SUPPORTING INFORMATION

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Part I: Experimental Procedures

General Procedures

^{1}H and ^{13}C NMR spectra were obtained on a Varian 300 MHz spectrometer (^{1}H 299.95 MHz, ^{13}C 75.43 MHz), 500 MHz spectrometer (^{1}H 500.10 MHz, ^{13}C 125.75 MHz) or 600 MHz spectrometer (^{1}H 599.98 MHz, ^{13}C 150.87 MHz). Chemical shifts (δ) are expressed in ppm relative to tetramethylsilane (TMS) using residual non-deuterated solvent ($CDCl_3$: ^{1}H 7.26 ppm, ^{13}C 77.0 ppm; CD_2Cl_2: ^{1}H 5.32 ppm, ^{13}C 54.0 ppm; DMSO–d_6: ^{1}H 2.50 ppm, ^{13}C 39.51 ppm). UV-Vis spectra were recorded on an HP 8453 UV-Vis spectrophotometer. Unless otherwise specified, all reagents were purchased and used as received. Dry solvents were obtained from distillation using published literature procedures directly before use. Fluorescence data was acquired with a Horiba Jobin-Yvon FluoroMax-4 fluorescence spectrophotometer in $CHCl_3$ prepared in the same manner as for UV-Vis; slit widths (ex/em) were 3 nm/3 nm. Compounds **1**, **2**, **3** and **6** were synthesized using previously reported procedures.[1]

Synthesis

Dianiline 4. A suspension of ethynylaniline **6** (2.262 g, 9.22 mmol) and K_2CO_3 (6.37 g, 46.1 mmol) in Et_2O (15 mL) and MeOH (30 mL) was stirred at room temperature and monitored by TLC until completion (30 min). The solution was diluted with DCM and washed three times with water and brine. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was dissolved in minimal THF and added to an N_2 purged solution of 1,3-diiodobenzene (1.39 g, 4.20 mmol), $Pd(PPh_3)_4$ (0.49 g, 0.42 mmol) and CuI (0.16 g, 0.84 mmol) in dry THF (45 mL) and *i*-Pr_2NH (45 mL). The solution was stirred at 50 °C for 8 h.

The reaction was concentrated *in vacuo* and the residue was taken up into DCM. The solution was filtered through a 3 cm silica gel plug and washed with additional DCM. The combined organics were concentrated *in vacuo* and the product was purified by column chromatography (2:1 hexanes/CH_2Cl_2) to afford **4** (1.01 g, 57%) as a pale brown solid. Mp: 132.1-133.0 °C; ^{1}H NMR (600 MHz, CD_2Cl_2): δ 1.28 (s, 18H), 4.22 (br s, 4H), 6.69 (d, *J* = 8.5 Hz, 2H), 7.21 (dd, *J* = 8.5, 2.4 Hz, 2H), 7.34-7.40 (m, 3H), 7.50 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.71 (t, *J* = 1.7 Hz, 1H); ^{13}C NMR (151 MHz, CD_2Cl_2) δ 146.37, 141.29, 134.56, 131.37, 129.26, 129.22, 128.00, 124.40, 114.73, 107.30, 93.69, 87.78, 34.35, 31.68; HRMS (ESI) for $C_{30}H_{33}N_2$ $[M+H]^+$: calcd 421.2625, found 421.2644.

Bisurea 5. All glassware was dried in a 150 °C oven for at least 1 h. Dianiline **4** (200 mg, 0.5 mmol) and *p*-methoxyphenyl isocyanate (177 mg, 1.2 mmol) in toluene (50 mL) were stirred at 50 °C for 8 h. The reaction became cloudy upon completion and acetone was added until the turbidity was removed. Hexanes was added until a slight turbidity returned and the suspension was left to precipitate overnight in the refrigerator. Filtration afforded **5** (320 mg, 93%) as a fine white powder. Mp: 158.5-160.0 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 1.29 (s, 18H), 3.70 (s, 6H), 6.86 (d, *J* = 8.9 Hz, 4H), 7.37 (d, *J* = 8.9 Hz, 3H), 7.42 (dd, *J* = 8.8, 2.4 Hz, 2H), 7.50 (d, *J* = 2.4 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.72 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.99 (t, *J* = 1.7 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 2H), 8.11 (s, 2H), 9.28 (s, 2H); ^{13}C NMR (151 MHz, DMSO-d_6): δ 154.61, 152.40, 144.38, 138.04, 134.33, 132.43, 131.77, 129.16, 128.69, 126.96, 122.94, 120.22, 119.64, 114.03, 110.73, 93.69, 86.75, 55.13, 33.94, 31.02; HRMS (ESI) for $C_{46}H_{47}N_4O_4$ $[M+H]^+$: calcd 719.3563, found 719.3597.

Part II: X-Ray Crystallography

Diffraction intensities were collected at 100(2) K on a Bruker Apex2 CCD diffractometer using MoKα radiation λ= 0.71073 Å. The systematic absences allow the space group to be Pnma or $Pna2_1$; $Pna2_1$ was chosen and confirmed by the analysis. Absorption corrections were 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 treated in calculated positions in a rigid group model. PLATON checks show that there is an 80% fit to a structure in space group Pccn. In this Pccn system, molecule **5** would have crystallographically-imposed twofold symmetry, with disordered t-butyl groups; in addition, two of the n-butyl moieties in the tetrabutylammonium cation would be disordered, as would be the chloroform of solvation. As the $Pna2_1$ structure shows no anomalous anisotropic displacement parameters, the obvious conclusion is that the reported nicely-ordered $Pna2_1$ structure is correct. All calculations were performed by the Bruker SHELXTL (v. 6.10) package.[3]

Crystallographic data for **5**: $C_{63}H_{83}Cl_4N_5O_4$, M_r = 1116.14, crystal size 0.25 x 0.19 x 0.13 mm^3, orthorhombic, space group $Pna2_1$, a = 24.2423(16), b = 25.3429(17), c = 9.7891(7) Å, V = 6014.1(17) $Å^3$, Z = 4, ρ_{calc} = 1.233 g cm^{-3}, μ = 0.247 mm^{-1}, F(000)=2384, MoKα radiation λ= 0.71073 Å, T = 100(2) K, $2\Theta_{max}$ = 54.00°, 90937 reflections measured [R_{int}=0.0396], 10521 reflections observed, 686 refined parameters, $R1$ = 0.0614, $wR2$ = 0.1674, and GOF = 1.054 for reflections with $I > 2\sigma(I)$, $R1$ = 0.0670, $wR2$ = 0.1737, and GOF = 1.054 for all data, max/min residual electron density +1.026/-1.258 e $Å^{-3}$, the Flack = 0.47(7). CCDC 929532 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.

Part III: Titrations

General Titration Procedures. Receptor concentration was kept constant by preparing a stock solution of receptor and preparing a guest serial dilution with the stock receptor solution. A constant receptor concentration was maintained during the titration to avoid concentration effects on the proton chemical shifts and provide clean isosbestic points in the UV spectra. Tetrabutylammonium salts were purchased from TCI America or Fluka and dried by heating to 70 °C *in vacuo* before use. Hamilton gas-tight syringes were used for all titrations and additions were made through septa when available. The reported binding constants represent the average of the fits from titrations performed in triplicate. Representative data are provided for each halide anion.

^{1}H NMR Titrations

NMR Titration Conditions. ^{1}H NMR titrations were carried out on an Inova 500 MHz spectrometer (^{1}H 500.10 MHz). Chemical shifts (δ) are expressed in ppm relative to tetramethylsilane (TMS) using residual non-deuterated solvent ($CDCl_3$: ^{1}H 7.26 ppm, ^{13}C 77.0 ppm). $CDCl_3$ was prepared by passing over activated alumina. 1:1 v/v $CDCl_3$ and deionized water was mixed in a separatory funnel and the organic layer was collected. Association constants were determined using non-linear regression fitting in MatLab.[4]

Tetrabutylammonium chloride with 5. A stock solution of **5** (1.48 mg, [R]=0.69 mM) in $CDCl_3$ (3 mL) was prepared and used in the dilution of TBACl guest solution (5.05 mg, [G]=7.57 mM). The remaining stock solution (0.6 mL) was used as the starting volume in an NMR tube. The calculated association constants for Cl^- with **5** had large error and were not

consistent across titrations; therefore, reported association constants were determined using UV-Vis titrations. The procedure for this titration is provided for comparison of structural characteristics apparent in the NMR (downfield shifts of urea and aryl protons) to crystallographic data.

Table S1. Representative titration data for Cl^- with **5**.

