Electronic Supplementary Information for

Chiral approach to investigate mechanism of highly efficient thermally activated delayed fluorescence†

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Section 1. Synthesis of chromophores

Enantiomers of 10,10'-bis[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-2,2'-dimethyl-10*H*,10'*H*-9,9'-spirobi[acridine] (**1**) consisting of a 2-2'-dimethyl-10*H*,10'*H*-9,9'-spirobi[acridine] moiety with chiral carbon as a donating unit and a 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine as an acceptor unit were synthesized. An achiral structure based on the conjugated back bone of **1** has been reported as a chromophore with a high external electroluminescence quantum yield of 35% in organic light emitting diodes.[5] Hence, we selected this state-of the-art back bone to study the influence of vibrations on f_f. To synthesize **1**, racemic 2-2′-dimethyl-10*H*,10′*H*-9,9′-spirobi[acridine] (**1d**) (Fig 1a) was first obtained by nucleophilic addition promoted by *n*-butyllithium (see Figs. S1-S10, ESI†).[14] Enantiomers of **1d** were separated by chiral column chromatography (see Fig. S11, ESI†). The enantiomers of **1** were synthesized by Buckwald–Hartwig amination with enantiomers of **1d** and 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (see Figs. S12-S15, ESI†). Chromophores were identified using proton nuclear magnetic resonance (^{1}H NMR) and ^{13}C NMR (ECA-500, JEOL, Japan) spectroscopy and high-resolution electrospray (ESI) analysis (JMS-T100 AccuTOF, Jeol). Detailed information regarding synthesis and purification procedures are as follows.

2-(*p*-Tolyamino)benzonic acid:

p-Toluidine (2.50 g, 23.4 mmol), 2-bromobenzonic acid (4.67 g, 23.3 mmol), copper(I) oxide (1.72 g, 12.0 mmol), *N*-methylmorpholine (3.90 mL, 35.5 mmol) were dissolved in dioxane (60 mL) and stirred under nitrogen at reflux (100 °C) for 3 h. After the mixture cooled to room temperature (RT), 1 N sodium hydroxide (NaOH, 155 mL) was added to the solution. The 1 N NaOH phase (155 mL) was extracted with dichloromethane (30 mL × 3). After addition of 1 N hydrochloric acid (HCl) the pH of the aqueous phase became 2 and a precipitate appeared on standing for 1 h, which was filtered to yield 2-(*p*-tolyamino)benzonic acid (4.48 g, 84.4%) as a pale yellow solid. ^{1}H NMR (DMSO-D_6, 500 MHz): δ = 9.57 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 15.0 Hz, 1H), 7.11–7.19 (m, 5H), 6.73 (t, *J* = 14.5 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (DMSO, 125 MHz): δ =170.53, 148.25, 138.23, 134.72, 133.07, 132.38, 130.48, 122.72, 117.41, 113.84, 112.45, 20.97; HRMS-ESI (m/z): $[M+H]^+$ calcd. for $C_{14}H_{14}N_1O_2$, 228.102; found, 228.101.

2-Methylacridin-9(10*H*)-one:

2-(*p*-Tolyamino)benzonic acid (5.00 g, 22.0 mmol) and polyphosphoric acid (45.7 g) were stirred at 120 °C for 3.5 h under ambient conditions. After the mixture cooled to RT, iced water (100 mL) was added followed by 1 N NaOH. The pH of the solution became 7, and a precipitate appeared on standing, which was filtered to yield 2-methylacridin-9(10*H*)-one (3.61 g, 78.3%) as a yellow solid. ^{1}H NMR (DMSO-D_6, 500 MHz): δ = 11.67 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.03 (s, 1H), 7.69–7.73 (m, 1H), 7.46–7.58 (m, 3H), 7.22–7.25 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (DMSO, 125 MHz): δ =177.08, 141.32, 139.52, 135.46, 133.76, 130.62, 126.54, 125.60, 121.26, 120.90, 120.88, 117.86, 117.81, 21.14; HRMS-ESI (m/z): $[M+H]^+$ calcd. for $C_{14}H_{12}N_1O_1$, 210.092; found, 210.091.

10-[(2-Methoxyethoxy)methyl]-2-methylacridin-9(10*H*)-one:

Sodium hydride (229.3 mg, 9.56 mmol) and 2-methylacridin-9(10*H*)-one (1.00 g, 4.80 mmol) were taken in anhydrous *N*,*N*-dimethylformamide (DMF) (15 mL), stirred under nitrogen at RT for 45 min. After slow addition of 1-(chloromethoxy)-2-methoxyethane (1.10 mL, 9.56 mmol) to the solution over 10 min, the solution was stirred at RT for 2 h. After addition of water to the solution, the aqueous phase was extracted with ethyl acetate (30 mL × 3) and the combined extracts were dried over sodium sulfate (Na_2SO_4) and filtered. Evaporation of the solvent gave the crude product. The resulting crude material was purified by column chromatography (silica gel, acetone/hexane; 20:80 v/v as the eluent) to yield 10-[(2-methoxyethoxy)methyl]-2-methylacridin-9(10*H*)-one as a pale yellow solid (811 mg, 56.8%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.53 (d, *J* = 8.0, 1H), 8.32 (s, 1H), 7.69–7.73 (m, 2H), 7.62 (d, *J* = 9.0, 1H), 7.54–7.56 (m, 1H), 7.29–7.33 (m, 1H), 5.81 (s, 2H), 3.84–3.86 (m, 2H), 3.62–3.64 (m, 2H), 3.44 (s, 3H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ =178.40, 142.34, 140.51, 135.39, 133.82, 131.75, 127.63, 126.92, 122.34, 122.27, 121.83, 115.24, 115.17, 76.96, 72.20, 67.26, 59.20, 20.63; HRMS-ESI (m/z): $[M+H]^+$ calcd. for $C_{18}H_{20}N_1O_3$, 298.144; found, 298.143.

***tert*-Butyl phenyl(*p*-tolyl)carbamate:**

4-Methyl-*N*-phenylaniline (2.01 g, 11.0 mmol) and di-*tert*-butyl dicarbonate (4.88 g, 22.4 mmol) were dissolved in anhydrous tetrahydrofuran (THF) (60 mL) and stirred under nitrogen at RT for 24 h. After addition of water to the solution, the aqueous phase was extracted with ethyl acetate (30 mL × 3) and the combined extracts were dried over Na_2SO_4 and filtered. Evaporation of the solvent gave the crude product. The resulting

crude material was purified by column chromatography (silica gel, dichloromethane/hexane; 40:60 v/v as an eluent) to yield *tert*-butyl phenyl(*p*-tolyl)carbamate as a white solid (2.07 g, 66.5 %). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.27–7.31 (m, 2H), 7.20–7.22 (m, 2H), 7.08–7.16 (m, 5H), 2.32 (s, 3H), 1.44 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ =153.95, 143.21, 140.48, 135.41, 129.35, 128.62, 126.92, 126.78, 125.41, 80.99, 28.25, 20.96; HRMS-ESI (m/z): $[M+Na]^+$ calcd. for $C_{18}H_{21}N_1Na_1O_2$, 306.147; found, 306.147.

2-2′ -dimethyl-10*H*,10′ *H*-9,9′ -spirobi[acridine] (1d):

tert-Butyl phenyl(*p*-tolyl)carbamate (700 mg, 2.35 mmol), *N*,*N*,*N*′,*N*′,-tetramethylethylenediamine (TMEDA) (0.56 mL, 3.77 mmol) were taken in anhydrous THF (5.5 mL) under nitrogen. *n*-Buthyllithium (*n*-BuLi) 1.6 M (3.53 mmol) in hexane (2.21 ml) was added to the solution at −78 °C under nitrogen and stirred for 3 h. 10-[(2-methoxyethoxy)methyl]-2-methylacridin-9(10*H*)-one (667 mg, 2.35 mmol) in THF (14 mL) was added to the solution with stirring at −78 °C under nitrogen for 4 h. After heating the solution to room-temperature, 0.5 N HCl (2.8 mL) was added and the resulting mixture stirred for 1 h before a further addition of 0.5 N HCl (14.0 mL) to the solution with stirring for 48 h. An aqueous K_2CO_3 solution was added to the mixture and the pH of the resulting solution became approximately 7. The aqueous phase was extracted with dichloromethane, dried over Na_2SO_4, and filtered. Evaporation of the solvent yielded the crude deuterated product. The resulting crude material was purified by column chromatography (silica gel, dichloromethane/hexane; 50:50 v/v as the eluent) to give a white solid. The white solid was again purified by column chromatography (silica gel, ethyl acetate/hexane; 16:84 v/v as the eluent) to yield **1d** as a white solid (186.3 mg, 21.2 %). ^{1}H NMR (DMSO-D_6, 500 MHz): δ = 8.90 (s, 2H), 6.91–6.94 (m, 2H), 6.73–6.79 (m 6H), 6.66–6.67 (m, 2H), 6.50-6.55 (m, 4H), 1.97 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ =135.81, 133.65, 132.58, 132.35, 130.76, 130.31, 129.81, 127.82, 126.75, 120.51, 113.00, 47.08, 20.82; HRMS-ESI (m/Z): $[M+H]^+$ calcd. for $C_{27}H_{23}N_2$, 375.186; found, 375.190. Enantiomers of **1d** were separated with a Shimadzu (Kyoto, Japan) HPLC system（an LC-10AT pump or an LC-6AD semi-preparative pump with a SPD-10A UV-detector) equipped with Chirakpak IA (Daicel, Japan) with hexane:isopropanol = 9:1. The chiral purities of the separated enantiomers 1 and 2 of **1d** were 89%ee and 83%ee (Figure

S1), respectively.

