

The Electronic Supplementary Information for

Photochemically assisted synthesis and photophysical properties of difluoroboronated β -diketones having fused four benzene rings; chrysene and pyrene

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Contents

1. Procedure for preparing compounds, 1-ChB, 3-ChB and 1-PyB (p. 2–7)

2. Absorption and fluorescence spectra in MeCN (p. 8)

3. Absorption and fluorescence spectra in DMSO (p. 9)

4. Decay profiles of fluorescence (p. 10)

5. Lippert-Mataga analysis data (p. 11–12)

6. Transient absorption spectra in MeCN (p. 13)

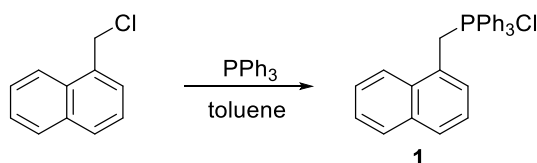
7. Results of DFT and TD-DFT calculations (absorption spectra, atom coordinates and sum of electronic and zero-point energies) (p. 14–20)

8. ¹H and ¹³C NMR spectra of new compounds (p. 21–28)

1. Procedure for preparing compounds, 1-ChB, 3-ChB and 1-PyB

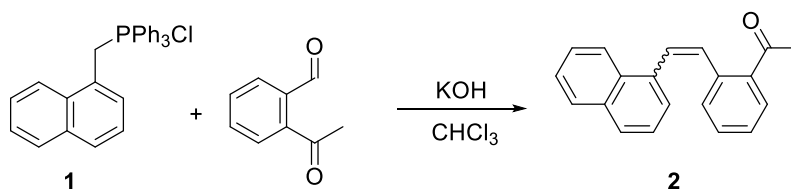
1.1. Preparation of 1-ChB

1.1.1 Preparation of compound 1



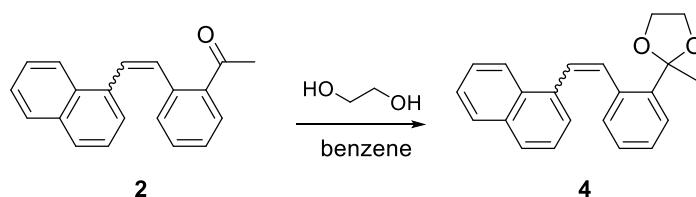
To 200 ml toluene, 1-chloromethylnaphthalene (3.5 g, 20 mmol) and triphenylphosphine (6.3 g, 24 mmol) were added, and the solution was refluxed for 24 h. The precipitate was filtered, washed with benzene and dried in vacuo. Compound **1** (1.9 g, 22 %) was obtained.¹

1.1.2 Preparation of compound 2



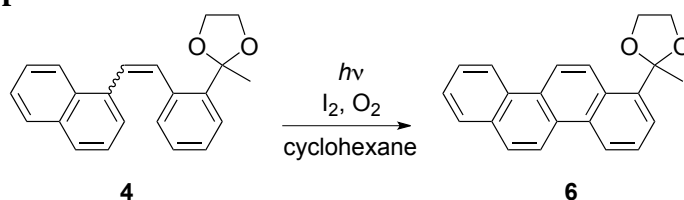
To 60 ml chloroform solution of compound **1** (3.1 g, 7.0 mmol) and 2-acetylbenzaldehyde (1.0 g, 6.8 mmol), 30 ml of aqueous KOH (50 %) was dropwise added. After the solution was stirred for 2 h at room temperature, 100 ml chloroform was added. The organic layer was separated, washed with brine, and evaporated under reduced pressure. The product **2** was obtained after silica gel chromatography using hexane/ethyl acetate (9:1, v/v) as a mixture of *E*- and *Z*-isomers (1.8 g, 99 %). The mixture was used in the following photoreaction without further separation and purification.

1.1.3 Synthesis of compound 4



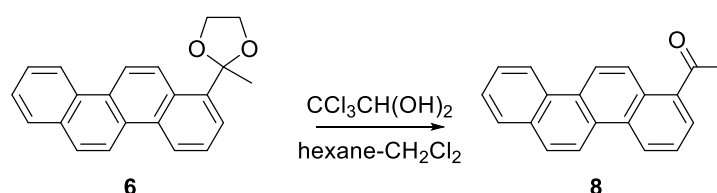
To 200 ml of benzene, compound **2** (1.8 g, 6.7 mmol), 30 ml ethylene glycol and *p*-toluenesulfonic acid (0.92 g, 4.8 mmol) were added, the solution was refluxed for 48 h. After cooling to room temperature, the solution was washed with water and brine. The product was separated by silica-gel chromatography using hexane / ethyl acetate (9:1, v/v) providing compound **4** (2.0 g, 98 %).

1.1.4 Synthesis of compound 6.



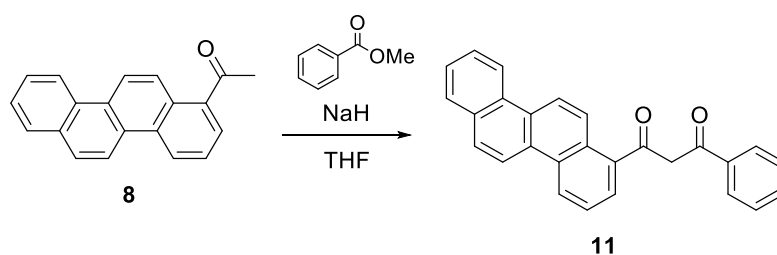
A cyclohexane solution (1000 ml) of compound **4** (1.2 g, 3.8 mmol) and 50 mg of I₂ was photolyzed using with a home-made microflow photoreactor.² The photolyzed solution was washed with aqueous Na₂S₂O₃ and brine. After usual work-up, compound **6** was obtained (1.2 g, 99 %). ¹H NMR (CDCl₃, 400 MHz) δ_H = 8.83-8.69 (m, 5H), 8.00-7.98 (m, 2H), 7.93 (dd, 1H, *J* = 0.9, 7.3), 7.73-7.61 (m, 3H), 4.16-4.13 (m, 2H), 3.88-3.84 (m, 2H), 1.97 (s, 3H). Since the acetal **6** was hydrolyzed during separation by silica-gel chromatography, it was used the following deprotection without purification.

1.1.5 Synthesis of compound **8**



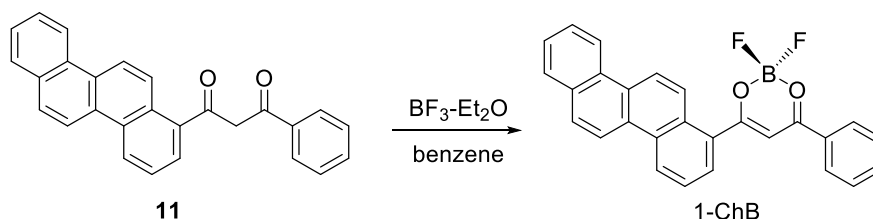
Compound **6** (300 mg, 1.0 mmol) and chloral hydrate (1.0 g, 6.6 mmol) were added in a mixture of 5 ml hexane and 3.4 ml CH₂Cl₂. The solution was stirred at room temperature under N₂ atmosphere for 5 h. After adding CH₂Cl₂ (100 ml), the solution was washed with water and brine. After evaporating the solvent, the residue was chromatographed on silica-gel using hexane/ethyl acetate (3:1, v/v) to give compound **8** (200 mg, 74 %). mp 207–208 °C. ¹H NMR (600 MHz, CDCl₃) δ_H = 8.98 (d, 1H, *J* = 8.4 Hz), 8.82 (m, 2H), 8.80 (d, 1H, *J* = 8.4 Hz), 8.70 (d, 1H, *J* = 9.2 Hz), 8.04–8.00 (m, 3H), 7.78–7.70 (m, 2H), 7.67 (ddd, 1H, *J* = 7.7, 6.9, 1.4 Hz), 2.82 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ_C = 202.6, 136.7, 132.4, 131.4, 130.4, 129.3, 128.6, 128.3, 128.13, 128.07, 127.9, 127.5, 127.1, 126.9, 125.3, 124.5, 123.42, 123.40, 121.2, 30.6; HRMS (FAB-TOF) *m/z* calcd. for C₂₀H₁₄O 270.1045 [M⁺], found 270.1046.

1.1.6 Synthesis of compound **11**



To 15 ml of dry THF, **8** (260 mg, 1.0 mmol) and NaH (60 % in oil, 1.0 g, 25 mmol) were added, and the mixture was stirred for 30 min at 0 °C. Methyl benzoate (0.25 ml, 2.0 mmol) was added to the solution, which was refluxed for 2 h. After cooling to room temperature, aqueous NH₄Cl (20 %, 30 ml) was added. The product was extracted with ethyl acetate, and the solution was washed with aqueous NH₄Cl and brine. The product was purified by silica-gel chromatography using hexane / ethyl acetate (9:1, v/v) to give **11** (130 mg, 36 %). mp 247–248 °C. ¹H NMR (600 MHz, CDCl₃) δ_H = 16.83 (s, 1H), 8.98 (d, 1H, *J* = 8.4 Hz), 8.85–8.79 (2H, two doublets overlapped), 8.74 (d, 1H, *J* = 9.2 Hz), 8.67 (d, 1H, *J* = 9.3 Hz), 8.05 (d, 1H, *J* = 9.2 Hz), 8.03–8.00 (m, 3H), 7.94 (dd, 1H, *J* = 7.2, 1.0 Hz), 7.77 (dd, 1H, *J* = 8.4, 7.2 Hz), 7.74 (ddd, 1H, *J* = 8.0, 7.0, 1.2 Hz), 7.67 (ddd, 1H, *J* = 8.0, 7.0, 1.0 Hz), 7.58 (m, 1H), 7.50 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ_C = 190.8, 184.5, 135.8, 135.0, 132.6, 132.2, 131.1, 130.3, 129.1, 128.7, 128.5, 128.2, 128.1, 127.8, 127.2, 127.0, 126.9, 126.7, 126.4, 125.7, 124.3, 123.2, 122.6, 121.1, 98.6; HRMS (FAB-TOF) *m/z* calcd. for C₂₇H₁₈O₂ 374.1307 [M⁺], found 374.1336.

