

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**

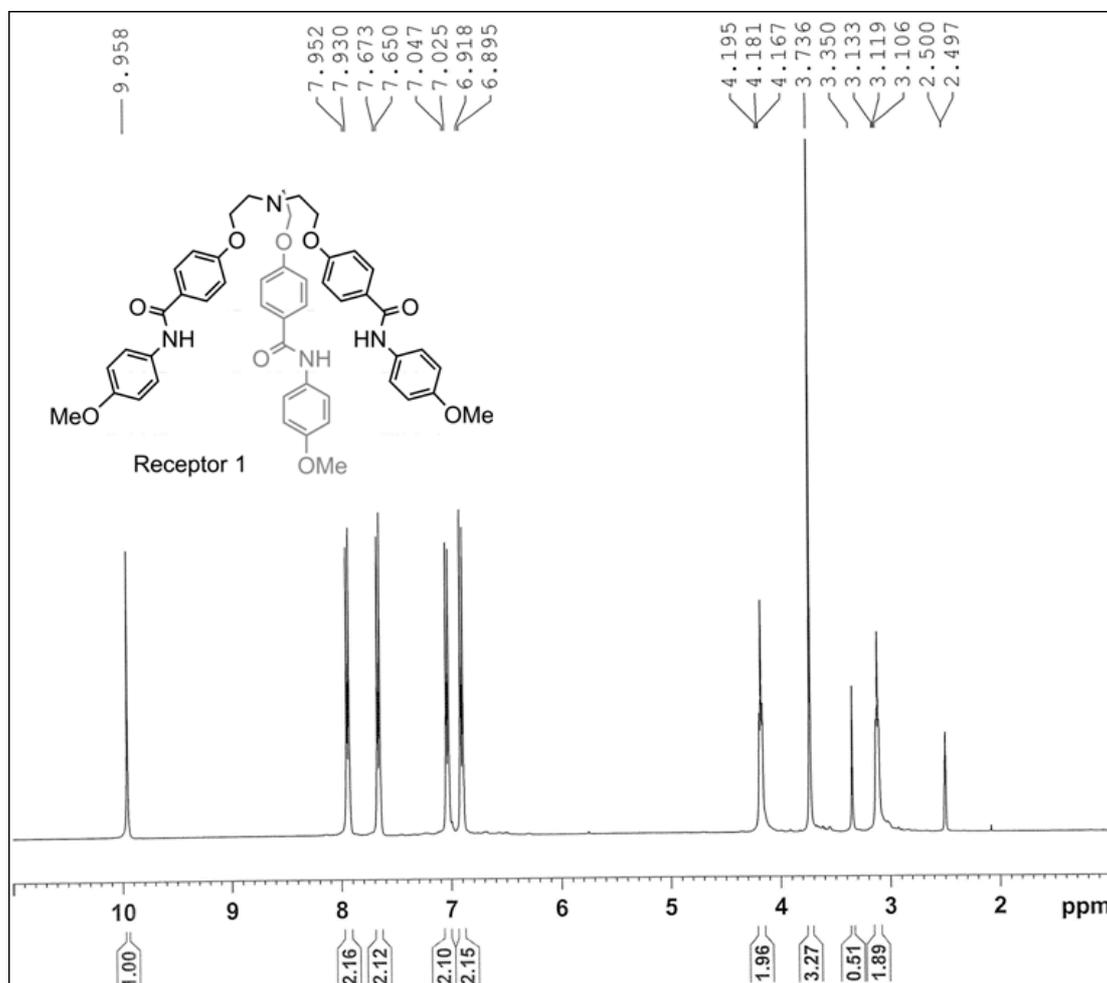
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*Institute of Chemistry, Academia Sinica, 115 Nankang, Taipei, Taiwan,  
Republic of China*

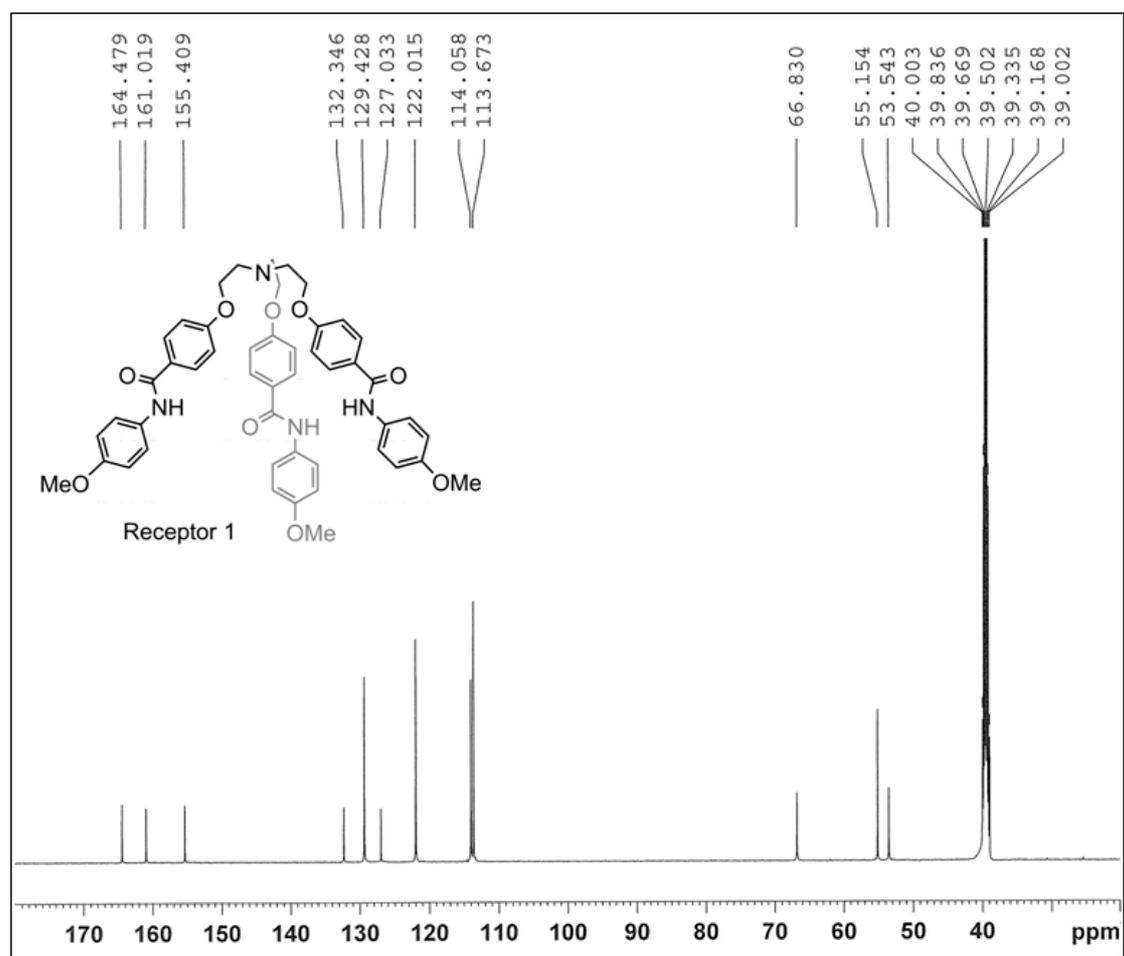
*E-mail: sssun@chem.sinica.edu.tw*

- Fig. S1-S47** Spectral characterization of receptors and anion complexes.
- Fig. S48-S56** HRESI mass spectra of nitrate complexes **1a-7a**, **1b** and **6b**.
- Fig. S57-S60** HRESI mass spectra of self-assemble capsule (**1'**)<sub>2</sub> formation.
- Fig. S61-S64** HRESI mass spectra of self-assemble capsule (**5**)<sub>2</sub> formation.
- Fig. S65-S67** HRESI mass spectra of self-assemble capsule (**6'**)<sub>2</sub> formation.
- Fig. S68** Titration spectra of mixture of nitrate complex **1a** and **1b** in DMSO-*d*<sub>6</sub> with varying amount of CDCl<sub>3</sub>.
- Fig. S69-S71** <sup>1</sup>H NMR titration of DMSO-*d*<sub>6</sub> solution of receptor **1'** with CDCl<sub>3</sub>, acetone-*d*<sub>6</sub> and CD<sub>3</sub>NO<sub>2</sub> respectively.
- Fig. S72-S74** <sup>1</sup>H NMR titration of DMSO-*d*<sub>6</sub> solution of nitrate complex **1b** with CDCl<sub>3</sub>, acetone-*d*<sub>6</sub> and CD<sub>3</sub>NO<sub>2</sub> respectively.
- Fig. S75-S76** <sup>1</sup>H NMR titration of DMSO-*d*<sub>6</sub> solution of receptor **5** with acetone-*d*<sub>6</sub> and CD<sub>3</sub>NO<sub>2</sub> respectively.
- Fig. S77-S79** <sup>1</sup>H NMR titration of DMSO-*d*<sub>6</sub> solution of nitrate complex **5a** with CDCl<sub>3</sub>, acetone-*d*<sub>6</sub> and CD<sub>3</sub>NO<sub>2</sub> respectively.
- Fig. S80** Titration spectra of mixture of nitrate complex **6a** and **6b** in DMSO-*d*<sub>6</sub> with varying amount of CDCl<sub>3</sub>.
- Fig. S81** <sup>1</sup>H NMR titration of DMSO-*d*<sub>6</sub> solution of receptor **6'** with CD<sub>3</sub>NO<sub>2</sub>.
- Fig. S82-S84** <sup>1</sup>H NMR titration of DMSO-*d*<sub>6</sub> solution of nitrate complex **6b** with CDCl<sub>3</sub>, acetone-*d*<sub>6</sub> and CD<sub>3</sub>NO<sub>2</sub> respectively.
- Fig. S85** Concentration dependent <sup>1</sup>H NMR spectra of receptor **5** in CDCl<sub>3</sub>.
- Fig. S86-S93** Titration spectra of perchlorate complexes of the corresponding receptors **1-7** and **1'** with TBANO<sub>3</sub> in acetone-*d*<sub>6</sub>.
- Fig. S94** Spectroscopic curves of titration of perchlorate complexes with TBANO<sub>3</sub> in acetone-*d*<sub>6</sub>.

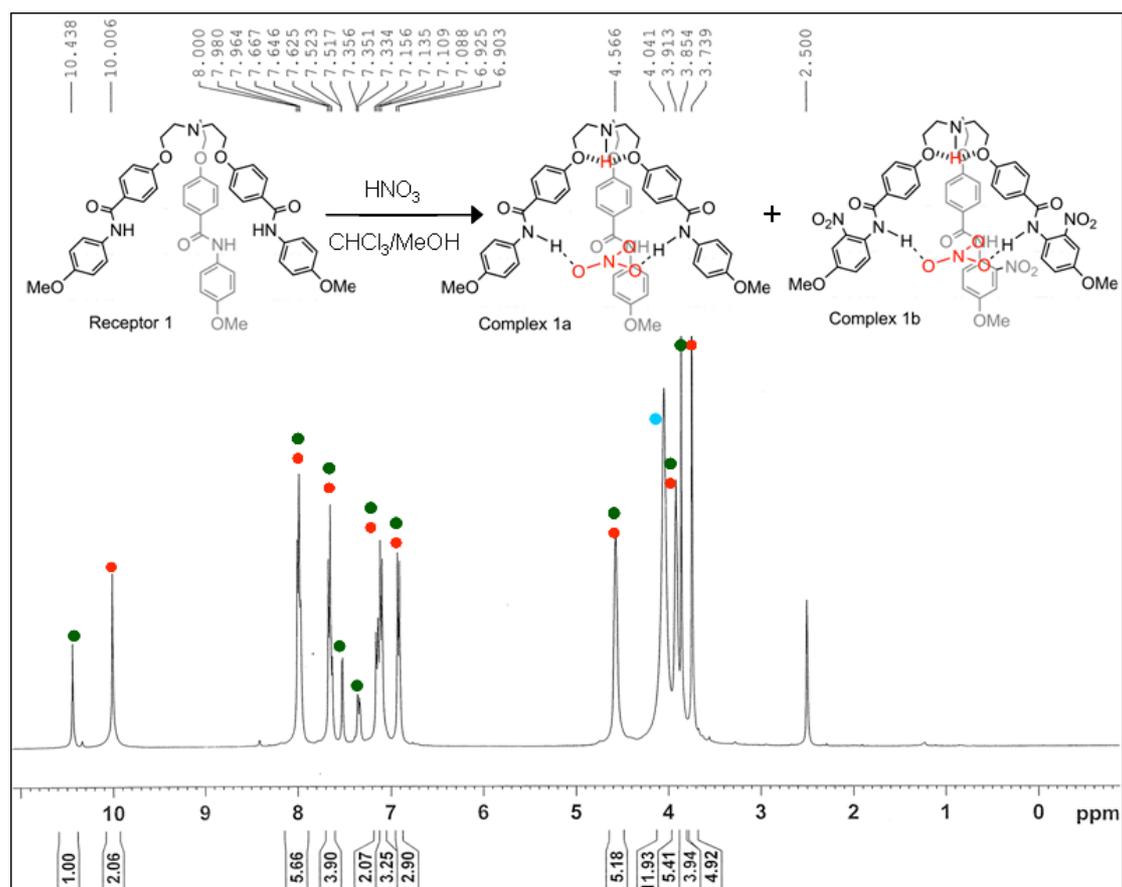
- Fig. S95** pH dependent reversible binding of nitrate anion by receptor **1'**.  
**Table S1** Crystallographic data and structure refinements for **1a**.  
**Table S2** Hydrogen bonding distances and Bond angles in complex **6a**.



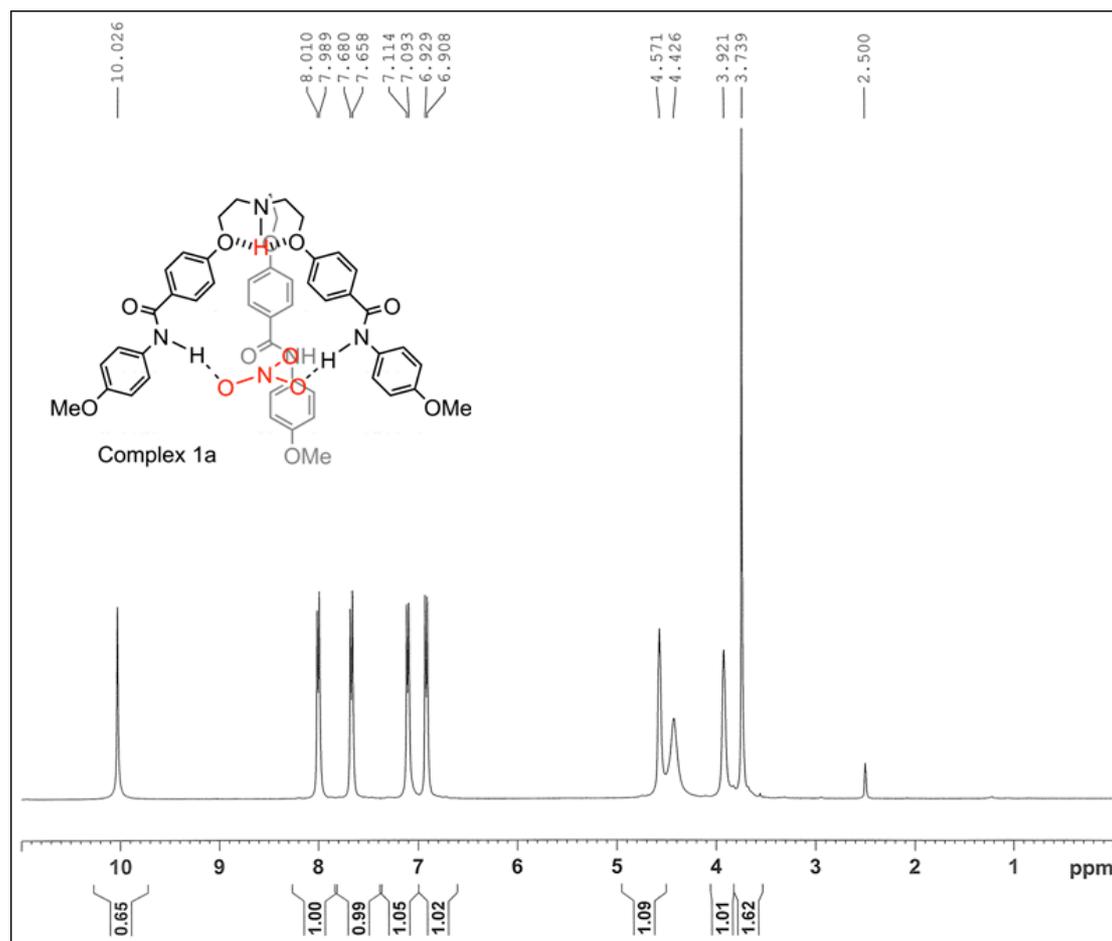
**Fig. S1** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 20 °C) spectrum of receptor **1**.



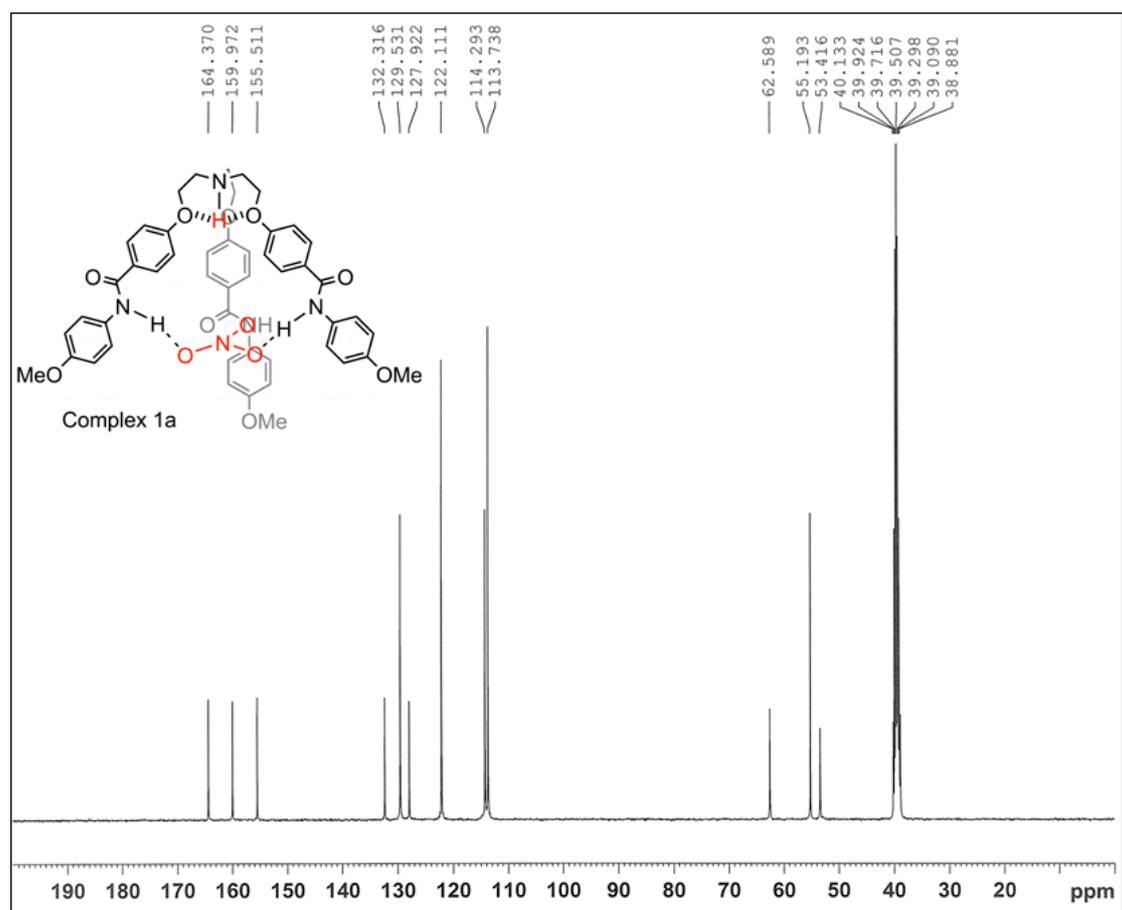
**Fig. S2**  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of receptor 1.



**Fig. S3** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 20 °C) 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<sub>3</sub>/MeOH (v/v = 1/1). The circle in blue color represents water peak from DMSO-*d*<sub>6</sub>.

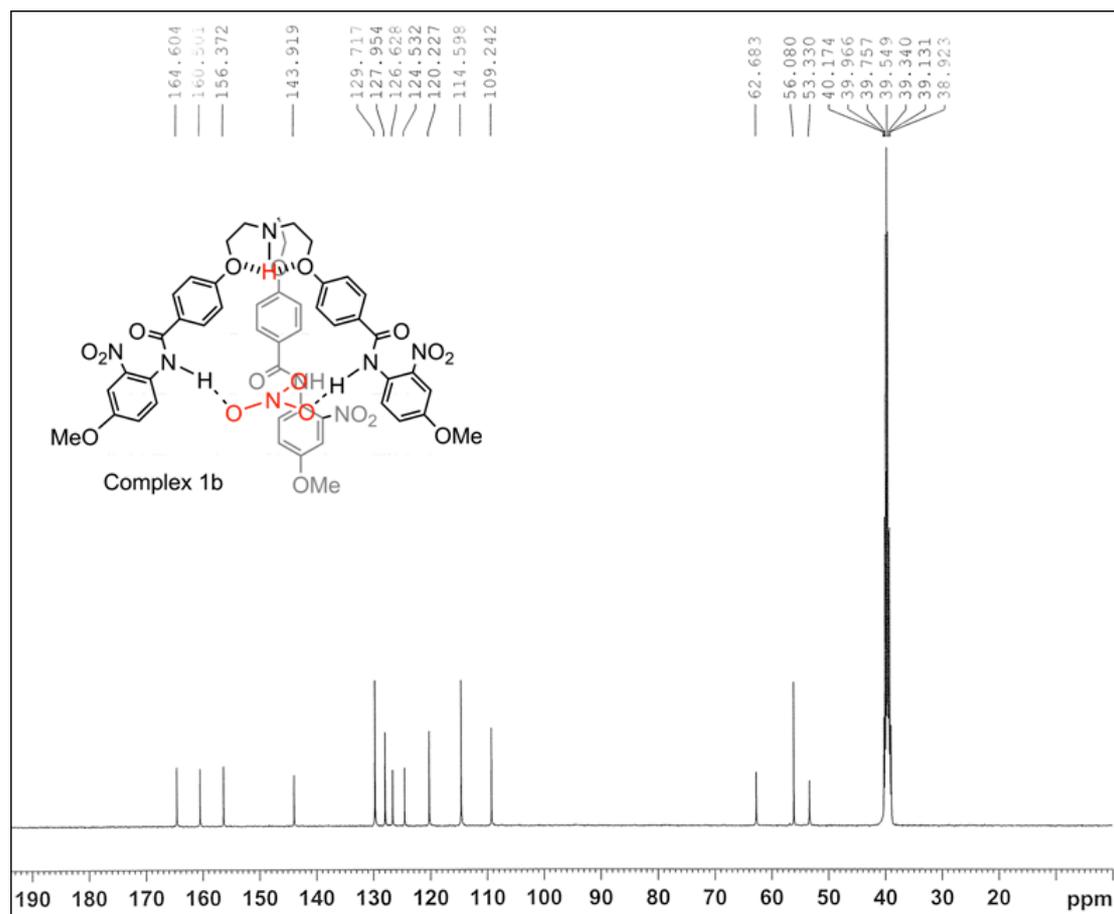


**Fig. S4** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 20 °C) spectrum of nitrate complex **1a**.

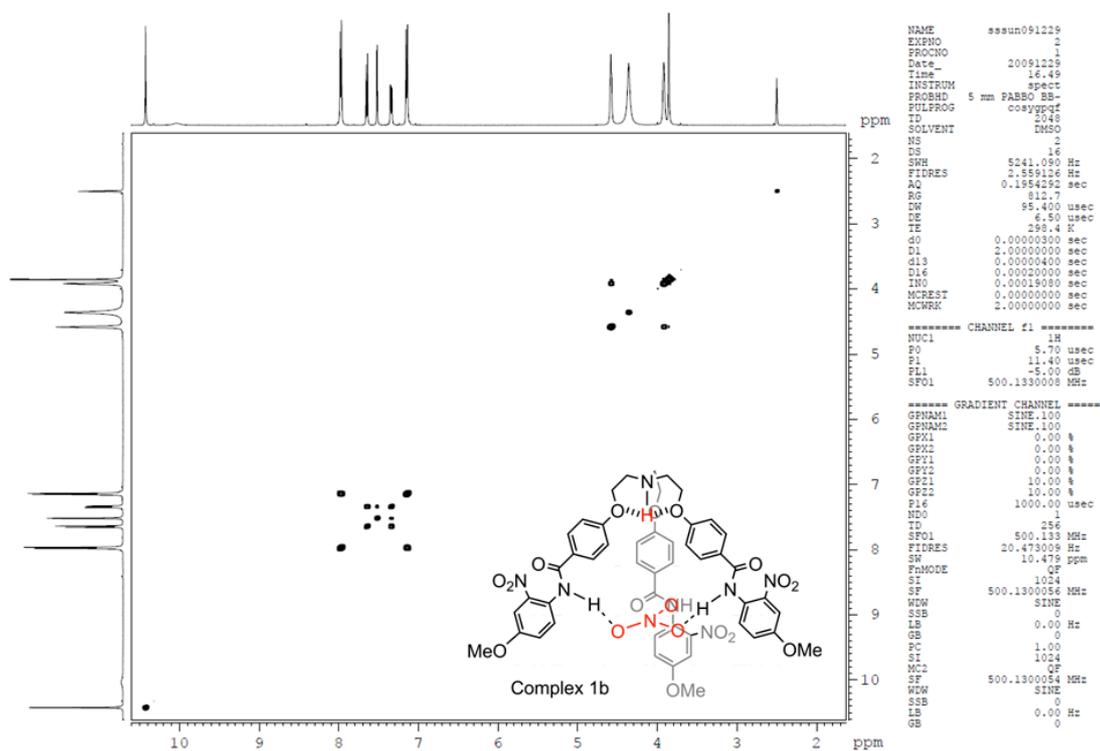


**Fig. S5**  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of nitrate complex **1a**.

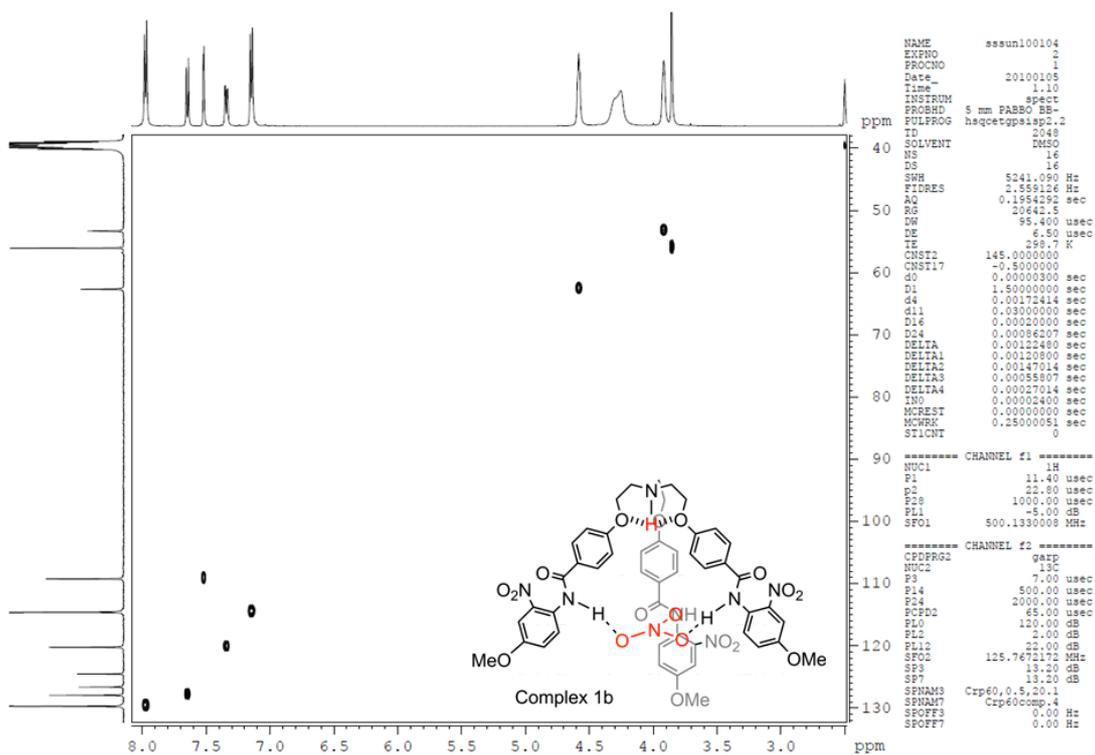




**Fig. S7** <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 20 °C) spectrum of nitrate complex **1b**.



**Fig. S8** The COSY spectrum of nitrate complex **1b** in DMSO-*d*<sub>6</sub>.



**Fig. S9** The HSQC spectrum of nitrate complex **1b** in DMSO-*d*<sub>6</sub>.

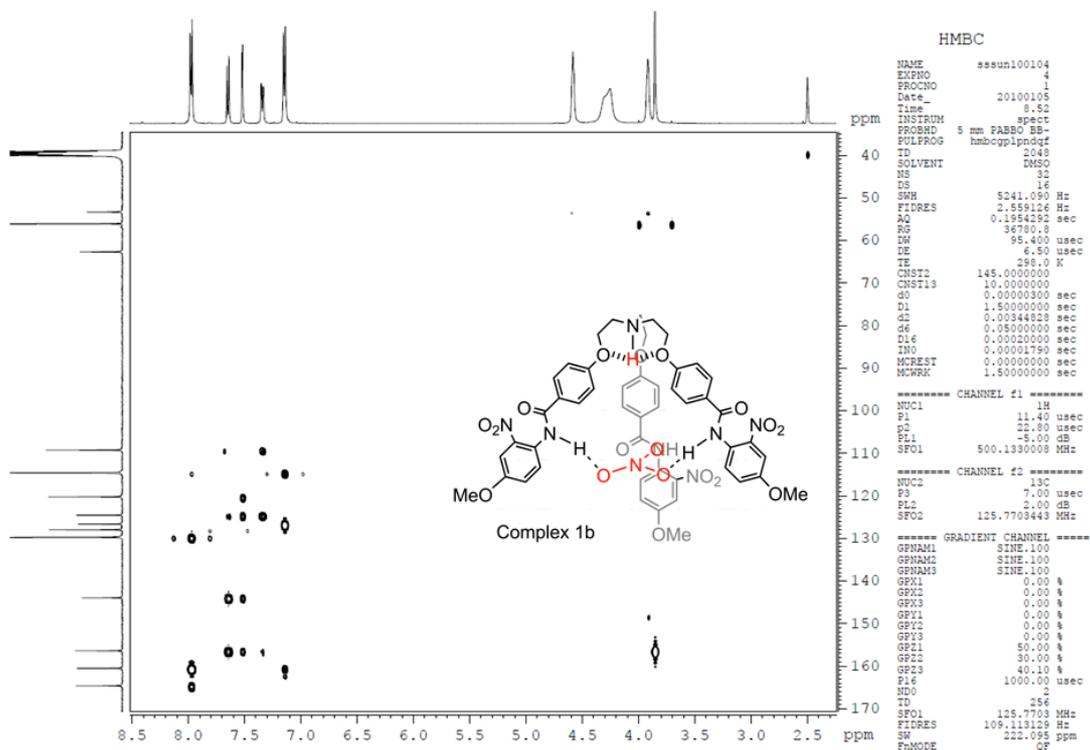


Fig. S10 The HMBC spectrum of nitrate complex **1b** in DMSO-*d*<sub>6</sub>.

