

# Supporting Information

## **Improvement of photostability of cycloalkylamine-7-sulfonyl-2,1,3-benzoxadiazole-based fluorescent dyes by replacing dimethylamino substituent with cyclic amino rings**

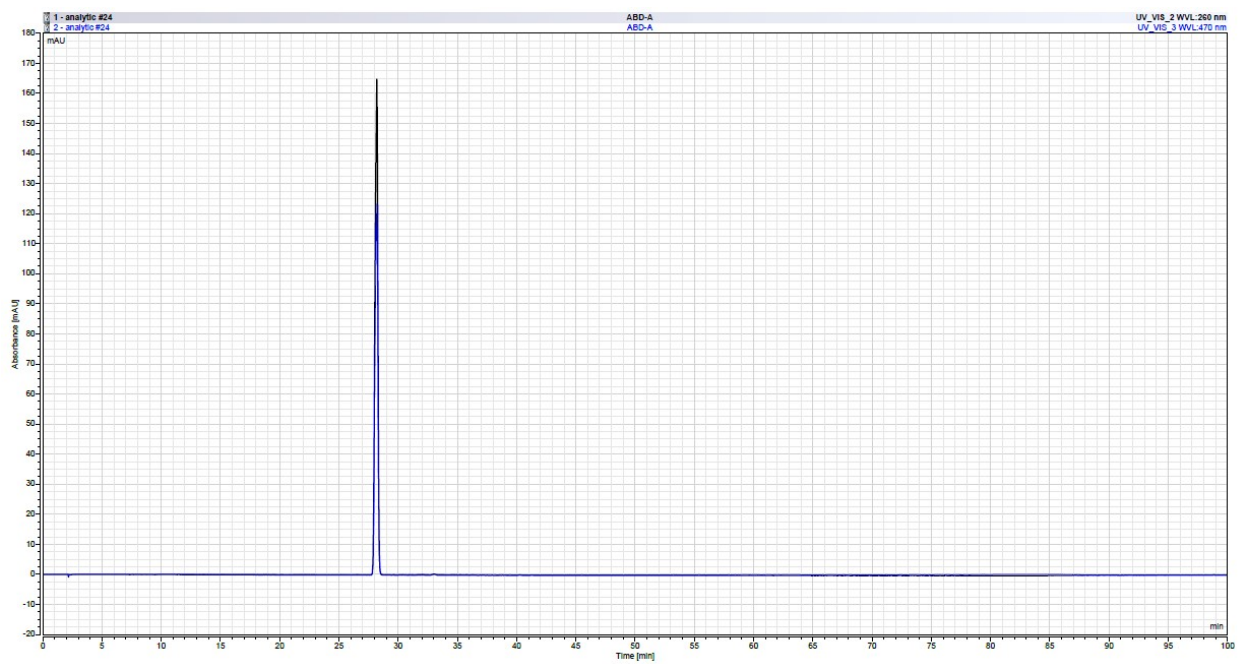
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Research Center for Controlling Intercellular Communication and Education and Research

Center for Smart Energy Materials and Process, Department of Chemistry and Chemical

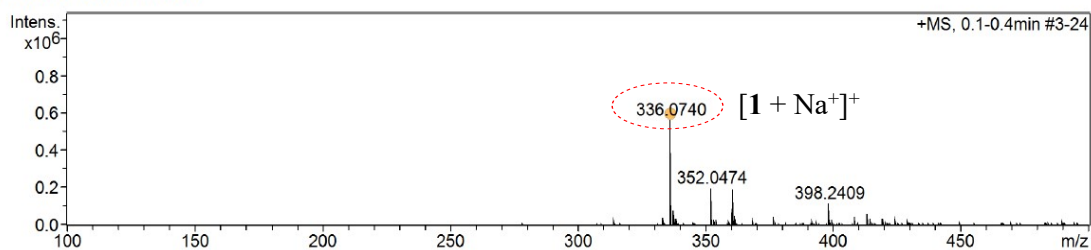
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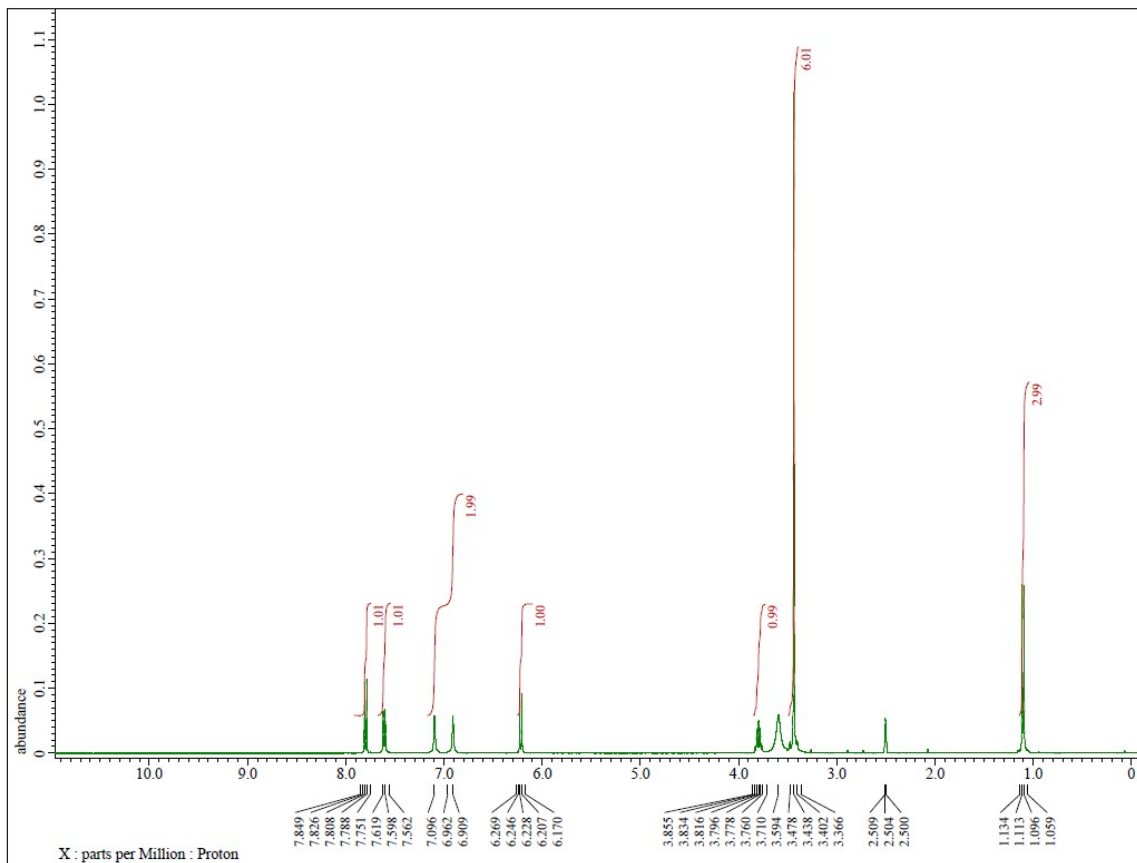
**Figure S1.** HPLC chromatogram of **1**

