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Supporting Information

fac-Re $(CO)_3$-based neutral heteroleptic tetrahedrons

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50. **Fig. S24.** Molecular structure of **2**. Tetrahedral skeleton of **2** with four ligands aligned along the four edges (Re1-Re^1 and Re2-Re^2 for two dianionic bis-chelating (RBC^{2-}) ligand motifs, Re1-Re2 and Re^2-Re^1 for two **L2** motifs, and Re1-Re^2 and Re2-Re^1 are the two missing edges) of the Re4 tetrahedron. (A) Ball and stick view of **2** (hydrogen atoms are omitted for clarity; bonds of **L2** are shown in blue; bonds of chelating atoms of RBC are shown in red). (B) Space-filling view of **2**. (C) **2** with chelating atoms (red), **L2** (blue) to show the orientation of chelating units around metal cores. Color code: C = gray; N = blue; O =red; Re = green; CO = green in C).

51. **Fig. S25.** Molecular structure of **3**. Tetrahedral skeleton of **3** with four ligands aligned along the four edges (Re1-Re2 and Re^1-Re^2 for two dianionic bis-chelating (RBC^{2-}) ligand motifs, Re1-Re^2 and Re2-Re^1 for two **L3** motifs, and Re1-Re^1 and Re2-Re^2 are the two missing edges) of the Re4 tetrahedron. (A) Ball and stick view of **3** (hydrogen atoms are omitted for clarity; bonds of **L3** are shown in blue; bonds of chelating atoms of RBC are shown in red). (B) Space-filling view of **3**. (C) Space-filling view of **3** showing cavity of face in which OCH_3 resides (D) **3** with chelating atoms (red), **L3** (blue) to show the orientation of chelating units around metal cores. Color code: C = gray; N = blue; O =red; Re = green; CO = green in C).

52. **Fig. S26.** Molecular structure of **4**. Bonds of **L4** are shown in blue; bonds of chelating atoms of RBC are shown in red). Color code: C = gray; N = blue; O =red; $Re(CO)_3$ = green).

53. **Fig. S27.** Molecular structure of **5**. Tetrahedral skeleton of **5** with four ligands aligned along the four edges (Re^1-Re^1 and Re^2-Re^2 for two dianionic bis-chelating (RBC^{2-}) ligand motifs, Re^1-Re^2 and Re^2-Re^1 for two **L5** motifs, and Re^1-Re^2 and Re^2-Re^1 are the two missing edges) of the Re4 tetrahedron. (A) Ball and stick view of **5** (hydrogen atoms are omitted for clarity; bonds of **L5** are shown in blue; bonds of chelating atoms of RBC are shown in red). (B) Space-filling view of **5**. (C) **5** with chelating atoms (red), **L5** (blue) to show the orientation of chelating units around metal cores. Color code: C = gray; N = blue; O =red; Re = green; CO = green in C).

54. **Fig. S28.** Molecular structure of **1** showing size of tetrahedron edges.

55. **Fig. S29.** Molecular structure of **2** showing size of tetrahedron edges.

56. **Fig. S30.** Molecular structure of **3** showing size of tetrahedron edges.

57. **Fig. S31.** Molecular structure of **4** showing size of tetrahedron edges.

58. **Fig. S32.** Molecular structure of **5** showing size of tetrahedron edges.

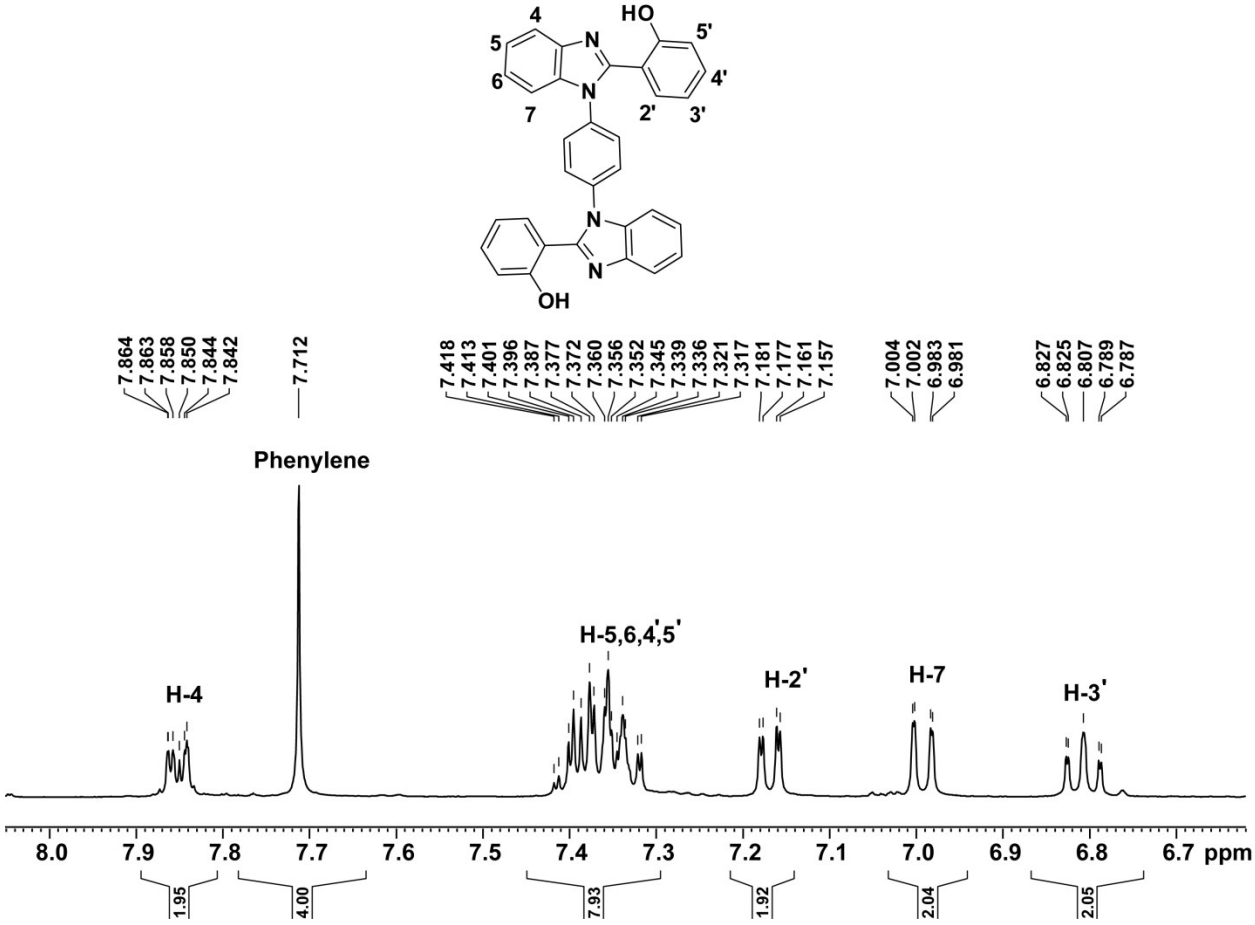

Fig. S1a. Partial ^{1}H NMR spectrum of **H_2-RBC** in dmso-d_6.

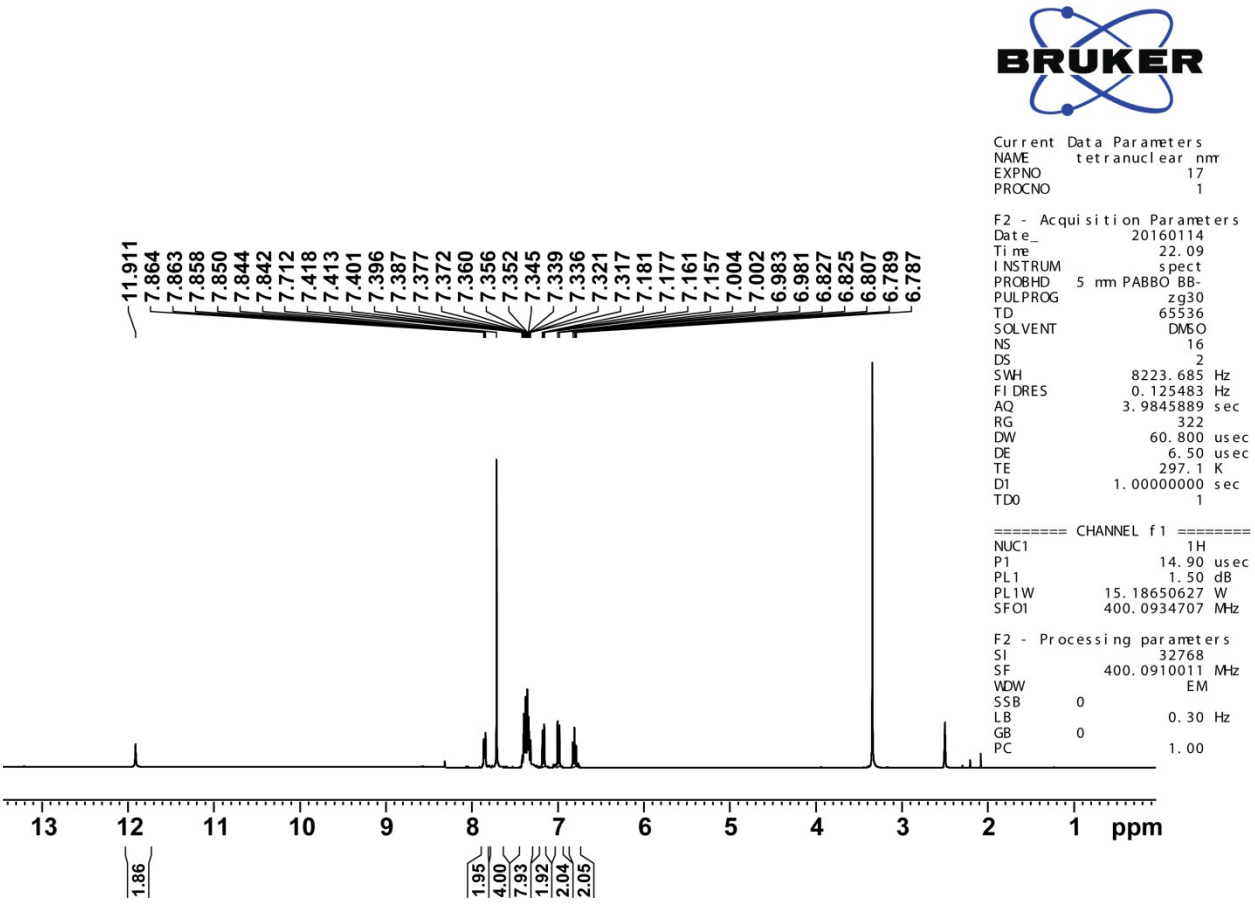

Fig. S1b. ^{1}H NMR spectrum of **H_2-RBC** in dmso-d_6.

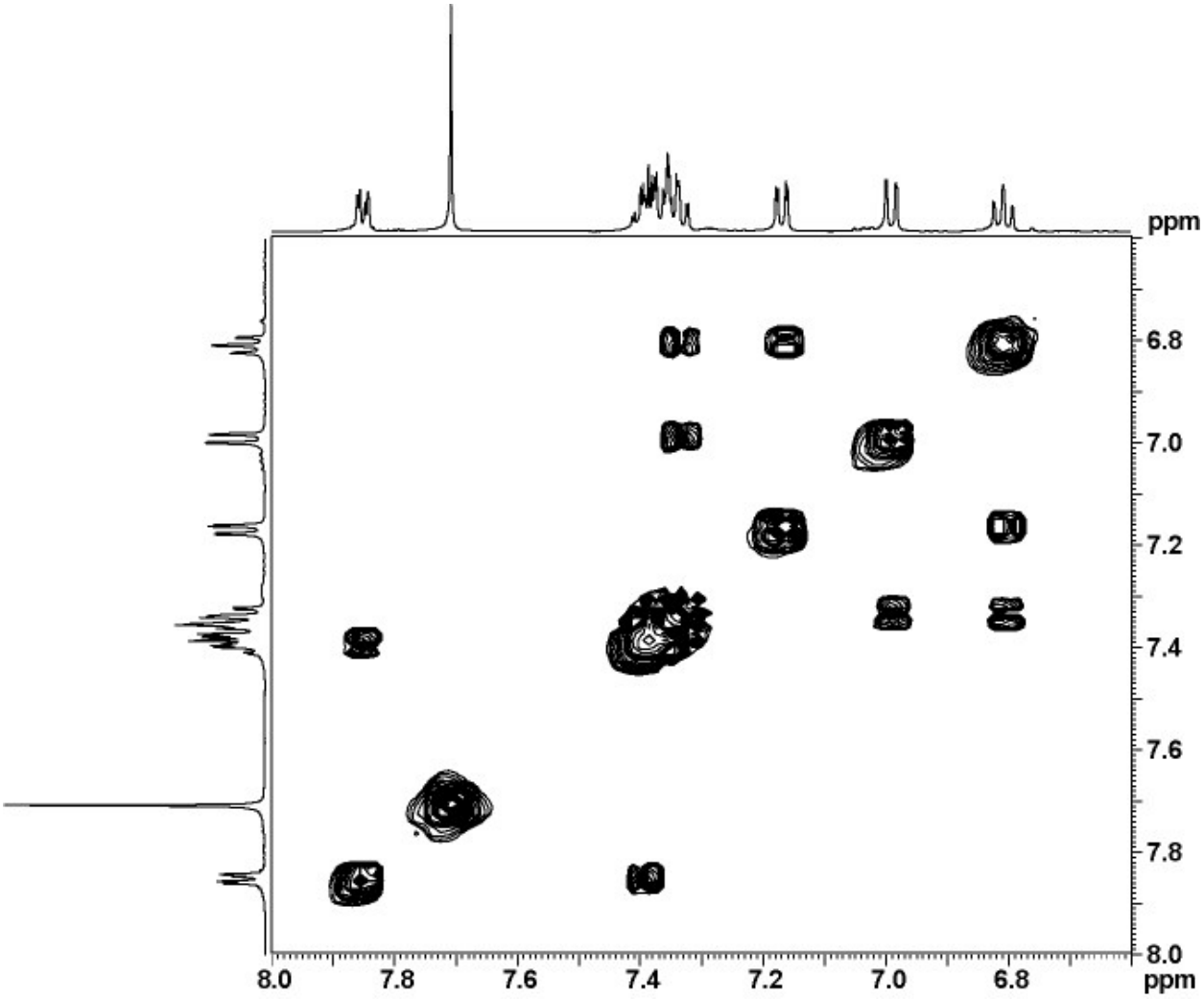

Fig. S1c. ^{1}H-^{1}H COSY NMR spectrum **H_2-RBC** in dmso-d_6.

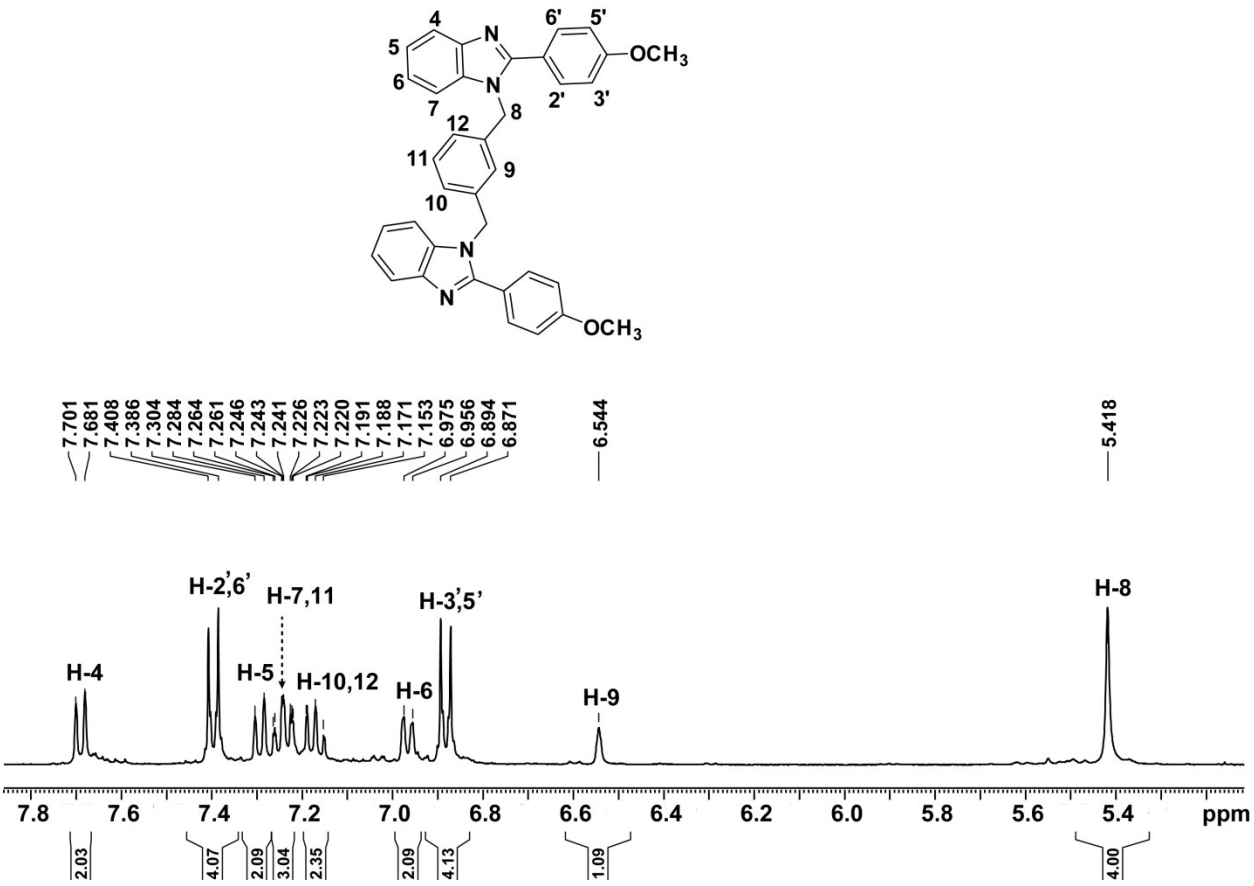

Fig. S2a. Partial ^{1}H NMR spectrum of **L2** in dmso-d_6.

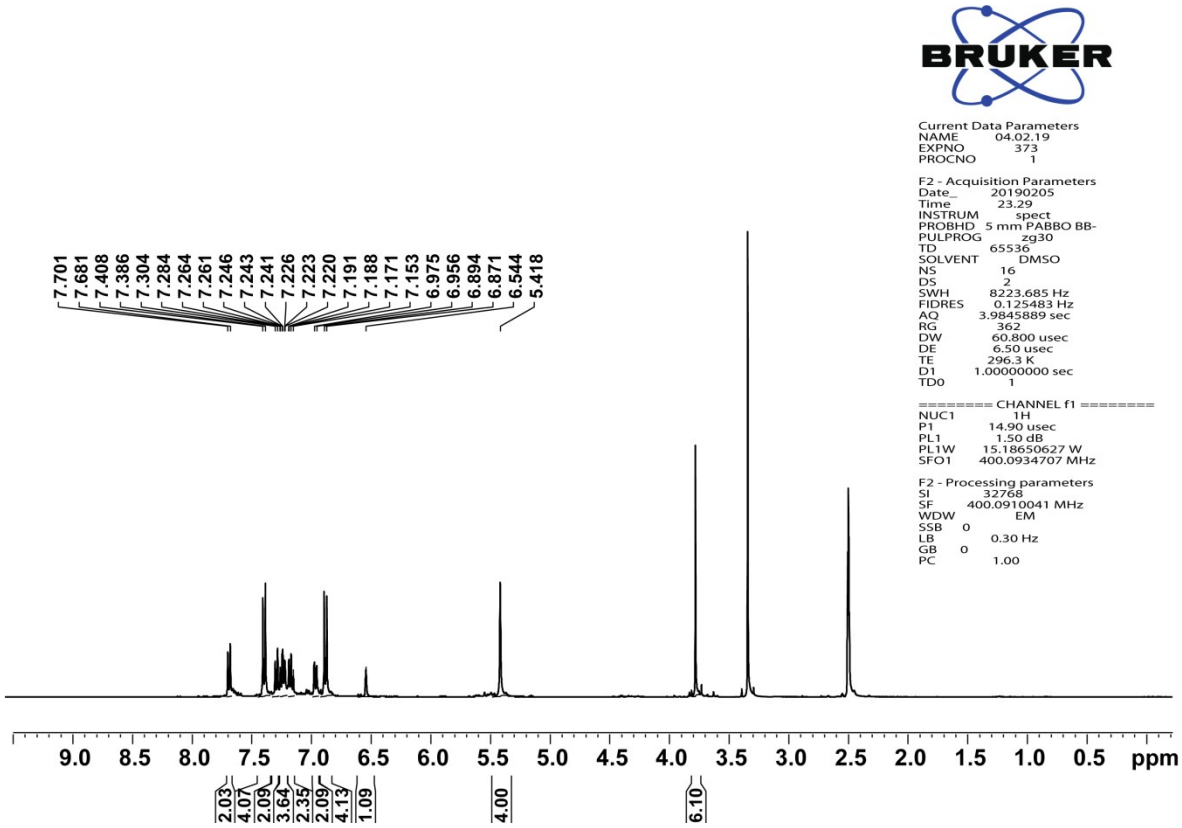

Fig. S2b. ^{1}H NMR spectrum of **L2** in dmso-d_6.

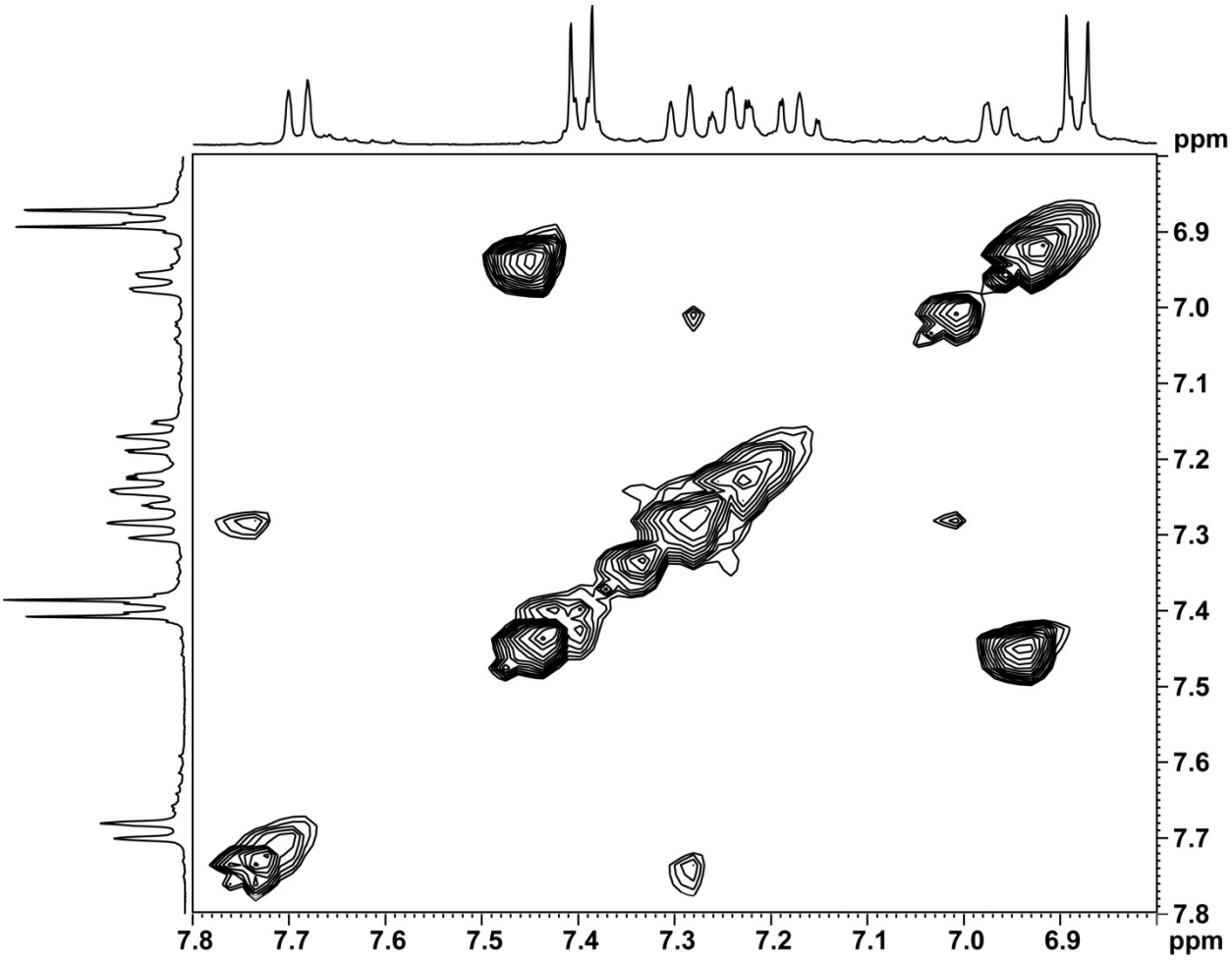

Fig. S2c. ^{1}H-^{1}H COSY NMR spectrum of L**2** in dmso-d_6.

