New indole based co-sensitizers for dye sensitized solar cells exceeding 10% efficiency

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Electronic Supplementary Information

DSSC fabrication and characterization

Fluorine-doped tin oxide (FTO) coated glasses (2.2 mm thickness, sheet resistance of 8 Ω cm^{-2}, TEC, Pilkington) were washed with detergent, water, acetone and ethanol, sequentially. After this thoroughly cleaned plates were immersed into an aqueous solution containing 40 mM of $TiCl_4$, maintained at 70 °C for 30 minutes and subsequently washed with water and ethanol. A thin layer (8-12 μm thick) of TiO_2 (Solaronix, Ti-Nanoxide T/SP) was deposited (active area, 0.18 cm^2) on transparent conducting glass by squeegee printing followed by drying at 125 °C for 5 minutes, 350 °C for 5 minutes and curing at 500 °C for 30 minutes. Next, scattering layer of (5 μm thick) TiO_2 particles (Solaronix, Ti-Nanoxide R/SP,) was printed. Then, TiO_2 electrodes were heated under an air flow at 350 °C for 10 minutes, followed by heating at 500 °C for 30 minutes. After cooling to room temperature, the TiO_2 electrodes were treated with 40 mM aqueous solution of $TiCl_4$ at 70 °C for 30 minutes and then washed with water and ethanol. The electrodes were heated again at 500 °C for 30 minutes and then allowed to cool to 80 °C. The dye solutions (0.5 mM) were prepared by dissolving the dye in 1:1 acetonitrile and tert-butyl alcohol. The co-adsorbate deoxycholic acid was added to the dye solution at a concentration of 1, 10 and 20 mM. The electrodes were immersed in the dye solutions and then kept at 25 °C for 20 hours to adsorb the dye onto the TiO_2 surface. For preparing the counter electrode, pre-cut TCO glasses were washed with water followed by 0.1M HCl in EtOH, and sonicated in acetone bath for 10 minutes. These washed TCO were then dried at 400 °C for 15 minutes. A thin layer of Pt-paste (Solaronix, Platisol T/SP) on TCO was printed and the printed electrodes were then cured at 450 °C for 10 minutes. The dye sensitized TiO_2 electrodes were sandwiched with Pt counter

electrodes and the electrolyte (Solaronix, Iodolyte AN-50) was then injected into the cell, while the two electrodes were held together with the clips. Co-sensitization was done as per the procedure reported by Han et al. [1]

Current-voltage plots of DSSCs were obtained using a Keithley 2400 source meter under illumination of AM 1.5 G solar light from solar simulator (SOL3A, Oriel), coupled with a 450 W xenon lamp (91160, Oriel). A reference Si solar cell (Newport Oriel, 91150V) was used to calibrate the incident light intensity to 1 Sun (100 mW cm^{-2}). The measurements were precisely controlled using Oriel IV Test Station software. Further, IPCE (incident monochromatic photon to current conversion efficiency) experiments were performed using a system (QEX10, PV Measurements, USA) connected to a 75 W short arc xenon lamp (UXL-75XE, USHIO, Japan) as a light source linked to a monochromater. Before measurements, calibration of incident light was performed with the help of a silicone photodiode (IF035, PV Measurements). All the measurements were carried out without the use of anti-reflecting film in DC mode.

The electrochemical impedance spectra were obtained using impedance analyzer potentiostat (Bio-Logic SP-150) under illumination with a solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91160, Oriel). Impedance spectra were recorded over a frequency range of 100 mHz to 200 kHz at 298 K. During the measurements, the applied bias voltage was fixed at the V_{oc} of the DSSCs, with AC amplitude set at 10 mV. The obtained spectra were fitted using Z-Fit software (Bio-Logic).

Calculation of GSOP by Cyclic Voltammetry

The experimental HOMO energy values for **DBA-3**, **DBA-4** and **DBA-5** dyes were measured using a cyclic voltammetry (CV). The CV measurements were carried out in anhydrous dichloromethane with 0.1 M [TBA][PF_6] as an electrolyte at a scan rate of 100 mVs^{-1}. Glassy

carbon was used as the working electrode (WE), Pt wire as counter electrode and Ag/Ag^{+} in ACN was used as the reference electrode. Fc/Fc^{+} was used as internal reference which was converted to NHE by addition of 0.63 V.

Nyquist and Bode plots for N719

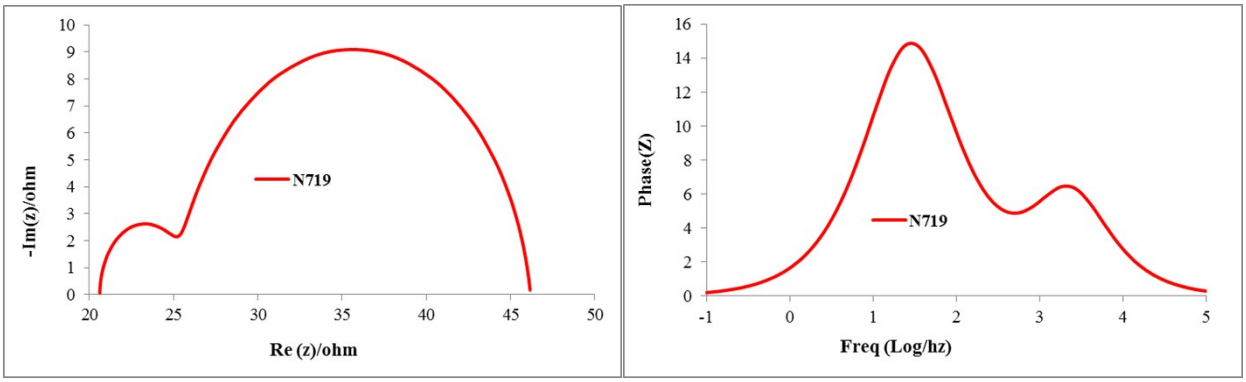

Figure 1S. Nyquist and Bode plots for **N719**

Table 1S. Cartesian coordinates for the optimized geometry of **DBA-3**

ATOM	CARTESIAN COORDINATES		
1 c	0.00873451220963	0.00725512226488	-0.02650524002574
2 c	2.67424416863803	0.05268035806099	-0.09826696952397
3 c	4.02869744477164	2.29118771249096	-0.10782286947904
4 c	2.66716505651788	4.53737933452189	-0.04186111556583
5 c	0.00922059429199	4.57259801801708	0.03608352005751
6 c	-1.30753760744957	2.29129674529872	0.03617064153100
7 n	3.49989656746038	7.03806054964013	-0.06910224894844
8 c	1.49115348846147	8.60166767909209	-0.00784532118671
9 c	-0.76071165987378	7.21864104609681	0.05929178939771
10 c	-3.31189499996092	7.99257073849242	0.14163125272800
11 c	-1.36362501134651	-2.43311948872798	-0.01491900087627
12 c	6.13247781221988	7.85121330039104	-0.05983188654521
13 c	7.32506709623295	7.84429119466482	2.57524011385927
14 c	10.09084701109201	8.67610747827448	2.52174445055341
15 c	11.32191640482385	8.72157469319262	5.13684390785072

