Supporting Information of

Light-emitting properties of donor–acceptor and donor–acceptor–donor dyes in solution, solid, and aggregated states: structure–property relationship of emission behavior

Tsutomu Ishi-i,*[a] Kei Ikeda,[b] Michiaki Ogawa[a] and Yutarou Kusakaki[b]

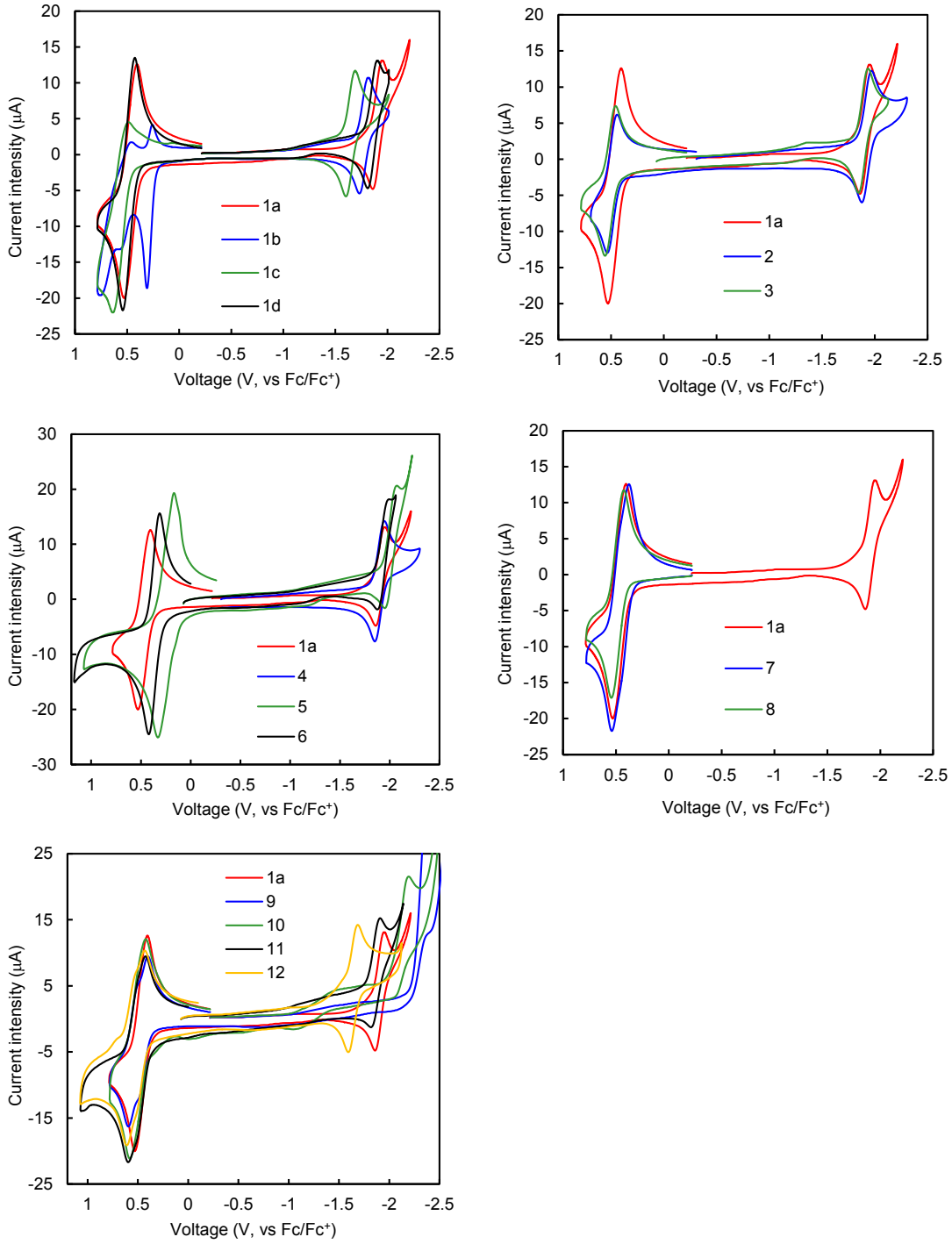


Fig. S1 Cyclic voltammograms of **1a**, **1b**, **1c**, **1d**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, and **12** in dichloromethane (5.0×10^{-4} M) in the presence of tetrabutylammonium hexafluoroborate (0.1 M) at the scan rate of 100 mVs^{-1}.

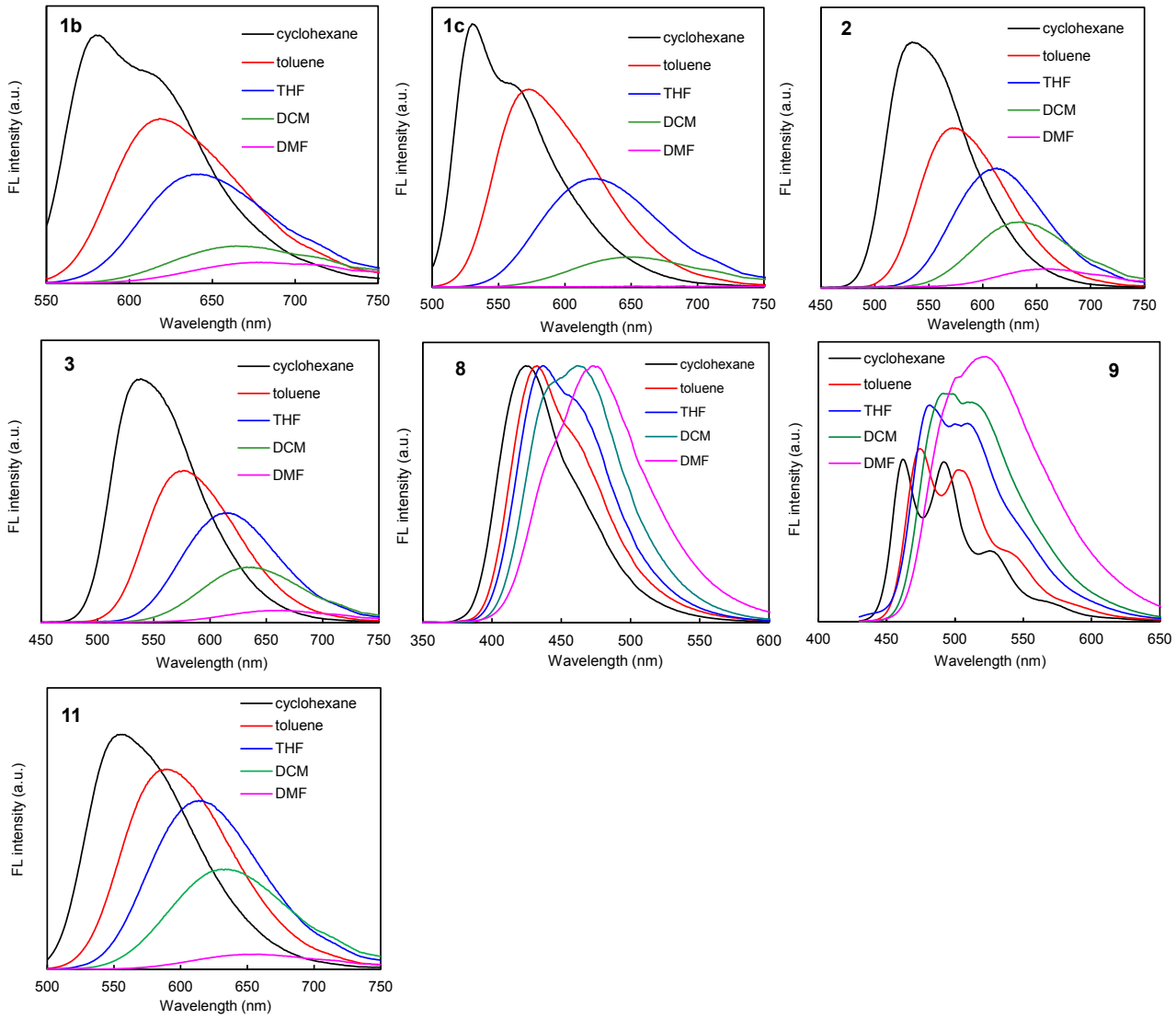


Fig. S2 Fluorescence spectra of **1b** (ex. 510 nm), **1c** (ex. 480 nm), **2** (ex. 440 nm), **3** (ex. 440 nm), **8** (ex. 340 nm), **9** (ex. 420 nm), and **11** (ex. 455 nm) in cyclohexane, toluene, THF, dichloromethane, and DMF at 1.0×10^{-6} M.

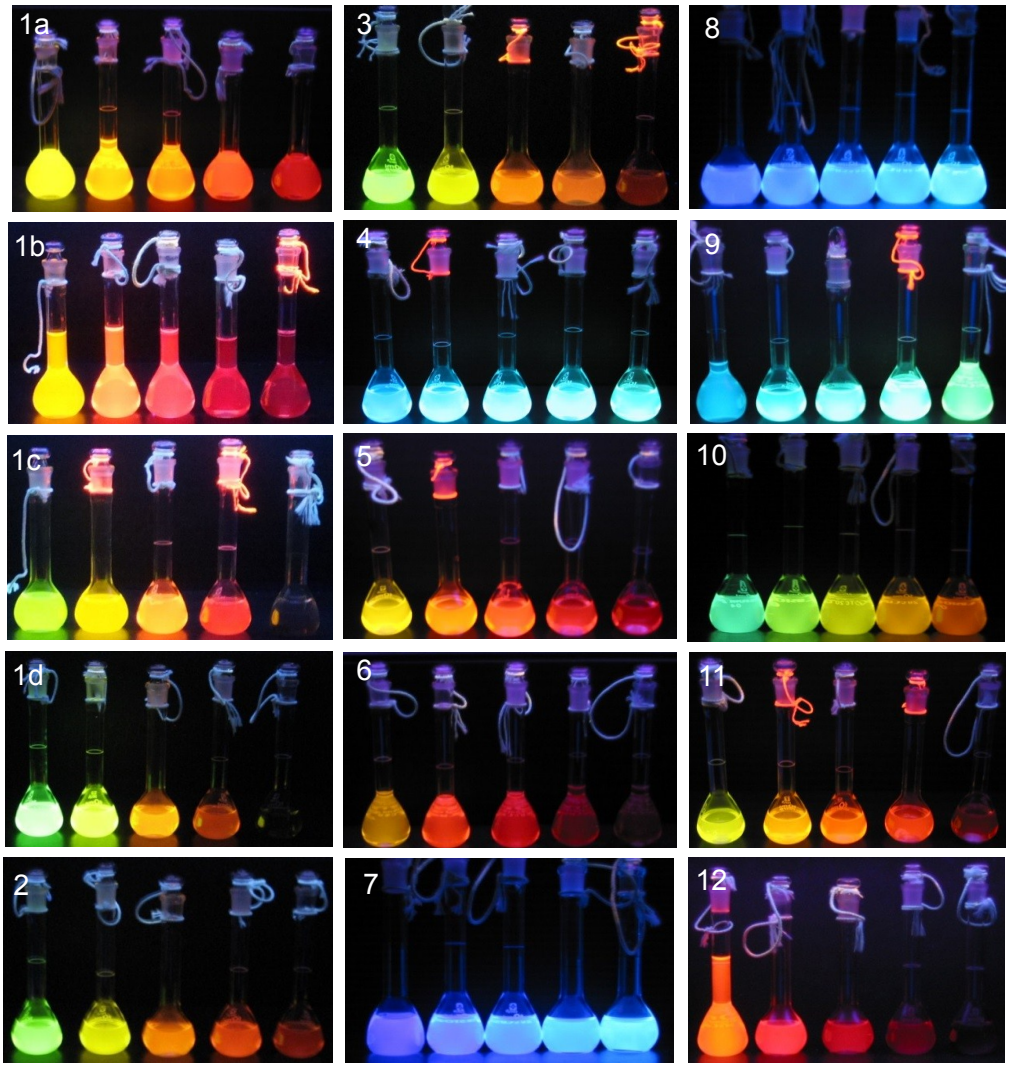


Fig. S3 Fluorescence images of **1a, 1b**, **1c**, **1d**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, and **12** under UV light irradiation at 1.0×10^{-5} M (cyclohexane, toluene, THF, DCM, and DMF from left to right).

