Supporting Information

Turn-on Exciplex Fluorescence Induced by Complexation of Nonfluorescent Pentafluorinated Dibenzoylmetanatoboron Difluoride with Benzene and Its Derivatives

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1. General Methods and Materials

All solvents were purified before use. Tetrahydrofurane was distilled from sodium/benzophenone. Dichloromethane was distilled over phosphorus pentoxide. Acetophenone, pentafluorobenzoyl chloride, LiHMDS (1M in THF) and boron trifluoride diethyl etherate were purchased from Acros Organics and used without purification. The reactions were monitored by thin-layer chromatography (TLC) using Fluka silica gel (60 F 254) plates (0.25 mm). Column chromatography was carried out using Merck 60 (230–400 mesh) silica gel. Visualization was made with UV light. Melting points of synthesized compounds were taken on a melting point tube. IR spectra were obtained using an IR spectrometer with a Fourier transformer Bruker "Tensor 37" (Germany). The samples were prepared by pressing KBr pellets. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance 400 (400 MHz; Germany) spectrometer. Chemical shifts are reported relative to chloroform (δ=7.25 ppm) for ^{1}H NMR and chloroform (δ=77.00 ppm) for ^{13}C NMR. High-resolution mass spectra (HRMS) were measured using a Bruker micrOTOF II instrument with electrospray ionization (ESI) (Germany). The absorption spectra were recorded on a Shimadzu UV-25001PC spectrophotometer (Japan). The fluorescence spectra in solution were measured on the scanning spectrofluorimeter developed and constructed at ISPM RAS equipped with a 150 W arc xenon lamp as the pumping source, two Seya-Namioka-type monochromators and two photoelectronic multipliers[1] and Agilent Cary Eclipse Fluorescence Spectrophotometer (USA). Spectroscopic grade solvents (Aldrich) were used in UV-vis absorption and fluorescence measurements. Optical densities were, typically, between 0.1 and 0.5 (corresponding to sample concentrations from 3×10^{-6} to 3×10^{-5} mole dm^{-3}) for absorption measurements and around 0.05-0.1 for fluorescence measurements. Quantum yield were measured using 9,10-DPA as a reference. The fluorescence spectra in solid state were recorded using Ocean Optics USB4000 fiberoptic spectrometer (USA). A 226 LEE U.V. light filter (LEE Filters) was located before the entrance slit of the spectrometer and a Nichia NSHU591A light diode with a UFS-2 filter ($\lambda_{ex} = 340$ nm) was used as a source.

2. Synthesis
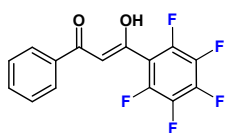
Pentafluorophenyl-DBM (**3**). To a solution of acetophenone **1** (0.004 mol) in dry THF (15 mL) at -70 °C a 1M solution of LiHMDS in THF (0.008 mol) under argon was added and the reaction mixture was stirred at -70 °C for 1 h. Then a solution of pentafluorobenzoyl chloride (0.0045 mol) was slowly added to the reaction mixture. After stirring at -70 °C for 1 h the temperature of the reaction mixture was raised up to room temperature and stirred for 2 h. Then the reaction mixture was poured into water (50 mL) and organic fraction was extracted by ethyl acetate (50 mL). Organic layer was separated by diluted funnel and washed with H_2O. After drying over Na_2SO_4, the solvent was evaporated in vacuo. The residual product was purified by column chromatography on silica with toluene as an eluent. **Yield**: 55 %. **Mp.** = 135-137 °C. **^{1}H NMR** (400 MHz, CDCl$_3$): δ 6.50 (s, 1H, CO-CH-CO), 7.49 (t, 2H, *J*=7.6 Hz, Ar), 7.59 (t, 1H, *J*=7.3 Hz, Ar), 7.93 (d, 2H, *J*=7.6 Hz, Ar), 15.90 (s, 1H, OH). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 99.7, 113.0, 127.4, 128.9, 133.3, 133.7, 136.5, 139.1, 141.3, 143.3, 143.9, 145.8, 178.7, 184.2. **^{19}F NMR** (376 MHz, CDCl$_3$): δ -160.32 (t, 2F, *J*=17.9 Hz, CF), -149.76 (t, 1F, *J*=20.6 Hz, CF), -139.58 (d, 2F, *J*=17.2 Hz, CF). **IR** (KBr): 1653, 1600, 1570, 1520, 1490, 1425, 1331, 1303, 1262, 1244, 1193, 1180, 1104, 1097, 1073, 1065, 1026, 998, 988, 944, 866, 846, 821, 781, 754, 718, 711, 688, 620, 602, 579, 489, 443 cm^{-1}. **HRMS** (ESI) *m/z* calcd. for $C_{15}H_7F_5O_2Na$ [(M+Na)$^+$]: 337.0258, found 337.0259.
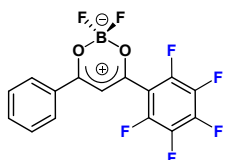