16 c	**14.08785103248215**	**9.55642870590700**	**5.09293409821111**
17 c	**15.30386690384078**	**9.60824755860825**	**7.71107755781351**
18 c	**-3.56298377836438**	**-2.76570089052963**	**1.40176829817758**
19 c	**-4.87473976298563**	**-5.04446099781243**	**1.41985336740406**
20 c	**-3.98939545704031**	**-7.07297294570810**	**-0.00847642613262**
21 c	**-1.78967320463824**	**-6.77954838573735**	**-1.43913150927314**
22 c	**-0.50895607618289**	**-4.50332912796762**	**-1.43389424114583**
23 o	**-5.11633425681743**	**-9.38145530354112**	**-0.12917488738041**
24 c	**-7.37415882911128**	**-9.77836535976815**	**1.25850371608136**
25 c	**-4.58501824959663**	**10.26019942965403**	**0.17945558299941**
26 c	**-3.43513383932330**	**12.76656827219468**	**0.10900162455364**
27 n	**-5.11275527507680**	**14.79765020421195**	**0.14480587948184**
28 h	**-4.32857585940001**	**16.53539958322261**	**0.09391646419650**
29 c	**-7.71826750655431**	**14.72591601252915**	**0.24443821601897**
30 n	**-8.70100248224615**	**12.31403375720375**	**0.31323513438072**
31 h	**-10.60220153342016**	**12.18325682860161**	**0.39060314691405**
32 c	**-7.37165486031334**	**10.04275785663872**	**0.29272471487625**
33 o	**-8.54230629698032**	**8.06350935198177**	**0.36959001837127**
34 o	**-1.17226759896172**	**13.22746762699193**	**0.02281987210099**
35 o	**-9.01654095035732**	**16.61087117445450**	**0.26940610824553**
36 h	**-7.94368212120473**	**-11.71370381095269**	**0.87285697162256**
37 h	**-8.87178410042627**	**-8.49195984277973**	**0.64944424517667**
38 h	**-7.06392270160799**	**-9.55098788035969**	**3.28857084096725**
39 h	**17.27336321089380**	**10.20975217642893**	**7.61413073013414**
40 h	**15.26253774770496**	**7.74189298857807**	**8.59191863103792**
41 h	**14.31335067536266**	**10.91115361846517**	**8.96871680992732**
42 h	**14.21602050965610**	**11.43429308058871**	**4.23525100078770**
43 h	**15.16159290160654**	**8.29063953246011**	**3.85841026037785**
44 h	**11.19045204391432**	**6.83984145168887**	**5.98953988847980**
45 h	**10.24684306158924**	**9.98546618983992**	**6.37419067151383**
46 h	**10.22372556527106**	**10.55957398532008**	**1.67315653287252**
47 h	**11.16631074020379**	**7.41292390918378**	**1.28322093914164**
48 h	**7.17488189976351**	**5.95237838548205**	**3.39079026454806**
49 h	**6.23365044041451**	**9.10039182599620**	**3.79995216359208**
50 h	**6.19020960900032**	**9.74601742879230**	**-0.86616996131753**
51 h	**7.18466771308757**	**6.61703475100717**	**-1.33457141808580**
52 h	**-4.62842164757738**	**6.41955647174085**	**0.19774051556331**
53 h	**1.70046229470668**	**10.62144465479003**	**-0.02188023945485**
54 h	**-1.13086323765489**	**-8.35759956652922**	**-2.55834294971589**
55 h	**-6.55865932352145**	**-5.21448690254933**	**2.55893081535349**
56 h	**1.16332366587601**	**-4.30992073524669**	**-2.59446874640754**
57 h	**-4.26034427756948**	**-1.22884077845920**	**2.55665507977627**
58 h	**6.07208146223050**	**2.26511357918141**	**-0.14473125066877**

59 h	-3.35203738718610	2.27644323144931	0.03256527734558
60 h	3.69410892720651	-1.71789370021449	-0.10206235647997

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Table 2S. Cartesian coordinates for the optimized geometry of **DBA-4**

ATOM	CARTESIAN COORDINATES		
1 c	0.03718266438195	0.03933452536168	-0.04348037524972
2 c	2.69503498039441	0.10684833765330	-0.18927428610477
3 c	3.98948259741490	2.37206279579069	-0.15822310265928
4 c	2.58073972991385	4.58853753536722	0.02062160904898
5 c	-0.06866900410301	4.56104572348524	0.16374175913254
6 c	-1.36156480039285	2.25461064595167	0.13239957067902
7 n	3.36073038853434	7.11099713701962	0.06488533975711
8 c	1.32627926355549	8.62360877929159	0.23483211412117
9 c	-0.89570855637264	7.18313191375960	0.30502029251310
10 c	-3.46055671161948	7.89053096316478	0.45324889067504
11 o	-0.98878291161566	-2.32102433666280	-0.09204363001347
12 c	-3.65459716750372	-2.56079880423758	0.05219616035605
13 c	5.97512622375275	7.97864888475464	0.03055001156792
14 c	7.27006783406742	7.83449874633510	2.61286399042747
15 c	10.01655523198358	8.72285946649991	2.50129349879122
16 c	11.35694000180297	8.62295898261986	5.06031057952627
17 c	14.10853658740053	9.49848239093271	4.95292592238271
18 c	15.43548931228495	9.40242937083271	7.51533450275819
19 c	-4.79149150784888	10.12182556438979	0.59389626714149
20 c	-3.70502186855752	12.65623326352090	0.63611890302502
21 n	-5.43319252419138	14.64075361618941	0.77869940738994
22 h	-4.69322155926013	16.39831673784463	0.80483573209086
23 c	-8.03533052450584	14.49816074225236	0.88355587390793
24 n	-8.95641241210490	12.06099363244571	0.84321077272441
25 h	-10.85337675955114	11.87842167381675	0.91829725592335
26 c	-7.56990384511183	9.82832191213896	0.70738101885894
27 o	-8.69077274968572	7.81795397728186	0.68836198098421
28 o	-1.45509265523352	13.17779739448391	0.55969040590566
29 o	-9.38143138173084	16.34590692847291	1.00119677997593
30 h	17.39315368380208	10.03277090540020	7.37274701356497
31 h	15.44977208811549	7.48444110586104	8.27832811866559
32 h	14.48776381761227	10.61244461600574	8.89314131706710
33 h	-4.04642054300854	-4.57571051687541	-0.01292962858545
34 h	-4.58408252457544	-1.63254396617488	-1.54262909498717
35 h	-4.38886940267254	-1.77825728061313	1.81763443925062
36 h	14.17867394982346	11.42812889212897	4.21125121759570
37 h	15.14213909265602	8.32749698861551	3.59665603416241

38 h	**11.28473666541115**	**6.68933864024956**	**5.79613258539703**
39 h	**10.32129414915722**	**9.79052280536155**	**6.41980616658681**
40 h	**10.08197771818377**	**10.65904642843732**	**1.77201008369480**
41 h	**11.05953942102527**	**7.56273087032251**	**1.14017682052260**
42 h	**7.18749064708874**	**5.89389574309360**	**3.31537710964413**
43 h	**6.20651193746173**	**8.99102659047630**	**3.95449409347402**
44 h	**5.96403353401473**	**9.92096064504063**	**-0.65567875209598**
45 h	**7.00383334199664**	**6.85057143947390**	**-1.35747602035270**
46 h	**-4.73937549293270**	**6.28583940173355**	**0.45676001974376**
47 h	**1.48871494458080**	**10.64680651819811**	**0.29196981881365**
48 h	**3.69461027439874**	**-1.66931667210900**	**-0.32541183762154**
49 h	**-3.39802383586041**	**2.20833426078871**	**0.23931711998411**
50 h	**6.03005657402482**	**2.39231544998920**	**-0.27093993293328**

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Table 3S. Cartesian coordinates for the optimized geometry of **DBA-5**

