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Synthesis and optical properties of new chalcones containing 4-[bis(2-hydroxyethyl)amino]phenyl fragment

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Materials and methods. ^{1}H NMR spectra were recorded on a Bruker AvanceNeo III HD (400 MHz) spectrophotometer using hexamethyldisiloxane (0.055 ppm) as the internal standard. NMR data are reported as follows: chemical shift, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *quint* = quintet, *m* = multiplet, *dd* = double doublet), integration, and coupling constants (Hz). Signals of benzene ring protons are denoted as *Ph*, thiophene ring protons – as *Th*, carbazole ring protons - as *Cz*. The IR spectra were run on a Perkin–Elmer Spectrum Two FTIR spectrometer (PerkinElmer, Inc, USA) in Nujol. The elemental analyses were obtained on a LECO CHNS-932 analyzer (Elementar, Germany). The UV spectra were measured on a Shimadzu UV-2600 spectrophotometer for $CHCl_3$ solutions of compounds with concentration of solutions with concentration of solutions from 1×10–5 to 5×10–5 mol dm^{-3}, cell dimensions 10×10×40 mm. The emission spectra were recorded on a Shimadzu RF-5301 spectrofluorophotometer (Shimadzu Corp., Japan) in $CHCl_3$ (*c* 10^{-5} mol dm^{-3}), cell dimensions 10×10×40 mm. Fluorescence quantum yield were determined relative to 3-aminophthalimide in EtOH (Φ_f = 60%)[S1] which was used as a standard. The reaction progress and individuality of the synthesized compounds were monitored by thin-layer chromatography (TLC): Sorbfil plates, different solvent systems, visualization by UV light (365 nm), iodine vapours, 2,4-dinitrophenylhydrazine solution (EtOH, H_3PO_4). The products were isolated by column chromatography on silica gel (Silicagel 60, 0.06–0.20 mm; from Lancaster). Ethylenedioxythiophene (EDOT, Clevios M V2, Heraeus), 2-bromothiophene, terephthalaldehyde, carbazole were purchased from AlfaAesar, and acetyl bromide - from Sigma–Aldrich.

4-(Bis(2-acetoxyethyl)amino)benzaldehyde **1**, 2-acetyl-3,4-ethylenedioxythiophene **2a**, 2-acetyl-5-bromothiophene **2b** were prepared according the known procedures.[S2-S4] The syntheses

of 1-(9-ethyl-9*H*-carbazol-3-yl)ethan-1-one **2c** and 1-(5-(9-ethyl-9*H*-carbazol-3-yl)thiophen-2-yl)ethan-1-one **2d** were performed similarly to a previously described protocol[S5].

Synthesis *1,3-Disubstituted prop-2-en-1-ones **(3a-d)** (general procedure).*[S6] Ethanol solution of KOH (10%, 25 ml) was poured into ethanol (25 ml) solution of 4-(bis(2-acetoxyethyl)amino)-benzaldehyde (1 g, 3.4 mmol) and the corresponding ketone **2a-d** (3.4 mmol). The mixture was refluxed for 12 h, then cooled, poured into water, and extracted with CH_2Cl_2. The solvent was removed, the residue was subjected to column chromatography on silica gel, a mixture of ethyl acetate and hexane was used as an eluent.

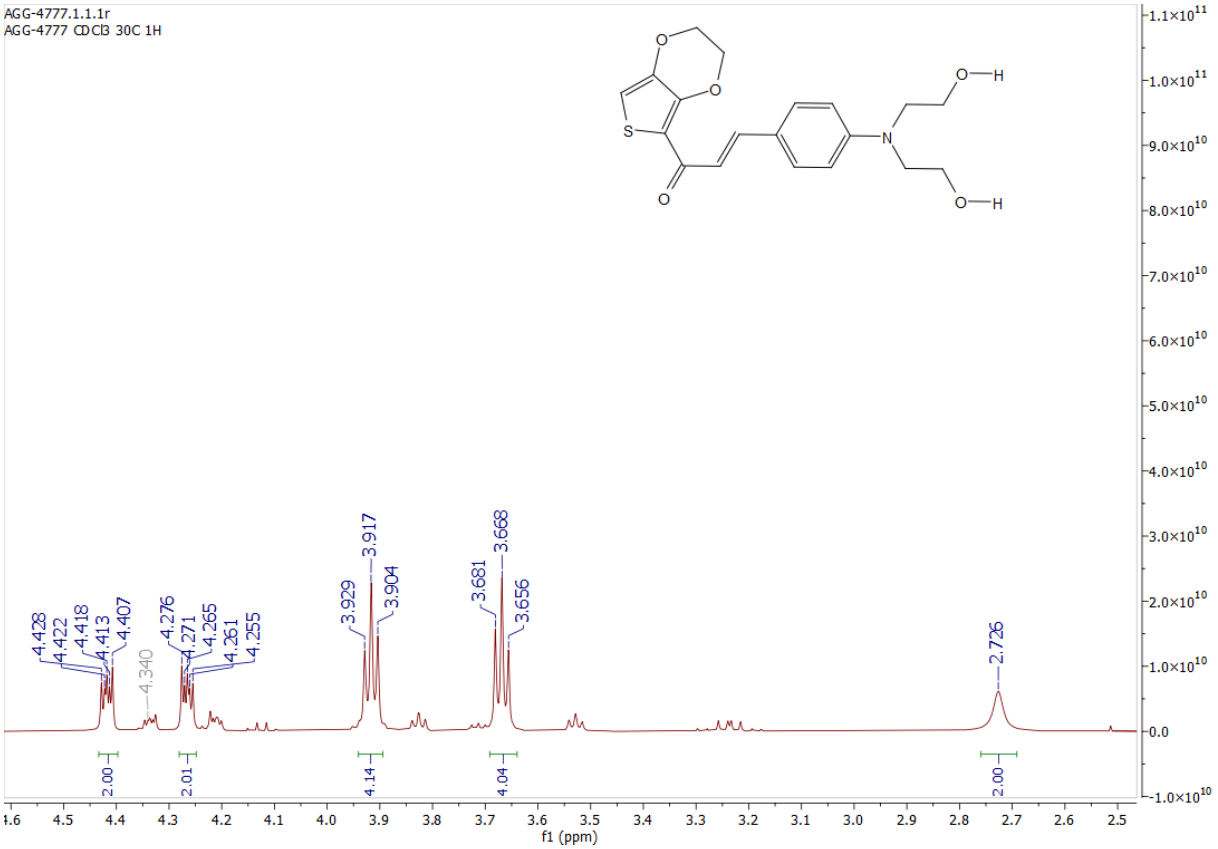
*3-[4-(Bis(2-hydroxyethyl)amino)phenyl]-1-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)prop-2-en-1-one (**3a**).* Yield 0.84 g (66%). Red crystals. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.73 s (2H, OH), 3.67 t (2H, CH_2N, *J* 5.0 Hz), 3.92 t (2H, CH_2O, *J* 5.2 Hz), 4.23-4.28 m (2H, OCH_2CH_2O), 4.40-4.43 m (2H, OCH_2CH_2O), 6.69 s (1H, Th), 6.71-6.73 d (2H, Ph, *J* 8.8 Hz), 7.44-7.48 d (1H, CH=CHCO, *J* 15.2 Hz), 7.51-7.51 d (2H, Ph, *J* 8.8 Hz), 7.44-7.48 d (1H, CH=CHCO, *J* 15.2 Hz). IR spectrum, ν, cm^{-1}: 3299 (OH). Found, %: C 60.78; H 5.64; N 3.73; S 8.54. $C_{19}H_{21}NO_5S$. Calculated, %: C 60.55; H 5.86; N 3.34; S 8.26. *M* 375.44.

