Supplementary Material (ESI) for New Journal of Chemistry
This journal is (c) The Royal Society of Chemistry and
The Centre National de la Recherche Scientifique, 2009

SUPPORTING INFORMATION

Photo-switch and INHIBIT Logic Gate Based on two Pyrazolone thiosemicarbazone Derivants

Xiangyun Xie [a], Lang Liu [a], Dianzeng Jia *[a], Jixi Guo [a], Dongling Wu [a], Xiaolin Xie[b]

[a]*Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, P. R.China*

[b]*National Anti-counterfeit Engineering Research Center,Department of Chemistry and Chemical Engineering,Huazhong University of Science and Technology, Wuhan 430074, China*

E–mail: jdz@xju.edu.cn

Table of Contents:

This journal is (c) The Royal Society of Chemistry and
The Centre National de la Recherche Scientifique, 2009

Spectroscopy

Synthesis of 1-phenyl-3-methyl-4-(2-fluorobenzal)-5-hydroxypyrazole 4-ethylthiosemi-carbazone(2)

1–Phenyl–3–methyl–4–(2–fluorobenzal)–5–hydroxypyrazole 4–ethylthiosemicarbazone was synthesized by refluxing PM2FHP (5 mmol) and N(4)–ethyl–3–thiosemicarbazide (5 mmol) in 30 ml of methanol at the presence of glacial acetic acid (1 ml) at 70 °C for ca. 3 h under magnetic stirring. After cooling down to room temperature in the dark, white powders were obtained. Then the resulting mixture was filtered, the white product was obtained in 90.07 % yield. m. p. 217.8–219.2 °C. The compound produced the crystals suitable for X–ray analysis in the methanol solution. The spectroscopic data are as follows. IR (ν/cm^{-1}): (a. the white powder before irradiation): 3304 υ(N–H), 3065–2593 υ(O–H), 1633 υ(C=N), 1555, 1496 υ(phenyl), 1408, 1369 υ(pyrazolone–ring), 1229 υ(C=S). (b the yellow powder after irradiation): 3304, υ(N–H), 1664 υ (C=O), 1633 υ(C=N), 1555, 1496 υ(phenyl), 1408, 1369 υ(pyrazolone–ring), 1229 υ(C=S). MS, m/z: [M+1] = 398.1 (formula weight: 397.47). ^{1}H NMR (DMSO–d_6) (δ, ppm): 1.144–1.109 (3H, CH_2CH_3), 1.659 (2H, CH_2CH_3), 3.612–3.544 (3H Pz–CH_3), 7.176–7.466 (5H, Ph), 7.768–7.513 (5H, C_6H_4F+N4–H), 7.929 (1H, N5–H), 8.266 (1H, Pz–NH).

