One-pot protocol for J-aggregated anthraimidazolediones catalyzed by phosphotungstic acid in PEG-400 under aerobic condition

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Supplementary Data

General information:

Melting points were determined in open capillary tubes on Kofler block apparatus and are uncorrected. IR spectra were recorded in cm^{-1} using KBr discs with a Perkin Elmer RXI FTIR spectrophotometer. NMR spectra (^{1}H, ^{13}C) were recorded in $CDCl_3$ or DMSO-D_6 solution in 5 mm BBO probe fitted with a pulse field gradient and working with Topsin 1.3 programme in a Bruker AV-300 Supercon NMR spectrometer (chemical shifts in δ ppm and J in Hz). Hitachi UV-vis U-3501 spectrometer was used for recording UV/VIS spectra in HPLC grade acetonitrile and toluene solution in the order of 10^{-5} mol L^{-1}concentration at room temperature. Perkin-Elmer LS-55 was used for recording fluorescence spectra using aforesaid solution with similar concentration. Field emission scanning electron microscopy (FESEM) was used to observe the surface morphology (both unused and used PTA). Previously, the samples were coated with a thin layer of gold to avoid electrical charging during examination. Zeiss Auriga instrument was used for FESEM study. Mass spectral analysis of **compound 3x** has been performed by Xevo-G2-S QTof instrument in methanol solvent. X-ray diffraction analysis of **3p** and **3t** were performed at room temperature by X-PERT-PRO Pan analytical diffractometer using Cu Kα (λ= 1.5406) as X-ray source of current 30 mA at a generator voltage of 40 kV. The rate of scanning was 1° min^{-1}. X-ray crystallographic data were taken on a Bruker Smart Apex 2 diffractometer equipped with a CCD area detector with graphite monochromatized Mo K_{α} radiation. Further information on the crystal structure investigations may be obtained from Cambridge Crystallographic Data Center CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax (+44-(0)1223-336033 or email: (deposit@ccdc.cam.ac.uk).

Preparation of samples for FESEM studies:

Samples for FESEM studies were prepared as follows. Stock solutions of fresh PTA and used PTA (1×10^{-5} M) in toluene were prepared and after twenty five minutes of sonication at room temperature, a small amount of aliquot was deposited onto a clean wafer and subjected to slow evaporation.

Preparation of samples for SEM studies:

Samples for SEM studies were prepared as follows. Stock solutions of **3p** and **3t** (1×10^{-5} M) in toluene were prepared and after twenty five minutes of sonication at room temperature, a small amount of aliquot was deposited onto a clean wafer and subjected to slow evaporation.

Spectral data of some new compounds:

2-(4-(methylthio)phenyl)-1H-anthra[1,2-d]imidazole-6,11-dione (3k). Yield: 222 mg, 82% dark brown solid; Mp: 294-295°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.19 (br s, 1H), 8.29-8.26 (m, 1H), 8.23-8.20 (m, 1H), 8.16 (d, J = 8.4 Hz, 1H), 8.04-7.98 (m, 3H), 7.77-7.73 (m, 2H), 7.34-7.12 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 183.9, 183.0, 157.6, 149.0, 143.3, 134.7, 134.6, 133.5, 133.3, 128.8, 128.2, 127.1, 126.6, 125.7, 125.5, 125.0, 121.4, 120.6, 118.9, 14.5; IR υ_{max} (KBr) cm^{-1} 2924, 2853, 1662, 1583, 1466; anal. calcd for $C_{22}H_{14}N_2O_2S$: C: 71.33, H: 3.81, N: 7.56 %, found: C: 71.31, H: 3.80, N: 7.53 %.

2-pentyl-1H-anthra[1,2-d]imidazole-6,11-dione (3o). Yield: 310 mg, 97%, yellow crystalline solid; Mp 158-160°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.06 (s, 1H), 8.22-8.18 (m, 2H), 8.02-7.97 (m, 2H), 7.92-7.89 (m, 2H), 2.96 (t, *J* = 7.5 Hz, 2H), 1.81-1.77 (m, 2H), 1.34-1.32 (m, 4H), ca. 0.88 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 183.6, 182.8, 162.9, 149.5, 134.7, 134.5, 133.5, 133.3, 132.3, 127.5, 127.0, 126.6, 126.5, 124.5, 120.5, 31.2, 28.5, 27.6, 22.1, 14.1; IR

υ_{max} (KBr) cm^{-1} 3326, 2925, 2854, 1660, 1583, 1519; anal. calcd for $C_{20}H_{18}N_2O_2$: C: 75.45, H: 5.70, N: 8.80 %, found: C: 75.44, H: 5.68, N: 8.81 %.

2-pentadecyl-1H-anthra[1,2-d]imidazole-6,11-dione (3q). Yield: 425 mg, 93%, yellow crystalline solid; Mp 122-123°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.84 (br. s, 1H), 8.36-8.33 (m, 1H), 8.29-8.26 (m, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.84-7.77 (m, 2H), 3.02 (t, *J* = 7.8 Hz, 2H), 1.98-1.88 (m, 2H), 1.46-1.25 (m, 24H, partially merged in HOD peak), ca. 0.89 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.8, 182.4, 160.4, 148.6, 134.4, 133.9, 133.6, 133.3, 132.9, 132.3, 127.8, 127.2, 126.1, 124.8, 121.1, 117.4, 31.5, 29.2, 29.2, 29.0, 28.9, 28.8, 27.5, 22.2, 13.6; IR υ_{max} (KBr) cm^{-1} 3851, 3348, 2916, 2848, 2347, 1655, 1648, 1578, 1517; anal. calcd for $C_{30}H_{38}N_2O_2$: C: 78.56, H: 8.35, N: 6.11 %, found: C: 78.54, H: 8.37, N: 6.10 %.

2-(thiophen-3-yl)-1H-anthra[1,2-d]imidazole-6,11-dione (3u). Yield: 260 mg, 86%, yellowish brown solid; Mp 284-285°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.13 (s, 1H), 8.85-8.84 (m, 1H), 8.17-8.13 (m, 2H), 8.01-8.00 (m, 2H), 7.97-7.96 (m, 1H), 7.88-7.86 (m, 2H), 7.72-7.70 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 183.4, 182.5, 154.2, 149.5, 134.7, 134.4, 133.4, 133.2, 132.8, 131.4, 128.9, 128.7, 127.7, 127.5, 126.9, 126.4, 124.9, 121.2, 118.7; IR υ_{max} (KBr) cm^{-1} 3433, 3079, 1667, 1584, 1561; anal. calcd for $C_{19}H_{10}N_2O_2S$: C: 69.08, H: 3.05, N: 8.48 %, found: C: 69.07, H: 3.04, N: 8.45 %.

2-(1H-pyrrol-2-yl)-1H-anthra[1,2-d]imidazole-6,11-dione (3v). Yield: 275 mg, 85%, dark orange solid; Mp 294-296°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.92 (s, 1H), 12.13 (s, 1H), 8.21-8.16 (m, 2H), 8.01-7.87 (m, 4H), 7.31 (s, 1H), 7.12 (s, 1H), 6.28 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 183.7, 182.3, 152.5, 150.2, 134.7, 134.3, 133.6, 133.3, 132.9, 127.1, 127.0, 126.4, 23.6, 123.5, 121.9, 121.4, 117.9, 113.4, 110.4; IR υ_{max} (KBr) cm^{-1} 3336, 3267, 3112,

3091,1657, 1588, 1515; anal. calcd for $C_{19}H_{11}N_3O_2$: C: 72.84, H: 3.54, N: 13.41 %, found: C: 72.81, H: 3.52, N: 13.40 %.