Enantiomer 1 of 10,10′-bis[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-2,2′-dimethyl-10*H*,10′*H*-9,9′-spirobi[acridine] (Enantiomer 1 of 1):

Enantiomer 1 of **1d** (31.0 mg, 0.083 mmol), 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (78.0 mg, 0.20 mmol), sodium t-butoxide (19.5 mg, 0.20 mmol), tris(dibenzylideneaceton)dipalladium(0) [$Pd_2(dba)_3$] (1.6 mg, 0.0017 mmol), tri-*t*-butylphosphine (0.010 mL, 0.0036 mmol) in dry toluene (1.0 mL) was heated at reflux (110 °C) under a nitrogen atmosphere for 24 h. After cooling, the solvent was evaporated to dryness, and dichloromethane was added. The organic phase was washed with H_2O (3 × 20 mL), dried over Na_2SO_4, and purified by column chromatography (silica gel; dichloromethane/hexane; 20/80 as the eluent) to yield enantiomer 1 of **1** as a yellow powder (26.7 mg, 32.6%). The powder was further purified by sublimation. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.12–9.09 (m, 4H), 8.84–8.86 (m, 8H), 7.69–7.72 (m, 4H), 7.61–7.68 (m, 12H), 7.21 (dd, *J* = 7.5, 1.5, 2H), 7.02 (d, *J* = 2.0, 2H), 6.91–6.94 (m, 2H), 6.78–6.81 (m, 2H), 6.74–6.78 (m, 2H), 6.40 (dd, *J* = 8.5, 1.0, 2H), 6.33 (d, *J* = 8.5, 2H), 2.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ =171.91, 171.12, 145.55, 138.25, 136.46, 136.32, 136.09, 133.02, 132.75, 132.72, 131.93, 131.85, 131.80, 131.50, 130.14, 129.06, 128.76, 127.64, 126.60, 120.83, 113.94, 113.81, 47.03, 20.74; HRMS-ESI (m/z): $[M+H]^+$ calcd. for $C_{69}H_{49}N_8$, 989.408; found, 989.406; Anal. Calcd. for $C_{69}H_{48}N_8$: C, 83.78; H, 4.89; N, 11.33. Found C, 84.01; H, 5.09; N, 11.59.

Enantiomer 2 of 10,10′-bis[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-2,2′-dimethyl-10*H*,10′*H*-9,9′-spirobi[acridine] (Enantiomer 2 of 1):

Enantiomer 1 of **1d** (20.3 mg, 0.054 mmol), 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (53.2 mg, 0.14 mmol), sodium *t*-butoxide (15.7 mg, 0.16 mmol), $Pd_2(dba)_3$ (1.8 mg, 0.0020 mmol), tri-*t*-butylphosphine (0.010 ml, 0.0036 mmol) in dry toluene (1.0 mL) was heated under reflux at approximately 110 °C under a nitrogen atmosphere for 24 h. After cooling, the solvent was evaporated to dryness, and dichloromethane was added. The organic phase was washed with H_2O (3 × 20 mL), dried over Na_2SO_4, and purified by column chromatography (silica gel; dichloromethane/hexane; 20/80 as the eluent) to yield enantiomer 2 of **1** as a yellow powder (25.0 mg, 44.6%). The powder was further purified by sublimation. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.12–9.09 (m, 4H), 8.84–8.86

(m, 8H), 7.70–7.72 (m, 4H), 7.61–7.68 (m, 12H), 7.21 (dd, J = 6.5, 1.5, 2H), 7.02 (d, J = 1.5, 2H), 6.91–6.94 (m, 2H), 6.78–6.81 (m, 2H), 6.75–6.78 (m, 2H), 6.40 (dd, J = 7.0, 1.0, 2H), 6.33 (d, J = 8.5, 2H), 2.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ =171.89, 171.10, 145.52, 138.21, 136.44, 136.30, 136.06, 133.02, 132.75, 132.72, 131.92, 131.84, 131.80, 131.48, 130.13, 129.05, 128.76, 127.63, 126.59, 120.83, 113.92, 113.80, 47.00, 20.74; HRMS-ESI (m/z): $[M+H]^+$ calcd. for $C_{69}H_{49}N_8$, 989.408; found, 989.407.

Section 2. Other experimental procedures

2-1. Film preparation

A solution of chromophore **1** (0.2 mg) and 1,3-bis(carbazol-9-yl)benzene (mCP) in chloroform (0.25 mL) was spin casted on to a quartz substrate in condition of 750 rpm for 60 s to prepare a 10 wt% chromophore **1**-doped mCP film. The mCP film doped with 10 wt% enantiomer 1 of chromophore **1** and an mCP film doped with 10 wt% enantiomer 2 of chromophore **1** were prepared by the same procedure.

2-2. Measurements of photophysical properties

Absorption spectra were measured with an absorption spectrometer (V−630, Jasco, Ltd., Tokyo, Japan). Emission spectra and quantum yields were measured with an absolute luminescence quantum yield measurement system (C9920−02G, Hamamatsu Photonics, Shizuoka, Japan). The emission lifetime was determined using a compact fluorescence lifetime spectrometer (Quantaurus−Tau, Hamamatsu Photonics). Circular dichroism (CD) and circularly polarized luminescence (CPL) spectra were measured using a circular dichroism dispersion meter (J-720, JASCO International Co., Ltd.) and a spectrofluoropolarimeter (CPL-200, JASCO International Co., Ltd.), respectively.

2-3. Quantum chemical calculations

The structure of (*S*)-chromophore **1** was optimized at the lowest singlet excited state (S_1) with Gaussian09 based on time-dependent density functional theory (TD-DFT) using the B3LYP functional and 6-31G(d) basis set. The energy difference between S_1 and T_1 (ΔE_{ST}) and the oscillator strength for fluorescence (f_f) was calculated based on the optimized S_1 structure. To calculate physical parameters relating to the dihedral angle between the donor and acceptor units (θ) and fluorescence, a variety of coordinates were constructed by changing θ based on the coordinates optimized at S_1. The energy change from the optimized S_1 coordinate (E), the probability of the chromophore based on the Boltzmann distribution at room-temperature (P), the optical rotation intensity for fluorescence (R_f), and f_f were calculated at each coordinate by TD-DFT [Gaussian09/B3LYP/6-31G(d)]. The average f_f ($\langle f_f \rangle$) was determined by integrating $f_f P$ over θ. To calculate physical parameters relating θ to the absorbance of the first absorption band, the S_0 geometry was optimized by DFT [Gaussian09/B3LYP/6-31G(d)]. After a variety of coordinates were constructed by changing θ based on the structure

optimized at S_0, the energy change (E_a) depending on θ was calculated by DFT [Gaussian09/B3LYP/6-31G(d)] and the probability of the chromophore existing at θ (P_a) was determined based on the Boltzmann distribution at room-temperature. The oscillator strength for absorption (f_a) and the optical rotation intensity for absorption (R_a) for the transition between the donor and acceptor with θ were calculated at each coordinate depending on θ by TD-DFT [Gaussian09/B3LYP/6-31G(d)]. The average f_a ($<f_a>$) was determined by integrating f_aP_a over θ.