Table S1 Spectral data of **1a**–**d**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, and **12**

comp.	solvent	λ_{abs} (nm) [a]	ε	λ_{em} (nm) [b]	Φ_F [c]	$\Delta\lambda$ (nm)
1a	cyclohexane	460	18,900	557	0.85	97
	toluene	461	20,500	592	0.80	131
	THF	460	20,700	614	0.71	154
	DCM	459	19,500	639	0.36	180
	DMF	460	18,700	657	0.22	197
	solid			580	0.55 [f]	
1b	cyclohexane	506	42,600	580, 620 (sh)	0.87 [d]	74
	toluene	511	39,480	618	0.64 [d]	107
	THF	510	38,550	640	0.32 [d]	130
	DCM	512	40,330	665	0.18 [d]	143
	DMF	512	39,520	679	0.12 [d]	167
	solid			683	0.07 [f]	
1c	cyclohexane	475	39,760	530, 560 (sh)	0.93	55
	toluene	480	37,110	573	0.87	97
	THF	479	40,160	619	0.52	140
	DCM	485	37,740	651	0.16	166
	DMF	480	37,900	680	<0.01	200
	solid			647	0.12 [f]	
1d	cyclohexane	424	26,930	527, 550 (sh)	0.79	103
	toluene	427	28,300	556	0.70	129
	THF	424	26,890	617	0.50	193
	DCM	422	26,980	643	0.14	221
	DMF	426	26,660	680	<0.01	254
	solid			547	0.53 [f]	
2	cyclohexane	437	15,610	535, 555 (sh)	0.86	98
	toluene	439	13,980	575	0.74	136
	THF	436	13,110	611	0.65	175
	DCM	436	13,560	636	0.30	200
	DMF	435	13,700	664	0.11	229
	solid			538	0.47 [f]	
3	cyclohexane	439	18,680	538	0.92	99
	toluene	440	15,960	577	0.83	137
	THF	436	14,720	613	0.77	177
	DCM	437	13,580	639	0.37	202
	DMF	435	13,650	664	0.07	229
	solid			570	0.58 [f]	

4	cyclohexane	380	9,600	477	0.71 [e]	97
	toluene	383	10,280	482	0.61 [e]	99
	THF	383	10,320	489	0.71 [e]	106
	DCM	381	10,010	491	0.76 [e]	110
	DMF	382	10,240	507	0.82 [e]	125
	solid			484	0.92 [f]	
5	cyclohexane	455	16,670	571	0.82	116
	toluene	461	17,140	610	0.63	149
	THF	462	17,020	625	0.59	163
	DCM	459	16,350	646	0.29	187
	DMF	464	16,590	666	0.17	202
	solid			625	0.53 [f]	
6	cyclohexane	462	11560	579	0.72	117
	toluene	473	11,360	623	0.50	150
	THF	476	11,200	645	0.46	169
	DCM	472	12,780	670	0.13	198
	DMF	481	13,140	679	0.05	198
	solid			686	0.25 [f]	
7	cyclohexane	354	53,140	401, 422	0.46 [e]	47
	toluene	358	54,650	409, 428	0.45 [e]	51
	THF	356	55,000	415, 430 (sh)	0.37 [e]	59
	DCM	357	53,270	426, 465 (sh)	0.50 [e]	69
	DMF	359	54,690	434, 470 (sh)	0.56 [e]	75
	solid			447	0.59 [f]	
8	cyclohexane	342	353,00	425, 460 (sh)	0.41 [e]	83
	toluene	345	32,270	432, 460 (sh)	0.42 [e]	87
	THF	343	33,810	437, 460 (sh)	0.48 [e]	93
	DCM	345	31,430	445 (sh), 462	0.55 [e]	117
	DMF	346	31,120	445 (sh), 473	0.55 [e]	127
	solid			420	0.59 [f]	
9	cyclohexane	421	69,260	462, 491, 525	0.33	41
	toluene	427	69,840	474, 503, 542	0.40	47
	THF	426	73,780	483, 509, 550 (sh)	0.41	57
	DCM	427	69,170	491, 513	0.51	64
	DMF	429	68,080	499 (sh), 522	0.60	93
	solid			609	0.15 [f]	
10	cyclohexane	419	14,660	517	0.78	98
	toluene	417	15,710	543	0.78	126
	THF	412	15,160	564	0.66	152

	DCM	414	14,010	596	0.44	182
	DMF	411	15,870	615	0.34	204
	solid			520	0.52 [f]	
11	cyclohexane	457	18,790	557	0.82	100
	toluene	458	21,460	590	0.81	132
	THF	455	20,730	614	0 68	159
	DCM	456	20,230	636	0.50	180
	DMF	453	20,380	659	0.11	206
	solid			590	0.71 [f]	
12	cyclohexane	508	26,910	607	0.63 [d]	99
	toluene	507	25,150	646	0.40 [d]	147
	THF	504	24,450	665	0.20 [d]	164
	DCM	506	23,070	683	0.07 [d]	177
	DMF	501	23,400	-	-	-
	solid			641	0.36 [f]	

[a] at 1.0×10^{-5} M.

[b] at 1.0×10^{-6} M.

[c] Determined relative to fluorescein (Φ_F 0.97, ex 455 nm) in ethanol at 0.001 mM.

[d] Determined relative to rhodamine B (Φ_F 0.65, ex 535 nm) in ethanol at 0.001 mM.

[e] Determined relative to quinine sulfate (Φ_F 0.55, ex 350 nm) in 1 N sulfuric acid at 0.001 mM.

[f] Absolute fluorescence quantum yield.

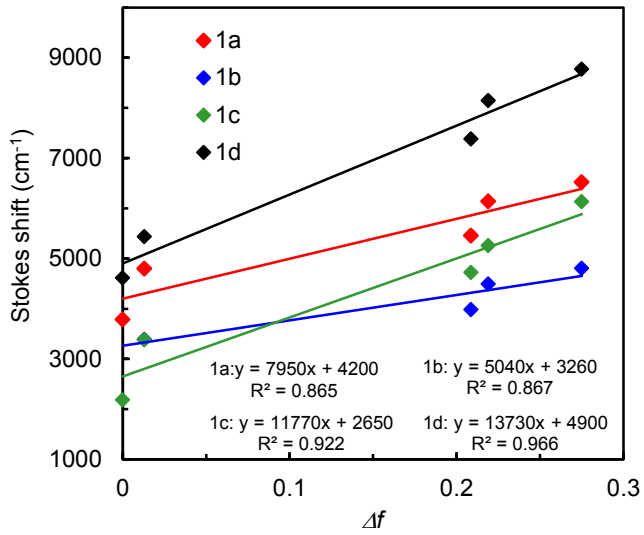


Fig. S4 Plots of the Stokes shift ($\Delta\nu = \nu_{abs}-\nu_{FL}$) against the solvent polarity parameter (Δf) for **1a**–**d** in cyclohexane, toluene, THF, DCM, and DMF. The relationship between the Stokes shift and the solvent polarity parameter is evaluated by Mataka-Lippert equations:

$\Delta\nu = \nu_{abs}-\nu_{FL} = 2\Delta f(\mu_e-\mu_g)^2/(hca^3)$

$\Delta f = (\varepsilon-1)/(2\varepsilon+1)-(n^2-1)/(2n^2+1)$,

h is the Plank constant, c is the speed of light, a is the Onsager cavity radius, μ_e and μ_g refer to the dipole moments in the excited and ground states, and ε and n are the dielectric constant and refractive index of the solvents.

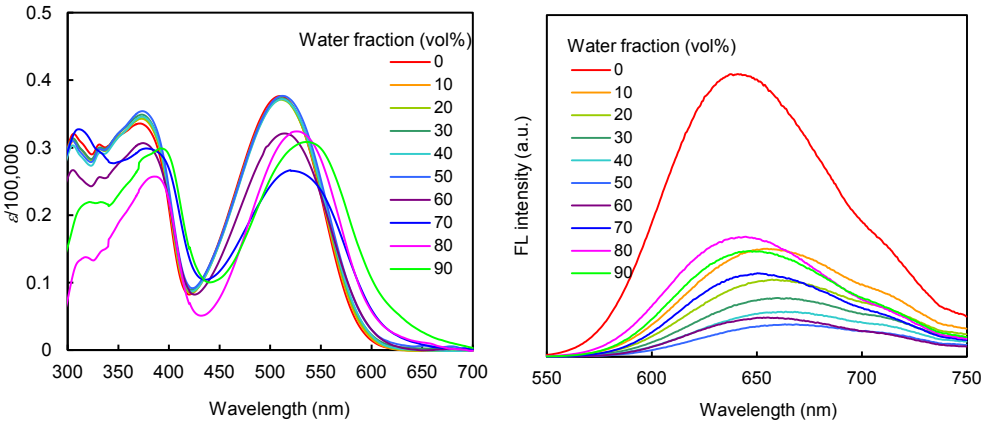


Fig. S5 UV/Vis and fluorescence (ex. 510 nm) spectra of **1b** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, (v/v)) at 1.0×10^{-5} M (1 cm width cell).

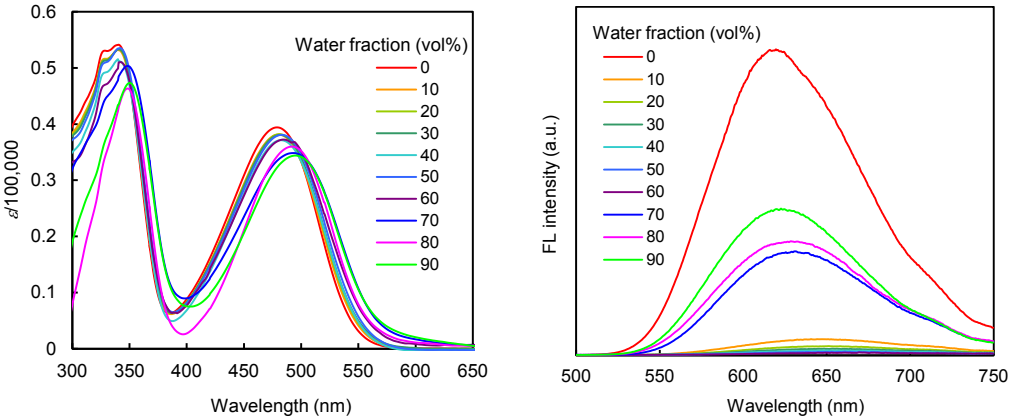


Fig. S6 UV/Vis and fluorescence (ex. 480 nm) spectra of **1c** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, (v/v)) at 1.0×10^{-5} M (1 cm width cell).