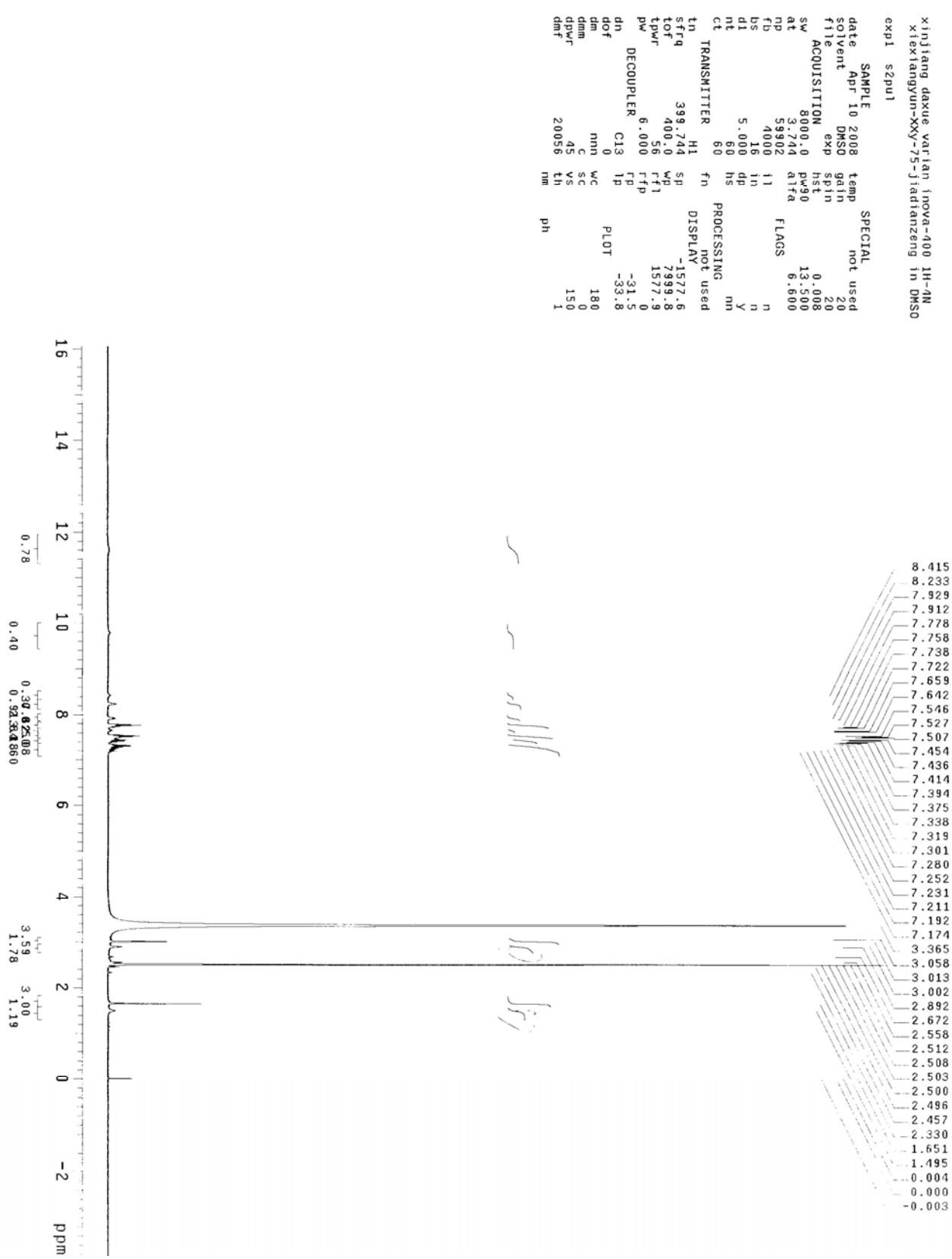

Figure S1. ^{1}H NMR spectra of **1** in DMSO-d_6

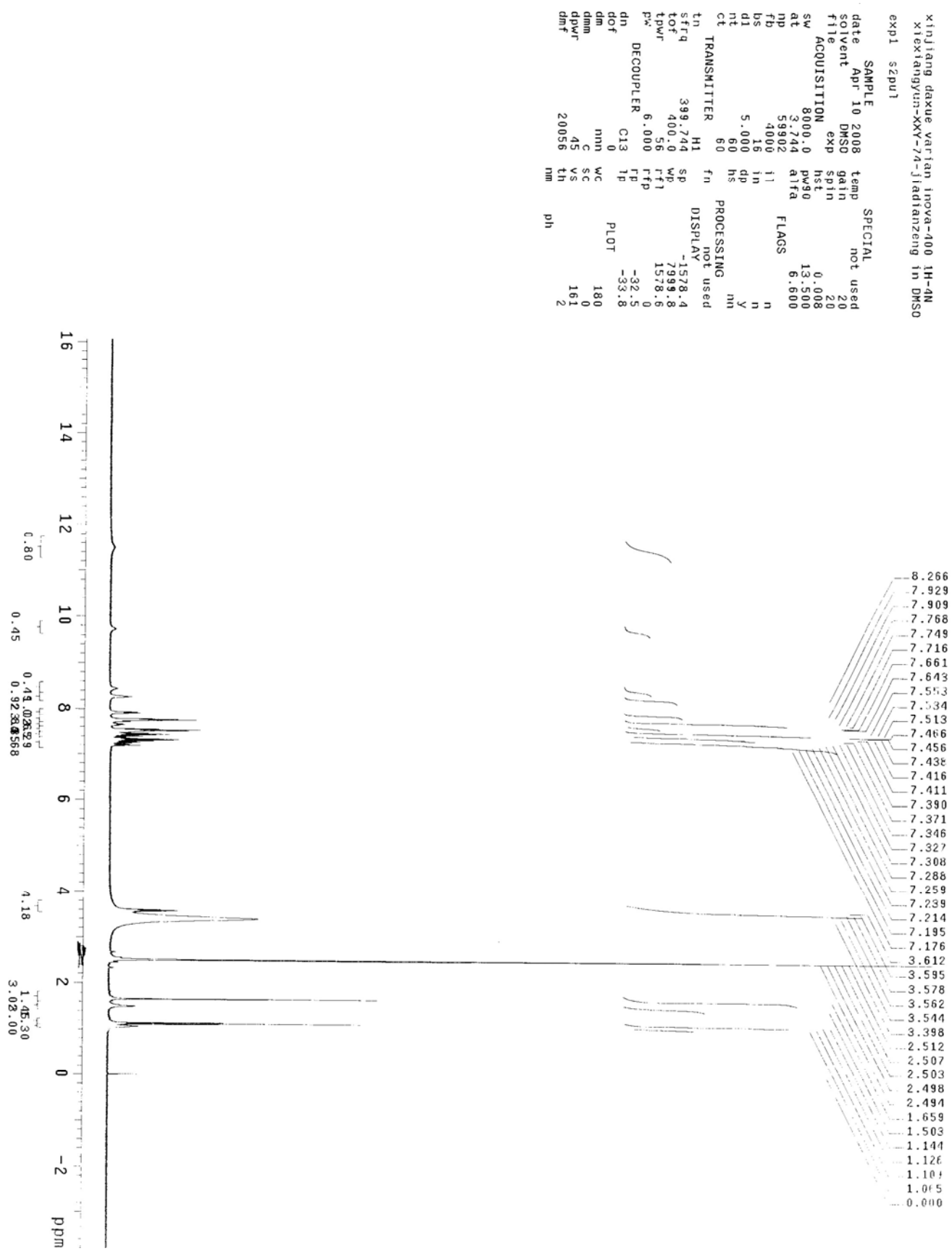

Figure S2. ^{1}H NMR spectra of **2** in DMSO-d_6

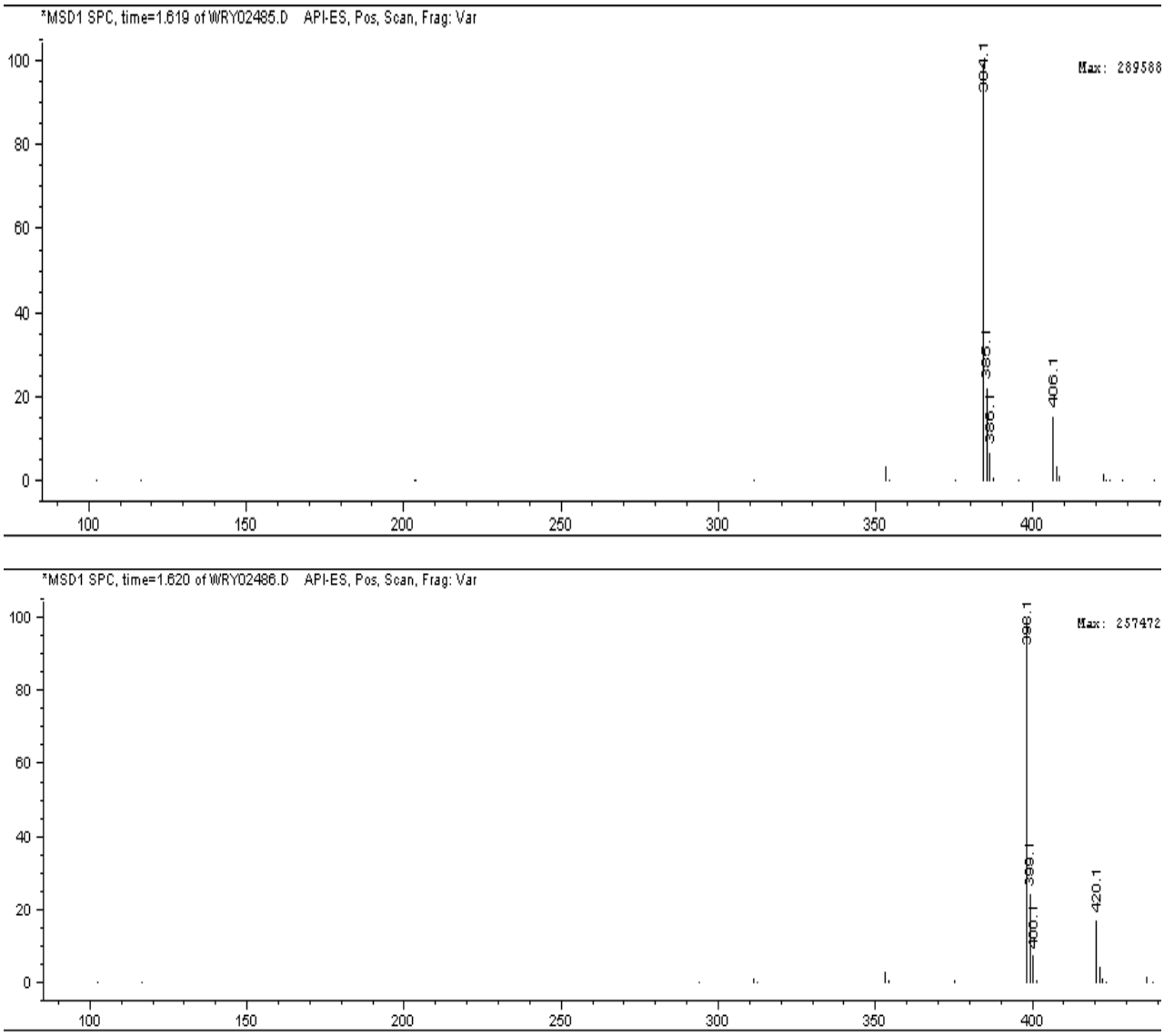

Figure S3. MS spectra of **1** and **2**.

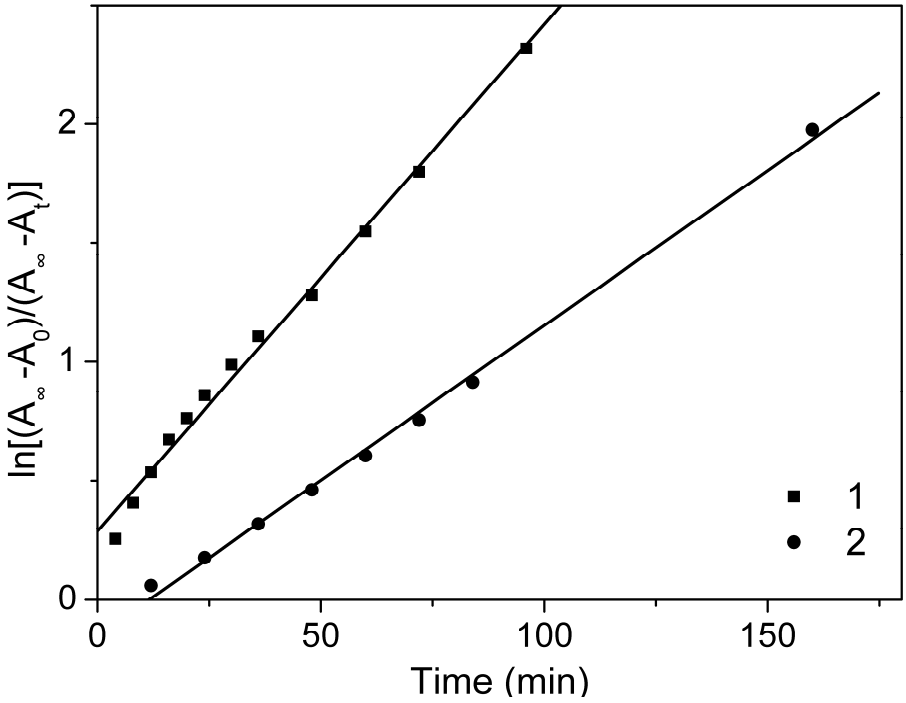

Figure S4. First-order kinetic plots of photoisomerization reactions of **1** and **2** induced by 365 nm light at room temperature.

This journal is (c) The Royal Society of Chemistry and
The Centre National de la Recherche Scientifique, 2009

X-Ray Crystallography

X-ray crystal structure determination:

Single crystals of **1** and **2** suitable for X-ray crystallographic work were grown by slow evaporation of their methanol solution at room temperature. The crystallographic data were collected on an imaging plate system (Rigaku R-AXIS SPIDER) with a graphite monochromatized Mo *Kα* radiation (λ = 0.71073 Å). The crystal was mounted with grease on the top of a glass fiber and cooled at 153 *K* in a liquid nitrogen stream. Cell constants and orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from reflections in the range 3.06 to 25.25 º for **1** (3.12 to 27.48 º for **2**). Crystal structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods with the *SHELXTL-97* program. All non-H atoms were refined anisotropically. The H atoms on oxygen atom and nitrogen atoms were located from the Fourier maps, the restraints in each of the refinements were used to restraint the H atoms. And all of the other H atoms were placed in geometrically idealized positions. The disordered part with small occupancy was refined isotropically and the bond lengths and geometry were restrained in the refinement.

