SUPPLEMENTARY INFORMATION

Bis-amidocarbazolyl urea receptor for short-chain dicarboxylate anions

M. Belén Jiménez,[a] Victoria Alcázar,[b] Rafael Peláez,[c] Francisca Sanz,[d] Ángel L. Fuentes de Arriba[a] and M. Cruz Caballero*[a]

[a] *Organic Chemistry Department, University of Salamanca, Plaza de los Caidos 1-5, 37008 Salamanca, Spain. Fax: +34 9232 94574; Tel: +34 9232 94481. Email: ccsa@usal.es*

[b] *Industrial Chemistry and Environmental Engineering Department, Politechnique University of Madrid, José Gutiérrez Abascal 2, 28006 Madrid, Spain.*

[c] *Pharmaceutical Chemistry Department, University of Salamanca, Campus Miguel de Unamuno, 37007 Salamanca, Spain.*

[d] *X-ray Diffraction Service, University of Salamanca, Plaza de los Caídos 1-5, 37008 Salamanca, Spain.*

TABLE OF CONTENTS: page

1. General information. S2

2. Structural determination of receptor 1 (Fig. S1-S6). S3
- Elemental analysis S3
- IR Spectra (Nujol) S3
- ^{1}H NMR spectrum (DMSO-d_6) S4
- ^{13}C NMR spectrum (DMSO-d_6) S4
- ROESY S5
- Asignation of NMR signals. Table S6

3. Job´s plot of complexes (Fig. S7). S7

4. Titration spectra (Fig. S8-S10). S8

5. Binding curves of titrations for receptor 1·malonate and receptor 1·succinate complexes (Fig. S11-S12). S10

6. ORTEP diagrams and X-ray crystal structure data (Fig. S13-S14). S12

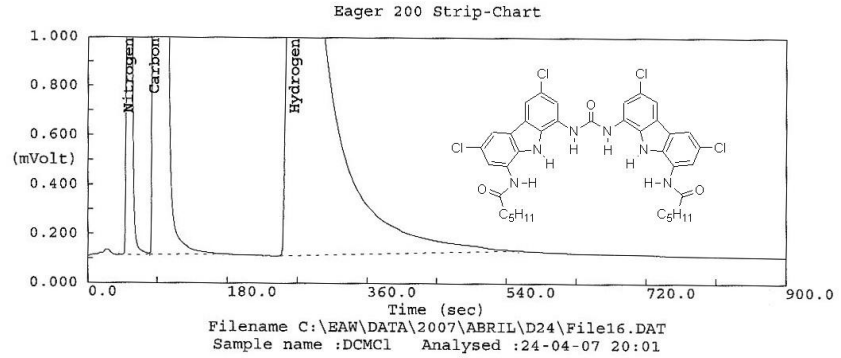
7. View of figure 6 (Fig. S15). S15

1. General information.

Melting points were measured with a Stuart Scientific SM3P capillary apparatus. IR spectra were recorded with a Bonem MB-100-FT IR spectrometer. NMR spectra were recorded at room temperature with Bruker Mod.WP-200-SY, Varian Mod. Mercury VS 2000 or Bruker Advance DRX spectrometers in deuterated chloroform or dimethylsulfoxide. *J* values are reported in Hertzs and chemical shifts in ppm with the solvent signal as internal standard. Electrospray ionization high resolution mass spectra (ESI-HRMS) were determined with an Applied Biosystems QSTAR XL spectrometer. Elemental analysis were recorded on an elemental analyzer Carlo Erba EA 1108 model. Suitable single crystals of both complexes were mounted on glass fibre for data collection on a Bruker Kappa APEX II CCD diffractometer. Data for oxalate complex were collected at 298 K using CuK_{α} radiation (λ = 1.54178 Å) and data for malonate complex were collected at 373 K using MoK_{α} radiation (λ = 0.71073 Å). Structure solution, refinement and data output were carried out with the SHELXTL and SIR2004 program package.

2. Structural determination of receptor 1.

Figure S1. Elemental analysis.



Eager 200 Report

S/W version : 1.06
Operator ID : W.D. Company Name : Carlo Erba Instr
Method Name : Sulfanilamide & Carbon Method File : CHNS.MTH
Analysed : 24-04-07 20:01 Printed : 24/04/2007 20:16

Sample ID : DCMCl (# 16) Channel : E.A. Channel A
Analysis Type : UnkNown (Area) Sample weight : 1.6899
Chromatogram : C:\EAW\DATA\2007\ABRIL\D24\FILE16.DAT

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	Element %	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	10.9041	53	349436	FU	14.471440	.187642E+07
Carbon	58.2032	87	5056845	FU	1.000000	.513794E+07
Hydrogen	4.6992	266	1204898	RS	4.196907	.151727E+08
Totals	73.8065		6611179			

Figure S2.- IR spectrum (Nujol).