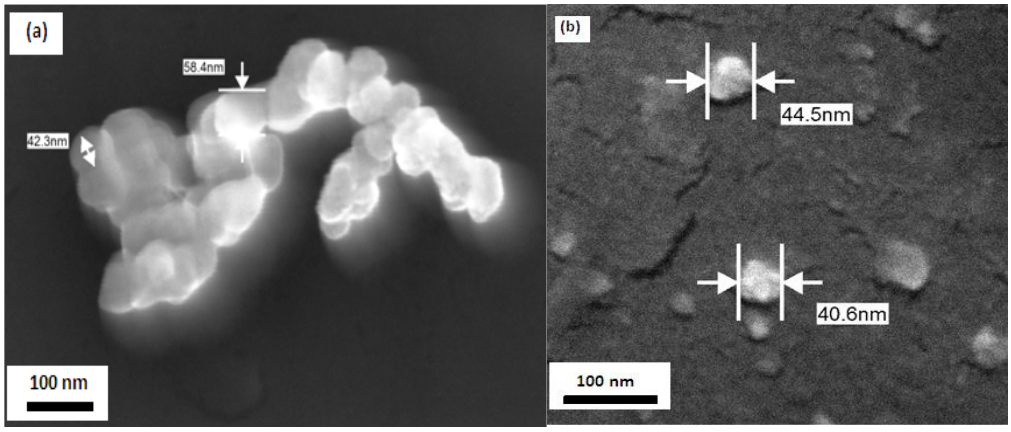


Figure S1: (a) FE-SEM images of fresh, (b) FE-SEM images of used catalyst

Crystallographic data collection and refinement

Suitable single crystal isolated by slow diffusion from ethanolic solution of the compound at room temperature and mounted it on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo-Kα (λ = 0.71073 Å) radiation. The crystal was positioned at 60 mm from the CCD. Frames (360) were measured with a counting time of 5 s. The structure was solved by Patterson method using the SHELXS 97 program. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. Absorption corrections were carried out using the SADABS program. All the calculations were carried out using SHELXS 97, SHELXL 97, PLATON 99, ORTEP-32 and WINGX system ver-1.64. Data

collection, structure refinement parameters and crystallographic data for the compound is given in Table 3.

Table S1. Crystal data and structure refinement for **3t** (**CCDC 1053279**)

Compound	**3t**
Formula	$C_{19}H_{12}N_2O_3$ S
M	347.28
Crystal System	Monoclinic
Space Group	$P2_1/c$
a/Å	12.513(5)
b/Å	14.980(6)
c/Å	8.251(4)
α/°	90
β/°	92.583(14)
γ/°	90
V/Å^3	1545.0(12)
Z	4
D_c/g cm^{-3}	1.493
μ/mm^{-1}	0.231
F (000)	718
R(int)	0.063
Total Reflections	16744
Unique reflections	2650
$I>2\sigma(I)$	1880
R1, *w*R2	0.1220, 0.3787
Temp (K)	296
GOF	1.49

Table S2. Hydrogen Bonding Interactions in compound **3t**

D–H···A	D–H (Å)	H···A (Å)	D···A	∠D–H···A (º)	Symmetry
O4–H102···O2	0.86(11)	2.25(12)	2.882(7)	131(10)	1-x,-y,1-z
O4–H101···N2A	0.81(10)	2.14(10)	2.944(7)	172(11)	1-x,-1/2+y,3/2-z
O4–H102···O4	0.86(11)	2.46(11)	3.244(8)	151(9)	1-x,-y,1-z
N1–H100···O4	0.84(6)	2.10(6)	2.924(7)	167(5)	……
C14–H14···O1	0.9300	2.4000	3.219(11)	147.00	2-x,-1/2+y,1/2-z

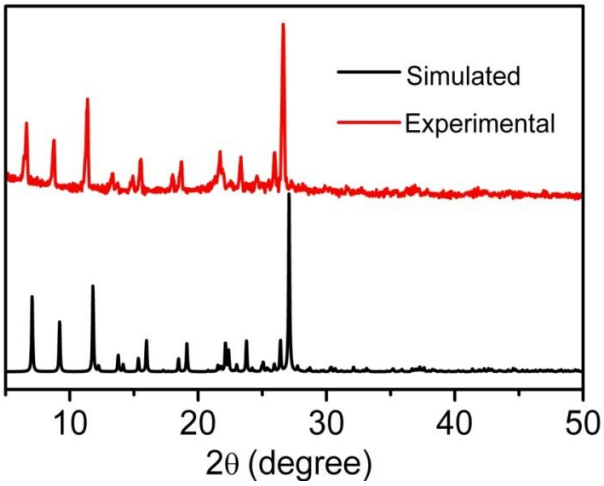


Figure S2: Powder XRD pattern of compound **3t** (Experimental and simulated)

Table S3: Peak List of Compound **3t** obtained from powder XRD data

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
6.6259	396.29	0.1584	13.32926	41.60
8.7485	295.78	0.1584	10.09950	31.05
11.3659	481.02	0.1584	7.77894	50.49
13.3269	87.08	0.6336	6.63838	9.14
15.5230	171.99	0.2376	5.70380	18.05
18.6521	161.32	0.2376	4.75340	16.93
21.6956	210.51	0.3168	4.09297	22.10
23.3124	183.47	0.2376	3.81262	19.26
25.9615	233.66	0.1980	3.42929	24.53
26.6335	952.72	0.2772	3.34427	100.00

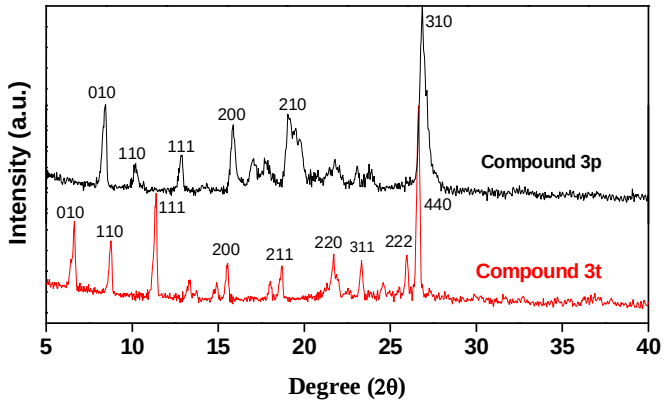


Figure S3: Powder XRD (PXRD) data of the molecules **3p** and **3t**

Table S4: Peak List of Compound **3p** obtained from powder XRD data

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
8.4324	442.37	0.3168	10.47740	49.14
10.1641	99.46	0.9504	8.69584	11.05
12.8303	181.18	0.2376	6.89419	20.13
15.8603	323.04	0.3168	5.58328	35.89
19.1256	372.58	0.3168	4.63677	41.39
26.8455	900.19	0.2772	3.31834	100.00

