Electronic Supplementary Material (ESI) for Dalton Transactions.

Boosting the salt recognition abilities of L-ornithine based multitopic molecular receptors by harnessing a double cooperative effect

by

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GENERAL INFORMATIONS

Unless specifically indicated, all other chemicals and reagents used in this study were purchased from commercial sources and used as received. 18-Aza-crown-6 was prepared according to literature procedure.[1] Compounds **1a**, **1c** and **S2** were prepared according to literature procedure.[2] Purification of products was performed using column chromatography on silica gel (Merck Kieselgel 60, 230-400 mesh) with mixtures of chloroform/methanol. Thin-layer chromatography (TLC) was performed on silica gel plates (Merck Kieselgel 60 F254).

^{1}H and ^{13}C NMR spectra used in the characterization of products were recorded on Varian Unity 200 spectrometer using a TMS (δ=0.00) or residual protonated solvent as internal standard. The following abbreviations are used to indicate the multiplicity: s - singlet; d - doublet; t - triplet; q - quartet; m - multiplet, b – broad signal.

High resolution mass spectra (HRMS) were measured on a Quattro LC Micromass unit using ESI technique.

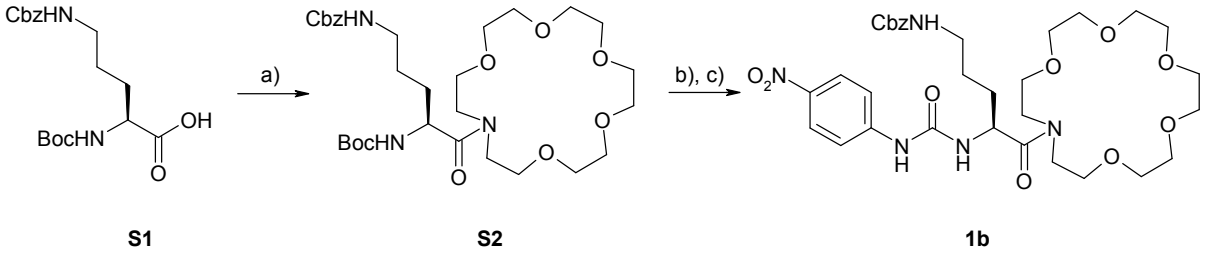
UV-vis analyses were performed using Thermo Spectronic Unicam UV500 Spectrophotometer.

Atomic absorption measurements were performed using Perkin Elmer AAnalyst 300 spectometer.

The conductance was measured using a conductance meter, Radiometer model CDM230, with a CDC241-9 conductivity cell.

SYNTHESIS

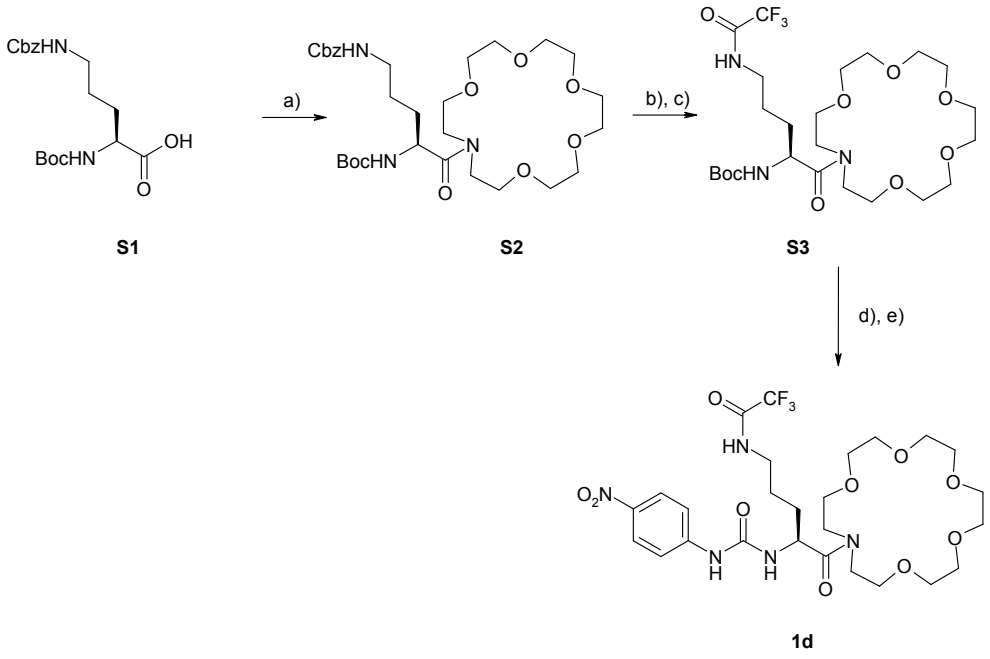
Receptor 1b



S1 **S2** **1b**

Scheme S1. Synthesis of receptor **1b**. *Reagents and conditions*: a) DCC, 1-aza-18-crown-6, CH_2Cl_2, 0˚C to r.t., 92%; b) TFA- CH_2Cl_2 (1:1), r.t., quantitative; c) 4-nitrophenyl isocyanate, THF, 73%.

