Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

An Efficient approach to Bis-benzoquinonylmethanes On Water Under Catalysis of the Bio-derived *O*-Carboxymethyl Chitosan

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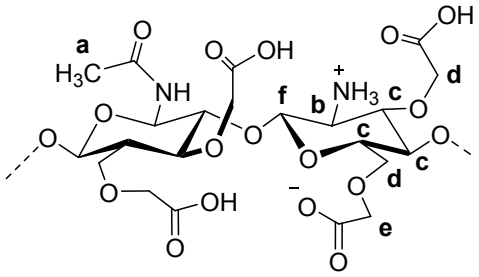
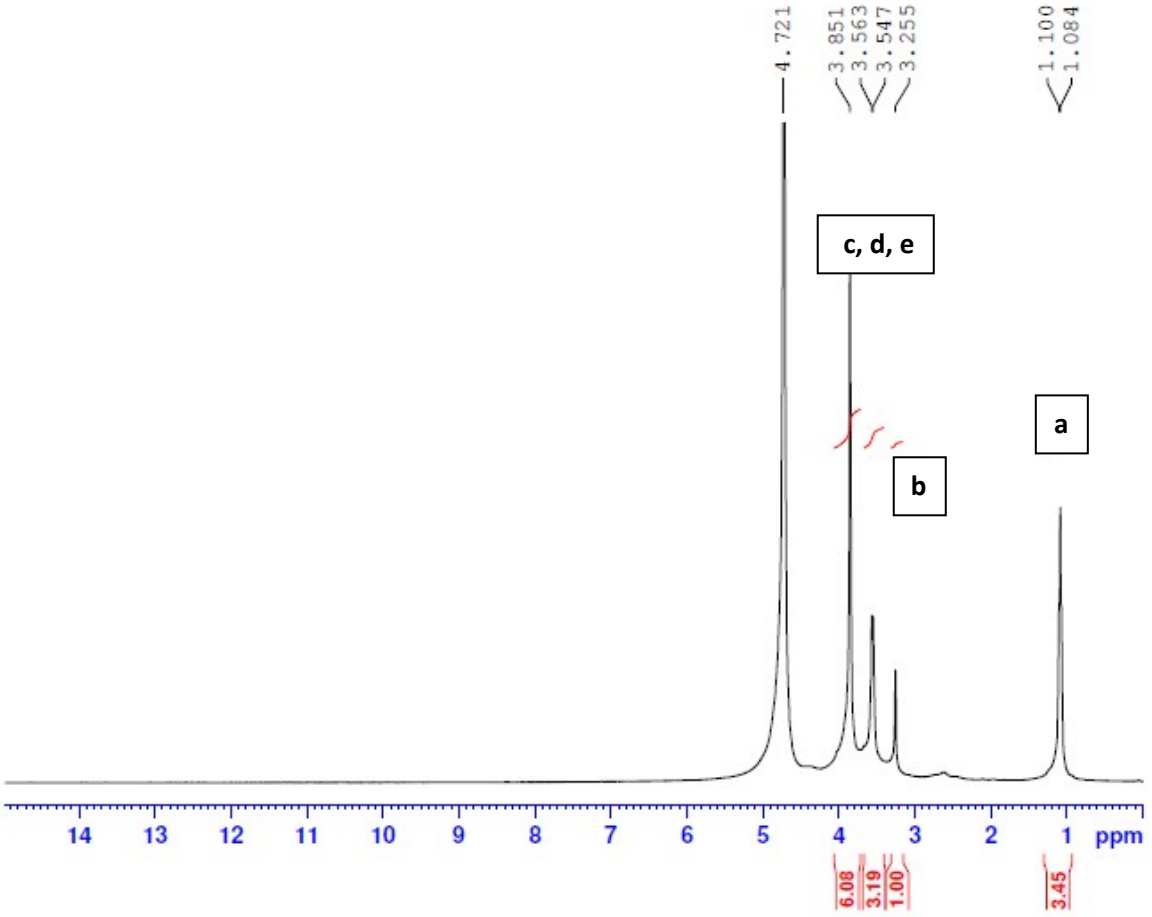
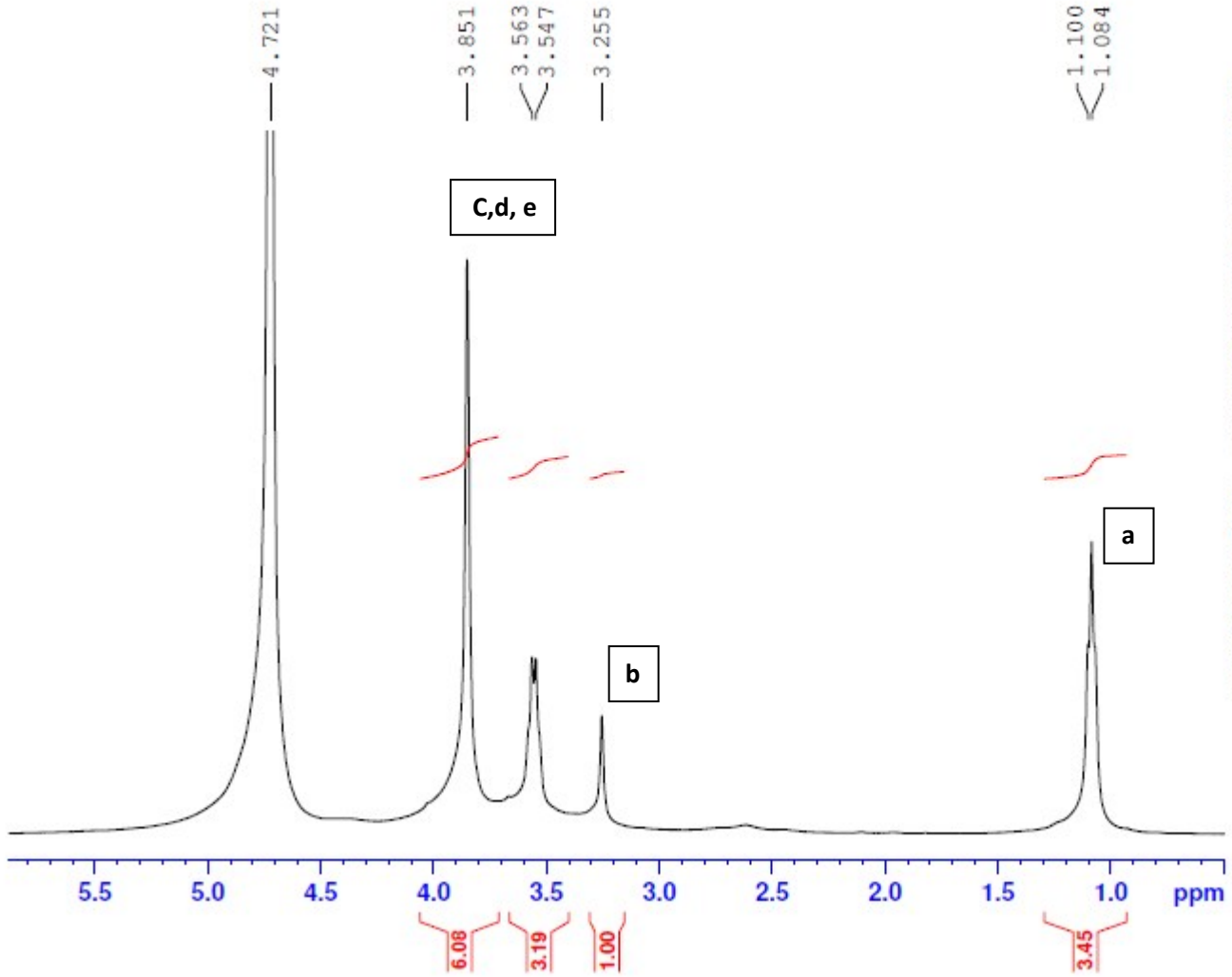
S_1 The ^1H NMR spectrum of *O*-cm-chitosan in D_2O



*The CH peak of **f** is overlapping with the solvent HOD signal at 4.72.



Sample code: I (haji)



BRUKER

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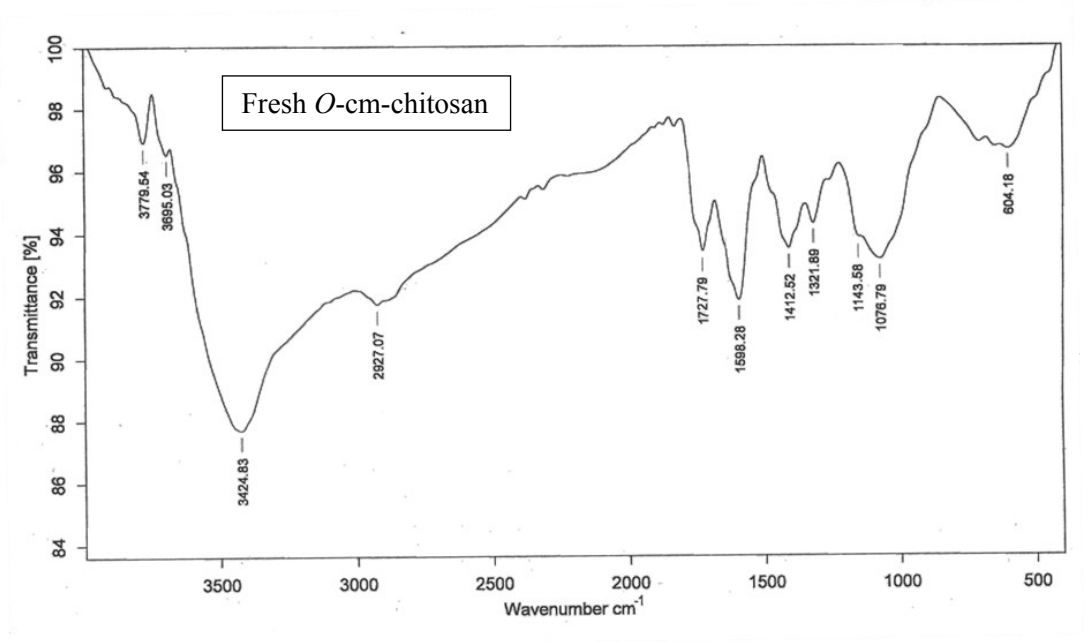
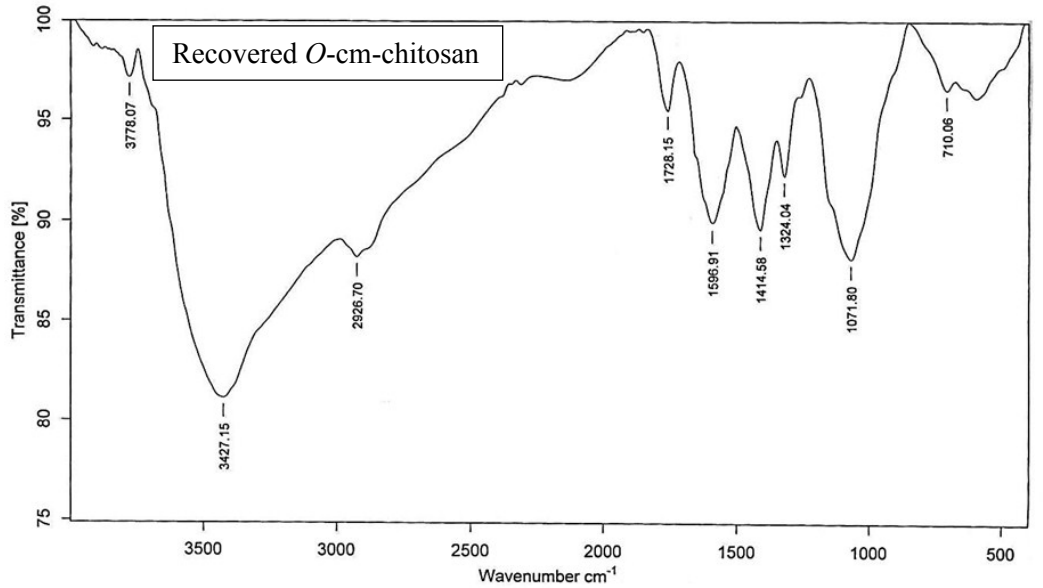
SOLVENT	D2O	
NS	20	
DS	0	
SWH	8012.820	Hz
FIDRES	0.122266	Hz
AQ	4.0894966	sec
RG	36	
DW	62.400	usec
DE	6.50	usec
TE	293.5	K
D1	4.00000000	sec
TD0	1	
======= CHANNEL f1 =======		
NUC1	1H	
P1	14.00	usec
PL1	-2.00	dB
PL1W	11.86359406	W
SFO1	400.2236020	MHz
SI	32768	
SF	400.2200000	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

