Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Ratiometric O_2 Sensing Based on Selective Self-Sensitized Photooxidation of Donor-Acceptor Fluorophores

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Materials and Methods

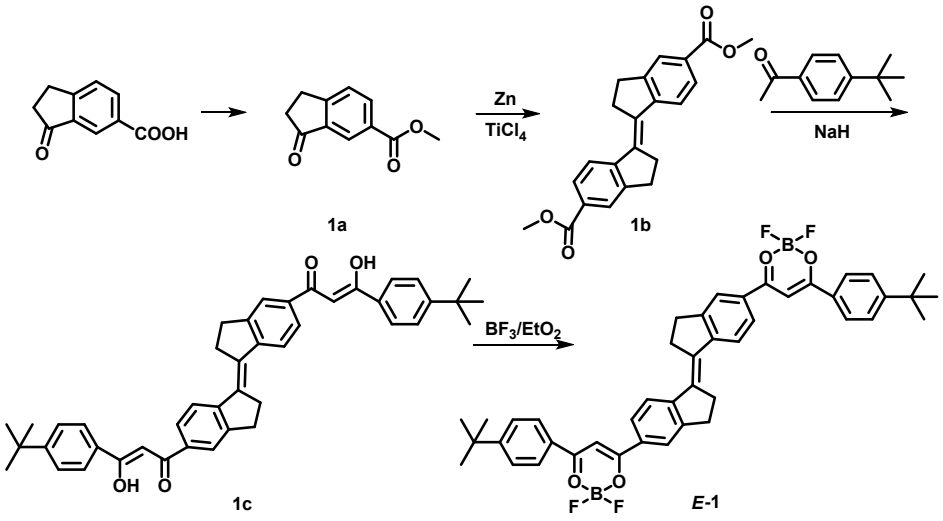
All chemicals were purchased from commercial suppliers and used without further purification. NMR spectra were recorded with JEOL-400 or JEOL-600 spectrometers. High-resolution mass spectra were measured on a Bruker Solarix XR Fourier Transform Ion Cyclotron Resonance Mass Spectrometer, absorption and photoluminescence spectra for the solutions were recorded with Hitachi UV-3900 and F-4600 spectrometer, respectively. The absolute fluorescence quantum yields and phosphorescence spectrum at 77 k was recorded with Edinburgh FLS980 Spectrometer. The electron spin resonance (ESR) experiments were determined on a Bruker E500 electron paramagnetic resonance spectrometer.

Photooxidation experiment. Aerated condition: 20 μM toluene solution of compounds ***E*-1**, ***Z*-1** and **2-6** were prepared in air. Anaerobic condition: 20 μM toluene solution of compound ***E*-1**, ***Z*-1** and **2-6** were prepared in glove box. A 365 nm THORLABS M365l2 LED Lamp was used as the excitation source.

Hydrogel. 1 mg of ***E*-1** in 1 ml THF was added to an aqueous solution of *F*-127 followed by an aqueous solution of polyvinyl alcohol. After stirring for 2 h in 110 °C, the hydrogel was cooled to 0 °C overnight. Irradiation of the same material for 5 min through a mask of a smiley face transferred this image to the hydrogel by photooxidizing the exposed areas only, engendering them with blue fluorescence.

Cell culture and fluorescence imaging. HeLa cells were cultured in culture media (DMEM/F12 supplemented with 10% FBS, 50 unit/mL penicillin, and 50 μg/mL of streptomycin) at 37 °C under a humidified atmosphere containing 5% CO_2 for 24 h. The cells were seeded in a 6-well plate at a density of 10^4 cells per well in culture media. The cells were treated and incubated with 1 μM of **6** at 37 °C under 5% CO_2 for 15 min, then were washed three times with phosphate buffered saline (PBS). For the control experiment, the cells were treated with 1 μM of **6** at 37 °C under 100 % CO_2 for 15 min then were washed three times with phosphate buffered saline (PBS). A 365 nm THORLABS M365l2 LED Lamp was used as the irradiation light, and the aerated and anaerobic cultured Hela cells were irradiated for 1 min at the corresponding conditions. Confocal fluorescence imaging was performed with Nikon A1R microscopy with a 60 × oilimmersion objective lens. The fluorophores were excited at 409 nm and emission was collected by 425-475 nm (blue channel) and 570-620 nm (red channel) band pass filter, respectively.

Synthesis and Characterization

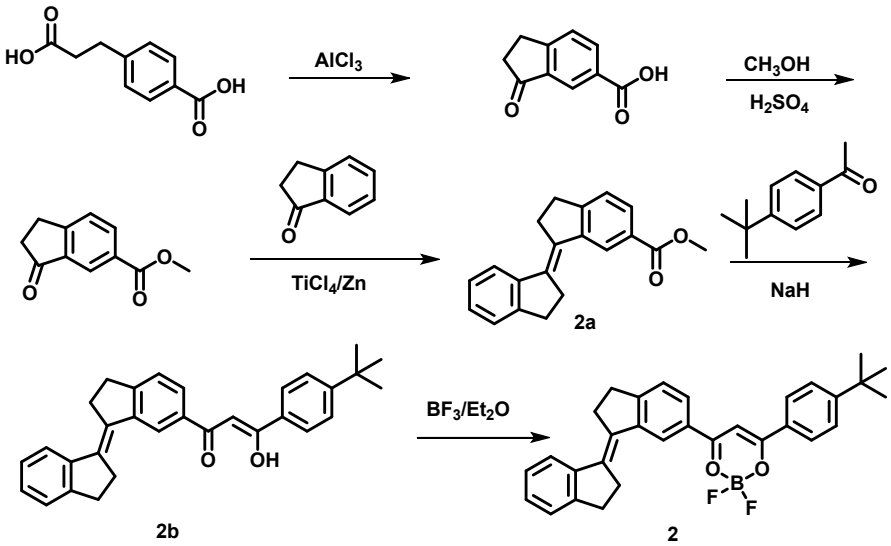


Synthesis of **1a**: Concentrated sulfuric acid (0.5 mL) was added to a solution of 6-carboxyl-1-indone (3 g, 17 mmol) in methanol (100ml). The mixture was refluxed for 2 h. Upon cooling to room temperature, pH was adjusted to 9 with saturated Na_2CO_3 (aq) and the product was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2 as the eluent afforded 2.65 g of **1a** as white solid (yield: 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 3.93 (s, 3H), 3.32 – 2.93 (m, 2H), 2.85 – 2.59 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.9, 166.3, 159.5, 137.4, 135.4, 129.9, 126.9, 125.3, 52.4, 36.5, 26.1. HRMS: calc. for [M+H$^+$] 191.0702, found 191.0701.

Synthesis of **1b**: To a stirred suspension of zinc powder (3.25 g, 50 mmol) in 120 mL dry THF, $TiCl_4$ (5.7 g, 30 mmol) was added slowly at 0 °C, the resulting slurry was refluxed for 3 h. A THF solution (10 mL) of **1a** (0.5 g, 2.6 mmol) was added to the refluxing reaction mixture. The reflux was continued for 2 h. Upon cooling to room temperature, 200 mL of water was added to the reaction mixture, and extracted with CH_2Cl_2. The combined organic phase was washed with water, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Column chromatography using CH_2Cl_2/CH_3OH (100:1, v/v) as the eluent afforded 0.4 g of **1b** (Yield: 89 %.) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 2H), 7.87 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 3.89 (s, 6H), 3.24 (d, *J* = 7.3 Hz, 4H), 3.21 – 3.14 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 154.7, 145.2, 137.5, 130.7, 130.4, 127.4, 126.9, 53.9, 33.9, 33.2. HRMS: calc. for [M+NH_4^+] 366.1699, found 366.1699.

Synthesis of **1c**: 4'-tert-butylacetophenone (423 mg, 2.4 mmol) in 5 mL anhydrous THF was added to a high-pressure tube. The solution was bubbled with N_2 for 5 min, and NaH (57-63% oil dispersion, 800 mg, 20.0 mmol) and **1b** (400 mg, 1.15 mmol) were added. The mixture was allowed to stir for 24 h at 60 °C under N_2 atmosphere. Upon cooling to room temperature, the reaction was quenched by water (100 mL). The pH was adjusted to 3 with HCl (aq) and the organic material was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2/petroleum ether (2:1, v/v) as the eluent afforded **1c** as yellow solid (0.19 g, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 17.02 (s, 2H), 8.22 (s, 2H), 7.93 (d, *J* = 8.0 Hz, 4H), 7.82 (d, *J* = 7.5 Hz,2H), 7.52 (d, *J* = 8.0 Hz, 4H), 7.43 (d, *J* = 7.9 Hz, 2H), 6.85 (s, 2H), 3.32 (d, *J* = 6.2 Hz, 4H), 3.23 (s, 4H), 1.36 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.5, 185.1, 156.3, 152.4, 143.7, 135.8, 134.5, 132.9, 127.1, 126.5, 125.8, 125.2, 123.2, 92.9, 58.9, 35.2, 32.1, 31.4, 31.2. HRMS: calc. for [M+H^+] 637.3314, found 637.3314.

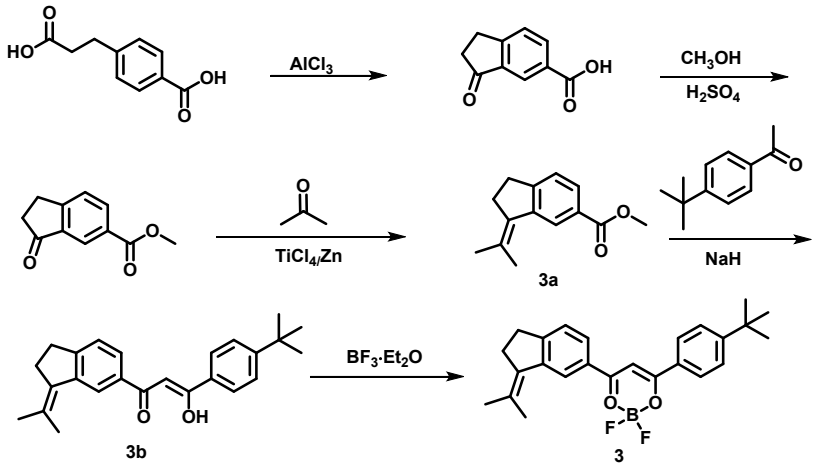
Synthesis of ***E*-1**: To a solution of **1c** (190 mg, 0.30 mmol) in 10 mL CH_2Cl_2 was added Et_3N (420 µL, 3 mmol). After stirring for 5 min at room temperature, BF_3/Et_2O (378 µL, 3.0 mmol) was added. After stirring 2 h at room temperature in the dark, 100 mL of water was added. The organic layers was collected, washed with saturated aqueous NH_4Cl and dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2 as the eluent afforded ***E*-1** as orange solid (0.13 g, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 2H), 8.09 (d, *J* = 8.5 Hz, 4H), 7.96 (d, *J* = 7.0 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 4H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.16 (s, 2H), 3.29 (s, 8H), 1.38 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.8, 182.7 , 159.8, 155.9 , 136.1 , 130.9 , 129.4, 129.0 , 128.3 , 126.3 , 125.8 , 124.6, 93.2, 35.6, 31.9, 31.7, 31.1 , 30.9, 29.6 . HRMS: calc. for [M+H^+] 733.3273, found: 733.3278.



Synthesis of **2a**: To a stirred suspension of zinc powder (6.5 g, 100 mmol) in 120 mL dry THF, $TiCl_4$ (11.4 g, 60 mmol) was added slowly at 0 °C. The resulting slurry was refluxed for 3 h. A THF solution (10 mL) of **1a** (1 g, 5.3 mmol) and 1-indonal (2.1 g, 15.9 mmol) was added to the refluxing reaction mixture. The reflux was continued for 0.5 h. Upon cooling to room temperature, 200 mL of water was added to the reaction mixture, and extracted with CH_2Cl_2. The combined organic phase was washed with water, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Column chromatography with CH_2Cl_2/petroleum ether (1:1, v/v) as the eluent afforded **2a** (0.4 g, 26 % yield:). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.22 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 3.88 (s, 3H), 3.21 – 3.16 (m, 4H), 3.16 – 3.10 (m, 4H). ^{13}C NMR (150 MHz, CD_2Cl_2) δ 167.3, 152.6, 147.5, 143.6, 142.9, 136.9, 134.1, 128.7, 128.2, 127.2, 126.3, 125.3, 125.1, 124.6, 51.9, 31.9, 31.9, 31.2, 31.0. HRMS: calc. for [M+H^+] 291.7319, found: 291.7318.

Synthesis of **2b**: 4'-tert-butylacetophenone (121.5 mg, 0.69 mmol) in 5 mL anhydrous THF was added to a high-pressure tube. The solution was bubbled with N_2 for 5 min, then NaH (57-63% oil dispersion, 400 mg, 10.0 mmol) and **2a** (200 mg, 0.69 mmol) were added. The mixture was stirred for 20 h at 60 °C under N_2 atmosphere. Upon cooling to room temperature, the reaction was quenched by water (100 mL). The pH was adjusted to 3 with HCl (aq) and extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography with CH_2Cl_2/petroleum ether (1:1, v/v) as the eluent afforded **2b** as yellow solid (0.21 g, 70% yield). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 17.12 (s, 1H), 8.19 (s, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 6.87 (s, 1H), 3.26 – 3.17 (m, 4H), 3.15 (dt, *J* = 9.3, 5.1 Hz, 4H), 1.35 (s, 9H). ^{13}C NMR (150 MHz, CD_2Cl_2) δ 186.4, 185.1, 156.4, 152.4, 147.5, 143.9, 142.9, 137.0, 134.2, 132.7, 128.1, 127.8, 126.9, 126.4, 126.2, 126.1, 125.7, 125.5 , 125.5, 125.1, 124.6, 122.9, 121.5, 92.8, 35.0, 31.9, 31.9, 31.3, 31.1, 30.9. HRMS: calc. for [M+H$^+$] 435.2318, found 435.2318.

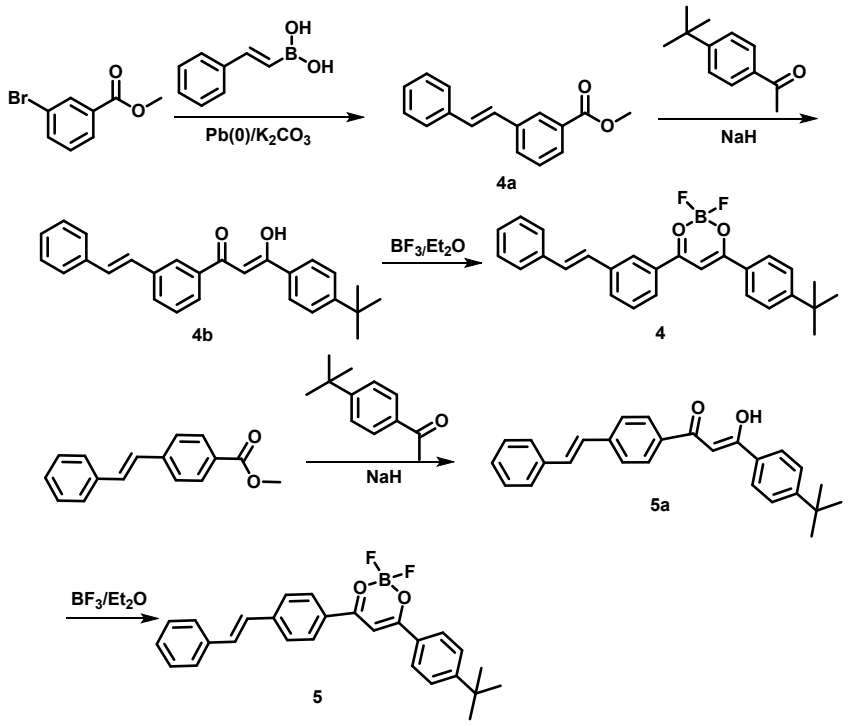
Synthesis of **2**: To a solution of **2b** (210 mg, 0.48 mmol) in 10 mL CH_2Cl_2 was added Et_3N (210 µL, 1.5 mmol). After stirring for 5 min at room temperature, BF_3/Et_2O (189 µL, 1.5 mmol) was added. After stirring at room temperature for 2 h in the dark, 100 ml of water was added. The organic layer was collected, washed with saturated aqueous NH_4Cl and dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography with CH_2Cl_2/petroleum ether (1:1, v/v) as the eluent afforded **2** as orange solid (0.19 g, yield: 82%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.30 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 3H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 6.8 Hz, 1H), 7.23 (dd, *J* = 14.9, 5.7 Hz, 3H), 3.20 (d, *J* = 11.6 Hz, 8H), 1.34 (s, 9H). ^{13}C NMR (150 MHz, CD_2Cl_2) δ 183.0, 182.3, 159.8, 155.9, 147.7, 144.6, 142.6, 138.2, 133.3, 130.6, 129.3, 128.8, 127.8, 127.6, 126.4, 126.3, 125.6, 125.1, 124.7, 124.1, 93.3, 35.4, 31.9, 31.8, 31.6, 31.1, 30.7. HRMS: calc. for [M+NH_4^+] 500.2566, found: 500.2564.



