Electronic Supporting Information (ESI)

Studies on interactions of X-ray structurally characterized Mo(VI) complexes of thiophene appended amide-imine conjugates: optical recognition of calcon and 2-aminobutyric acid

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1. General method of UV-Vis and fluorescence titration

Stock solution of **M1** and **M2** (20 μM) are prepared in DMSO/H_2O (4/1, v/v, PBS buffer) media, pH 7.4 for UV-Vis and fluorescence titrations. Working solutions of **M1**, **M2**, calcon and 2-aminobutyric acid are prepared from their respective stock solutions. For absorption and emission studies, cells having path length 1cm are used. Fluorescence measurements have been performed using 5 nm x 5 nm slit width.

2. Job's plot from fluorescence experiment

A series of solutions containing **M1**, **M2** and calcon, 2-aminobutyric acid are prepared such that the total concentration of calcon, 2-aminobutyric acid and **M1**, **M2** remained constant (20 μM) in all the sets. The mole fractions (**x**) of calcon and 2-aminobutyric acid are varied from 0.1 to 0.9. The fluorescence intensity at 484 nm for **M1**-calcon and **M2** -2-aminobutyric acid at 489 nm are plotted respectively against the mole fraction of calcon and 2-aminobutyric acid.

3. Determination of binding constant

The binding constants of **M1** and **M2** towards sensed molecules (analyte) are determined using Benesi-Hildebrand equation:

$$\frac{F_{max} - F_{min}}{F_X - F_{min}} = 1 + \frac{1}{K[C]^n}$$

Here, $\mathbf{F_{min}}$, $\mathbf{F_x}$ and $\mathbf{F_{max}}$ are the emission intensities of **M1** and **M2** in absence of analyte, at an intermediate analyte concentration, and at a concentration of complete interaction with analyte respectively. **K** is the binding constant, **C** is the concentration of analyte and **n** is the number of analyte bound per crystal molecule (here, **n** = 1). The value of **K** can be determined from the slopes of the plots.

