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Supporting Information

Do CH–Anion and Anion–π Interactions Alter the Mechanism of 2:1 Host–Guest Complexation in Arylethynyl Monourea Anion Receptors?

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SUPPORTING INFORMATION

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Experimental Procedures

General methods. ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained on a Varian Mercury 300 MHz (^{1}H: 300.09 MHz), Inova 500 MHz (^{1}H: 500.10 MHz, ^{13}C 125.75 MHz, ^{19}F: 470.56 MHz), or Bruker Avance III HD 600 MHz NMR spectrometer with Prodigy multinuclear broadband BBO CryoProbe (^{1}H: 600.02 MHz, ^{13}C: 150.89 MHz). Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane (TMS) using non-deutrated solvent present in the bulk deutrated solvent ($CDCl_3$, ^{1}H 7.26 ppm, ^{13}C 77.16 ppm; *d*$_6$-DMSO: ^{1}H 2.50 ppm, ^{13}C 39.52 ppm; *d*$_6$-acetone ^{1}H 2.05 ppom, ^{13}C 206.7 ppm, 29.9 ppm). Mixed solvent systems were referenced to the most abundant solvent. All NMR spectra were processed using MestReNova NMR processing software. Unless otherwise specified, all materials were obtained from TCI-America, Sigma-Aldrich, or Acros and used as received. Tetrabutylammonium salts were dried at 50 °C in vacuo prior to use. Aniline **5** was synthesized and desilated following known procedures.[1]

3,5-Dinitrophenyl aniline 6. In a sealable flask, 1-iodo-3,5-dinitrobenzene (1.20 g, 4.08 mmol) was dissolved in DIPA (20 mL) and THF (20 mL). The mixture was purged with N_2 for 30 min, then CuI (0.076 g, 0.408 mmol) was added. The mixture was purged for an additional 30 min, followed by the addition of $Pd(PPh_3)_4$ (0.38 g, 0.327 mmol). An N_2-purged solution of 4-*tert*-butyl-2-ethynylaniline (1.05 g, 6.05 mmol) in DIPA (10 mL) and THF (10 mL) was then transferred into the flask via cannula. The flask was sealed and the mixture was stirred overnight at 50 °C. The cooled solution was filtered through a 6 cm silica gel plug eluting with CH_2Cl_2 and the concentrated *in vacuo*. Column chromatography (2:1 EtOAc:hexanes) of the crude material afforded **6** (1.24 g, 87%) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (t, J = 1.8 Hz, 1H), 8.64 (d, J = 2.0 Hz, 2H), 7.41 (d, J = 2.1 Hz, 1H), 7.17 (d, J = 7.5 Hz, 1H), 6.72 (d, J = 8.4 Hz, 1H), 4.21 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.94, 146.56, 141.69, 140.39, 129.54, 129.43, 127.77, 117.84, 115.17, 105.45, 93.43, 90.39, 34.40, 31.74. HRMS (TOF-MS-ES$^-$) for $C_{18}H_{16}N_3O_4$ $[M–H]^-$: calcd 338.1141, found 338.1157.

Pentafluorophenyl aniline 7. Following the procedure for the synthesis of **6**, iodopentafluorobenzene (1.25 g, 4.25 mmol) was reacted with 4-*tert*-butyl-2-ethynylaniline (1.11 g, 6.38 mmol) in the presence of THF (25 mL), DIPA (25 mL), CuI (0.040 g, 0.21 mmol), and

$Pd(PPh_3)_4$ (0.393 g, 0.340 mmol). Product **7** was obtained via a silica plug (2:1 hexanes:EtOAc) as a black-brown solid and used without further purification (1.04 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 2.3 Hz, 1H), 7.21 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.73 (d, *J* = 8.7 Hz, 1H), 4.52 (s, 2H), 1.26 (s, 9H). ^{13}C{^{19}F} NMR (126 MHz, $CDCl_3$) δ 147.25, 146.24, 141.08, 129.62, 128.91, 128.73, 128.22, 114.60, 106.01, 105.56, 80.31, 78.72, 34.08, 31.47. ^{19}F NMR (471 MHz, $CDCl_3$) δ –136.62 (dd, *J* = 22.1, 7.7 Hz), –153.44 (t, *J* = 41.0 Hz), –161.86 (m). HRMS (TOF-MS-ES$^+$) for $C_{18}H_{15}NF_5$ $[M–H]^+$: calcd 340.1125, found 340.1137.

3,5-Dinitrophenyl receptor 3. In flame dried glassware, aniline **6** (0.250 g, 0.737 mmol) and *p*-nitrophenyl isocyanate (0.212 g, 1.29 mmol) was dissolved in freshly distilled toluene (75 mL). The reaction mixture was stirred for 48 h at 50 °C. The reaction was quenched with acetone, allowed to cool, and concentrated *in vacuo*. Product **3** was precipitated with acetone from a hexanes solution (0.271 g, 73%) as an orange solid. ^{1}H NMR (500 MHz, *d*$_6$-acetone) δ 9.18 (s, 1H), 8.91 (t, *J* = 2.1 Hz, 1H), 8.34 (s, 1H), 8.24 (d, *J* = 9.1 Hz, 2H), 8.19 (d, *J* = 2.6 Hz, 1H), 7.80 (d, *J* = 9.2 Hz, 2H), 7.72 (d, *J* = 2.4 Hz, 1H), 7.57 (dd, *J* = 8.9, 2.4 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, *d*$_6$-acetone) δ 152.65, 149.82, 147.10, 146.93, 143.21, 139.15, 132.21, 130.51, 129.23, 127.29, 125.98, 121.14, 119.19, 118.85, 111.74, 92.10, 91.43, 35.08, 31.63. HRMS (TOF-MS-ES$^–$) for $C_{25}H_{20}N_5O_7$ $[M–H]^–$: calcd 502.1363, found 502.1358.

Pentafluorophenyl receptor 4. In flame dried glassware, aniline **7** (0.500 g, 1.47 mmol) and *p*-nitrophenyl isocyanate (0.423 g, 2.58 mmol) was dissolved in freshly distilled toluene (150 mL). The reaction mixture was stirred for 72 h at 50 °C. The reaction was quenched with acetone, allowed to cool, and concentrated *in vacuo*. Pure product **4** was precipitated out of hot EtOAc (0.574 g, 71%) as a yellow solid. ^{1}H NMR (500 MHz, *d*$_6$-DMSO/$CDCl_3$) δ 9.52 (s, 1H), 8.04 (s, 1H), 7.86 (dd, *J* = 9.2, 2.1 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.37 (dd, *J* = 9.1, 2.3 Hz, 2H), 7.18 (d, *J* = 2.3 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.4 Hz, 1H), 1.05 (s, 9H). ^{13}C{^{19}F} (125.75 MHz, *d*$_6$-DMSO/$CDCl_3$) 151.99, 145.76, 145.63, 145.57, 145.55, 138.52, 129.46, 127.91, 127.79, 124.96, 124.77, 120.10, 117.24, 110.03, 109.80, 79.91, 79.26, 39.99, 30.88. ^{19}F NMR (471 MHz, *d*$_6$-DMSO/$CDCl_3$) δ –135.24 (m), –152.00 (m), –161.49 (m). HRMS (TOF-MS-ES$^+$) for $C_{25}H_{18}F_5N_3O_7$ $[M–H]^+$: calcd 504.1347, found 504.1350.

X-Ray Crystallography

General details. Diffraction intensities were collected at 173 K on a Bruker Apex2 CCD diffractometer using CuKα radiation, λ = 1.54178 Å. Space group was determined based on systematic absences. Absorption correction was applied by SADABS.[2] Structure was 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. All H atoms were refined in calculated positions in a rigid group model. There are two symmetrically independent molecules in the crystal structure. One of the terminal –Me groups in the $[N(n\text{-}Bu)_4]^+$ cation is disordered over two positions in the ratio 0.69/0.31. The Br^- anion forms H-bonds to the two main molecules. Crystals of the investigated compound were very small needles and even using a strong *Incoatec IμS Cu* source the diffraction data were collected only up to $2\theta_{max} = 100°$. The reflections at high angles were very weak and as a result reflection statistics at high angles is poor and value of R_{int} is high. While the found X-ray structure is not precise, it provides clear chemical information about the formed complex. All calculations were performed by the Bruker SHELXL-2013 package.[3]

Crystal structure 3_2•(*n*-Bu)$_4$NBr. $C_{68}H_{84}BrN_{11}O_{15}S$, M = 1407.43, 0.23 x 0.01 x 0.01 mm, T = 173 K, Monoclinic, space group $P2_1/c$, a = 20.6647(10) Å, b = 10.3192(5) Å, c = 35.0367(16) Å, β = 104.992(3)°, V = 7217.0(6) Å^3, Z = 4, D_c = 1.295 Mg/m^3, μ(Cu) = 1.630 mm^{-1}, F(000) = 2960, $2\theta_{max}$ = 100.0°, 25199 reflections, 7300 independent reflections [R_{int} = 0.3631], R1 = 0.1166, wR2 = 0.2657 and GOF = 0.974 for 7300 reflections (850 parameters) with I>2σ(I), R1 = 0.3173, wR2 = 0.3633 and GOF = 0.974 for all reflections, max/min residual electron density +1.343/–0.516 eÅ^3. CCDC 1507418 contains the supplementary crystallographic data for these compounds. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Titrations

General Titration Procedures. Concentration of receptor was kept constant by preparing a stock solution of the receptor and performing a serial dilution with the receptor stock solution to dissolve the guest. Receptor concentration was maintained constant throughout the titration to avoid concentration effects on the proton chemical shifts. Tetrabutylammonium salts, purchased from TCI America or SigmaAldrich, were dried by heating to 50 °C *in vacuo* before use. Hamilton gas-tight syringes were used for all titrations. Titrations were performed in triplicate and the reported association constants represent the average fits across all titrations. Representative data are provided for each receptor and halide.

^{1}H NMR Titration Conditions. ^{1}H NMR titrations were carried out on an Inova 500 MHz NMR spectrometer (^{1}H: 500.10 MHz). Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane (TMS) using non-deutrated solvent present in the bulk deutrated solvent ($CDCl_3$, ^{1}H 7.26 ppm; *d*$_6$-DMSO: ^{1}H 2.50 ppm). Mixed solvent systems were referenced to the most abundant solvent. All NMR spectra were processed using MestReNova NMR processing software. Association constants were determined using step-wise non-linear regression fitting in MatLab.[4]

Tetrabutylamamonium chloride with 3. A concentrated solution of **3** (2.45 mg, [R]=4.87 mM) in 10% *d*$_6$-DMSO/$CDCl_3$ (1.00 mL) was prepared. A serial dilution was then performed with 250 μL of 4.87 mM solution of **3** diluted to 3 mL to yield the stock solution of **3** ([R]=0.406 mM). This solution was used in the dilution of TBACl guest solution (6.53 mg, [G]= 9.98 mM). The remaining stock solution (0.600 mL) was used as the starting volume in the NMR tube.

Table S1. Representative titration data for Cl^- with **3**.

	Guest (µL)	[**1**] (M)	[Cl^-] (M)	Equiv.	H^c δ (ppm)	H^a δ (ppm)	H^b δ (ppm)
1	0	4.06E-04	0.00E+00	0.00	9.553	8.725	8.126
2	5	4.06E-04	8.25E-05	0.20	9.634	8.737	8.167
3	10	4.06E-04	1.64E-04	0.40	9.713	8.751	8.208
4	15	4.06E-04	2.43E-04	0.60	9.783	8.759	8.244
5	20	4.06E-04	3.22E-04	0.79	9.844	8.771	8.276
6	25	4.06E-04	3.99E-04	0.98	9.901	8.779	8.304
7	30	4.06E-04	4.75E-04	1.17	9.950	8.785	8.329
8	35	4.06E-04	5.50E-04	1.36	9.998	8.794	8.354
9	40	4.06E-04	6.24E-04	1.54	10.039	8.800	8.375
10	50	4.06E-04	7.67E-04	1.89	10.114	8.813	8.417
11	60	4.06E-04	9.07E-04	2.24	10.186	8.824	8.452
12	80	4.06E-04	1.17E-03	2.89	10.295	8.842	8.508
13	100	4.06E-04	1.43E-03	3.51	10.385	8.857	8.556
14	150	4.06E-04	2.00E-03	4.92	10.550	8.885	8.641
15	200	4.06E-04	2.49E-03	6.15	10.661	8.903	8.709
16	300	4.06E-04	3.33E-03	8.20	10.789	8.929	8.770
17	400	4.06E-04	3.99E-03	9.84	10.873	8.939	8.810
18	600	4.06E-04	4.99E-03	12.30	10.926	8.952	8.840

