Supplementary Information

Synthesis and photophysical properties of photostable 1,8-naphthalimide dyes incorporating benzotriazole-based UV absorbers

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Contents

1. Characterization data

1.1 Compound 1

Melting point: over 300 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 10.51 (s, 1H), 10.46 (s, 1H), 8.77-8.78 (d, *J* = 8.4 Hz, 1H), 8.56-8.57 (d, *J* = 7.2 Hz, 1H), 8.51-8.52 (d, *J* = 7.2 Hz, 1H), 8.35-8.36 (d, *J* = 8.4 Hz, 1H), 8.04-8.05 (m, 2H), 7.93-7.95 (m, 2H), 7.53-7.56 (m, 3H), 7.18-7.21 (dd, *J* = 8.4, 8.4 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 170.19, 164.11, 163.52, 148.38, 144.19 (2C), 141.05, 132.81, 132.19, 131.42 (2C), 130.02, 129.56, 129.04, 128.03 (2C), 126.97, 126.27, 125.84, 124.73, 123.50, 119.94, 119.74, 118.60 (2C), 24.67. FT-IR (ATR, cm^{-1}): 3240, 3040, 1708, 1670, 1538, 1371, 1340, 1239, 1197, 780, 748, 734. MS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{26}H_{17}N_5NaO_4$ 486.12; Found 486.08. Anal. Calcd for $C_{26}H_{17}N_5O_4$: C, 67.38; H, 3.70; N, 15.11. Found: C, 67.43; H, 4.02; N, 15.17.

1.2 Compound 3

Melting point: over 300 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 10.46 (s, 1H), 10.31 (s, 1H), 8.78-8.79 (d, *J* = 8.4 Hz, 1H), 8.57-8.58 (d, *J* = 7.8 Hz, 1H), 8.52-8.53 (d, *J* = 8.4 Hz, 1H), 8.36-8.37 (d, *J* = 8.4 Hz, 1H), 8.14-8.16 (m, 2H), 7.93-7.95 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.73-7.74 (d, *J* = 1.8 Hz, 1H), 7.52-7.54 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.48-7.50 (dd, *J* = 2.1, 8.7 Hz, 1H), 7.10-7.12 (d, *J* = 9.0 Hz, 1H), 2.30 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 170.17, 164.47, 163.89, 149.40, 144.27, 143.70, 142.59, 141.06, 135.46, 132.26, 131.49, 130.01, 129.60, 129.45, 128.78, 127.49, 126.95, 124.72, 123.44, 122.79, 119,92, 119.16, 118.75, 118.52, 118.02, 34.49, 31.69 (3C), 24.66. FT-IR (ATR, cm^{-1}): 3249, 2959, 1668, 1657, 1377, 1240, 1195, 779. MS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{30}H_{26}N_5O_4$ 520.20; Found 520.19. Anal. Calcd for $C_{30}H_{25}N_5O_4$: C, 69.35; H, 4.85; N, 13.48. Found: C, 69.13; H, 5.16; N, 13.24.

1.3 Compound 4

Melting point: over 300 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 10.43 (s, 1H), 8.74-8.75 (d, *J* = 7.8 Hz, 1H), 8.51-8.53 (d, *J* = 7.2 Hz, 1H), 8.46-8.48 (d, *J* = 7.8 Hz, 1H), 8.33-8.34 (d, *J* = 7.8 Hz, 1H), 7.90-7.92 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.52-7.53 (d, *J* = 7.8 Hz, 2H), 7.27-7.28 (d, *J* = 7.8 Hz, 2H), 2.29 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (150 MHz, DMSO-d_6): δ 170.16, 164.36, 163.79, 150.95, 140.93, 133.87, 132.19, 131.40 (2C), 129.88, 129.27, 129.06 (2C), 126.90, 126.19, 124.63, 123.31, 119.87, 118.42, 34.98, 31.73 (3C), 24.64. FT-IR (ATR, cm^{-1}): 3332, 2951, 1712, 1663, 1506, 1374, 1237, 1199, 783, 562. MS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{22}N_2NaO_3$ 409.15; Found 409.11. Anal. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.73; H, 5.88; N, 7.32.

1.4 Compound 5

Melting point: 129 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 10.53 (s, 1H), 8.02-8.04 (m, 2H), 7.80-7.81 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.52-7.54 (m, 2H), 7.42-7.45 (m, 1H), 7.16-7.17 (d, *J* = 7.8 Hz, 1H), 7.03-7.06 (dd, *J* = 8.1, 8.1 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6): δ 151.47, 144.09 (2C), 131.65, 131.63, 127.87 (2C), 125.83, 120.09, 118.52 (2C), 118.44. FT-IR (ATR, cm^{-1}): 3097, 1490, 1256, 1221, 741, 684, 656, 472. MS (ESI) *m/z*: $[2M-H]^-$ Calcd for $C_{24}H_{17}N_6O_2$ 421.14; Found 420.57. Anal. Calcd for $C_{12}H_9N_3O$: C, 68.24; H, 4.29; N, 19.89. Found: C, 68.59; H, 4.46; N, 19.94.

1.5 Compound 6

Melting point: 153°C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.51 (s, 1H), 8.07-8.08 (m, 2H), 7.54-7.57 (m, 3H), 7.15 (s, 1H), 3.47 (br, 2H), 1.71 (s, 2H), 1.34 (s, 6H), 0.74 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 143.76 (2C), 142.11, 138.96, 129.87, 128.29 (2C), 126.69, 119.18, 118.49

(2C), 115.07, 56.60, 38.40, 32.64, 32.14 (3C), 31.76 (2C). FT-IR (ATR, cm^{-1}): 3445, 3364, 3059, 2955, 1512, 1219, 751, 725, 659. MS (ESI) *m/z*: $[M]^+$ Calcd for $C_{20}H_{26}N_4O$ 338.21; Found 338.56.

2. Absorption and fluorescence spectra in various solvents

Table S1 Optical properties of **1-5** and the equimolar mixture of **4** and **5** in various solvents.[a]

Compd	Solvent	λ_{abs} (nm)	ε_{max}	λ_F (nm)	λ_{EX} (nm)	Stokes shift (cm^{-1})	Φ_F (%)	τ (ns) (χ^2)[d]	k_r (ns^{-1})	k_{nr} (ns^{-1})
1	CH_3OH	337	27000	466	370	5570	56.2	5.2 (1.03)	0.11	0.084
	$CHCl_3$	340	27700	443	372	4310	27.8	2.1 (1.09)	0.13	0.34
	DMSO	370	16200	464	373	5260	27.8	2.5 (1.07)	0.11	0.28
2	CH_3OH	342	28000	468	373	5440	7.5	0.79 (1.01)	0.10	1.2
	$CHCl_3$	350	28500	473	379	5240	2.8	1.4 (1.02)	0.020	0.68
	DMSO	364	17600	465	375	5160	7.4	0.68 (1.04)	0.11	1.4
3	CH_3OH	356	20200	466	376	5140	41.7	4.3 (1.06)	0.10	0.14
	$CHCl_3$	359	31500	444	380	3790	5.1	0.82 (1.08)	0.062	1.2
	DMSO	371	17700	464	375	5120	39.1	2.8 (1.02)	0.14	0.22
4[b]	CH_3OH	364	14900	465	368	5670	82.6	7.3 (1.04)	0.11	0.024
	$CHCl_3$	365	15100	444	370	4510	46.5	2.9 (1.02)	0.16	0.19
	DMSO	374	15000	464	373	5260	54.6	3.8 (1.09)	0.14	0.12
5[c]	CH_3OH	328	17300	392	313	6440	0.8	0.057 (1.08)	0.14	18
	$CHCl_3$	333	18600	392	315	6240	0.6	1.1 (1.04)	0.0054	0.90
	DMSO	289	13100	419	285	11220	1.2	0.26 (1.05)	0.046	3.8
4 + **5**[b]	CH_3OH	335	13400	468	370	5660	87.1	8.1 (1.05)	0.11	0.016
	$CHCl_3$	339	15300	444	372	4360	48.2	3.2 (1.09)	0.15	0.16
	DMSO	372	8000	464	374	5190	56.5	4.2 (1.05)	0.14	0.10

[a]Conc. 20 μM. [b]Conc. 30 μM. [c]Conc. 50 μM. [d]Lifetimes were determined by fitting the decay curves with a single-exponential decay function. The quantities that express the mismatch between data and fitted function (χ^2) are shown in parentheses.

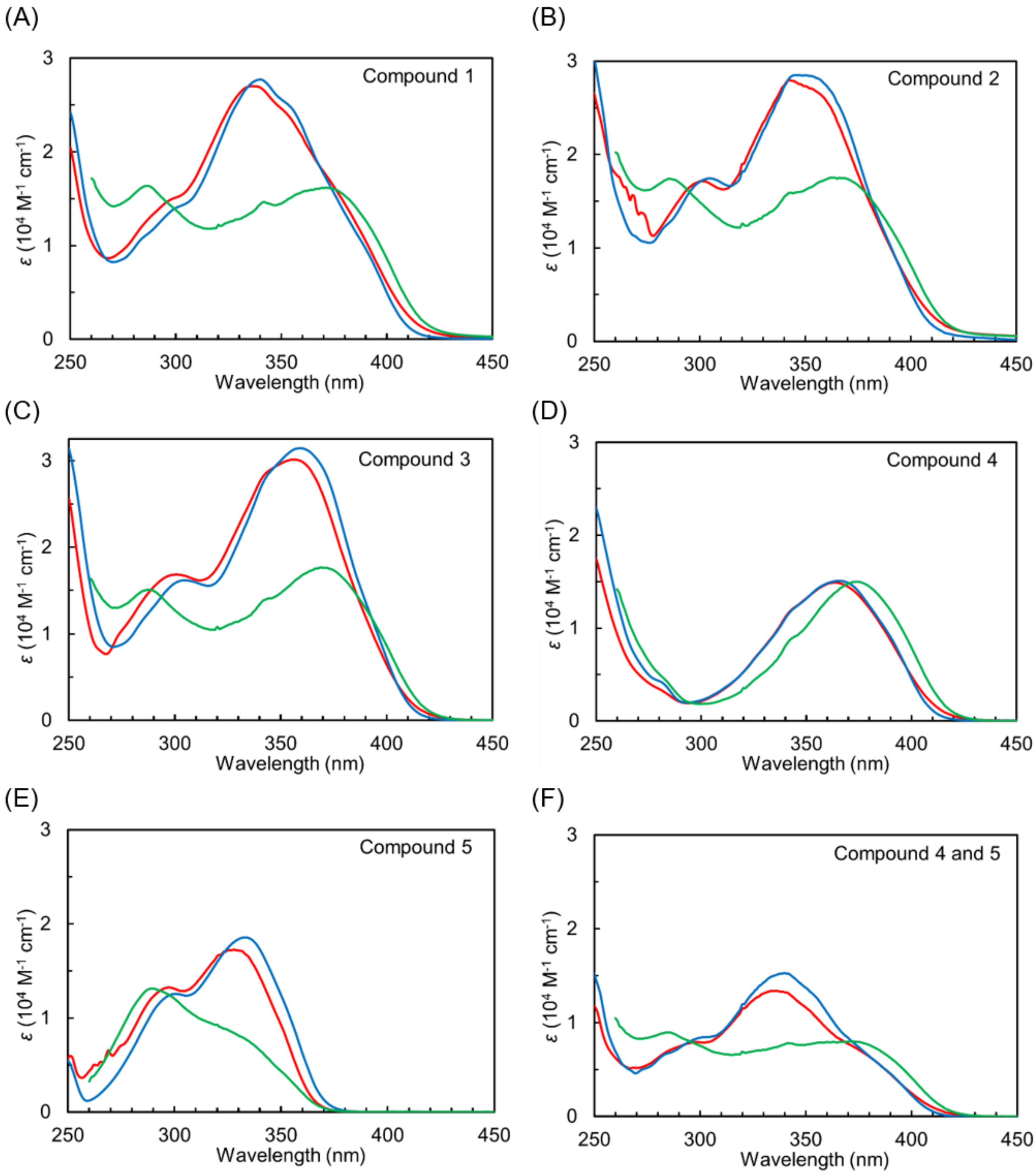

Fig. S1 UV-vis absorption spectra of **1** (A), **2** (B), **3** (C), **4** (D), **5** (E), and the equimolar mixture of **4** and **5** (F) in CH_3OH (red), $CHCl_3$ (blue), and DMSO (green).