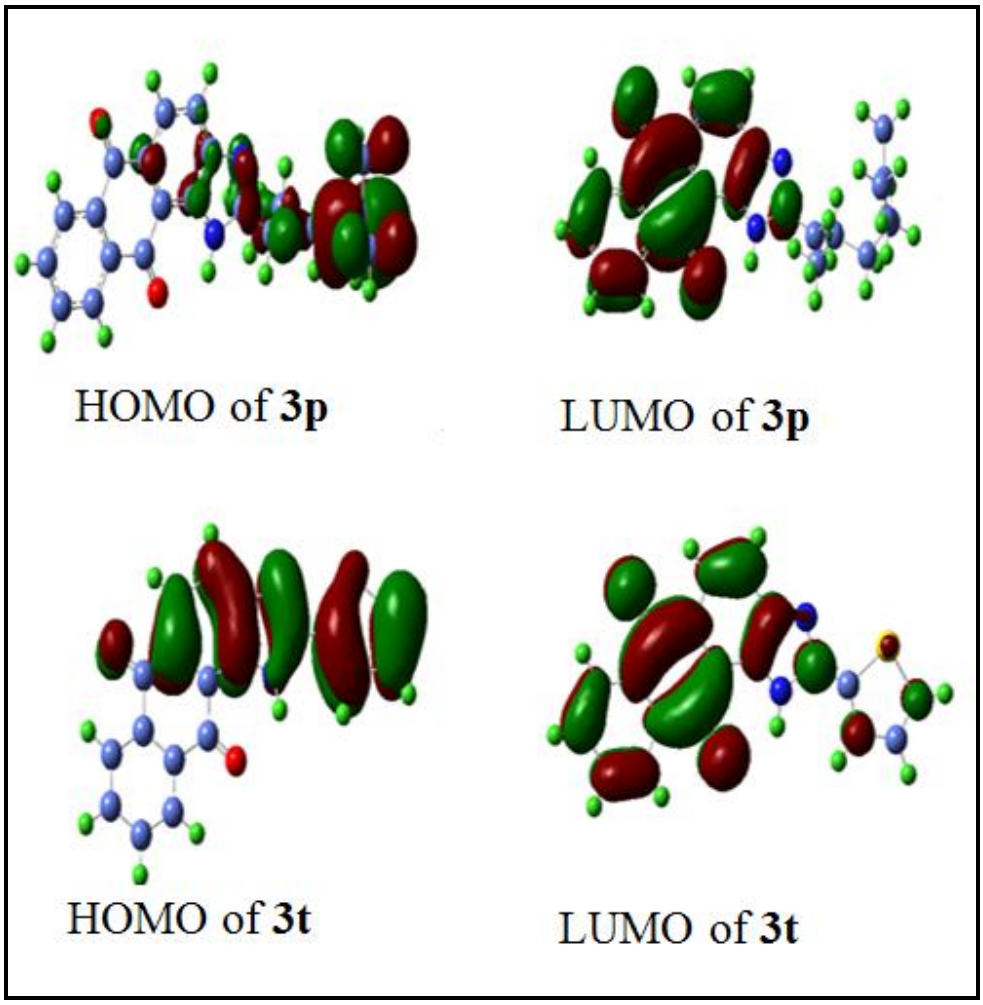
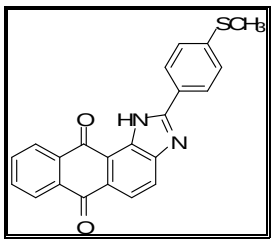
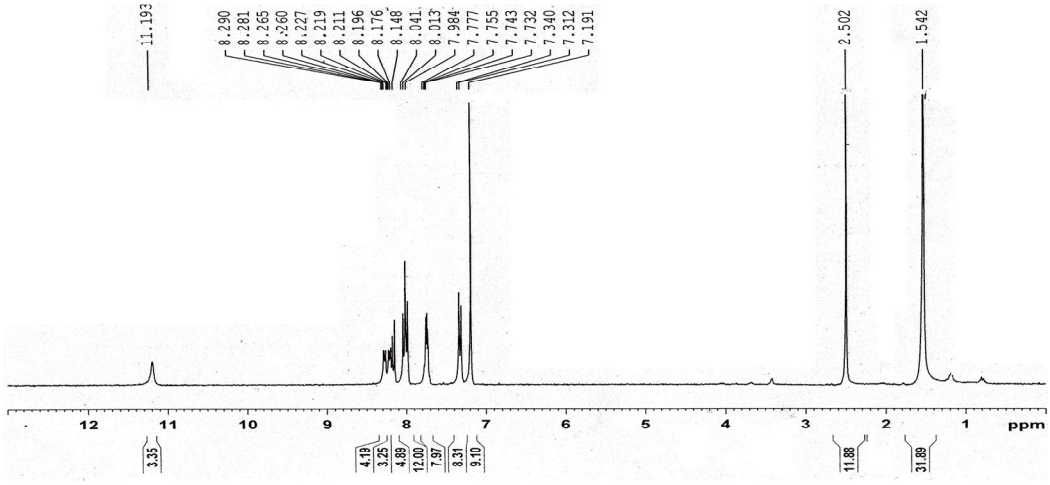


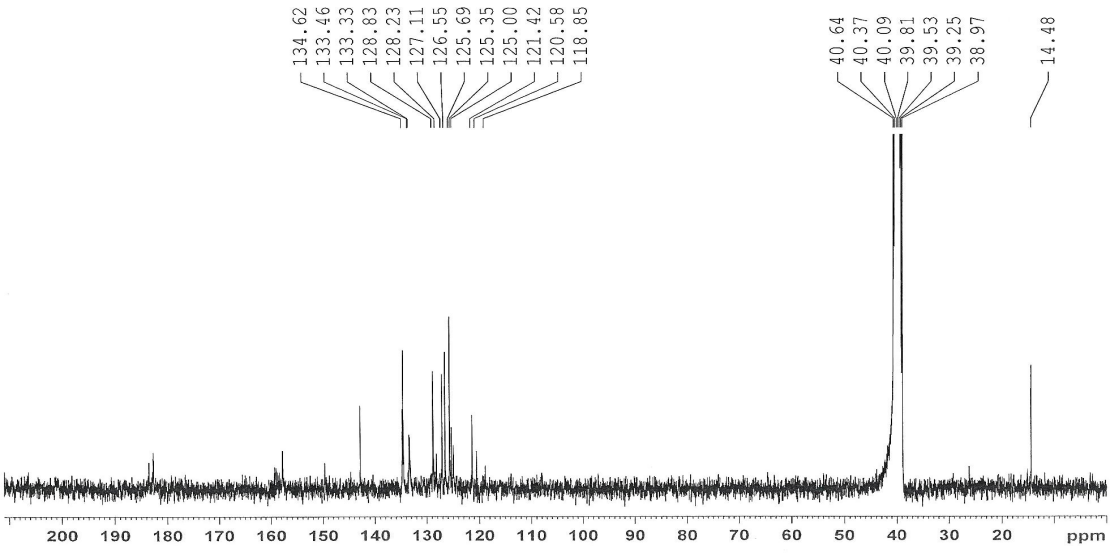
Figure S4: HOMO-LUMO of compound **3p** and **3t** form Gaussian 09W using B3LYP/6-311++G as functional and basis set



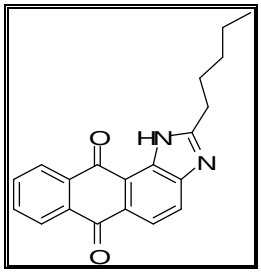
2-(4-(methylthio)phenyl)-1*H*-anthra[1,2-*d*]imidazole-6,11-dione **(3k)**



