Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Chromenoquinoline-Based Thiol Probes: A Study on Quencher Position for Controlling Fluorescent *Off-On* Characteristics

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Supporting Information

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I. Theoretical Calculations:

The molecular geometries of **5** and **6** were fully optimized at a level of density functional theory employing the hybrid functional B3LYP[S1] with Pople's basis set 6-311G(d,p) where polarization functions were added to all the atoms and diffuse functions to the heavy atoms. All the calculations were performed with the development version of Gaussian 09.[S2]

Table S1. Atomic coordinates calculated for **5** from DFT B3LYP/6-311G(d,p) geometry optimization.

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Atom #	Atom Type	x	y	z
1	C	3.375847	-1.818948	-0.00538
2	C	3.180032	-0.414779	-0.047826
3	C	1.910106	0.119132	-0.032958
4	C	0.779936	-0.732779	0.021573
5	C	0.974737	-2.144062	0.075089
6	C	2.292004	-2.658264	0.060468
7	N	-0.455049	-0.162336	0.022986
8	C	-1.526053	-0.932946	0.091628
9	C	-1.421565	-2.362648	0.16183
10	C	-0.187472	-2.949817	0.138436
11	C	-2.887966	-0.35972	0.017336
12	C	-3.908259	-1.227693	-0.377345
13	O	-3.716377	-2.569664	-0.546825
14	C	-2.700271	-3.131099	0.288306
15	C	-3.221887	1.032406	0.217303
16	C	-4.557339	1.474039	-0.060316
17	C	-5.521823	0.54501	-0.531858
18	C	-5.211215	-0.77639	-0.679133
19	C	-2.305857	2.000196	0.708366
20	C	-2.684863	3.30986	0.90178
21	C	-3.995183	3.739421	0.612542
22	C	-4.910667	2.831492	0.140731
23	N	4.318363	0.441395	-0.124334
24	C	4.40717	1.612831	-0.911795
25	C	5.776581	2.172475	-0.669125
26	C	6.419843	1.389398	0.192872
27	C	5.525983	0.250812	0.581131
28	O	3.551313	2.061971	-1.628377
29	O	5.778803	-0.650023	1.340132
30	H	4.379483	-2.218256	-0.010613
31	H	1.741952	1.184617	-0.086004
32	H	2.44148	-3.732056	0.098435
33	H	-0.088574	-4.031051	0.177239
34	H	-3.059412	-3.114278	1.328184
35	H	-2.587689	-4.168424	-0.026025
36	H	-6.522732	0.898531	-0.75564
37	H	-5.935862	-1.507544	-1.014935

38	H	-1.292794	1.695327	0.912673
39	H	-1.95979	4.021124	1.282181
40	H	-4.275838	4.775386	0.764971
41	H	-5.927536	3.138317	-0.081619
42	H	6.107258	3.075785	-1.160219
43	H	7.41603	1.483266	0.59944

Table S2. Atomic coordinates calculated for **6** from DFT B3LYP/6-311G(d,p) geometry optimization.

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Atom #	Atom Type	x	y	z
1	C	4.284985	2.073499	-0.332478
2	C	4.075632	0.688757	-0.16795
3	C	2.803739	0.169842	-0.094675
4	C	1.663614	1.024761	-0.182878
5	C	1.891869	2.426411	-0.335575
6	C	3.212131	2.927572	-0.413735
7	N	0.420967	0.488494	-0.094202
8	C	-0.631665	1.286957	-0.151892
9	C	-0.499856	2.708596	-0.274347
10	C	0.746548	3.259846	-0.363246
11	C	-2.000158	0.757131	0.010931
12	C	-2.953246	1.644748	0.511649
13	O	-2.706287	2.980744	0.653522
14	C	-1.771178	3.500894	-0.299356
15	C	-2.392532	-0.612616	-0.207695
16	C	-3.692347	-1.038535	0.21744
17	C	-4.571145	-0.103006	0.825839
18	C	-4.222847	1.212691	0.951848
19	C	-1.57809	-1.556913	-0.884188
20	C	-2.013145	-2.845741	-1.0978
21	C	-3.275916	-3.27285	-0.63871
22	C	-4.098254	-2.379526	0.003228
23	N	2.625467	-1.222934	0.136016
24	C	2.071932	-2.137294	-0.774354
25	C	1.981344	-3.442299	-0.03843
26	C	2.440699	-3.277515	1.199845
27	C	2.865254	-1.850236	1.376313
28	O	3.327318	-1.329774	2.358141
29	O	1.756516	-1.910359	-1.915078

30	H	5.2971	2.455988	-0.386854
31	H	4.922144	0.018025	-0.088659
32	H	3.363255	3.995591	-0.530259
33	H	0.872689	4.335235	-0.450227
34	H	-2.23523	3.460663	-1.295628
35	H	-1.609515	4.543438	-0.027363
36	H	-5.545038	-0.442591	1.162059
37	H	-4.892759	1.949877	1.376542
38	H	-0.609844	-1.253063	-1.247629
39	H	-1.375026	-3.535085	-1.639757
40	H	-3.599974	-4.293574	-0.807504
41	H	-5.083262	-2.68239	0.343193
42	H	1.598821	-4.332631	-0.515198
43	H	2.527029	-3.994329	2.003189

Table S3. Atomic coordinates calculated for **6+Cys** from DFT B3LYP/6-311G(d,p) geometry optimization.

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Atom #	Atom Type	x	y	z
1	C	-0.2146	4.7245	-0.0920
2	C	0.5557	3.6383	0.3741
3	C	0.0334	2.3678	0.3955
4	C	-1.2968	2.1157	-0.0503
5	C	-2.0704	3.2267	-0.5028
6	C	-1.5048	4.5231	-0.5195
7	N	-1.7812	0.8499	-0.0063
8	C	-3.0221	0.6218	-0.4007
9	C	-3.8834	1.6772	-0.8445
10	C	-3.4067	2.9567	-0.8889
11	C	-3.6137	-0.7265	-0.3000
12	C	-5.0015	-0.7857	-0.1680
13	O	-5.8005	0.3090	-0.3326
14	C	-5.2740	1.2848	-1.2407
15	C	-2.8666	-1.9566	-0.2157
16	C	-3.5555	-3.1636	0.1305
17	C	-4.9567	-3.1282	0.3625
18	C	-5.6700	-1.9744	0.1966
19	C	-1.4835	-2.0520	-0.5208
20	C	-0.8250	-3.2603	-0.4577
21	C	-1.4977	-4.4379	-0.0718
22	C	-2.8403	-4.3845	0.2118
23	N	0.8045	1.2886	0.9242
24	C	0.9523	1.0721	2.3072
25	C	1.6855	-0.2488	2.4856
26	C	2.1077	-0.6768	1.0759

27	C	1.3793	0.2883	0.1400
28	O	0.5505	1.8066	3.1683
29	O	1.3194	0.2190	-1.0628
30	S	3.9333	-0.5166	0.8828
31	C	4.1609	-1.1927	-0.8210
32	C	5.6504	-1.4056	-1.1293
33	N	6.2137	-2.4635	-0.3084
34	C	6.4341	-0.0862	-1.0733
35	O	7.3826	0.1259	-0.3635
36	O	5.9508	0.8199	-1.9528
37	H	0.2174	5.7178	-0.1003
38	H	1.5665	3.7999	0.7280
39	H	-2.1072	5.3554	-0.8679
40	H	-4.0427	3.7746	-1.2151
41	H	-5.2835	0.8542	-2.2526
42	H	-5.9626	2.1285	-1.2103
43	H	-5.4633	-4.0455	0.6430
44	H	-6.7438	-1.9345	0.3305
45	H	-0.9479	-1.1659	-0.8226
46	H	0.2246	-3.3058	-0.7274
47	H	-0.9616	-5.3786	-0.0184
48	H	-3.3818	-5.2838	0.4867
49	H	2.5125	-0.1182	3.1849
50	H	0.9882	-0.9623	2.9307
51	H	1.8232	-1.7001	0.8320
52	H	3.6627	-2.1616	-0.8712
53	H	3.7090	-0.5072	-1.5333
54	H	5.6892	-1.7251	-2.1780
55	H	7.2067	-2.5537	-0.4982
56	H	6.1367	-2.2164	0.6740
57	H	6.4863	1.6217	-1.8559

Table S4. Atomic coordinates calculated for **6+GSH** from DFT B3LYP/6-311G(d,p) geometry optimization.

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Atom #	Atom Type	x	y	z
1	C	-3.4293	-4.8277	1.2783
2	C	-2.3403	-4.1102	0.7394
3	C	-2.5030	-2.8179	0.3031
4	C	-3.7669	-2.1671	0.3947
5	C	-4.8714	-2.9221	0.8920
6	C	-4.6746	-4.2496	1.3391
7	N	-3.8760	-0.8769	-0.0061
8	C	-5.0600	-0.2899	0.0397
9	C	-6.2419	-0.9924	0.4419
10	C	-6.1376	-2.2857	0.8705
11	C	-5.2322	1.1025	-0.4117
12	C	-6.4916	1.4412	-0.9051

13	O	-7.5643	0.6013	-0.7955
14	C	-7.5300	-0.2276	0.3734
15	C	-4.1897	2.0958	-0.4500
16	C	-4.4452	3.3403	-1.1113
17	C	-5.7154	3.5681	-1.7055
18	C	-6.7254	2.6533	-1.5886
19	C	-2.9410	1.9419	0.2067
20	C	-2.0028	2.9506	0.2033
21	C	-2.2451	4.1578	-0.4856
22	C	-3.4434	4.3430	-1.1312
23	N	-1.4175	-2.1396	-0.3340
24	C	-0.5334	-1.2797	0.3015
25	C	0.5052	-0.8403	-0.7357
26	C	-0.1254	-1.2163	-2.0807
27	C	-1.2296	-2.1999	-1.7349
28	O	-1.8642	-2.8939	-2.4792
29	O	-0.5718	-0.9637	1.4684
30	O	5.0330	0.3554	-3.0507
31	C	5.4849	0.0151	-1.9686
32	N	6.8060	0.1503	-1.6730
33	C	7.4998	-0.1076	-0.4306
34	C	8.9625	-0.3779	-0.7197
35	O	9.6102	-0.7697	0.3930
36	O	9.4954	-0.2326	-1.7893
37	C	4.5681	-0.5935	-0.8796
38	C	3.2220	-0.9528	-1.5288
39	S	2.0665	-1.7518	-0.3363
40	N	4.4167	0.3268	0.2385
41	C	4.7075	-0.0352	1.5327
42	C	4.1416	0.9128	2.5829
43	C	2.6090	0.7191	2.7495
44	C	1.7866	2.0166	2.8241
45	N	0.3394	1.7842	2.8055
46	C	2.0879	2.9906	1.6841
47	O	2.0190	2.4001	0.4444
48	O	2.3298	4.1603	1.8010
49	O	5.3564	-1.0306	1.8082
50	H	-3.2790	-5.8444	1.6203
51	H	-1.3690	-4.5810	0.6485
52	H	-5.5228	-4.8066	1.7230
53	H	-7.0167	-2.8370	1.1918
54	H	-7.6480	0.4162	1.2572
55	H	-8.3936	-0.8879	0.3010
56	H	-5.8885	4.5046	-2.2252
57	H	-7.7135	2.8287	-1.9952
58	H	-2.7354	1.0238	0.7351
59	H	-1.0878	2.8160	0.7699
60	H	-1.4965	4.9422	-0.4844
61	H	-3.6545	5.2748	-1.6459
62	H	0.5590	-1.6573	-2.8033
63	H	-0.6005	-0.3480	-2.5485

