Supplementary Information

Synthesis, Characterization and Anti-Cancer Properties of Water-Soluble bis(PYE) Pro-ligands and Derived Palladium(II) Complexes

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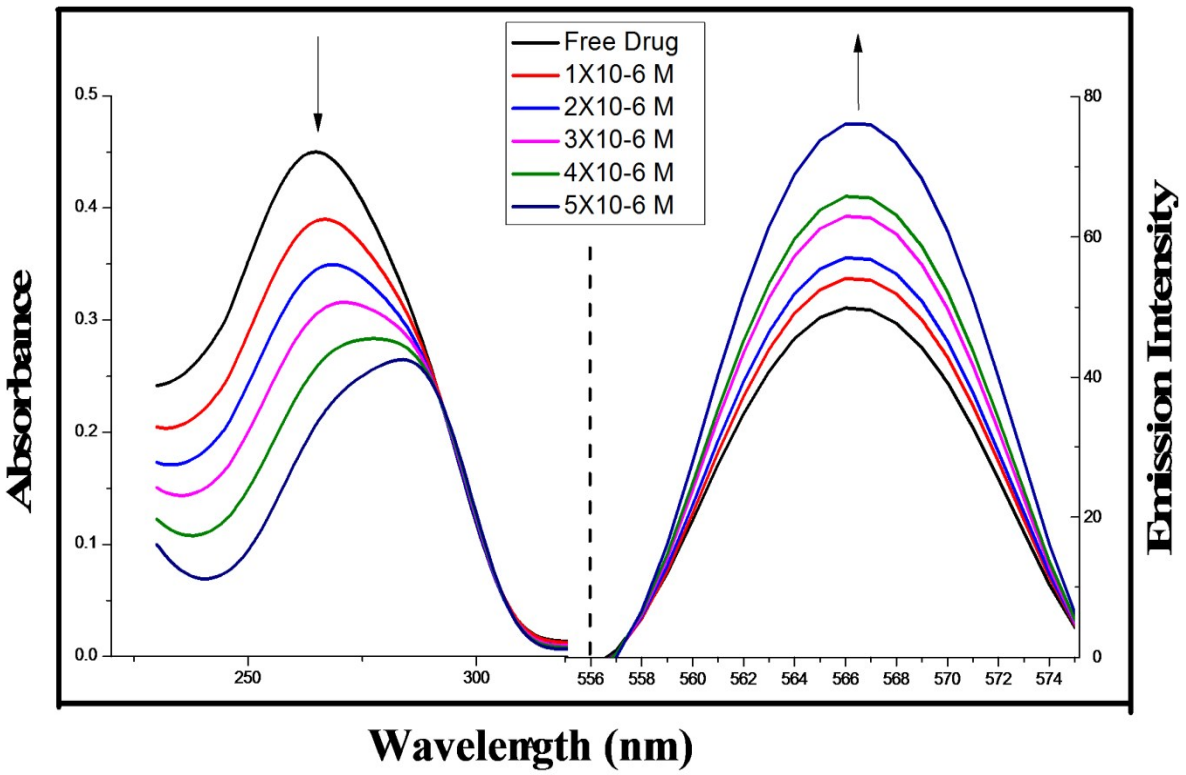


Figure S1. Absorption and emission spectra of **2**–CT-DNA complex with varying concentrations of CT-DNA.

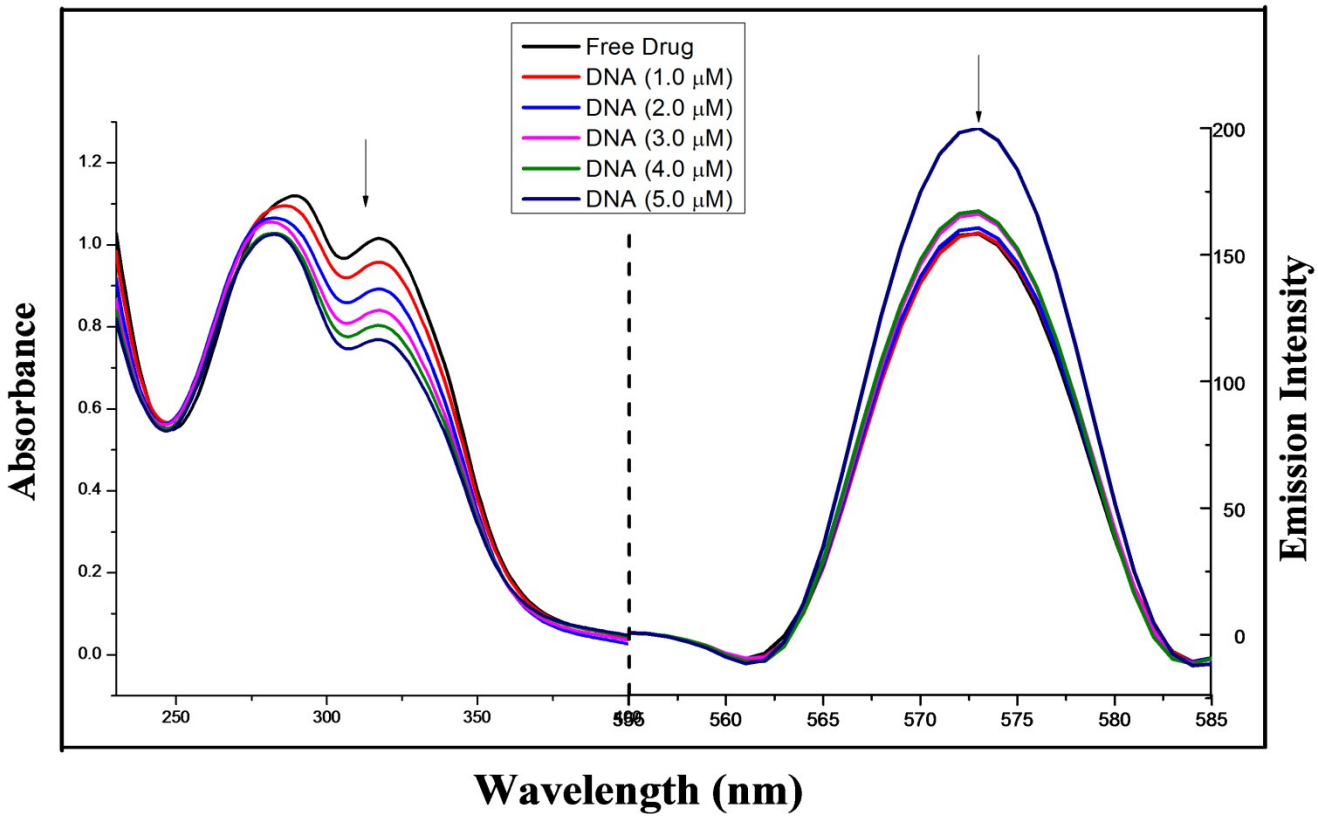


Figure S2. Absorption and emission spectra of **4**–CT-DNA complex with varying concentrations of CT-DNA

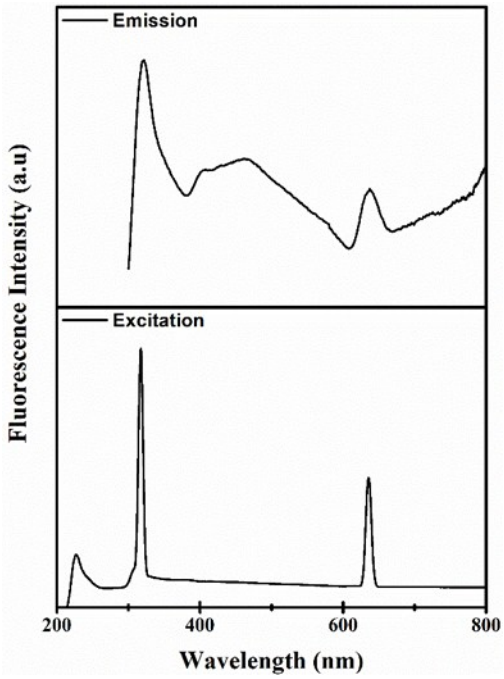


Figure S3. Excitation and Emission Spectra of **2** (Excitation at 284 nm)

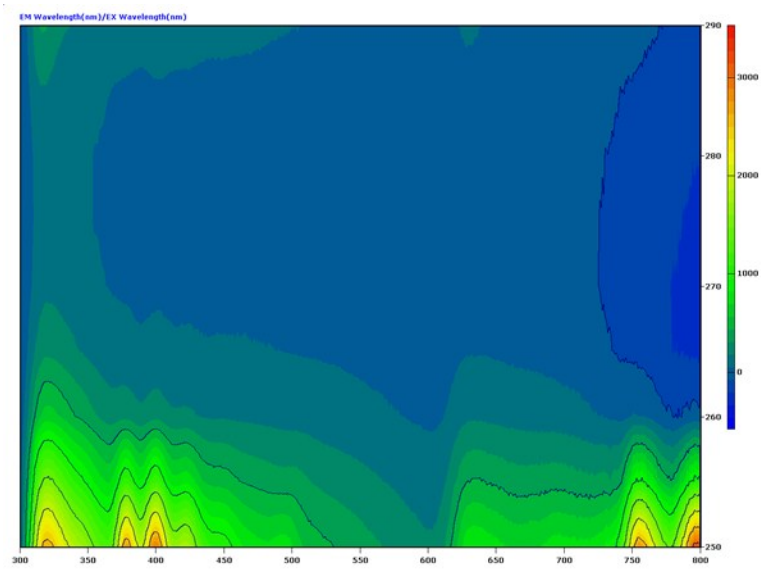


Figure S4. 3-D Emission Spectrum of **2** (Excitation range 250-300 nm)