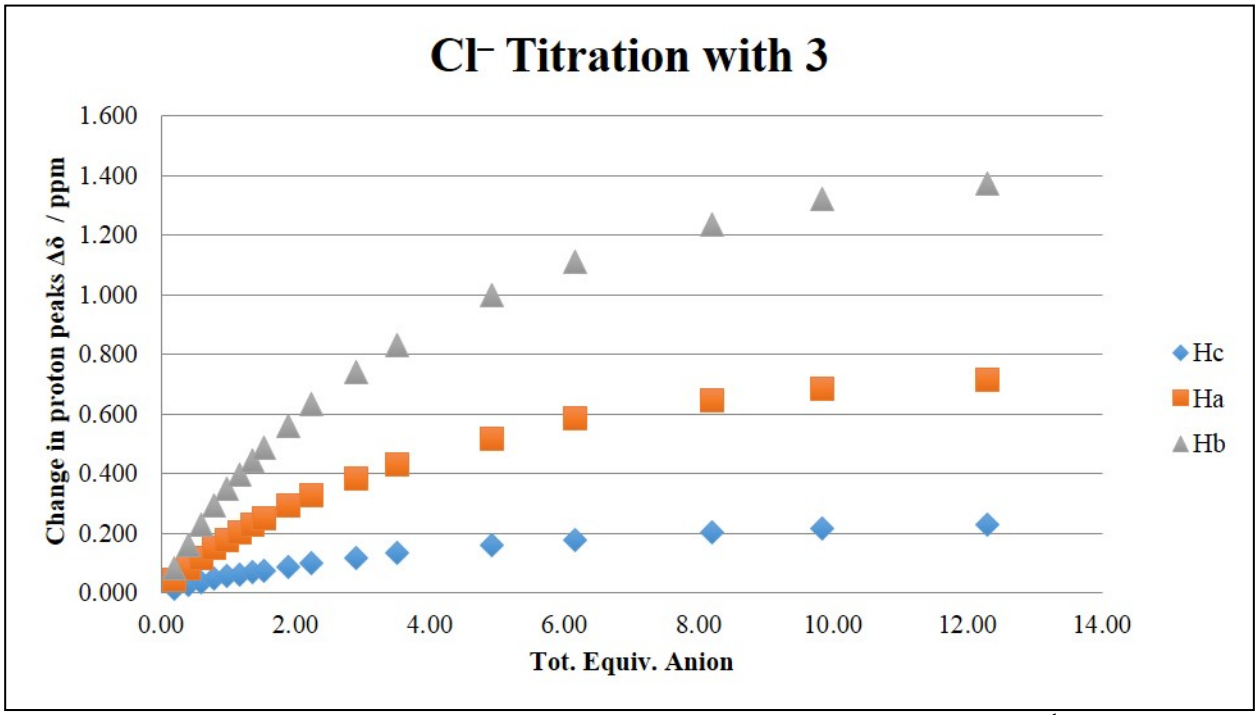


Figure S1. Binding isotherm for Cl^- titration with **3** in 10% d_6-DMSO/$CDCl_3$ by ^1H NMR.

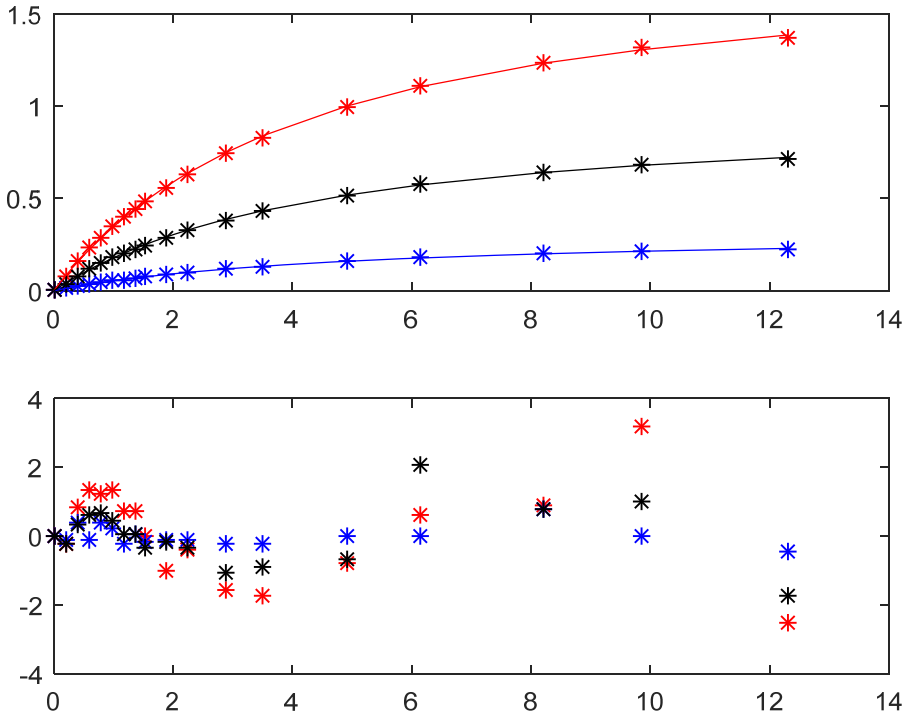


Figure S2. MatLab fit of binding isotherm for Cl^- titration with **3**.

Tetrabutylamamonium bromide with 3. A concentrated solution of **3** (5.16 mg, [R]=5.12 mM) in 10% *d*$_6$-DMSO/$CDCl_3$ (2.00 mL) was prepared. A serial dilution was then performed with 590 µL of 5.12 mM solution of **3** diluted to 3 mL to yield the stock solution of **3** ([R]=1.01 mM). This solution was used in the dilution of TBABr guest solution (45.03 mg, [G]=6.00 mM). The remaining stock solution (0.600 mL) was used as the starting volume in the NMR tube.

Table S2. Representative titration data for Br^- with **3**.

	Guest (μL)	[**1**] (M)	[Br^-] (M)	Equiv.	H^c δ (ppm)	H^a δ (ppm)	H^b δ (ppm)
1	0	1.01E-03	0.00E+00	0.00	9.590	8.730	8.144
2	5	1.01E-03	4.95E-04	0.49	9.743	8.759	8.225
3	10	1.01E-03	9.83E-04	0.98	9.828	8.770	8.270
4	15	1.01E-03	1.46E-03	1.45	9.900	8.784	8.310
5	20	1.01E-03	1.93E-03	1.92	9.943	8.793	8.333
6	25	1.01E-03	2.40E-03	2.38	9.984	8.799	8.356
7	30	1.01E-03	2.85E-03	2.83	10.024	8.805	8.377
8	35	1.01E-03	3.30E-03	3.28	10.058	8.810	8.395
9	40	1.01E-03	3.75E-03	3.72	10.089	8.816	8.412
10	50	1.01E-03	4.61E-03	4.58	10.139	8.825	8.440
11	60	1.01E-03	5.45E-03	5.41	10.194	8.834	8.470
12	80	1.01E-03	7.05E-03	7.00	10.258	8.846	8.506
13	100	1.01E-03	8.56E-03	8.50	10.312	8.855	8.534
14	150	1.01E-03	1.20E-02	11.90	10.415	8.873	8.592
15	200	1.01E-03	1.50E-02	14.87	10.458	8.885	8.616
16	300	1.01E-03	2.00E-02	19.83	10.544	8.896	8.662
17	400	1.01E-03	2.40E-02	23.79	10.581	8.904	8.682
18	600	1.01E-03	3.00E-02	29.74	10.589	8.904	8.693

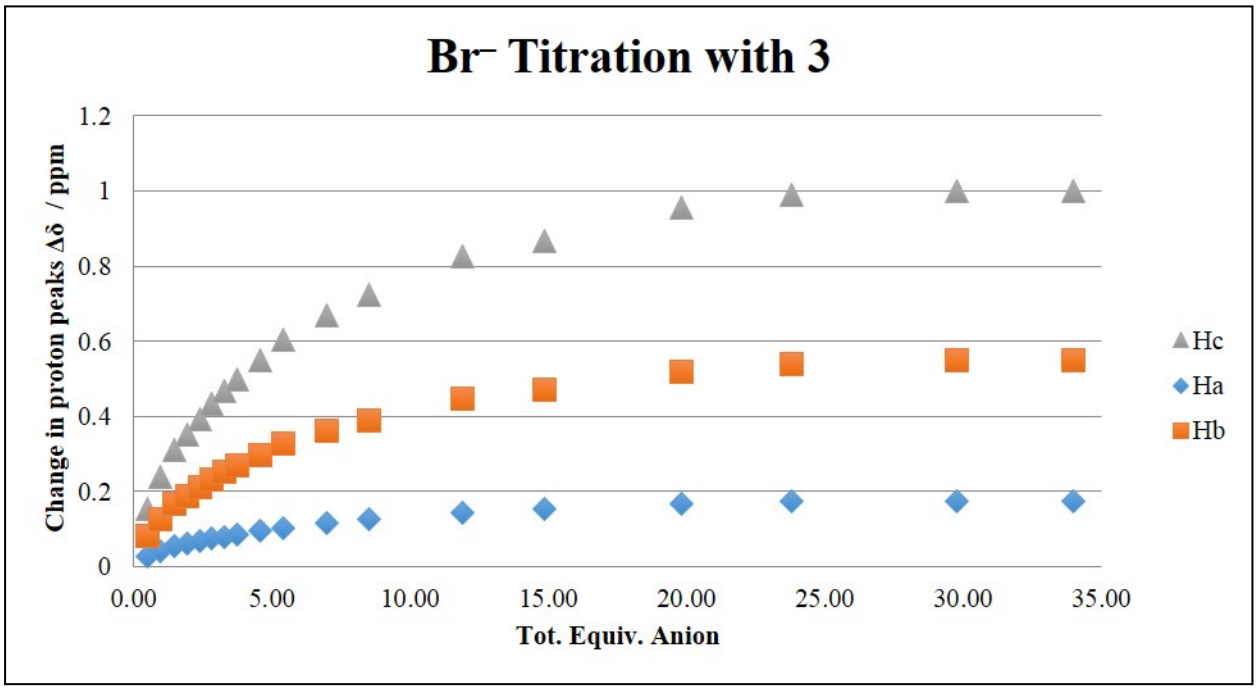


Figure S3. Binding isotherm for Br^- titration with **3** in 10% d_6-DMSO/$CDCl_3$ by ^1H NMR.

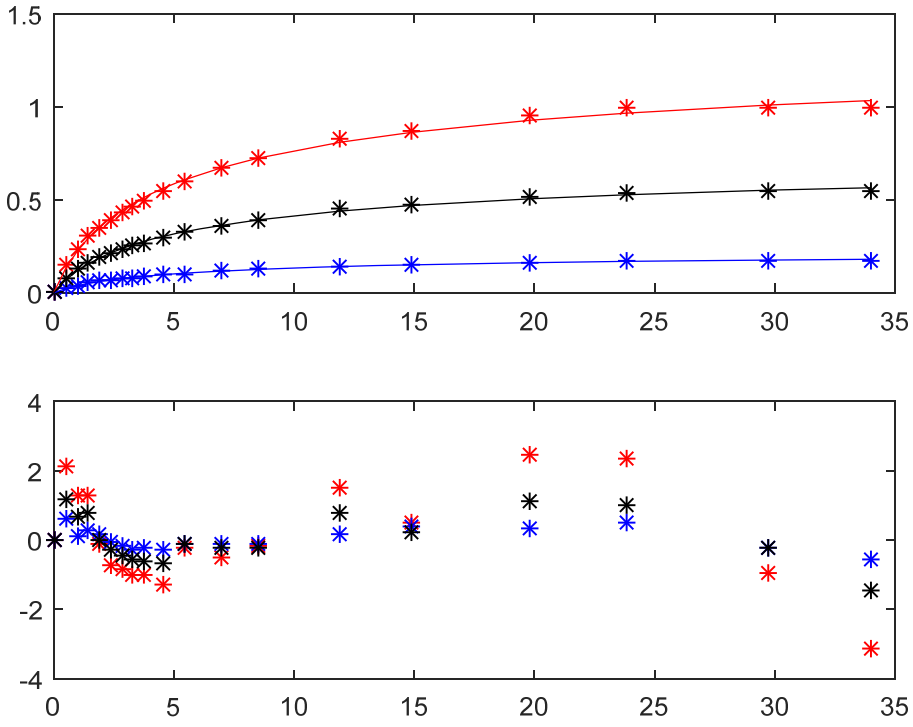


Figure S4. MatLab fit of binding isotherm for Br^- titration with **3**.

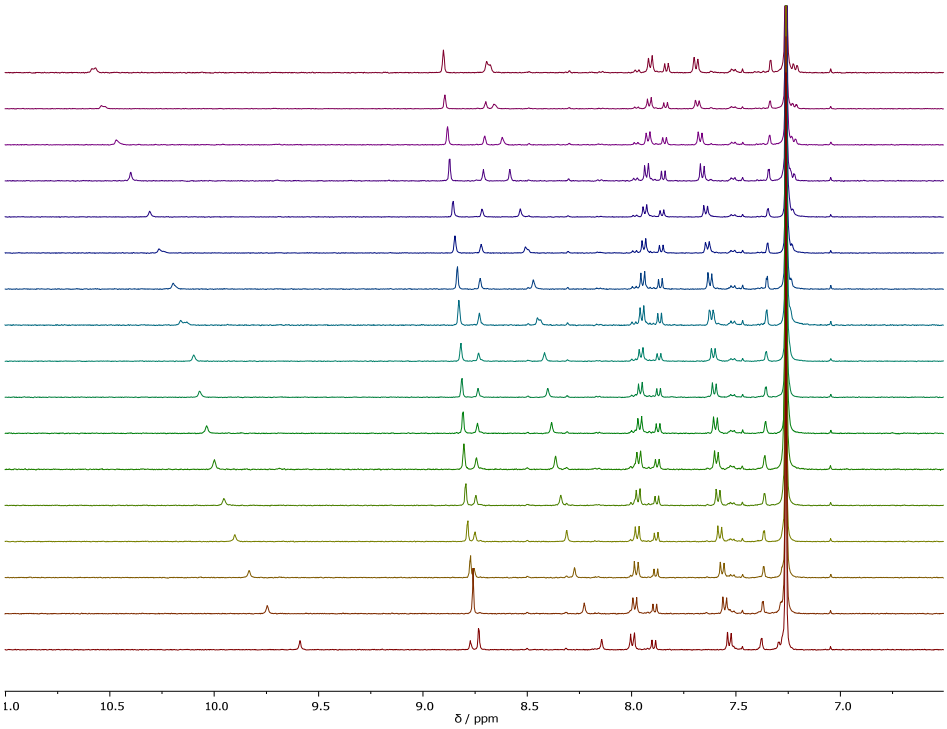


Figure S5. ^1H NMR spectra of Br^- titration with **3**.