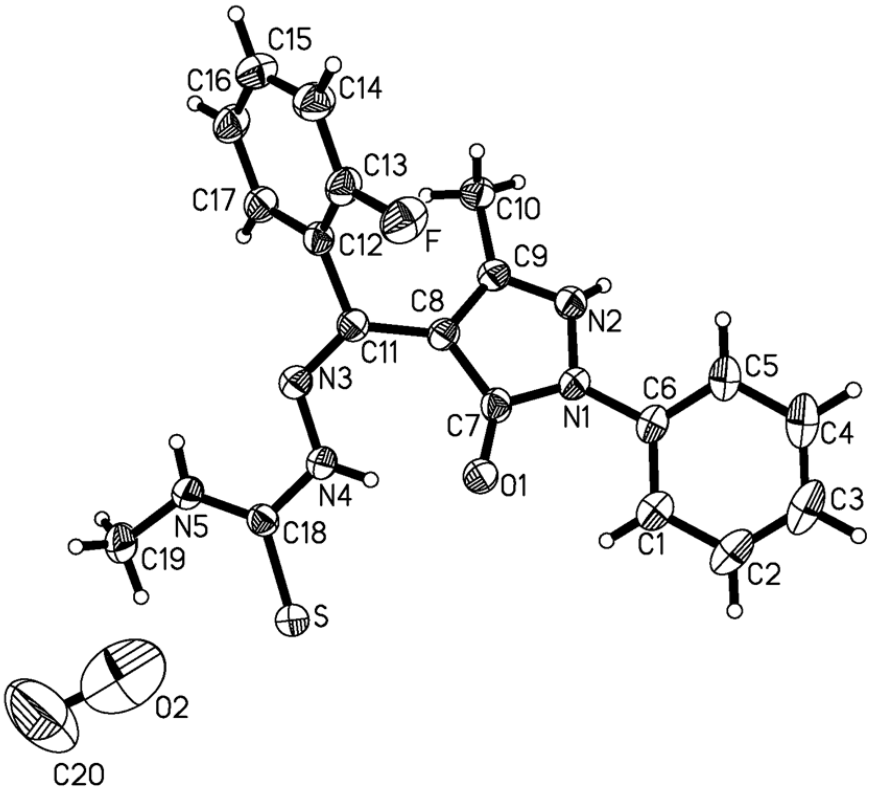

Figure S5. Molecular structure of **1 (**keto form, **II)** with atom numberings (30% probability ellipsoids).

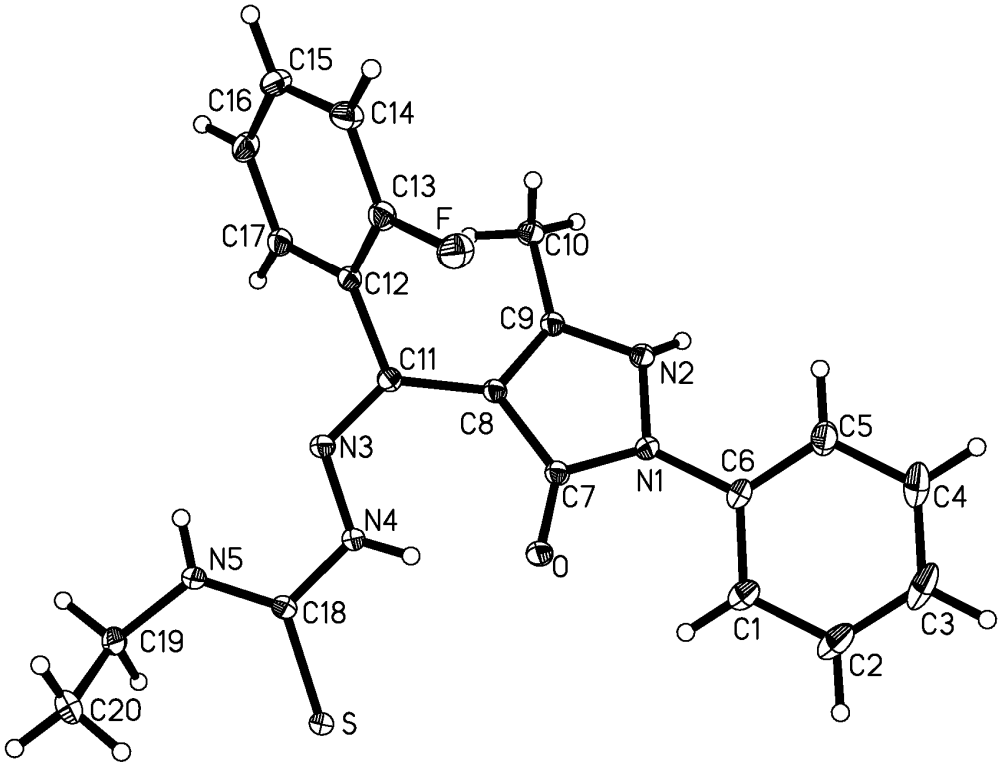

Figure S6. Molecular structure of **2 (**keto form, **II)** with atom numberings (30% probability ellipsoids)