Pentafluorophenyl-DBMBF$_2$ (**4**). 2-Fold excess of boron trifluoride diethyl etherate (0.04 mol) was added to a solution of 1,3-diketone **3** (0.02 mol) in dry dichloromethane (50 mL). The reaction mixture was stirred for 2 h at room temperature. After the reaction was complete the solvent was removed by evaporation in vacuo and the residue was purified by column chromatography on silica with a mixture hexane-toluene as an eluent. **Yield**: 75 %. **Mp.** = 118-120 °C. **^{1}H NMR** (400 MHz, CDCl$_3$): δ 6.98 (s, 1H, CO-CH-CO), 7.60 (t, 2H, *J*=7.8 Hz, Ar), 7.78 (t, 1H, *J*=7.4 Hz, Ar), 8.15 (d, 2H, *J*=7.8 Hz, Ar). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 100.1, 109.5, 129.5, 129.8, 130.9, 136.92, 136.93, 139.3, 142.8, 144.4, 145.4, 146.9, 174.1, 186.3. **^{19}F NMR** (376 MHz, CDCl$_3$): δ -158.82 (t, 2F, *J*=16.8 Hz, CF), -144.50 (t, 1F, *J*=19.0 Hz, CF), -138.08 (80%, ^{11}B-F), -138.02 (20%, ^{10}B-F), -135.75 (d, 2F, *J*=16.9 Hz, CF). **IR** (KBr): 3147, 3078, 1653, 1592, 1562, 1544, 1518, 1491, 1452, 1431, 1395, 1357, 1319, 1296, 1230, 1205, 1179, 1101, 