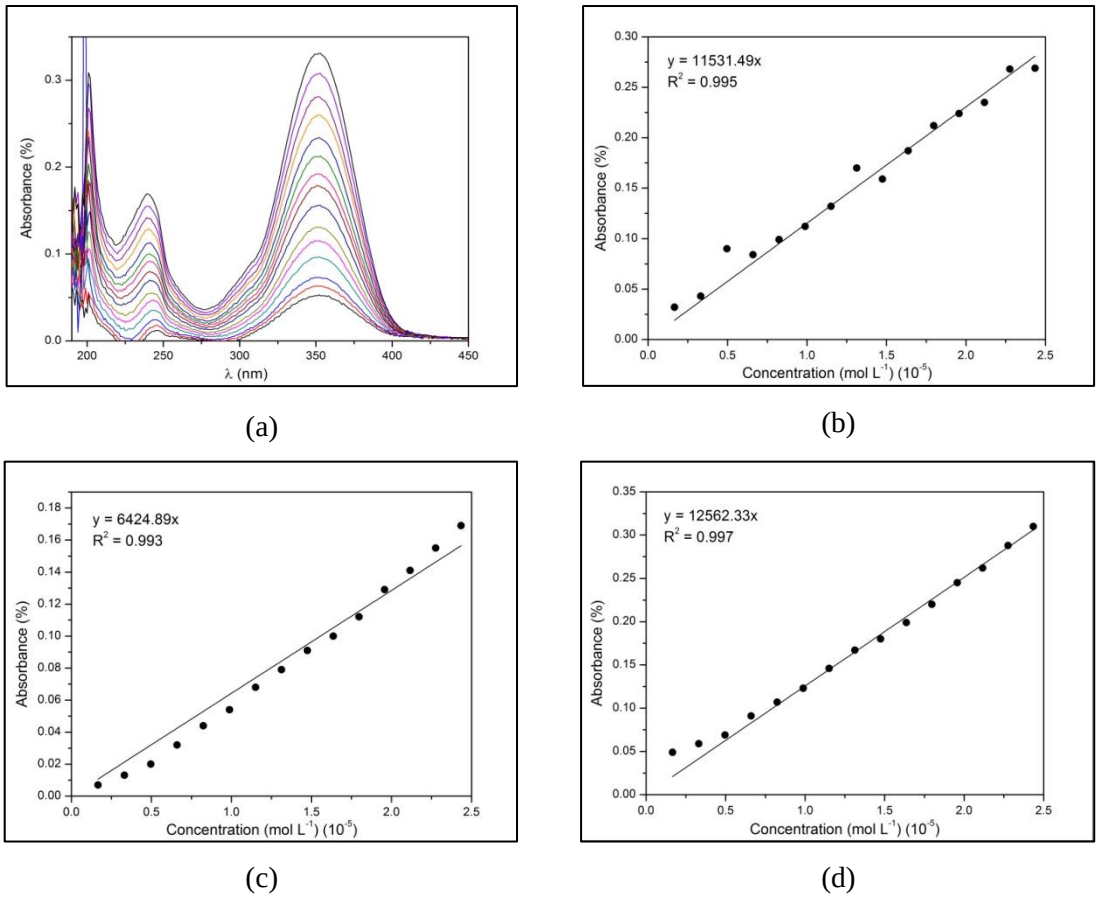


Figure S29. (a) Absorbance *versus* wavelength (λ) plots from 190 to 450 nm and straight lines of absorbance *versus* concentration at (b) 200 nm, (c) 240 nm and (d) 360 nm for **2** in ethanol at 25 °C.