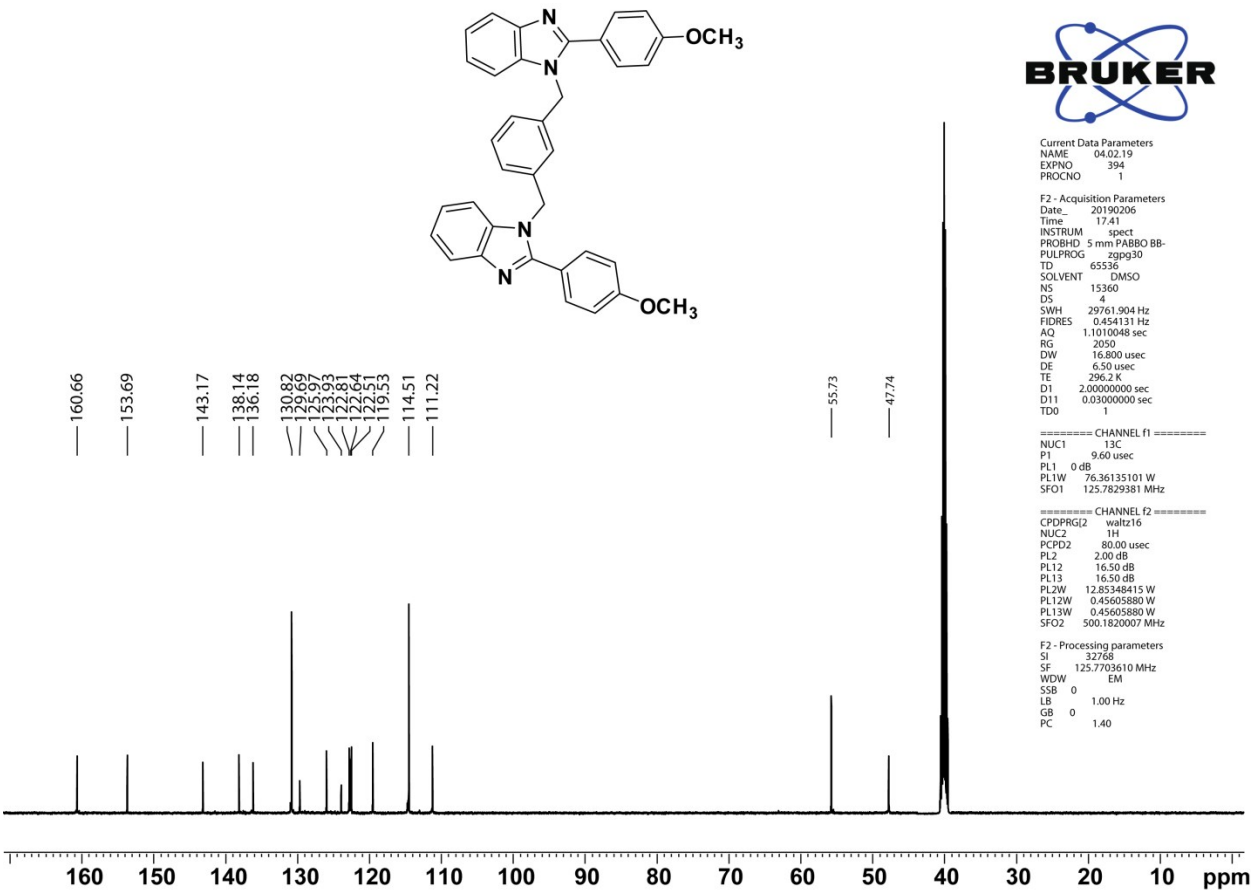

Fig. S2d. ^{13}C NMR spectrum of L**2** in dmso-d_6.

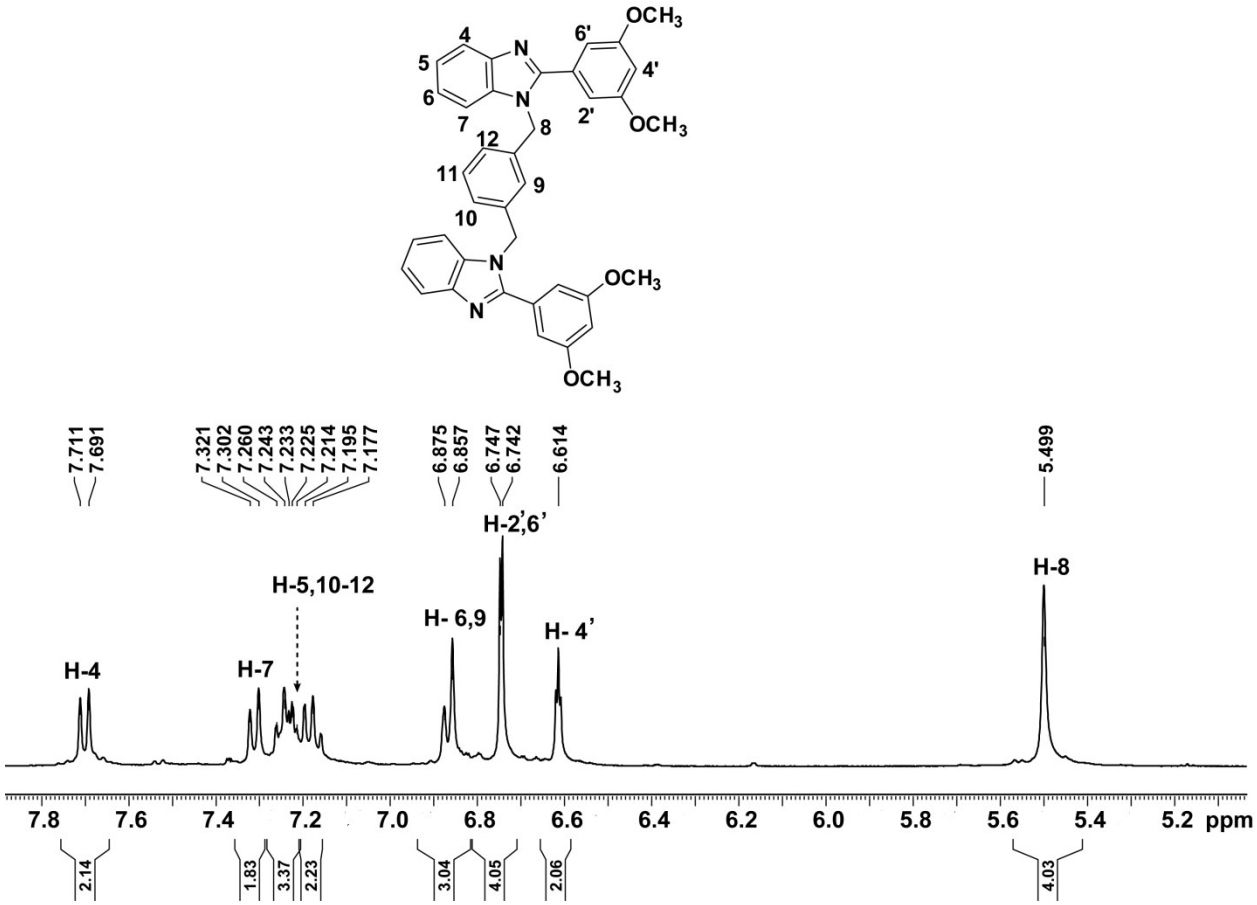

Fig. S3a. Partial ^{1}H NMR spectrum of **L3** in dmso-d_6.

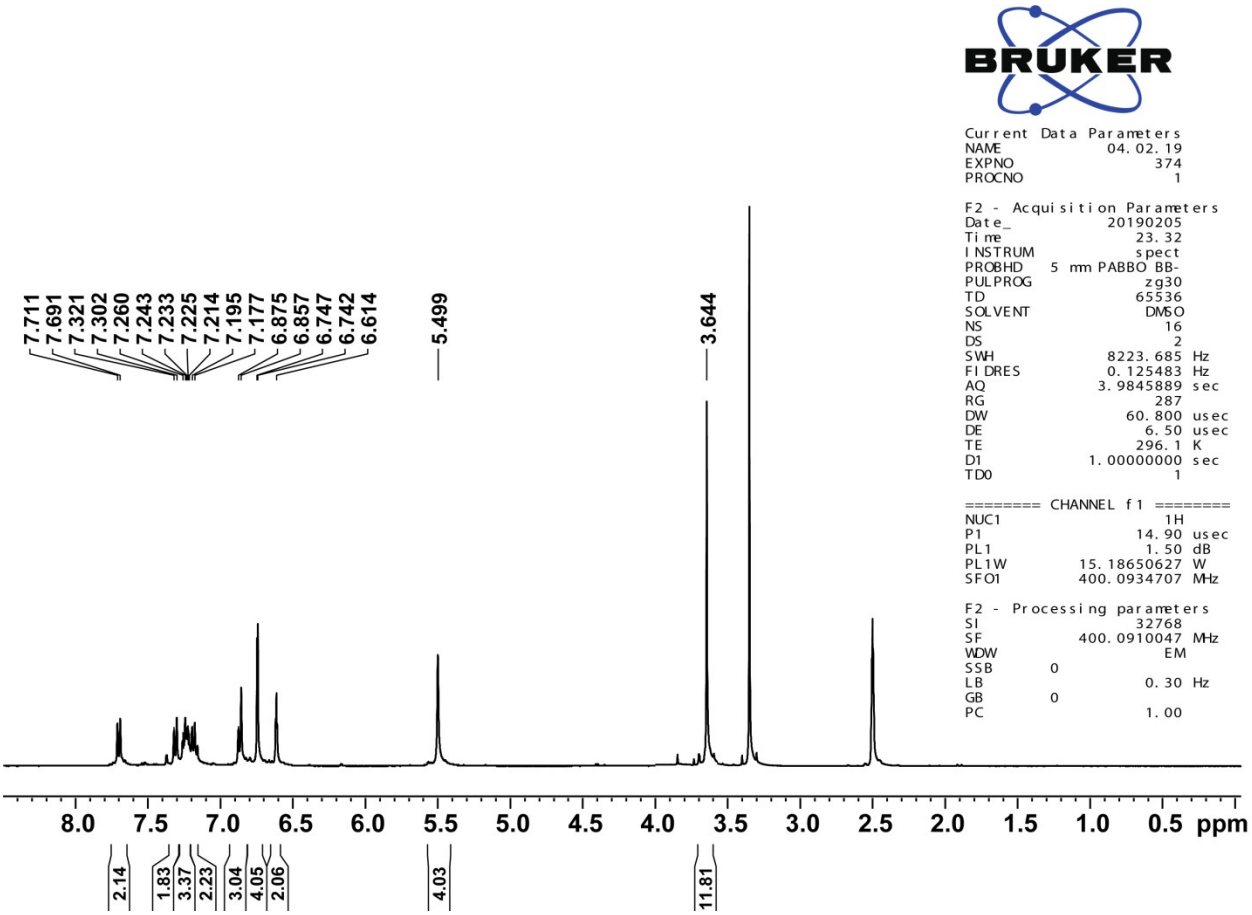

Fig. S3b. ^{1}H NMR spectrum of **L3** in dmso-d_6.

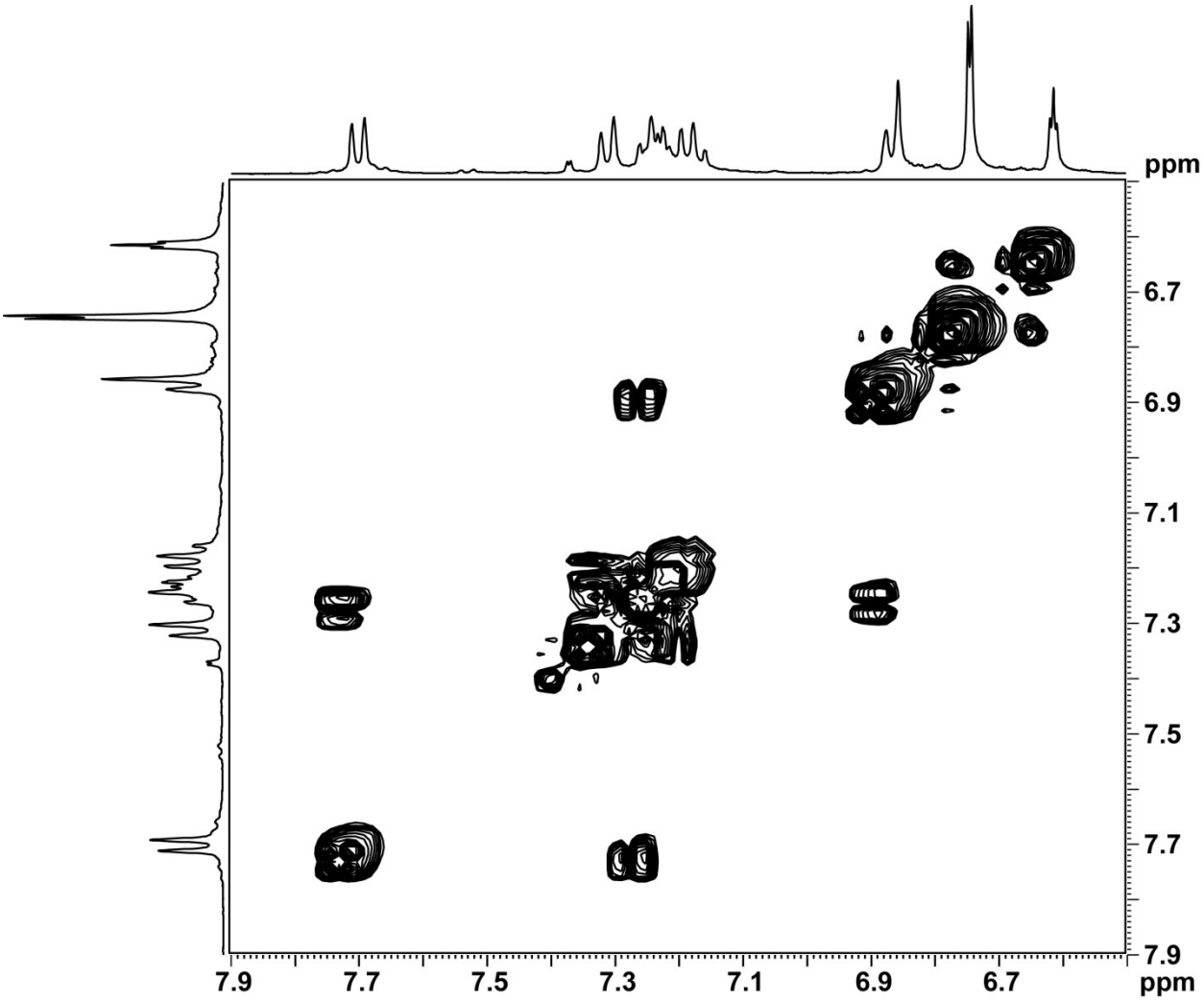

Fig. S3c. ^{1}H-^{1}H COSY NMR spectrum of L**3** in dmso-d_6.

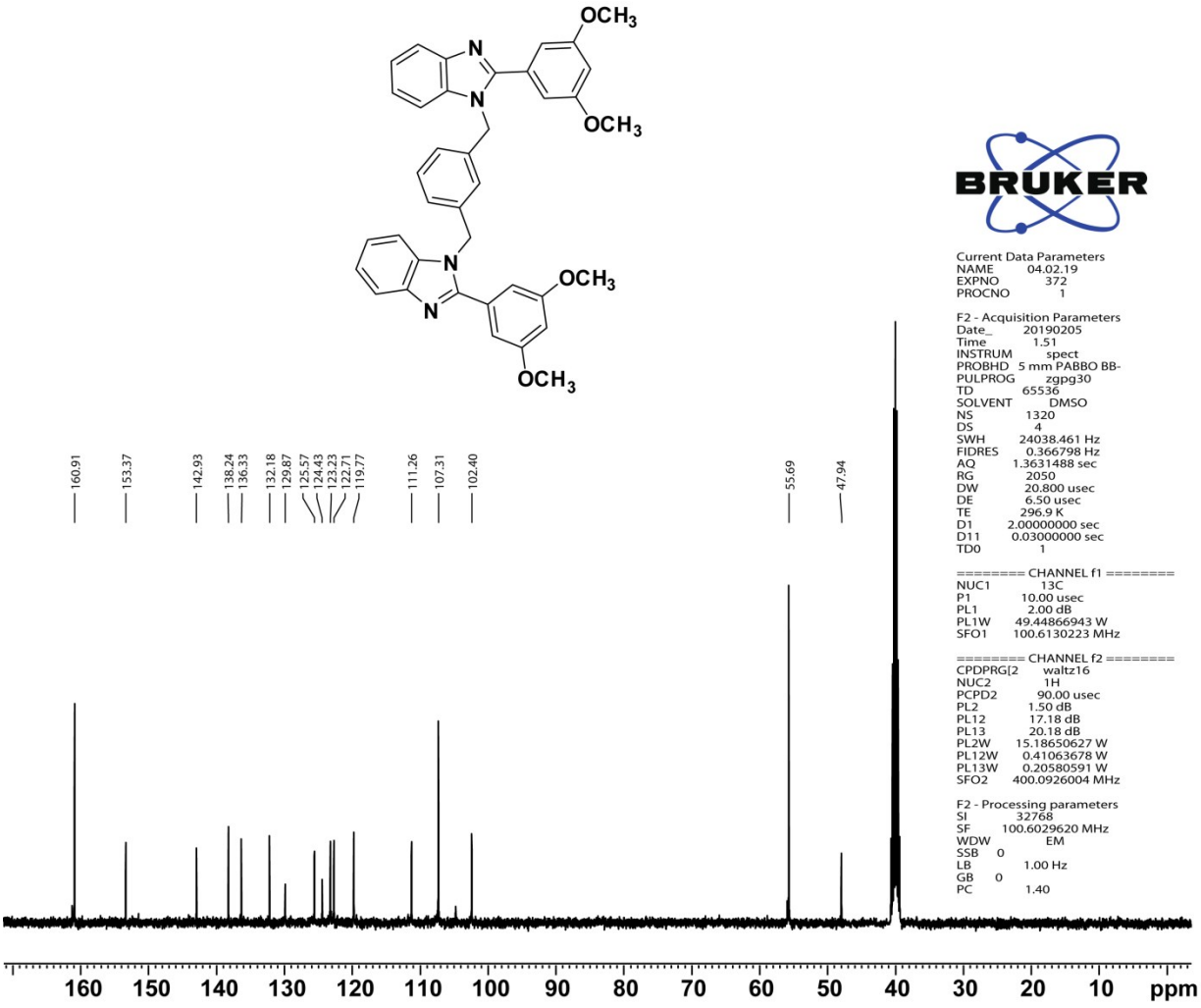

Fig. S3d. ^{13}C NMR spectrum of L**3** in dmso-d_6.

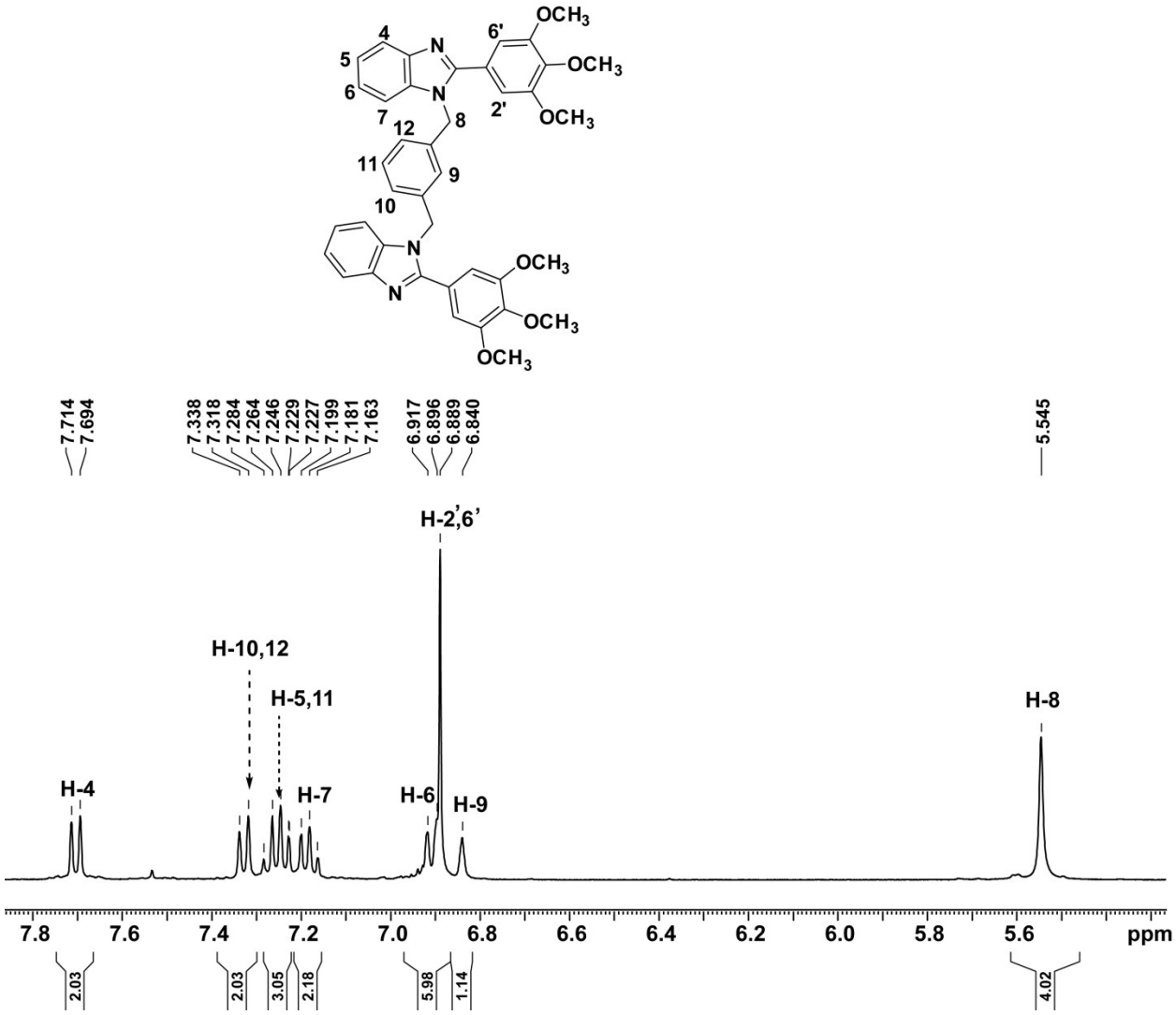

Fig. S4a. Partial ^{1}H NMR spectrum of **L4** in dmso-d_6.

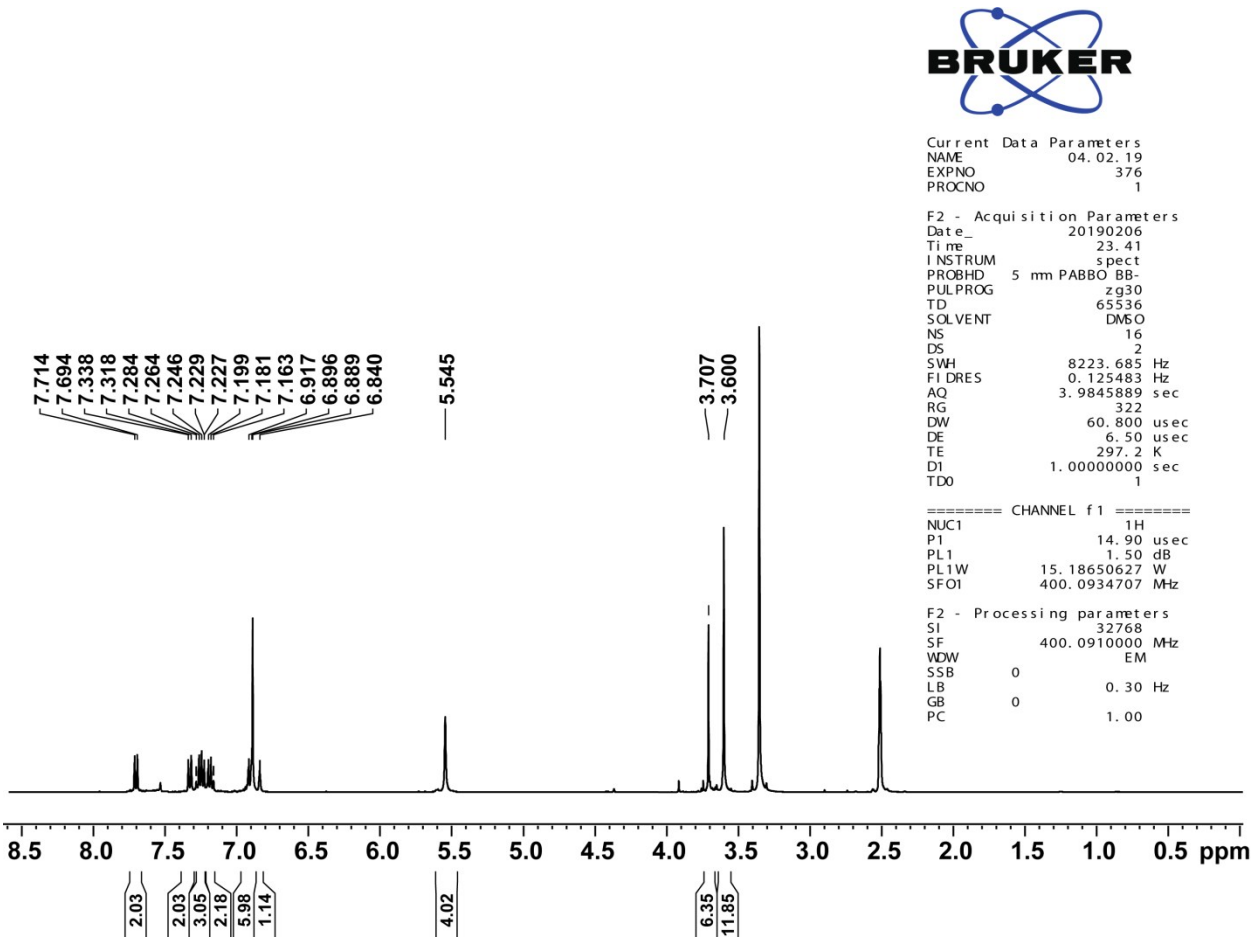

Fig. S4b. ^{1}H NMR spectrum of **L4** in dmso-d_6.