Tetrabutylamamonium iodide with 3. A concentrated solution of **3** (5.22 mg, [R]=5.18 mM) in 10% d_6-DMSO/$CDCl_3$ (2.00 mL) was prepared. A serial dilution was then performed with 590 μL of 5.18 mM solution of **3** diluted to 3 mL to yield the stock solution of **3** ([R]=1.02 mM). This solution was used in the dilution of TBAI guest solution (51.76 mg, [G]=5.94 mM). The remaining stock solution (0.600 mL) was used as the starting volume in the NMR tube.

Table S3. Representative titration data for I^- with **3**.

	Guest (μL)	[**1**] (M)	[I^-] (M)	Equiv.	H^c δ (ppm)	H^a δ (ppm)	H^b δ (ppm)
1	0	1.01E-03	0.00E+00	0.00	9.590	8.730	8.144
2	5	1.01E-03	4.95E-04	0.49	9.743	8.759	8.225
3	10	1.01E-03	9.83E-04	0.98	9.828	8.770	8.270
4	15	1.01E-03	1.46E-03	1.45	9.900	8.784	8.310
5	20	1.01E-03	1.93E-03	1.92	9.943	8.793	8.333
6	25	1.01E-03	2.40E-03	2.38	9.984	8.799	8.356
7	30	1.01E-03	2.85E-03	2.83	10.024	8.805	8.377
8	35	1.01E-03	3.30E-03	3.28	10.058	8.810	8.395
9	40	1.01E-03	3.75E-03	3.72	10.089	8.816	8.412
10	50	1.01E-03	4.61E-03	4.58	10.139	8.825	8.440
11	60	1.01E-03	5.45E-03	5.41	10.194	8.834	8.470
12	80	1.01E-03	7.05E-03	7.00	10.258	8.846	8.506
13	100	1.01E-03	8.56E-03	8.50	10.312	8.855	8.534
14	150	1.01E-03	1.20E-02	11.90	10.415	8.873	8.592
15	200	1.01E-03	1.50E-02	14.87	10.458	8.885	8.616
16	300	1.01E-03	2.00E-02	19.83	10.544	8.896	8.662
17	400	1.01E-03	2.40E-02	23.79	10.581	8.904	8.682
18	600	1.01E-03	3.00E-02	29.74	10.589	8.904	8.693

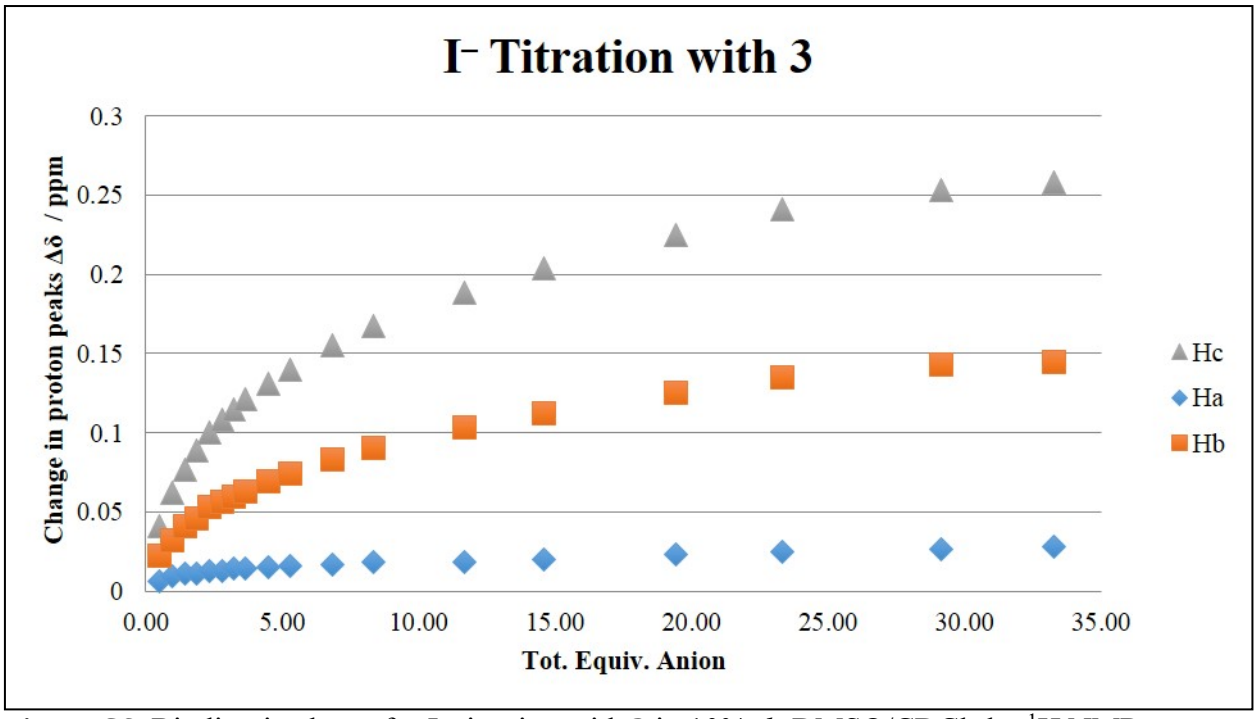


Figure S6. Binding isotherm for I^- titration with **3** in 10% d_6-DMSO/$CDCl_3$ by ^1H NMR.

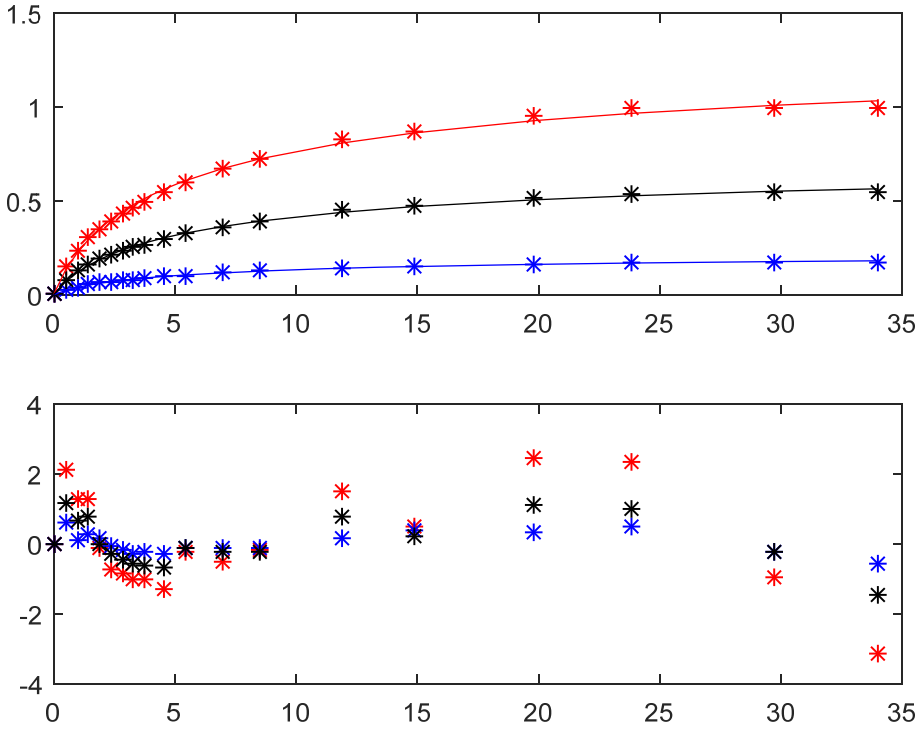


Figure S7. MatLab fit of binding isotherm for I^- titration with **3**.

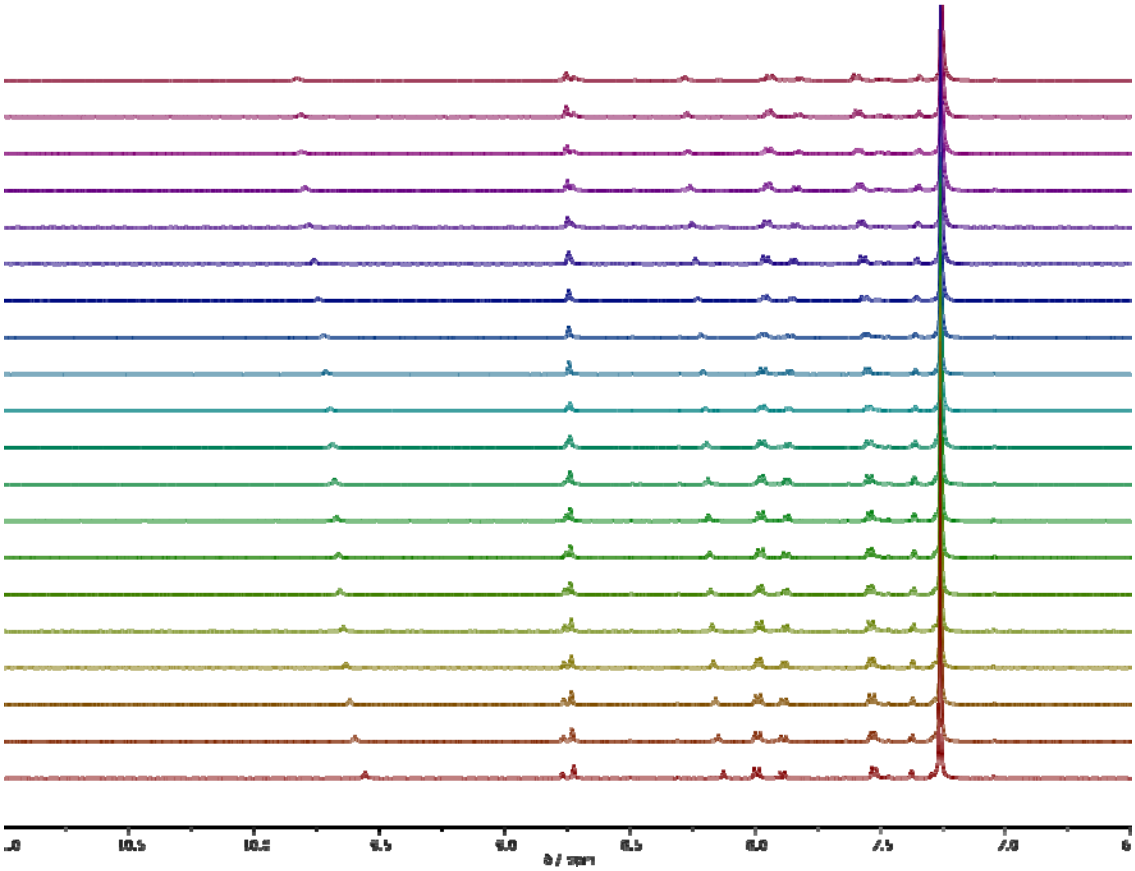


Figure S8. ^{1}H NMR spectra of I^{-} titration with **3**.

Tetrabutylamamonium chloride with 4. A concentrated solution of **4** (2.96mg, [R]=5.88 mM) in 10% *d*$_6$-DMSO/$CDCl_3$ (1.00 mL) was prepared. A serial dilution was then performed with 511 µL of 5.88 mM solution of **4** diluted to 3 mL to yield the stock solution of **4** ([R]=1.00 mM). This solution was used in the dilution of TBACl guest solution (9.56 mg, [G]=14.9 mM). The remaining stock solution (0.600 mL) was used as the starting volume in the NMR tube. The calculated association constants for the titration of TBACl with **4** were at the limits of ^{1}H NMR titrations, although errors were less than 15% across three titrations. The µM concentrations needed to obtain UV-Vis spectroscopy titration data dilute out the expected 2:1 host-guest model, however, leading to titrations only appropriately fit to a 1:1 host-guest model.

Table S4. Representative titration data for Cl^- with **4**.