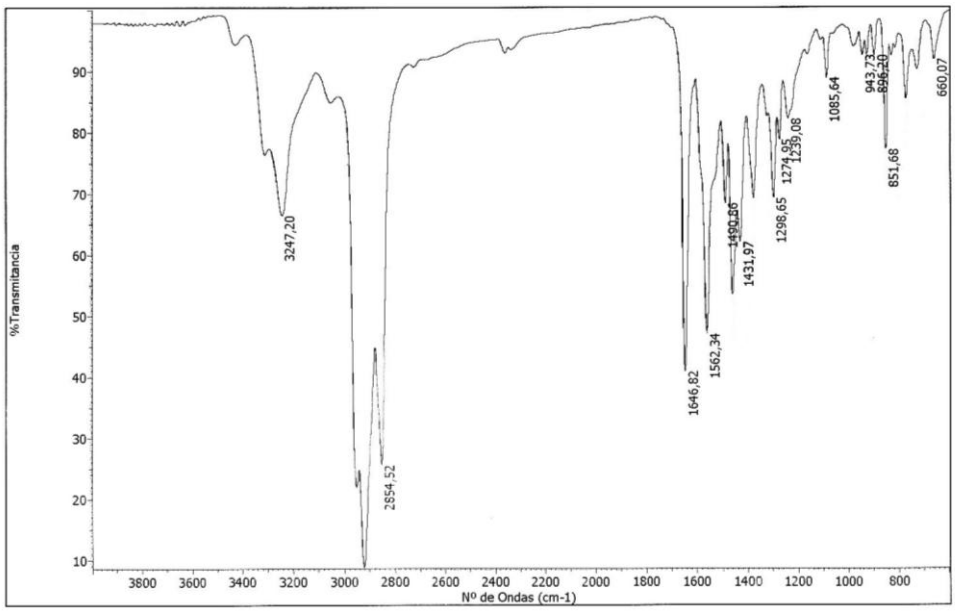


Figure S3. ^{1}H NMR spectrum (200MHz, DMSO-d_6).

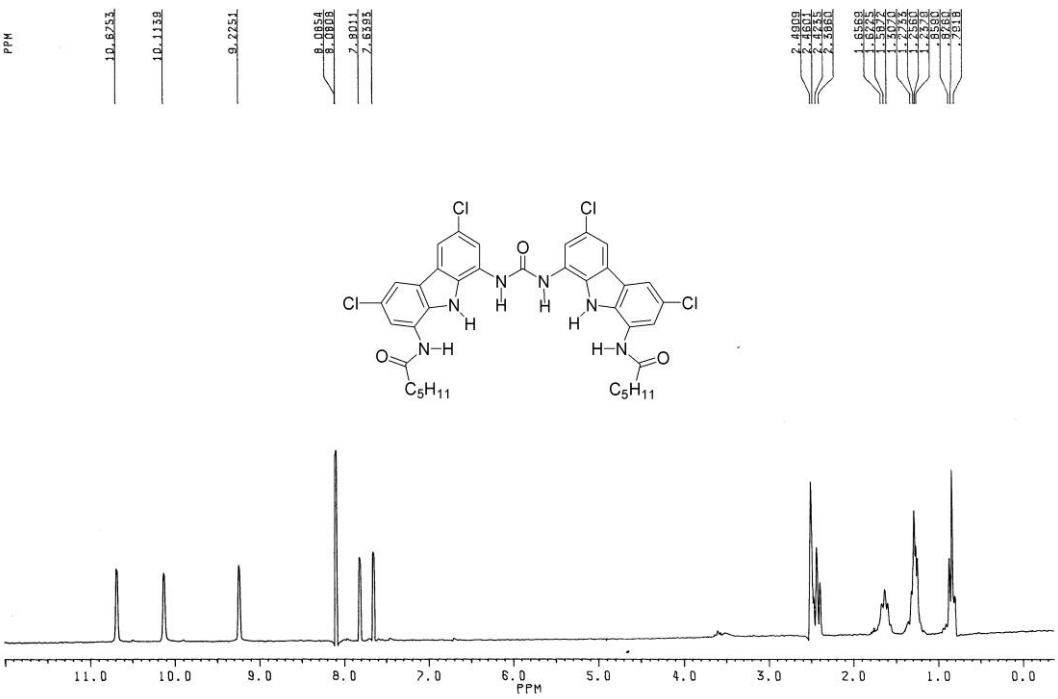


Figure S4. ^{13}C NMR spectrum (50MHz, DMSO-d_6).

