Electronic Supporting Information

Boosting Triplet Activity for Heavy-Atom-Free Difluoroboron Dibenzoylmethane via sp3 Oxygen-Bridged Electron Donor

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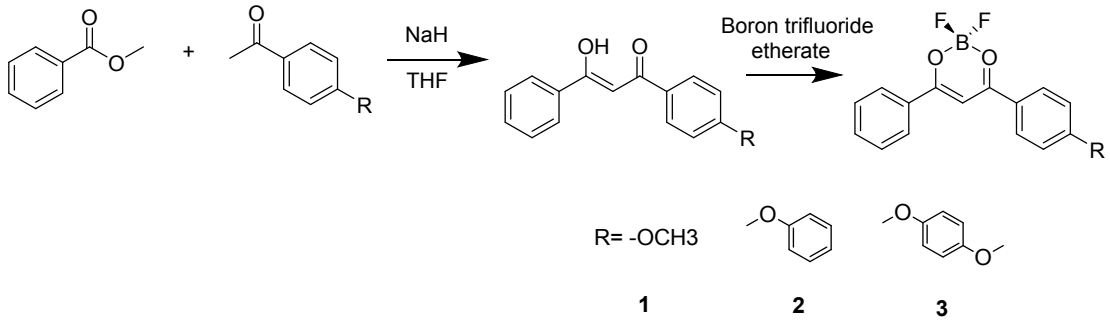
1.Materials and Synthesis

Materials. Extra dry THF and all other reagents and solvents were obtained from Aladdin Reagent and were used as received. Dichloromethane was dried over calcium hydride ~3h. Sodium hydride (95%) and boron trichloride solution (1.0 M in CH_2Cl_2) were purchased from Sigma-Aldrich.

Methods. ^1H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker AV400 NMR spectrometer operated in the Fourier transform mode at 400MHZ. Electrospray ionization (ESI) mass spectra were recorded on a LTQ ORBITRAP XL mass spectrometer (Thermo Scientific). UV/Vis spectra were recorded on a UV–1800 Shimadzu spectrometer. Steady-state emission spectra were recorded on a Horiba FluoroMax-4 spectrofluorometer (Japan). Fluorescence quantum yields were measured on a Hamamatsu Quantaurus-QY spectrometer. Fluorescence lifetime data were acquired with a 1 MHz LED laser with the excitation peak at 372 nm (NanoLED-370). Lifetime data were analyzed with DataStation v6.6 (Horiba Scientific).



Scheme S1. Chemical synthesis of BF_2dbm model complexes

(Z)-3-hydroxy-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (Cp1). Methyl benzoate (1.5 ml, 12 mmol), 1-(4-methoxyphenyl)ethan-1-one (2.42 g, 10 mmol), Sodium hydride (0.36 g, 15 mmol)and 10 ml extra dry THF were added into a round-bottomed flask, reflux 5 h under N_2,cool to room temperature. The reaction mixture was concentrated in vacuo to remove THF, 10 ml ultra-

pure water was added. The pH of the solution was adjusted to seven by the addition of a saturated aqueous solution of sodium bicarbonate then extracted with ethyl acetate (3 × 25 mL), and the combined organic layer was washed with brine (1 × 100 mL) and dried over sodium sulfate. The solution was filtered, and solvent was removed in vacuo. The crude product was purified by column chromatography (1:20 EtOAc/Hex) to provide the desired product as white solid : 1.8 g (60%).δ (ppm) H (400 MHz, $CDCl_3$) 16.99 (1 H, s), 8.02 – 7.94 (4 H, m), 7.53 (1 H, ddd, J 6.1, 3.5, 1.2), 7.50 – 7.42 (2 H, m), 7.00 – 6.94 (2 H, m), 6.79 (1 H, s), 3.86 (3 H, d, J 6.2). δ C (101 MHz, $CDCl_3$) 186.23, 184.04, 163.28, 135.57, 132.20, 129.35, 128.76, 128.67, 128.21, 127.02, 114.01, 113.97, 92.40, 55.51. ESI-MS m/z: $[M + Na]^+$, 277.0833;calculated mass for $C_{16}H_{14}NaO_3^+$: 277.0841amu.

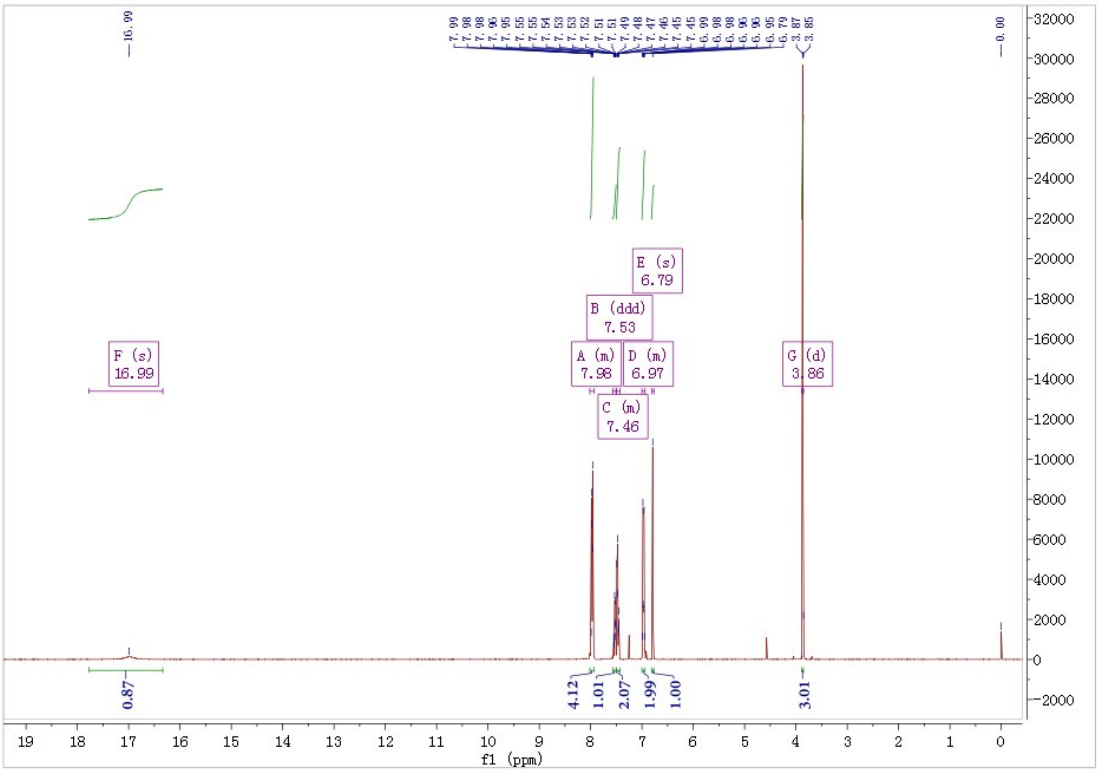


Figure S1. ^1H NMR spectrum (300 MHz, $CDCl_3$) of **Cp1**

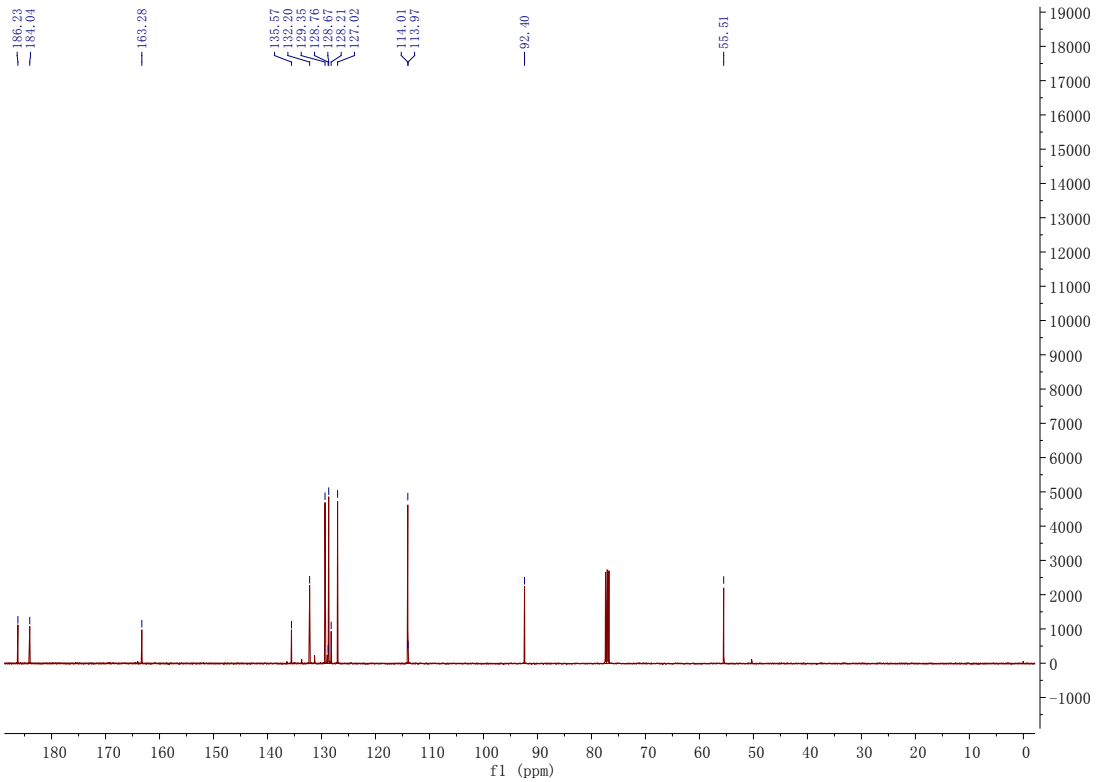


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **Cp1**

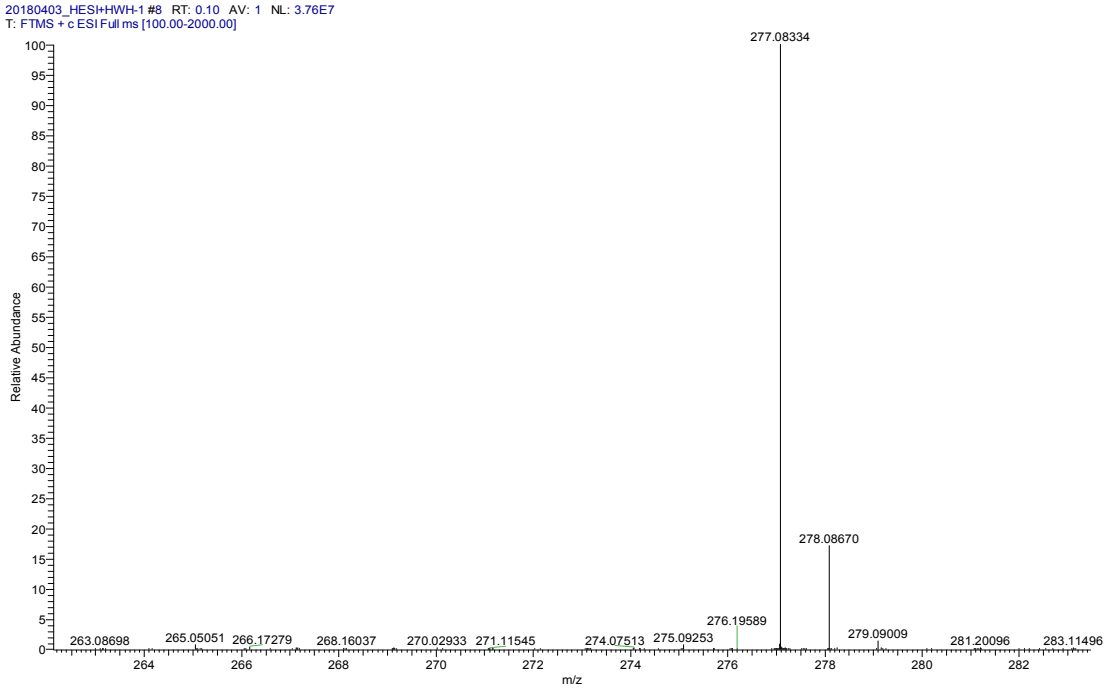


Figure S3. ESI-MS spectrum of **Cp1**

(Z)-3-hydroxy-1-(4-phenoxyphenyl)-3-phenylprop-2-en-1-one (Cp2). Synthesized according to the above method for (Z)-3-hydroxy-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one: 2.21 g (70%). δ (ppm) H (400 MHz, $CDCl_3$) 16.90 (1 H, s), 8.00 – 7.95 (4 H, m), 7.54 (1 H, dt, J 2.8, 2.1), 7.51 – 7.45 (2 H, m), 7.43 – 7.36 (2 H, m), 7.20 (1 H, ddt, J 8.5, 7.1, 1.1), 7.11 – 7.02 (4 H, m), 6.81 (1 H, s). δ C (101 MHz, $CDCl_3$) 185.71, 184.64, 161.60, 155.68, 135.50, 132.34, 130.07, 129.34, 128.70, 127.08, 124.54, 120.08, 117.71, 92.65. ESI-MS *m/z*: $[M + Na]^+$,339.0986;

calculated mass for $C_{21}H_{16}NaO_3^+$: 339.0997amu.

