Supplementary Information

Dynamic Self-Assembly of Molecular Capsules *via* Solvent Polarity Controlled Reversible Binding of Nitrate Anion with C_3 Symmetric Tripodal Receptors

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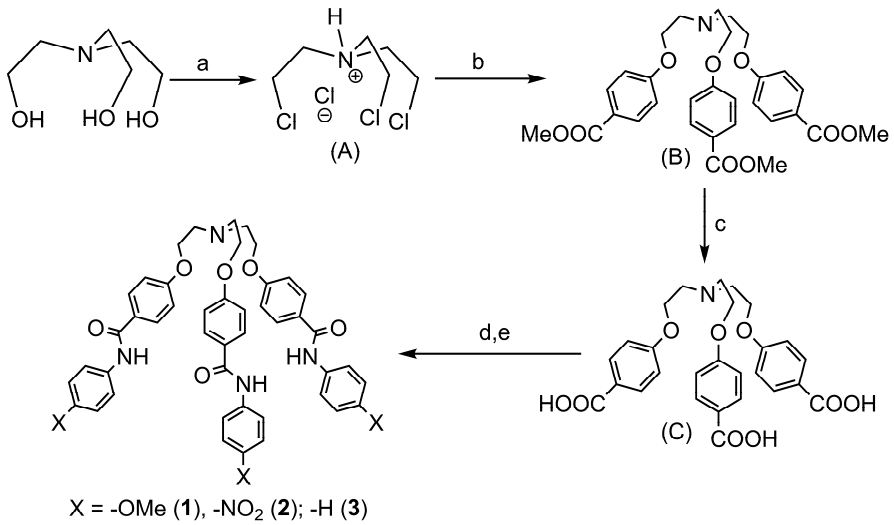
Contents:

Synthetic Scheme:



(a) $SOCl_2$, $CHCl_3$, 54%. (b) *p*-OH-C_6H_4COOMe, KOH, DMSO, 80 ºC, 75%. (c) 5 N NaOH/MeOH (1:1, v/v), 100 ºC, 12 h, dil HCl, 92%. (d) $SOCl_2$, CH_2Cl_2, DMF (cat.), reflux, 2-3 h. (e) X-$C_6H_4NH_2$, CH_2Cl_2, Et_3N, reflux, 8 h, 89-95%.

General procedures for the synthesis of receptors 1–3. Receptors **1–3** were synthesized from previously reported tris(2-chloroethyl)amine hydrochloride[1] (A) by simple SN_2 substitution with 4-hydroxy methylbenzoate in DMSO followed by basic hydrolysis to yield corresponding triacid (C). Subsequent condensation of triacid with thionyl chloride in dichloromethane yielded corresponding acid chloride. Subsequently, the acid chloride solution in dichloromethane was slowly added to a mixture of the corresponding amino derivative and Et_3N in dichloromethane and refluxed for 8-12 h. Solvent was removed under reduced pressure. Ice-cold water was added to the residue and stirred at room temperature for 2-3 h to precipitate the target compounds (**1-3**). The crude product was purified by flash chromatography with

$CHCl_3$/MeOH mixture solution as eluent to yield desired receptors. The desired receptors **1-3** were isolated in 89-95% yields.

1: Creamy white solid (yield 95%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 3.12 (t, 6H, J = 5.6 Hz), 3.73 (s, 9H), 4.18 (t, 6H, J = 5.6 Hz), 6.90 (d, 6H, J = 8.8 Hz), 7.03 (d, 6H, J = 8.8 Hz), 7.65 (d, 6H, J = 8.8 Hz), 7.93 (d, 6H, J = 8.8 Hz), 9.96 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 53.5, 55.2, 66.8, 113.7, 114.1, 122.0, 127.0, 129.4, 132.4, 155.4, 161.0, 164.5. HRESIMS m/z 825.3494 (calcd m/z 825.3500 for $[M+H]^+$).

1a: Pale yellow solid (yield 92%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 3.74 (s, 9H), 3.92 (s, 6H), 4.57 (s, 6H), 6.92 (d, 6H, J = 8.4 Hz), 7.10 (d, 6H, J = 8.4 Hz), 7.67 (d, 6H, J = 8.4 Hz), 8.00 (d, 6H, J = 8.4 Hz), 10.03 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 53.4, 55.2, 62.6, 113.7, 114.3, 122.1, 127.9, 129.5, 132.3, 155.5, 160.0, 164.4. HRESIMS *m/z* 886.3306 (calcd *m/z* 886.3299 for $[M-H]^-$).

1b: Orange color solid (yield 92%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 3.86 (s, 9H), 3.92 (s, 6H), 4.58 (s, 6H), 7.15 (d, 6H, J = 8.8 Hz), 7.35 (d, 3H, J = 9.2 Hz), 7.52 (s, 3H), 7.64 (d, 3H, J = 9.2 Hz), 7.98 (d, 6H, J = 8.8 Hz) 10.44 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 53.3, 56.1, 62.7, 109.2, 114.6, 120.2, 124.5, 126.6,

128.0, 129.7, 143.9, 156.4, 160.5, 164.4. HRESIMS *m/z* 1021.2855 (calcd *m/z* 1021.2852 for $[M-H]^-$).

1': Deep yellow solid (yield 87%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 3.13 (t, 6H, *J* = 5.2 Hz), 3.85 (s, 9H), 4.20 (t, 6H, *J* = 5.2 Hz),7.08 (d, 6H, *J* = 8.8 Hz), 7.33 (d, 3H, *J* = 9 Hz), 7.51 (s, 3H), 7.65 (d, 3H, *J* = 8.8 Hz), 7.92 (d, 6H, *J* = 8.8 Hz), 10.39 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 53.4, 56.0, 66.9, 109.1, 114.3, 120.2, 124.6, 125.7, 127.7, 129.6, 143.6, 156.1, 161.5, 164.6. HRESIMS *m/z* 960.3060 (calcd *m/z* 960.3052 for $[M+H]^+$).

2: Yellow solid (yield 85%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 3.88 (s, 6H), 4.64 (s, 6H), 7.13 (d, 6H, *J* = 8.4 Hz), 8.04-8.09 (m, 9H), 8.21 (d, 6H, *J* = 9.2 Hz), 10.75 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 52.6, 62.7, 114.4, 119.8, 124.6, 126.8, 130.1, 142.2, 145.7, 160.5, 165.3. HRESIMS *m/z* 870.2730 (calcd *m/z* 870.2735 for $[M+H]^+$).

2a: Yellow solid (yield 87%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 3.93 (s, 6H), 4.58 (s, 6H), 7.13 (d, 6H, *J* = 8.8 Hz), 8.01-8.05 (m, 9H), 8.22 (d, 6H, *J* = 9.2 Hz), 10.65 (s, 3 H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 53.4, 62.7, 114.4, 119.8, 124.7, 126.9, 130.0, 142.3, 145.6, 160.5, 165.4. HRESIMS *m/z* 931.2539 (calcd *m/z* 931.2535 for $[M-H]^-$).

3: Creamy white solid (yield 89%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 3.13 (t, 6H, J = 5.6 Hz), 4.19 (s, 6H, J = 5.6 Hz), 7.07 (m, 9H), 7.33 (3, 6H, J = 7.6 Hz), 7.76 (d, 6H, J = 8.0 Hz), 7.95 (d, 6H, J = 8.0 Hz), 10.07 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 53.6, 66.9, 114.2, 120.5, 123.5, 127.0, 128.6, 129.7, 139.3, 161.2, 165.0. HRESIMS *m/z* 735.3174 (calcd *m/z* 735.3183 for $[M+H]^+$).

3a: Creamy yellow solid (yield 85%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 3.90 (s, 6H), 4.56 (s, 6H), 7.07-7.13 (m, 9H), 7.34 (t, 6H, J = 8.0 Hz), 7.77 (d, 6H, J = 8.0 Hz), 8.01 (d, 6H, J = 8.4 Hz), 10.12 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 53.4, 62.6, 114.3, 120.5, 123.6, 127.8, 128.6, 129.7, 139.2, 160.1, 164.7. HRESIMS *m/z* 796.2977 (calcd *m/z* 796.2983 for $[M-H]^-$).

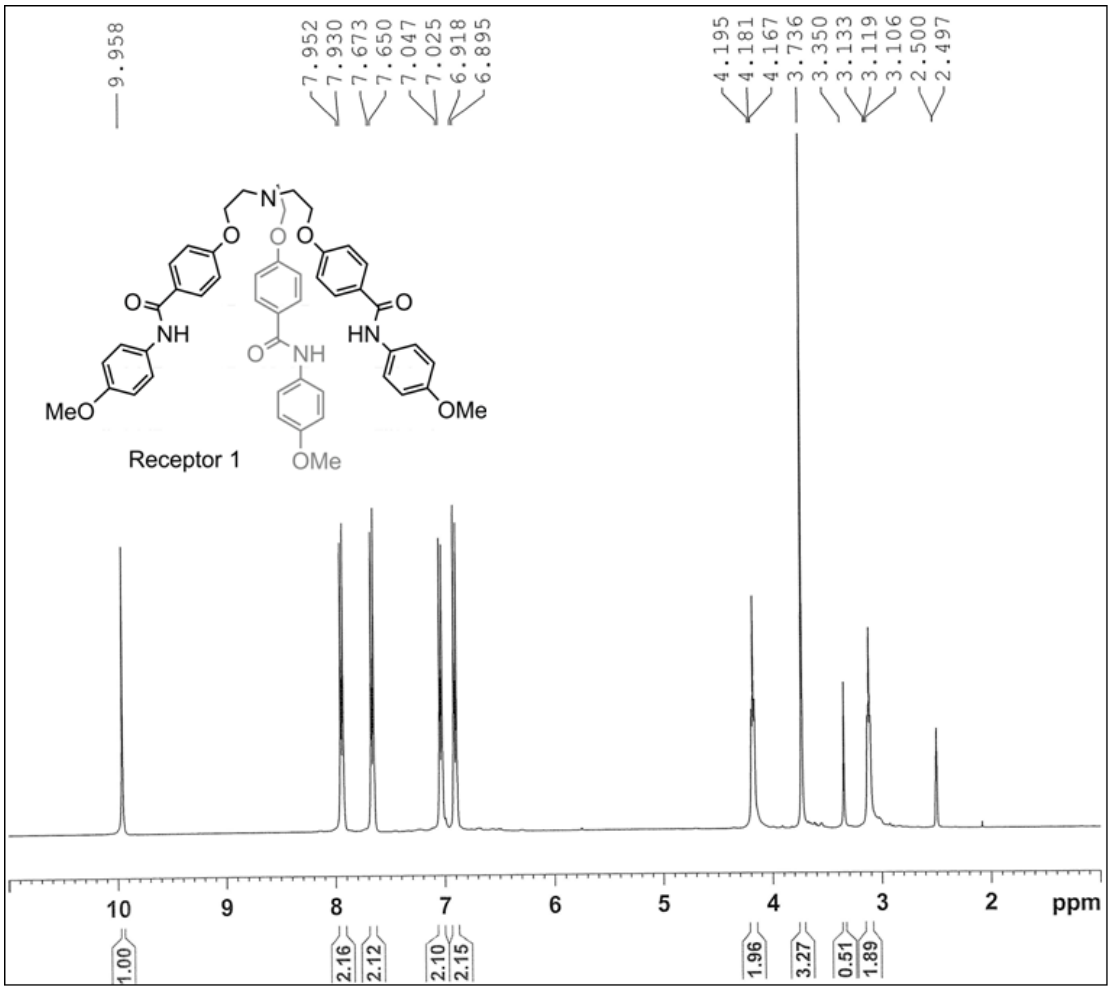


Fig. S1 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **1**.

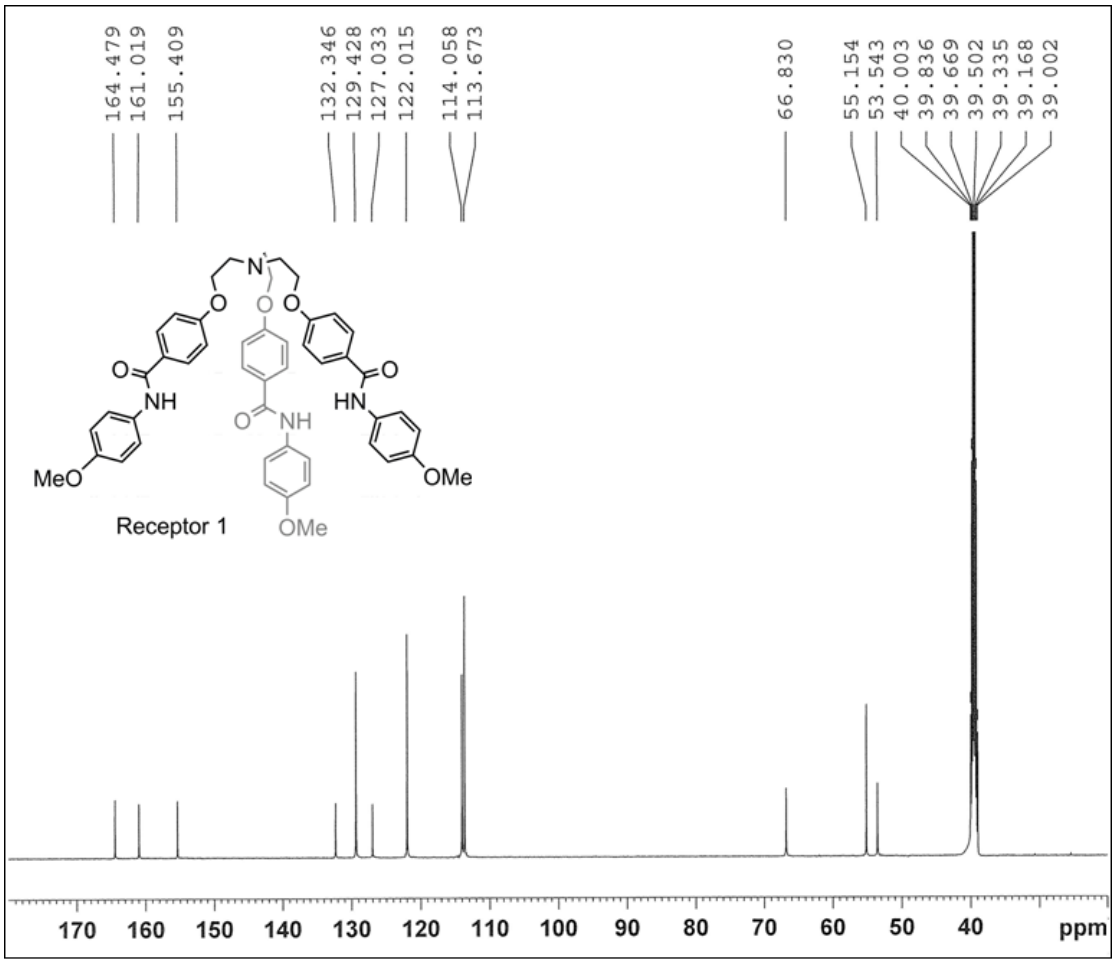


Fig. S2 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **1**.