	Guest (μL)	[**2**] (M)	[Cl^-] (M)	Equiv.	H^a δ (ppm)	H^b δ (ppm)
1	0	1.00E-03	0.00E+00	0.00	9.617	8.119
2	5	1.00E-03	1.23E-04	0.12	9.888	8.230
3	10	1.00E-03	2.44E-04	0.24	10.145	8.335
4	15	1.00E-03	3.62E-04	0.36	10.379	8.428
5	20	1.00E-03	4.79E-04	0.48	10.562	8.502
6	25	1.00E-03	5.94E-04	0.59	10.695	8.555
7	30	1.00E-03	7.08E-04	0.71	10.775	8.587
8	35	1.00E-03	8.19E-04	0.82	10.819	8.604
9	40	1.00E-03	9.29E-04	0.93	10.847	8.615
10	50	1.00E-03	1.14E-03	1.14	10.877	8.626
11	60	1.00E-03	1.35E-03	1.35	10.892	8.631
12	80	1.00E-03	1.75E-03	1.75	10.910	8.637
13	100	1.00E-03	2.12E-03	2.12	10.919	8.640
14	150	1.00E-03	2.97E-03	2.97	10.929	8.643
15	200	1.00E-03	3.71E-03	3.71	10.933	8.643
16	300	1.00E-03	4.95E-03	4.95	10.939	8.645
17	400	1.00E-03	5.94E-03	5.93	10.941	8.645
18	600	1.00E-03	7.43E-03	7.42	10.944	8.646

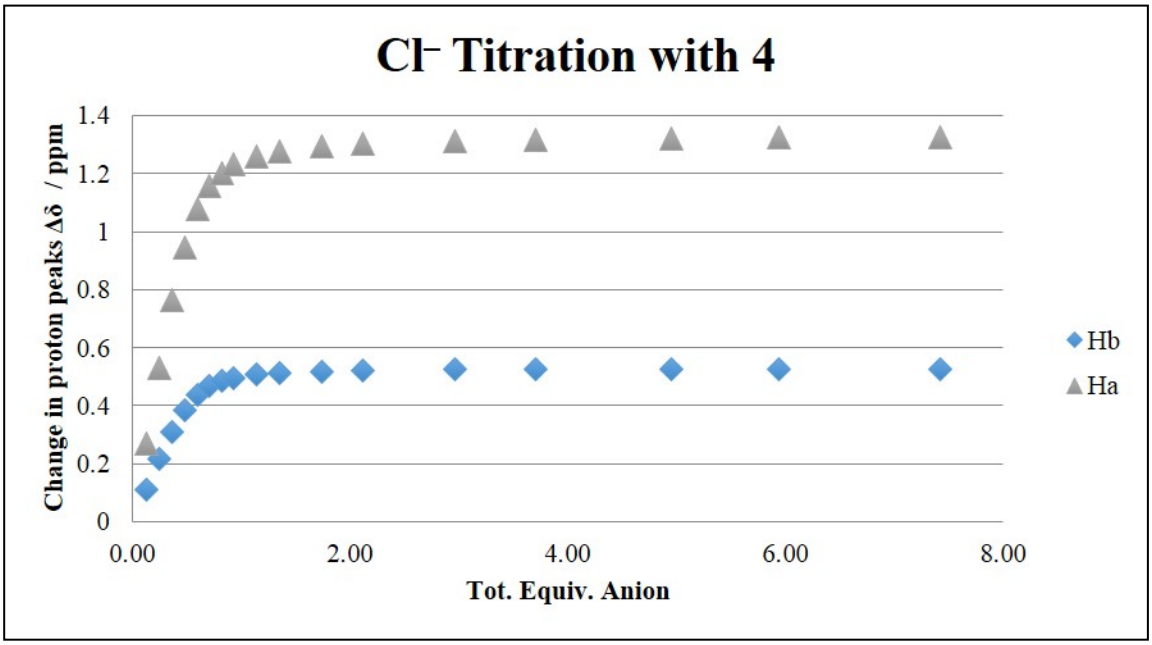


Figure S9. Binding isotherm for Cl^- titration with **4** in 10% d_6-DMSO/$CDCl_3$ by ^1H NMR.

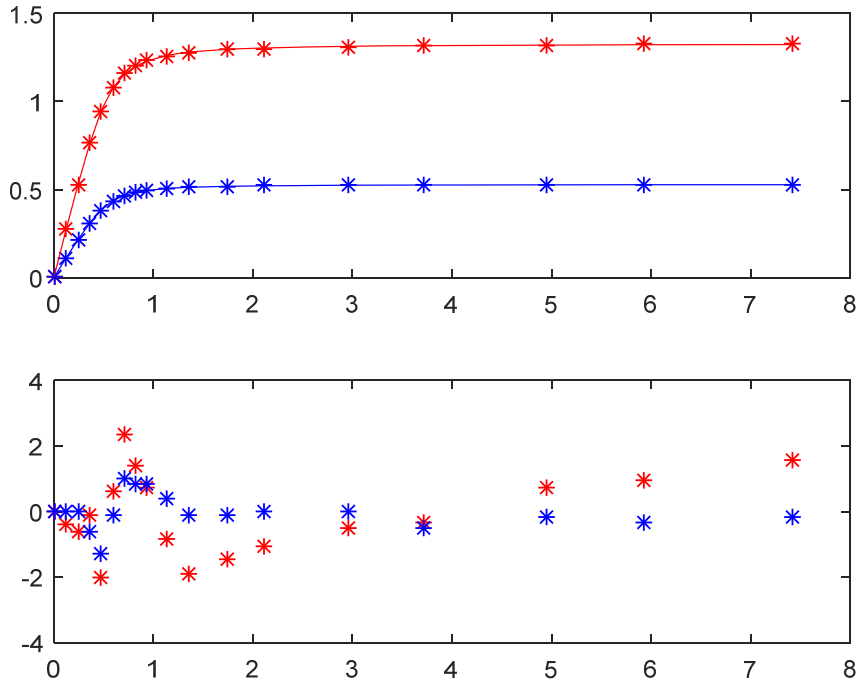


Figure S10. MatLab fit of binding isotherm for Cl^- titration with **4**.

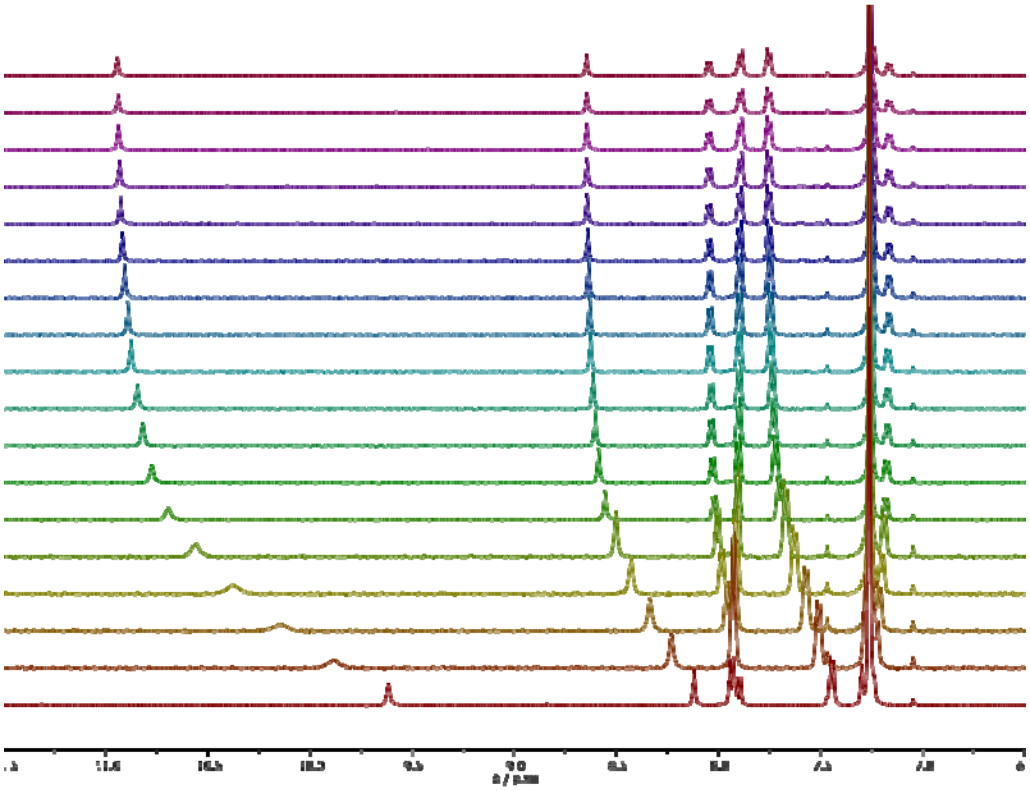


Figure S11. ^1H NMR spectra of Cl^- titration with **4**.

Tetrabutylamamonium bromide with 4. A concentrated solution of **4** (5.21 mg, [R]=5.17 mM) in 10% d_6-DMSO/$CDCl_3$ (2.00 mL) was prepared. A serial dilution was then performed with 590 μL of 5.17 mM solution of **4** diluted to 3 mL to yield the stock solution of **4** ([R]=1.02 mM). This solution was used in the dilution of TBABr guest solution (23.01 mg, [G]=31.0 mM). The remaining stock solution (0.600 mL) was used as the starting volume in the NMR tube.

Table S5. Representative titration data for Br^- with **2**.

	Guest (μL)	[**2**] (M)	[Br^-] (M)	Equiv.	H^a δ (ppm)	H^b δ (ppm)
1	0	1.02E-03	0.00E+00	0.25	9.754	8.178
2	5	1.02E-03	2.56E-04	0.50	9.975	8.285
3	10	1.02E-03	5.08E-04	0.74	10.101	8.345
4	15	1.02E-03	7.55E-04	0.98	10.181	8.382
5	20	1.02E-03	9.99E-04	1.22	10.233	8.407
6	25	1.02E-03	1.24E-03	1.45	10.266	8.422
7	30	1.02E-03	1.47E-03	1.68	10.290	8.434
8	35	1.02E-03	1.71E-03	1.90	10.307	8.441
9	40	1.02E-03	1.94E-03	2.34	10.322	8.447
10	50	1.02E-03	2.38E-03	2.77	10.341	8.456
11	60	1.02E-03	2.82E-03	3.58	10.356	8.463
12	80	1.02E-03	3.64E-03	4.35	10.369	8.468
13	100	1.02E-03	4.42E-03	6.09	10.377	8.472
14	150	1.02E-03	6.19E-03	7.61	10.388	8.477
15	200	1.02E-03	7.74E-03	10.14	10.391	8.478
16	300	1.02E-03	1.03E-02	12.17	10.394	8.478
17	400	1.02E-03	1.24E-02	15.21	10.398	8.480
18	600	1.02E-03	1.55E-02	0.25	10.398	8.480

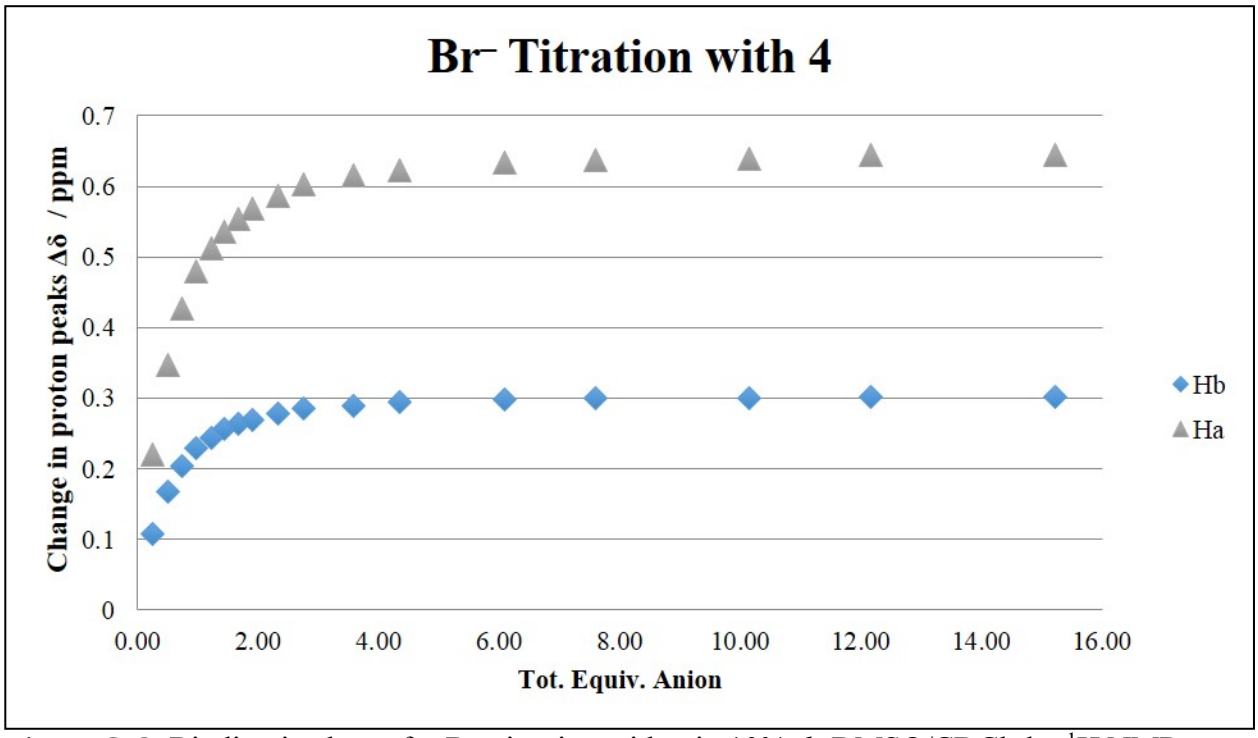


Figure S12. Binding isotherm for Br^- titration with **4** in 10% d_6-DMSO/$CDCl_3$ by ^1H NMR.

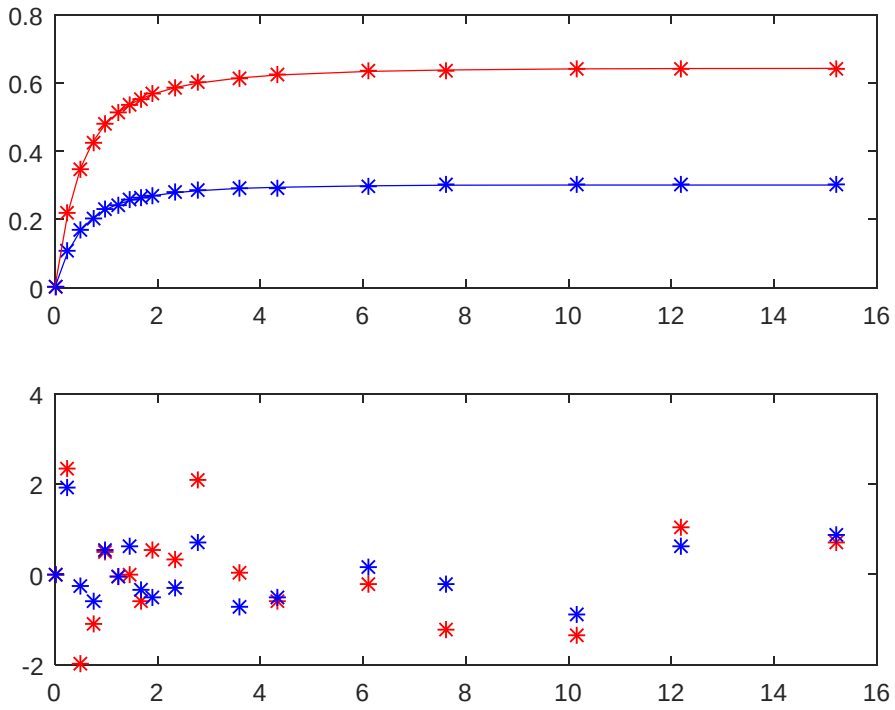


Figure S13. MatLab fit of binding isotherm for Br^- titration with **4**.