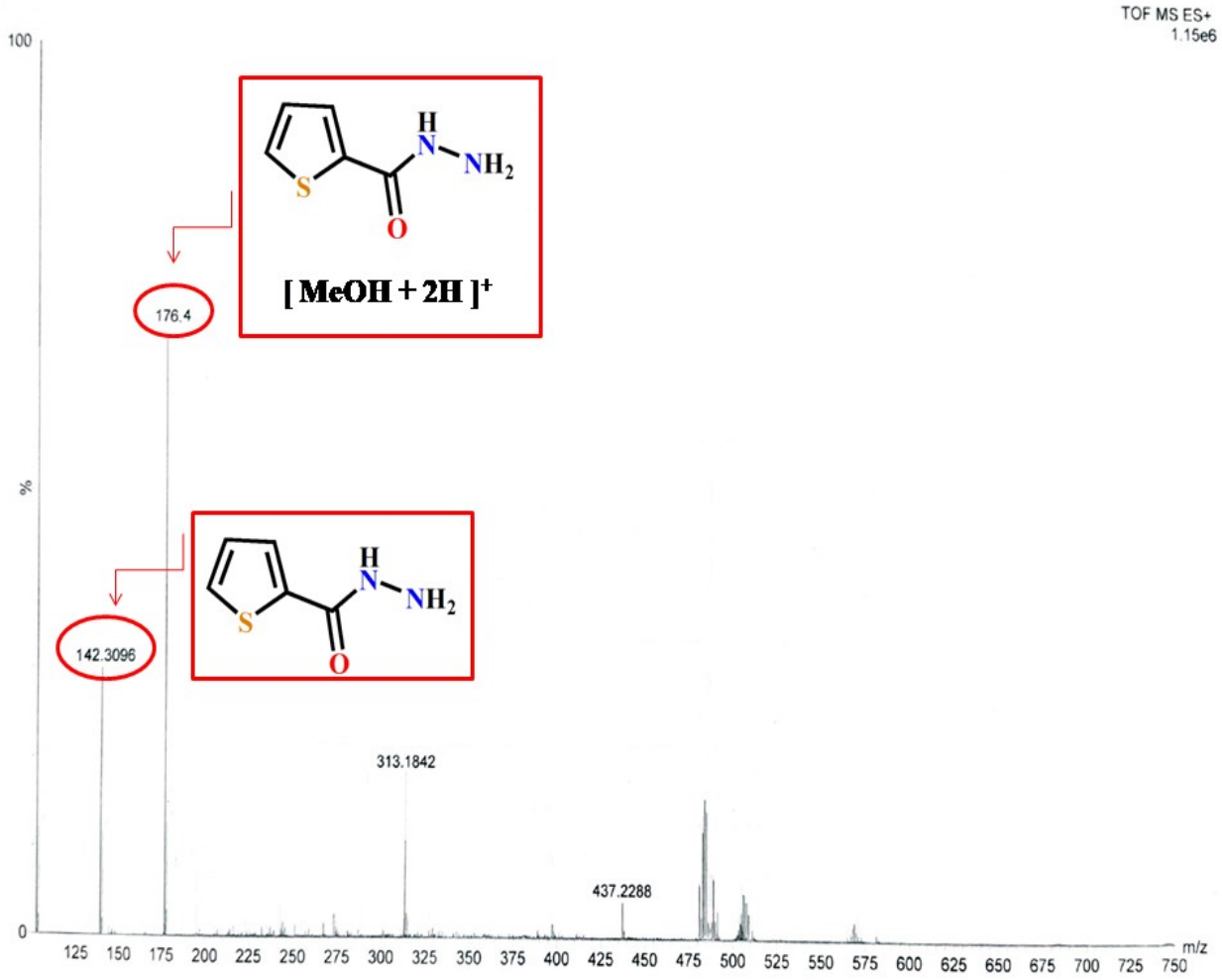

Figure S1a QTOF mass spectrum of **TCA**

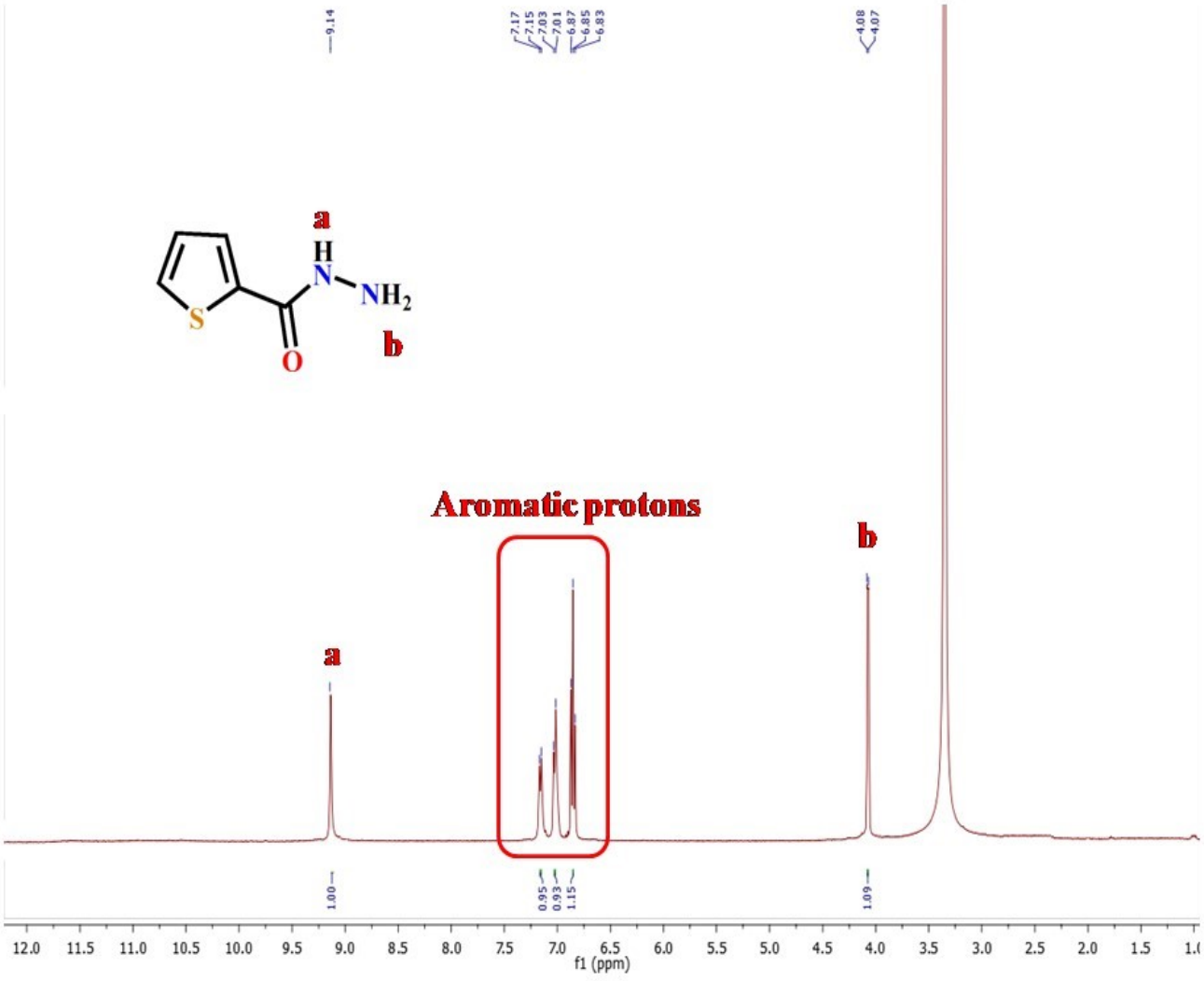

Figure S1b ^{1}H NMR spectrum of **TCA** in DMSO-d_6

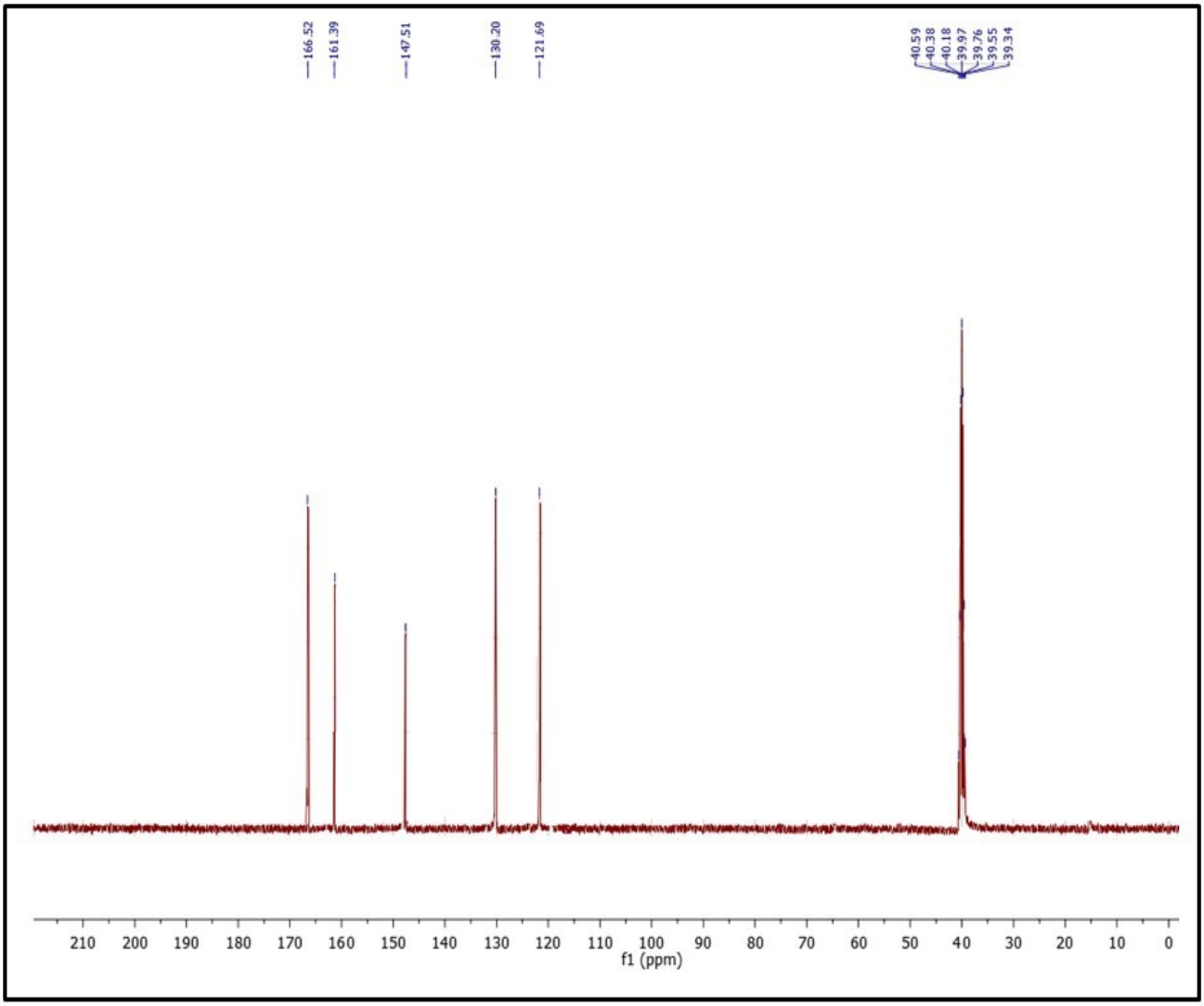

Figure S1c ^{13}C NMR spectrum of **TCA**

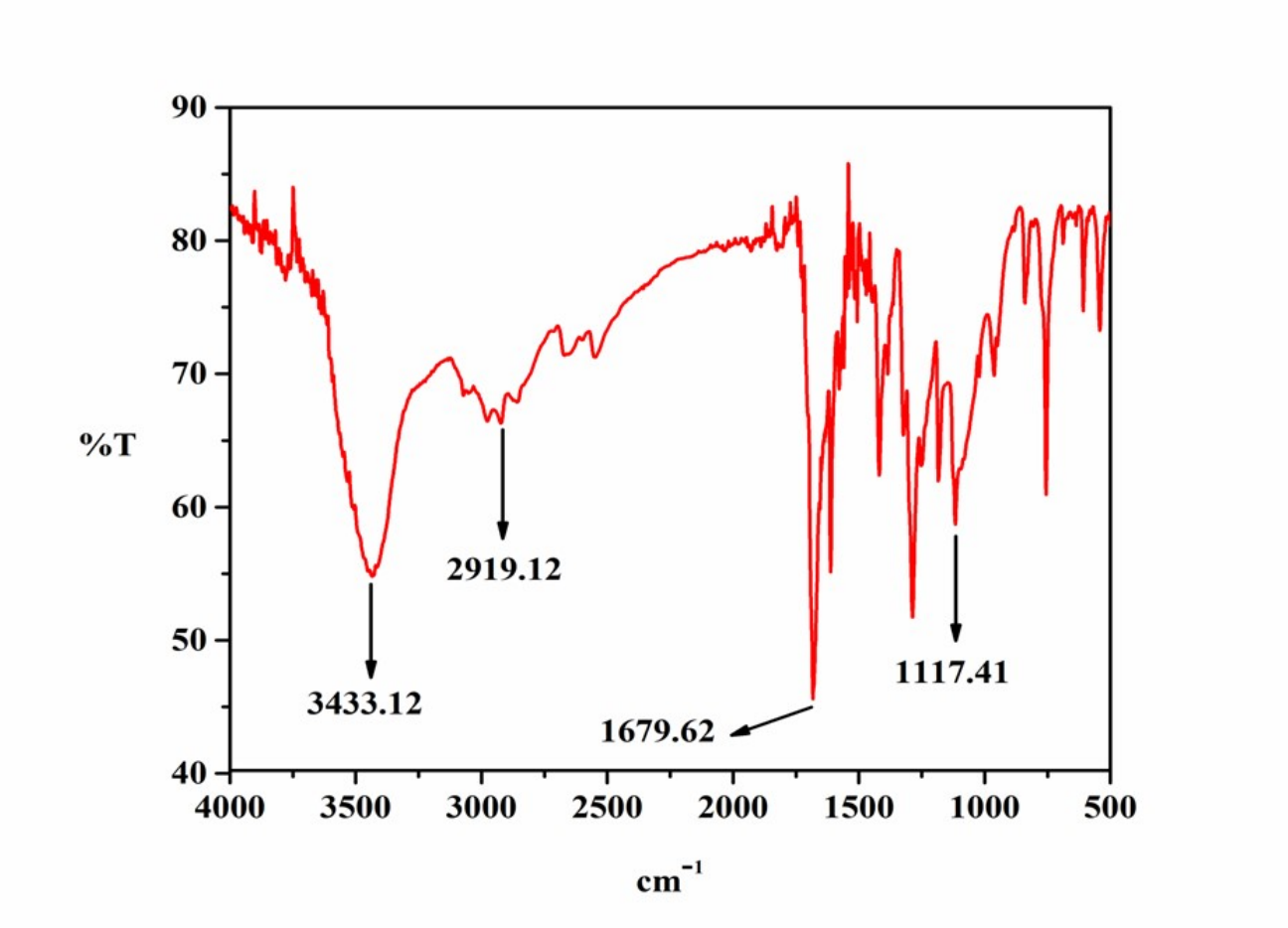

Figure S1d FTIR spectrum of **TCA**

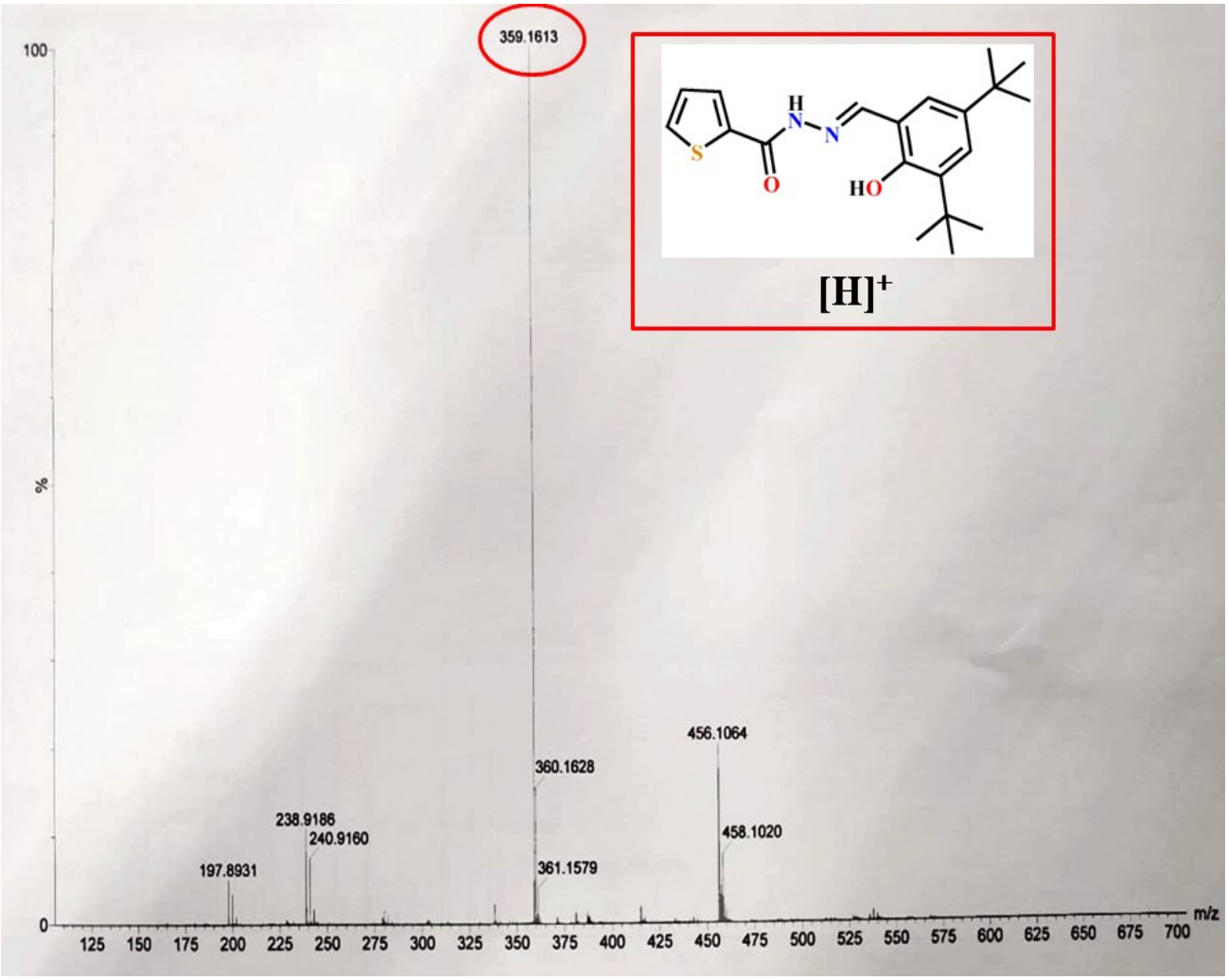

Figure S2a QTOF mass spectrum of **L1**

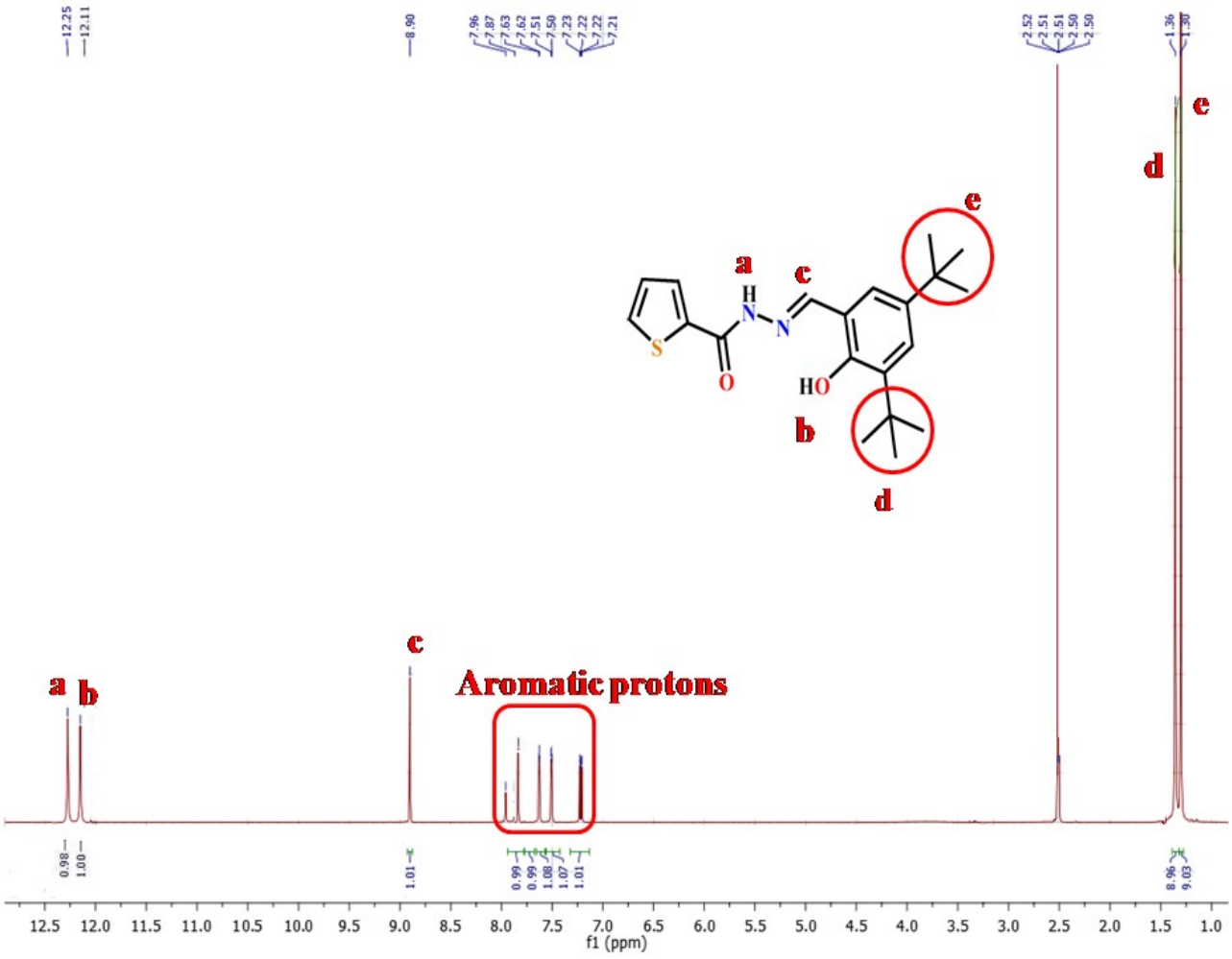

Figure S2b [1]HNMR spectrum of **L1** in DMSO-d_6

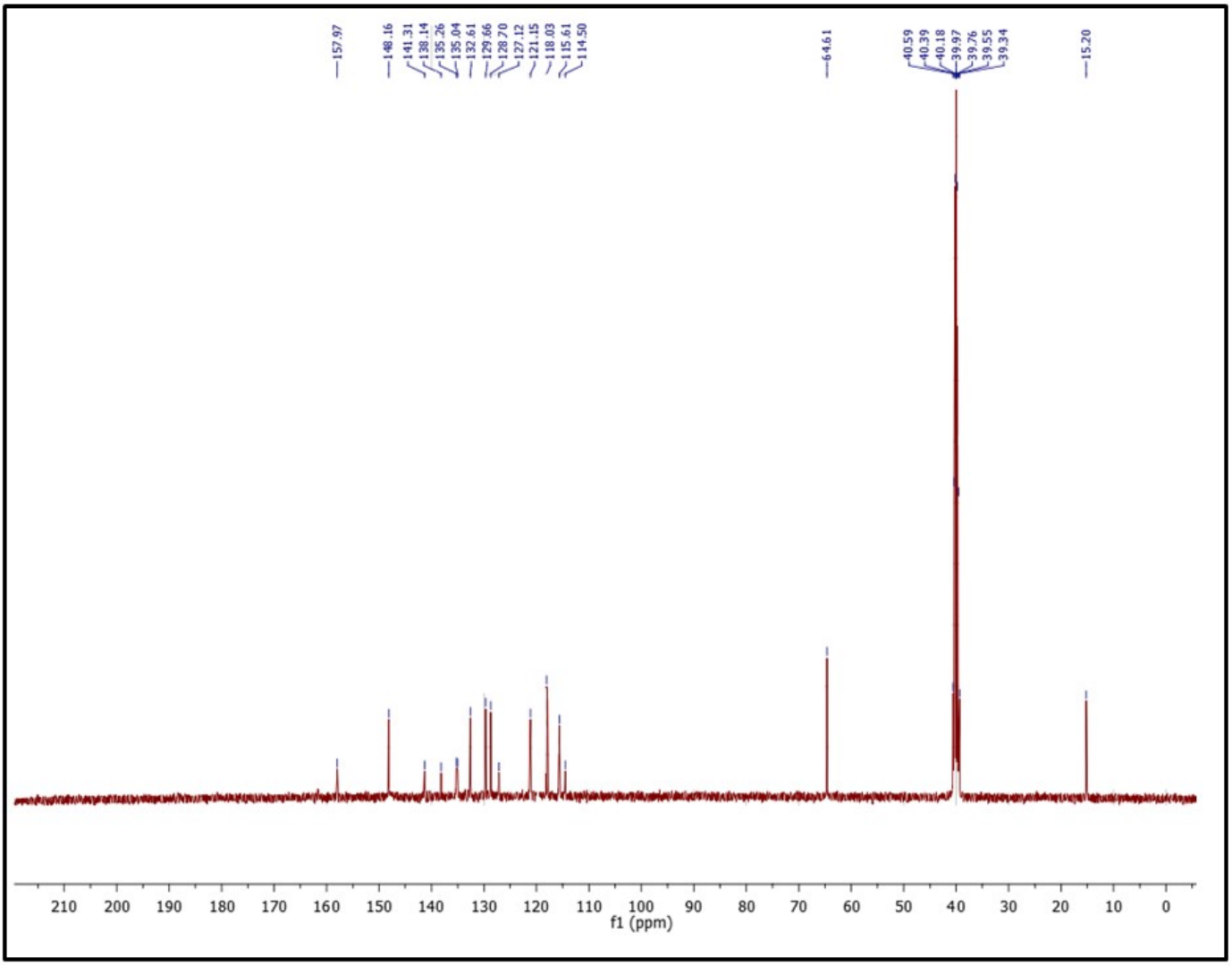

Figure S2c ^{13}CNMR spectrum of **L1**

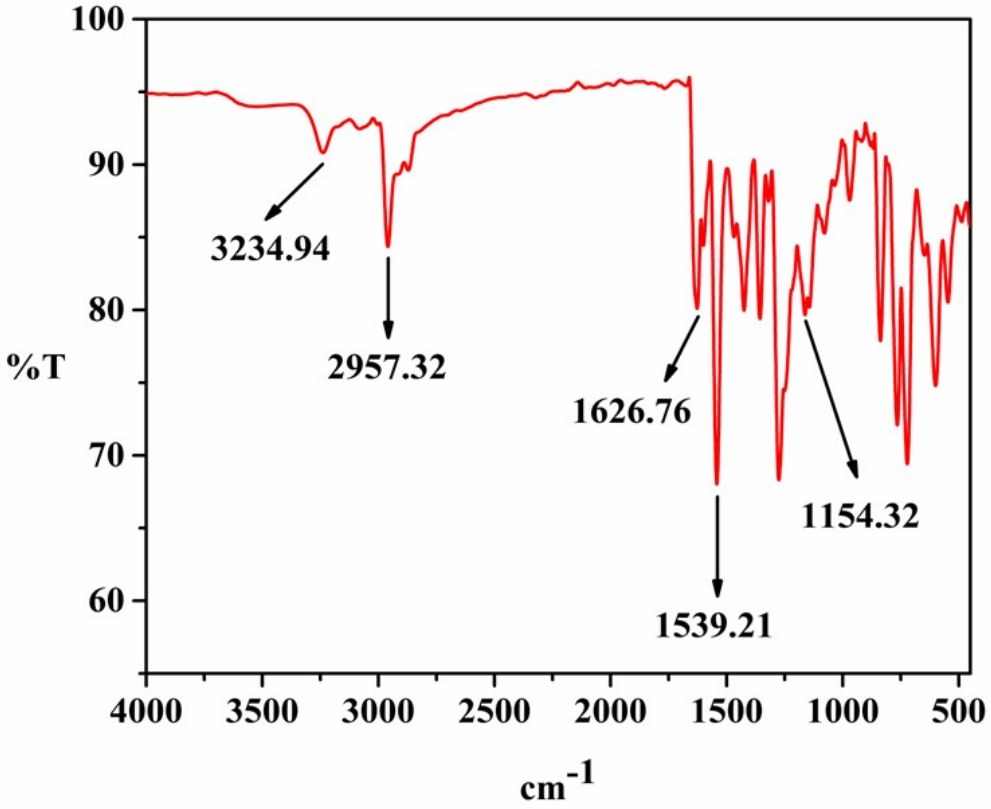

Figure S2d FTIR spectrum of **L1**

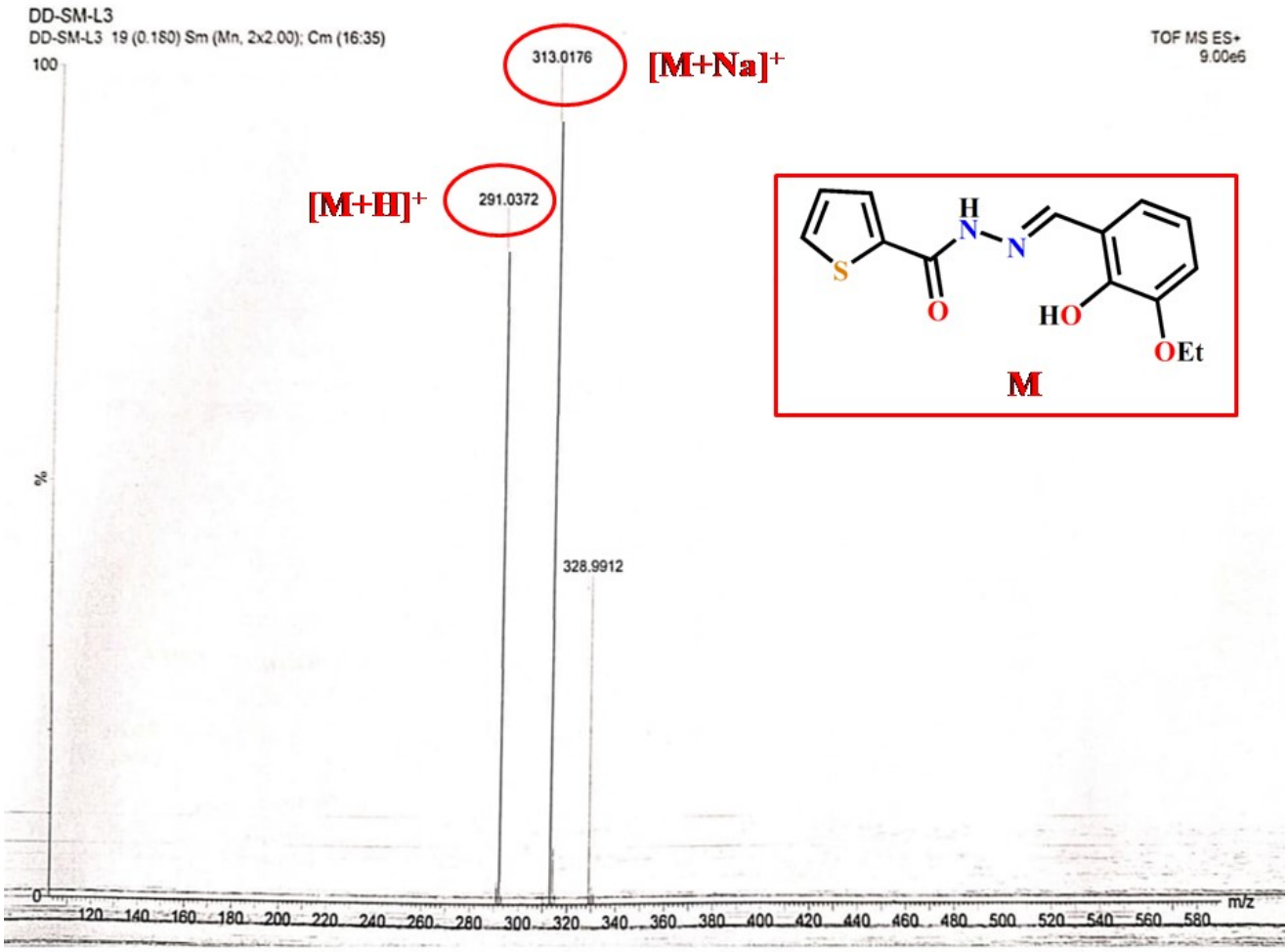