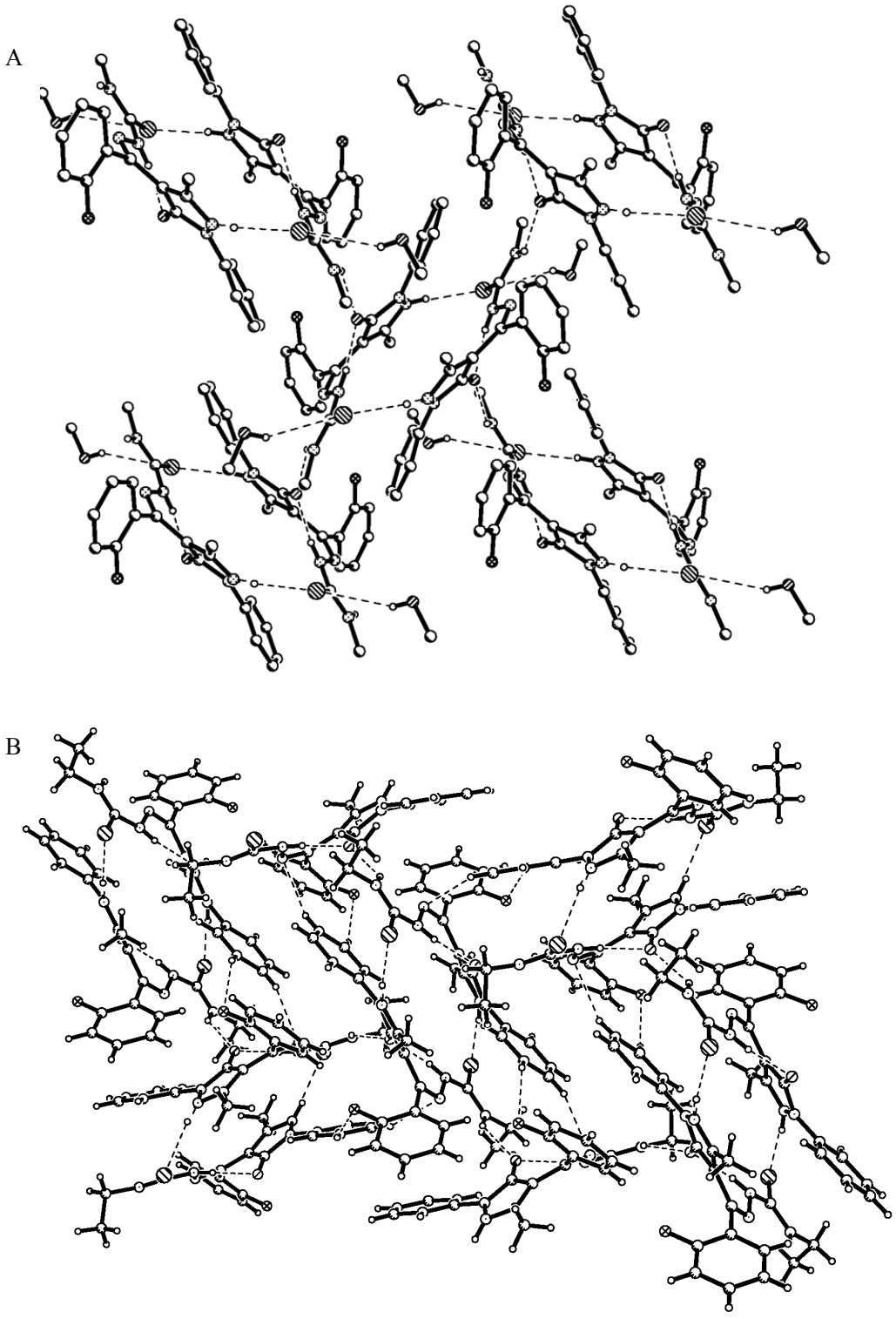

Figure S7. Crystal packing in unit cell along c axis for **1(A)** and **2(B)**.

Table S1. Crystal data and structure refinement details for compounds **1** and **2**

Compounds	**1** (**keto form, II**)	**2** (**keto form, II**)
Empirical formula	$C_{19.50}H_{20}N_5O_{1.50}SF$	$C_{20}H_{20}N_5OSF$
FW	399.46	397.47
Temperature/K	293(2)	153(2)
Wavelength/ Å	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbcn*	*Pbcn*
Unit cell dimensions	a = 13.4486(8) Å α = 90 °	a = 13.9254(3) Å α = 90 °
	b = 13.3331(9) Å β = 90 °	b = 13.0617(3) Å β = 90 °
	c = 21.6910(12)Å γ = 90 °	c = 21.3133(4) Å γ = 90 °
Volume/A^3	3889.4(4)	3876.66(14)
Z	8	8
Density (Calculated)/ Mg/m^3	1.364	1.362
Absorption coefficient/mm^{-1}	0.199 mm	0.197
F(000)	1672	1664
Crystal size	0.28 x 0.28 x 0.08 mm	0.60 x 0.57 x 0.40 mm
Theta range for data collection/º	3.06 to 25.25	3.12 to 27.48
Limiting indices	-13 ≤h≤16	-18≤h≤18
	-16≤k≤15	-16≤k≤16
	-26≤l≤25	-27≤l≤27
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.9843 and 0.9464	0.9252 and 0.8908
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3519 / 3 / 272	4443 / 3 / 269
Reflections collected / unique	26179 / 3519 [R(int) = 0.0901]	34491 / 4443 [R(int) = 0.0256]
GOF on F^2	0.999	1.000
Final R indices [I >2 σ (I)]	R_1 = 0.0603, wR_2 = 0.1543	R_1 = 0.0334, wR_2 = 0.0909
R indices (all data)	R_1 = 0.0973, wR_2 = 0.1748	R_1 = 0.0385, wR_2 = 0.0946
Extinction coefficient	0.0092(14)	0.0015(4)
Largest diff. peak and hole	0.466 and -0.333 e $Å^{-3}$	0.375 and -0.219