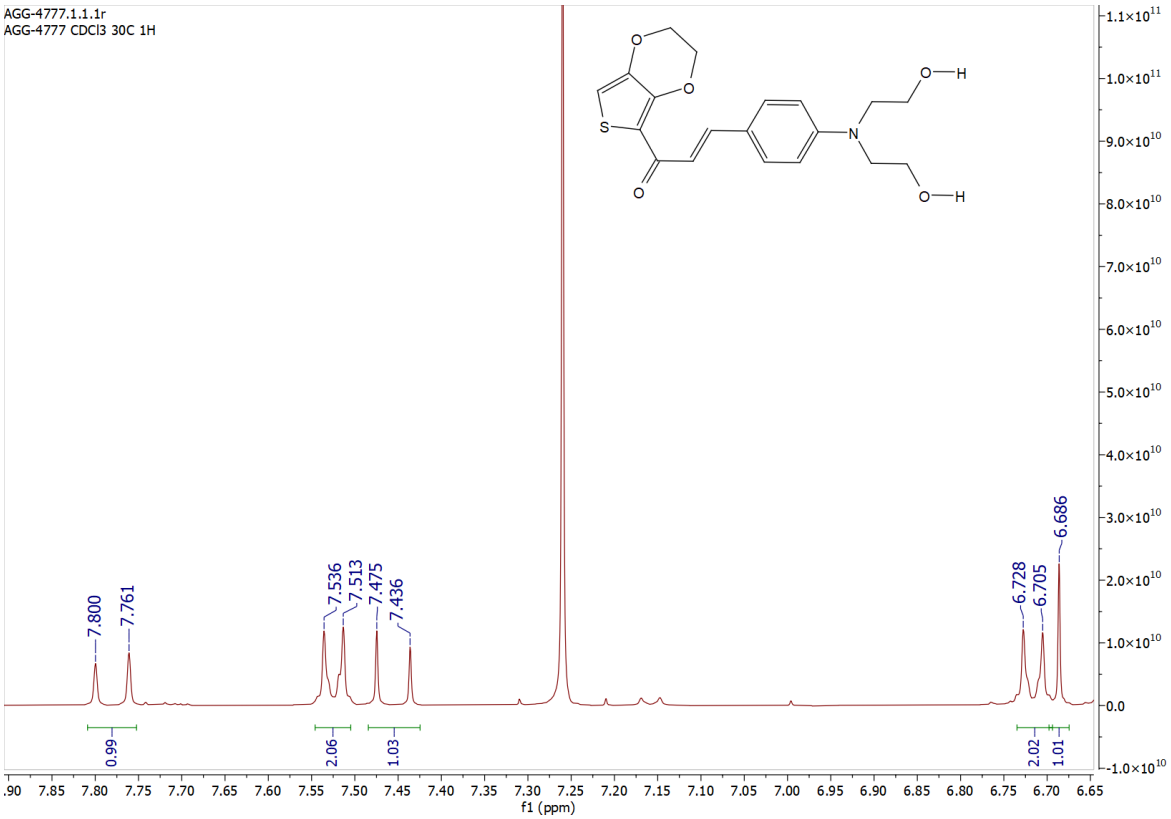
*1-(5-Bromothiophen-2-yl)-3-[4-(bis(2-hydroxyethyl)amino)phenyl)]prop-2-en-1-one (**3b**).* Yield 0.91 g (68%). Dark red crystals. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.66 s (2H, OH), 3.67 t (2H, CH_2N, *J* 4.8 Hz), 3.91 t (2H, CH_2O, *J* 5.2 Hz), 6.70-6.72 d (2H, Ph, *J* 8.8 Hz), 7.08-7.12 d (1H, CH=CHCO, *J* 15.2 Hz), 7.11-7.12 d (2H, Th, *J* 4 Hz), 7.49-7.51 d (2H, Ph, *J* 8.8 Hz), 7.53-7.54 d (2H, Th, *J* 4 Hz), 7.76-7.80 d (1H, CH=CHCO, *J* 15.2 Hz). IR spectrum, ν, cm^{-1}: 3336 (OH). Found, %: C 51.52; H 4.58; N 3.53; S 8.09. $C_{17}H_{18}BrNO_3S$. Calculated, %: C 51.69; H 4.47; N 3.36; S 8.17. *M* 396.30.

