Supplementary Information

Reversible Encapsulation of a Nitrate Guest via Hydrogen bonded Self-Assembled Capsule Formation by Flexible Tripodal Receptor in Polar Solvent through Dynamic Self-Assembly

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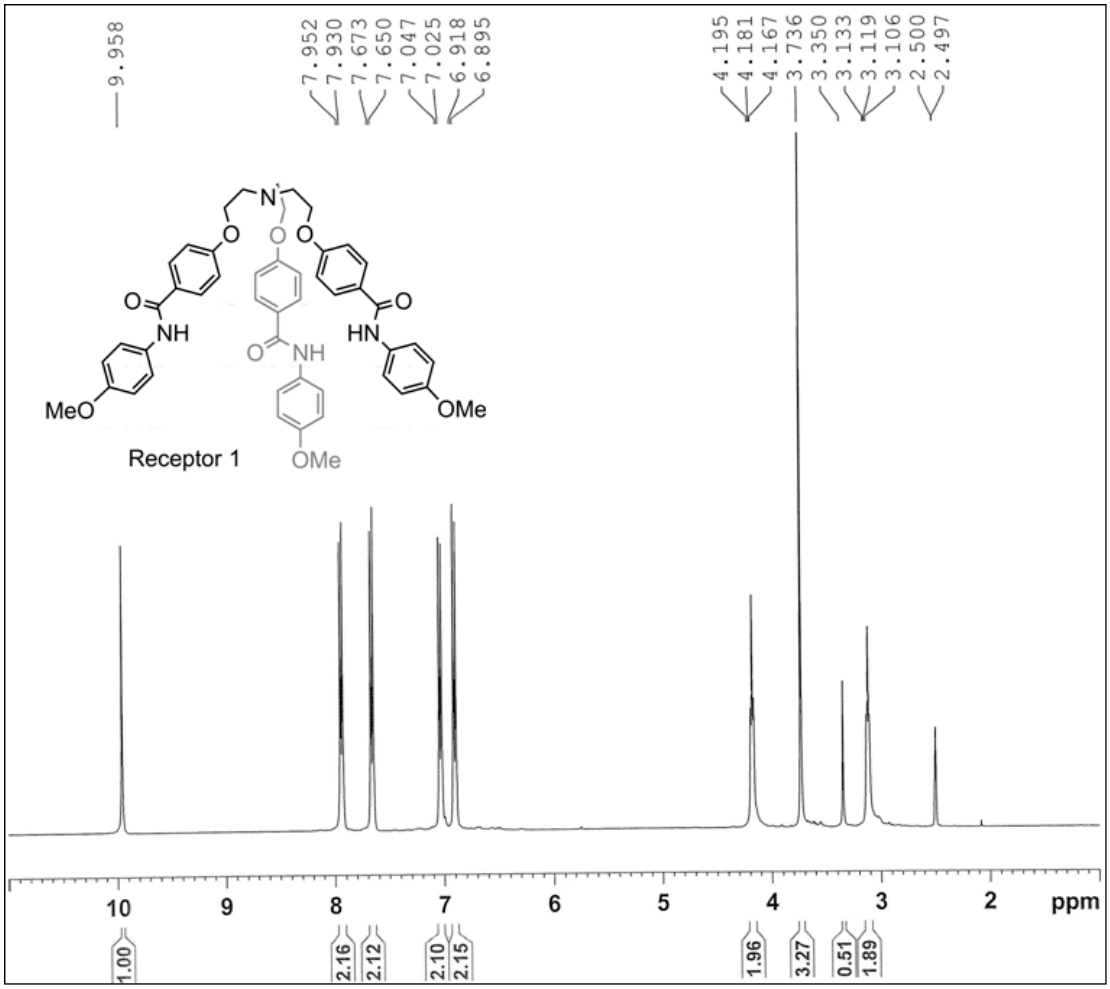

Fig. S1 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **1**.

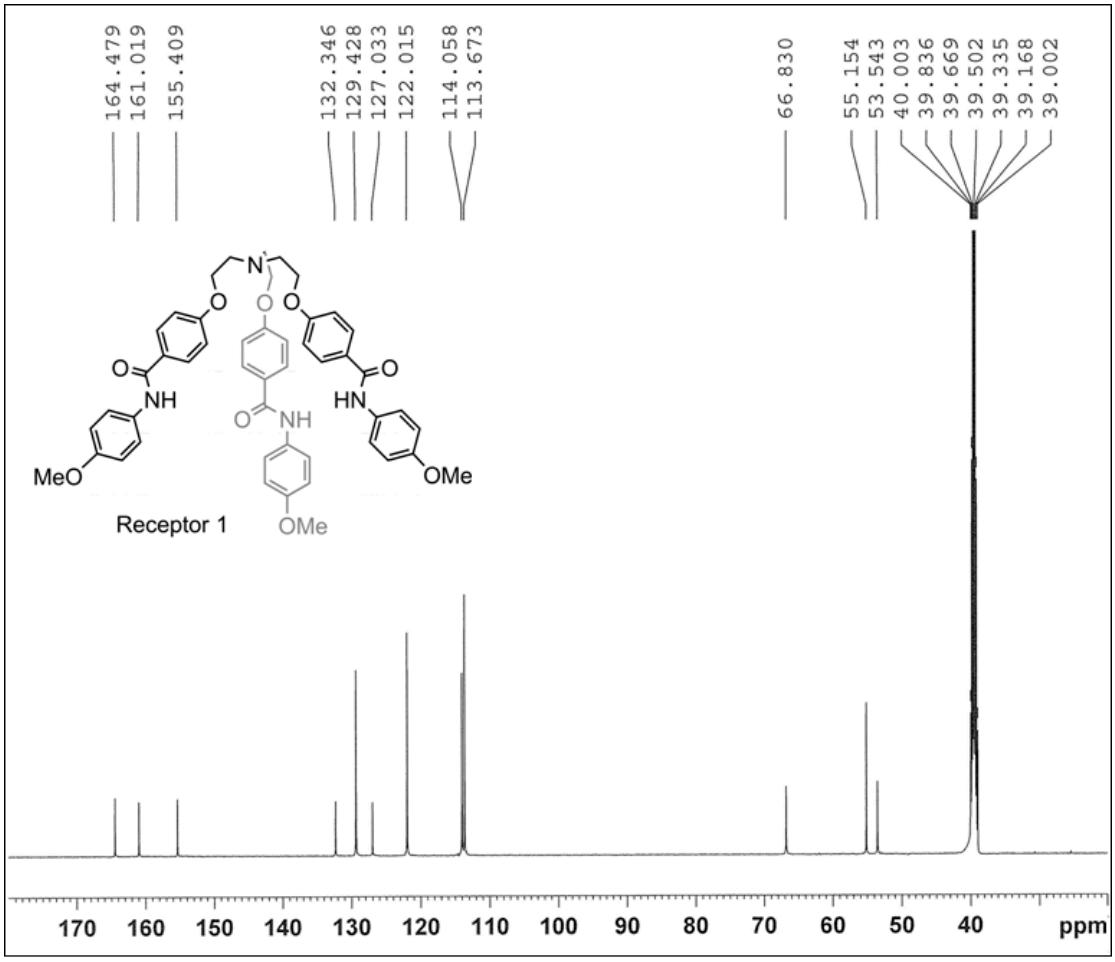

Fig. S2 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **1**.

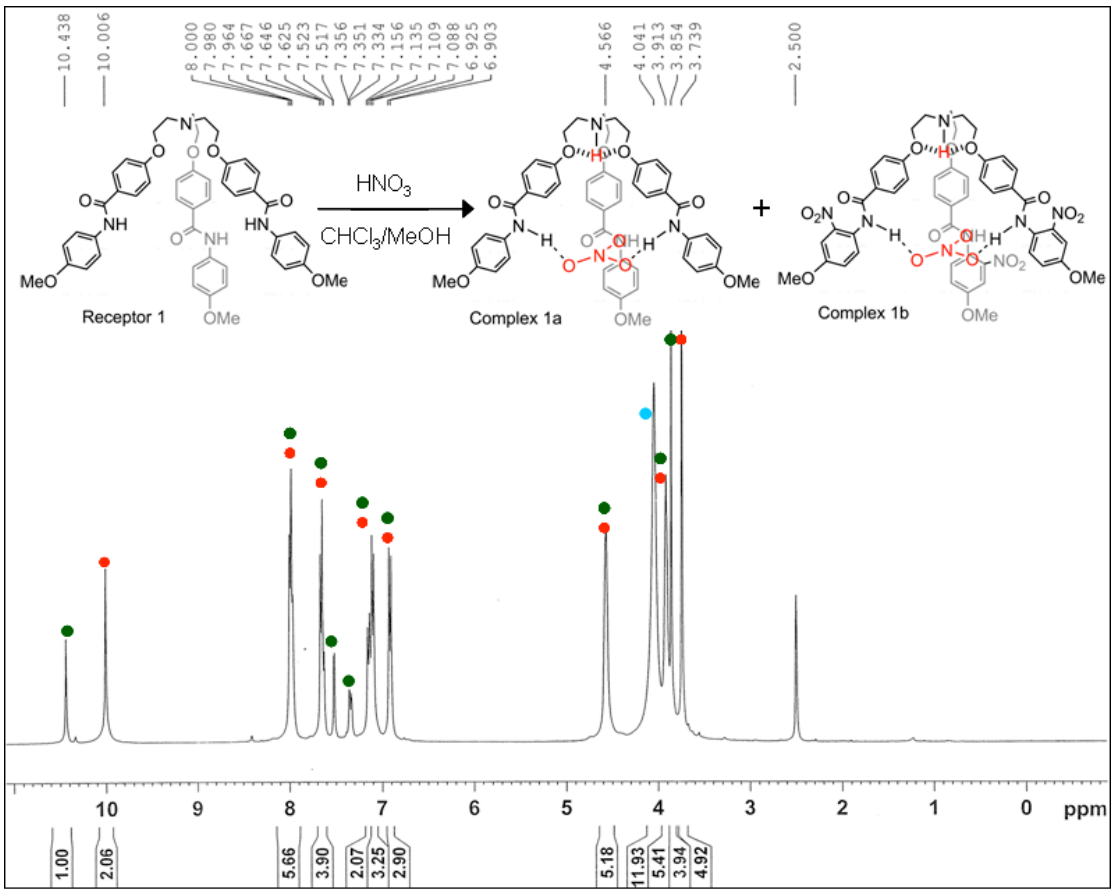

Fig. S3 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of a mixture of complexes **1a** (peaks represented by red circles) and **1b** (peaks represented by green circles) obtained by treating receptor **1** with nitric acid in $CHCl_3$/MeOH (v/v = 1/1). The circle in blue color represents water peak from DMSO-d_6.

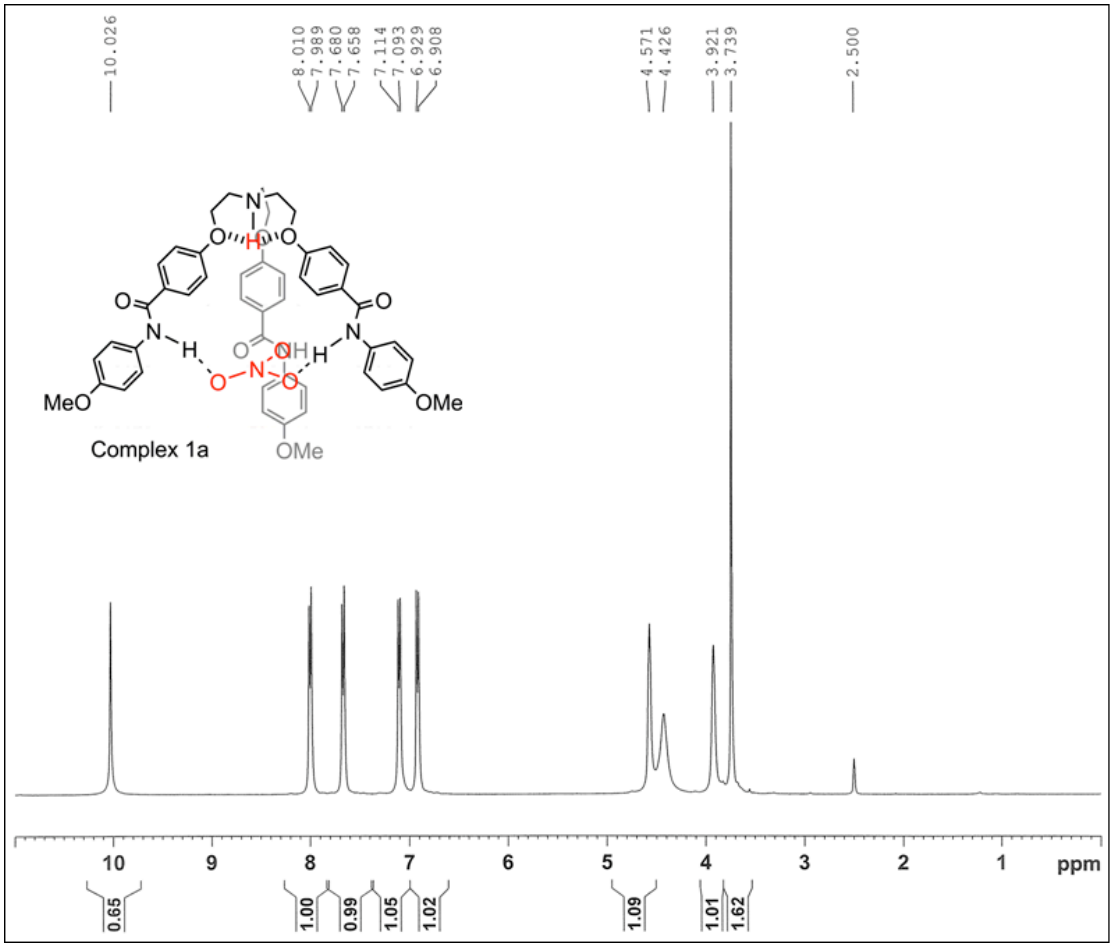

Fig. S4 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **1a**.

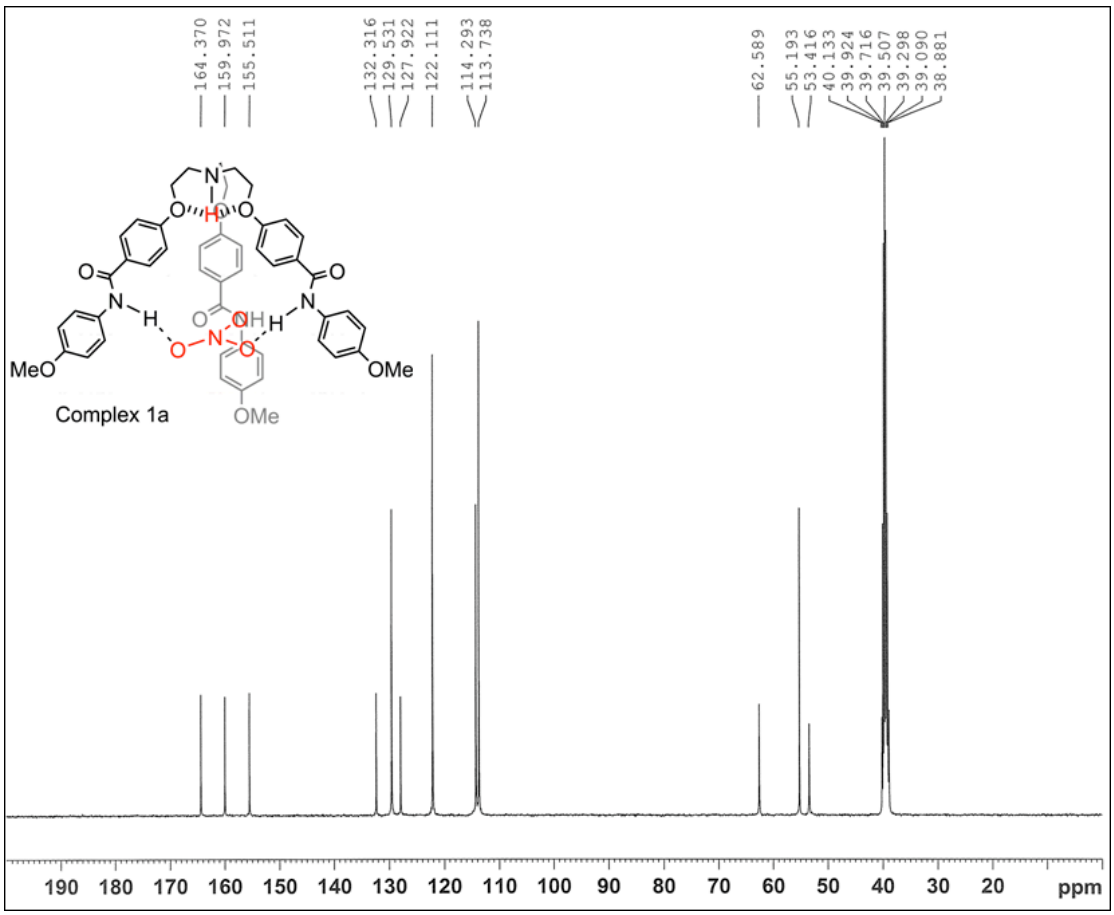

Fig. S5 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **1a**.

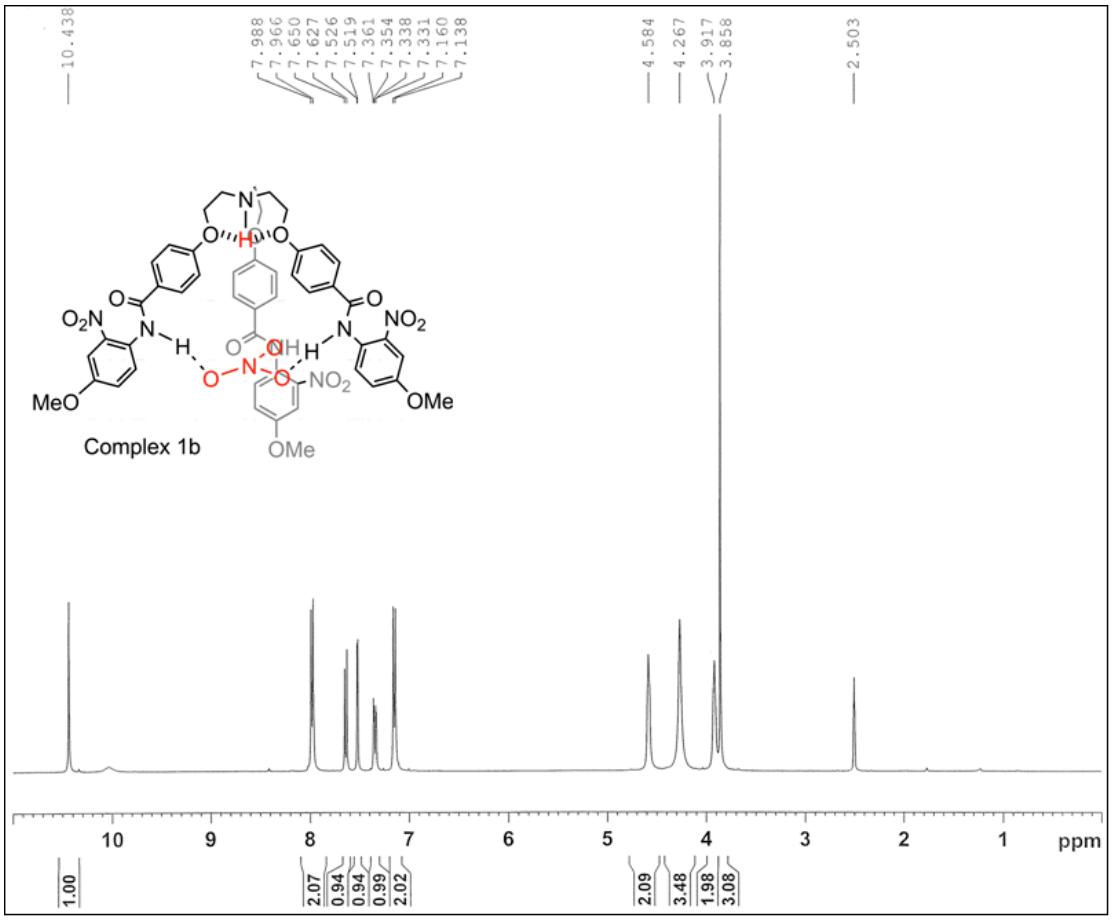

Fig. S6 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **1b**.

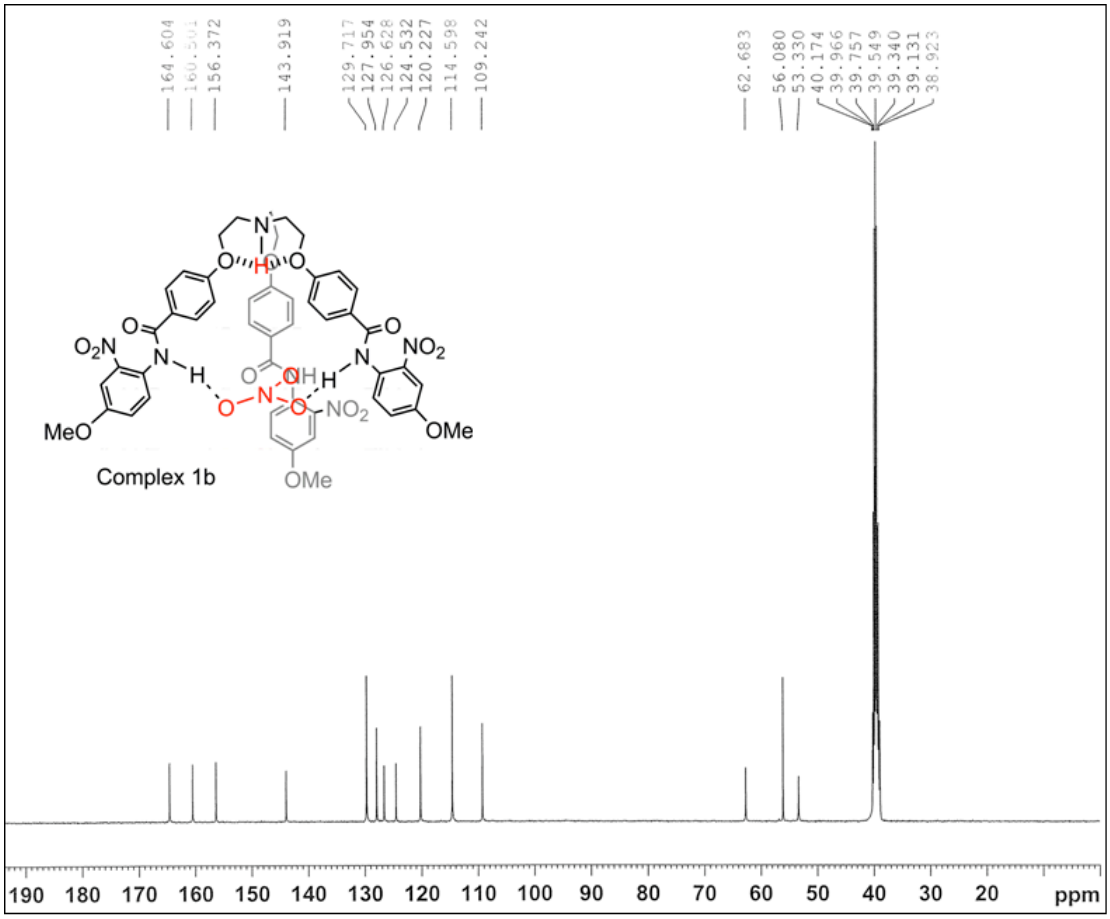

Fig. S7 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **1b**.

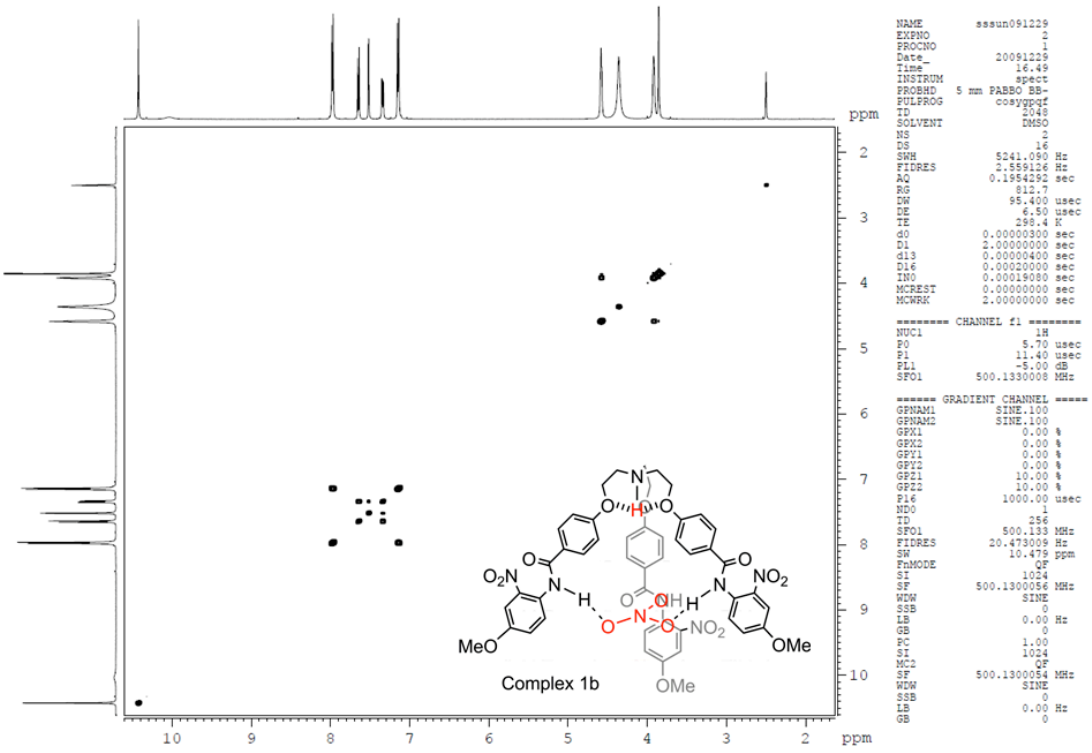

Fig. S8 The COSY spectrum of nitrate complex **1b** in DMSO-d_6.

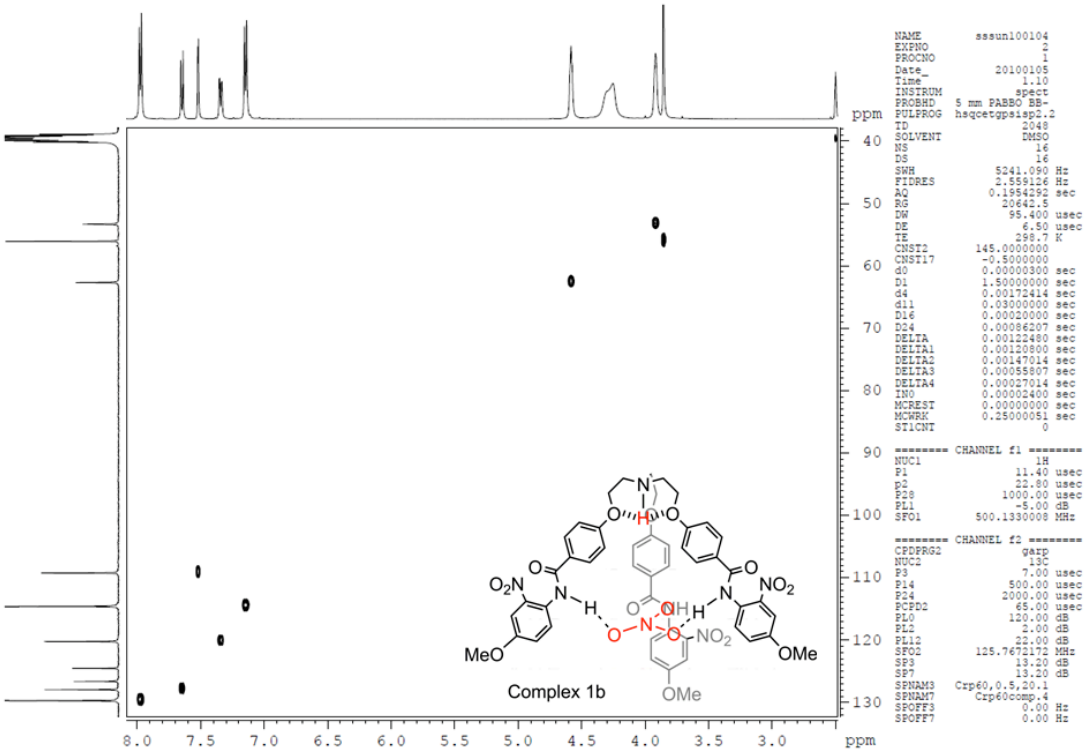

Fig. S9 The HSQC spectrum of nitrate complex **1b** in DMSO-d_6.

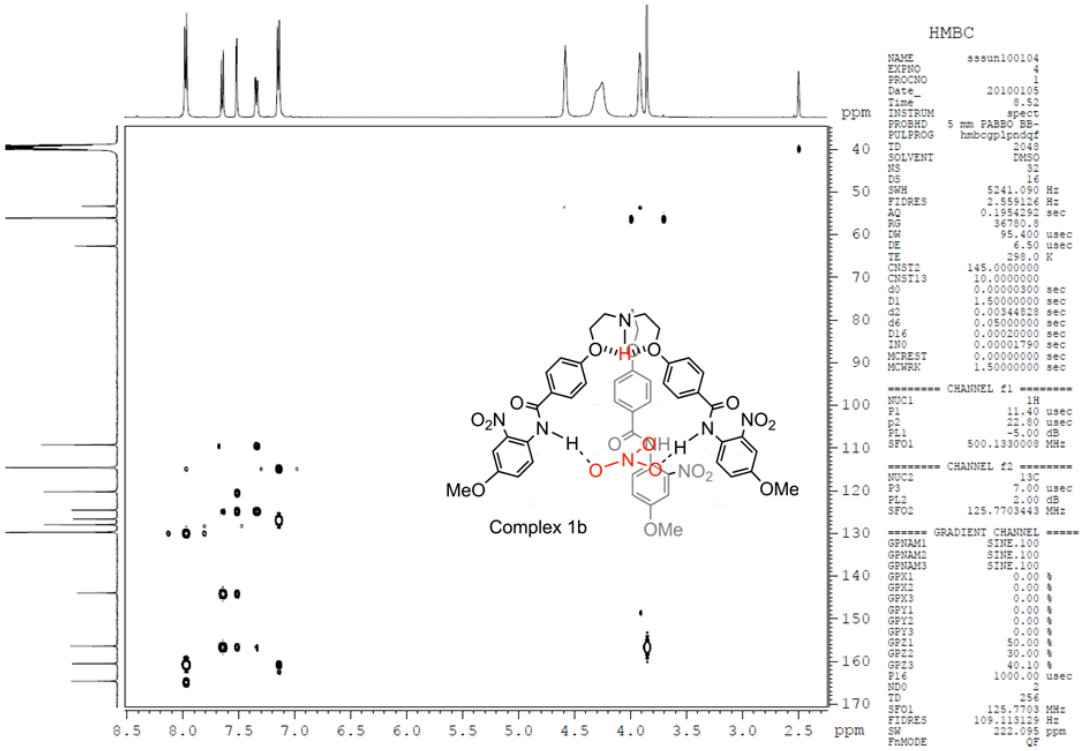

Fig. S10 The HMBC spectrum of nitrate complex **1b** in DMSO-d_6.

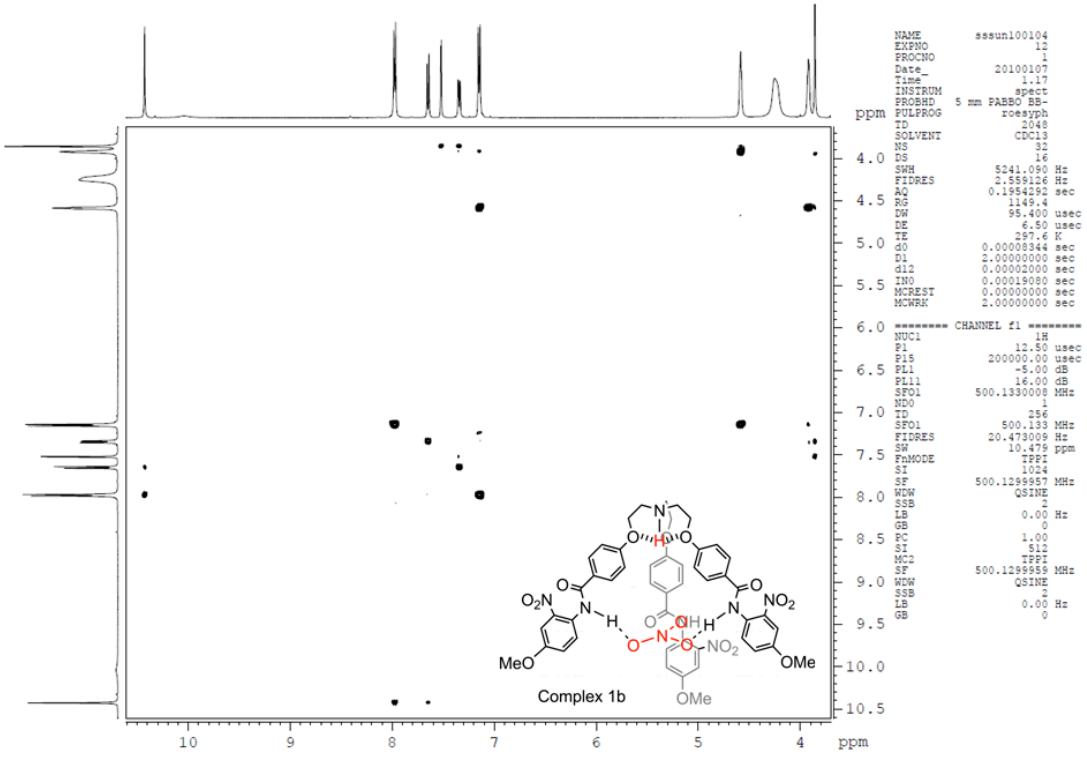

Fig. S11 The ROESY spectrum of nitrate complex **1b** in DMSO-d_6.

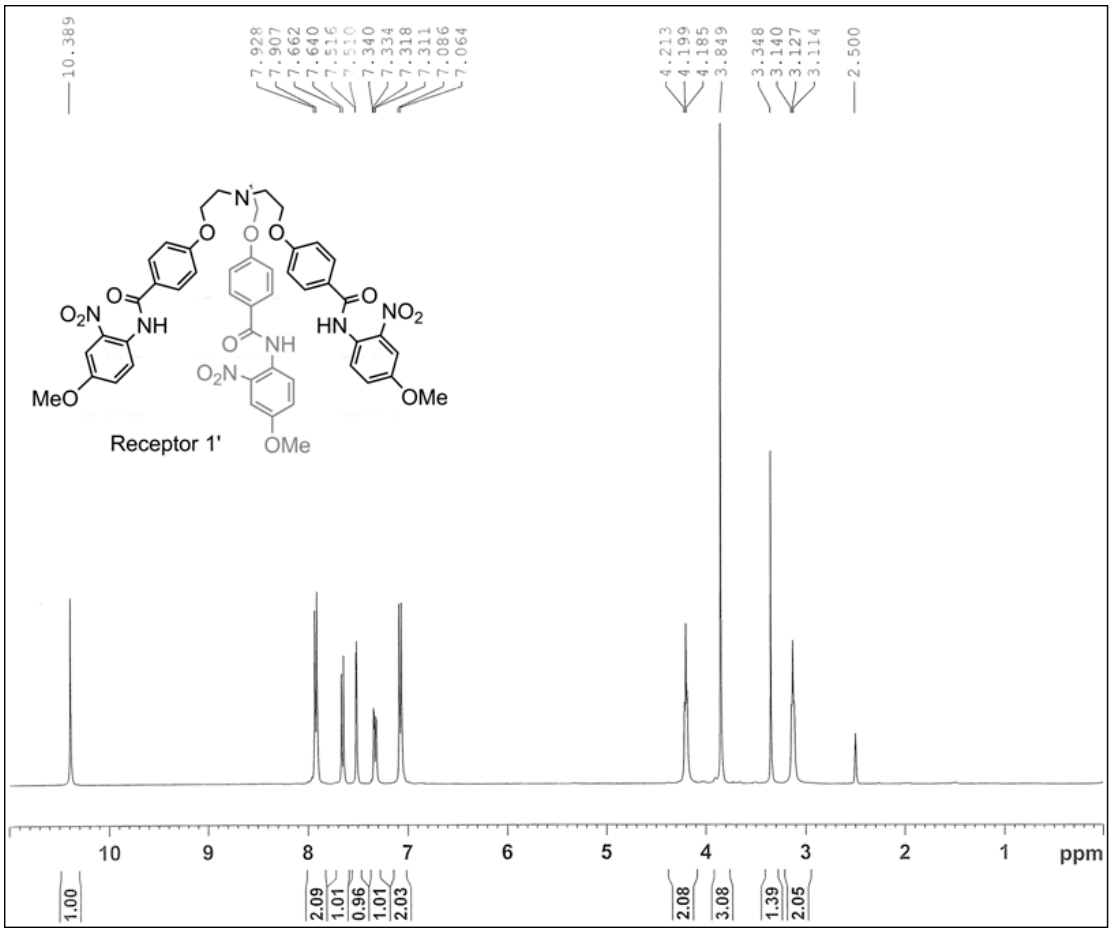

Fig. S12 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **1'**.

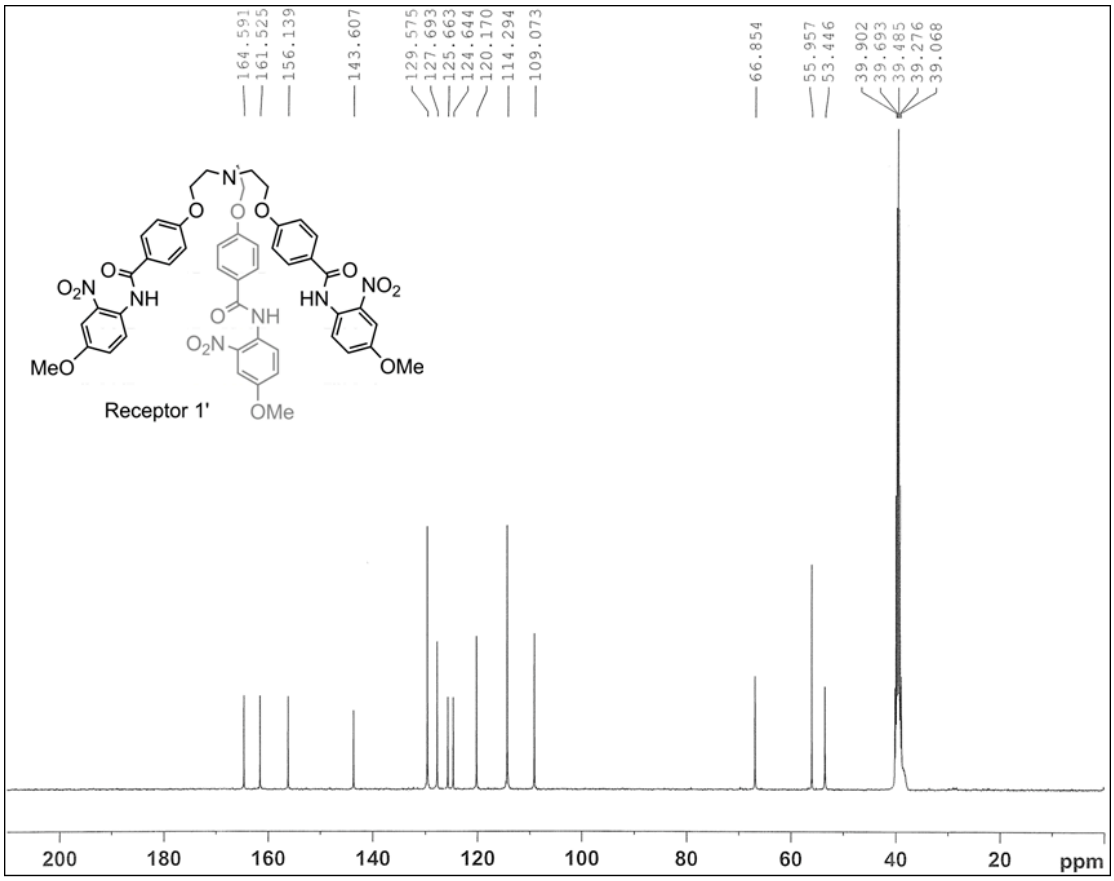

Fig. S13 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **1'**.