+MS, 0.1-0.4min #3-24

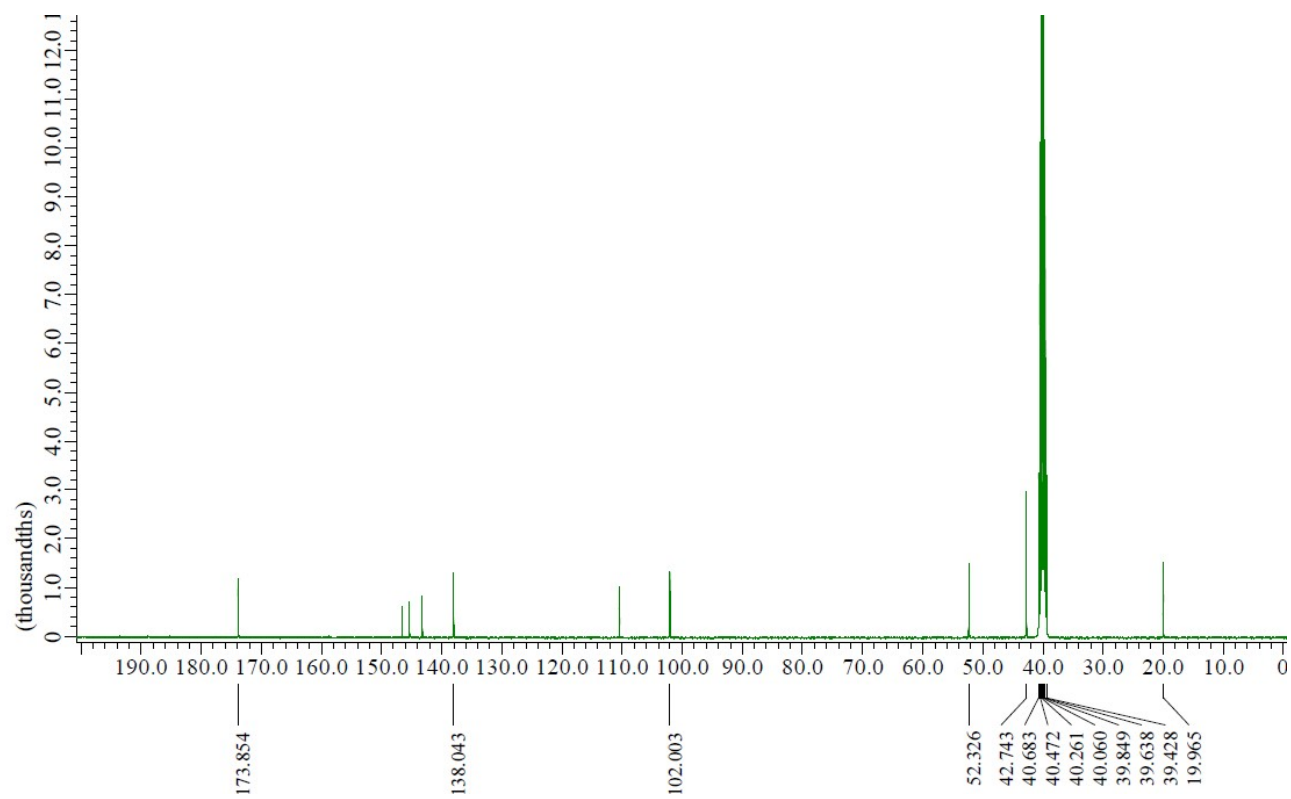


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
336.0740	1	C <sub>9</sub> H <sub>10</sub> N <sub>11</sub> O <sub>2</sub> S	336.0734	-1.7	3.0	1	100.00	10.5	even	ok
	2	C <sub>12</sub> H <sub>18</sub> NO <sub>8</sub> S	336.0748	-2.3	7.0	2	83.11	4.5	even	ok
	3	C <sub>8</sub> H <sub>14</sub> N <sub>7</sub> O <sub>6</sub> S	336.0721	5.6	9.4	3	39.31	5.5	even	ok
	4	C <sub>13</sub> H <sub>14</sub> N <sub>5</sub> O <sub>4</sub> S	336.0761	6.3	14.8	4	29.78	9.5	even	ok
	5	C <sub>7</sub> H <sub>18</sub> N <sub>3</sub> O <sub>10</sub> S	336.0707	-9.6	21.4	5	9.53	0.5	even	ok
	6	C <sub>14</sub> H <sub>10</sub> N <sub>9</sub> S	336.0774	10.3	26.0	6	6.78	14.5	even	ok
	7	C <sub>16</sub> H <sub>18</sub> NO <sub>3</sub> S <sub>2</sub>	336.0723	-5.1	35.1	7	31.84	8.5	even	ok
	8	C <sub>9</sub> H <sub>18</sub> N <sub>7</sub> O <sub>5</sub> S <sub>3</sub>	336.0729	3.1	40.2	8	43.11	4.5	even	ok
	9	C <sub>8</sub> H <sub>22</sub> N <sub>3</sub> O <sub>5</sub> S <sub>3</sub>	336.0716	7.0	42.8	9	15.63	-0.5	even	ok
	10	C <sub>13</sub> H <sub>22</sub> NO <sub>3</sub> S <sub>3</sub>	336.0756	4.9	45.7	10	24.77	3.5	even	ok
	1	C <sub>11</sub> H <sub>15</sub> N <sub>5</sub> NaO <sub>4</sub> S	336.0737	0.8	4.3	1	100.00	6.5	even	ok
	2	C <sub>7</sub> H <sub>11</sub> N <sub>11</sub> NaO <sub>2</sub> S	336.0710	-8.8	8.0	2	14.55	7.5	even	ok
	3	C <sub>10</sub> H <sub>19</sub> NNaO <sub>8</sub> S	336.0724	-4.8	9.8	3	42.72	1.5	even	ok
	4	C <sub>12</sub> H <sub>11</sub> N <sub>9</sub> NaS	336.0750	-3.1	15.1	4	54.99	11.5	even	ok
	5	C <sub>8</sub> H <sub>19</sub> N <sub>5</sub> NaO <sub>4</sub> S <sub>2</sub>	336.0771	9.2	22.4	5	12.09	1.5	even	ok
	6	C <sub>16</sub> H <sub>15</sub> N <sub>3</sub> NaO <sub>2</sub> S	336.0777	-11.1	26.8	6	4.39	10.5	even	ok
	7	C <sub>7</sub> H <sub>19</sub> N <sub>7</sub> NaOS <sub>3</sub>	336.0705	-10.2	39.1	7	5.63	1.5	even	ok
	8	C <sub>11</sub> H <sub>23</sub> NNaO <sub>3</sub> S <sub>3</sub>	336.0732	2.2	42.1	8	42.71	0.5	even	ok

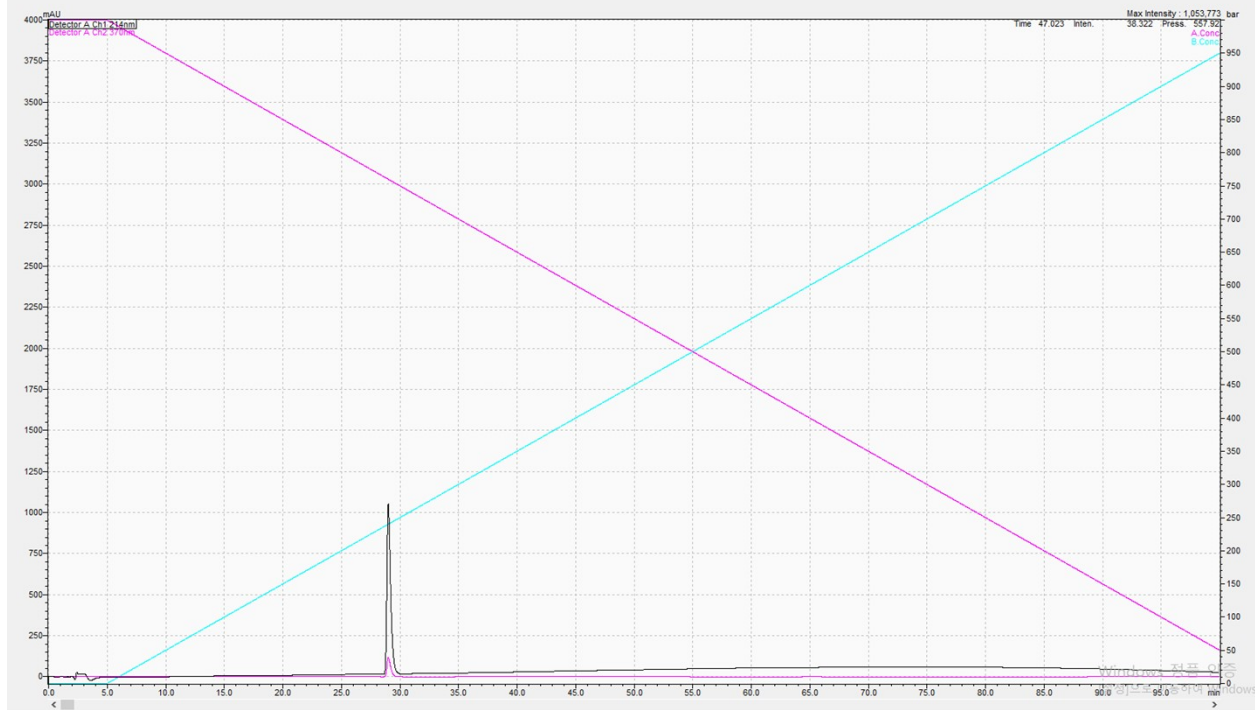
Figure S2. HRMS (ESI-TOF) spectrum of 1



**Figure S3.**  $^1\text{H}$ -NMR spectrum of **1** in DMSO-D<sub>6</sub>



**Figure S4.**  $^{13}\text{C}$ -NMR spectrum of **1** in  $\text{DMSO-}d_6$



**Figure S5.** HPLC chromatogram of **2**

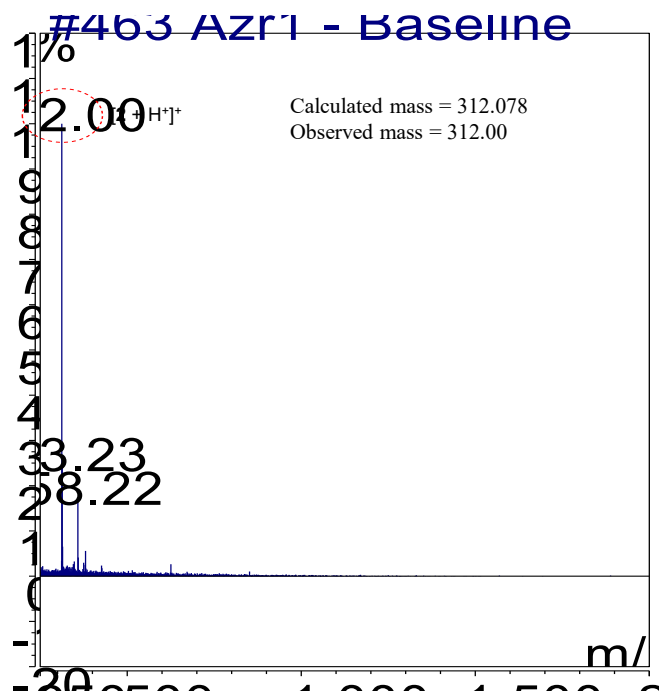


Figure S6a. ESI-MS spectrum of 2

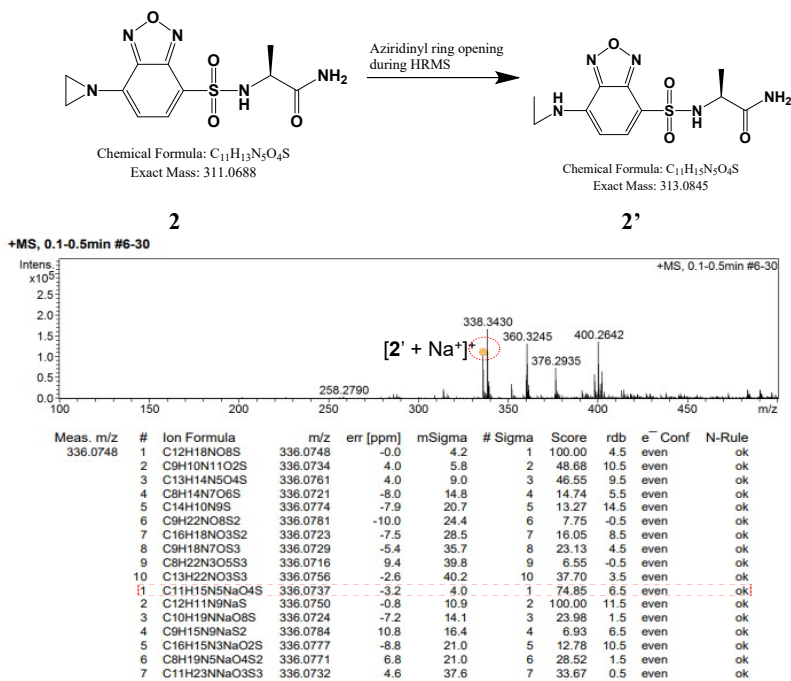


Figure S6b. Aziridinyll ring opening and HRMS (ESI-TOF) spectrum of 2'