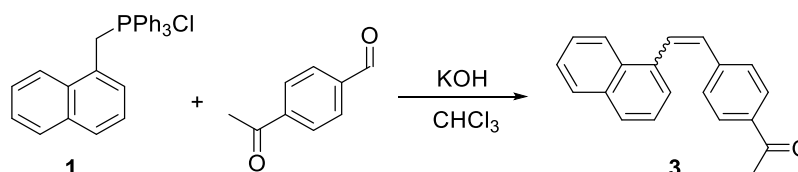
1.1.7 Synthesis of 1-ChB



Compound **11** (70 mg, 0.19 mmol) and a Et₂O solution of boron trifluoride diethyl etherate (46 %, 0.1 ml, 0.37 mmol) were added to 5 ml of benzene, and the solution was refluxed for 1 h. The product was purified by silica-gel chromatography using hexane / ethyl acetate (3:1, v/v) to give 1-ChB (66 mg, 83 %). mp 267–268 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ_{H} = 9.41 (d, 2H, *J* = 8.4 Hz), 9.15 (d, 2H, *J* = 9.5 Hz), 9.03–8.98 (2H, two doublets overlapped), 8.65 (d, 1H, *J* = 9.5 Hz), 8.43 (m, 2H), 8.21 (d, 1H, *J* = 9.1 Hz), 8.15 (dd, 1H, *J* = 7.8, 1.0 Hz), 7.97 (dd, 1H, *J* = 8.4, 7.3 Hz), 7.89 (s, 1H), 7.88 (ddd, 1H, *J* = 8.2, 7.0, 1.0 Hz), 7.77 (ddd, 1H, *J* = 7.8, 7.0, 1.0 Hz), 7.71 (m, 2H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ_{C} = 187.1, 183.0, 136.2, 132.0, 131.2, 131.0, 130.8, 130.6, 130.0, 129.7, 129.6, 129.5, 129.0, 128.5, 128.4, 127.9, 127.8, 127.4, 127.3, 126.2, 124.3, 123.7, 123.3, 121.5, 99.4; HRMS (FAB-TOF) *m/z* calcd. for C₂₇H₁₇BF₂O₂ 422.1290 [M⁺], found 422.1303.

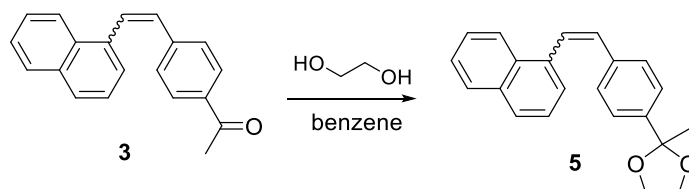
1.2 Synthesis of 3-ChB

1.2.1 Preparation of compound 3



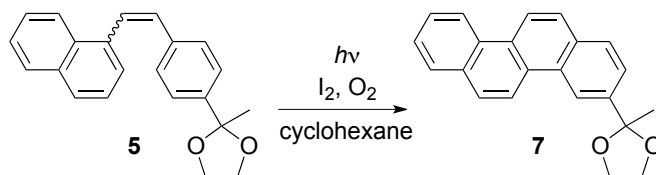
To 60 ml chloroform solution of compound **1** (3.1 g, 7.0 mmol) and 4-acetylbenzaldehyde (1.0 g, 6.8 mmol), 30 ml of aqueous KOH (50 %) was dropwise added. After the solution was stirred for 2 h at room temperature, 100 ml chloroform was added. The organic layer was separated, washed with brine, and evaporated under reduced pressure. The product **3** was obtained after silica gel chromatography using hexane/ethyl acetate (9:1, v/v) as a mixture of *E*- and *Z*-isomers (1.8 g, 99 %). The mixture was used in the following photoreaction without further separation and purification.

1.2.2 Synthesis of compound 5.



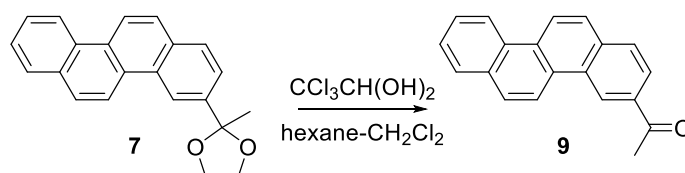
To 200 ml of benzene, compound **3** (1.8 g, 6.7 mmol), 30 ml ethylene glycol and *p*-toluenesulfonic acid (0.92 g, 4.8 mmol) were added, the solution was refluxed for 48 h. After cooling to room temperature, the solution was washed with water and brine. The product **5** was separated by silica-gel chromatography using hexane/ethyl acetate (9:1, v/v) providing compound (2.0 g, 98 %).

1.2.3 Synthesis of compound 7.



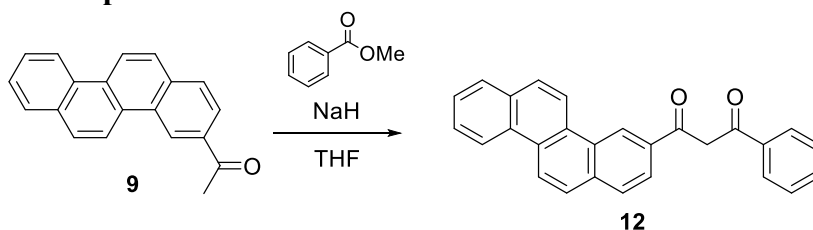
A cyclohexane solution (1000 ml) of compound **5** (1.2 g, 3.8 mmol) and 50 mg I_2 was photolyzed using with a home-made microflow photoreactor.² The photolyzed solution was washed with aqueous $Na_2S_2O_3$ and brine. After usual work-up, compound **7** was obtained (1.2 g, 99 %). 1H NMR ($CDCl_3$, 400 MHz) δ_H = 9.43 (s, 1H), 8.85-8.79 (m, 3H), 8.17 (dd, 1H, J = 1.6, 8.5), 8.09-7.99 (m, 4H), 7.67-7.61 (m, 2H), 4.15-4.12 (m, 2H), 3.90-3.86 (m, 2H), 1.83 (s, 3H). Since the acetal **7** was hydrolyzed during separation by silica-gel chromatography, it was used the following deprotection without purification.

1.2.4 Synthesis of compound 9



Compound **7** (610 mg, 1.9 mmol) and chloral hydrate (2.1 g, 13 mmol) were added to a mixture of 8 ml of hexane and 8 ml of CH_2Cl_2 . The solution was stirred at room temperature under N_2 atmosphere for 5 h. After adding CH_2Cl_2 (100 ml), the solution was washed with water and brine. After evaporating the solvent, the residue was chromatographed on silica-gel using hexane / ethyl acetate (3:1, v/v) to give **9** (387 mg, 79 %). mp 155–159 °C. 1H NMR (600 MHz, $CDCl_3$) δ_H = 9.41 (bs, 1H), 8.82 (d, 1H, J = 9.1), 8.80–8.76 (2H, two doublets overlapped), 8.17 (dd, 1H, J = 8.7, 1.7 Hz), 8.07 (d, 1H, J = 9.1 Hz), 8.05–8.00 (m, 3H), 7.74 (ddd, 1H, J = 8.3, 7.7, 1.4 Hz), 7.67 (ddd, 1H, J = 7.7, 7.0, 1.0 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ_C = 198.4, 135.0, 134.9, 132.4, 130.5, 130.0, 129.08, 129.05, 128.8, 128.7, 128.3, 127.1, 126.91, 129.85, 125.1, 124.8, 124.1, 123.2, 121.0, 27.1; HRMS (FAB-TOF) m/z calcd. for $C_{20}H_{14}O$ 270.1045 [M^+], found 270.1073.

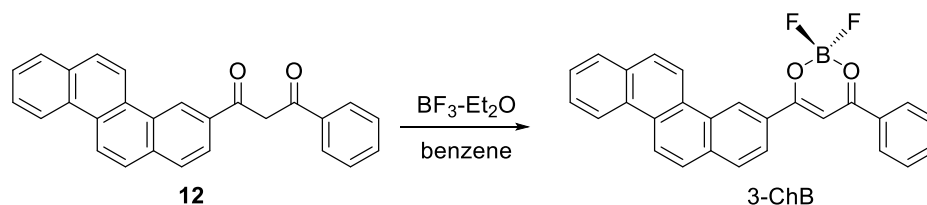
1.2.5 Preparation of compound 12



To 20 ml of dry THF, compound **9** (400 mg, 1.5 mmol) and NaH (60 % in oil, 1.5 g, 38 mmol) were added, and the mixture was stirred for 10 min at room temperature. Methyl benzoate (0.25 ml, 2.0 mmol) was added to the solution, which was refluxed for 3 h. After cooling to room temperature, aqueous NH_4Cl (20 %, 30 ml) was added. The product was extracted with ethyl acetate, and the solution was washed with aqueous NH_4Cl and brine. The product was purified by silica-gel chromatography using hexane/ethyl acetate (9:1, v/v) to give compound **12** (230 mg, 41 %). mp 217–220 °C. 1H NMR (600 MHz, $CDCl_3$) δ_H = 17.10 (s, 1H), 9.47 (s, 1H), 8.85–8.80 (2H, two

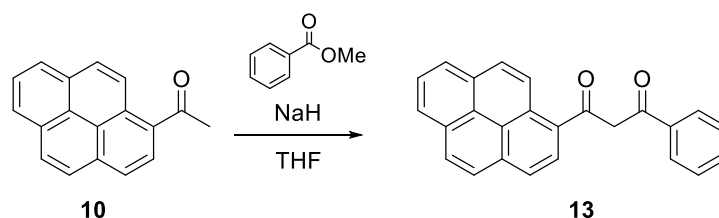
doublets overlapped), 8.78 (d, 1H, $J = 8.2$ Hz), 8.15 (d, 1H, $J = 8.1$ Hz), 8.10–8.00 (m, 6H), 7.74 (ddd, 1H, $J = 8.2, 7.5, 1.0$), 7.67 (t, 1H, $J = 7.5$ Hz), 7.60 (m, 1H), 7.54 (m, 2H), 7.09; ^{13}C NMR (150 MHz, CDCl_3) $\delta_{\text{C}} = 186.1, 185.8, 135.8, 134.6, 133.4, 132.7, 132.5, 130.6, 130.3, 129.1, 129.0, 128.9, 128.83, 128.80, 1288.2, 127.4, 127.1, 126.9, 126.9, 124.1, 123.8, 123.4, 123.3, 121.2, 93.8$; HRMS (FAB-TOF) m/z calcd. for $\text{C}_{27}\text{H}_{18}\text{O}_2$ 374.1307 [M^+], found 374.1287.