Synthesis of **3a**: To a stirred suspension of zinc powder (6.5 g, 100 mmol) in 120 mL dry THF, $TiCl_4$ (11.4 g, 60 mmol) was added slowly at 0 °C. The resulting slurry was refluxed for 3 h. A THF solution (10 mL) of **1a** (1 g, 5.3 mmol) and acetone (1 mL, 13.5 mmol) was added to the refluxing reaction mixture. The reflux was continued for 0.5 h. Upon cooling to room temperature, 200 mL of water was added to the reaction mixture, and extracted with CH_2Cl_2. The combined organic phase was washed with water, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Column chromatography with CH_2Cl_2/petroleum ether (1:1, v/v) as the eluent afforded **3a** (0.6 g, Yield: 56 %.) ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.16 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 3.85 (s, 3H), 2.97 – 2.89 (m, 2H), 2.73 (t, *J* = 6.3 Hz, 2H), 2.09 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (150 MHz, CD_2Cl_2) δ 154.9, 144.3, 136.4, 130.3, 129.4, 129.1, 127.1, 126.8, 53.8, 32.8, 32.2, 25.7, 23.2. HRMS: calc. for [M+H$^+$] 361.2162, found 361.2173.

Synthesis of **3b**: 4'-tert-butylacetophenone (121.5 mg, 0.69 mmol) was added to a high-pressure tube in 5 mL anhydrous THF. The solution was bubbled with N_2 for 5 min, then NaH (57-63% oil dispersion, 400 mg, 10.0 mmol) and **3a** (200 mg, 0.93 mmol) was added. The mixture was stirred for 24 h at 60 °C under N_2 atmosphere. Upon cooling to room temperature, the reaction was quenched by water (100 mL). The pH was adjusted to 3 with HCl (aq) and extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2/petroleum ether (1:1, v/v) as the eluent afforded **3b** as yellow solid (0.16 g, yield: 47.9%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 16.96 (s, 1H), 8.15 (s, 1H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 6.81 (s, 1H), 3.02 – 2.96 (t, *J* =7.2 Hz, 2H), 2.77 (t, *J* =6.0 Hz, 2H), 2.16 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 186.6, 184.9, 156.3, 152.8, 142.7, 134.6, 133.9, 132.8, 127.3, 126.9, 125.7, 125.3, 125.1, 122.8, 92.7, 35.0, 30.9, 30.9, 30.3, 23.8, 21.4. HRMS: calc. for [M+NH_4^+] 426.2410, found 426.2408.

Synthesis of **3**: To a solution of **3b** (160 mg, 0.44 mmol) in 10 mL CH_2Cl_2 was added Et_3N (210 µL, 1.5 mmol). After stirring for 5 min at room temperature, BF_3/Et_2O (189 µL, 1.5 mmol) was added. After stirring at room temperature for 2 h in the dark, 100 mL of water was added. The organic layer was collected, washed with saturated aqueous NH_4Cl, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2/ petroleum ether (1:1, v/v) as the eluent afforded **3** as yellow solid (0.15 g, yield: 83.3%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.24 (s, 1H), 8.09 – 8.03 (m, 2H), 7.90 (s, 1H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 1.6 Hz, 1H), 3.01 (s, 2H), 2.78 (s, 2H), 2.16 (s, 3H), 1.91 (s, 3H), 1.35 (d, *J* = 1.7 Hz, 9H). ^{13}C NMR (150 MHz, CD_2Cl_2) δ 183.3, 182.2 159.7, 156.5, 143.4, 133.9, 130.3, 129.4, 128.7, 127.2, 126.3, 125.7, 124.1, 93.2, 35.4, 30.8, 30.7, 30.6, 23.9, 21.5. HRMS: calc. for [M+H$^+$] 217.1223, found: 217.1228.



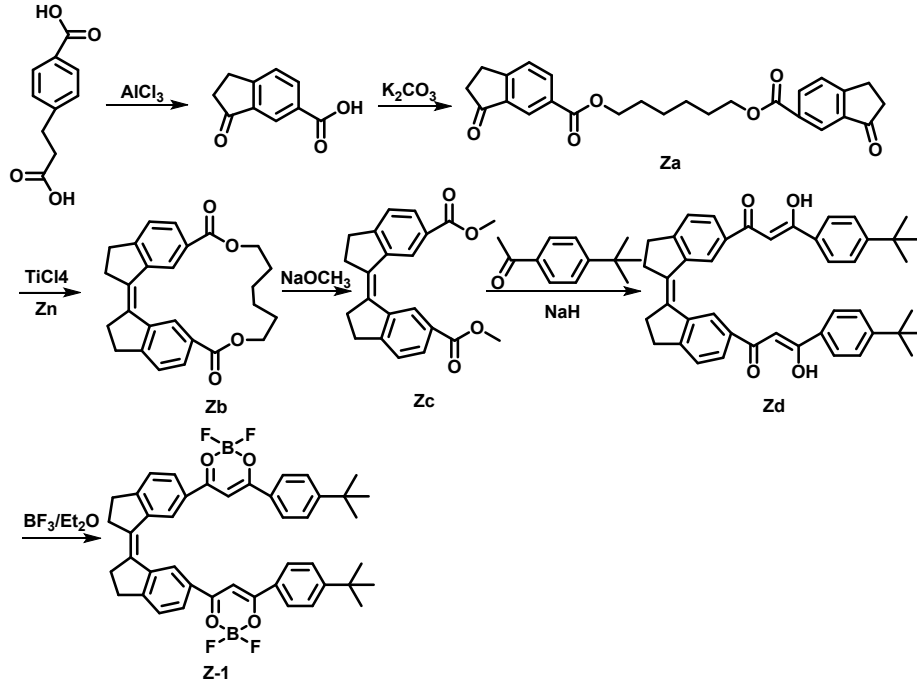
Synthesis of **4b**: 4'-tert-butylacetophenone (147.9 mg, 0.84 mmol) was added to a high-pressure tube in 5mL anhydrous THF. The solution was bubbled with N_2 for 5 min, then NaH (57-63% oil dispersion, 200 mg, 5.0 mmol) and **4a**[1] (200 mg, 0.84 mmol) was added to the mixture. The reaction mixture was allowed to stir for 24 h at 60 °C under N_2 atmosphere. Upon cooling to room temperature, the reaction was quenched by water (100 mL). The pH was adjusted to 3 with HCl (aq) and extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2/ petroleum ether (1:1, v/v) as eluent afforded **4b** as yellow solid (0.21 g yield: 68%).^{1}H NMR (400 MHz, $CDCl_3$) δ 16.93 (s, 1H), 8.11 (d, *J* = 1.3 Hz, 1H), 7.95 (d, *J* = 8.5 Hz,2H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.45 (m, 5H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.24 – 7.13 (m, 2H), 6.87 (s, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 185.4, 156.5, 138.0, 137.0, 136.3, 132.8, 130.2, 130.1, 129.1, 128.9, 128.1, 127.8, 127.2, 126.7, 126.2, 125.8, 125.2, 93.2, 35.2, 31.2. HRMS: calc. for [M+H$^+$] 383.2005, found 383.2001.

Synthesis of **4**: To a solution of **4b** (210 mg, 0.57 mmol) in 10 mL CH_2Cl_2 was added Et_3N (420 µL, 3.0 mmol) and BF_3/Et_2O (378 µL, 3.0 mmol). After stirring at room temperature for 2 h in the dark, 100 mL of water was added. The organic layers was collected, washed with saturated aqueous NH_4Cl and dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2 as eluent afforded **4** as yellow solid (0.20 g yield: 81.3%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.60 – 7.49 (m, 5H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.26 – 7.12 (m, 3H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.4, 182.5, 160.1, 138.7, 136.7, 132.8, 132.7, 131.0, 129.5, 129.2, 128.9, 128.4, 127.6, 126.9, 126.9, 126.7, 126.4, 93.4, 35.6, 31.1. HRMS: calc. for [M+NH_4^+] 448.2253, found: 448.2253.

Synthesis of **5a**: 4'-tert-butylacetophenone (147.9 mg, 0.84 mmol) was added to a high-pressure tube in 5mL anhydrous THF. The solution was bubbled with N_2 for 5 min, then NaH (57-63% oil dispersion, 200 mg, 5.0 mmol) and (E)-methyl 4-styrylbenzoate (200 mg, 0.84 mmol) was added to the mixture. The reaction mixture was stirred for 24 h at 60 °C under N_2 atmosphere. Upon cooling to room temperature, the reaction was quenched by water (100 mL). The pH was adjusted to 3 with HCl (aq) and the solution was extracted with CH_2Cl_2. The combined organic

phase was dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2/ petroleum ether (1:1, v/v) as eluent afforded **5a** as yellow solid (0.25 g, yield: 78%).^{1}H NMR (400 MHz, $CDCl_3$) δ 16.96 (s, 1H), 7.96 (dd, *J* = 18.5, 8.4 Hz, 4H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.53 (dd, *J* = 15.2, 8.1 Hz, 4H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.27 – 7.11 (m, 2H), 6.85 (s, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 184.7, 156.3, 141.5, 136.9, 134.5, 133.0, 131.2, 128.9, 128.3, 127.7, 127.2, 127.1, 126.9, 126.7, 125.8, 92.9, 35.2, 31.2. HRMS: calc. for [M+H$^+$] 383.2005, found 383.2002.

Synthesis of **5**: To a solution of **5a** (250 mg, 0.65 mmol) in 10 mL CH_2Cl_2 was added Et_3N (420 μL, 3.0 mmol) and BF_3/Et_2O (378 μL, 3.0 mmol). After stirring at room temperature for 2 h in the dark, 100 mL of water was added. The organic layers was collected, washed with saturated aqueous NH_4Cl and dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2 as eluent afforded **5** as yellow solid (0.22 g yield: 78.7%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (d, *J* = 8.5 Hz, 2H), 8.22 (d, *J* = 8.5 Hz, 2H), 7.83 – 7.74 (m, 3H), 7.59 (d, *J* = 8.2 Hz, 4H), 7.50 (d, *J* = 16.4 Hz, 1H), 7.33 (dd, *J* = 13.2, 5.8 Hz,3H), 7.24 (d, *J* = 7.1 Hz, 1H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 182.5, 160.2 , 145.2, 137.1, 133.8, 133.4, 130.6, 130.0, 129.5, 129.4, 129.3, 127.9, 127.8, 127.0, 116.0, 94.8, 35.9, 31.3. HRMS: calc. for [M+NH_4^+] 448.2253, found: 448.2254.



Synthesis of **Za**: To a solution of 6-carboxylic-1-indone (2 g, 11.4 mmol) of acetonitrile (50 mL) was added 1, 6-dibromohexane (1.39 g, 5.7 mmol) and K_2CO_3 (3.15 g, 22.8 mmol), and the mixture was stirred at reflux for 8 h. After cooling to room temperature, 100 mL of water was added to the solution and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and column chromatography using CH_2Cl_2/CH_3OH (100:1, v/v) as eluent afforded **Za** as white solid (2.1 g, yield: 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 2H), 8.24 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 4.33 (t, *J* = 6.6 Hz, 4H), 3.27 – 3.04 (m, 4H), 2.78 – 2.68 (m, 4H), 1.84 – 1.72 (m, 4H), 1.51 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 165.9, 159.5, 137.4, 135.5, 130.1, 126.9, 125.2, 65.3, 36.5, 28.7, 26.1, 25.8. HRMS: calc. for [M+NH_4^+] 452.2067, found: 452.2066.

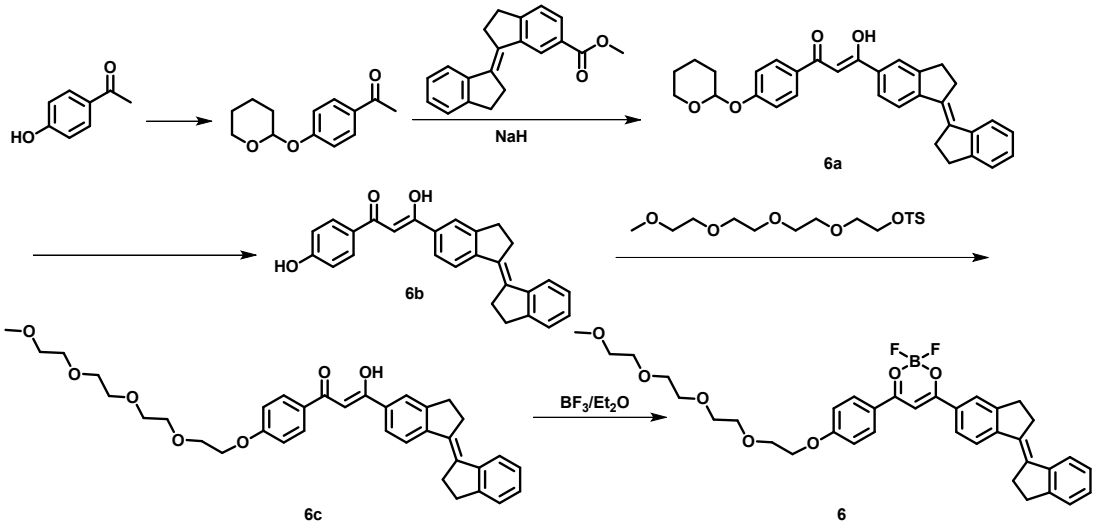
Synthesis of ***Z*b**: To a stirred suspension of zinc powder (3.9 g, 60 mmol) in 120 mL dry THF, $TiCl_4$ (5.5 mL, 9.5 g, 50 mmol) was added over 2 min at 0 °C. The resulting slurry was heated at reflux for 3 h. A THF solution (200 mL) of ***Z*a** (2.1 g, 4.8 mmol) was added over 3 h by dropping funnel to the refluxing reaction mixture. The reflux was continued for 0.5 h after the addition completing. Upon cooling to room temperature, 200 mL of water was added to the reaction mixture, and extracted with CH_2Cl_2. The combined organic phase was washed with water, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Column chromatography using CH_2Cl_2/CH_3OH (100:0.5, v/v) as eluent afforded ***Z*b** (1.2 g Yield: 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (s, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 4.42 – 4.24 (m, 4H), 3.09 – 2.98 (m, 4H), 2.88 – 2.76 (m, 4H), 1.87 – 1.70 (m, 4H), 1.50 (s, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.9, 153.7, 140.7, 135.2, 129.6, 128.5, 125.3, 123.4, 64.9, 35.3, 30.9, 28.6, 25.8. HRMS: calc. for [M+H$^+$] 403.1903, found 403.1899.

Synthesis of ***Z*c**: To a solution of ***Z*b** (200 mg, 0.5 mmol) of methanol was added sodium methoxide (400 mg, 7.4 mmol), then the mixture was stirred at reflux for 10 h. After cooling to room temperature, the methanol was

removed under reduced pressure and column chromatography using CH_2Cl_2/CH_3OH (100:0.5, v/v) as eluent afforded ***Zc*** as white solid (0.15 g Yield: 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (s, 2H), 7.88 (d, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 3.86 (s, 6H), 3.05 – 2.98 (m, 4H), 2.85 (t, *J* = 6.8 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.2, 153.5, 140.5, 135.2, 129.0, 128.2, 125.2, 124.4, 51.9, 34.7, 30.8. HRMS: calc. for [M+NH_4^+] 366.1699, found 366.1692.

Synthesis of ***Zd***: 4'-tert-butylacetophenone (158.6 mg, 0.90 mmol) was added to a high-pressure tube in 5mL anhydrous THF. The solution was bubbled with N_2 for 5 min, then NaH (57-63% oil dispersion, 800 mg, 20.0 mmol) and ***Zc*** (150 mg, 0.43 mmol) was added to the mixture. The reaction mixture was stirred for 24 h at 60 °C under N_2 atmosphere. Upon cooling to room temperature, the reaction was quenched by water (100 mL). The pH was adjusted to 3 with HCl (aq) and extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2/petroleum ether (2:1, v/v) as eluent afforded ***Zd*** as yellow solid (0.19 g yield: 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 17.10 (s, 2H), 8.80 (s, 2H), 7.96 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 4H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 4H), 6.90 (s, 2H), 3.11 – 3.02 (m, 4H), 2.88 (t, *J* = 6.7 Hz, 4H), 1.22 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.5, 185.2, 156.1, 153.5, 140.9, 135.3, 133.6, 132.5, 127.1, 126.9, 125.8, 125.5, 121.5, 92.2, 34.9, 31.1, 30.9. HRMS: calc. for [M+H^+] 637.3312, found: 637.3315.