Figure S3a QTOF mass spectrum of **L2**

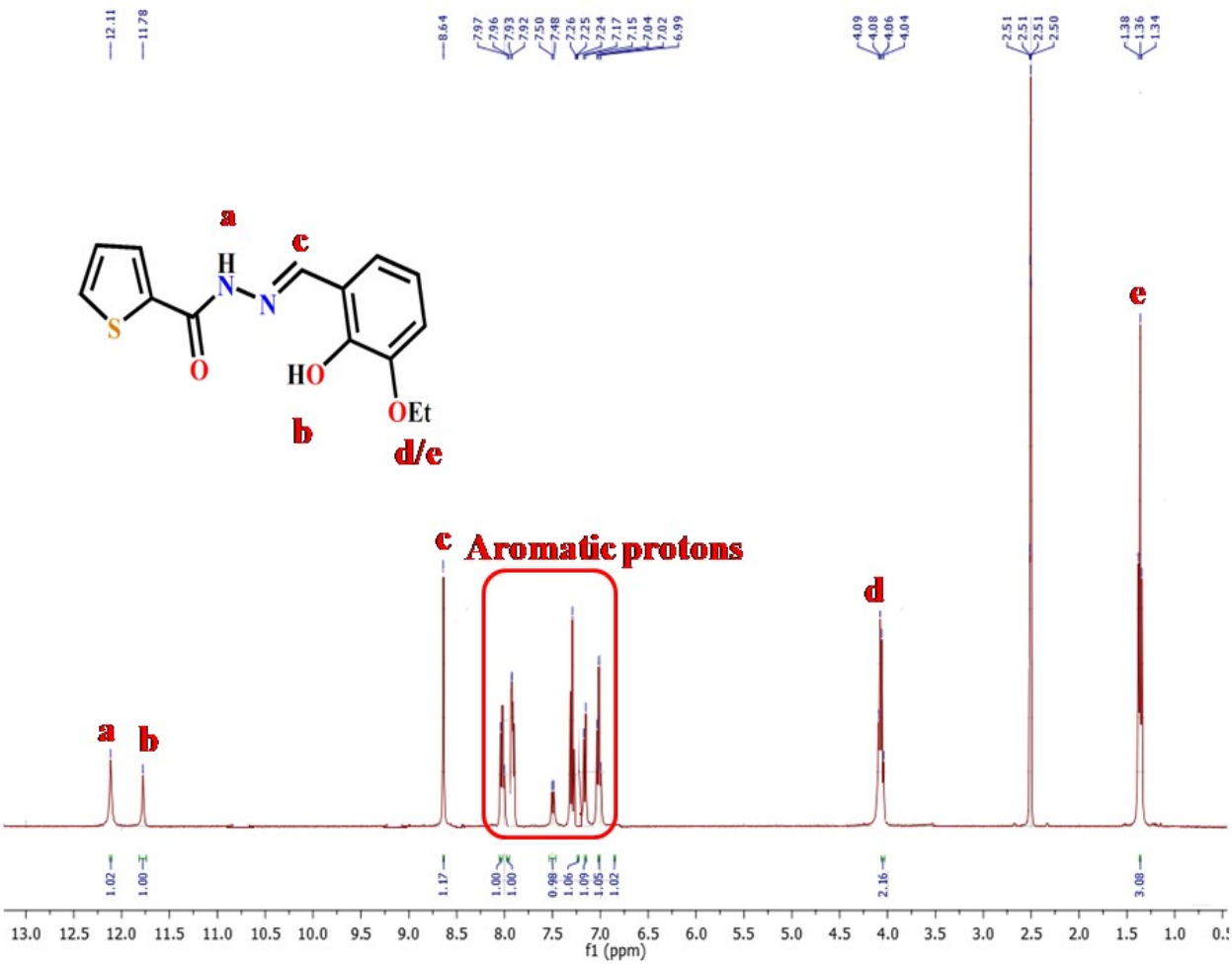

Figure S3b ^{1}HNMR spectrum of **L2** in DMSO-d_6

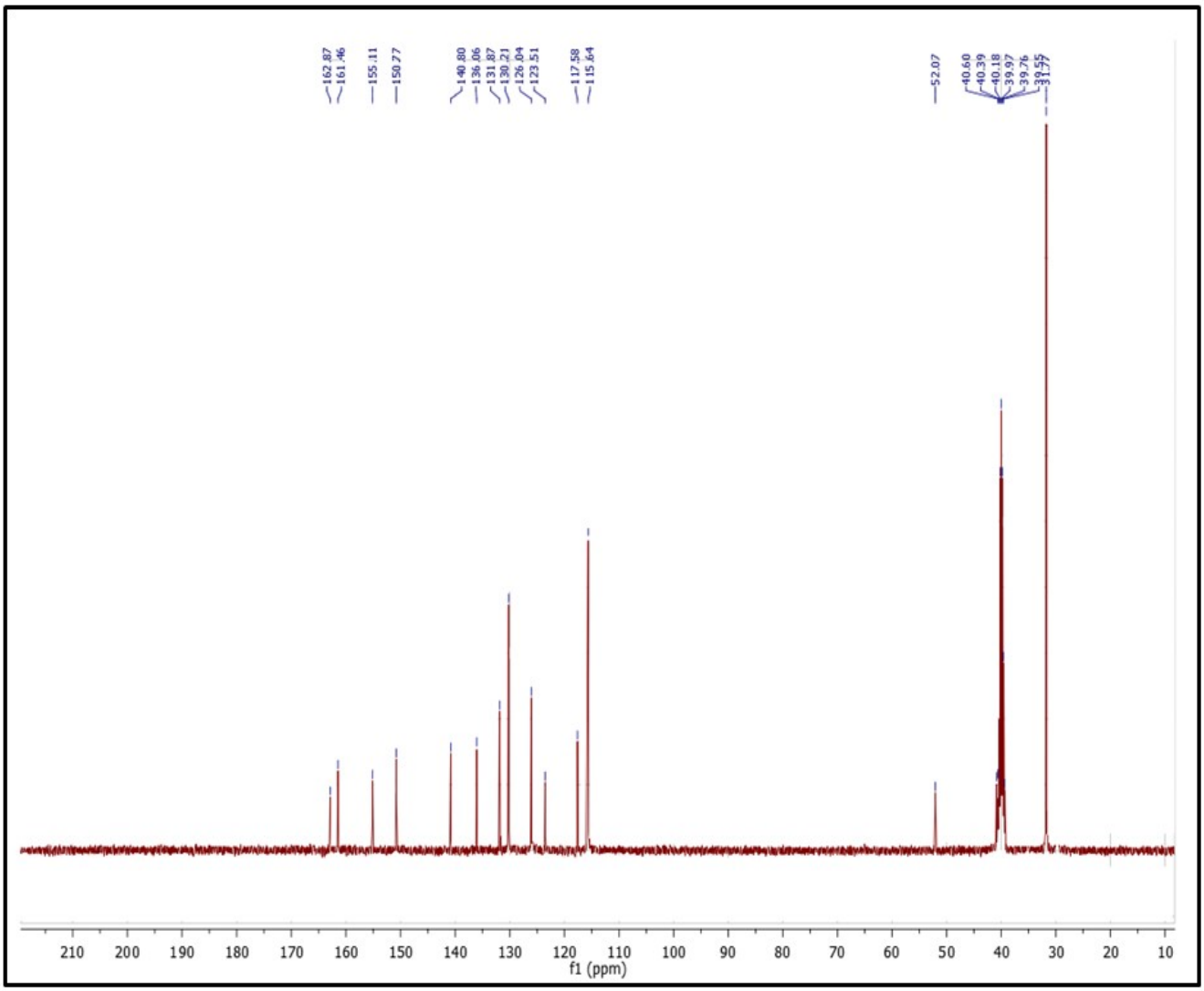

Figure S3c ^{13}CNMR spectrum of **L2**

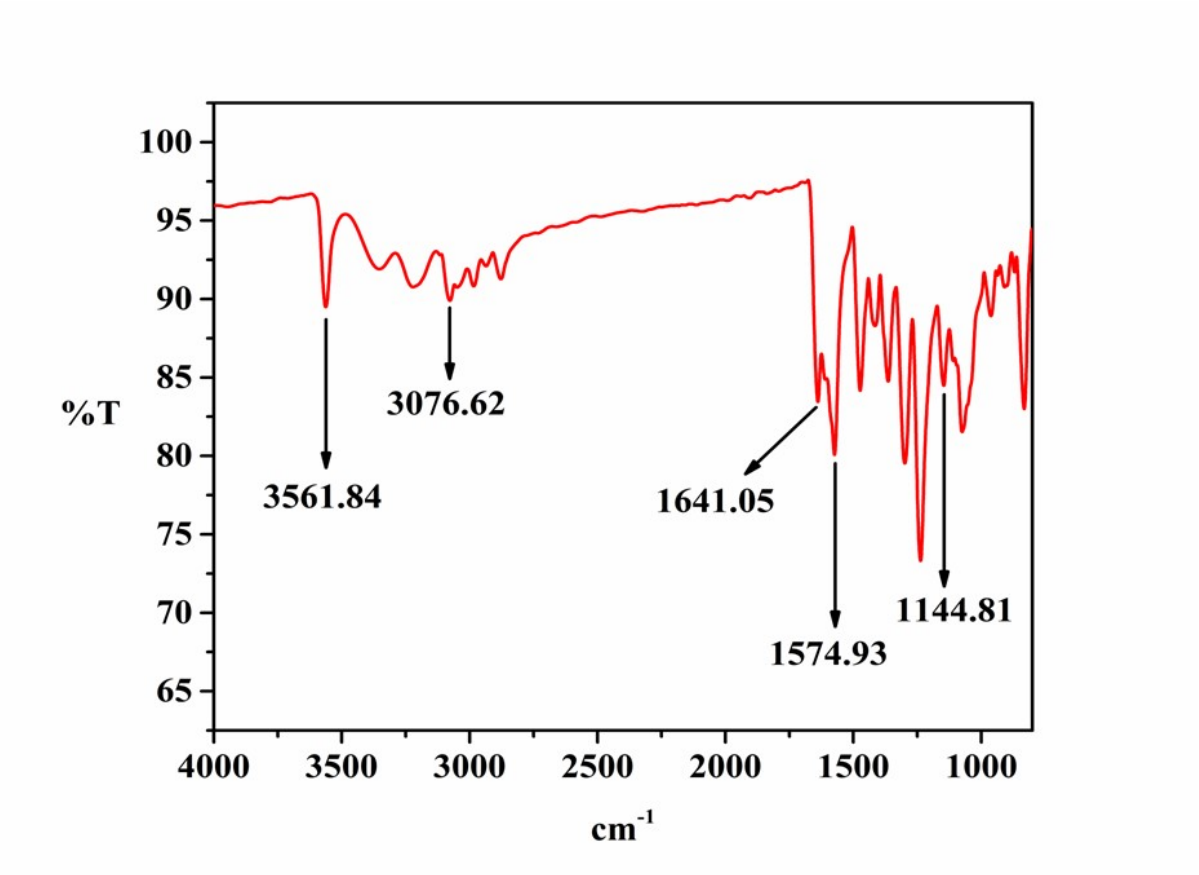

Figure S3d FTIR spectrum of **L2**

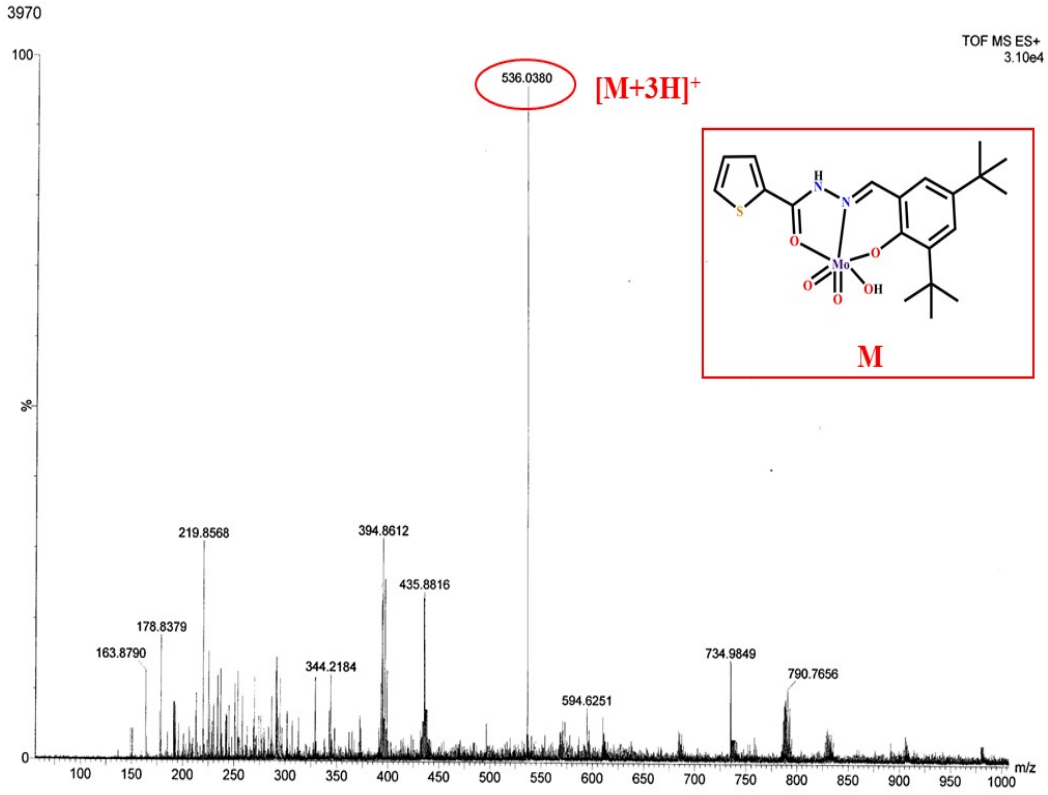

Figure S4a QTOF mass spectrum of **M1**

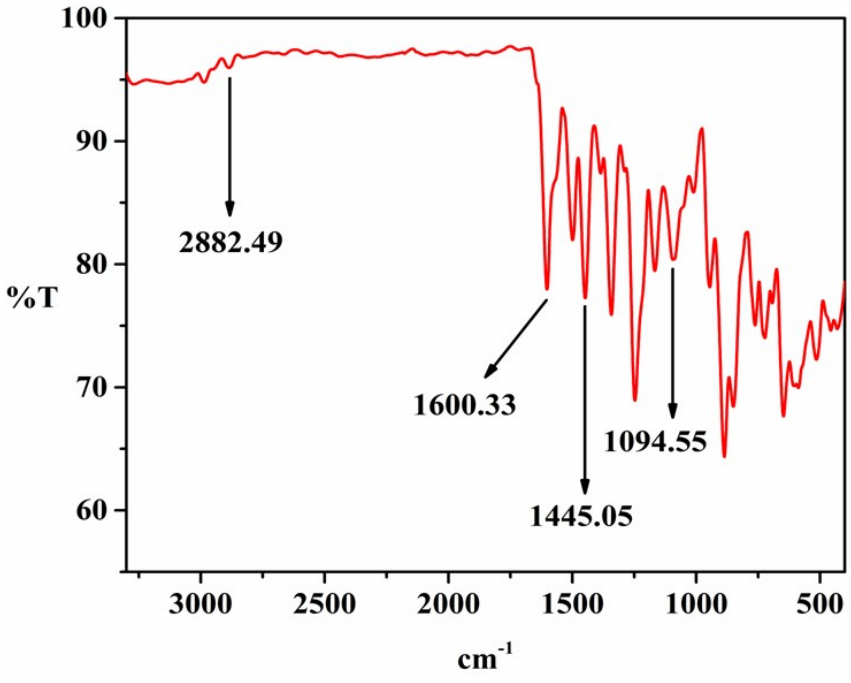

Figure S4b FTIR spectrum of **M1**

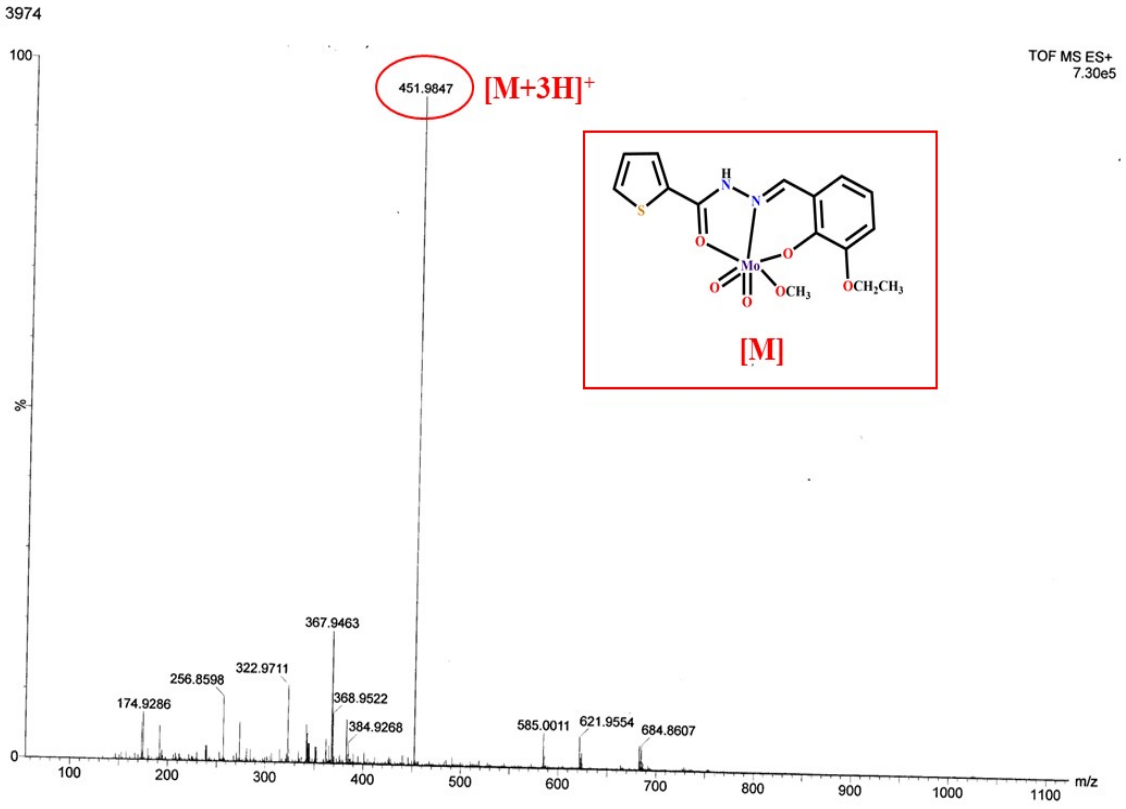

Figure S5a QTOF mass spectrum of **M2**

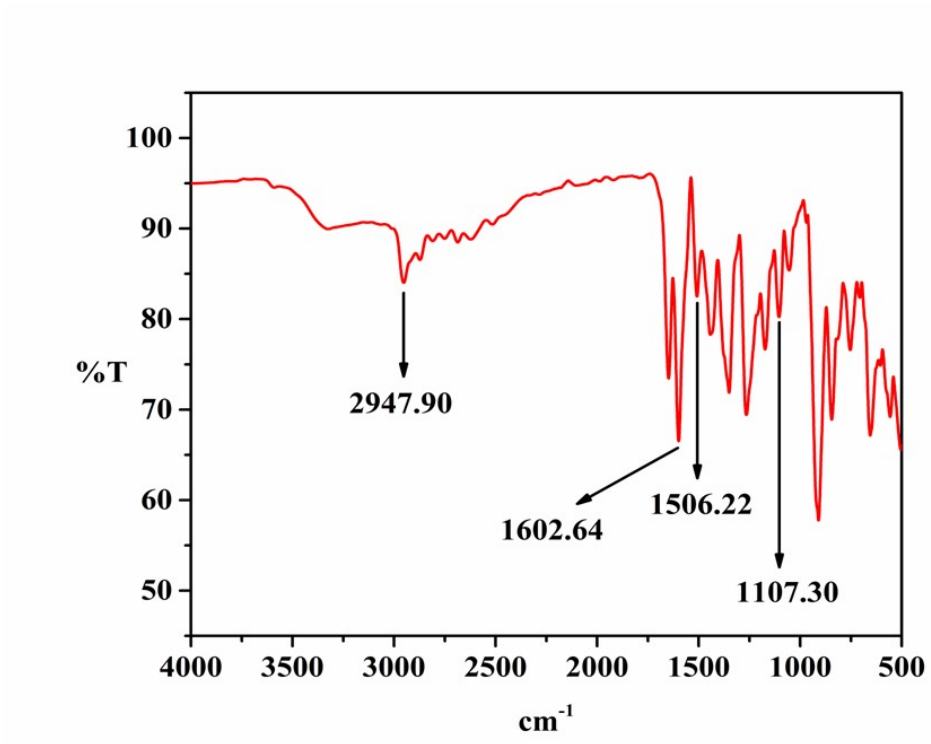

Figure S5b FTIR spectrum of **M2**

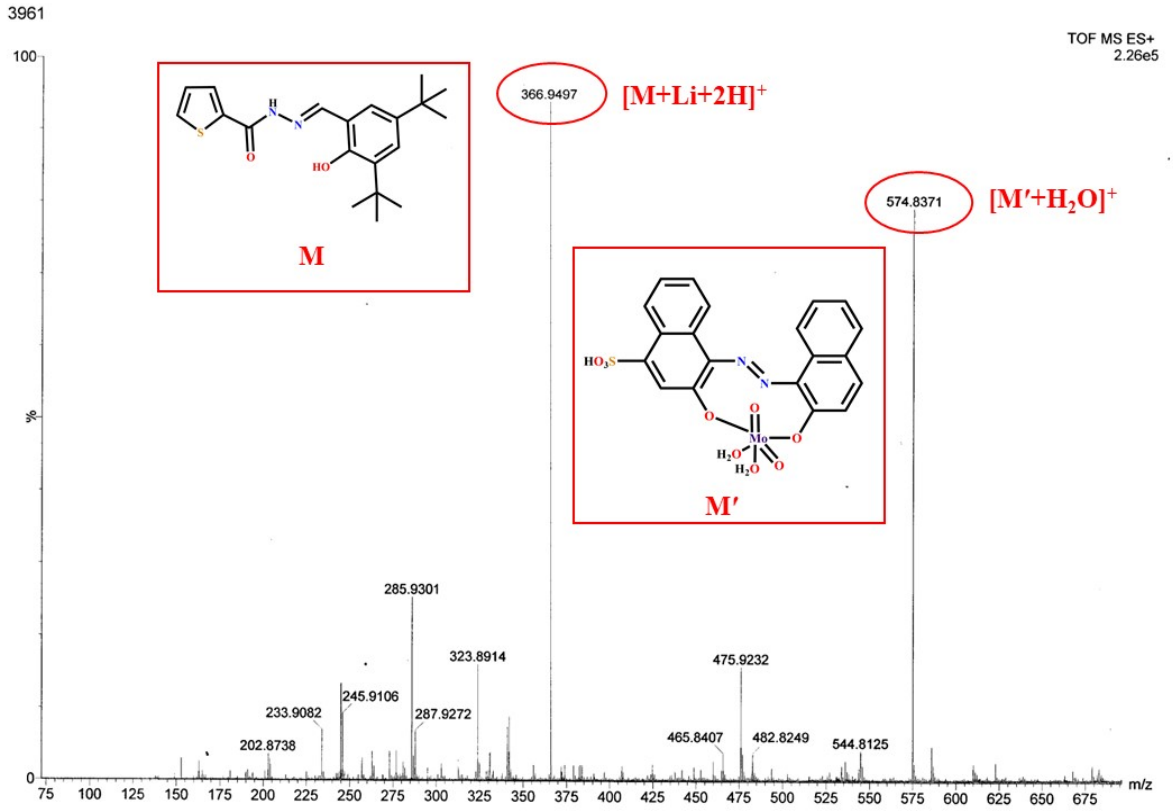

Figure S6a QTOF mass spectrum of **C1**

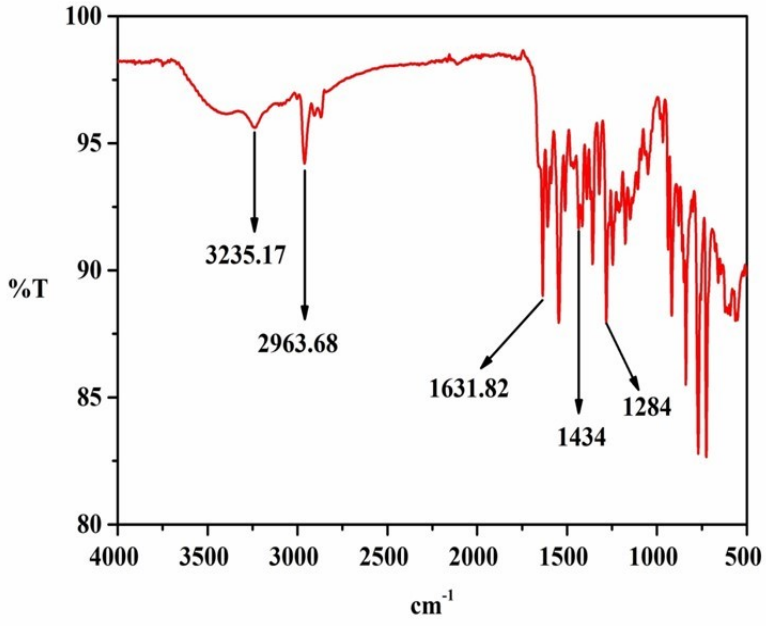