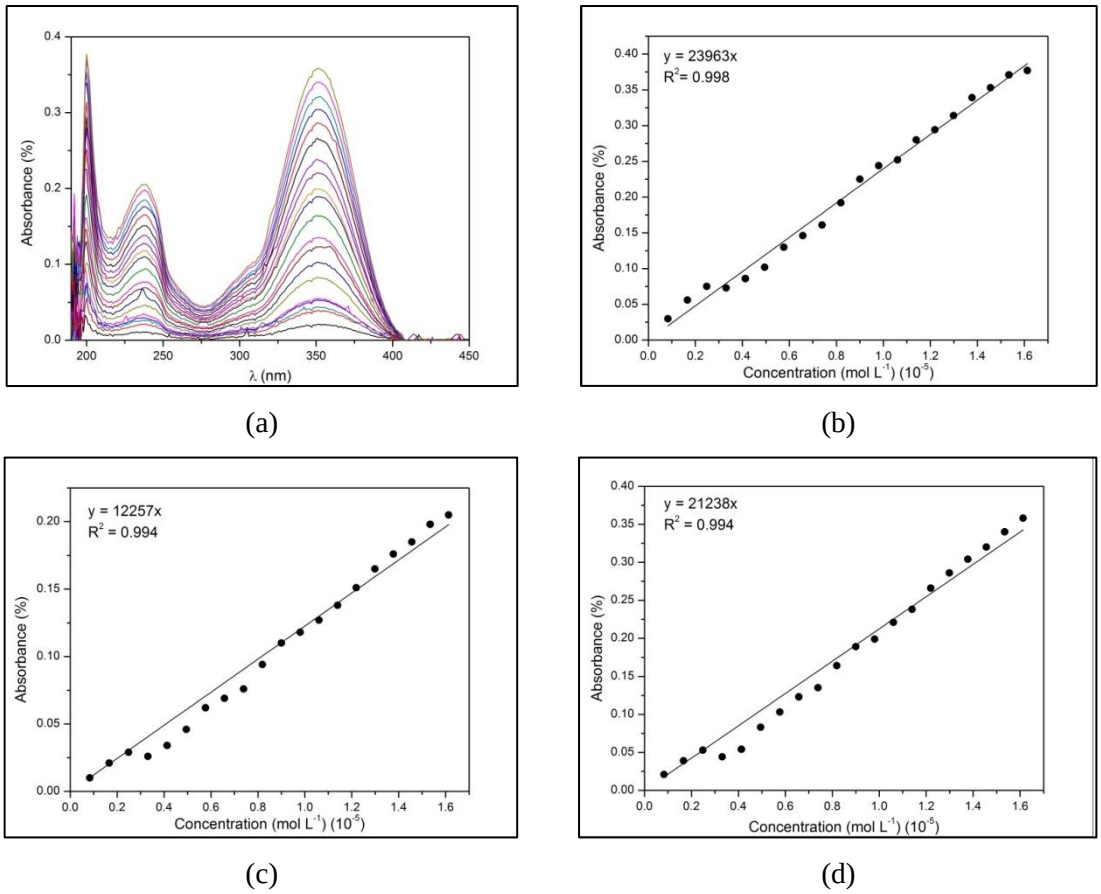


Figure S30. (a) Absorbance *versus* wavelength (λ) plots from 190 to 450 nm and straight lines of absorbance *versus* concentration at (b) 200 nm, (c) 238 nm and (d) 352 nm for **3** in ethanol at 25 °C.