	Guest (μL)	[**5**] (M)	[Cl^-] (M)	Equiv.	δ (ppm)
0	0	6.86E-04	0.00E+00	0.00	7.443
1	10	6.86E-04	1.24E-04	0.18	7.545
2	20	6.86E-04	2.44E-04	0.36	7.640
3	30	6.86E-04	3.61E-04	0.53	7.726
4	40	6.86E-04	4.73E-04	0.69	7.798
5	50	6.86E-04	5.82E-04	0.85	7.852
6	60	6.86E-04	6.88E-04	1.00	7.900
7	80	6.86E-04	8.91E-04	1.30	7.973
8	100	6.86E-04	1.08E-03	1.58	8.016
9	120	6.86E-04	1.26E-03	1.84	8.047
10	140	6.86E-04	1.43E-03	2.09	8.065
11	180	6.86E-04	1.75E-03	2.55	8.084
12	220	6.86E-04	2.03E-03	2.96	8.097
13	260	6.86E-04	2.29E-03	3.34	8.106
14	300	6.86E-04	2.52E-03	3.68	8.112
15	400	6.86E-04	3.03E-03	4.41	8.122
16	600	6.86E-04	3.79E-03	5.52	8.130
17	1000	6.86E-04	4.73E-03	6.90	8.137

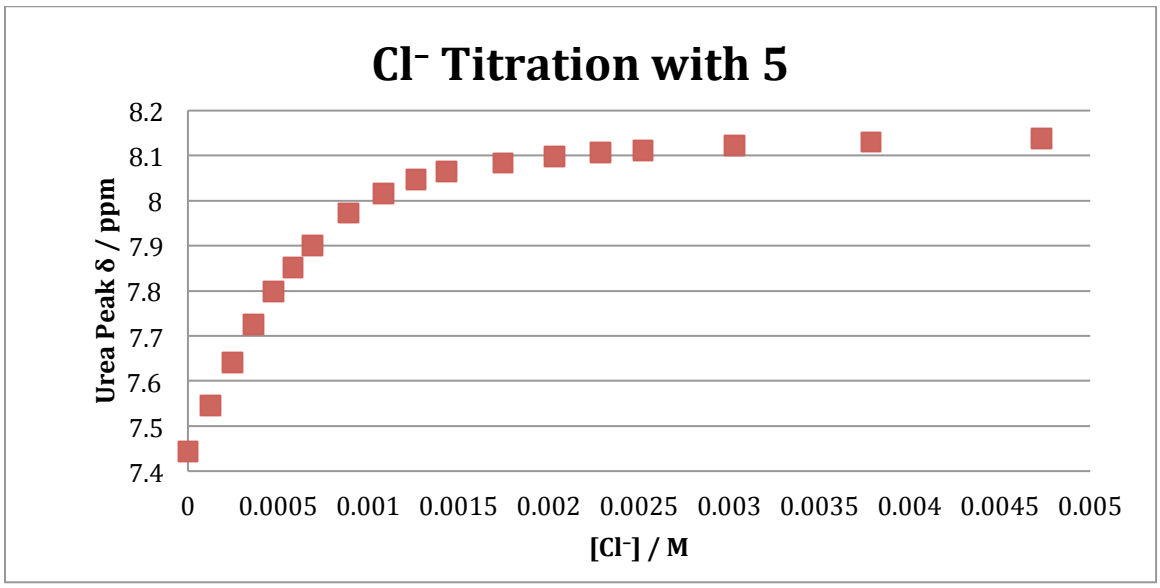

Figure S1. Binding isotherm for Cl^- titration of **5** in $CDCl_3$ by ^1H NMR.

Tetrabutylammonium bromide with 5. A stock solution of **5** (1.98 mg, [R]=0.92 mM) in $CDCl_3$ (3 mL) was prepared and used in the dilution of TBABr guest solution (19.58 mg, [G]=26.41 mM). The remaining stock solution (0.6 mL) was used as the starting volume in an NMR tube.

Table S2. Representative titration data for Br^- with **5**.

	Guest (μL)	[**5**] (M)	[Br^-] (M)	Equiv.	δ (ppm)
0	0	9.18E-04	0.00E+00	0.00	7.443
1	5	9.18E-04	2.18E-04	0.24	7.528
2	10	9.18E-04	4.33E-04	0.47	7.597
3	15	9.18E-04	6.44E-04	0.70	7.652
4	20	9.18E-04	8.52E-04	0.93	7.699
5	25	9.18E-04	1.06E-03	1.15	7.739
6	30	9.18E-04	1.26E-03	1.37	7.773
7	35	9.18E-04	1.46E-03	1.59	7.805
8	45	9.18E-04	1.84E-03	2.01	7.842
9	55	9.18E-04	2.22E-03	2.42	7.871
10	65	9.18E-04	2.58E-03	2.81	7.894
11	80	9.18E-04	3.11E-03	3.38	7.916

12	100	9.18E-04	3.77E-03	4.11	7.939
13	125	9.18E-04	4.55E-03	4.96	7.955
14	150	9.18E-04	5.28E-03	5.75	7.968
15	200	9.18E-04	6.60E-03	7.19	7.977
16	250	9.18E-04	7.77E-03	8.46	7.990
17	300	9.18E-04	8.80E-03	9.59	8.000
18	375	9.18E-04	1.02E-02	11.06	8.008
19	450	9.18E-04	1.13E-02	12.33	8.013
20	550	9.18E-04	1.26E-02	13.76	8.017

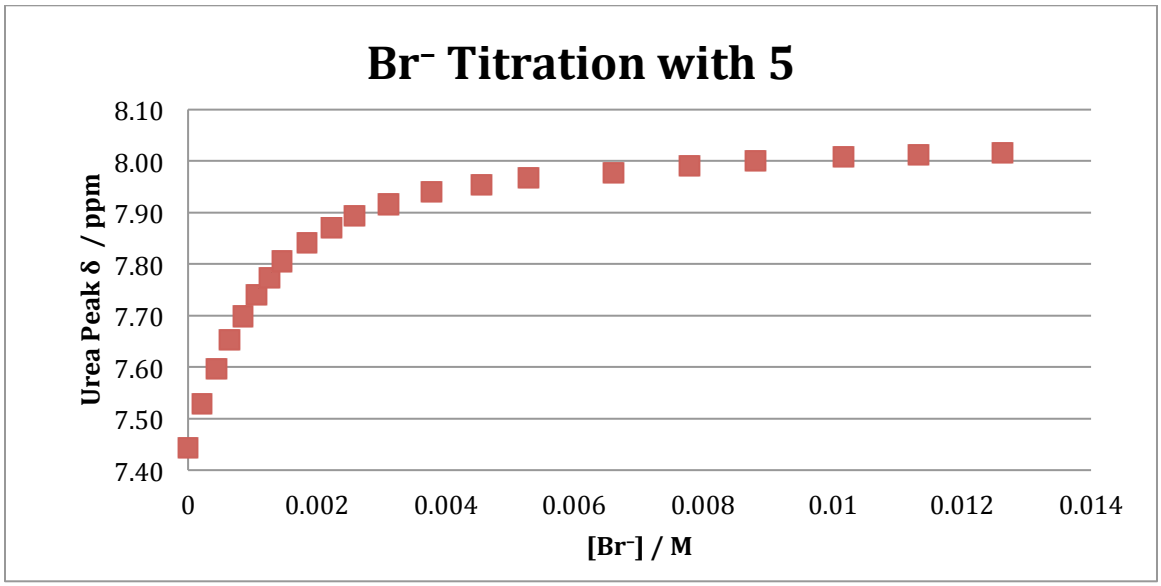

Figure S2. Binding isotherm for Br^- titration of **5** in $CDCl_3$ by ^1H NMR.

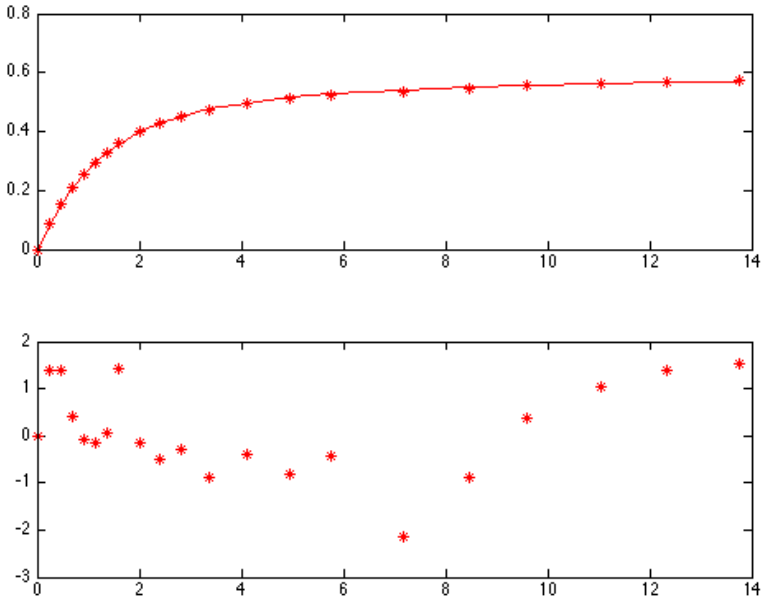

Figure S3. Matlab fit for the binding isotherm of Br^- titration with **5**.