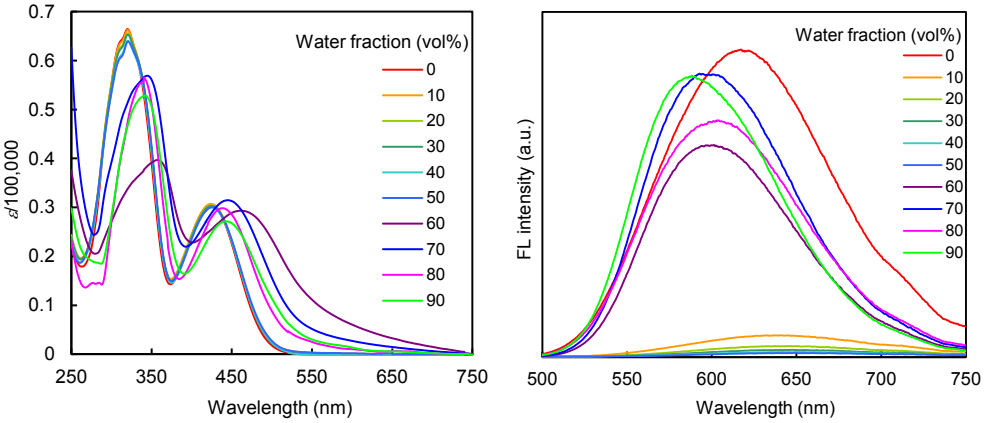


Fig. S7 UV/Vis and fluorescence (ex. 420 nm) spectra of **1d** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, (v/v)) at 1 x 10^{-5} M (1 cm width cell). At 60 and 70% water fraction, precipitates were formed.

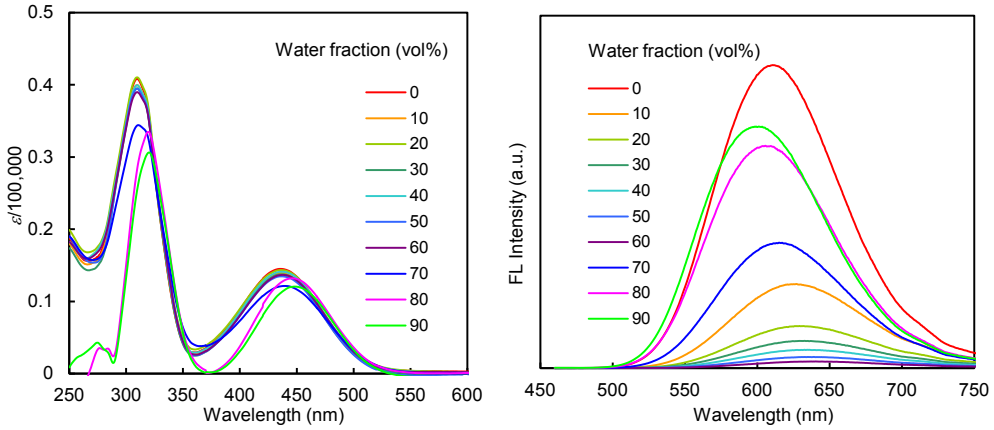


Fig. S8 UV/Vis and fluorescence (ex. 440 nm) spectra of **2** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, (v/v)) at 1.0×10^{-5} M (1 cm width cell).

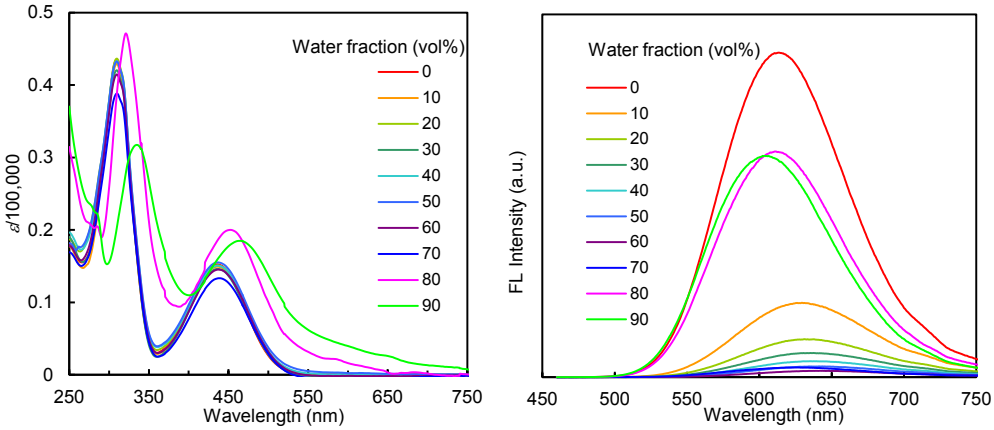


Fig. S9 UV/Vis and fluorescence (ex. 440 nm) spectra of **3** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, (v/v)) at 1.0×10^{-5} M (1 cm width cell).

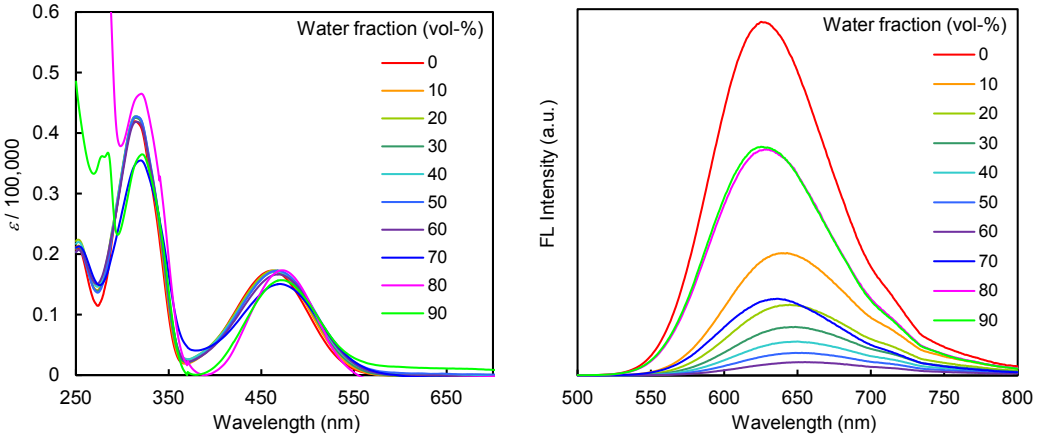


Fig. S10 UV/Vis and fluorescence (ex. 450 nm) spectra of **5** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, (v/v)) at 1.0×10^{-5} M (1 cm width cell).

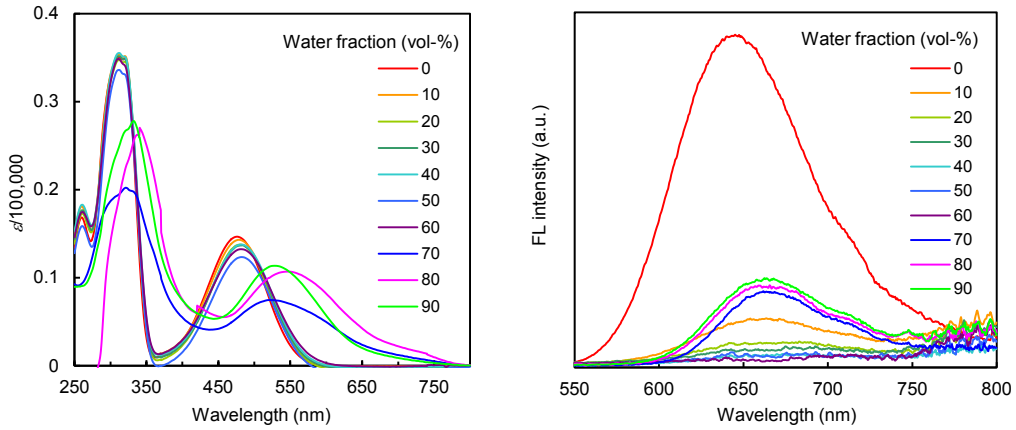


Fig. S11 UV/Vis and fluorescence (ex. 500 nm) spectra of **6** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, (v/v)) at 1.0×10^{-5} M (1 cm width cell).

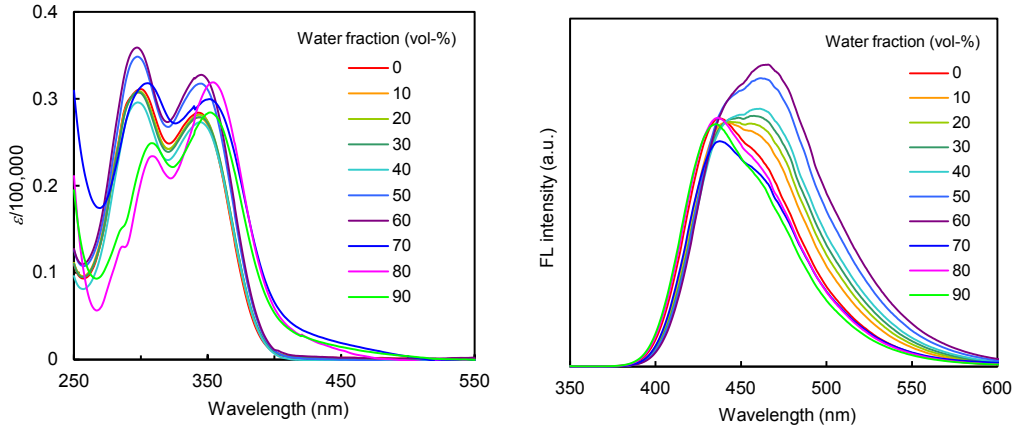


Fig. S12 UV/Vis and fluorescence (ex. 340 nm) spectra of **8** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, (v/v)) at 1.0×10^{-5} M (1 cm width cell).

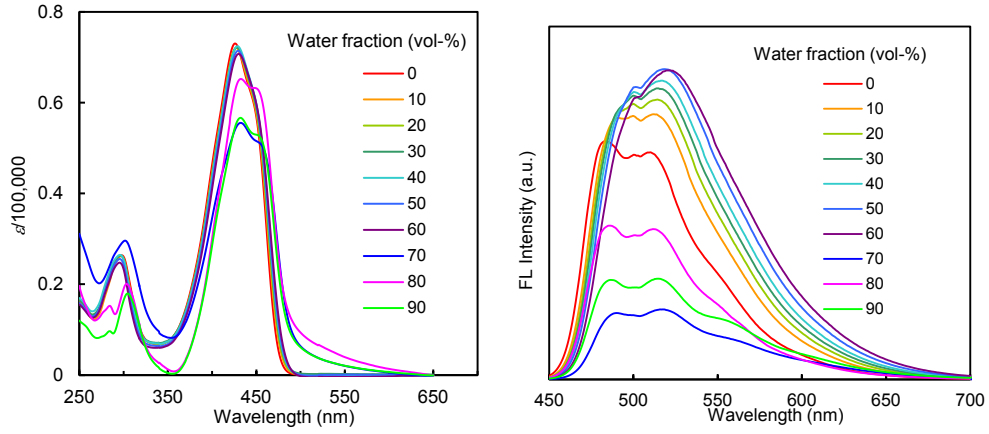


Fig. S13 UV/Vis and fluorescence (ex. 430 nm) spectra of **9** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, (v/v)) at 1.0×10^{-5} M (1 cm width cell).

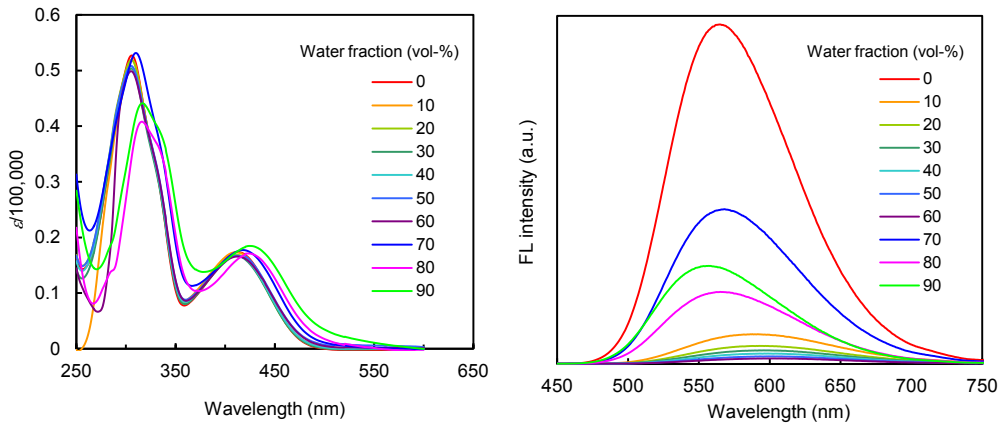


Fig. S14 UV/Vis and fluorescence (ex. 420 nm) spectra of **10** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, (v/v)) at 1.0×10^{-5} M (1 cm width cell).