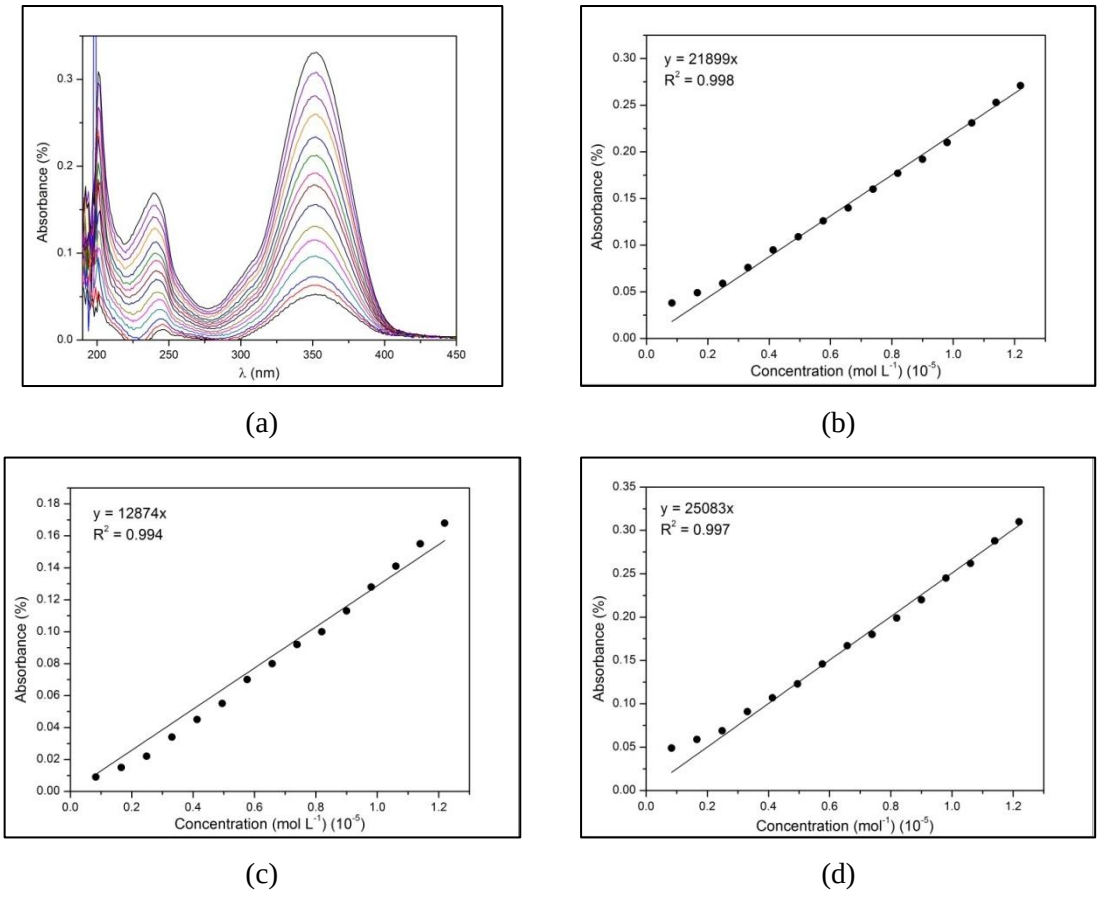


Figure S31. (a) Absorbance *versus* wavelength (λ) plots from 190 to 450 nm and straight lines of absorbance *versus* concentration at (b) 203 nm, (c) 241 nm and (d) 360 nm for **4** in ethanol at 25 °C.

^{13}C NMR and ^{1}H NMR Spectra

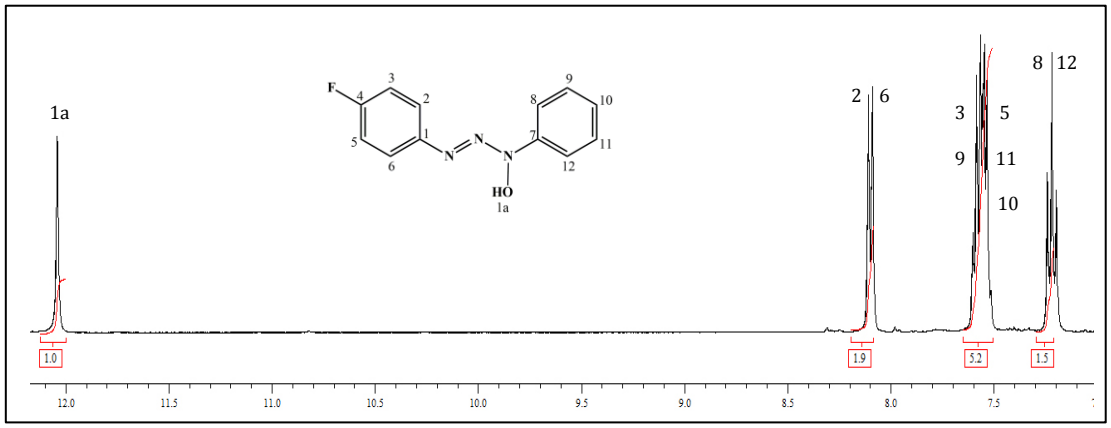


Figure S32. ^{1}H NMR spectra of compound **1** in DMSO – d_6 on 400 MHz.

