Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Supporting Information

Photodimerization of HCl salts of azastilbenes in solid state

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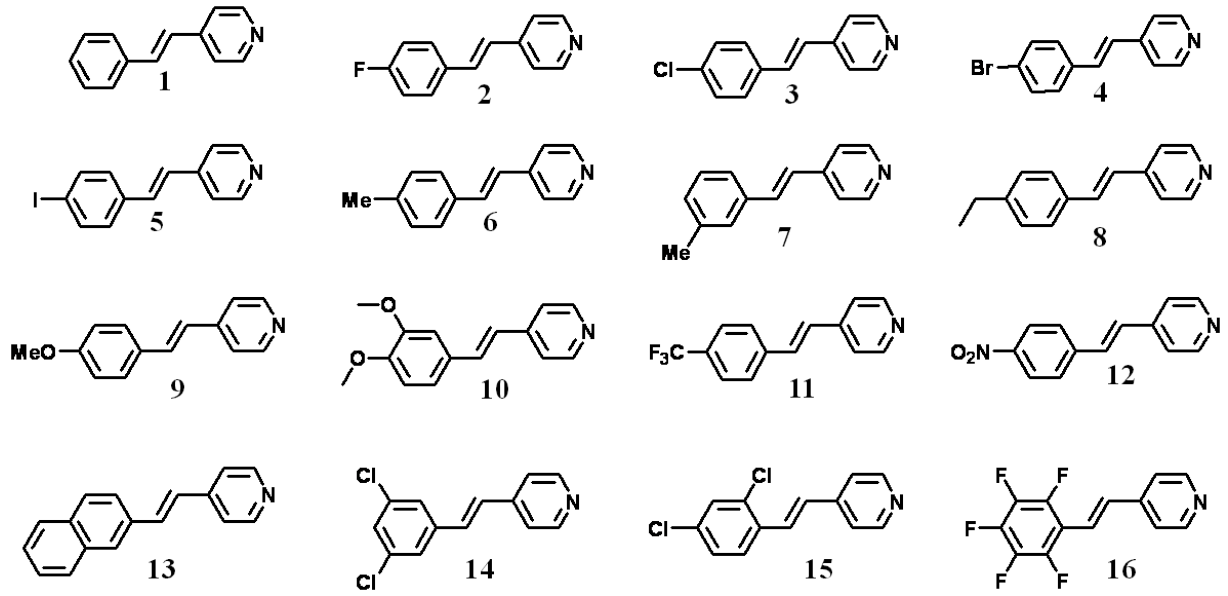

Scheme 1: Structure of molecules investigated in this study.

Experimental Section

Materials: All starting materials were purchased from Aldrich and used for synthesis of stilbazole derivatives following literature procedures.[1-2] 4-Iodo stilbazole was synthesized as described in the reference 3.[3] Stilbazole. HCl salts were prepared by adding 2 equivalents of conc. HCl to stilbazoles in a mortar and ground well with a pestle to give a pasty mass. This pasty mass was air dried overnight to give stilbazole.HCl salts. On addition of conc. HCl most of stilbazoles showed color change indicative of formation of HCl salts.

Irradiation Techniques: Irradiations were performed using a 450 W medium pressure mercury arc lamp placed in a water-cooled Pyrex immersion well. Light emitted from a Hanovia lamp was filtered through Pyrex (transmission $\lambda \geq 290$ nm).

About 8-10 mg of powdered stilbazole.HCl salts were spread uniformly between two Pyrex glass plates sealed with Parafilm and irradiated. The plates were turned around every 6 hours. The same experiments were also done in hexane, where stilbazole.HCl salts were

suspended in hexane in a Pyrex tube and irradiated with stirring. In most cases, irradiation in hexane suspension was faster than in Pyrex plates. After irradiation the crude product was dissolved in H_2O and neutralized with 1N NaOH. For experiments in hexane suspension, hexane was evaporated by purging with N_2, and the crude product was dissolved in H_2O and neutralized with 1N NaOH. This neutral solution was extracted with $CHCl_3$ four times and the combined organic layer was dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a product that was characterized by ^1H NMR and mass spec. ^1H NMR of the product was recorded in $CDCl_3$.

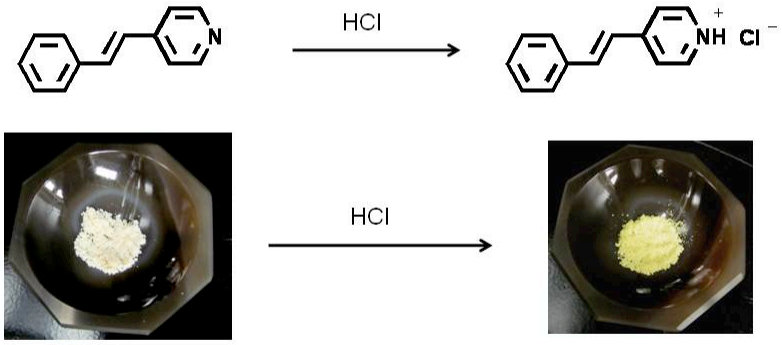

Figure S1 (a): White stilbazole turns yellow upon addition of HCl.

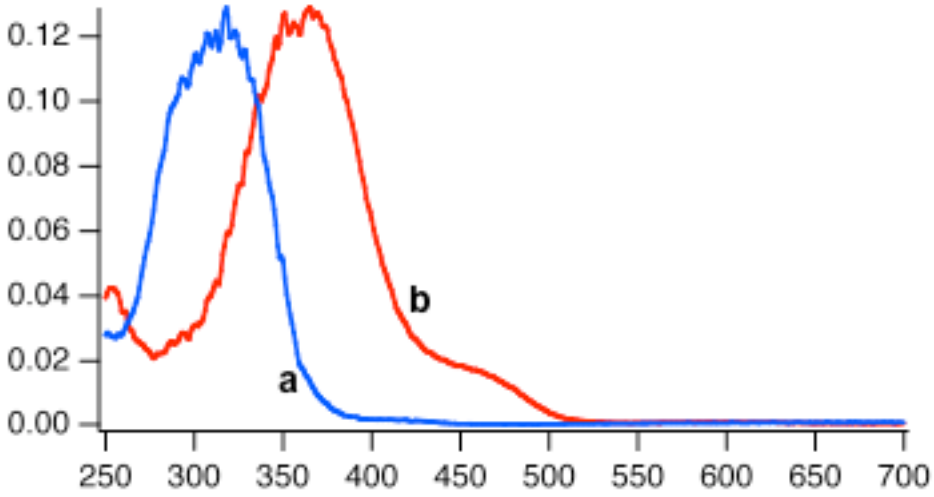

Figure S1 (b)

Diffuse reflectance spectra (y axis:Kubelka-Munk and x-axis wavelength) of (a) 4-methoxy stilbazole (b) and 4-methoxy-stilbazole.HCl dispersed in $BaSO_4$ powder

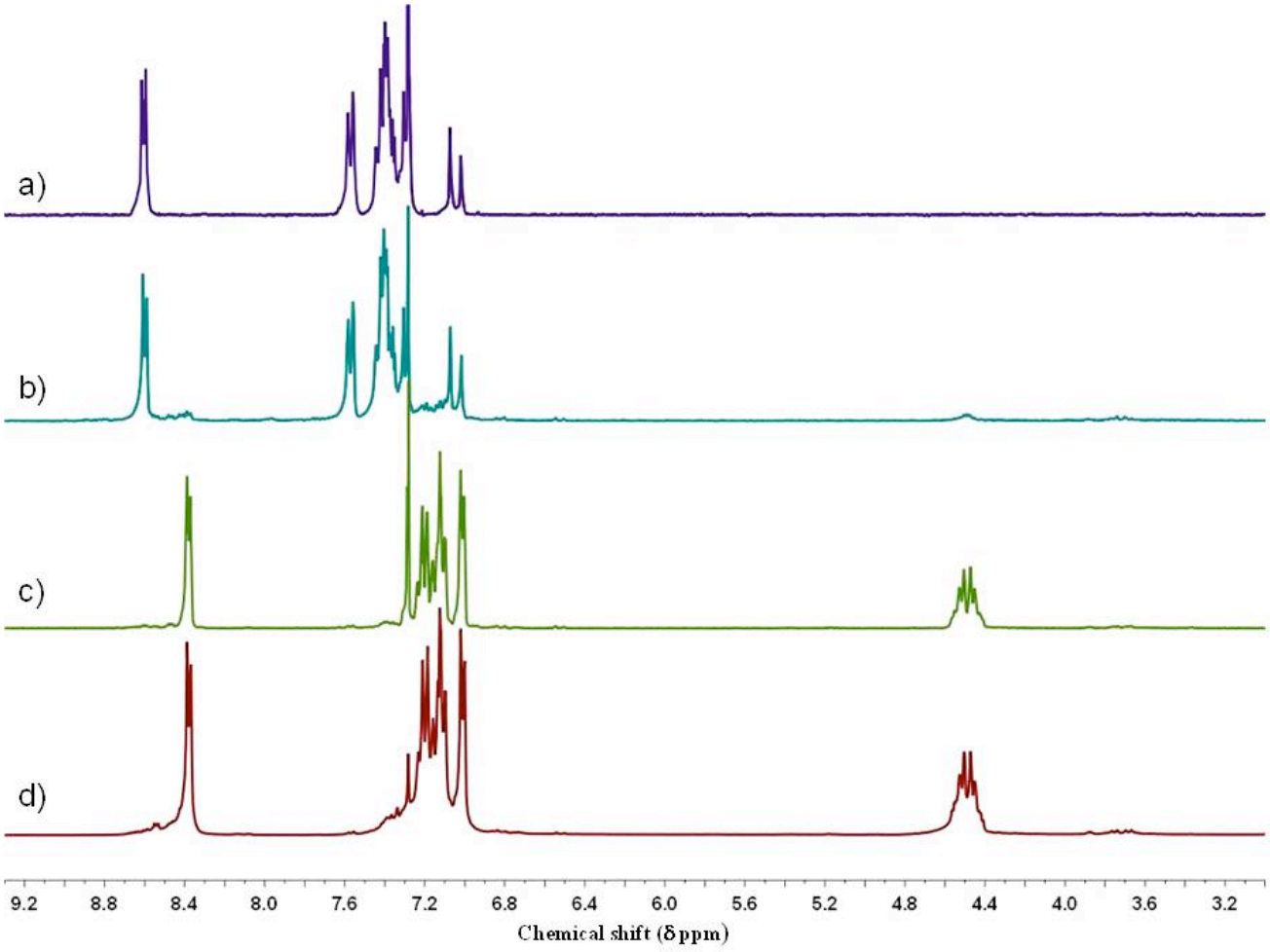

Figure S2 (a) ^{1}H NMR in $CDCl_3$ of 4-stilbazole, **1** (b) after irradiation of 4-stilbazole for 20 h in solid state, (c) neutral extract of 4-Stilbazole.HCl, irradiated for 37 h in solid state, (d) neutral extract of 4-Stilbazole.HCl irradiated for 10 h as suspension in hexane.

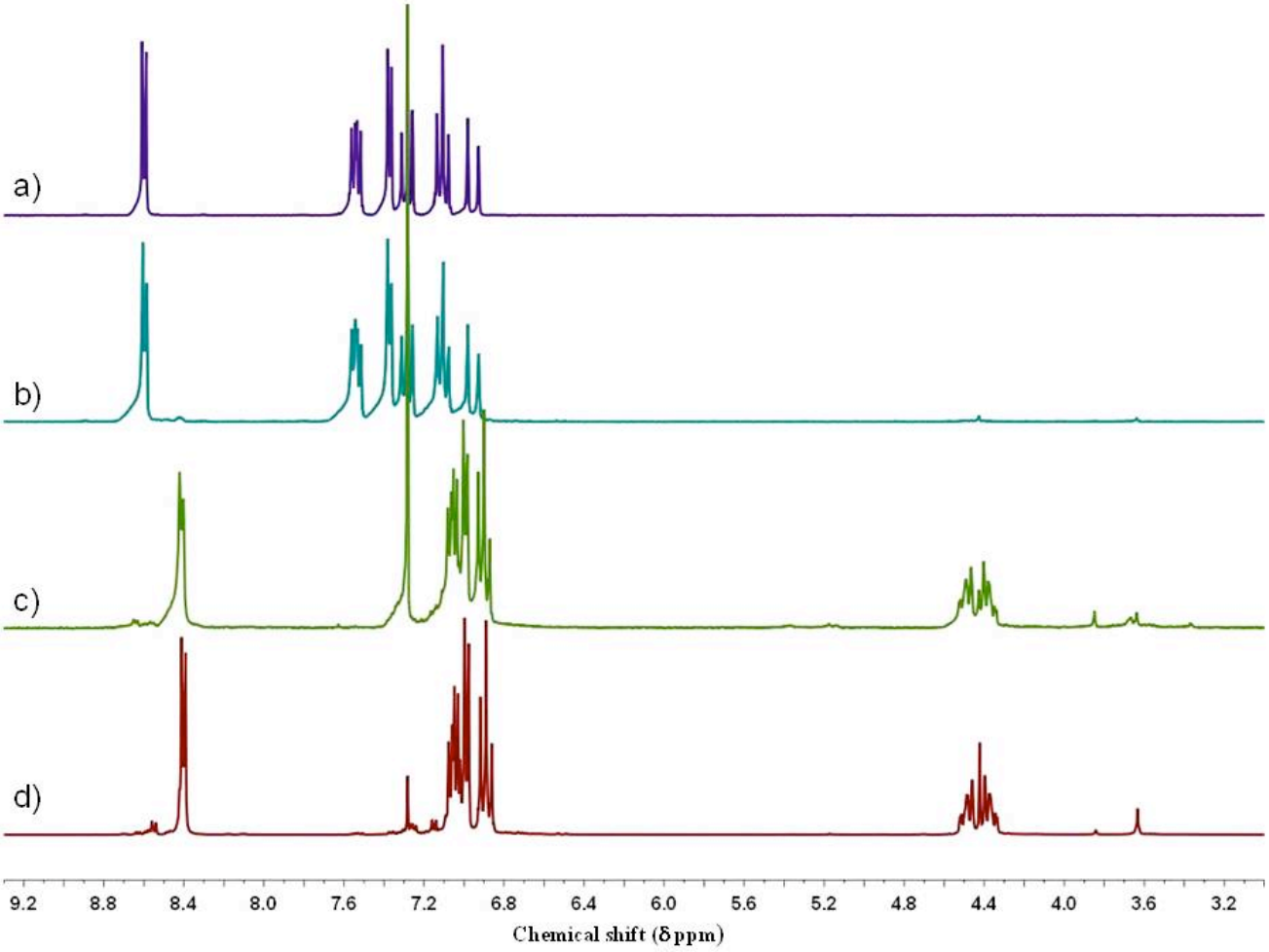

Figure S3 (a) ^{1}H NMR in $CDCl_3$ of 4F-stilbazole, **2** (b) after irradiation of 4F-stilbazole for 52 h in solid state, (c) neutral extract of 4F-stilbazole.HCl, irradiated for 62 h in solid state, (d) neutral extract of 4F-stilbazole.HCl irradiated for 12 h as suspension in hexane.

