D-A-D type chromophores with aggregation-induced emission and two-photon absorption: synthesis, optical characteristics and cell imaging

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Content

1. Tables and Figures for OPEF

Table S1 The one-photon optical data of **1**, **2,** and **3** in various solvents [a]

		1					**2**					**3**				
solvent	Δf	λ_{ab}(nm)	λ_{em}(nm)	$\Delta\nu/10^3$ (cm^{-1})	Φ_f(%)	τ (ns)	λ_{ab}(nm)	λ_{em}(nm)	$\Delta\nu/10^3$ (cm^{-1})	Φ_f(%)	τ (ns)	λ_{ab}(nm)	λ_{em}(nm)	$\Delta\nu/10^3$ (cm^{-1})	Φ_f(%)	τ (ns)
HEX	~ 0	415	488	3.65	2.9	0.86354	n.d.	n.d.	N/A	n.d.	n.d.	407	467	3.2	1.0	0.54778
TOL	0.014	418	553	5.91	4.0	1.25964	429	584	6.18	4.1	1.31737	402	494	4.63	1.1	0.60814
EtOAc	0.201	418	590	7.00	3.9	1.22795	425	604	6.95	2.0	0.77832	399	514	5.2	1.1	0.61221
THF	0.210	420	592	7.09	4.1	1.23467	430	611	6.89	2.0	0.74315	401	516	5.65	0.8	0.62329
DCM	0.218	426	611	7.13	2.5	0.93382	430	609	6.84	1.1	0.68217	397	528	5.87	0.8	0.75276
DMF	0.275	428	617	7.18	1.0	0.61353	431	604	6.59	0.7	0.61537	399	547	6.94	1.1	0.71406
AN	0.306	421	626	7.75	0.6	0.59633	422	615	7.44	0.5	0.60274	394	554	6.91	1.0	0.66786

[a] Abbreviations: λ_{ab}= absorption maximum, λ_{em} = emission maximum, Δν = Stock's shift in cm^{-1}, Φ_F = fluorescence quantum yield, τ = fluorescence lifetime, and n.d. = not detected.

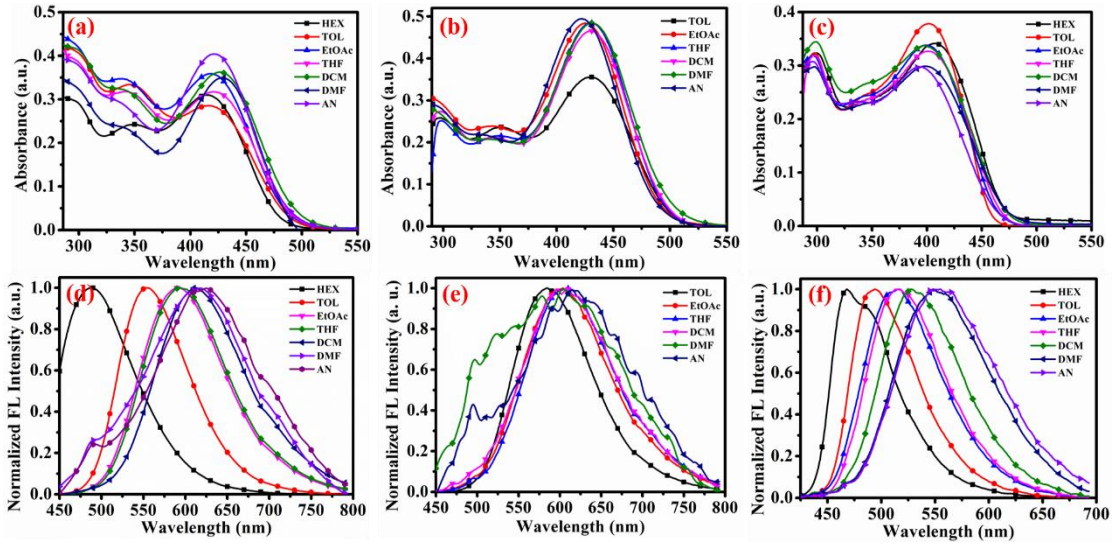

Figure S1 One-photon absorption spectra and excited fluorescence of **1** (a, d), **2** (b, e), and **3** (c, f) in various solvents with different polarity. *Concentration* = 10 μM.

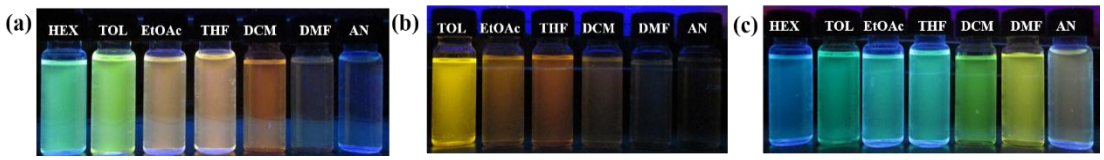

Figure S2 Photographs of **1** (a), **2** (b), and **3** (c) taken under UV 365 nm illumination in different solvents labeled on the top of the bottle. *Concentration* = 10 μM.

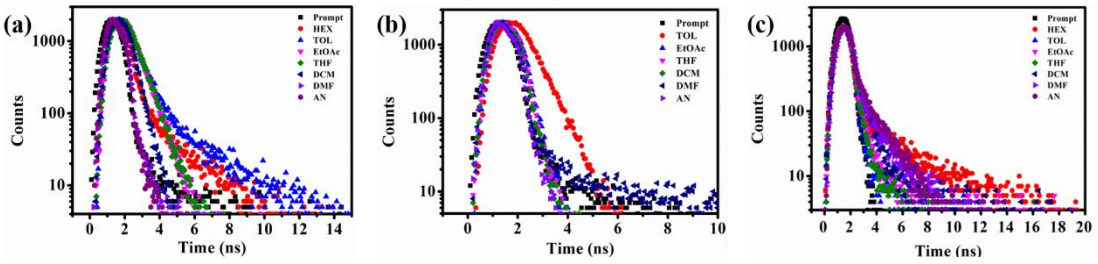

Figure S3 Fluorescence decay curves of **1** (a), **2** (b), and **3** (c) in different solvents. *Concentration* = 10 μM.

Table S2 The k_f and k_{nr} for **1**, **2** and **3** in different solvents.

Solvent	**1**		**2**		**3**	
	k_f	k_{nr}	k_f	k_{nr}	k_f	k_{nr}
HEX	0.0336	1.124	N/A	N/A	0.0183	1.807
TOL	0.0318	0.762	0.0311	0.728	0.0181	1.626
EtOAc	0.0318	0.783	0.0257	1.259	0.0180	1.615
THF	0.0332	0.777	0.0269	1.319	0.0128	1.592
DCM	0.0268	1.044	0.0161	1.450	0.0106	1.318
DMF	0.0163	1.614	0.0114	1.614	0.0154	1.185
AN	0.0101	1.667	0.0083	1.651	0.0150	1.482

k_f and k_{nr} represent radiative rate and non-radiative rate, respectively.

2. Tables and Figures for theoretical calculations

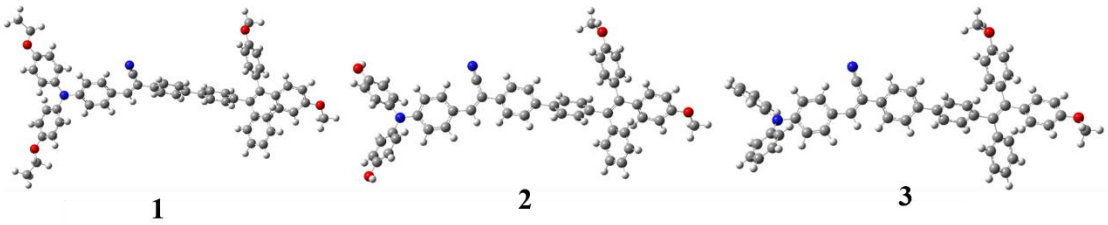

Figure S4 Optimized structures of **1**, **2,** and **3**, respectively. The planarity of the three conformations are sequenced as **3** > **2** > **1**.

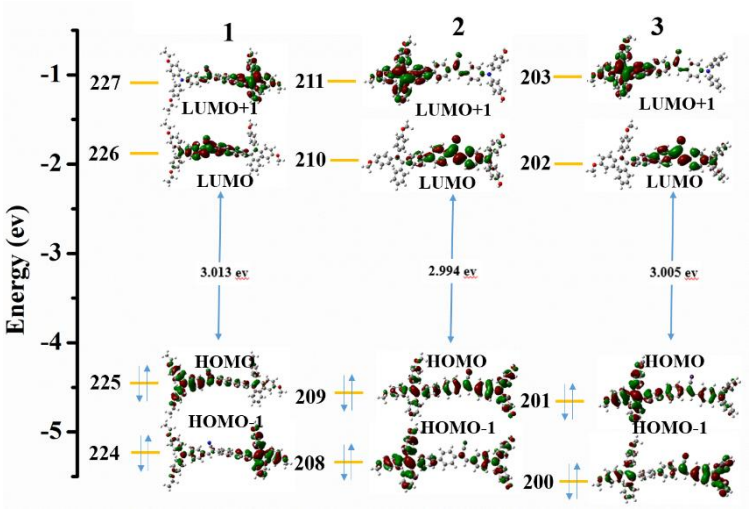

Figure S5 Electron cloud distributions and molecular orbital energy diagrams of **1** ~ **3**.

Table S3 Experimental and calculated optical data for chromophores **1**, **2**, and **3**.

Compd	Transitions (S. no.)	OI[a] (Tc)[b]	E^c (eV)	Cal. λmax[d] (nm)	Obs. λmax[d] (nm)	Character
	1	225 (H) → 226 (L)	3.013	415	429	π → π* (ICT)
TPEOM-1	2	224 (H-1) → 226 (L)	3.664	338	346	π → π* (ICT)
	3	224 (H-1) → 227 (L+1)	3.855	302	294	π → π*
	1	209 (H) → 210 (L)	2.994	415	429	π → π* (ICT)
TPEOM-2	2	208 (H-1) → 210 (L)	3.747	331	351	π → π* (ICT)
	3	207 (H-1) → 211 (L+1)	3.901	306	296	π → π*
	1	201 (H) → 202 (L)	3.005	413	402	π → π* (ICT)
TPEOM-3	2	200 (H-1) → 202 (L)	3.770	329	345	π → π* (ICT)
	3	200 (H-1) → 203 (L+1)	3.980	312	298	π → π*

(a) Orbitals involved in the excitations; (b) Transition coefficients; (c) Excitation energies (eV); (d) Calculated peak position of the longest absorption; (e) Observed peak position of the longest absorption.