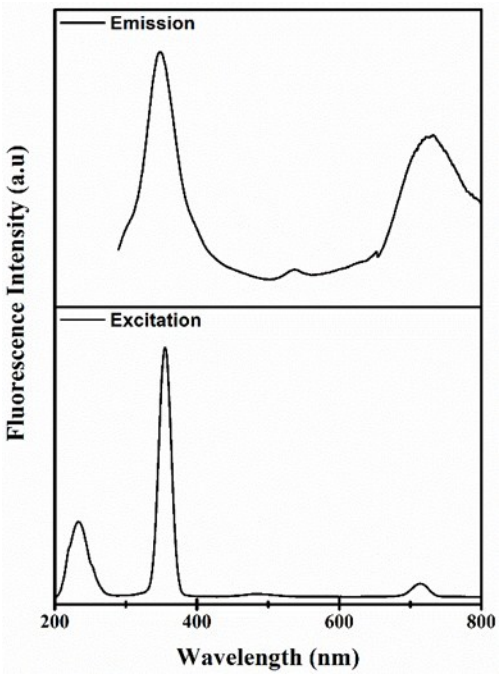


Figure S5. Excitation and Emission Spectra of **3** (Excitation at 275 nm)

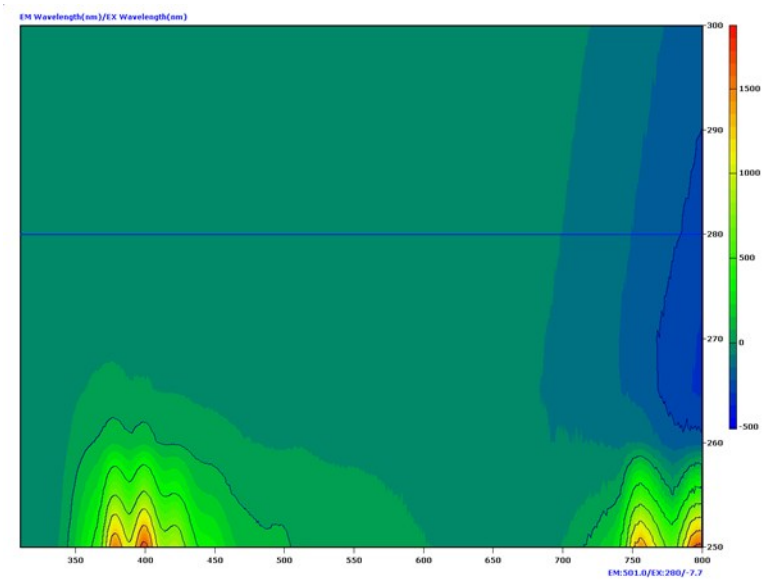


Figure S6. 3-D Emission Spectrum of **3** (Excitation range 250-300 nm)

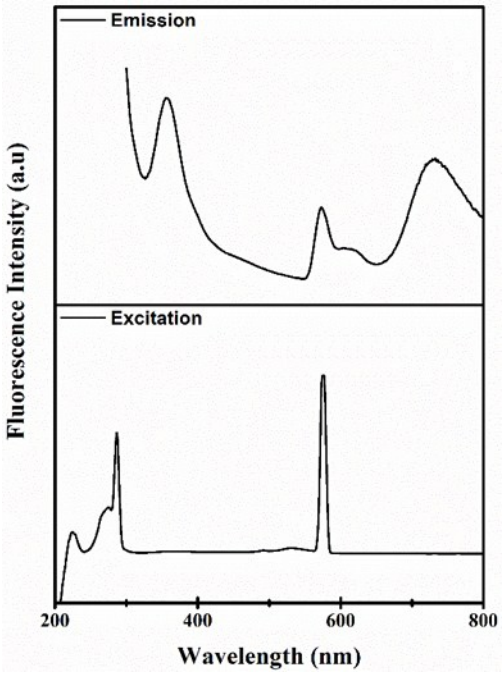


Figure S7. Excitation and Emission Spectra of **4** (Excitation at 287 nm)

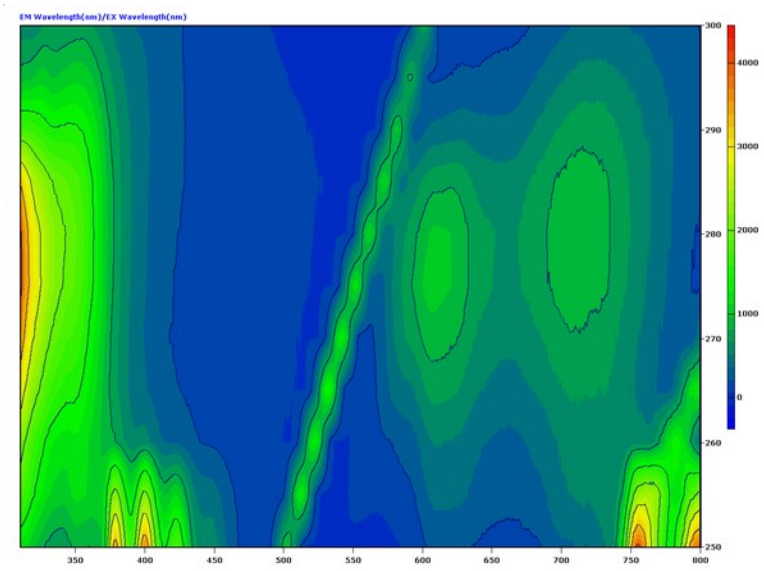


Figure S8. 3-D Emission Spectrum of **4** (Excitation range 250-300 nm)

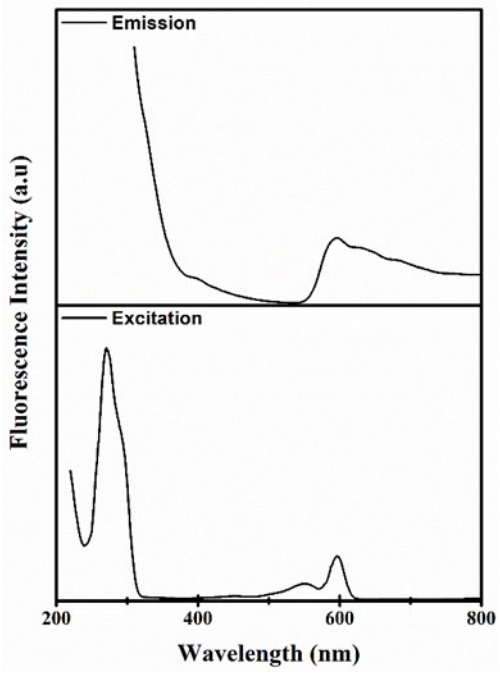


Figure S9. Excitation and Emission Spectra of **5** (Excitation at 290 nm)

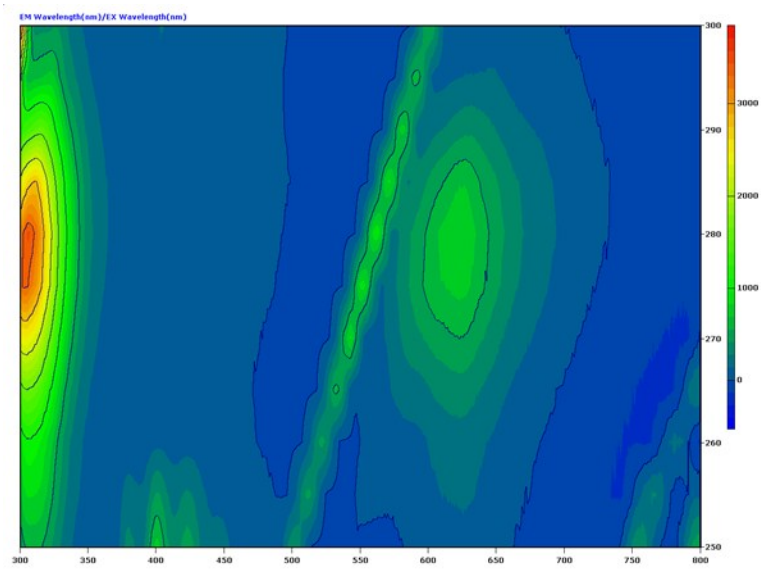


Figure S10. 3-D Emission Spectrum of **5** (Excitation range 250-300 nm)