Although the calculation of the transition dipole moment by TD-DFT based on the B3LYP functional may generally cause slightly different values because of different delocalization of HOMO and LUMO (E. R. Johnson, P. Mori-Sanchez, A. J. Cohen, W. T. Yang, *J. Chem. Phys*., 2008, **129**, 204112), the estimated $<f_f>$ based on TD-DFT with the B3LYP functional without intermolecular interactions was comparable to that optically measured f_f in toluene solution, for which restriction of the conformation change was not considered.

2-4. Determination of theoretical dissymmetry factors of CPL and CD

The dissymmetry factor of CPL (g_{lum}) and the dissymmetry factor of CD (g_{abs}) are generally respectively expressed as[17]:

$$g_{lum} = \frac{4|M_f|}{|\mu_f|} cos\delta_f , \quad (1)$$

$$g_{abs} = \frac{4|M_a|}{|\mu_a|} cos\delta_a , \quad (2)$$

where $\boldsymbol{M}_{\mathbf{f(a)}}$ is the magnetic transition dipole moment for fluorescence (absorption), $\boldsymbol{\mu}_{\mathbf{f(a)}}$ is the electric transition dipole moment for fluorescence (absorption), $\delta_{f(a)}$ is the angle between $\boldsymbol{M}_{\mathbf{f(a)}}$ and $\boldsymbol{\mu}_{\mathbf{f(a)}}$. The optical rotation intensity for fluorescence (absorption) [$R_{f(a)}$] is expressed as[17]:

$$R_{f(a)} = |\mu_{f(a)}||M_{f(a)}| cos\delta_{f(a)}. \quad (3)$$

Equations (1)-(2) convert into the following equation:

$$g_{lum(abs)} = 4\frac{R_{f(a)}}{|\mu_{f(a)}|^2}. \quad (4)$$

f_f and f_a are generally respectively expressed as[15]:

$$f_f = \left(\frac{8\pi^2 m_e c\langle\nu_f\rangle}{3he^2}\right)|\mu_f|^2, \quad (5)$$

$$f_a = \left(\frac{8\pi^2 m_e c\langle\nu_a\rangle}{3he^2}\right)|\mu_a|^2, \quad (6)$$

where m_e is the quantity of electron, c is the velocity of light, $\langle\nu_f\rangle$ is the average of fluorescence energy, $\langle\nu_f\rangle$ is the average of absorption energy at first absorption band, h is Planck constant, and e is the elementary charge. Equations (1)–(6) convert into the following equation

$$g_{lum(abs)} = A\frac{R_{f(a)}}{\mu_{f(a)}}, \quad (7)$$

where A is a constant.

The f_f and R_f values of a reference chiral compound with a known g_{lum} were calculated by TD-DFT [Gaussian09/B3LYP/6-31G(d)] with $A = 4.11\times10^{-6}$.[18] The calculated f_f and R_f values of (*S*)-chromophore **1** and $A = 4.11\times10^{-6}$ values were used to determine the theoretical g_{lum} of the (*S*)-chromophore **1**. The determination procedures were performed for the (*S*)-chromophore **1** at a variety of θ values to construct the relationship between g_{lum} and θ. The average g_{lum} ($<g_{lum}>$) was determined by integrating $g_{lum}P$ as a function of θ. The calculated f_a and R_a values of the (*S*)-chromophore **1** and $A = 4.11\times10^{-6}$ values were used to determine the theoretical g_{abs} of (*S*)-chromophore **1**. The determination procedures were performed for the (*S*)-chromophore **1** with a range of θ values to construct the relationship between g_{abs} and θ.

Section 3. Supporting Figures.

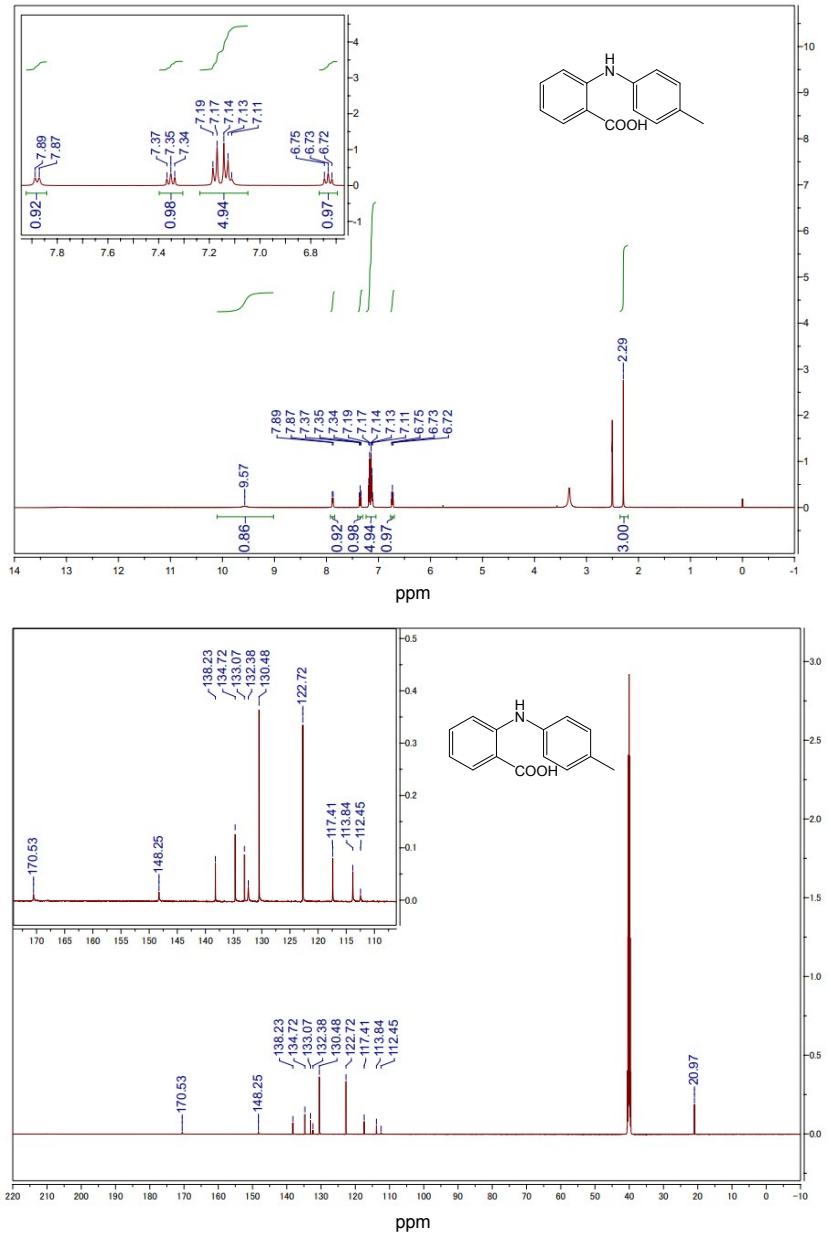

Figure S1. 1H and 13C NMR spectra of 2-(*p*-Tolyamino)benzonic acid.

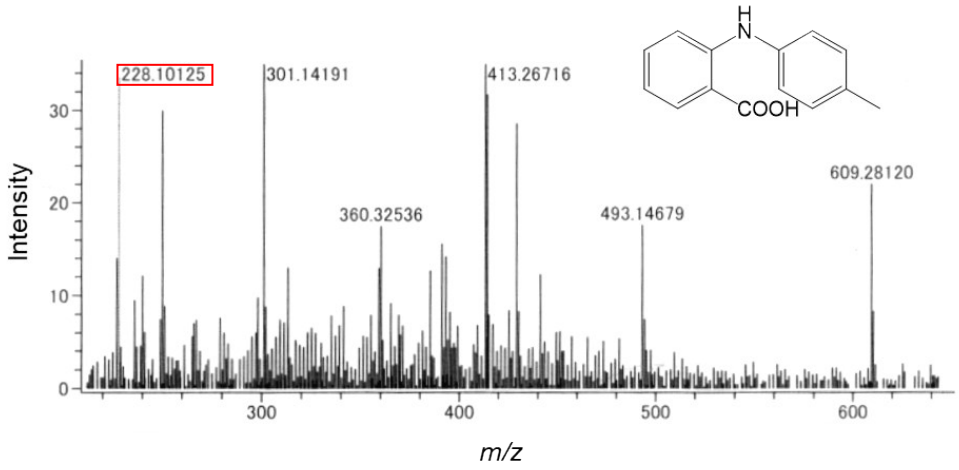

Figure S2. HRMS-ESI spectra of 2-(*p*-tolyamino)benzonic acid. Reserpine was added as a reference to check accuracy of values in equipment.