Tetrabutylamamonium iodide with 4. A concentrated solution of **4** (5.21 mg, [R]=5.17 mM) in 10% d_6-DMSO/$CDCl_3$ (2.00 mL) was prepared. A serial dilution was then performed with 576 µL of 5.17 mM solution of **4** diluted to 3 mL to yield the stock solution of **4** ([R]=0.994 mM). This solution was used in the dilution of TBAI guest solution (26.11mg, [G]=31.21 mM). The remaining stock solution (0.600 mL) was used as the starting volume in the NMR tube.

Table S6. Representative titration data for I^- with **4**.

	Guest (µL)	[**2**] (M)	[I^-] (M)	Equiv.	H^a δ (ppm)	H^b δ (ppm)
1	0	9.94E-04	0.00E+00	0.26	9.644	8.131
2	5	9.94E-04	2.58E-04	0.51	9.651	8.135
3	10	9.94E-04	5.12E-04	0.77	9.661	8.141
4	15	9.94E-04	7.61E-04	1.01	9.668	8.146
5	20	9.94E-04	1.01E-03	1.26	9.675	8.151
6	25	9.94E-04	1.25E-03	1.50	9.681	8.154
7	30	9.94E-04	1.49E-03	1.73	9.685	8.156
8	35	9.94E-04	1.72E-03	1.96	9.689	8.160
9	40	9.94E-04	1.95E-03	2.42	9.691	8.161
10	50	9.94E-04	2.40E-03	2.86	9.698	8.166
11	60	9.94E-04	2.84E-03	3.70	9.708	8.170
12	80	9.94E-04	3.67E-03	4.49	9.718	8.177
13	100	9.94E-04	4.46E-03	6.28	9.726	8.183
14	150	9.94E-04	6.24E-03	7.85	9.750	8.197
15	200	9.94E-04	7.80E-03	10.47	9.767	8.206
16	300	9.94E-04	1.04E-02	12.57	9.778	8.214
17	400	9.94E-04	1.25E-02	15.71	9.788	8.223
18	600	9.94E-04	1.56E-02	0.26	9.803	8.230

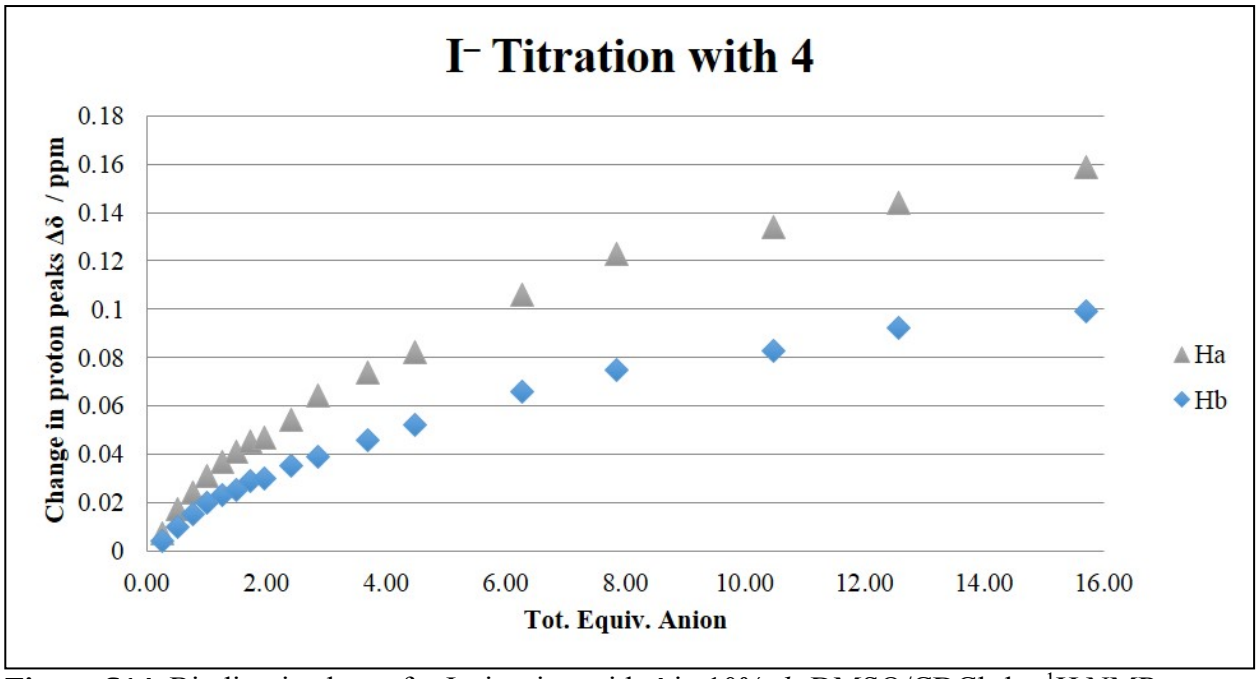


Figure S14. Binding isotherm for I^- titration with **4** in 10% *d*$_6$-DMSO/$CDCl_3$ by ^1H NMR.

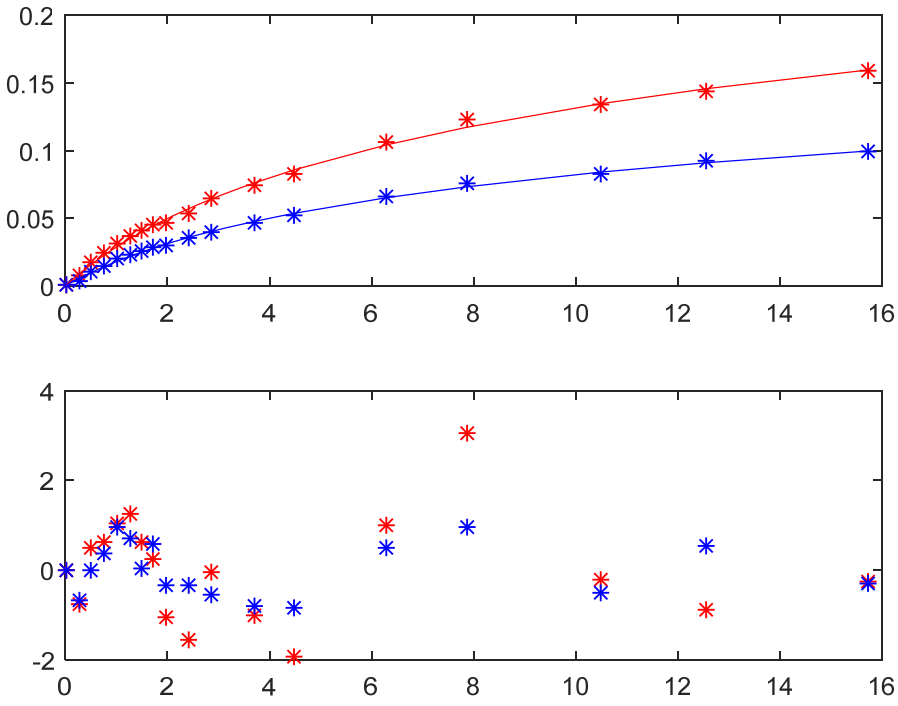


Figure S15. MatLab fit of binding isotherm for I^- titration with **4**.

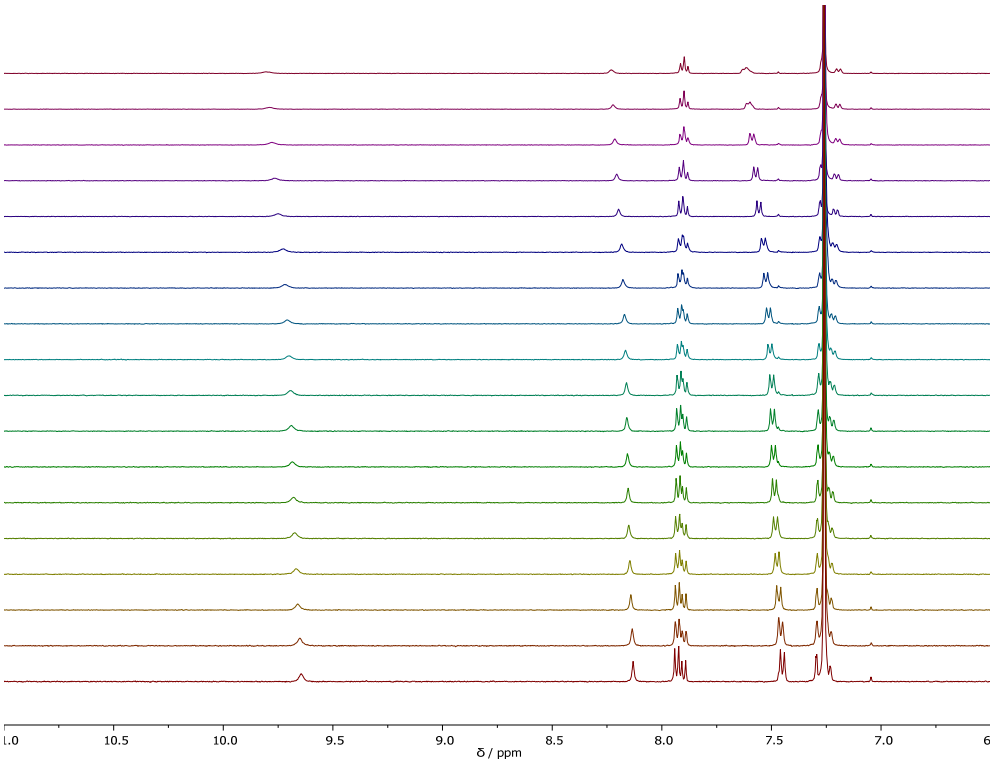


Figure S16. ^{1}H NMR spectra of I^{-} titration with **4**.

UV-Vis Titrations

General Conditions. UV-Vis titrations were carried out on an HP 8453 UV-Vis spectrometer. Water-saturated 10% DMSO/$CHCl_3$ was prepared in the same manner as for the ^1H NMR titrations. Association constants were determined by non-linear regression using Open Data Fit.[5]

Tetrabutylammonium chloride with 4. A concentrated solution of **4** (2.00 mg, [R]=0.199 mM) in 10% DMSO/$CHCl_3$ (20.00 mL) was prepared. A serial dilution was then performed with 50 μL of 0.199 mM solution of **4** diluted to 5 mL to yield the stock solution of **4** ([R]= 1.99 μM). A 2 mL solution of TBACl (2.53 mg, [G]=0.984 mM) was prepared by serial dilution with the stock solution of **4**. The starting volume in the cuvette was 2.0 mL.

Table S7. Representative titration data for Cl^- with **4**.

	Guest (μL)	[**2**] (M)	[Cl^-] (M)	Equiv.
1	0	1.99E-06	0.00E+00	0.00
2	5	1.99E-06	2.45E-06	1.23
3	10	1.99E-06	4.89E-06	2.46
4	15	1.99E-06	9.74E-06	4.90
5	20	1.99E-06	1.93E-05	9.71
6	25	1.99E-06	2.87E-05	14.42
7	30	1.99E-06	3.78E-05	19.05
8	40	1.99E-06	4.68E-05	23.58
9	50	1.99E-06	5.79E-05	29.13
10	60	1.99E-06	6.86E-05	34.55
11	70	1.99E-06	8.94E-05	45.02
12	80	1.99E-06	1.09E-04	55.03
13	100	1.99E-06	1.28E-04	64.60
14	120	1.99E-06	1.47E-04	73.76
15	140	1.99E-06	1.64E-04	82.54
16	180	1.99E-06	1.97E-04	99.05
17	220	1.99E-06	2.27E-04	114.28
18	300	1.99E-06	2.55E-04	128.39
19	400	1.99E-06	3.05E-04	153.69
20	600	1.99E-06	3.49E-04	175.73
21	800	1.99E-06	4.22E-04	212.24

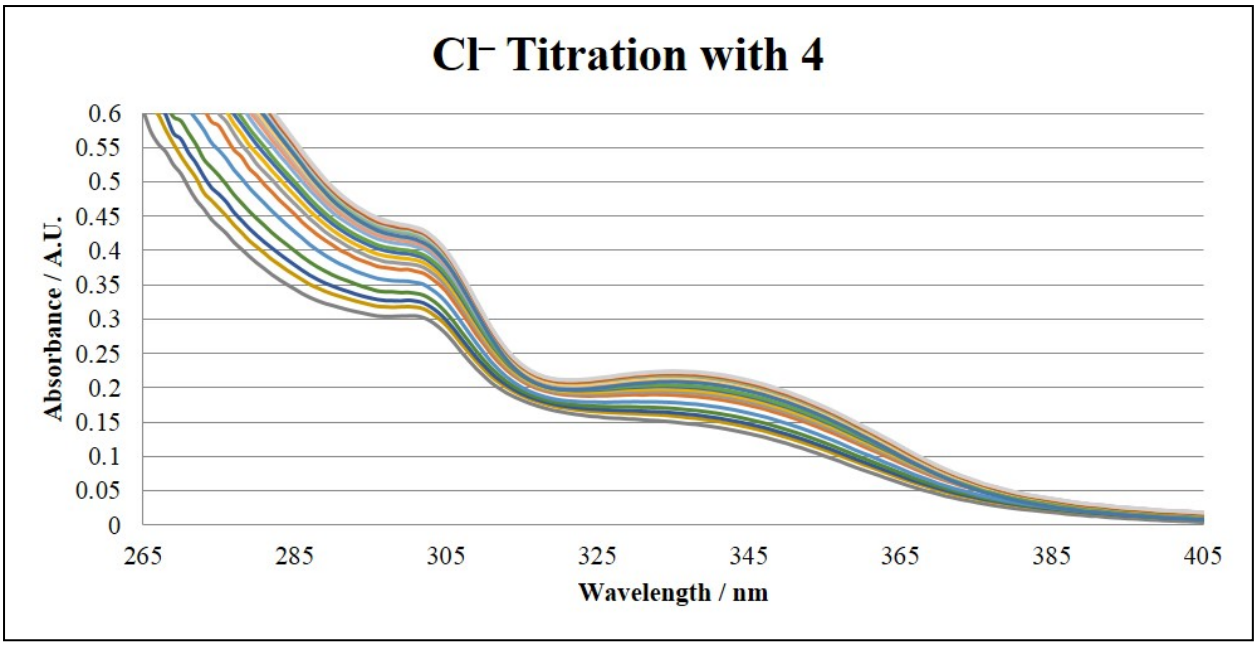


Figure S17. UV-Vis spectra of **4** titrated with Cl^- in 10% -DMSO/$CHCl_3$.

