Supporting Information

Expanding Reversible Chalcogenide Binding: Supramolecular Receptors for the Hydroselenide (HSe^-) Anion

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Experimental Details

Materials and Methods.

All manipulations were performed under an inert atmosphere using an Innovative Atmospheres N_2-filled glove box unless otherwise noted. All reagents were purchased from commercial sources and used as received, unless otherwise noted. Solvents were degassed by sparging with Ar followed by passage through a Pure Process Technologies solvent purification system to remove water and stored over 4Å molecular sieves in an inert atmosphere glove box. CD_3CN and DMSO-d_6 were distilled from calcium hydride then deoxygenated by three freeze-pump-thaw cycles and stored in an inert atmosphere glove box. Tetrabutylammonium hydrosulfide ($NBu_4(SH)$)[1] and host **1**^{tBu} were all synthesized according to previous reports.[1,2] Note: Hydrogen sulfide, hydrogen selenide, and related salts are highly toxic and should be handled carefully to avoid exposure. MS was collected on a Xevo Waters ESI LC/MS instrument. The following naming conventions were used to describe NMR couplings: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (dd) doublet of doublets, (m) multiplet, (b) broad.

Guest and Receptor Synthesis.

Tetrabutylammonium hydroselenide (NBu$_4$SeH). This preparation was adapted from previous reports.[3] NBu_4BH_4 (0.743 g, 2.90 mmol) was dissolved in dry CH_3CN (10 mL) and treated with Se^0 (0.242 g, 3.10 mmol) in a dry box. After stirring for 7 d, the solvent was removed *in vacuo* and the resulting yellow oil was washed with THF. The resulting white powder was filtered using a fine porosity glass-fritted funnel and redissolved in CH_3CN and layered under Et_2O to afford colorless crystals (0.152 g, 0.500 mmol, 16% yield). ^{1}H NMR (600 MHz, CD_3CN) δ: 3.09 (m, 8H), 1.60 (p, *J* = 7.9 Hz, 8H), 1.35 (h, *J* = 7.3 Hz, 8H), 0.97 (t, *J* = 7.4 Hz, 12H), –6.61 (SeH, s, 1H). ^{13}C{^{1}H} NMR (150 MHz, CD_3CN) δ: 59.3, 24.32, 20.34, 13.79.

N,N',N''-(Nitrilotris(ethane-2,1-diyl))tris(3,5-bis(trifluoromethyl)benzamide) (2^{CF3}). This preparation was adapted from previous reports.[4,5] Tris(2-aminoethyl)amine (0.0770 g, 0.530 mmol) and NaOH (0.230 g, 5.75 mmol) were dissolved in H_2O (20 mL), and a solution of 3,5-bis(trifluoromethyl)benzoyl chloride (0.437 g, 1.58 mmol) in ethyl acetate (EtOAc, 20 mL) was added dropwise and the reaction mixture was stirred overnight under N_2 at room temperature. The organic layer was washed three times with H_2O (30 mL) then dried with Na_2SO_4. After filtration, the solvent was removed under vacuum to afford a white powder (0.246 g, 54% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.86 (NH, t, *J* = 5.5 Hz, 3H), 8.29 (s, 6H), 8.14 (s, 3H), 3.34 (q, *J* = 5.9 Hz, 6H), 2.75 (t, *J* = 6.2 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ: 163.36, 136.37, 130.14 (q, *J* = 33.3 Hz), 127.78, 124.49, 122.98 (q, *J* = 272.8 Hz), 53.44, 38.10.

NMR Studies.

General Methods. NMR spectra were acquired on a Brüker Avance-III-HD 600 spectrometer with a Prodigy multinuclear broadband cryoProbe at 25.0 °C or on a Varian 500 MHz spectrometer. Chemical shifts are reported in parts per million (δ) and are referenced to residual solvent resonances (CD_3CN ^{1}H 1.94 ppm, ^{13}C{^{1}H} 118.26 ppm and DMSO-d_6 ^{1}H 2.50 ppm, ^{13}C{^{1}H} 39.52 ppm).

General Procedure for NMR Titrations. Method A. A solution of host in 10% DMSO-d_6/CD_3CN or CD_3CN (1.8-2.2 mM, 3 mL) was prepared and 500 µL was added to a septum-sealed NMR tube. The remaining host solution (2.5 mL) was used to prepare a host/guest (10-25 mM) stock solution. Aliquots of the host/guest solution were added to the NMR tube using Hamilton

gas-tight syringes, and ^{1}H NMR spectra were recorded at 25 °C after each addition of guest. The Δδ of the various NH and aromatic CH protons were used to follow the progress of the titration, and association constants were determined using the Thordarson method.[6,7]

Method B. A solution of receptor $\mathbf{1}^{tBu}$ in 10% DMSO-d_6/CD_3CN (0.8-1.2 mM) was prepared and 500 μL was added to a septum-sealed NMR tube. A stock solution of guest (NBu_4SeH) was prepared in 10% DMSO-d_6/CD_3CN (18.6-27.0 mM). Aliquots of the guest solution were added to the NMR tube using Hamilton gas-tight syringes, and ^{1}H NMR spectra were recorded at 25 °C after each addition of guest. The Δδ of the NH and the central aromatic CH proton was used to follow the progress of the titration, and association constants were determined using the Thordarson method.[6,7]

Decomposition Studies with $\mathbf{1}^{tBu}$ and HSe^-.

Stock solutions in 10% DMSO-d_6/CD_3CN of $\mathbf{1}^{tBu}$ (2 mM,) and $NBu_4(SeH)$ (25 mM) were prepared. A septum sealed NMR tube was charged with 500 μL of the $\mathbf{1}^{tBu}$ solution. 20 equiv. NBu_4SeH was added to the receptor solution using a Hamilton gas-tight syringe, and the δ of the NH and various aromatic CH protons were monitored by ^{1}H NMR at 25 °C to determine the effect of HSe^- binding on $\mathbf{1}^{tBu}$ (Figure S3). These samples were then collected and the solvent removed under vacuum for MS analysis.

HSe^- Binding Reversibility Studies with $\mathbf{1}^{tBu}$ and $Zn(OAc)_2$.

Stock solutions in 10% DMSO-d_6/CD_3CN of receptor $\mathbf{1}^{tBu}$ (2 mM,) and NBu_4SeH (11 mM) were prepared, as was a stock solution of $Zn(OAc)_2$ (78 mM) in DMSO-d_6. A septum sealed NMR tube was charged with 500 μL of $\mathbf{1}^{tBu}$. After 6 equiv. NBu_4SeH was added using a Hamilton gas-tight syringe, the δ of the NH and various aromatic CH protons were monitored by ^{1}H NMR at 25 °C over the course of 3 h. (Figure S5) 20 equiv. $Zn(OAc)_2$ was added using a Hamilton gas-tight syringe to determine the effect of $Zn(OAc)_2$ on HSe^- binding.

HSe^- Binding Reversibility Studies with $\mathbf{2}^{CF3}$ and $Zn(OAc)_2$.