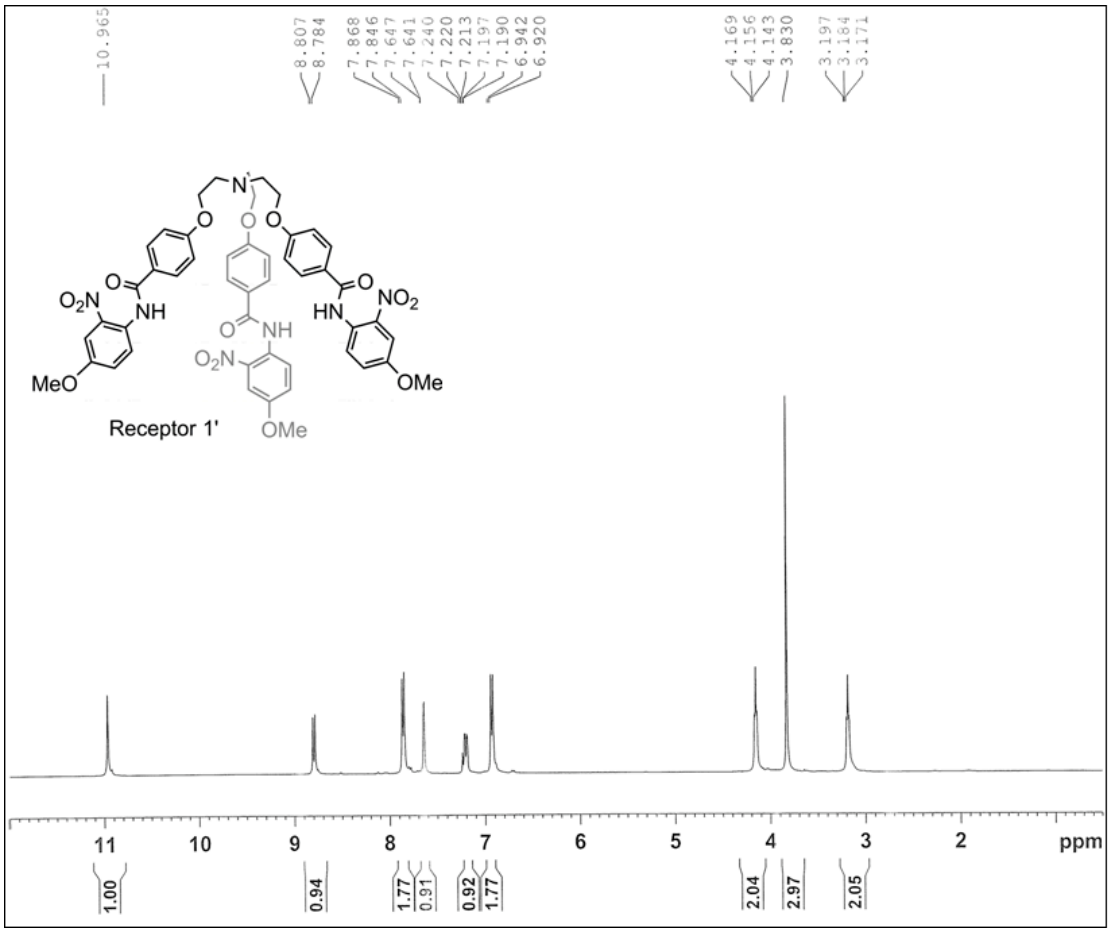

Fig. S14 ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) spectrum of receptor **1'**.

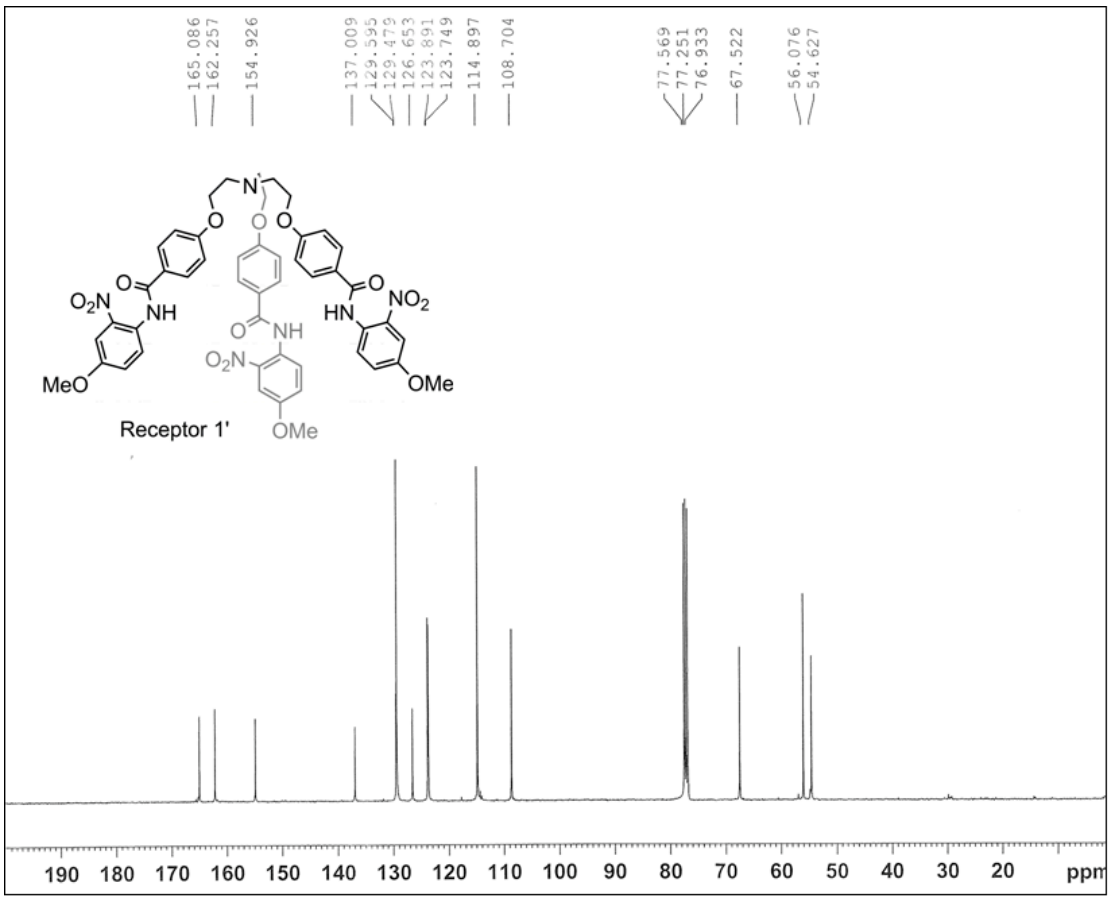

Fig. S15 ^{13}C NMR (100 MHz, $CDCl_3$, 20 ºC) spectrum of receptor **1'**.

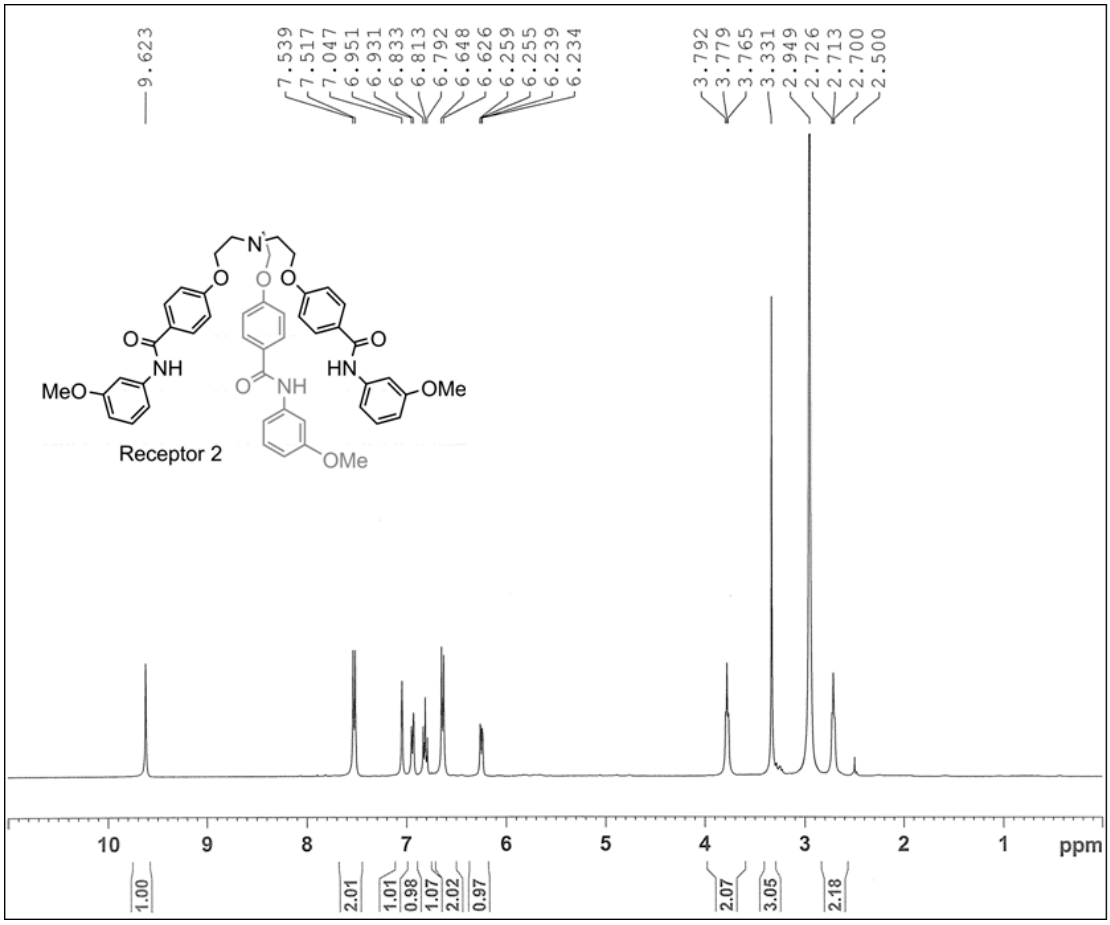

Fig. S16 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **2**.

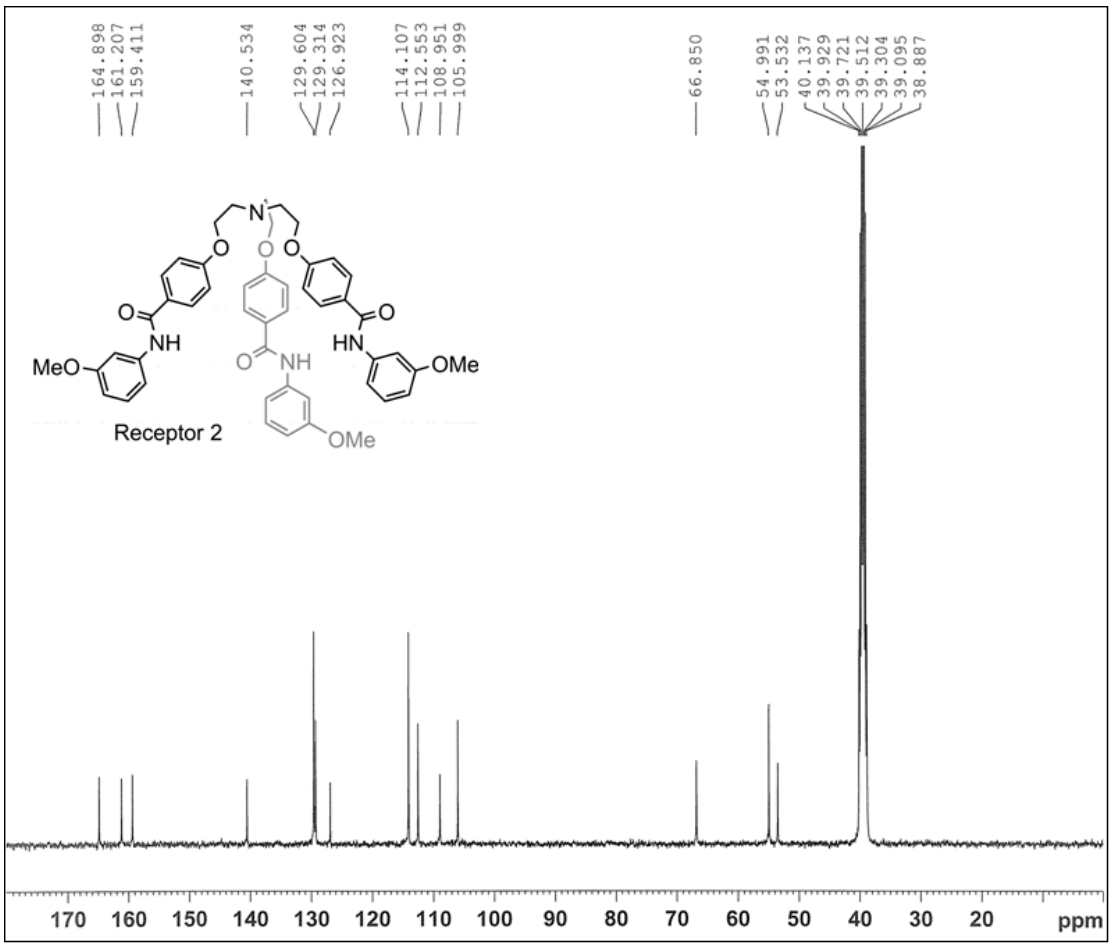

Fig. S17 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **2**.

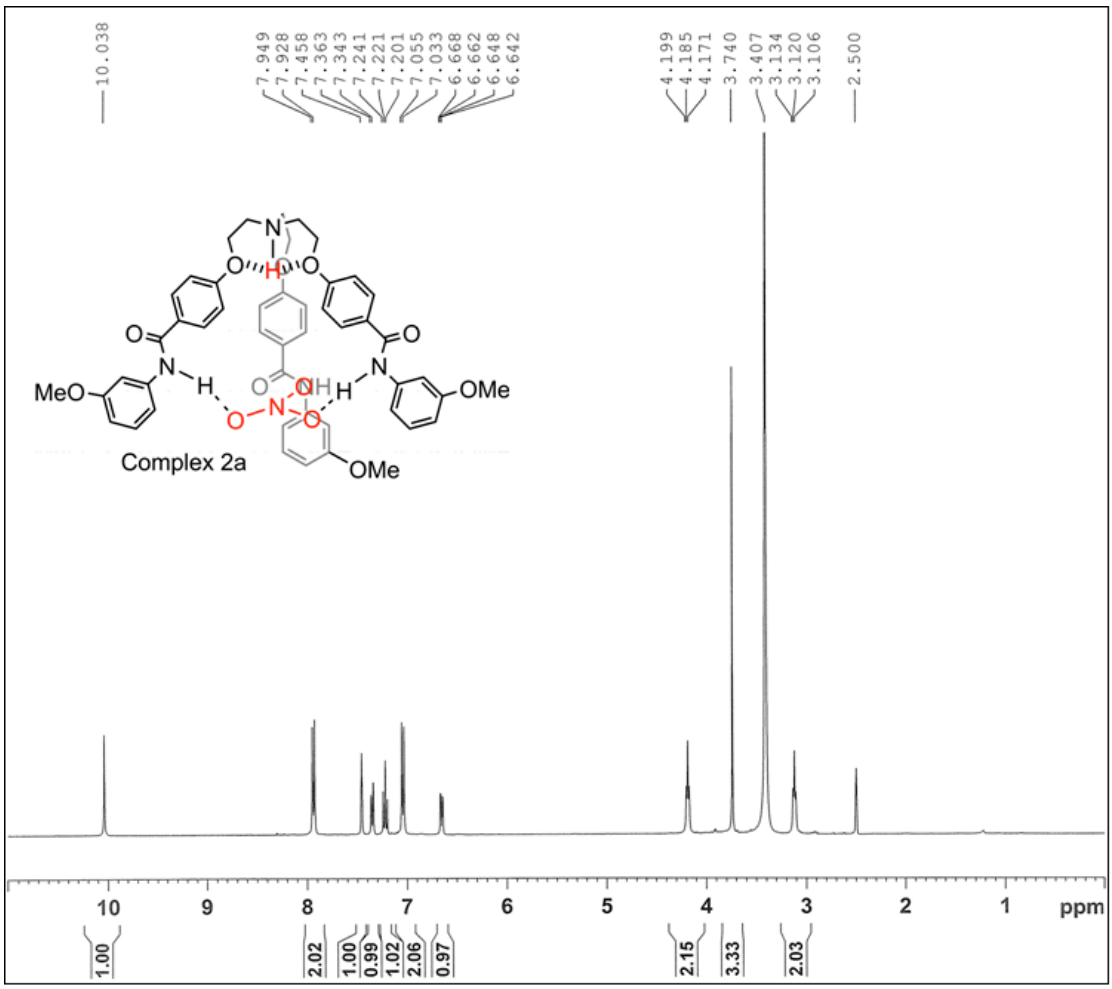

Fig. S18 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **2a**.

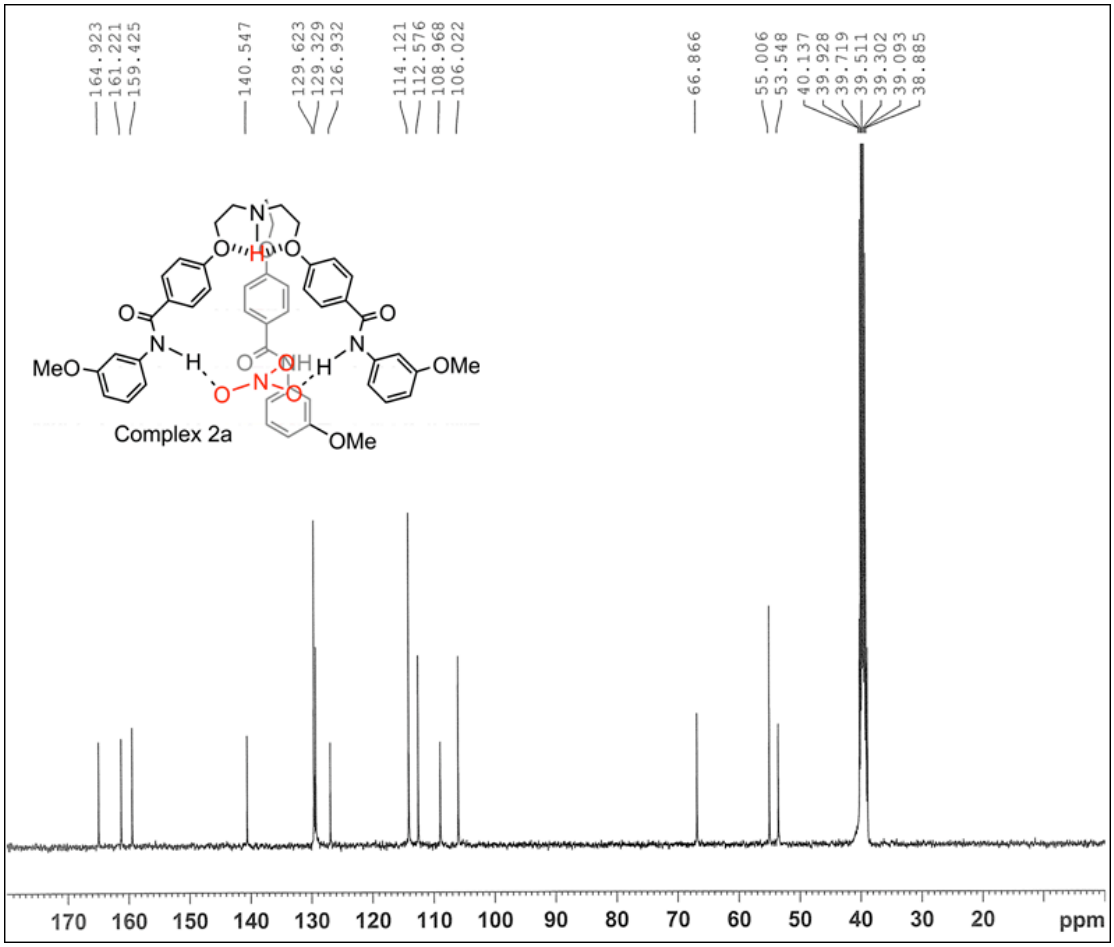

Fig. S19 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **2a**.

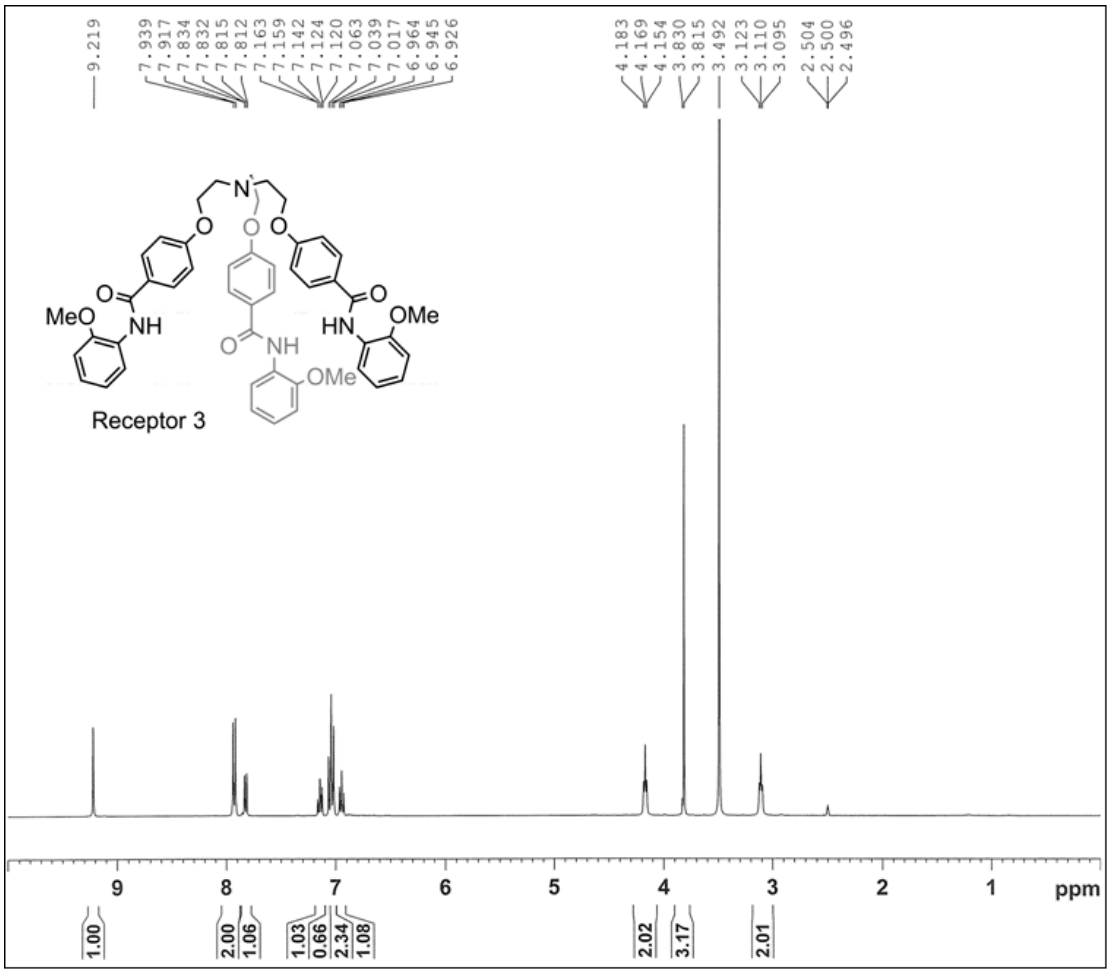

Fig. S20 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **3**.

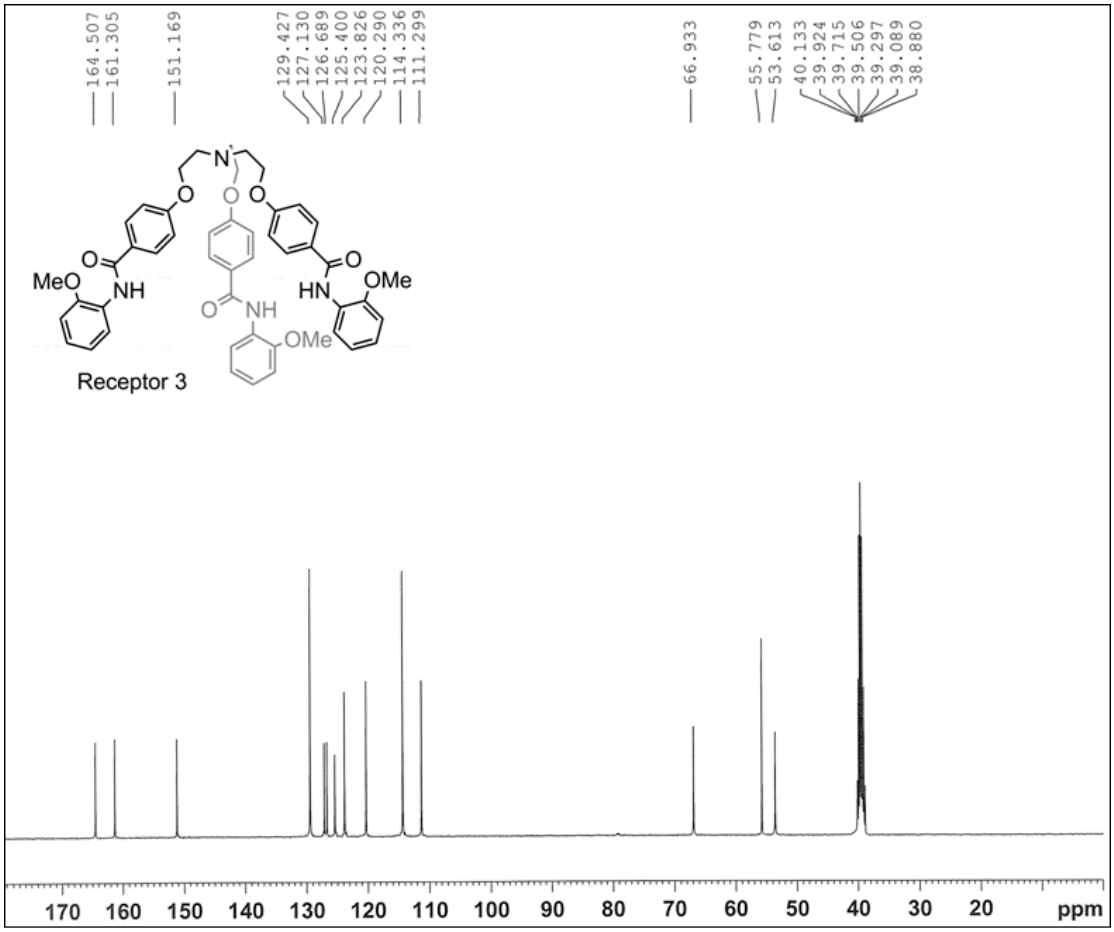

Fig. S21 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **3**.

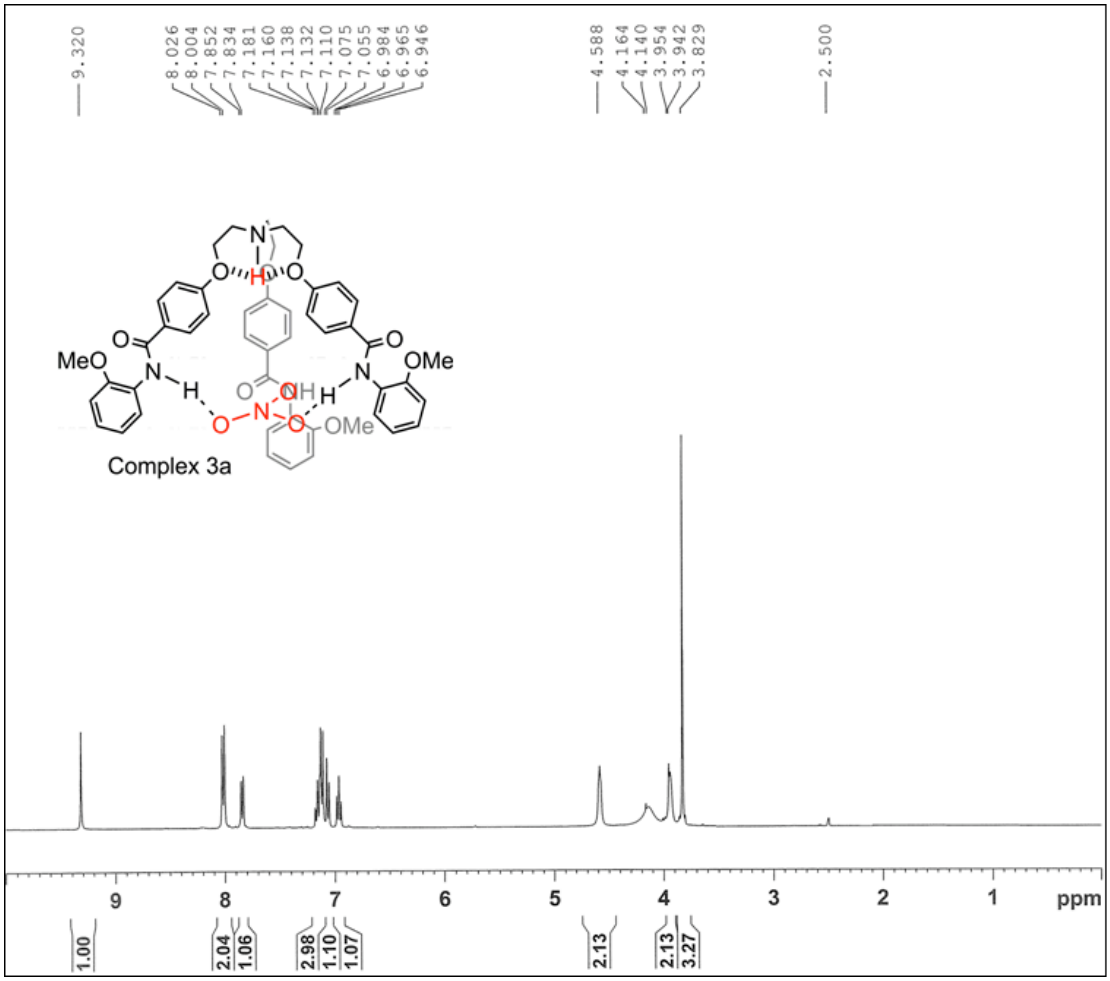

Fig. S22 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **3a**.

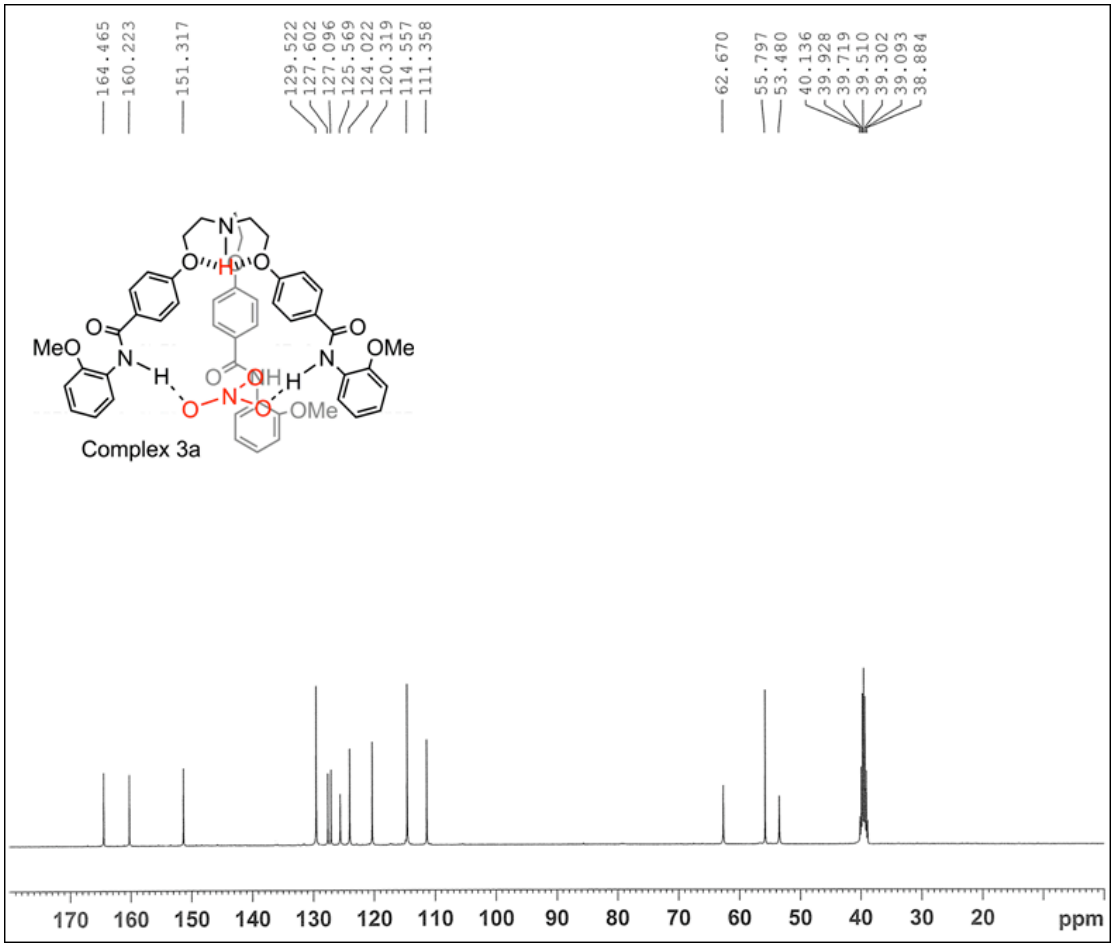

Fig. S23 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **3a**.

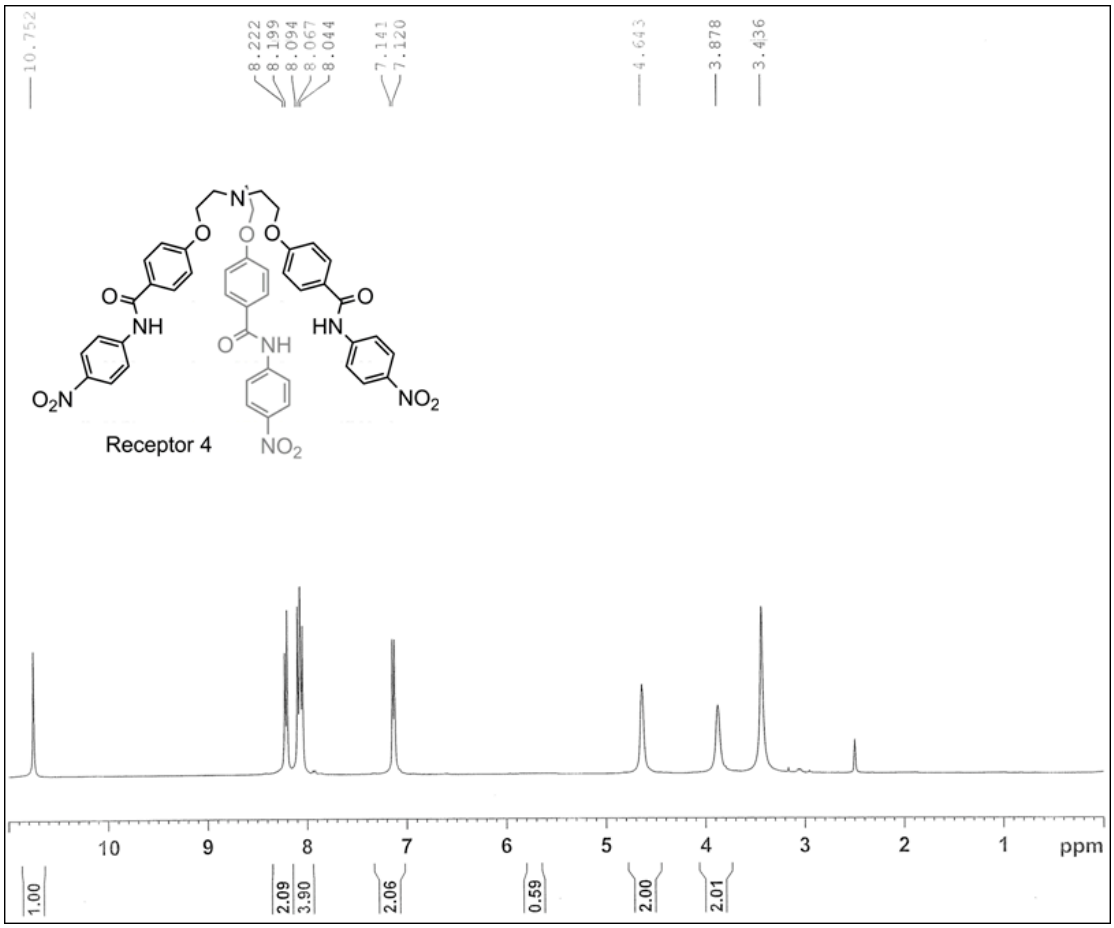

Fig. S24 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **4**.