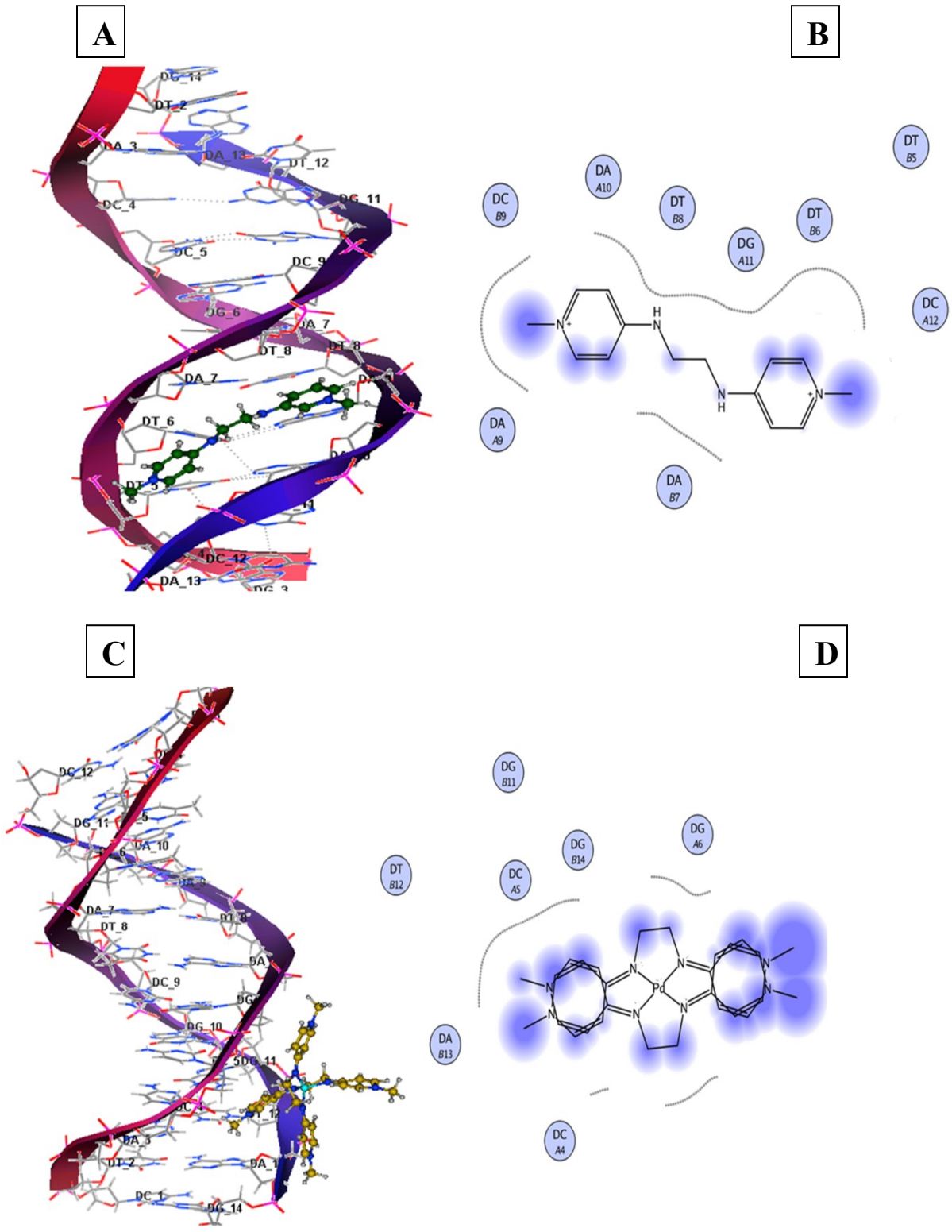


Figure S11. Visual representations of docking interactions of CT-DNA with (A) **2** and (C) **4**, as well as 2-D plots showing CT-DNA base pair interactions with (B) **2** and (D) **4.**

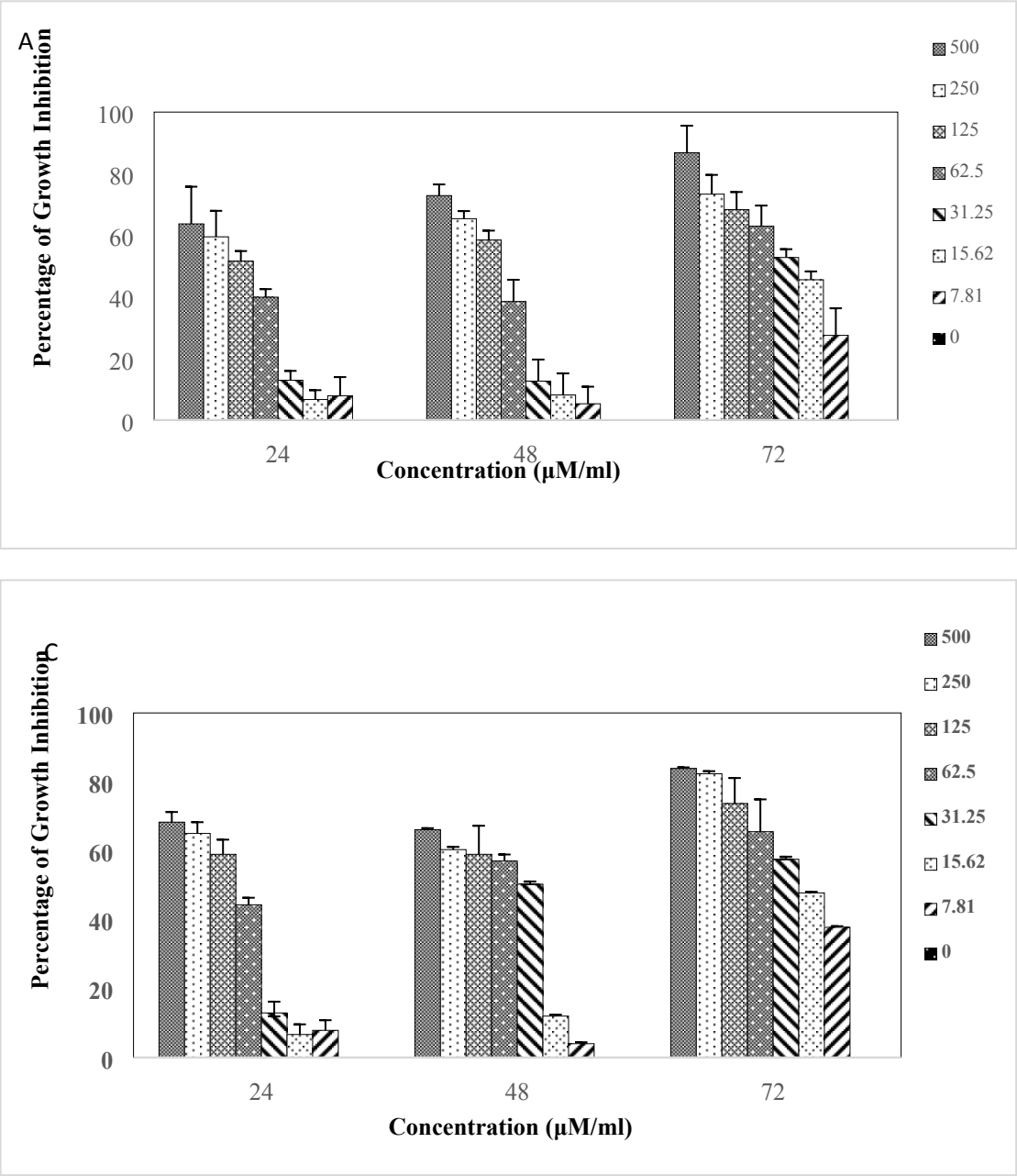
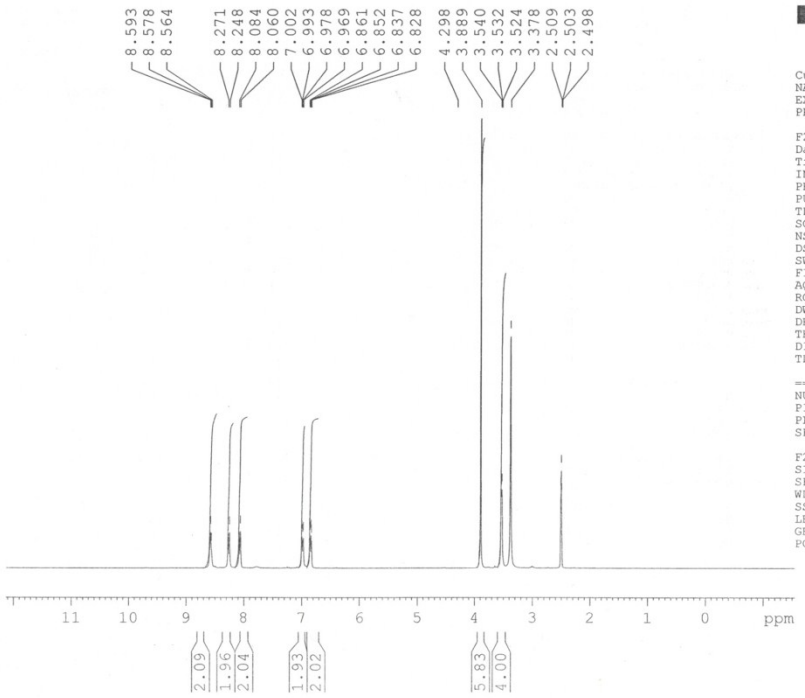


Figure S12. Percentage of growth inhibition for **2** (A) and **4** (C) against MCF-7 at 24 hr, 48 hr, and 72 hr. Error bars show one standard deviation.

DR.NAVEED ZAFAR/SARA/SM-03_1HNMR_DMSO



BRUKER

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PROCNO 1

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SOLVENT DMSO
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FIDRES 0.094190 Hz
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DW 81.000 usec
DE 6.00 usec
TE 294.9 K
D1 1.00000000 sec
TD0 1

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PL1 2.00 dB
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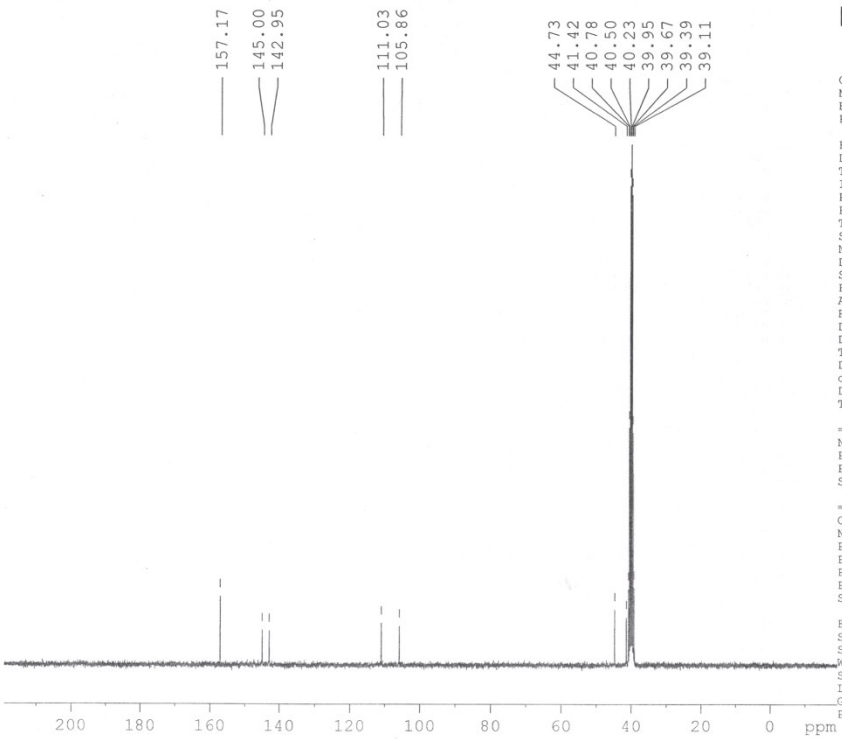
DR.NAVEED ZAFAR/SARA/SM-03_13CNMR_DMSO