S_2 The FT-IR spectrum of fresh and recovered *O*-cm-chitosan

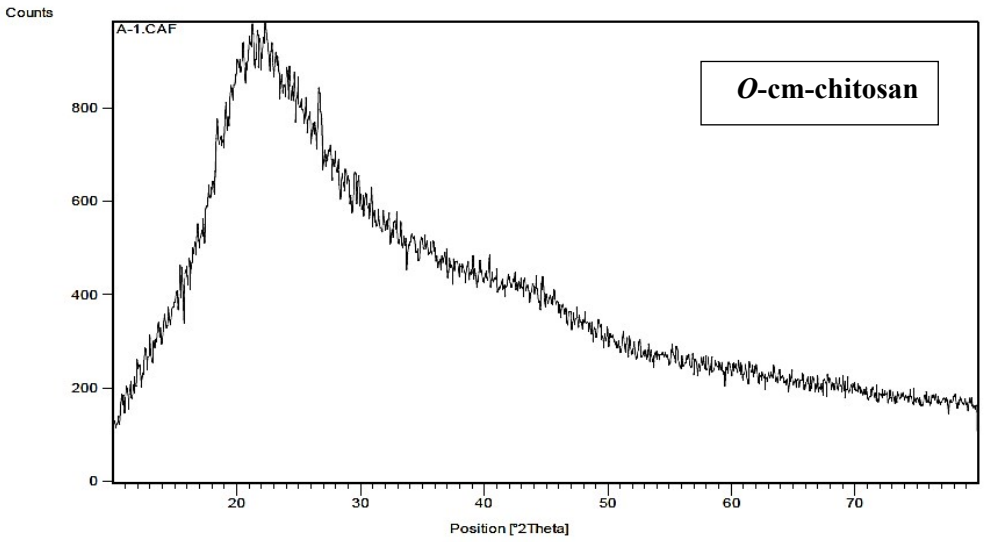
The FT-IR spectrum shows the basic characteristic absorptions at: 3424 cm^{-1} (O–H stretch.), 2927 cm^{-1} (C–H stretch.), 1598 cm^{-1} (N–H bend), 1727 cm^{-1} (–COOH), 1076–1143 cm^{-1} (–C–O sretch.).

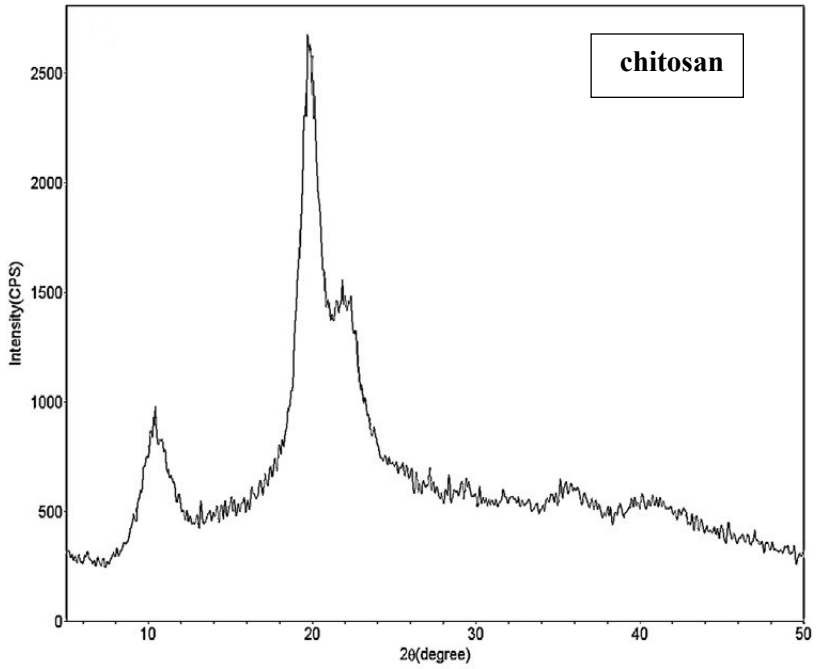




S_3 The X-ray diffraction (XRD) patterns of chitosan and *O*-cm-chitosan

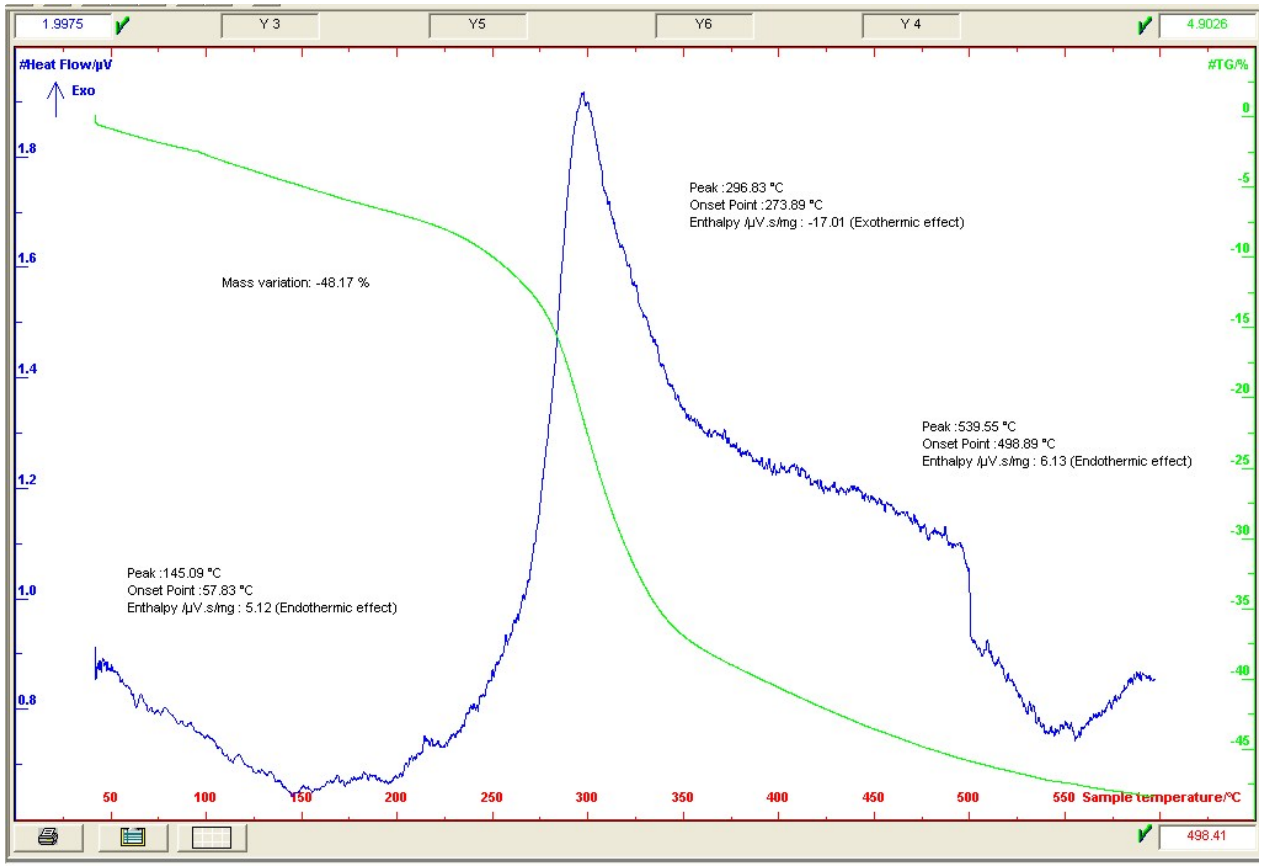
The XRD of original chitosan displays two characteristic peaks at 2θ =10° (weak diffraction peak) and 2θ =20° (strong diffraction peak) indicating a considerably high degree of crystallinity for chitosan. However, as the XRD of *O*-cm-chitosan shows, much (but not all) of the crystallinity was lost on *O*-carboxymethylation of chitosan. Therefore, the synthesized *O*-cm-chitosan is rather an amorphous bio-derived polymer, very likely due to a large change in intermolecular hydrogen bonding between the individual chains of chitoan on *O*-carboxymethylation.





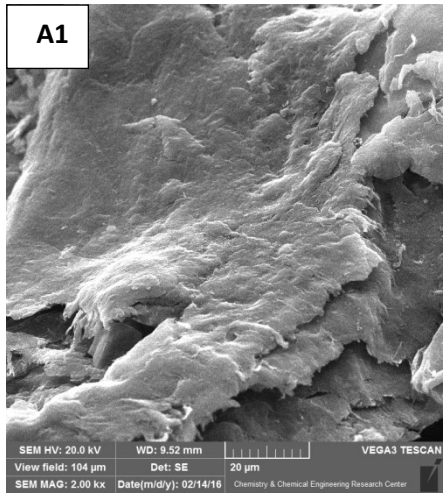
S$_4$ The TGA & DSC thermograms of *O*-cm-chitosan

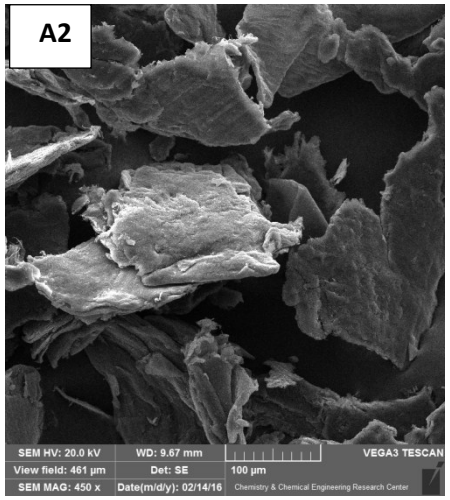
The TGA and DSC traces of *O*-cm-chitosan display a smooth endothermic weight loss at 60-274 °C, presumably due to dehydration and decarboxylation of *O*-cm-chitosan. The large weight loss at 296 °C in the TGA thermogram of *O*-cm-chitosan corresponds to a strong exothermic decomposition peak in the DSC trace of this compound. In an earlier study, the maximum thermal decomposition temperature of chitosan was reported to be 302 °C which is slightly greater than the value of 296 °C determined by the present study for *O*-cm-chitosan.[26] The lower thermal stability of *O*-cm-chitosan with respect to that of chitosan can be attributed to the less crystallinity and presence of carboxyl groups in this compound.

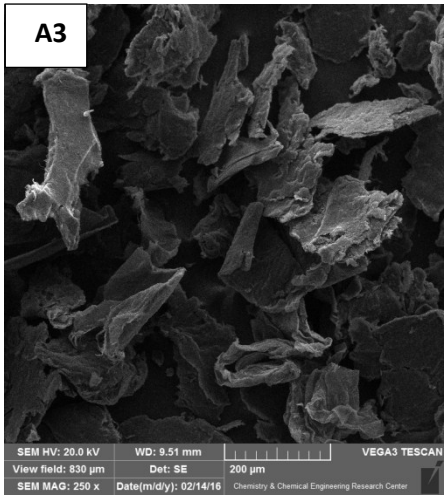


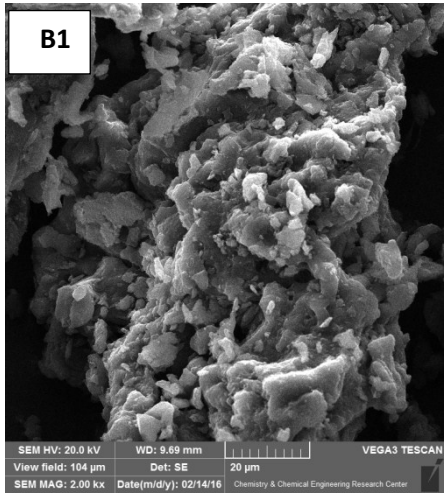
S_5 The scanning electron microscopy (SEM) images of chitosan and *O*-cm-chitosan

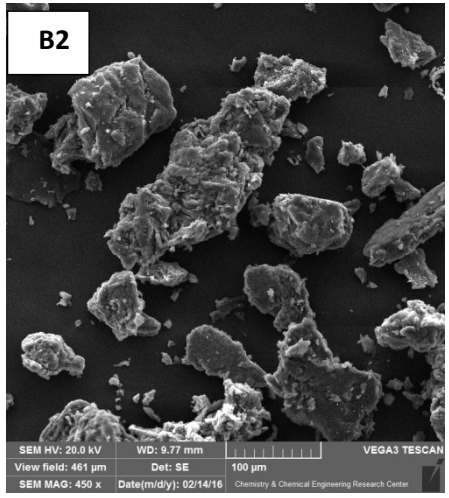
The SEM images showed a smooth surface morphology for chitosan (A1, A2, A3) before being carboxymethylated. Upon *O*-carboxymethylation (B1, B2, B3), the surface of chitosan was completely changed, indicating that the desired modification was achieved.

