Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Lithium Sensors Based on Photophysical Changes of 1-Aza-12-crown-4 Naphthalene Derivatives Synthesized via Buchwald-Hartwig Amination

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DFT Calculations

The compound 1: Summary of geometry optimization

Calculation method = B3LYP
Basis set = 6-31G*
Charge = 0
Spin = Singlet
Final single point energy = -979.519883133685 a.u.
Dipole moment = 2.78446 Debye
Total Run Time = 0 days 3 hours 32 minutes 52 seconds 287 msec
Cartesian coordinates (Å) of the optimized **1**

C	-3.691230	1.362149	-1.168708
C	-4.653922	1.410662	-0.185960
C	-4.488505	0.653819	0.998403
C	-3.389768	-0.163480	1.155448
C	-2.399095	-0.274554	0.141392
C	-2.535781	0.544482	-1.029919
H	-3.792871	1.965231	-2.068621
H	-5.528448	2.045082	-0.306493
H	-5.226054	0.728570	1.793686
H	-3.249513	-0.710222	2.081678
C	-1.499066	0.559331	-2.000864
C	-0.367903	-0.200479	-1.812483
C	-0.249212	-1.054983	-0.692625
C	-1.248231	-1.131704	0.264731
H	0.619579	-1.695129	-0.586582
H	-1.607353	1.194097	-2.877319
H	0.435660	-0.174570	-2.545064
N	-1.132882	-1.990771	1.390218
C	-2.075728	-3.091345	1.566982
C	-1.838365	-4.350550	0.723524
H	-3.087034	-2.738820	1.339796
H	-2.066768	-3.381862	2.628152
O	-2.140485	-4.044127	-0.630842
H	-2.513647	-5.147373	1.088029
H	-0.811607	-4.708269	0.814695
C	-1.786125	-5.039970	-1.572198
C	-0.325568	-4.982085	-2.011301
H	-2.413836	-4.857830	-2.453295
H	-2.017901	-6.048768	-1.193476
O	0.505237	-5.530198	-0.995996
H	-0.062573	-3.933304	-2.205750
H	-0.206674	-5.549730	-2.951005
C	1.845684	-5.072495	-0.946355
C	2.154784	-4.604342	0.468581
H	2.007204	-4.241433	-1.646657

H	2.532265	-5.887252	-1.224599
O	1.412728	-3.422168	0.714840
H	3.235869	-4.420571	0.586905
H	1.865470	-5.397055	1.175250
C	1.035180	-3.209142	2.060040
C	0.097873	-1.996737	2.168853
H	1.917554	-3.015264	2.695302
H	0.544661	-4.111969	2.459246
H	0.654899	-1.093932	1.902321
H	-0.151601	-1.912459	3.241970

The compound 2: Summary of geometry optimization

Calculation method = B3LYP
Basis set = 6-31G*
Charge = 0
Spin = Singlet
Final single point energy = -1417.385692212674 a.u.
Dipole moment = 7.18132 Debye
Total Run Time = 0 days 8 hours 44 minutes 37 seconds 905 msec
Cartesian coordinates (Å) of the optimized **2**

C	-2.445175	-0.307957	0.733830
C	-3.492932	-0.713394	1.542983
C	-3.396181	-1.914986	2.270891
C	-2.278452	-2.718975	2.148922
C	-1.206399	-2.366221	1.288578
C	-1.279696	-1.109081	0.609994
C	-0.175915	-0.641395	-0.147562
C	0.976138	-1.407656	-0.215218
C	1.045832	-2.670051	0.399236
C	-0.029995	-3.182786	1.119022
H	-4.367259	-0.075193	1.619508
H	-4.199372	-2.202896	2.943559
H	-2.191131	-3.619193	2.747180
H	1.815181	-1.030120	-0.791432
H	1.928865	-3.288064	0.276339
C	-2.549229	0.986770	0.012870
N	-1.445456	1.372195	-0.760602
C	-0.235572	0.658115	-0.850613
O	-3.547001	1.696391	0.078811
O	0.705176	1.109762	-1.494074
C	-1.534898	2.653805	-1.483959
C	-1.075322	3.847703	-0.638747
H	-2.578339	2.777474	-1.780088
H	-0.911550	2.556699	-2.374510
C	-1.176281	5.171484	-1.408184