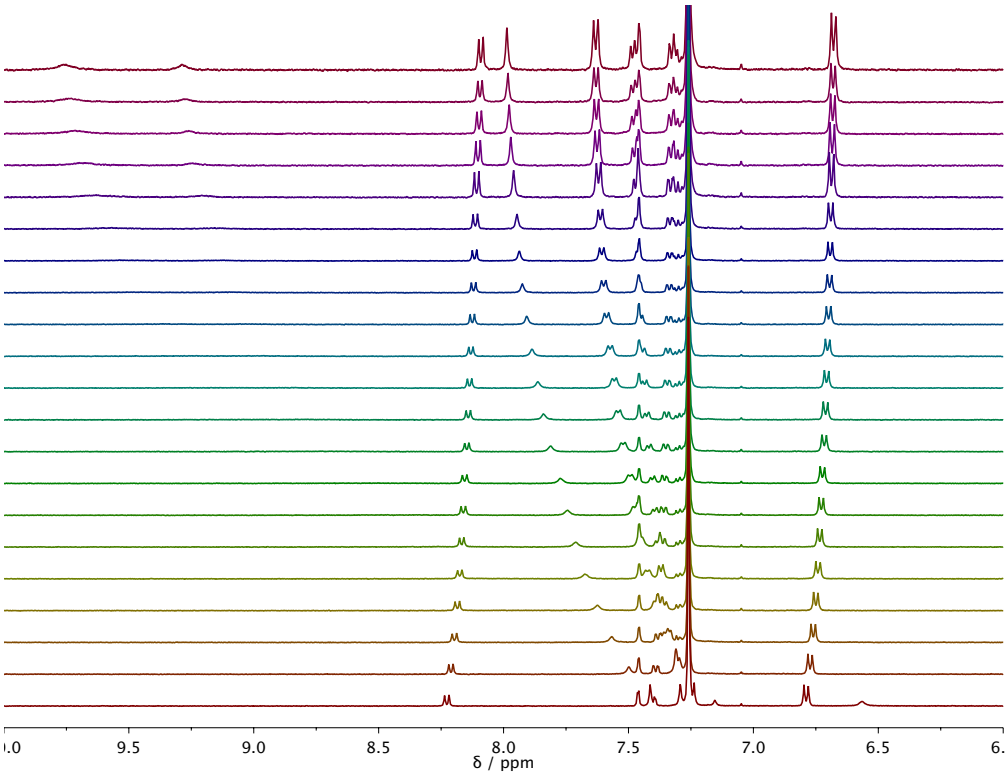

Figure S4. ^1H NMR spectra of Br^- titration with **5**.

Tetrabutylammonium iodide with 5. A stock solution of **5** (4.05 mg, [R]=1.88 mM) in $CDCl_3$ (3 mL) was prepared and used in the dilution of TBAI guest solution (50.21 mg, [G]=58.47 mM). The remaining stock solution (0.6 mL) was used as the starting volume in an NMR tube.

Table S3. Representative titration data for I^- with **5**.

	Guest (μL)	[**5**] (M)	[I^-] (M)	Equiv.	δ (ppm)
0	0	1.88E-03	0.00E+00	0.00	7.418
1	5	1.88E-03	4.83E-04	0.26	7.442
2	10	1.88E-03	9.58E-04	0.51	7.460
3	15	1.88E-03	1.43E-03	0.76	7.486
4	20	1.88E-03	1.89E-03	1.00	7.505
5	25	1.88E-03	2.34E-03	1.25	7.524
6	30	1.88E-03	2.78E-03	1.48	7.540
7	35	1.88E-03	3.22E-03	1.72	7.555
8	40	1.88E-03	3.65E-03	1.95	7.570
9	50	1.88E-03	4.50E-03	2.39	7.594
10	60	1.88E-03	5.32E-03	2.83	7.616
11	70	1.88E-03	6.11E-03	3.25	7.635
12	80	1.88E-03	6.88E-03	3.66	7.650
13	90	1.88E-03	7.63E-03	4.06	7.666
14	115	1.88E-03	9.40E-03	5.01	7.693
15	140	1.88E-03	1.11E-02	5.89	7.715
16	190	1.88E-03	1.41E-02	7.49	7.744
17	240	1.88E-03	1.67E-02	8.90	7.765
18	290	1.88E-03	1.91E-02	10.14	7.776
19	390	1.88E-03	2.30E-02	12.26	7.794
20	590	1.88E-03	2.90E-02	15.44	7.812
21	1090	1.88E-03	3.77E-02	20.08	7.824
22	1590	1.88E-03	4.24E-02	22.60	7.828

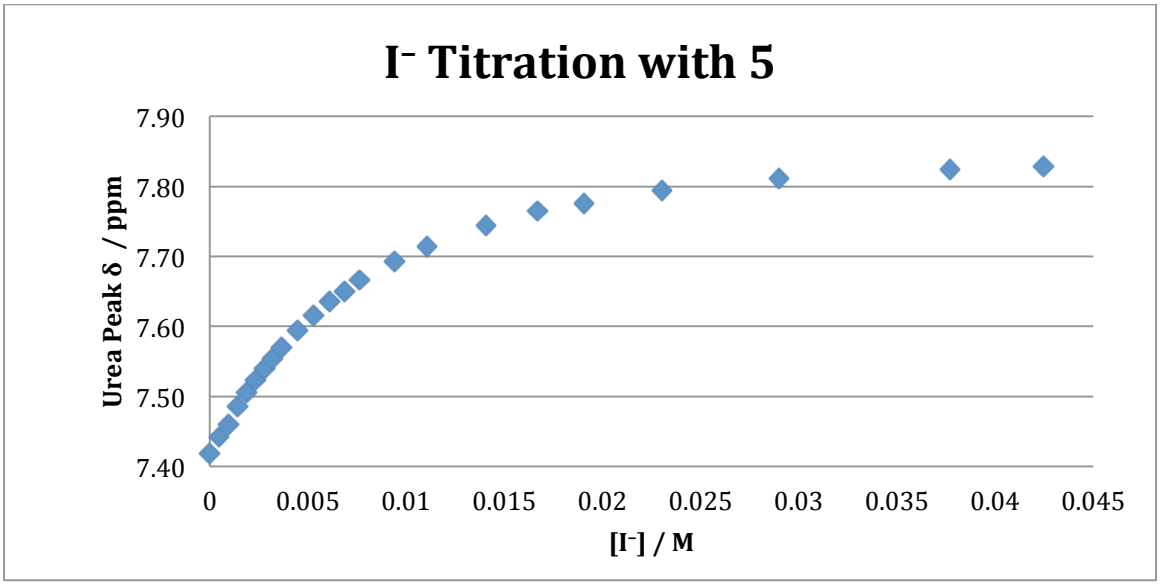

Figure S5. Binding isotherm for I^- titration of **5** in $CDCl_3$ by ^1H NMR.

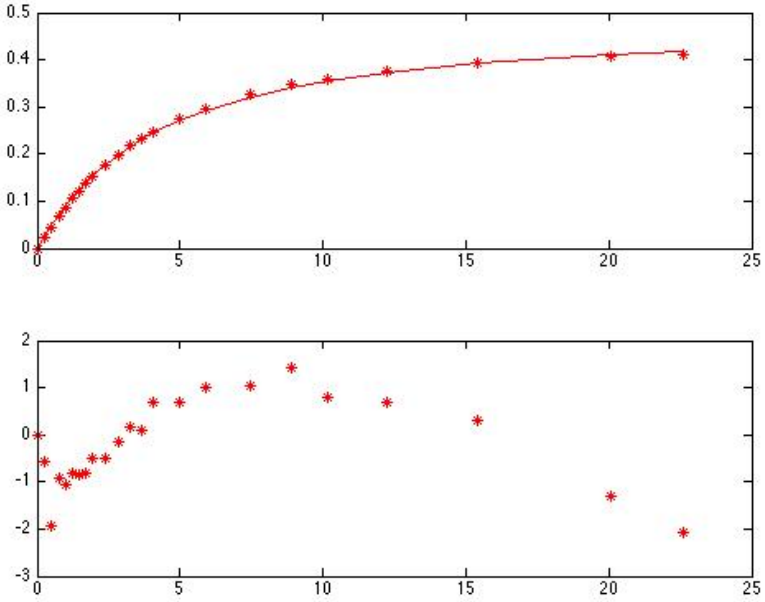

Figure S6. Matlab fit for the binding isotherm of I^- titration with **5**.

