Supplementary Information for

Electrochemiluminescence of dimethylaminonaphthalene-oxazaborine donor-acceptor luminophores

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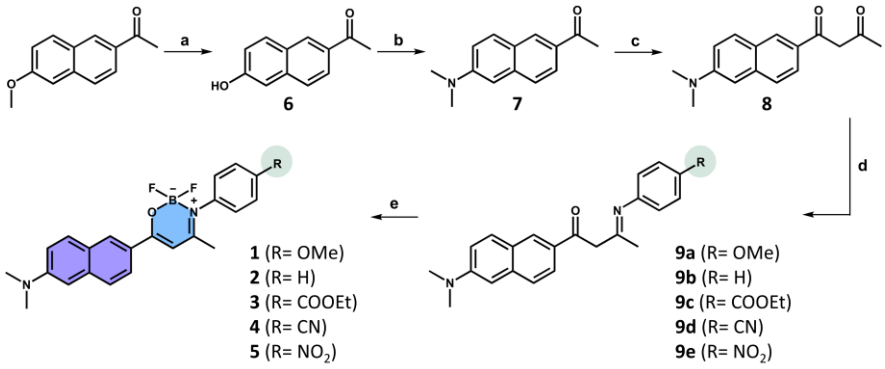
1. Synthesis and characterization

Synthesis of compounds 1–5



a) Conc. HCl, TEA, DCM, 100°C; b) $Na_2S_2O_5$, 40% Me_2NH, H_2O, 150°C; c) NaH, EtOAc, THF, 60°C
d) Aniline derivatives, Sulfamic acid, 90°C; e) TEA, boron trifluoride diethyl etherate, DCM, 0°C to rt

Scheme S1. Synthetic scheme of compounds **1**–**5**.

1.1. Synthesis of compound 6

To a solution of 2-acetyl-6-methoxynaphthalene (2 g, 10 mmol) in dichloromethane (4 mL) was added concentrated hydrochloric acid (80 mL). Then, triethylamine (0.75 mL) was added dropwise to the reaction mixture and stirred at 100°C for 4 h. The hot solution was filtered through cotton wool. After cooling down to room temperature, precipitates were formed and vacuum-filtered. The solid was re-dissolved with ethyl acetate and washed with H_2O and brine, and dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1:5) to give compound **6** (971 mg, 52% yield). 500 MHz ^{1}H NMR ($CDCl_3$): δ 8.42 (s, 1H), 8.01 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.22 – 7.14 (m, 2H), 2.72 (s, 3H).

1.2. Synthesis of compound 7

A mixture of compound **6** (541 mg, 2.9 mmol), dimethylamine (40% aqueous solution) (1.8 mL, 5.5 mmol), $Na_2S_2O_5$ (1104 mg, 5.8 mmol), and H_2O (2 mL) was added into a sealed tube and stirred at 150 °C for 72 h. After cooling down to room temperature, the reaction mixture was extracted with dichloromethane (CH_2Cl_2). The combined organic phase was washed with H_2O and brine, and dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1:5) to afford compound **7**. (322 mg, 52% yield). 400 MHz ^{1}H NMR ($CDCl_3$): δ 8.30 (s, 1H), 7.91 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.79 (d, *J* = 9.1 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.16 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.86 (d, *J* = 2.1 Hz, 1H), 3.10 (s, 6H), 2.65 (s, 3H)

1.3. Synthesis of compound 8

To a solution of compound **7** (300 mg, 1.41 mmol) dissolved in 10 mL tetrahydrofuran (THF) in a nitrogen

atmosphere was added NaH (60 % dispersion in mineral oil) (211 mg, 7.03 mmol) and ethyl acetate (0.18 mL, 1.83 mmol), and the reaction mixture was stirred at 60 °C for 12 h. The reaction was quenched by the addition of water and acidified with hydrochloric acid to pH 3. The solution was diluted with H_2O (30 mL) and extracted with dichloromethane (CH_2Cl_2). The solution was washed with H_2O and brine, and dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1:5) to afford compound **8** (268 mg, 74% yield). 400 MHz ^{1}H NMR ($CDCl_3$): δ 8.29 (s, 1H), 7.81 – 7.74 (m, 2H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.16 – 7.12 (m, 1H), 6.86 (s, 1H), 6.26 (s, 1H), 3.10 (d, *J* = 5.2 Hz, 6H), 2.19 (s, 3H). MALDI-TOF-MS m/z 255.719 ($[M]^+$), calcd 255.126.

1.4. General synthesis of compounds (9a–e)

A mixture of compound **8** (1 equiv), aniline derivative (1 equiv), and catalytic amount of sulfamic acid (0.1 equiv) was heated at 90 ℃ for 4 h under solvent-free condition. After cooling down to room temperature, crude product was dissolved in acetone and filtered through cotton wool for the removal of sulfamic acid. Then filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1:5) to give compound **9a**–**e** (65-88%).

1.4.1. Synthesis of compound **9a**

Following the general synthetic procedure, compound **8** (30 mg, 0.117 mmol), *p*-anisidine (15 mg, 0.123 mmol), and sulfamic acid (1 mg, 0.01 mmol) were used. The reaction mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1:2) to give compound **9a** (37 mg, 88% yield). 500 MHz ^{1}H NMR ($CDCl_3$): δ 12.99 (s, 1H), 8.33 (s, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.79 (t, *J* = 24.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.21 – 7.15 (m, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 3H), 6.02 (s, 1H), 3.83 (s, 3H), 3.09 (s, 6H), 2.11 (s, 3H). 125 MHz ^{13}C NMR ($CDCl_3$): δ 188.36, 162.19, 157.65, 149.50, 136.54, 133.50, 131.77, 130.28, 127.50, 126.51, 125.95, 125.80, 124.62, 116.25, 114.29, 105.64, 93.53, 55.49, 40.65, 20.34. MALDI-TOF-MS m/z 361.143 ($[M+H]^+$), calcd 360.184.

1.4.2. Synthesis of compound **9b**

Following the general synthetic procedure, compound **8** (30 mg, 0.117 mmol), aniline (11 μL, 0.117 mmol), and sulfamic acid (1 mg, 0.01 mmol) were used. The reaction mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1:2) to give compound **9b** (31 mg, 80% yield). 500 MHz ^{1}H NMR ($CDCl_3$): δ 13.16 (s, 1H), 8.34 (s, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 8.9 Hz, 4H), 6.94 (s, 1H), 6.05 (s, 1H), 3.11 (s, 7H), 2.20 (s, 3H). 125 MHz ^{13}C NMR ($CDCl_3$): δ 188.61, 161.23, 149.53, 138.96, 136.62, 133.35, 130.31, 129.26, 129.13, 127.64, 125.98, 125.77, 125.42, 124.58, 116.26, 105.70, 94.33, 40.63, 20.56. MALDI-TOF-MS: m/z 331.141 ($[M+H]^+$), calcd 330.173.

1.4.3. Synthesis of compound **9c**

Following the general synthetic procedure, compound **8** (12 mg, 0.05 mmol), ethyl 4-aminobenzoate (8 mg, 0.05 mmol), and sulfamic acid (0.5 mg, 0.005 mmol) were used. The reaction mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1:2) to give compound **9c** (13 mg, 69% yield). 500 MHz ^{1}H NMR ($CDCl_3$): δ 13.36 (s, 1H), 8.32 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 2H), 7.93 (dd, *J* = 8.7, 1.3 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.90 (s, 1H), 6.10 (s, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.10 (s, 6H), 2.30 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). 125 MHz ^{13}C NMR ($CDCl_3$): δ 189.12, 166.05, 159.44, 149.63, 143.38, 137.09, 136.78, 132.88, 130.79, 130.42, 127.94, 126.26, 126.09, 124.50, 122.50, 116.28, 105.57, 96.12, 60.94, 40.58, 21.05, 14.36. MALDI-TOF-MS m/z 403.183 ($[M+H]^+$), calcd 402.194.

1.4.4. Synthesis of compound **9d**

Following the general synthetic procedure, compound **8** (35 mg, 0.137 mmol), 4-aminobenzonitrile (16 mg, 0.137 mmol), and sulfamic acid (1 mg, 0.01 mmol) were used. The reaction mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1:2) to give compound **9d** (42 mg, 86% yield). 500 MHz ^{1}H NMR ($CDCl_3$): δ 13.40 (s, 1H), 8.32 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.65 (dd, *J* = 27.5, 7.9 Hz, 3H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.91 (s, 1H), 6.14 (s, 1H), 3.10 (s, 6H), 2.30 (s, 3H). 125 MHz ^{13}C NMR ($CDCl_3$): δ 189.50, 158.37, 149.81, 143.55, 136.96, 133.31, 132.53, 130.46, 128.19, 126.15, 125.54, 124.41, 122.64, 118.83, 116.30, 107.00, 105.46, 97.11, 40.56, 21.13. MALDI-TOF-MS m/z 356.236 ($[M+H]^+$), calcd 355.168.

1.4.5. Synthesis of compound **9e**

Following the general synthetic procedure, compound **8** (35 mg, 0.137 mmol), 4-nitroaniline (19 mg, 0.137 mmol), and sulfamic acid (1 mg, 0.01 mmol) were used. The reaction mixture was purified by silica gel column chromatography (ethyl acetate/hexane = 1:2) to give compound **9e** (34 mg, 65% yield). 500 MHz ^{1}H NMR ($CDCl_3$): δ 13.52 (s, 1H), 8.34 (s, 1H), 8.24 (d, *J* = 9.0 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 5.9 Hz, 2H), 7.22 (s, 1H), 6.95 (s, 1H), 6.19 (s, 1H), 3.13 (s, 7H), 2.39 (s, 3H). 125 MHz ^{13}C NMR ($CDCl_3$): δ 189.64, 157.81, 149.85, 145.54, 143.20, 137.03, 135.92, 132.31, 130.48, 128.33, 126.16, 125.23, 124.37, 121.54, 116.27, 105.38, 97.85, 40.52, 21.37. MALDI-TOF-MS m/z 375.077 ($[M]^+$), calcd 375.158.

1.5. General synthesis of compounds 1–5

A solution of compounds **9a**–**e** (1 equiv) and trimethylamine (2 equiv) dissolved in anhydrous dichloromethane (CH_2Cl_2) was cooled to 0°C in a nitrogen atmosphere. Then boron trifluoride diethyl etherate (3 equiv) was slowly added to the solution via syringe, and the resulting mixture was stirred at room temperature for 18 h. After the reaction was finished, H_2O (20 mL) was added to the solution and extracted with dichloromethane (CH_2Cl_2). The solution was washed with H_2O and brine, and dried over anhydrous Na_2SO_4, and concentrated

in vacuo. The residue was purified by silica gel column chromatography (dichloromethane /hexane = 1:50) to afford compounds **1**–**5** (66-81%).

1.5.1. Synthesis of compound **1**

Following the general synthetic procedure, compound **9a** (37 mg, 0.1 mmol), trimethylamine (29 μL, 0.21 mmol), boron trifluoride diethyletherate (38 μL, 0.31 mmol), and anhydrous dichloromethane (1 mL) were used. The reaction mixture was purified by silica gel column chromatography (dichloromethane /hexane = 1:50) to give compound **1** (34 mg, 81% yield). 500 MHz ^{1}H NMR (DMSO-d_6): δ 8.46 (s, 1H), 7.90 (dd, J = 15.6, 8.9 Hz, 2H), 7.72 (d, J = 8.6 Hz, 1H), 7.28 (d, J = 8.9 Hz, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.96 (s, 1H), 6.72 (s, 1H), 3.79 (s, 3H), 3.06 (s, 7H), 2.09 (s, 3H). 125 MHz ^{13}C NMR (DMSO-d_6): δ 172.76, 169.20, 158.98, 150.56, 137.40, 132.95, 130.90, 128.68, 127.74, 126.68, 125.43, 125.35, 123.99, 117.09, 114.69, 105.27, 95.77, 55.80, 40.41, 21.97. HRMS (ESI): calc'd m/z 409.1899 ($[M+H]^+$), found 409.1881.

1.5.2. Synthesis of compound **2**

Following the general synthetic procedure, compound **9b** (32 mg, 0.10 mmol), trimethylamine (28 μL, 0.20 mmol), boron trifluoride diethyletherate (37 μL, 0.30 mmol), and anhydrous dichloromethane (1 mL) were used. The reaction mixture was purified by silica gel column chromatography (dichloromethane /hexane = 1:50) to give compound **2** (26 mg, 71% yield). 500 MHz ^{1}H NMR (DMSO-d_6): δ 8.48 (s, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.90 (dd, J = 8.8, 1.8 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.29 (d, J = 7.4 Hz, 3H), 6.98 (d, J = 2.3 Hz, 1H), 6.76 (s, 1H), 3.08 (s, 6H), 2.10 (s, 3H). 125 MHz ^{13}C NMR (DMSO-d_6): δ 172.50, 169.49, 150.59, 140.28, 137.46, 130.94, 129.58, 128.80, 128.32, 126.75, 126.70, 125.42, 125.26, 124.01, 117.09, 105.26, 95.78, 40.41, 21.98. HRMS (ESI): calc'd m/z 379.1793 ($[M+H]^+$), found 379.1779.

1.5.3. Synthesis of compound **3**

Following the general synthetic procedure, compound **9c** (12 mg, 0.03 mmol), trimethylamine (8 μL, 0.06 mmol), boron trifluoride diethyletherate (11 μL, 0.09 mmol), and anhydrous dichloromethane (0.5 mL) were used. The reaction mixture was purified by silica gel column chromatography (dichloromethane /hexane = 1:50) to give compound **3** (8 mg, 66% yield). 400 MHz ^{1}H NMR ($CDCl_3$): δ 8.47 (s, 1H), 8.13 (d, J = 8.4 Hz, 2H), 7.81 (dd, J = 14.9, 5.7 Hz, 2H), 7.63 (d, J = 8.8 Hz, 1H), 7.36 (d, J = 8.3 Hz, 2H), 7.16 (dd, J = 9.1, 2.4 Hz, 1H), 6.86 (s, 1H), 6.29 (s, 1H), 4.39 (q, J = 7.1 Hz, 2H), 3.11 (s, 6H), 2.07 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). 125 MHz ^{13}C NMR (DMSO-d_6): δ 172.51, 170.15, 165.54, 150.69, 144.51, 137.60, 131.03, 130.51, 129.78, 129.08, 127.40, 126.73, 125.40, 125.05, 124.04, 117.11, 105.24, 96.06, 61.42, 40.40, 22.05, 14.62. HRMS (ESI): calc'd m/z 451.2005 ($[M+H]^+$), found 451.1985.