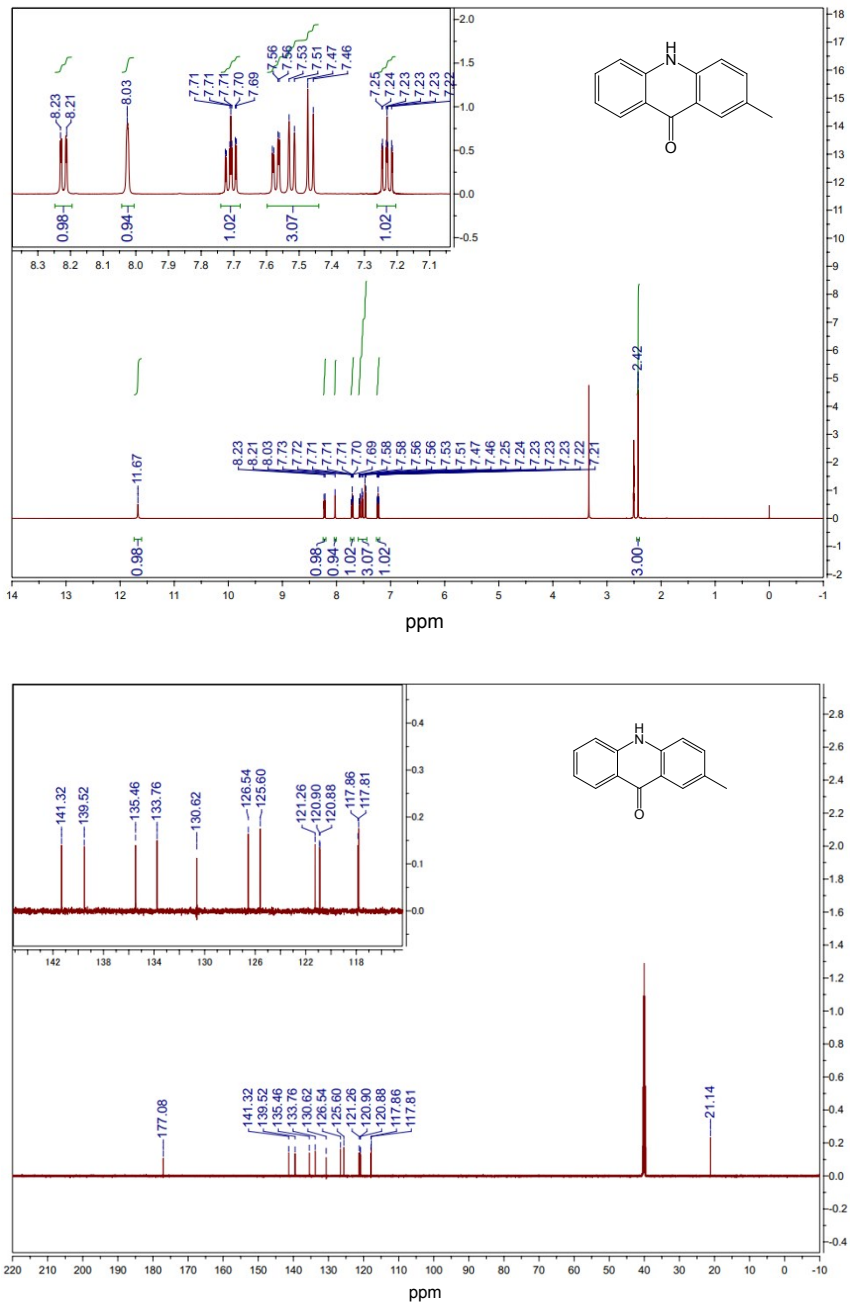

Figure S3. 1H and 13C NMR spectra of 2-methylacridin-9(10*H*)-one.

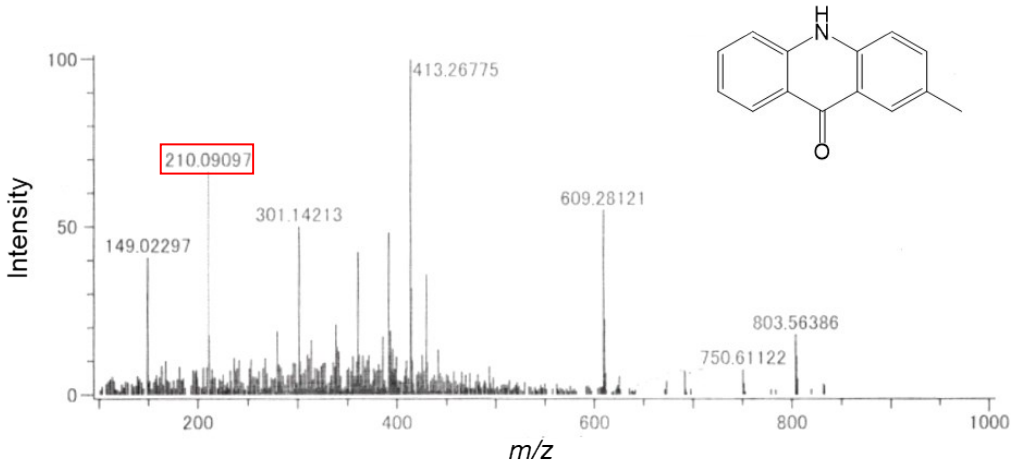

Figure S4. HRMS-ESI spectra of 2-methylacridin-9(10*H*)-one. Reserpine was added as a reference to check accuracy of values in equipment.

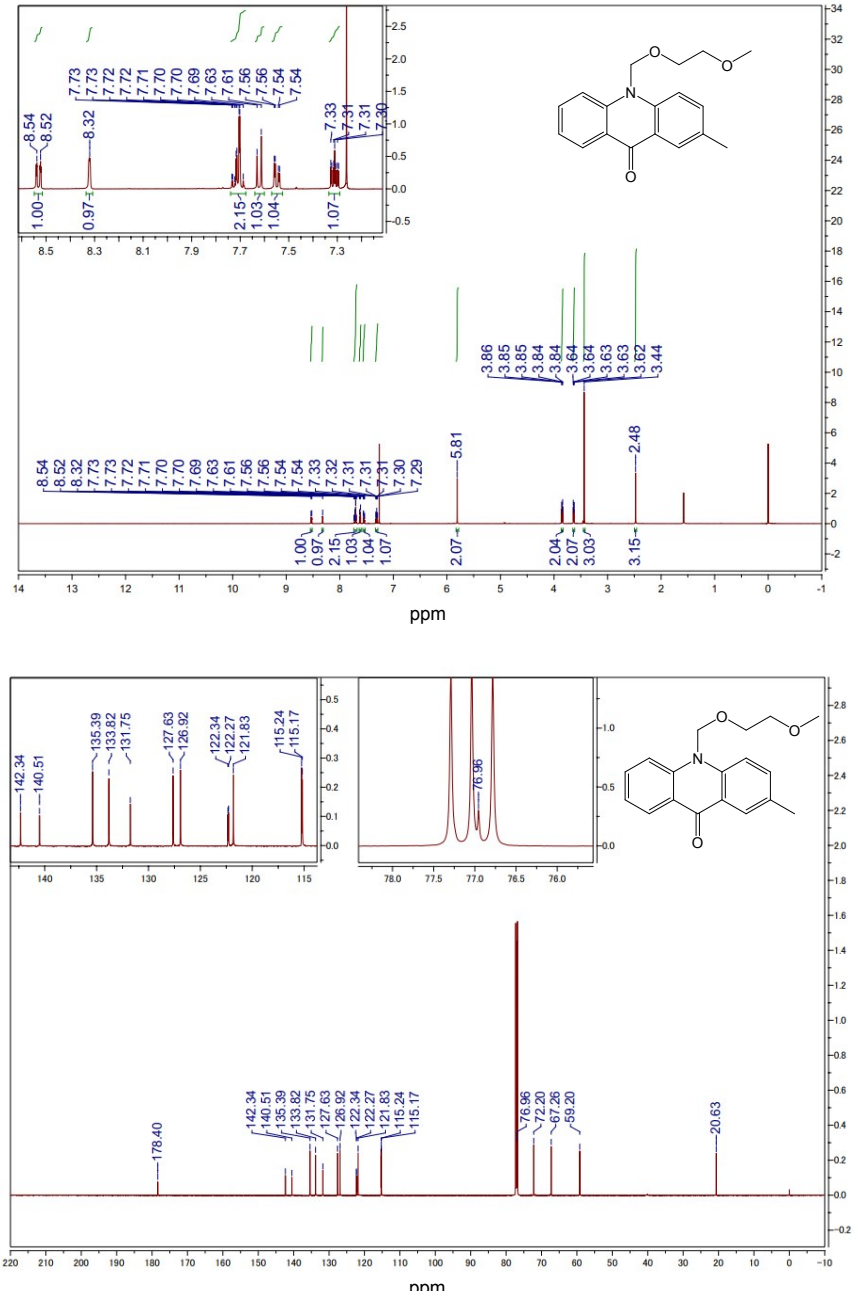

Figure S5. 1H and 13C NMR spectra of 10-[(2-methoxyethoxy)methyl]-2-methylacridin-9(10*H*)-one.