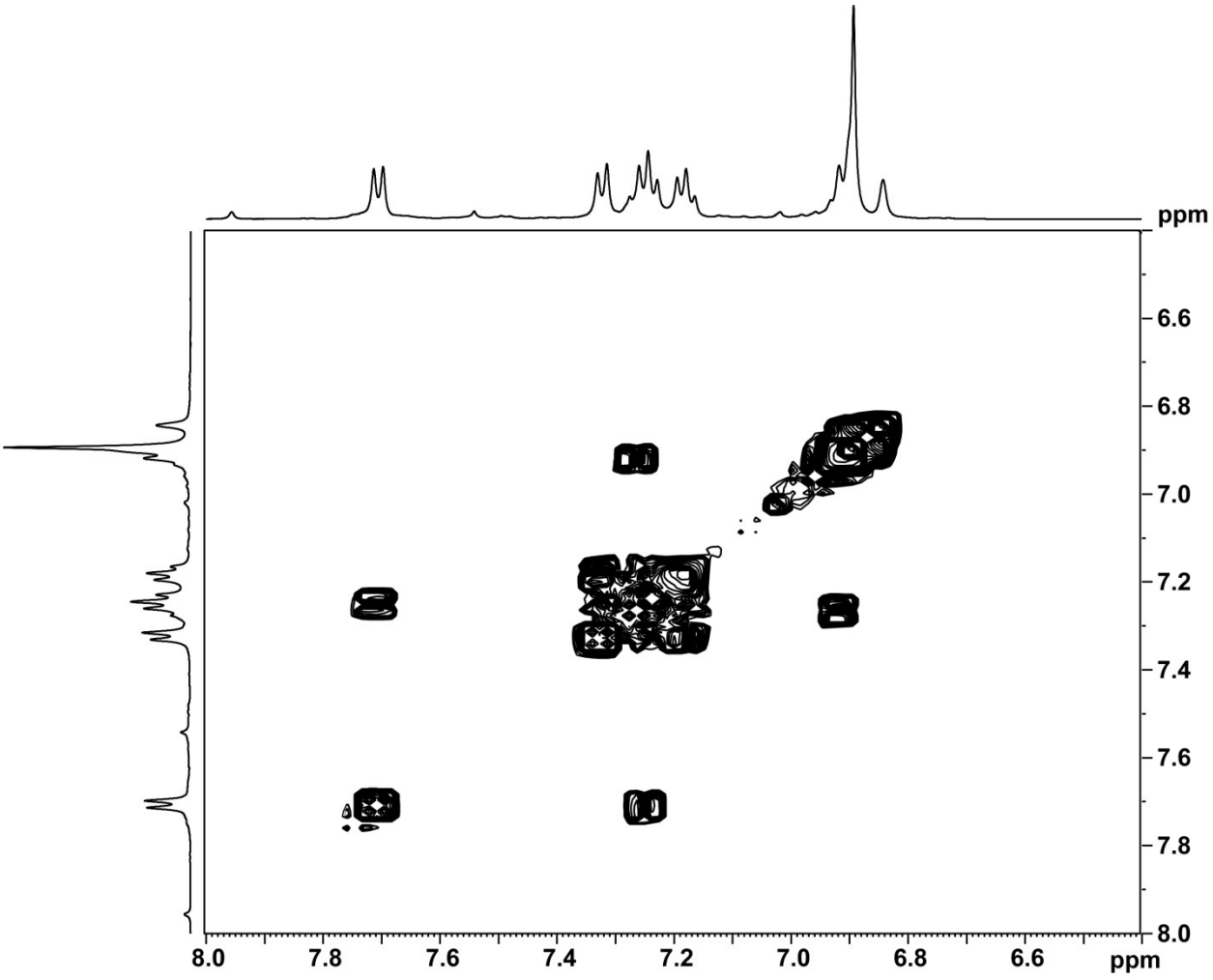

Fig. S4c. ^{1}H-^{1}H COSY NMR spectrum of L**4** in dmso-d_6.

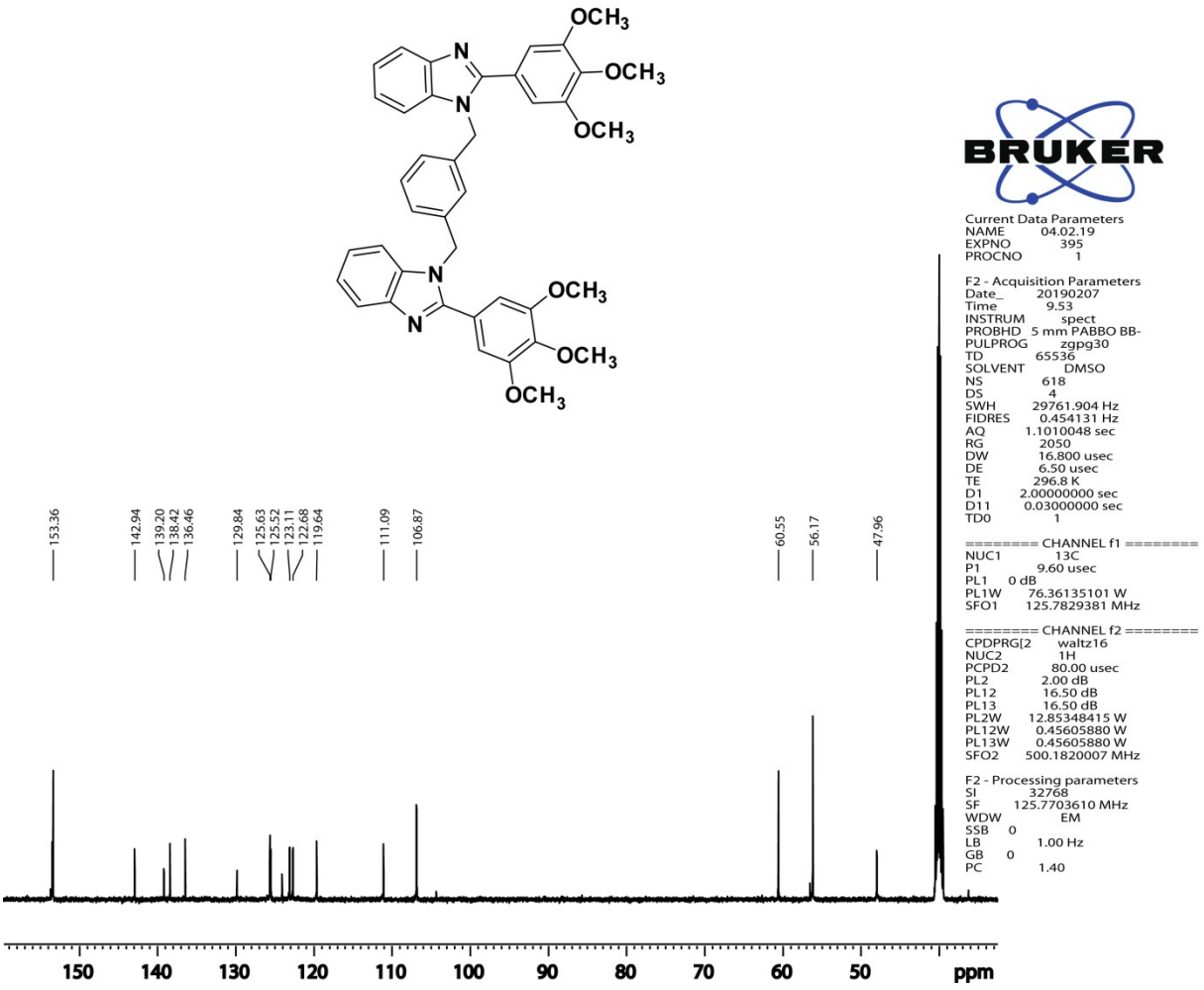

Fig. S4d. ^{13}C NMR spectrum of L**4** in dmso-d_6.

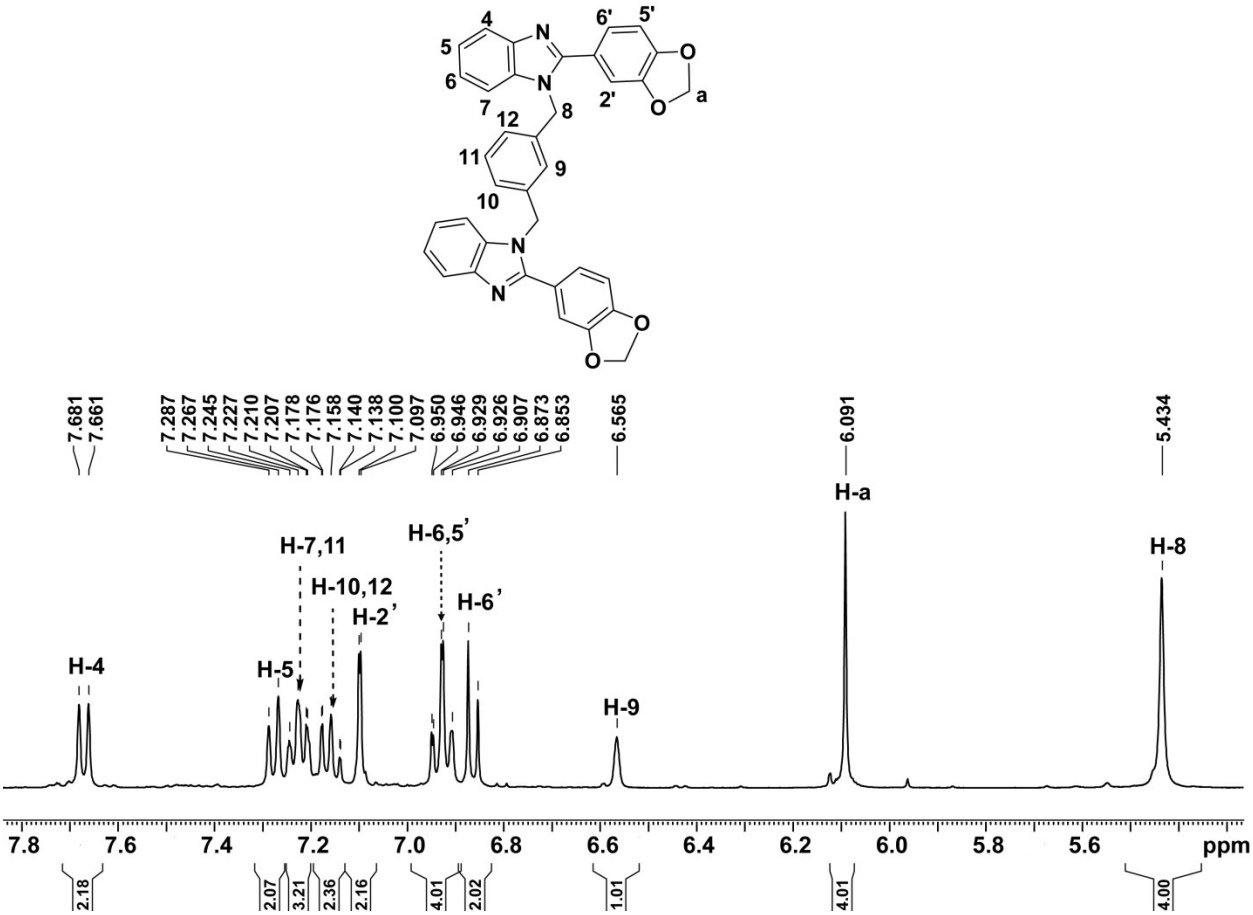

Fig. S5a. Partial ^{1}H NMR spectrum of **L5** in dmso-d_6.

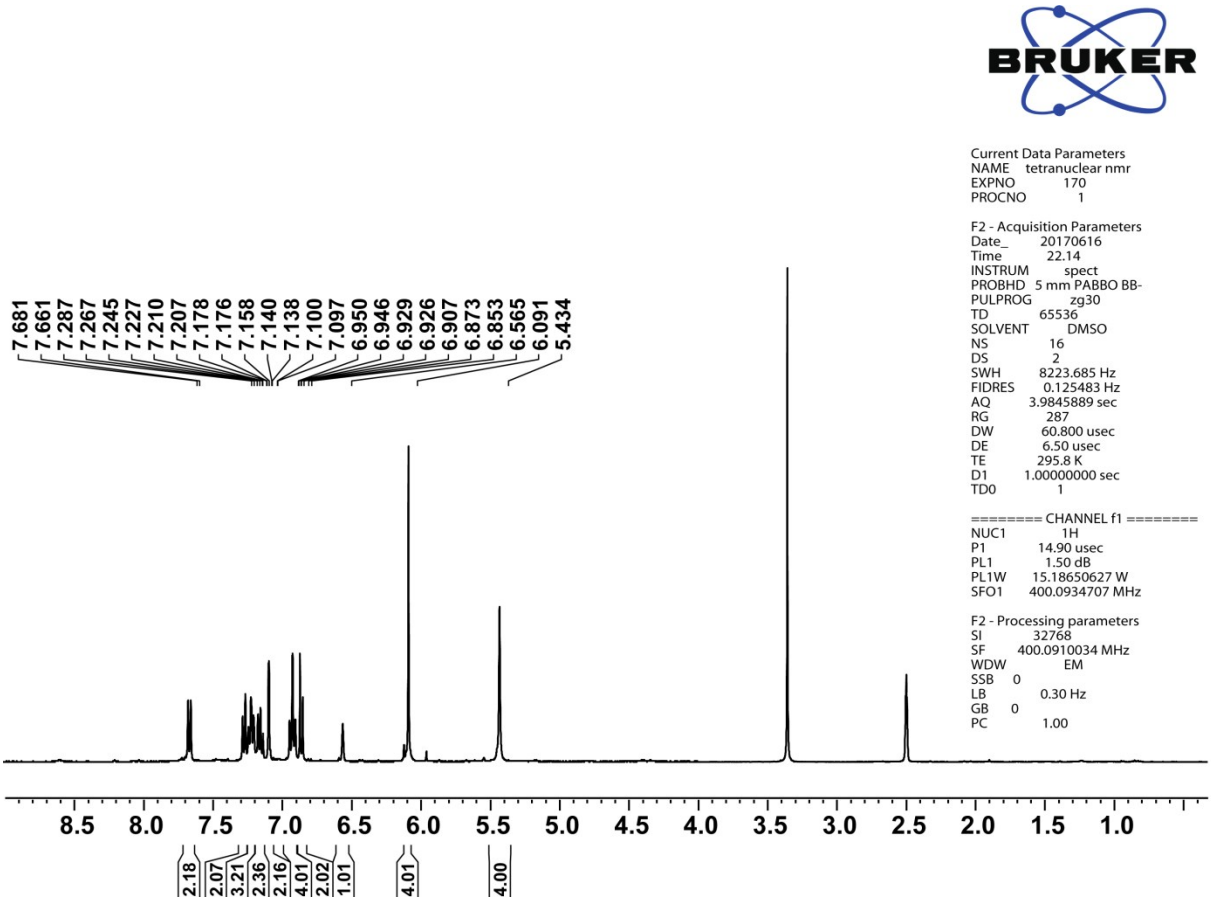

Fig. S5b. ^{1}H NMR spectrum of **L5** in dmso-d_6.

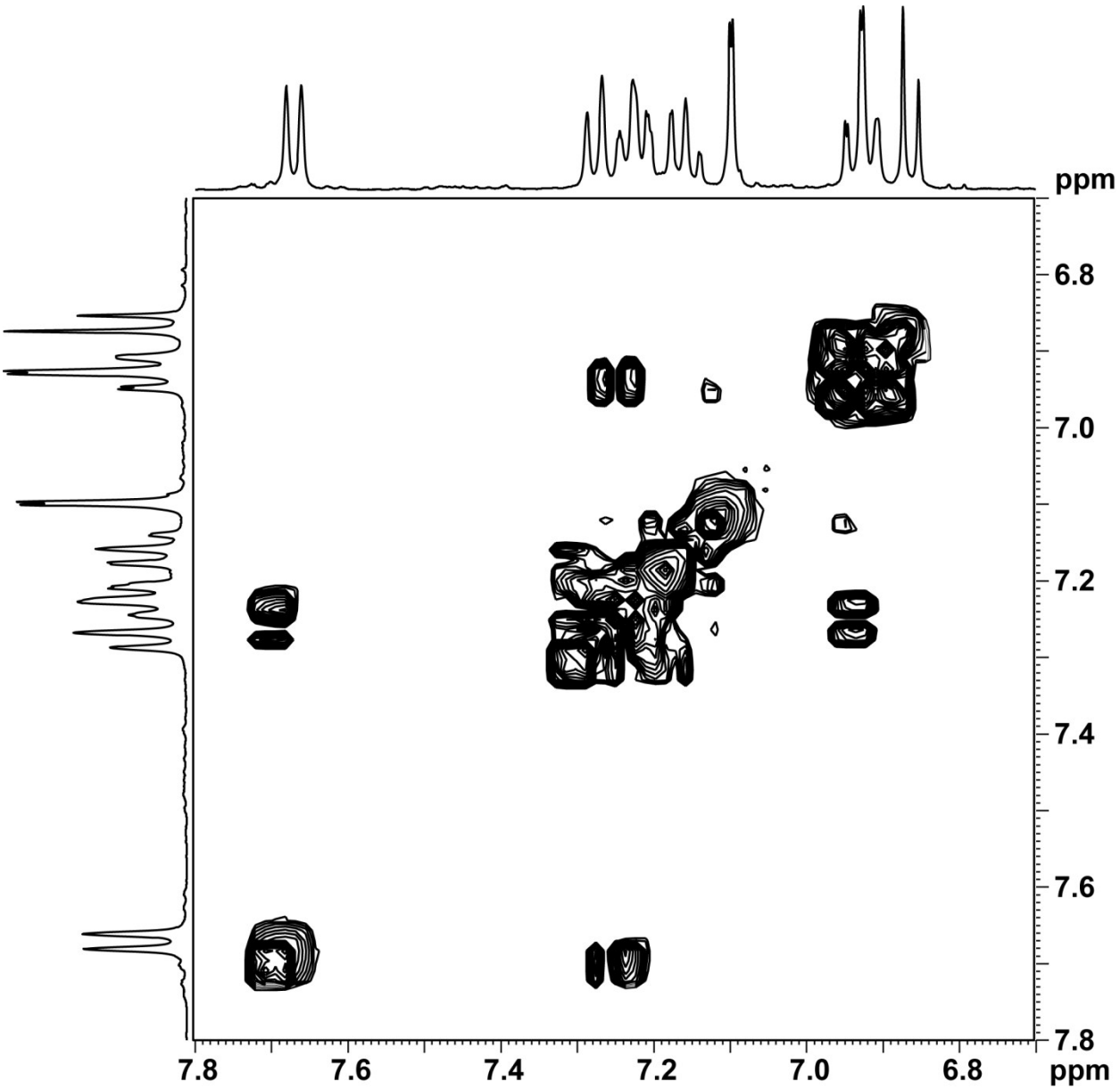

Fig. S5c. ^{1}H-^{1}H COSY NMR spectrum of L**5** in dmso-d_6.

UOH -SCHOOL OF CHEMISTRY -HRMS

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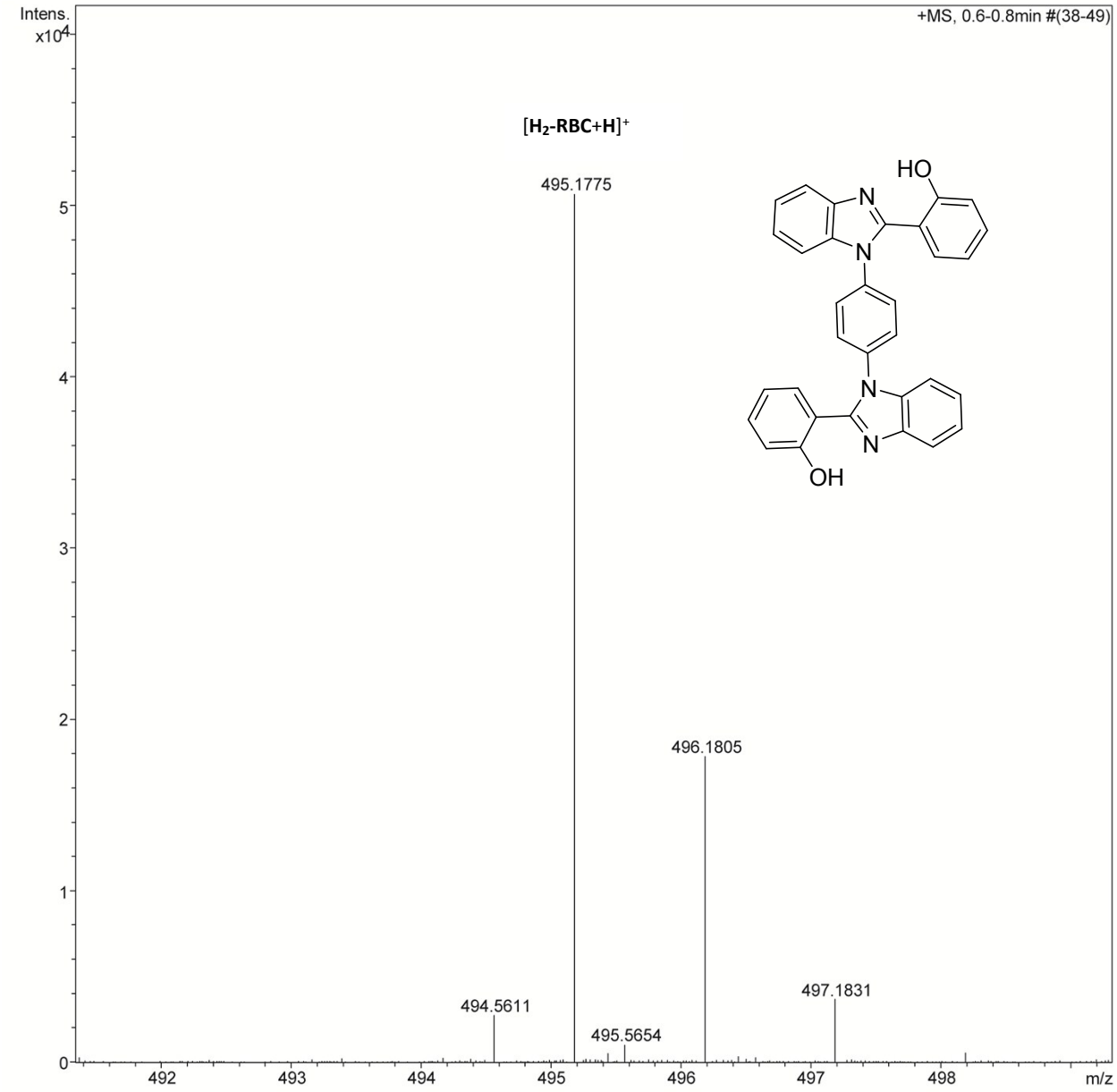

Fig. S6. ESI mass spectrum of **H_2-RBC** in positive ion mode.

UOH -SCHOOL OF CHEMISTRY -HRMS

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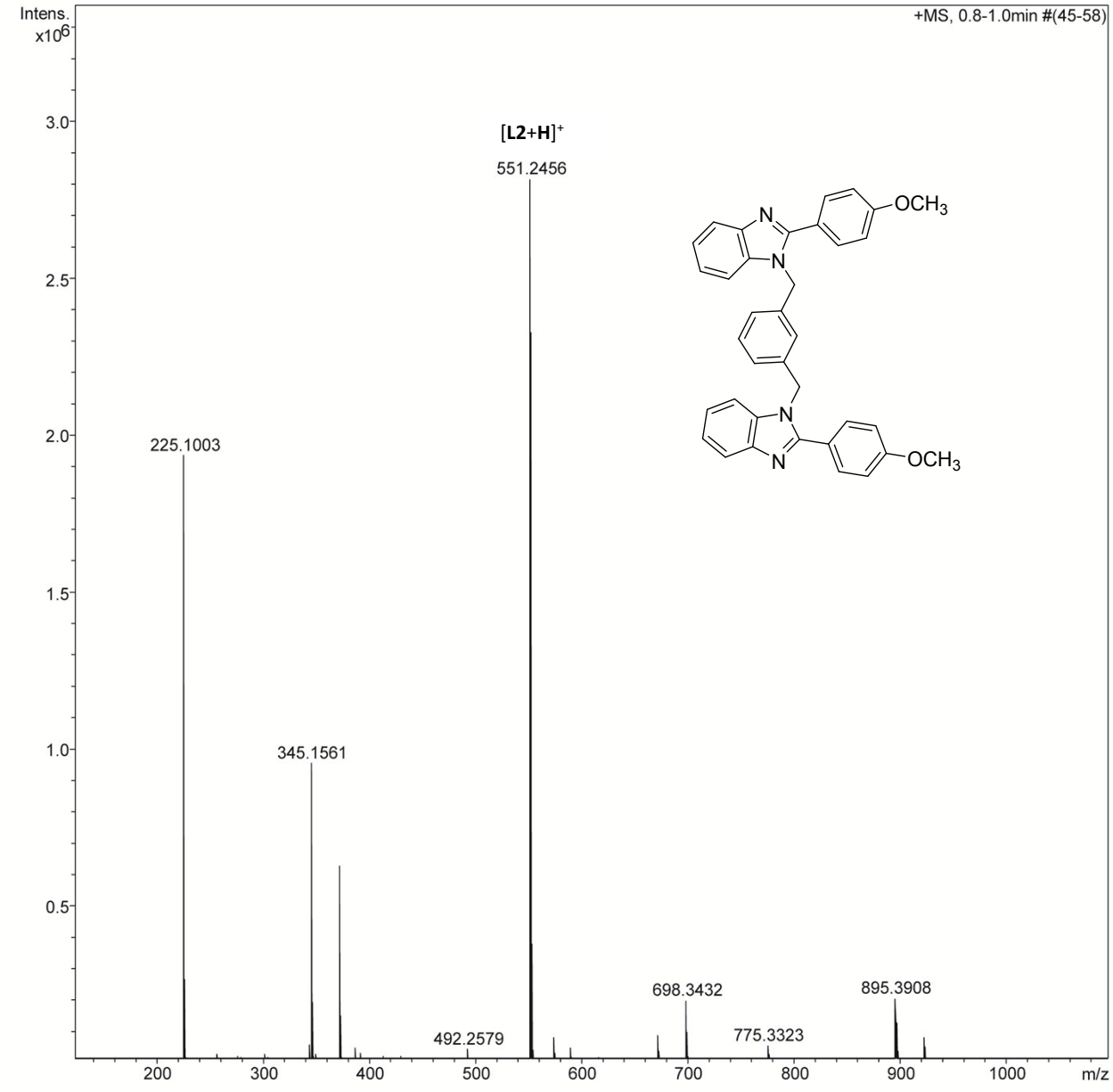

Fig. S7. ESI mass spectrum of **L2** in positive ion mode.

