Electronic Supplementary Material (ESI) for RSC Advances.

Bromine substituted aminonaphthoquinones: Synthesis, Characterization, DFT and metal ion binding studies

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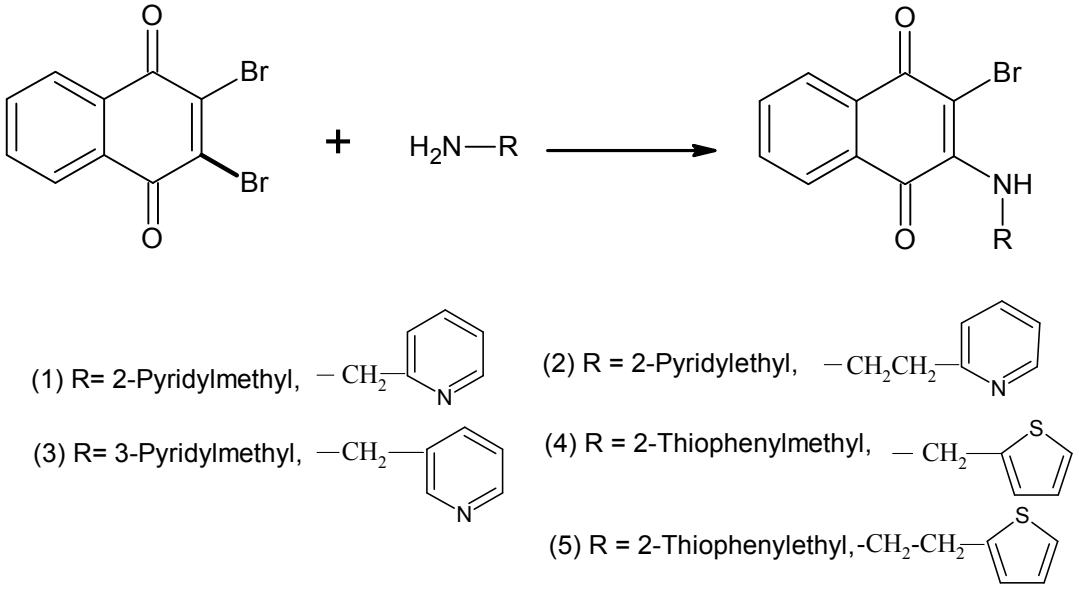

Scheme 2 General reaction for the synthesis of ligands

Figure Legends

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Fig.S7f	^{13}CNMR spectrum of 2AET in $CDCl_3$ between 123-180 ppm
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Fig.S8	UV-visible spectra for

Table S9	Bond lengths and Bond angles for 3MPA
Table S10	Anisotropic displacement parameters for 3MPA
Table S11	Torsion angles for 3MPA

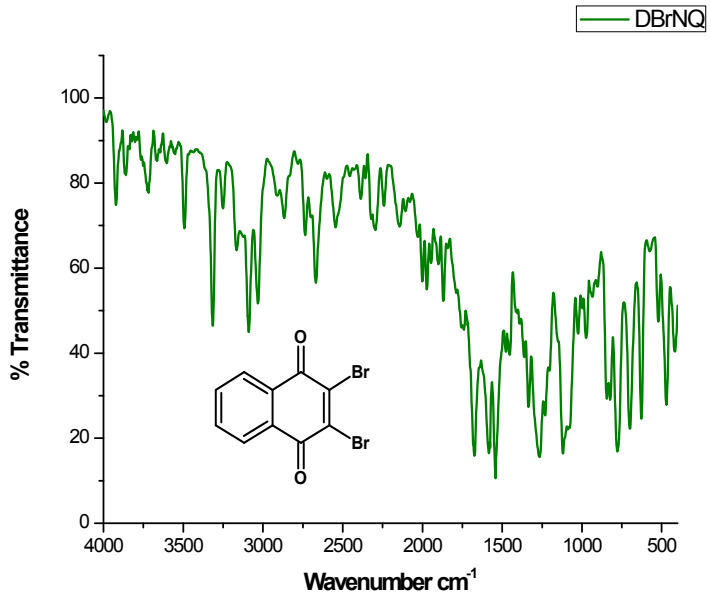

Fig S1a FT-IR spectrum of DBrNQ in the region 4000 to 400 cm^{-1}

Table S12	Atomic coordinates and equivalent isotropic displacement parameters for 2AMT
Table S13	Bond lengths and Bond angles for 2AMT
Table S14	Anisotropic displacement parameters for 2AMT
Table S15	Torsion angles for 2AMT
Table S16	Atomic coordinates and equivalent isotropic displacement parameters for 2EPA
Table S17	Bond lengths and Bond angles for 2EPA
Table S18	Anisotropic displacement parameters for 2EPA
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Table S20	Atomic coordinates and equivalent isotropic displacement parameters for 2AET
Table S21	Bond lengths and Bond angles for 2AET
Table S22	Anisotropic displacement parameters for 2AET
Table S23	Torsion angles for 2AET

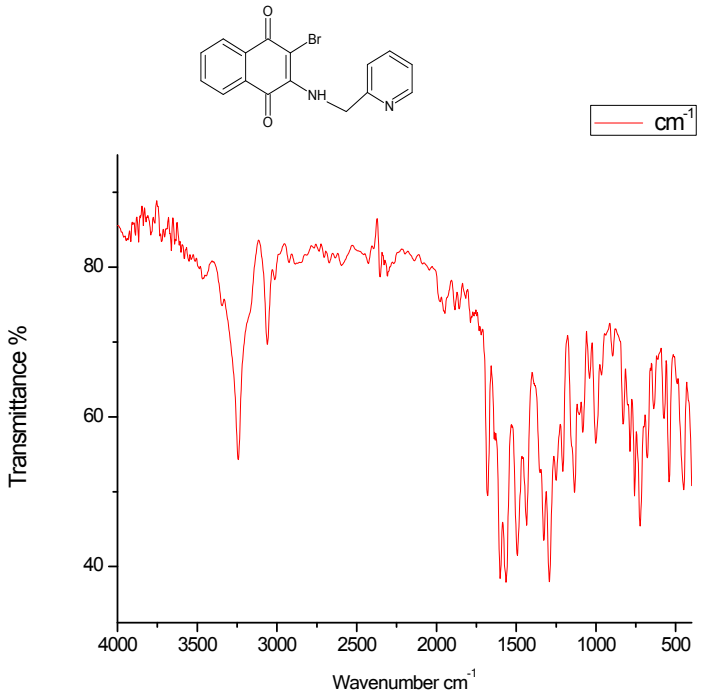


Fig.S1b FT-IR spectrums of 2MPA in the region 4000 cm^{-1} to 400 cm^{-1}

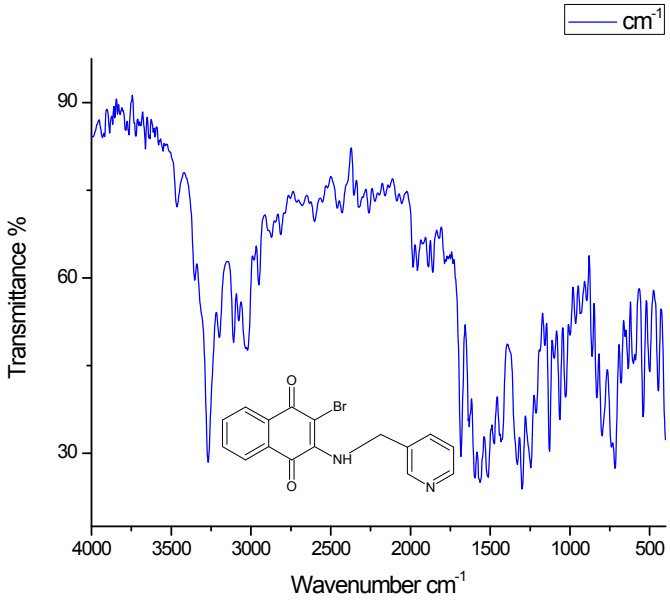


Fig.S1c FT-IR spectrums of 3MPA in the region 4000 cm^{-1} to 400 cm^{-1}

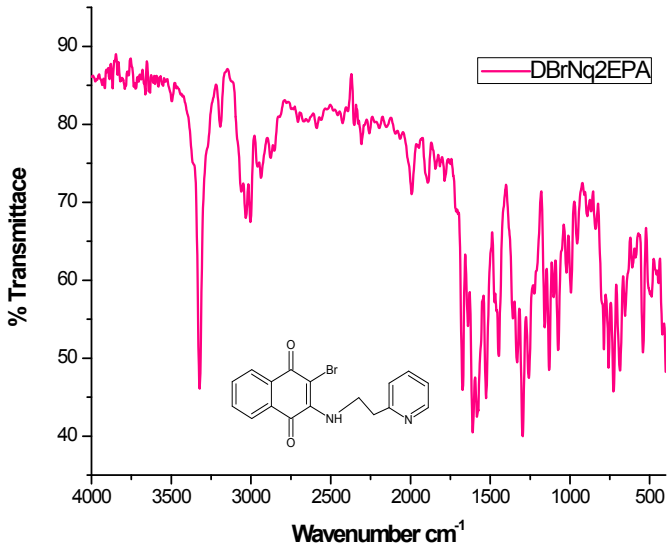


Fig.S1d FT-IR spectrums of 2EPA in the region 4000 cm^{-1} to 400 cm^{-1}

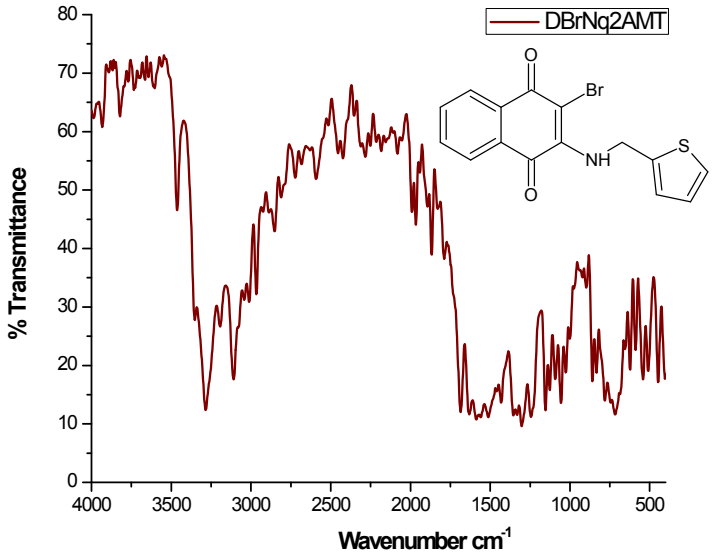


Fig.S1e FT-IR spectrums of 2AMT in the region 4000 cm^{-1} to 400 cm^{-1}

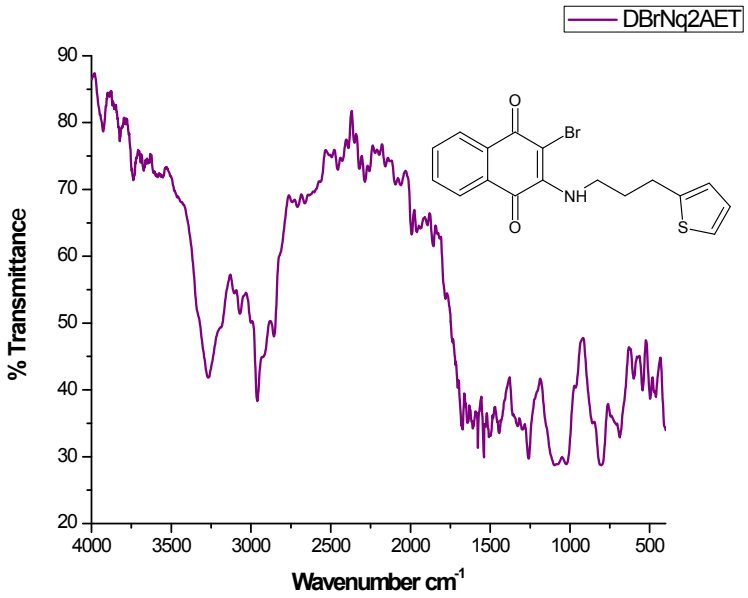
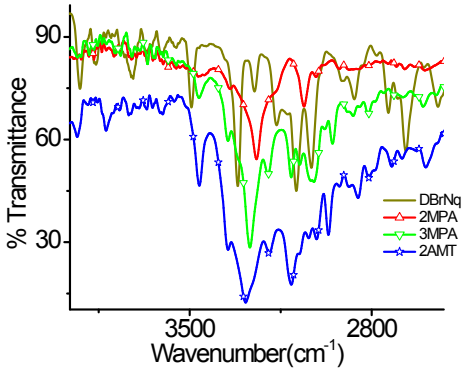


Fig.S1f FT-IR spectrums of 2AET in the region 4000 cm^{-1} to 400 cm^{-1}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3500
2800
Wavenumber(cm-1)
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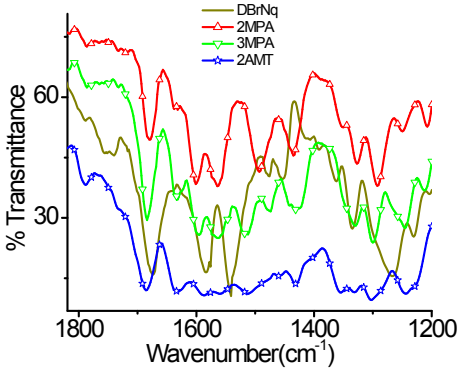
3MPA
2AMT


DBrNq
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3MPA
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30
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1800
1600
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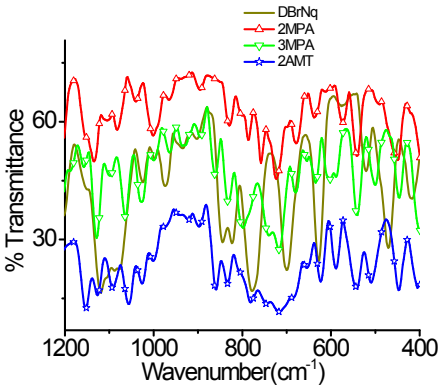
1200
Wavenumber(cm-1)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2AMT
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30
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1200
1000
800
600
400
Wavenumber(cm-1)

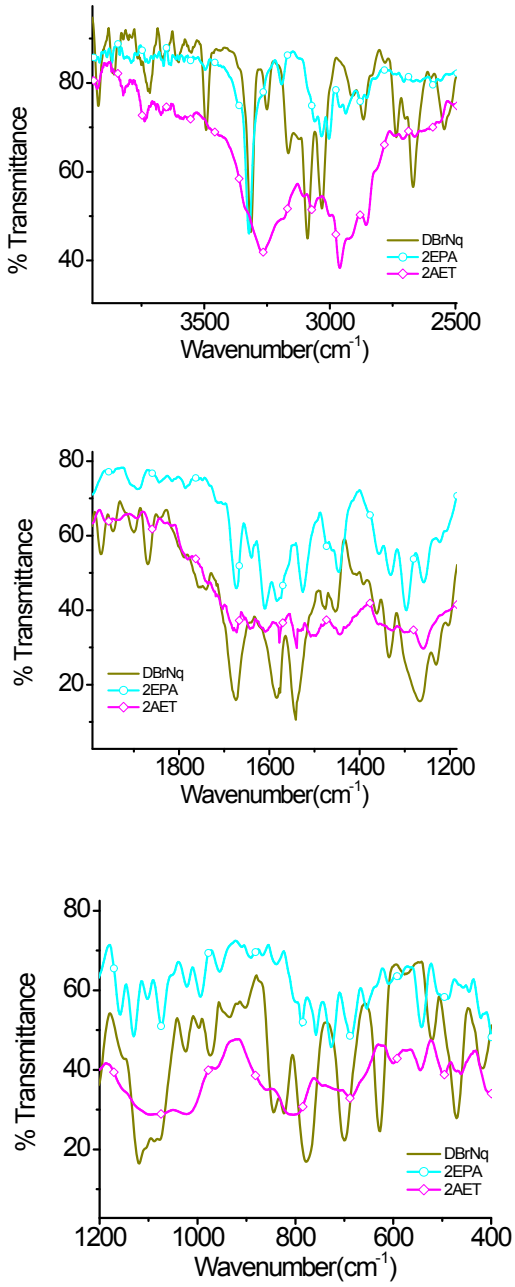


Fig.S2 FT-IR spectra in various regions of 2MPA, 3MPA, 2AMT, 2EPA and 2AET

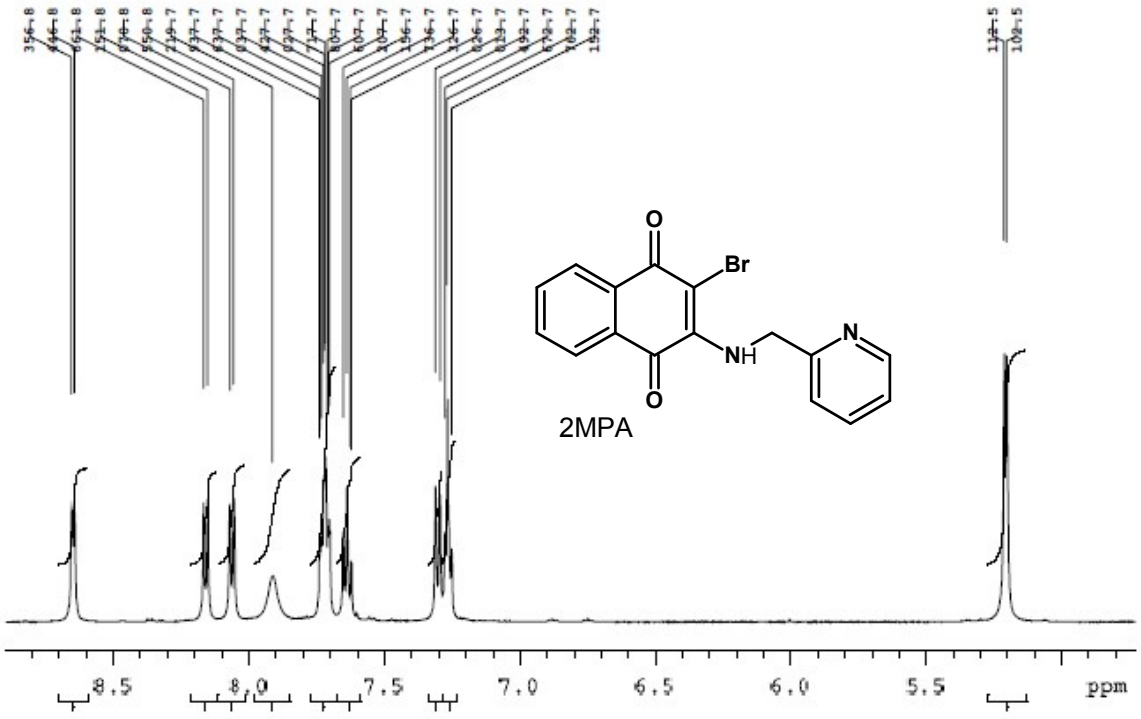


Fig.S3a ^{1}HNMR spectrum of 2MPA in $CDCl_3$

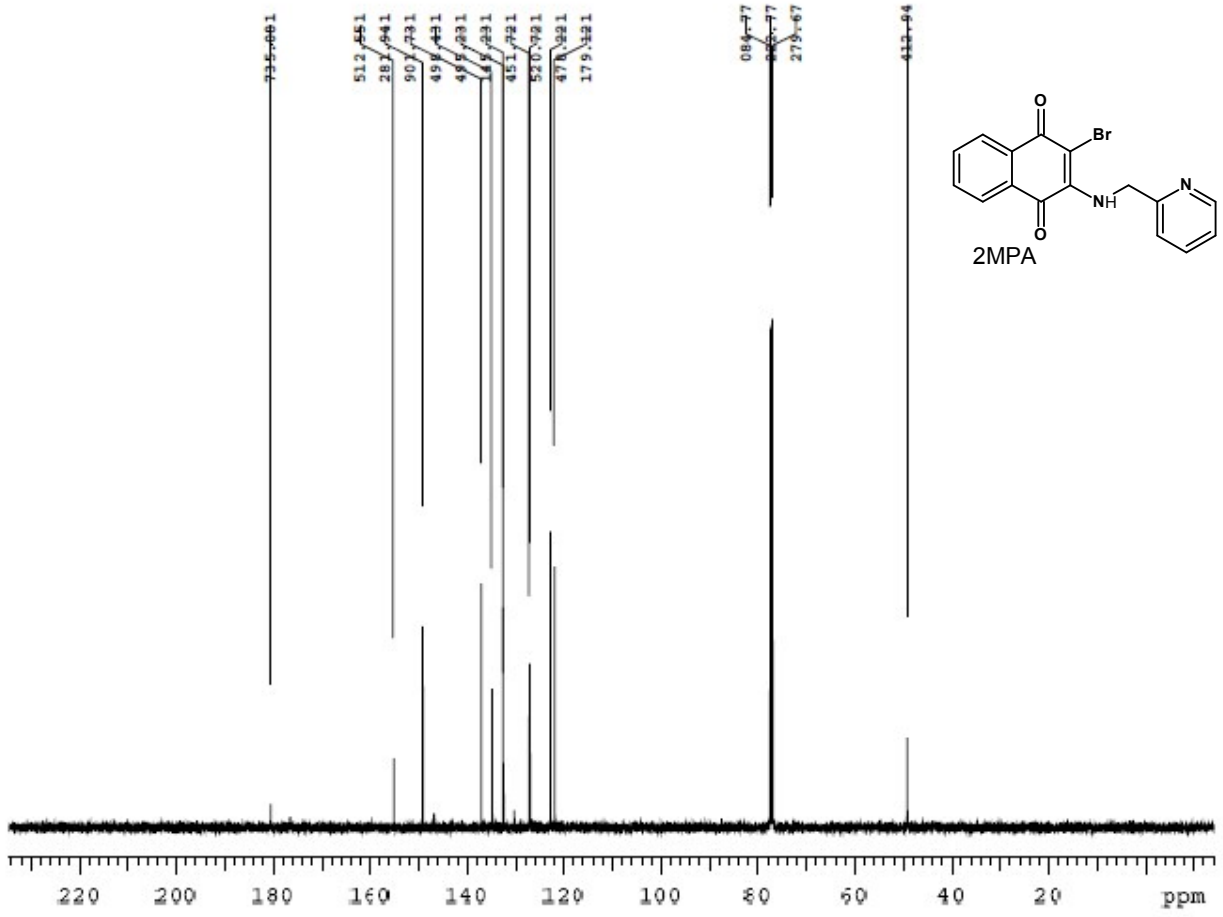


Fig.S3b ^{13}C NMR of 2MPA in $CDCl_3$

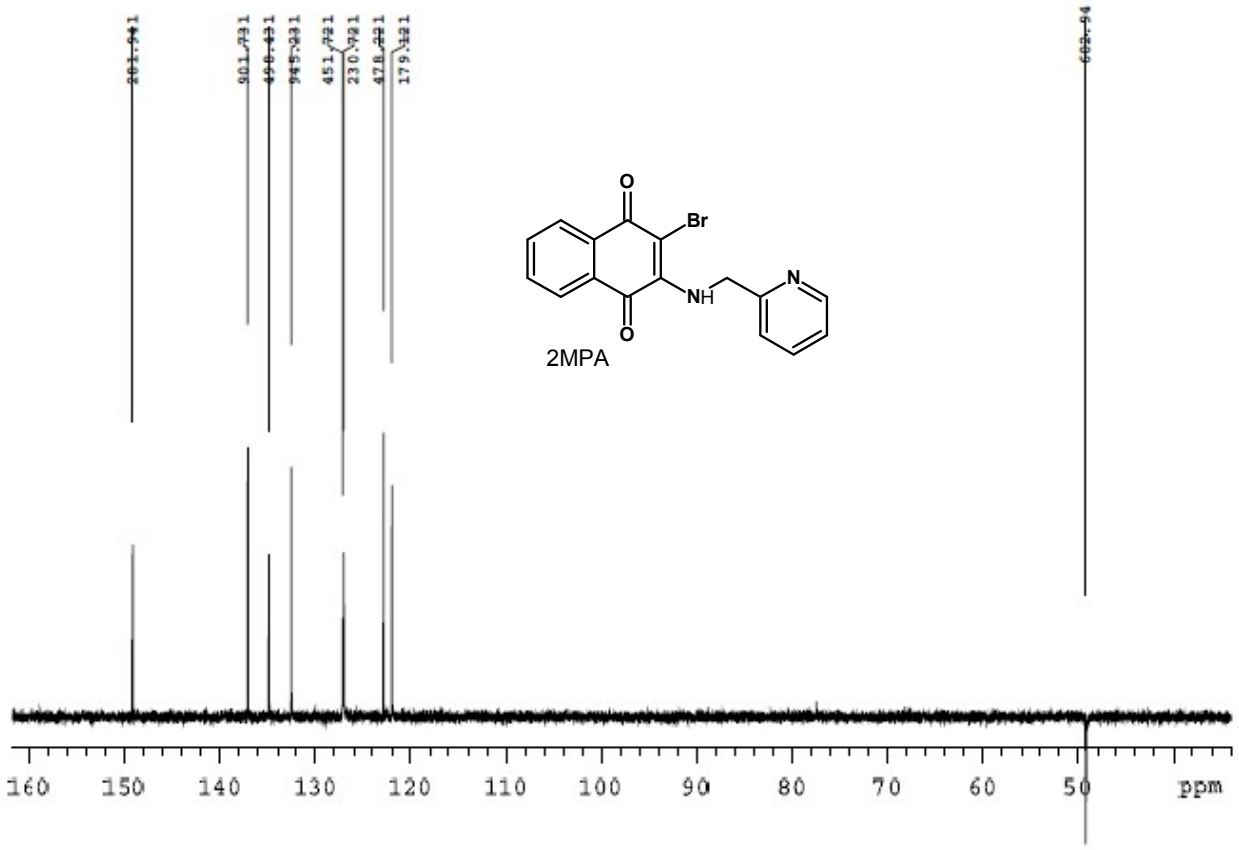


Fig.S3c DEPT NMR spectrum of 2MPA in $CDCl_3$

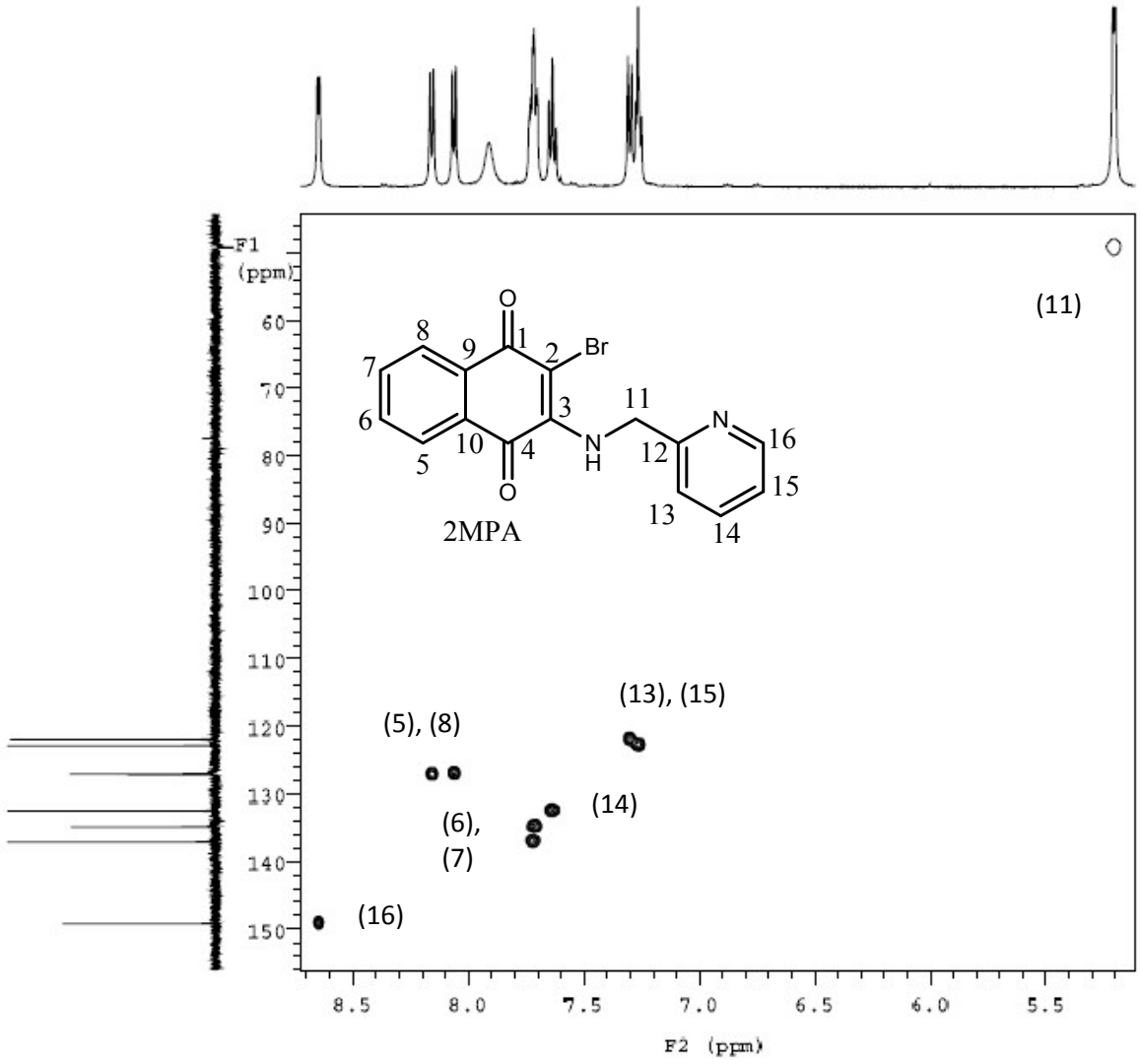


Fig.S3d gHSQCAD NMR spectrum of 2MPA in $CDCl_3$ showing correlation between the Carbons and Protons

Interpretation of the 2D gHSQCAD NMR spectrum of DBrNq2MPA-

Spot (5,8) show the correlation between the protons i.e. observed at 8.16 ppm and 8.06 ppm and the carbon C5 and C8 both absorbing at 127.154 ppm in ^{13}CNMR.

Spot (6,7) shows a close correlation between the protons i.e. observed within 7.72 ppm (H-C6 and H-C7) in proton NMR and the carbons C6 and C7 which absorb at 134.894 and 137.109 respectively in carbon NMR.

Spots (11) show the correlation between the protons observed at 5.21 ppm (H-C11) and the carbons which absorb at 49.214 ppm in ^{13}CNMR. Hence it is inferred from the 2D spectrum that

this proton is attached to the carbons C11. Similarly other spots can be correlated to their respective carbons.

