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Synthesis of Thiosemicarbazone Derivatives of Benzo-15-crown-5 and Their Anion Recognition Properties

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*A series of thiosemicarbazone derivatives of benzo-15-crown-5 were synthesized efficiently at room temperature using hydrogenchloride acid (HCl) as catalyst. Their anion recognition properties of **a**, **b** and **c** were studied, the result show they exhibit highly selective binding and sensing of F^- , $MeCO_2^-$ and $n-C_3H_7CO_2^-$ in CH_3CN ($F^- > n-C_3H_7CO_2^- > MeCO_2^- \gg Cl^-, Br^-$ and I^-). Especially receptor **c** shows different UV-Vis spectrum of F^- from $MeCO_2^-$ and $C_3H_7CO_2^-$, in addition to the color of the solution change from colorless to yellow upon the addition of F^- , these two points make it suitable to be used as colorimetric anion sensor to identify fluoride anion from other halide anions and carboxylate anions by naked-eye. The connection between receptor and anion is by hydrogen bonding interactions, the binding ratio is 1:1, which have been confirmed by UV-vis inspection spectra in CH_3CN and ¹HMR in DMSO-*d*₆.*

Keywords Anion recognition; synthesis; thiosemicarbazone derivatives of Benzo-15-crown-5

INTRODUCTION

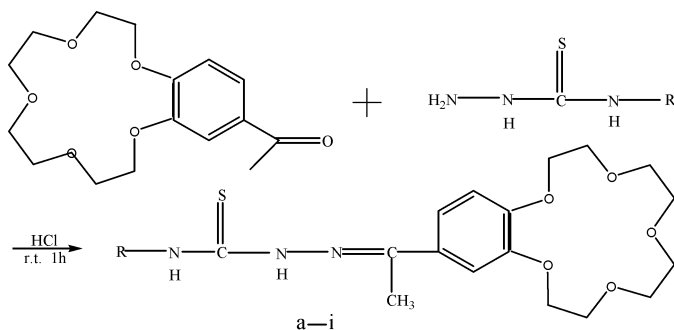
The design and synthesis of efficient artificial receptors for selective binding of biologically or environmentally important anionic species is an important work with many applications such as sensors, homogeneous catalysis, and membrane transport¹. It is noteworthy that

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thioureas are good hydrogen-bond donors and are excellent receptors for Y-shaped anions such as carboxylate through the formation of two hydrogen bonds^{1,2,3}. However, during our study, we find the title compounds exhibit specific UV-Vis spectrum of fluoride anion, a sphere anion, yet this substrate is crucial for biological processes, and the color of the solutions change from colorless to yellow, which show that they can be used as a powerful naked-eye sensor for fluoride anion. Herein, we report the synthesis and anion recognition properties of these highly selective and sensitive anion receptors to continue and develop our previous work on the synthesis and crystal structure of crown ether.^{4,5}



SCHEME 1

RESULTS AND DISCUSSION

Synthesis of **a-i**

The synthetic route is shown in Scheme 1. In general, thiosemicarbazones are prepared under refluxing solvent for several hours, however, in this reaction, we find the 4-acetyl benzo-15-crown-5 react with thiosemicarbazides using concentrated hydrogenchloride (HCl) as catalyst at room temperature to afford the target products almost in quantitative yield within an hour, in addition, the products, which need only a simple washing with 10ml ethanol three times, can be used to characterize (Table I). In order to find out the most ideal reaction condition, we selected **a** as an example to study the influence of catalyst on this reaction. Then two experiments were carried out at room temperature with AcOH as catalyst and without any catalyst separately. After 12h, the reaction catalyzed by AcOH began, but it did not go to completion after 24h and gave the product in 11% yield, the reaction without any catalyst did not take place at all after 24 h. Apparently, the HCl is an efficient catalyst for this reaction.