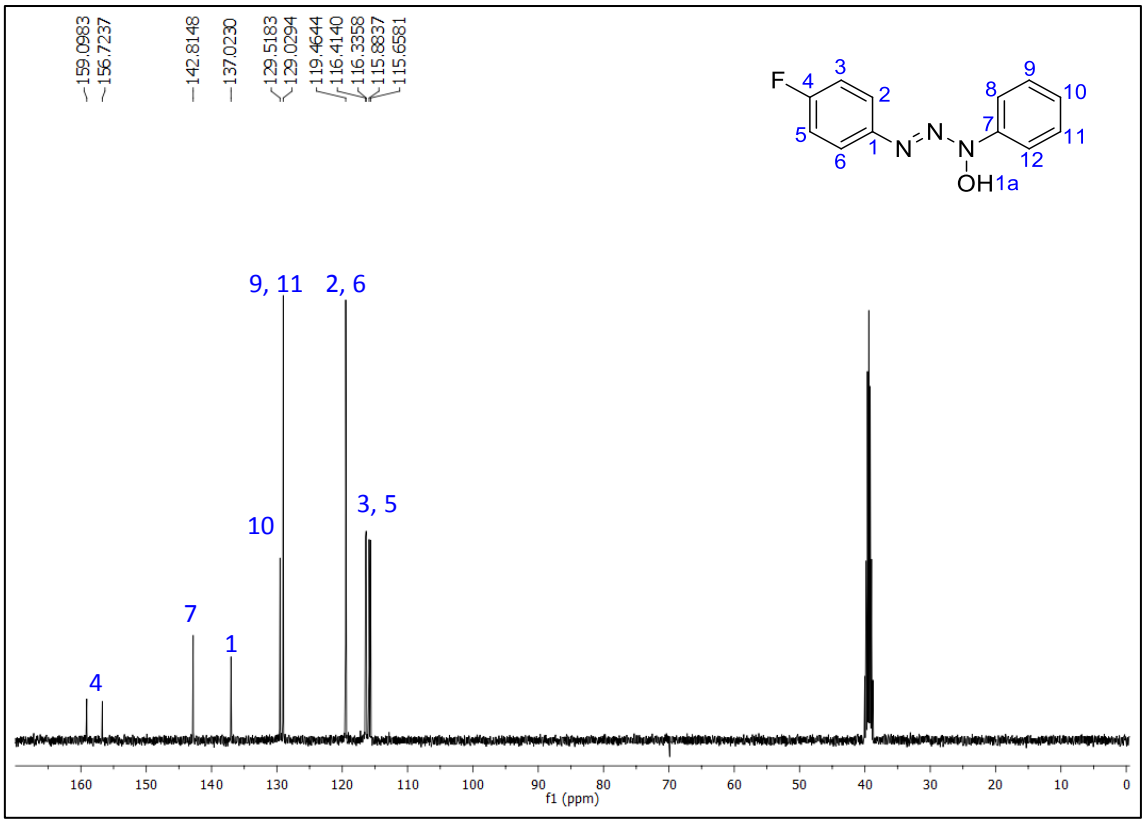


Figure S33. ^{13}C NMR spectra of compound **1** in DMSO – d_6 on 400 MHz.

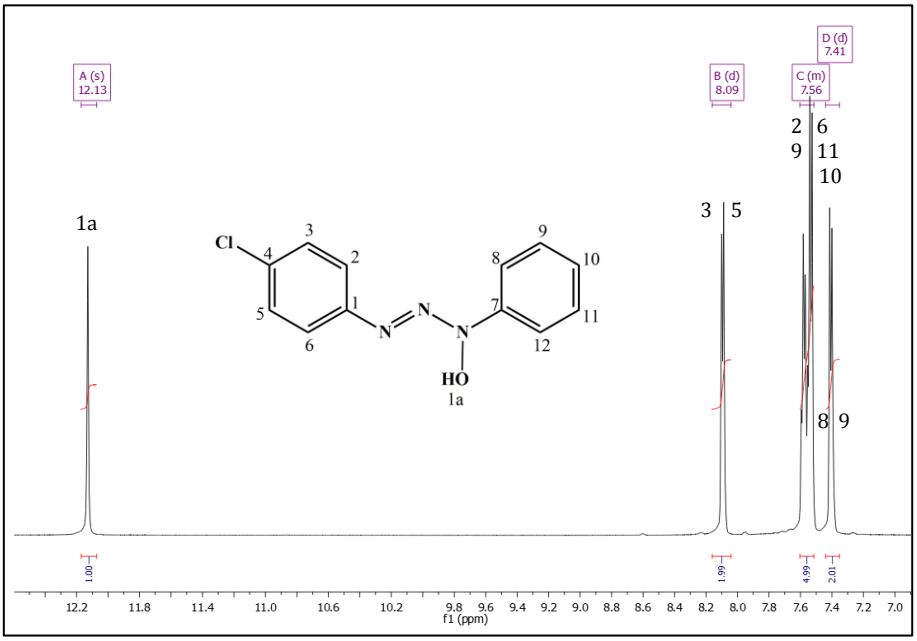


Figure S34. ^{1}H NMR spectra of compound **2** in DMSO – d_6 on 600 MHz.