Synthesis of ***Z*-1**: To a solution of **Zd** (190 mg, 0.30 mmol) in 10 mL CH_2Cl_2 was added Et_3N (420 µL, 3 mmol) and BF_3/Et_2O (378 µL, 3.0 mmol). After stirring at room temperature for 2 h in the dark, 100 mL of water was added. The organic layers was collected, washed with saturated aqueous NH_4Cl and dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2 as eluent afforded ***Z*-1** as orange solid (0.13 g yield: 59%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83 (s, 2H), 8.25 (d, *J* = 7.9 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 4H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 4H), 7.05 (s, 2H), 3.15 (d, *J* = 6.5 Hz, 4H), 2.95 (d, *J* = 6.4 Hz, 4H), 1.28 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.9, 181.3, 160.1, 157.2, 141.2, 135.5, 130.1, 129.2, 128.5, 126.8, 126.2, 122.1, 91.7, 35.5, 35.0, 31.2, 30.8, 29.4. HRMS: calc. for [M+NH_4^+] 750.3543, found: 750.3535.



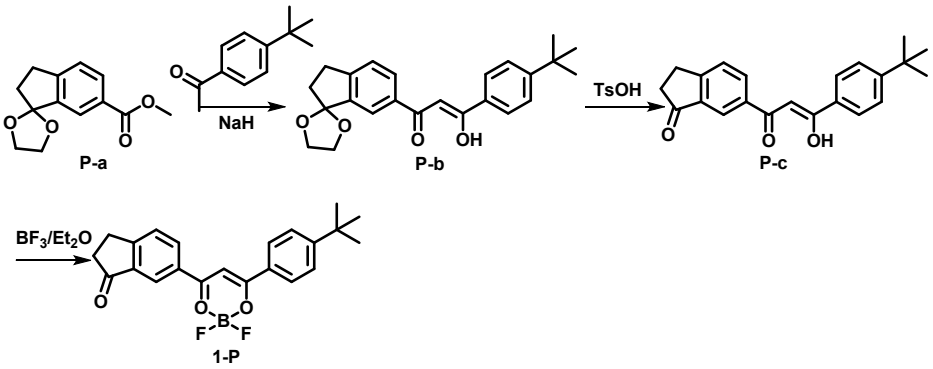
Synthesis of **6a**: 1-(4-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)ethanone (200 mg, 0.9 mmol) was added to a high-pressure tube in 5mL anhydrous THF. The solution was bubbled with N_2 for 5 min, then NaH (57-63% oil dispersion, 400 mg, 10.0 mmol) and **2a** (261 mg, 0.9 mmol) was added to the mixture. The reaction mixture stirred for 24 h at 60 °C under N_2 atmosphere. Upon cooling to room temperature, the reaction was quenched by water (100 mL). The pH was adjusted to 3 with HCl (aq) and extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2/CH_3OH (100:1, v/v) as eluent afforded **6a** as yellow solid (0.32 g, yield: 65%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 17.19 (s, 1H), 8.18 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.80 (s, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.83 (s, 1H), 5.51 (t, *J* = 2.9 Hz, 1H), 3.87 – 3.80 (m, 1H), 3.59 (dt, *J* = 10.8, 4.2 Hz, 1H), 3.19 (ddd, *J* = 29.5, 16.1, 4.6 Hz, 8H), 2.02 – 1.94 (m, 1H), 1.86 (dq, *J* = 11.0, 3.6 Hz, 2H), 1.67 (ddt, *J* = 13.4, 8.0, 4.1 Hz, 2H), 1.58 (dq, *J* = 10.5, 6.7, 5.2 Hz, 1H). ^{13}C NMR (150 MHz, CD_2Cl_2) δ 185.4, 160.9, 152.3, 147.5, 143.9, 142.9, 137.0, 134.2, 129.5, 129.0, 127.3, 126.4, 125.9, 125.1, 124.6, 122.8, 116.3, 115.5, 96.4, 92.3, 62.2, 31.9, 31.9, 31.2, 31.1, 30.2, 25.2, 18.7.HRMS: calc. for [M+H^+] 479.2216, found: 479.2215.

Synthesis of **6b**: **6a** (0.32 g, 0.65 mmol) was dissolved in THF/H_2O/ acetic acid (1/1/2, v/v/v), the mixture was stirred overnight at 45°C. THF was removed and the pH was adjusted to 6 by saturated $NaHCO_3$, followed by extraction with ethyl acetate. The combined organic phase was dried over anhydrous Na_2SO_4, followed by filtration and

evaporation of the solvent. Column chromatography using CH_2Cl_2/CH_3OH (100:1, v/v) as eluent afforded **6b** as yellow solid (0.20 g yield: 78%)^{1}H NMR (400 MHz, DMSO-d_6) δ 17.52 (s, 1H), 10.39 (s, 1H), 8.14 (s, 1H), 8.01 (t, *J* = 9.3 Hz, 3H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.22 (dt, *J* = 17.9, 7.1 Hz, 2H), 7.13 (s, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.08 (d, *J* = 12.3 Hz, 8H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 186.2, 184.3, 162.7, 152.5, 147.5, 143.8, 142.8, 136.9, 134.3, 133.9, 130.5, 127.9, 127.0, 126.2, 125.7, 125.6, 124.9, 122.8, 116.1 , 92.5, 55.4, 31.9, 31.2, 31.0. HRMS: calc. for [M+H$^+$] 395.1641, found 395.1646.

Synthesis **6**: **6b** (0.2 g, 0.5 mmol) and 4-(2,5,8,11-tetraoxatetradecan-14-yl) benzenesulfonic acid (181 mg, 0.5 mmol) were dissolved in 20 mL of acetonitrile, potassium carbonate(1.38 g, 10 mmol) was added to the solution and the mixture was refluxed for 10 h. After cooling to room temperature the solid were filtered off, and the organic phase was dried over anhydrous Na_2SO_4. The solvent was evaporated, the solids were redissolved in 10 mL of DCM, and Et_3N (210 µL, 1.5 mmol) and BF_3/Et_2O (189 µL, 1.5 mmol) were added to the solution. After stirring at room temperature for 2 h in the dark, 100 mL saturated NH_4Cl solution was added. The organic layer was collected, washed with saturated aqueous NH_4Cl 3 times. The organic phase was dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2 as eluent afforded **6** as orange solid (0.13 g yield: 59%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.30 (s, 1H), 8.15 (d, *J* = 8.9 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 7.24 (dt, *J* = 15.0, 7.0 Hz, 2H), 7.15 (s, 1H), 7.09 (d, *J* = 8.9 Hz, 2H), 4.27 – 4.18 (m, 2H), 3.88 – 3.82 (m, 2H), 3.67 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.61 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.59 – 3.53 (m, 6H), 3.47 (dd, *J* = 5.7, 3.4 Hz, 2H), 3.31 (s, 3H), 3.28 – 3.15 (m, 8H). ^{13}C NMR (150 MHz, CD_2Cl_2) δ 182.0, 181.5, 165.1, 155.6, 147.7, 144.6, 142.6, 138.1, 133.4, 131.5, 130.8, 127.6, 127.6, 126.4, 125.6, 125.1, 124.7, 124.4, 123.9, 115.2, 92.6, 71.9, 70.9, 70.6, 70.6, 70.5, 70.4, 69.3, 68.2, 58.6, 31.9, 31.8, 31.6, 31.2. HRMS: calc. for [M+NH_4^+] 630.2156, found: 630.2160.

Preparative photooxidation of ***E*-1**: 5 mg of ***E*-1** was dissolved in 100 mL toluene, the solution was saturated with O_2 by bubbling for 20 min, and irradiation with a xenon lamp with a 365 nm filter for 10 min. The solvent was removed under the reduced pressure, and the residue was purified by column chromatography using CH_2Cl_2/petroleum ether (2:1, v/v) as eluent to afford 2 mg of **1-P** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.1 Hz, 2H), 8.03 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.15 (s, 1H), 3.26 – 3.14 (m, 2H), 2.78 – 2.60 (m, 2H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1, 181.4, 175.8, 161.7, 160.6, 137.9, 134.6, 131.9, 129.5, 129.1, 126.6, 124.3, 93.4, 90.2, 36.7, 35.8, 31.2, 26.6. HRMS: calc. for [M+NH_4^+] 400.1890, found: 400.1885.



Synthesis of **P-b**: 4'-tert-butylacetophenone (120.0 mg, 0.64 mmol) in 5mL anhydrous THF was added to a high-pressure tube. The solution was bubbled with N_2 for 5 min, then NaH (57-63% oil dispersion, 200 mg, 5.0 mmol) and compound **P-a**[2](150 mg, 0.64 mmol) was added to the mixture. The reaction mixture was stirred for 24 h at 60 °C under N_2 atmosphere. Upon cooling to room temperature, the reaction was quenched by water (100 mL). The pH was adjusted to 3 with HCl (aq) and extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2/CH_3OH (100:1, v/v) as eluent afforded **P-b** as yellow solid (0.19 g, yield: 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 16.85 (s, 1H), 8.30 (s, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 6.87 (s, 1H), 3.25 – 3.16 (m, 2H), 2.80 – 2.69 (m, 2H), 1.35 (s, 9H).^{13}C NMR (150 MHz, $CDCl_3$) δ 206.2, 185.9, 184.4, 158.9, 156.7, 137.5, 135.4, 133.3, 132.5, 127.3, 127.2, 125.8, 122.5, 92.9, 49.9, 49.7, 36.6, 35.2, 31.2, 26.1. HRMS: calc. for [M+H$^+$] 379.1903, found 379.1905.

Synthesis of **P-c**: 0.19 g of **P-b** was dissolved in THF/water (3:2, 10ml total) and TsOH (0.2eq) was added. The resulting mixture was stirred at room temperature overnight and the product was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent to afford 0.12 g of **P-c** as yellow solid, which was sufficiently pure for subsequent steps without additional

purification. (yield: 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.79 (s, 1H), 8.22 (s, 1H), 8.20 – 8.13 (m, 1H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 6.80 (s, 1H), 3.17 – 3.09 (m, 2H), 2.69 (dd, *J* = 7.0, 4.9 Hz, 2H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.1, 184.6, 159.2, 156.8, 137.6, 135.5, 133.4, 132.6, 127.4, 125.9, 122.6, 93.1, 68.2, 53.6, 36.7, 35.3, 31.3, 26.3. HRMS: calc. for [M+H$^+$] 335.1641, found 335.1644.

Synthesis of **1-P**: To a solution of **P-c** (120 mg, 0.36 mmol) in 10 mL CH_2Cl_2 was added Et_3N (210 µL, 1.5 mmol) and BF_3/Et_2O (189 µL, 1.5 mmol). After stirring at room temperature for 2 h in the dark, 100 mL of water was added. The organic phase was separated, washed with saturated aqueous NH_4Cl and dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent. Column chromatography using CH_2Cl_2 as eluent afforded of **1-P** as white solid (0.05 g yield: 33%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.1 Hz, 2H), 8.03 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.15 (s, 1H), 3.26 – 3.14 (m, 2H), 2.78 – 2.60 (m, 2H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1, 181.4, 175.8, 161.7, 160.6, 137.9, 134.6, 131.9, 129.5, 129.1, 126.6, 124.3, 93.4, 90.2, 36.7, 35.8, 31.2, 26.6. HRMS: calc. for [M+NH_4^+] 400.1890, found: 400.1885.

Supplementary Figures and Tables.

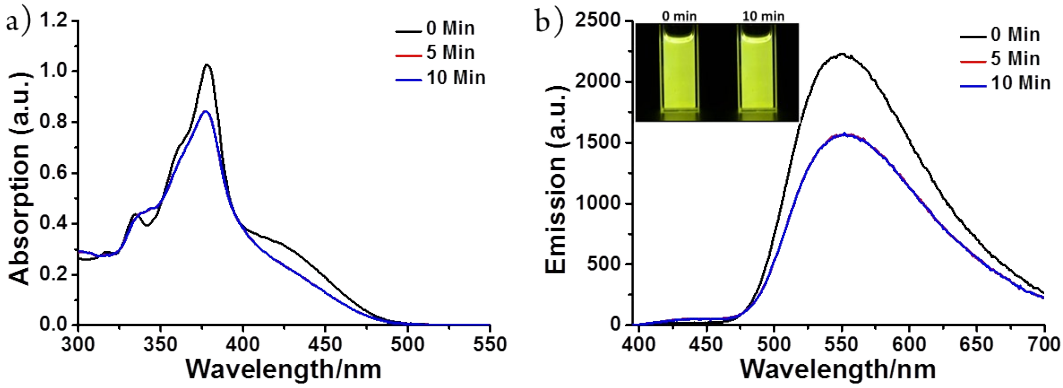


Figure S1: Time-dependent **a**) UV-Vis and **b**) fluorescence spectra of compound ***E*-1** in N_2 saturated toluene solution (20 µM) irradiated by a 365nm LED lamp (inset: fluorescence images of ***E*-1** in N_2 saturated toluene solution (20 µM) irradiated by a 365nm LED lamp, before (left) and after 5 min (right) irradiation).

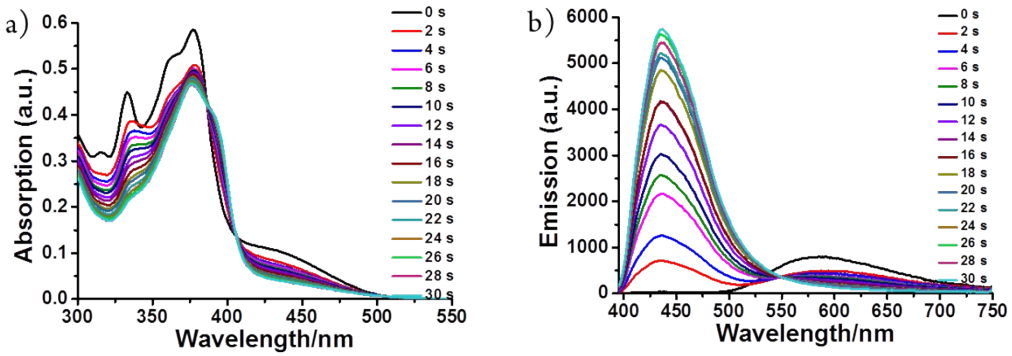


Figure S2: Time-dependent **a**) UV-Vis and **b**) fluorescence spectra of **2** in air saturated toluene (20 µM) solution irradiated by a 365nm LED lamp.

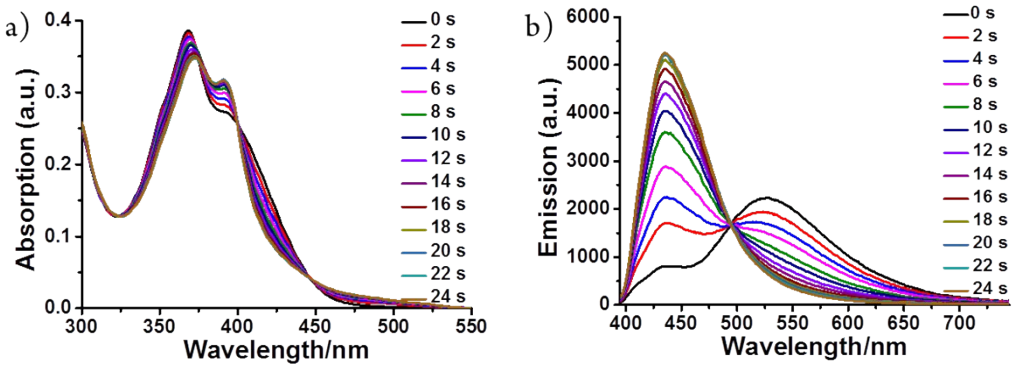


Figure S3: Time-dependent **a**) UV-Vis and **b**) fluorescence spectra of **3** in air saturated toluene (20 µM) solution irradiated by a 365nm LED lamp.