3. Tables and Figures for AIE

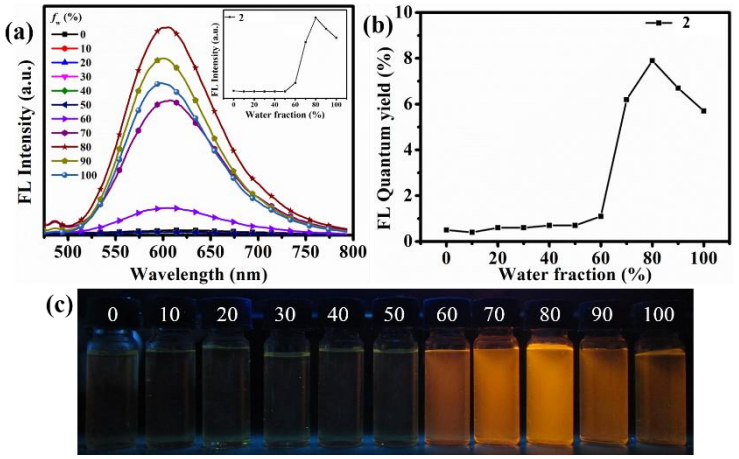

Figure S6 (a) FL spectra of **2** in the AN/Water mixtures, λ_{ex} = 420 nm; (b) Plots of FL quantum yield *vs* water fraction; (c) Photographs taken under UV 365 nm illumination, the number labeled on the top of the bottle represent the water fraction (%). Inset: The FL intensity as a function *vs* the water fraction. *Concentration* = 10 μM.

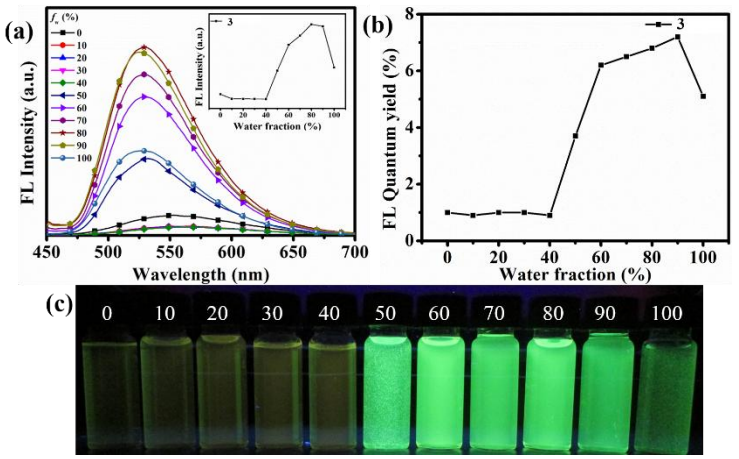

Figure S7 (a) FL spectra of **3** in the AN/Water mixtures, λ_{ex} = 420 nm; (b) Plots of FL quantum yield *vs* water fraction; (c) Photographs taken under UV 365 nm illumination, the number labeled on the top of the bottle represent the water fraction (%). Inset: The FL intensity as a function *vs* the water fraction. *Concentration* = 10 μM.

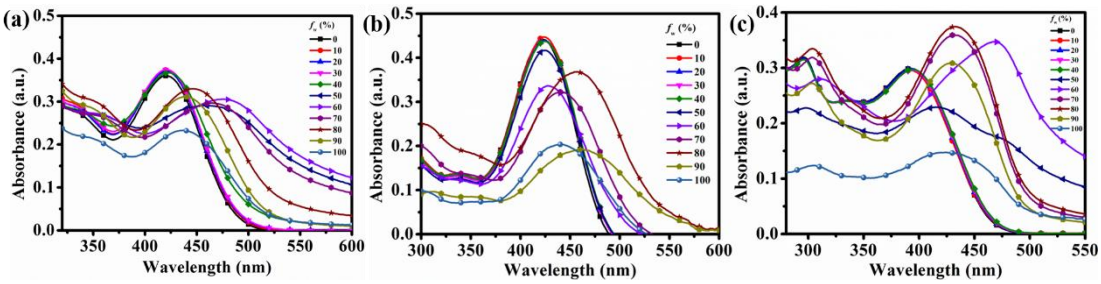

Figure S8 UV-Vis spectra of **1** (a), **2** (b), and **3** (c) in the AN/water mixtures with different water fractions, *Concentration* = 10 μM.

Table S4 Average diameter and PDI of the chromophores in AN/water mixtures with different water fraction[a]

f_w(%)	**1**		**2**		**3**	
	d (nm)	PDI	*d* (nm)	PDI	*d* (nm)	PDI
60	579.8	0.098	211.4	0.089	360.6	0.037
80	303.4	0.254	507.2	0.005	289.4	0.006
100	1533.8	0.367	2626.7	0.526	176.5	0.345

[a] Abbreviations: *d* = average diameter, PDI = polydispersity index

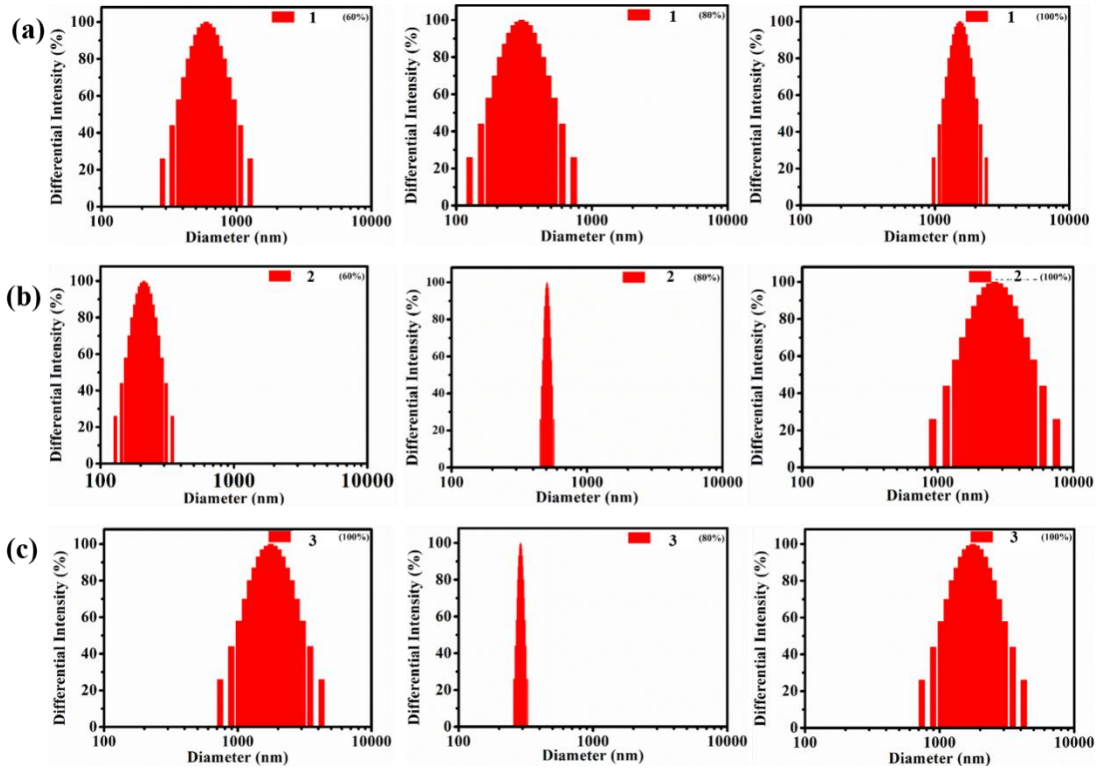

Figure S9 Particle size distributions of **1** (a), **2** (b) and **3** (c) in AN/water mixtures with f_w = 60%, 80% and 100%. *Concentration* = 10 μM.

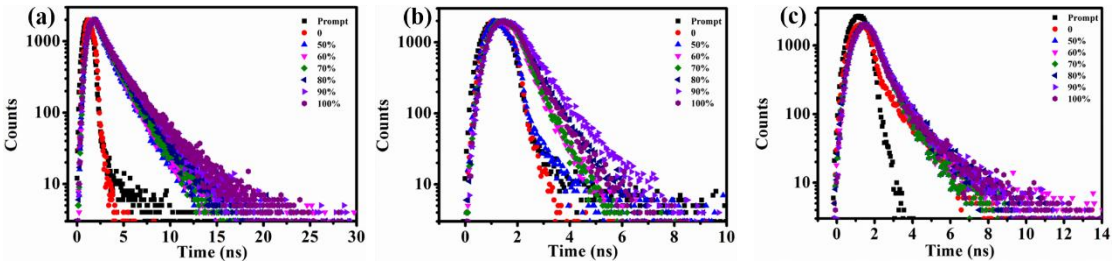

Figure S10 FL lifetime profiles of **1** (a), **2** (b), and **3** (c) in pure and AN/water mixtures with varying f_w from 50 ~ 100%. *Concentration* = 10 μM.

4. Figures for TPEF

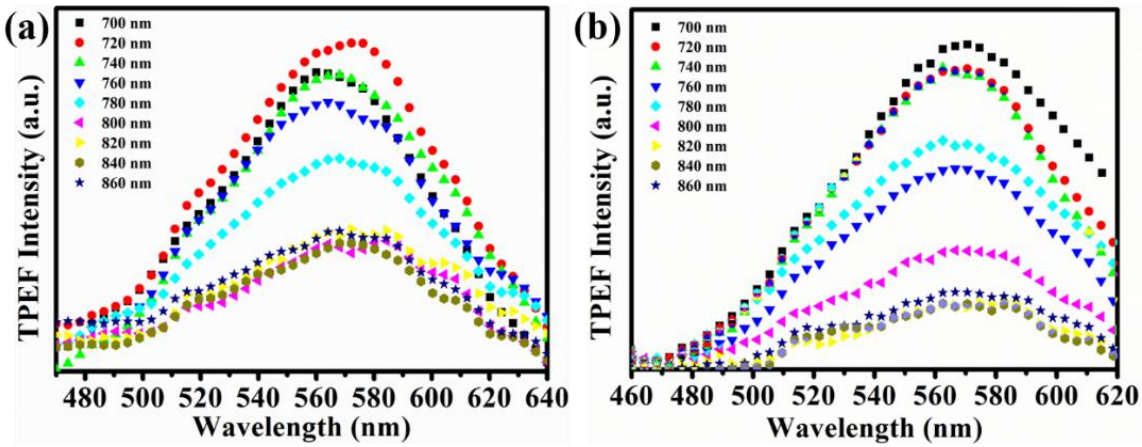

Figure S11 TPEF spectra of chromophores **1** (a) and **2** (b) in toluene pumped by femto-second laser at 300 mW under varying excitation energies from 700-860 nm. *Concentration* = 1 mM.