1.2.6 Synthesis of 3-ChB



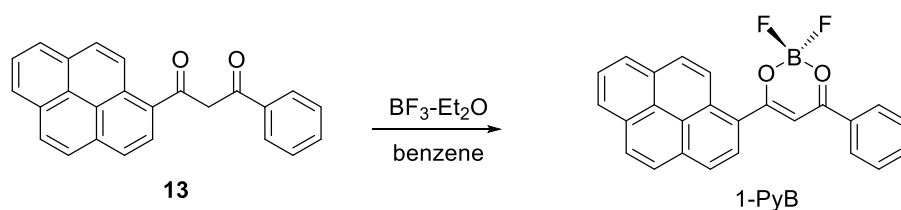
Compound **12** (130 mg, 0.35 mmol) and a Et_2O solution of boron trifluoride diethyl etherate (46 %, 0.3 ml, 1.1 mmol) were added to 5 ml of benzene, and the solution was refluxed for 1 h. The product was purified by silica-gel chromatography using hexane/ethyl acetate (3:1, v/v) to give 3-ChB (70 mg, 47 %). mp 252–253 °C. ^1H NMR (600 MHz, $\text{DMSO}-d_6$) $\delta_{\text{H}} = 9.90$ (s, 1H), 9.24 (d, 1H, $J = 8.8$ Hz), 9.17 (d, 1H, $J = 8.8$ Hz), 9.01 (d, 1H, $J = 8.4$ Hz), 8.51 (3H, two doublets overlapped), 8.36 (d, 1H, $J = 8.4$ Hz), 8.33 (s, 1H), 8.31–8.25 (2H, two doublets overlapped), 8.18 (d, 1H, $J = 7.1$ Hz), 7.88 (t, 1H, $J = 7.1$ Hz), 7.81 (t, 1H, $J = 7.1$ Hz), 7.78–7.73 (m, 3H); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) $\delta_{\text{C}} = 182.6, 182.4, 135.9, 132.1, 131.5, 129.8, 129.6, 129.51, 129.46, 129.43, 128.61, 128.57, 128.54, 128.4, 127.4, 127.3, 127.0, 126.8, 126.0, 125.0, 123.6, 121.7, 95.1$; HRMS (FAB-TOF) m/z calcd. for $\text{C}_{27}\text{H}_{17}\text{BF}_2\text{O}_2$ 422.1290 [M^+], found 422.1322.

1.3.1 Synthesis of 1-PyDK



To 15 ml of dry THF, 1-acetylpyrene **10** (735 mg, 3 mmol) and NaH 700 mg (60 % in oil, 1.0 g, 25 mmol) were added, and the mixture was stirred for 15 min at room temperature. Methyl benzoate 0.40 ml (3.3 mmol) was added to the mixture, which was then refluxed for 24 h. After cooling to room temperature, aqueous NH_4Cl (20 %, 30 ml) was added. The product was extracted with ethyl acetate, and the solution was washed with aqueous NH_4Cl and brine. After removal of the solvent, the product was purified by silica-gel chromatography using hexane/ethyl acetate (9:1, v/v) to give compound **13** (990 mg, 95 %). mp 230–234 °C. ^1H NMR (600 MHz, CDCl_3) $\delta_{\text{H}} = 17.01$ (s, 1H), 8.85 (d, 1H, $J = 9.4$), 8.31 (d, $J = 8.1$), 8.31–8.22 (2H, two doublets overlapped), 8.23 (d, 1H, $J = 8.1$ Hz), 8.19 (d, 1H, $J = 8.9$ Hz), 8.11 (d, 1H, $J = 8.9$ Hz), 8.07 (t, 1H, $J = 7.5$ Hz), 8.05–8.01 (m, 3H), 7.58 (m, 2H), 7.51 (m, 2H), 6.89 (s, 1H); ^{13}C NMR (150 MHz, CDCl_3) $\delta_{\text{C}} = 190.8, 184.2, 135.2, 133.4, 132.5, 131.6, 131.2, 130.6, 129.2, 129.1, 129.0, 128.7, 127.2$ (two signals overlapped), 126.4, 126.15, 126.13, 126.0, 124.9, 124.7, 124.5, 124.4, 98.8; HRMS (FAB-TOF) m/z calcd. for $\text{C}_{25}\text{H}_{16}\text{O}_2$ 348.1150 [M^+], found 348.1174.

1.3.2 Synthesis of 1-PyB



Compound **13** (420 mg, 1.0 mmol) and boron trifluoride diethyl etherate (46 %, 0.55 ml, 2.0 mmol) were added to 10 ml benzene, and the solution was refluxed for 1 h. The precipitated product was filtrated and washed with benzene to give 1-PyB (50 mg, 13 %). mp 131–133 °C. ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ_{H} = 8.92 (d, 1H, J = 9.4 Hz), 8.80 (d, 1H, J = 8.1 Hz), 8.53–8.48 (m, 4H), 8.47 (d, 1H, J = 8.9 Hz), 8.43 (d, 2H, J = 7.6 Hz), 8.35 (d, 1H, J = 8.9 Hz), 8.23 (t, 1H, J = 7.5 Hz), 7.98 (s, 1H), 7.86 (t, 1H, J = 7.5 Hz), 7.70 (t, 2H, J = 7.5 Hz); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ_{C} = 186.6, 181.9, 135.9, 135.3, 131.4, 131.1, 130.6, 130.1, 129.9, 129.51, 129.46, 129.29, 127.7, 127.31, 127.28, 127.25, 126.0, 124.9, 124.0, 123.8, 123.2, 99.3; HRMS (FAB-TOF) m/z calcd. for $\text{C}_{25}\text{H}_{15}\text{BF}_2\text{O}_2$ 396.1133 [M^+], found 396.1139.

2. Absorption and fluorescence spectra in MeCN

Figure S1 shows absorption and fluorescence spectra of the used compounds in acetonitrile (MeCN).

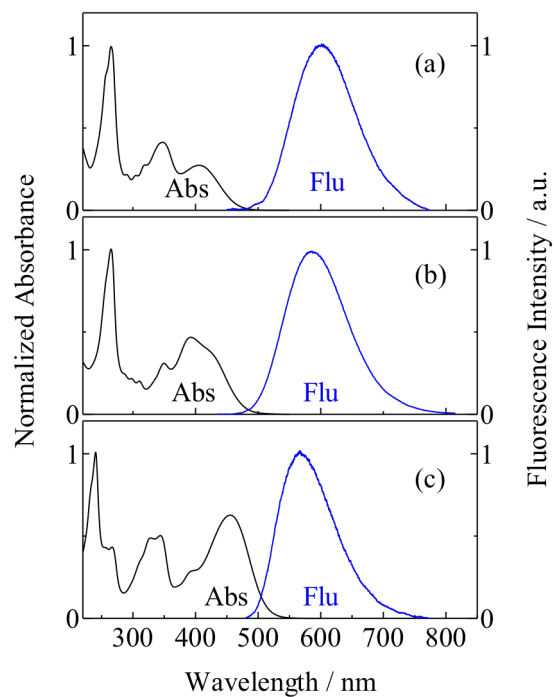


Figure S1. Absorption (black) and fluorescence (blue) spectra in MeCN for 1-ChB (a), 3-ChB (b) and 1-PyB (c). The fluorescence spectra are not corrected.

3. Absorption and fluorescence spectra in DMSO

Figure S2 shows absorption and fluorescence spectra of 1-PyB in DMSO. The shapes and maximum wavelengths of the fluorescence were similar to each other. A 1 mm path length cuvette was used on the spectroscopic measurements for a highly concentrated DMSO solution of 1-PyB.

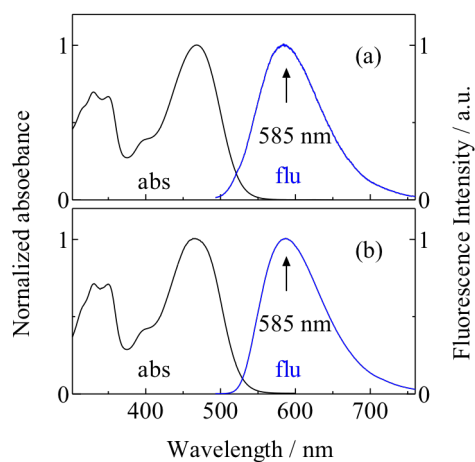


Figure S2. Absorption (black) and fluorescence (blue) spectra in DMSO solution of 1-PyB at concentrations of $3.0 \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (a) and $1.0 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (b). The fluorescence spectra are not corrected.

4. Decay profiles of fluorescence

Figure S3 shows decay profiles of fluorescence of 1-ChB, 3-ChB and 1-PyB in CHCl_3 and MeCN. The decay profiles except for 1-PyB in MeCN were analyzed by fitting a single-exponential function whereas that for 1-PyB in MeCN was analyzed with a double-exponential function (Figure S3f).