1.5.4. Synthesis of compound **4**

Following the general synthetic procedure, compound **9d** (42 mg, 0.12 mmol), trimethylamine (33 μL, 0.24 mmol), boron trifluoride diethyletherate (44 μL, 0.36 mmol), and anhydrous dichloromethane (1 mL) were used. The reaction mixture was purified by silica gel column chromatography (dichloromethane /hexane = 1:50) to give compound **4** (36 mg, 74% yield). 300 MHz ^{1}H NMR (DMSO-d_6): δ 8.52 (s, 1H), 8.02 (d, J = 8.0 Hz, 2H), 7.98 – 7.89 (m, 2H), 7.75 (d, J = 9.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.7 Hz, 1H), 7.00 (s, 1H), 6.85 (s, 1H), 3.10 (s, 6H), 2.15 (s, 3H). 125 MHz ^{13}C NMR (DMSO-d_6): δ 172.65, 170.45, 150.75, 144.52, 137.67, 133.83, 131.08, 129.22, 128.29, 126.76, 125.40, 124.95, 124.06, 118.78, 117.13, 111.26, 105.24, 96.18, 40.40, 22.12. HRMS (ESI): calc'd m/z 404.1746 ([M+H]$^{+}$), found 404.1730.

1.5.5. Synthesis of compound **5**

Following the general synthetic procedure, compound **9e** (34 mg, 0.09 mmol), trimethylamine (40 μL, 0.29 mmol), boron trifluoride diethyletherate (54 μL, 0.44 mmol), and anhydrous dichloromethane (1 mL) were used. The reaction mixture was purified by silica gel column chromatography (dichloromethane /hexane = 1:50) to give compound **5** (25 mg, 66% yield). 500 MHz ^{1}H NMR (DMSO-d_6): δ 8.52 (s, 1H), 8.36 (d, J = 9.0 Hz, 2H), 7.93 (dd, J = 14.3, 5.5 Hz, 2H), 7.74 (d, J = 8.9 Hz, 1H), 7.63 (d, J = 8.8 Hz, 2H), 7.30 (dd, J = 9.2, 2.5 Hz, 1H), 6.98 (d, J = 2.2 Hz, 1H), 6.86 (s, 1H), 3.09 (s, 6H), 2.16 (s, 3H). 125 MHz ^{13}C NMR (DMSO-d_6): δ 172.70, 170.63, 150.76, 147.18, 146.15, 137.70, 131.10, 129.31, 128.53, 126.76, 125.38, 124.99, 124.88, 124.06, 117.12, 105.22, 96.28, 40.39, 22.16. HRMS (ESI): calc'd m/z 424.1644 ([M+H]$^{+}$), found 424.1628.

2. Experimental section

2.1. Materials and instruments

All chemicals were purchased from Sigma-Aldrich (Sigma-Aldrich Corp., MO, USA), TCI (Tokyo Chemical Industry, Tokyo, Japan), or Alfa (Alfa Aesar, MA, USA) and were used without further purification. Organic solvents were purchased from Samchun (Samchun Chemical Co., Seoul, Korea). Thin layer chromatography was performed on TLC plates (aluminum sheets coated with Merck silica gel 60 F-254). Silica gel 60 (230-400 mesh) from SILICYCLE was used for the stationary phase in column chromatography. Deuterated solvents for NMR spectra were purchased from CIL (Cambridge Isotopic Laboratories, MA, USA). All ^{1}H and ^{13}C NMR spectra were recorded from Agilent NMR system 400 MHz DD2MR400 or Varian NMR System 500MHz instruments. The chemical shifts of NMR spectra were given in parts per million (ppm) calibrated using the residual solvent signals as an internal reference. High-resolution mass spectral (HRMS) data were obtained with the Thermo Scientific Orbitrap Exploris 120 mass spectrometer coupled to the Thermo Scientific Vanquish Core HPLC system. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained using the Microflex from Bruker Daltonics. UV-Vis absorption spectra were recorded with a JASCO V-730 spectrometer.

The photoluminescence (PL) spectra were measured in a JASCO FP-8300 spectrometer. The PL quantum yields (Φ_{PL}) of compounds **1**–**5** were obtained by comparing their integrated PL intensity and their absorbance of the compounds with the standard of coumarin 343 (Φ=63%). Stock solutions of compounds (2 mM) were prepared in dimethyl sulfoxide (DMSO) and diluted with acetonitrile.

2.2. Determination of photoluminescence quantum yield (Φ_{PL})

The PL quantum yields (Φ_{PL}) of compounds **1**–**5** were obtained by comparing their integrated PL intensity and their absorbance of the compounds with the standard of coumarin 343 (Φ=63%). Coumarin 343 was dissolved in EtOH (refractive index, η = 1.36). The Φ_{pL} was estimated by the following equation[1]:

$$\Phi_{PL} = 63\% \frac{I_x A_{st}}{I_{st} A_x} \left(\frac{\eta_x}{\eta_{st}}\right)^2$$

Where the Φ_{PL} is the PL quantum yield, I is the integrated PL emission intensity, A is the absorbance, and η is the refractive index of the solvent. The subscript x and st refers to the compounds **1**–**5** and the standard coumarin 343, respectively. Stock solutions of each compound (2 mM) were prepared in dimethyl sulfoxide (DMSO) and diluted with acetonitrile (CH_3CN, η = 1.34).

2.3. Electrochemical and electrochemiluminescent (ECL) measurements

To investigate electrochemical properties, cyclic voltammetry (CV) with a scan rate of 0.1 V/s was applied to individual samples with a CH Instruments 650B Electrochemical Analyzer (CH Instruments, Inc., TX, USA). All redox potential values were calibrated against the oxidation of 1 mM ferrocene (Fc/Fc^+) as a standard and then referenced to SCE. The ECL signal was measured along with CV scan (scan range: 0−1.9 V *vs.* SCE, scan rate: 0.1 V/s) by a low-voltage photomultiplier tube module (H-6780, Hamamatsu photonics K.K., Tokyo, Japan) on which a 250 μL volume home-made ECL flow cell was directly mounted. All solutions for ECL experiments contained 10 mM tripropylamine (TPrA) (Sigma-Aldrich) and 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (TCI) as the co-reactant for ECL and supporting electrolyte, respectively, in CH_3CN (ACROS). The glassy carbon (GC) working electrode was polished with 0.05 μm alumina (Buehler, IL, USA) on a felt pad. Then the electrode was sonicated in a 1:1 (v/v) mixture of distilled H_2O and ethanol (Samchun Chemical) for 5 min and was dried by ultra-pure N_2 gas for 1 min. The samples for electrochemical and ECL experiments were freshly prepared in each experiment. All ECL data were the average of the values from at least three experiments.

2.4. Determination of electrochemiluminescence efficiency (Φ_{ECL})

The ECL quantum yields (Φ_{PL}) of compounds **1**–**5** were obtained by comparing their integrated ECL intensity and their faradaic current values with the standard of $Ru(bpy)_3^{2+}$ (Φ^o = 100%). The Φ_{ECL} was estimated by the

$$\Phi_{ECL} = \Phi^o{}_{ECL} \frac{IQ^o}{I^o Q}$$

following equation[2]:

Where Φ_{ECL} is the ECL efficiency, I and I^o are the integrated ECL intensity of compounds **1**–**5** and $Ru(bpy)_3^{2+}$ as a standard, Q and Q^o are the faradaic charge values for compounds **1**–**5** and the standard, respectively.

3. Additional figures and tables

Table S1. Calculated excited state, energy, oscillator strength (*f*), and transition analyses of compounds **1**–**5** by TD-DFT based on the optimized molecular geometries at the ground state.

Compound	State	λ_{cal} (nm)	*f*	Orbital transition
1	S_1	488.51	1.1877	HOMO → LUMO (98.34%)
2	S_1	489.62	1.0769	HOMO → LUMO (98.77%)
3	S_1	510.96	1.1644	HOMO → LUMO (98.70%)
4	S_1	517.19	1.1537	HOMO → LUMO (98.77%)
5	S_1/ S_2	607.10/ 468.14	0.6474/ 0.6466	HOMO → LUMO (99.60%)/ HOMO-2 → LUMO (3.07%), HOMO → LUMO+1 (95.87%)

Table S2. Photophysical data of compounds **1**–**5**.

Compound	Absorbance		Photoluminescence		
	λ_{abs} (nm)	$\varepsilon \times 10^4$ [M^{-1} cm^{-1}] at λ_{abs}	^aE_s (eV)	λ_{em} (nm)	Φ_{PL} (%)
1	423	3.70	2.18	568	22.6
2	424	4.15	2.16	575	35.4
3	432	3.16	2.06	603	15.0
4	436	4.46	2.02	614	13.1
5	439	5.13	2.09	594	0.05

[a]The energy of singlet excited state (E_s) was calculated following the equation: E_s (eV)=1239.81/λ_{max} (nm, PL)

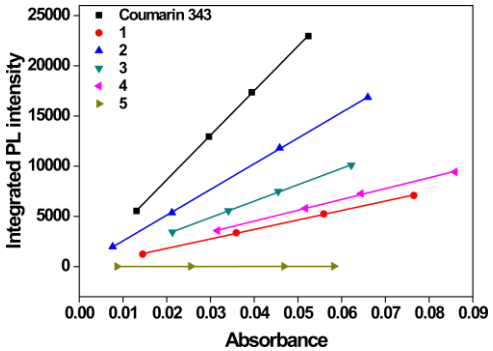


Figure S1. Photoluminescence and absorbance of compounds **1**–**5** and coumarin 343 standard in CH_3CN.

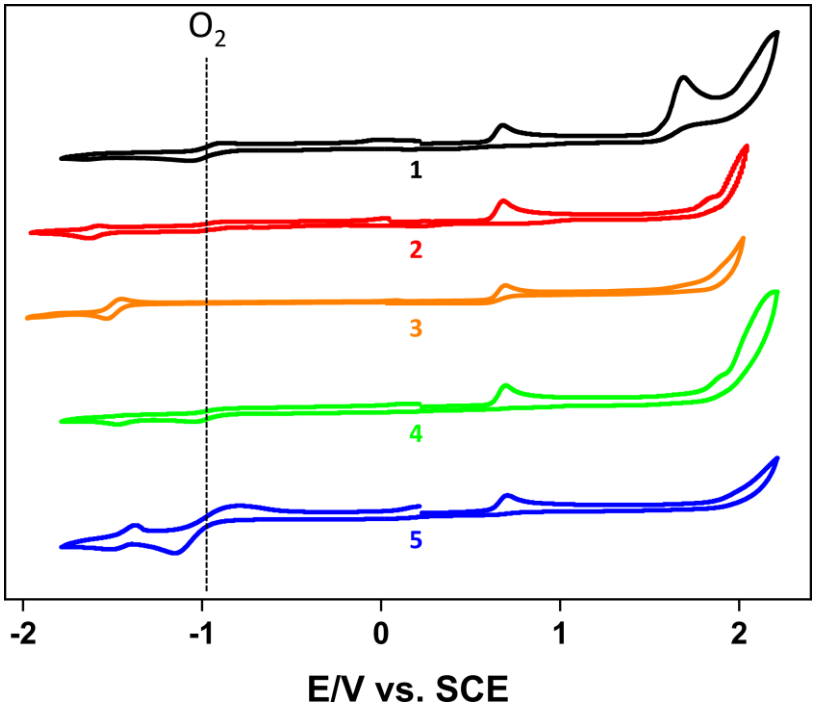


Figure S2. Cyclic voltammetry traces for 1 mM compounds **1**–**5** in MeCN containing $TBAPF_6$ as the supporting electrolyte (scan rate: 0.1 V/s, working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: $Ag/AgNO_3$). The values were calibrated against the oxidation of 1 mM ferrocene (Fc/Fc^+) as a standard and then referenced to SCE.

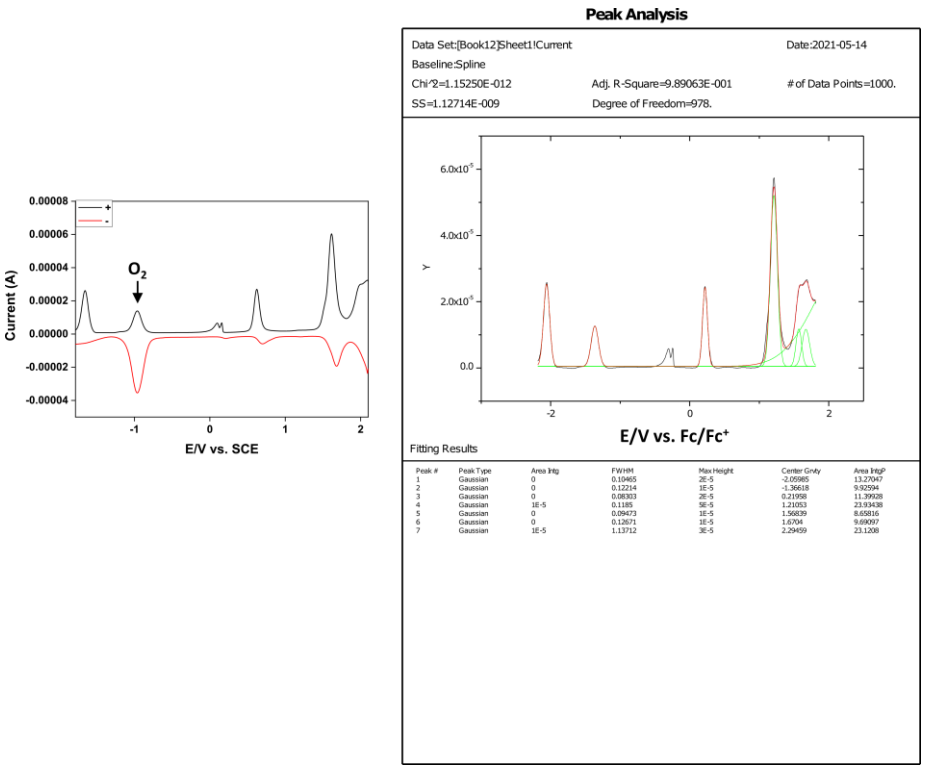


Figure S3. Differential pulse voltammetry (DPV) of **1** (1 mM) in MeCN containing $TBAPF_6$ as the supporting electrolyte.