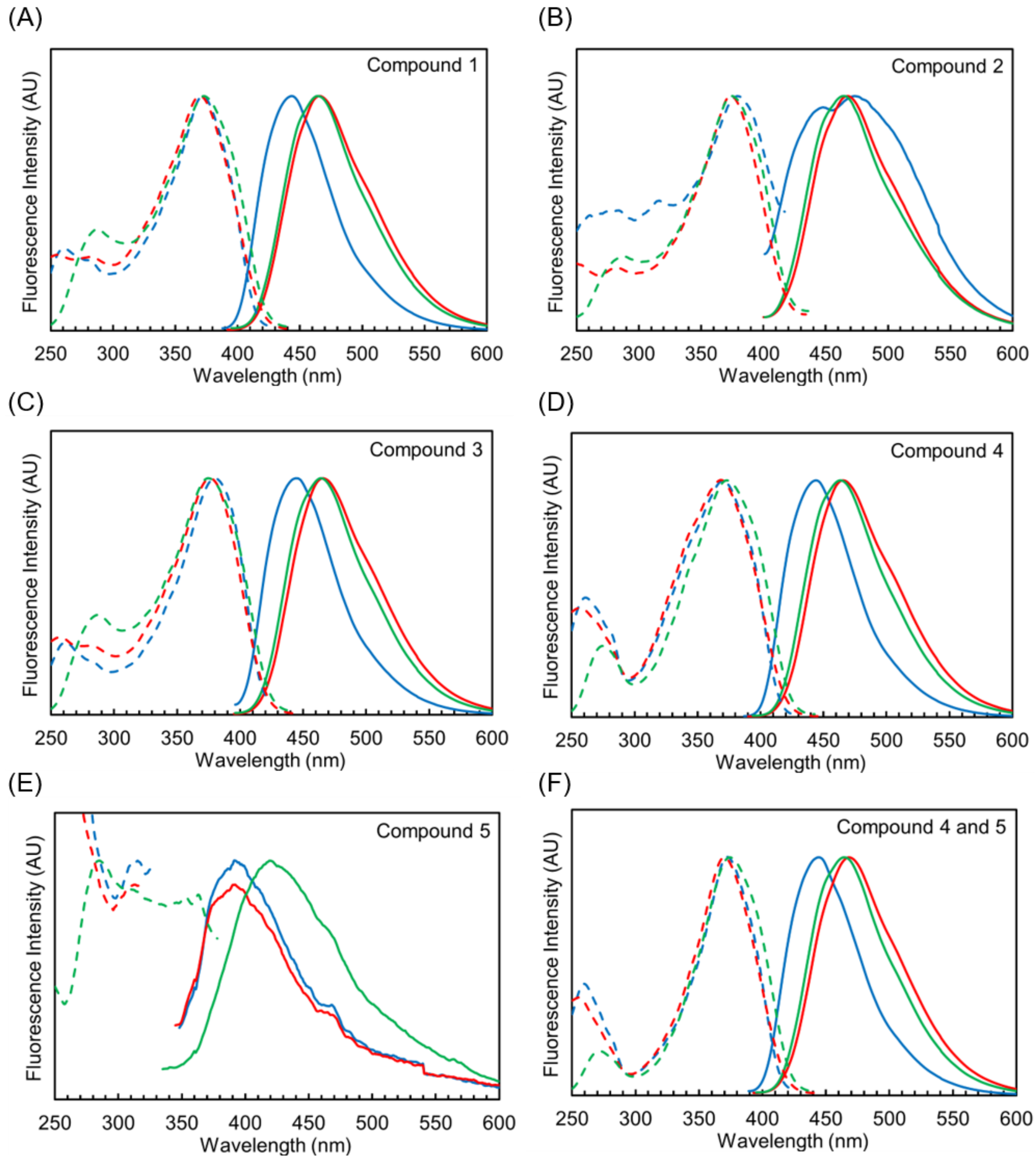

Fig. S2 Fluorescence (solid-line) and excitation (dot-line) spectra of **1** (A), **2** (B), **3** (C), **4** (D), **5** (E), and the equimolar mixture of **4** and **5** (F) in CH_3OH (red), $CHCl_3$ (blue), and DMSO (green).

3. Phosphorescence spectra

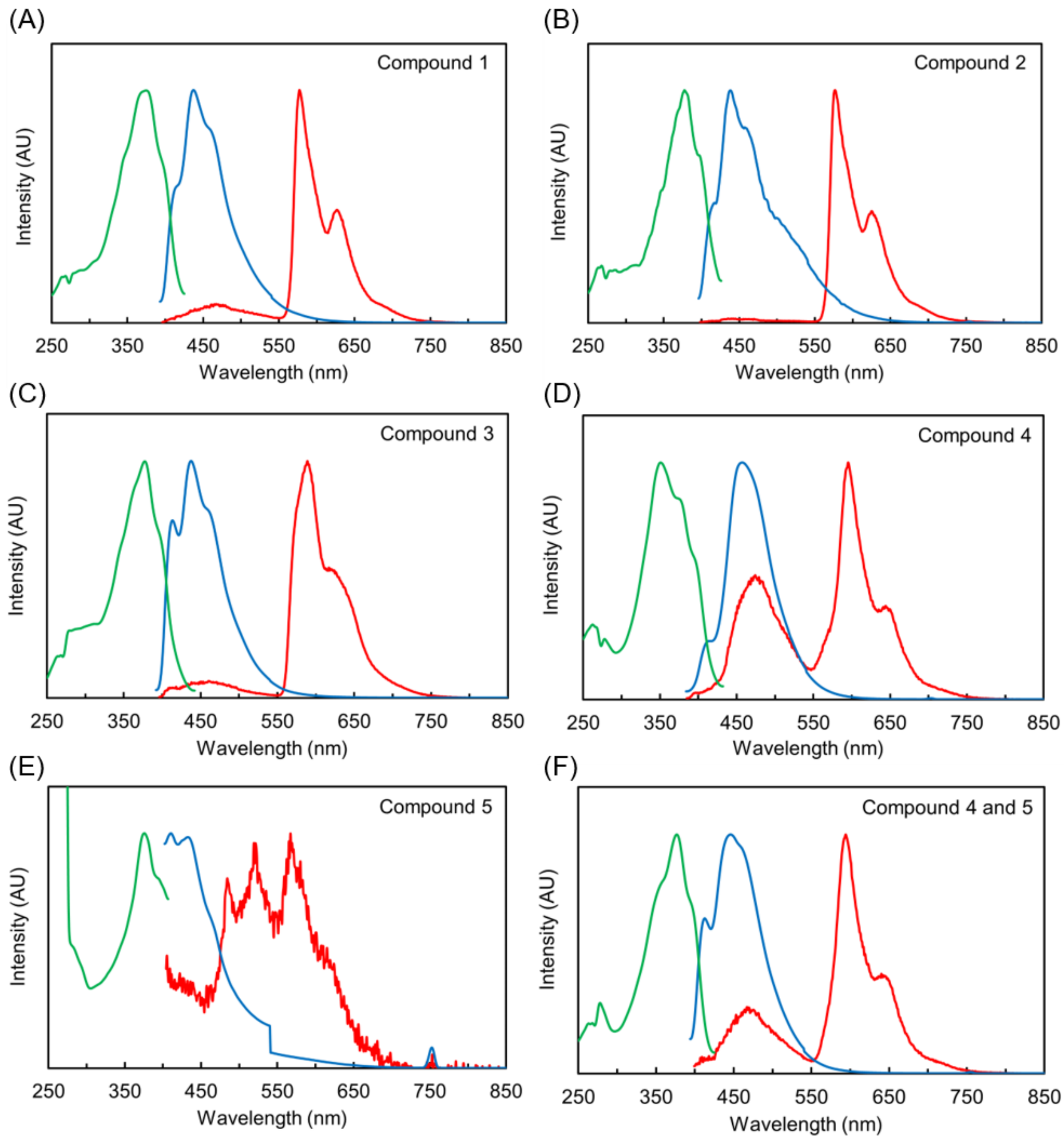

Fig. S3 Phosphorescence (red), fluorescence (blue), and excitation (green) spectra of **1** (A), **2** (B), **3** (C), **4** (D), **5** (E), and the equimolar mixture of **4** and **5** (F) in toluene at 77 K.

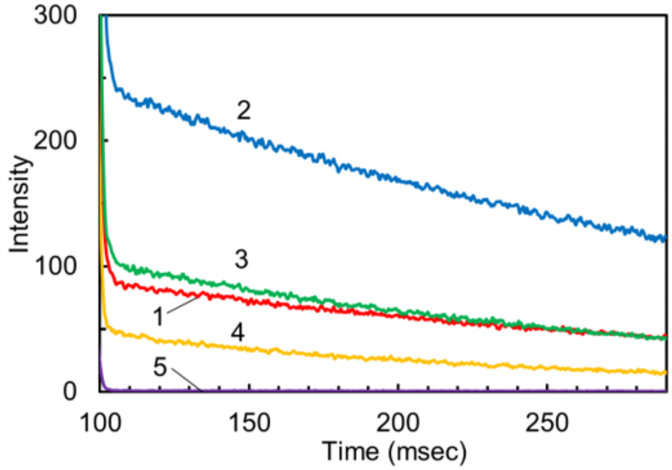

Fig. S4 Phosphorescence lifetimes of **1**-**5**. After 100 msec, the excitation light was shut off.