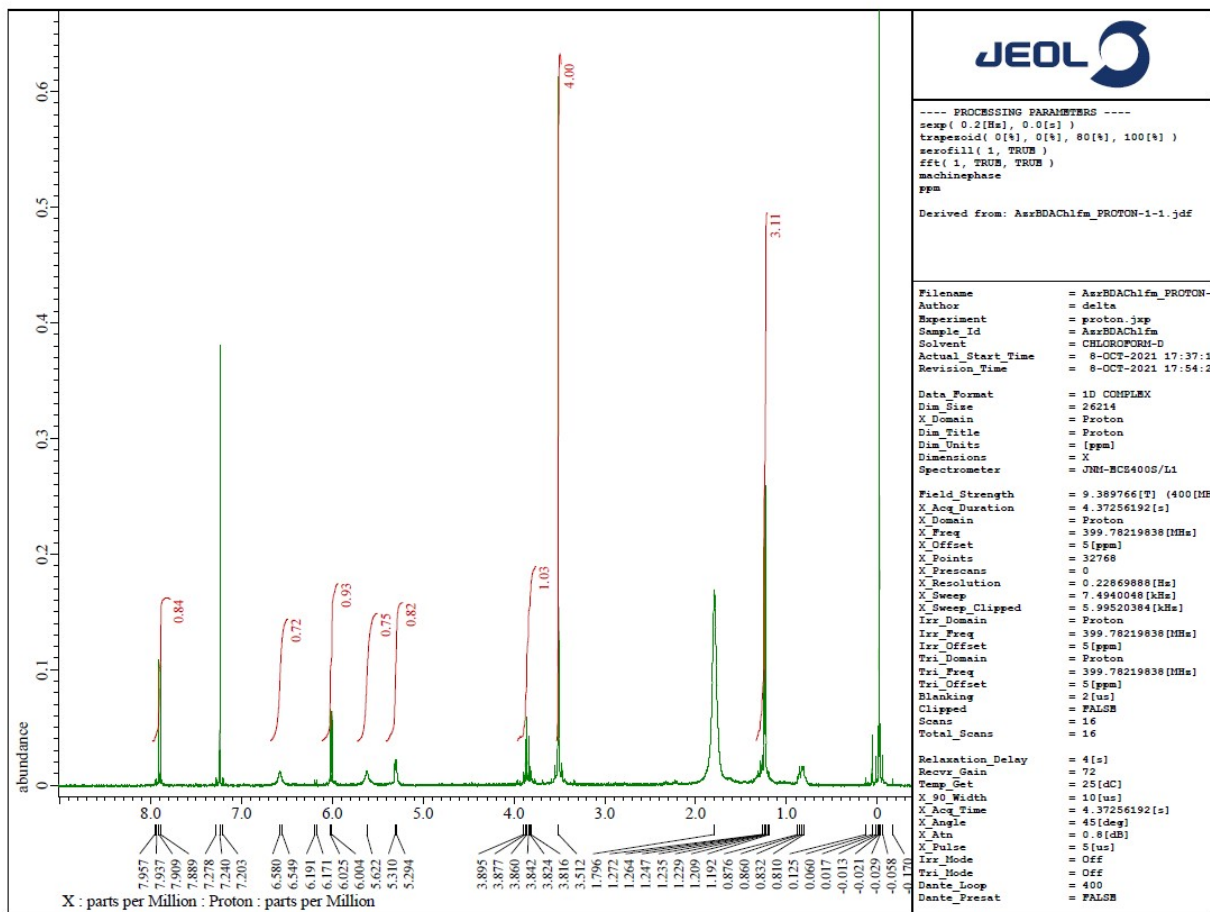
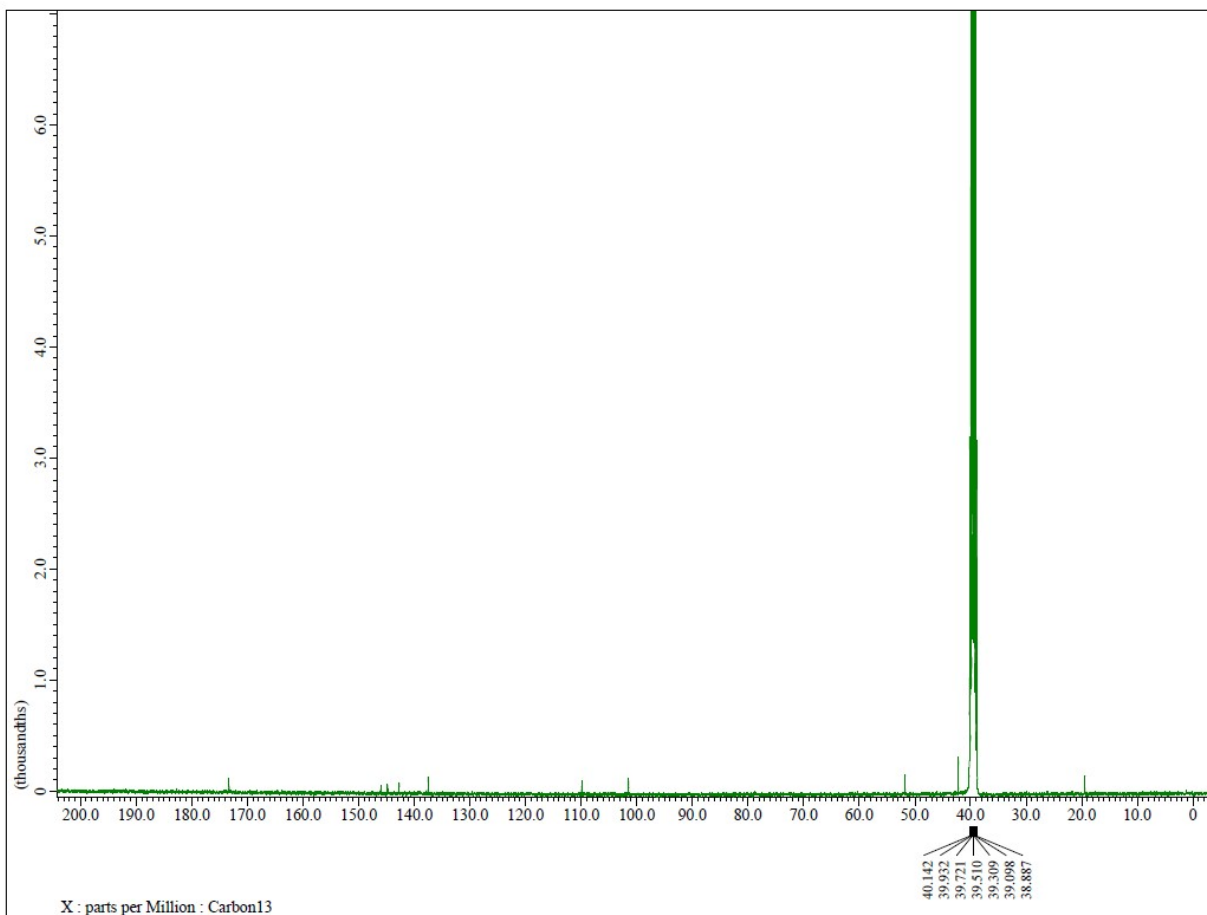
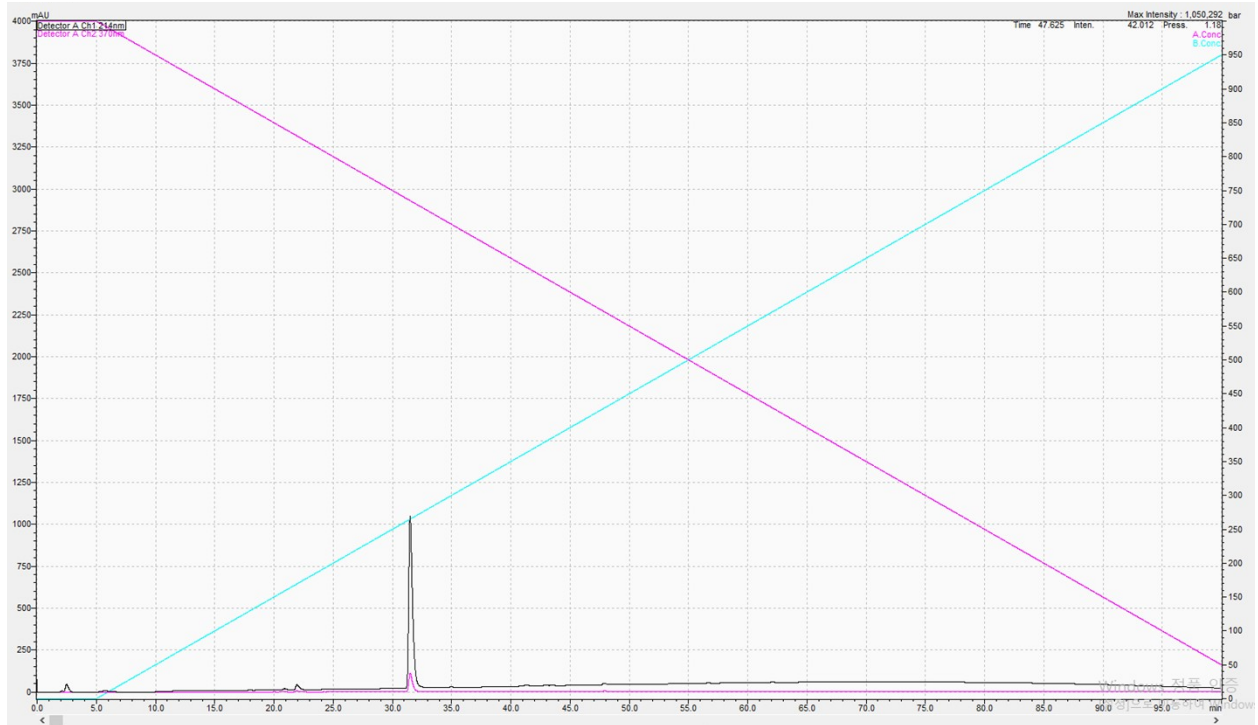


Figure S7. <sup>1</sup>H-NMR spectrum of **2** in CDCl<sub>3</sub>



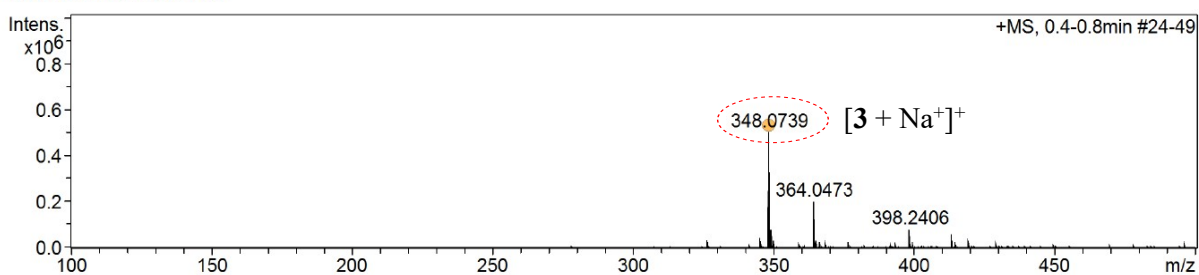


**Figure S8.**  $^{13}\text{C}$ -NMR spectrum of **2** in DMSO-D6



**Figure S9.** HPLC chromatogram of **3**

+MS, 0.4-0.8min #24-49



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
348.0739	1	C <sub>10</sub> H <sub>10</sub> N <sub>11</sub> O <sub>2</sub> S	348.0734	1.3	1.1	1	100.00	11.5	even	ok
	2	C <sub>13</sub> H <sub>18</sub> N <sub>8</sub> O <sub>8</sub> S	348.0748	-2.5	5.4	2	75.22	5.5	even	ok
	3	C <sub>9</sub> H <sub>14</sub> N <sub>7</sub> O <sub>6</sub> S	348.0721	-5.2	11.8	3	37.26	6.5	even	ok
	4	C <sub>14</sub> H <sub>14</sub> N <sub>5</sub> O <sub>4</sub> S	348.0761	-6.4	11.8	4	27.13	10.5	even	ok
	5	C <sub>15</sub> H <sub>10</sub> N <sub>9</sub> S	348.0774	-10.2	23.1	5	6.06	15.5	even	ok
	6	C <sub>17</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub>	348.0723	4.7	32.8	6	33.32	9.5	even	ok
	7	C <sub>10</sub> H <sub>18</sub> N <sub>7</sub> O <sub>5</sub> S <sub>3</sub>	348.0729	-2.7	39.1	7	43.36	5.5	even	ok
	8	C <sub>9</sub> H <sub>22</sub> N <sub>3</sub> O <sub>5</sub> S <sub>3</sub>	348.0716	6.5	42.3	8	15.89	0.5	even	ok
	9	C <sub>14</sub> H <sub>22</sub> N <sub>3</sub> O <sub>3</sub> S <sub>3</sub>	348.0756	-5.0	44.2	9	22.42	4.5	even	ok
	10	C <sub>10</sub> H <sub>26</sub> N <sub>3</sub> S <sub>5</sub>	348.0725	4.0	79.3	10	8.51	-0.5	even	ok
	1	C <sub>12</sub> H <sub>15</sub> N <sub>5</sub> NaO <sub>4</sub> S	348.0737	-0.5	1.7	1	100.00	7.5	even	ok
	2	C <sub>11</sub> H <sub>19</sub> NNaO <sub>8</sub> S	348.0724	4.4	11.8	2	40.30	2.5	even	ok
	3	C <sub>13</sub> H <sub>11</sub> N <sub>9</sub> NaS	348.0750	3.3	12.4	3	50.51	12.5	even	ok
	4	C <sub>9</sub> H <sub>19</sub> N <sub>5</sub> NaO <sub>4</sub> S <sub>2</sub>	348.0771	9.1	22.3	4	10.13	2.5	even	ok
	5	C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> NaO <sub>2</sub> S	348.0777	-11.0	23.9	5	3.88	11.5	even	ok
	6	C <sub>12</sub> H <sub>23</sub> NNaO <sub>3</sub> S <sub>3</sub>	348.0732	1.9	41.0	6	42.48	1.5	even	ok

