Supporting Information

Spectroscopic, Structural, and Theoretical Studies of Halide Complexes with a Urea-based Tripodal Receptor

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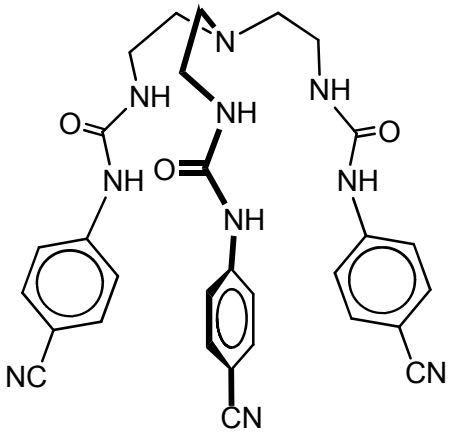

L

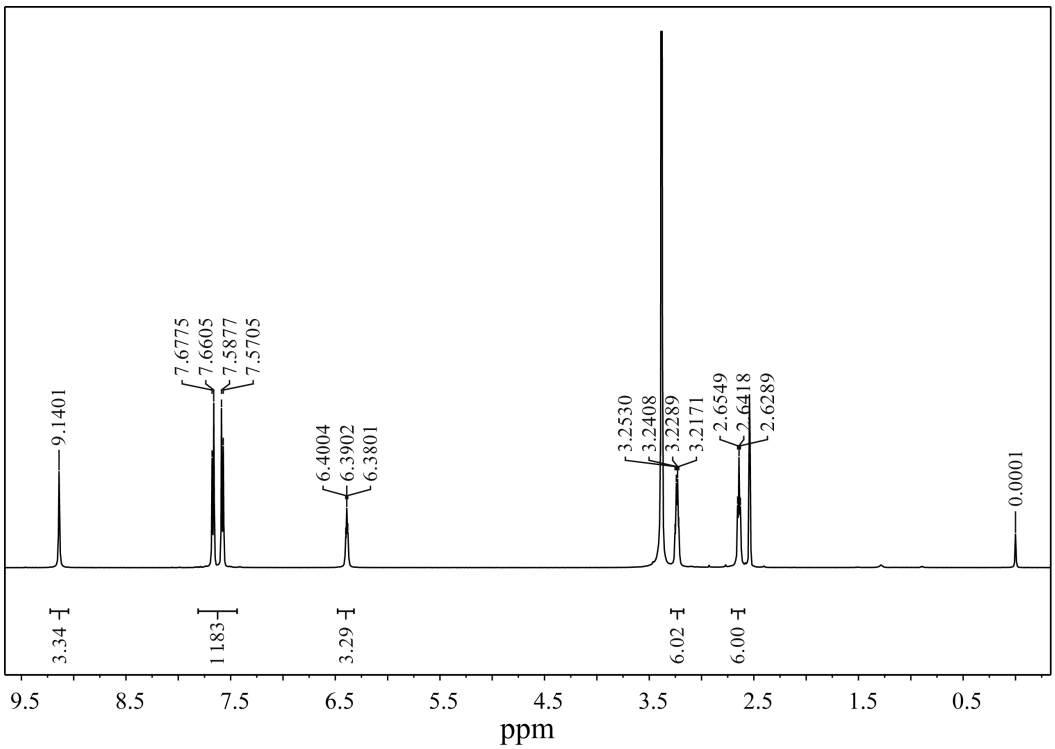

Figure S1. ^{1}H NMR spectrum of **L** in DMSO-d_6.