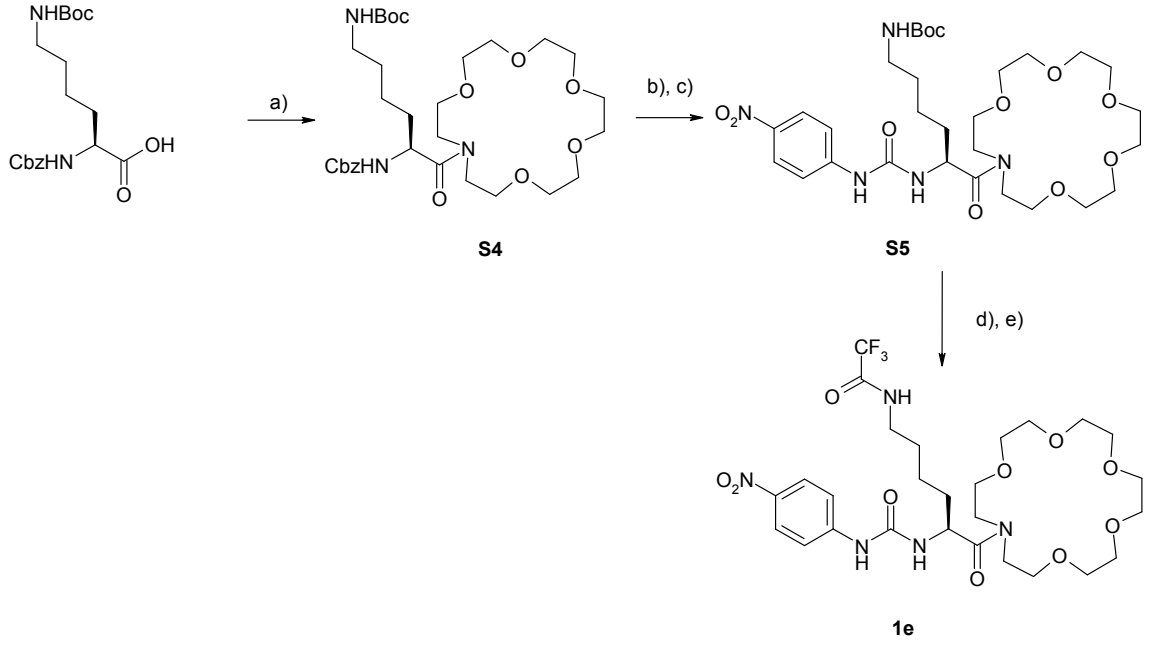
Receptor 1d



S1 **S2** **S3** **1d**

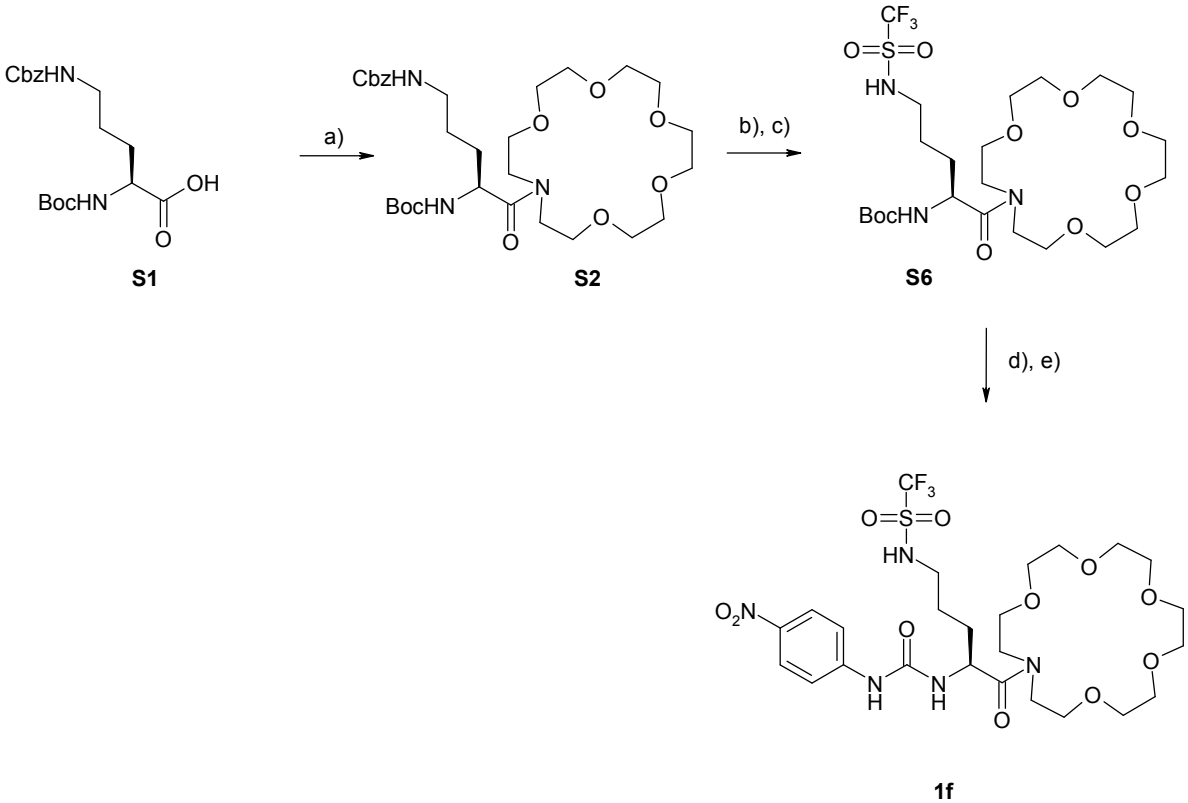
Scheme S2. Synthesis of receptor **1d**. *Reagents and conditions*: a) DCC, 1-aza-18-crown-6, CH_2Cl_2, 0˚C to r.t., 92%; b) H_2, Pd/C, MeOH-THF, r.t., quantitative; c) trifluoroacetyl anhydride, Et_3N, CH_2Cl_2, 0˚C to r.t., 72%; d) TFA- CH_2Cl_2 (1:1), r.t., quantitative; e) 4-nitrophenyl isocyanate, Et_3N, THF, 60%.

Receptor 1e



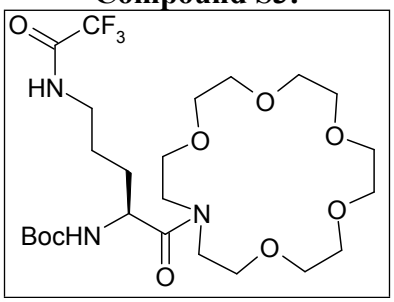
Scheme S3. Synthesis of receptor **1e**. *Reagents and conditions*: a) DCC, 1-aza-18-crown-6, CH_2Cl_2, 0˚C to r.t., 91%; b) H_2, Pd/C, MeOH-THF, r.t., quantitative; c) 4-nitrophenyl isocyanate, THF, 81%; d) TFA- CH_2Cl_2 (1:1), r.t., quantitative; e) trifluoroacetyl anhydride, Et_3N, CH_2Cl_2, 0˚C to r.t., 73%.

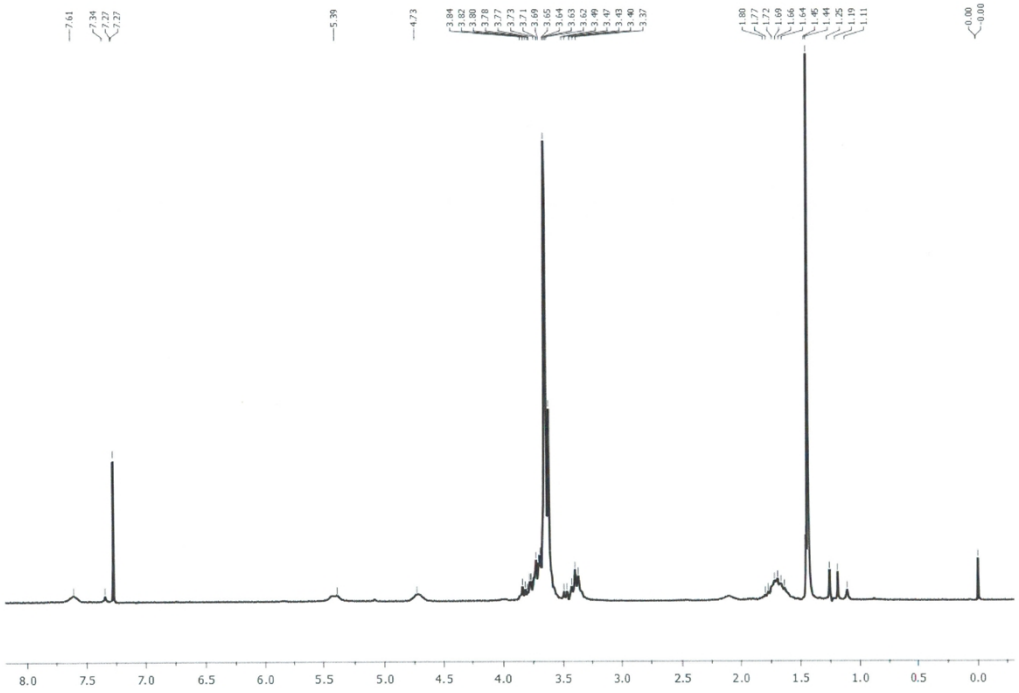
Receptor 1f



Scheme S4. Synthesis of receptor **1f**. *Reagents and conditions*: a) DCC, 1-aza-18-crown-6, CH_2Cl_2, 0˚C to r.t., 92%; b) H_2, Pd/C, MeOH-THF, r.t., quantitative; c) trifluoromethanesulfonyl chloride, Et_3N, CH_2Cl_2, 0˚C to r.t., 91%; d) TFA- CH_2Cl_2 (1:1), r.t., quantitative; e) 4-nitrophenyl isocyanate, Et_3N, THF, 72%.

Compound S3:


O
CF3
HN
O
O
O
O
N
O
BocHN
O


7.61
7.34
7.27
7.27
5.39
4.73
3.84
3.82
3.80
3.78
3.77
3.73
3.71
3.69
3.65
3.64
3.63
3.62
3.49
3.47
3.43
3.40
3.37
1.80
1.77
1.72
1.68
1.66
1.64
1.45
1.44
1.25
1.19
1.11
0.00
0.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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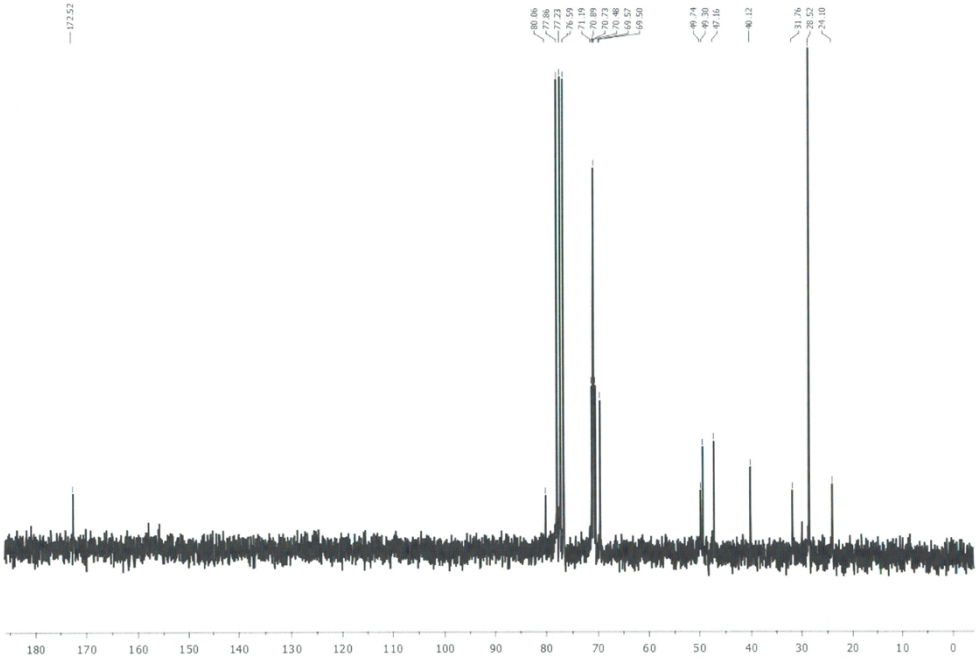
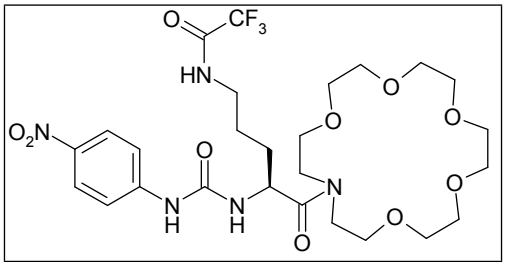
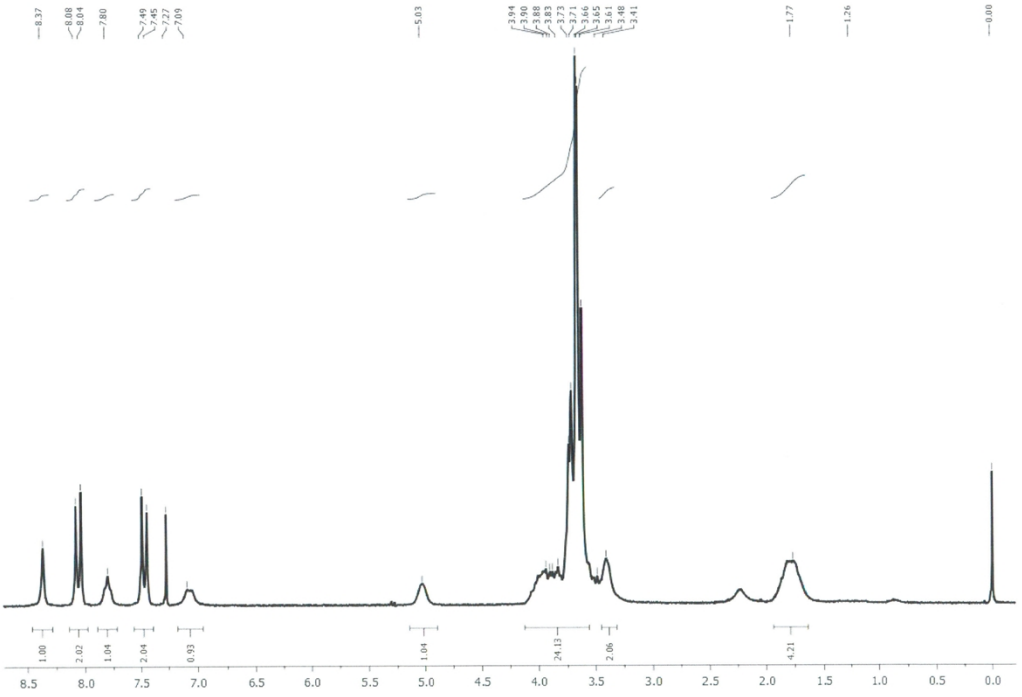
0.5
0.0