Figure S10. HRMS (ESI-TOF) spectrum of **3**

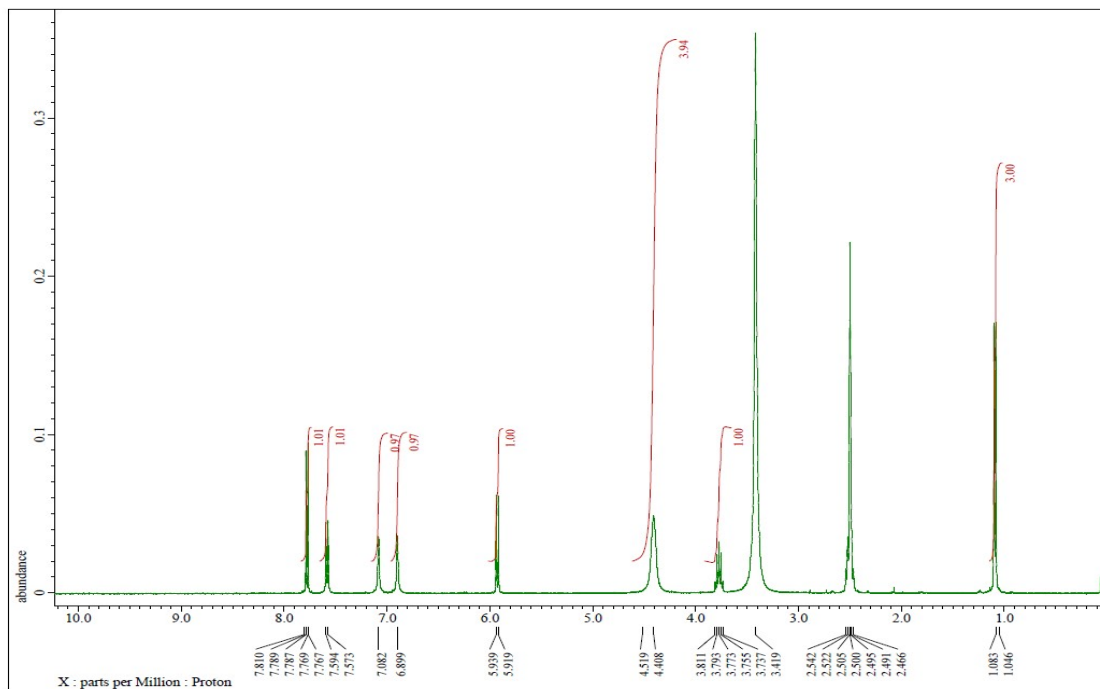


Figure S11a. <sup>1</sup>H-NMR spectrum of 3 in DMSO-D<sub>6</sub>

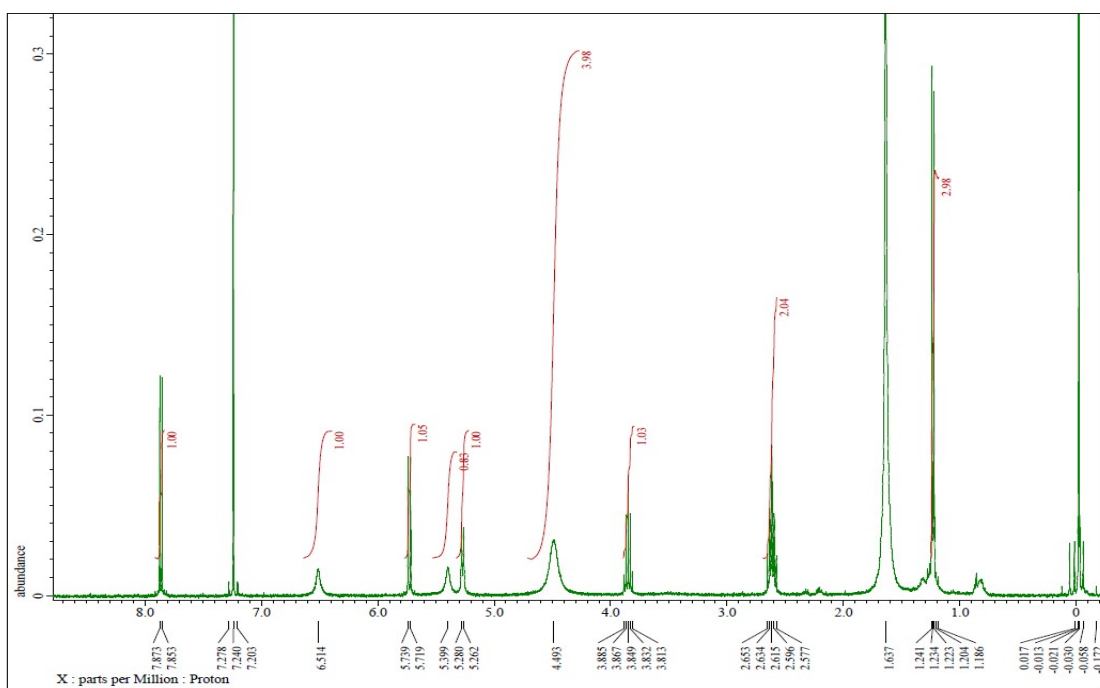
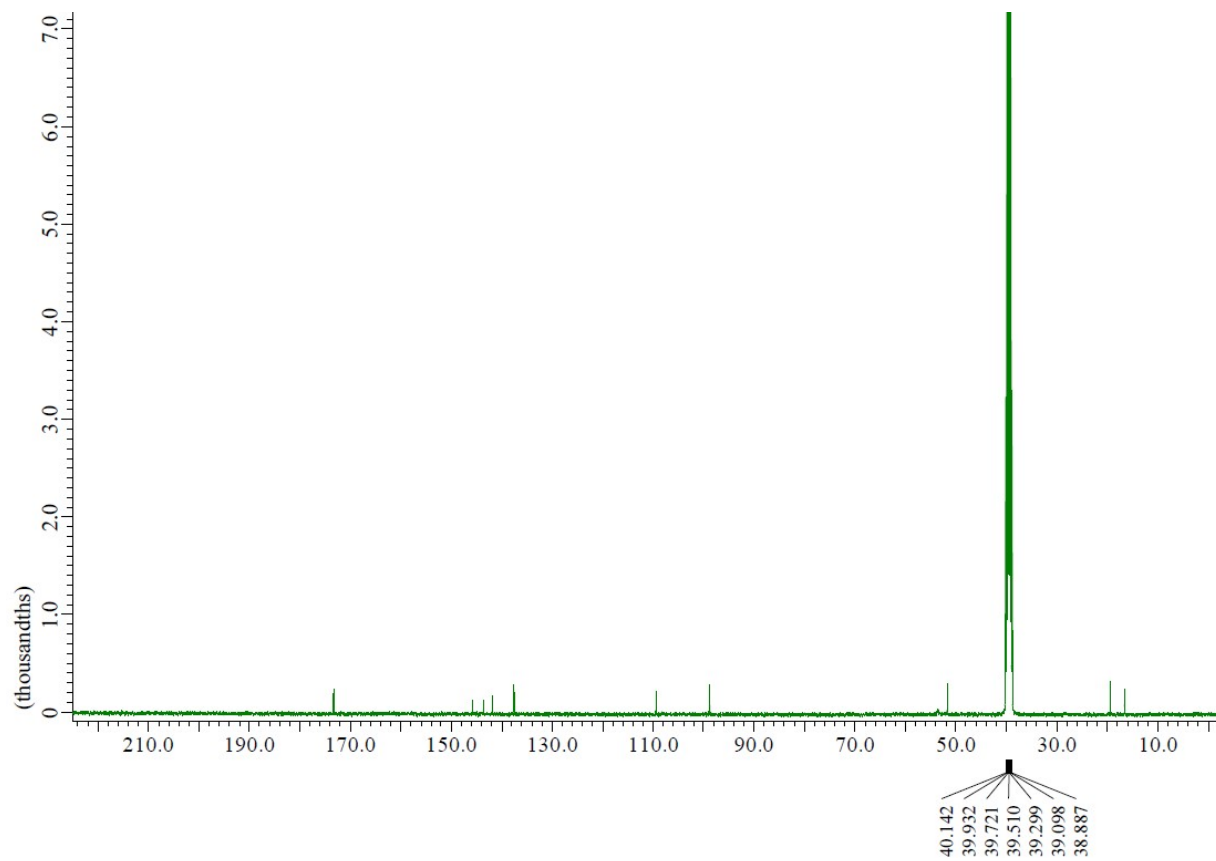
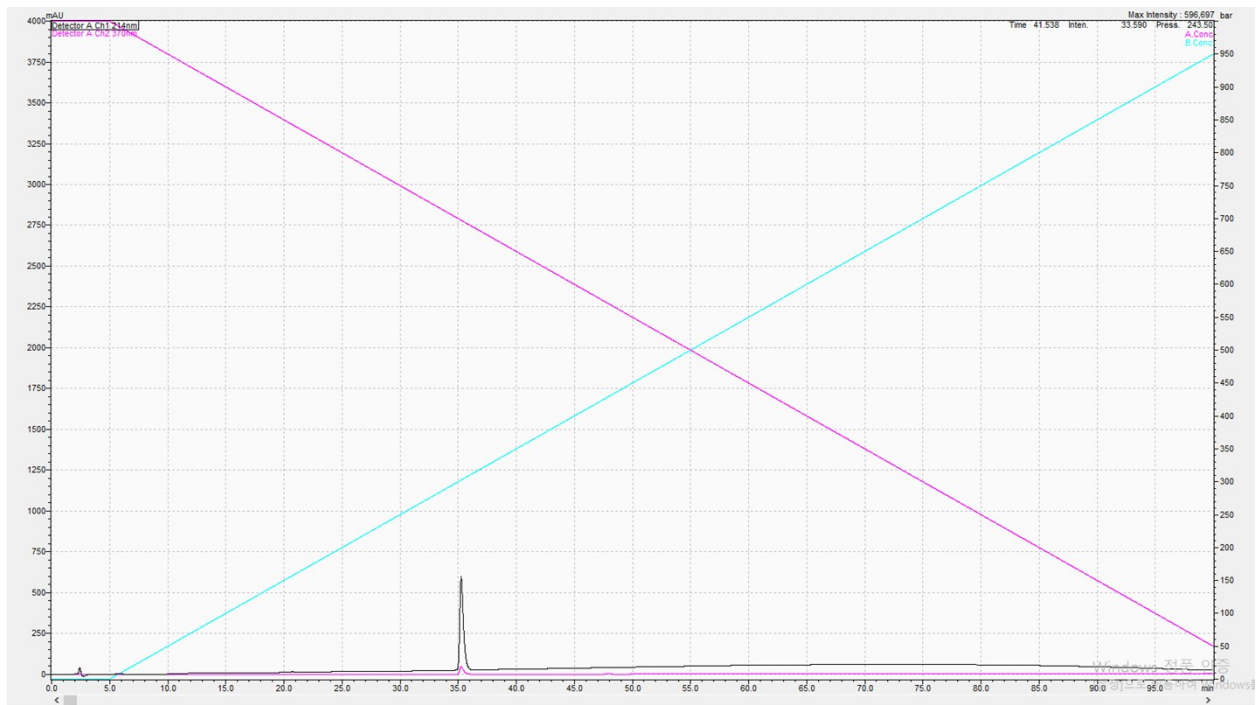