UOH -SCHOOL OF CHEMISTRY -HRMS

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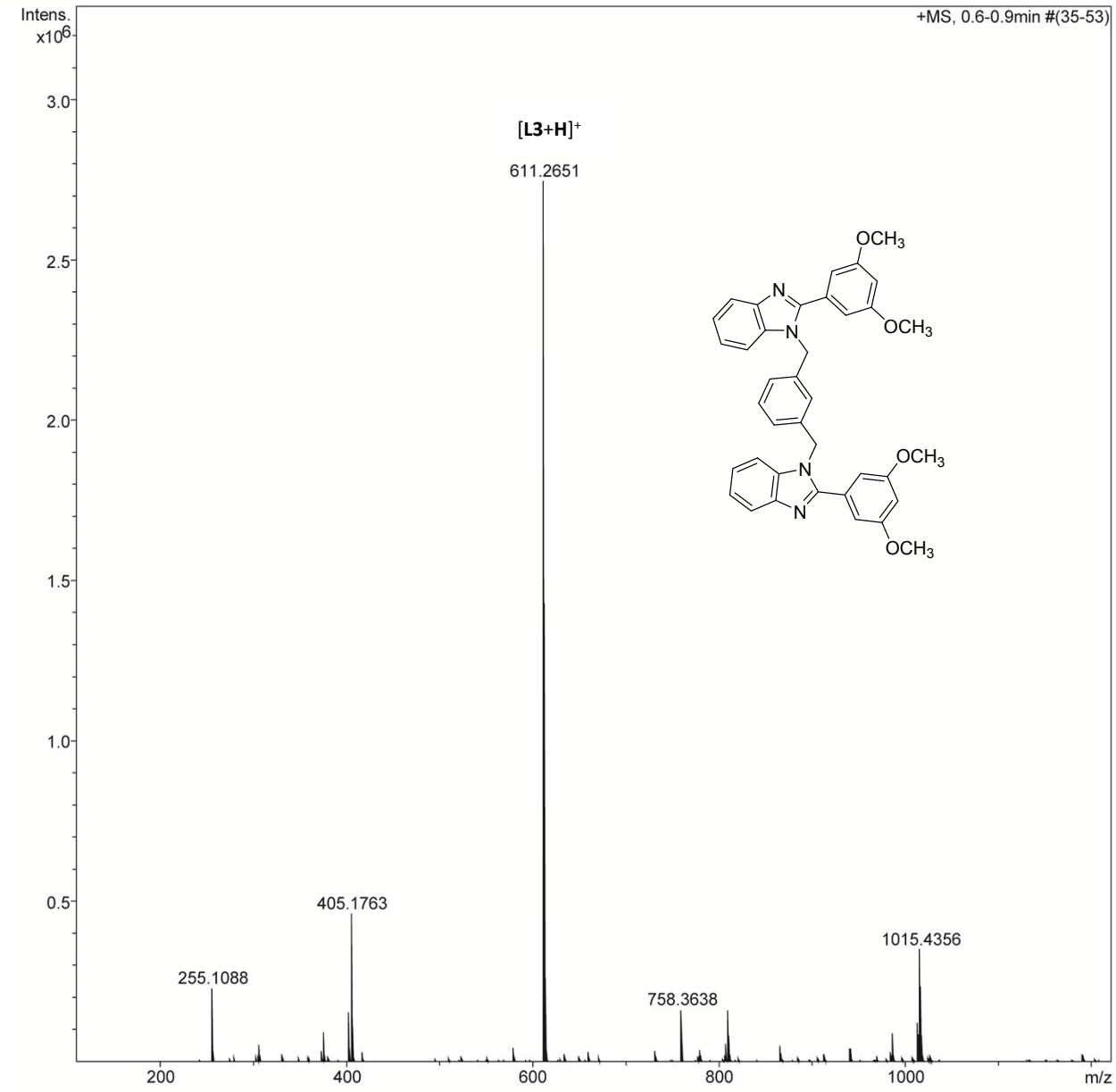

Fig. S8. ESI mass spectrum of **L3** in positive ion mode.

UOH -SCHOOL OF CHEMISTRY -HRMS

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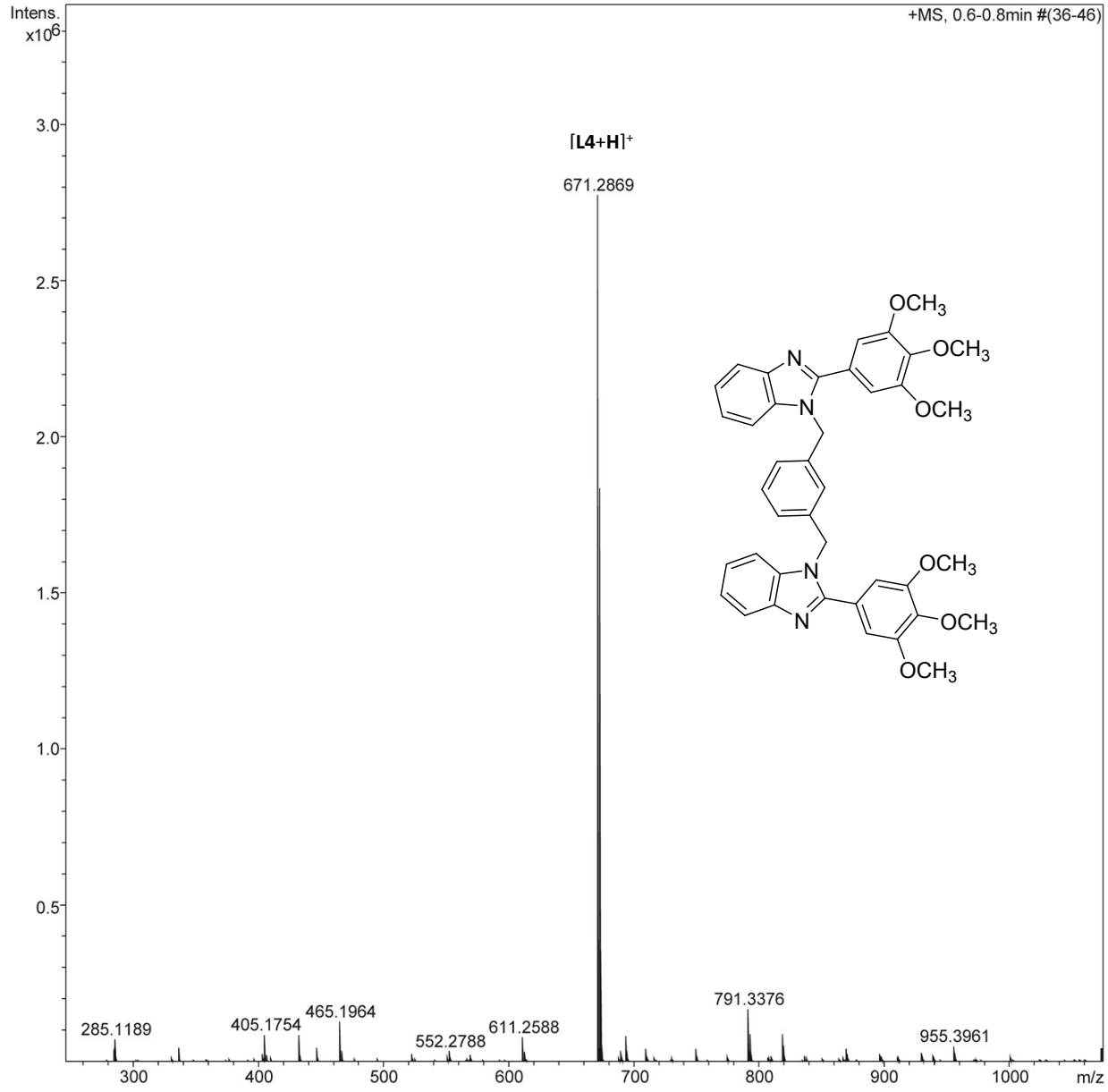

Fig. S9. ESI mass spectrum of **L4** in positive ion mode.

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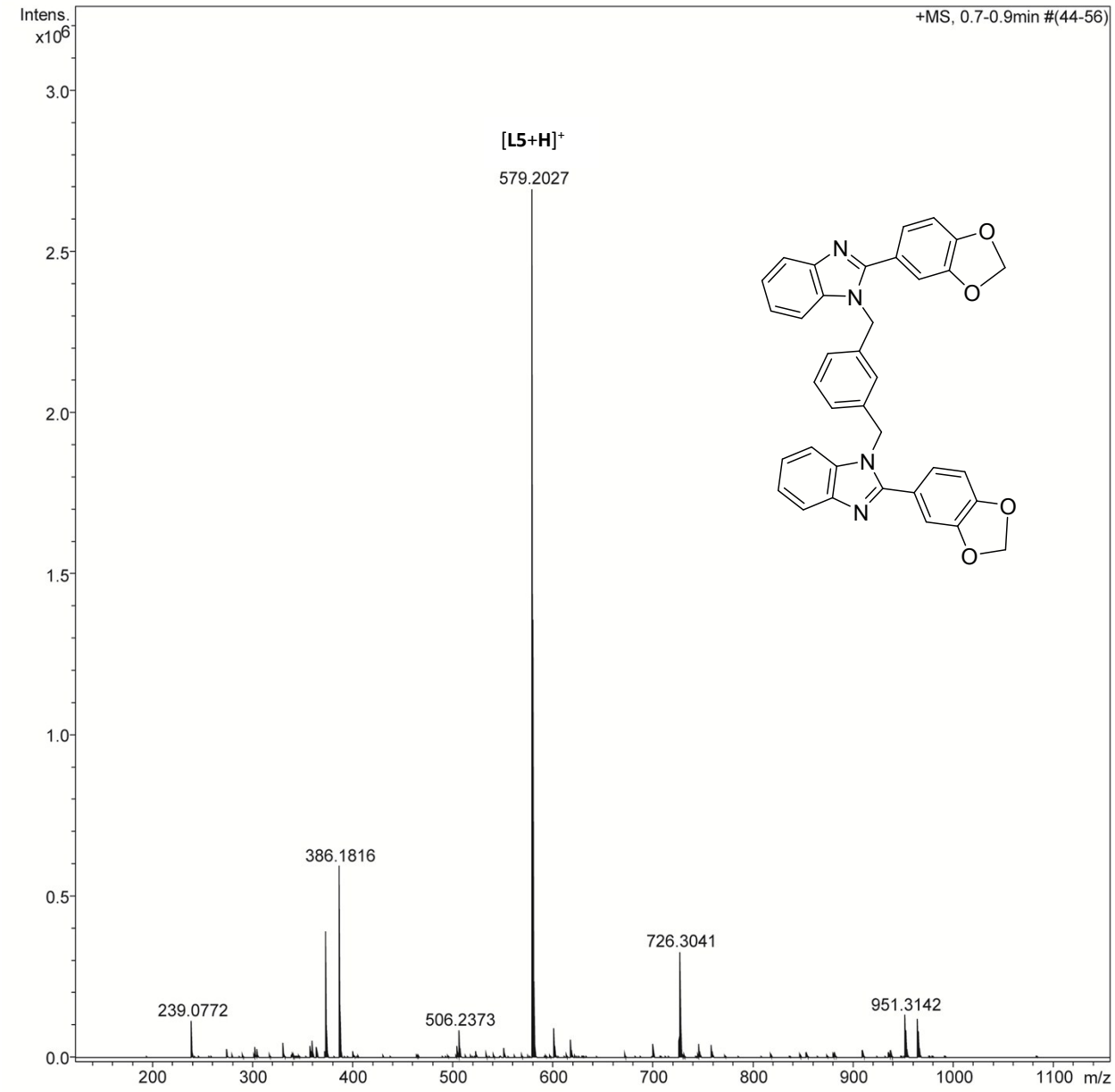

Fig. S10. ESI mass spectrum of **L5** in positive ion mode.

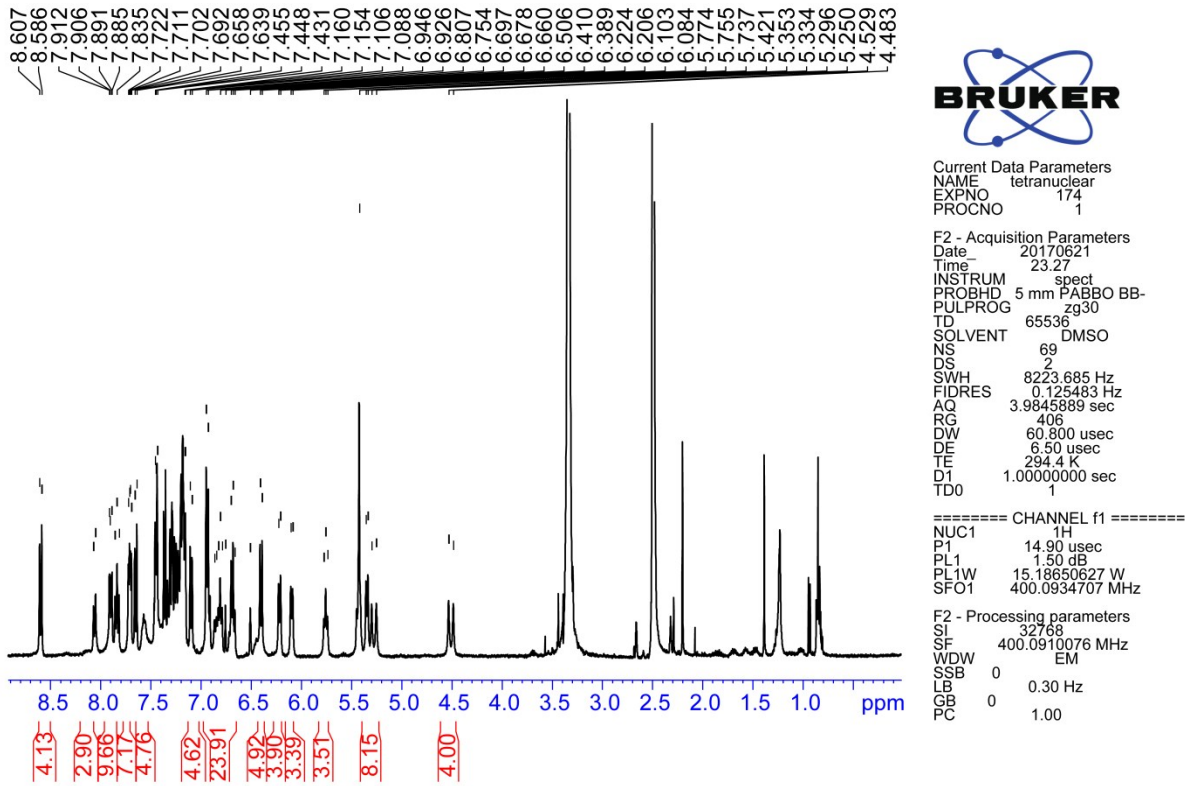

Fig. S11a. ^{1}H NMR spectrum of **1** in dmso-d_6.

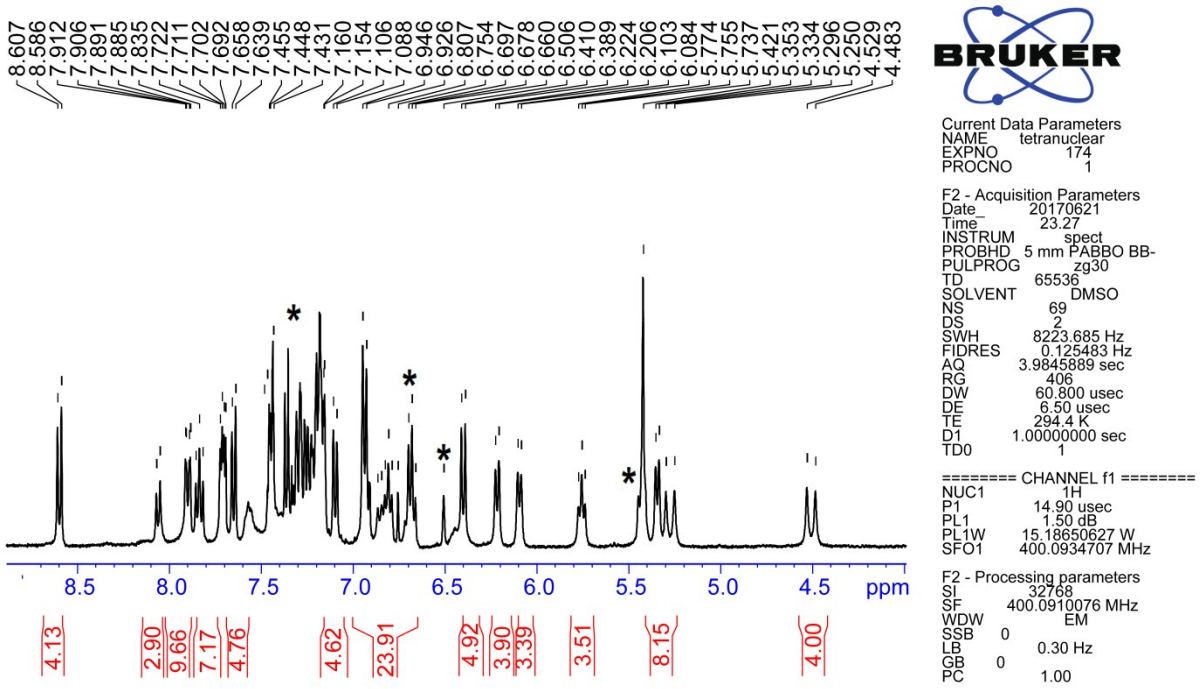

Fig. S11b. Partial ^{1}H NMR spectrum of **1** in dmso-d_6 (∗ indicates free ligand).

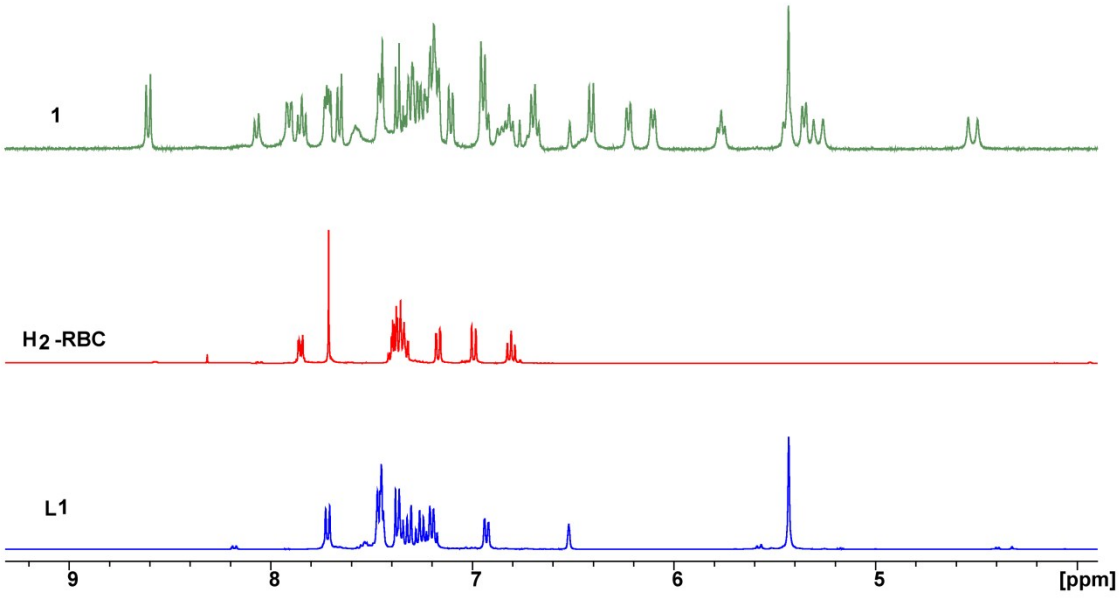

Fig. S11C. ^{1}H NMR spectra of **L1** (blue), **H_2-RBC** (red) and **1(**green**)** in dmso-d_6.

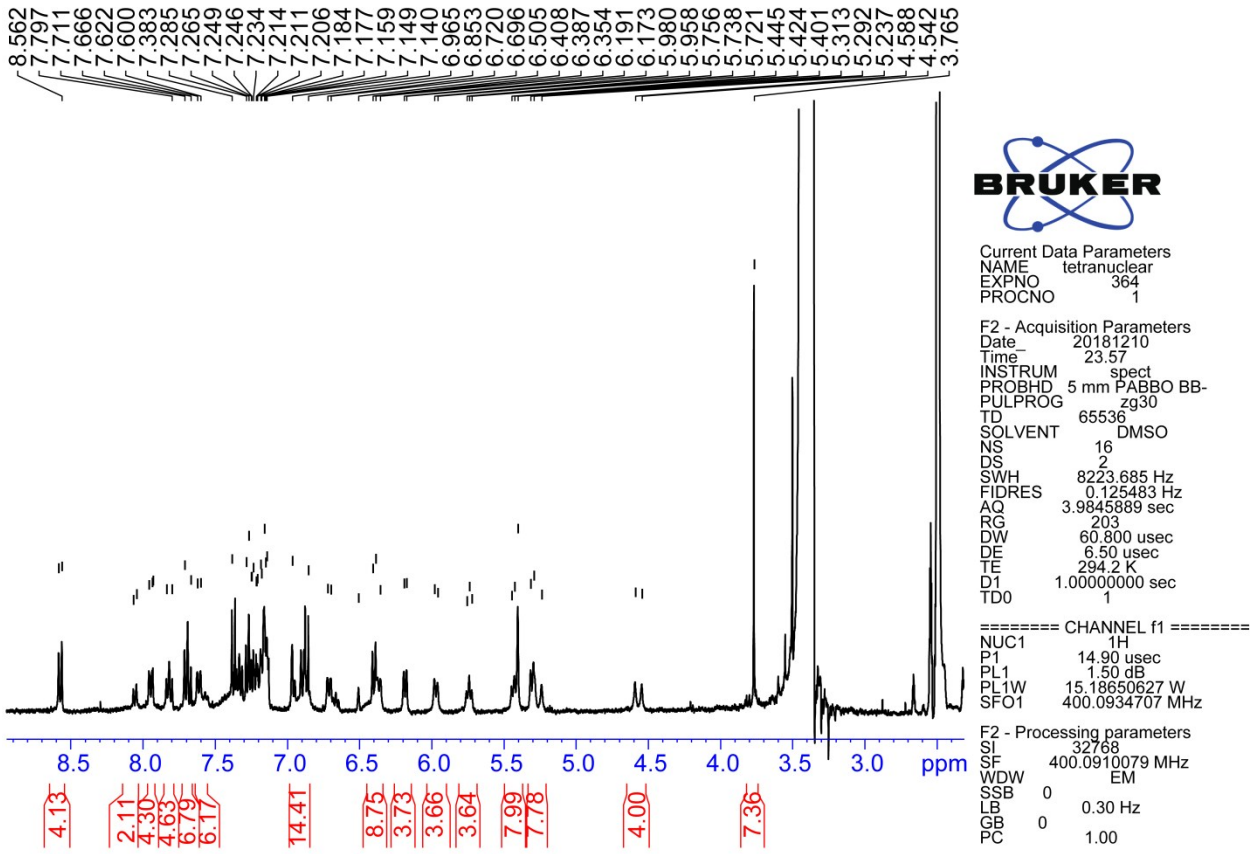

Fig. S12a. ^{1}H NMR spectrum of **2** in dmso-d_6.

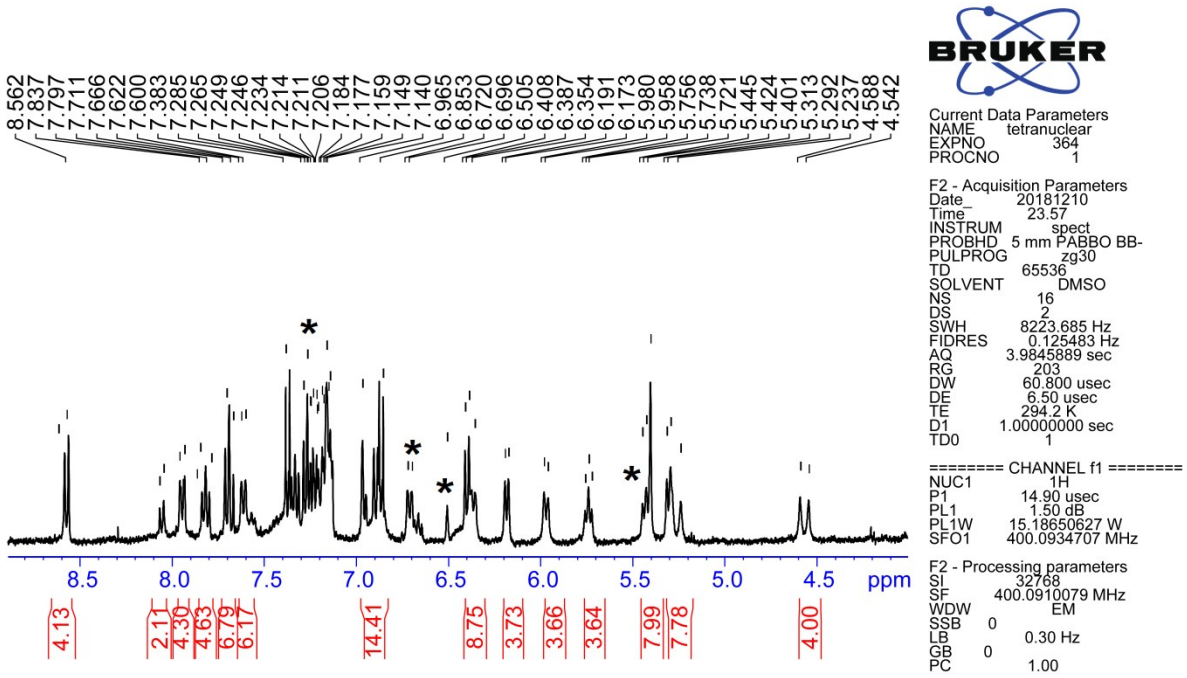

Fig. S12b. Partial ^{1}H NMR spectrum of **2** in dmso-d_6 (∗ indicates free ligand).

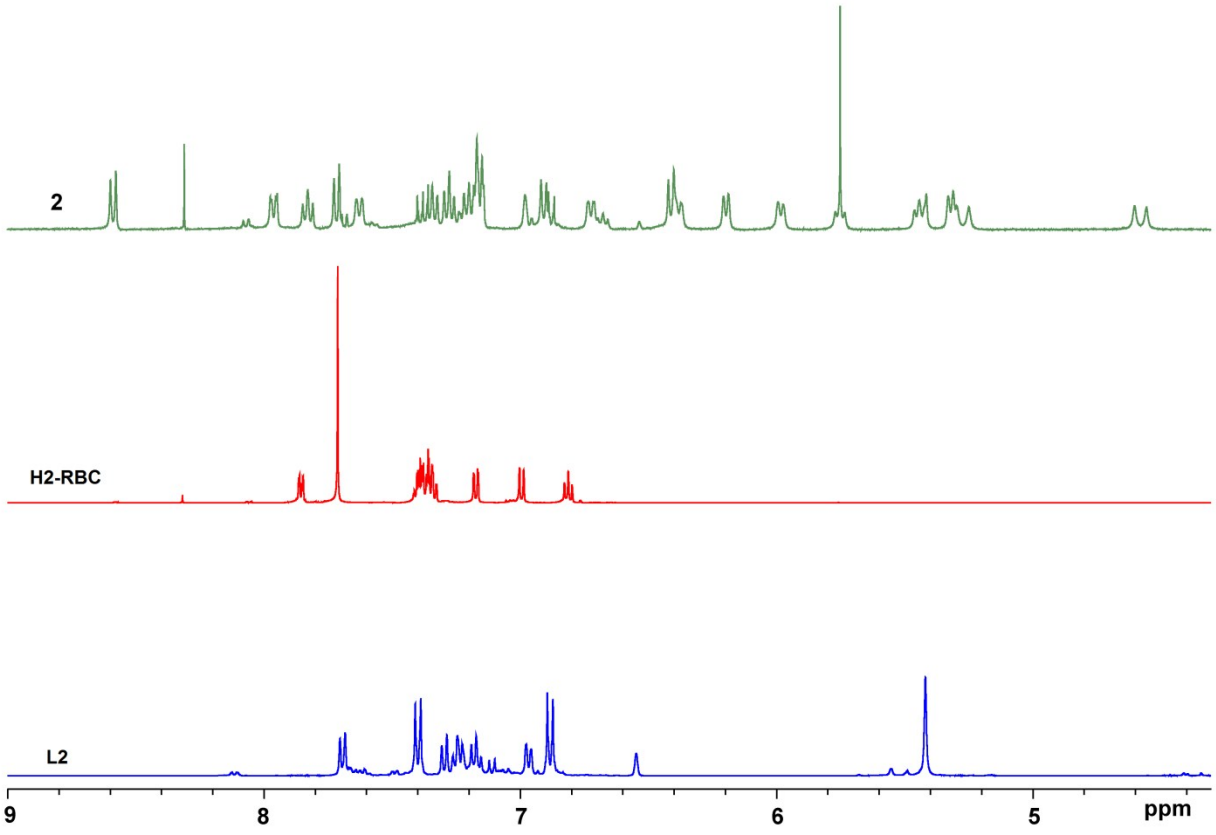

Fig. S12C. ^{1}H NMR spectra of **L2** (blue), **H_2-RBC** (red) and **2(**green**)** in dmso-d_6.