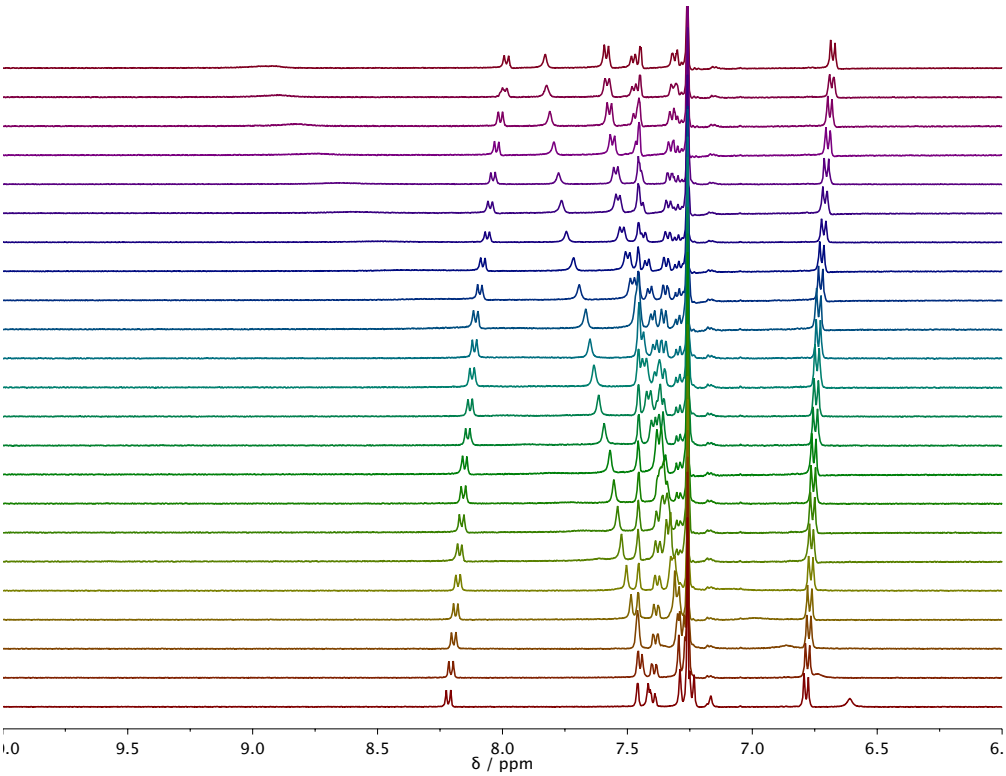

Figure S7. ^{1}H NMR spectra of I^- titration with **5**.

Tetrabutylammonium chloride with 2. A stock solution of **2** (2.87 mg, [**2**]=1.33 mM) in $CDCl_3$ (3 mL) was prepared and used in the dilution of TBACl guest solution (21.34 mg, [G]=33.38 mM). The remaining stock solution (0.6 mL) was used as the starting volume in an NMR tube.

Table S4. Representative titration data for Cl^- with **5**.

	Guest (μL)	[**2**] (M)	[Cl^-] (M)	δ H1 (ppm)	δ H2 (ppm)
0	0	1.33E-03	0.00E+00	7.716	7.716
1	5	1.33E-03	2.76E-04	8.017	7.827
2	10	1.33E-03	5.47E-04	8.226	7.920
3	15	1.33E-03	8.14E-04	8.422	7.995
4	20	1.33E-03	1.08E-03	8.574	8.060
5	25	1.33E-03	1.34E-03	8.692	8.111
6	30	1.33E-03	1.59E-03	8.816	8.158
7	40	1.33E-03	2.09E-03	8.990	8.231

8	50	1.33E-03	2.57E-03	9.112	8.286
9	60	1.33E-03	3.03E-03	9.230	8.331
10	70	1.33E-03	3.49E-03	9.301	8.368
11	100	1.33E-03	4.77E-03	9.484	8.449
12	125	1.33E-03	5.76E-03	9.593	8.494
13	150	1.33E-03	6.68E-03	9.655	8.529
14	200	1.33E-03	8.35E-03	9.766	8.581
15	250	1.33E-03	9.82E-03	9.837	8.615
16	350	1.33E-03	1.23E-02	9.936	8.664
17	450	1.33E-03	1.43E-02	9.995	8.695
18	650	1.33E-03	1.74E-02	10.073	8.733
19	850	1.33E-03	1.96E-02	10.107	8.758
20	1050	1.33E-03	2.12E-02	10.140	8.773

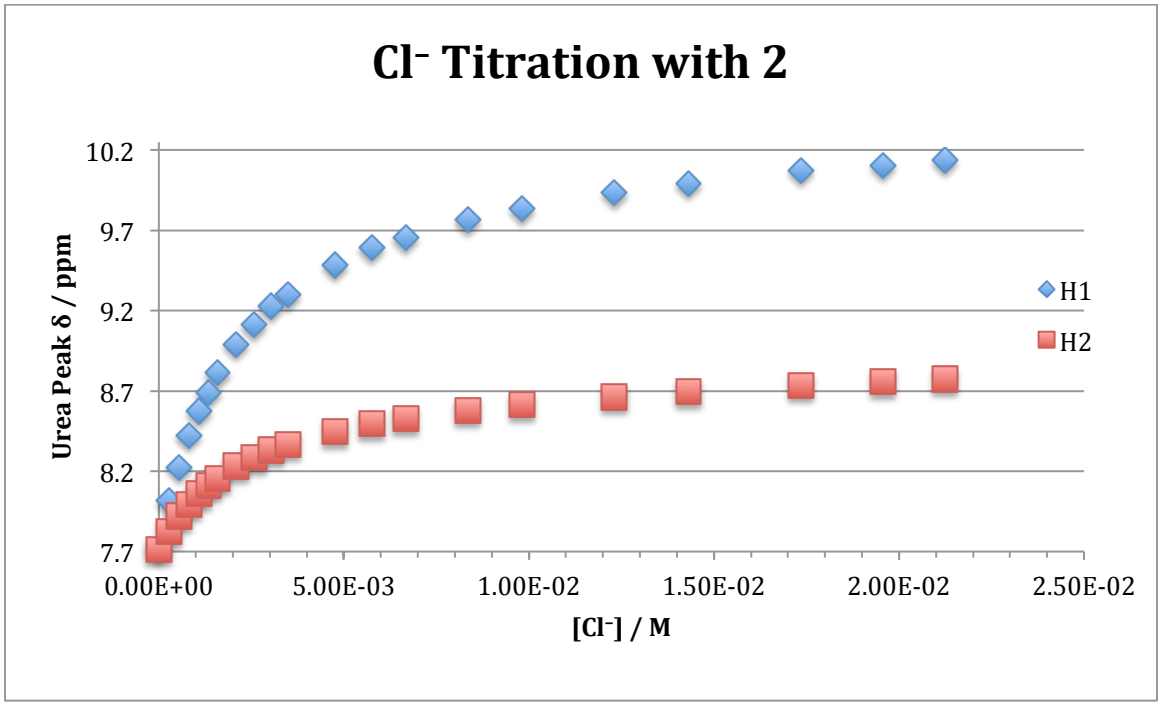

Figure S8. Binding isotherm for Cl^- titration of **2** in $CDCl_3$ by ^1H NMR.

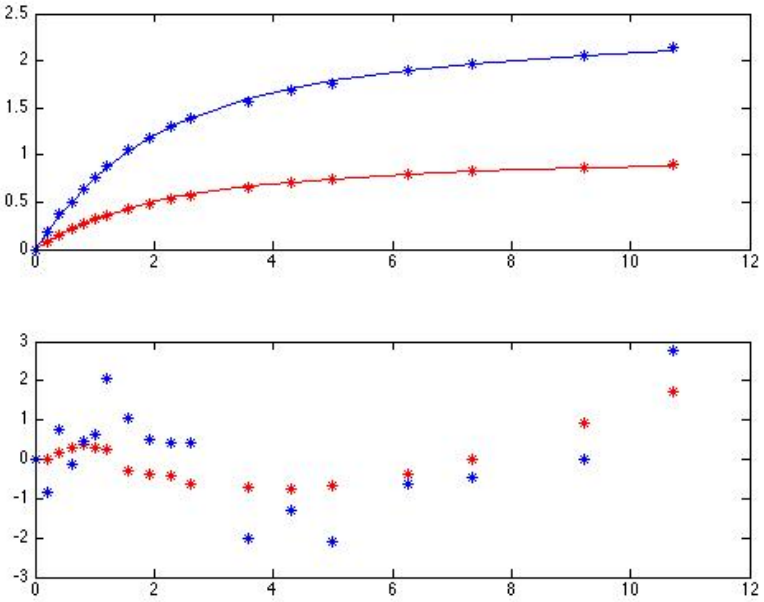

Figure S9. Matlab fit for the binding isotherm of Cl^- titration with **2**.

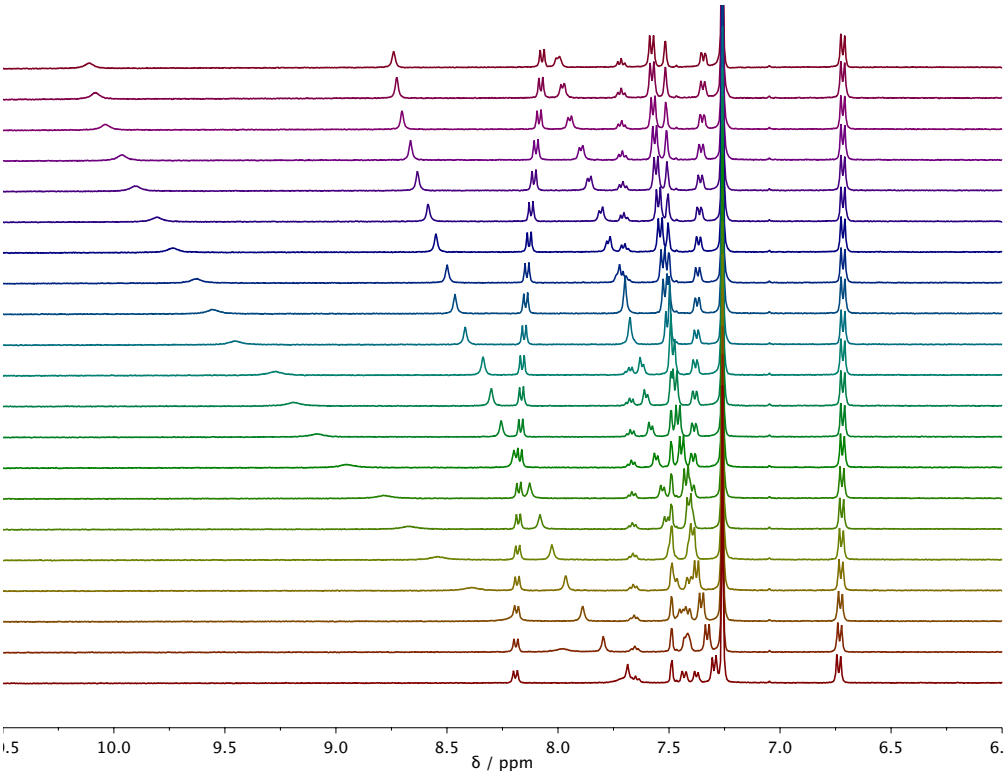

Figure S10. ^1H NMR spectra of Cl^- titration with **2**.