4. DFT calculations

The geometries of the ground states and excited states for **1-3** were optimized in CH_3OH by DFT and time-dependent DFT (TD-DFT) calculations with the Gaussian 09 program.[1] The calculations were performed with the CAM-B3LYP exchange-correlation functional under a 6-31G+(d) basis set.

Table S2 Geometrical parameters and total energies of optimized structures for S_0, neutral S_1, and zwitterionic S_1 of **1-3** calculated at the CAM-B3LYP/6-31G+(d) (solvent: CH_3OH). The calculations of **2** were performed on the models in which 1,1,3,3-tetramethylbutyl groups were replaced with *tert*-butyl groups.

Compd	Optimized structures	$\varphi_{\text{BTA-NI}}$ (°)[a]	$\varphi_{\text{BT-PH}}$ (°)[b]	C-N (Å)[c]	O-H (Å)[d]	N-H (Å)[e]	Total energies (hartree)
1	S_0	87.4	0.23	1.44	0.99	1.76	-1575.01637
	neutral S_1	87.9	0.35	1.43	0.99	1.76	-1574.89759
	zwitterionic S_1	85.0	11.2	1.43	1.99	1.02	-1574.89575
2	S_0	87.6	0.14	1.44	0.99	1.76	-1732.17643
	neutral S_1	87.0	0.16	1.44	0.99	1.76	-1732.05764
	zwitterionic S_1	86.7	13.7	1.43	2.02	1.02	-1732.05857
3	S_0	87.3	1.82	1.44	0.99	1.78	-1732.17562
	neutral S_1	87.0	1.09	1.44	0.99	1.78	-1732.05707
	zwitterionic S_1	88.6	15.6	1.44	2.01	1.03	-1732.05817

[a]Dihedral angles between the 2-(2-hydroxyphenyl)-2*H*-benzotoriazole and the 1,8-naphthalimide.
[b]Dihedral angles between the benzotriazole group and the phenyl group.
[c]Bond lengths between the carbon atom of the 2-(2-hydroxyphenyl)-2*H*-benzotoriazole and the nitrogen atom of the 1,8-naphthalimide.
[d]Bond lengths of the hydroxy group.
[e]Bond lengths between the nitrogen atom of the benzotriazole group and the hydrogen atom of the hydroxy group.

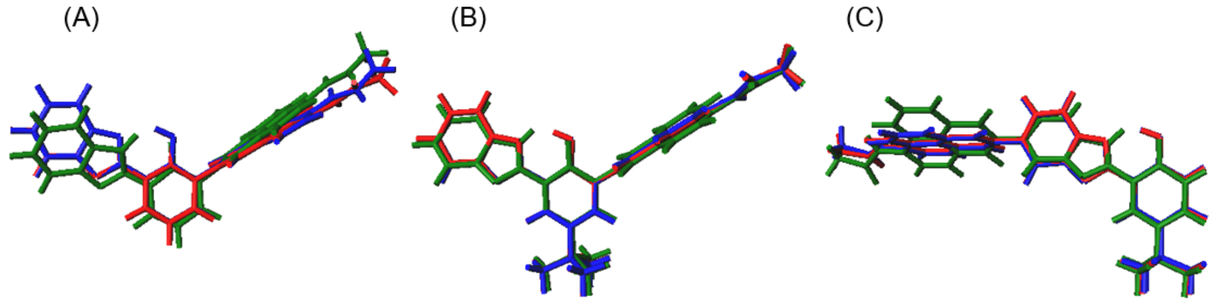

Fig. S5 Comparisons of the optimized structures of the S_0 (red), the neutral S_1 (blue), and the zwitterionic S_1 (green) for **1** (A), **2** (B), and **3** (C) calculated at the CAM-B3LYP/6-31G+(d) (solvent: CH_3OH). The calculations of **2** were performed on the models in which 1,1,3,3-tetramethylbutyl groups were replaced with *tert*-butyl groups.

5. Properties of PMMA Films

Table S3 Optical properties of **1-5** and the equimolar mixture of **4** and **5** in PMMA films[a].

Compd	λ_{abs} (nm)	λ_F (nm)	λ_{EX} (nm)	Stokes shift (cm^{-1})	Φ_F (%)
1	340	449	375	4400	32.7
2	349	475	403	3760	17.9
3	361	450	389	3490	19.6
4	370	447	370	4660	51.2
5	333	394	305	7410	0.1
4 and **5**	339	445	376	4120	58.6

[a]2.5 wr% doped films.

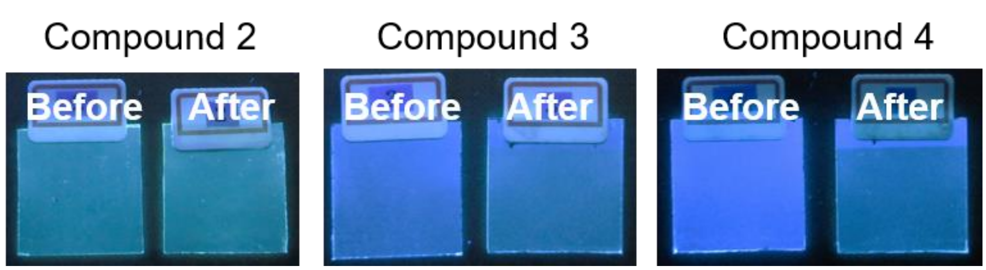

Fig. S6 The photographs under UV light (365nm) of PMMA films doped with **2-4** before and after simulated solar light irradiation.

6. NMR and MS spectra

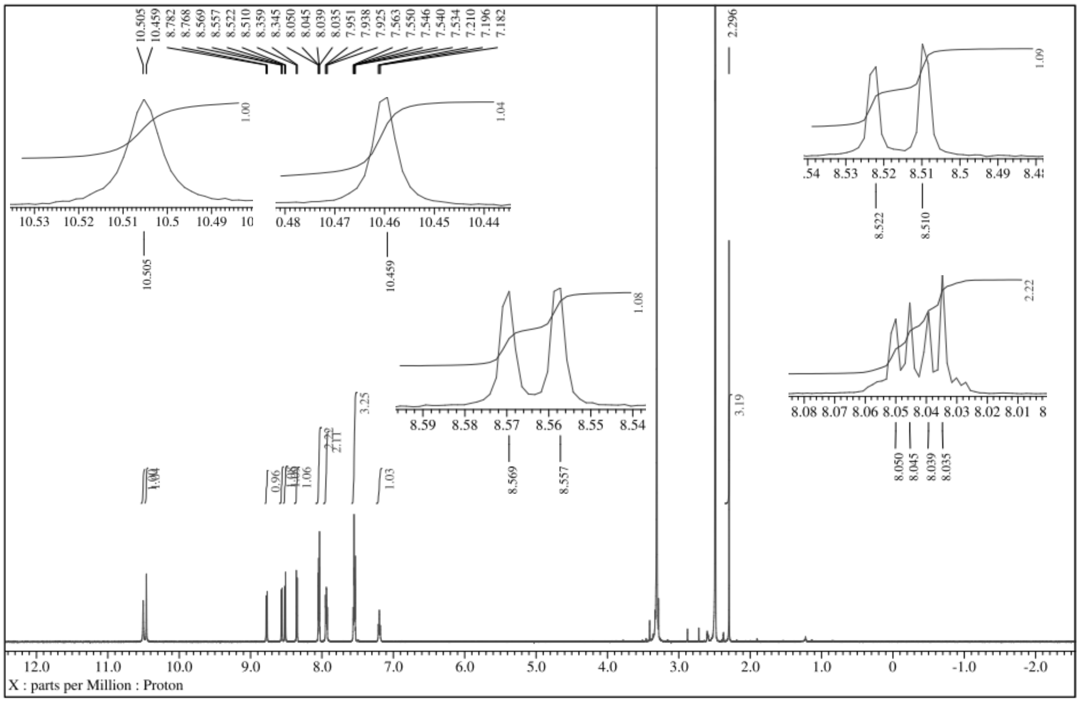

Fig. S7 [1]H NMR spectra of **1** (600 MHz, DMSO-d_6, 298K).

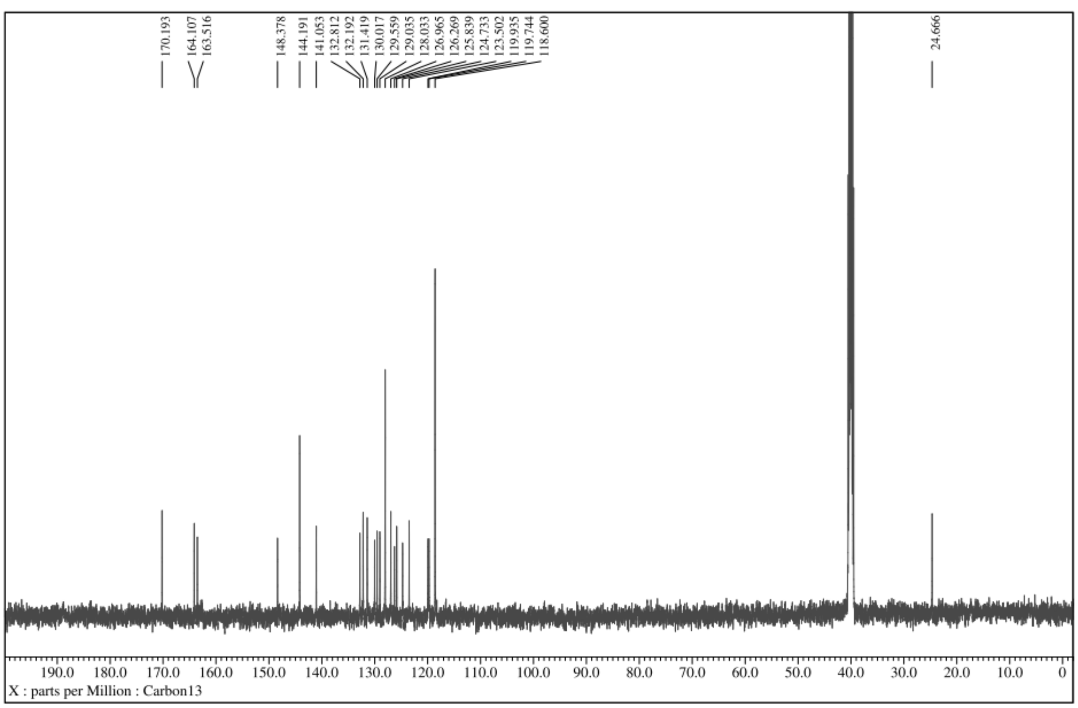

Fig. S8 [13]C NMR spectra of **1** (125 MHz, DMSO-d_6, 298K).