Table S2. Selected bond lengths (Å) and angles (°) for **1** and **2**

1 (**keto form**)		**2** (**keto form**)	
Bond Lengths (Å)			
S-C(18)	1.697(3)	S-C(18)	1.7044(12)
O(1)-C(7)	1.251(3)	O(1)-C(7)	1.2498(14)
C(20)-O(2)#1	1.421(15)	N(1)-C(7)	1.3838(16)
C(20)-O(2)	1.421(15)	N(2)-C(9)	1.3386(16)
N(1)-C(7)	1.381(4)	N(4)-C(18)	1.3616(15)
N(2)-C(9)	1.334(4)	N(5)-C(18)	1.3169(16)
N(4)-C(18)	1.360(4)	N(3)-N(4)	1.3798(14)
N(5)-C(18)	1.316(4)	C(7)-C(8)	1.4451(16)
N(3)-N(4)	1.381(3)	C(8)-C(9)	1.3879(16)
C(7)-C(8)	1.438(4)		
C(8)-C(9)	1.390(4)		
Bond angles(°)			
N(2)-N(1)-C(7)	108.2(2)	N(2)-N(1)-C(7)	109.09(9)
N(2)-N(1)-C(6)	120.6(2)	N(2)-N(1)-C(6)	120.19(10)
C(7)-N(1)-C(6)	129.2(3)	C(7)-N(1)-C(6)	128.62(10)
C(9)-N(2)-N(1)	109.4(2)	C(9)-N(2)-N(1)	108.86(10)
C(11)-N(3)-N(4)	117.5(2)	C(11)-N(3)-N(4)	117.21(10)
C(18)-N(4)-N(3)	117.9(2)	C(18)-N(4)-N(3)	117.65(10)
C(7)-C(8)-C(11)	128.2(2)	C(7)-C(8)-C(11)	128.08(10)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,y,-z+3/2

Table S3. Intra- and intermolecular hydrogen bonding data in keto-form crystals for **1** and **2.**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
1				
N(4)-H(4N)···O(1)#1	0.864(10)	1.879(14)	2.704(3)	159(3)
N(2)-H(2N)···S#2	0.855(10)	2.410(11)	3.261(3)	174(3)
N(5)-H(5N)···O(1)#3	0.850(10)	2.310(2)	2.966(3)	134(3)
O(2)-H(2A) ···S	0.820	2.810	3.524(12)	147.1
2				
N(4)-H(4N)···O	0.869(9)	1.869(10)	2.7118(13)	163.0(16)
N(2)-H(2N)···S#1	0.866(9)	2.345(10)	3.2057(11)	172.6(17)
N(5)-H(5N)···O(1)#2	0.863(9)	2.328(13)	3.0107(13)	136.2(14)

Symmetry codes: For 1 *#1 -x+2,y,-z+3/2* *#2 -x+1,-y+1,-z+1* *#3 -x+3/2,y+1/2,z*
For 2 *#1 -x+1,-y+1,-z+1* *#2 -x+3/2,y+1/2,z*

This journal is (c) The Royal Society of Chemistry and
The Centre National de la Recherche Scientifique, 2009

Theoretical Calculation

Computational details: we emphasized molecular energy of keto and enol forms according to the results calculated at the B3LYP/6-31G* level, as implemented in the GAUSSIAN 03W [1] program package both in gas phase and in methanol solution. Full geometry optimizations have been performed on the basis of the structure data of the keto form along with analytic real vibrational frequencies in order to conform to the structure obtained as minima on the potential energy surface. The reactions described here took place in methanol solution because single crystals are obtained by evaporating its methanol solution. So the methanol is chosen to study the effect of the solvent on the relative energy order of the isomers. It is known that the use of optimized gas phase structures does not introduce large errors for solutes of limited conformational changes.[2] Estimation of the solvent effects on energies was carried out using the polarizable continuum model (PCM) method.[3]

1 Frisch, M. J. *GAUSSIAN 03, Revision B.04*, Gaussian, Inc., Pittsburgh, PA, 2003. 13

2 a) Luque, F. J.; Negre, M. J.; Orozco, M. *J. Phys. Chem*. 1993, **97**, 4386–4391. b) Luque, F. J.; Zhang, Y.; Alemn, C.; Bachs, M.; Gao, J.; Orozco, M. *J. Phys. Chem.* 1996, **100**, 4269–4276;

3 a) Cammi, R.; Tomasi, J. *J. Comput. Chem.* 1995, **16**, 1449–1458. b) Tomasi, J.; Bonaccorsi, R. *Croat. Chem. Acta.* 1992, **65**, 29–54.

Table S4. Electronic energy (E), relative energy (ΔE), ZPE corrected energy (E_{corr}), Dipole moments in gas phase, electronin energy (E^{PCM}), relative energy (ΔE^{PCM}) in methanol solution.

	1 (enol form)	**1** (keto form)	**2** (enol form)	**2** (keto form)
E (a.u.)	-1581.840187	-1581.839647	-1621.156569	-1621.156144
ΔE(kcal/mol)	0.00	0.34	0.00	0.27
E_{corr} (a.u.)	-1581.490529	-1581.490122	-1620.778091	-1620.777764
Dipole moments (Debye)	5.23	9.28	5.13	9.22
E^{PCM} (a.u.)	-1581.865175	-1581.873474	-1621.181563	-1621.189458
ΔE^{PCM} (kcal/mol)	5.21	0.00	4.95	0.00