Stock solutions in 10% DMSO-d_6/CD_3CN of $\mathbf{2}^{CF3}$ (2 mM,), NBu_4SeH (20 mM), and $Zn(OAc)_2$ (40 mM) were prepared. A septum sealed NMR tube was charged with 350 μL of the $\mathbf{2}^{CF3}$ solution, then 2 equiv. NBu_4SeH and 12 equiv. $Zn(OAc)_2$ were sequentially added using Hamilton gas-tight syringes. The δ of the NH and various aromatic CH protons were monitored by ^{1}H NMR at 25 °C to determine the effect of $Zn(OAc)_2$ on HSe^- binding.

X-ray Crystallography

General Methods. Diffraction intensities for NBu_4SeH, $\mathbf{2}^{CF_3}$, and $NBu_4[\mathbf{1}^{tBu}(SeH)]$ were collected at 173 K on a Bruker Apex2 CCD diffractometer using CuKα radiation, λ= 1.54178 Å. Space groups were determined based on systematic absences (NBu_4SeH, $NBu_4[\mathbf{1}^{tBu}(SeH)]$) and intensity statistics ($\mathbf{2}^{CF}$). Absorption corrections were applied by SADABS.[8] Structures were solved by direct methods and Fourier techniques and refined on F^2 using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. H atoms in all structures were refined in calculated positions in a rigid group model, except the H atom bonded to the Se atom in NBu_4SeH. Position of this H atom was found on the residual density map and refined with isotropic thermal parameters. Solvent molecules (hexane in $\mathbf{2}^{CF_3}$ and diethyl ether in $NBu_4[\mathbf{1}^{tBu}(SeH)]$) fill out a large empty space between the main molecules in the packing. They are highly disordered and were treated by SQUEEZE.[9] The corrections of the X-ray data by SQUEEZE are 132 and 212

electron/cell; the expected values are 100 and 168 electron/cell, respectively, for $\mathbf{2}^{CF_3}$ and $NBu_4[\mathbf{1}^{tBu}(SeH)]$. Due to a lot of disordered $-CF_3$ groups in the structure of $\mathbf{2}^{CF_3}$, diffraction at high angles from crystals of this compound is very weak and reflection statistics at high angles are poor. Even using a strong *Incoatec* IμS Cu source it was possible to collected data only up to $2\theta_{max}$ = 99.98°. However, diffraction data collected for $\mathbf{2}^{CF_3}$ provide appropriate numbers of measured reflections per refined parameters: 8261 per 1118. Thermal parameters for the F atoms in the disordered $-CF_3$ groups are significantly elongated displaying their significant disorder. Diffraction data for $NBu_4[\mathbf{1}^{tBu}(SeH)]$ has been collected up to $2\theta_{max}$ = 133.46° but reflection at high angles are also very weak due to disordered terminal groups in a counter-ion NBu_4 and solvent Et_2O molecule. The disordered fragments have been refined with restrictions on its geometry and using RIGU option in SHELXL. All calculations were performed by the Bruker SHELXL-2014 package.[10]

In contrast to the structure of NBu_4SH,[1] determined in high symmetry *R*-3*c* with the H atom at the S atom disordered over several positions, the structure of NBu_4SeH was determined in monoclinic system with one position for the H atom on the Se atom. The difference in size of the S and Se atoms appear to provide the difference in crystal packing and as a result crystal symmetry in case of the Se atom is reduced from hexagonal to monoclinic.

Table S1. Crystallographic data for NBu_4SeH, $\mathbf{2}^{CF_3}$, and $NBu_4[\mathbf{1}^{tBu}(SeH)]$.

	NBu_4SeH	$\mathbf{2}^{CF_3}$	$NBu_4[\mathbf{1}^{tBu}(SeH)]$
formula	$C_{16}H_{37}NSe$	$C_{36}H_{31}F_{18}N_4O_3$	$C_{74}H_{111}N_5O_6Se$
fw	322.42	909.65	1245.63
T (K)	173(2)	173(2)	173(2) K
crystal system	Monoclinic	Triclinic	Monoclinic
space group	*C*2/*c*	*P*-1	*P*2$_1$/*n*
a (Å)	14.1628(5)	13.8015(7)	9.5547(4)
b (Å)	14.0547(5)	18.0488(9)	30.3155(13)
c (Å)	19.8443(7)	18.1383(9)	26.1228(10)
α (°)	90	103.008(3)	90
β (°)	110.832(2)	102.996(3)	90.476(2)
γ (°)	90	105.924(3)	90
Z	8	4	4
V (Å^3)	3691.9(2)	4030.4(4)	7566.4(5)
δ_{calc} (mg/m^3)	1.160	1.499	1.093
indep. reflections	3260	8261	13148
R1	0.0442	0.0656	0.0921
R1(I>2σ(I))	0.0722	0.0899	0.1124
wR2	0.1118	0.1674	0.2381
GOF	1.025	1.047	1.050
max/min res. e$^-$ den. (eÅ^{-3})	+0.377/–0.337	+0.672/–0.343	+1.061/–0.814
CCDC#	1846890	1846891	1846892

$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

GOF = S = $[\Sigma[w(F_o^2–F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

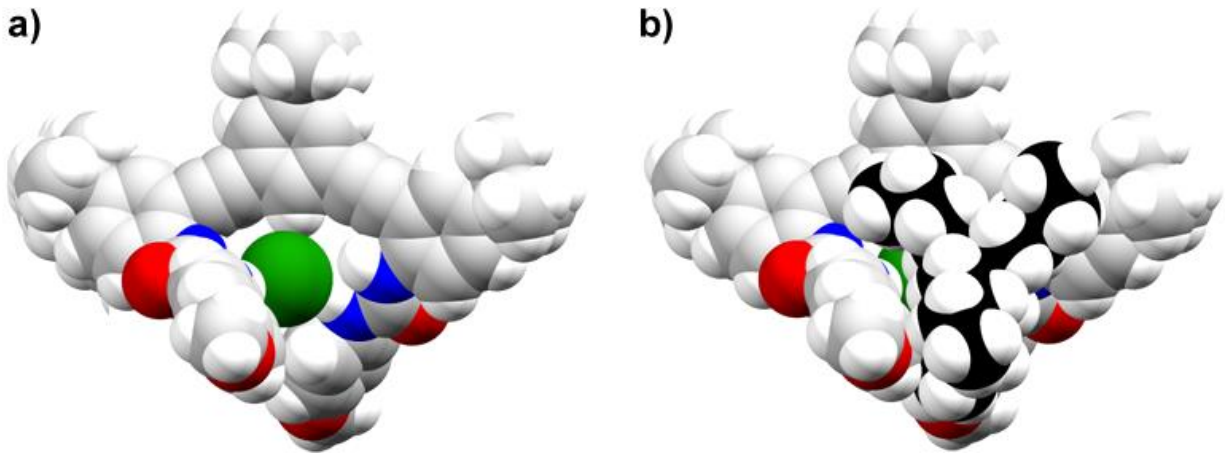


Figure S1. Space-filling model of (a) $[\mathbf{1}^{\mathbf{tBu}}(SeH)]^-$ and (b) NBu_4 $[\mathbf{1}^{\mathbf{tBu}}(SeH)]$, (C atoms of NBu_4^+ in black) demonstrating that the aliphatic C–H bonds of NBu_4^+ counter ion interacts with the bound HSe^- anion.