ATOM	**CARTESIAN COORDINATES**		
1 c	**0.05777891712790**	**0.02057259377347**	**-0.14081896544037**
2 c	**2.70260227682016**	**0.06806798201826**	**-0.27099055362859**
3 c	**4.01764693440494**	**2.33407074461162**	**-0.20597726347878**
4 c	**2.60612087779350**	**4.54363575190931**	**-0.00898127804175**
5 c	**-0.05320787059931**	**4.54057864073715**	**0.12115794122347**
6 c	**-1.33188197805891**	**2.23296840580924**	**0.05269976847401**
7 n	**3.40224644124266**	**7.05550862822968**	**0.07313335027100**
8 c	**1.37331632179828**	**8.58449758822791**	**0.25431195099501**
9 c	**-0.85687843643001**	**7.16848804831417**	**0.29427686620234**
10 c	**-3.41899447493671**	**7.90174483062172**	**0.44430711628727**
11 c	**6.02247382168463**	**7.90824154805079**	**0.05785094465250**
12 c	**7.30605189570638**	**7.73083859724357**	**2.64339764166480**
13 c	**10.05560827538701**	**8.61191234727840**	**2.55249357930774**
14 c	**11.39439822956646**	**8.45224337503608**	**5.10918933769570**
15 c	**14.14205167712888**	**9.34248541027247**	**5.02630199305096**
16 c	**15.47708540420314**	**9.15763073390114**	**7.57951913553408**
17 c	**-4.72027582094671**	**10.14597792470597**	**0.61257696797674**
18 c	**-3.60286755222558**	**12.66788906688515**	**0.69011573744884**
19 n	**-5.30574252136510**	**14.67033176316269**	**0.85588715973438**
20 h	**-4.54410979340397**	**16.41814839414796**	**0.90735347265606**
21 c	**-7.91042397989699**	**14.55940073722256**	**0.95610889771254**
22 n	**-8.86245104060155**	**12.13519949189134**	**0.88211713317735**
23 h	**-10.76183607774400**	**11.97571561050902**	**0.95325401173902**
24 c	**-7.50509859223158**	**9.88662775875583**	**0.71864334837615**
25 o	**-8.64912900903276**	**7.89162274772791**	**0.67267725391550**
26 o	**-1.34653679381307**	**13.16196470407299**	**0.62368630037016**

27 o	-9.23171453289152	16.42281257387619	1.09708397021773
28 h	17.42927402668640	9.80853561010018	7.45621531153118
29 h	15.50875471857082	7.21154131255457	8.26712993987522
30 h	14.52418692269833	10.30548722245720	9.00611642060173
31 h	14.20195527714971	11.29838111329091	4.35595573356325
32 h	15.17645165917832	8.22651633283266	3.62499924605306
33 h	11.33020346787158	6.49971213986781	5.79412267831008
34 h	10.35309762817345	9.57947445593210	6.49810437102833
35 h	10.12770527025292	10.56275660301448	1.86402290028722
36 h	11.09562681896536	7.47719673754274	1.16785859878291
37 h	7.21469308078651	5.78243855710107	3.32297550399281
38 h	6.24126791535633	8.87512416318979	3.99452643747304
39 h	6.02514175961747	9.85714861074920	-0.60961146543560
40 h	7.04978507056852	6.78808464629800	-1.33723999691328
41 h	-4.71424808369748	6.31025089338069	0.42256262145701
42 h	1.55491142247818	10.60522121438803	0.33967460505327
43 h	3.73557794123931	-1.68940276999521	-0.42355953202813
44 h	-0.91390789407592	-1.77741563326141	-0.19416556323007
45 h	-3.37331435000031	2.15705865145274	0.14670533101969
46 h	6.05863013271034	2.36253062429245	-0.30484230531800