Spot (13) and (15) are very closely related showing the correlation between the proton i.e. observed as a doublet at 7.30 ppm (C13-H) and a triplet at 7.27 ppm (C15-H) in proton NMR and the carbon C13 observed at 121.971 ppm and C15 appearing at 122.874 ppm in carbon NMR.

Spot (14) show the correlation between the proton i.e. observed at 7.64 ppm (C14-H) in proton NMR and the carbon observed at 132.154 ppm in carbon NMR.

Spot (16) show the correlation between the proton i.e. observed at 8.65 ppm (C16-H) in proton NMR and the carbon observed at 149.182 ppm in carbon NMR.

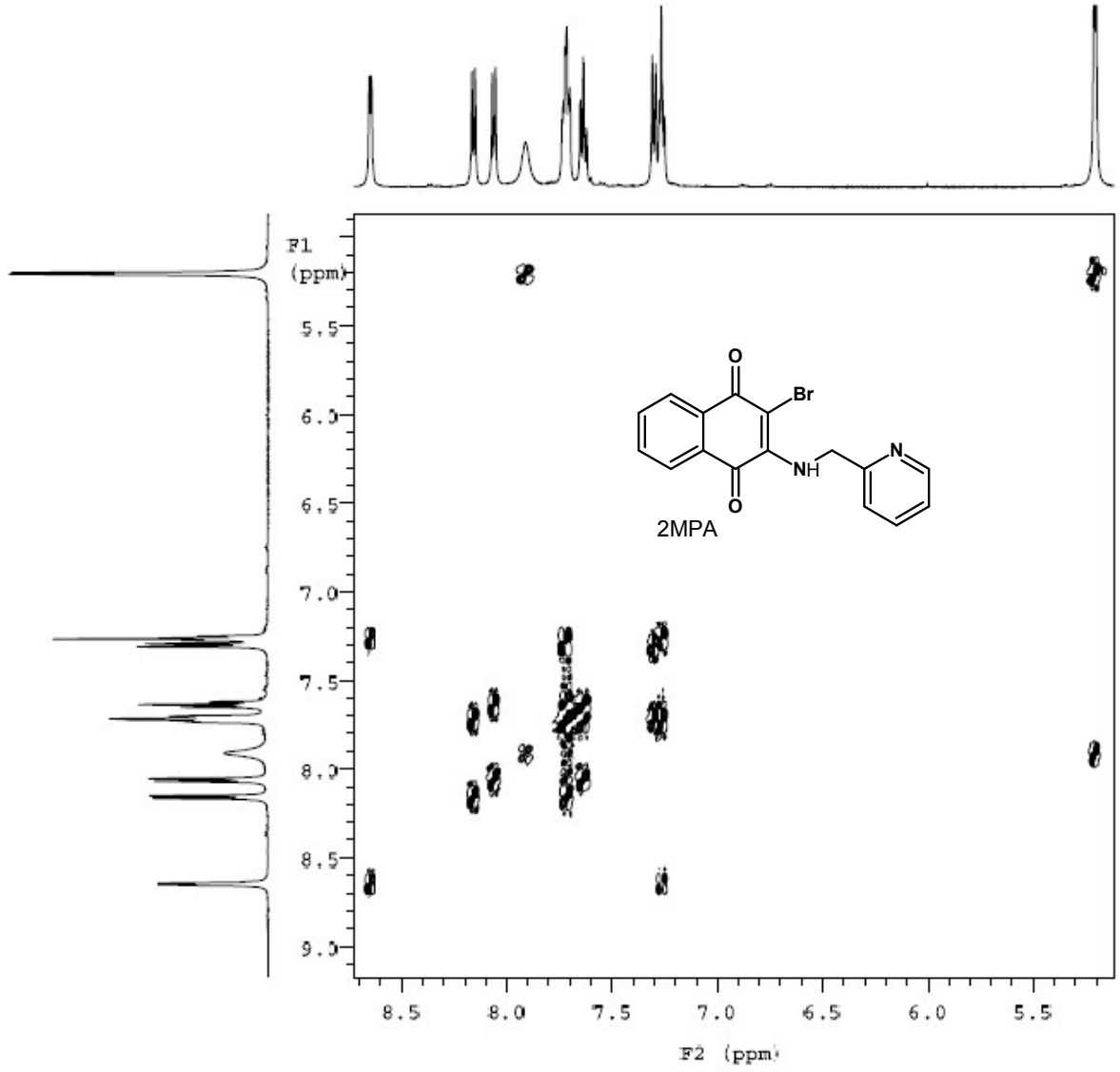


Fig.S3e gDQCOSY spectrum of 2MPA in $CDCl_3$ showing homonuclear correlation between protons

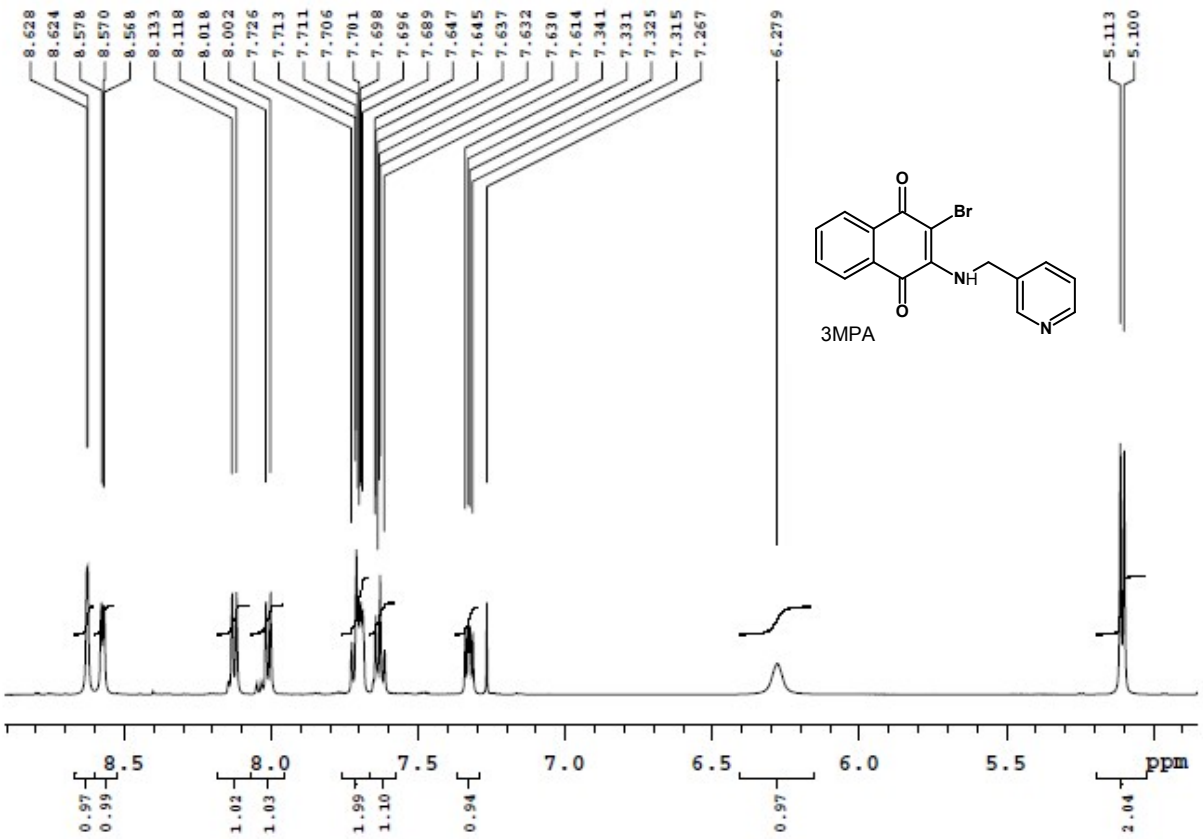


Fig.S4a ^{1}HNMR spectrum of 3MPA in $CDCl_3$

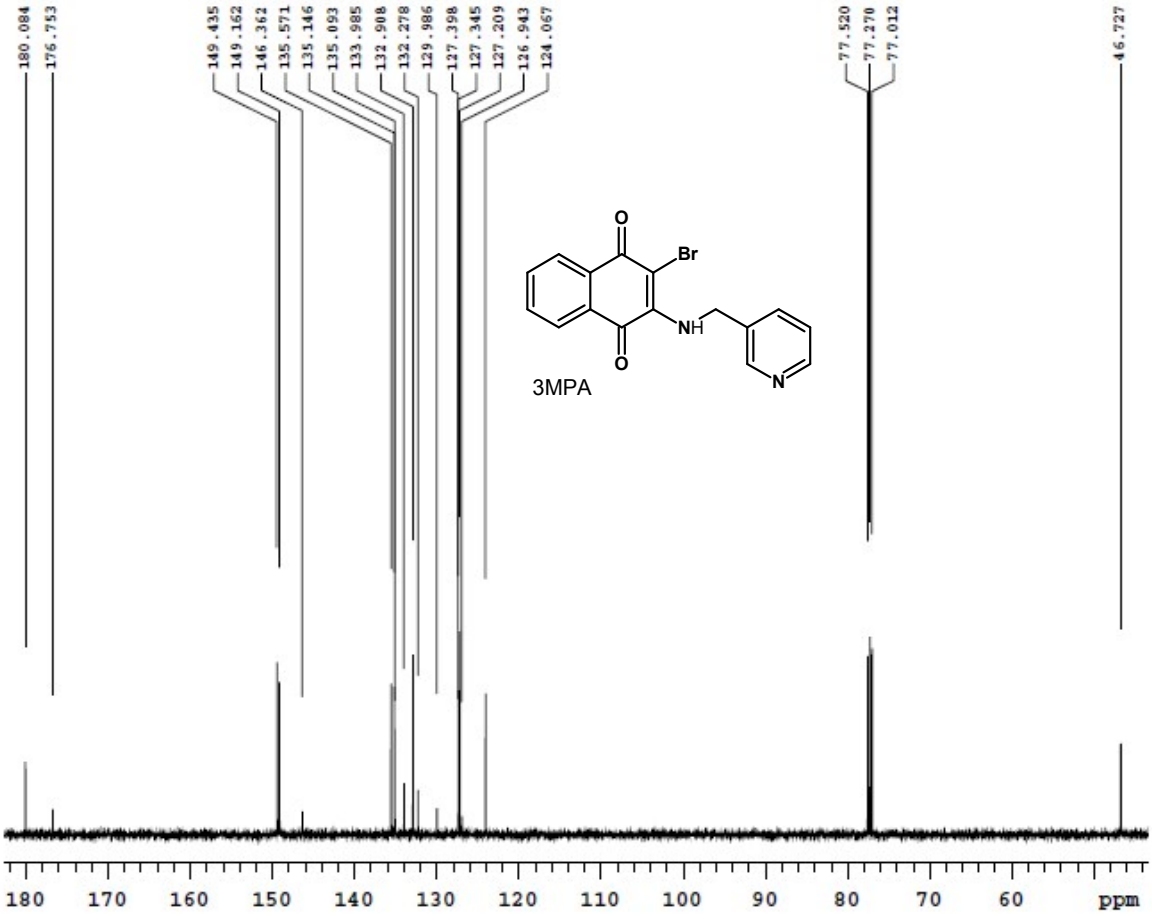


Fig.S4b ^{13}CNMR spectrum of 3MPA in $CDCl_3$

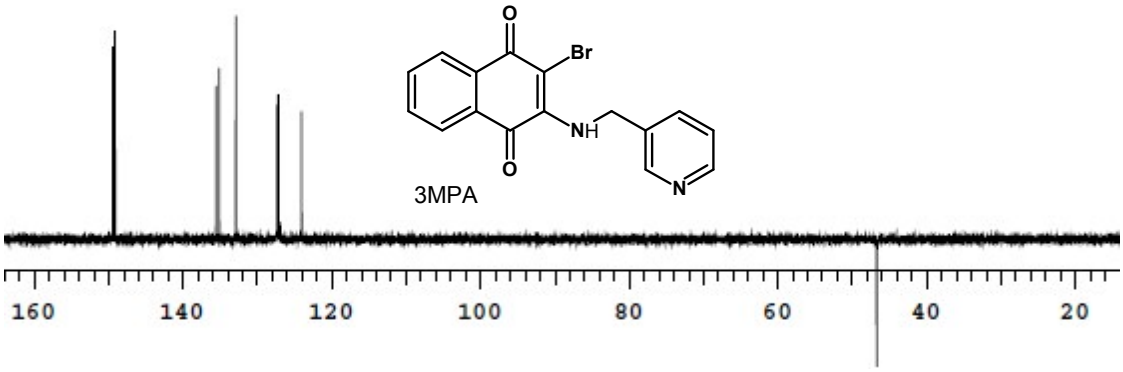


Fig.S4c DEPT NMR spectrum of 3MPA (20-160 ppm) in $CDCl_3$

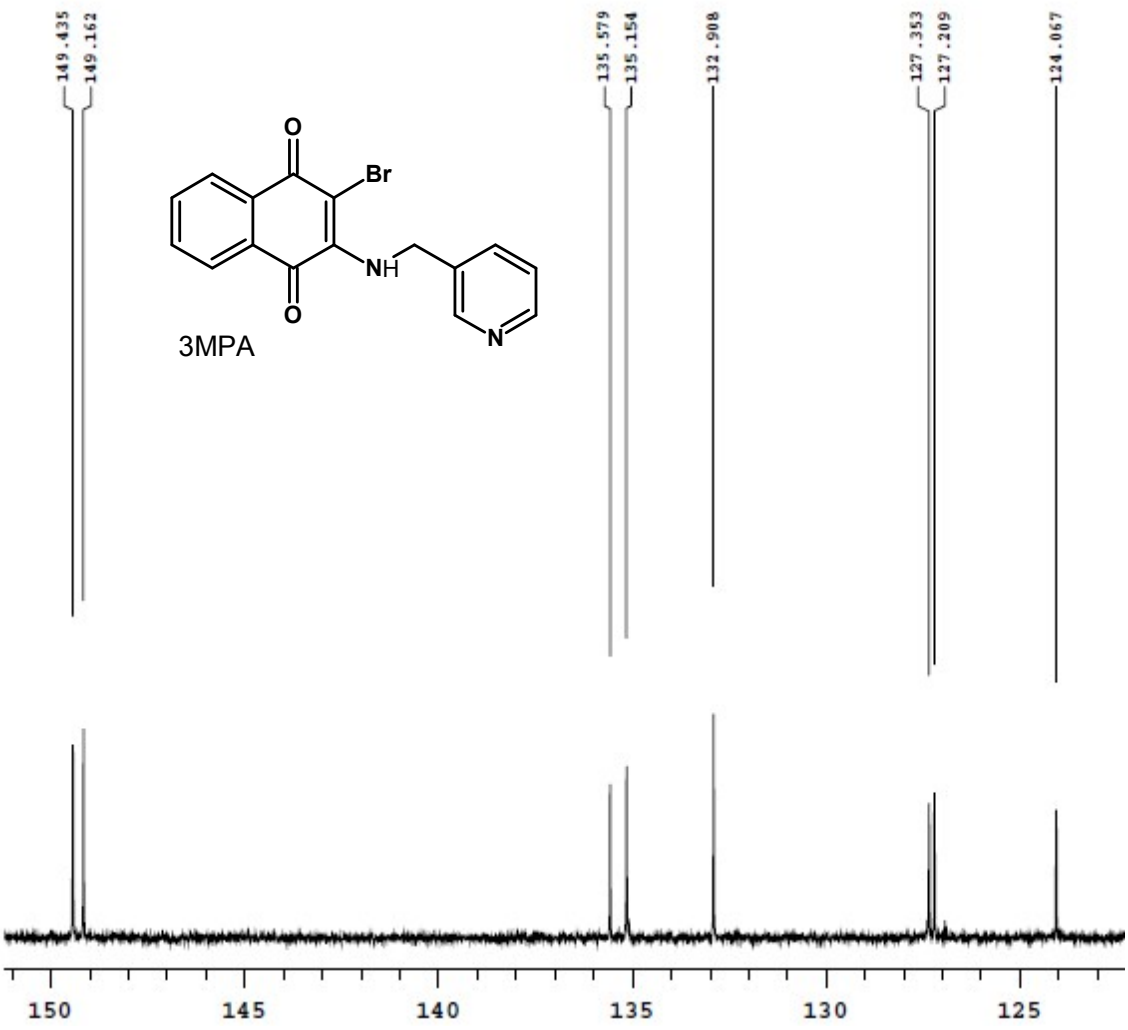


Fig S4d Zoomed view of DEPT NMR spectrum of 3MPA (122-150 ppm) in $CDCl_3$

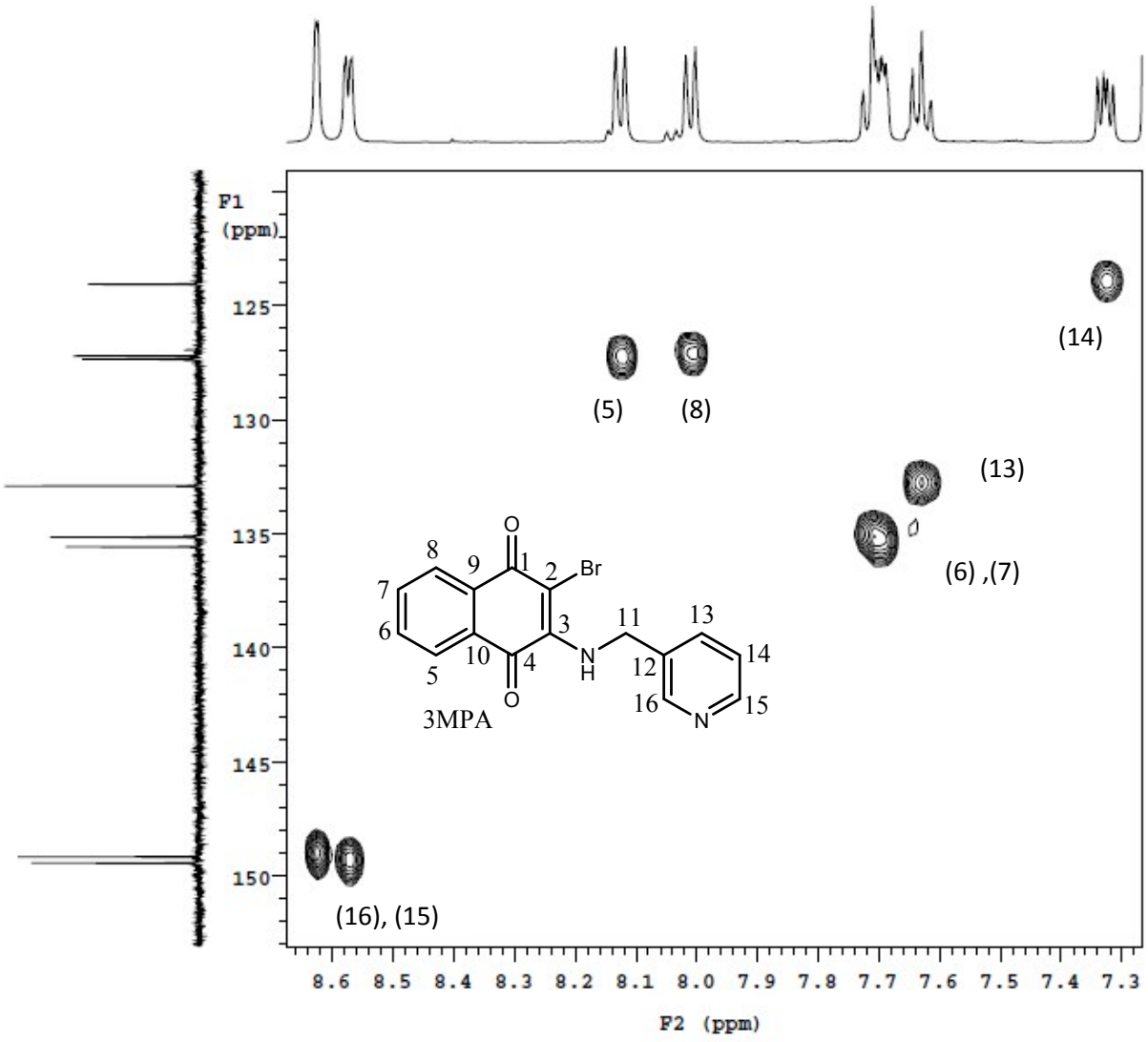


Fig.S4e gHSQCAD NMR spectrum of 3MPA in $CDCl_3$ showing the correlation between the Carbon and Proton

Interpretation of the 2D gHSQCAD NMR of 3MPA

Spot (5) shows the correlation between the proton observed at 8.12 ppm (H-C5) and the carbon C5 which absorb at 127.371 ppm in ^{13}CNMR. Hence it is inferred from the 2D spectrum that this proton is attached to the carbons C5.

Spot (8) shows the correlation between the proton i.e. observed at 8.01 ppm and the carbon C8 which absorb at 127.209 ppm in ^{13}CNMR. Hence it is inferred from the 2D spectrum that this proton is attached to the carbon C8.

Spot (6,7) show a close correlation between the protons i.e. observed within 7.70 ppm (H-C6 and H-C7) in proton NMR and the carbons C6 and C7 which absorb at 135.119 and 135.571 respectively in ^{13}CNMR.
Spot (13) shows the correlation between the proton i.e. observed as a doublet at 7.64 ppm (C13-H) in proton NMR and the carbon observed at 132.908 ppm in carbon NMR.
Spot (14) show the correlation between the proton i.e. observed at 7.33ppm (C14-H) in proton NMR and the carbon observed at 124.067 ppm in carbon NMR.
Spot (15) shows the correlation between the protons i.e. observed as a double for C15-H at 8.57 ppm which corresponds to the carbon absorbing at 149.435 ppm.
Spot (16) shows the correlation between the protons i.e. observed as a singlet for C16-H at 8.62 ppm which corresponds to the carbon absorbing at 149.162 ppm.

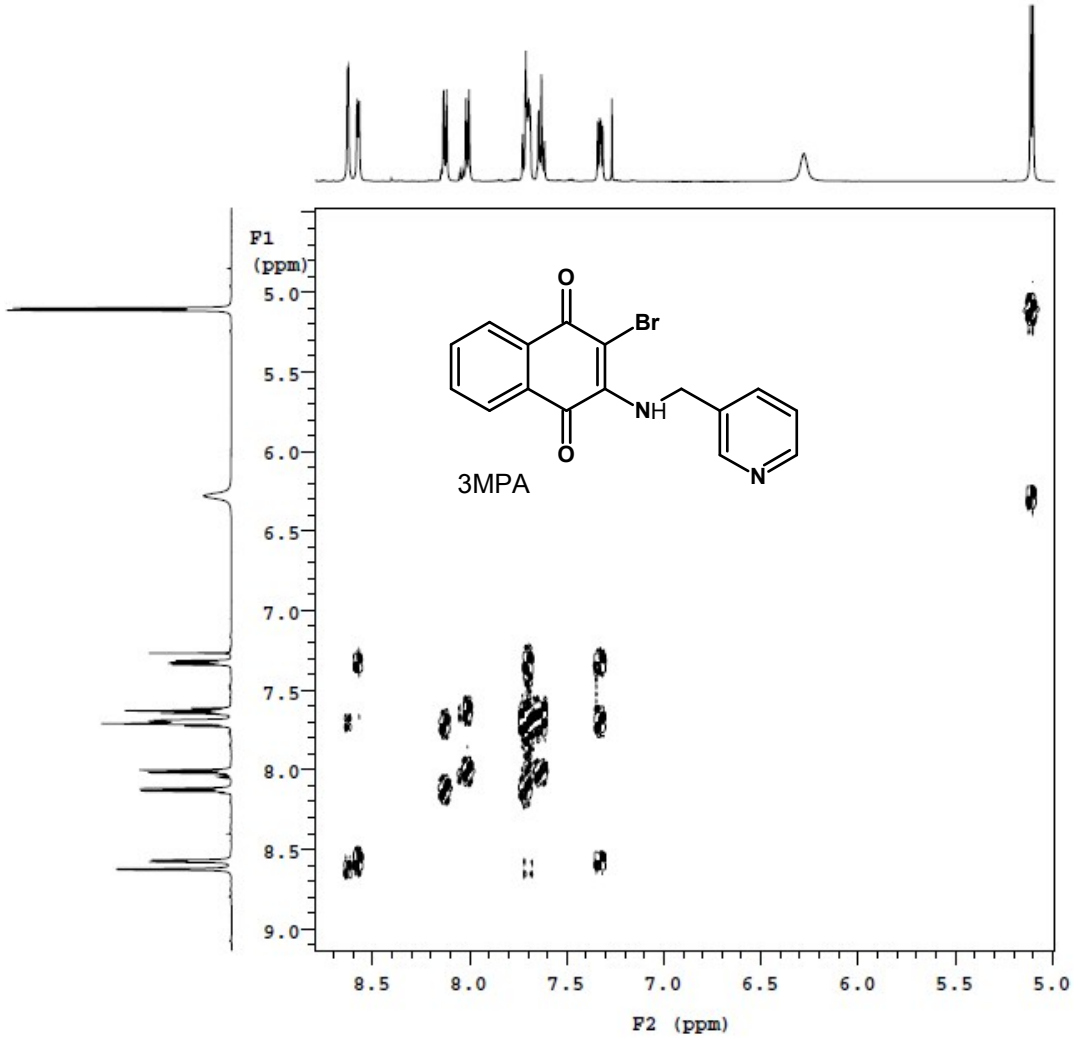


Fig.S4f gDQCOSY spectrum of 3MPA in $CDCl_3$ showing homonuclear correlation between protons

