Benzo[α]phenoxazines and Benzo[α]phenothiazine of Vitamin K3: Synthesis, molecular structures, DFT studies and cytotoxic activity

Dattatray Chadar[a], Soniya S. Rao[a], Ayesha Khan [a], Shridhar P. Gejji[a], Kiesar Sideeq Bhat[a], Thomas Weyhermüller[b] and Sunita Salunke Gawali*[a]

[a] *Department of Chemistry, Savitribai Phule Pune University, Pune 411007, India; Fax: +912025693981 ; Tel: +912025601397 -Ext-531; E-mail: sunitas@chem.unipune.ac.in*

[b] *MPI für Chemische Energiekonversion, Stiftstr. 34-36, 45470 Mülheim an der Ruhr, Germany*

Supplementary material

Figure Legends

Fig.S1 FT-IR spectrum of **MQ** in region 4000 cm^{-1} to 400 cm^{-1}

Fig.S2 FT-IR spectrum of **M-1B** in region 4000 cm^{-1} to 400 cm^{-1}

Fig.S3 FT-IR spectrum of **M-2B** in region 4000 cm^{-1} to 400 cm^{-1}

Fig.S4 FT-IR spectrum of **M-3B** in region 4000 cm^{-1} to 400 cm^{-1}

Fig.S5 FT-IR spectrum of **M-4B** in region 4000 cm^{-1} to 400 cm^{-1}

Fig.S6 GC-MS spectra of **M-1B**

Fig.S7 GC-MS spectra of **M-2B**

Fig.S8 GC-MS spectra of **M-3B**

Fig.S9 GC-MS spectra of **M-4B**

Fig.S10 DSC plot of **M-1B**

Fig.S11 DSC plot of **M-2B**

Fig.S12 DSC plot of **M-3B**

Fig.S13 DSC plot of **M-4B**

Fig.S14 a) ^{1}H, b) ^{13}C NMR spectra of **M-1B**

Fig.S15 a) ^{1}H, b) ^{13}C NMR spectra of **M-2B**

Fig.S16 a) ^{1}H, b) ^{13}C NMR spectra of **M-3B**

Fig.S17 a) ^{1}H, b) ^{13}C NMR spectra of **M-4B**

Fig.S18 2D gHSQCAD NMR spectra of **M-1B**

Fig.S19 2D gHSQCAD NMR spectra of **M-2B**

Fig.S20 2D gHSQCAD NMR spectra of **M-3B**

Fig.S21 2D gHSQCAD NMR spectra of **M-4B**

Fig.S22 (a) FT-IR spectra of **M-1B**, **M-2B**, **M-3B**, M-4B in region 3500-2500 cm^{-1} and (b) in region of 1850 to 1550 cm^{-1}

Fig.S23 Molecular association of **M-1B** via C-H···O, C-H···Cl, Cl···Cl and π-π stacking interactions

Fig.S24 Slipped π-π stacking interactions in **M-1B**. b) Cl···Cl interactions in **M-1B** down the c-axis

Fig.S25 Molecular association accompanying **M-2B**

Fig.S26 Interactions from neighboring molecules in M-4B

Fig.S27 Butterfly like arrangement of molecules of **M-4B** down c-axis

Fig.S28 Concentration dependent cytotoxicity of compounds **M-1B** to **M-4B** against normal skin cell line evaluated by MTT assay after 24, 48, 72, and 96 hours. Results are mean values

Table Legends

Table S1 FT-IR stretching frequencies of **M-1B**, **M-2B**, **M-3B**, **M-4B**

Table S2 Chemical Shift (δ) in ppm and coupling constant *J* in Hz for **M-1B**, **M-2B**, **M-3B** and **M-4B**

Table S3 ^{13}C NMR chemical shifts of **M-1B**, **M-2B**, **M-3B** and **M-4B** in $CDCl_3$

Table S4 Bond lengths [Å] and angles [°] for **M-2B**

Table S5 Anisotropic displacement parameters ($Å^2x10^3$) for **M-2B**. The anisotropic Displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Table S6 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2x\ 10^3$) for **M-2B**.

Table S7 Bond lengths [Å] and angles [°] for **M-1B**

Table S8 Anisotropic displacement parameters ($Å^2x\ 10^3$) for **M-1B**. The anisotropic Displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

Table S9 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2x\ 10^3$) For **M-1B**.

Table S10 Bond lengths [Å] and angles [°] for **M-4B**

Table S11 Anisotropic displacement parameters ($Å^2x\ 10^3$) for **M-4B**. The anisotropic Displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Table S12 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2x\ 10^3$) For **M-4B**.