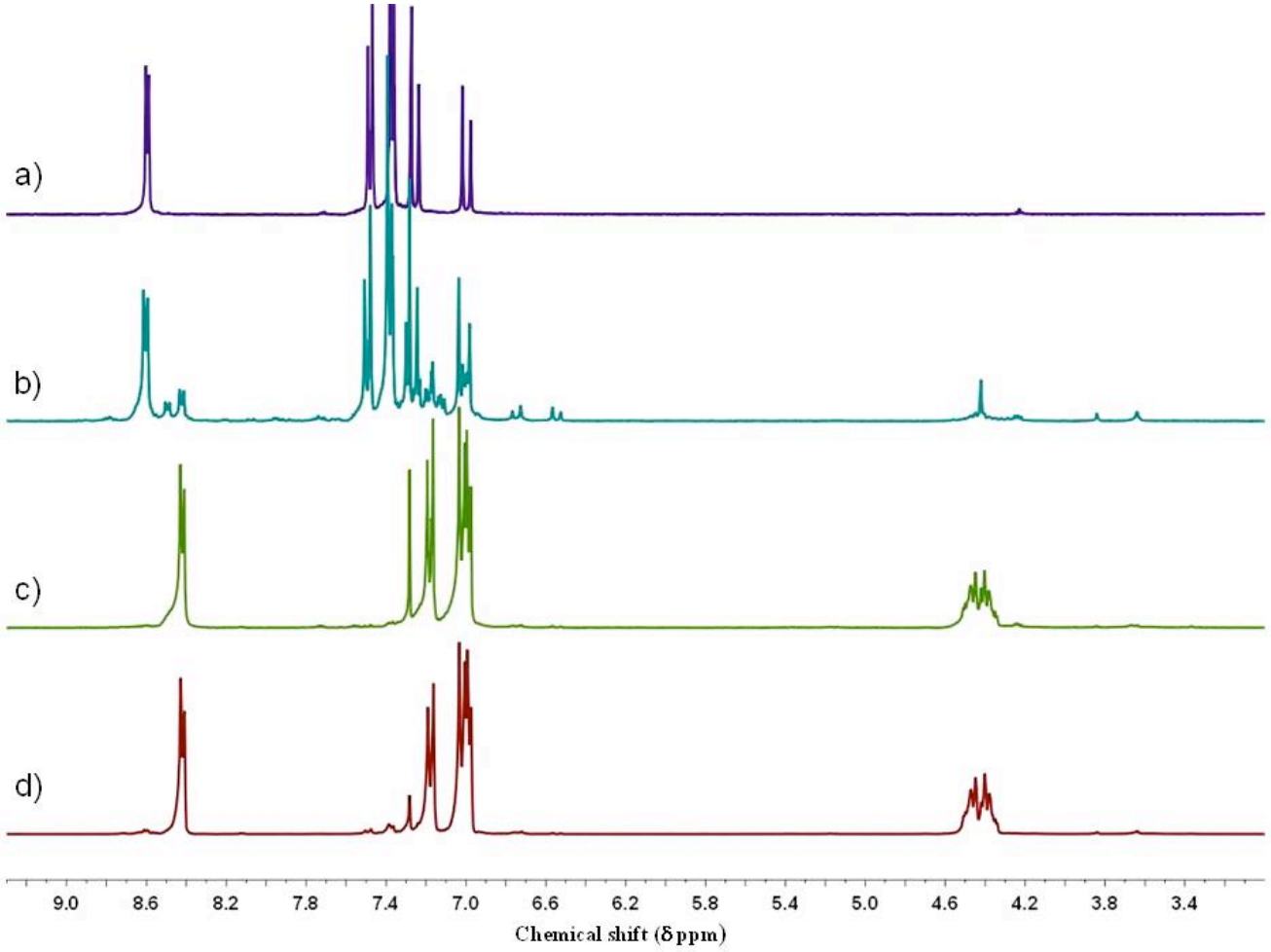

Figure S4 (a) ^{1}H NMR in $CDCl_3$ of 4Cl-stilbazole,**3** (b) after irradiation of 4Cl-stilbazole for 52 h in solid state, (c) neutral extract of 4Cl-stilbazole.HCl, irradiated for 44 h in solid state, (d) neutral extract of 4Cl-stilbazole.HCl irradiated for 6 h as suspension in hexane.

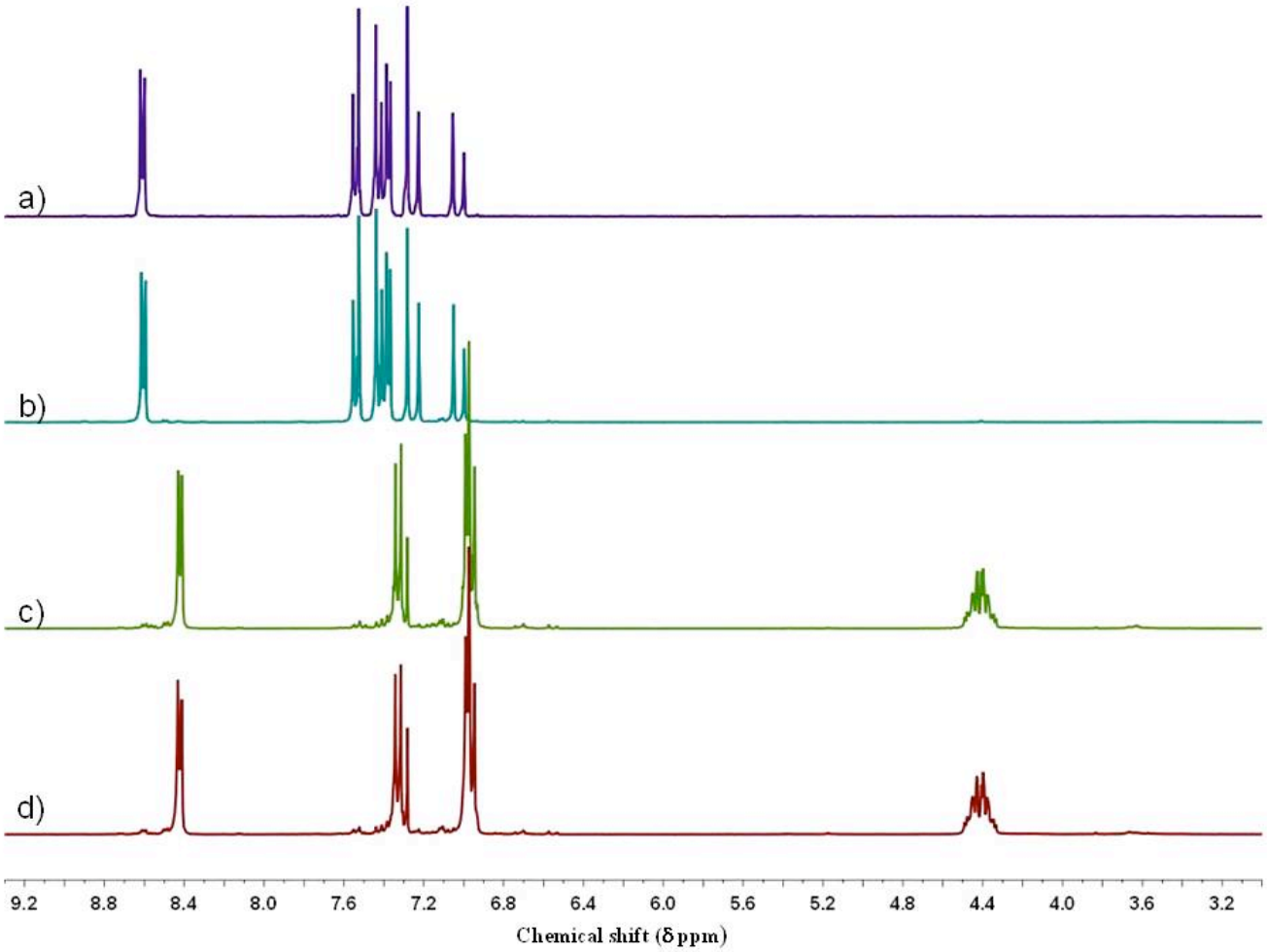

Figure S5 (a) ^{1}H NMR in $CDCl_3$ of 4Br-stilbazole, **4** (b) after irradiation of 4Br-stilbazole for 10 h in solid state, (c) neutral extract of 4Br-stilbazole.HCl, irradiated for 5 h in solid state, (d) neutral extract of 4Br-Stilbazole.HCl irradiated for 3 h as suspension in hexane.

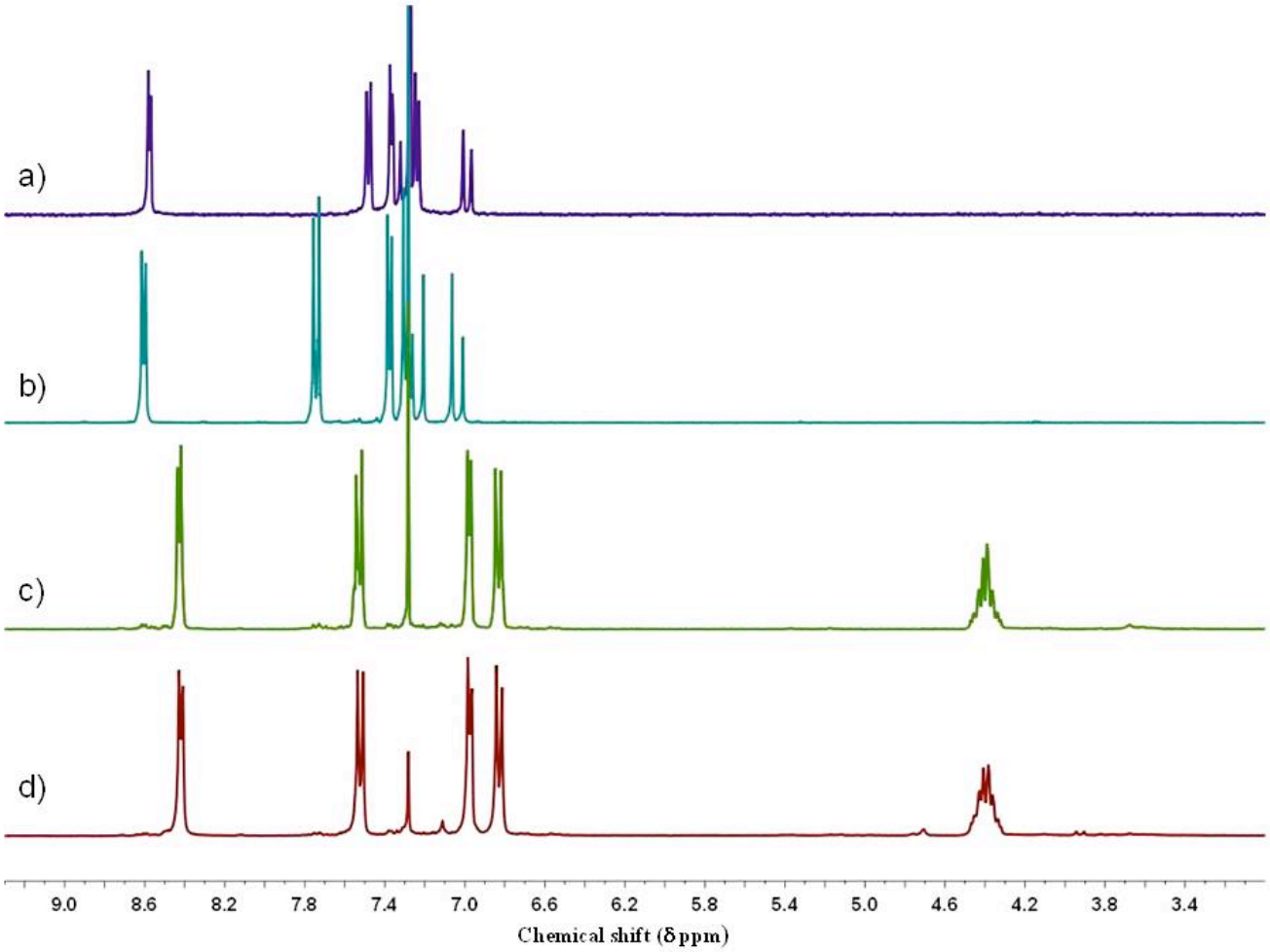

Figure S6 (a) ^{1}H NMR in $CDCl_3$of 4I-stilbazole, **5** (b) after irradiation of 4I-stilbazole for 91 h in solid state, (c) neutral extract of 4I-stilbazole.HCl, irradiated for 91 h in solid state, (d) neutral extract of 4I-stilbazole.HCl irradiated for 31 h as suspension in hexane.

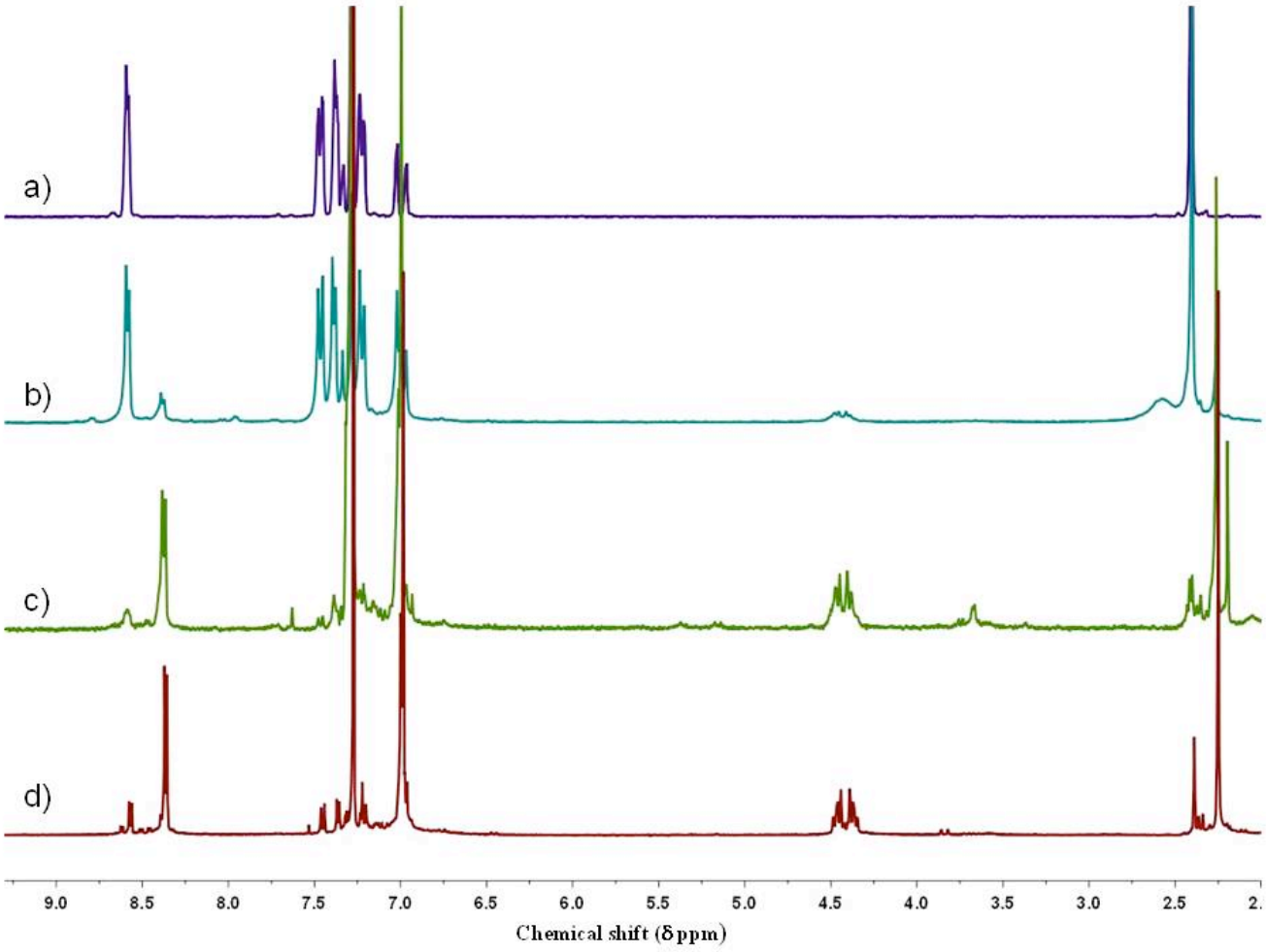

Figure S7 (a) ^{1}H NMR in $CDCl_3$ of 4-methyl-stilbazole, **6** (b) after irradiation of 4-methyl-stilbazole for 98 h in solid state, (c) neutral extract of 4-methyl-stilbazole.HCl, irradiated for 37 h in solid state, (d) neutral extract of 4-methyl-stilbazole.HCl irradiated for 23 h as suspension in hexane.