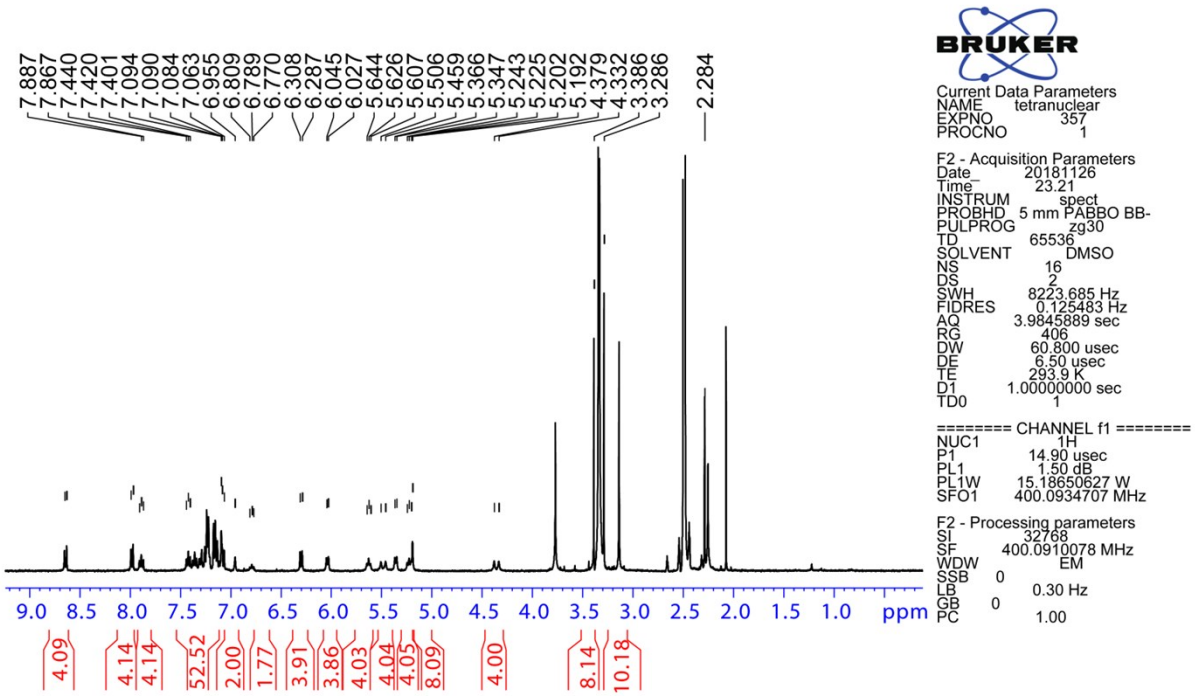

Fig. S13a. ^{1}H NMR spectrum of **4** in dmso-d_6.

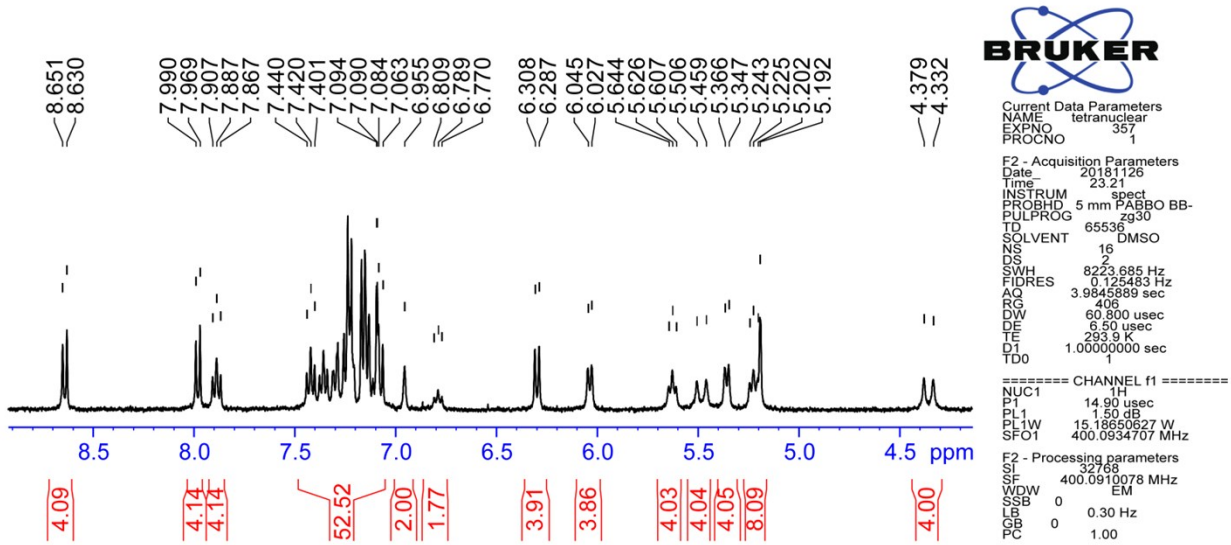

Fig. S13b. Partial ^{1}H NMR spectrum of **4** in dmso-d_6.

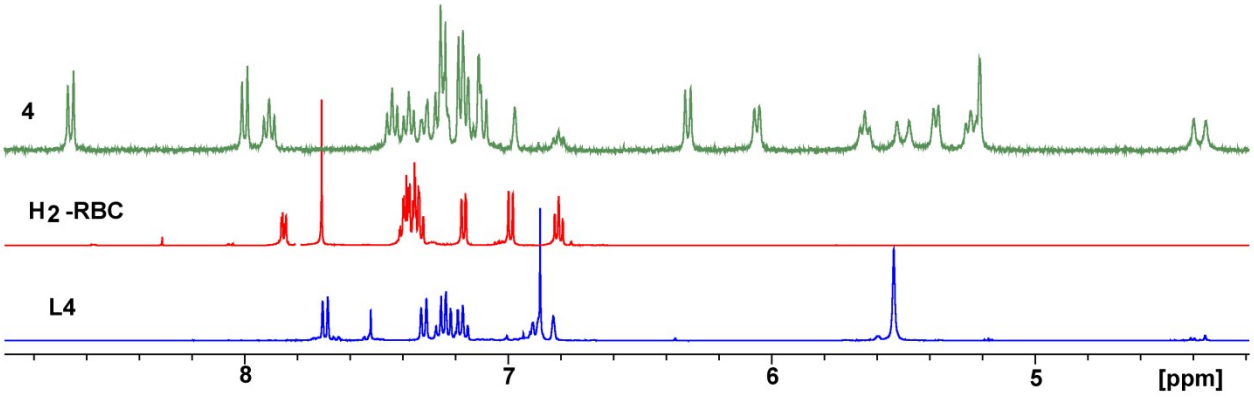

Fig. S13C. ^{1}H NMR spectra of **L4** (blue), **H_2-RBC** (red) and **4(**green**)** in dmso-d_6.

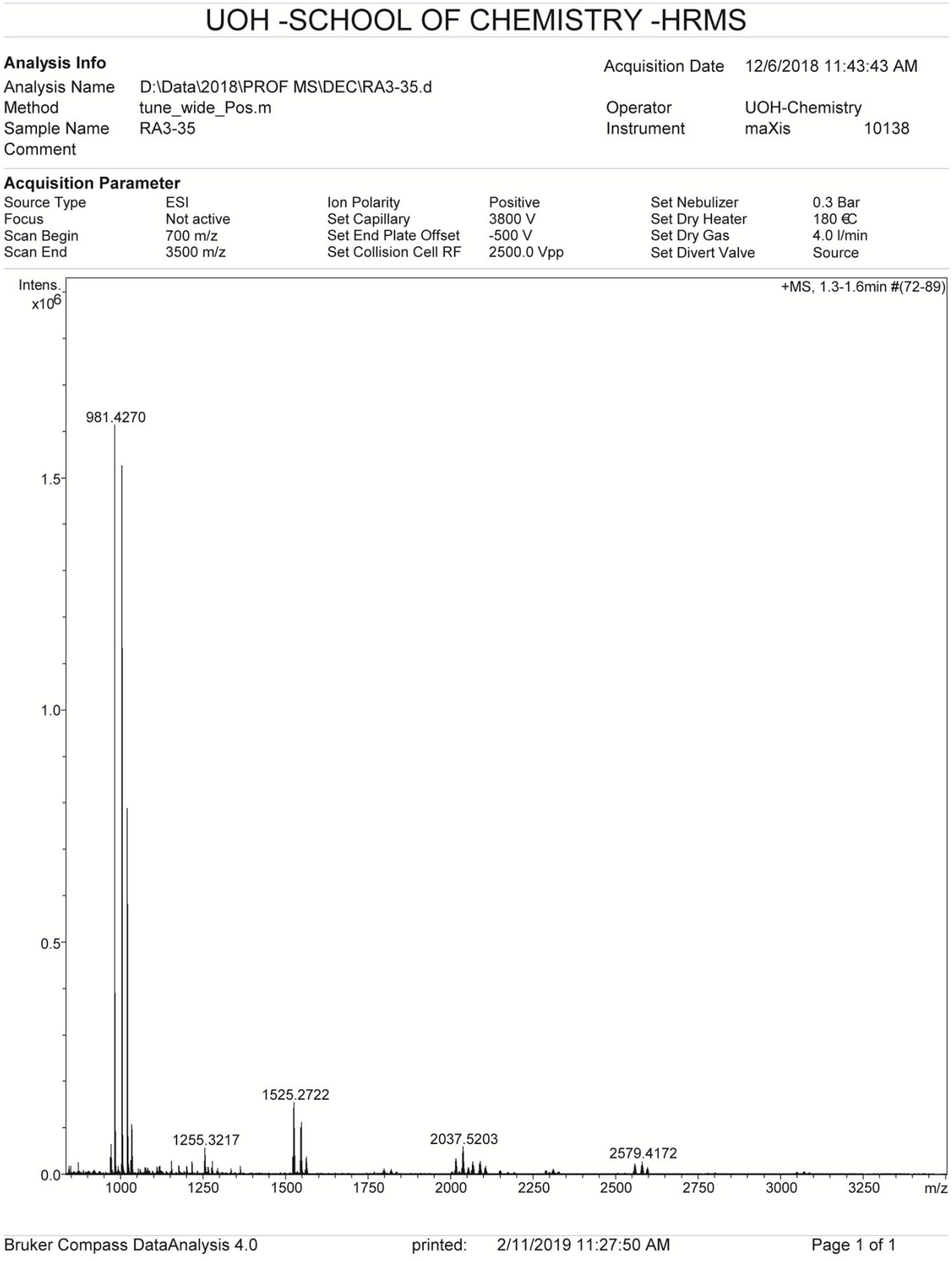

Fig. S14a. ESI mass spectrum of **1** in positive ion mode.

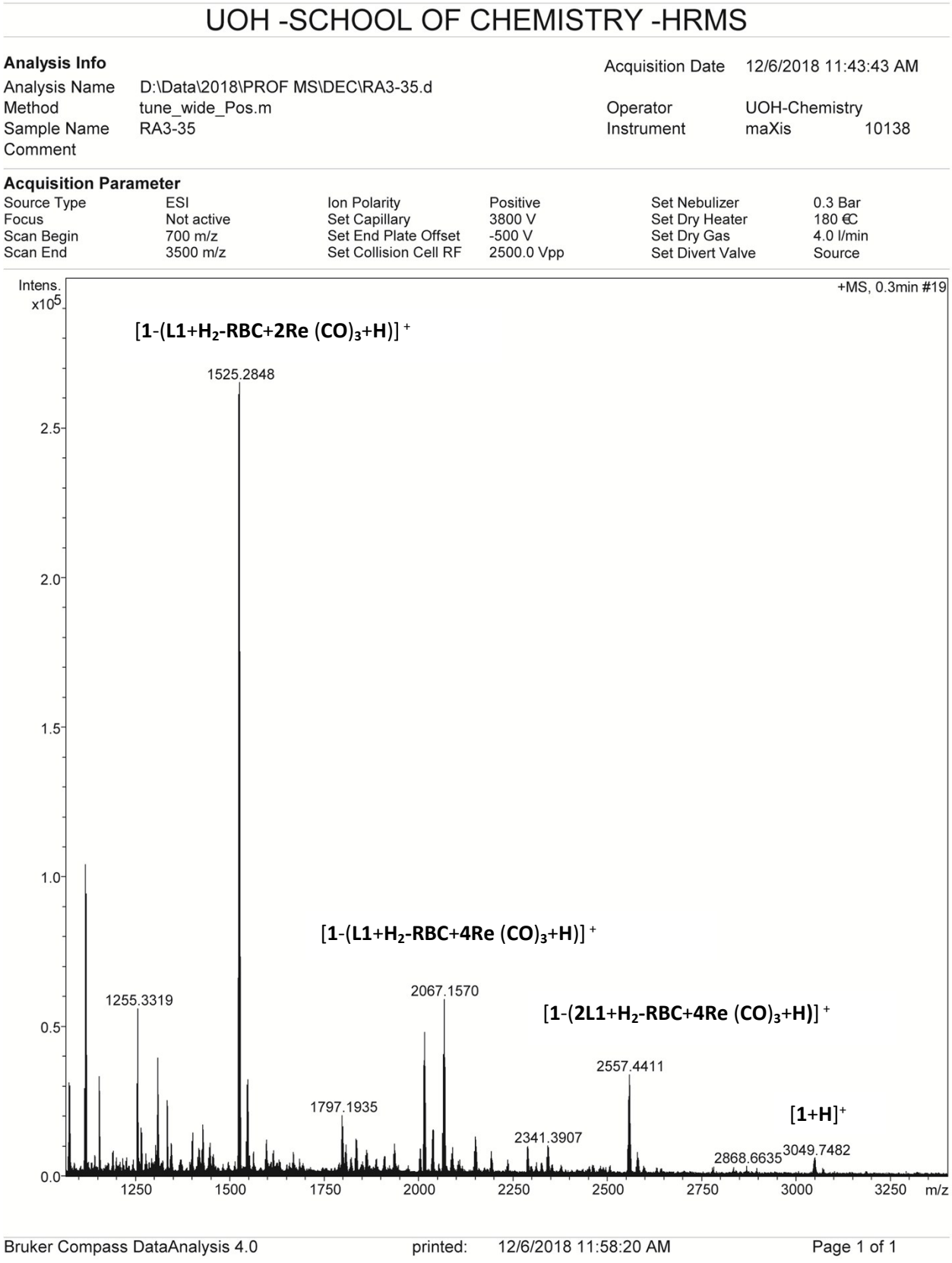

Fig. S14b. ESI mass spectrum of **1** in positive ion mode.

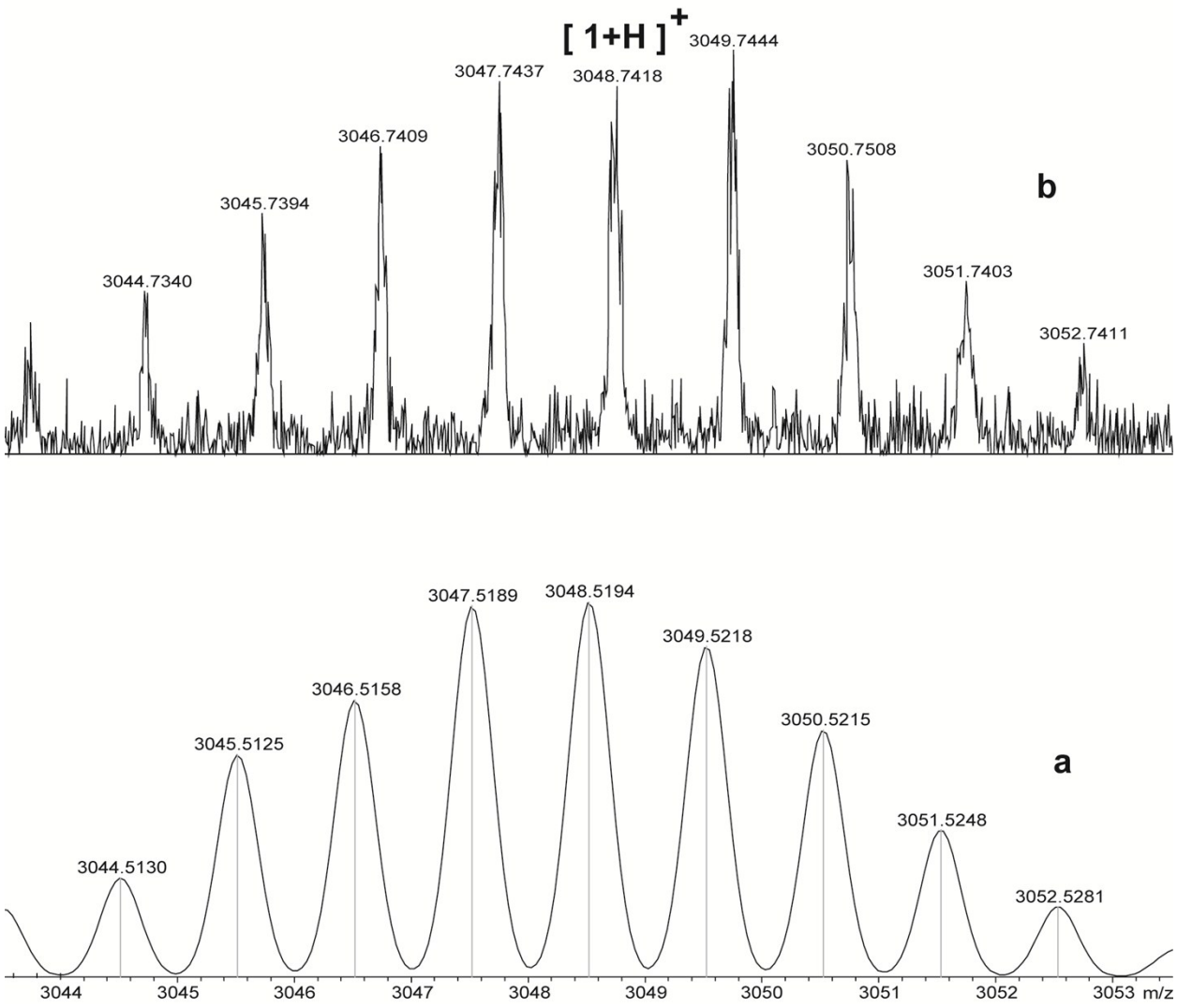

Fig. S14c. Experimental (a) and calculated (b) ESI-TOF mass spectra of [**1**+**H**]$^{+}$.

UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF MS\DEC\RA3-37.d	Acquisition Date	12/6/2018 12:07:05 PM
Method	tune_high_Pos.m	Operator	UOH-Chemistry
Sample Name	RA3-37	Instrument	maXis 10138
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
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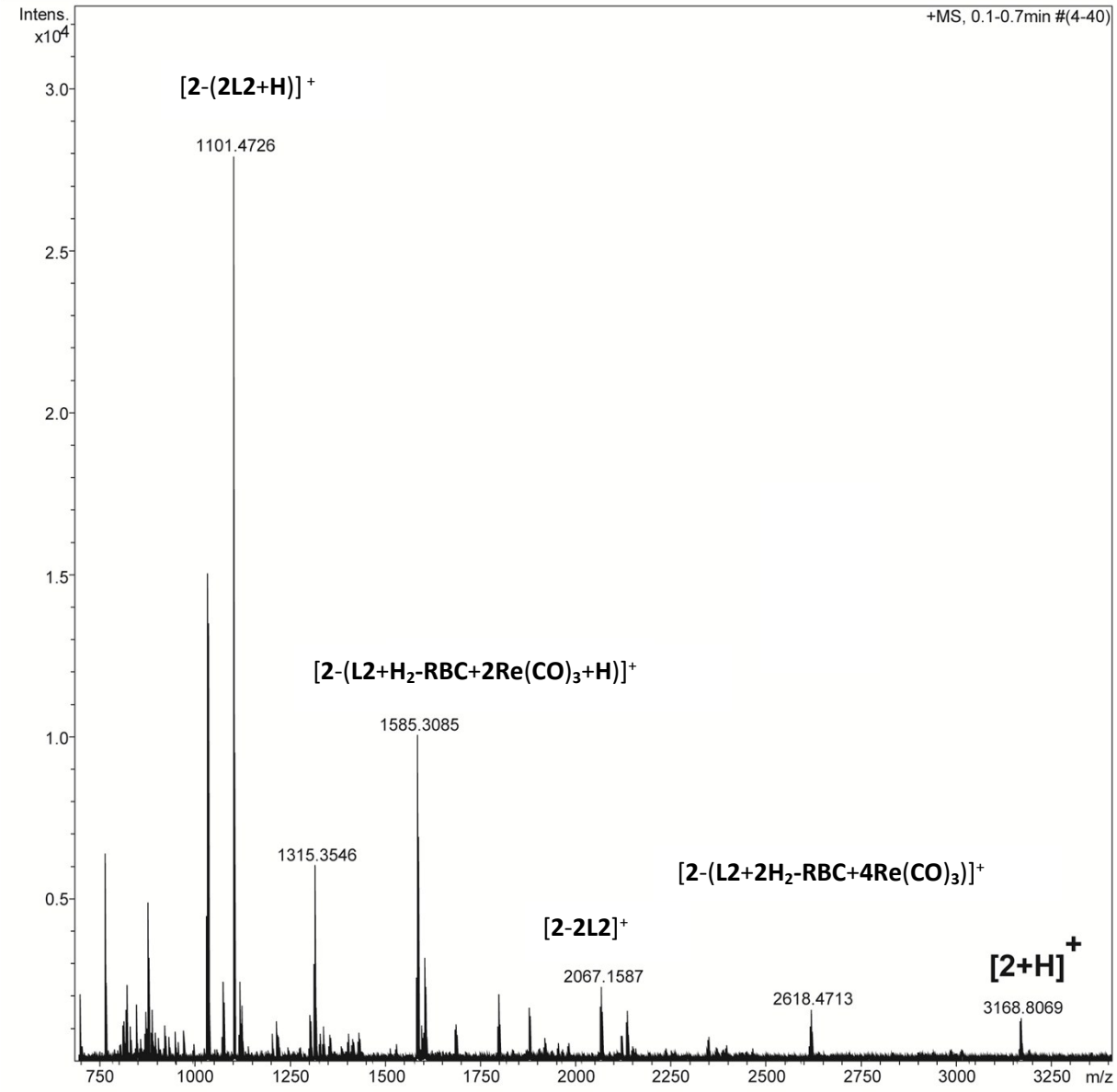
Scan End	3500 m/z	Set Collision Cell RF	2500.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 12/6/2018 12:12:59 PM Page 1 of 1

Fig. S15a. ESI mass spectrum of **2** in positive ion mode.

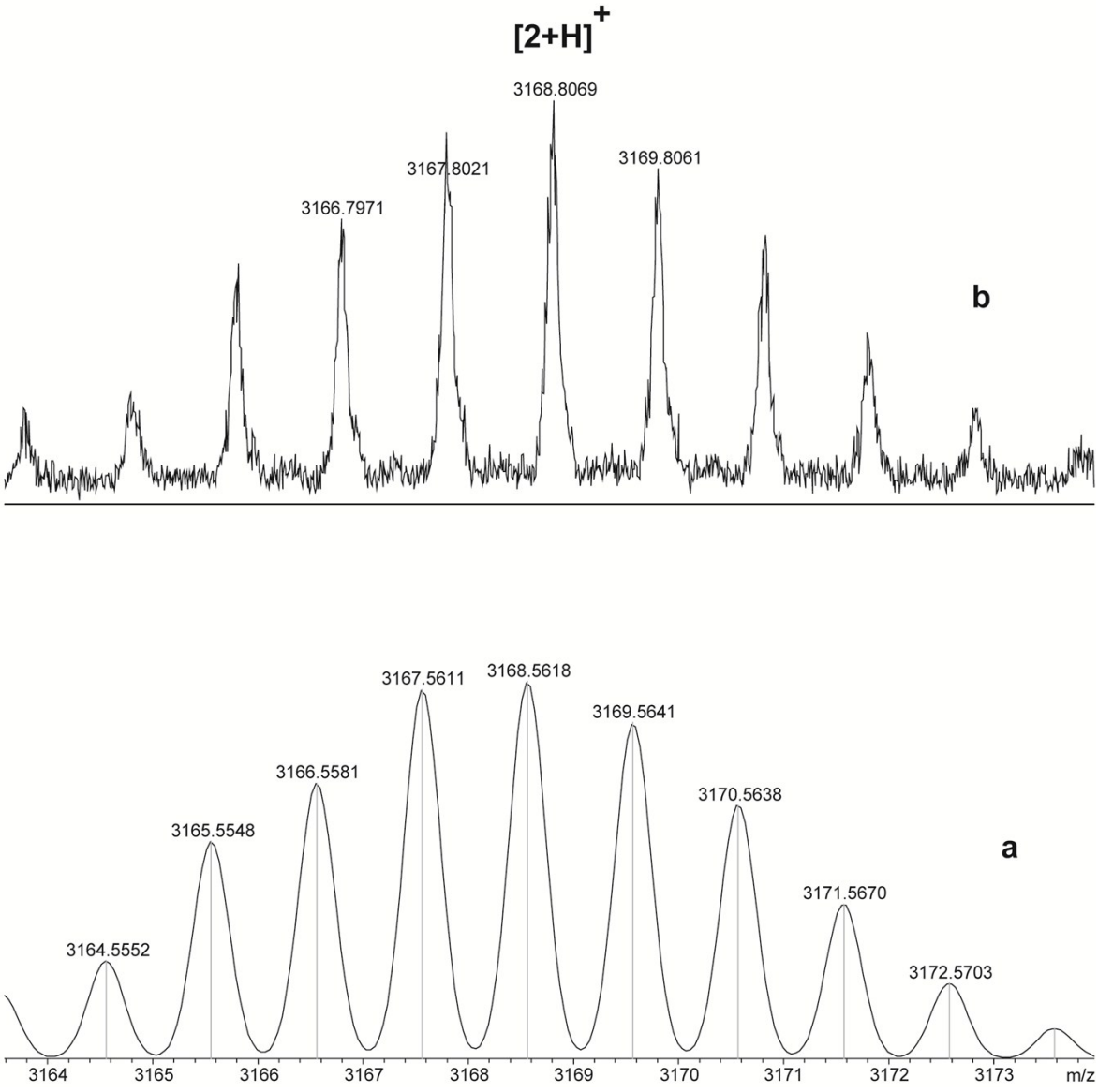


Fig. S15b. Experimental (a) and calculated (b) ESI-TOF mass spectra of [**2**+**H**]$^+$.

UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF MS\DEC\RA3-27.d	Acquisition Date	12/8/2018 2:47:00 PM
Method	tune_high_Pos.m	Operator	UOH-Chemistry
Sample Name	RA3-27	Instrument	maXis 10138
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
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Scan End	3500 m/z	Set Collision Cell RF	2500.0 Vpp	Set Divert Valve	Waste

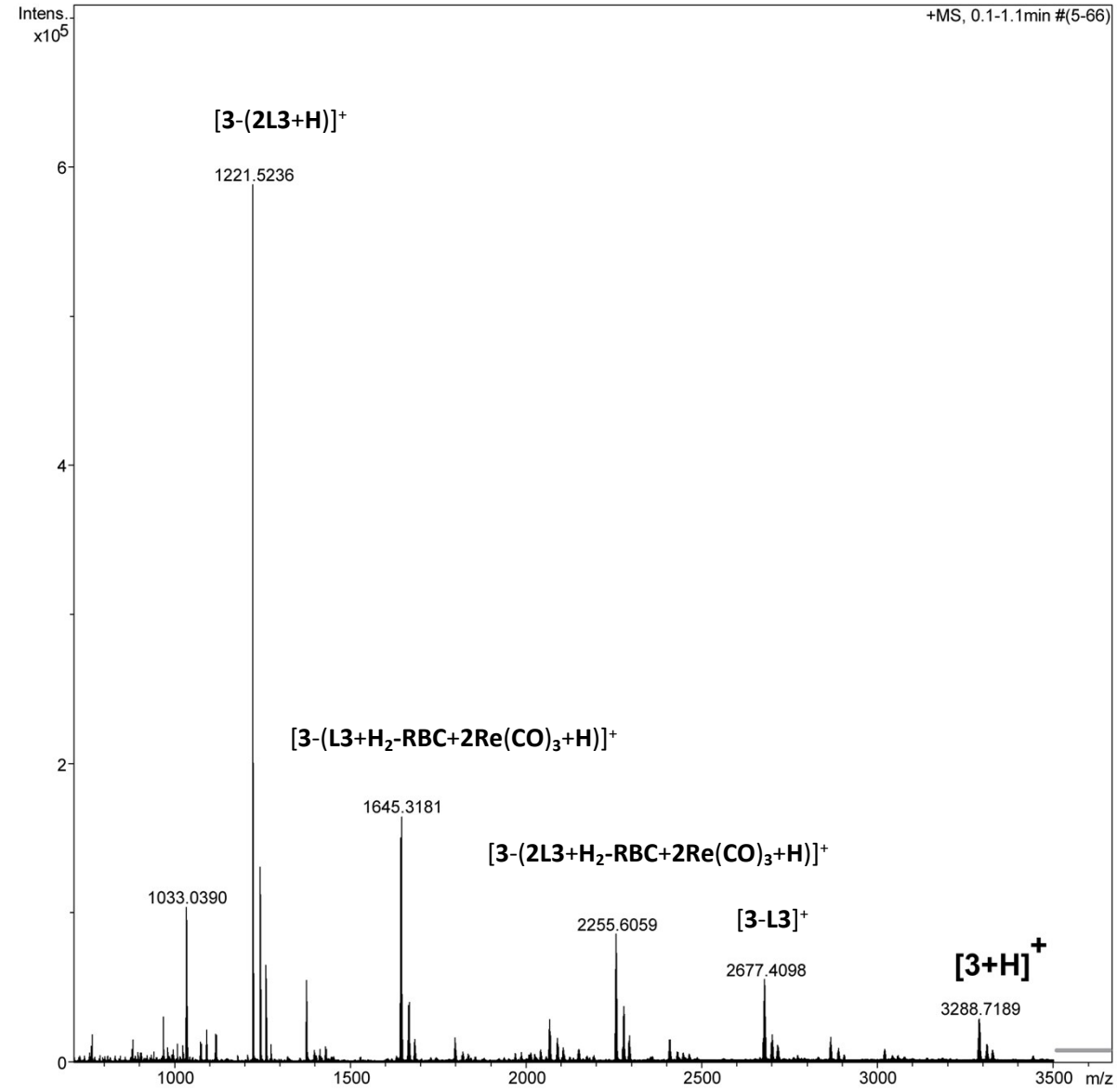

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Fig. S16a. ESI mass spectrum of **3** in positive ion mode.

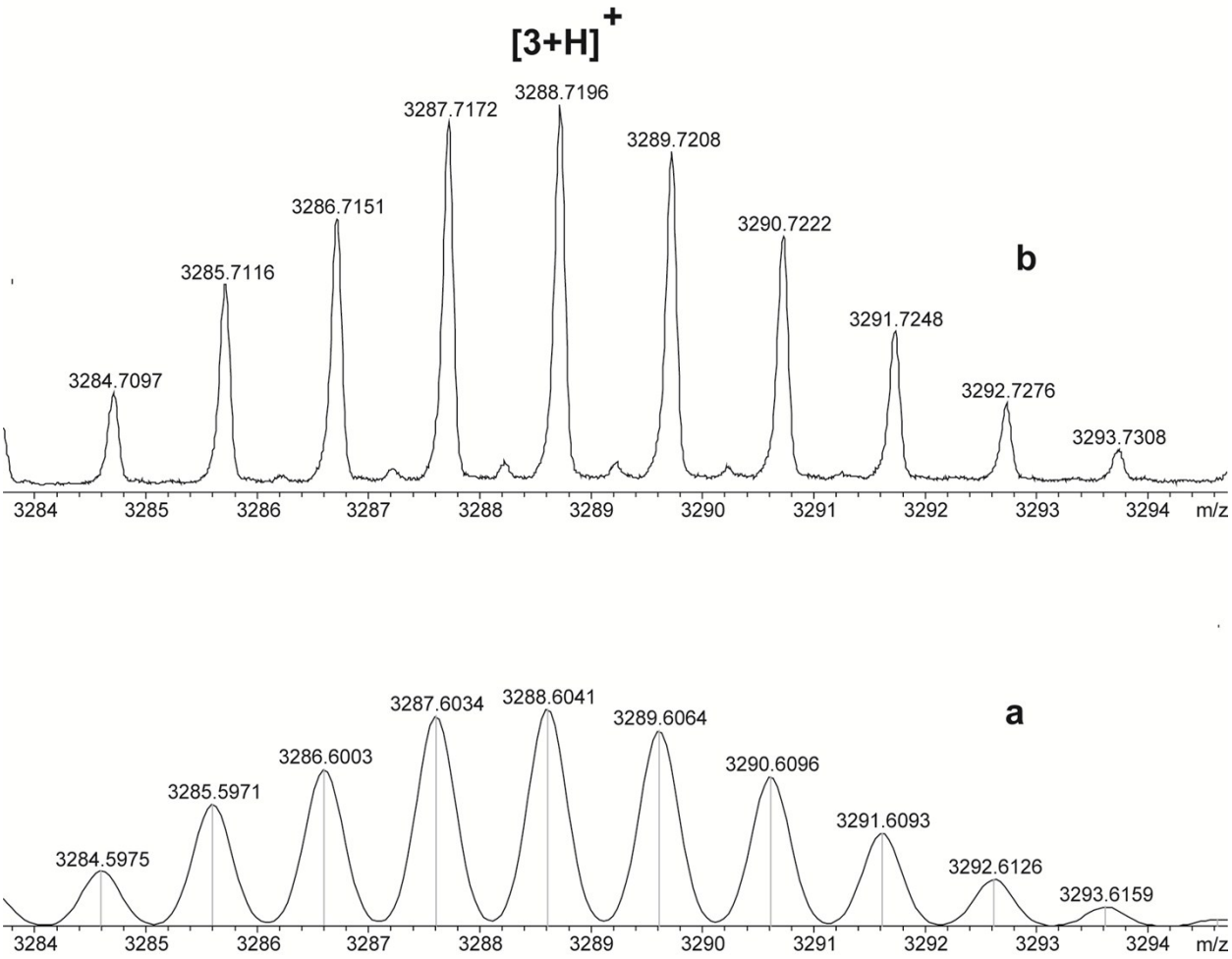

Fig. S16b. Experimental (a) and calculated (b) ESI-TOF mass spectra of [**3**+**H**]$^{+}$.

UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF MS\DEC\RA5-129.d	Acquisition Date	12/4/2018 12:52:26 PM
Method	tune_high_Pos.m	Operator	UOH-Chemistry
Sample Name	RA5-129-ACN	Instrument	maXis 10138
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4200 V	Set Dry Heater	180 ℃
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Scan End	4000 m/z	Set Collision Cell RF	2500.0 Vpp	Set Divert Valve	Waste

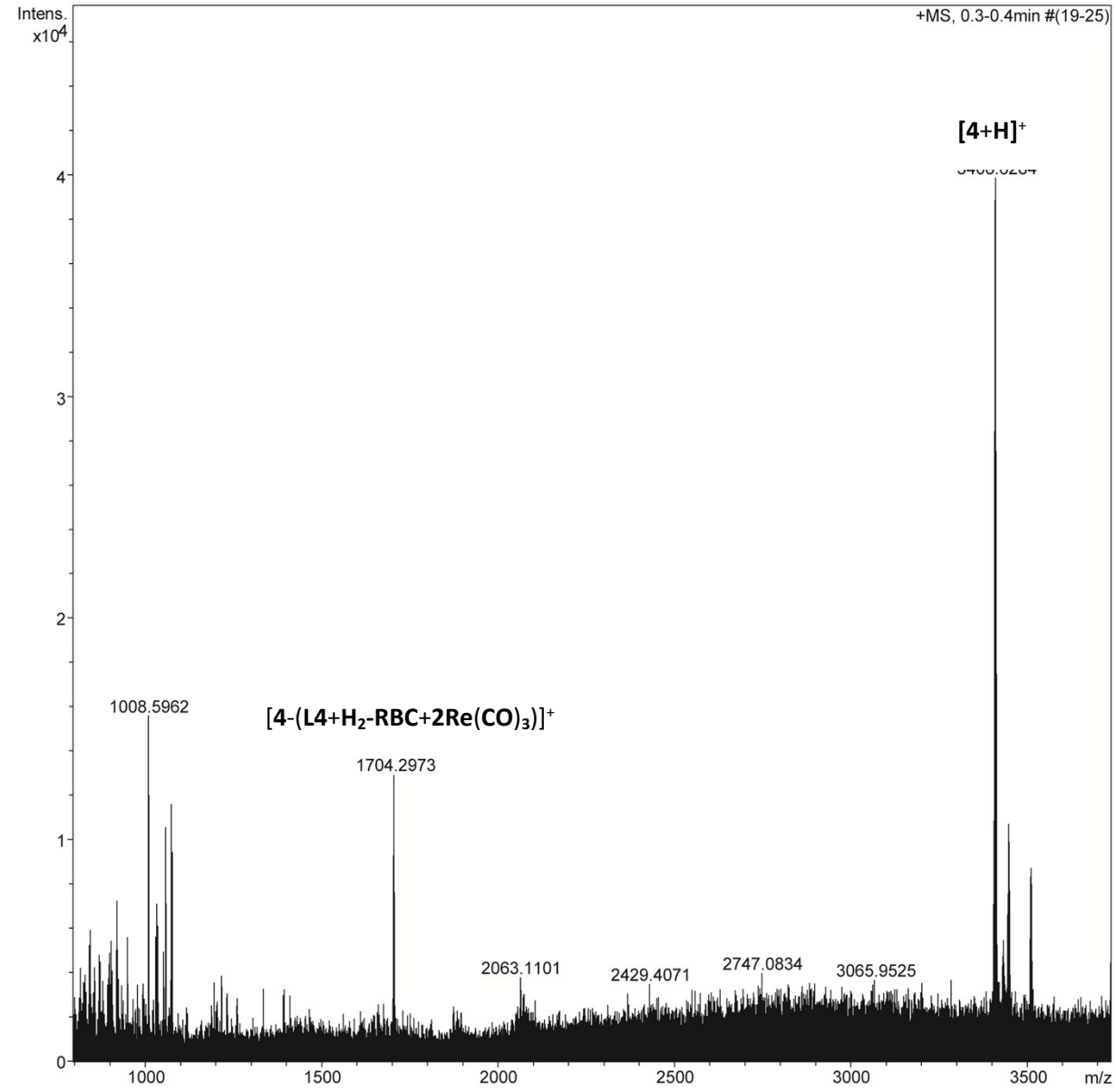

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Fig. S17a. ESI mass spectrum of **4** in positive ion mode.

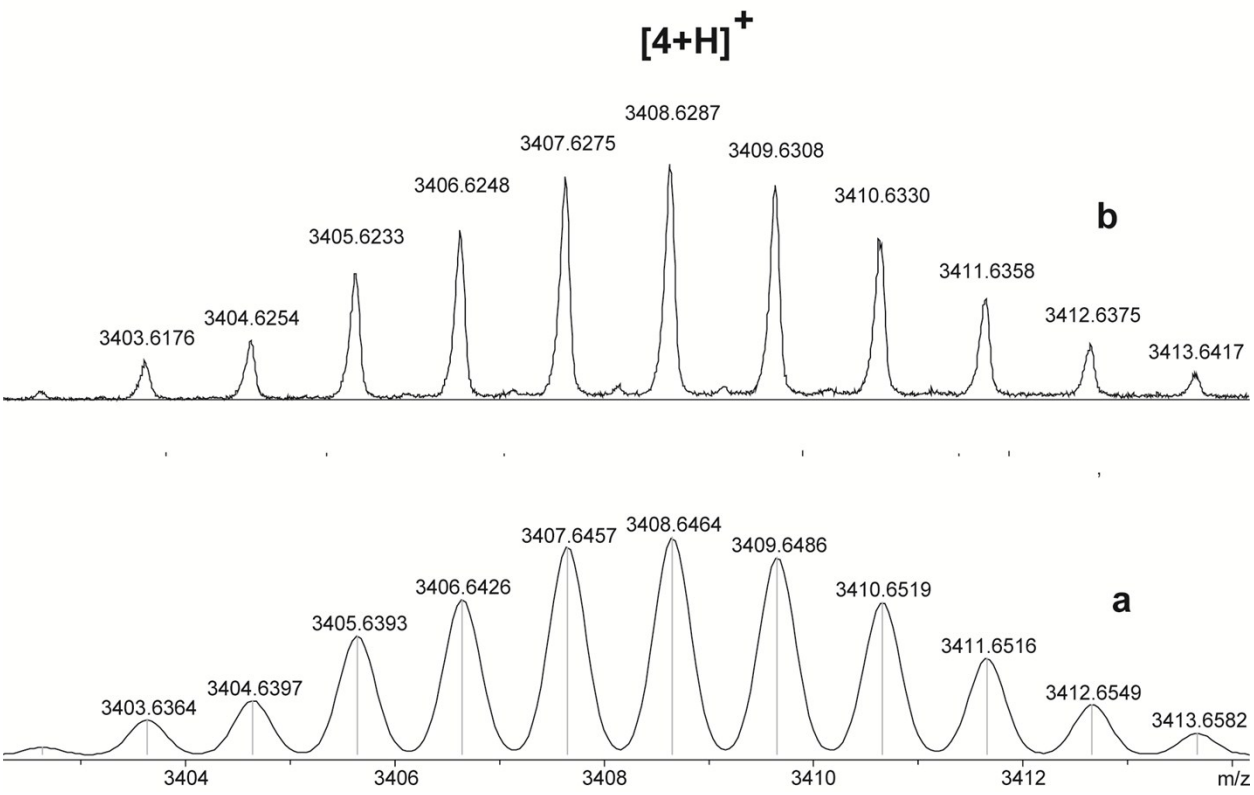


Fig. S17b. Experimental (a) and calculated (b) ESI-TOF mass spectra of [**4**+**H**]$^{+}$.

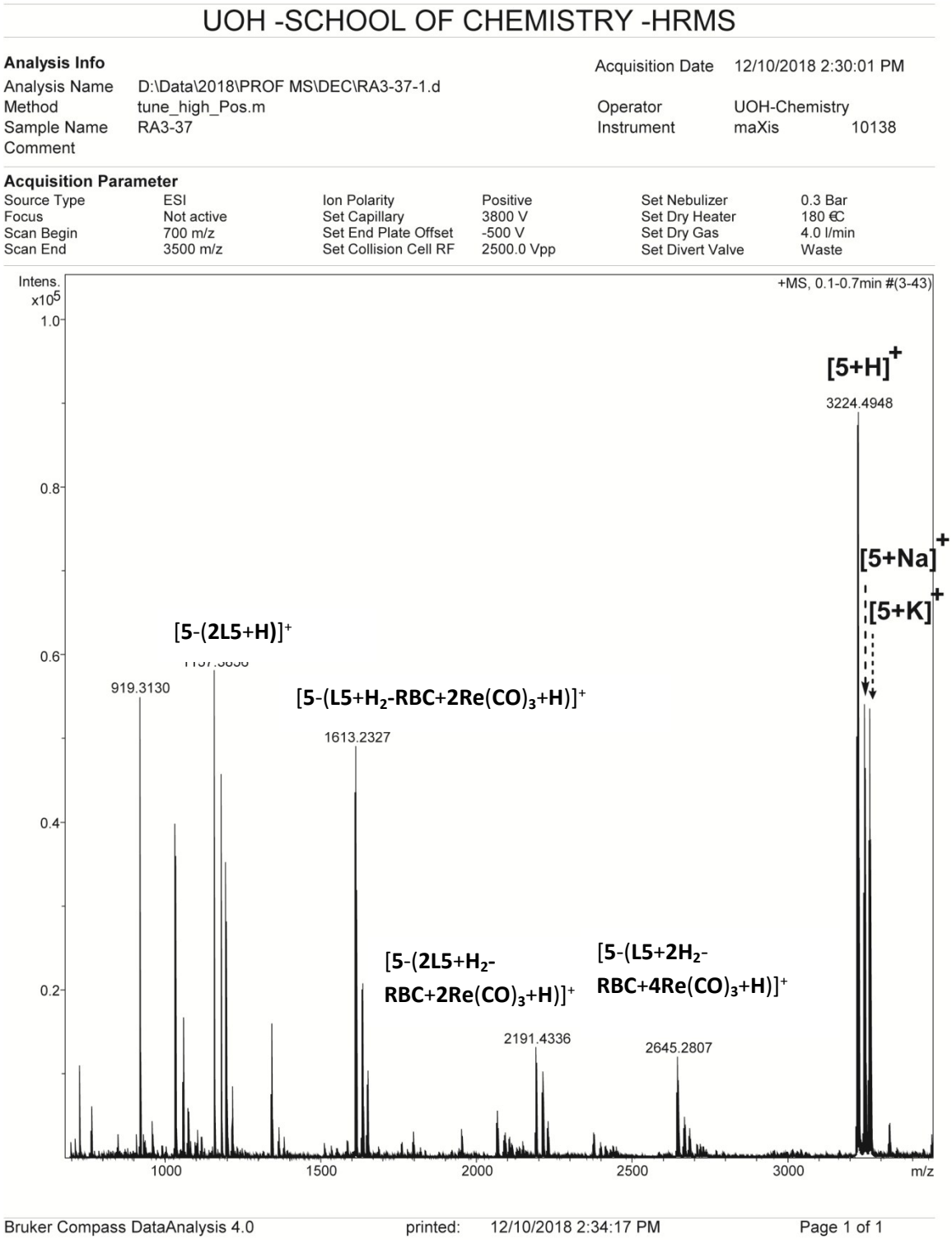


Fig. S18a. ESI mass spectrum of **5** in positive ion mode.

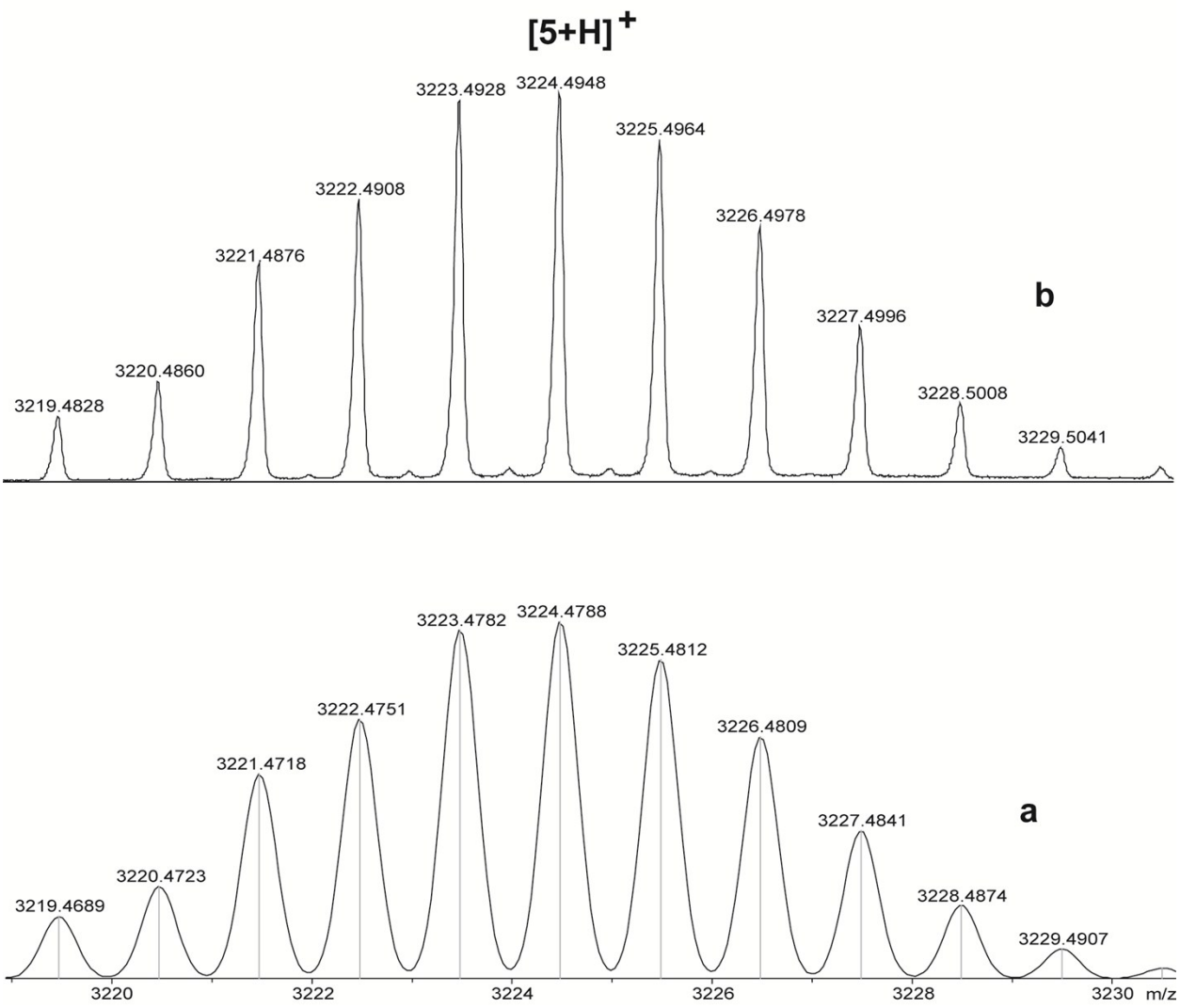
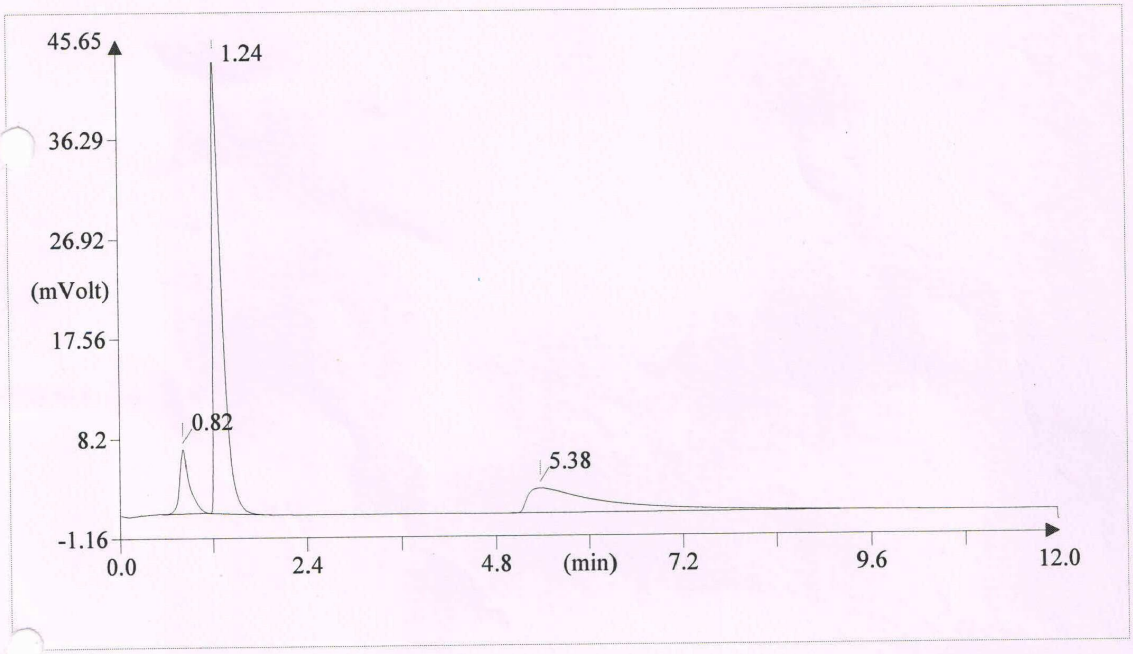


Figure S18b. Experimental (a) and calculated (b) ESI-TOF mass spectra of [**5**+**H**]$^{+}$.