64	H	7.3723	0.5217	-2.4263
65	H	7.4609	0.7498	0.2549
66	H	7.0750	-0.9466	0.1231
67	H	10.5407	-0.8941	0.1528
68	H	5.0358	-1.4909	-0.4680
69	H	2.7541	-0.0498	-1.9213
70	H	3.3947	-1.6179	-2.3733
71	H	3.7641	1.0902	0.1104
72	H	4.6682	0.7145	3.5154
73	H	4.3729	1.9435	2.2918
74	H	2.2186	0.1216	1.9232
75	H	2.4032	0.1449	3.6557
76	H	2.0446	2.5800	3.7237
77	H	0.1038	0.8829	2.3966
78	H	-0.0553	1.8295	3.7355
79	H	2.1019	3.1224	-0.1979
80	H	0.6997	0.2249	-0.6140

Table S5. Atomic coordinates calculated for **6+HCy** from DFT B3LYP/6-311G(d,p) geometry optimization.

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Atom #	Atom Type	x	y	z
1	C	1.0167	3.9638	-0.1974
2	C	1.4352	2.6374	0.0432
3	C	0.5151	1.6186	0.1078
4	C	-0.8733	1.8726	-0.0857
5	C	-1.2849	3.2220	-0.2986
6	C	-0.3179	4.2529	-0.3536
7	N	-1.7430	0.8333	-0.0555
8	C	-3.0335	1.0653	-0.2192
9	C	-3.5448	2.3912	-0.4052
10	C	-2.6769	3.4461	-0.4399
11	C	-4.0202	-0.0291	-0.1253
12	C	-5.3195	0.3365	0.2298
13	O	-5.7220	1.6383	0.3077
14	C	-5.0270	2.5234	-0.5779
15	C	-3.7211	-1.4339	-0.2624
16	C	-4.7298	-2.3944	0.0731
17	C	-6.0010	-1.9482	0.5233
18	C	-6.2985	-0.6165	0.5851
19	C	-2.4885	-1.9285	-0.7648
20	C	-2.2664	-3.2809	-0.9037
21	C	-3.2506	-4.2218	-0.5386
22	C	-4.4601	-3.7790	-0.0627
23	N	0.9357	0.2832	0.3801
24	C	0.7190	-0.3466	1.6229
25	C	1.1046	-1.8088	1.4548

26	C	1.8620	-1.8685	0.1234
27	C	1.4947	-0.5632	-0.5760
28	O	0.2966	0.1969	2.6059
29	O	1.6654	-0.2936	-1.7404
30	S	3.6745	-1.9575	0.4805
31	C	6.1779	0.1494	-0.7915
32	N	7.2871	-0.7927	-0.9147
33	C	5.8914	0.5212	0.6660
34	O	6.4193	0.0161	1.6233
35	O	4.9913	1.5297	0.7784
36	H	1.7571	4.7532	-0.2462
37	H	2.4859	2.4120	0.1821
38	H	-0.6454	5.2734	-0.5225
39	H	-3.0424	4.4594	-0.5800
40	H	-5.3204	2.2798	-1.6096
41	H	-5.3792	3.5268	-0.3407
42	H	-6.7485	-2.6864	0.7932
43	H	-7.2710	-0.2551	0.8949
44	H	-1.7215	-1.2242	-1.0447
45	H	-1.3230	-3.6261	-1.3134
46	H	-3.0568	-5.2828	-0.6466
47	H	-5.2384	-4.4855	0.2063
48	H	1.6720	-2.1509	2.3206
49	H	0.1791	-2.3899	1.4082
50	H	1.5869	-2.7126	-0.5077
51	H	6.4636	1.0870	-1.2796
52	H	8.1686	-0.3000	-0.8166
53	H	7.2594	-1.4435	-0.1342
54	H	4.8643	1.6774	1.7282
55	C	4.4459	-1.7598	-1.1880
56	H	5.2781	-2.4653	-1.2119
57	H	3.7097	-2.0918	-1.9199
58	C	4.9264	-0.3528	-1.5490
59	H	5.2039	-0.3763	-2.6076
60	H	4.1130	0.3650	-1.4466

II. Crystal Structures:[S3]

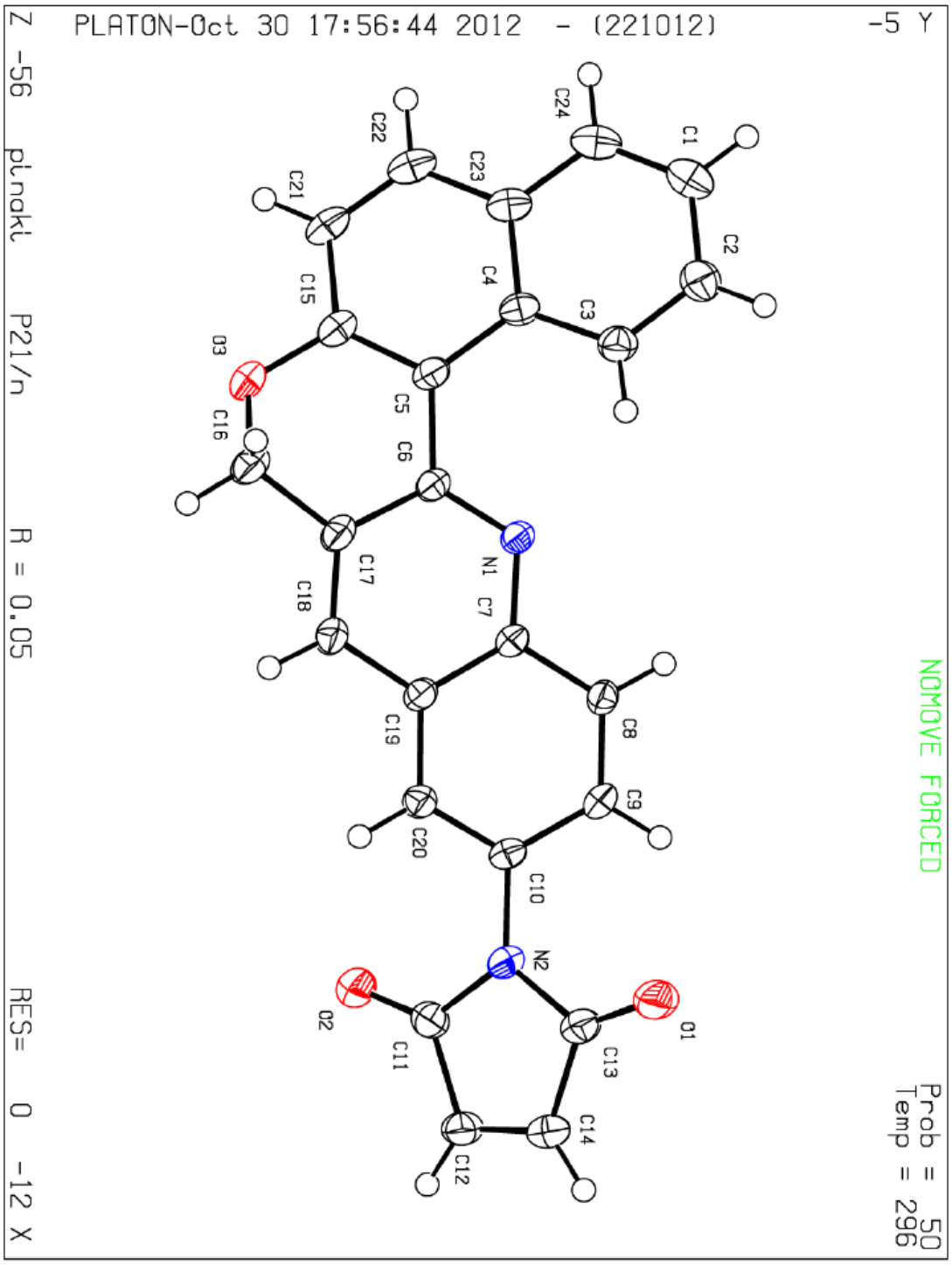

Figure S1. ORTEP diagram of chromenoquinoline-based thiol probe **4**.