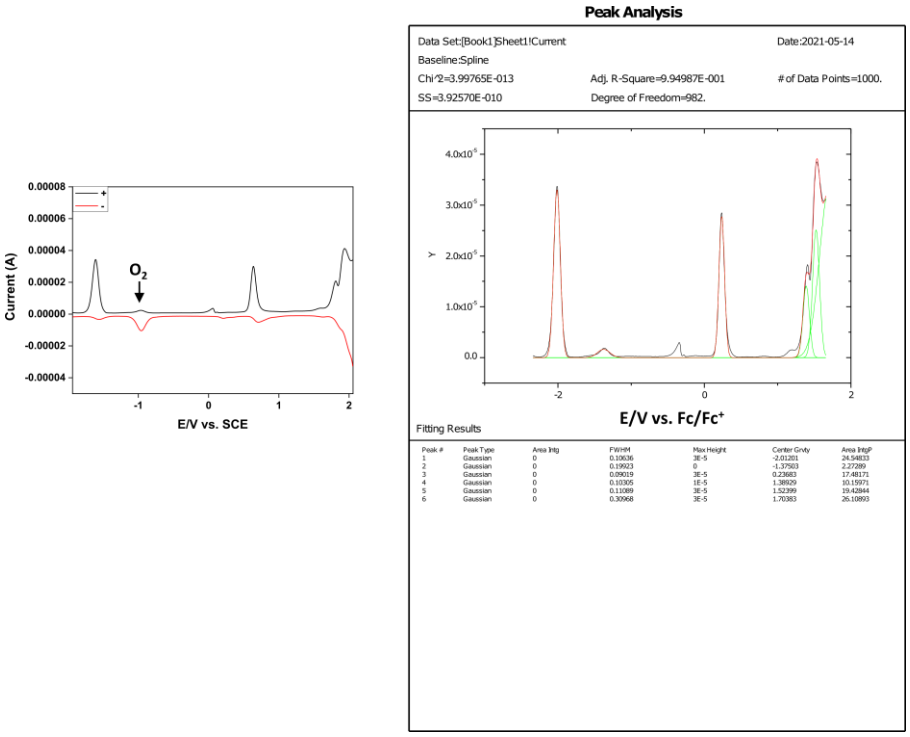


Figure S4. Differential pulse voltammetry (DPV) of **2** (1 mM) in MeCN containing $TBAPF_6$ as the supporting electrolyte.

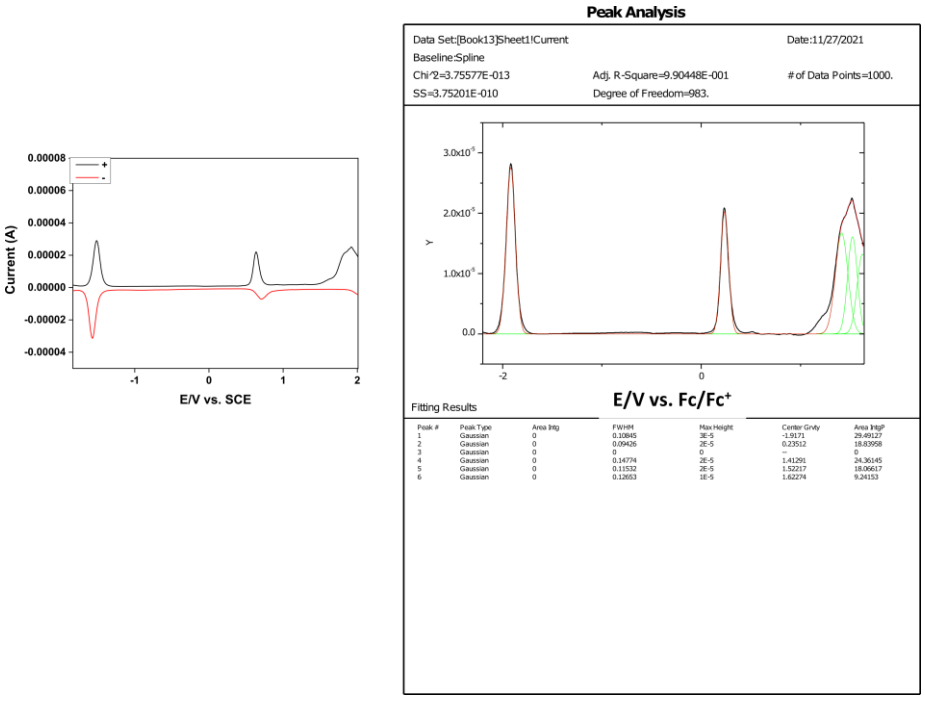


Figure S5. Differential pulse voltammetry (DPV) of **3** (1 mM) in MeCN containing $TBAPF_6$ as the supporting electrolyte.

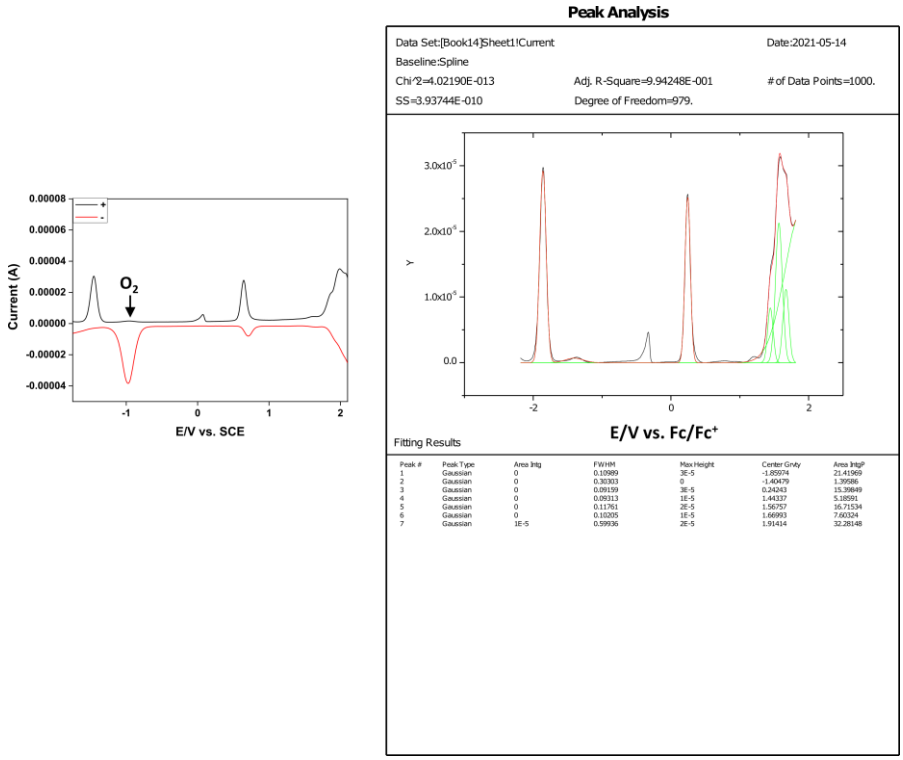


Figure S6. Differential pulse voltammetry (DPV) of **4** (1 mM) in MeCN containing $TBAPF_6$ as the supporting electrolyte.

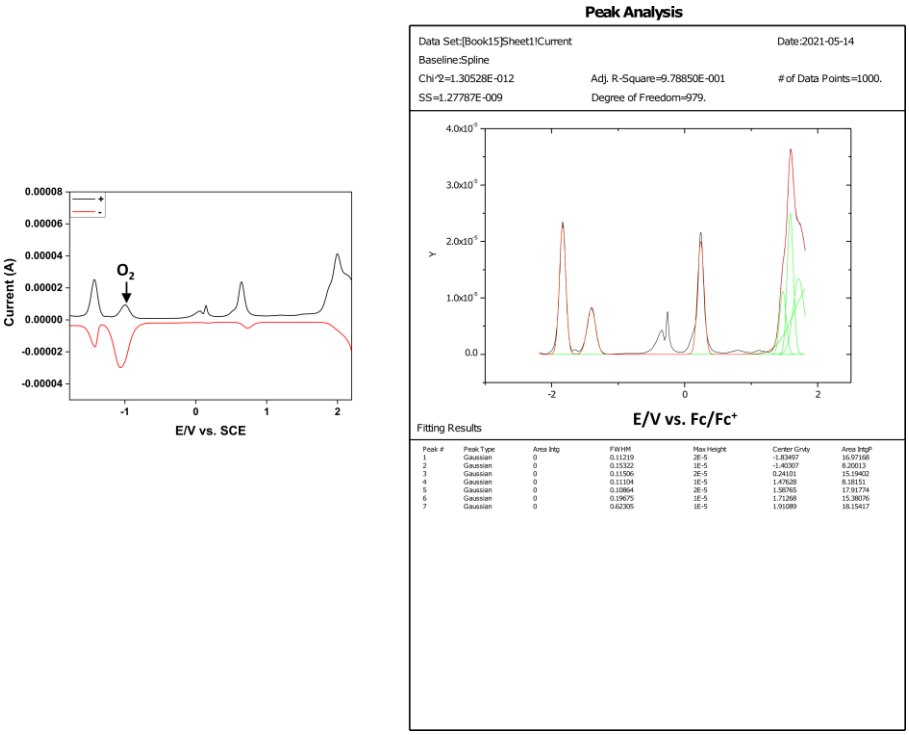


Figure S7. Differential pulse voltammetry (DPV) of **5** (1 mM) in MeCN containing $TBAPF_6$ as the supporting electrolyte.

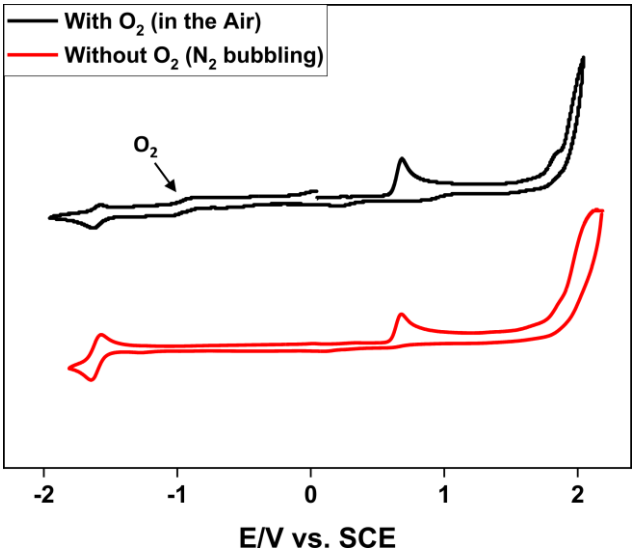


Figure S8. Cyclic voltammograms for compound **1** (1 mM) in the presence of oxygen (top) and in the absence of oxygen (bottom) in MeCN containing $TBAPF_6$ as the supporting electrolyte (scan rate: 0.1 V/s, working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: $Ag/AgNO_3$). The values were calibrated against the oxidation of 1 mM ferrocene (Fc/Fc^+) as a standard and then referenced to SCE.

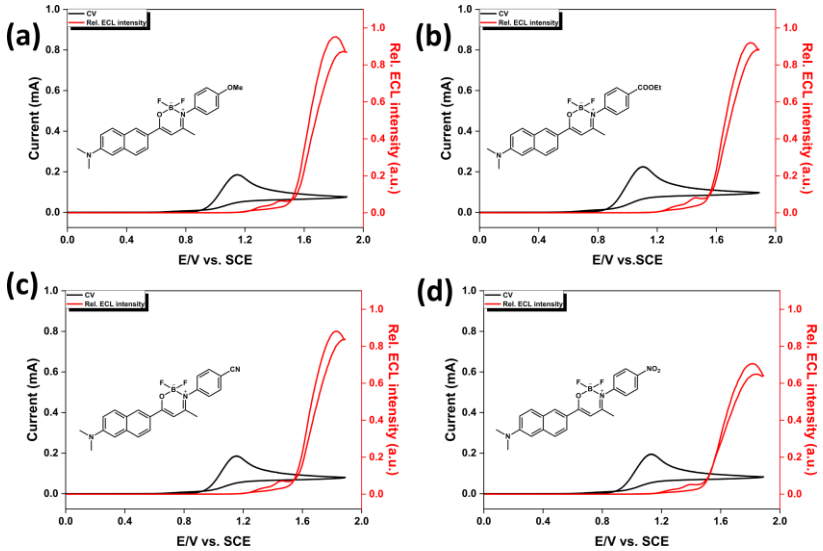


Figure S9. Cyclic voltammograms and the corresponding ECL-voltage curves of 10 μM compounds: (a) **1**, (b) **3**, (c) **4**, and (d) **5** in CH_3CN with 10 mM TPrA and 0.1 M $TBAPF_6$ while the potential is swept at a GC disk electrode (diameter 2 mm) at a scan rate of 0.1 V/s.

Table S3. Electrochemical and ECL properties of compounds **1**–**5**.

Compounds	Electrochemistry		[d]Enthalphy of reaction	ECL	
	[a]E_{red} (V *vs.* SCE)/ [c]LUMO (eV)	[b]$E_{Ox1,2}$ (V *vs.* SCE)/ [c]HOMO (eV)	[d]-ΔH_{TPrA} (eV)	Rel. ECL intensity at V_{max} (%)	[e]Φ_{ECL} (%)
1	−1.57/−2.83	0.61, 1.61/−5.01	2.15	95.1	119.4
2	−1.53/−2.87	0.64, 1.79/−5.04	2.18	106.6	135.9
3	−1.45/−2.95	0.62, 1.81/−5.02	2.16	92.0	83.5
4	−1.41/−2.99	0.64, 1.84/−5.04	2.18	88.0	102.3
5	−1.40/−3.00	0.64, 1.88/−5.04	2.18	70.5	89.7

[a]Cyclic voltammetric measurements of compounds **1**–**5** (1 mM) for getting reduction potential values were performed in CH_3CN solution with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte at the scan rate of 0.1 V/s. [b]The oxidation potentials were measured using DPV with the following conditions: pulse amplitude, 50 mV; sample width, 17 ms; pulse width, 50 mV; pulse period, 200 ms; and quiet time, 2 s. The values were calibrated against the oxidation of 1 mM ferrocene (Fc/Fc^+) as a standard and then referenced to SCE. [c]The corresponding HOMO/LUMO energy levels of compounds were calculated using the equation: $E_{HOMO/LUMO}$ (eV) = $-(E_{ox/red} - E_{Fc/Fc^+}) - 4.80$ eV.[3] [d]The enthalphy ($-\Delta H_{TPrA}$) values of the radical reaction were calculated following the equation:[1] $-\Delta H_{TPrA} = E_{Ox1} - E(TPrA^{\bullet}) - 0.16$, where $E(TPrA^{\bullet}) \approx -2.1$ V *vs.* Fc/Fc^+.[4] [e]The ECL efficiencies were measured in comparison with $Ru(bpy)_3^{2+}$ (Φ_{ECL} = 100%).