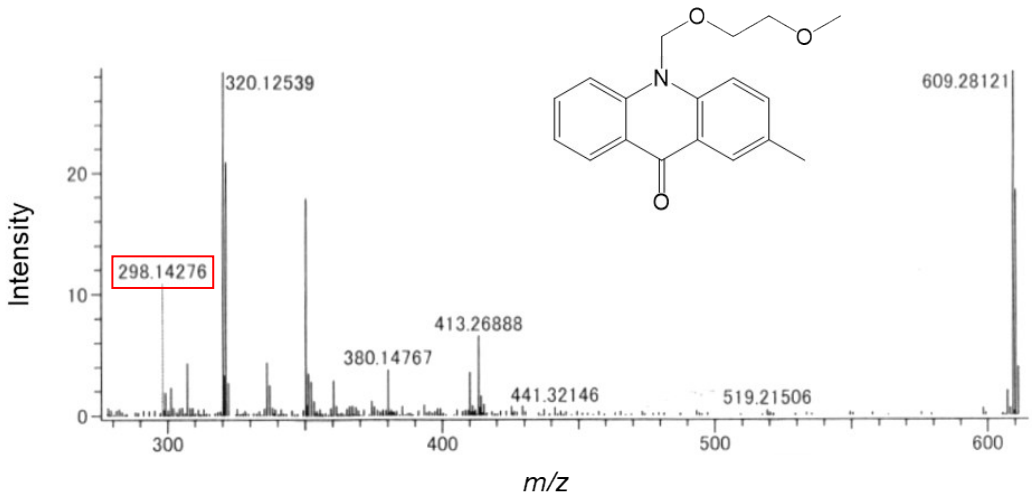

Figure S6. HRMS-ESI spectra of 10-[(2-methoxyethoxy)methyl]-2-methylacridin-9(10*H*)-one. Reserpine was added as a reference to check accuracy of values in equipment.

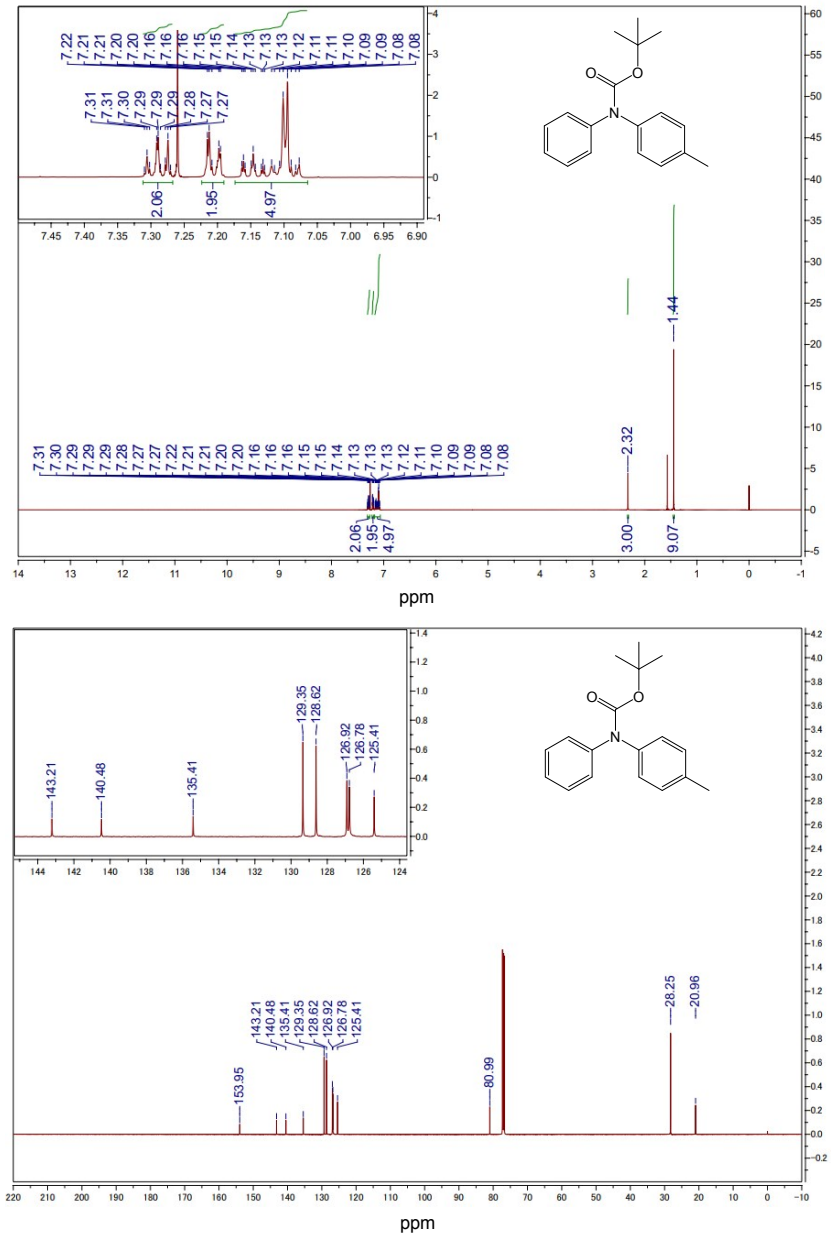

Figure S7. 1H and 13C NMR spectra of *tert*-Butyl phenyl(*p*-tolyl)carbamate.

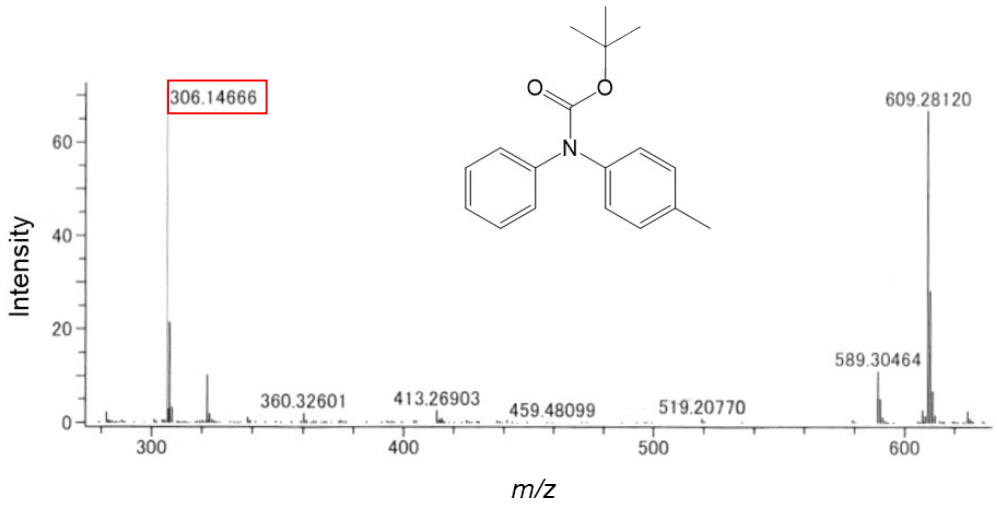

Figure S8. HRMS-ESI spectra of *tert*-butyl phenyl(*p*-tolyl)carbamate. Reserpine was added as reference to check accuracy of values in equipment.