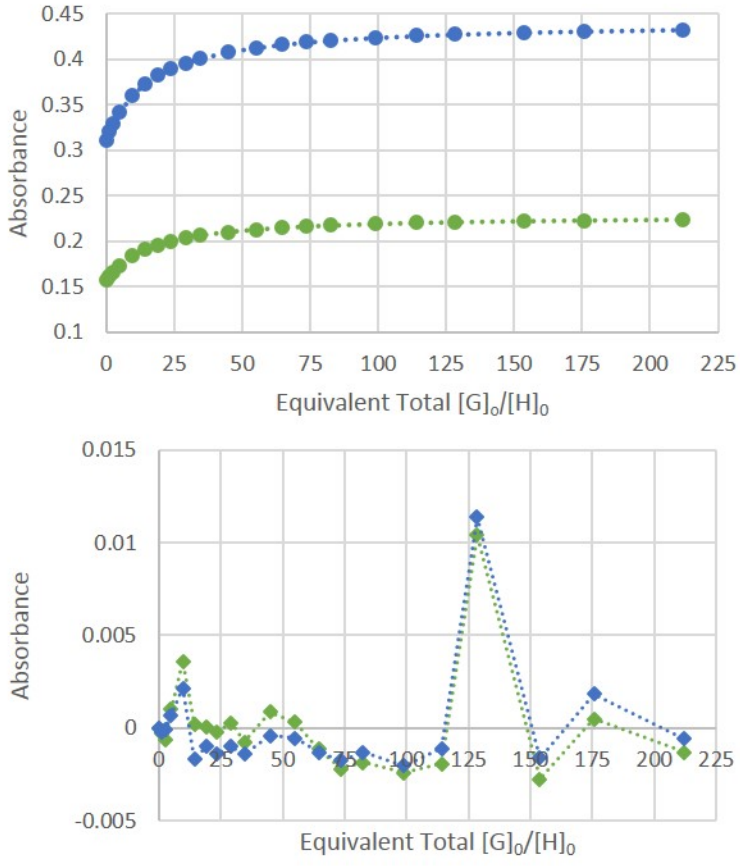


Figure S18. Open Data Fit fit of binding isotherm for Cl^- titration with **4**.

Job's Plot Analysis

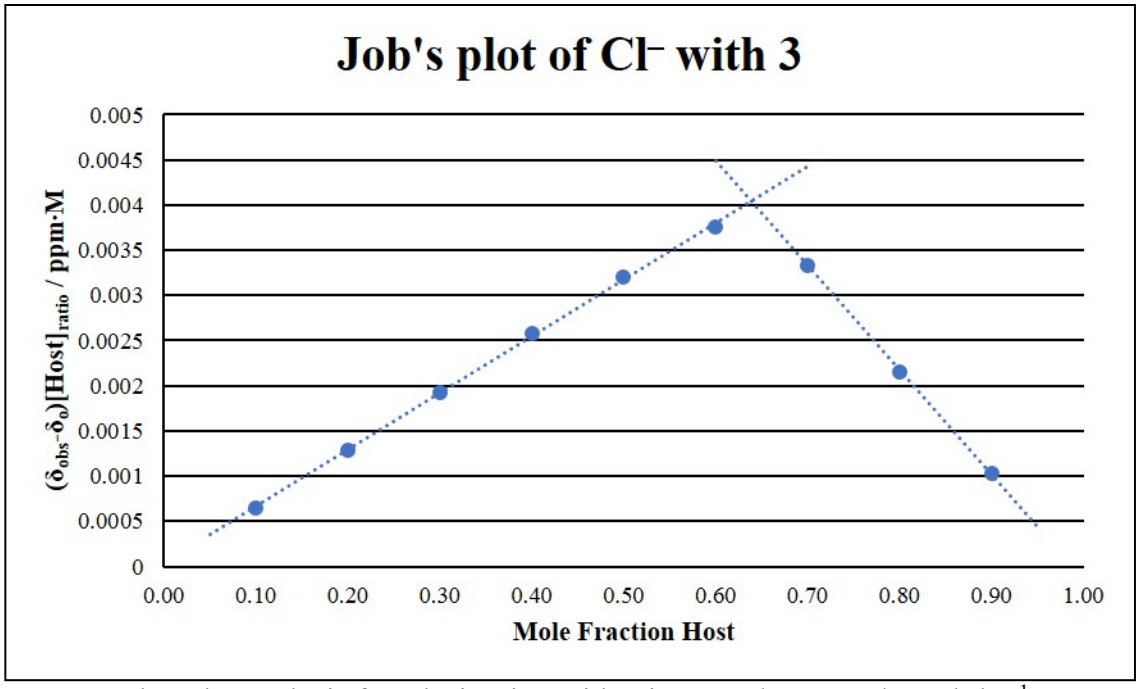


Figure S18. Job's plot analysis for Cl^- titration with **3** in 10% *d*$_6$-DMSO/$CDCl_3$ by ^1H NMR.

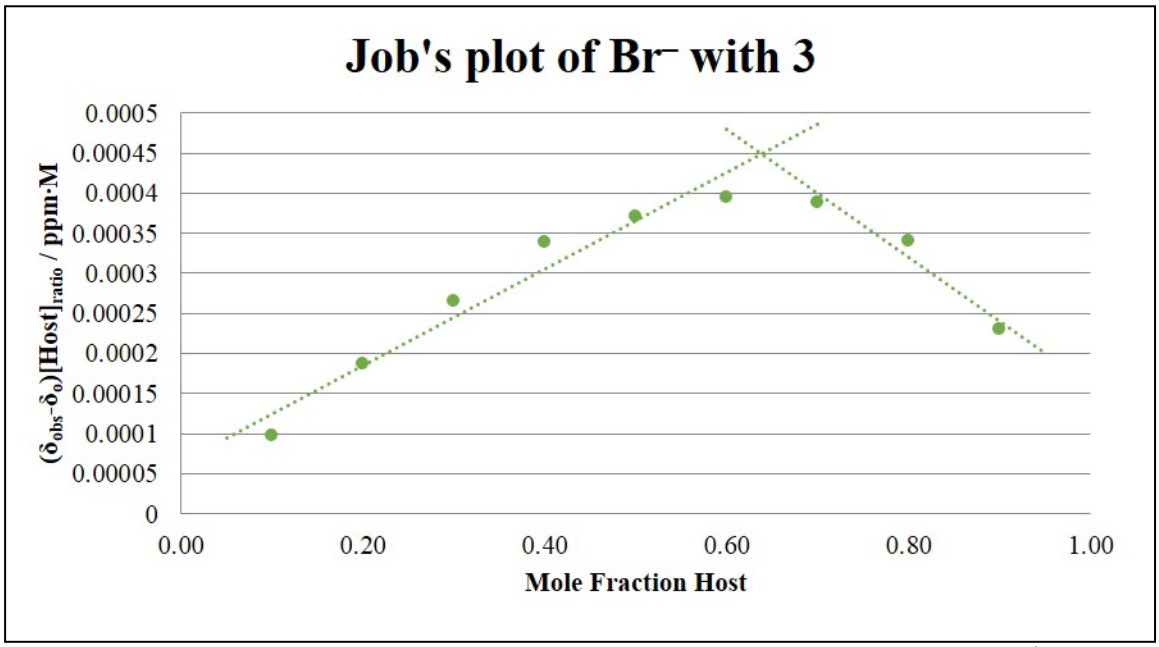


Figure S19. Job's plot analysis for Br^- titration with **3** in 10% *d*$_6$-DMSO/$CDCl_3$ by ^1H NMR.

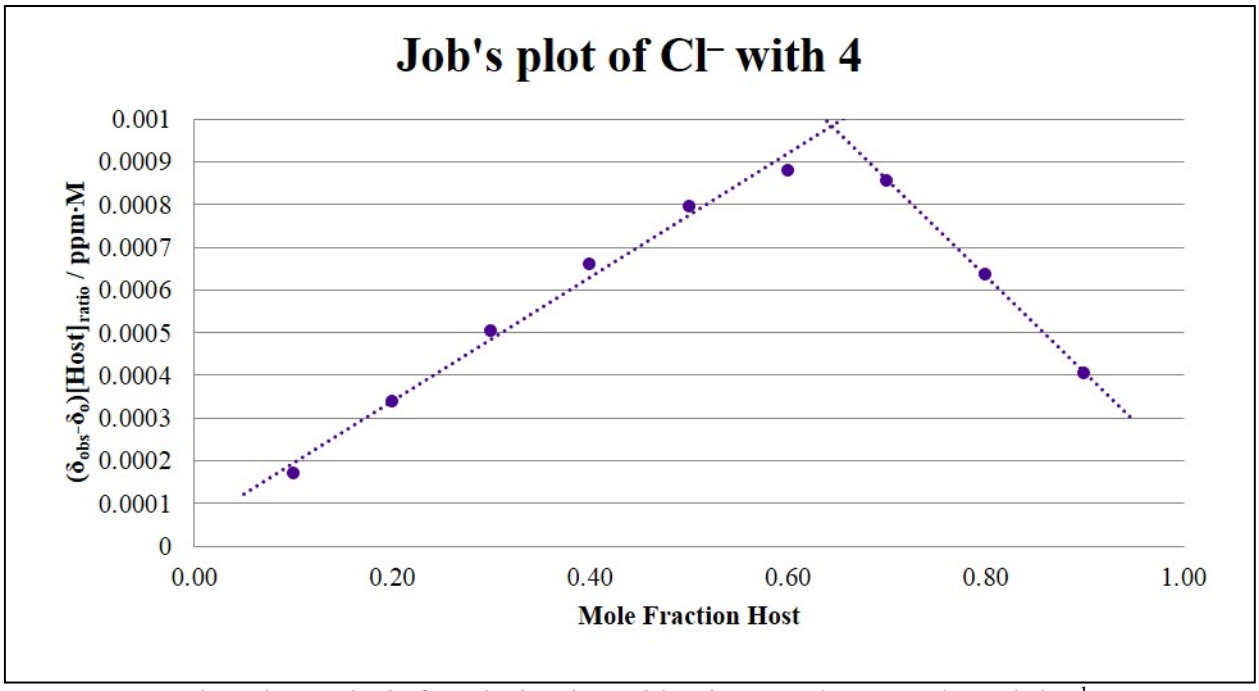


Figure S20. Job's plot analysis for Cl^- titration with **4** in 10% *d*$_6$-DMSO/$CDCl_3$ by ^1H NMR.

