

Electronic Supporting Information (ESI)

An Improved Organic/Inorganic Solid Receptor for Colorimetric Cyanide-Chemosensing in Water: Towards New Mechanism Aspects, Simplistic Use and Portability

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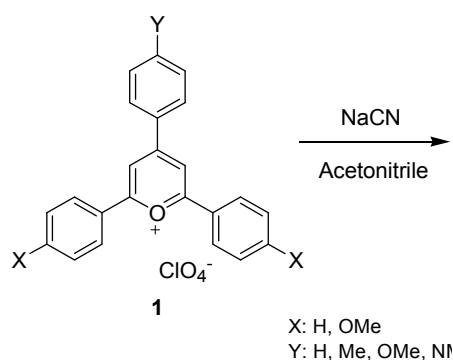
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1. Experimental

1.1. General

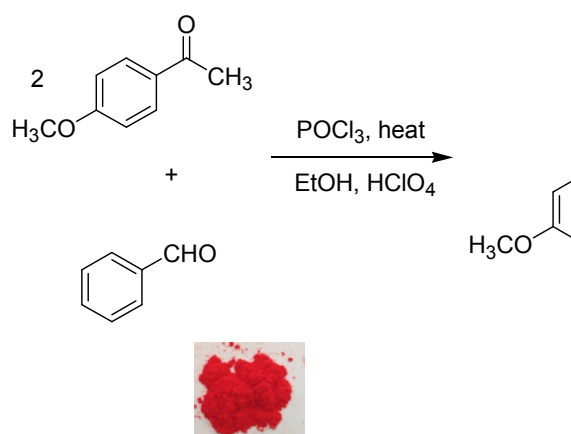
Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. Monitoring of the reactions was accomplished by TLC. IR spectra were obtained on a Bomem MB:102 FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer at 400 and 100 MHz, respectively, in CDCl_3 or DMSO-d_6 with tetramethylsilane as an internal standard. MS spectra were measured on an Agilent 5975 Mass Spectrophotometer. All absorption measurements and absorption spectra were performed using PG instrument UV-Vis spectrophotometer model T80 (UK). Fluorescence measurements were performed using a Cary Eclipse Fluorescence Spectrophotometer. The X-ray measurement of the product **2a** was made on a Bruker-Nonius X8 ApexII diffractometer equipped with a CCD area detector by using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) generated from a sealed tube source. Data were collected and reduced by SAINT software in the Bruker package [1]. The structure was solved by direct methods [2] and then developed by least squares refinement on F^2 [3, 4]. All non-H atoms were placed in calculated positions and refined as isotropic with the "riding-model technique".



Scheme S1. Transformation of triarylpyrylium derivatives **1** into corresponding aromatic cyanodienones **2**

1.2. Synthesis of 2,6-bis(4-methoxyphenyl)-4-phenylpyrylium perchlorate (**1a**)

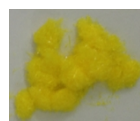
Benzaldehyde (0.06 mol) and 4-methoxy acetophenone (0.12 mol) were stirred at room temperature; POCl_3 (5 mL) was added dropwise during 30 min. The mixture was stirred at 65°C for 2 h. Then, ethanol (31.5 mL) and perchloric acid 70% (7.5 mL) was added respectively. The mixture was excluded in order to form a precipitate for 24 h. The precipitates recrystallized from acetic acid. The final product was isolated as deep red solid (49% yield, m.p. $285\text{-}286^\circ\text{C}$). ^1H NMR (400 MHz, CDCl_3): $\delta = 3.99$ (s, 6H, OCH_3), 7.22-7.25, 7.67-8.35 (m, 13H, Ar-H), 8.36 (s, 2H, H^1 , H^2) ppm; ^{13}C NMR (100MHz, DMSO-d_6): $\delta = 56.5$ (OCH_3), 112.9, 115.8, 121.7 (ArC), 129.9, 130.1 (ArC_q), 131.4 (ArC), 133.1, 135.0, 163.5 (ArC_q), 165.2, 169.2 (ArC) ppm.



Scheme S2. The synthetic procedure for **1a**

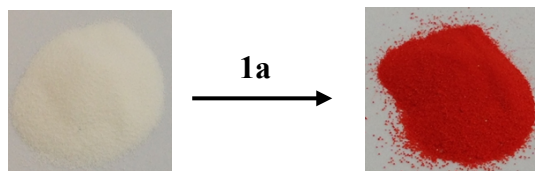
1.3. Synthesis of (2Z,4E)-6-oxo-2,4,6-triphenyl-2,4-hexadienenitrile (**2a**)

The 2,6-bis(4-methoxyphenyl)-4-phenylpyrylium perchlorate **1a** (1 mmol) were stirred with sodium cyanide (2 mmol) at room temperature in acetonitrile (10 mL), the reaction were monitored by TLC using a 20:80 mixture of ether:*n*-hexan as eluent. After completion of the reaction, the solvent was evaporated under vacuum and the product **2a** recrystallized from EtOH. The final product was isolated as light yellow solid (86% yield, m.p. 127-129 °C). MS *m/z*: 395.2 [M^+]; IR (neat): $\nu = 2217$ (CN), 1638 (CO) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta = 3.87, 3.91$ (s, 6H, OCH_3), 7.24 (s, 1H, H^1), 6.95-7.00, 7.49-8.04 (m, 13H, Ar-H), 8.35 (s, 1H, H^2) ppm; ^{13}C NMR (100MHz, CDCl_3): $\delta = 55.4, 55.5$ (OCH_3), 113.9 (C-5), 114.3 (ArC), 115.7 (C-2), 118.5 (C-1), 125.8 (ArC), 126.3 (ArC_q), 127.9, 128.7, 128.8, 129.9, 130.7 (ArC), 131.5(ArC_q), 138.9 (C-3), 139.4, 151.0 (ArC_q), 160.9 (C-4), 163.5 (ArC_q), 188.7 (C-6) ppm.



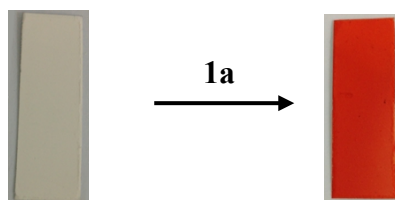
1.4. Sensitizing the neutral Al_2O_3

A 50-ml round-bottom flask was charged with 0.25 g (0.54 mmol) of compound **1a** suspended in 50 ml of dichloromethane, and then 4.0 g of γ -Alumina was added. The flask was transferred to a rotary evaporator, and the dichloromethane was removed under reduced pressure, keeping the bath temperature below 65 °C. Dye-impregnated γ -alumina was then dried at room temperature.



1.5. Sensitizing the Al_2O_3 TLC strips

Compound **1a** was absorbed into Al_2O_3 TLC strip by immersing the TLC in a suspension of the compound **1a** (5 mM) in dichloromethane maintained in the refrigerator. It was allowed to stand for another 12 h so the dye could impregnate the TLC strip. A deep red **1a**/ Al_2O_3 TLC strip was obtained.