H	-0.037337	3.680345	-0.323116
H	-1.691005	3.899163	0.268465
C	-0.721834	6.378031	-0.578795
H	-2.214822	5.323484	-1.735875
H	-0.571228	5.107813	-2.324025
H	-1.331671	6.486892	0.326708
H	-0.803640	7.309795	-1.150751
H	0.323591	6.270193	-0.263777
N	0.012163	-4.471919	1.693129
C	-0.917575	-5.493332	1.201593
C	-0.888565	-5.741477	-0.308209
H	-1.953972	-5.231599	1.452396
H	-0.694913	-6.428080	1.727543
O	0.321661	-6.363067	-0.697411
H	-1.012481	-4.782376	-0.834356
H	-1.749889	-6.377581	-0.579157
C	0.560690	-6.272093	-2.091917
C	1.850991	-6.996548	-2.443917
H	0.639448	-5.215884	-2.393455
H	-0.270383	-6.726654	-2.660587
O	2.986656	-6.356333	-1.891009
H	1.961881	-6.990215	-3.536739
H	1.788145	-8.045646	-2.120872
C	3.558913	-6.960626	-0.744634
C	1.188519	-4.906364	2.446759
C	2.204462	-5.838217	1.779623
H	0.832113	-5.434637	3.345550
H	1.708667	-4.008224	2.793452
O	2.973254	-5.131868	0.823708
H	1.684757	-6.687953	1.320534
H	2.866462	-6.231104	2.572631
C	4.019689	-5.883281	0.232346
H	4.640095	-6.357268	1.013412
H	4.640338	-5.157735	-0.303038
H	4.439033	-7.561273	-1.032413
H	2.844508	-7.637100	-0.259097

The compound 1 + LiCl: Summary of geometry optimization

Calculation method = B3LYP
Basis set = 6-31G*
Charge = 0
Spin = Singlet
Final single point energy = -1447.304911232912 a.u.
Dipole moment = 9.82921 Debye
Total Run Time = 0 days 7 hours 46 minutes 23 seconds 316 msec

Cartesian coordinates (Å) of the optimized **1** + LiCl

C	-3.583815	3.018562	0.514386
C	-4.395599	3.188483	-0.583923
C	-4.497666	2.159312	-1.549605
C	-3.788669	0.986577	-1.401911
C	-2.937085	0.775471	-0.280678
C	-2.838356	1.822229	0.698915
C	-2.000902	1.645790	1.833635
C	-1.284491	0.484779	2.000764
C	-1.373474	-0.550758	1.039135
C	-2.174369	-0.427787	-0.081496
N	-2.217387	-1.520926	-1.021386
C	-3.459055	-2.316370	-1.003339
C	-3.571323	-3.139173	0.287884
O	-2.481569	-4.056031	0.315073
C	-1.934983	-4.462889	1.560430
C	-0.493539	-4.887271	1.280359
O	0.124274	-3.743188	0.689064
C	1.375969	-3.894261	0.018075
C	1.552913	-2.611268	-0.793162
O	0.419899	-2.510867	-1.643119
C	-0.000471	-1.229388	-2.101239
C	-1.521757	-1.276322	-2.299039
H	-3.499436	3.802489	1.263728
H	-4.959285	4.108582	-0.712146
H	-5.141003	2.294852	-2.414979
H	-3.883300	0.211272	-2.153575
H	-1.938096	2.447193	2.566157
H	-0.644638	0.353924	2.869581
H	-0.805939	-1.467375	1.168813
H	-3.428716	-3.011192	-1.851021
H	-4.372171	-1.707490	-1.098298
H	-4.526090	-3.682857	0.296861
H	-3.534928	-2.484272	1.169113
H	-2.501115	-5.302072	1.989167
H	-1.948360	-3.626211	2.274268
H	-0.476413	-5.731294	0.576793
H	0.012598	-5.177465	2.212712
H	1.343138	-4.764626	-0.652161
H	2.201418	-4.014856	0.734912
H	2.484034	-2.657813	-1.375779
H	1.601064	-1.743542	-0.119109
H	0.487162	-0.988456	-3.056028
H	0.271119	-0.458507	-1.367128
H	-1.755104	-2.105113	-2.977657
H	-1.828605	-0.339946	-2.790910

Li	-1.085711	-3.688918	-1.065129
Cl	-1.277815	-5.224744	-2.622417

LOD Calculations

Limit of detection (LOD) was calculated according to the following equation:

$$LOD = 3 * (RMS_{noise} / slope)$$

$$RMS_{noise} = \sqrt{V_{x^2}/N}$$

$$V_{x^2} = \sum (y_i - y)^2$$

In order to obtain the LOD, we first took ten consecutive blank UV-vis data points (absorption at 317 nm) of the compound **1** prior to the exposure to the lithium ions. These values were plotted and fitted to the fifth order polynomial. In the equation to obtain V_{x^2}, y_i means the actual value of each blank data point, and y indicates the corresponding value from the fifth order polynomial fit. The slope was calculated from the linear fit of the concentration-signal graph (black curve) in Figure 3d, wherein a lithium concentration at zero was excluded. The RMS_{noise} (0.0004670) and the slope (0.06763 mM^{-1}) were obtained, resulting in the LOD of 21 μM.