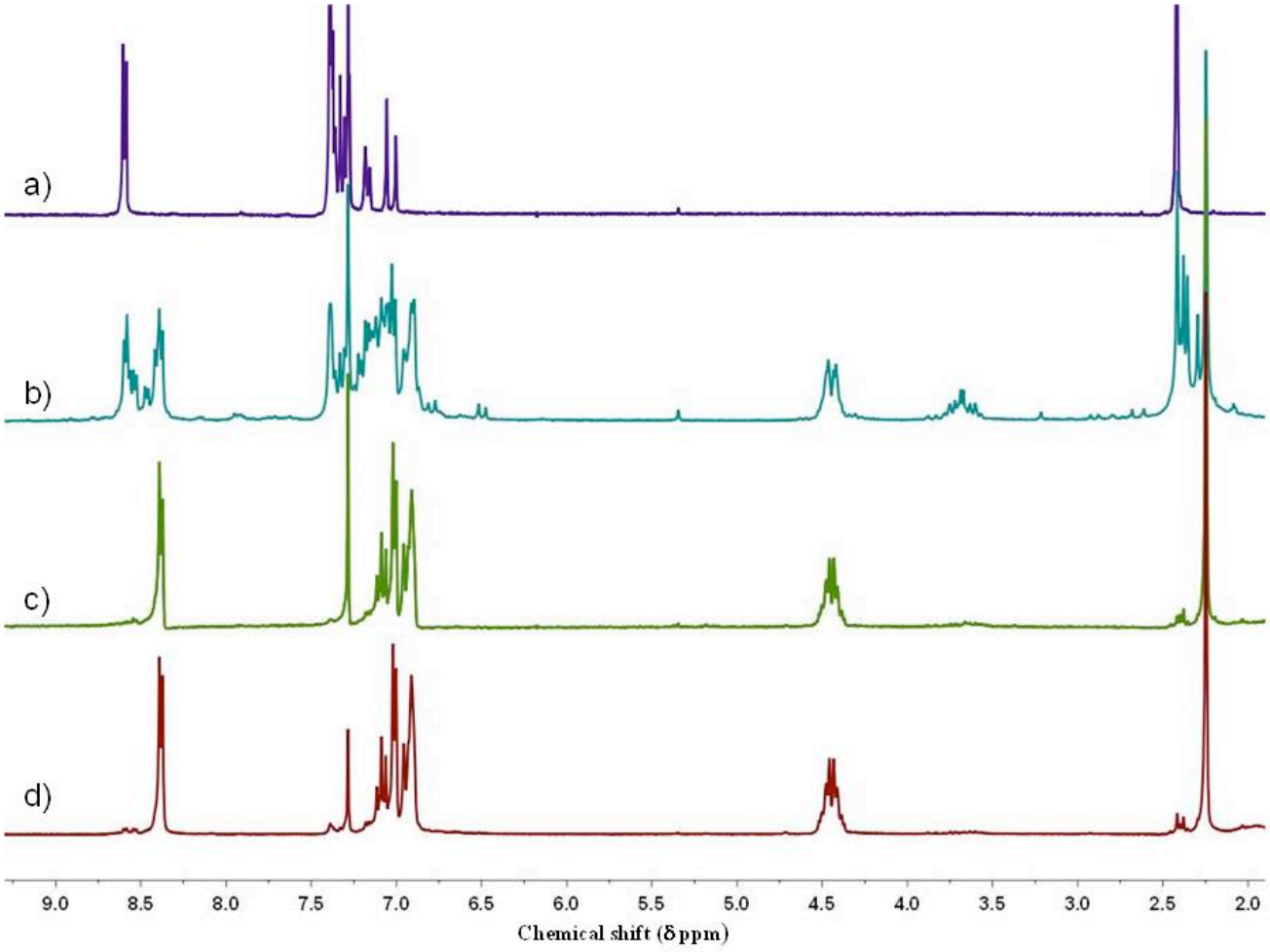

Figure S8 (a) ^{1}H NMR in $CDCl_3$ of 3-methyl-stilbazole, **7** (b) after irradiation of 3-methyl-stilbazole for 37 h in solid state, (c) neutral extract of 3-methyl-stilbazole.HCl, irradiated for 19 h in solid state, (d) neutral extract of 3-methyl-stilbazole.HCl irradiated for 19 h as suspension in hexane.

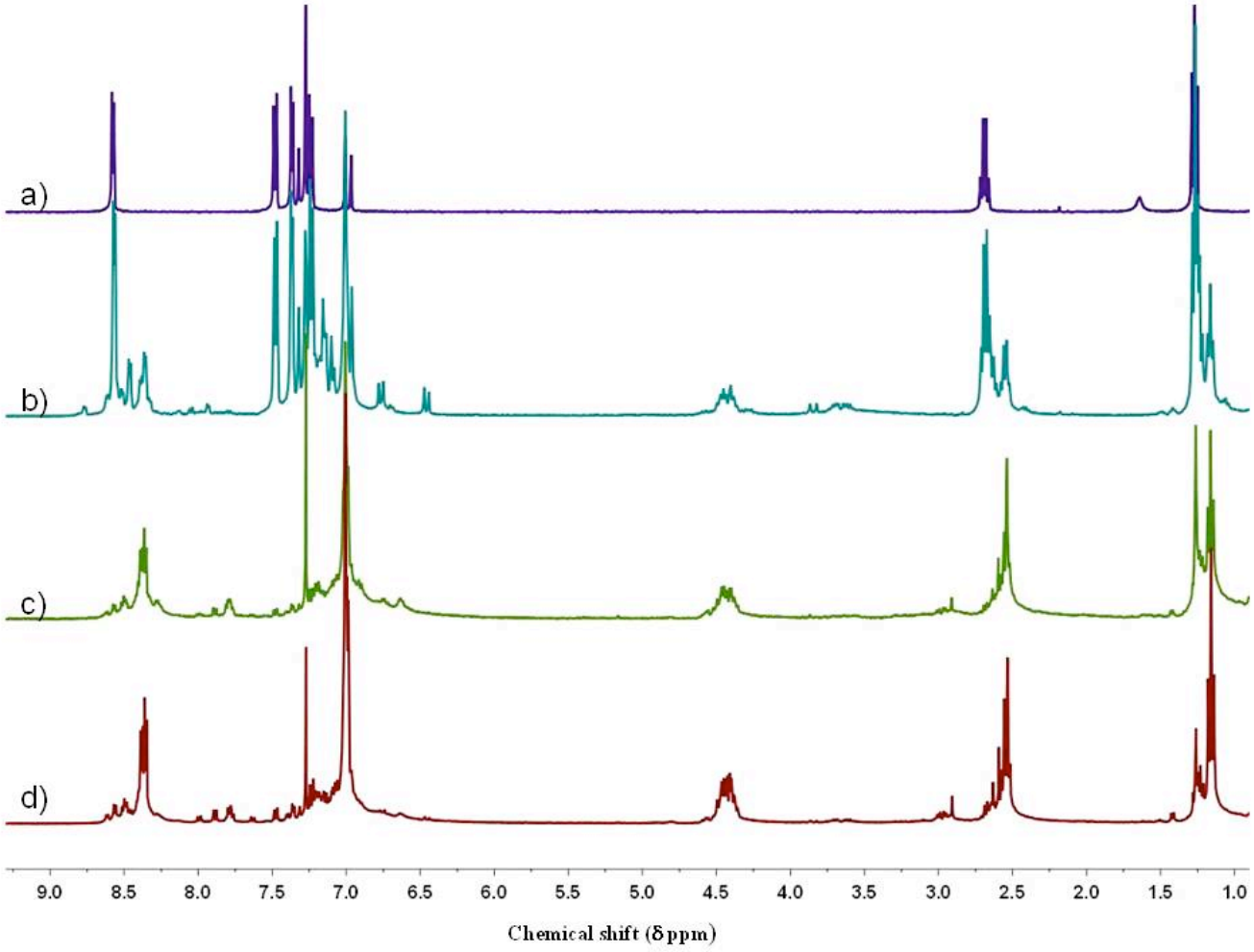

Figure S9 (a) ^{1}H NMR in $CDCl_3$ of 4-ethyl-stilbazole, **8** (b) after irradiation of 4-ethyl-stilbazole for 20 h in solid state, (c) neutral extract of 4-ethyl-stilbazole.HCl, irradiated for 130 h in solid state, (d) neutral extract of 4-ethyl-stilbazole.HCl irradiated for 112 h as suspension in hexane.

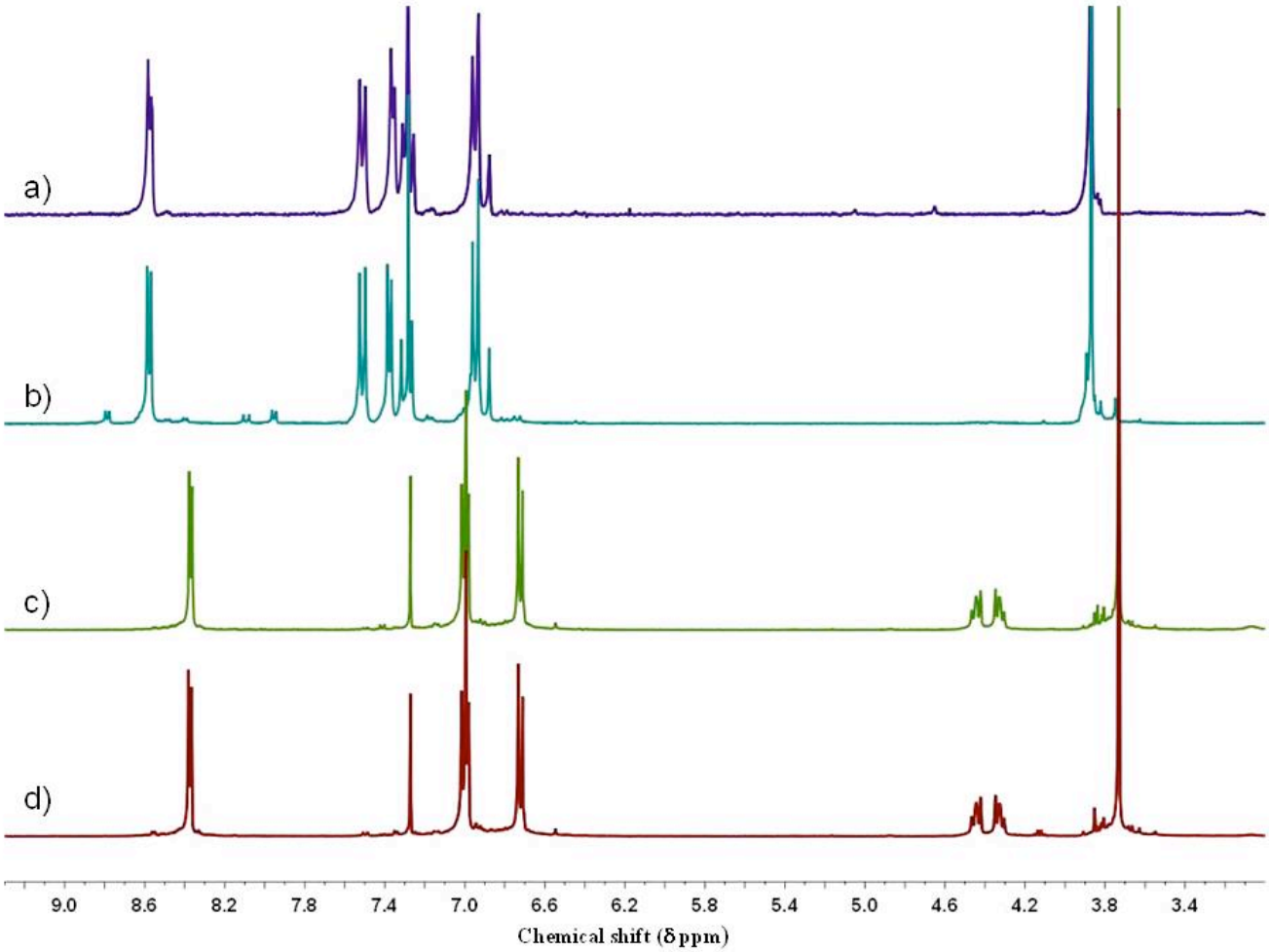

Figure S10 (a) ^{1}H NMR in $CDCl_3$ of 4-methoxy-stilbazole, **9** (b) after irradiation of 4-methoxy-stilbazole for 52 h in solid state, (c) neutral extract of 4-methoxy-stilbazole.HCl, irradiated for 60 h in solid state, (d) neutral extract of 4-methoxy-stilbazole.HCl irradiated for 46 h as suspension in hexane.