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d11 0.03000000 sec
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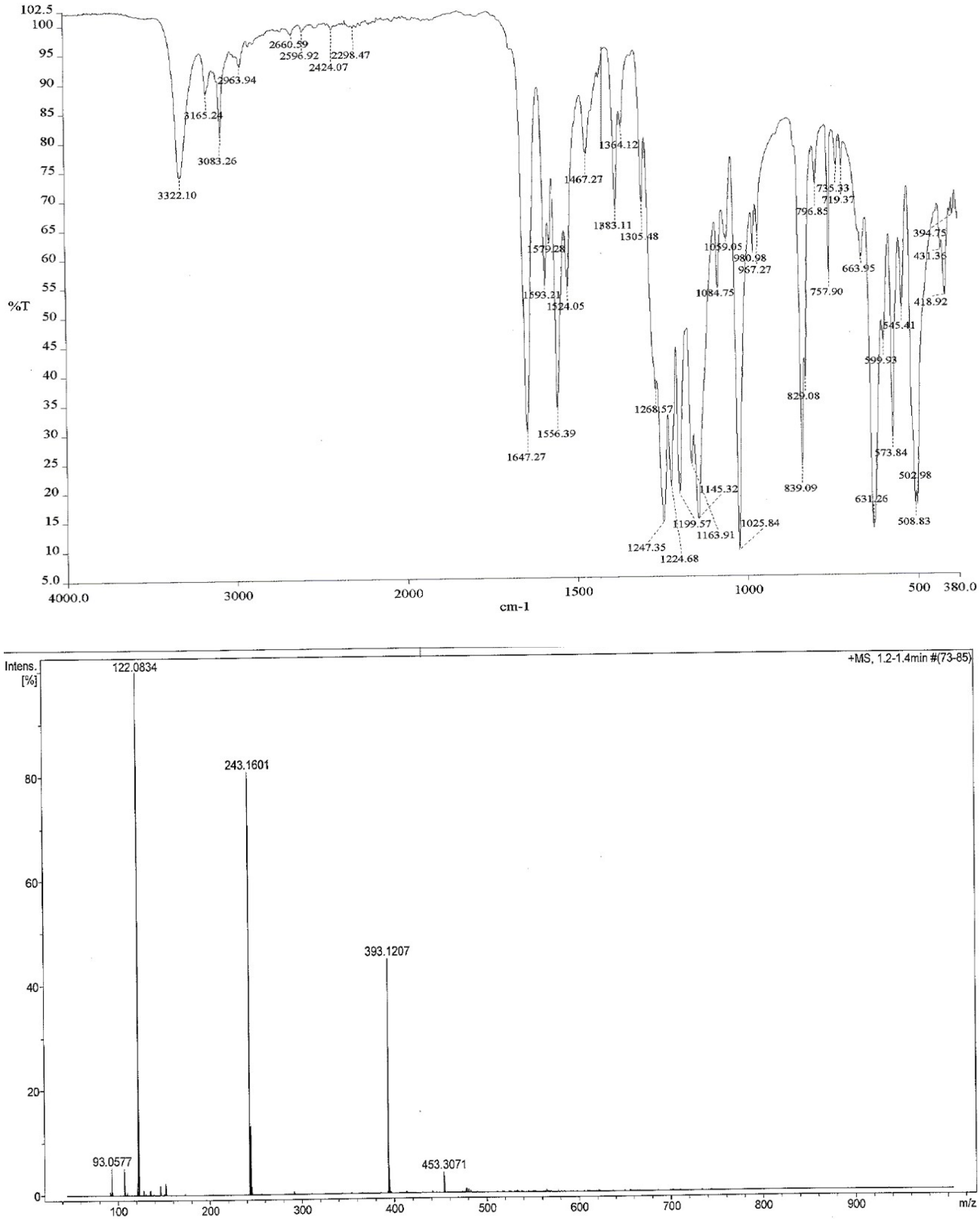
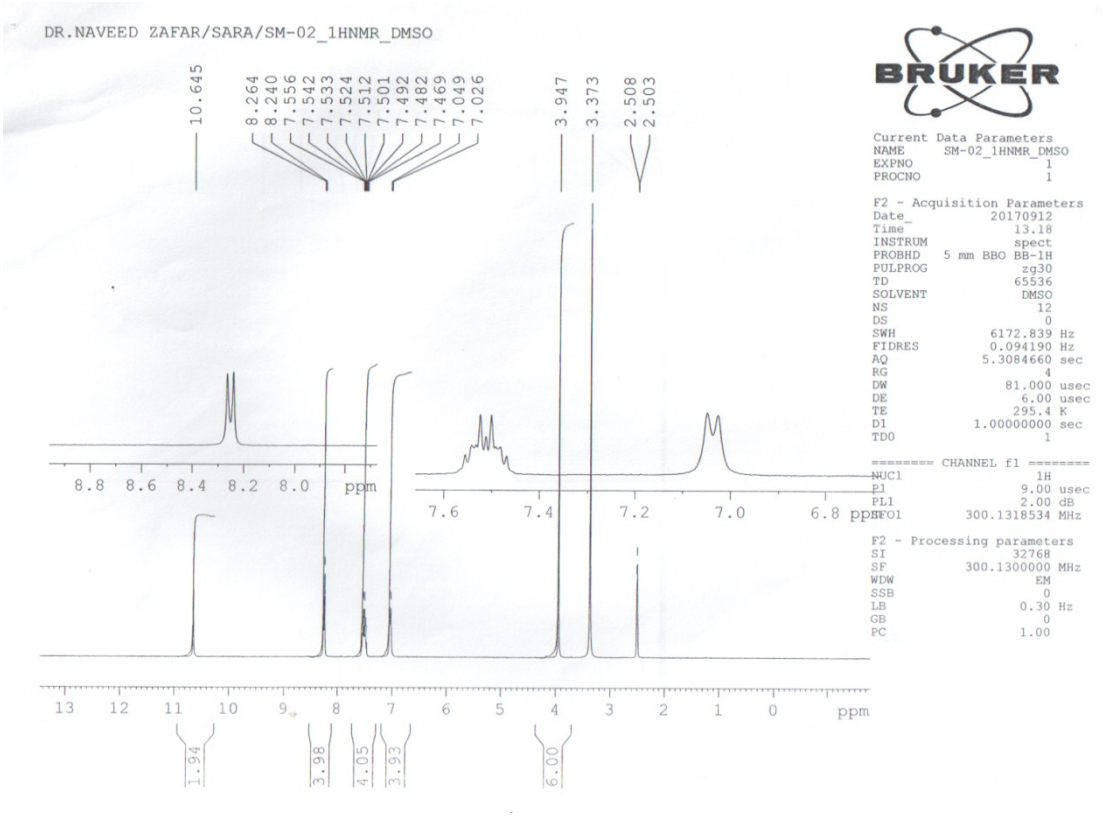