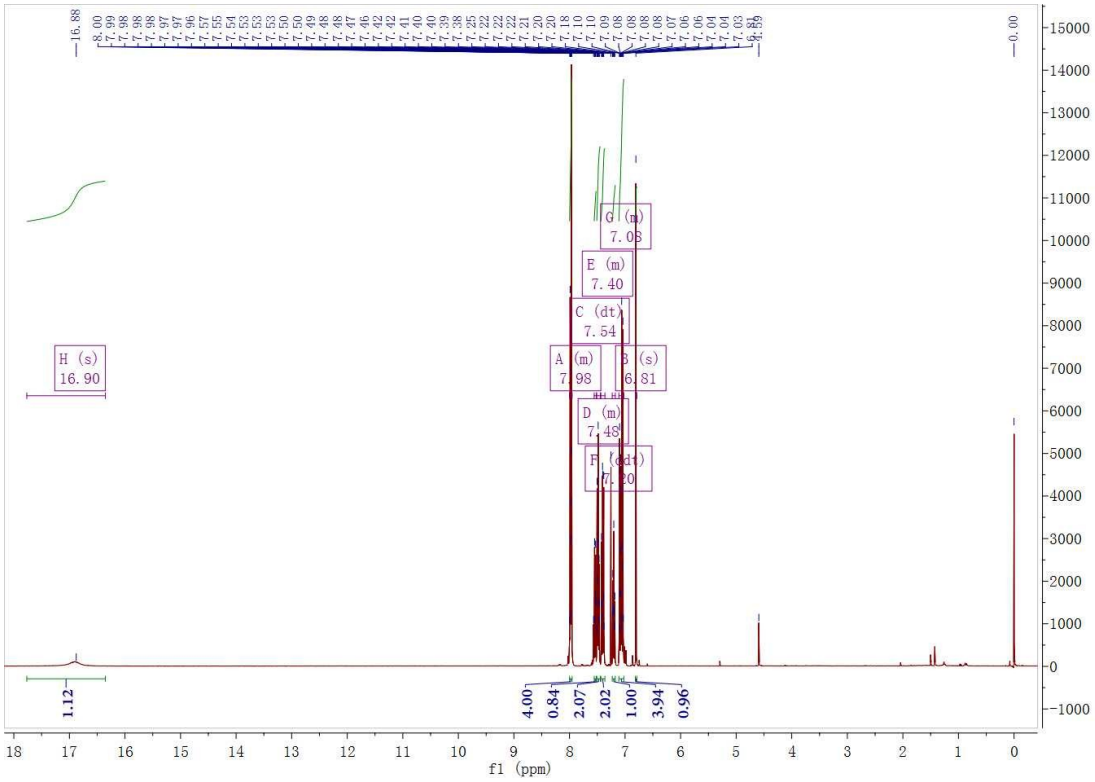


Figure S4. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **Cp2**

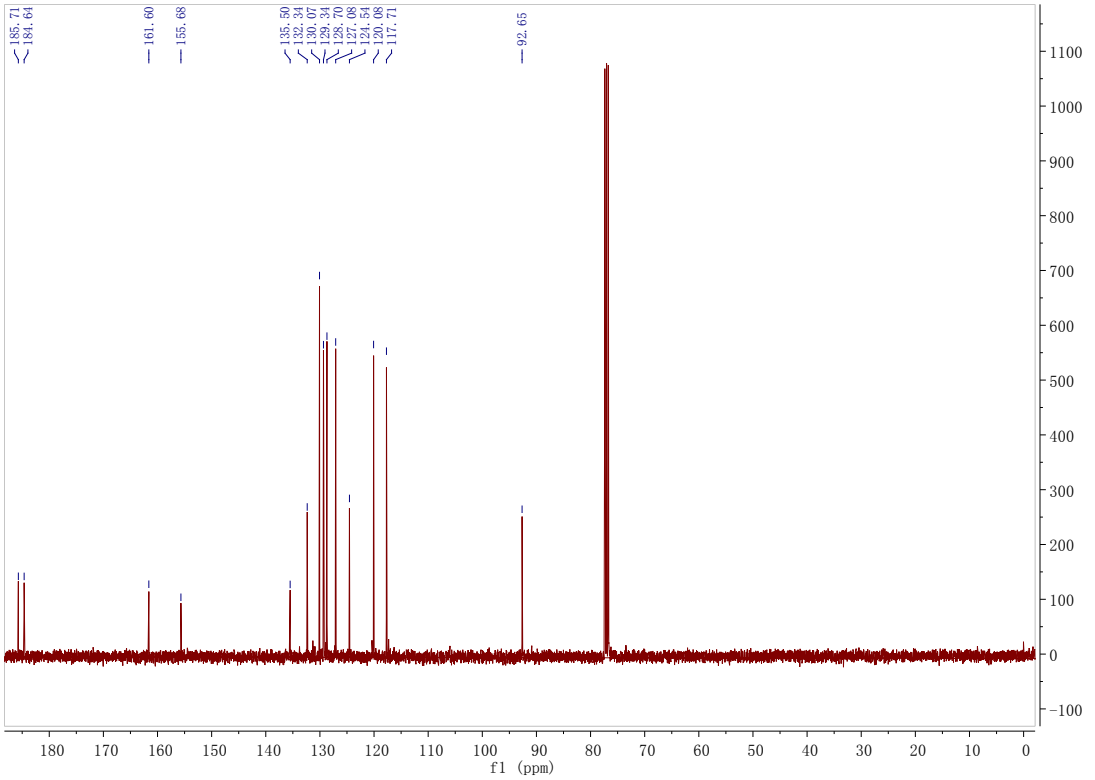


Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **Cp2**

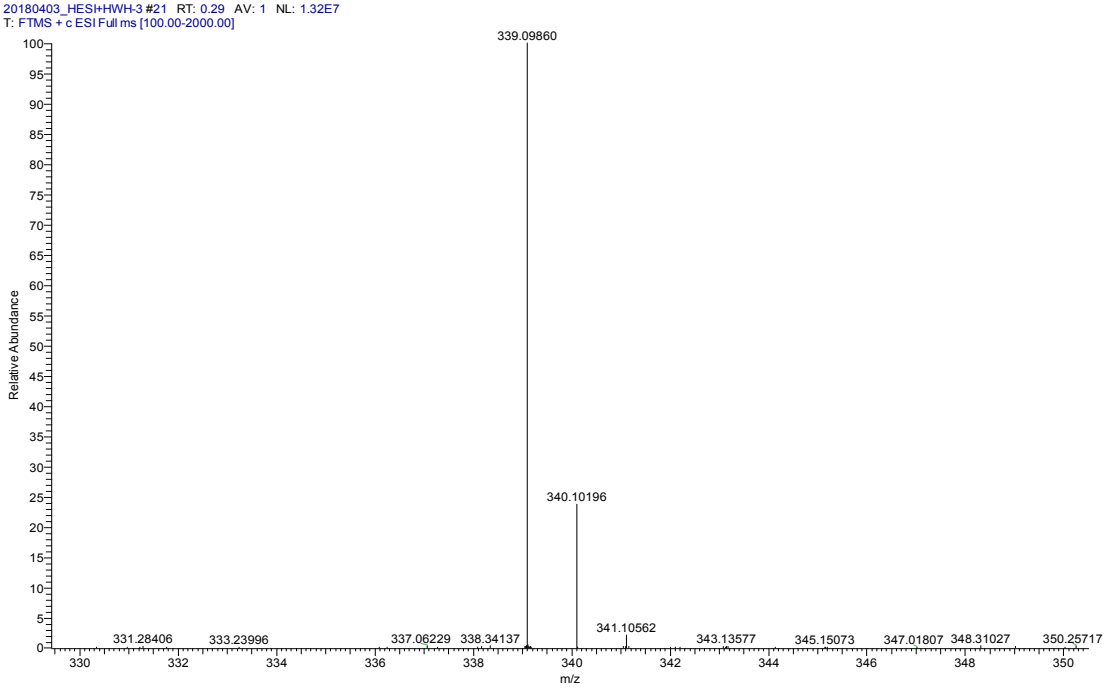


Figure S6. ESI-MS spectrum of **Cp2**

(Z)-3-hydroxy-1-(4-(4-methoxyphenoxy)phenyl)-3-phenylprop-2-en-1-one (Cp3). Synthesized according to the above method for (Z)-3-hydroxy-1-(4-methoxyphenyl)-3-pheny-lprop-2-en-1-one: 1.42 g (40%). δ (ppm) H (400 MHz, $CDCl_3$) 17.07 – 16.84 (1 H, m), 8.01 – 7.93 (4 H, m), 7.59 – 7.52 (1 H, m), 7.52 – 7.46 (2 H, m), 7.08 – 6.97 (4 H, m), 6.97 – 6.90 (2 H, m), 6.80 (1 H, s), 3.83 (3 H, d, J 3.8). δ C (101 MHz, $CDCl_3$) 185.84, 184.45, 162.62, 156.67, 148.65, 135.52, 132.29, 129.51, 129.31, 128.68, 127.06, 121.65, 116.74, 115.10, 92.57, 55.69. ESI-MS *m*/*z*: $[M + Na]^+$, 369.1096； calculated mass for $C_{22}H_{18}NaO_4^+$: 369.1103amu.