Absorption Spectroscopy

Changes in absorbance of **1** and **2** with only one input

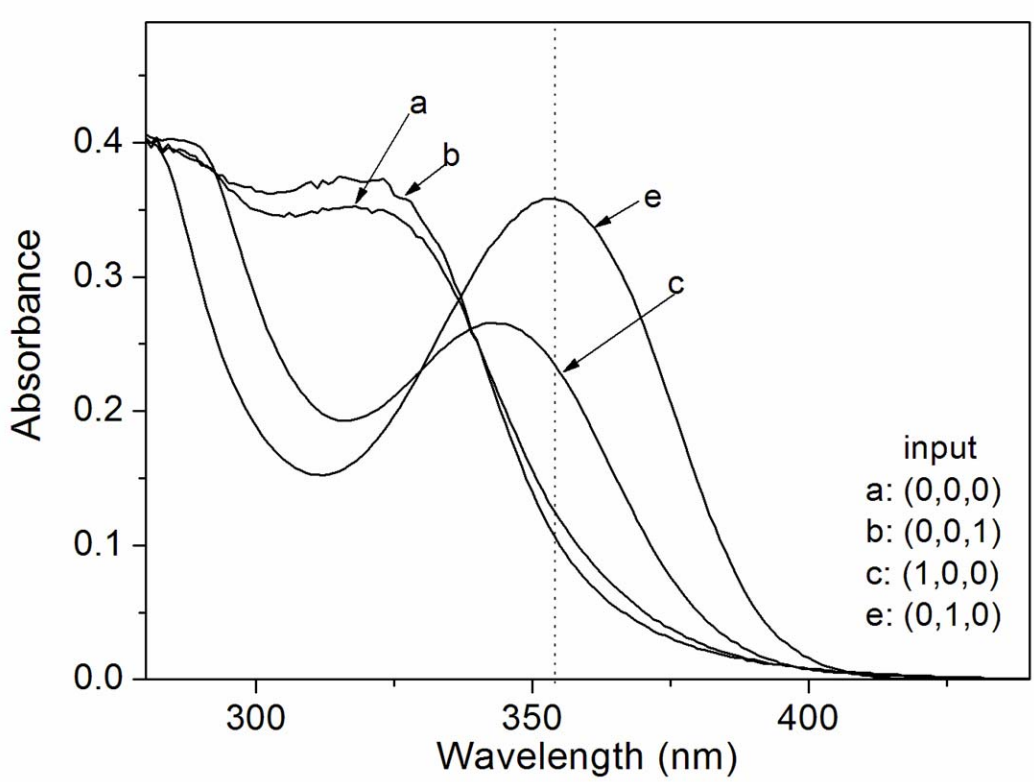

Figure S8. (A) Changes in the absorption spectra of **1** (2×10^{-5} mol/l, CH_3OH) (a) none, (b) in presence of HCl (0.1 M), (c) in presence of NaOH(0.1 M), (e) in presence of $ZnCl_2$ (0.1 M).

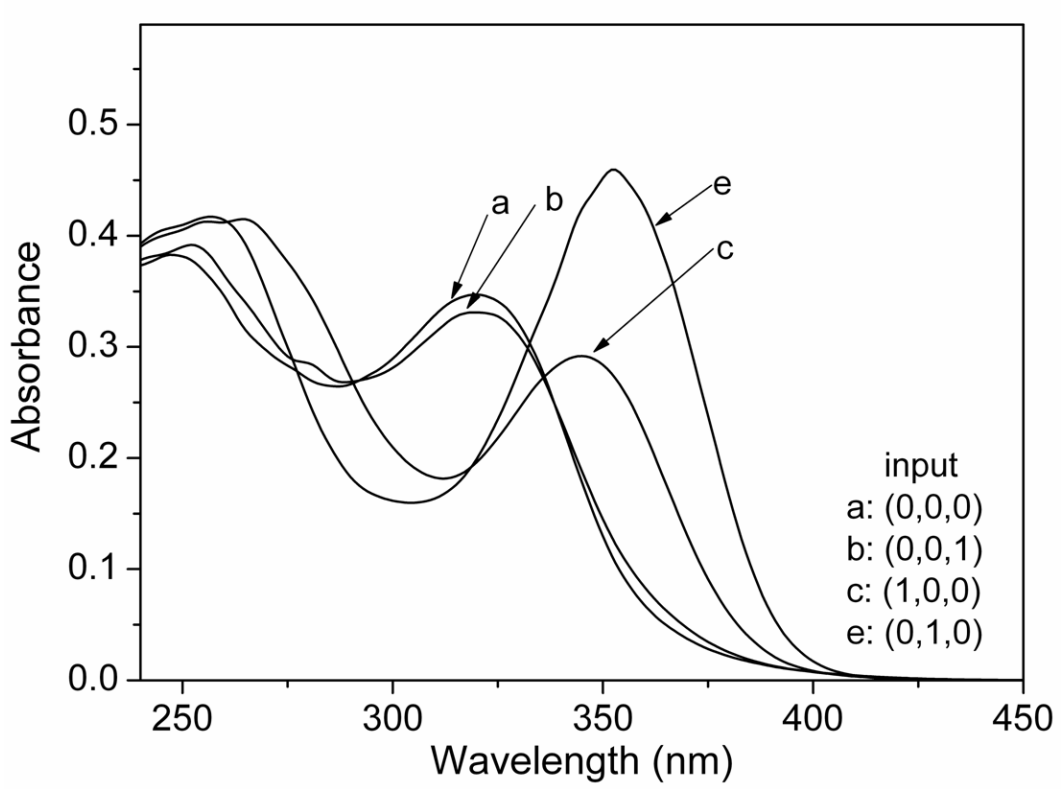

Figure S9. (A) Changes in the absorption spectra of **2** (2×10^{-5} mol/l, CH_3OH) (a) none, (b) in presence of HCl (0.1 M), (c) in presence of NaOH(0.1 M), (e) in presence of $ZnCl_2$ (0.1 M).