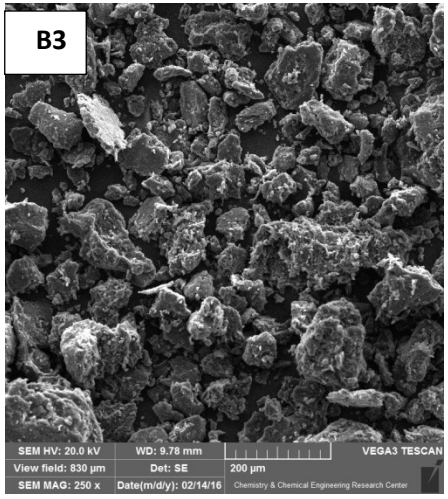




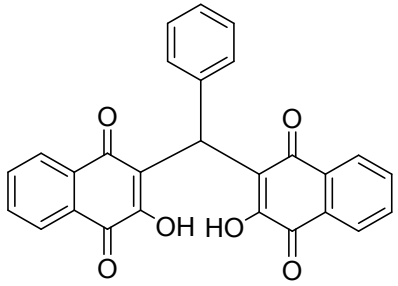




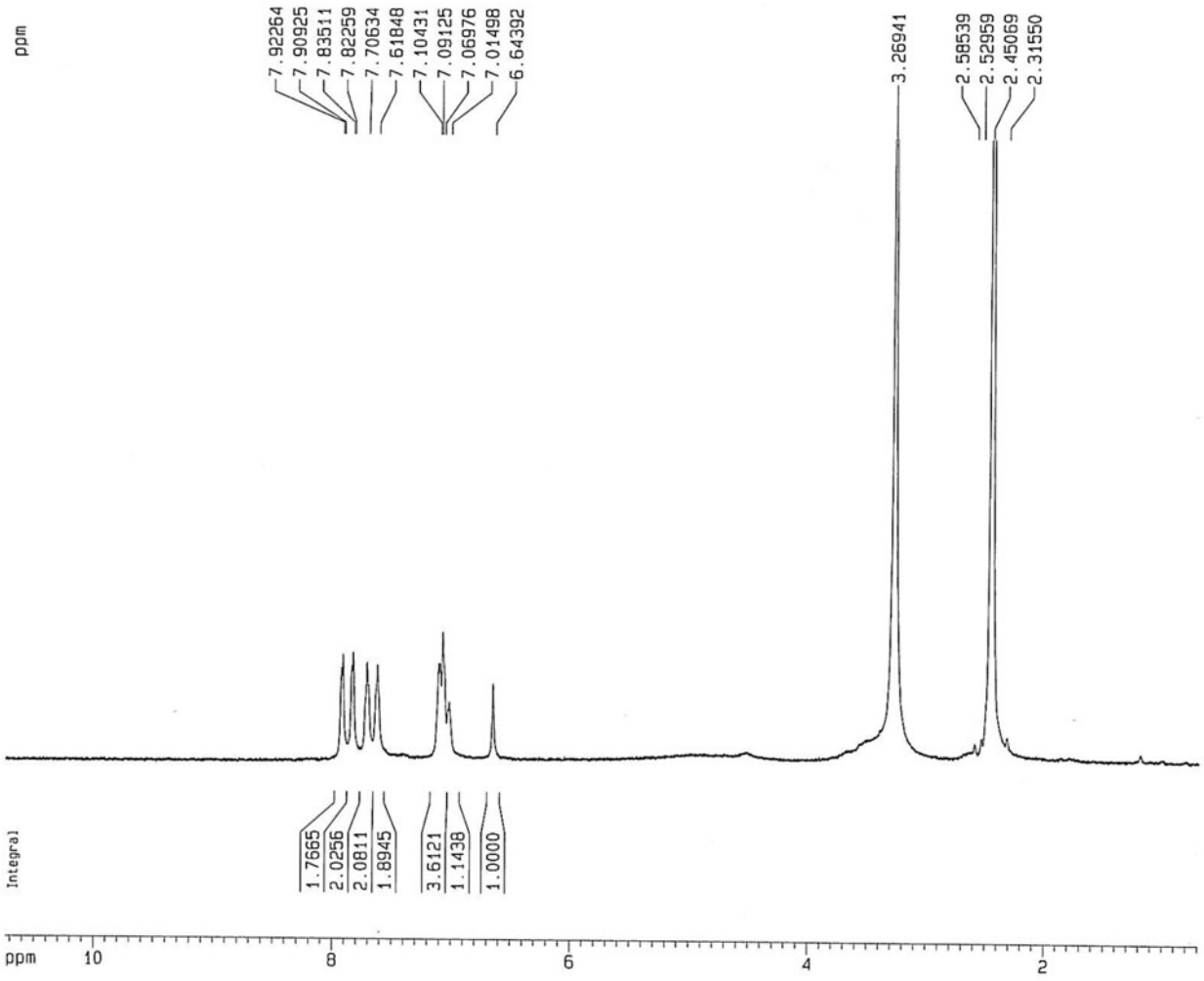




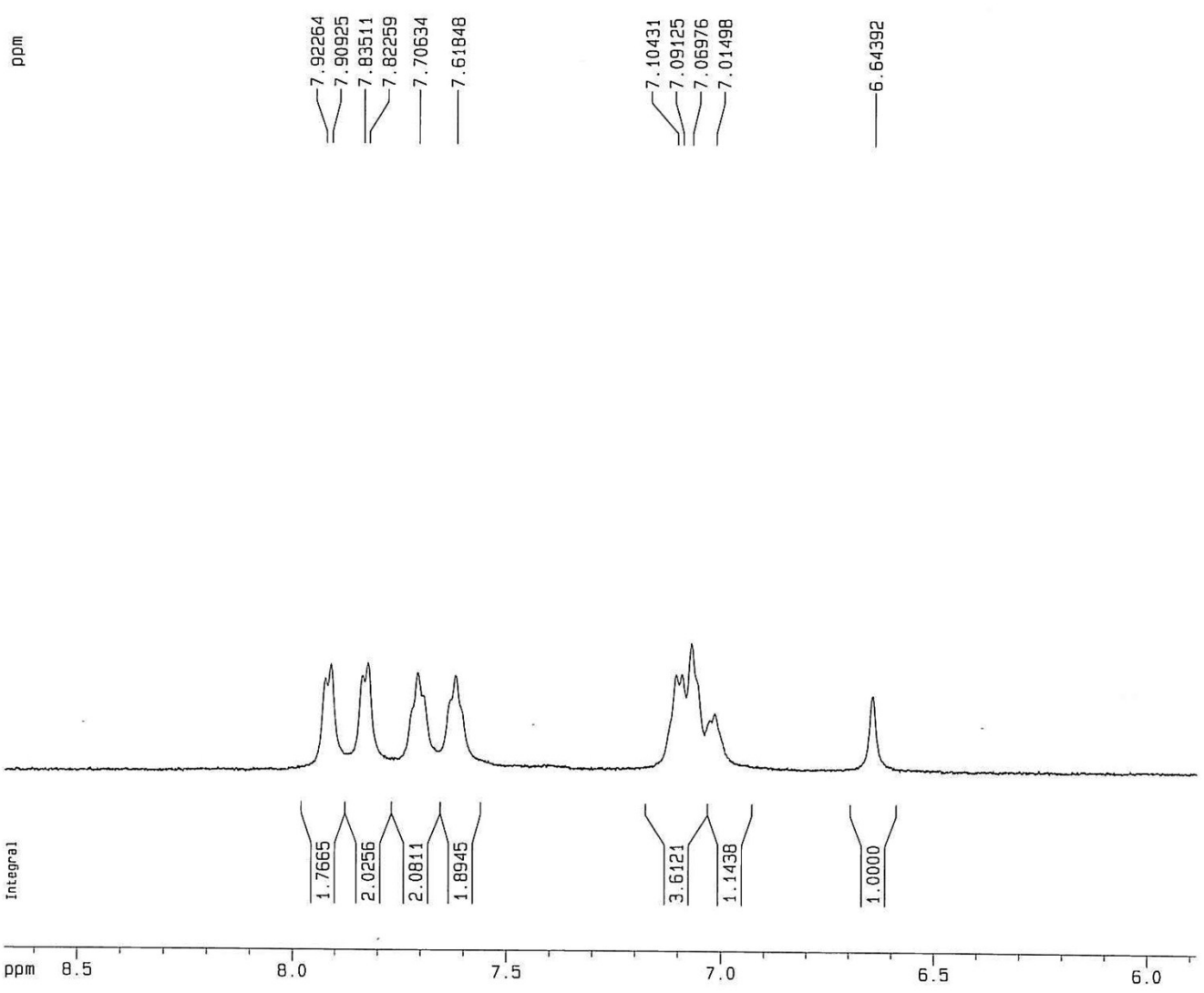
S$_6$ The ^{1}H NMR spectrum of 3,3′-(phenylmethylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-d_6 **(3a)**



^{1}H NMR (500 MHz, DMSO-d_6): δ_H 7.91 (d, *J* 6.7 Hz, 2H), 7.83 (d, *J* 6.3 Hz, 2H), 7.71 (br t, 2H), 7.62 (br t, 2H), 7.10-7.01 (m, 7H, Ph), 6.64 (1H, s, Aliph. CH) ppm.