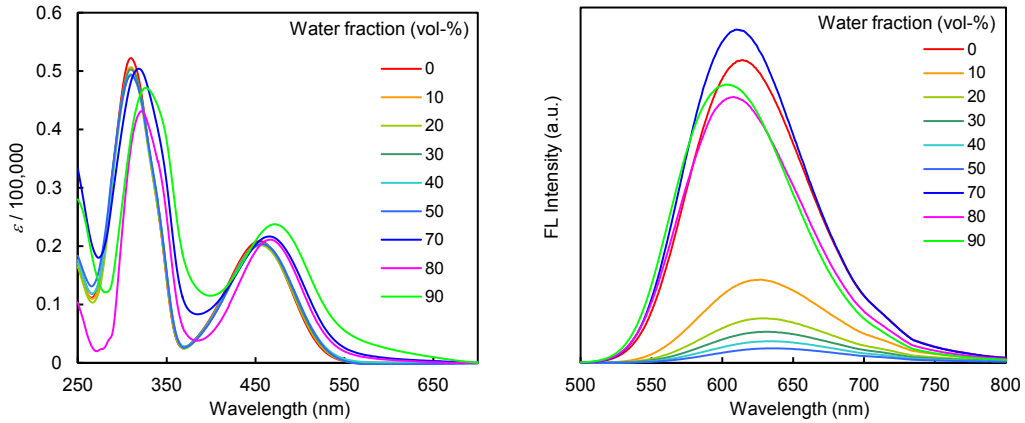


Fig. S15 UV/Vis and fluorescence (ex. 455 nm) spectra of **11** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, (v/v)) at 1.0×10^{-5} M (1 cm width cell). At 60% water fraction, precipitate was formed.

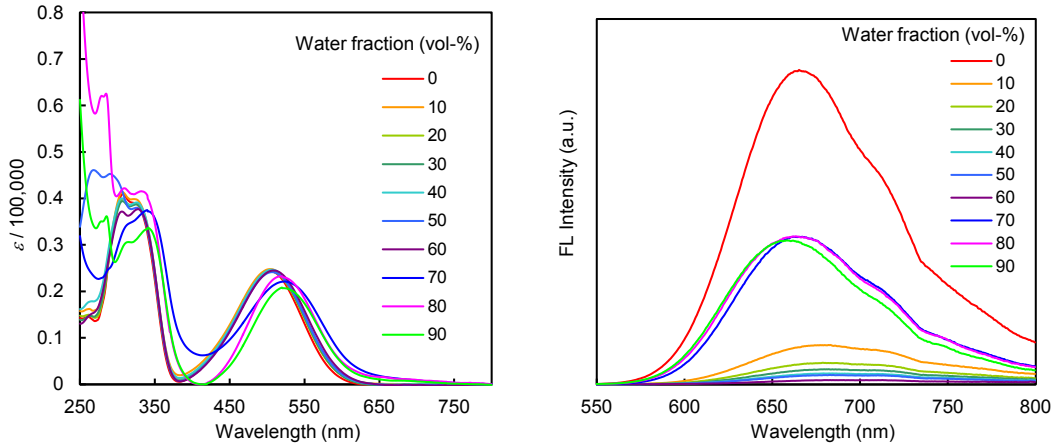


Fig. S16 UV/Vis and fluorescence (ex. 500 nm) spectra of **12** in THF/water (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, (v/v)) at 1.0×10^{-5} M (1 cm width cell).

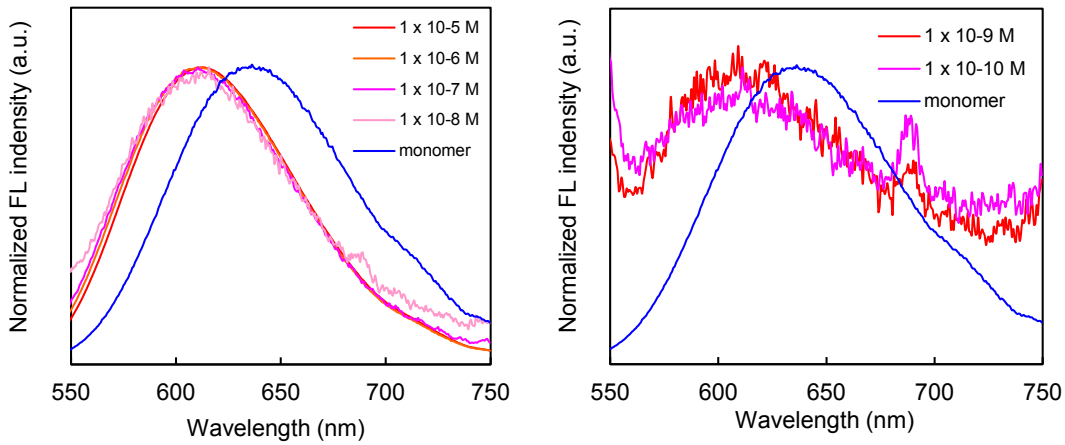


Fig. S17 Fluorescence spectra of **1a** in THF/water (1:9, v/v) at 1×10^{-5}, 1×10^{-6}, 1×10^{-7}, 1×10^{-8}, 1×10^{-9}, and 1.0×10^{-10} M. The emission band was scarcely changed around 610 nm, which was different to the monomer emission around 640 nm in THF/water (5:5, v/v)

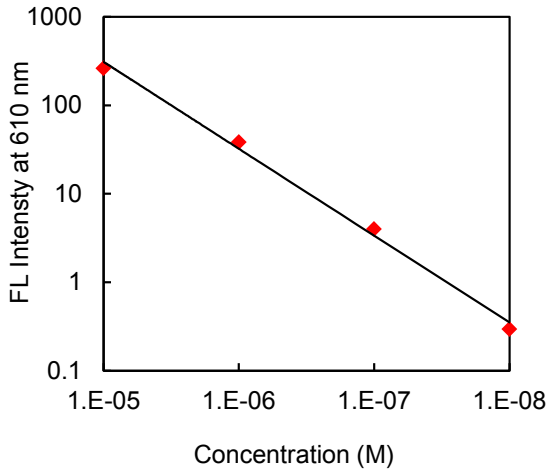


Fig. S18 Plot of the fluorescence intensity (at 610 nm) *versus* the concentration of **1a** in THF/water (1:9, v/v).

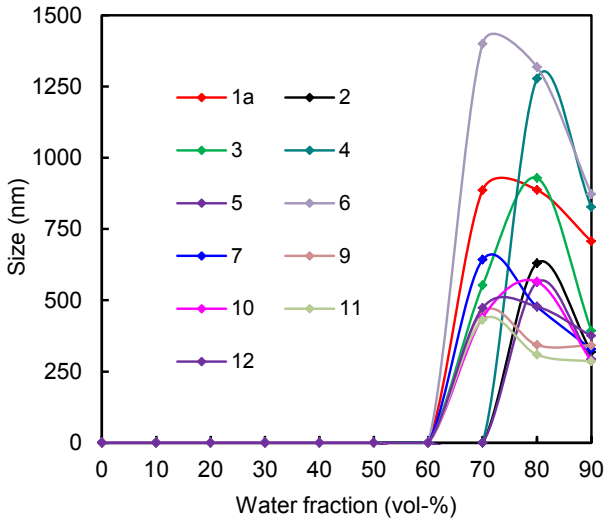


Fig. S19 Plots of the aggregate size measured by DLS *versus* the water fraction (vol%) of **1a**, **2**, **3**, **4**, **5**, **6**, **7**, **9**, **10**, **11**, and **12** in THF/water at 1.0×10^{-5} M. Aggregate size at 90% water fraction: 700 nm for **1a**, 320 nm for **2**, 390 nm for **3**, 830 nm for **4**, 290 nm for **5**, 870 nm for **6**, 330 nm for **7**, 340 nm for **9**, 290 nm for **10**, 290 nm for **11**, and 380 nm for **12**.

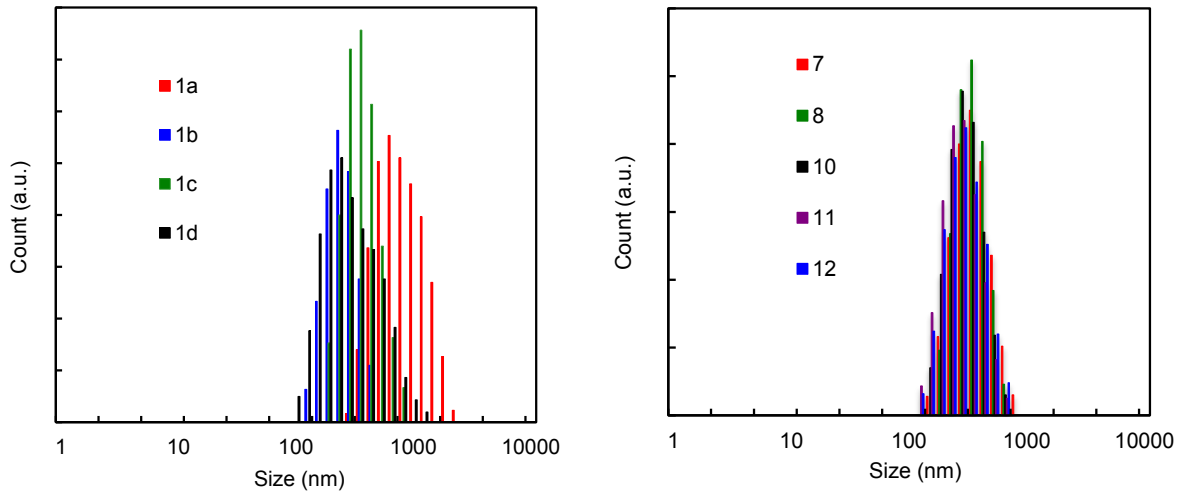


Fig. S20 DLS charts of **1a** (700 nm), **1b** (270 nm), **1c** (350 nm), **1d** (250 nm), **7** (330 nm), **8** (320 nm), **10** (290 nm), **11** (290 nm), and **12** (380 nm) in THF/water (1:9, v/v) at 1.0×10^{-5} M.

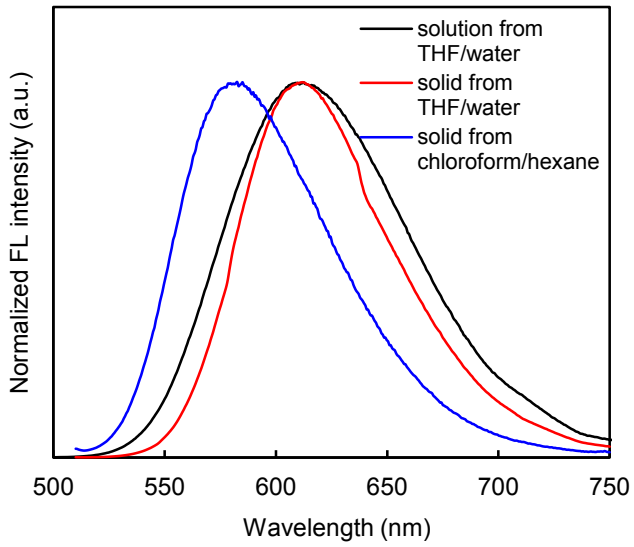


Fig. S21 Fluorescence spectra of **1a** in the solution and solid state: aggregate solution in THF/water (90% water fraction), powder-like solid sample from THF/water (90% water fraction), and crystalline-like solid sample from chloroform/hexane. The fluorescence spectrum (610 nm) of the powder-like sample was similar to that (610 nm) of the aggregate solution, but not to that (580 nm) of the crystalline-like sample. Thus, the aggregate structure formed in THF/water media is preserved in the powder-like solid state. In the THF/water media, less-ordered aggregation proceeded owing to the nonplanar triphenylamine moieties, preventing an ordered packing of the molecules and thus producing an increased number of conformations of the molecules. In contrast, one of the conformer was obtained mainly in the crystalline-like sample, leading to the difference of emission band.