1086, 1051, 1000, 979, 942, 894, 847, 826, 785, 742, 718, 688, 614, 575 cm^{-1}. **HRMS** (ESI) *m/z* calcd. for $C_{15}H_6BF_7O_2Na$ [(M+Na)$^+$]: 385.0244, found 385.0244.
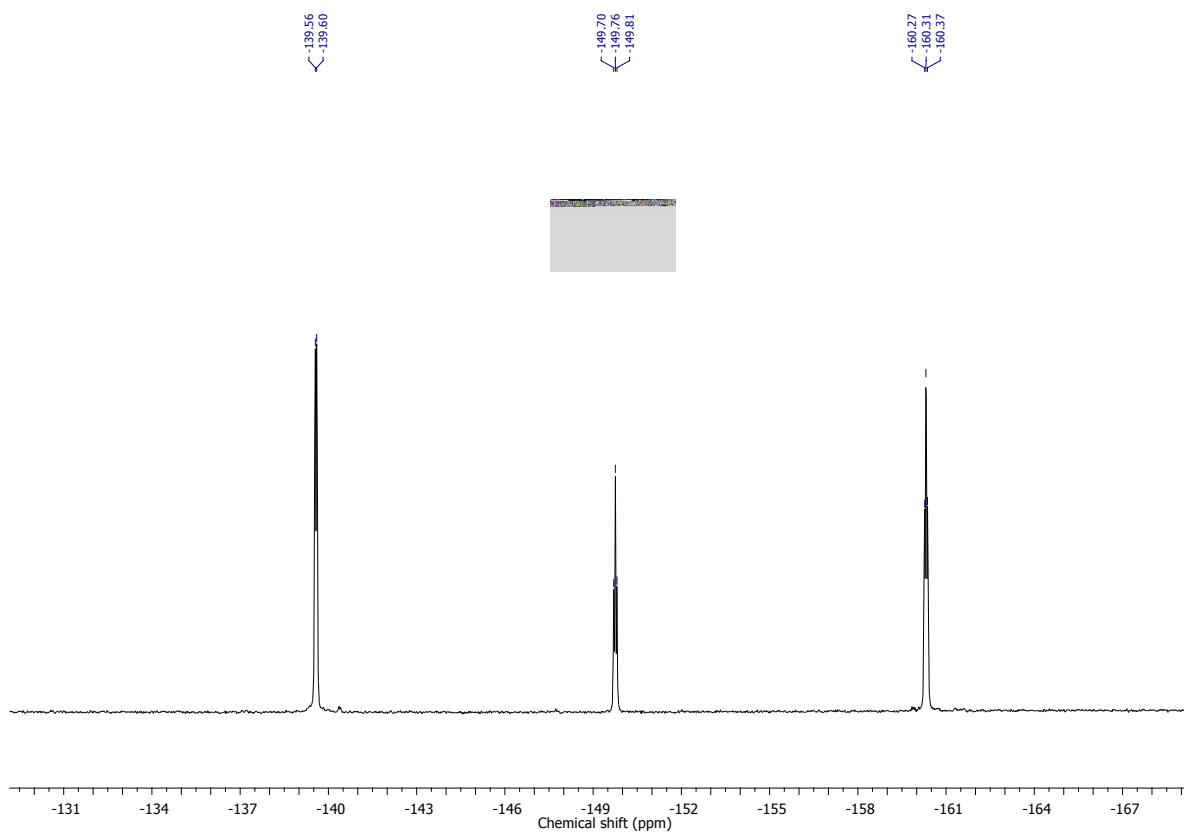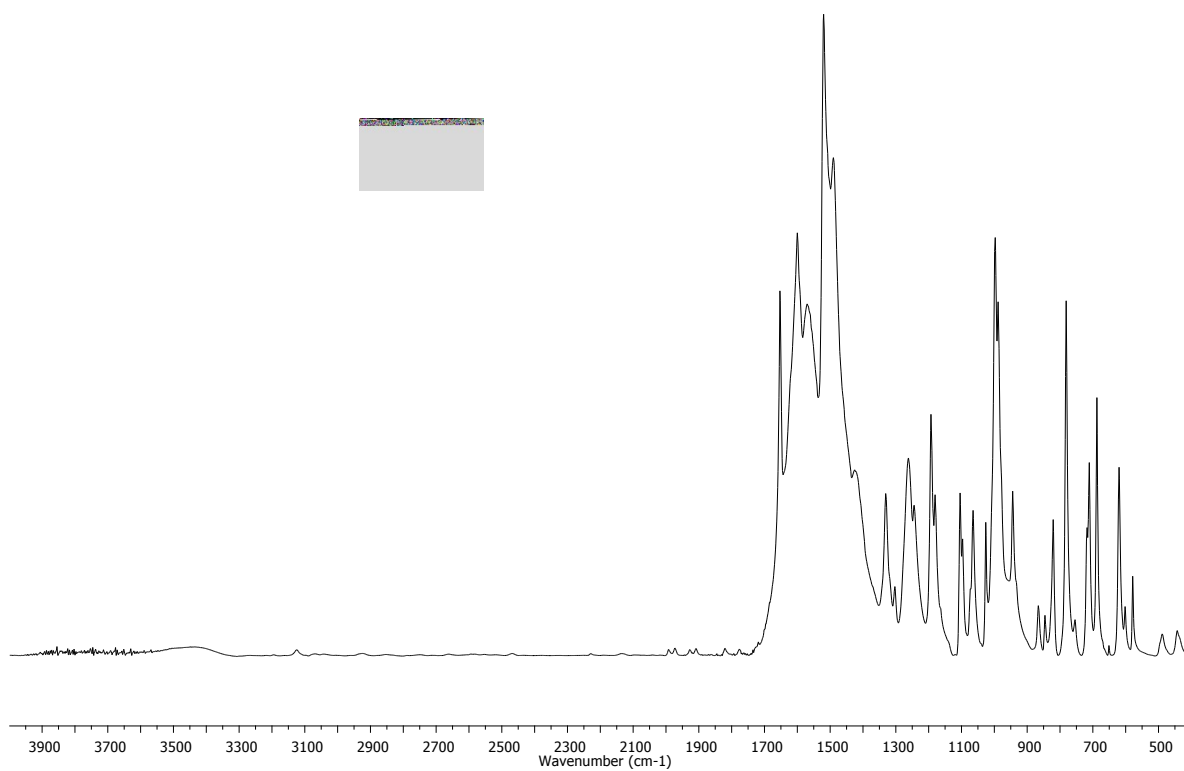
3. Spectral Data
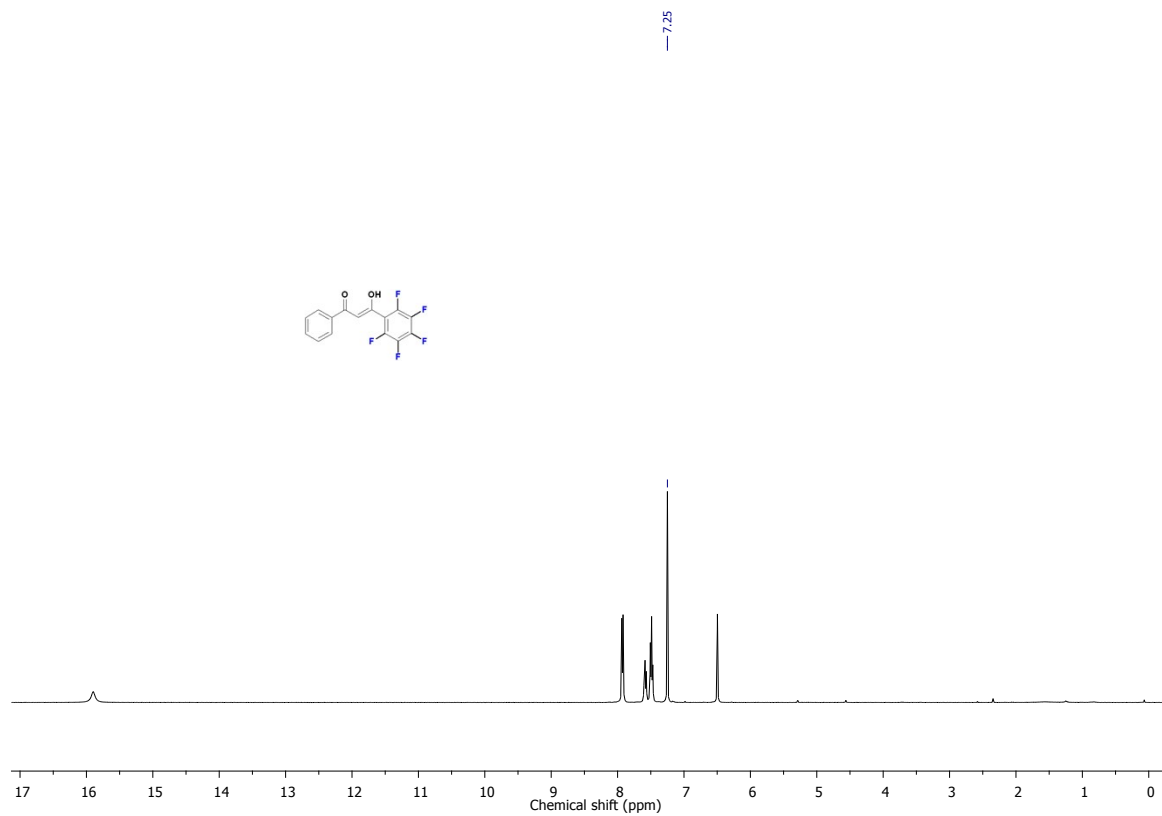
Figure S1. ^{1}H NMR spectrum of **3** in CDCl$_3$.
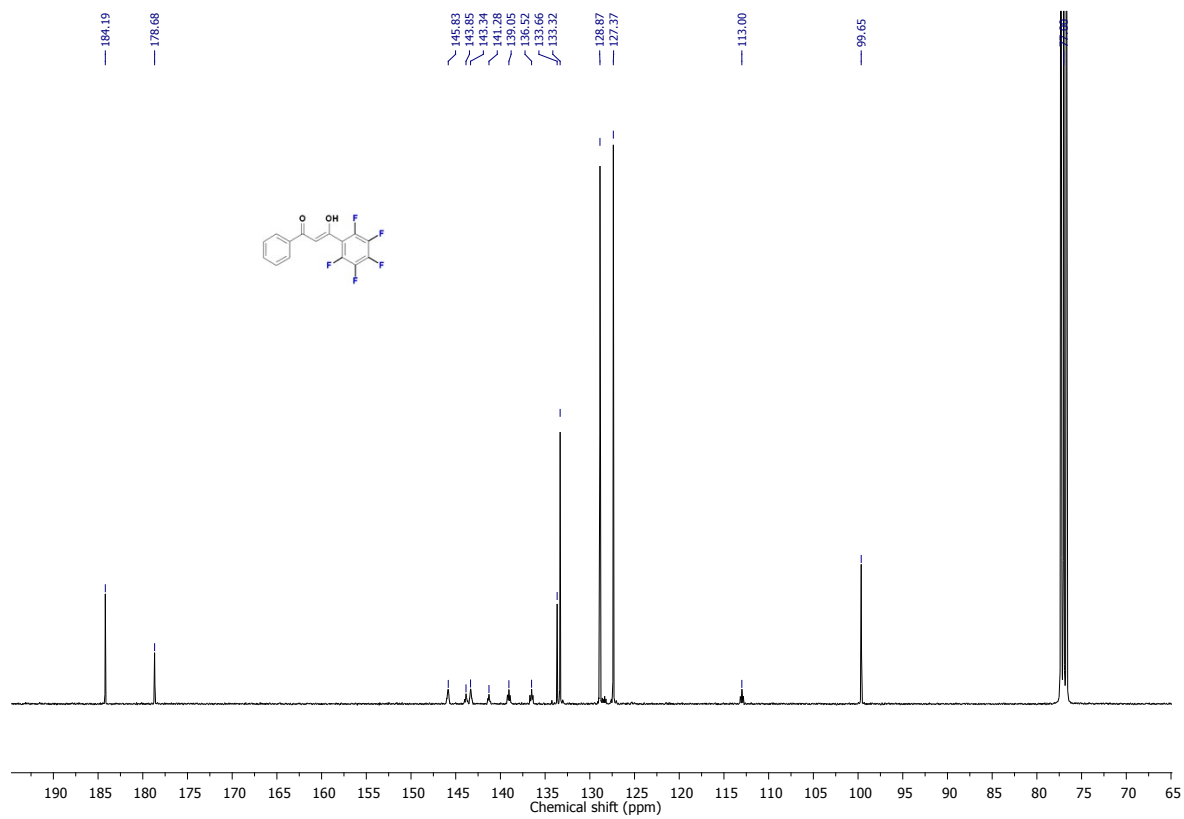
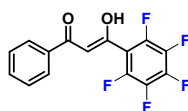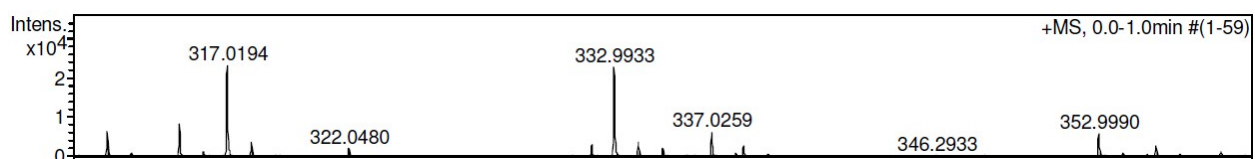**Figure S2.** ^{13}C NMR spectrum of **3** in CDCl$_3$.