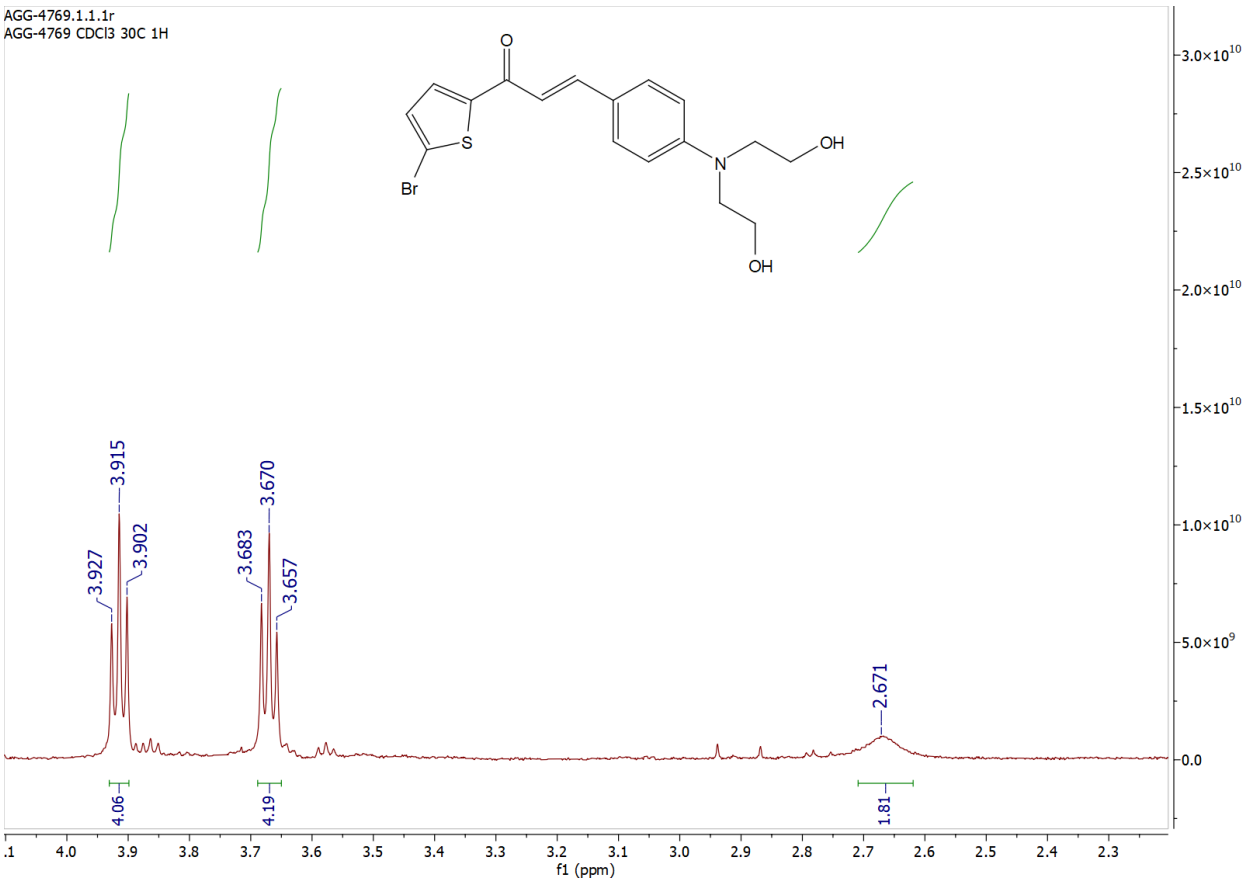
*1-(9-Ethyl-9H-carbazol-3-yl)-3-[4-(bis(2-hydroxyethyl)amino)phenyl]prop-2-en-1-one (**3c**).* Yield 0.76 g (52%). Bright orange crystals. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.46 t (3H, CH_3, *J* 7.2 Hz), 3.06 s (2H, OH), 3.66 t (2H, CH_2N, *J* 5.0 Hz), 3.91 t (2H, CH_2O, *J* 5.2 Hz), 4.39 q (2H, NCH_2, *J* 7.2 Hz), 6.72-6.74 d (2H, Ph, *J* 8.8 Hz), 7.29 t (1H, Cz, *J* 8 Hz), 7.42-7.44 d (2H, Ph, *J* 8.3 Hz), 7.48-7.50 dd (1H, Cz, *J* 7.2, 1.2 Hz), 7.53-7.56 d (1H, CH=CHCO, *J* 15.2 Hz), 7.56-7.58 d (2H, Cz, *J* 8 Hz), 7.79-7.83 d (1H, CH=CHCO, *J* 15.2 Hz), 8.19 td (2H, Cz, *J* 8.2, 1.2 Hz), 8.81 d (1H, Cz, *J* 1.6). IR spectrum, ν, cm^{-1}: 3182, 3320 (OH). Found, C 75.68; H 6.59; N 6.54. Calculated, %: C 75.89; H 6.41; N 6.32. *M* 428.53.

*1-[5-(9-Ethyl-9H-carbazol-3-yl)thiophen-2-yl]-3-[4-(bis(2-hydroxyethyl)amino)phenyl]prop-2-en-1-one (**3d**).* Yield 0.69 g (40%). Dark red crystals. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.45 t (3H, CH_3, *J* 7.2 Гц), 3.35 s (2H, OH), 3.70 t (2H, CH_2N, *J* 5.0 Hz), 3.92 t (2H, CH_2O, *J* 5.2 Hz), 4.21 q (2H, NCH_2, *J* 7.2 Hz), 7.27-7.29 d (1H, Cz, *J* 7.6 Hz), 7.30-7.34 d (1H, CH=CHCO, *J* 15.2 Hz), 7.41-7.43 d (2H, Ph, *J* 8.8 Hz), 7.50-7.52 d (2H, Cz, 1H, Th), 7.60-7.62 d (2H, Ph, *J* 8.8 Hz), 7.68-7.70 м (2H, Cz), 7.79-7.83 д (1H, CH=CHCO, *J* 15.6 Hz), 7.83-7.84 д (1H, Th, *J* 4 Hz), 8.12-8.14 д (1H, Cz, *J* 7.6), 8.40 с (1H, Cz), ИК, ν, см$^{-1}$: 3400 (OH). Found, %: C 72.91; H 5.92; N 5.49; S 6.28. Calculated, %: 72.74; H 5.63; N 5.58; S 6.04. *M* 510.65.