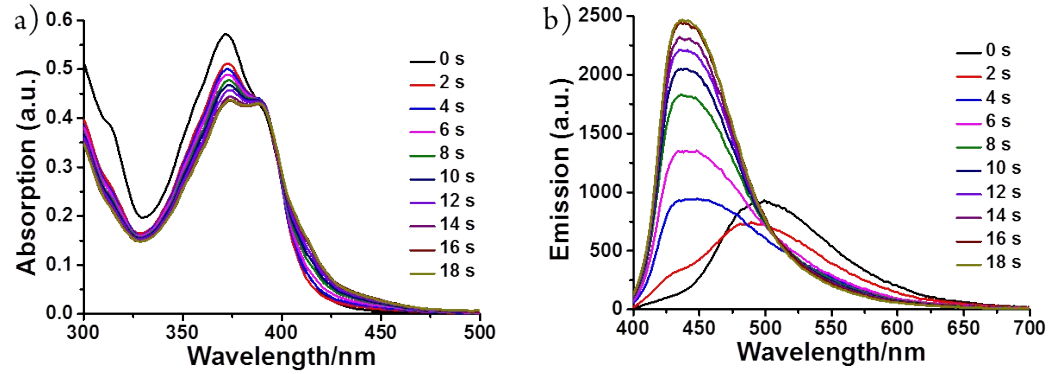


Figure S4: Time-dependent **a**) UV-Vis and **b**) fluorescence spectra of **4** in air saturated toluene (20 µM) solutions irradiated by a 365nm LED lamp.

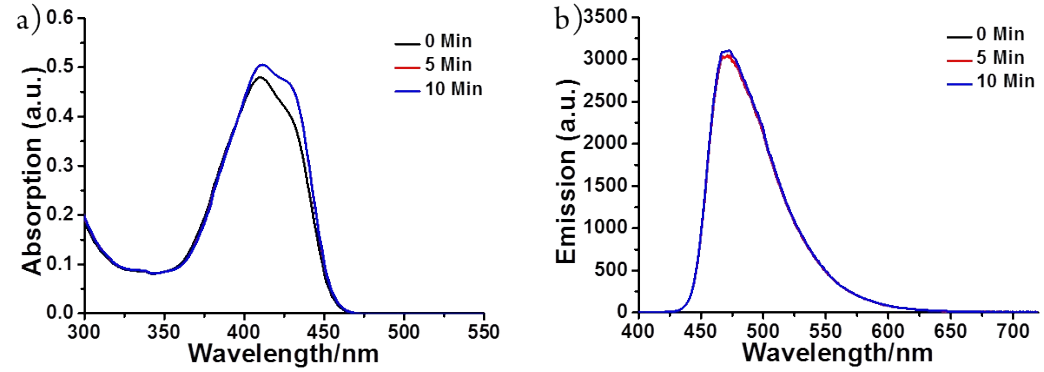


Figure S5: Time-dependent **a**) UV-Vis and **b**) fluorescence spectra of **5** in air saturated toluene (20 µM) solution irradiated by a 365nm LED lamp.

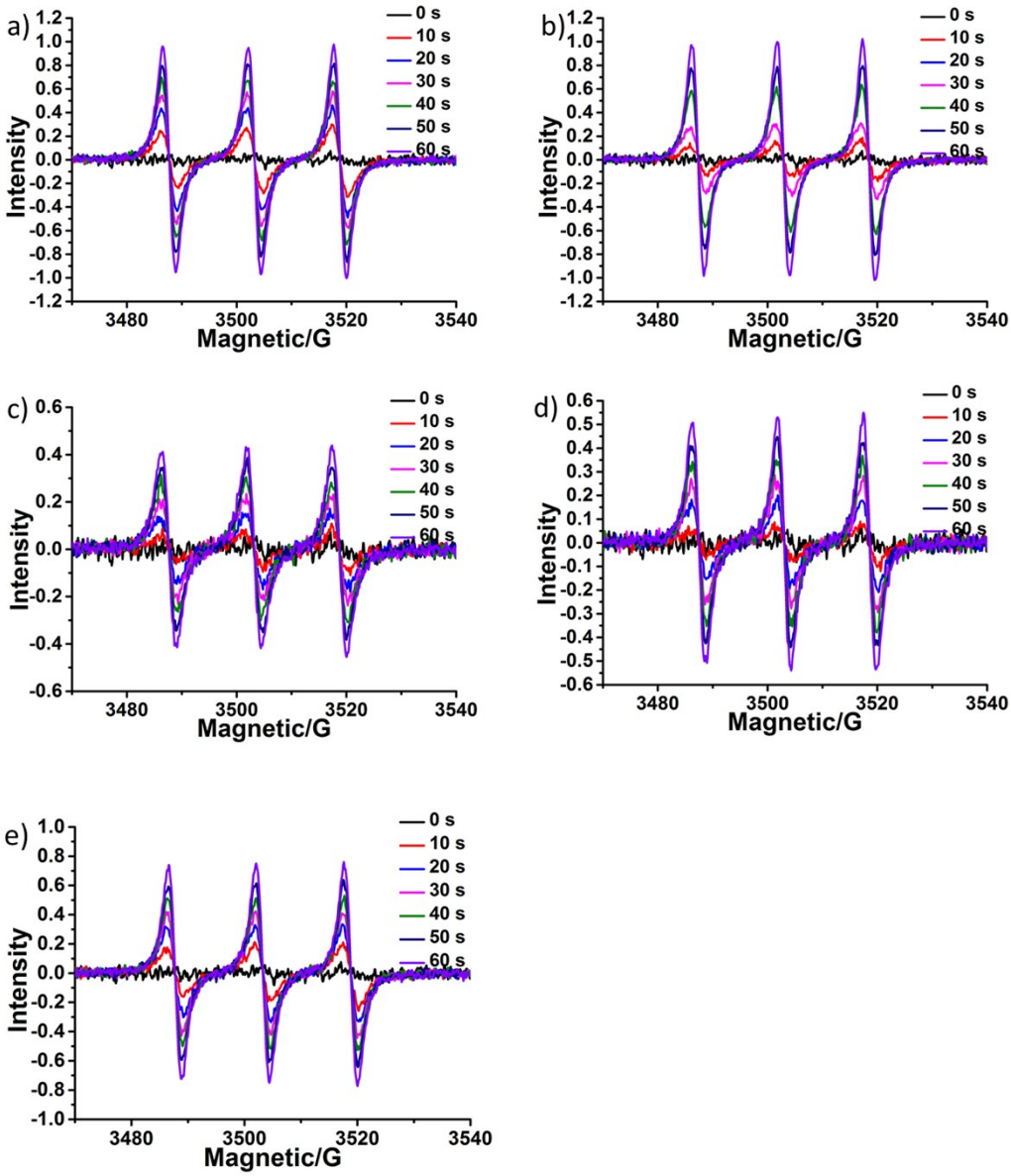


Figure S6: ESR spectra of air-saturated toluene solutions of **a**) ***Z*-1**, **b**) **2**, **c**) **3**, **d**) **4** and **e**) **6** (1×10^{-4} M) with TEMP (2×10^{-4} M) after increasingly long irradiation by a 365 nm LED lamp at room temperature.

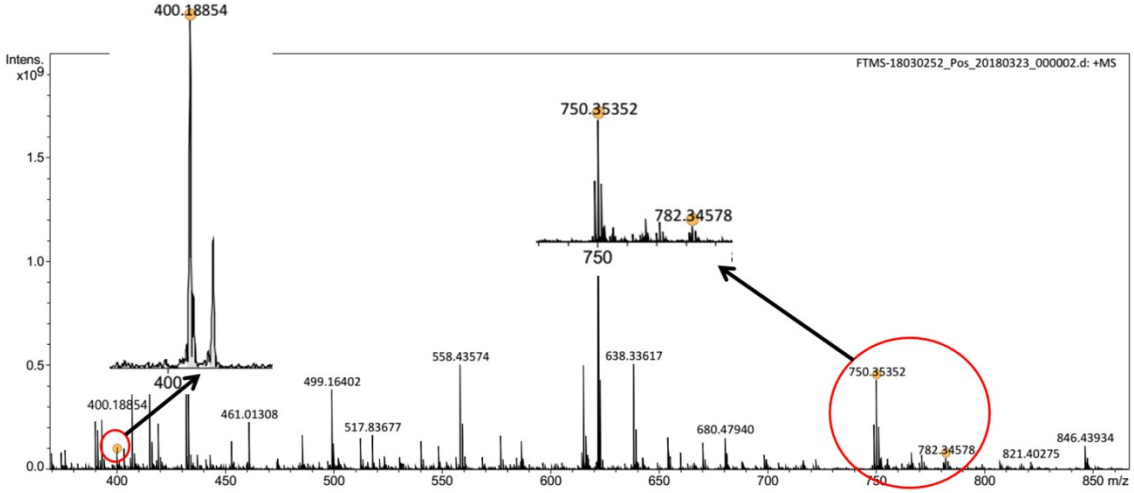


Figure S7: High-resolution mass spectrum of a solution of ***E*-1** after irradiation of its aerated solution at 365 nm.

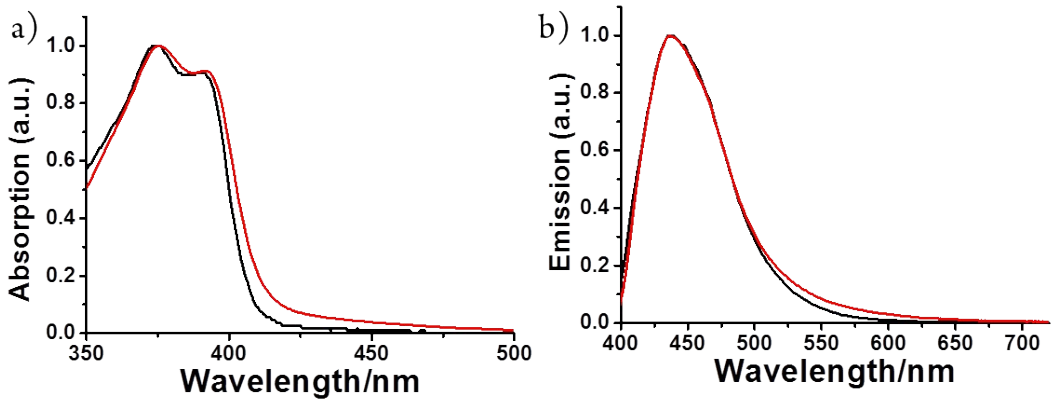


Figure S8: a) UV-Vis and **b**) fluorescence spectra of independently synthesized **1-P** (black line) and the product of the photooxidation ***E*-1** (red line). The spectral intensities were normalized to 1 to facilitate comparison.

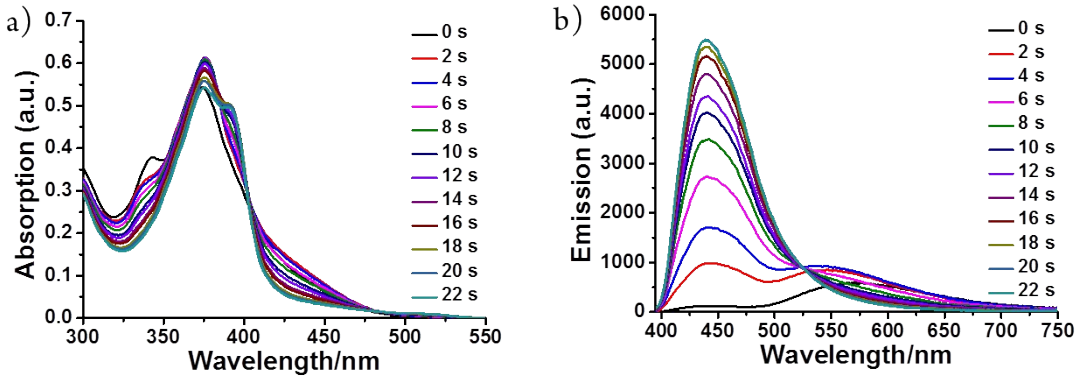


Figure S9: Time-dependent **a**) UV-Vis and **b**) fluorescence spectra of ***Z*-1** in air saturated toluene (20 µM) solutions irradiated by a 365nm LED lamp.

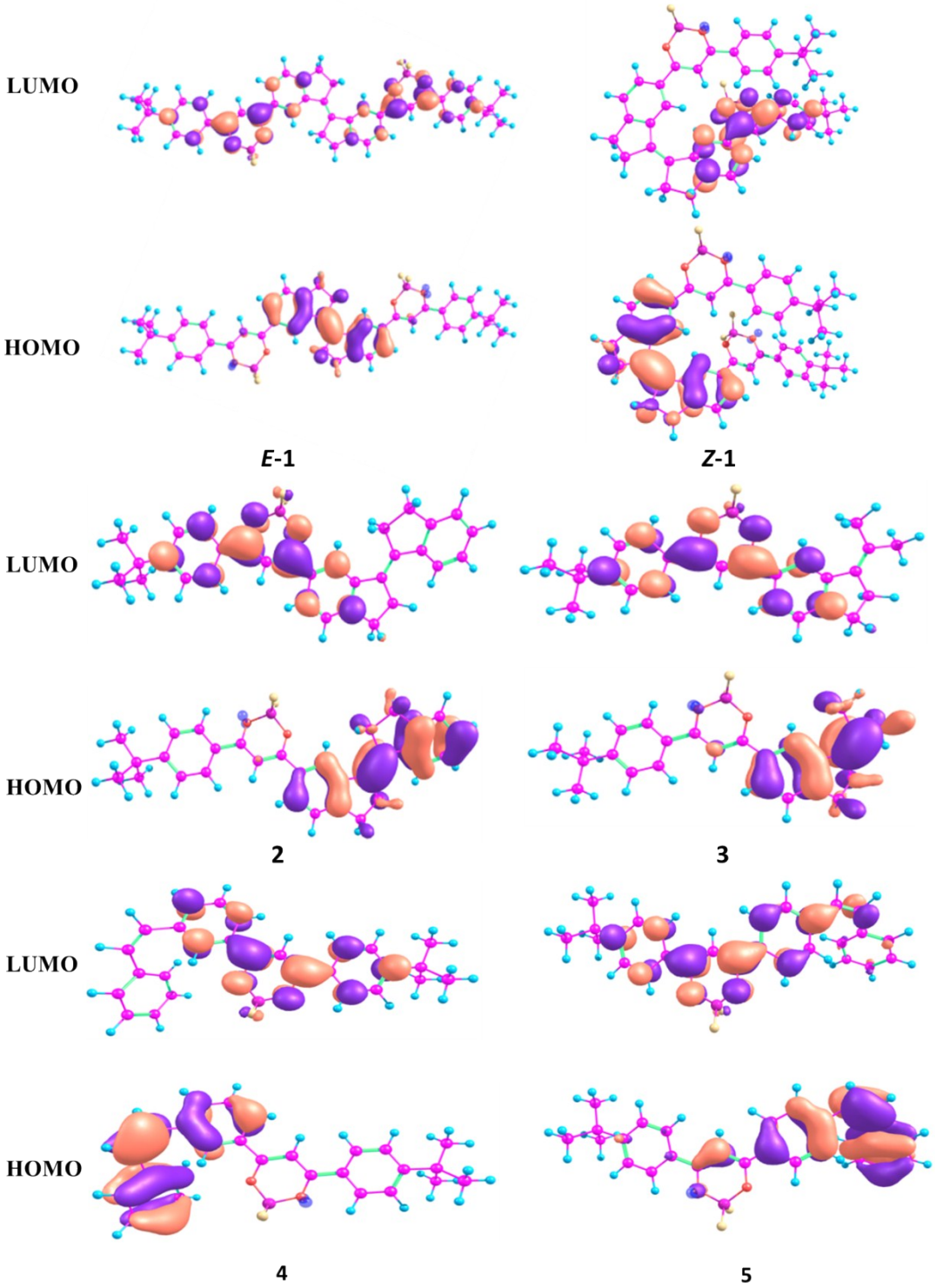


Figure S10: The converged geometries and calculated HOMO and LUMO density maps for compounds ***E*-1, *Z*-1** and **2-5** at the B3LYP/6-31G(d) level of DFT.