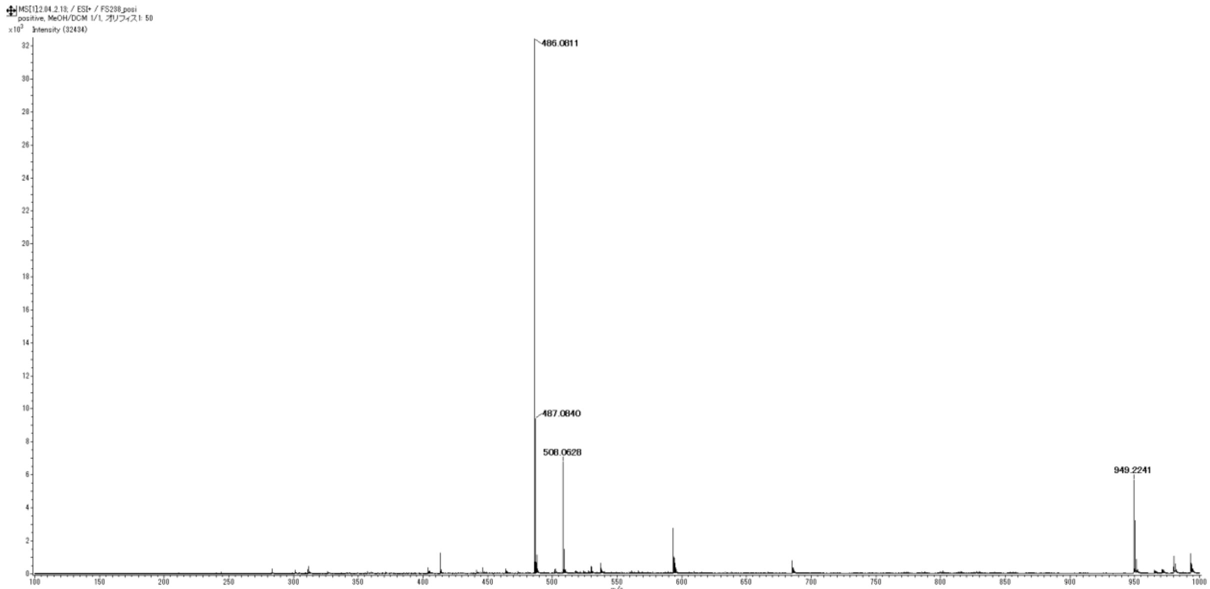

Fig. S9 ESI MS-spectra for **1**.

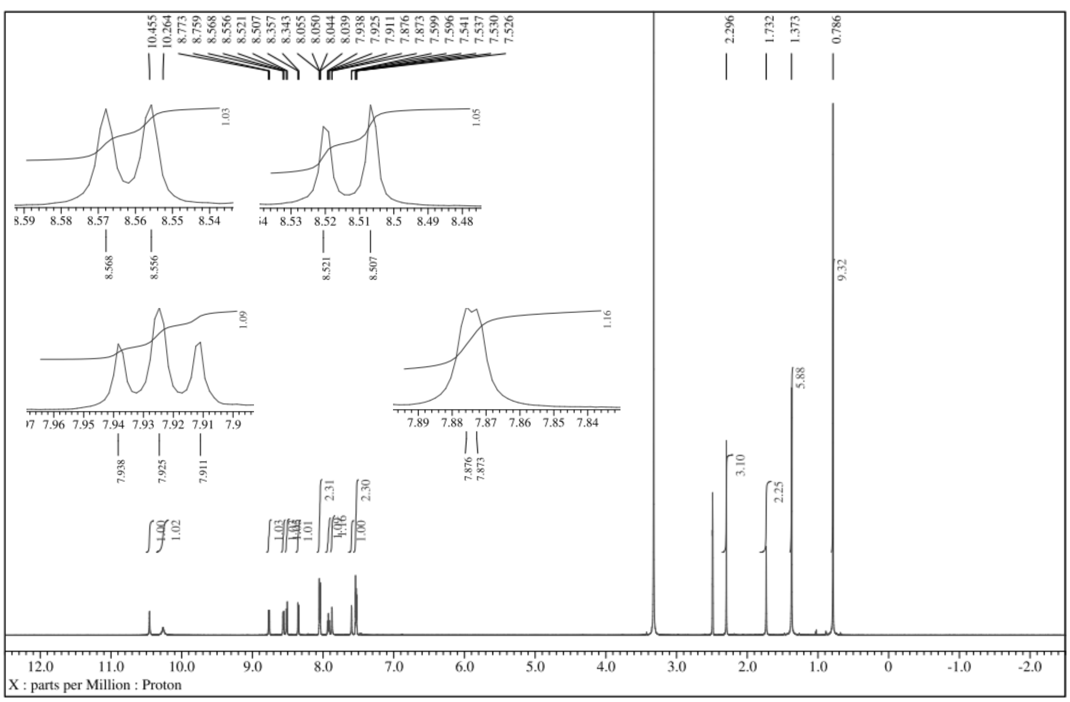

Fig. S10 ^{1}H NMR spectra of **2** (600 MHz, DMSO-d_6, 298K).

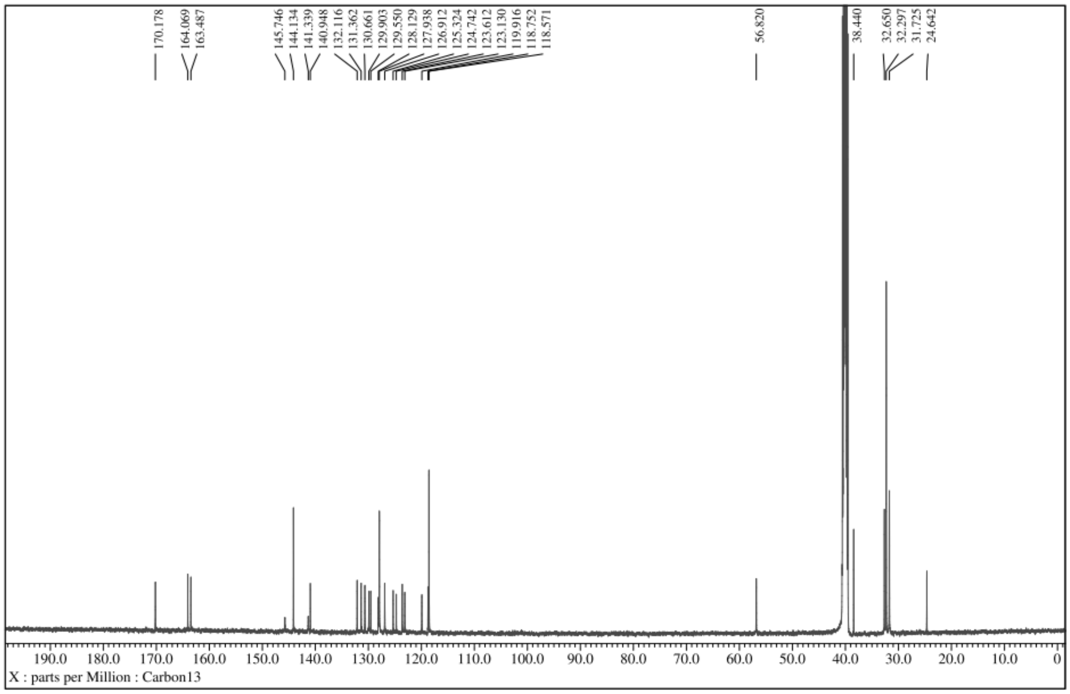

Fig. S11 ^{13}C NMR spectra of **2** (125 MHz, DMSO-d_6, 298K).

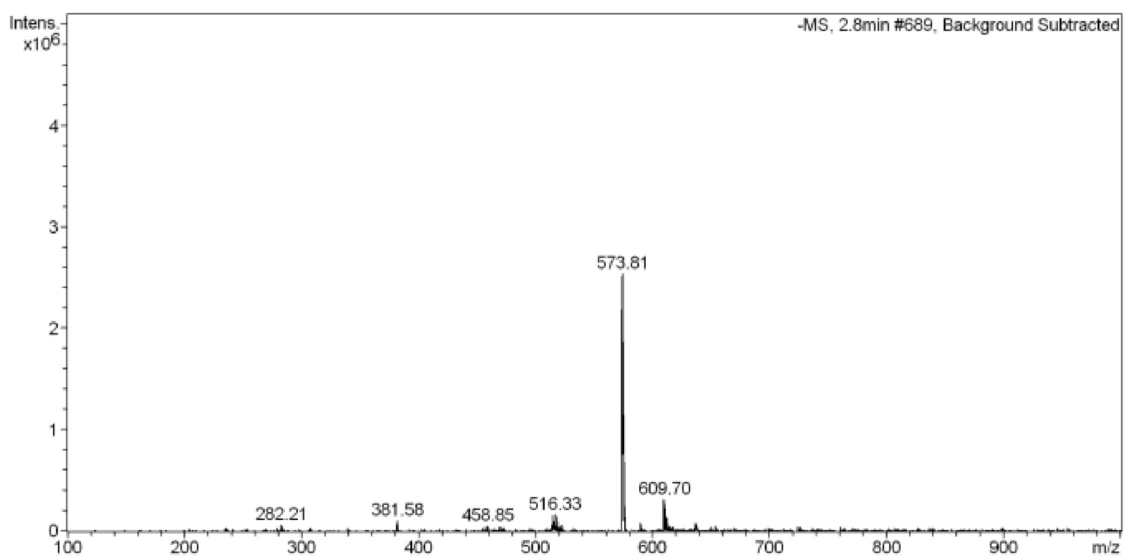

Fig. S12 ESI MS-spectra for **2**.

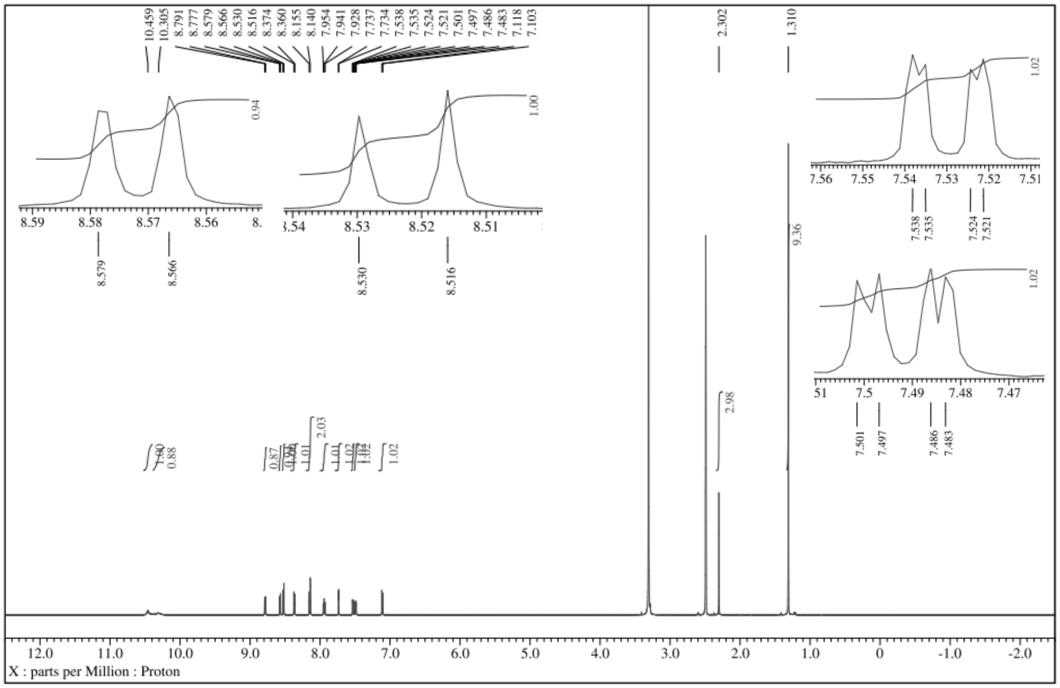

Fig. S13 ^{1}H NMR spectra of **3** (600 MHz, DMSO-d_6, 298K).