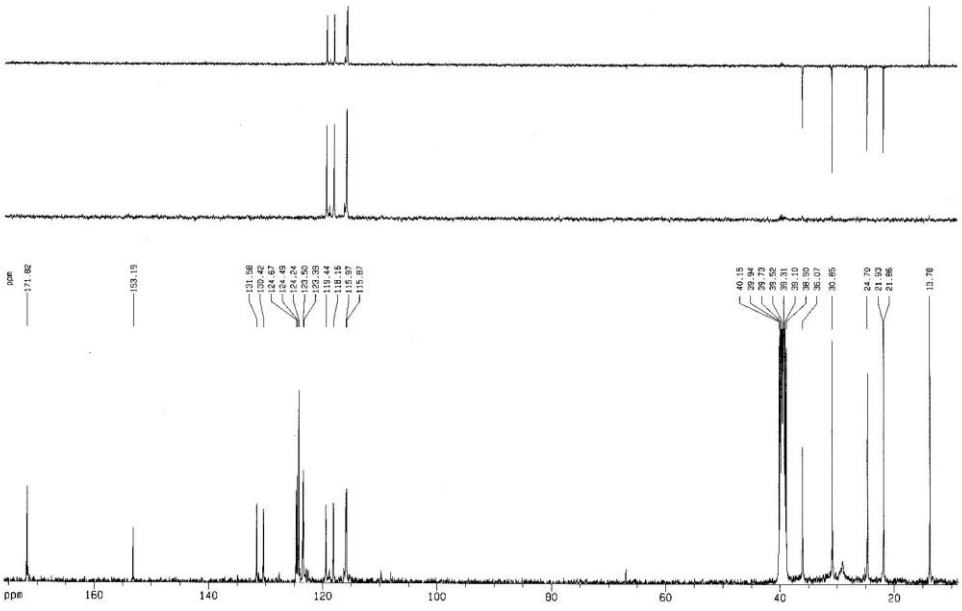


Figure S5. ROESY.

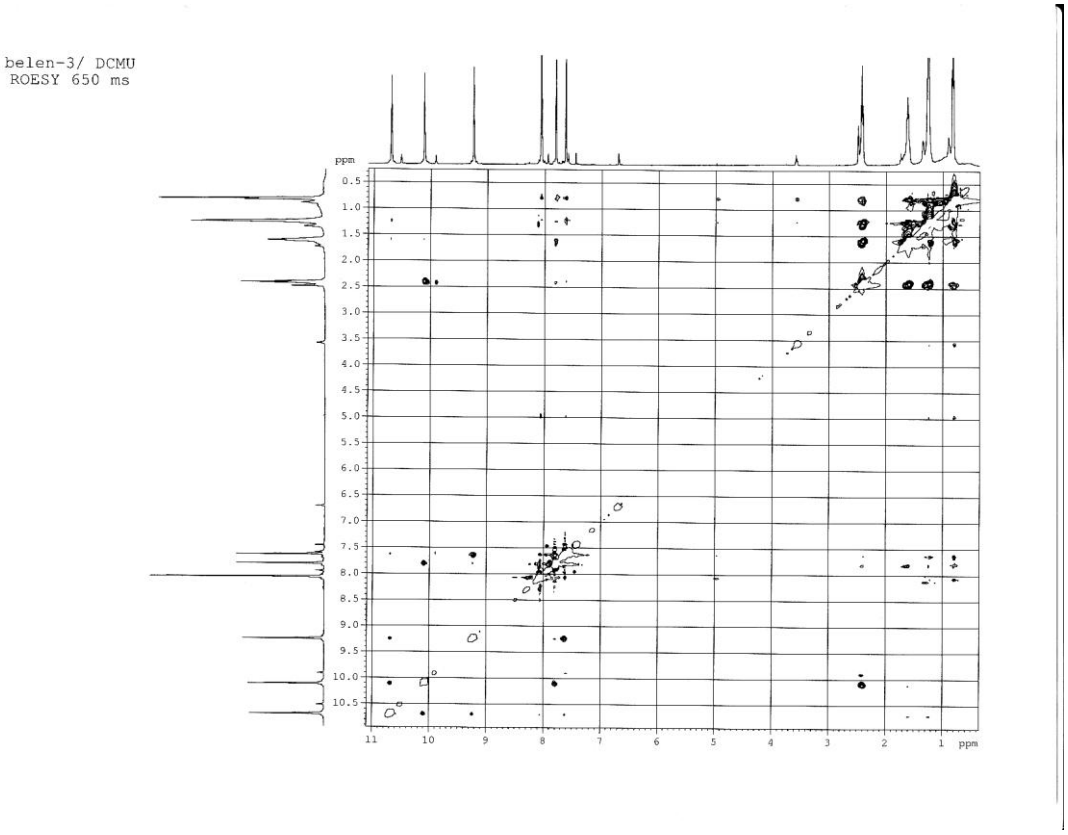


Figure S6. Assignation of ^{1}H and ^{13}C NMR signals.

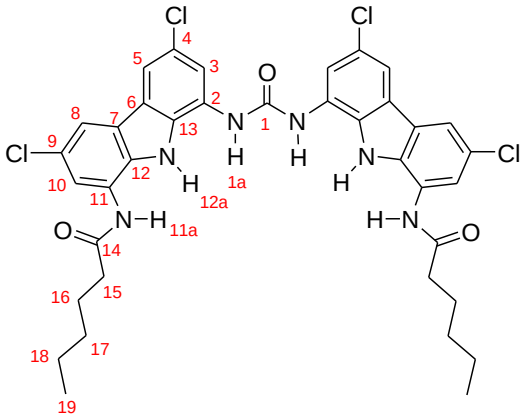


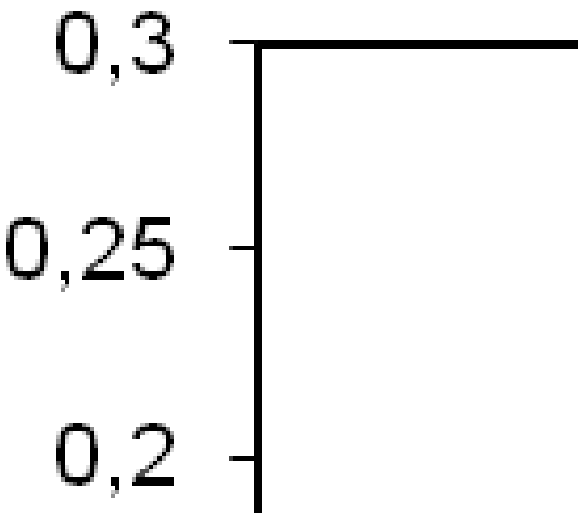
Table: Assignation of the signals of ^{1}H NMR and ^{13}C NMR spectra for receptor **1** (DMSO-d_6).