Figure S13. ^{1}H, ^{13}C NMR, IR and MS spectra for **2**.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7.501
7.492
7.482
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7.049
7.026
3.947
3.373
2.508
2.503
8.8 8.6 8.4 8.2 8.0 ppm
7.6 7.4 7.2 7.0 6.8 ppm
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
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3.98
4.05
3.93
6.00
BRUKER
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PROCNO 1
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FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 4
DW 81.000 usec
DE 6.00 usec
TE 295.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 2.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
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SF 300.1300000 MHz
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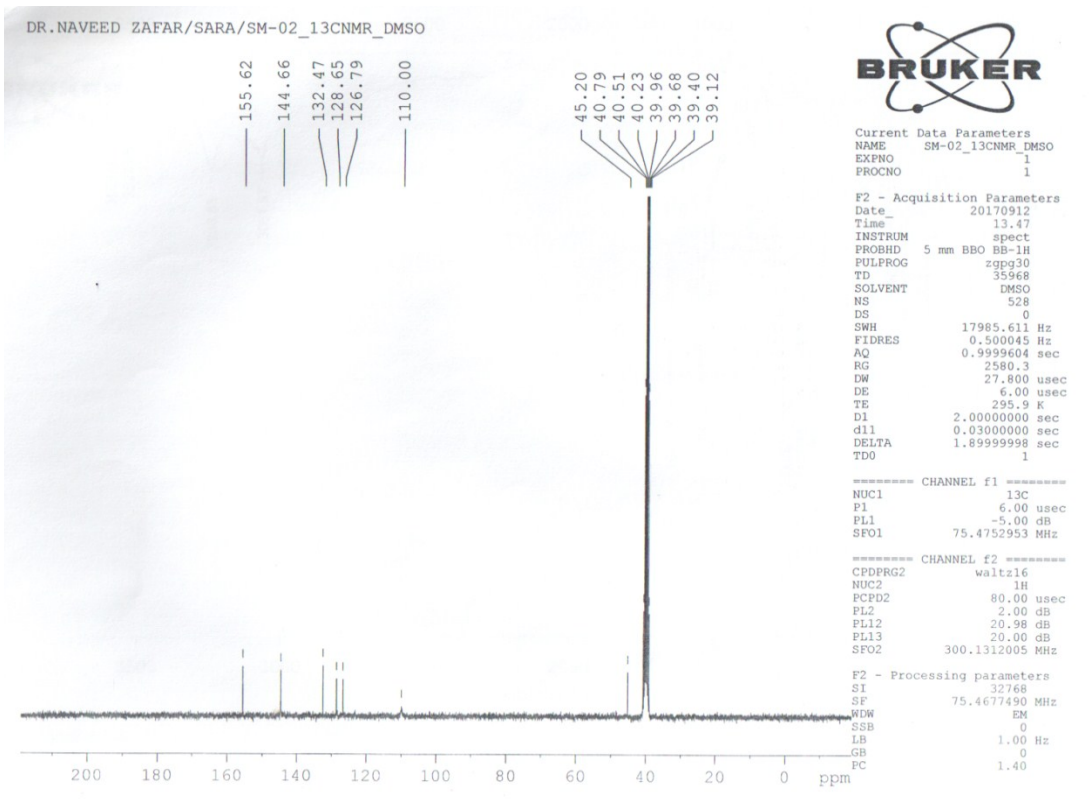
PC 1.00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126.79
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40.79
40.51
40.23
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39.68
39.40
39.12
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BRUKER
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PROCNO 1
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SOLVENT DMSO
NS 528
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FIDRES 0.500045 Hz
AQ 0.9999604 sec
RG 2580.3
DW 27.800 usec
DE 6.00 usec
TE 295.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 6.00 usec
PL1 -5.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.00 dB
PL12 20.98 dB
PL13 20.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
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LB 1.00 Hz
GB 0
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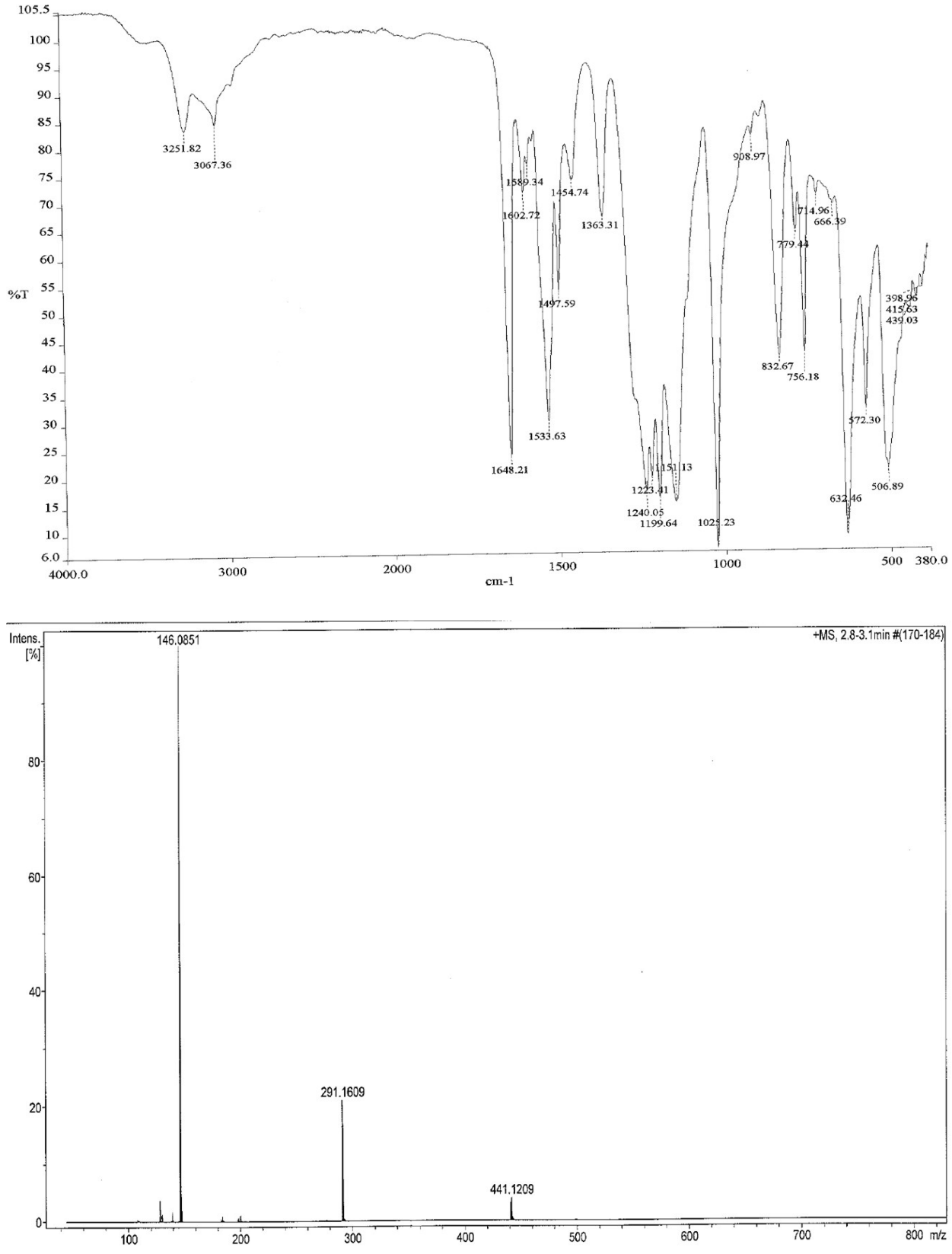
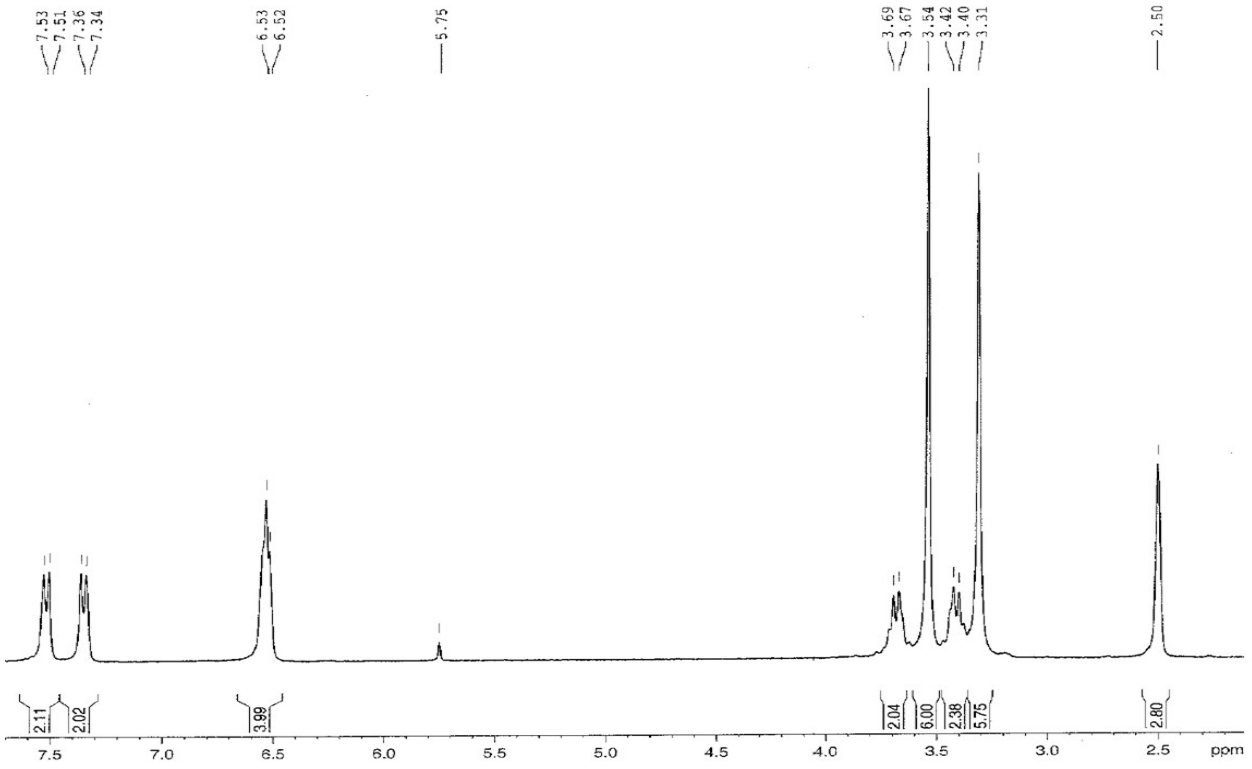