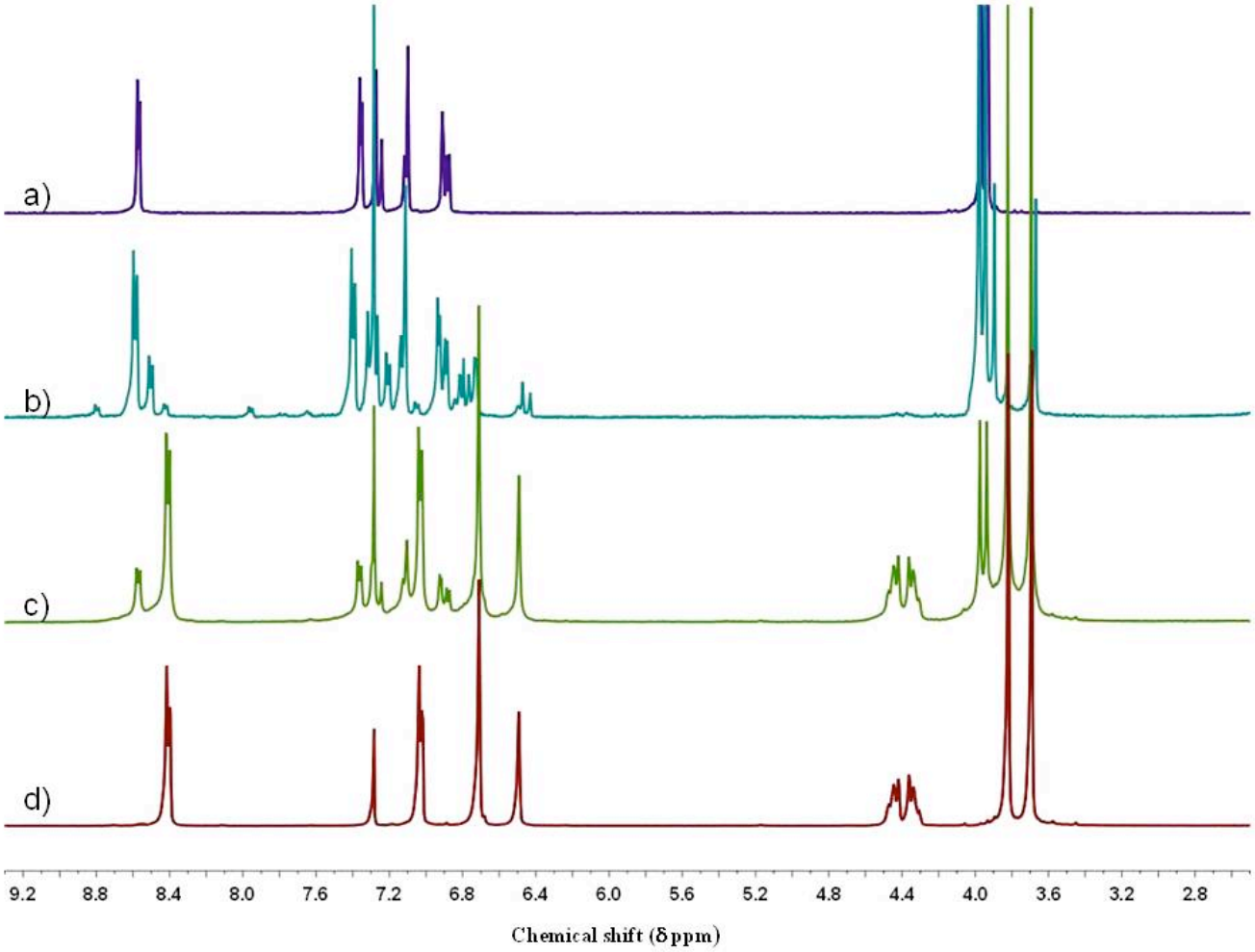

Figure S11 (a) ^{1}H NMR in $CDCl_3$ of 3, 4-dimethoxy-stilbazole, **10** (b) after irradiation of 3, 4-dimethoxy-stilbazole for 72 h in solid state, (c) neutral extract of 3, 4-dimethoxy-stilbazole.HCl, irradiated for 168 h in solid state, (d) neutral extract of 3, 4-dimethoxy-stilbazole.HCl irradiated for 72 h as suspension in hexane.

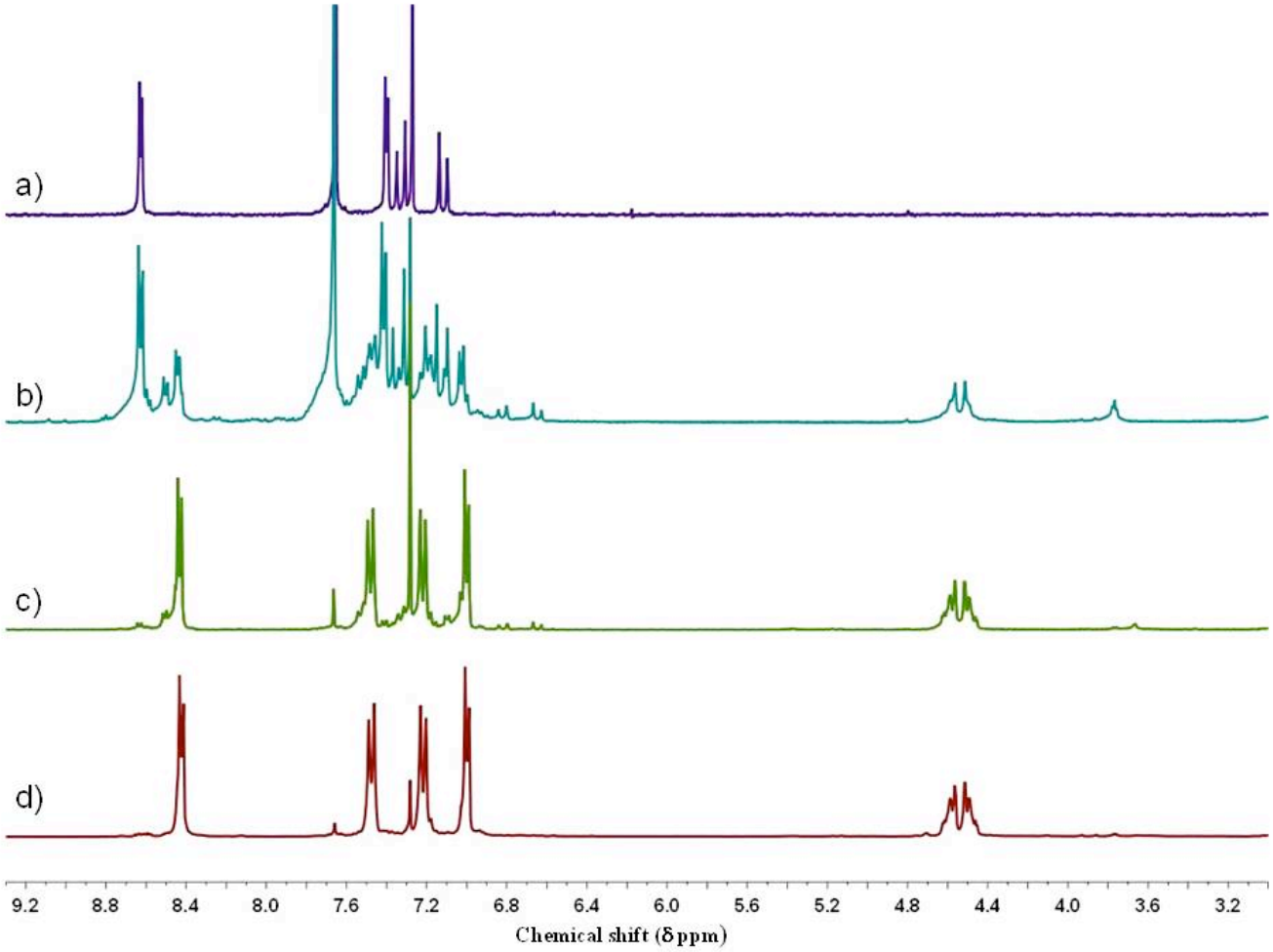

Figure S12 (a) ^{1}H NMR in $CDCl_3$ of 4-CF_3-stilbazole, **11**(b) after irradiation of 4-CF_3-stilbazole for 52 h in solid state, (c) neutral extract of 4-CF_3-stilbazole.HCl, irradiated for 37 h in solid state, (d) neutral extract of 4-CF_3-stilbazole.HCl irradiated for 42 h as suspension in hexane.

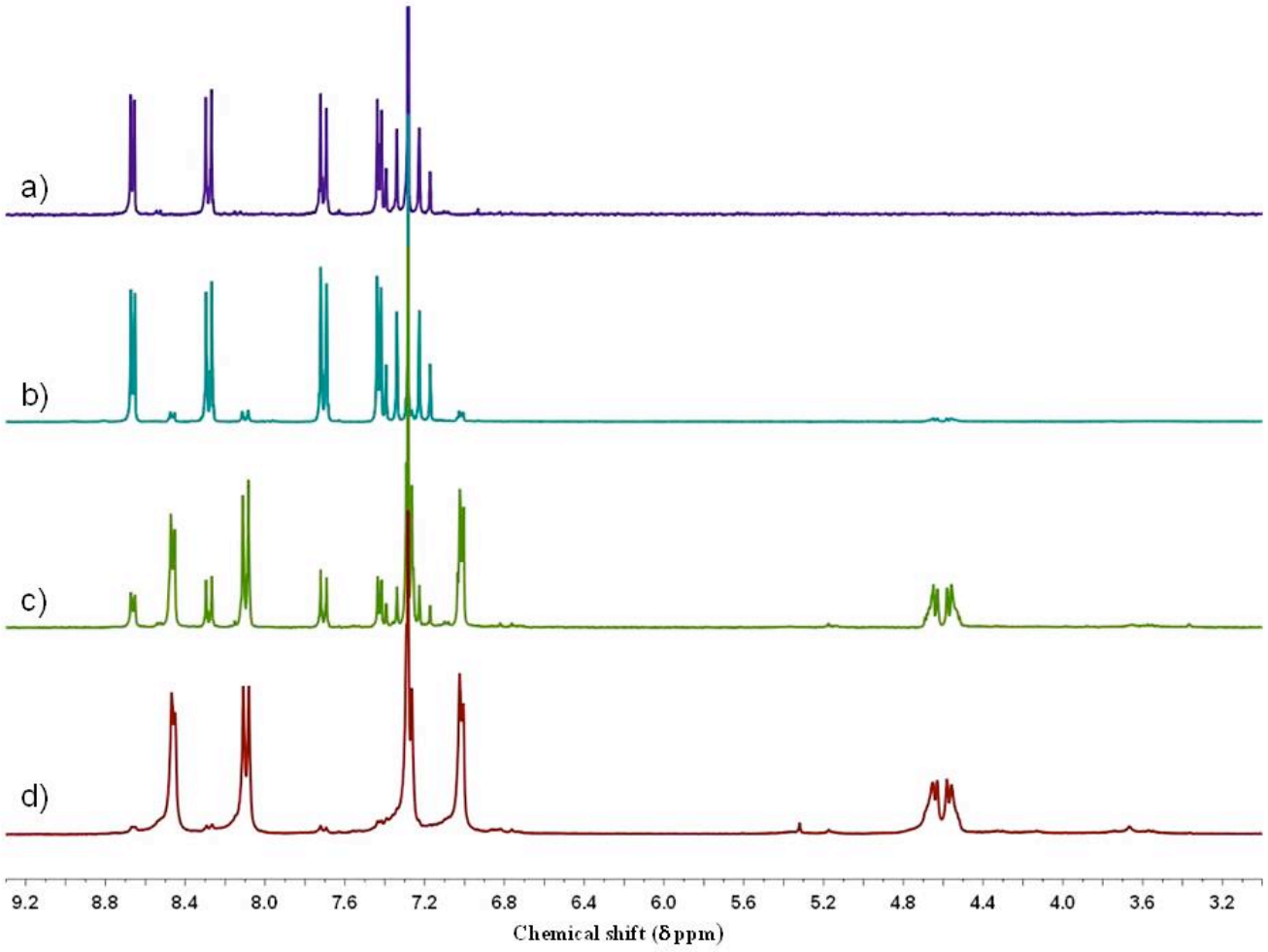

Figure S13 (a) ^{1}H NMR in $CDCl_3$ of 4-NO_2-stilbazole, **12** (b) after irradiation of 4-NO_2-stilbazole for 69 h in solid state, (c) neutral extract of 4-NO_2 -stilbazole.HCl, irradiated for 65 h in solid state, (d) neutral extract of 4-NO_2-stilbazole.HCl irradiated for150 h as suspension in hexane.

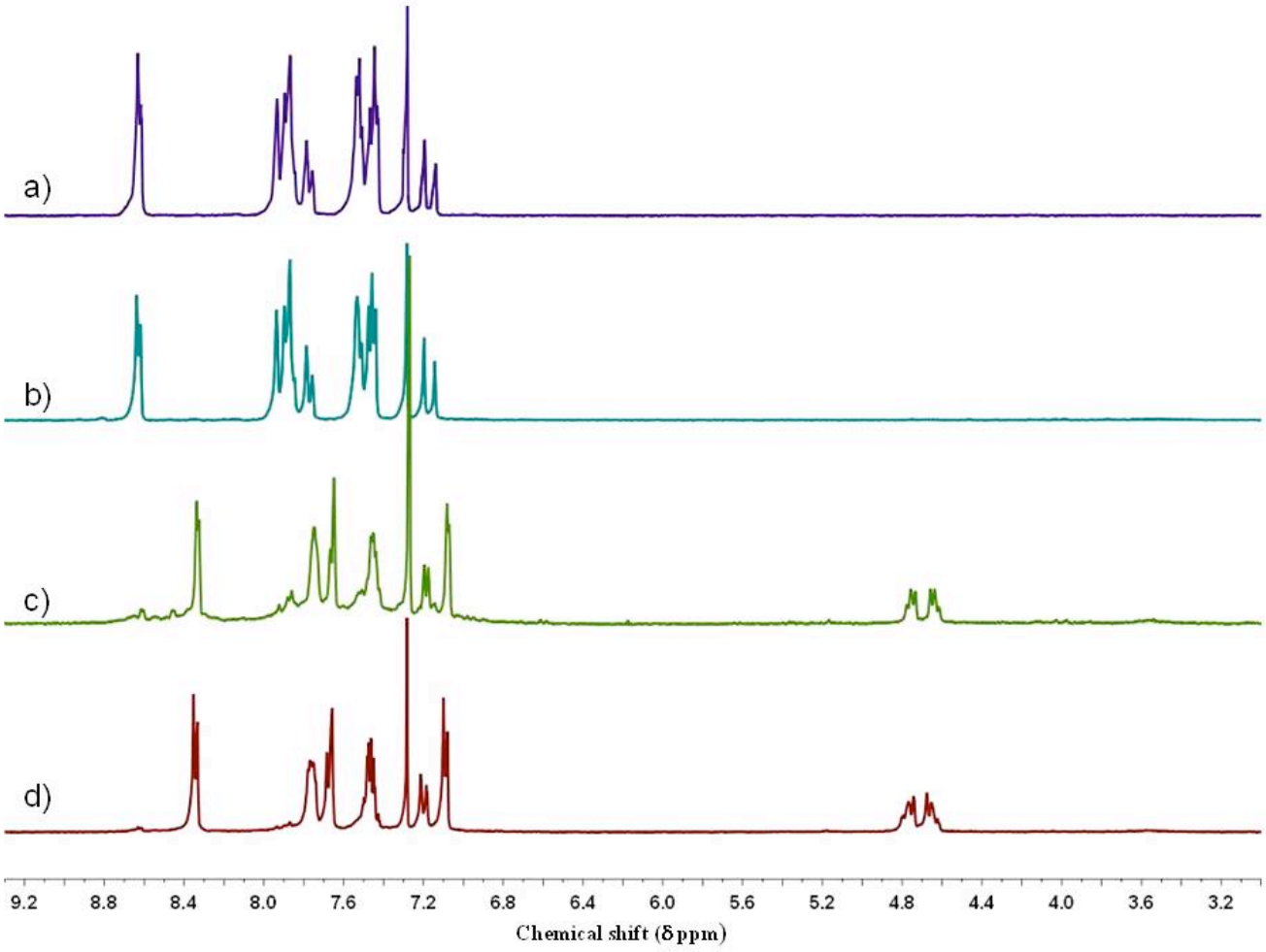

Figure S14 (a) ^{1}H NMR of in $CDCl_3$ 2-naphthyl-stilbazole,**13** (b) after irradiation of 2-naphthyl-stilbazole for 40 h in solid state, (c) neutral extract of 2-naphthyl-stilbazole.HCl, irradiated for 140 h in solid state, (d) neutral extract of 2-naphthyl-stilbazole.HCl irradiated for 22 h as suspension in hexane.