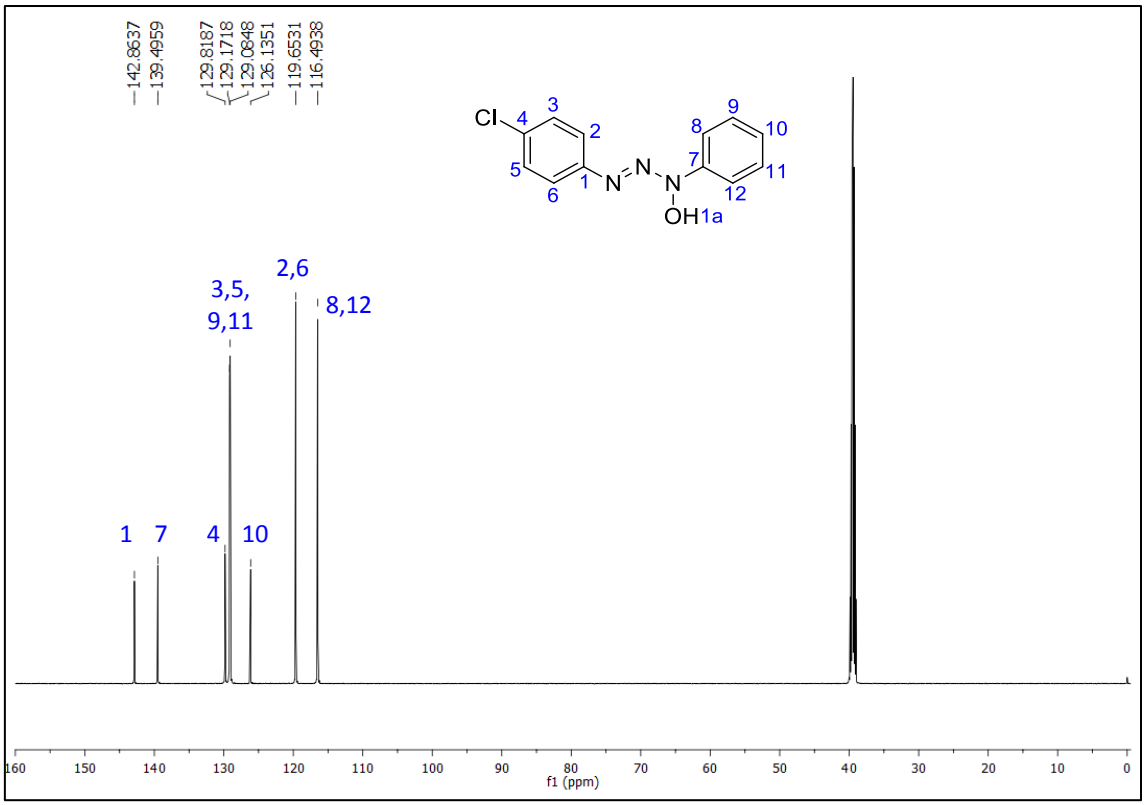


Figure S35. ^{13}C NMR spectra of compound **2** in DMSO – d_6 on 600 MHz.