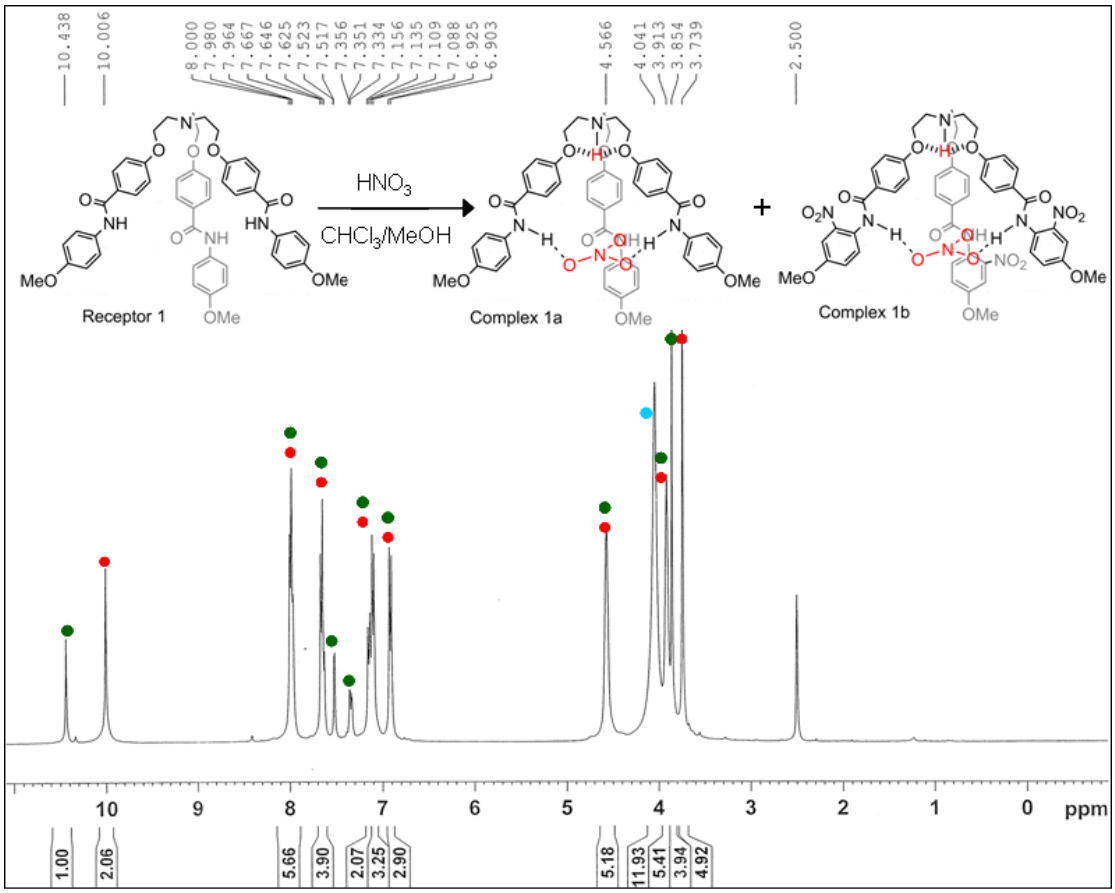


Fig. S3 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of mixture of complexes **1a** (represented by red circle) and **1b** (represented by green circle), obtained by treating compound **1** with nitric acid in $CHCl_3$/MeOH (v/v) in ratio 1:1. The circle in blue color represents water peak from DMSO-d_6.

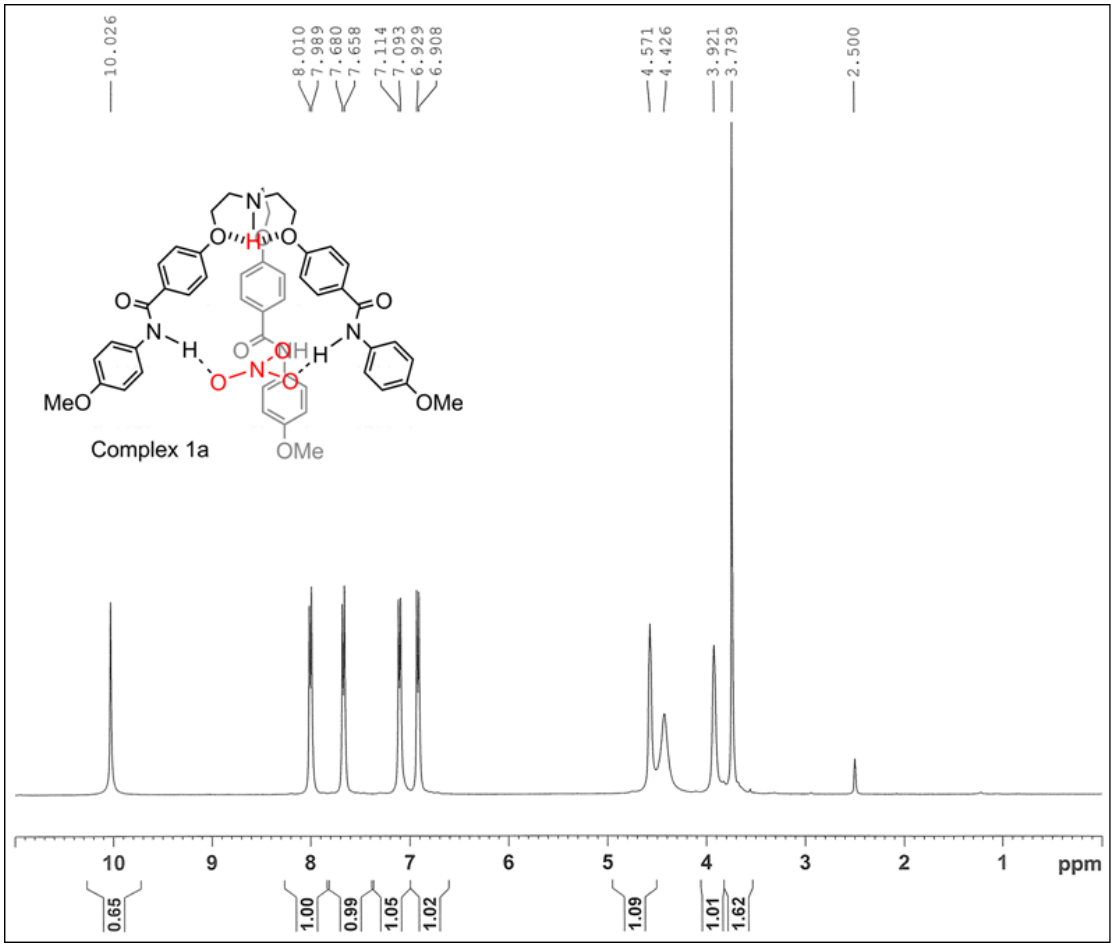


Fig. S4 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **1a**.

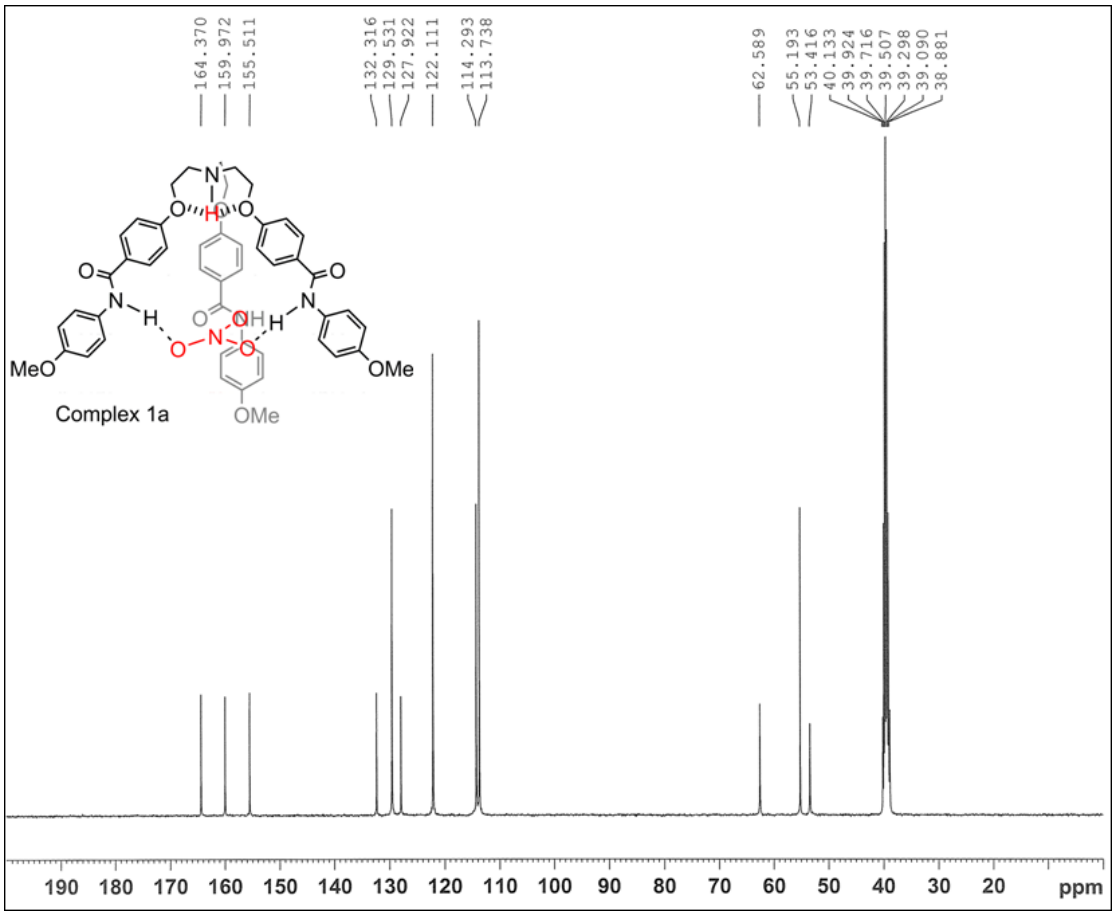


Fig. S5 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **1a**.

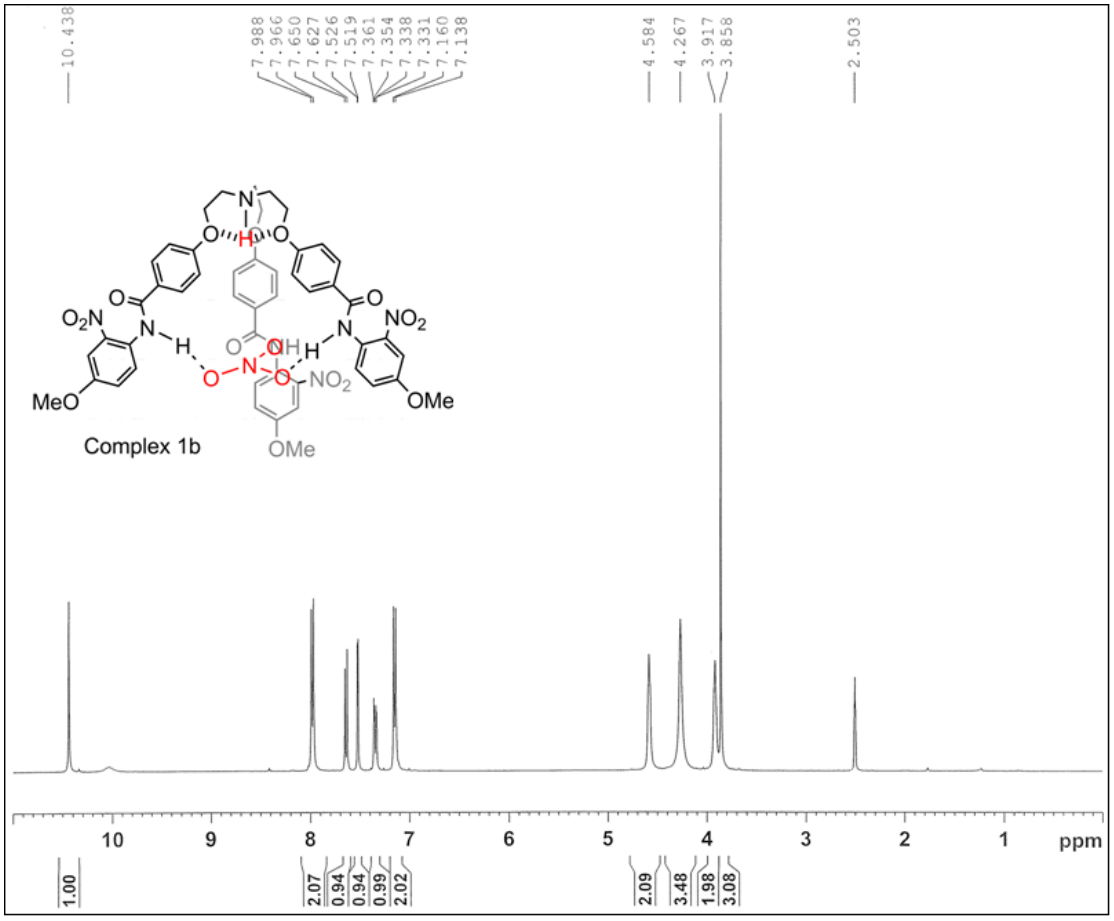


Fig. S6 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **1b**.