172.52
80.06
77.86
77.23
76.59
71.19
70.89
70.73
70.48
69.57
69.50
49.74
49.30
47.16
40.12
31.76
28.52
24.10
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Receptor 1d:


O
CF3
HN
O2N
O
N
H
N
H
O
N
O
O
O
O
O
O


8.37
8.08
8.04
7.80
7.49
7.46
7.27
7.09
5.03
3.94
3.90
3.88
3.83
3.73
3.71
3.66
3.65
3.61
3.48
3.41
1.77
1.26
0.00
1.00
2.02
1.04
2.04
0.93
1.04
24.13
2.06
4.21
8.5
8.0
7.5
7.0
6.5
6.0
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2.0
1.5
1.0
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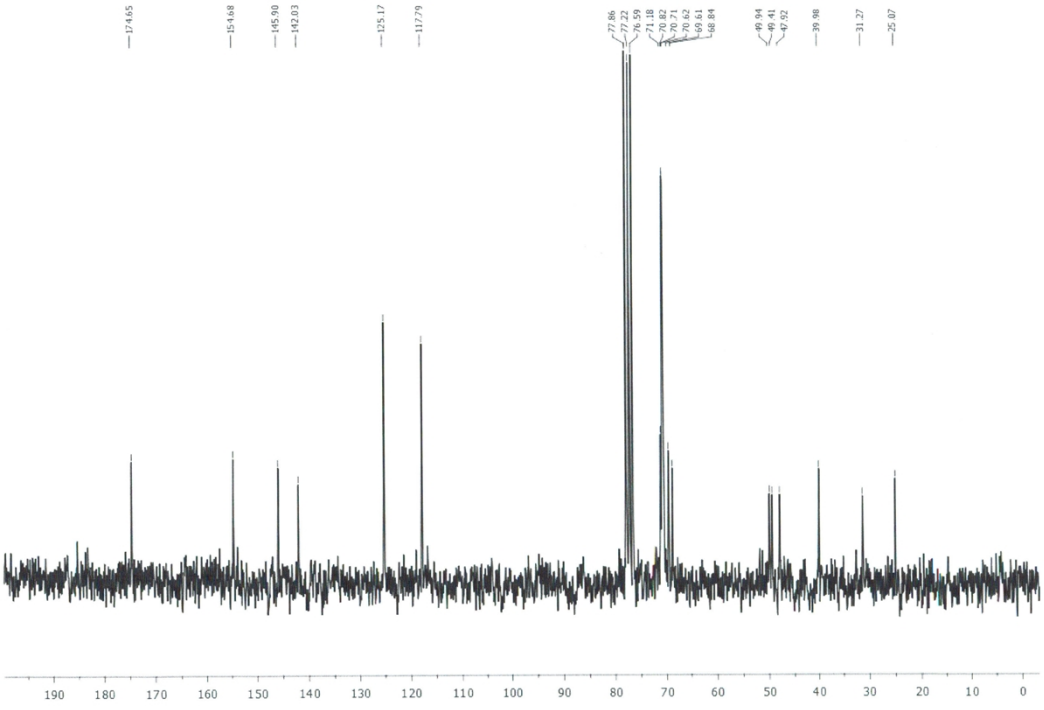
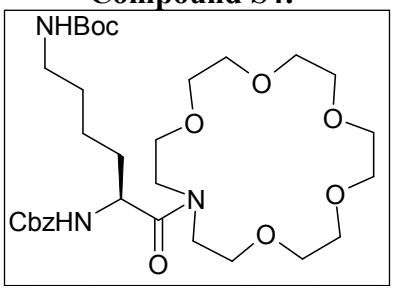
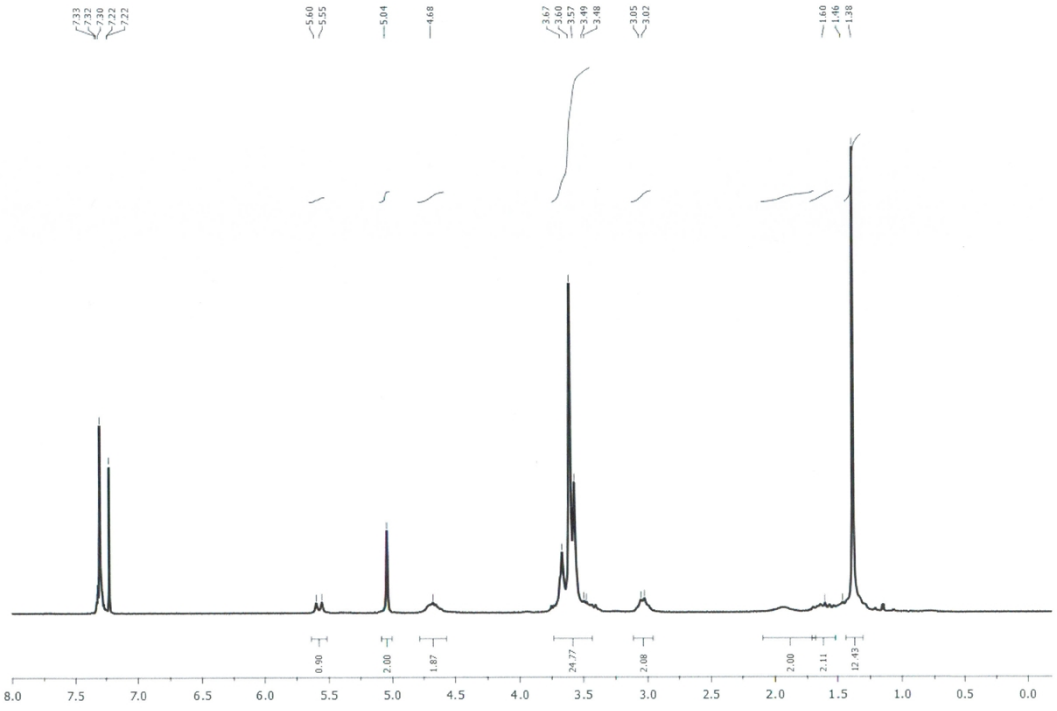
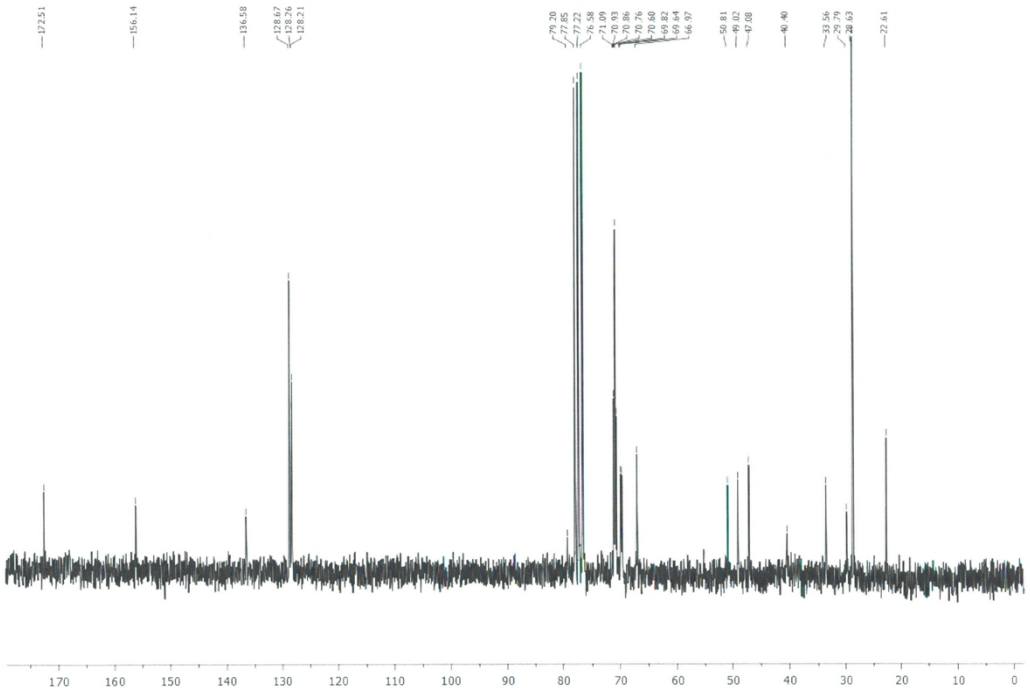