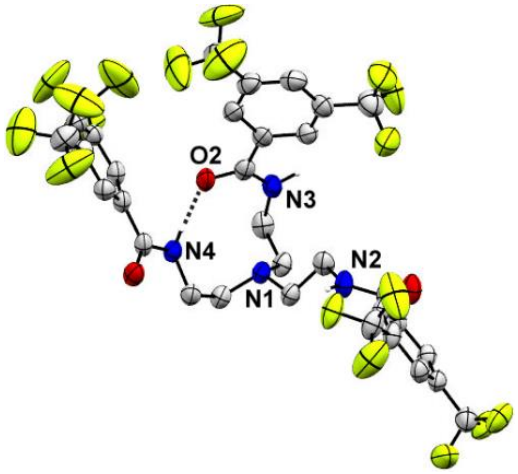


Figure S2. Thermal ellipsoid diagram (at 50% probability) depicting the molecular structure of 2^{CF_3}. Only N–H hydrogen atoms are shown for clarity.

NMR Studies

Decomposition Studies with ***1^{tBu}*** *and* HSe^-. Stock solutions in 10% DMSO-d_6/CD_3CN of **1^{tBu}** (2 mM,) and $NBu_4(SeH)$ (25 mM) were prepared. A septum sealed NMR tube was charged with 500 μL of the **1^{tBu}** solution. 20 equiv. NBu_4SeH was added to the receptor solution using a Hamilton gas-tight syringe, and the δ of the NH and various aromatic CH protons were monitored by ^1H NMR at 25 °C to determine the effect of HSe^- binding on **1^{tBu}** (Figure S3).

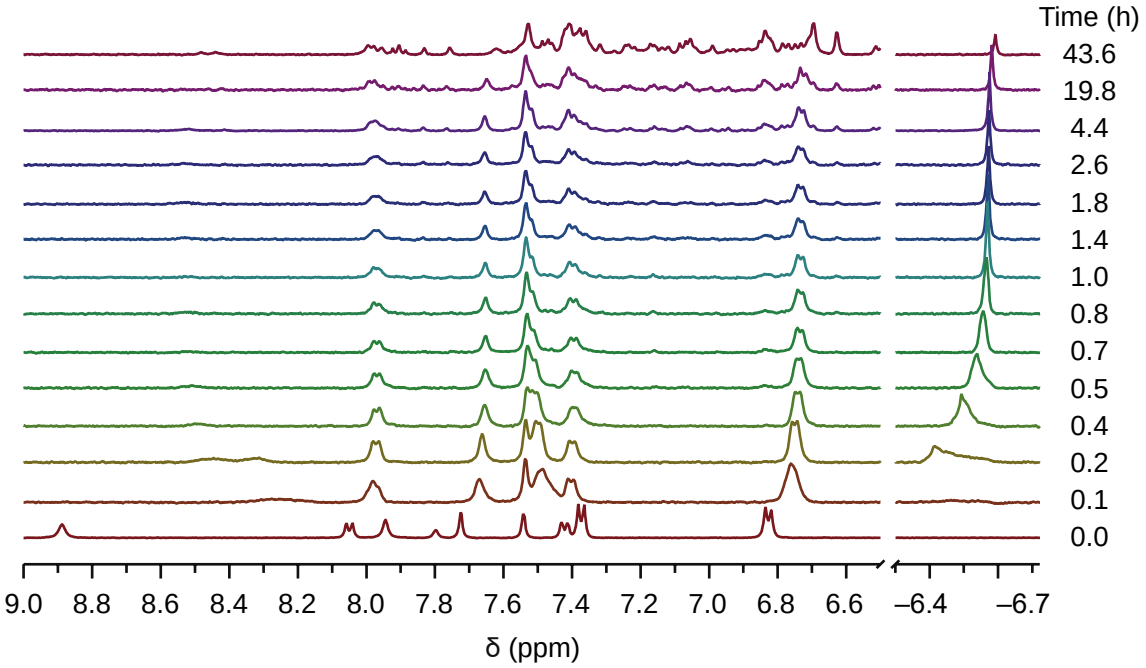


Figure S3. Stacked ^1H spectrum of receptor **1^{tBu}** and subsequent decomposition over 43 h upon addition of 20 equiv. NBu_4SeH.