Additional Data

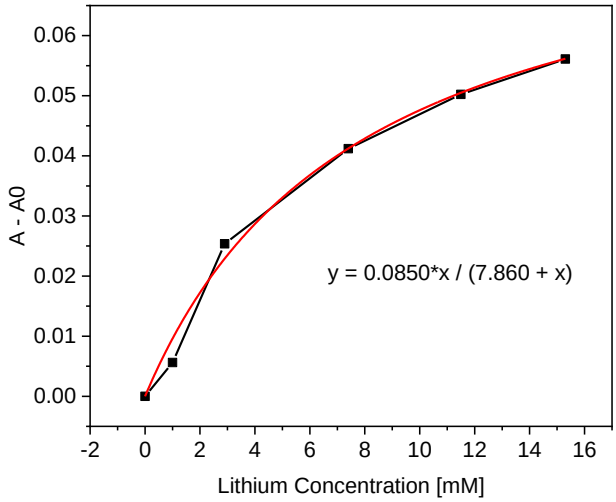

Figure S1. The plot of the absorption difference at 282 nm and the lithium concentration for the calculation of the binding constant.

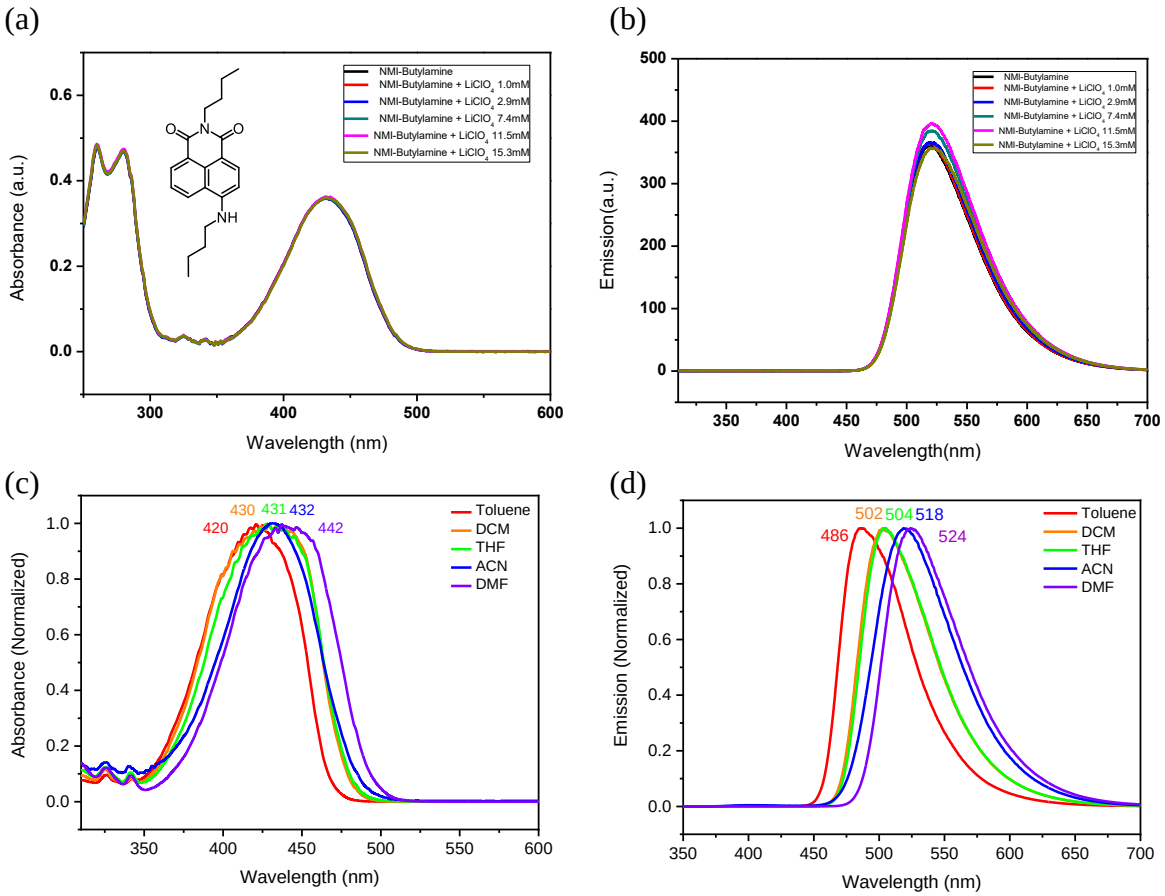

Figure S2. Characterization of NMI-NH-Bu. (a) Upon the addition of lithium ions, the absorption of this compound did not change. (b) The emission spectra did not generate additional fluorescence peaks upon the addition of lithium ions, indicating that this reporter is inert to lithium ions. Solvatochromic