TABLE I The Reaction Time, Yield, and Melting Points of a-i

Entry	R	Time/yield (%)		M.p. (°)
a	C ₆ H ₅	1 h	98	114
b	4-FC ₆ H ₄	1 h	100	166–168
c	4-CH ₃ CH ₂ OC ₆ H ₄	1 h	100	156–158
d	2-CH ₃ OC ₆ H ₄	1 h	96	108–110
e	2-CH ₃ C ₆ H ₄	1 h	99	160–161
f	3-CH ₃ C ₆ H ₄	1 h	94	156–158
g	4-CH ₃ C ₆ H ₄	1 h	90	168–170
h	2-ClC ₆ H ₄	1 h	95	182–183
i	4-ClC ₆ H ₄	1 h	85	165–167

UV-vis Absorption Spectra

The effect of various anions as N(C₄H₉)₄⁺ salt on absorption spectrum of **c** (2.0×10^{-5} M) was examined in CH₃CN, and result are shown in Figure1. Spectrum (c) is measured in the absence of anions, where **c** has a UV-vis spectrum with λ_{max} at 323nm, which can be assigned as an intramolecular charge transfer absorption band. As shown in spectrum (Cl⁻), (Br⁻) and (I⁻), **c** does not show any obvious spectral change even in the presence of 50 equiv. of Cl⁻, Br⁻, and I⁻. By contrast, significant changes are observed in the presence of 50 equiv. of MeCO₂⁻, n-C₃H₇CO₂⁻ and F⁻, as shown in spectrum (MeCO₂⁻), n-C₃H₇CO₂⁻ and (F⁻), in fact, there are some differences among them: after F⁻ is added,

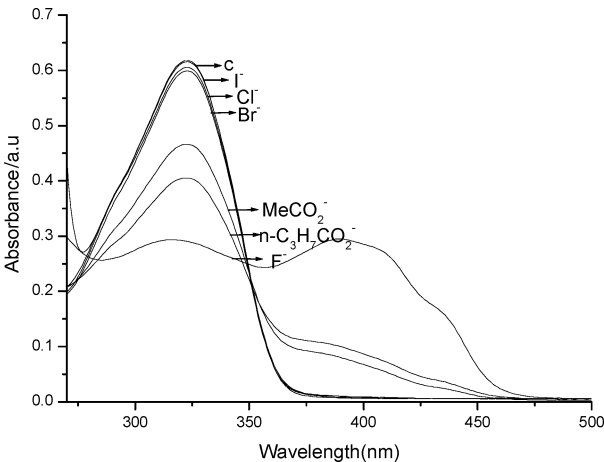


FIGURE 1 UV-vis absorption spectra of **c** recorded in CH₃CN (2.0×10^{-5} M) after the addition of 50 equivalents of representative anions.

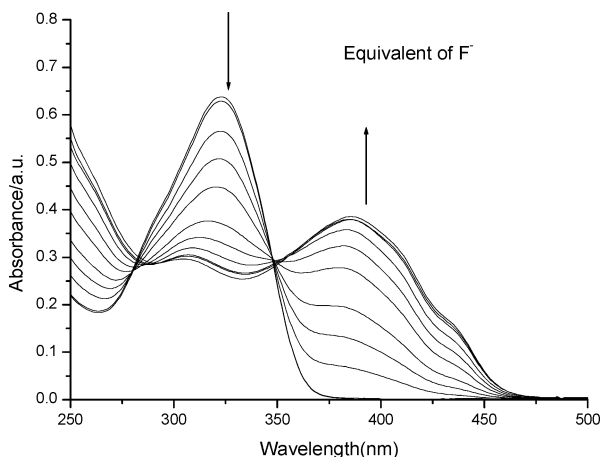


FIGURE 2 UV-vis absorption spectra of **c** in CH_3CN (2.0×10^{-5} M) upon the addition of various equivalents of $\text{Bu}_4\text{N}^+\text{F}^-$: 0, 0.5, 6.0, 12, 20, 40, 60, 80, 100, 120, and 140.

the peak at 323 nm produces a hypsochromic shift (from 323 to 305 nm), a new peak appears at 379 nm, and the color of the solution changes from colorless to yellow obviously, however, addition of MeCO_2^- and $\text{n-C}_3\text{H}_7\text{CO}_2^-$ cause a very small hypsochromic shift (from 323 to 322 nm), no new peak appears and no clear color change is found. It is apparent that the specific spectra property and the resulting color change of receptor **c** upon the addition of F^- under the solution-phase conditions can be used as colorimetric anion sensor.