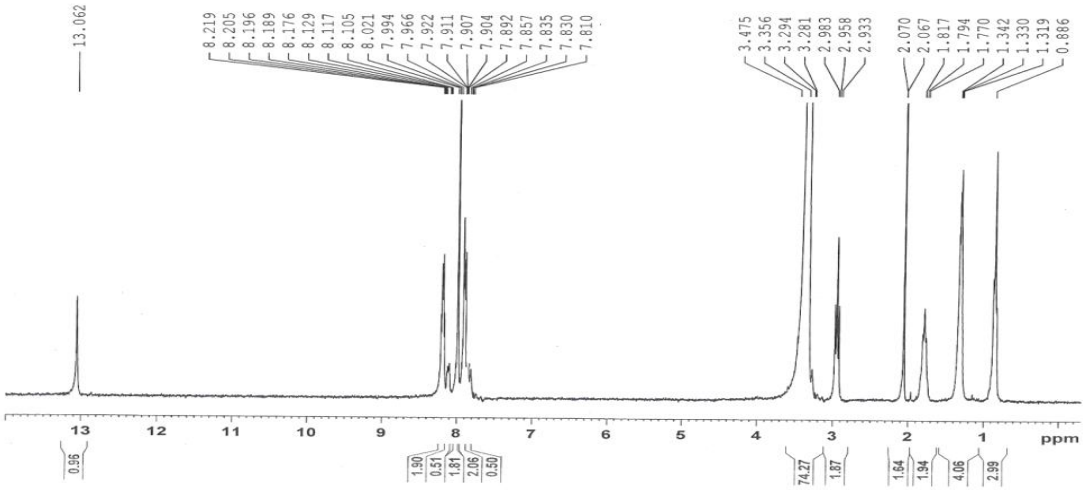
^{1}H- NMR, 300 MHz, $CDCl_3$



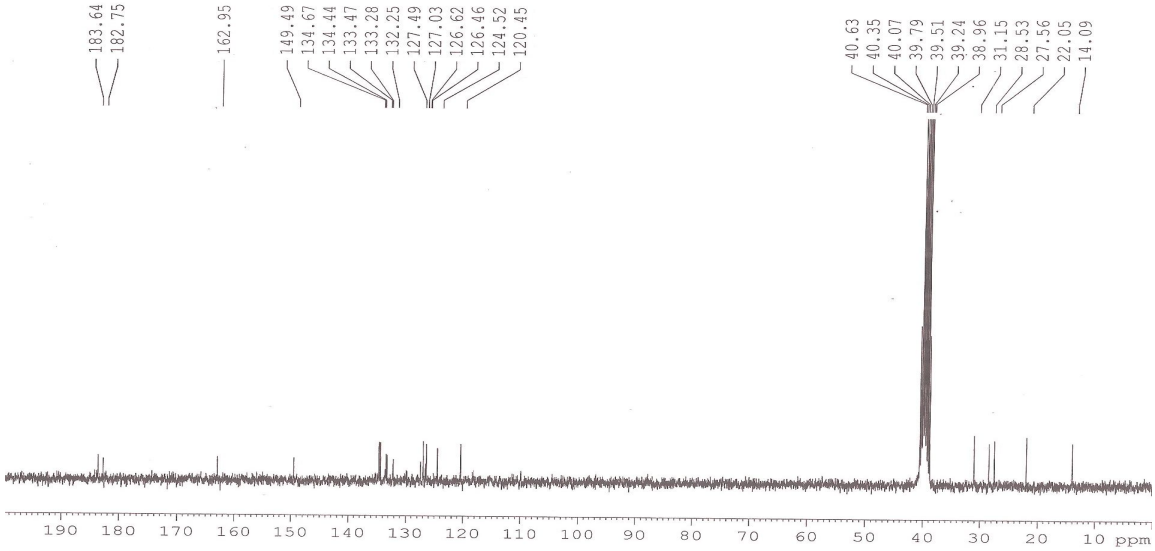
^{13}C- NMR, 75 MHz, DMSO-d_6



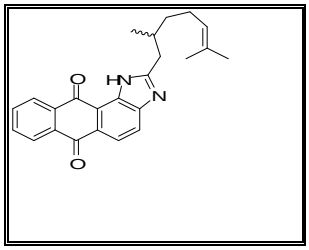
2-pentyl-1*H*-anthra[1,2-*d*]imidazole-6,11-dione **(3o)**