5. Flow cytometric assay

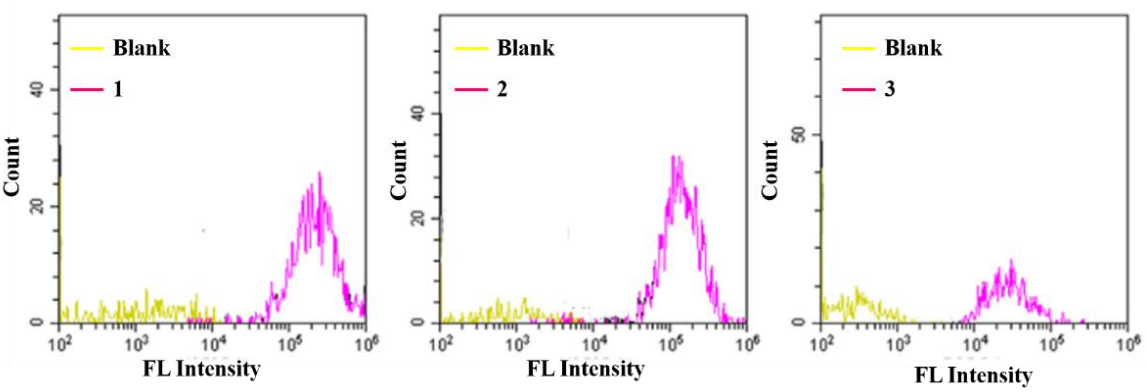

Figure S12 Flow cytometric profiles of HpeG2 cells incubated with **1**, **2** and **3** for 4 h. [Dyes] = 10 μM.

6. Cell localized study

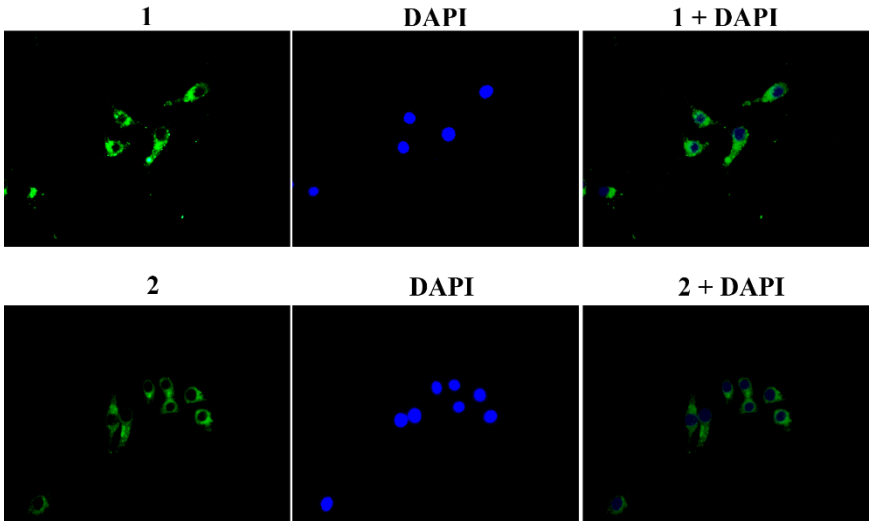

Figure S13 CLSM images of HpeG2 cells after 4 h incubation with DPAI (1 mg/mL) and chromophores (10 μM).

6. Characteristic spectra for newly synthesized compounds

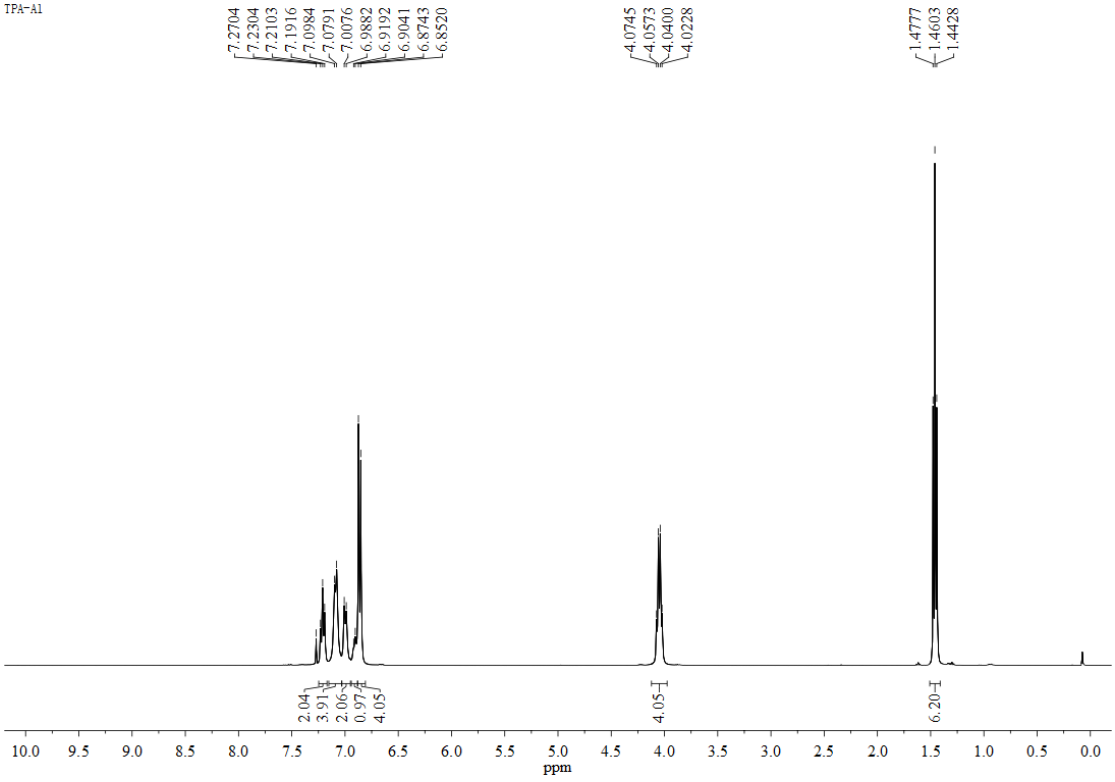

Figure S14 ^{1}H NMR spectrum of compound **4** ($CDCl_3$).

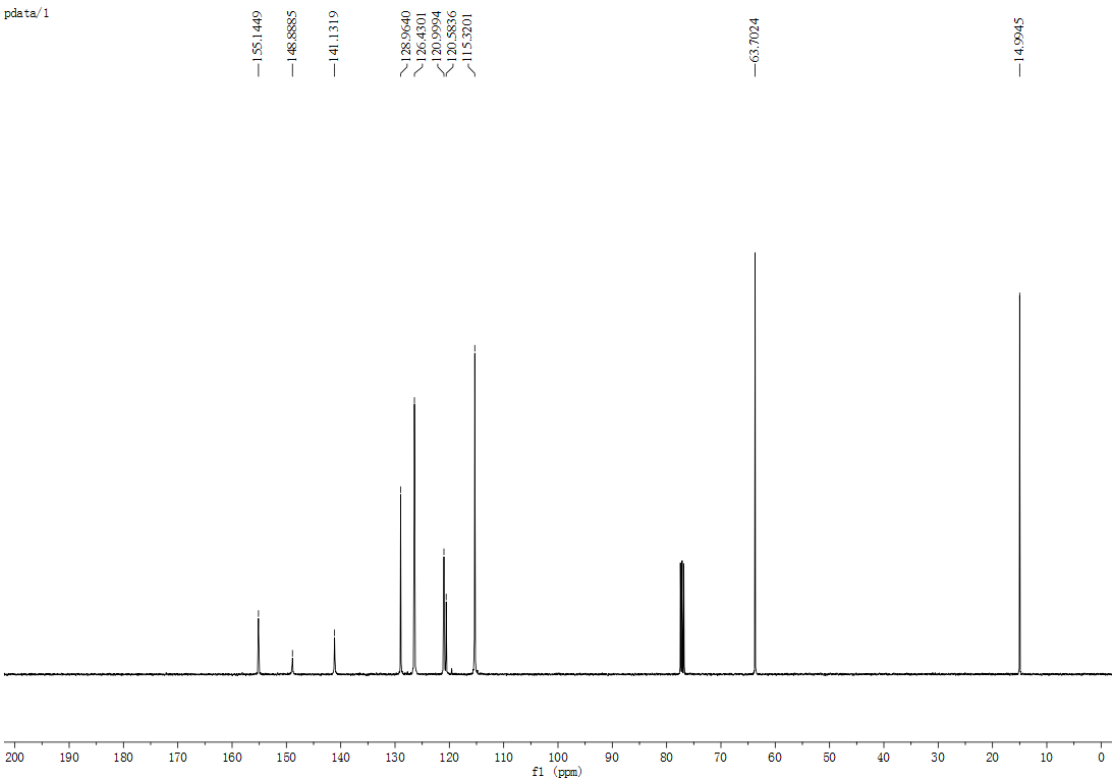

Figure S15 ^{13}C NMR spectrum of compound **4** ($CDCl_3$).