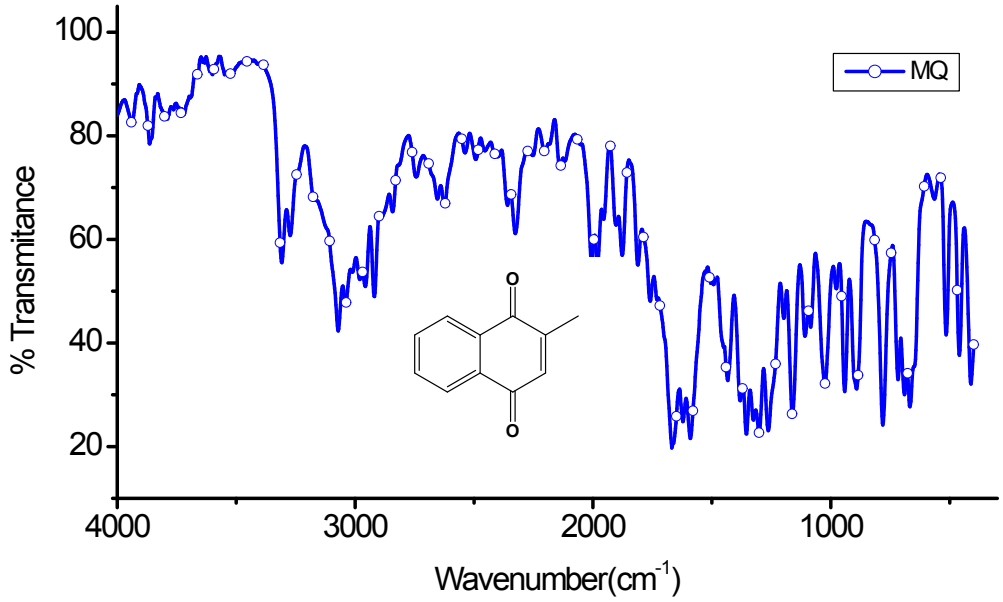


Fig.S1 FT-IR spectrums of MQ in region 4000 cm^{-1} to 400 cm^{-1}

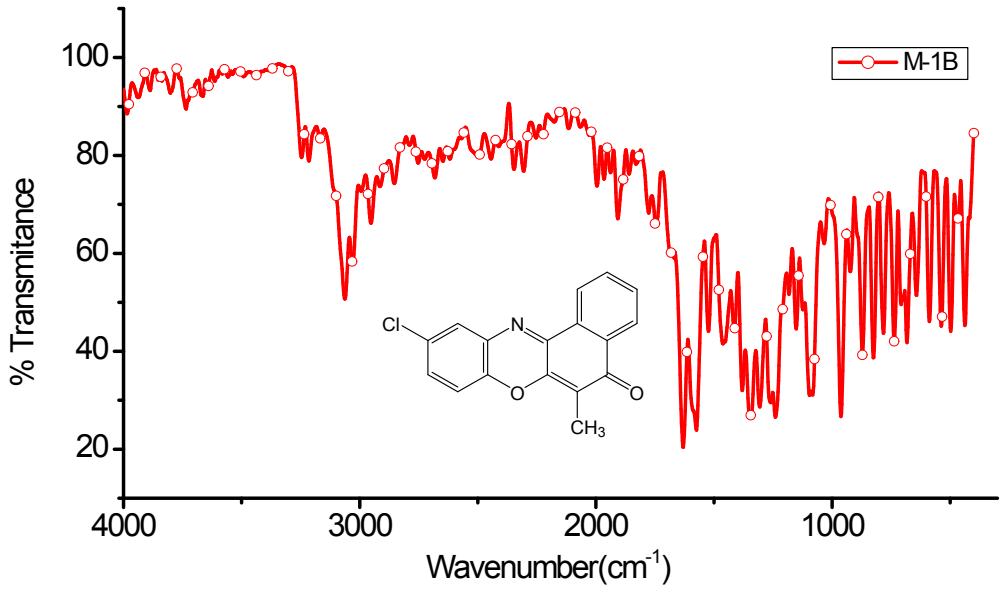


Fig.S2 FT-IR spectrums of **M-1B** in region 4000 cm^{-1} to 400 cm^{-1}

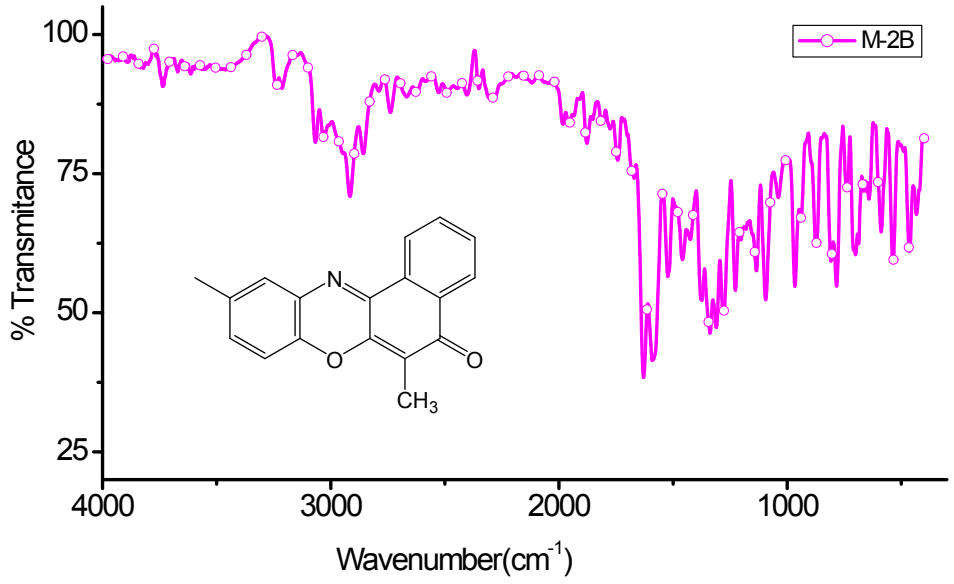


Fig.S3 FT-IR spectrums of **M-2B** in region 4000 cm^{-1} to 400 cm^{-1}

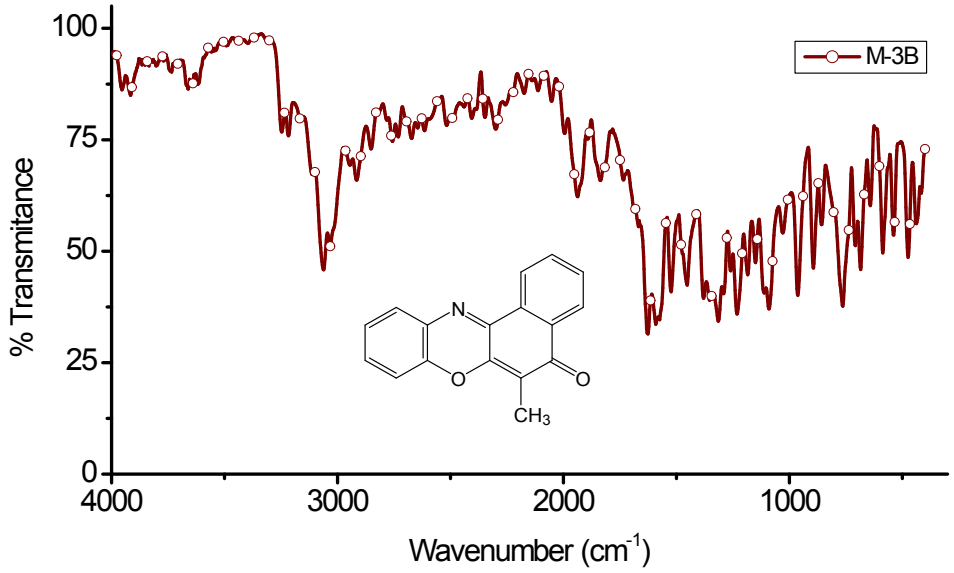


Fig.S4 FT-IR spectrums of **M-3B** in region 4000 cm^{-1} to 400 cm^{-1}

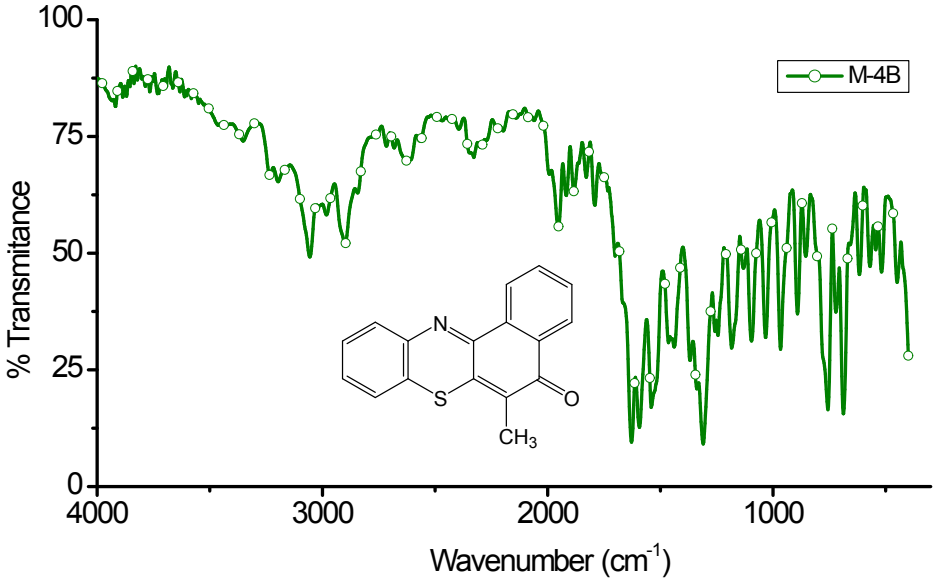


Fig.S5 FT-IR spectrums of **M-4B** in region 4000 cm^{-1} to 400 cm^{-1}

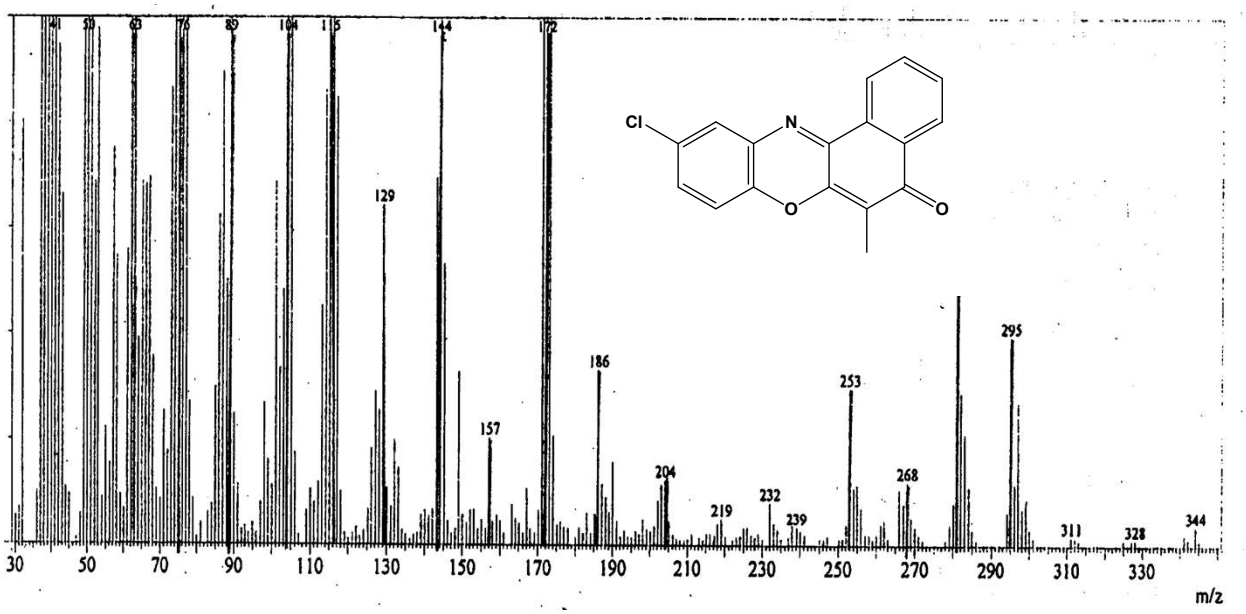


Fig.S6 GC-MS spectra of **M-1B**

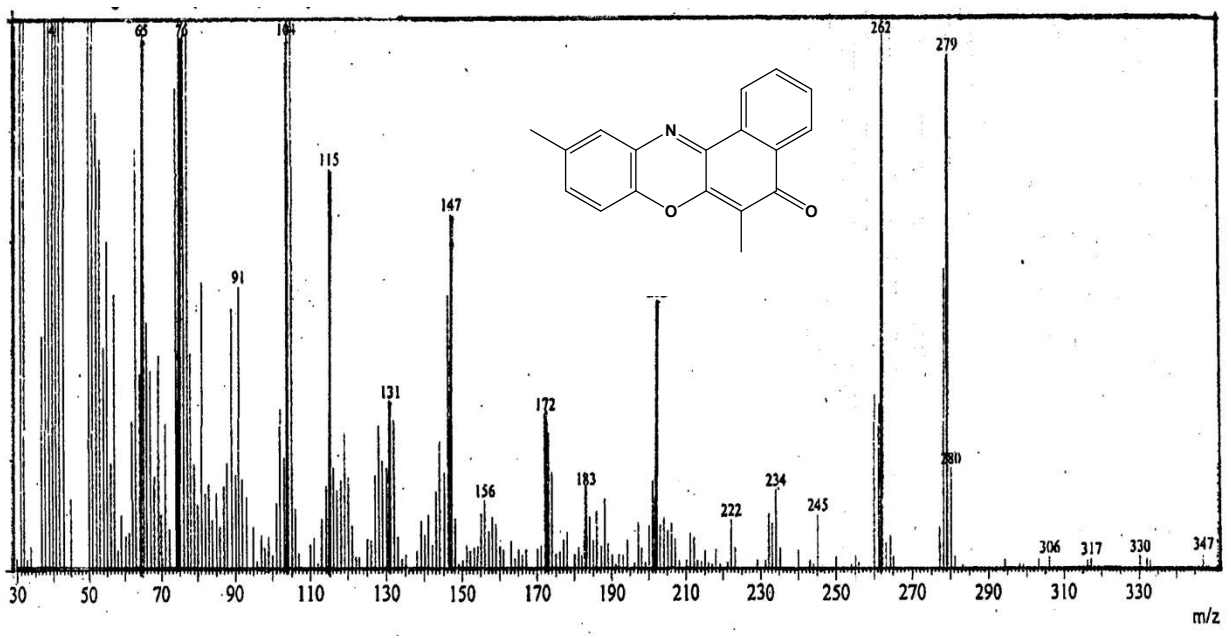


Fig.S7 GC-MS spectra of **M-2B**

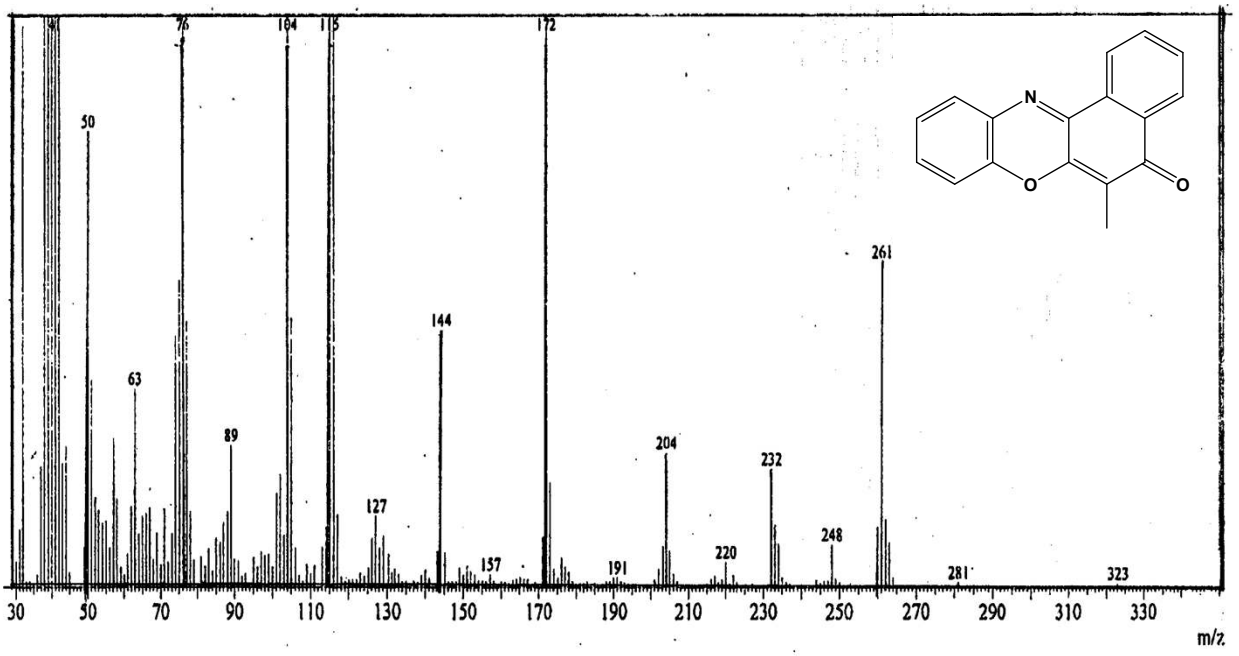


Fig.S8 GC-MS spectra of **M-3B**