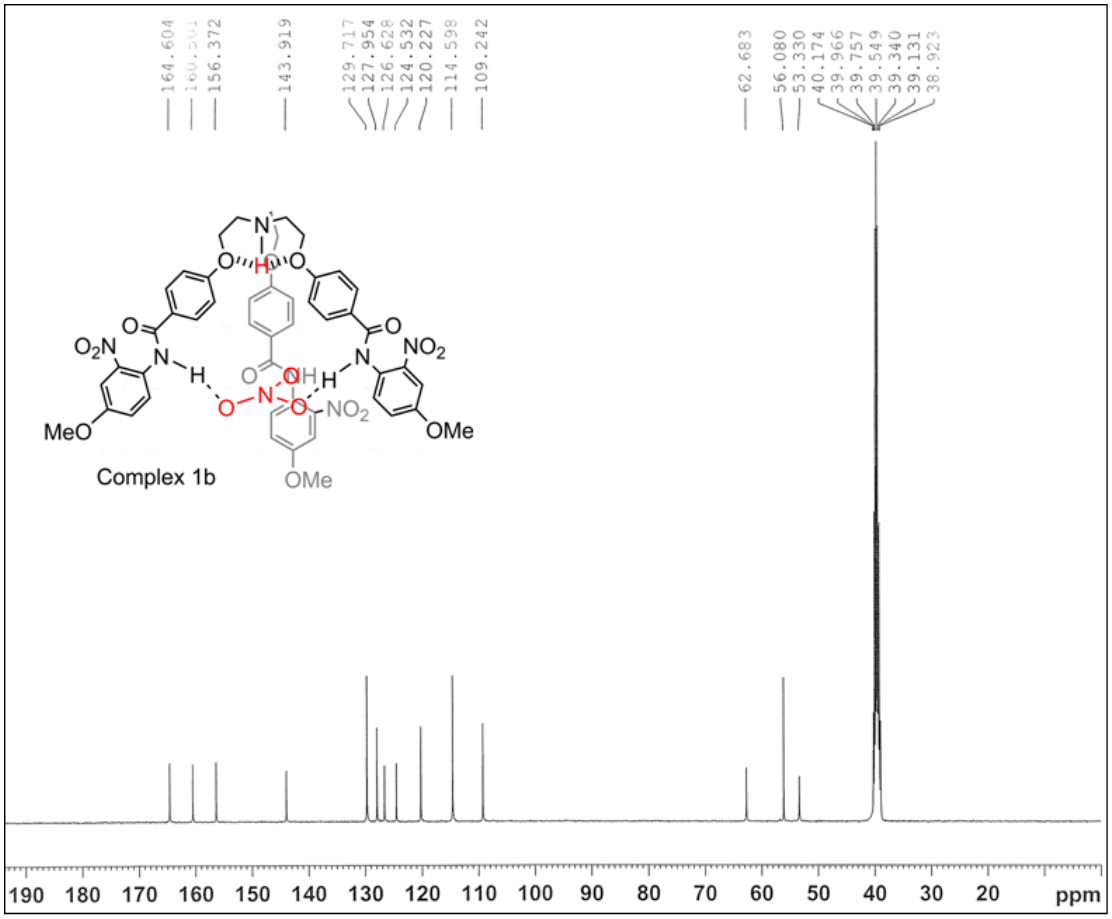


Fig. S7 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **1b**.

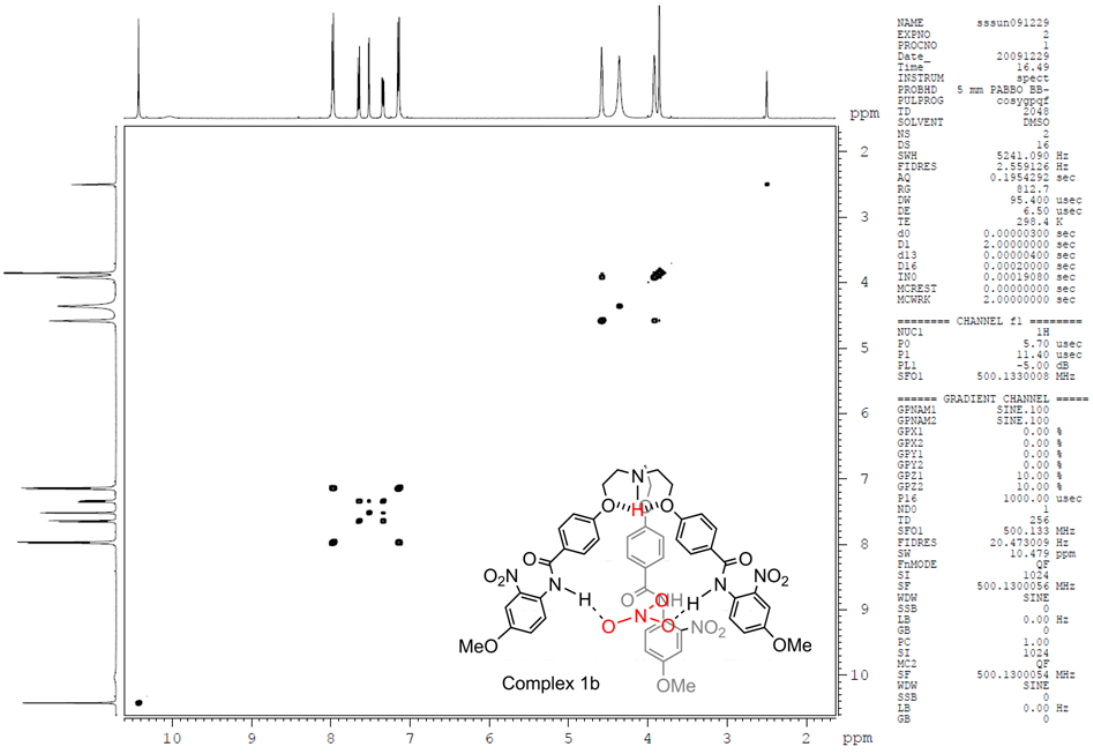


Fig. S8 COSY spectra of nitrate complex **1b** in DMSO-d_6.

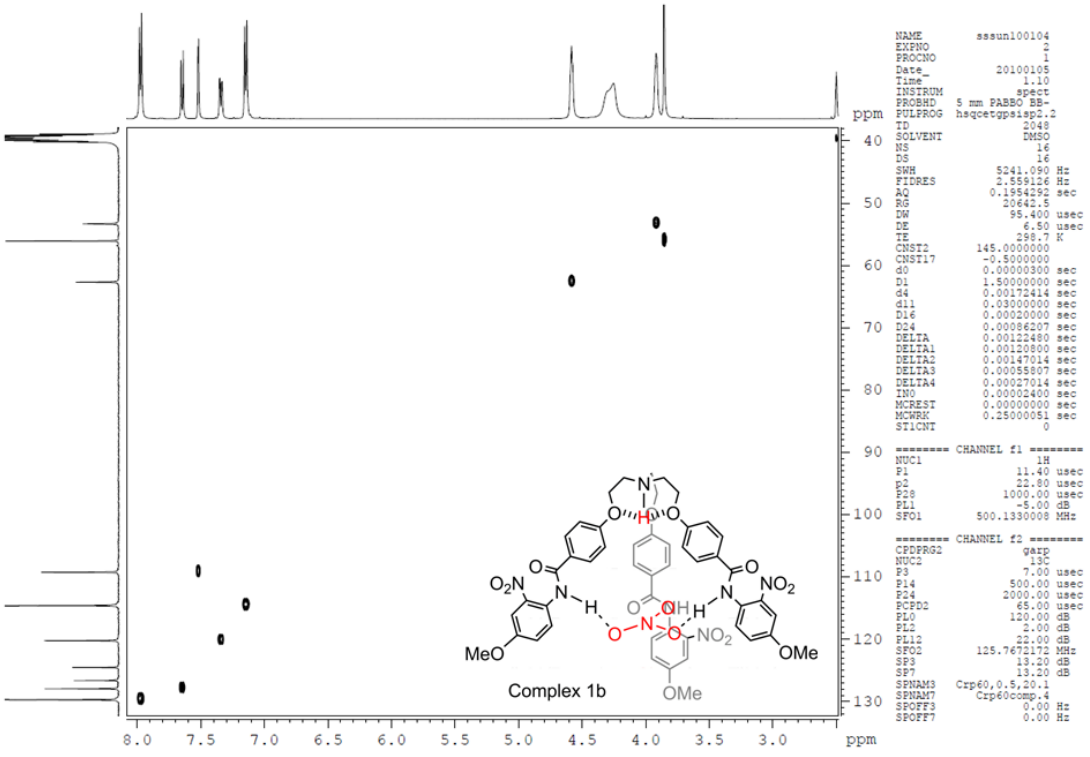


Fig. S9 HSQC spectra of nitrate complex **1b** in DMSO-d_6.

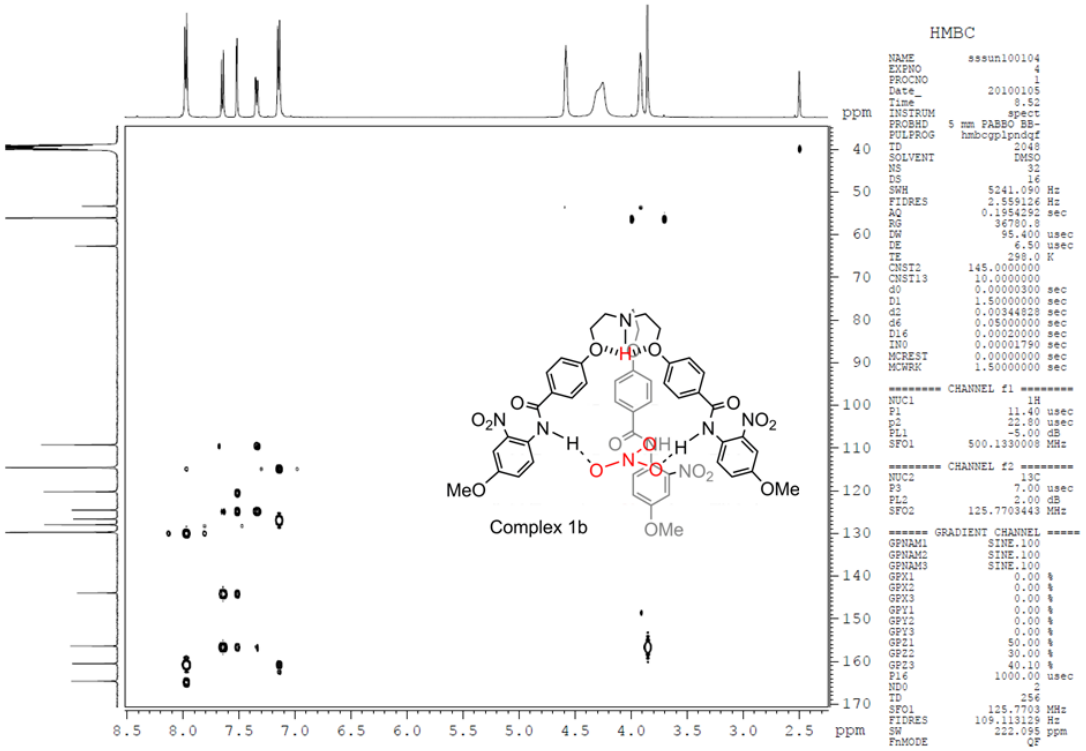


Fig. S10 HMBC spectra of nitrate complex **1b** in DMSO-d_6.

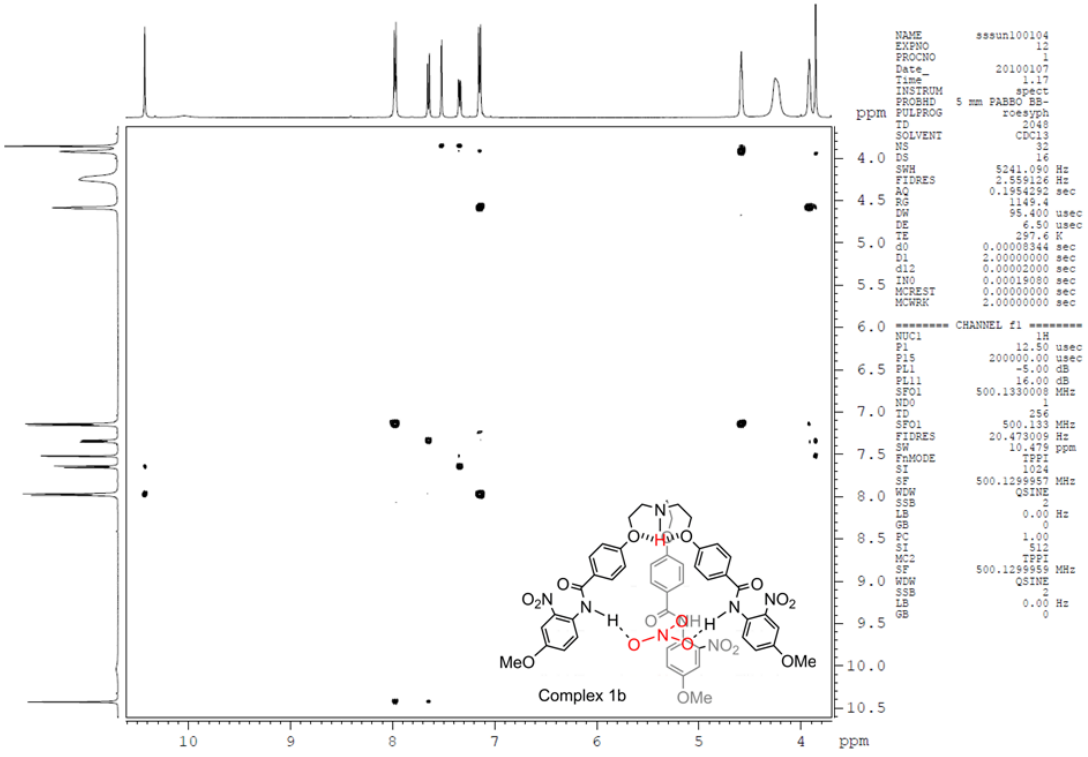


Fig. S11 ROESY spectra of nitrate complex **1b** in DMSO-d_6.