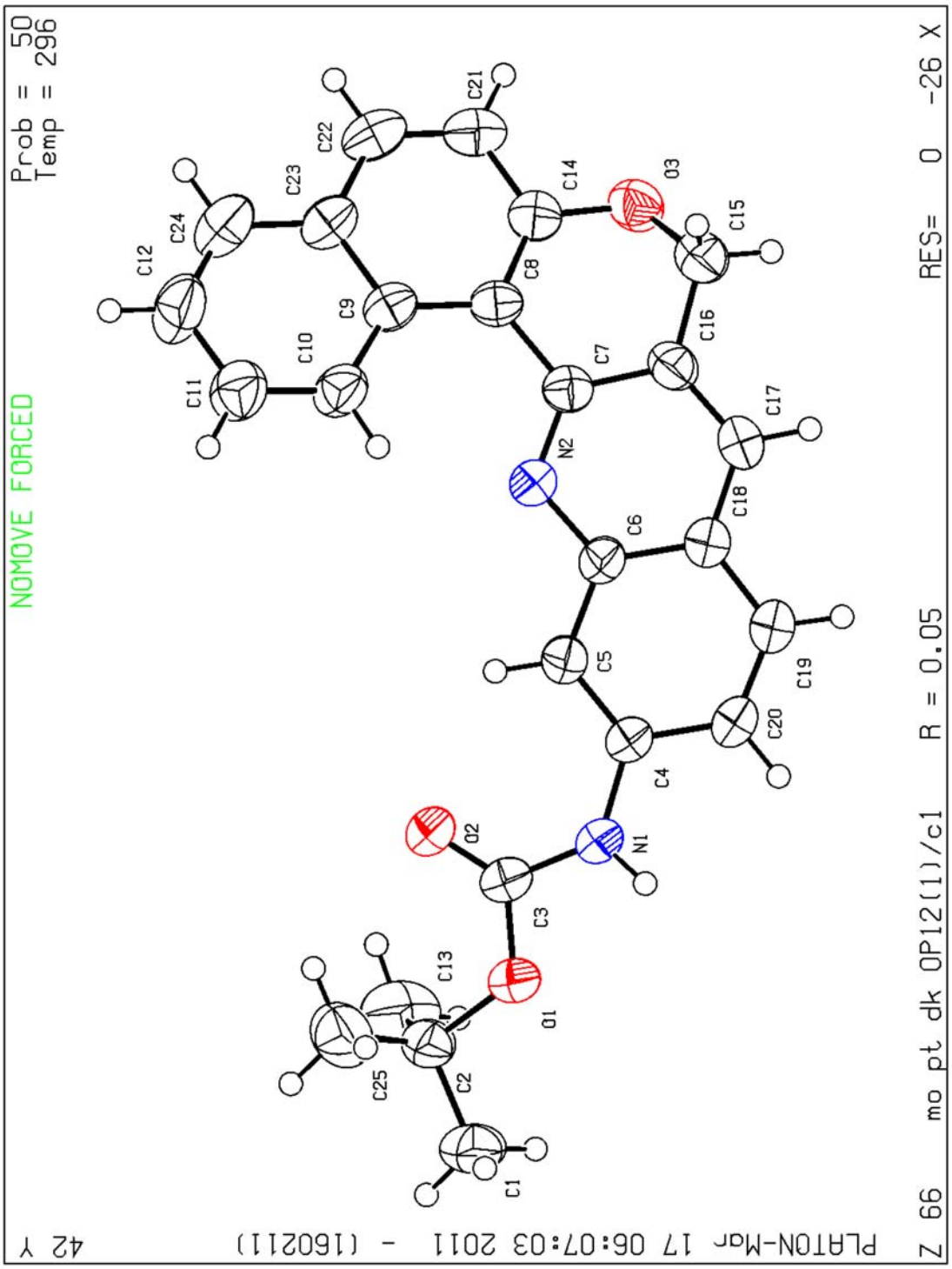

Figure S2. ORTEP diagram of chromenoquinoline **12**.

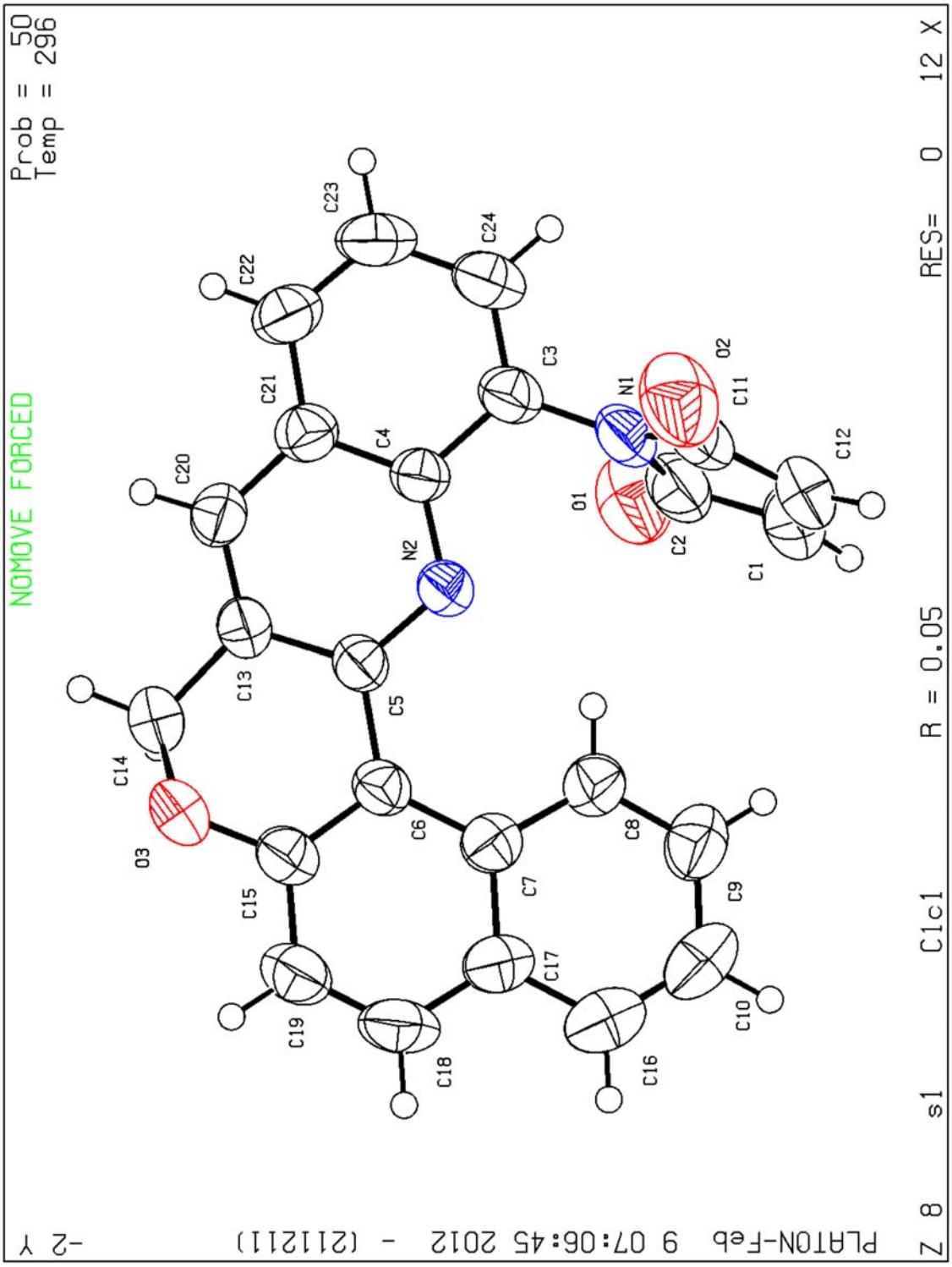

Figure S3. ORTEP diagram of chromenoquinoline-based thiol probe **6**.

III. Photophysical Properties of Probes:

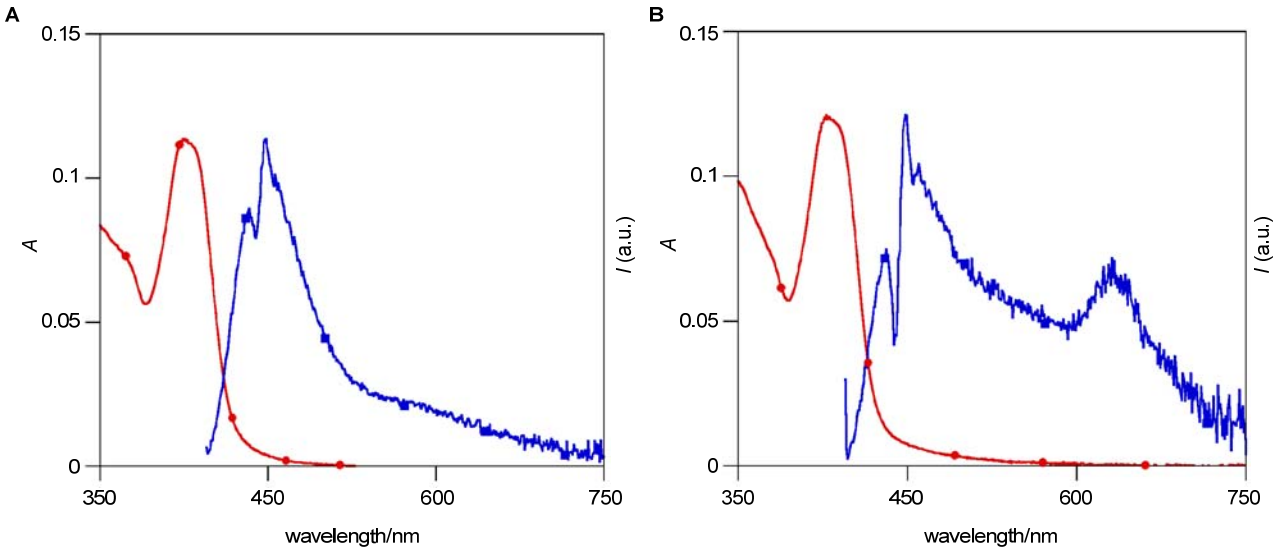

Figure S4. Photophysical properties of the chromenoquinoline-based probes **5** (**A**) and **6** (**B**) recorded in HEPES buffer (10 mM, pH 7.4, 1% DMSO).

Table S6. Quantum yields in different solvents.

Compounds	Solvents								
	$CHCl_3$ [a]			CH_3CN/10 mM HEPES buffer pH = 7.4 (70:30)			HEPES Buffer		
	λ_{max} (nm)	λ_{em} [b] (nm)	Φ	λ_{max} (nm)	λ_{em} [b] (nm)	Φ	λ_{max} (nm)	λ_{em} [b] (nm)	Φ
5	385	432	0.0075	380	440	0.009	374	455	0.009
5+Cys	ND	ND	ND	380	444	0.24	383	460	0.22
5+GSH	ND	ND	ND	380	444	0.27	383	460	0.28
5+Hcy	ND	ND	ND	ND	ND	ND	383	460	0.21
6	380	435	0.0033	377	433	0.004	382	457	0.0052
6+Cys	ND	ND	ND	377	435	0.32	383	460	0.38
6+GSH	ND	ND	ND	377	436	0.30	383	460	0.33
6+Hcy	ND	ND	ND	ND	ND	ND	383	460	0.48

[a] Thiol addition reaction in $CHCl_3$ was not successful as pH could not be maintained in the pure organic solvent. [b] For all cases λ_{ex} = 383 nm was used. ND = Not determined.