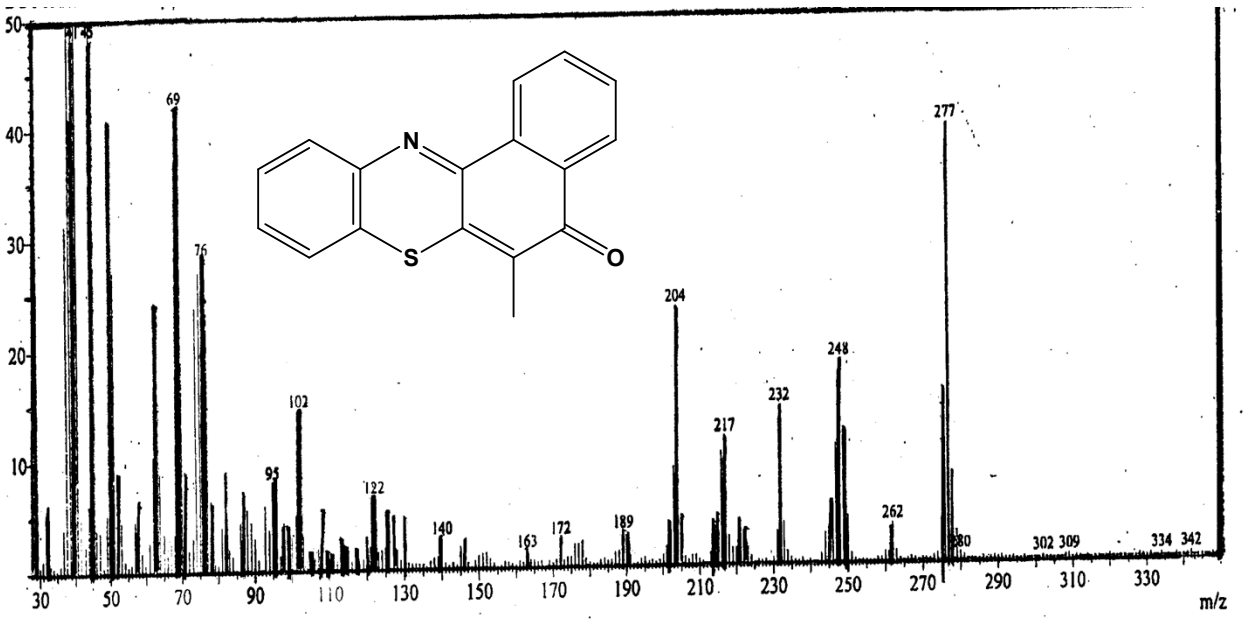


Fig.S9 GC-MS spectra of **M-4B**

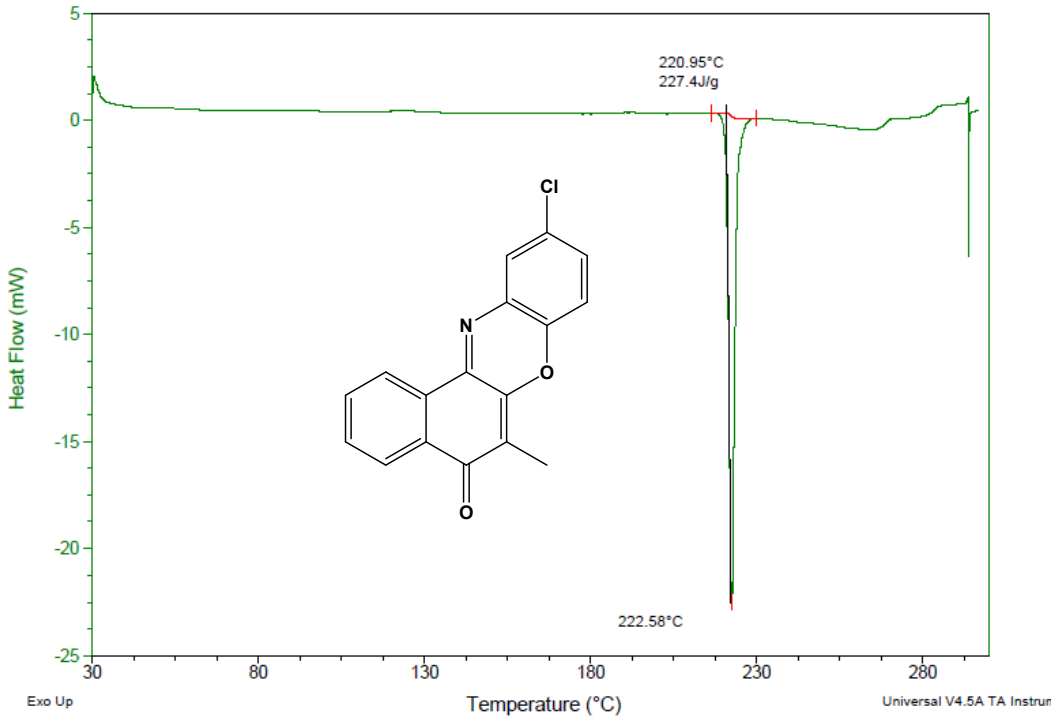


Fig.S10 DSC plot of **M-1B**

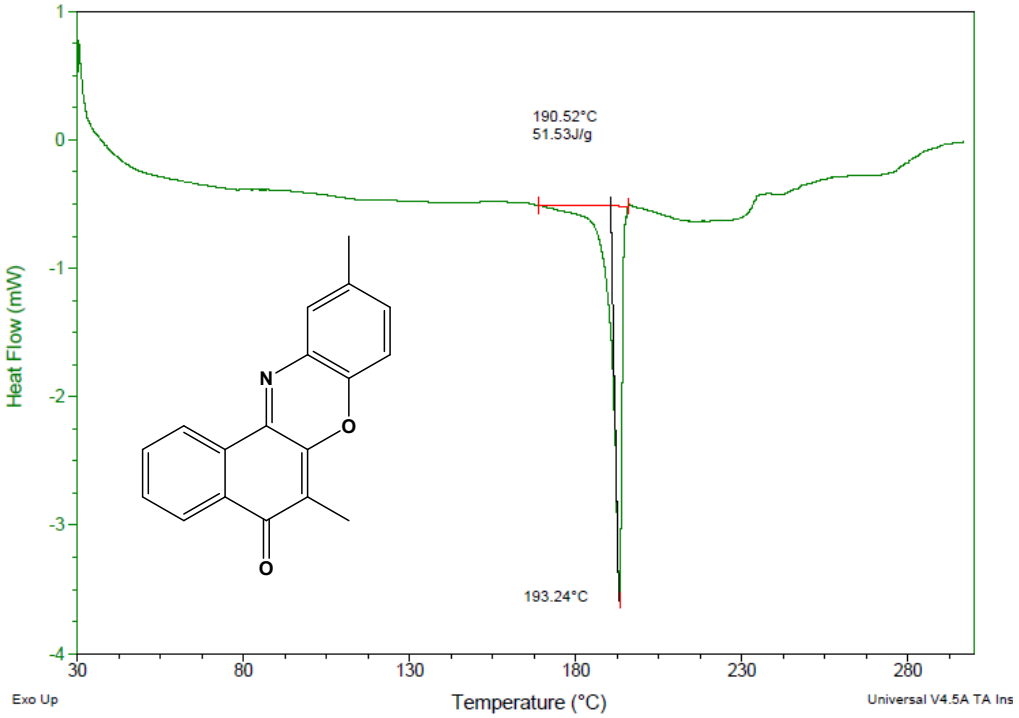


Fig.S11 DSC plot of **M-2B**

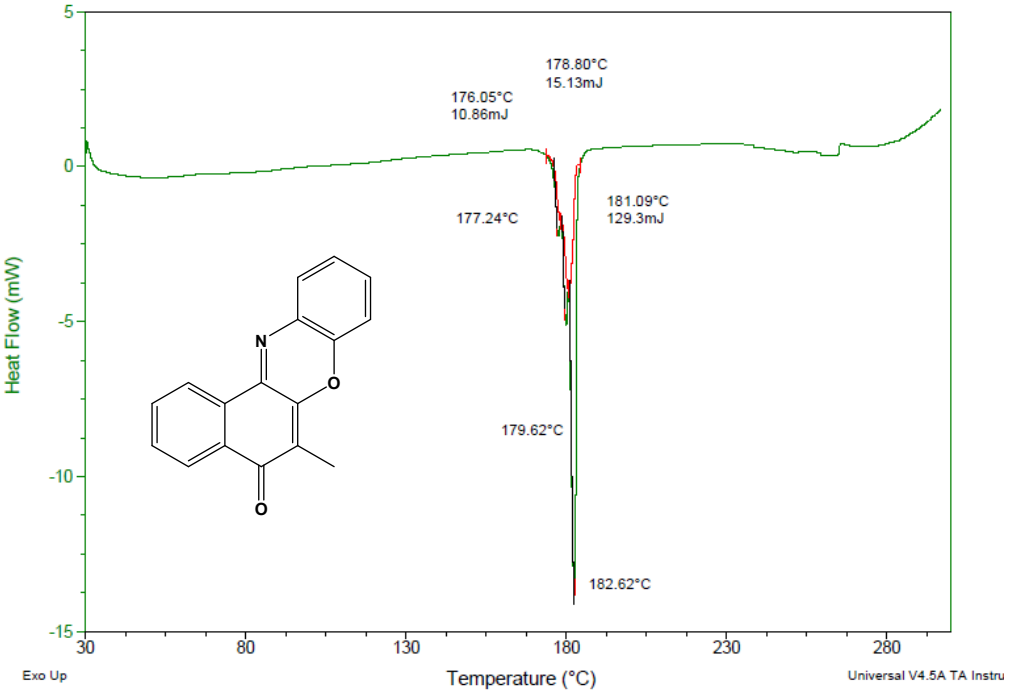


Fig.S12 DSC plot of **M-3B**

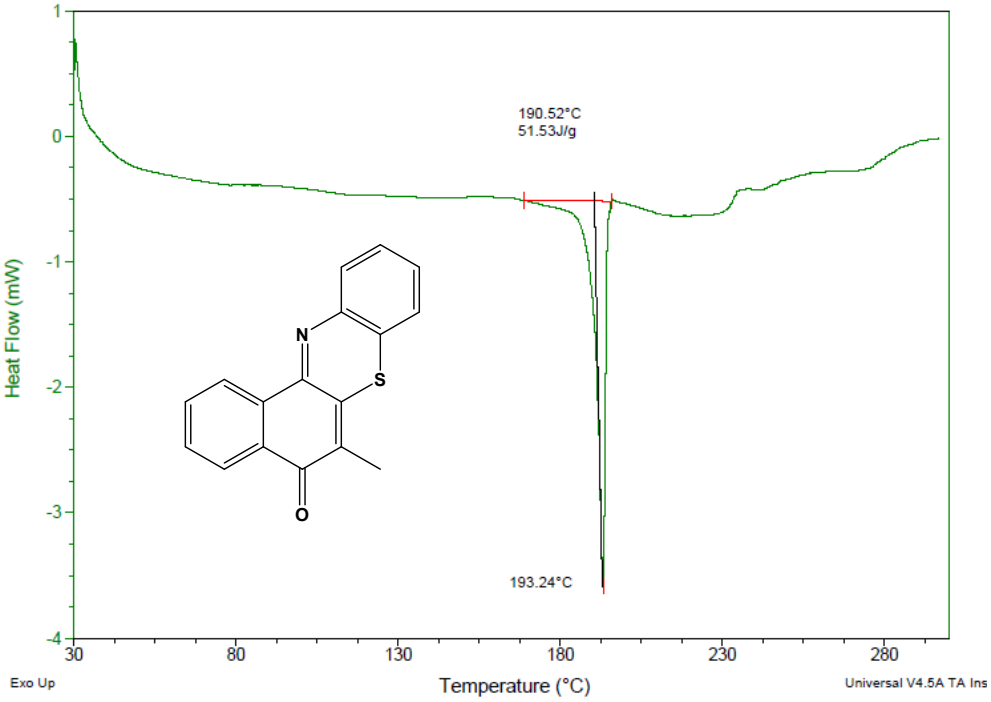
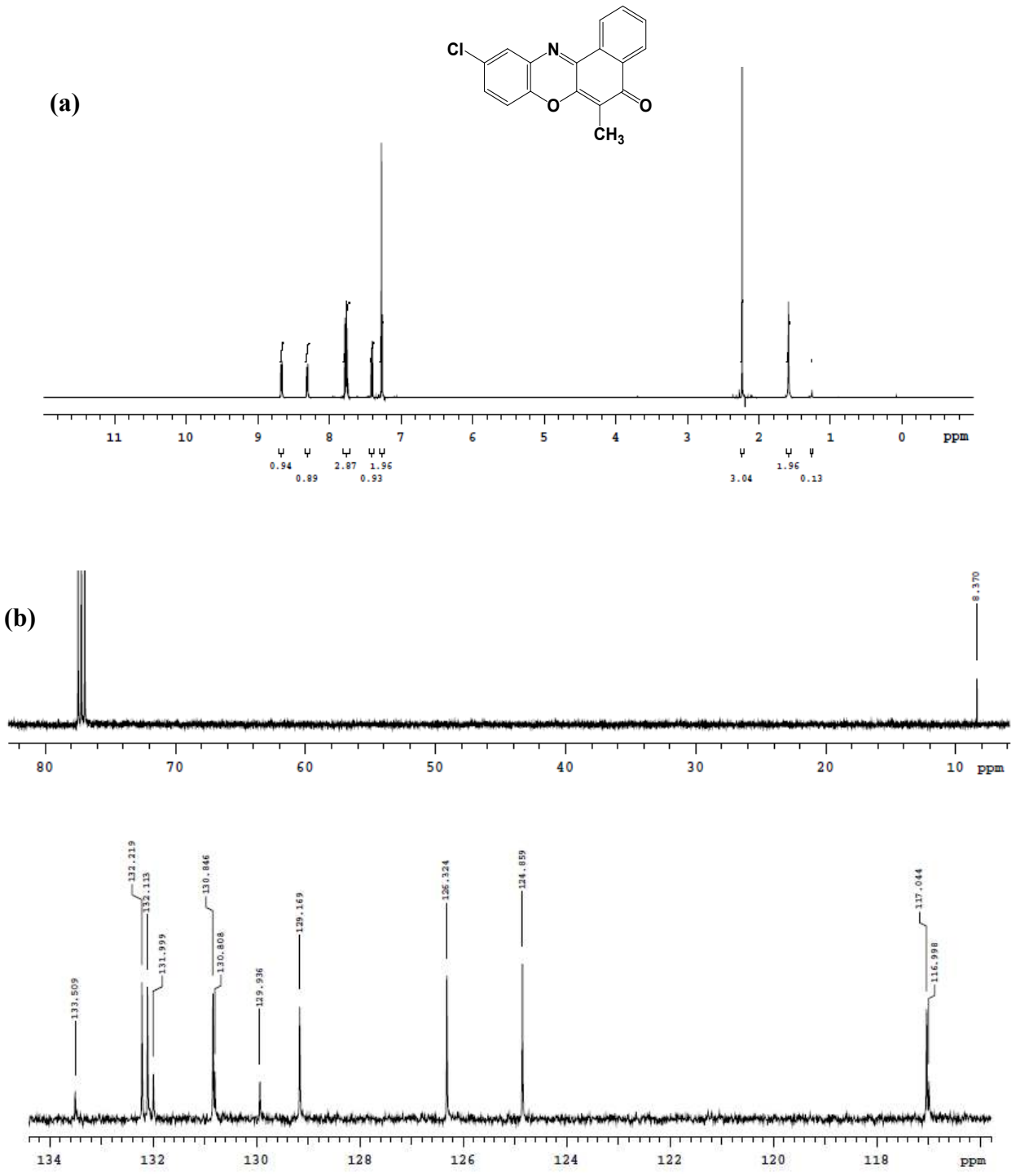


Fig.S13 DSC plot of **M-4B**


(a)
Cl
N
O
O
CH3
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.94 0.89 2.87 1.96 0.93
3.04 1.96 0.13
(b)
8.370
80 70 60 50 40 30 20 10 ppm
133.509
132.219
132.113
131.999
130.846
130.808
129.936
129.169
126.324
124.859
117.044
116.998
134 132 130 128 126 124 122 120 118 ppm

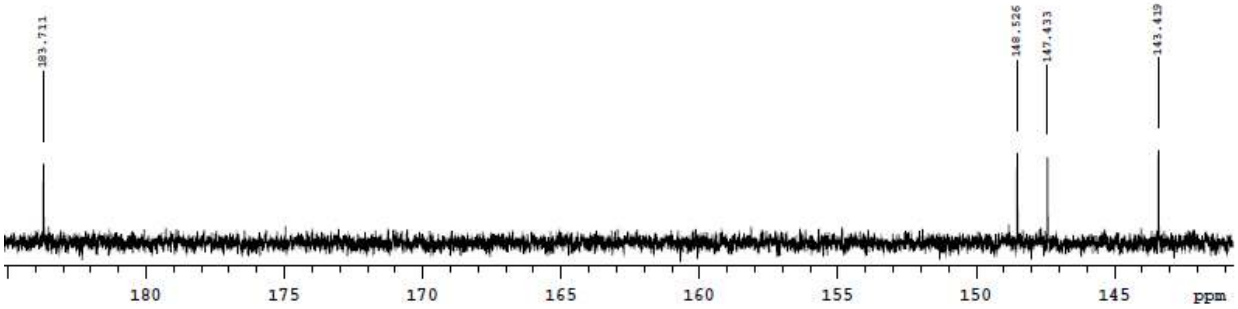
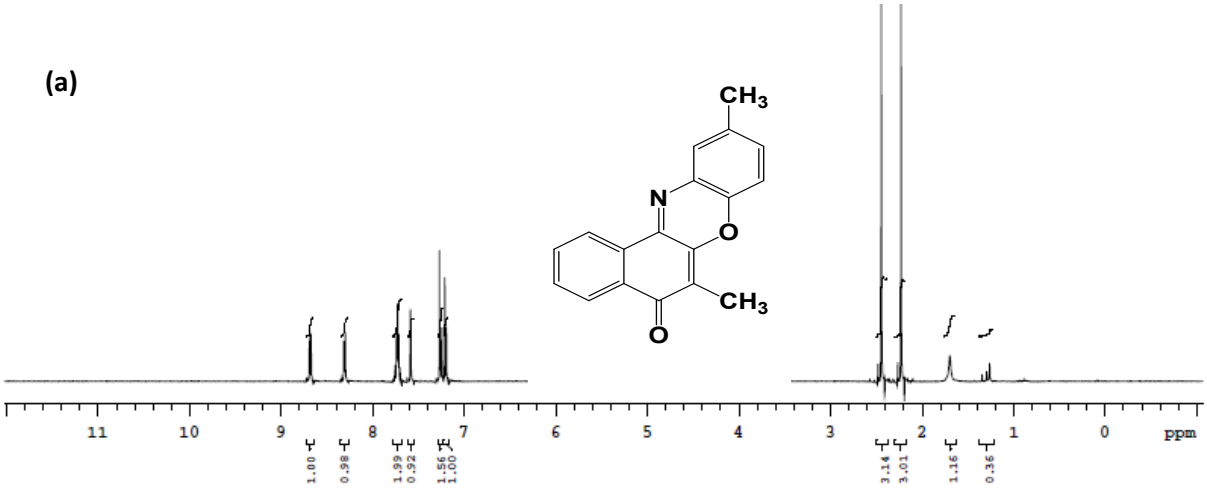
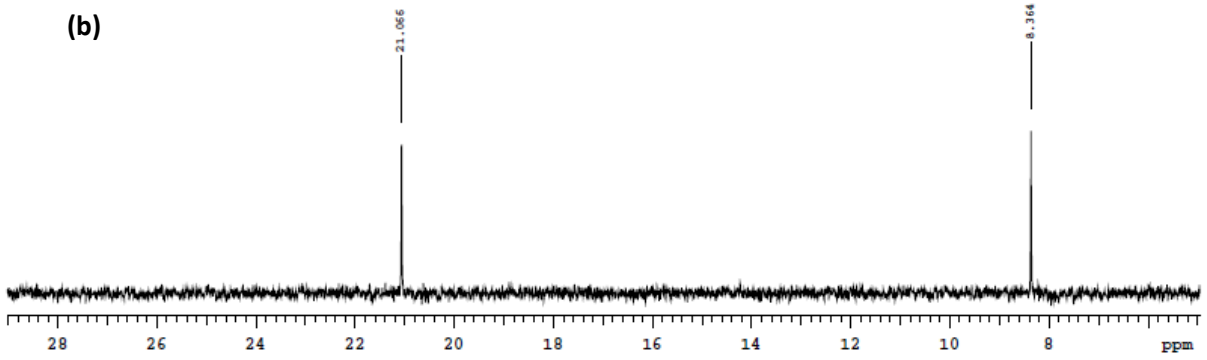