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NMR Spectra

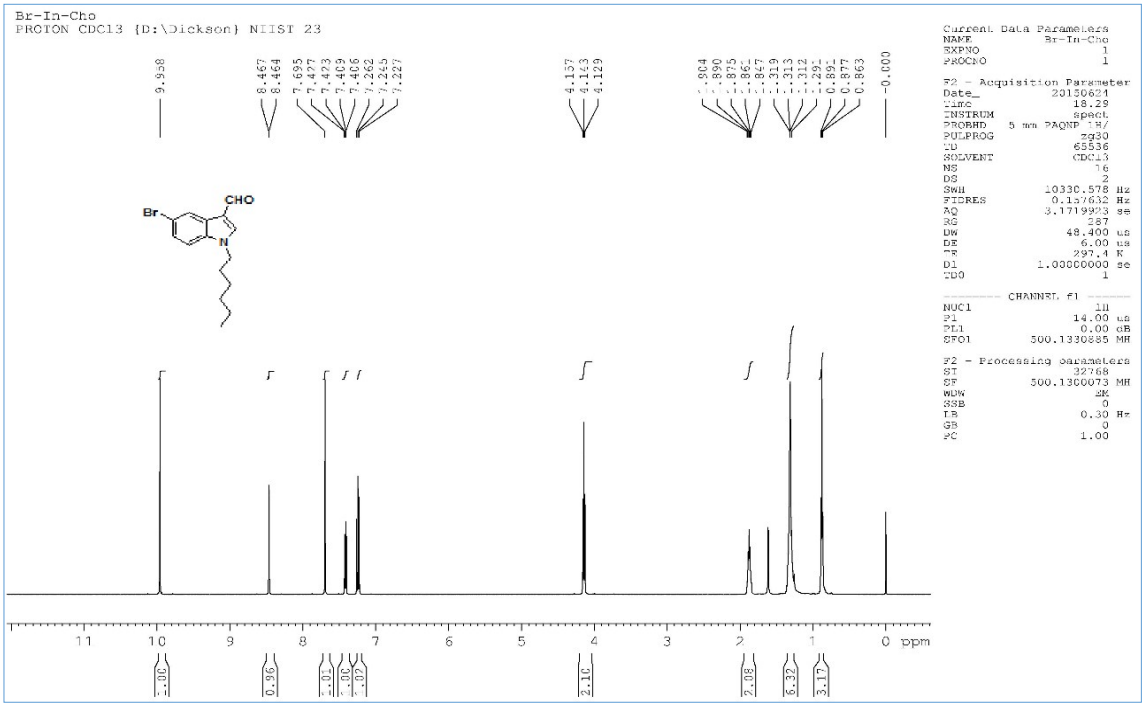

Figure 2S. ^{1}H NMR spectrum of **2** in $CDCl_3$

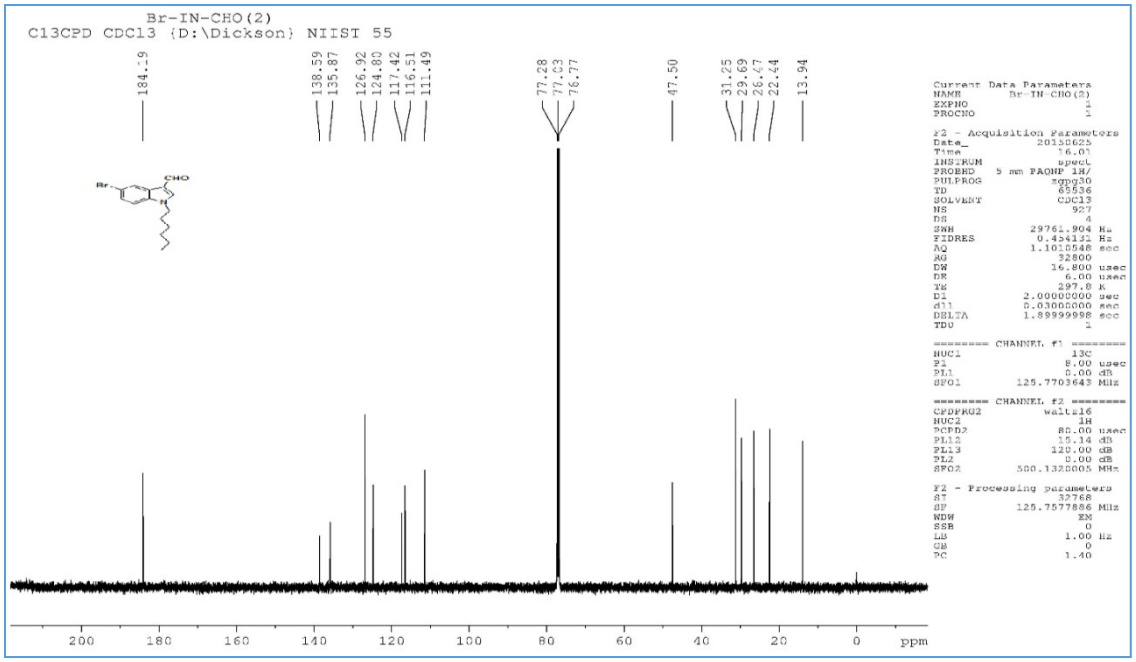

Figure 3S. ^{13}C NMR spectrum of **2** in $CDCl_3$

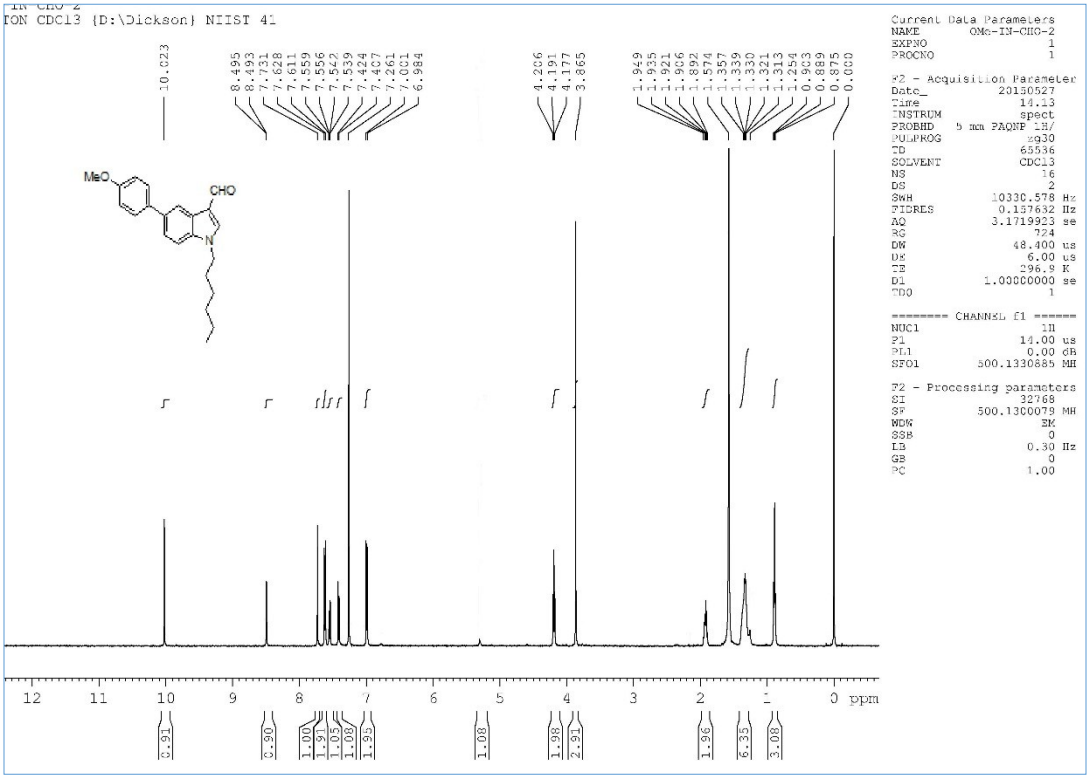

Figure 4S. ^{1}H NMR spectrum of **3** in $CDCl_3$