Figure S6b FTIR spectrum of **C1**

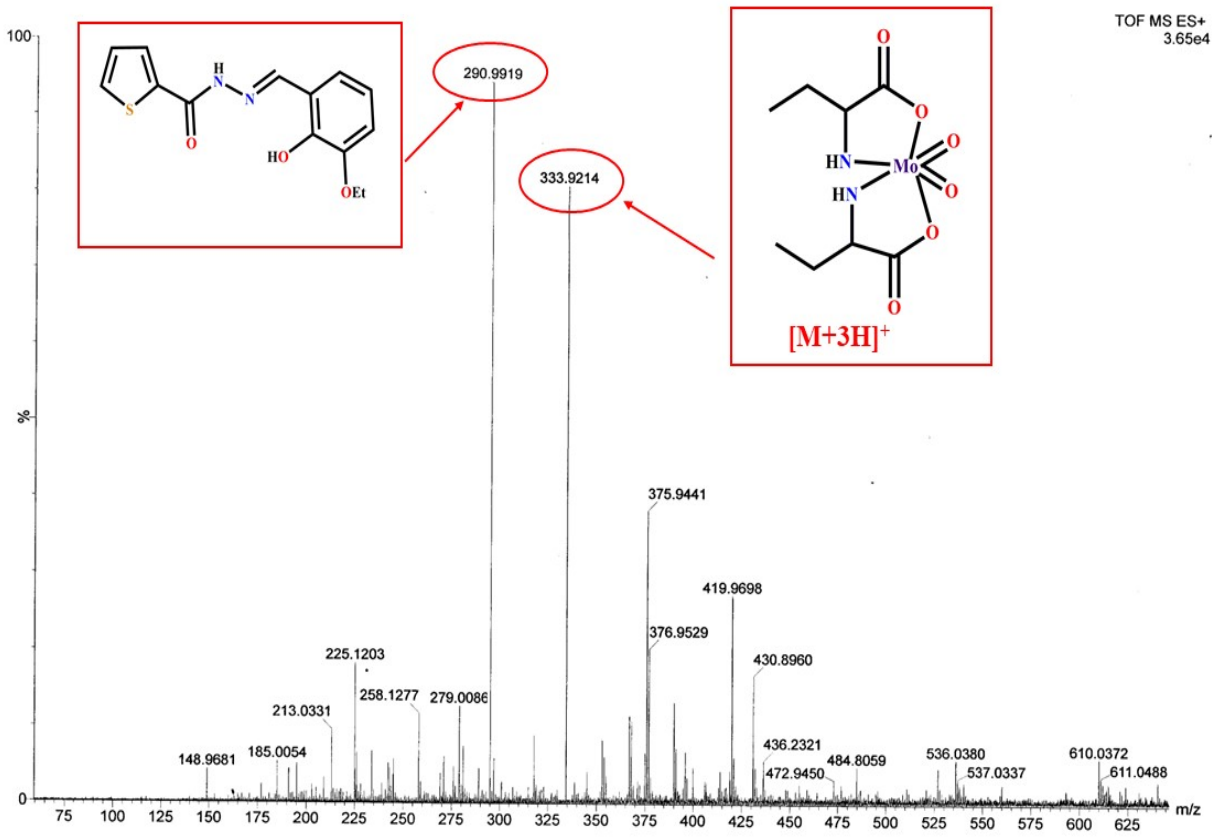

Figure S7a QTOF mass spectrum of **A1**

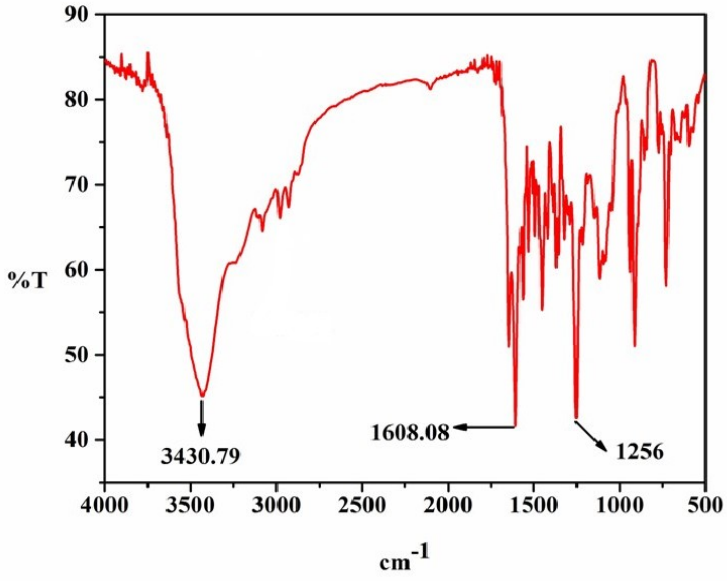

Figure S7b FTIR spectrum of **A1**

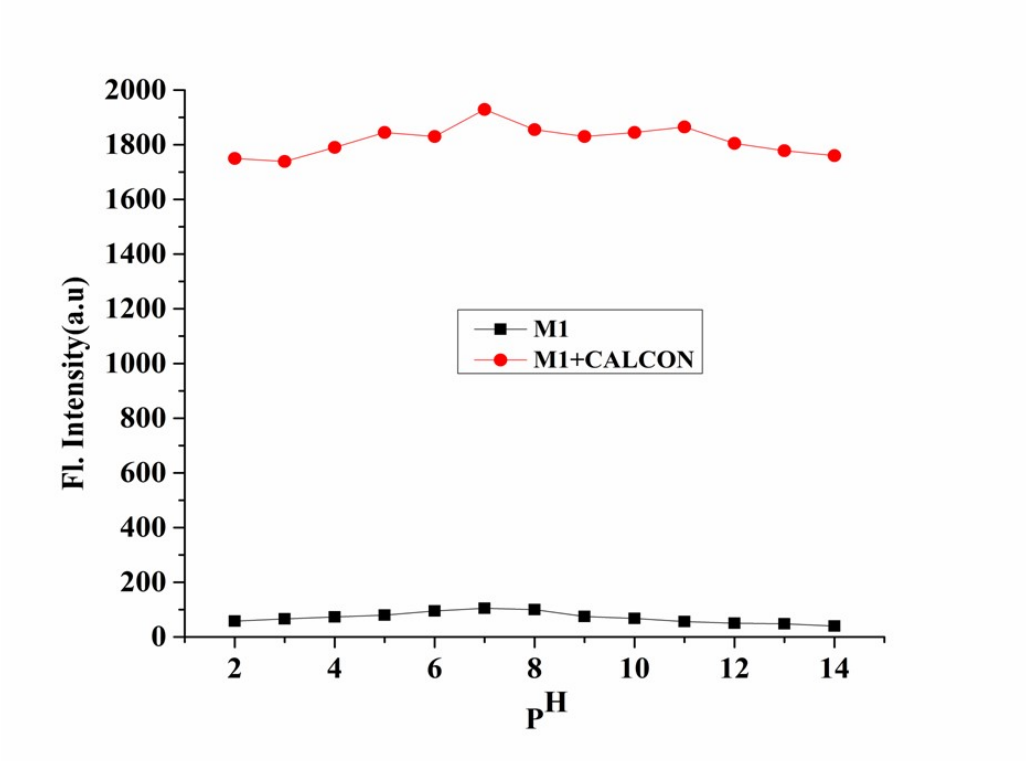

Figure S8a Effect of pH on the emission intensities of **M1** (λ_{ex} = 285 nm, λ_{em} = 484 nm) in presence and absence of calcon

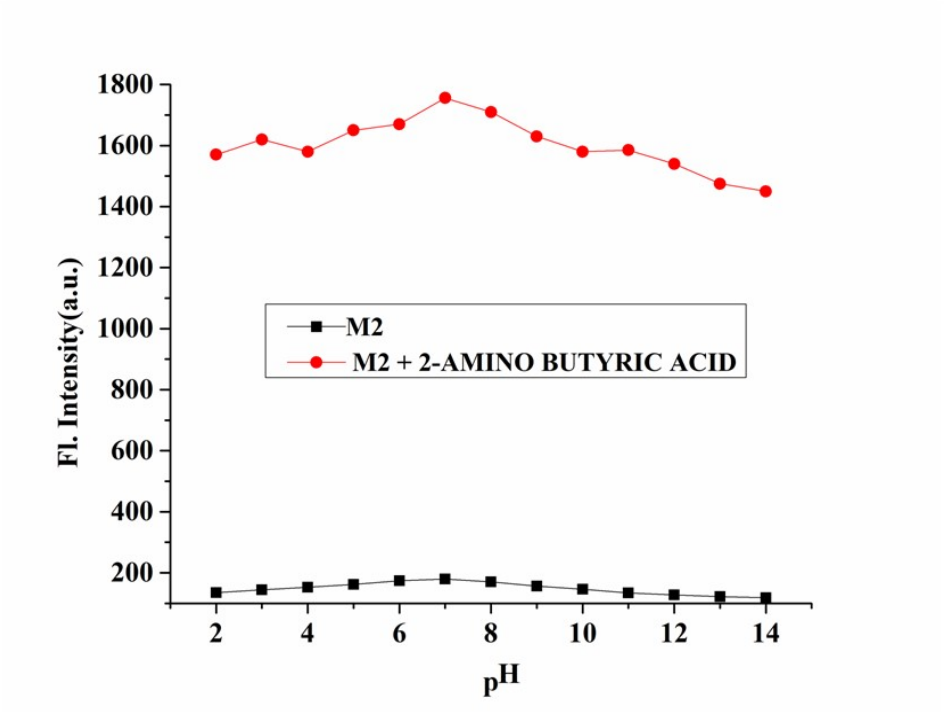

Figure S8b Effect of pH on the emission intensities of **M2** (λ_{ex} = 290 nm, λ_{em} = 489 nm) in presence and absence of 2-amino butyric acid

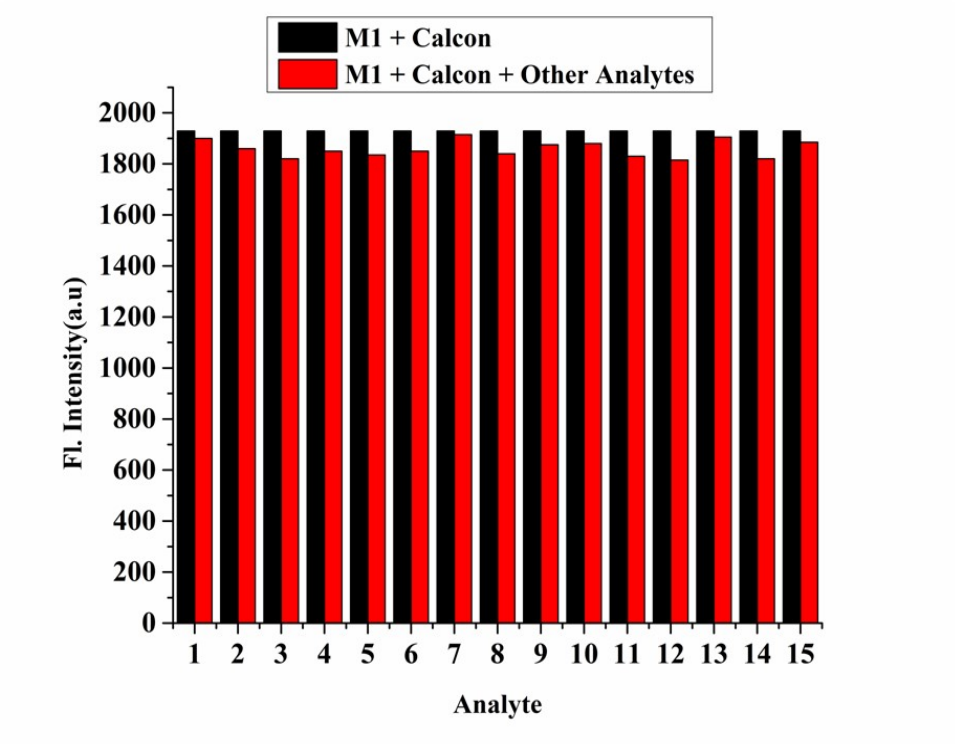

Figure S9a Plot for interference from common indicators during fluorescence recognition of calcon using **M1** (λ_{ex} = 285 nm, λ_{em} = 484 nm). 