Fig.S14 a) ^{1}H, b) ^{13}C NMR spectra of **M-1B**





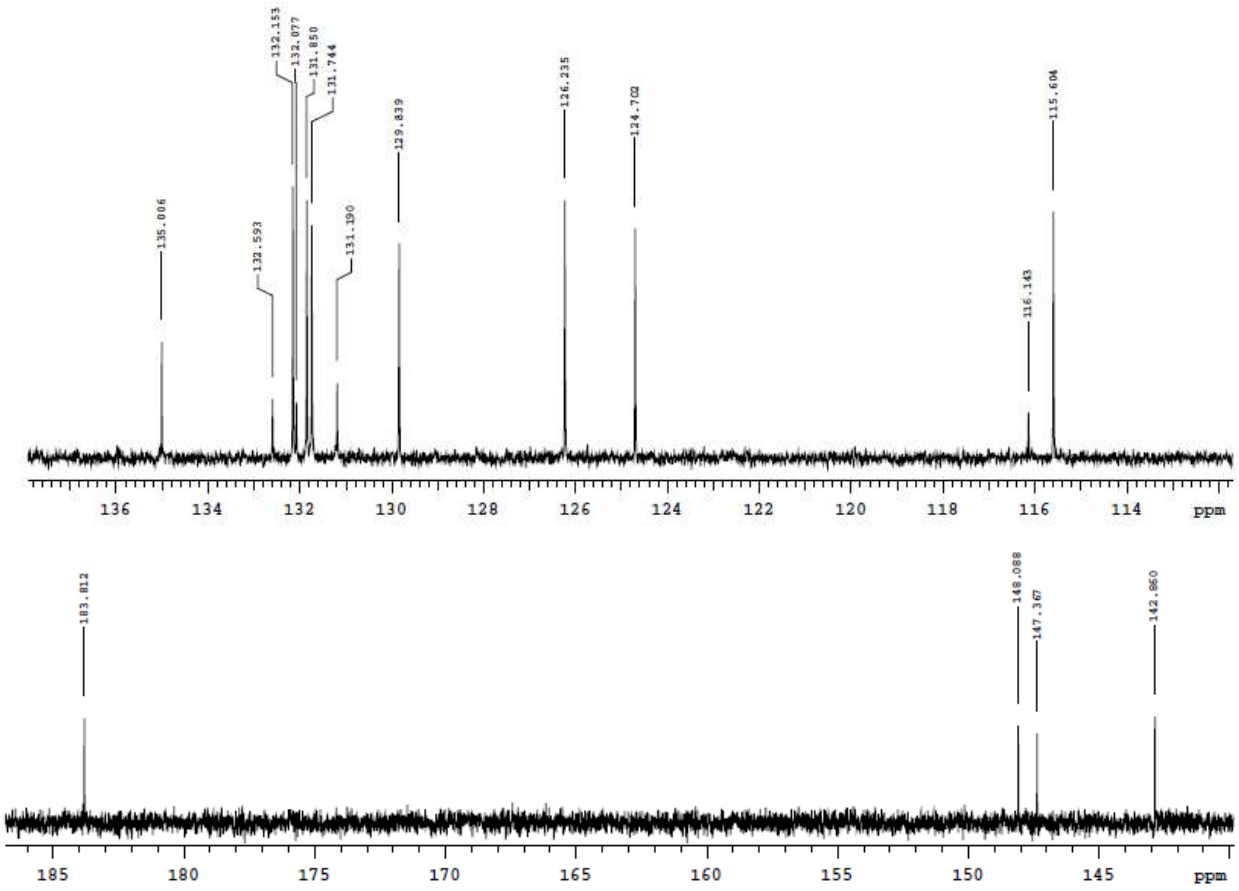


Fig.S15 a) ^{1}H, b) ^{13}C NMR spectra of **M-2B**

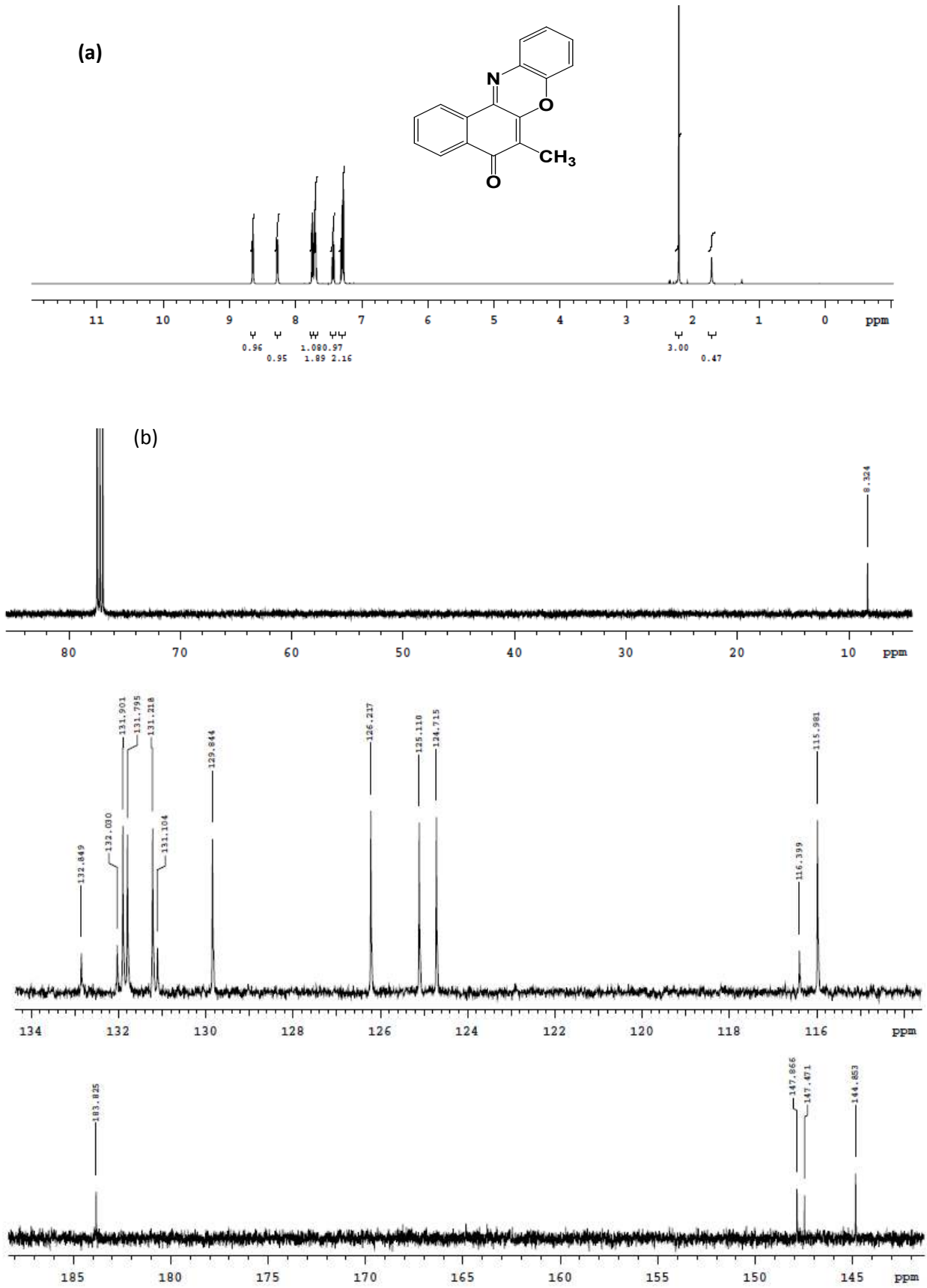


Fig.S16 a) ^{1}H, b) ^{13}C NMR spectra of **M-2B**

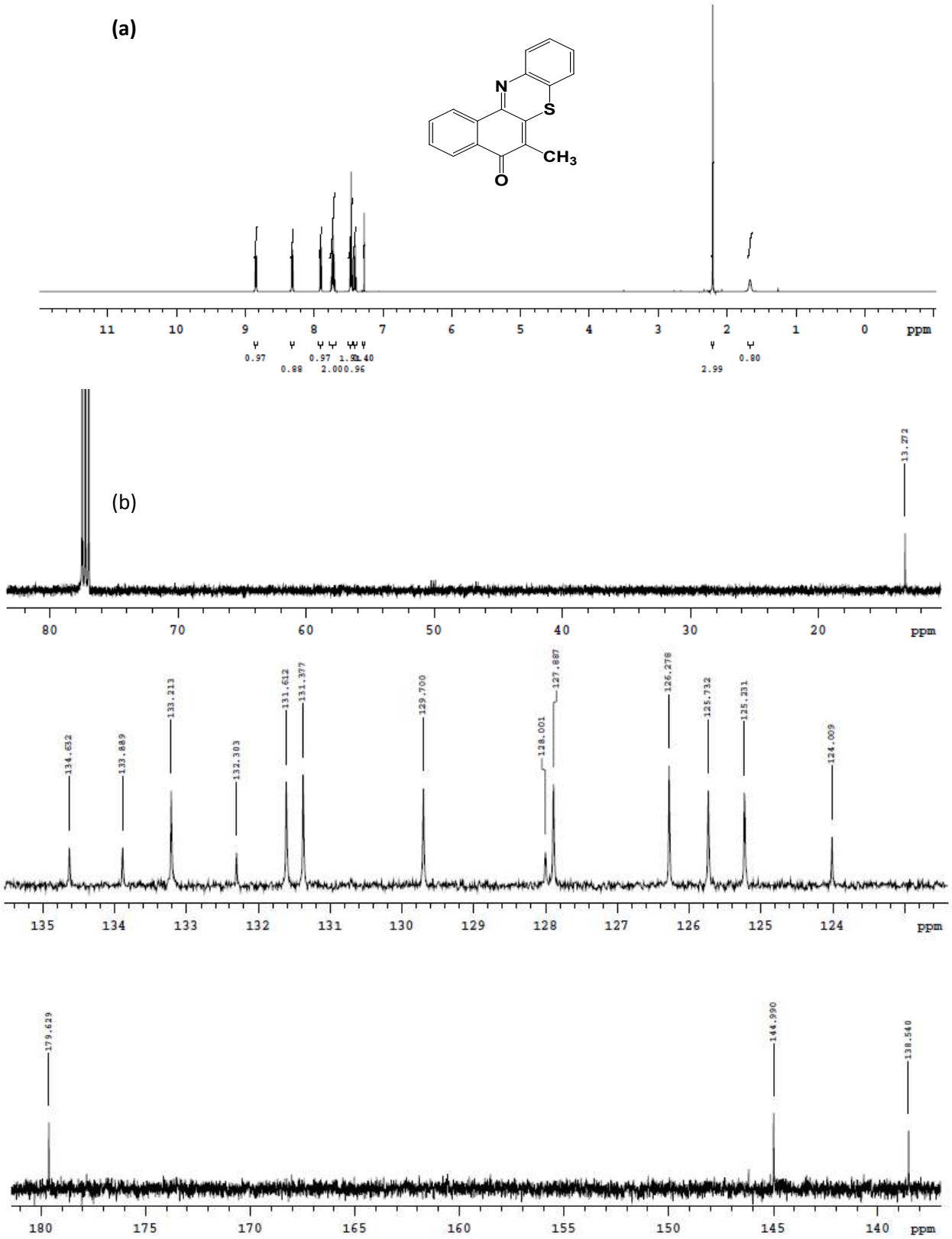


Fig.S17 a) ^{1}H, b) ^{13}C NMR spectra of **M-4B**

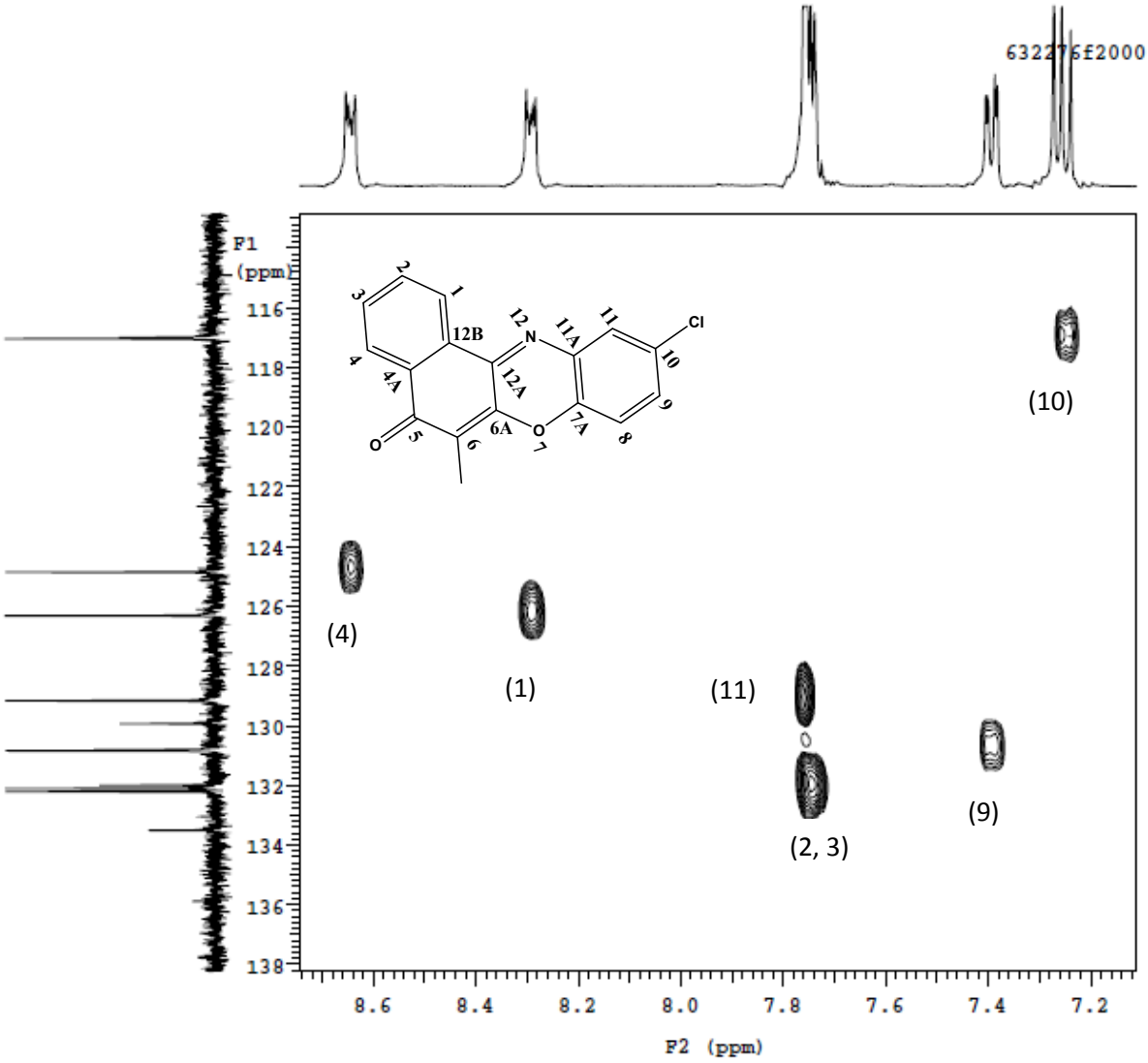


Fig.S18 2D gHSQCAD NMR spectra of **M-1B**

Interpretation of the 2D gHSQCAD NMR of M-1B that shows the correlation between the Carbon and Proton

Spot (8) show the correlation between the proton i.e. observed at 7.264 ppm (C8-H) in proton NMR and the carbons observed at 117.04 ppm in carbon NMR.

Spot (9) show the correlation between the proton i.e. observed at 7.794 ppm (C9-H) in proton NMR and the carbon observed at 130.84 ppm in carbon NMR.

Spot (4) show the correlation between the proton i.e. observed at 8.646 ppm (C4-H) in proton NMR and the carbon observed at 126.32 ppm in carbon NMR.

Spot (1) show the correlation between the proton i.e. observed at 8.239 ppm (C1-H) in proton NMR and the carbon observed at 124.85 ppm in carbon NMR.

Spot (2, 3) show the correlation between the protons i.e. observed multiplate at 7.756 ppm (C2-H, C3-H) in proton NMR and the carbon observed at 132.11 (C2) ppm and 132.21 (C3) ppm carbons NMR.