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	RA3-35 (# 44)
Analysis type:	UnkNown
Chromatogram filename:	UNK-13062017-4.dat
Sample weight:	1.206

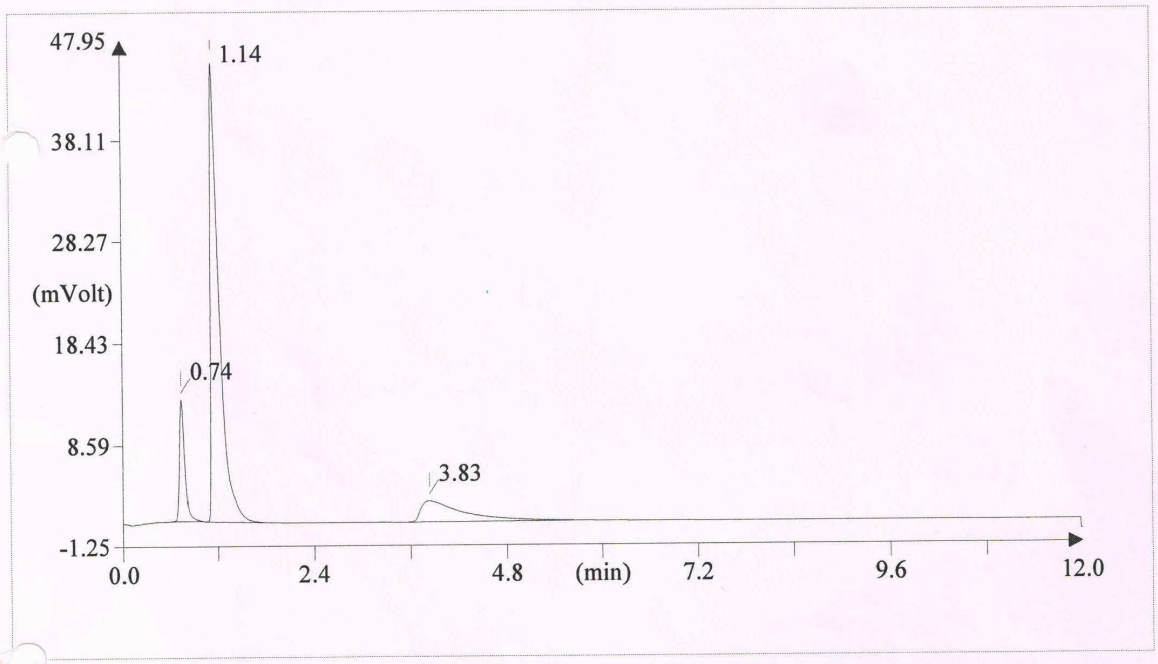


Element Name	Element %	Ret. Time
Nitrogen	7. 41	0. 82
Carbon	56. 69	1. 24
Hydrogen	3. 12	5. 38

Fig. S19. Elemental analysis of **1**.

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	RA3-36 (# 45)
Analysis type:	UnkNown
Chromatogram filename:	UNK-13062017-5.dat
Sample weight:	1.223



Element Name	Element %	Ret. Time
Nitrogen	7. 23	0. 74
Carbon	56. 27	1. 14
Hydrogen	3. 12	3. 83

Fig. S20. Elemental analysis of **2**.

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
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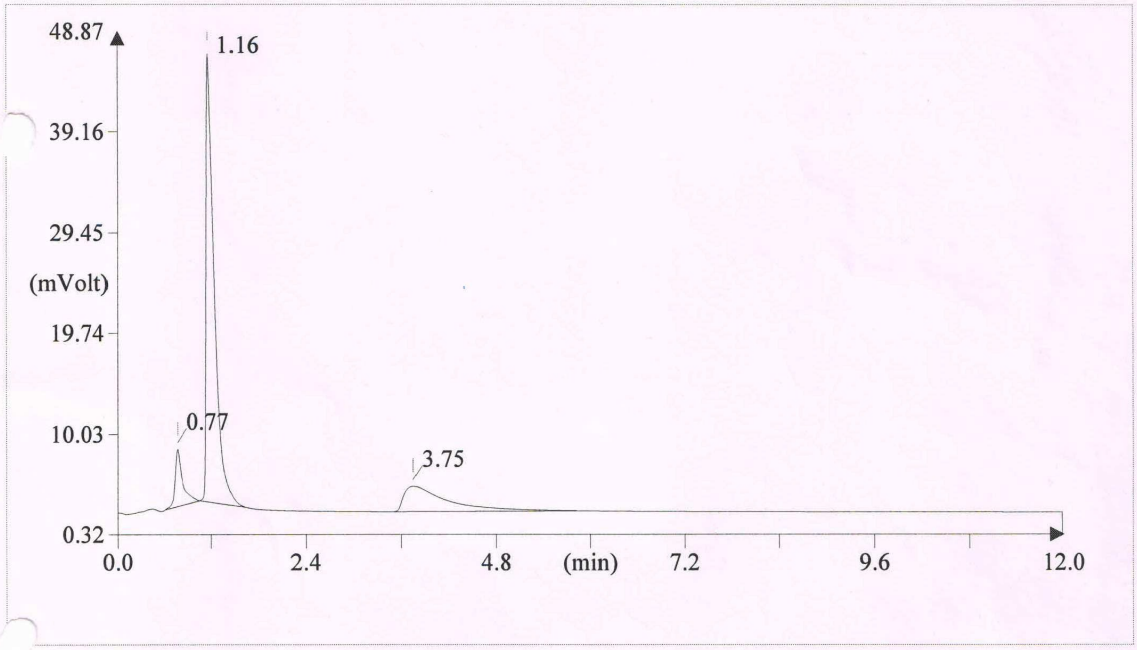
Analysis type:	UnkNown
Chromatogram filename:	UNK-13062017-2.dat
Sample weight:	1.265

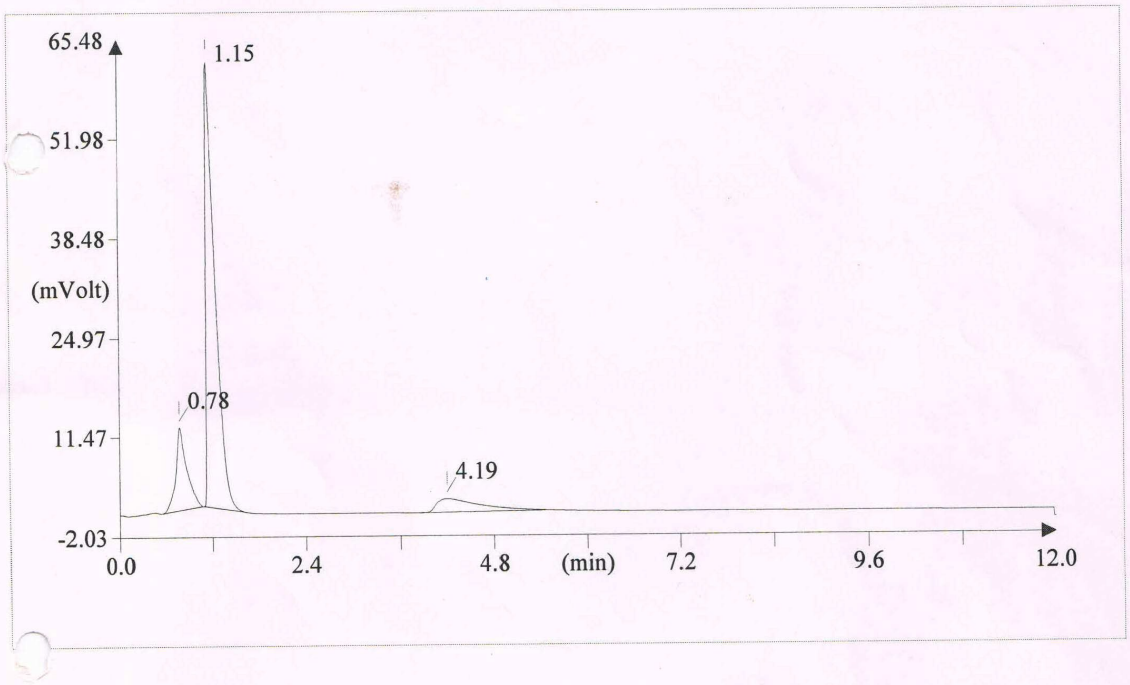


Element Name	Element %	Ret. Time
Nitrogen	6. 75	0. 77
Carbon	55. 43	1. 16
Hydrogen	3. 38	3. 75

Fig. S21. Elemental analysis of **3**.

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: SR2-20 (# 41)
Analysis type: UnkNown
Chromatogram filename: UNK-13062017-1.dat
Sample weight: 1412



Element Name	Element %	Ret. Time
Nitrogen	6. 48	0. 78
Carbon	54. 85	1. 15
Hydrogen	3. 47	4. 19

Fig. S22. Elemental analysis of **4**.

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
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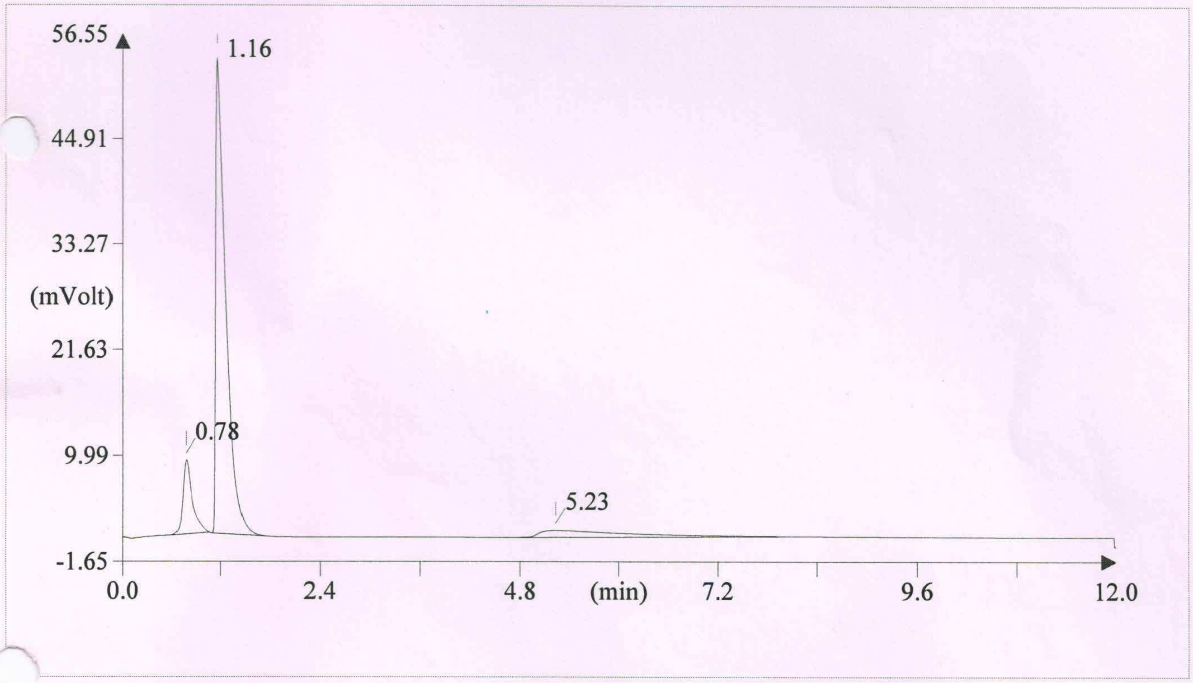
Analysis type:	UnkNown
Chromatogram filename:	UNK-13062017-3.dat
Sample weight:	1.323



Element Name	Element %	Ret. Time
Nitrogen	7. 06	0. 78
Carbon	55. 21	1. 16
Hydrogen	2. 83	5. 23

Fig. S23. Elemental analysis of **5**.

Table S1a. Crystallographic Data of **1**, **2** and **4** (the parameters are calculated with/without the solvent molecules).

	1	**2**	**2** with solvents	**4**
formula	$C_{144}H_{92}N_{16}O_{16}Re_4$	$C_{148}H_{100}N_{16}O_{20}Re_4$	$C_{169}H_{123}N_{16}O_{20}Re_4$	$C_{156}H_{116}N_{16}O_{28}Re_4$
M_r	3047.13	3167.23	3442.63	3407.44
crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
space group	*Pccn*	*Pccn*	*Pccn*	*Pbcn*
a (Å)	18.7295(17)	19.1389(13)	19.1389(13)	20.942(2)
b (Å)	24.537(2)	24.4265(13)	24.4265(13)	23.014(2)
c (Å)	34.743(3)	35.133(2)	35.133(2)	34.149(3)
a(deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	90	90	90
V (Å^3)	15967(2)	16424.4(17)	16424.4(17)	16458(3)
Z	4	4	4	4
T (K)	296(2)	296(2)	296(2)	296(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
D_{calc} (gcm^{-3})	1.268	1.281	1.392	1.375
μ (mm^{-1})	3.080	2.999	3.005	3.001
F(000)	5984	6240	6836	6752
goodness-of-fit	1.052	1.056	1.140	1.106
R1[a]/wR2[b] [$I > 2\sigma(I)$]	0.0562/0.1130	0.0845	0.0981/0.2266	0.0858/0.1538
R1[a]/wR2[b] (all data)	0.1056/0.1408	0.2128	0.1756/0.2685	0.1358/0.1718
Larg. Res. (e Å^{-3})	1.858	2.051	2.216	1.560

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$. [b] $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$

Table S1b. Crystallographic Data of **3** and **5** (the parameters are calculated with/without the solvent molecules).

	3	**3 with solvents**	**5**	**5 with solvents**
formula	$C_{166}H_{124}N_{16}O_{24}Re_4$	$C_{180}H_{140}N_{16}O_{24}Re_4$	$C_{148}H_{92}N_{16}O_{24}Re_4$	$C_{183}H_{90}N_{16}O_{24}Re_4$
M_r	3471.6	3655.87	3223.17	3641.50
crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
space group	*Pbcn*	*Pbcn*	*Pccn*	*Pccn*
a (Å)	20.820(3)	20.820(3)	18.7918(6)	18.7918(6)
b (Å)	22.790(3)	22.790(3)	23.7918(7)	23.7918(7)
c (Å)	33.942(4)	33.942(4)	35.3639(11)	35.3639(11)
a(deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	90	90	90
V (Å^3)	16106(4)	16106(4)	15810.9(8)	15810.9(8)
Z	4	4	4	4
T (K)	296(2)	296(2)	296(2)	296(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
D_{calc} (gcm^{-3})	1.432	1.508	1.354	1.530
μ (mm^{-1})	3.067	3.071	3.118	3.128
F(000)	6896	7296	6336	7168
goodness-of-fit	1.004	1.020	1.046	1.079
R1[a]/wR2[b] [$I > 2\sigma(I)$]	0.0543/0.1214	0.0570/0.1299	0.0369/0.0793	0.0484/0.1266
R1[a]/wR2[b] (all data)	0.1211/0.1594	0.1251/0.1696	0.0497/0.0858	0.0631/0.1379
Larg. Res. (e Å^{-3})	1.293	1.377	1.691	1.703

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$. [b] $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$

† = data obtained from solvent molecules

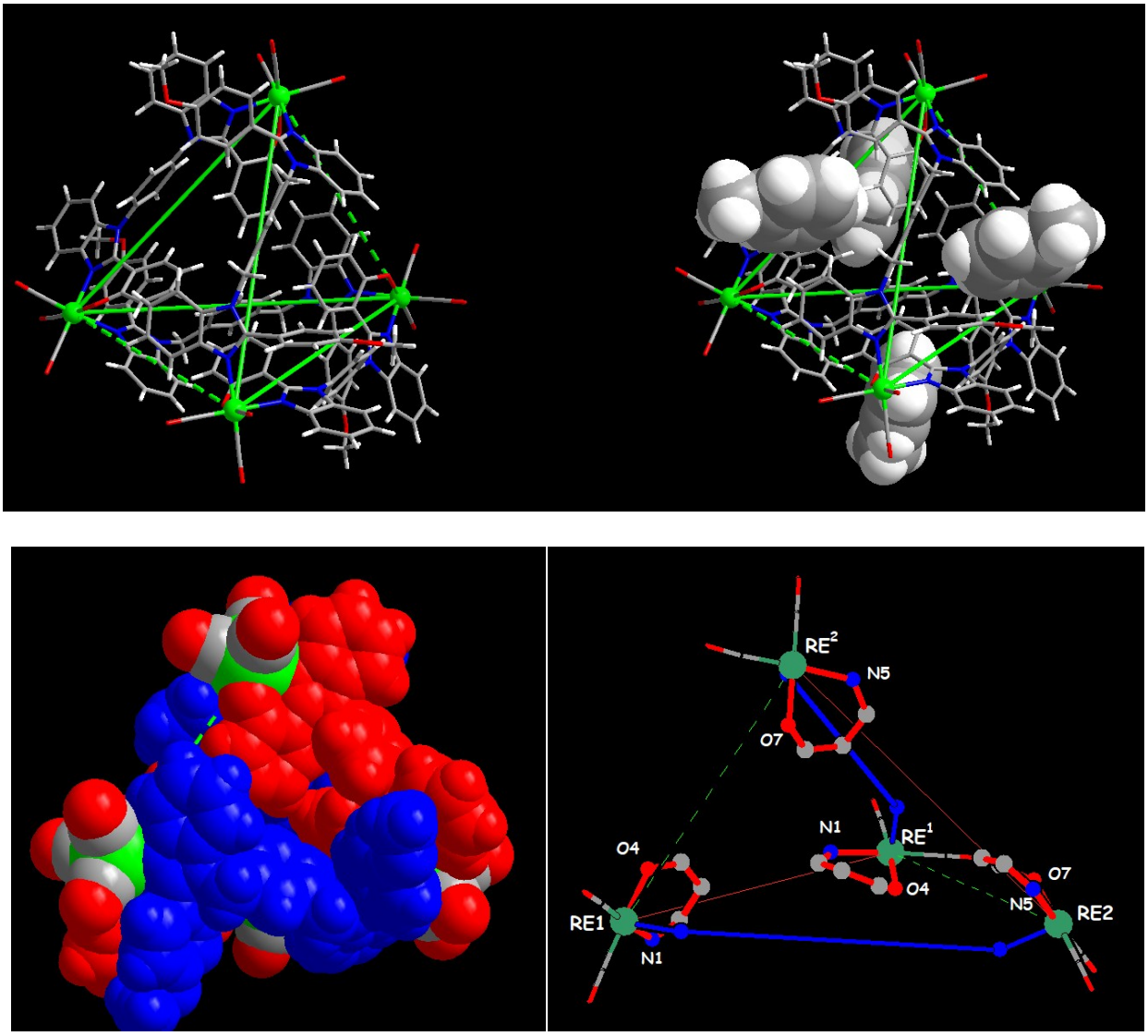


Fig. S24. Molecular structure of **2**. Tetrahedral skeleton of **2** with four ligands aligned along the four edges (Re1-Re^1 and Re2-Re^2 for two dianionic bis-chelating (RBC^{2-}) ligand motifs, Re1-Re2 and Re^2-Re^1 for two **L2** motifs, and Re1-Re^2 and Re2-Re^1 are the two missing edges) of the Re4 tetrahedron. Top: Ball and stick view of **2** without/with solvent molecules (left/right). Bottom: (left) Space-filling view of **2** (**L2** = blue; RBC^{2-} = red) and (right) **L2** is blue stick and chelating atoms of RBC are shown in red to show the orientation of chelating units around metal cores. Two 4-methoxyphenyl units are disordered in **2**. Only one of the occupancy of methoxyphenyl unit is shown for clarity. Color code: C = gray; N = blue; O =red; Re = green; CO = green in C).

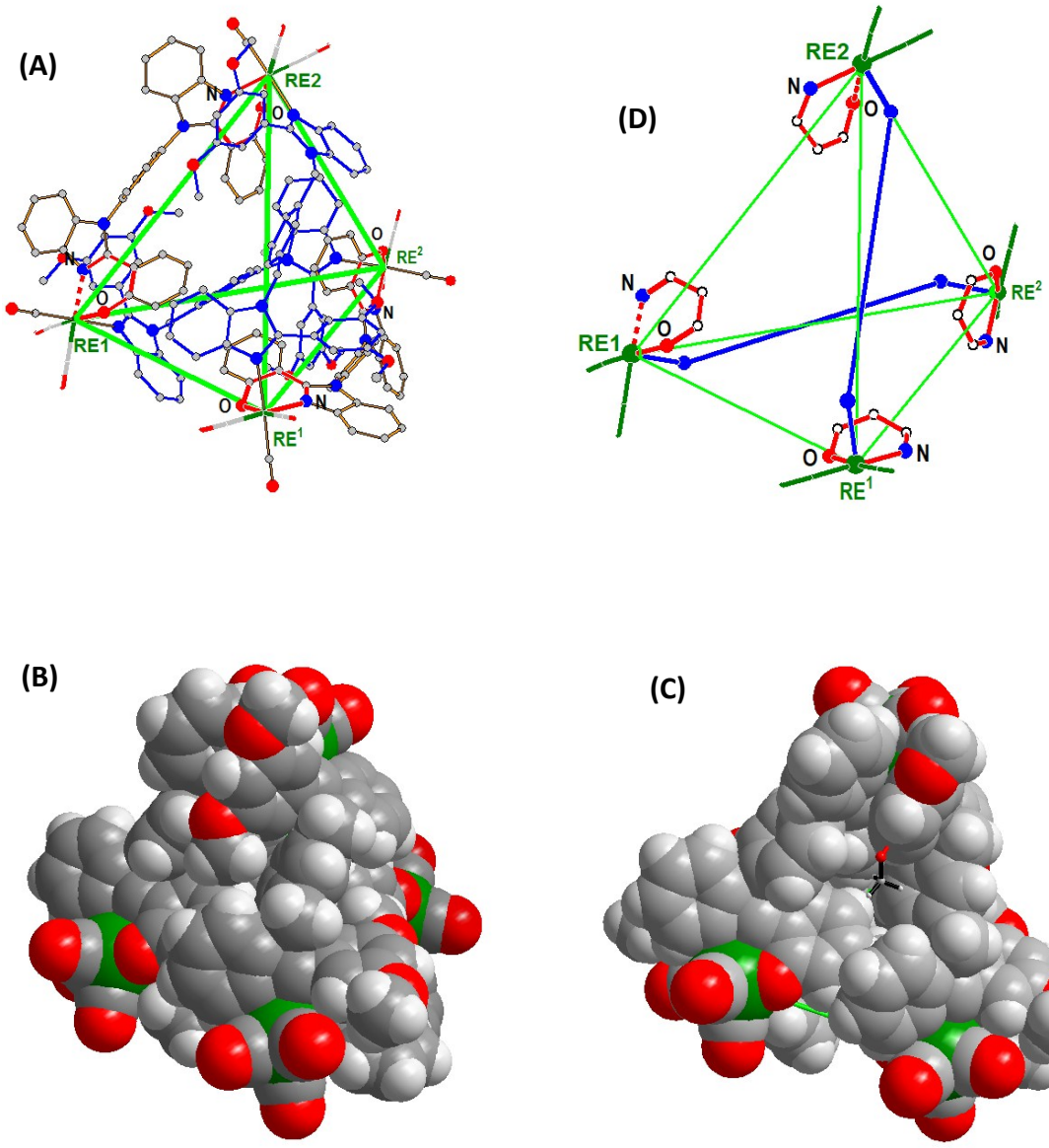


Fig. S25a. Molecular structure of **3**. Tetrahedral skeleton of **3** with four ligands aligned along the four edges (Re1-Re2 and Re^1-Re^2 for two dianionic bis-chelating (RBC^{2-}) ligand motifs, Re1-Re^2 and Re2-Re^1 for two **L3** motifs, and Re1-Re^1 and Re2-Re^2 are the two missing edges) of the Re4 tetrahedron. (A) Ball and stick view of **3** (hydrogen atoms are omitted for clarity; bonds of **L3** are shown in blue; bonds of chelating atoms of RBC are shown in red). (B) Space-filling view of **3**. (C) Space-filling view of **3** showing cavity of face in which OCH_3 resides (D) **3** with chelating atoms (red), **L3** (blue) to show the orientation of chelating units around metal cores. Two of the disordered methoxy units in **3** are not shown for clarity. Color code: C = gray; N = blue; O =red; Re = green; CO = green in C).

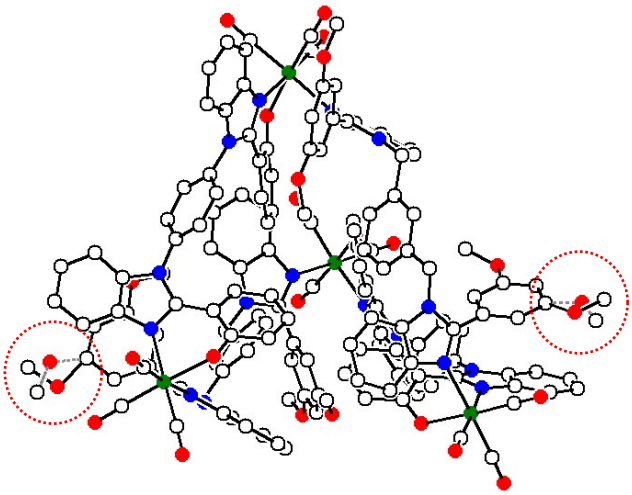


Fig. S25b. Molecular structure of **3** with disordered two methoxy units. Hydrogen atoms and solvents molecules are removed for clarity (picture drawn from data of **3.solvents**).