1; murexide, 2; phenolphthalein, 3; EBT, 4; methyl red, 5; methyl orange, 6; thymol blue, 7; bromocresol green, 8; methyl violet, 9; alizarin yellow R, 10; bromothymol blue, 11; anthraquinone, 12; methylene blue, 13; malachite green, 14; picric acid, 15; rhodamin B.

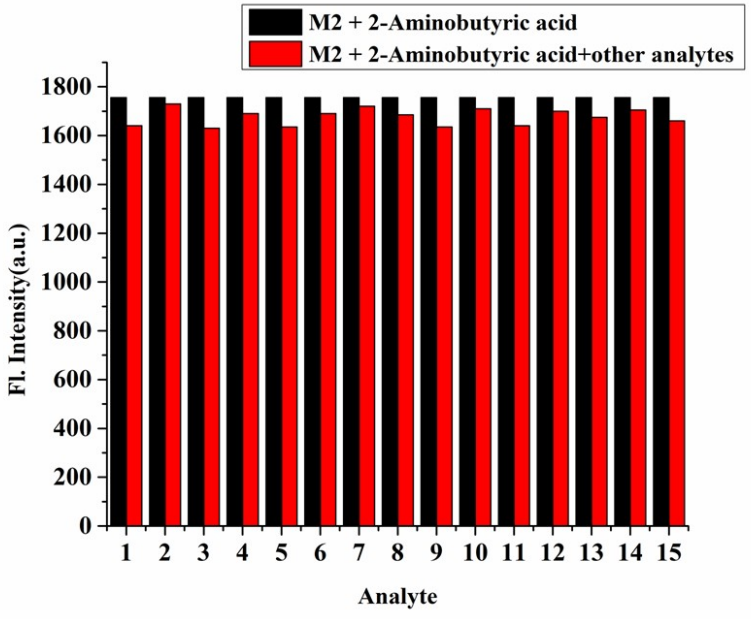

Figure S9b Plot for interference from common bio-molecules during fluorescence recognition of 2-aminobutyric acid using **M2** (λ_{ex} = 290 nm, λ_{em} = 489 nm) . 1; methionine, 2; arginine, 3; cysteine, 4; proline, 5; lysine, 6; tryptophan, 7; phenylalanine, 8; glycine, 9; aspartic acid, 10; creatinine, 11; Alanine, 12; superoxide dismutase,13; bisphenol, 14; glutathione, 15; cytochrome C