Spot (11) show the correlation between the proton i.e. observed at 7.239 ppm (C11-H) in proton NMR and the carbon observed at 129.16 ppm in carbon NMR

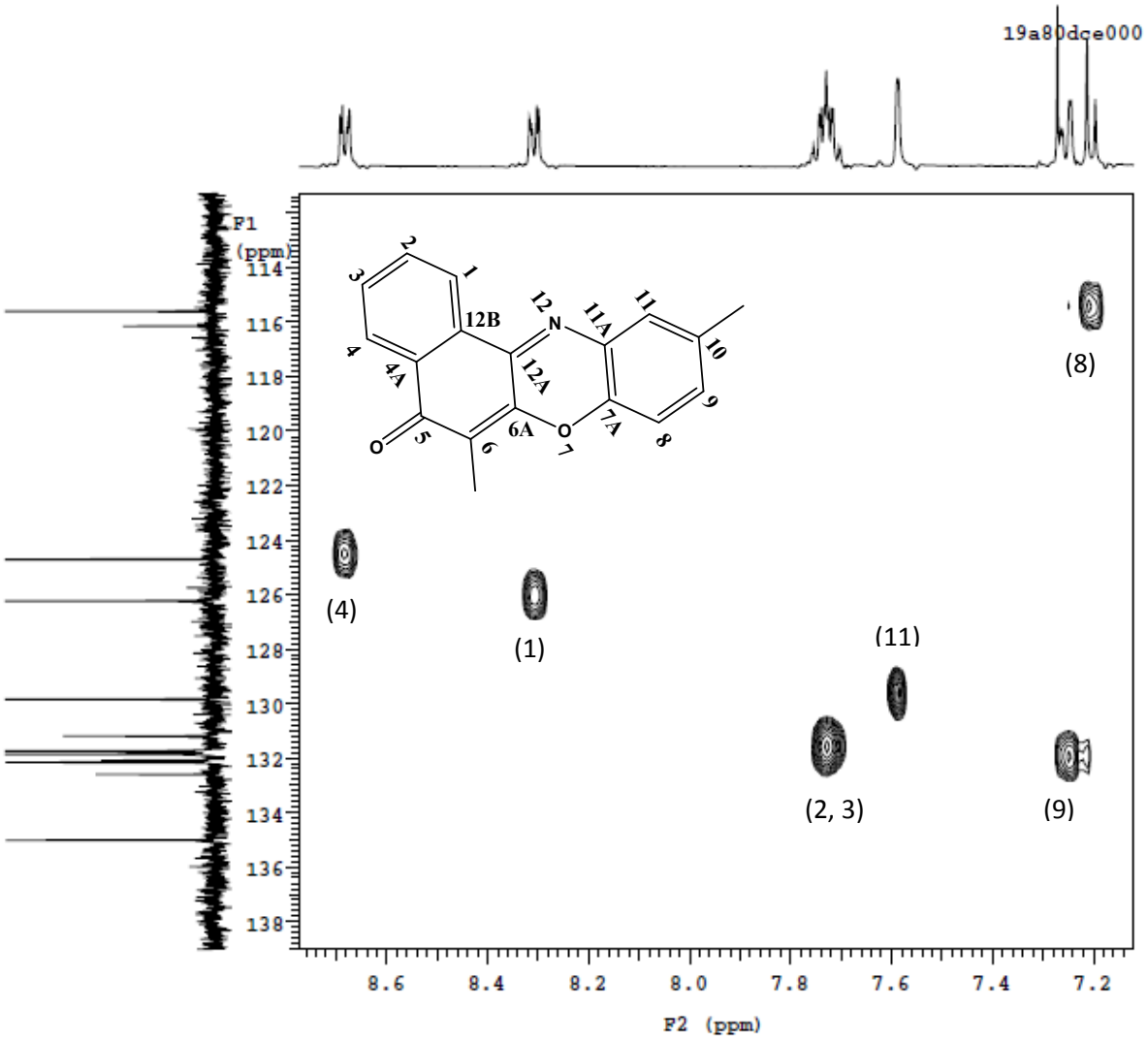


Fig.S19 2D gHSQCAD NMR spectra of **M-2B**

Interpretation of the 2D gHSQCAD NMR of M-2B that shows the correlation between the Carbon and Proton

Spot (8) show the correlation between the proton i.e. observed at 7.205 ppm (C8-H) in proton NMR and the carbon observed at 115.60 ppm in carbon NMR.

Spot (9) show the correlation between the proton i.e. observed at 7.261 ppm (C9-H) in proton NMR and the carbon observed at 131.19 ppm in carbon NMR.

Spot (4) show the correlation between the proton i.e. observed at 8.769 ppm (C4-H) in proton NMR and the carbon observed at 126.30 ppm in carbon NMR.

Spot (1) show the correlation between the protons i.e. observes at 8.311 ppm (C1-H) in proton NMR and the carbon observed at 124.70 ppm in carbon NMR.

Spot (11) show the correlation between the proton i.e. observed at 7.589 ppm (C11-H) in proton NMR and the carbon observed at 129.83 ppm in carbon NMR.

Spot (2, 3) show the correlation between the proton i.e. observed multiplate for 2H at 7.729 ppm (C-2, 3) in proton NMR and the carbon observed at 131.74 (C2-H) and 131.85 (C3-H) ppm in carbon NMR.

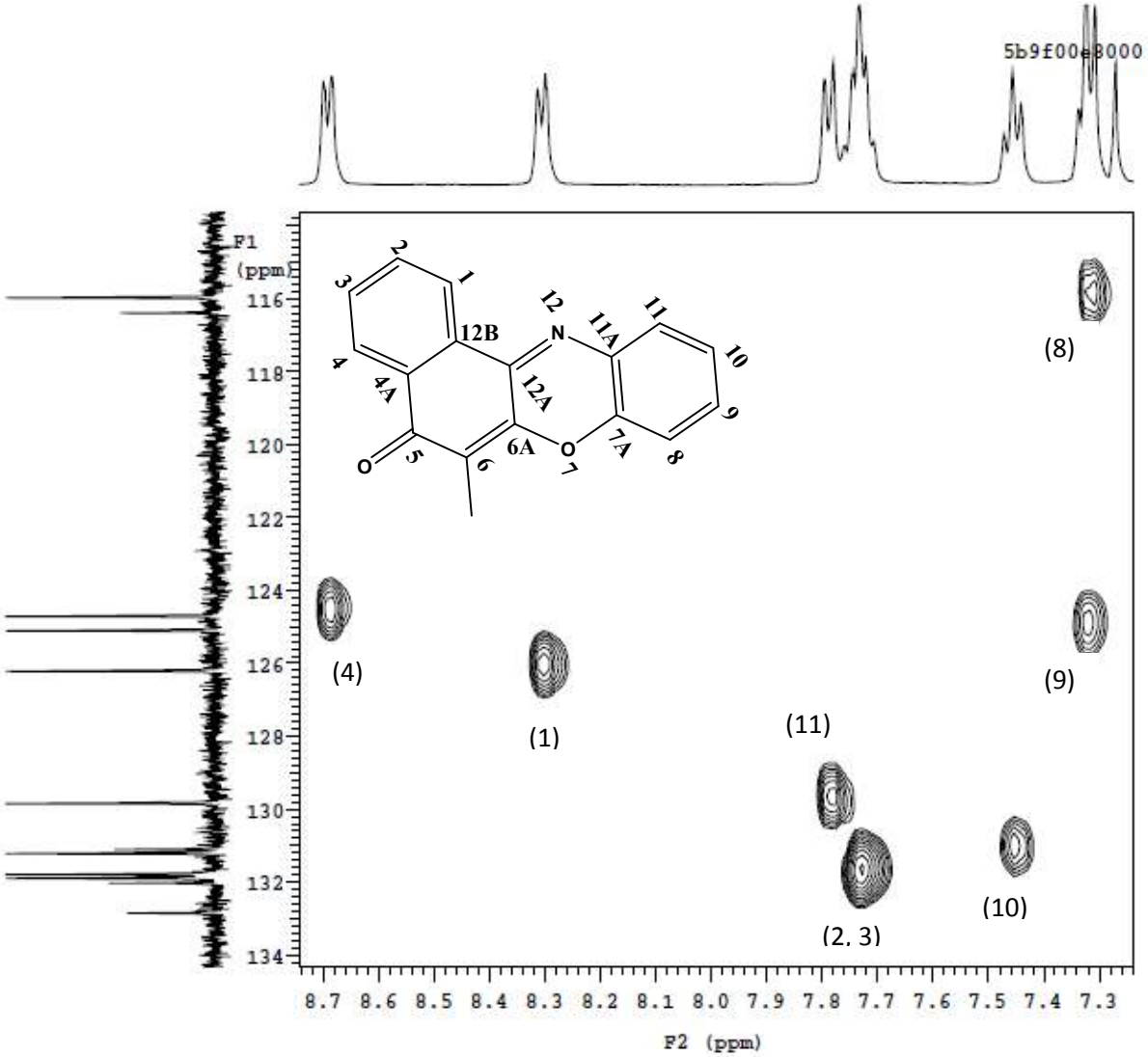


Fig.S20 2D gHSQCAD NMR spectra of **M-3B**

Interpretation of the 2D gHSQCAD NMR of M-3B that shows the correlation between the Carbon and Proton

Spot (8) show the correlation between the proton i.e. observed at 7.270 ppm (C8-H) in proton NMR and the carbon observed at 115.98 ppm in carbon NMR.

Spot (9) show the correlation between the proton i.e. observed at 7.324 ppm (C9-H) in proton NMR and the carbon observed at 125.11 ppm in carbon NMR. 7.324

Spot (10) show the correlation between the proton i.e. observed at 7.457 ppm (C10-H) in proton NMR and the carbon observed at 131.21ppm in carbon NMR.

Spot (11) show the correlation between the proton i.e. observed at 7.795 ppm (C11-H) in proton NMR and the carbon observed at 129.84 ppm in carbon NMR.

Spot (1) show the correlation between the proton i.e. observed at 8.307 ppm (C1-H) in proton NMR and the carbon observed at 124.71 ppm in carbon NMR.

Spot (4) show the correlation between the proton i.e. observed at 8.935 ppm (C4-H) in proton NMR and the carbon observed at 126.21 ppm in carbon NMR.

Spot (2, 3) show the correlation between the proton i.e. observed multiplate for 2H at 7.766 ppm (C-2, 3) in proton NMR and the carbon observed at 131.79 (C2-H) and 131.90 (C3-H) ppm in carbon NMR.

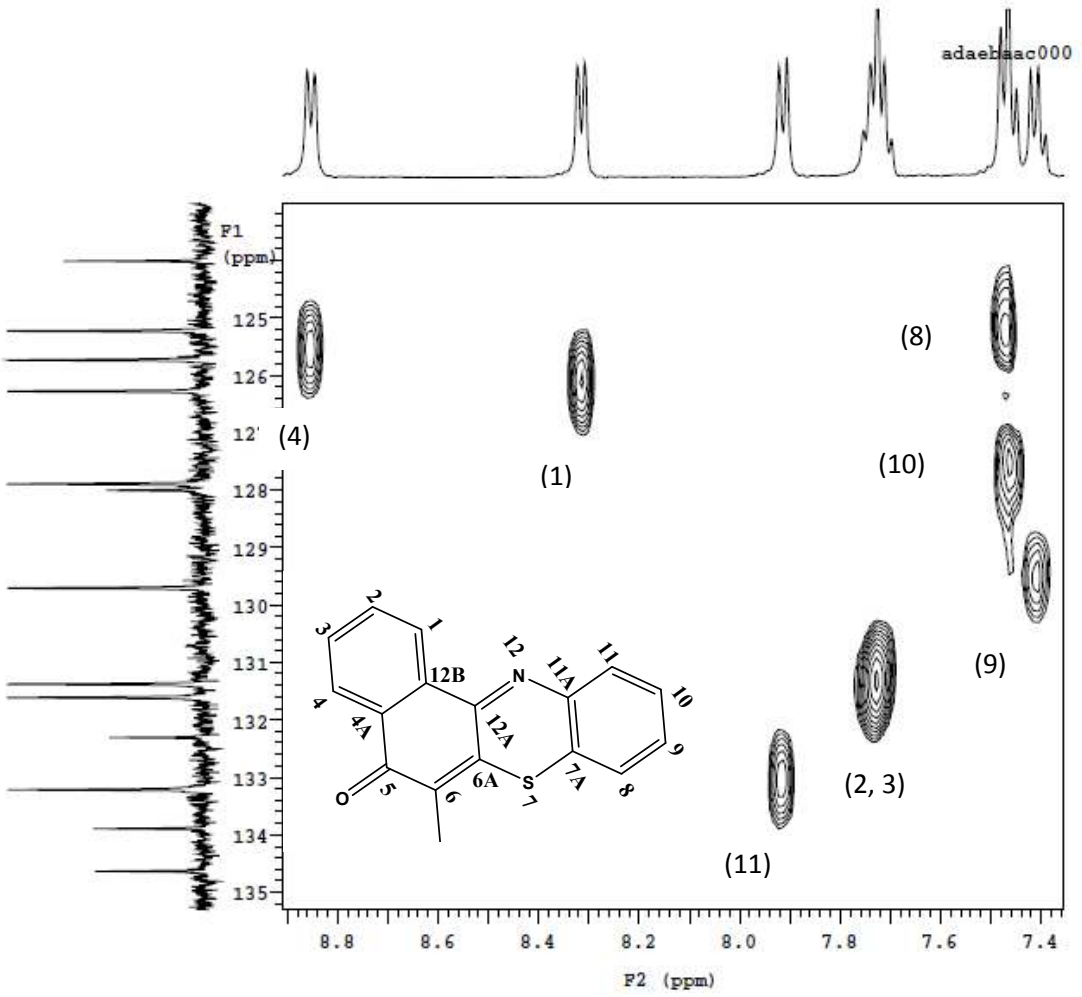


Fig.S21 2D gHSQCAD NMR spectra of **M-4B**

Interpretation of the 2D gHSQCAD NMR of M-4B that shows the correlation between the Carbon and Proton.

Spot (8) show the correlation between the proton i.e. observed at 7.271 ppm (C8-H) in proton NMR and the carbon observed at 125.73 ppm in carbon NMR.

Spot (9) show the correlation between the proton i.e. observed at 7.405 ppm (C9-H) in proton NMR and the carbon observed at 127.78 ppm in carbon NMR.

Spot (10) show the correlation between the proton i.e. observed at 7.465 ppm (C10-H) in proton NMR and the carbon observed at 129.70 ppm in carbon NMR.

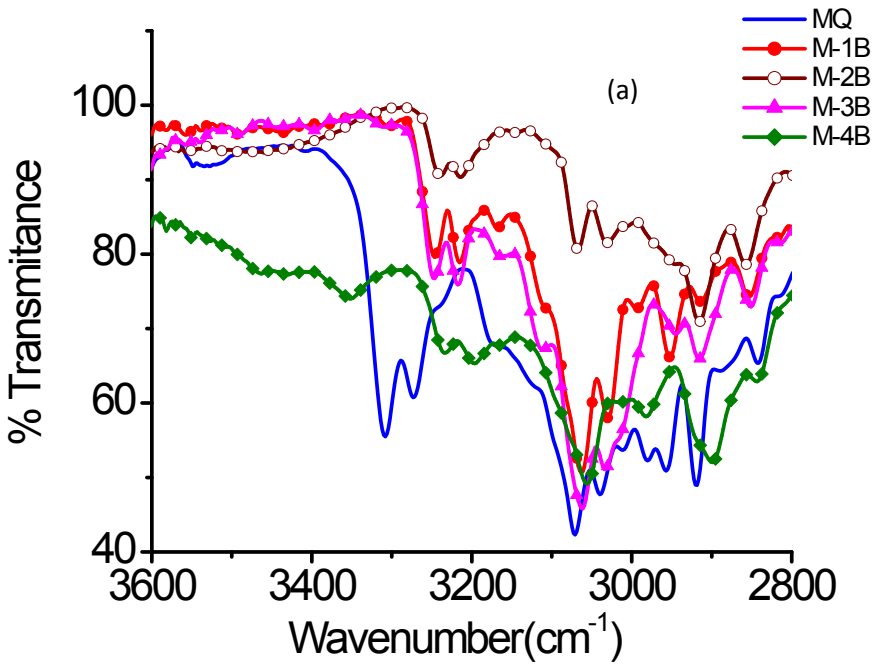
Spot (11) show the correlation between the proton i.e. observed at 7.914 ppm (C11-H) in proton NMR and the carbon observed at 133.21 ppm in carbon NMR.