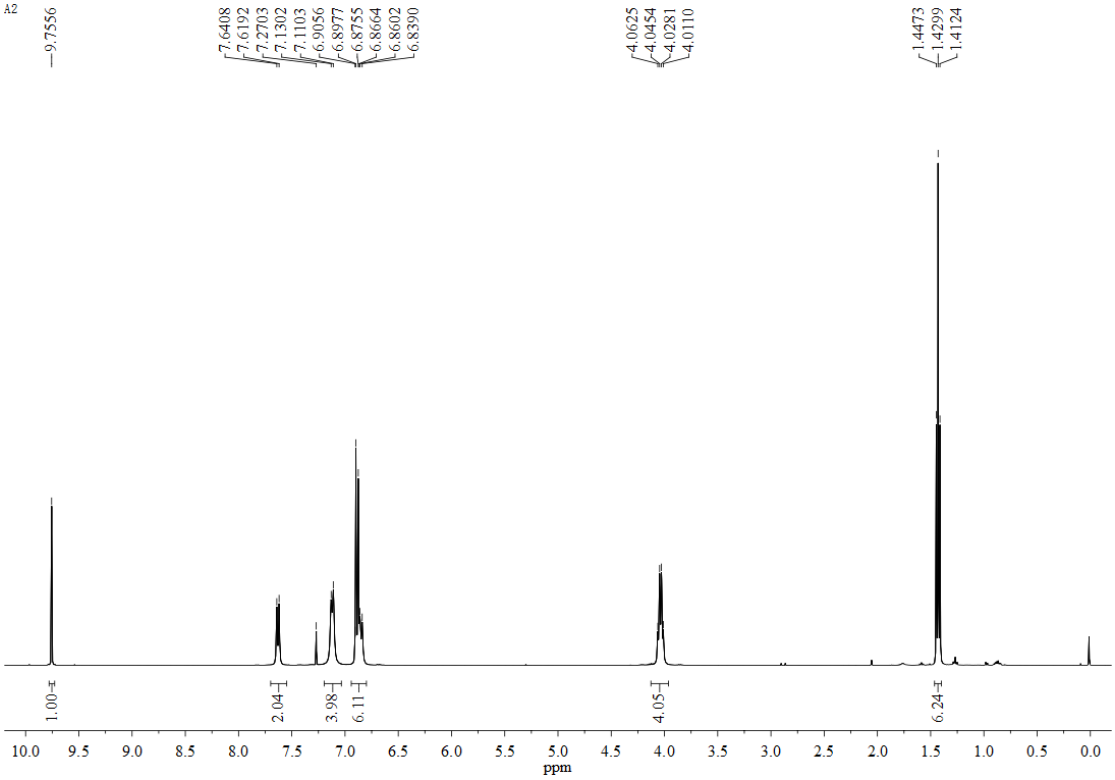

Figure S16 ^{1}H NMR spectrum of compound **7** ($CDCl_3$).

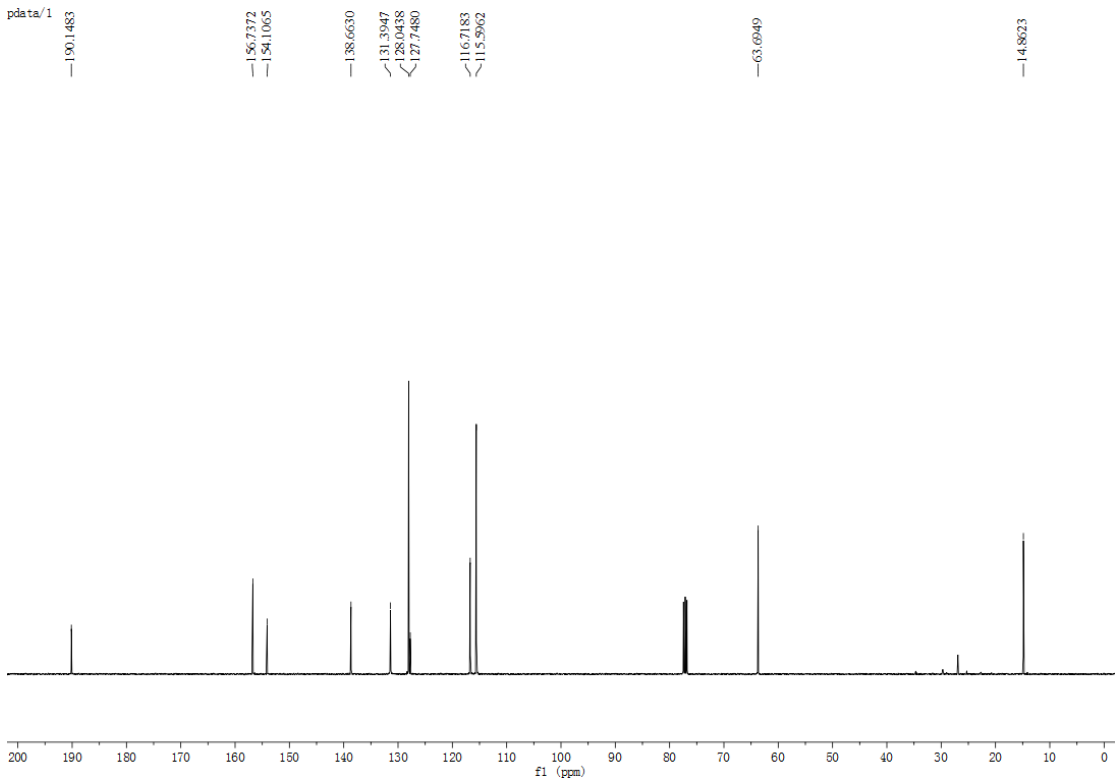

Figure S17 ^{13}C NMR spectrum of compound **7** ($CDCl_3$).

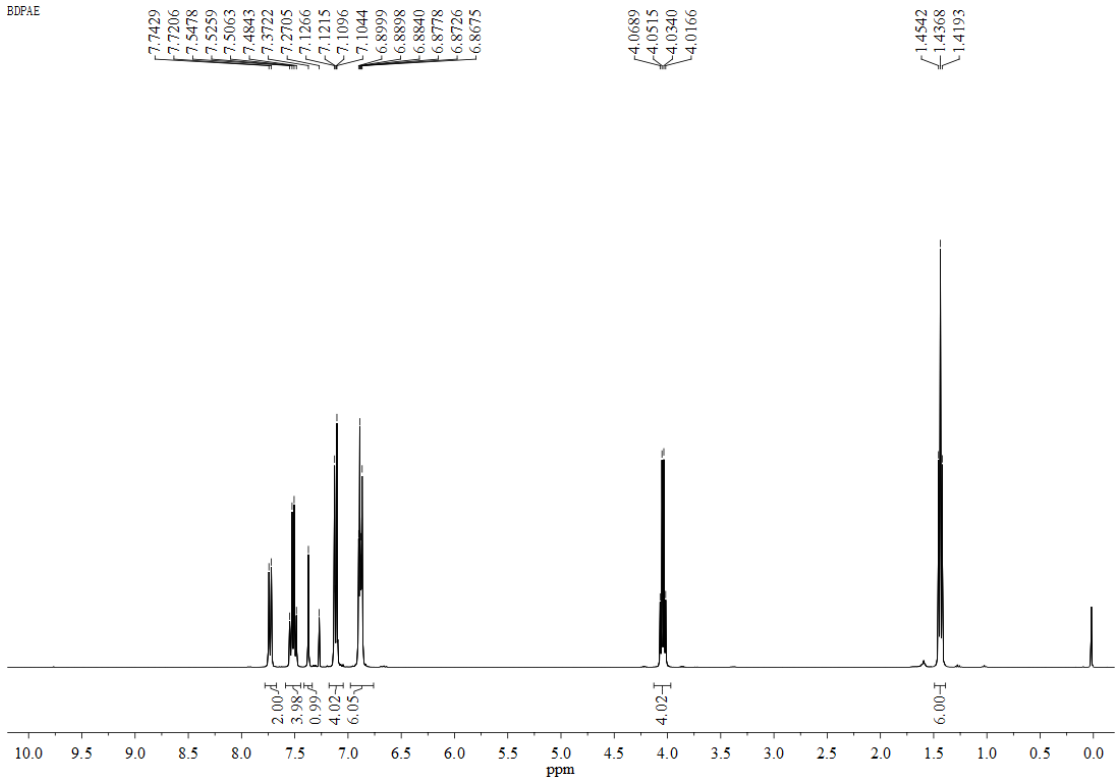

Figure S18 ^{1}H NMR spectrum of compound **10** ($CDCl_3$).

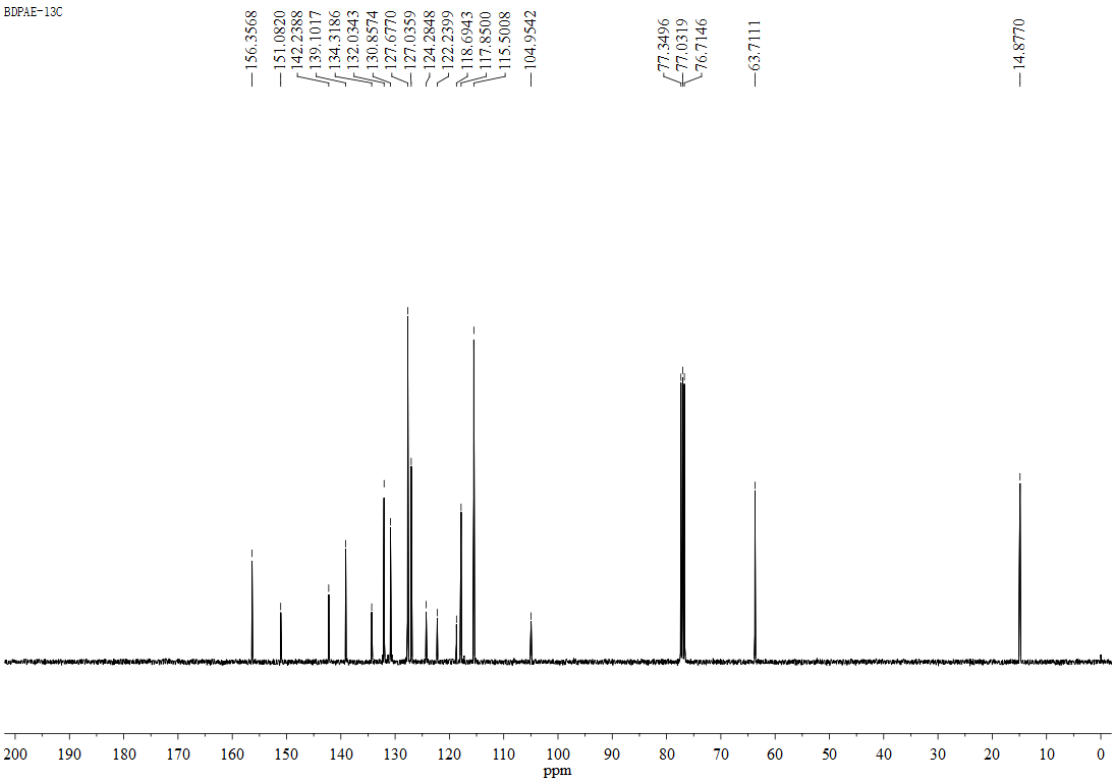

Figure S19 ^{13}C NMR spectrum of compound **10** ($CDCl_3$).