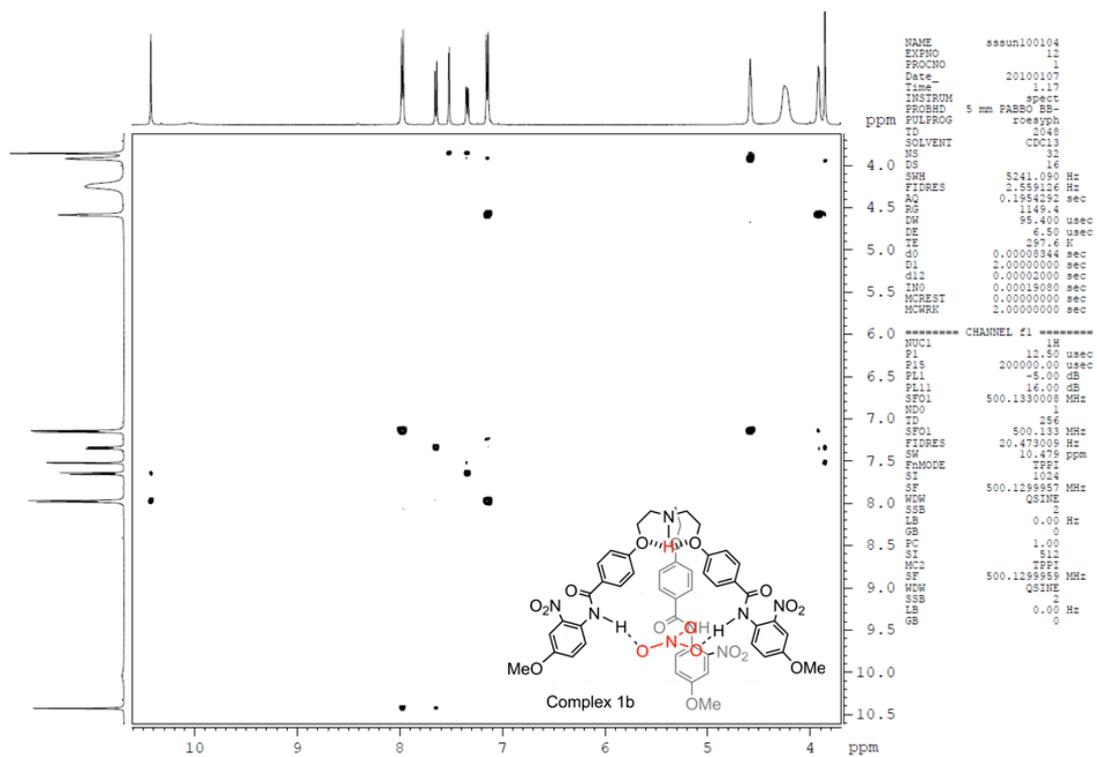
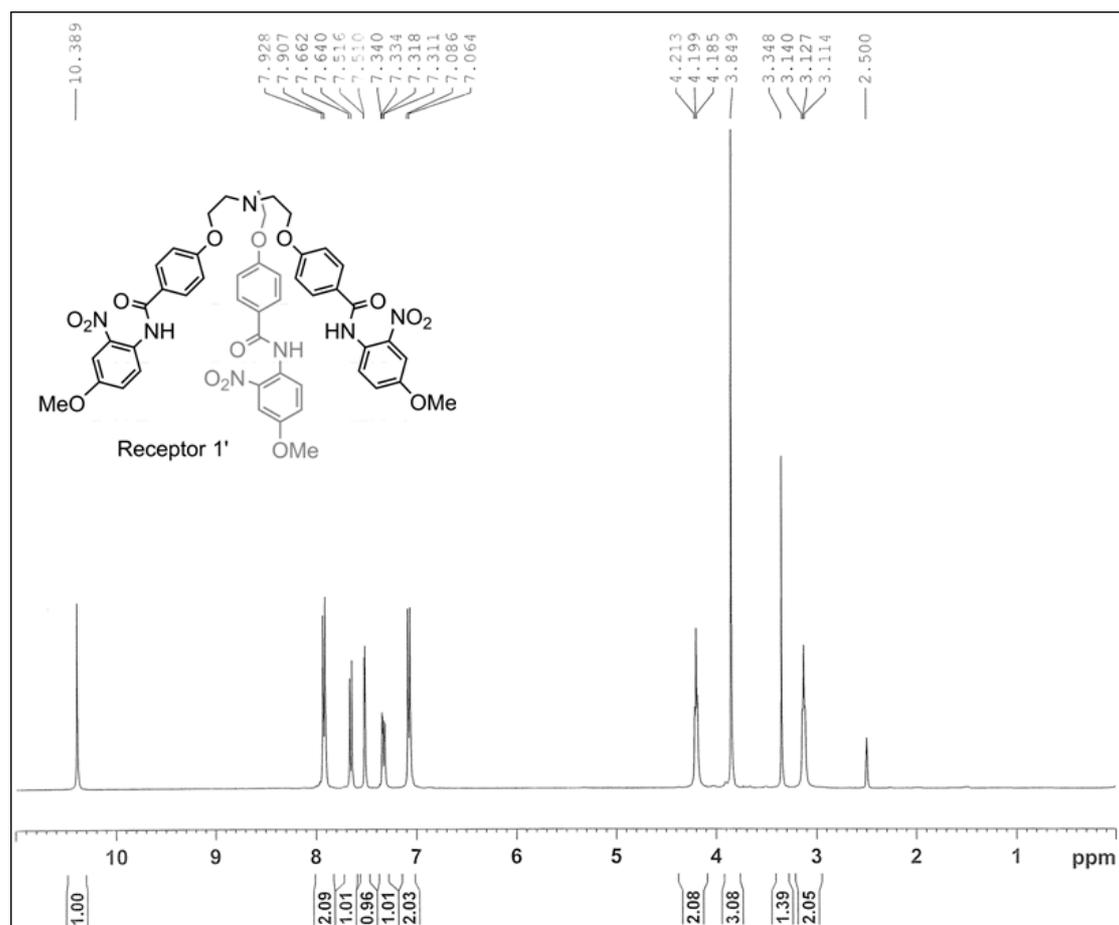
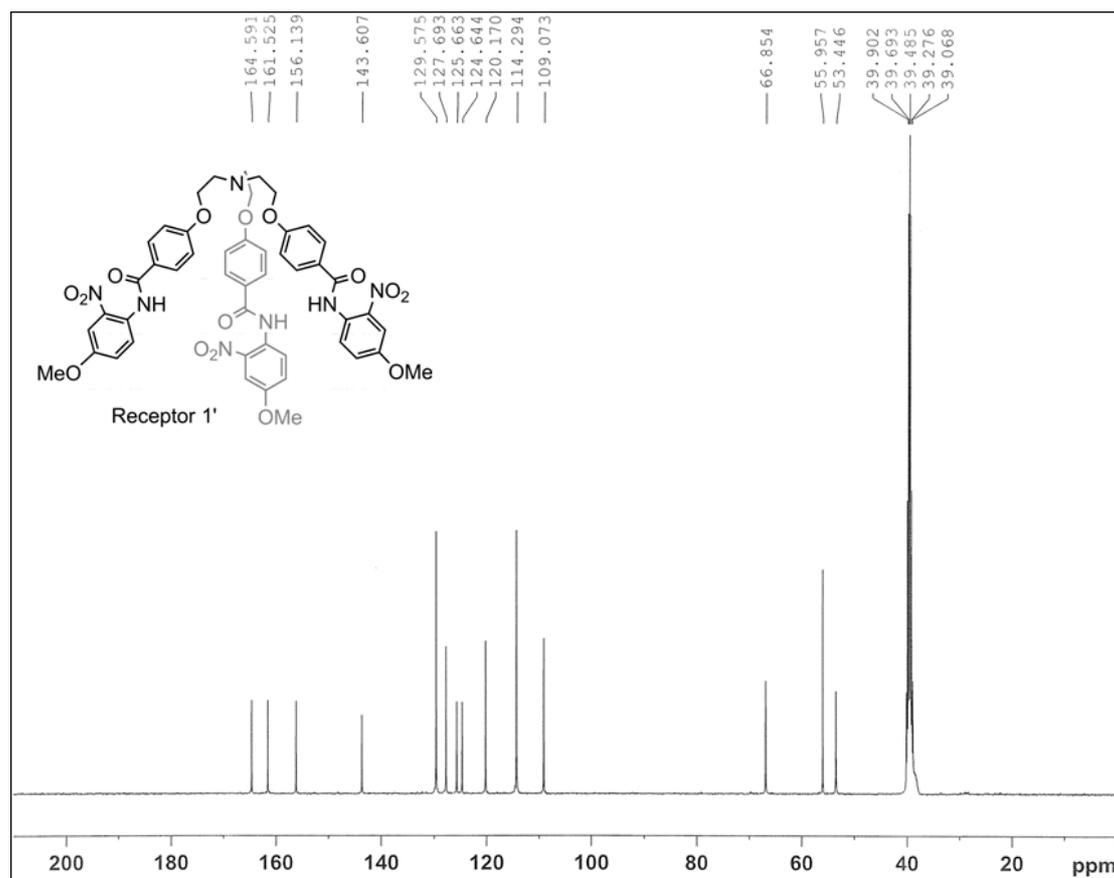


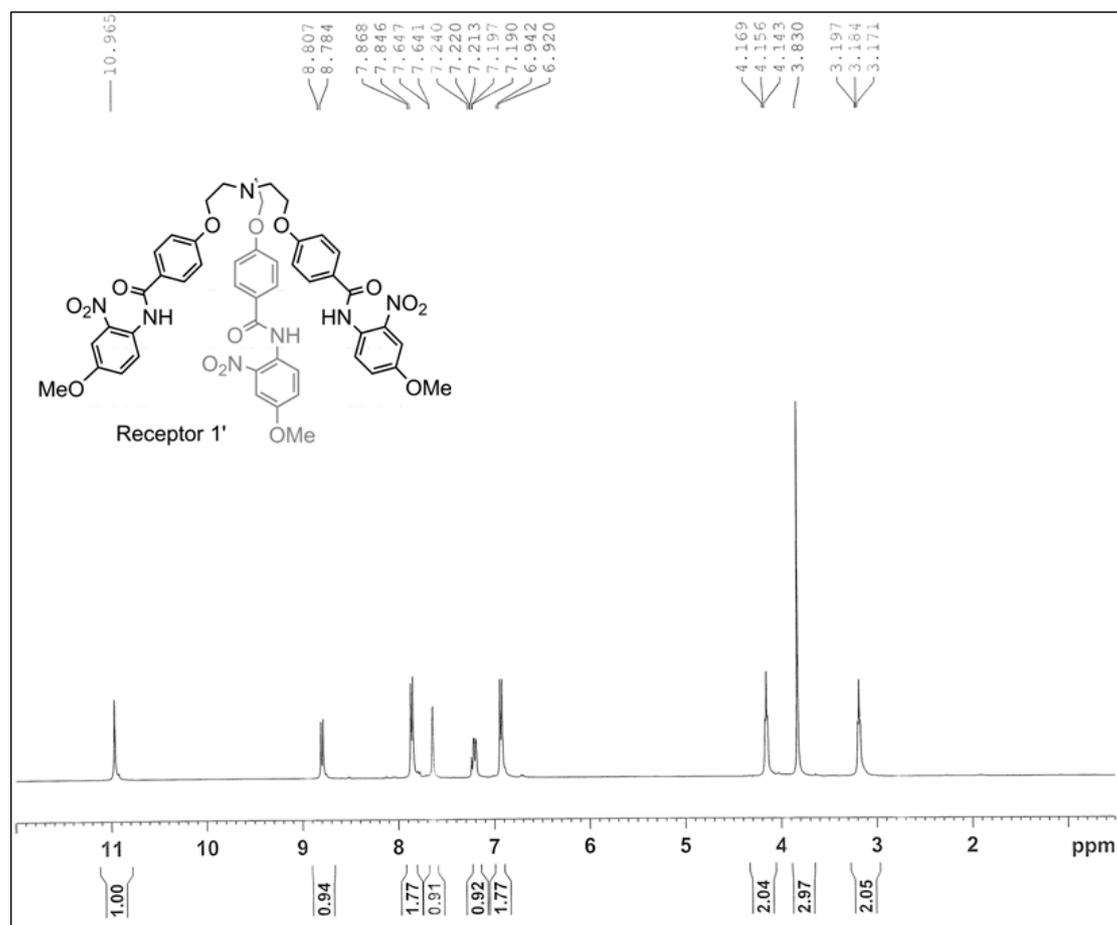
Fig. S11 The ROESY spectrum of nitrate complex **1b** in DMSO-*d*<sub>6</sub>.



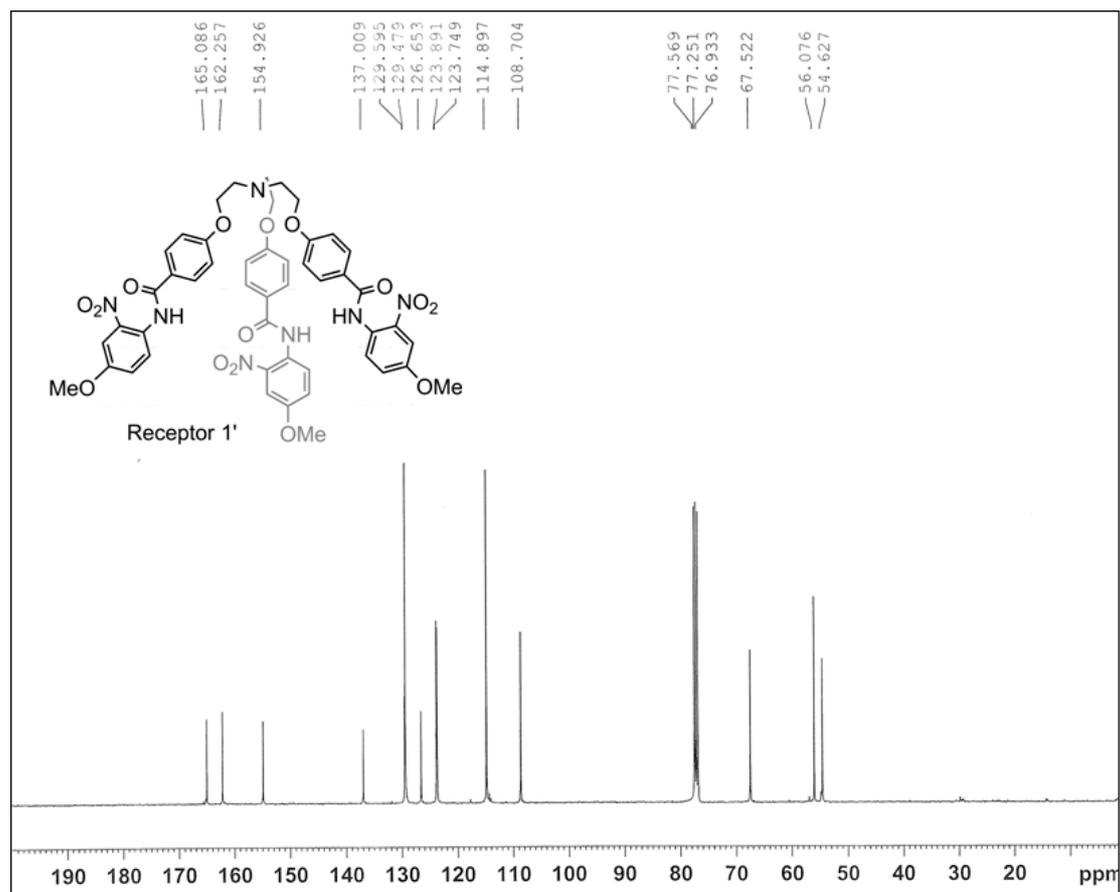
**Fig. S12**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ,  $20^\circ\text{C}$ ) spectrum of receptor 1'.



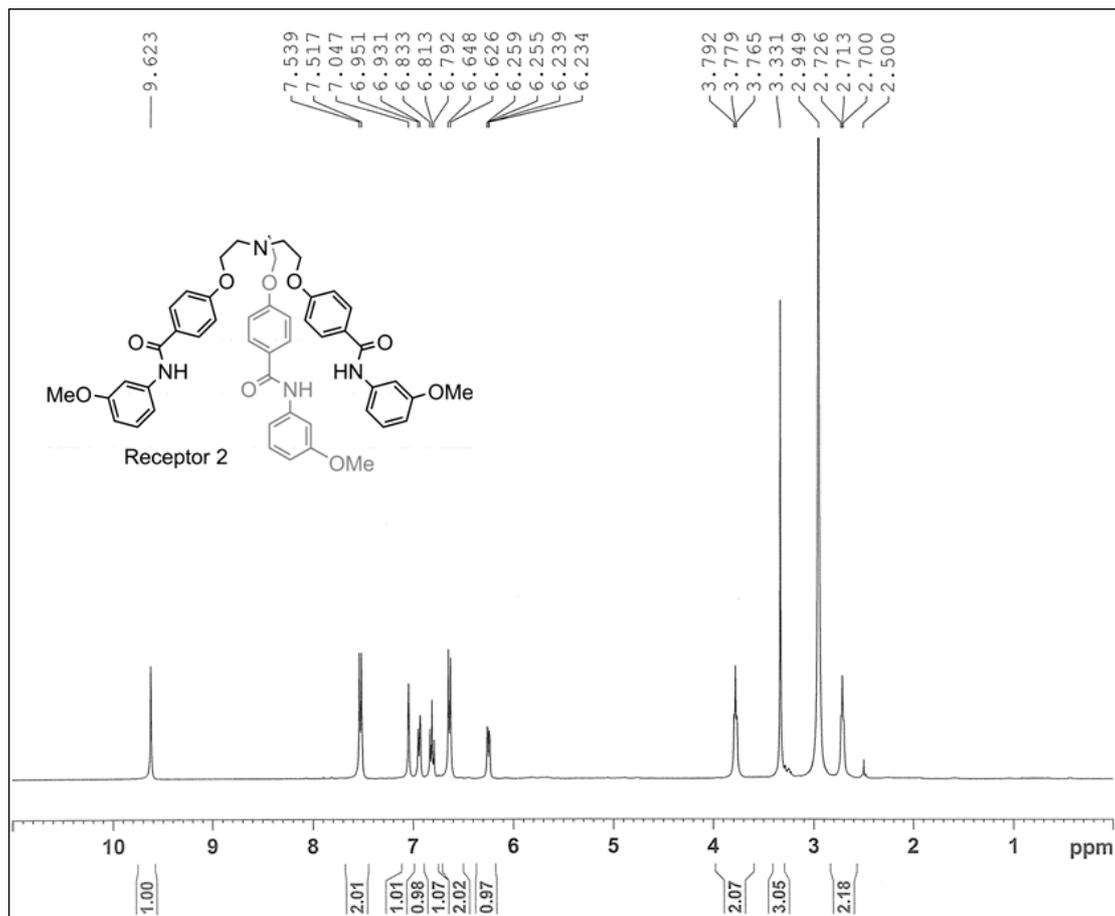
**Fig. S13**  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of receptor 1'.



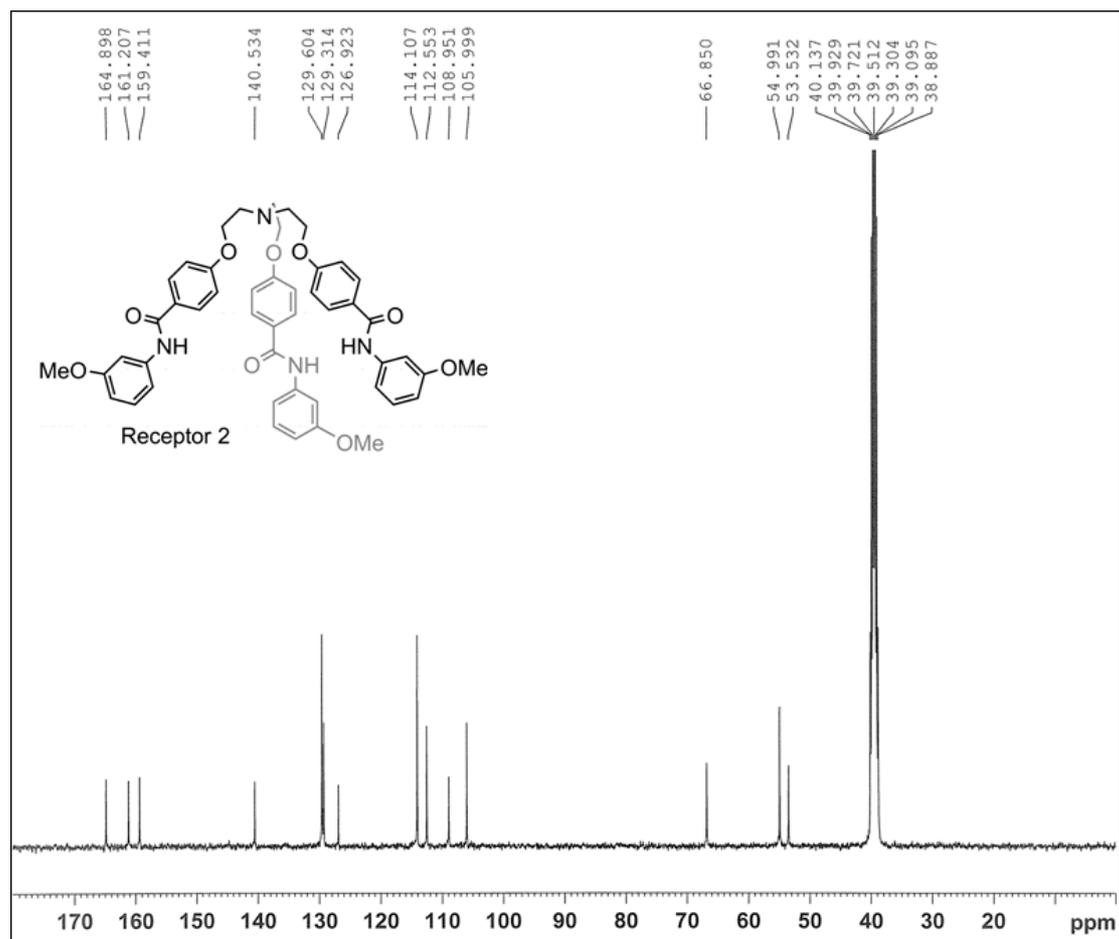
**Fig. S14** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20 °C) spectrum of receptor 1'.



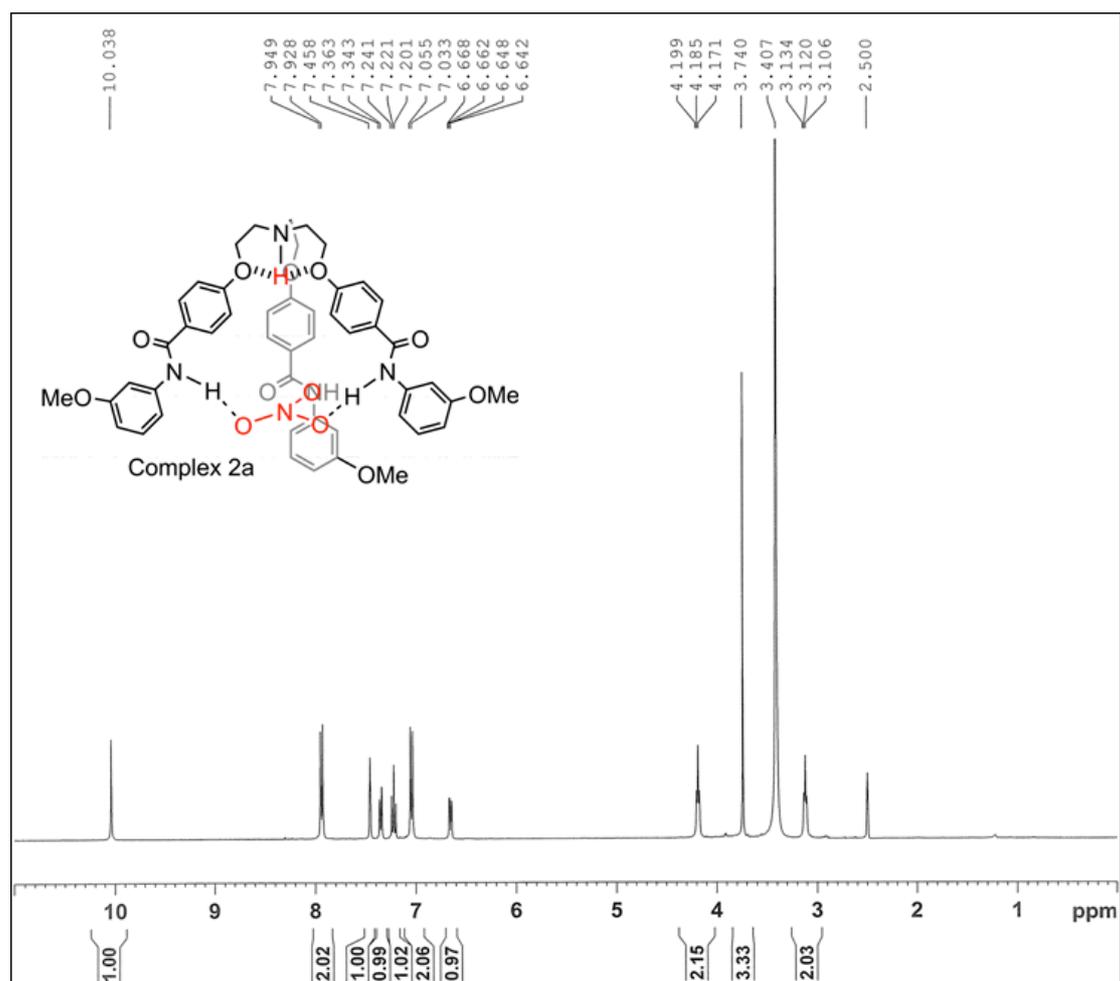
**Fig. S15** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C) spectrum of receptor 1'.



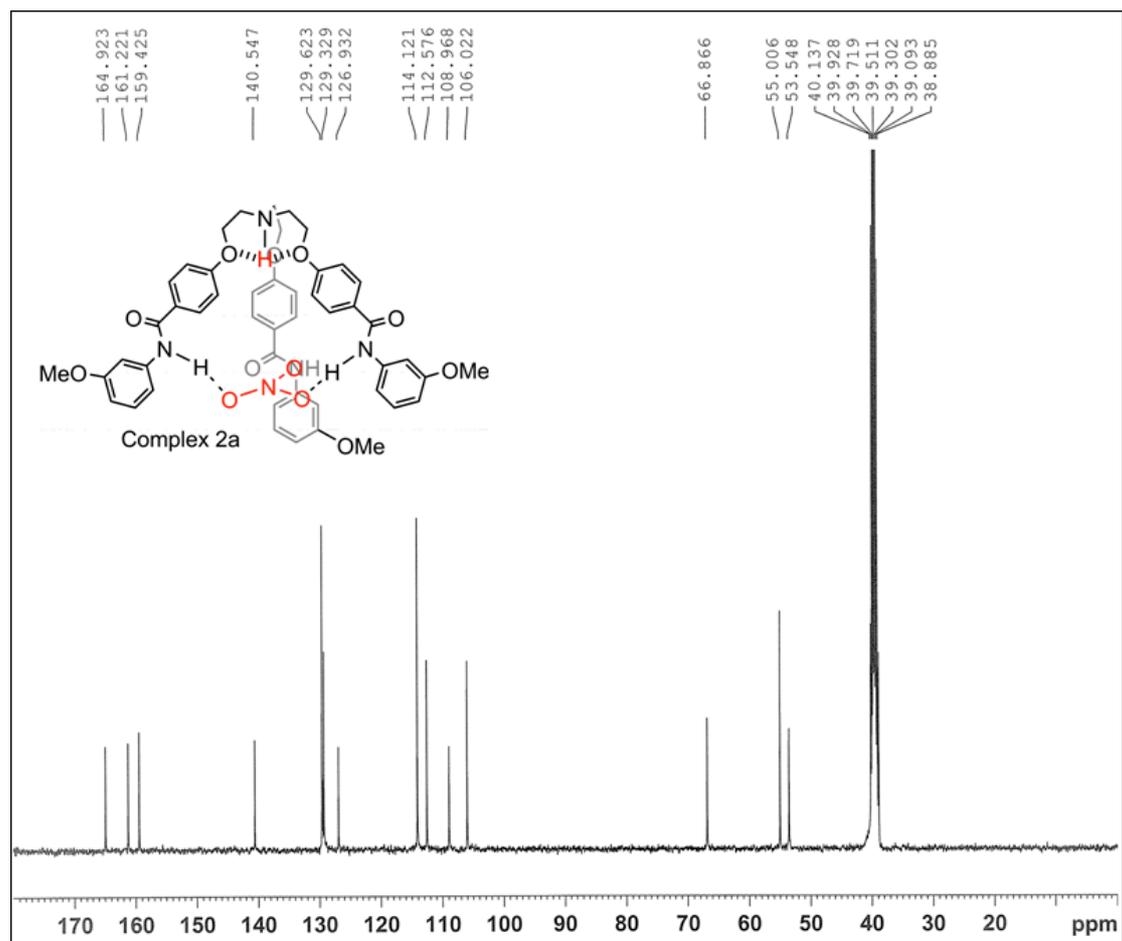
**Fig. S16**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of receptor 2.



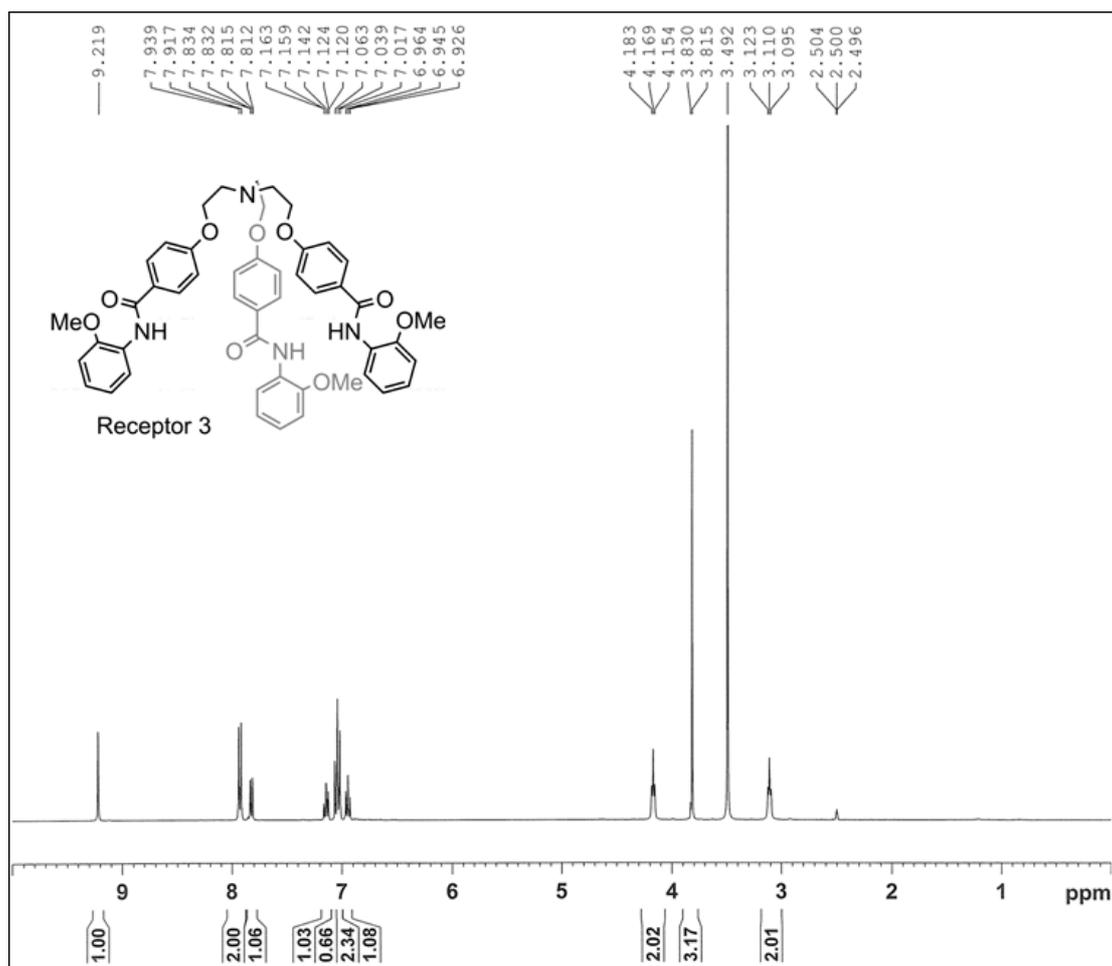
**Fig. S17** <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 20 °C) spectrum of receptor 2.



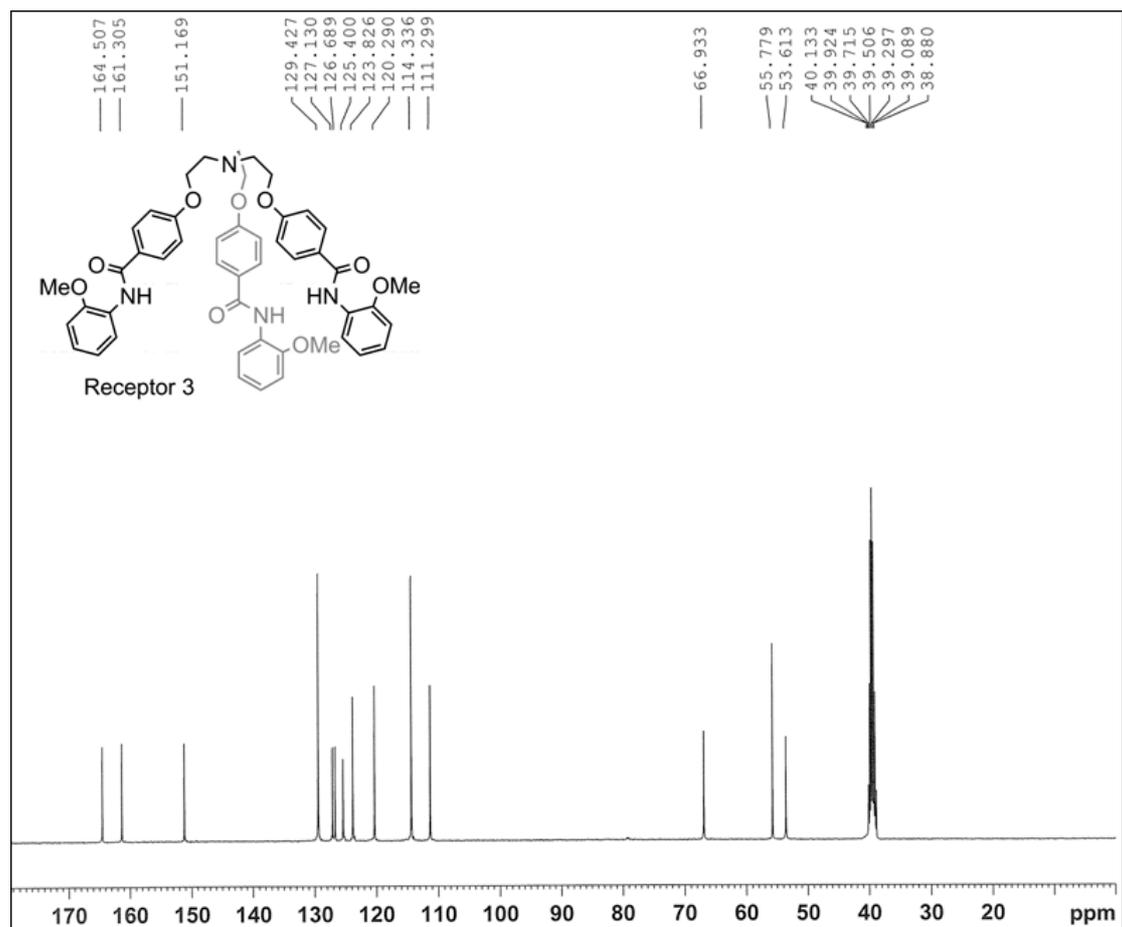
**Fig. S18**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of nitrate complex **2a**.



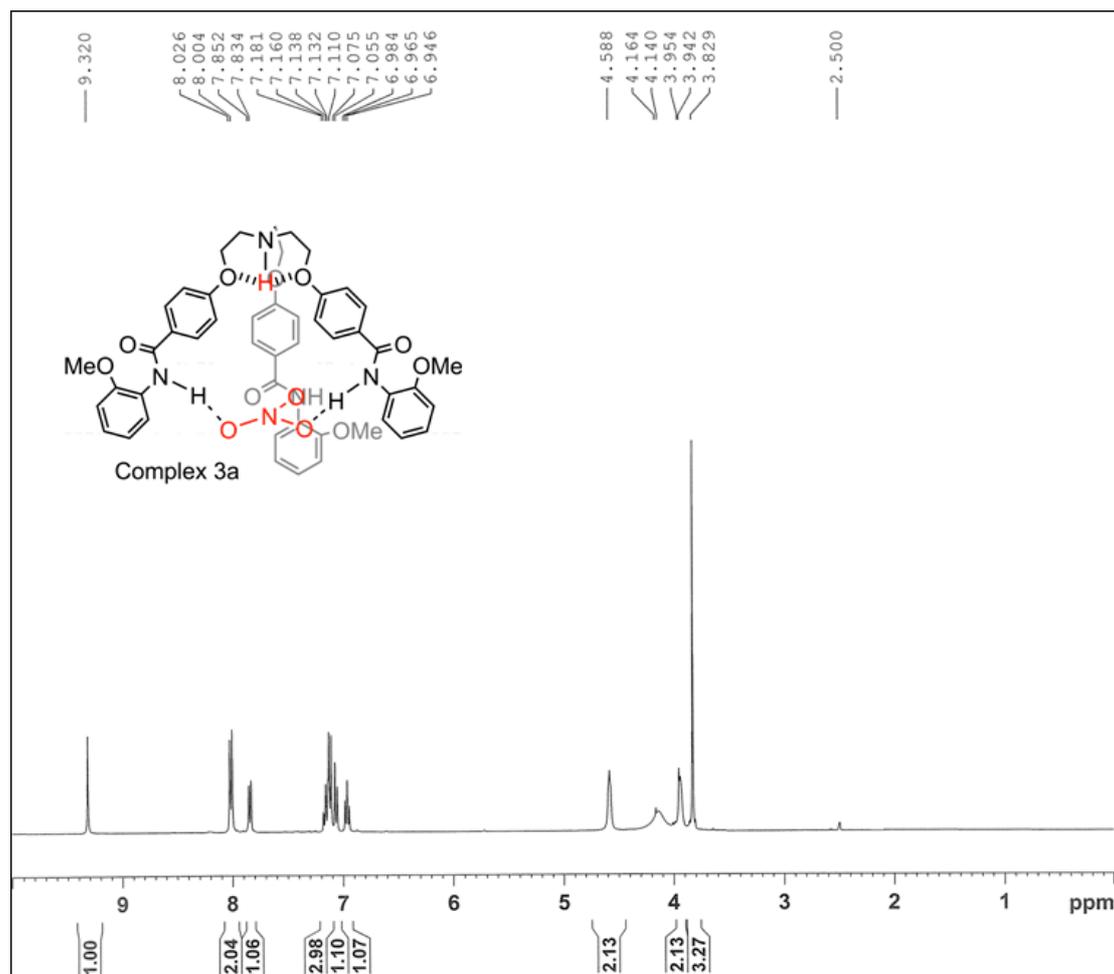
**Fig. S19**  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of nitrate complex 2a.