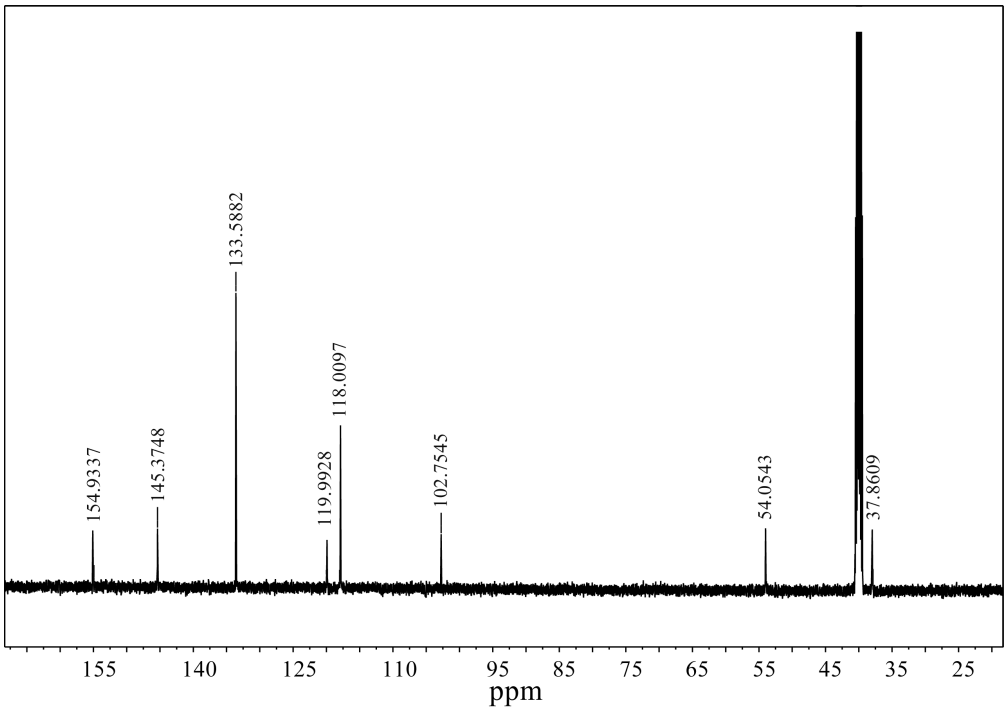

Figure S2. ^{13}C NMR spectrum of **L** in DMSO-d_6.