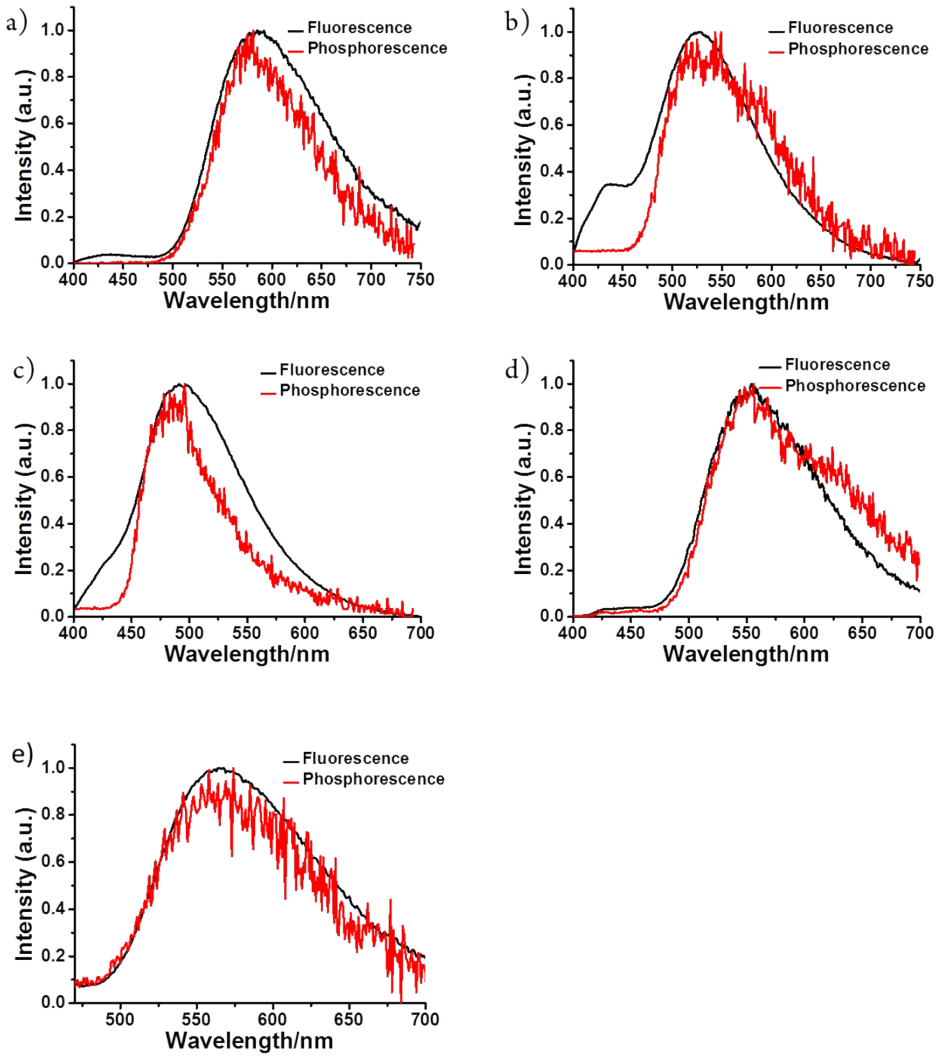


Figure 11: Fluorescence (at room temperature) and phosphorescence (at 77 k, after a 0.1 ms delay) spectra of **2**, **3**, **4**, **6** and ***Z*-1** (**a-e**, respectively) in anaerobic toluene (20 μM) solutions.

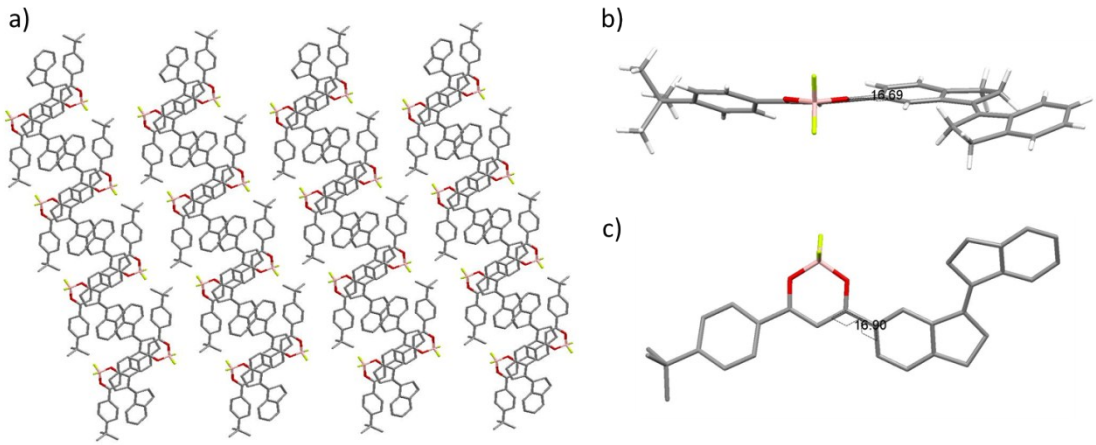


Figure S12: a) The aggregate form (2 × 2 × 2), **b**) and **c**) the molecular structure viewed along the long and front molecules axis of **2**, respectively.

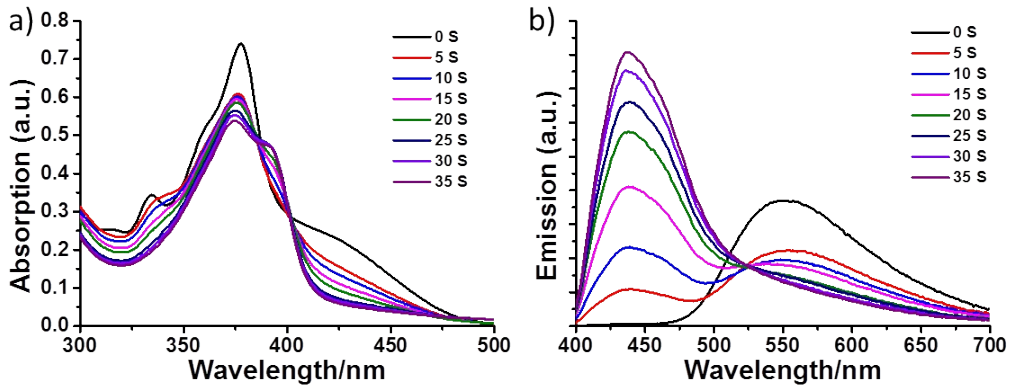


Figure S13: Time-dependent (a) absorption and (b) emission spectra of ***E*-1** in an air-saturated toluene 20 μM solution upon irradiation under a xenon lamp with a ＞400 nm filter.

Table S1: The photophysical data of 1-6, 1-P, 4-P and 6-P.

Compounds	[a]λ_{abs} (nm)	[b]ε ($cm^{-1}M^{-1}$)	[c]λ_{em}(nm)	[d]Φ (%)
***E*-1**	**377**	**4.4×10^4**	**556**	**32**
***Z*-1**	**375**	**3.2×10^4**	**580**	**25**
2	**377**	**3.1×10^4**	**577**	**24**
3	**368**	**2.0×10^4**	**526**	**46**
4	**370**	**2.8×10^4**	**495**	**24**
5	**405**	**3.1×10^4**	**467**	**93**
6	**377**	**4.3×10^4**	**560**	**26**
[e]**1-P**	**374**	**3.2×10^4**	**430**	**84**
[f]**4-P**	**374**	**2.2×10^4**	**436**	**36**
[f]**6-P**	**377**	**3.5×10^4**	**430**	**88**

a. Absorption maxima, b. extinction coefficients at the absorption maxima, c. emission maxima, d. the absolute fluorescence quantum yields, e. the photooxidation product of **1-3**, f. the photooxidation products (without further purification) after fully irradiation of **4** and **6**, respectively. All the data were measured in toluene.

Crystallographic data of compound 2

CCDC 1915963 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2: Single crystal data of compound 2 .

Empirical formula	**$C_{31}H_{29}BF_2O_2$**
Formula weight	**482.35**
Color of crystal	**orange**
Temperature/k	**153.15**
Crystal system	**Triclinic**
Space group	**$P2_1/n$**
Unit cell dimensions	**a = 8.706 (17) Å** **b = 10.639 (2) Å** **c = 15.826 (3) Å** **α= 71.80(3)°** **β= 81.15(3) °** **γ= 83.26(3)°**
Volume (Å^3)	**1372.3(5)**
Z	**2**
ρ_{calc} g/cm^3	**1.167**

MS Spectra

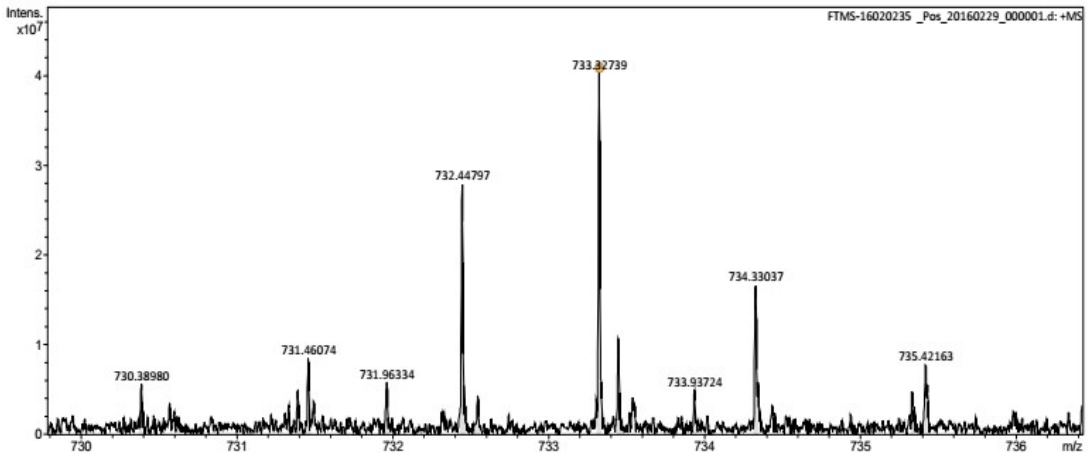


Figure S14: High-resolution mass spectrum of ***E*-1**.

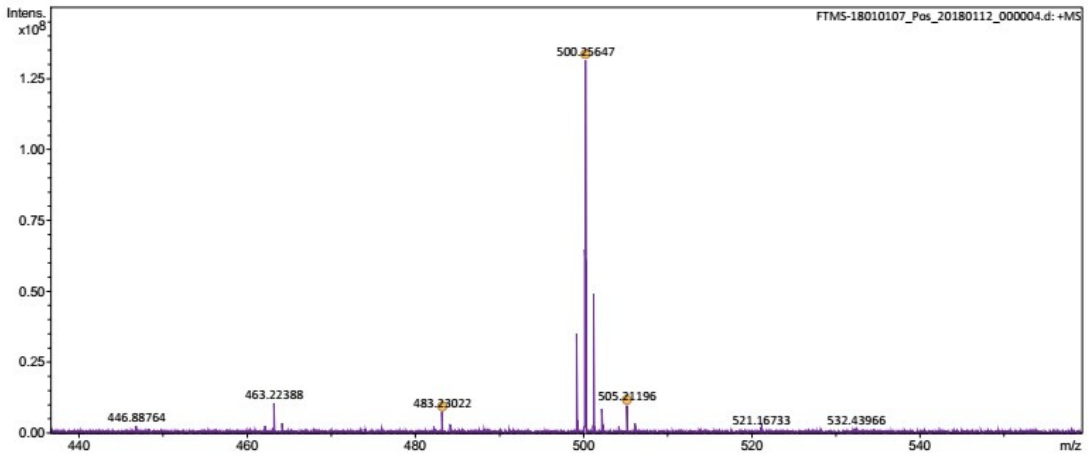


Figure S15: High-resolution mass spectrum of **2**.

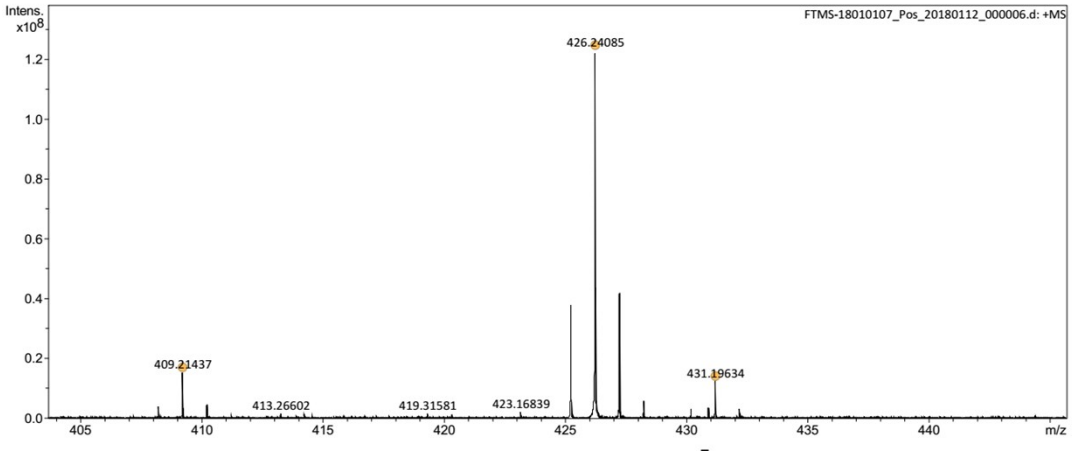


Figure S16: High-resolution mass spectrum of **3**.

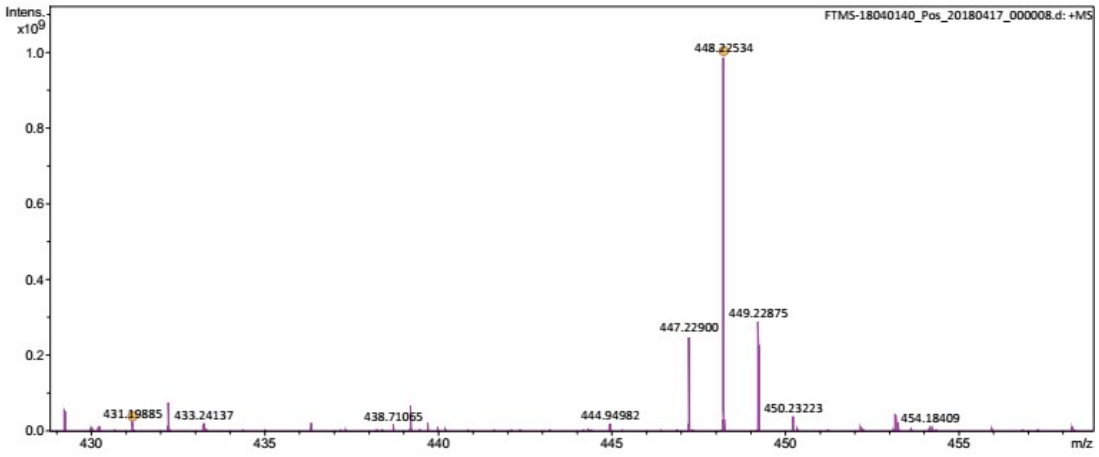


Figure S17: High-resolution mass spectrum of **4**.

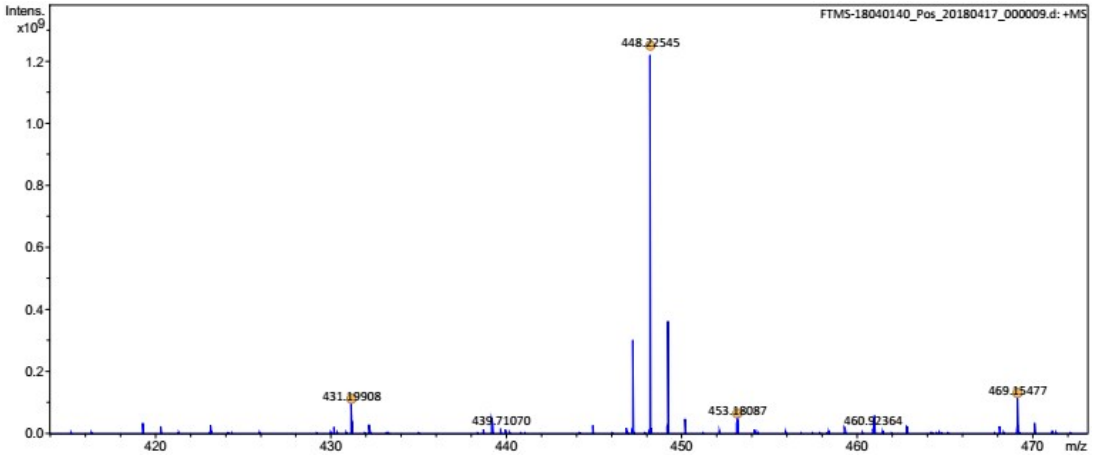


Figure S18: High-resolution mass spectrum of **5**.

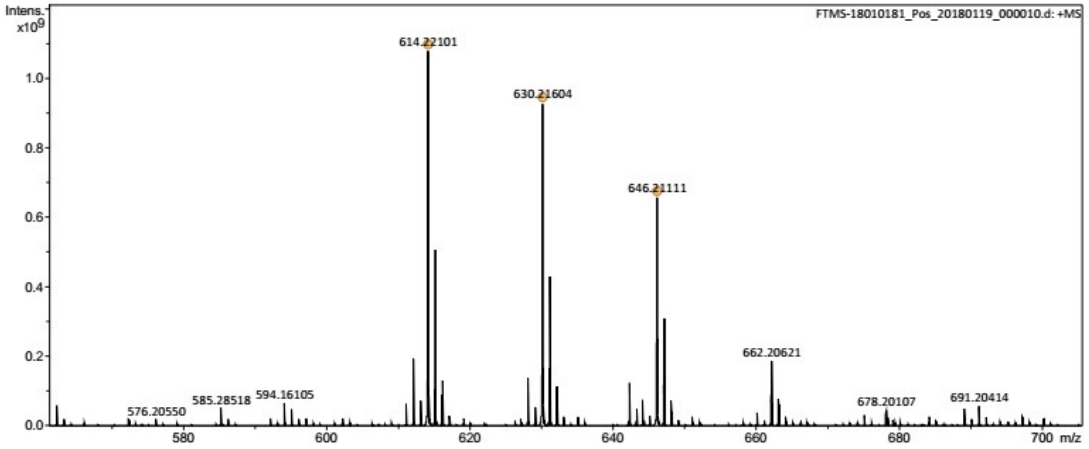


Figure S19: High-resolution mass spectrum of **6**.