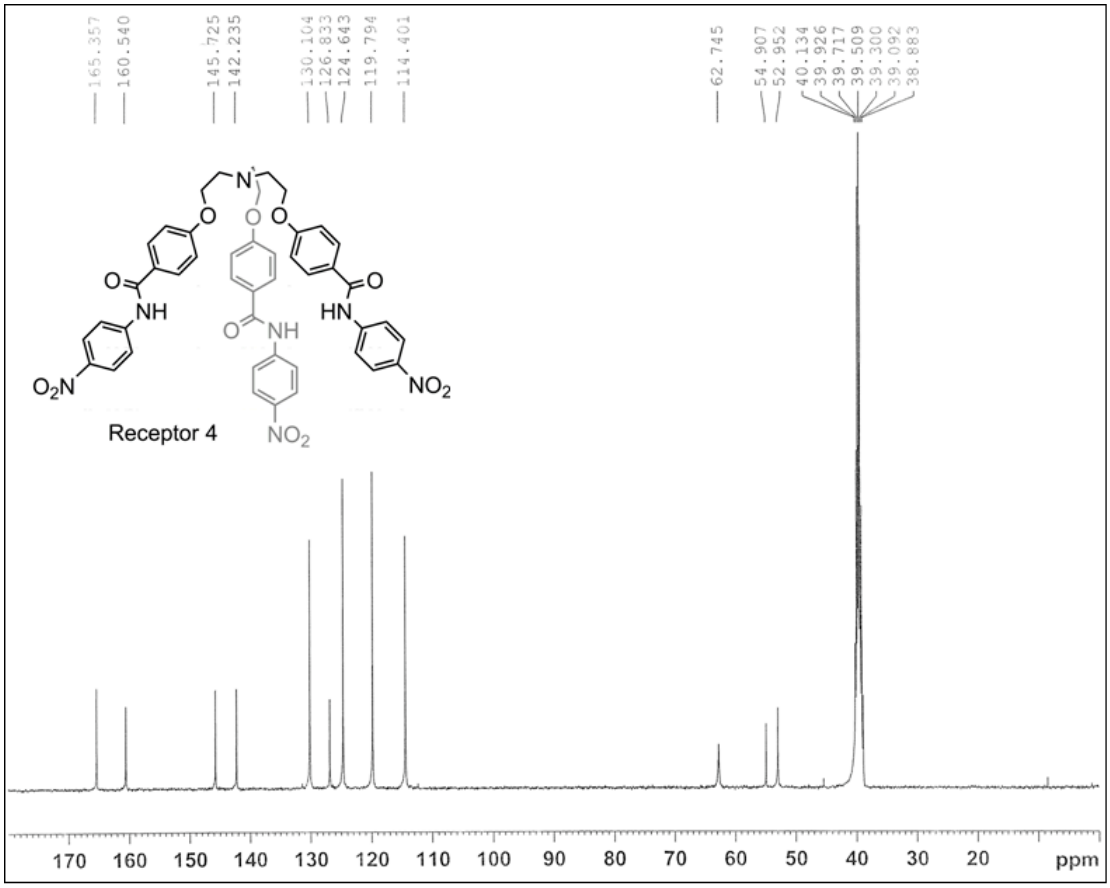

Fig. S25 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **4**.

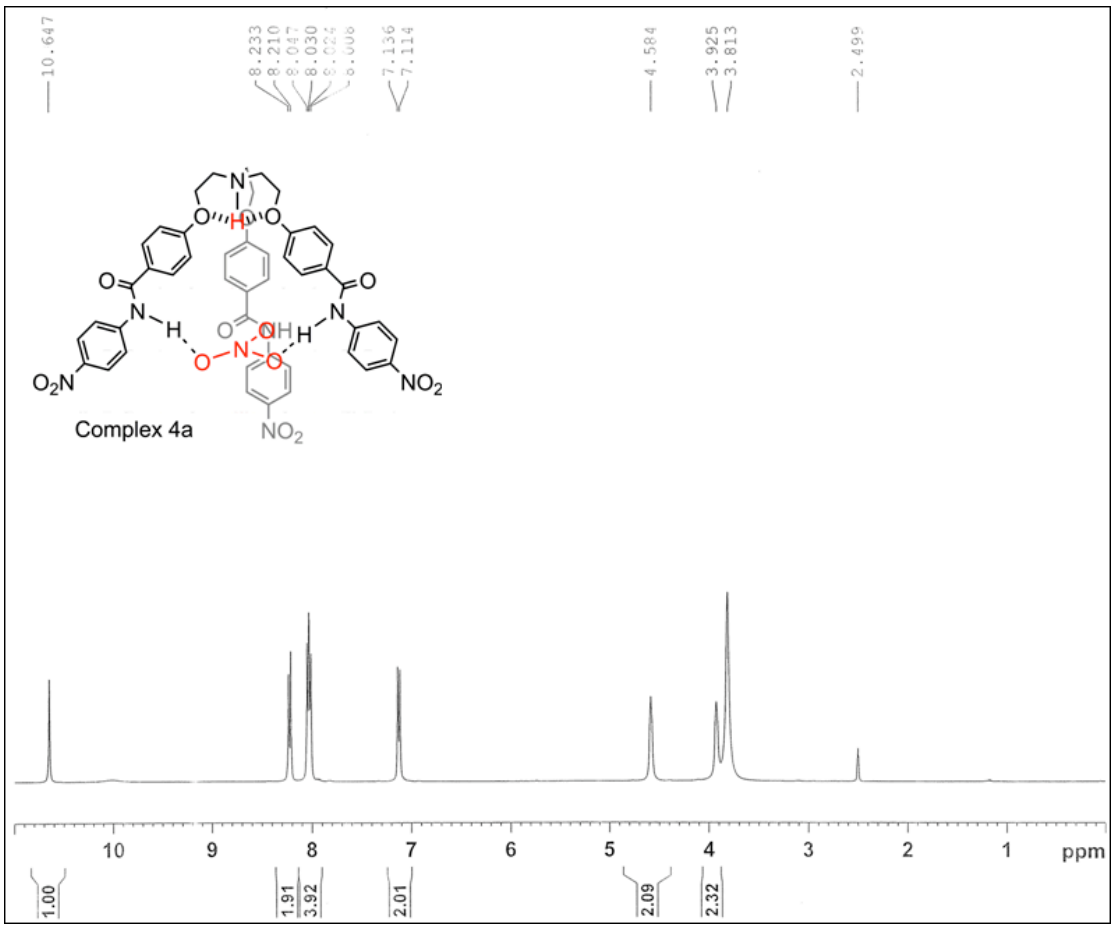

Fig. S26 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **4a**.

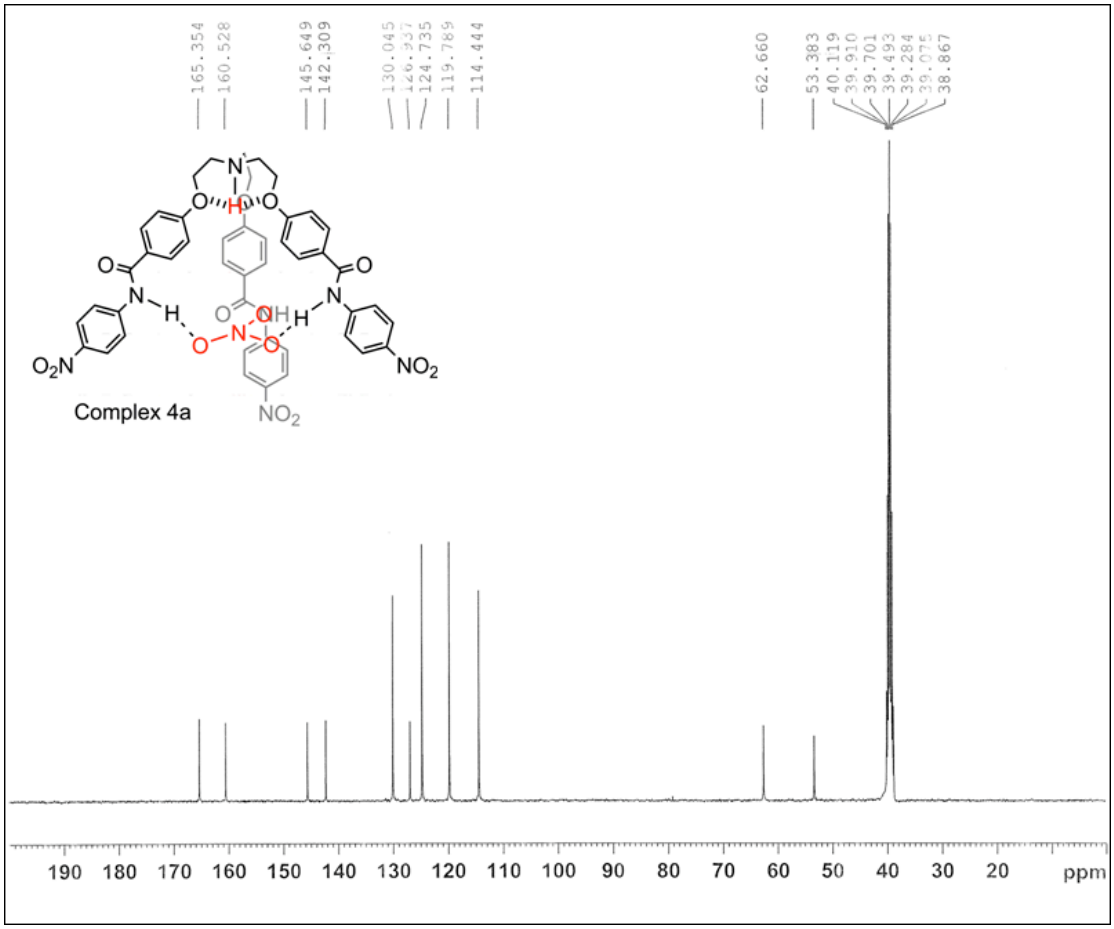

Fig. S27 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **4a**.

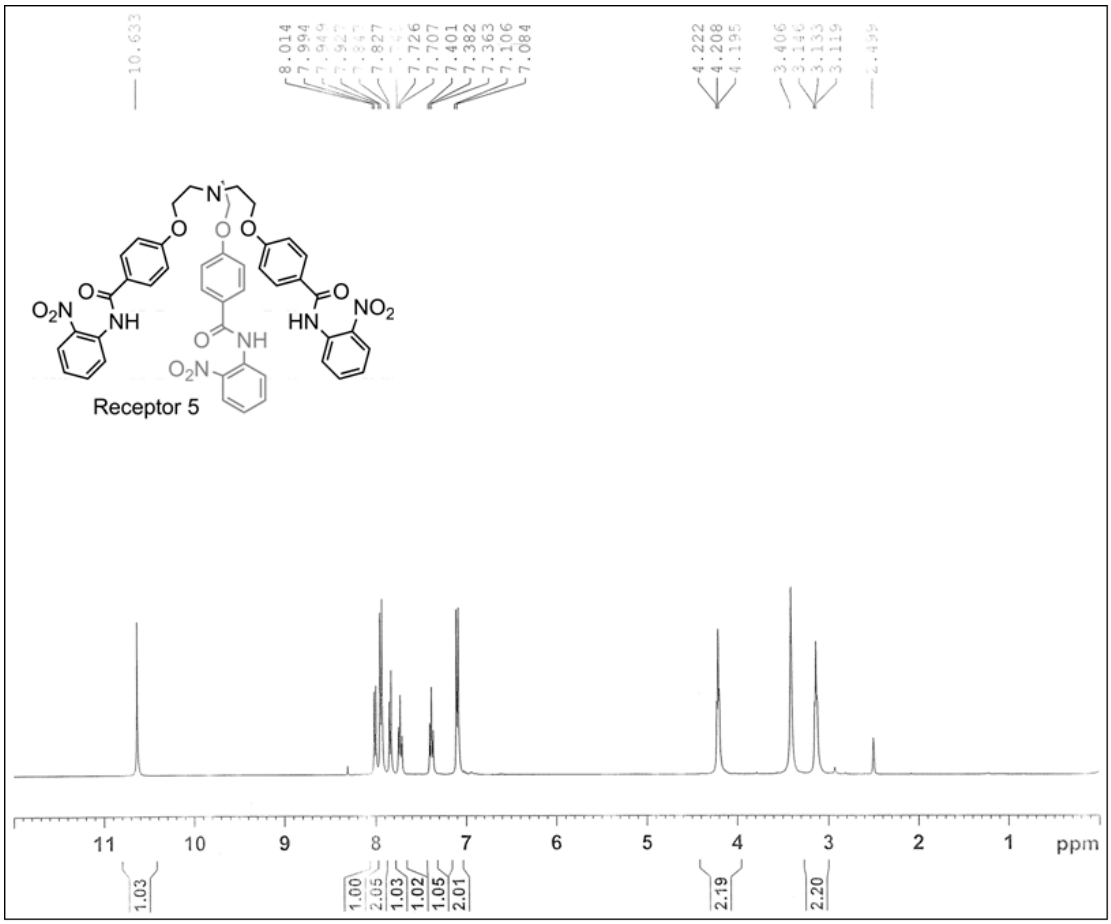

Fig. S28 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **5**.

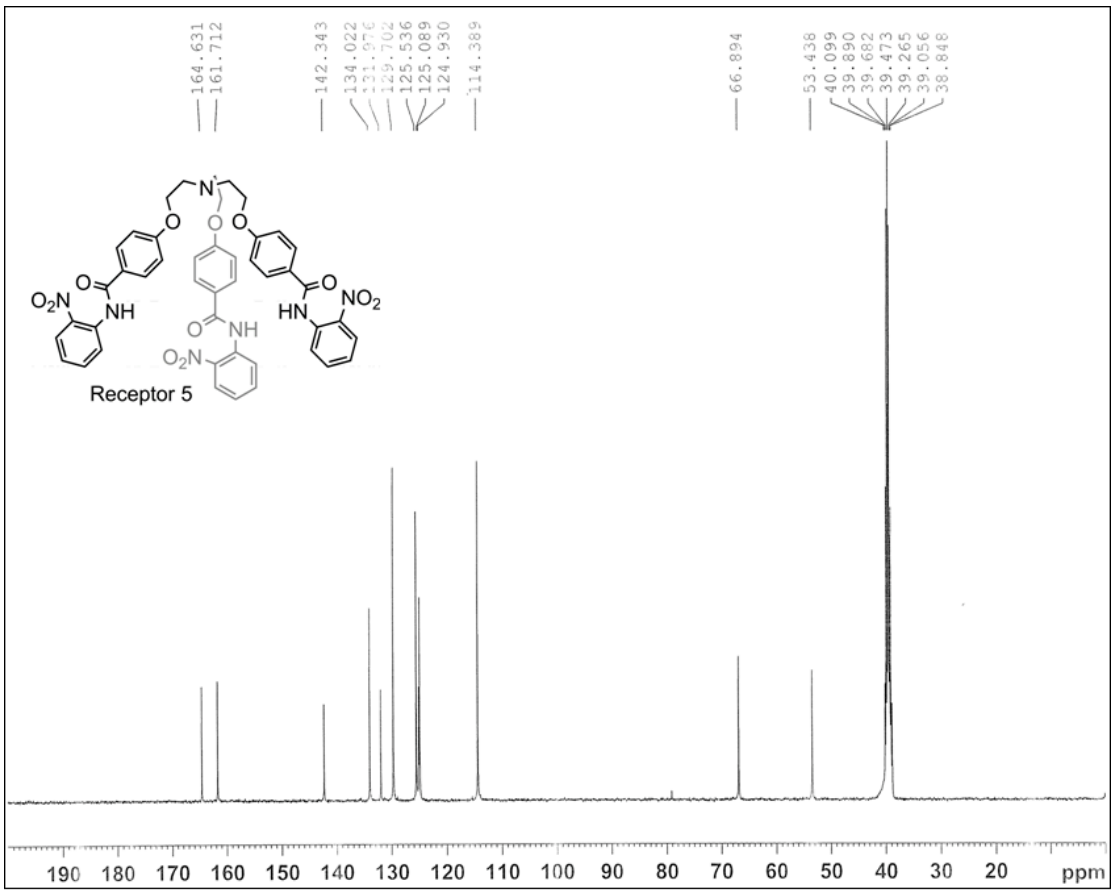

Fig. S29 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **5**.

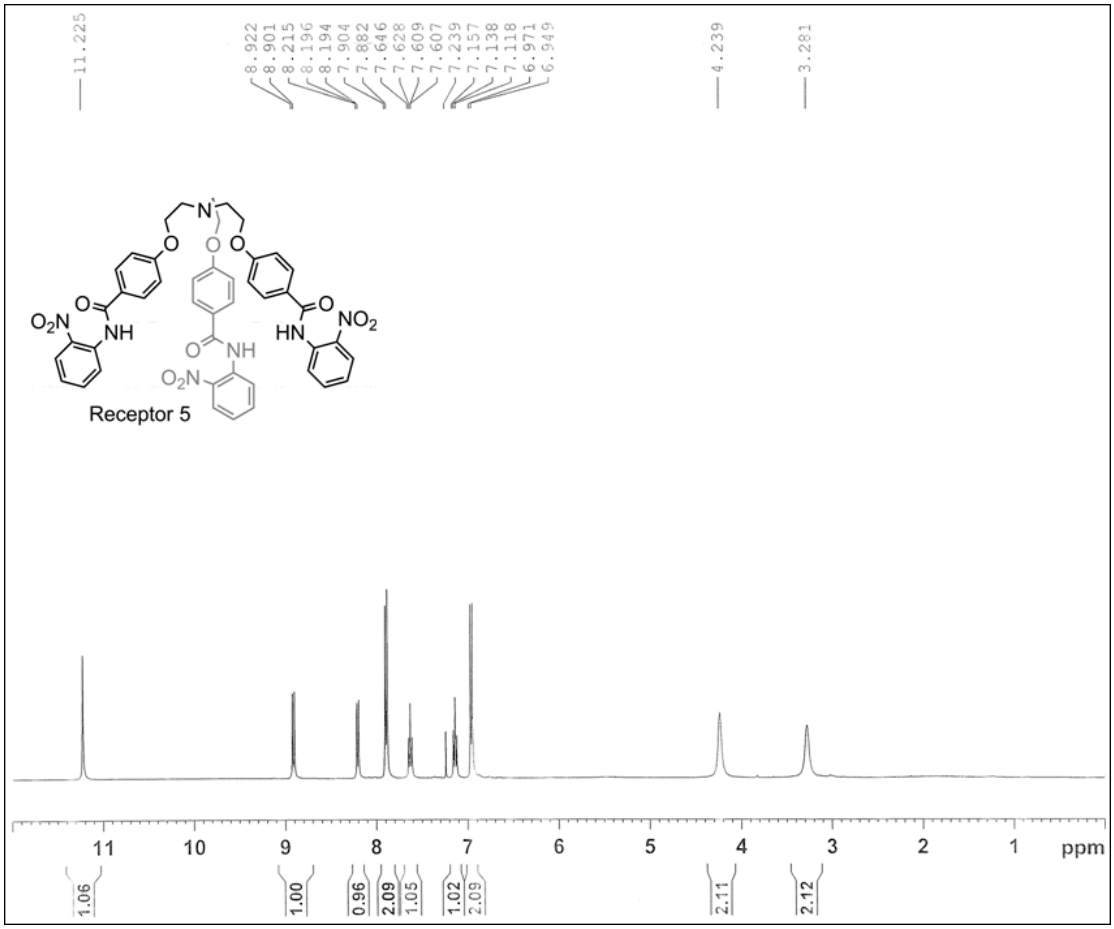

Fig. S30 ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) spectrum of receptor **5**.

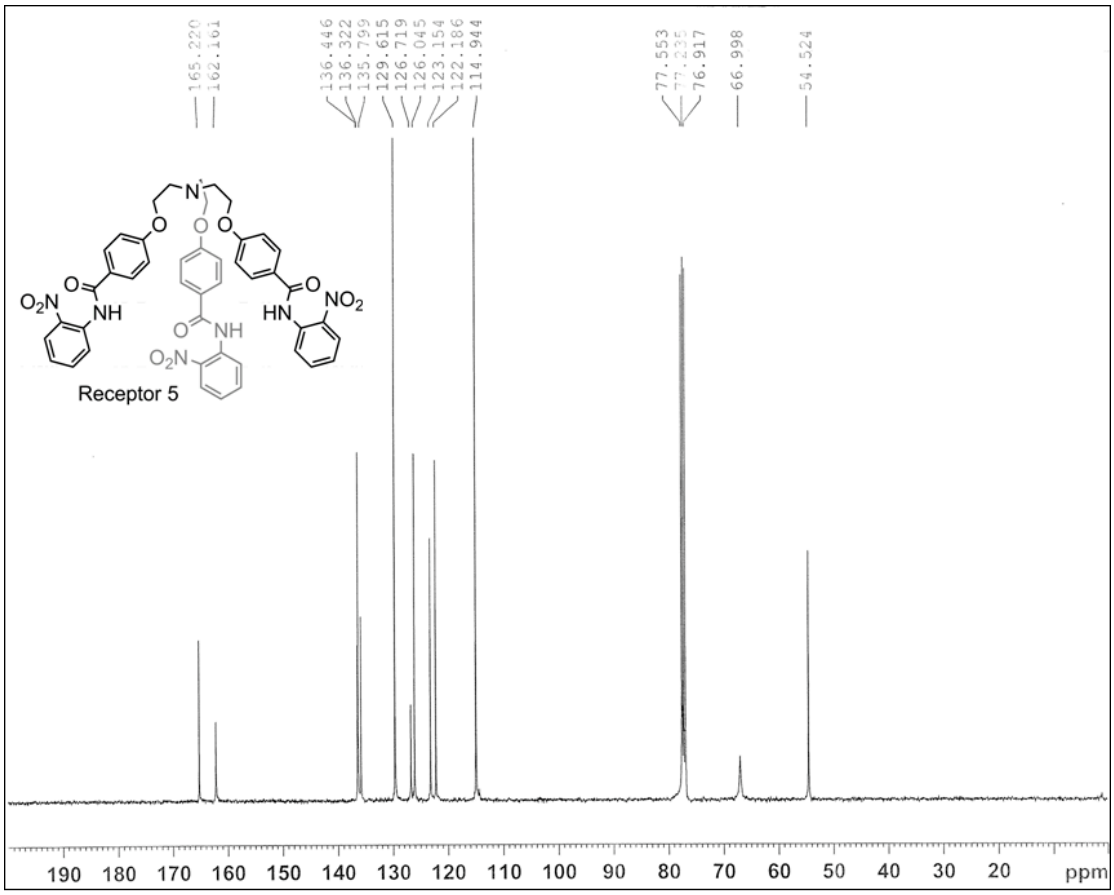

Fig. S31 ^{13}C NMR (100 MHz, $CDCl_3$, 20 ºC) spectrum of receptor **5**.

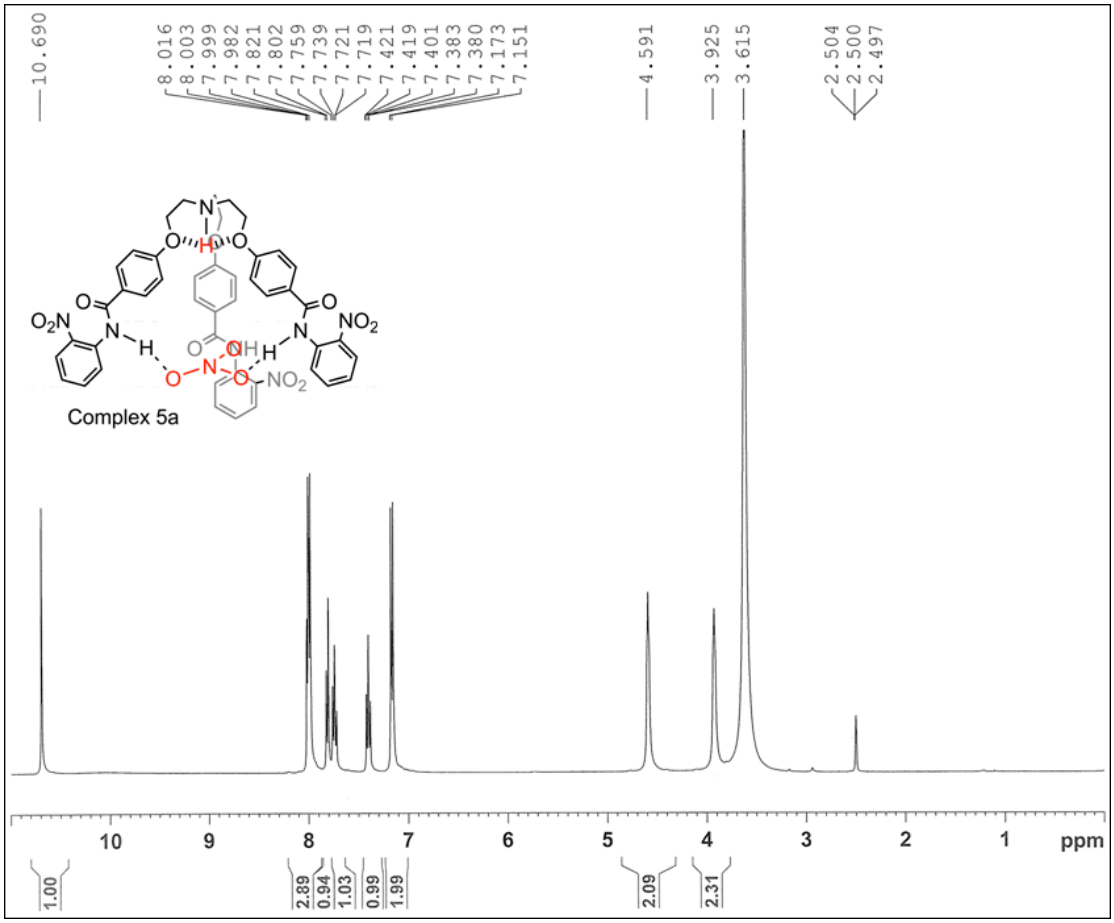

Fig. S32 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **5a**.

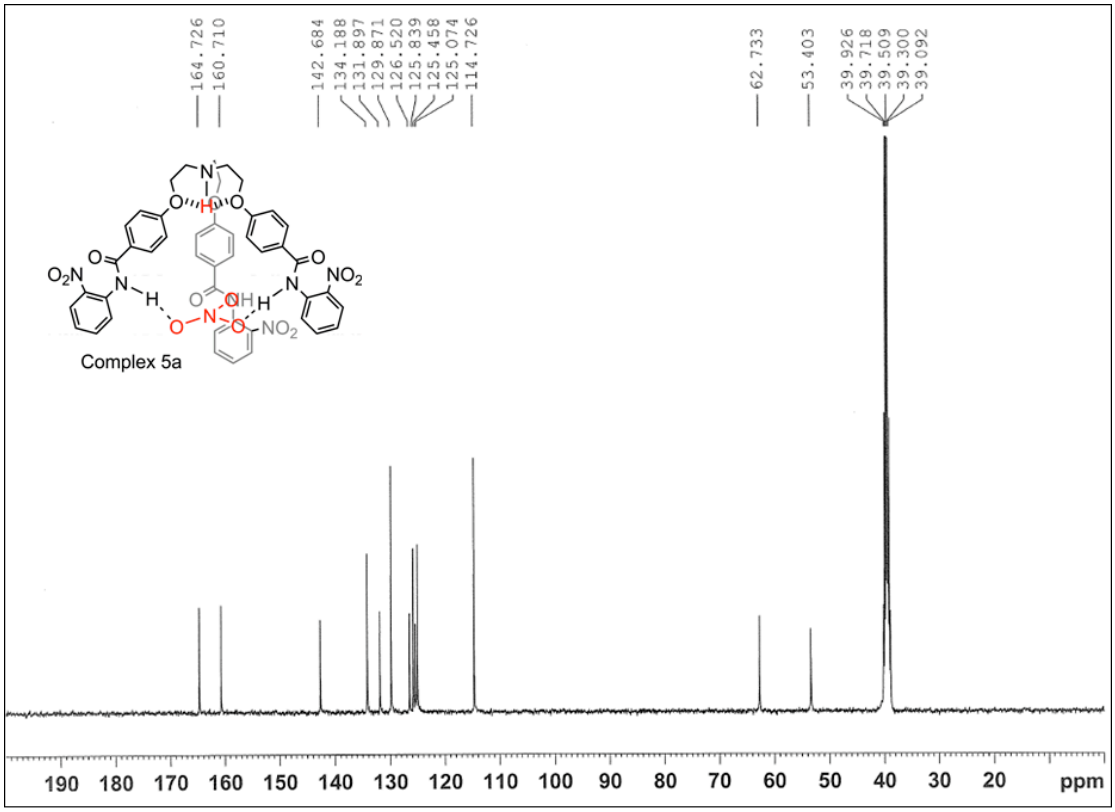

Fig. S33 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **5a**.

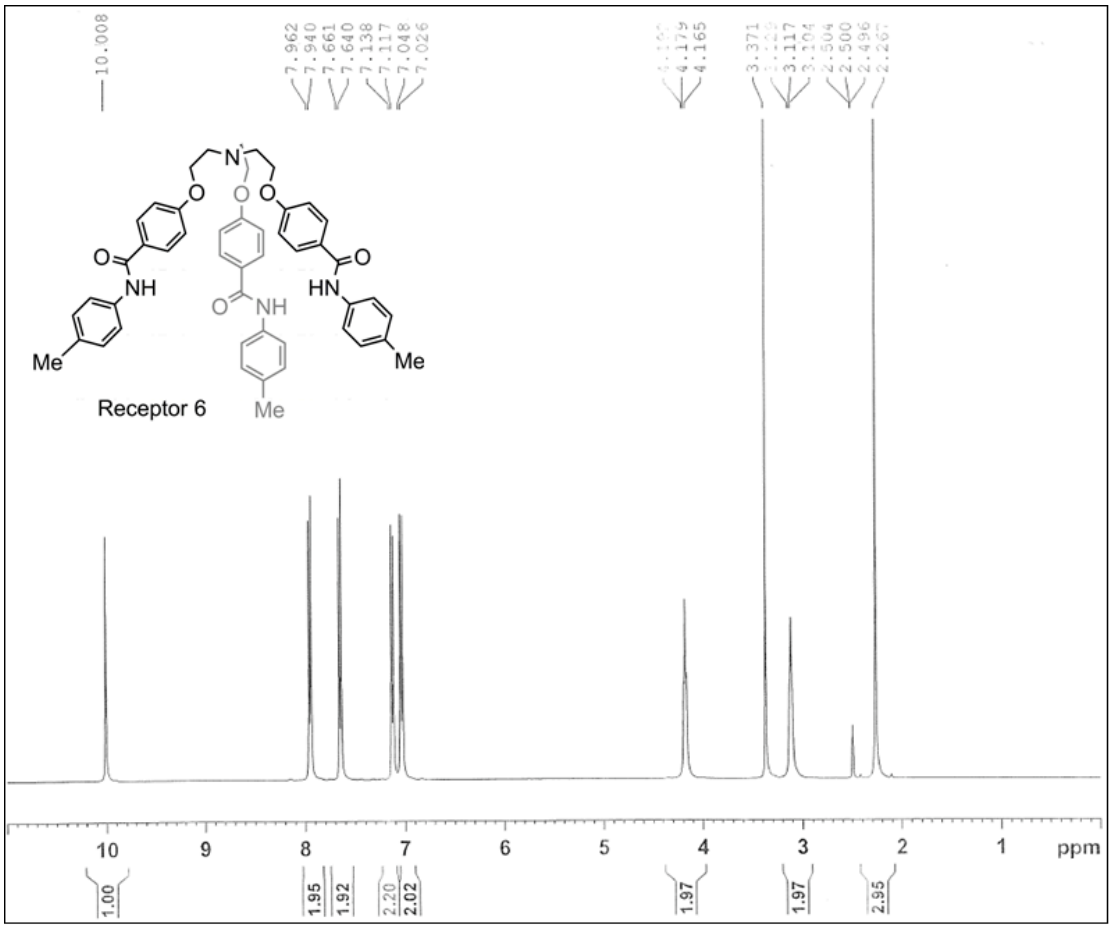

Fig. S34 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **6**.

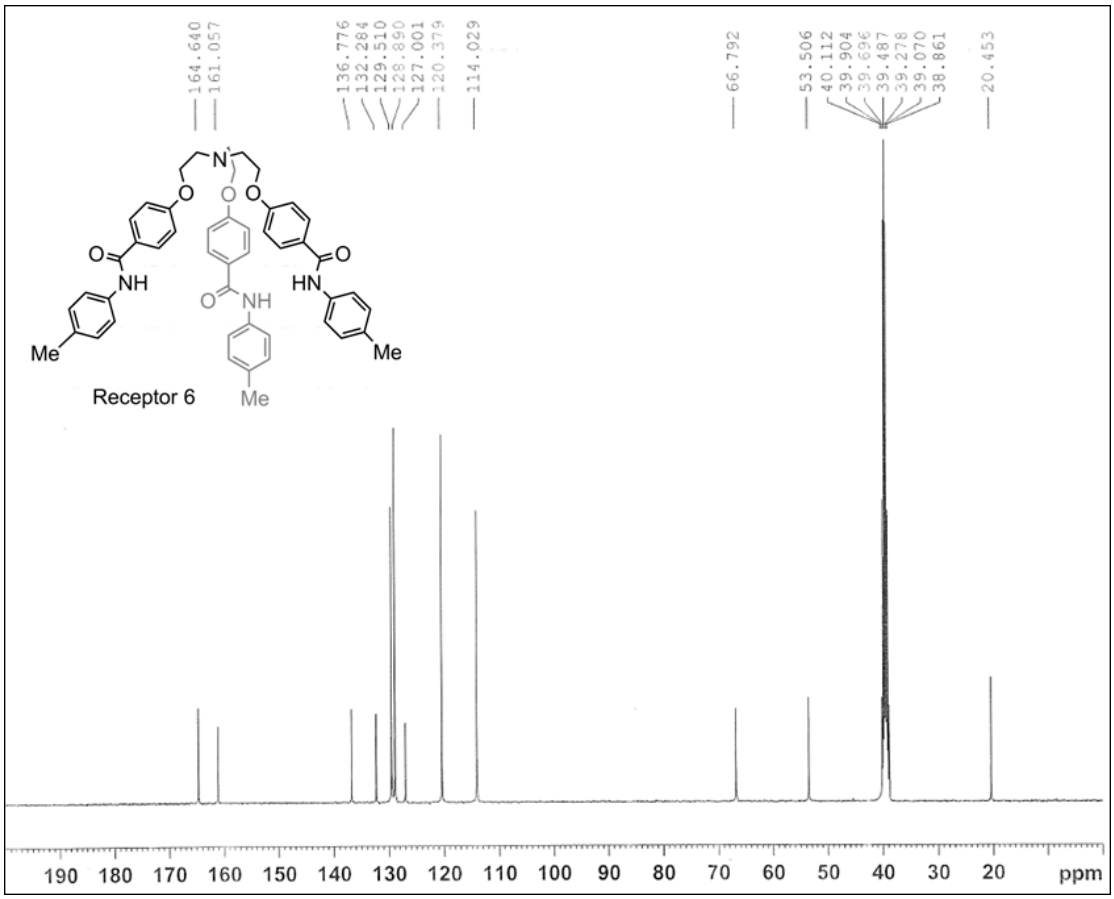

Fig. S35 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **6**.

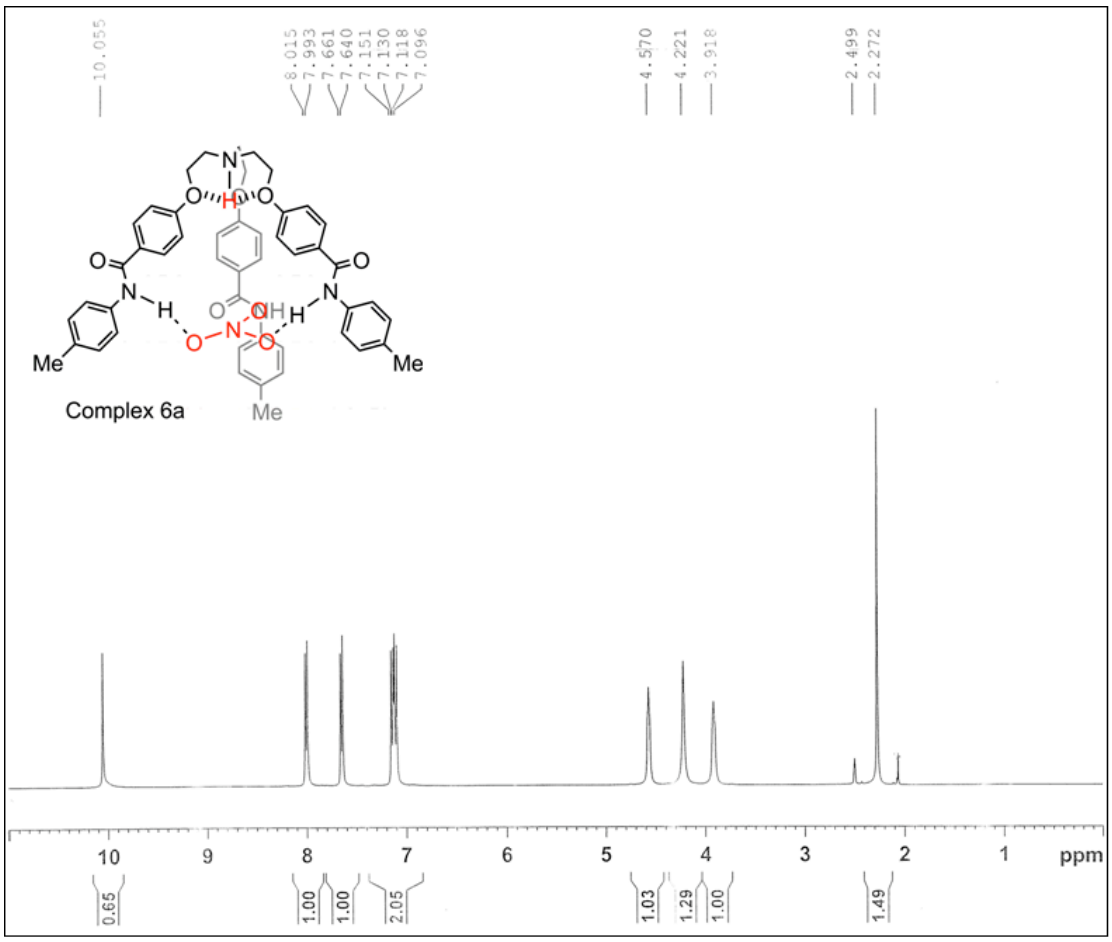

Fig. S36 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **6a**.

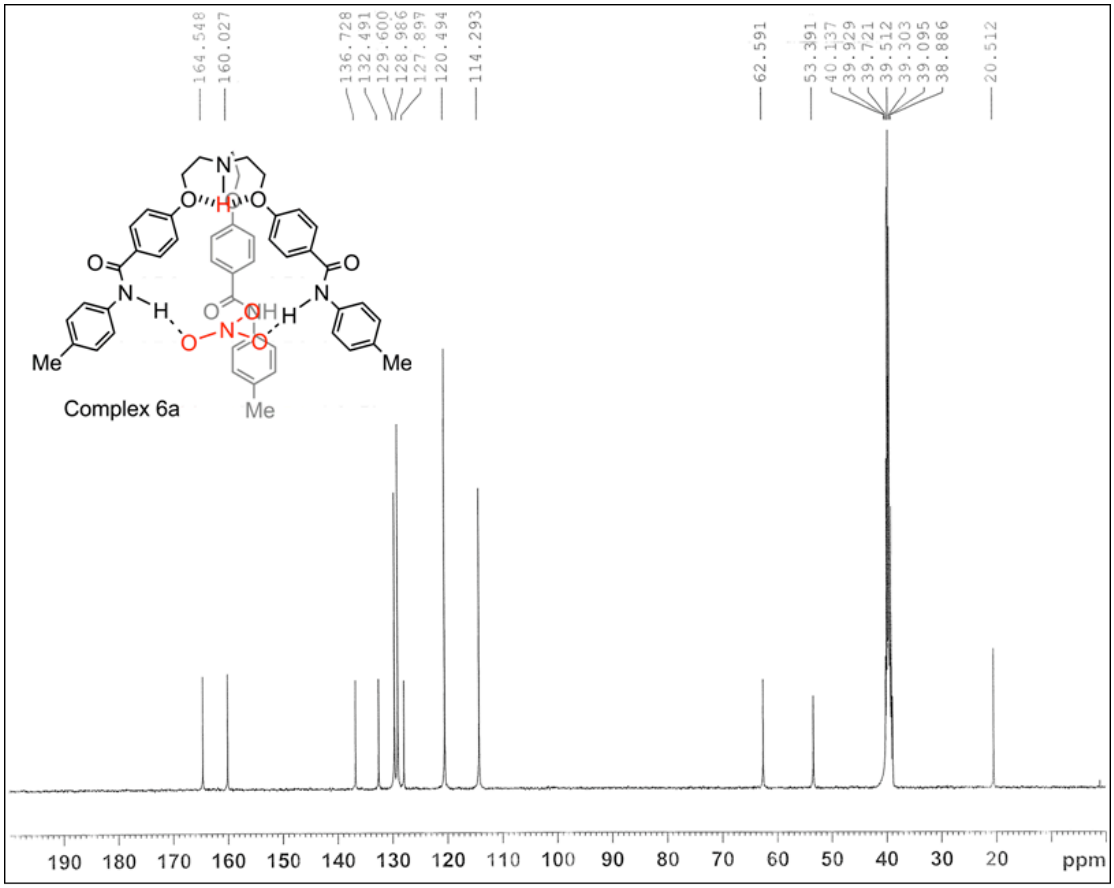

Fig. S37 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **6a**.