The binding properties of **c** with F^- , MeCO_2^- and $\text{n-C}_3\text{H}_7\text{CO}_2^-$ were further assessed by UV-vis spectroscopy. Figure 2 show the dependence of UV-vis spectra of **c** in CH_3CN on the concentration of F^- . Increasing the concentration of F^- the peak at 323 nm decreases, and produces a significant hypsochromic shift from 323 to 305 nm, at the same time, a new peak at 379 nm appears, which is ascribed to the formation of the complex between **c** and F^- , and produces a bathochromic shift from 379 to 386 nm, indicating that the combination of **c** with F^- promotes the charge transfer interaction, and two clear isosbestic points appear at 280 nm and 347 nm, respectively. A Job plot experiment was conducted, the result show the absorption of **c**- F^- complex approaches a maximum when the molar fraction of $[\text{F}^-]/([\text{c}] + [\text{F}^-])$ is about 0.5 (Figure 3), indicating that 1:1 complex is formed. The association constant (K_{ass}) calculated according to the titration experiment is 1890 (Table II). The satisfactory result of the nonlinear curve fitting (the correlation coefficient $R > 0.99$) confirms further the 1:1 binding ratio⁶ (Figure 4).

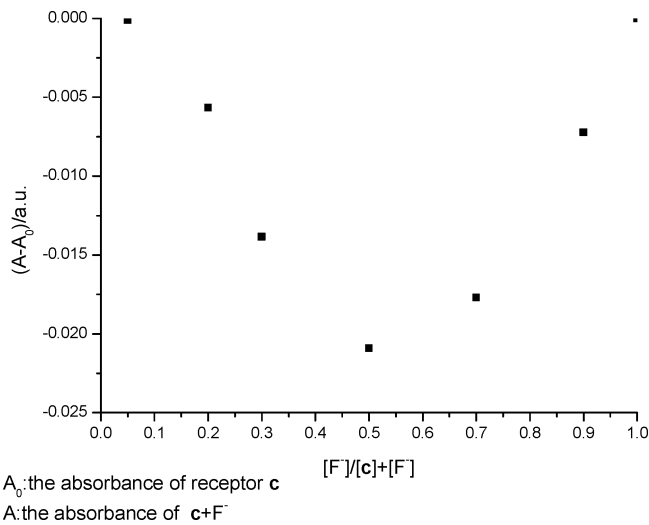


FIGURE 3 Job’s plot between receptor **c** and $Bu_4N^+ F^-$ in CH_3CN . $[c] + [F^-] = 4.0 \times 10^{-5} M$.

Differently, less hypsochromic shift (from 323 to 322 nm) are seen upon the addition of excess $MeCO_2^-$, no new peak appears, no obvious color changes, but two clear isosbestic points appears at 275nm and 350nm, the binding ratio between receptor **c** and $MeCO_2^-$ is still 1:1, the association constant is 1680 (Figure 5). $n-C_3H_7CO_2^-$ shows the same properties as $MeCO_2^-$, two clear isosbestic points appears at 279nm and 348nm, its association constant is 1740 (Figure 6). From these association constants data and Figure1, we draw the conclusion that the binding ability of receptor **c** recognizes anions in the following order : $F^- > n-C_3H_7CO_2^- > MeCO_2^- >> Cl^-, Br^-$ and I^- .

In the case of receptor **b**, the addition of $MeCO_2^-$ and $n-C_3H_7CO_2^-$ show the similar tendency with F^- , all of the three anions cause the

TABLE II Association Constants $K_{ass}((mol\ L^{-1})^{-1})$ for Receptor **a, Receptor **b** and Receptor **c** with Anions and Their Correlation Coefficients R**

Anion	Receptor a		Receptor b		Receptor c	
	K_{ass}	R	K_{ass}	R	K_{ass}	R
F^-	4310	0.9988	4590	0.9918	1890	0.9995
$n-C_3H_7CO_2^-$	3400	0.9993	4330	0.997	1740	0.9994
$CH_3CO_2^-$	3240	0.9990	3580	0.9987	1680	0.9983