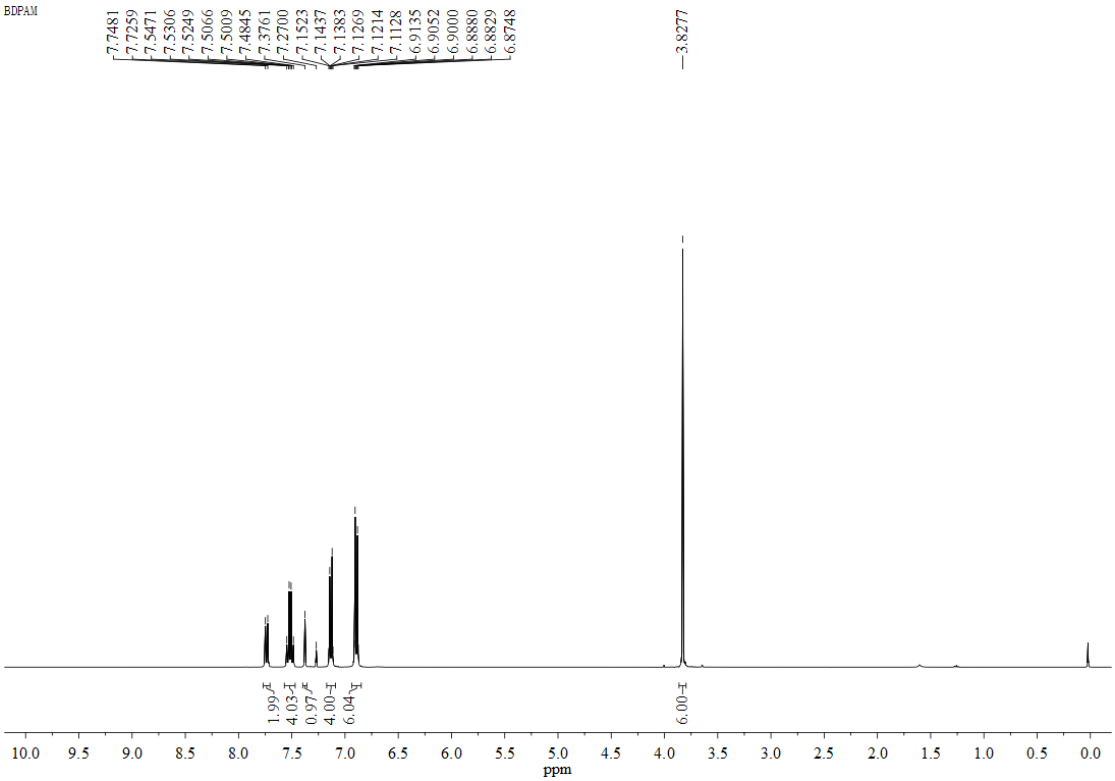

Figure S20 ^{1}H NMR spectrum of compound **11** ($CDCl_3$).

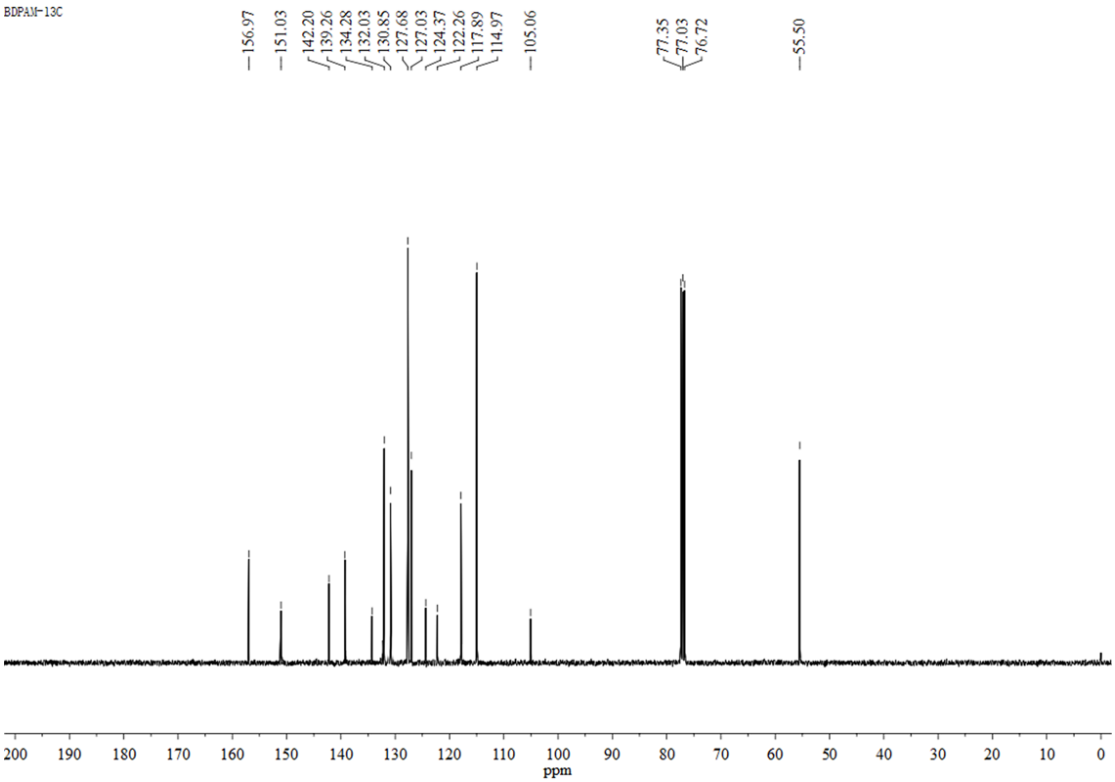

Figure S21 ^{13}C NMR spectrum of compound **11** ($CDCl_3$).

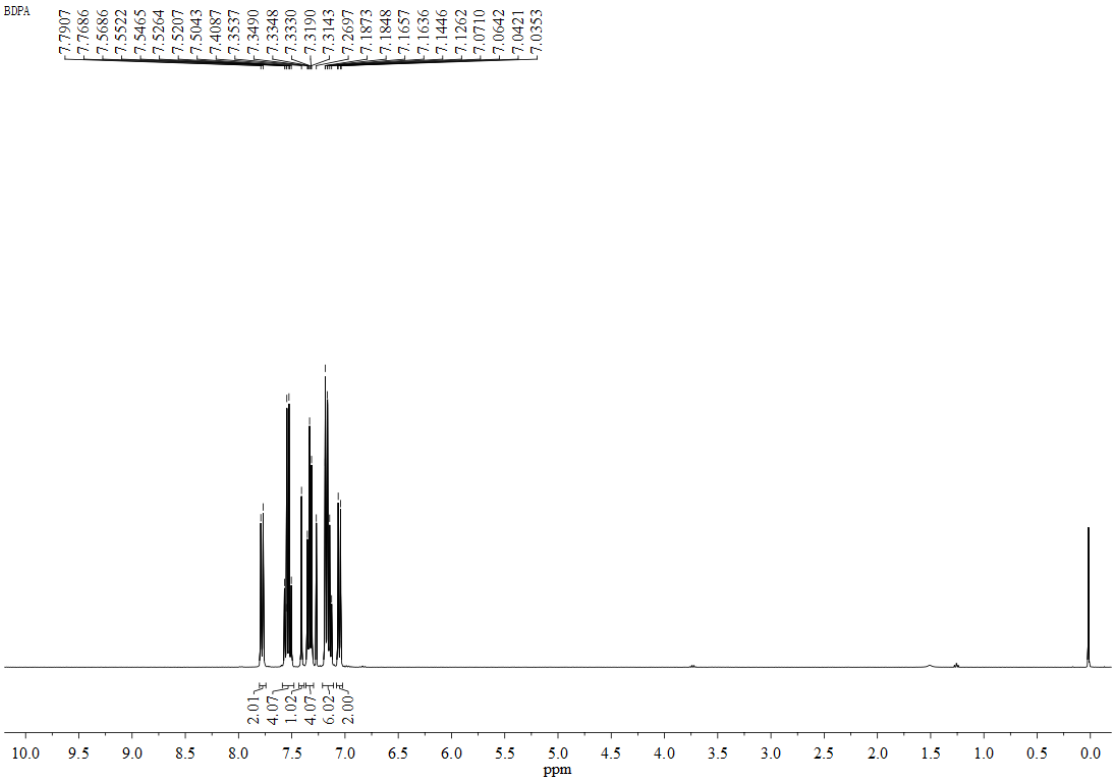

Figure S22 ^{1}H NMR spectrum of compound **12** ($CDCl_3$).