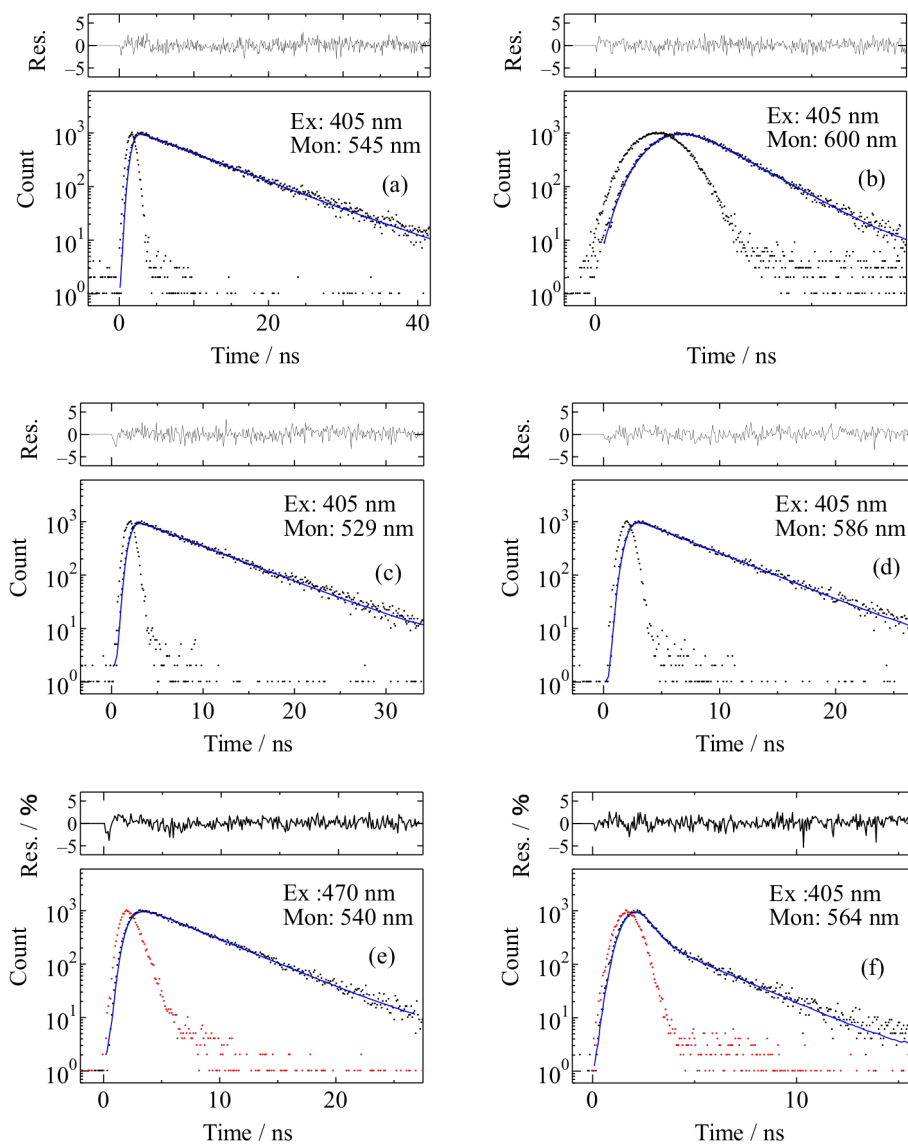


Figure S3. Decay profiles of fluorescence for 1-ChB in CHCl_3 (a) and MeCN (b), 3-ChB in CHCl_3 (c) and MeCN (d), and 1-PyB in CHCl_3 (e) and MeCN (f) at 295 K. Ex. and Mon. in the figures indicate the excitation and monitoring wavelengths, respectively.

5. Lippert-Mataga analysis data

Spectroscopic data of absorption and fluorescence for the BF₂DKs in various solvents and the solvent properties are listed in Tables S1-3 for performing the Lippert-Mataga analysis.

Table S1. Spectroscopic data and solvent properties on performing Lippert-Mataga plot for 1-ChB.

Solvent	F (ϵ_r , n)	λ_{abs}^0 ^a / nm	λ_{em}^0 ^b / nm	$\Delta\bar{\nu}$ ^c /cm ⁻¹
Benzene	0.006	415	519	4830
CCl ₄	0.022	409	486	3870
Toluene	0.268	415	521	4900
Chloroform	0.296	416	544	5660
Diethyl ether	0.329	403	517	5470
THF	0.419	408	544	6130
Dichloromethane	0.444	414	567	6520
Ethanol	0.578	408	577	7180
Acetonitrile	0.609	406	602	8020

a) The maximum wavelength of the first absorption band. b) The maximum wavelength of the first fluorescence band. c) The energy difference between the energies estimated from λ_{abs}^0 and λ_{em}^0 in cm⁻¹ unit.

Table S2. Spectroscopic data and solvent properties on performing Lippert-Mataga plot for 3-ChB.

Solvent	F (ϵ_r , n)	λ_{abs}^0 ^a / nm	λ_{em}^0 ^b / nm	$\Delta\bar{\nu}$ ^c /cm ⁻¹
Benzene	0.006	431	500	3200
CCl ₄	0.022	433	460	1360
Toluene	0.268	431	498	3120
Chloroform	0.296	430	529	4350
Diethyl ether	0.329	421	500	3750
THF	0.419	428	528	4430
Dichloromethane	0.444	431	557	5250
Ethanol	0.578	431	559	5310
Acetonitrile	0.609	426	586	6410

a) The maximum wavelength of the first absorption band. b) The maximum wavelength of the first fluorescence band. c) The energy difference between the energies estimated from λ_{abs}^0 and λ_{em}^0 in cm⁻¹ unit.

Table S3. Spectroscopic data and solvent properties on performing Lippert-Mataga plot for 1-PyB.

Solvent	F (ϵ_r , n)	λ_{abs}^0 ^a / nm	λ_{em}^0 ^b / nm	$\Delta\bar{\nu}$ ^c /cm ⁻¹
Benzene	0.006	463	522	2440
CCl ₄	0.022	461	496	1530
Toluene	0.268	462	520	2410
Chloroform	0.296	465	542	3060
Diethyl ether	0.329	450	515	2800
THF	0.419	455	537	3360
Dichloromethane	0.444	464	558	3630
Ethanol	0.578	456	550	3750
Acetonitrile	0.609	455	567	4340

a) The maximum wavelength of the first absorption band. b) The maximum wavelength of the first fluorescence band. c) The energy difference between the energies estimated from λ_{abs}^0 and λ_{em}^0 in cm⁻¹ unit.

6. Transient absorption spectra in MeCN

Figure S4 shows transient absorption spectra obtained upon 266 nm laser pulsing in the MeCN solution of the BF₂DKs.

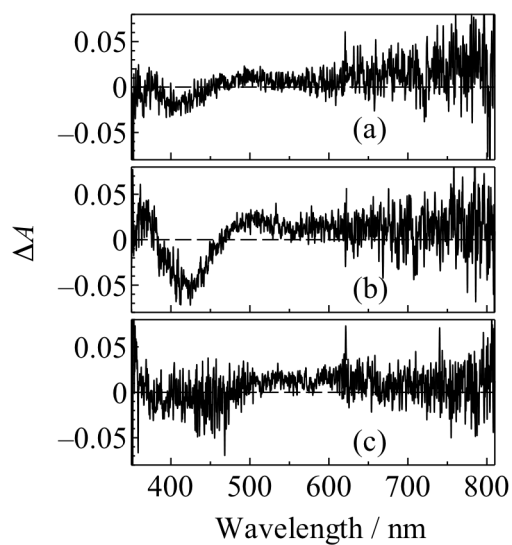


Figure S4 Transient absorption spectra obtained at 200 ns upon 266 nm laser pulsing in the Ar-purged MeCN solution of 1-ChB (a), 3-ChB (b) and 1-PyB (c) at 295 K.

7. Results of DFT and TD-DFT calculations (absorption spectra, atom coordinates and sum of electronic and zero-point energies)

The calculation was carried out at the DFT level, using the Gaussian 09 software package.³ The geometries of the difluoroboronated β -diketones were fully optimized by using the 6-31G(d) base set at the B3LYP method considering dielectric constants of CHCl_3 and MeCN on the CPCM model. Figure S5 compares experimental absorption spectra in CHCl_3 with the calculated ones considering the dielectric constant of CHCl_3 on the CPCM model. Atom coordinates for the optimized geometries of the difluoroboronated β -diketones in CHCl_3 and MeCN are listed in Tables S4-9.

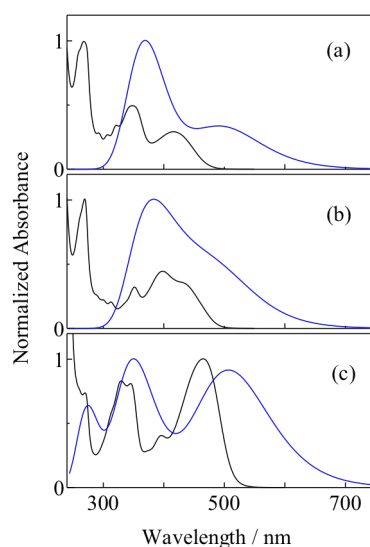


Figure S5. Absorption spectra of 1-ChB (a), 3-ChB (b) and 1-PyB (c) in CHCl_3 (black) and calculated ones by considering the CHCl_3 dielectric constant (blue).

Table S4. Atom coordinates for the optimized geometry of 1-ChB in CHCl₃.

	X	Y	Z
C	5.00313	-0.62715	-0.40465
C	6.06819	0.31603	-0.27654
C	5.75932	1.66956	0.06118
C	4.47047	2.07804	0.25964
C	3.36758	1.16977	0.14062
C	3.6347	-0.18205	-0.19165
C	1.99436	1.60762	0.34883
C	0.92133	0.66245	0.2566
C	1.23856	-0.68475	-0.10014
C	2.53002	-1.07888	-0.31703
C	1.67948	2.96186	0.63058
C	0.37423	3.38423	0.79944
C	-0.68074	2.46418	0.70818
C	-0.42814	1.1169	0.46025
C	-1.58801	0.20479	0.45412
C	-2.81663	0.56738	-0.10373
C	-3.92473	-0.27449	0.04474
C	-5.28094	0.05927	-0.41464
C	-5.61368	1.35649	-0.854
C	-6.90729	1.64208	-1.28521
C	-7.88558	0.64099	-1.28602
C	-7.56596	-0.64967	-0.84927
C	-6.27491	-0.94007	-0.41393
O	-1.43326	-0.95618	1.04024
O	-3.79622	-1.43841	0.6321
B	-2.47347	-2.02124	0.97978
F	-2.56461	-2.6236	2.22728
F	-2.11271	-2.94621	-0.00397
H	6.57551	2.38096	0.16184
H	4.29689	3.11539	0.51799
H	0.4454	-1.41256	-0.20728
H	2.70405	-2.11199	-0.59392
H	2.46806	3.69991	0.71133
H	0.16305	4.4275	1.01372
H	-1.69821	2.80228	0.87565
H	-2.9028	1.50327	-0.63378
H	-4.87548	2.15089	-0.84735
H	-7.15348	2.64658	-1.61671
H	-8.89314	0.86679	-1.62421
H	-8.32254	-1.42901	-0.8499
H	-6.02455	-1.94025	-0.07856
C	7.40917	-0.09832	-0.48218
C	5.34157	-1.96579	-0.73654
C	7.70453	-1.40829	-0.80656
H	8.73468	-1.71683	-0.96276
C	6.65758	-2.34743	-0.93318
H	6.88468	-3.37958	-1.18644
H	4.56741	-2.71749	-0.84122
H	8.20392	0.63701	-0.37948

Sum of electronic and zero-point energies = -1414.310434 Hartree

Table S5. Atom coordinates for the optimized geometry of 1-ChB in MeCN.