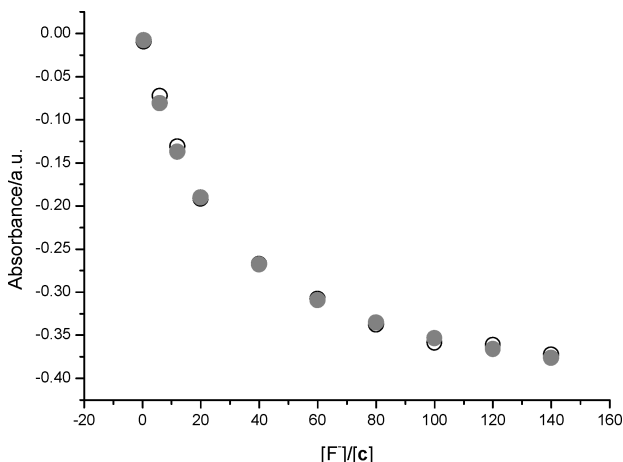


FIGURE 4 Plot of absorbance change of receptor **c** vs. equivalents of $\text{Bu}_4\text{N}^+ \text{F}^-$ added (the hollow spheres are the fitting curve).

color of the solution change from colorless to yellow. For receptor **a**, the addition of $\text{n-C}_3\text{H}_7\text{CO}_2^-$ show the similar tendency with F^- , and the color of the solution change from colorless to yellow, the addition of MeCO_2^- show the similar tendency with that of receptor **c**, and no obvious color changes is found.

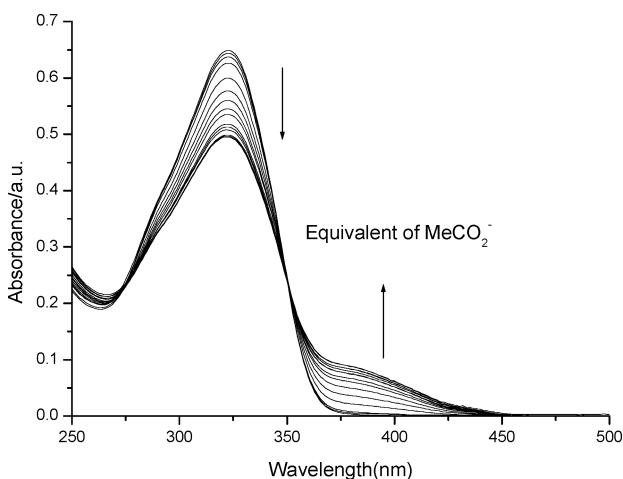


FIGURE 5 UV-vis absorption spectra of **c** in CH_3CN ($2.0 \times 10^{-5} \text{ M}$) upon the addition of various equivalents of $\text{Bu}_4\text{N}^+ \text{MeCO}_2^-$: 0, 0.75, 2.0, 5.0, 10, 20, 30, 40, 60, 80, 110, 130, 150, 200, and 250.

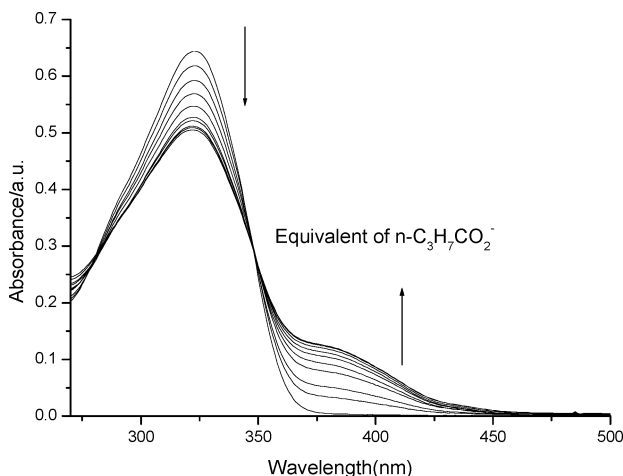


FIGURE 6 UV-vis absorption spectra of **c** in CH_3CN ($2.0 \times 10^{-5} \text{ M}$) upon the addition of various equivalents of $\text{Bu}_4\text{N}^+\text{C}_3\text{H}_7\text{CO}_2^-$: 0, 0.5, 6.0, 15, 30, 50, 80, 110, 140, 200, and 250.