IV. Thiols Sensing:

Procedures:

Preparation of the medium: Deionized water was used throughout all experiments. Conjugate addition reactions were carried out in HEPES buffer (10 mM, pH 7.4) with/without 1.0% DMSO (maximum).

Preparation of the solution of 5 and 6: Stock solutions of **5** and **6** (1255 μM each) were prepared in DMSO. The stock solutions of **5** and **6** were then diluted to 100 μM in DMSO. Final concentration of **5** and **6** during each assay was 10 μM with 1% DMSO (maximum).

Preparation of the solution of amino acids: Stock solutions of amino acids were prepared in H_2O with varied concentrating ranging from 1952 μM to 12234 μM. Calculated volumes of amino acids were added from respective stock solutions to fluorescence each cuvette to provide 100 μM. Conjugate addition reactions were carried out in HEPES buffer (10 mM, pH 7.4) with maximum 1.0% DMSO. Spectra data were recorded 20 min in an indicated time after the addition of amino acids by exciting at 383 nm. The excitation and emission slit width was 3 nm and 3 nm respectively.

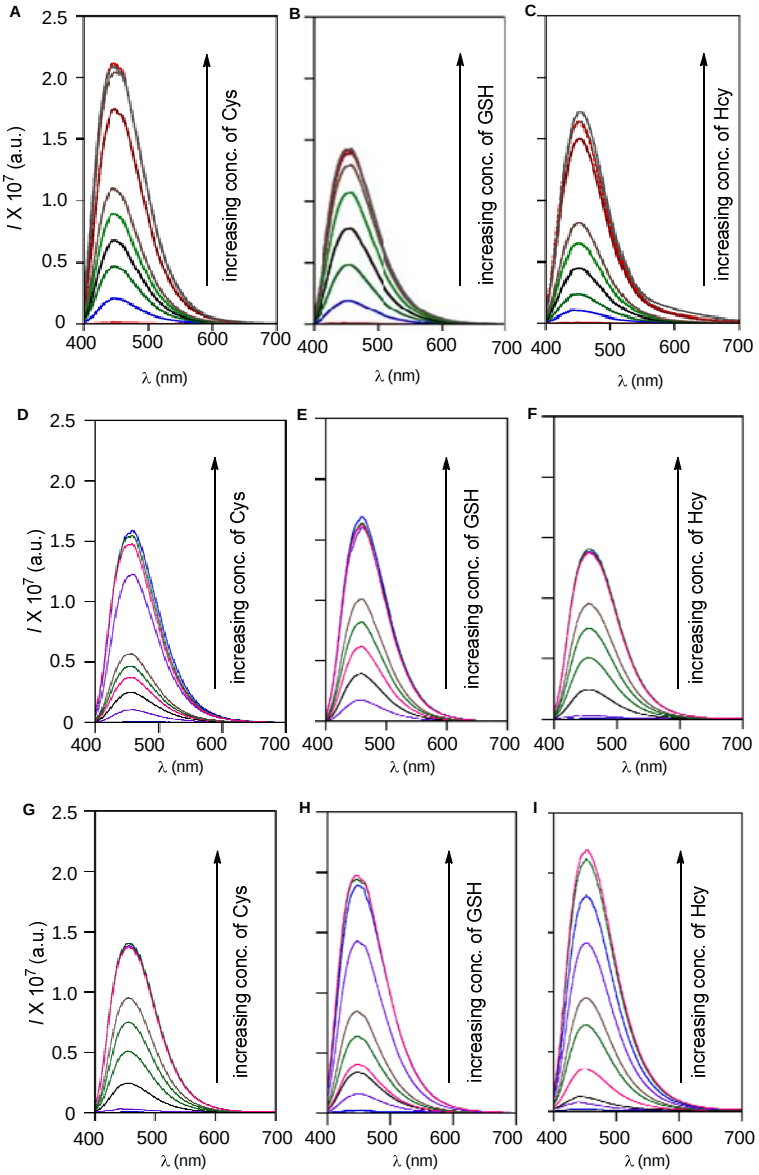

Figure S5. Fluorometric titrations of probes **4** in response to biological thiols (Cys, GSH and Hcy). (**A**) Fluorescence responses of **4** (10 μM) toward various concentrations (0, 2, 4, 6, 8, 10, 20, 40 and 100 μM) of Cys in HEPES buffer (10 mM, pH 7.4, 1% DMSO). Each spectrum was recorded at 20 min after addition of Cys to **4**. The same experiment was carried out for 4 with GSH (**B**) and Hcy (**C**); for **5** with Cys (**D**), GSH (**E**) and Hcy (**F**); for **6** with Cys (**G**), GSH (**H**) and Hcy (**I**).

Detection limit: The detection limits were determined based on the fluorescence titrations.[S4] To improve the sensitivity, probes **5** and **6** were employed at 10 μM and the slit was adjusted to 3.0 nm/3.0 nm. To determine the *S/N* ratio, the emission intensity of each probe without thiol was measured by 3-4 times and the standard deviation of blank measurements was determined. Under the present conditions, a good linear relationship between the fluorescence intensity and the thiol

concentration could be obtained in the 2 - 10 μM, as shown in figure S4 and figure S5. The detection limits were then calculated with the equation: detection limit = $3\sigma_{bi}/m$, where σ_{bi} is the standard deviation of blank measurements, m is the slope between intensity versus sample concentration (Table S3).

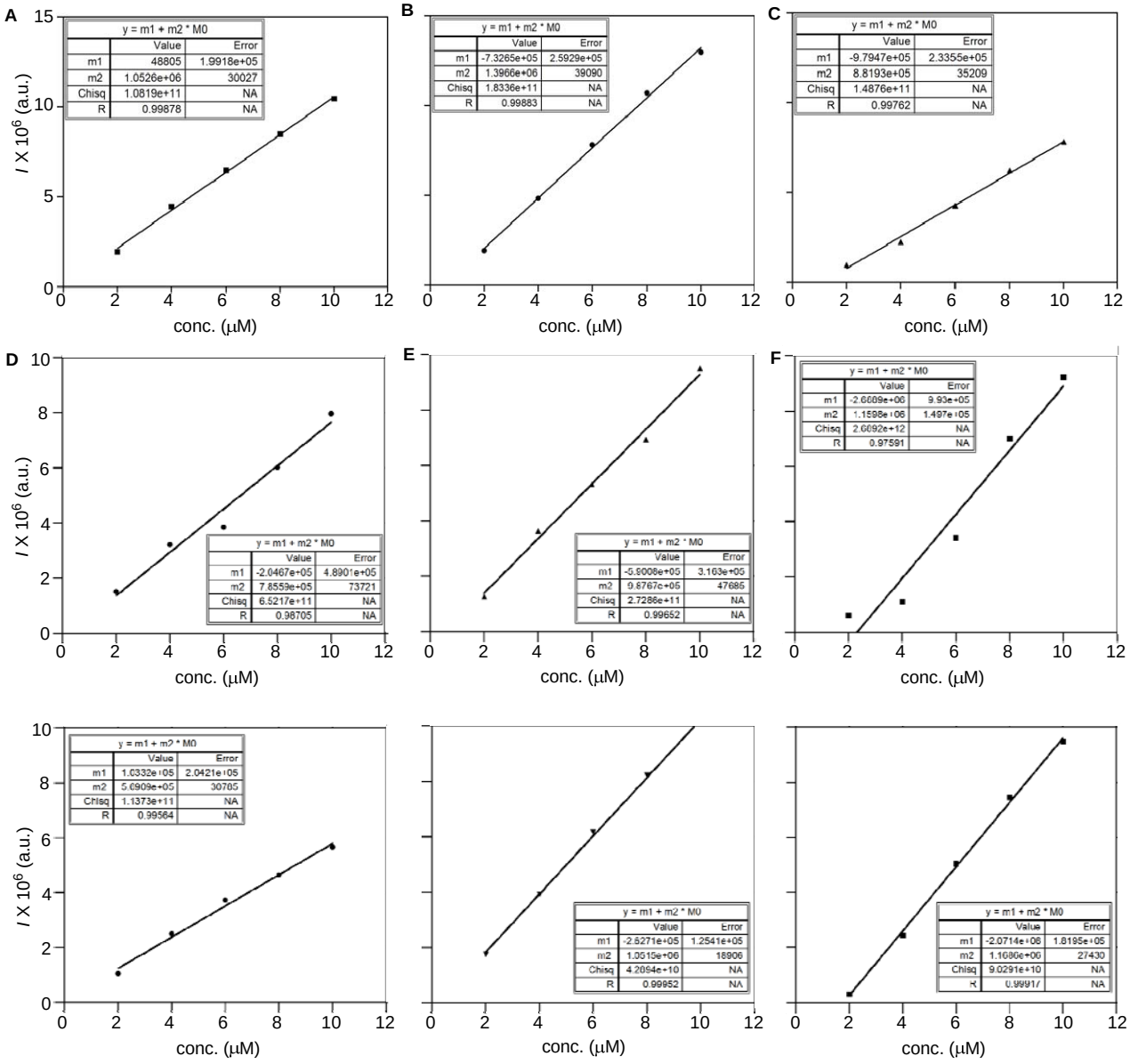

Figure S6. The linearity of the Cys (**A**), GSH (**B**) and Hcy (**C**) titration assay of probe **4**; The same experiment was carried out for **5** with Cys (**D**), GSH (**E**) and Hcy (**F**); for **6** with Cys (**G**), GSH (**H**) and Hcy (**I**).

Table S7. Calculation of detection limit of Cys, GSH and Hcy with probes **4**, **5** and **6**.