A-Asghari 1HNMR in DMSO at 298 K 93/6/22



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MCWRK	0.01500000 sec

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F2 - Processing parameters

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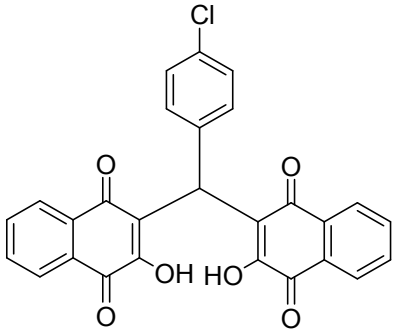
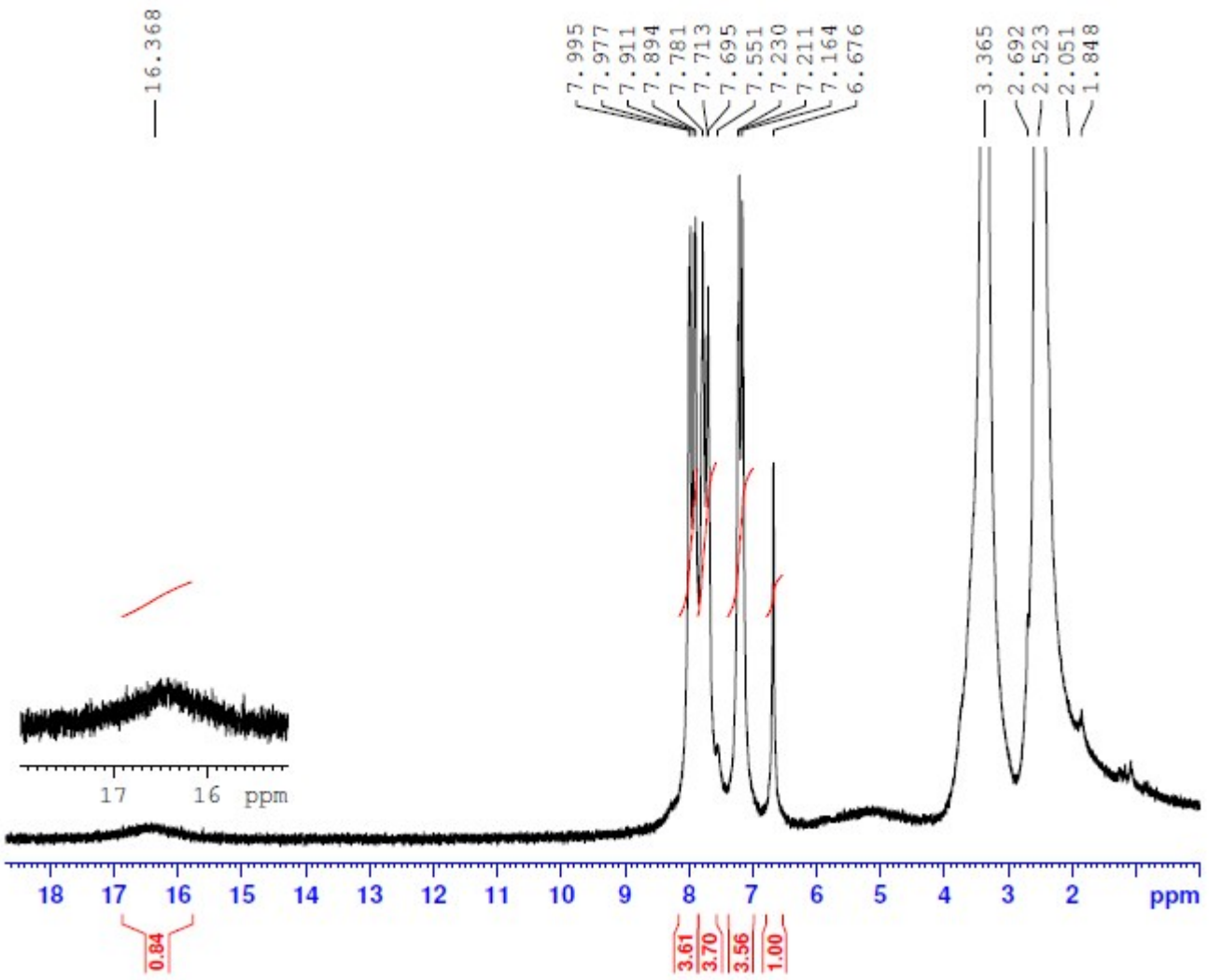
1D NMR plot parameters

CX	20.00 cm
CY	33.23 cm
F1P	8.669 ppm
F1	4335.56 Hz
F2P	5.886 ppm
F2	2943.84 Hz
PPMCM	0.13914 ppm/cm
HZCM	69.58583 Hz/cm

S_7 The ^{1}H NMR spectrum of 3,3′-((4-Chlorophenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-d_6 **(3b)**



^{1}H NMR (400 MHz, DMSO-d_6): δ_H 16.37 (br s , 2 Enolic OH), 7.99 (d, *J* 7.2 Hz, 2H), 7.90 (d, *J* 6.8 Hz, 2H), 7.78 (br t, 2H), 7.69 (br t, 2H), 7.22 (br d, 2H, Ar), 7.15 (br d, 2H, Ar), 6.68 (1H, s, Aliph. CH) ppm.



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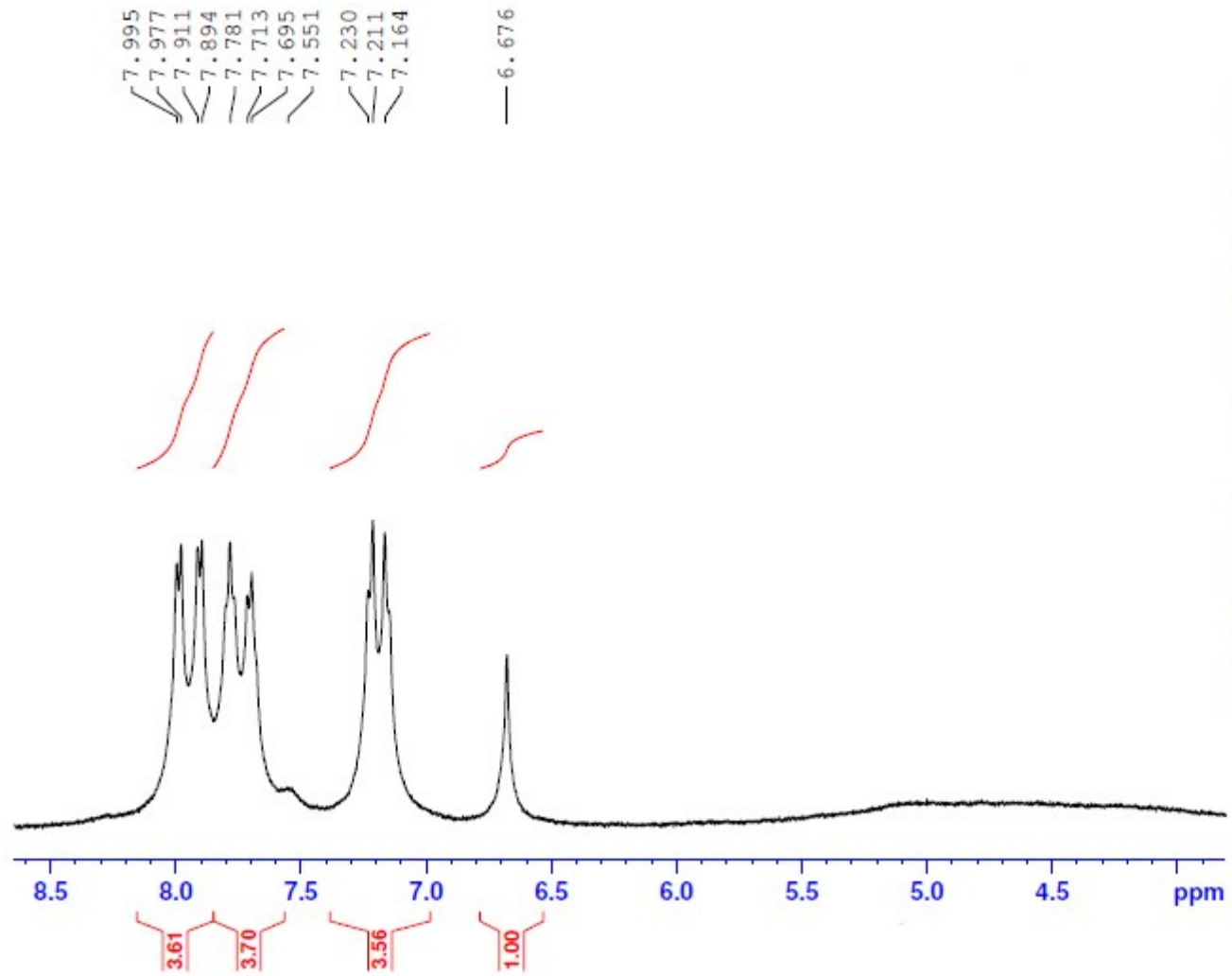

BRUKER

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TE	294.9 K
D1	4.00000000 sec
TD0	1
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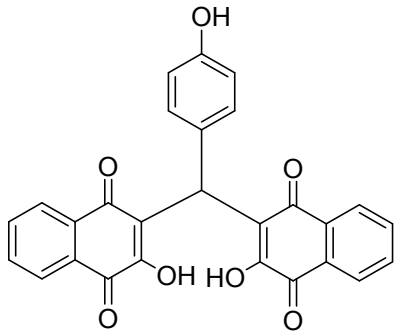
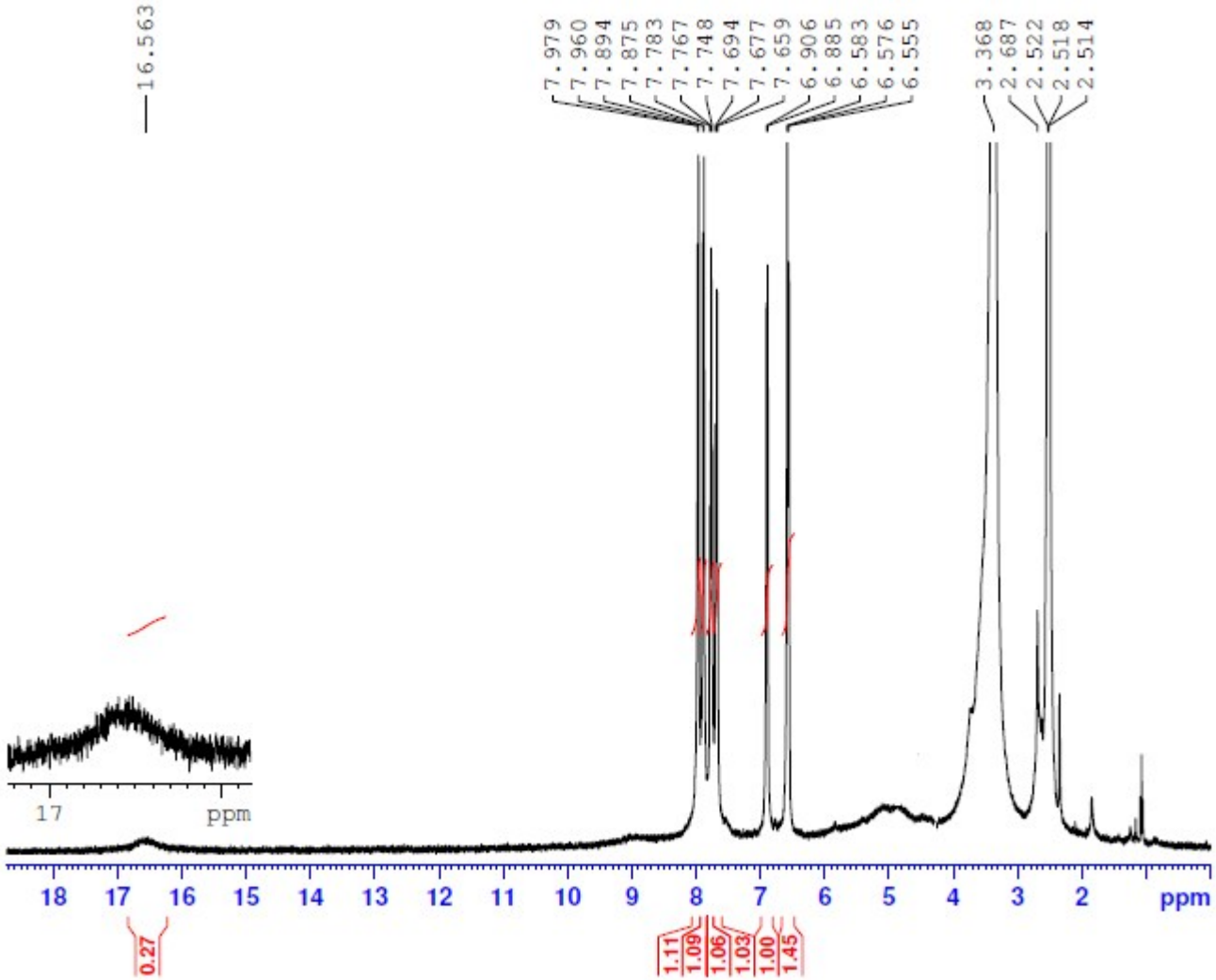
NUC1	1H
P1	14.00 usec
PL1	-2.00 dB
PL1W	11.86359406 W
SFO1	400.2236020 MHz
SI	32768
SF	400.2200000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

S$_8$ The ^{1}H NMR spectrum of 3,3′-((4-Hydroxyphenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-d_6 **(3c)**



^{1}H NMR (400 MHz, DMSO-d_6): δ_H 16.56 (br s, 2 Enolic OH), 7.97 (d, *J* 7.6 Hz, 2H), 7.88 (d, *J* 7.6 Hz, 2H), 7.77 (t, *J* 7.6 Hz, 2H), 7.68 (t, *J* 7.6 Hz, 2H), 6.90 (d, *J* 8.4 Hz, Ar), 6.58 (s, 1H, Phenolic OH), 6.56 (d, *J* 8.4 Hz, Ar), 6.58 (1H, s, Aliph. CH) ppm.