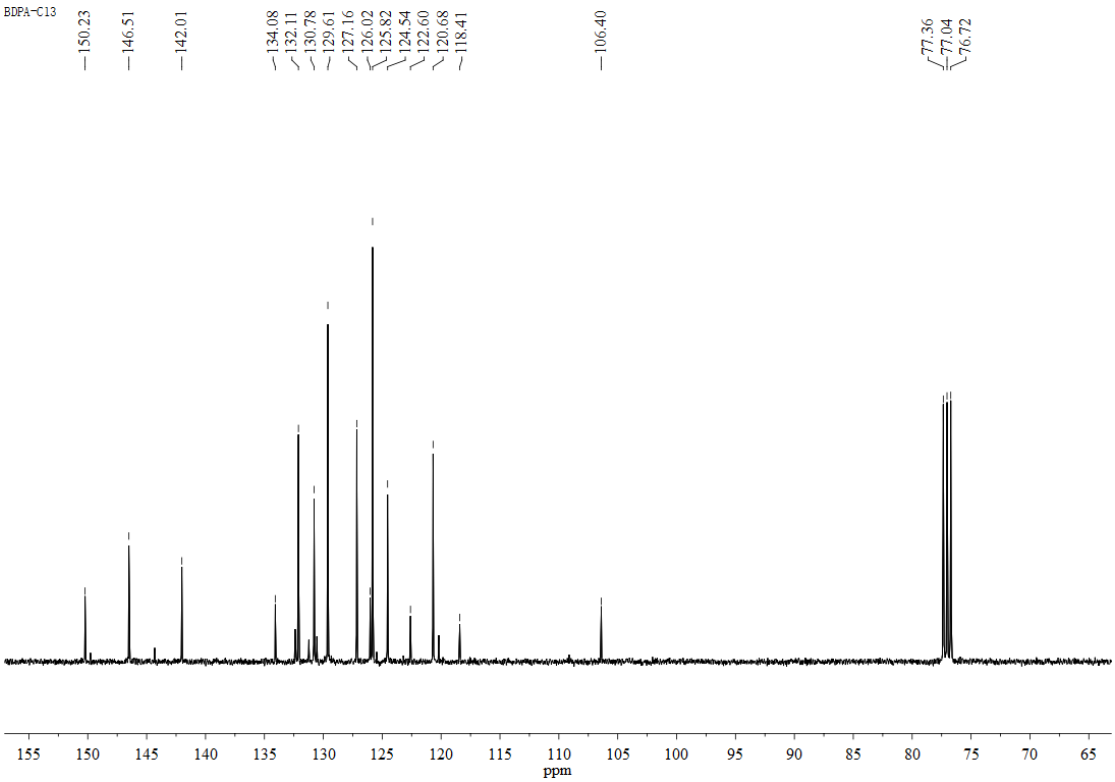

Figure S23 ^{13}C NMR spectrum of compound **12** ($CDCl_3$).

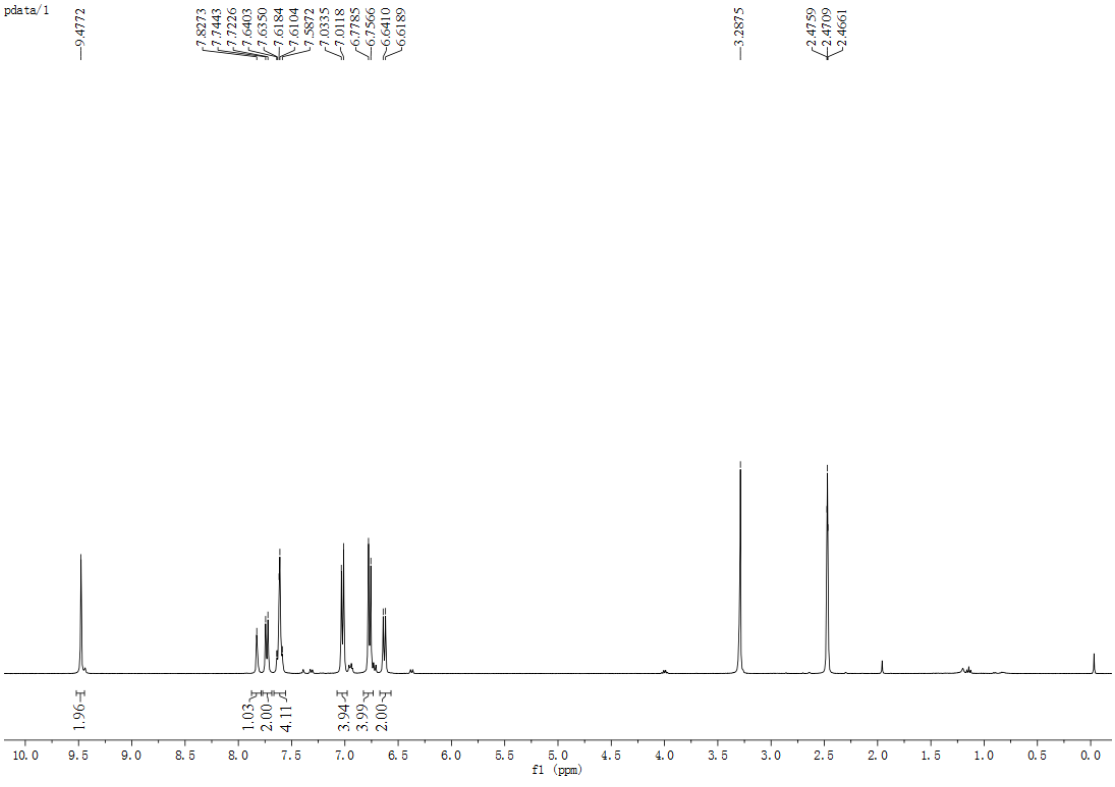

Figure S24 ^{1}H NMR spectrum of compound **13** (DMSO-d_6).

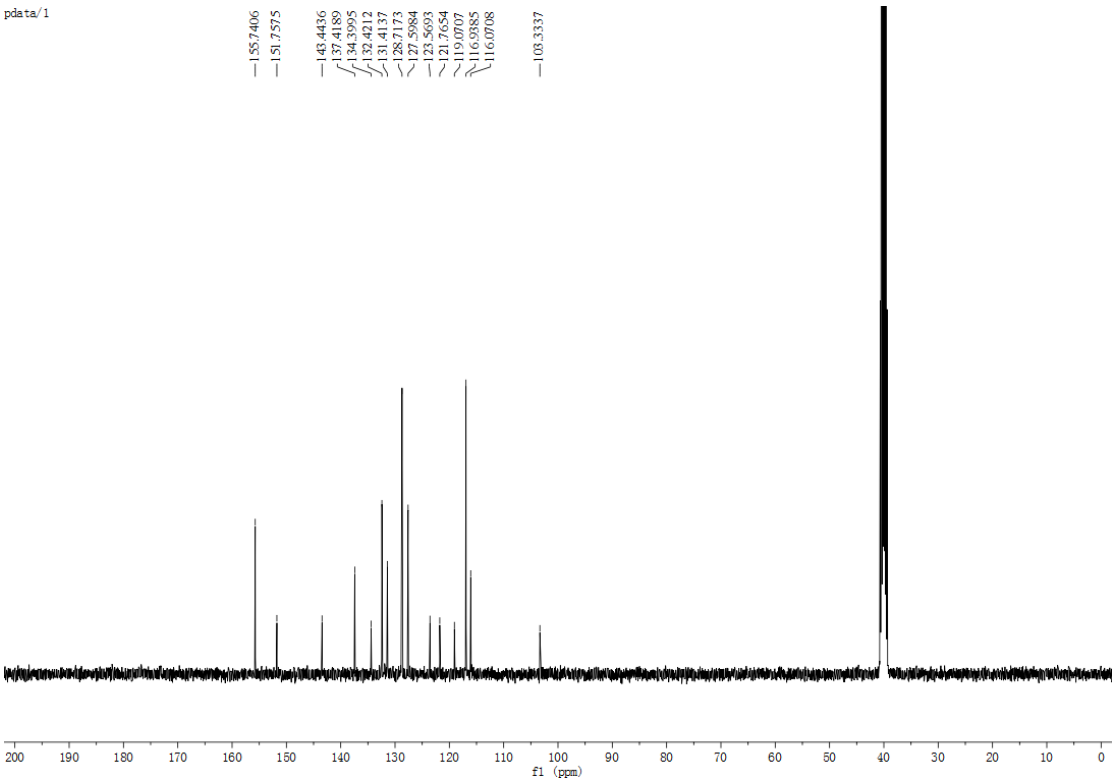

Figure S25 ^{13}C NMR spectrum of compound **13** (DMSO-d_6).

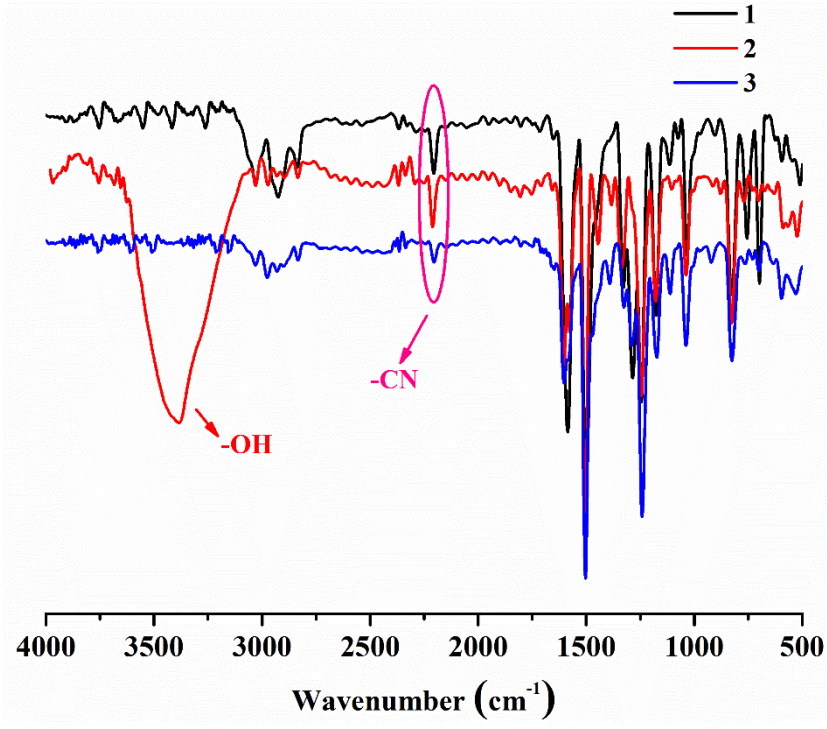

Figure S26 FT-IR spectra of chromophores **1** ~ **3**.