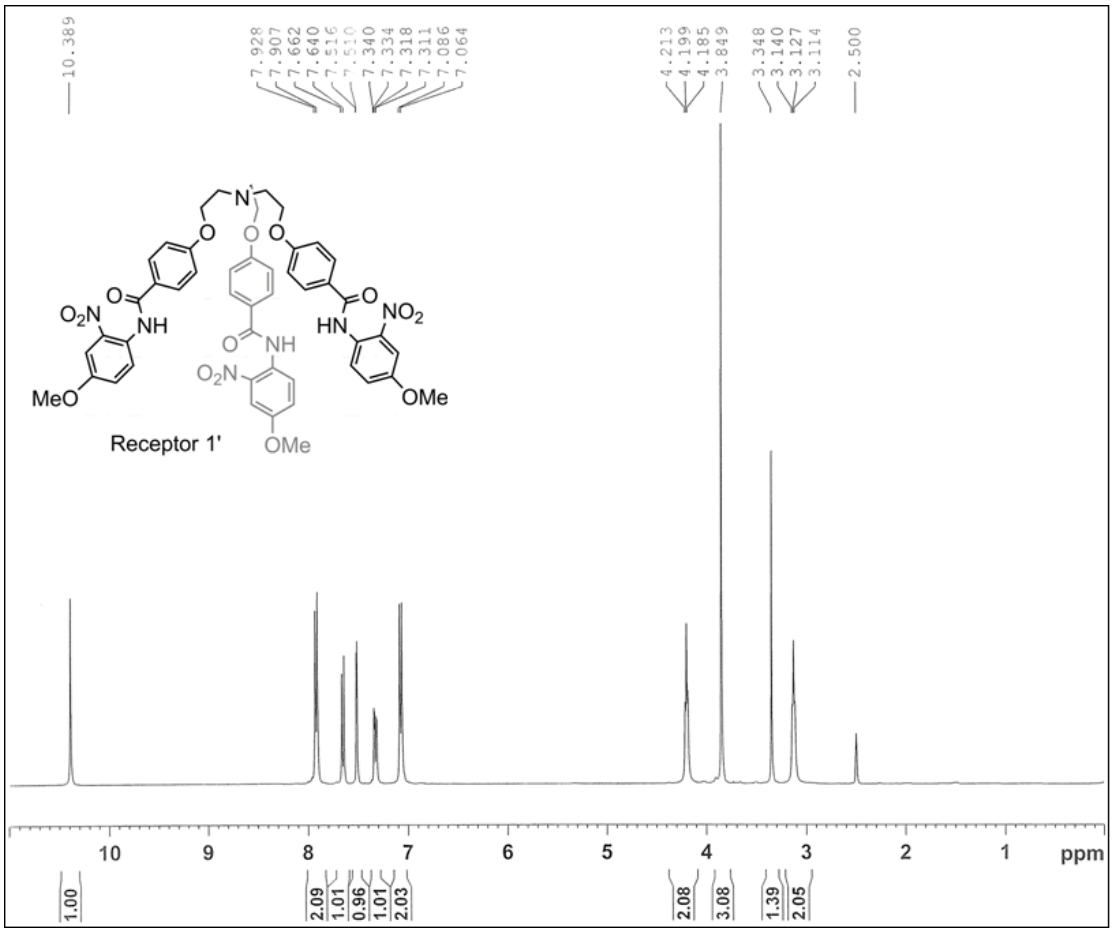


Fig. S12 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of substituted receptor **1'**.

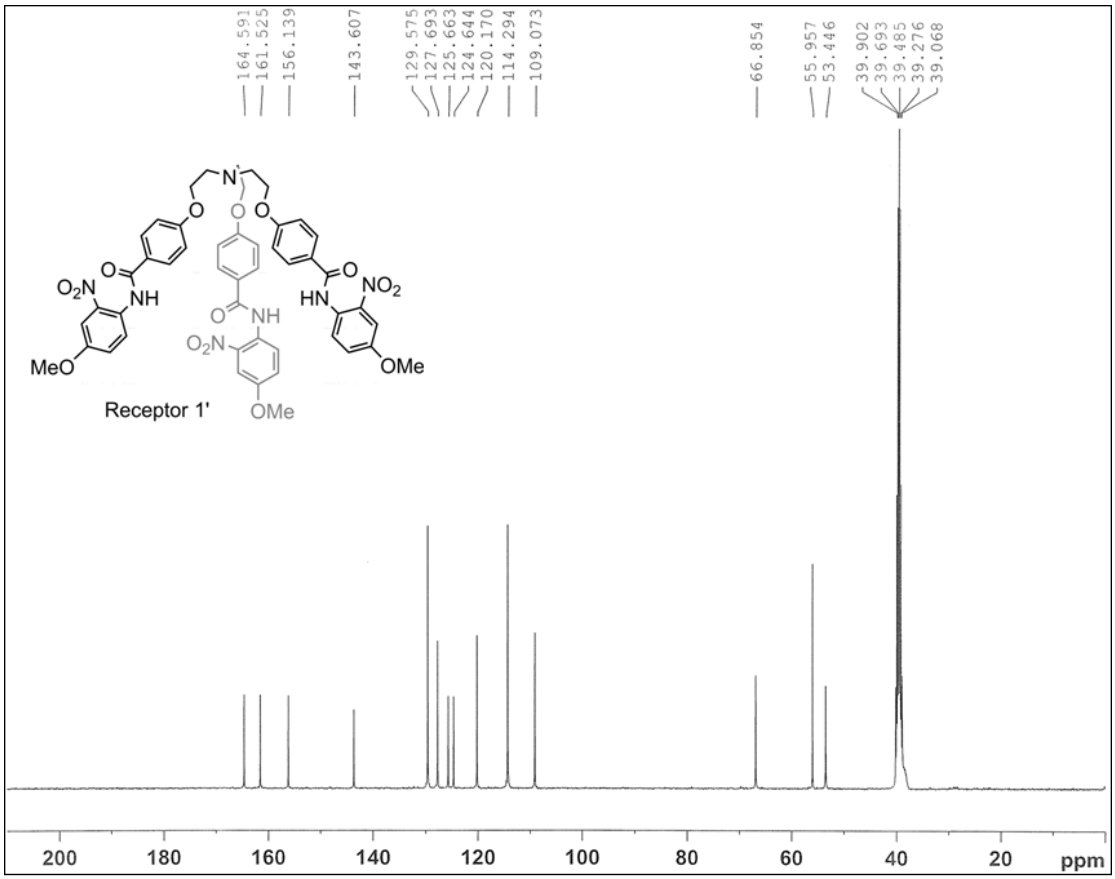


Fig. S13 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of substituted receptor **1'**.

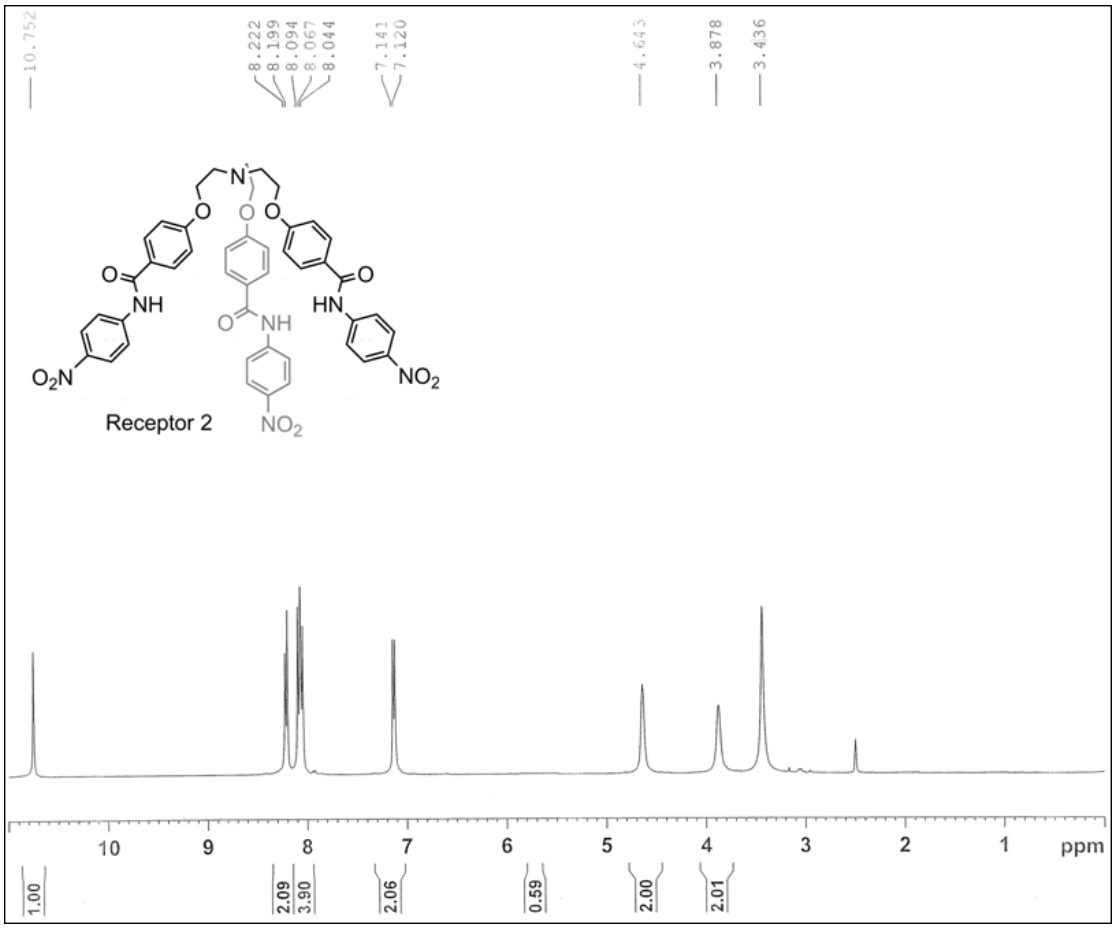


Fig. S14 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **2**.

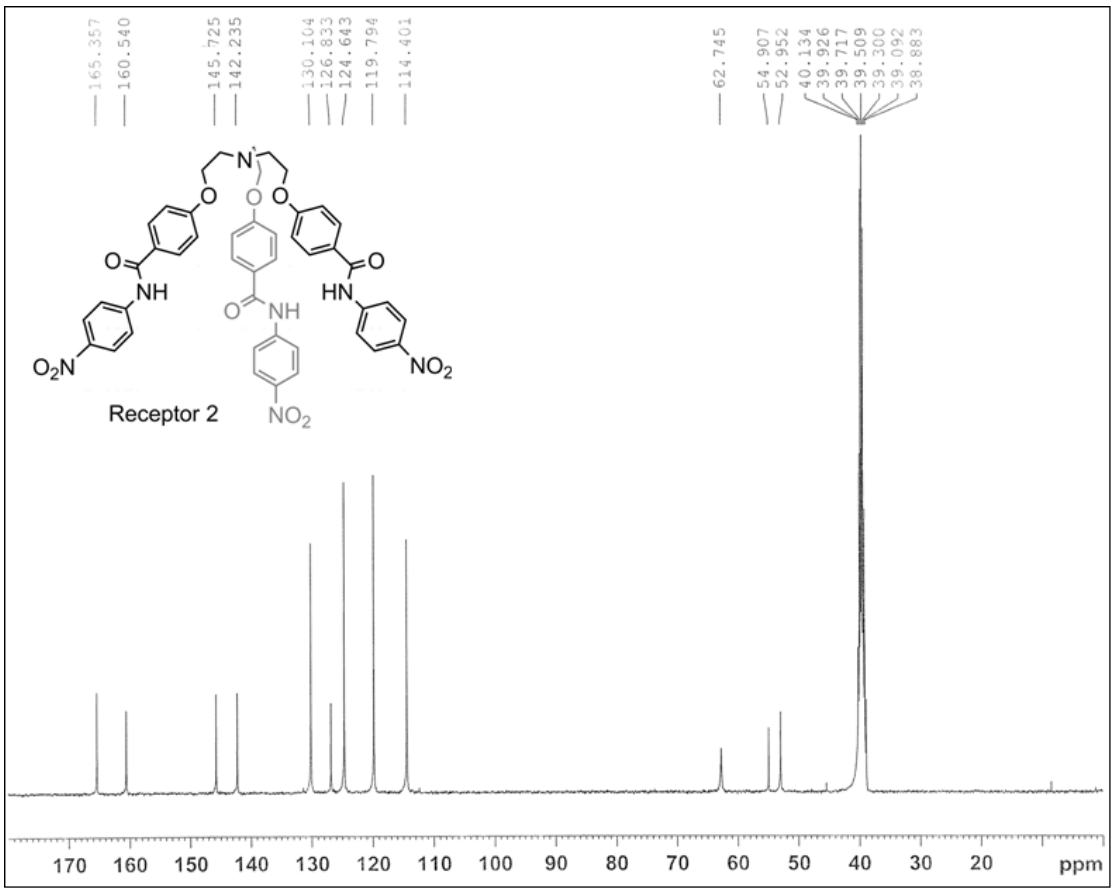


Fig. S15 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **2**.

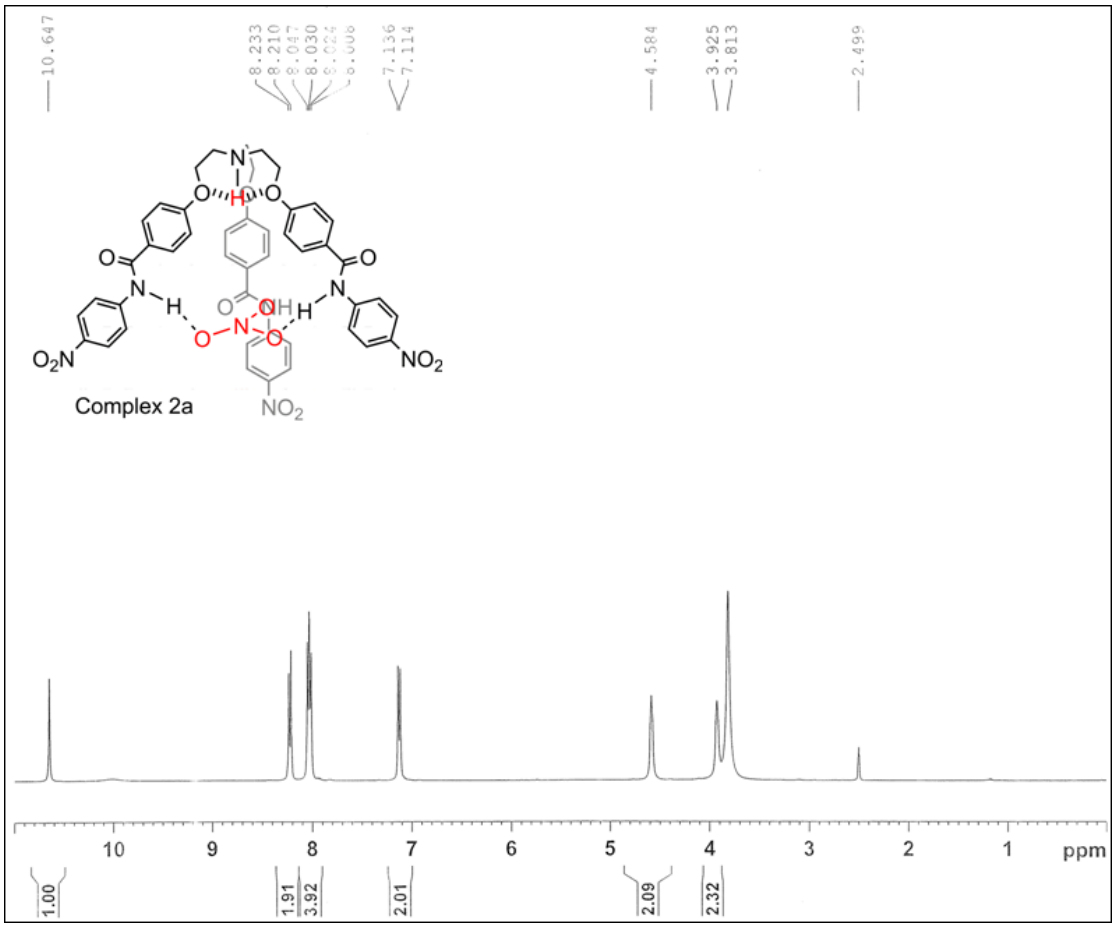


Fig. S16 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **2a**.