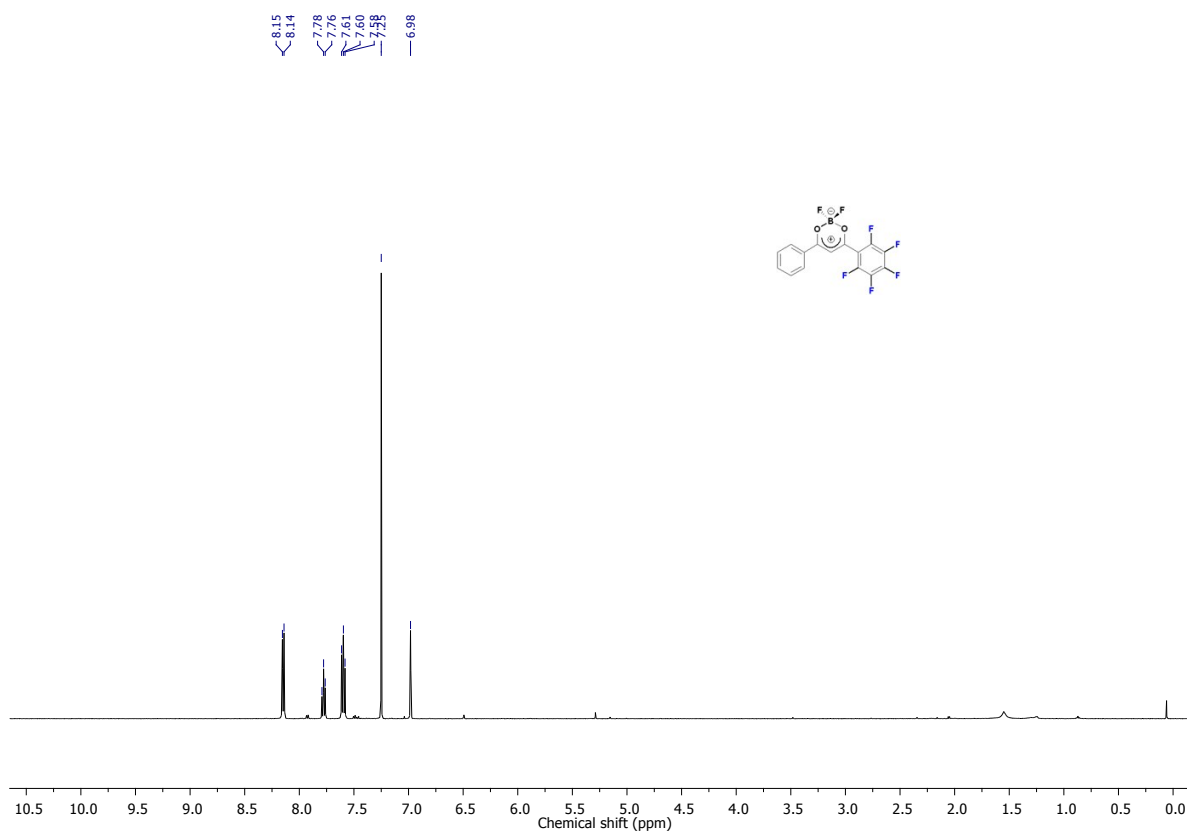**Figure S3.** ^{19}F NMR spectrum of **3** in CDCl$_3$.
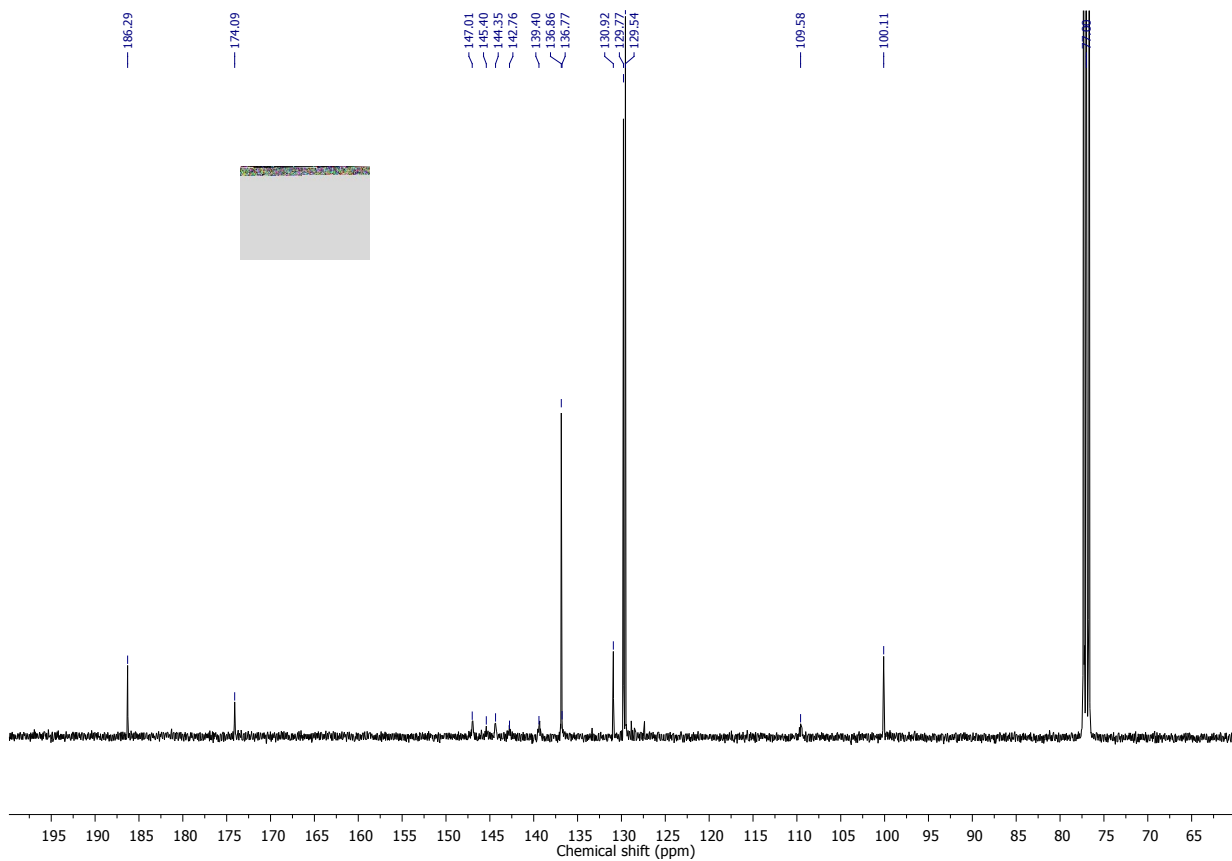