	X	Y	Z
C	4.98434	-0.63406	-0.40591
C	6.05181	0.31033	-0.32219
C	5.74969	1.6705	-0.01001
C	4.46607	2.08271	0.20783
C	3.3611	1.17344	0.13422
C	3.62104	-0.18456	-0.17487
C	1.99337	1.61468	0.36399
C	0.91835	0.66913	0.30361
C	1.22673	-0.68644	-0.02784
C	2.51411	-1.0832	-0.25719
C	1.68332	2.97014	0.64094
C	0.38275	3.39429	0.83487
C	-0.67389	2.47392	0.76581
C	-0.42607	1.12717	0.52013
C	-1.58693	0.20948	0.51314
C	-2.8023	0.56396	-0.08628
C	-3.91353	-0.27635	0.05987
C	-5.26727	0.05866	-0.42513
C	-5.59665	1.34711	-0.88572
C	-6.88367	1.62584	-1.34067
C	-7.85965	0.62364	-1.34284
C	-7.54322	-0.65872	-0.88377
C	-6.25792	-0.94104	-0.42571
O	-1.44559	-0.92852	1.1234
O	-3.8022	-1.42303	0.66231
B	-2.46444	-2.03633	0.99224
F	-2.5624	-2.69365	2.18685
F	-2.08018	-2.84127	-0.06712
H	6.56813	2.38392	0.05529
H	4.29681	3.12618	0.44544
H	0.43216	-1.41767	-0.09494
H	2.68411	-2.12358	-0.50831
H	2.47525	3.70696	0.70176
H	0.17726	4.43895	1.0508
H	-1.69009	2.80937	0.95007
H	-2.87151	1.48733	-0.64113
H	-4.85751	2.14151	-0.87737
H	-7.12697	2.62565	-1.68955
H	-8.86278	0.84302	-1.69905
H	-8.29825	-1.44002	-0.88394
H	-6.00414	-1.93332	-0.06969
C	7.38694	-0.10995	-0.54558
C	5.31672	-1.97927	-0.7125
C	7.67595	-1.42643	-0.84396
H	8.70292	-1.73913	-1.01318
C	6.62717	-2.36681	-0.92657
H	6.84865	-3.40526	-1.15868
H	4.53964	-2.73202	-0.78167
H	8.18393	0.62729	-0.47647

Sum of electronic and zero-point energies = -1414.31541927 Hartree

Table S6. Atom coordinates for the optimized geometry of 3-ChB in CHCl₃.

	X	Y	Z
C	5.65270	0.18931	0.04086
C	5.69000	-1.23907	0.06872
C	4.46134	-1.96768	0.05636
C	3.25440	-1.32713	0.01929
C	3.16648	0.10133	-0.00859
C	4.36397	0.86286	0.00179
C	1.88112	0.78433	-0.04796
C	1.84349	2.21340	-0.07450
C	3.06803	2.94135	-0.06349
C	4.27172	2.29171	-0.02662
C	0.65004	0.09355	-0.06008
C	-0.57469	0.76209	-0.09097
C	-0.59290	2.18401	-0.12022
C	0.59161	2.88242	-0.11367
C	-1.81349	-0.02548	-0.08897
C	-3.08581	0.52377	0.10396
C	-4.21969	-0.28387	-0.02346
C	-5.60072	0.21958	0.04057
C	-6.66407	-0.7001	0.13887
C	-7.98101	-0.25064	0.20649
C	-8.25707	1.12089	0.17144
C	-7.20870	2.04247	0.06740
C	-5.88955	1.59859	0.00295
O	-1.67240	-1.31316	-0.29782
O	-4.09832	-1.57317	-0.22772
B	-2.79146	-2.27291	-0.11650
F	-2.71677	-3.23886	-1.11240
F	-2.69406	-2.85117	1.15375
H	4.49930	-3.05416	0.07684
H	2.35175	-1.92650	0.01095
H	3.03383	4.02751	-0.08391
H	5.17630	2.88818	-0.01859
H	0.62852	-0.98746	-0.03666
H	-1.52923	2.72829	-0.16817
H	0.58144	3.96875	-0.14357
H	-3.19375	1.57412	0.32136
H	-6.44814	-1.76212	0.16956
H	-8.79187	-0.96874	0.28825
H	-9.28448	1.47066	0.22267
H	-7.41935	3.10732	0.03177
H	-5.09413	2.32942	-0.09471
C	6.89214	0.88266	0.05329
C	6.93717	-1.91408	0.10759
C	8.12493	-1.20913	0.11897
H	9.07561	-1.73449	0.14903
C	8.09695	0.20249	0.09132
H	9.02848	0.76211	0.10008
H	6.91500	1.96627	0.03310
H	6.94083	-3.00139	0.12832

Sum of electronic and zero-point energies = 1414.31773972 Hartree

Table S7. Atom coordinates for the optimized geometry of 3-ChB in MeCN.

	X	Y	Z
C	5.65150	0.18618	0.03113
C	5.68560	-1.24176	0.03316
C	4.45553	-1.96620	0.01105
C	3.25040	-1.32369	-0.01124
C	3.16555	0.10474	-0.01361
C	4.36480	0.86262	0.00689
C	1.88188	0.78963	-0.03726
C	1.84587	2.21806	-0.03944
C	3.07188	2.94283	-0.01970
C	4.27386	2.29110	0.00292
C	0.64945	0.10050	-0.05681
C	-0.57369	0.76809	-0.07373
C	-0.58992	2.18865	-0.07974
C	0.59460	2.88716	-0.06404
C	-1.81259	-0.02911	-0.07969
C	-3.08820	0.51844	0.11494
C	-4.21687	-0.29505	-0.03819
C	-5.60337	0.21251	0.00972
C	-6.66040	-0.70710	0.14067
C	-7.97918	-0.26071	0.19966
C	-8.26251	1.10636	0.12164
C	-7.21927	2.02780	-0.01787
C	-5.89898	1.58576	-0.07270
O	-1.66539	-1.30322	-0.29990
O	-4.09667	-1.57199	-0.25130
B	-2.78190	-2.29079	-0.07228
F	-2.69000	-3.28378	-1.01020
F	-2.70695	-2.73996	1.23356
H	4.49094	-3.05313	0.01231
H	2.34571	-1.91990	-0.02786
H	3.03944	4.02973	-0.02224
H	5.18043	2.88494	0.01811
H	0.62076	-0.98072	-0.05321
H	-1.52782	2.73235	-0.11559
H	0.58555	3.97446	-0.07539
H	-3.20196	1.56515	0.34876
H	-6.43208	-1.76547	0.20121
H	-8.78648	-0.97986	0.30753
H	-9.29162	1.45324	0.16564
H	-7.43525	3.09025	-0.08988
H	-5.10402	2.31316	-0.20223
C	6.89262	0.87443	0.05336
C	6.93073	-1.91915	0.05679
C	8.11995	-1.21885	0.07809
H	9.06918	-1.74758	0.09617
C	8.09546	0.19204	0.07628
H	9.02850	0.74929	0.09303
H	6.91742	1.95844	0.05287
H	6.93148	-3.00686	0.05785

Sum of electronic and zero-point energies = -1414.32360393 Hartree

Table S8. Atom coordinates for the optimized geometry of 1-PyB in CHCl₃.

	X	Y	Z
C	-5.37434	1.88296	-0.86440
C	-6.55107	1.13843	-0.78925
C	-6.51072	-0.20702	-0.42190
C	-5.28971	-0.83514	-0.12092
C	-4.07859	-0.07824	-0.18924
C	-4.13121	1.29556	-0.56933
C	-2.82346	-0.69205	0.11733
C	-1.61088	0.07363	0.06570
C	-1.70078	1.45140	-0.34327
C	-2.90064	2.02635	-0.64426
C	-2.79475	-2.07652	0.47481
C	-1.55859	-2.68378	0.75594
C	-0.38342	-1.95241	0.69266
C	-0.38003	-0.58228	0.36794
C	0.91810	0.11685	0.37198
C	2.09903	-0.50541	-0.06184
C	3.32311	0.15506	0.08910
C	4.63001	-0.45435	-0.23030
C	4.77150	-1.83413	-0.46810
C	6.01981	-2.37328	-0.77204
C	7.14397	-1.54378	-0.84408
C	7.01427	-0.17210	-0.60558
C	5.76819	0.37046	-0.29772
O	0.93831	1.33436	0.82895
O	3.37099	1.37424	0.54216
B	2.13986	2.23319	0.66020
F	2.25711	3.02802	1.76735
F	1.98029	2.93620	-0.52345
H	-5.40847	2.93070	-1.15364
H	-7.50394	1.60784	-1.01871
H	-7.43067	-0.78441	-0.36533
H	-0.79899	2.04479	-0.40659
H	-2.93422	3.06940	-0.95026
H	-1.53124	-3.73346	1.03757
H	0.55412	-2.43704	0.94712
H	2.05332	-1.48927	-0.50358
H	3.91386	-2.49555	-0.39942
H	6.11714	-3.44109	-0.94801
H	8.11659	-1.96620	-1.08265
H	7.88468	0.47592	-0.66065
H	5.65905	1.43334	-0.11265
C	-5.21971	-2.21943	0.25420
C	-4.02560	-2.81316	0.53733
H	-6.14397	-2.79042	0.30603
H	-3.98451	-3.86312	0.81732

Sum of electronic and zero-point energies = -1336.90128577 Hartree

Table S9. Atom coordinates for the optimized geometry of 1-PyB in MeCN.

	X	Y	Z
C	5.40437	-1.87834	-0.82006
C	6.57706	-1.12902	-0.72344
C	6.52450	0.21870	-0.36280
C	5.29498	0.84443	-0.08989
C	4.08770	0.08271	-0.17867
C	4.15340	-1.29250	-0.55228
C	2.82461	0.69403	0.10094
C	1.61524	-0.07570	0.03168
C	1.71939	-1.45279	-0.37548
C	2.92678	-2.02688	-0.65194
C	2.78553	2.08135	0.44857
C	1.54208	2.68811	0.70149
C	0.37066	1.95334	0.62521
C	0.37602	0.57817	0.31292
C	-0.91811	-0.11932	0.31892
C	-2.10734	0.50425	-0.08454
C	-3.32868	-0.15556	0.07504
C	-4.63765	0.45179	-0.21963
C	-4.77933	1.83595	-0.44054
C	-6.03153	2.37943	-0.72005
C	-7.15861	1.55216	-0.78502
C	-7.02879	0.17663	-0.56433
C	-5.77934	-0.37118	-0.28043
O	-0.93351	-1.35232	0.75745
O	-3.36647	-1.38717	0.51861
B	-2.14041	-2.22427	0.63908
F	-2.23906	-3.00014	1.78097
F	-2.01302	-3.00682	-0.50998
H	5.44765	-2.92658	-1.10528
H	7.53595	-1.59570	-0.93141
H	7.44089	0.79936	-0.29020
H	0.82093	-2.04793	-0.46244
H	2.96932	-3.06928	-0.95857
H	1.50597	3.73984	0.97247
H	-0.56976	2.44084	0.86007
H	-2.07191	1.49572	-0.50879
H	-3.92147	2.49681	-0.37750
H	-6.12920	3.44900	-0.88235
H	-8.13355	1.9788	-1.00456
H	-7.90094	-0.46895	-0.61513
H	-5.67504	-1.43725	-0.11235
C	5.21417	2.23118	0.27537
C	4.01205	2.82330	0.53053
H	6.13519	2.80526	0.34175
H	3.96166	3.87470	0.80207