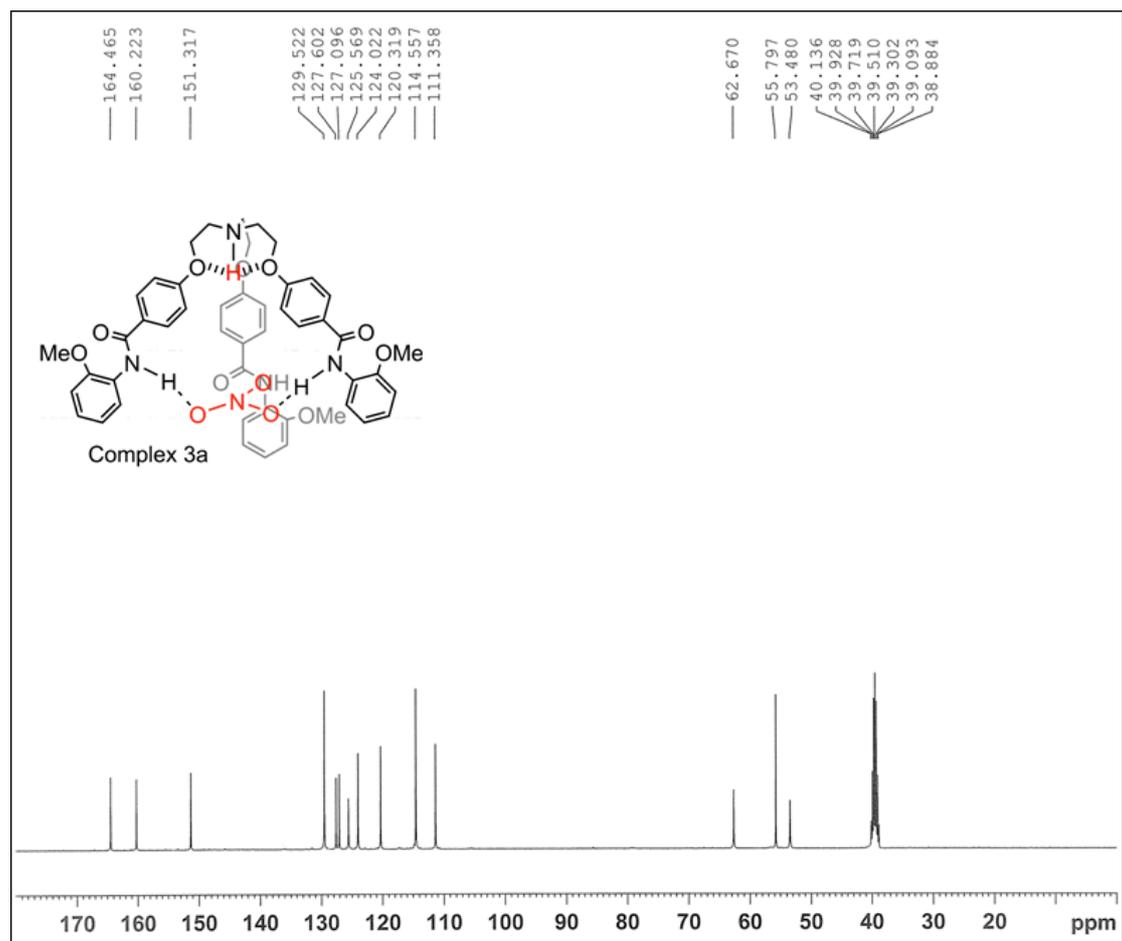
**Fig. S20** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 20 °C) spectrum of receptor **3**.



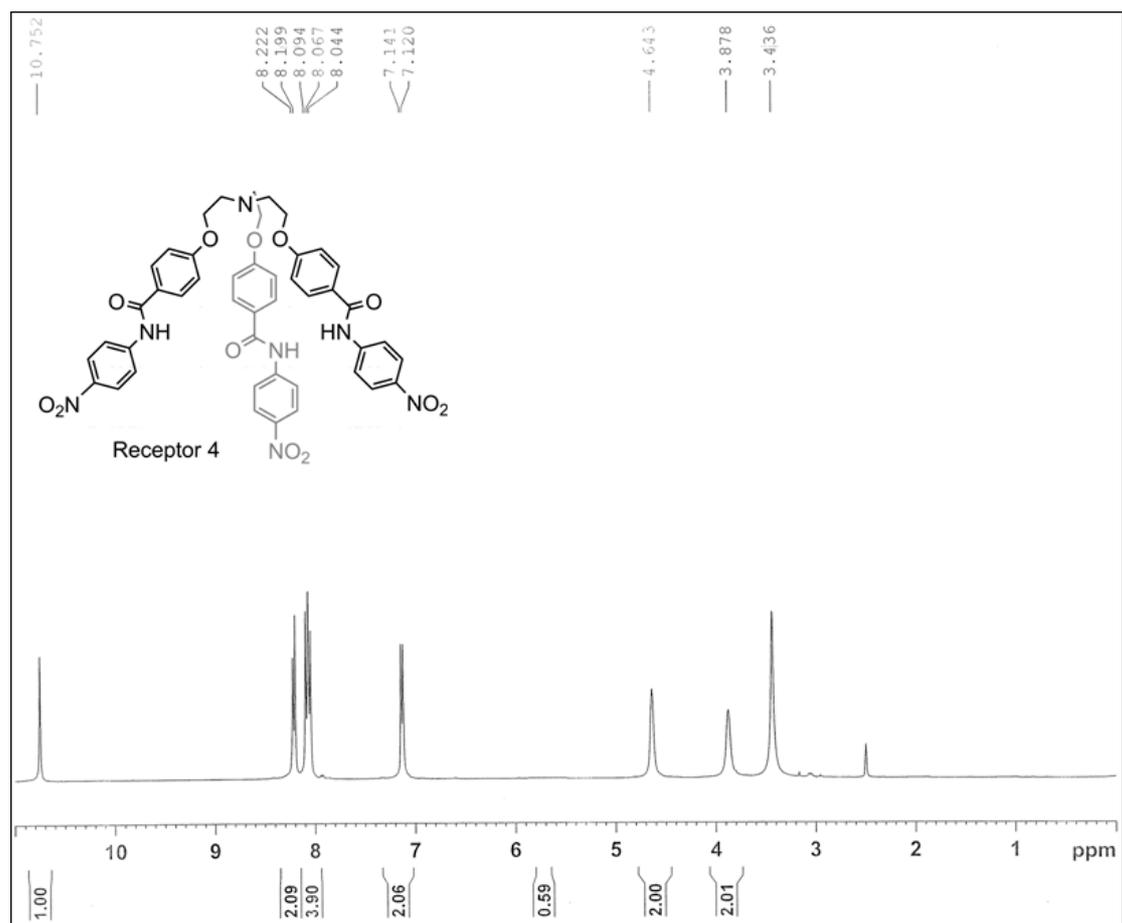
**Fig. S21**  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of receptor **3**.



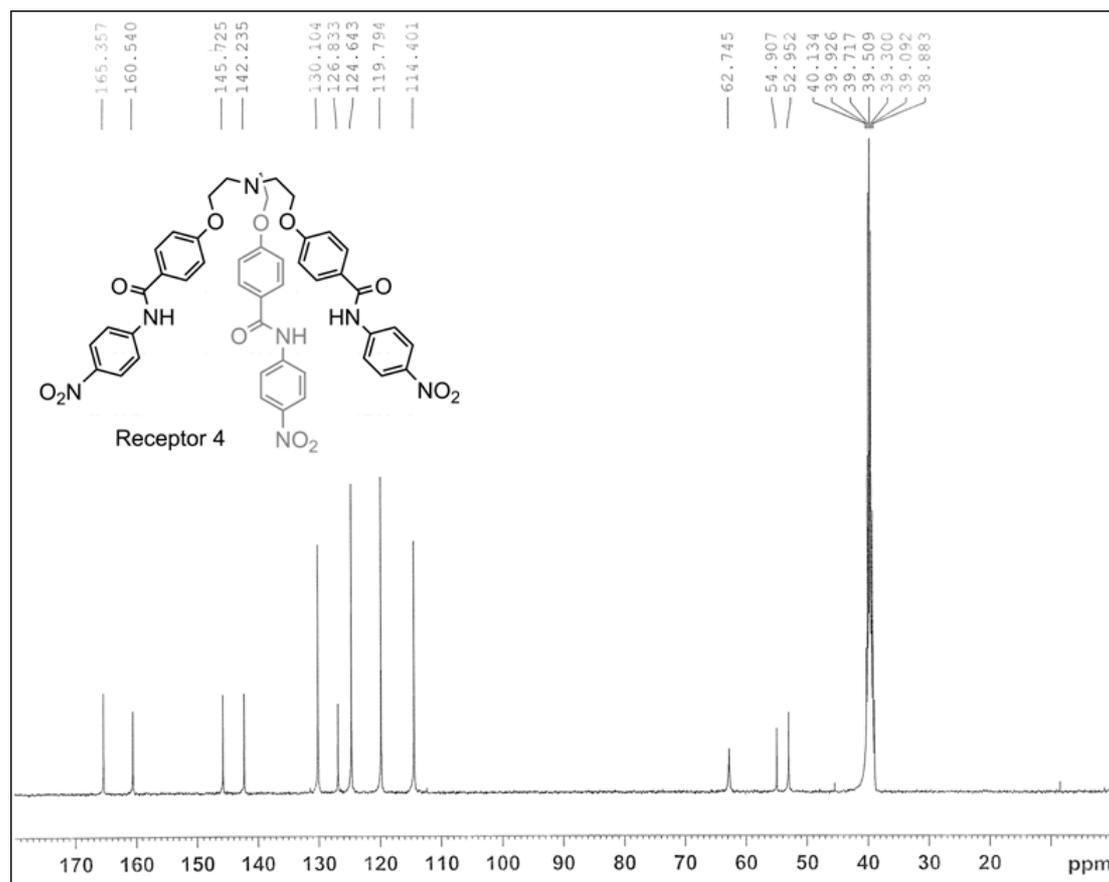
**Fig. S22**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of nitrate complex **3a**.



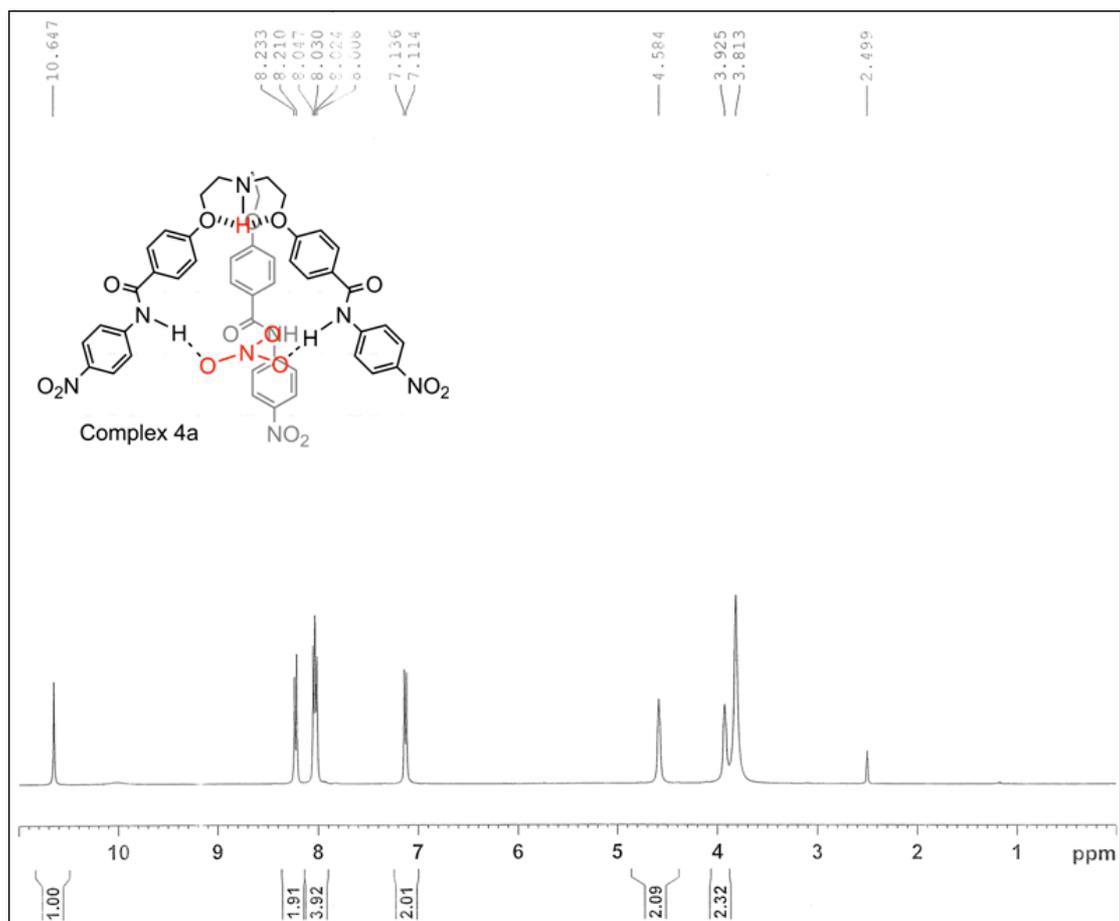
**Fig. S23** <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 20 °C) spectrum of nitrate complex **3a**.



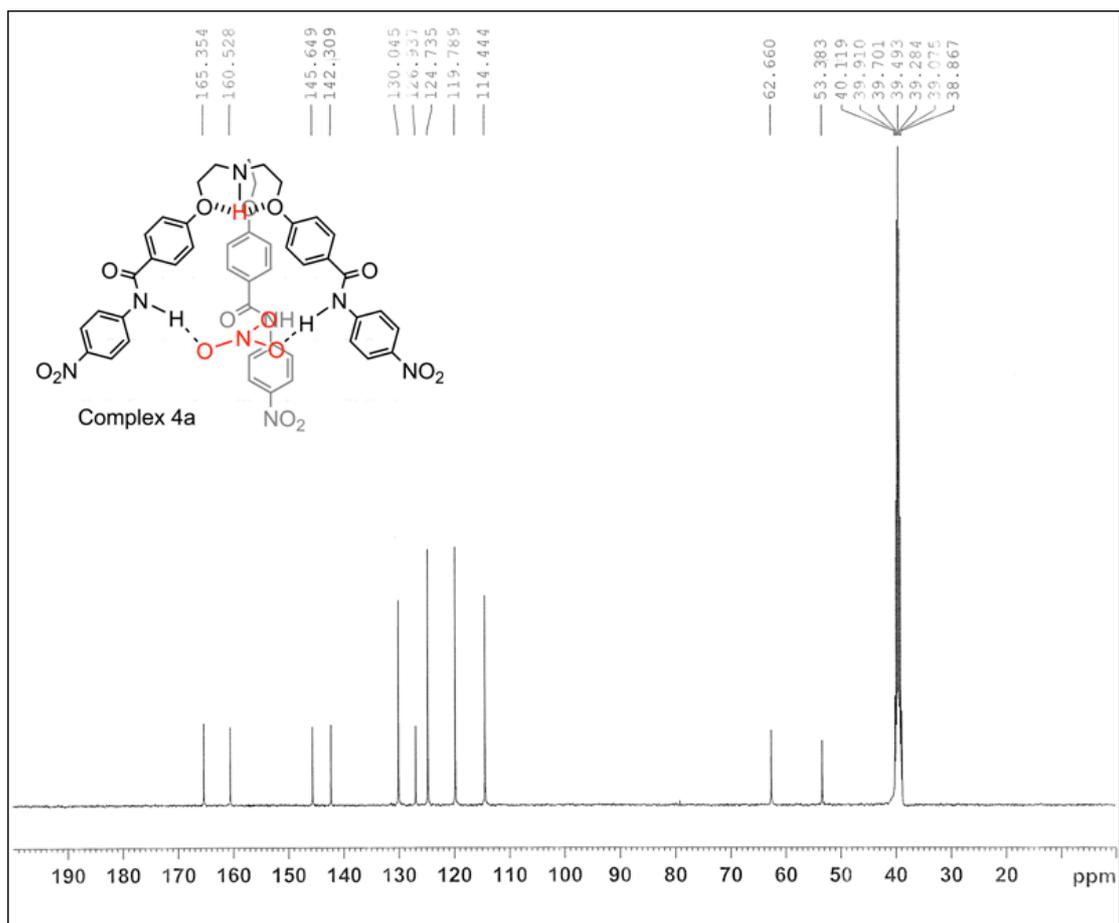
**Fig. S24**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of receptor 4.



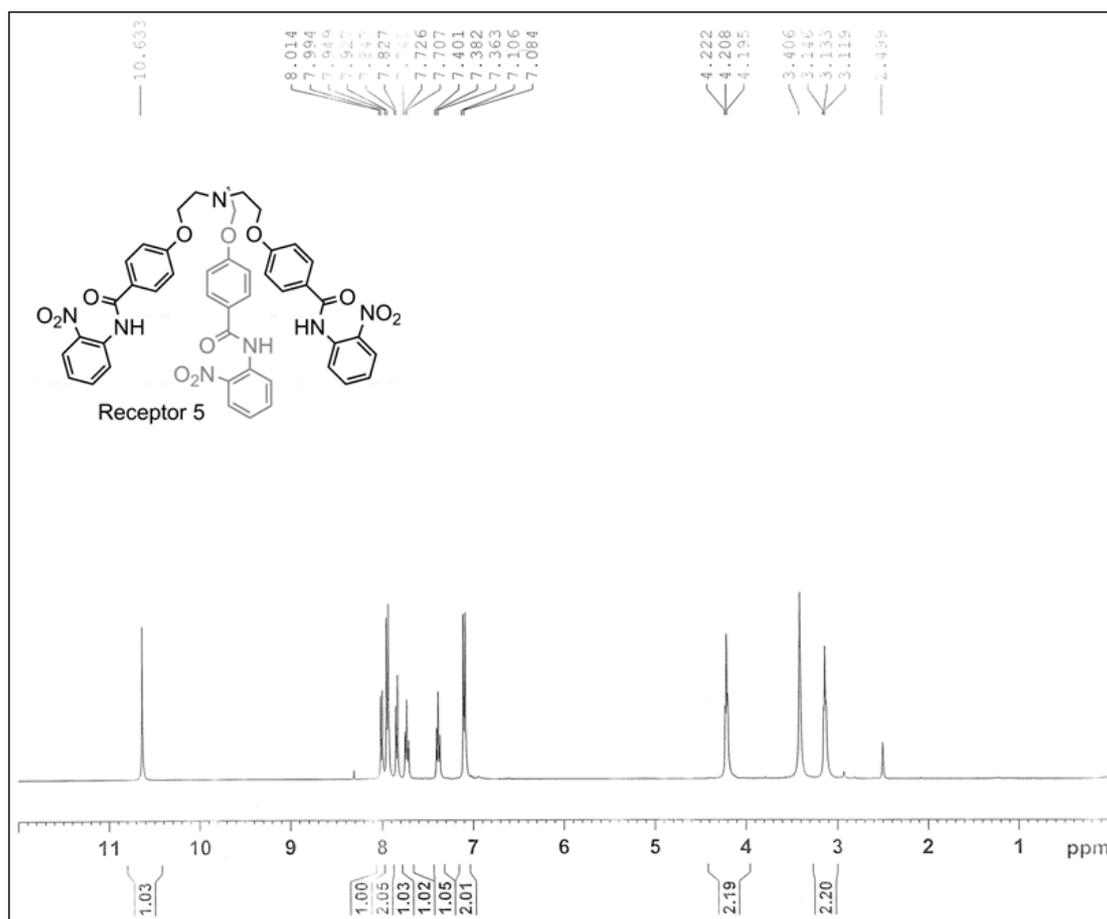
**Fig. S25**  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of receptor 4.



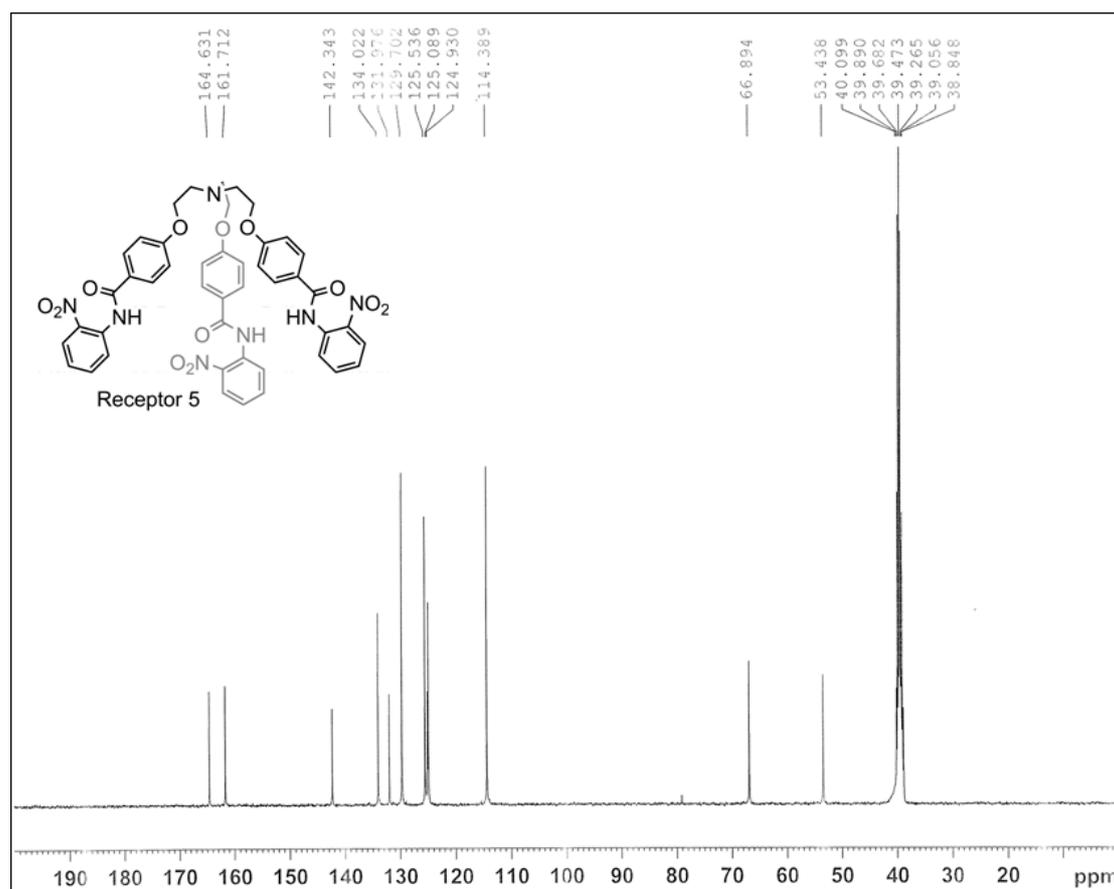
**Fig. S26** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 20 °C) spectrum of nitrate complex **4a**.



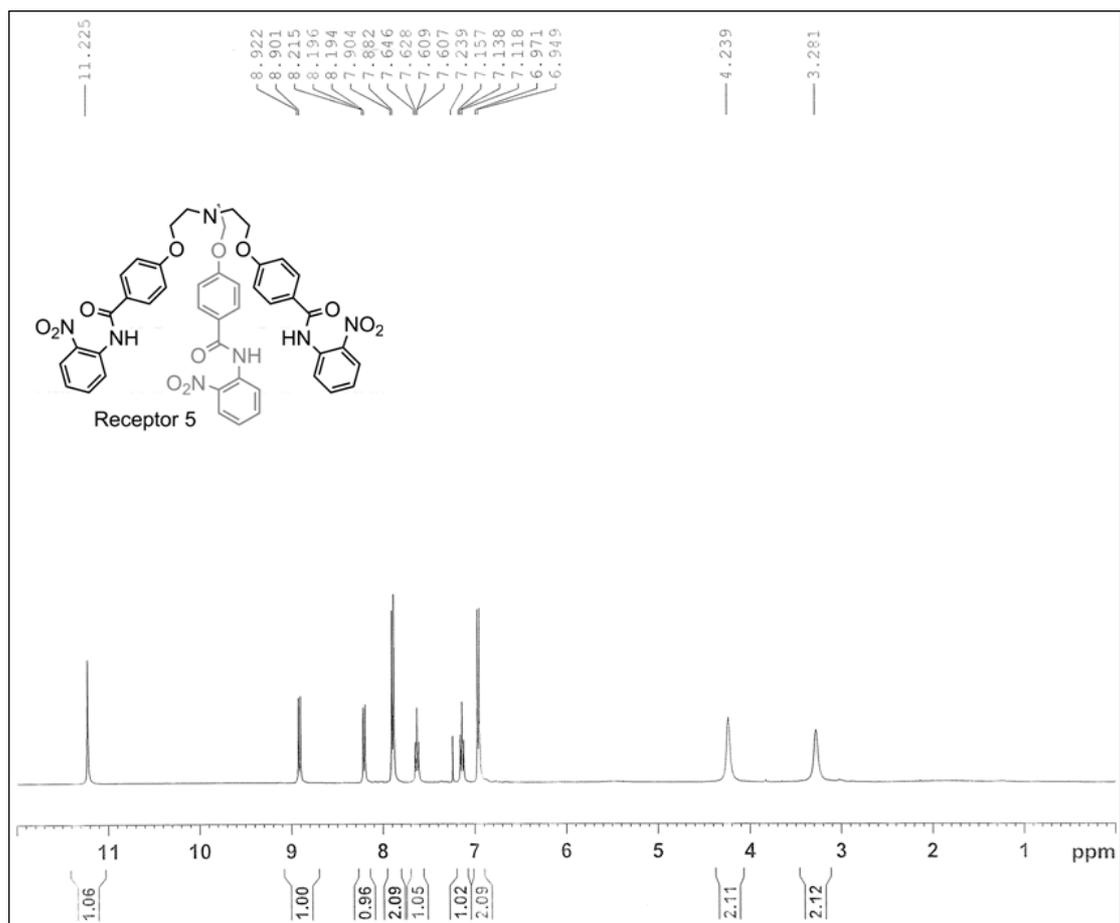
**Fig. S27**  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ , 20 °C) spectrum of nitrate complex 4a.



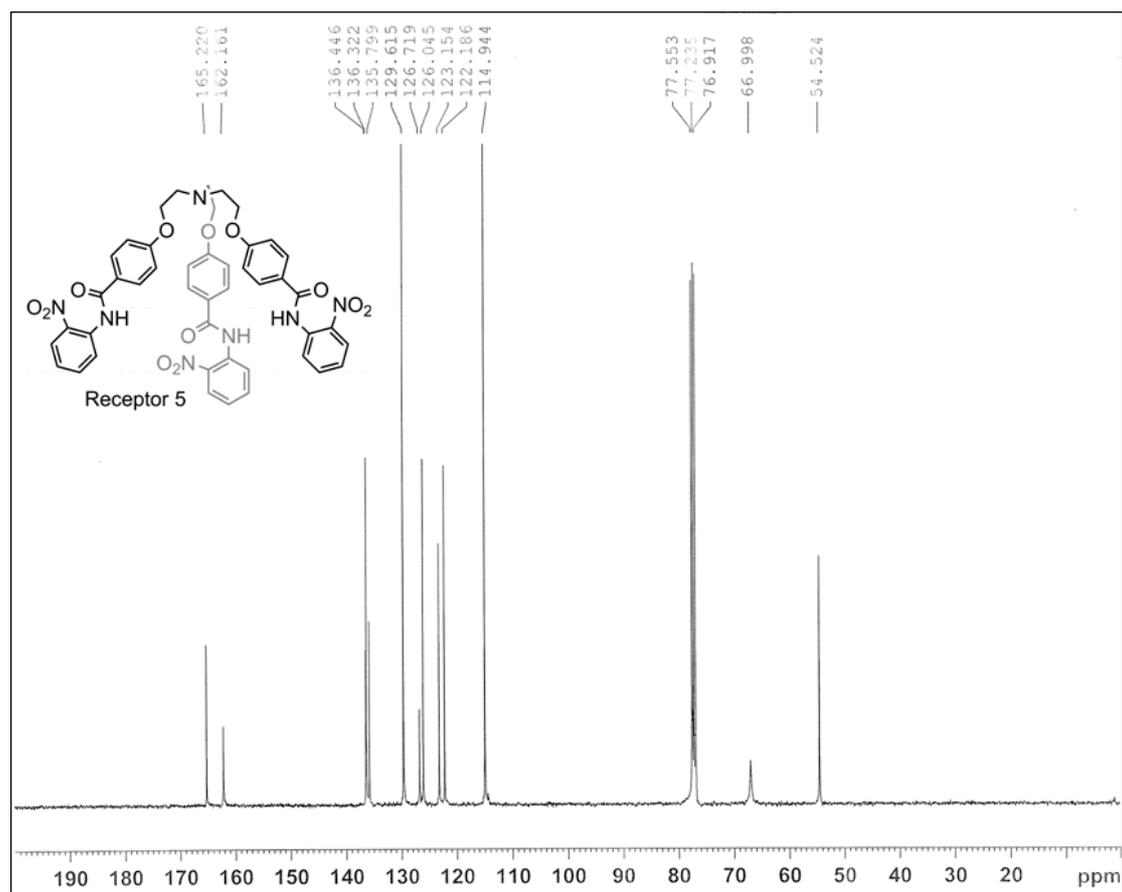
**Fig. S28**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of receptor 5.



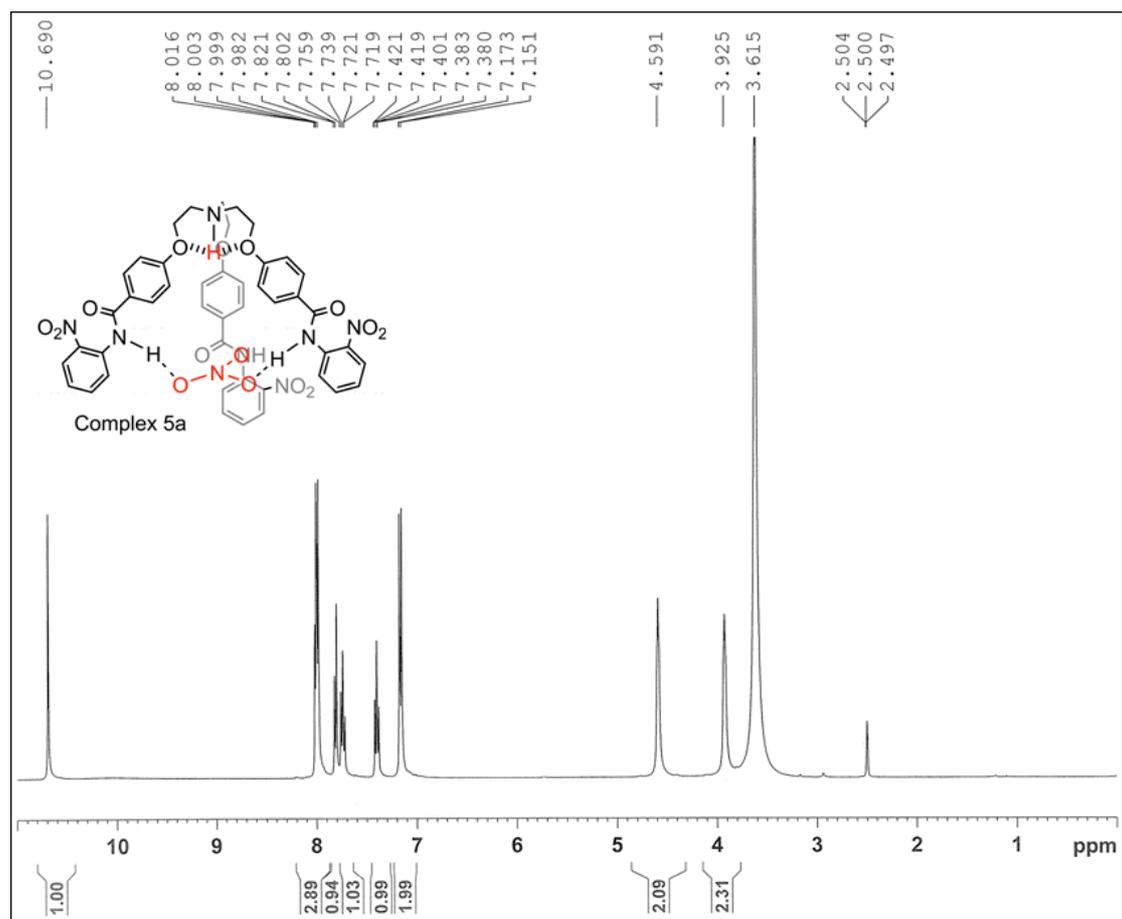
**Fig. S29**  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of receptor **5**.



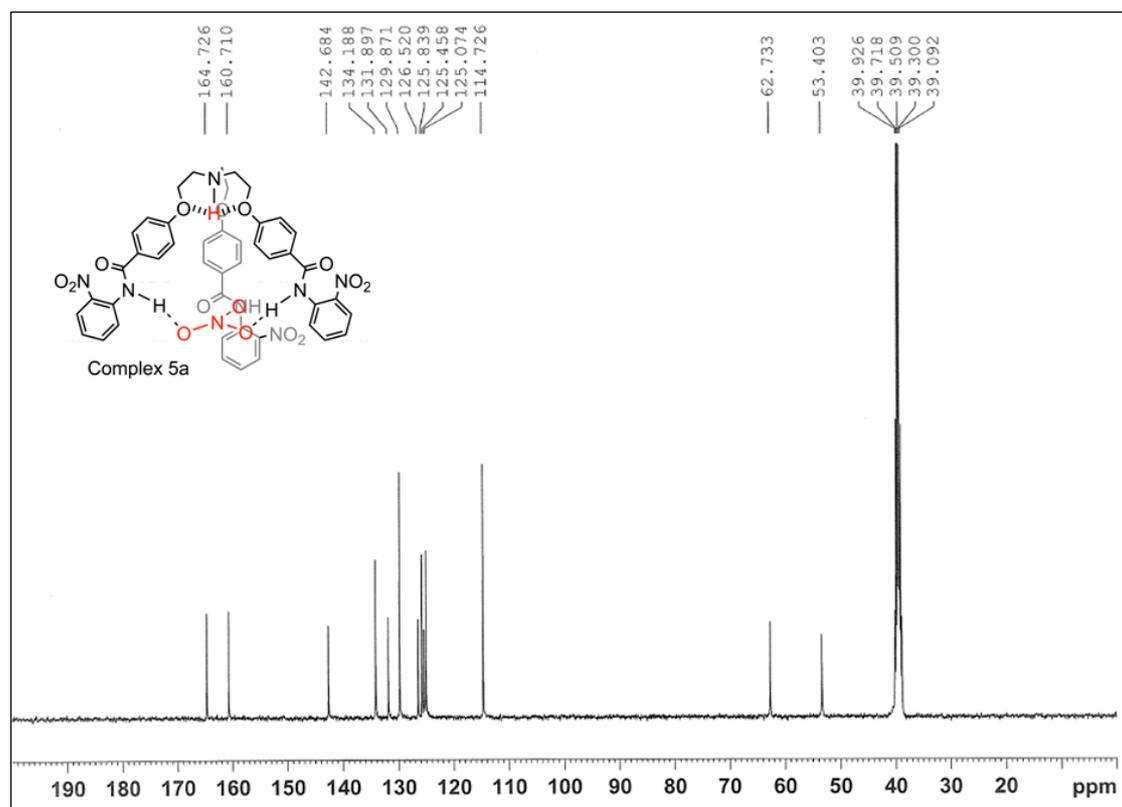
**Fig. S30**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ) spectrum of receptor **5**.



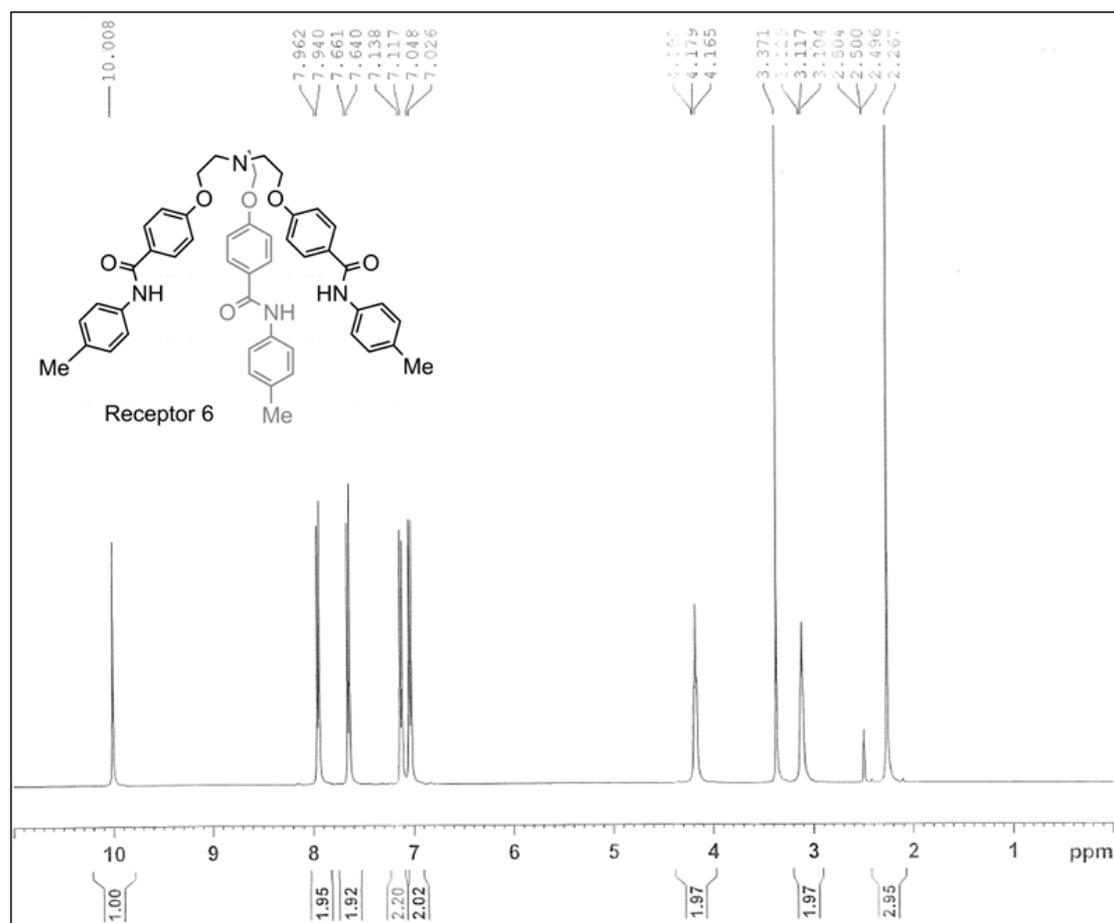
**Fig. S31**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 20 °C) spectrum of receptor **5**.