Spot (1) show the correlation between the proton i.e. observed at 8.316 ppm (C1-H) in proton NMR and the carbon observed at 125.23 ppm in carbon NMR.

Spot (4) show the correlation between the proton i.e. observed at 8.853 ppm (C4-H) in proton NMR and the carbon observed at 126.27 ppm in carbon NMR.

Spot (10) show the correlation between the proton i.e. observed at 7.475 ppm (C10-H) in proton NMR and the carbon observed at 125.45 ppm in carbon NMR.

Spot (2, 3) show the correlation between the proton i.e. observed multiplate for 2H at 7.727 ppm (C-2, 3) in proton NMR and the carbon observed at 131.37 (C2-H) and 131.61 (C3-H) ppm in carbon NMR.



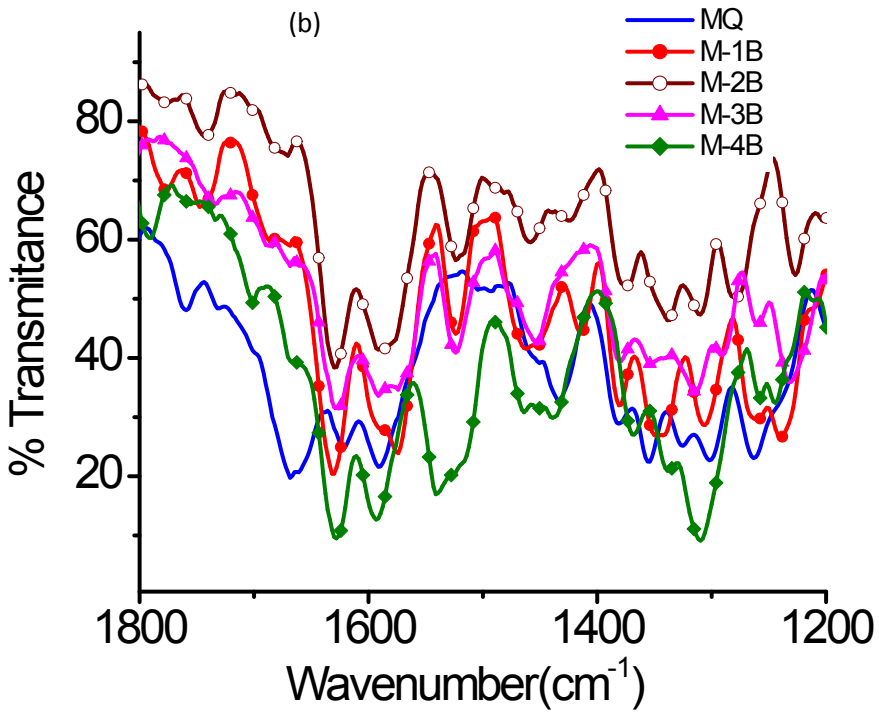


Fig.S22 (a) FT-IR spectra of M-1B, M-2B, M-3B, M-4B in region 3500-2500 cm^{-1} and (b) in region of 1850 to 1550 cm^{-1}

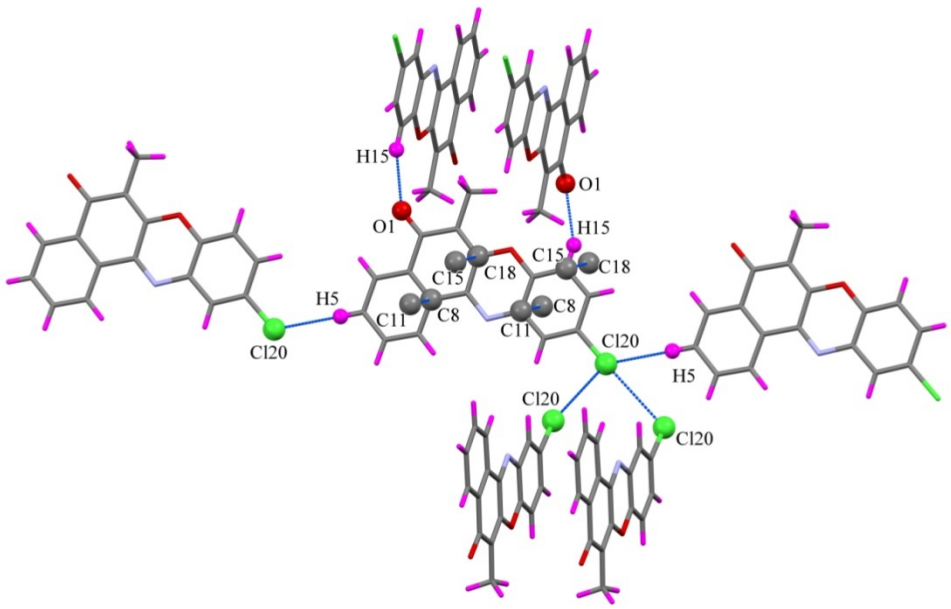


Fig.S23 Molecular association of **M-1B** via C-H···O, C-H···Cl, Cl···Cl (Table 2) and π-π stacking interactions

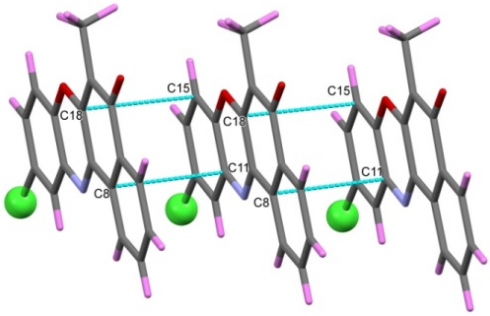
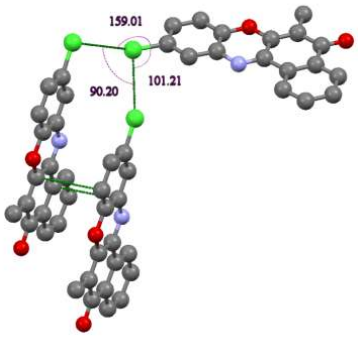