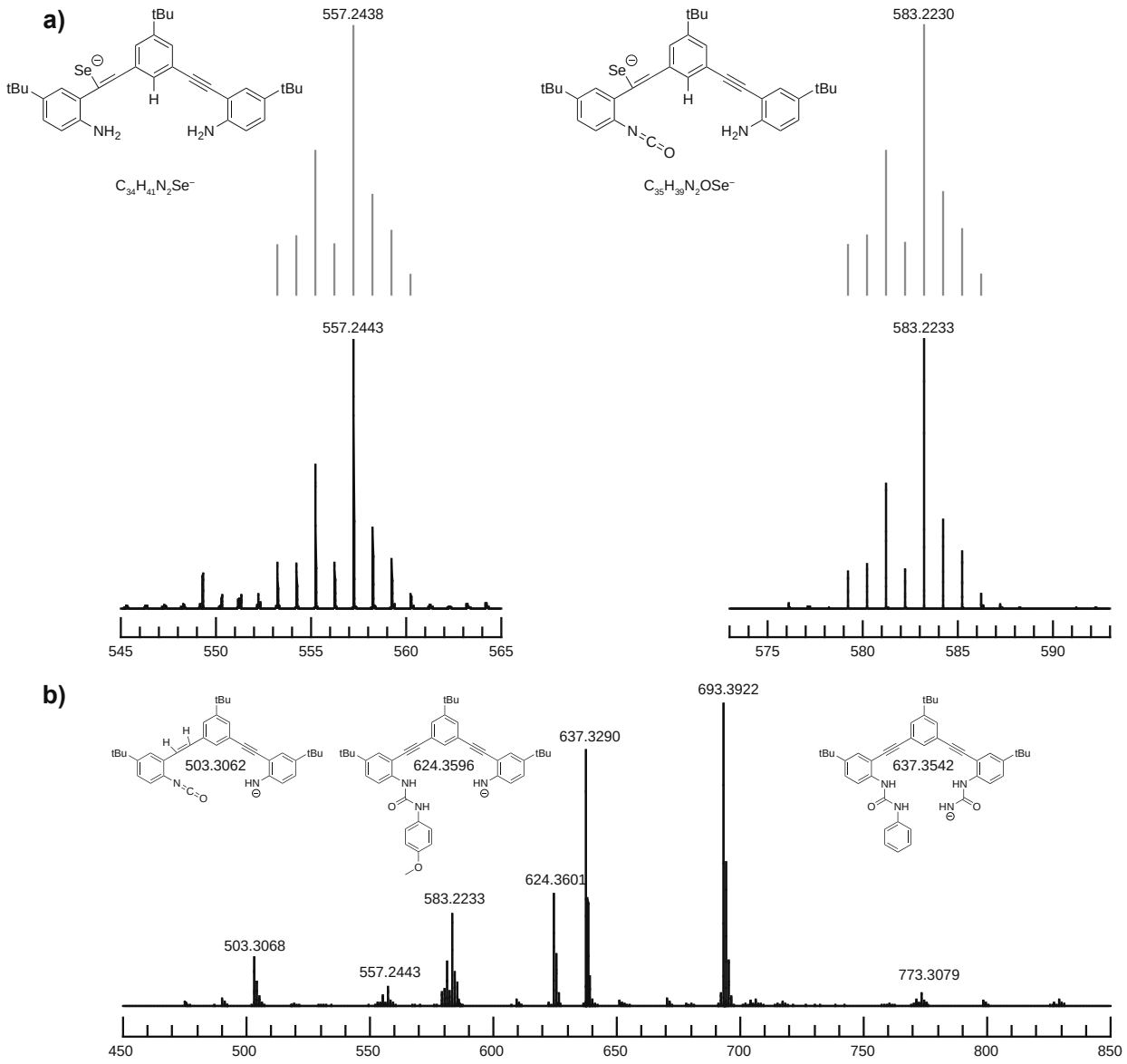


Figure S4. (a) Zoomed MS (negative mode, ESI) of further reacted products, with the proposed identity of these fragments, from the reaction of receptor **1**$^{\mathbf{tBu}}$ with 20 equiv. NBu_4SeH. Simulated spectra are in grey above the experimental spectra. (b) Full MS (negative mode, ESI) with the proposed identity of certain peaks specified.

HSe^- Binding Reversibility Studies with ***1^{tBu}*** *and Zn(OAc)$_2$.* Stock solutions in 10% DMSO-d_6/CD_3CN of receptor **1^{tBu}** (2 mM,) and NBu_4SeH (11 mM) were prepared, as was a stock solution of $Zn(OAc)_2$ (78 mM) in DMSO-d_6. A septum sealed NMR tube was charged with 500 μL of **1^{tBu}**. After 6 equiv. NBu_4SeH was added using a Hamilton gas-tight syringe, the δ of the NH and various aromatic CH protons were monitored by ^{1}H NMR at 25 °C over the course of 3 h. (Figure S5) 20 equiv. $Zn(OAc)_2$ was added using a Hamilton gas-tight syringe to determine the effect of $Zn(OAc)_2$ on HSe^- binding.

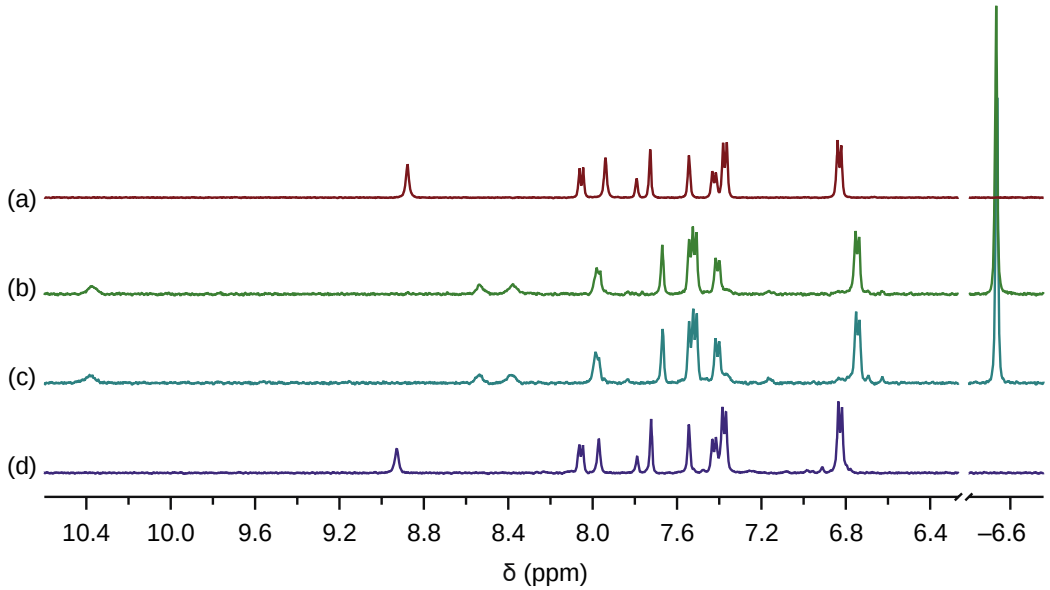


Figure S5. (a) ^{1}H spectrum of unbound **1^{tBu}**. (b) ^{1}H spectrum of **1^{tBu}** bound with HSe^- after 1 h and (c) after 3 h. (d) Addition of Zn(OAc) shows a return to the original, unbound spectrum of **1^{tBu}**, demonstrating reversibility.

HSe^- Binding Reversibility Studies with $\mathbf{2}^{\mathbf{CF_3}}$ and $Zn(OAc)_2$. Stock solutions in 10% DMSO-d_6/CD_3CN of $\mathbf{2}^{\mathbf{CF_3}}$ (2 mM,), NBu_4SeH (20 mM), and $Zn(OAc)_2$ (40 mM) were prepared. A septum sealed NMR tube was charged with 350 μL of the $\mathbf{2}^{\mathbf{CF_3}}$ solution, then 2 equiv. NBu_4SeH and 12 equiv. $Zn(OAc)_2$ were sequentially added using Hamilton gas-tight syringes. The δ of the NH and various aromatic CH protons were monitored by ^1H NMR at 25 °C to determine the effect of $Zn(OAc)_2$ on HSe^- binding.

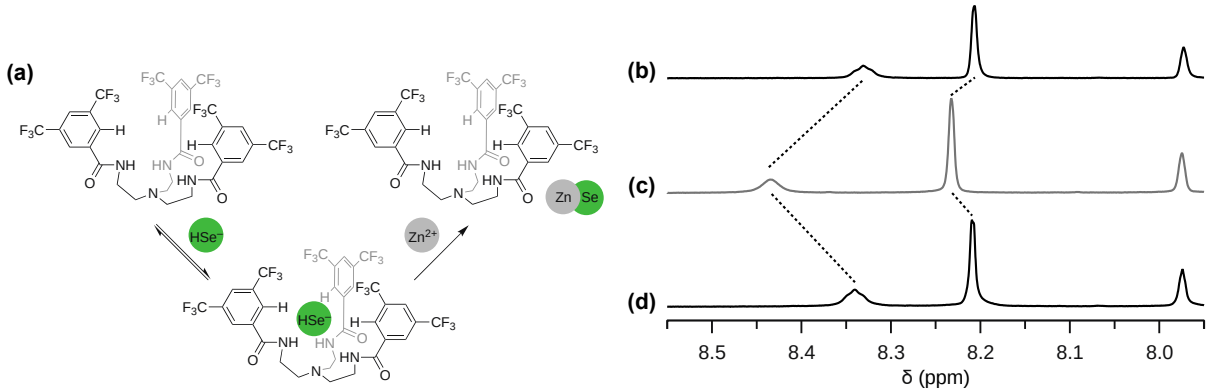


Figure S6. (a) Molecular depiction of Zn extrusion to show reversibility of receptor $\mathbf{2}^{\mathbf{CF_3}}$. (b) ^1H spectrum of unbound $\mathbf{2}^{\mathbf{CF_3}}$. (c) ^1H spectrum of $\mathbf{2}^{\mathbf{CF_3}}$ bound with HSe^-. (d) Addition of $Zn(OAc)_2$ shows a return to the original, unbound spectrum of $\mathbf{2}^{\mathbf{CF_3}}$, demonstrating reversibility.