Figure S11b. <sup>1</sup>H-NMR spectrum of 3 in CDCl<sub>3</sub>

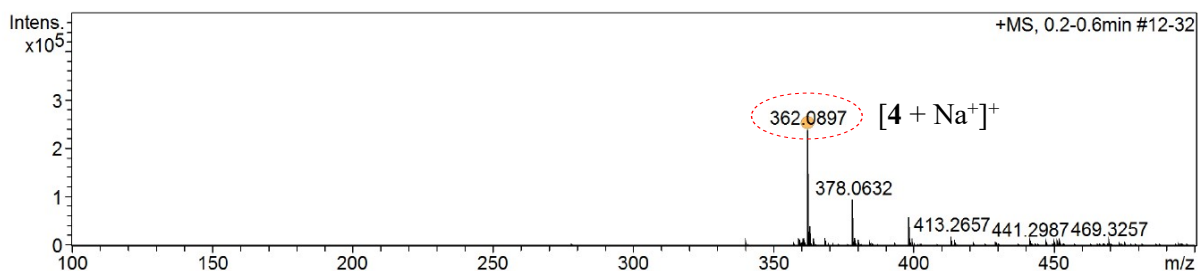


**Figure S12.**  $^{13}\text{C}$ -NMR spectrum of **3** in DMSO- $\text{D}_6$



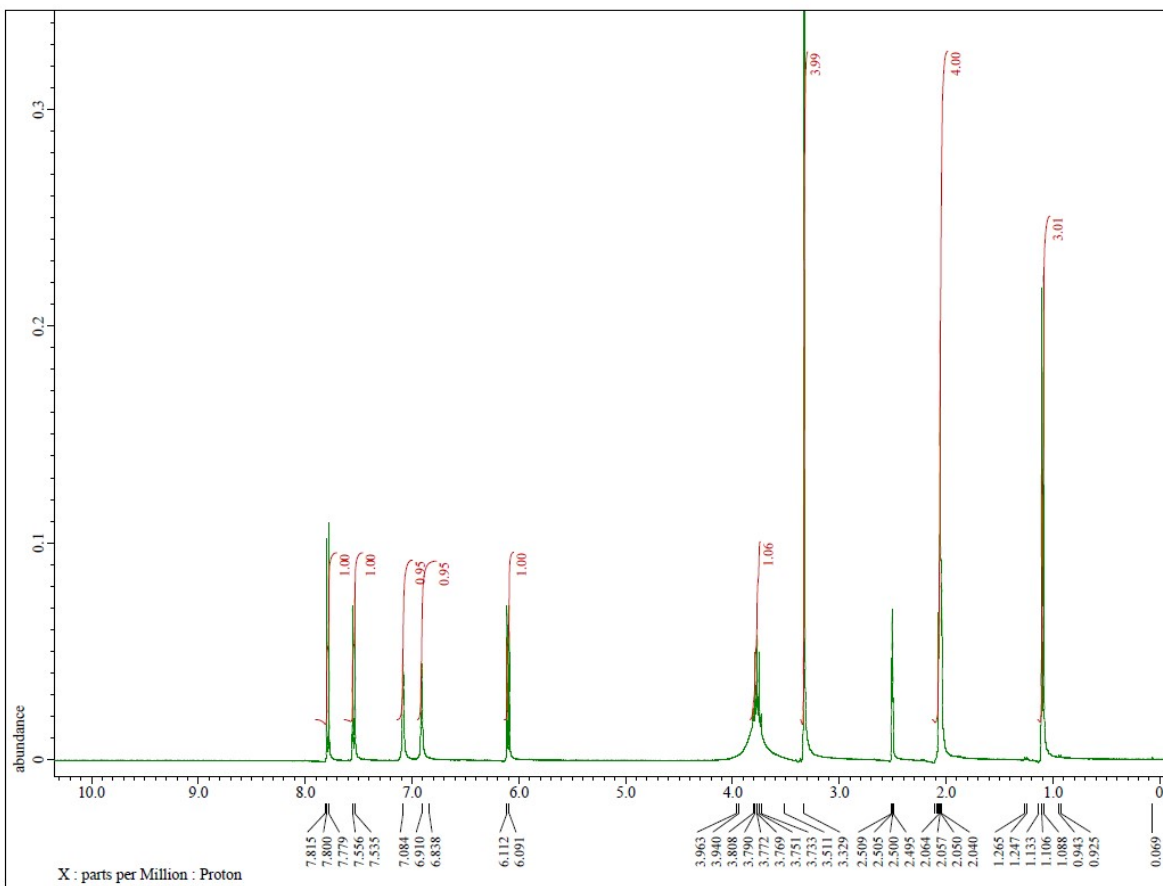
**Figure S13.** HPLC chromatogram of **4**

+MS, 0.2-0.6min #12-32



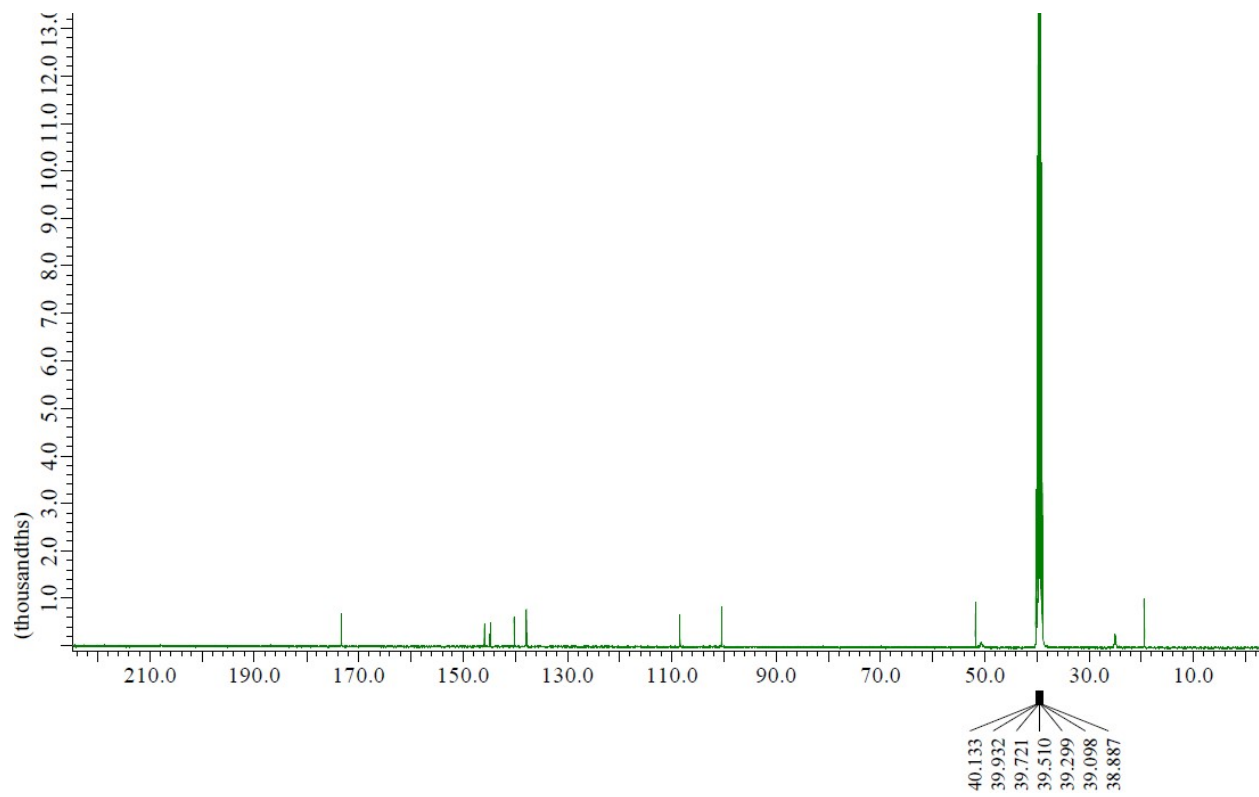
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
362.0897	1	C11H12N11O2S	362.0891	1.7	3.2	1	100.00	11.5	even	ok
	2	C14H20NO8S	362.0904	2.0	6.3	2	89.32	5.5	even	ok
	3	C15H16N5O4S	362.0918	-5.7	9.8	3	35.32	10.5	even	ok
	4	C10H16N7O6S	362.0877	-5.4	14.3	4	35.43	6.5	even	ok
	5	C16H12N9S	362.0931	-9.4	20.9	5	8.31	15.5	even	ok
	6	C18H20NO3S2	362.0879	4.9	31.6	6	34.43	9.5	even	ok
	7	C11H20N7OS3	362.0886	-3.0	39.1	7	44.29	5.5	even	ok
	8	C10H24N3O5S3	362.0873	6.7	42.7	8	15.43	0.5	even	ok
	9	C15H24NO3S3	362.0913	-4.4	43.9	9	27.97	4.5	even	ok
	10	C11H28N3S5	362.0881	4.3	79.3	10	8.56	-0.5	even	ok
	1	C13H17N5NaO4S	362.0893	-0.9	3.0	1	100.00	7.5	even	ok
	2	C14H13N9NaS	362.0907	2.8	10.2	2	62.65	12.5	even	ok
	3	C12H21NNaO8S	362.0880	-4.6	14.1	3	37.94	2.5	even	ok
	4	C18H17N3NaO2S	362.0934	-10.2	21.6	4	5.26	11.5	even	ok
	5	C10H21N5NaO4S2	362.0927	8.4	23.3	5	12.53	2.5	even	ok
	6	C13H25NNaO3S3	362.0889	-2.2	41.1	6	42.86	1.5	even	ok