^{1}H NMR spectra of compounds 3a-d



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Br
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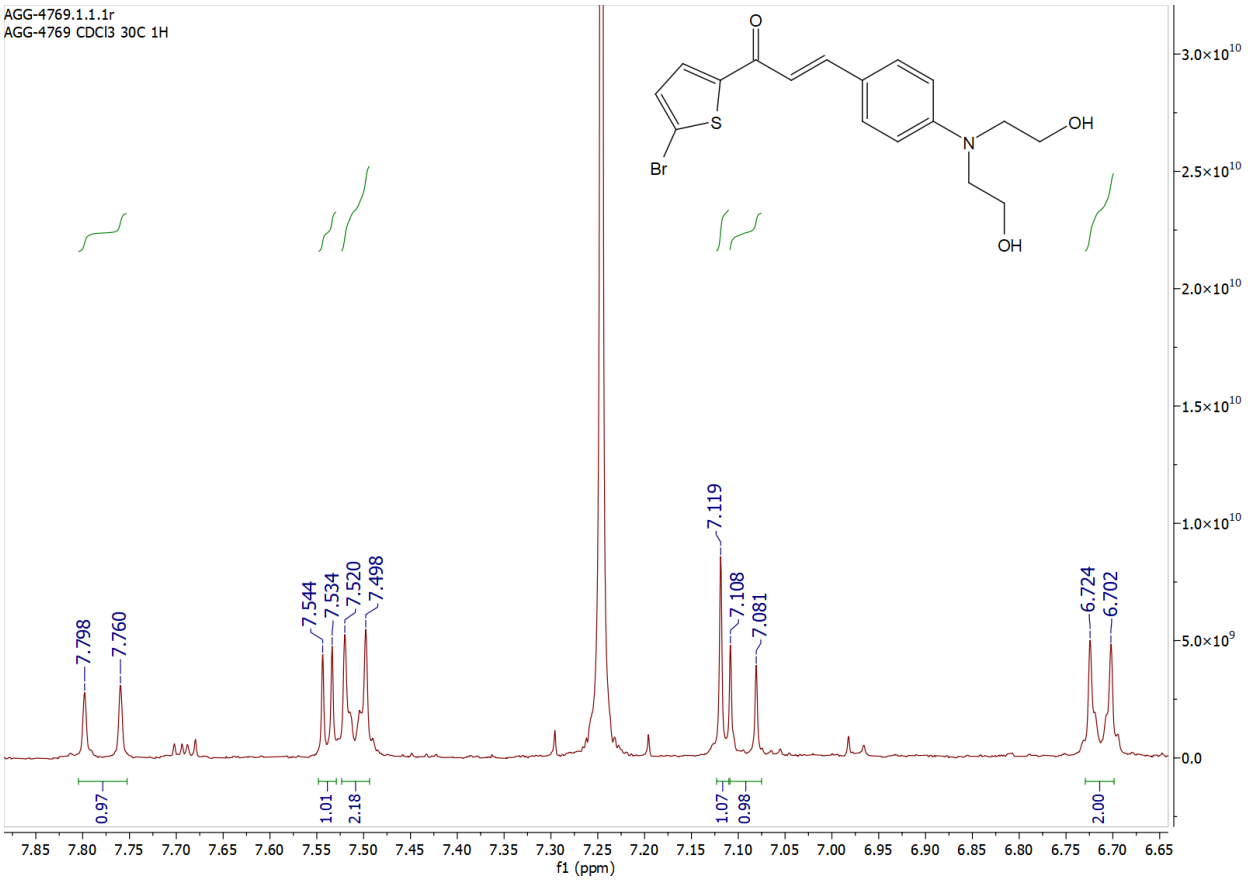
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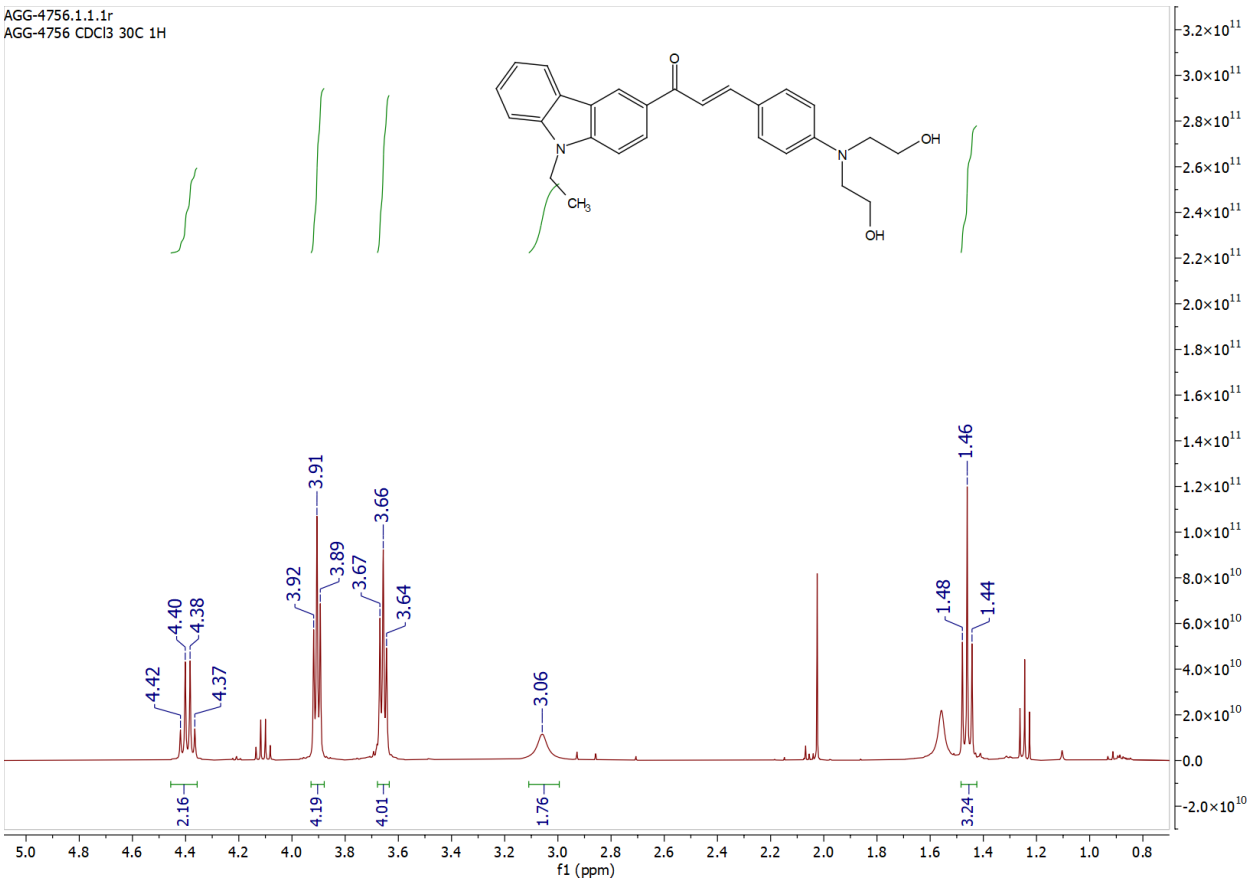
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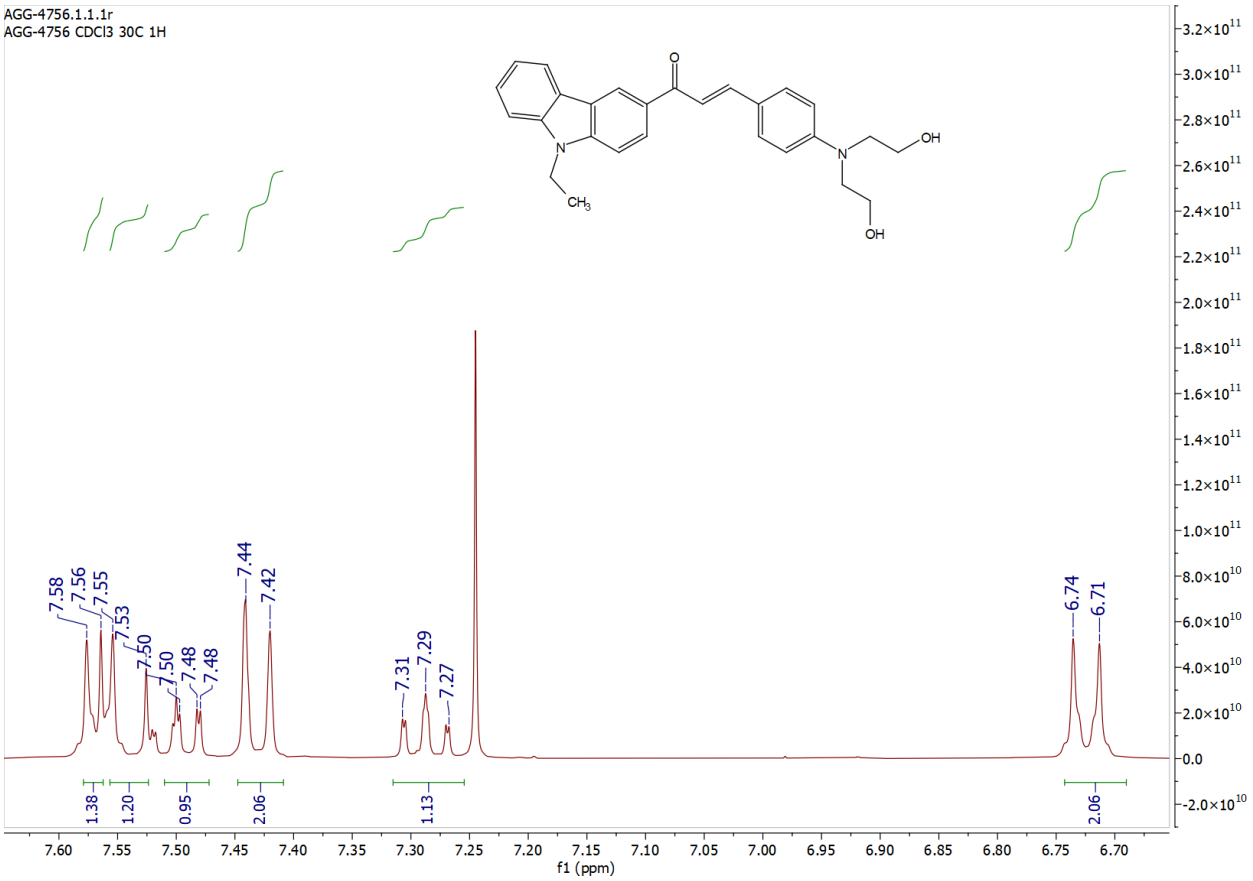