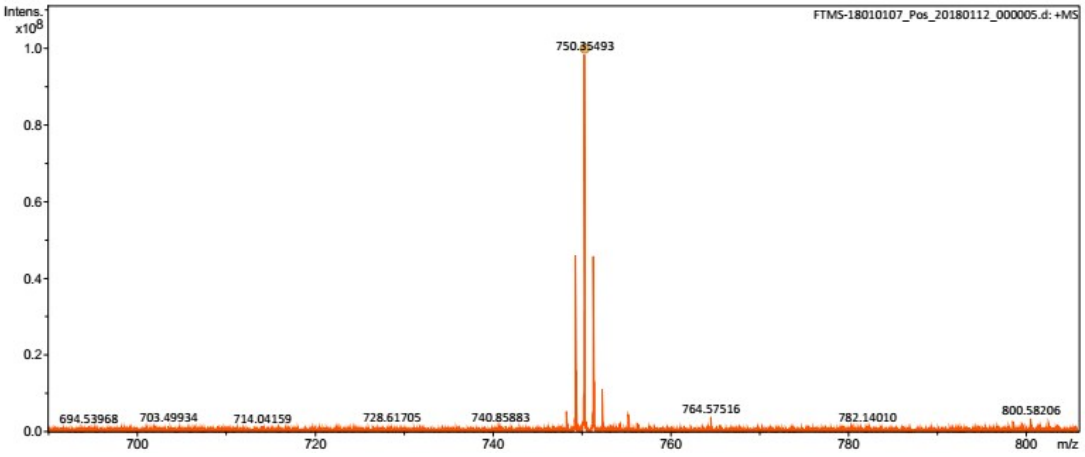


Figure S20: High-resolution mass spectrum of ***Z*-1**.

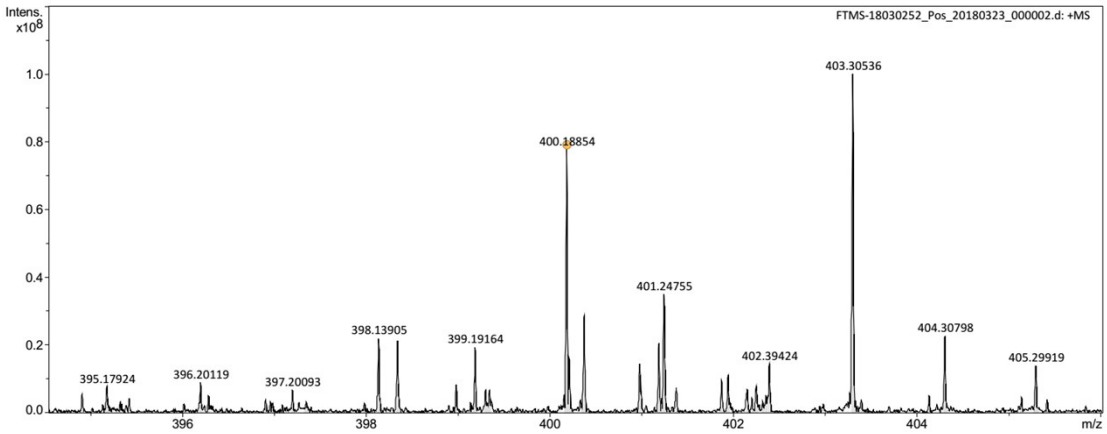


Figure S21: High-resolution mass spectrum of **1-P**.

NMR Spectra

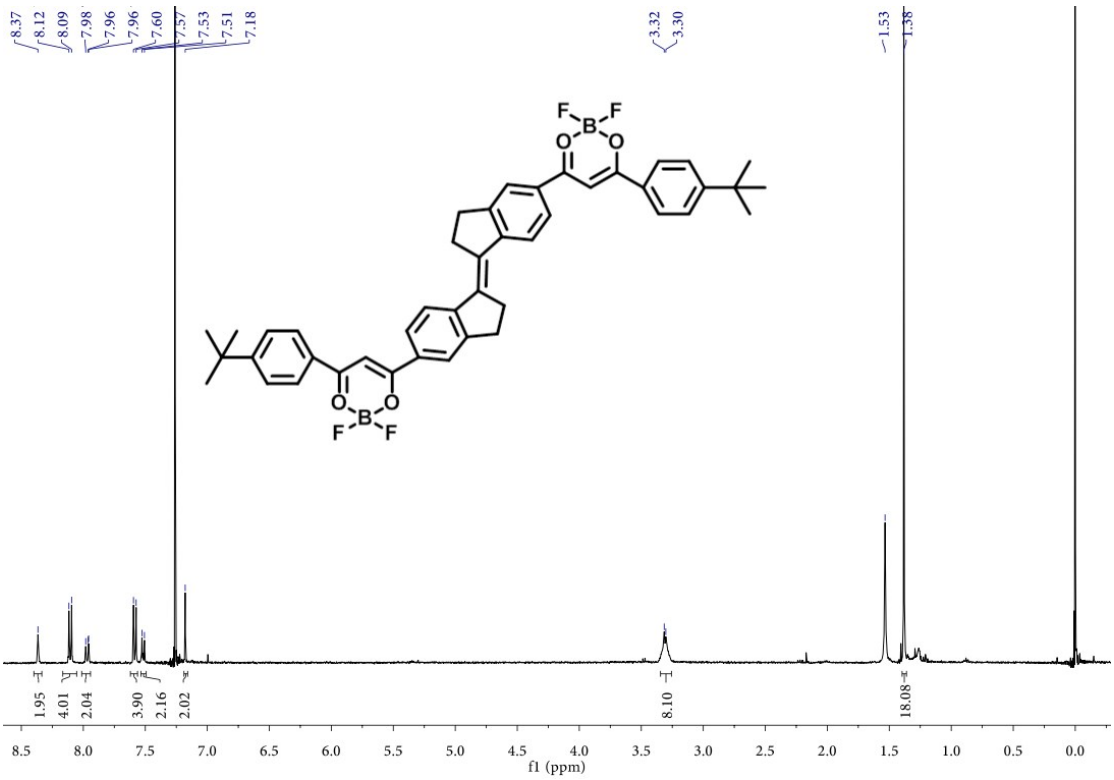


Figure S22: ^{1}H NMR spectrum of ***E*-1** in $CDCl_3$ (500µL).

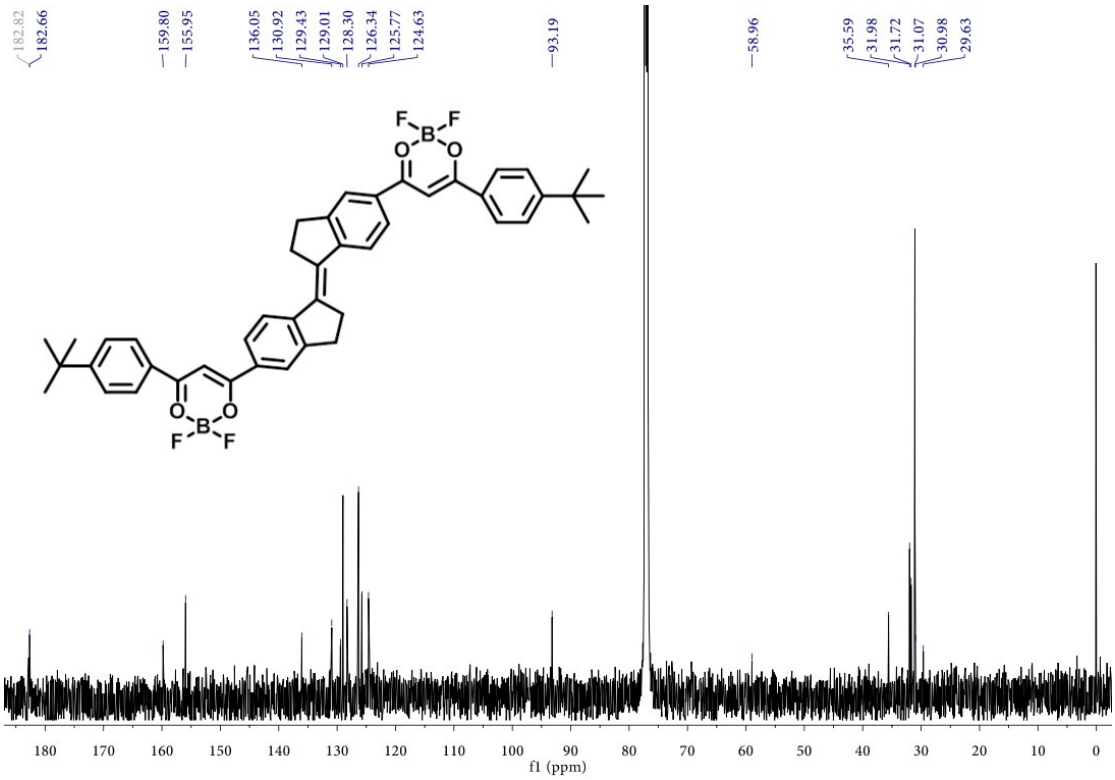


Figure S23: ^{13}C NMR spectrum of ***E*-1** in $CDCl_3$ (500µL).

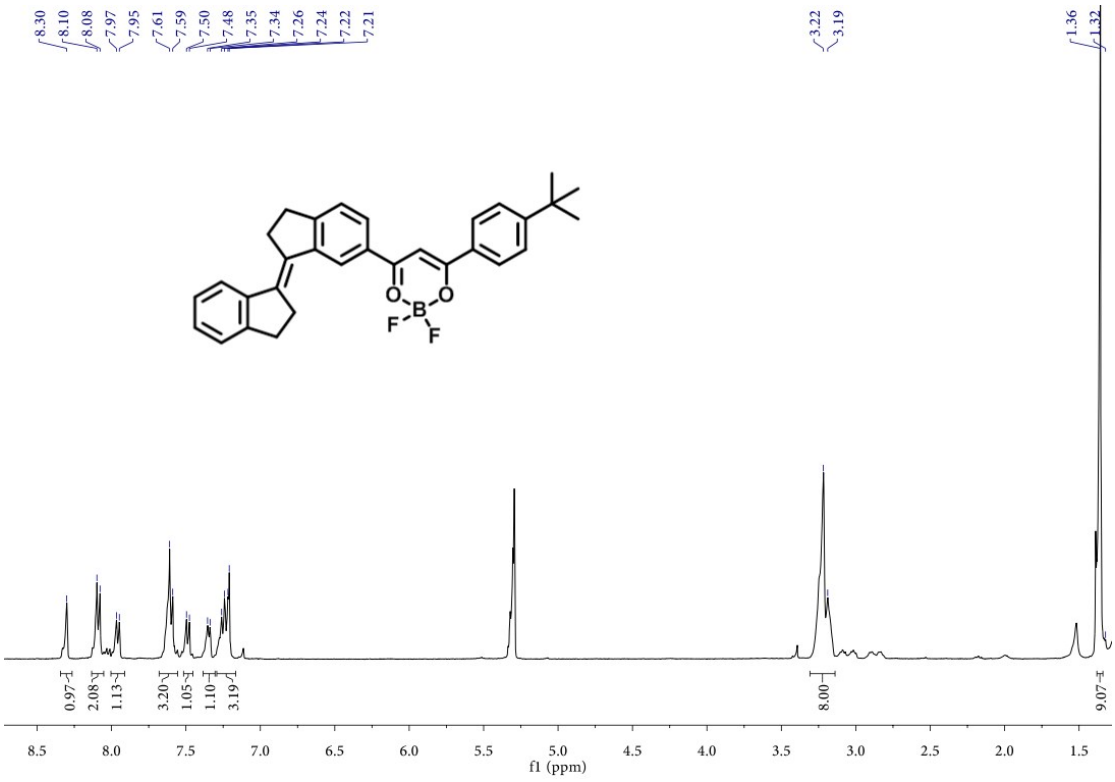


Figure S24: ^{1}H NMR spectrum of **2** in CD_2Cl_2 (500µL).

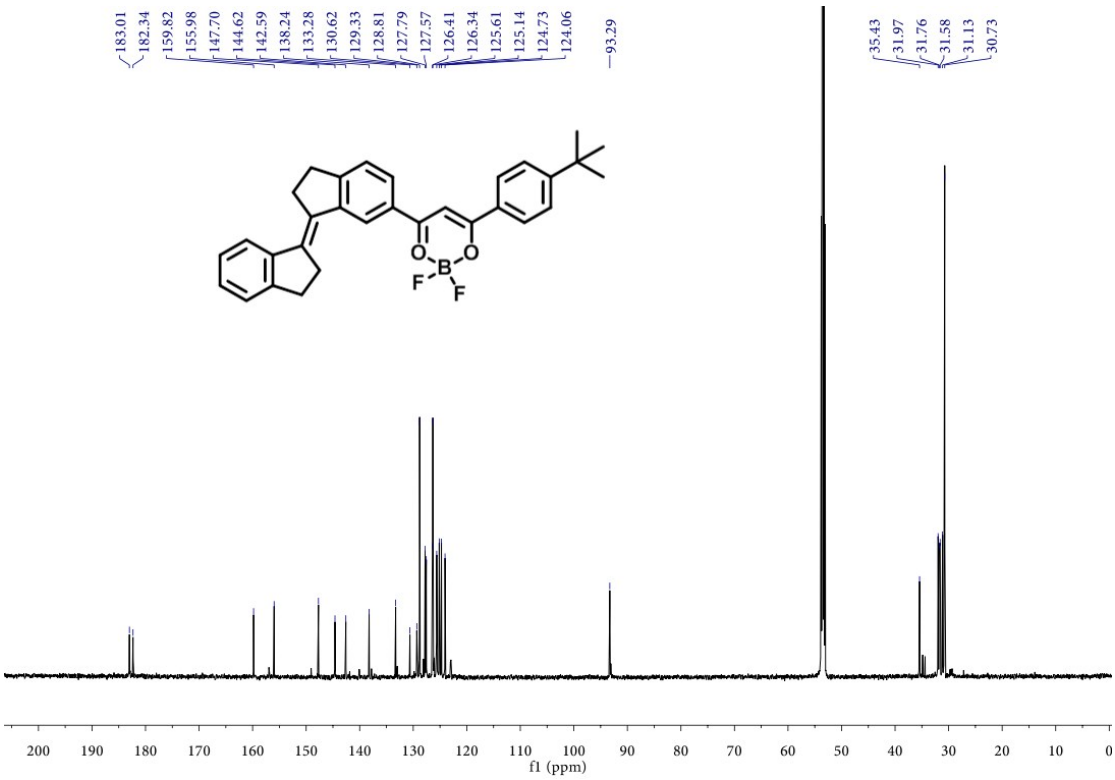


Figure S25: ^{13}C NMR spectrum of **2** in CD_2Cl_2 (500µL).