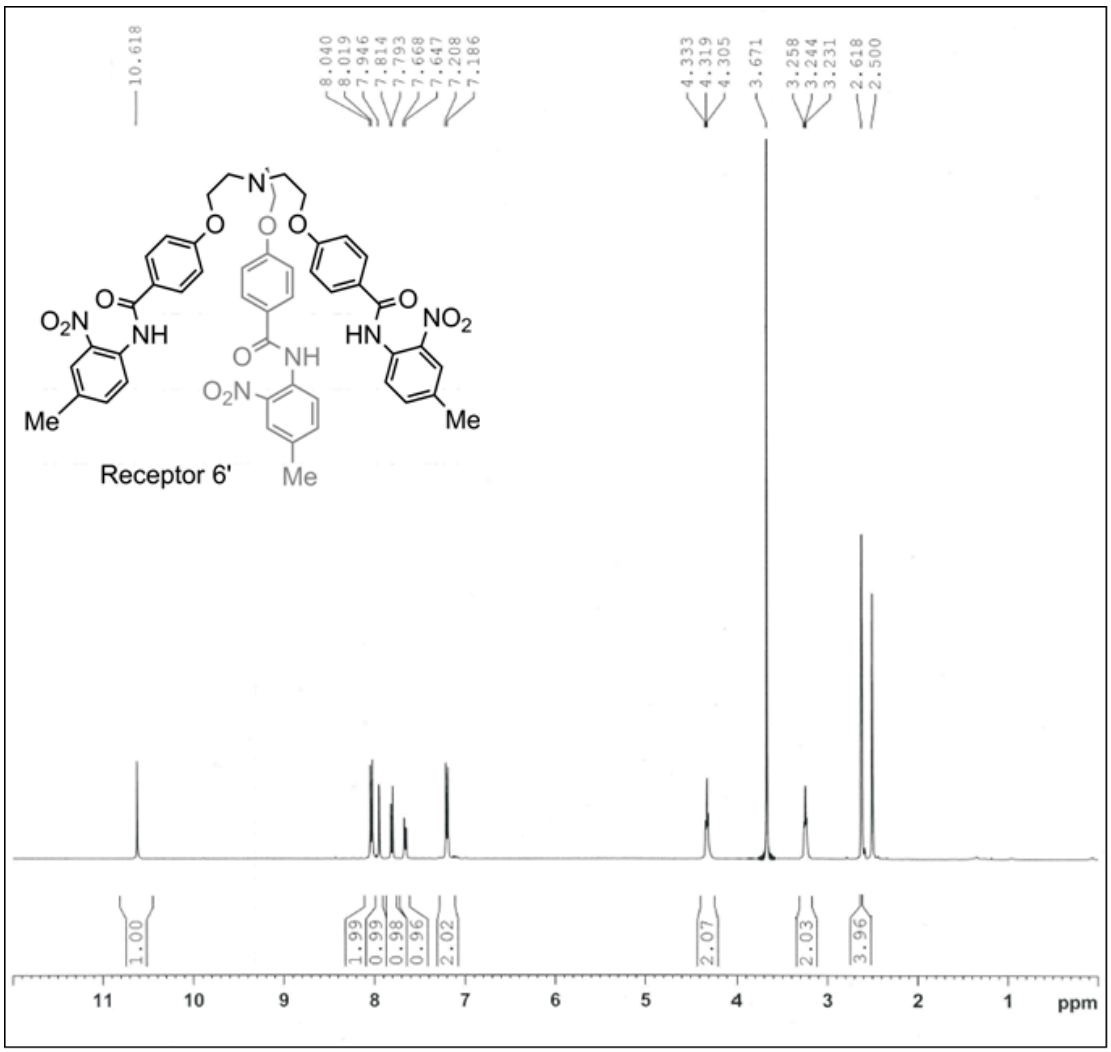

Fig. S38 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **6'**.

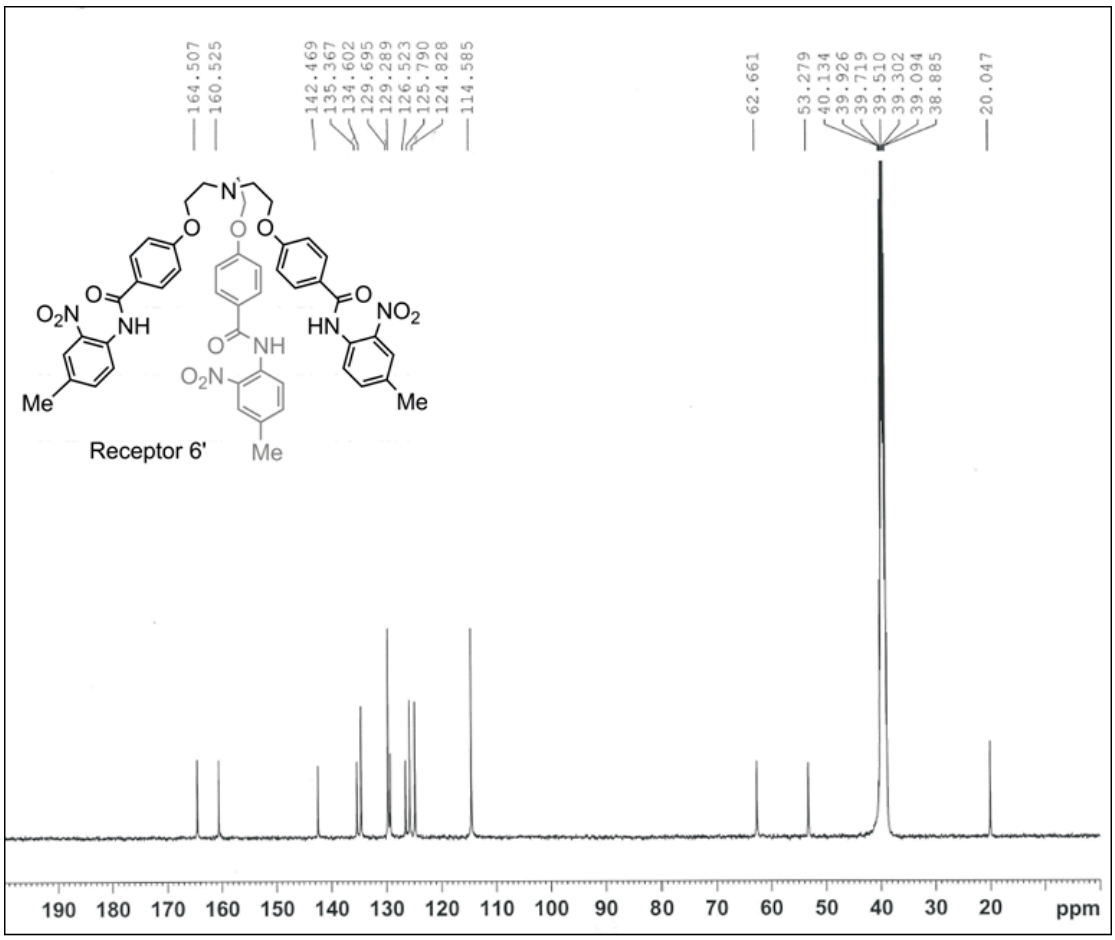

Fig. S39 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **6'**.

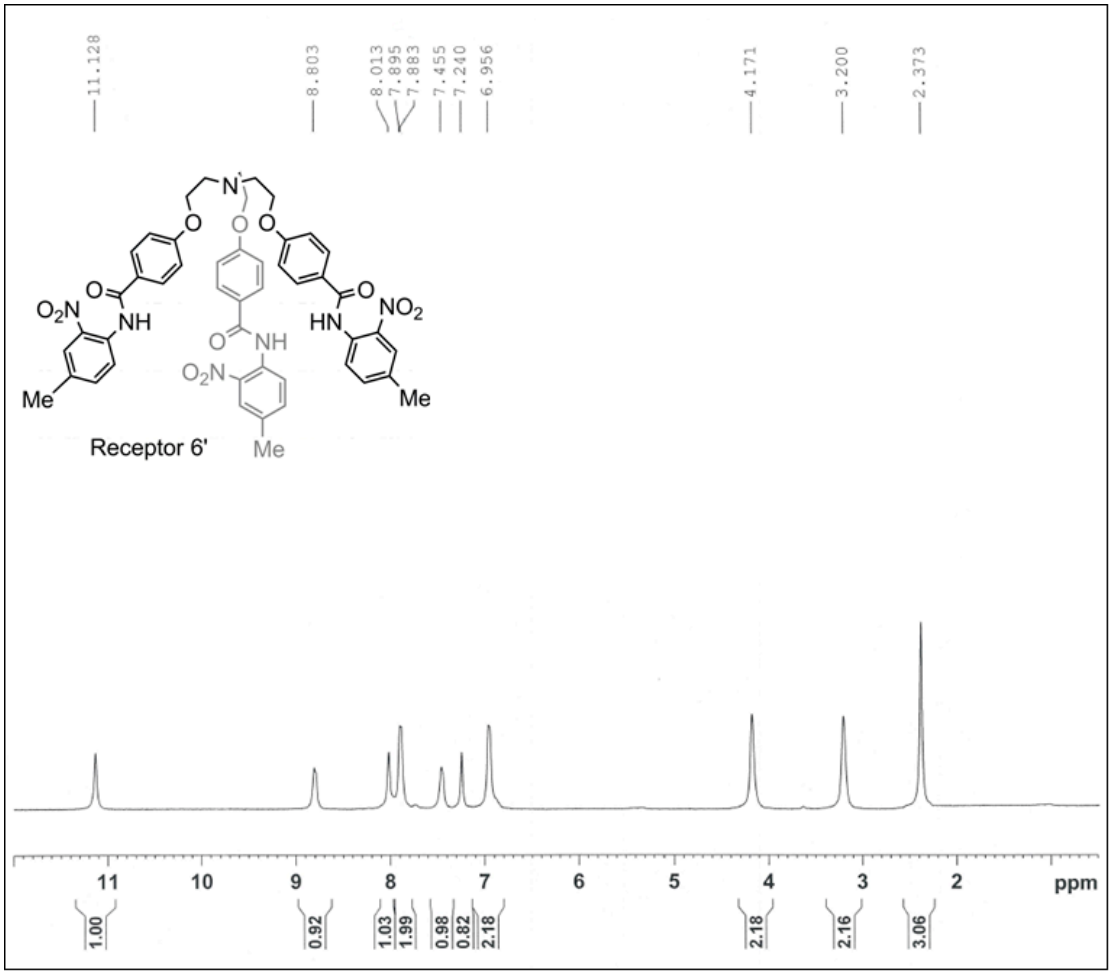

Fig. S40 ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) spectrum of receptor **6'**.

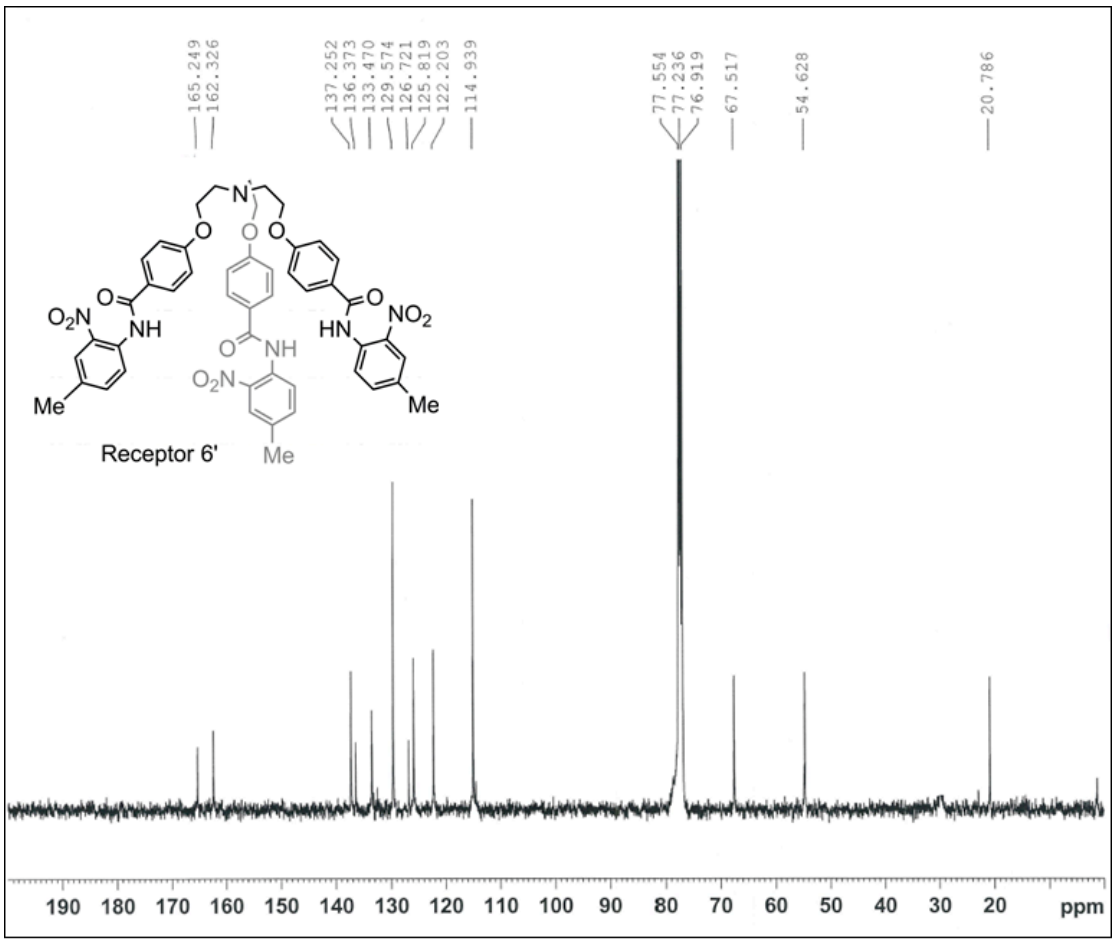

Fig. S41 ^{13}C NMR (100 MHz, $CDCl_3$, 20 ºC) spectrum of receptor **6'**.

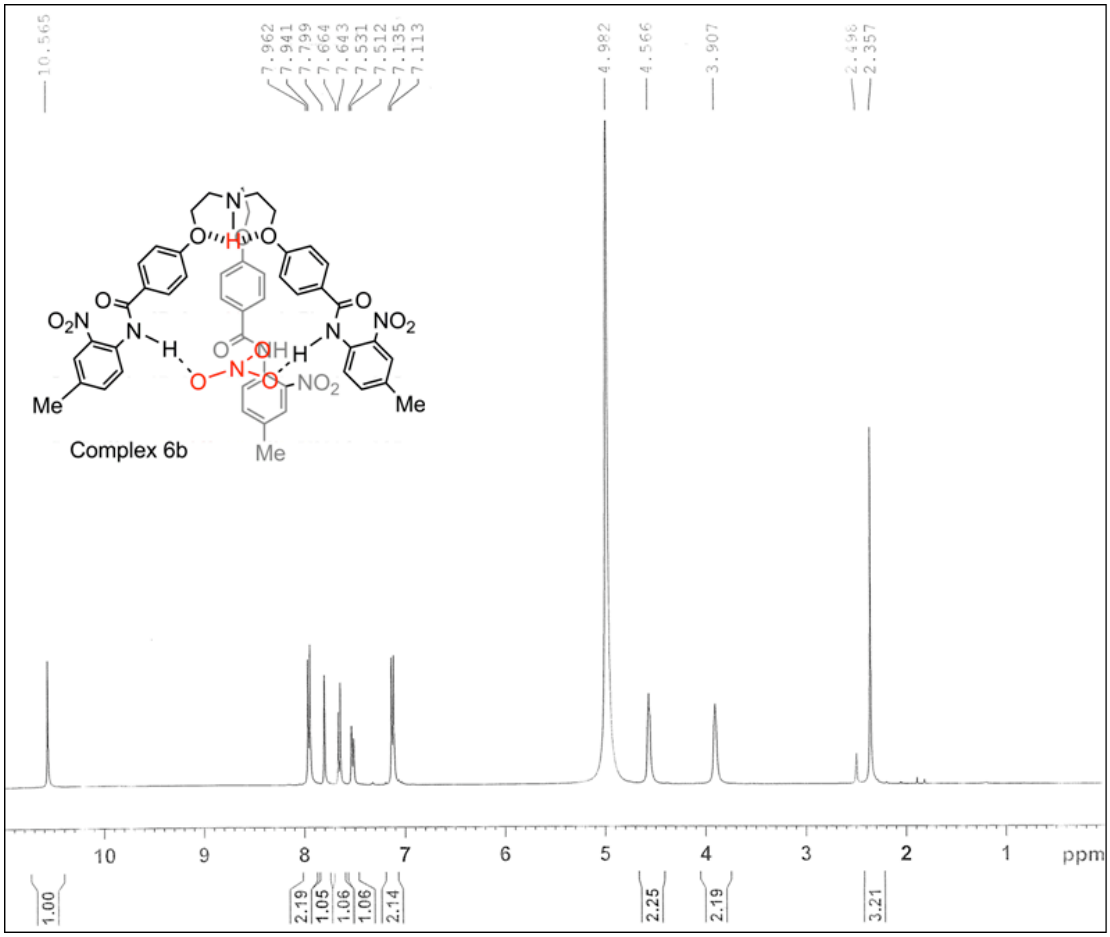

Fig. S42 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **6b**.

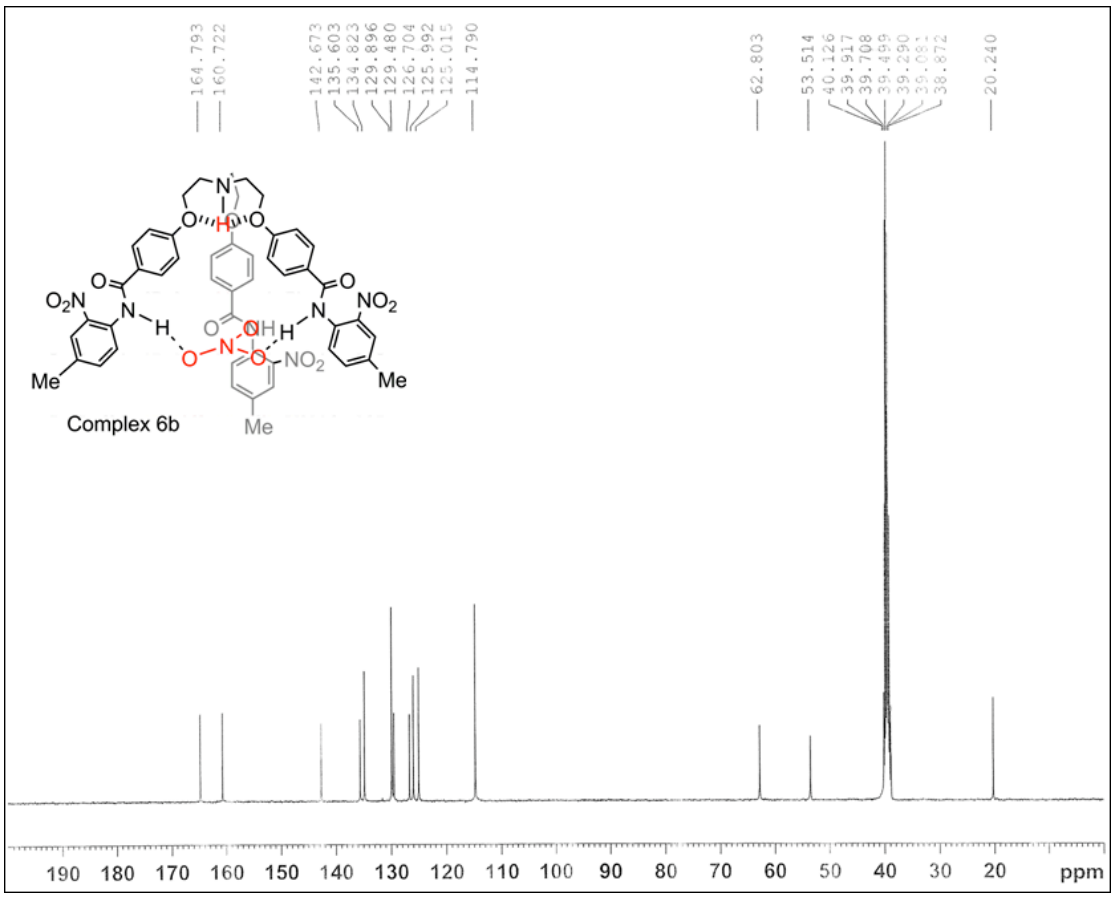

Fig. S43 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **6b**.

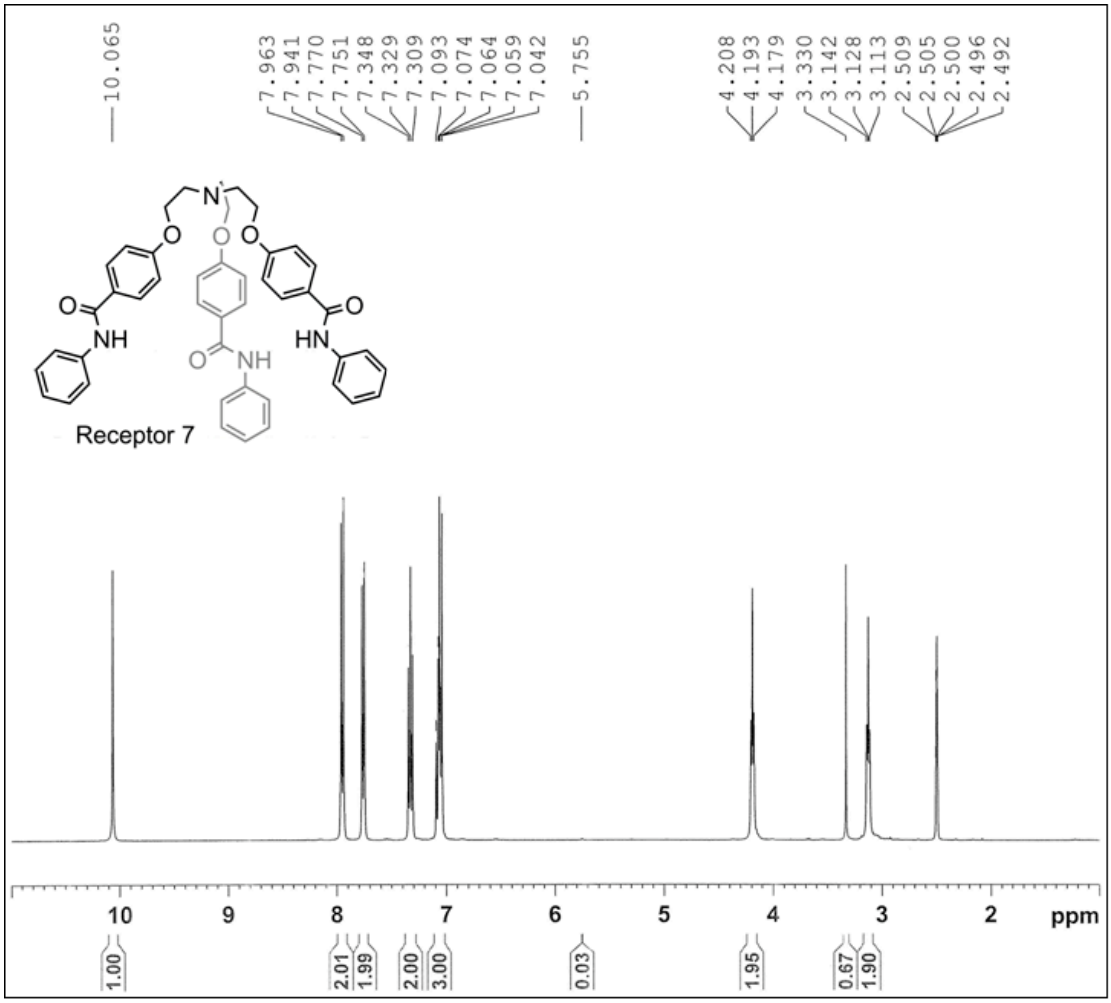

Fig. S44 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **7**.

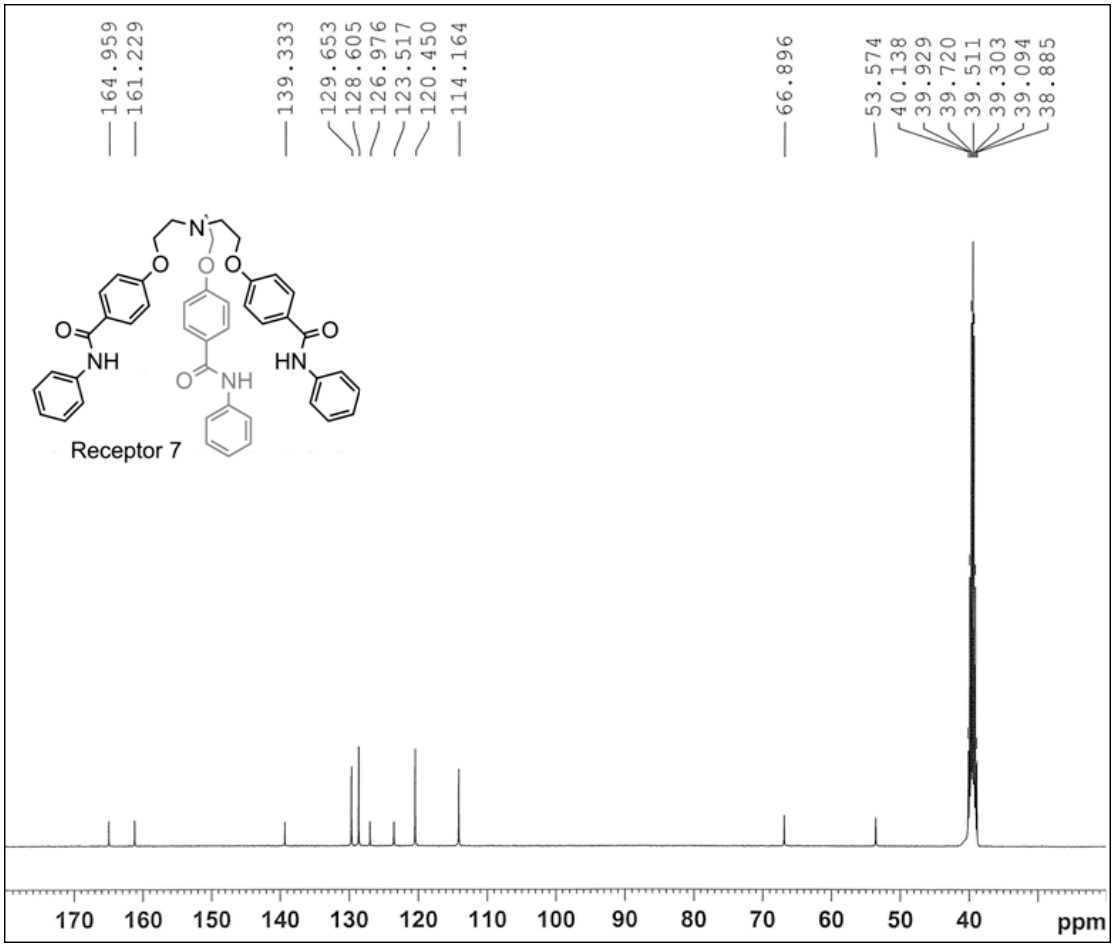

Fig. S45 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **7**.

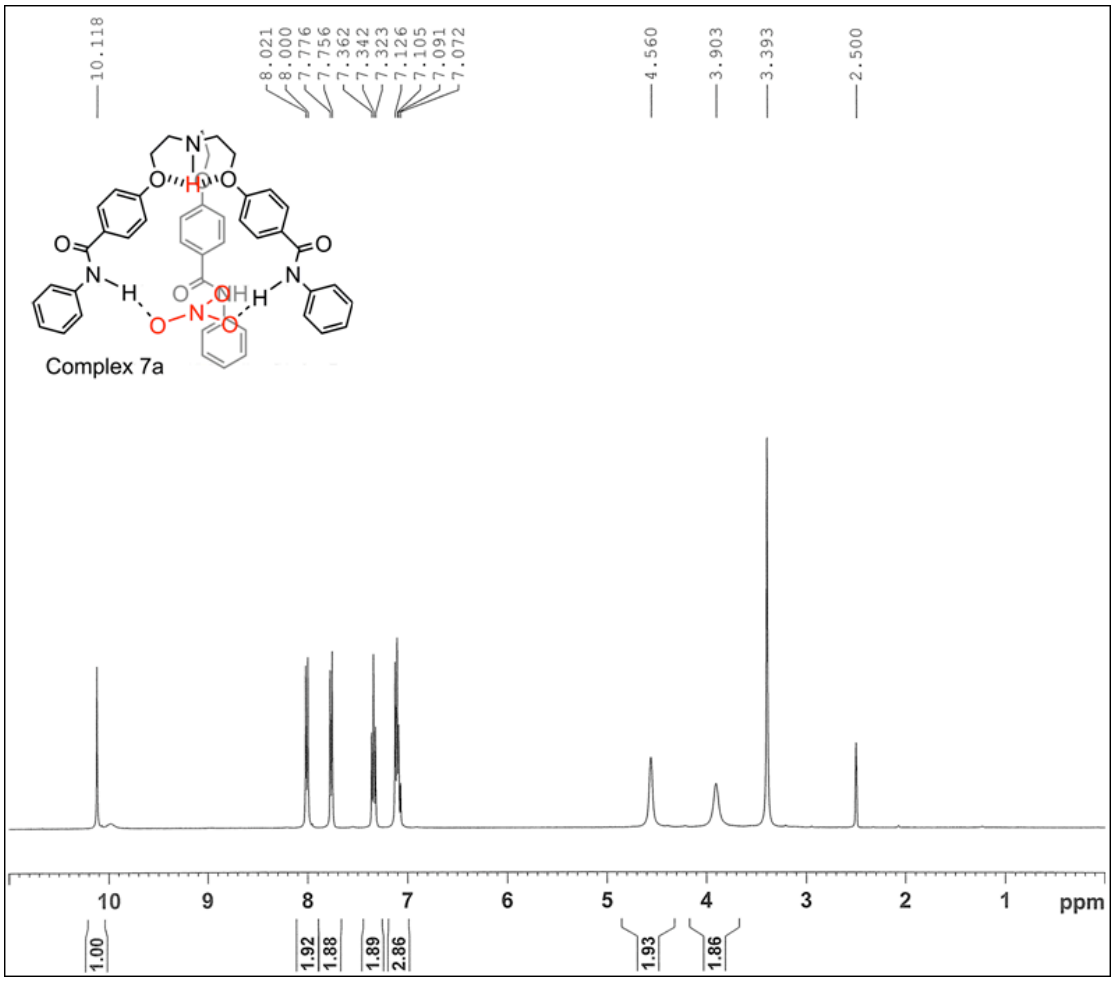

Fig. S46 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **7a**.

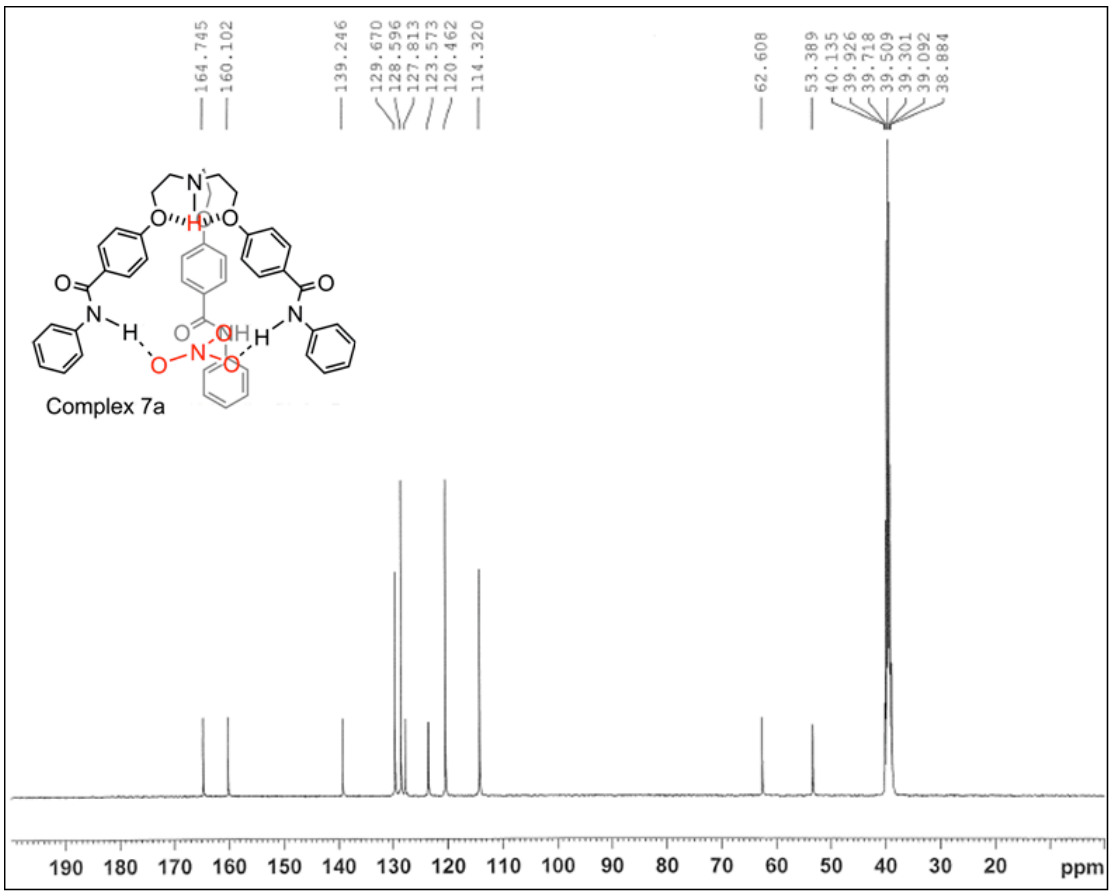

Fig. S47 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **7a**.

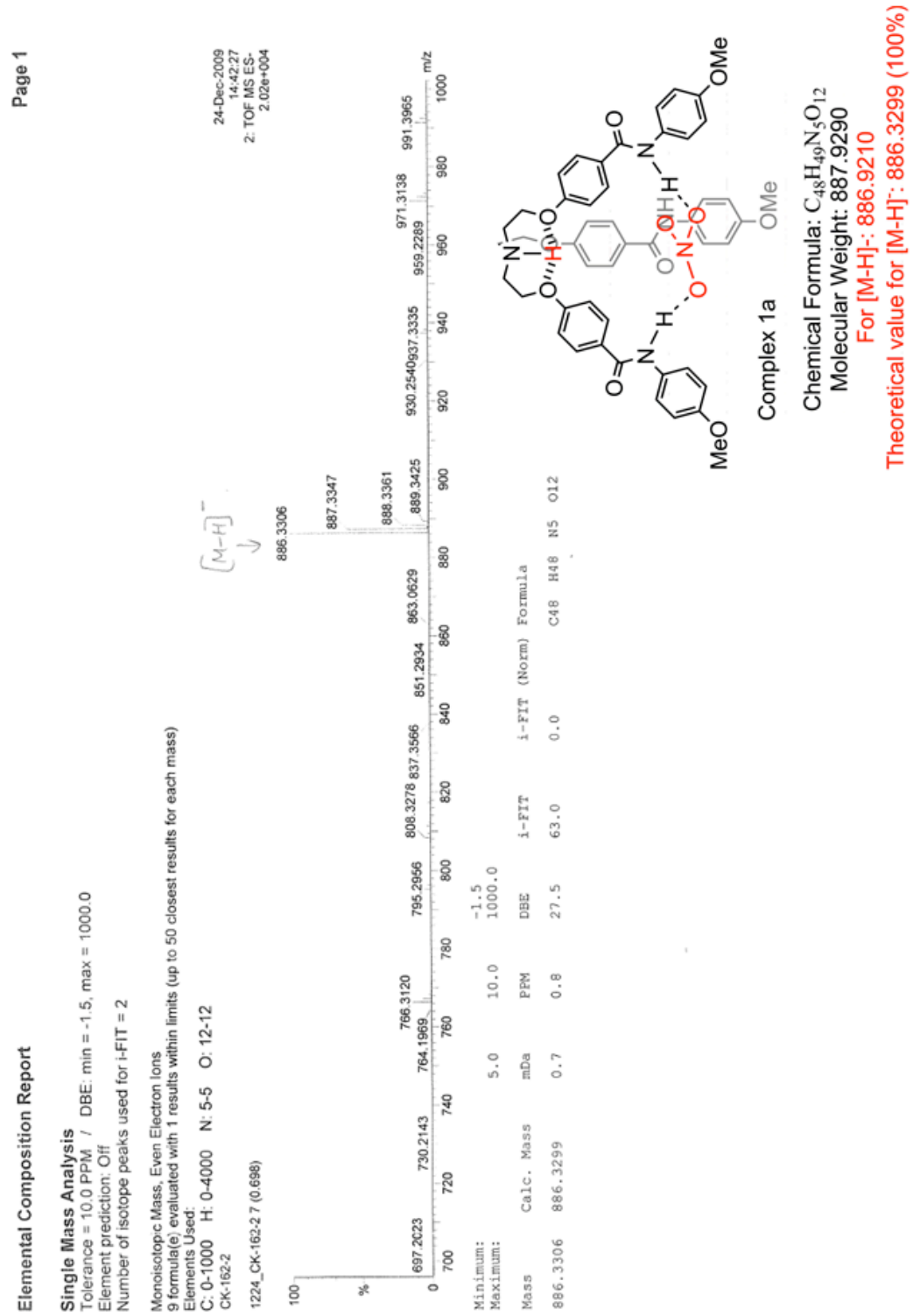

Fig. S48 HRESI mass spectrum of complex **1a**.