Probe	σ_{bi}	*S/N*	Slope From linear plots, *m*			Detection limit (M)		
			Cys	GSH	Hcy	Cys	GSH	Hcy
4	6797.083	3.0	1.05×10^{6}	1.40×10^{6}	8.82×10^{5}	1.94×10^{-8}	1.46×10^{-8}	2.31×10^{-8}
5	34410.17039	3.0	7.86×10^{5}	9.88×10^{5}	1.16×10^{6}	13.13×10^{-8}	10.45×10^{-8}	8.90×10^{-8}
6	10108.32080	3.0	5.69×10^{5}	1.05×10^{6}	1.17×10^{6}	5.33×10^{-8}	2.89×10^{-8}	2.59×10^{-8}

Mass Spectrometric Analysis of Thiol Addition Reactions:

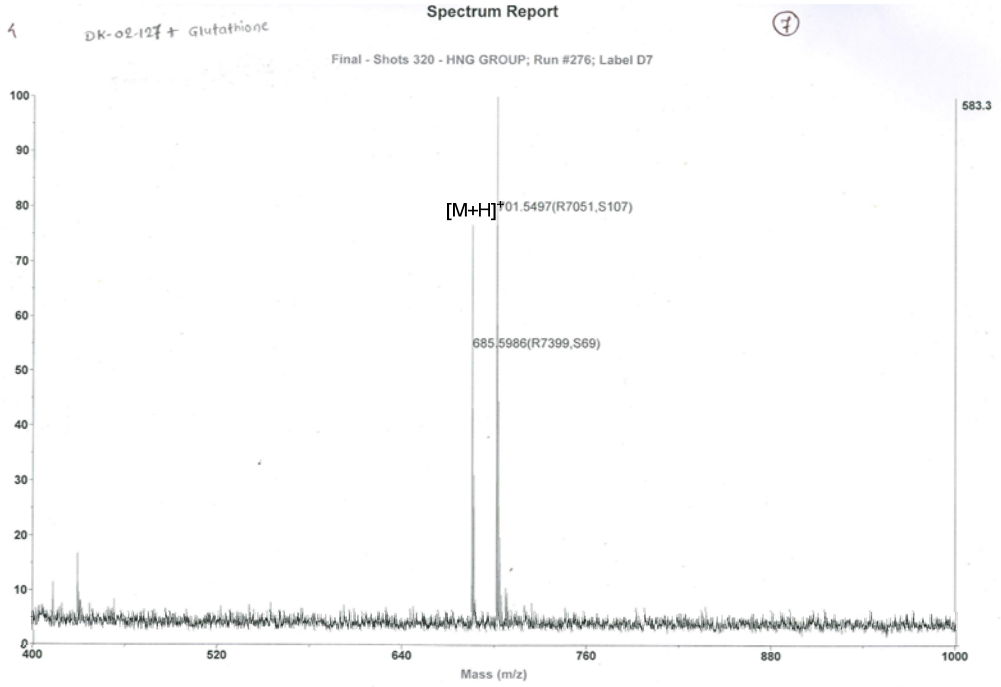

Figure S7. ESI-MS of the probe **5** (10 μM) titrated with GSH (100 μM) in HEPES buffer (10 mM, pH 7.4, 1% DMSO).

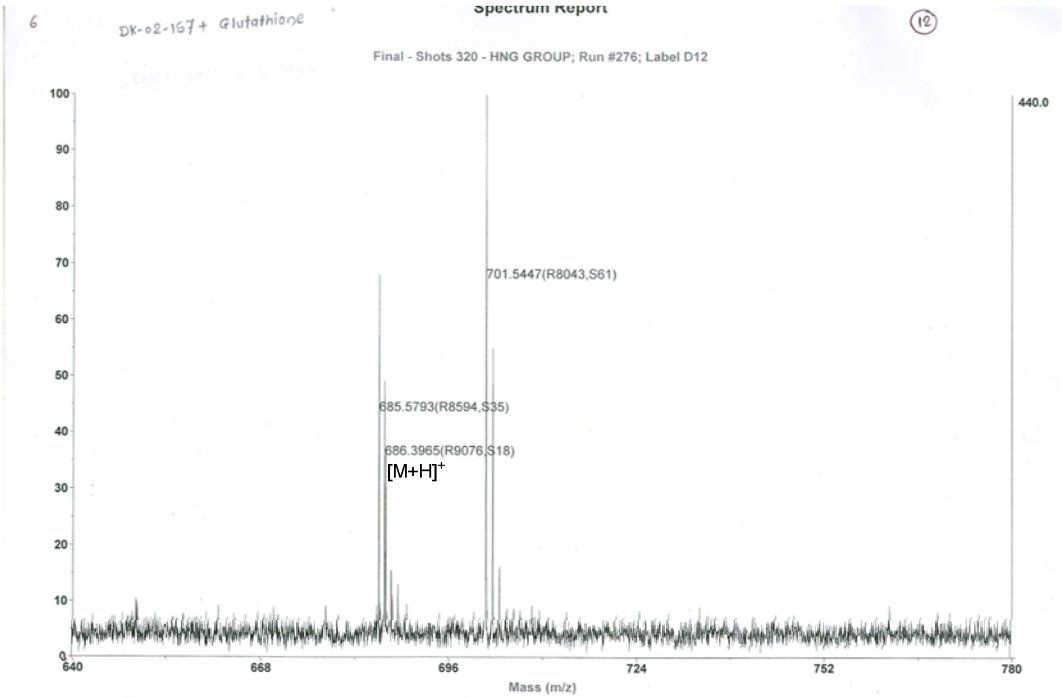

Figure S8. ESI-MS of the probe **6** (10 μM) titrated with GSH (100 μM) in HEPES buffer (10 mM, pH 7.4, 1% DMSO).

V. NMR Data.

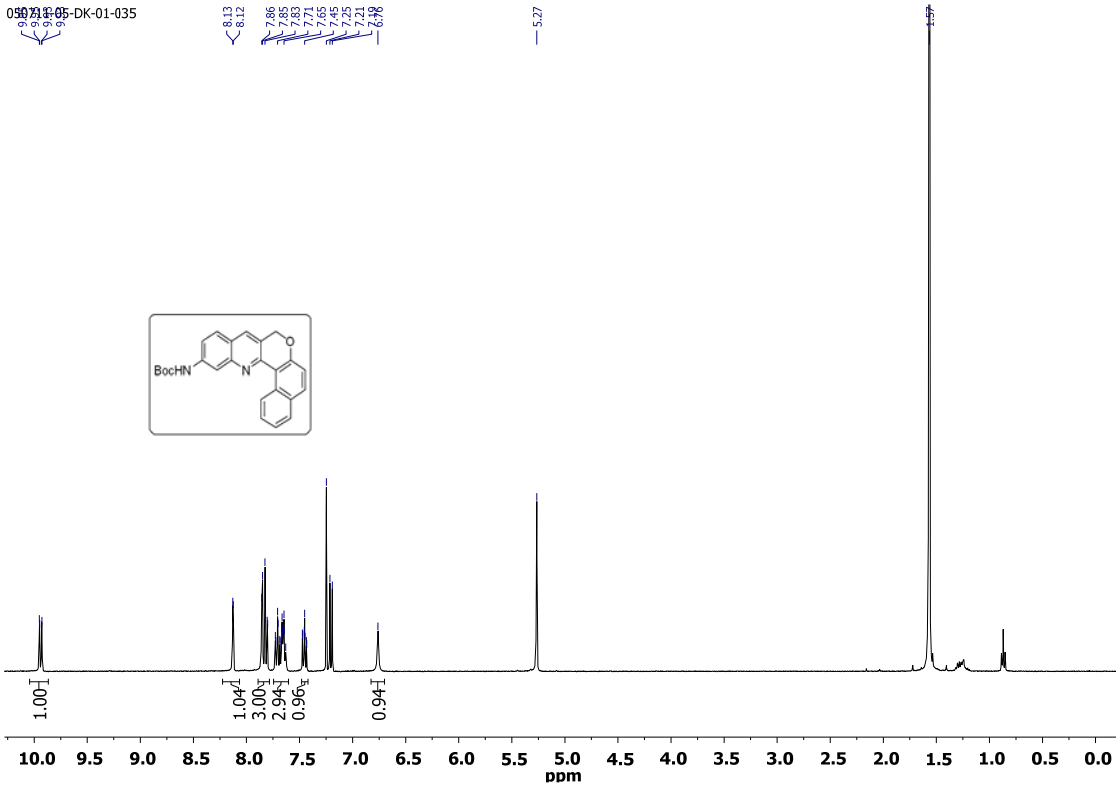

Figure S9. ^{1}H NMR spectra of **12** in $CDCl_3$.

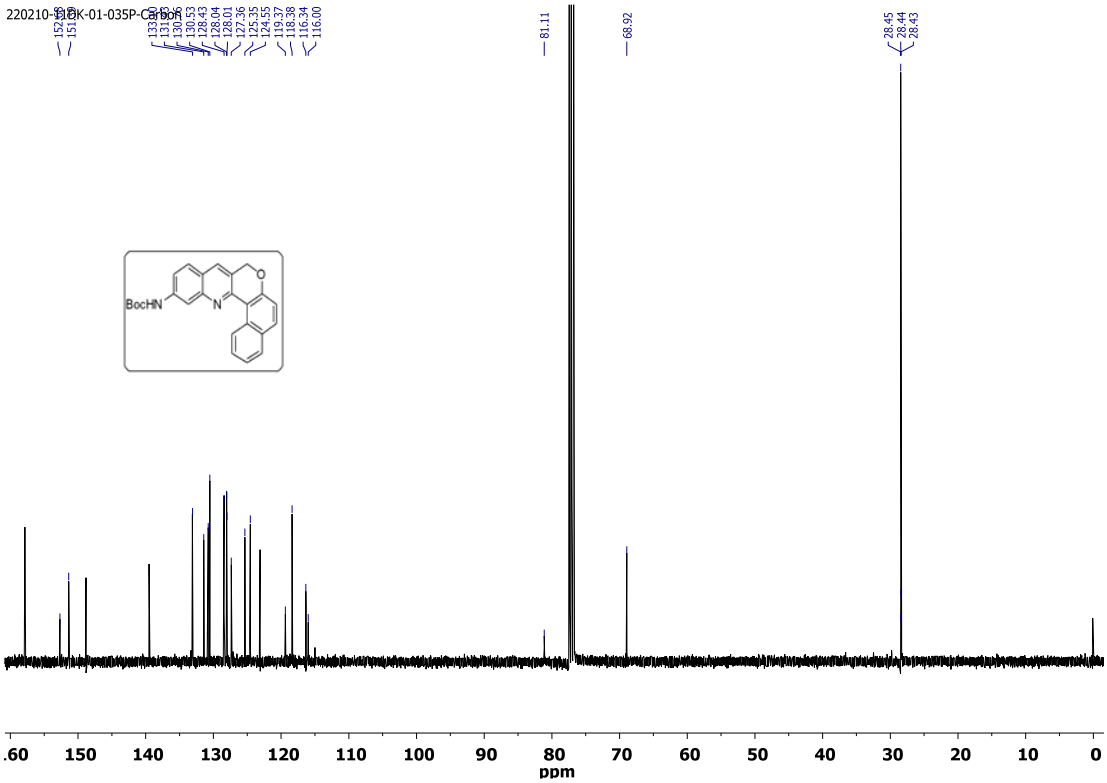

Figure S10. ^{13}C NMR spectra of **12** in $CDCl_3$.