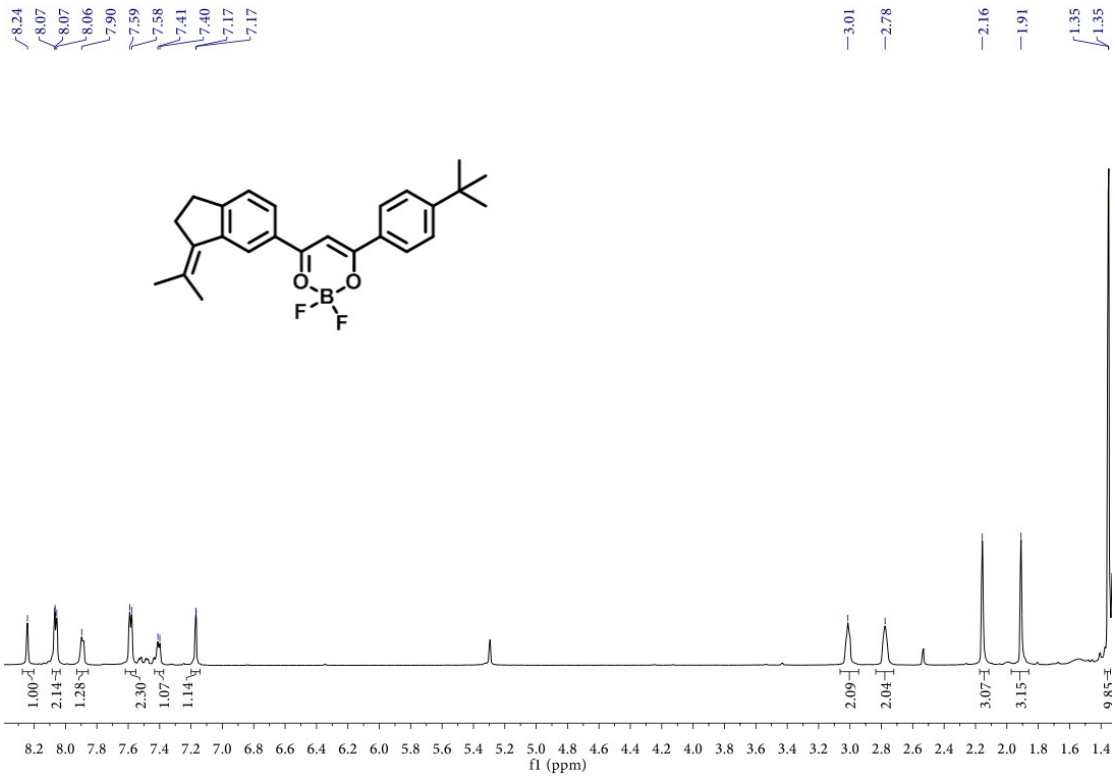


Figure S26: ^{1}H NMR spectrum of **3** in CD_2Cl_2 (500µL).

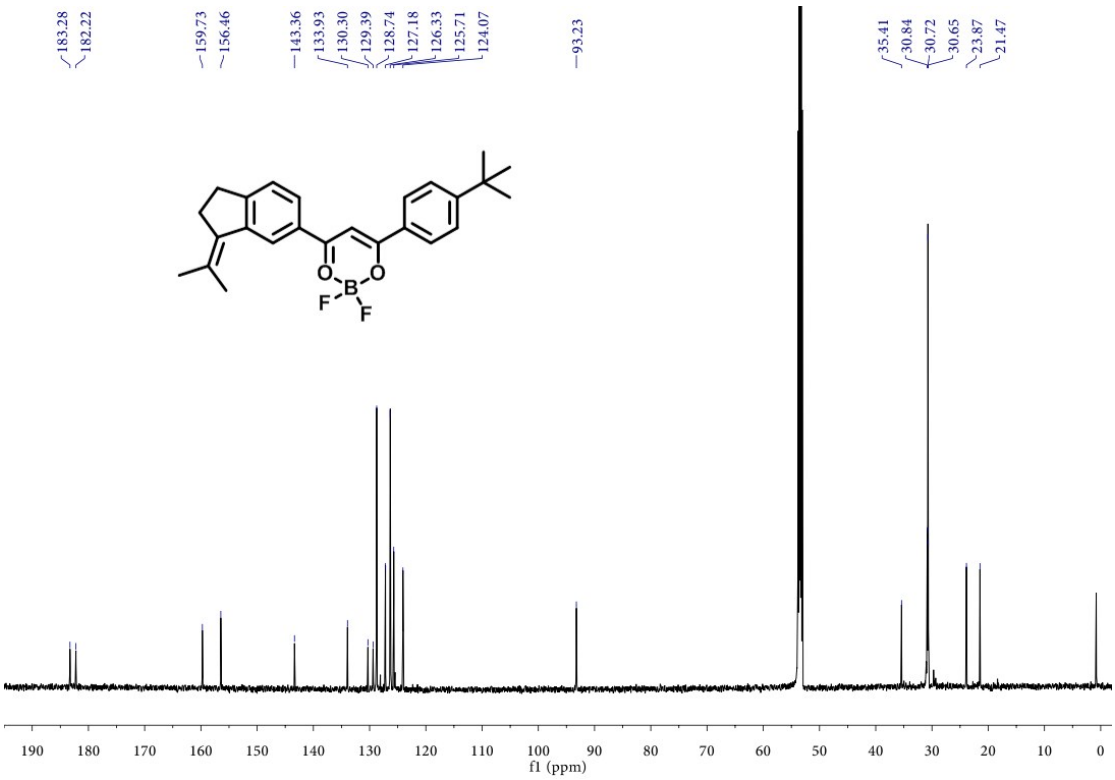


Figure S27: ^{13}C NMR spectrum of **3** in CD_2Cl_2 (500µL).

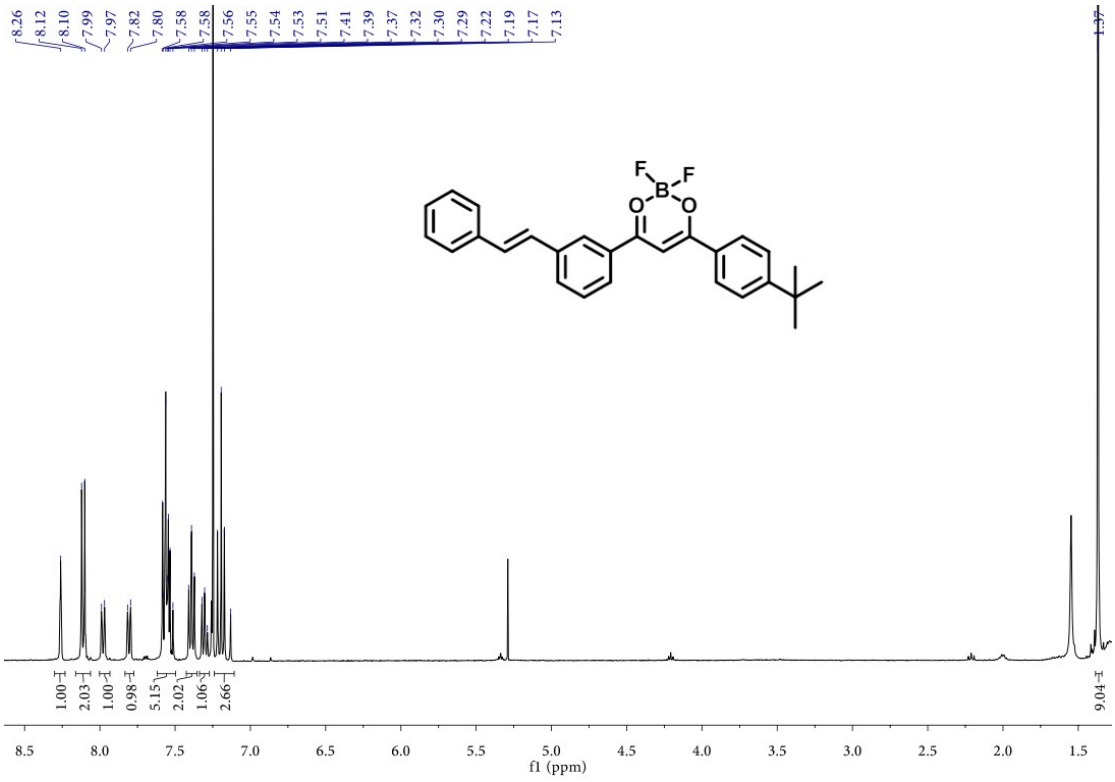


Figure S28: ^{1}H NMR spectrum of **4** in $CDCl_3$ (500µL).

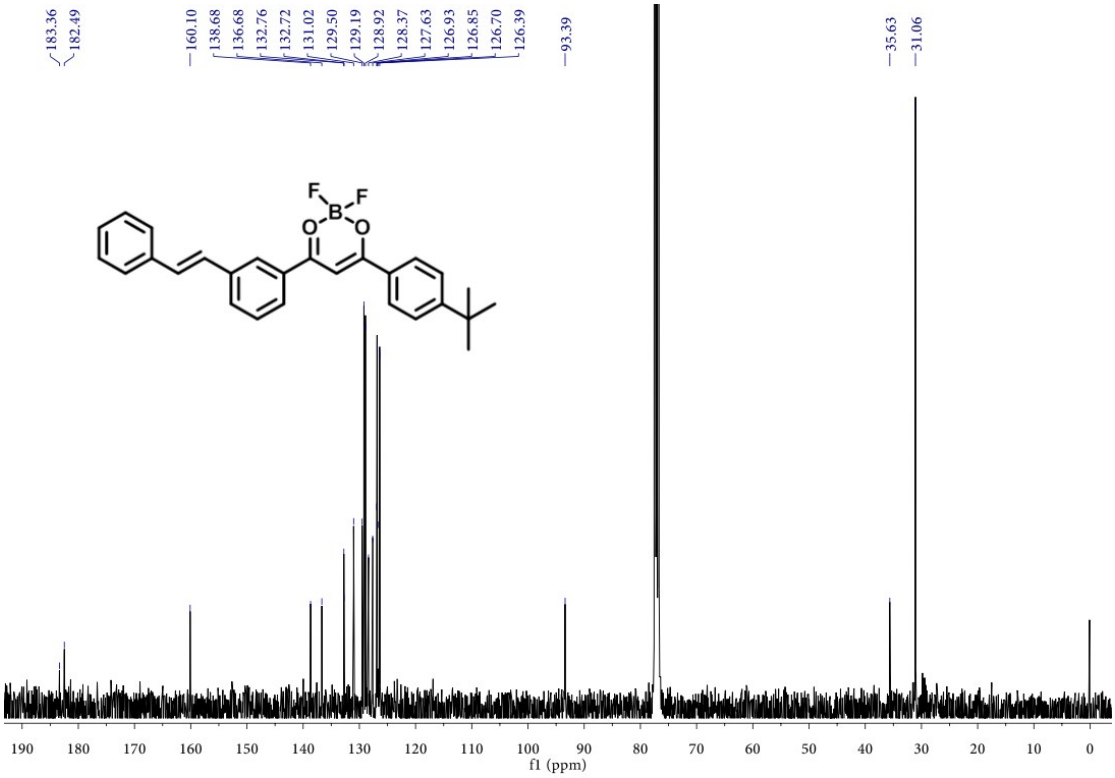


Figure S29: ^{13}C NMR spectrum of **4** in $CDCl_3$ (500µL).

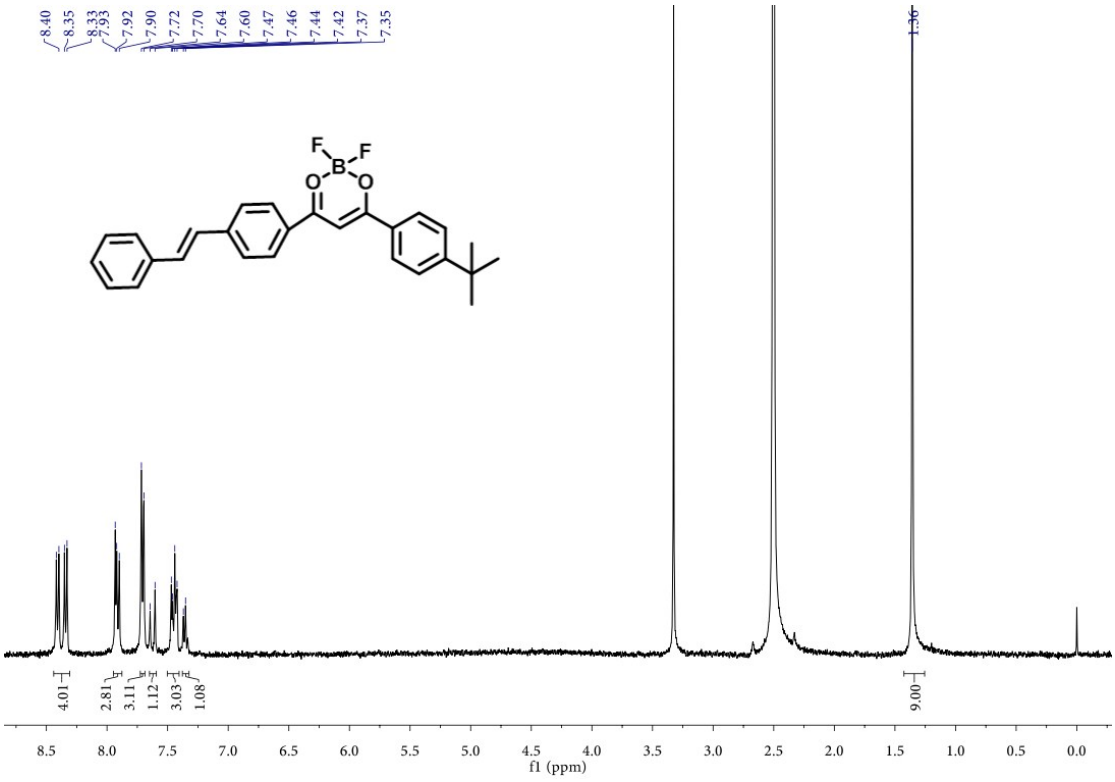


Figure S30: ^{1}H NMR spectrum of **5** in DMSO (500µL).

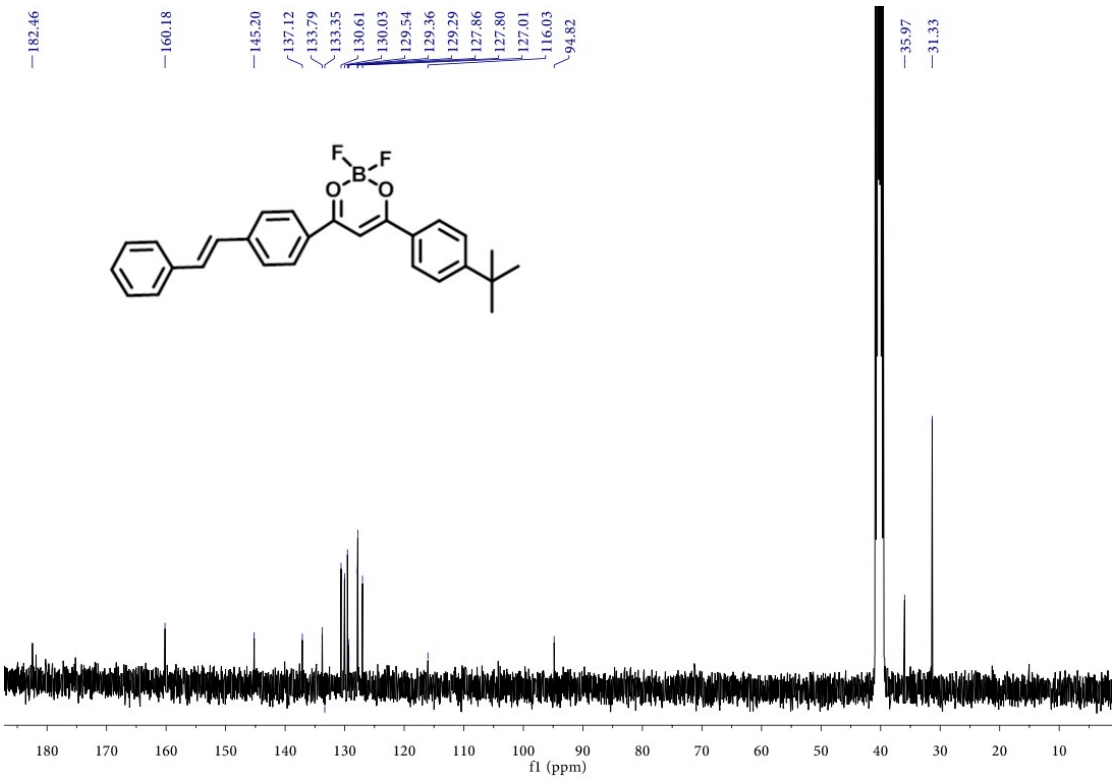


Figure S31: ^{13}C NMR spectrum of **5** in DMSO (500µL).