Figure S4. IR spectrum of **3**.
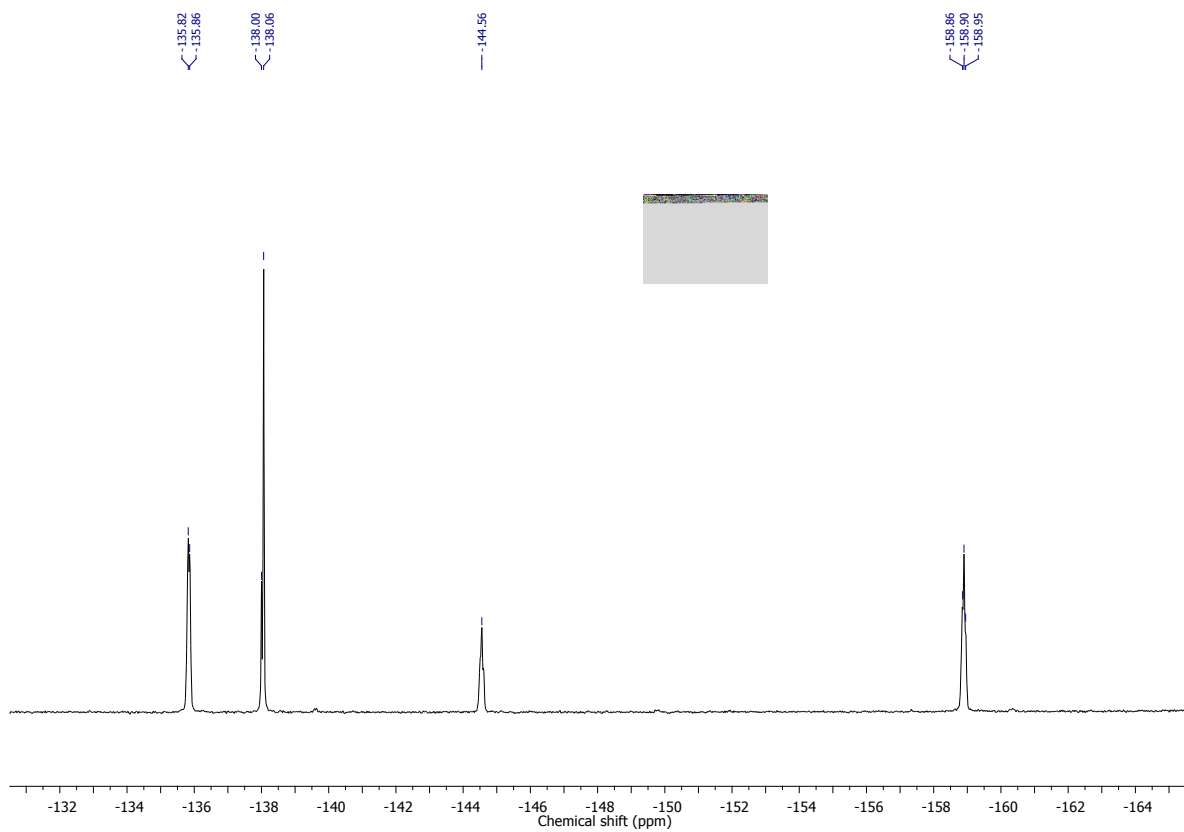
m/z calcd. for $C_{15}H_7F_5O_2Na$ [(M+Na)$^+$]: 337.0258
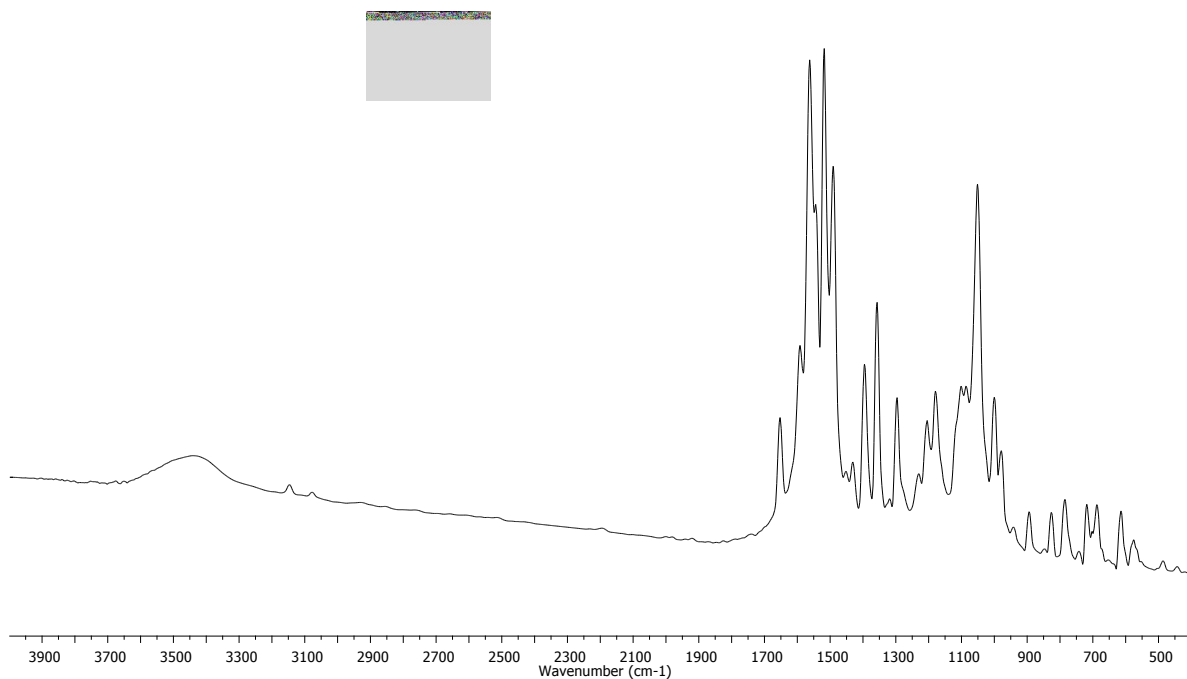
Figure S5. MS spectrum of **3**.

