Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Neighbouring group participation of thiol through aldehyde group assisted thiolysis of active ether: ratiometric and vapor phase fast detection of hydrogen sulfide in mixed aqueous media

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Calculation of the detection limit:

The detection limit (DL) of **R1** in emission and absorption spectra for HS^- was determined from the following equation[1]:

DL = K* Sb1/S

Where K = 2 or 3 (we take 2 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

From the graph Fig.S1(a), we get slope = 60382, and Sb1 value is 20898.96.

Thus using the formula we get the Detection Limit for H_2S/HS^- = 0.69 μM in emission.

From the graph Fig.S1(b), we get slope = 0.096, and Sb1 value is 0.080289.

Thus using the formula we get the Detection Limit for H_2S/HS^- = 1.67 μM in absorption.

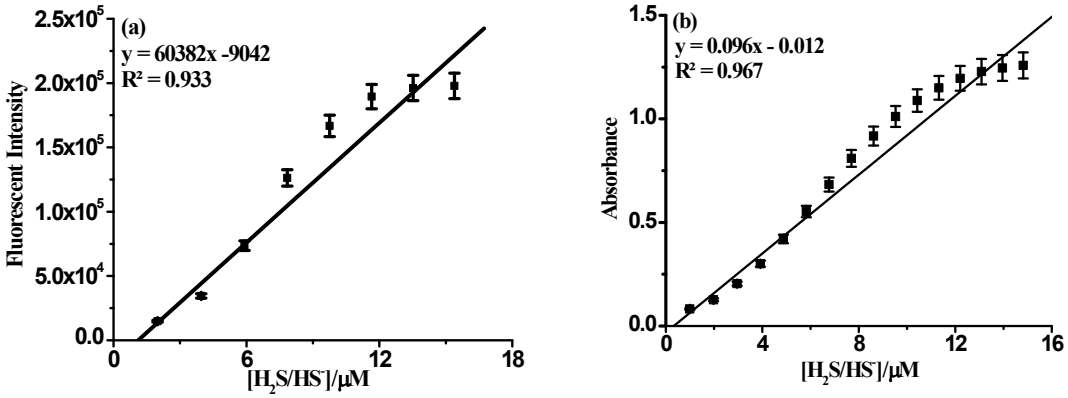


Figure S1 (a) Changes of emission intensity of **R1** (c = 2 x10^{-5}M) as a function of [H_2S/HS^-](*c* = 2x10^{-4}M) at 462 nm. **(b)** Changes of absorbance of **R1** (c= 2x10^{-5}M) as a function of [H_2S/HS^-] (*c* = 2x10^{-4}M) at 410 nm.

The changes of absorption curve of R1 (c = 2x10^{-5}M) at different time interval by addition of HS$^-$ (c =2x10^{-4}) and calculation of first order rate constant:

Fig S2(a) represents the changes of absorbance at different time interval by addition of HS$^-$.

From the time vs. absorbance plot (Fig.S2(b)) at fixed wavelength at 410 mm by using first order rate equation we get the rate constant K=slope x 2.303= 0.083x 2.303=19.11x10^{-2} Sec^{-1}.

(a) (b)

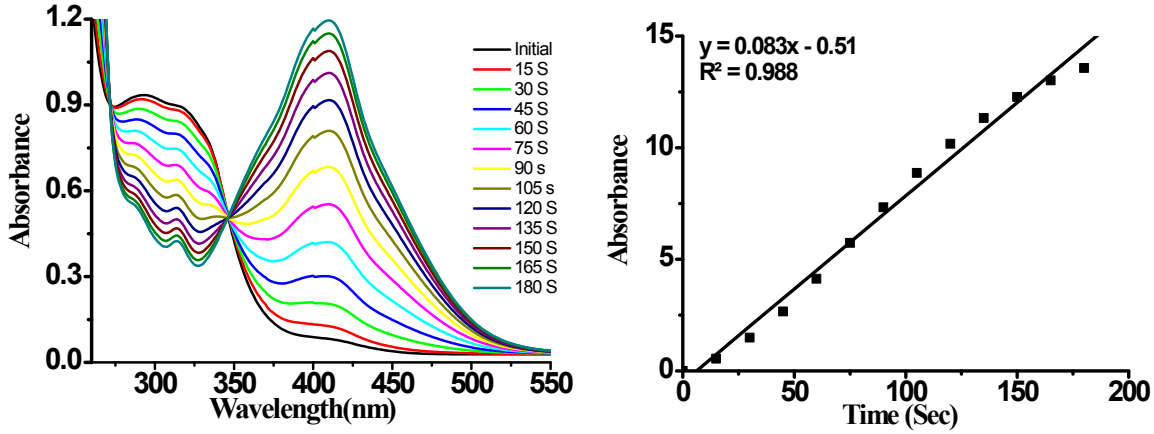


Figure S2: (a) The changes of absorbance at different wavelength of **R1** in presence of HS$^-$ in CH_3CN-HEPES buffer (50/50, v/v, 25°C) at pH 7.4. **Inset**-Different time intervals are shown in the rectangle ('S' denotes Second). (b) The first order rate equation by using Time vs. absorbance plot at 410 nm.

$_P$H Titration:

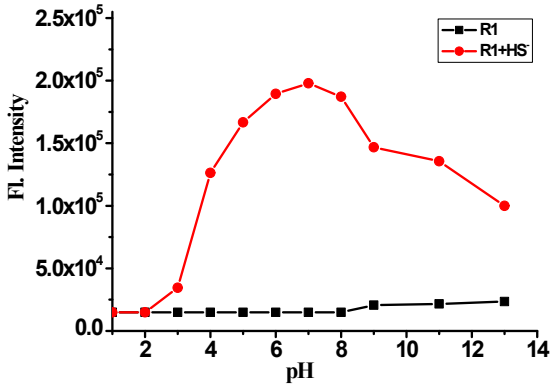


Figure S3: The effect of pH on the fluorescence intensity changes of **R1** (c = 2×10^{-5} M) in presence and absence of [H_2S/HS$^-$] (c = 2×10^{-4}M).