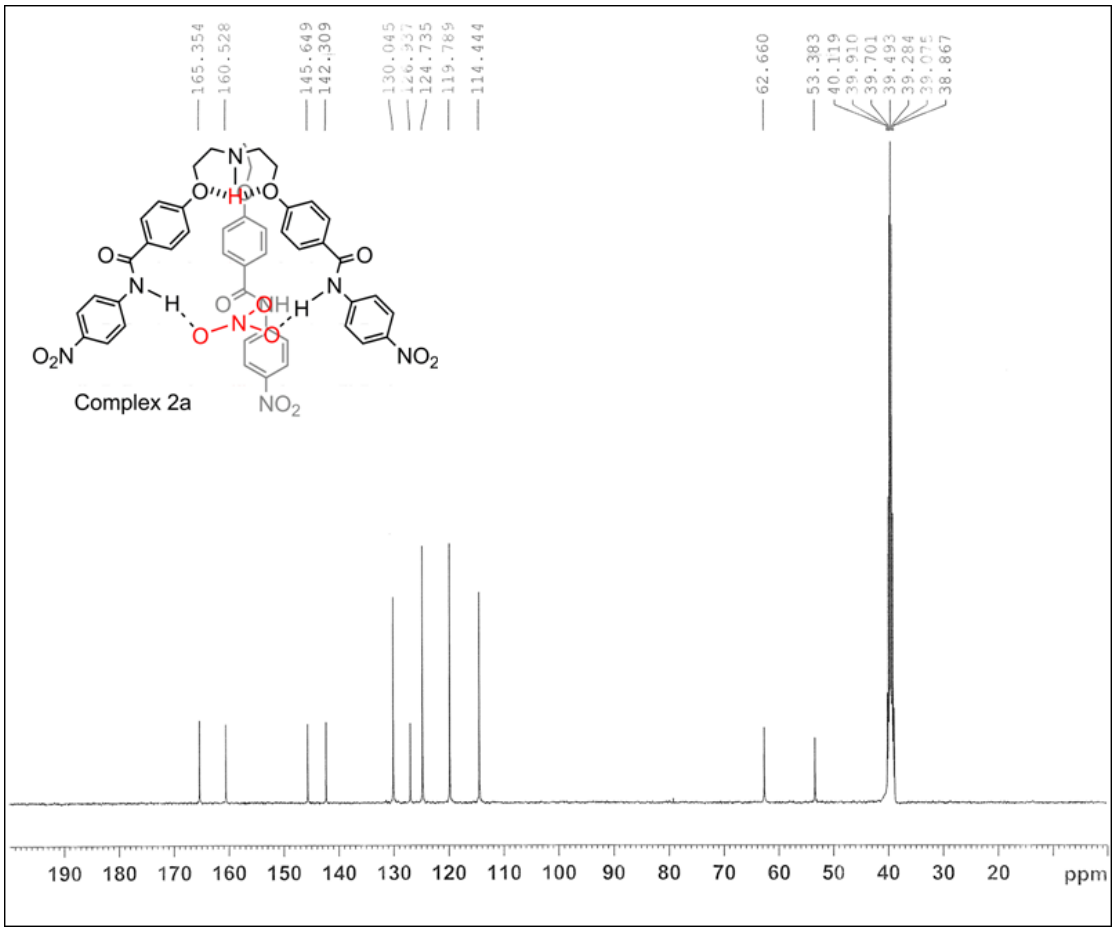


Fig. S17 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **2a**.

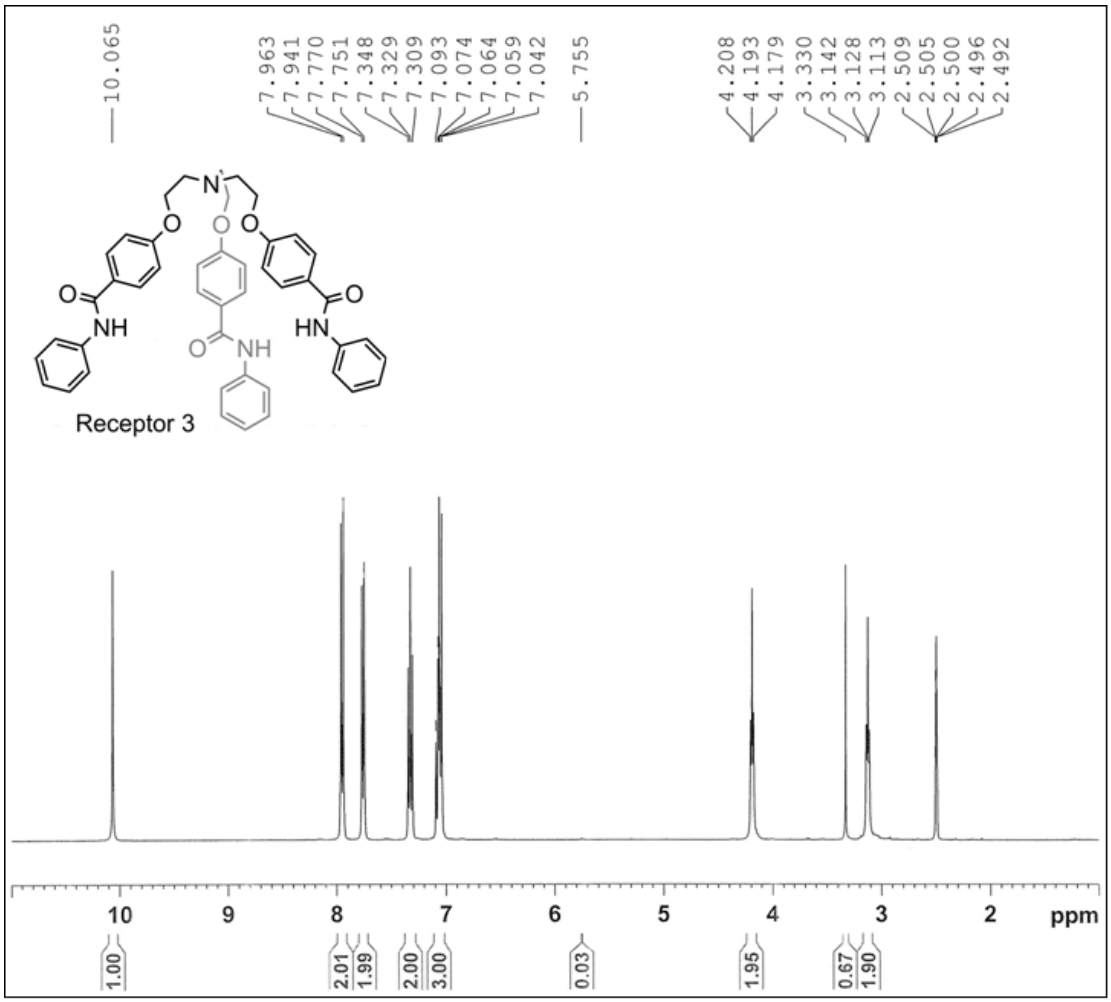


Fig. S18 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **3**.

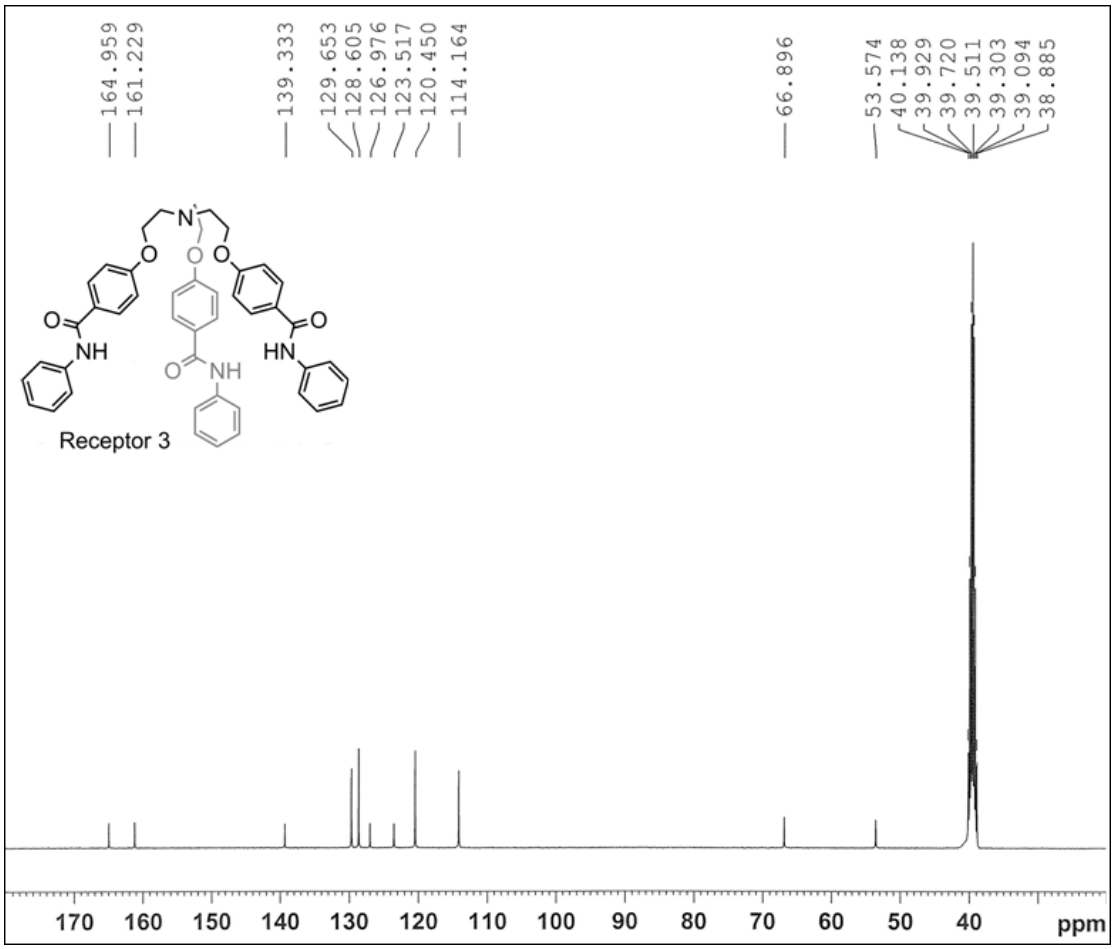


Fig. S19 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **3**.

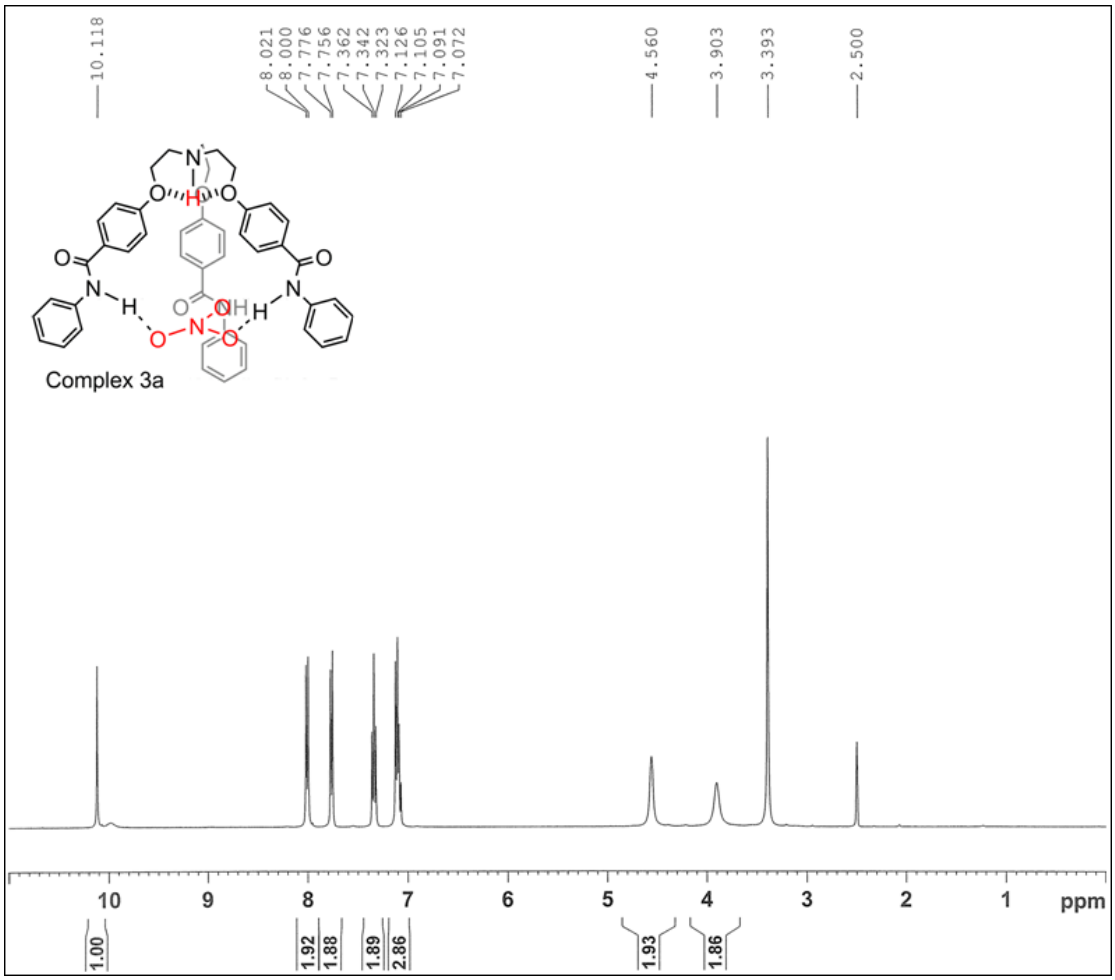


Fig. S20 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **3a**.