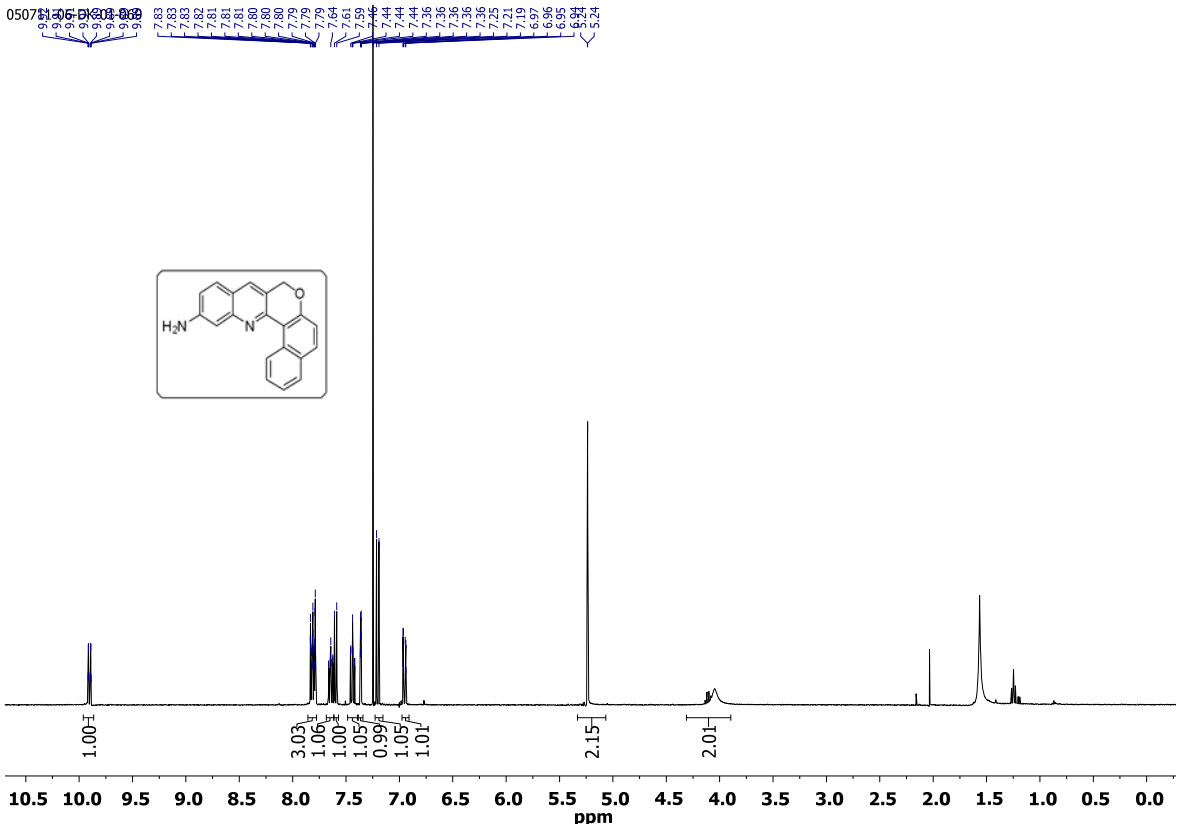

Figure S11. ^{1}H NMR spectra of **13** in $CDCl_3$.

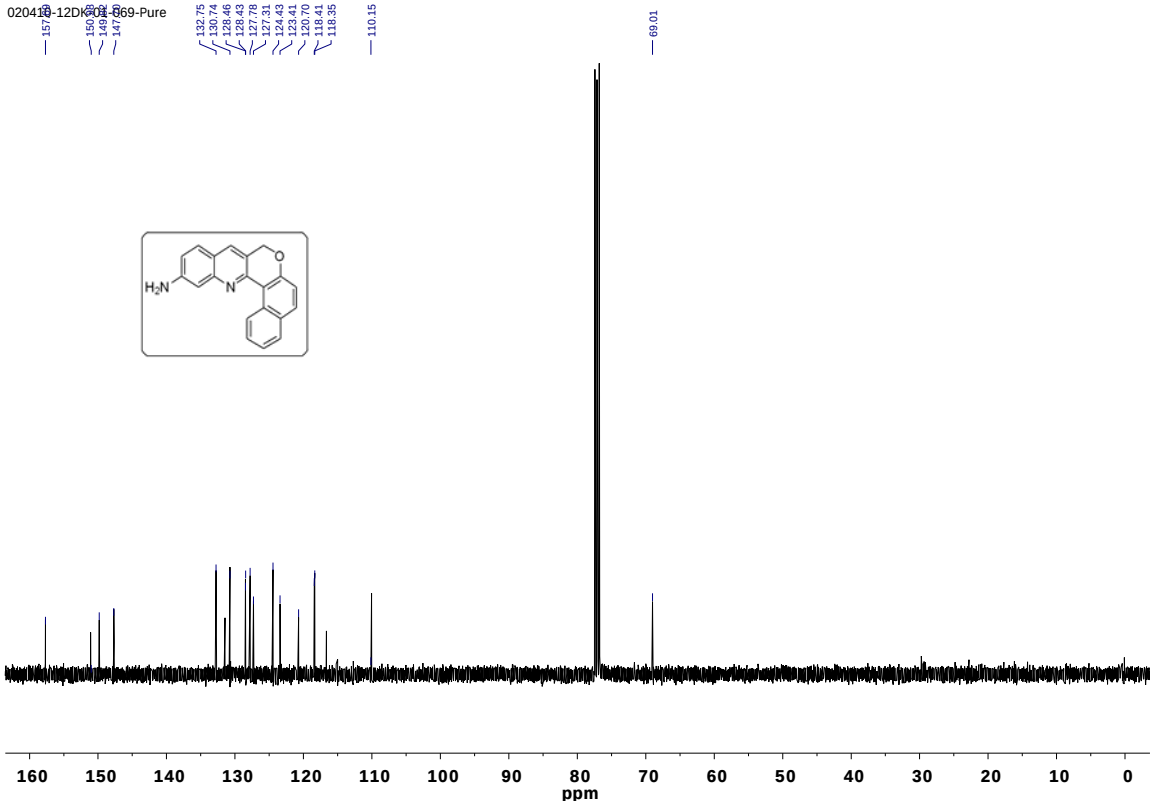

Figure S12. ^{13}C NMR spectra of **13** in $CDCl_3$.

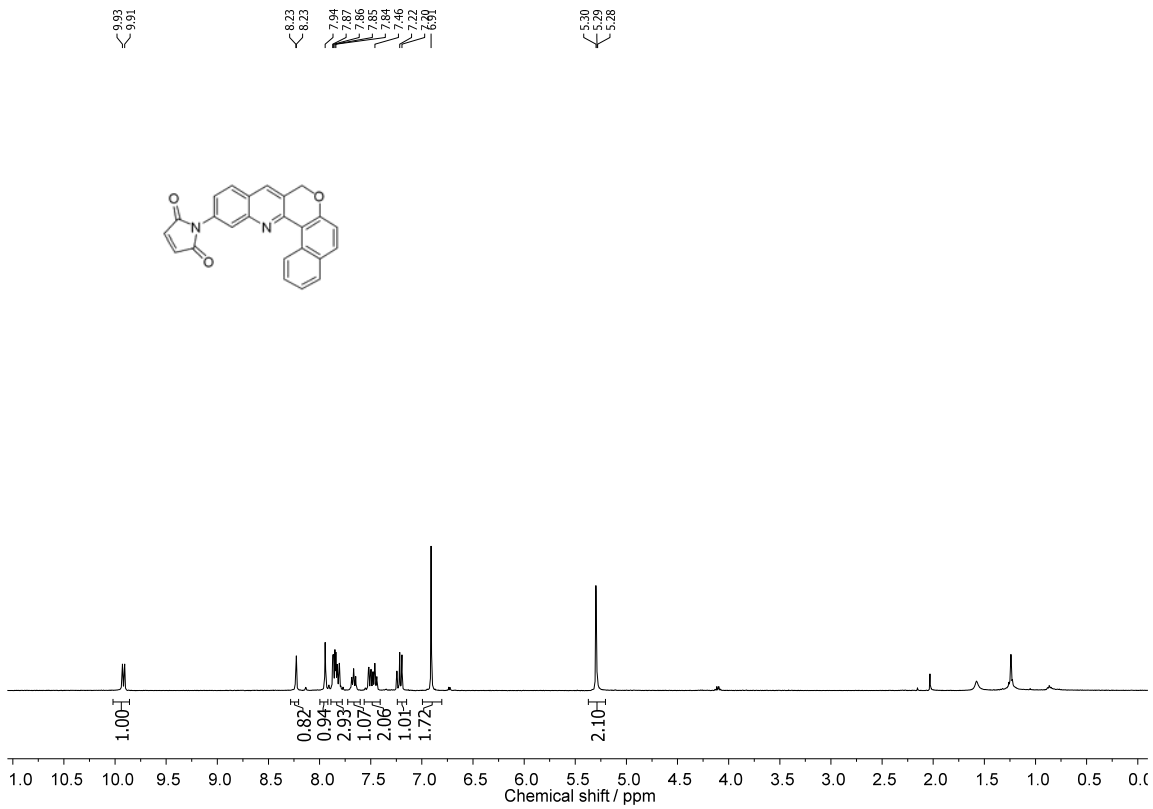

Figure S13. ^{1}H NMR spectra of **5** in $CDCl_3$.