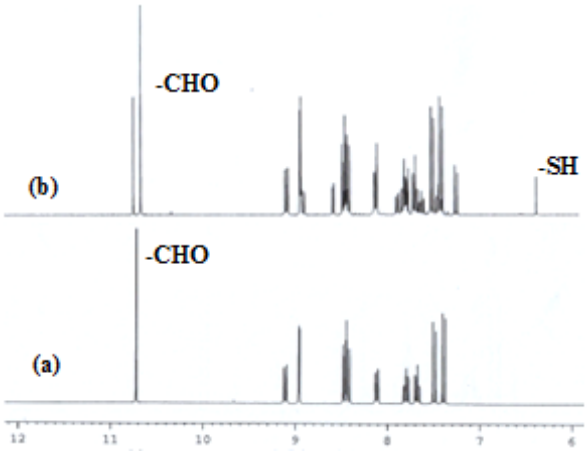
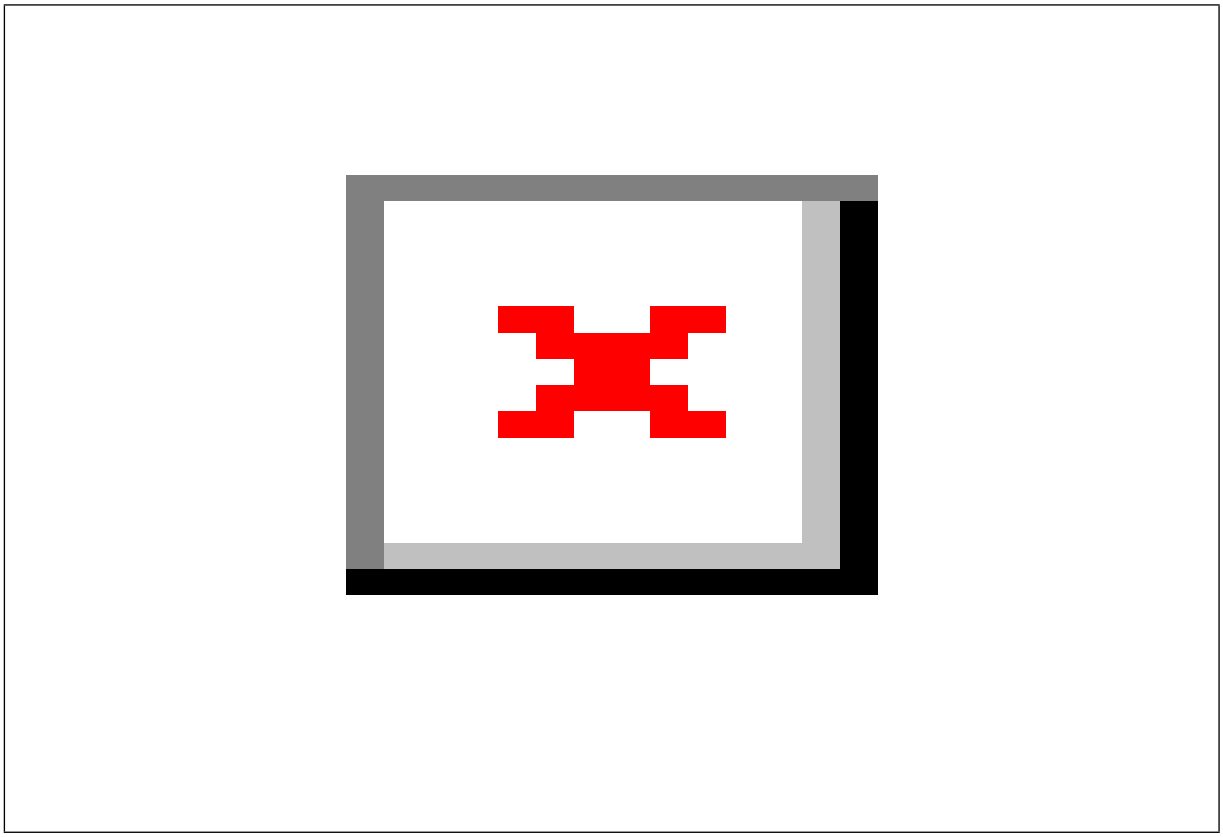


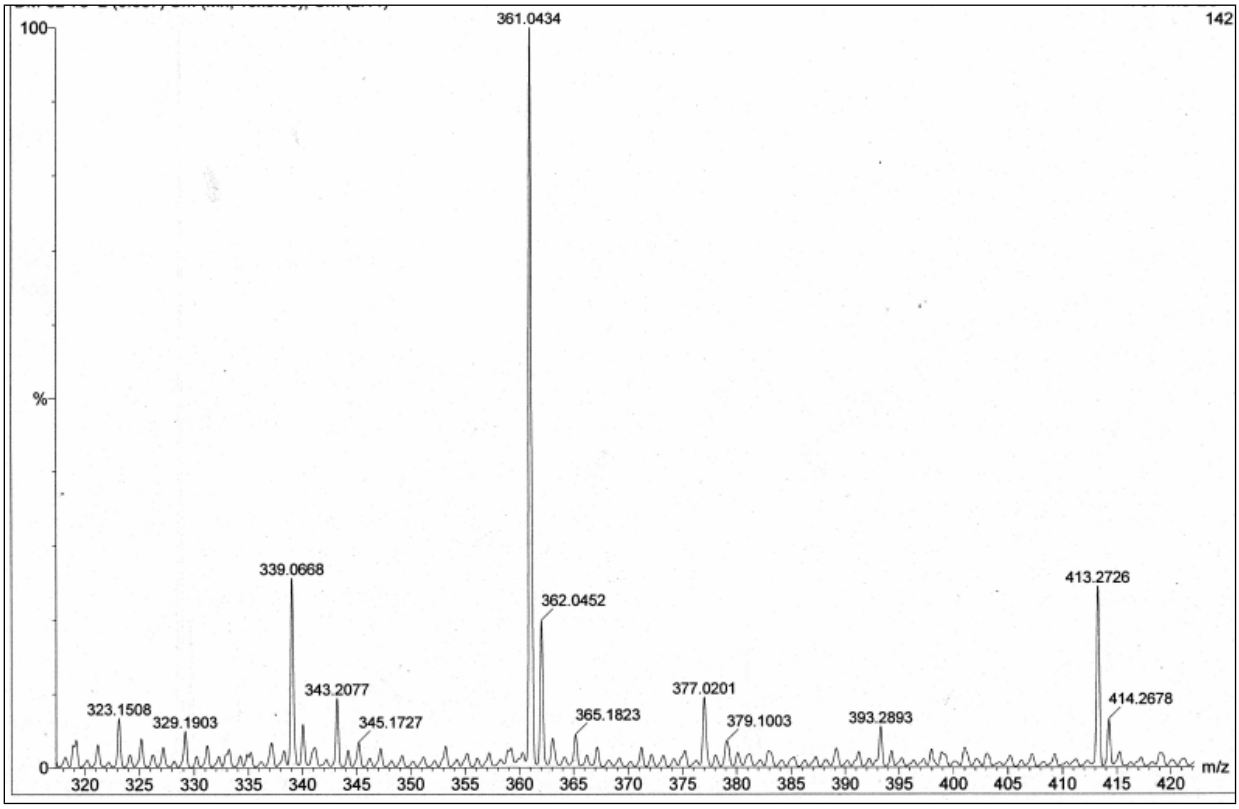
Figure S4: Partial ^{1}H NMR spectra of receptor (a) **R1 and** (b) **R1** + H_2S in d^6-DMSO: D_2O.