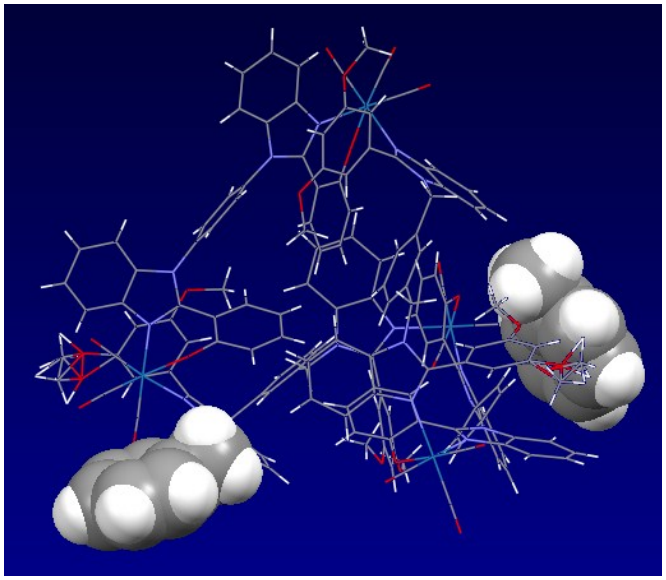


Fig. S25c. Molecular structure of **3** with disordered two methoxy units. Two toluene solvent molecules are shown as space filling view (picture drawn from data of **3.solvents**).

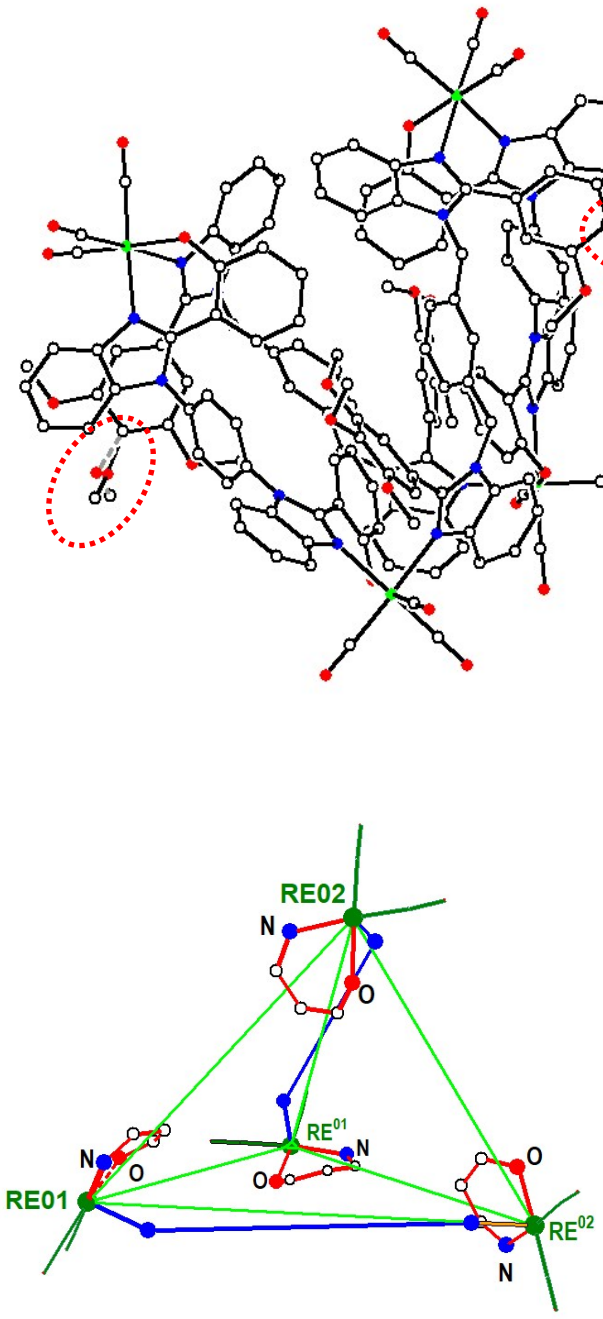


Fig. S26. Top: Molecular structure of **4** with disordered two methoxy units. Hydrogen atoms and solvents molecules are removed for clarity. Molecular structure of **4**. Bottom: Bonds of **L4** are shown in blue; bonds of chelating atoms of RBC are shown in red. Color code: C = gray; N = blue; O =red; $Re(CO)_3$ = green).

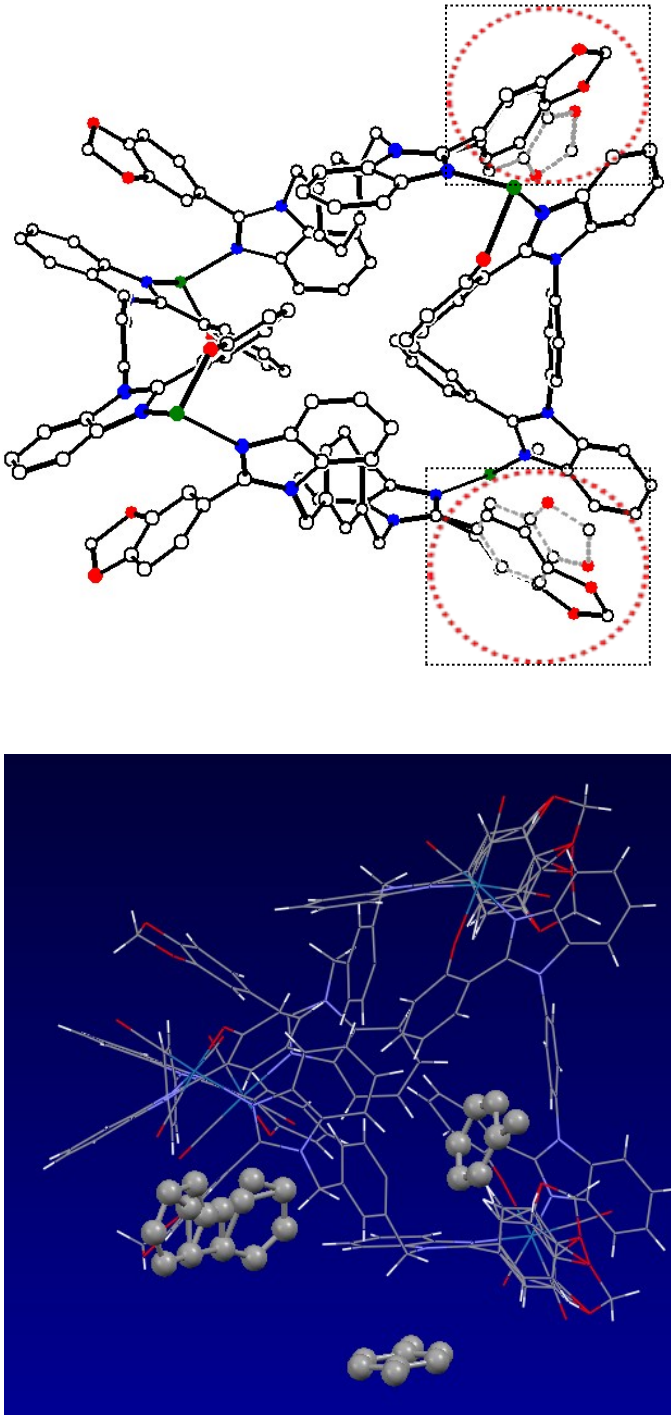


Fig. S27a. Top: Asymmetric unit of **5** showing two disordered 1,3-benzodioxole rings (hydrogen atoms, CO umits and solvent molecules are removed for clarity). Molecular structure of **5** with solvent molecules.

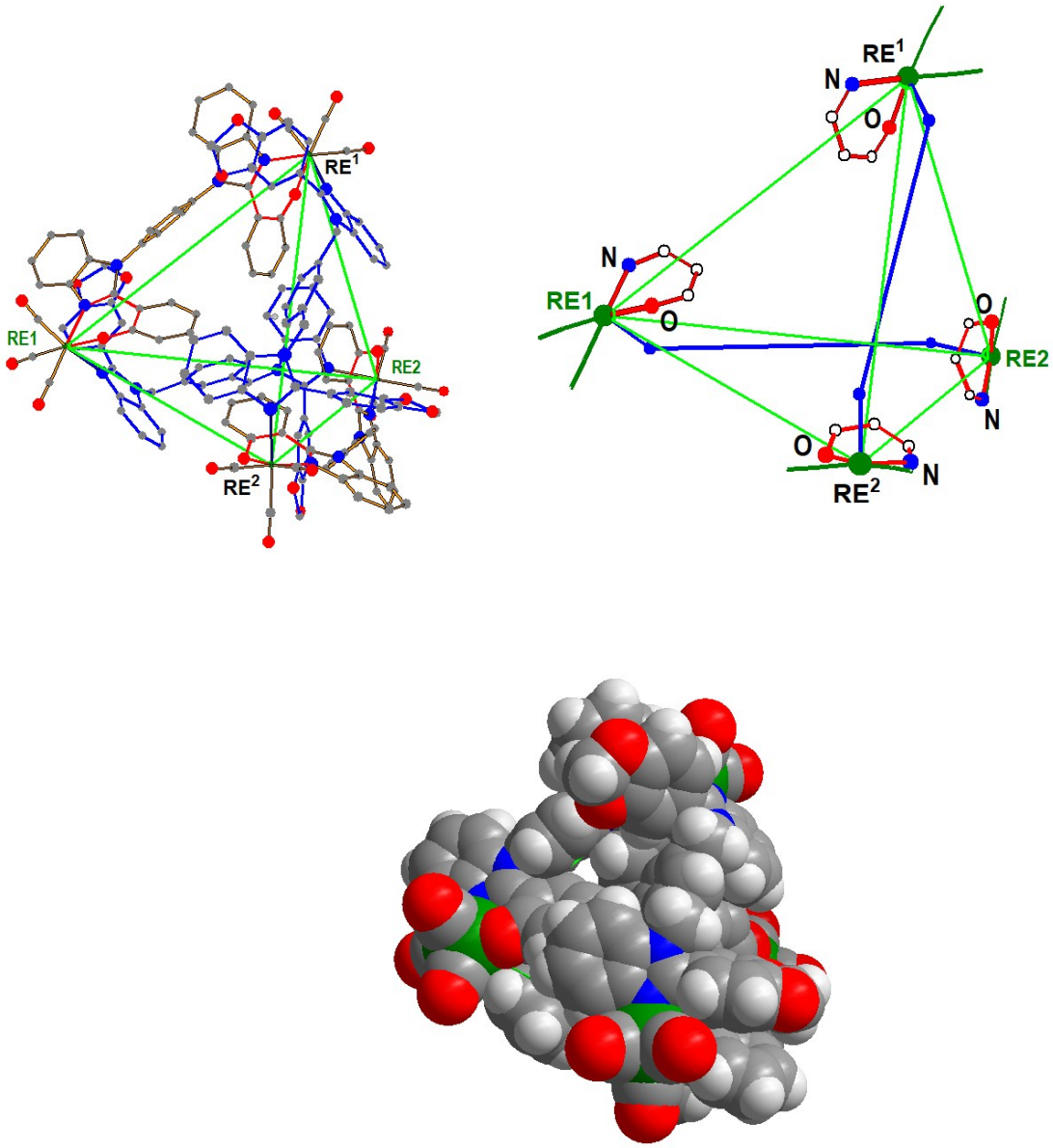


Fig. S27. Molecular structure of **5**. Tetrahedral skeleton of **5** with four ligands aligned along the four edges (Re1-Re^{1} and Re2-Re^{2} for two dianionic bis-chelating (RBC^{2-}) ligand motifs, Re1-Re2 and Re^{2}-Re^{1} for two **L5** motifs, and Re1-Re^{2} and Re2-Re^{1} are the two missing edges) of the Re4 tetrahedron. (A) Ball and stick view of **5** (hydrogen atoms are omitted for clarity; bonds of **L5** are shown in blue; bonds of chelating atoms of RBC are shown in red). (B) Space-filling view of **5**.(C) **5** with chelating atoms (red), **L5** (blue) to show the orientation of chelating units around metal cores. Only one of the occupancy of 1,3-benzodioxole unit is shown for clarity. Color code: C = gray; N = blue; O =red; Re = green; CO = green in C).

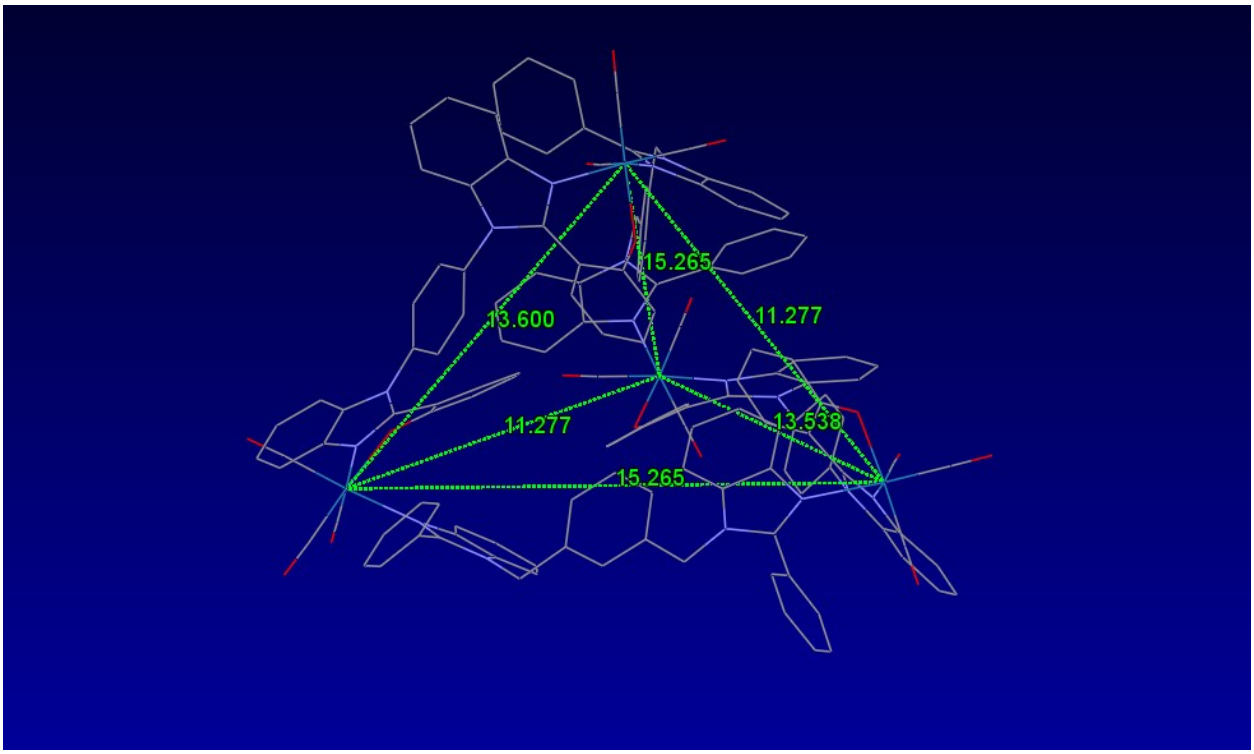


Fig. S28. Molecular structure of **1** showing size of tetrahedron edges.

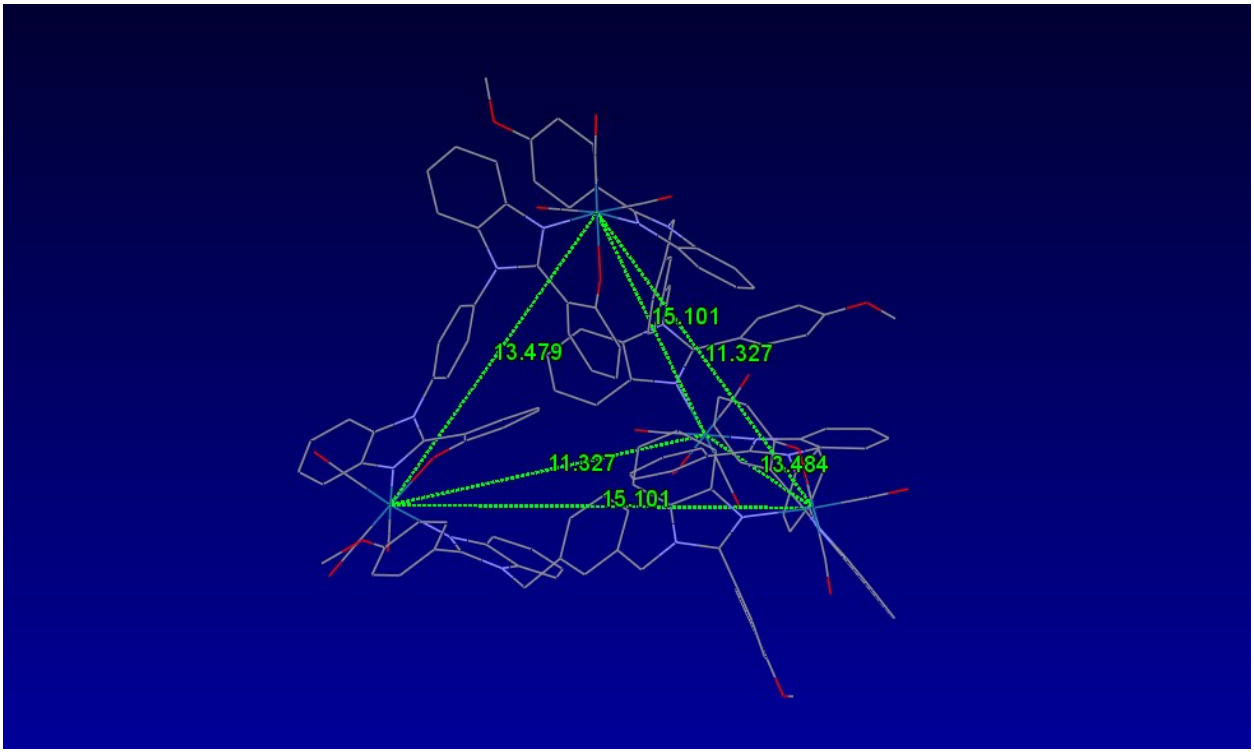


Fig. S29. Molecular structure of **2** showing size of tetrahedron edges.

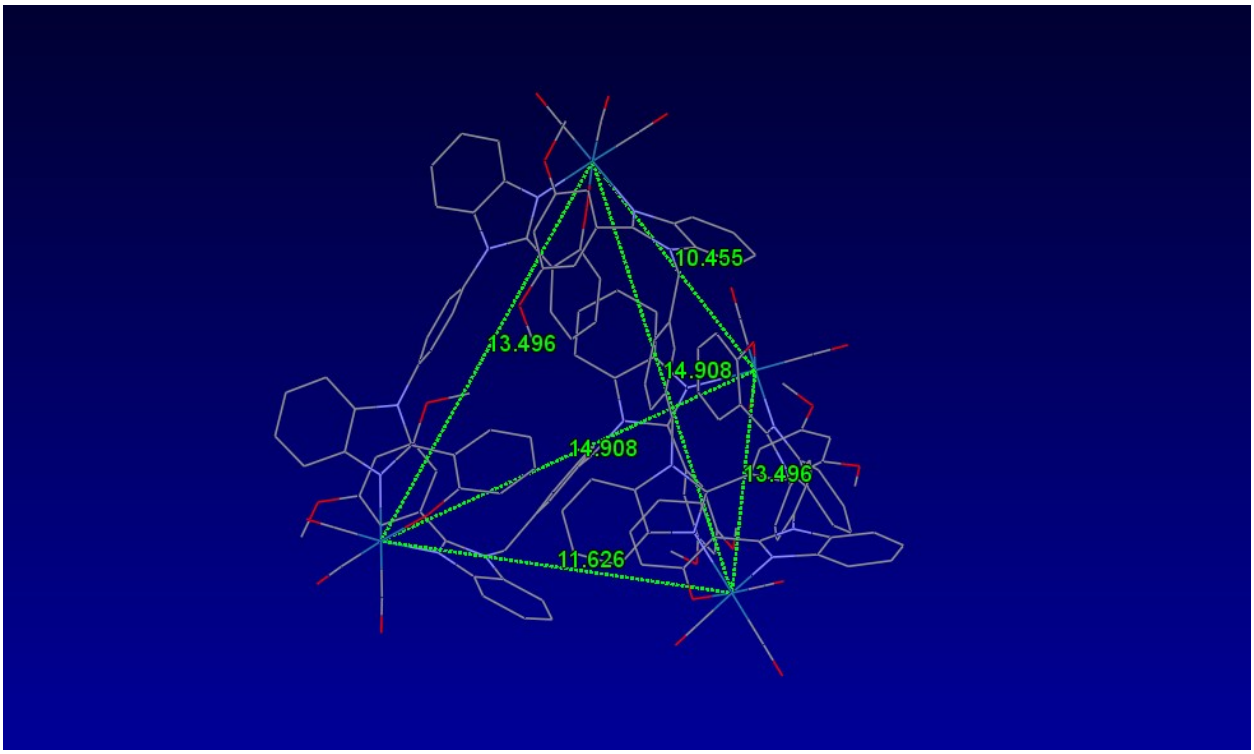


Fig. S30. Molecular structure of **3** showing size of tetrahedron edges.

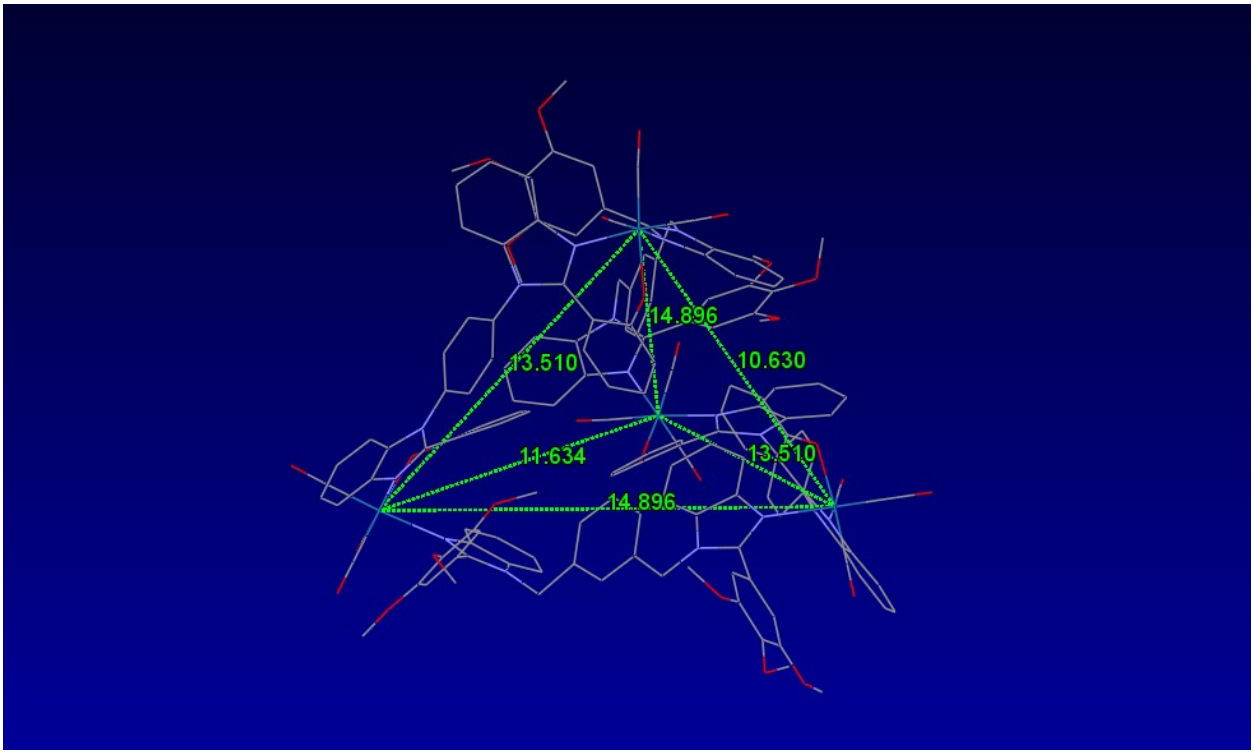


Fig. S31. Molecular structure of **4** showing size of tetrahedron edges.

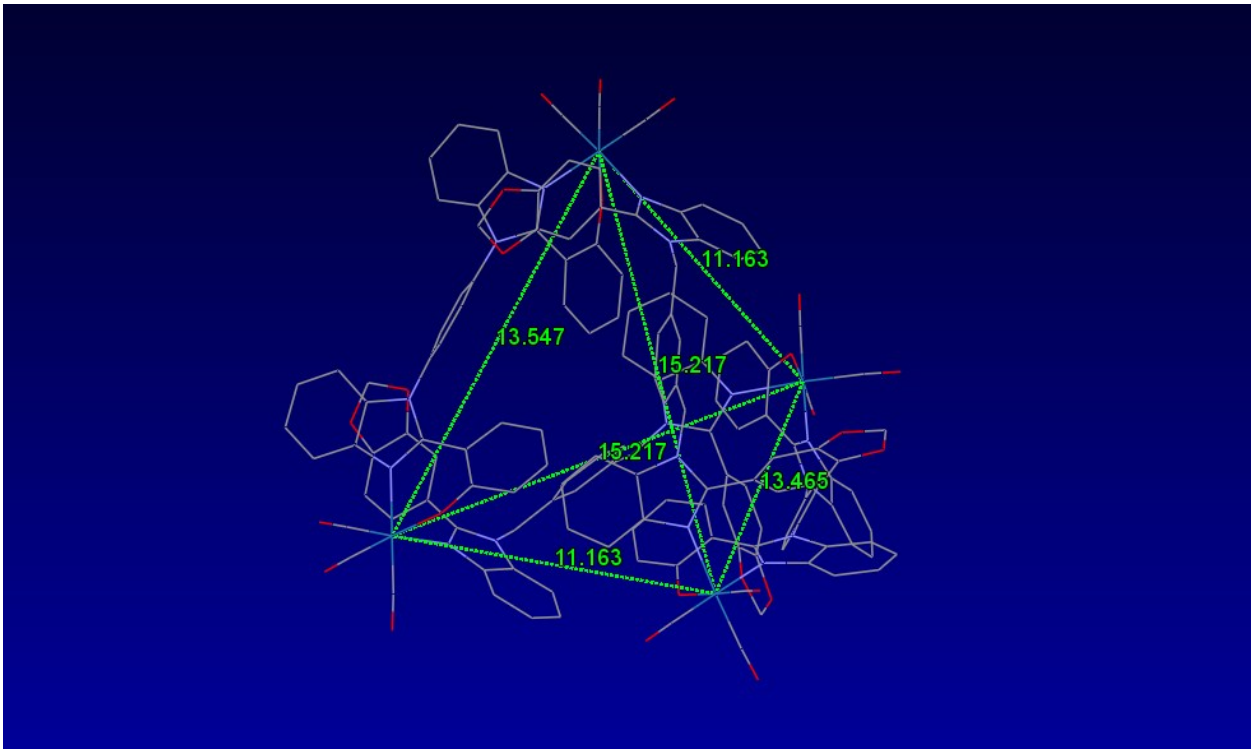


Fig. S32. Molecular structure of **5** showing size of tetrahedron edges.