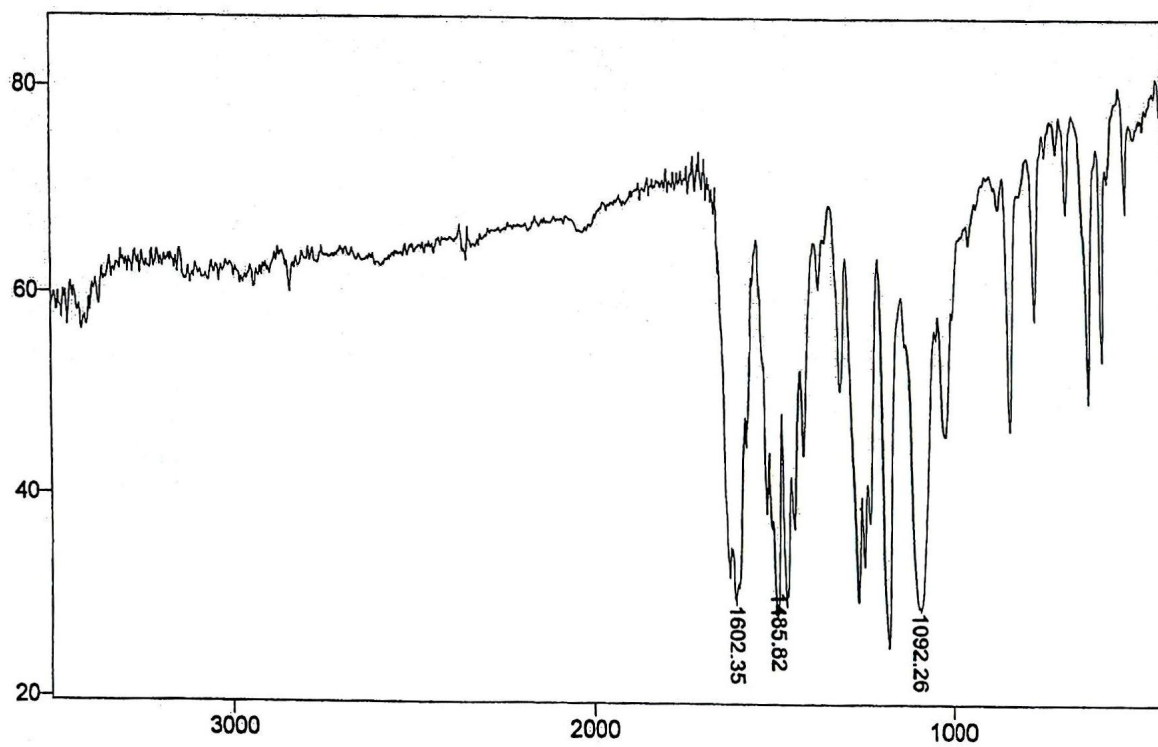


1.6. References

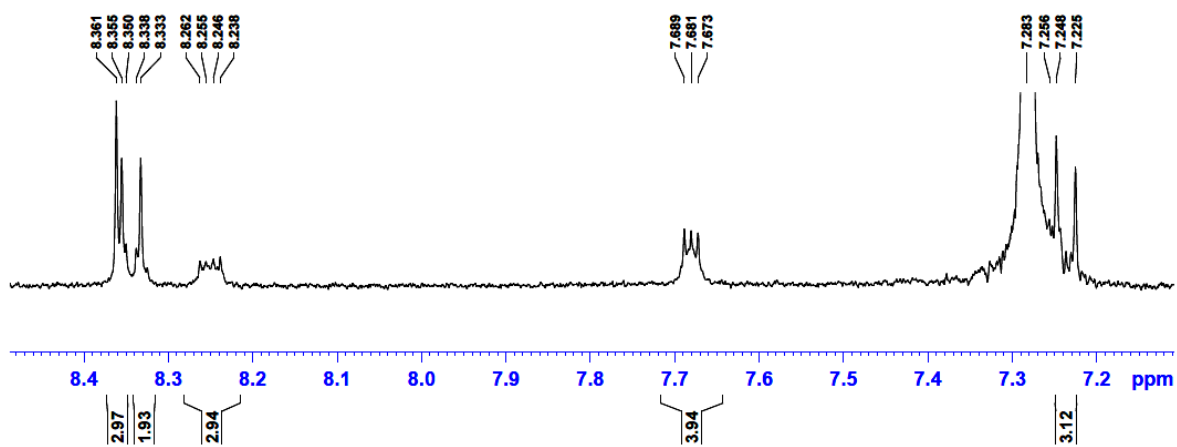
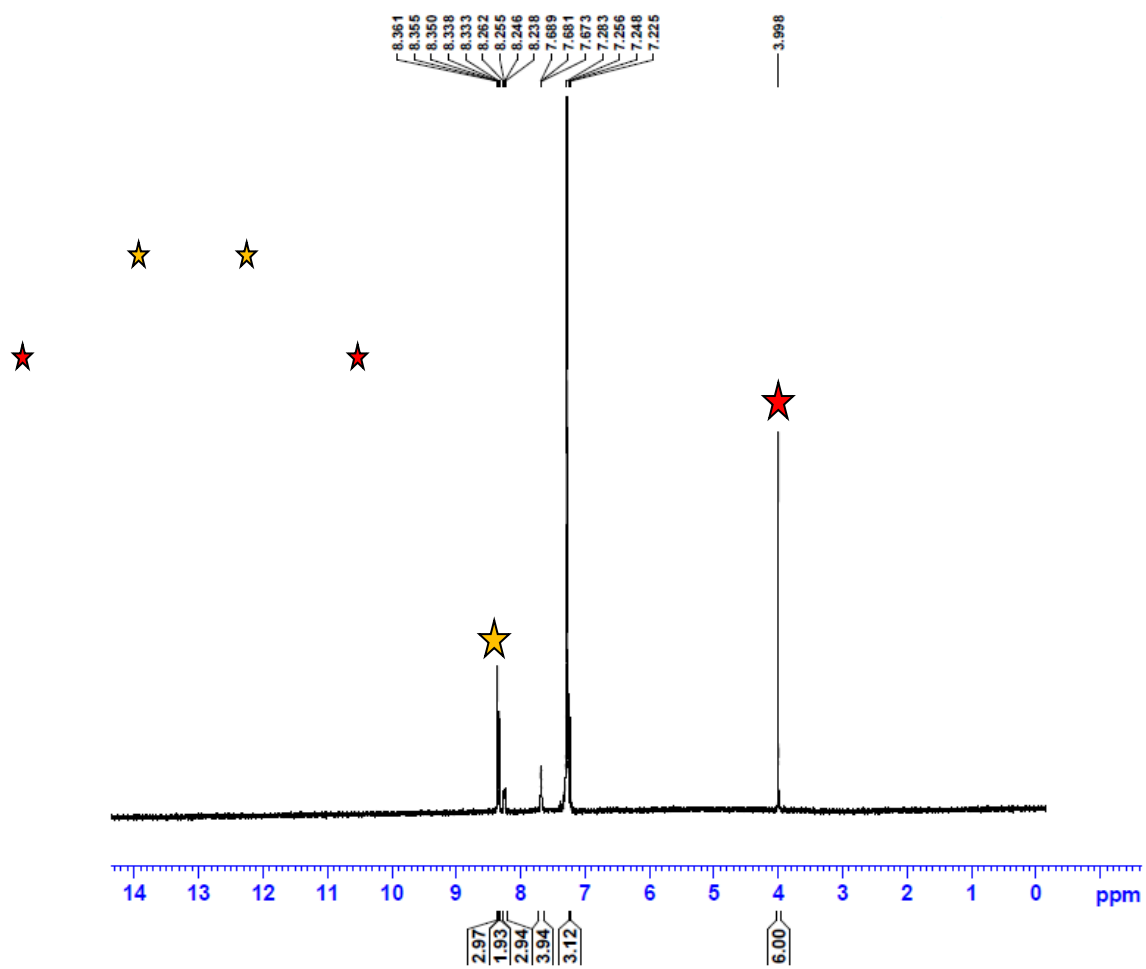
- [1] Bruker AXS Inc., SAINT (Version 6.02), Madison, Wisconsin, USA, 1999.
- [2] M.C. Burla, R. Caliendo, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 38 (2005) 381–388.
- [3] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [4] SHELXT LN, Version 5.10, Bruker Analytical X-ray Inc., Madison, WI, USA, 1998.