^{1}H NMR Data

Table S2. Representative titration of receptor **1** with HSe^- in 10% DMSO-d_6/CD_3CN.

Entry	V_{Guest} (μL)	[Host] (M)	[HSe^-] (M)	Equiv.	δ NH_f (ppm)	δ NH_g (ppm)	δ CH_a (ppm)
0	0	2.0E-03	0.0E+00	0.00	8.873	7.937	7.790
1	5	2.0E-03	2.7E-04	0.13	8.991	7.969	7.854
2	10	2.0E-03	5.3E-04	0.27	9.098	8.000	7.906
3	15	2.0E-03	7.9E-04	0.40	9.187	8.028	7.950
4	25	1.9E-03	1.3E-03	0.67	9.343	8.071	8.035
5	35	1.9E-03	1.8E-03	0.94	9.475	8.101	8.101
6	55	1.8E-03	2.7E-03	1.47	9.670	8.165	8.201
7	95	1.7E-03	4.3E-03	2.55	9.913	8.229	8.327
8	145	1.6E-03	6.1E-03	3.89	10.078	8.274	8.405
9	205	1.4E-03	7.8E-03	5.50	10.176	8.312	8.456
10	265	1.3E-03	9.3E-03	7.10	10.254	8.336	8.489
11	325	1.2E-03	1.1E-02	8.71	10.307	8.354	8.507
12	385	1.1E-03	1.2E-02	10.32	10.331	8.361	8.516
13	485	1.0E-03	1.3E-02	13.00	10.367	8.380	8.525

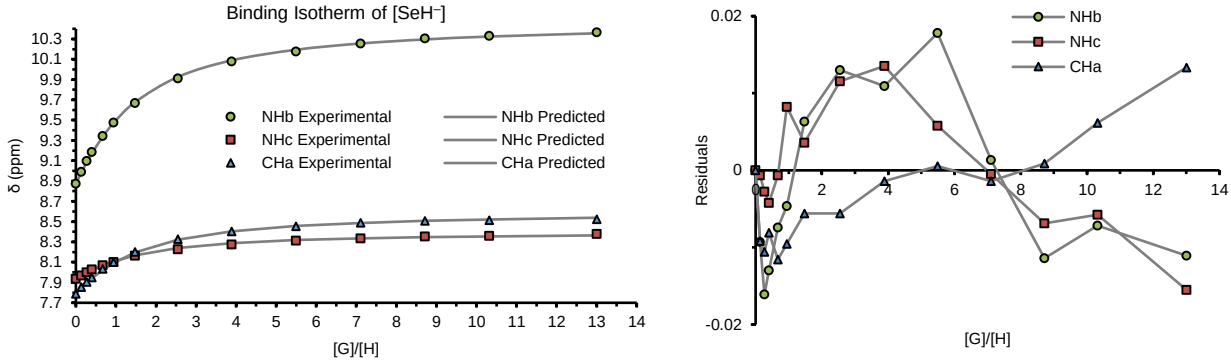


Figure S7. Representative binding isotherm for HSe^- titration of receptor **1** in 10% DMSO-d_6/CD_3CN determined by ^{1}H NMR spectroscopy.

Table S3. Representative titration of receptor **1** with HS^- in 10% DMSO-d_6/CD_3CN.

Entry	V_{Guest} (μL)	[Host] (M)	[HS^-] (M)	Equiv.	δ NH_f (ppm)	δ NH_g (ppm)	δ CH_a (ppm)
0	0	1.0E-03	0.0E+00	0.00	8.868	7.934	7.790
1	5	1.0E-03	1.8E-04	0.18	9.205	8.003	7.969
2	10	1.0E-03	3.6E-04	0.36	9.507	8.060	8.153
3	15	1.0E-03	5.3E-04	0.53	9.770	8.116	8.313
4	20	1.0E-03	7.0E-04	0.70	9.999	8.161	8.448
5	30	1.0E-03	1.0E-03	1.04	10.363	8.233	8.644
6	40	1.0E-03	1.4E-03	1.36	10.580	8.282	8.758
7	50	1.0E-03	1.7E-03	1.67	10.723	8.314	8.835
8	65	1.0E-03	2.1E-03	2.11	10.857	8.340	8.908
9	80	1.0E-03	2.5E-03	2.53	10.944	8.361	8.953
10	95	1.0E-03	2.9E-03	2.93	10.993	8.373	8.963
11	115	1.0E-03	3.4E-03	3.43	11.036	8.385	8.970
12	140	1.0E-03	4.0E-03	4.01	11.080	8.410	9.002
13	170	1.0E-03	4.7E-03	4.65	11.110	8.407	9.005
14	210	1.0E-03	5.4E-03	5.42	11.130	8.419	9.005
15	260	1.0E-03	6.3E-03	6.27	11.155	8.413	9.013
16	360	1.0E-03	7.7E-03	7.67	11.174	8.434	9.022
17	510	1.0E-03	9.3E-03	9.25	11.206	8.445	9.032
18	710	1.0E-03	1.1E-02	10.75	11.223	8.467	9.028

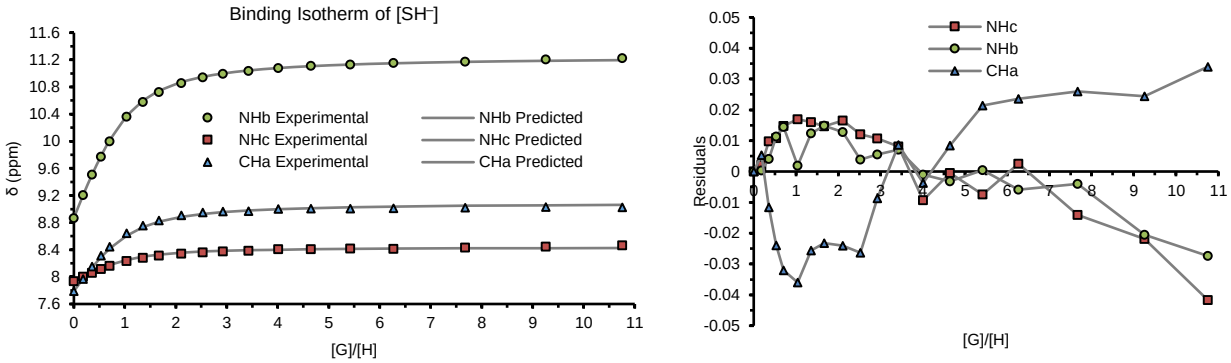


Figure S8. Representative binding isotherm for HS^- titration of receptor **1** in 10% DMSO-d_6/CD_3CN determined by ^1H NMR spectroscopy.