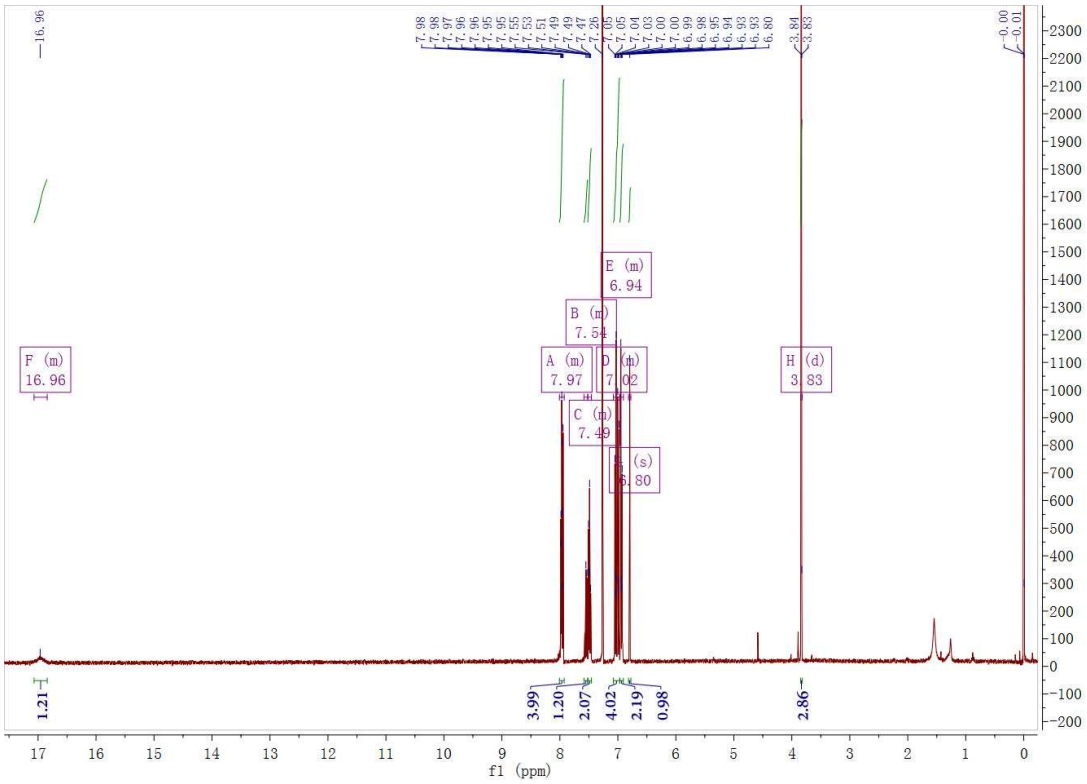


Figure S7. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **Cp3**

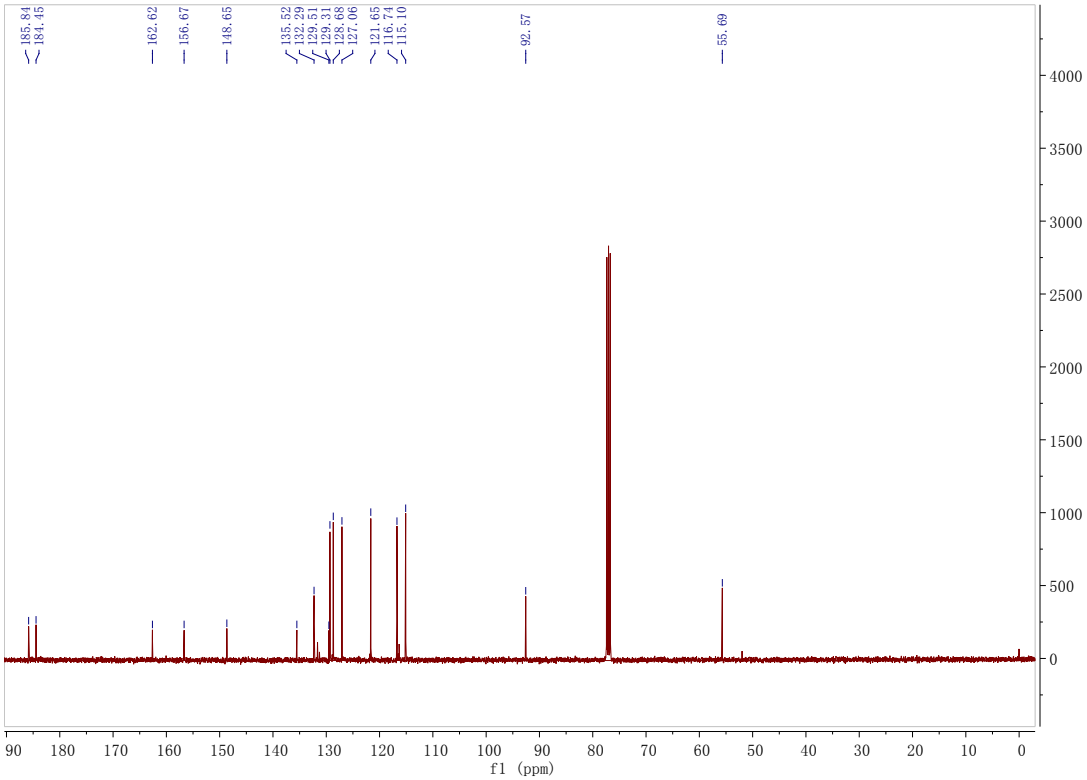


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **Cp3**

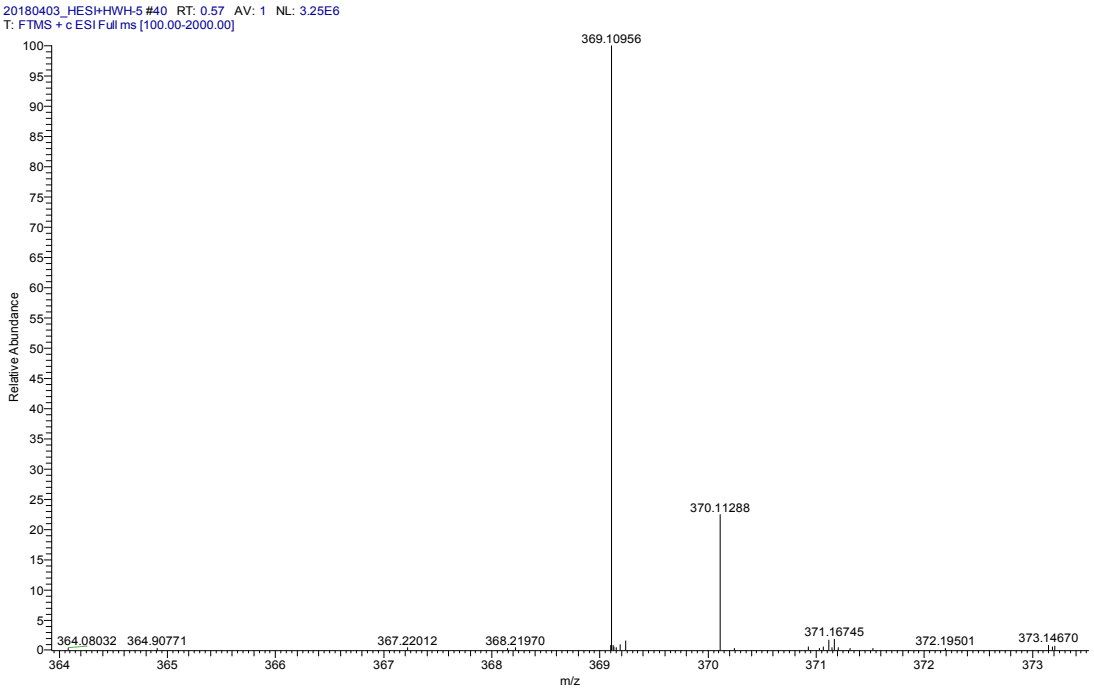


Figure S9. ESI-MS spectrum of **Cp3**

2,2-difluoro-4-(4-methoxyphenyl)-6-phenyl-2H-1,3l3,2l4-dioxaborinine(1). (Z)-3-hydroxy-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (3.76 g,14.8 mmol) and boron trifluoride dietherate (2.00 mL, 16.0 mmol) were added to 20 ml CH_2Cl_2 and stirred under N_2 at room temperature overnight. The solution was then purged with N_2 to remove excess boron trifluoride (absorbed with NaOH aq. solution). The desired product was obtained by silica gel chromateography with CH_2Cl_2/hexanes as bright yellow powder (3.61g, 81%). δ (ppm) H (400 MHz, $CDCl_3$) 8.44 – 8.02 (4 H, m), 7.61 (3 H, d, J 49.9), 7.18 – 6.91 (3 H, m), 3.94 (3 H, s). δ C (101 MHz, $CDCl_3$) 186.23, 184.04, 163.28, 135.57, 132.20, 129.35, 128.76, 128.67, 128.21, 127.02, 114.01, 113.97, 92.40, 55.51.ESI-MS *m*/*z*: $[M + Na]^+$, 325.0813； calculated mass for $C_{16}H_{13}BF_2NaO_3^+$: 325.0824 amu.