Fig.S24 Slipped π-π stacking interactions in **M-1B**



b) Cl···Cl interactions in **M-1B** down the c-axis

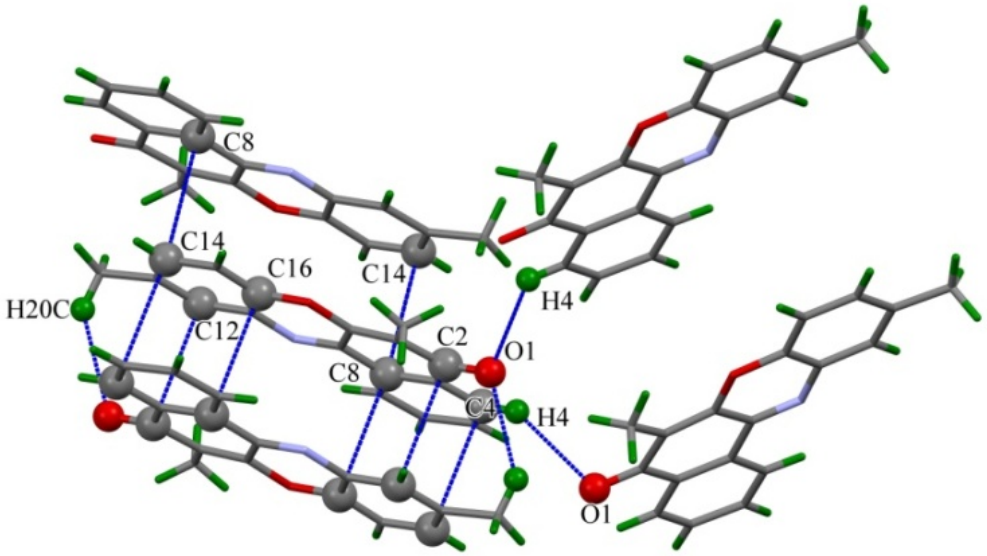


Fig.S25 Molecular association accompanying **M-2B**

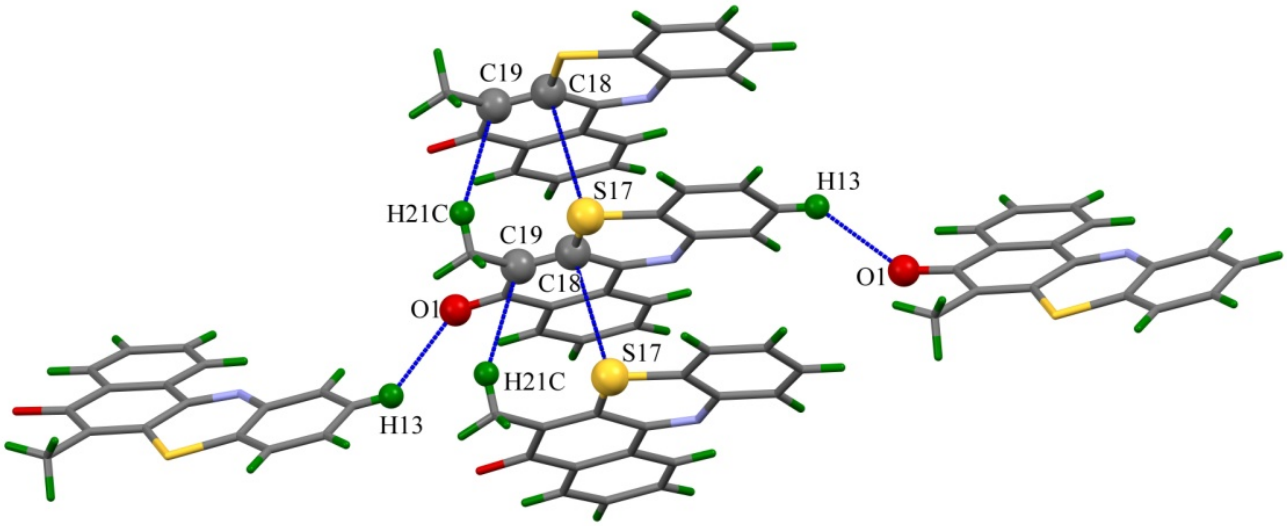


Fig.S26 Interactions from neighboring molecules in **M-4B**

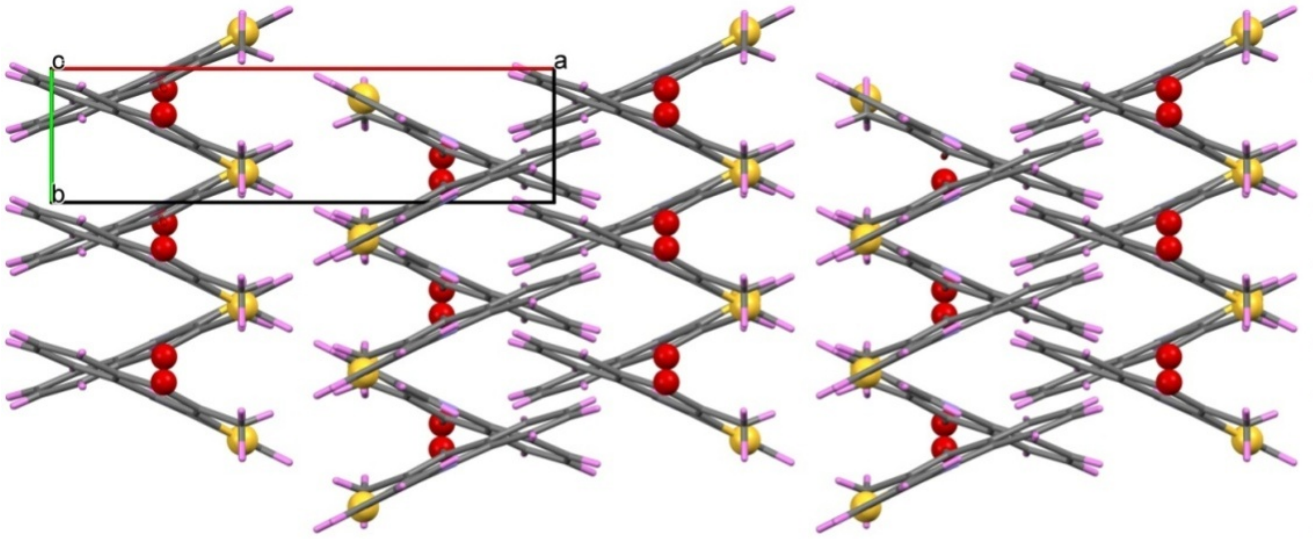


Fig.S27 Butterfly like arrangement of molecules of **M-4B** down c-axis

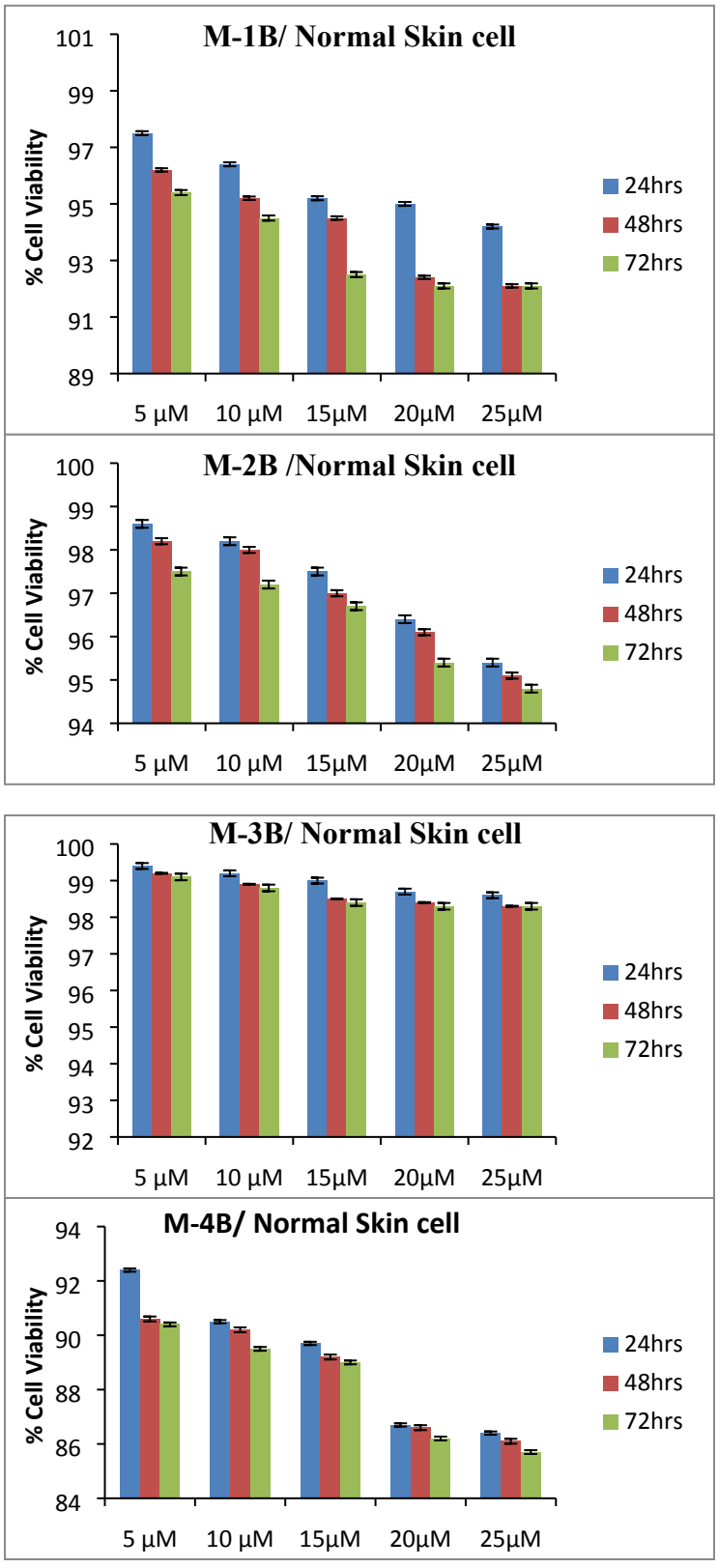
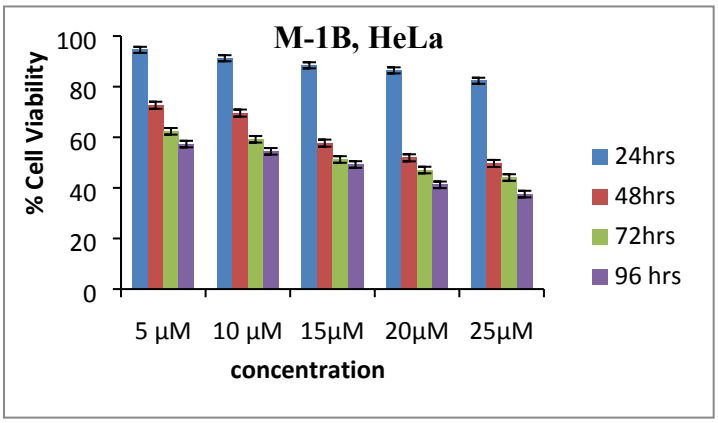
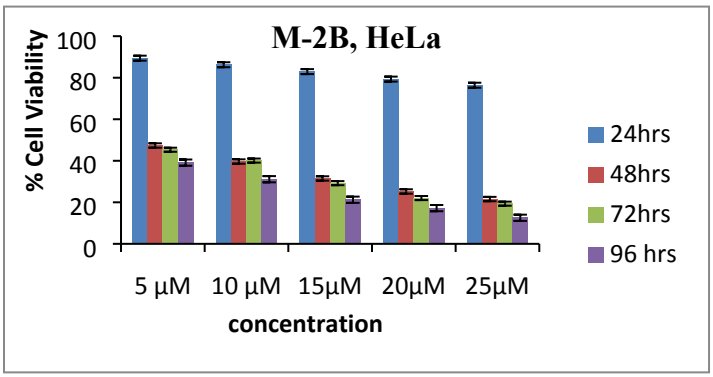
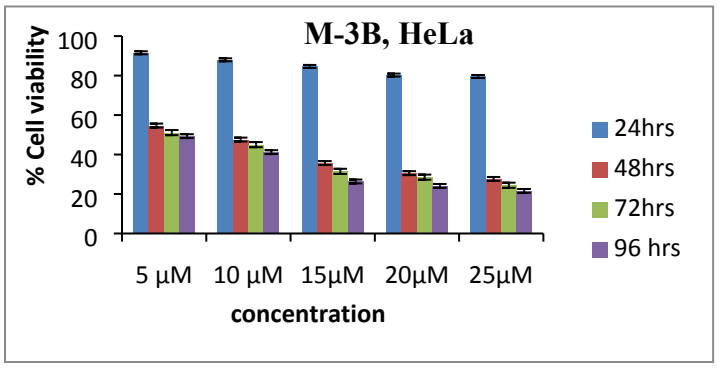


Fig.S28 Concentration dependent cytotoxicity of compounds **M-1B** to **M-4B** against normal skin cell line evaluated by MTT assay after 24, 48, 72, and 96 hours. Results are mean values of 3 identical experiments


M-1B, HeLa
% Cell Viability
100
80
60
40
20
0
5 µM
10 µM
15µM
20µM
25µM
concentration
24hrs
48hrs
72hrs
96 hrs


M-2B, HeLa
% Cell Viability
100
80
60
40
20
0
5 µM
10 µM
15µM
20µM
25µM
concentration
24hrs
48hrs
72hrs
96 hrs


M-3B, HeLa
% Cell viability
100
80
60
40
20
0
5 µM
10 µM
15µM
20µM
25µM
concentration
24hrs
48hrs
72hrs
96 hrs

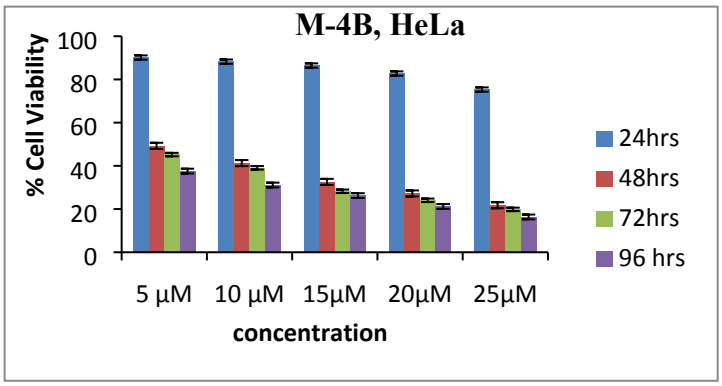

M-4B, HeLa
% Cell Viability
100
80
60
40
20
0
5 µM
10 µM
15µM
20µM
25µM
concentration
24hrs
48hrs
72hrs
96 hrs

Fig.S29 Concentration dependent cytotoxicity of compounds **M-1B** to **M-4B** against MCF-7 cell lines evaluated by MTT assay after 24, 48, 72, and 96 hours. Results are mean values of 3 identical experiments

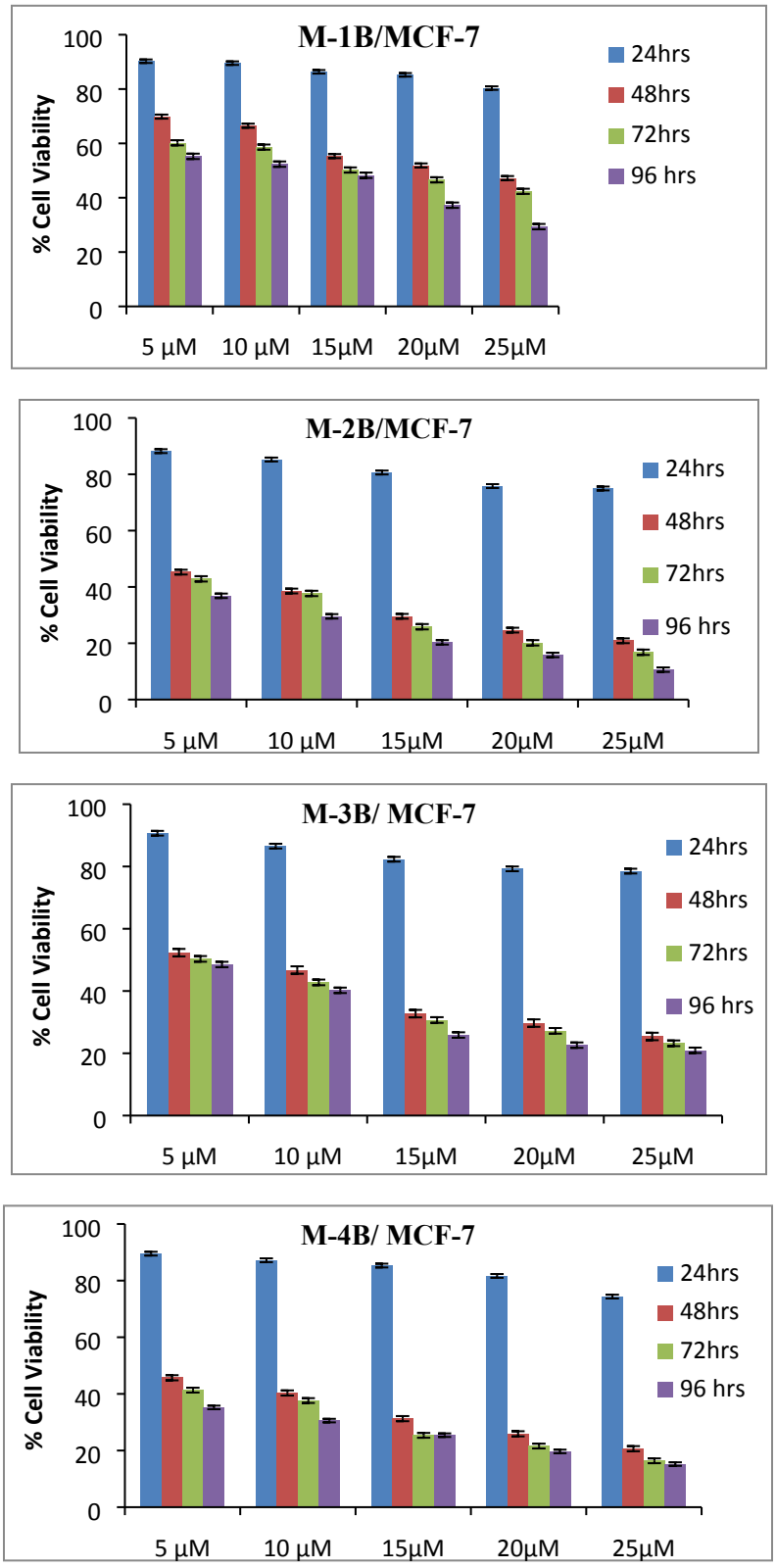


Fig.S30 Concentration dependent cytotoxicity of compounds **M-1B** to **M-4B** against MCF-7 cell lines evaluated by MTT assay after 24, 48, 72, and 96 hours. Results are mean values of 3 identical experiments

Table S1. Stretching frequencies of **M-1B**, **M-2B**, **M-3B**, **M-4B**

Comp.	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{C=C}$	$\nu_{C-H\ (Ar-H)}$	ν_{C-O}	ν_{p-NQ}	ν_{C-Cl}
MQ	1660, 1622	…	1523, 1348	3308, 3070, 2956,2918	…	1240	….
M-1B	1630	1573	1523, 1348	3063,3030,2953,2852	1095	1240	736
M-2B	1629	1585	1524, 1338	3066,3030, 2916, 2856	1093	1226	….
M-3B	1628	1591	1523, 1313	3061,2955,2914, 2850	1095	1240	….
M-4B	1628	1593	1541, 1338	3055, 2982, 2899, 2843	1095	1244	….

Table S2. Chemical Shift (δ) in ppm and coupling constant *J* in Hz for **M-1B**, **M-2B**, **M-3B** and **M-4B**

Comp.	**M-1B**	**M-2B**	**M-3B**	**M-4B**
Ar-H (d) (C1)	8.29 (7.25 Hz)	8.311 (8.00 Hz)	8.307 (7.00 Hz)	8.316 (7.50 Hz)
Ar-H (m) (C2)	7.756 (8.00 Hz)	7.729 (8.25 Hz)	7.773 (8.00 Hz)	8.853 (7.50 Hz)
Ar-H (m) (C3)	7.756 (8.00 Hz)	7.729 (8.25 Hz)	7.773 (8.00 Hz)	7.272 (8.00 Hz)
Ar-H (d) (C4)	8.646 (8.00 Hz)	8.679 (8.00 Hz)	8.933 (7.50 Hz)	7.272 (8.00 Hz)
Ar-H (d) (C8)	7.264 (8.00 Hz)	7.205 (7.50 Hz)	7.270 (8.00 Hz)	7.271 (7.75 Hz)
Ar-H (d) (C9)	7.794 (8.00 Hz)	7.261 (8.25 Hz)	7.795 (7.75 Hz)	7.405 (7.50 Hz)
Ar-H (t) (C9)	**…**	**…**	7.234 (7.50 Hz)	7.465 (7.75 Hz)
Ar-H (t) (C10)	**…**	**…**	7.457 (7.50 Hz)	7.46 (7.50 Hz)
Ar-H (s) (C11)	7.230 (s, 1H)	7.589 (s, 1H)	**…**	**...**
Ar-CH_3(s) (C13)	2.223 (s, 3H)	2.230 (s, 3H)	2.239 (s, 3H)	2.210 (s, 3H)
CH_3 (s) (C13')	…	2.445 (s, 3H)	…	…

Table S3. ^{13}C NMR chemical shifts of **M-1B**, **M-2B**, **M-3B** and **M-4B** in $CDCl_3$.

Carbon No.	M-1B	M-2B	M-3B	M-4B
C1	124.85	124.70	124.71	125.23
C2	132.11	131.74	131.79	131.37
C3	132.21	131.85	131.90	131.61
C4	126.32	126.30	126.21	126.27
C4a	131.99	132.59	132.03	133.88
C5	183.71	183.81	183.82	179.62
C6	116.99	116.14	116.39	124.00
C6a	143.41	142.86	144.85	134.63
C7a	133.50	135.00	132.84	128.00
C8	117.04	115.60	115.98	125.73
C9	130.84	132.15	125.11	127.88
C10	129.93	131.19	131.21	129.70
C11	129.16	129.83	129.84	133.21
C11a	147.43	147.36	147.47	138.54
C12a	148.52	148.08	147.86	144.99
C12b	130.80	132.07	131.10	132.30
C13	8.37	8.36	8.24	13.27
C13’	…	21.06	…	…

Table S4 Bond lengths [Å] and angles [°] for M-1B

O(1)-C(2)	**1.230(2)**
C(2)-C(19)	**1.464(3)**
C(2)-C(3)	**1.493(3)**
C(3)-C(8)	**1.395(3)**
C(3)-C(4)	**1.398(3)**
C(4)-C(5)	**1.386(3)**
C(5)-C(6)	**1.389(3)**
C(6)-C(7)	**1.384(3)**
C(7)-C(8)	**1.398(3)**
C(8)-C(9)	**1.467(2)**
C(9)-N(10)	**1.296(2)**
C(9)-C(18)	**1.464(3)**
N(10)-C(11)	**1.396(2)**
C(11)-C(12)	**1.394(2)**
C(11)-C(16)	**1.395(3)**
C(12)-C(13)	**1.387(3)**
C(13)-C(14)	**1.401(3)**
C(13)-C(20)	**1.500(2)**
C(14)-C(15)	**1.384(3)**
C(15)-C(16)	**1.384(3)**
C(16)-O(17)	**1.374(2)**
O(17)-C(18)	**1.375(2)**
C(18)-C(19)	**1.349(3)**
C(19)-C(21)	**1.503(3)**
O(1)-C(2)-C(19)	**121.19(17)**
O(1)-C(2)-C(3)	**120.77(17)**
C(19)-C(2)-C(3)	**118.04(16)**
C(8)-C(3)-C(4)	**119.62(17)**
C(8)-C(3)-C(2)	**120.70(16)**
C(4)-C(3)-C(2)	**119.65(17)**
C(5)-C(4)-C(3)	**120.01(18)**
C(4)-C(5)-C(6)	**120.30(18)**
C(7)-C(6)-C(5)	**120.08(18)**
C(6)-C(7)-C(8)	**120.06(18)**