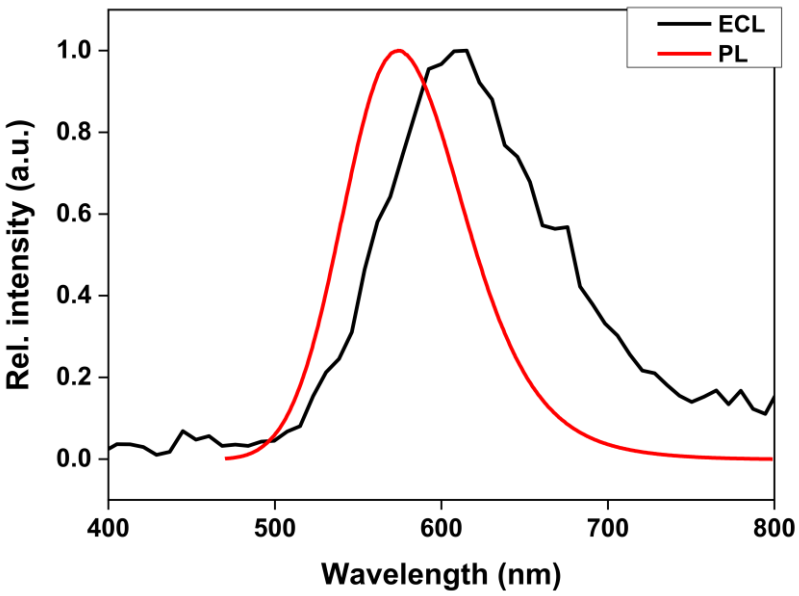


Figure S10. Normalized PL (red line) and ECL spectra (black line) of **2** in CH_3CN. The PL spectrum of compound **2** (10 μM) was obtained in CH_3CN solution. ECL spectrum was recorded in CH_3CN solution containing 1 mM compound **2**, 100 mM $TBAPF_6$ with 100 mM TPrA as a co-reactant.

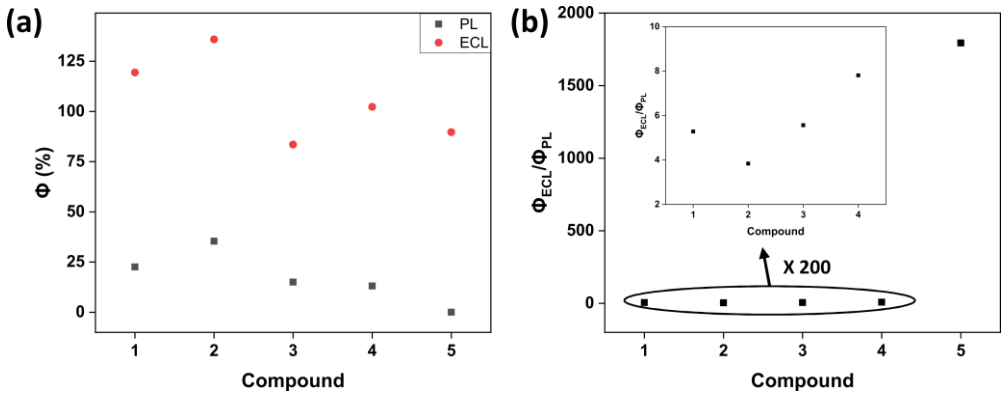


Figure S11. (a) PLQYs (black dot) and ECL efficiencies (red dot), and (b) The Φ_{ECL}/Φ_{PL} values of the compounds **1**–**5**. The PLQYs of the compounds (10 μM) were obtained in CH_3CN solution. ECL efficiencies were recorded in CH_3CN solution containing 10 μM compounds, 100 mM $TBAPF_6$ with 10 mM TPrA as a co-reactant.

4. Copies of NMR spectra

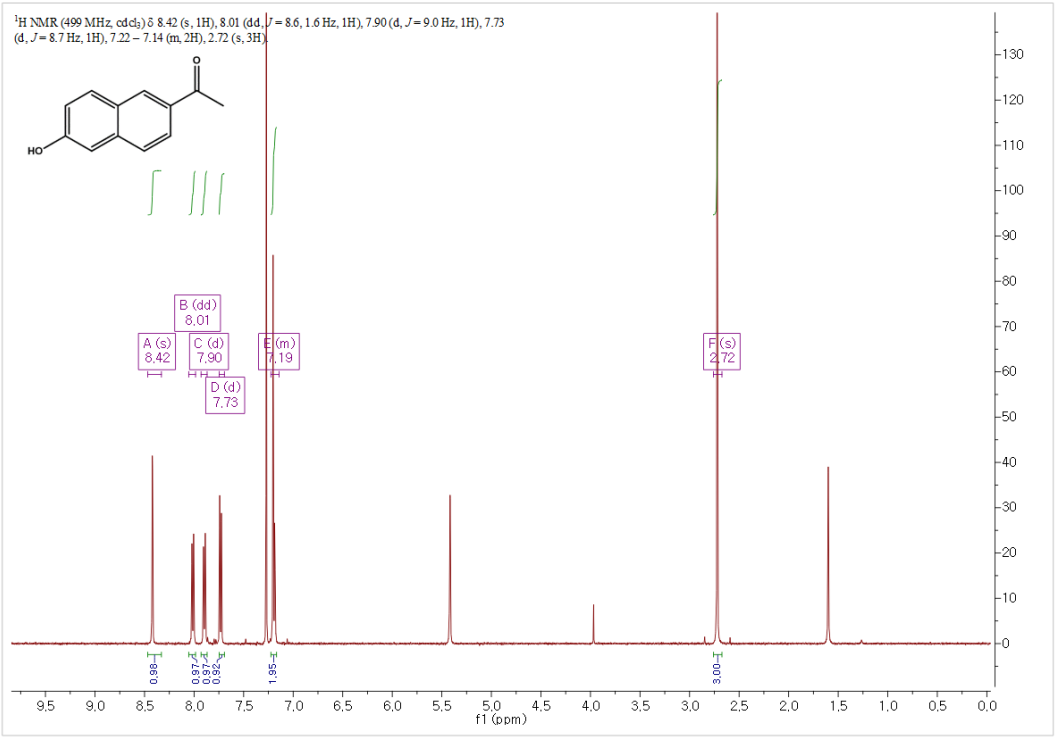


Figure S12. ^{1}H NMR spectrum of compound **6** (500 MHz, $CDCl_3$).

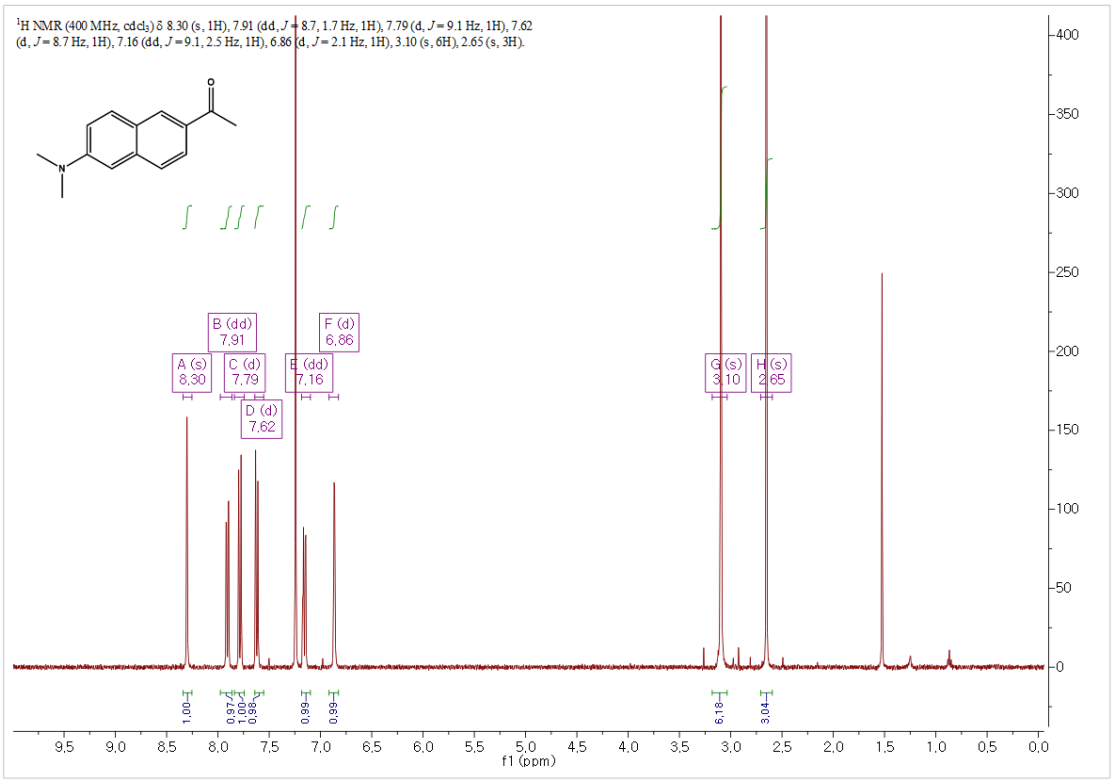


Figure S13. ^{1}H NMR spectrum of compound **7** (400 MHz, $CDCl_3$).

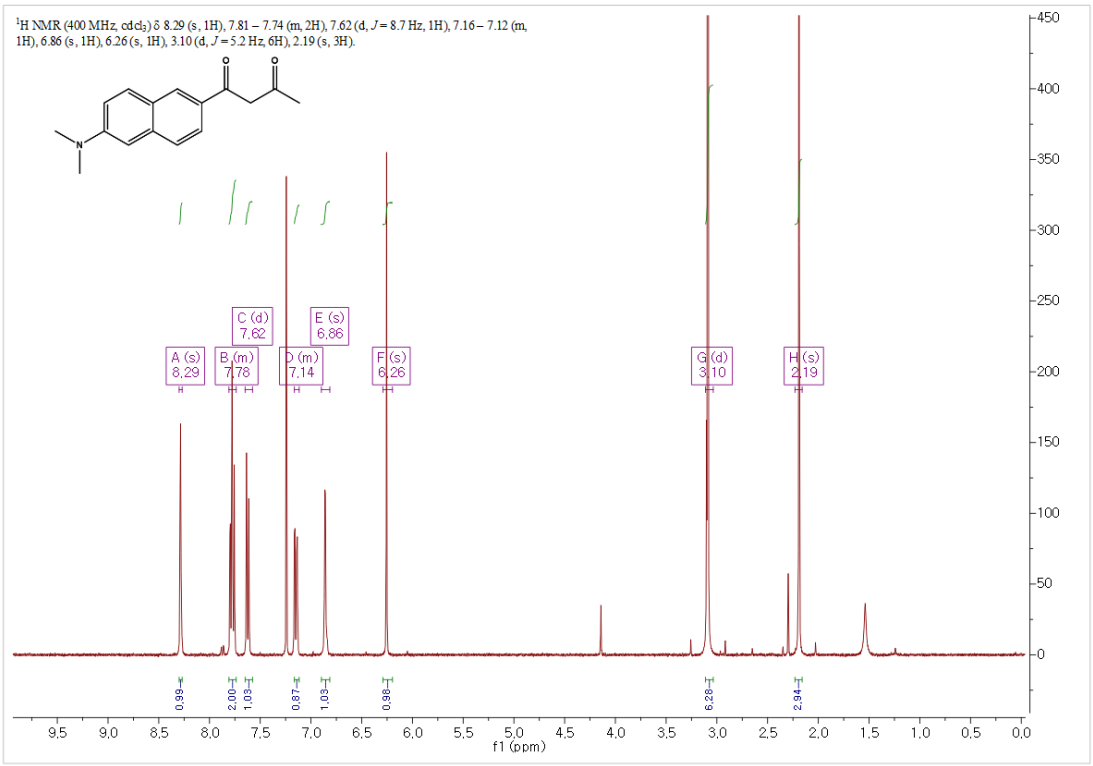


Figure S14. ^{1}H NMR spectrum of compound **8** (400 MHz, $CDCl_3$).

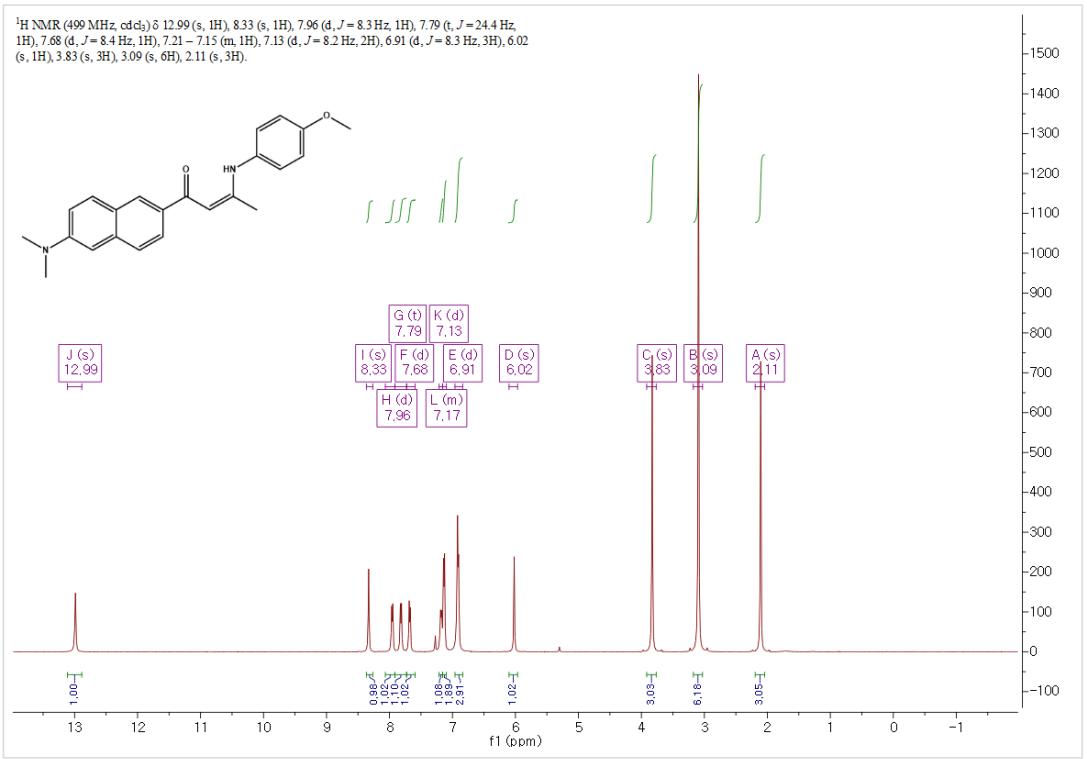


Figure S15. ^{1}H NMR spectrum of compound **9a** (500 MHz, $CDCl_3$).