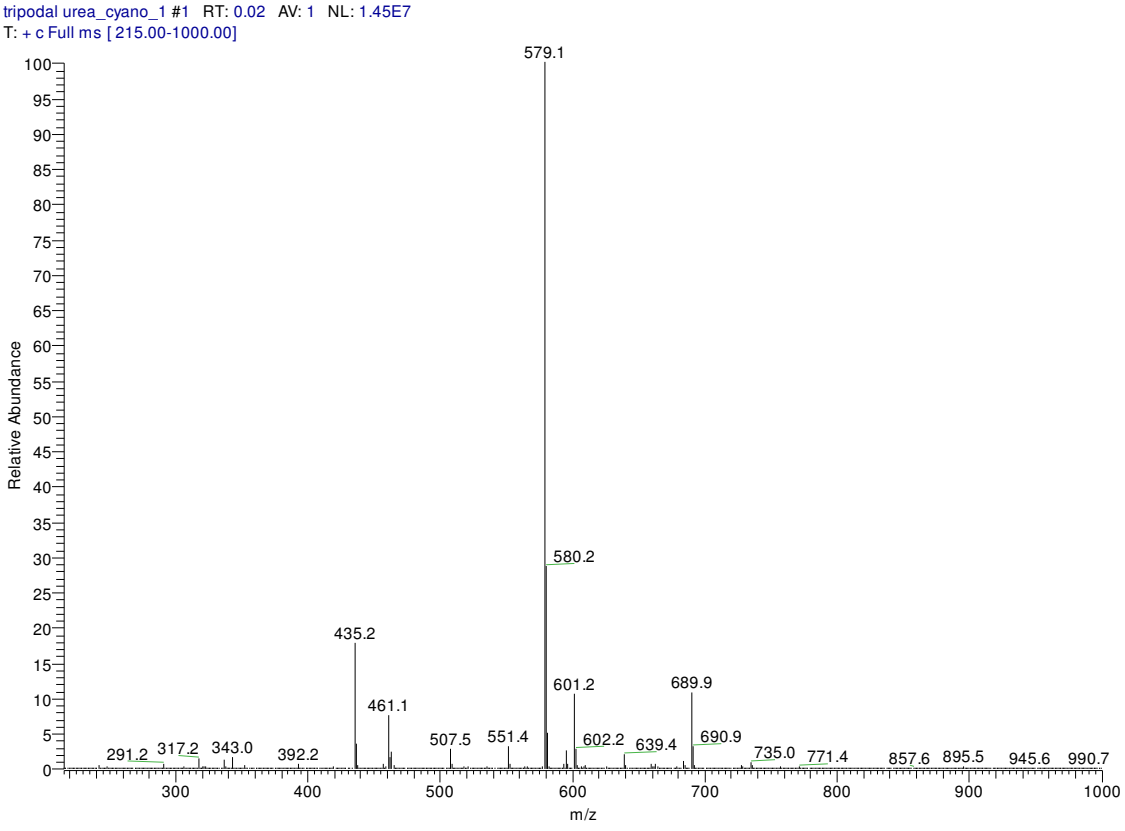

Figure S3. ESI-MS spectrum of ligand **L**

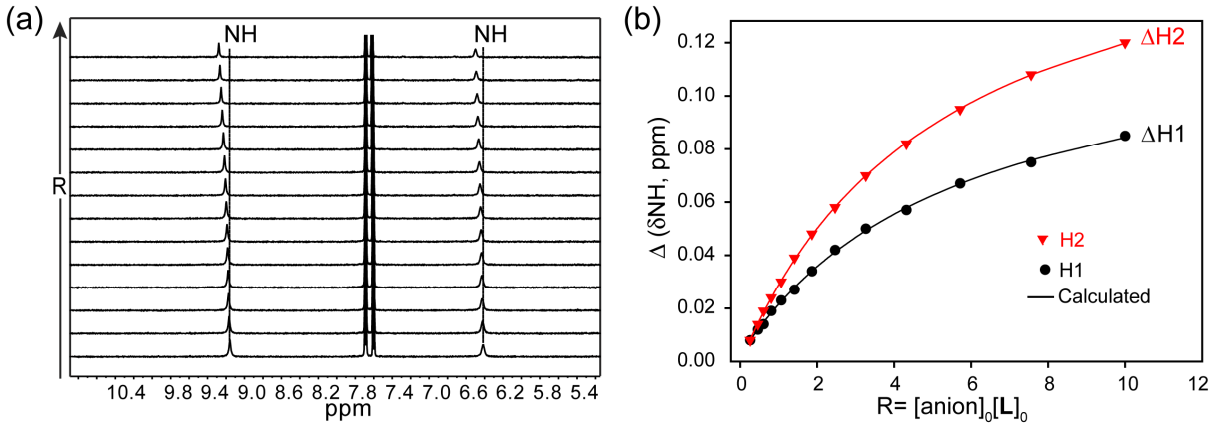

Figure S4. (a) ^{1}H NMR spectra of **L** (2 mM) with an increasing amount of TBABr (R = $[TBABr]_0/[\mathbf{L}]_0$) in DMSO-d_6. (b) Titration curves of **L** with TBABr showing changes in the chemical shifts of NH are shown against an increasing amount of anions. H1 = CH_2NHCO and H2 = CONHAr.

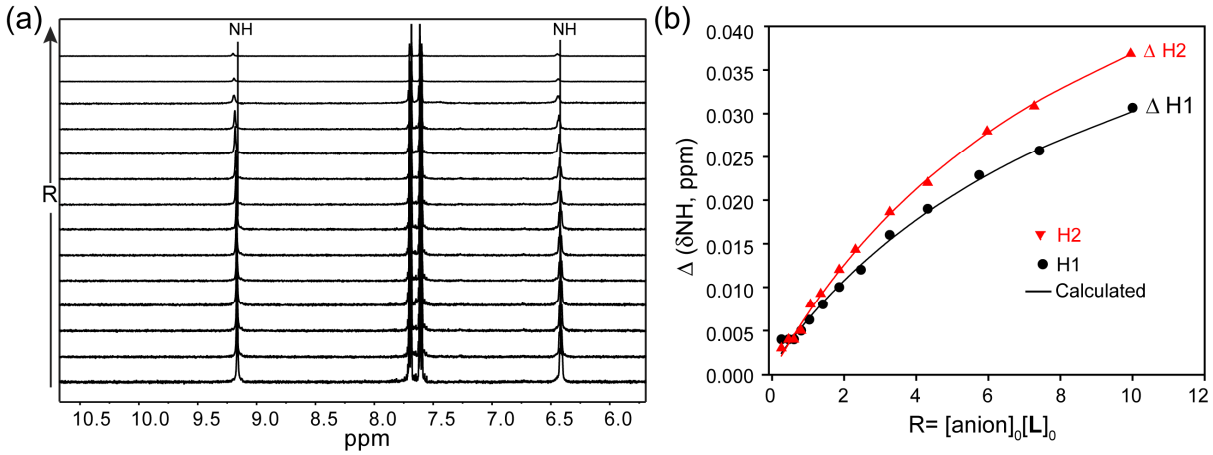

Figure S5. ^{1}H NMR spectra of **L** (2mM) with an increasing amount of (a) TBAI (R = $[TBAI]_0/[\mathbf{L}]_0$) and (b) TBAI (R = $[TBAI]_0/[\mathbf{L}]_0$) in DMSO-d_6. (No apparent binding was observed from these titrations)

Job plot

The binding stoichiometry was determined by a Job's plot analysis of the ^{1}H NMR spectra of **L** with varying amounts of an anion in DMSO-d_6. Stock solutions (10 mM) of ligands and anion solution were prepared separately. Ten NMR samples were prepared with different proportions of the ligand and anion solution so that the final concentration ([**L**] + [anion]) of each sample became 10 mM. Sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3,-d_4 acid (TSP) in DMSO-d_6 was used as an external reference in a sealed capillary tube. The stoichiometric ratio of **L** to anion in the complex was estimated by plotting Δδ ([**L**]/ ([**L**] + [A]) with ([**L**]/ [**L**] + [A]).