UV–Vis Titrations

UV-Vis Titration Conditions. UV-Vis titrations were carried out on an HP 8453 UV-Vis spectrometer. Water saturated $CHCl_3$ was prepared in the same manner as for ^1H. Association constants were determined by non-linear regression using HYPerquad.[5]

Tetrabutylammonium chloride with 5. A stock solution of **5** was prepared using serial dilution to a final volume of 5 mL (1.28 mg, [**5**] = 10.68 μM). A 2 mL solution of TBACl (2.96 mg, 2.13 mM) was prepared by serial dilution with the stock solution of **5**. The starting volume in the cuvette was 2.0 mL.

Table S5. Representative titration data for Cl^- with **5**.

	Guest (μL)	[**5**] (M)	[Cl^-] (M)	Equiv.
00	0	1.07E-05	0.00E+00	0.00
01	5	1.07E-05	5.31E-06	0.50
02	10	1.07E-05	1.06E-05	0.99
03	15	1.07E-05	1.59E-05	1.48
04	20	1.07E-05	2.11E-05	1.97
05	25	1.07E-05	2.63E-05	2.46
06	30	1.07E-05	3.15E-05	2.95
07	40	1.07E-05	4.18E-05	3.91
08	50	1.07E-05	5.20E-05	4.86
09	60	1.07E-05	6.20E-05	5.81
10	70	1.07E-05	7.20E-05	6.74
11	80	1.07E-05	8.19E-05	7.67
12	100	1.07E-05	1.01E-04	9.49
13	120	1.07E-05	1.21E-04	11.29
14	140	1.07E-05	1.39E-04	13.04
15	180	1.07E-05	1.76E-04	16.46
16	220	1.07E-05	2.11E-04	19.76
17	300	1.07E-05	2.78E-04	26.01
18	400	1.07E-05	3.55E-04	33.23
19	600	1.07E-05	4.92E-04	46.01
20	800	1.07E-05	6.09E-04	56.97

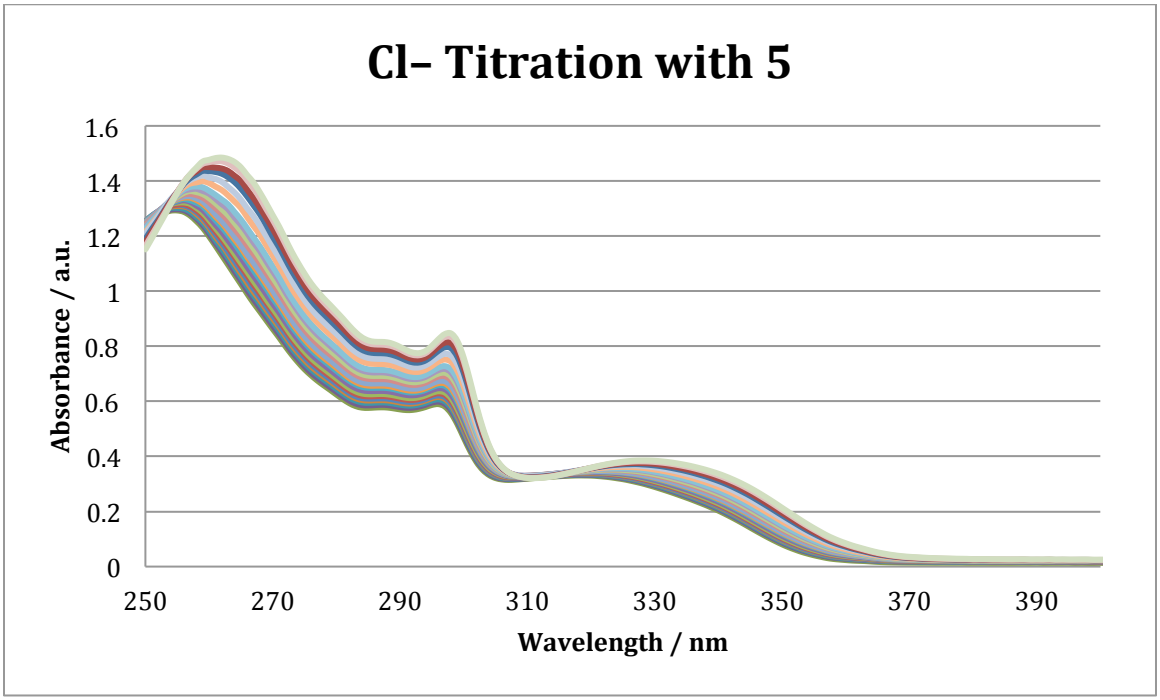

Figure S11. UV-Vis spectra of **5** titrated with Cl^- in water saturated $CHCl_3$.

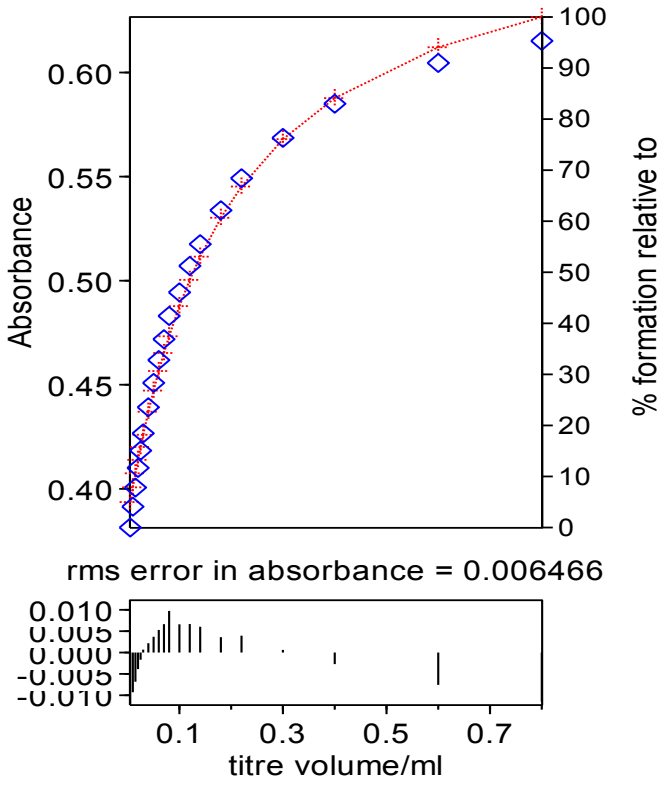

Figure S12. HyperQuad fit for the binding isotherm of Cl^- titration with **5**.

Tetrabutylammonium chloride with 3. A stock solution of **3** was prepared using serial dilution to a final volume of 5 mL (1.50 mg, [**3**] = 14.99 μM). A 2 mL solution of TBACl (7.20 mg, 2.07 mM) was prepared by serial dilution with the stock solution of **3**. The starting volume in the cuvette was 2.0 mL.

Table S6. Representative titration data for Cl^- with **3**.