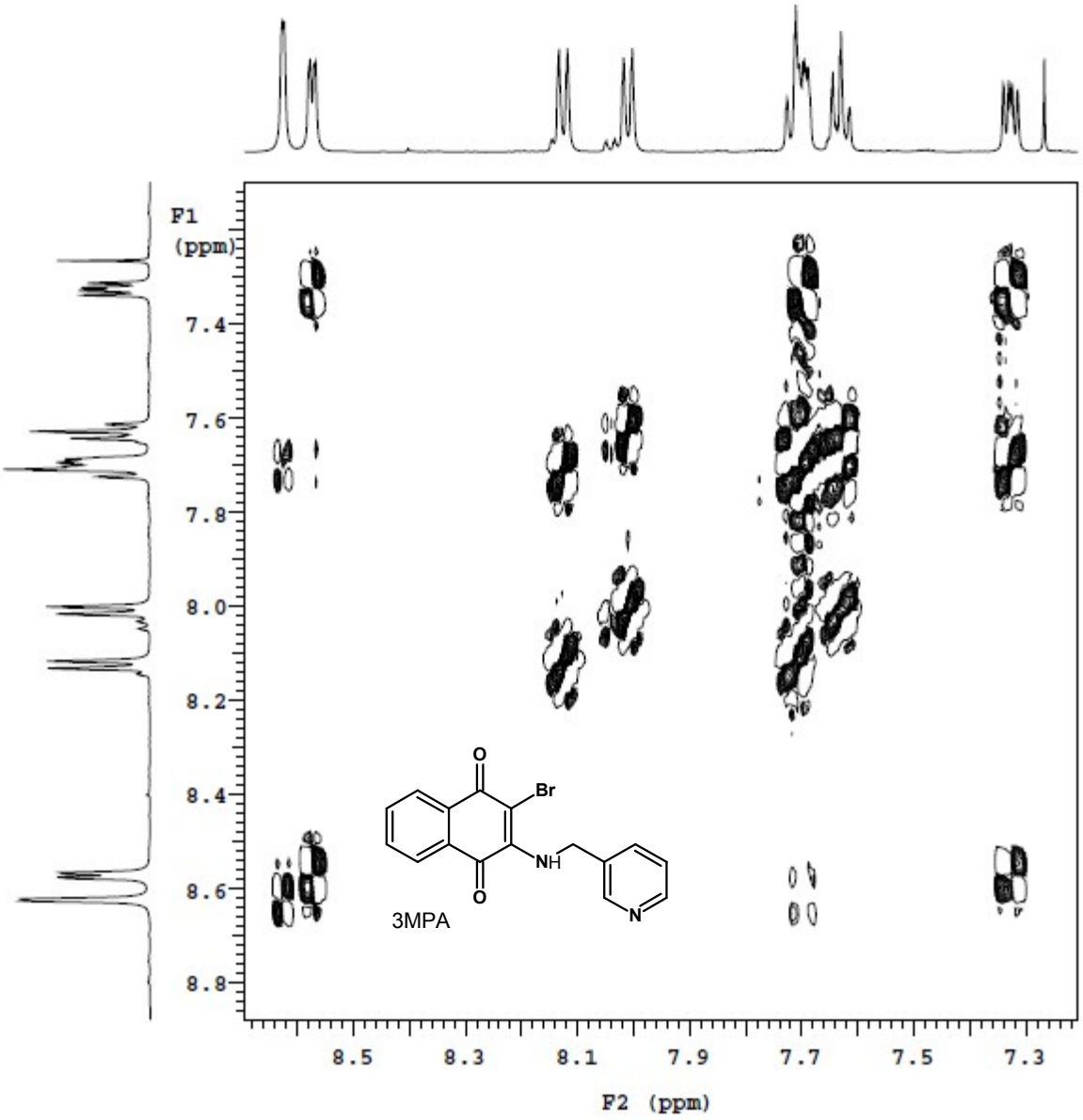


Fig S4g Magnified view of the gDQCOSY spectrum of 3MPA in $CDCl_3$

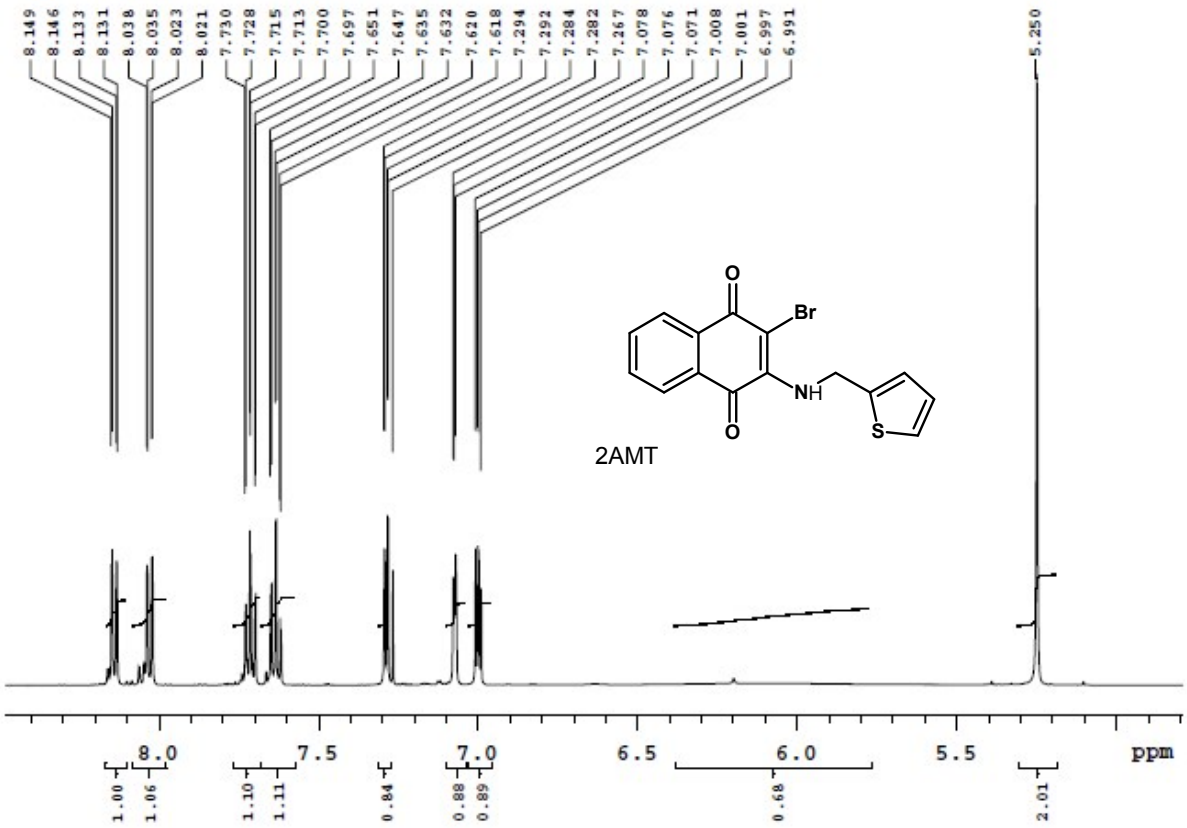


Fig.S5a ^{1}HNMR spectrum of 2AMT in $CDCl_3$

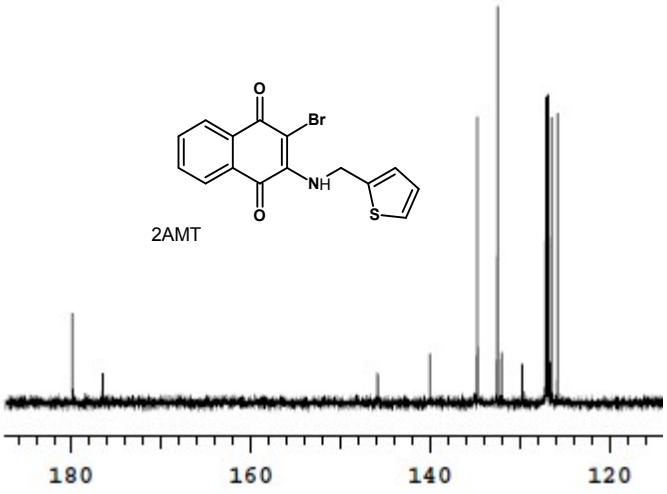


Fig.S5b ^{13}CNMR spectrum of 2AMT in $CDCl_3$ in the region 120-180 ppm

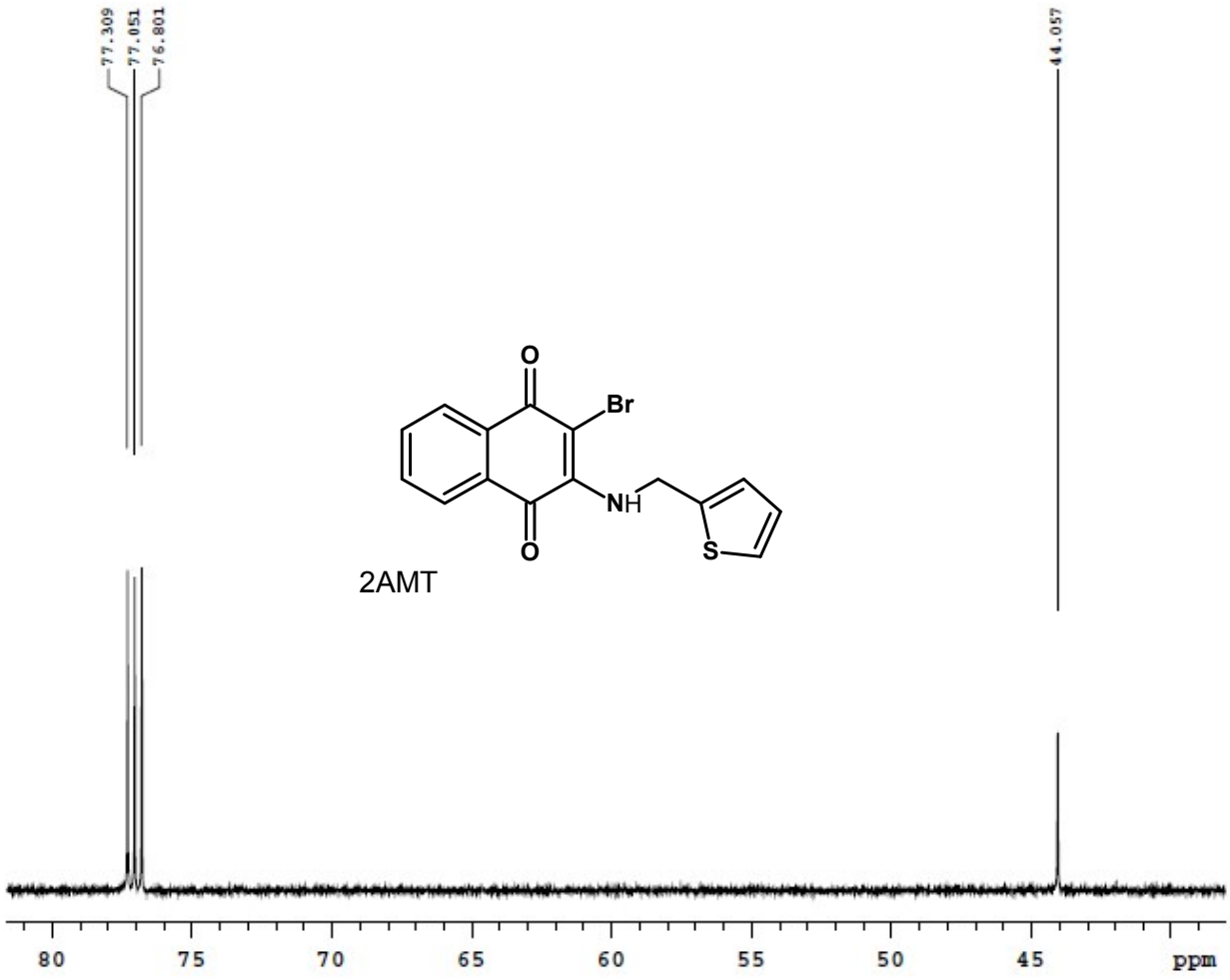


Fig.S5c ^{13}CNMR spectrum of 2AMT in $CDCl_3$ in the region 43-80 ppm

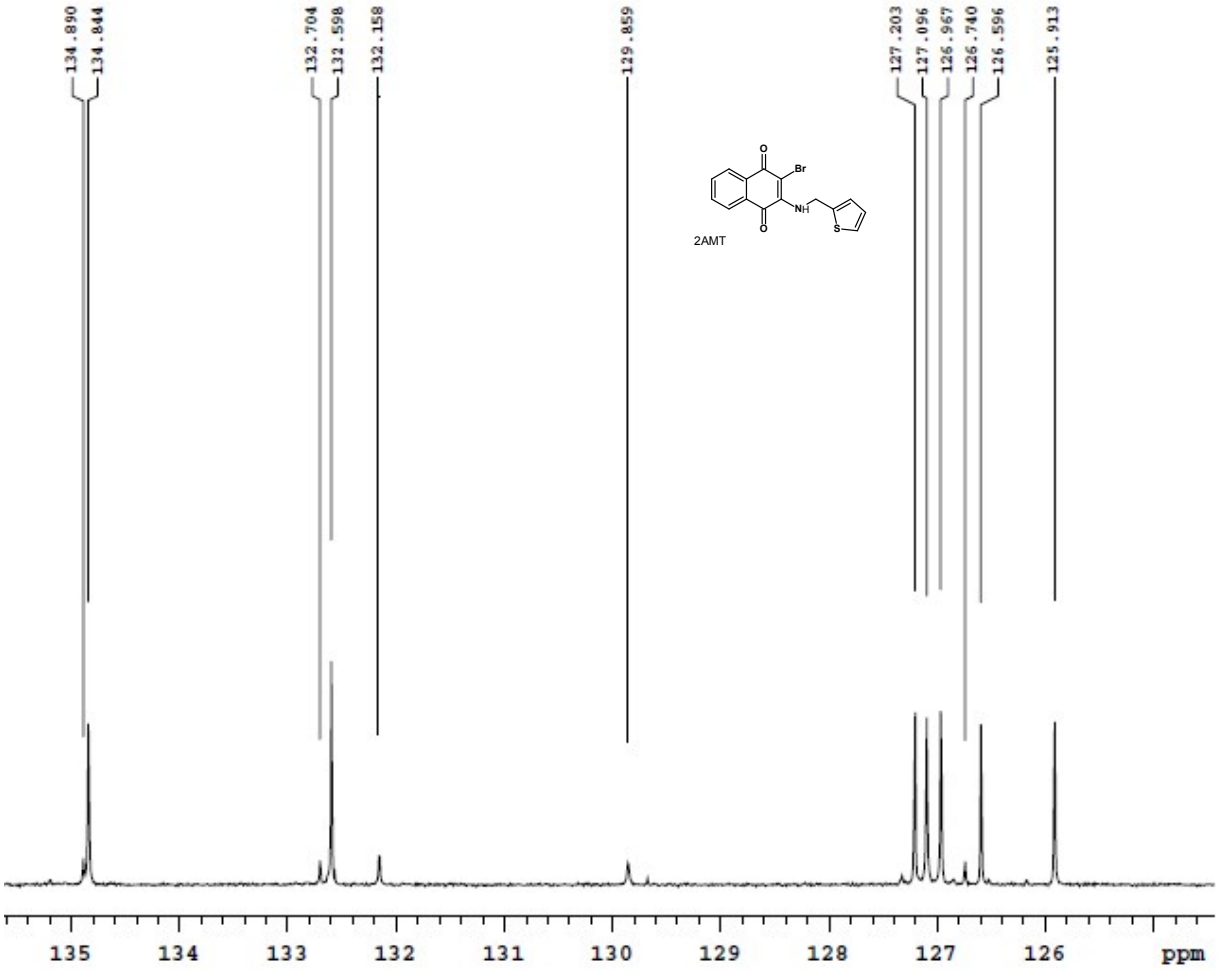


Fig.S5d ^{13}CNMR spectrum of 2AMT in $CDCl_3$ in the region 125-135 ppm

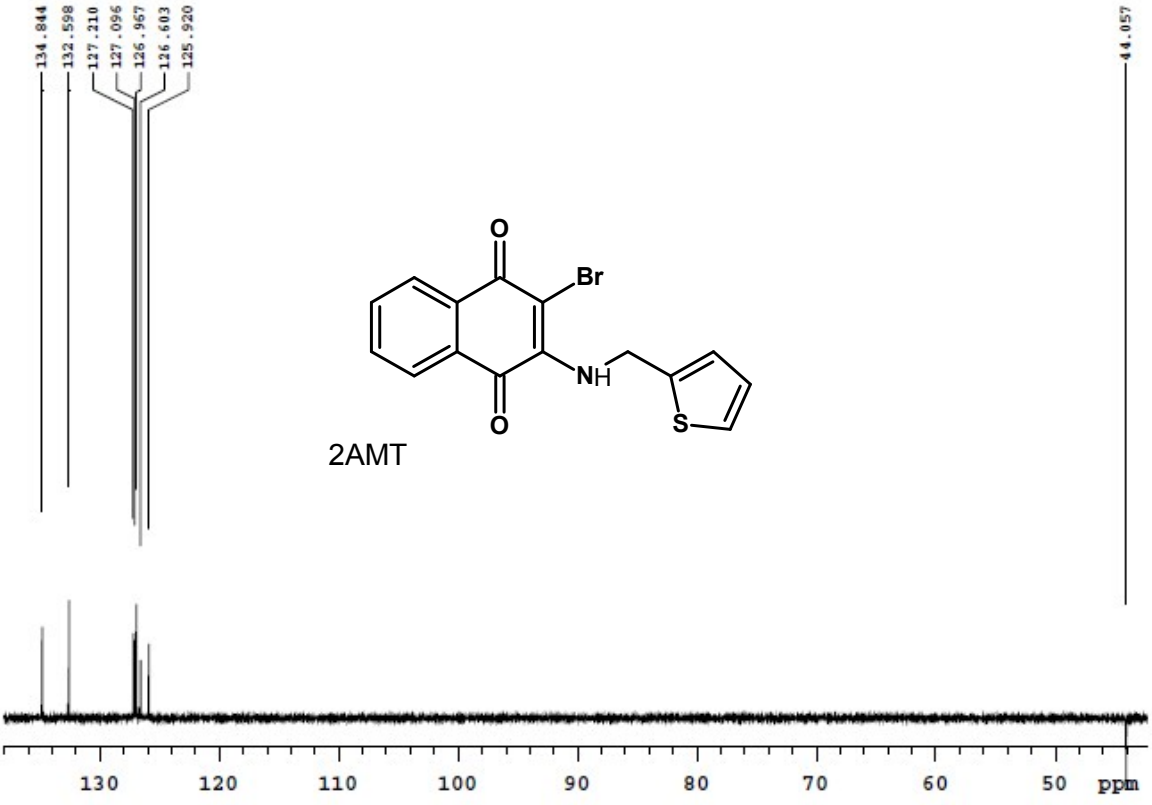


Fig.S5e DEPT NMR spectrum of 2AMT in $CDCl_3$

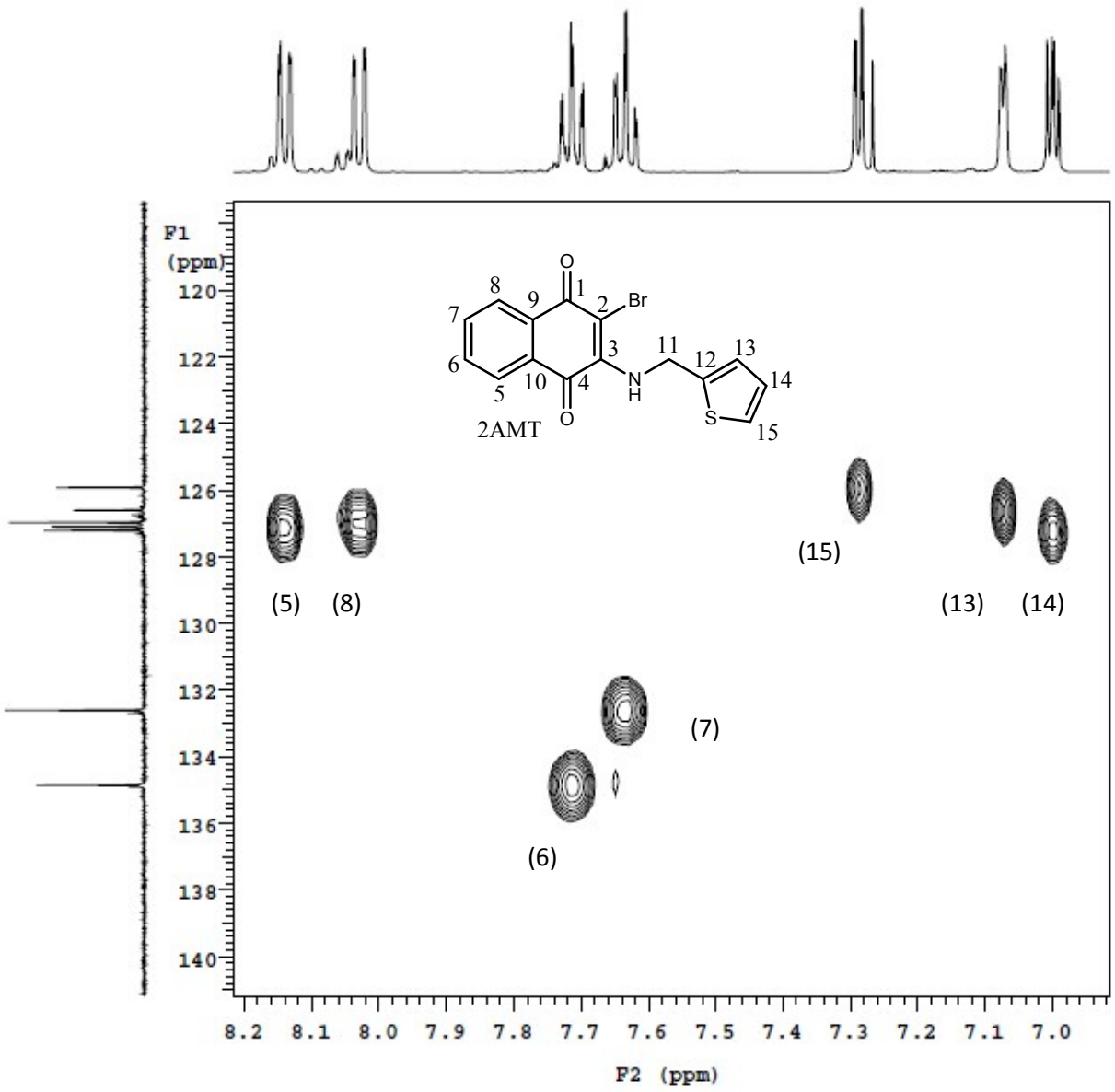


Fig S5f gHSQCAD NMR spectrum of 2AMT in $CDCl_3$ showing correlation between carbons and protons

Interpretation of the 2DgHSQCAD Spectrum of 2AMT

Spot (5) shows the correlation between the proton observed at 8.14 ppm (H-C5) and the carbon C5 which absorb at 127.096 ppm in ^{13}CNMR. Hence it is inferred from the 2D spectrum that this proton is attached to the carbons C5 .

Spot (6) shows the correlation between the proton i.e. observed at 7.72 ppm and the carbon C6 which absorb at 134.867 ppm in ^{13}CNMR.

Spot (7) shows a close correlation between the proton observed at 7.64 ppm (H-C7) in proton NMR and the carbon C7 absorbs at 132.651 in ^{13}CNMR.

Spot (8) shows the correlation between the proton observed at 8.03 ppm (C8-H) in proton NMR and the carbon observed at 126.967 ppm in ^{13}C NMR.
Spot (13) show the correlation between the proton i.e. observed at 7.07 ppm (C13-H) in proton NMR and the carbon observed at 126.596 ppm in carbon NMR.
Spot (14) shows the correlation between the protons observed at (C14-H) at 7.00 ppm which corresponds to the carbon absorbing at 127.203 ppm.
Spot (15) shows the correlation between the protons i.e. observed as a singlet for (C15-H) at 7.29 ppm which corresponds to the carbon absorbing at 125.913 ppm.

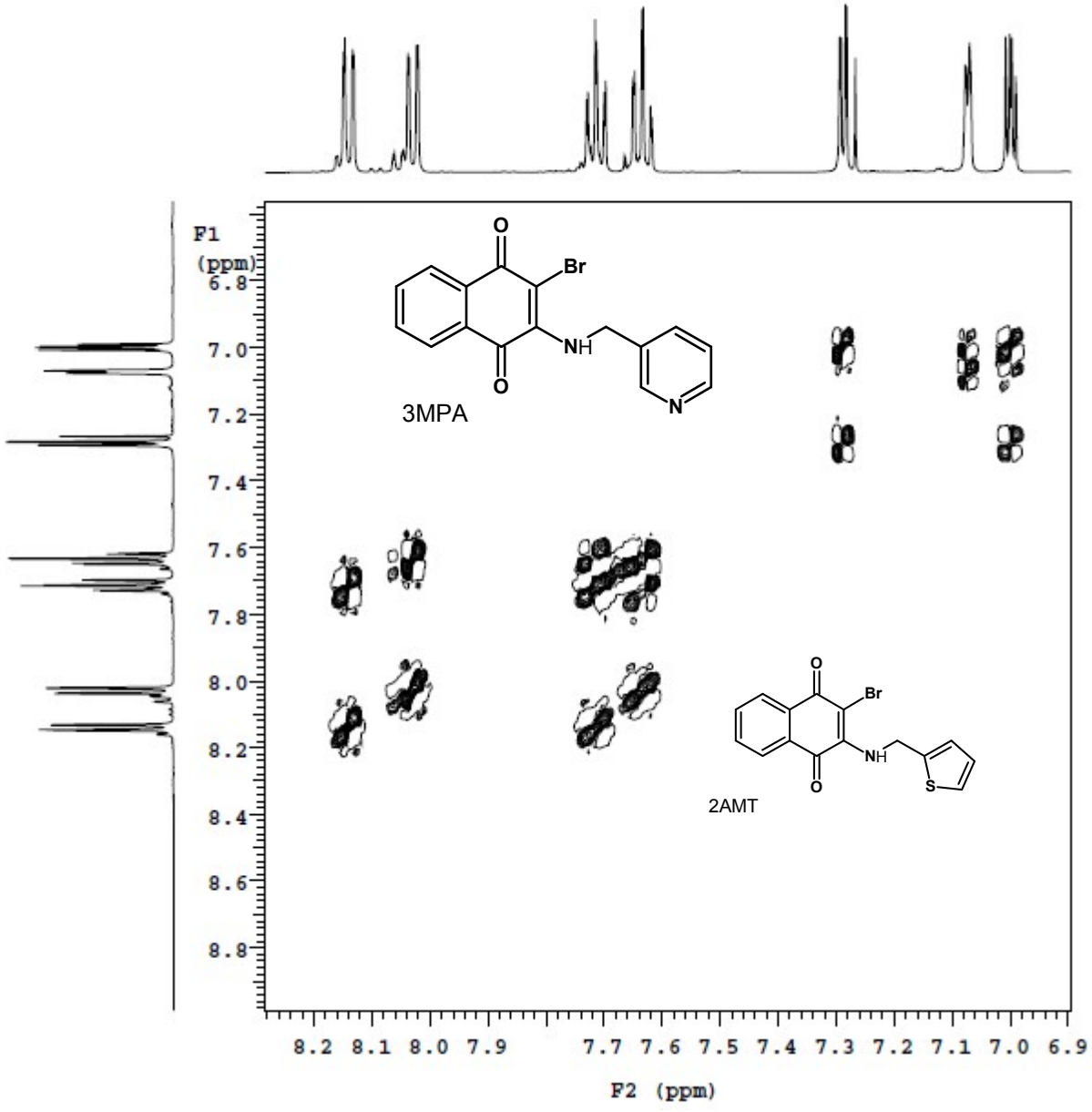


Fig.S5g gDQCOSY NMR spectrum of 2AMT in $CDCl_3$ showing homonuclear correlation between protons