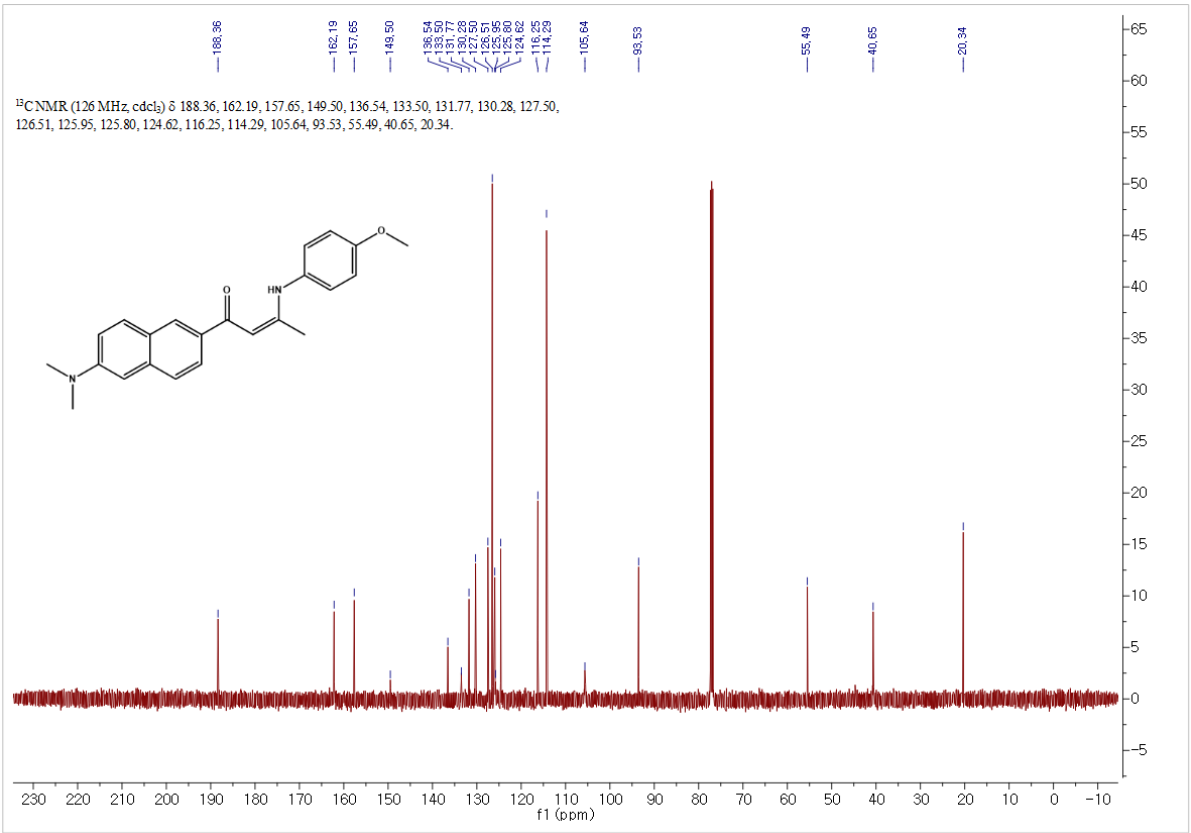


Figure S16. ^{13}C NMR spectrum of compound **9a** (125 MHz, $CDCl_3$).

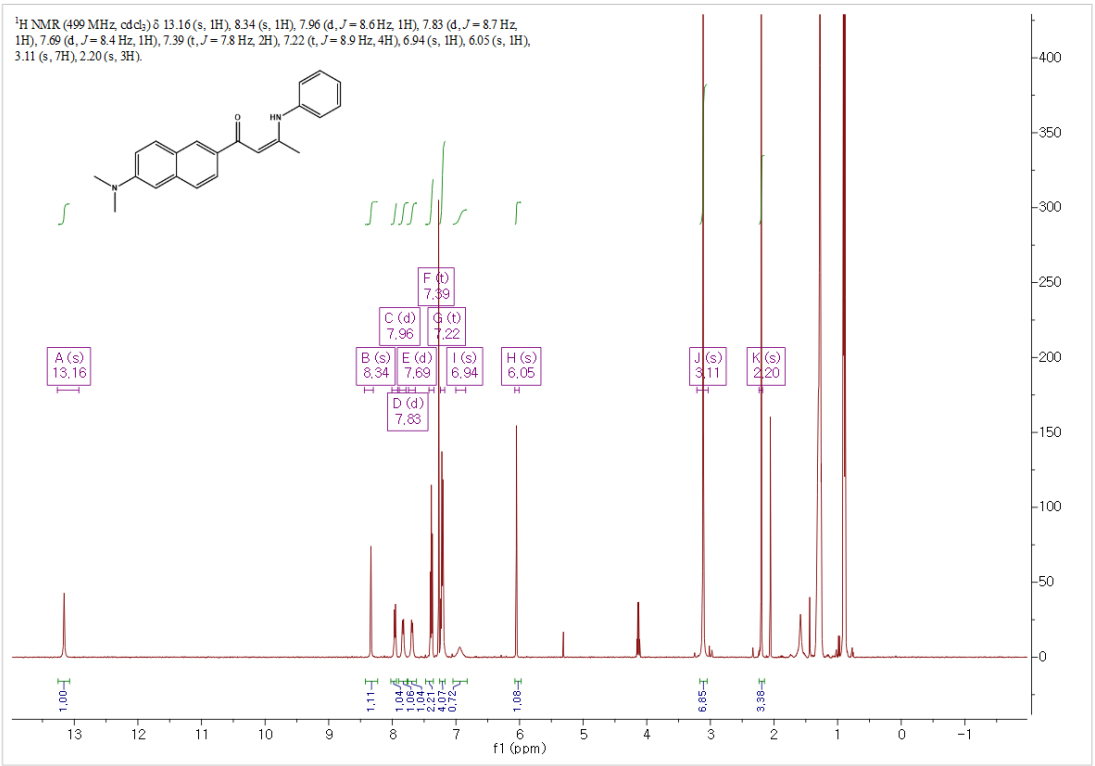


Figure S17. ^{1}H NMR spectrum of compound **9b** (500 MHz, $CDCl_3$).

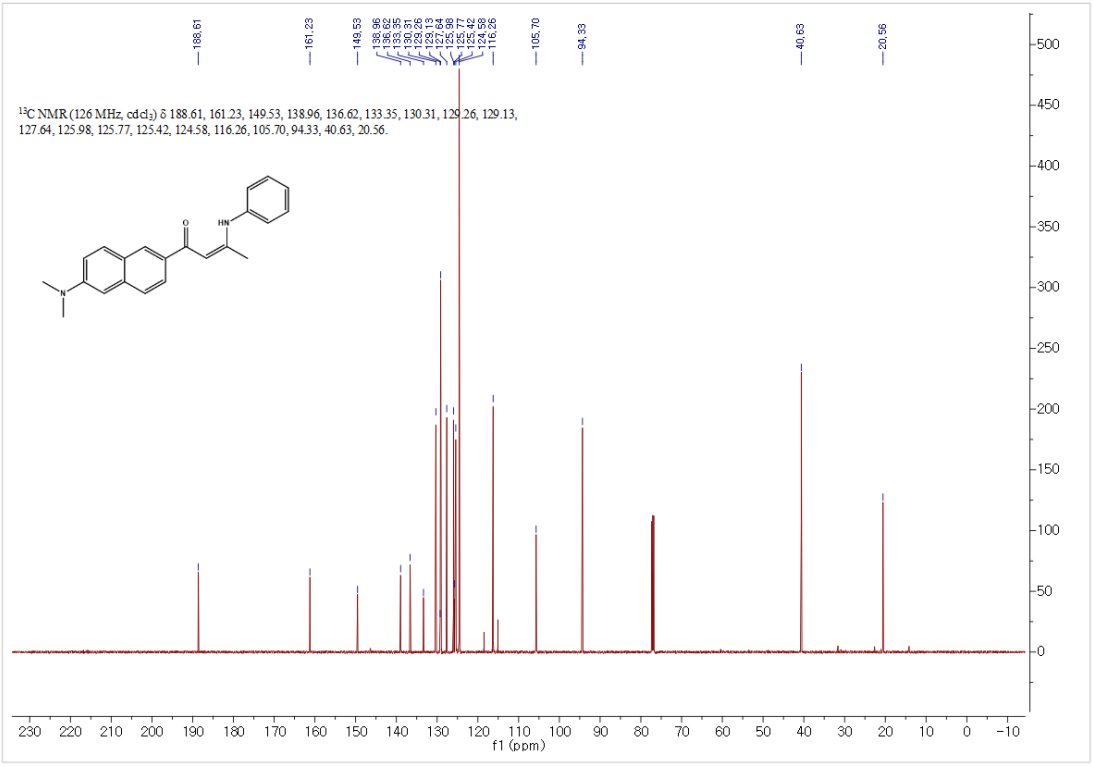


Figure S18. ^{13}C NMR spectrum of compound **9b** (125 MHz, $CDCl_3$).

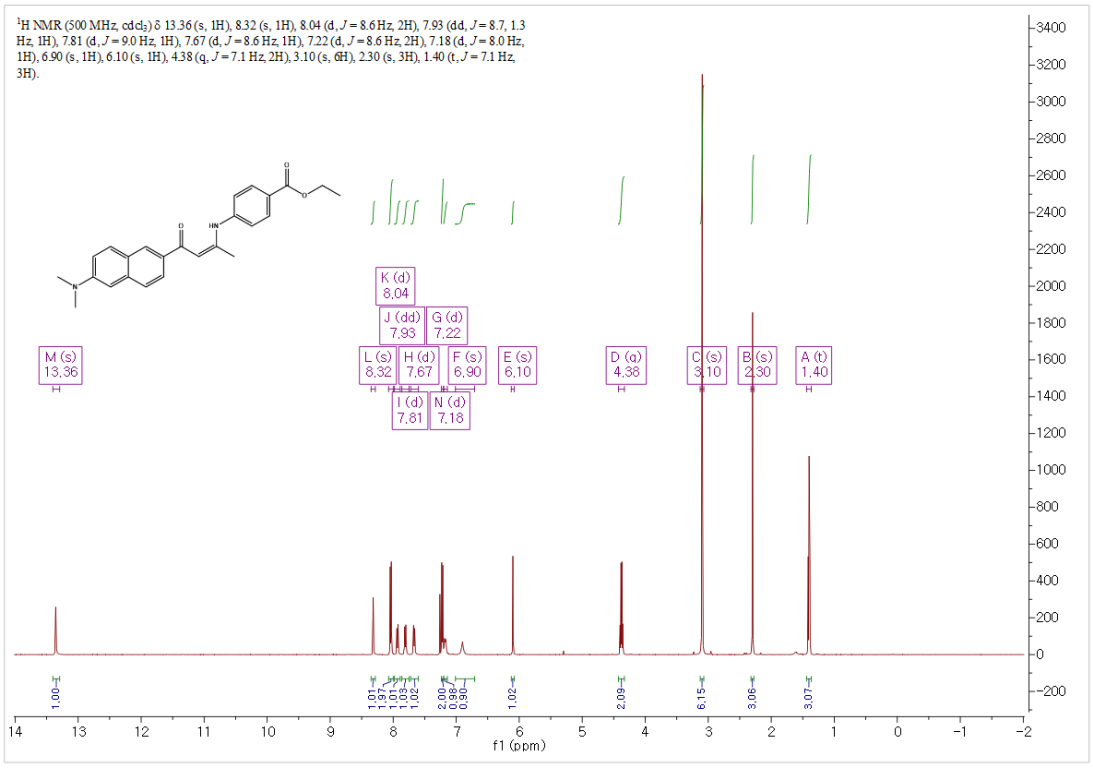


Figure S19. ^{1}H NMR spectrum of compound **9c** (500 MHz, $CDCl_3$).