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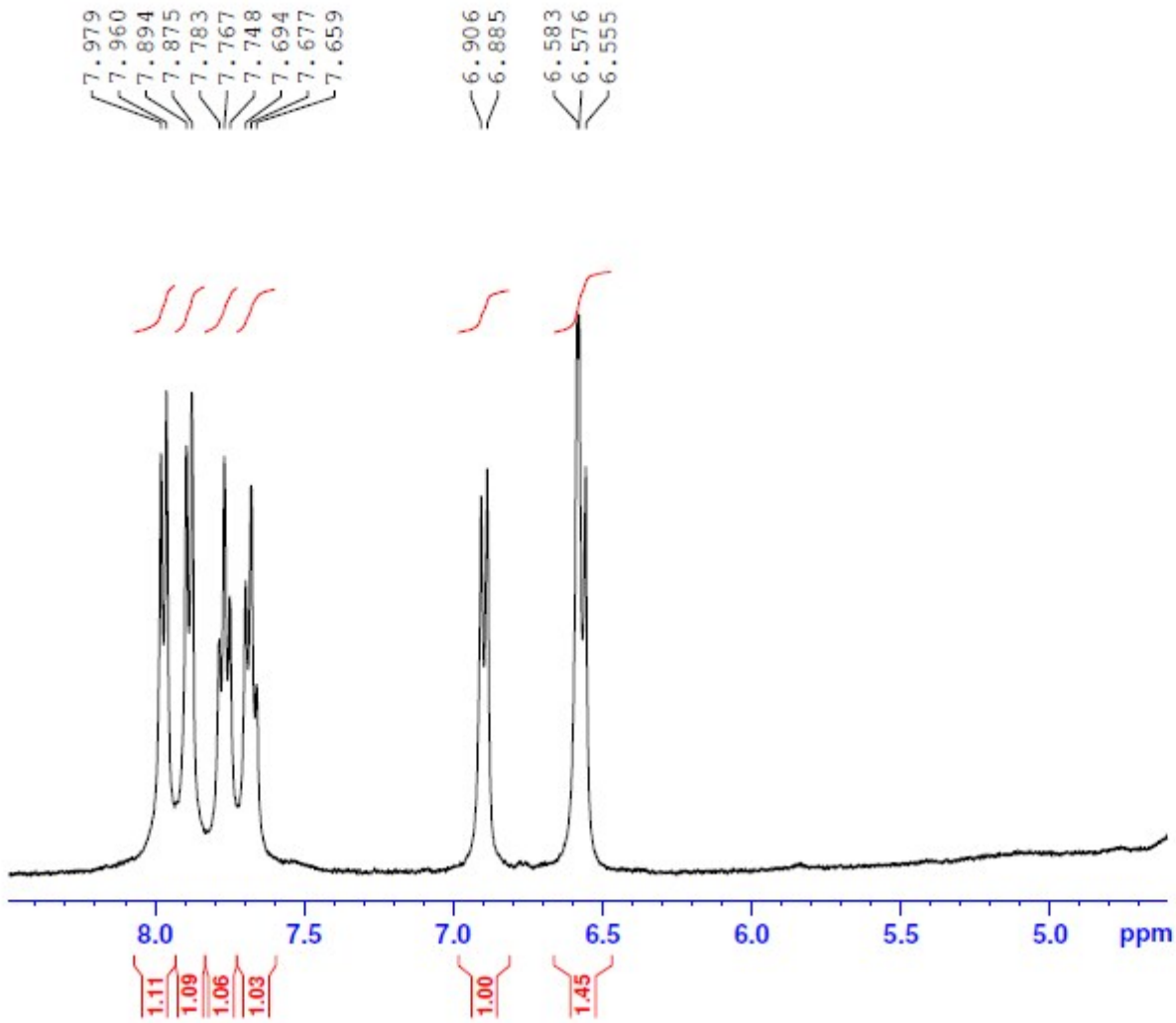

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FIDRES	0.122266	Hz
AQ	4.0894966	sec
RG	181	
DW	62.400	usec
DE	6.50	usec
TE	293.6	K
D1	4.00000000	sec
TD0	1	
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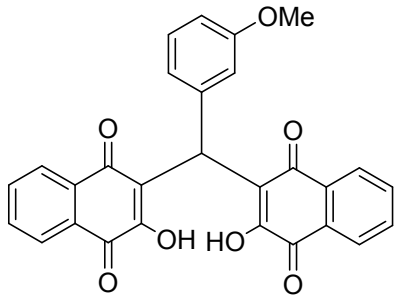
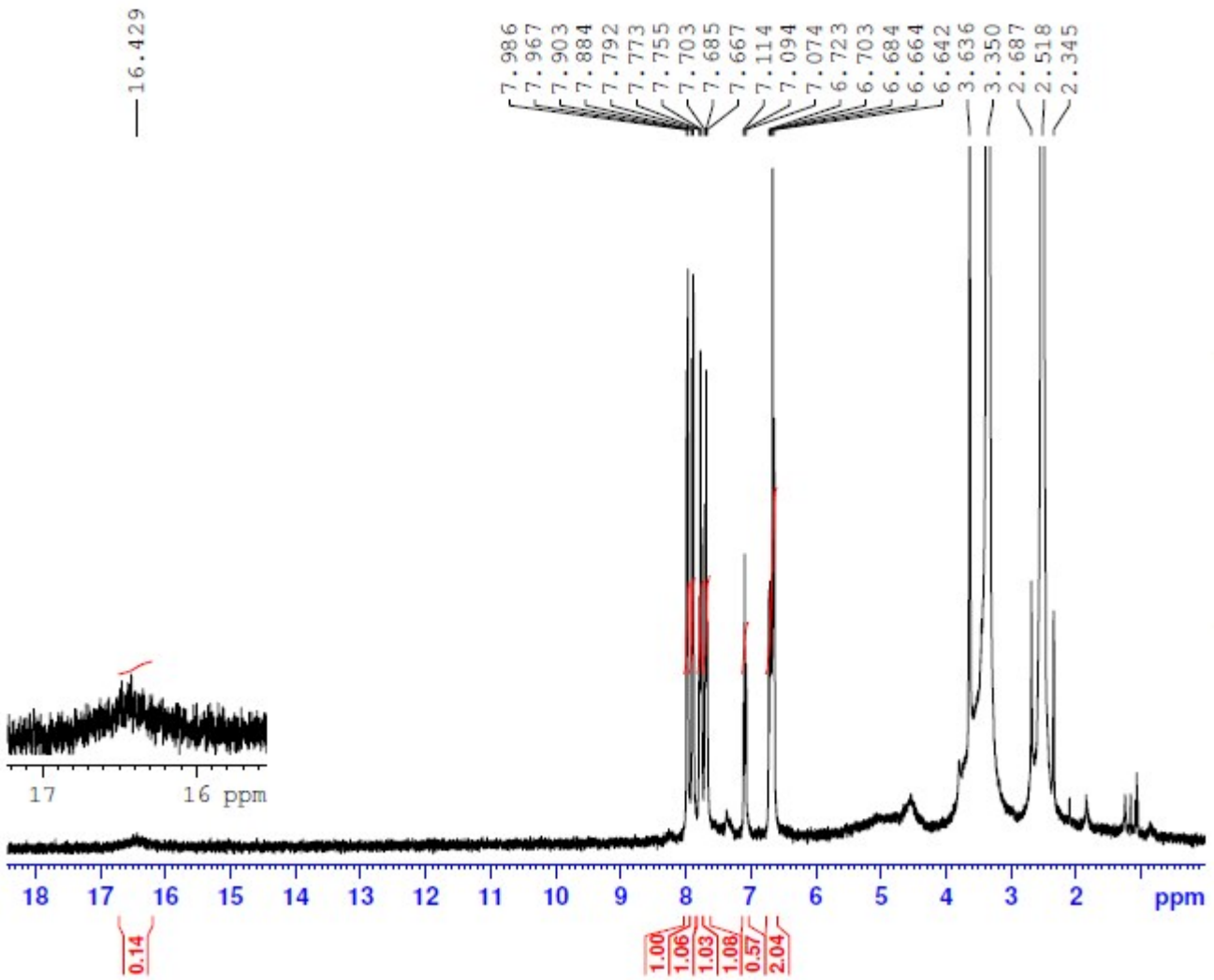
NUC1	1H	
P1	14.00	usec
PL1	-2.00	dB
PL1W	11.86359406	W
SFO1	400.2236020	MHz
SI	32768	
SF	400.2200000	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

S9 The ^{1}H NMR spectrum of 3,3′-((3-Methoxyphenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-d_6 **(3d)**



^{1}H NMR (400 MHz, DMSO-d_6): δ_H 16.45 (br s, 2 Enolic OH), 7.98 (d, *J* 7.6 Hz, 2H), 7.89 (d, *J* 7.6 Hz, 2H), 7.77 (t, *J* 7.6 Hz, 2H), 7.68 (t, *J* 7.6 Hz, 2H), 7.09 (t, *J* 8.0 Hz, 1H, Ar 5-H), 6.72-6.64 (m, 3H, Ar), 3.64 (s, 3H, OCH_3), 6.66 (s, 1H, Aliph. CH) ppm.



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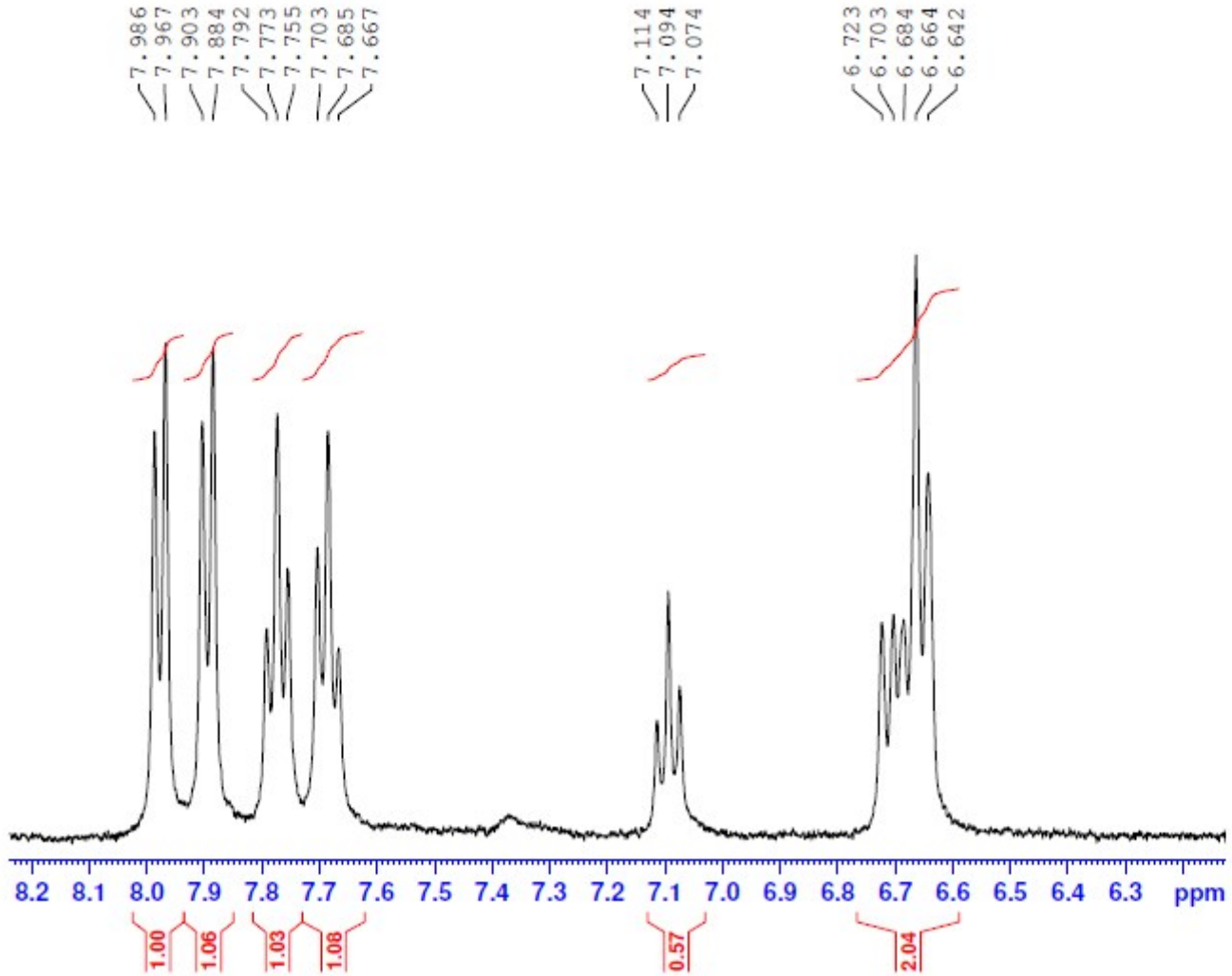