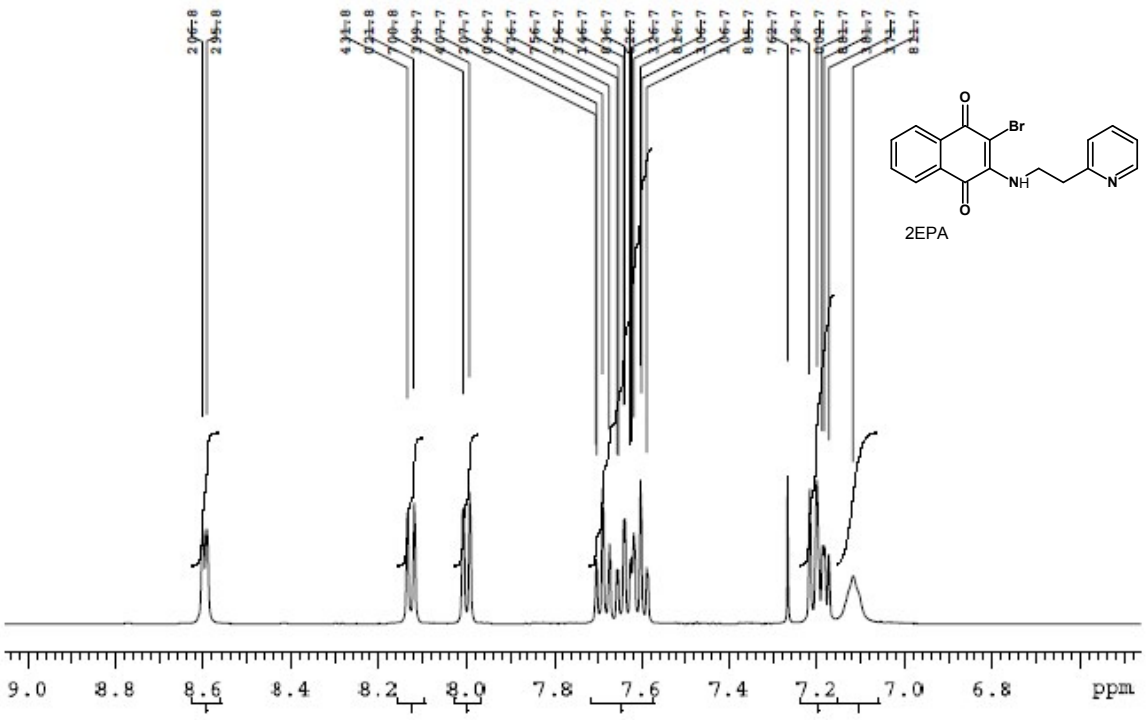


Fig.S6a ^{1}HNMR spectrum of 2EPA (6.6-9.0 ppm) in $CDCl_3$

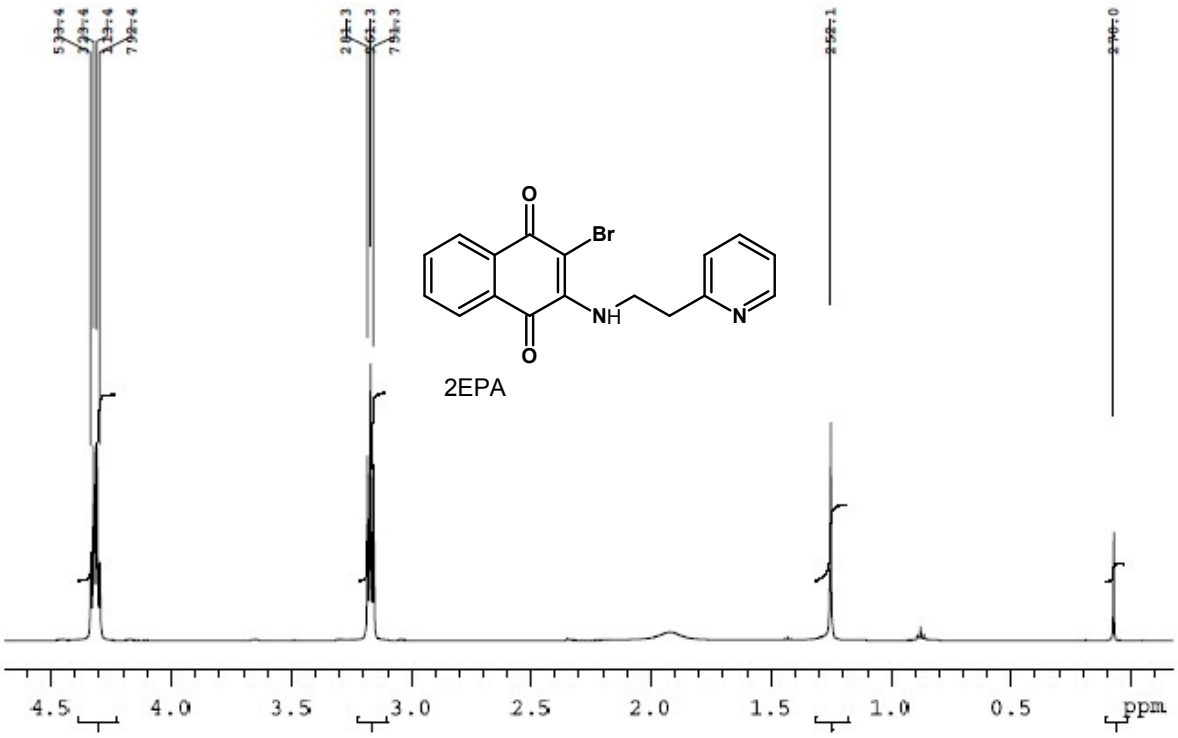


Fig.S6b ^{1}HNMR spectrum of 2EPA (0.0 – 4.5 ppm) in $CDCl_3$

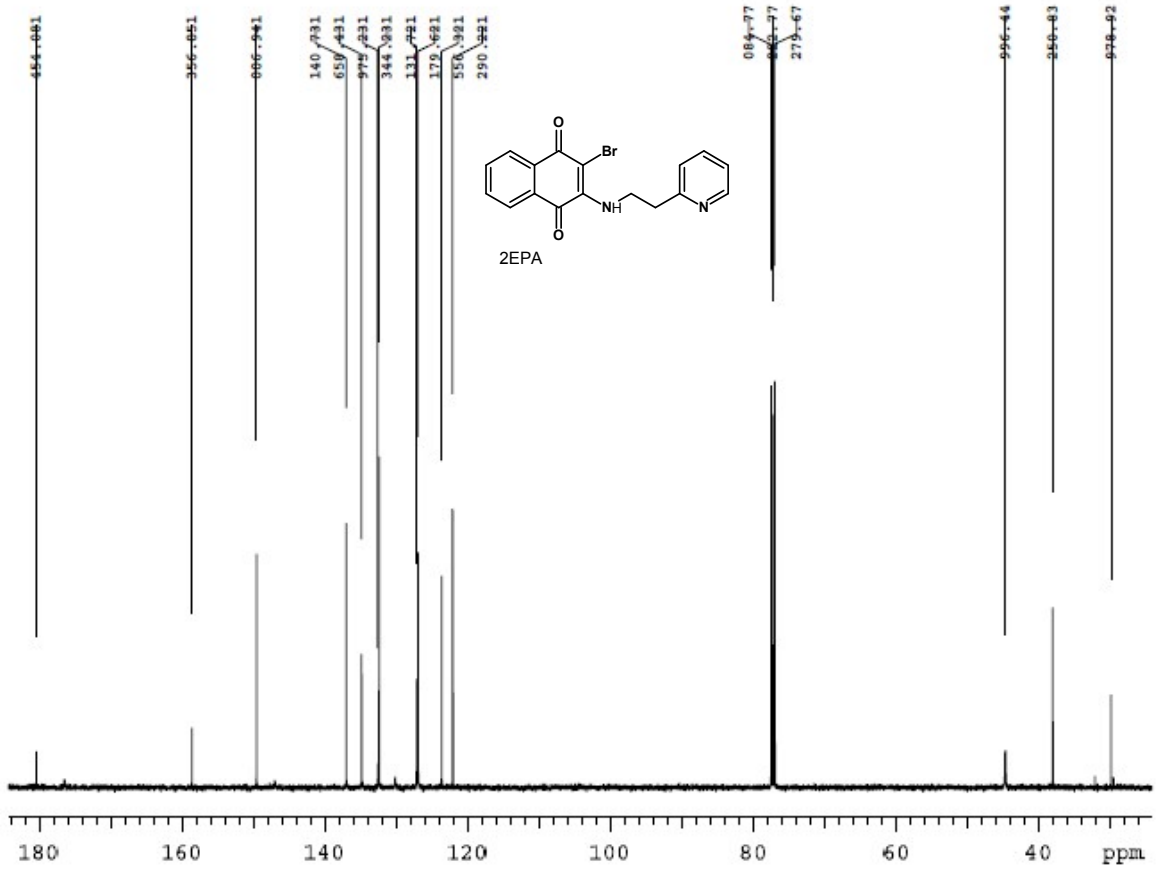


Fig.S6c ^{13}CNMR spectrum of 2EPA in $CDCl_3$

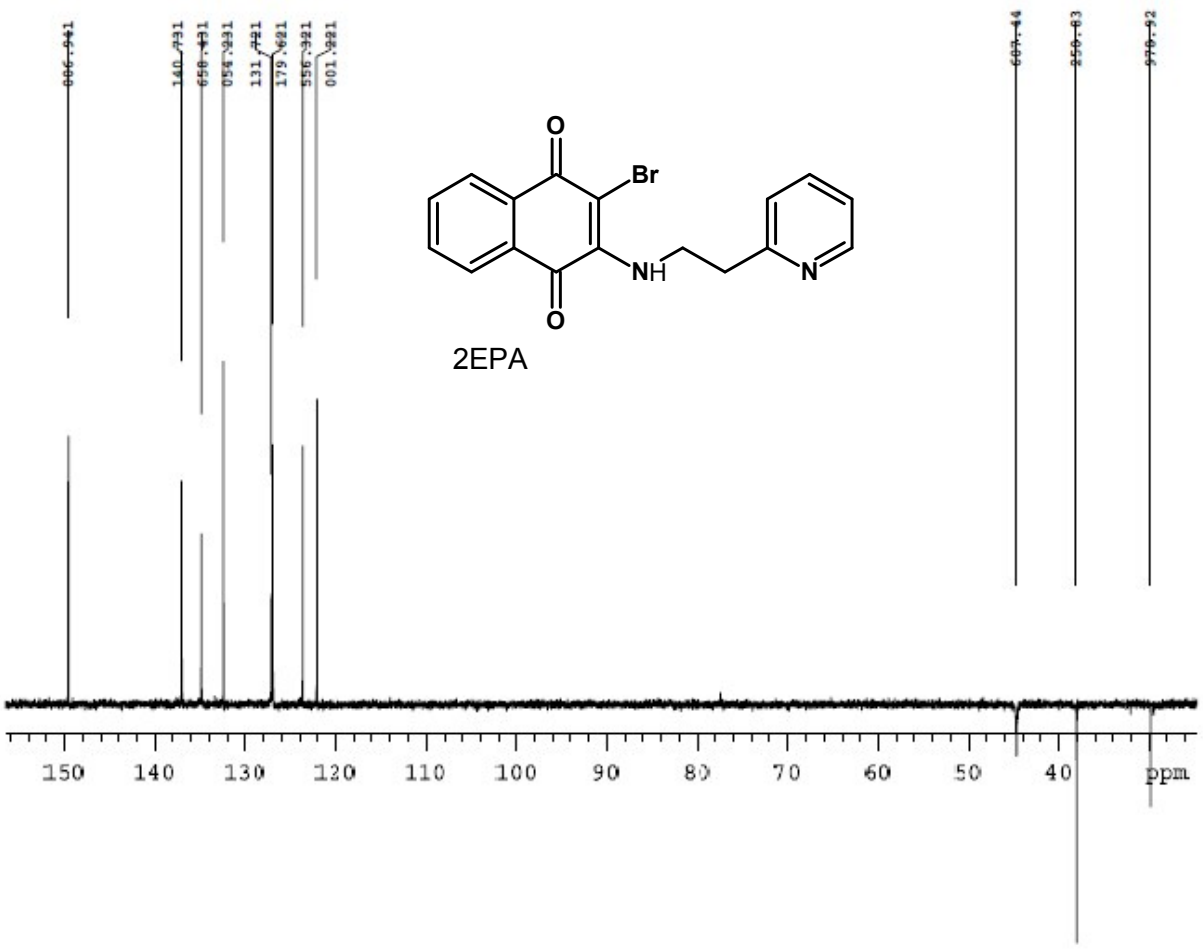


Fig.S6d DEPT NMR spectrum of 2EPA in $CDCl_3$

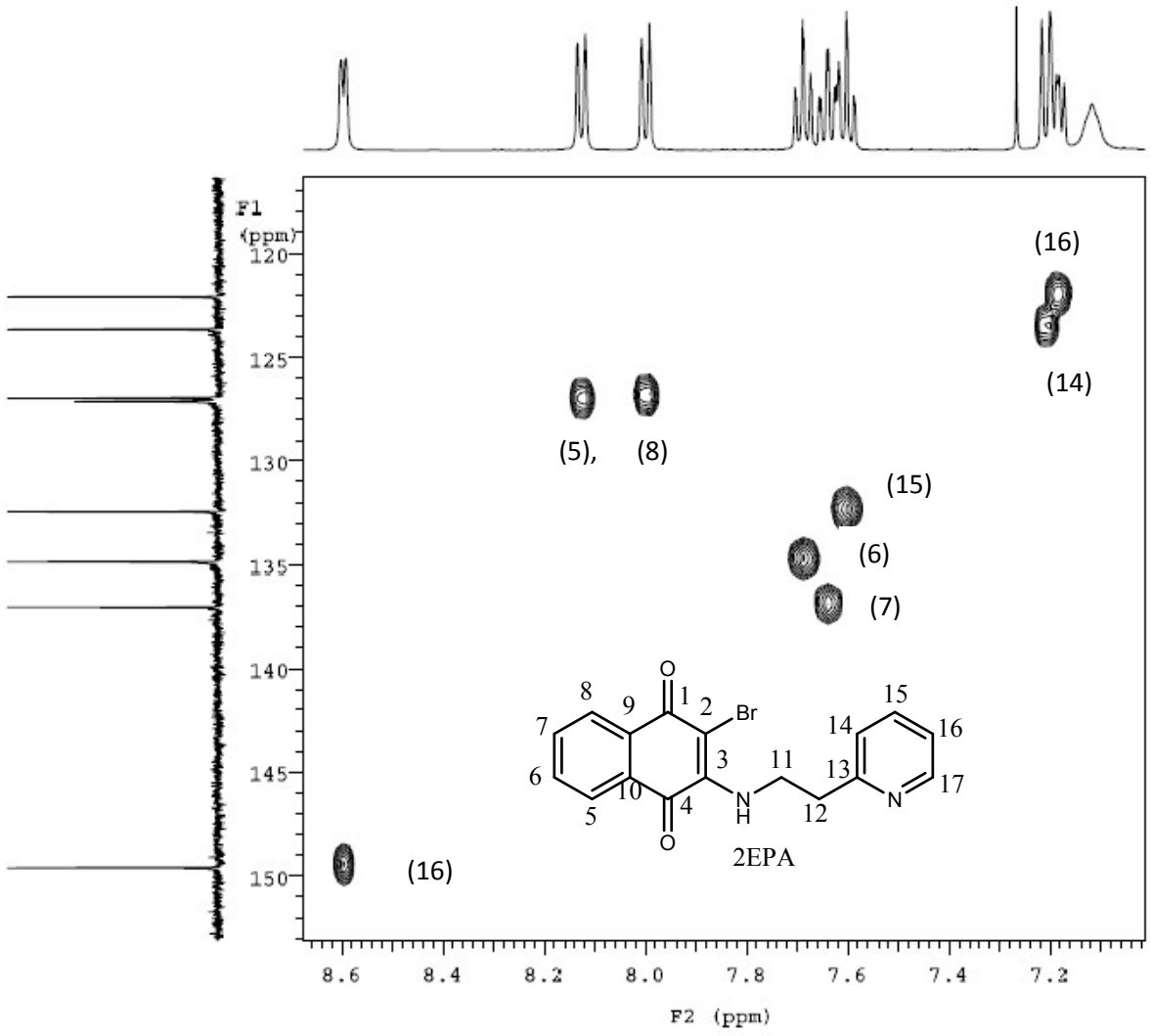


Fig.S6e gHSQCAD NMR spectrum of 2EPA in $CDCl_3$ showing the correlation between the Carbon and Proton.

Interpretation of the 2D gHSQCAD NMR of 2EPA-

Spots (5) show the correlation between the proton observed at 8.13 ppm (H-C5) and the carbons C5 which absorb at 127.131 ppm in ^{13}CNMR. Hence it is inferred from the 2D spectrum that this proton is attached to the carbons C5.

(8) Show the correlation between the protons i.e. observed at 8.00 ppm and the carbon C8 which absorb at 126.971 ppm in ^{13}CNMR. Hence it is inferred from the 2D spectrum that this proton is attached to the carbon C8.

Spot (6) shows correlation between the proton observed at 7.69 ppm (H-C6) in proton NMR and the carbons C6 absorbs at 134.856 in carbon NMR.

Spot (7) shows correlation between the proton observed at 7.64 ppm (H-C7) in proton NMR and the carbons C7 absorbs at 137.041 ppm in carbon NMR. Both C6 and C7 absorb closely with

C15 which appears at 7.60 ppm and corresponds to a carbon absorbing at 132.443 ppm in ^{13}C NMR.

Spot (14) and (16) show close correlation between protons appearing at 7.21 and 7.18 ppm respectively which correspond to the carbons absorbing at 123.655 and 122.092 ppm.

Spot (17) shows the correlation between the proton observed as a doublet at 8.59 ppm (C17-H) in proton NMR and the carbon observed at 149.660 ppm in carbon NMR.

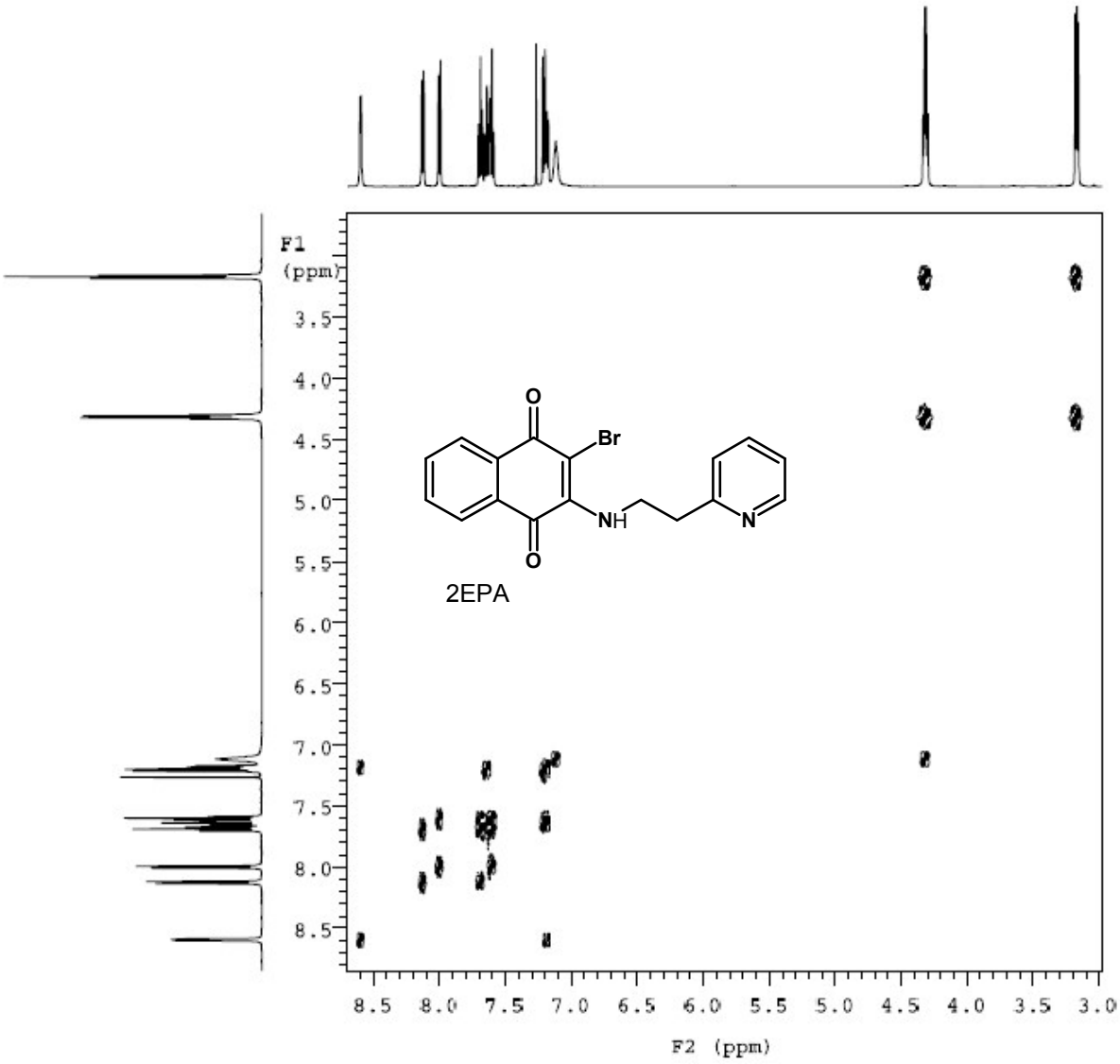


Fig.S6f gDQCOSY NMR spectrum of 2EPA in $CDCl_3$ showing the homonuclear correlation between protons

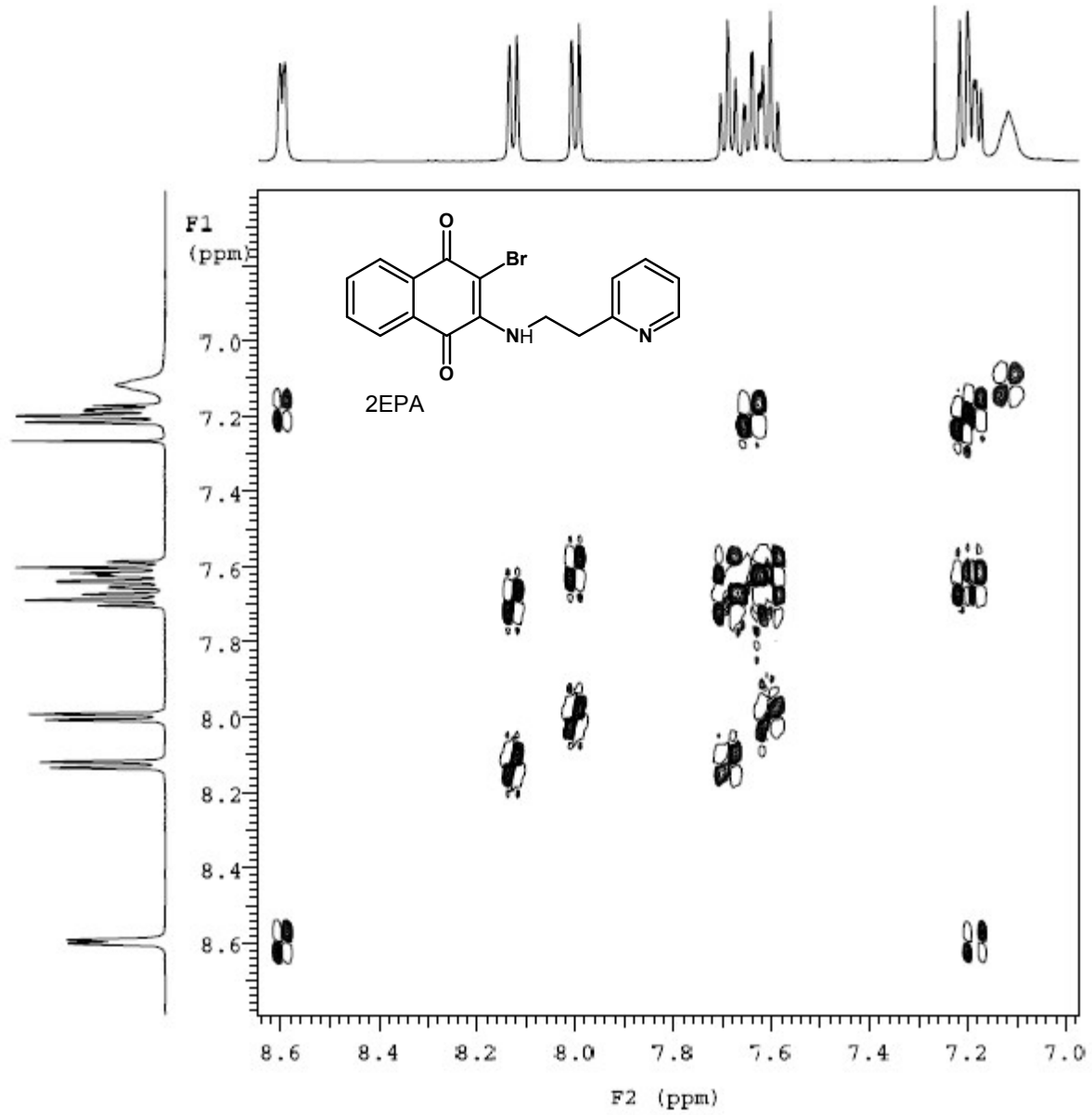


Fig.S6g Magnified View of gDQCOSY NMR spectrum of 2EPA in $CDCl_3$

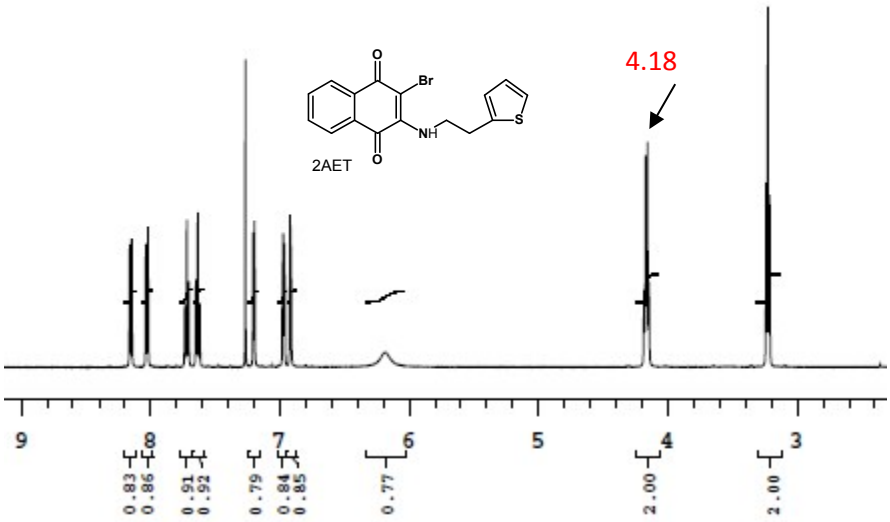


Fig.S7a ^{1}HNMR spectrum of 2AET in $CDCl_3$ (3.0-9.0 ppm)

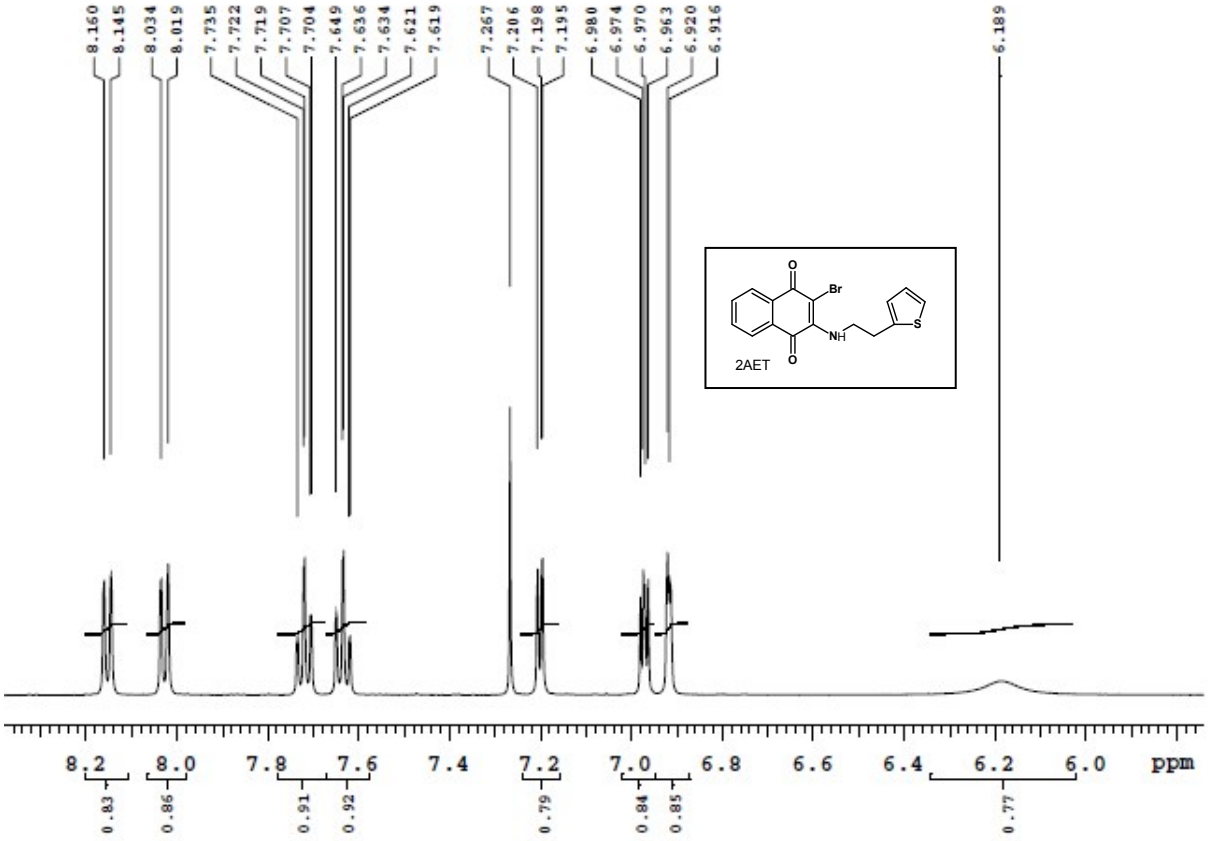


Fig S7b ^{1}HNMR spectrum of 2AET in $CDCl_3$ (6.0-8.5 ppm)

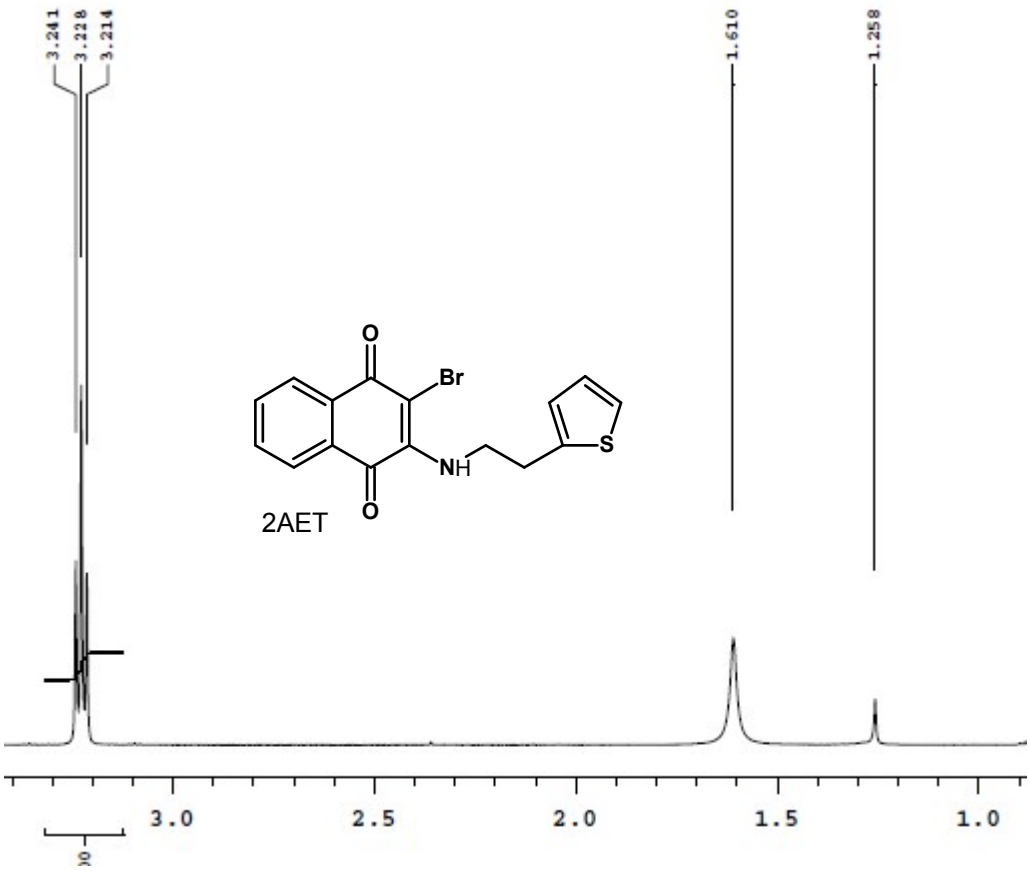


Fig.S7c ^{1}HNMR spectrum of 2AET in $CDCl_3$ (1.0-3.5 ppm)

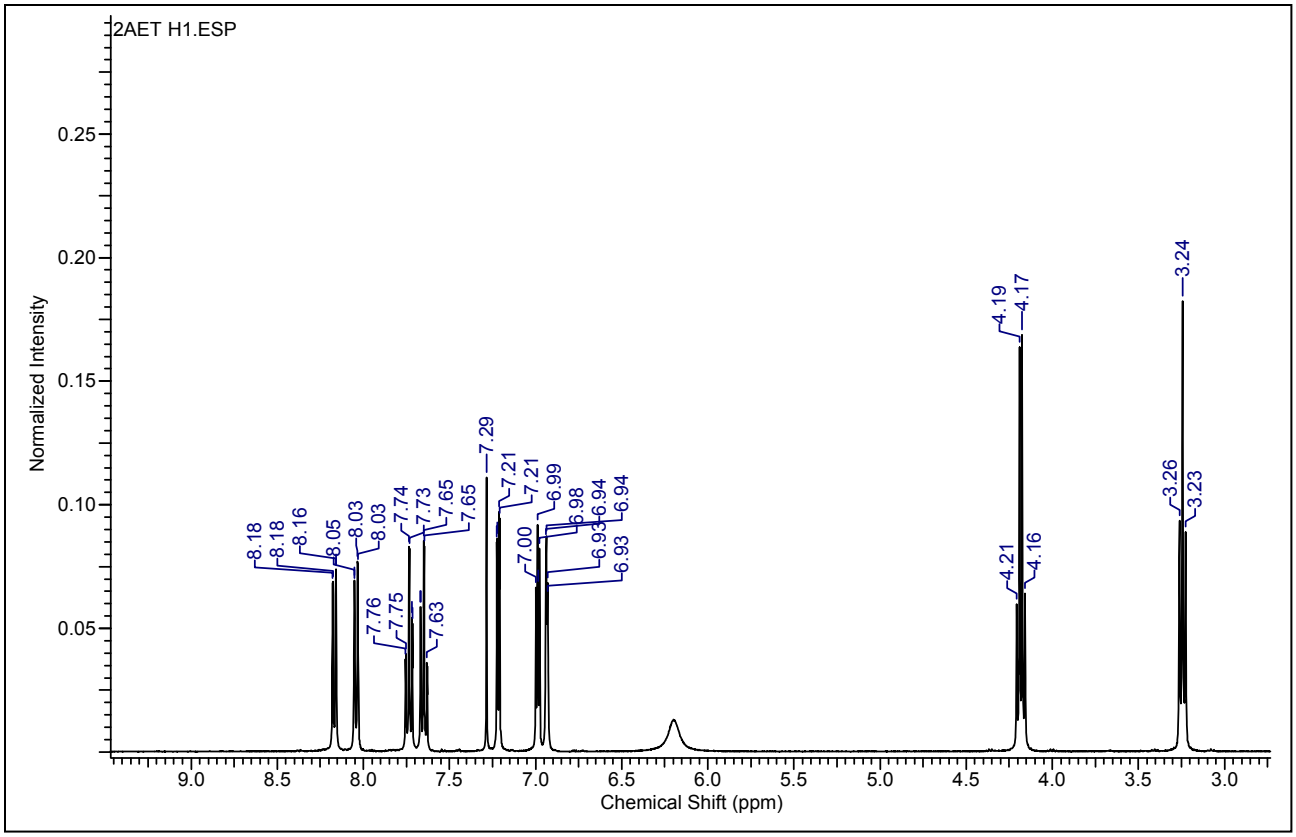


Fig.S7d Another ^{1}HNMR spectrum of 2AET in $CDCl_3$ (3.0-9.0 ppm)