	Guest (μL)	[**3**] (M)	[Cl^-] (M)	Equiv.
00	0	1.50E-05	0.00E+00	0.00
01	5	1.50E-05	5.17E-06	0.34
02	10	1.50E-05	1.03E-05	0.69
03	15	1.50E-05	1.54E-05	1.03
04	20	1.50E-05	2.05E-05	1.37
05	25	1.50E-05	2.56E-05	1.71
06	30	1.50E-05	3.06E-05	2.04
07	40	1.50E-05	4.06E-05	2.71
08	50	1.50E-05	5.05E-05	3.37
09	60	1.50E-05	6.04E-05	4.03
10	70	1.50E-05	7.01E-05	4.68
11	80	1.50E-05	7.97E-05	5.32
12	90	1.50E-05	8.92E-05	5.95
13	100	1.50E-05	9.87E-05	6.58
14	120	1.50E-05	1.17E-04	7.83
15	140	1.50E-05	1.36E-04	9.05
16	160	1.50E-05	1.54E-04	10.24
17	200	1.50E-05	1.88E-04	12.57
18	250	1.50E-05	2.30E-04	15.36
19	300	1.50E-05	2.70E-04	18.03
20	350	1.50E-05	3.09E-04	20.59

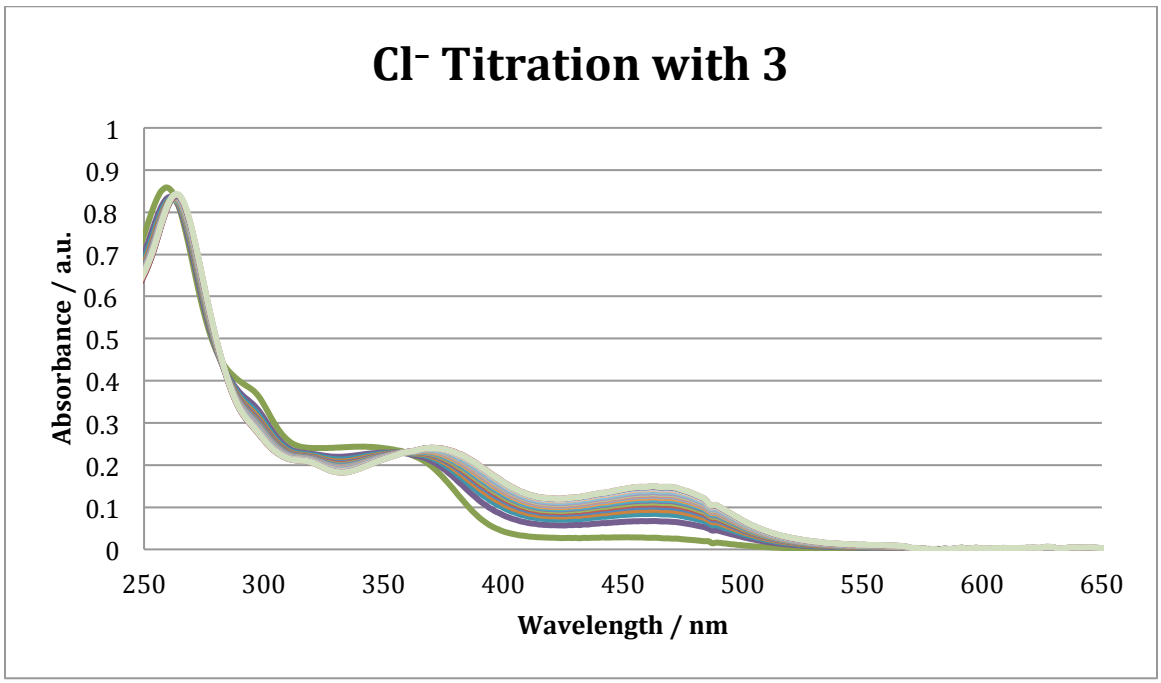

Figure S13. UV-Vis spectra of **3** titrated with Cl^- in water saturated $CHCl_3$.

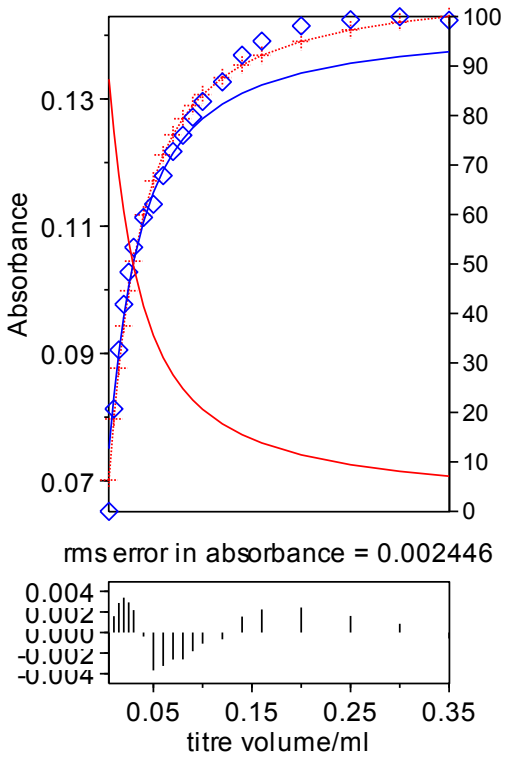

Figure S14. HyperQuad fit for the binding isotherm of Cl^- titration with **3**.

Part IV: Fluorescence Spectra

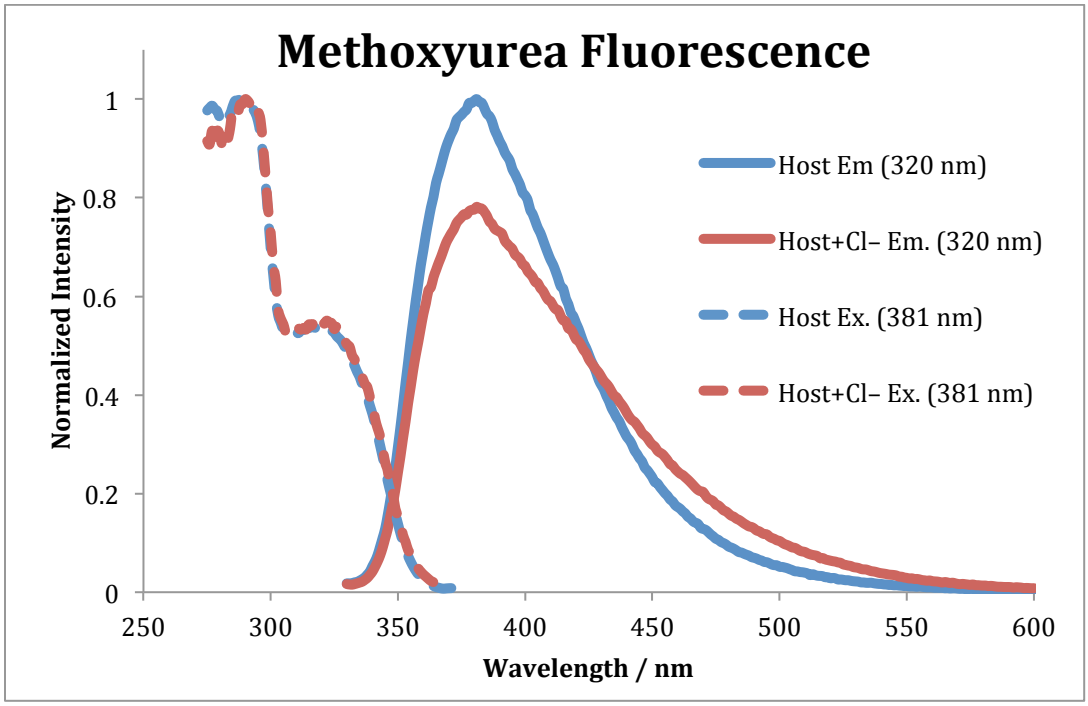

Figure S15. Fluorescence emission and excitation spectra of **5** and **5** with one equivalent of TBACl in $CHCl_3$.

Part V: NMR Spectra

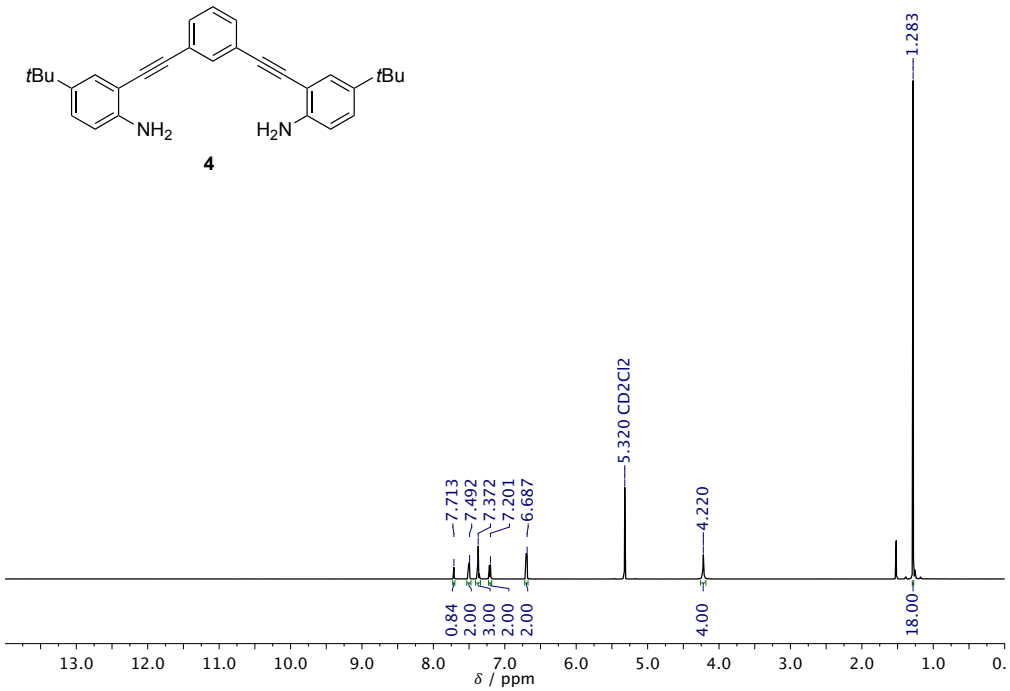

Figure S16. ^{1}H NMR spectra of **4** in CD_2Cl_2.