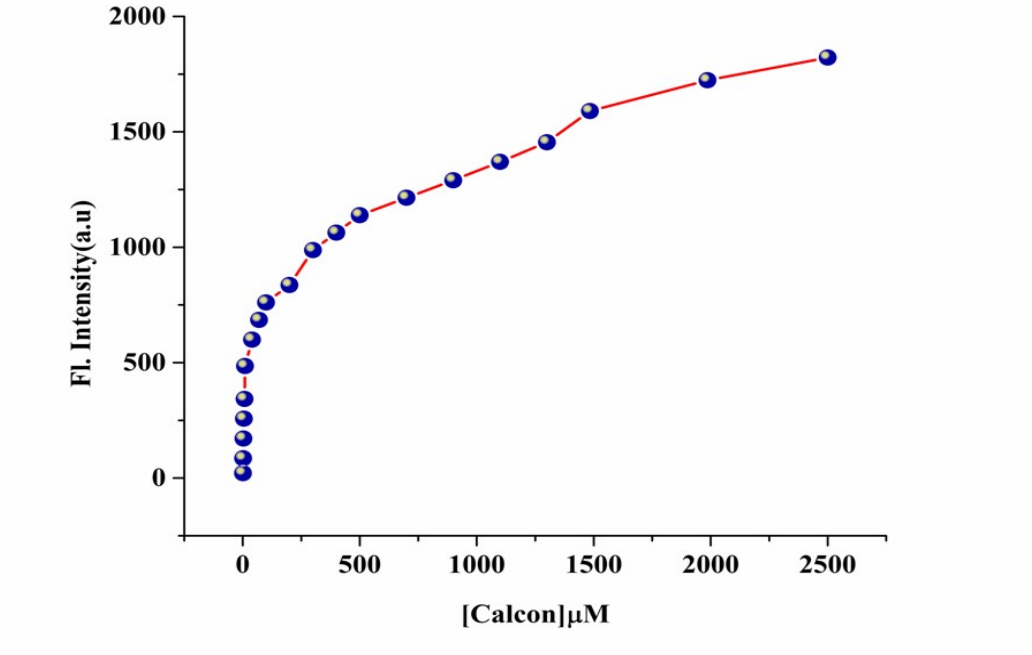

Figure S10a Plot of emission intensities of **M1** (20 μM, λ_{ex} = 285 nm, λ_{em} = 484 nm) as a function of externally added calcon (1.0-2500 μM)

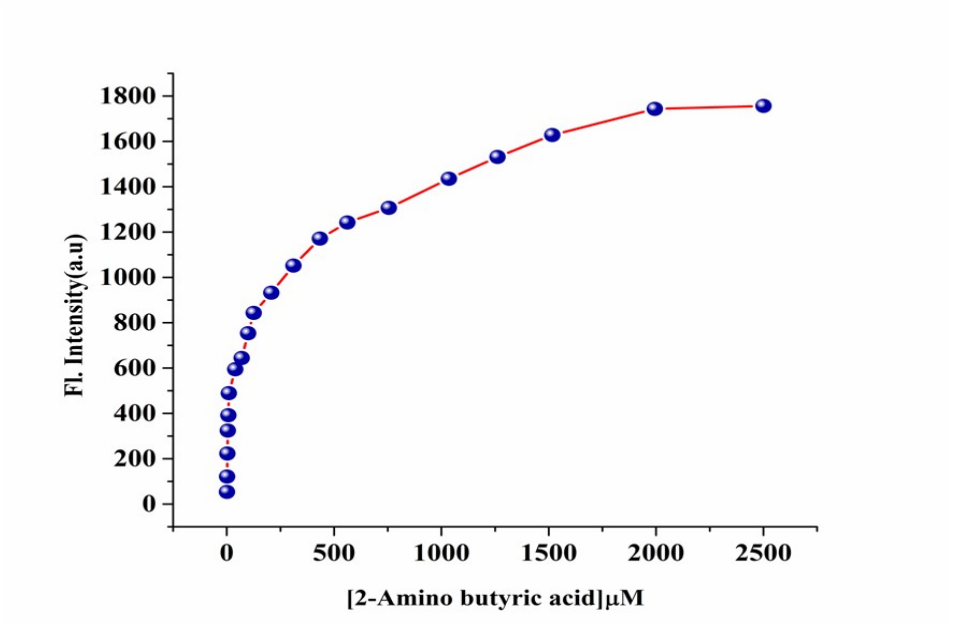

Figure S10b Plot of emission intensities of **M2** (20 μM, λ_{ex} = 290 nm, λ_{em} = 489 nm) as a function of externally added 2-aminobutyric acid (1.0-2500 μM)

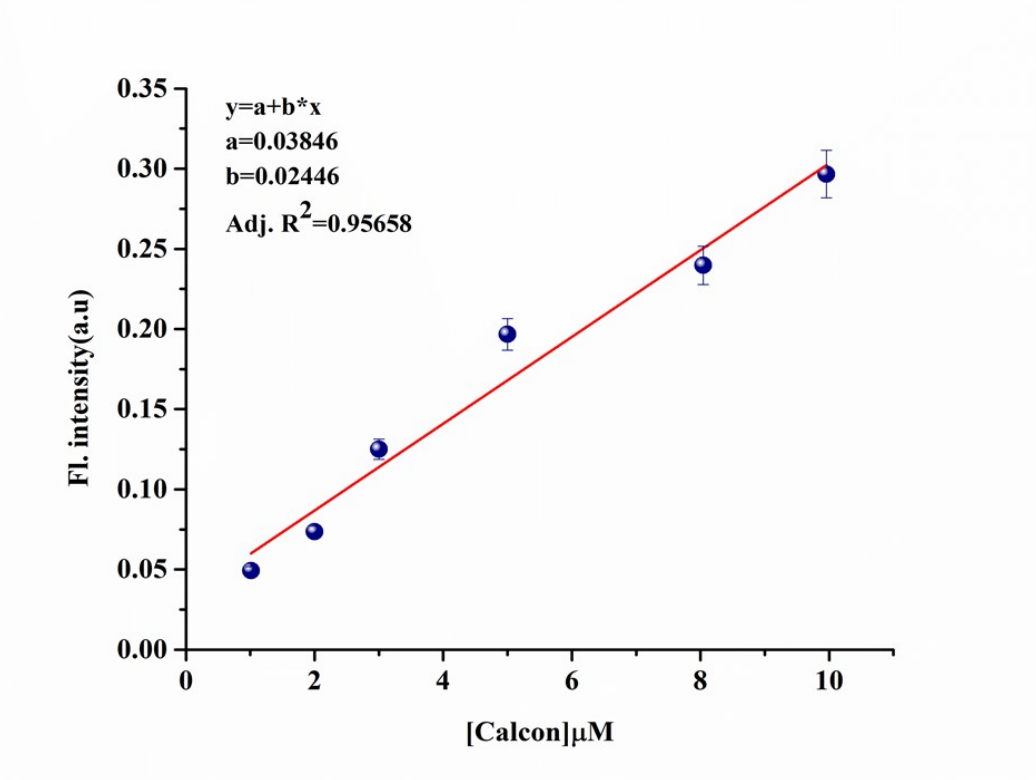

Figure S11a Determination of the detection limit of calcon (λ_{ex} = 285 nm, λ_{em} = 484 nm) using **M1** (20 μM)

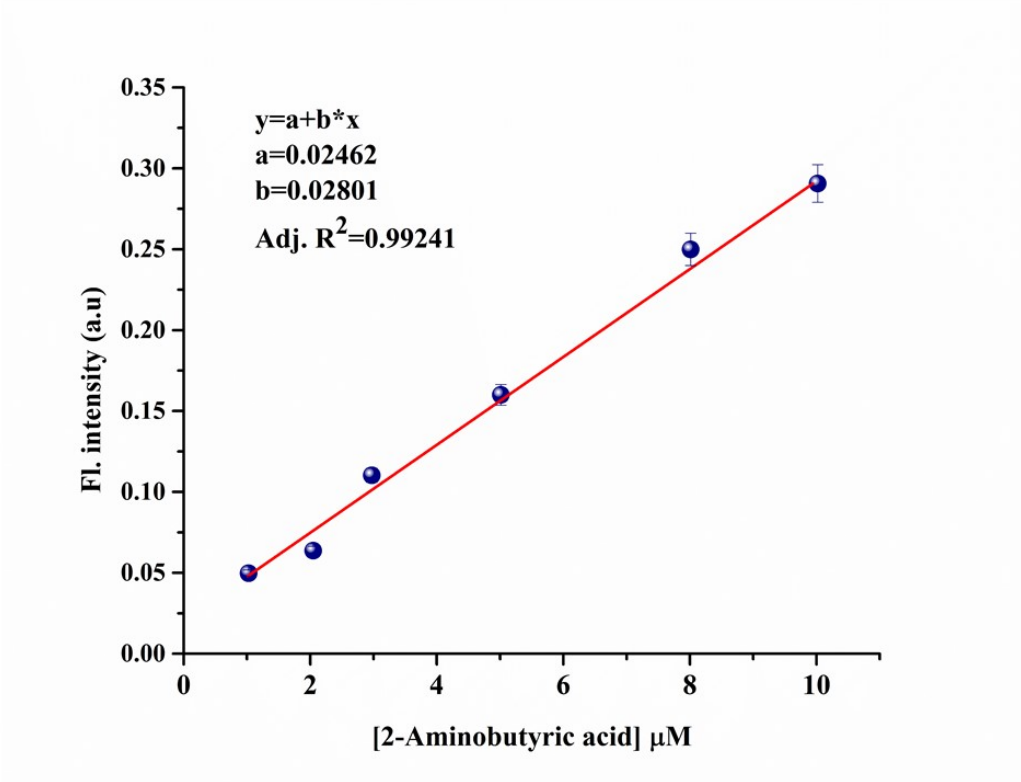

Figure S11b Determination of the detection limit based of 2-aminobutyric acid (λ_{ex} = 290 nm, λ_{em} = 489 nm) using **M2** (20 μM).

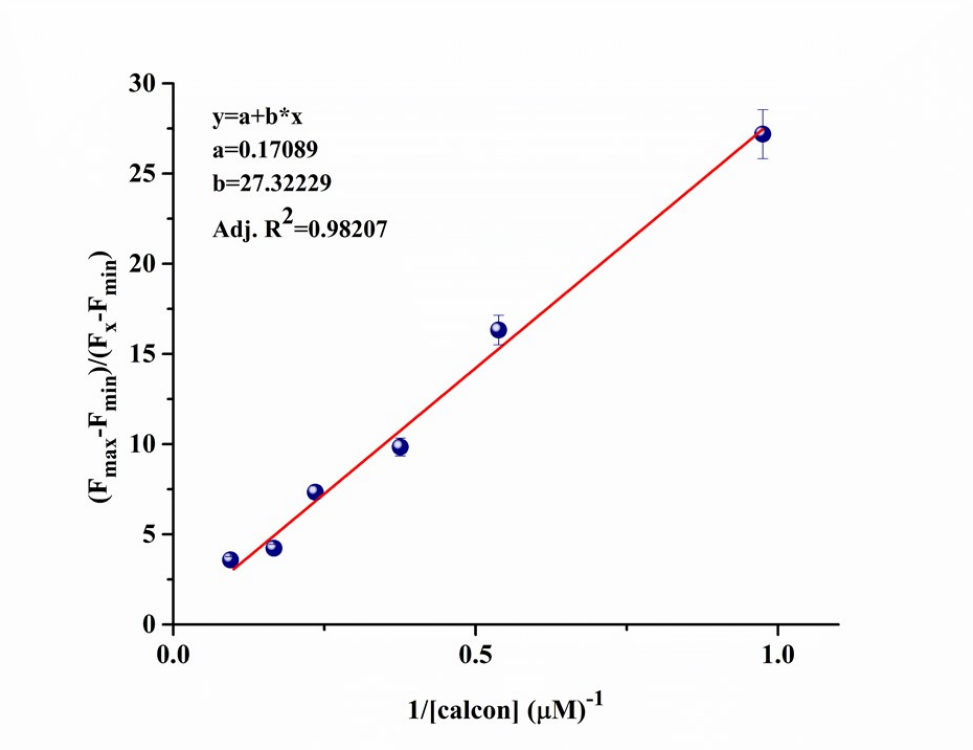

Figure S12a Benesi−Hildebrand plot for determination of displacement binding constant for calcon using **M1** (liner portion only) (λ_{ex} = 285 nm, λ_{em} = 484 nm)

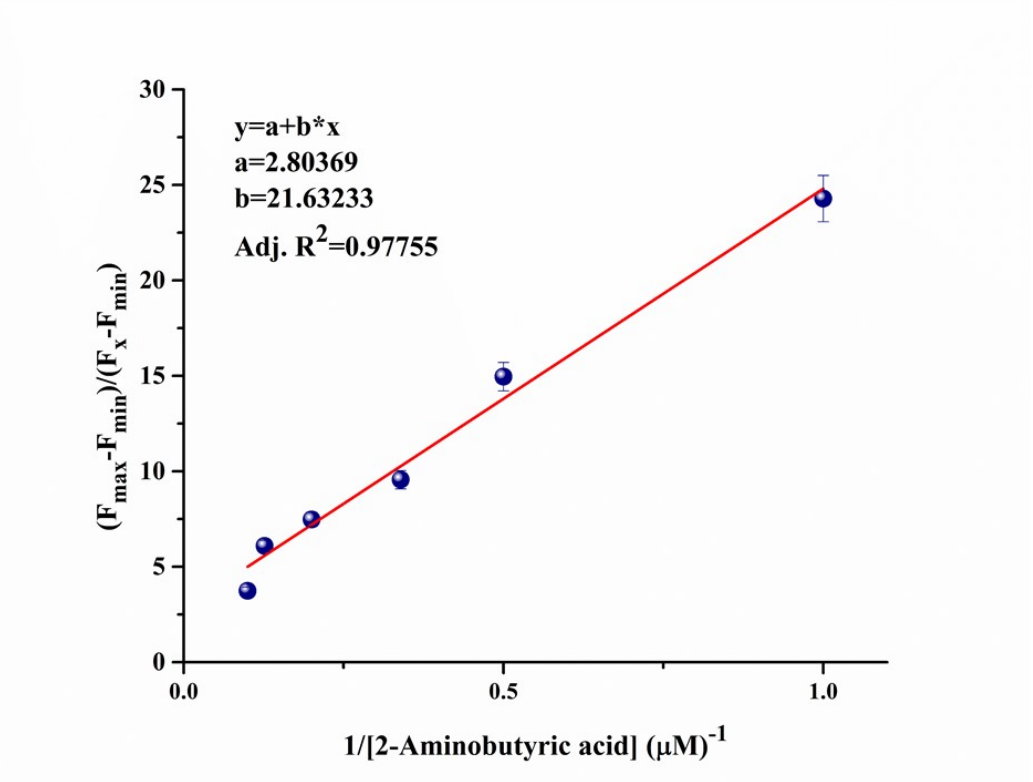

Figure S12b Benesi−Hildebrand plot for determination of displacement binding constant for 2-aminobutyric acid using **M2** (liner portion only) (λ_{ex} = 290 nm, λ_{em} = 489 nm)