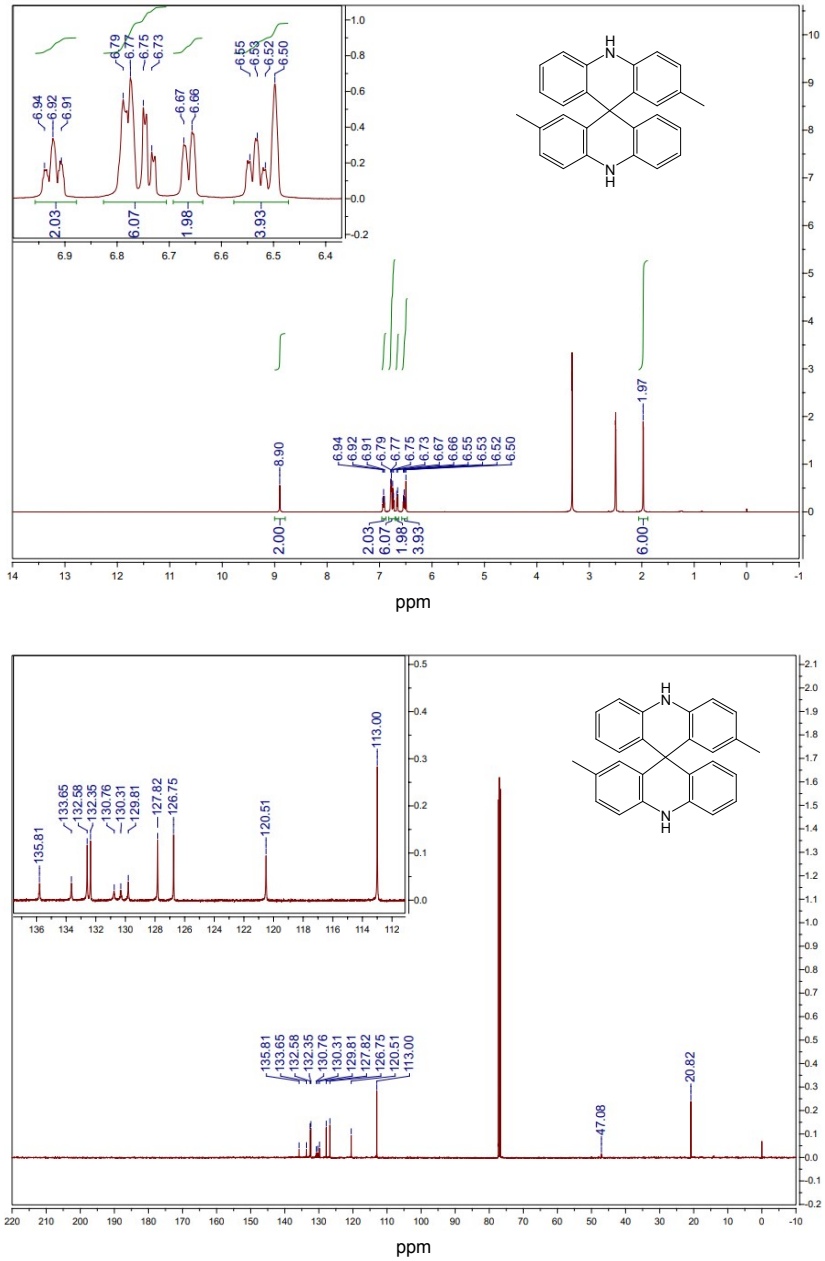

Figure S9. 1H and 13C NMR spectra of 2-2′-dimethyl-10*H*,10′*H*-9,9′-spirobi[acridine] (1d).

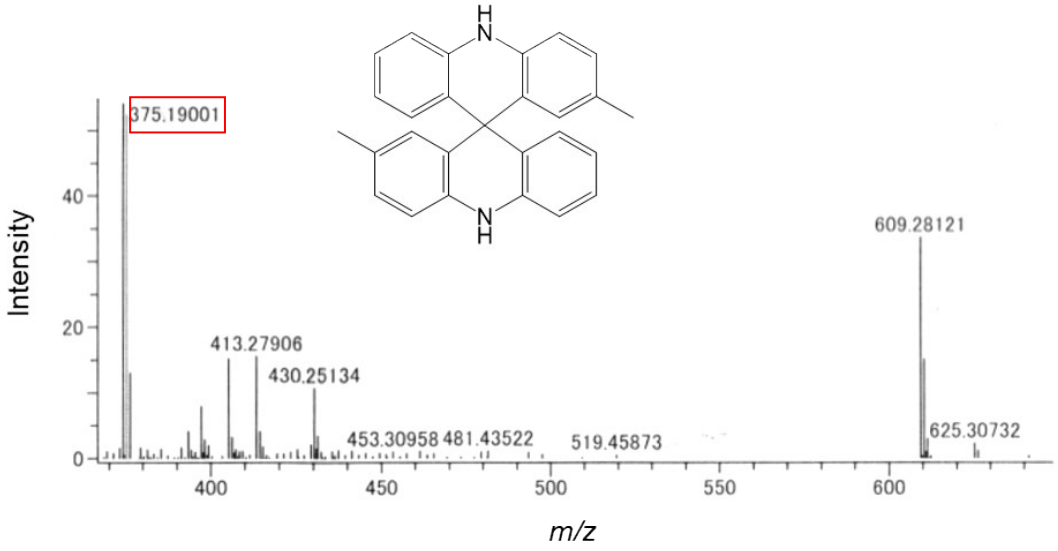

Figure S10. HRMS-ESI spectra of 2-2′-dimethyl-10*H*,10′*H*-9,9′-spirobi[acridine] (**1d**). Reserpine was added as a reference to check accuracy of values in equipment.

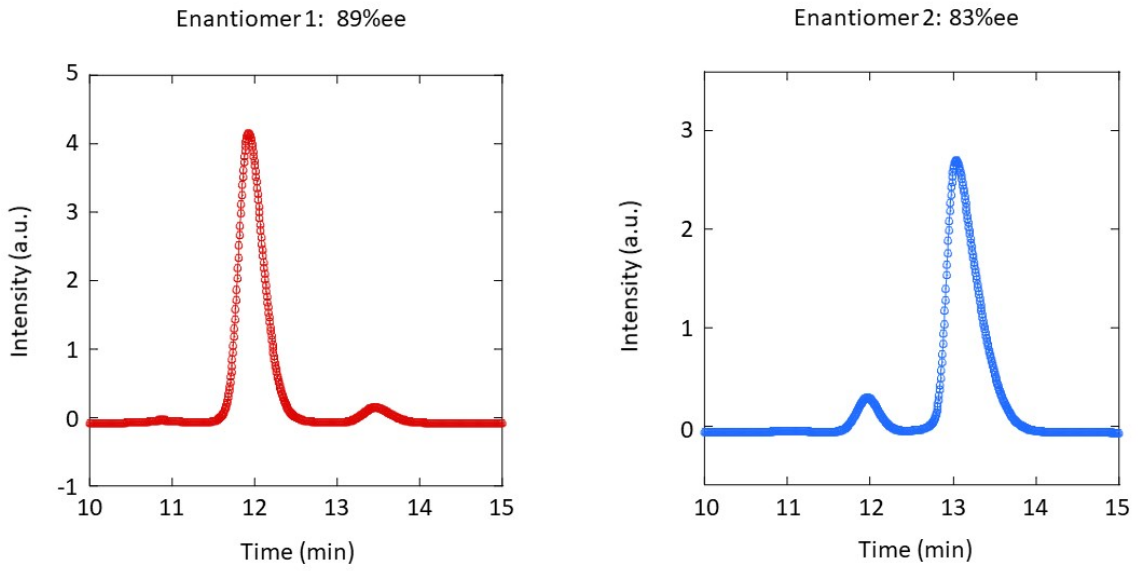

Figure S11. Profiles of high-performance liquid chromatography for the prepared enantiomers of **1d**. Chiral purities of the separated enantiomers 1 (left) and 2 (right) were 89%ee and 83ee%, respectively.