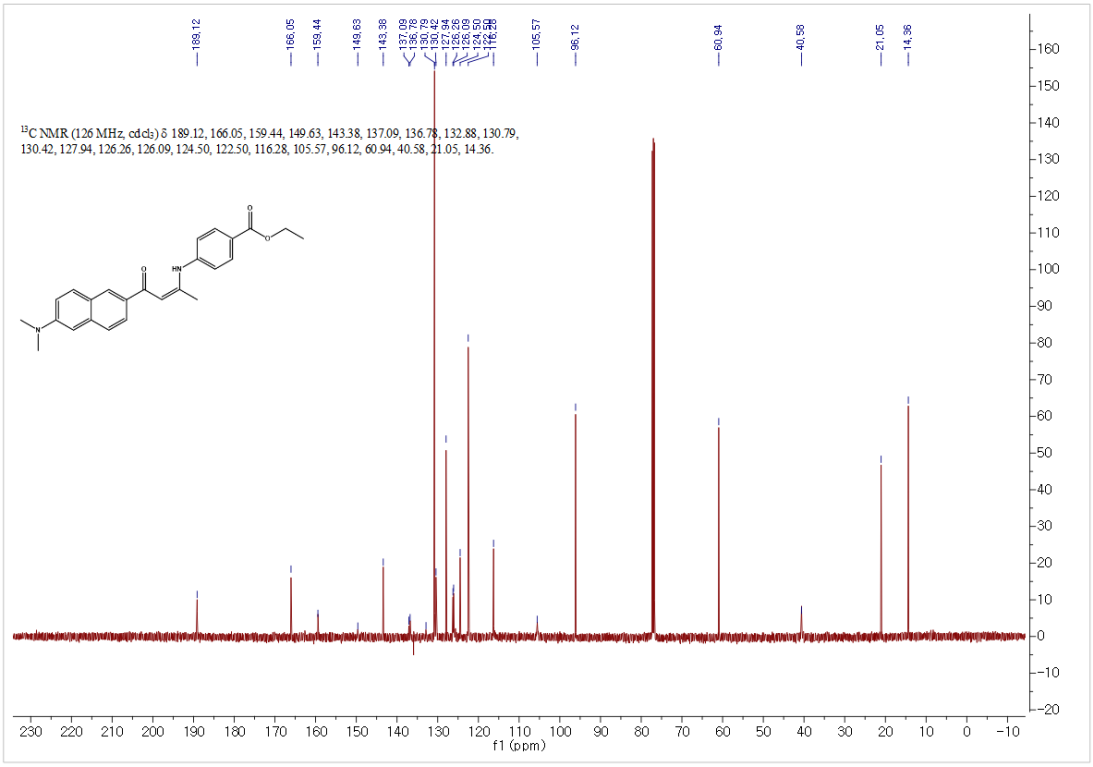


Figure S20. ^{13}C NMR spectrum of compound **9c** (125 MHz, $CDCl_3$).

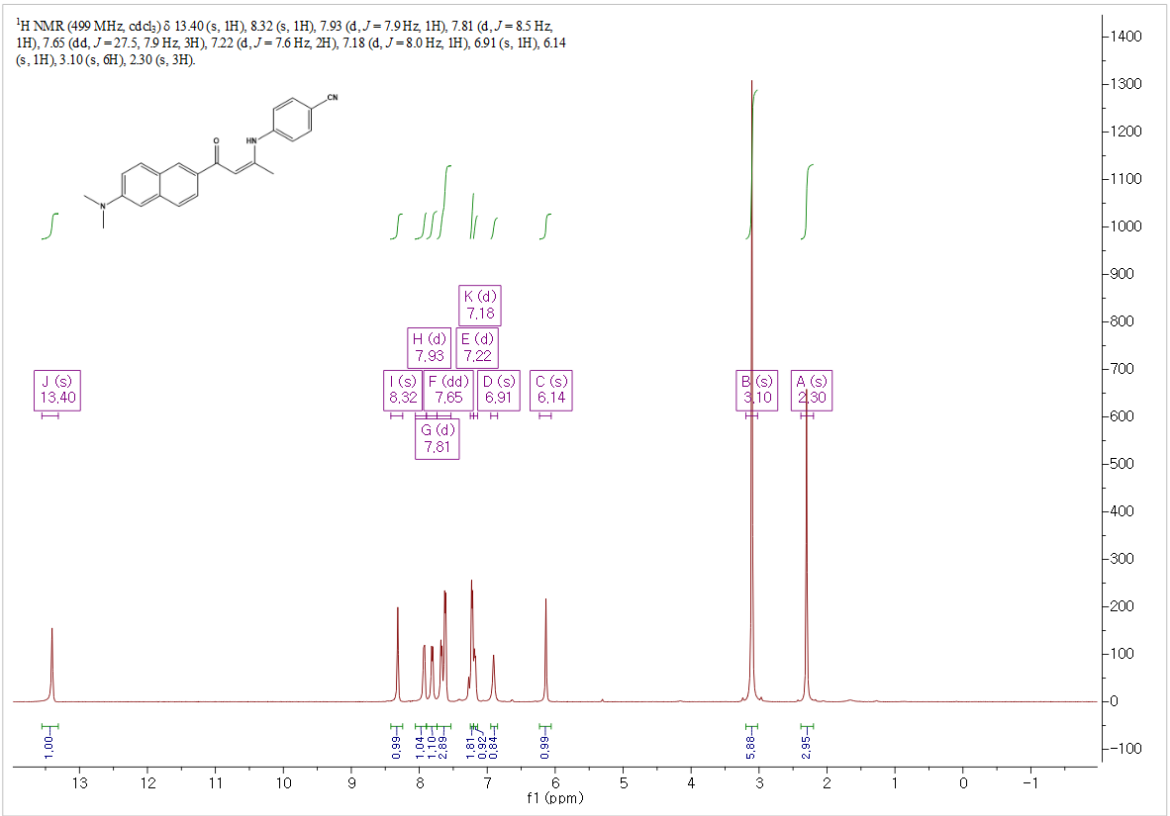


Figure S21. ^{1}H NMR spectrum of compound **9d** (500 MHz, $CDCl_3$).

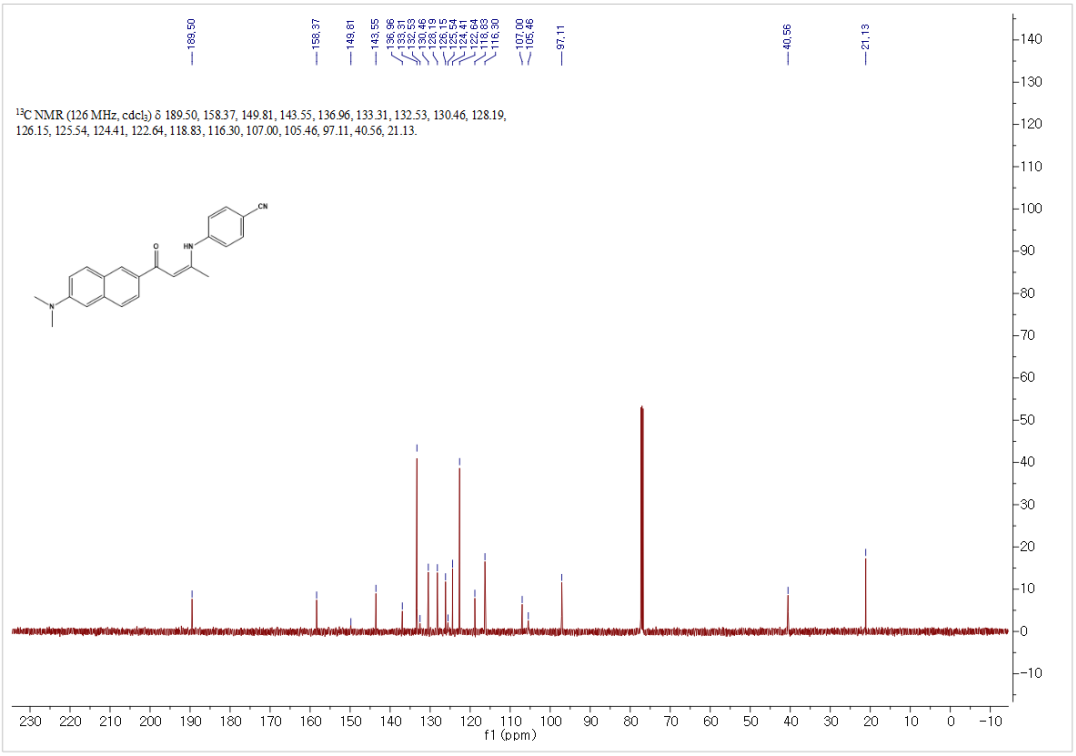


Figure S22. ^{13}C NMR spectrum of compound **9d** (125 MHz, $CDCl_3$).

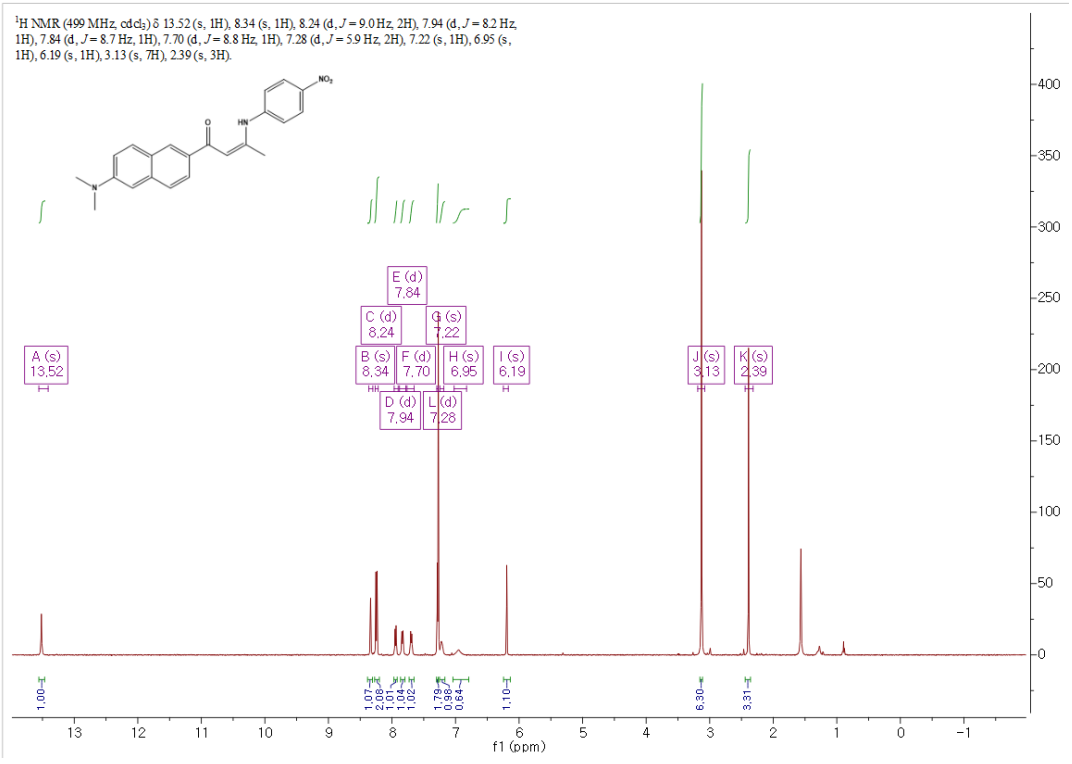


Figure S23. ^{1}H NMR spectrum of compound **9e** (500 MHz, $CDCl_3$).

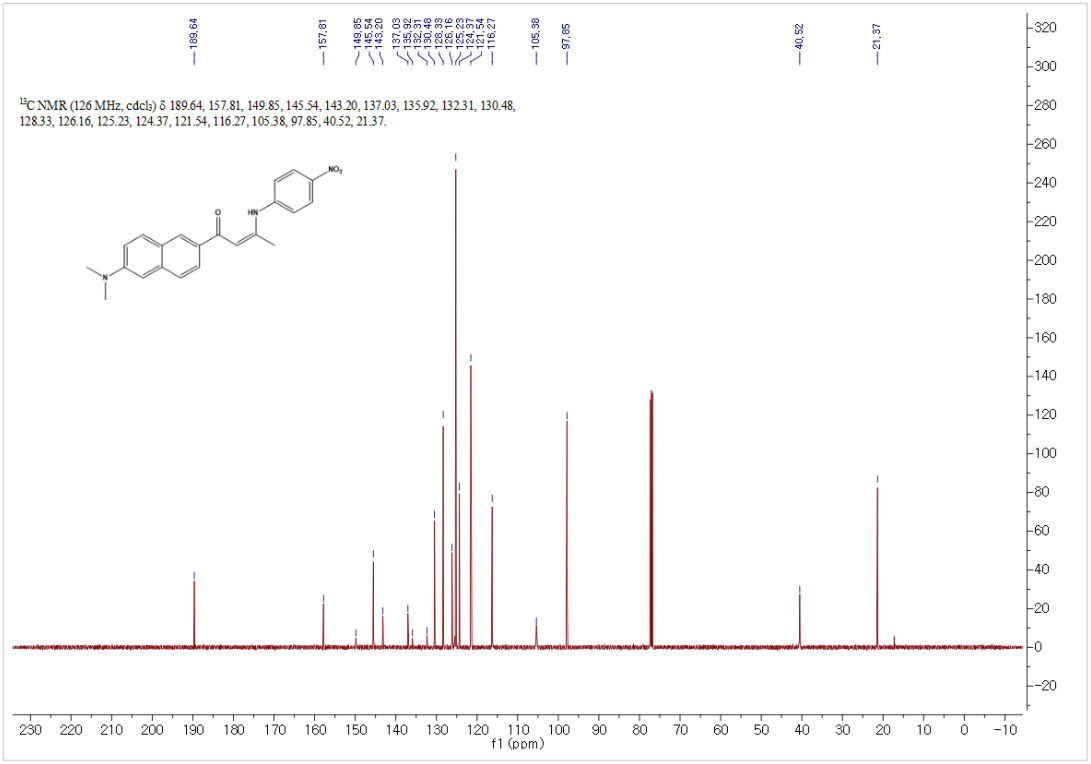


Figure S24. ^{13}C NMR spectrum of compound **9e** (125 MHz, $CDCl_3$).

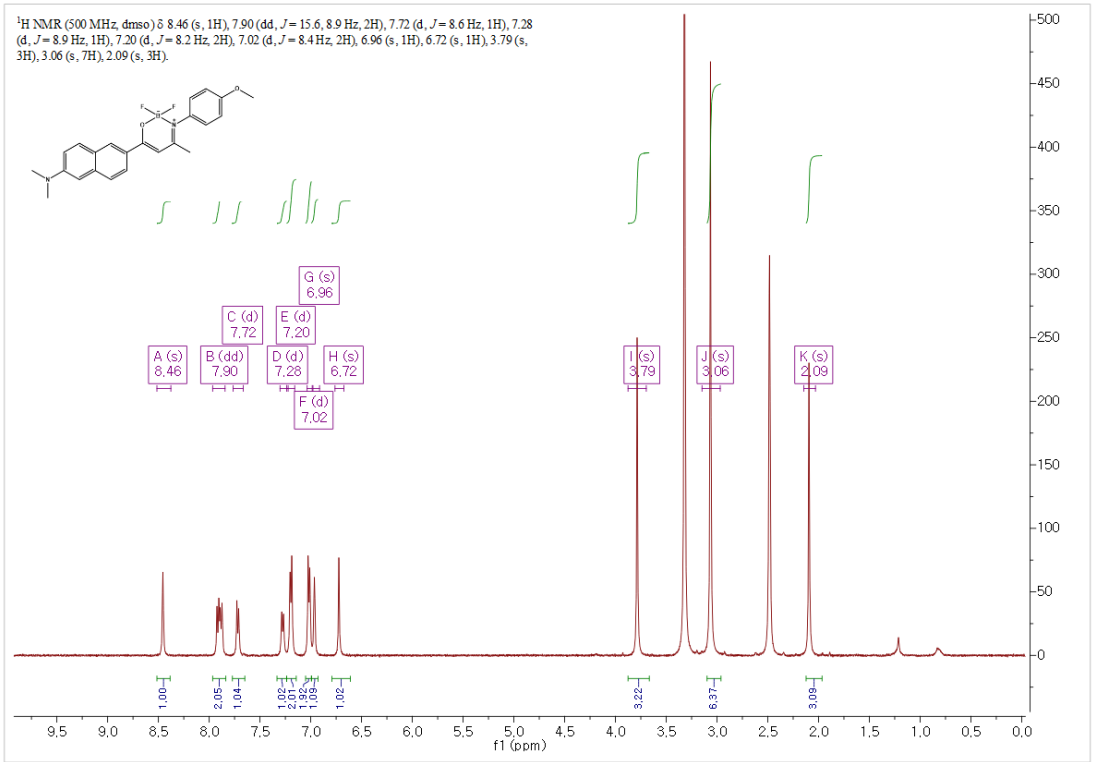


Figure S25. ^{1}H NMR spectrum of compound **1** (500 MHz, DMSO-d_6).