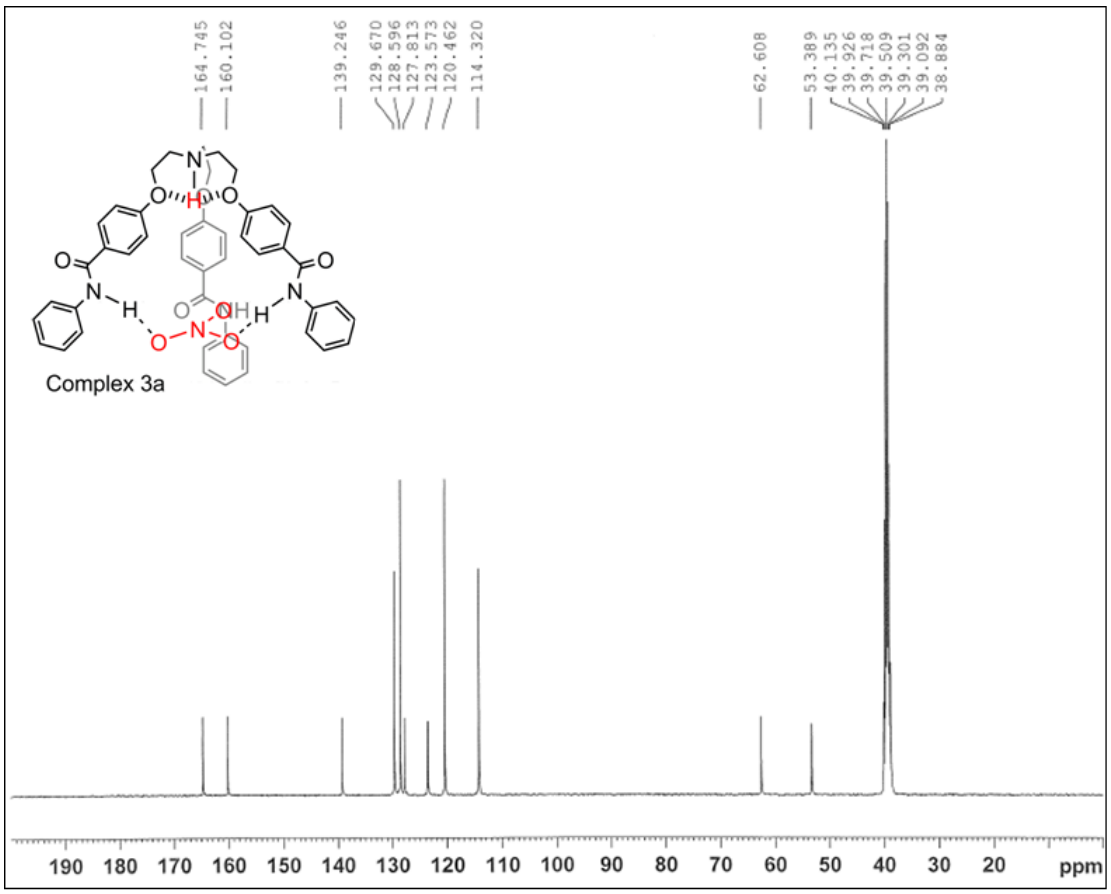


Fig. S21 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of nitrate complex **3a**.

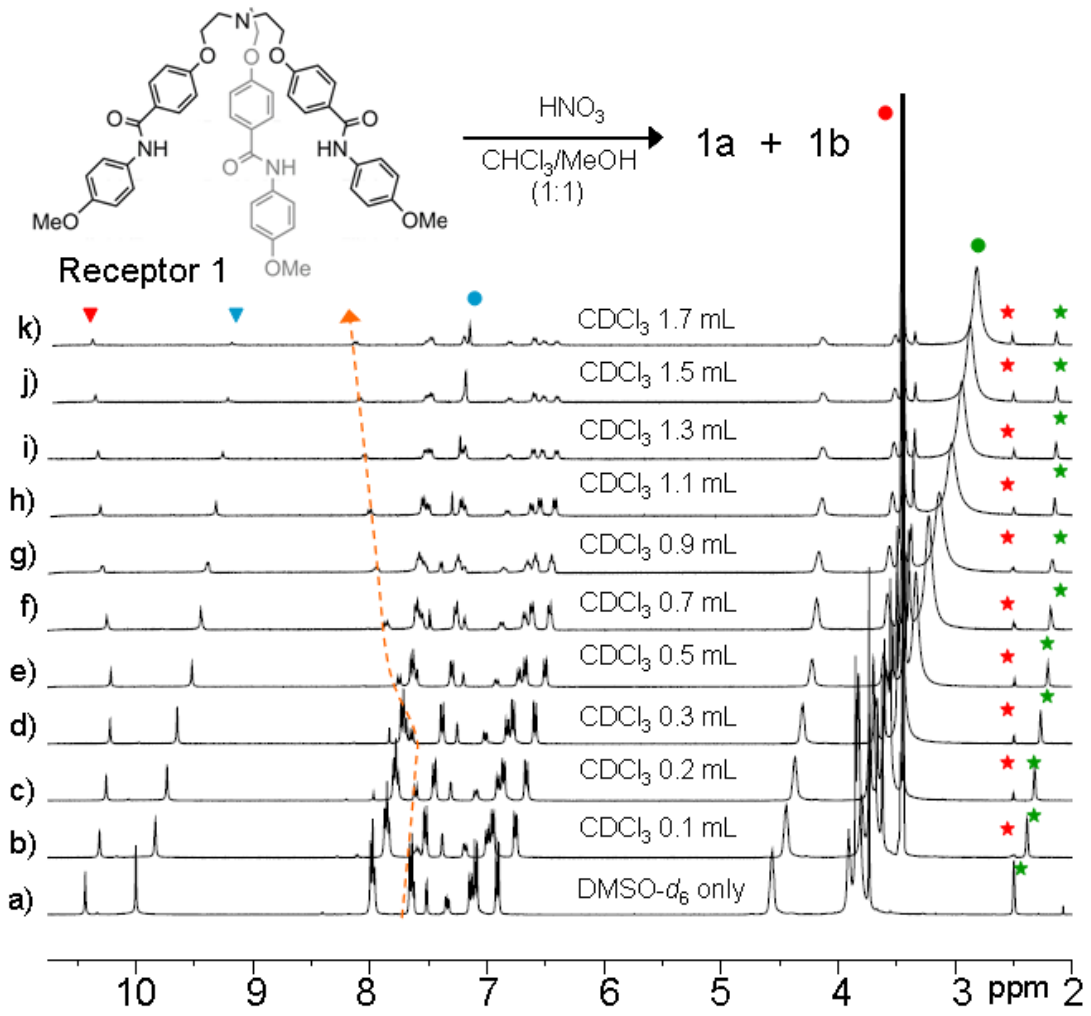


Fig. S22 ^{1}H NMR titration spectra of nitrate complex (in DMSO-d_6 with varying amount of $CDCl_3$), obtained after addition of nitric acid in aqueous methanol to suspension of receptor **1** in $CHCl_3$. Star mark in green color represents peak corresponding to DMSO-d_6 (as solvent) and the same in red color represents for DMSO-d_6 (as internal reference). 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 solvent). Triangle in red color represents amide N-H peak of nitrate complex **1b** and the same in blue color represents the same for complex **1a**. Circle in blue color represents peak for $CDCl_3$.

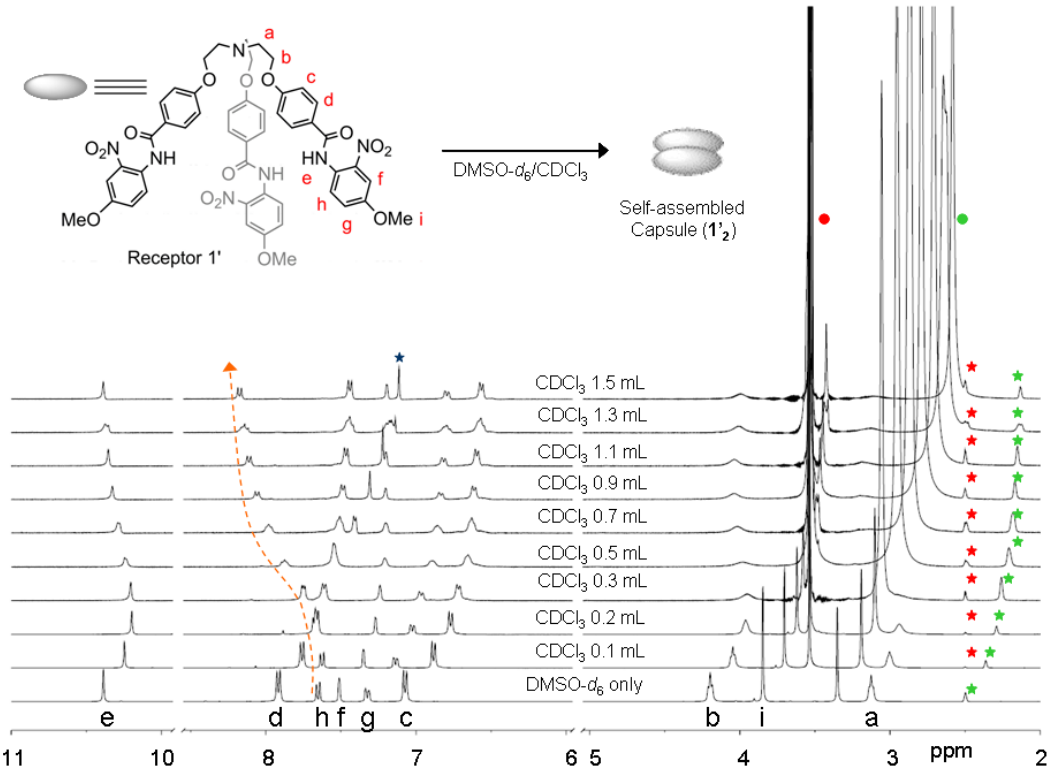


Fig. S23 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **1'** (52 mM) in a DMSO-d_6 solution upon addition of varying amount of $CDCl_3$ using TMS as the internal reference. The star marks in red, green, and blue color represent solvent peaks for DMSO-d_6 from internal reference, solvent used to dissolve receptor **1'**, and $CDCl_3$, 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 solvent).

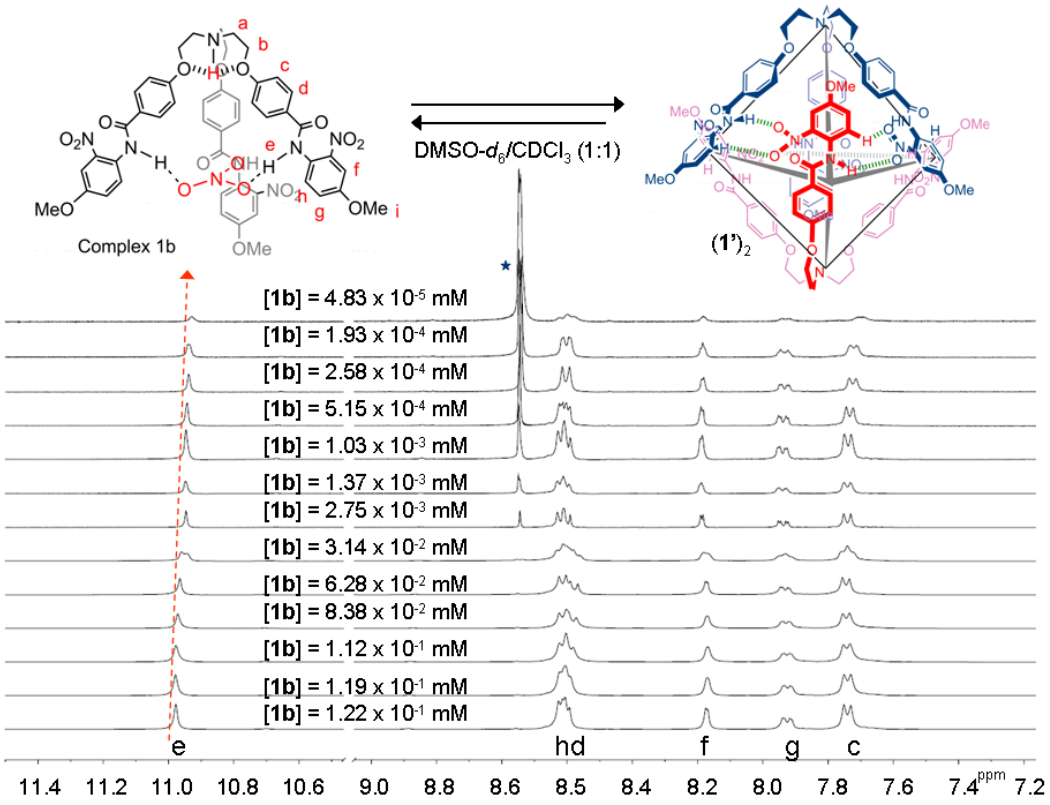


Fig. S24 Concentration-dependent ^{1}H NMR titration spectra of nitrate complex **1b** in a mixture solution of DMSO-d_6/CDCl$_3$ (1:1). A star mark in blue color represents peak for CDCl$_3$.