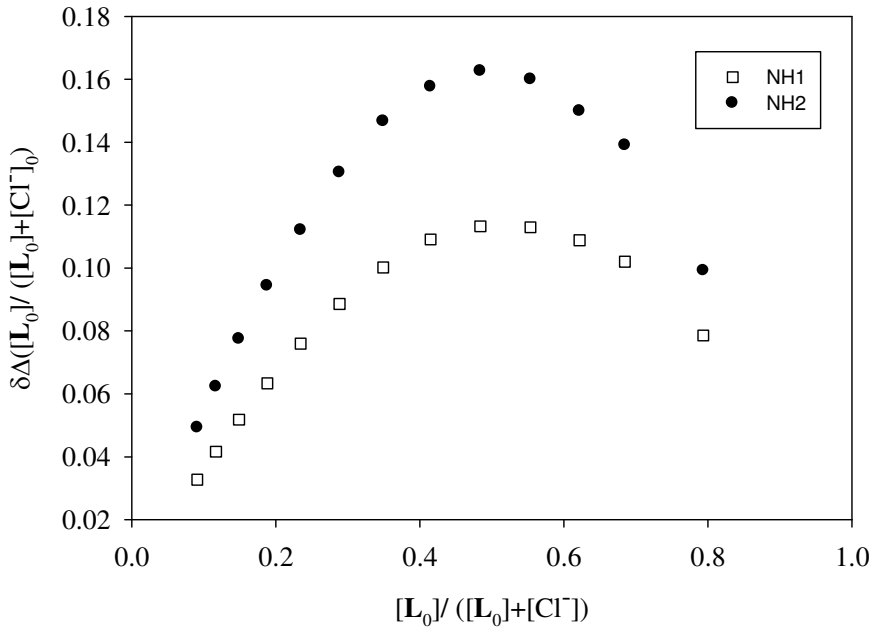

Figure S6. Job's plot of **L** with TBACl in DMSO-d_6 showing a maximum at 0.5 mole fraction of **L**. The shift change (δΔ) in the H1 (CH_2NHCO) and H2 ($CONHAr$) were followed for the Job's plot.

DFT calculations

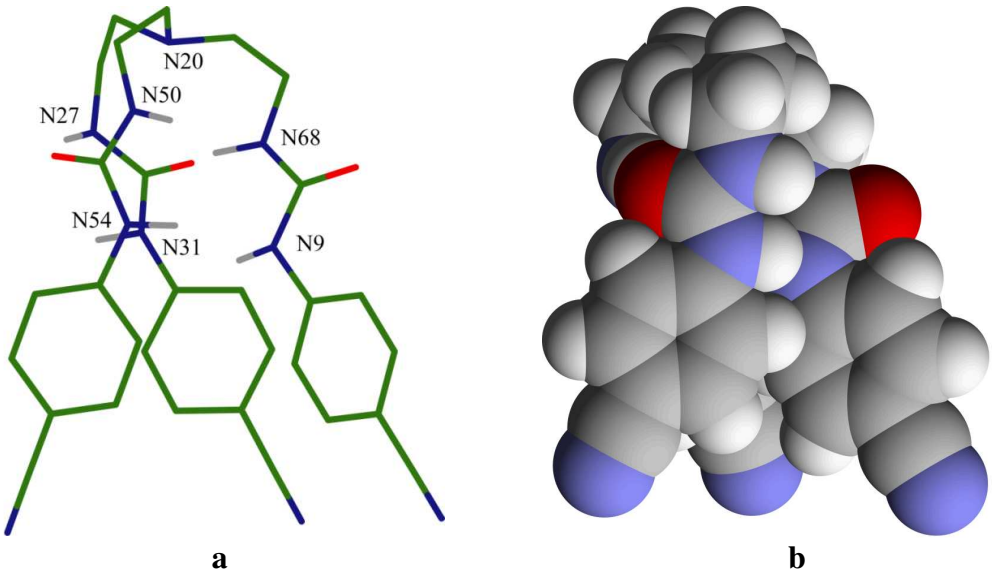

Figure S7. Optimized structures: (a) perspective view and (b) space filling model of **L**