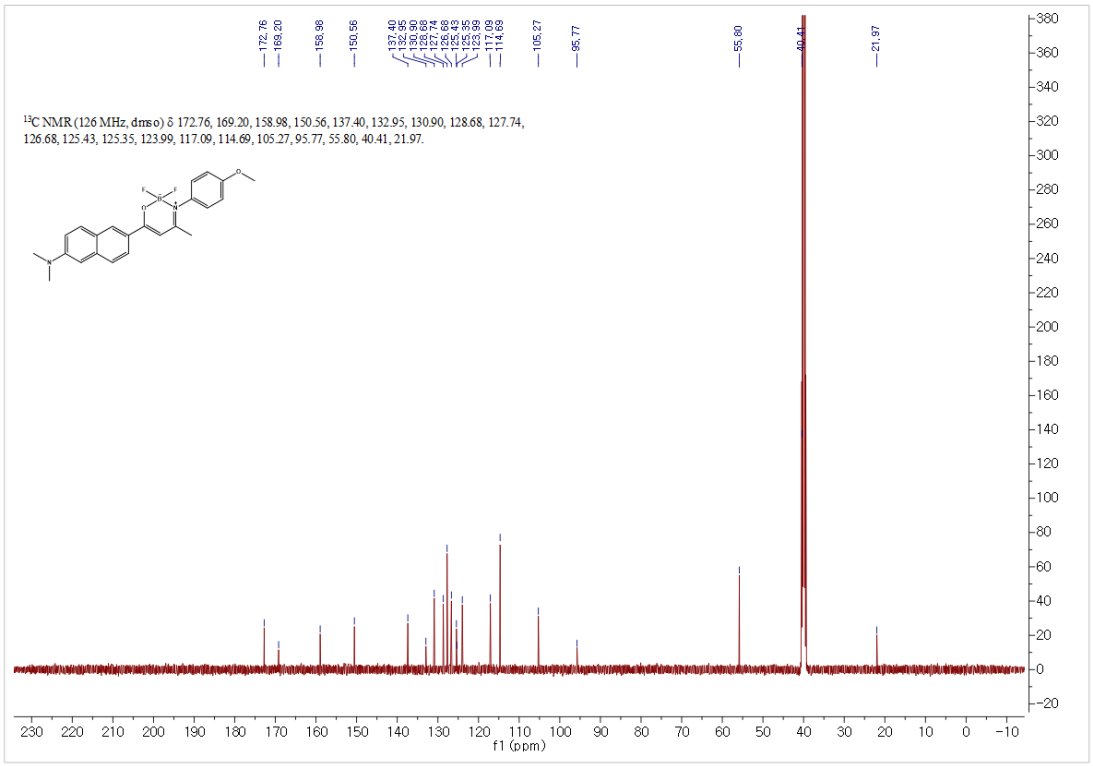


Figure S26. ^{13}C NMR spectrum of compound **1** (125 MHz, DMSO-d_6).

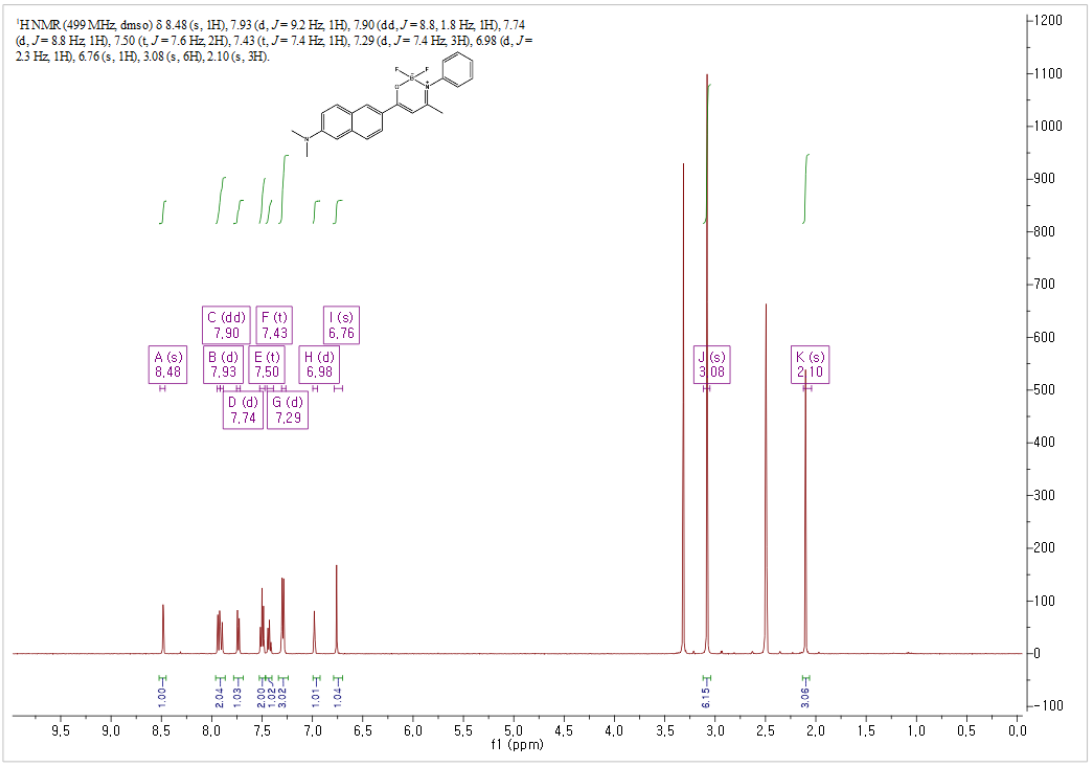


Figure S27. ^{1}H NMR spectrum of compound **2** (500 MHz, DMSO-d_6).

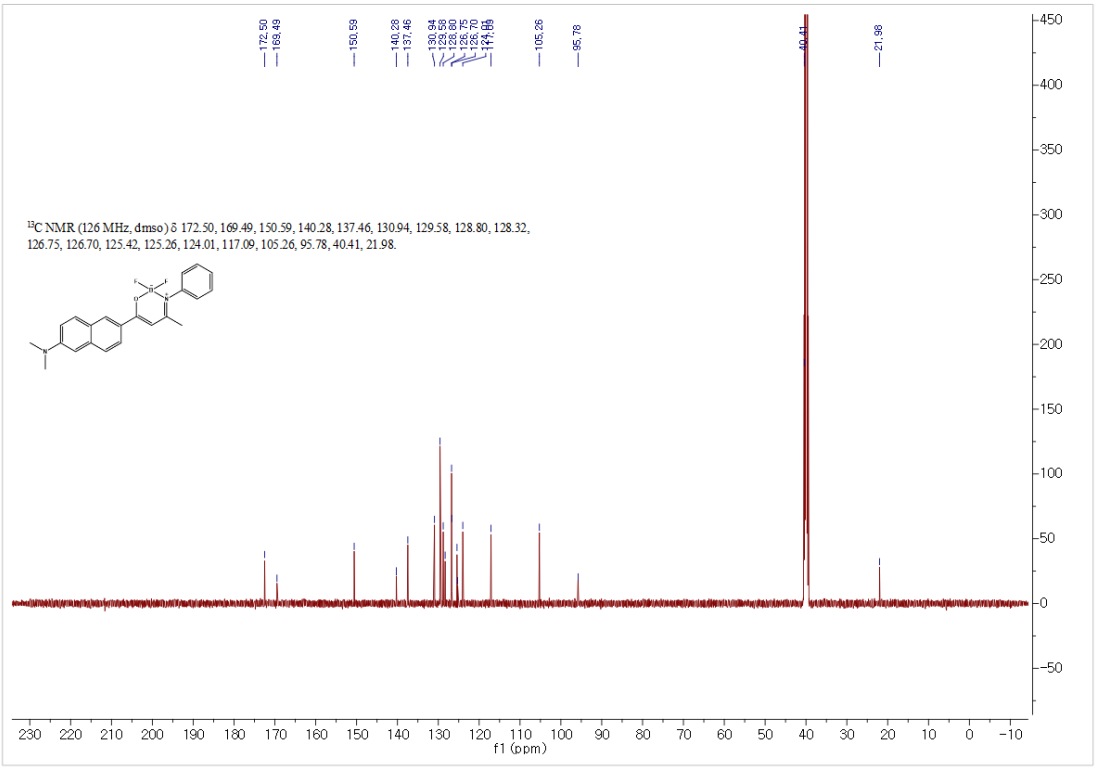


Figure S28. ^{13}C NMR spectrum of compound **2** (125 MHz, DMSO-d_6).

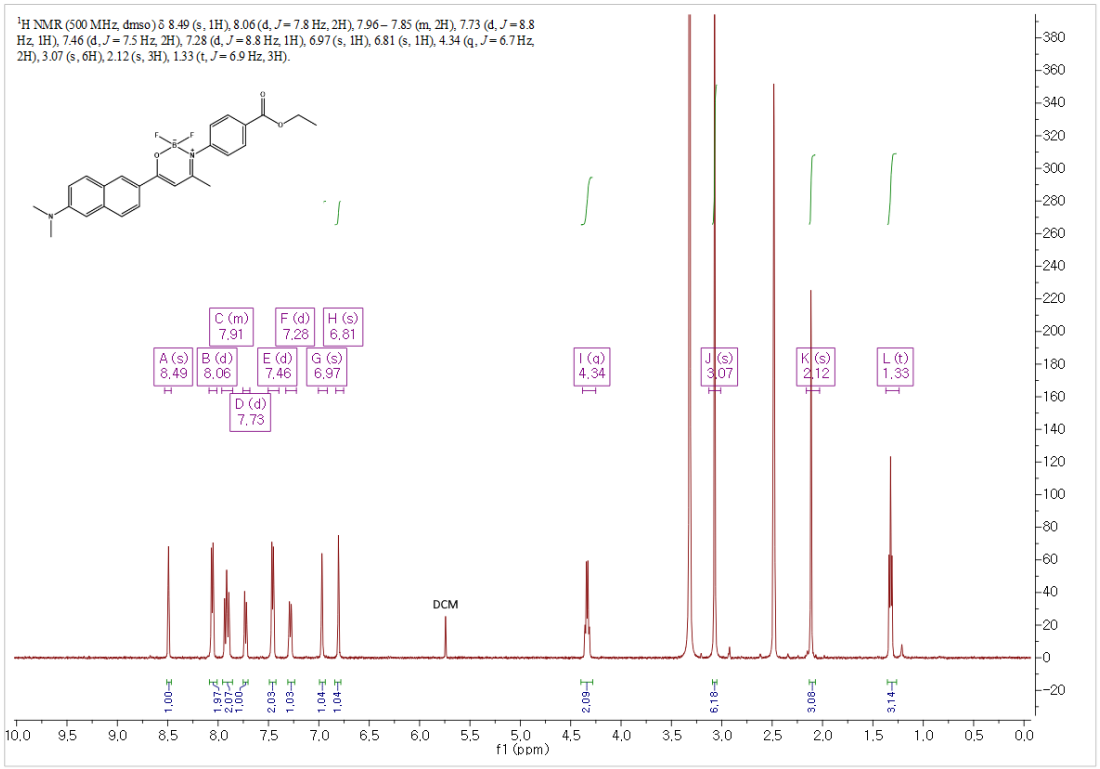


Figure S29. ^{1}H NMR spectrum of compound **3** (500 MHz, DMSO-d_6).

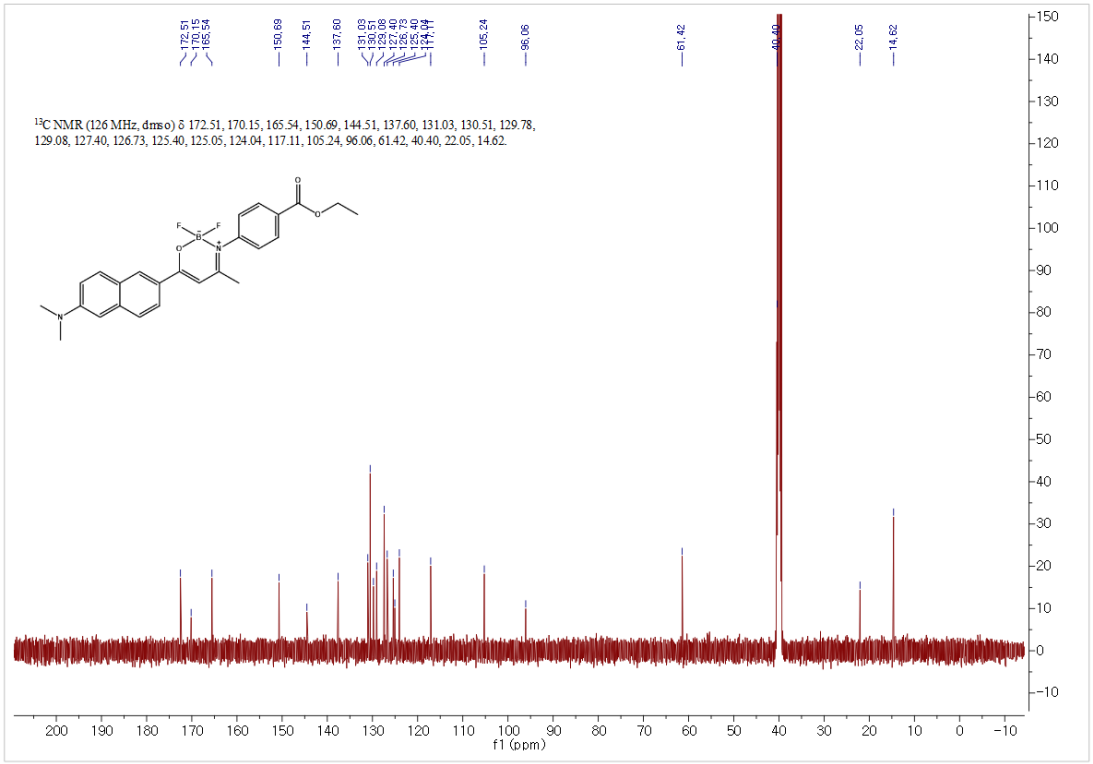


Figure S30. ^{13}C NMR spectrum of compound **3** (125 MHz, DMSO-d_6).