174.65
154.68
145.90
142.03
125.17
117.79
77.86
77.22
76.59
71.18
70.82
70.71
70.62
69.61
68.84
49.94
49.41
49.02
39.98
31.27
25.07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Compound S4:







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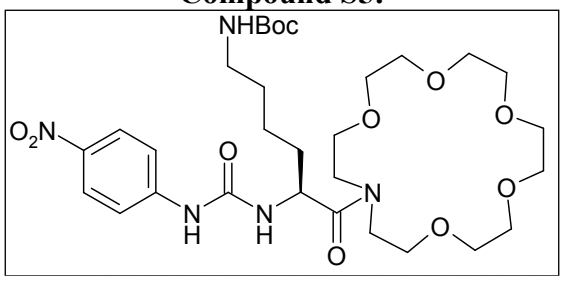
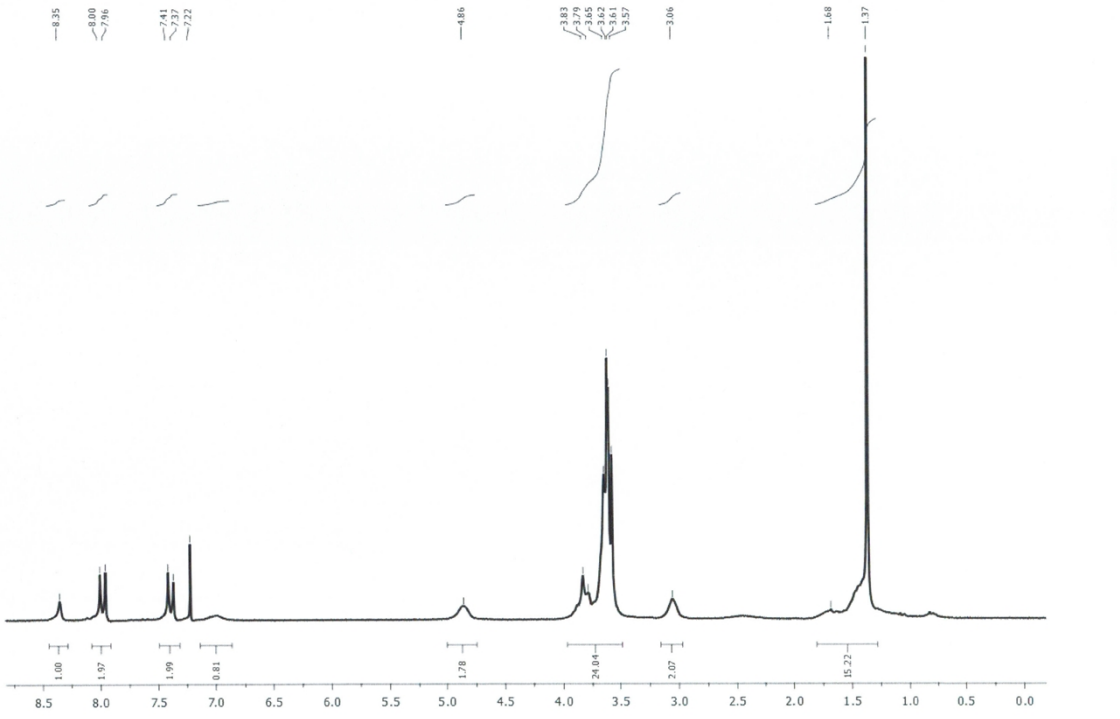
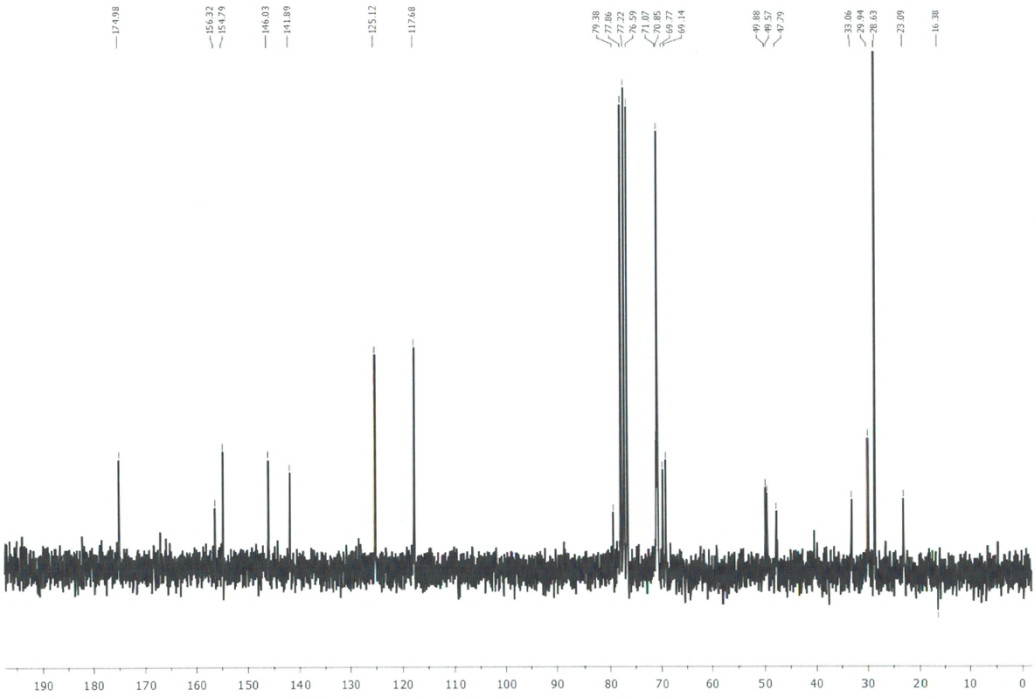