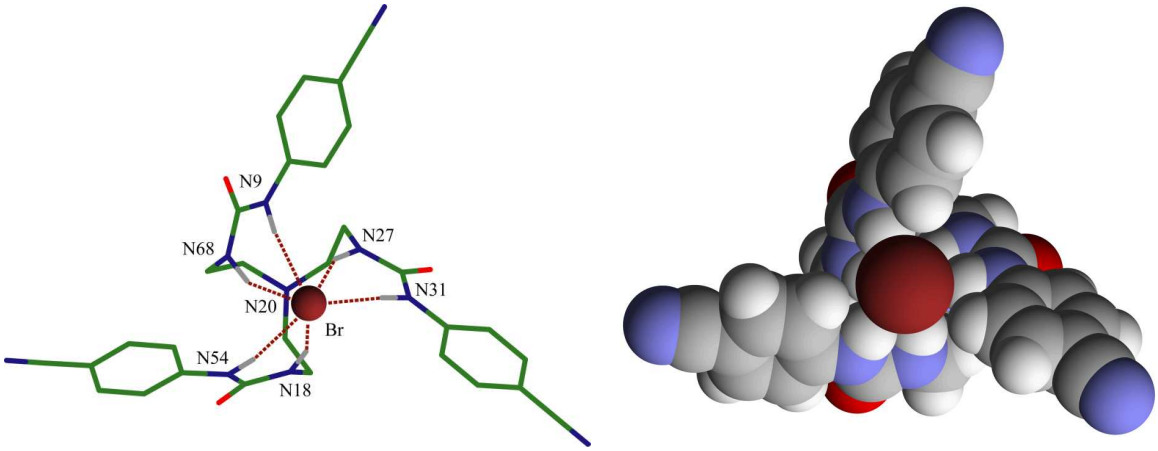

Figure S8. Optimized structures: (a) perspective view and (b) space filling model of bromide complex of **L**

Table S1. Reference Cartesian coordinates (in Å) and total energy (in Hartrees) for **L**.

Total energy: -1934.33017480

1	C1	8.4985	11.9640	0.6015 C
2	N2	8.7988	10.8461	0.5961 N
3	N3	0.0345	12.3391	2.6296 N
4	N4	5.2543	11.4578	6.4502 N
5	C5	6.7930	13.7247	0.8172 C
6	H6	6.0273	12.9642	0.9300 H
7	C7	6.4499	15.0634	0.8668 C
8	O8	3.4648	18.9734	3.6559 O
9	N9	4.7906	17.1804	3.0217 N
10	C10	3.7628	16.2136	2.9703 C
11	C11	2.4454	16.5339	2.6209 C
12	H12	2.1737	17.5623	2.4316 H
13	C13	1.4945	15.5262	2.5496 C
14	H14	0.4710	15.7689	2.2856 H
15	C15	1.8386	14.1959	2.8094 C
16	C16	3.1575	13.8754	3.1474 C
17	H17	3.4287	12.8466	3.3609 H
18	C18	4.1087	14.8798	3.2247 C
19	C19	0.8409	13.1648	2.7160 C
20	N20	7.8498	20.9025	3.2825 N
21	C21	9.2613	21.1862	3.5221 C
22	H22	9.4090	22.1905	3.9594 H
23	H23	9.7653	21.1883	2.5491 H
24	C24	9.9556	20.1469	4.4061 C
25	H25	11.0328	20.3399	4.3878 H
26	H26	9.6319	20.2055	5.4461 H

27	N27	9.6883	18.7970	3.9506 N
28	H28	9.7423	18.6574	2.9446 H
29	C29	8.7428	18.0657	4.6101 C
30	O30	8.3230	18.3231	5.7256 O
31	N31	8.2807	16.9667	3.8659 N
32	H32	8.8032	16.7646	3.0187 H
33	C33	7.6688	15.8454	4.4596 C
34	C34	6.7578	15.9675	5.5203 C
35	H35	6.5399	16.9453	5.9278 H
36	C36	6.1628	14.8287	6.0459 C
37	H37	5.4583	14.9181	6.8655 H
38	C38	6.4431	13.5658	5.5134 C
39	C39	7.3334	13.4477	4.4400 C
40	H40	7.5496	12.4717	4.0171 H
41	C41	7.9407	14.5807	3.9220 C
42	H42	8.6408	14.4883	3.0971 H
43	C43	5.7902	12.3979	6.0394 C
44	C44	7.3643	21.6592	2.1340 C
45	H45	7.7566	22.6914	2.1251 H
46	H46	6.2754	21.7403	2.1941 H
47	C47	7.7144	20.9751	0.8137 C
48	H48	7.3931	21.6031	-0.0231 H
49	H49	8.7902	20.8189	0.7141 H
50	N50	7.0924	19.6717	0.6874 N
51	H51	6.1130	19.6256	0.4498 H
52	C52	7.7798	18.5202	0.8943 C
53	O53	8.9902	18.4806	1.1111 O
54	N54	6.9899	17.3849	0.8161 N
55	H55	5.9949	17.4975	0.9764 H
56	C56	7.4297	16.0608	0.7497 C
57	C57	8.7676	15.6910	0.5356 C
58	H58	9.5259	16.4509	0.4112 H
59	C59	9.1030	14.3444	0.4721 C
60	H60	10.1353	14.0566	0.3039 H
61	C61	8.1289	13.3527	0.6269 C
62	C62	7.0282	21.0930	4.4787 C
63	H63	6.9376	22.1582	4.7552 H
64	H64	7.5162	20.5688	5.3045 H
65	C65	5.6293	20.5070	4.3158 C
66	H66	5.1245	20.5195	5.2870 H
67	H67	5.0016	21.1013	3.6413 H
68	N68	5.7181	19.1423	3.8307 N
69	H69	6.6192	18.8244	3.4930 H
70	C70	4.5702	18.4821	3.5222 C
71	H71	5.6855	16.7902	3.3074 H
72	H72	5.1356	14.6350	3.4813 H
73	H73	5.4094	15.3447	0.9995 H