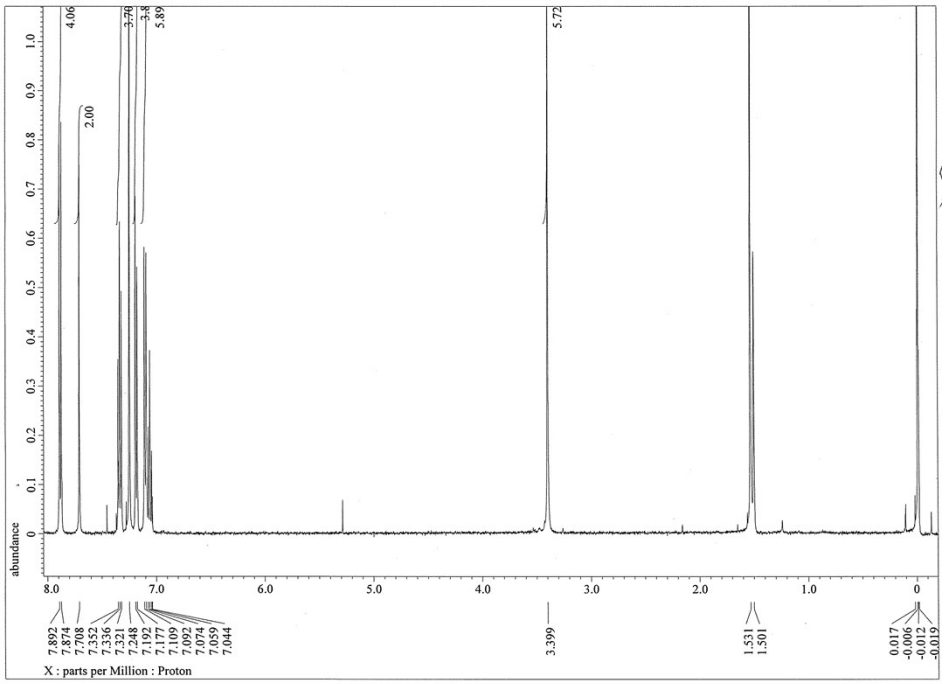


Fig. S22 ^{1}H NMR spectrum of **5** in $CDCl_3$.

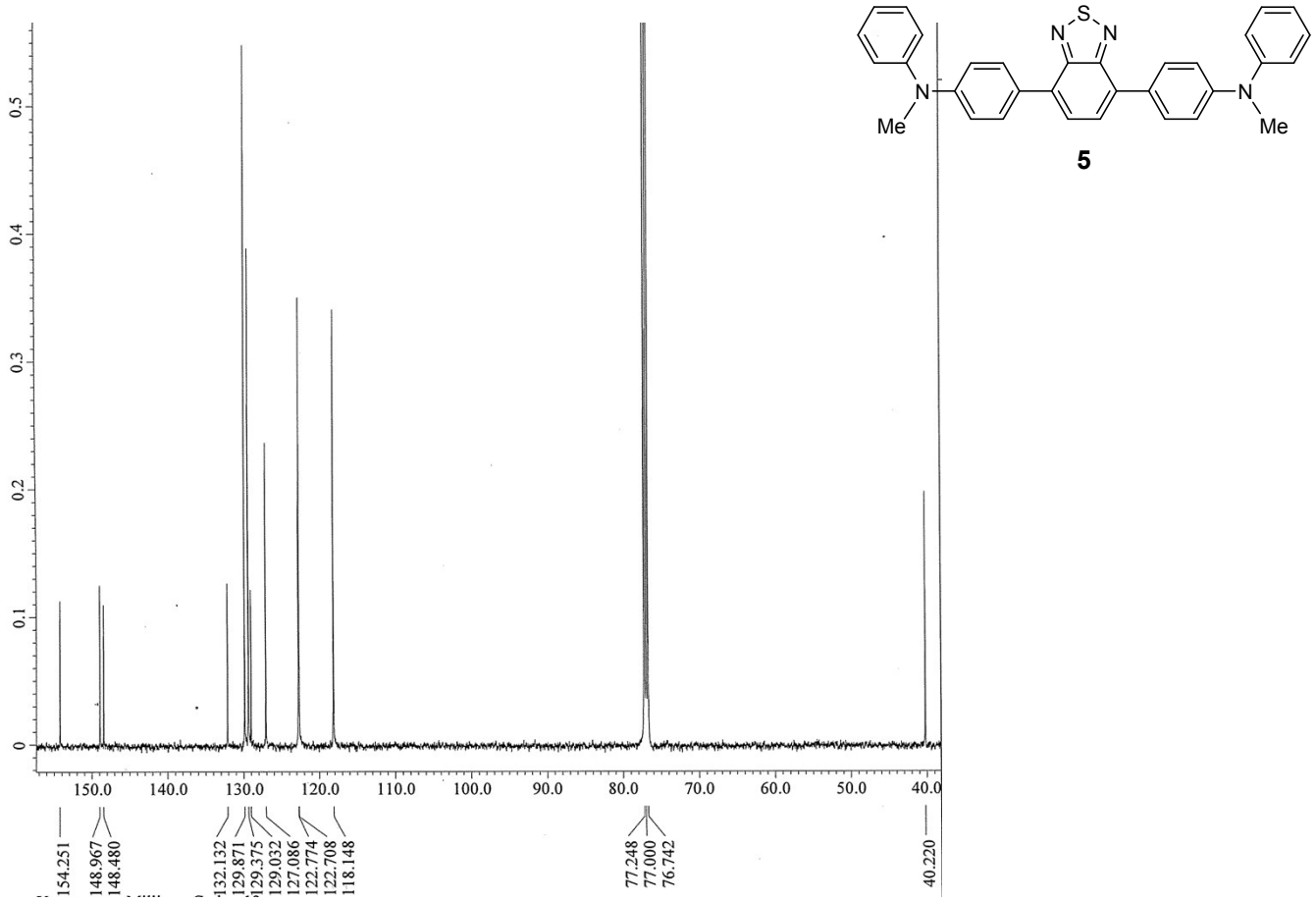


Fig. S23 ^{13}C NMR spectrum of **5** in $CDCl_3$.

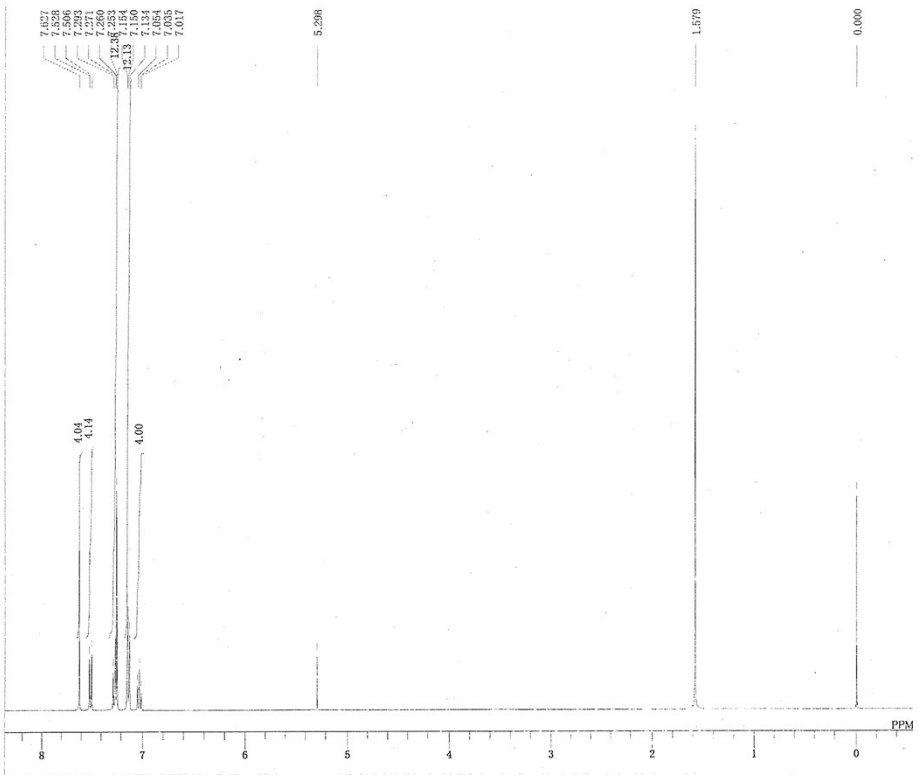
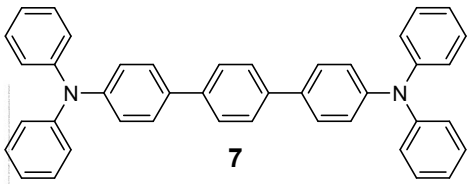


Fig. S24 ^{1}H NMR spectrum of **7** in $CDCl_3$.



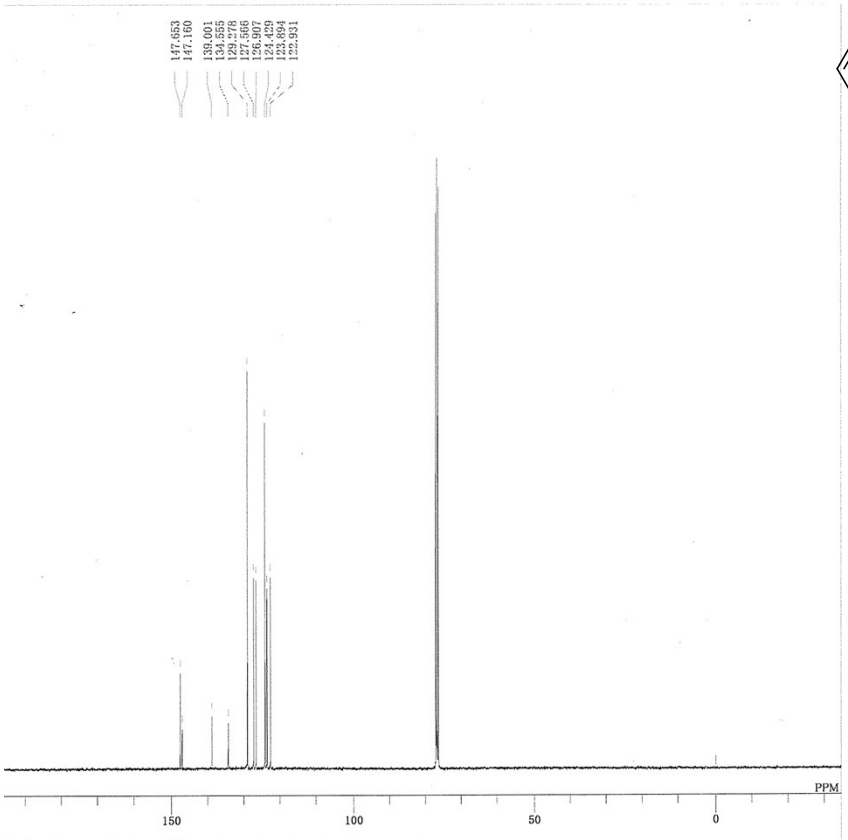


Fig. S25 ^{13}C NMR spectrum of **7** in $CDCl_3$.