studies in (c) absorption and (d) emission displayed red-shifted peaks as the solvent polarity increases, which could result from the polar excited structures generated by intramolecular charge transfer.

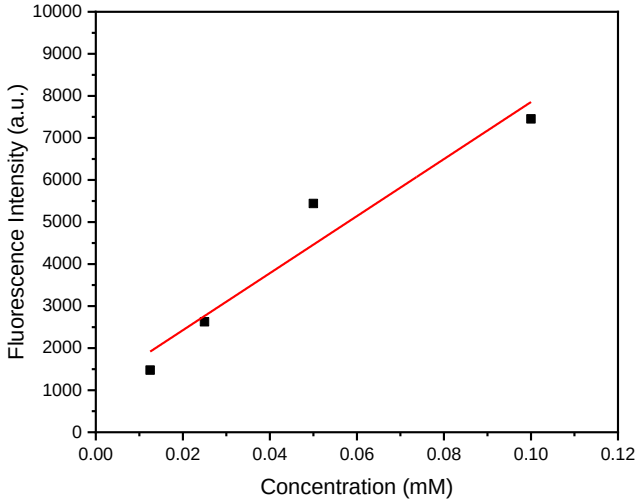

Figure S3. Fluorescence intensity depending on the concentration of Naph-Crown (**1**), indicative of no self-quenching at a concentration of 0.1 mM.

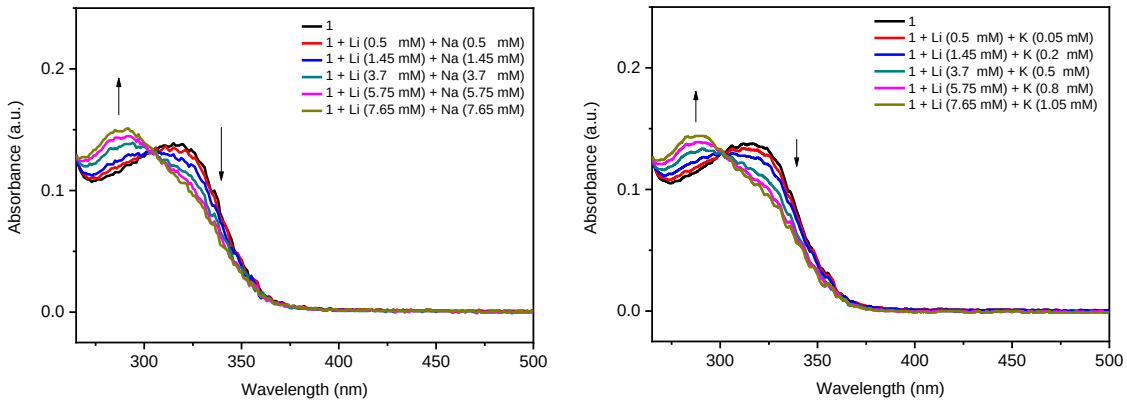

Figure S4. Absorption spectra in the co-existence of lithium/sodium (left) and lithium/potassium (right).