Receptor 1					
Position[a]	**δ_H (ppm)**	**δ_C (ppm)**	**Position**[a]	**δ_H (ppm)**	**δ_C (ppm)**
1		153.2 s			
2		124.7 s	**14**		171.8 s
3	7.64 (s)	119.4 d	**15**	2.42 (t)	36.1 t
4		130.4 s	**16**	1.62 (m)	24.7 t
5	8.09 (s)	116.0 d	**17**	1.26 (m)	30.9 t
6		124.2 s	**18**	1.26 (m)	21.9 t
7		124.2 s	**19**	0.82 (t)	13.8 c
8	8.08 (s)	116.0 d	**N*H* 1a**	9.23 (s)	
9		123.4 s	**N*H* 12a**	10.68 (s)	
10	7.80 (s)	118.2 d	**N*H* 11a**	10.11 (s)	
11		124.5 s			
12		130.4 s			
13		131.6 s			

[a] The numbering is not systematic. urea N*H* =1a, carbazole N*H* =12a, amide N*H* =11a

3. Job´s plot of complexes.

Figure S7. Job´s plots of receptor 1·oxalate, receptor 1·malonate and receptor 1·succinate, measured by ^{1}H NMR.



4. Titration spectra.

Figure S8. Titration spectra of receptor **1** with **oxalate** diTBA salt, in DMSO-d_6.

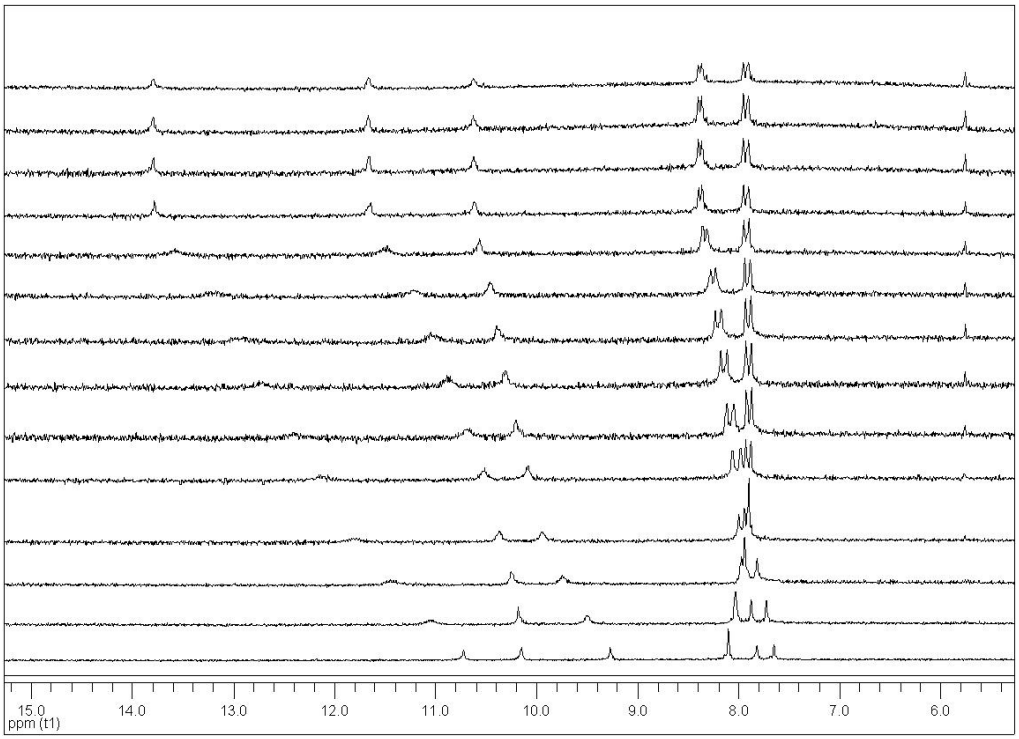


Figure S9. Titration spectra of receptor **1** with **malonate** diTBA salt, in DMSO-d_6.