Sum of electronic and zero-point energies = -1336.90638036 Hartree

8. ^1H and ^{13}C NMR spectra

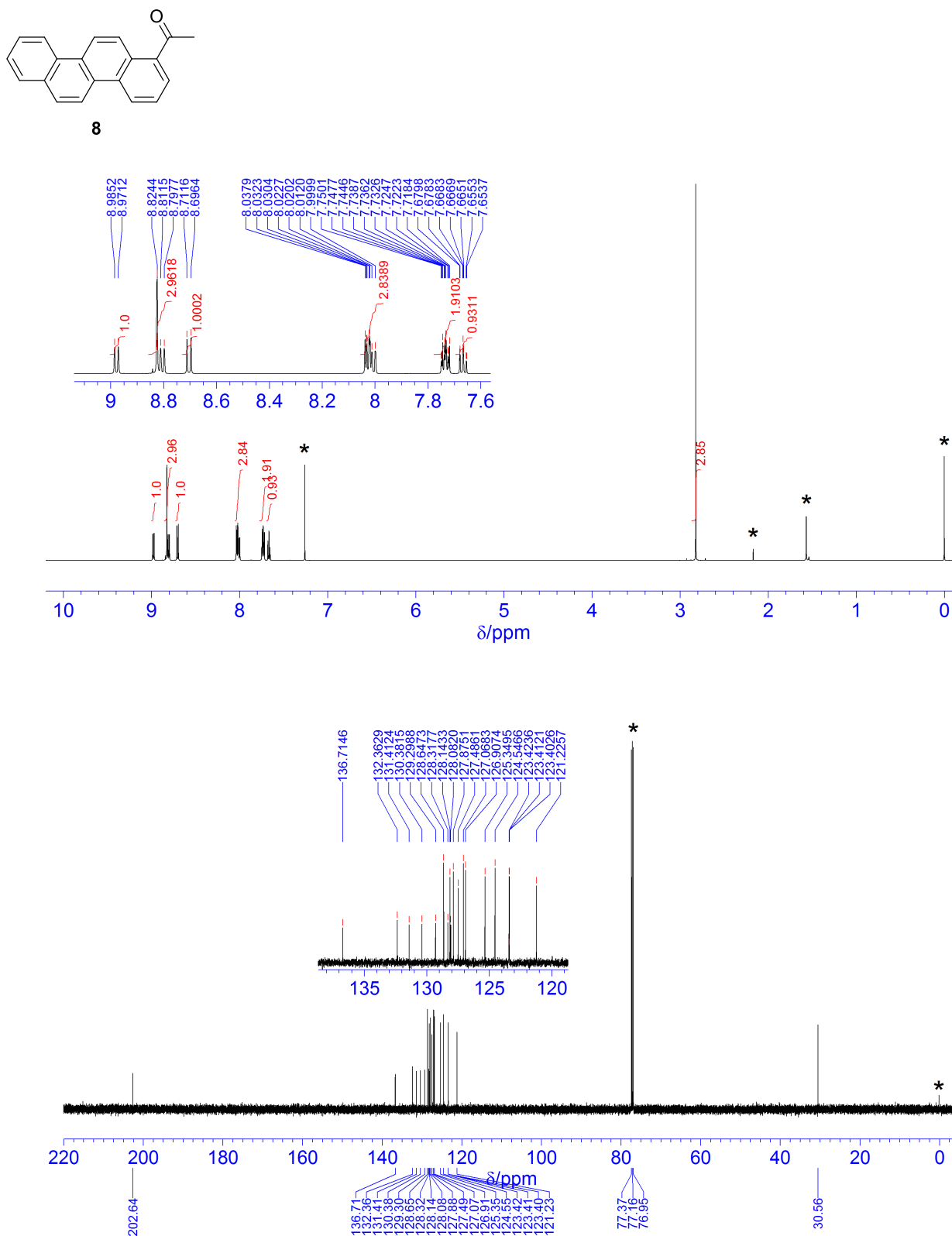
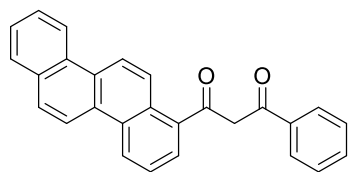


Figure S6. ^1H - (600 MHz) (upper) and ^{13}C (150 MHz) NMR spectra (lower) of **8** in CDCl_3 . The asterisked peaks are due to the solvent, TMS, H_2O included in the solvent, and other impurity.



11

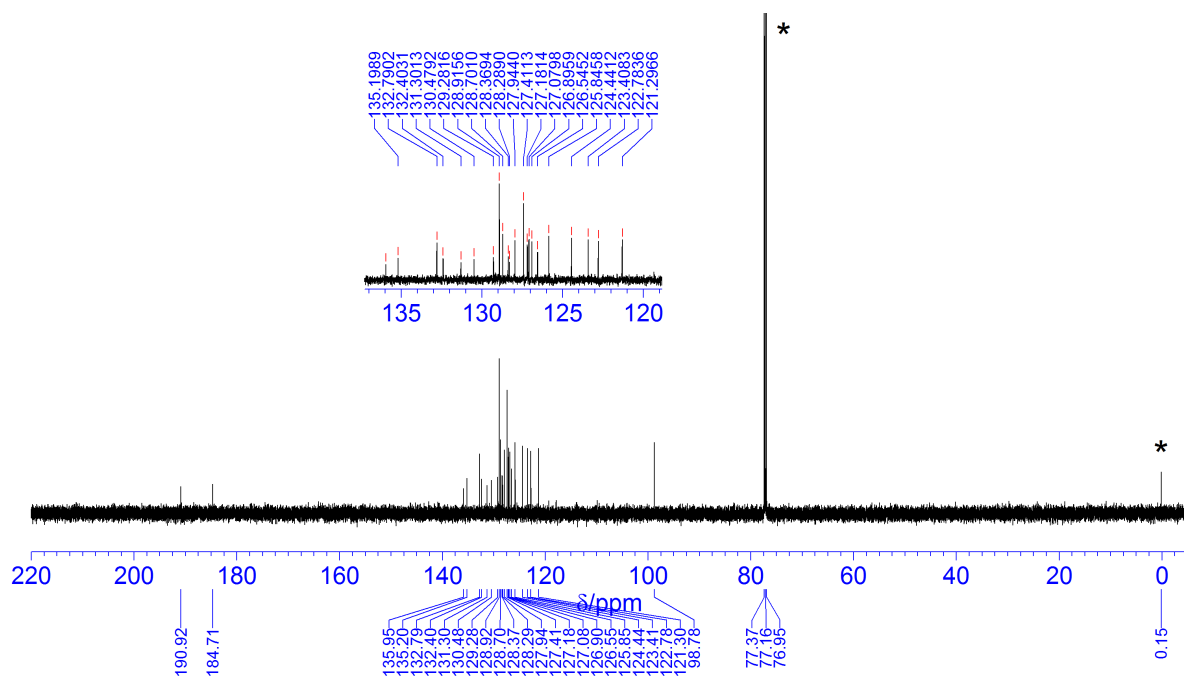
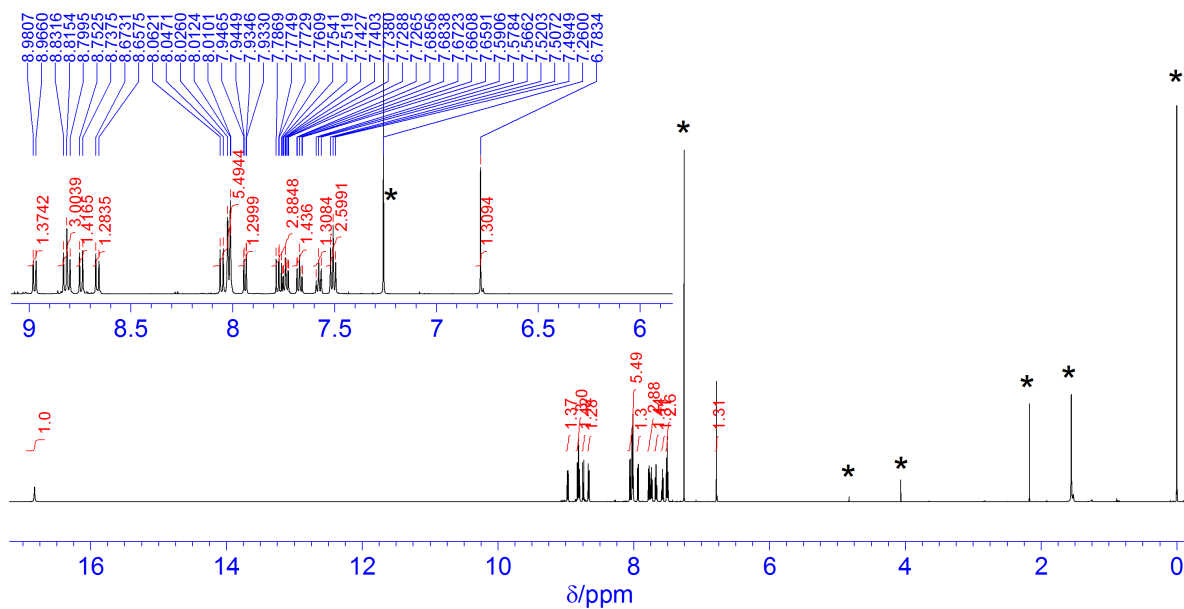
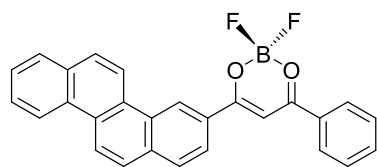


Figure S7. ^1H - (600 MHz) (upper) and ^{13}C (150 MHz) NMR spectra (lower) of **11** in CDCl_3 . The asterisked peaks are due to the solvent, TMS, H_2O included in the solvent, and other impurity.