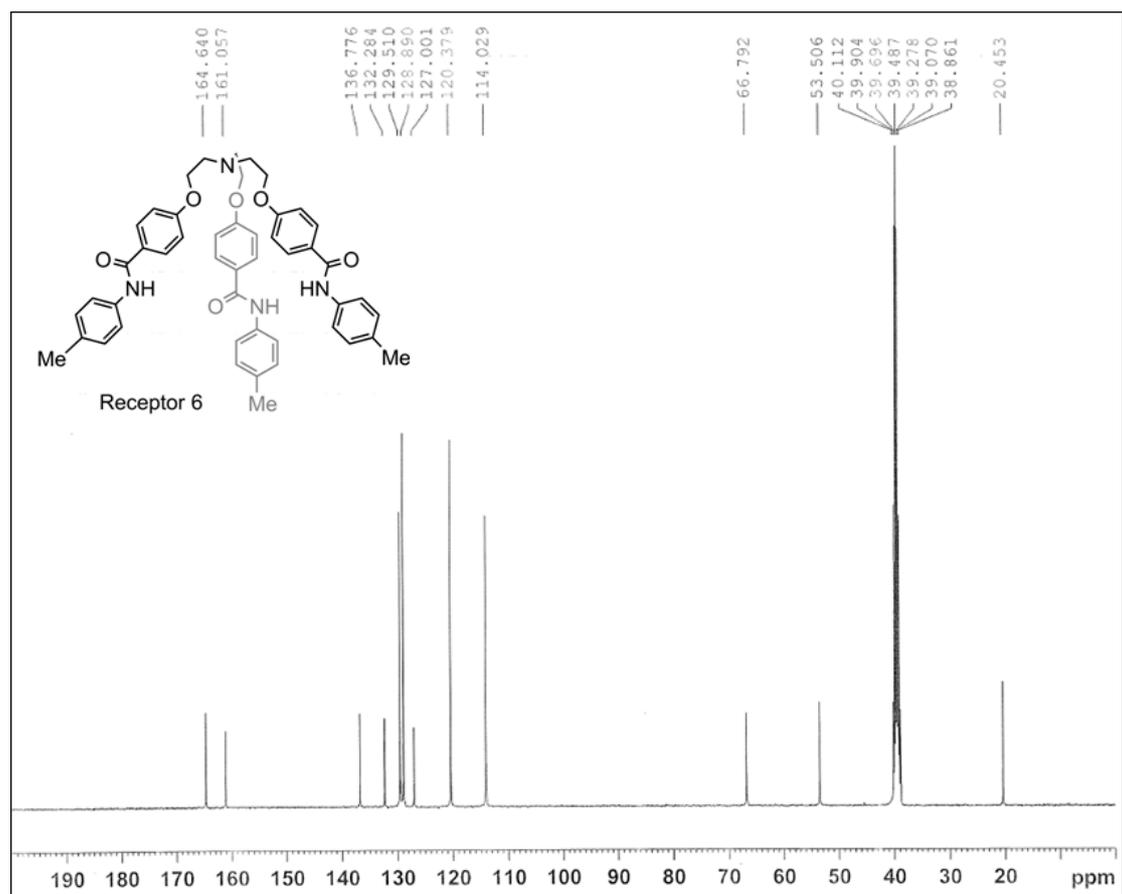
**Fig. S32**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of nitrate complex **5a**.



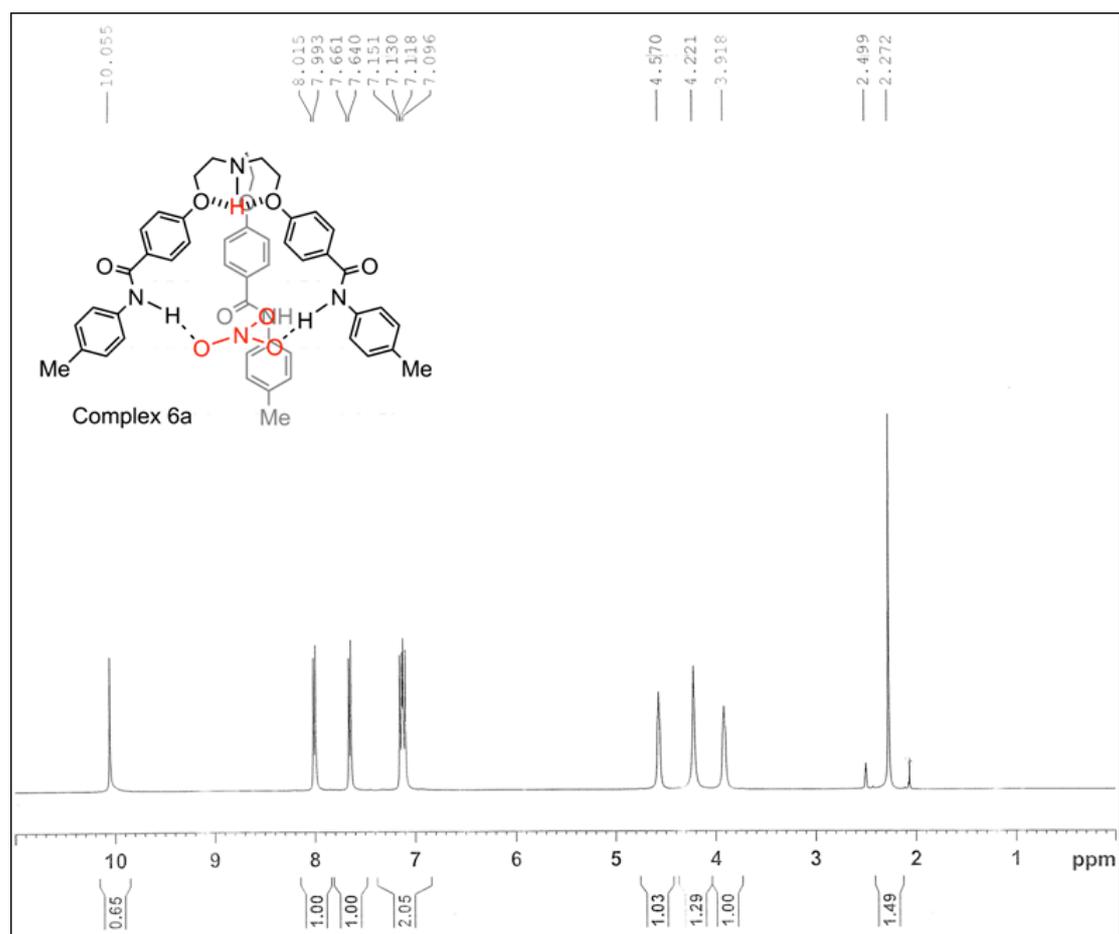
**Fig. S33**  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of nitrate complex **5a**.



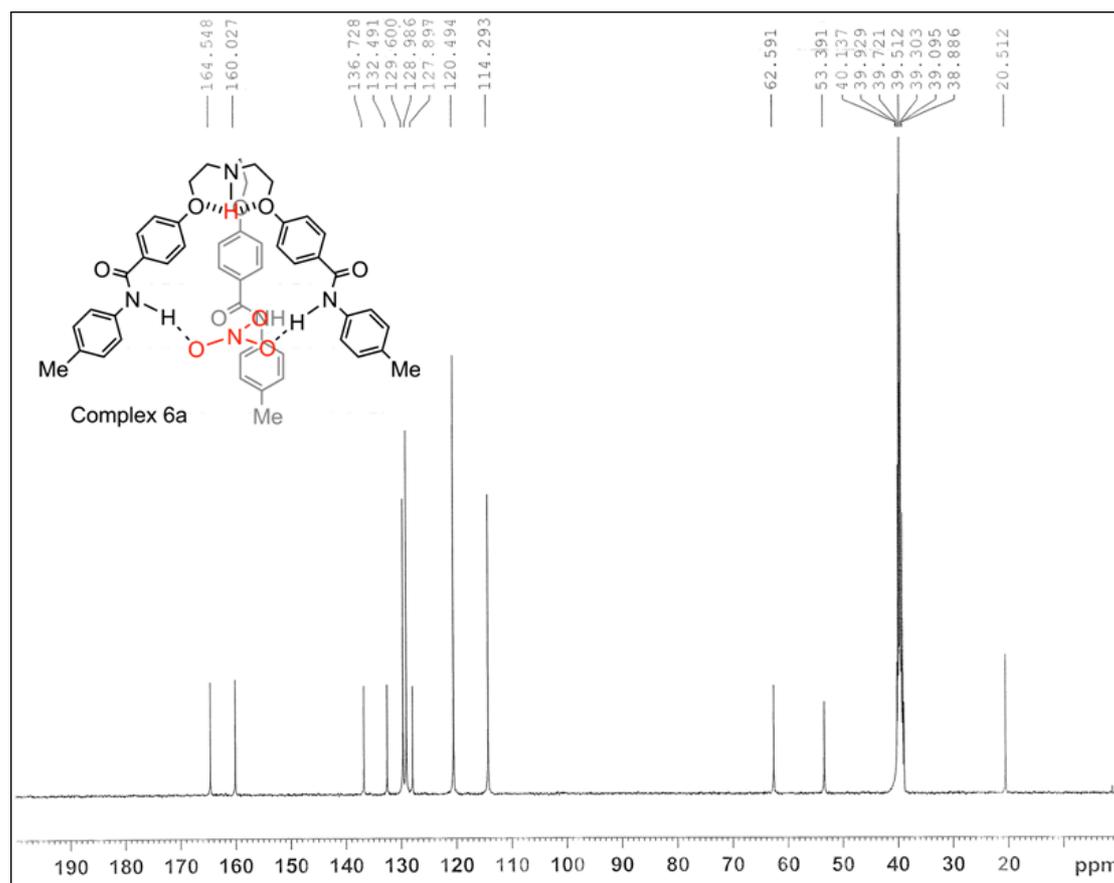
**Fig. S34** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 20 °C) spectrum of receptor 6.



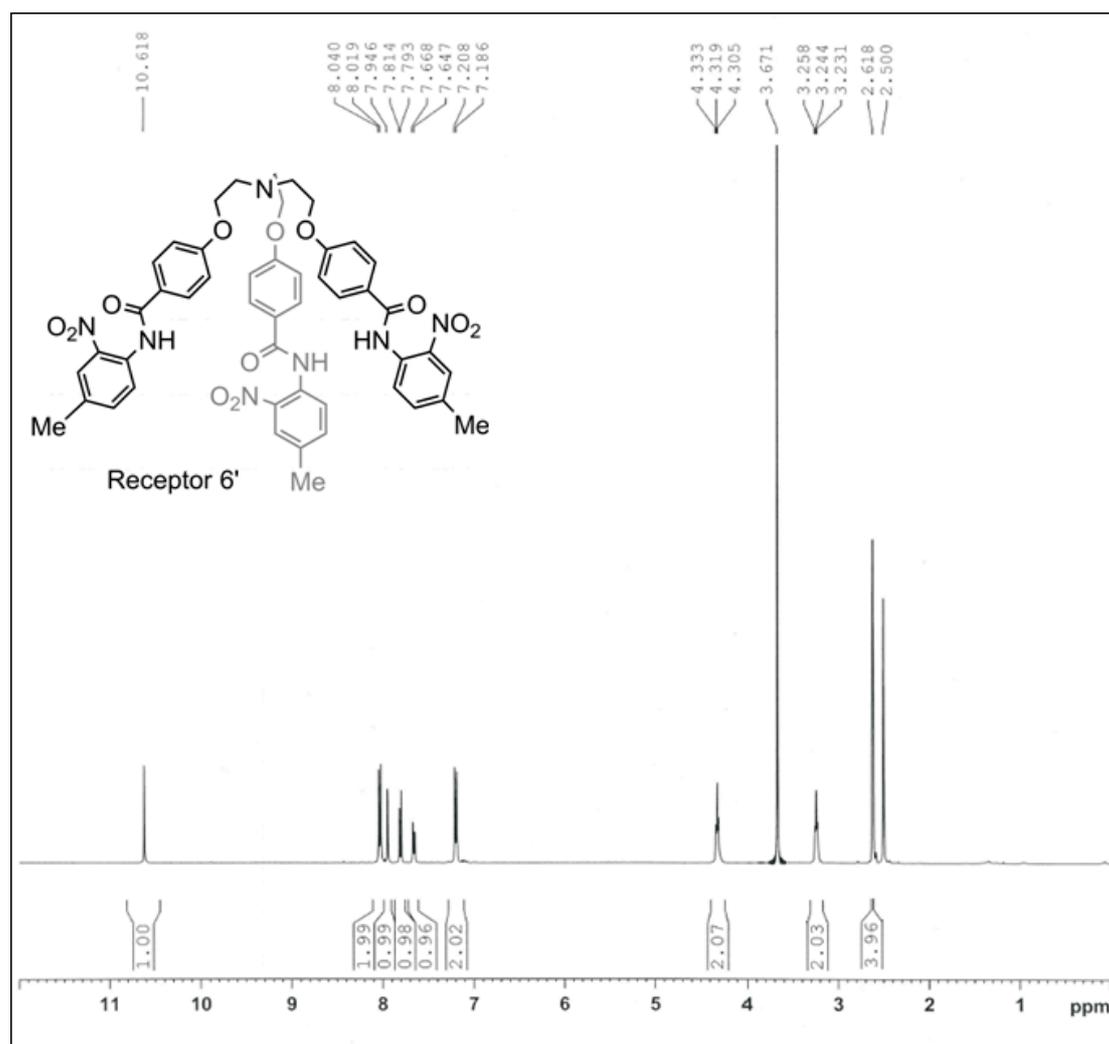
**Fig. S35** <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 20 °C) spectrum of receptor 6.



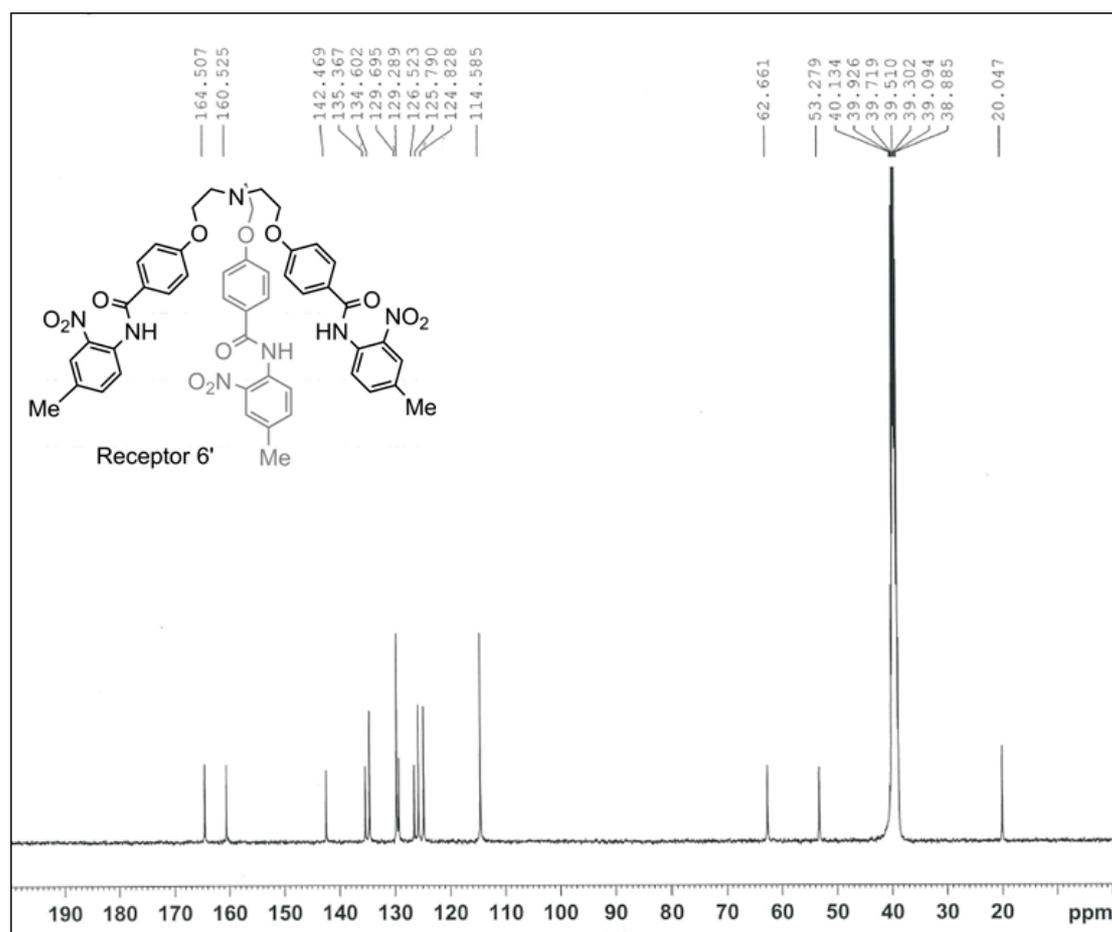
**Fig. S36**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of nitrate complex **6a**.



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

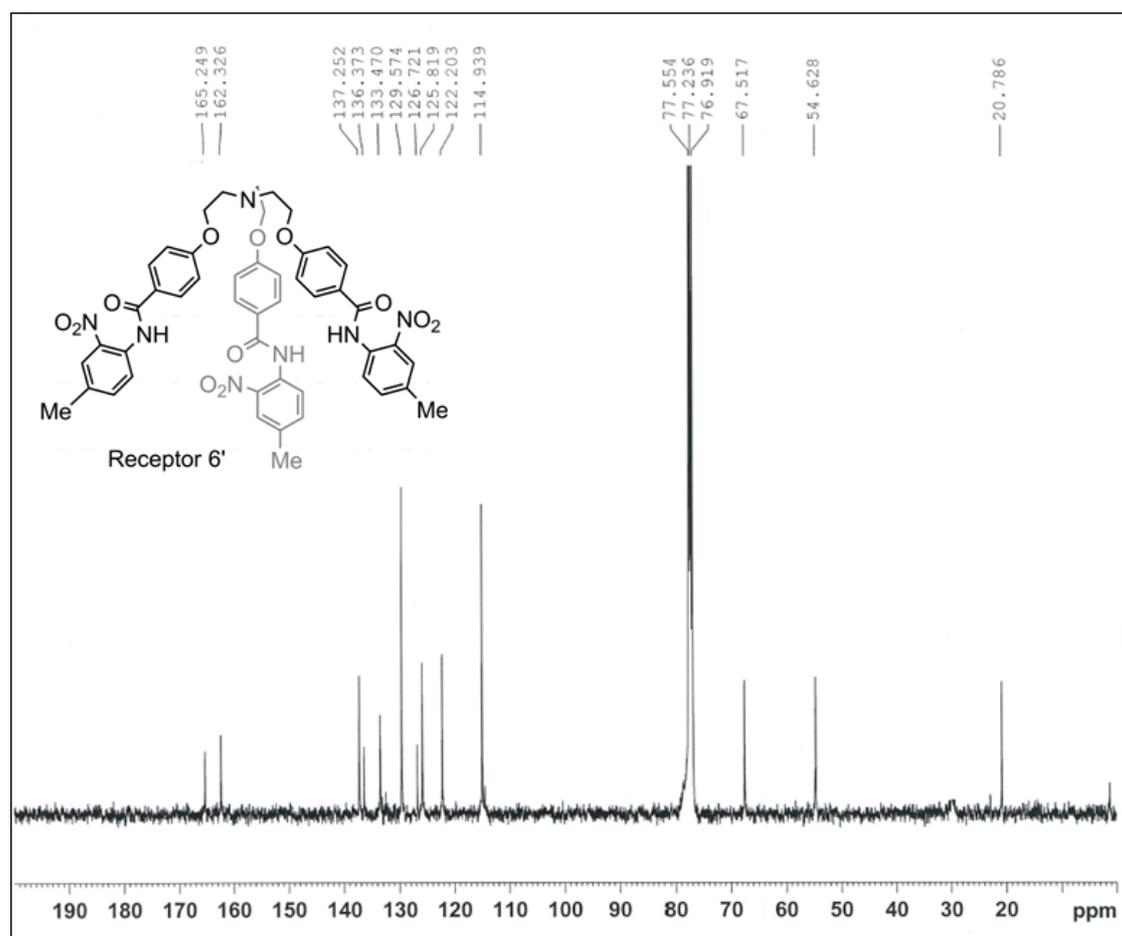


**Fig. S38** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 20 °C) spectrum of receptor 6'.

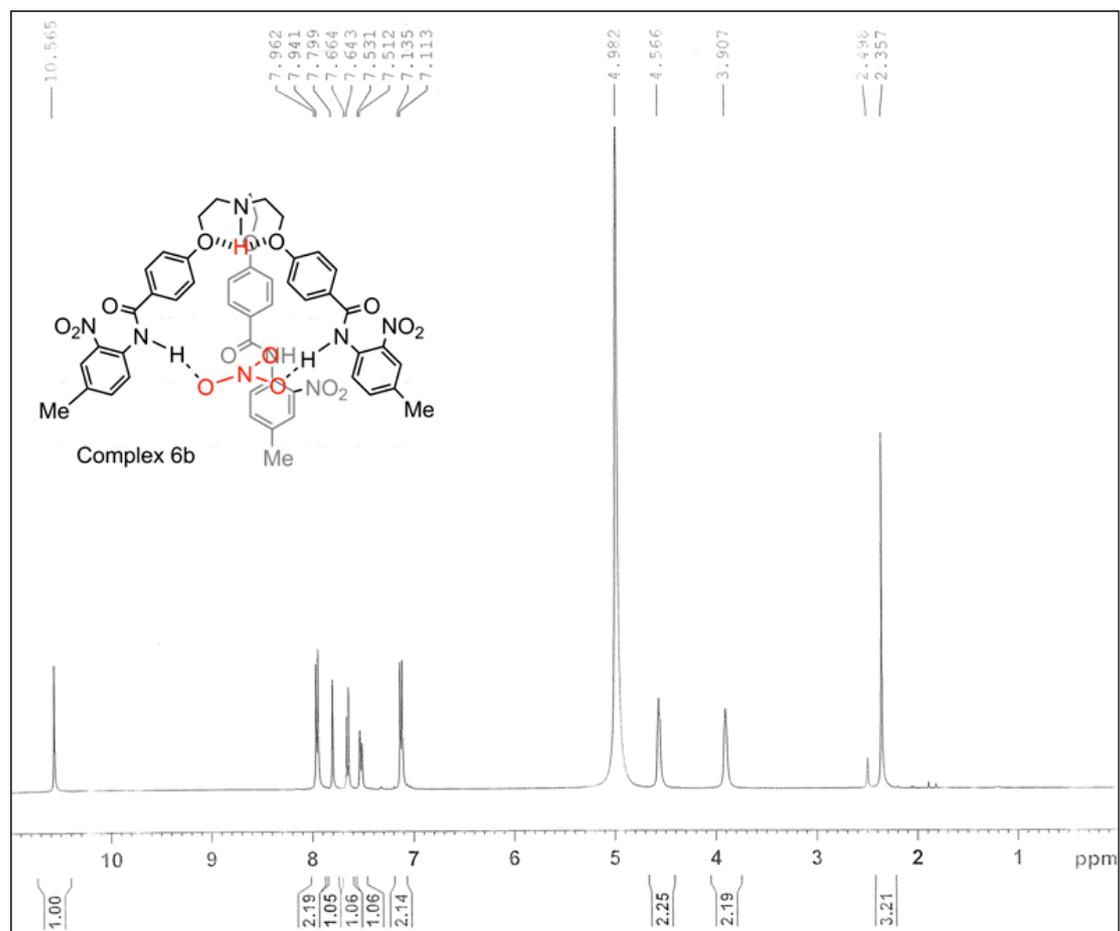


**Fig. S39**  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of receptor 6'.

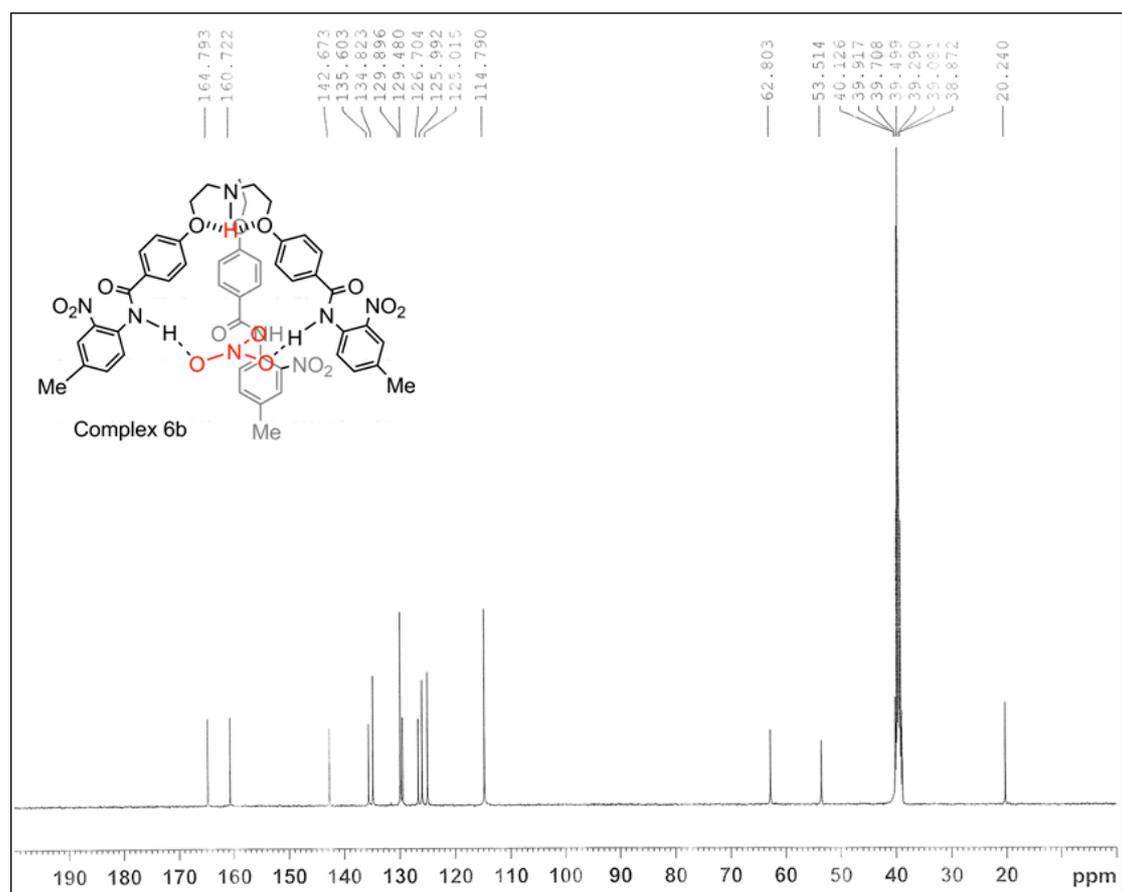




**Fig. S41** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20 °C) spectrum of receptor **6'**.



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



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

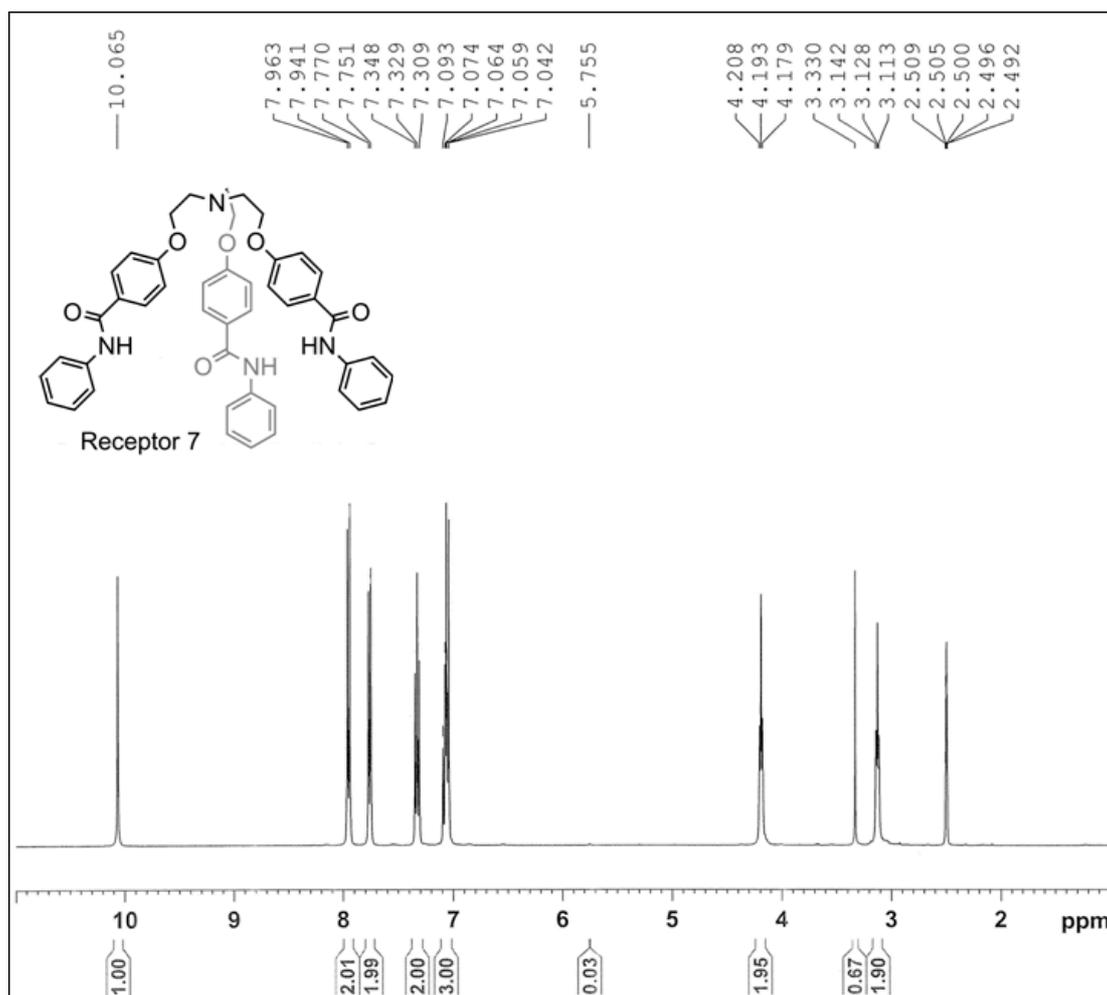
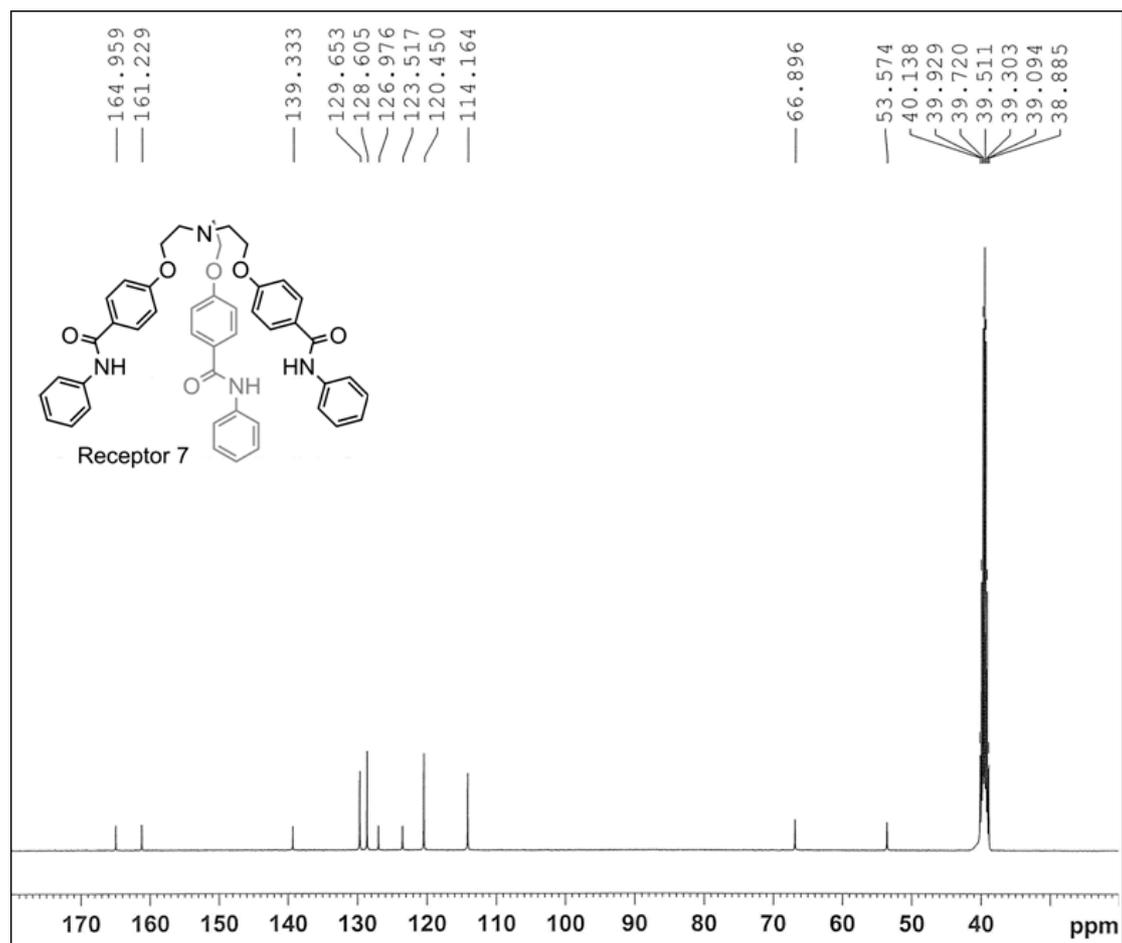
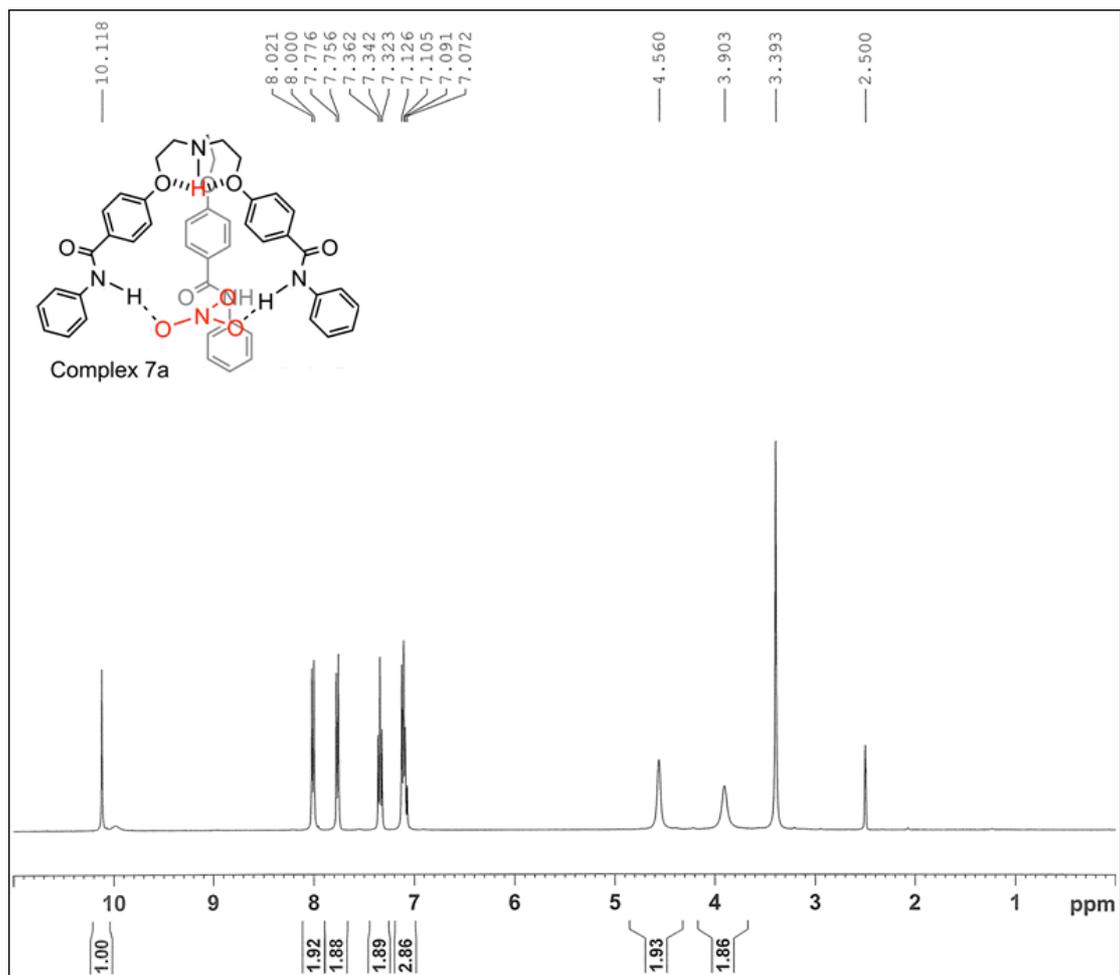


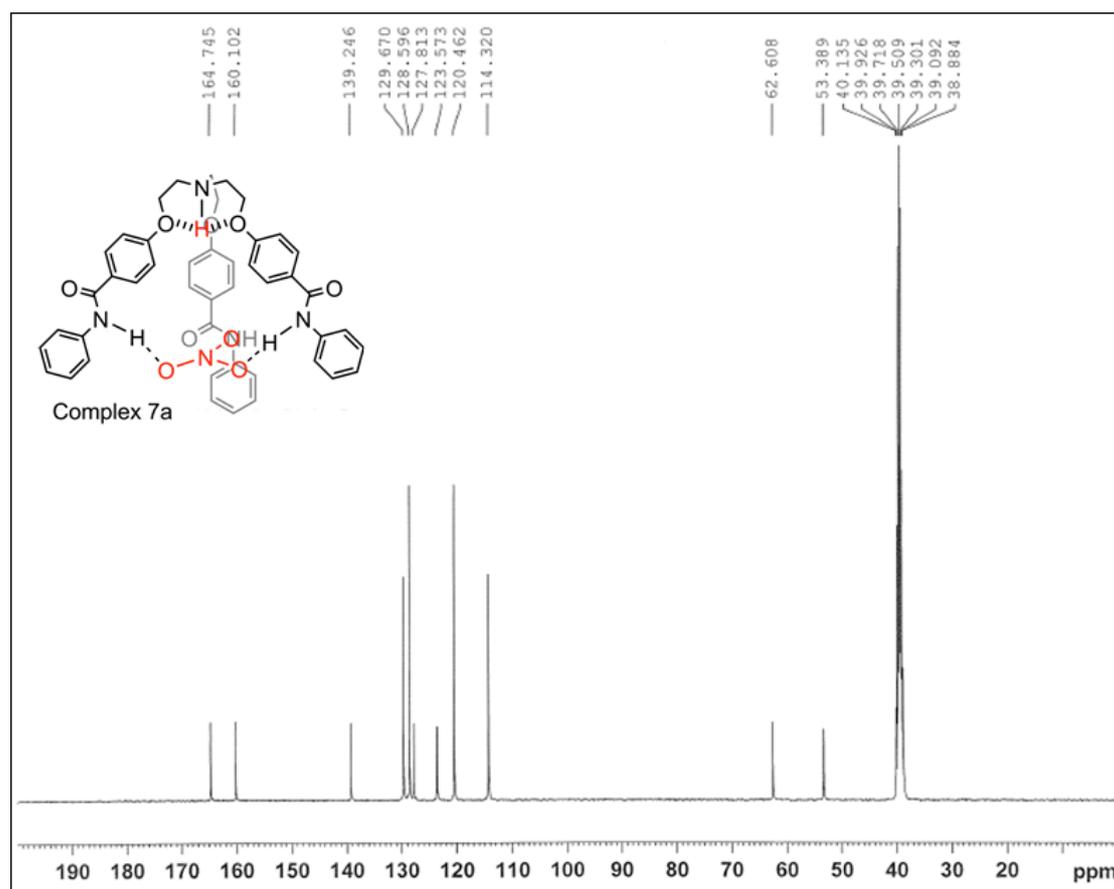
Fig. S44  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 20 °C) spectrum of receptor 7.