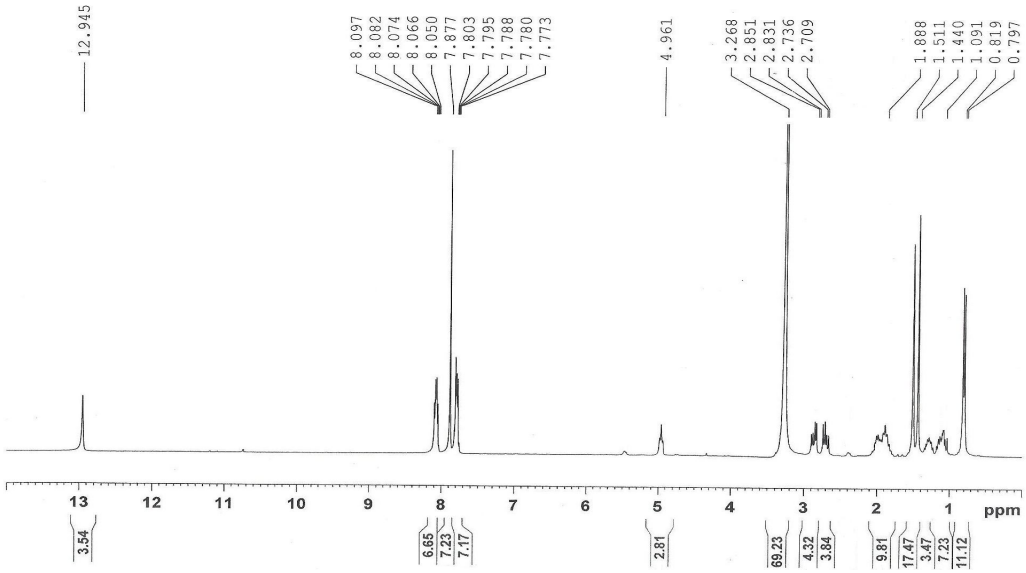
^{1}H- NMR, 300 MHz, DMSO-d_6



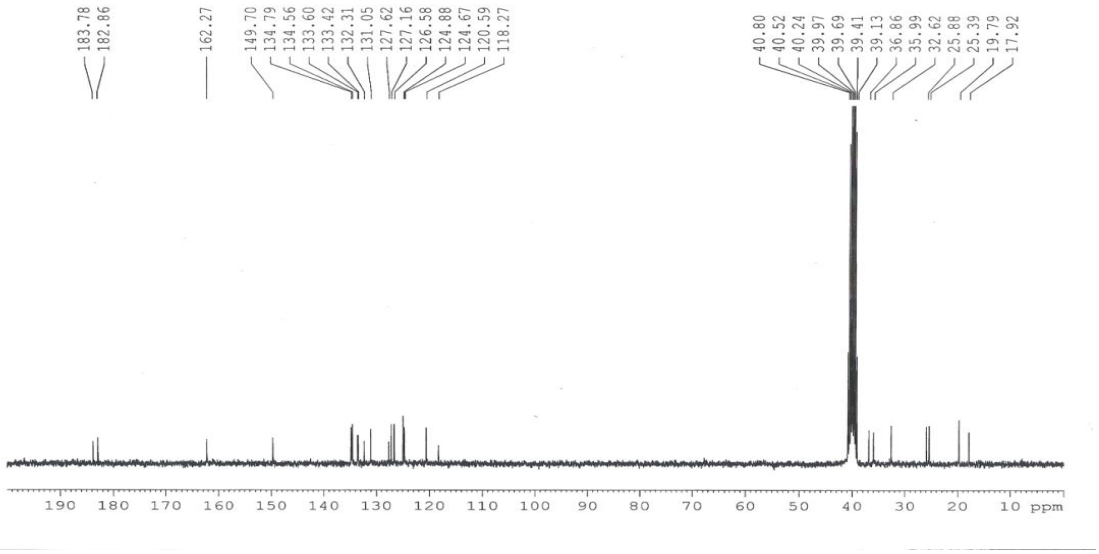
^{13}C- NMR, 75 MHz, DMSO-d_6



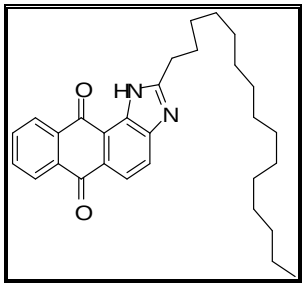
(±)2-(2,6-dimethylhept-5-enyl)-1*H*-anthra[1,2-*d*]imidazole-6,11-dione (**3p)**



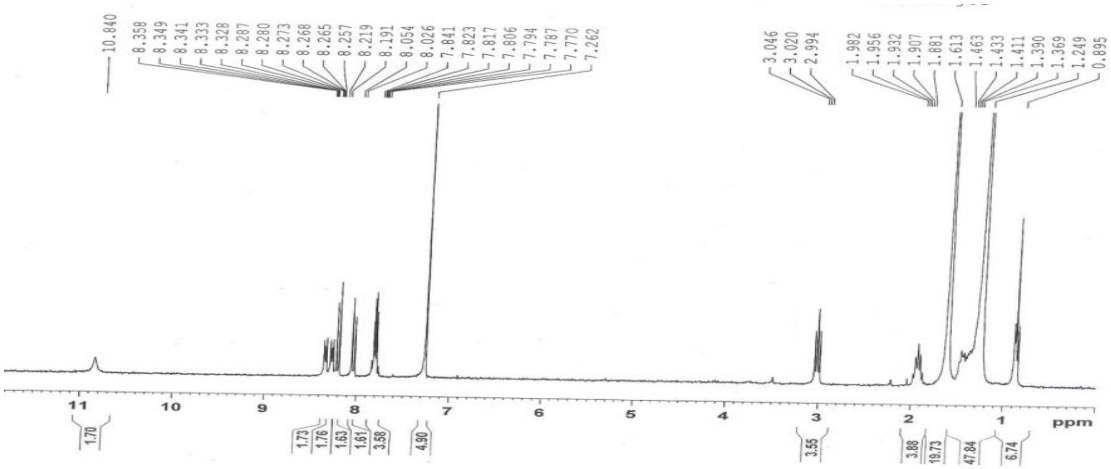
^{1}H- NMR, 300 MHz, DMSO-d_6



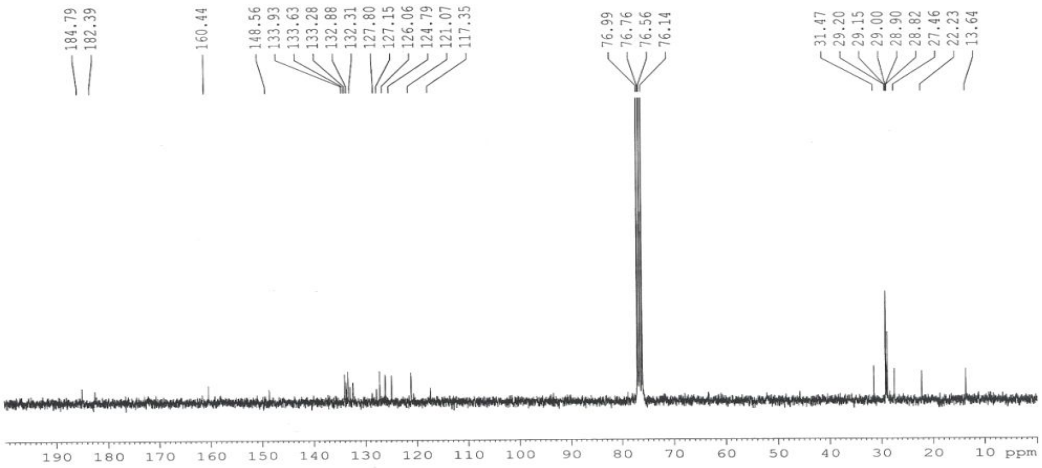
^{13}C- NMR, 75 MHz, DMSO-d_6



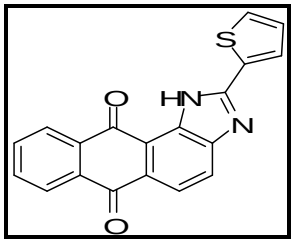
2-pentadecyl-1*H*-anthra[1,2-*d*]imidazole-6,11-dione **(3q)**