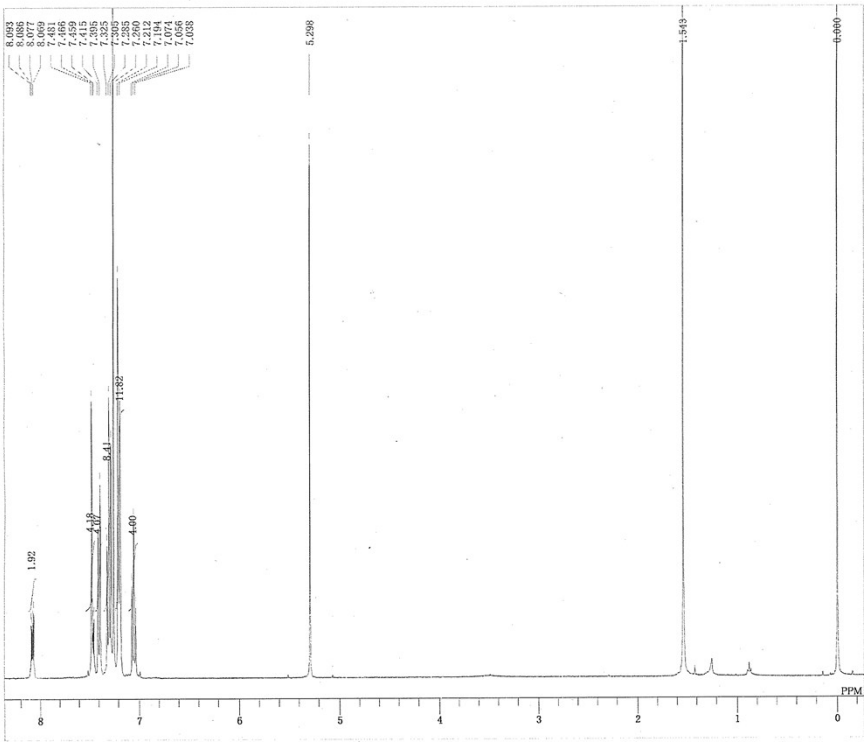
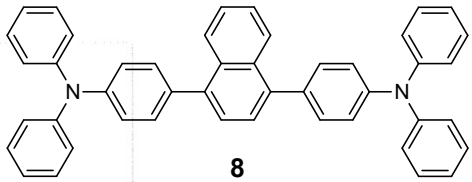


Fig. S26 ^{1}H NMR spectrum of **8** in $CDCl_3$.



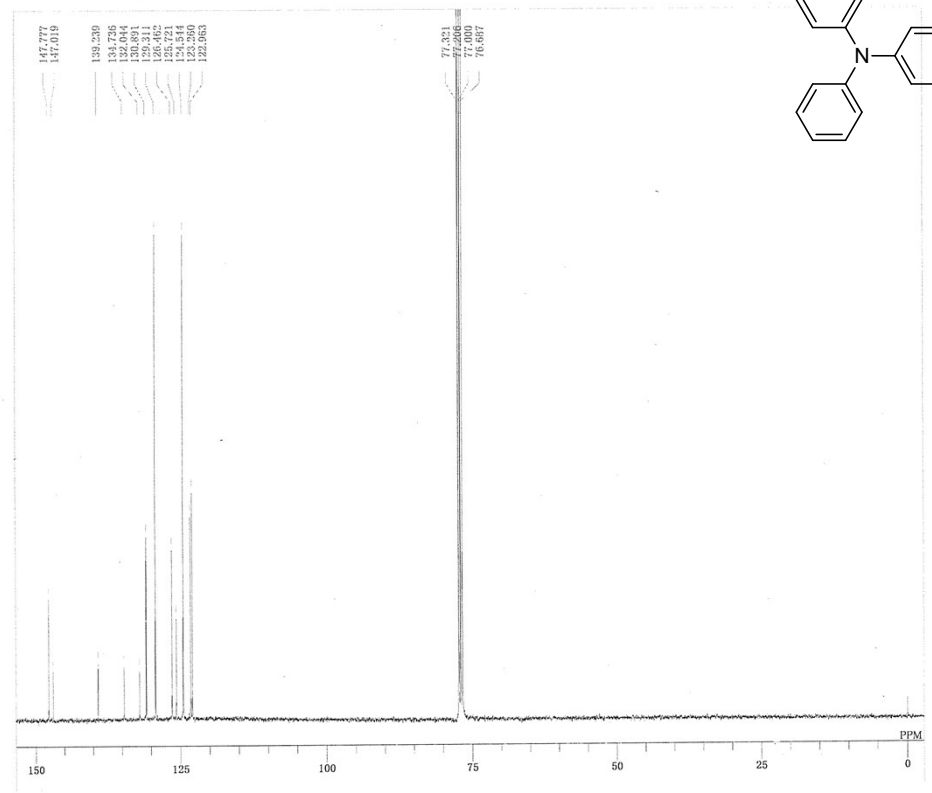


Fig. S27 ^{13}C NMR spectrum of **8** in $CDCl_3$.

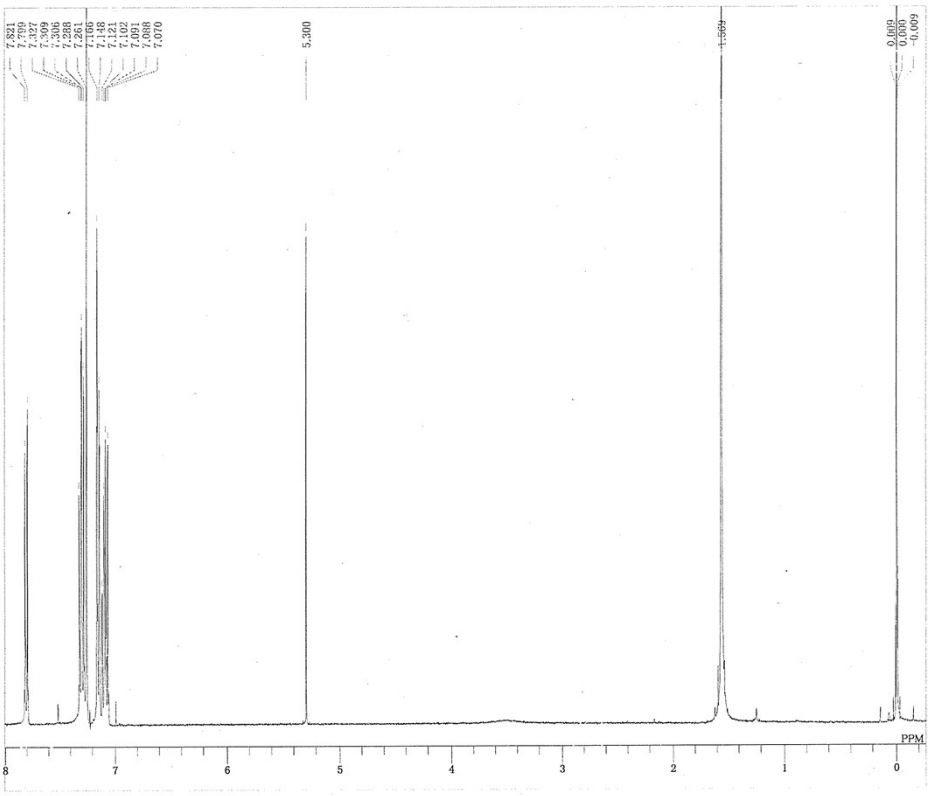
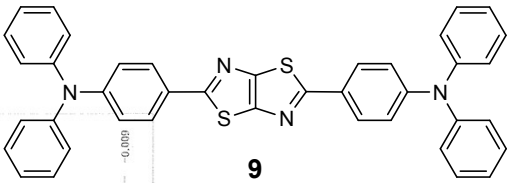


Fig. S28 ^{1}H NMR spectrum of **9** in $CDCl_3$.



9

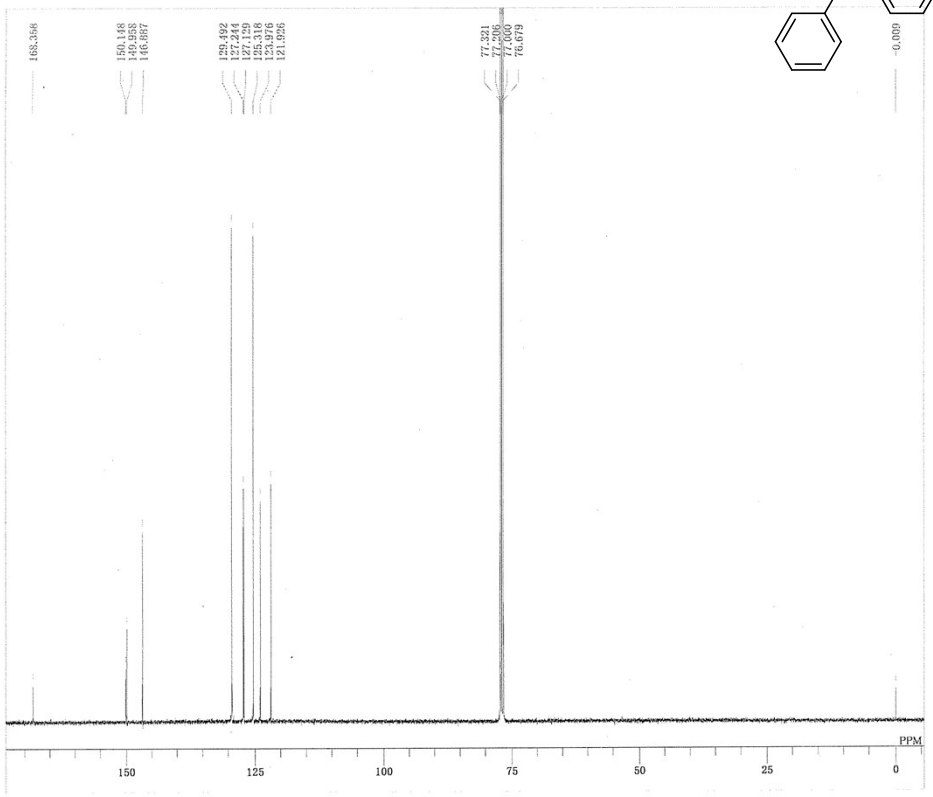


Fig. S29 ^{13}C NMR spectrum of **9** in $CDCl_3$.