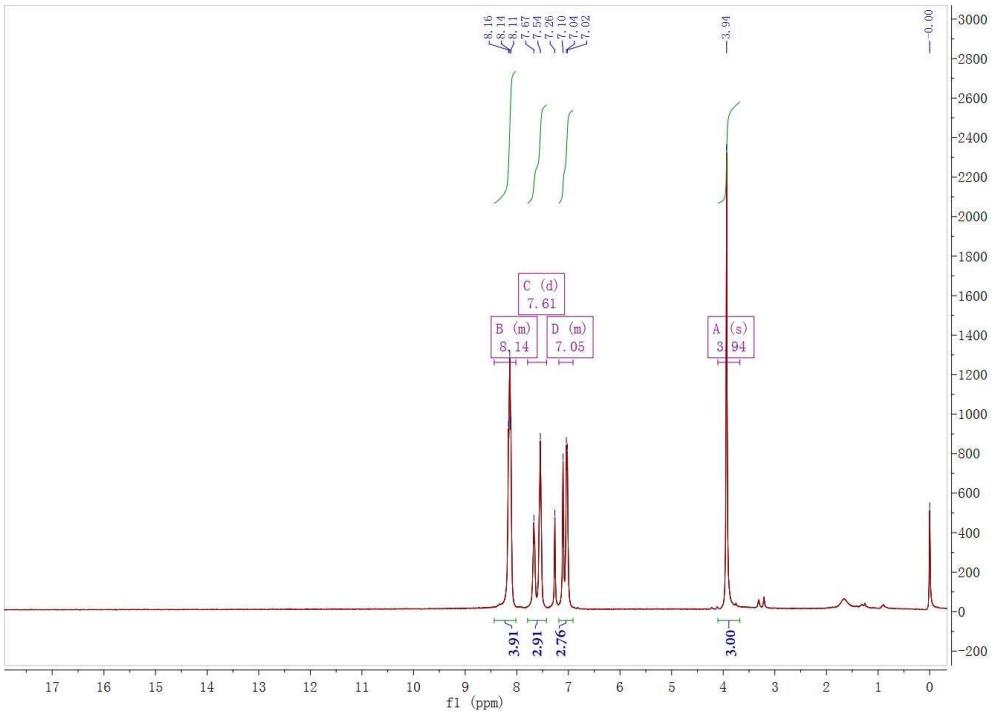


Figure S10. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **1**

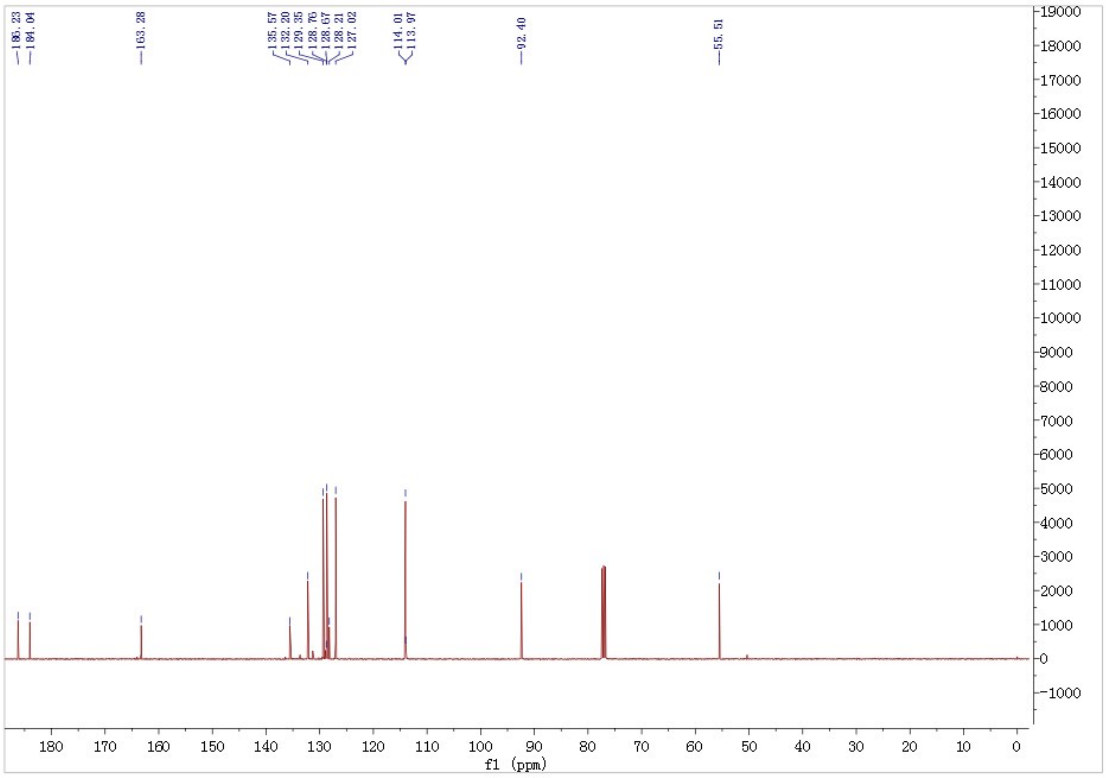


Figure S11. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1**

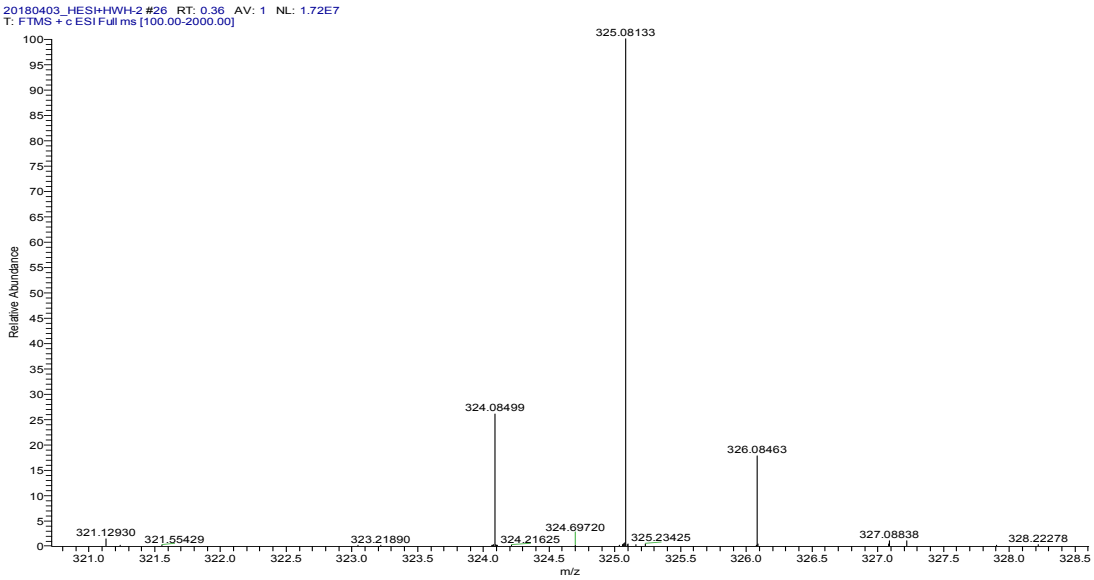


Figure S12. ESI-MS spectrum of **1**

2,2-difluoro-4-(4-phenoxyphenyl)-6-phenyl-2H-1,3l3,2l4-dioxaborinine(2).

Synthesized according to the above method for 2,2-difluoro-4-(4-methoxyphenyl)-6-phenyl-2H-1,3l3,2l4-dioxaborinine (1): 4.58g, 85%,δ(ppm) H (400 MHz, $CDCl_3$) 8.14 (4 H, ddd, J 8.5, 5.0, 2.1), 7.68 (1 H, t, J 7.4), 7.55 (2 H, t, J 7.8), 7.49 – 7.40 (2 H, m), 7.30 – 7.25 (1 H, m), 7.19 – 7.01 (5 H, m). δ C (101 MHz, $CDCl_3$) 182.10, 164.42, 154.62, 134.97, 132.15, 131.58, 130.31, 129.15, 128.75, 125.70, 125.41, 120.61, 117.54, 92.77. ESI-MS *m/z*: $[M + Na]^+$, 387.0975； calculated mass for: $C_{21}H_{15}BF_2NaO_3^+$: 387.0980 amu.

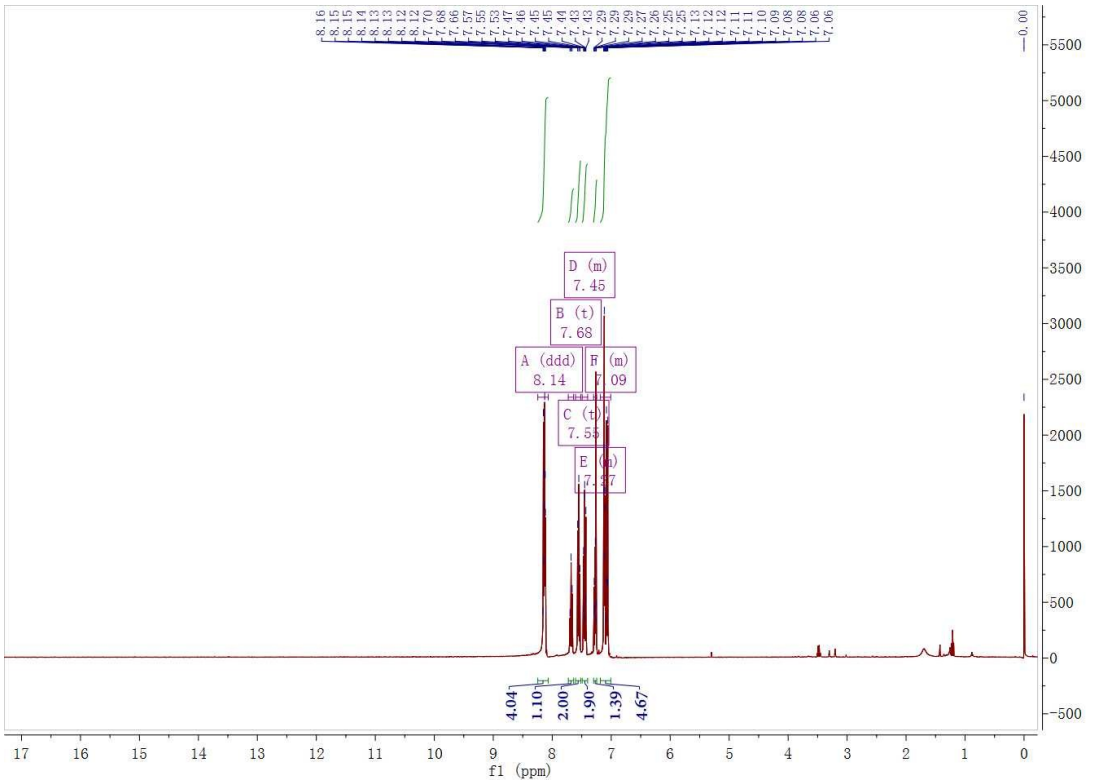


Figure S13. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2**

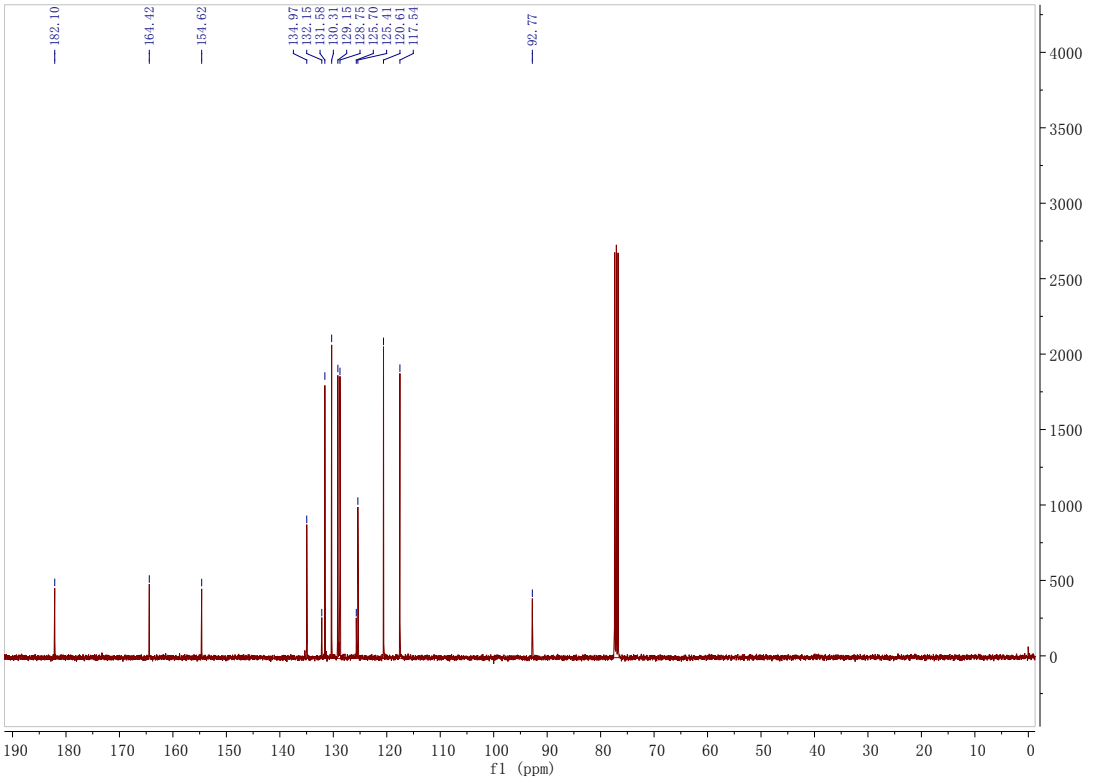


Figure S14. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2**

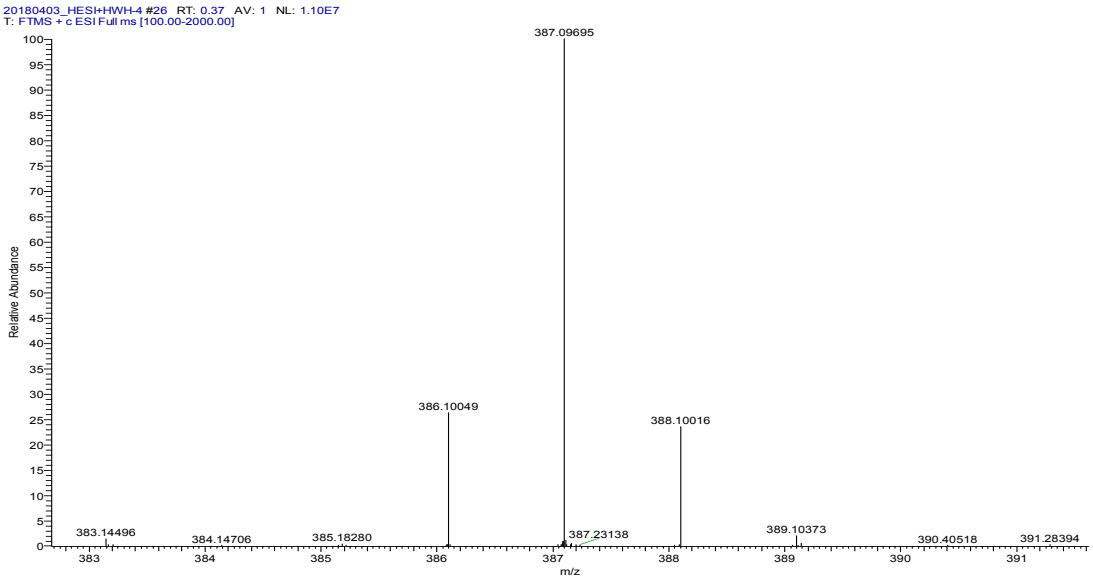


Figure S15. ESI-MS spectrum of **2**

2,2-difluoro-4-(4-(4-methoxyphenoxy)phenyl)-6-phenyl-2H-1,3l3,2l4-dioxaborinine(3)

Synthesized according to the above method for 2,2-difluoro-4-(4-methoxyphenyl)-6-phenyl -2H-1,3l3,2l4-dioxaborinine(1):4.31g,71%.δ (ppm) H (400 MHz, $CDCl_3$) 8.16 – 8.08 (4 H, m), 7.68 (1 H, t, J 7.4), 7.55 (2 H, t, J 7.8), 7.11 (1 H, s), 7.08 – 6.90 (6 H, m), 3.84 (3 H, d, J 9.4). δ C (101 MHz, $CDCl_3$) 182.16, 181.94, 165.27, 157.16, 147.74, 134.89, 132.22, 131.59, 129.13, 128.97, 128.72, 125.29, 121.89, 116.90, 115.27, 92.69, 55.71. ESI-MS *m*/*z*: $[M + Na]^+$, 417.1075 calculated mass for: $C_{22}H_{17}BF_2NaO_4^+$: 417.1086 amu.