Mechanism of Recognition

Receptor **b** was selected as a model to study the mechanism of recognition between receptors and anions. The color of the solution **b** + F^- is yellow; however, as a protic solvent methanol was added gradually, the yellow color of the solution faded, at the same time, the absorbance of the solution **b** + F^- at 323 nm went back to the value of receptor **b** and the peak of complex **b**· F^- at 369 nm disappeared. The reason is that the addition of methanol resulted in the hydrogen bond between NH of thiourea and anions replaced by a new hydrogen bond between NH of thiourea and methanol, in view of this point, the hydrogen bonds between NH of thiourea and anions come into being.

In order to reveal the forming of the hydrogen bond, a ^1H NMR titration experiment was carried out. ^1H NMR spectroscopy of **b** was recorded in DMSO-d_6 ($1.0 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$) after the addition of 1.0 equivalent of representative anions. Addition of F^- , $\text{n-C}_3\text{H}_7\text{CO}_2^-$ and MeCO_2^- to compound **b** caused the NH proton signals of thiourea group to be changed. Upon addition of F^- and $\text{n-C}_3\text{H}_7\text{CO}_2^-$, the NH peaks of the thiourea disappeared. In the case of MeCO_2^- , NH(adjacent to imine) disappeared, another NH showed a downfield shift from 9.9 to 10.0 ppm. These results illustrate that the connection between receptor **b** and those anions was by hydrogen bonding interactions.

CONCLUSION

We have succeeded in preparing a new class of receptors that exhibit highly selective binding and sensing of F^- , $n-C_3H_7CO_2^-$ and $MeCO_2^-$ in CH_3CN , the highly sensing properties and unique color change upon addition of F^- of receptor **c** make it can be explored as a colorimetric sensor for F^- in application.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded in KBr on a Digilab FTS-3000 spectrophotometer and 1H NMR spectra on an mercury plus-400MHz or mercury plus-300MHz Varian instrument using $CDCl_3$ or $DMSO-d_6$ as solvent and TMS as internal reference. Elemental analysis was determined on PE-2400 CHN instrument. UV-vis spectra were taken on an Agilent-8453 spectrometer.

Materials

The thiosemicarbazides have been prepared by following the method of Shukla et al.⁷ and 4-acetyl benzo-15-crown-5 has been prepared by following the method of Lai-xin Zhang⁸. The anionic substrates were used as the tetrabutylammonium salts, which were analytical reagents. The CH_3CN was refluxed with K_2CO_3 , $KMnO_7$ and then P_2O_5 . All other commercially available reagents were used without further purification.

Synthesis of a–i

This reaction was carried out by adding a thiosemicarbazide (2 mmol), 4-acetyl benzo-15-crown-5 (2 mmol) and 1–2 drops of HCl to a round-bottomed flask containing 20 ml ethanol and a magnetic stirring bar and stirred at room temperature. Several minutes later, substantial precipitation took place. In order to make it completed, the reaction lasted for 1 h. When the reaction finished, the precipitation was filtered and washed with 10 ml ethanol three times. By this simple treatment, pure product, Suitable for characterization, was obtained.

a ($C_{23}H_{29}N_3SO_5$)

Elemental analysis, found: C 60.28, H 6.72, N 9.31; Calc: C 60.11, H 6.36, N 9.14%. IR: 3439, 3283 (N-H), 3060, 3026 (Ar-H), 2925 (CH_3), 2866 (CH_2), 1596 (C=N), 1551, 1516 (Ar), 1272, 1059 (Ar-O- CH_2), 1183 (C=S), 1131 (CH_2 -O- CH_2), cm^{-1} . 1H NMR ($CDCl_3$), δ_H : 2.3 (s,

3H, $-\text{CH}_3$), 3.75–4.21 (m, 16H, $4 \times \text{OCH}_2\text{CH}_2\text{O}$), 6.87–7.69 (m, 8H, Ar-H), 8.69 (s, 1H, NH), 9.34 (s, 1H, NH).