C(3)-C(8)-C(7)	**119.88(17)**
C(3)-C(8)-C(9)	**120.18(16)**
C(7)-C(8)-C(9)	**119.93(16)**
N(10)-C(9)-C(18)	**123.45(16)**
N(10)-C(9)-C(8)	**119.49(16)**
C(18)-C(9)-C(8)	**117.04(16)**
C(9)-N(10)-C(11)	**117.70(15)**
C(12)-C(11)-C(16)	**118.83(16)**
C(12)-C(11)-N(10)	**119.73(16)**
C(16)-C(11)-N(10)	**121.42(16)**
C(13)-C(12)-C(11)	**121.40(17)**
C(12)-C(13)-C(14)	**117.92(16)**
C(12)-C(13)-C(20)	**120.89(17)**
C(14)-C(13)-C(20)	**121.15(17)**
C(15)-C(14)-C(13)	**122.04(17)**
C(14)-C(15)-C(16)	**118.63(17)**
O(17)-C(16)-C(15)	**118.29(16)**
O(17)-C(16)-C(11)	**120.56(16)**
C(15)-C(16)-C(11)	**121.15(17)**
C(16)-O(17)-C(18)	**119.09(14)**
C(19)-C(18)-O(17)	**118.09(16)**
C(19)-C(18)-C(9)	**124.14(16)**
O(17)-C(18)-C(9)	**117.74(15)**
C(18)-C(19)-C(2)	**119.58(16)**
C(18)-C(19)-C(21)	**121.84(16)**
C(2)-C(19)-C(21)	**118.58(16)**

Table S5 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for M-1B. The anisotropic Displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	27(1)	28(1)	16(1)	4(1)	-2(1)	9(1)
C(2)	16(1)	17(1)	12(1)	2(1)	0(1)	0(1)
C(3)	14(1)	13(1)	14(1)	1(1)	0(1)	-2(1)
C(4)	16(1)	14(1)	16(1)	1(1)	-3(1)	2(1)
C(5)	15(1)	14(1)	22(1)	-3(1)	0(1)	4(1)
C(6)	16(1)	15(1)	13(1)	-4(1)	1(1)	-1(1)
C(7)	13(1)	15(1)	13(1)	-2(1)	-2(1)	0(1)
C(8)	10(1)	10(1)	11(1)	0(1)	-1(1)	-2(1)
C(9)	12(1)	12(1)	10(1)	1(1)	0(1)	-4(1)
N(10)	12(1)	12(1)	10(1)	-1(1)	1(1)	-1(1)
C(11)	10(1)	12(1)	13(1)	-1(1)	1(1)	-1(1)
C(12)	13(1)	13(1)	10(1)	-1(1)	1(1)	-1(1)
C(13)	13(1)	13(1)	13(1)	2(1)	-4(1)	-1(1)
C(14)	13(1)	15(1)	16(1)	-3(1)	2(1)	1(1)
C(15)	17(1)	16(1)	11(1)	-4(1)	1(1)	-1(1)
C(16)	13(1)	14(1)	12(1)	-1(1)	-2(1)	-1(1)
O(17)	17(1)	18(1)	10(1)	0(1)	1(1)	6(1)
C(18)	12(1)	15(1)	12(1)	0(1)	2(1)	-1(1)
C(19)	14(1)	19(1)	11(1)	0(1)	0(1)	1(1)
Cl(20)	16(1)	15(1)	15(1)	2(1)	0(1)	4(1)
C(21)	22(1)	27(1)	11(1)	2(1)	1(1)	4(1)

Table S6 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for M-1B

	x	y	z	U(eq)
H(4)	3784	7172	1895	35
H(5)	2270	6789	-723	36
H(6)	1126	5776	-1149	36
H(7)	1326	5160	1034	32
H(12)	708	3767	3930	29
H(14)	2221	3586	8730	32
H(15)	3459	4585	9148	31
H(20A)	-661	2891	5155	48
H(20B)	556	2758	7032	48
H(20C)	1632	2665	5776	48
H(21A)	5304	6216	8508	46
H(21B)	5288	6897	7840	46
H(21C)	7104	6442	8002	46

Table S7 Bond lengths [Å] and angles [°] for M-2B

O(1)-C(2)	**1.233(3)**
C(2)-C(19)	**1.461(3)**
C(2)-C(3)	**1.490(3)**
C(3)-C(4)	**1.397(3)**
C(3)-C(8)	**1.404(3)**
C(4)-C(5)	**1.382(3)**
C(5)-C(6)	**1.391(3)**
C(6)-C(7)	**1.377(3)**
C(7)-C(8)	**1.402(3)**
C(8)-C(9)	**1.465(3)**
C(9)-N(10)	**1.303(3)**
C(9)-C(18)	**1.468(3)**
N(10)-C(11)	**1.395(3)**
C(11)-C(16)	**1.396(3)**
C(11)-C(12)	**1.398(3)**
C(12)-C(13)	**1.379(3)**
C(13)-C(14)	**1.396(3)**
C(13)-Cl(20)	**1.732(2)**
C(14)-C(15)	**1.386(3)**
C(15)-C(16)	**1.383(3)**
C(16)-O(17)	**1.373(3)**
O(17)-C(18)	**1.370(3)**
C(18)-C(19)	**1.354(3)**
C(19)-C(21)	**1.504(3)**
O(1)-C(2)-C(19)	**121.2(2)**
O(1)-C(2)-C(3)	**120.1(2)**
C(19)-C(2)-C(3)	**118.7(2)**
C(4)-C(3)-C(8)	**119.7(2)**
C(4)-C(3)-C(2)	**119.5(2)**
C(8)-C(3)-C(2)	**120.8(2)**
C(5)-C(4)-C(3)	**120.1(2)**
C(4)-C(5)-C(6)	**120.1(2)**
C(7)-C(6)-C(5)	**120.7(2)**
C(6)-C(7)-C(8)	**119.9(2)**

C(7)-C(8)-C(3)	**119.5(2)**
C(7)-C(8)-C(9)	**120.8(2)**
C(3)-C(8)-C(9)	**119.7(2)**
N(10)-C(9)-C(8)	**119.5(2)**
N(10)-C(9)-C(18)	**123.2(2)**
C(8)-C(9)-C(18)	**117.3(2)**
C(9)-N(10)-C(11)	**117.19(19)**
N(10)-C(11)-C(16)	**122.1(2)**
N(10)-C(11)-C(12)	**119.3(2)**
C(16)-C(11)-C(12)	**118.5(2)**
C(13)-C(12)-C(11)	**119.4(2)**
C(12)-C(13)-C(14)	**121.4(2)**
C(12)-C(13)-Cl(20)	**118.98(18)**
C(14)-C(13)-Cl(20)	**119.56(19)**
C(15)-C(14)-C(13)	**119.7(2)**
C(16)-C(15)-C(14)	**118.6(2)**
O(17)-C(16)-C(15)	**117.5(2)**
O(17)-C(16)-C(11)	**120.1(2)**
C(15)-C(16)-C(11)	**122.3(2)**
C(18)-O(17)-C(16)	**119.30(18)**
C(19)-C(18)-O(17)	**117.4(2)**
C(19)-C(18)-C(9)	**124.5(2)**
O(17)-C(18)-C(9)	**118.0(2)**
C(18)-C(19)-C(2)	**118.9(2)**
C(18)-C(19)-C(21)	**122.4(2)**
C(2)-C(19)-C(21)	**118.7(2)**

Table S8 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for M-2B. The anisotropic Displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	32(1)	28(1)	36(1)	-2(1)	17(1)	-1(1)
C(2)	19(1)	28(1)	30(1)	0(1)	13(1)	4(1)
C(3)	21(1)	29(1)	26(1)	2(1)	12(1)	4(1)
C(4)	26(1)	31(1)	34(1)	5(1)	15(1)	5(1)
C(5)	28(1)	38(1)	28(1)	9(1)	14(1)	7(1)
C(6)	24(1)	42(1)	22(1)	3(1)	8(1)	3(1)
C(7)	22(1)	35(1)	24(1)	1(1)	9(1)	2(1)
C(8)	16(1)	31(1)	25(1)	2(1)	9(1)	3(1)
C(9)	17(1)	28(1)	24(1)	-1(1)	9(1)	2(1)
N(10)	18(1)	29(1)	24(1)	1(1)	9(1)	2(1)
C(11)	16(1)	30(1)	24(1)	1(1)	9(1)	2(1)
C(12)	18(1)	29(1)	26(1)	-2(1)	9(1)	1(1)
C(13)	18(1)	30(1)	30(1)	1(1)	10(1)	1(1)
C(14)	23(1)	32(1)	28(1)	4(1)	13(1)	1(1)
C(15)	22(1)	33(1)	24(1)	0(1)	10(1)	1(1)
C(16)	17(1)	27(1)	26(1)	-1(1)	10(1)	1(1)
O(17)	24(1)	28(1)	22(1)	-1(1)	10(1)	-3(1)
C(18)	18(1)	29(1)	22(1)	3(1)	10(1)	3(1)
C(19)	20(1)	29(1)	25(1)	-2(1)	10(1)	1(1)
C(20)	29(1)	30(1)	37(1)	1(1)	14(1)	-2(1)
C(21)	30(1)	34(1)	28(1)	-3(1)	11(1)	-4(1)

Table S9 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for M-2B

x	y	z	U(eq)
H(4)	21981	-5454	1478	18
H(5)	23011	-5781	675	21
H(6)	20727	-4462	97	18
H(7)	17356	-2838	312	16
H(12)	11041	176	339	14
H(14)	6733	2060	1404	18
H(15)	9183	746	1971	18
H(21A)	17212	-1910	2687	30
H(21B)	15665	-3378	2715	30
H(21C)	13905	-2015	2588	30

Table S10 Bond lengths [Å] and angles [°] for M-4B

O(1)-C(2)	1.246(3)
C(2)-C(19)	1.468(4)
C(2)-C(3)	1.476(4)
C(3)-C(4)	1.399(4)
C(3)-C(8)	1.405(4)
C(4)-C(5)	1.387(4)
C(5)-C(6)	1.398(4)
C(6)-C(7)	1.382(4)
C(7)-C(8)	1.402(4)
C(8)-C(9)	1.481(4)
C(9)-N(10)	1.294(3)
C(9)-C(18)	1.465(4)
N(10)-C(11)	1.392(3)
C(11)-C(12)	1.404(4)
C(11)-C(16)	1.408(4)
C(12)-C(13)	1.380(4)
C(13)-C(14)	1.396(4)
C(14)-C(15)	1.386(4)
C(15)-C(16)	1.389(4)
C(16)-S(17)	1.741(3)
S(17)-C(18)	1.754(3)
C(18)-C(19)	1.359(4)
C(19)-C(21)	1.500(4)
O(1)-C(2)-C(19)	120.4(2)
O(1)-C(2)-C(3)	120.3(2)
C(19)-C(2)-C(3)	119.3(2)
C(4)-C(3)-C(8)	119.9(2)
C(4)-C(3)-C(2)	120.4(2)
C(8)-C(3)-C(2)	119.7(2)
C(5)-C(4)-C(3)	120.7(2)
C(4)-C(5)-C(6)	119.5(3)
C(7)-C(6)-C(5)	120.2(2)
C(6)-C(7)-C(8)	120.9(2)
C(7)-C(8)-C(3)	118.7(2)

C(7)-C(8)-C(9)	**120.4(2)**
C(3)-C(8)-C(9)	**120.8(2)**
N(10)-C(9)-C(18)	**127.1(2)**
N(10)-C(9)-C(8)	**116.2(2)**
C(18)-C(9)-C(8)	**116.7(2)**
C(9)-N(10)-C(11)	**123.1(2)**
N(10)-C(11)-C(12)	**116.1(2)**
N(10)-C(11)-C(16)	**125.1(2)**
C(12)-C(11)-C(16)	**118.8(2)**
C(13)-C(12)-C(11)	**120.7(3)**
C(12)-C(13)-C(14)	**119.9(3)**
C(15)-C(14)-C(13)	**120.3(3)**
C(14)-C(15)-C(16)	**120.1(3)**
C(15)-C(16)-C(11)	**120.2(2)**
C(15)-C(16)-S(17)	**118.1(2)**
C(11)-C(16)-S(17)	**121.6(2)**
C(16)-S(17)-C(18)	**103.57(13)**
C(19)-C(18)-C(9)	**123.6(2)**
C(19)-C(18)-S(17)	**117.3(2)**
C(9)-C(18)-S(17)	**119.08(19)**
C(18)-C(19)-C(2)	**119.6(2)**
C(18)-C(19)-C(21)	**122.0(3)**
C(2)-C(19)-C(21)	**118.4(2)**

Table S11 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for M-4B. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	30(1)	29(1)	24(1)	0(1)	15(1)	0(1)
C(2)	21(1)	11(1)	22(1)	-3(1)	6(1)	-3(1)
C(3)	22(1)	10(1)	23(1)	-2(1)	9(1)	-4(1)
C(4)	26(1)	13(1)	18(1)	-1(1)	7(1)	-2(1)
C(5)	23(1)	14(1)	23(1)	1(1)	4(1)	1(1)
C(6)	20(1)	14(1)	27(1)	-2(1)	9(1)	-1(1)
C(7)	22(1)	14(1)	19(1)	-1(1)	8(1)	-3(1)
C(8)	21(1)	11(1)	19(1)	-1(1)	6(1)	-2(1)
C(9)	18(1)	9(1)	20(1)	-2(1)	7(1)	-2(1)
N(10)	20(1)	15(1)	20(1)	0(1)	6(1)	0(1)
C(11)	17(1)	12(1)	23(1)	1(1)	5(1)	0(1)
C(12)	21(1)	16(1)	25(1)	0(1)	8(1)	0(1)
C(13)	26(1)	16(1)	26(1)	0(1)	10(1)	-2(1)
C(14)	24(1)	15(1)	25(1)	2(1)	6(1)	-3(1)
C(15)	18(1)	14(1)	28(1)	0(1)	6(1)	0(1)
C(16)	19(1)	11(1)	23(1)	-1(1)	8(1)	-3(1)
S(17)	19(1)	14(1)	24(1)	-1(1)	8(1)	1(1)
C(18)	18(1)	9(1)	22(1)	-3(1)	4(1)	-3(1)
C(19)	20(1)	14(1)	24(1)	-3(1)	11(1)	-4(1)
C(21)	20(1)	18(1)	30(1)	-3(1)	13(1)	-1(1)

Table S12 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) For M-4B

	x	y	z	U(eq)
H(4)	601	13776	-2184	23
H(5)	-767	15224	-1967	25
H(6)	-854	14576	-930	24
H(7)	418	12553	-121	22
H(12)	1955	10810	1547	25
H(13)	3013	8803	2484	26
H(14)	4393	6144	2459	26
H(15)	4718	5547	1499	24
H(21A)	4339	9189	-763	32
H(21B)	3770	9394	-1503	32
H(21C)	3787	5847	-1120	32