2. Structure characterizations for 1a

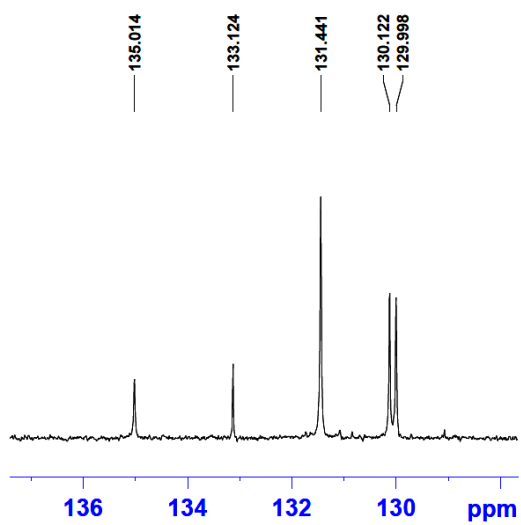
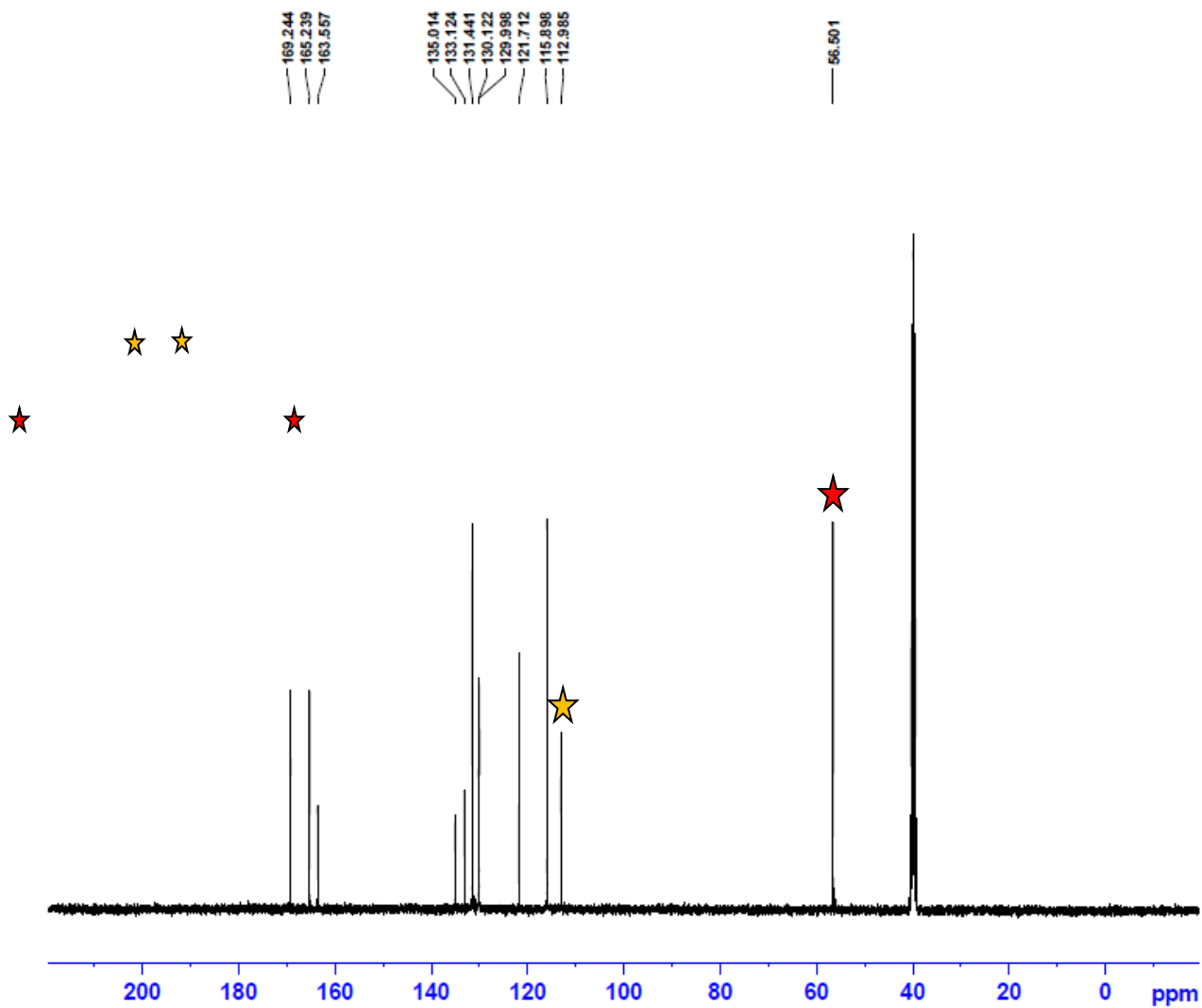
2.1. IR spectra