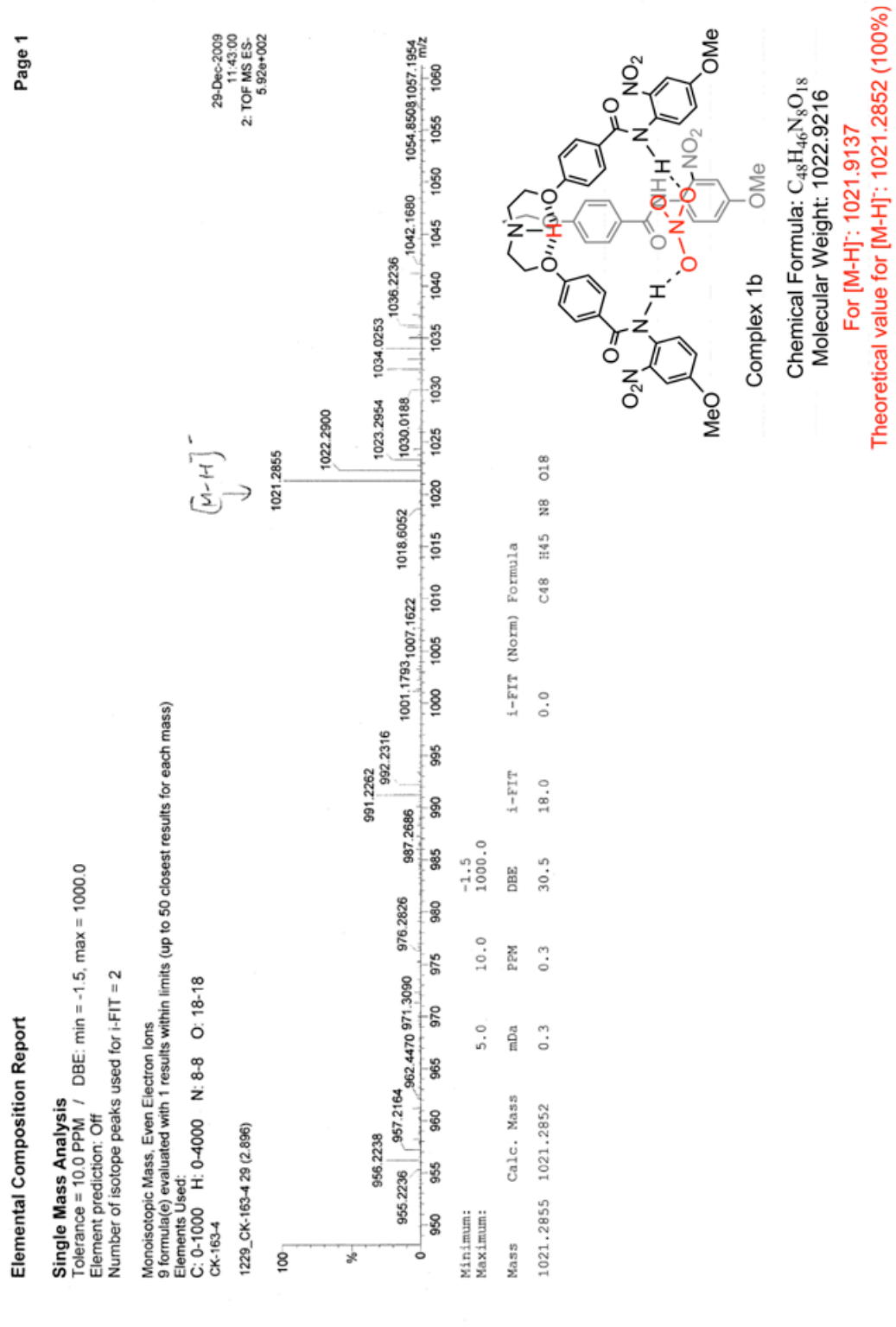

Fig. S49 HRESI mass spectrum of complex **1b**.

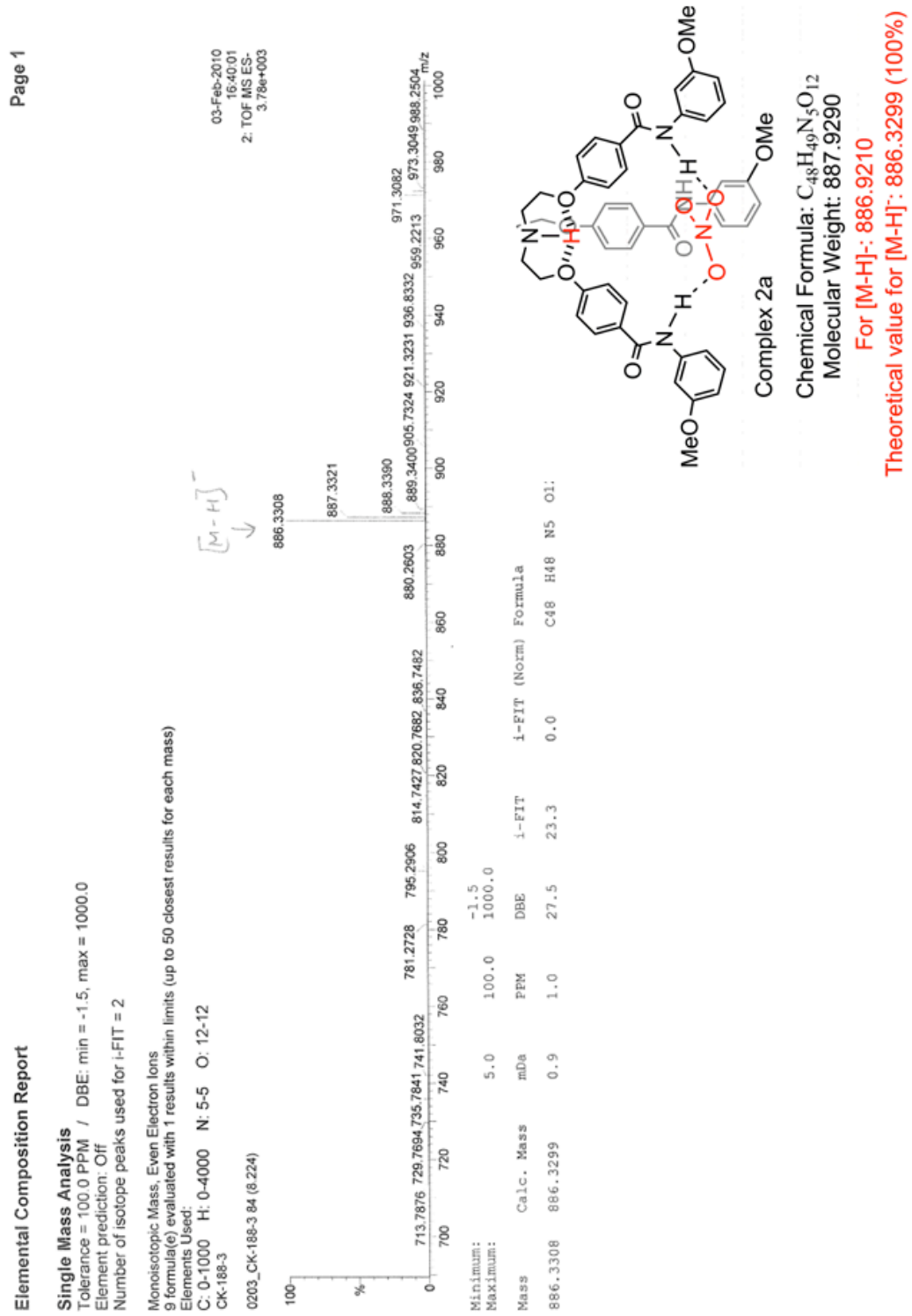

Fig. S50 HRESI mass spectrum of complex **2a**.

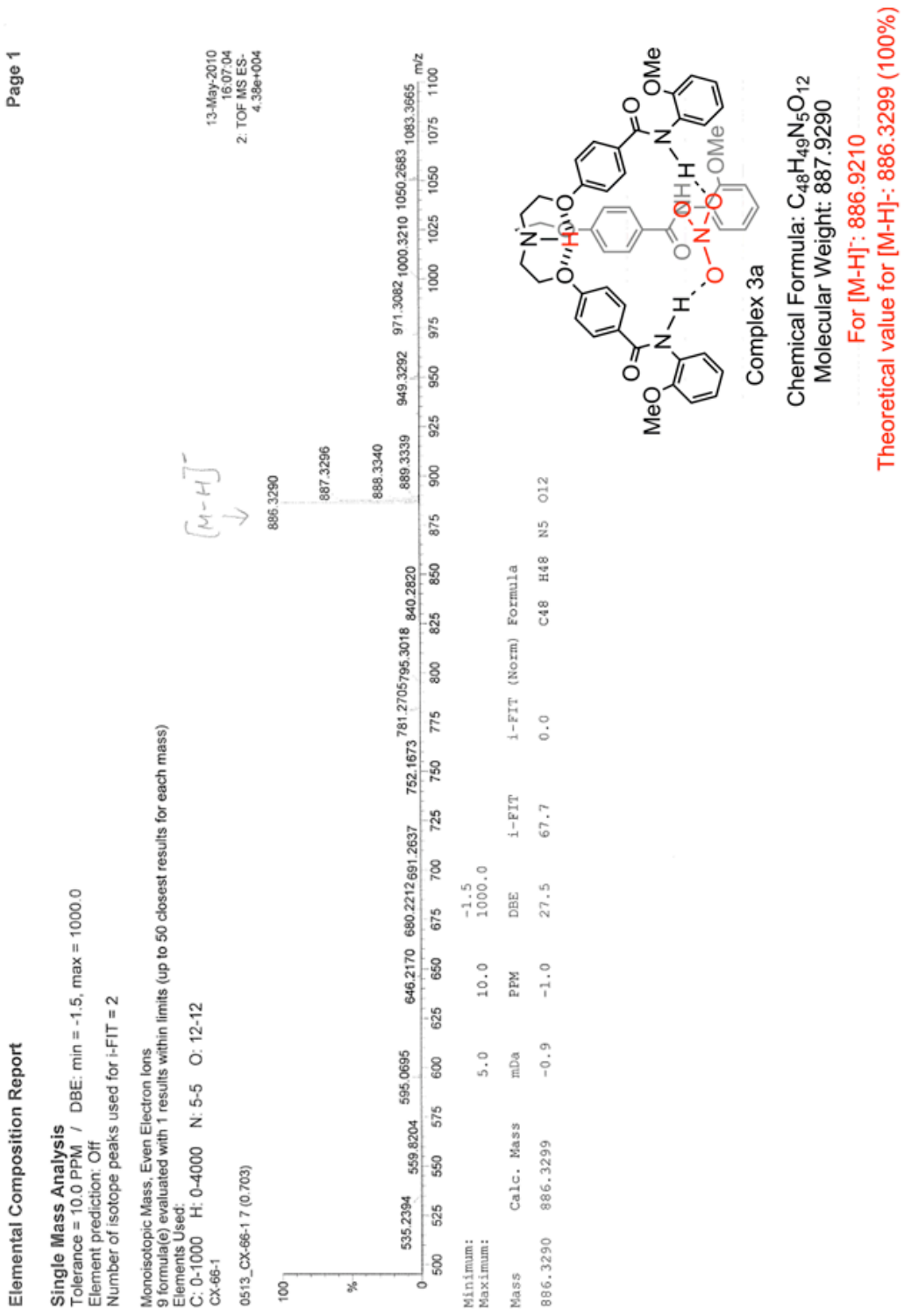

Fig. S51 HRESI mass spectrum of complex **3a**.

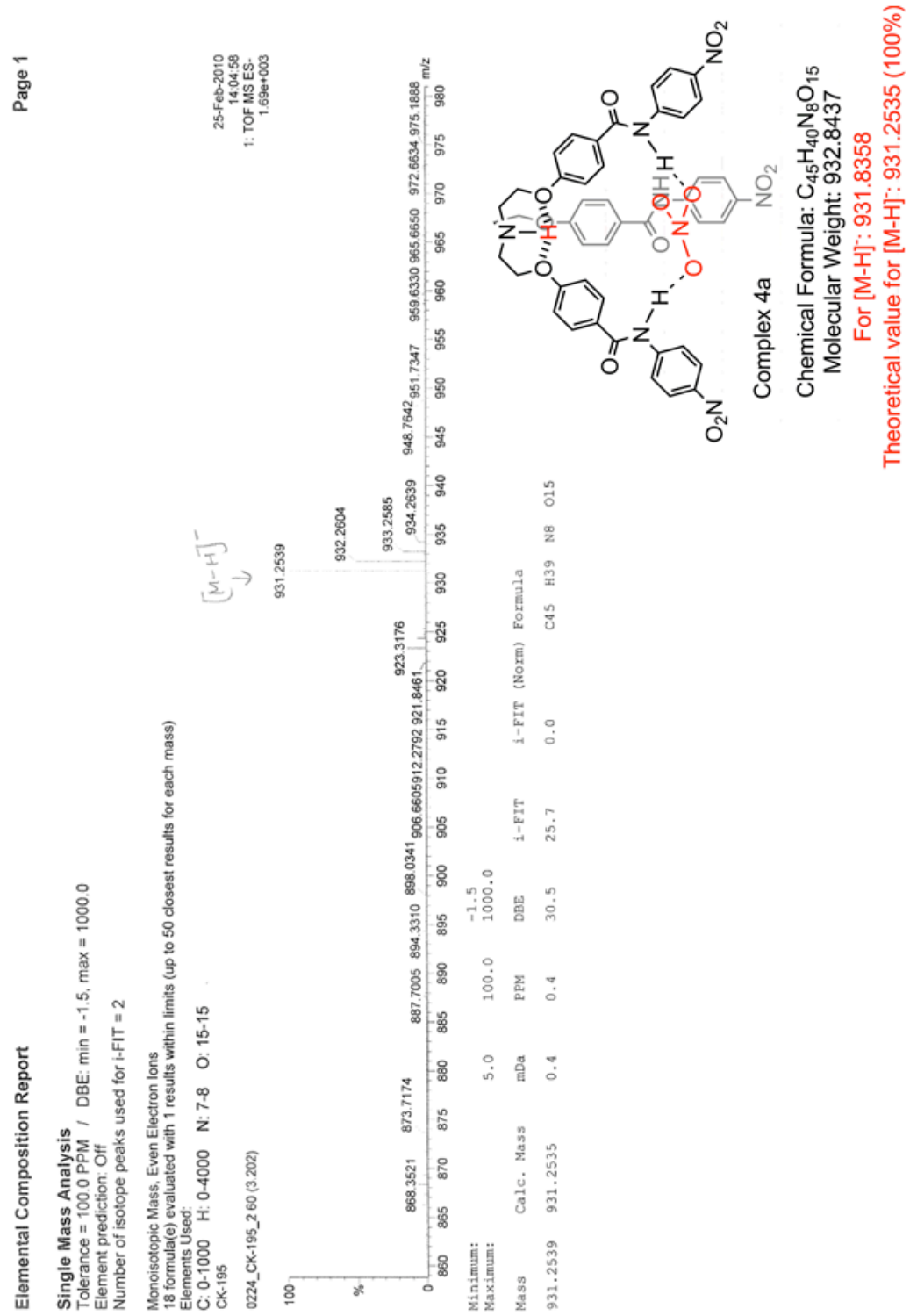

Fig. S52 HRESI mass spectrum of complex **4a**.

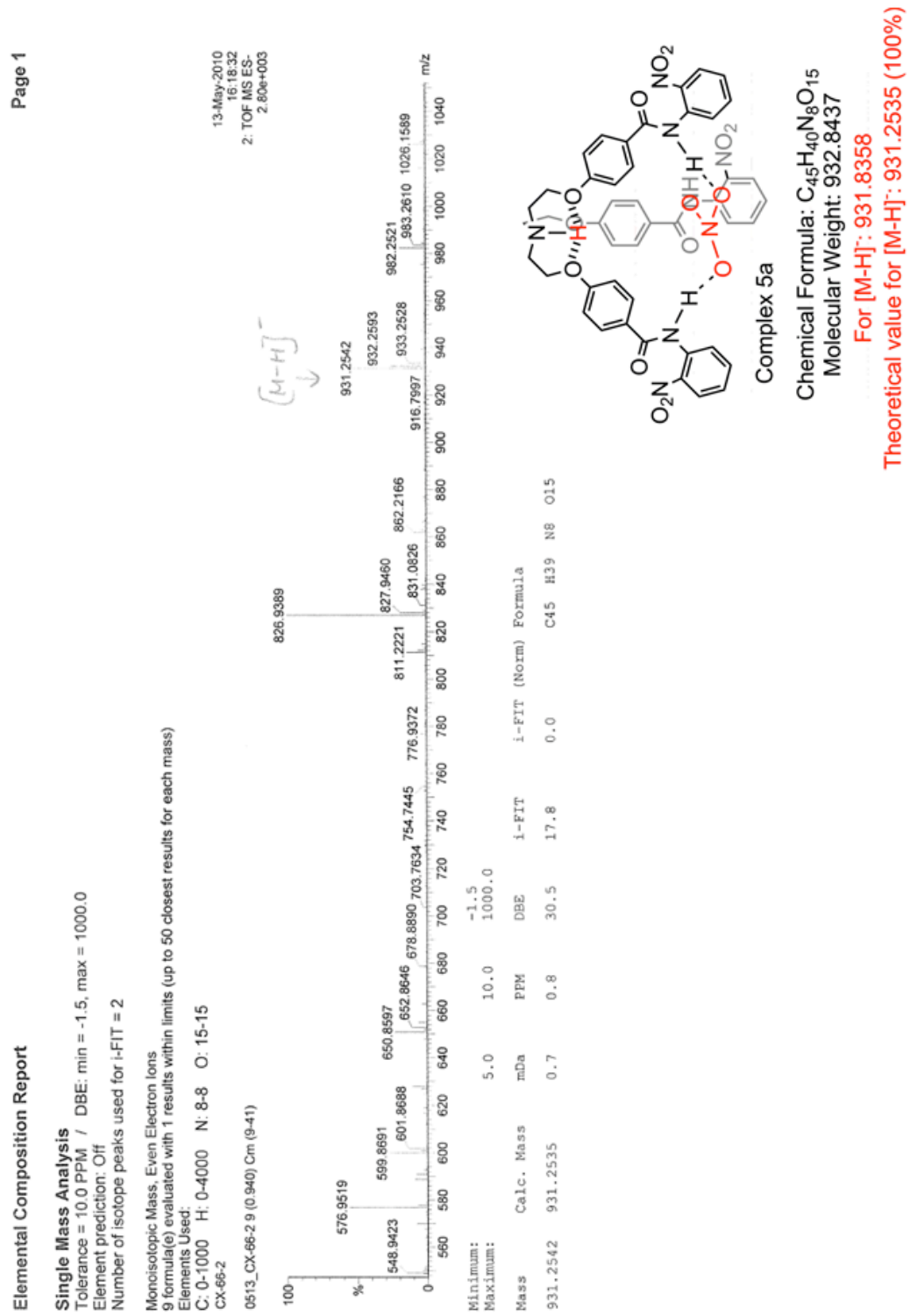

Fig. S53 HRESI mass spectrum of complex **5a**.

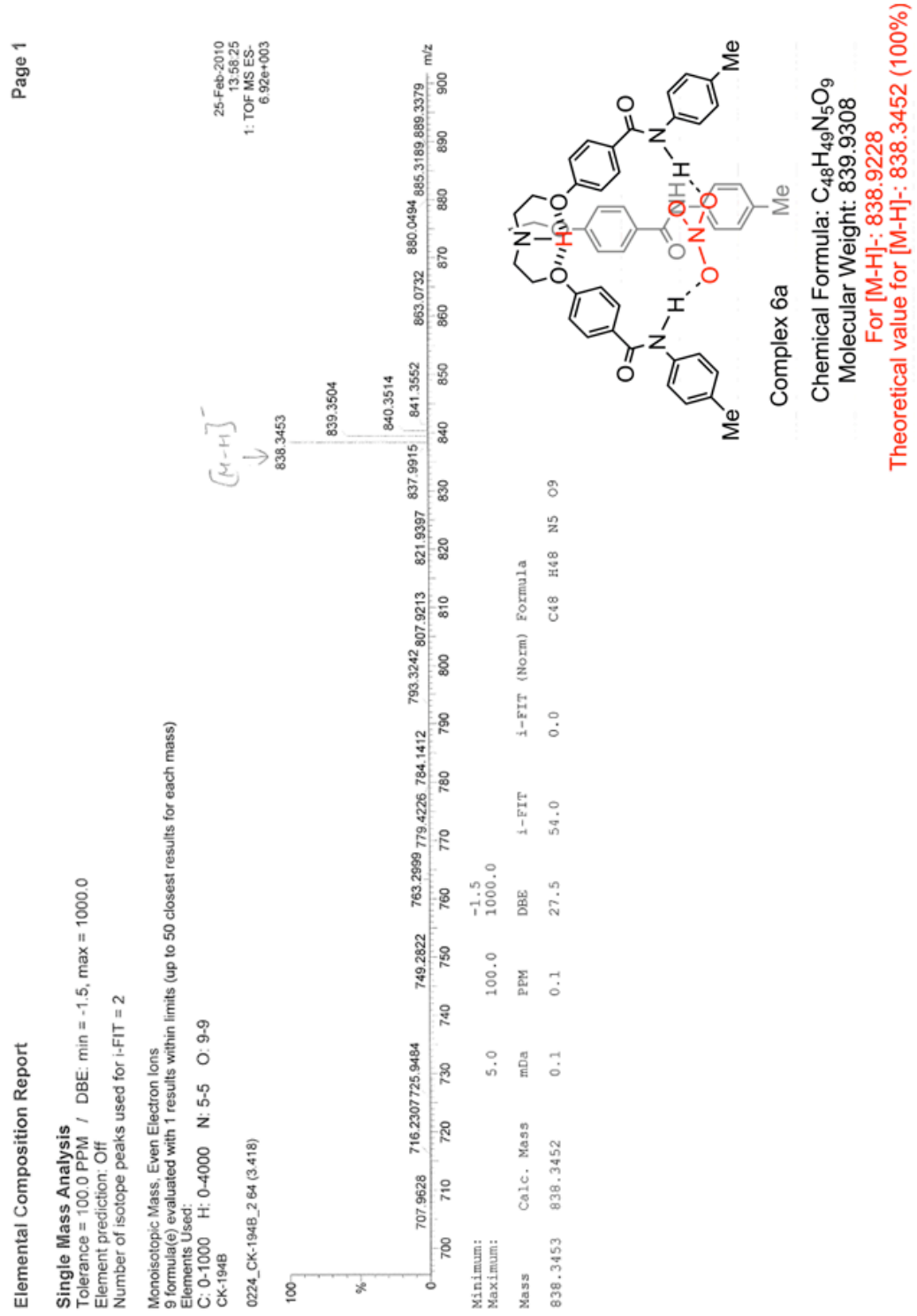

Fig. S54 HRESI mass spectrum of complex **6a**.

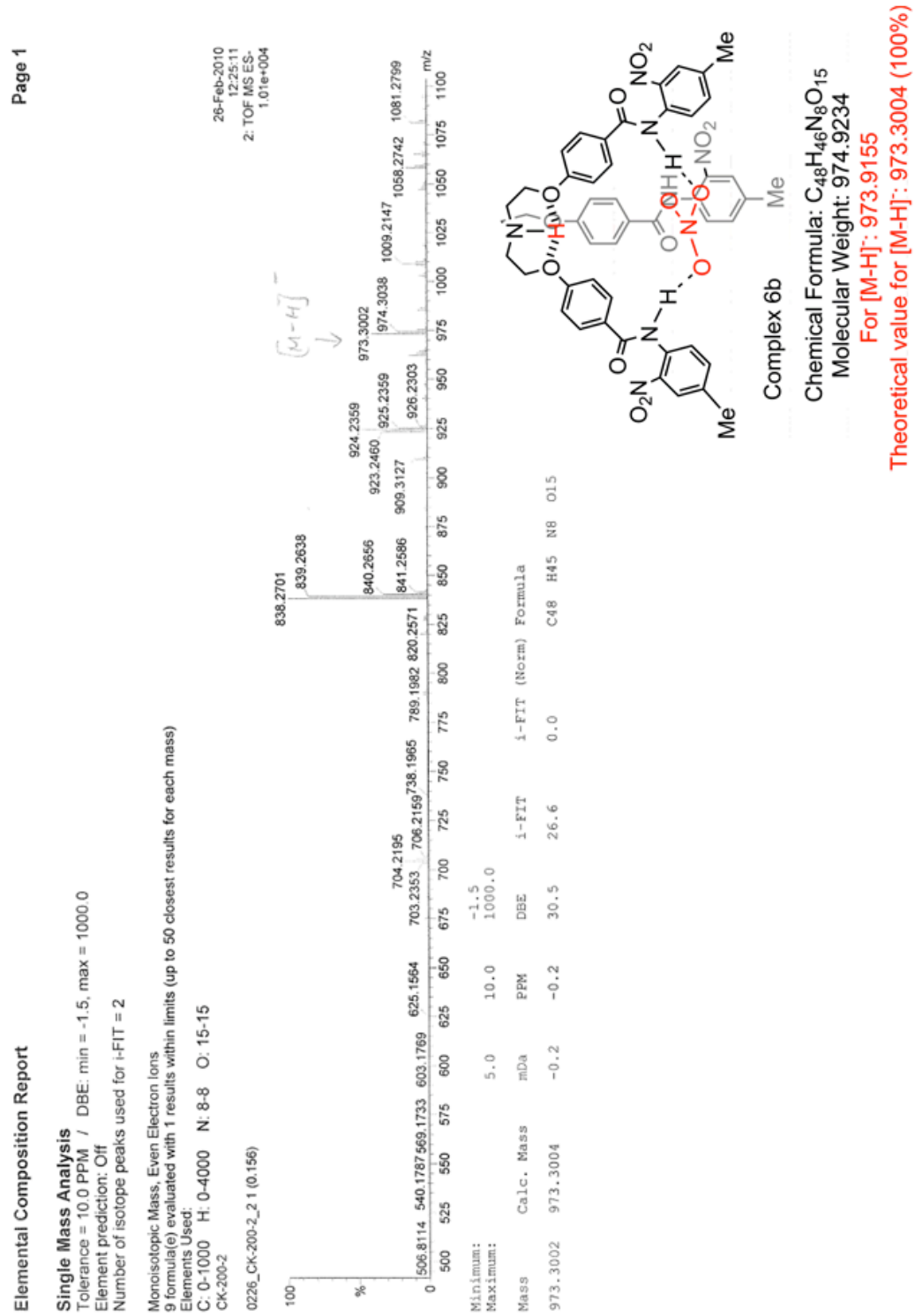

Fig. S55 HRESI mass spectrum of complex **6b**.

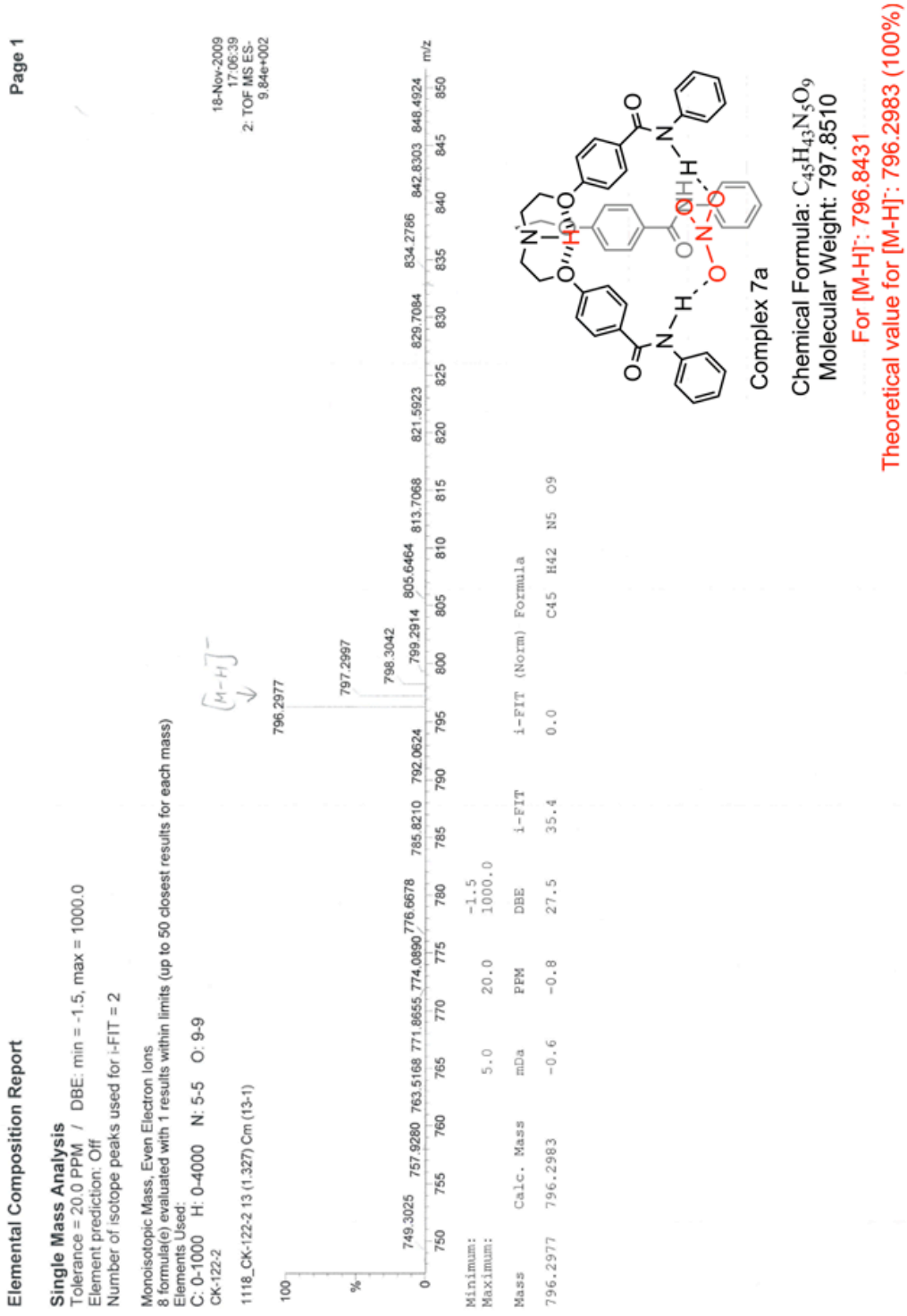

Fig. S56 HRESI mass spectrum of complex **7a**.

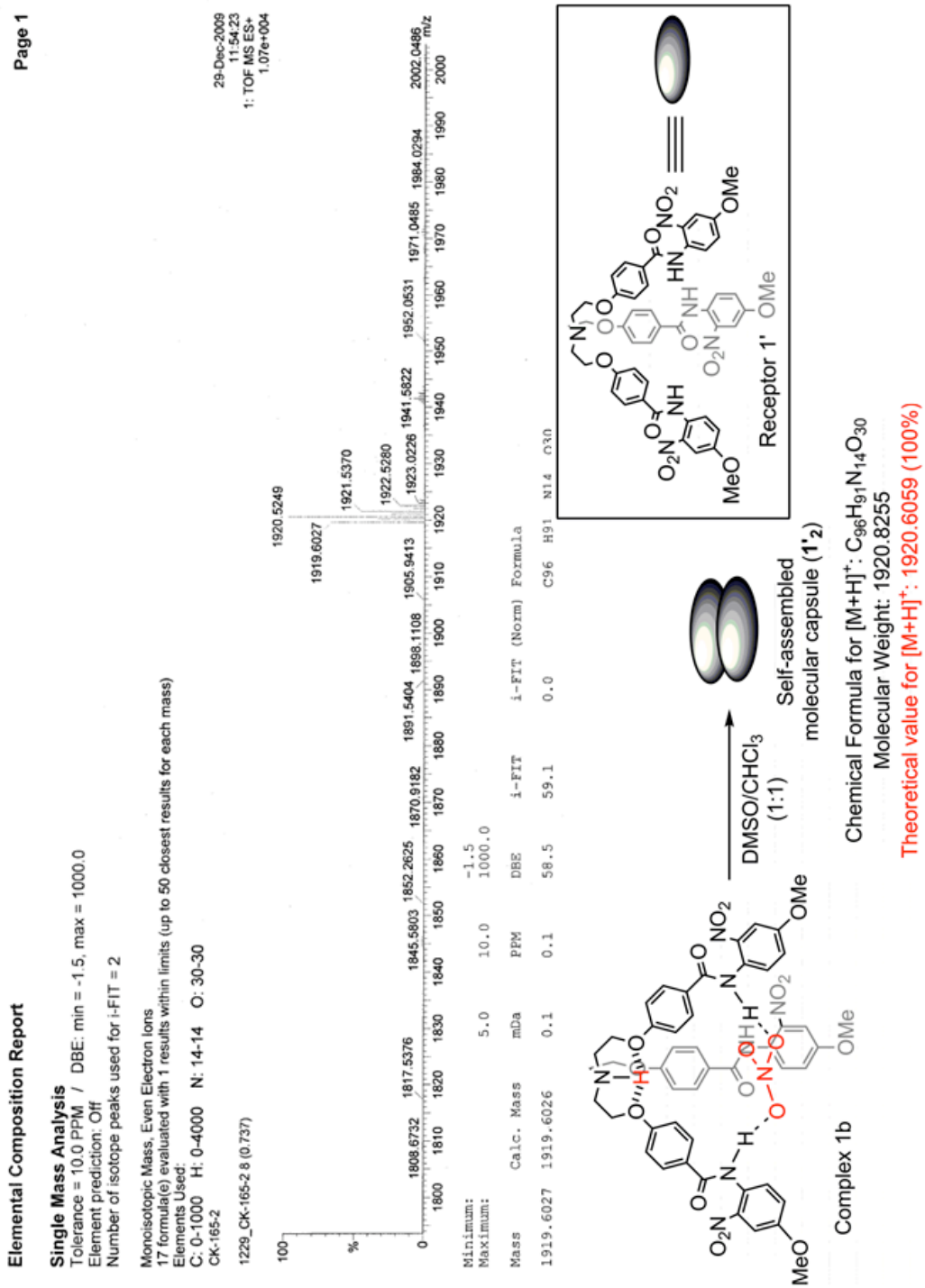

Fig. S57 HRESI mass spectrum of the self-assembled capsule (**1'$_2$**) recorded after dissolving nitrate complex **1b** in a mixture solution of DMSO/$CHCl_3$ (1:1).

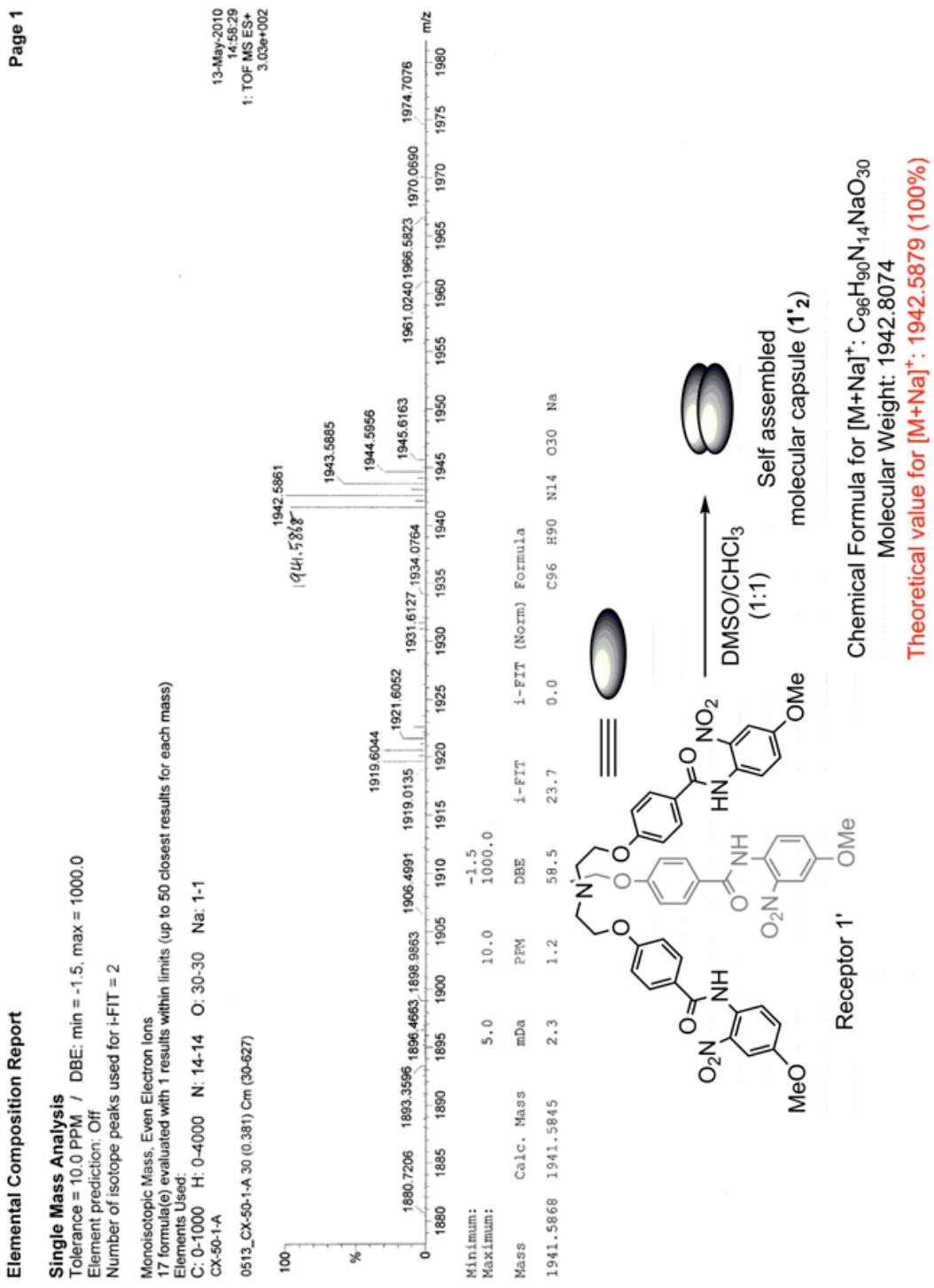

Fig. S58 HRESI mass spectrum of the self-assembled capsule (**1'$_2$**) recorded after dissolving receptor **1'** in a mixture solution of DMSO/$CHCl_3$ (1:1).