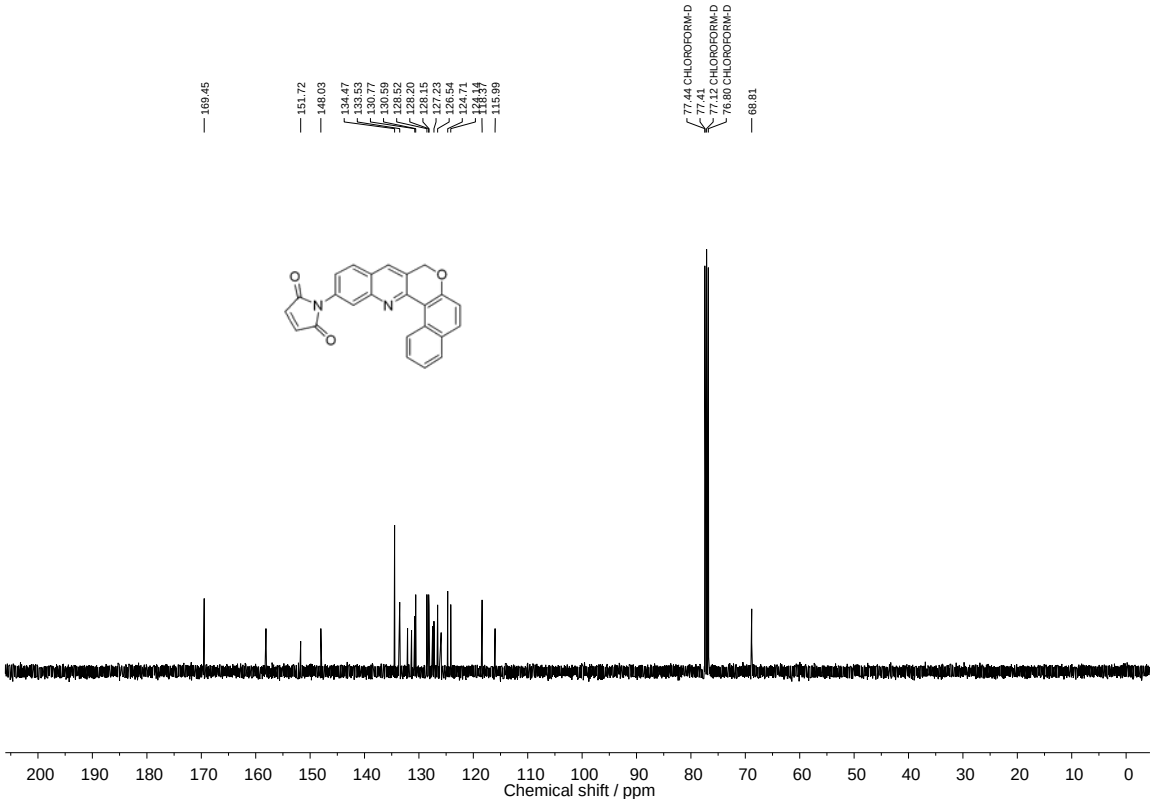

Figure S14. ^{13}C NMR spectra of **5** in $CDCl_3$.

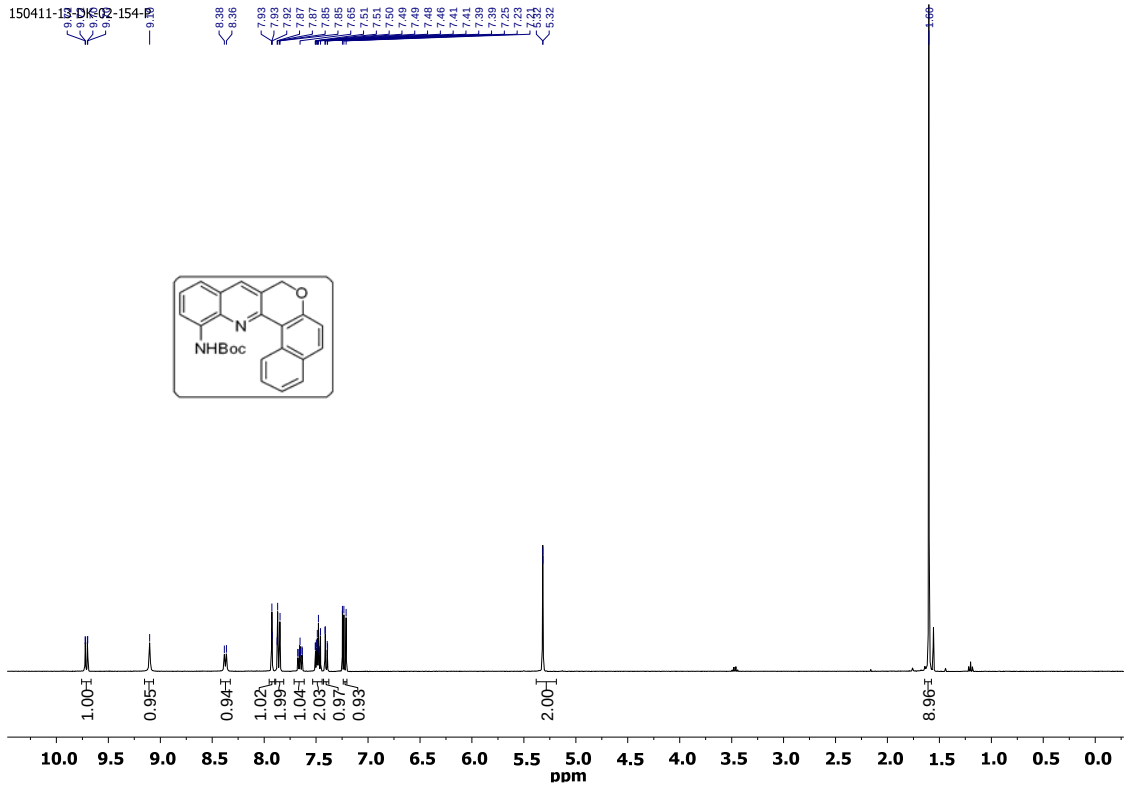

Figure S15. ^{1}H NMR spectra of **15** in $CDCl_3$.

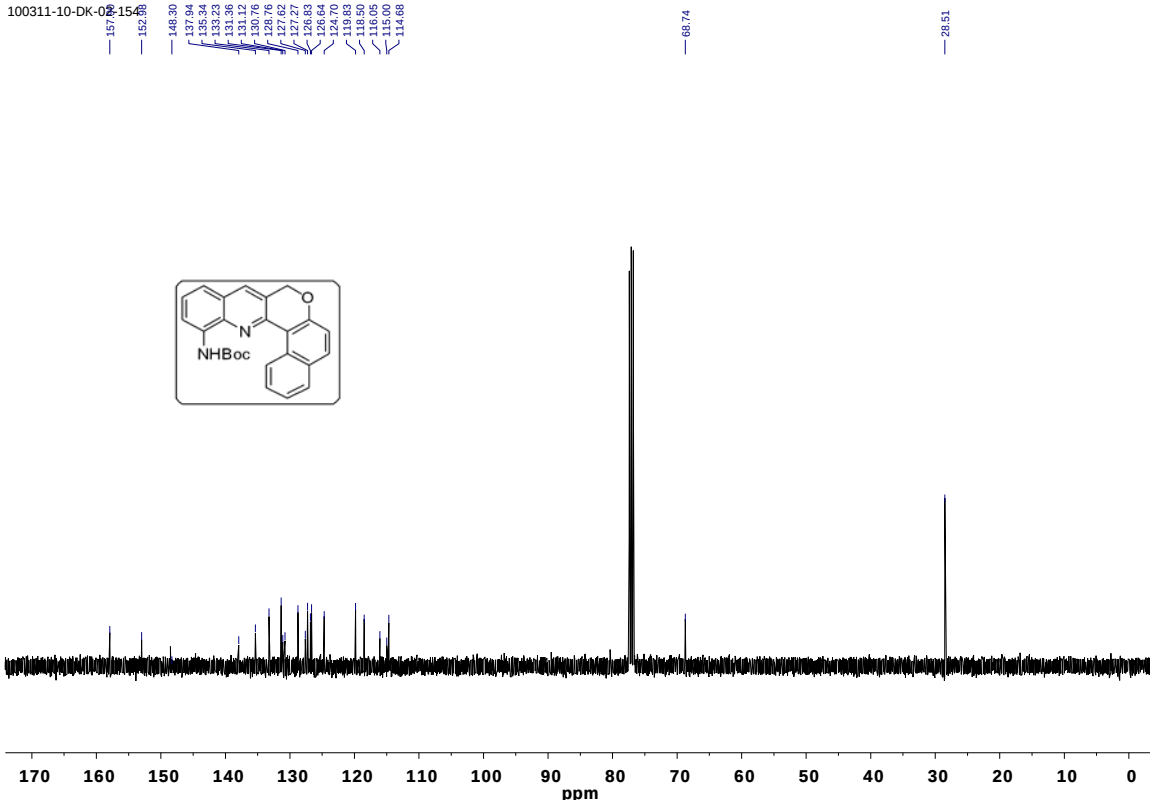

Figure S16. ^{13}C NMR spectra of **15** in $CDCl_3$.

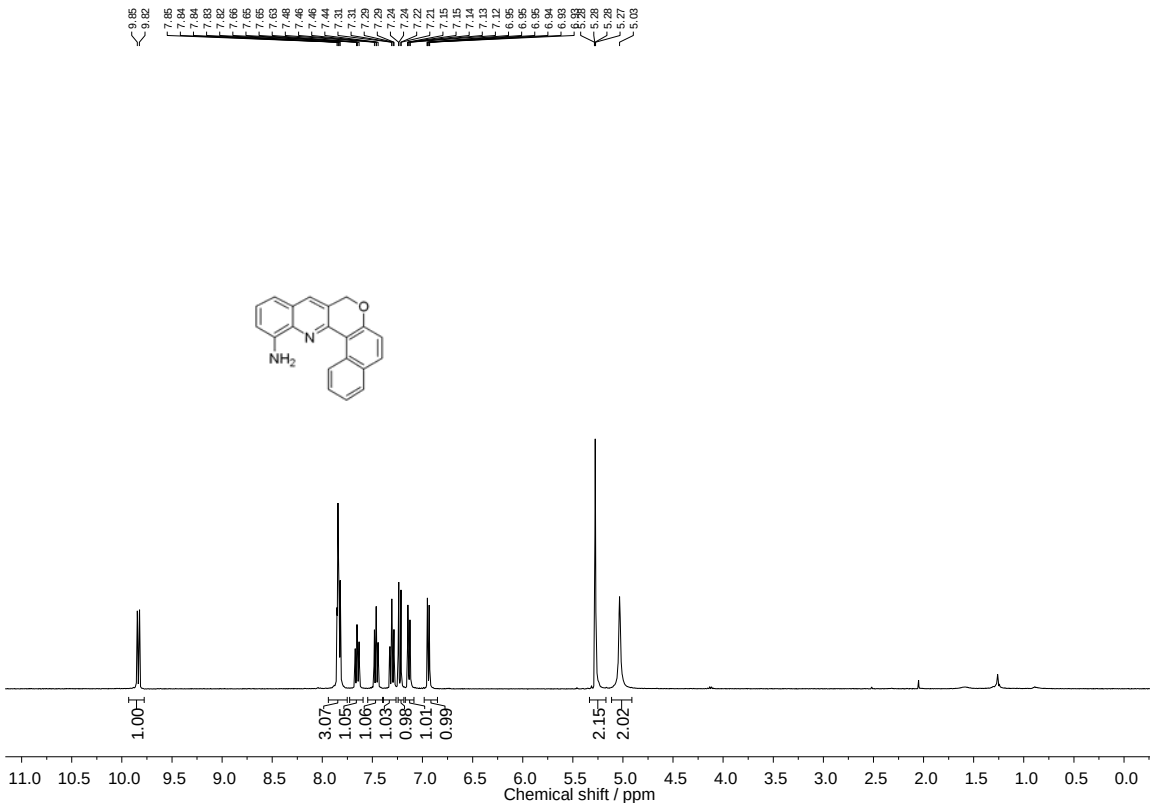

Figure S17. ^{1}H NMR spectra of **16** in $CDCl_3$.