2.2. ^1H NMR spectra in CDCl_3

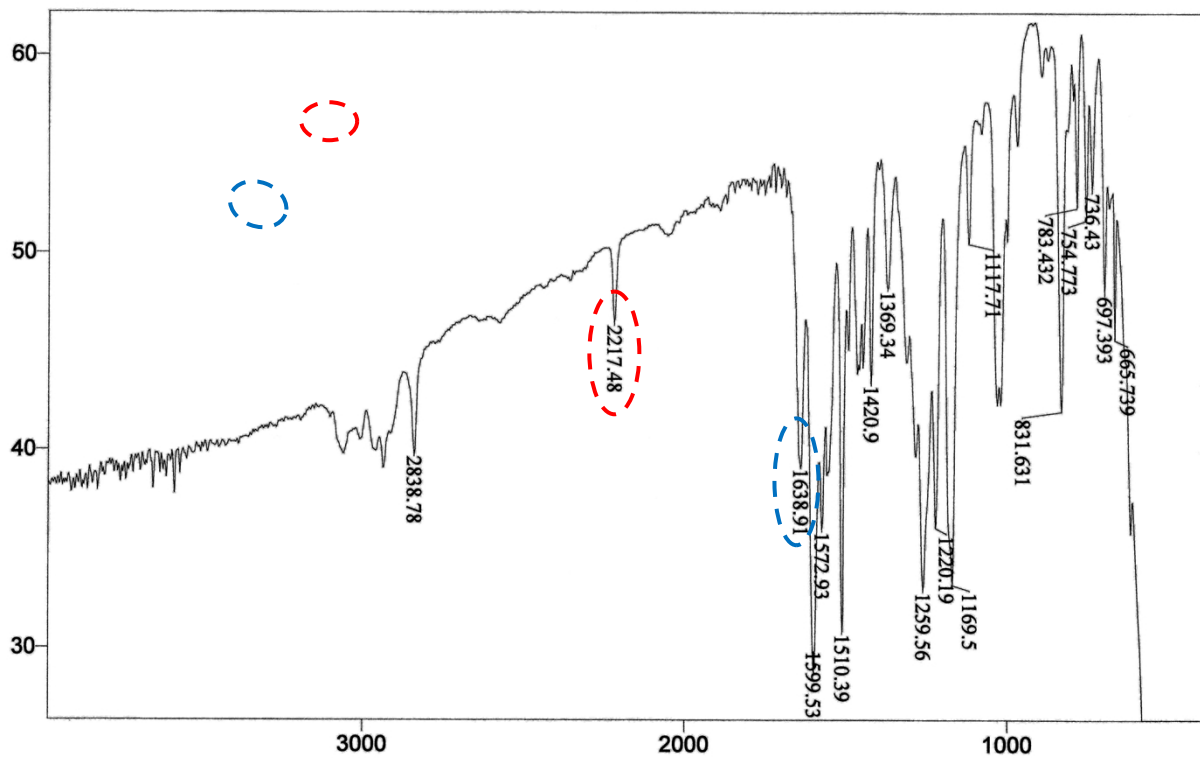


2.3. ^{13}C NMR spectra in $\text{DMSO-}d_6$

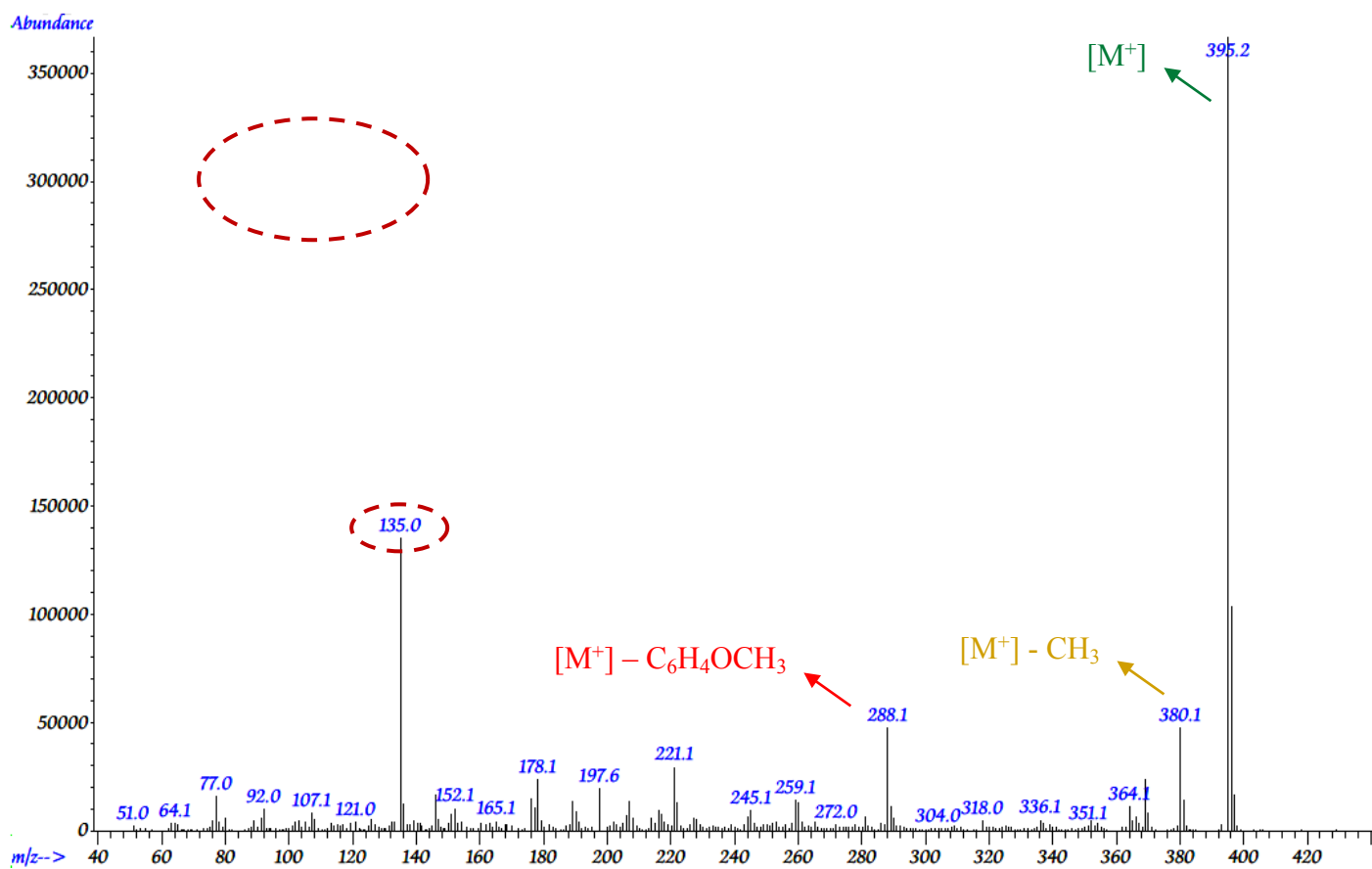


3. Structure characterizations for 2a

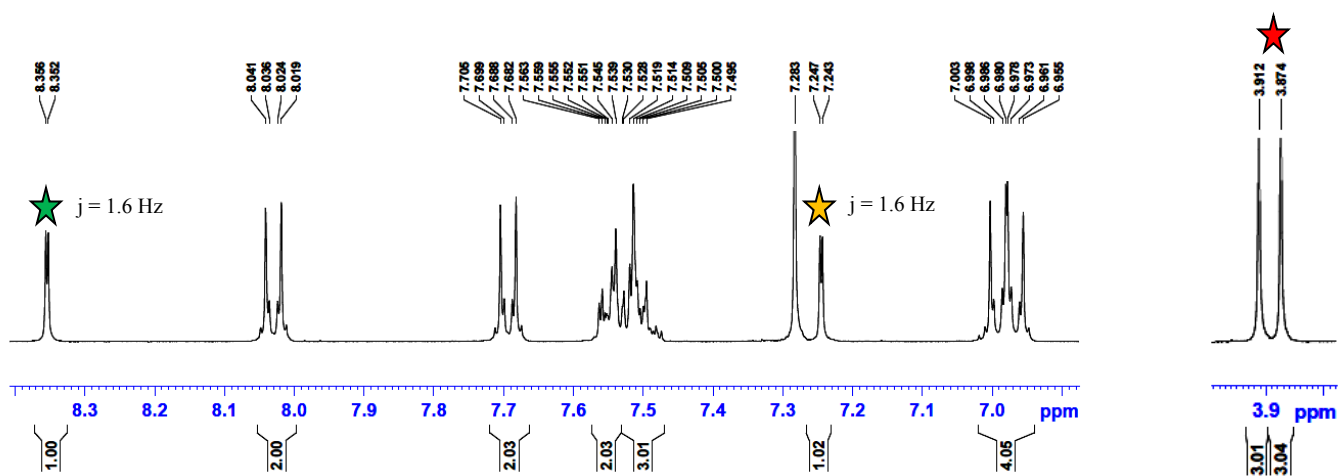
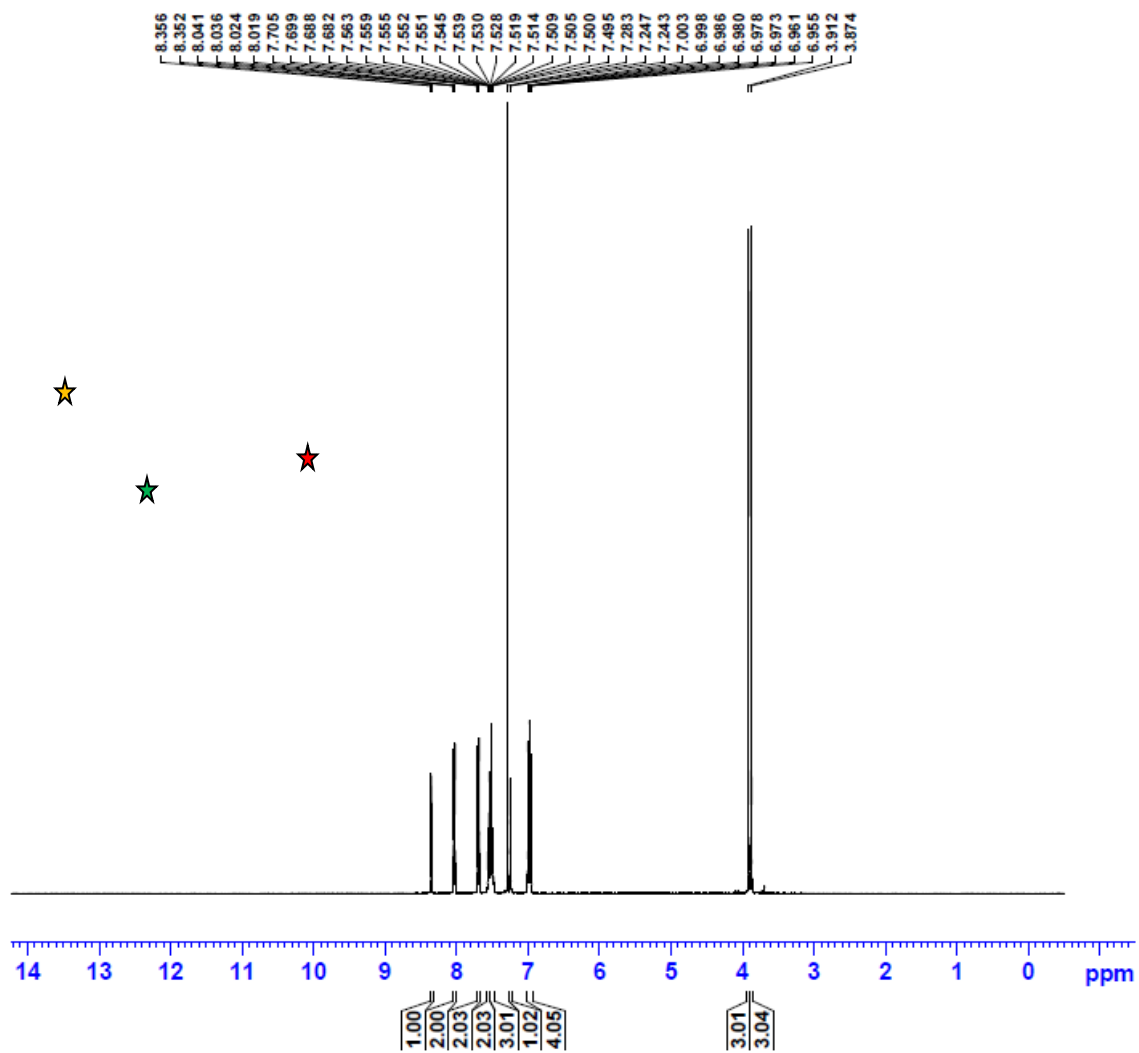
3.1. IR spectra