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



**Fig. S46** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 20 °C) spectrum of nitrate complex **7a**.



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

### Elemental Composition Report

#### Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0  
Element prediction: Off  
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions  
9 formulae) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

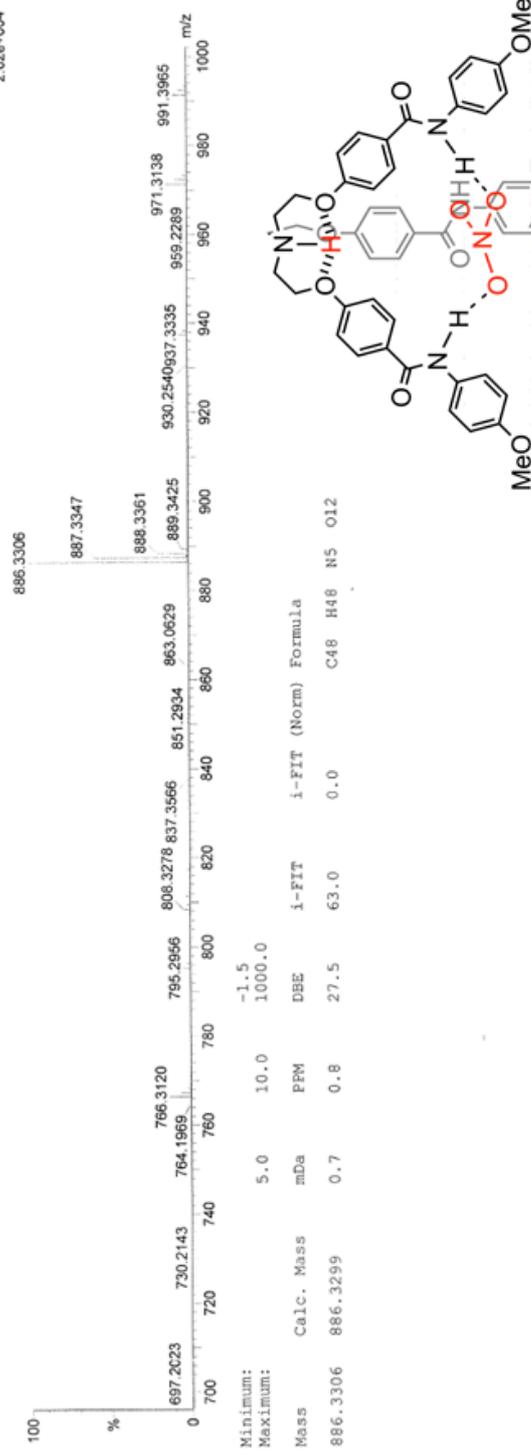
C: 0-1000 H: 0-4000 N: 5-5 O: 12-12

CK-162-2

1224\_CK-162-2 (0.698)

24-Dec-2009  
14:42:27  
2: TOF MS ES-  
2.02e+004

$[M-H]^-$



Complex 1a

Chemical Formula:  $C_{48}H_{48}N_5O_{12}$

Molecular Weight: 887.9290

For  $[M-H]^-$ : 886.9210

Theoretical value for  $[M-H]^-$ : 886.3299 (100%)

Fig. S48 HRESI mass spectrum of complex 1a.

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

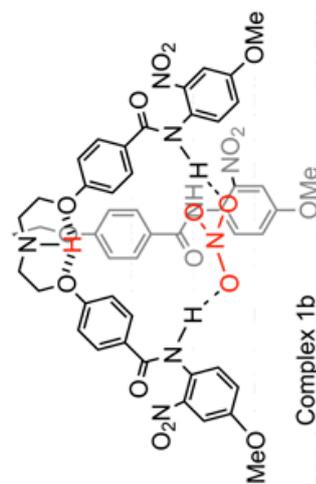
C: 0-1000 H: 0-4000 N: 8-8 O: 18-18

CK-163-4

1229\_CK-163-4 29 (2.896)



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1021.2855	1021.2852	0.3	0.3	30.5	18.0	0.0	C48 H45 N8 O18



Chemical Formula: C<sub>48</sub>H<sub>46</sub>N<sub>8</sub>O<sub>18</sub>  
 Molecular Weight: 1022.9216

For [M-H]<sup>-</sup>: 1021.9137

Theoretical value for [M-H]<sup>-</sup>: 1021.2852 (100%)

Fig. S49 HRESI mass spectrum of complex 1b.

### Elemental Composition Report

#### Single Mass Analysis

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Element prediction: Off  
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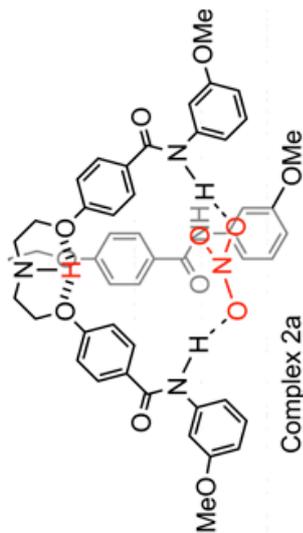
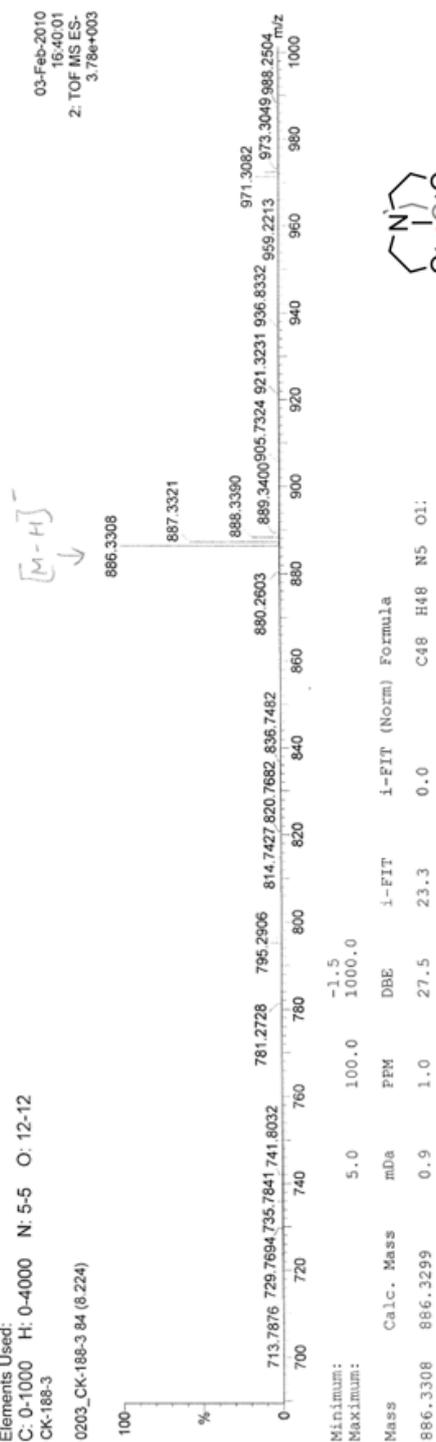
Monoisotopic Mass, Even Electron Ions  
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-1000 H: 0-4000 N: 5-5 O: 12-12

CK-188-3

0203\_CK-188-3 84 (8.224)



Chemical Formula:  $C_{48}H_{49}N_5O_{12}$   
Molecular Weight: 887.9290

For  $[M-H]^-$ : 886.9210

Theoretical value for  $[M-H]^-$ : 886.3299 (100%)

Fig. S50 HRESI mass spectrum of complex 2a.

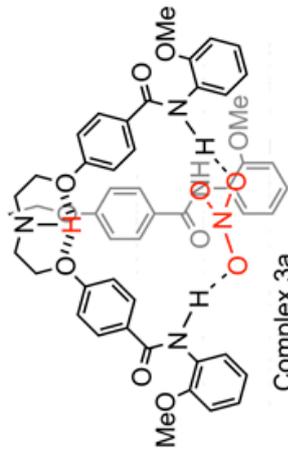
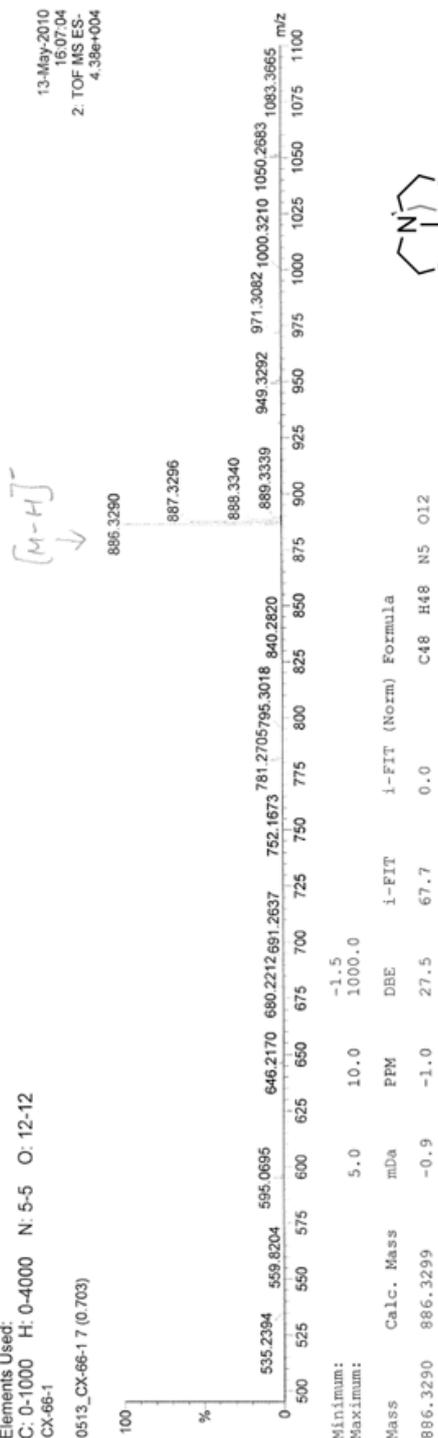
Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions  
 9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)  
 Elements Used:  
 C: 0-1000 H: 0-4000 N: 5-5 O: 12-12  
 CX-66-1

0513\_CX-66-1 7 (0.703)



Chemical Formula: C<sub>48</sub>H<sub>49</sub>N<sub>5</sub>O<sub>12</sub>  
 Molecular Weight: 887.9290

For [M-H]<sup>-</sup>: 886.9210

Theoretical value for [M-H]<sup>-</sup>: 886.3299 (100%)

Fig. S51 HRESI mass spectrum of complex 3a.

Elemental Composition Report

Single Mass Analysis

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

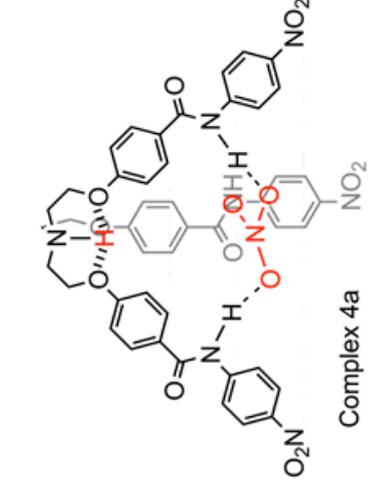
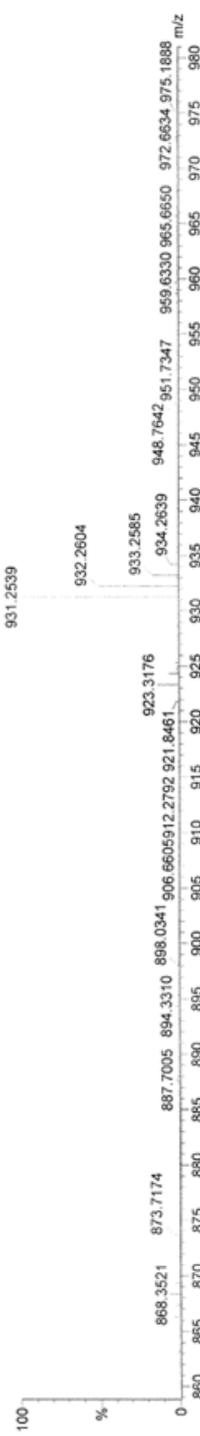
18 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)  
 Elements Used:

C: 0-1000 H: 0-4000 N: 7-8 O: 15-15

CK-195

0224\_CK-195\_2.60 (3.202)

25-Feb-2010  
 14:04:58  
 1: TOF MS ES-  
 1.69e+003



Chemical Formula: C<sub>45</sub>H<sub>40</sub>N<sub>8</sub>O<sub>15</sub>  
 Molecular Weight: 932.8437

For [M-H]<sup>-</sup>: 931.8358

Theoretical value for [M-H]<sup>-</sup>: 931.2535 (100%)

Fig. S52 HRESI mass spectrum of complex 4a.

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

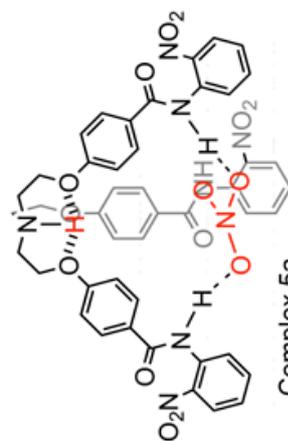
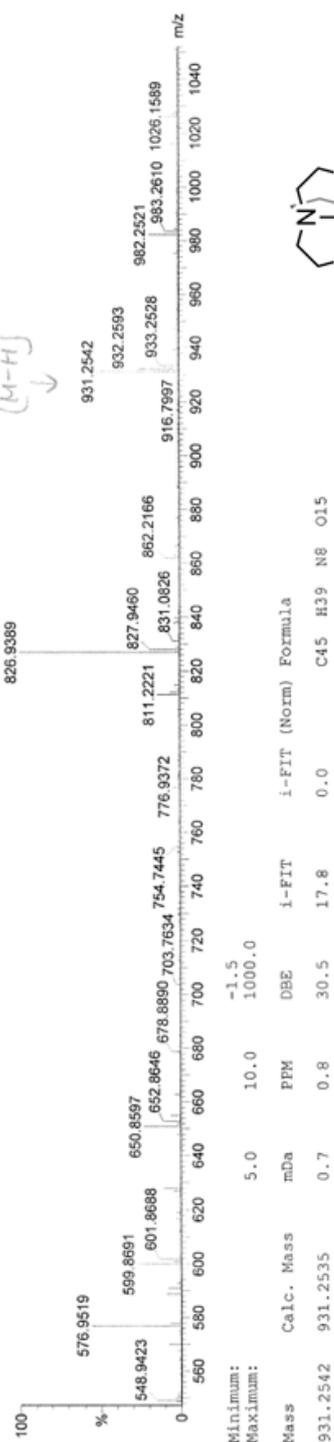
Monoisotopic Mass, Even Electron Ions  
 9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-1000 H: 0-4000 N: 8-8 O: 15-15

CX-66-2

0513\_CX-66-2 9 (0.940) Cm (9.41)



Chemical Formula: C<sub>45</sub>H<sub>40</sub>N<sub>8</sub>O<sub>15</sub>  
 Molecular Weight: 932.8437

For [M-H]<sup>-</sup>: 931.8358

Theoretical value for [M-H]<sup>-</sup>: 931.2535 (100%)

Fig. S53 HRESI mass spectrum of complex 5a.

Elemental Composition Report

Single Mass Analysis

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

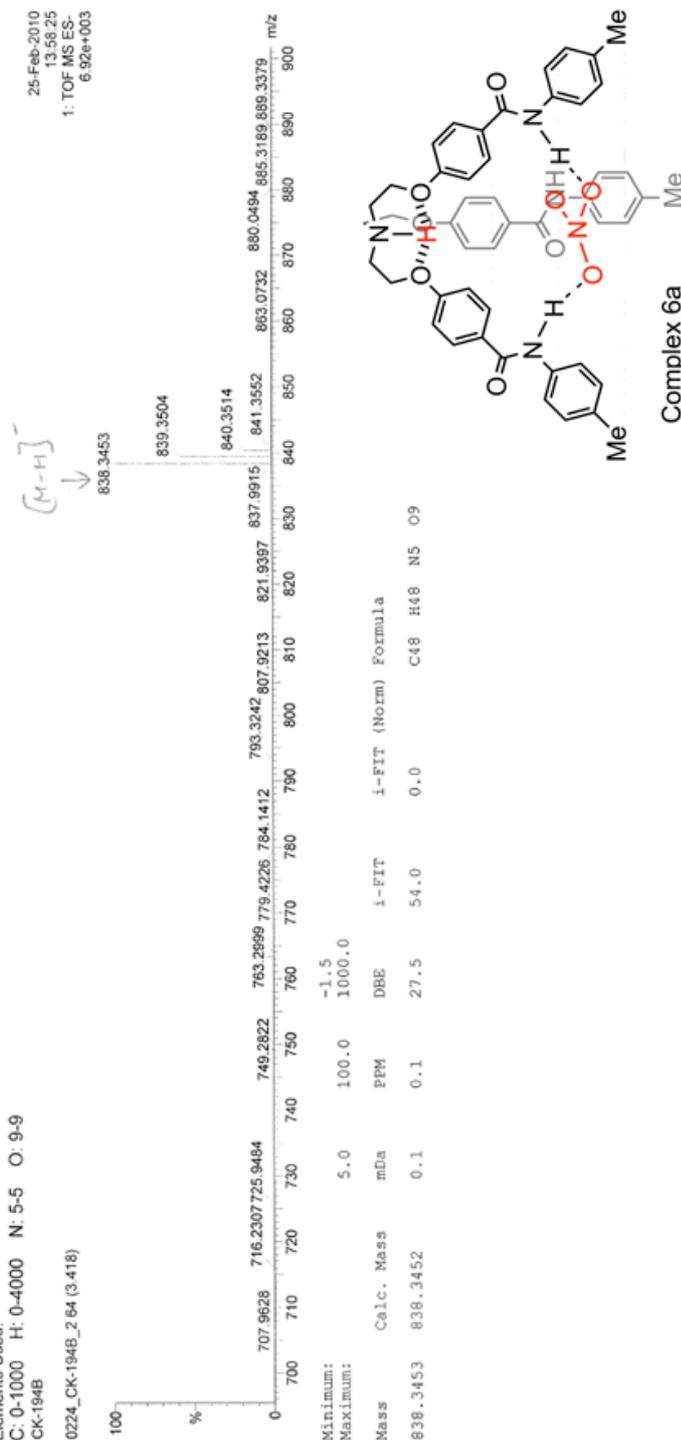
Monoisotopic Mass, Even Electron Ions  
 9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-1000 H: 0-4000 N: 5-5 O: 9-9

CK-194B

0224\_CK-194B\_2.64 (3.418)



Chemical Formula: C<sub>48</sub>H<sub>48</sub>N<sub>5</sub>O<sub>9</sub>

Molecular Weight: 839.9308

For [M-H]<sup>-</sup>: 838.9228

Theoretical value for [M-H]<sup>-</sup>: 838.3452 (100%)

Fig. S54 HRESI mass spectrum of complex 6a.

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

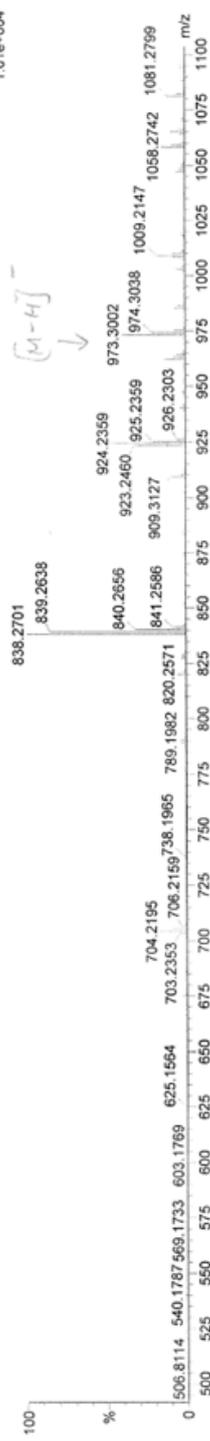
Elements Used:

C: 0-1000 H: 0-4000 N: 8-8 O: 15-15

CK-200-2

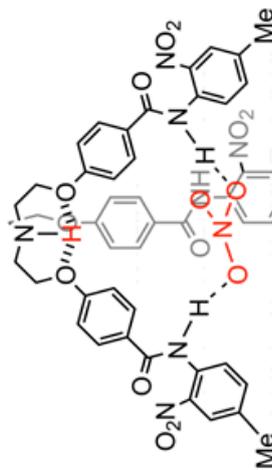
0226\_CK-200-2\_2 1 (0.156)

26-Feb-2010  
 12:25:11  
 2: TOF MS ES-  
 1.01e+004



Minimum: -1.5  
 Maximum: 1000.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
973.3002	973.3004	-0.2	-0.2	30.5	26.6	0.0	C48 H45 N8 O15



Complex 6b

Chemical Formula: C<sub>48</sub>H<sub>46</sub>N<sub>8</sub>O<sub>15</sub>

Molecular Weight: 974.9234

For [M-H]<sup>-</sup>: 973.9155

Theoretical value for [M-H]<sup>-</sup>: 973.3004 (100%)

Fig. S55 HRESI mass spectrum of complex 6b.

### Elemental Composition Report

#### Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 1000.0  
Element prediction: Off  
Number of isotope peaks used for iFIT = 2

Monoisotopic Mass, Even Electron Ions  
8 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

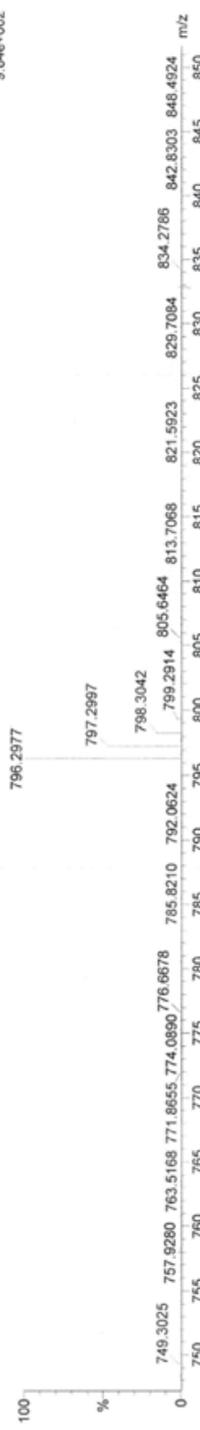
C: 0-1000 H: 0-4000 N: 5-5 O: 9-9

CK-122-2

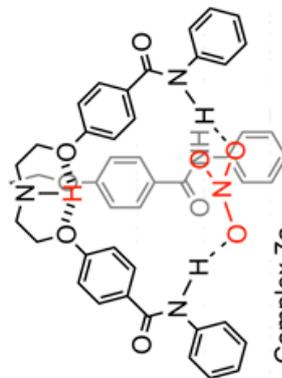
1118\_CK-122-2 13 (1.327) Cm (13-1)

$[M-H]^-$

18-Nov-2009  
17:06:39  
2: TOF MS ES-  
9.84e+002



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	(Norm)	Formula
796.2977	796.2983	-0.6	-0.8	27.5	35.4	0.0	C45 H42 N5 O9



Complex 7a

Chemical Formula: C<sub>45</sub>H<sub>43</sub>N<sub>5</sub>O<sub>9</sub>  
Molecular Weight: 797.8510

For [M-H]<sup>-</sup>: 796.8431

Theoretical value for [M-H]<sup>-</sup>: 796.2983 (100%)

Fig. S56 HRESI mass spectrum of complex 7a.

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass: Even Electron Ions

17 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-1000 H: 0-4000 N: 14-14 O: 30-30

CK-165-2

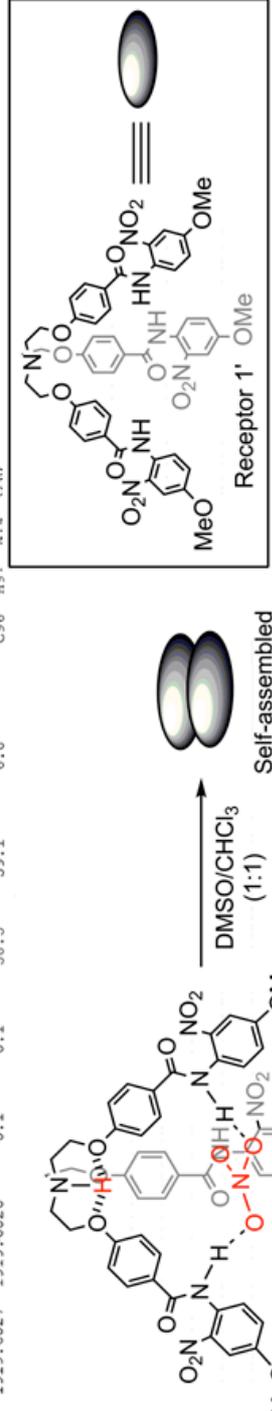
1229\_CK-165-2 8 (0.737)



Minimum: 5.0 10.0 -1.5 1000.0  
 Maximum: 1919.6027 1919.6026 0.1 0.1 58.5 59.1 0.0

Mass Calc. Mass mDa PPM DBE i-FIT i-FIT (Norm) Formula

1919.6027 1919.6026 0.1 0.1 58.5 59.1 0.0 C<sub>96</sub>H<sub>91</sub>N<sub>14</sub>O<sub>30</sub>



Complex 1b

Self-assembled  
molecular capsule (1'2)

Chemical Formula for [M+H]<sup>+</sup>: C<sub>96</sub>H<sub>91</sub>N<sub>14</sub>O<sub>30</sub>  
 Molecular Weight: 1920.8255  
**Theoretical value for [M+H]<sup>+</sup>: 1920.6059 (100%)**

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<sub>3</sub> (1:1).

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

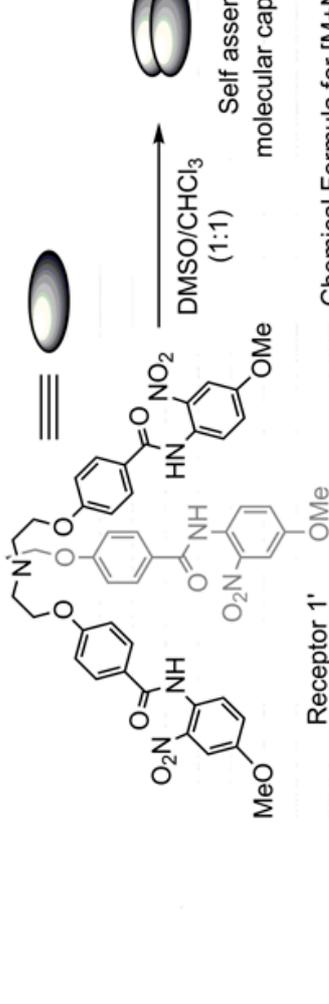
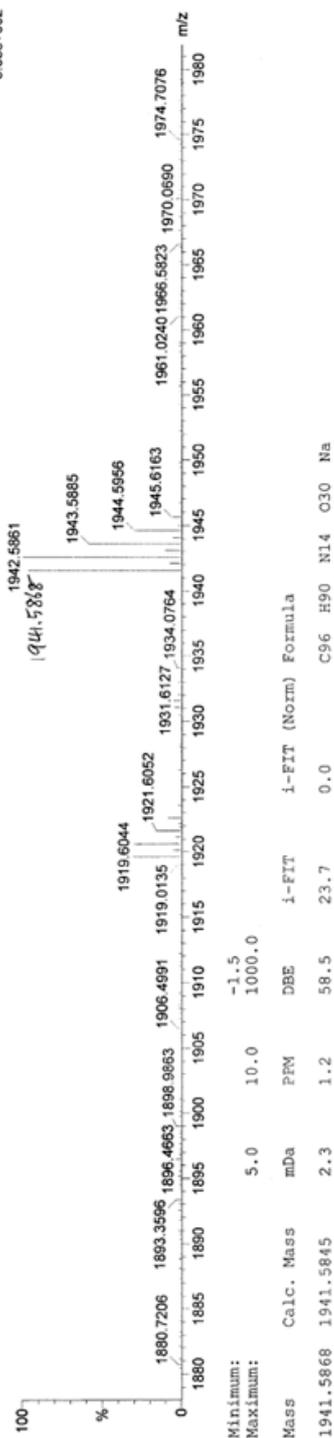
17 formulae evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-1000 H: 0-4000 N: 14-14 O: 30-30 Na: 1-1

CX-50-1-A

0513\_CX-50-1-A 30 (0.381) Cm (30-627)



Chemical Formula for  $[M+Na]^+$ : C<sub>96</sub>H<sub>90</sub>N<sub>14</sub>NaO<sub>30</sub>

Molecular Weight: 1942.8074

Theoretical value for  $[M+Na]^+$ : 1942.5879 (100%)

Fig. S58 HRESI mass spectrum of the self-assembled capsule (1'2) recorded after dissolving receptor 1' in a mixture solution of DMSO/CHCl<sub>3</sub> (1:1).

Elemental Composition Report

Single Mass Analysis

Tolerance = 40.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

17 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

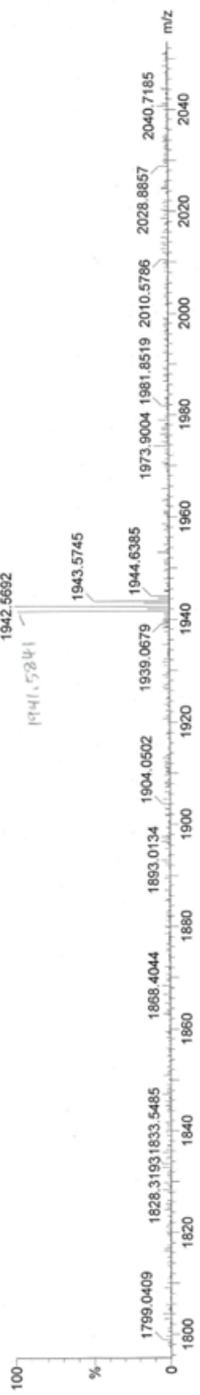
C: 0-400 H: 0-1000 N: 14-14 O: 30-30 Na: 1-1

CX-183-3

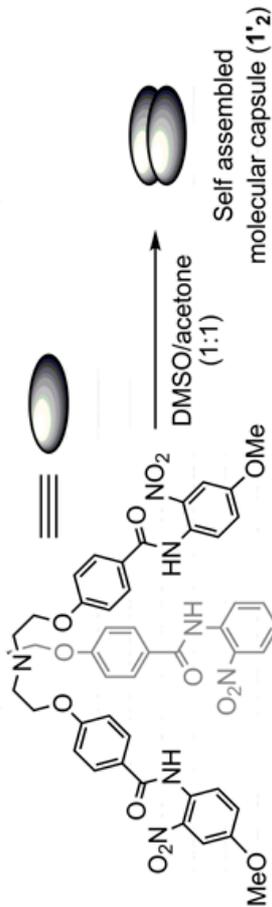
0330\_CX-183-3 5 (0.245)

KE267

30-Mar-2011  
 11:46:57  
 1: TOF MS ES+  
 9.56e+001



Mass	Calc. Mass	DBE	i-FIT	i-FIT (Norm)	Formula
1941.5841	1941.5845	-0.4	0.0	0.0	C <sub>96</sub> H <sub>90</sub> N <sub>14</sub> O <sub>30</sub> Na
		58.5	15.8	0.0	
		40.0			
		5.0			
		-1.5			
		1000.0			



Receptor 1'

Self assembled molecular capsule (1'2)

Chemical Formula for [M+Na]<sup>+</sup>: C<sub>96</sub>H<sub>90</sub>N<sub>14</sub>NaO<sub>30</sub>  
 Molecular Weight: 1942.8074  
**Theoretical value for [M+Na]<sup>+</sup>: 1942.5879 (100%)**

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).