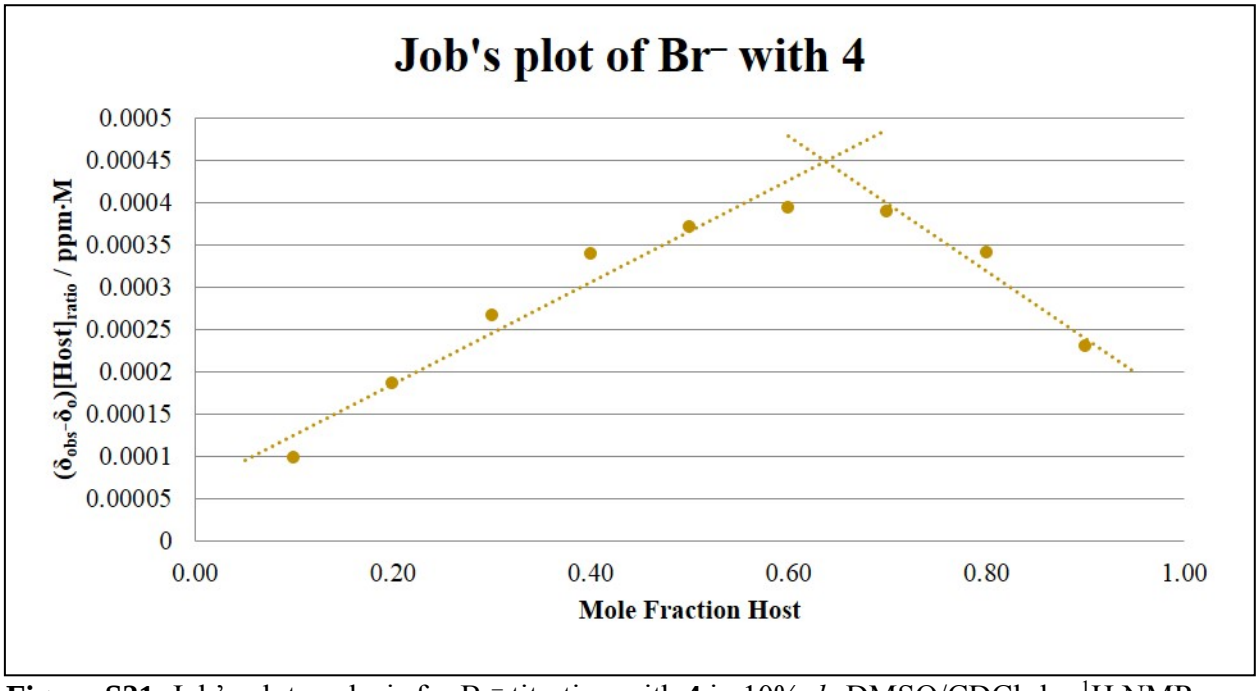


Figure S21. Job's plot analysis for Br^- titration with **4** in 10% *d*$_6$-DMSO/$CDCl_3$ by ^1H NMR.

References

1. (a) C. N. Carroll, B. A. Coombs, S. P. McClintock, C. A. Johnson, O. B. Berryman, D. W. Johnson, M. M. Haley, *Chem. Commun.* **2011**, *47*, 5539–5541; (b) C. N. Carroll, O. B. Berryman, C. A. Johnson, L. N. Zakharov, M. M. Haley, D. W. Johnson, *Chem. Commun.* **2009**, 2520–2522.

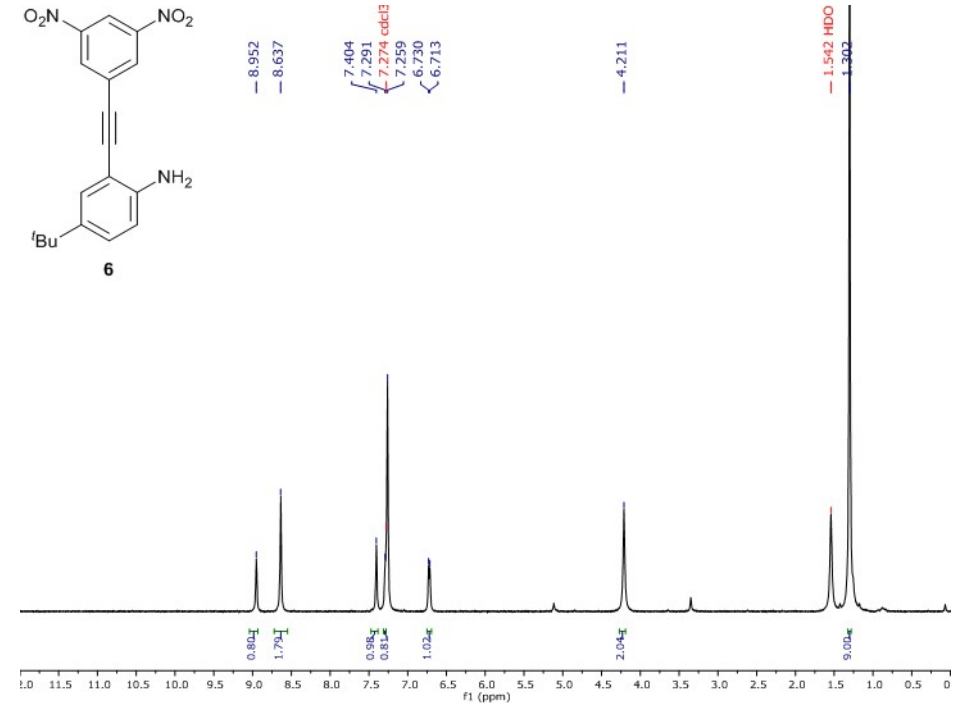
2. G. M. Sheldrick, *Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, WI, 1998.