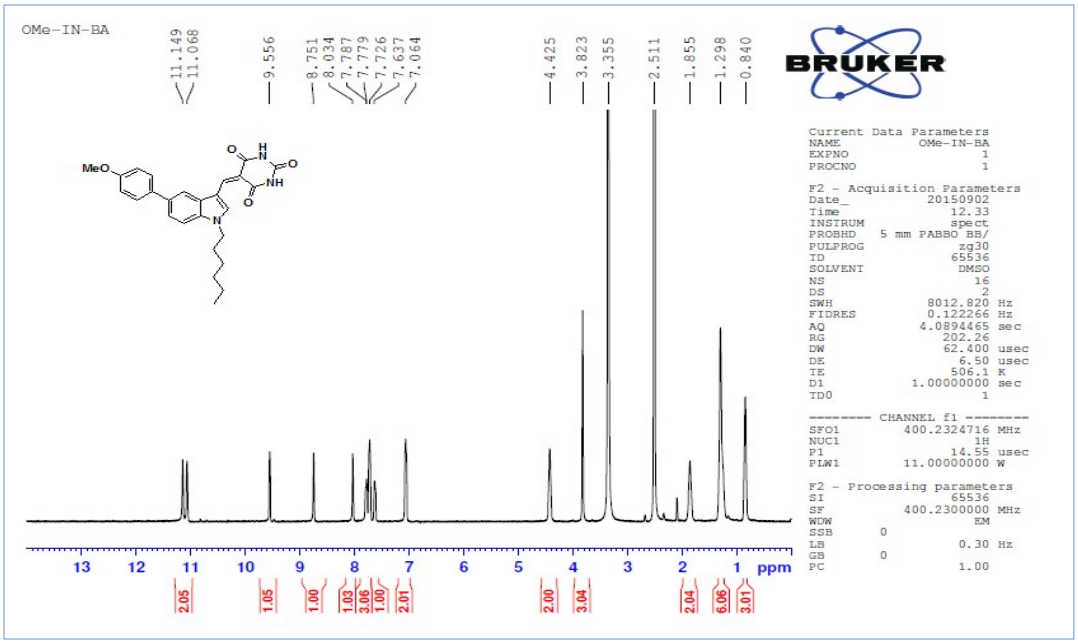

Figure 5S. [1]H NMR spectrum of **DBA-3** in DMSO

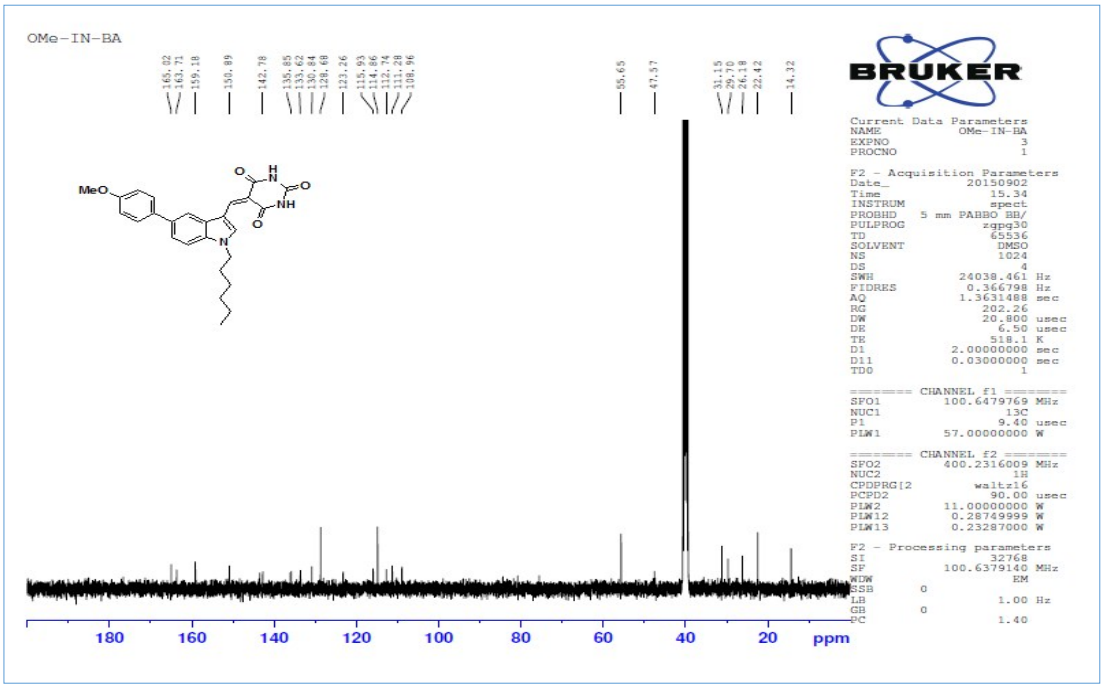

Figure 6S. [13]C NMR spectrum of **DBA-3** in DMSO

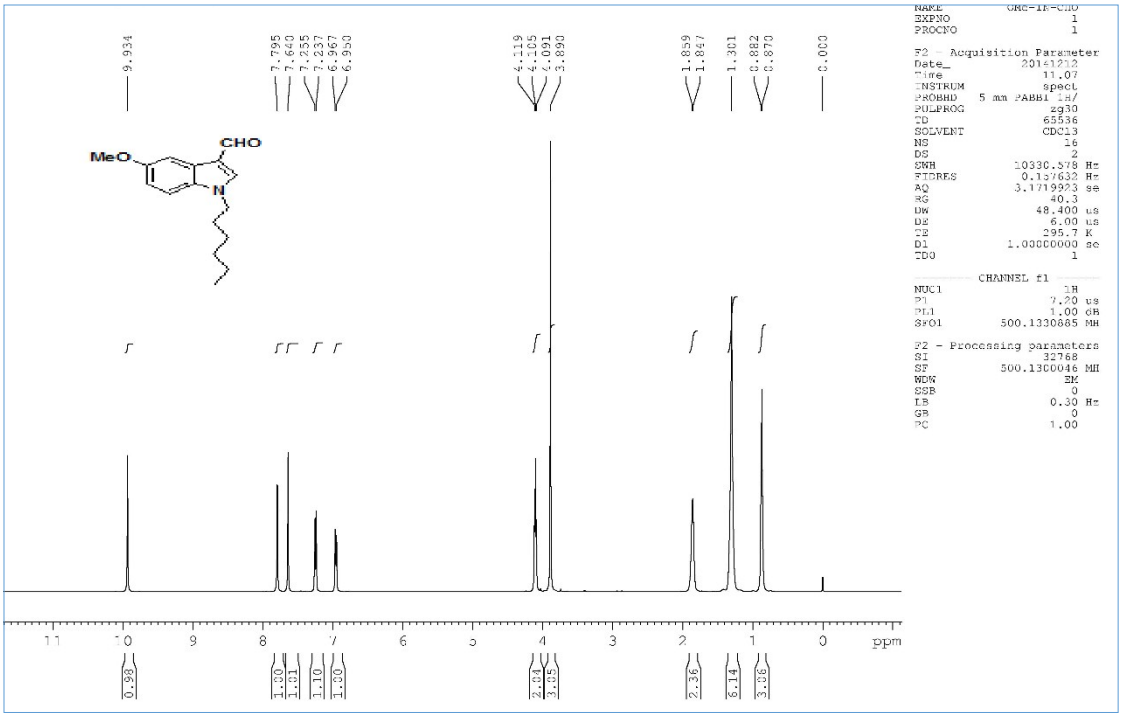

Figure 7S. ^{1}H NMR spectrum of **5a** in $CDCl_3$

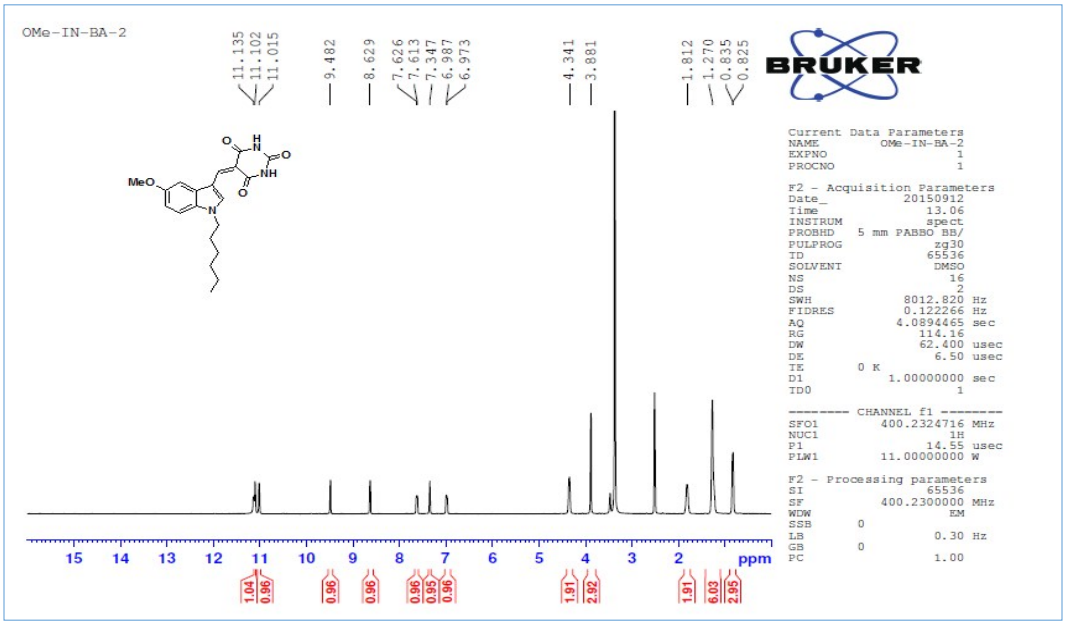

Figure 8S. ^{1}H NMR spectrum of **DBA-4** in DMSO