Table S4. Representative titration of receptor **1** with Br^- in 10% DMSO-d_6/CD_3CN.

Entry	V_{Guest} (μL)	[Host] (M)	[Br^-] (M)	Equiv.	δ NH_f (ppm)	δ NH_g (ppm)	δ CH_a (ppm)
0	0	1.0E-03	0.0E+00	0.00	8.878	7.936	7.797
1	5	1.0E-03	2.5E-04	0.25	8.906	7.941	7.820
2	10	1.0E-03	4.9E-04	0.49	8.923	7.945	7.836
3	15	1.0E-03	7.2E-04	0.72	8.946	7.947	7.854
4	20	1.0E-03	9.5E-04	0.95	8.967	7.952	7.875
5	30	1.0E-03	1.4E-03	1.40	9.003	7.956	7.906
6	40	1.0E-03	1.8E-03	1.83	9.035	7.962	7.939
7	50	1.0E-03	2.3E-03	2.25	9.069	7.965	7.965
8	65	1.0E-03	2.9E-03	2.85	9.108	7.971	8.002
9	80	1.0E-03	3.4E-03	3.41	9.143	7.976	8.033
10	95	1.0E-03	4.0E-03	3.95	9.177	7.982	8.066
11	115	1.0E-03	4.6E-03	4.63	9.214	7.987	8.105
12	135	1.0E-03	5.3E-03	5.26	9.247	7.991	8.132
13	160	1.0E-03	6.0E-03	6.00	9.281	7.995	8.164
14	190	1.0E-03	6.8E-03	6.82	9.318	8.001	8.196
15	225	1.0E-03	7.7E-03	7.68	9.352	8.006	8.225
16	265	1.0E-03	8.6E-03	8.58	9.385	8.011	8.256
17	315	1.0E-03	9.6E-03	9.57	9.420	8.016	8.289
18	375	1.0E-03	1.1E-02	10.61	9.455	8.022	8.316
19	455	1.0E-03	1.2E-02	11.79	9.488	8.022	8.345
20	555	1.0E-03	1.3E-02	13.02	9.516	8.030	8.367
21	695	1.0E-03	1.4E-02	14.40	9.530	8.036	8.383
22	885	1.0E-03	1.6E-02	15.82	9.560	8.036	8.410

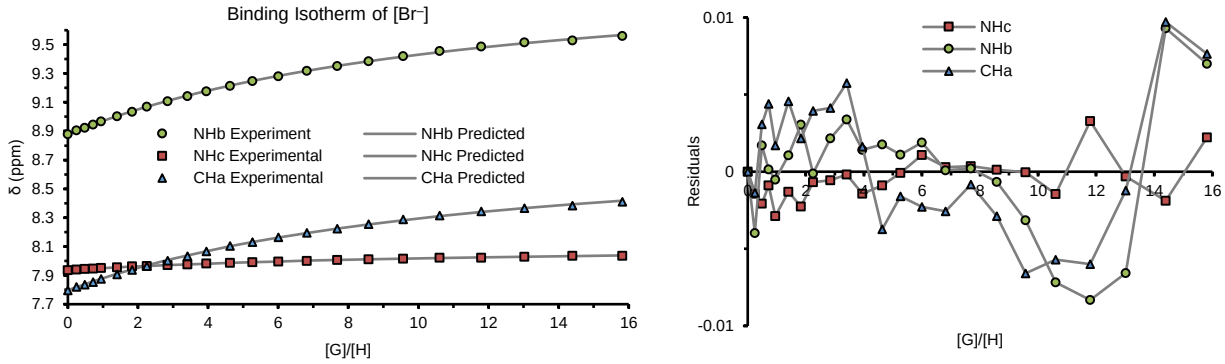


Figure S9. Representative binding isotherm for Br^- titration of receptor **1** in 10% DMSO-d_6/CD_3CN determined by ^1H NMR spectroscopy.

Table S5. Representative titration of receptor **1** with Cl^- in 10% DMSO-d_6/CD_3CN.

Entry	V_{Guest} (μL)	[Host] (M)	[Cl^-] (M)	Equiv.	δ NH_f (ppm)	δ NH_g (ppm)	δ CH_a (ppm)
0	0	8.8E-04	0.0E+00	0.00	8.866	7.934	7.788
1	5	8.8E-04	2.0E-04	0.23	9.083	7.956	7.969
2	10	8.8E-04	4.0E-04	0.45	9.256	7.973	8.117
3	15	8.8E-04	5.9E-04	0.67	9.397	7.989	8.238
4	20	8.8E-04	7.7E-04	0.88	9.514	8.001	8.336
5	30	8.8E-04	1.1E-03	1.30	9.696	8.018	8.484
6	40	8.8E-04	1.5E-03	1.70	9.820	8.031	8.593
7	50	8.8E-04	1.8E-03	2.09	9.910	8.039	8.667
8	65	8.8E-04	2.3E-03	2.64	10.006	8.050	8.746
9	80	8.8E-04	2.8E-03	3.17	10.069	8.061	8.800
10	100	8.8E-04	3.4E-03	3.83	10.130	8.062	8.847
11	125	8.8E-04	4.0E-03	4.59	10.181	8.073	8.891
12	155	8.8E-04	4.8E-03	5.43	10.219	8.080	8.920
13	195	8.8E-04	5.7E-03	6.44	10.259	8.082	8.946
14	245	8.8E-04	6.6E-03	7.55	10.293	8.090	8.969
15	345	8.8E-04	8.2E-03	9.38	10.328	8.100	8.988
16	495	8.8E-04	1.0E-02	11.42	10.361	8.108	9.006
17	695	8.8E-04	1.2E-02	13.36	10.374	8.114	9.013

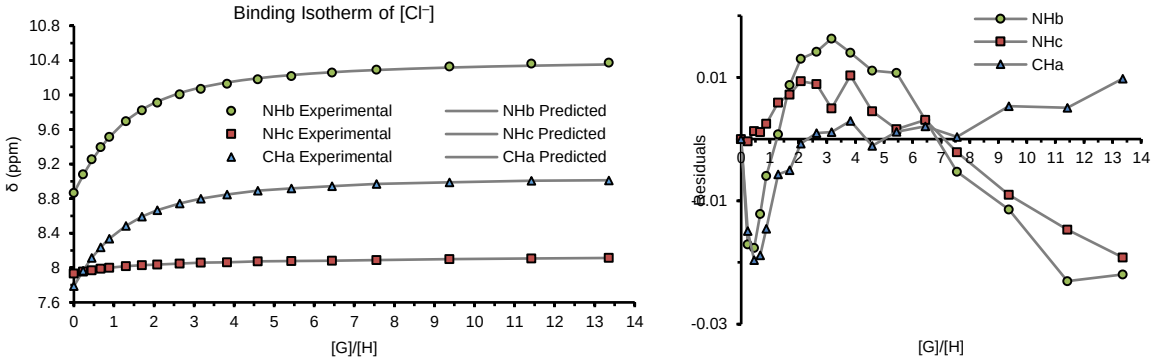


Figure S10. Representative binding isotherm for Cl^- titration of receptor **1** in 10% DMSO-d_6/CD_3CN determined by ^1H NMR spectroscopy.