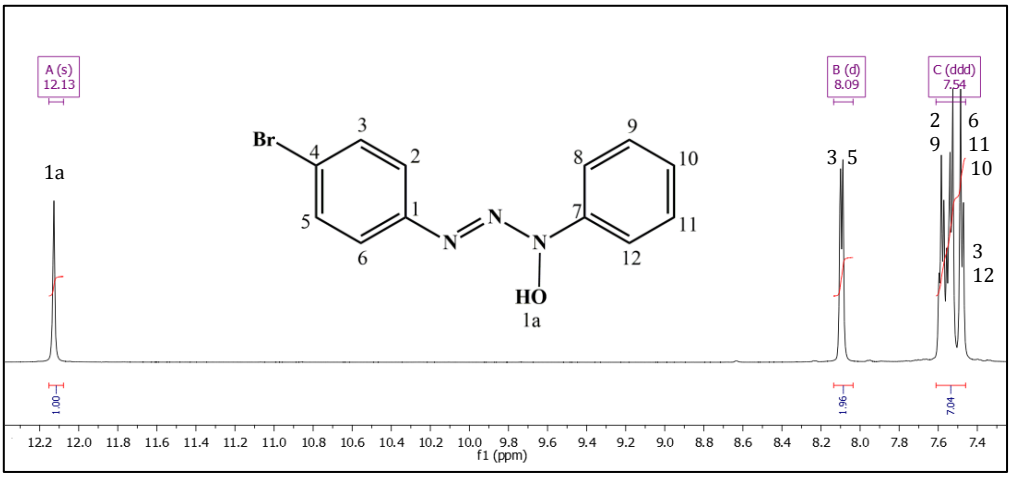


Figure S36. ^{1}H NMR spectra of compound **3** in DMSO – d_6 on 600 MHz.

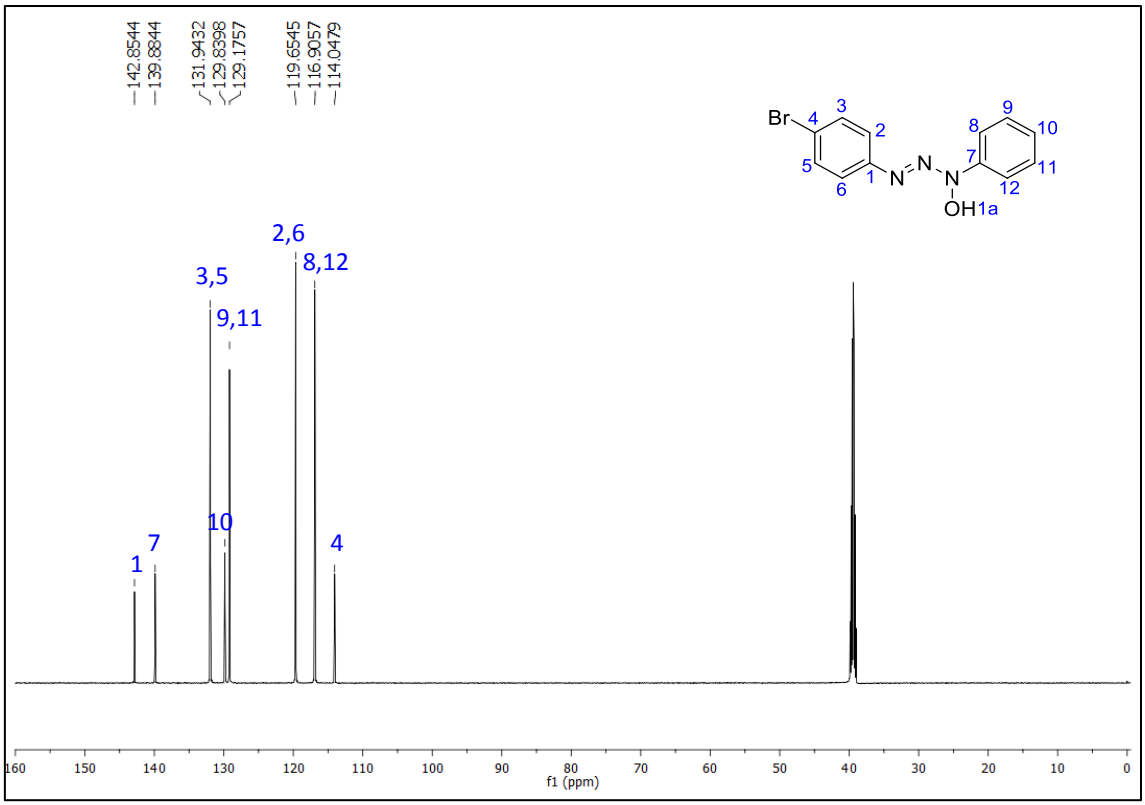


Figure S37. ^{13}C NMR spectra of compound **3** in DMSO – d_6 on 600 MHz.