Figure S8. ^{1}H, ^{13}C NMR, IR and MS spectra for **3**.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2.50
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2.02
3.99
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6.00
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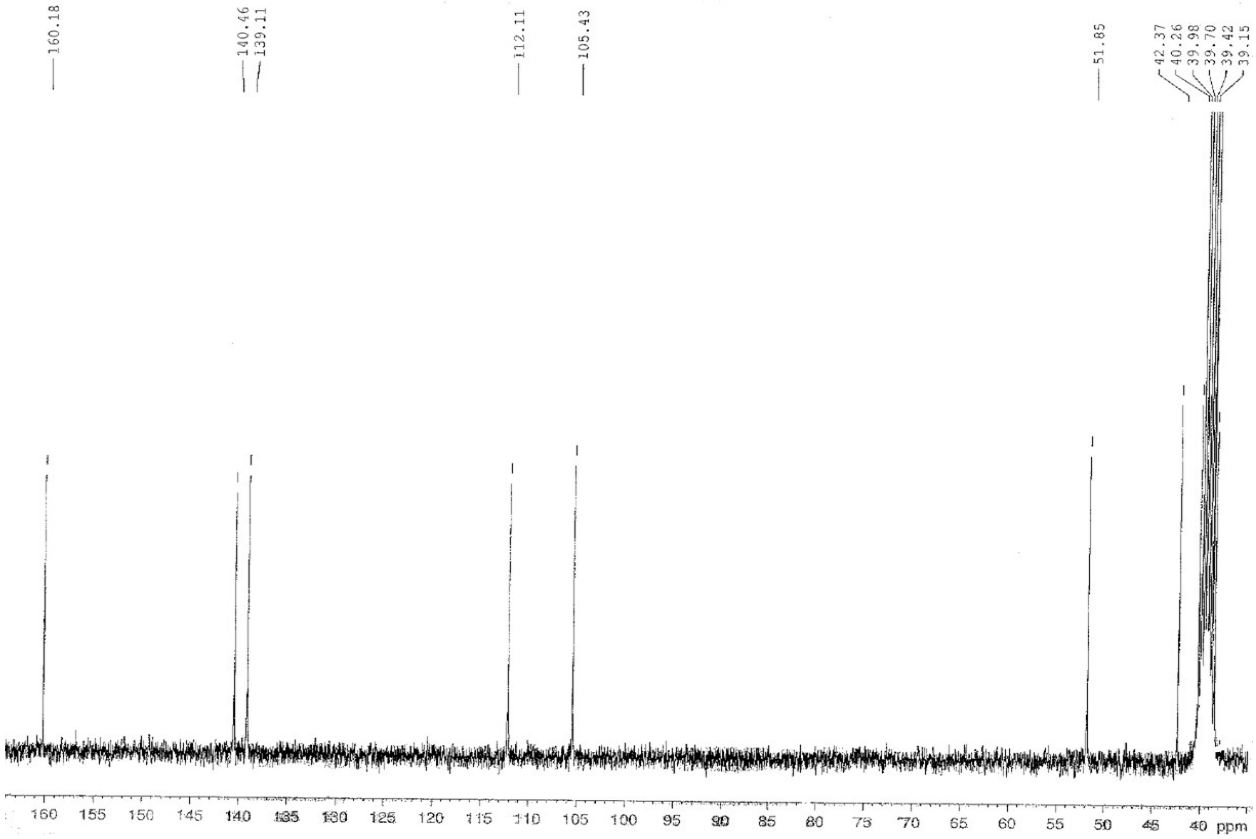
3.5
3.0
2.5
ppm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155
150
145
140
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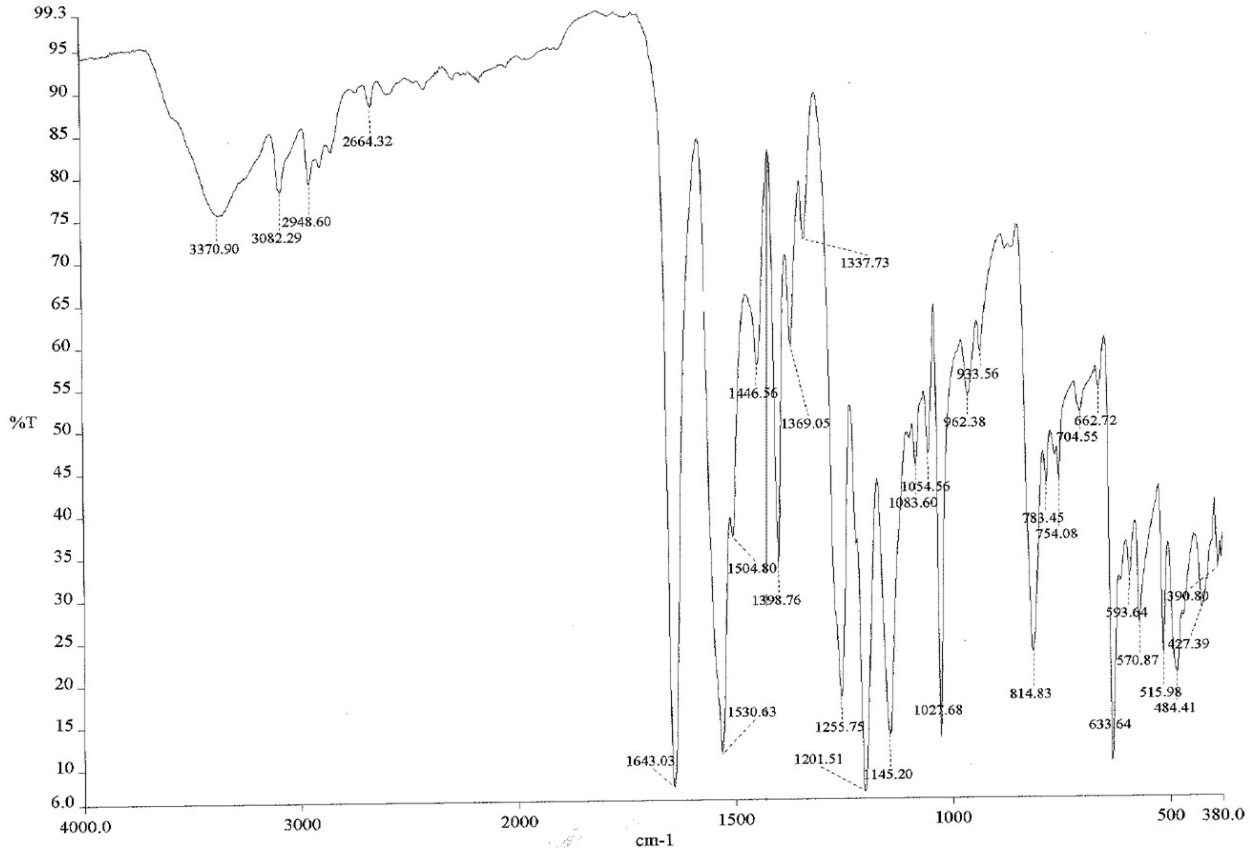


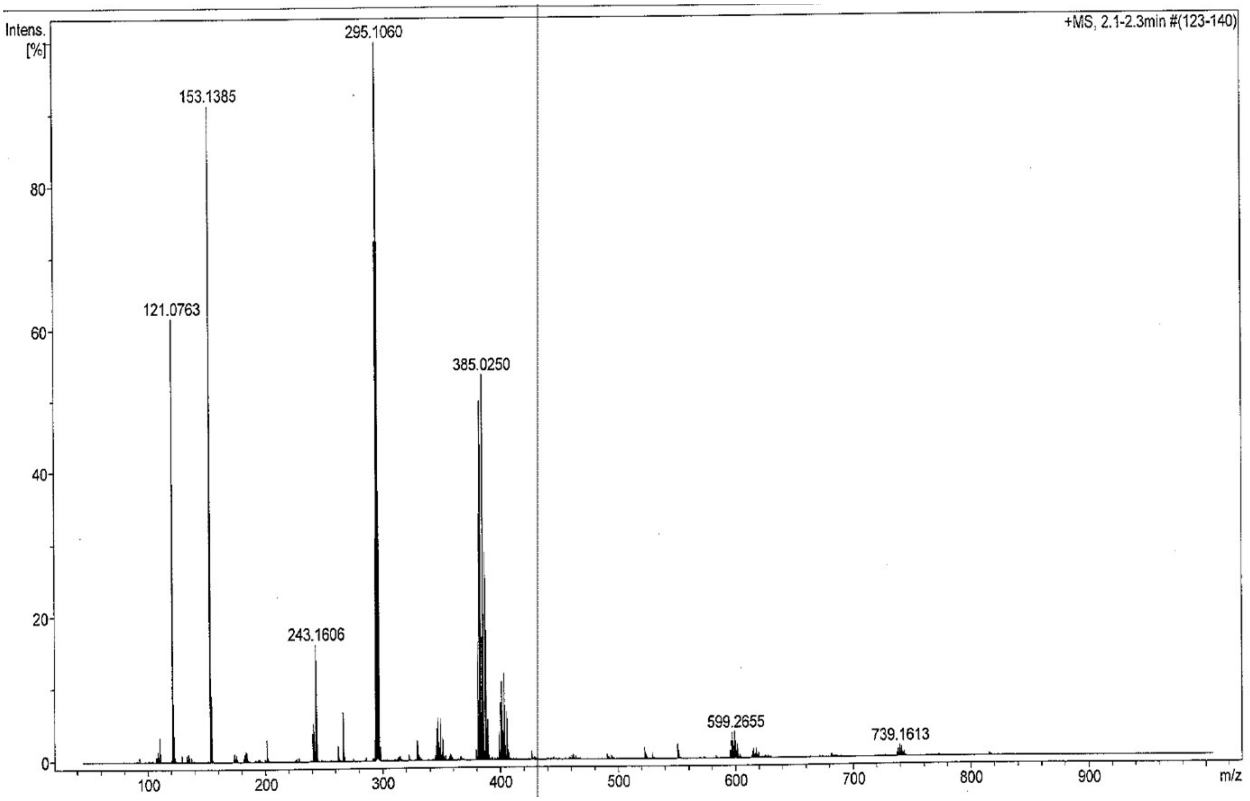
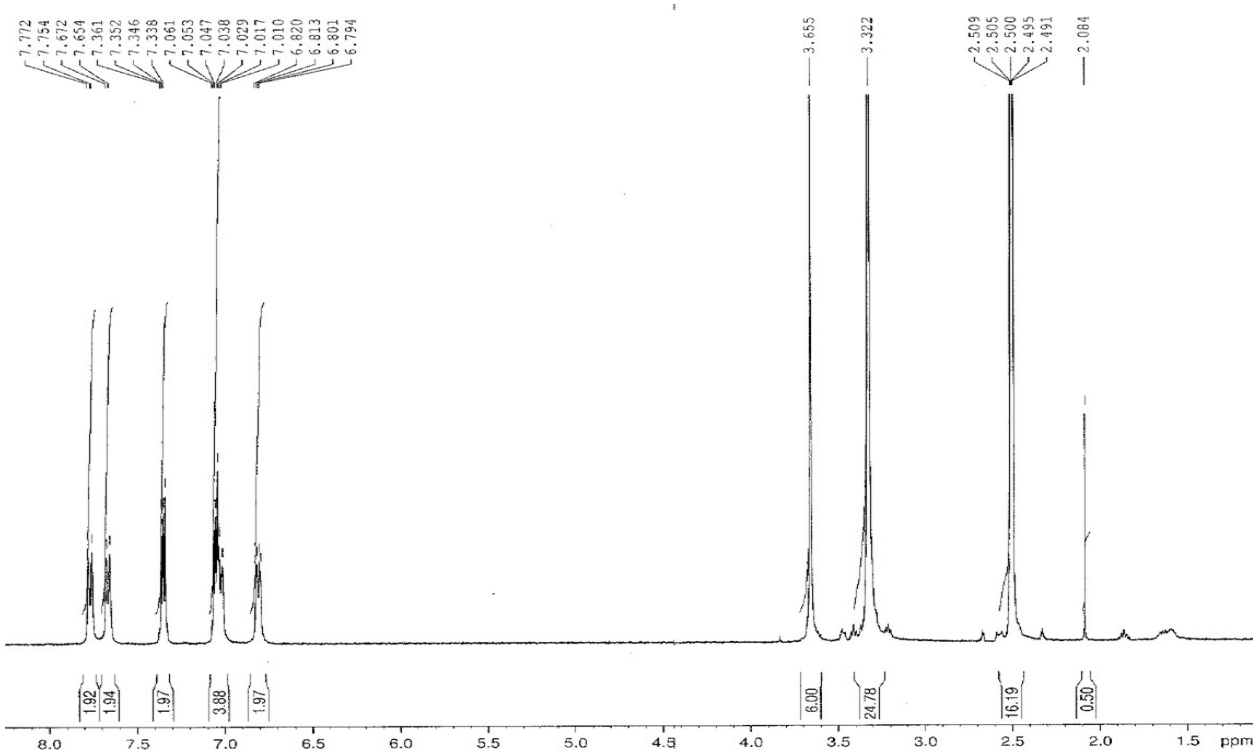