3-ChB

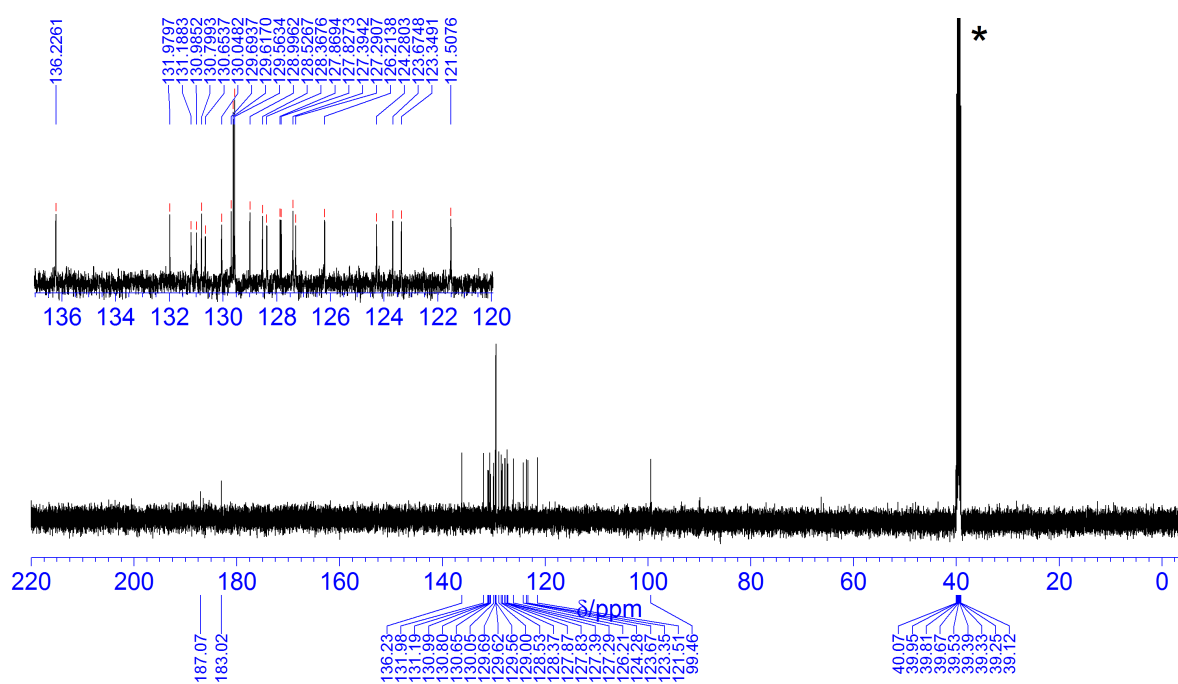
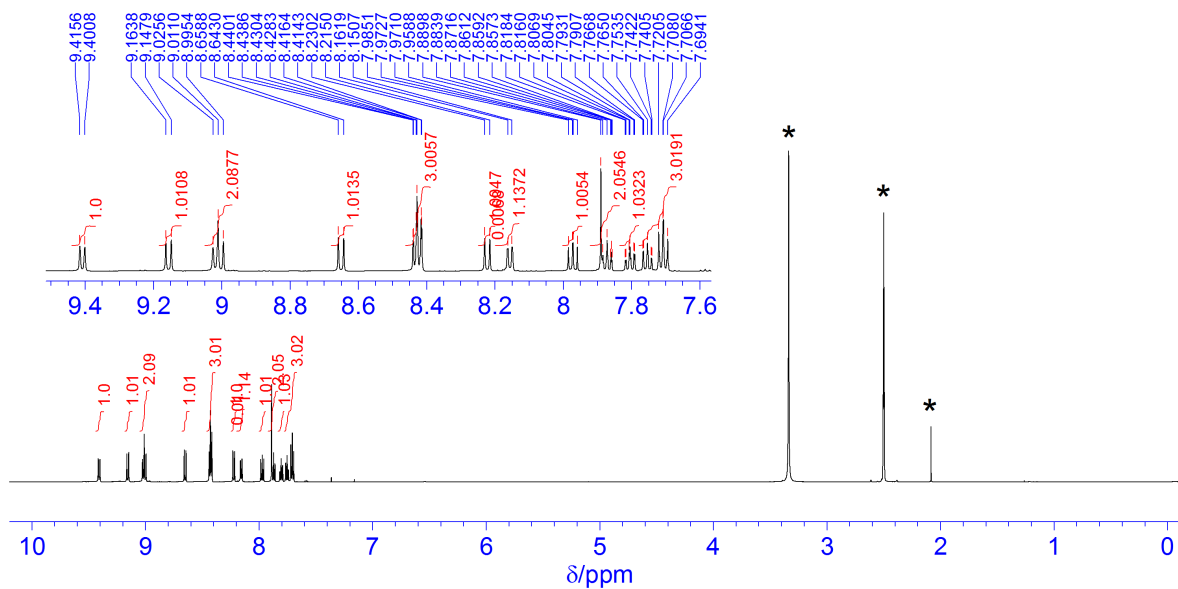


Figure S8. ^1H - (600 MHz) (upper) and ^{13}C (150 MHz) NMR spectra (lower) of 1-ChB in $\text{DMSO-}d_6$. The asterisked peaks are due to the solvent, H_2O included in the solvent, and other impurity.

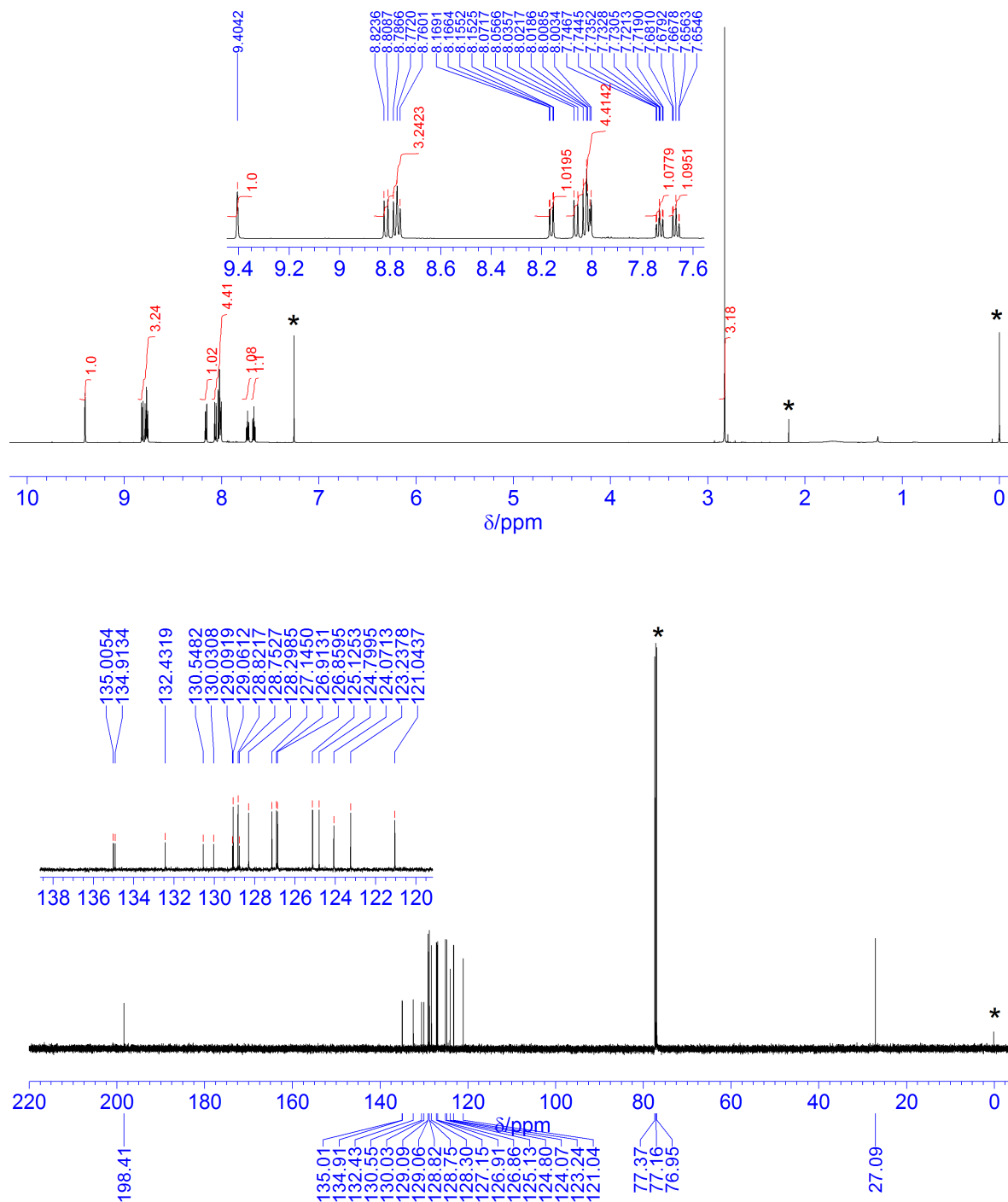
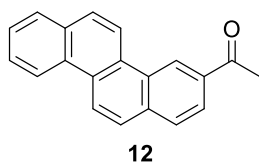
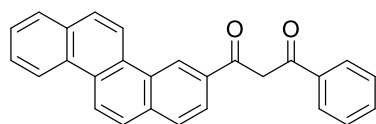


Figure S9. ¹H- (600 MHz) (upper) and ¹³C (150 MHz) NMR spectra (lower) of **12** in CDCl₃. The asterisked peaks are due to the solvent, TMS, and H₂O included in the solvent.