NMR Spectra

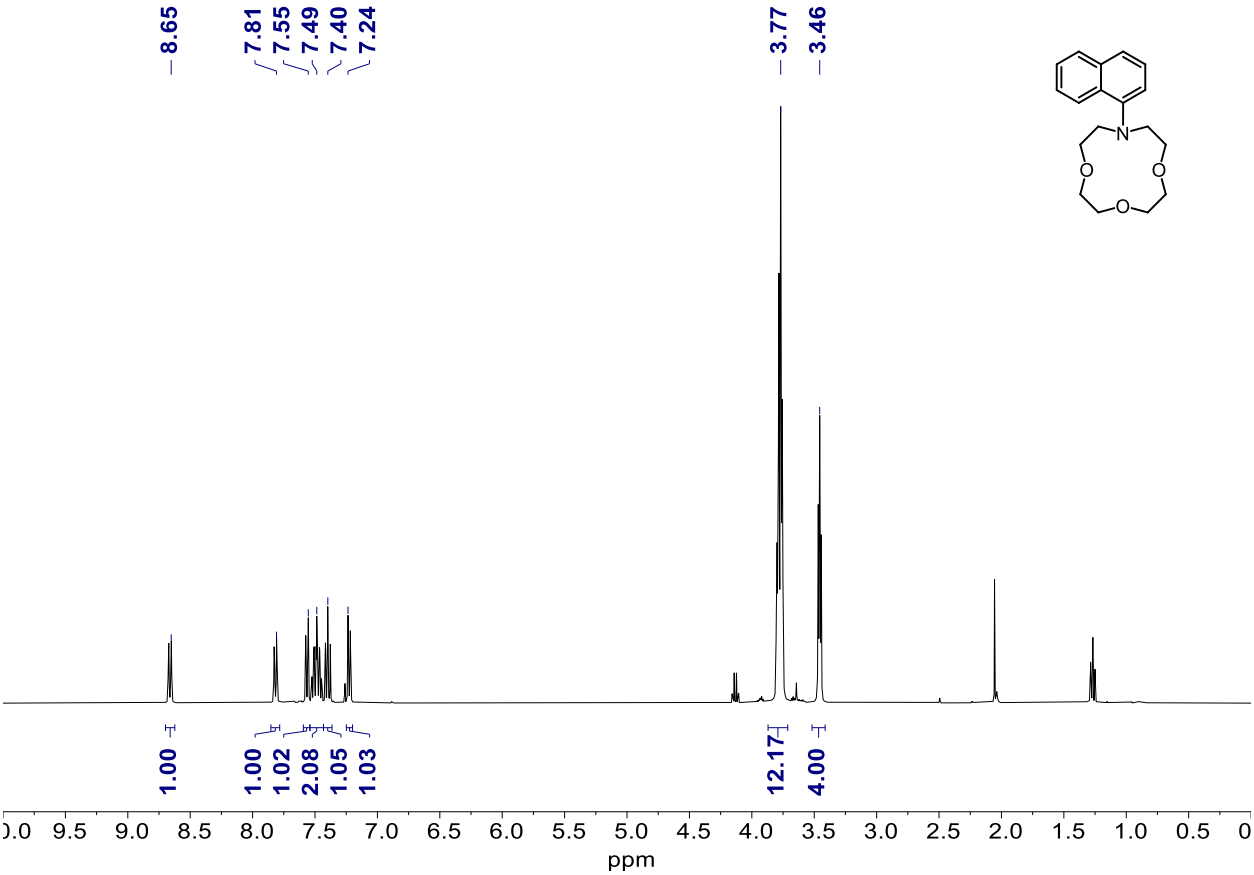

Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

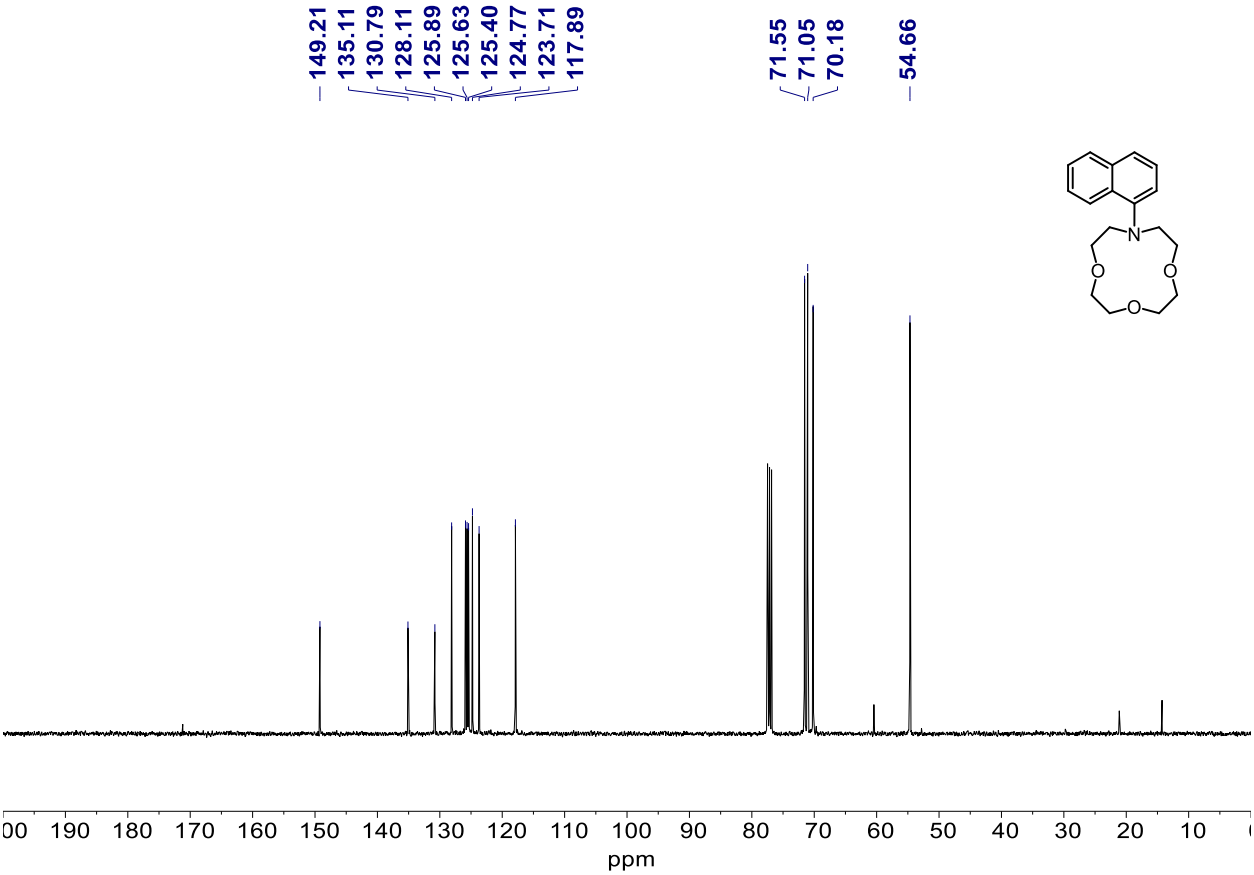

Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$.