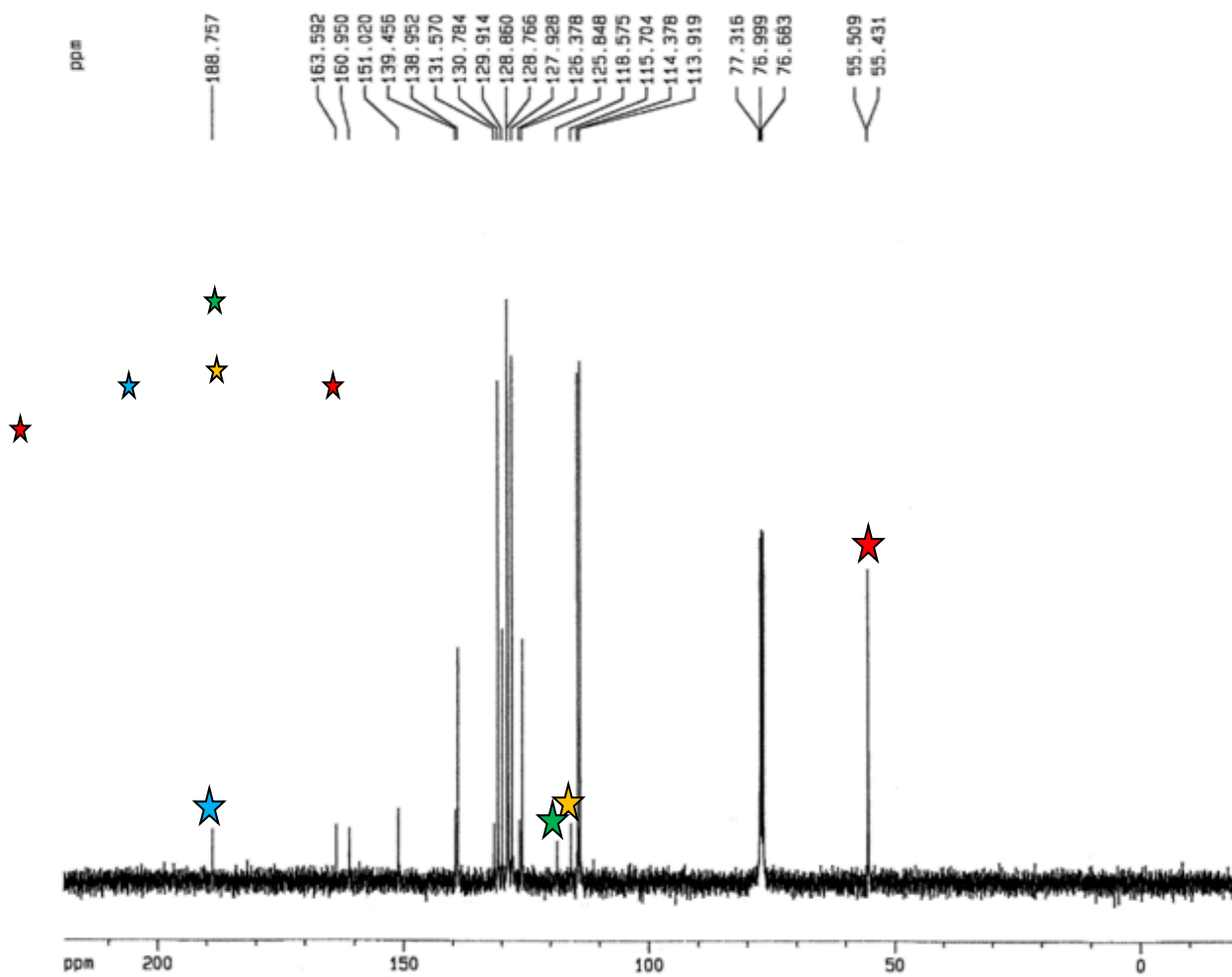
3.2. Mass spectra



3.3. ^1H NMR spectra in CDCl_3

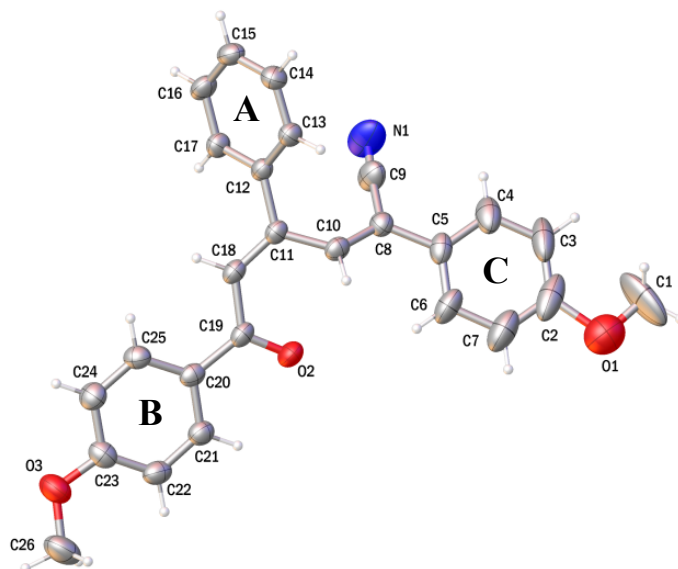


3.4. ^{13}C NMR spectra in CDCl_3



3.5. X-ray structure data

CCDC 995679 contains the supplementary crystallographic data for compound **2a**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Three phenyl rings are not coplanar and the central ring A is twisted by a large dihedral angle (56.18°), relative to the lateral ring B, and the dihedral angle between benzene rings A and C is even larger (60.24°) due to the higher steric congestion between them. The carbonyl oxygen O(2) is involved in a non-classical intramolecular interaction, C(10)-H...O(2), with a H...O distance of 2.365 Å and an C(10)-H...O(2) angle of 101.83° . Adjacent molecules are linked together via non-classic C(15)H...O(2) intermolecular hydrogen bonds with H...O distance of 2.66 Å. Repetition of these hydrogen bonds leads to the formation of a 1D chain structure which extends to a single 3D-network structure by the intermolecular C-H... π interactions.