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

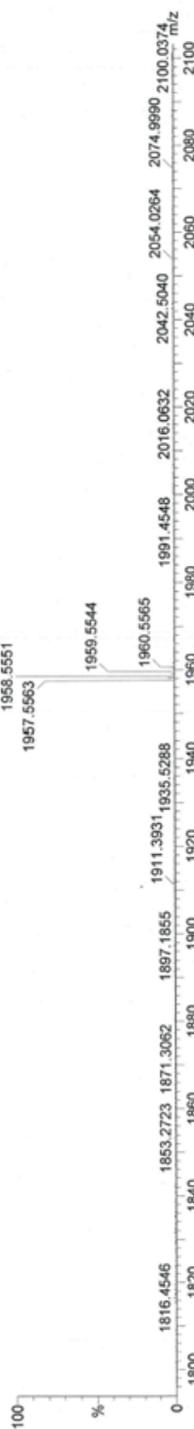
Monoisotopic Mass, Even Electron Ions

17 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)  
 Elements Used:

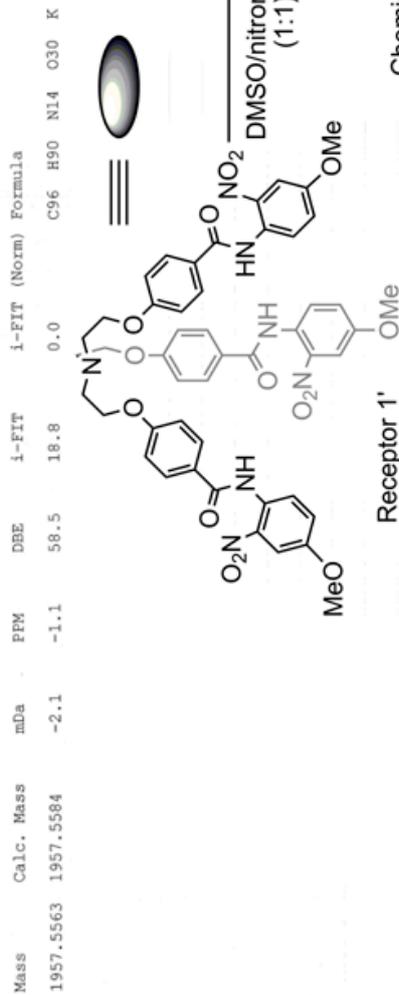
C: 0-400 H: 0-1000 N: 14-14 O: 30-30 K: 1-1  
 CX-183-7

0401\_CX-183-7 11 (0.489) Cm (9:11)

01-Apr-2011  
 16:06:22  
 1: TOF MS ES+  
 1.12e+003



Minimum: -1.5  
 Maximum: 1000.0



Chemical Formula for [M+K]<sup>+</sup>: C<sub>96</sub>H<sub>90</sub>N<sub>14</sub>KO<sub>30</sub>  
 Molecular Weight: 1958.9159

Theoretical value for [M+K]<sup>+</sup>: 1958.5618 (100%)

Fig. S60 HRESI mass spectrum of the self-assembled capsule (1'2) recorded by dissolving receptor 1' to a mixture solution of DMSO/CH<sub>3</sub>NO<sub>2</sub> (1:1, v/v).

Elemental Composition Report

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions  
 10 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-1000 H: 0-4000 N: 14-14 O: 24-24

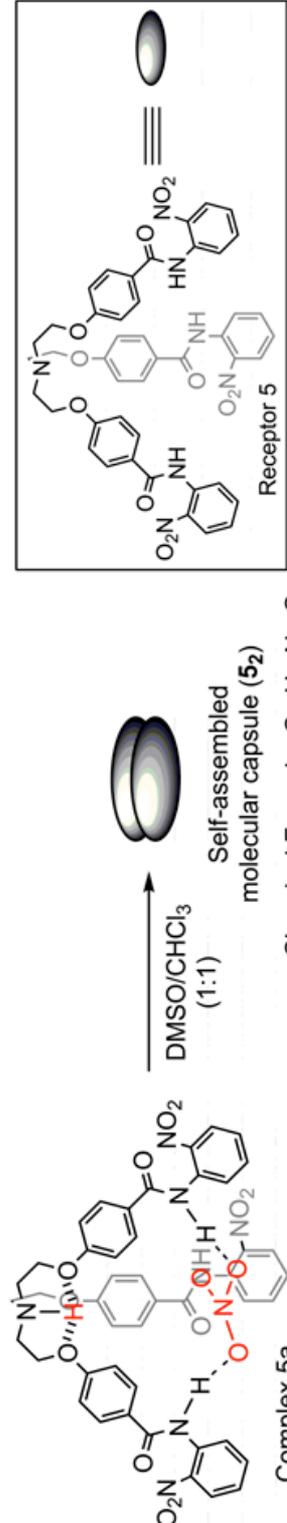
CX-19-2B

0407\_CX-19-2B 11 (1.057) Cm (11-1)

07-Apr-2010  
 14:13:14  
 1: TOF MS ES+  
 3.86e+003



Mass	Calc. Mass	mDa	DBE	i-FIT	i-FIT (Norm)	Formula
1739.5383	1739.5392	-0.9	58.5	34.8	0.0	C <sub>90</sub> H <sub>78</sub> N <sub>14</sub> O <sub>24</sub>



**Fig. S61** HRESI mass spectrum of the self-assembled capsule (**5<sub>2</sub>**) recorded after dissolving nitrate complex **5<sub>a</sub>** in mixture solution of DMSO/CHCl<sub>3</sub> (1:1).

Elemental Composition Report

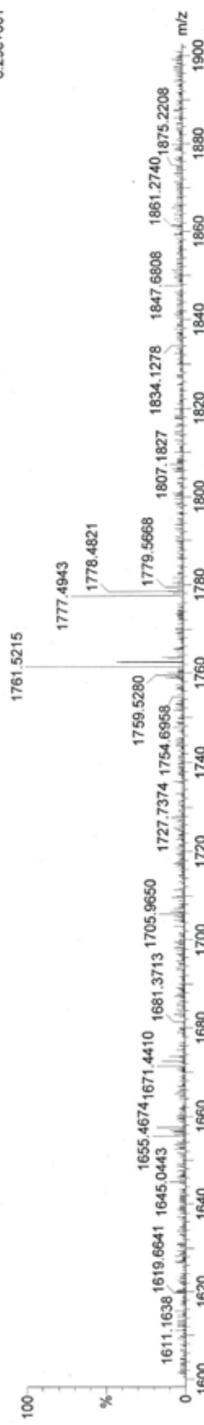
Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

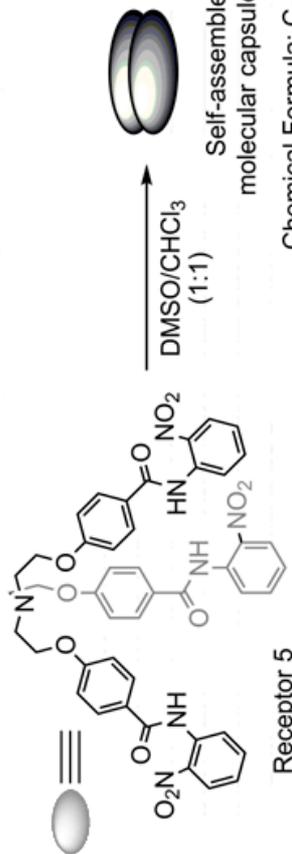
Monoisotopic Mass, Even Electron Ions  
 16 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)  
 Elements Used:

C: 0-400 H: 0-1000 N: 14-14 O: 24-24 Na: 1-1  
 CX-183-1

0328\_CX-183-1 10 (0.454) Cm (10:11)



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1761.5215	1761.5211	0.4	0.2	58.5	24.2	0.0	C90 H78 N14 O24 Na



Self-assembled  
 molecular capsule (**52**)

Chemical Formula: C<sub>90</sub>H<sub>78</sub>N<sub>14</sub>O<sub>24</sub>  
 Molecular Weight: 1739.6617

Theoretical value for [M+Na]<sup>+</sup>: 1761.5211 (100%)

Fig. S62 HRESI mass spectrum of the self-assembled capsule (**52**) recorded by dissolving receptor **5** to a mixture solution of DMSO/CHCl<sub>3</sub> (1:1, v/v).

Elemental Composition Report

Single Mass Analysis

Tolerance = 40.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions  
 16 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

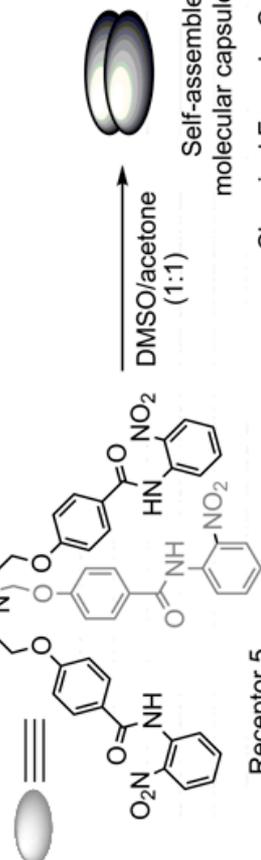
Elements Used:

C: 0-400 H: 0-1000 N: 14-14 O: 24-24 Na: 1-1  
 CX-183-4

0330\_CX-183-4 24 (1.049)



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1761.5193	1761.5211	-1.8	-1.0	58.5	12.6	0.0	C90 H78 N14 O24 Na



Chemical Formula: C<sub>90</sub>H<sub>78</sub>N<sub>14</sub>O<sub>24</sub>

Molecular Weight: 1739.6617

Theoretical value for [M+Na]<sup>+</sup>: 1761.5211 (100%)

Fig. S63 HRESI mass spectrum of the self-assembled capsule (5<sub>2</sub>) recorded by dissolving receptor 5 to a mixture solution of DMSO/acetone-*d*<sub>6</sub> (1:1, v/v).

Elemental Composition Report

Single Mass Analysis

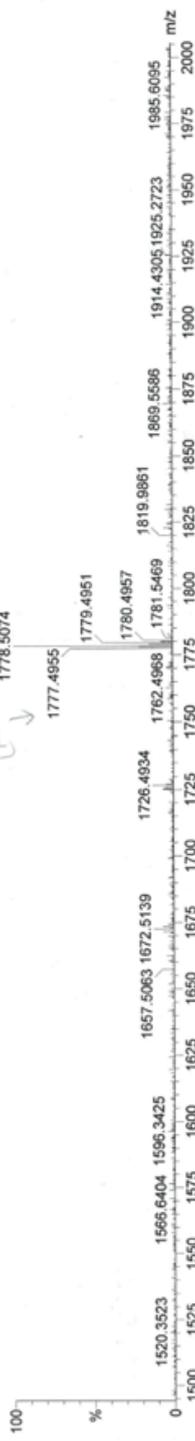
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions  
 16 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

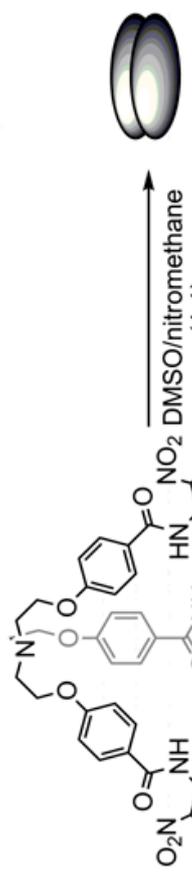
Elements Used:  
 C: 0-400 H: 0-1000 N: 14-14 O: 24-24 K: 1-1  
 CX-183-8

0401\_CX-183-8 40 (1.749)

01-Apr-2011  
 16:17:37  
 1: TOF MS ES+  
 9.62e+001



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1777.4955	1777.4950	0.5	0.3	58.5	23.2	0.0	C90 H78 N14 O24 K
Minimum:	5.0		10.0	-1.5			
Maximum:				1000.0			



Self-assembled  
 molecular capsule (**5<sub>2</sub>**)

Chemical Formula for [M+K]<sup>+</sup>: C<sub>90</sub>H<sub>78</sub>N<sub>14</sub>KO<sub>24</sub>  
 Molecular Weight: 1778.7600  
 Theoretical value for [M+K]<sup>+</sup>: 1777.4950 (100%)

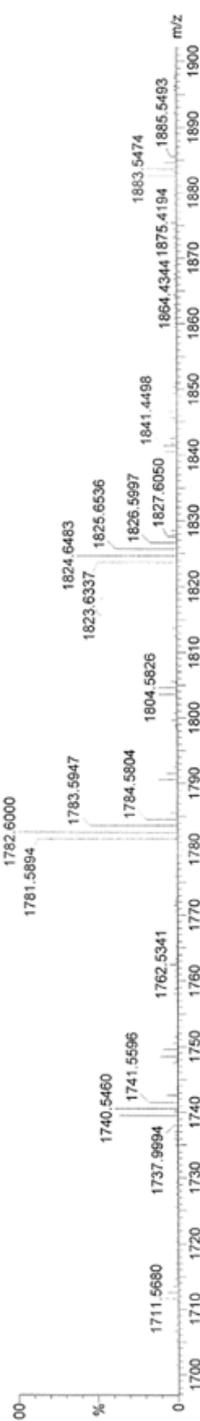
Fig. S64 HRESI mass spectra of the self-assembled capsule (**5<sub>2</sub>**) recorded by dissolving receptor **5** to a mixture solution of DMSO/CH<sub>3</sub>NO<sub>2</sub> (1:1, v/v).

Elemental Composition Report

**Single Mass Analysis**  
 Tolerance = 50.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions  
 17 formulae evaluated with 1 results within limits (up to 50 closest results for each mass)  
 Elements Used:  
 C: 0-1000 H: 0-4000 N: 14-14 O: 24-24  
 CX-19-3

0407\_CX-19-3 (0.901)



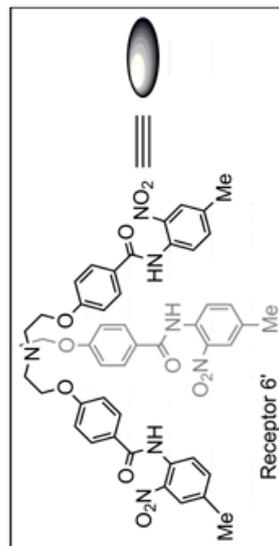
Minimum: -1.5  
 Maximum: 1000.0

Mass	Calc. Mass	mDa	PFM	DBE	i-FIT	i-FIT (Norm)	Formula
1823.6337	1823.6331	0.6	0.3	58.5	17.4	0.0	C <sub>96</sub> H <sub>90</sub> N <sub>14</sub> O <sub>24</sub>

Self-assembled  
 molecular capsule (**6'**)

Chemical Formula: C<sub>96</sub>H<sub>90</sub>N<sub>14</sub>O<sub>24</sub>  
 Molecular Weight: 1823.8212

Theoretical value for M<sup>+</sup>: 1823.6286 (100%)  
 Theoretical value for [M+H]<sup>+</sup>: 1824.6364 (100%)



Complex **6b**

Chemical Formula: C<sub>96</sub>H<sub>90</sub>N<sub>14</sub>O<sub>24</sub>  
 Molecular Weight: 1823.8212

Theoretical value for M<sup>+</sup>: 1823.6286 (100%)

Theoretical value for [M+H]<sup>+</sup>: 1824.6364 (100%)

**Fig. S65** HRESI mass spectrum of the self-assembled capsule (**6'**) recorded after dissolving the nitrate complex **6b** in a mixture solution of DMSO/CHCl<sub>3</sub> (1:1).

Elemental Composition Report

**Single Mass Analysis**  
 Tolerance = 40.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for iFIT = 2

Monoisotopic Mass, Even Electron Ions  
 17 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)  
 Elements Used:

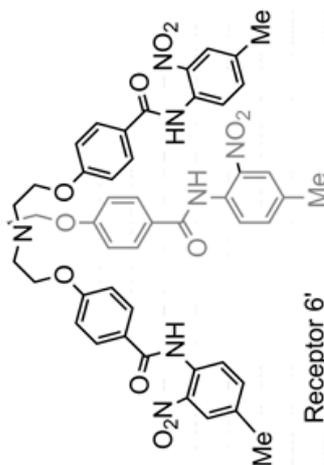
C: 0-400 H: 0-1000 N: 14-14 O: 24-24 Na: 1-1  
 CX-183-5

0330\_CX-183-5.12 (0.523) Cm (12)



Minimum: -1.5  
 Maximum: 1000.0

Mass	Calc. Mass	mDa	DBE	i-FIT	i-FIT (Norm)	Formula
1845.6069	1845.6150	-8.1	58.5	11.6	0.0	C <sub>96</sub> H <sub>90</sub> N <sub>14</sub> O <sub>24</sub> Na



Chemical Formula: C<sub>96</sub>H<sub>90</sub>N<sub>14</sub>O<sub>24</sub>  
 Molecular Weight: 1823.8212

Theoretical value for M<sup>+</sup>: 1823.6286 (100%)  
 Theoretical value for [M+Na]<sup>+</sup>: 1846.6184 (100%)

**Fig. S66** HRESI mass spectra of the self-assembled capsule (6'<sub>2</sub>) recorded by dissolving receptor 6' to a mixture solution of DMSO/acetone (1:1, v/v).

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0  
 Element prediction: Off  
 Number of isotope peaks used for iFIT = 2

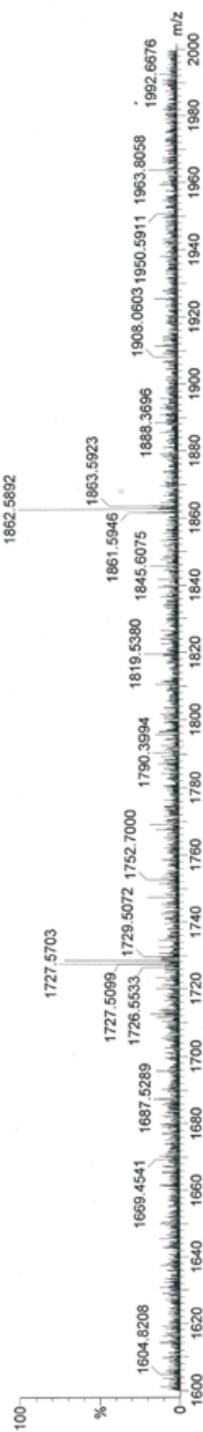
Monoisotopic Mass, Even Electron Ions  
 17 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)  
 Elements Used:

C: 0-400 H: 0-1000 N: 14-14 O: 24-24 K: 1-1  
 CX-183-9

0401\_CX-183-9\_2.14 (0.630) Cm (11:15)

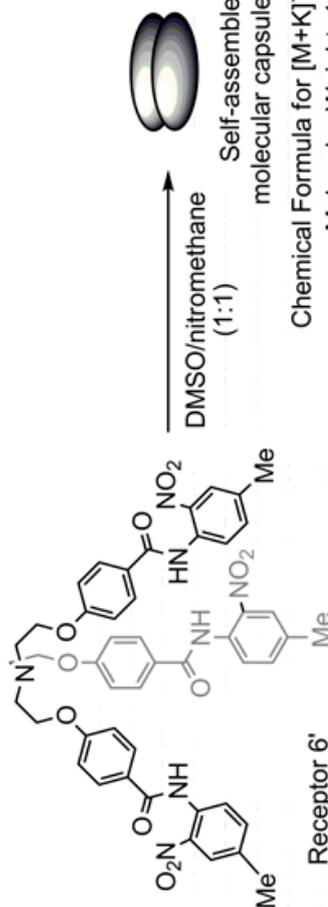
01-Apr-2011  
 16:36:02  
 1: TOF MS ES+  
 5.63e+001

KE267



Minimum: -1.5  
 Maximum: 1000.0

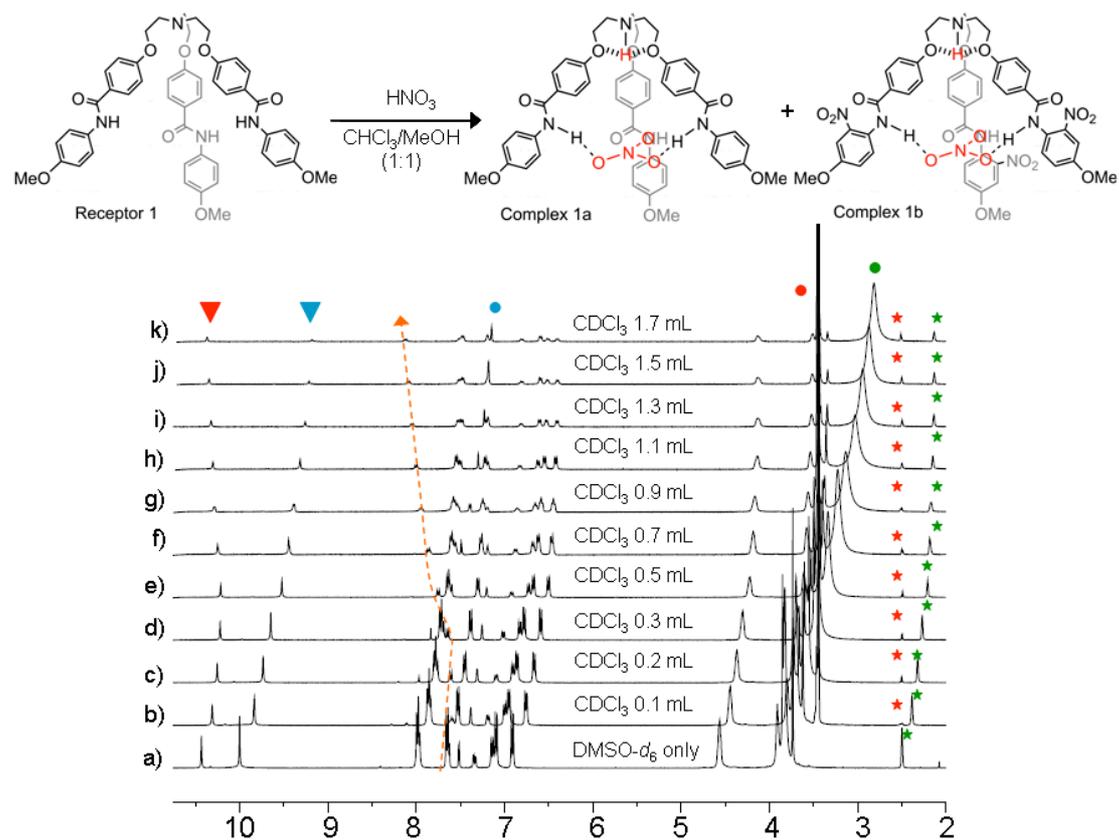
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1861.5946	1861.5889	5.7	3.1	58.5	44.7	0.0	C <sub>96</sub> H <sub>90</sub> N <sub>14</sub> O <sub>24</sub> K



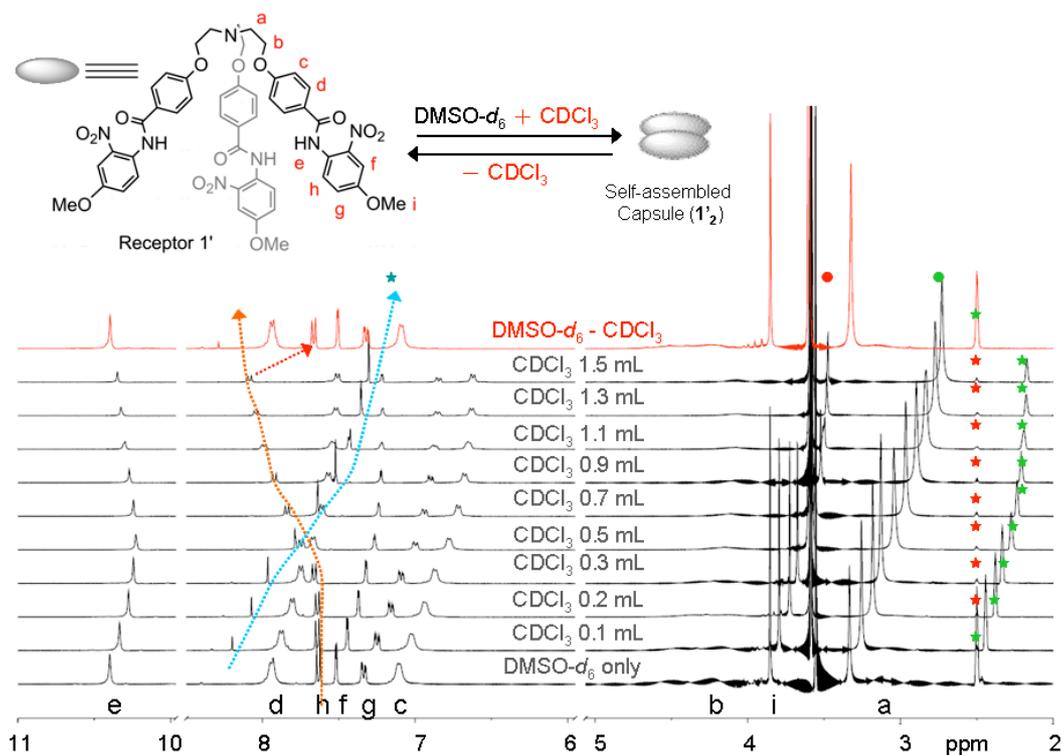
Chemical Formula for [M+K]<sup>+</sup>: C<sub>96</sub>H<sub>90</sub>N<sub>14</sub>KO<sub>24</sub>  
 Molecular Weight: 1862.9195

Theoretical value for [M+K]<sup>+</sup>: 1862.5923 (100%)

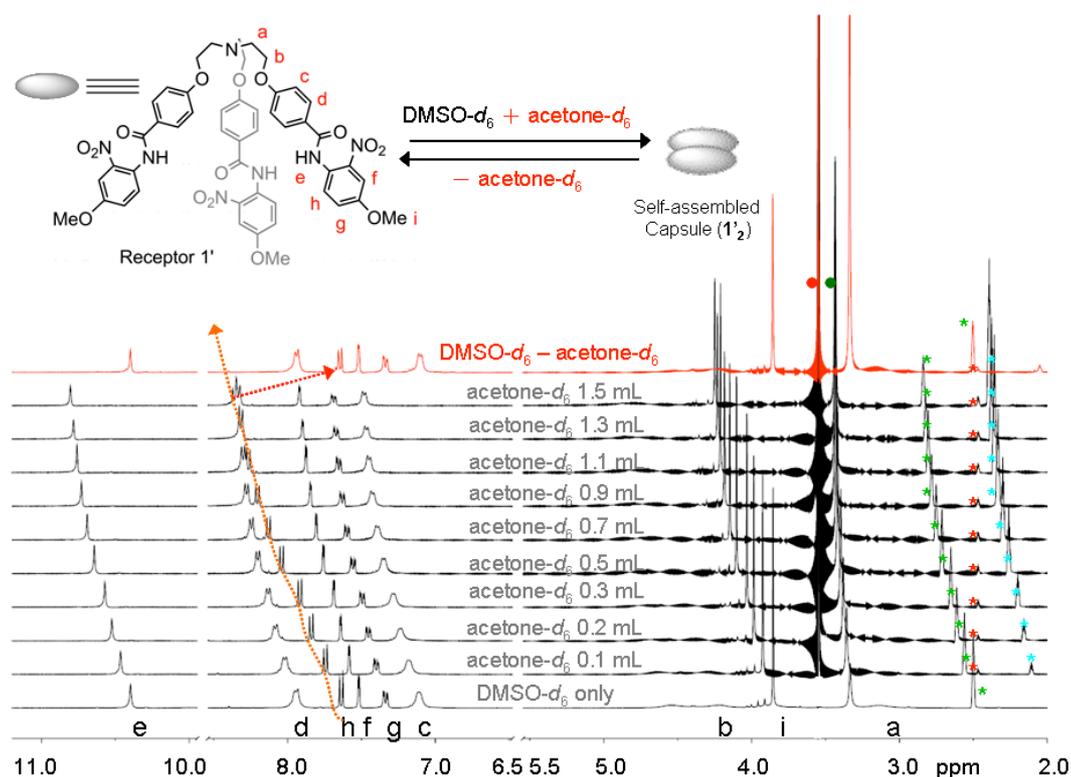
Fig. S67 HRESI mass spectra of the self-assembled capsule (6'2) recorded by dissolving receptor 6' to a mixture solution of DMSO/CH<sub>3</sub>NO<sub>2</sub> (1:1, v/v).



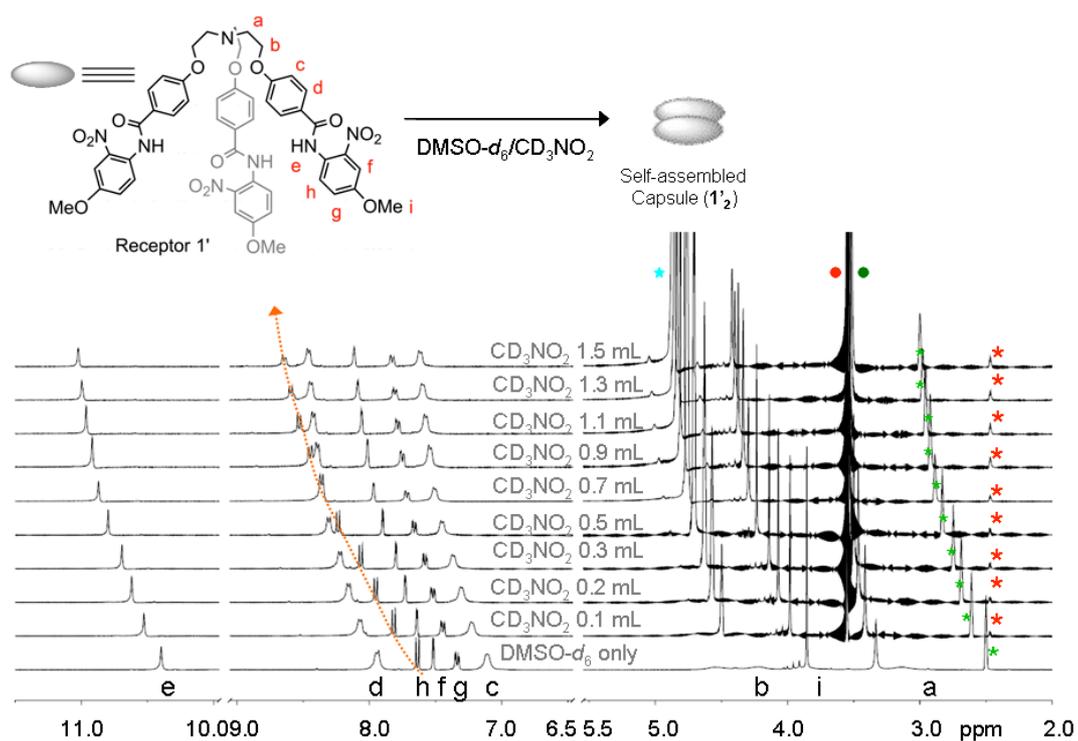
**Fig. S68** <sup>1</sup>H NMR titration spectra of a mixture of nitrate complexes (in DMSO-*d*<sub>6</sub> with varying amount of CDCl<sub>3</sub>) obtained after addition of nitric acid in aqueous methanol to a suspension of receptor **1** in CHCl<sub>3</sub>. The star marks in green and red color represent the peaks for DMSO-*d*<sub>6</sub> (as solvent) and DMSO-*d*<sub>6</sub> (as internal reference, TMS in DMSO-*d*<sub>6</sub>), respectively. The circles in green and red color represent water peaks from DMSO-*d*<sub>6</sub> (as solvent) and from DMSO-*d*<sub>6</sub> (as internal reference, TMS in DMSO-*d*<sub>6</sub>), 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<sub>3</sub>.



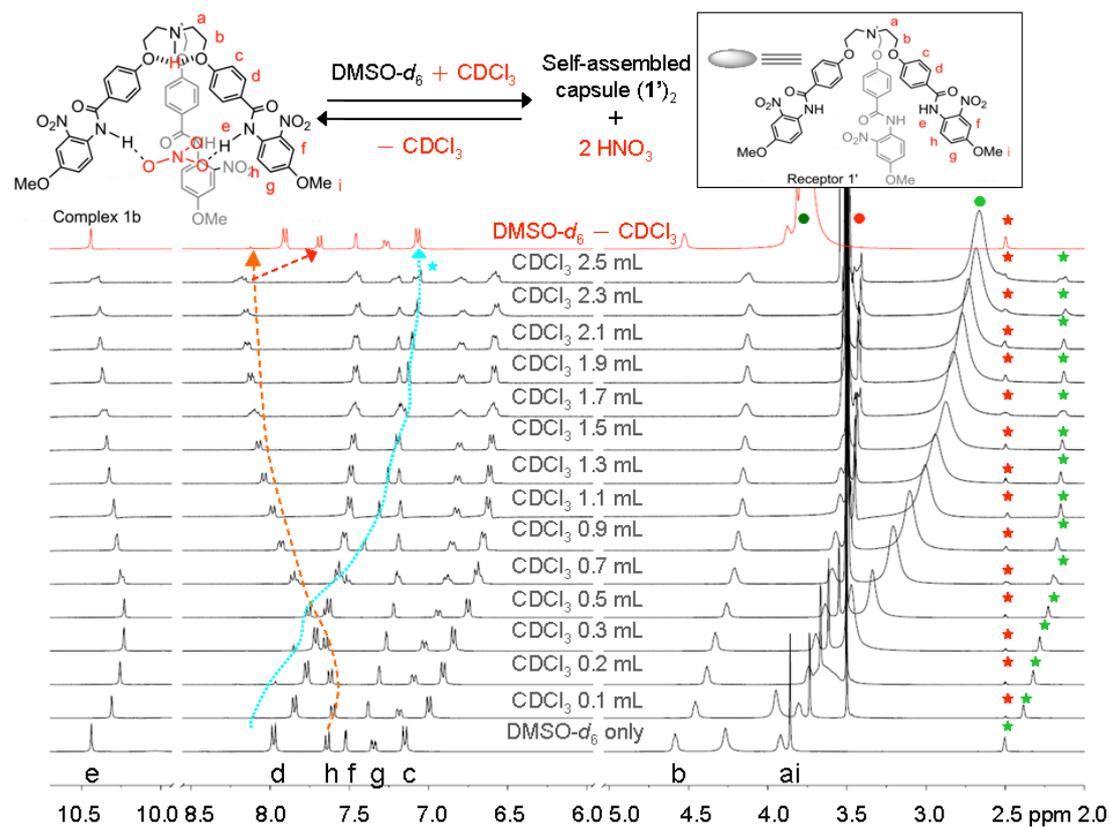
**Fig. S69**  $^1\text{H}$  NMR (400 MHz, 20 °C) titration spectra of receptor **1'** (10.3 mM) in  $\text{DMSO-}d_6$  with varying amount of  $\text{CDCl}_3$  with TMS (in  $\text{DMSO-}d_6$ ) as the internal reference. Green stars represent the peaks of  $\text{DMSO-}d_6$  used as solvent. Red stars represent the peaks of  $\text{DMSO-}d_6$  from the internal reference. Circles in green and red color represent the peaks for water from solvent  $\text{DMSO-}d_6$  and from internal reference, respectively. A star mark in blue color represents peak for  $\text{CDCl}_3$ . The spectrum in red color was recorded after partial evaporation of  $\text{CDCl}_3$  from the mixture solution, showing reversible capsule formation through dynamic self-assembly of receptor **1'**.