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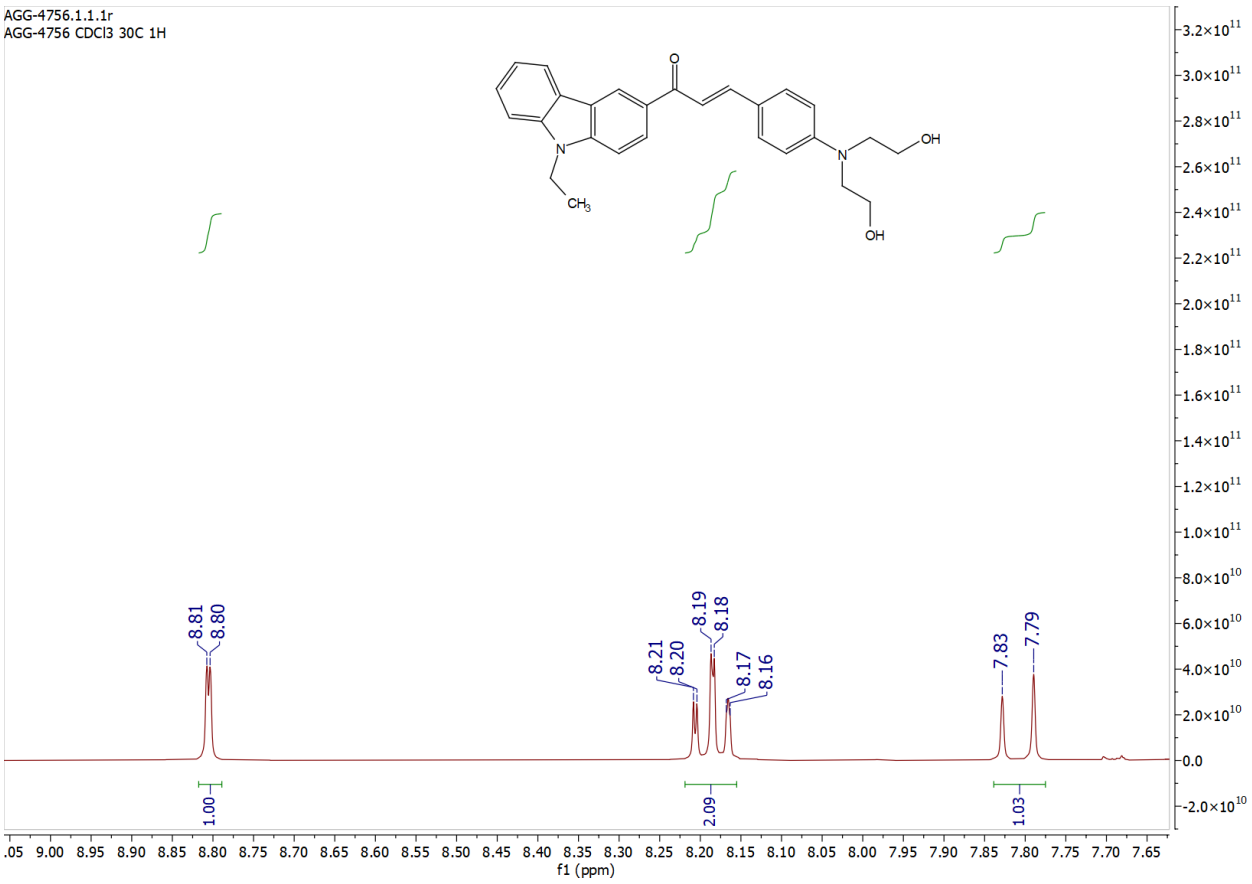
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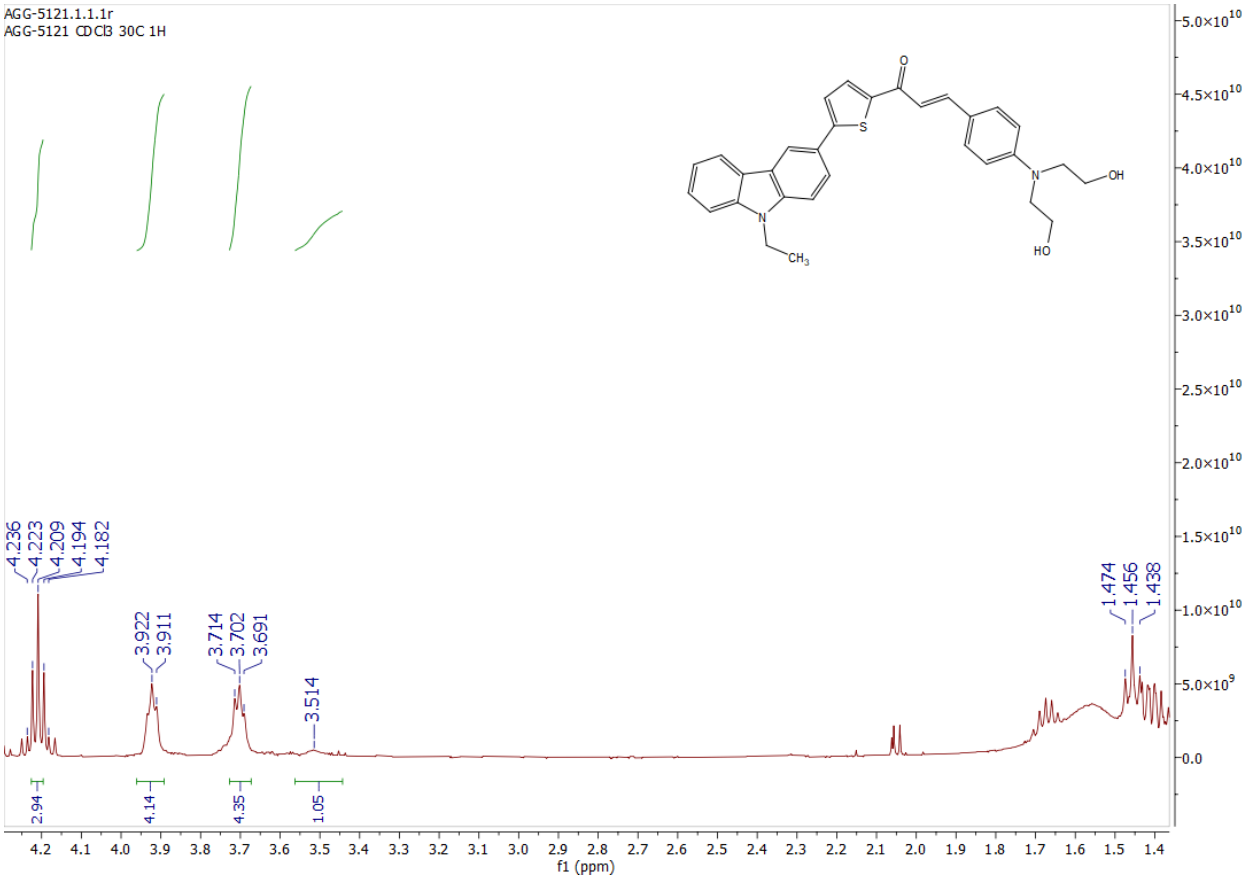
f1 (ppm)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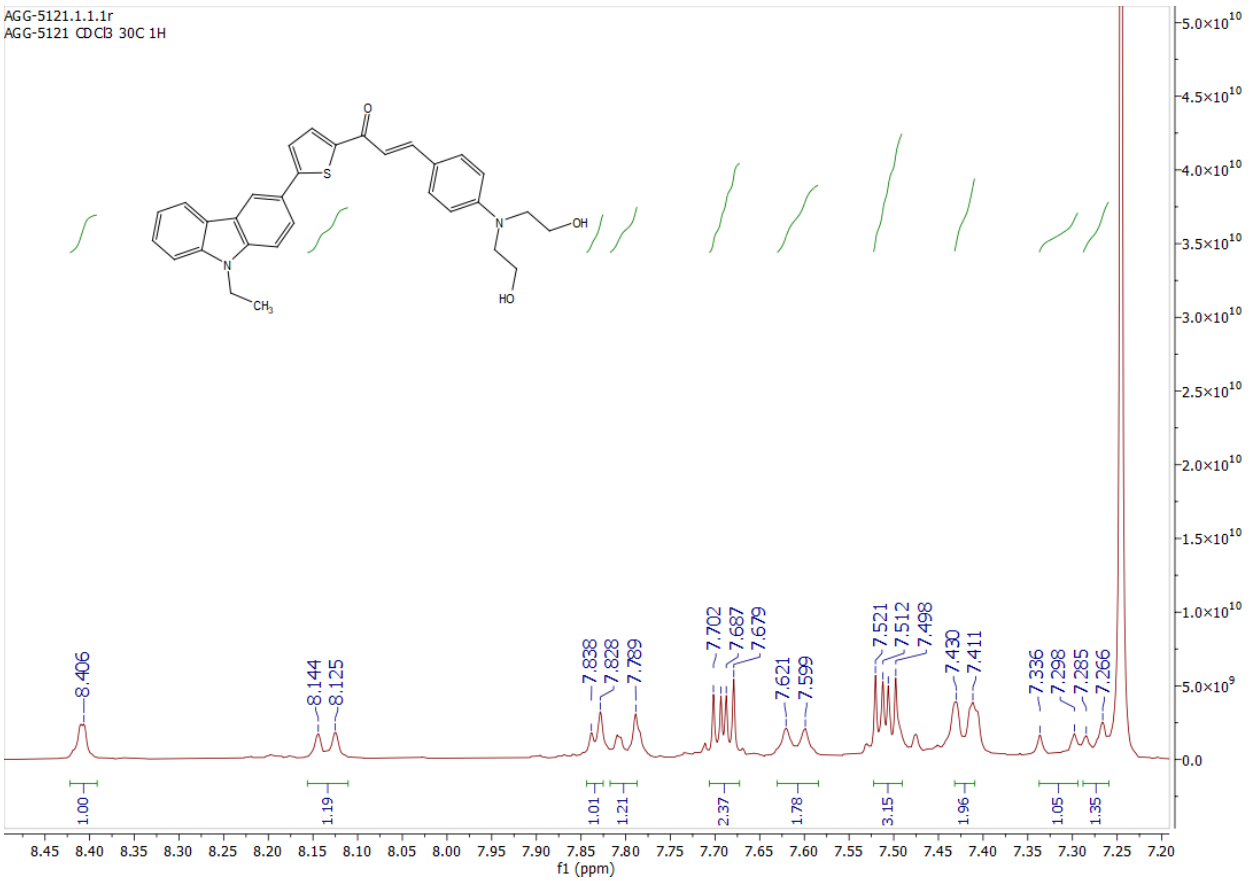