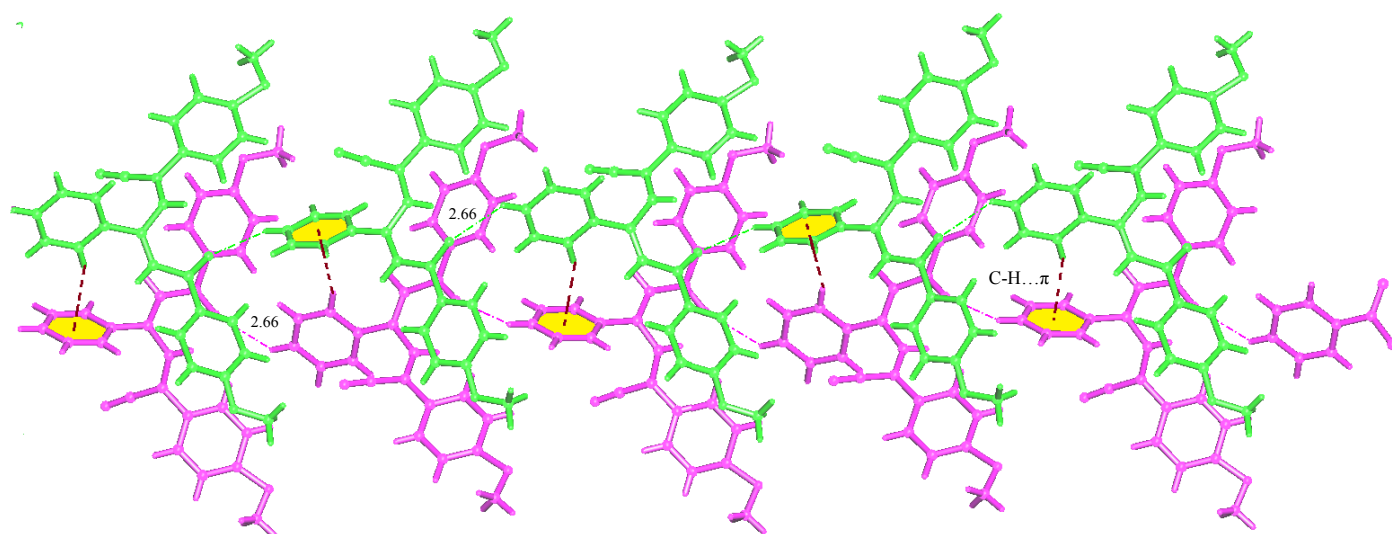


Table 1Crystal data and structure refinement for **2a**

Chemical formula	C ₂₆ H ₂₁ N O ₃
Formula weight	395.44
Temperature (K)	298(2)
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> (Å)	7.4208(15)
<i>b</i> (Å)	19.207(4)
<i>c</i> (Å)	29.746(6)
<i>V</i> (Å ³)	4239.7(15)
<i>Z</i>	8
Absorption coefficient (mm ⁻¹)	0.081
D _x (Mg/m ³)	1.239
Crystal size (mm)	0.26 × 0.18 × 0.10
<i>F</i> (000)	1664
θ Ranges (°)	2.52–25.00
Reflections collected	15918
Independent reflections (<i>R</i> _{int})	3729 (<i>R</i> _(int) = 0.0659)
Data/restraints/parameters	3729/0/259
Goodness-of-fit on <i>F</i> ²	0.724
Final <i>R</i> indices	<i>R</i> ₁ = 0.0550, <i>wR</i> ₂ = 0.1200
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1727, <i>wR</i> ₂ = 0.1450
Range of <i>h, k, l</i>	–8 / 8, –22 / 22, –35 / 33

Table 2Selected bond lengths and angles for **2a**

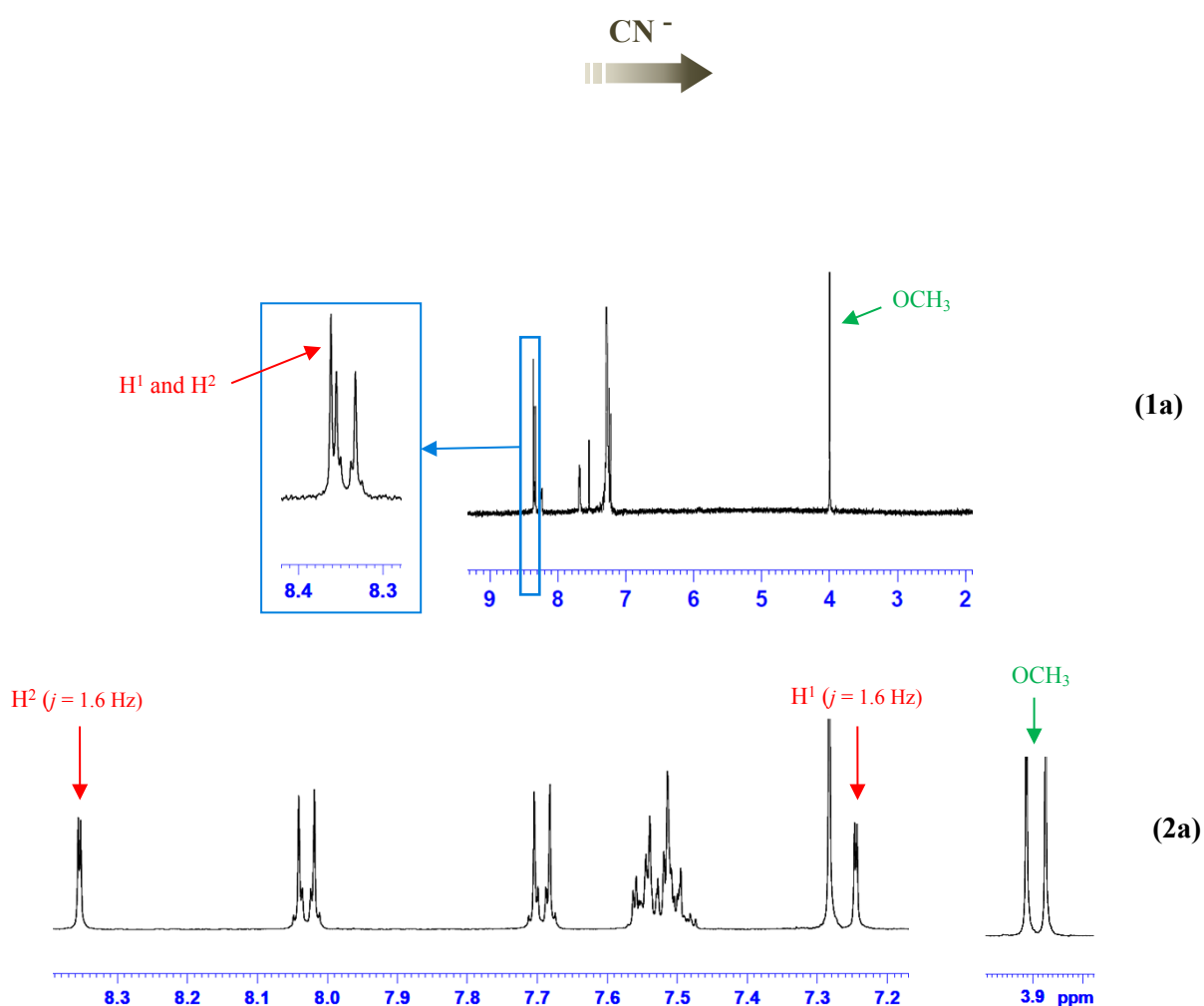
<i>Bond lengths (Å)</i>		<i>Bond lengths (Å)</i>	
C(2)-C(3)	1.3900	C(12)-C(17)	1.396(4)
C(2)-C(7)	1.3900	C(13)-C(14)	1.380(4)
C(2)-O(1)	1.516(5)	C(14)-C(15)	1.371(5)
C(3)-C(4)	1.3900	C(15)-C(16)	1.371(5)
C(4)-C(5)	1.3900	C(16)-C(17)	1.382(5)
C(5)-C(6)	1.3900	C(18)-C(19)	1.476(4)
C(5)-C(8)	1.489(4)	C(19)-O(2)	1.230(4)
C(6)-C(7)	1.3900	C(19)-C(20)	1.492(5)
C(1)-O(1)	1.261(5)	C(20)-C(21)	1.380(4)
C(8)-C(10)	1.334(5)	C(20)-C(25)	1.387(5)
C(8)-C(9)	1.438(6)	C(21)-C(22)	1.376(5)
C(9)-N(1)	1.128(5)	C(22)-C(23)	1.367(5)
C(10)-C(11)	1.459(4)	C(23)-O(3)	1.366(4)
C(11)-C(18)	1.338(5)	C(23)-C(24)	1.390(5)
C(11)-C(12)	1.492(4)	C(24)-C(25)	1.370(5)
C(12)-C(13)	1.387(5)	C(26)-O(3)	1.426(5)
<i>Bond angles (°)</i>		<i>Bond angles (°)</i>	
C(3)-C(2)-C(7)	120.0	C(14)-C(13)-C(12)	120.4(3)
C(3)-C(2)-O(1)	131.1(4)	C(15)-C(14)-C(13)	120.8(4)
C(7)-C(2)-O(1)	108.9(4)	C(16)-C(15)-C(14)	119.4(4)
C(4)-C(3)-C(2)	120.0	C(15)-C(16)-C(17)	120.6(4)
C(3)-C(4)-C(5)	120.0	C(16)-C(17)-C(12)	120.2(4)
C(6)-C(5)-C(4)	120.0	C(11)-C(18)-C(19)	125.9(3)
C(6)-C(5)-C(8)	118.7(3)	O(2)-C(19)-C(18)	119.9(4)
C(4)-C(5)-C(8)	121.2(3)	O(2)-C(19)-C(20)	119.3(3)
C(5)-C(6)-C(7)	120.0	C(18)-C(19)-C(20)	120.8(3)
C(6)-C(7)-C(2)	120.0	C(21)-C(20)-C(25)	117.8(4)
C(10)-C(8)-C(9)	120.2(3)	C(21)-C(20)-C(19)	118.7(3)
C(10)-C(8)-C(5)	123.0(3)	C(25)-C(20)-C(19)	123.5(3)
C(9)-C(8)-C(5)	116.4(4)	C(22)-C(21)-C(20)	121.8(4)