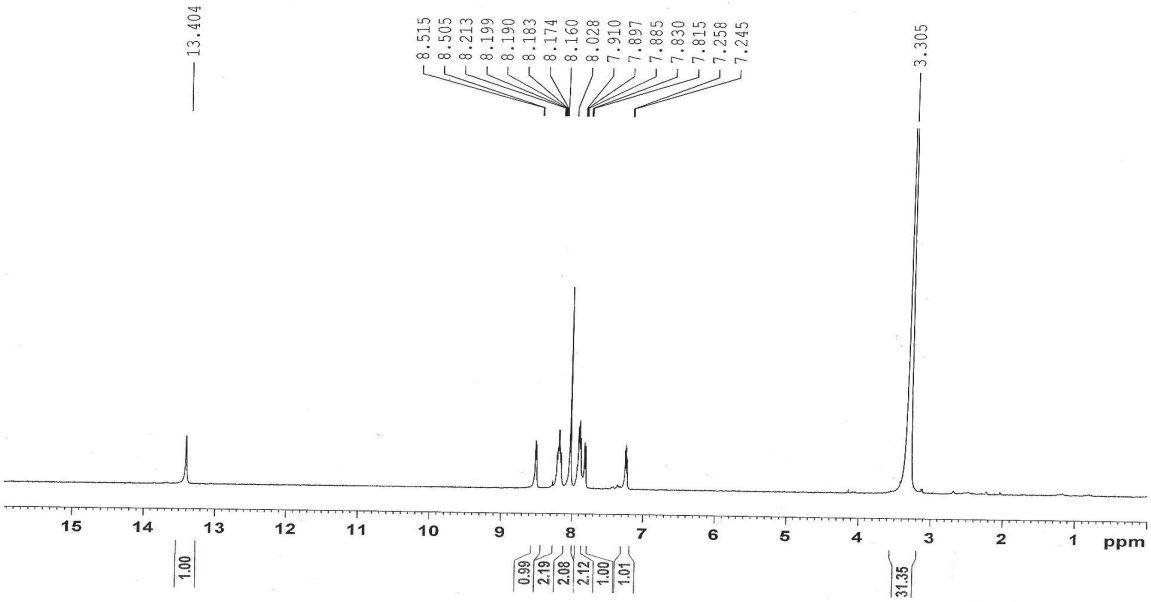
^{1}H- NMR, 300 MHz, $CDCl_3$



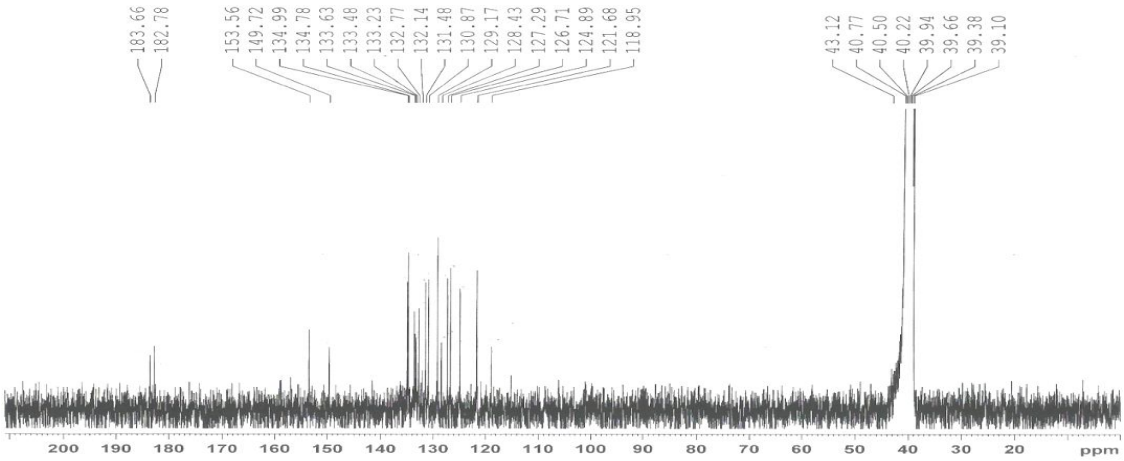
^{13}C- NMR, 75 MHz, $CDCl_3$



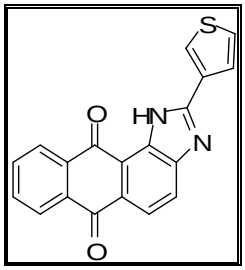
2-(thiophen-2-yl)-1*H*-anthra[1,2-*d*]imidazole-6,11-dione **(3t)**



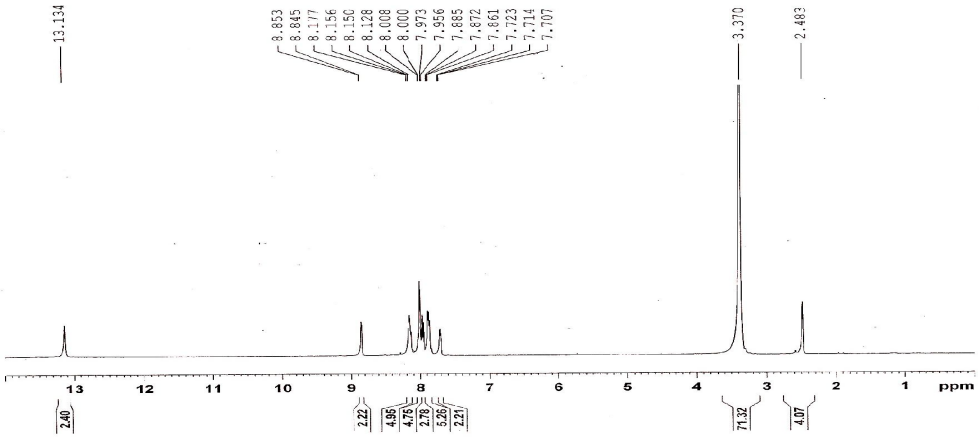
^{1}H- NMR, 300 MHz, DMSO-d_6



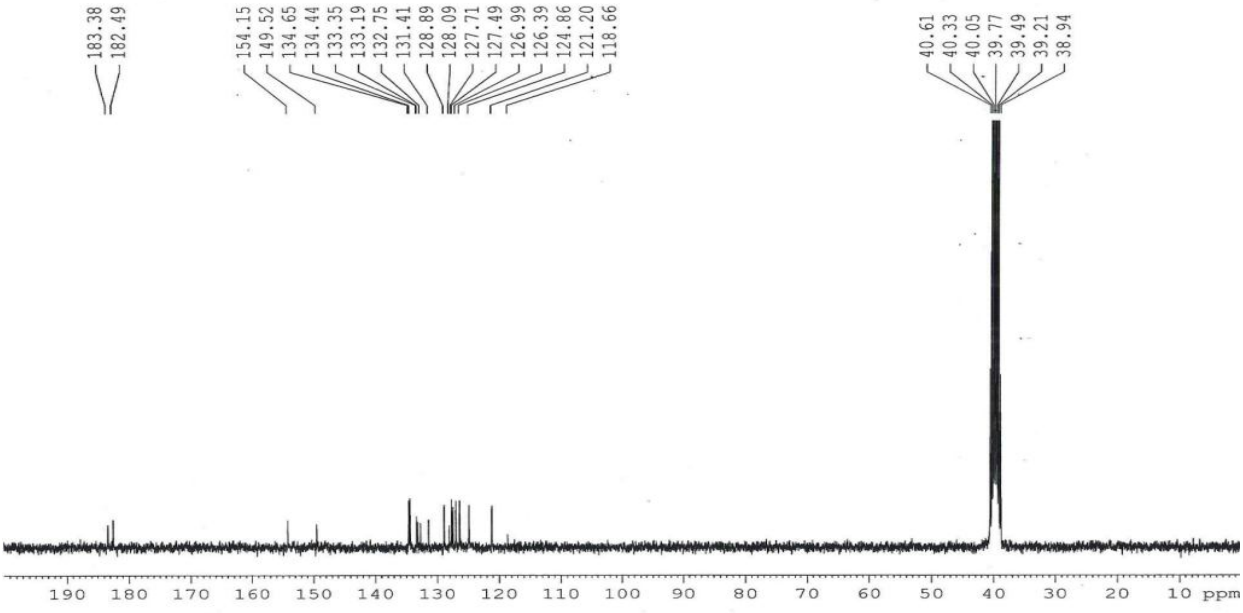
^{13}C- NMR, 75 MHz, DMSO-d_6



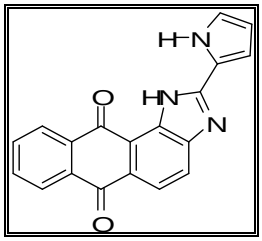
2-(thiophen-3-yl)-1*H*-anthra[1,2-*d*]imidazole-6,11-dione **(3u)**