NHBoc
O_2N
O
N
H
N
H
O
O
O
O
O
N
O
O


8.35
8.00
7.96
7.41
7.37
7.22
4.86
3.83
3.79
3.65
3.62
3.61
3.57
3.06
1.68
1.37
1.00
1.97
1.99
0.81
1.78
24.04
2.07
15.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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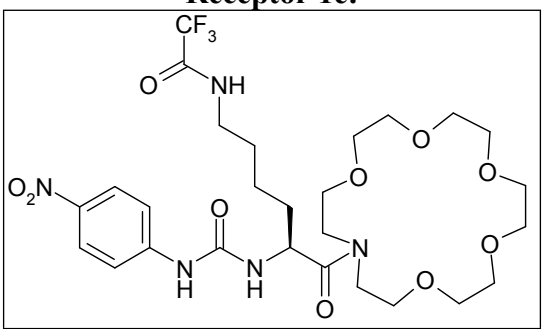
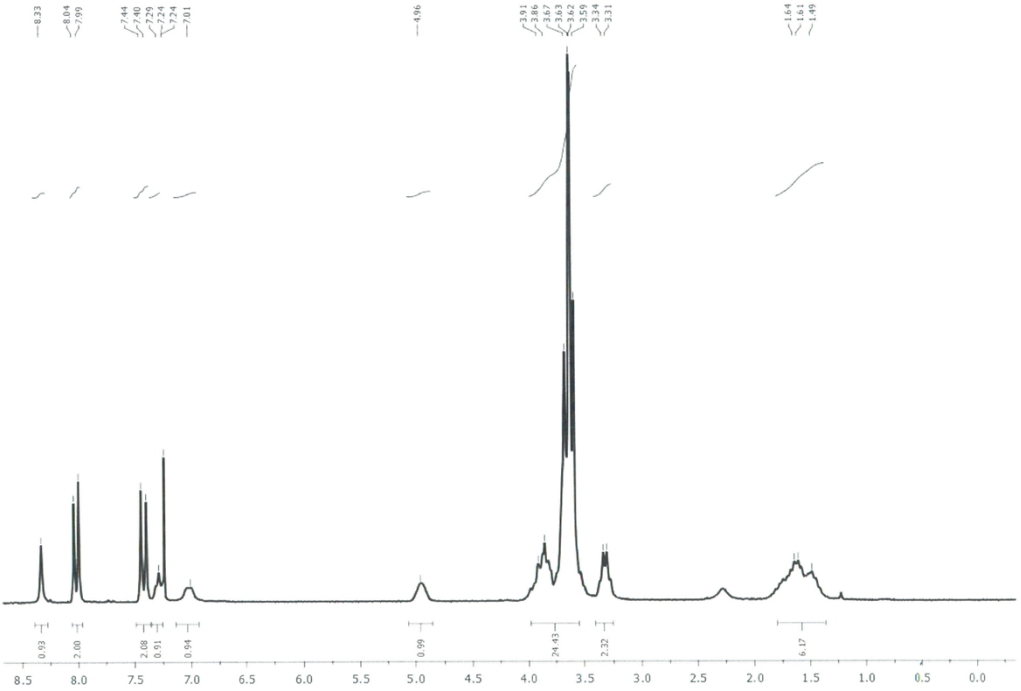
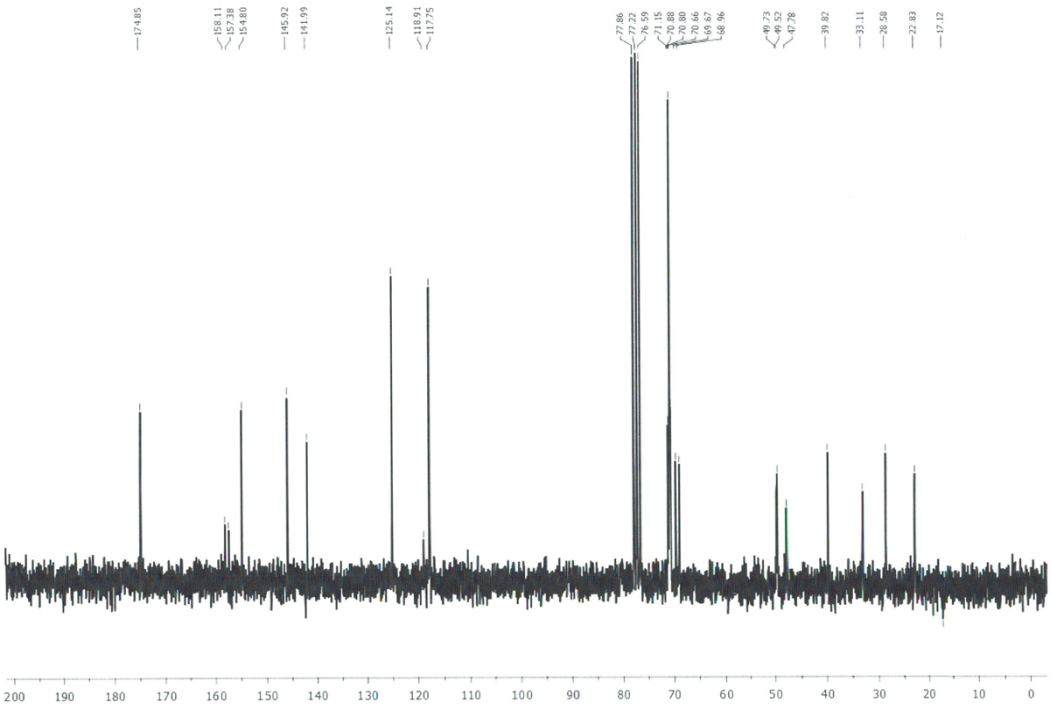
156.32
154.79
146.03
141.89
125.12
117.68
79.38
77.06
77.22
76.59
71.07
70.85
69.77
69.14
49.88
49.57
47.79
33.06
29.94
28.63
23.09
16.38
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Receptor 1e:


CF3
O
NH
O2N
O
N
H
N
H
O
O
O
O
O
O
N
O


8.33
8.04
7.99
7.44
7.40
7.29
7.24
7.24
7.01
4.96
3.91
3.86
3.67
3.63
3.62
3.59
3.34
3.31
1.64
1.61
1.49
0.93
2.00
2.08
0.91
0.94
0.99
24.43
2.32
6.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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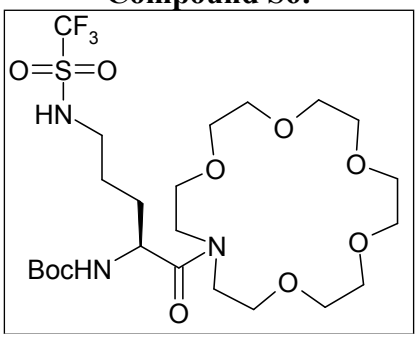
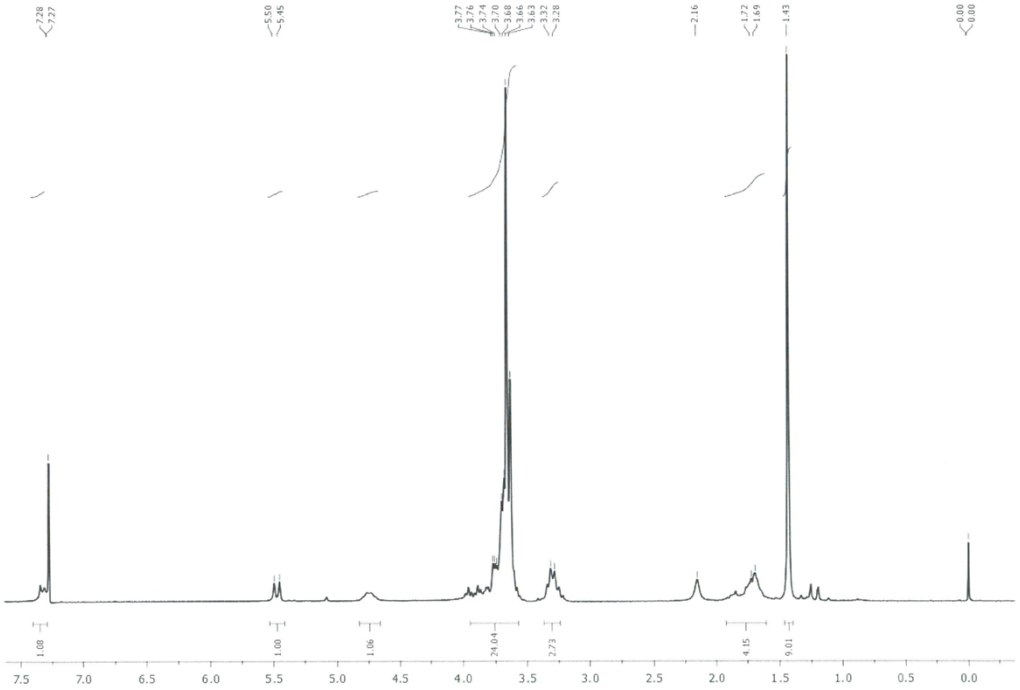
125.14
118.91
117.75
77.86
77.22
76.59
71.15
70.88
70.80
70.66
66.67
66.56
60.96
49.73
49.52
47.78
39.82
33.11
26.58
22.83
17.12
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Compound S6:


CF3
O=S=O
HN
BocHN
N
O
O
O
O
O
O
O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3.76
3.74
3.70
3.68
3.66
3.63
3.32
3.28
2.16
1.72
1.69
1.43
0.00
0.00
1.08
1.00
1.06
24.04
2.73
4.15
9.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
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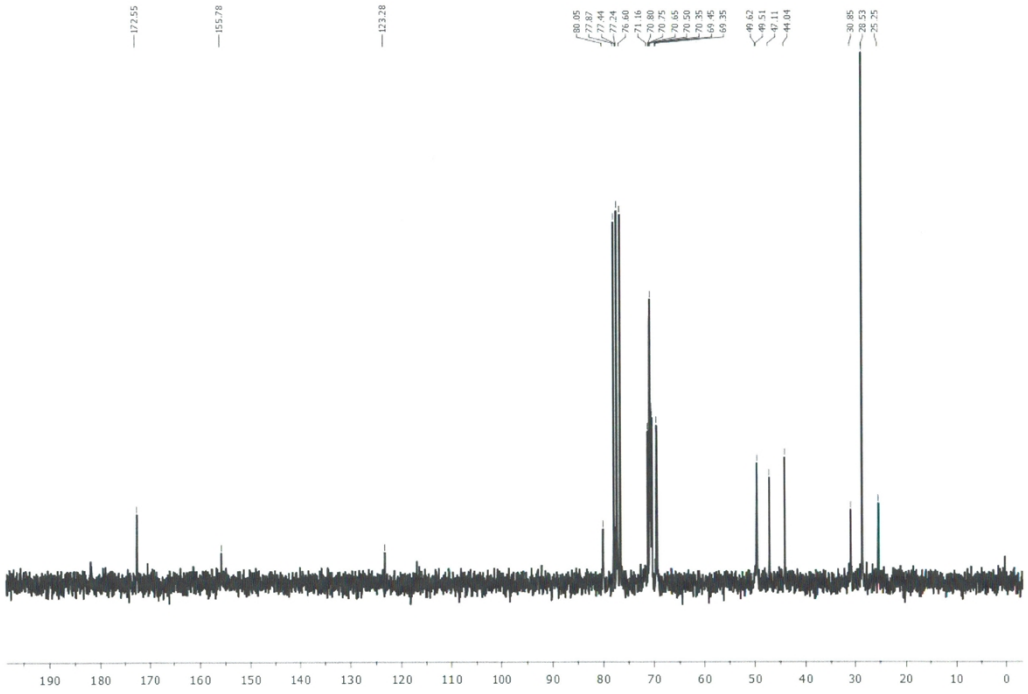
0.0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70.80
70.75
70.65
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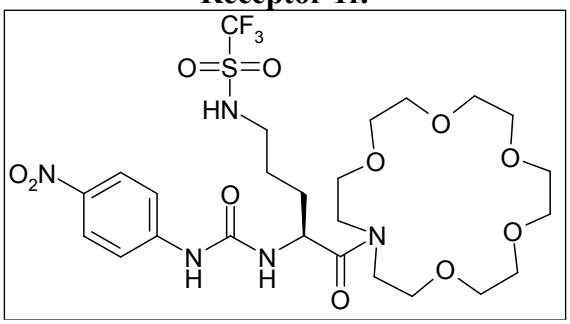
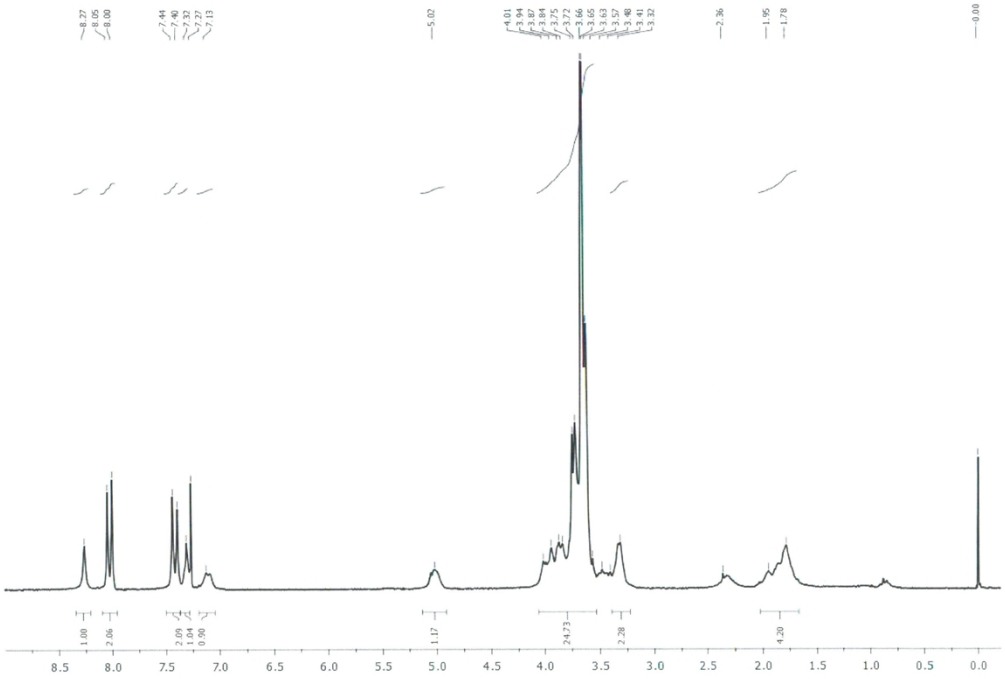
70.35
69.46
69.35
49.62
49.51
47.11
44.04
30.05
28.53
25.25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Receptor 1f:


CF3
O=S=O
HN
O2N
O
N
H
N
H
O
O
O
O
O
O
N
O
O


8.27
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8.00
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7.40
7.32
7.27
7.13
5.02
4.01
3.94
3.87
3.84
3.75
3.72
3.66
3.65
3.63
3.57
3.48
3.41
3.32
2.36
1.95
1.78
0.00
1.00
2.06
2.09
1.04
0.90
1.17
24.73
2.28
4.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
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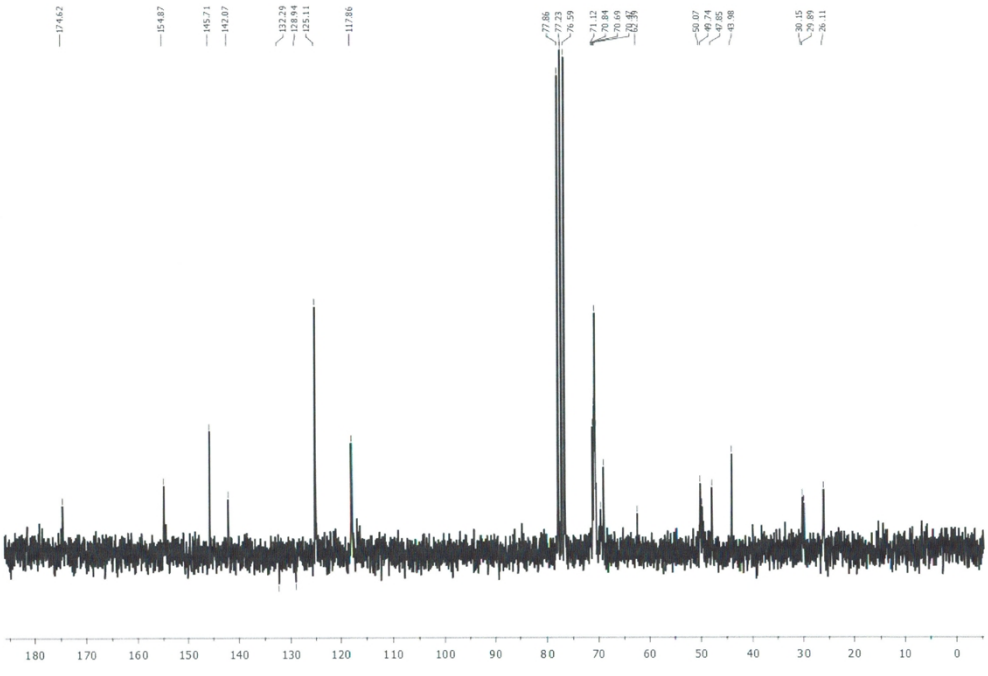
2.0
1.5
1.0
0.5
0.0


174.62
154.87
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132.29
128.94
125.11
117.86
77.86
77.23
76.59
71.12
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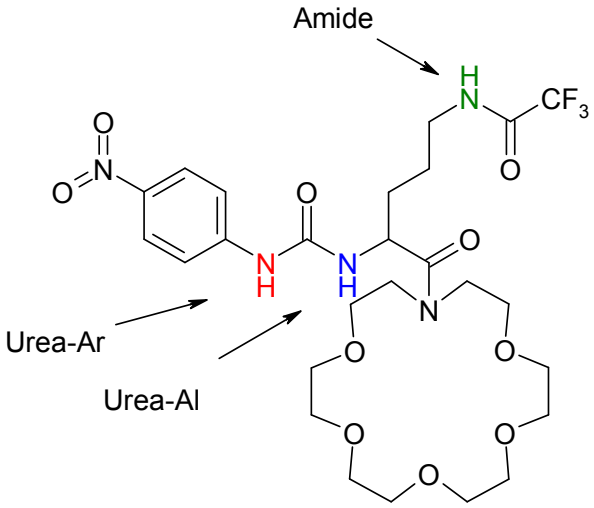
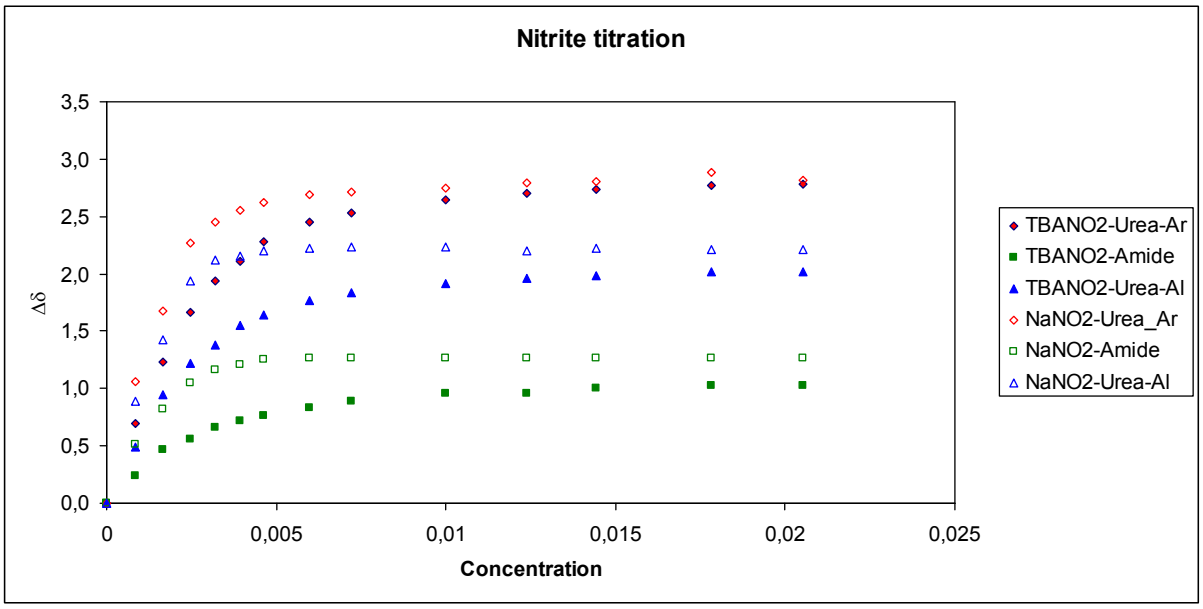
70.69
50.07
49.74
47.65
45.98
30.15
29.89
26.11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