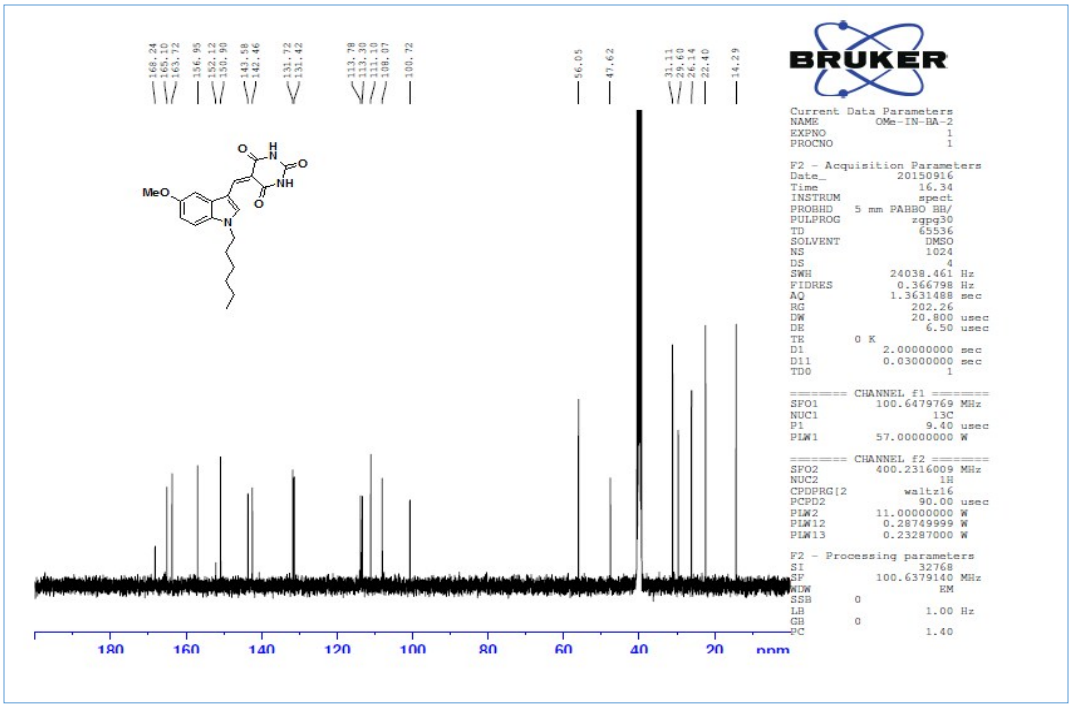

Figure 9S. ^{13}C NMR spectrum of **DBA-4** in DMSO

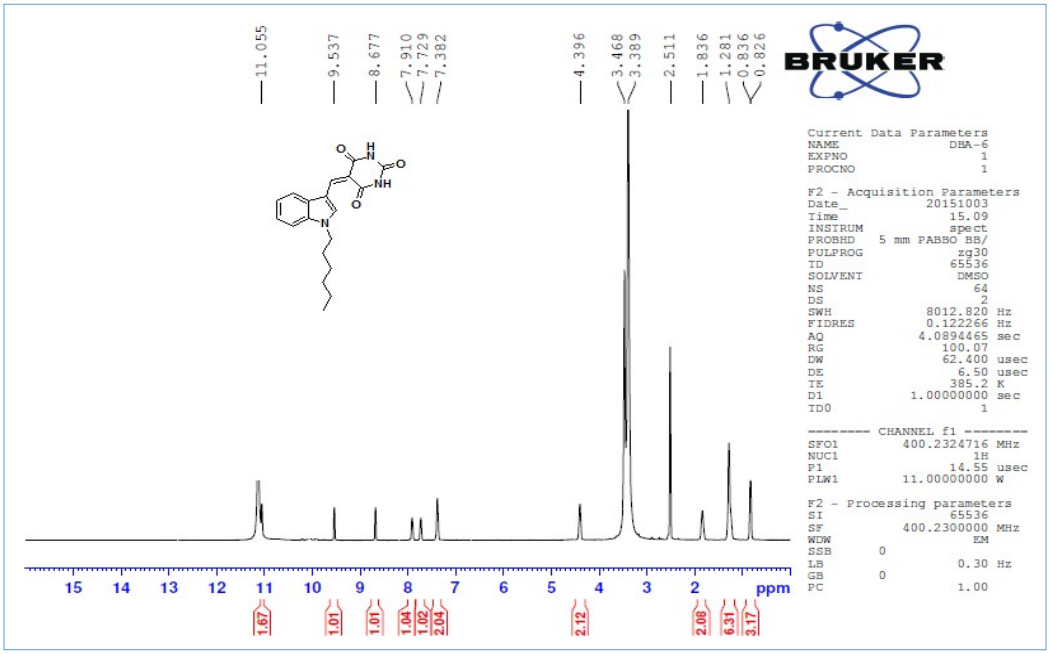

Figure 10S. ^{1}H NMR spectrum of **DBA-5** in DMSO

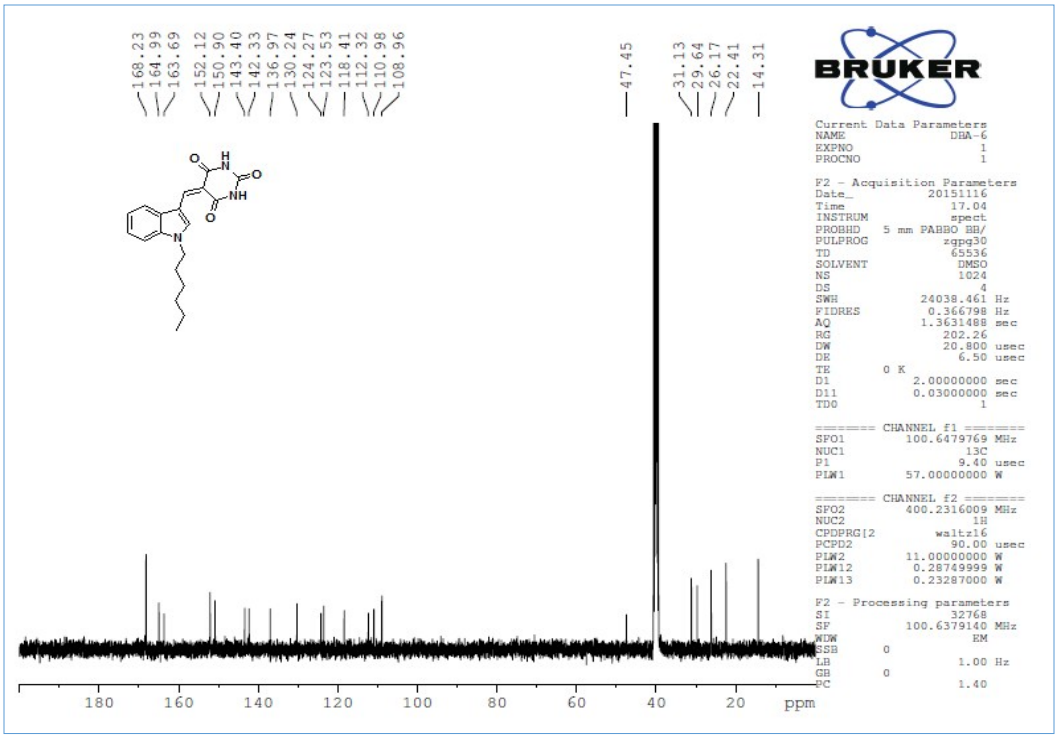

Figure 11s. ^{13}C NMR spectrum of **DBA-5** in DMSO

Mass Spectra

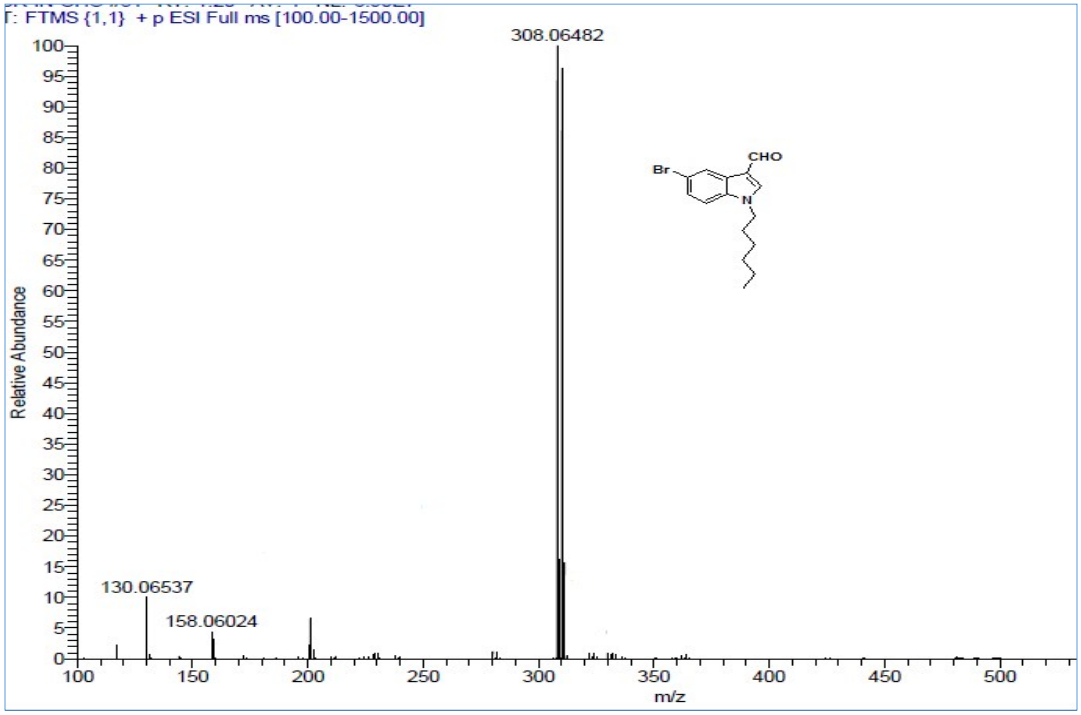