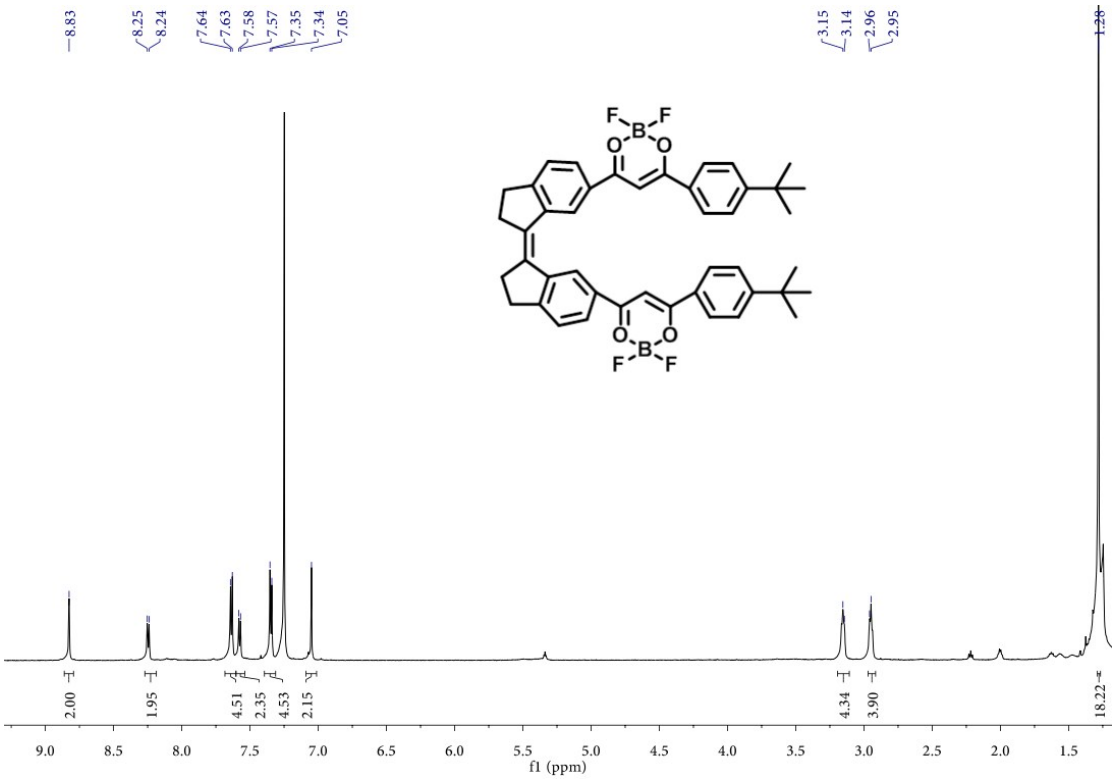


Figure S32: ^{1}H NMR spectrum of **Z-1** in $CDCl_3$ (500µL).

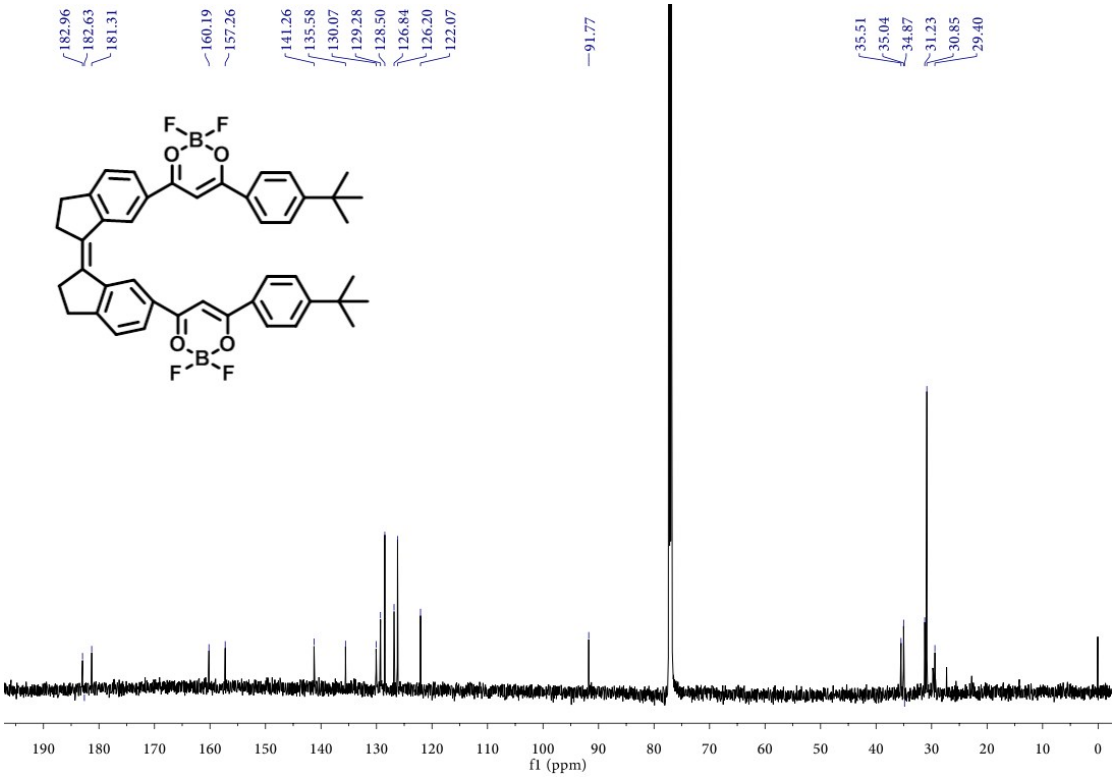


Figure S33: ^{13}C NMR spectrum of **Z-1** in $CDCl_3$ (500µL).

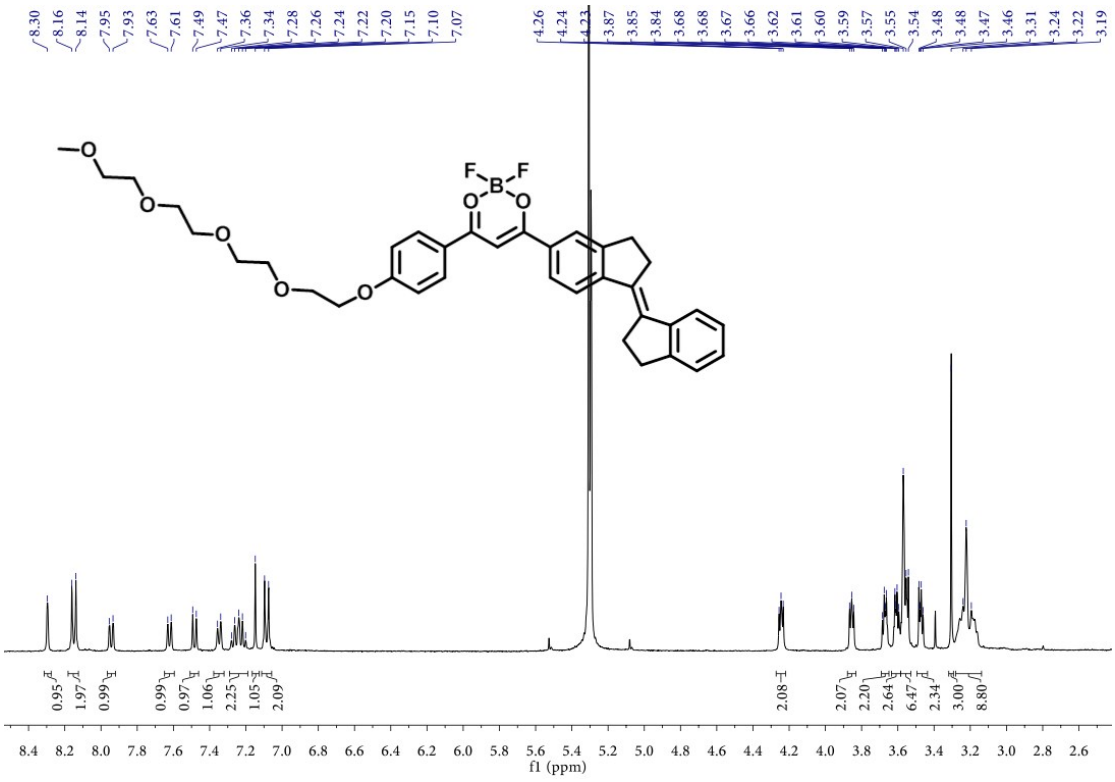


Figure S34: ^{1}H NMR spectrum of **6** in CD_2Cl_2 (500µL).

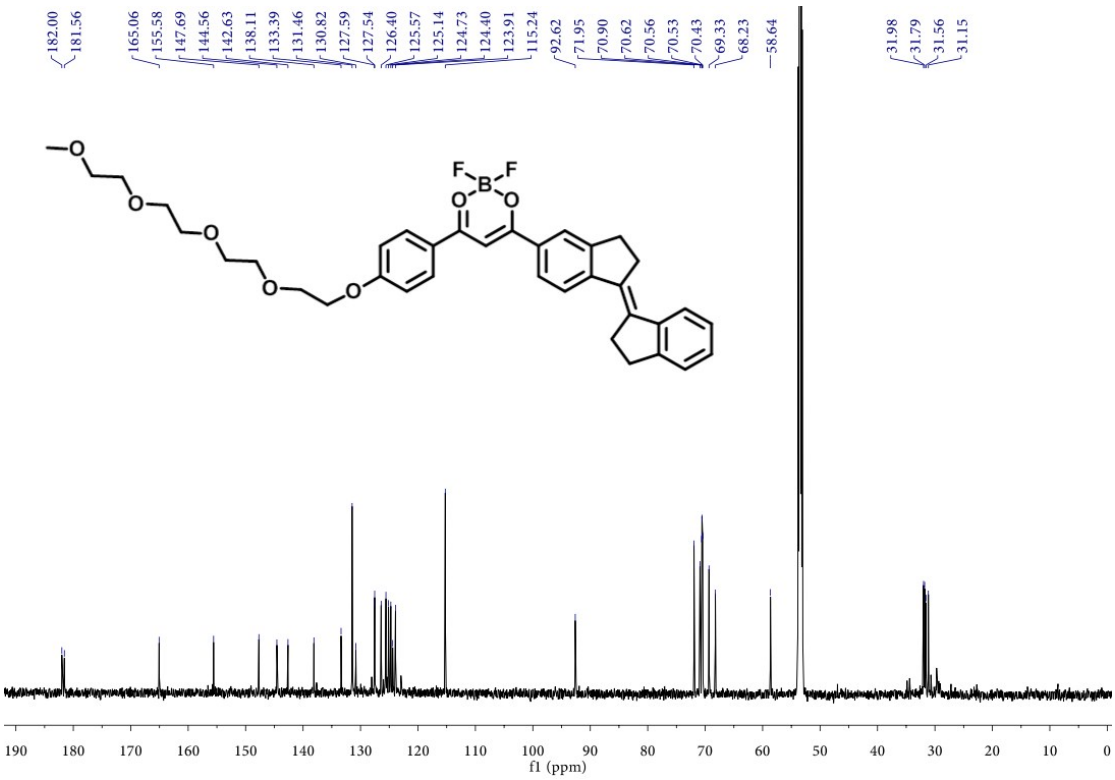


Figure S35: ^{13}C NMR spectrum of **6** in CD_2Cl_2 (500µL).

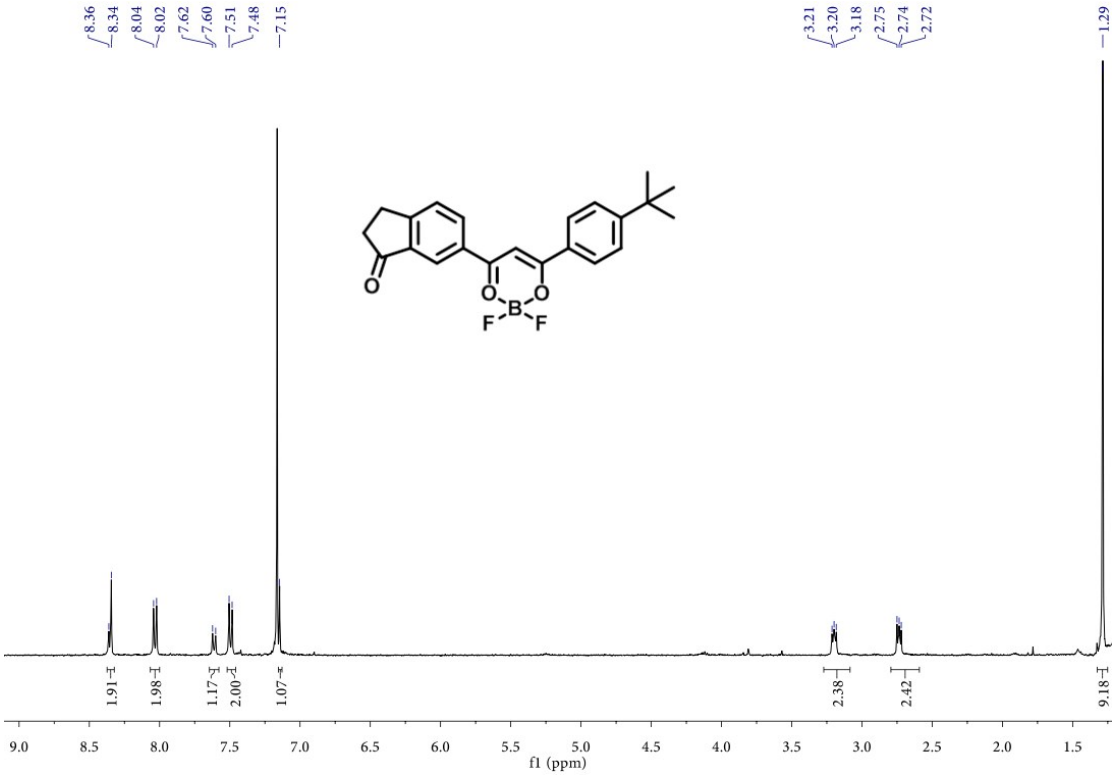


Figure S36: ^{1}H NMR spectrum of **1-P** in $CDCl_3$ (500µL).

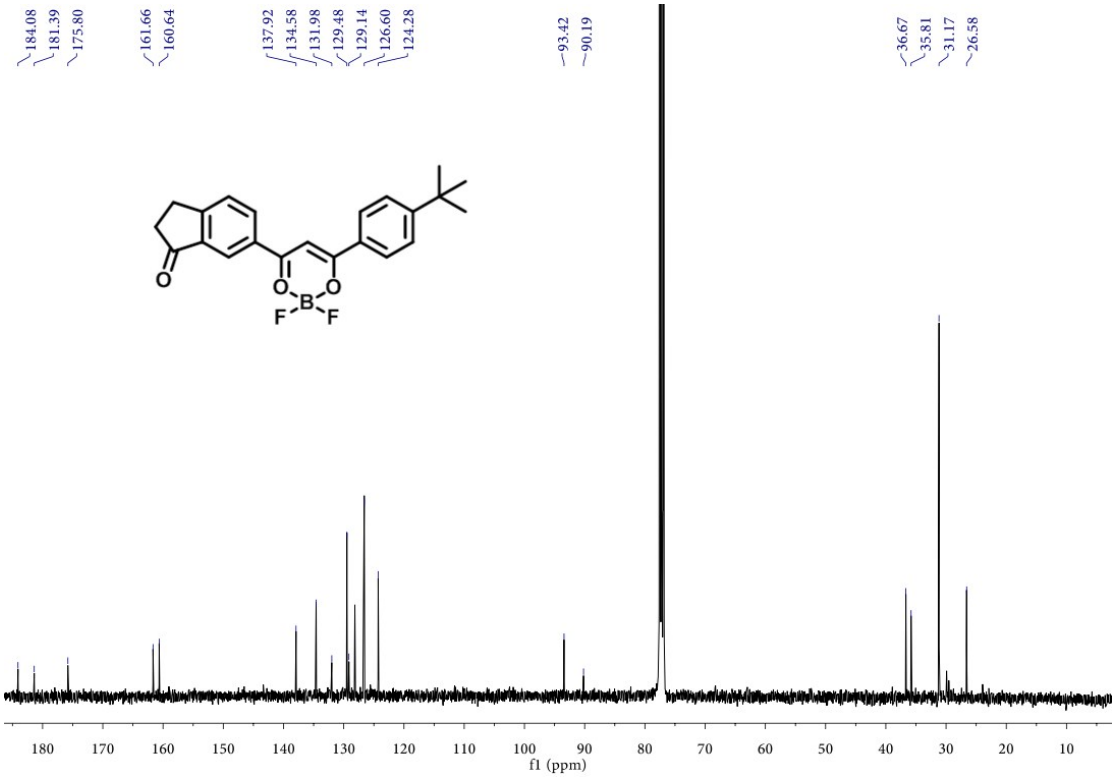


Figure S37: ^{13}C NMR spectrum of **1-P** in $CDCl_3$ (500µL).

Supplementary References

1. R. M. Brady, A. Vom, M. J. Roy, N. Toovey, B. J. Smith, R. M. Moss, E. Hatzis, D. C. Huang, J. P. Parisot, H. Yang, I. P. Street, P. M. Colman, P. E. Czabotar, J. B. Baell and G. Lessene, *J. Med. Chem.*, 2014, **57**, 1323-1343.
2. Q.-Z. Y. Zhen Huang, Daria Khvostichenko, Timothy J. Kucharski, Joseph Chen, and Roman Boulatov, *J. Am. Chem. Soc.*, 2009, 1407-1409.