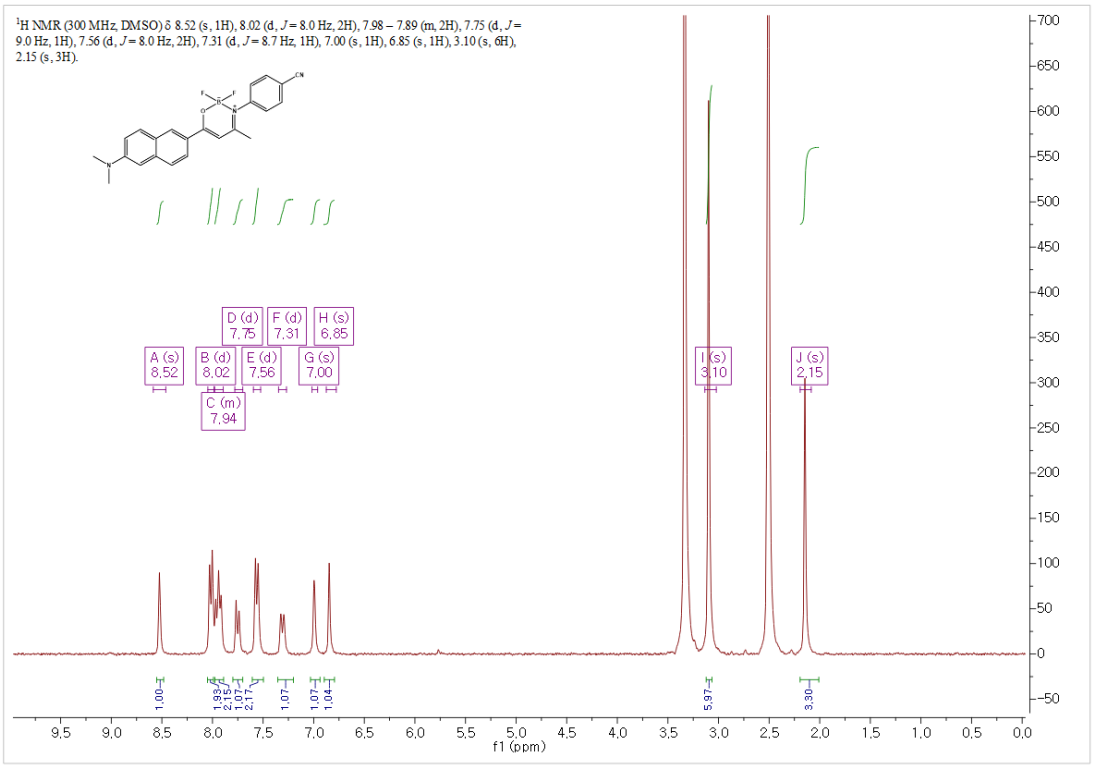


Figure S31. ^{1}H NMR spectrum of compound **4** (300 MHz, DMSO-d_6).

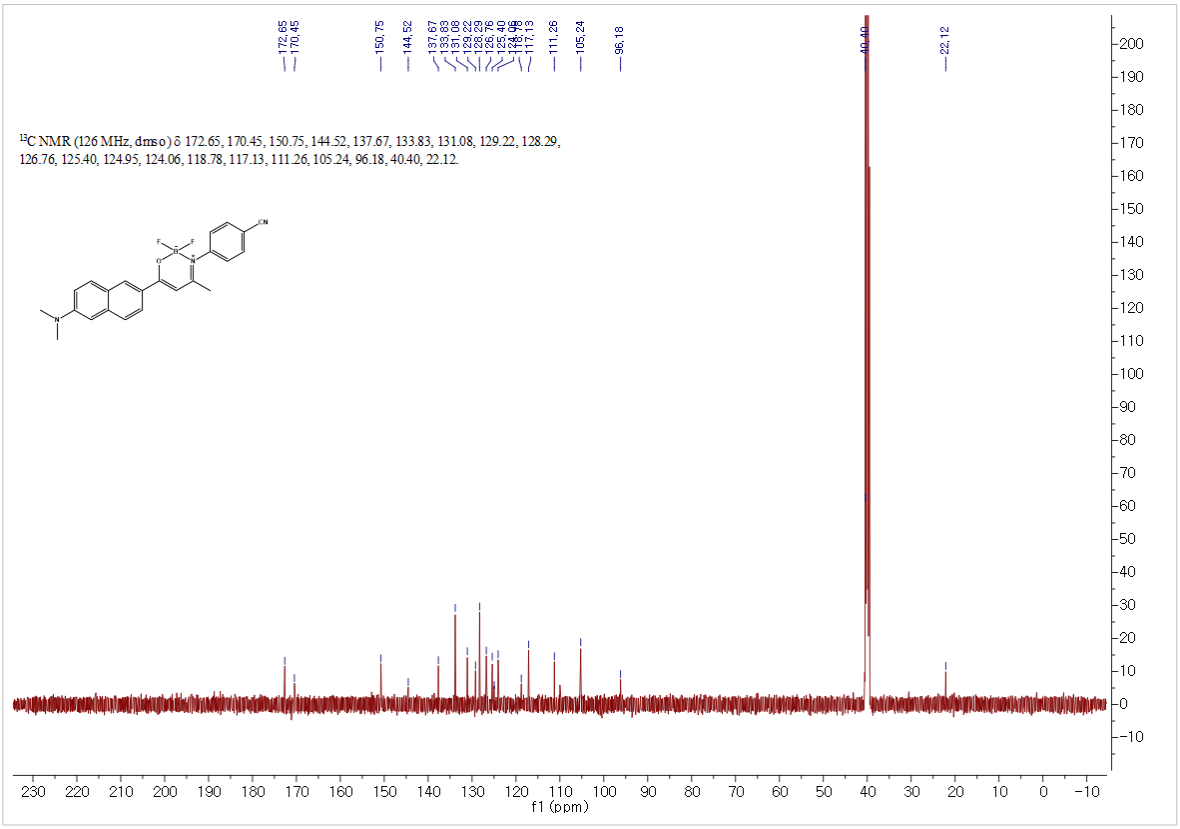


Figure S32. ^{13}C NMR spectrum of compound **4** (125 MHz, DMSO-d_6).

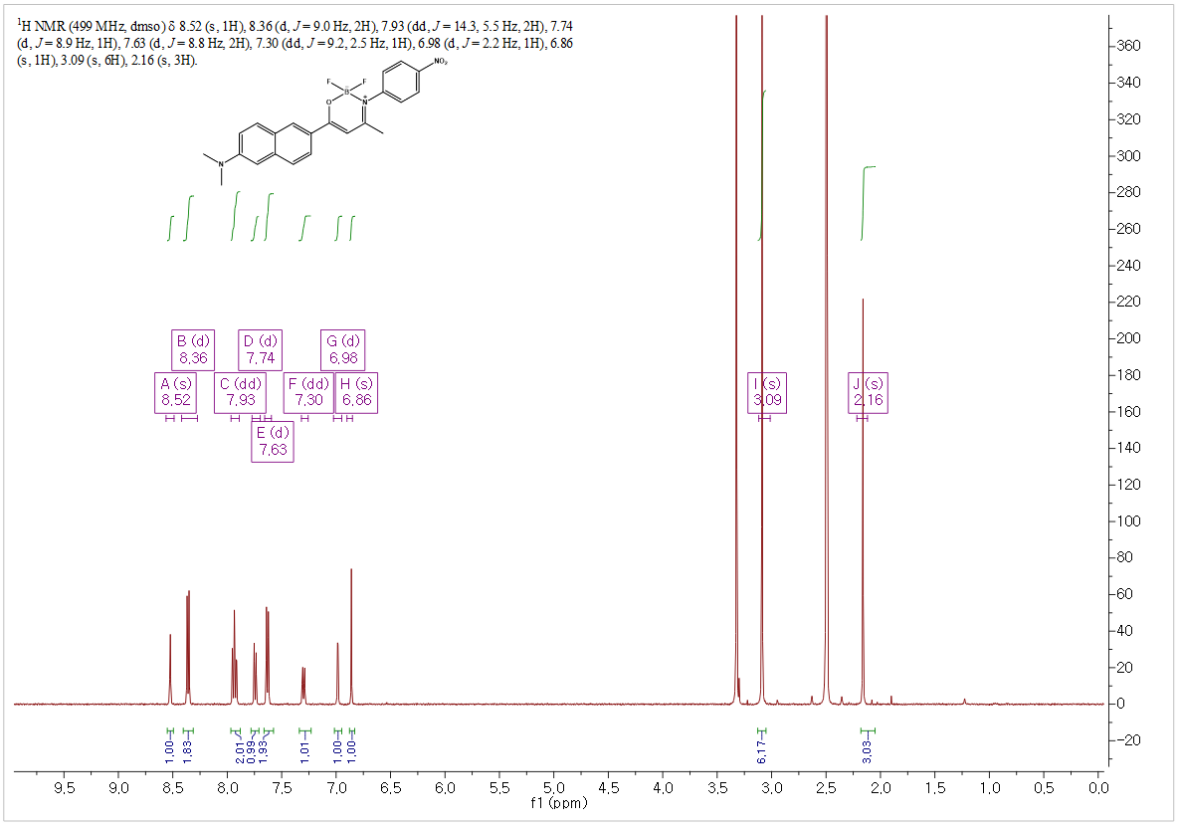


Figure S33. ^{1}H NMR spectrum of compound **5** (500 MHz, DMSO-d_6).

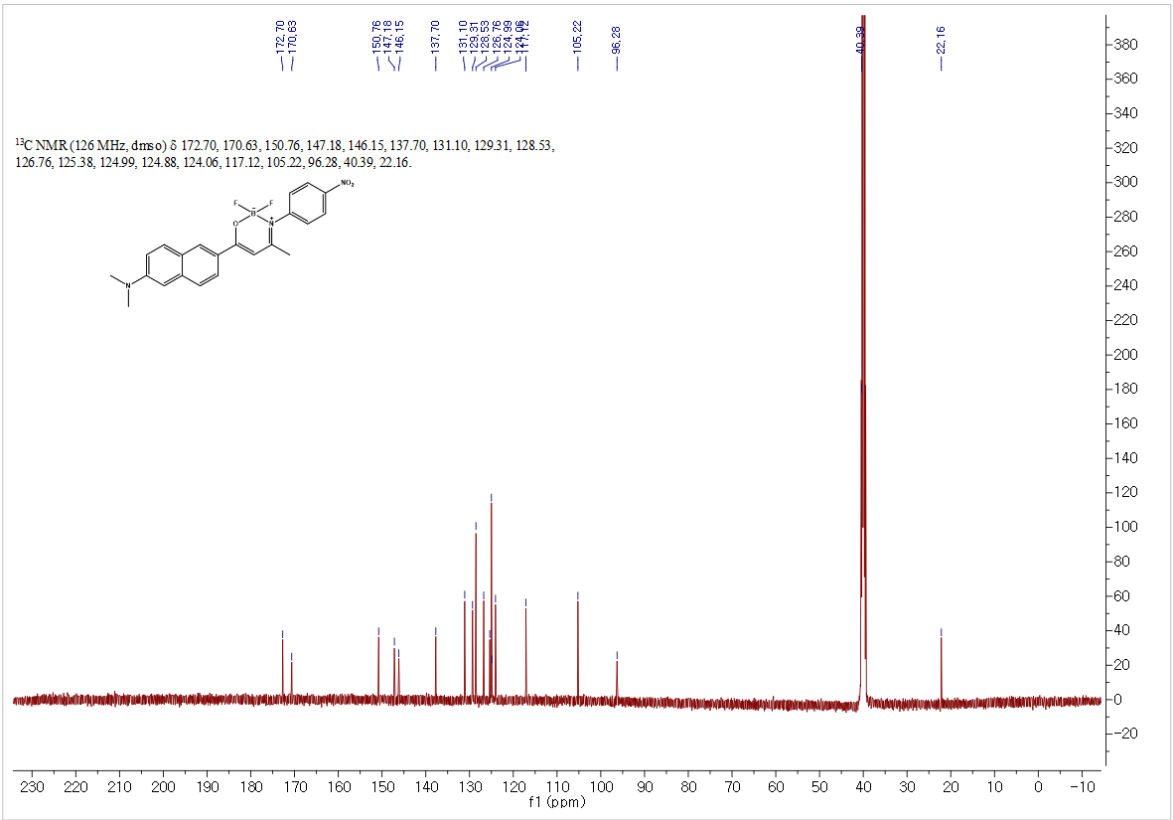


Figure S34. ^{13}C NMR spectrum of compound **5** (125 MHz, DMSO-d_6).

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(2) M. M. Richter, J. D. Debad, D. R. Striplin, G. A. Crosby and A. J. Bard, *Anal. Chem.*, 1996, **68**, 4370-4376.

(3) L. V. Brownell, K. A. Robins, Y. Jeong, Y. Lee and D.-C. Lee, *J. Phys. Chem. C*, 2013, **117**, 25236-25247.

(4) B. Newman, L. Chen, L. C. Henderson, E. H. Doeven, P. S. Francis and D. J. Hayne, *Front. Chem.*, 2020, **8**, 583631.