Figure S6. ^{1}H NMR spectrum of **4** in CDCl$_3$.
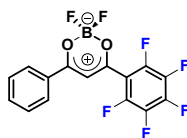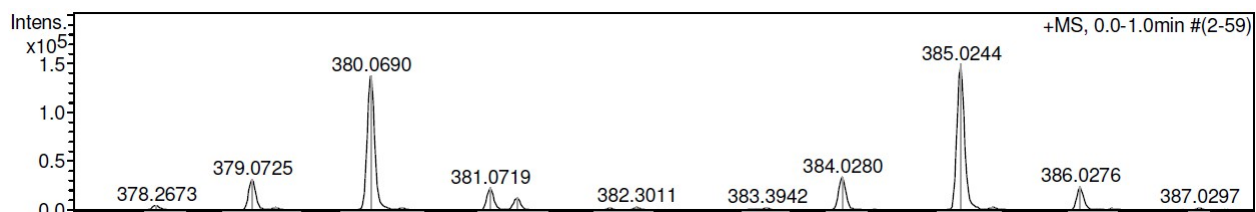
Figure S7. ^{13}C NMR spectrum of **4** in CDCl$_3$.

Figure S8. ^{19}F NMR spectrum of **4** in CDCl$_3$.

Figure S9. IR spectrum of **4**.