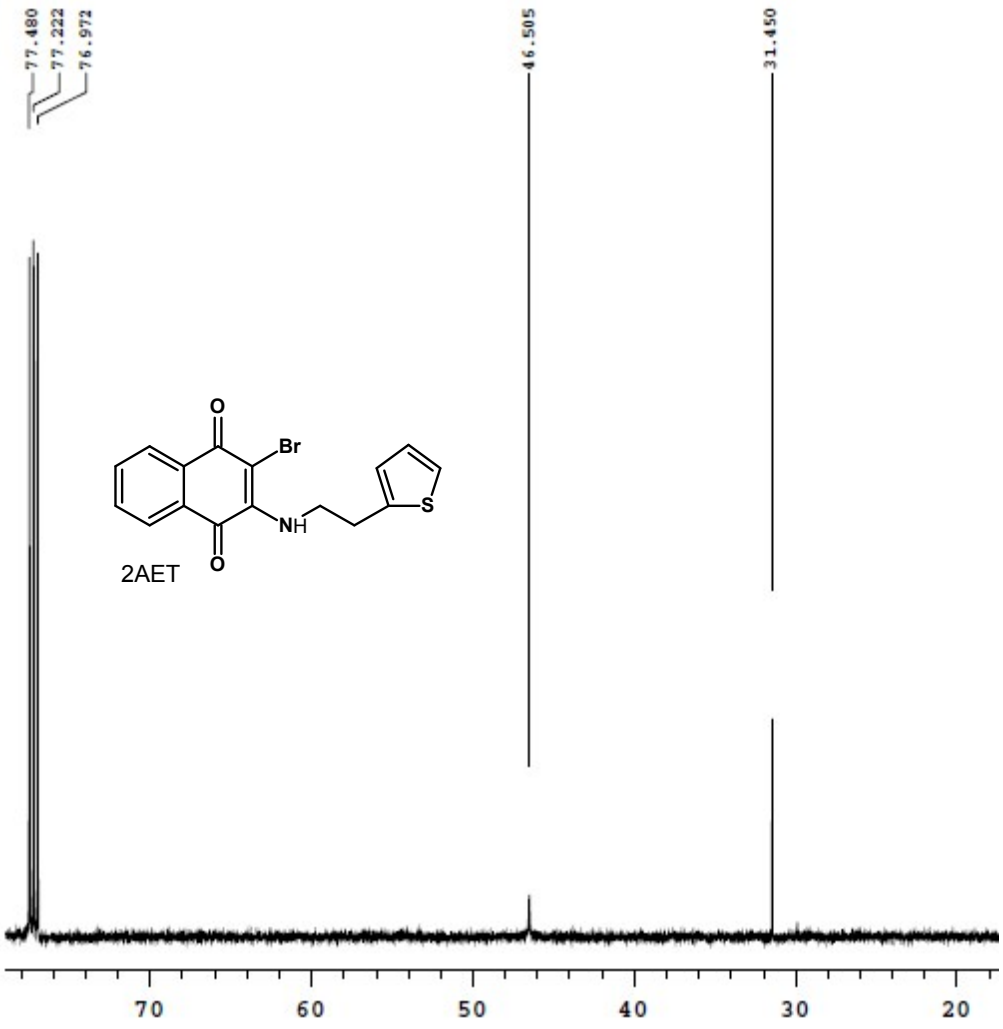


Fig S7e ^{13}CNMR spectrum of 2AET in $CDCl_3$ (20-80 ppm)

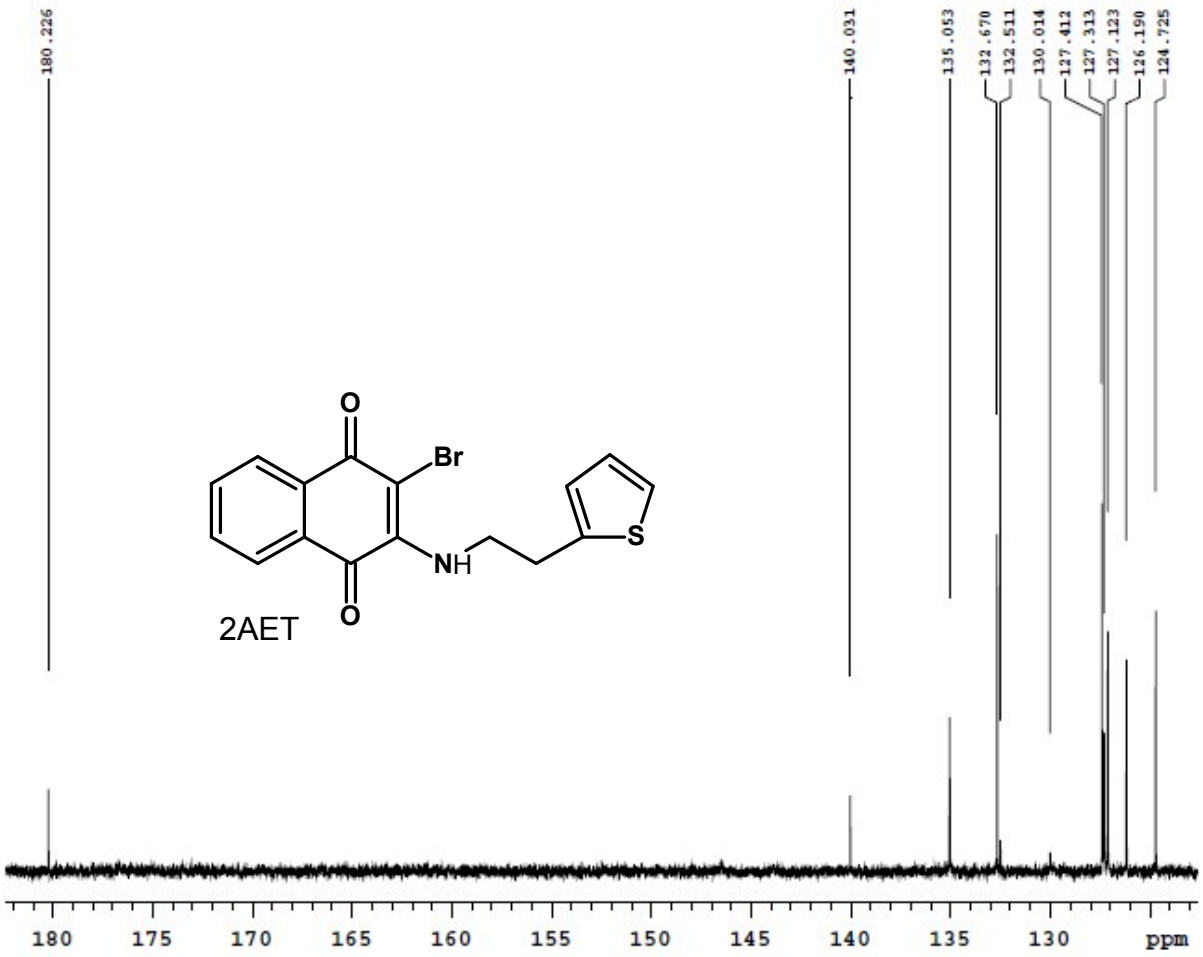


Fig.S7f ^{13}CNMR spectrum of 2AET in $CDCl_3$ (123-180 ppm)

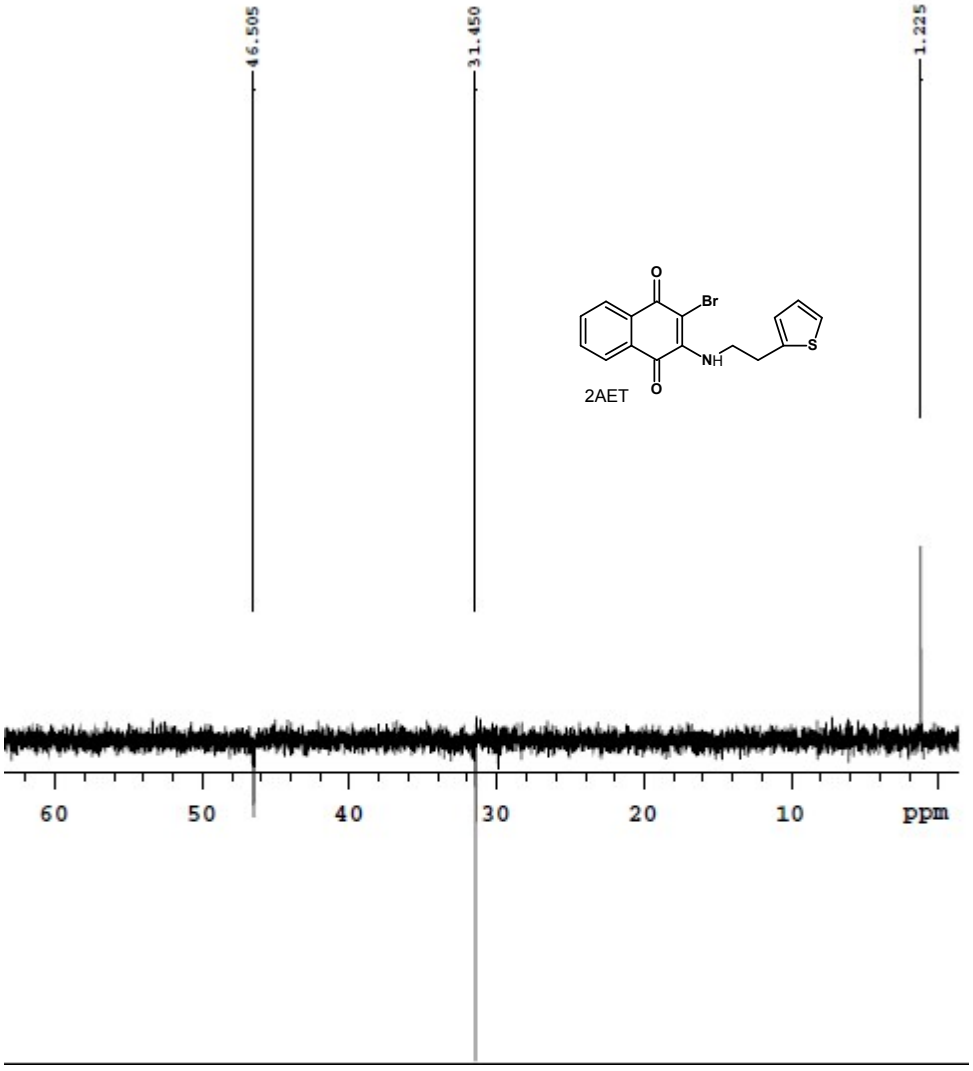


Fig.S7g DEPT NMR spectrum of 2AET in $CDCl_3$ (0-60 ppm)

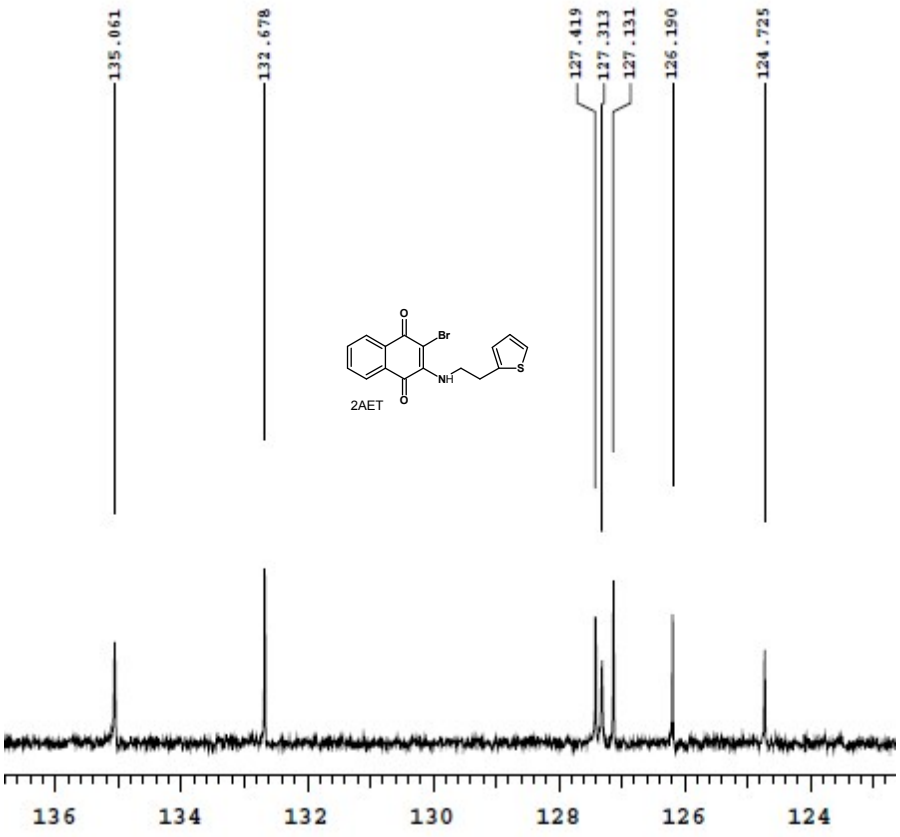


Fig.S7h DEPT NMR spectrum of 2AET in $CDCl_3$ (124-136 ppm)

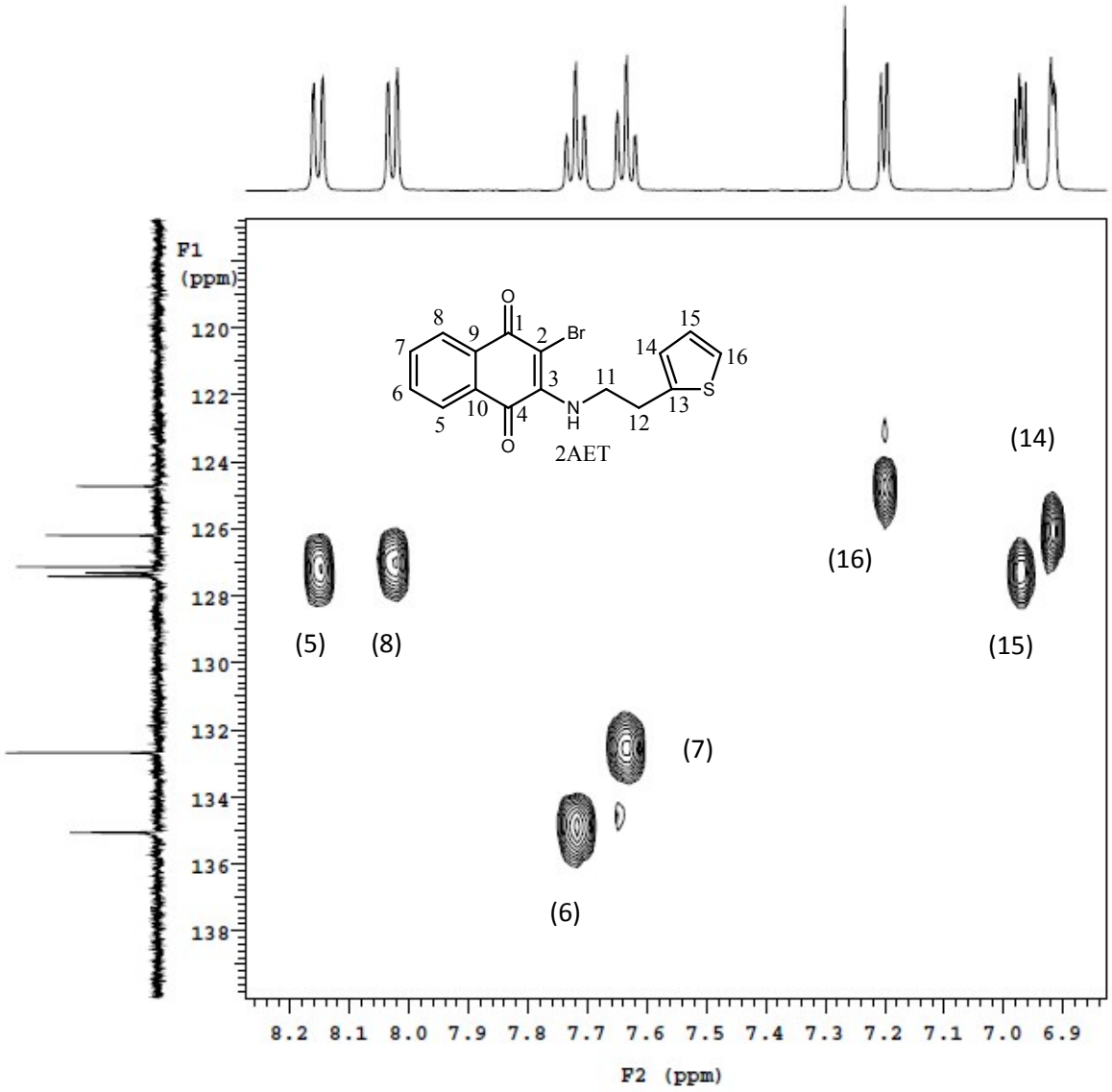


Fig.S7i gHSQCAD NMR spectrum of 2AET in $CDCl_3$ showing correlation between carbons and protons

Interpretation of the 2DgHSQCAD Spectrum of 2AET

Spot (5) shows the correlation between the proton observed at 8.15 ppm (H-C5) and the carbon C5 which absorb at 127.313 ppm in ^{13}CNMR. Hence it is inferred from the 2D spectrum that this proton is attached to the carbons C5 .

Spot (6) shows the correlation between the proton i.e. observed at 7.72 ppm and the carbon C6 which absorb at 135.053 ppm in ^{13}CNMR.

Spot (7) shows a close correlation between the proton observed at 7.63 ppm (H-C7) in proton NMR and the carbon C7 absorbs at 132.670 in ^{13}CNMR.

Spot (8) shows the correlation between the proton observed at 8.02 ppm (C8-H) in proton NMR and the carbon observed at 127.123 ppm in ^{13}C NMR.

Spot (14) shows the correlation between the proton i.e. observed at 6.92 ppm (C14-H) in proton NMR and the carbon observed at 126.190 ppm in carbon NMR.
Spot (15) shows the correlation between the protons observed at (C15-H) at 6.97 ppm which corresponds to the carbon absorbing at 127.412 ppm.
Spot (16) shows the correlation between the protons i.e. observed as a singlet for (C16-H) at 7.20 ppm which corresponds to the carbon absorbing at 124.725 ppm.

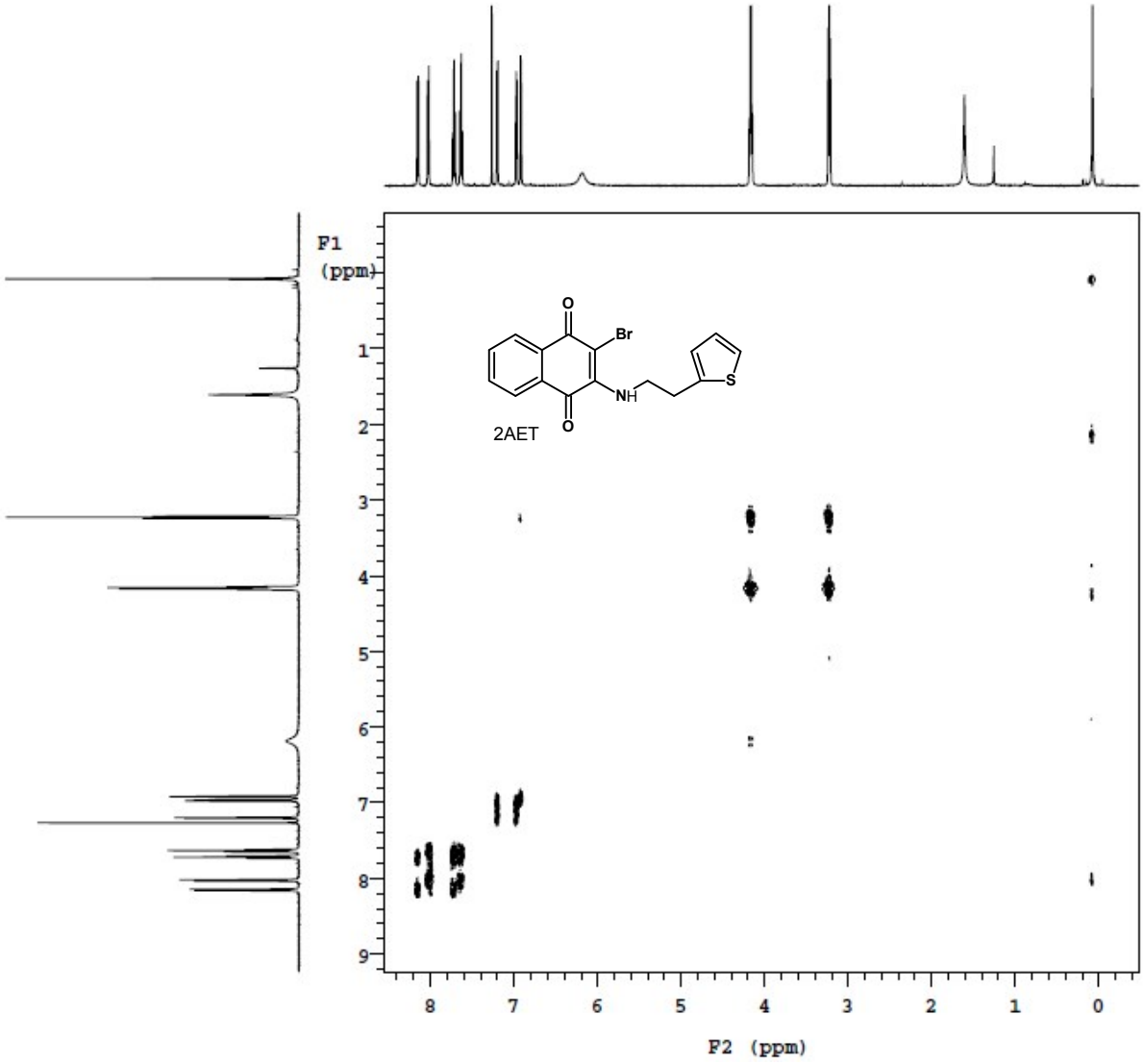


Fig.S7j gDQCOSY NMR spectrum of 2AET in $CDCl_3$ showing homonuclear correlation between protons

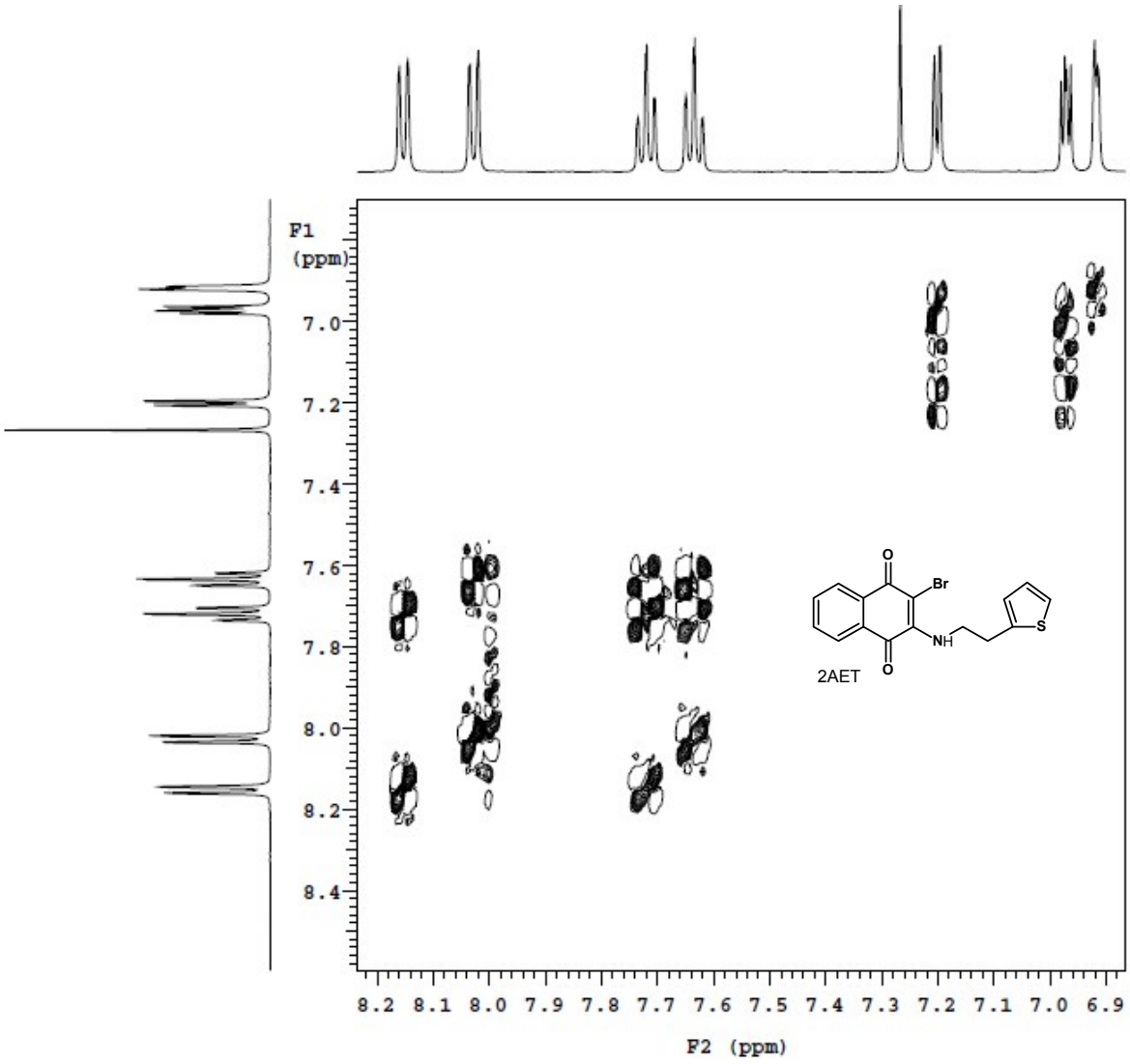


Fig.S7k Magnified view of the gDQCOSY NMR spectrum of 2AET in $CDCl_3$

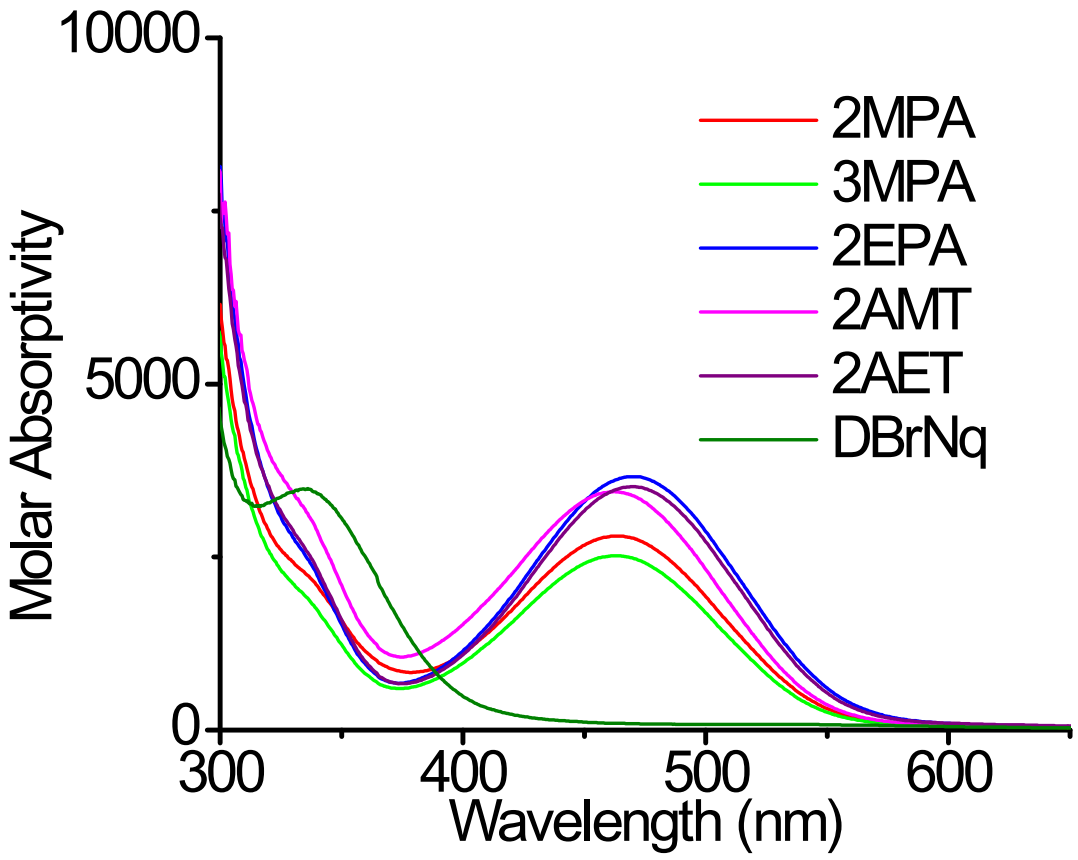


Fig.S8 UV-visible spectra of aminonaphthoquinones in DMSO

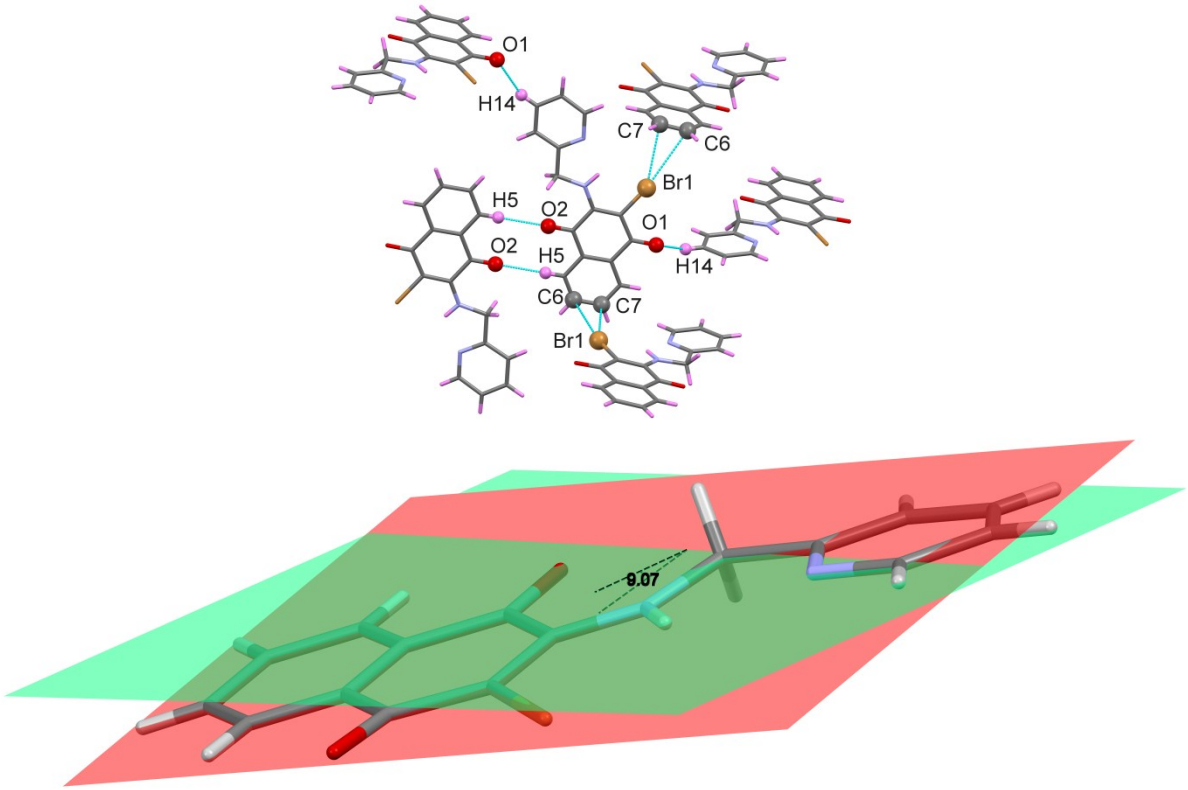
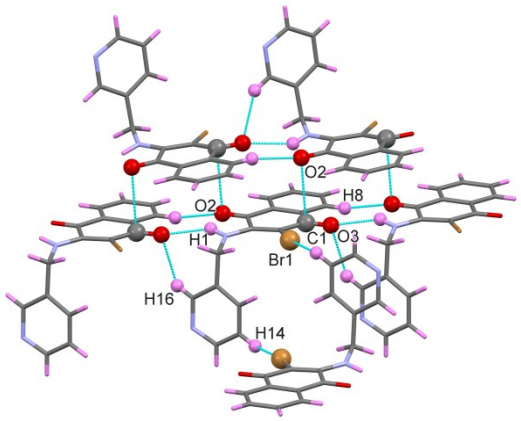
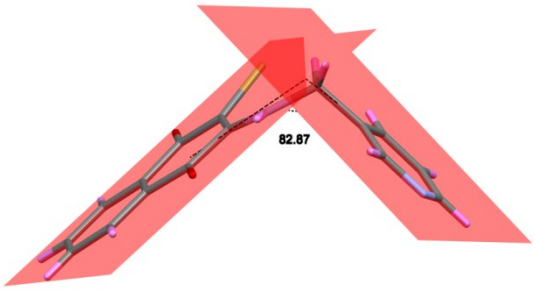