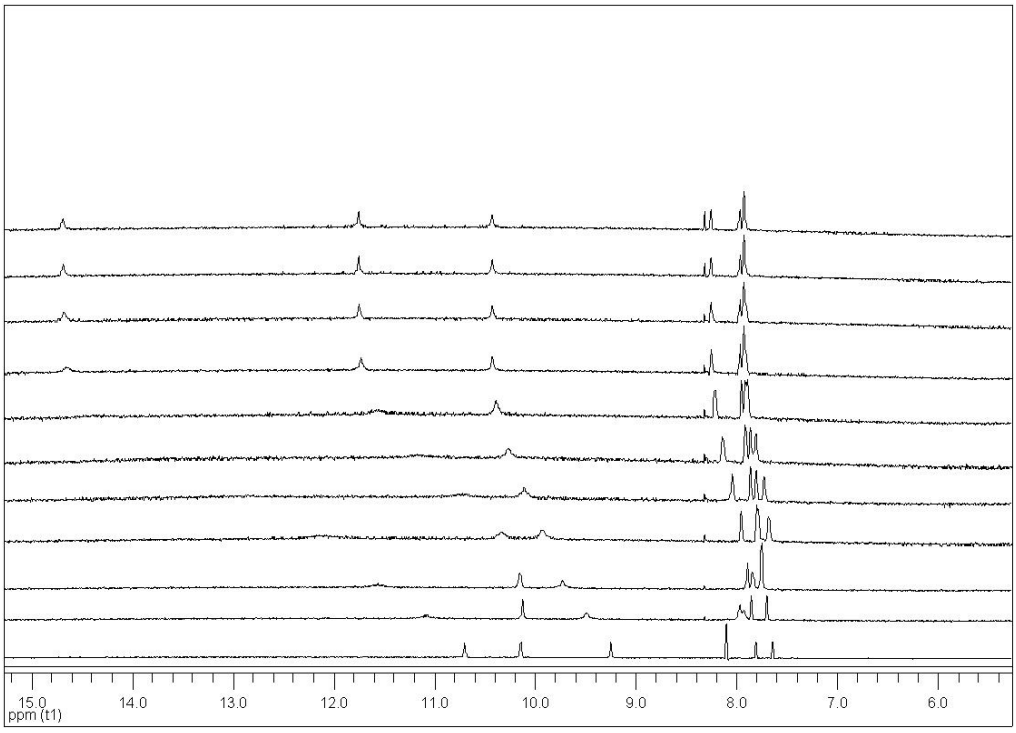
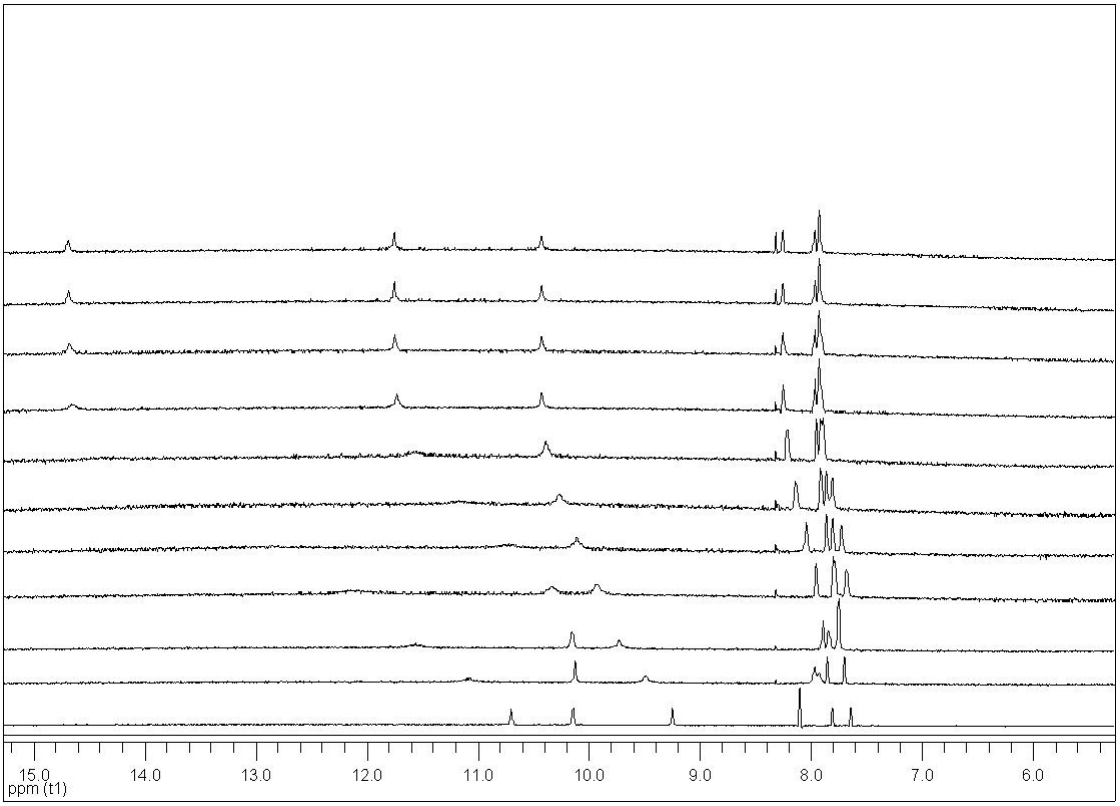


Figure S10. Titration spectra of receptor **1** with **succinate** diTBA salt, in DMSO-d_6



5. Binding curves of titrations between receptor 1 and ditetrabutylammonium malonate and succinate.

Figure S11. Binding curve of titration for receptor**1·malonate** ditetrabutylammonium salt.