Table S6. Representative titration of receptor **2** with HSe^- in CD_3CN.

Entry	V_{Guest} (μL)	[Host] (M)	[HSe^-] (M)	Equiv.	δ NH (ppm)	δ CH (ppm)
0	0	1.1E-03	0.00E+00	0.00	7.79	8.13
1	5	1.1E-03	8.99E-05	0.08	7.81	8.14
2	10	1.1E-03	1.78E-04	0.16	7.82	8.14
3	20	1.1E-03	3.49E-04	0.32	7.85	8.15
4	30	1.1E-03	5.14E-04	0.47	7.87	8.15
5	45	1.1E-03	7.49E-04	0.68	7.91	8.16
6	60	1.1E-03	9.72E-04	0.89	7.94	8.17
7	80	1.1E-03	1.25E-03	1.14	7.97	8.17
8	100	1.1E-03	1.51E-03	1.38	8.01	8.18
9	130	1.1E-03	1.87E-03	1.71	8.06	8.19
10	160	1.1E-03	2.20E-03	2.01	8.1	8.2
11	200	1.1E-03	2.59E-03	2.37	8.15	8.21
12	250	1.1E-03	3.03E-03	2.76	8.19	8.22
13	310	1.1E-03	3.47E-03	3.17	8.23	8.23
14	380	1.1E-03	3.92E-03	3.57	8.25	8.25
15	460	1.1E-03	4.35E-03	3.97	8.27	8.27
16	560	1.1E-03	4.79E-03	4.37	8.28	8.28
17	710	1.1E-03	5.33E-03	4.86	8.3	8.29
18	910	1.1E-03	5.86E-03	5.34	8.31	8.31
19	1160	1.1E-03	6.34E-03	5.78	8.32	8.32

Figure S11. Representative binding isotherm for HSe^- titration of receptor **2** in CD_3CN determined by ^1H NMR spectroscopy.

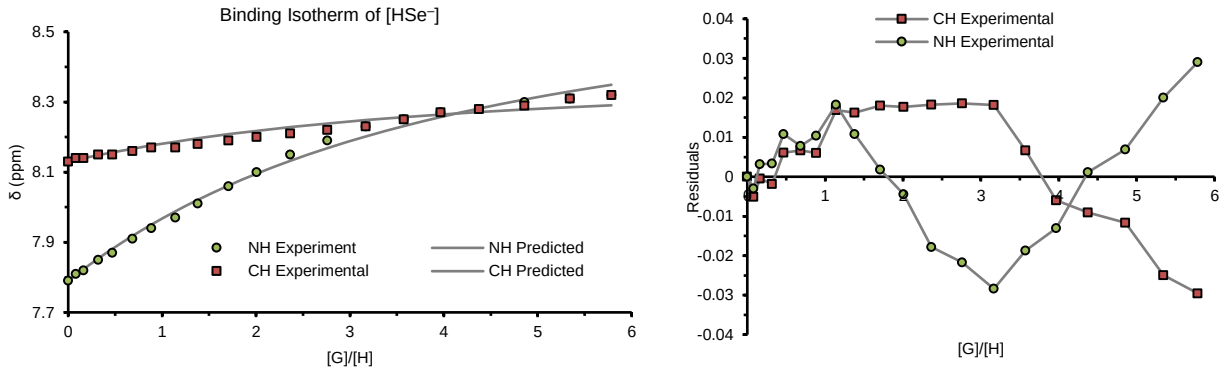


Table S7. Representative titration of receptor $\mathbf{2}^{\mathbf{CF_3}}$ with HS^- in CD_3CN.

Entry	V_{Guest} (μL)	[Host] (M)	[HS^-] (M)	Equiv.	δ NH (ppm)	δ CH (ppm)
0	0	1.2E-03	0.0E+00	0.00	7.79	8.14
1	10	1.2E-03	2.3E-04	0.19	7.99	8.18
2	20	1.2E-03	4.5E-04	0.37	8.12	8.21
3	30	1.2E-03	6.6E-04	0.54	8.28	8.24
4	45	1.2E-03	9.6E-04	0.79	8.47	8.29
5	60	1.2E-03	1.2E-03	1.03	8.65	8.32
6	80	1.2E-03	1.6E-03	1.32	8.83	8.37
7	100	1.2E-03	1.9E-03	1.60	8.99	8.4
8	125	1.2E-03	2.3E-03	1.92	9.14	8.43
9	150	1.2E-03	2.7E-03	2.21	9.24	8.46
10	180	1.2E-03	3.1E-03	2.54	9.35	8.48
11	210	1.2E-03	3.4E-03	2.83	9.43	8.5
12	250	1.2E-03	3.9E-03	3.19	9.50	8.51
13	300	1.2E-03	4.4E-03	3.59	9.58	8.53
14	360	1.2E-03	4.9E-03	4.01	9.63	8.54
15	440	1.2E-03	5.4E-03	4.49	9.68	8.56
16	540	1.2E-03	6.0E-03	4.98	9.72	8.57
17	640	1.2E-03	6.5E-03	5.38	9.75	8.57
18	790	1.2E-03	7.1E-03	5.87	9.80	8.58
19	990	1.2E-03	7.7E-03	6.37	9.79	8.58
20	1240	1.2E-03	8.3E-03	6.83	9.82	8.14

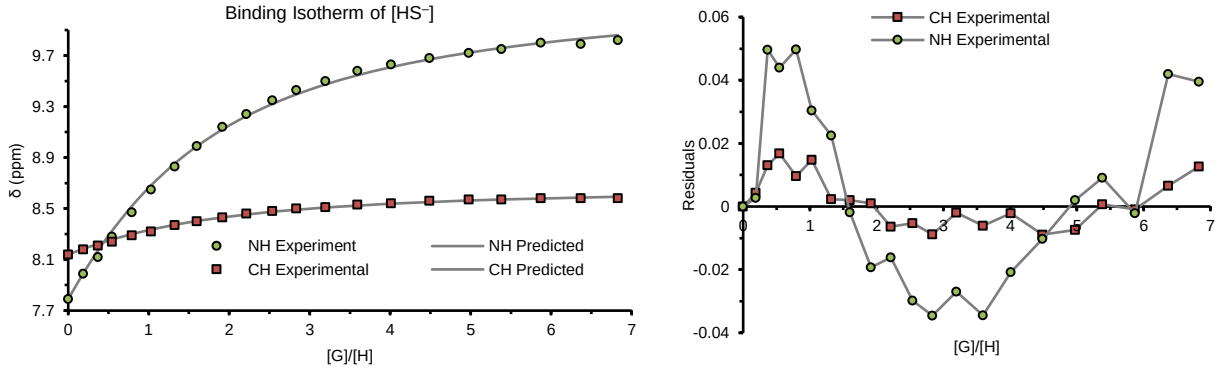


Figure S12. Representative binding isotherm for HS^- titration of receptor $\mathbf{2}^{\mathbf{CF_3}}$ in CD_3CN determined by ^1H NMR spectroscopy.