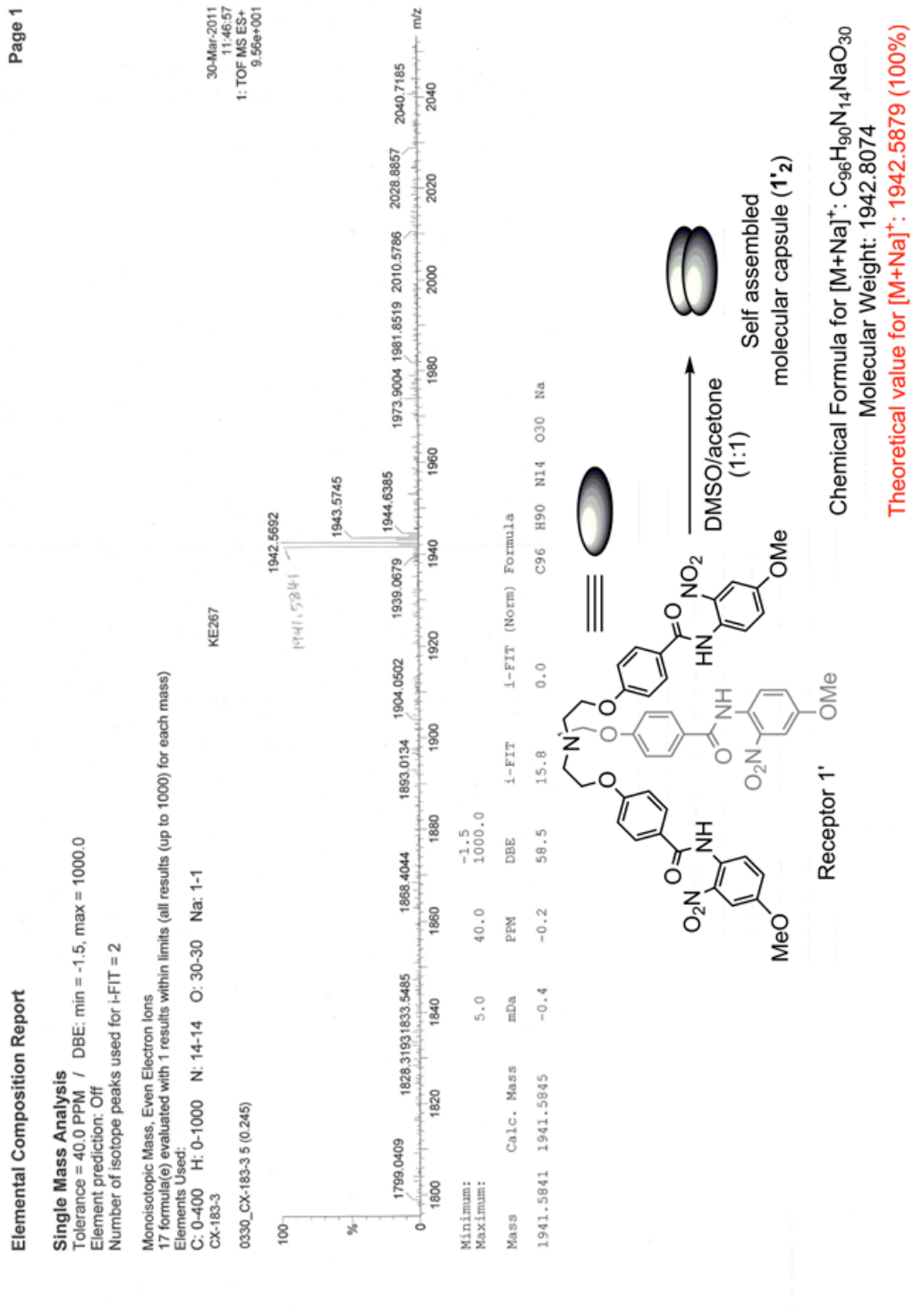

Fig. S59 HRESI mass spectrum of the self-assembled capsule (**1'$_2$**) recorded by dissolving receptor **1'** to a mixture solution of DMSO/acetone (1:1, *v/v*).

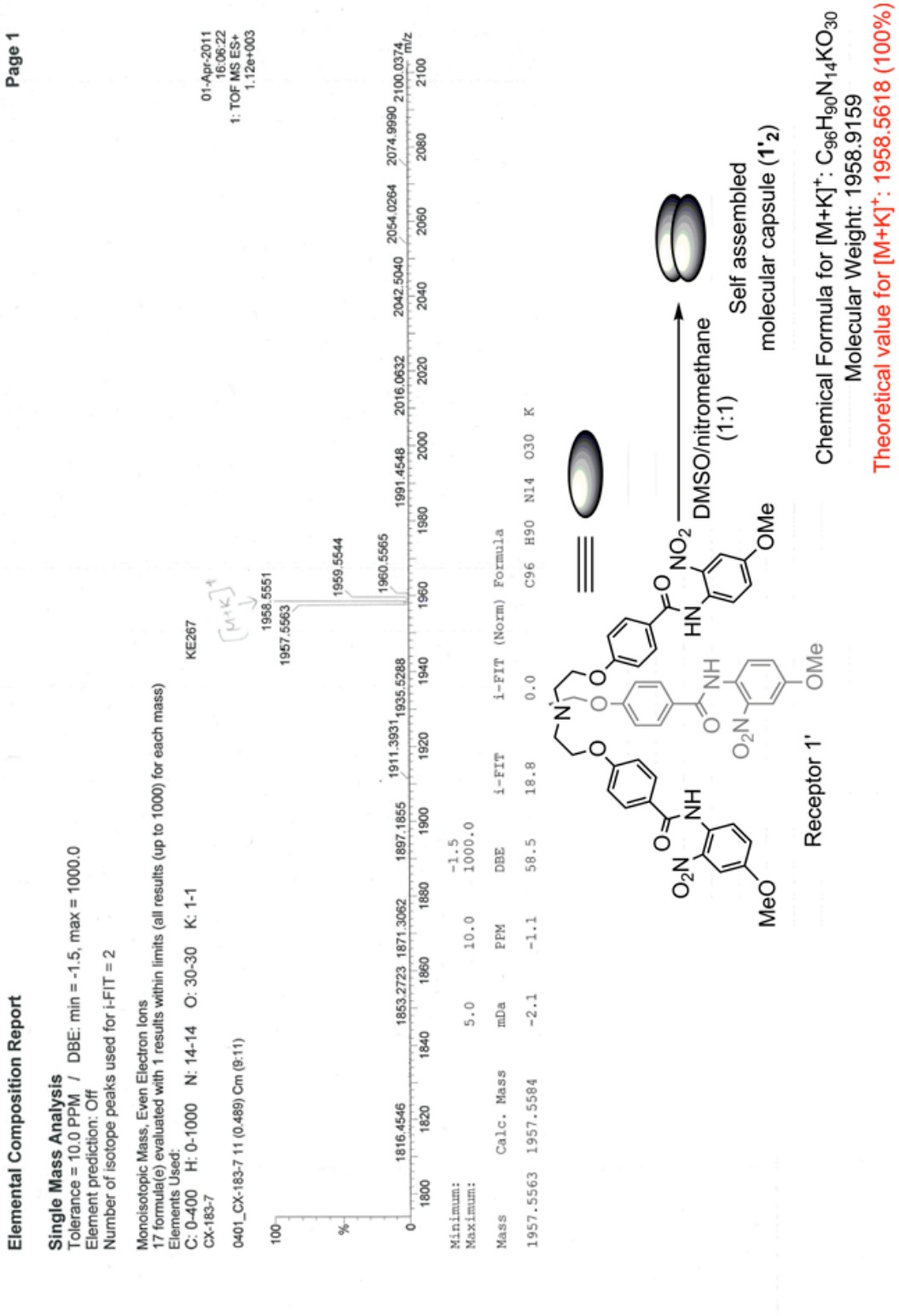

Fig. S60 HRESI mass spectrum of the self-assembled capsule (**1'$_2$**) recorded by dissolving receptor **1'** to a mixture solution of DMSO/CH_3NO_2 (1:1, *v/v*).

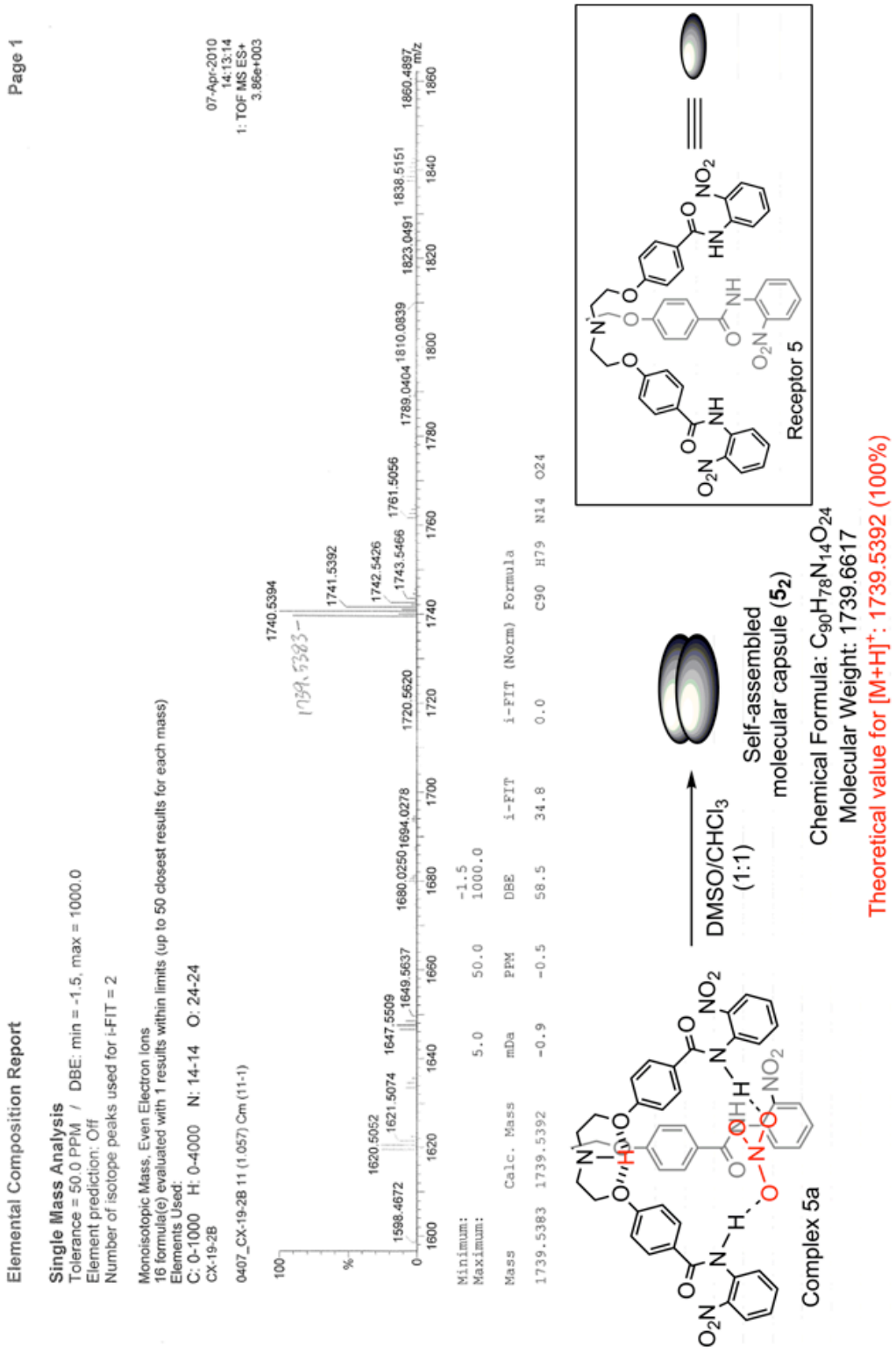

Fig. S61 HRESI mass spectrum of the self-assembled capsule (**5_2**) recorded after dissolving nitrate complex **5a** in mixture solution of DMSO/$CHCl_3$ (1:1).

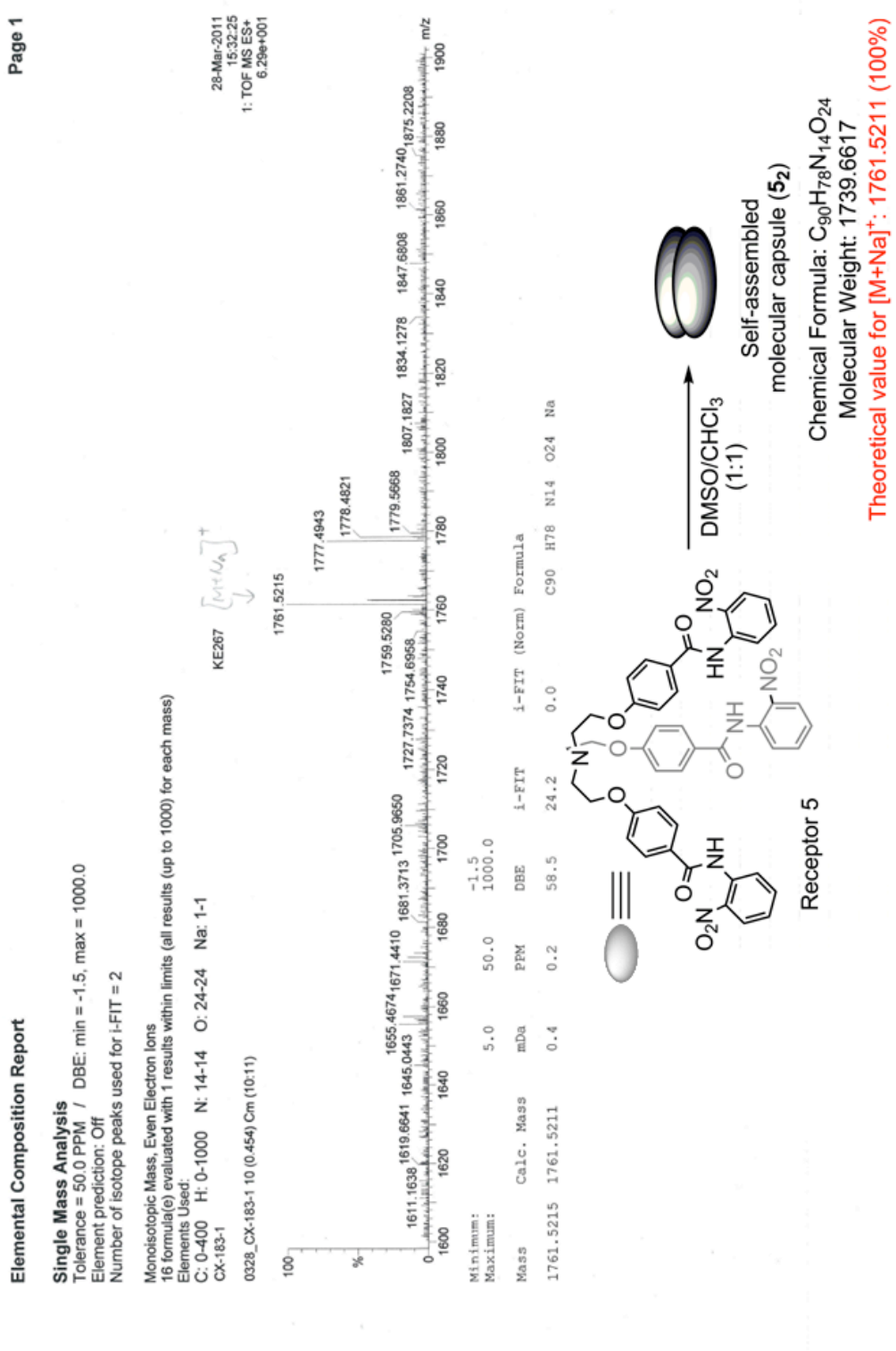

Fig. S62 HRESI mass spectrum of the self-assembled capsule ($\mathbf{5_2}$) recorded by dissolving receptor **5** to a mixture solution of DMSO/$CHCl_3$ (1:1, *v/v*).

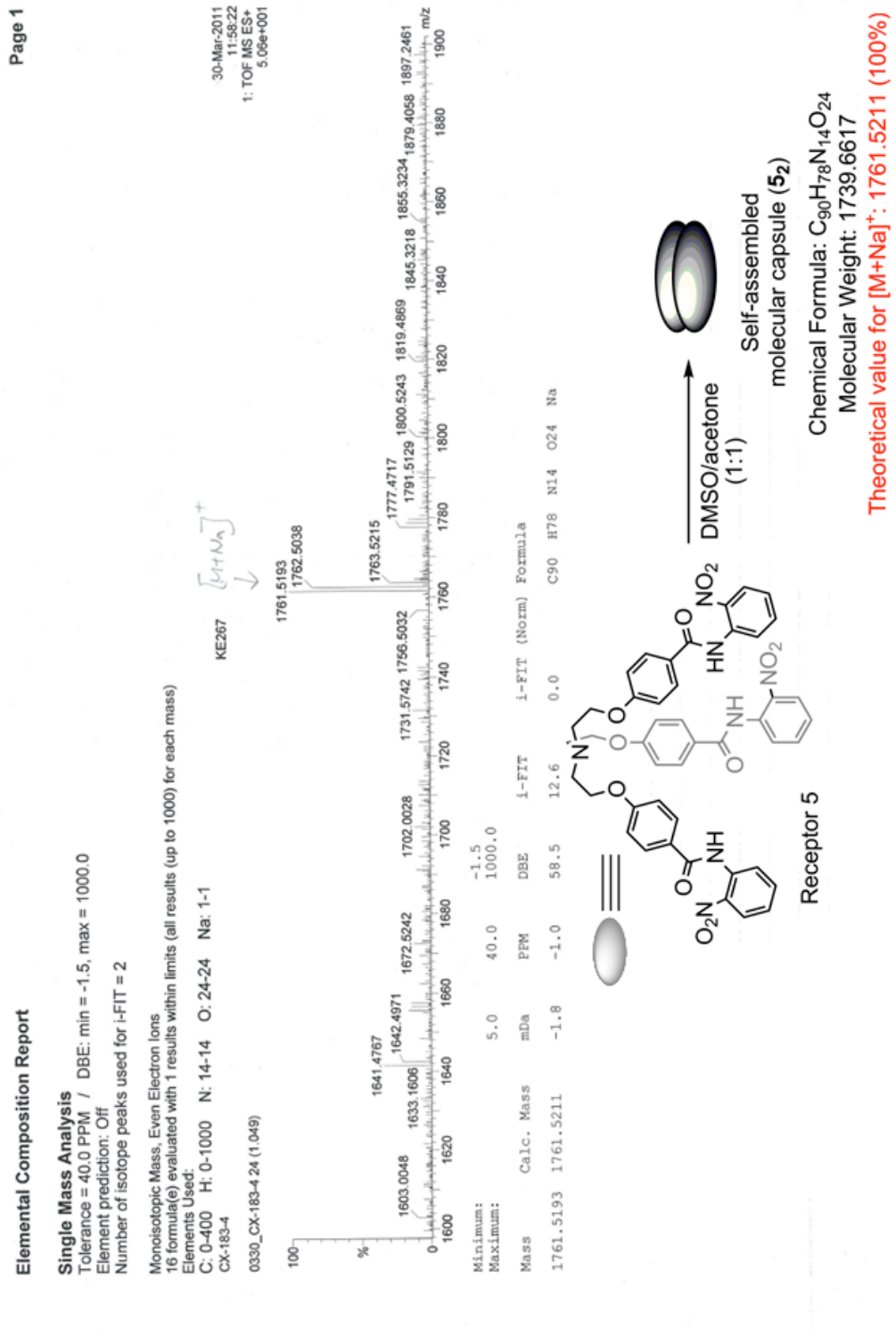

Fig. S63 HRESI mass spectrum of the self-assembled capsule (**5'$_2$**) recorded by dissolving receptor **5** to a mixture solution of DMSO/acetone-d_6 (1:1, *v/v*).

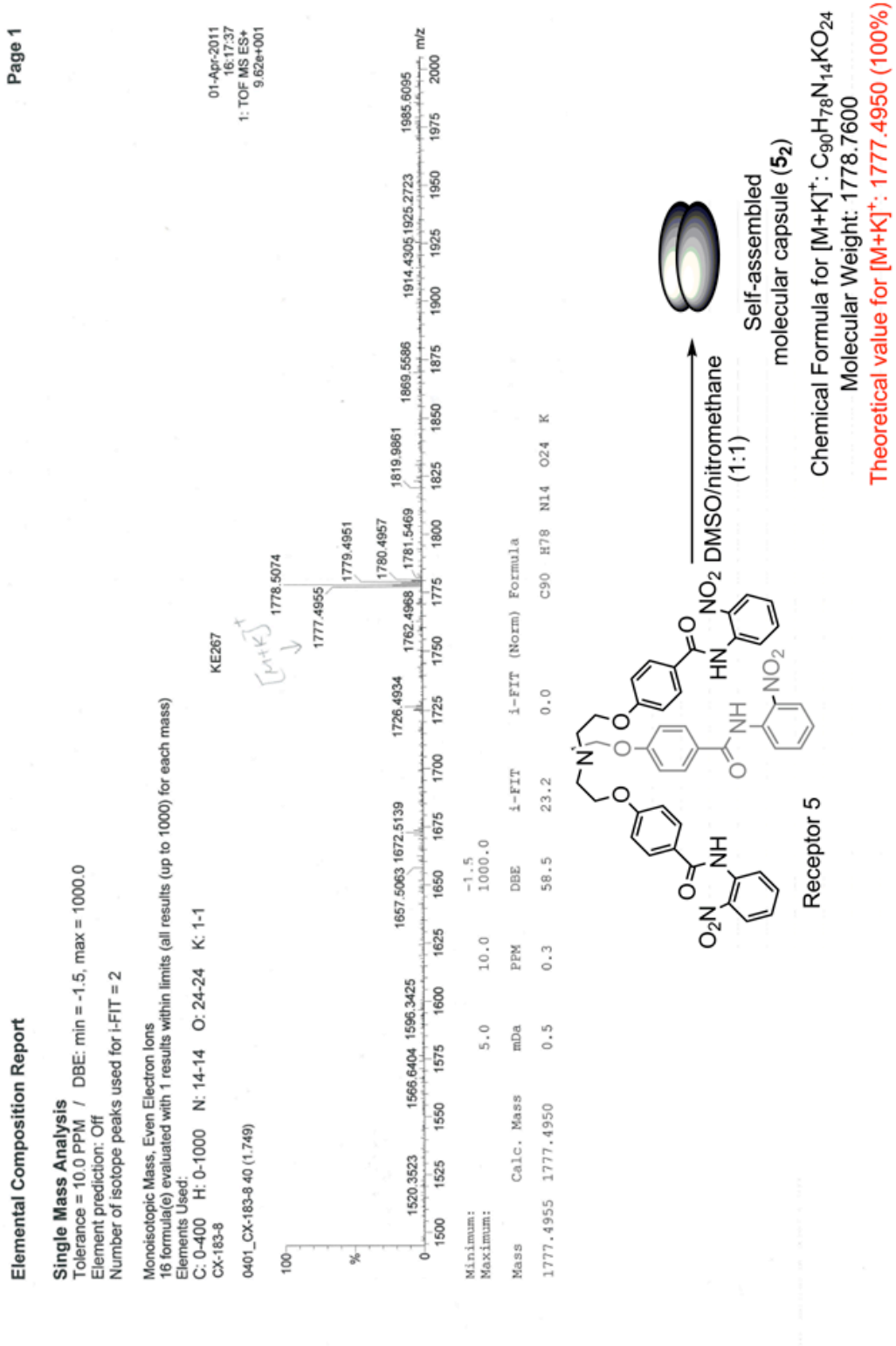

Fig. S64 HRESI mass spectra of the self-assembled capsule (**5₂**) recorded by dissolving receptor **5** to a mixture solution of DMSO/CH_3NO_2 (1:1, *v/v*).

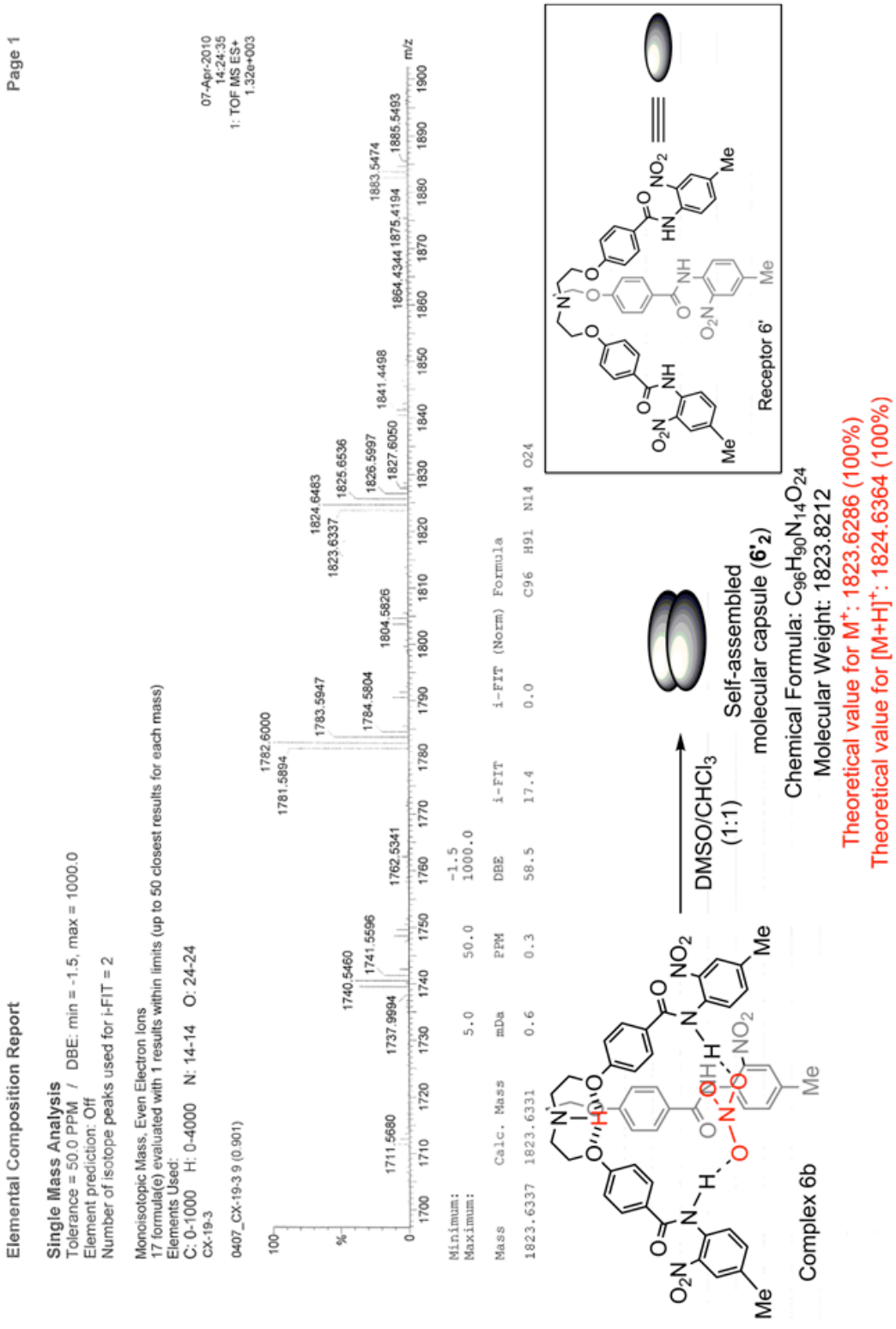

Fig. S65 HRESI mass spectrum of the self-assembled capsule (**6'$_2$**) recorded after dissolving the nitrate complex **6b** in a mixture solution of DMSO/$CHCl_3$ (1:1).

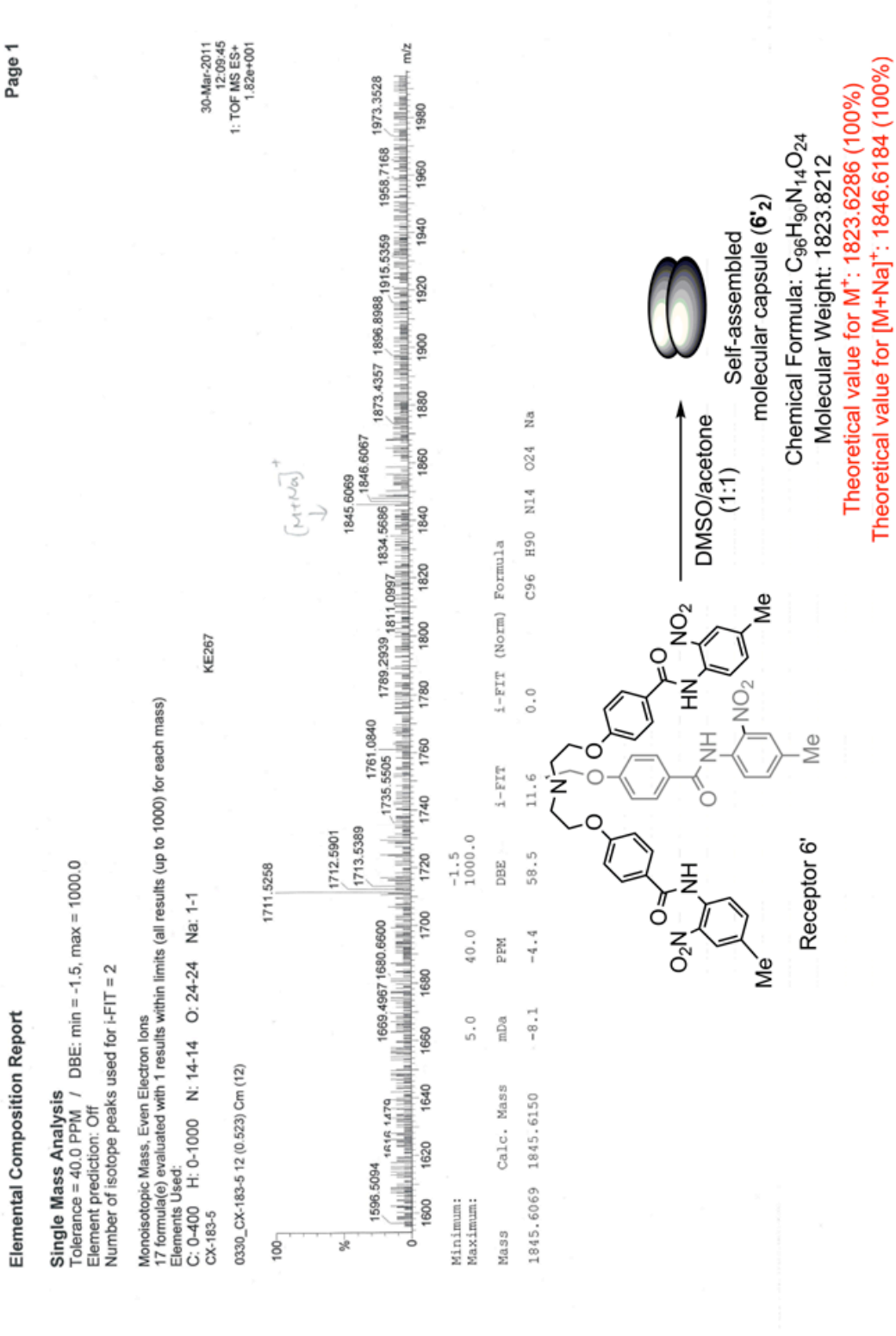

Fig. S66 HRESI mass spectra of the self-assembled capsule (**6'$_2$**) recorded by dissolving receptor **6'** to a mixture solution of DMSO/acetone (1:1, *v/v*).

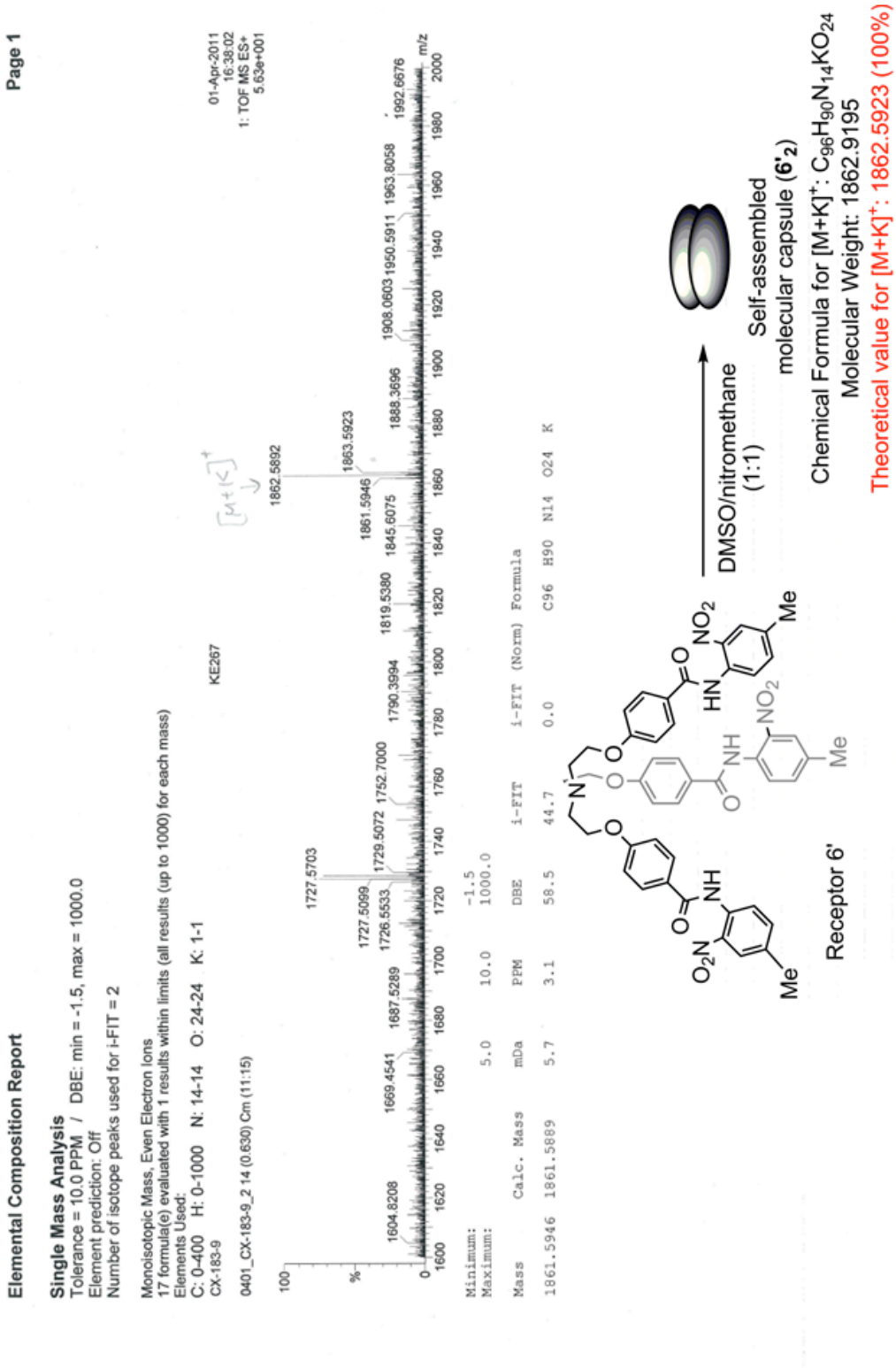

Fig. S67 HRESI mass spectra of the self-assembled capsule (**6'$_2$**) recorded by dissolving receptor **6'** to a mixture solution of DMSO/CH_3NO_2 (1:1, *v/v*).

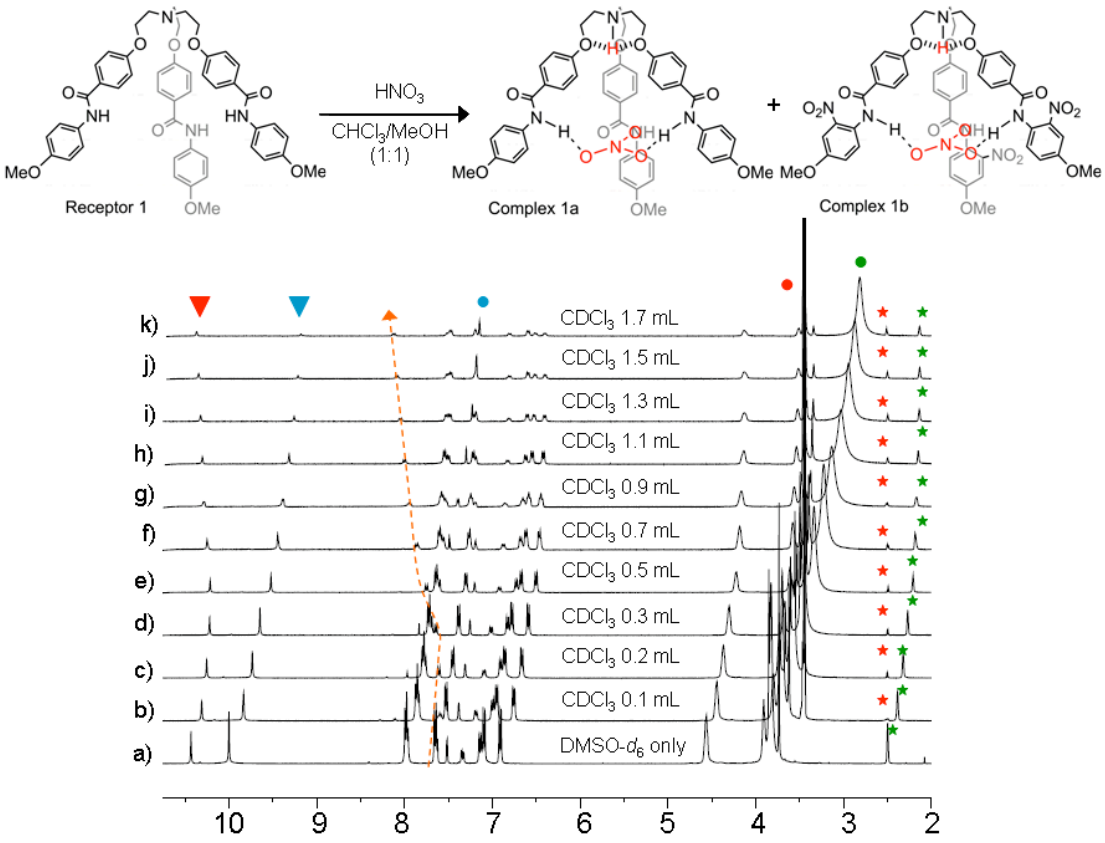

Fig. S68 ^{1}H NMR titration spectra of a mixture of nitrate complexes (in DMSO-d_6 with varying amount of $CDCl_3$) obtained after addition of nitric acid in aqueous methanol to a suspension of receptor **1** in $CHCl_3$. The star marks in green and red color represent the peaks for DMSO-d_6 (as solvent) and DMSO-d_6 (as internal reference, TMS in DMSO-d_6), respectively. The circles in green and red color represent water peaks from DMSO-d_6 (as solvent) and from DMSO-d_6 (as internal reference, TMS in DMSO-d_6), respectively. The triangles in red and blue color represent amide N-H peaks of nitrate complexes **1b** and **1a**, respectively. The circle in blue color represents peak for $CDCl_3$.

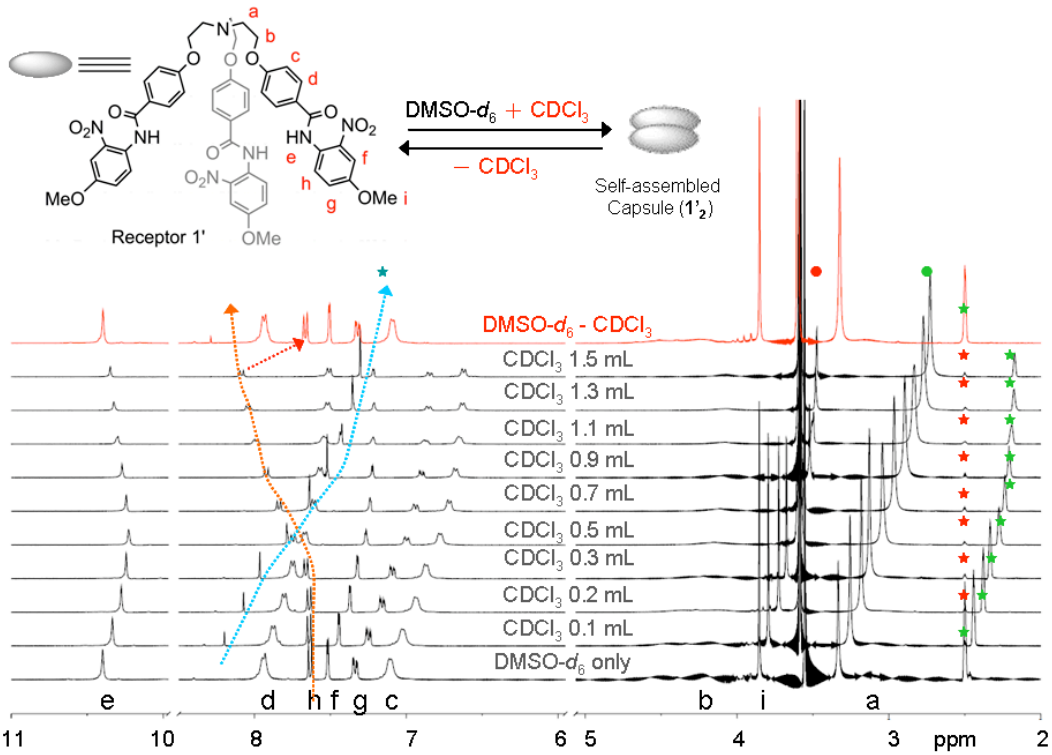

Fig. S69 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **1'** (10.3 mM) in DMSO-d_6 with varying amount of $CDCl_3$ with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A star mark in blue color represents peak for $CDCl_3$. The spectrum in red color was recorded after partial evaporation of $CDCl_3$ from the mixture solution, showing reversible capsule formation through dynamic self-assembly of receptor **1'**.