Single crystal X-ray analysis of compound 3a

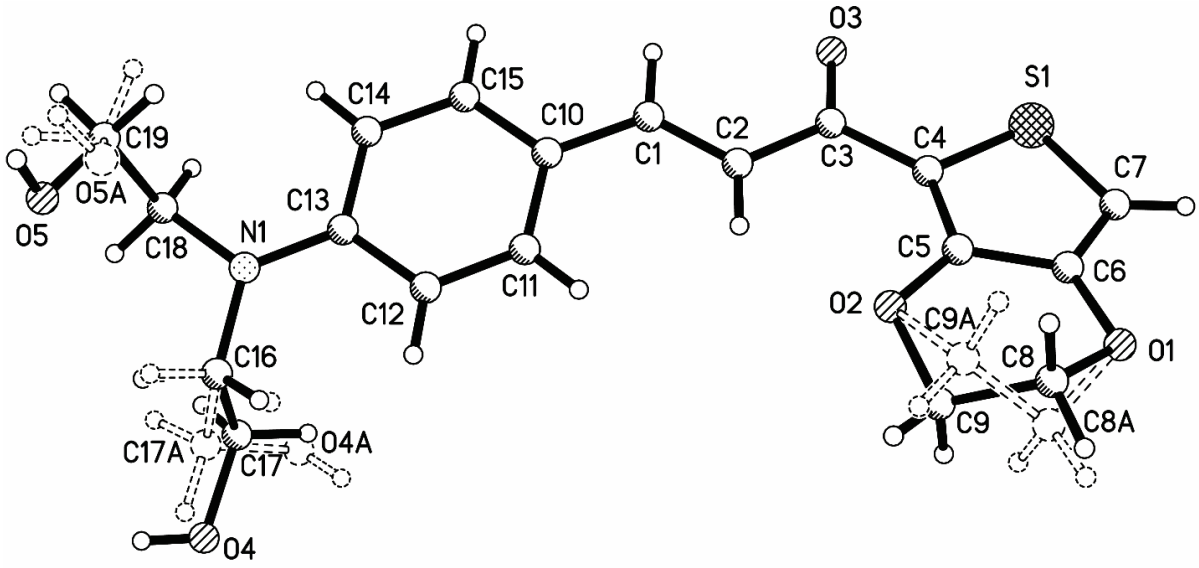

Figure S1 Molecular structure of compound **3a** (CCDC 2094902).