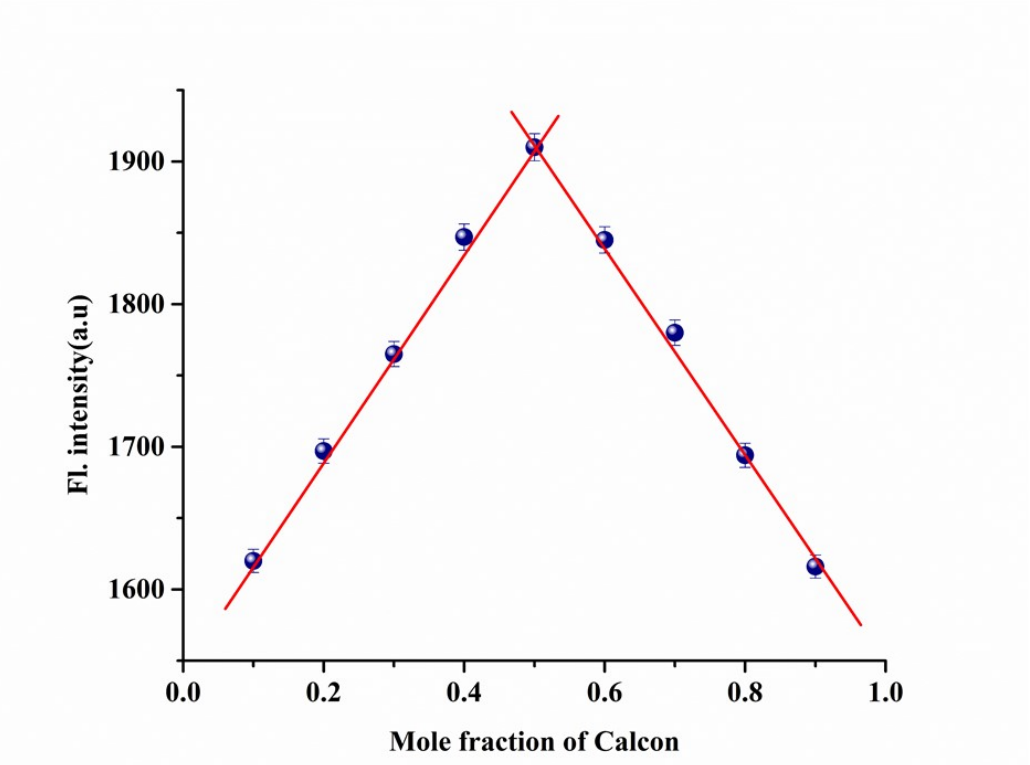

Figure S13a Job's plot for stoichiometry determination of **C1** (λ_{ex} = 285 nm λ_{em} = 484 nm)

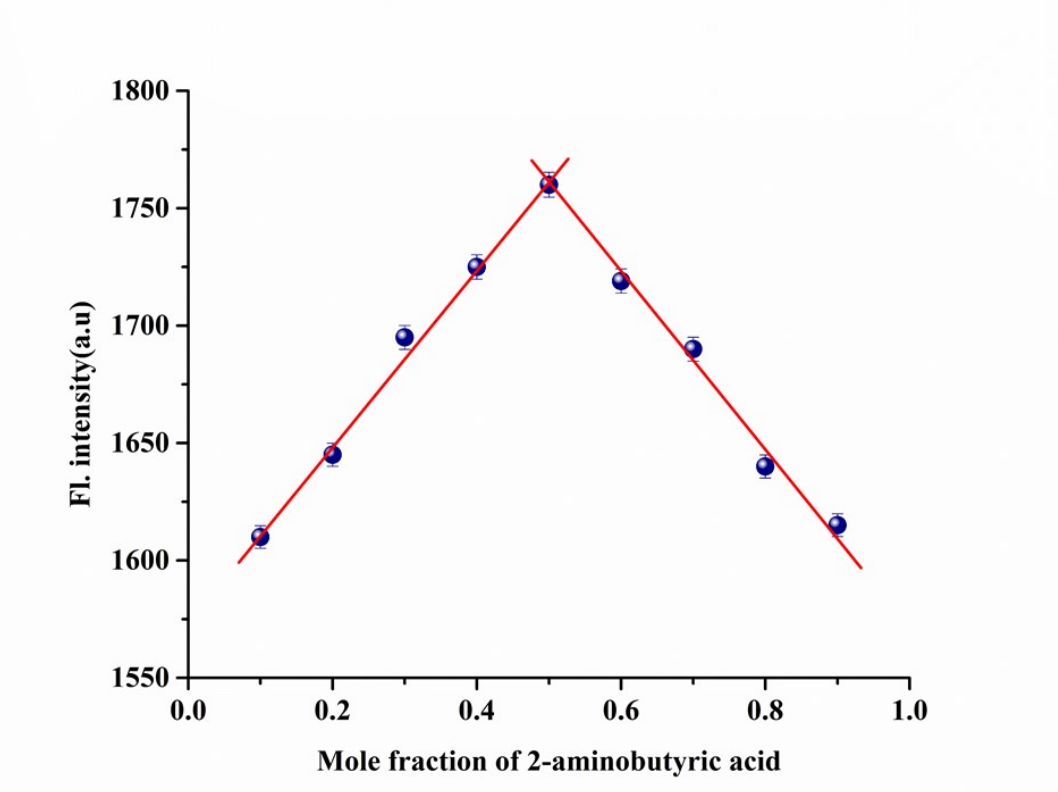

Figure S13b Job's plot for stoichiometry determination of **A1** (λ_{ex} = 290 nm, λ_{em} = 489 nm)

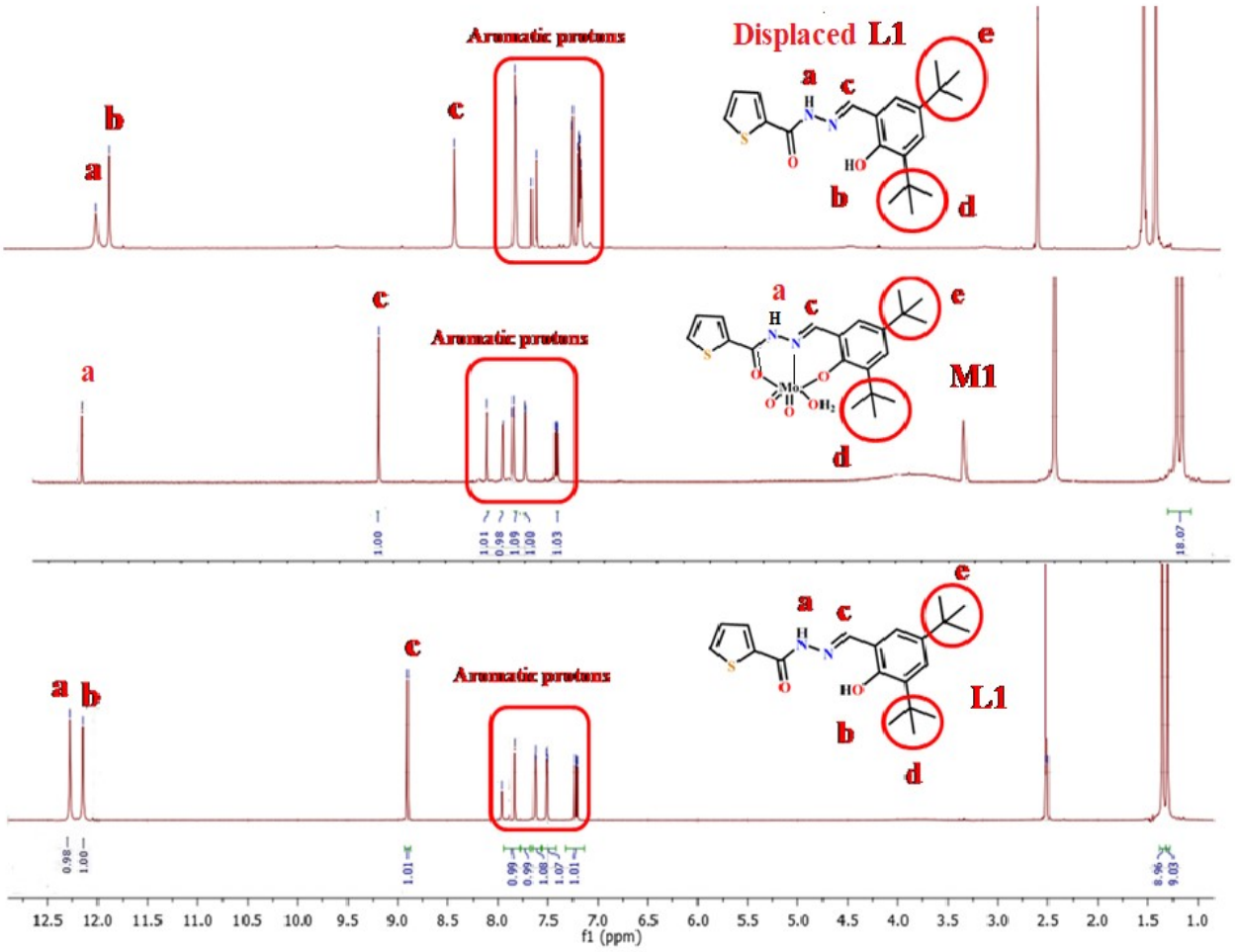

Figure S14a Changes in the ^{1}HNMR spectra of **L1** and **M1** upon interaction with Mo(VI) and calcon respectively

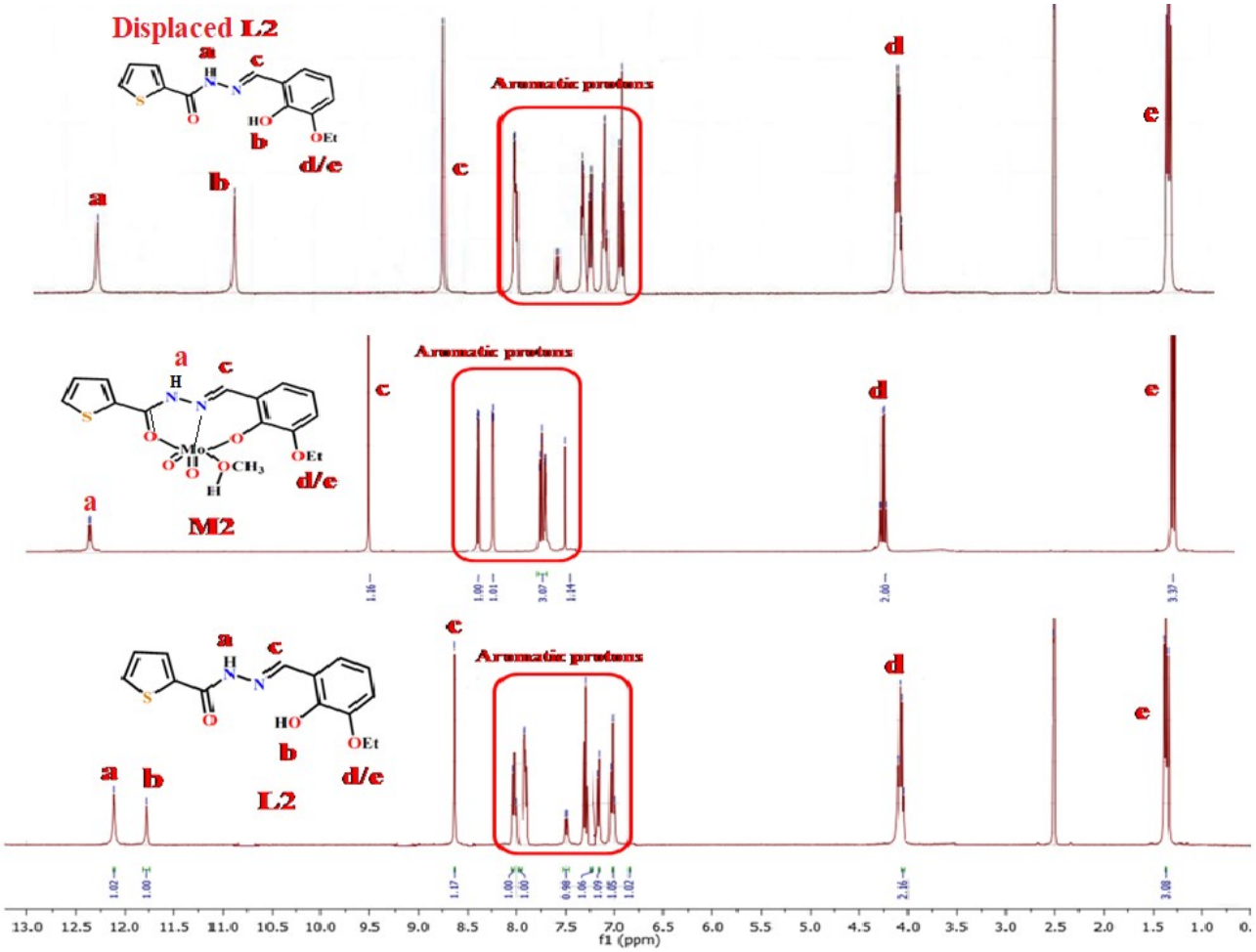

Figure S14b Changes in the ^{1}HNMR spectra of **L2** and **M2** upon interaction with Mo(VI) and 2-aminobutyric acid respectively

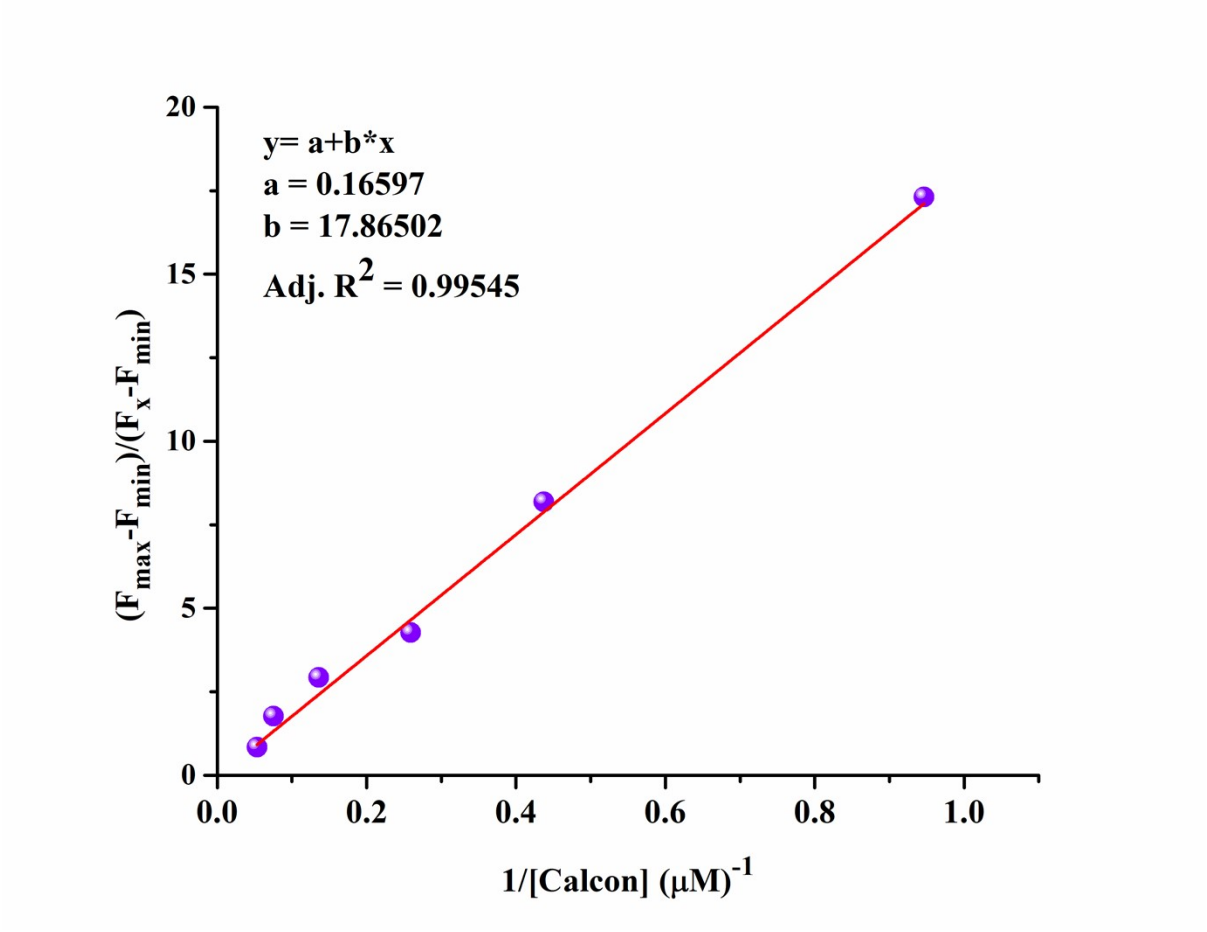

Figure S15a Benesi−Hildebrand plot for determination of binding constant for calcon and Mo(VI) ion in presence of L1.