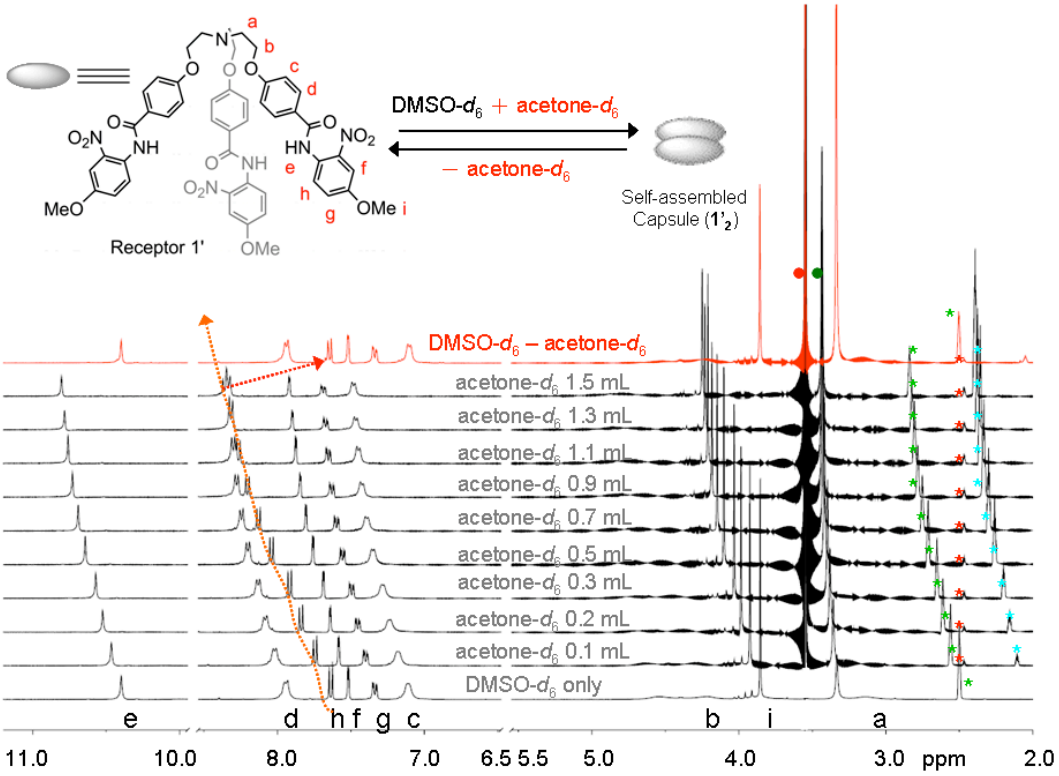

Fig. S70 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **1'** (10.3 mM) in DMSO-d_6 with varying amount of acetone-d_6 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. Star marks in blue color represent the peaks for acetone-d_6. The spectrum in red color was recorded after partial evaporation of acetone-d_6 from the mixture solution, showing reversible capsule formation through dynamic self-assembly of receptor **1'**.

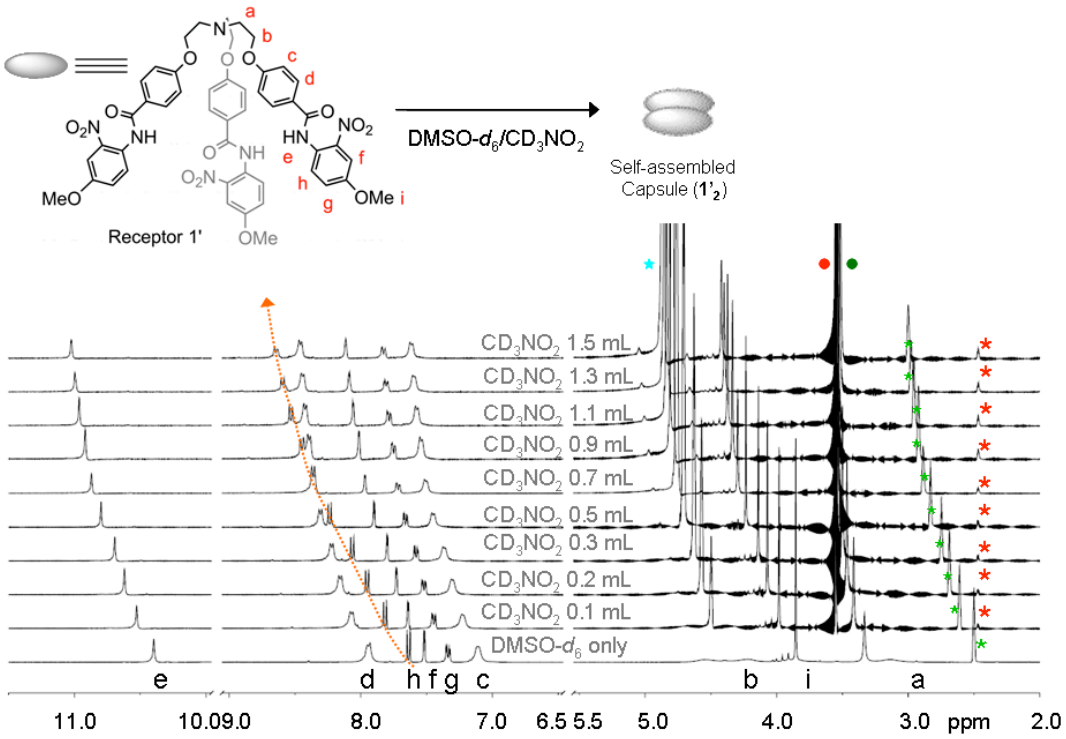

Fig. S71 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **1'** (10.3 mM) in DMSO-d_6 with varying amount of CD_3NO_2 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A star mark in blue color represents peak for CD_3NO_2.

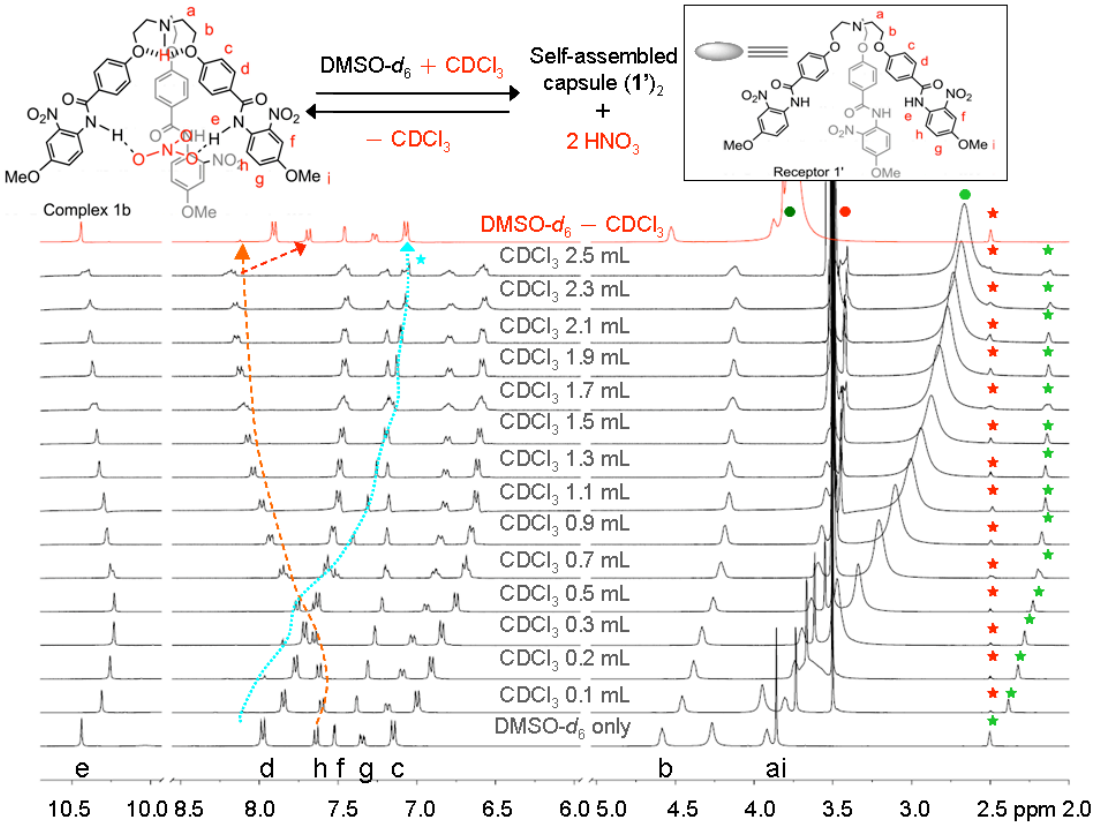

Fig. S72 ^{1}H NMR (400 MHz, 20 °C) titration spectra of nitrate complex **1b** (10.3 mM) in DMSO-d_6 with varying amount of $CDCl_3$ with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A star mark in blue color represents peak for $CDCl_3$. The spectrum in red color was recorded after partial evaporation of $CDCl_3$ from the mixture solution, showing reversible binding of nitrate anion by receptor **1'**.

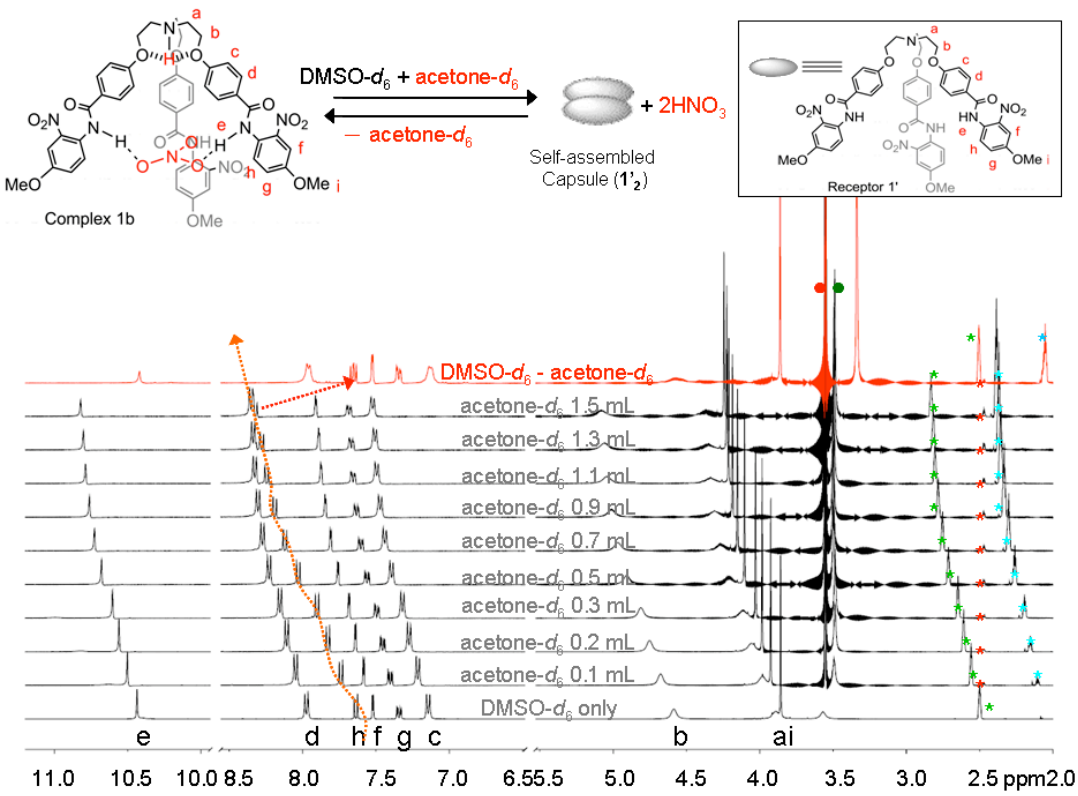

Fig. S73 ^{1}H NMR (400 MHz, 20 °C) titration spectra of nitrate complex **1b** (10.3 mM) in DMSO-d_6 with varying amount of acetone-d_6 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A star mark in blue color represents the peak for acetone-d_6. The spectrum in red color was recorded after partial evaporation of acetone-d_6 from the mixture solution, showing reversible binding of nitrate anion by receptor **1'**.

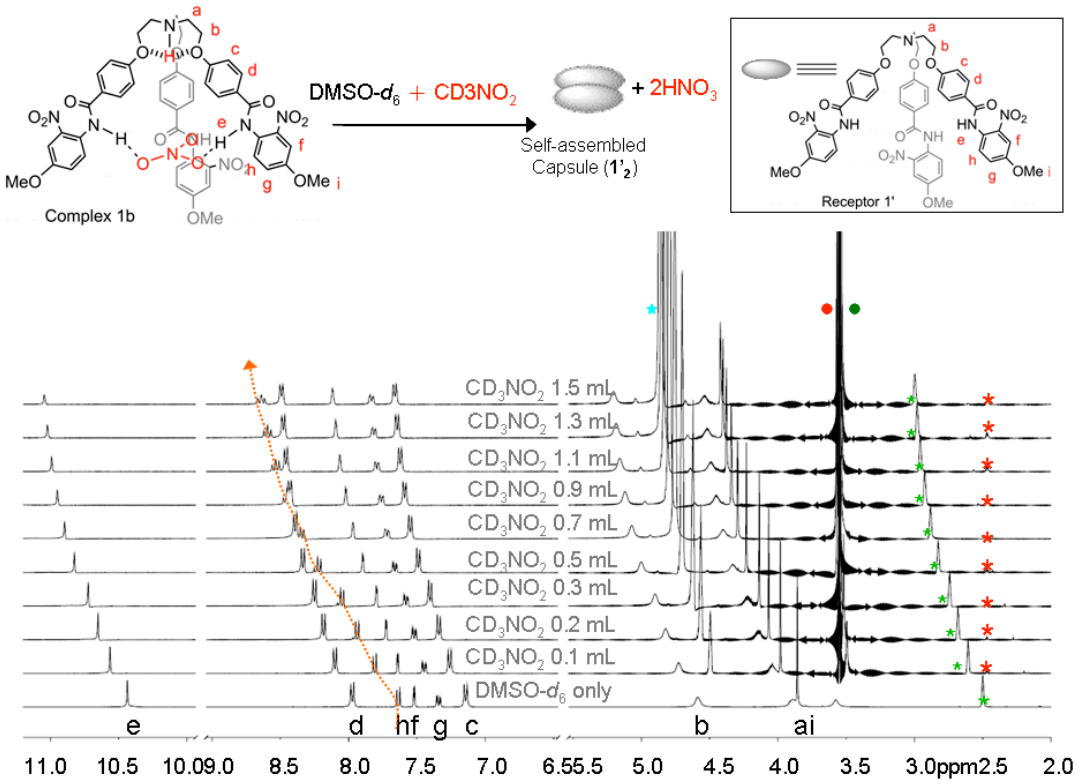

Fig. S74 ^{1}H NMR (400 MHz, 20 °C) titration spectra of nitrate complex **1b** (10.3 mM) in DMSO-d_6 with varying amount of CD_3NO_2 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A star mark in blue color represents the peak for CD_3NO_2.

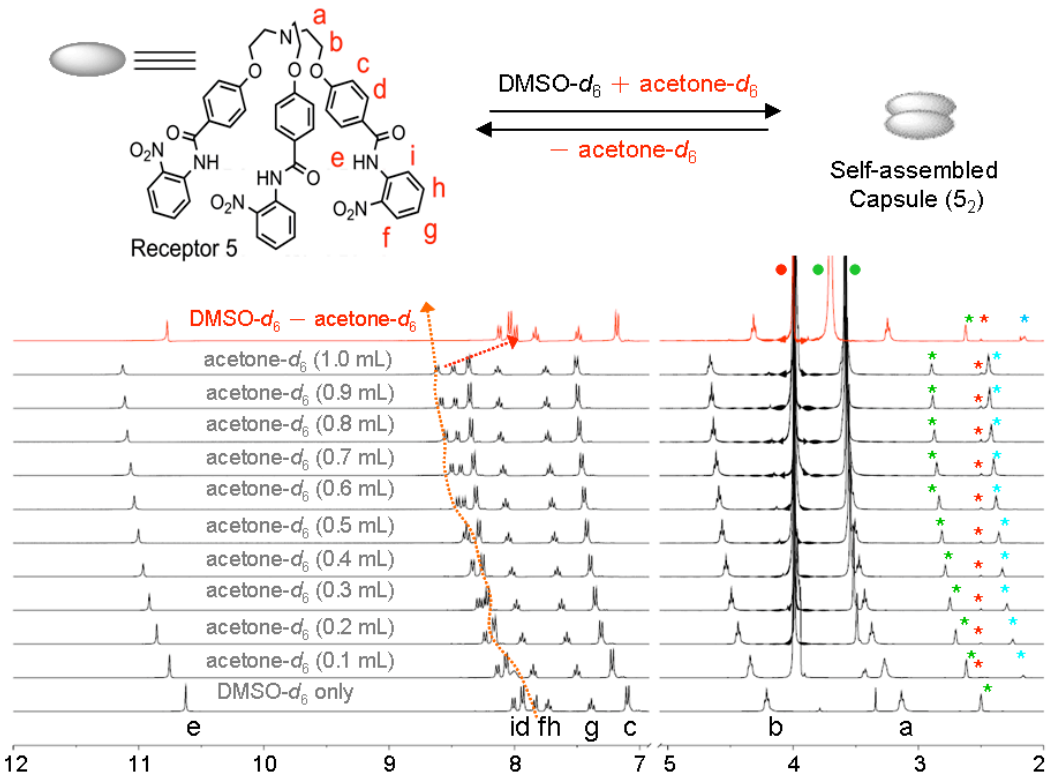

Fig. S75 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **5** (10.3 mM) in DMSO-d_6 with varying amount of acetone-d_6 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A star mark in blue color represents the peak for acetone-d_6.

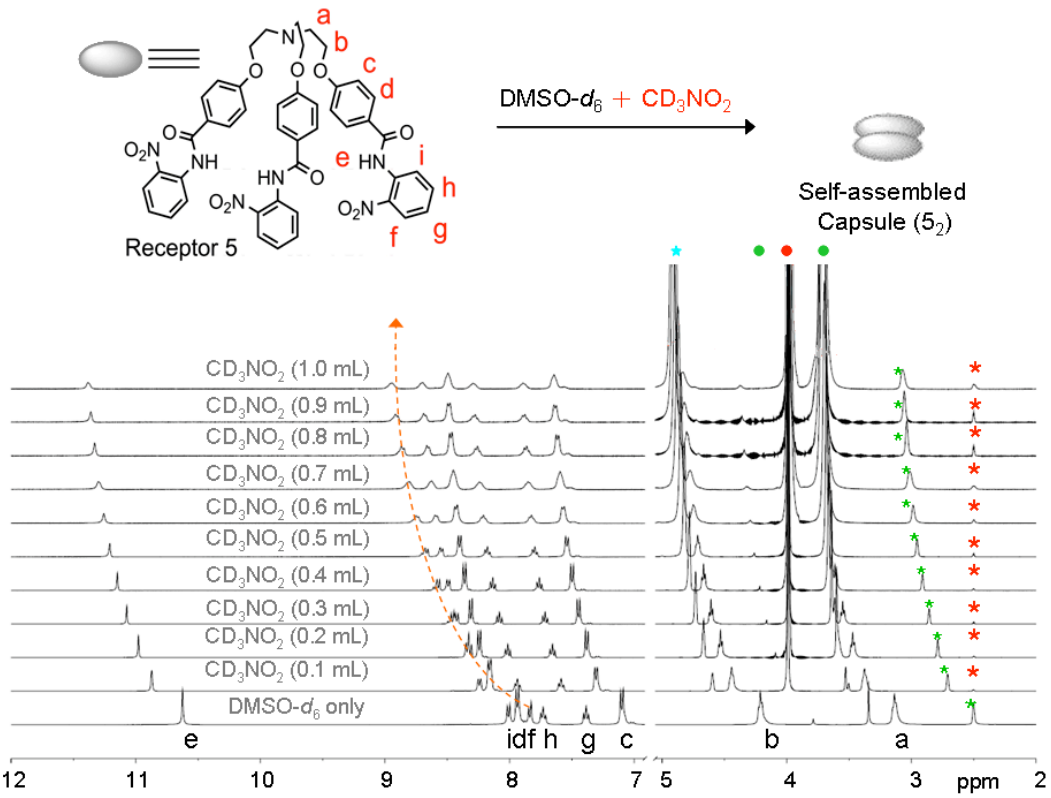

Fig. S76 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **5** (10.3 mM) in DMSO-d_6 with varying amount of CD_3NO_2 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A star mark in blue color represents the peak for CD_3NO_2.

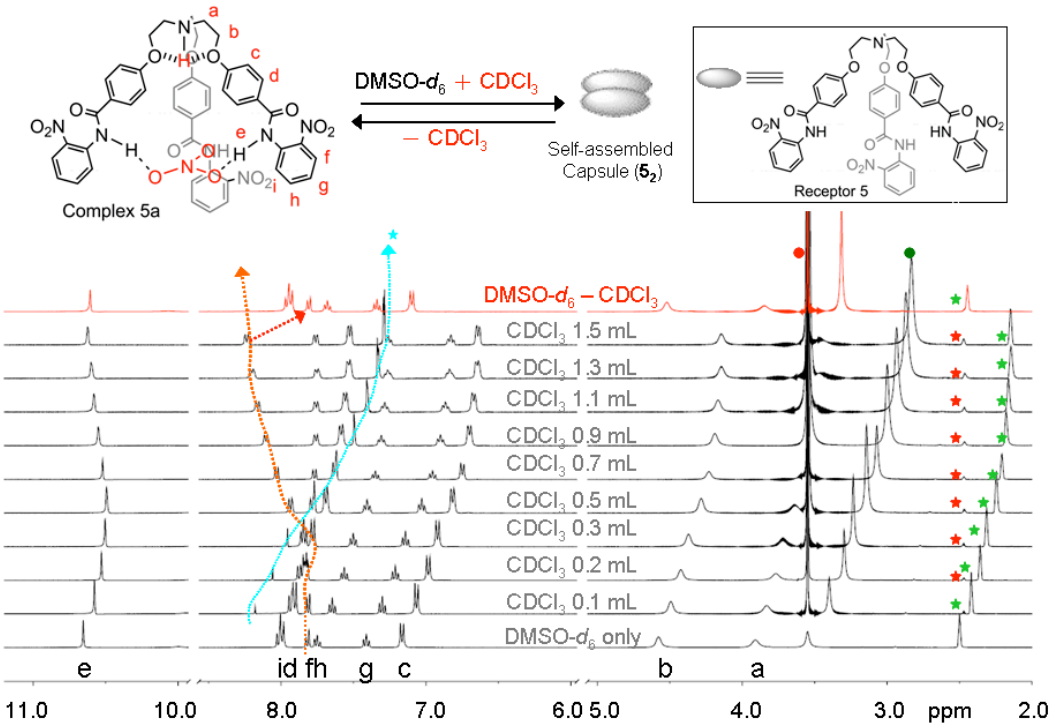

Fig. S77 ^{1}H NMR (400 MHz, 20 °C) titration spectra of nitrate complex **5a** (10.3 mM) in DMSO-d_6 with varying amount of $CDCl_3$ with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A star mark in blue color represents the peak for $CDCl_3$. The spectrum in red color was recorded after partial evaporation of $CDCl_3$ from the mixture solution, showing reversible binding of nitrate anion by receptor **5**.

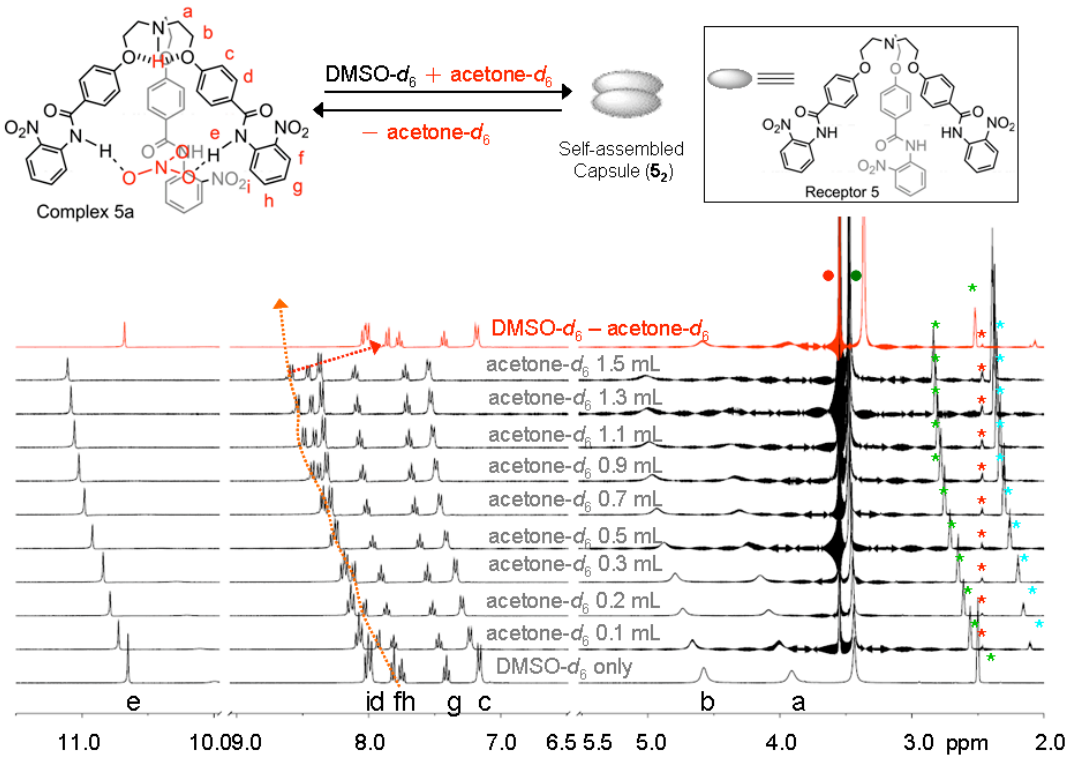

Fig. S78 ^{1}H NMR (400 MHz, 20 °C) titration spectra of nitrate complex **5a** (10.3 mM) in DMSO-d_6 with varying amount of acetone-d_6 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A star mark in blue color represents the peak for acetone-d_6. The spectrum in red color was recorded after partial evaporation of acetone-d_6 from the mixture solution, showing reversible binding of nitrate anion by receptor **5**.

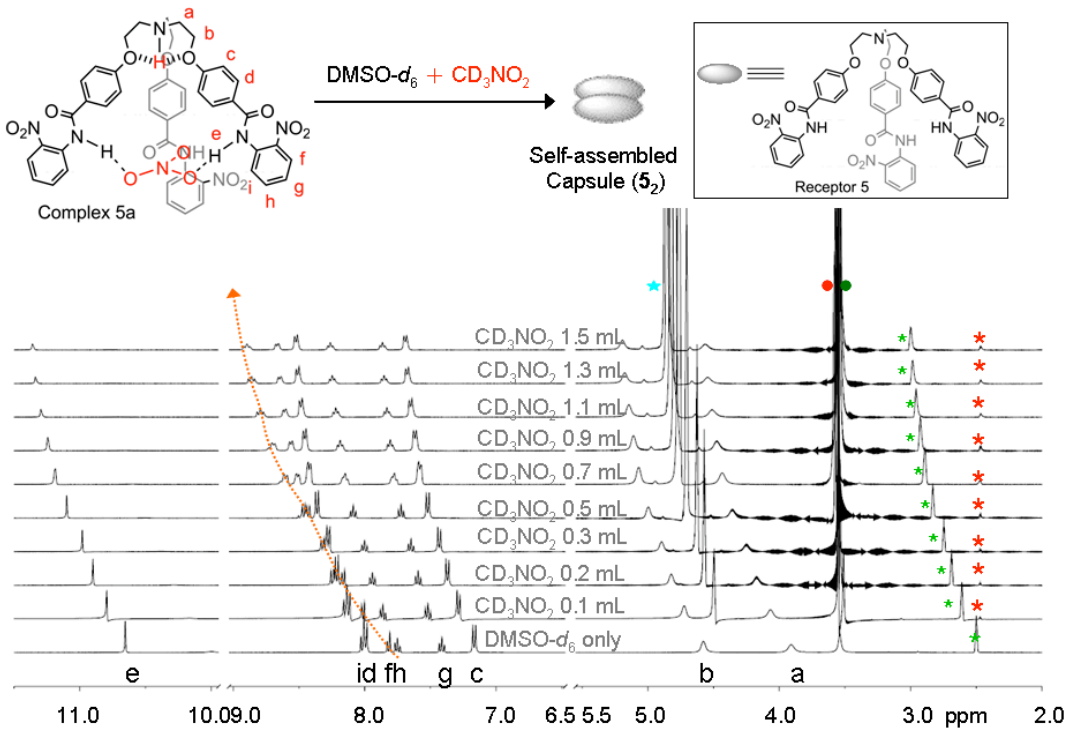

Fig. S79 ^{1}H NMR (400 MHz, 20 °C) titration spectra of nitrate complex **5a** (10.3 mM) in DMSO-d_6 with varying amount of CD_3NO_2 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A star mark in blue color represents peak for CD_3NO_2.

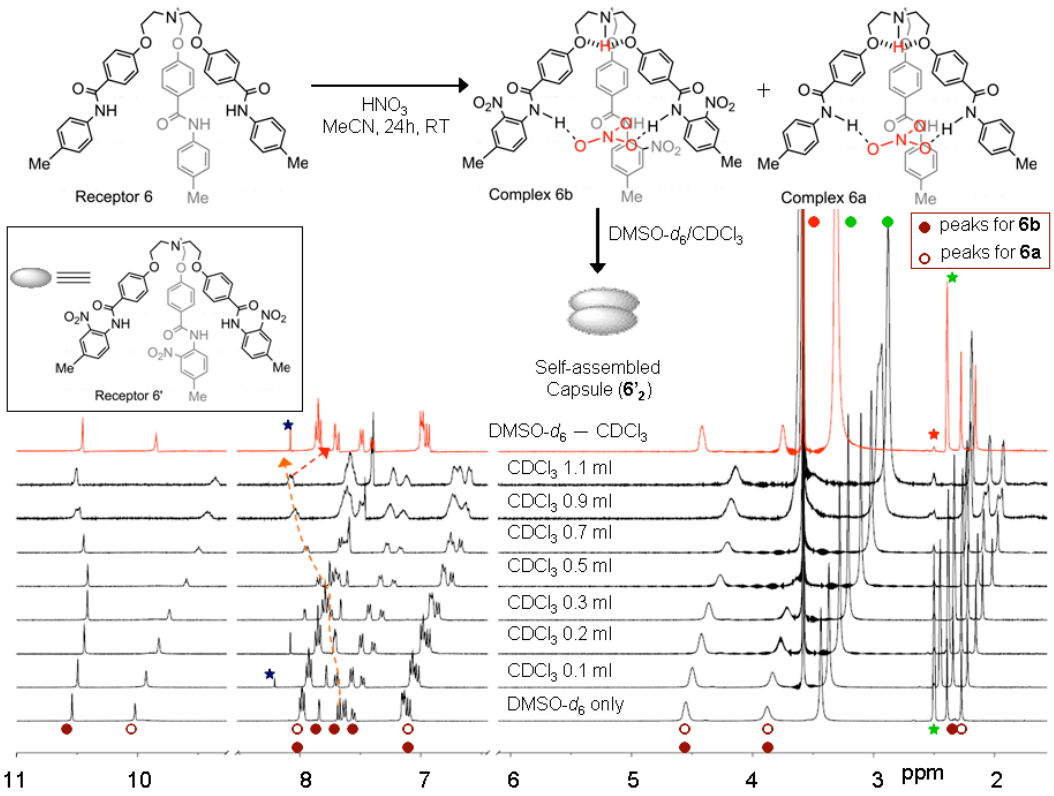

Fig. S80 ^{1}H NMR titration spectra of mixture of nitrate complex (in DMSO-d_6 with varying amount of $CDCl_3$), obtained after addition of nitric acid in an aqueous methanol to the suspension of receptor **6** in $CHCl_3$. The star marks in green and red color represents peak corresponding to DMSO-d_6 (as solvent) and DMSO-d_6 (as internal reference, TMS in DMSO-d_6), respectively. Circle in green color represents water peak from DMSO-d_6 (as solvent) and the same in red color represents water peak from DMSO-d_6 (as internal reference, TMS in DMSO-d_6). A star mark in blue color represents peak for $CDCl_3$.

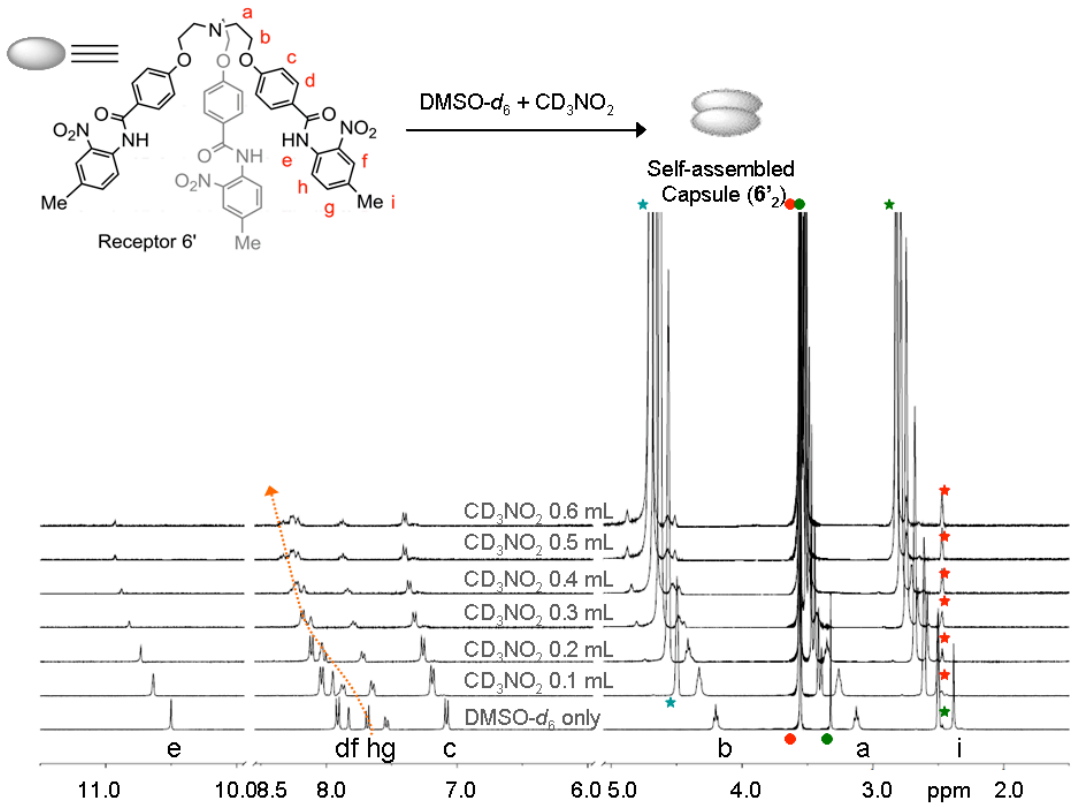

Fig. S81 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **6'** (10.3 mM) in DMSO-d_6 with varying amount of CD_3NO_2 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A star mark in blue color represents the peak for CD_3NO_2.

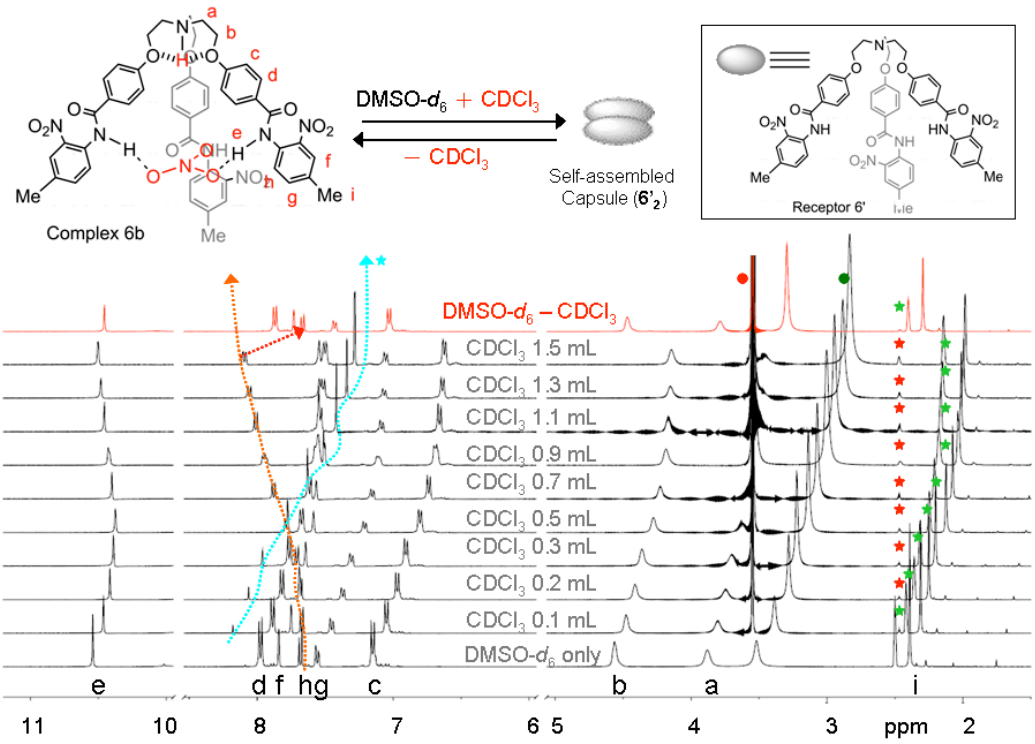

Fig. S82 ^{1}H NMR (400 MHz, 20 °C) titration spectra of nitrate complex **6b** (10.3 mM) in DMSO-d_6 with varying amount of $CDCl_3$ with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A star mark in blue color represents the peak for $CDCl_3$. The spectrum in red color was recorded after partial evaporation of $CDCl_3$ from the mixture solution, showing reversible binding of nitrate anion by receptor **6'**.