Fig.S9 a) Neighboring molecules of 2MPA, b) The planes of naphthoquinone ring and the pyridyl ring of 2MPA

a)



b)



c)

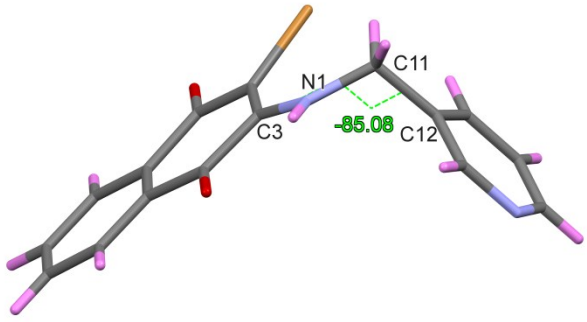
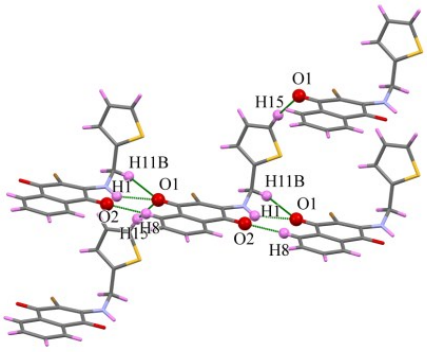


Fig.S10 3a) Neigboring molecules of 3MPA, b) Planes of naphthoquinone ring with pyridyl ring, c) Torsion angle of 3MPA

a)



b)

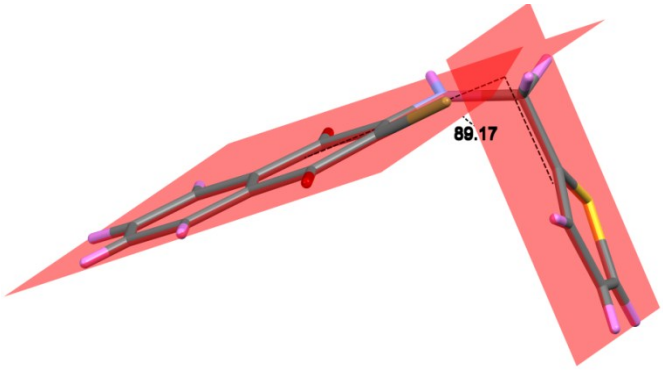


Fig.S11 a) Neighboring molecules of 2AMT, b) The planes of naphthoquinone ring and the pyridyl ring of 2AMT

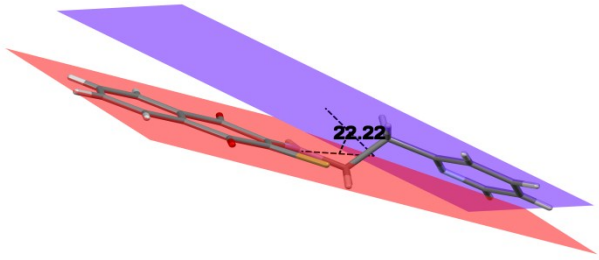
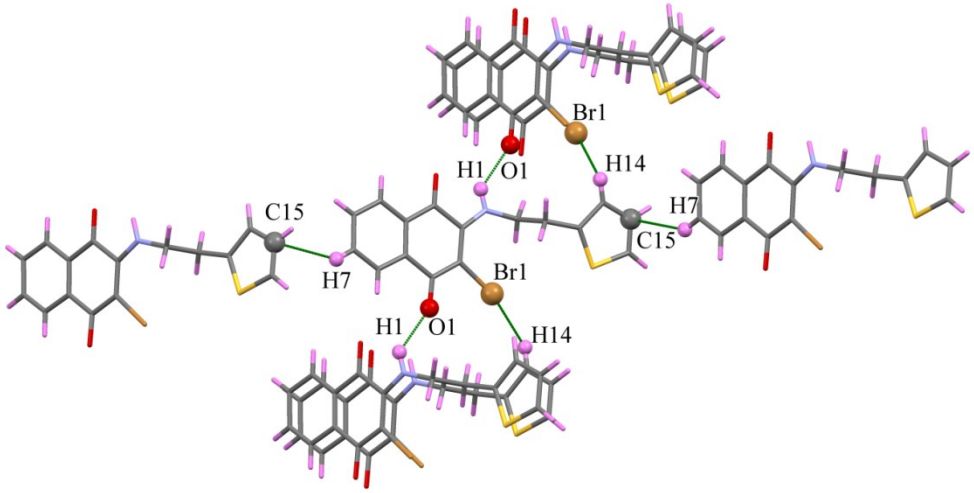


Fig.S12 The planes of naphthoquinone ring and the pyridyl ring of 2EPA

a)



b)

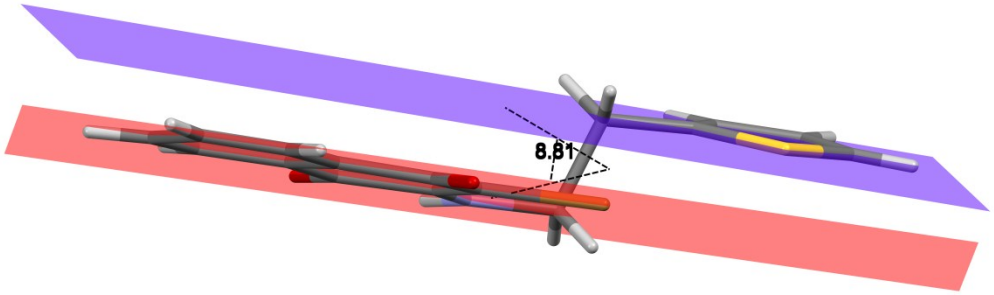


Fig.S13 a) Neighbouring contacts of 2AET molecules, b) The planes of naphthoquinone ring and the pyridyl ring of 2AET

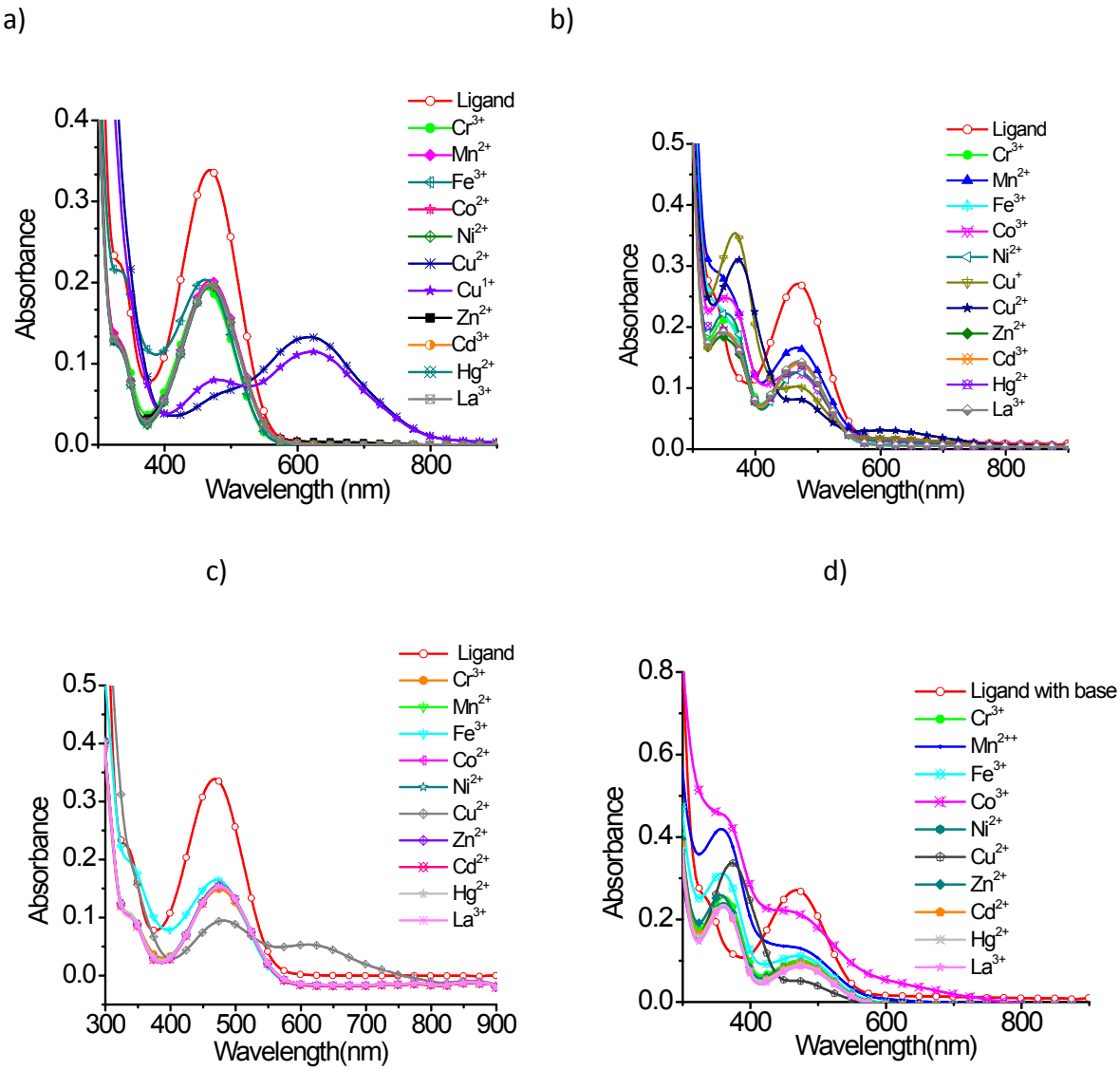


Fig.S14 UV-Visible spectra of a)2EPA (10^{-4} M) with metal ions (10^{-4} M) in methanol, b) In methanol and triethylamine, c) 2EPA in methanol and with metal ions (10^{-4} M) in water, d) 2EPA in methanol and with metal ions (10^{-4} M) in water and triethylamine

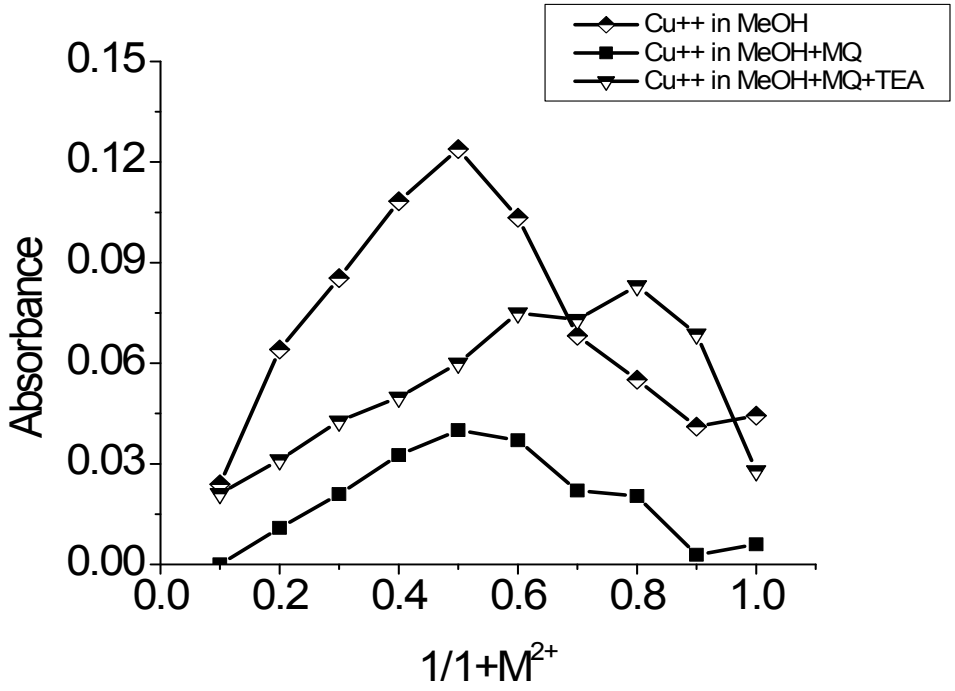


Fig.S15 Job plots obtained for 2MPA with Cu^{2+} ions in methanol, methanol-water, and methanol-water-triethylamine

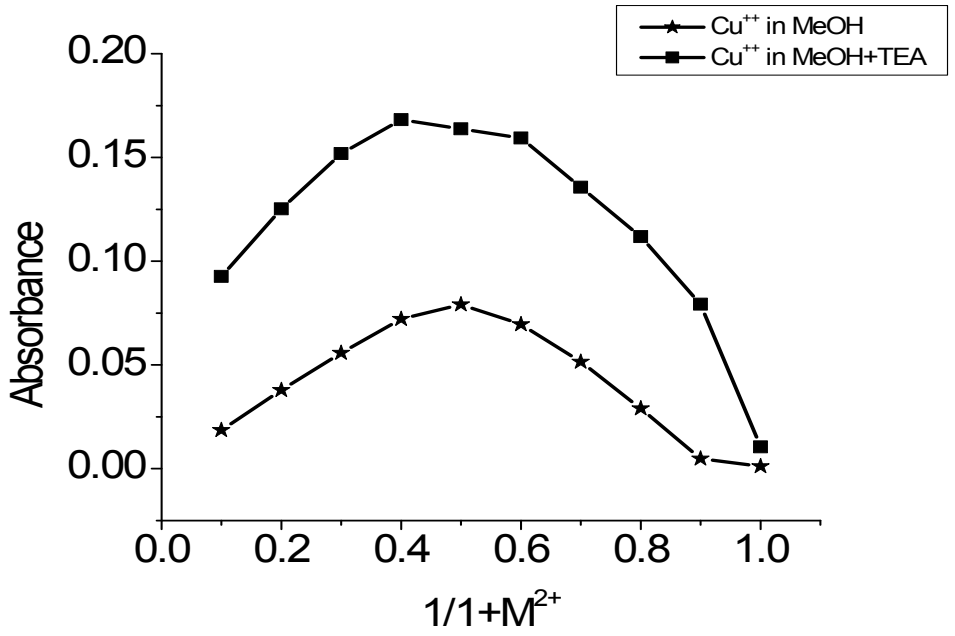


Fig.S16 Job plots obtained for 2EPA with Cu^{2+} ions in methanol and methanol-triethylamine

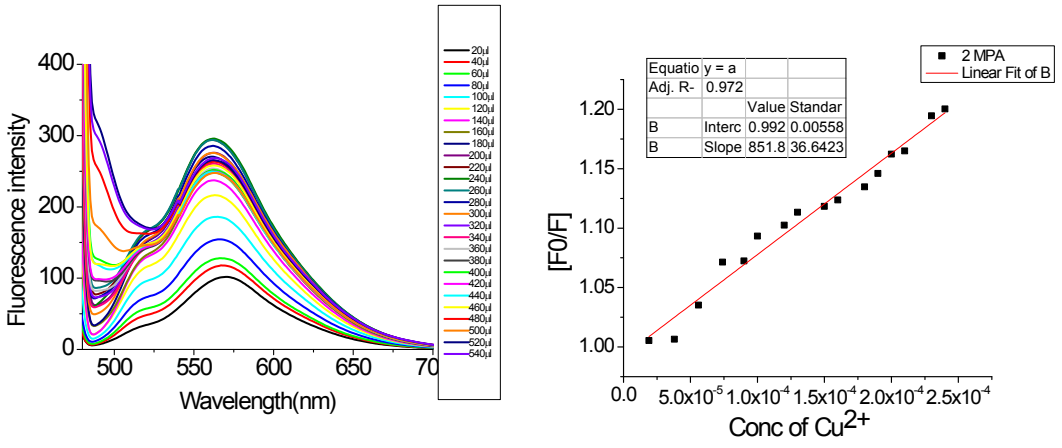


Fig.S17 Fluorescence spectra of binding constant of Cu^{2+} ion with 2MPA

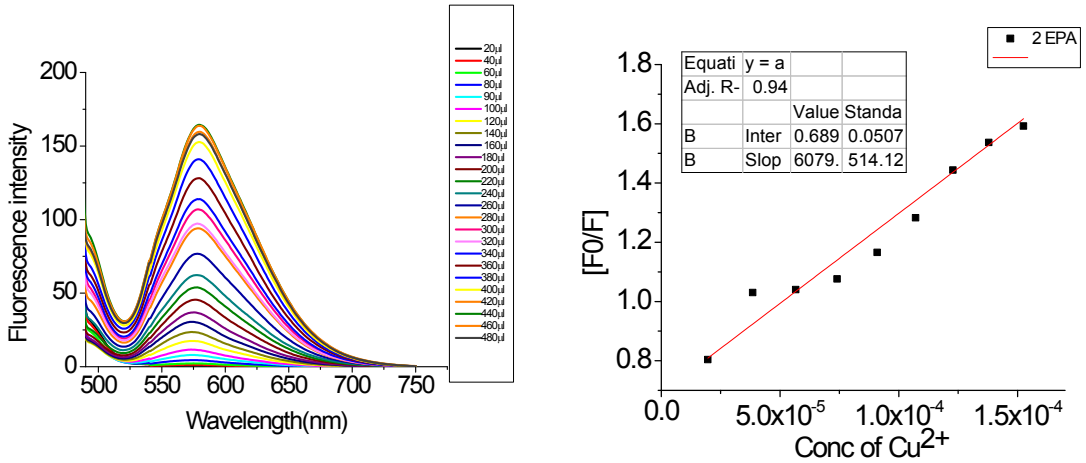
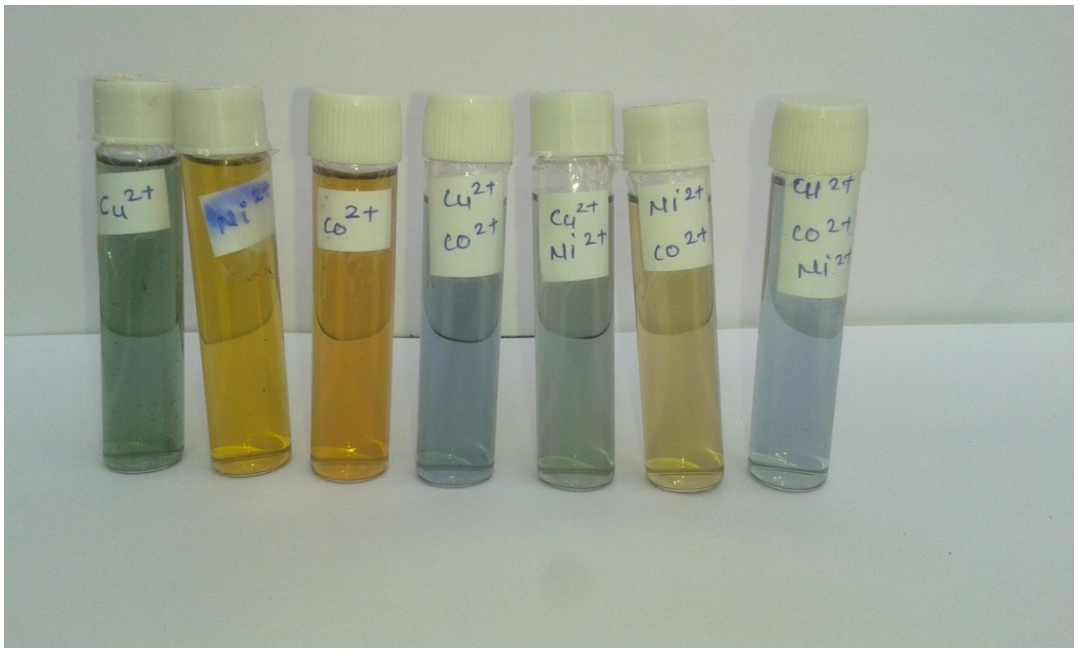


Fig.S18 Fluorescence spectra of binding constant of Cu^{2+} ion with 2EPA

a)



b)

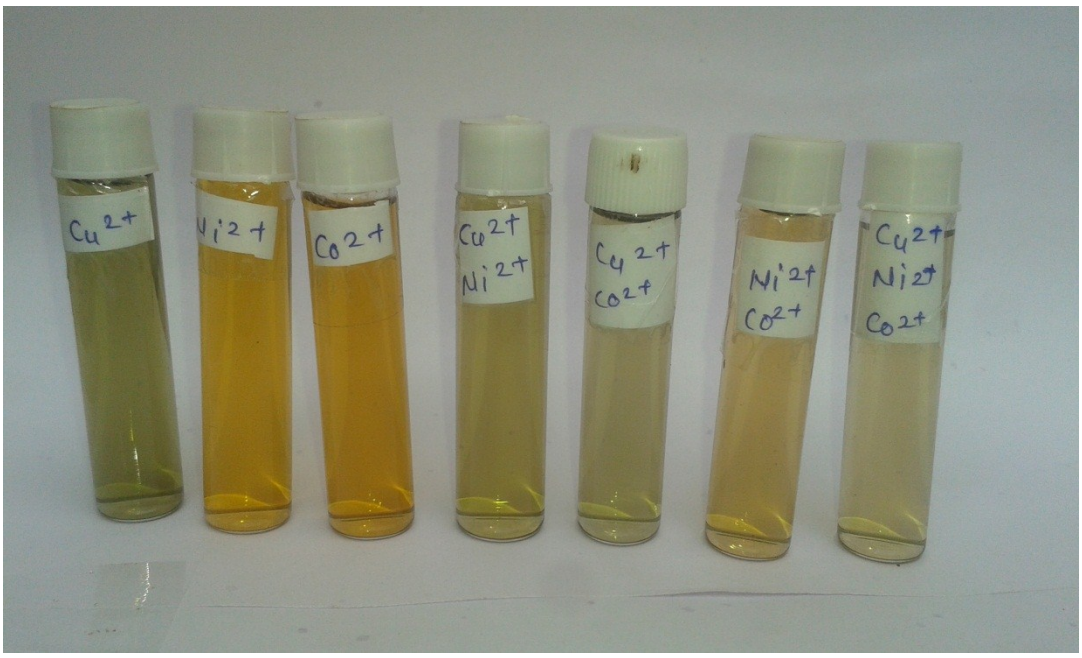


Fig.S19 Colour changes observed to a) 2MPA and b) 2EPA and metal ion ($5*10^{-4}$M) in methanol

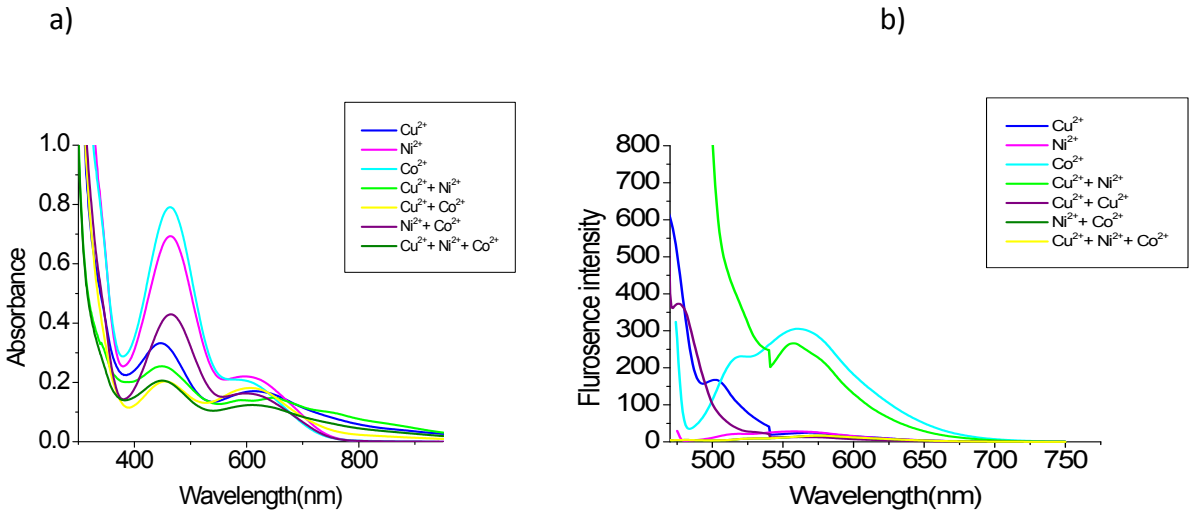


Fig.S20 UV-visible of competitive binding of selected metal ions with 2MPA in methanol a) Absorption spectra, b) fluorescence spectra

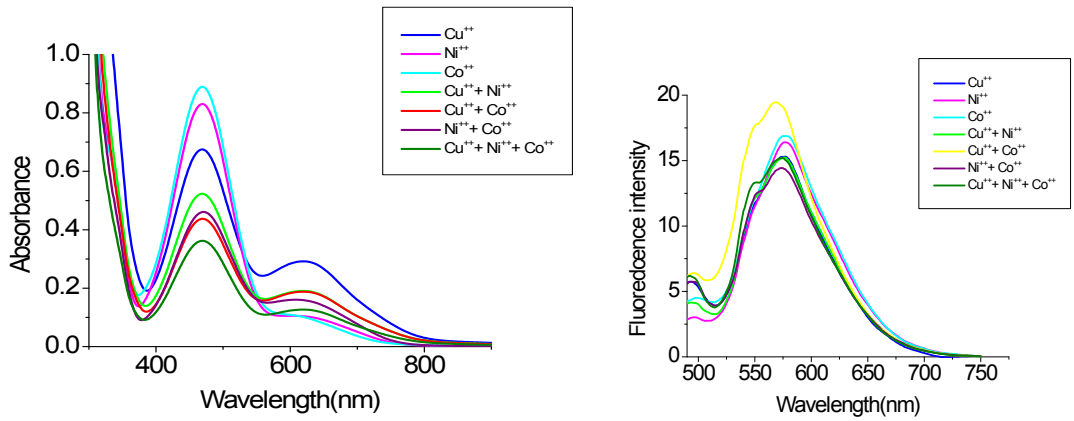


Fig.S21 UV-visible of competitive binding of selected metal ions with 2MPA in methanol a) absorption spectra, b) fluorescence spectra

Table S1a FT- IR Frequencies for 2MPA, 3MPA, 2EPA, 2AMT, 2AET

Ligand	ν_{N-H}	$\nu_{C=O}$	ν_{C-N}	ν_{p-Nq}	ν_{C-Br}	ν_{C-HAr}	Ring stretching ($\nu_{C=C,}\nu_{C=N,}$ $\nu_{C=S)}$
2MPA	3242	1680	1600	1292, 1249	638	3061,3012	1564,1492, 1435
3MPA	3267	1683	1593	1300, 1246	643	3076, 3022	1564, 1512, 1473
2EPA	3321	1672	1610	1296, 1257	653	3061,3003	1572, 1525, 1446
2AMT	3284	1685	1595	1300, 1244	623	3082, 3012	1570, 1510, 1431
2AET	3263	1678	1577	1300, 1259	686	3068,2960	1577, 1539, 1442

Table S1b FT- IR Frequencies for 2MPA, 3MPA, 2EPA, 2AMT, 2AET

Ligand	ν_{N-H}	ν_{C-HAr}	$\nu_{C=O}$	ν_{C-N}	($\nu_{C=C,}$)	ν_{p-Nq}	ν_{C-Br}
DBrNQ			1676				627
2MPA	3242	3061,3012	1680	1600	1599 1564	1249	638
3MPA	3267	3076, 3022	1683	1593	1564	1246	643
2AMT	3284	3082, 3012	1685	1595	1570	1244	623
2EPA	3321	3061,3003	1672	1610	1572	1257	653
2AET	3263	3068,2960	1678	1577	1577	1259	686

Table S2 Chemical Shift (δ) in ppm and Coupling constant *J* in Hz for 2MPA, 3MPA, 2EPA, 2AMT, 2AET

H bearing Carbon No.	2MPA δ(ppm) and *J*(Hz)	3MPA δ(ppm) and *J*(Hz)	2AMT δ(ppm) and *J*(Hz)	2EPA δ(ppm) and *J*(Hz)	2AET δ(ppm) and *J*(Hz)
H-C5	8.16(d),7.50	8.12(d),7.50	8.14(d), 7.50	8.13 (d), 7.00	8.15(d), 7.50
H-C6	7.72(m)	7.70(m),	7.72(t) 7.74	7.69(t),7.25	7.72(t),7.50
H-C7	7.72(m)	7.70(m),	7.64(t), 7.50	7.64(t), 7.75	7.63(t), 7.25
H-C8	8.06(d),7.50	8.01(d), 8.00	8.03(d), 7.00	8.00(d), 7.00	8.02(d), 7.50
H-C11	5.21(d), 5.00	5.11(d),6.50	5.25(s)	4.32(q), 6.33	4.18(q), 6.66
H-C12	-	-	-	3.17(t), 3.75	3.23(t), 6.25
H-C13	7.30(d), 8.00	7.64(t),8.00	7.07(d), 3.00	-	-
H-C14	7.64 (t), 7.50	7.33(t), 6.50	7.00(t), 4.25	7.21(d),8.49	6.92(d), 4.99
H-C15	7.27(t), 6.25	8.57(d), 4.50	7.29 (d), 5.00	7.60(t), 7.50	6.97(t), 4.25
H-C16	8.65(d), 4.50	8.62 (s)	-	7.18(d), 3.75	7.20(d), 4.99
H-C17	-	-	-	8.59(d), 5.00	-
N-H	7.91	6.28	6.10	7.12	6.18

Table S3 Chemical Shift (δ) in ppm in ^{13}C-NMR for 2MPA, 3MPA, 2EPA, 2AMT, 2AET

Carbon No.	2MPA δ(ppm)	3MPA δ(ppm)	2AMT δ(ppm)	2EPA δ(ppm)	2AET δ(ppm)
C1	176.680	176.753	176.200	176.200	176.600
C2	128.240	126.943	126.740	-	overlapped
C3	146.200	146.362	146.000	146.500	146.500
C4	180.537	180.084	180.000	180.454	180.226
C5	127.020	127.371	127.096	127.131	127.313
C6	134.894	135.119	134.867	134.856	135.053
C7	137.109	135.571	132.651	137.041	132.670
C8	127.154	127.209	126.967	126.971	127.123
C9	132.541	132.278	132.158	132.579	132.511
C10	130.000	129.986	129.859	130.200	130.014
C11	49,214	48.727	44.057	44.699	46.505
C12	155.215	133.985	140.100	38.052	31.450
C13	121.971	132.908	126.596	158.653	140.031
C14	132.154	124.067	127.203	123.655	126.190
C15	122.874	149.435	125.913	132.443	127.412
C16	149.182	149.162	-	122.092	124.725
C17	-	-	-	149.600	-

Table S4 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 2MPA. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	4982(1)	2050(1)	2731(1)	47(1)
O(1)	9077(9)	604(3)	3284(2)	56(1)
O(2)	7737(10)	522(3)	523(2)	65(1)
N(1)	4578(10)	1739(3)	1188(2)	44(1)
N(2)	609(13)	2913(3)	876(3)	56(1)
C(1)	8846(11)	620(3)	2654(3)	38(1)
C(2)	6973(10)	1213(3)	2242(2)	34(1)
C(3)	6454(10)	1206(3)	1535(3)	33(1)
C(4)	8113(11)	549(3)	1153(2)	38(1)
C(5)	11829(12)	-626(4)	1208(3)	45(1)
C(6)	13735(14)	-1174(4)	1575(4)	55(2)
C(7)	14123(13)	-1143(4)	2287(4)	52(2)
C(8)	12496(12)	-566(4)	2637(3)	45(1)
C(9)	10569(10)	-9(3)	2273(3)	35(1)
C(10)	10193(11)	-37(3)	1554(3)	38(1)
C(11)	3771(13)	1841(4)	444(3)	44(1)
C(12)	1638(13)	2587(4)	332(3)	45(1)
C(13)	885(19)	2909(5)	-334(4)	69(2)
C(14)	-1040(20)	3598(6)	-432(5)	84(3)
C(15)	-2179(17)	3933(5)	113(5)	81(2)
C(16)	-1283(15)	3572(5)	763(4)	65(2)

Table S5 Bond lengths [Å] and angles [°] for 2MPA.