Figure S9. ^{1}H, ^{13}C NMR, IR and MS spectra for **4**.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2.500
2.495
2.491
2.084
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1.94
1.97
3.88
1.97
6.00
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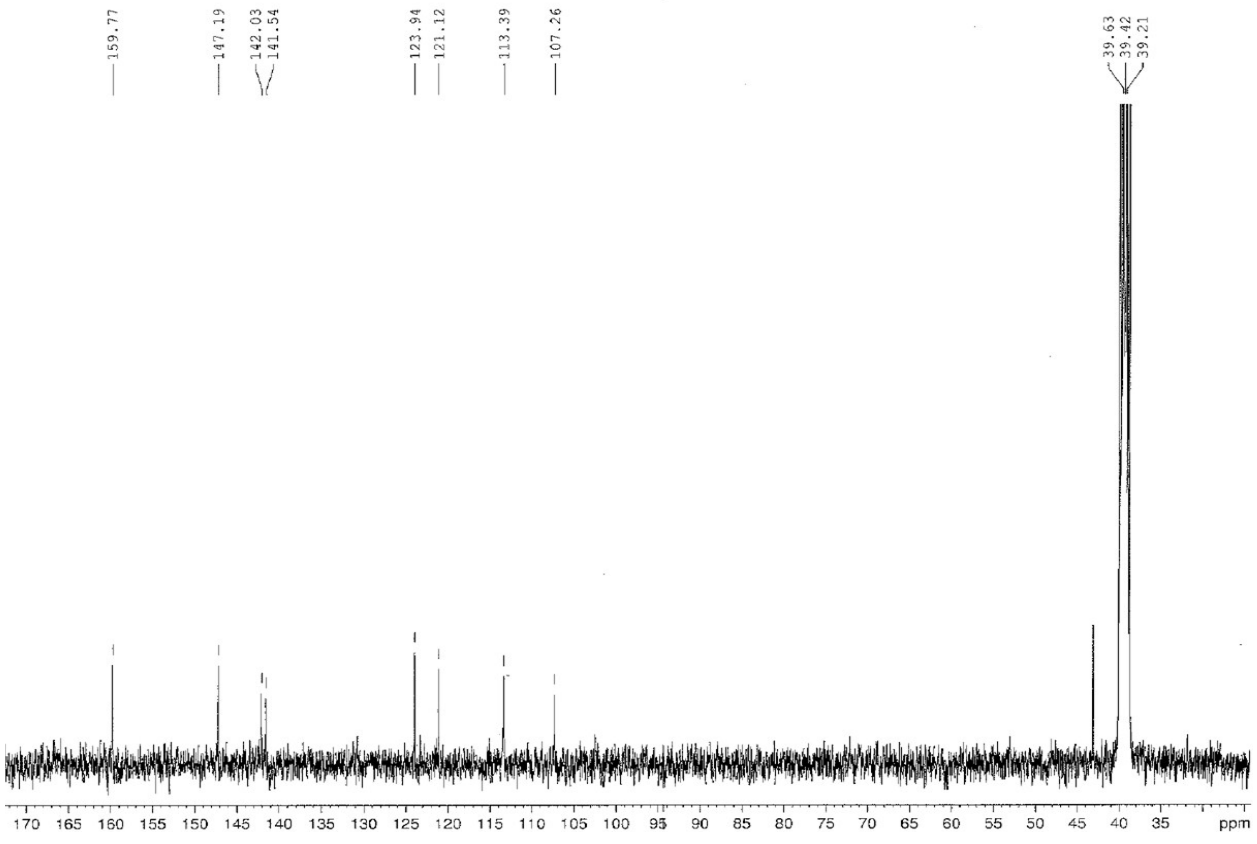
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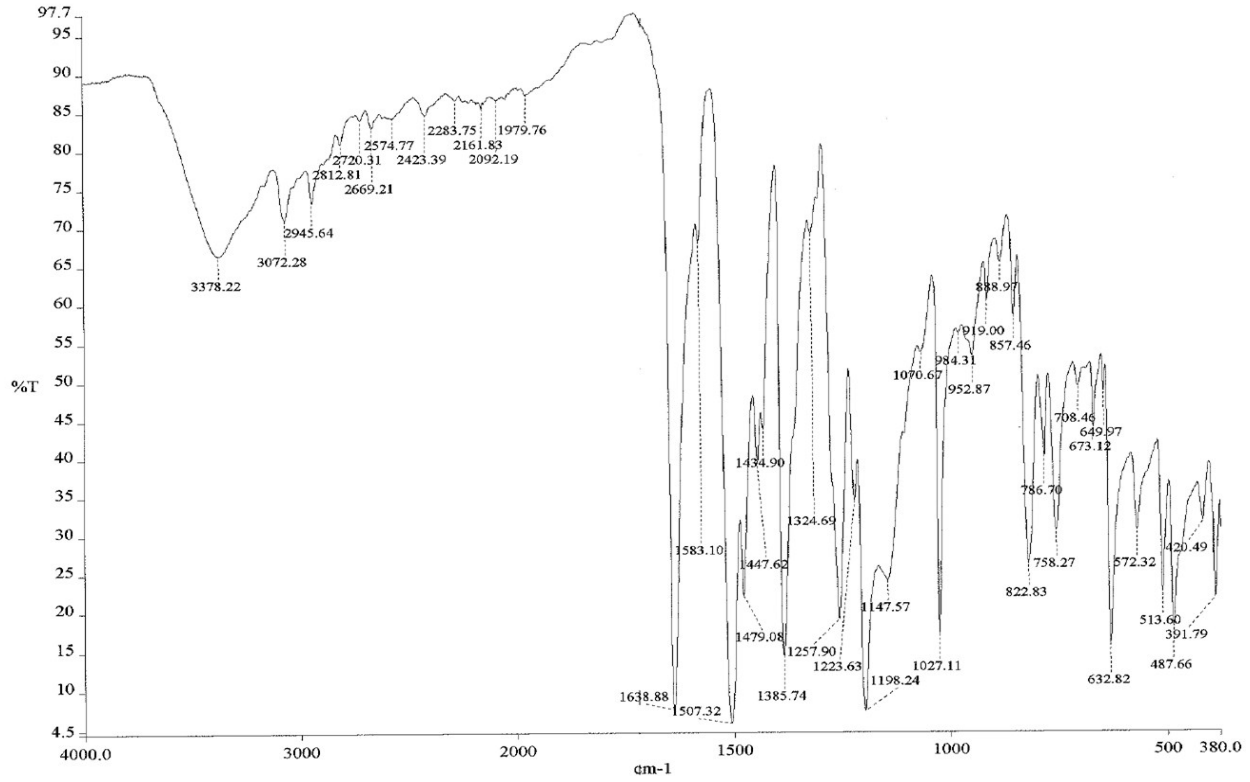

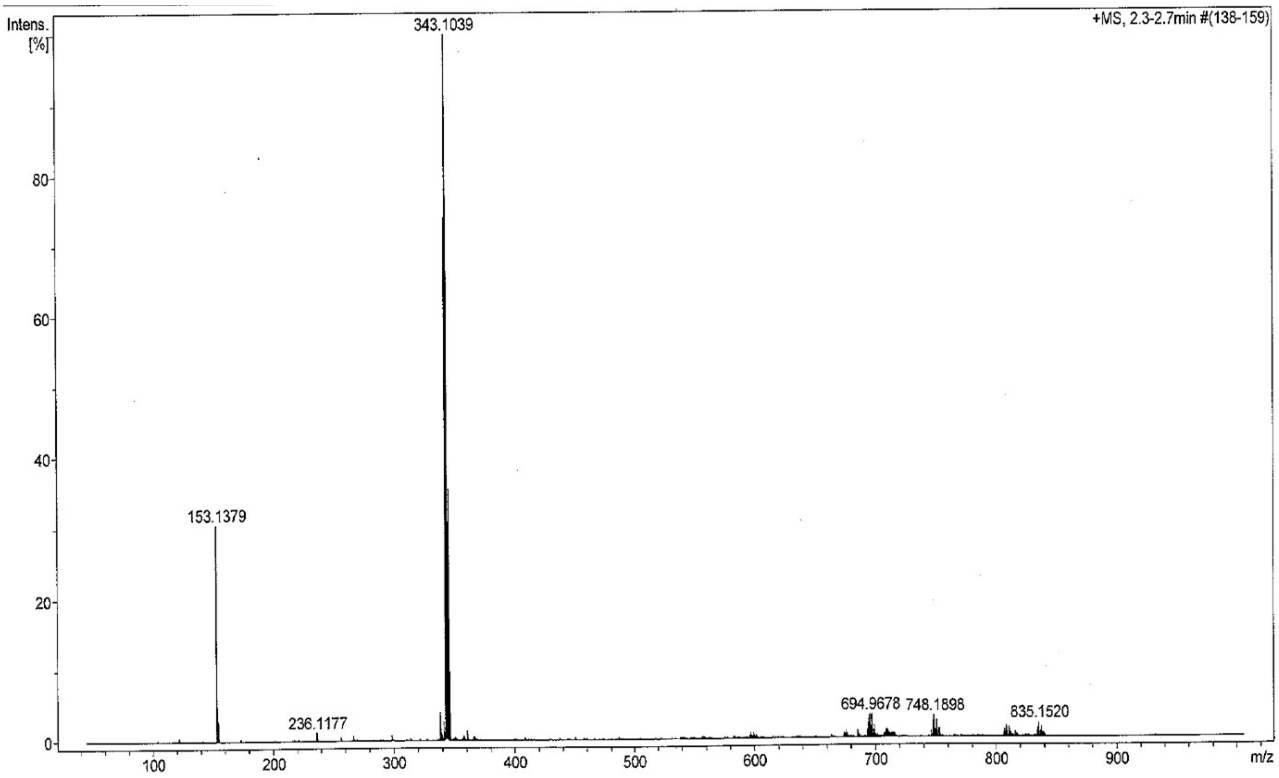

Figure S10. ^{1}H, ^{13}C NMR, IR and MS spectra for **5**.