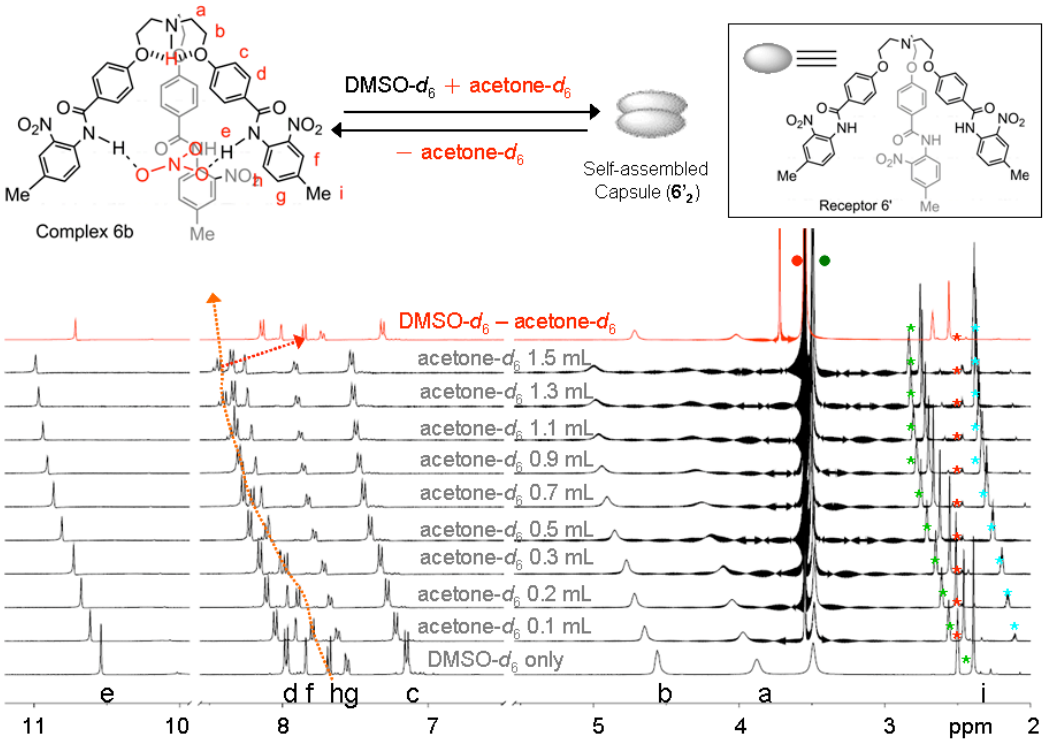

Fig. S83 ^{1}H NMR (400 MHz, 20 °C) titration spectra of nitrate complex **6b** (10.3 mM) in DMSO-d_6 with varying amount of acetone-d_6 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A star mark in blue color represents peak for acetone-d_6. The spectrum in red color was recorded after partial evaporation of acetone-d_6 from the mixture solution, showing reversible binding of nitrate anion by receptor **6'**.

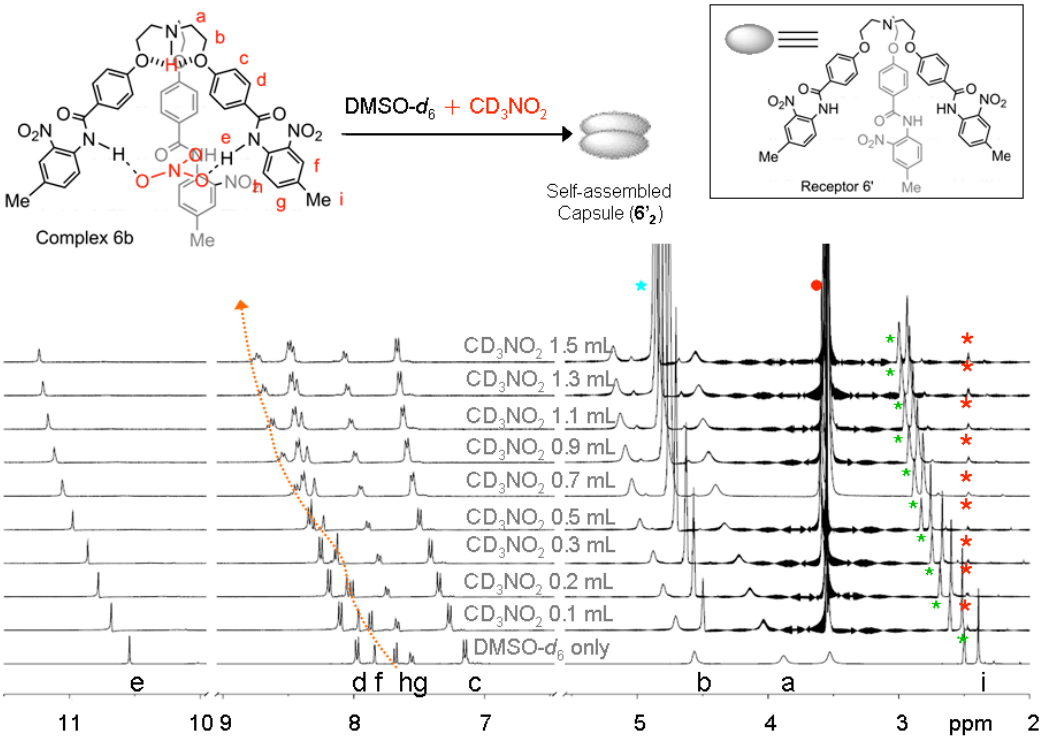

Fig. S84 ^{1}H NMR (400 MHz, 20 °C) titration spectra of nitrate complex **6b** (10.3 mM) in DMSO-d_6 with varying amount of CD_3NO_2 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in red color represent the peaks for water from DMSO-d_6 (internal reference). A star mark in blue color represents the peak for CD_3NO_2.

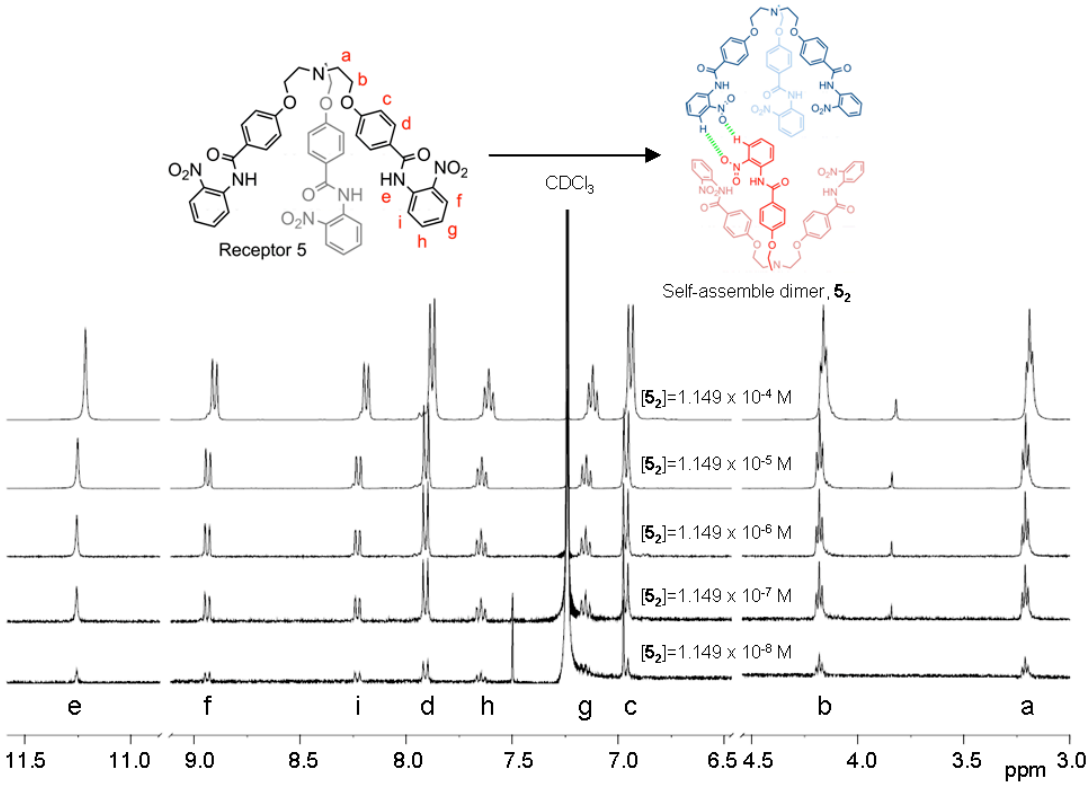

Fig. S85 Concentration dependent ^{1}H NMR of $\mathbf{5}_2$ in $CDCl_3$ showing the self-assembled capsule exists till 1×10^{-8} M concentration without formation of any side products.

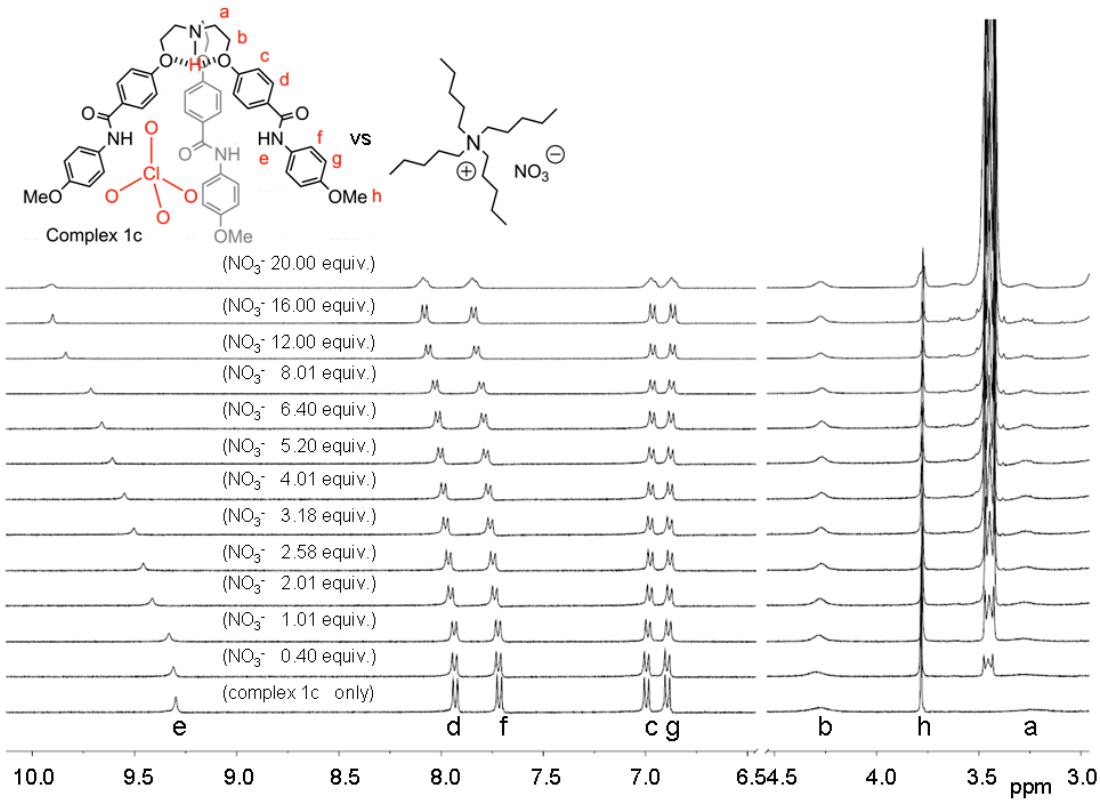

Fig. S86 Partial ^{1}H NMR titration spectra of perchlorate complex **1c** (2.96×10^{-3} M) with tetrabutylammonium nitrate in acetone-d_6.

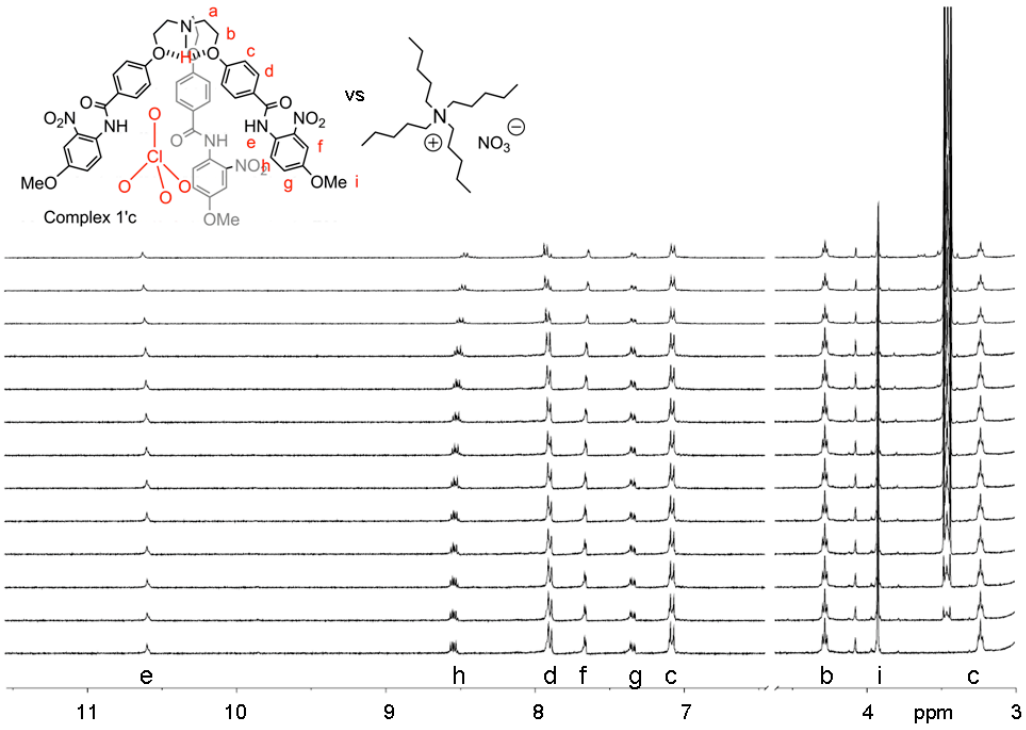

Fig. S87 Partial ^{1}H NMR titration spectra of perchlorate complex **1'c** (1.48×10^{-3} M) with tetrabutylammonium nitrate in acetone-d_6.

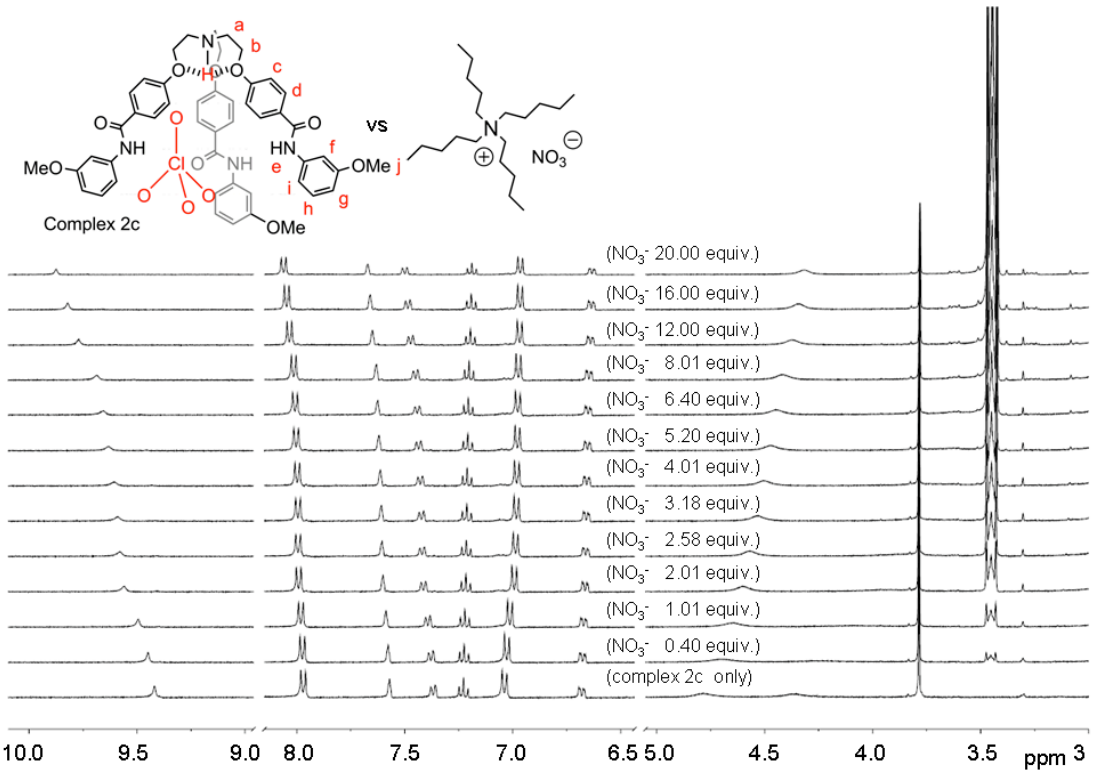

Fig. S88 Partial ^{1}H NMR titration spectra of perchlorate complex **2c** (1.48×10^{-3} M) with tetrabutylammonium nitrate in acetone-d_6.

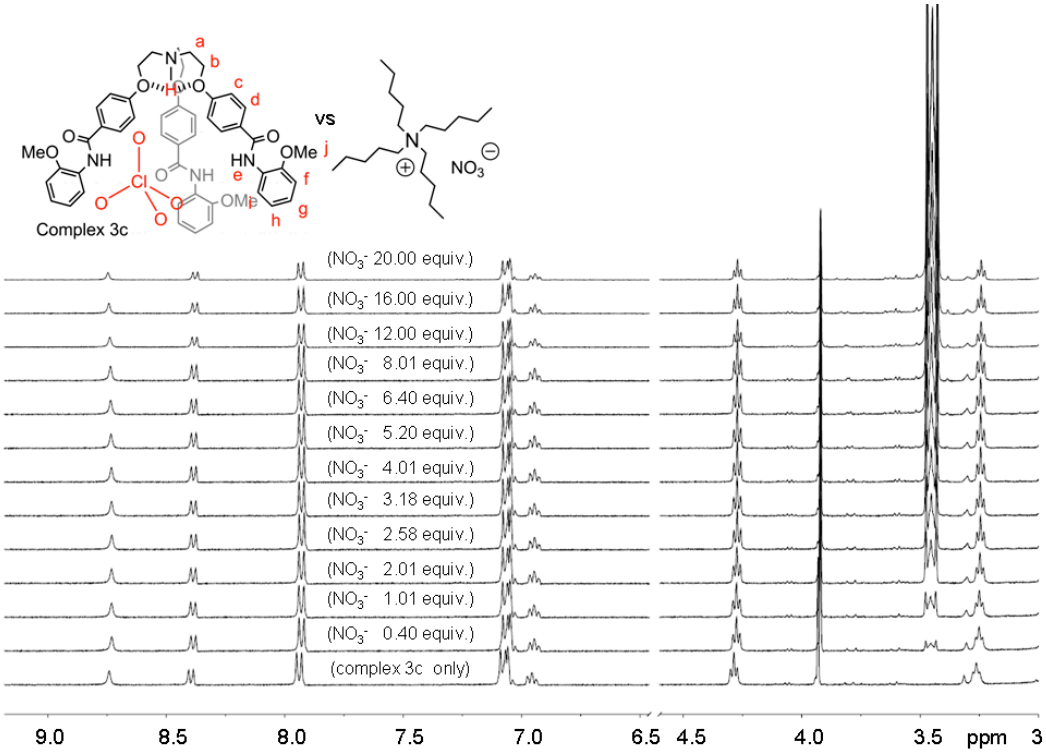

Fig. S89 Partial ^{1}H NMR titration spectra of perchlorate complex **3c** (1.48×10^{-3} M) with tetrabutylammonium nitrate in acetone-d_6.

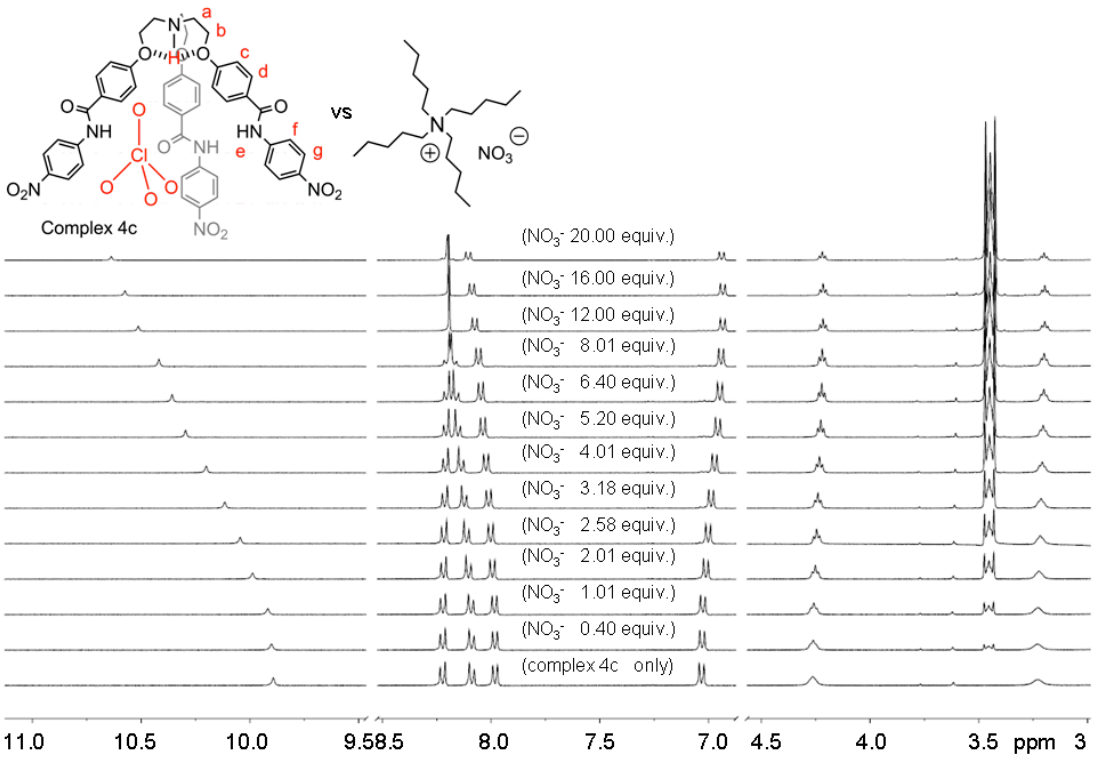

Fig. S90 Partial ^{1}H NMR titration spectra of perchlorate complex **4c** (1.48×10^{-3} M) with tetrabutylammonium nitrate in acetone-d_6.

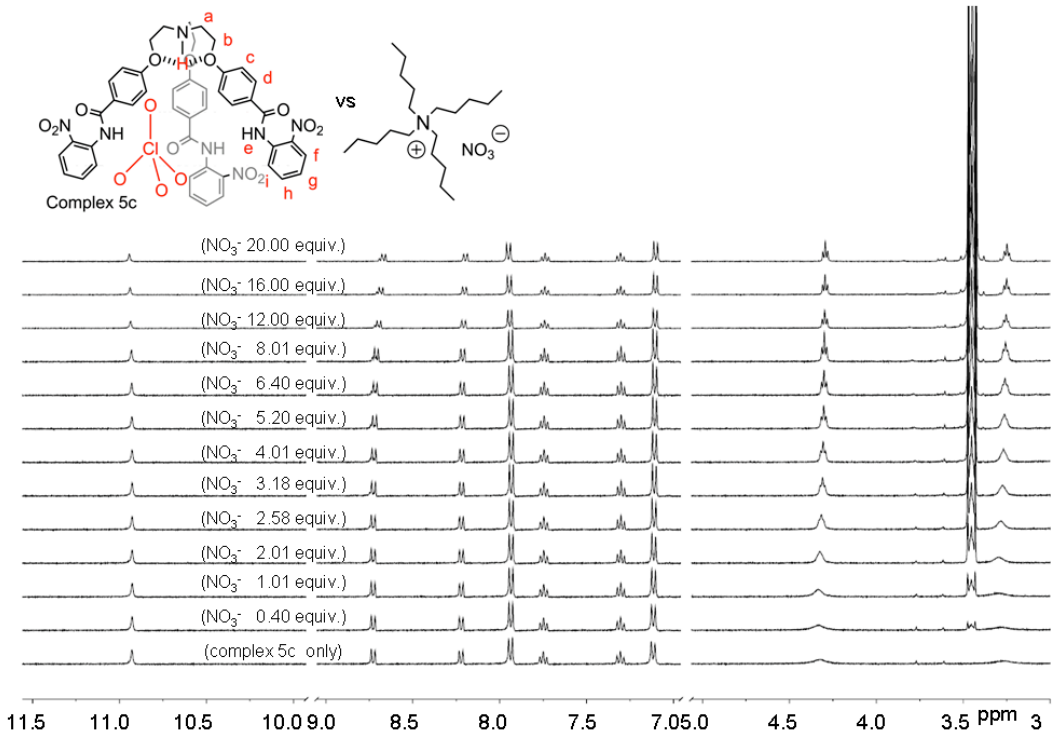

Fig. S91 Partial ^{1}H NMR titration spectra of perchlorate complex **5c** (1.48×10^{-3} M) with tetrabutylammonium nitrate in acetone-d_6.

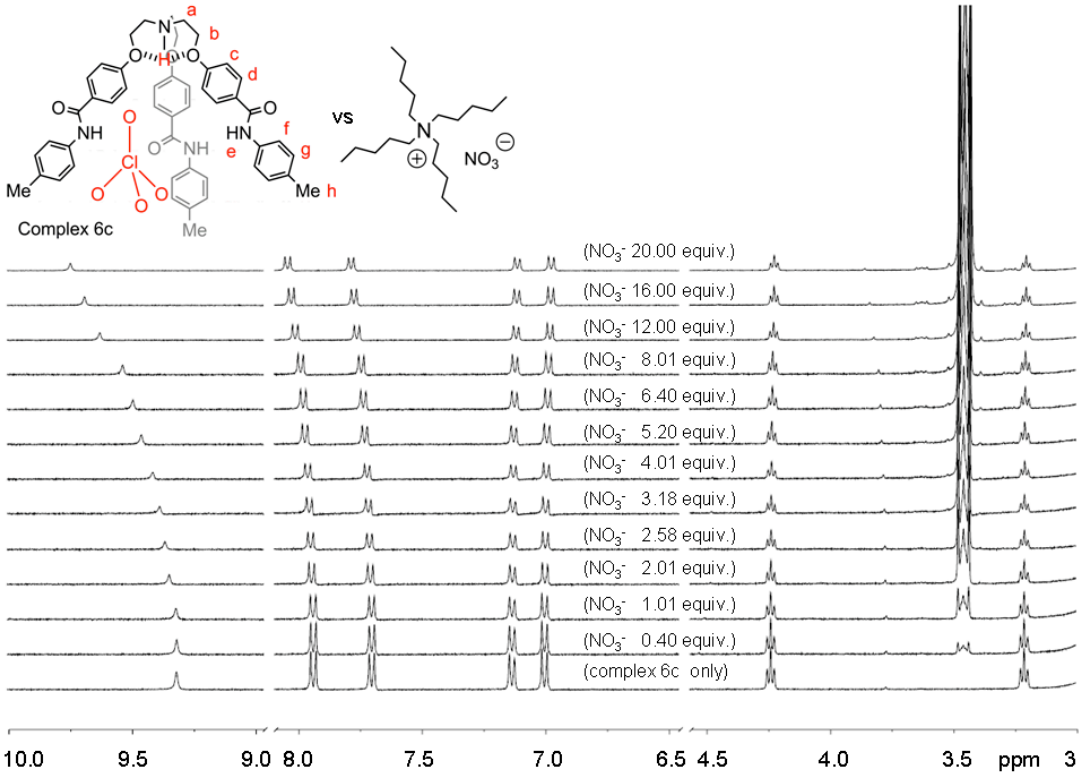

Fig. S92 Partial ^{1}H NMR titration spectra of perchlorate complex **6c** (1.48×10^{-3} M) with tetrabutylammonium nitrate in acetone-d_6.

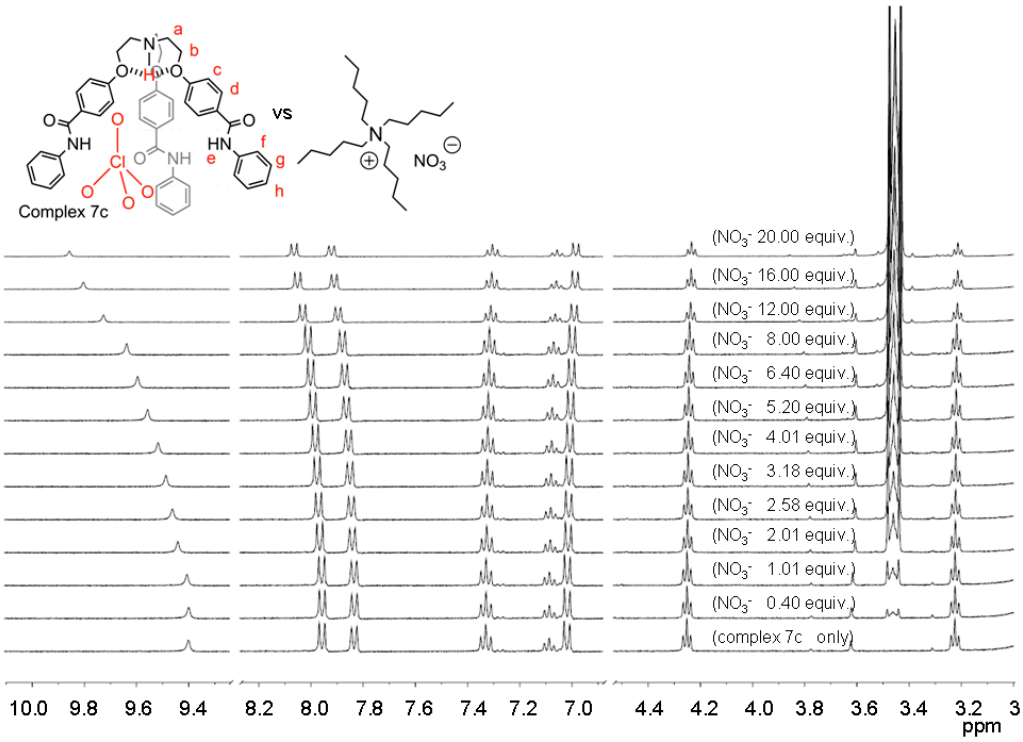

Fig. S93 Partial ^{1}H NMR titration spectra of perchlorate complex **7c** (1.48×10^{-3} M) with tetrabutylammonium nitrate in acetone-d_6.

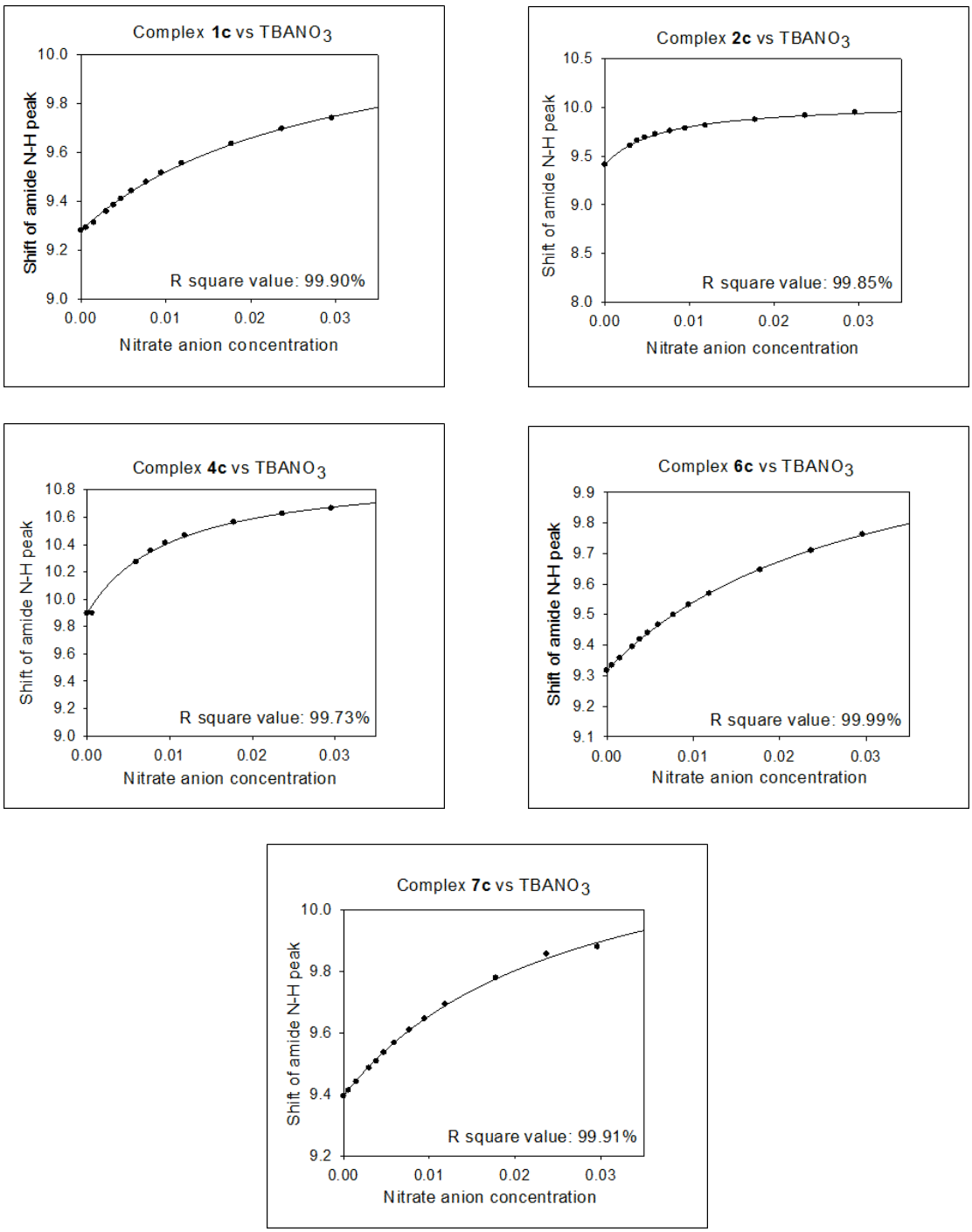

Fig. S94 ^{1}H NMR titration curves of perchlorate complexes (1.48×10^{-3} M) with tetrabutylammonium nitrate in acetone-d_6.

pH dependent reversible binding of NO_3 anion by compound **1'**:

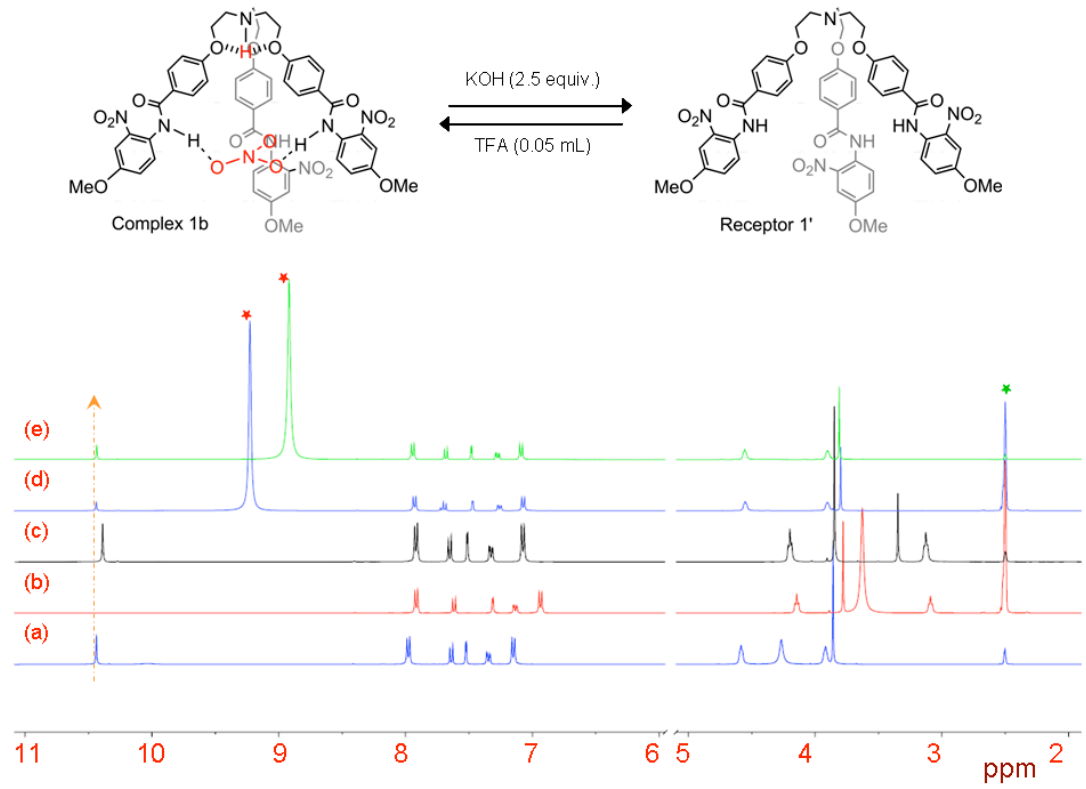

Fig. S95 ^{1}H NMR spectra (400 MHz, DMSO-d_6, 20 °C) of complex **1b** (49 mM) showing proton-induced reversible binding of nitrate anion. (a) ^{1}H NMR spectrum of complex **1b** in DMSO-d_6. (b) After treating with 2.5 equiv. of KOH. (c) ^{1}H NMR spectrum of compound **1'** in DMSO-d_6. (d) Acidification with trifluoroacetic acid retained its yellow color. (e) Compound **1'** in DMSO-d_6 in presence of trifluoroacetic acid. The star mark in green and red color represent the peaks for DMSO-d_6 and for trifluoroacetic acid.

Table T1. Crystallographic data and structure refinements for **6a** and $\mathbf{5_2}$.

	6a	$\mathbf{5_2}$
Empirical formula	$C_{48}\ H_{49}\ N_5\ O_9$	$C_{45}\ H_{39}\ N_7\ O_{12}$
Formula weight	839.92	869.83
Crystal system	Trigonal	Monoclinic
Space group	P -3	P 21/c
a (Å)	15.5323(6)	23.327 (14)
b (Å)	15.5323(6)	11.333 (6)
c (Å)	11.4631(6)	15.245 (9)
α (°)	90	90
β (°)	90	99.7
γ (°)	120	90
V ($Å^3$)	2394.99(18)	3973 (4)
Z	2	4
Temperature	200(2) K	200(2) K
Wavelength (Å)	0.71073	0.71073
ρ_{cal} Mg/m^3	1.165	1.454
μ, mm^{-1}	0.081	0.108
F (000)	888	1816
Independent reflection	2791	4927
Reflection used	15166	6537
R_{int} value	0.0626	0.0554
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
GOOF	1.079	1.651
R indices[I>2sigma(I)]	R1 = 0.1807, wR2 = 0.4861	R1 = 0.1700, wR2 = 0.4652
R indices(all data)	R1 = 0.2109, wR2 = 0.4985	R1 = 0.2315, wR2 = 0.4923

Table T2. Hydrogen bonding distances (Å) and Bond angles (°) in complex **6a**

Bond distances (Å)		Bond angles (°)	
N1-H1…N3	6.970	N1-H1…O3	180.00
N2-H2…O3	2.234	N2-H2…O3	159.77
C7-H7…O3	2.567	C7-H7…O3	160.13
C1-H1A…O3	2.636	C1-H1A…O3	148.15
C11-H11…O3	2.561	C11-H11…O3	130.25