Compound **3a** crystallizes in the centrosymmetric space group of the monoclinic crystal system (Figure S1). The chalcone moiety is non-planar and has a propeller-like conformation, the angle between the planes of the thiophene and phenyl rings is 20.3 °. The dioxane ring is disordered over two positions with occupancy factors of 0.898(7) and 0.102(7). The dioxane conformation for both components is a half-chair. The O1C6C5O2 moiety is planar, the C8 and C9 atoms are deviated to different sides of the plane by 0.44 and 0.31 Å, respectively, the C8A and C9A atoms are deviated by 0.40 and 0.49 Å, respectively. The hydroxyethyl groups are located on opposite

sides of the plane of the phenyl ring and both are partially disordered. One of the hydroxyl groups was refined as disordered over two positions with occupancies of 0.797(13) and 0.203(13) for O5 and O5A, respectively. The O5–H5 and O5A–H5A groups of both conformers form intermolecular hydrogen bonds with the same carbonyl group (C3=O3) of an adjacent molecule (Table S1, Figure S2). The C17–O4 hydroxymethyl group is also disordered over two positions with occupancy of 0.445(6) for C17A–O4A. The conformer with the O4A–H4A group is located near the conformer with the O4 atom and forms the O4A–H4A···O4 hydrogen bond (Table S1, Figure S2). The O4–H4 group forms a hydrogen bond with the O5 atom (Table S1, Figure S2). The close values of the occupancies for the O4–H4 and O4A–H4A groups suggest that these conformers regularly alternate in the crystal. As a result, the molecules are linked via hydrogen bonds forming a two-dimensional network (Figure S3, Figure S4) parallel to the plane (011).

The presence of the aliphatic fragments, which are covalently bound with aromatic rings, probably complicates the formation of infinite stacks via to π-π interactions. Nevertheless, the thiophene rings of the adjacent molecules are close together in pairs (Figure 5). Heterocycles lie in parallel planes, the distance between planes is 3.51 Å, the distance between centroids is 3.76 Å.

Table S1 Hydrogen bon geometry (Å, º)

D–H···A	D–H	H···A	D···A	D–H···A
O4–H4···O5^{i}	0.82	2.01	2.807 (7)	164
O4A–H4A···O4^{ii}	0.82	1.912	2.700(7)	161
O5–H5···O3^{iii}	0.82	2.01	2.786 (3)	158
O5A–H5A···O3^{iii}	0.82	2.07	2.756 (12)	142

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

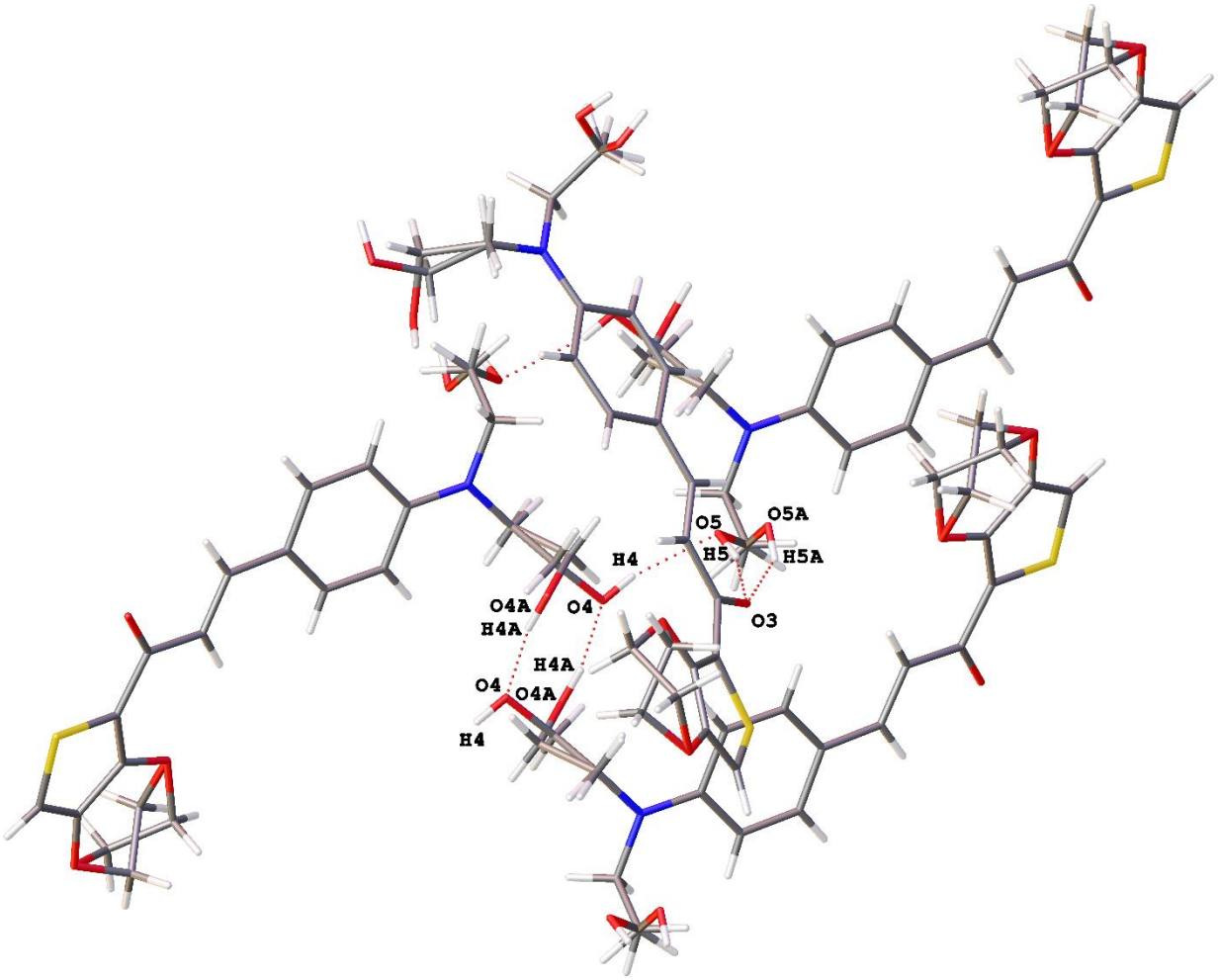

Figure S2 H-bond formation in crystal of compound **3a**.