Figure S14. HRMS (ESI-TOF) spectrum of 4

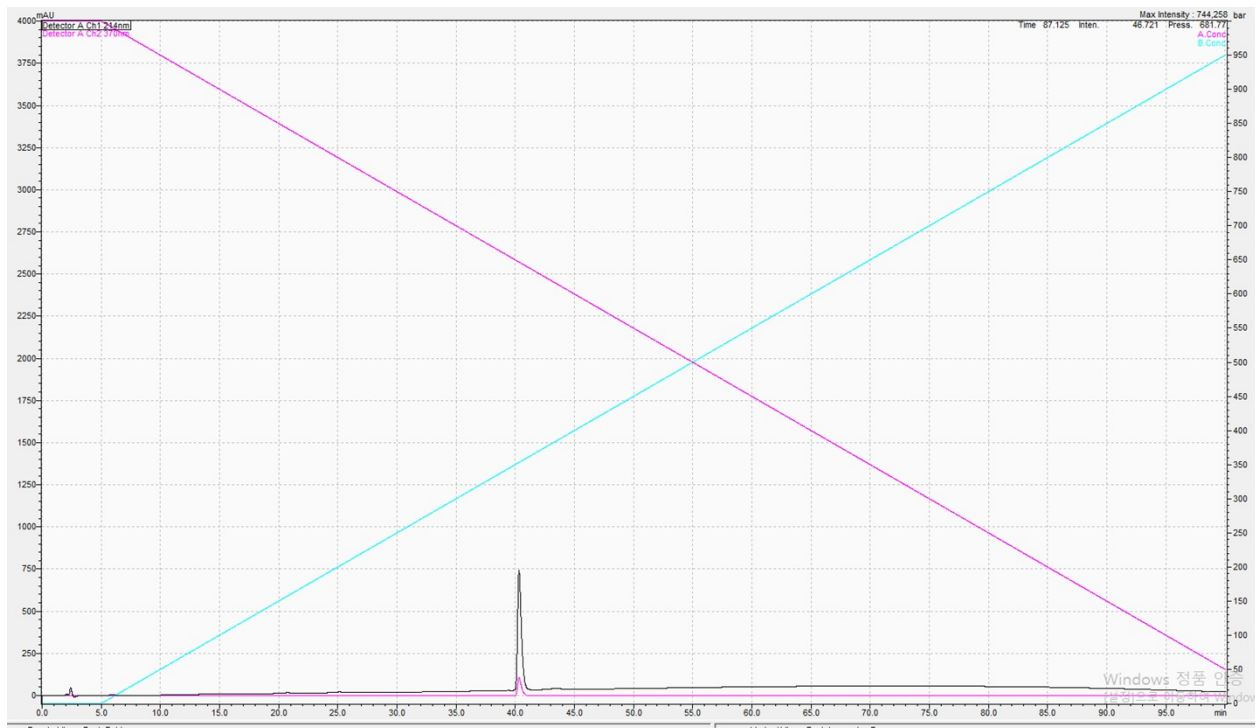


**Figure S15.** <sup>1</sup>H-NMR spectrum of **4** in DMSO-D6



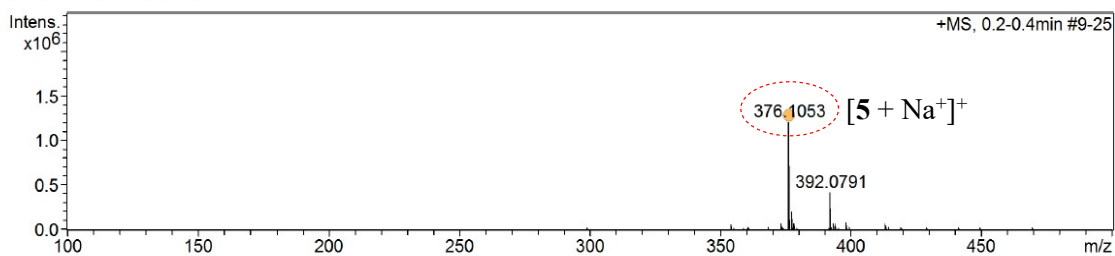


**Figure S16.**  $^{13}\text{C}$ -NMR spectrum of **4** in DMSO- $\text{D}_6$



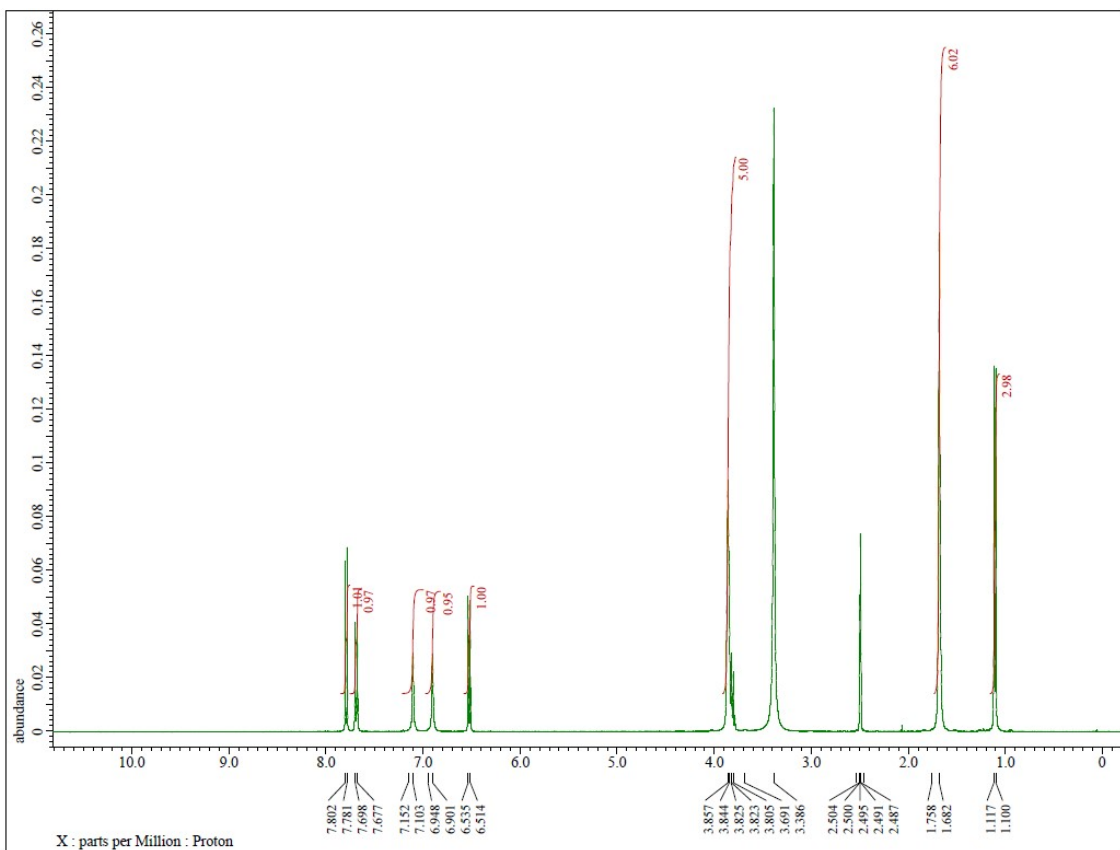
**Figure S17.** HPLC chromatogram of **5**

+MS, 0.2-0.4min #9-25

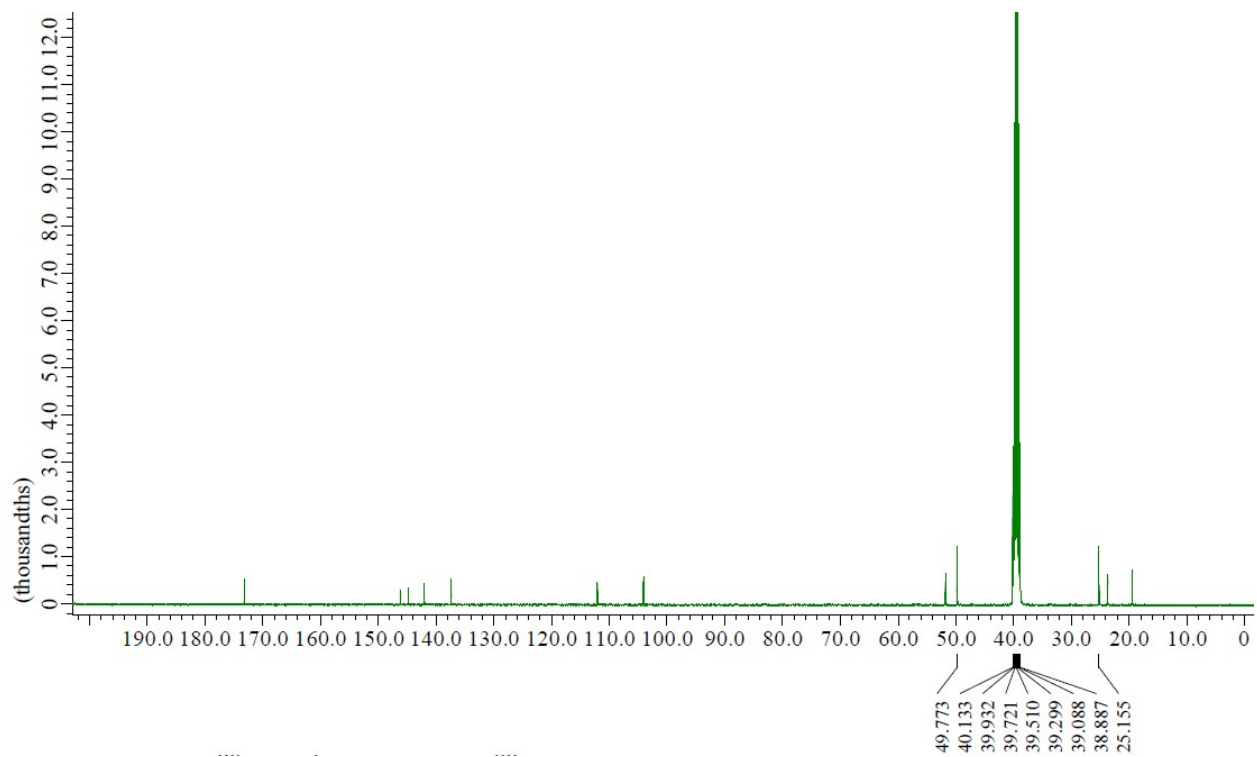


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
376.1053	1	C12H14N11O2S	376.1047	1.7	4.2	1	100.00	11.5	even	ok
	2	C15H22NO8S	376.1061	1.9	8.3	2	88.55	5.5	even	ok
	3	C11H18N7O6S	376.1034	5.2	8.7	3	39.95	6.5	even	ok
	4	C16H18N5O4S	376.1074	5.5	16.2	4	32.14	10.5	even	ok
	5	C10H22N3O10S	376.1020	8.8	20.5	5	9.57	1.5	even	ok
	6	C17H14N9S	376.1087	-9.0	27.2	6	7.46	15.5	even	ok
	7	C19H22NO3S2	376.1036	4.7	37.0	7	30.43	9.5	even	ok
	8	C12H22N7OS3	376.1042	-2.9	41.4	8	42.24	5.5	even	ok
	9	C11H26N3O5S3	376.1029	-6.5	43.5	9	15.30	0.5	even	ok
	10	C16H26NO3S3	376.1069	4.2	47.4	10	25.95	4.5	even	ok
	11	C12H30N3S5	376.1038	4.2	74.6	11	10.47	-0.5	even	ok
	1	C14H19N5NaO4S	376.1050	-0.9	5.7	1	100.00	7.5	even	ok
	2	C10H15N11NaO2S	376.1023	-8.1	6.9	2	14.69	8.5	even	ok
	3	C13H23NNaO8S	376.1037	4.5	9.3	3	43.44	2.5	even	ok
	4	C15H15N9NaS	376.1063	2.6	16.2	4	59.00	12.5	even	ok
	5	C11H23N5NaO4S2	376.1084	-8.0	22.7	5	13.52	2.5	even	ok
	6	C19H19N3NaO2S	376.1090	9.8	28.1	6	4.84	11.5	even	ok
	7	C10H23N7NaOS3	376.1018	9.3	39.8	7	5.44	2.5	even	ok
	8	C14H27NNaO3S3	376.1045	-2.2	43.4	8	41.97	1.5	even	ok