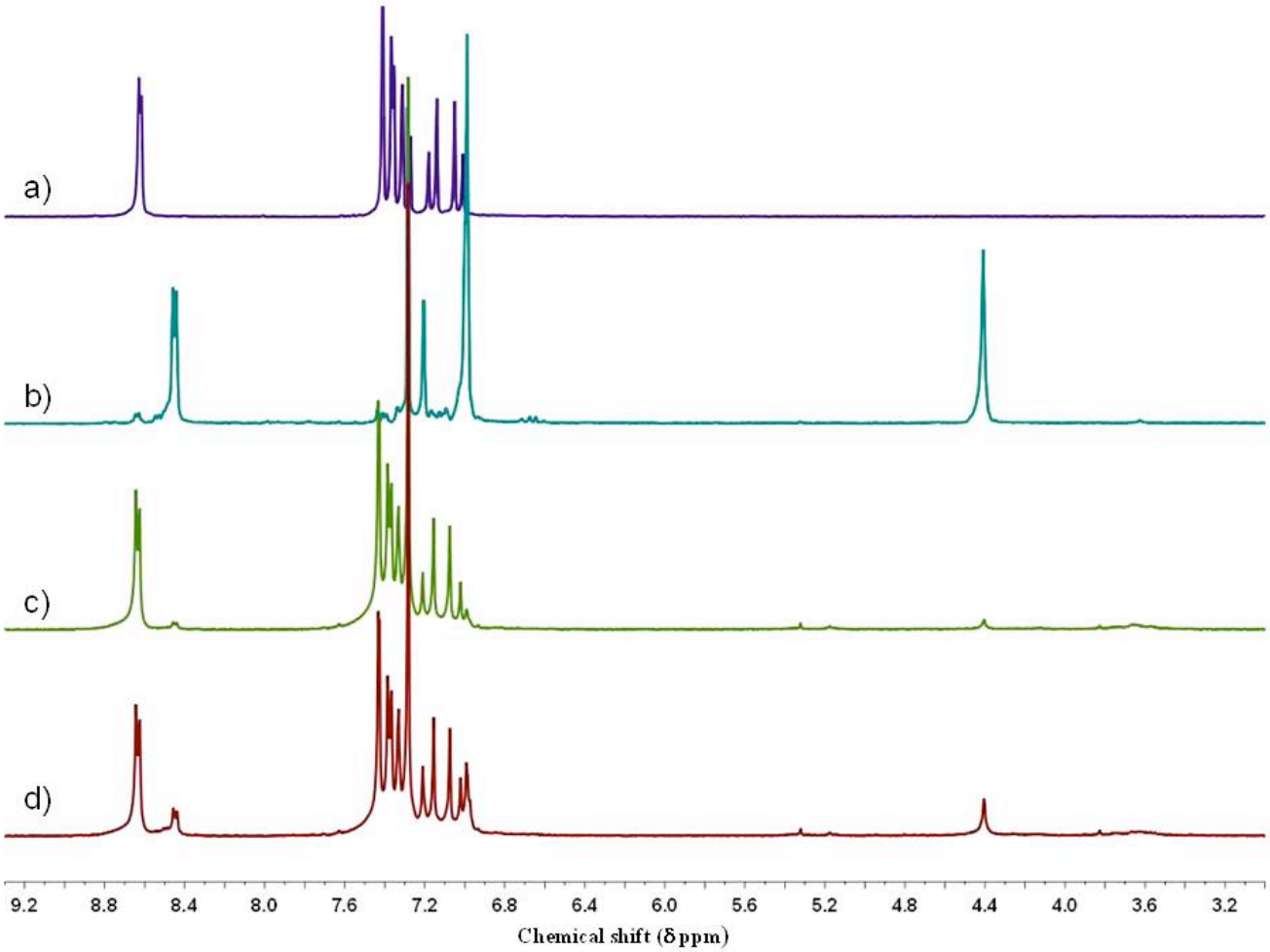

Figure S15 (a) ^{1}H NMR in $CDCl_3$ of 3,5-dichloro-stilbazole, **14** (b) after irradiation of 3,5-dichloro–stilbazole for 96 h in solid state, (c) neutral extract of 3,5-dichloro-stilbazole.HCl, irradiated for 150 h in solid state, (d) neutral extract of 3,5-dichloro-stilbazole.HCl irradiated for 150 h as suspension in hexane.

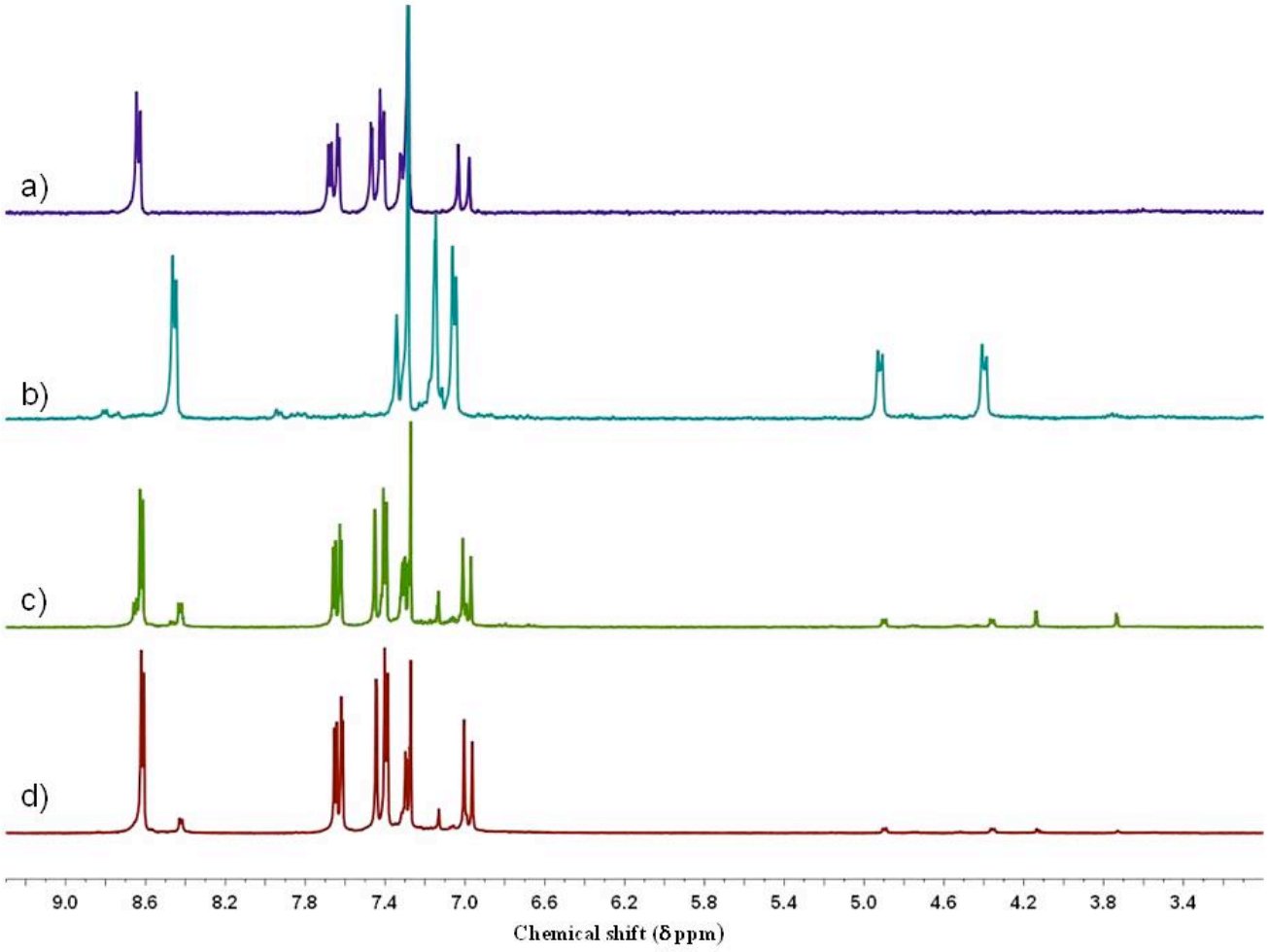

Figure S16 (a) ^{1}H NMR in $CDCl_3$ of 2,4-dichloro-stilbazole, **15** (b) after irradiation of 2,4-dichloro-stilbazole for 96 h in solid state, (c) neutral extract of 2,4-dichloro-stilbazole.HCl, irradiated for 183 h in solid state, (d) neutral extract of 2,4-dichloro-stilbazole.HCl irradiated for 158 h as suspension in hexane.

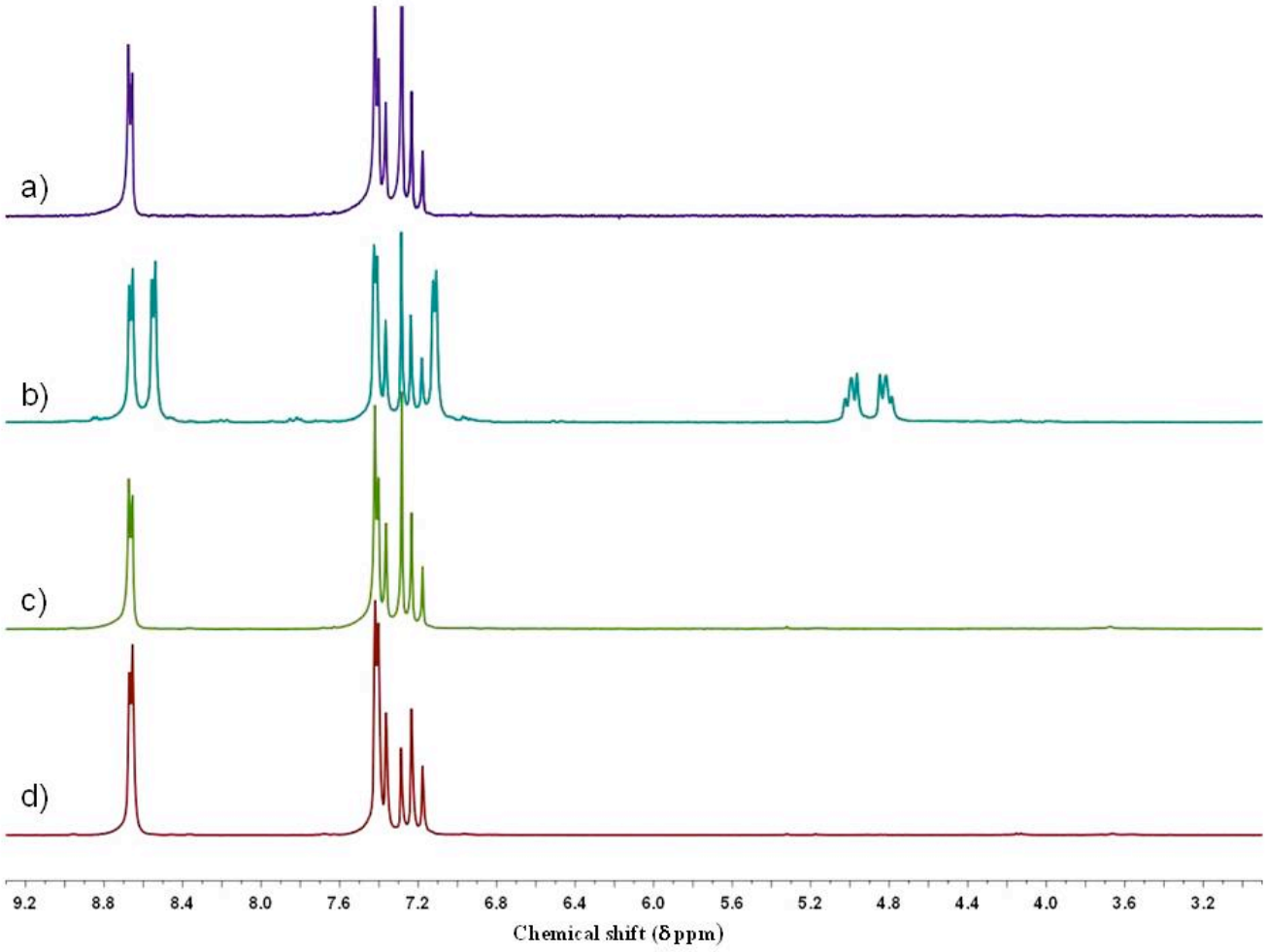

Figure S17 (a) ^{1}H NMR in $CDCl_3$ of 2,3,4,5,6 pentafluoro-stilbazole, **16** (b) after irradiation of 2,3,4,5,6 pentafluoro-stilbazole for 84 h in solid state, (c) neutral extract of 2,3,4,5,6 pentafluoro-stilbazole.HCl, irradiated for 129 h in solid state, (d) neutral extract of 2,3,4,5,6 pentafluoro-stilbazole.HCl irradiated for 84 h as suspension in hexane.