Br(1)-C(2)	1.888(4)
O(1)-C(1)	1.222(7)
O(2)-C(4)	1.223(7)
N(1)-C(3)	1.325(7)
N(1)-C(11)	1.466(7)
N(1)-H(1)	0.8600
N(2)-C(12)	1.317(8)
N(2)-C(16)	1.333(9)
C(1)-C(2)	1.434(7)
C(1)-C(9)	1.500(7)
C(2)-C(3)	1.373(7)
C(3)-C(4)	1.507(6)
C(4)-C(10)	1.478(7)
C(5)-C(6)	1.364(9)
C(5)-C(10)	1.401(7)
C(5)-H(5)	0.9300
C(6)-C(7)	1.380(10)
C(6)-H(6)	0.9300
C(7)-C(8)	1.392(8)
C(7)-H(7)	0.9300
C(8)-C(9)	1.376(7)
C(8)-H(8)	0.9300
C(9)-C(10)	1.395(7)
C(11)-C(12)	1.503(8)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.390(10)
C(13)-C(14)	1.373(10)
C(13)-H(13)	0.9300
C(14)-C(15)	1.350(12)
C(14)-H(14)	0.9300
C(15)-C(16)	1.395(12)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300

C(3)-N(1)-C(11)	130.9(4)
C(3)-N(1)-H(1)	114.6
C(11)-N(1)-H(1)	114.6
C(12)-N(2)-C(16)	116.8(6)
O(1)-C(1)-C(2)	123.5(5)
O(1)-C(1)-C(9)	119.9(5)
C(2)-C(1)-C(9)	116.6(4)
C(3)-C(2)-C(1)	126.1(4)
C(3)-C(2)-Br(1)	117.9(4)
C(1)-C(2)-Br(1)	116.0(3)
N(1)-C(3)-C(2)	122.9(4)
N(1)-C(3)-C(4)	120.0(5)
C(2)-C(3)-C(4)	117.1(5)
O(2)-C(4)-C(10)	121.7(4)

O(2)-C(4)-C(3)	119.5(5)
C(10)-C(4)-C(3)	118.8(4)
C(6)-C(5)-C(10)	119.9(6)
C(6)-C(5)-H(5)	120.1
C(10)-C(5)-H(5)	120.1
C(5)-C(6)-C(7)	120.9(5)
C(5)-C(6)-H(6)	119.5
C(7)-C(6)-H(6)	119.5
C(6)-C(7)-C(8)	119.7(6)
C(6)-C(7)-H(7)	120.1
C(8)-C(7)-H(7)	120.1
C(9)-C(8)-C(7)	119.9(6)
C(9)-C(8)-H(8)	120.0
C(7)-C(8)-H(8)	120.0
C(8)-C(9)-C(10)	120.2(5)
C(8)-C(9)-C(1)	119.6(5)
C(10)-C(9)-C(1)	120.2(5)
C(9)-C(10)-C(5)	119.3(5)
C(9)-C(10)-C(4)	121.0(4)
C(5)-C(10)-C(4)	119.7(5)
N(1)-C(11)-C(12)	108.5(4)
N(1)-C(11)-H(11A)	110.0
C(12)-C(11)-H(11A)	110.0
N(1)-C(11)-H(11B)	110.0
C(12)-C(11)-H(11B)	110.0
H(11A)-C(11)-H(11B)	108.4
N(2)-C(12)-C(13)	123.3(6)
N(2)-C(12)-C(11)	118.0(5)
C(13)-C(12)-C(11)	118.7(6)
C(14)-C(13)-C(12)	118.5(7)
C(14)-C(13)-H(13)	120.8
C(12)-C(13)-H(13)	120.8
C(15)-C(14)-C(13)	119.7(8)
C(15)-C(14)-H(14)	120.2
C(13)-C(14)-H(14)	120.2
C(14)-C(15)-C(16)	117.8(7)
C(14)-C(15)-H(15)	121.1
C(16)-C(15)-H(15)	121.1
N(2)-C(16)-C(15)	123.9(7)
N(2)-C(16)-H(16)	118.1
C(15)-C(16)-H(16)	118.1

Symmetry transformations used to generate equivalent atoms:

Table S6 Anisotropic displacement parameters ($Å^2 \times 10^3$) for 2MPA. The anisotropic displacement factor exponent takes the form:$-2\pi^2$ [h^2 a^{*2} U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	54(1)	44(1)	45(1)	-11(1)	11(1)	4(1)
O(1)	61(3)	75(3)	31(2)	2(2)	3(2)	11(2)
O(2)	78(3)	86(3)	32(2)	-2(2)	6(2)	33(3)
N(1)	51(3)	48(2)	34(2)	1(2)	9(2)	10(2)
N(2)	57(4)	52(3)	57(3)	-6(2)	1(3)	8(2)
C(1)	38(3)	42(3)	34(3)	3(2)	6(2)	-7(2)
C(2)	29(3)	37(2)	36(2)	-1(2)	7(2)	1(2)
C(3)	32(3)	30(2)	38(2)	2(2)	6(2)	-1(2)
C(4)	44(3)	41(2)	31(2)	-2(2)	6(2)	2(2)
C(5)	48(3)	37(3)	52(3)	-1(2)	11(3)	2(2)
C(6)	53(4)	37(3)	77(4)	-4(3)	22(3)	3(3)
C(7)	38(3)	42(3)	75(4)	7(3)	3(3)	8(2)
C(8)	45(3)	40(3)	48(3)	9(2)	-1(2)	-3(2)
C(9)	33(3)	30(2)	43(3)	5(2)	2(2)	-9(2)
C(10)	42(3)	34(2)	41(3)	-2(2)	12(2)	-6(2)
C(11)	50(4)	47(3)	34(3)	2(2)	3(2)	7(3)
C(12)	43(3)	41(3)	50(3)	1(2)	-8(2)	-5(2)
C(13)	77(6)	74(5)	51(4)	6(3)	-10(4)	20(4)
C(14)	110(7)	71(5)	67(5)	14(4)	-8(5)	29(5)
C(15)	71(5)	53(4)	110(7)	1(4)	-18(4)	26(4)
C(16)	58(4)	60(4)	74(5)	-15(3)	-5(3)	11(3)

Table S7 Torsion angles [°] for 2MPA

O(1)-C(1)-C(2)-C(3)	-174.0(5)
C(9)-C(1)-C(2)-C(3)	5.7(7)
O(1)-C(1)-C(2)-Br(1)	3.9(7)
C(9)-C(1)-C(2)-Br(1)	-176.3(3)
C(11)-N(1)-C(3)-C(2)	178.7(6)
C(11)-N(1)-C(3)-C(4)	-1.8(9)
C(1)-C(2)-C(3)-N(1)	176.0(5)
Br(1)-C(2)-C(3)-N(1)	-1.9(6)
C(1)-C(2)-C(3)-C(4)	-3.5(7)
Br(1)-C(2)-C(3)-C(4)	178.6(3)
N(1)-C(3)-C(4)-O(2)	1.0(8)
C(2)-C(3)-C(4)-O(2)	-179.5(5)
N(1)-C(3)-C(4)-C(10)	179.9(4)
C(2)-C(3)-C(4)-C(10)	-0.5(7)
C(10)-C(5)-C(6)-C(7)	-1.4(9)
C(5)-C(6)-C(7)-C(8)	1.9(9)
C(6)-C(7)-C(8)-C(9)	-2.0(8)
C(7)-C(8)-C(9)-C(10)	1.6(7)
C(7)-C(8)-C(9)-C(1)	-179.3(5)
O(1)-C(1)-C(9)-C(8)	-3.2(7)
C(2)-C(1)-C(9)-C(8)	177.1(4)
O(1)-C(1)-C(9)-C(10)	175.9(5)
C(2)-C(1)-C(9)-C(10)	-3.8(7)
C(8)-C(9)-C(10)-C(5)	-1.1(7)
C(1)-C(9)-C(10)-C(5)	179.8(4)
C(8)-C(9)-C(10)-C(4)	179.3(4)
C(1)-C(9)-C(10)-C(4)	0.2(7)
C(6)-C(5)-C(10)-C(9)	1.0(8)
C(6)-C(5)-C(10)-C(4)	-179.4(5)
O(2)-C(4)-C(10)-C(9)	-179.0(5)
C(3)-C(4)-C(10)-C(9)	2.0(7)
O(2)-C(4)-C(10)-C(5)	1.4(8)
C(3)-C(4)-C(10)-C(5)	-177.6(5)
C(3)-N(1)-C(11)-C(12)	-176.7(5)
C(16)-N(2)-C(12)-C(13)	1.3(10)
C(16)-N(2)-C(12)-C(11)	-179.9(6)
N(1)-C(11)-C(12)-N(2)	-9.1(8)
N(1)-C(11)-C(12)-C(13)	169.8(6)
N(2)-C(12)-C(13)-C(14)	-0.3(12)
C(11)-C(12)-C(13)-C(14)	-179.2(7)
C(12)-C(13)-C(14)-C(15)	-1.2(14)
C(13)-C(14)-C(15)-C(16)	1.6(14)
C(12)-N(2)-C(16)-C(15)	-0.8(11)
C(14)-C(15)-C(16)-N(2)	-0.6(13)

Symmetry transformations used to generate equivalent atoms:

Table S8 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 3MPA. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	3011(1)	-380(1)	8468(1)	54(1)
O(2)	-133(2)	3801(3)	8604(2)	58(1)
O(3)	1327(2)	-2666(3)	8692(2)	51(1)
N(1)	1860(2)	3506(3)	8644(2)	35(1)
N(2)	4040(3)	5744(6)	11371(3)	71(1)
C(1)	999(3)	-1176(4)	8684(2)	33(1)
C(2)	1668(2)	306(4)	8615(2)	32(1)
C(3)	1345(2)	1993(4)	8642(2)	28(1)
C(4)	189(2)	2311(4)	8645(2)	32(1)
C(5)	-1555(3)	1144(4)	8717(2)	41(1)
C(6)	-2209(3)	-236(5)	8796(3)	47(1)
C(7)	-1814(3)	-1919(5)	8836(2)	44(1)
C(8)	-771(3)	-2223(4)	8812(2)	39(1)
C(9)	-111(2)	-835(4)	8738(2)	30(1)
C(10)	-514(2)	841(4)	8693(2)	30(1)
C(11)	3009(2)	3913(4)	8831(2)	38(1)
C(12)	3616(2)	4126(4)	9896(2)	35(1)
C(13)	4293(3)	2834(5)	10442(3)	50(1)
C(14)	4810(3)	2946(5)	11387(2)	48(1)
C(15)	4677(3)	4375(6)	11823(3)	58(1)
C(16)	3498(3)	5608(5)	10381(3)	47(1)

Table S9 Bond lengths [Å] and angles [°] for 3MPA

Br(1)-C(2)	1.893(3)	N(1)-C(3)-C(4)	110.4(2)
O(2)-C(4)	1.216(4)	C(2)-C(3)-C(4)	117.6(3)
O(3)-C(1)	1.222(4)	O(2)-C(4)-C(10)	121.6(3)
N(1)-C(3)	1.341(4)	O(2)-C(4)-C(3)	118.3(3)
N(1)-C(11)	1.454(4)	C(10)-C(4)-C(3)	120.1(2)
N(1)-H(1)	0.86	C(10)-C(5)-C(6)	120.0(3)
N(2)-C(15)	1.368(6)	C(10)-C(5)-H(5)	120
N(2)-C(16)	1.389(5)	C(6)-C(5)-H(5)	120
C(1)-C(2)	1.456(4)	C(5)-C(6)-C(7)	119.6(3)
C(1)-C(9)	1.486(4)	C(5)-C(6)-H(6)	120.2
C(2)-C(3)	1.370(4)	C(7)-C(6)-H(6)	120.2
C(3)-C(4)	1.517(4)	C(8)-C(7)-C(6)	120.4(3)
C(4)-C(10)	1.468(4)	C(8)-C(7)-H(7)	119.8
C(5)-C(10)	1.379(4)	C(6)-C(7)-H(7)	119.8
C(5)-C(6)	1.386(5)	C(7)-C(8)-C(9)	120.0(3)
C(5)-H(5)	0.93	C(7)-C(8)-H(8)	120
C(6)-C(7)	1.388(5)	C(9)-C(8)-H(8)	120
C(6)-H(6)	0.93	C(10)-C(9)-C(8)	119.2(3)
C(7)-C(8)	1.380(5)	C(10)-C(9)-C(1)	121.1(3)
C(7)-H(7)	0.93	C(8)-C(9)-C(1)	119.6(3)
C(8)-C(9)	1.394(4)	C(5)-C(10)-C(9)	120.8(3)
C(8)-H(8)	0.93	C(5)-C(10)-C(4)	119.7(3)
C(9)-C(10)	1.385(4)	C(9)-C(10)-C(4)	119.5(3)
C(11)-C(12)	1.504(4)	N(1)-C(11)-C(12)	111.8(3)
C(11)-H(11A)	0.97	N(1)-C(11)-H(11A)	109.3
C(11)-H(11B)	0.97	C(12)-C(11)-H(11A)	109.3
C(12)-C(16)	1.378(5)	N(1)-C(11)-H(11B)	109.3
C(12)-C(13)	1.391(5)	C(12)-C(11)-H(11B)	109.3
C(13)-C(14)	1.325(5)	H(11A)-C(11)-H(11B)	107.9
C(13)-H(13)	0.93	C(16)-C(12)-C(13)	116.9(3)
C(14)-C(15)	1.311(6)	C(16)-C(12)-C(11)	120.9(3)
C(14)-H(14)	0.93	C(13)-C(12)-C(11)	122.2(3)
C(15)-H(15)	0.93	C(14)-C(13)-C(12)	124.0(4)
C(16)-H(16)	0.93	C(14)-C(13)-H(13)	118
C(3)-N(1)-C(11)	131.6(3)	C(12)-C(13)-H(13)	118
C(3)-N(1)-H(1)	114.2	C(15)-C(14)-C(13)	117.4(3)
C(11)-N(1)-H(1)	114.2	C(15)-C(14)-H(14)	121.3
C(15)-N(2)-C(16)	117.6(4)	C(13)-C(14)-H(14)	121.3

O(3)-C(1)-C(2)	121.7(3)	C(14)-C(15)-N(2)	124.5(4)
O(3)-C(1)-C(9)	120.2(3)	C(14)-C(15)-H(15)	117.7
C(2)-C(1)-C(9)	118.1(2)	N(2)-C(15)-H(15)	117.7
C(3)-C(2)-C(1)	123.3(3)	C(12)-C(16)-N(2)	119.7(3)
C(3)-C(2)-Br(1)	124.6(2)	C(12)-C(16)-H(16)	120.1
C(1)-C(2)-Br(1)	112.1(2)	N(2)-C(16)-H(16)	120.1
N(1)-C(3)-C(2)	132.0(3)		

Table S10 Anisotropic displacement parameters ($Å^2$ x 10^3) for 3MPA.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Br(1)	46(1)	45(1)	78(1)	-12(1)	32(1)	3(1)
O(2)	45(1)	22(1)	101(2)	-1(1)	17(1)	5(1)
O(3)	55(2)	22(1)	80(2)	0(1)	26(1)	8(1)
N(1)	36(1)	24(1)	41(1)	2(1)	5(1)	-4(1)
N(2)	67(2)	74(3)	68(2)	-11(2)	15(2)	-8(2)
C(1)	42(2)	22(1)	33(1)	0(1)	11(1)	2(1)
C(2)	35(1)	28(1)	34(1)	-1(1)	11(1)	3(1)
C(3)	32(1)	27(1)	22(1)	0(1)	4(1)	0(1)
C(4)	34(1)	21(1)	37(2)	-1(1)	6(1)	2(1)
C(5)	36(2)	35(2)	48(2)	0(1)	9(1)	3(1)
C(6)	36(2)	53(2)	53(2)	2(2)	16(2)	-4(2)
C(7)	48(2)	42(2)	45(2)	0(1)	18(2)	-15(2)
C(8)	52(2)	25(1)	42(2)	0(1)	17(1)	-3(1)
C(9)	38(2)	23(1)	28(1)	-1(1)	9(1)	-1(1)
C(10)	34(1)	24(1)	28(1)	-1(1)	5(1)	0(1)
C(11)	38(2)	38(2)	40(2)	2(1)	13(1)	-8(1)
C(12)	26(1)	36(2)	41(2)	2(1)	11(1)	-7(1)
C(13)	45(2)	48(2)	55(2)	2(2)	15(2)	7(2)
C(14)	38(2)	60(2)	38(2)	10(2)	1(1)	17(2)
C(15)	40(2)	86(3)	39(2)	6(2)	0(2)	2(2)
C(16)	48(2)	39(2)	49(2)	1(1)	7(2)	1(2)

Table S11 Torsion angles [°] for 3MPA

O(3)-C(1)-C(2)-C(3)	-177.4(3)	C(2)-C(1)-C(9)-C(8)	-179.5(3)
C(9)-C(1)-C(2)-C(3)	3.1(4)	C(6)-C(5)-C(10)-C(9)	0.6(5)
O(3)-C(1)-C(2)-Br(1)	3.4(4)	C(6)-C(5)-C(10)-C(4)	-177.8(3)
C(9)-C(1)-C(2)-Br(1)	-176.1(2)	C(8)-C(9)-C(10)-C(5)	-0.2(4)
C(11)-N(1)-C(3)-C(2)	-15.6(5)	C(1)-C(9)-C(10)-C(5)	178.3(3)
C(11)-N(1)-C(3)-C(4)	166.2(3)	C(8)-C(9)-C(10)-C(4)	178.1(3)
C(1)-C(2)-C(3)-N(1)	175.8(3)	C(1)-C(9)-C(10)-C(4)	-3.4(4)
Br(1)-C(2)-C(3)-N(1)	-5.1(5)	O(2)-C(4)-C(10)-C(5)	-1.7(5)
C(1)-C(2)-C(3)-C(4)	-6.1(4)	C(3)-C(4)-C(10)-C(5)	178.5(3)
Br(1)-C(2)-C(3)-C(4)	173.0(2)	O(2)-C(4)-C(10)-C(9)	180.0(3)
N(1)-C(3)-C(4)-O(2)	3.3(4)	C(3)-C(4)-C(10)-C(9)	0.2(4)
C(2)-C(3)-C(4)-O(2)	-175.2(3)	C(3)-N(1)-C(11)-C(12)	-85.1(4)
N(1)-C(3)-C(4)-C(10)	-176.9(2)	N(1)-C(11)-C(12)-C(16)	-75.9(4)
C(2)-C(3)-C(4)-C(10)	4.6(4)	N(1)-C(11)-C(12)-C(13)	102.3(4)
C(10)-C(5)-C(6)-C(7)	-1.0(5)	C(16)-C(12)-C(13)-C(14)	0.8(5)
C(5)-C(6)-C(7)-C(8)	1.0(5)	C(11)-C(12)-C(13)-C(14)	-177.4(3)
C(6)-C(7)-C(8)-C(9)	-0.6(5)	C(12)-C(13)-C(14)-C(15)	-0.8(6)
C(7)-C(8)-C(9)-C(10)	0.2(4)	C(13)-C(14)-C(15)-N(2)	0.4(7)
C(7)-C(8)-C(9)-C(1)	-178.3(3)	C(16)-N(2)-C(15)-C(14)	-0.1(7)
O(3)-C(1)-C(9)-C(10)	-177.5(3)	C(13)-C(12)-C(16)-N(2)	-0.4(5)
C(2)-C(1)-C(9)-C(10)	2.0(4)	C(11)-C(12)-C(16)-N(2)	177.8(3)
O(3)-C(1)-C(9)-C(8)	0.9(4)	C(15)-N(2)-C(16)-C(12)	0.1(6)

Table S12 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 2AMT. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	7096(1)	5025(1)	8919(1)	69(1)
S(1)	11652(2)	11274(2)	8292(1)	69(1)
O(1)	7415(5)	2481(3)	7175(2)	63(1)
O(2)	7601(7)	8722(4)	5502(2)	88(1)
N(1)	7626(4)	8678(4)	7553(2)	38(1)
C(1)	7454(6)	3925(5)	6794(3)	42(1)
C(2)	7431(5)	5481(5)	7452(3)	38(1)
C(3)	7552(5)	7117(4)	7060(3)	33(1)
C(4)	7545(6)	7286(5)	5859(3)	44(1)
C(5)	7488(7)	5896(6)	4077(3)	53(1)
C(6)	7467(7)	4441(6)	3424(3)	60(1)
C(7)	7459(8)	2841(6)	3859(4)	65(1)
C(8)	7465(7)	2662(5)	4946(4)	59(1)
C(9)	7487(6)	4112(5)	5618(3)	40(1)
C(10)	7497(6)	5727(5)	5171(3)	39(1)
C(11)	8302(5)	9244(5)	8615(3)	40(1)
C(12)	10352(5)	9422(5)	8680(3)	40(1)
C(13)	11475(5)	8157(5)	9003(3)	36(1)
C(14)	13343(7)	8855(7)	8918(4)	63(1)
C(15)	13626(7)	10461(8)	8546(4)	69(1)

Table S13 Bond lengths [Å] and angles [º] for 2AMT.

Br(1)-C(2)	1.894(3)	N(1)-C(3)-C(2)	131.3(3)
S(1)-C(15)	1.680(6)	N(1)-C(3)-C(4)	111.1(3)
S(1)-C(12)	1.705(4)	C(2)-C(3)-C(4)	117.5(3)
O(1)-C(1)	1.225(4)	O(2)-C(4)-C(10)	122.0(3)
O(2)-C(4)	1.206(4)	O(2)-C(4)-C(3)	118.2(3)
N(1)-C(3)	1.339(4)	C(10)-C(4)-C(3)	119.8(3)
N(1)-C(11)	1.462(4)	C(6)-C(5)-C(10)	119.7(4)
N(1)-H(1)	0.86	C(6)-C(5)-H(5)	120.2
C(1)-C(2)	1.446(5)	C(10)-C(5)-H(5)	120.2
C(1)-C(9)	1.488(5)	C(7)-C(6)-C(5)	119.9(4)
C(2)-C(3)	1.364(5)	C(7)-C(6)-H(6)	120.1
C(3)-C(4)	1.517(5)	C(5)-C(6)-H(6)	120.1
C(4)-C(10)	1.464(5)	C(6)-C(7)-C(8)	120.8(4)
C(5)-C(6)	1.375(6)	C(6)-C(7)-H(7)	119.6
C(5)-C(10)	1.384(5)	C(8)-C(7)-H(7)	119.6
C(5)-H(5)	0.93	C(7)-C(8)-C(9)	120.2(4)
C(6)-C(7)	1.366(6)	C(7)-C(8)-H(8)	119.9
C(6)-H(6)	0.93	C(9)-C(8)-H(8)	119.9
C(7)-C(8)	1.376(6)	C(8)-C(9)-C(10)	118.6(4)
C(7)-H(7)	0.93	C(8)-C(9)-C(1)	120.6(3)
C(8)-C(9)	1.386(5)	C(10)-C(9)-C(1)	120.8(3)
C(8)-H(8)	0.93	C(5)-C(10)-C(9)	120.8(4)
C(9)-C(10)	1.383(5)	C(5)-C(10)-C(4)	119.3(3)
C(11)-C(12)	1.494(6)	C(9)-C(10)-C(4)	119.9(3)
C(11)-H(11A)	0.97	N(1)-C(11)-C(12)	112.0(3)
C(11)-H(11B)	0.97	N(1)-C(11)-H(11A)	109.2
C(12)-C(13)	1.421(5)	C(12)-C(11)-H(11A)	109.2
C(13)-C(14)	1.415(6)	N(1)-C(11)-H(11B)	109.2
C(13)-H(13)	0.93	C(12)-C(11)-H(11B)	109.2
C(14)-C(15)	1.332(7)	H(11A)-C(11)-H(11B)	107.9
C(14)-H(14)	0.93	C(13)-C(12)-C(11)	127.8(3)
C(15)-H(15)	0.93	C(13)-C(12)-S(1)	111.2(3)
C(15)-S(1)-C(12)	92.5(2)	C(11)-C(12)-S(1)	121.0(3)
C(3)-N(1)-C(11)	130.0(3)	C(14)-C(13)-C(12)	109.0(4)
C(3)-N(1)-H(1)	115	C(14)-C(13)-H(13)	125.5
C(11)-N(1)-H(1)	115	C(12)-C(13)-H(13)	125.5
O(1)-C(1)-C(2)	122.1(4)	C(15)-C(14)-C(13)	115.0(5)
O(1)-C(1)-C(9)	119.9(4)	C(15)-C(14)-H(14)	122.5

C(2)-C(1)-C(9)	118.0(3)	C(13)-C(14)-H(14)	122.5
C(3)-C(2)-C(1)	123.8(3)	C(14)-C(15)-S(1)	112.4(4)
C(3)-C(2)-Br(1)	122.7(3)	C(14)-C(15)-H(15)	123.8
C(1)-C(2)-Br(1)	113.4(2)	S(1)-C(15)-H(15)	123.8

Symmetry transformations used to generate equivalent atoms:

Table S14 Anisotropic displacement parameters ($Å^2$ x 10^3) for 2AMT. The anisotropic displacement factor exponent takes the form; $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Br(1)	117(1)	50(1)	37(1)	13(1)	4(1)	-5(1)
S(1)	73(1)	62(1)	70(1)	14(1)	6(1)	-6(1)
O(1)	106(3)	31(2)	53(2)	12(1)	0(2)	9(2)
O(2)	197(4)	29(2)	40(2)	5(1)	-5(2)	21(2)
N(1)	53(2)	30(2)	33(2)	-2(1)	-8(1)	10(1)
C(1)	51(3)	31(2)	44(2)	7(2)	-2(2)	3(2)
C(2)	52(2)	34(2)	27(2)	7(1)	-2(2)	2(2)
C(3)	37(2)	31(2)	32(2)	0(1)	-3(2)	6(2)
C(4)	67(3)	30(2)	35(2)	3(2)	-5(2)	9(2)
C(5)	80(3)	43(2)	36(2)	1(2)	1(2)	10(2)
C(6)	84(4)	60(3)	36(2)	-7(2)	1(2)	10(3)
C(7)	100(4)	47(3)	49(3)	-16(2)	-1(3)	15(3)
C(8)	92(4)	31(2)	55(3)	-2(2)	-5(2)	12(2)
C(9)	51(2)	29(2)	40(2)	1(2)	-3(2)	7(2)
C(10)	49(2)	32(2)	35(2)	2(2)	-1(2)	7(2)
C(11)	48(2)	39(2)	33(2)	-7(2)	0(2)	5(2)
C(12)	46(2)	44(2)	27(2)	-5(2)	3(2)	-2(2)
C(13)	27(2)	53(2)	29(2)	-4(2)	-5(2)	12(2)
C(14)	52(3)	84(4)	55(3)	-5(3)	1(2)	19(3)
C(15)	47(3)	98(4)	57(3)	-3(3)	2(2)	-11(3)

Table S15 Torsion angles [°] for 2AMT

O(1)-C(1)-C(2)-C(3)	177.1(4)	C(2)-C(1)-C(9)-C(10)	0.1(6)
C(9)-C(1)-C(2)-C(3)	-4.2(6)	C(6)-C(5)-C(10)-C(9)	0.0(7)
O(1)-C(1)-C(2)-Br(1)	-5.8(5)	C(6)-C(5)-C(10)-C(4)	179.2(4)
C(9)-C(1)-C(2)-Br(1)	172.9(3)	C(8)-C(9)-C(10)-C(5)	0.0(7)
C(11)-N(1)-C(3)-C(2)	26.9(7)	C(1)-C(9)-C(10)-C(5)	-178.6(4)
C(11)-N(1)-C(3)-C(4)	-155.3(4)	C(8)-C(9)-C(10)-C(4)	-179.2(4)
C(1)-C(2)-C(3)-N(1)	-176.9(4)	C(1)-C(9)-C(10)-C(4)	2.3(6)
Br(1)-C(2)-C(3)-N(1)	6.2(6)	O(2)-C(4)-C(10)-C(5)	-1.0(7)
C(1)-C(2)-C(3)-C(4)	5.4(6)	C(3)-C(4)-C(10)-C(5)	179.9(4)
Br(1)-C(2)-C(3)-C(4)	-171.5(3)	O(2)-C(4)-C(10)-C(9)	178.2(5)
N(1)-C(3)-C(4)-O(2)	-0.1(6)	C(3)-C(4)-C(10)-C(9)	-1.0(6)
C(2)-C(3)-C(4)-O(2)	178.0(4)	C(3)-N(1)-C(11)-C(12)	73.2(5)
N(1)-C(3)-C(4)-C(10)	179.1(4)	N(1)-C(11)-C(12)-C(13)	-93.3(4)
C(2)-C(3)-C(4)-C(10)	-2.8(6)	N(1)-C(11)-C(12)-S(1)	83.9(4)
C(10)-C(5)-C(6)-C(7)	-0.1(8)	C(15)-S(1)-C(12)-C(13)	-0.3(3)
C(5)-C(6)-C(7)-C(8)	0.2(8)	C(15)-S(1)-C(12)-C(11)	-178.0(3)
C(6)-C(7)-C(8)-C(9)	-0.2(8)	C(11)-C(12)-C(13)-C(14)	178.4(4)
C(7)-C(8)-C(9)-C(10)	0.1(7)	S(1)-C(12)-C(13)-C(14)	1.0(4)
C(7)-C(8)-C(9)-C(1)	178.7(5)	C(12)-C(13)-C(14)-C(15)	-1.3(5)
O(1)-C(1)-C(9)-C(8)	0.3(7)	C(13)-C(14)-C(15)-S(1)	1.1(6)
C(2)-C(1)-C(9)-C(8)	-178.4(4)	C(12)-S(1)-C(15)-C(14)	-0.5(4)
O(1)-C(1)-C(9)-C(10)	178.8(4)		