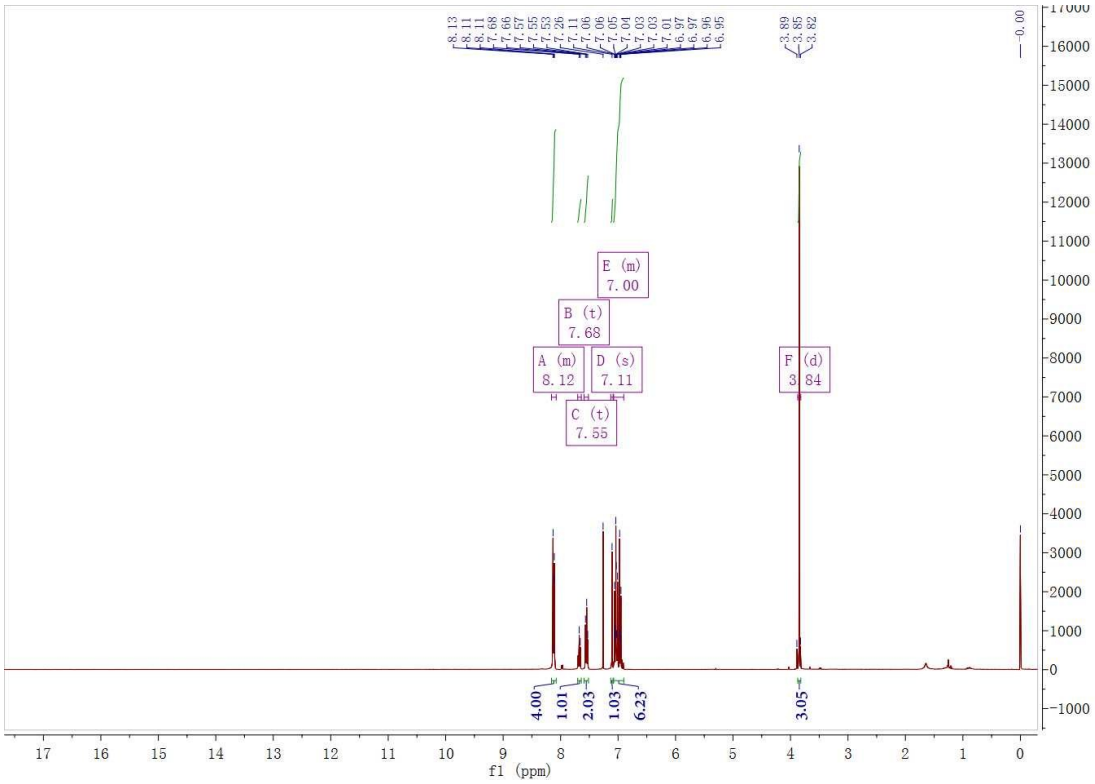


Figure S16. ^1H NMR spectrum (300 MHz, $CDCl_3$) of **3**

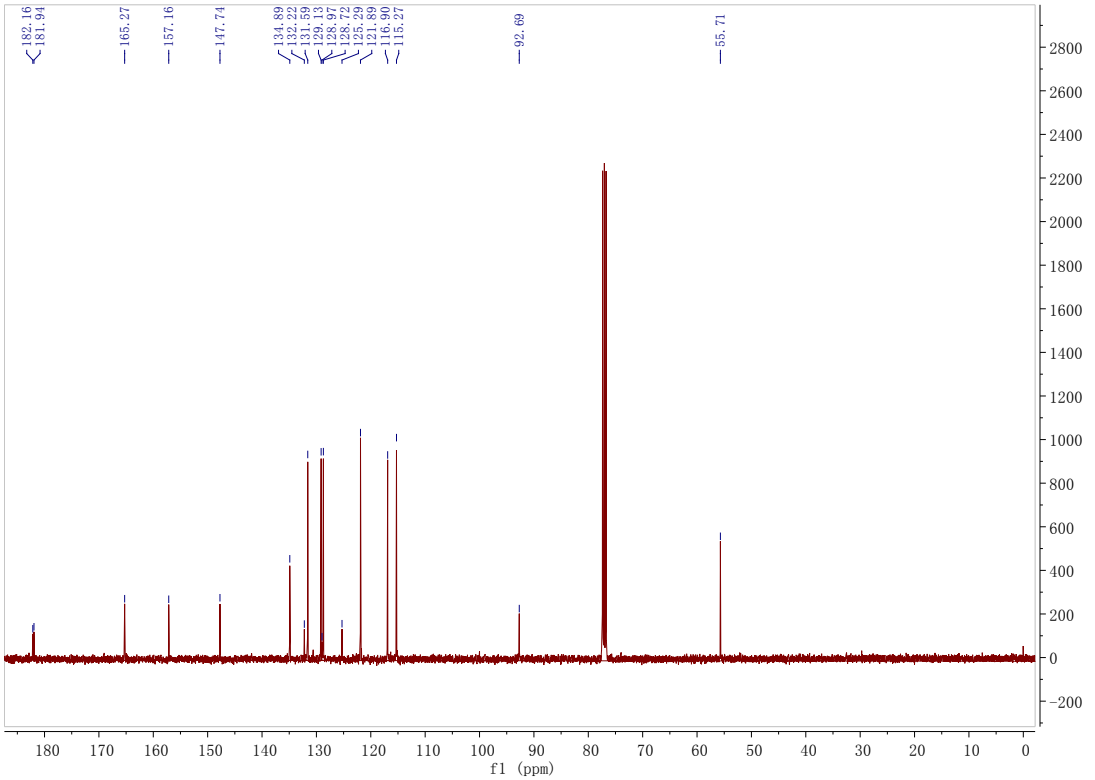


Figure S17. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3**

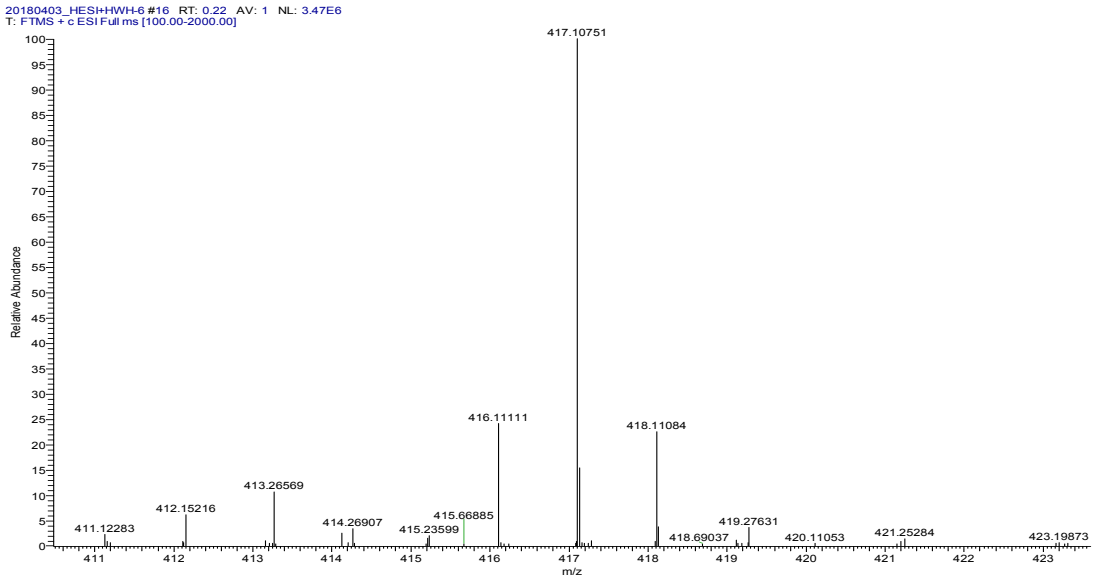


Figure S18. ESI-MS spectrum of **3**

2. Theoretical Calculations

Table S1. The singlet and triplet excited state transition configurations of **1** that contain the same orbital transition components of S_1

Excited State	Energy (ev)	Transtion configuration (%)
S1	3.2485	H→L (70.4)
T1	2.3935	H-4→L (10.3),H-1→L (14.9),H→L (67.0)
T2	3.0297	H-2→L+3 (11.2),H-1→L (61.8)
T3	3.4159	H-3→L (19.1),H-2→L (44.0),H-2→L+3 (19.4)
T4	3.5310	H-4→L (33.1),H-2→L (50.6),H-1→L+1 (15.3)
T5	3.6892	H-4→L (30.0),H-3→L (59.5),H-3→L+1 (17.3)
T6	3.9271	H-1→L (22.2),H-1→L+2 (11.4),H→L+1 (49.5),H→L+5 (13.5)
T7	4.2417	H-4→L (20.9),H-2→L+3 (35.8),H-1→L+2 (23.2)
T8	4.3066	H-4→L (17.2),H-2→L+3 (36.9),H→L+1 (17.7),H→L+2 (48.7)
T9	4.4659	H-3→L+1 (10.9),H-3→L+2 (39.0),H-2→L+3 (28.1),H→L+2 (28.8)

Table S2. The singlet and triplet excited state transition configurations of **2** that contain the same orbital transition components of S_1

Excited State	Energy (ev)	Transtion configuration (%)
S1	3.2751	H→L (70.3)
T1	2.4169	H-6→L (11.0),H-2→L (13.6),H-1→L (66.8)
T2	3.0580	H-4→L+3 (11.7),H-2→L (45.8)
T3	3.4094	H-5→L (16.7),H-4→L (47.2),H-4→L+3 (17.9),H-3→L+1 (10.1)
T4	3.5198	H-6→L (36.6),H-4→L (47.6),H-2→L+1 (12.0)
T5	3.6677	H-6→L (26.6),H-5→L (51.5),H-5→L+1 (15.5),H-3→L (27.8),H-2→L (13.3)
T6	3.7175	H-5→L (15.6),H-3→L+2 (19.7),H-2→L+2 (20.5),H-1→L+4 (48.5)
T7	3.7960	H-1→L (69.3)
T8	3.9355	H-2→L (25.6),H→L+1 (47.8)
T9	4.0987	H-3→L (47.6),H-2→L (39.7)

Table S3. The singlet and triplet excited state transition configurations of **3** that contain the same orbital transition components of S_1

Excited State	Energy (ev)	Transtion configuration (%)
S1	3.0461	H→L (70.5)

T1	2.4117	H-6→L (10.8),H-2→L (14.3),H-1→L (66.5)
T2	3.0213	H-1→L+1 (12.1),H→L (59.1)
T3	3.0721	H-3→L (20.0),H-2→L (46.9),H→L (37.2)
T4	3.4147	H-5→L (17.7),H-4→L (45.6),H-4→L+3 (18.4)
T5	3.5241	H-6→L (34.6),H-4→L (49.1),H-2→L+1 (14.3)
T6	3.6272	H-3→L+2 (22.3),H-2→L+4 (12.4),H→L+2 (17.7),H→L+5 (48.5)
T7	3.6682	H-6→L (28.1),H-5→L (52.4),H-5→L+1 (16.0)
T8	3.9346	H-3→L+2 (11.9),H-2→L (25.7),H-1→L+1 (47.9)
T9	3.9949	H→L+2 (48.5)