3. G. M. Sheldrick, *Acta Cryst,* **2015**, *C71*, 3–8.

4. P. Thordarson, *Chem. Soc. Rev.* **2011**, *40*, 1305–1323.

5. http://supramolecular.org

NMR Spectra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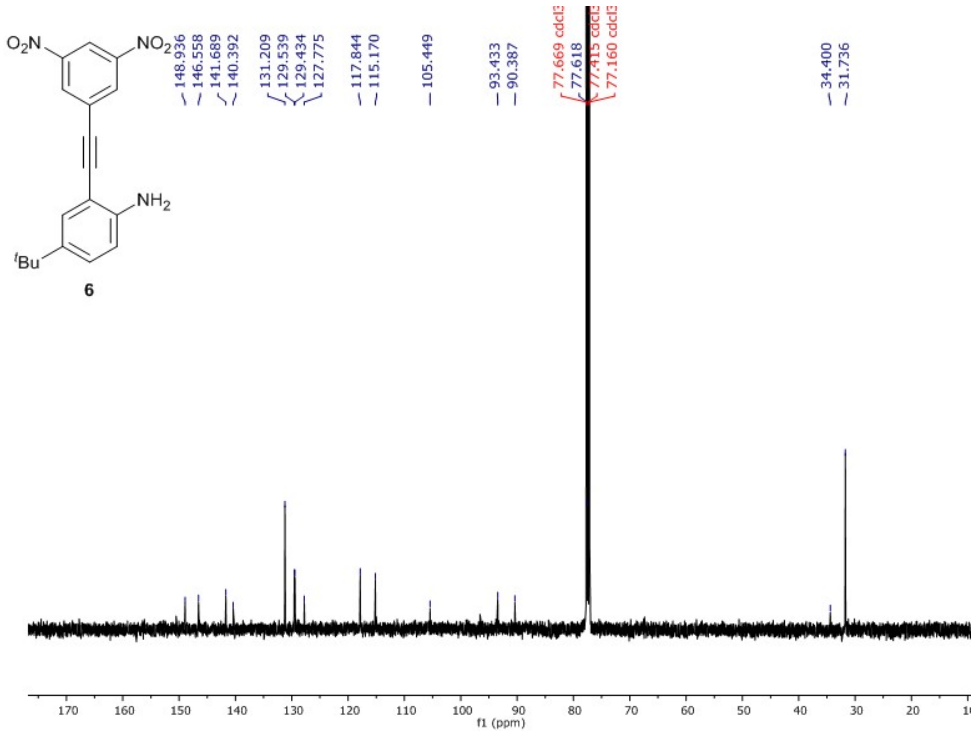
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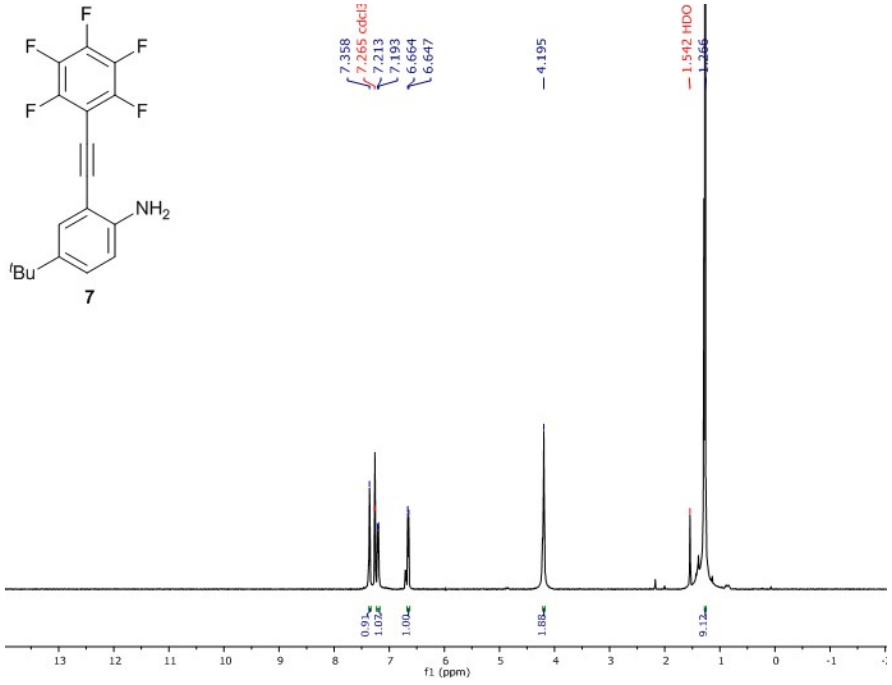
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9.12
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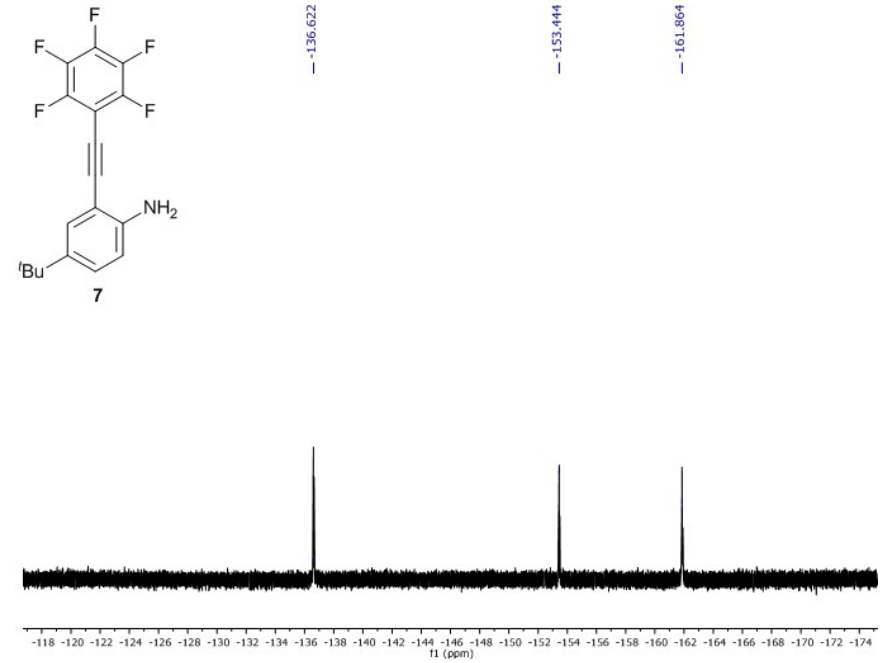
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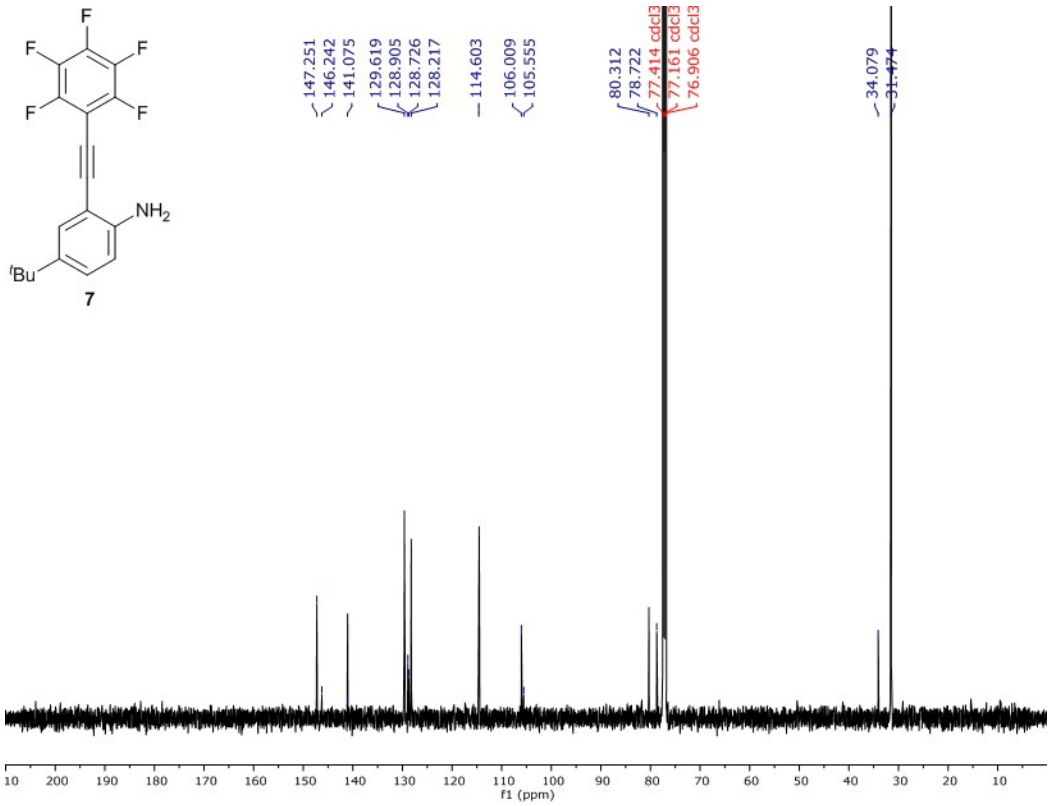
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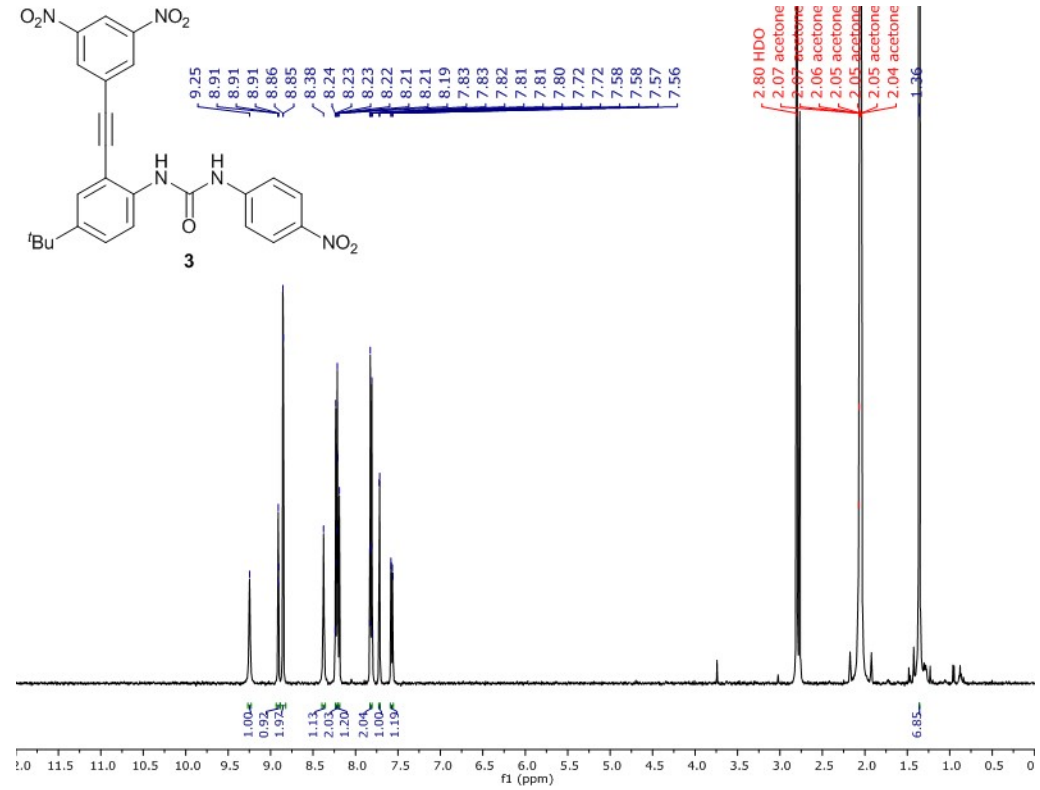
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2.05 acetone
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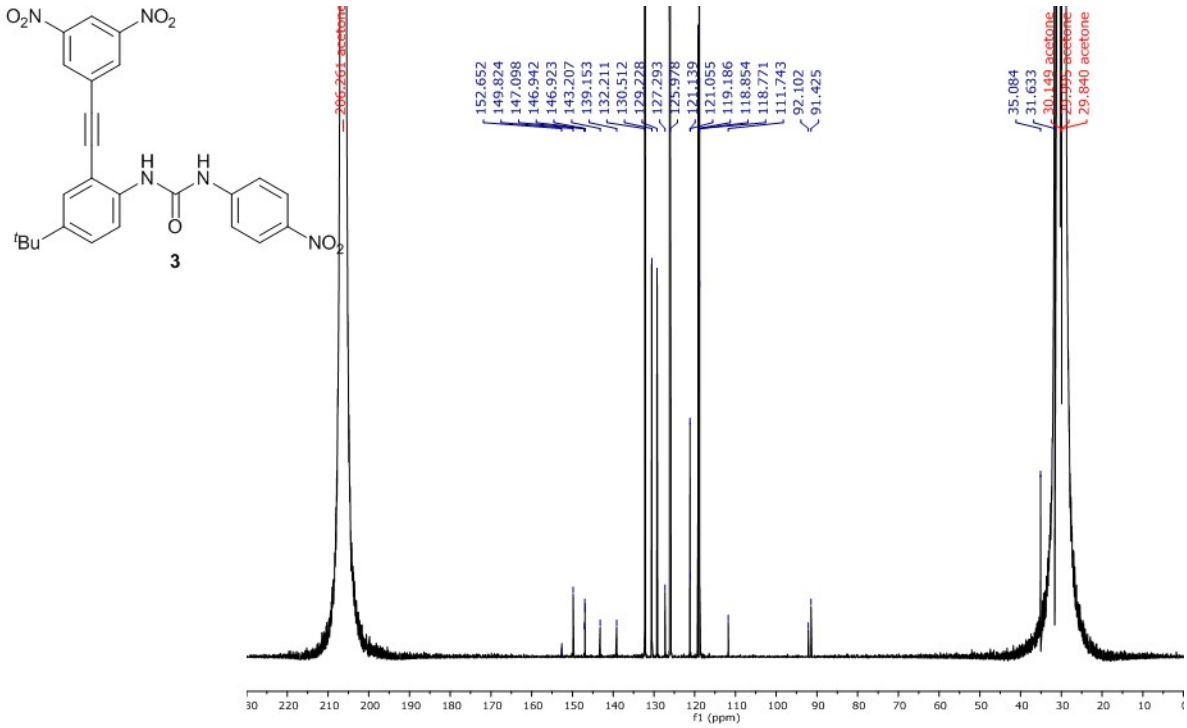
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N
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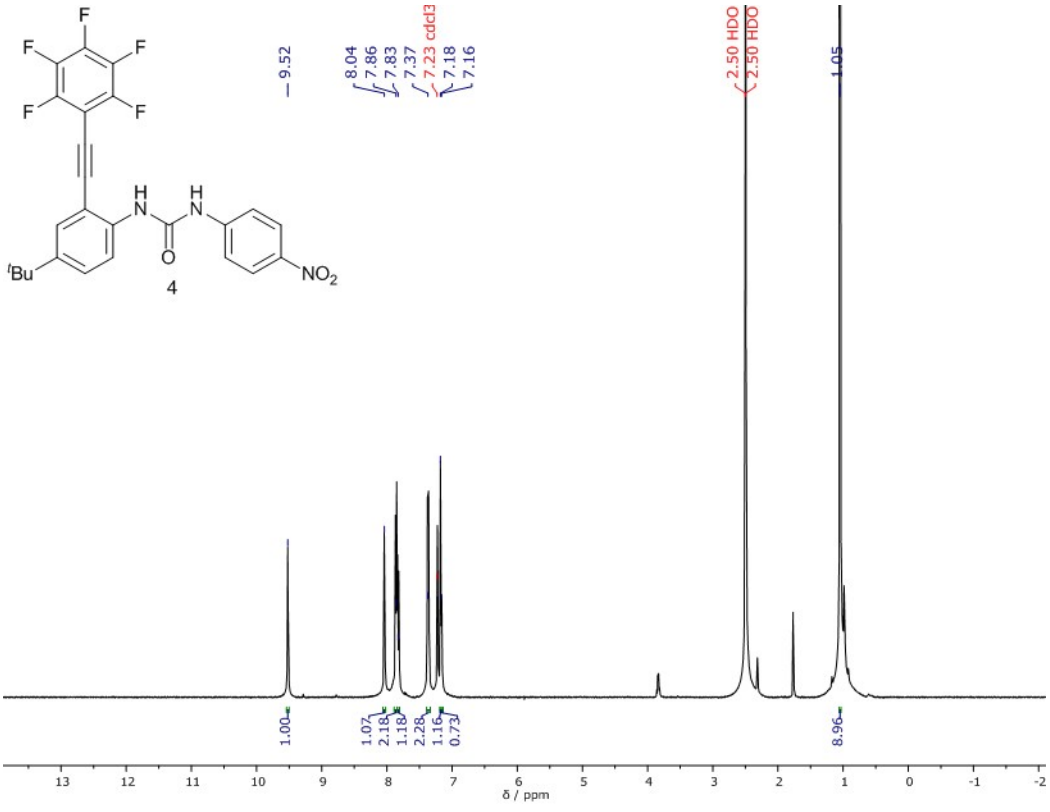
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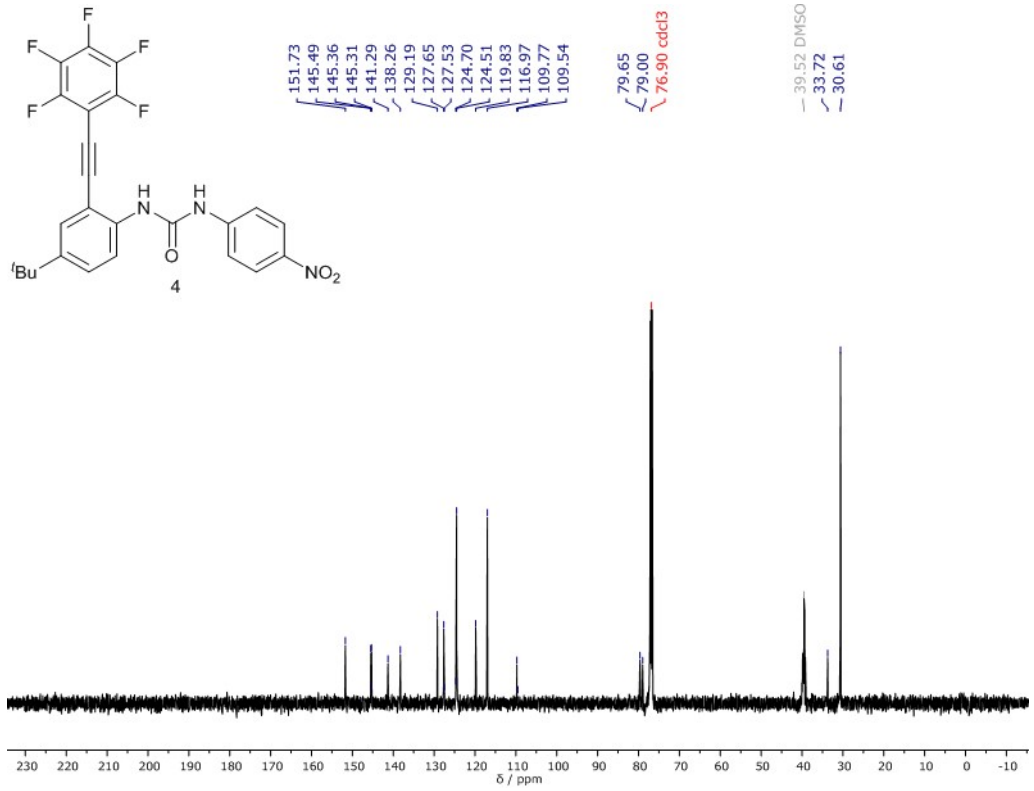
δ / ppm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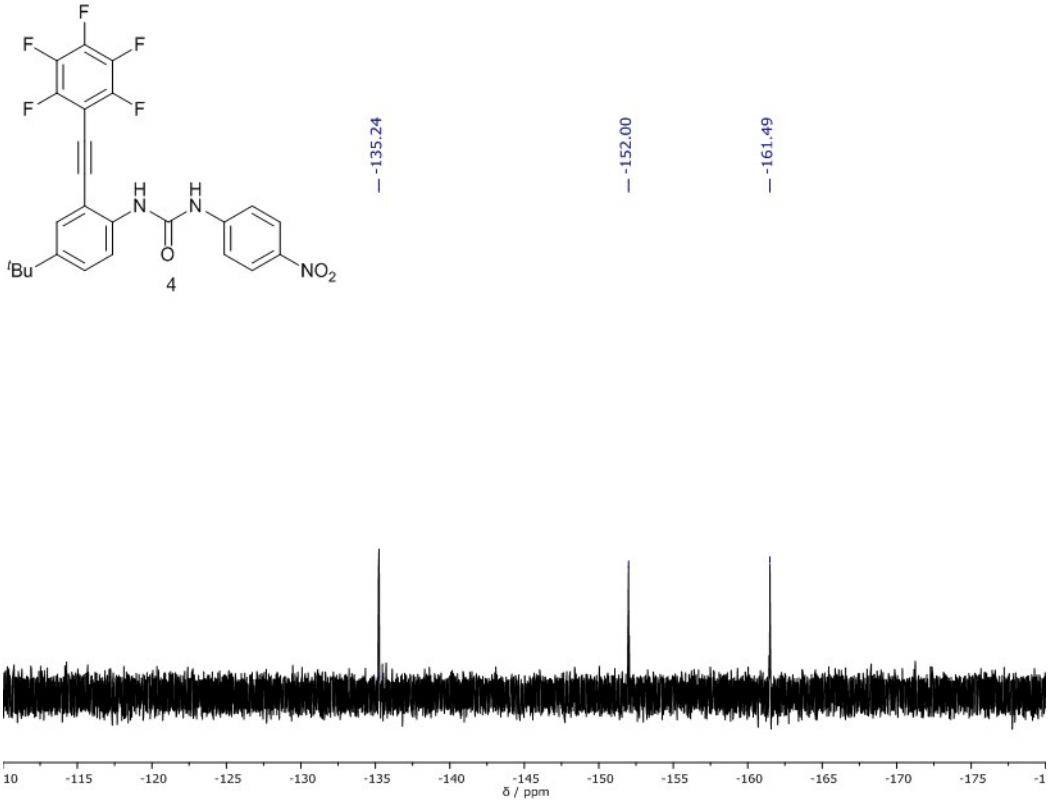
138.26
129.19
127.65
127.53
124.70
124.51
119.83
116.97
109.77
109.54
79.65
79.00
76.90 cdcl3
39.52 DMSO
33.72
30.61
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ / ppm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H
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δ / ppm