Without separation the resulting product by the reaction of H_2S with **R1**, the mechanistic view of the sensing of H_2S in **R1** platform can also be verified by the ^{1}H-NMR titration spectra. The NMR peak of aldehyde proton at δ 10.72 ppm group of **R1** splits into two signals due to the probable rapid equilibrium of 2-hydroxy-1-naphthaldehyde with its deprotonation form of the naphthyl-hydroxyl group in presence of H_2S which is shown in Route 1. The proton signal of –SH group appears at δ 6.33 ppm of 2,4-dinitrothiophenol (though –SH peak is exchangeable with D_2O, the excess presence of H_2S over D_2O could not possibly make the peak to disappear). All the others aromatic protons signals of 2-hydroxy-1-naphthaldehyde and 2,4-dinitrothiophenol shifted slightly on breaking the ether linkage of **R1** and the number of the total proton signal increases for the rapid equilibrium.

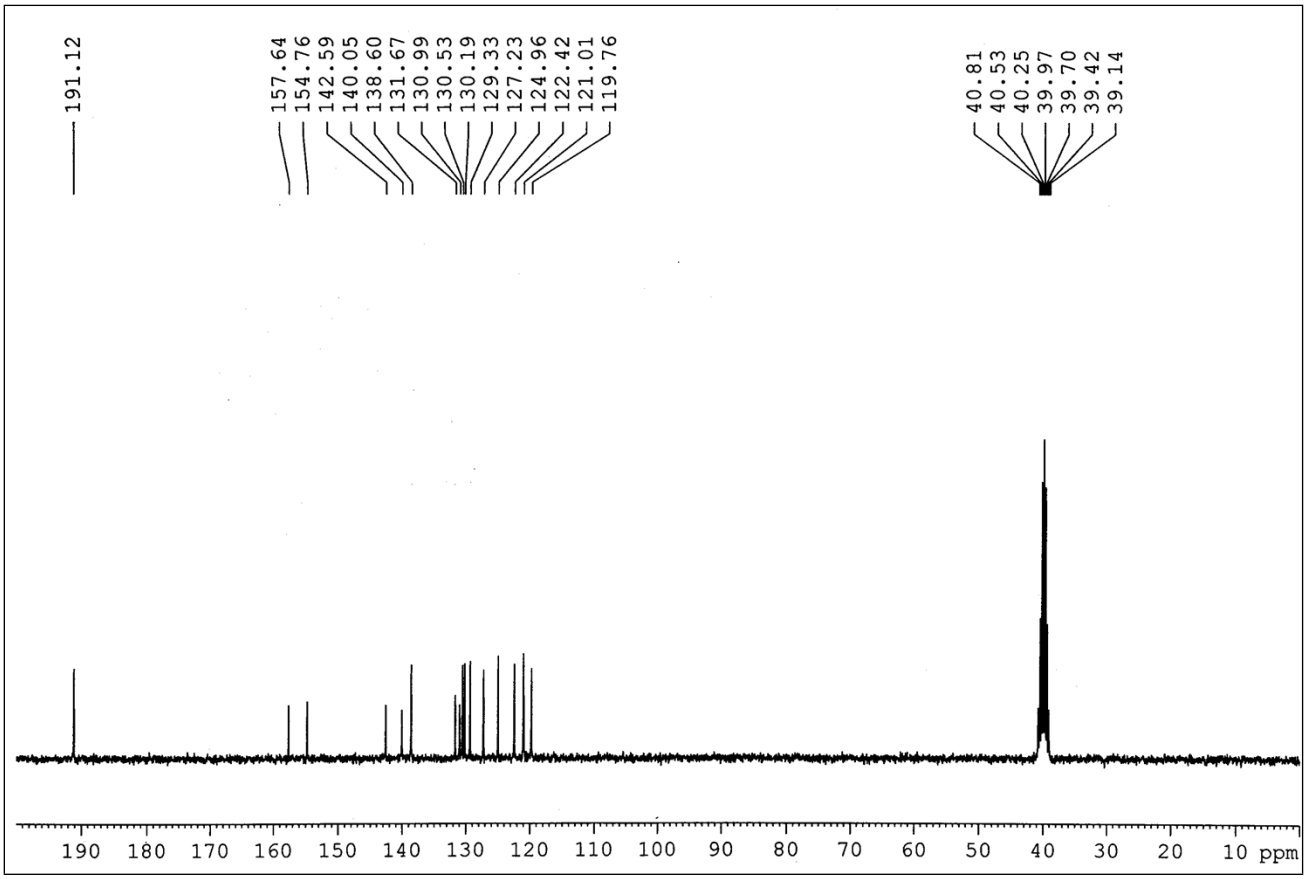
^{1}H NMR spectra (S5) of R1:



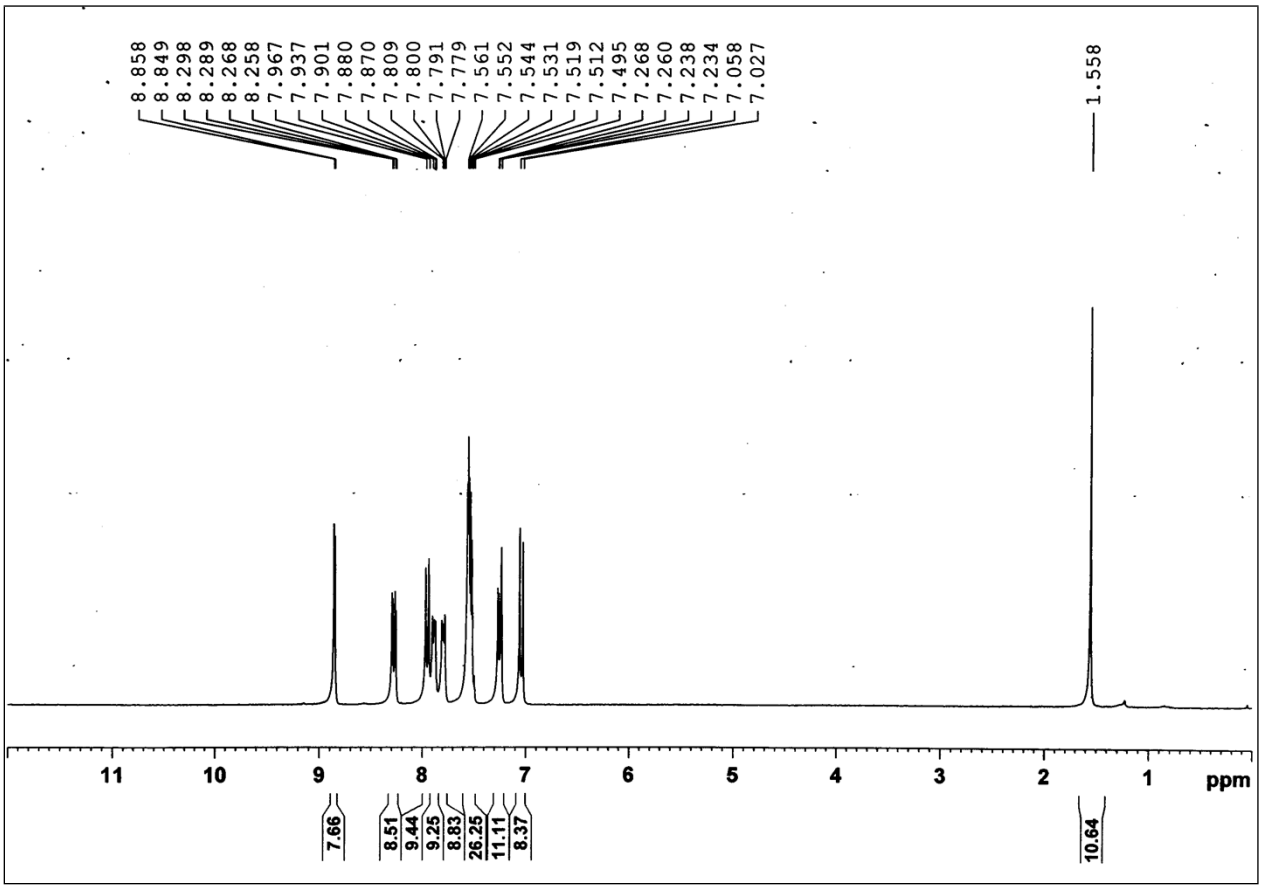
Mass spectra (S6) of R1:



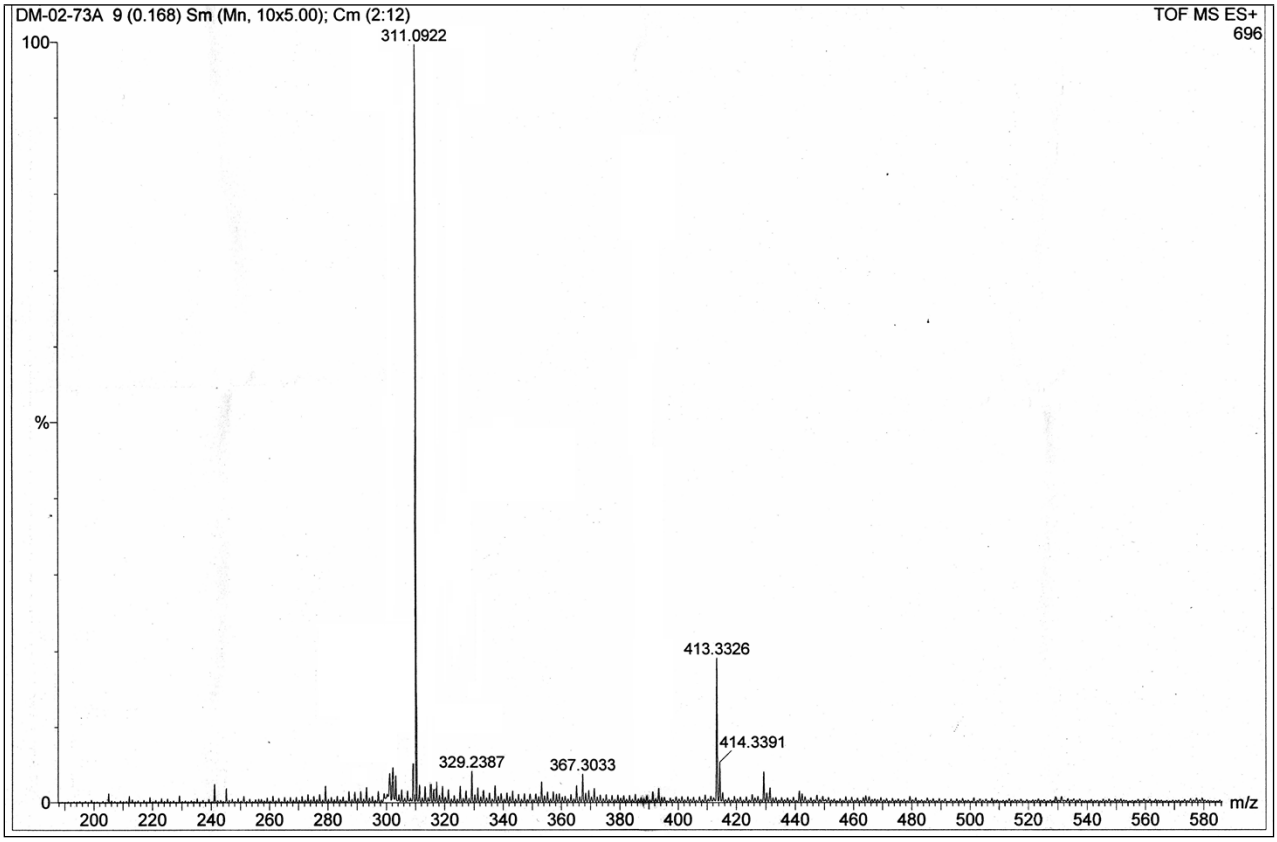
^{13}C NMR spectra (S7) of R1:



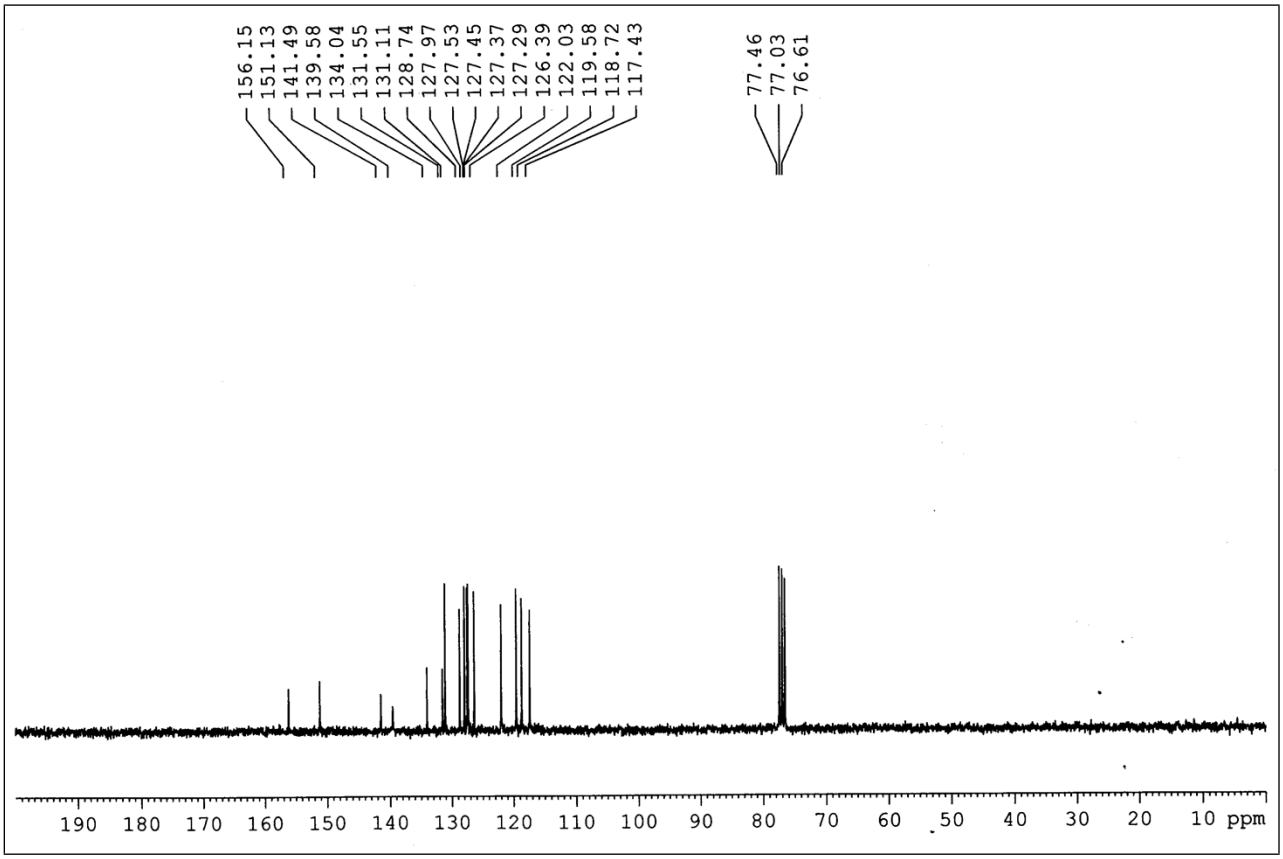
^{1}H NMR spectra (S8) of R2:



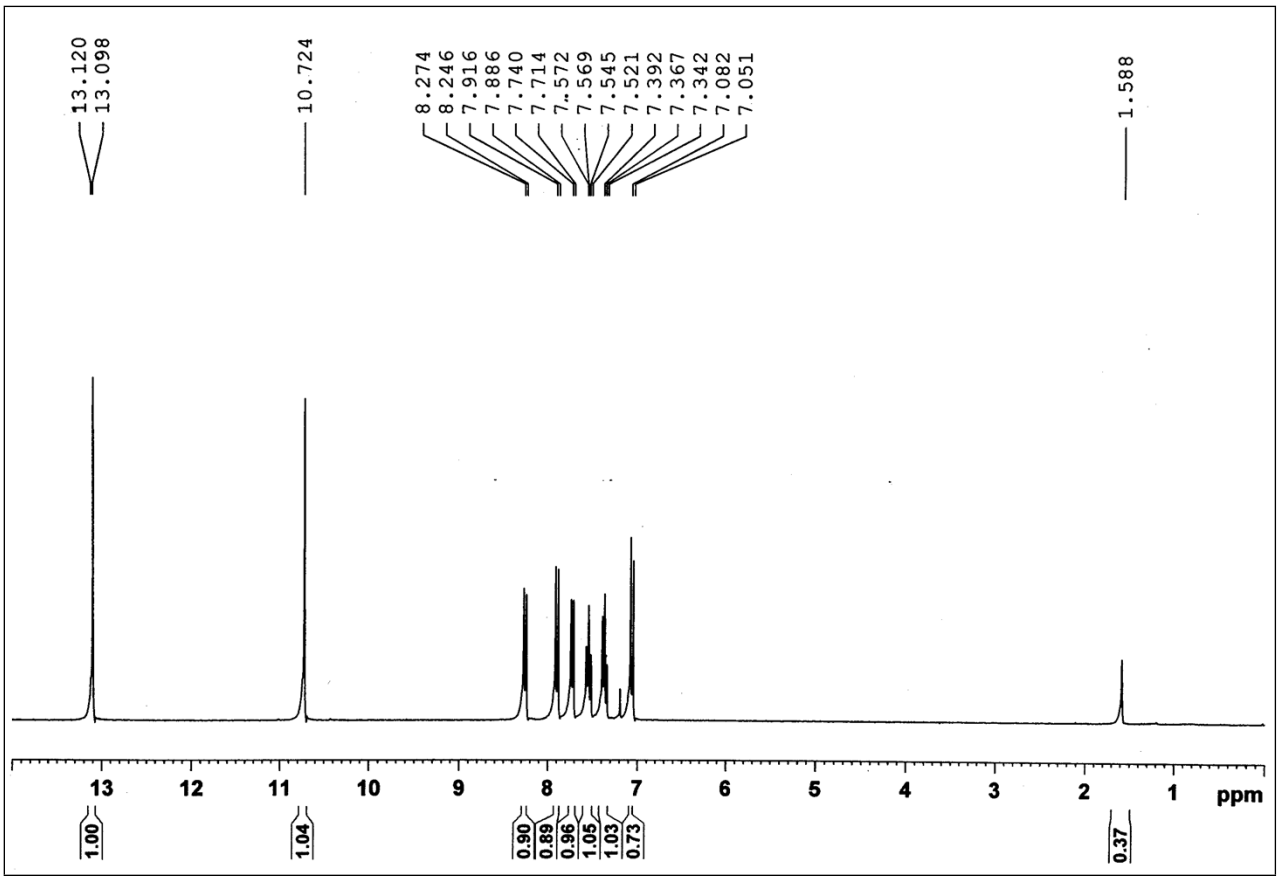
Mass spectra (S9) of R2:



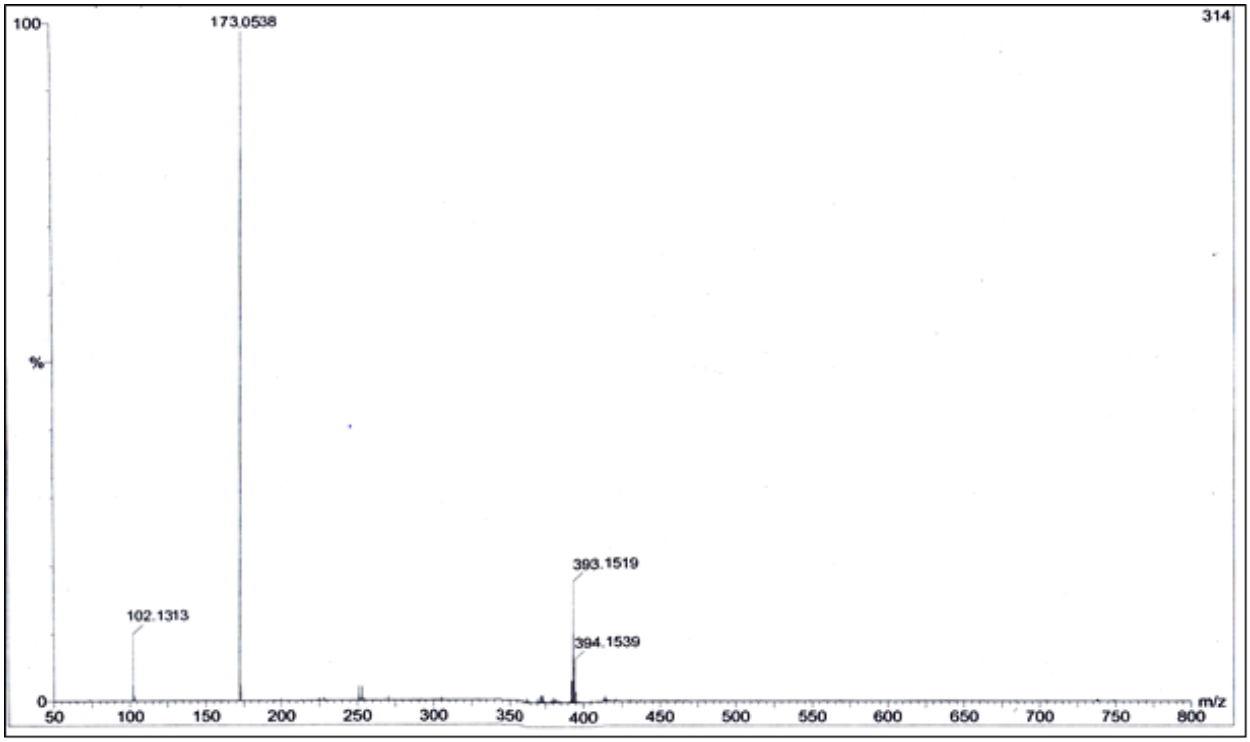
^{13}C NMR spectra (S10) of R2:



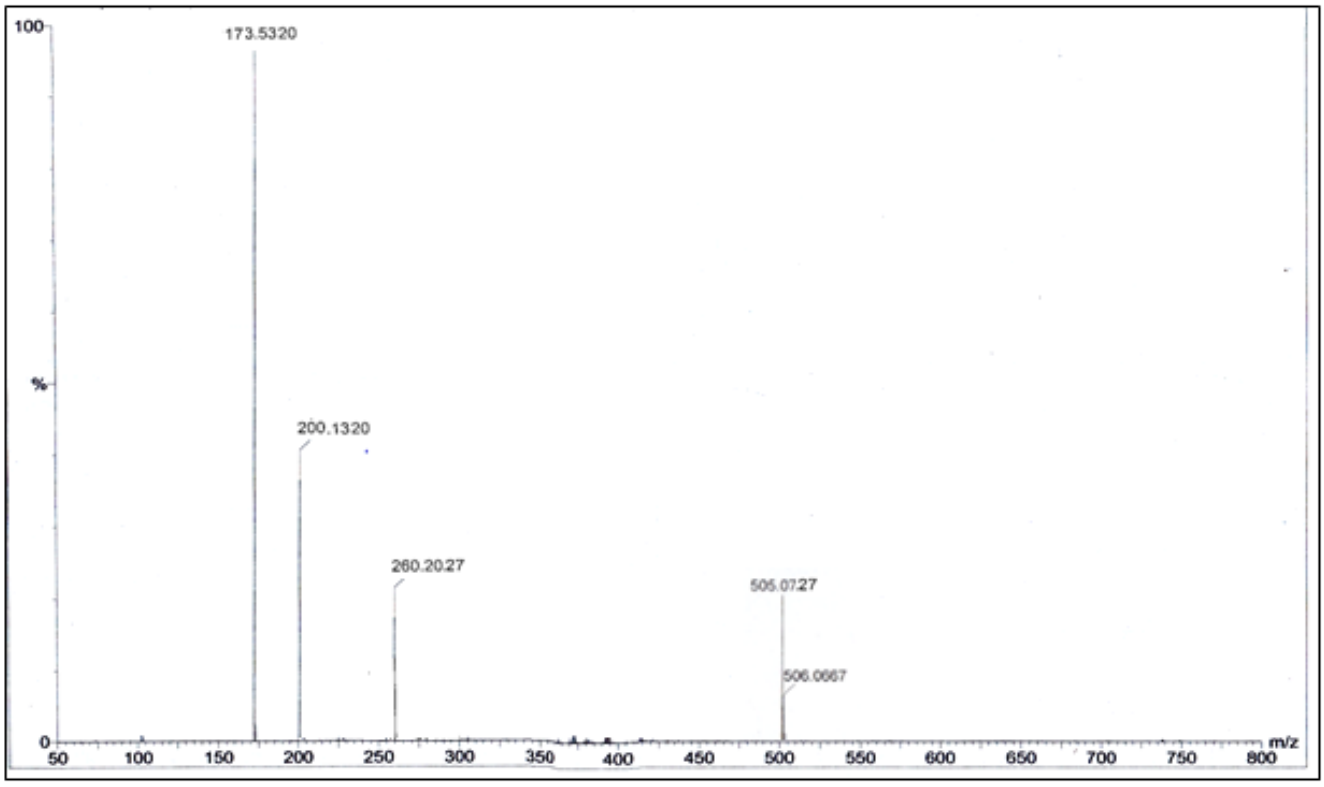
^{1}H NMR spectra (S11) of isolated product R1P from R1:



Mass spectra (S12) of the isolated product R1P from R1:



Mass spectra (S13) of the resulting crude product of R1 on treatment with H_2S/HS^-:



X-ray crystal structure analysis:

A yellow, block shaped single crystal of the compound **R1**, with dimensions of 0.351 mm × 0.280 mm × 0.168 mm, and a yellow, plate shaped single crystal of the compound **R2**, with dimensions of 0.624 mm × 0.129 mm × 0.074 mm, were selected and mounted on a Bruker APEX-II DUO CCD diffractometer with fine-focus sealed tube graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) at room temperature. The data were processed with SAINT and corrected for absorption using SADABS [2]. The structure was solved by direct method using the program SHELXTL [3] and was refined by full-matrix least squares technique on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were positioned geometrically [C—H = 0.93 Å] and refined using riding model with isotropic displacement parameters set to 1.2 times the equivalent isotropic *U* values of the parent carbon atoms. A summary of crystal data and parameters for structure refinement details are given in Table S1 whereas the hydrogen-bond geometry can be found in Table S2. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with CCDC 1033193 (**R1**) and CCDC 1045108 (R2). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK. Fax: +44-(0)1223-336033 or e-mail:deposit@ccdc.cam.ac.uk

Table S1 Experimental details for X-ray Crystallography

Crystal data	**R1 (CCDC 1033193)**	**R2 (CCDC 1045108)**
Chemical formula	$C_{17}H_{10}N_2O_6$	$C_{16}H_{10}N_2O_5$
M_r	338.27	310.26
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	294	294
a, b, c (Å)	8.2271 (12), 13.429 (2), 13.894 (2)	21.9055 (19), 4.6272 (4),13.7499 (12)
β (°)	101.830 (3)	92.655 (2)
V (Å^3)	1502.4 (4)	1392.2 (2)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.12	0.11
Crystal size (mm)	0.35 × 0.28 × 0.17	0.62 × 0.13 × 0.07
Data collection		
Diffractometer	Bruker *SMART APEX* II DUO CCD area-detector diffractometer	
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)	
T_{min}, T_{max}	0.960, 0.981	0.933, 0.992
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7157, 2742, 1997	18679, 2898, 1973
R_{int}	0.019	0.042
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.606	0.629
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.126, 1.05	0.051, 0.160, 1.05
No. of reflections	2742	2898
No. of parameters	226	208
H-atom treatment	H-atom parameters constrained	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.21	0.40, −0.19

Table S2 Hydrogen-bond geometry (Å, º)

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
Compound R1				
C3—H3*A*···O6	0.93	2.25	2.885 (3)	125
C8—H8*A*···O6^{i}	0.93	2.47	3.341 (2)	155
C12—H12*A*···O4^{ii}	0.93	2.43	3.340 (3)	166
Compound R2				
C13—H13A···O4^{iii}	0.93	2.50	3.397 (3)	161
C16—H16A···O3^{iv}	0.93	2.45	3.144 (3)	131

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*, −*y*+3/2, *z*−1/2; (iii) −x+1, −y+1, −z+1; (iv) x, −y+3/2, z−1/2.