Table S2. Reference Cartesian coordinates (in Å) and total energy (in Hartrees) for the fluoride complex of L.

Total energy: -2034.36081621

1 C1	7.0364	14.7731	-4.5160 C
2 N2	6.6806	14.3072	-5.5157 N
3 N3	1.0155	15.0050	8.1314 N
4 N4	7.4086	10.6746	8.8967 N
5 C5	6.9901	14.8749	-2.0566 C
6 H6	6.2633	14.0697	-2.0453 H
7 C7	7.4238	15.4382	-0.8725 C
8 O8	3.7453	18.7673	2.0096 O
9 N9	4.8234	16.8925	2.8422 N
10 C10	3.9867	16.5436	3.8930 C
11 C11	2.8012	17.2251	4.2180 C
12 H12	2.4900	18.0652	3.6156 H
13 C13	2.0519	16.8143	5.3090 C
14 H14	1.1403	17.3456	5.5621 H
15 C15	2.4521	15.7296	6.0964 C
16 C16	3.6264	15.0407	5.7663 C
17 H17	3.9529	14.1993	6.3689 H
18 C18	4.3716	15.4377	4.6729 C
19 C19	1.6613	15.3270	7.2247 C
20 N20	7.2946	20.4043	2.5361 N
21 C21	7.0607	20.8703	3.8977 C
22 H22	6.5909	21.8701	3.9176 H
23 H23	8.0296	20.9533	4.4019 H
24 C24	6.2110	19.8729	4.6810 C
25 H25	6.1064	20.1823	5.7234 H
26 H26	5.1998	19.8039	4.2508 H
27 N27	6.8610	18.5827	4.6649 N
28 H28	7.0454	18.1778	3.7524 H
29 C29	6.7955	17.7329	5.7335 C
30 O30	6.3831	18.0484	6.8396 O
31 N31	7.3047	16.4792	5.4051 N
32 H32	7.5617	16.3585	4.4156 H
33 C33	7.2985	15.3428	6.1839 C
34 C34	6.8957	15.2994	7.5317 C
35 H35	6.5642	16.2092	8.0115 H
36 C36	6.9220	14.0936	8.2141 C
37 H37	6.6106	14.0600	9.2531 H
38 C38	7.3416	12.9130	7.5882 C
39 C39	7.7354	12.9546	6.2437 C
40 H40	8.0561	12.0438	5.7489 H
41 C41	7.7123	14.1509	5.5546 C
42 H42	8.0071	14.1935	4.5090 H
43 C43	7.3746	11.6754	8.3133 C
44 C44	8.5816	20.8040	1.9862 C
45 H45	8.8595	21.8308	2.2851 H

46	H46	8.5194	20.7928	0.8941 H
47	C47	9.6965	19.8309	2.3800 C
48	H48	10.6386	20.1637	1.9337 H
49	H49	9.8242	19.8050	3.4666 H
50	N50	9.4208	18.4756	1.9486 N
51	H51	8.8651	17.8735	2.5529 H
52	C52	9.3447	18.2092	0.6119 C
53	O53	9.7444	18.9772	-0.2567 O
54	N54	8.7589	16.9728	0.3600 N
55	H55	8.3568	16.5149	1.1874 H
56	C56	8.3621	16.4866	-0.8741 C
57	C57	8.8533	16.9657	-2.1009 C
58	H58	9.5666	17.7768	-2.1035 H
59	C59	8.4085	16.3989	-3.2844 C
60	H60	8.7869	16.7681	-4.2320 H
61	C61	7.4810	15.3513	-3.2798 C
62	C62	6.1761	20.6447	1.6329 C
63	H63	6.2755	21.6074	1.1009 H
64	H64	5.2505	20.6881	2.2136 H
65	C65	6.0192	19.5027	0.6237 C
66	H66	5.1529	19.7017	-0.0135 H
67	H67	6.9026	19.4203	-0.0200 H
68	N68	5.8383	18.2230	1.2795 N
69	H69	6.6724	17.7289	1.5853 H
70	C70	4.7224	18.0273	2.0450 C
71	H71	5.7477	16.4514	2.8309 H
72	H72	5.2786	14.8982	4.4173 H
73	H73	7.0319	15.0901	0.0791 H
74	F74	7.5612	16.5307	2.7290 F