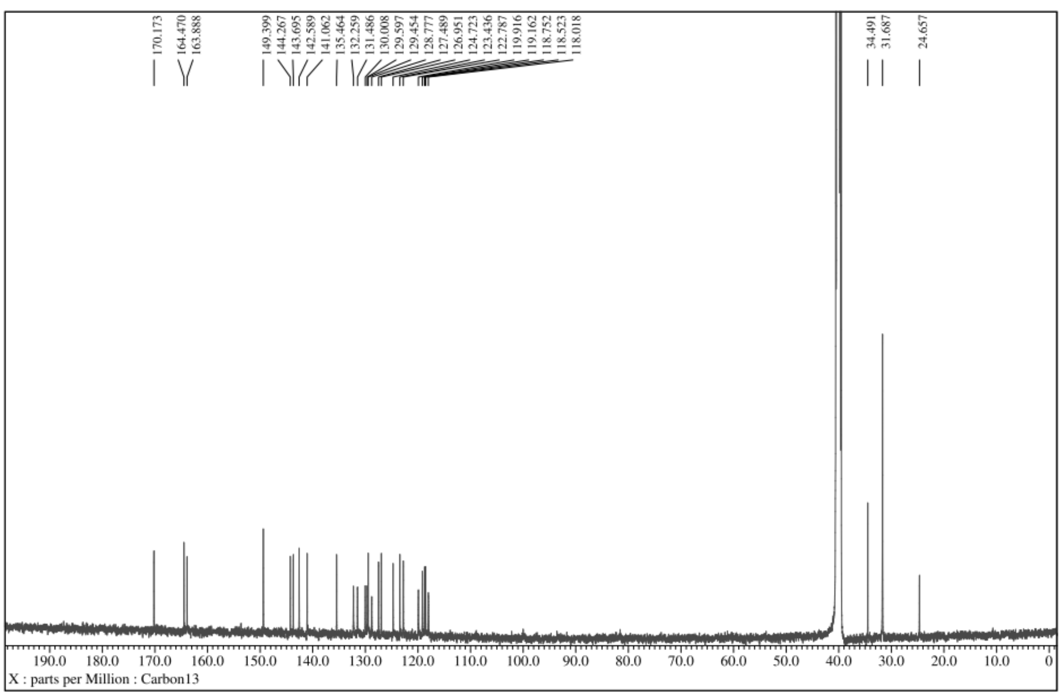

Fig. S14 ^{13}C NMR spectra of **3** (125 MHz, DMSO-d_6, 298K).

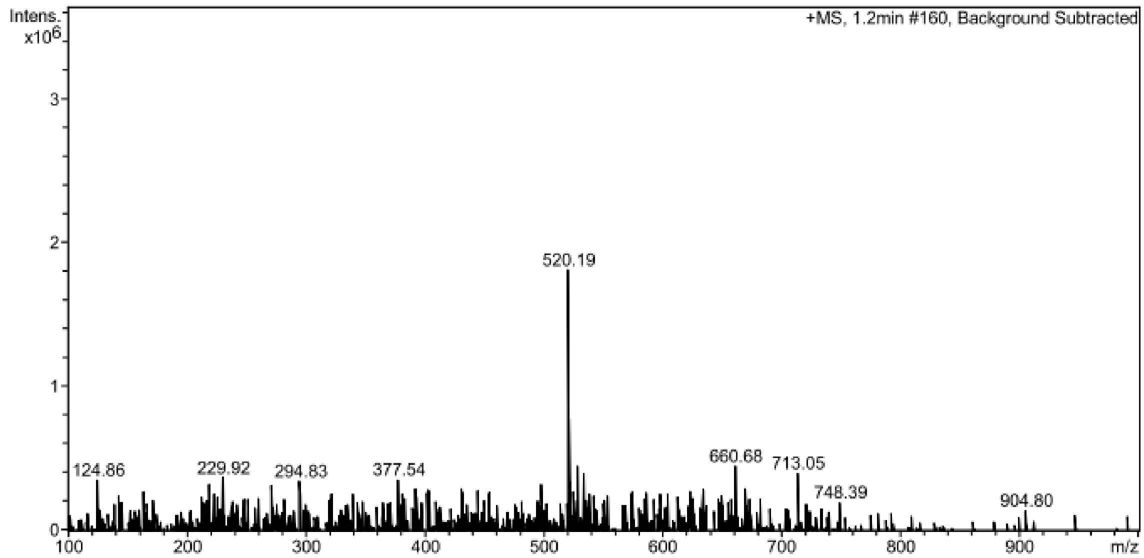

Fig. S15 ESI MS-spectra for **3**.

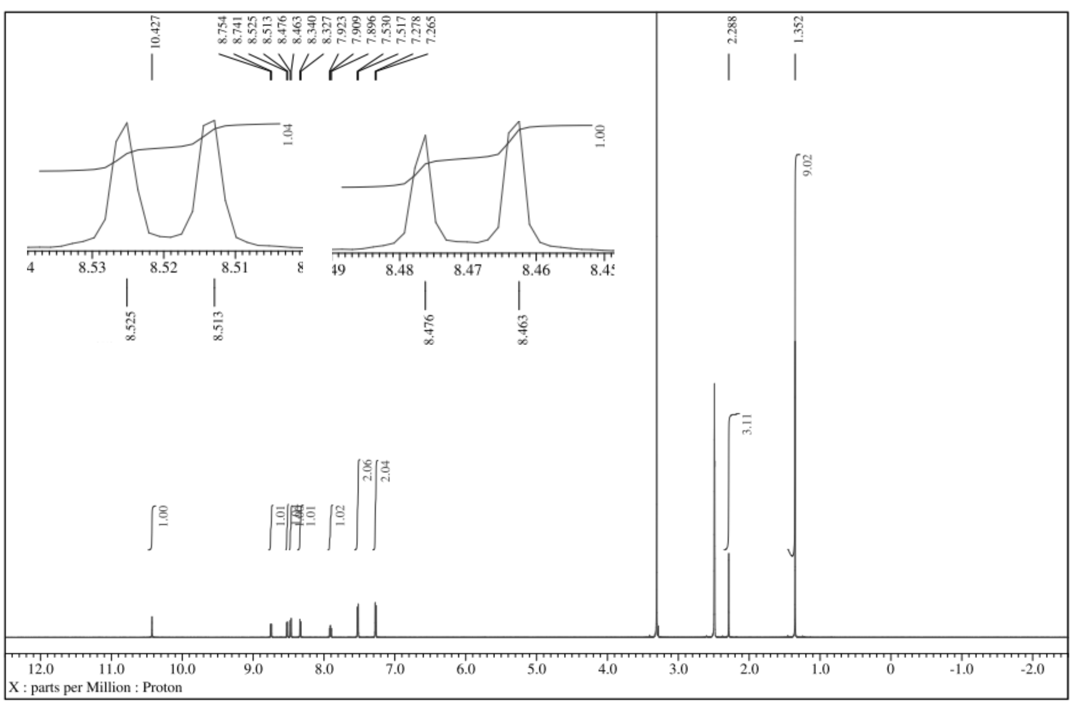

Fig. S16 [1]H NMR spectra of **4** (600 MHz, DMSO-d_6, 298K).

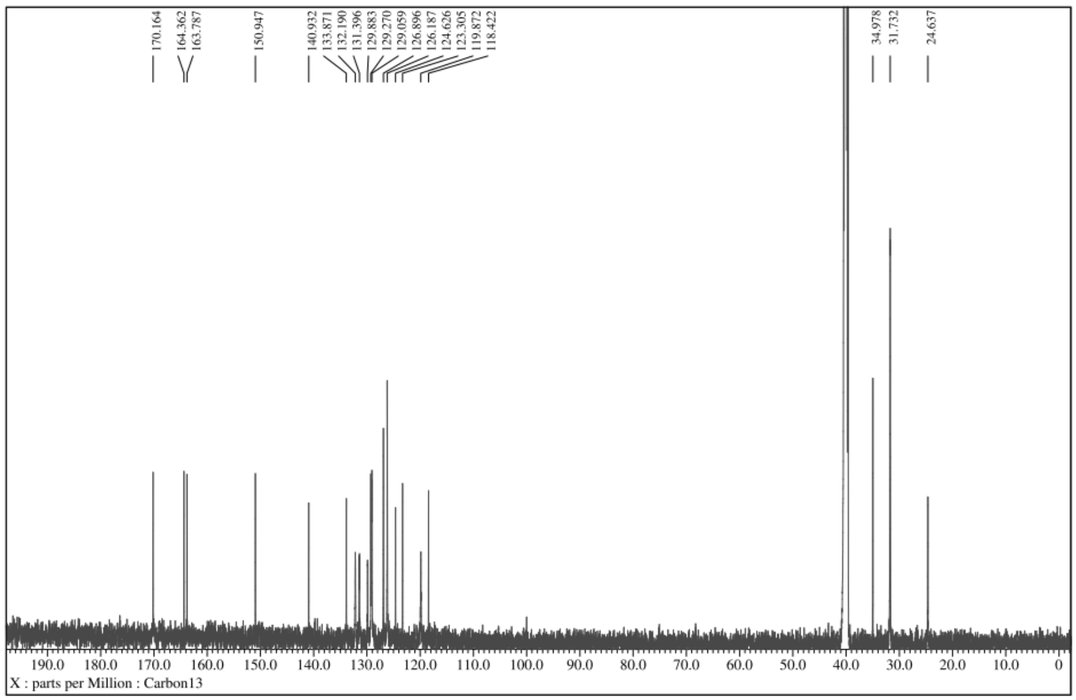

Fig. S17 ^{13}C NMR spectra of **4** (150 MHz, DMSO-d_6, 298K).