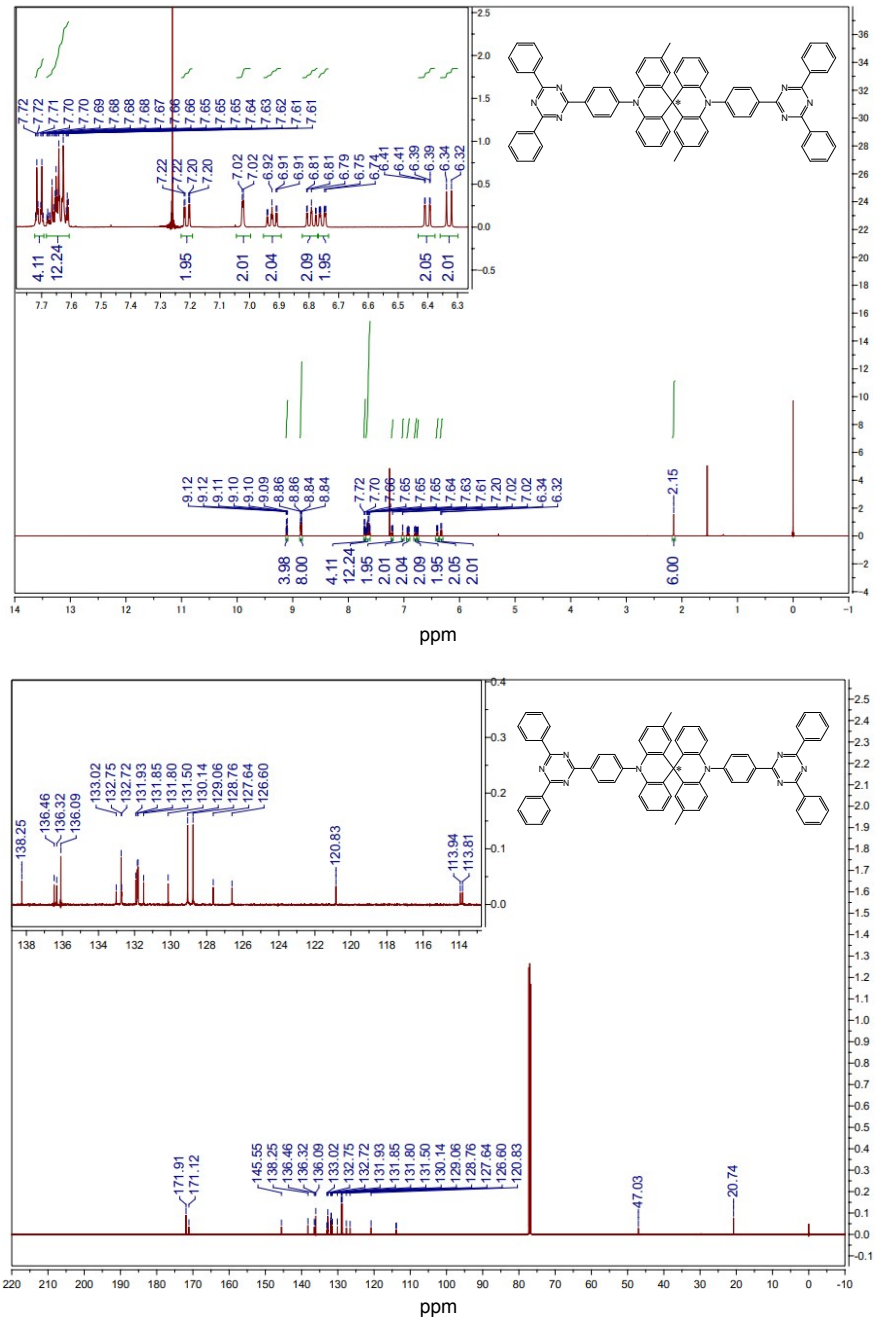

Figure S12. 1H and 13C NMR spectra of Enantiomer 1 of 10,10′-bis[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-2,2′-dimethyl-10*H*,10′*H*-9,9′-spirobi[acridine] (Enantiomer 1 of **1**).

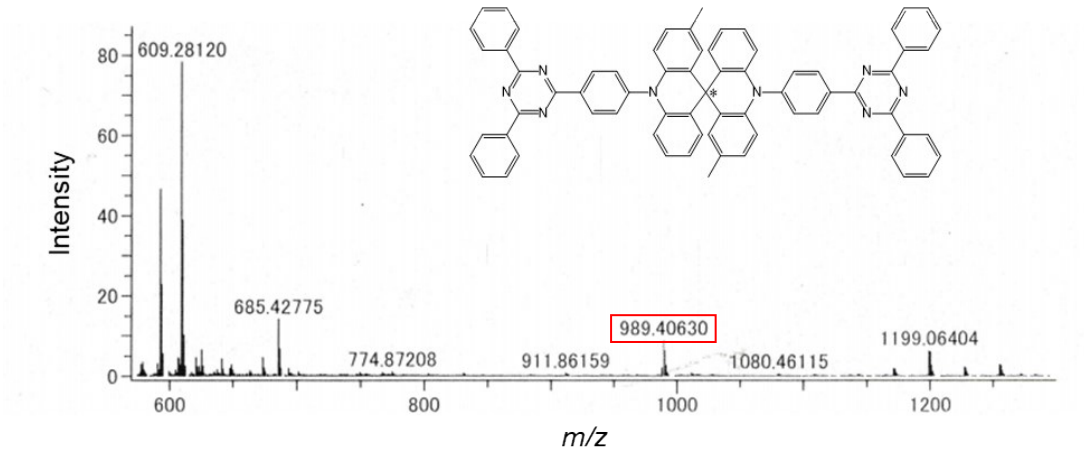

Figure S13. HRMS-ESI spectra of enantiomer 1 of 10,10′-bis[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-2,2′-dimethyl-10*H*,10′*H*-9,9′-spirobi[acridine] (enantiomer 1 of **1**). Reserpine was added as a reference to check accuracy of values in equipment.

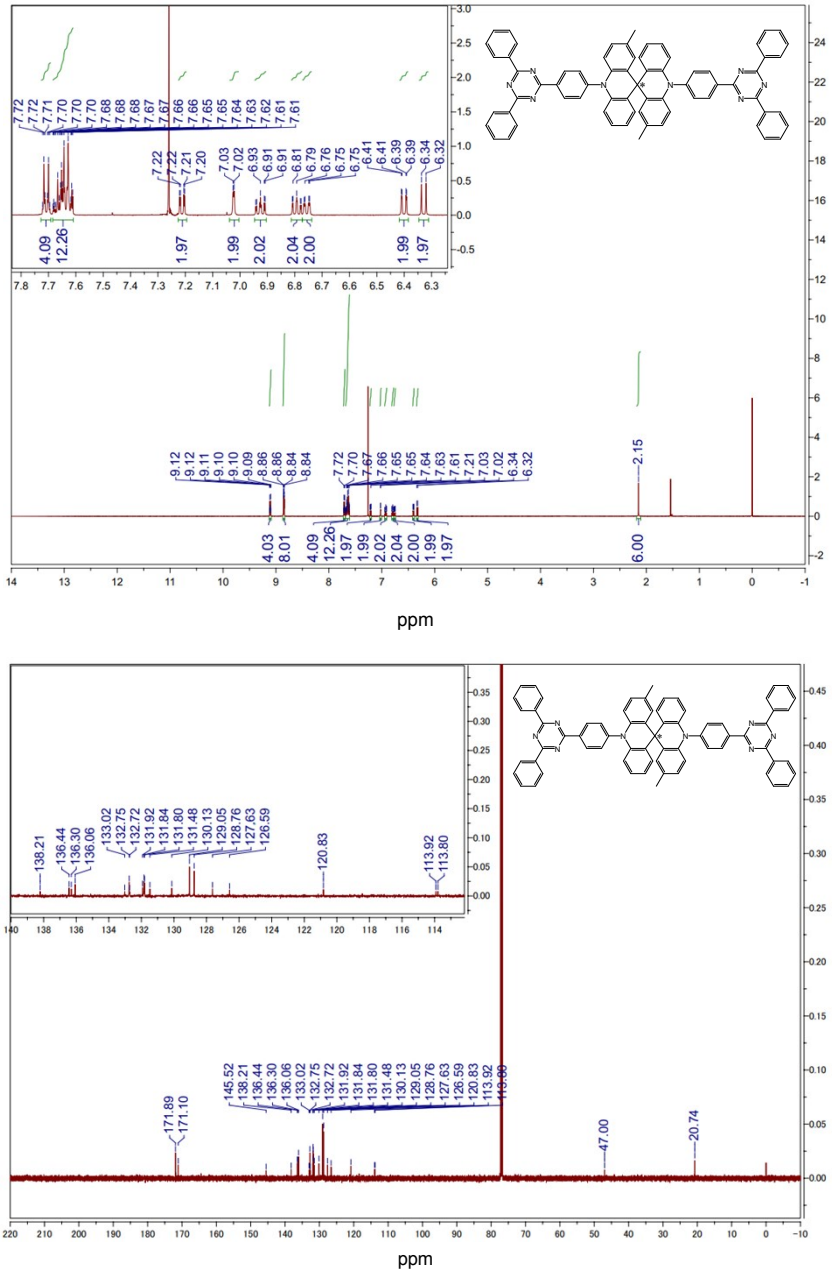

Figure S14. ^{1}H and ^{13}C NMR spectra of enantiomer 2 of 10,10′-bis[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-2,2′-dimethyl-10*H*,10′*H*-9,9′-spirobi[acridine] (enantiomer 2 of **1**).