BRUKER

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PROCNO	1	
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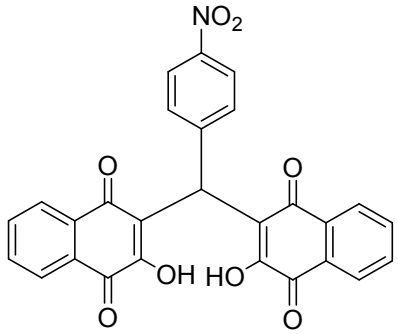
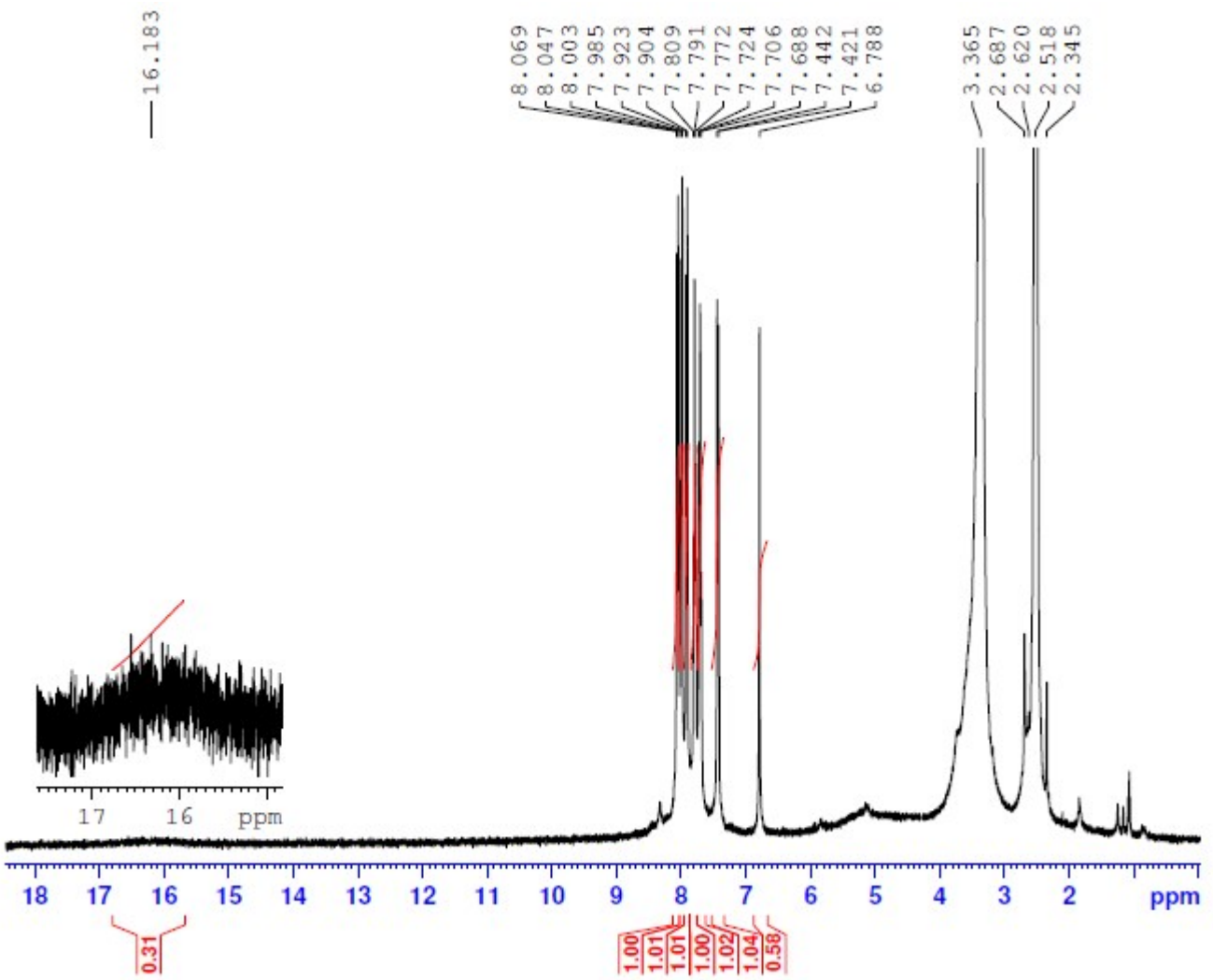
DS	0	
SWH	8012.820	Hz
FIDRES	0.122266	Hz
AQ	4.0894966	sec
RG	181	
DW	62.400	usec
DE	6.50	usec
TE	293.5	K
D1	4.00000000	sec
TD0	1	
======= CHANNEL f1 =======		
NUC1	1H	
P1	14.00	usec
PL1	-2.00	dB
PL1W	11.86359406	W
SFO1	400.2236020	MHz
SI	32768	
SF	400.2200000	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

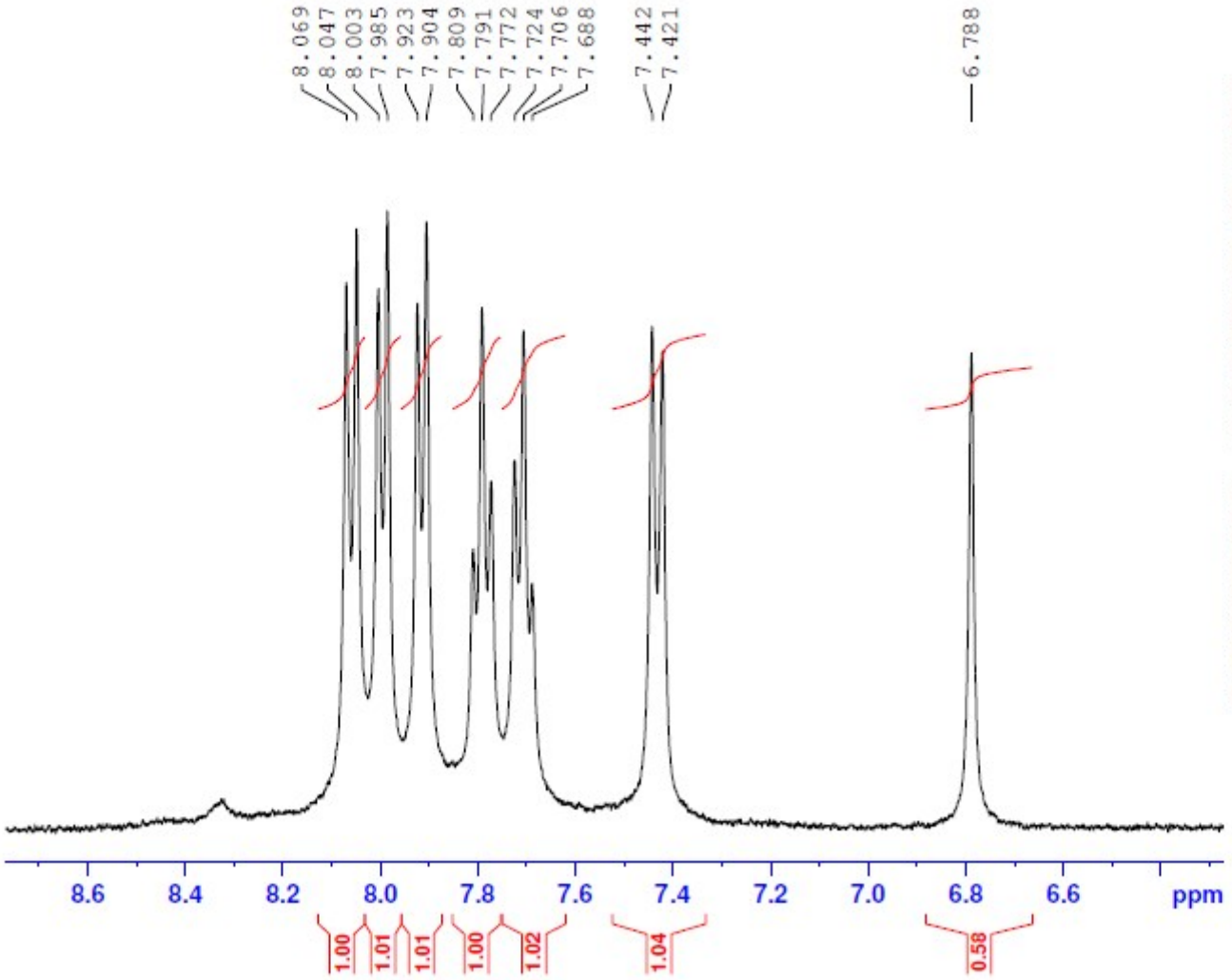
S_{10} The ^{1}H NMR spectrum of 3,3′-((4-Nitrophenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-d_6 **(3e)**



^{1}H NMR (400 MHz, DMSO-d_6): δ_H 16.18 (br s, 2 Enolic OH), 8.06 (d, *J* 8.6 Hz, 2H, Ar), 7.99 (d, *J* 7.2 Hz, 2H), 7.91 (d, *J* 7.6 Hz, 2H), 7.79 (t, *J* 7.4 Hz, 2H), 7.71 (t, *J* 7.2 Hz, 2H), 7.43 (d, *J* 8.6 Hz, 2H, Ar), 6.79 (s, 1H, Aliph. CH) ppm.



Sample code: E (haji)



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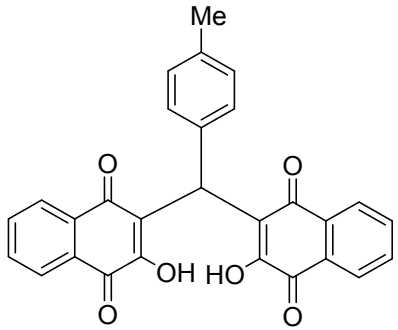
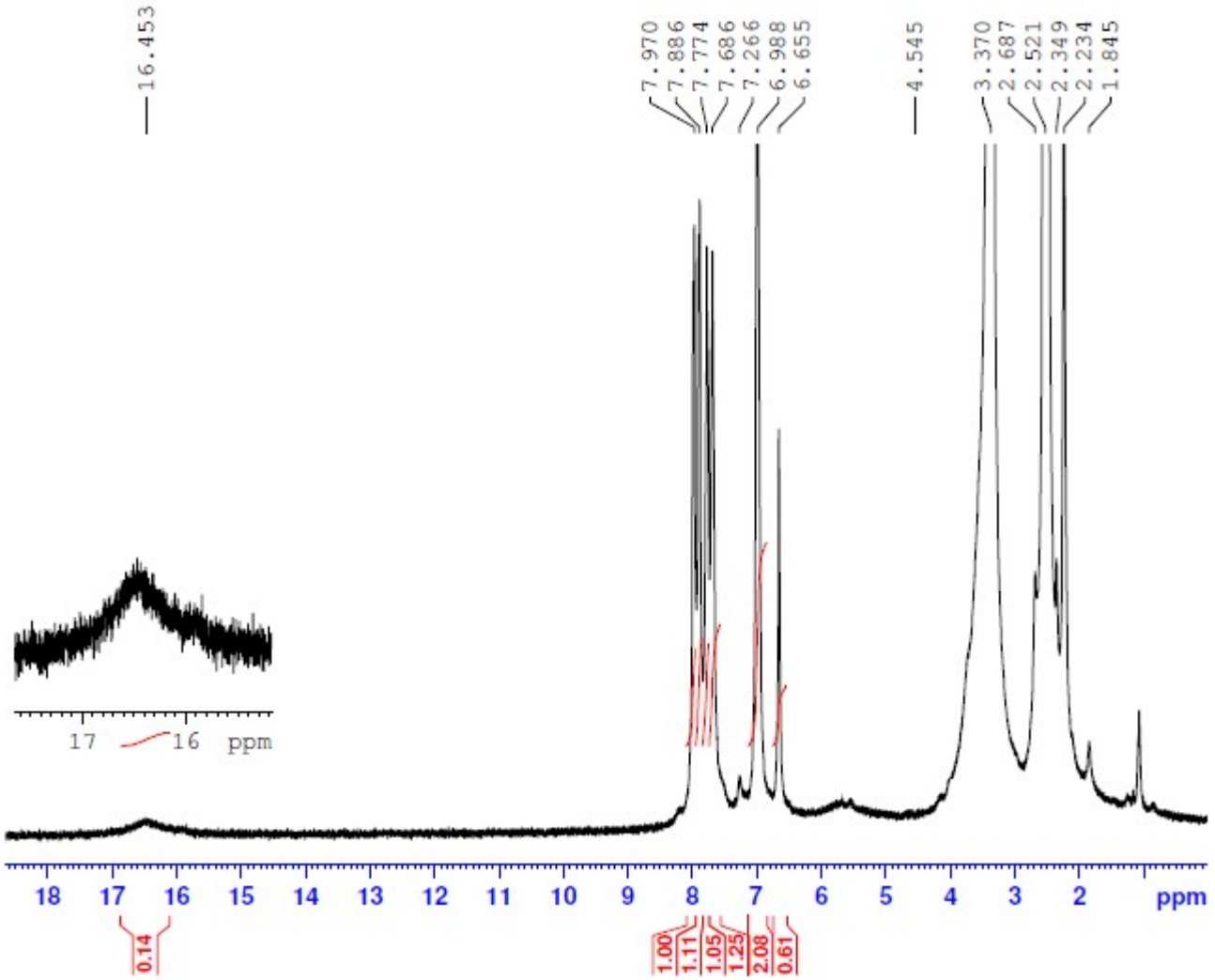
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	181
DW	62.400 usec
DE	6.50 usec
TE	293.5 K
D1	4.00000000 sec
TD0	1
=======	CHANNEL f1 =======
NUC1	1H
P1	14.00 usec
PL1	-2.00 dB
PL1W	11.86359406 W
SFO1	400.2236020 MHz
SI	32768
SF	400.2200000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