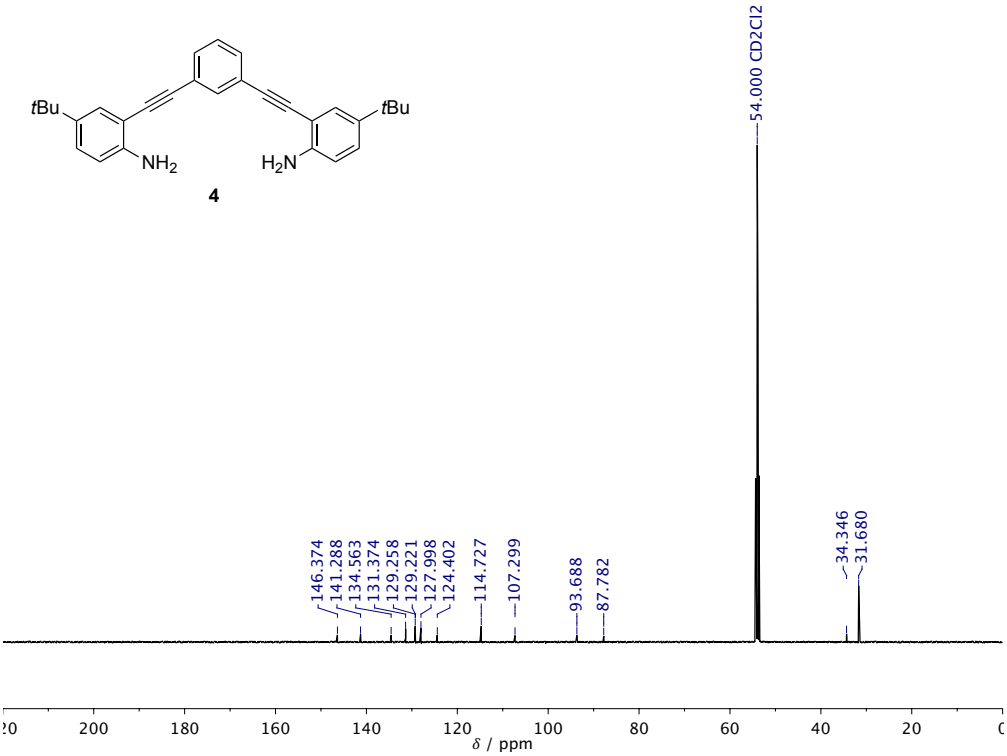

Figure S17. ^{13}C NMR spectra of **4** in CD_2Cl_2.

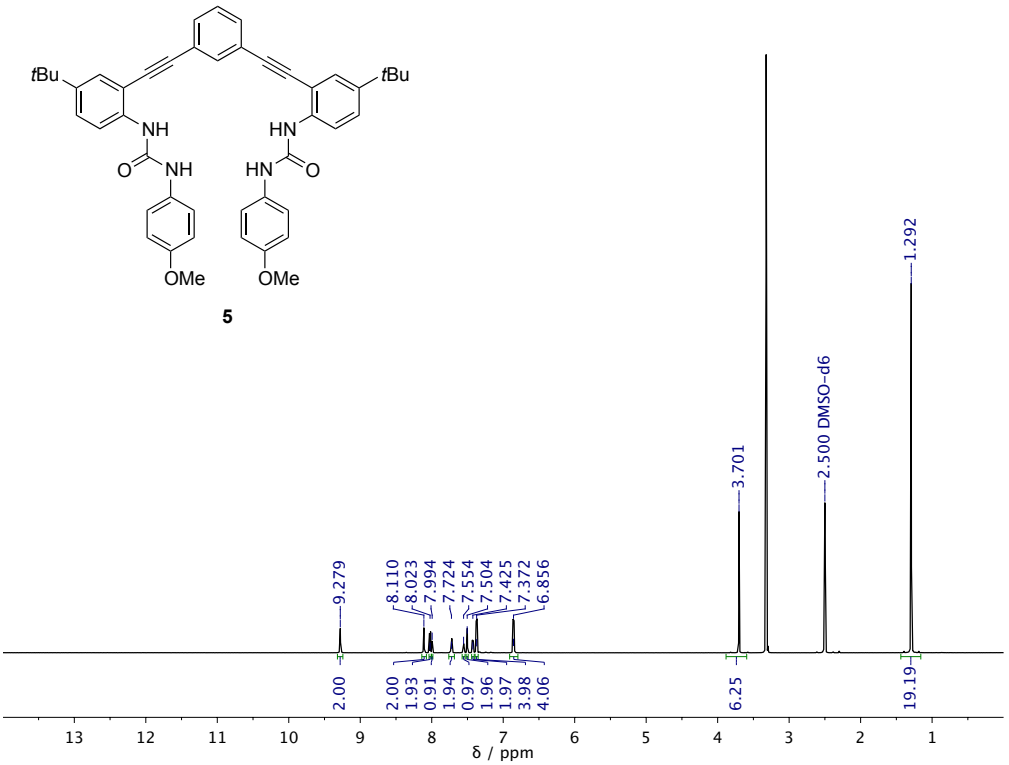

Figure S18. ^{1}H NMR spectra of **5** in DMSO–d_6.

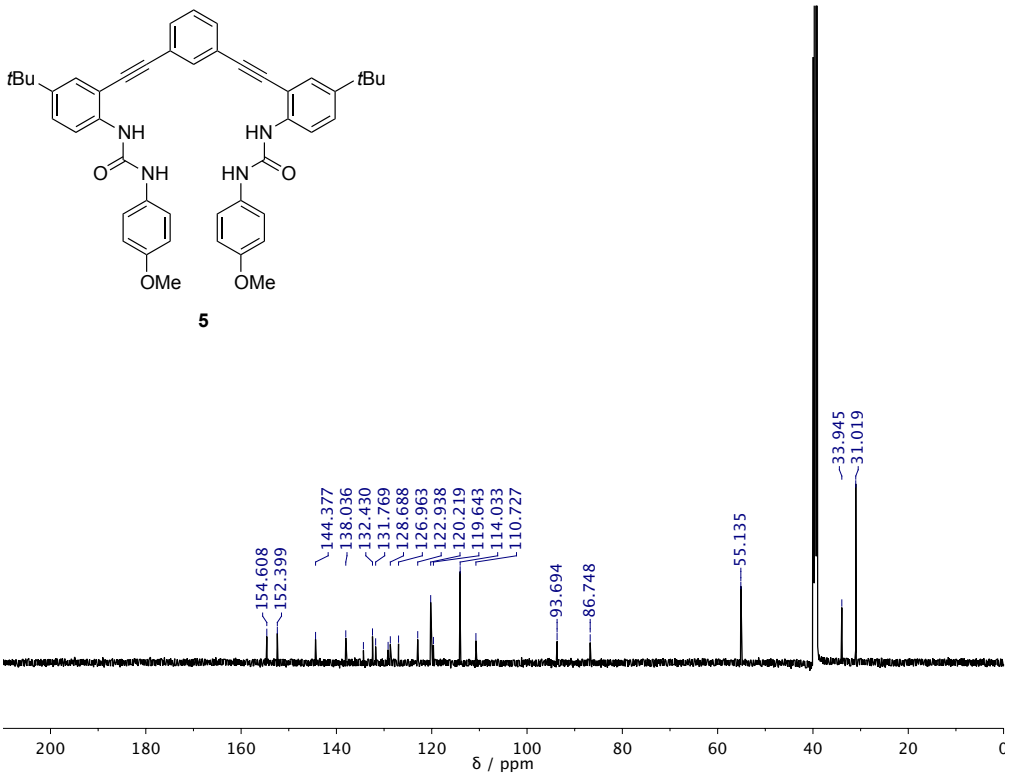

Figure S19. ^{13}C NMR spectra of **5** in DMSO–d_6.