Figure 12S. Mass spectrum of **2**

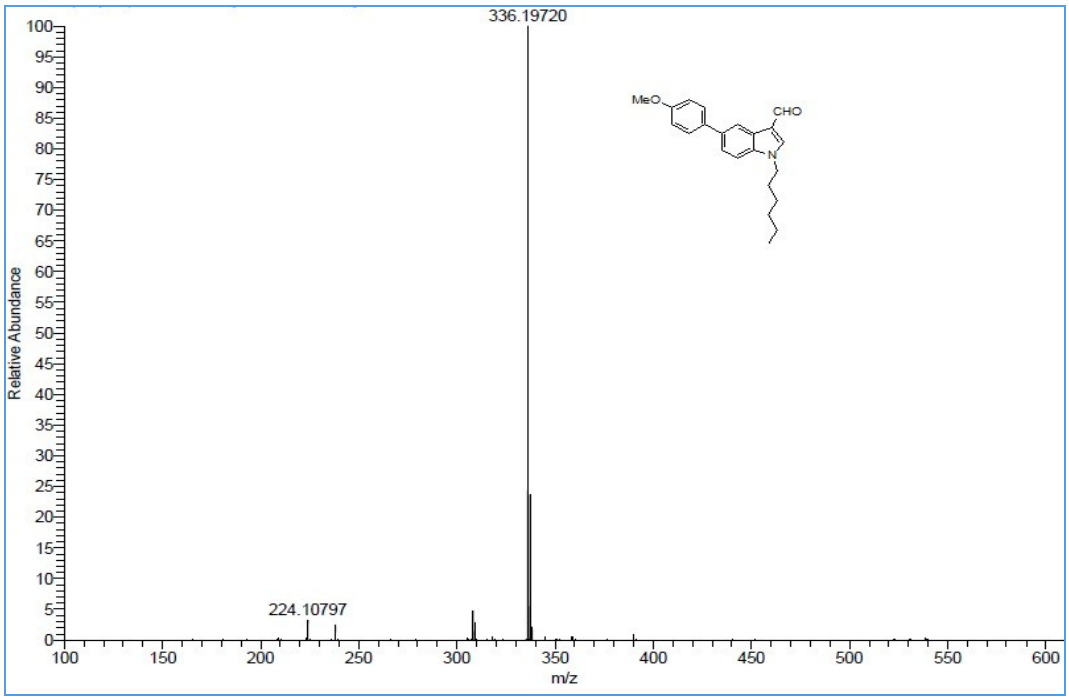

Figure 13S. Mass spectrum of **3**

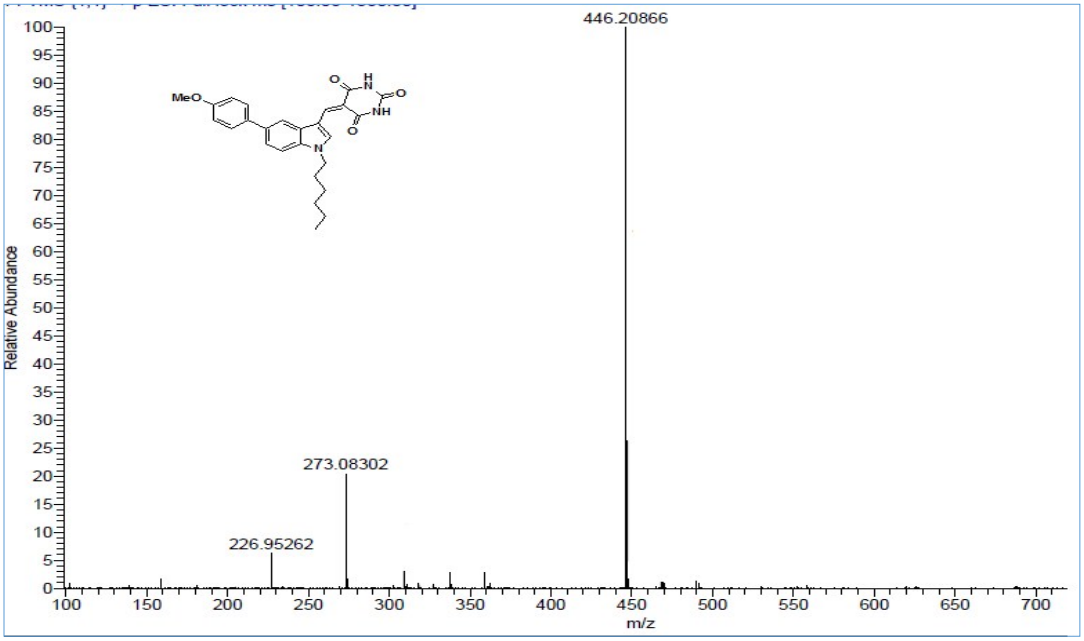

Figure 14S. Mass spectrum of **DBA-3**

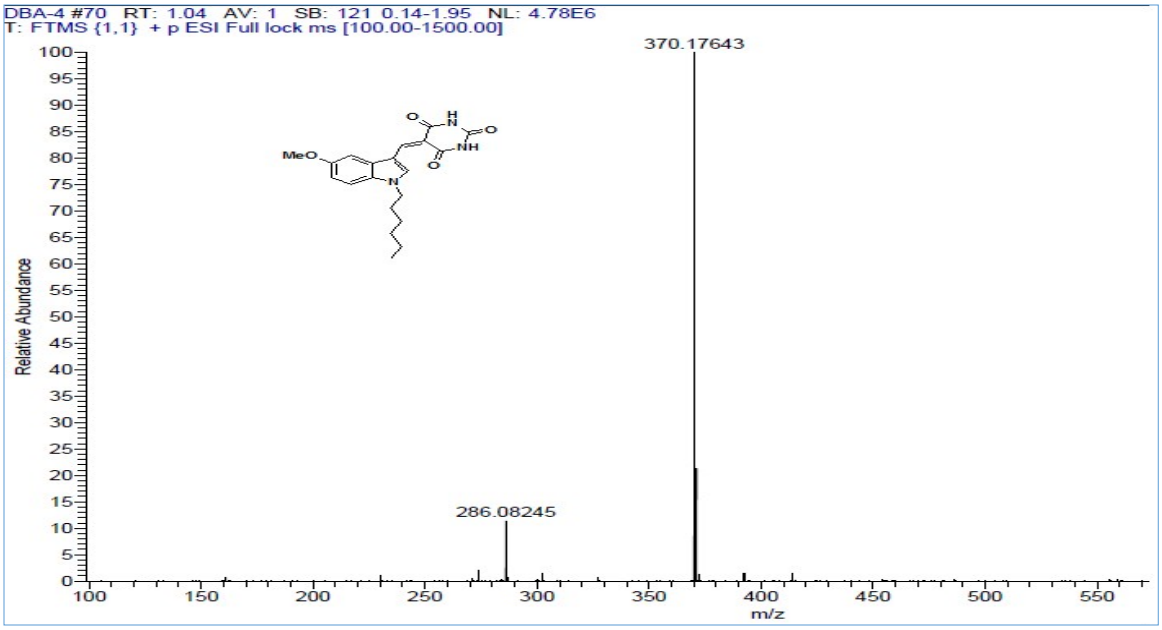

Figure 15S. Mass spectrum of **DBA-4**

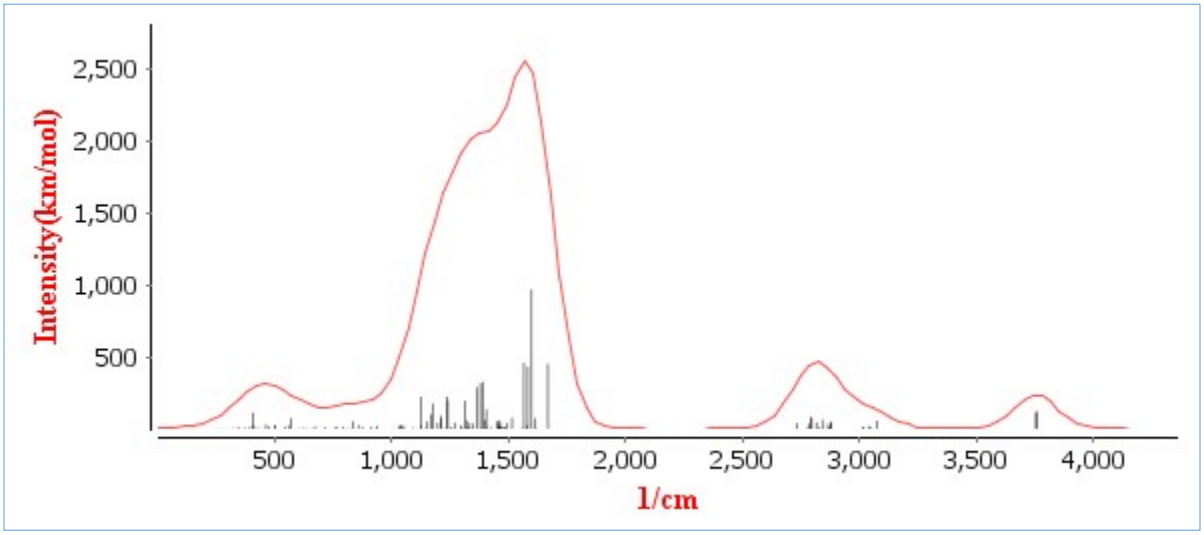

Figure 16S. Theoretically obtained FT-IR spectrum of **DBA-3**