Table S1. Crystal data and structure refinement for **2.**

Crystal data and structure refinement for 2	
Identification code	nztfh6_final
Empirical formula	$C_{16}H_{20}F_6N_4O_6S_2$
Formula weight	542.48
Temperature/K	89(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	11.1143(3)
b/Å	18.9059(5)
c/Å	10.9462(3)
α/°	90.00
β/°	105.989(2)
γ/°	90.00
Volume/Å^3	2211.10(10)
Z	4
ρ_{calc}g/cm^3	1.630
μ/mm^{-1}	0.333
F(000)	1112.0
Crystal size/mm^3	0.5 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.38 to 51.98
Index ranges	$-13 \leq h \leq 13$, $-23 \leq k \leq 22$, $-11 \leq l \leq 13$
Reflections collected	24654
Independent reflections	4341 [R_{int} = 0.0519]
Data/restraints/parameters	4341/0/309
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0353, wR_2 = 0.0819
Final R indexes [all data]	R_1 = 0.0496, wR_2 = 0.0889
Largest diff. peak/hole / e Å^{-3}	0.32/-0.37

Table S2. Crystal data and structure refinement for **3.**

Crystal data and structure refinement for 3	
Identification code	nz323_final
Empirical formula	$C_{20}H_{22}F_6N_4O_7S_2$
Formula weight	608.54
Temperature/K	88(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	12.7108(1)
b/Å	12.4777(1)
c/Å	16.4443(2)
α/°	90.00
β/°	98.012(1)
γ/°	90.00
Volume/Å^3	2582.63(4)
Z	4
ρ_{calc}g/cm^3	1.616
μ/mm^{-1}	0.309
F(000)	1280.0
Crystal size/mm^3	0.43 × 0.33 × 0.20
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.8 to 52
Index ranges	$-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-19 \leq l \leq 20$
Reflections collected	30554
Independent reflections	5078 [R_{int} = 0.0345]
Data/restraints/parameters	5078/0/362
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0356, wR_2 = 0.0883
Final R indexes [all data]	R_1 = 0.0432, wR_2 = 0.0935
Largest diff. peak/hole / e Å^{-3}	0.65/-0.50

Table S3. Crystal data and structure refinement for **4.**

Crystal data and structure refinement for 4	
Identification code	nz360_final
Empirical formula	$C_{30}H_{35.5}F_6N_8O_{7.5}PdS_2$
Formula weight	912.68
Temperature/K	89(2)
Crystal system	Triclinic
Space group	P-1
a/Å	9.609(5)
b/Å	13.660(5)
c/Å	15.003(5)
α/°	106.473(5)
β/°	93.890(5)
γ/°	101.967(5)
Volume/Å^3	1830.5(13)
Z	2
ρ_{calc}g/cm^3	1.656
μ/mm^{-1}	0.710
F(000)	927.0
Crystal size/mm^3	0.30 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.86 to 55.92
Index ranges	$-12 \leq h \leq 12$, $-17 \leq k \leq 18$, $-19 \leq l \leq 19$
Reflections collected	40793
Independent reflections	8775 [R_{int} = 0.0429]
Data/restraints/parameters	8775/43/603
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0492, wR_2 = 0.1226
Final R indexes [all data]	R_1 = 0.0679, wR_2 = 0.1349
Largest diff. peak/hole / e Å^{-3}	1.25/-0.88

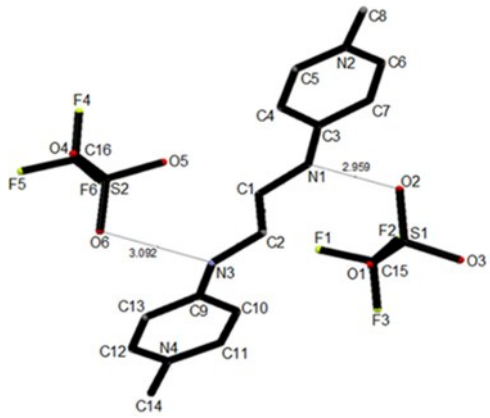

Figure S11. Capped stick diagram of $[H_2L_{en}][OTf]_2$ (**2**) showing hydrogen bonding

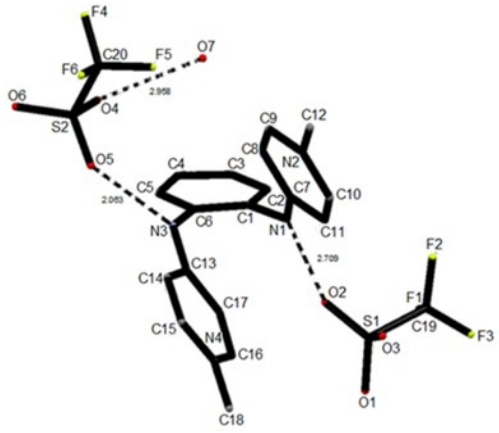

Figure S12. Capped stick diagram of $[H_2L_{phen}][OTf]_2$ (**3**) showing hydrogen bonding

Table S4: Selected bond lengths and bond angles for **2**.

Bond	Length	Bond	Length	Bond	Length	Bond	Length
C(1)-N(1)	1.453(2)	C(4)-C(5)	1.364(2)	C(9)-N(3)	1.337(2)	C(12)-N(4)	1.360(2)
C(1)-C(2)	1.532(3)	C(5)-N(2)	1.350(2)	C(9)-C(10)	1.422(2)	C(14)-N(4)	1.474(2)
C(2)-N(3)	1.459(2)	C(6)-C(7)	1.357(3)	C(10)-C(11)	1.360(3)	C(8)-N(2)	1.482(2)
C(3)-N(1)	1.337(2)	C(6)-N(2)	1.357(2)	C(11)-N(4)	1.355(2)	C(3)-C(4)	1.416(2)

Bond	Angle	Bond	Angle
N(1)-C(1)-C(2)	112.27(15)	C(9)-N(3)-C(2)	123.64(15)
N(1)-C(3)-C(4)	123.70(16)	N(3)-C(9)-C(13)	120.60(16)
N(1)-C(3)-C(7)	119.50(16)	N(3)-C(9)-C(10)	122.78(17)
C(3)-N(1)-C(1)	125.17(15)	N(3)-C(2)-C(1)	110.67(15)

Table S5: Selected bond lengths and bond angles for **3**.

Bond	Length	Bond	Length	Bond	Length	Bond	Length
C(1)-C(2)	1.386(7)	C(5)-C(6)	1.413(7)	C(9)-N(2)	1.355(8)	C(13)-C(17)	1.404(7)
C(1)-C(6)	1.400(8)	C(6)-N(4)	1.389(7)	C(10)-N(2)	1.349(8)	C(14)-C(15)	1.375(9)
C(1)-N(1)	1.461(6)	C(7)-C(8)	1.389(9)	C(10)-C(11)	1.373(9)	C(15)-N(3)	1.356(8)
C(2)-C(3)	1.397(8)	C(7)-N(1)	1.399(7)	C(12)-N(2)	1.484(8)	C(16)-N(3)	1.345(8)
C(3)-C(4)	1.378(9)	C(7)-C(11)	1.406(9)	C(13)-C(14)	1.393(9)	C(16)-C(17)	1.374(8)
C(4)-C(5)	1.394(8)	C(8)-C(9)	1.379(8)	C(13)-N(1)	1.400(7)	C(18)-N(3)	1.488(7)

Bond	Angle	Bond	Angle	Bond	Angle
C(2)-C(1)-N(1)	119.3(5)	N(1)-C(7)-C(11)	120.3(5)	C(7)-N(1)-C(13)	122.3(4)
C(6)-C(1)-N(1)	118.2(5)	C(14)-C(13)-N(1)	120.2(5)	C(7)-N(1)-C(1)	119.3(4)
C(8)-C(7)-N(1)	121.2(5)	N(1)-C(13)-C(17)	121.7(5)	C(13)-N(1)-C(1)	117.5(4)

Table S6: Selected bond lengths and bond angles for **4**.

Bond	Length	Bond	Length	Bond	Length
C(1)-N(1)	1.474(5)	C(5)-N(2)	1.365(6)	C(10)-C(11)	1.348(11)
C(1)-C(2)	1.501(6)	C(6)-N(2)	1.349(6)	C(11)-N(4)	1.369(11)
C(2)-N(3)	1.454(5)	C(6)-C(7)	1.350(6)	C(14)-N(4)	1.460(14)
C(3)-N(1)	1.318(5)	C(8)-N(2)	1.471(6)	N(4)-C(12)	1.294(9)
C(3)-C(4)	1.431(6)	C(9)-N(3)	1.310(5)	C(12)-C(13)	1.347(5)
C(3)-C(7)	1.446(5)	C(9)-C(10)	1.381(8)	N(1)-Pd(1)	2.044(3)
C(4)-C(5)	1.348(6)	C(9)-C(13)	1.426(5)	N(3)-Pd(1)	2.022(3)

Bond	Angle	Bond	Angle	Bond	Angle
C(1)-N(1)-Pd(1)	112.6(2)	N(1)-C(1)-C(2)	109.5(3)	N(3)-C(9)-C(10)	125.0(5)
C(3)-N(1)-Pd(1)	129.7(3)	N(1)-C(3)-C(4)	122.0(3)	N(3)-C(9)-C(13)	121.2(3)
C(9)-N(3)-Pd(1)	129.7(3)	N(1)-C(3)-C(7)	123.7(4)	N(3)-C(2)-C(1)	108.3(3)
C(2)-N(3)-Pd(1)	106.4(2)	C(3)-N(1)-C(1)	116.3(3)	C(9)-N(3)-C(2)	123.0(3)
N(3)-Pd(1)-N(1)	78.32(12)	N(1)-Pd(1)-N(1)'	180.0	N(3)-Pd(1)-N(3)'	180.0