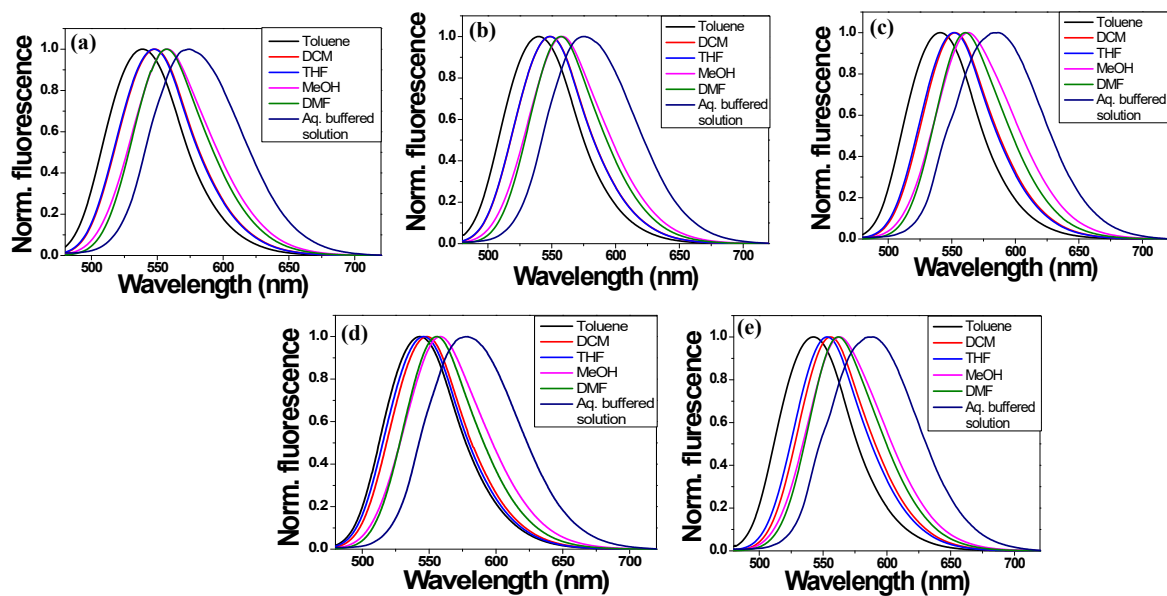
Figure S18. HRMS (ESI-TOF) spectrum of 5



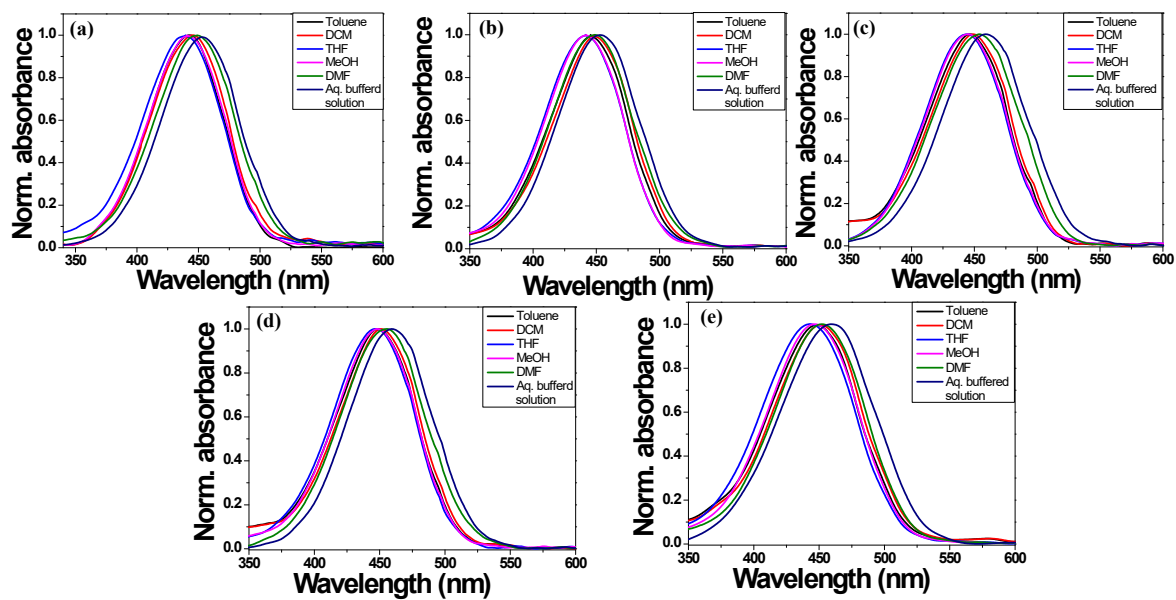
**Figure S19.**  $^1\text{H-NMR}$  spectrum of **5** in  $\text{DMSO-D}_6$



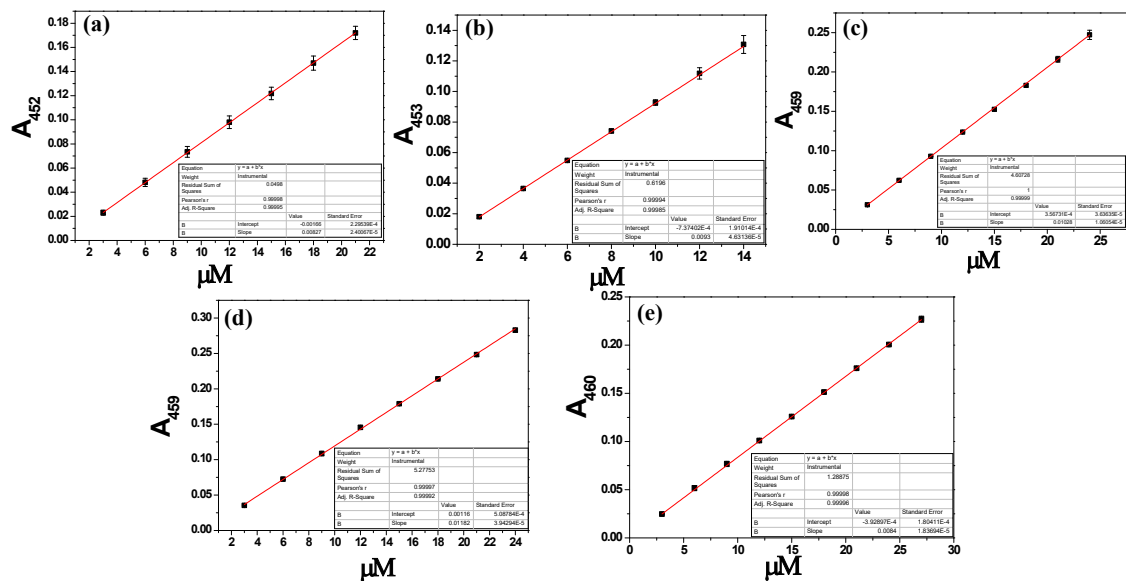
**Figure S20.**  $^{13}\text{C}$ -NMR spectrum of **5** in DMSO- $\text{D}_6$



**Figure S21.** Normalized fluorescence emission spectra of 1-5 [20  $\mu\text{M}$ ] in various solvents. (a; 1, b; 2, c; 3, d; 4, and e; 5).

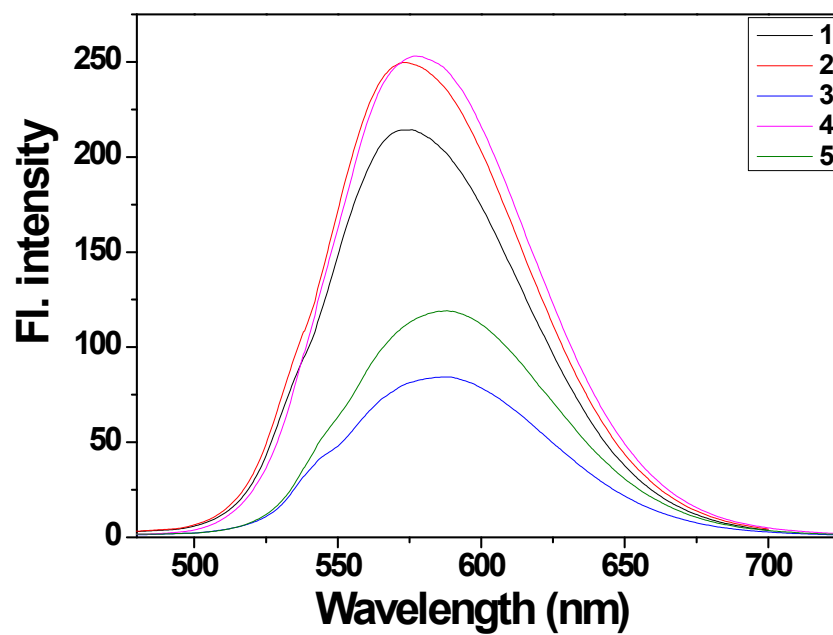


**Figure S22.** Normalized UV-visible emission spectra of probes 1-5 [20  $\mu$ M] in different solvent system. (a; 1, b; 2, c; 3, d; 4, and e; 5).

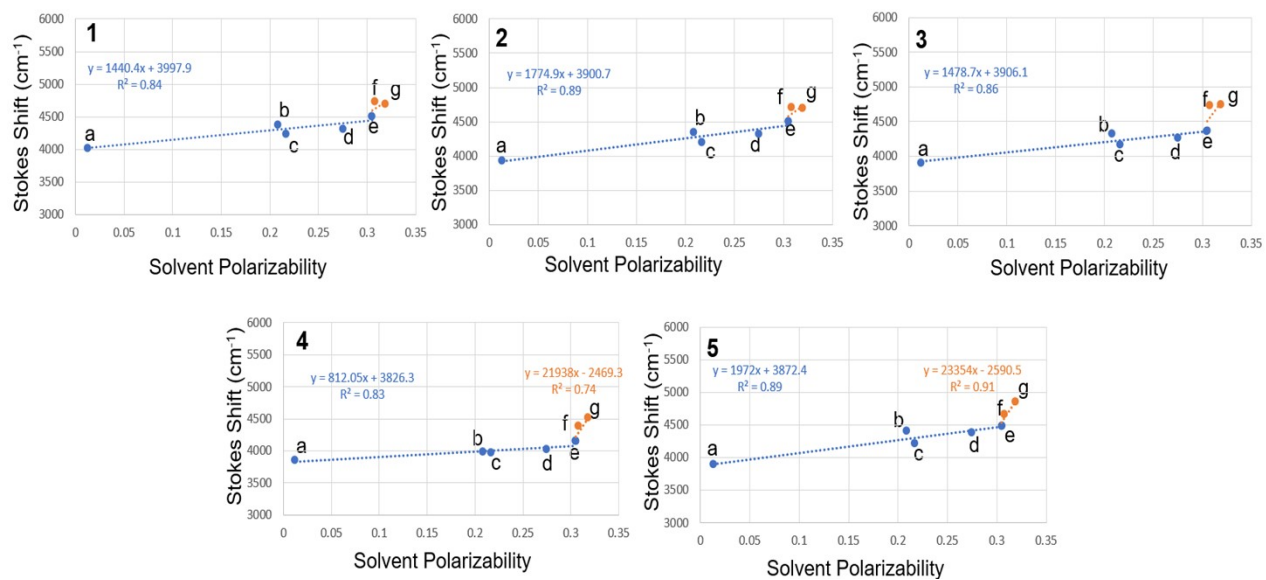


**Figure S23.** Linear plot of absorption band as a function of concentration of 1-5 in aqueous buffered solution (10 mM HEPES at pH 7.4) containing 0.5% DMF (a; 1, b; 2, c; 3, d; 4, and e; 5).