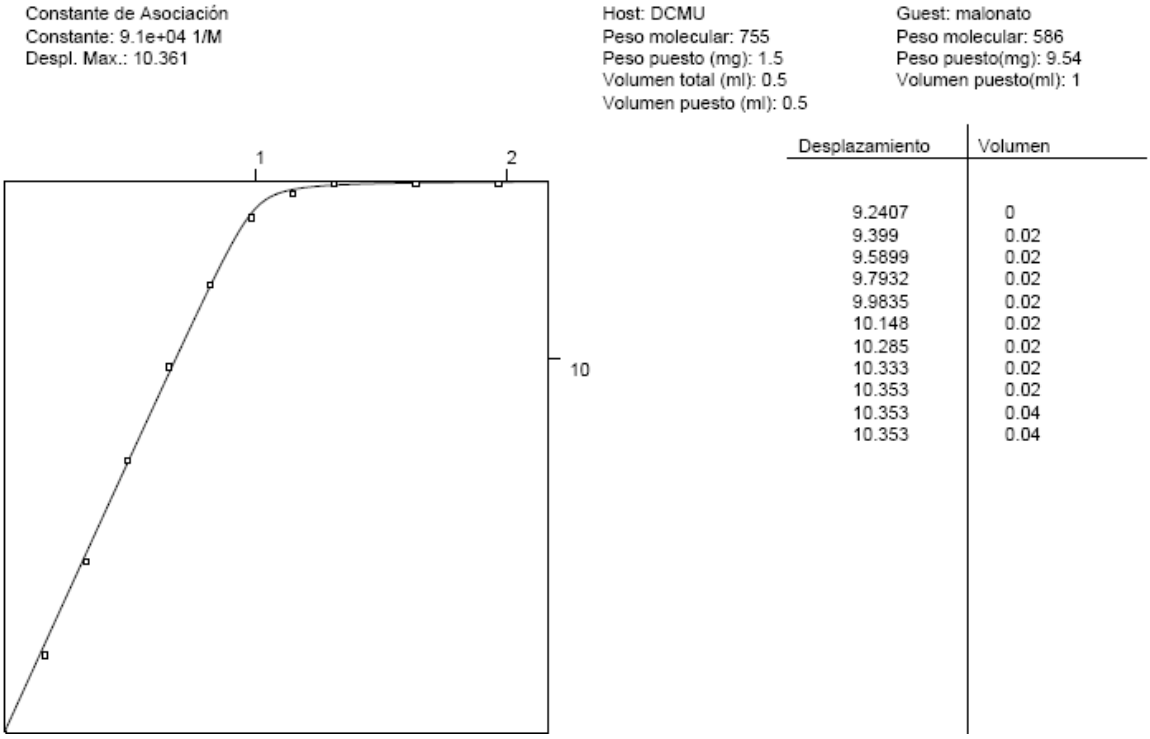
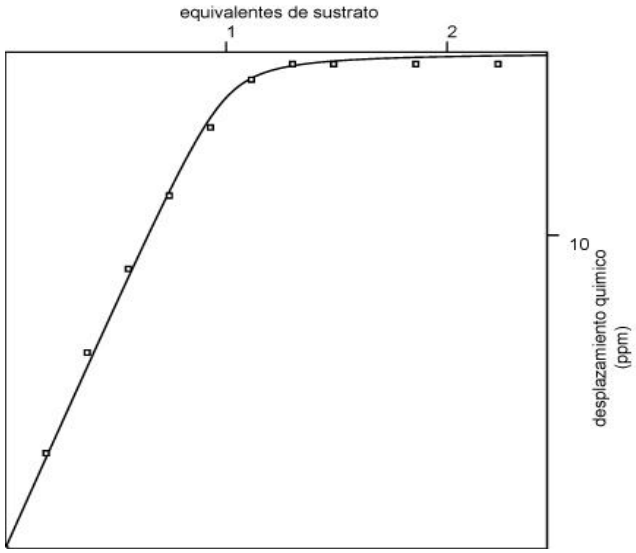


Figure S12. Binding curve of titration for receptor **1·succinate** ditetrabutylammonium salt.