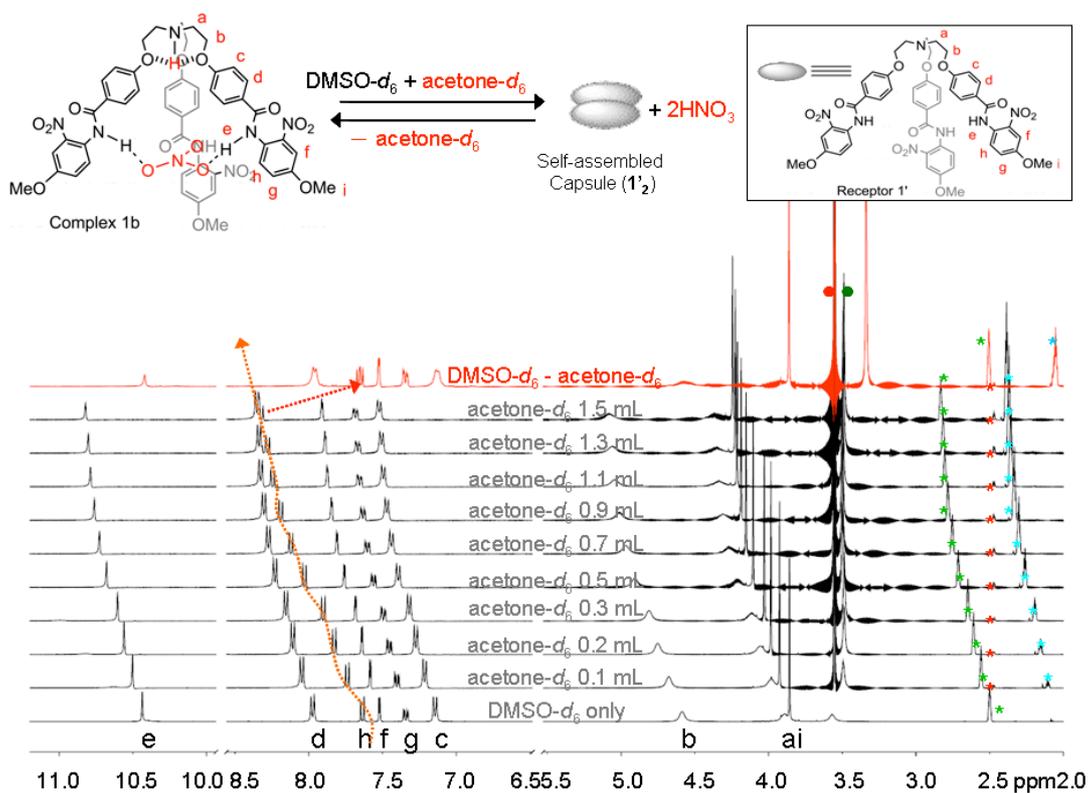
**Fig. S70**  $^1\text{H}$  NMR (400 MHz, 20 °C) titration spectra of receptor **1'** (10.3 mM) in  $\text{DMSO-}d_6$  with varying amount of  $\text{acetone-}d_6$  with TMS (in  $\text{DMSO-}d_6$ ) as the internal reference. Green stars represent the peaks of  $\text{DMSO-}d_6$  used as solvent. Red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



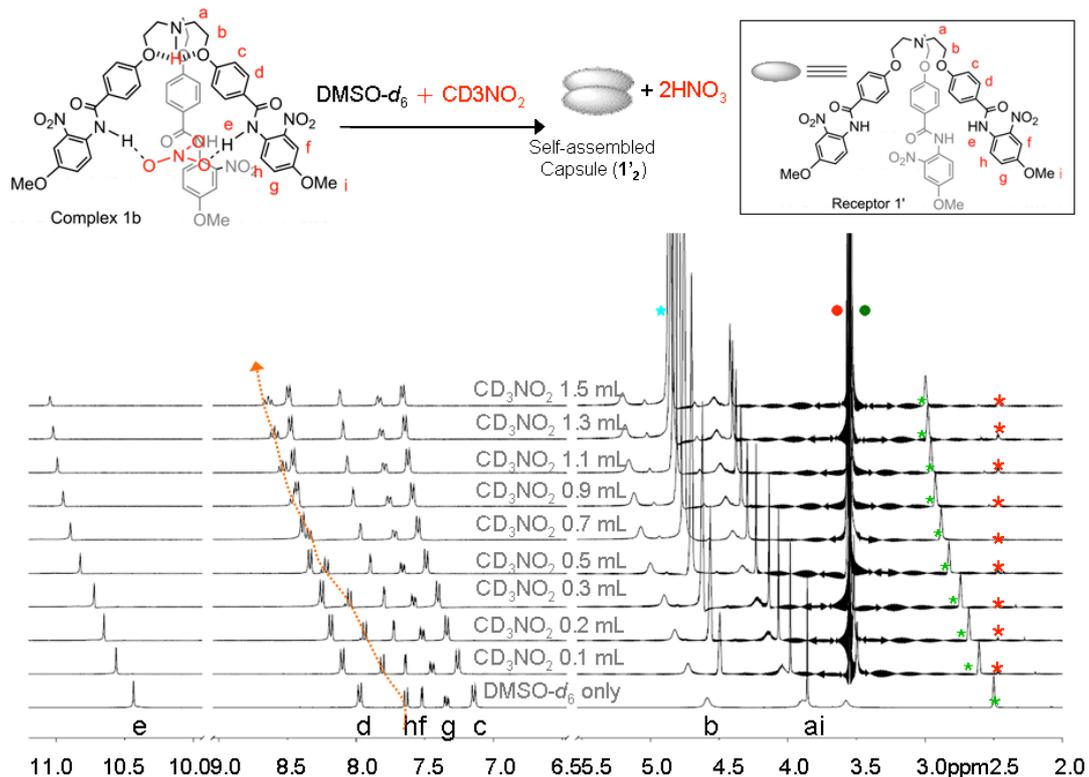
**Fig. S71** <sup>1</sup>H NMR (400 MHz, 20 °C) titration spectra of receptor 1' (10.3 mM) in DMSO-*d*<sub>6</sub> with varying amount of CD<sub>3</sub>NO<sub>2</sub> with TMS (in DMSO-*d*<sub>6</sub>) as the internal reference. Green stars represent the peaks of DMSO-*d*<sub>6</sub> used as solvent. Red stars represent the peaks of DMSO-*d*<sub>6</sub> from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-*d*<sub>6</sub> and from internal reference, respectively. A star mark in blue color represents peak for CD<sub>3</sub>NO<sub>2</sub>.



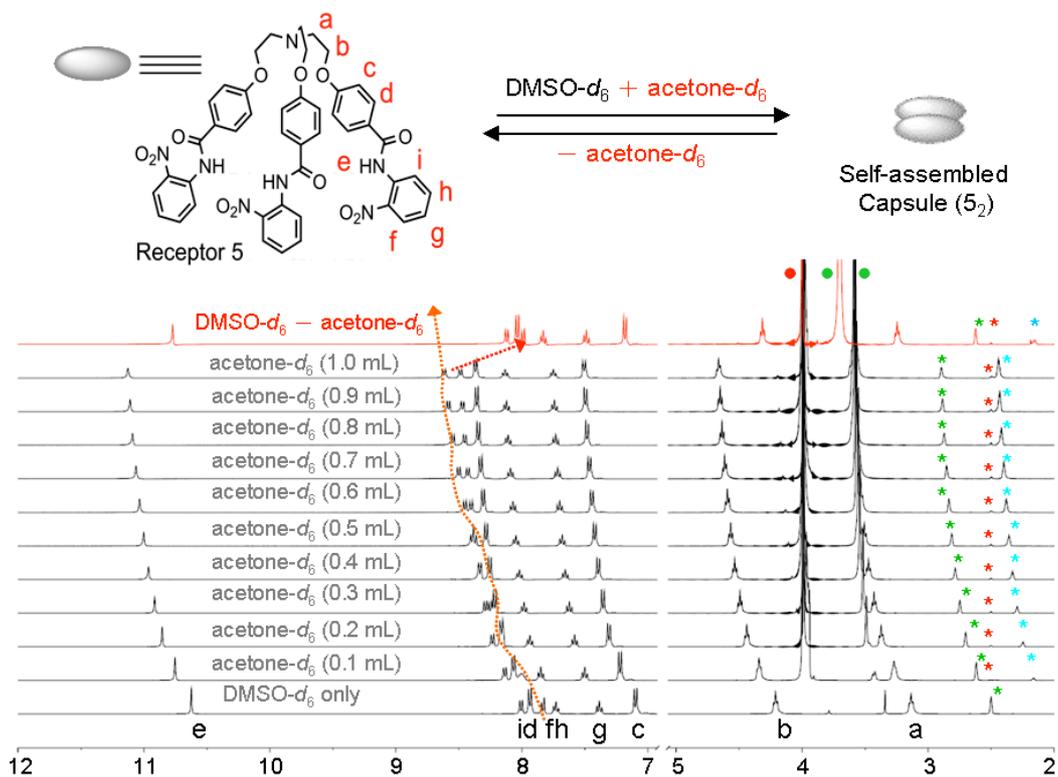
**Fig. S72**  $^1\text{H}$  NMR (400 MHz, 20 °C) titration spectra of nitrate complex **1b** (10.3 mM) in  $\text{DMSO-}d_6$  with varying amount of  $\text{CDCl}_3$  with TMS (in  $\text{DMSO-}d_6$ ) as the internal reference. Green stars represent the peaks of  $\text{DMSO-}d_6$  used as solvent. Red stars represent the peaks of  $\text{DMSO-}d_6$  from the internal reference. Circles in green and red color represent the peaks for water from solvent  $\text{DMSO-}d_6$  and from internal reference, respectively. A star mark in blue color represents peak for  $\text{CDCl}_3$ . The spectrum in red color was recorded after partial evaporation of  $\text{CDCl}_3$  from the mixture solution, showing reversible binding of nitrate anion by receptor **1'**.



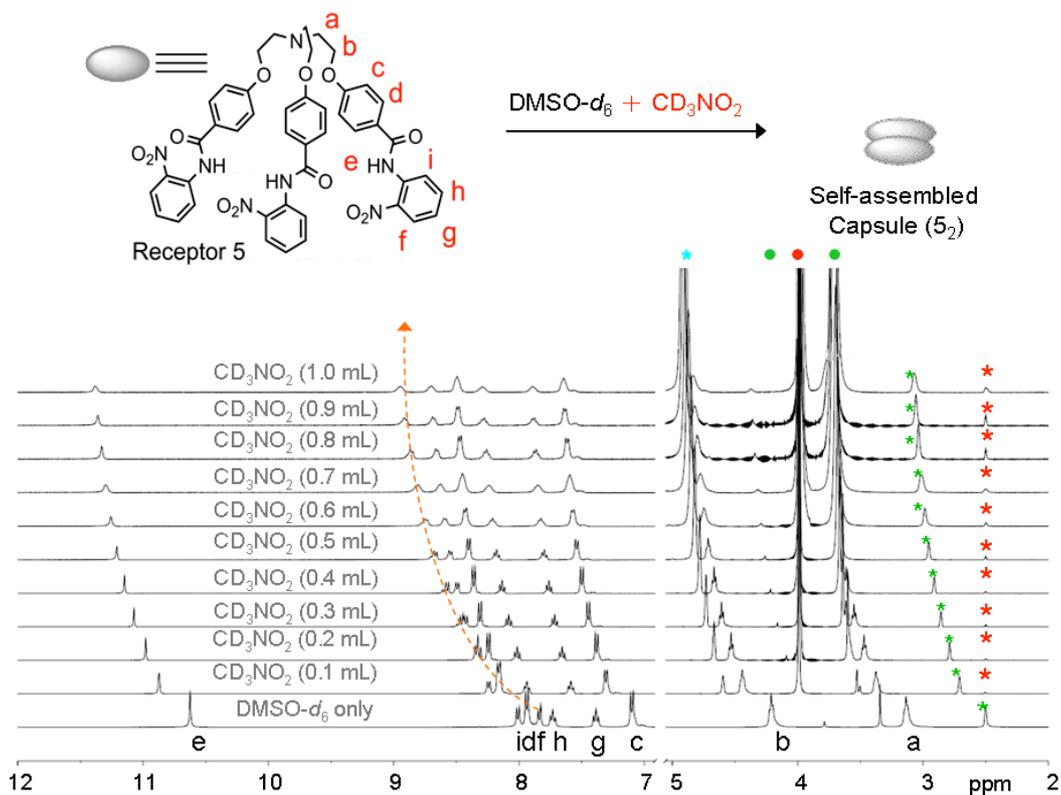
**Fig. S73**  $^1\text{H}$  NMR (400 MHz, 20 °C) titration spectra of nitrate complex **1b** (10.3 mM) in  $\text{DMSO-}d_6$  with varying amount of  $\text{acetone-}d_6$  with TMS (in  $\text{DMSO-}d_6$ ) as the internal reference. Green stars represent the peaks of  $\text{DMSO-}d_6$  used as solvent.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



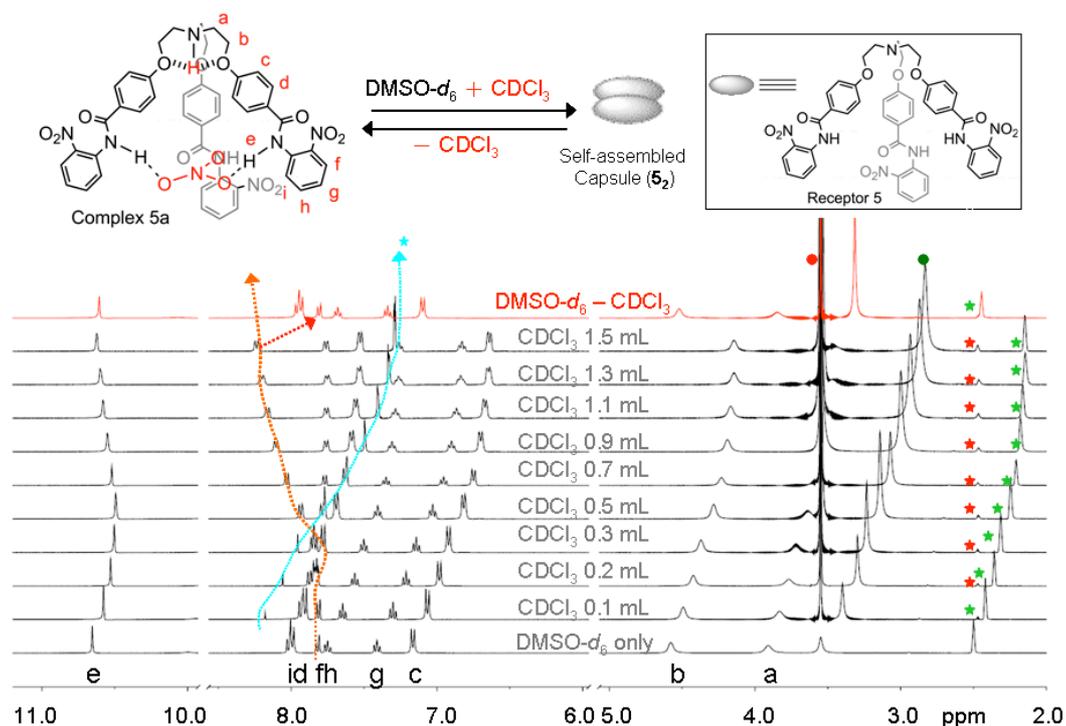
**Fig. S74**  $^1H$  NMR (400 MHz, 20 °C) titration spectra of nitrate complex **1b** (10.3 mM) in DMSO- $d_6$  with varying amount of  $CD_3NO_2$  with TMS (in DMSO- $d_6$ ) as the internal reference. Green stars represent the peaks of DMSO- $d_6$  used as solvent. Red stars represent the peaks of DMSO- $d_6$  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  $CD_3NO_2$ .



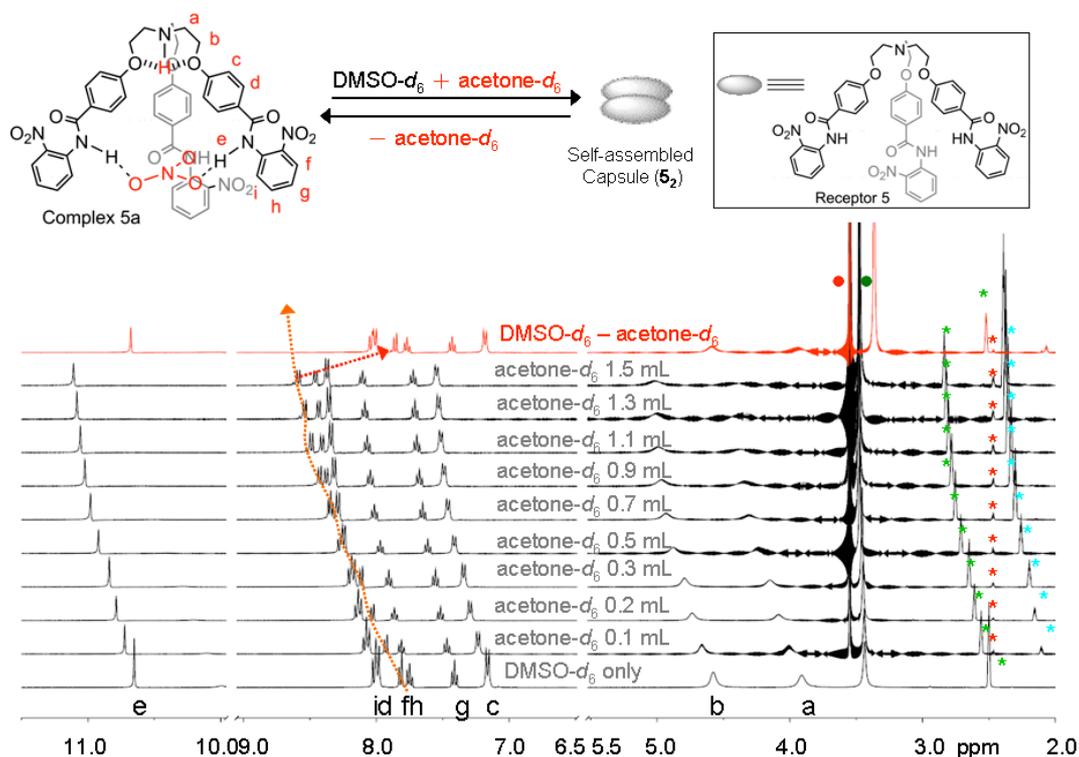
**Fig. S75**  $^1\text{H}$  NMR (400 MHz, 20 °C) titration spectra of receptor **5** (10.3 mM) in DMSO- $d_6$  with varying amount of acetone- $d_6$  with TMS (in DMSO- $d_6$ ) as the internal reference. Green stars represent the peaks of DMSO- $d_6$  used as solvent. Red stars represent the peaks of 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- $d_6$ .



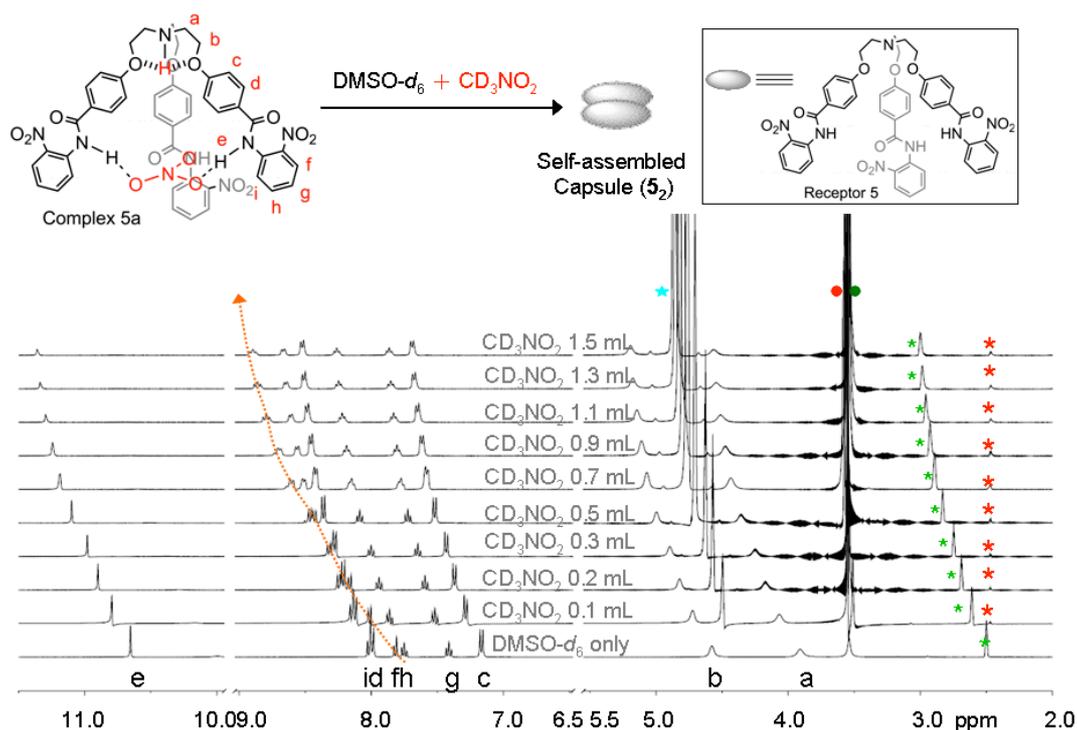
**Fig. S76**  $^1\text{H}$  NMR (400 MHz, 20 °C) titration spectra of receptor **5** (10.3 mM) in  $\text{DMSO-}d_6$  with varying amount of  $\text{CD}_3\text{NO}_2$  with TMS (in  $\text{DMSO-}d_6$ ) as the internal reference. Green stars represent the peaks of  $\text{DMSO-}d_6$  used as solvent. Red stars represent the peaks of  $\text{DMSO-}d_6$  from the internal reference. Circles in green and red color represent the peaks for water from solvent  $\text{DMSO-}d_6$  and from internal reference, respectively. A star mark in blue color represents the peak for  $\text{CD}_3\text{NO}_2$ .



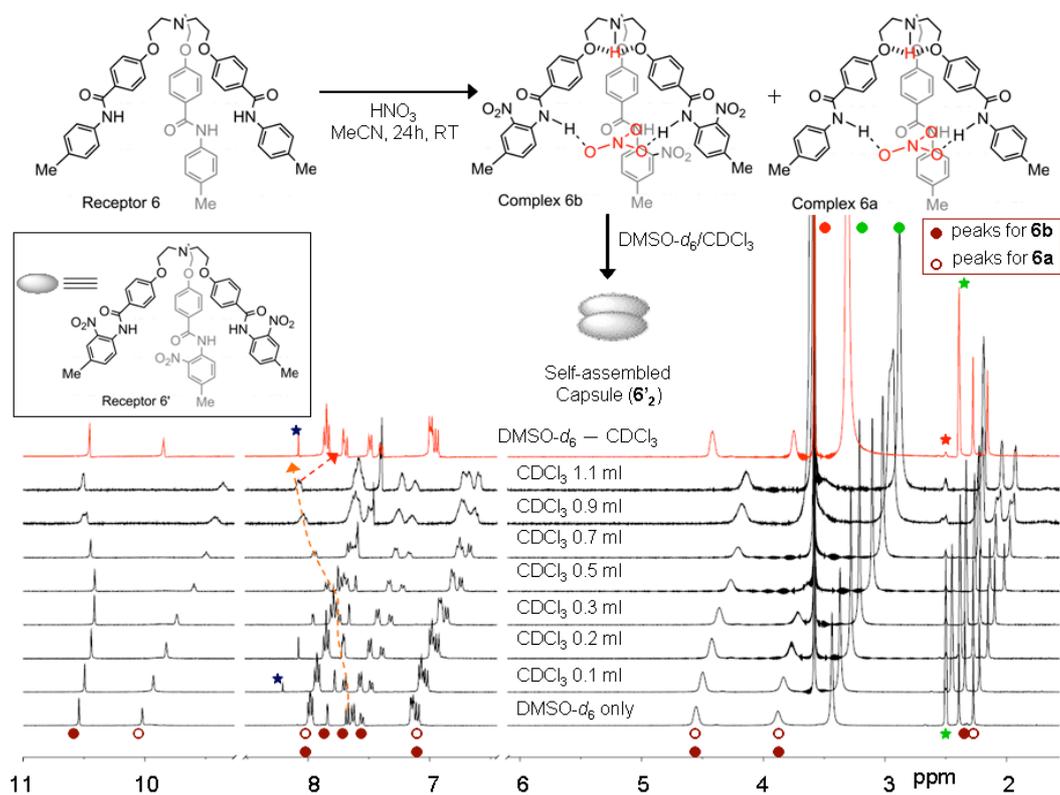
**Fig. S77** <sup>1</sup>H NMR (400 MHz, 20 °C) titration spectra of nitrate complex **5a** (10.3 mM) in DMSO-*d*<sub>6</sub> with varying amount of CDCl<sub>3</sub> with TMS (in DMSO-*d*<sub>6</sub>) as the internal reference. Green stars represent the peaks of DMSO-*d*<sub>6</sub> used as solvent. Red stars represent the peaks of DMSO-*d*<sub>6</sub> from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-*d*<sub>6</sub> and from internal reference, respectively. A star mark in blue color represents the peak for CDCl<sub>3</sub>. The spectrum in red color was recorded after partial evaporation of CDCl<sub>3</sub> from the mixture solution, showing reversible binding of nitrate anion by receptor **5**.



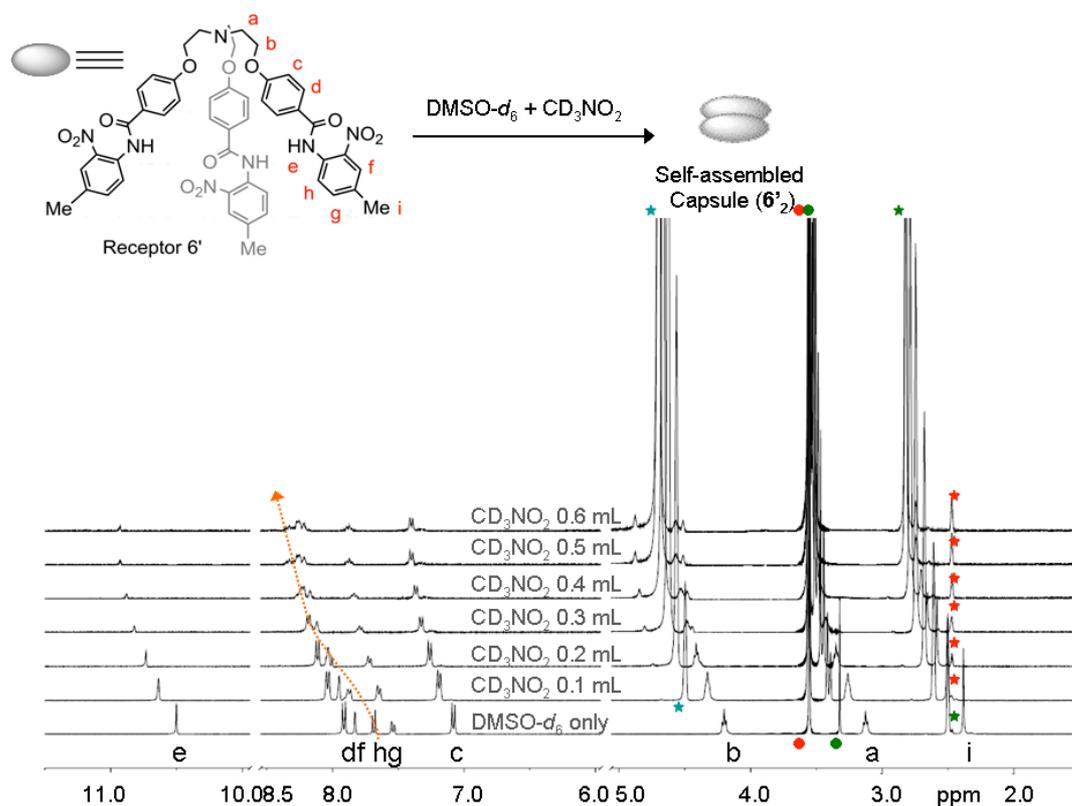
**Fig. S78**  $^1\text{H}$  NMR (400 MHz, 20 °C) titration spectra of nitrate complex **5a** (10.3 mM) in  $\text{DMSO-}d_6$  with varying amount of  $\text{acetone-}d_6$  with TMS (in  $\text{DMSO-}d_6$ ) as the internal reference. Green stars represent the peaks of  $\text{DMSO-}d_6$  used as solvent.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



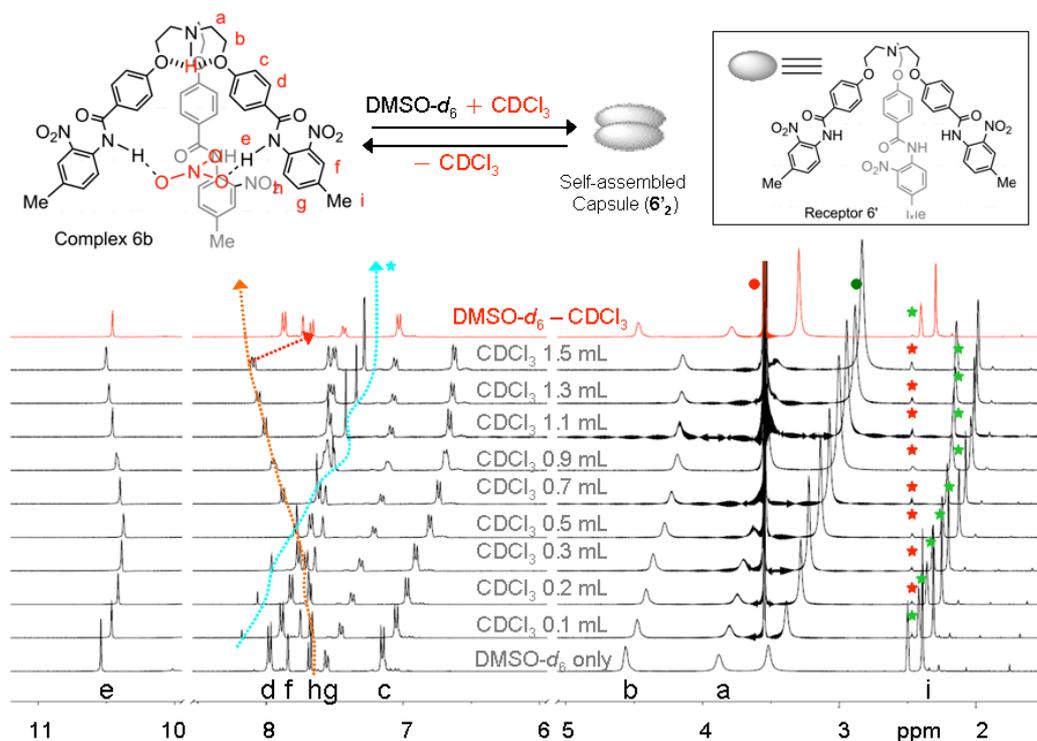
**Fig. S79**  $^1H$  NMR (400 MHz, 20 °C) titration spectra of nitrate complex **5a** (10.3 mM) in DMSO- $d_6$  with varying amount of  $CD_3NO_2$  with TMS (in DMSO- $d_6$ ) as the internal reference. Green stars represent the peaks of DMSO- $d_6$  used as solvent. Red stars represent the peaks of DMSO- $d_6$  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  $CD_3NO_2$ .



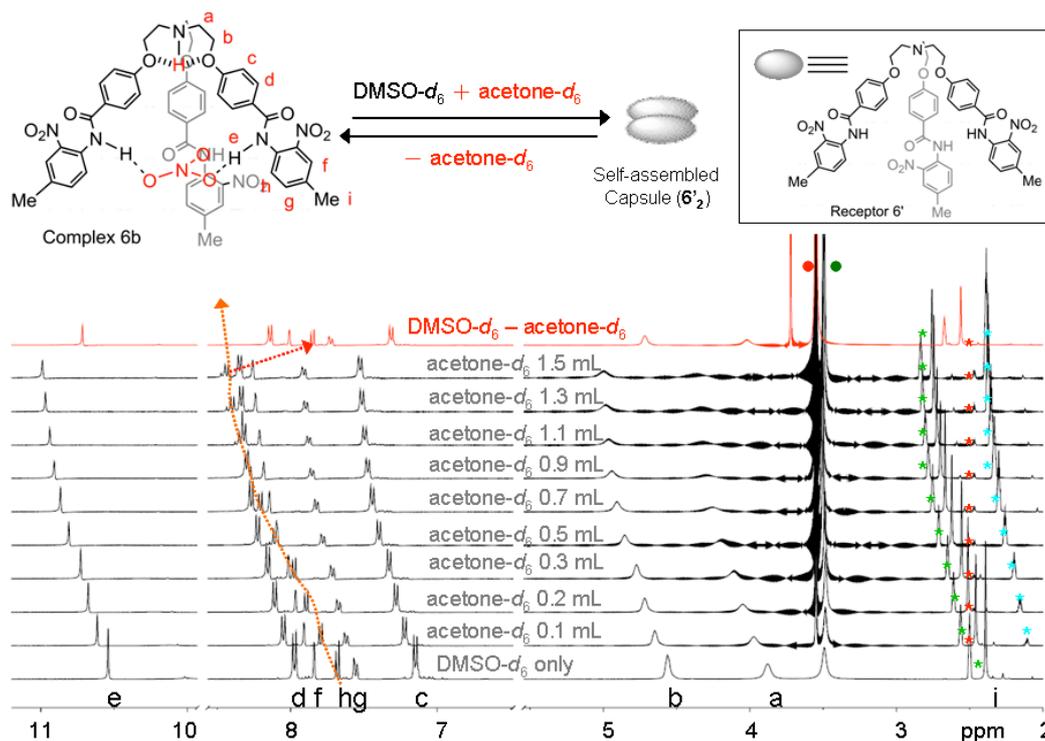
**Fig. S80**  $^1\text{H}$  NMR titration spectra of mixture of nitrate complex (in  $\text{DMSO-}d_6$  with varying amount of  $\text{CDCl}_3$ ), obtained after addition of nitric acid in an aqueous methanol to the suspension of receptor 6 in  $\text{CHCl}_3$ . The star marks in green and red color represents peak corresponding to  $\text{DMSO-}d_6$  (as solvent) and  $\text{DMSO-}d_6$  (as internal reference, TMS in  $\text{DMSO-}d_6$ ), respectively. Circle in green color represents water peak from  $\text{DMSO-}d_6$  (as solvent) and the same in red color represents water peak from  $\text{DMSO-}d_6$  (as internal reference, TMS in  $\text{DMSO-}d_6$ ). A star mark in blue color represents peak for  $\text{CDCl}_3$ .



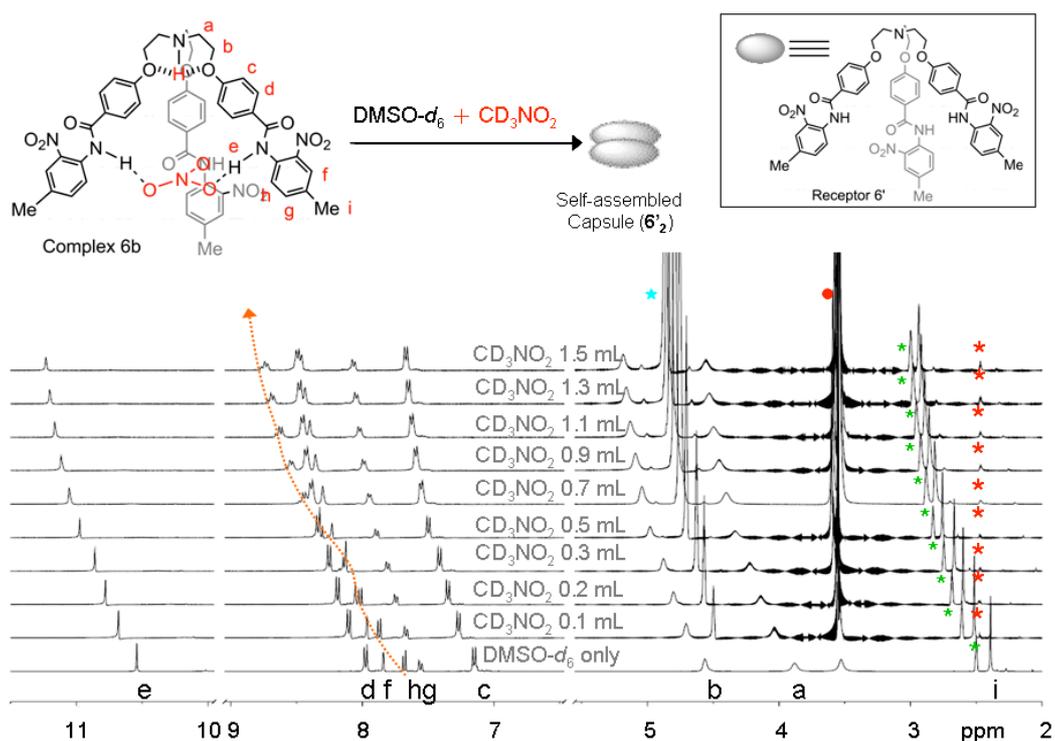
**Fig. S81**  $^1\text{H}$  NMR (400 MHz, 20 °C) titration spectra of receptor **6'** (10.3 mM) in  $\text{DMSO-}d_6$  with varying amount of  $\text{CD}_3\text{NO}_2$  with TMS (in  $\text{DMSO-}d_6$ ) as the internal reference. Green stars represent the peaks of  $\text{DMSO-}d_6$  used as solvent. Red stars represent the peaks of  $\text{DMSO-}d_6$  from the internal reference. Circles in green and red color represent the peaks for water from solvent  $\text{DMSO-}d_6$  and from internal reference, respectively. A star mark in blue color represents the peak for  $\text{CD}_3\text{NO}_2$ .