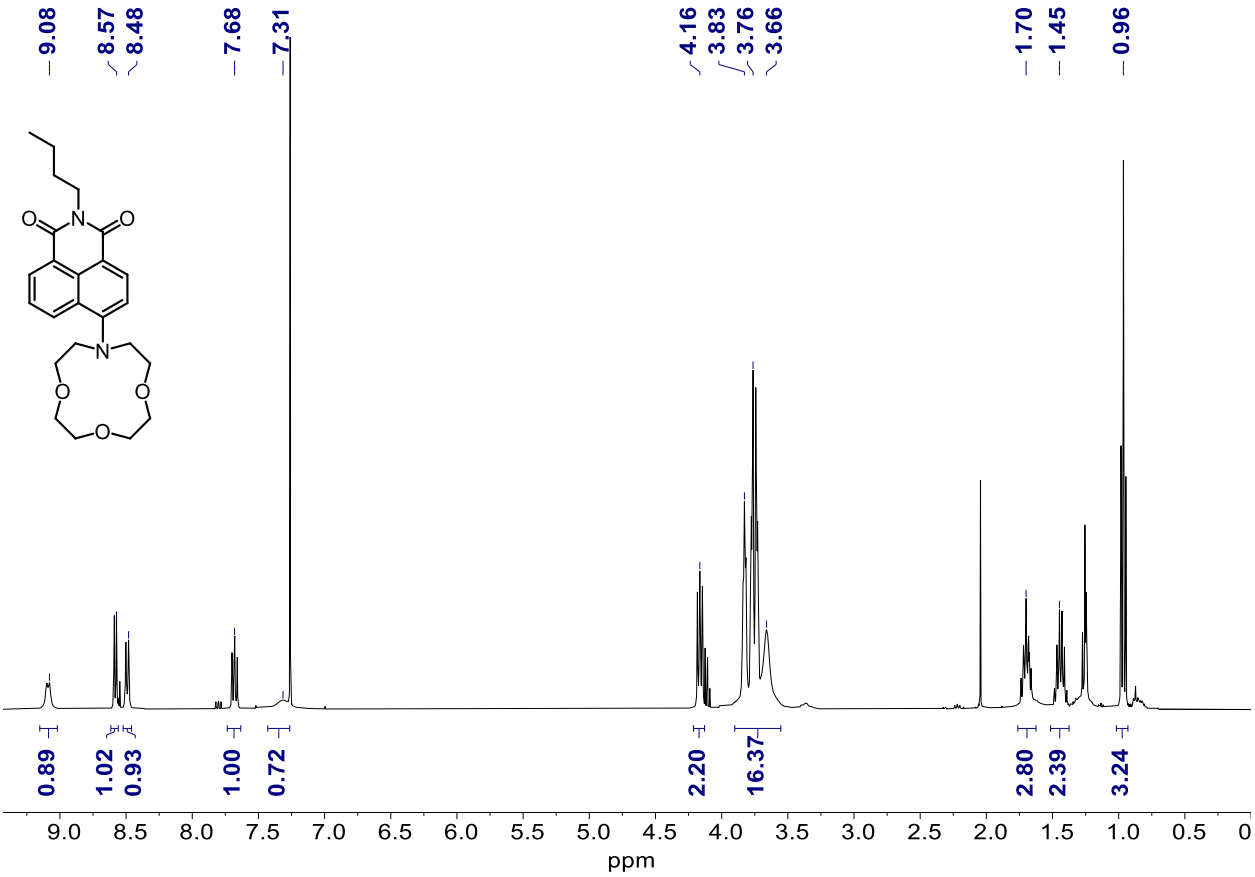

Figure S3. ^{1}H NMR spectrum of **2** in $CDCl_3$.