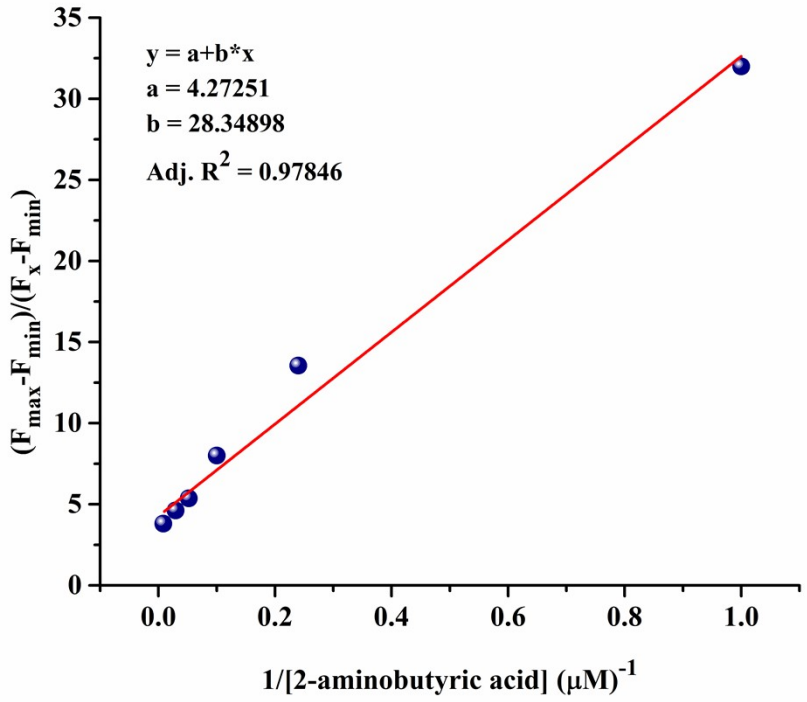

Figure S15b Benesi−Hildebrand plot for determination of binding constant for 2-aminobutyric acid with Mo(VI) ion in presence of L2

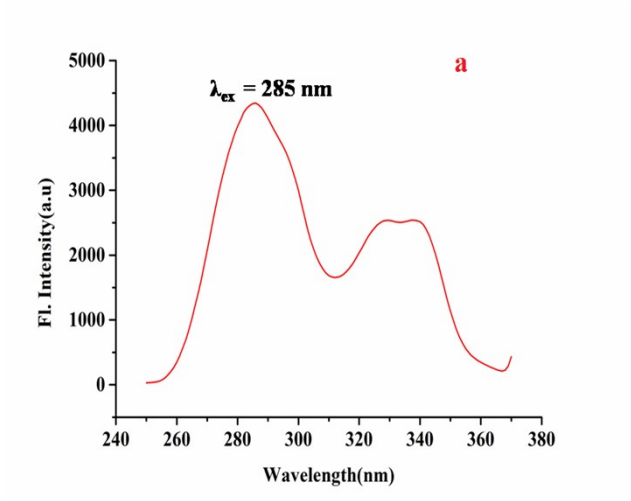

Figure S16a Excitation spectra of **C1** (a) and **A1** (b); media and pH mentioned *supra*

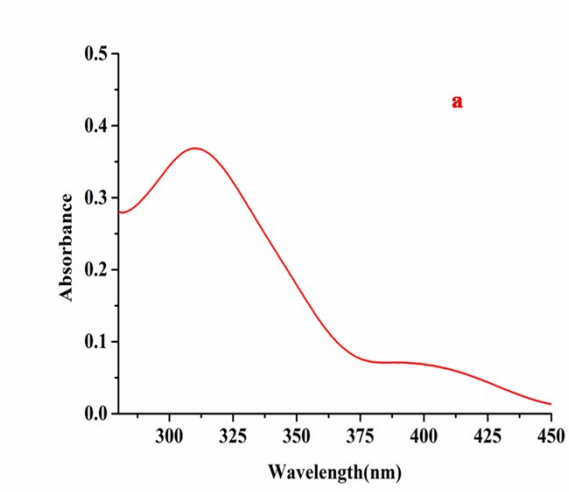

Figure S16b Absorption spectra of **C1** (a) and **A1** (b); media and pH mentioned *supra*

Table S1 Crystal data and structure refinement for **M1** and **M2**

Crystal parameters	**M1**	**M2**
CCDC	**2365489**	**2365810**
Empirical formula	$C_{20}H_{25}MoN_2O_7S$	$C_{15}H_{16}MoN_2O_6S$
Formula weight	533.42	448.30
Crystal system	Triclinic	Triclinic
Space group	P -1	P -1
Hall group	-P 1	-P 1
Temparature	296 K	296 K

Wavelength	0.71073	0.71073
a/Å	9.9045(9)	8.2019(8)
b/Å	10.4697(8)	8.5271(9)
c/Å	14.7351(12)	12.8130(13)
α/°	72.154(5)	93.903(5)
β/°	85.084(5)	92.557(5)
γ/°	65.666(5)	96.706(5)
Volume/Å^3	1323.8(2)	886.68(16)
Z	2	2
ρ_{calc} g/cm^3	1.338	1.679
μ/mm^{-1}	0.611	0.891
F(000)	546.0	452.0
F(000′)	543.04	448.99
Θmax	28.530	28.487
Index ranges (h,k,lmax)	13,14,19	11,11,17
Reflections collected (R)	0.0931 (5157)	0.0815 (3936)
wR_2 (Reflection)	0.2867 (6571)	0.2638 (4397)
S	2.020	2.235
Npar	286	228
Data completeness	0.977	0.982

Table S2a Selected bond lengths and angles of **M1**

Atoms	**Bond length**	**Atoms**	**Bond angle**
Mo O3	1.678(5)	O3 Mo1 O2	105.9(3)
Mo O2	1.705(5)	O3 Mo1 O4	99.3(3)
Mo O4	1.913(4)	O2 Mo1 O4	102.9(2)
Mo O5	2.028(4)	O3 Mo1 O5	94.8(2)
Mo O1	2.300(4)	O2 Mo1 O5	98.6(2)
Mo N6	2.254(4)	O4 Mo1 O5	149.88(17)
S2 CP	1.693(8)	O3 Mo1 N6	95.9(2)
S2 CM	1.720(6)	O2 Mo1 N6	157.0(2)
O4 CB	1.343(7)	O4 Mo1 N6	80.33(16)
O5 CH	1.310(7)	O5 Mo0 N6	71.82(17)
N6 CG	1.288(7)	O3 Mo1 O1	170.2(2)
N6 N8	1.396(6)	O2 Mo1 O1	81.8(2)

N8 CH	1.300(7)	O4 Mo1 O1	84.44(17)
CA CB	1.413(7)	O5 Mo1 O1	77.89(17)
CA CE	1.415(8)	N6 Mo1 O1	75.74(16)
CA CG	1.447(7)	CP S2 CM	92.2(3)
CB CD	1.417(8)	CB O4 Mo1	135.6(4)
CC CE	1.363(8)	CH O5 Mo1	119.5(4)
CC CF	1.429(8)	CG N6 N8	117.4(4)
CC CL	1.537(8)	CG N6 Mo1	127.9(4)
CD CF	1.376(9)	N8 N6 Mo1	114.7(3)
CD CK	1.535(8)	CH N8 N6	110.1(4)
CH CM	1.438(8)	CB CA CE	119.4(5)
CJ CO	1.393(9)	CB CA CG	122.8(5)
CJ CM	1.431(8)	CE CA CG	117.8(5)
CK CR	1.507(10)	O4 CB CD	119.3(5)
CK CV	1.532(12)	O4 CB CA	120.5(5)
CK CU	1.546(11)	CD CB CA	120.2(5)
CL CQ	1.501(9)	CE CC CF	116.8(5)
CL CS	1.520(10)	CE CC CL	123.7(5)
CL CT	1.518(10)	CF CC CL	119.5(5)
CO CP	1.339(11)	CB CD CF	117.0(5)
		CB CD CK	122.3(6)
		CF CD CK	120.7(5)
		CC CE CA	121.8(5)
		CC CF CD	124.5(5)
		N6 CG CA	123.9(5)
		N8 CH O5	123.8(5)
		N8 CH CM	119.8(5)
		O5 CH CM	116.5(5)
		CO CJ CM	110.5(6)
		CR CK CD	113.6(6)
		CR CK CV	108.6(7)
		CD CK CV	109.3(6)
		CR CK CU	107.5(7)
		CD CK CU	109.5(6)
		CV CK CU	108.2(8)

		CQ CL CS	108.6(6)
		CQ CL CC	112.0(5)
		CS CL CC	109.9(6)
		CQ CL CT	107.9(6)
		CS CL CT	109.1(6)
		CC CL CT	109.2(6)
		CH CM CJ	130.4(5)
		CH CM S2	119.5(4)
		CJ CM S2	110.0(4)
		CP CO CJ	114.8(6)
		CO CP S2	112.4(5)

Table S2b Selected bond lengths and angles of **M2**

Atoms	**Bond length**	**Atoms**	**Bond angle**
Mo01 O2	1.693(5)	O2 Mo01 O1	106.6(2)
Mo01 O1	1.695(4)	O2 Mo01 O006	99.6(2)
Mo01 O006	1.921(4)	O1 Mo01 O006	104.34(19)
Mo01 O004	2.024(4)	O2 Mo01 O004	97.6(2)
Mo01 N007	2.231(4)	O1 Mo01 O004	95.97(19)
Mo01 O005	2.351(4)	O006 Mo01 O004	148.25(16)
S1 C00J	1.576(8)	O2 Mo01 N007	94.3(2)
S1 C00F	1.668(6)	O1 Mo01 N007	157.0(2)
C1 C00K	1.567(8)	O006 Mo01 N007	81.05(16)
C1 C00F	1.618(6)	O004 Mo01 N007	71.20(14)
O004 C00C	1.307(6)	O2 Mo01 O005	170.6(2)
O005 C00M	1.478(8)	O1 Mo01 O005	82.46(19)
O006 C00G	1.344(7)	O006 Mo01 O005	80.21(17)
N007 C00E	1.290(7)	O004 Mo01 O005	78.54(16)
N007 N009	1.399(6)	N007 Mo01 O005	76.36(15)
N009 C00C	1.306(7)	C00J S1 C00F	94.1(4)
O3 C00H	1.417(8)	C00K C1 C00F	94.7(4)
O3 C00O	1.411(8)	C00C O004 Mo01	120.2(3)
C00C C00F	1.456(7)	C00M O005 Mo01	121.6(4)
C00D C00G	1.368(9)	C00G O006 Mo01	131.6(4)
C00D C00L	1.438(8)	C00E N007 N009	116.7(4)

C00D C00E	1.449(8)	C00E N007 Mo01	126.4(4)
C00G C00H	1.434(7)	N009 N007 Mo01	116.5(3)
C00H C00I	1.383(10)	C00C N009 N007	108.5(4)
C00I C00N	1.335(12)	C00H O3 C00O	116.0(6)
C00J C00K	1.346(12)	N009 C00C O004	123.5(5)
C00L C00N	1.361(11)	N009 C00C C00F	120.7(5)
C00O C00P	1.531(13)	O004 C00C C00F	115.8(4)
		C00G C00D C00L	118.7(6)
		C00G C00D C00E	123.3(5)
		C00L C00D C00E	118.0(6)
		N007 C00E C00D	123.0(5)
		C00C C00F C1	120.6(4)
		C00C C00F S1	123.0(4)
		C1 C00F S1	116.3(3)
		O006 C00G C00H	116.4(5)
		O006 C00G C00D	123.3(5)
		C00H C00G C00D	120.2(5)
		O3 C00H C00G	115.9(6)
		O3 C00H C00I	126.8(6)
		C00G C00H C00I	117.3(6)
		C00N C00I C00H	123.2(7)
		C00K C00J S1	116.5(5)
		C00J C00K C1	118.3(5)
		C00N C00L C00D	120.0(7)
		C00I C00N C00L	120.4(7)
		O3 C00O C00P	107.7(7)

Table S3a Selected DFT parameters of **L1**, **M1** and **C1**

Compounds → **Parameters ↓**	**L1**	**M1**	**C1**
Multiplicity	1	2	1
No. of electrons	192	257	280
No. of alpha electrons	96	115	126
No. of beta electrons	96	114	126

No. basis functions	281	377	520
No. of independent functions	281	377	520
No. of point charges	0	0	0
No. of translation vectors	0	0	0
No. of atoms	51	54	49
Calculation type	SP	SP	OPT
Calculation method	TD RB3LYP	TD RB3LYP	OPT RB3LYP
Basis set	6-31G	SDD	6-31g(d)+sdd
Charge	0	0	0
Spin	singlet	doublet	singlet
Solvation	None	None	None
Dipole moment	6.7620 Debye	12.7086 Debye	8.8303 Debye
Point group	C1	C1	C1
RMS Gradient Norm	0 Hartree/Bohr	0 Hartree/Bohr	0 Hartree/Bohr
E(TD-HF/TD-DFT) in -ve	1435.111368 Hartrees	1728.59856935 Hartrees	2024.73585870 Hartrees

Table S3b Selected DFT parameters of **L2**, **M2** and **A1**

Compounds / **Parameters** ↓ →	**L2**	**M2**	**A1**
Multiplicity	1	1	1
No. of electrons	152	198	216
No. of alpha electrons	76	99	70
No. of beta electrons	76	99	70
No. basis functions	212	319	231
No. of independent functions	212	319	231
No. of point charges	0	0	0
No. of translation vectors	0	0	0
No. of atoms	34	41	33

Calculation type	SP	SP	SP
Calculation method	TD RB3LYP	TD RB3LYP	TD RB3LYP
Basis set	6-31G	SDD	SDD
Charge	0	0	0
Spin	Singlet	Singlet	Singlet
Solvation	None	None	None
Dipole movement	5.4635 Debye	9.9011Debyee	11.8197 Debyee
Point group	C1	C1	C1
RMS Gradient Norm	0 Hartree/Bohr	0 Hartree/Bohr	0 Hartree/Bohr
E(TD-HF/TD-DFT) in -ve	1274.57133864 Hartrees	1607.96370844 Hartrees	943.467667363 Hartrees