Table S3. Reference Cartesian coordinates (in Å) and total energy (in Hartrees) for the chloride complex of L.

Total energy: -2394.72975290

1	C1	7.4777	14.9410	-4.7836 C
2	N2	7.2998	14.6358	-5.8873 N
3	N3	-1.5567	16.1648	6.3522 N
4	N4	11.9355	12.5663	9.1007 N
5	C5	7.0075	14.6715	-2.3828 C
6	H6	6.2984	13.8852	-2.6189 H
7	C7	7.2255	15.0383	-1.0694 C
8	O8	3.6340	19.4473	1.7068 O
9	N9	3.8615	17.2675	2.4288 N
10	C10	2.7269	17.1143	3.2129 C
11	C11	1.7105	18.0772	3.3292 C
12	H12	1.7927	19.0036	2.7800 H
13	C13	0.6186	17.8217	4.1444 C

14	H14	-0.1673	18.5642	4.2360 H
15	C15	0.5091	16.6190	4.8499 C
16	C16	1.5244	15.6603	4.7326 C
17	H17	1.4498	14.7274	5.2811 H
18	C18	2.6184	15.9062	3.9268 C
19	C19	-0.6330	16.3683	5.6826 C
20	N20	7.2809	19.8842	2.9940 N
21	C21	6.8579	20.2601	4.3327 C
22	H22	6.5592	21.3216	4.3926 H
23	H23	7.6941	20.1211	5.0245 H
24	C24	5.7112	19.3773	4.8305 C
25	H25	5.4112	19.7011	5.8314 H
26	H26	4.8392	19.4567	4.1721 H
27	N27	6.0908	17.9780	4.8933 N
28	H28	5.9217	17.3944	4.0826 H
29	C29	7.0282	17.5868	5.8037 C
30	O30	7.4478	18.3265	6.6865 O
31	N31	7.4528	16.2773	5.6209 N
32	H32	7.0297	15.7633	4.8473 H
33	C33	8.3852	15.5794	6.3735 C
34	C34	8.9991	16.0842	7.5325 C
35	H35	8.7494	17.0777	7.8741 H
36	C36	9.9111	15.2995	8.2202 C
37	H37	10.3817	15.6876	9.1176 H
38	C38	10.2330	14.0113	7.7805 C
39	C39	9.6232	13.5106	6.6226 C
40	H40	9.8703	12.5140	6.2729 H
41	C41	8.7134	14.2849	5.9290 C
42	H42	8.2426	13.9047	5.0262 H
43	C43	11.1757	13.2113	8.5095 C
44	C44	8.7176	19.9300	2.7827 C
45	H45	9.1898	20.7791	3.3075 H
46	H46	8.9185	20.0588	1.7157 H
47	C47	9.3946	18.6283	3.2192 C
48	H48	10.4717	18.7015	3.0383 H
49	H49	9.2414	18.4505	4.2893 H
50	N50	8.8734	17.4733	2.5118 N
51	H51	8.1378	16.9319	2.9512 H
52	C52	9.0309	17.3853	1.1602 C
53	O53	9.7427	18.1492	0.5170 O
54	N54	8.2966	16.3511	0.5958 N
55	H55	7.7517	15.7757	1.2392 H
56	C56	8.1422	16.0577	-0.7508 C
57	C57	8.8348	16.7084	-1.7858 C
58	H58	9.5390	17.4902	-1.5425 H
59	C59	8.6061	16.3345	-3.1009 C
60	H60	9.1406	16.8357	-3.9012 H
61	C61	7.6988	15.3180	-3.4163 C
62	C62	6.4979	20.4816	1.9255 C
63	H63	6.9771	21.3868	1.5128 H

64 H64	5.5245	20.7839	2.3214 H
65 C65	6.2398	19.4839	0.7924 C
66 H66	5.6366	19.9625	0.0151 H
67 H67	7.1823	19.1581	0.3383 H
68 N68	5.5486	18.2931	1.2567 N
69 H69	6.1208	17.5166	1.5683 H
70 C70	4.2964	18.4191	1.7884 C
71 H71	4.4976	16.4695	2.4169 H
72 H72	3.4164	15.1732	3.8414 H
73 H73	6.6851	14.5480	-0.2640 H
74 Cl74	6.2879	15.1863	2.8146 Cl

Table S4. Reference Cartesian coordinates (in Å) and total energy (in Hartrees) for the bromide complex of **L**.