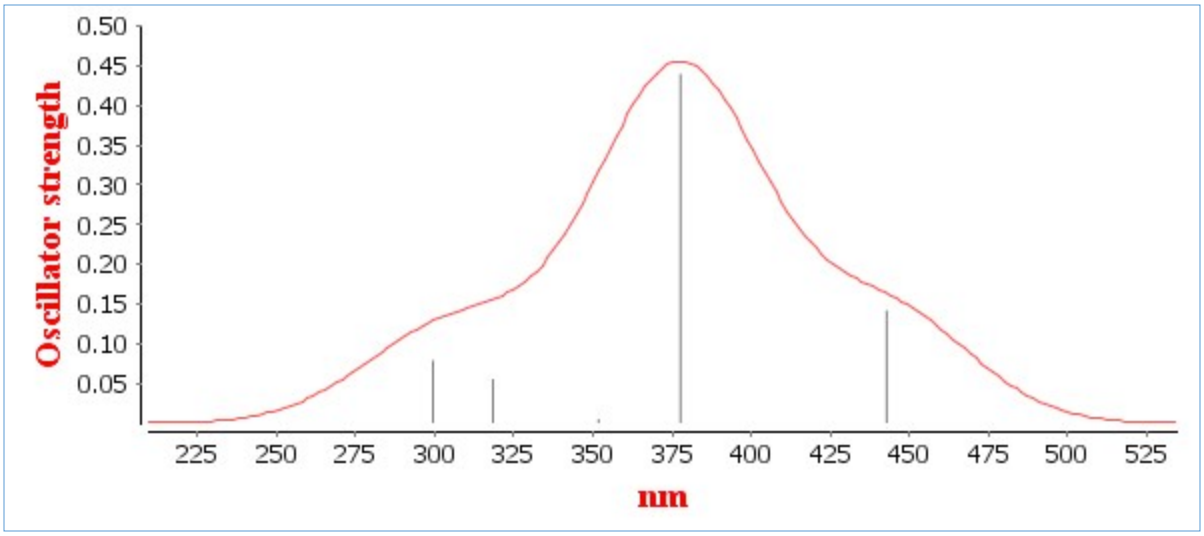

Figure 17S. Simulated absorption spectrum of **DBA-3**

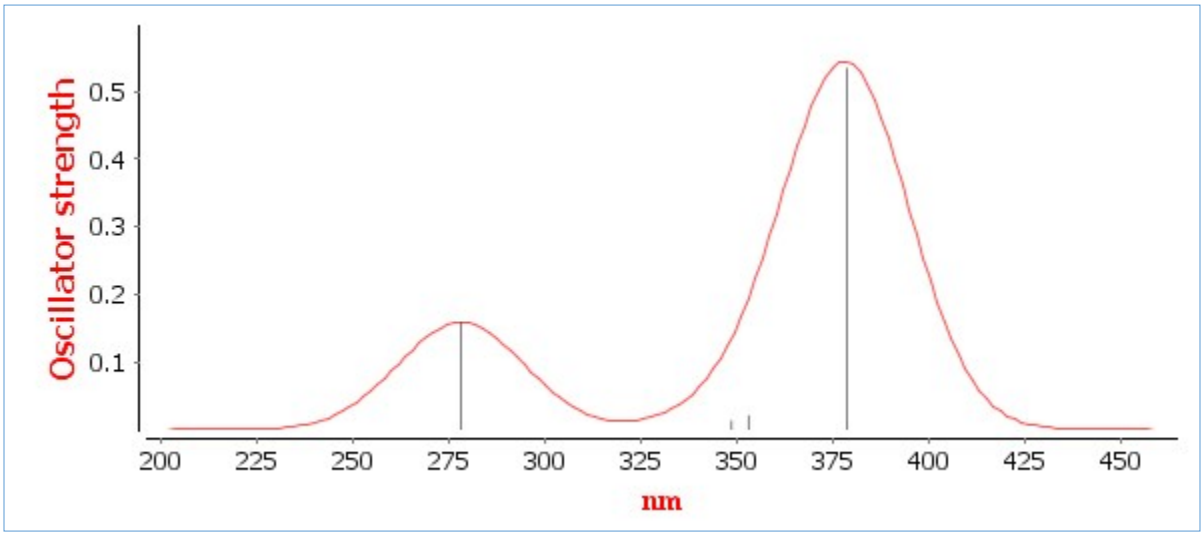

Figure 18S. Simulated absorption spectrum of **DBA-5**

REFERENCES

1. L. Han, A. Islam, H. Chen, C. Malapaka, B. Chiranjeevi, S. Zhang, X. Yang and M. Yanagida, *Energy Environ. Sci.*, 2012, **5**, 6057–6060.