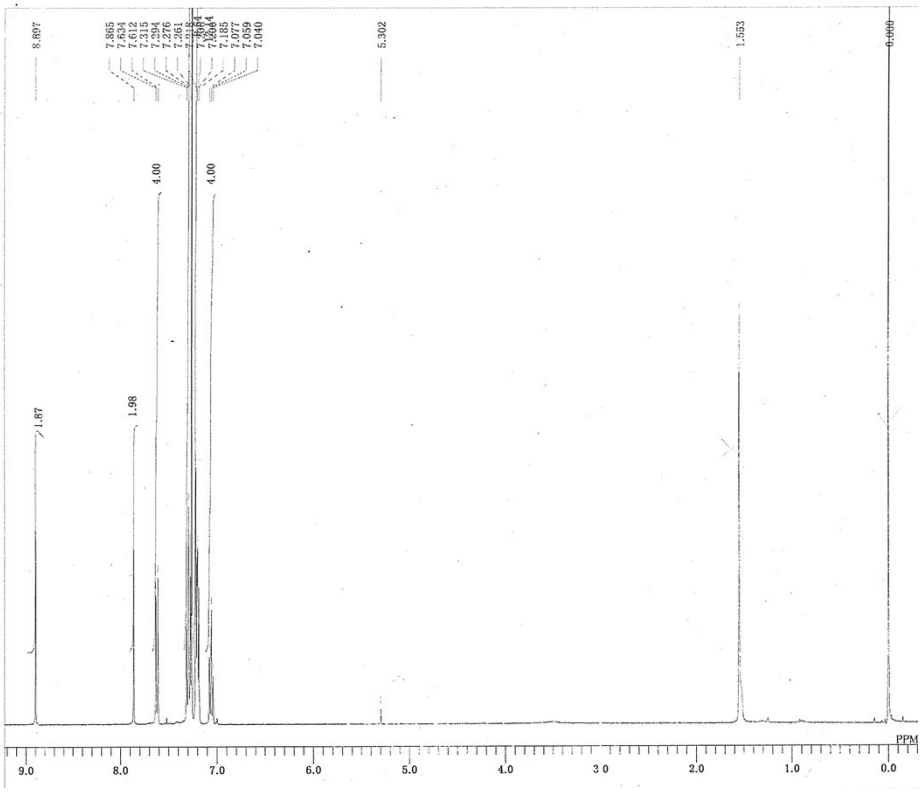
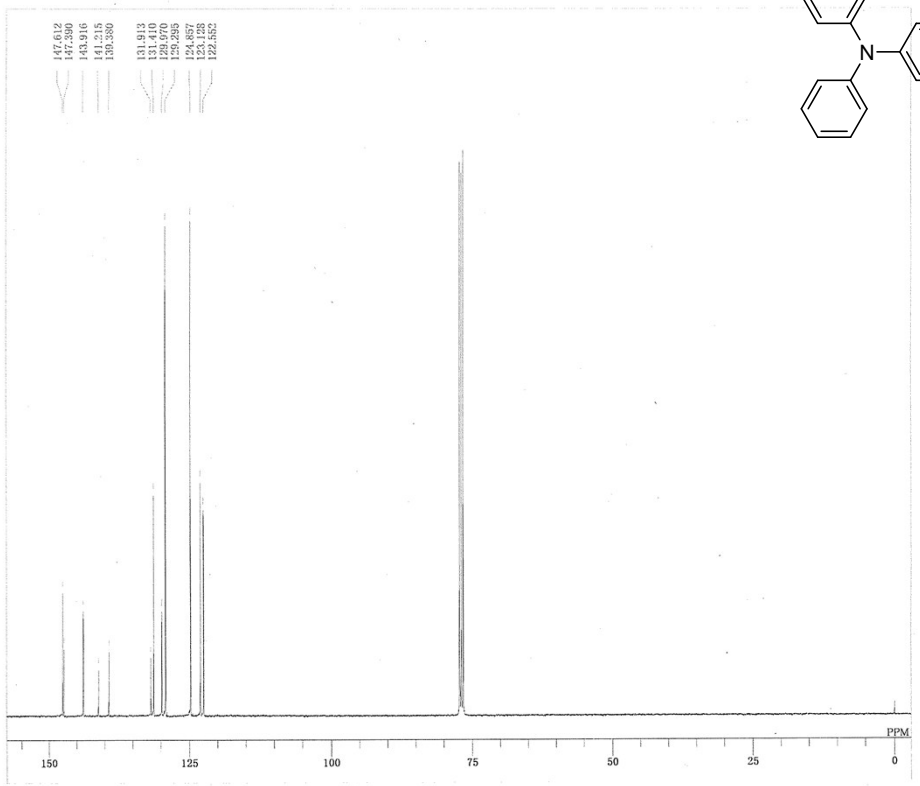
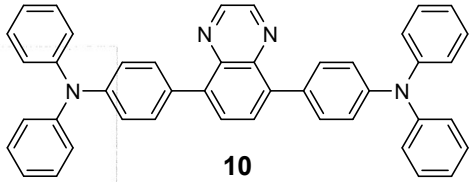


Fig. S30 ^{1}H NMR spectrum of **10** in $CDCl_3$.





10

Fig. S31 ^{13}C NMR spectrum of **10** in $CDCl_3$.

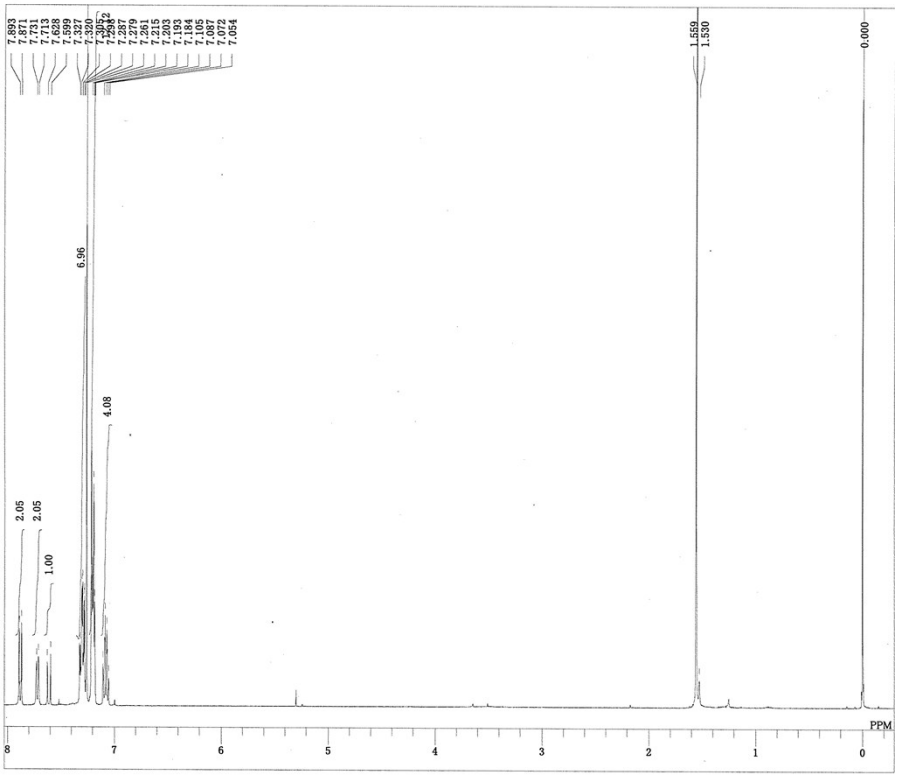
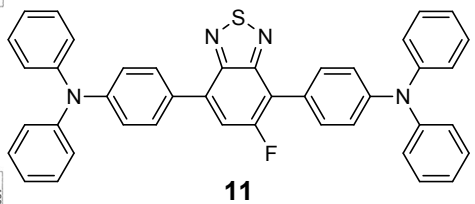


Fig. S32 ^{1}H NMR spectrum of **11** in $CDCl_3$.



11

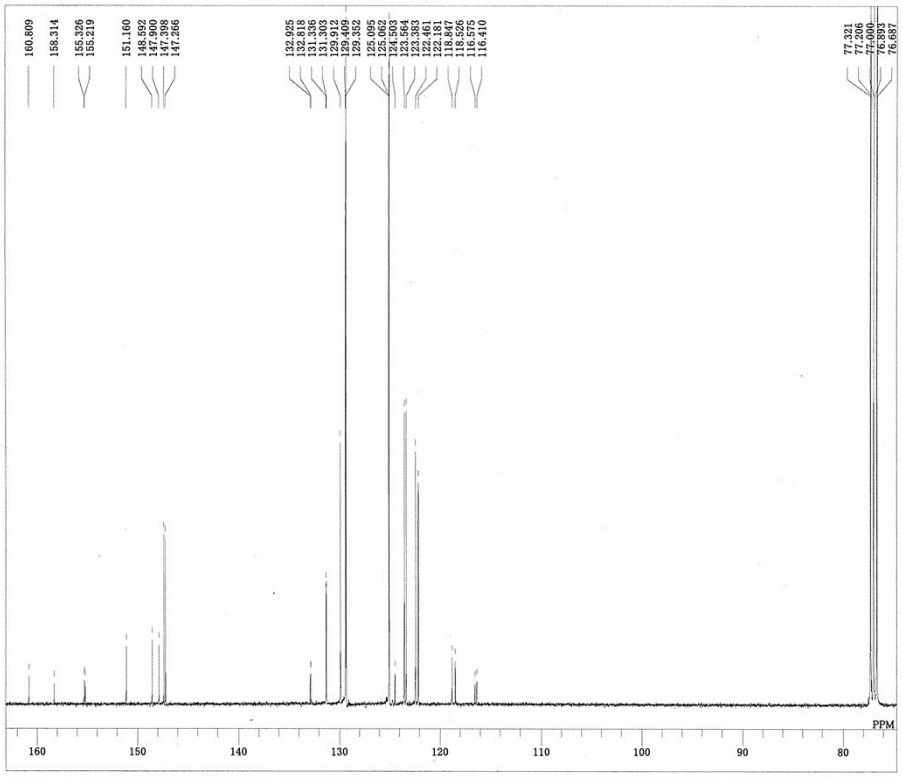


Fig. S33 ^{13}C NMR spectrum of **11** in $CDCl_3$.

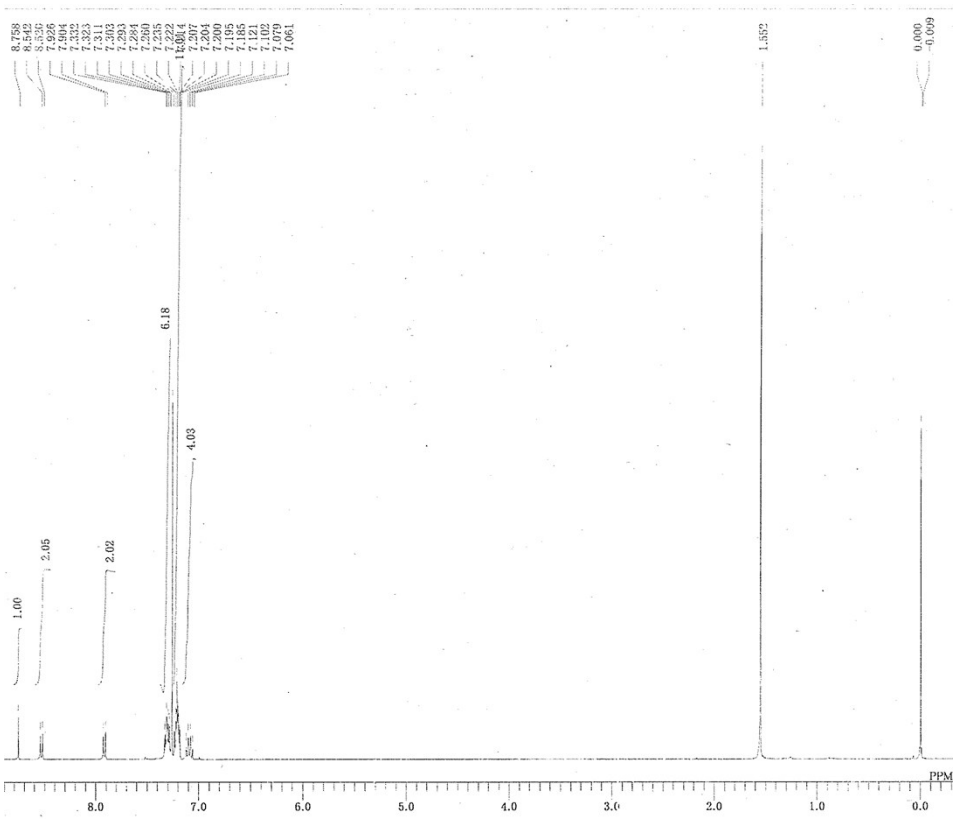
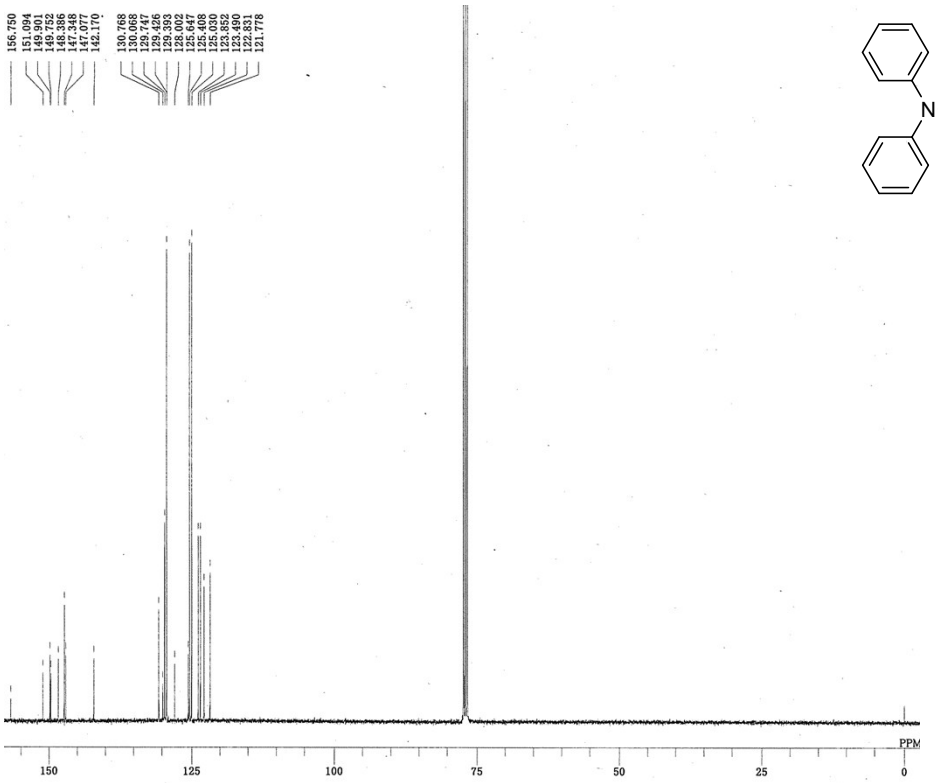
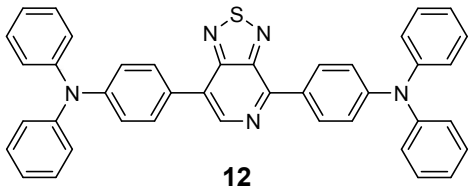