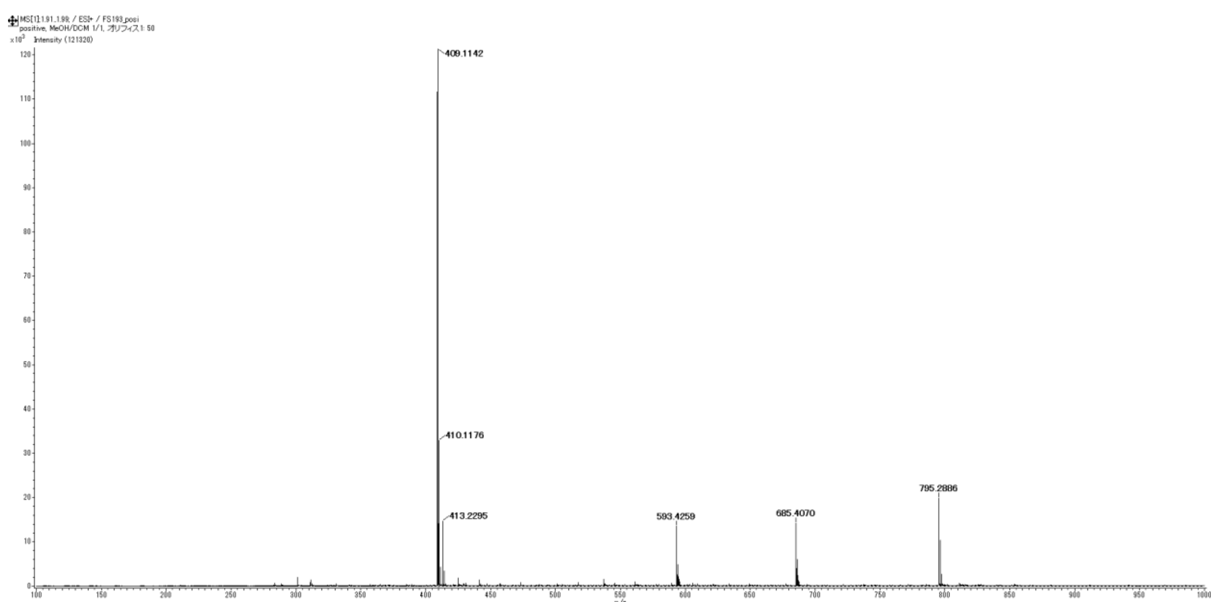

Fig. S18 ESI MS-spectra for **4**.

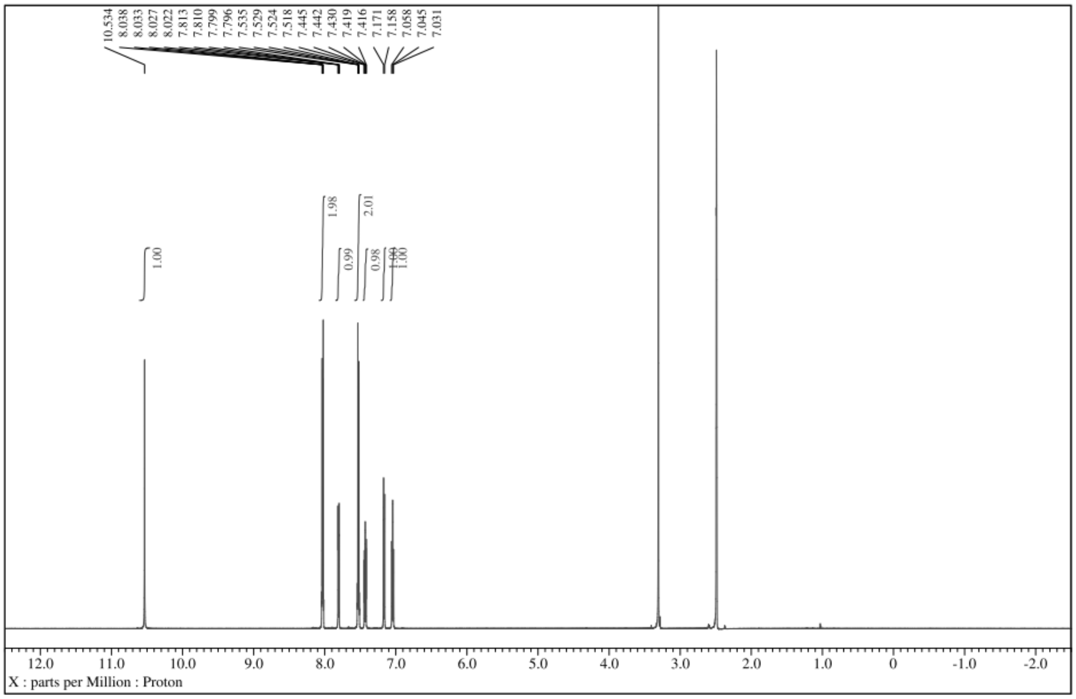

Fig. S19 ^{1}H NMR spectra of **5** (600 MHz, DMSO-d_6, 298K).

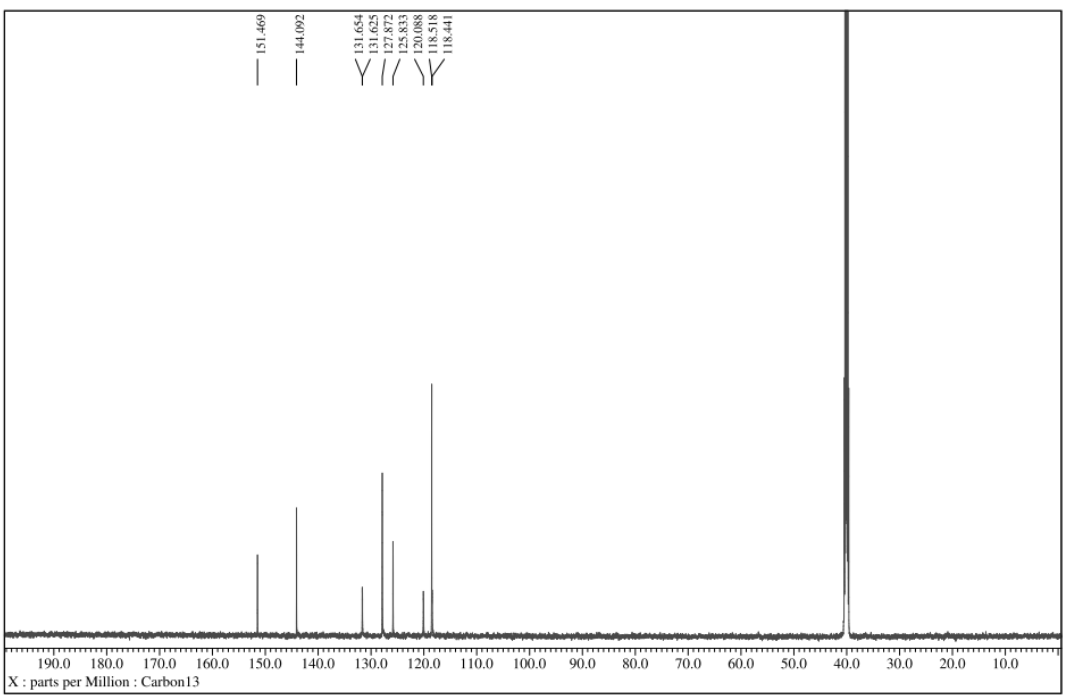

Fig. S20 ^{13}C NMR spectra of **5** (150 MHz, DMSO-d_6, 298K).

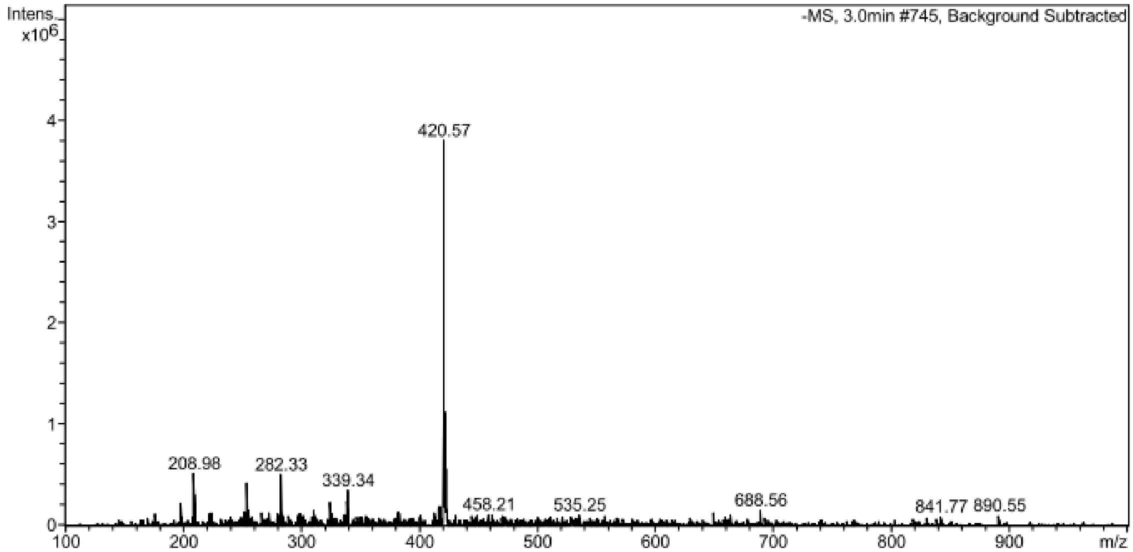

Fig. S21 ESI MS-spectra for **5**.

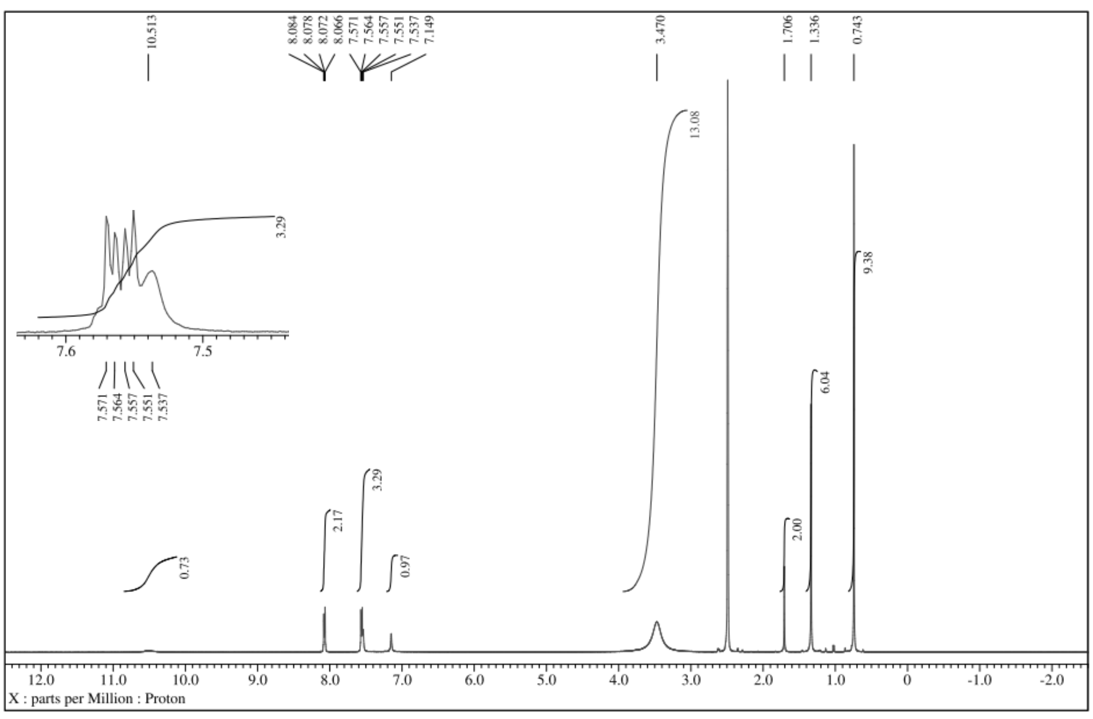

Fig. S22 ^{1}H NMR spectra of **6** (500 MHz, DMSO-d_6, 298K).