Changes in absorbance of **1** and **2** with NaOH, $ZnCl_2$ and HCl

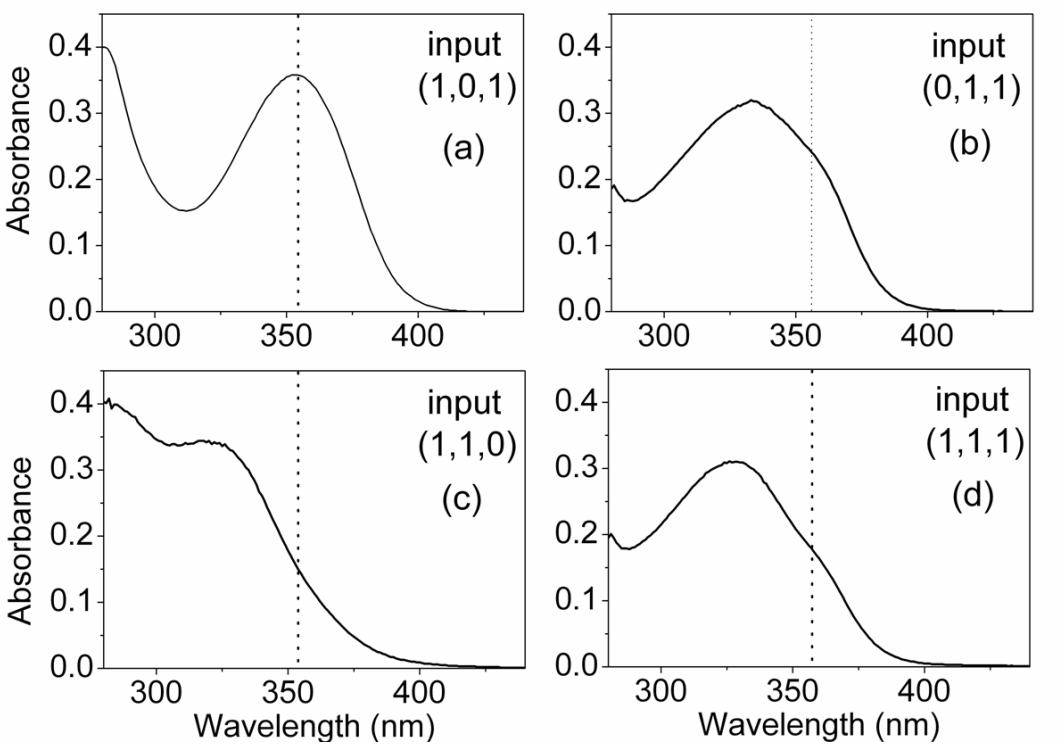

Figure S10. Absorption spectra of **1** (2×10^{-5} mol/l, CH_3OH) in presence of equimolar mixture HCl(0.1 M) and NaOH(0.1 M) (a), in presence of mixture $ZnCl_2$(0.1 M) and HCl(b), in presence of mixture NaOH and $ZnCl_2$(c) and in presence of mixture NaOH, $ZnCl_2$ and HCl(d).

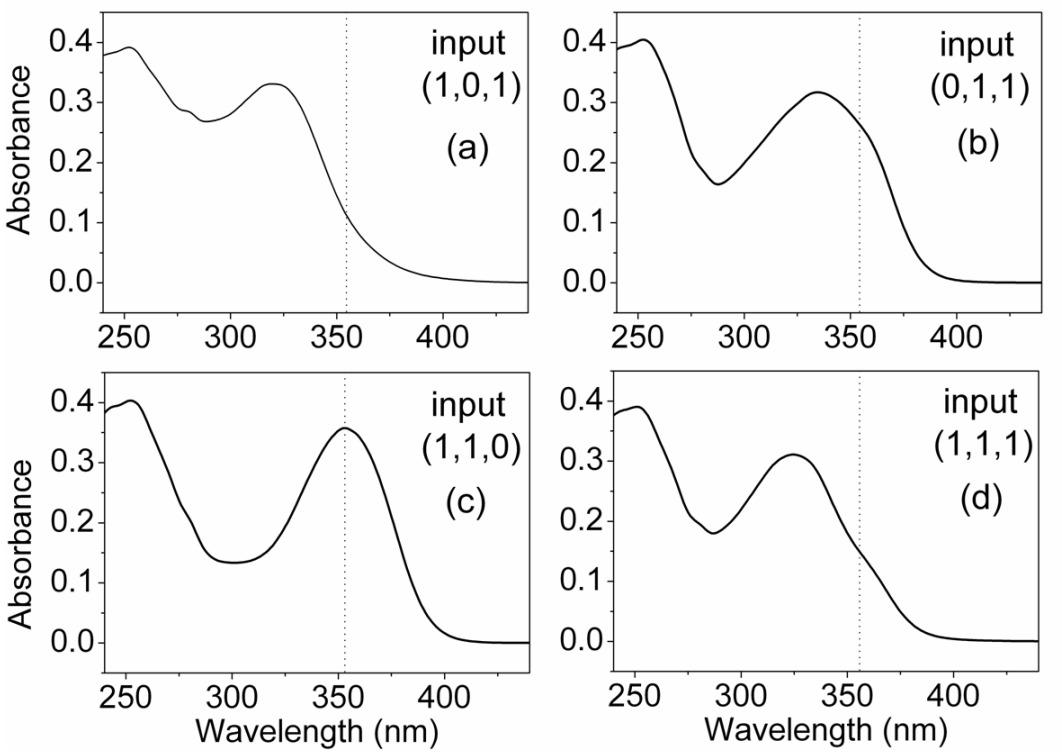

Figure S11. Absorption spectra of **2** (2×10^{-5} mol/l, CH_3OH) in presence of equimolar mixture HCl (0.1 M) and NaOH(0.1 M) (a), in presence of mixture $ZnCl_2$(0.1 M) and HCl(b), in presence of mixture NaOH and $ZnCl_2$(c) and in presence of mixture NaOH, $ZnCl_2$ and HCl(d).