b ($\text{C}_{23}\text{H}_{28}\text{N}_3\text{SO}_5\text{F}$)

Elemental analysis, found: C 57.75, H 6.04, N 8.82; Calc: C 57.85, H 5.91, N 8.79%. IR: 3445, 3293 (N-H), 3080 (Ar-H), 2924 (CH_3), 2866 (CH_2), 1605 ($\text{C}=\text{N}$), 1545, 1512 (Ar), 1273, 1057 (Ar-O- CH_2), 1188 ($\text{C}=\text{S}$), 1133 ($\text{CH}_2\text{-O-CH}_2$), cm^{-1} . $^1\text{HNMR}$ ($\text{DMSO-}d_6$), δ_H : 2.35 (s, 3H, $-\text{CH}_3$), 3.62–4.15 (m, 16H, $4 \times \text{OCH}_2\text{CH}_2\text{O}$), 6.94–7.61 (m, 7H, Ar-H), 9.99 (s, 1H, NH), 10.50 (s, 1H, NH).

c ($\text{C}_{25}\text{H}_{33}\text{N}_3\text{SO}_6$)

Elemental analysis, found: C 59.70, H 6.57, N 8.42; Calc: C 59.62, H 6.6, N 8.34%. IR: 3441, 3225 (N-H), 3080 (Ar-H), 2930 (CH_3), 2974, 2866 (CH_2), 1595 ($\text{C}=\text{N}$), 1539, 1512 (Ar), 1272, 1046 (Ar-O- CH_2), 1180 ($\text{C}=\text{S}$), 1136 ($\text{CH}_2\text{-O-CH}_2$), cm^{-1} . $^1\text{HNMR}$ ($\text{DMSO-}d_6$), δ_H : 1.31–1.35 (t, 3H, $-\text{CH}_3$), 2.34 (s, 3H, CH_3), 2.49–2.50 (d, 2H, $-\text{OCH}_2-$), 3.55–4.15 (m, 16H, $4 \times \text{OCH}_2\text{CH}_2\text{O}$), 6.89–7.61 (m, 7H, Ar-H), 9.87 (s, 1H, NH), 10.36 (s, 1H, NH).

d ($\text{C}_{24}\text{H}_{31}\text{N}_3\text{SO}_6$)

Elemental analysis, found: C 58.92, H 6.50, N 8.68; Calc: C 58.88, H 6.38, N 8.58%. IR: 3375, 3249 (N-H), 3073 (Ar-H), 2999, 2990 (CH_3), 2871 (CH_2), 1647 ($\text{C}=\text{N}$), 1602, 1540, 1510 (Ar), 1274, 1052 (Ar-O- CH_2), 1190 ($\text{C}=\text{S}$), 1150 ($\text{CH}_2\text{-O-CH}_2$), cm^{-1} . $^1\text{HNMR}$ ($\text{DMSO-}D_6$), δ_H : 2.37 (s, 3H, $-\text{CH}_3$), 3.89 (s, 3H, $-\text{OCH}_3$), 3.62–4.14 (m, 16H, $4 \times \text{OCH}_2\text{CH}_2\text{O}$), 6.94–7.51 (m, 7H, Ar-H), 10.19 (s, 1H, NH), 10.71 (s, 1H, NH).

e ($\text{C}_{24}\text{H}_{31}\text{N}_3\text{SO}_5$)

Elemental analysis, found: C 60.79, H 6.64, N 8.93; Calc: C 60.87, H 6.59, N 8.87%. IR: 3439, 3304 (N-H), 3078 (Ar-H), 2927 (CH_3), 2866 (CH_2), 1589 ($\text{C}=\text{N}$), 1551, 1514 (Ar), 1273, 1057 (Ar-O- CH_2), 1171 ($\text{C}=\text{S}$), 1131 ($\text{CH}_2\text{-O-CH}_2$), cm^{-1} . $^1\text{HNMR}$ (CDCl_3), δ_H : 2.31 (s, 3H, $-\text{CH}_3$), 2.36 (s, 3H, $-\text{CH}_3$), 3.76–4.19 (m, 16H, $4 \times \text{OCH}_2\text{CH}_2\text{O}$), 6.86–7.86 (m, 7H, Ar-H), 8.74 (s, 1H, NH), 9.18 (s, 1H, NH).