Table S8. Representative titration of receptor $\mathbf{2}^{\mathbf{CF_3}}$ with Br^- in CD_3CN.

Entry	V_{Guest} (μL)	[Host] (M)	[HS^-] (M)	Equiv.	δ NH (ppm)	δ CH (ppm)
0	0	1.2E-03	0.0E+00	0	7.79	8.14
1	5	1.2E-03	2.6E-04	0.21	7.81	8.14
2	10	1.2E-03	5.1E-04	0.42	7.83	8.15
3	20	1.2E-03	1.0E-03	0.83	7.86	8.15
4	30	1.2E-03	1.5E-03	1.22	7.89	8.16
5	45	1.2E-03	2.2E-03	1.78	7.93	8.17
6	60	1.2E-03	2.8E-03	2.30	7.97	8.18
7	80	1.2E-03	3.6E-03	2.97	8.01	8.19
8	100	1.2E-03	4.3E-03	3.58	8.05	8.2
9	130	1.2E-03	5.4E-03	4.44	8.1	8.21
10	160	1.2E-03	6.3E-03	5.21	8.13	8.22
11	200	1.2E-03	7.4E-03	6.14	8.17	8.23
12	240	1.2E-03	8.5E-03	6.97	8.21	8.24
13	290	1.2E-03	9.7E-03	7.89	8.25	8.25
14	350	1.2E-03	1.1E-02	8.85	8.28	8.26
15	430	1.2E-03	1.2E-02	9.94	8.32	8.27
16	530	1.2E-03	1.3E-02	11.07	8.35	8.27
17	680	1.2E-03	1.5E-02	12.39	8.38	8.28
18	880	1.2E-03	1.7E-02	13.71	8.42	8.29
19	1130	1.2E-03	1.8E-02	14.91	8.43	8.29
20	1380	1.2E-03	1.9E-02	15.79	8.45	8.3

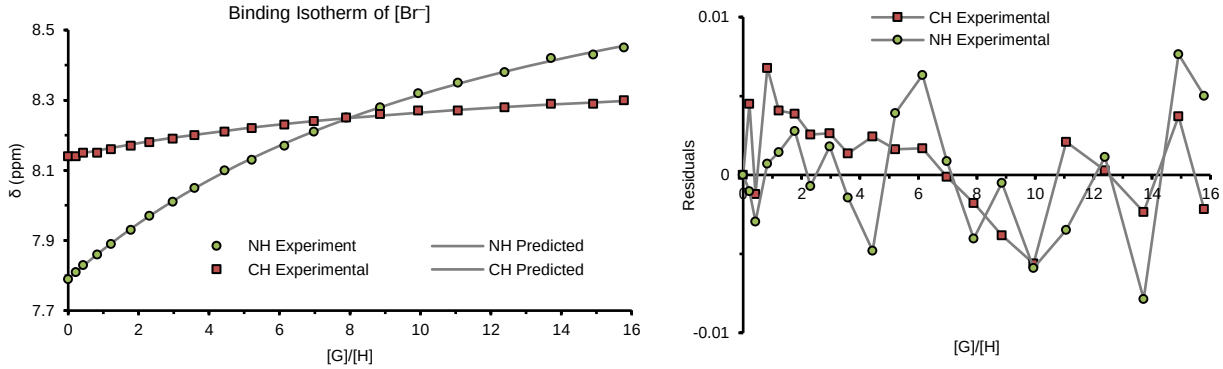
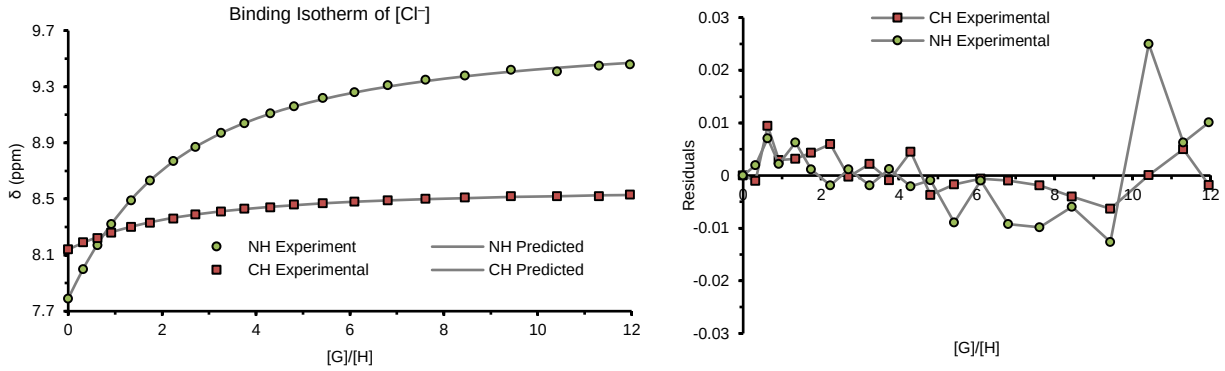


Figure S13. Representative binding isotherm for Br^- titration of receptor $\mathbf{2}^{\mathbf{CF_3}}$ in CD_3CN determined by ^1H NMR spectroscopy.

Table S9. Representative titration of receptor $\mathbf{2}^{\mathbf{CF_3}}$ with Cl^- in CD_3CN.

Entry	V_{Guest} (μL)	[Host] (M)	[HS^-] (M)	Equiv.	δ NH (ppm)	δ CH (ppm)
0	0	1.33E-03	0.00E+00	0.00	7.79	8.14
1	10	1.33E-03	4.23E-04	0.32	8	8.19
2	20	1.33E-03	8.30E-04	0.63	8.17	8.22
3	30	1.33E-03	1.22E-03	0.92	8.32	8.26
4	45	1.33E-03	1.78E-03	1.34	8.49	8.3
5	60	1.33E-03	2.31E-03	1.74	8.63	8.33
6	80	1.33E-03	2.98E-03	2.24	8.77	8.36
7	100	1.33E-03	3.60E-03	2.71	8.87	8.39
8	125	1.33E-03	4.32E-03	3.25	8.97	8.41
9	150	1.33E-03	4.98E-03	3.75	9.04	8.43
10	180	1.33E-03	5.71E-03	4.31	9.11	8.44
11	210	1.33E-03	6.39E-03	4.81	9.16	8.46
12	250	1.33E-03	7.20E-03	5.42	9.22	8.47
13	300	1.33E-03	8.10E-03	6.10	9.26	8.48
14	360	1.33E-03	9.04E-03	6.81	9.31	8.49
15	440	1.33E-03	1.01E-02	7.61	9.35	8.5
16	540	1.33E-03	1.12E-02	8.45	9.38	8.51
17	690	1.33E-03	1.25E-02	9.43	9.42	8.52
18	890	1.33E-03	1.38E-02	10.42	9.41	8.52
19	1140	1.33E-03	1.50E-02	11.31	9.45	8.52
20	1390	1.33E-03	1.59E-02	11.96	9.46	8.53

Figure S14. Representative binding isotherm for Cl^- titration of receptor $\mathbf{2}^{\mathbf{CF_3}}$ in CD_3CN determined by ^1H NMR spectroscopy.



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