Symmetry transformations used to generate equivalent atoms:

Table S16 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ ×10^3) for 2EPA. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	2137(1)	403(1)	542(1)	67(1)
O(1)	2431(1)	3113(8)	1556(1)	67(1)
O(2)	309(1)	5772(8)	584(1)	65(1)
N(1)	777(1)	2115(8)	122(1)	49(1)
N(2)	507(1)	-1328(8)	-1376(1)	50(1)
C(1)	1941(2)	3692(9)	1333(2)	43(1)
C(2)	1660(2)	2585(9)	822(1)	39(1)
C(3)	1110(2)	3076(8)	571(1)	35(1)
C(4)	793(2)	5123(9)	819(1)	39(1)
C(5)	769(2)	8163(9)	1559(1)	42(1)
C(6)	1025(2)	9241(10)	2041(2)	50(1)
C(7)	1574(2)	8500(10)	2293(2)	51(1)
C(8)	1868(2)	6720(10)	2063(2)	47(1)
C(9)	1618(1)	5615(9)	1579(1)	35(1)
C(10)	1062(1)	6331(8)	1329(1)	34(1)
C(11)	865(2)	81(9)	-252(1)	45(1)
C(12)	1023(2)	1693(9)	-672(2)	49(1)
C(13)	1015(2)	-366(9)	-1098(1)	42(1)
C(14)	1492(2)	-1311(10)	-1194(2)	52(1)
C(15)	1450(2)	-3281(11)	-1586(2)	63(1)
C(16)	936(2)	-4243(11)	-1871(2)	63(1)
C(17)	479(2)	-3224(11)	-1752(2)	59(1)

Table S17 Bond lengths [Å] and angles [°] for 2EPA

Br(1)-C(2)	1.896(4)	C(2)-C(3)-C(4)	117.6(3)
O(1)-C(1)	1.226(4)	O(2)-C(4)-C(10)	120.8(3)
O(2)-C(4)	1.227(4)	O(2)-C(4)-C(3)	118.7(3)
N(1)-C(3)	1.338(5)	C(10)-C(4)-C(3)	120.5(3)
N(1)-C(11)	1.448(5)	C(6)-C(5)-C(10)	119.7(4)
N(1)-H(1)	0.86	C(6)-C(5)-H(5)	120.1
N(2)-C(17)	1.328(5)	C(10)-C(5)-H(5)	120.1
N(2)-C(13)	1.345(5)	C(5)-C(6)-C(7)	119.9(4)
C(1)-C(2)	1.460(5)	C(5)-C(6)-H(6)	120
C(1)-C(9)	1.488(5)	C(7)-C(6)-H(6)	120
C(2)-C(3)	1.363(5)	C(8)-C(7)-C(6)	120.4(4)
C(3)-C(4)	1.514(5)	C(8)-C(7)-H(7)	119.8
C(4)-C(10)	1.468(5)	C(6)-C(7)-H(7)	119.8
C(5)-C(6)	1.379(5)	C(7)-C(8)-C(9)	120.5(4)
C(5)-C(10)	1.384(5)	C(7)-C(8)-H(8)	119.8
C(5)-H(5)	0.93	C(9)-C(8)-H(8)	119.8
C(6)-C(7)	1.385(6)	C(8)-C(9)-C(10)	119.0(4)
C(6)-H(6)	0.93	C(8)-C(9)-C(1)	120.1(3)
C(7)-C(8)	1.370(6)	C(10)-C(9)-C(1)	120.9(3)
C(7)-H(7)	0.93	C(5)-C(10)-C(9)	120.4(3)
C(8)-C(9)	1.385(5)	C(5)-C(10)-C(4)	120.4(3)
C(8)-H(8)	0.93	C(9)-C(10)-C(4)	119.2(3)
C(9)-C(10)	1.395(5)	N(1)-C(11)-C(12)	112.7(3)
C(11)-C(12)	1.523(6)	N(1)-C(11)-H(11A)	109.1
C(11)-H(11A)	0.97	C(12)-C(11)-H(11A)	109.1
C(11)-H(11B)	0.97	N(1)-C(11)-H(11B)	109.1
C(12)-C(13)	1.493(6)	C(12)-C(11)-H(11B)	109.1
C(12)-H(12A)	0.97	H(11A)-C(11)-H(11B)	107.8
C(12)-H(12B)	0.97	C(13)-C(12)-C(11)	111.8(3)
C(13)-C(14)	1.380(5)	C(13)-C(12)-H(12A)	109.3
C(14)-C(15)	1.376(6)	C(11)-C(12)-H(12A)	109.3
C(14)-H(14)	0.93	C(13)-C(12)-H(12B)	109.3
C(15)-C(16)	1.362(7)	C(11)-C(12)-H(12B)	109.3
C(15)-H(15)	0.93	H(12A)-C(12)-H(12B)	107.9
C(16)-C(17)	1.373(6)	N(2)-C(13)-C(14)	121.8(4)
C(16)-H(16)	0.93	N(2)-C(13)-C(12)	115.3(3)
C(17)-H(17)	0.93	C(14)-C(13)-C(12)	122.9(4)
C(3)-N(1)-C(11)	132.7(3)	C(13)-C(14)-C(15)	119.3(4)

C(3)-N(1)-H(1)	113.7	C(13)-C(14)-H(14)	120.3
C(11)-N(1)-H(1)	113.7	C(15)-C(14)-H(14)	120.3
C(17)-N(2)-C(13)	117.6(4)	C(16)-C(15)-C(14)	119.1(4)
O(1)-C(1)-C(2)	121.9(4)	C(16)-C(15)-H(15)	120.4
O(1)-C(1)-C(9)	120.1(4)	C(14)-C(15)-H(15)	120.4
C(2)-C(1)-C(9)	118.0(3)	C(15)-C(16)-C(17)	118.5(4)
C(3)-C(2)-C(1)	123.5(3)	C(15)-C(16)-H(16)	120.8
C(3)-C(2)-Br(1)	123.4(3)	C(17)-C(16)-H(16)	120.8
C(1)-C(2)-Br(1)	113.1(3)	N(2)-C(17)-C(16)	123.8(5)
N(1)-C(3)-C(2)	131.9(4)	N(2)-C(17)-H(17)	118.1
N(1)-C(3)-C(4)	110.5(3)	C(16)-C(17)-H(17)	118.1

Symmetry transformations used to generate equivalent atoms:

°

Table S18 Anisotropic displacement parameters ($Å^2$ x 10^3) for 2EPA. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2}$ U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	43(1)	89(1)	66(1)	-16(1)	12(1)	22(1)
O(1)	30(2)	104(3)	56(2)	-10(2)	-4(1)	21(2)
O(2)	35(2)	107(3)	41(2)	-18(2)	-6(1)	24(2)
N(1)	34(2)	68(2)	37(2)	-10(2)	1(2)	9(2)
N(2)	46(2)	56(2)	48(2)	-3(2)	13(2)	13(2)
C(1)	31(2)	50(3)	42(2)	7(2)	3(2)	3(2)
C(2)	30(2)	45(2)	40(2)	1(2)	11(2)	6(2)
C(3)	30(2)	41(2)	32(2)	5(2)	7(2)	4(2)
C(4)	30(2)	49(3)	35(2)	4(2)	4(2)	4(2)
C(5)	34(2)	55(3)	35(2)	3(2)	7(2)	7(2)
C(6)	47(2)	63(3)	40(2)	-8(2)	16(2)	1(2)
C(7)	44(2)	68(3)	34(2)	-9(2)	3(2)	-11(2)
C(8)	30(2)	64(3)	39(2)	-1(2)	0(2)	-4(2)
C(9)	26(2)	43(2)	34(2)	4(2)	5(2)	-2(2)
C(10)	30(2)	42(2)	28(2)	5(2)	7(2)	-4(2)
C(11)	46(2)	44(2)	40(2)	-8(2)	7(2)	-1(2)
C(12)	55(3)	43(2)	47(2)	3(2)	12(2)	2(2)
C(13)	47(2)	39(2)	39(2)	7(2)	13(2)	10(2)
C(14)	45(2)	56(3)	57(3)	9(2)	18(2)	9(2)
C(15)	68(3)	68(3)	65(3)	13(3)	38(3)	27(3)
C(16)	88(4)	62(3)	38(2)	-1(2)	20(3)	21(3)
C(17)	60(3)	67(3)	44(3)	-6(2)	5(2)	10(2)

Table S19 Torsion angles [°] for 2EPA

O(1)-C(1)-C(2)-C(3)	177.1(4)	C(6)-C(5)-C(10)-C(9)	-1.2(6)
C(9)-C(1)-C(2)-C(3)	-3.9(6)	C(6)-C(5)-C(10)-C(4)	179.0(4)
O(1)-C(1)-C(2)-Br(1)	-3.0(5)	C(8)-C(9)-C(10)-C(5)	1.1(6)
C(9)-C(1)-C(2)-Br(1)	175.9(3)	C(1)-C(9)-C(10)-C(5)	-178.9(3)
C(11)-N(1)-C(3)-C(2)	3.9(8)	C(8)-C(9)-C(10)-C(4)	-179.0(3)
C(11)-N(1)-C(3)-C(4)	-177.6(4)	C(1)-C(9)-C(10)-C(4)	1.0(5)
C(1)-C(2)-C(3)-N(1)	-175.6(4)	O(2)-C(4)-C(10)-C(5)	1.8(6)
Br(1)-C(2)-C(3)-N(1)	4.6(6)	C(3)-C(4)-C(10)-C(5)	-178.9(3)
C(1)-C(2)-C(3)-C(4)	6.0(6)	O(2)-C(4)-C(10)-C(9)	-178.1(4)
Br(1)-C(2)-C(3)-C(4)	-173.9(3)	C(3)-C(4)-C(10)-C(9)	1.2(5)
N(1)-C(3)-C(4)-O(2)	-4.0(5)	C(3)-N(1)-C(11)-C(12)	-95.2(5)
C(2)-C(3)-C(4)-O(2)	174.7(4)	N(1)-C(11)-C(12)-C(13)	-170.1(3)
N(1)-C(3)-C(4)-C(10)	176.6(3)	C(17)-N(2)-C(13)-C(14)	-0.4(6)
C(2)-C(3)-C(4)-C(10)	-4.6(5)	C(17)-N(2)-C(13)-C(12)	-178.4(4)
C(10)-C(5)-C(6)-C(7)	0.3(6)	C(11)-C(12)-C(13)-N(2)	69.0(5)
C(5)-C(6)-C(7)-C(8)	0.6(7)	C(11)-C(12)-C(13)-C(14)	-108.9(5)
C(6)-C(7)-C(8)-C(9)	-0.6(7)	N(2)-C(13)-C(14)-C(15)	0.3(6)
C(7)-C(8)-C(9)-C(10)	-0.2(6)	C(12)-C(13)-C(14)-C(15)	178.1(4)
C(7)-C(8)-C(9)-C(1)	179.8(4)	C(13)-C(14)-C(15)-C(16)	0.2(7)
O(1)-C(1)-C(9)-C(8)	-0.9(6)	C(14)-C(15)-C(16)-C(17)	-0.6(7)
C(2)-C(1)-C(9)-C(8)	-179.9(4)	C(13)-N(2)-C(17)-C(16)	0.0(7)
O(1)-C(1)-C(9)-C(10)	179.1(4)	C(15)-C(16)-C(17)-N(2)	0.5(7)
C(2)-C(1)-C(9)-C(10)	0.1(5)		

Symmetry transformations used to generate equivalent atoms:

Table S20 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 2AET. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	9944(1)	6929(4)	7441(1)	88(1)
S(2)	11258(2)	9422(15)	9330(4)	127(2)
O(1)	9155(4)	3380(30)	6306(6)	86(3)
O(2)	8269(4)	4170(20)	9630(6)	78(3)
N(1)	9232(4)	6960(20)	9406(6)	57(2)
C(1)	8968(5)	3510(30)	7098(7)	56(3)
C(2)	9248(5)	5130(30)	7815(7)	51(2)
C(3)	9033(4)	5460(20)	8681(7)	47(2)
C(4)	8469(5)	3900(30)	8880(7)	54(3)
C(5)	7668(6)	610(30)	8324(10)	72(3)
C(6)	7398(7)	-990(30)	7634(12)	83(4)
C(7)	7645(7)	-1280(40)	6783(12)	90(5)
C(8)	8142(6)	170(30)	6616(10)	74(4)
C(9)	8426(5)	1880(30)	7300(8)	57(3)
C(10)	8183(5)	2090(30)	8143(8)	53(3)
C(11)	9758(5)	8630(30)	9584(8)	55(3)
C(12)	10259(5)	6550(30)	9854(9)	63(3)
C(13)	10792(5)	8310(30)	10119(10)	64(3)
C(14)	10957(4)	9380(30)	11020(9)	57(3)
C(15)	11467(10)	10930(50)	10960(20)	132(9)
C(16)	11672(10)	11260(50)	10140(30)	154(14)

Table S21 Bond lengths [Å] and angles [º] for 2AET

Br(1)-C(2)	1.899(11)	C(2)-C(3)-C(4)	117.7(10)
S(2)-C(13)	1.678(13)	O(2)-C(4)-C(10)	122.4(11)
S(2)-C(16)	1.71(3)	O(2)-C(4)-C(3)	118.9(11)
O(1)-C(1)	1.248(13)	C(10)-C(4)-C(3)	118.7(9)
O(2)-C(4)	1.207(13)	C(6)-C(5)-C(10)	119.0(14)
N(1)-C(3)	1.326(14)	C(6)-C(5)-H(5)	120.5
N(1)-C(11)	1.450(14)	C(10)-C(5)-H(5)	120.5
N(1)-H(1)	0.86	C(5)-C(6)-C(7)	120.7(15)
C(1)-C(2)	1.417(16)	C(5)-C(6)-H(6)	119.6
C(1)-C(9)	1.491(17)	C(7)-C(6)-H(6)	119.6
C(2)-C(3)	1.380(14)	C(8)-C(7)-C(6)	119.5(15)
C(3)-C(4)	1.519(15)	C(8)-C(7)-H(7)	120.2
C(4)-C(10)	1.488(17)	C(6)-C(7)-H(7)	120.2
C(5)-C(6)	1.37(2)	C(7)-C(8)-C(9)	121.3(14)
C(5)-C(10)	1.398(17)	C(7)-C(8)-H(8)	119.3
C(5)-H(5)	0.93	C(9)-C(8)-H(8)	119.3
C(6)-C(7)	1.39(2)	C(10)-C(9)-C(8)	118.4(12)
C(6)-H(6)	0.93	C(10)-C(9)-C(1)	121.1(10)
C(7)-C(8)	1.35(2)	C(8)-C(9)-C(1)	120.5(11)
C(7)-H(7)	0.93	C(9)-C(10)-C(5)	120.9(12)
C(8)-C(9)	1.408(17)	C(9)-C(10)-C(4)	120.0(10)
C(8)-H(8)	0.93	C(5)-C(10)-C(4)	119.1(11)
C(9)-C(10)	1.372(17)	N(1)-C(11)-C(12)	112.0(9)
C(11)-C(12)	1.532(16)	N(1)-C(11)-H(11A)	109.2
C(11)-H(11A)	0.97	C(12)-C(11)-H(11A)	109.2
C(11)-H(11B)	0.97	N(1)-C(11)-H(11B)	109.2
C(12)-C(13)	1.509(18)	C(12)-C(11)-H(11B)	109.2
C(12)-H(12A)	0.97	H(11A)-C(11)-H(11B)	107.9
C(12)-H(12B)	0.97	C(13)-C(12)-C(11)	112.1(10)
C(13)-C(14)	1.444(18)	C(13)-C(12)-H(12A)	109.2
C(14)-C(15)	1.38(3)	C(11)-C(12)-H(12A)	109.2
C(14)-H(14)	0.93	C(13)-C(12)-H(12B)	109.2
C(15)-C(16)	1.32(4)	C(11)-C(12)-H(12B)	109.2
C(15)-H(15)	0.93	H(12A)-C(12)-H(12B)	107.9
C(16)-H(16)	0.93	C(14)-C(13)-C(12)	127.0(11)
C(13)-S(2)-C(16)	91.7(13)	C(14)-C(13)-S(2)	111.6(10)
C(3)-N(1)-C(11)	132.7(9)	C(12)-C(13)-S(2)	121.2(11)
C(3)-N(1)-H(1)	113.7	C(15)-C(14)-C(13)	108.5(16)

C(11)-N(1)-H(1)	113.7	C(15)-C(14)-H(14)	125.7
O(1)-C(1)-C(2)	123.1(11)	C(13)-C(14)-H(14)	125.7
O(1)-C(1)-C(9)	118.5(11)	C(16)-C(15)-C(14)	116(2)
C(2)-C(1)-C(9)	118.4(9)	C(16)-C(15)-H(15)	121.8
C(3)-C(2)-C(1)	124.0(10)	C(14)-C(15)-H(15)	121.8
C(3)-C(2)-Br(1)	123.6(9)	C(15)-C(16)-S(2)	111.7(18)
C(1)-C(2)-Br(1)	112.3(7)	C(15)-C(16)-H(16)	124.2
N(1)-C(3)-C(2)	131.1(10)	S(2)-C(16)-H(16)	124.2
N(1)-C(3)-C(4)	111.3(9)		

Symmetry transformations used to generate equivalent atoms:

Table S22 Anisotropic displacement parameters ($Å^2$ x 10^3) for 2AET.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2$ [h^2 a^{*2} U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	89(1)	118(1)	60(1)	-10(1)	28(1)	-31(1)
S(2)	96(3)	143(5)	145(5)	53(4)	26(3)	-6(3)
O(1)	95(6)	128(9)	35(4)	-11(5)	5(4)	-3(6)
O(2)	72(5)	104(7)	58(5)	-15(5)	22(4)	-29(5)
N(1)	55(5)	76(6)	39(5)	-4(5)	9(4)	-9(5)
C(1)	65(7)	69(7)	35(5)	5(5)	2(5)	4(6)
C(2)	57(6)	58(6)	36(5)	4(5)	5(4)	5(5)
C(3)	53(6)	50(6)	38(5)	3(5)	-2(4)	1(5)
C(4)	55(6)	64(7)	44(6)	5(5)	5(5)	2(5)
C(5)	71(8)	75(9)	71(8)	10(7)	-6(7)	-9(7)
C(6)	83(9)	65(9)	98(12)	-2(8)	-18(9)	-13(8)
C(7)	95(11)	81(11)	93(12)	-17(9)	-32(9)	-14(9)
C(8)	91(10)	67(9)	63(8)	-12(7)	-16(7)	5(8)
C(9)	64(7)	58(7)	50(6)	-2(5)	-10(5)	14(5)
C(10)	54(6)	53(6)	53(6)	4(5)	-6(5)	5(5)
C(11)	65(7)	58(7)	43(6)	-5(5)	3(5)	-6(5)
C(12)	61(7)	56(7)	72(8)	-2(6)	-1(6)	-2(6)
C(13)	57(6)	50(7)	83(9)	11(6)	4(6)	8(5)
C(14)	35(5)	59(7)	78(8)	-20(6)	-8(5)	6(5)
C(15)	111(17)	88(14)	190(30)	-1(16)	-63(18)	16(12)
C(16)	89(14)	103(16)	270(40)	90(20)	-79(19)	-33(12)

Table S23 Torsion angles [°] for 2AET.

O(1)-C(1)-C(2)-C(3)	175.9(12)	C(2)-C(1)-C(9)-C(8)	-178.2(11)
C(9)-C(1)-C(2)-C(3)	-4.0(18)	C(8)-C(9)-C(10)-C(5)	0.6(17)
O(1)-C(1)-C(2)-Br(1)	-2.2(16)	C(1)-C(9)-C(10)-C(5)	178.7(11)
C(9)-C(1)-C(2)-Br(1)	177.9(8)	C(8)-C(9)-C(10)-C(4)	-179.5(11)
C(11)-N(1)-C(3)-C(2)	-4(2)	C(1)-C(9)-C(10)-C(4)	-1.4(16)
C(11)-N(1)-C(3)-C(4)	176.1(11)	C(6)-C(5)-C(10)-C(9)	-2(2)
C(1)-C(2)-C(3)-N(1)	-177.8(11)	C(6)-C(5)-C(10)-C(4)	178.3(12)
Br(1)-C(2)-C(3)-N(1)	0.0(19)	O(2)-C(4)-C(10)-C(9)	179.4(12)
C(1)-C(2)-C(3)-C(4)	1.7(17)	C(3)-C(4)-C(10)-C(9)	-0.8(16)
Br(1)-C(2)-C(3)-C(4)	179.6(8)	O(2)-C(4)-C(10)-C(5)	-0.7(18)
N(1)-C(3)-C(4)-O(2)	0.2(16)	C(3)-C(4)-C(10)-C(5)	179.0(11)
C(2)-C(3)-C(4)-O(2)	-179.5(11)	C(3)-N(1)-C(11)-C(12)	-81.9(15)
N(1)-C(3)-C(4)-C(10)	-179.6(10)	N(1)-C(11)-C(12)-C(13)	-175.0(10)
C(2)-C(3)-C(4)-C(10)	0.8(15)	C(11)-C(12)-C(13)-C(14)	89.7(15)
C(10)-C(5)-C(6)-C(7)	3(2)	C(11)-C(12)-C(13)-S(2)	-86.6(12)
C(5)-C(6)-C(7)-C(8)	-4(2)	C(16)-S(2)-C(13)-C(14)	0.2(12)
C(6)-C(7)-C(8)-C(9)	3(2)	C(16)-S(2)-C(13)-C(12)	177.1(12)
C(7)-C(8)-C(9)-C(10)	-1.0(19)	C(12)-C(13)-C(14)-C(15)	-178.8(14)
C(7)-C(8)-C(9)-C(1)	-179.1(13)	S(2)-C(13)-C(14)-C(15)	-2.2(14)
O(1)-C(1)-C(9)-C(10)	-176.1(11)	C(13)-C(14)-C(15)-C(16)	4(3)
C(2)-C(1)-C(9)-C(10)	3.8(17)	C(14)-C(15)-C(16)-S(2)	-4(3)
O(1)-C(1)-C(9)-C(8)	1.9(18)	C(13)-S(2)-C(16)-C(15)	2(2)

Table 24 Selected bond distances (in Å) in 2MPA, 3MPA, 2AMT and 2AETin the gas phase (G) and solvent, Dimethylsulfoxide (D)

	2MPA			3MPA			2EPA			2AMT			2AET		
	Theoretical		Obs.	Theoretical		Obs.	Theoretical		Obs.	Theoretical		Obs.	Theoretical		Obs.
	G	D		G	D		G	D		G	D		G	D	
$C=O_1$	1.221	1.221	1.227(8)	1.218	1.218	1.222(4)	1.220	1.220	1.226(4)	1.218	1.218	1.225(4)	1.224	1.224	1.24(2)
$C=O_2$	1.218	1.218	1.227(8)	1.218	1.218	1.216(4)	1.218	1.218	1.227(4)	1.219	1.219	1.206(4)	1.218	1.218	1.21(2)
C- Br	1.875	1.875	1.885(5)	1.879	1.879	1.893(3)	1.881	1.881	1.896(4)	1.878	1.878	1.894(3)	1.881	1.881	1.90(1)
N-H	1.083	1.081	0.86	1.016	1.016	0.86	1.014	1.014	0.86	1.016	1.016	0.86	1.014	1.014	0.86
C11-H11	1.095	1.095	0.97	1.094	1.094	0.97	1.091	1.091	0.97	1.089	1.089	0.97	1.096	1.096	0.97
C12-H12							1.096	1.096	0.97				1.096	1.096	0.97
C-H	1.086	1.086	0.97	1.086	1.086	0.97	1.086	1.086	0.97	1.086	1.086	0.97	1.086	1.086	0.93

Table 25 Selected vibrational frequencies in ($\nu(cm^{-1})$) of 2MPA, 3MPA, 2AMT, 2EPA and 2AET

	2MPA (cm^{-1})	3MPA (cm^{-1})	2EPA (cm^{-1})	2AMT (cm^{-1})	2AET (cm^{-1})
νCH)ar	2988 (3061, 3012)*	2986(3076, 3022)	2982(3061, 3003)	2986(3082, 3012)	2986(3068, 2960)
ν (C-H11)		2864	2874	2870	2892
ν (C-H12)			2838		2814
ν (C1=O1)	1640	1649	1644	1651	1641
ν (C1=O2)	1664(1680)	1663(1683)	1662(1672)	1662(1685)	1664(1678)
ν (C=C)	1554(1564)	1561(1564)	1556(1572)	1564(1570)	1558(1577)
ν (NH)	3242(3242)	3283(3267)	3309(3321)	3285(3284)	3301(3263)
ν (C-Br)	766(638)	752(643)	753(653)	757(623)	751(686)

*Experimental values

Table 26^{1}H chemical shift (in ppm) in solvent Dimethylsulfoxide and observed ^{1}H chemical shifts in $CDCl_3$

	2MPA δ(ppm)		3MPA δ(ppm)		2EPA δ(ppm)		2AMT δ(ppm)		2AET δ(ppm)	
	Theoretical	Obs.	Theoretical	Obs.	Theoretical	Obs.	Theoretical	Obs.	Theoretical	Obs.
H1	8.3	7.91	6.7	6.28	6.8	7.12	6.6	6.10	6.7	6.18
H5	9.0	8.16	8.8	8.12	9.0	8.13	8.9	8.14	9.0	8.15
H6	8.4	7.72	8.3	7.70	8.4	7.69	8.3	7.72	8.4	7.72
H7	8.5	7.72	8.4	7.70	8.5	7.64	8.4	7.64	8.5	7.63
H8	9.0	8.06	9.0	8.01	9.0	8.00	8.9	8.03	9.0	8.02
H11	5.5	5.21	5.3	5.11	4.4	4.32	5.3	5.25	4.2	4.18
H12					3.2	3.17			3.3	3.23
H13	8.1	7.30	8.8	7.64			7.7	7.07		
H14	8.6	7.64	7.9	7.33	8.0	7.21	7.4	7.00	7.8	6.92
H15	8.5	7.27	8.9	8.57	8.4	7.60	8.0	7.29	7.5	6.97
H16	9.2	8.65	9.1	8.62	7.8	7.18			7.6	7.20
H17					9.1	8.59				

Table 27 Wavelength maxima (λ_{max}), oscillator strengths (*f*)and assignments of bands in the electronic spectra of the 2MPA, 3MPA,2AMT,2EPA and 2AET in methanol from TDDFT

Transition	2MPA			3MPA			2EPA			2AMT			2AET		
	E_{ex} (eV)	λ_{max} (nm)	(*f*)	Eex (eV)	λ_{max} (nm)	(*f*)	E_{ex} (eV)	λ_{max} (nm)	(*f*)	E_{ex} (eV)	λ_{max} (nm)	(*f*)	E_{ex} (eV)	λ_{max} (nm)	(*f*)
Homo→Lumo	3.1	401 (467)*	0.1369	3.2	385 (471)	0.0721	3.1	394 (477)	0.0756	3.2	384 (463)	0.0681	3.1	402 (472)	0.0911
Homo→ Lumo+1	5.5	223	0.3378	5.7	218	0.3396	5.6	223	0.3817	5.6	221	0.4029	5.5	226	0.2298
Homo→ Lumo+2	7.0	177	0.0391	6.5	191	0.0407				5.6	220	0.0358			
Homo-1→Lumo	5.9	210	0.1428	5.6	221	0.0286	6.3	196	0.1463	4.9	254	0.1373	4.3	286	0.0564
Homo-1→ Lumo+1	6.3	196	0.3419										6.9	180	0.0096
Homo-1→ Lumo+2	5.5	225	0.3443	5.5	225	0.1083	5.5	226	0.1734	5.7	216	0.1116	5.6	219	0.3022
Homo-2 →Lumo	4.5	278	0.1183	4.4	281	0.1167	4.4	279	0.116				4.8	258	0.1965
Homo-2 → Lumo+1				6.2	199	0.0643	6.2	200	0.0168						
Homo-2 → Lumo+2													6.0	207	0.1477
Homo-3→Lumo	7.8	259	0.3451	6.6	186	0.0118				4.4	281	0.1174	4.5	275	0.0683
Homo-3→ Lumo+1	6.1	202	0.1220							6.2	199	0.0884	6.2	197	0.1647
Homo-3→ Lumo+2				5.3	233	0.0190	5.4	231	0.0126						
Homo-4→Lumo				4.8	259	0.3019	4.8	258	0.3009	4.7	263	0.1689			

* Observed values

Table 28 Separation of HOMO, LUMO energies and global indices of 2MPA, 3MPA, 2AMT, 2EPA and 2AETwB97x/6-31+G(d,p)

Molecular properties	2MPA	2MPA[a]	3MPA	3MPA[a]	2EPA	2EPA[a]	2AMT	2AMT[a]	2AET	2AET[a]
$\Delta E_{HOMO-LUMO}$	0.267	0.223	0.276	0.235	0.271	0.233	0.276	0.233	0.268	0.249
Softness(σ)	7.496	8.983	7.235	8.524	7.371	8.566	7.239	8.602	7.468	8.032
Global Hardness(ŋ)	0.133	0.111	0.138	0.117	0.136	0.117	0.138	0.116	0.134	0.124
Electronic chemical potential(μ)	-0.172	-0.009	-0.188	-0.019	-0.178	-0.012	-0.184	-0.015	-0.171	-0.021
Electronegativity(χ)	0.172	0.009	0.188	0.019	0.178	0.012	0.184	0.015	0.171	0.021
Global electrophilicity index(ω)	0.015	0.000	0.018	0.000	0.016	0.000	0.017	0.000	0.015	0.000

[a] anionic form