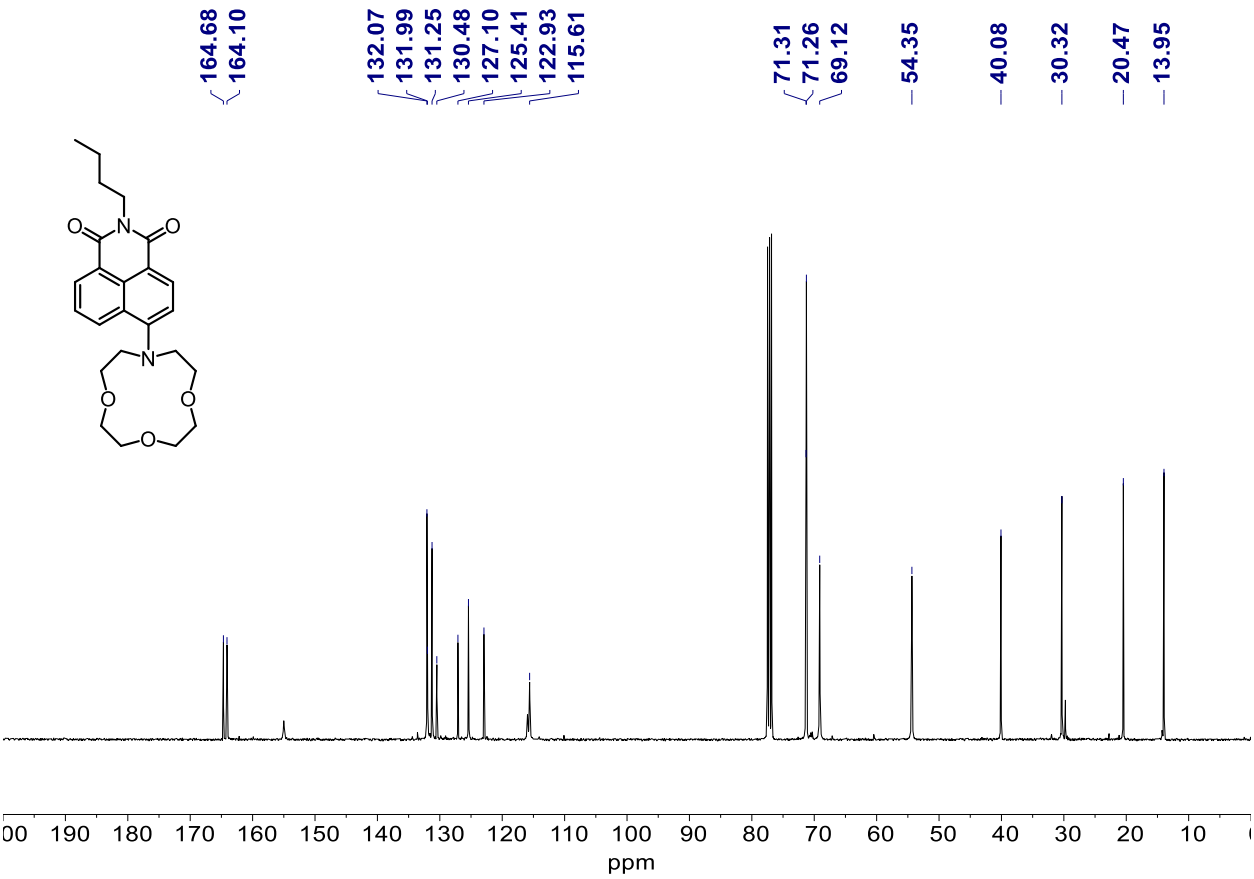

Figure S4. ^{13}C NMR spectrum of **2** in $CDCl_3$.