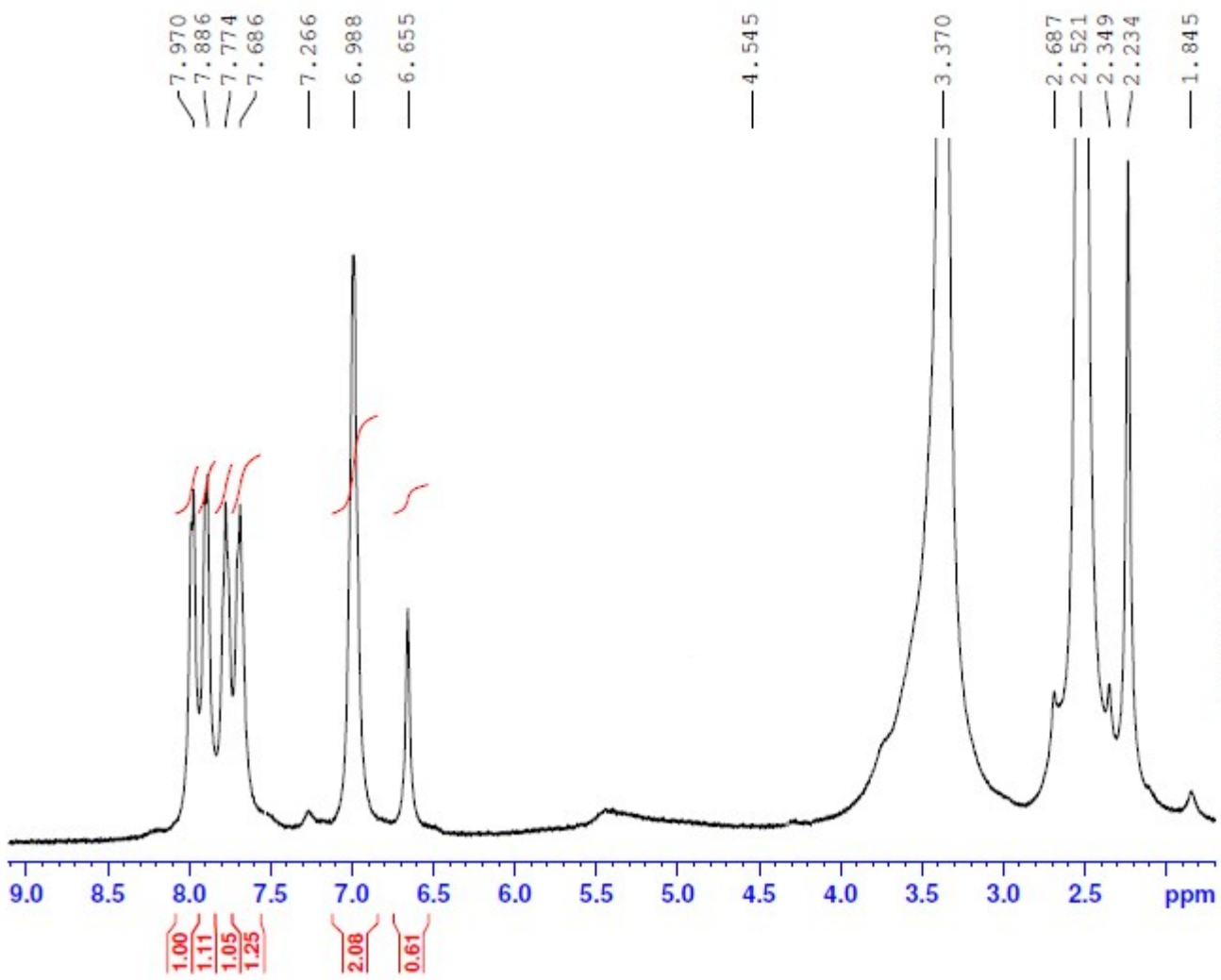
S_{11} The ^{1}H NMR spectrum of 3,3′-((4-Methylphenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-d_6 **(3f)**



^{1}H NMR (400 MHz, DMSO-d6): δ_H 16.45 (br s, 2 Enolic OH), 7.97-6.99 (m, 12H), 6.65 (s, 1H, Aliph. CH), 2.23 (s, 3H, CH_3) ppm.



Sample code: F (haji)



BRUKER

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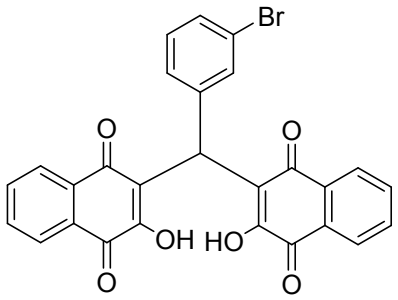
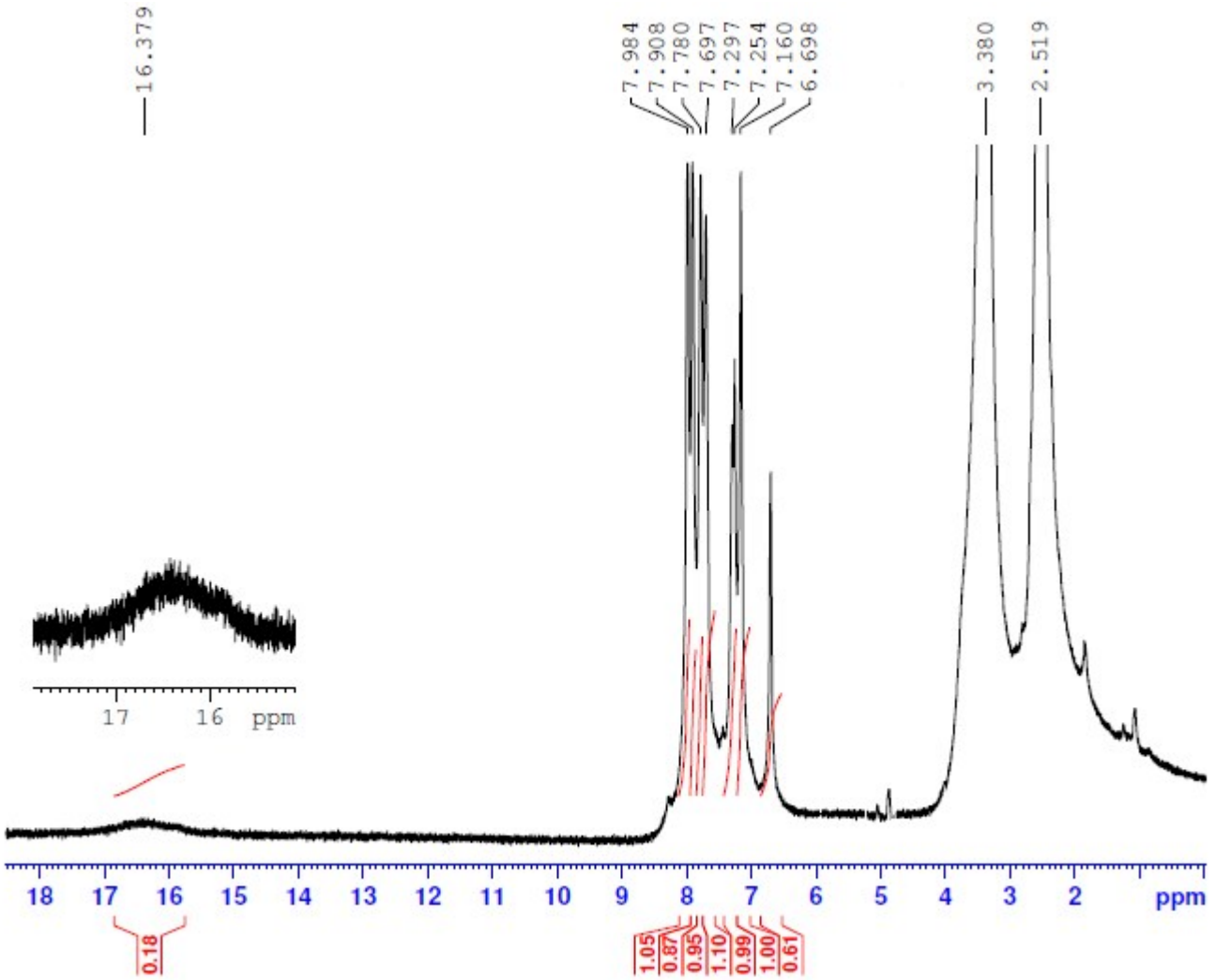
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	181
DW	62.400 usec
DE	6.50 usec
TE	293.5 K
D1	4.00000000 sec
TD0	1
====== CHANNEL f1 ======	
NUC1	1H
P1	14.00 usec
PL1	-2.00 dB
PL1W	11.86359406 W
SFO1	400.2236020 MHz
SI	32768
SF	400.2200000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