3. lifetime data

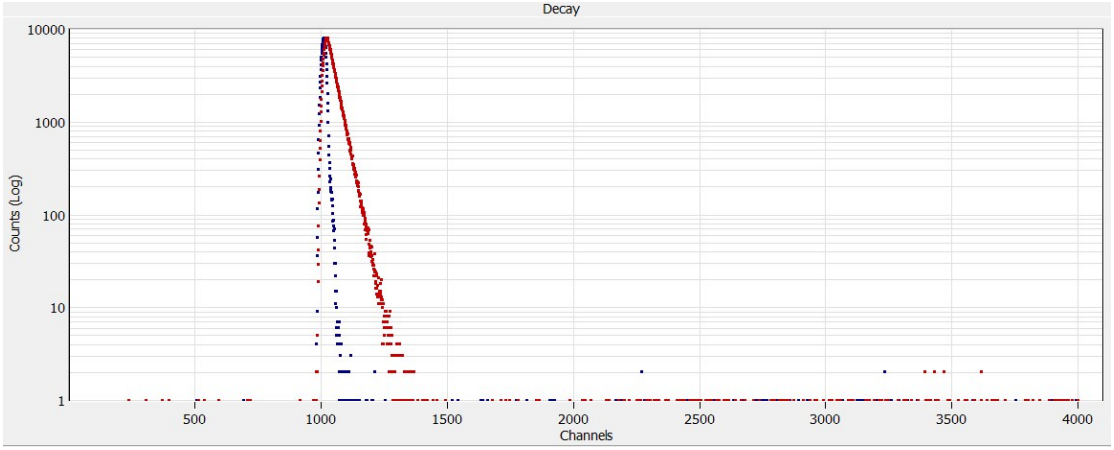


Figure S19. Fluorescence lifetime decay of **1** monotored at 420 nm (77 K, m-THF, Time calibration = 5.486969E-11 sec/ch, λ_{ex} = 372 nm nanoLED).

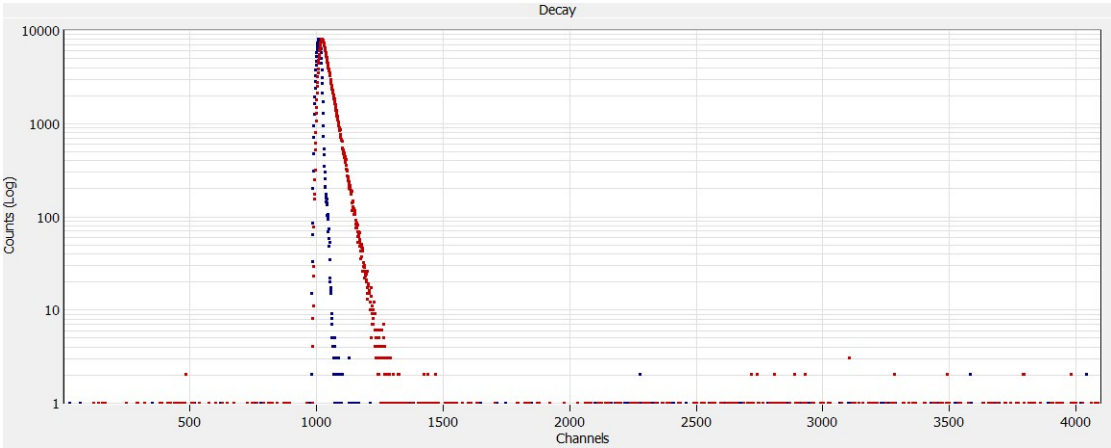


Figure S20. Fluorescence lifetime decay of **2** monotored at 414 nm (77K, m-THF, Time calibration = 5.486969E-11 sec/ch, λ_{ex} = 372 nm nanoLED).

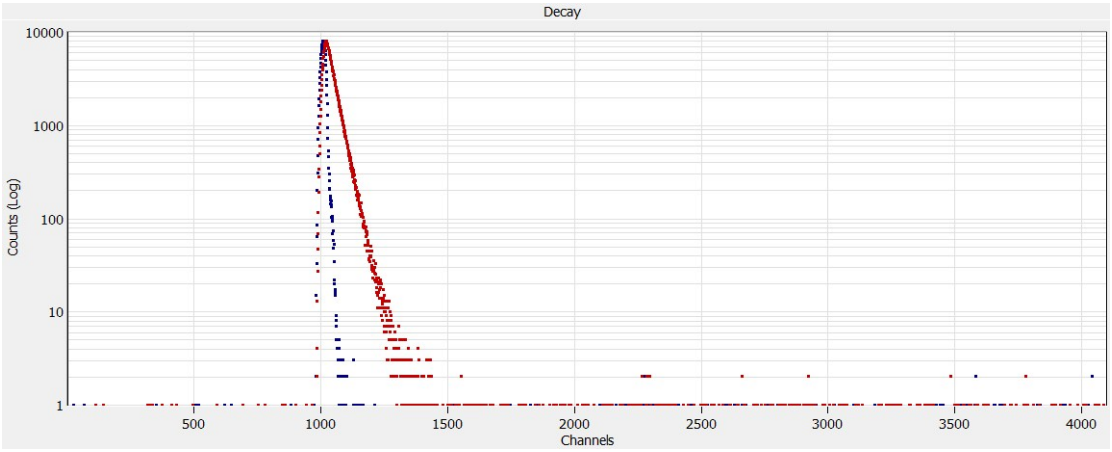


Figure S20. Fluorescence lifetime decay of **3** monitored at 415 nm (77K, m-THF, Time calibration = 5.486969E-11 sec/ch, λ_{ex} = 372 nm nanoLED).

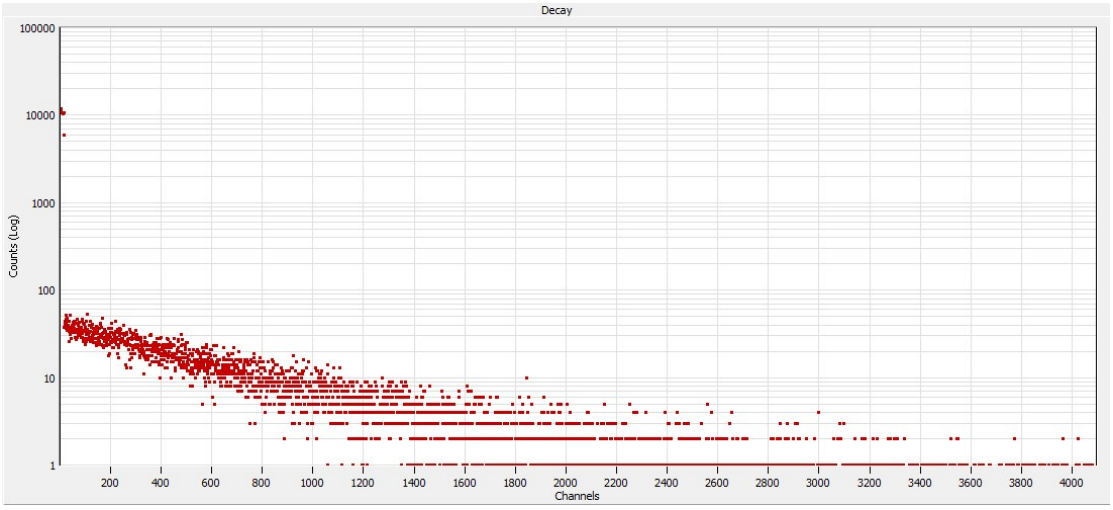


Figure S21. LP lifetime decay of **1** monitored at 502 nm (77 K, m-THF, Time calibration = 2.730672E-03 sec/ch, λ_{ex} = 374 nm spectraLED).

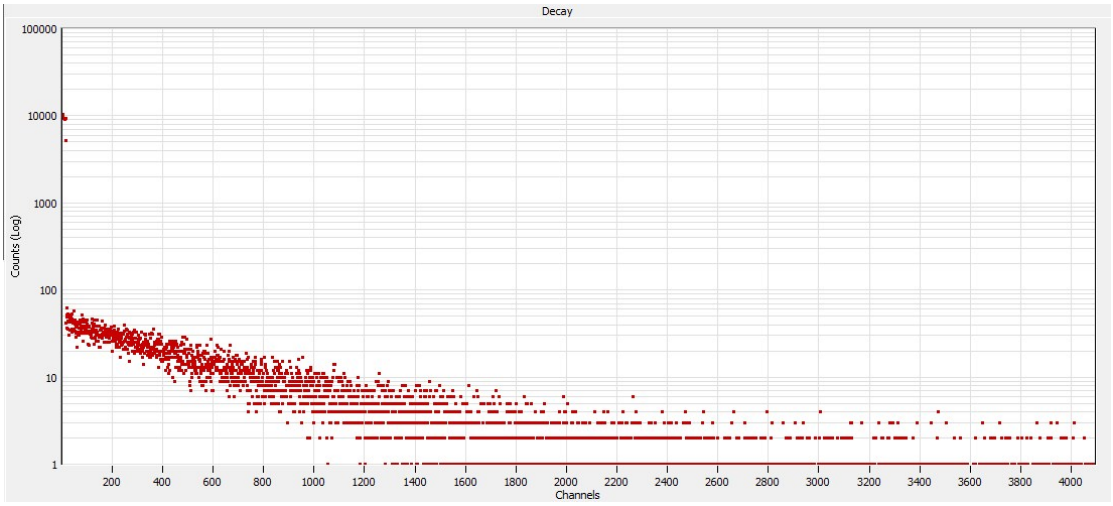


Figure S22. LP lifetime decay of **2** monitored at 497 nm (77 K, m-THF, Time calibration =2.730672E-03 sec/ch, λ_{ex} = 374 nm spectraLED)

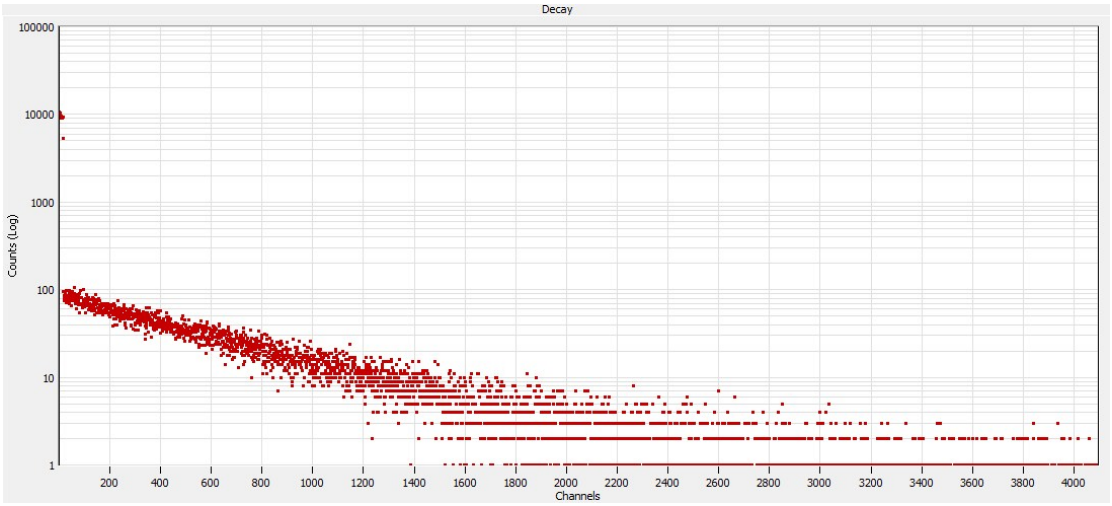


Figure S23. LP lifetime decay of **3** monitored at 539 nm (77 K, m-THF, Time calibration =2.730672E-03 sec/ch, λ_{ex} = 374 nm spectraLED)