NMR TITRATIONS

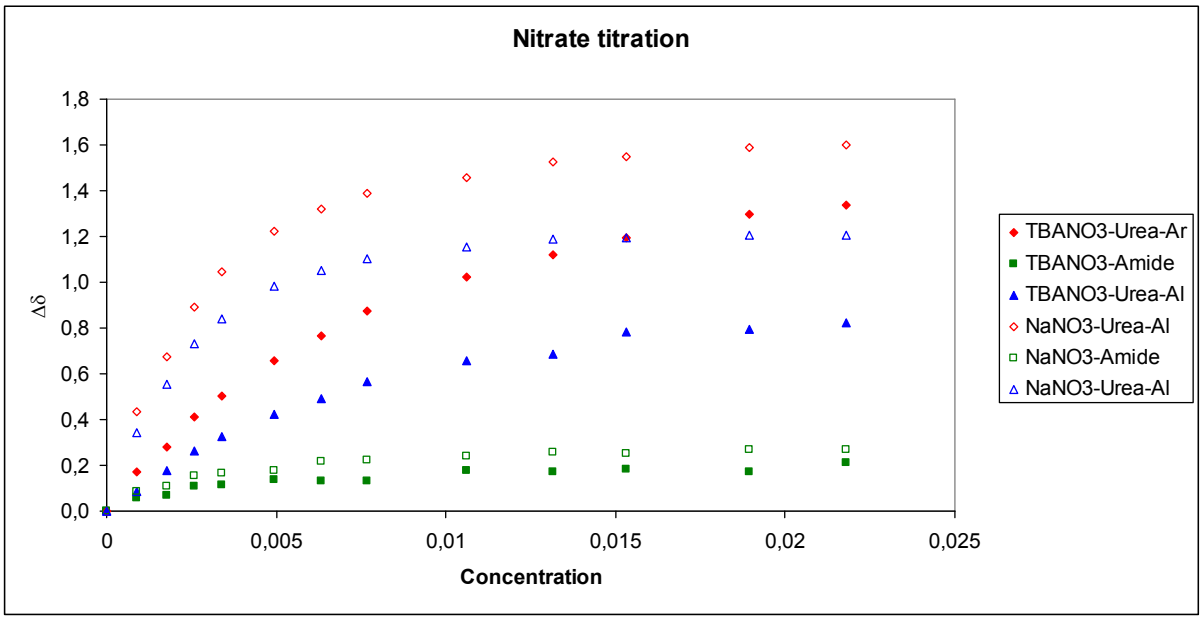
The ^{1}H NMR titrations were performed on a Varian UnityPlus 200MHz spectrometer, at 298K in CD_3CN. The anion TBA and cation PF6 salts were dried under high vacuum at 30−45 °C prior to use. In each case, a 500 µL of freshly prepared 2.7 mM solution of receptor **1** was added to a 5mm NMR tube. Where applicable the solution also contained 1 molar equivalent of sodium hexafluorophosphate. Small aliquots of 10-20 mM solution of tetrabutylammonium anion salts, containing **1** at 2.7 mM concentration, were added and a spectrum was acquired after each addition. Titration isotherms for NH protons were fitted to a 1:1 binding model using the HypNMR 2000 program. The 1:1 binding stoichiometries were verified by a Job plot analysis.

Selected binding isotherms:

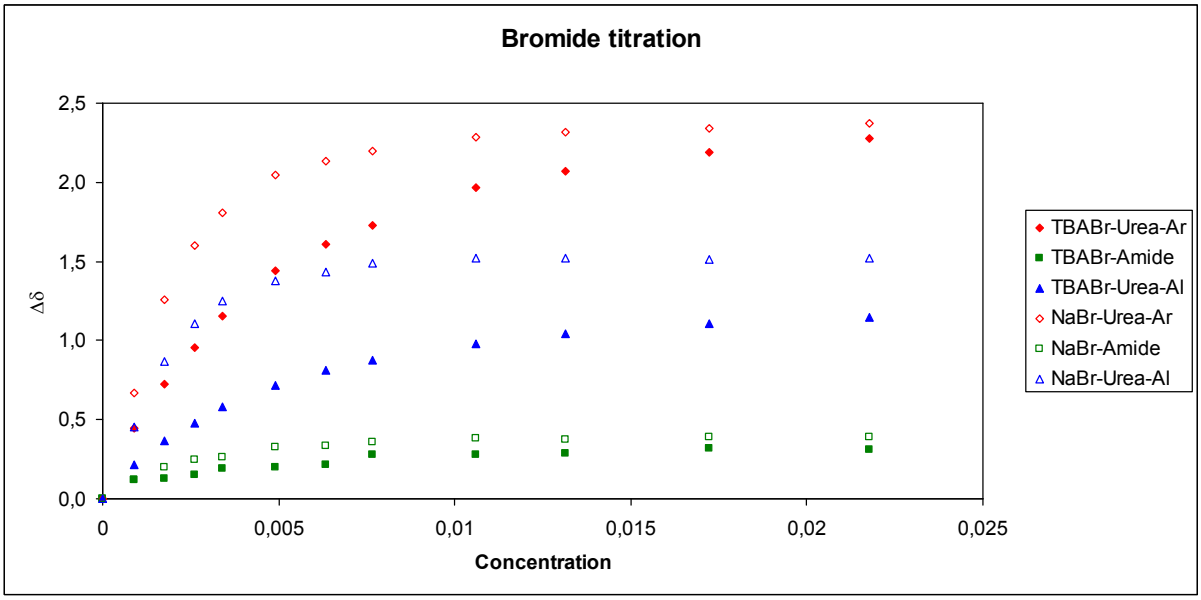




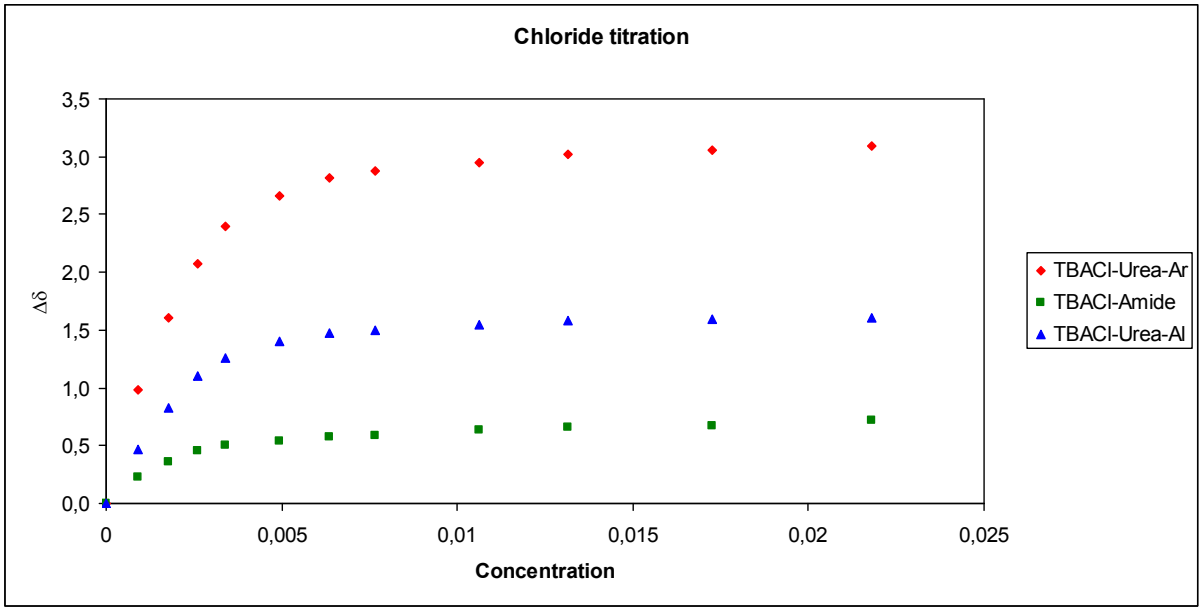
	K_{TBA}	K_{Na}	K_{Na}/K_{TBA}
NO_2^-	1 450	19 000	13,1