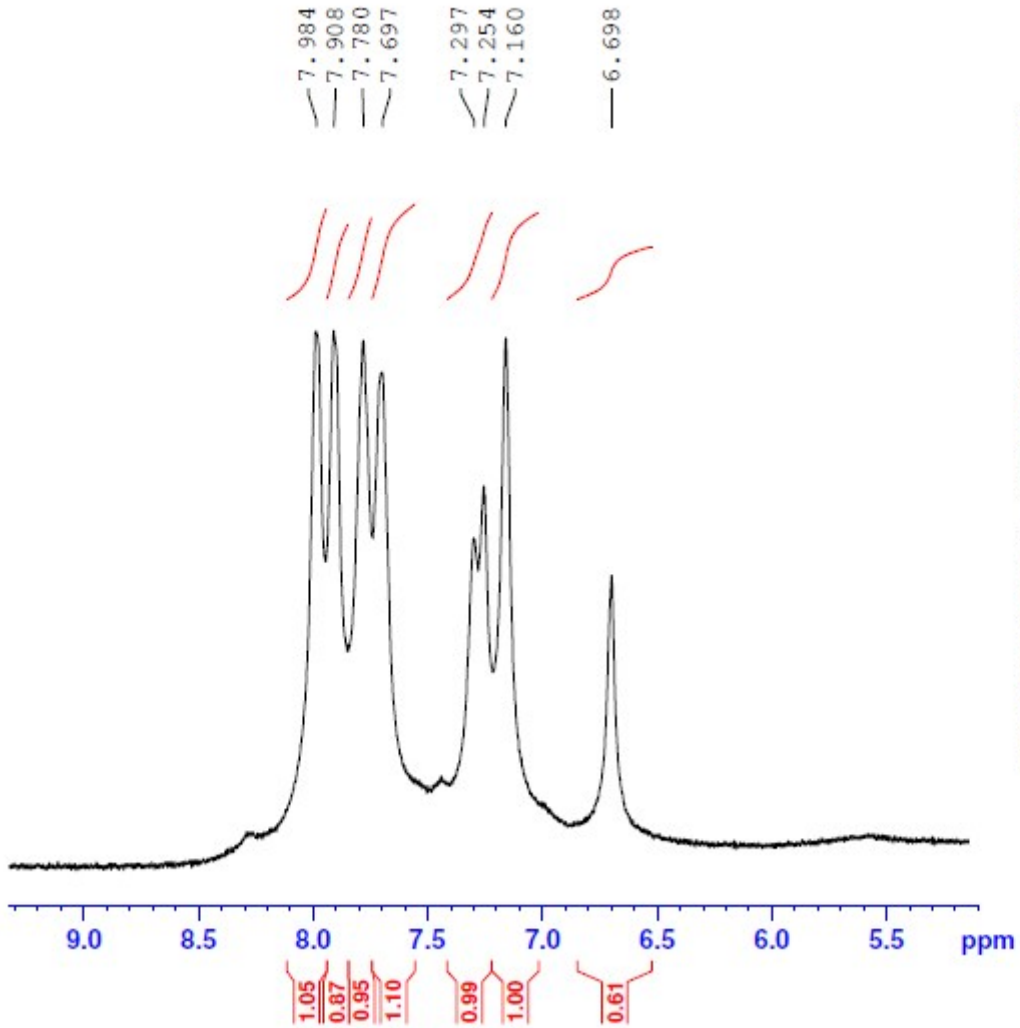
S_{12} The ^{1}H NMR spectrum of 3,3′-((3-Bromophenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-d_6 **(3g)**



^{1}H NMR (400 MHz, DMSO-d_6): δ_H 16.38 (br s, 2 Enolic OH), 7.98-7.70 (m, 8H), 7.30-7.16 (m, 4H, Ar), 6.70 (s, 1H, Aliph. CH) ppm.



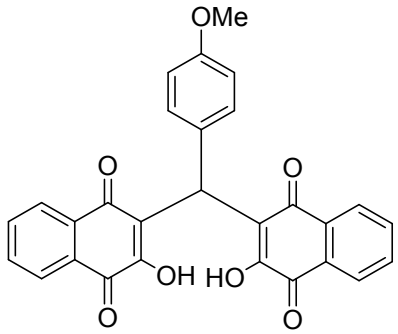
Sample code: G (haji)



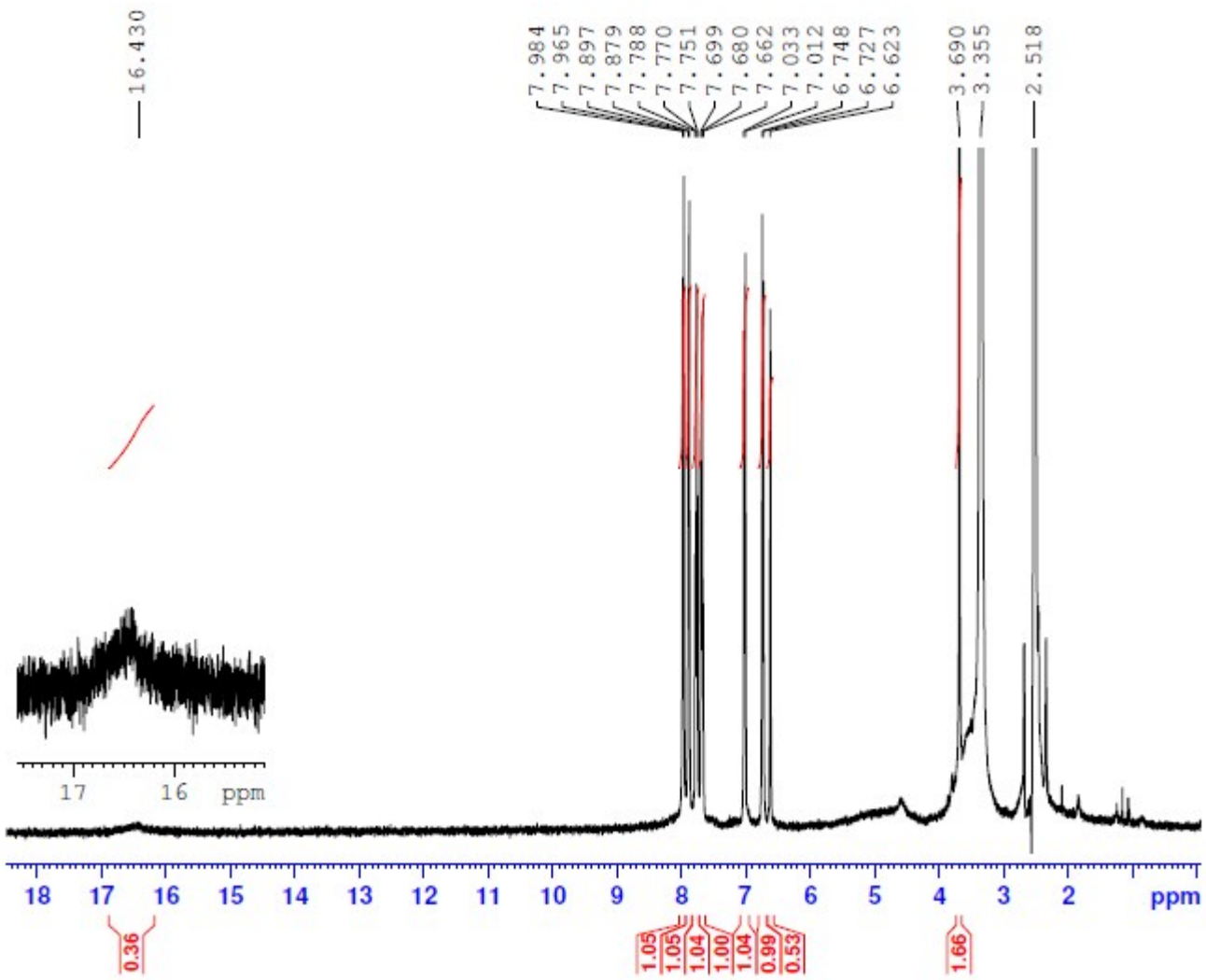
BRUKER

NAME	Gilan UN	
EXPNO	1771	
PROCNO	1	
Date_	20150125	
Time	14.49	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	65536	
SOLVENT	DMSO	
NS	20	
DS	0	
SWH	8012.820	Hz
FIDRES	0.122266	Hz
AQ	4.0894966	sec
RG	181	
DW	62.400	usec
DE	6.50	usec
TE	293.6	K
D1	4.00000000	sec
TD0	1	
=======	CHANNEL f1	=======
NUC1	1H	
P1	14.00	usec
PL1	-2.00	dB
PL1W	11.86359406	W
SFO1	400.2236020	MHz
SI	32768	
SF	400.2200000	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

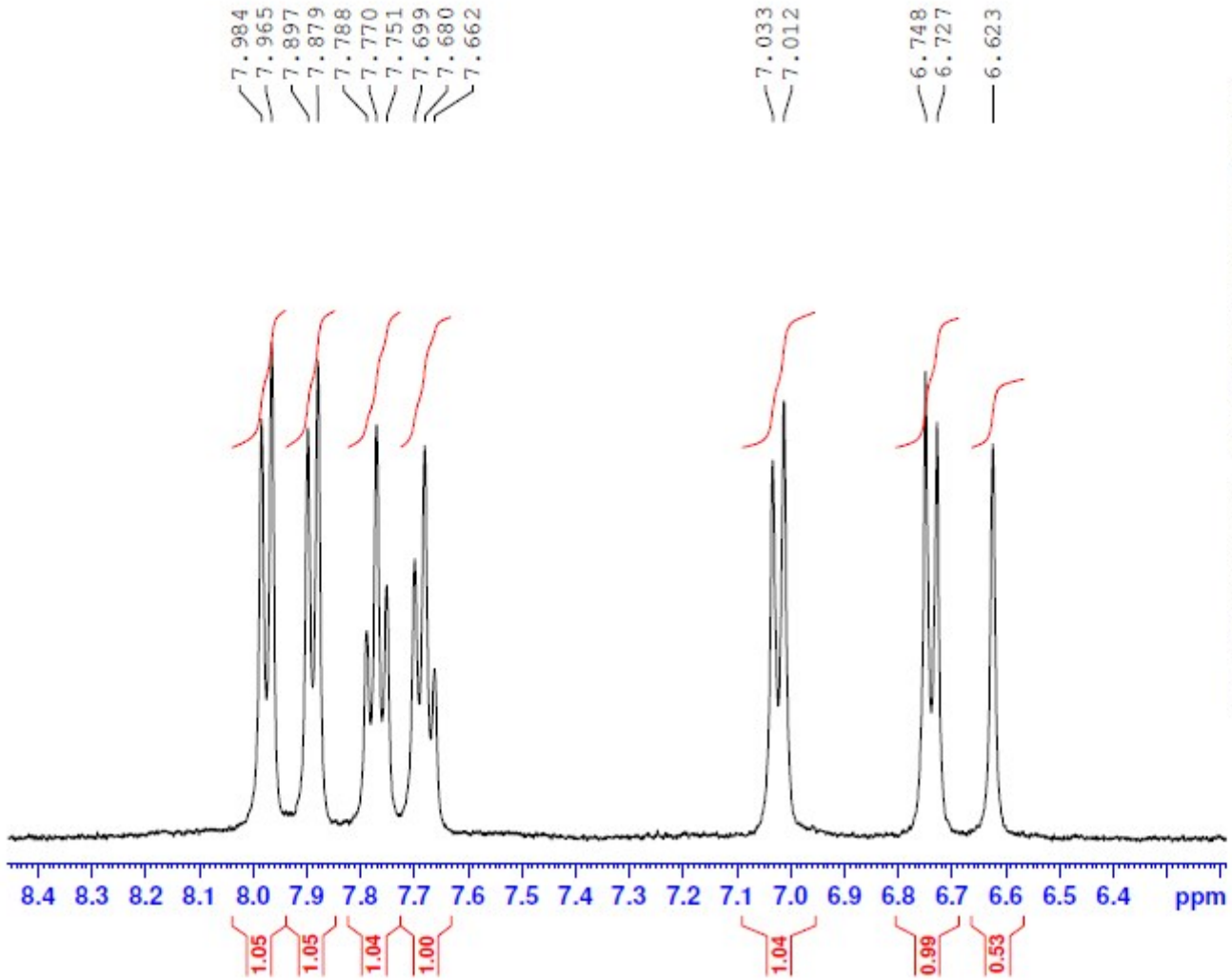
S_{13} The ^{1}H NMR spectrum of 3,3′-((4-chlorophenyl)methylene)bis(2-hydroxynaphthalene-1,4-dione) in DMSO-d_6 **(3h)**



^{1}H NMR (400 MHz, DMSO-d_6): δ_H 16.43 (br s, 2 Enolic OH), 7.97 (d, *J* 7.6 Hz, 2H), 7.89 (d, *J* 7.2 Hz, 2H), 7.77 (t, *J* 7.4 Hz, 2H), 7.68 (t, *J* 7.4 Hz, 2H), 7.02 (d, *J* 8.4 Hz, 2H, Ar), 6.74 (d, *J* 8.4 Hz, 2H, Ar), 6.62 s, 1H, Aliph. CH), 3.69 (s, 3H, OCH_3) ppm.



Sample code: H (haji)



BRUKER

NAME	Gilan UN
EXPNO	1772
PROCNO	1
Date_	20150125
Time	14.55
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	20
DS	0
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	181
DW	62.400 usec
DE	6.50 usec
TE	293.6 K
D1	4.00000000 sec
TD0	1
====== CHANNEL f1 ======	
NUC1	1H
P1	14.00 usec
PL1	-2.00 dB
PL1W	11.86359406 W
SFO1	400.2236020 MHz
SI	32768
SF	400.2200000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00