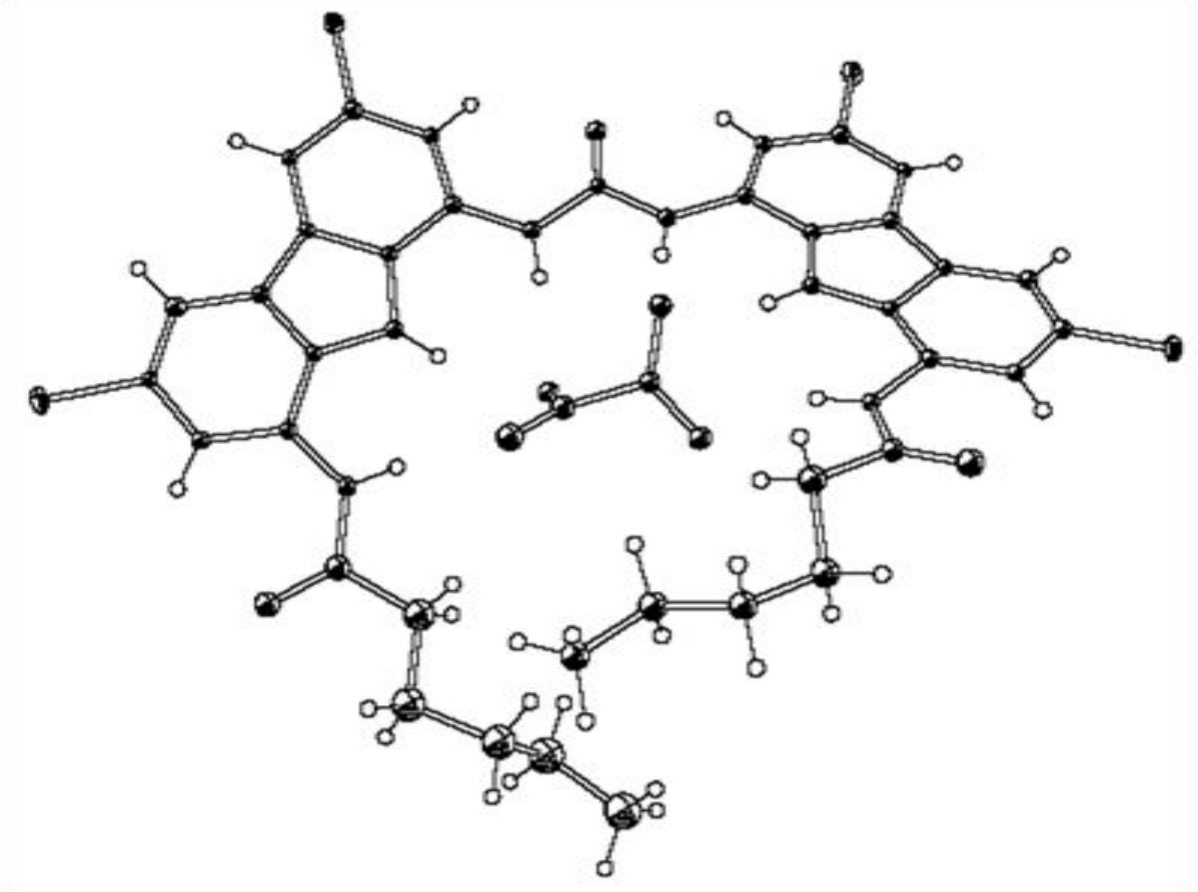
Host: dicarbazol monourea
Peso molecular: 755
Peso puesto (mg): 1.3
Volumen total (ml): 0.5
Volumen puesto (ml): 0.5

Guest: succinato
Peso molecular: 600
Peso puesto(mg): 9.6
Volumen puesto(ml): 1

Desplazamiento	Volumen
9.2367	0
9.4696	0.02
9.7144	0.02
9.9177	0.02
10.096	0.02
10.262	0.02
10.378	0.02
10.416	0.02
10.416	0.02
10.416	0.04
10.416	0.04

6. ORTEP diagrams and X-ray crystal structure data.

Figure S13a. ORTEP diagram and X-ray crystal structure data for the receptor **1**·diTBA oxalate complex. Ditetrabutylammonium counter-cations have been omitted for clarity.



Crystal data: $C_{37}H_{36}N_6O_3Cl_4$ x $2(C_{16}H_{36}N)$ x C_2O_4, M = 1327.45, monoclinic, space group $P2_1/c$ (nº 14), a = 27.892(3) Å, b = 17.1340(18) Å, c = 30.726(3) Å, $\alpha = \gamma = 90$ °, $\beta =$ 94.856(5) °, V = 14631(3) Å3, Z = 8, Dc = 1.205 Mg/m^3, m = (Mo-K_α) = 0.218 mm^{-1}, F(000) = 5712. 26060 reflections were collected at $0.73 \leq 2\theta \leq 22.12$ and merged to give 18233 unique reflections (R_{int} = 0.0475), of which 15610 with $I > 2\sigma(I)$ were considered to be observed. Final values are R1 = 0.1454, *w*R2 = 0.3771, GOF = 1.056 max/min residual electron density 0.608 and -0.899 e. $Å^{-3}$. **CCDC 837724** contains the Supplementary crystallographic data for this complex. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre http://www.ccdc.cam.ac.uk/data_request/cif.

Figure S13b. X-ray crystal structure of receptor **1**·diTBA oxalate complex, showing the ditetrabutylammonium counter-cations.