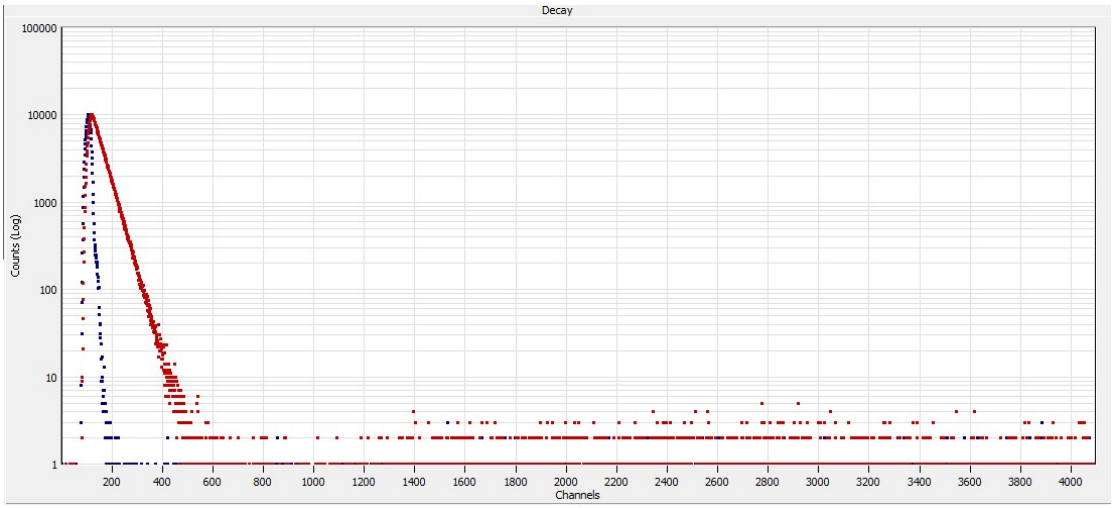


Figure S24. Fluorescence lifetime decay of **1** monitored at 434 nm (298 K, vacuum ,PMMA,0.1%, Time calibration = 5.486969E-11 sec/ch, λ_{ex} = 372 nm nanoLED).

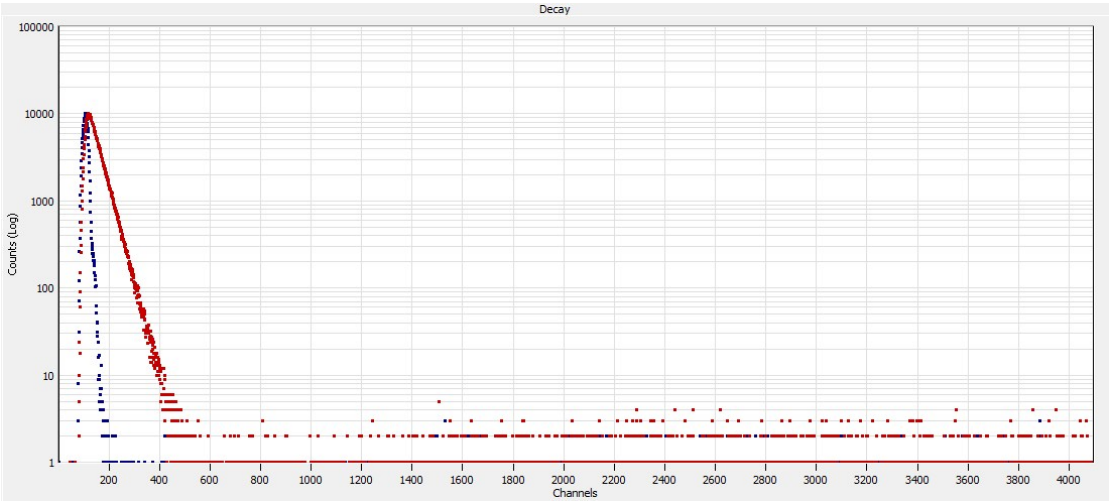


Figure S25. Fluorescence lifetime decay of **2** monitored at 433 nm (298K, vacuum ,PMMA,0.1%, Time calibration = 5.486969E-11 sec/ch, λ_{ex} = 372 nm nanoLED)

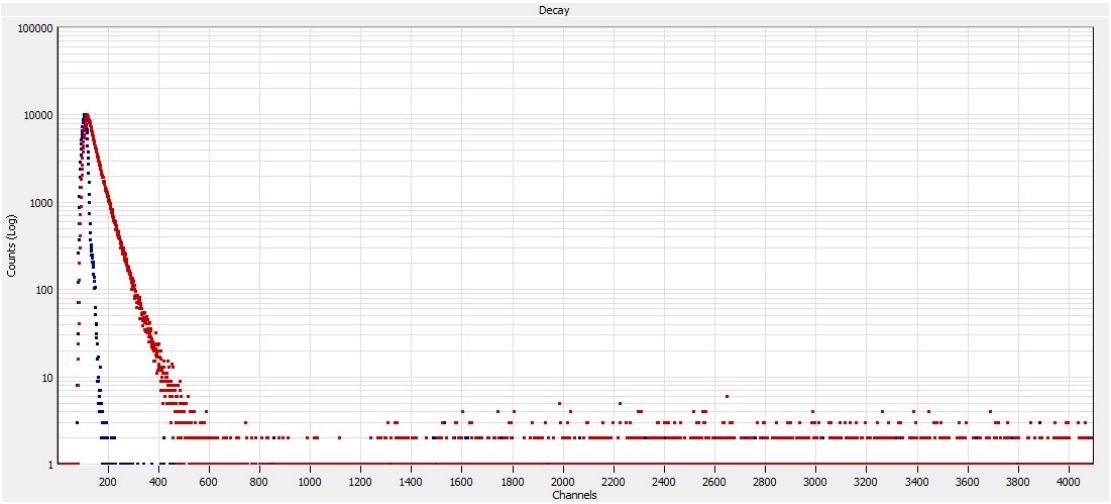


Figure S25. Fluorescence lifetime decay of **3** monitored at 440 nm (298 K, vacuum ,PMMA,0.1%, Time calibration = 5.486969E-11 sec/ch, λ_{ex} = 372 nm nanoLED)

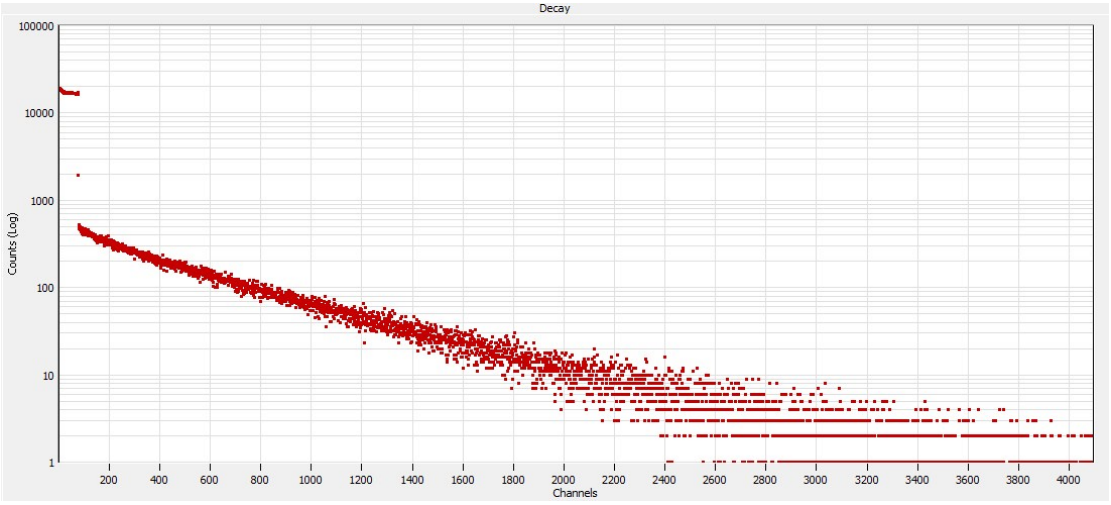


Figure S26. LP lifetime decay of **1** monitored at 510 nm (298 K, vacuum ,PMMA,0.1%, Time calibration =1.365336E-03 sec/ch, λ_{ex} = 374 nm spectraLED)

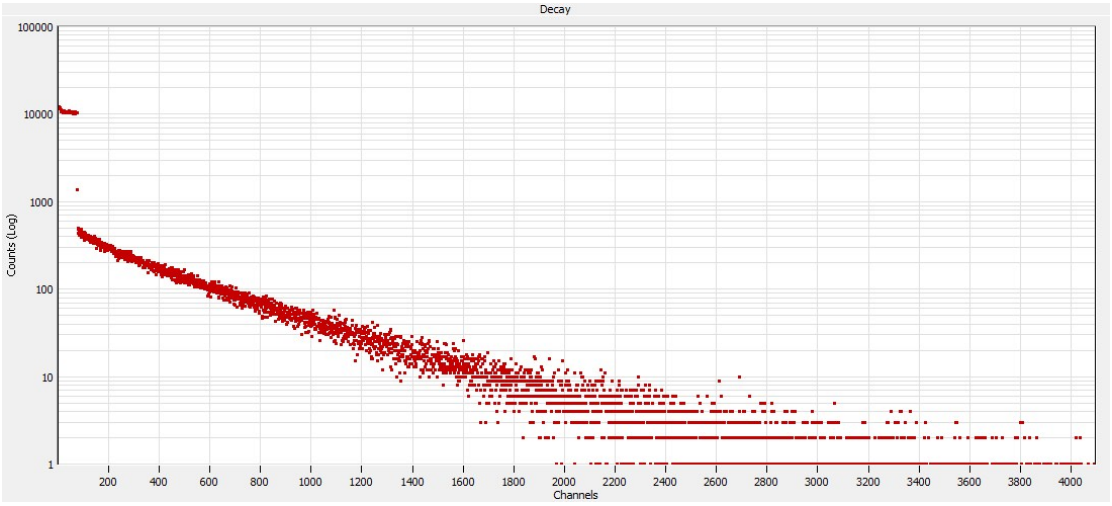


Figure S27. LP lifetime decay of **2** monitored at 510 nm (298 K, vacuum ,PMMA,0.1%, Time calibration = 1.365336E-03sec/ch, λ_{ex} = 374 nm spectraLED)

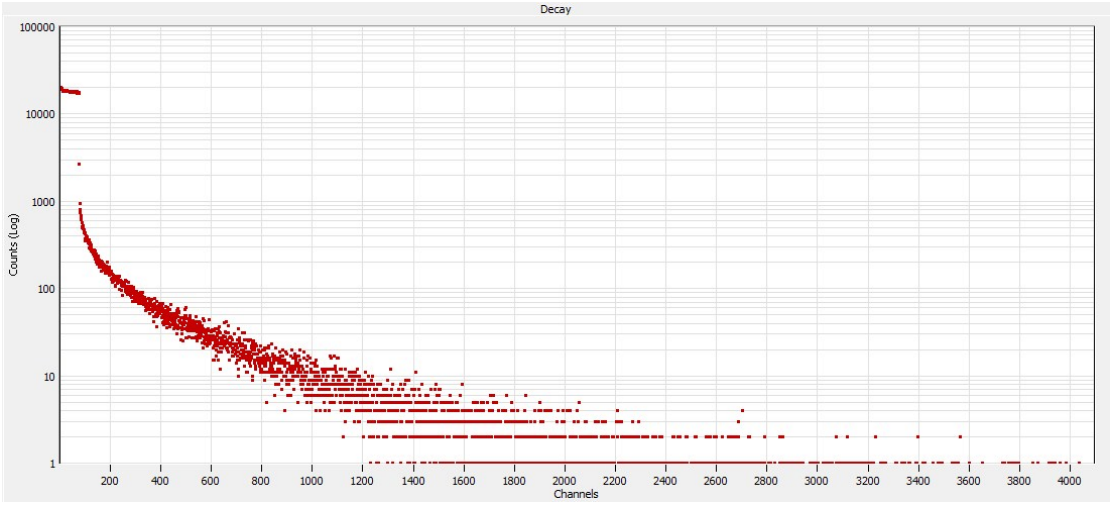


Figure S28. LP lifetime decay of **3** monitored at 510 nm (298 K, vacuum ,PMMA, 0.1%, Time calibration =1.365336E-03 sec/ch, λ_{ex} = 374 nm spectraLED)