Fig. S34 ^{1}H NMR spectrum of **12** in $CDCl_3$.





12

Fig. S35 ^{13}C NMR spectrum of **12** in $CDCl_3$.

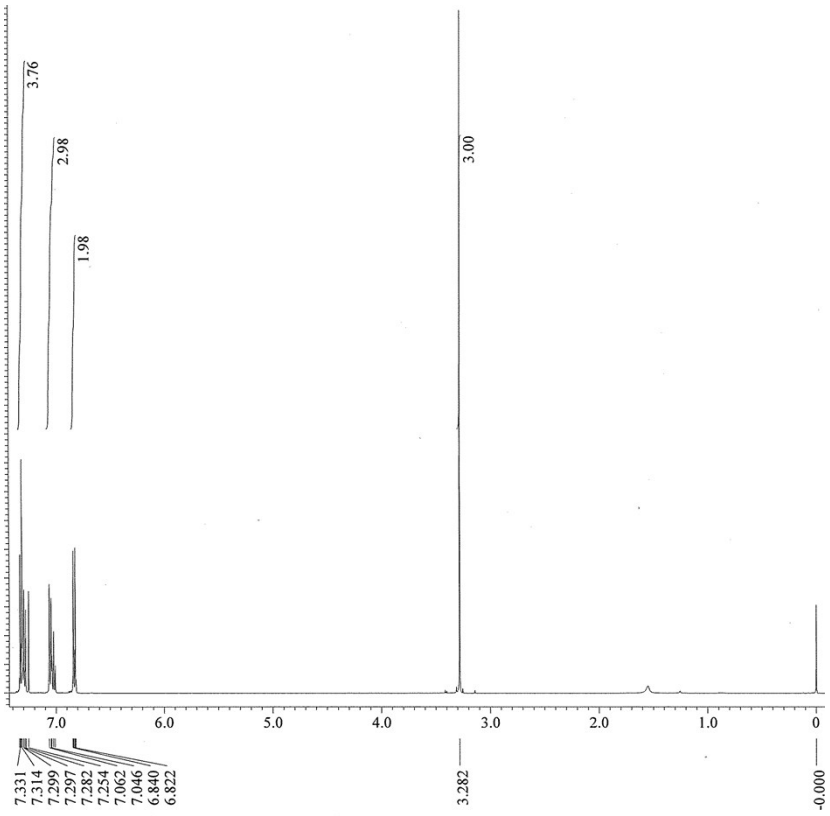
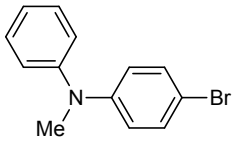


Fig. S36 ^{1}H NMR spectrum of **14** in $CDCl_3$.



14

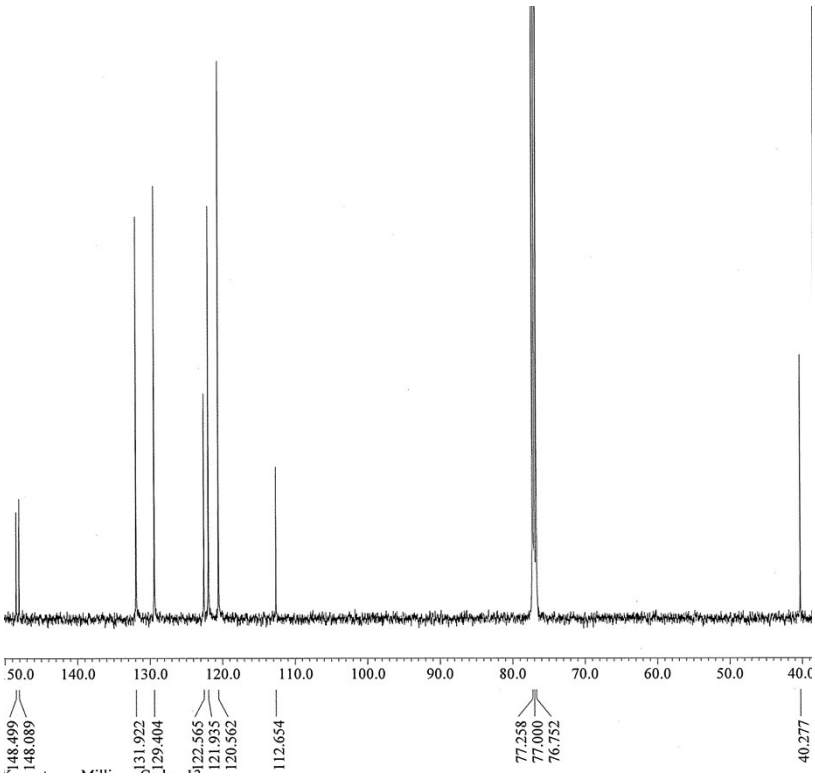


Fig. S37 ^{13}C NMR spectrum of **14** in $CDCl_3$.

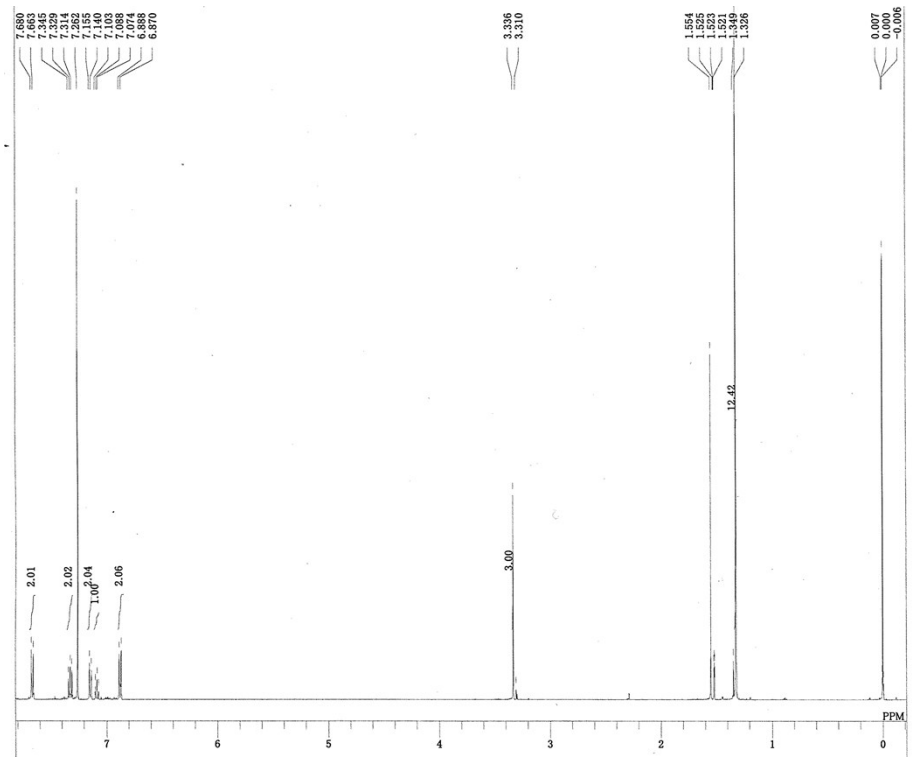
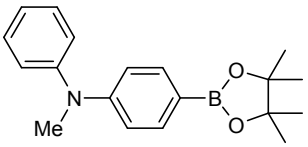


Fig. S38 ^{1}H NMR spectrum of **15** in $CDCl_3$.



15

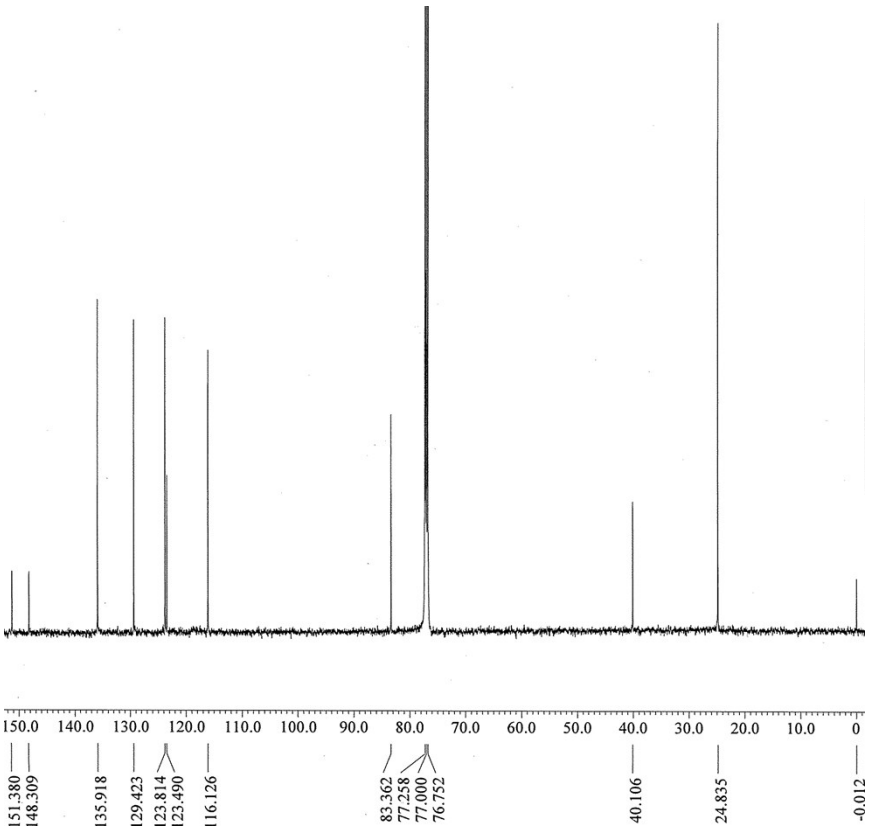


Fig. S39 ^{13}C NMR spectrum of **15** in $CDCl_3$.