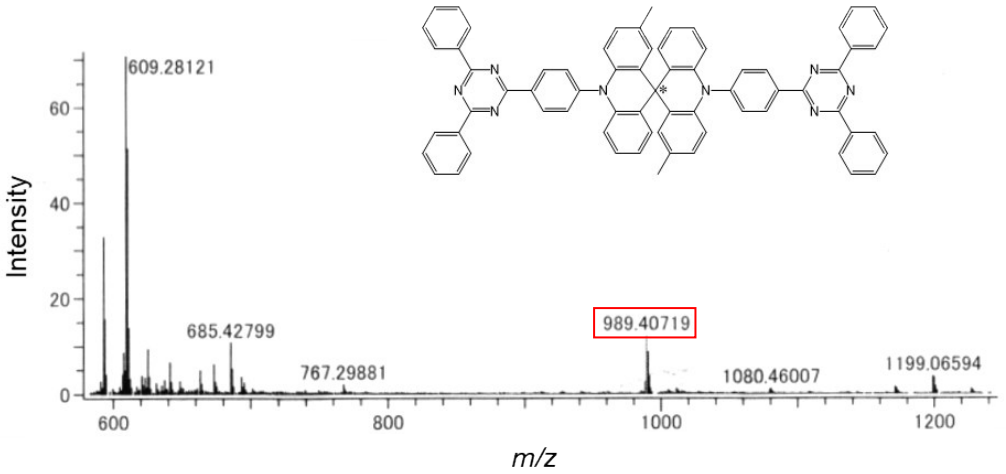

Figure S15. HRMS-ESI spectra of enantiomer 2 of 10,10′-bis[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-2,2′-dimethyl-10*H*,10′*H*-9,9′-spirobi[acridine] (enantiomer 2 of **1**). Reserpine was added as reference to check accuracy of values in equipment.

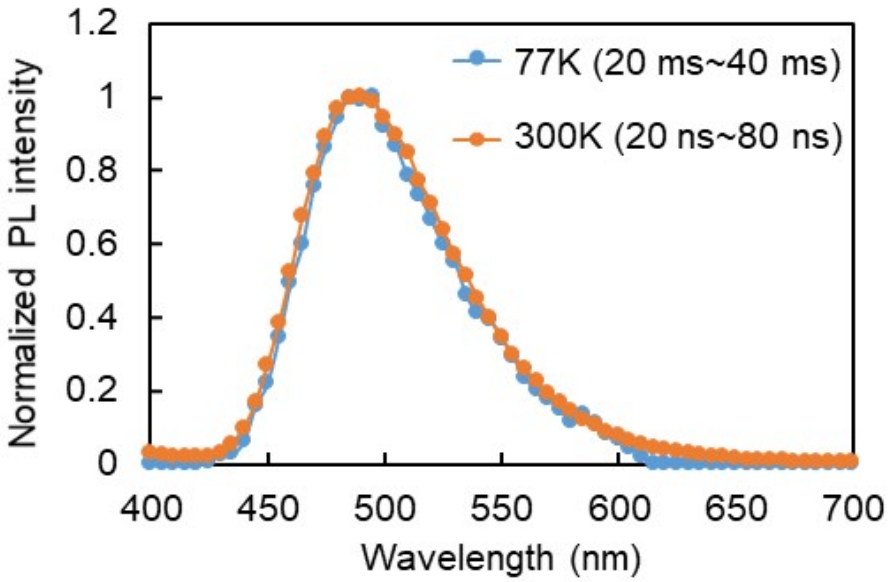

Figure S16. Spectra of prompt fluorescence at RT and delayed emission spectra at 77 K of 10 wt% **1**-doped mCP film.

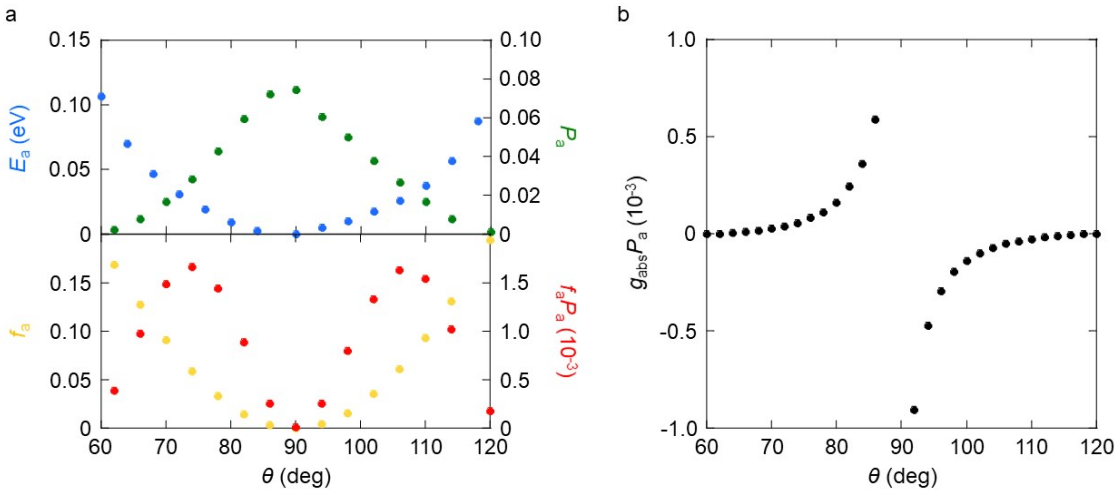

Figure S17. Dependence of calculated photophysical parameters on θ for **1**. The value of θ was changed from the optimized S_0 geometry without changing other bond lengths or angles between atoms. a) E_a vs θ plots (blue), P_a vs θ plots (green), f_a vs θ plots (yellow), and f_aP_a vs θ plots (red). b) $g_{abs}P_a$ vs θ plots. Calculated average value of f_a of chromophore **1** by integrating f_aP_a was 0.028. Optically measured f_a was determined to be 0.43 by substituting optically measured $\varepsilon(v)$ (in toluene) into $f_a = 4.32\times10^{-9}n^{-1}\int\varepsilon(v)dv$, where n is the refractive index of toluene. Thus, f_a was greater than f_f in both the calculation and optical measurements.

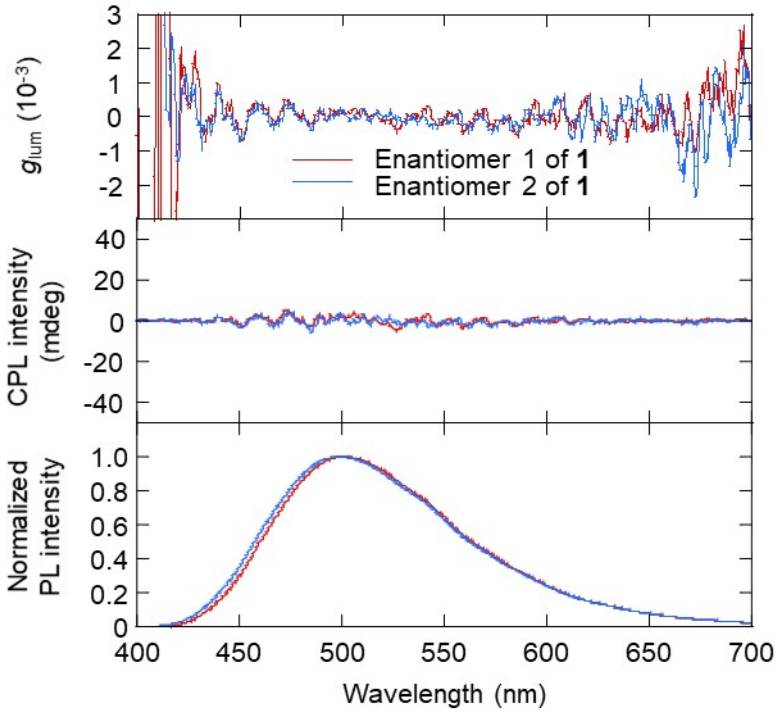

Figure S18. g_{lum} (top), CPL (middle) and emission (bottom) spectra of mCP films doped with 10 wt% of the enantiomers of **1**.