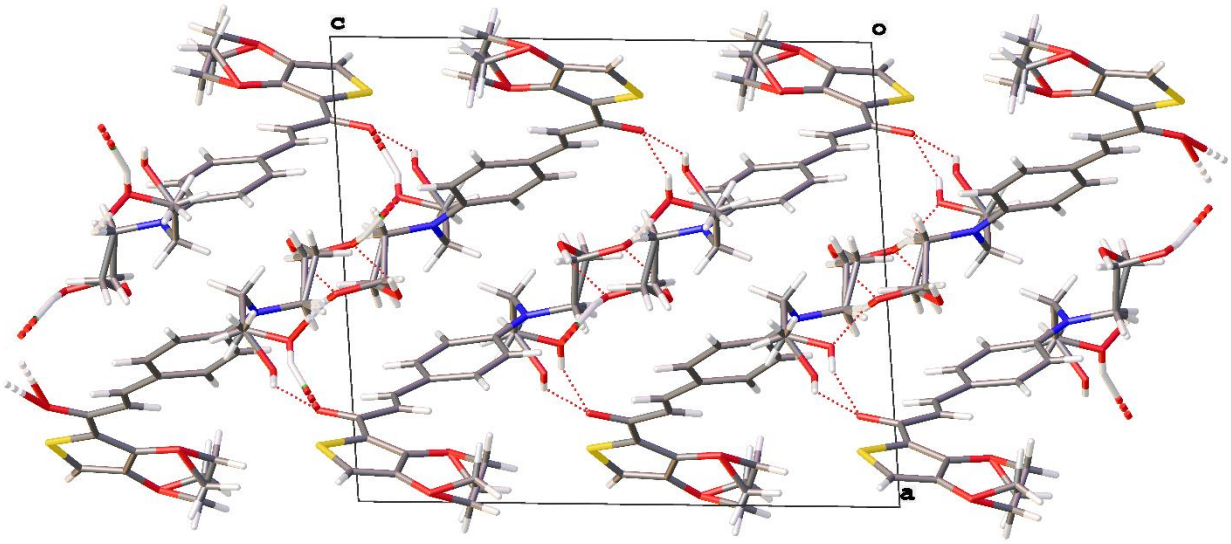

Figure S3 Crystal packing of compound **3a**, view along b axis.

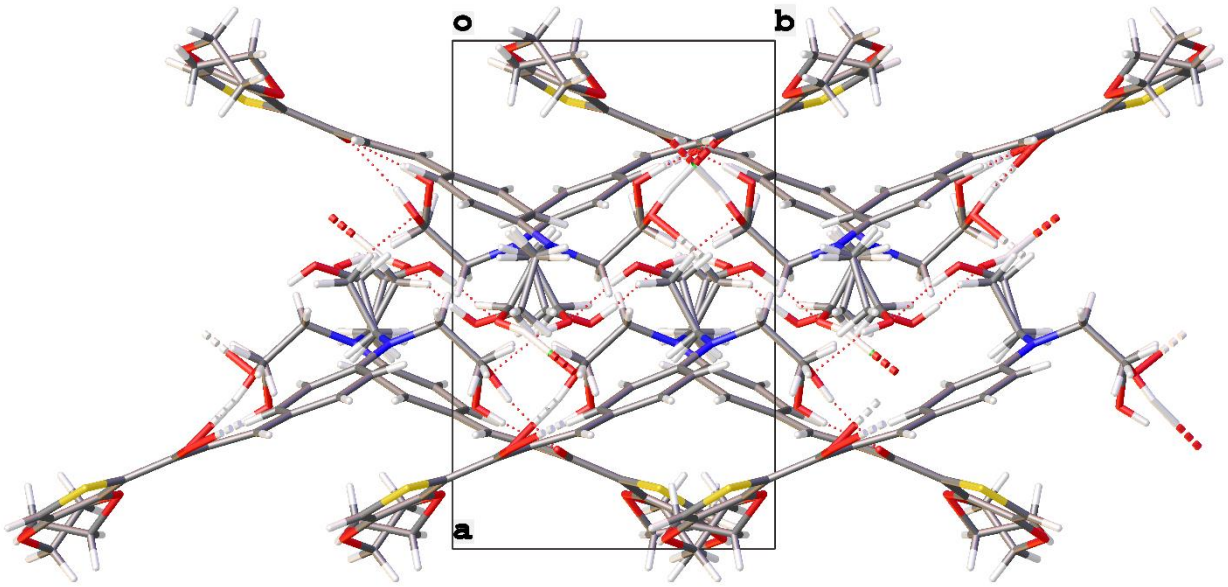

Figure S4 Crystal packing of compound **3a**, view along c axis.

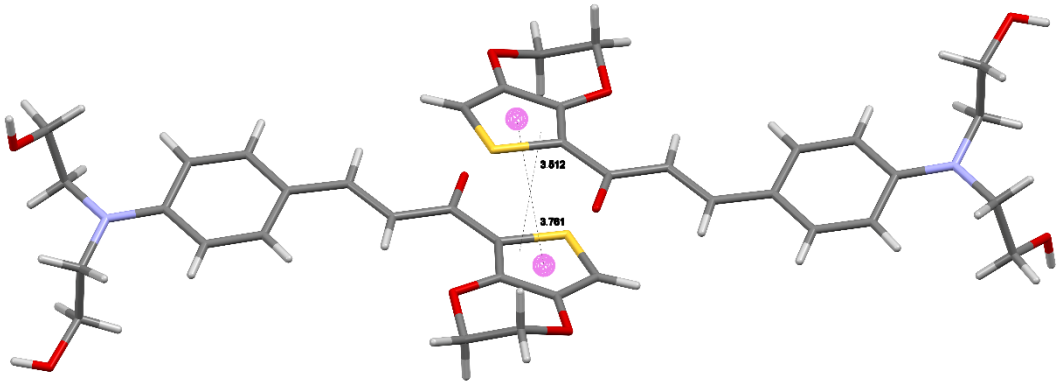

Figure S5 π-π Interaction in crystal of compound **3a**.

Crystal structure determination

The unit cell parameters and the X-ray diffraction intensities were measured on a Xcalibur Ruby diffractometer. The empirical absorption correction was introduced by multi-scan method using SCALE3 ABSPACK algorithm[S7]. Using OLEX2[S8], the structure was solved with the SHELXS[S9] program and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms using the SHELXL[S10] program. Hydrogen atoms were located from the Fourier synthesis of the electron density and refined using a riding model. For some of the disordered atoms, SADI, SIMU and DELU instructions were applied.

Table S2 Crystal data and structure refinement for 3a.

Empirical formula	$C_{19}H_{21}NO_5S$
Formula weight	375.43
Temperature, K	295.15
Crystal system	monoclinic

Space group	$P2_1/c$
a, Å	13.394(3)
b, Å	8.4623(19)
c, Å	15.555(3)
α, °	90
β, °	94.12(2)
γ, °	90
Volume, $Å^3$	1758.6(6)
Z	4
ρ_{calc}, g/cm^3	1.418
μ, mm^{-1}	0.215
F(000)	792.0
Crystal size, mm^3	0.55 × 0.25 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection, °	5.698 to 58.636
Index ranges	$-12 \le h \le 18$, $-7 \le k \le 11$, $-21 \le l \le 21$
Reflections collected	9411
Independent reflections	4179 [R_{int} = 0.0316]
Data/restraints/parameters	4179/7/287
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0514, wR_2 = 0.1131
Final R indexes [all data]	R_1 = 0.0817, wR_2 = 0.1360
Largest diff. peak/hole, $eÅ^{-3}$	0.21/-0.32

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