f ($\text{C}_{24}\text{H}_{31}\text{N}_3\text{SO}_5$)

Elemental analysis, found: C 60.92, H 6.76, N 8.94; Calc: C 60.87, H 6.59, N 8.87%. IR: 3454, 3276 (N-H), 3079 (Ar-H), 2920 (CH_3), 2866 (CH_2), 1609 ($\text{C}=\text{N}$), 1554, 1514 (Ar), 1273, 1057 (Ar-O- CH_2), 1110 ($\text{C}=\text{S}$), 1136 ($\text{CH}_2\text{-O-CH}_2$), cm^{-1} . $^1\text{HNMR}$ ($\text{DMSO-}D_6$), δ_H : 2.32 (s, 3H,

—CH₃), 2.35 (s, 3H, —CH₃) 3.61–4.15 (m, 16H, 4 × OCH₂CH₂O), 6.94–7.59 (m, 7H, Ar-H), 9.93 (s, 1H, NH), 10.45 (s, 1H, NH).

g (C₂₄H₃₁N₃SO₅)

Elemental analysis, found: C 60.81, H 6.73, N 8.90; Calc: C 60.87, H 6.59, N 8.87%. IR: 3443, 3285 (N-H), 3081, 3021 (Ar-H), 2926 (CH₃), 2866 (CH₂), 1591 (C=N), 1544, 1517 (Ar), 1272, 1059 (Ar—O—CH₂), 1180 (C=S), 1136(CH₂—O—CH₂), cm⁻¹. ¹HNMR (CDCl₃), δ_H: 2.30 (s, 3H, —CH₃), 2.37 (s, 3H, —CH₃) 3.76–4.21 (m, 16H, 4 × OCH₂CH₂O), 7.20–7.32 (m, 7H, Ar-H), 8.68 (s, 1H, NH), 9.24 (s, 1H, NH).

h(C₂₃H₂₈N₃SO₅Cl)

Elemental analysis, found: C 56.00, H 5.61, N 8.62; Calc: C 55.92, H 5.71, N 8.51%. IR: 3437, 3261 (N-H), 3077 (Ar-H), 2928 (CH₃), 2867 (CH₂), 1597 (C=N), 1543,1515 (Ar), 1274, 1057 (Ar—O—CH₂), 1185 (C=S), 1130(CH₂—O—CH₂), cm⁻¹. ¹HNMR (DMSO-D₆), δ_H: 2.38 (s, 3H, —CH₃), 3.62–4.14 (m, 16H, 4 × OCH₂CH₂O), 6.96–8.12 (m, 7H, Ar-H), 10.08 (s, 1H, NH), 10.81 (s, 1H, NH).

i (C₂₃H₂₈N₃SO₅Cl)

Elemental analysis, found: C 56.04, H 5.63, N 8.64; Calc: C 55.92, H 5.71, N 8.51%. IR: 3460, 3285 (N-H), 3079 (Ar-H), 2923 (CH₃), 2865 (CH₂), 1590 (C=N), 1532,1513 (Ar), 1273, 1059 (Ar—O—CH₂), 1191 (C=S), 1129(CH₂—O—CH₂), cm⁻¹. ¹HNMR (CDCl₃), δ_H: 2.29 (s, 3H, —CH₃), 3.76–4.21 (m, 16H, 4 × OCH₂CH₂O), 6.86–7.65 (m, 7H, Ar-H), 8.80 (s, 1H, NH), 9.30 (s, 1H, NH).

BINDING STUDIES

UV-vis spectral studies of the three receptors using CH₃CN as solvent were carried out by addition of anions to a 2.0 × 10⁻⁵ M solution of receptor. The job plot study was performed on a total concentration of 4.0 × 10⁻⁵ M in CH₃CN. The ¹HNMR study was recorded by adding equivalent amounts of anions to receptor **b** in DMSO-d₆(mercury plus-300MHz Varian instrument).

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