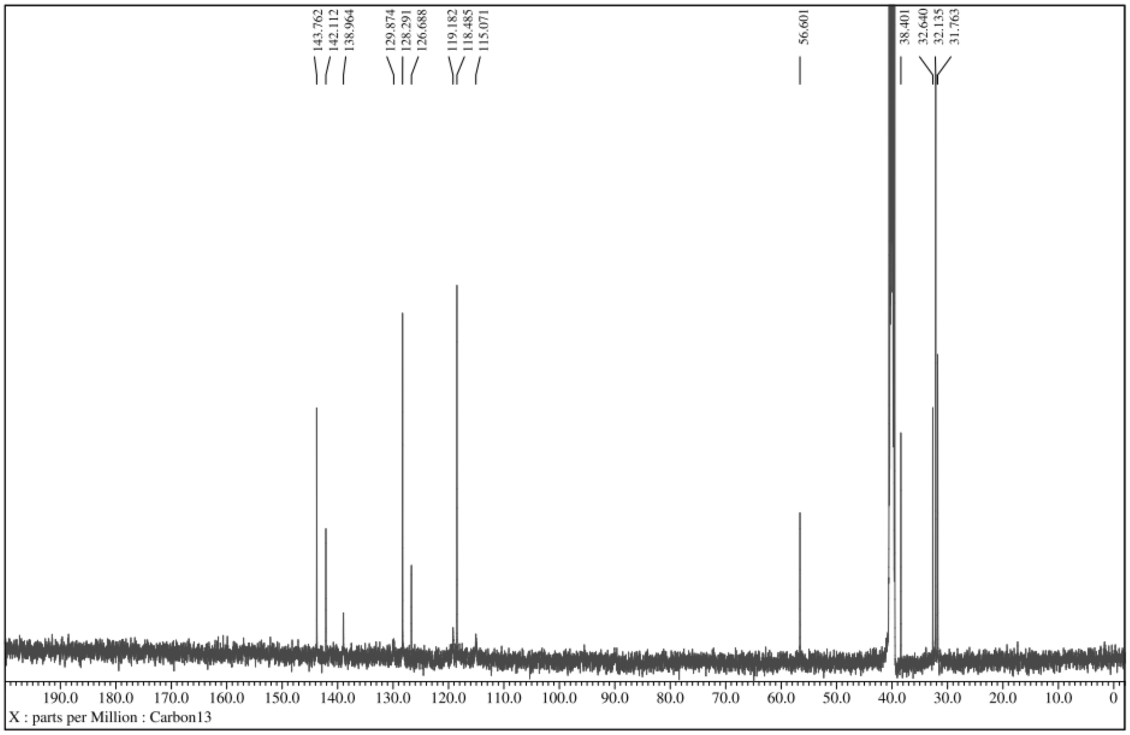

Fig. S23 ^{13}C NMR spectra of **6** (125 MHz, DMSO-d_6, 298K).

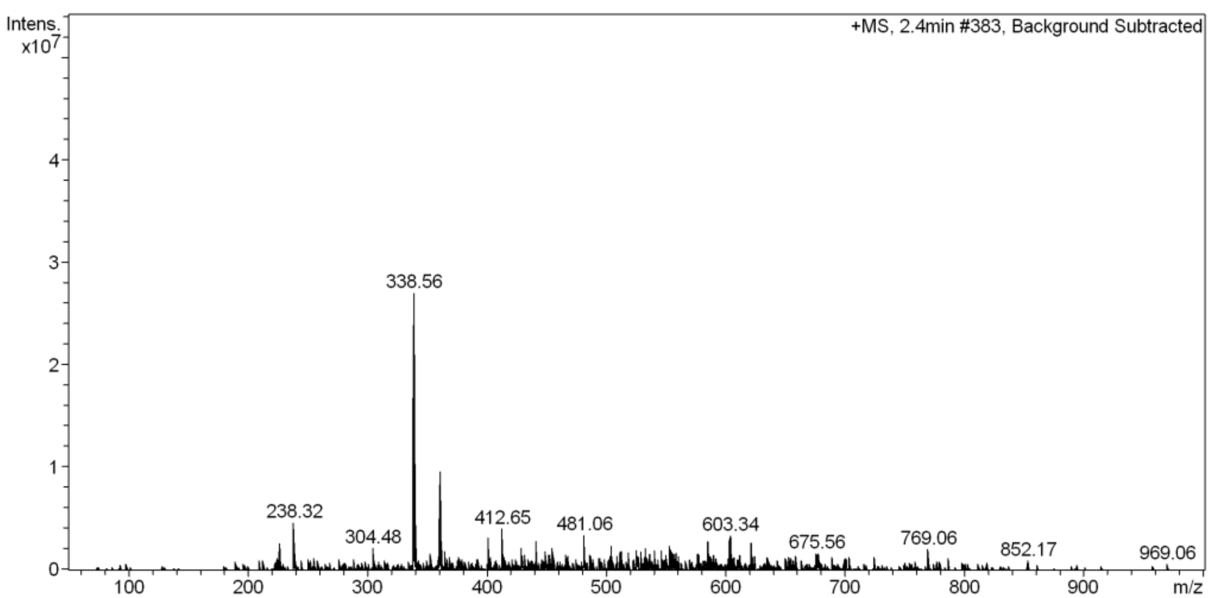

Fig. S24 ESI MS-spectra for **6**.

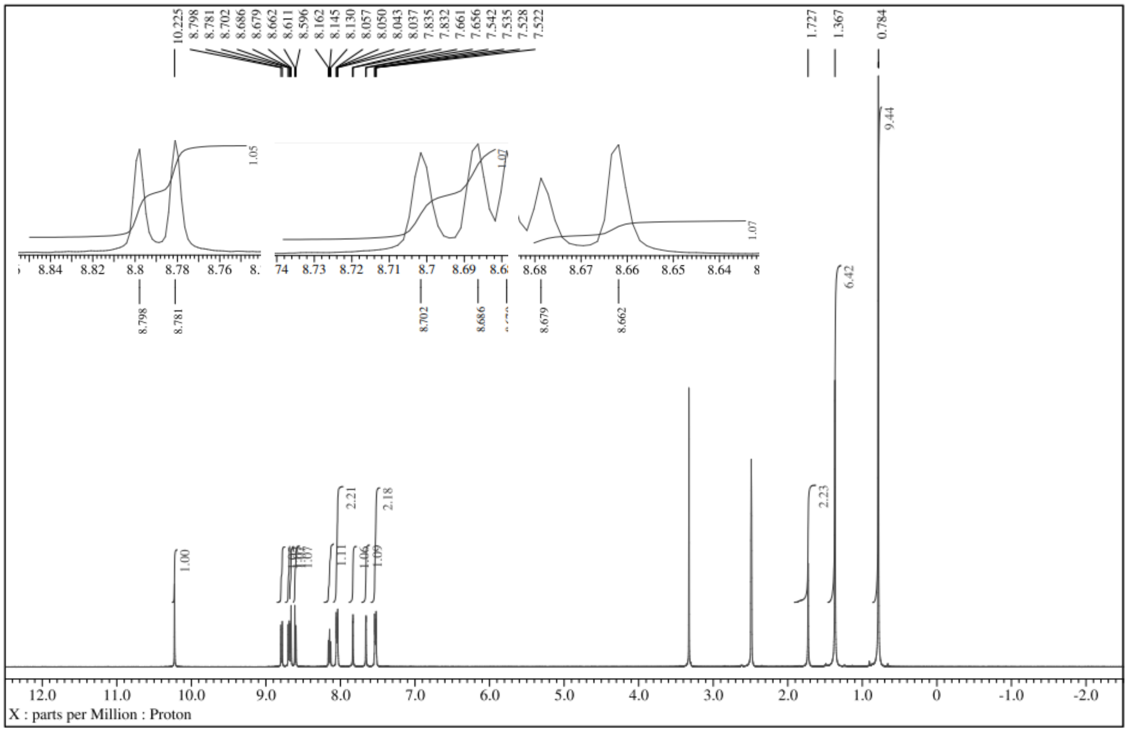

Fig. S25 [1]H NMR spectra of **7** (500 MHz, DMSO-d$_6$, 298K).

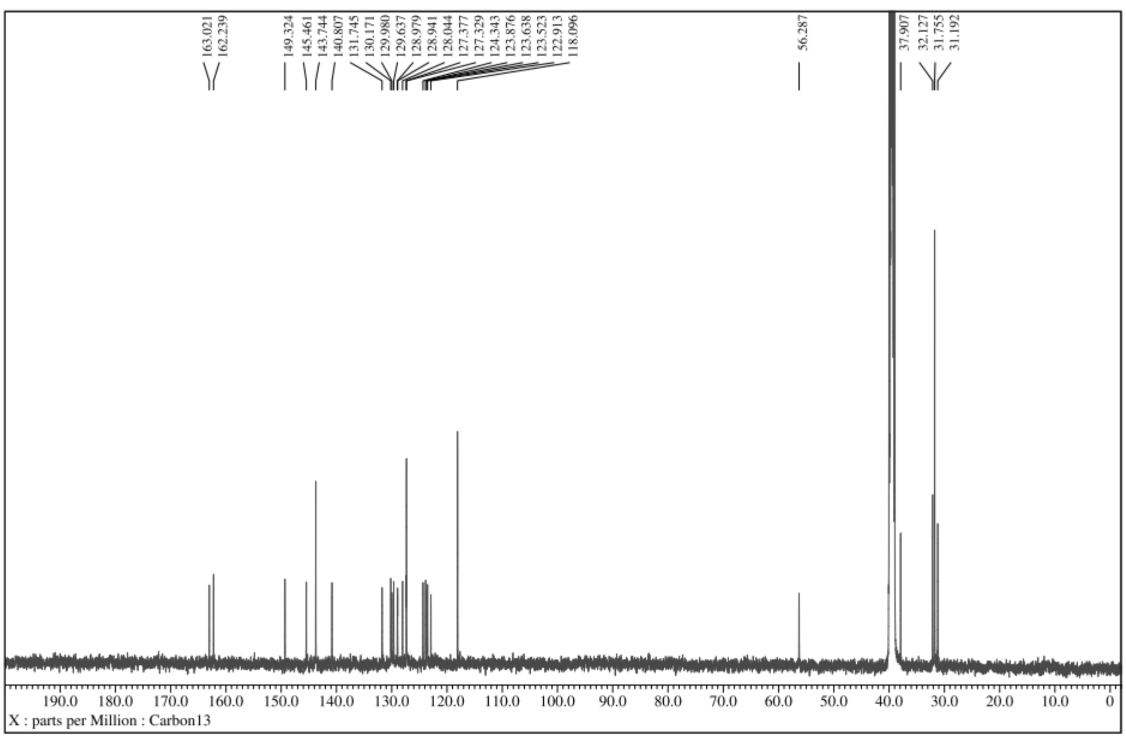

Fig. S26 ^{13}C NMR spectra of **7** (125 MHz, DMSO-d_6, 298K).