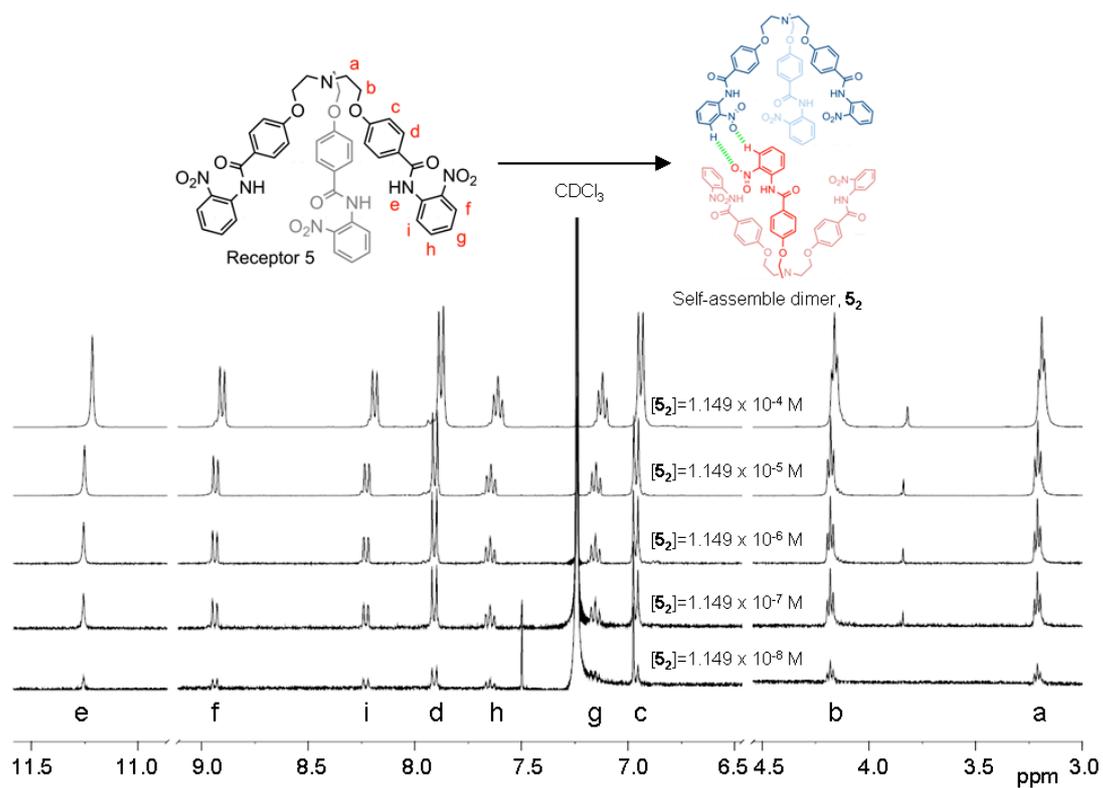
**Fig. S82**  $^1\text{H NMR}$  (400 MHz,  $20^\circ\text{C}$ ) titration spectra of nitrate complex **6b** (10.3 mM) in  $\text{DMSO-}d_6$  with varying amount of  $\text{CDCl}_3$  with TMS (in  $\text{DMSO-}d_6$ ) as the internal reference. Green stars represent the peaks of  $\text{DMSO-}d_6$  used as solvent. Red stars represent the peaks of  $\text{DMSO-}d_6$  from the internal reference. Circles in green and red color represent the peaks for water from solvent  $\text{DMSO-}d_6$  and from internal reference, respectively. A star mark in blue color represents the peak for  $\text{CDCl}_3$ . The spectrum in red color was recorded after partial evaporation of  $\text{CDCl}_3$  from the mixture solution, showing reversible binding of nitrate anion by receptor **6'**.



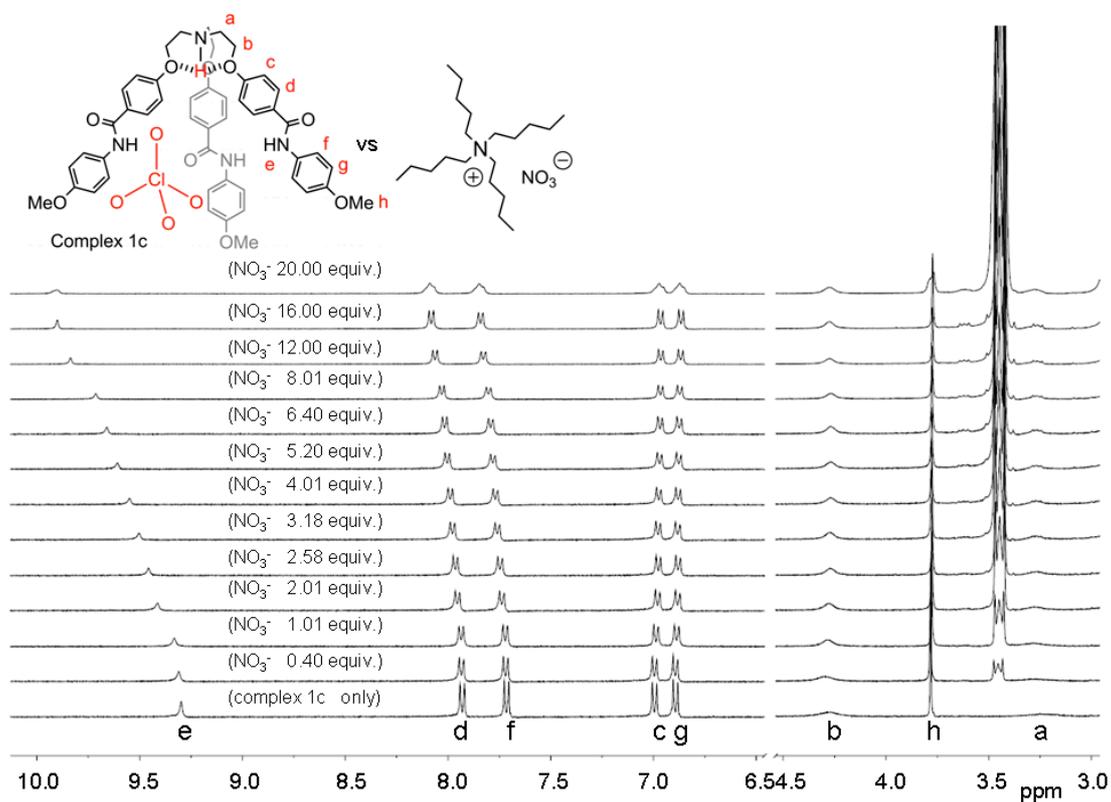
**Fig. S83**  $^1\text{H}$  NMR (400 MHz, 20 °C) titration spectra of nitrate complex **6b** (10.3 mM) in DMSO- $d_6$  with varying amount of acetone- $d_6$  with TMS (in DMSO- $d_6$ ) as the internal reference. Green stars represent the peaks of DMSO- $d_6$  used as solvent. Red stars represent the 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'**.



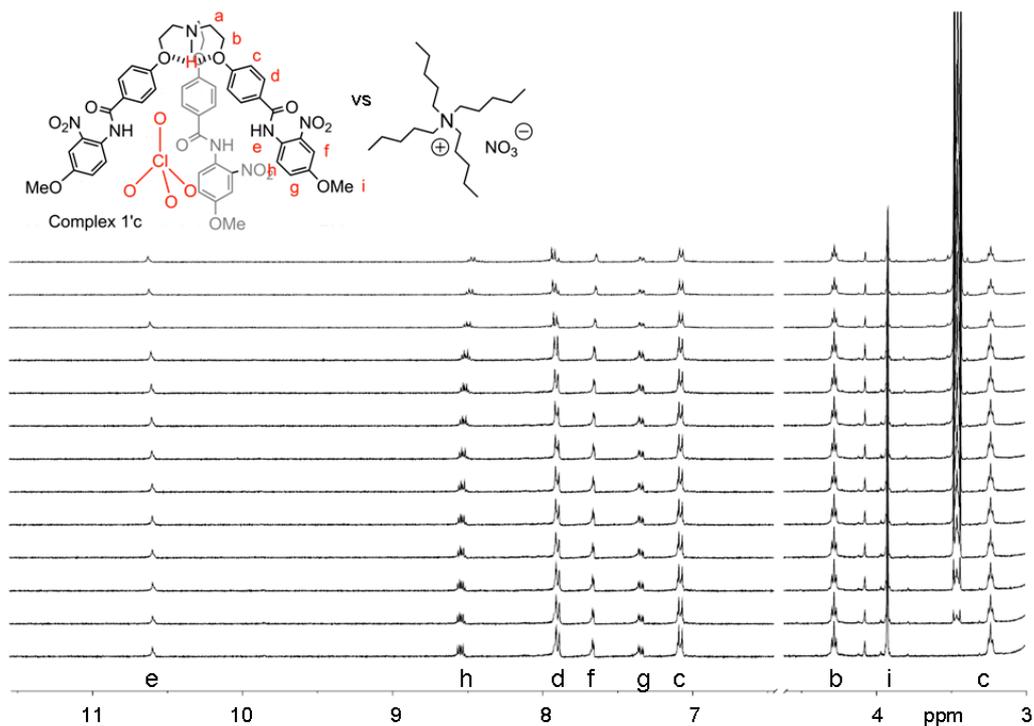
**Fig. S84**  $^1\text{H}$  NMR (400 MHz, 20 °C) titration spectra of nitrate complex **6b** (10.3 mM) in  $\text{DMSO-}d_6$  with varying amount of  $\text{CD}_3\text{NO}_2$  with TMS (in  $\text{DMSO-}d_6$ ) as the internal reference. Green stars represent the peaks of  $\text{DMSO-}d_6$  used as solvent. Red stars represent the peaks of  $\text{DMSO-}d_6$  from the internal reference. Circles in red color represent the peaks for water from  $\text{DMSO-}d_6$  (internal reference). A star mark in blue color represents the peak for  $\text{CD}_3\text{NO}_2$ .



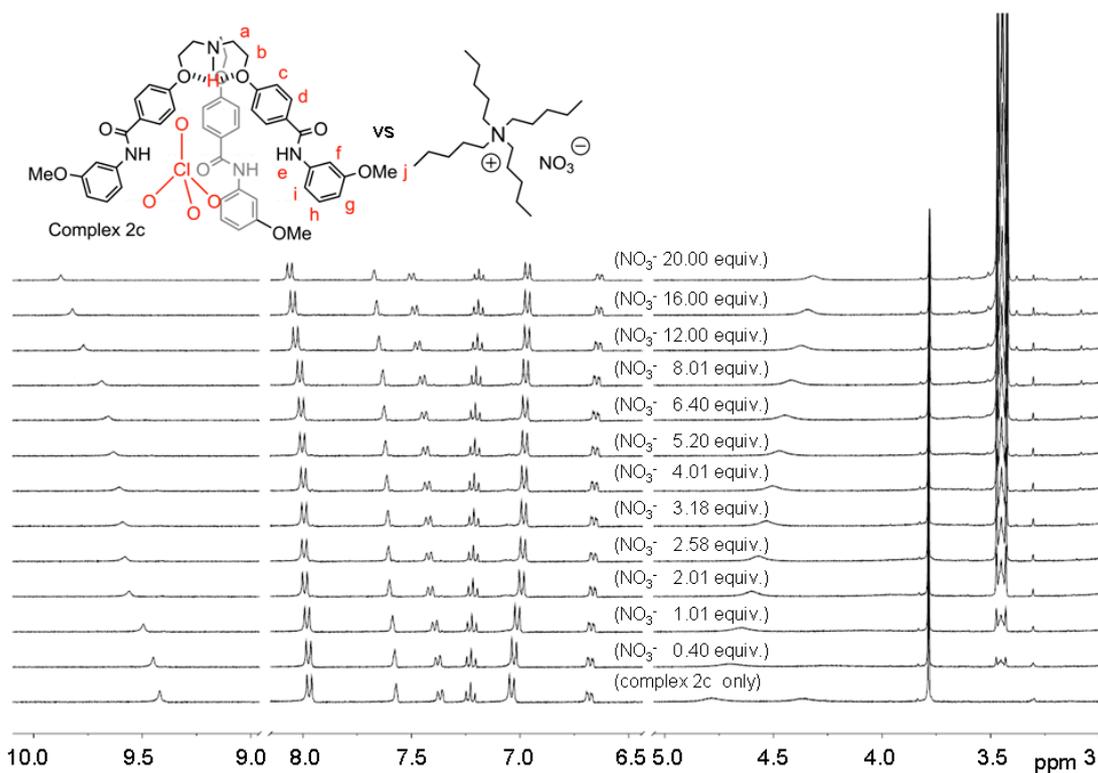
**Fig. S85** Concentration dependent <sup>1</sup>H NMR of **5**<sub>2</sub> in CDCl<sub>3</sub> showing the self-assembled capsule exists till 1 × 10<sup>-8</sup> M concentration without formation of any side products.



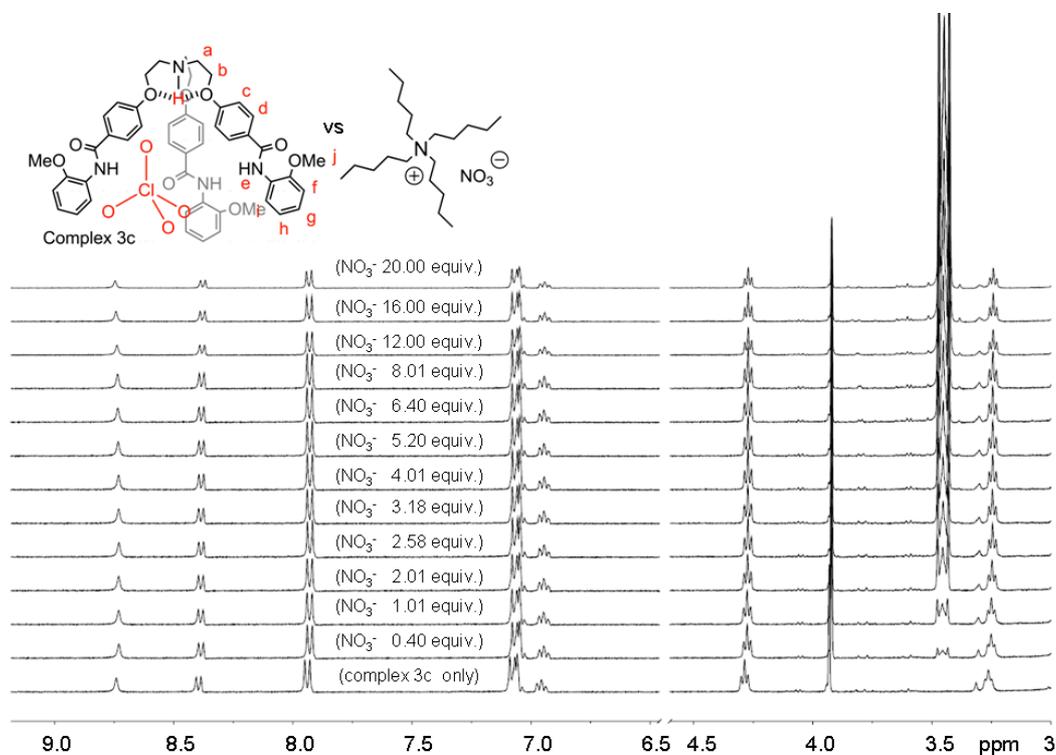
**Fig. S86** Partial <sup>1</sup>H NMR titration spectra of perchlorate complex **1c** ( $2.96 \times 10^{-3}$  M) with tetrabutylammonium nitrate in acetone-*d*<sub>6</sub>.



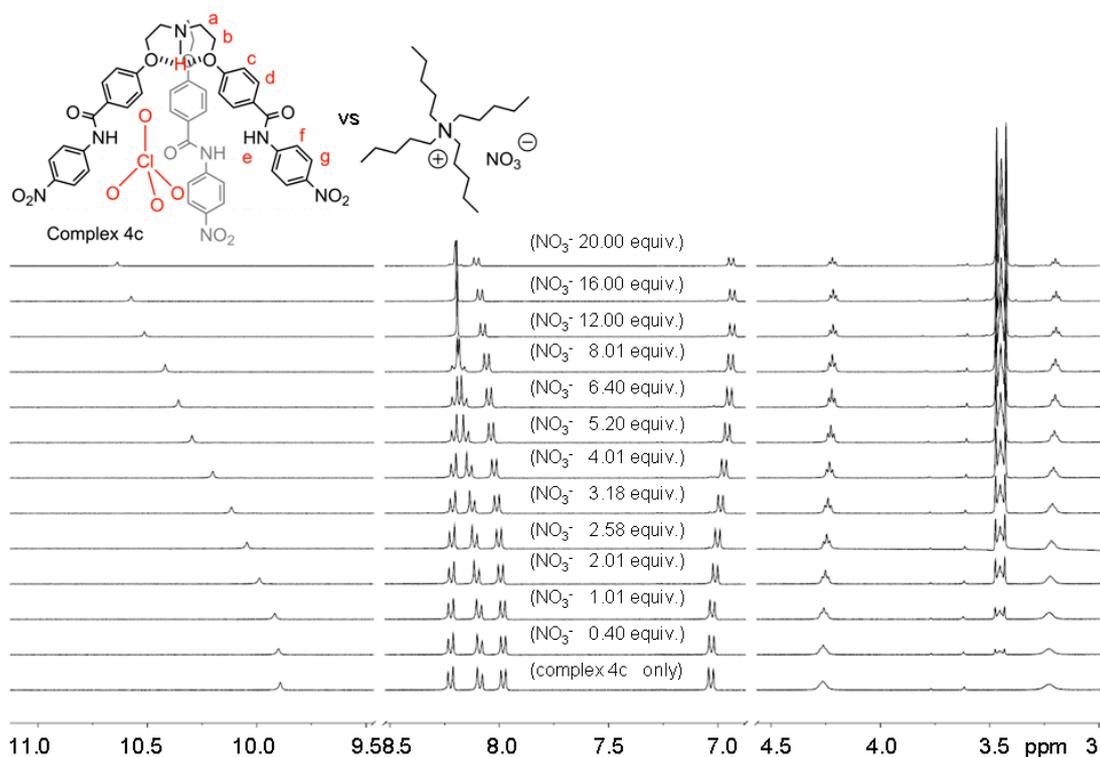
**Fig. S87** Partial <sup>1</sup>H NMR titration spectra of perchlorate complex **1'c** ( $1.48 \times 10^{-3}$  M) with tetrabutylammonium nitrate in acetone-*d*<sub>6</sub>.



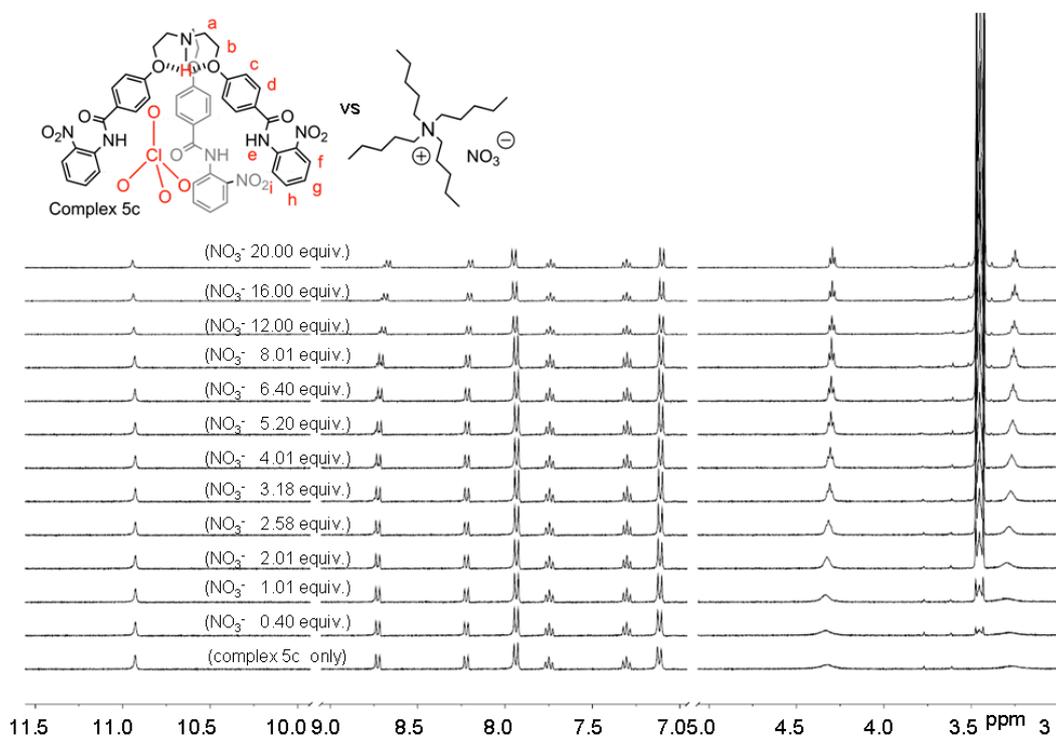
**Fig. S88** Partial  $^1\text{H}$  NMR titration spectra of perchlorate complex **2c** ( $1.48 \times 10^{-3}$  M) with tetrabutylammonium nitrate in acetone- $d_6$ .



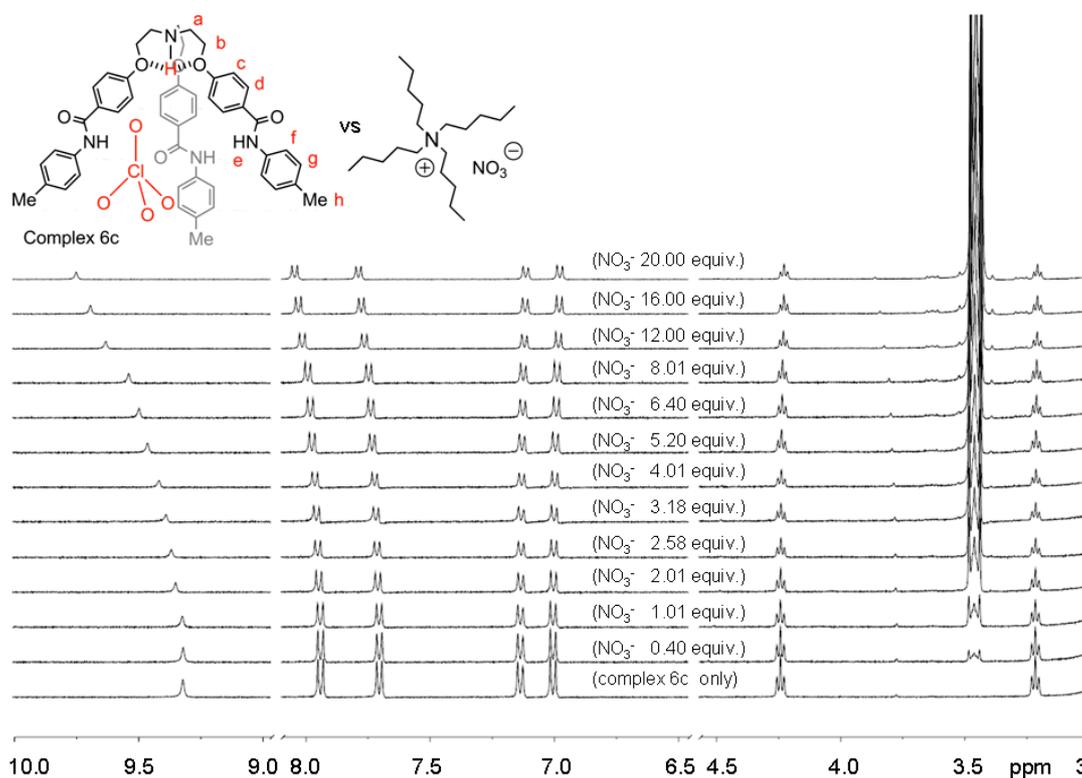
**Fig. S89** Partial  $^1\text{H}$  NMR titration spectra of perchlorate complex **3c** ( $1.48 \times 10^{-3}$  M) with tetrabutylammonium nitrate in acetone- $d_6$ .



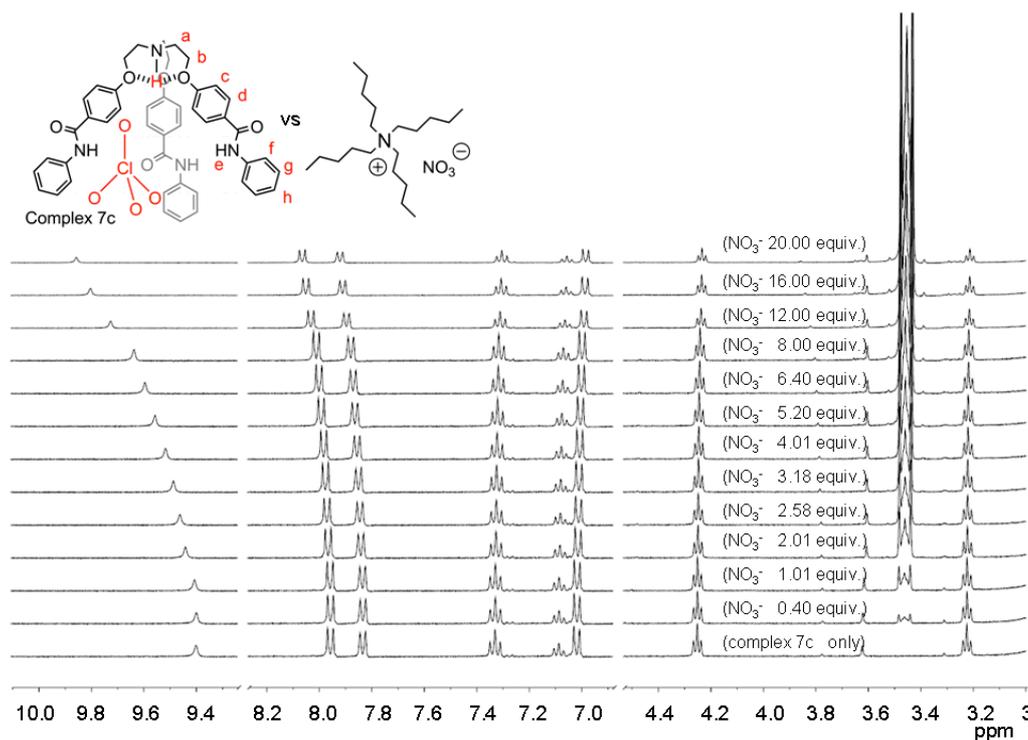
**Fig. S90** Partial <sup>1</sup>H NMR titration spectra of perchlorate complex **4c** ( $1.48 \times 10^{-3}$  M) with tetrabutylammonium nitrate in acetone-*d*<sub>6</sub>.



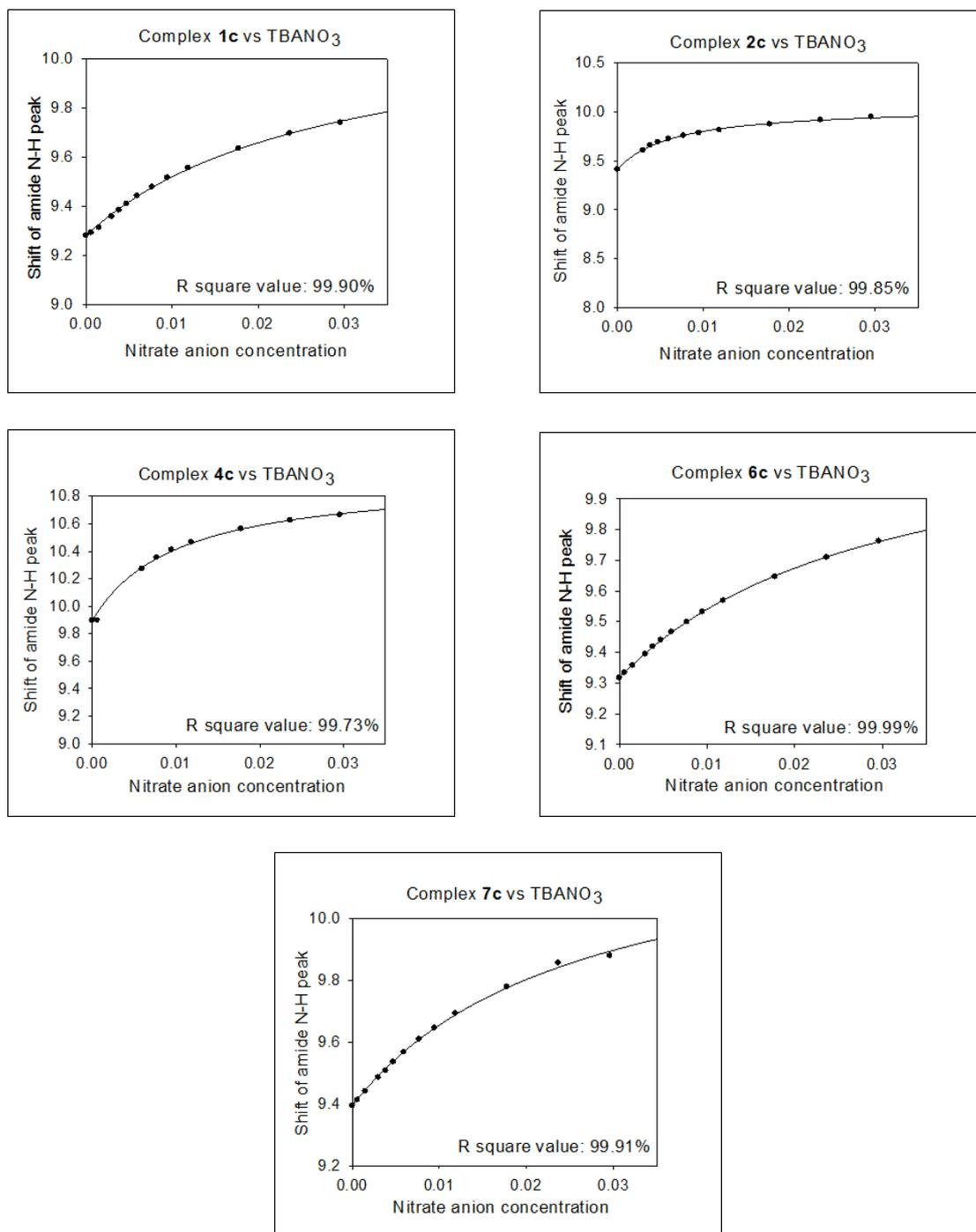
**Fig. S91** Partial <sup>1</sup>H NMR titration spectra of perchlorate complex **5c** ( $1.48 \times 10^{-3}$  M) with tetrabutylammonium nitrate in acetone-*d*<sub>6</sub>.



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

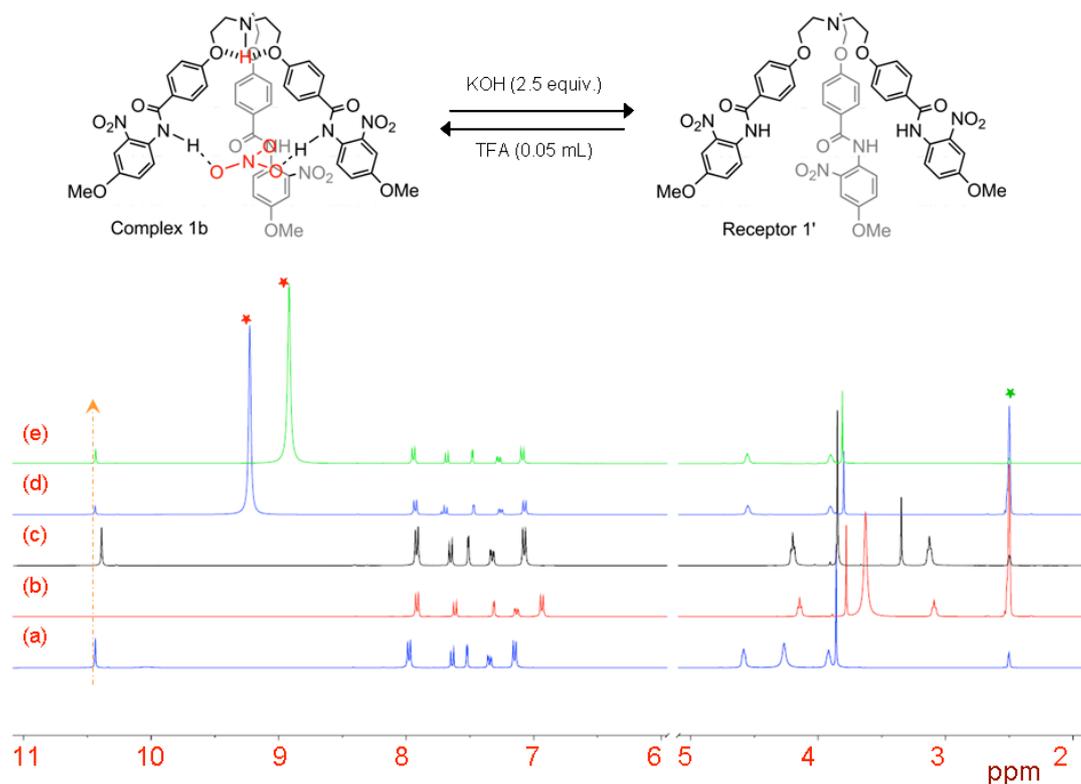


**Fig. S93** Partial  $^1\text{H}$  NMR titration spectra of perchlorate complex **7c** ( $1.48 \times 10^{-3}$  M) with tetrabutylammonium nitrate in acetone- $d_6$ .



**Fig. S94** <sup>1</sup>H NMR titration curves of perchlorate complexes ( $1.48 \times 10^{-3}$  M) with tetrabutylammonium nitrate in acetone-*d*<sub>6</sub>.

pH dependent reversible binding of NO<sub>3</sub> anion by compound 1':



**Fig. S95** <sup>1</sup>H NMR spectra (400 MHz, DMSO-*d*<sub>6</sub>, 20 °C) of complex **1b** (49 mM) showing proton-induced reversible binding of nitrate anion. (a) <sup>1</sup>H NMR spectrum of complex **1b** in DMSO-*d*<sub>6</sub>. (b) After treating with 2.5 equiv. of KOH. (c) <sup>1</sup>H NMR spectrum of compound **1'** in DMSO-*d*<sub>6</sub>. (d) Acidification with trifluoroacetic acid retained its yellow color. (e) Compound **1'** in DMSO-*d*<sub>6</sub> in presence of trifluoroacetic acid. The star mark in green and red color represent the peaks for DMSO-*d*<sub>6</sub> and for trifluoroacetic acid.

**Table T1.** Crystallographic data and structure refinements for **6a** and **5<sub>2</sub>**.

	<b>6a</b>	<b>5<sub>2</sub></b>
Empirical formula	C <sub>48</sub> H <sub>49</sub> N <sub>5</sub> O <sub>9</sub>	C <sub>45</sub> H <sub>39</sub> N <sub>7</sub> O <sub>12</sub>
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 <sup>3</sup> )	2394.99(18)	3973 (4)
Z	2	4
Temperature	200(2) K	200(2) K
Wavelength (Å)	0.71073	0.71073
ρ <sub>cal</sub> Mg/m <sup>3</sup>	1.165	1.454
μ, mm <sup>-1</sup>	0.081	0.108
F (000)	888	1816
Independent reflection	2791	4927
Reflection used	15166	6537
R <sub>int</sub> value	0.0626	0.0554
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
GOOF	1.079	1.651
R indices[I > 2σ(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