N(1)-C(9)-C(8)	176.7(5)	C(23)-C(22)-C(21)	119.6(4)
C(8)-C(10)-C(11)	128.3(3)	O(3)-C(23)-C(22)	126.1(4)
C(18)-C(11)-C(10)	121.7(3)	O(3)-C(23)-C(24)	114.2(4)
C(18)-C(11)-C(12)	120.2(3)	C(22)-C(23)-C(24)	119.7(4)
C(10)-C(11)-C(12)	118.1(3)	C(25)-C(24)-C(23)	120.1(4)
C(13)-C(12)-C(17)	118.4(3)	C(24)-C(25)-C(20)	120.9(4)
C(13)-C(12)-C(11)	120.6(3)	C(1)-O(1)-C(2)	102.4(5)
C(17)-C(12)-C(11)	120.9(3)	C(23)-O(3)-C(26)	118.9(4)

Symmetry operator i): -x, -y, -z

4. Comparison of the ^1H NMR spectra of **1a** and **2a**

The ^1H NMR spectra of receptor **1a** were characterized by the presence of the aromatic resonances in the 7.22-8.36 range. The most characteristic signal in this zone is a singlet at *ca.* 8.36 ppm, attributed to equivalent protons of the pyrylium ring (H^1 , H^2). Also the presence of a singlet centred at *ca.* 3.99 ppm is indicative of the presence of equivalent protons of the methoxy groups. The ^1H NMR spectra of product **2a** show two distinct singlets for the nonequivalent protons of methoxy and two singlets at *ca.* 7.24 and 8.35 ppm ($j = 1.6$ Hz) for H^1 and H^2 , respectively.



5. Absorption spectra

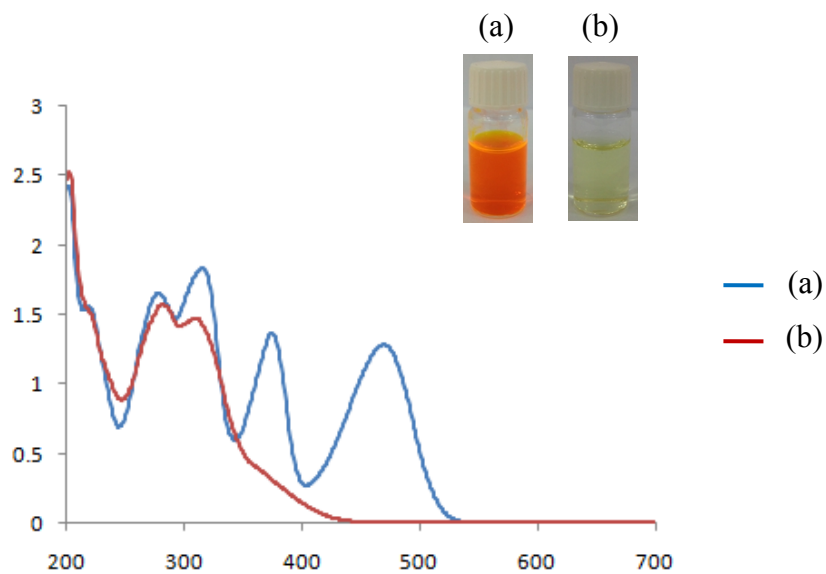


Figure S1. Steady-state absorption spectra (1 mM, MeCN) of (a) **1a** and (b) **2a**

6. Fluorescence emission spectra

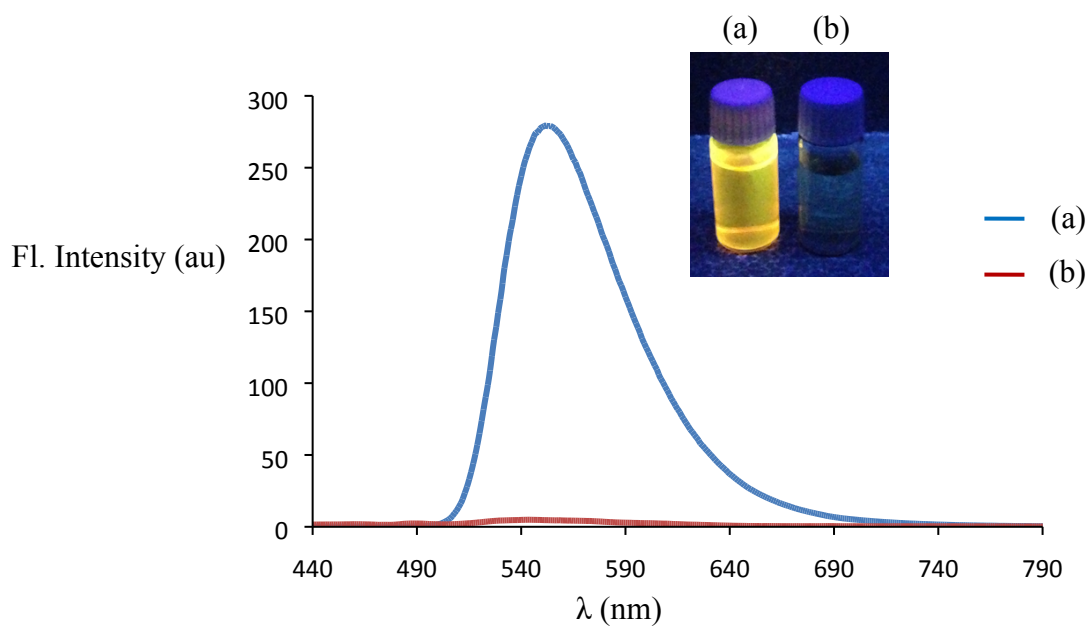


Figure S2. Fluorescence emission spectra (10 μ M, MeCN) of (a) **1a** and (b) **2a**

7. Determination of detection limit of CN^-

The detection limit was calculated by UV-Vis spectroscopy. To determine the standard deviation of blank measurements, the absorption intensity of **1a**/ γ - Al_2O_3 without CN^- was measured by 8 times. Under the present conditions, a good linear relationship between the absorption intensity and CN^- concentration could be obtained in the 0.5 – 4 ppm ($R = 0.9964$). The detection limit is then calculated with the equation: detection limit = $3\sigma_{bi}/m$, where σ_{bi} is the standard deviation of blank measurements; m is the slope between intensity versus sample concentration. The detection limit was measured to be 0.23 ppm.