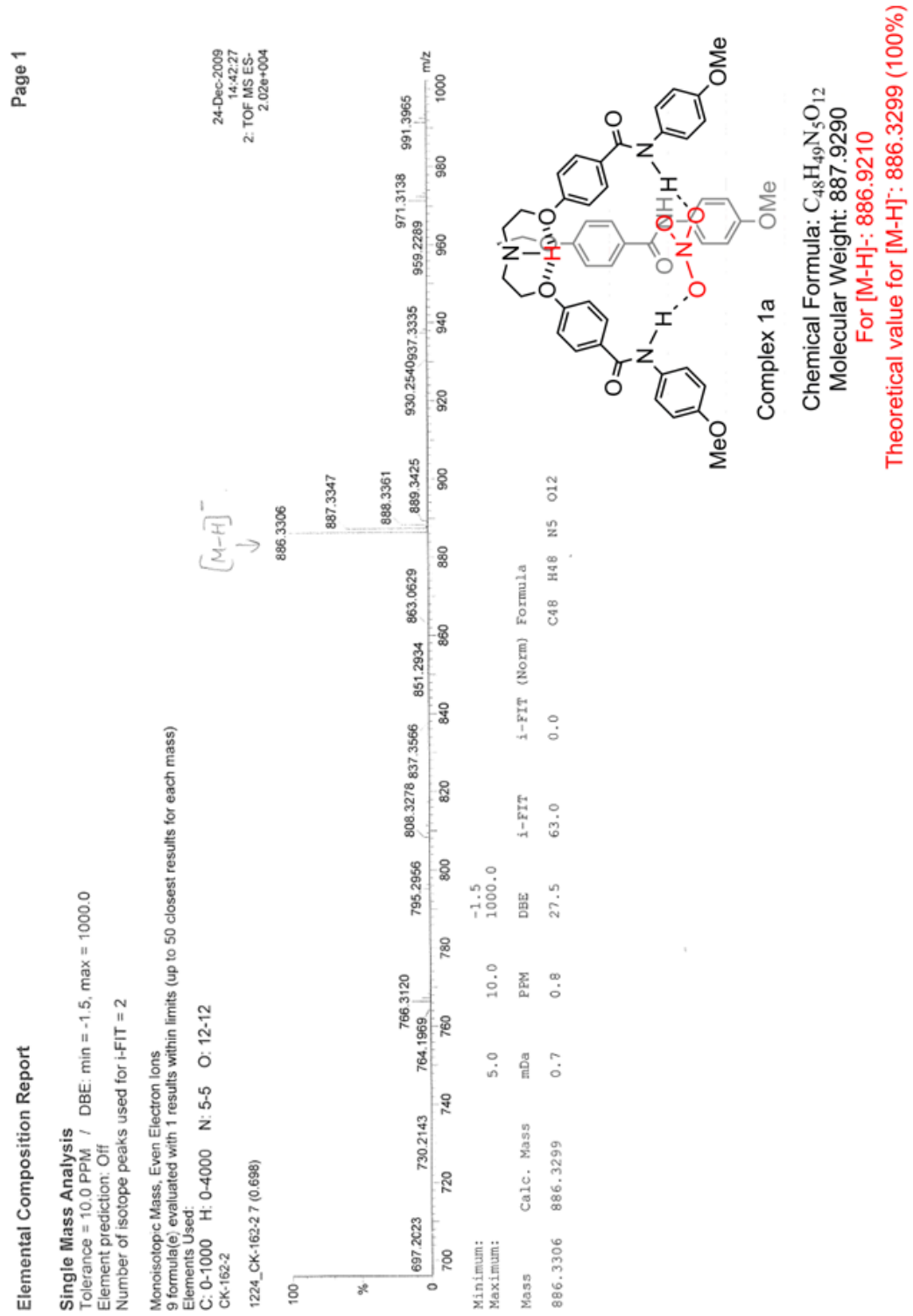


Fig. S25 HRESI mass spectrum of complex **1a** recorded in DMSO.

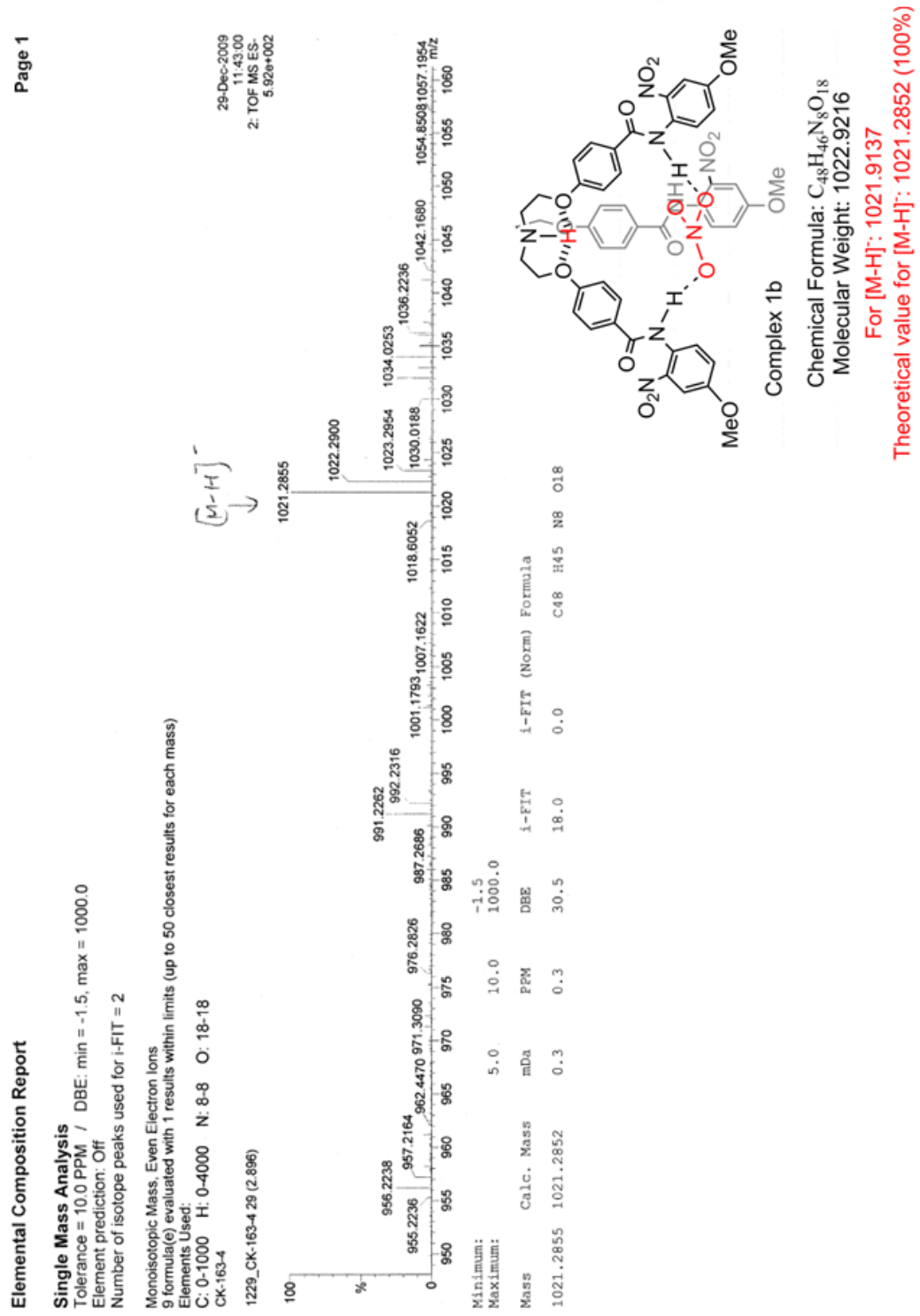


Fig. S26 HRESI mass spectrum of complex **1b** recorded in DMSO.

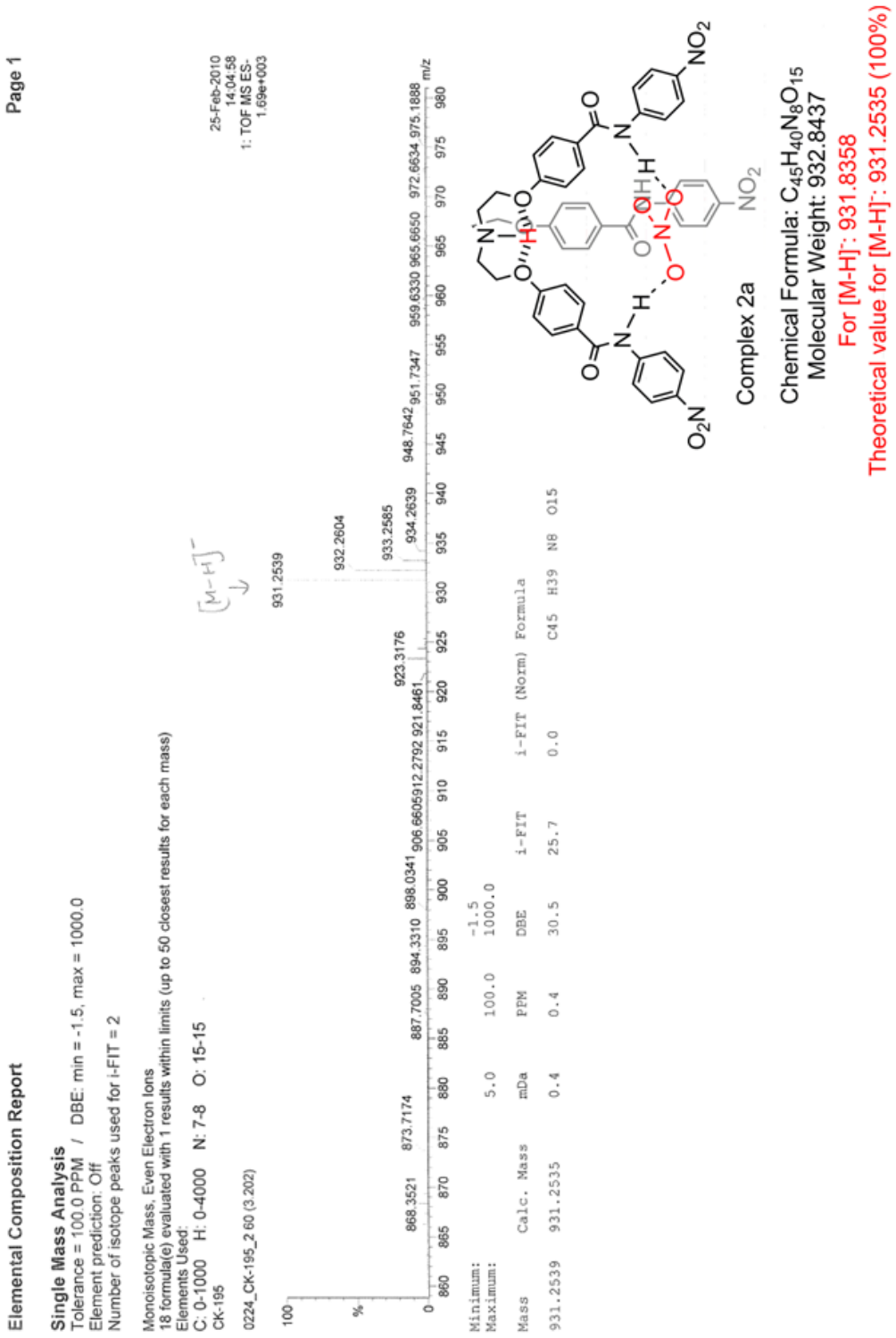


Fig. S27 HRESI mass spectrum of complex **2a** recorded in DMSO.

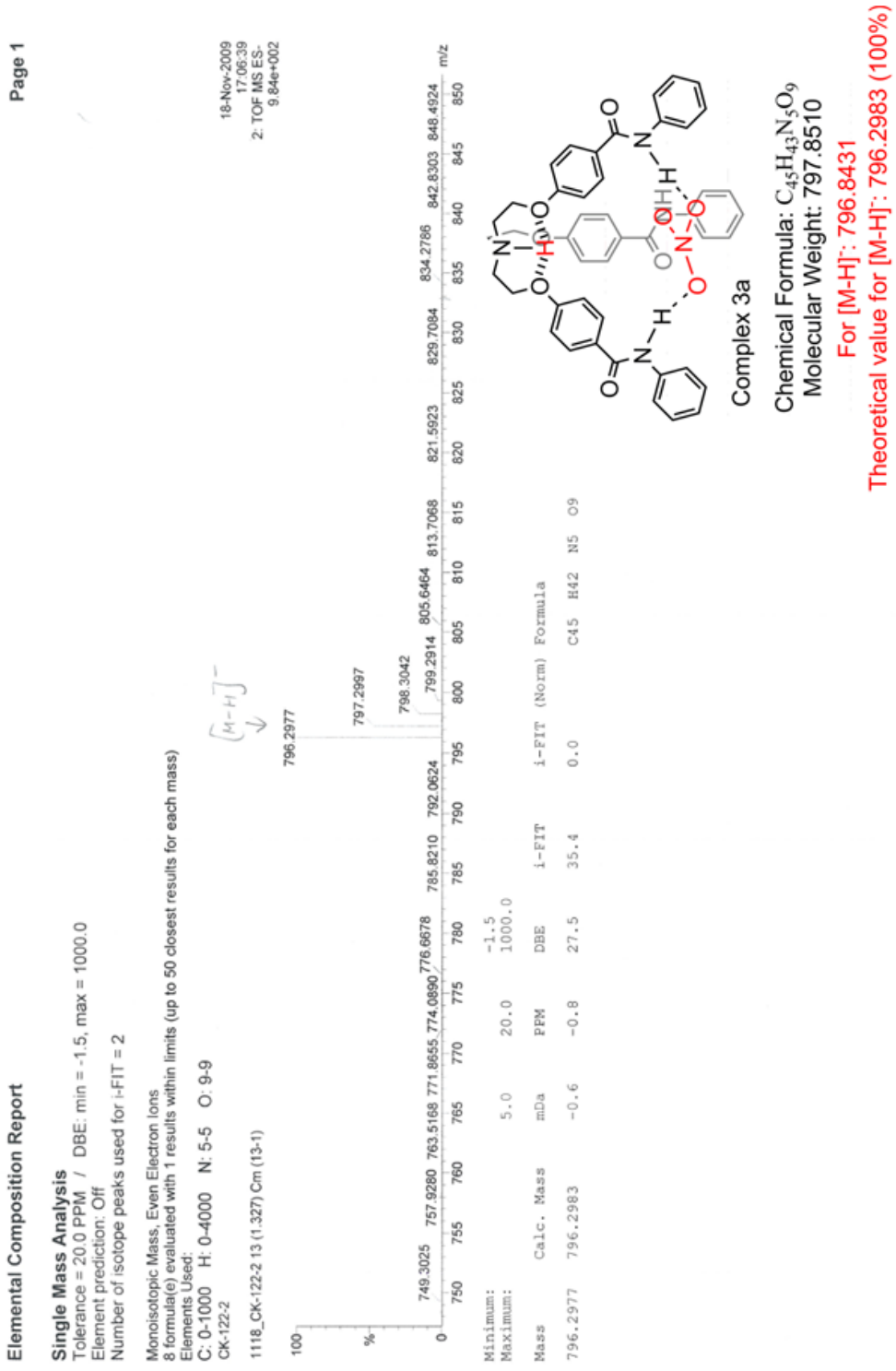


Fig. S28 HRESI mass spectrum of complex **3a** recorded in DMSO.