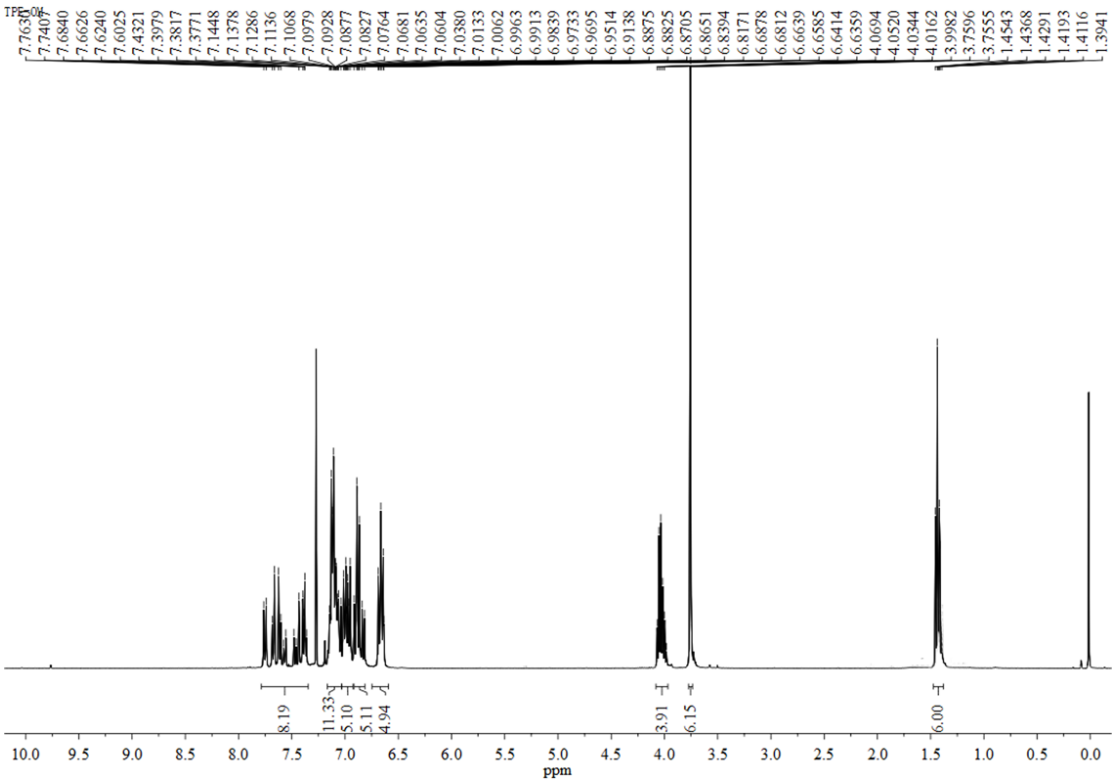

Figure S27 ^{1}H NMR spectrum of chromophore **1** ($CDCl_3$).

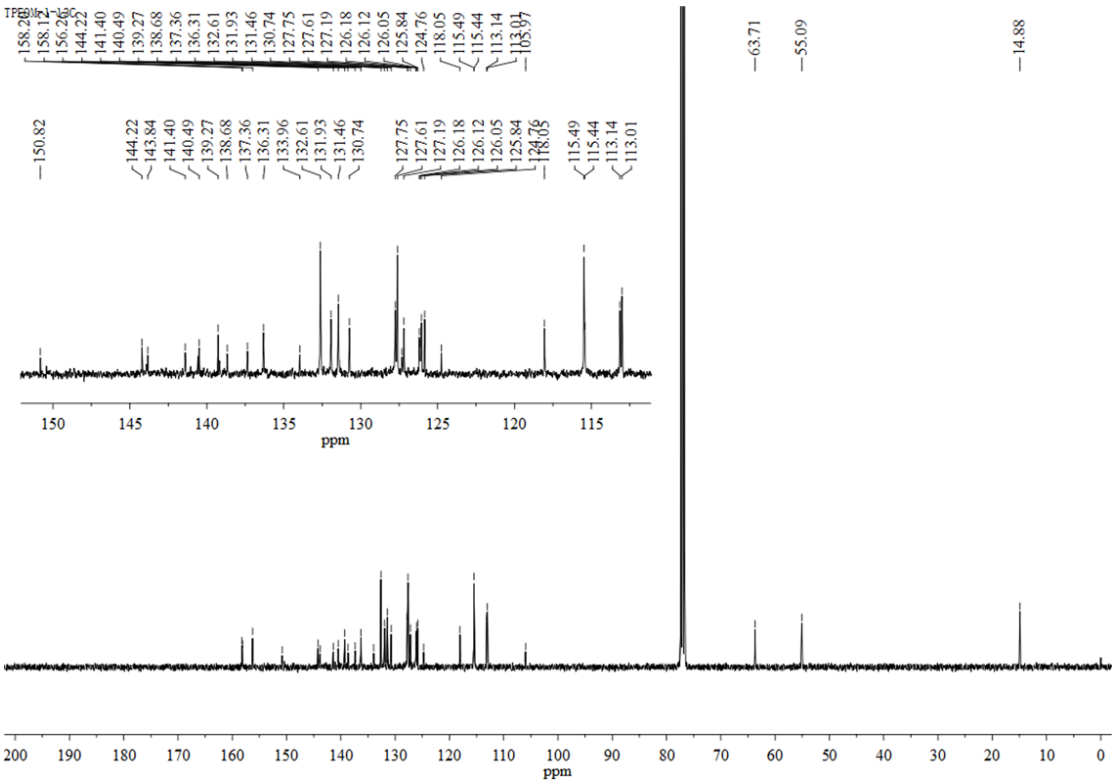

Figure S28 ^{13}C NMR spectrum of chromophore **1** ($CDCl_3$).

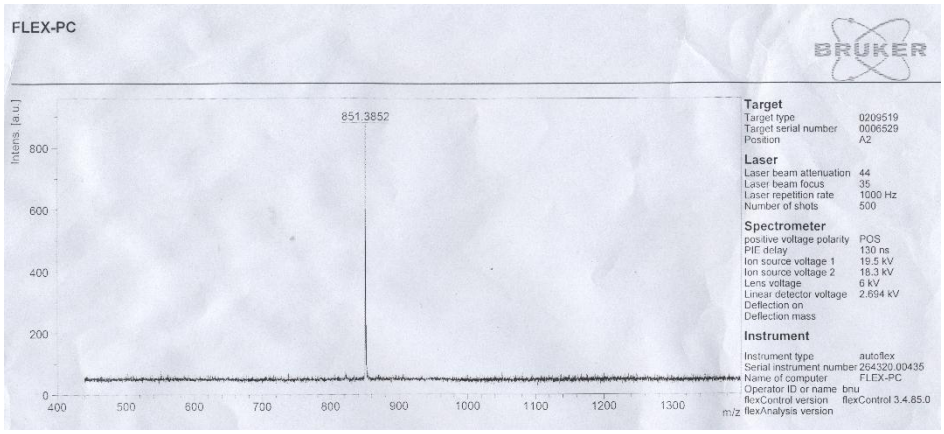

Figure S29 MALDI-TOF spectrum of chromophore **1**.

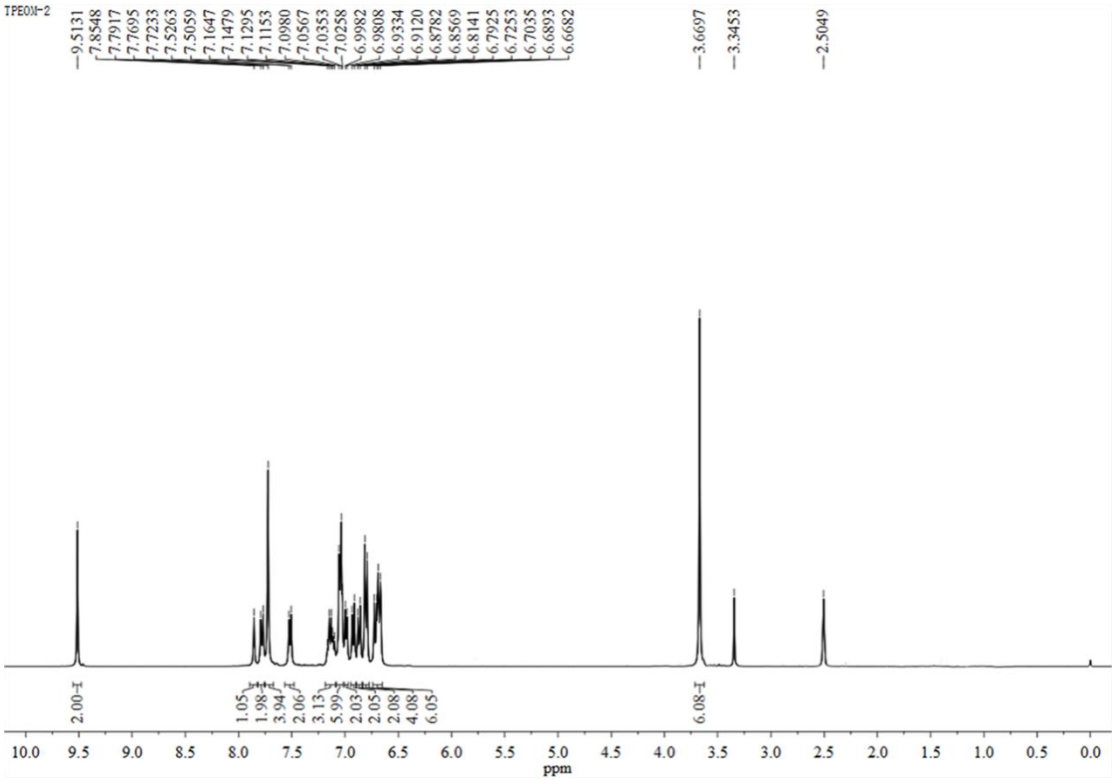

Figure S30 ^{1}H NMR spectrum of chromophore **2** (DMSO-d_6).