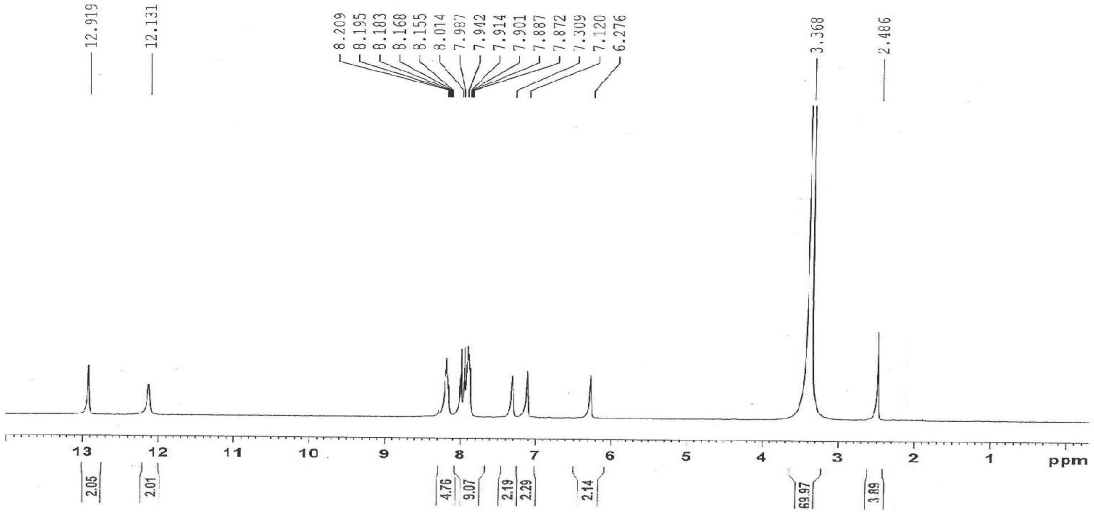
^{1}H- NMR, 300 MHz, DMSO-d_6



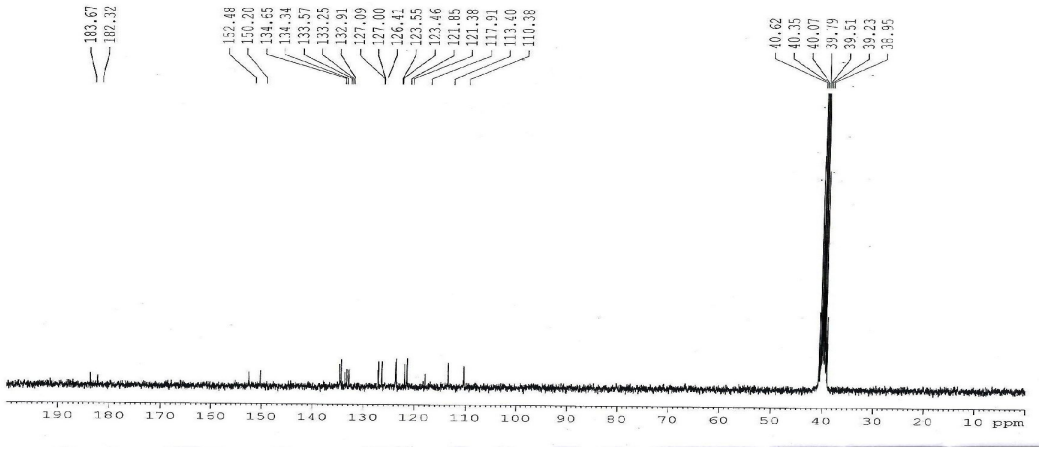
^{13}C- NMR, 75 MHz, DMSO-d_6



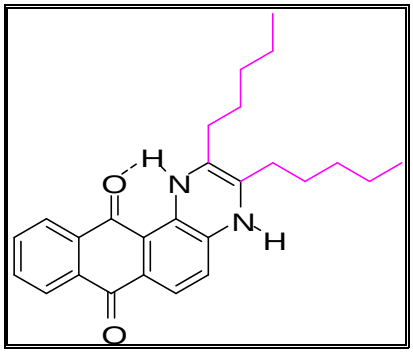
2-(1*H*-pyrrol-2-yl)-1*H*-anthra[1,2-*d*]imidazole-6,11-dione **(3v)**