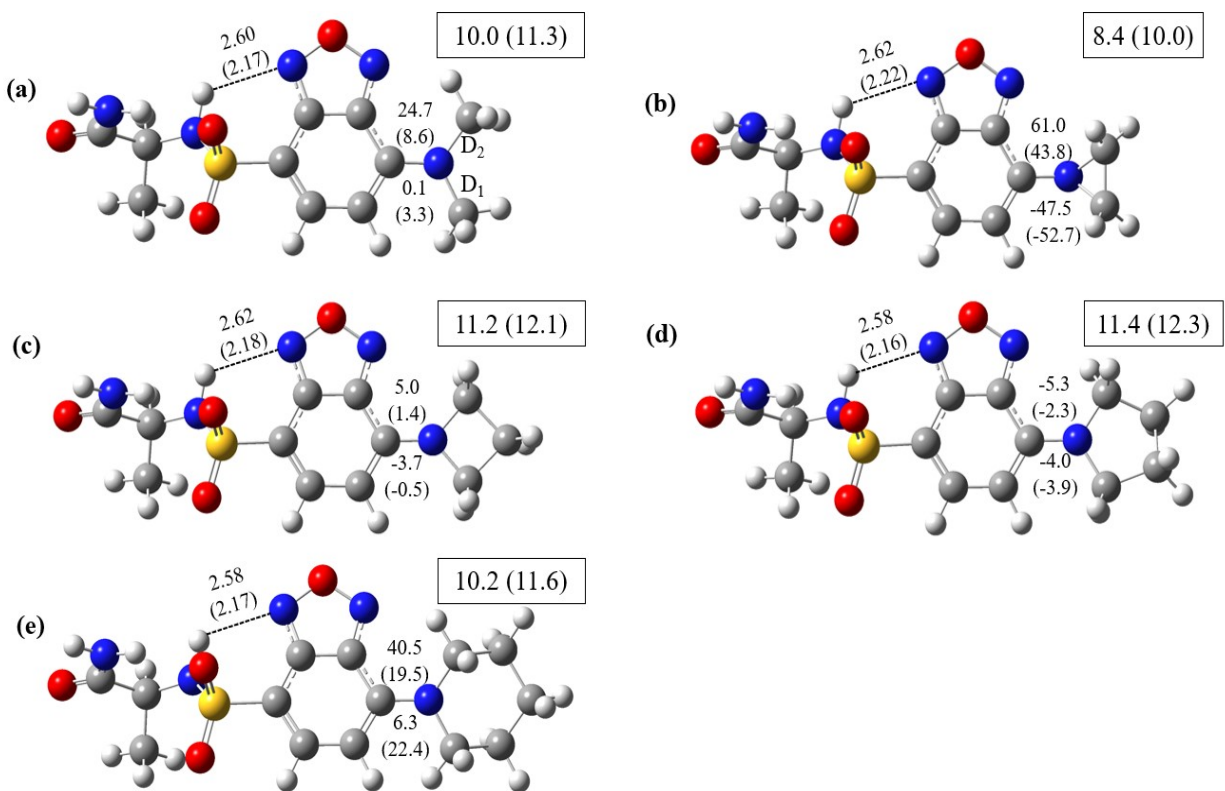




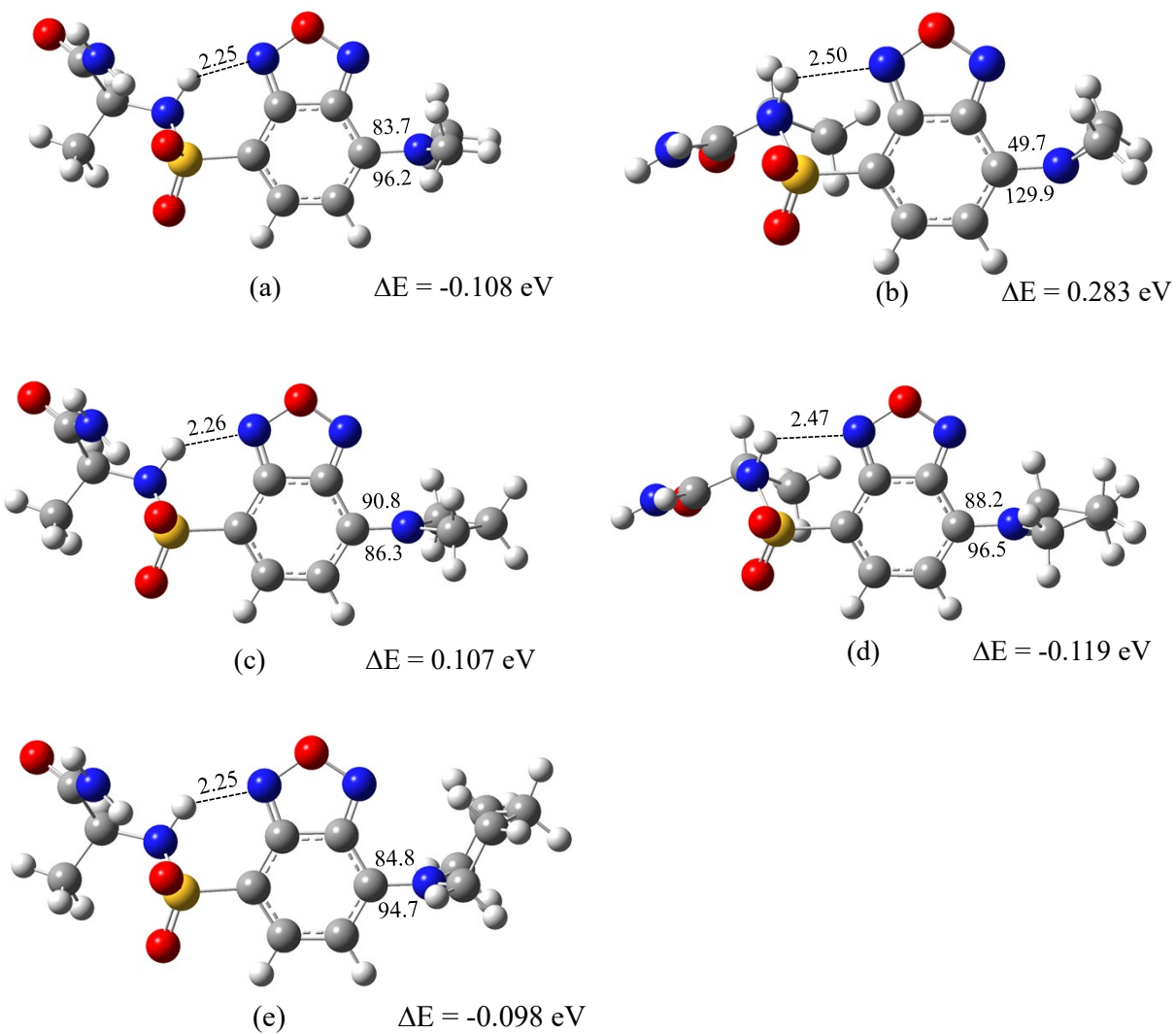
**Figure S24.** Fluorescence emission spectra of **1-5** [20  $\mu$ M] in aqueous buffered solution (10 mM HEPES, pH 7.4) containing 0.5% DMF (Sensitivity high, slit=10/10).



**Figure S25.** Lippert-Mataga plot of **1-5** in different solvents (a; toluene, b; THF, c; DCM, d; DMF, e; ACN, f; methanol; and g; aqueous buffered solution [10 mM HEPES, pH 7.4 containing 0.5% DMF]) showing the variation of Stokes shift as a function of orientation polarizability of the solvents



**Figure S26.** Optimized structures of (a) **1**, (b) **2**, (c) **3**, (d) **4**, and (e) **5** in the ground and excited states. Two torsional angles (in °), D<sub>1</sub> and D<sub>2</sub>, are shown in each figure. Dipole moments (in D) are shown in the rectangular box and some important bond lengths (in Å) of the probes are also shown. The values in parentheses are for the excited states. Dipole



**Figure S27.** Optimized TICT structures for (a) **1**, (b) **2**, (c) **3**, (d) **4**, and (e) **5** in the excited states. Two torsional angles (in  $^{\circ}$ ) and some important bond lengths (in  $\text{\AA}$ ) are shown in each figure.  $\Delta E$  denotes energy difference between LE and TICT states.

**Table**

Stokes

Solvent	Probe	$\lambda_{Ex}$ (nm)	$\lambda_{Em}$ (nm)	$\Delta\lambda$ (nm)	$\Delta\nu$ (cm <sup>-1</sup> )
<b>Aqueous buffered solution (pH=7.4)</b>	<b>1</b>	452	574	122	4702
	<b>2</b>	453	575.5	122.5	4699
	<b>3</b>	459	587	128	4751
	<b>4</b>	459.5	579	119.5	4507
	<b>5</b>	458.5	589.5	131	4847
<b>DMF</b>	<b>1</b>	449	557	108	4318
	<b>2</b>	449	557	108	4318
	<b>3</b>	454	560.5	106.5	4185
	<b>4</b>	455.5	556	100.5	3968
	<b>5</b>	451.5	562	110.5	4379
<b>MeOH</b>	<b>1</b>	441	557.5	116.5	4739
	<b>2</b>	442	558.5	116.5	4719
	<b>3</b>	444.5	563	118.5	4735
	<b>4</b>	448.5	558.5	110	4391
	<b>5</b>	446	563	117	4660
<b>ACN</b>	<b>1</b>	444.5	557	112.5	4544
	<b>2</b>	444.5	557.5	113	4509
	<b>3</b>	450.5	561	110.5	4372
	<b>4</b>	452	557	105	4170
	<b>5</b>	449.5	563	113.5	4485
<b>THF</b>	<b>1</b>	439.5	547.5	108	4488
	<b>2</b>	441.5	548.5	107	4419
	<b>3</b>	444	551.5	107.5	4390
	<b>4</b>	447.5	546	98.5	4031
	<b>5</b>	443	553	110	4490
<b>DCM</b>	<b>1</b>	445	548	103	4224
	<b>2</b>	448.5	549	100.5	4082
	<b>3</b>	449	552.5	103.5	4172
	<b>4</b>	451.5	548.5	97	3917

**S1:** Absorption maxima, emission maxima and shift of **1-5** in various solvents.

	<b>5</b>	451	555.5	104.5	4171
<b>Toluene</b>	<b>1</b>	443	539	96	4020
	<b>2</b>	445.5	540	94.5	3928
	<b>3</b>	446.5	541	94.5	3912
	<b>4</b>	449	543	94	3856
	<b>5</b>	448	542.5	94.5	3888

Table S2. Quantum yields in methanol, DMF, and DCM.

Probe	$\phi$ (Methanol)	$\phi$ (DMF)	$\phi$ (DCM)
<b>1</b>	0.049	0.246	0.688
<b>2</b>	0.032	0.282	0.775
<b>3</b>	0.021	0.161	0.309
<b>4</b>	0.044	0.375	0.697
<b>5</b>	0.036	0.231	0.667