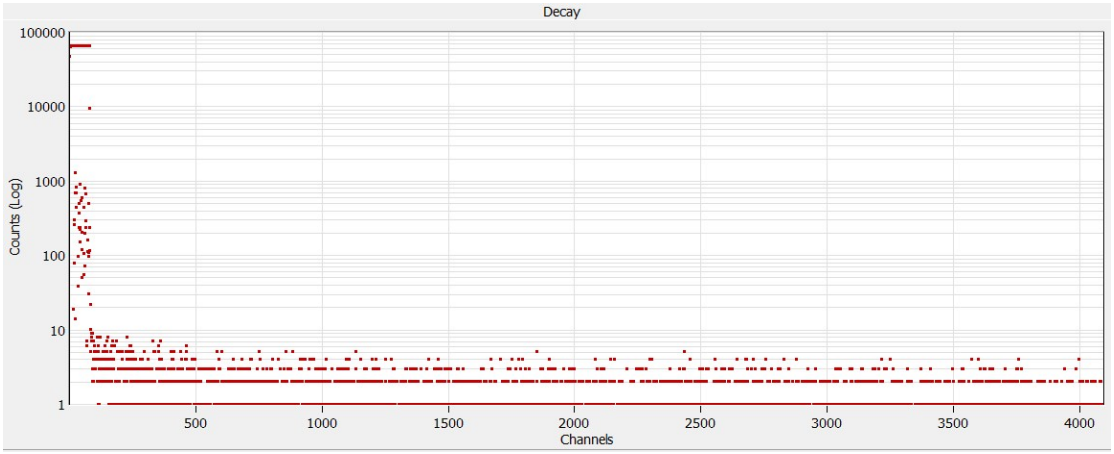


Figure S29. LP lifetime decay of **1** monitored at 510 nm (298 K, air ,PMMA, 0.1%, Time calibration = 1.333336E-06 sec/ch, λ_{ex} = 374 nm spectraLED)

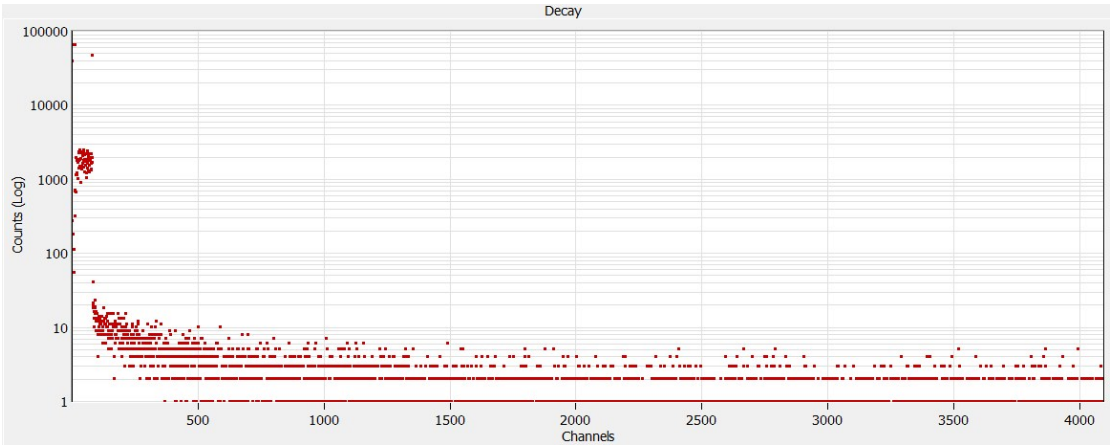


Figure S30. LP lifetime decay of **2** monitored at 510 nm (298K, air ,PMMA, 0.1%, Time calibration = 1.333336E-06 sec/ch, λ_{ex} = 374 nm spectraLED)

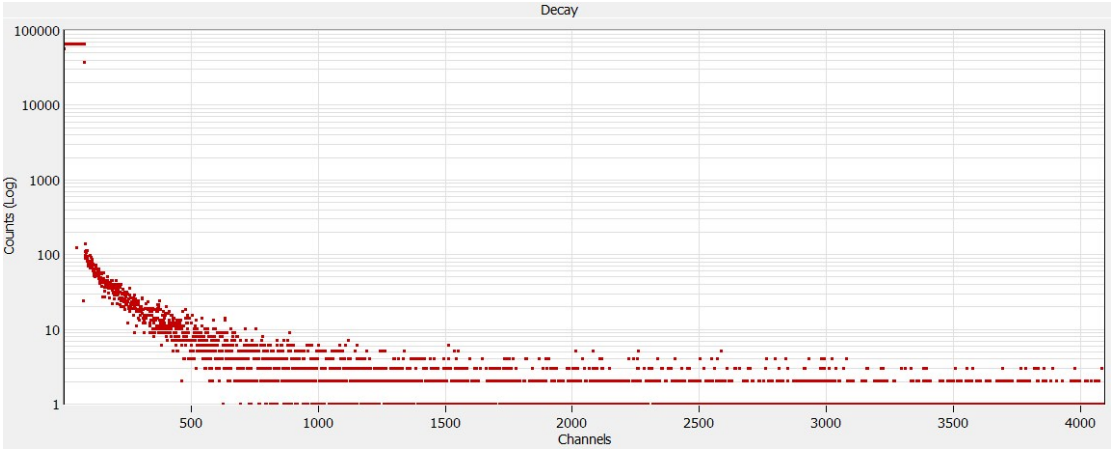


Figure S30. LP lifetime decay of **3** monitored at 510 nm (298 K, air ,PMMA, 0.1%, Time calibration = 1.333336E-06 sec/ch, λ_{ex} = 374 nm spectraLED)

4. Supplement Figure

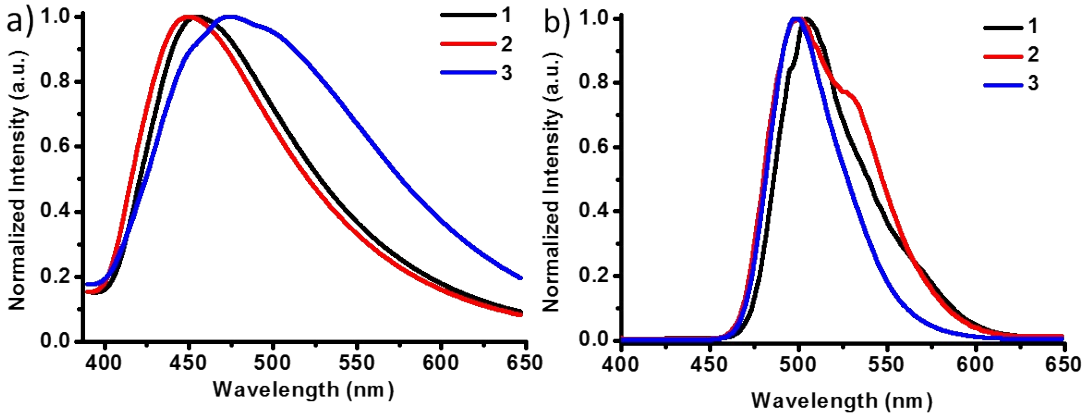


Figure S31.a) steady-state emission spectra of model complexes in 2-methyltetrahydrofuran at 77K in air (λ_{ex} = 372 nm) b) delayed (Δt = 100ms) emission spectra of model complexes in 2-methyltetrahydrofuran at 77K in air (λ_{ex} = 372 nm).

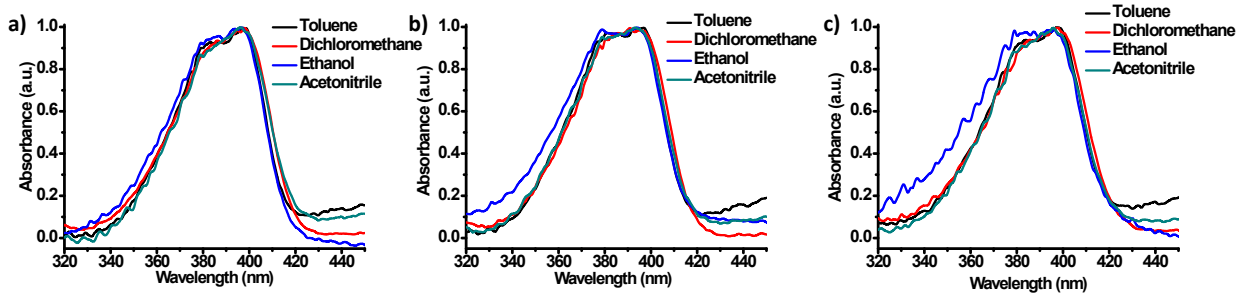


Figure S32. UV/Vis absorbance spectra of model complexes **1** (a), **2** (b), **3** (c) in different solvents (5.0 μM) at room temperature.

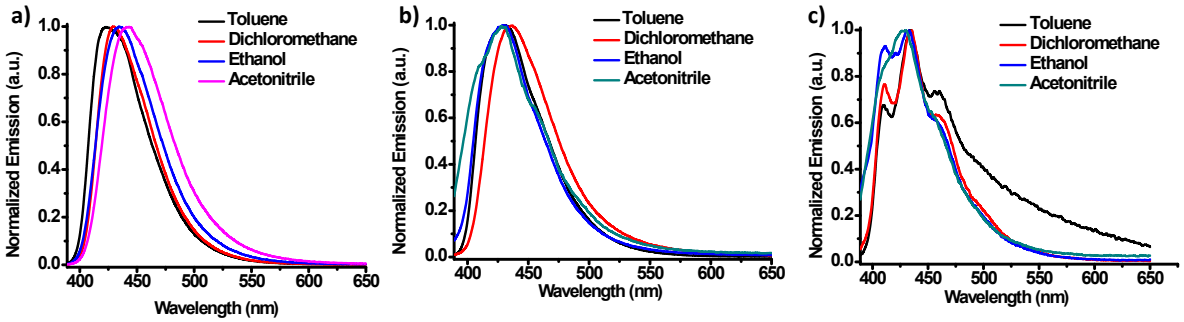


Figure S33. Steady-state emission (λ_{ex} = 372 nm) spectra of model complexes **1** (a), **2** (b), **3** (c) in different solvents (5.0 μM) at room temperature.

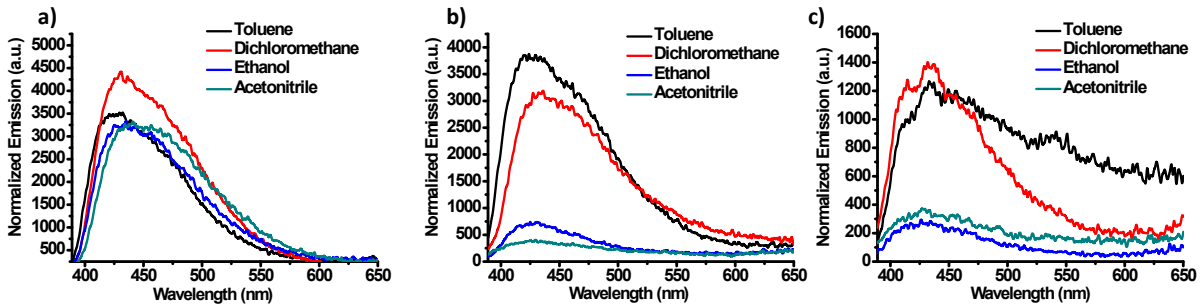


Figure S34. Delayed emission (λ_{ex} = 372 nm, Δt = 50 μs) spectra of model complexes **1** (a), **2** (b), **3** (c) in different solvents (5.0 μM) at room temperature.