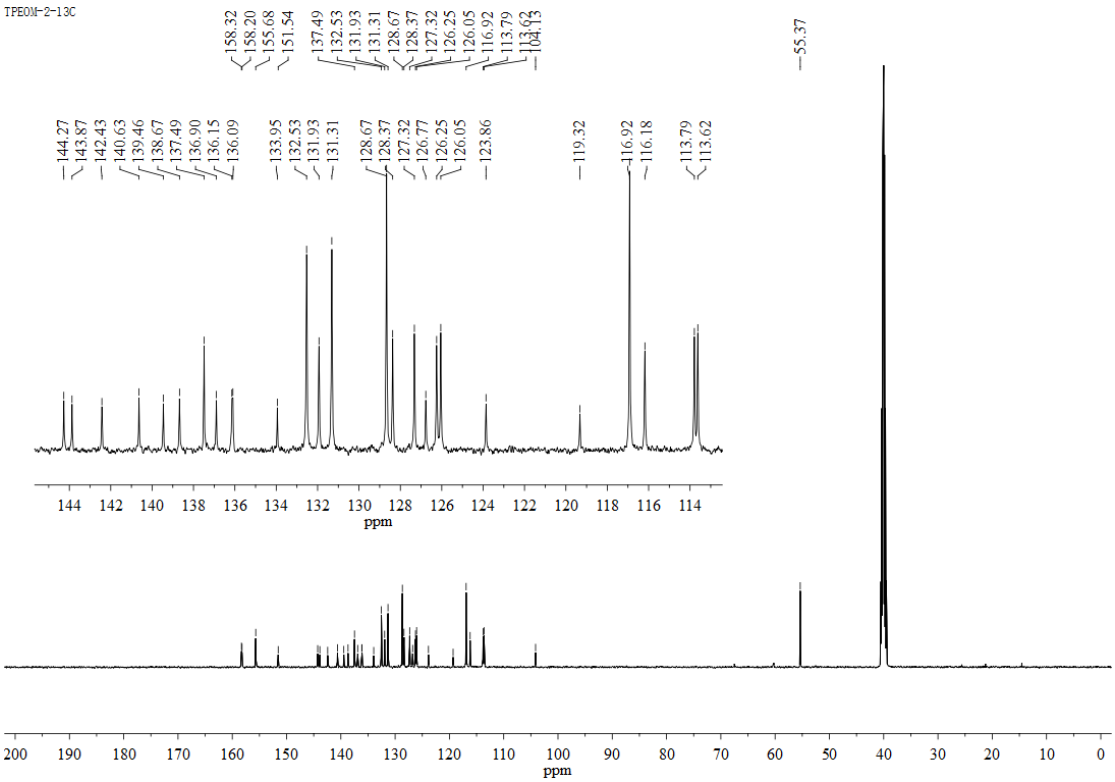

Figure S31 ^{13}C NMR spectrum of chromophore **2** (DMSO-d_6).

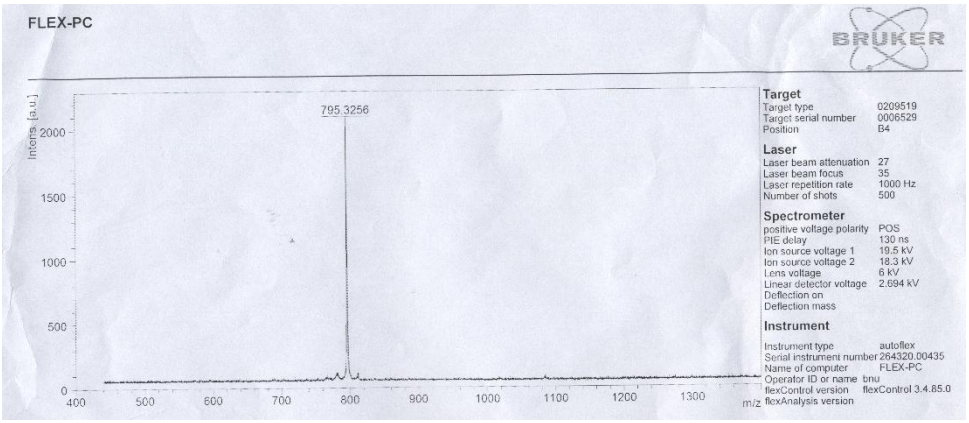

Figure S32 MALDI-TOF spectrum of chromophore **2**.

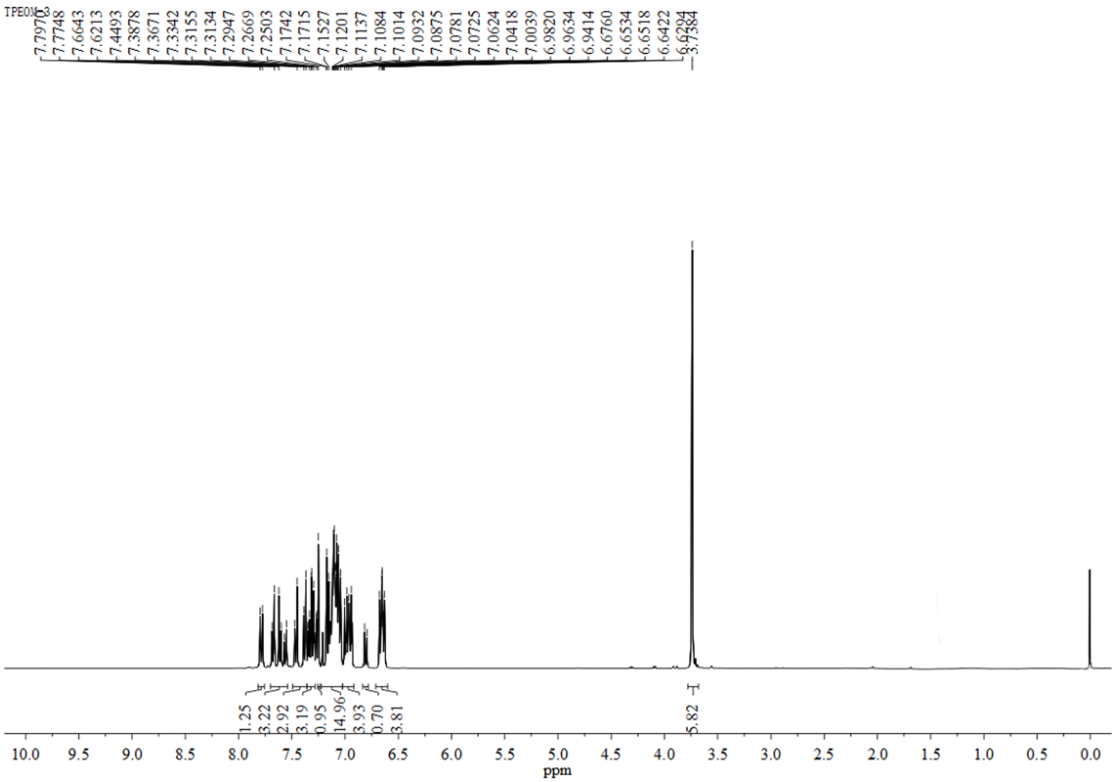

Figure S33 ^{1}H NMR spectrum of chromophore **3** ($CDCl_3$).

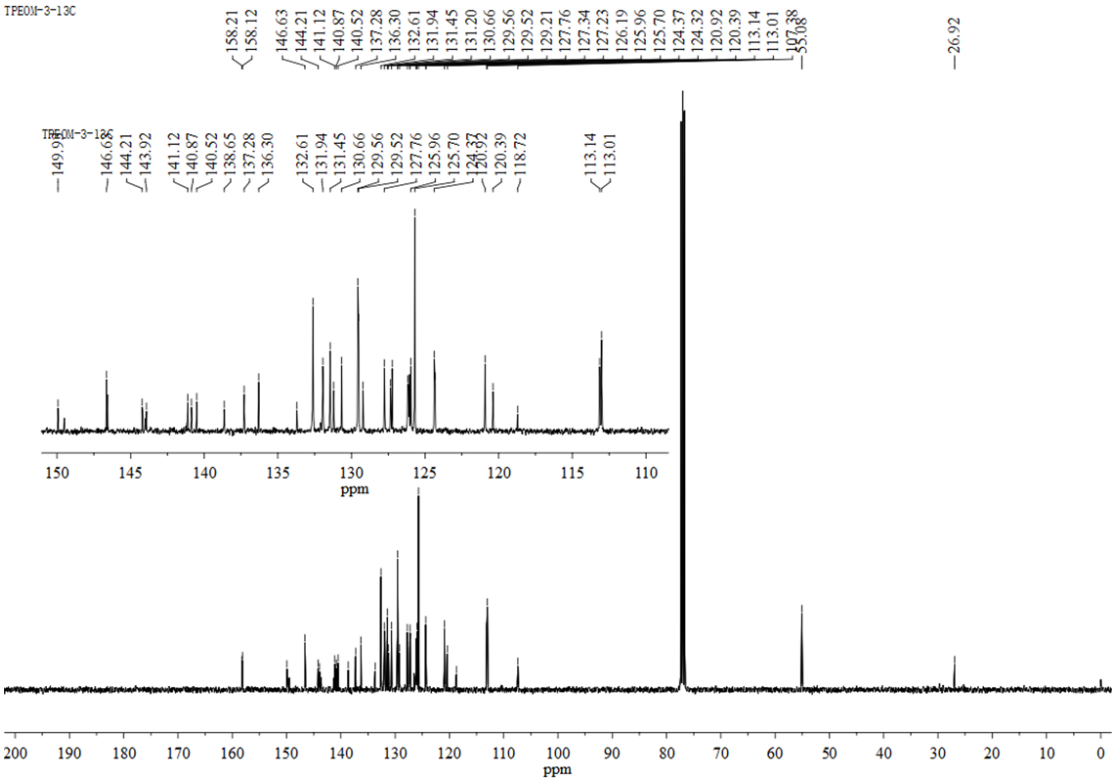

Figure S34 ^{13}C NMR spectrum of chromophore **3** ($CDCl_3$).

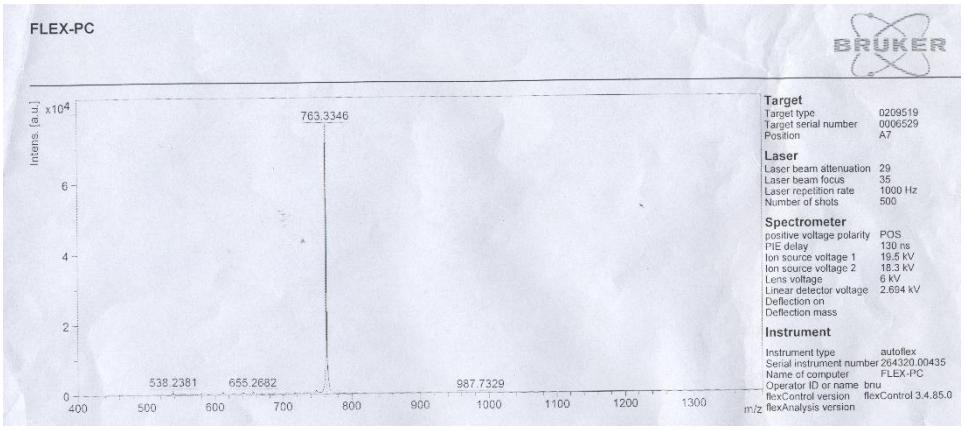

Figure S35 MALDI-TOF spectrum of chromophore **3**.