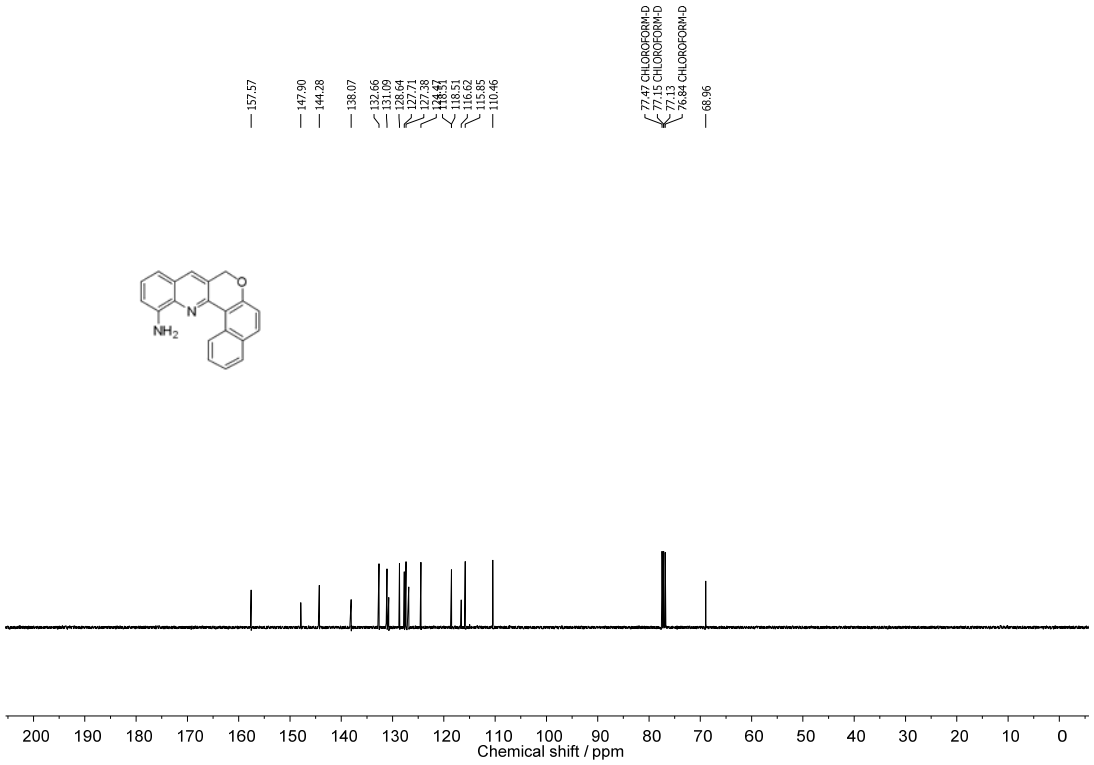

Figure S18. ^{13}C NMR spectra of **16** in $CDCl_3$.

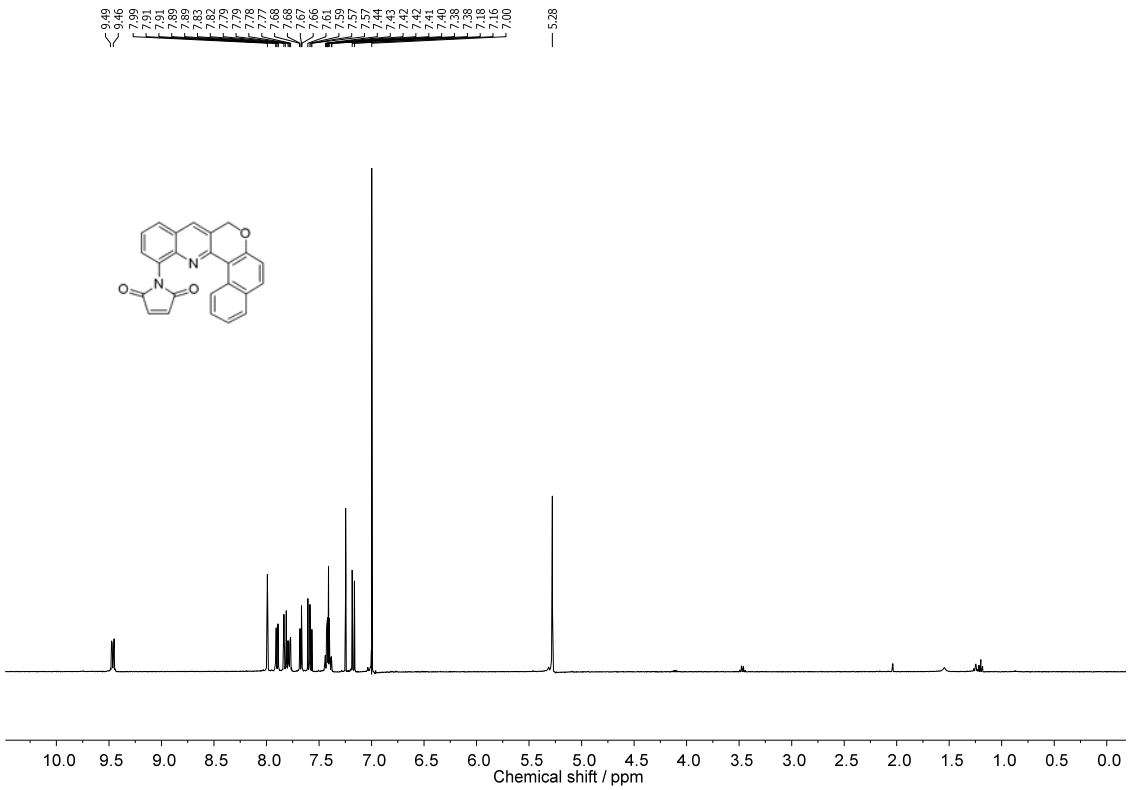

Figure S19. ^{1}H NMR spectra of **6** in $CDCl_3$.

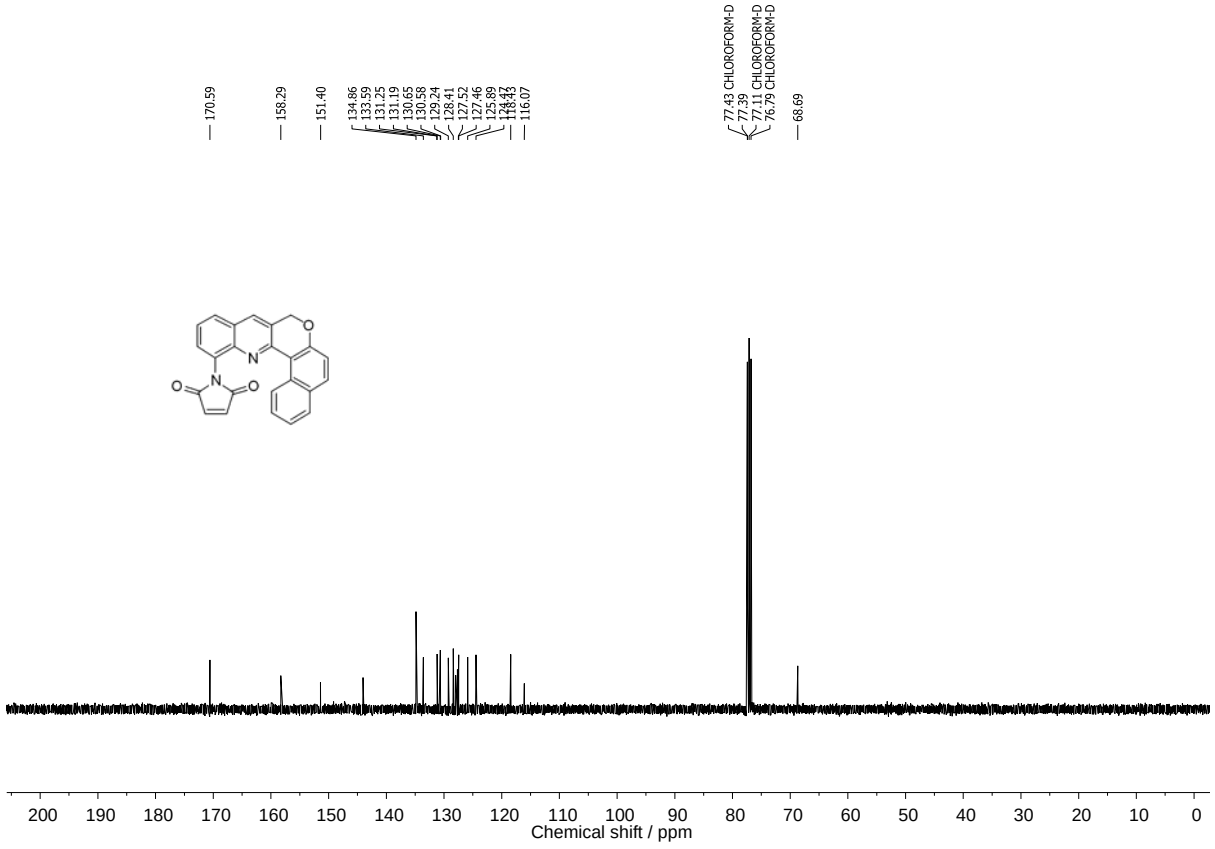

Figure S20. ^{13}C NMR spectra of **6** in $CDCl_3$.

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