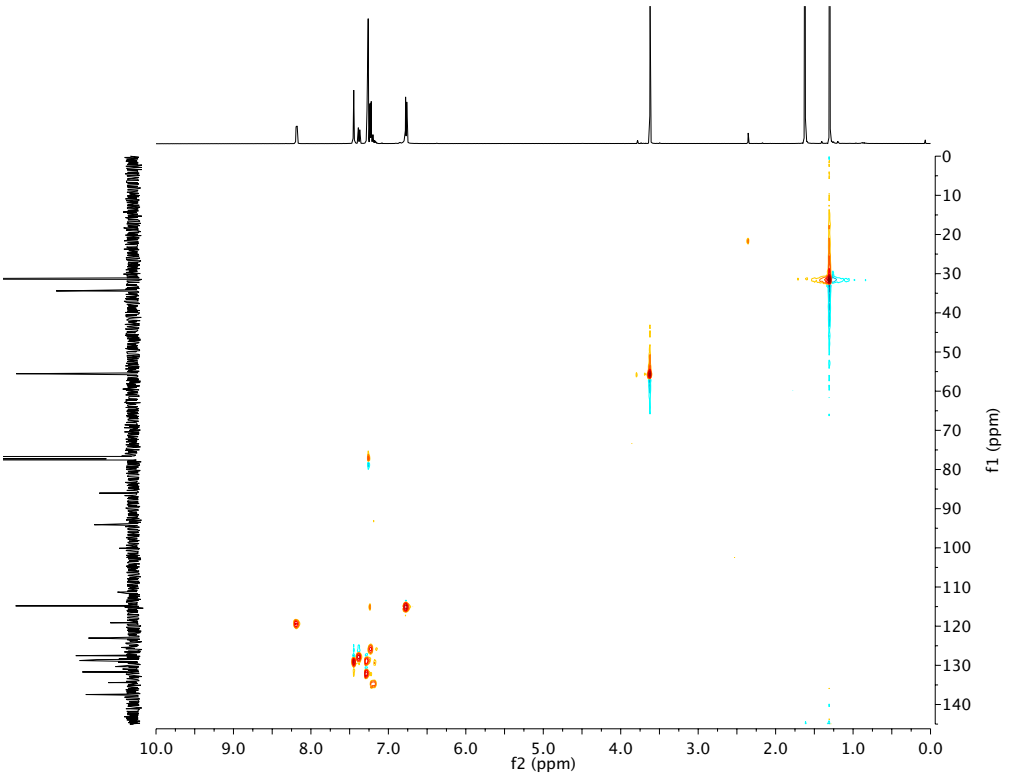

Figure S20. 2D ^{1}H–^{13}C HSQC NMR spectra of **5** in $CDCl_3$.

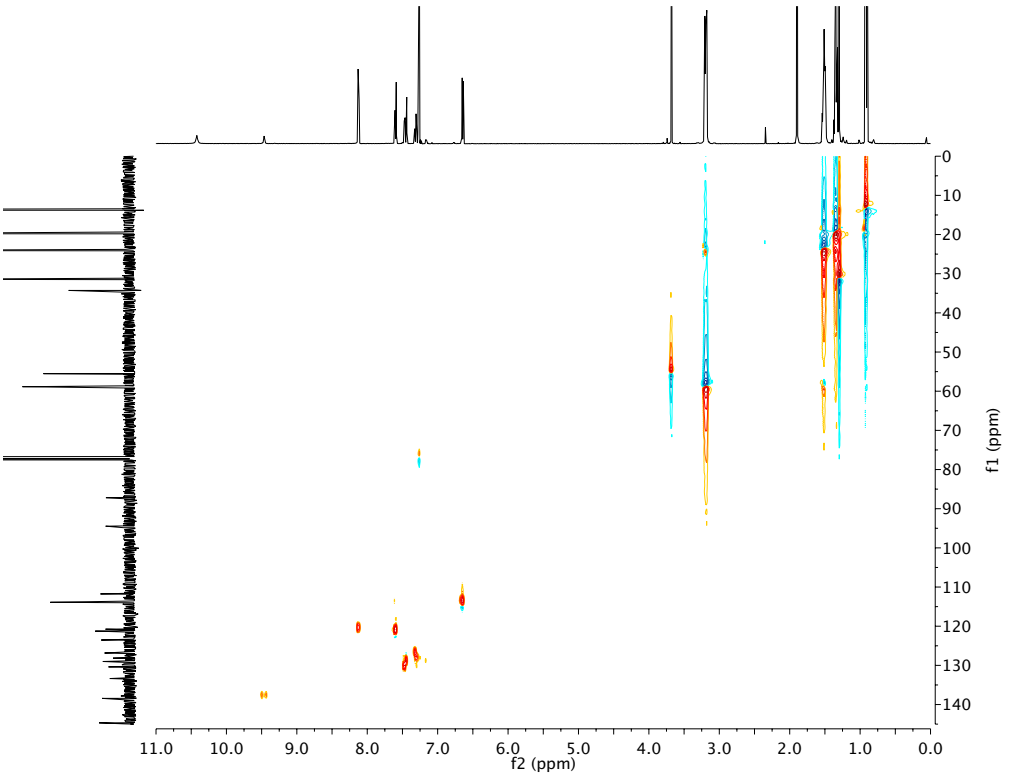

Figure S21. 2D ^{1}H–^{13}C HSQC NMR spectra of **5•Cl**$^{-}$ in $CDCl_3$.

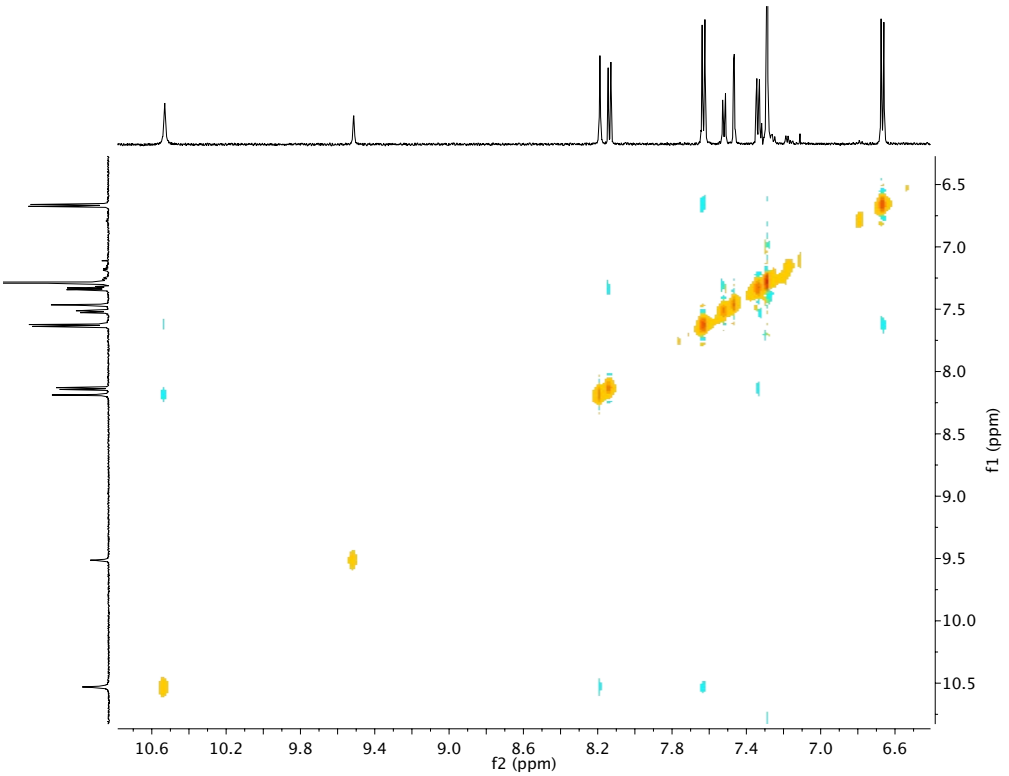

Figure S22. 2D ^{1}H–^{1}H ROESY NMR spectra of **5•Cl**$^{-}$ in $CDCl_3$.

Part VI: High Resolution MS of 4 and 5

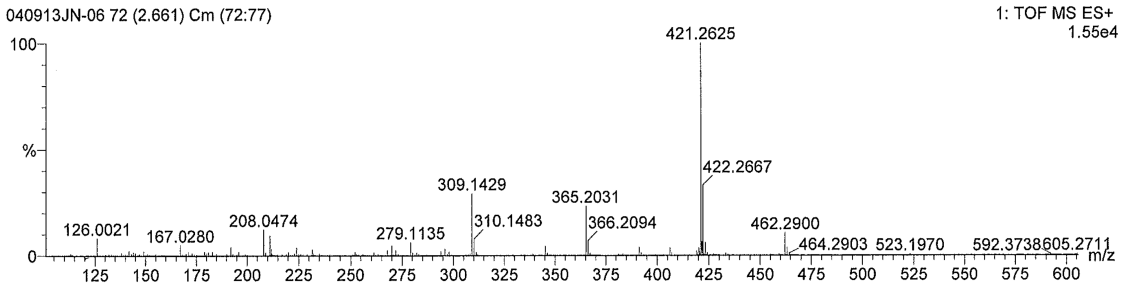

Figure S23. High resolution MS of **4**.

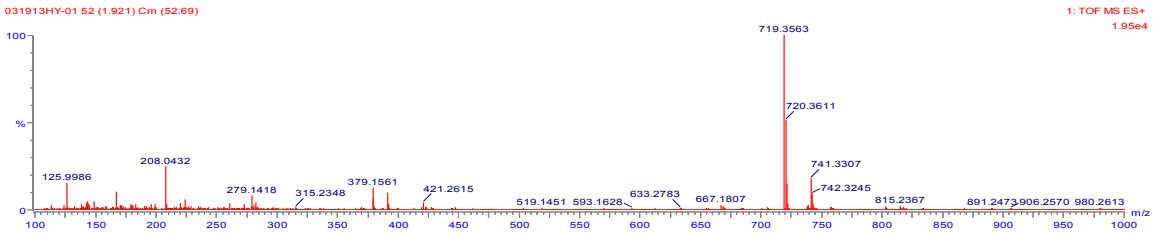

Figure S24. High resolution MS of **5**.

Part VII. References and Acknowledgments

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