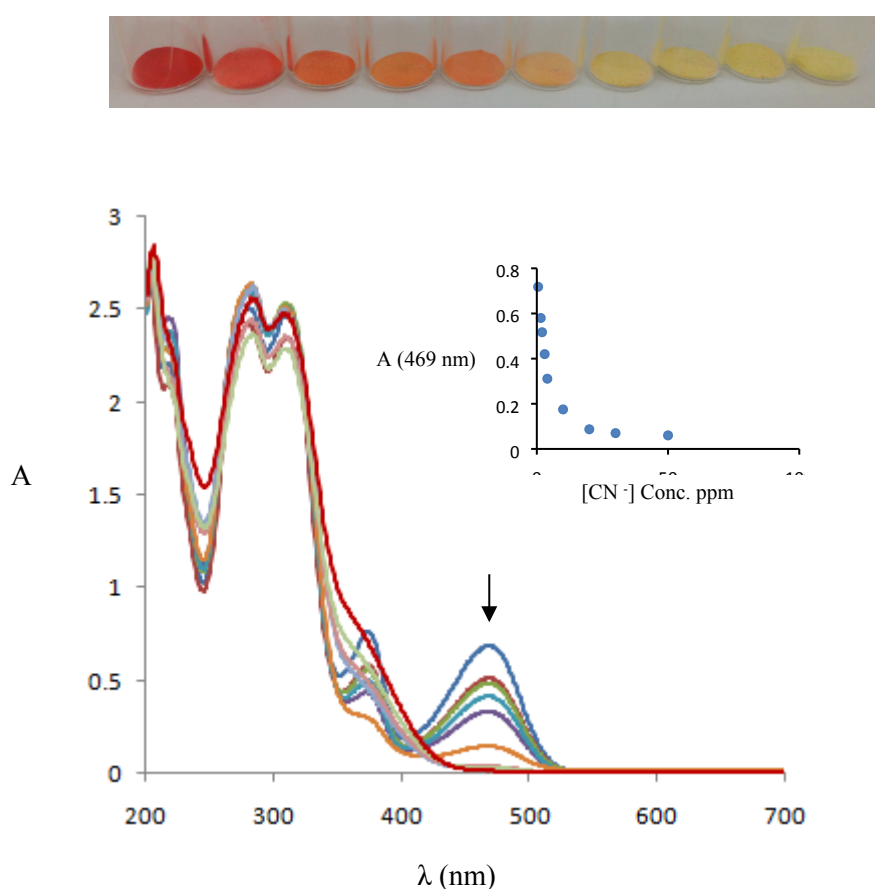
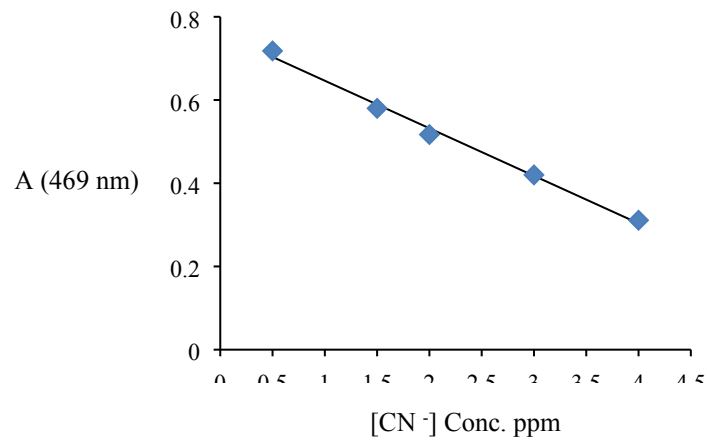
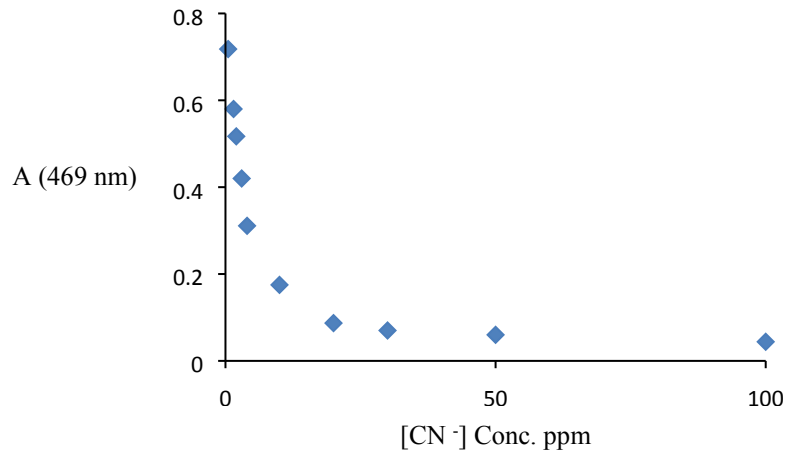


Figure S3. Selected UV/Vis titration curve of heterogeneous **1a**/ γ -alumina with cyanide in water (inset: cyanide concentration abs. at 469 nm).



8. Selectivity towards other common anions

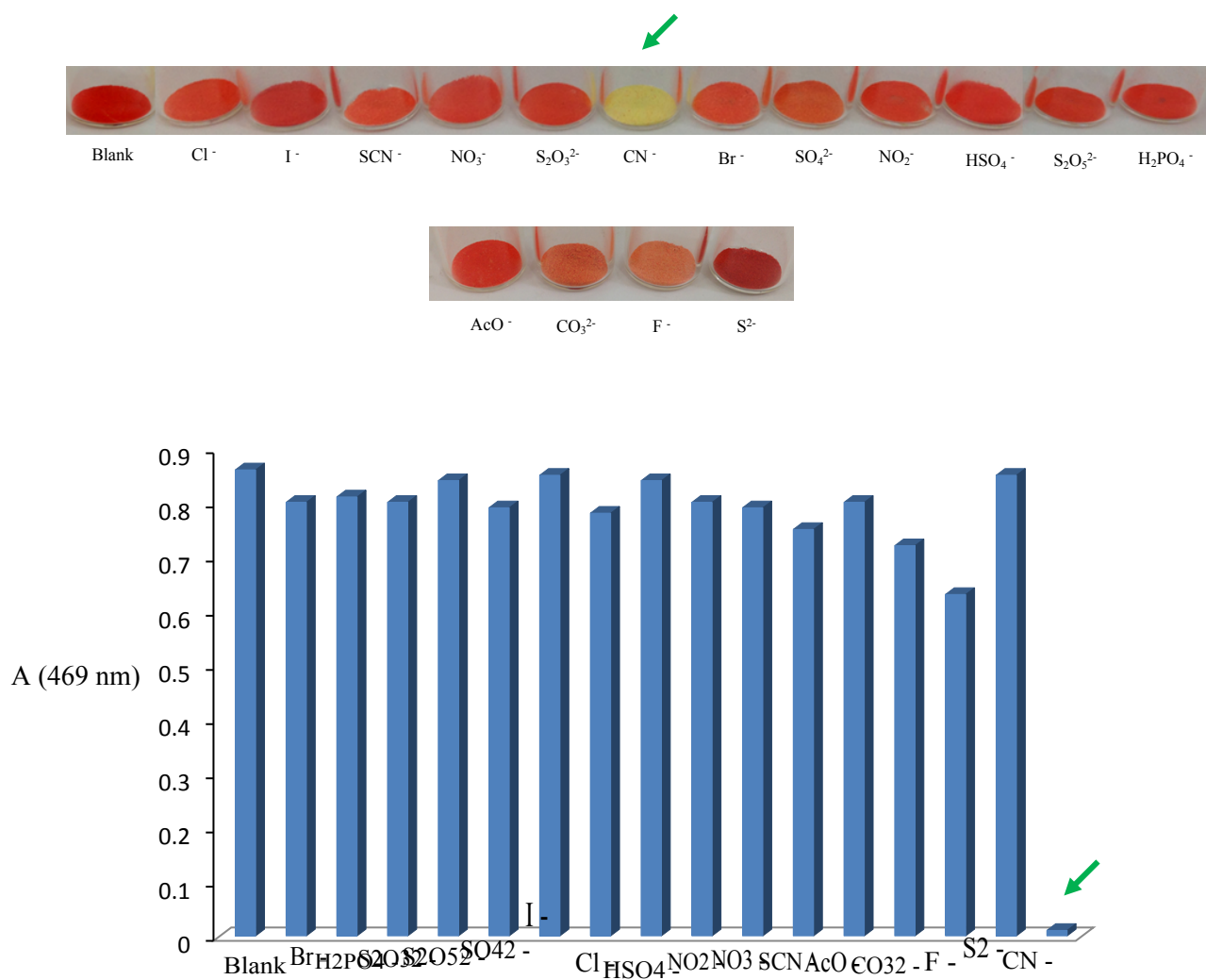


Figure S4. The absorption of chromoreactand **1a**/ γ -Al₂O₃ (at 469 nm in water) in the presence of 1 equiv. of cyanide and 10 equiv. of other anions