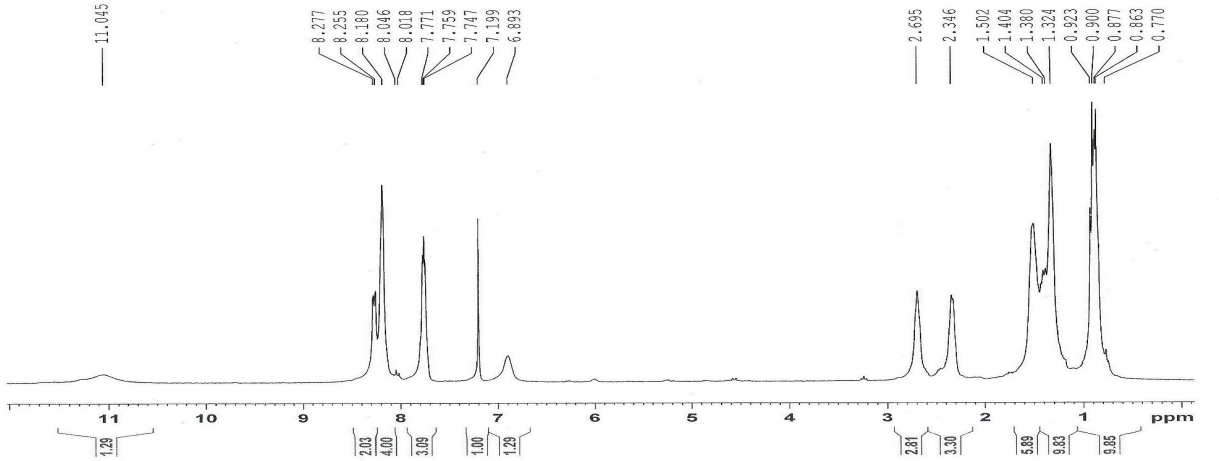
^{1}H- NMR, 300 MHz, DMSO-d_6



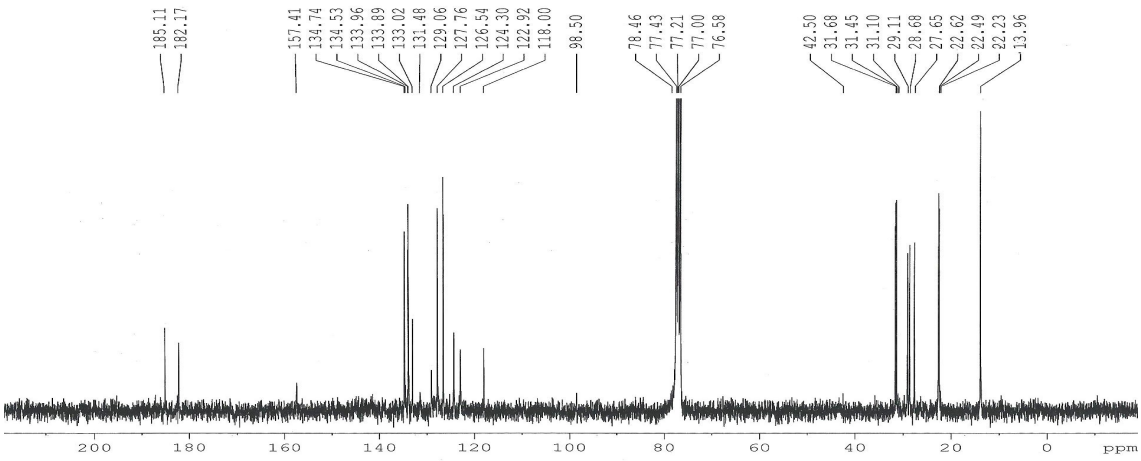
^{13}C- NMR, 75 MHz, DMSO-d_6



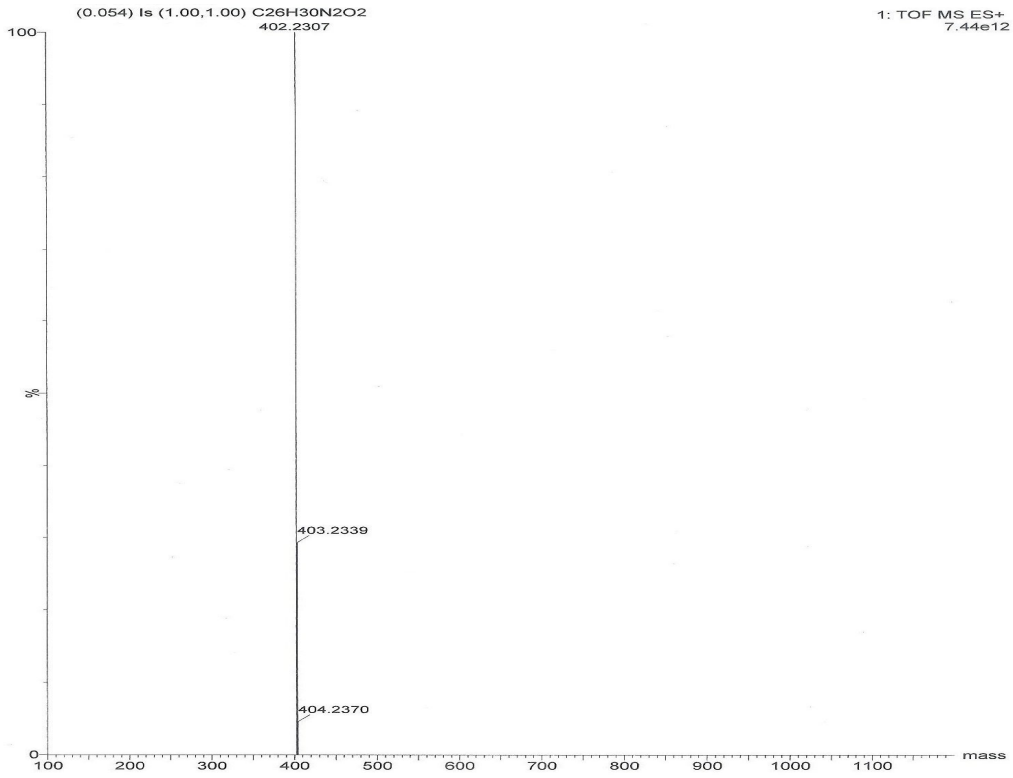
2,3-dipentylnaphtho[2,3-*f*]quinoxaline-7,12(1*H*,4*H*)-dione **(3x)**



^{1}H- NMR, 300 MHz, $CDCl_3$



^{13}C- NMR, 75 MHz, $CDCl_3$


(0.054) Is (1.00,1.00) C26H30N2O2
402.2307
1: TOF MS ES+
7.44e12
100
%
0
403.2339
404.2370
100
200
300
400
500
600
700
800
900
1000
1100
mass

HRMS, CH_3CN

- **Systematic concentration dependant UV-VIS spectroscopy experiments of 3p and 3t**

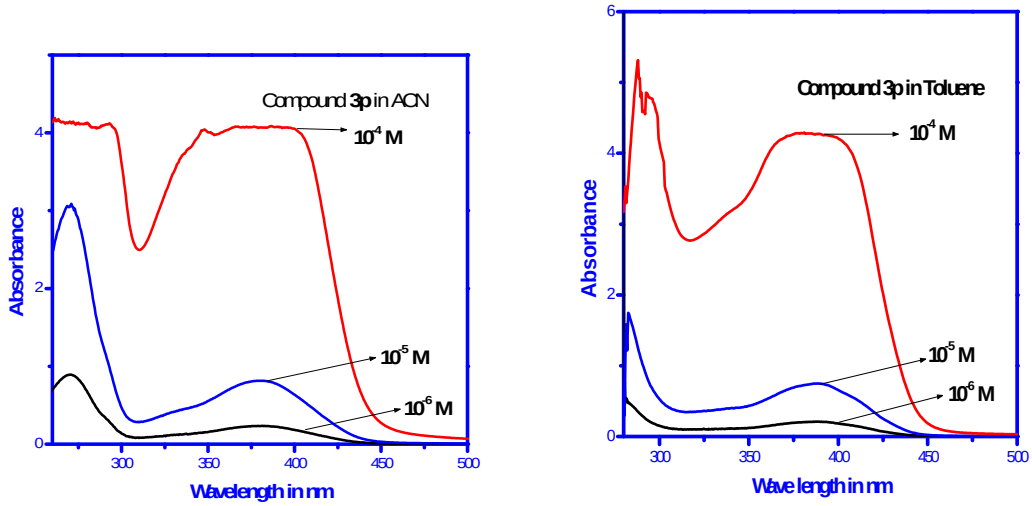


Fig. SA: (a) Comparison of UV-VIS spectra of the compound **3p** in acetonitrile and toluene solution of different concentrations (10^{-6} M, 10^{-5} M and 10^{-4} M)

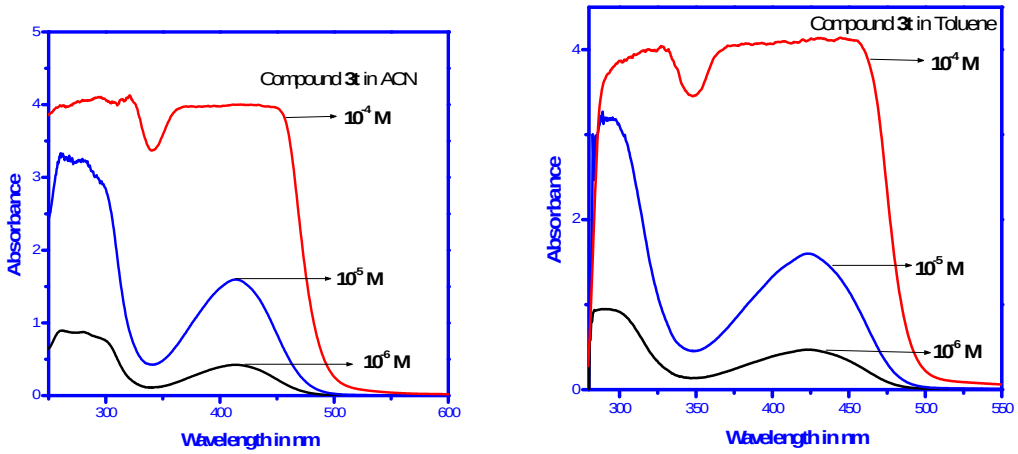


Fig. SB: (a) Comparison of UV-VIS spectra of the compound **3t** in acetonitrile and toluene solution of different concentrations (10^{-6} M, 10^{-5} M and 10^{-4} M).