Total energy: -4508.70325449

1 C1	6.9063	14.7399	-4.1977 C
2 N2	6.6275	14.4377	-5.2811 N
3 N3	-2.6720	16.2071	4.5054 N
4 N4	13.3137	12.9900	7.6364 N
5 C5	6.5078	14.6469	-1.7700 C
6 H6	5.6500	14.0062	-1.9445 H
7 C7	6.8547	15.0104	-0.4836 C
8 O8	3.6128	19.4439	1.4213 O
9 N9	3.6406	17.3135	2.3102 N
10 C10	2.3323	17.1599	2.7359 C
11 C11	1.2940	18.0540	2.4266 C
12 H12	1.5109	18.9298	1.8322 H
13 C13	0.0136	17.7972	2.8902 C
14 H14	-0.7918	18.4844	2.6522 H
15 C15	-0.2623	16.6606	3.6583 C
16 C16	0.7760	15.7711	3.9669 C
17 H17	0.5691	14.8910	4.5664 H
18 C18	2.0566	16.0194	3.5141 C
19 C19	-1.5954	16.4095	4.1271 C
20 N20	7.3604	19.7842	3.2948 N
21 C21	7.0284	20.2841	4.6216 C
22 H22	6.7380	21.3491	4.5992 H
23 H23	7.9087	20.2042	5.2646 H
24 C24	5.9134	19.4707	5.2820 C
25 H25	5.7016	19.8886	6.2717 H
26 H26	4.9940	19.5192	4.6897 H
27 N27	6.2559	18.0671	5.4193 N
28 H28	5.9359	17.4237	4.7026 H
29 C29	7.3386	17.7038	6.1652 C
30 O30	7.9538	18.4764	6.8912 O
31 N31	7.6701	16.3644	6.0061 N

32	H32	7.0821	15.8308	5.3684 H
33	C33	8.8529	15.7394	6.3746 C
34	C34	9.7481	16.2532	7.3260 C
35	H35	9.5289	17.1977	7.8031 H
36	C36	10.8963	15.5393	7.6339 C
37	H37	11.5912	15.9302	8.3698 H
38	C38	11.1714	14.3151	7.0155 C
39	C39	10.2778	13.8083	6.0618 C
40	H40	10.4923	12.8656	5.5701 H
41	C41	9.1350	14.5148	5.7423 C
42	H42	8.4455	14.1499	4.9846 H
43	C43	12.3584	13.5831	7.3567 C
44	C44	8.7918	19.8009	3.0197 C
45	H45	9.2846	20.6844	3.4615 H
46	H46	8.9512	19.8515	1.9395 H
47	C47	9.4769	18.5273	3.5200 C
48	H48	10.5441	18.5738	3.2847 H
49	H49	9.3738	18.4261	4.6059 H
50	N50	8.9189	17.3330	2.9103 N
51	H51	8.1194	16.9052	3.3657 H
52	C52	9.0403	17.1672	1.5580 C
53	O53	9.7673	17.8614	0.8569 O
54	N54	8.2549	16.1327	1.0730 N
55	H55	7.6773	15.6488	1.7588 H
56	C56	7.9649	15.8434	-0.2526 C
57	C57	8.7155	16.3186	-1.3393 C
58	H58	9.5633	16.9627	-1.1553 H
59	C59	8.3541	15.9531	-2.6267 C
60	H60	8.9322	16.3145	-3.4710 H
61	C61	7.2580	15.1150	-2.8573 C
62	C62	6.5655	20.3815	2.2304 C
63	H63	7.0201	21.3145	1.8499 H
64	H64	5.5774	20.6437	2.6238 H
65	C65	6.3448	19.4029	1.0767 C
66	H66	5.8113	19.9074	0.2674 H
67	H67	7.2989	19.0376	0.6805 H
68	N68	5.5597	18.2536	1.4836 N
69	H69	6.0368	17.5017	1.9691 H
70	C70	4.2227	18.4246	1.7178 C
71	H71	4.2688	16.5447	2.5384 H
72	H72	2.8755	15.3475	3.7600 H
73	H73	6.2691	14.6779	0.3702 H
74	Br74	6.0198	15.2229	3.3501 Br