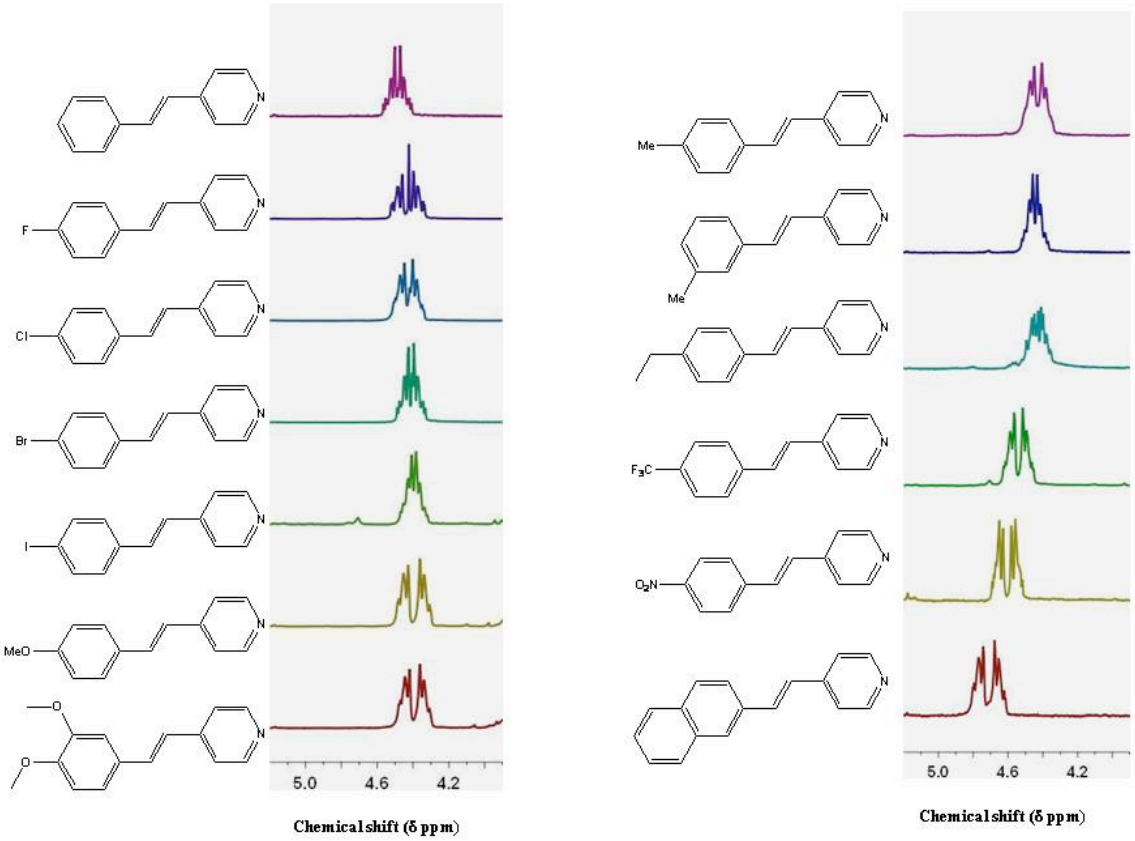

Figure S18 ^{1}H NMR ($CDCl_3$) of cyclobutane protons in dimer products obtained from **HCl** salts of stilbazole derivatives.

Crystallographic Analyses:

Yellow single crystals of **2.HCl (4F-Stilbazole.HCl), 3.HCl (4Cl-Stilbazole.HCl), 4.HCl (4Br-Stilbazole.HCl), 5.HCl (4I-Stilbazole.HCl), 9.HCl (4MeO-Stilbazole.HCl) and 16.HCl (2,3,4,5,6 penta F-Stilbazole.HCl)** suitable for X - ray diffraction analyses were obtained by evaporation of solvent from an ethanol/ toluene solvent mixture at 25 °C. Colorless single crystals of **2 (4F-Stilbazole) and 10 (3,4 diMeO-Stilbazole)** suitable for X - ray diffraction analyses were obtained by evaporation of solvent from chloroform/ toluene solvent mixture at 25 °C. Yellow single crystals of **dimer of 3 (4Cl-Stilbazole), dimer of 4 (4Br-Stilbazole), dimer of 5 (4I-Stilbazole) and 16 (2,3,4,5,6 penta F-Stilbazole)** suitable for X - ray diffraction analyses was obtained by evaporation from chloroform solvent at 25 °C. Colorless single crystals of **11.HCl (4CF_3-Stilbazole.HCl)** suitable for X - ray diffraction analyses were obtained by evaporation of solvent from an acetonitrile/ toluene solvent mixture at 25 °C. Pale yellow single crystals of **14.HCl 3,5 diCl-Stilbazole.HCl)** suitable for X - ray diffraction analyses were obtained by evaporation of solvent from a methanol/ toluene/chloroform solvent mixture at 25 °C.

Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX2 CCD-based diffractometer using Mo Kα radiation (λ = 0.71073 Å).[4] The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.[1] Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2, by using the SHELXTL software package.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the analyses are listed in Tables S1-S5.

Compound 1 (Stilbazole_HCl Salt) crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. The alkene group of the stilbazole molecule is disordered two orientations which were refined in a 70:30 ratio. There are three water molecules that cocrystallized with the complex.

Reasonable peak positions for the H atoms on the water molecules were located in the difference map and then refined with geometric restraints.

Compound 2 (4Fluoro Monomer) crystallized in the orthorhombic crystal system. The systematic absences in the intensity data were consistent with the unique space group *Pbca*. During the final stages of the structural analysis, the nitrogen atom N1 was found to be disordered at both ends of the molecule. This can be viewed as the whole molecule being disordered over two orientations such that the two molecules lie on top of each other. Appropriately, the N1 site and the C1 site were refined as a mixed N/C site in the ratio 50:50. The atomic coordinates and thermal parameters at these two mixed sites were constrained (SHELX: EXYZ and EADP instructions) to remain equal during the refinement cycles.

Compound 3 (4Chloro_HCl_Salt) crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. There are two water molecules that cocrystallized with the complex. Reasonable peak positions for the H atoms on the water molecules were located in the difference map and then refined with geometric restraints.

Compound 4 (4Chloro_StilbazoleDimer) crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/n$

Compound 5 (4Bromo_Stilbazole_HCl_Salt) crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. There are two water molecules that cocrystallized with the complex. Reasonable peak positions for the H atoms on the water molecules were located in the difference map and then refined with geometric restraints.

Compound 6 (4Bromo_StilbazoleDimer) crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/n$

Compound 7 (4Iodo_Stilbazole_HCl_Salt) crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. There are two water molecules that cocrystallized with the complex. Reasonable peak

positions for the H atoms on the water molecules were located in the difference map and then refined.

Compound 8 (4Iodo_StilbazoleDimer) crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/n$

9.HCl (4MeO-Stilbazole.HCl) crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. The asymmetric crystal units contain three molecules of the 4methoxy-Stilbazole salts. In two of the 4methoxy-Stilbazole cationic molecules, the alkene group is disordered over two orientations which were refined in the ratio 80:20. There are eight water molecules that cocrystallized with the complex. Reasonable peak positions for the H atoms on the water molecules were located in the difference map and then refined with geometric restraints. There is also an additional peak in the difference map which was assigned as Cl, resulting from excess HCl present under the crystallization conditions.

Compound **10 (3,4 diMeO-Stilbazole)** crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/c$.

Compound **11.HCl (4CF_3-Stilbazole.HCl)** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. The CF_3 group is disordered over two orientations and was refined in the ratio 70:30. There are three water molecules that cocrystallized with the complex. Reasonable peak positions for the H atoms on the water molecules were located in the difference map and then refined with geometric restraints.

Compound **14.HCl 3,5 diCl-Stilbazole.HCl)** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. The alkene group of the cationic **3,5 diChloro-Stilbazole** molecule is disordered two orientations which were refined in a 68:32 ratio.

Compound **16 (2,3,4,5,6 penta F-Stilbazole)** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure.

Compound **16.HCl (2,3,4,5,6 penta F-Stilbazole.HCl)** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. The alkene group of the cationic **2,3,4,5,6 penta F-Stilbazole** molecule is disordered two orientations which were refined in a 70:30 ratio.

Compound **2.HCl (4F-Stilbazole.HCl)** crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/c$. The alkene group of the cationic **4Fluoro-Stilbazole** molecule is disordered two orientations which were refined in a 60:40 ratio. There are three water molecules that cocrystallized with the complex. Reasonable peak positions for the H atoms on the water molecules were located in the difference map and then refined with geometric restraints. The R values during the final stage of the refinement are high due to poor crystal quality. Repeated attempts to grow high quality crystals were unsuccessful. The structure reported is the 'best' we were able to obtain.

Table S1. Crystallographic Data for Compounds 1-3.HCl salts

	Stilbazole_HCl	4_Fluoro Monomer	4_Chloro_HCl_Salt
Empirical formula	$C_{13}H_{12}N\bullet Cl\ 3H_2O$	$C_{13}H_{10}NF$	$C_{13}H_{11}NCl\bullet Cl\ 2H_2O$
Formula weight	271.73	199.22	288.16
Crystal system	Triclinic	Orthorhombic	Triclinic
Lattice parameters			
a (Å)	7.0919(5)	7.5432(6)	7.6093(5)
b (Å)	10.1566(7)	11.7934(9)	9.1045(6)
c (Å)	10.9322(7)	11.8041(9)	10.7778(6)
α (deg)	69.8118(9)	90	102.5029(8)
β (deg)	82.7066(10)	90	101.8363(9)
γ (deg)	79.1375(10)	90	92.2888(9)
V ($Å^3$)	724.18(9)	1050.09(14)	710.68(7)
Space group	$P\bar{1}$ (# 2)	*P*bca (# 61)	$P\bar{1}$ (# 2)
Z value	2	4	2
ρ_{calc} (g / cm^3)	1.246	1.260	1.347
μ (Mo Kα) (mm^{-1})	0.264	0.086	0.450
Temperature (K)	296	296	296
$2\Theta_{max}$ (°)	50.00	50.98	56.00
No. Obs. ($I > 2\sigma(I)$)	2227	757	2789
No. Parameters	187	74	167
Goodness of fit	1.051	1.071	1.040
Max. shift in cycle	0.001	0.001	0.001
Residuals*:R1; wR2	0.0550; 0.1553	0.0486; 0.1263	0.0453; 0.1339
Absorption Correction, Max/min	Multi-scan 0.7465; 0.6619	Multi-scan 0.9931; 0.9564	Multi-scan 0.7465; 0.0.6625
Largest peak in Final Diff. Map ($e^- / Å^3$)	0.329	0.221	0.301

*$R = \Sigma_{hkl}(\big|\,|F_{obs}|-|F_{calc}|\,\big|)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/\Sigma_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

Table S2. Crystallographic Data for Compounds 4.HCl salt and dimers from 3.HCl and 4.HCl

	4_ChloroStilbazole Dimer	4_Bromo_HCl_Salt	4_BromoStilbazole Dimer
Empirical formula	$C_{26}H_{20}N_2Cl_2$	$C_{13}H_{11}NBr\bullet Cl$ $2H_2O$	$C_{26}H_{20}N_2Br_2$
Formula weight	431.34	332.62	520.26
Crystal system	Monoclinic	Triclinic	Monoclinic
Lattice parameters			
a (Å)	9.6675(6)	8.0476(5)	9.8477(5)
b (Å)	13.8938(8)	9.7384(6)	9.4161(5)
c (Å)	16.3247(9)	9.9178(6)	24.1091(12)
α (deg)	90	99.575(1)	90
β (deg)	94.2639(8)	98.575(1)	90.2071(9)
γ (deg)	90	108.029(1)	90
V ($Å^3$)	2186.6(2)	711.93(8)	2235.5(2)
Space group	$P2_1/n$ (#14)	$P\bar{1}$ (# 2)	$P2_1/n$ (#14)
Z value	4	2	4
ρ_{calc} (g / cm^3)	1.310	1.552	1.546
μ (Mo Kα) (mm^{-1})	0.312	3.068	3.641
Temperature (K)	296	296	296
$2\Theta_{max}$ (°)	58.00	50.10	56.00
No. Obs. (I > 2σ(I))	4201	2309	3737
No. Parameters	271	167	271
Goodness of fit	1.024	1.082	1.028
Max. shift in cycle	0.001	0.001	0.001
Residuals*:R1; wR2	0.0463; 0.1127	0.0406; 0.1100	0.0432; 0.1070
Absorption Correction, Max/min	Multi-scan 0.9815/0.8646	Multi-scan 0.7465; 0.5846	Multi-scan 0.7461; 0.4780
Largest peak in Final Diff. Map (e^- / $Å^3$)	0.496	1.807	1.013

*$R = \Sigma_{hkl}(\big|\,|F_{obs}|-|F_{calc}|\,\big|)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/\Sigma_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

Table S3. Crystallographic Data for Compounds 5.HCl, 9.HCl and dimer from 5.HCl

	4_Iodo_HCl_Salt	4_IodoStilbazole Dimer	4_Methoxy_HCl_Salt
Empirical formula	$C_{13}H_{11}NI\bullet Cl\ 2H_2O$	$C_{26}H_{20}N_2I_2$	$C_{42}H_{42}N_3O_3\bullet 4Cl\ 8H_2O$
Formula weight	379.61	614.24	922.71
Crystal system	Triclinic	Monoclinic	Triclinic
Lattice parameters			
a (Å)	8.0309(3)	9.5861(4)	9.4503(4)
b (Å)	9.9249(4)	9.7404(4)	12.2691(5)
c (Å)	10.0973(4)	24.7898(10)	21.7240(9)
α (deg)	97.9228(5)	90	78.4586(6)
β (deg)	99.4160(5)	90.1197(7)	86.8176(6)
γ (deg)	108.9995(5)	90	84.1447(6)
V ($Å^3$)	734.79(5)	2314.68	2453.43(18)
Space group	$P\bar{1}$ (# 2)	$P2_1/n$ (# 14)	$P\bar{1}$ (# 2)
Z value	2	4	2
ρ_{calc} (g / cm^3)	1.716	1.763	1.249
μ (Mo Kα) (mm^{-1})	2.355	2.732	0.297
Temperature (K)	296	296(2)	296(2)
$2\Theta_{max}$ (°)	58.00	60.00	50.00
No. Obs. (I > 2σ(I))	3707	4849	6738
No. Parameters	179	271	645
Goodness of fit	1.122	1.015	1.035
Max. shift in cycle	0.001	0.002	0.007
Residuals*:R1; wR2	0.0277; 0.0758	0.0386; 0.0975	0.0451; 0.1201
Absorption Correction, Max/min	Multi-scan 0.8340/0.4105	Multi-scan 0.8532/0.4078	Multi-scan 0.7461/0.6876
Largest peak in Final Diff. Map (e^- / $Å^3$)	1.542	1.682	0.273

*$R = \Sigma_{hkl}(\big|\,|F_{obs}|-|F_{calc}|\,\big|)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/\Sigma_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/(n_{data}-n_{vari})]^{1/2}$.