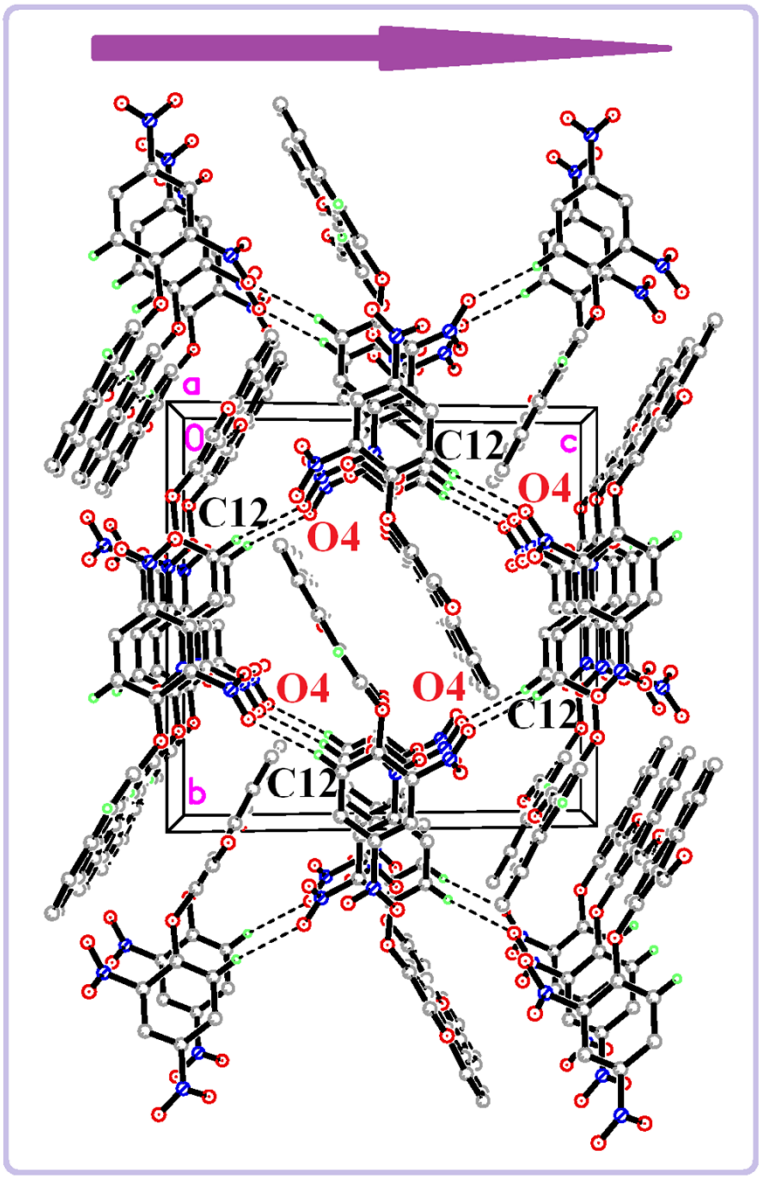


Figure S14. The crystal packing of **R1** viewed along the *a* axis. H atoms not involved in intermolecular interactions (dashed lines) have been omitted for clarity.

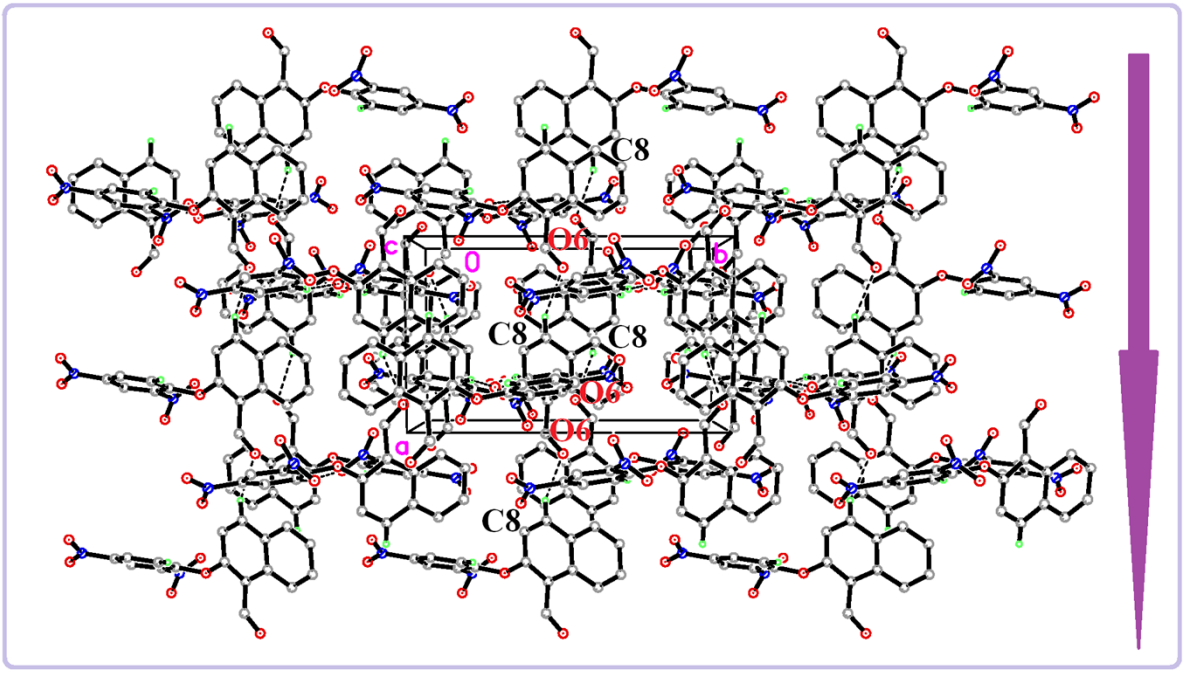


Figure S15. The crystal packing of **R1** viewed along the *c* axis. H atoms not involved in intermolecular interactions (dashed lines) have been omitted for clarity.

References:

1. M. Shortreed, R. Kopelman, M. Kuhn, B. Hoyland, *Anal. Chem*., 1996, **68**, 1414. (b) W. Lin,; Yuan, L.; Cao, Z.; Feng, Y.; Long, L. *Chem. Eur. J*. 2009, **15**, 5096.(c) Zhu, M.; Yuan, M.; Liu, X.; Xu, J.; Lv, J.; Huang, C.; Liu, H.; Li, Y.; Wang, S.; Zhu, D. *Org. Lett.* 2008, **10**, 1481-1484.

2. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Winconsin, USA.2009.

3. Sheldrick, G.M. A short history of SHELX. Acta Cryst.2008, A64, 112.