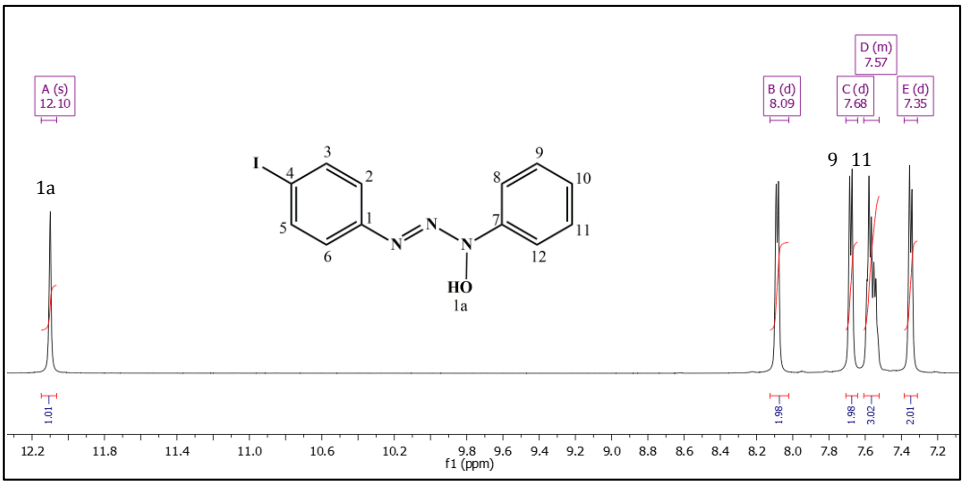


Figure S38. ^{1}H NMR spectra of compound **4** in DMSO – d_6 on 600 MHz.