Table S4. Crystallographic Data for Compounds 10, 11.HCl and 14.HCl

	3,4-DiMethoxyStilbazole Monomer	4-CF3Stilbazole HCl Salt	3,5-Dichloro HCl_Salt
Empirical formula	$C_{15}H_{15}NO_2$	$C_{14}H_{11}NF_3$•Cl $3H_2O$	$C_{13}H_{10}NCl_2$•Cl
Formula weight	241.28	339.74	286.57
Crystal system	Monoclinic	Triclinic	Triclinic
Lattice parameters			
a (Å)	8.7901(5)	7.4124(3)	4.9487(3)
b (Å)	7.8000(4)	9.5475(4)	7.8558(4)
c (Å)	19.3873(10)	12.2010(5)	16.9993(9)
α (deg)	90	80.0619(6)	96.3056(8)
β (deg)	96.962(1)	82.0762(6)	91.9793(8)
γ (deg)	90	75.3538(6)	93.8669(8)
V ($Å^3$)	1319.45(12)	818.84(6)	654.78(6)
Space group	$P2_1/c$ (# 14)	$P\bar{1}$ (# 2)	$P\bar{1}$ (# 2)
Z value	4	2	2
ρ_{calc} (g / cm^3)	1.215	1.378	1.453
μ (Mo Kα) (mm^{-1})	0.081	0.274	0.675
Temperature (K)	296(2)	296(2)	296(2)
$2\Theta_{max}$ (°)	53.00	52.00	50.00
No. Obs. ($I > 2\sigma(I)$)	2265	2960	2129
No. Parameters	166	234	173
Goodness of fit	1.038	1.041	1.078
Max. shift in cycle	0.000	0.000	0.000
Residuals*:R1; wR2	0.0436; 0.1183	0.0485; 0.1336	0.0593; 0.1463
Absorption Correction, Max/min	Multi-scan 0.9840/0.9623	Multi-scan 0.7465/0.6418	Multi-scan 0.8769/0.7037
Largest peak in Final Diff. Map (e^- / $Å^3$)	0.215	0.514	0.639

*$R = \Sigma_{hkl}(\left|\left|F_{obs}\right| - \left|F_{calc}\right|\right|)/\Sigma_{hkl}\left|F_{obs}\right|$; $R_w = [\Sigma_{hkl}w(\left|F_{obs}\right| - \left|F_{calc}\right|)^2/\Sigma_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(\left|F_{obs}\right| - \left|F_{calc}\right|)^2/(n_{data} - n_{vari})]^{1/2}$.

Table S5. Crystallographic Data for Compounds 16.HCl, 16 and 2.HCl

	PentafluoroStilbazole HCl_Salt	PentafluoroStilbazole Monomer	4_Fluoro_HCl_Salt
Empirical formula	$C_{13}H_7NF_5$•Cl	$C_{13}H_6NF_5$	$C_{13}H_{11}NF$•Cl $3H_2O$
Formula weight	307.65	271.19	281.73
Crystal system	Triclinic	Triclinic	Monoclinic
Lattice parameters			
a (Å)	8.3749(5)	5.8613(4)	7.0809(4)
b (Å)	8.3985(5)	9.2231(6)	9.6992(6)
c (Å)	10.2024(7)	10.9709(7)	22.3919(14)
α (deg)	66.6060(8)	71.3900(9)	90
β (deg)	71.9947(9)	85.3708(9)	98.4170(10)
γ (deg)	84.0524(9)	80.5834(9)	90
V ($Å^3$)	626.21(7)	554.24(6)	1521.29(16)
Space group	$P\bar{1}$ (# 2)	$P\bar{1}$ (# 2)	$P2_1/c$ (# 14)
Z value	2	2	4
ρ_{calc} (g / cm^3)	1.632	1.625	1.2230
μ (Mo Kα) (mm^{-1})	0.354	0.155	0.260
Temperature (K)	296(2)	296(2)	296(2)
$2\Theta_{max}$ (°)	52.00	58.00	50.00
No. Obs. (I > 2σ(I))	2145	2170	2115
No. Parameters	200	173	212
Goodness of fit	1.070	1.079	1.717
Max. shift in cycle	0.000	0.000	0.000
Residuals*: R1; wR2	0.0565; 0.1532	0.0477; 0.1394	0.1094
Absorption Correction, Max/min	Multi-scan 0.9722/0.8263	Multi-scan 0.9846/0.9236	Multi-scan 0.9845/0.8765
Largest peak in Final Diff. Map (e^- / $Å^3$)	0.438	0.259	1.267

*$R = \Sigma_{hkl}(\,|\,|F_{obs}| - |F_{calc}|\,|)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

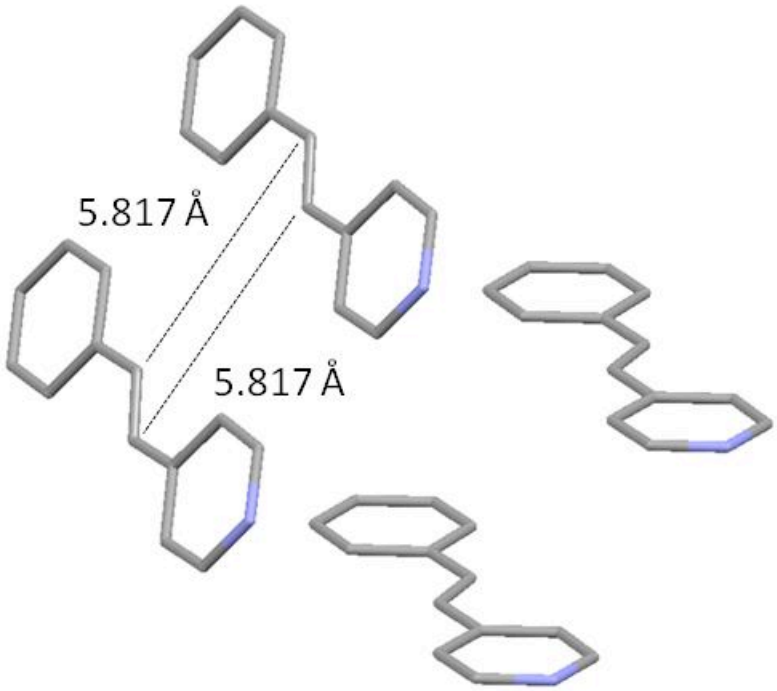

Figure S19 Packing arrangement of stibazole (**1**) based on literature report (E. Cariati, D. Roberto, R. Ugo, V. I. Srdanov, S. Galli, P. Macchi, A. Sironi *New J. Chem.* 2002, **26**, 13-15)

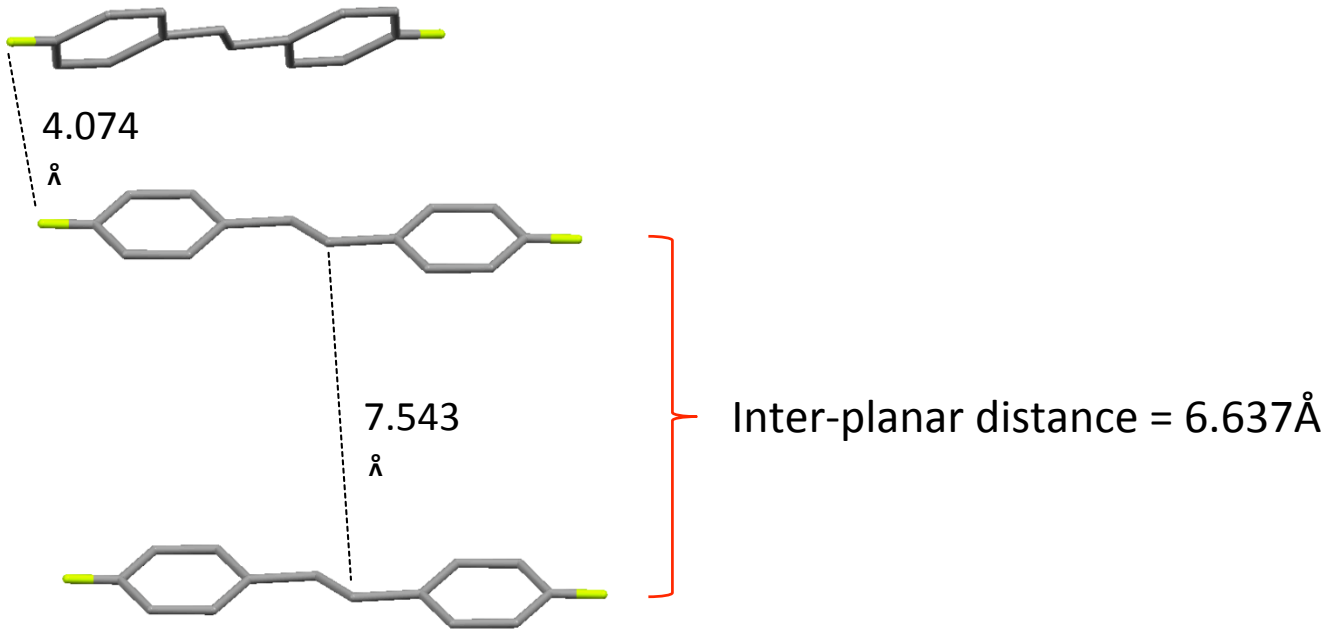

Figure S20 Packing arrangement of 4-fluoro-stibazole (**2**)**.** (Whole molecule disorder over two orientations, with N and C mixed sites).

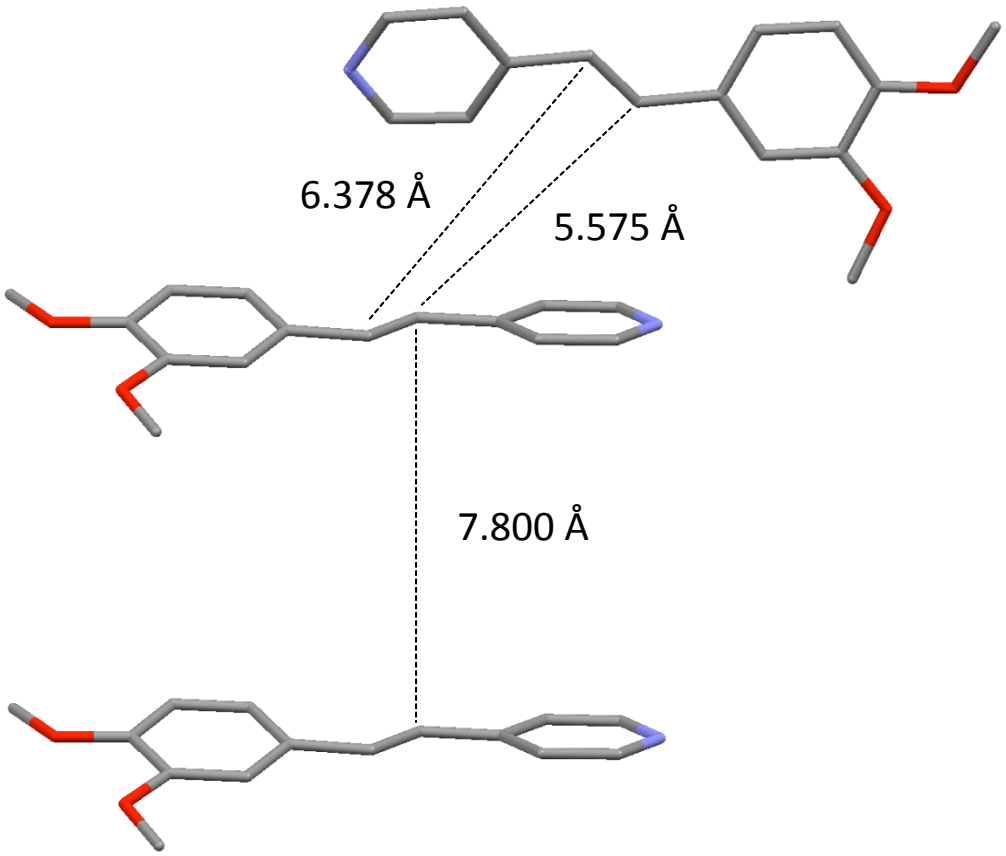

Figure S21 Packing arrangement of 3.4 -dimethoxy-stibazole (**10**)

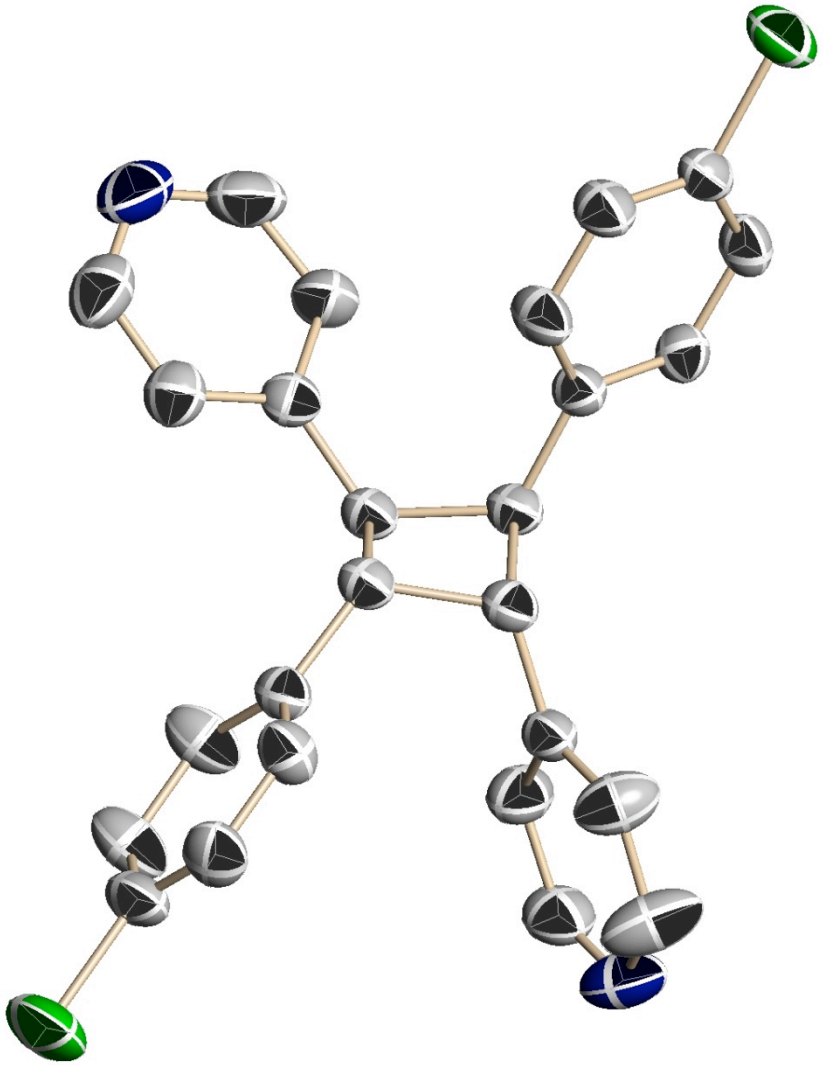

Figure S22 Structure of dimer obtained (following NaOH neutralization) upon irradiation of 4-chloro stilbazole.HCl salt.