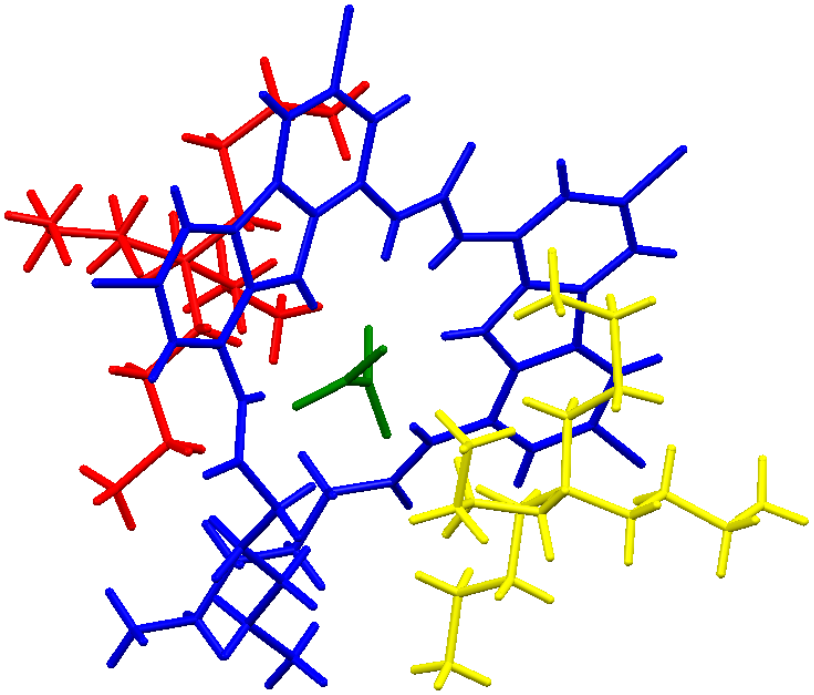
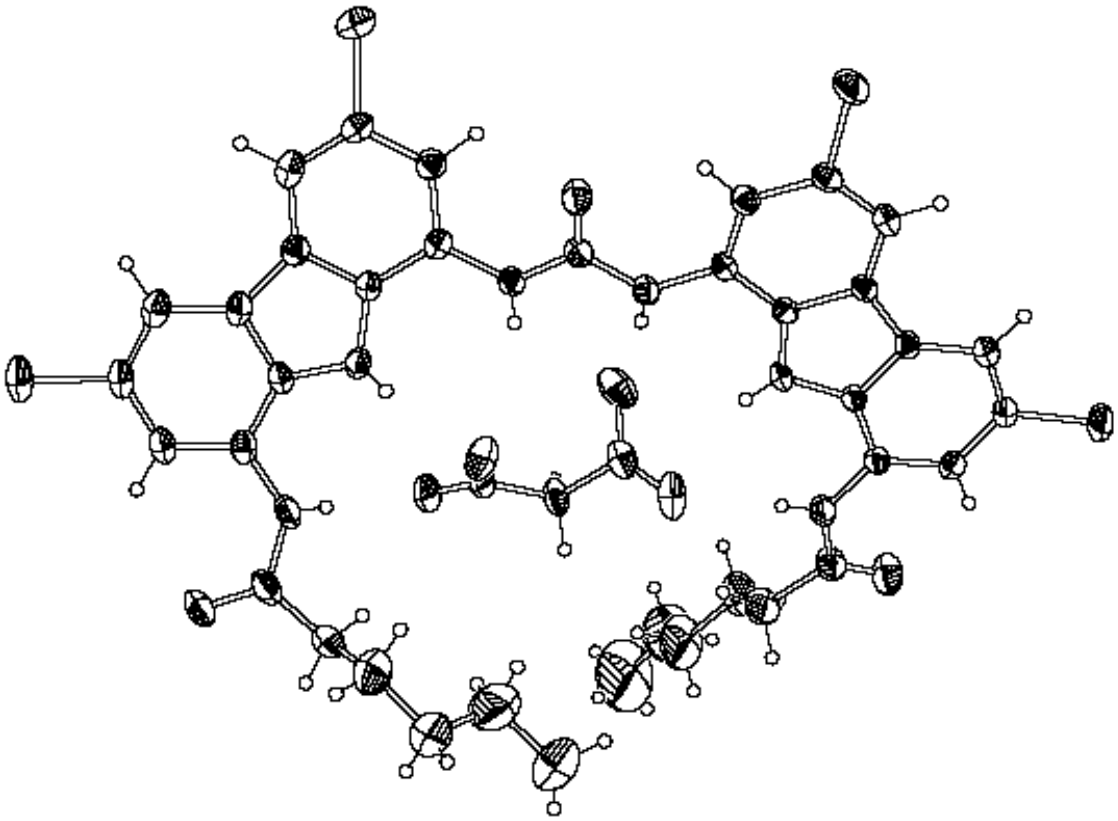


Figure S14. ORTEP diagram and X-ray crystal structure data for the receptor **1**·diTBA malonate complex. Ditetrabutylammonium counter-cations have been omitted for clarity.



Crystal data: $C_{37}H_{36}N_6O_3Cl_4$ x 2($C_{16}H_{36}N$) x $C_3H_2O_4$, M = 1341.48, monoclinic, space group $P2_1/n$ (nº 14), a = 18.8187(3) Å, b = 16.0647(3) Å, c = 26.4451(3) $Å^{-3}$, $\alpha = \gamma = 90°$, β = 93.0620(10) °, V = 7983.4(2) Å3, Z = 4, Dc = 1.116 Mg/m^3, m = (Cu-K_α) = 1.754 mm^{-1}, F(000) = 2888. 17057 reflections were collected at $2.81 \leq 2\theta \leq 48.05$ and merged to give 6410 unique reflections (R_{int} = 0.0190), of which 4879 with $I > 2\sigma(I)$ were considered to be observed. Final values are R1 = 0.0715, *w*R2 = 0.2180, GOF = 1.046, max/min residual electron density 1.049 and -0.317 e. $Å^{-3}$. **CCDC 837725** contains the Supplementary crystallographic data for this complex. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre http://www.ccdc.cam.ac.uk/data_request/cif.

7. View of figure 6.

Figure S15. View of minimized structure of complex between receptor **1** and diTBA succinate, showing five H-bonds (from 2.65 to 2.78 Å). One carbazole NH of the receptor and one carboxylate oxygen of the guest do not participate in the H-bond network.

Complementary to figure 6 in the text.