m/z calcd. for C$_{15}$H$_6$BF$_7$O$_2$Na [(M+Na)$^+$]: 385.0244

Figure S10. MS spectrum of **4**.

4. X-ray Analysis

Single crystals of **4** ($C_{15}H_6BF_7O_2$) were prism. A suitable crystal was selected, and X-ray dataset was collected on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 120K during data collection. Using Olex2[2], the structure was solved with the ShelXT[3] structure solution program using Intrinsic Phasing and refined with the ShelXL[4] refinement package using Least Squares minimisation.

Crystal Data for **4**: $C_{15}H_6BF_7O_2$ (M =362.01 g/mol): monoclinic, space group P2$_1$/n (no. 14), a = 10.084(4) Å, b = 13.499(6) Å, c = 10.890(5) Å, β = 110.210(10)°, V = 1391.1(10) Å^3, Z = 4, T = 120 K, μ(MoKα) = 0.175 mm-1, Dcalc = 1.729 g/cm3, 8329 reflections measured (4.75° ≤ 2Θ ≤ 61.288°), 4170 unique (Rint = 0.0359, Rsigma = 0.0625) which were used in all calculations. The final R1 was 0.0502 (I > 2σ(I)) and wR2 was 0.1243 (all data), GOF = 1.036.

5. Computational Methods

Structures and electronic spectra of $DBMBF_2$ molecule, its mono- and pentafluorinated derivatives, and exciplexes of these molecules with benzene, toluene, and m-xylene were studied theoretically using quantum-chemicals calculations. For excited state structures and emission spectra we used combined procedure proposed early by us[5,6]. Geometry optimization in the excited state was performed using the CIS-D method including the Grimme's dispersion correction with the double-zeta def2-SVP basis set. For the ground-state complexes, geometry optimization was performed by the HF-D method with the same basis set. Electron transition energies at the optimized geometries were calculated by the TDDFT method with the double-hybrid functional mPW2PLYP and the triple-zeta def2-TZVP basis set. Positions of absorption and fluorescence bands were calculated as electronic transition energies at the geometries optimized for the ground and excited states, respectively. All calculations were performed using the Orca program[7].

6. References

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