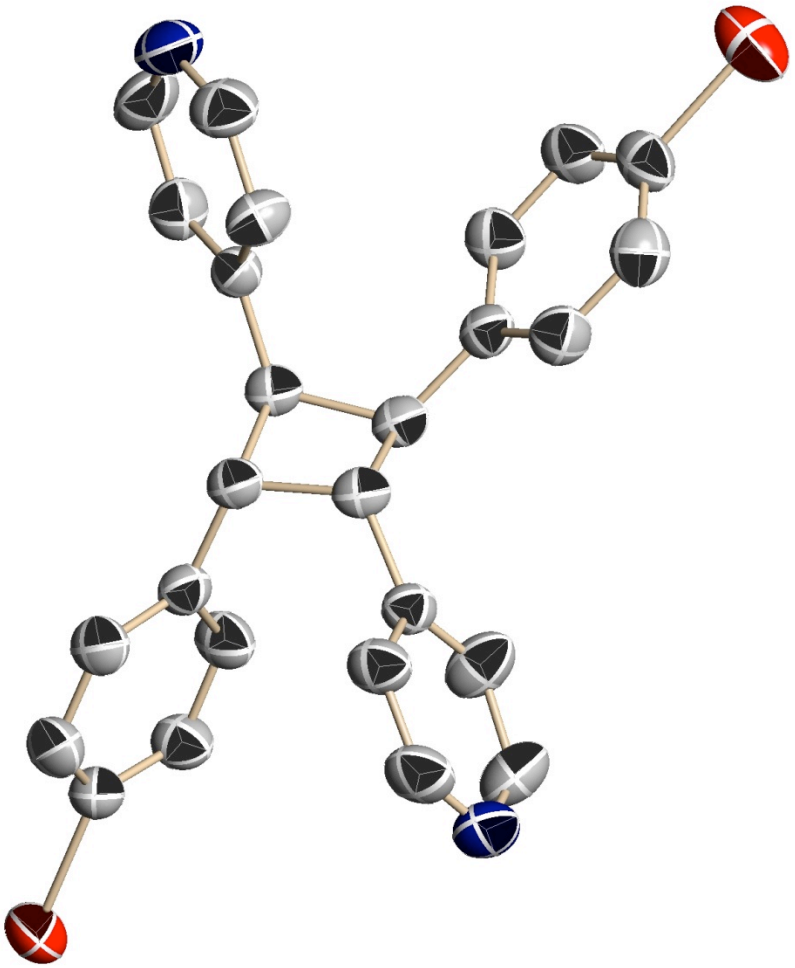

Figure S23 Structure of dimer obtained (following NaOH neutralization) upon irradiation of 4-bromo stilbazole.HCl salt.

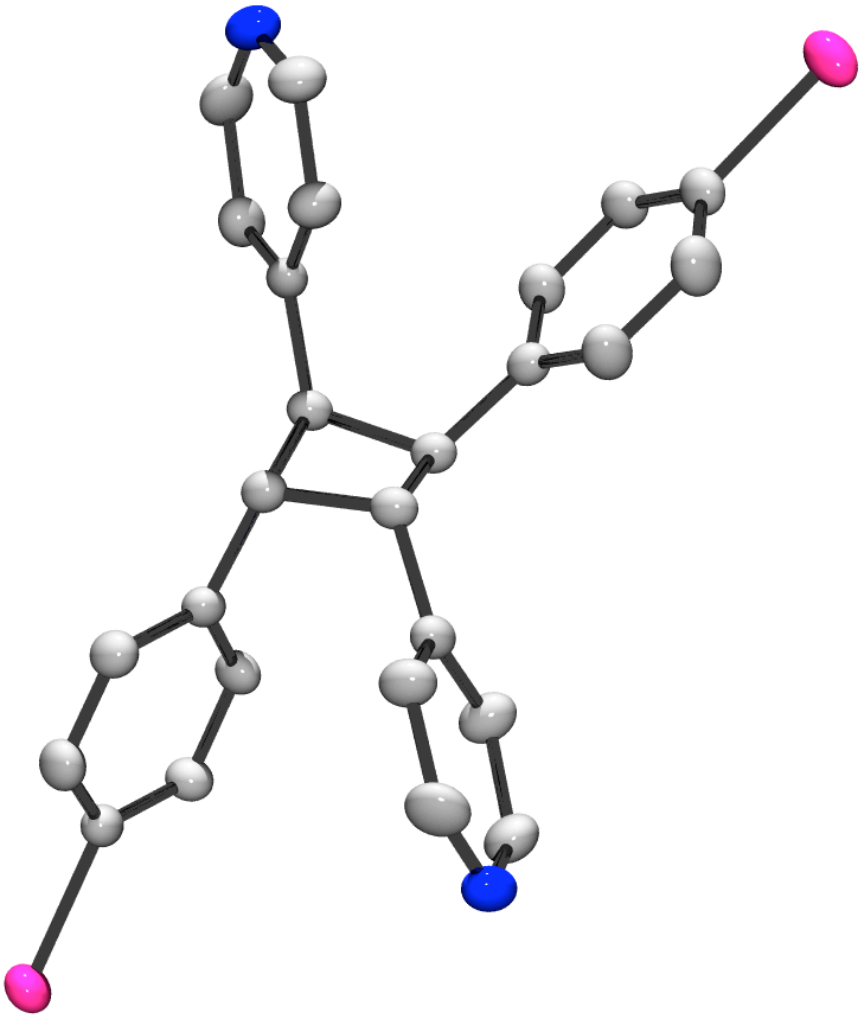

Figure S24 Structure of dimer obtained (following NaOH neutralization) upon irradiation of 4-iodo stilbazole.HCl salt.

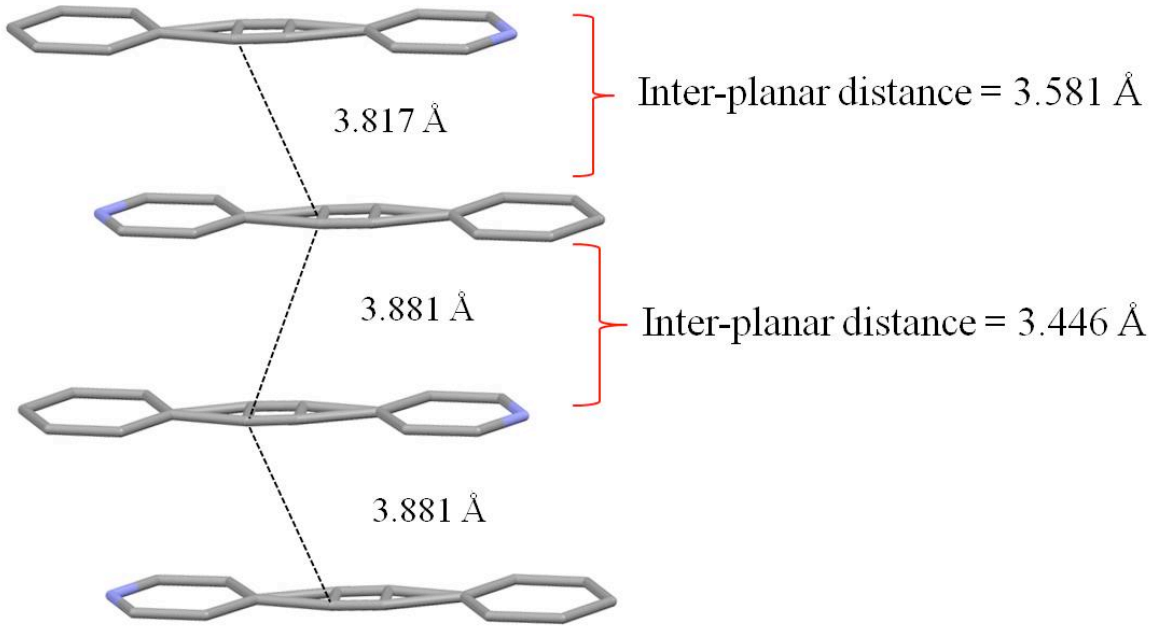

Figure S25 Packing arrangment of stilbazole.HCl salt. Note the disorder of the olefinic carbons.

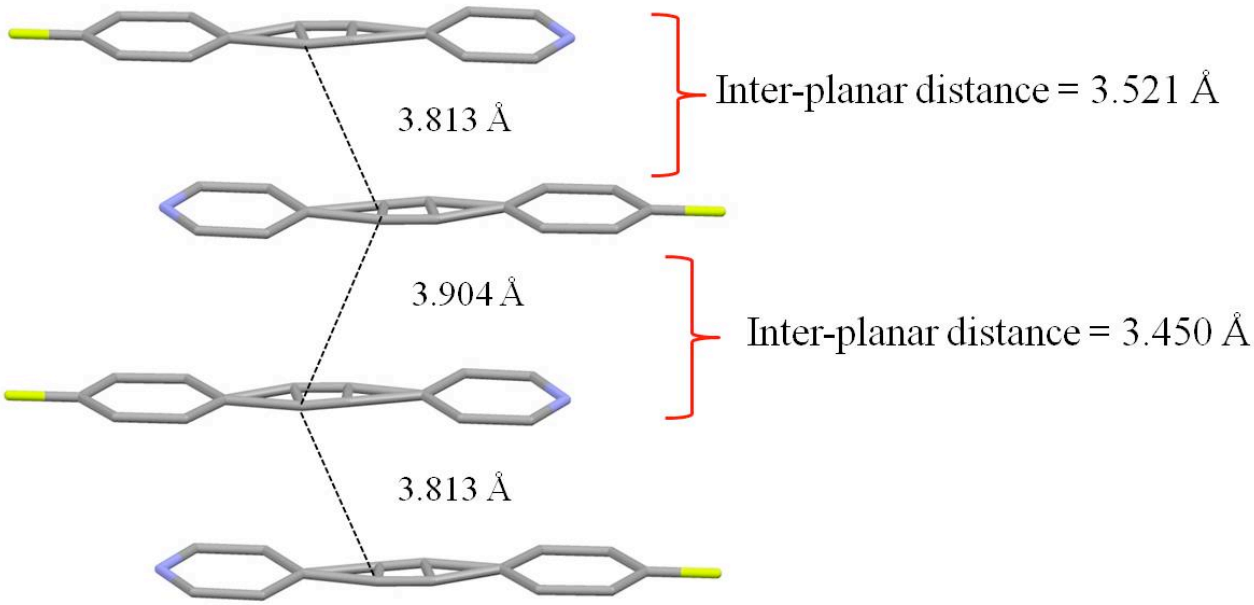

Figure S26 Packing arrangment of 4-flouro stilbazole.HCl salt. Note the disorder of the olefinic carbons.

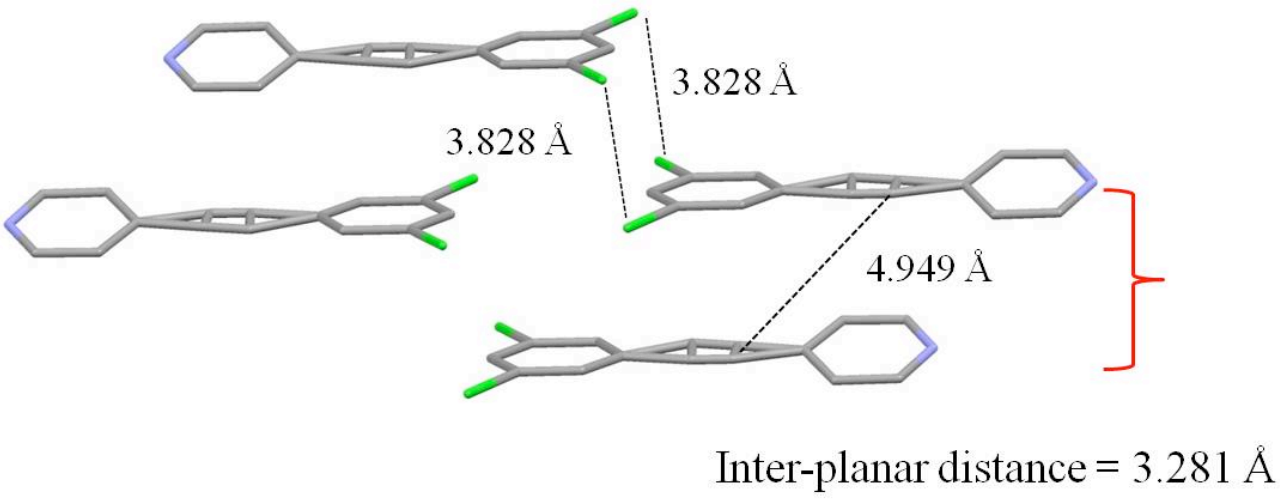

Figure S27 Packing arrangment of 3, 5- dichloro stilbazole.HCl salt. Note the disorder of the olefinic carbons.

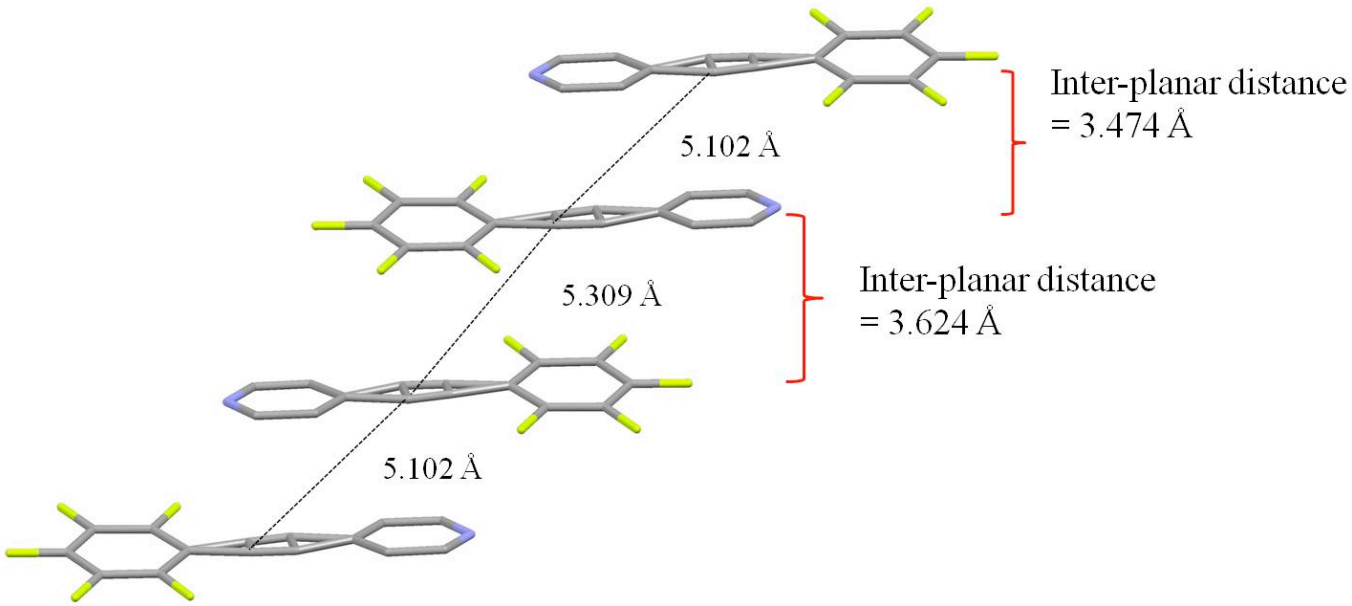

Figure S28 Packing arrangment of pentafluoro stilbazole.HCl salt. Note the disorder of the olefinic carbons.

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