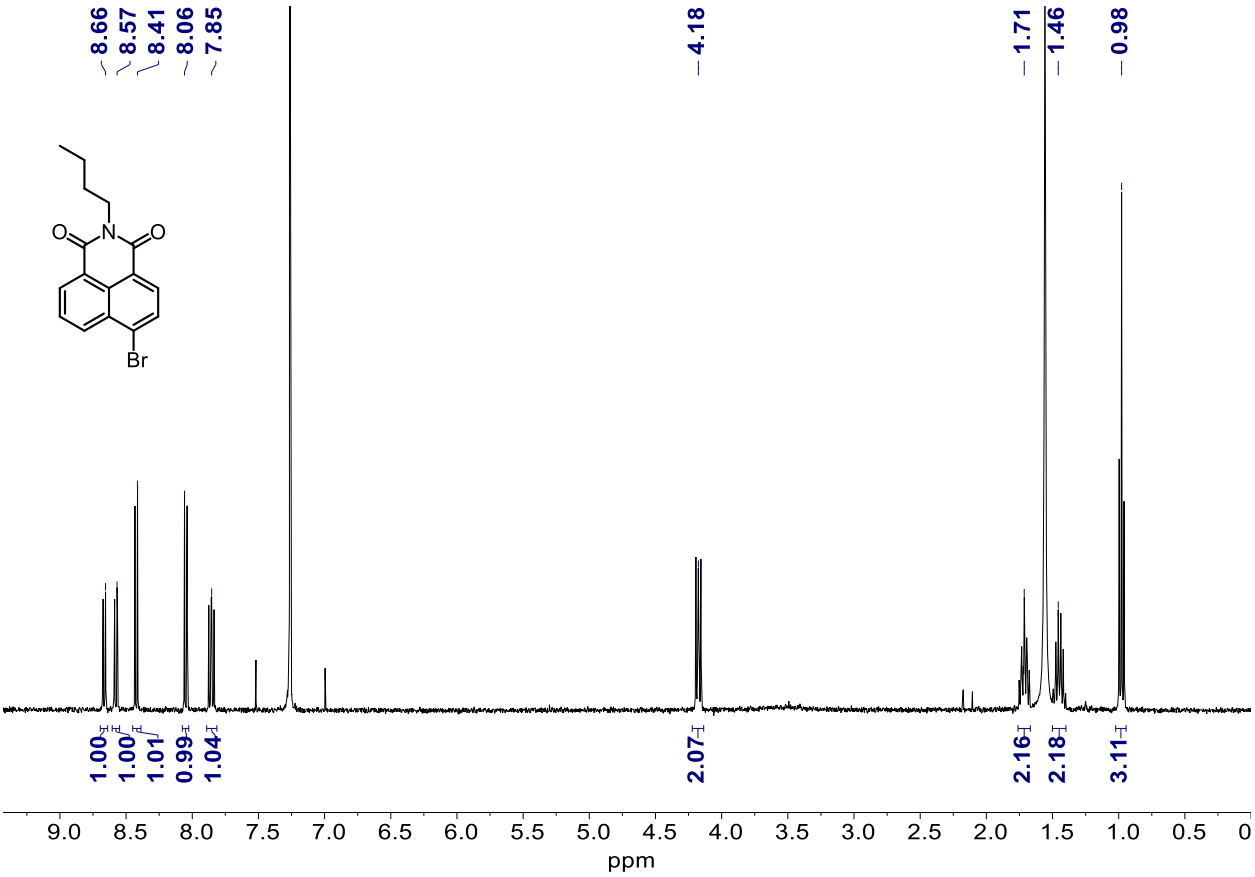

Figure S5. ^{1}H NMR spectrum of **3** in $CDCl_3$.