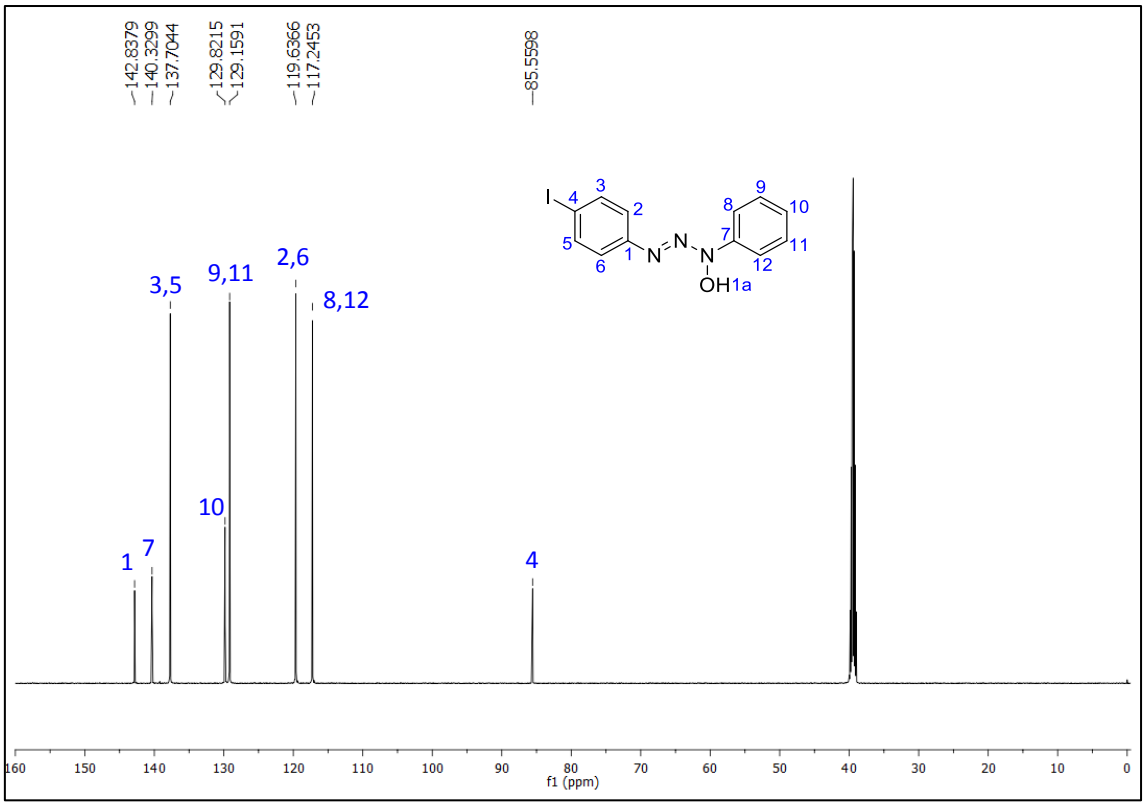
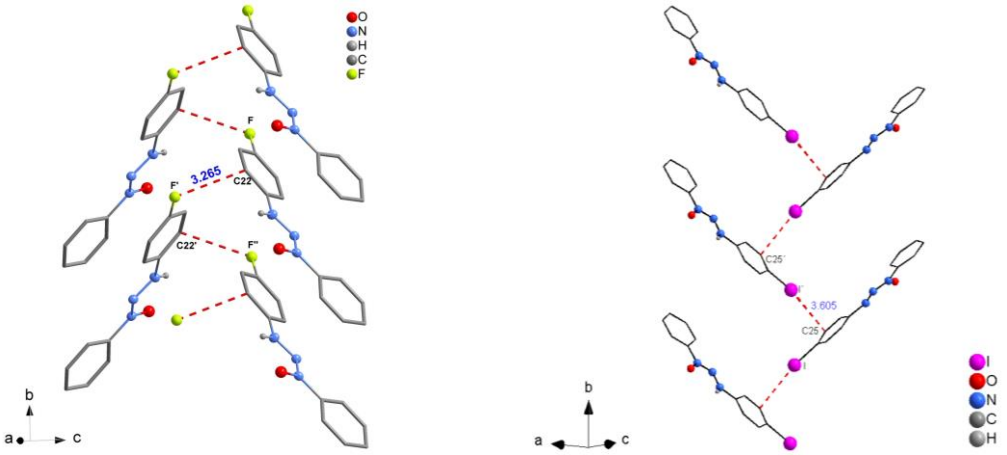
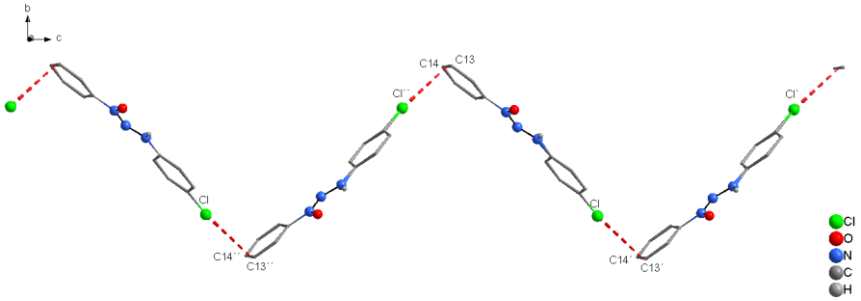


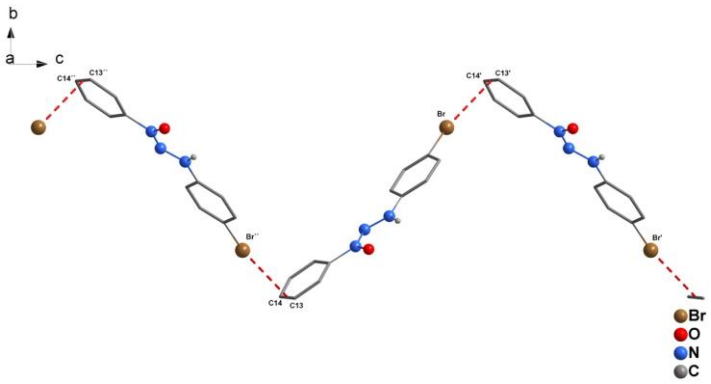
Figure S39. ^{13}C NMR spectra of compound **4** in DMSO – d_6 on 600 MHz.



1 **4**



2



3

Figure S40: Projection of the halogen···π interactions for the compounds **1**, **2**, **3** and **4**. Symmetry operators: ('): 2-x, -½ + y, -z for **1**; (') 1 + x, -½ + y, 1½-z for **4**; ('): 1 + x, -½-y, ½ + z for **2**; ('): 1 + x, ½-y, ½ + z for **3**.