	K_{TBA}	K_{Na}	K_{Na}/K_{TBA}
NO_3^-	150	1 250	8,2



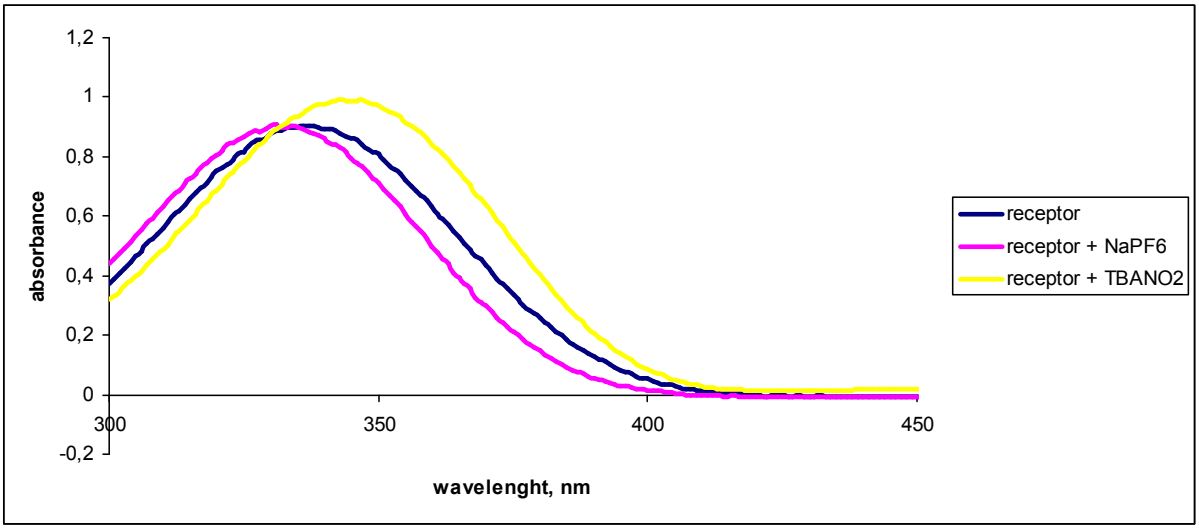
	K_{TBA}	K_{Na}	K_{Na}/K_{TBA}
Br^-	390	3 450	8,8



	K_{TBA}
Cl^-	3 100

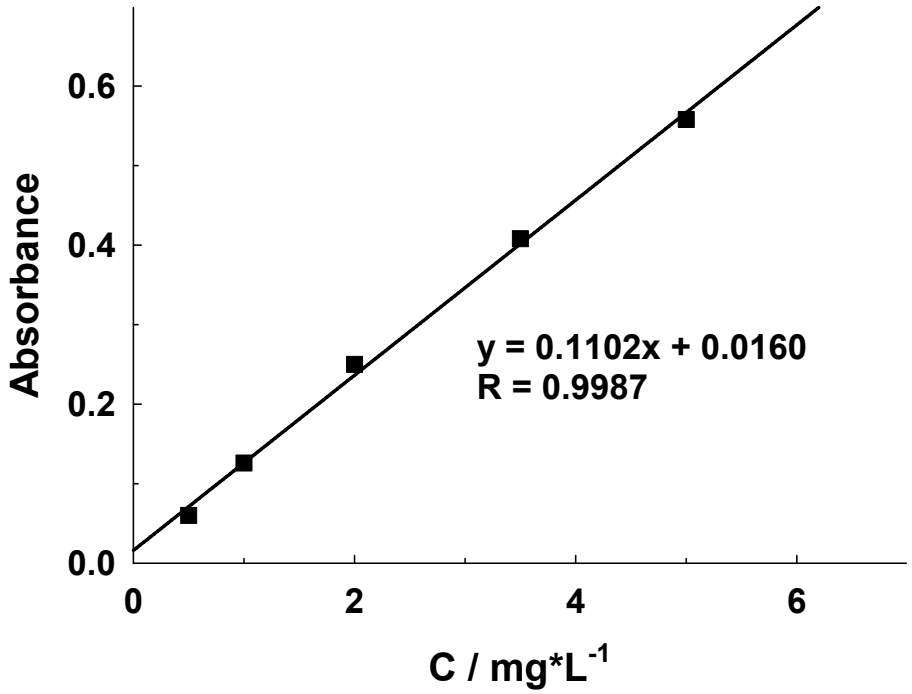
UV-VIS MEASUREMENTS

UV/vis spectra changes of receptor **1d** CH_3CN solution in the presence of excess of $NaPF_6$ and $TBANO_2$.



EXTRACTION and TRANSPORT EXPERIMENTS

The 1.5 mM aqueous solution of $NaNO_2$ or selected solid salts was extracted with 14 mM of $CHCl_3$ solution of **1d**. After phase separation a sample of organic phase was diluted with ethyl acetate and methanol (1:9:2 v:v:v, chloroform, ethyl acetate, methanol) and the content of extracted sodium cation was determined *via* atomic absorption spectroscopy. A calibration curve was generated using a standard solution of sodium hexafluorophosphate in chloroform/ ethyl acetate/methanol (1:9:2 v:v:v). The results are summarized in Table below.



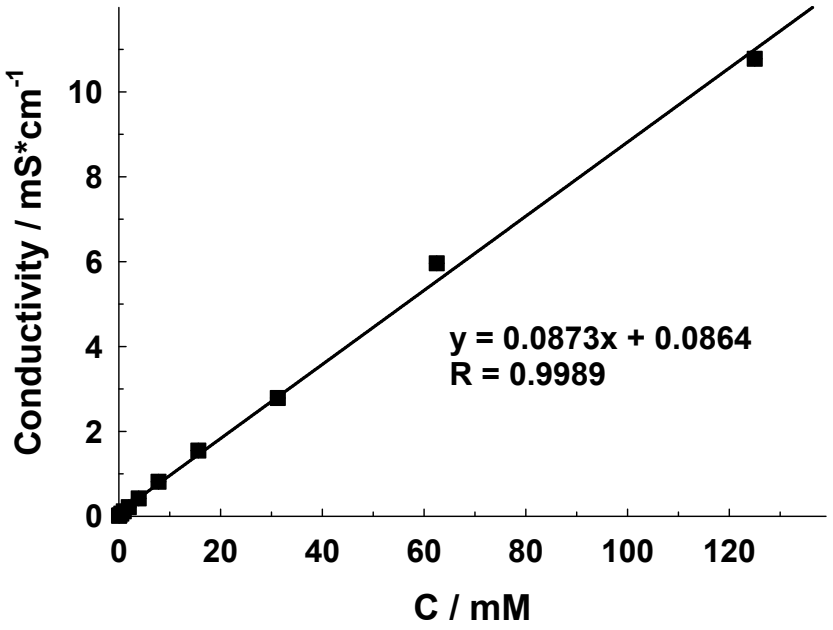
Calibration curve generated by measuring the peak intensities produced by $NaPF_6$ standard solutions.

Summary of extraction data.

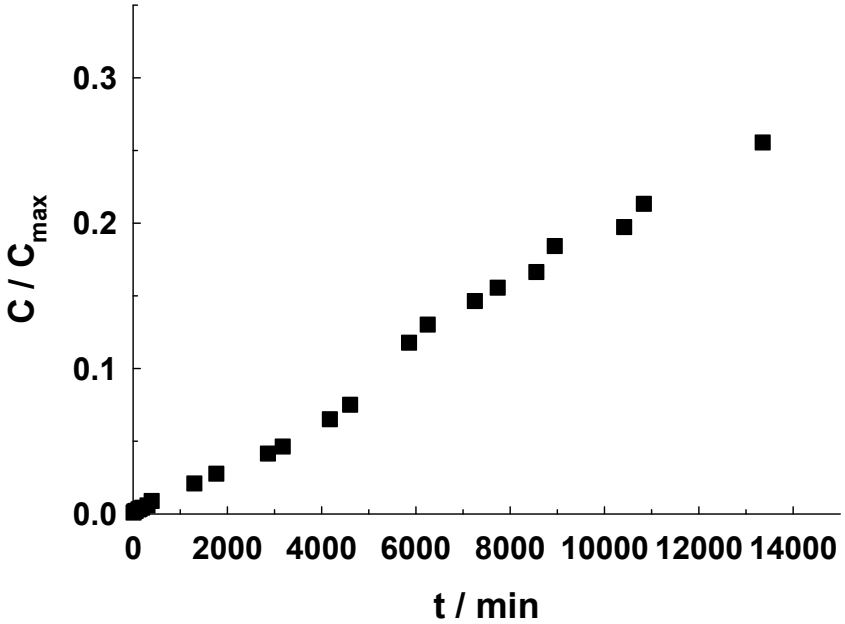
1d	1.5M $NaNO_2$	$NaNO_2$	NaBr	$NaNO_3$	NaCl
Extraction efficiency [%]	3.1	47.2	30.1	40.5	26.3

Membrane transport procedure.

Membrane transport experiments were performed with magnetic stirring in a conventional U-tube glass cell at room temperature. The feed phase was a 2 ml of 1M $NaNO_2$ salt; the membrane phase consisted of $3.9 \cdot 10^{-2}$M solution (3 ml) of **1d** in chloroform and the receiving phase consisted of 2 ml of distilled water. The salt concentration was determined by conductivity at appropriate intervals.



Calibration curve generated by measuring the conductivity produced by $NaNO_2$ standard solutions.



Concentration of sodium nitrite in receiving phase in funtion of time.

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[1] Maeda, H. Furuyoshi, S. Nakatsuji, Y. Okahara, M. *Bull. Chem. Soc. Jpn.*, **1983**, *56*, 212-218.

[2] a) Romański, J.; Trzaskowski, B.; Piątek, P. *Dalton Trans.* **2013**, *42*, 15271-15274; b) Romański, J. Piątek, P. *Chem. Commun.* **2012**, *48*, 11346-11348.