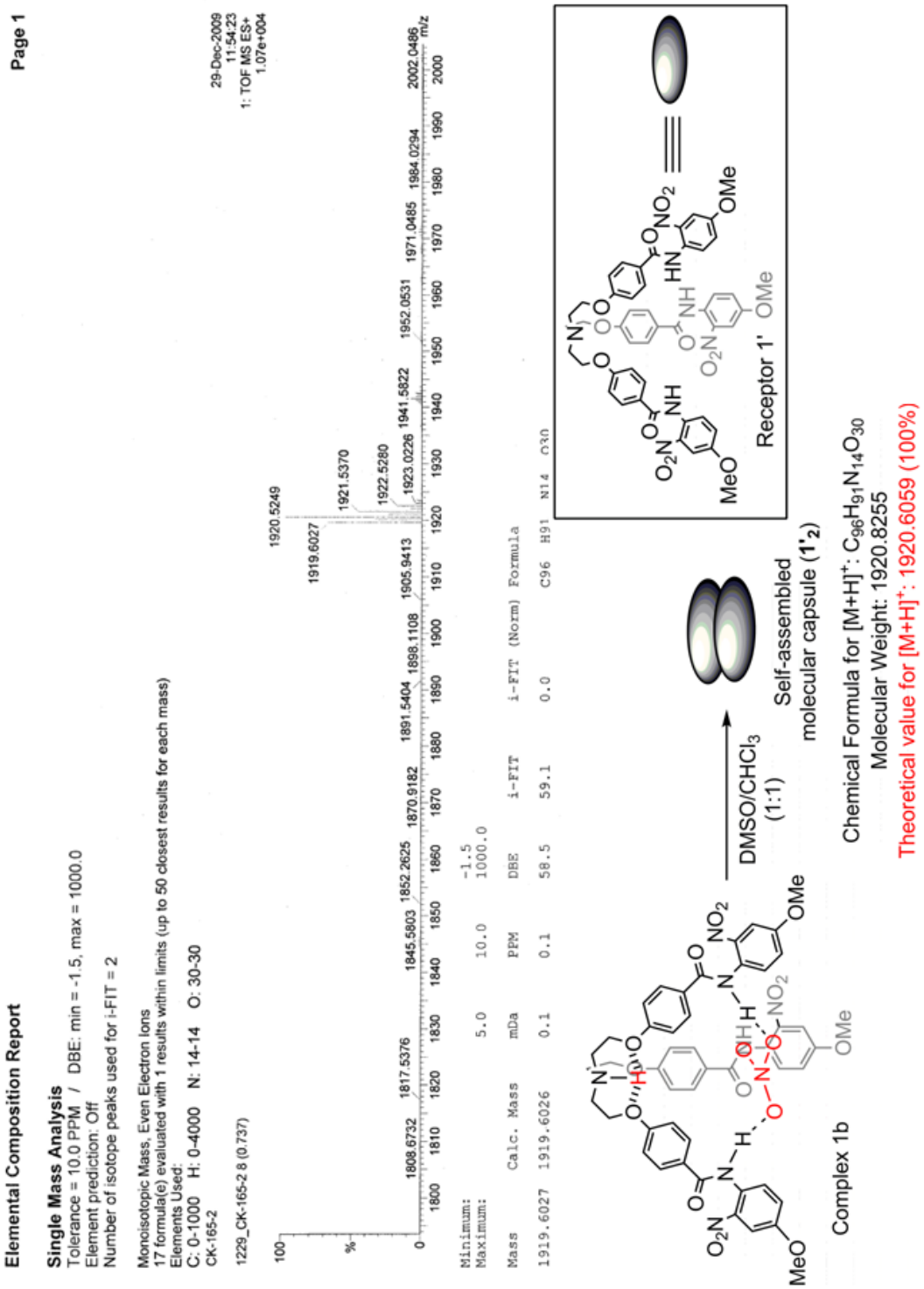


Fig. S29 HRESI mass spectrum of self-assembled capsule (**1'$_2$**) recorded after dissolving nitrate complex **1b** in mixture solution of DMSO/$CHCl_3$ (1:1).

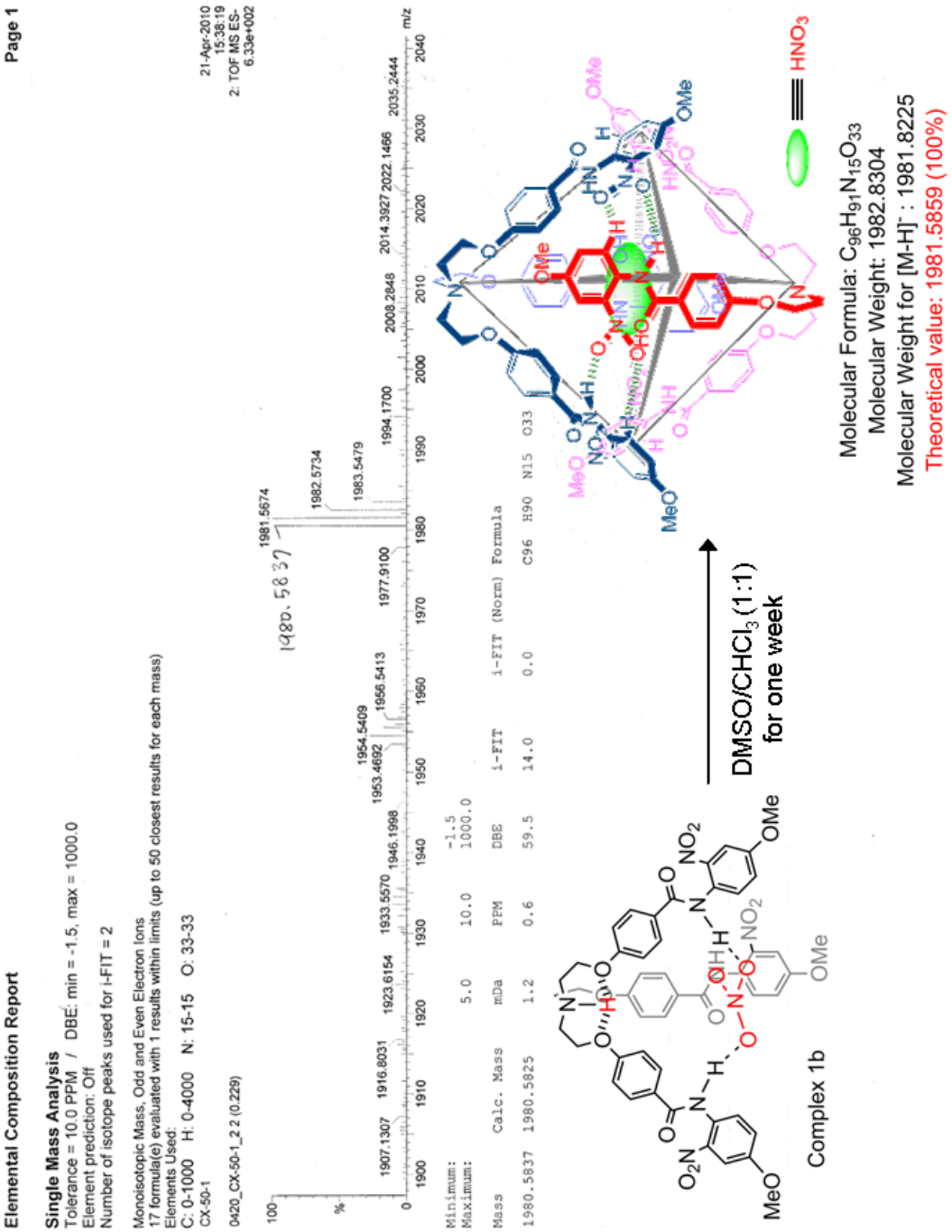


Fig. S30 HRESI mass spectrum of self-assembled capsule encapsulating nitrate anion (**1'$_2$a**) recorded after dissolving nitrate complex **1b** in mixture solution of DMSO/$CHCl_3$ (1:1) and keeping the mixture solution at room temperature (25 ºC) over a period of one week.

Table S1. Crystallographic data and structure refinements for **1a**

	1a
Empirical formula	C_{48} H_{49} N_5 O_{12}
Formula weight	887.92
Crystal system	Trigonal
Space group	P -3
a (Å)	15.7160(5)
b (Å)	15.7160(5)
c (Å)	11.4490(5)
α (°)	90
β (°)	90
γ (°)	120
V ($Å^3$)	2448.96(15)
Z	2
Temperature	200(2) K
Wavelength (Å)	0.71073
ρ_{cal} Mg/m^3	1.204
μ, mm^{-1}	0.087
F (000)	936
Independent reflection	2845
Reflection used	13438
R_{int} value	0.1221
Refinement method	Full-matrix least-squares on F2
GOOF	1.837
R indices[I>2sigma(I)]	R1 = 0.1953, wR2 = 0.5241
R indices(all data)	R1 = 0.2508, wR2 = 0.5372

Table S2. Hydrogen bonding distances (Å) and Bond angles (°) in complex **1a**

Bond distances (Å)		Bond angles (°)	
N1-H1'…N3	6.821	N1-H1'…N3	180.00
N2-H2…O3	2.215	N2-H2…O3	157.25
C7-H7…O3	2.476	C7-H7…O3	158.25
C1-H1A…O3	2.630	C1-H1A…O3	147.10
C11-H11…O3	2.674	C11-H11…O3	137.10

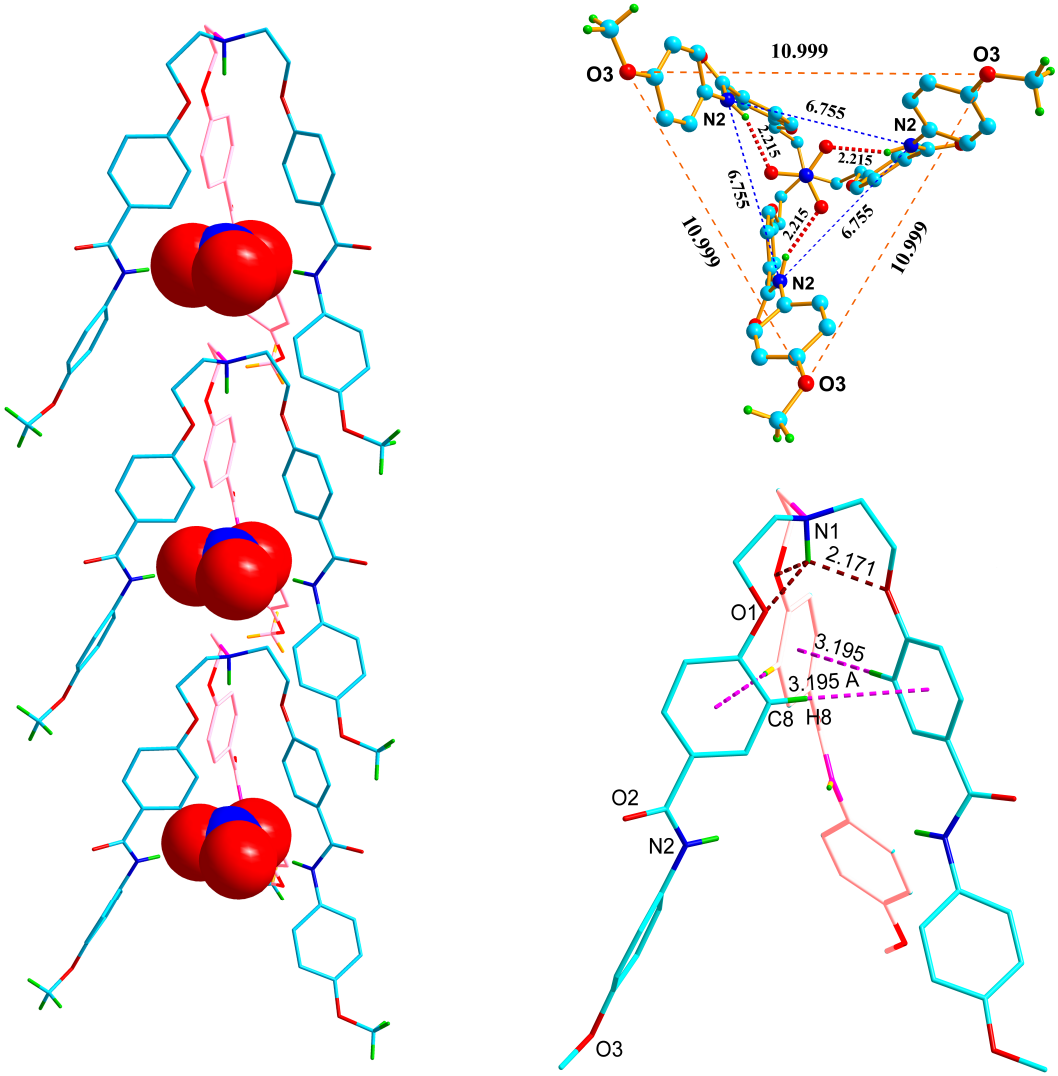


Fig. S31 Crystal structure of nitrate complex **1a** showing: packing of discrete nitrate complex (left); end of each arm lie at the apex of equilateral triangle (right, top); and interior cavity formed (right, bottom) by hydrogen bonding interactions between proton of centrally bridged N-atom and O-atoms of aliphatic arm (shown by brown color dotted lines) and aromatic C-H···π interactions (shown by purple color dotted lines) respectively.

Reference:

1. A. S. Singh, B.-Y. Chen, Y.-S. Wen, C. Tsai and S.-S. Sun, *Org. Lett.* 2009, **11**, 1867-1870.