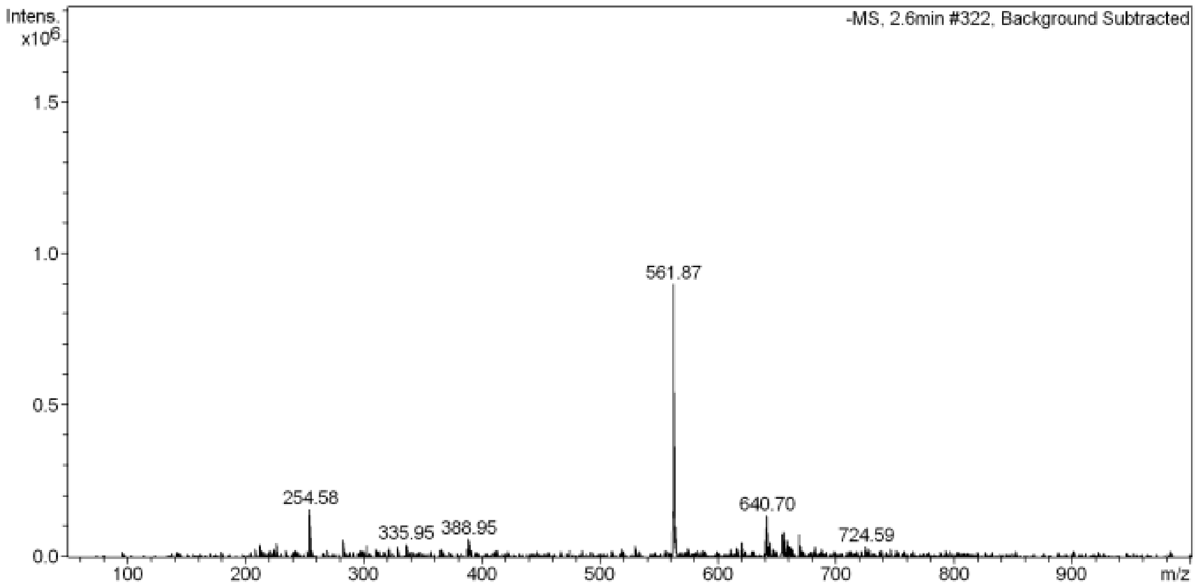

Fig. S27 ESI MS-spectra for **7**.

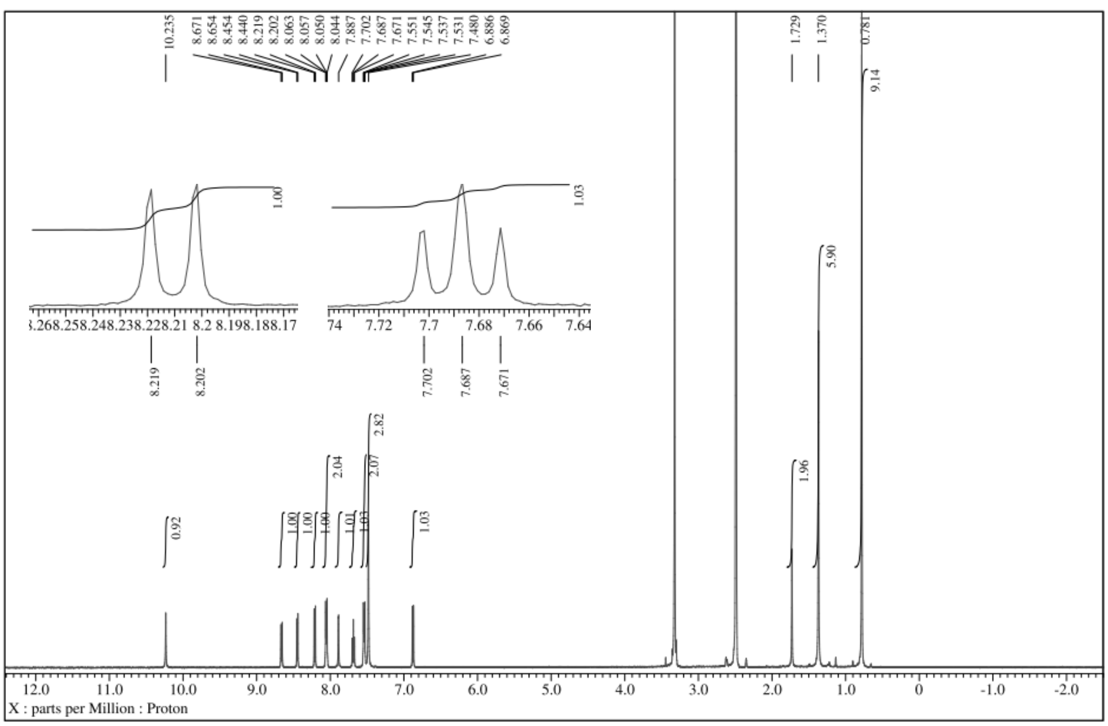

Fig. S28 ^{1}H NMR spectra of **8** (500 MHz, DMSO-d_6, 298K).

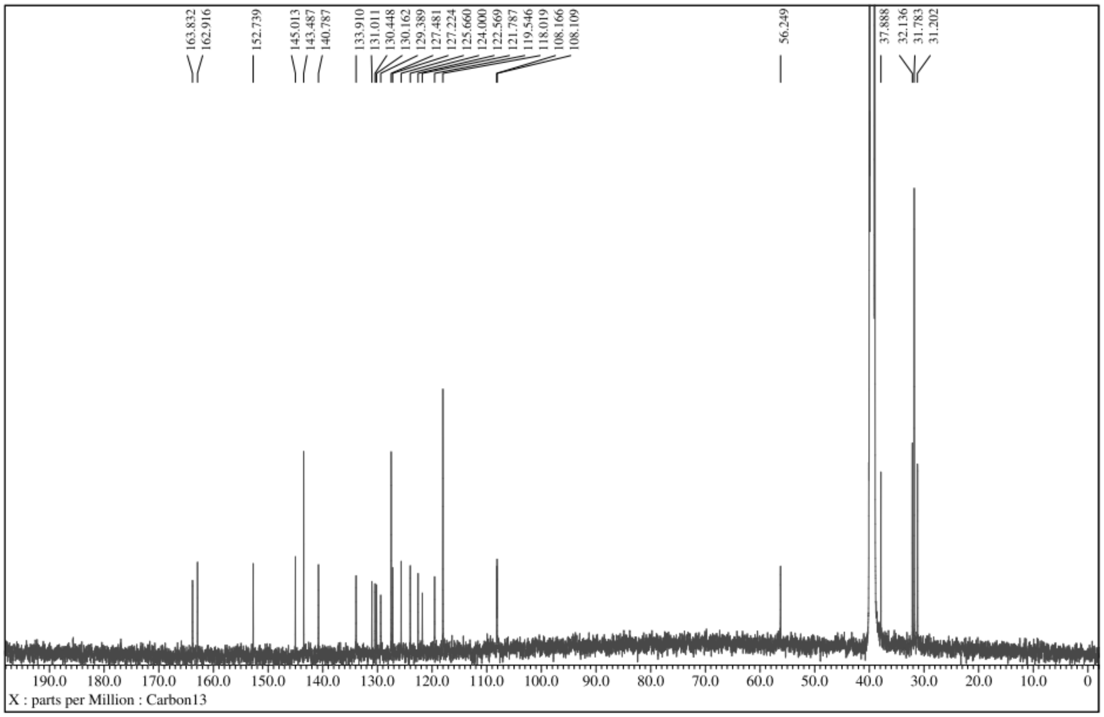

Fig. S29 ^{13}C NMR spectra of **8** (125 MHz, DMSO-d_6, 298K).

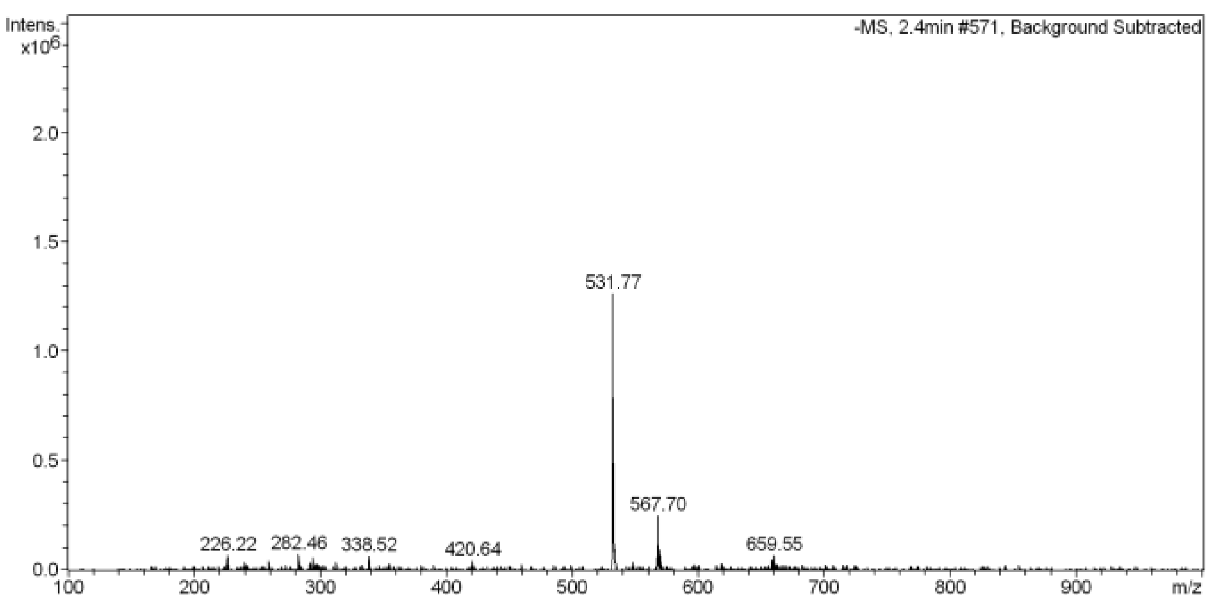

Fig. S30 ESI MS-spectra for **8**.

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