12

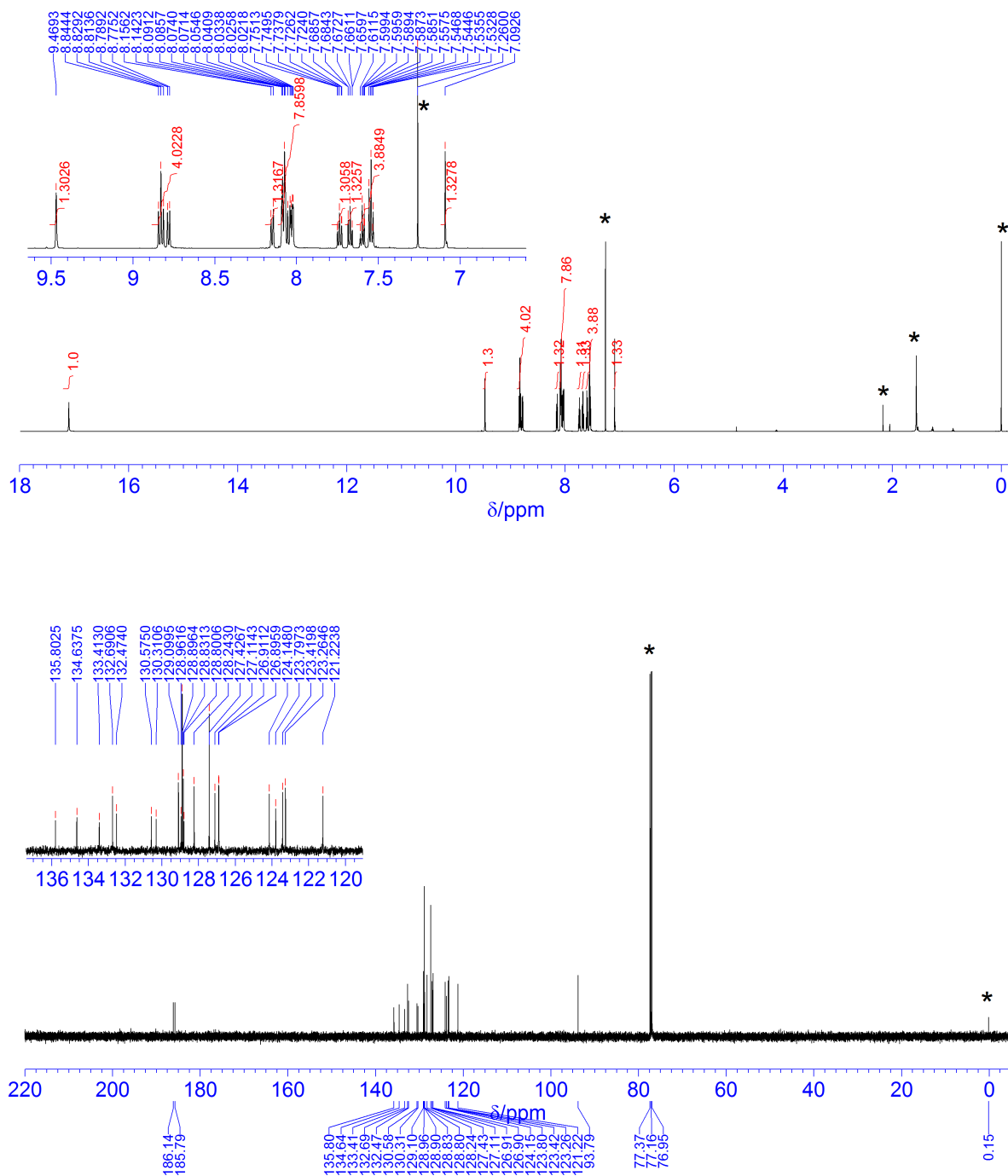
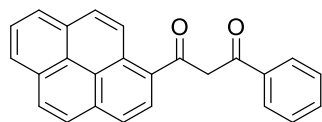


Figure S10. ¹H- (600 MHz) (upper) and ¹³C (150 MHz) NMR spectra (lower) of **12** in CDCl₃. The asterisked peaks are due to the solvent, TMS, H₂O included in the solvent, and other impurity.



13

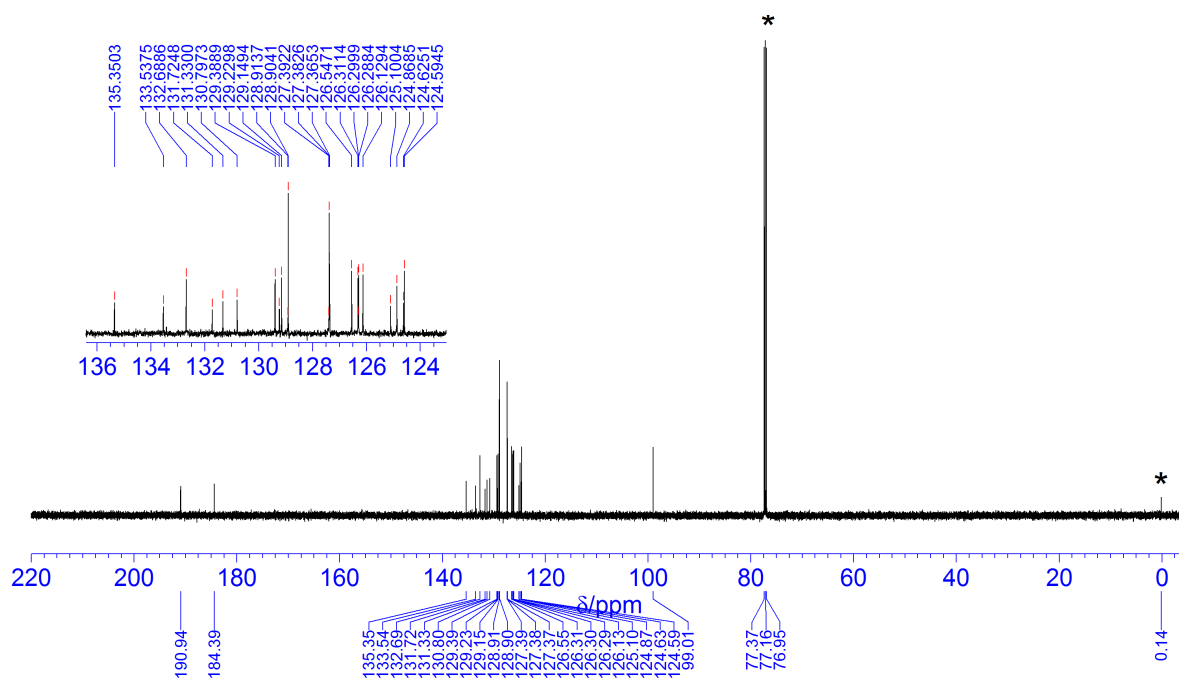
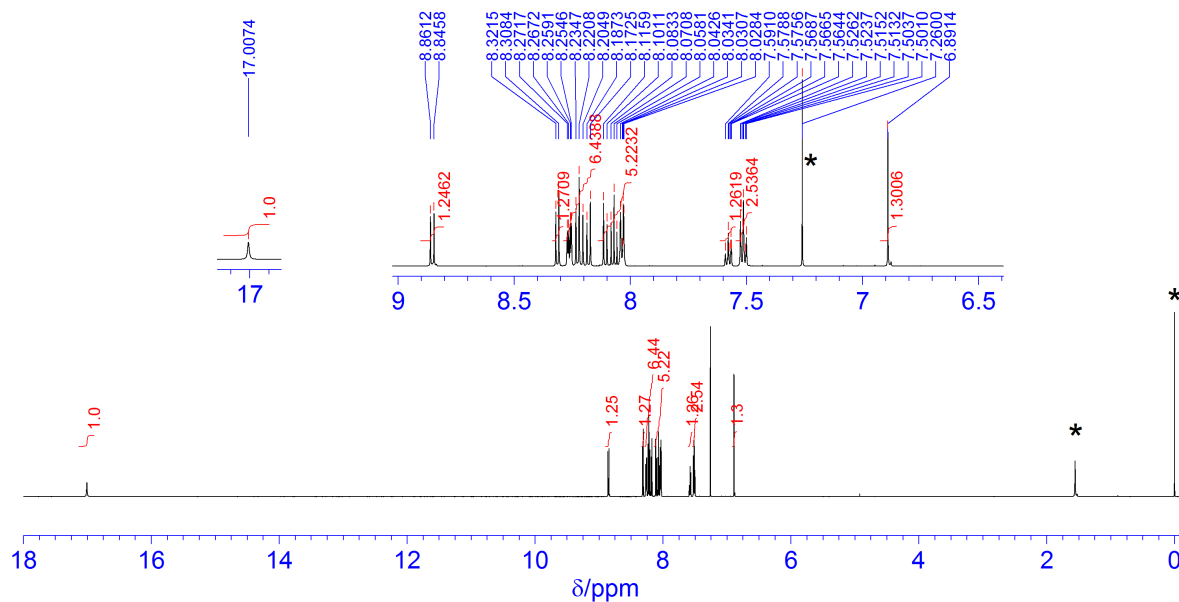


Figure S12. ^1H - (600 MHz) (upper) and ^{13}C (150 MHz) NMR spectra (lower) of **13** in CDCl_3 . The asterisked peaks are due to the solvent, TMS, and H_2O included in the solvent.

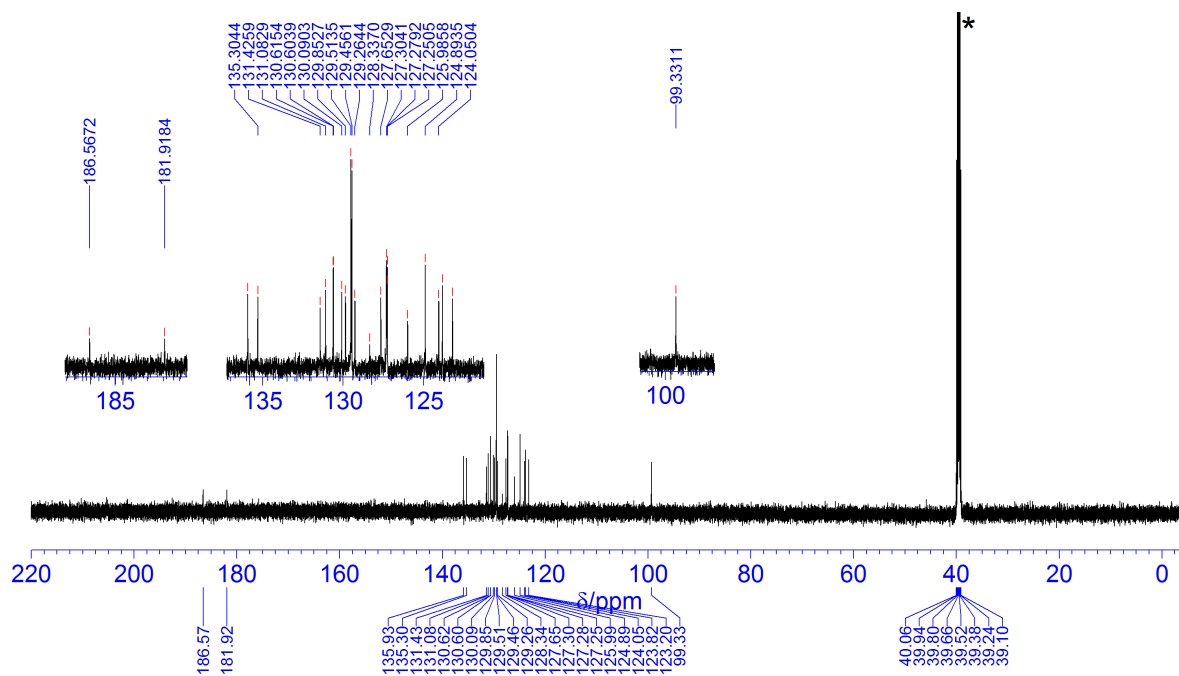
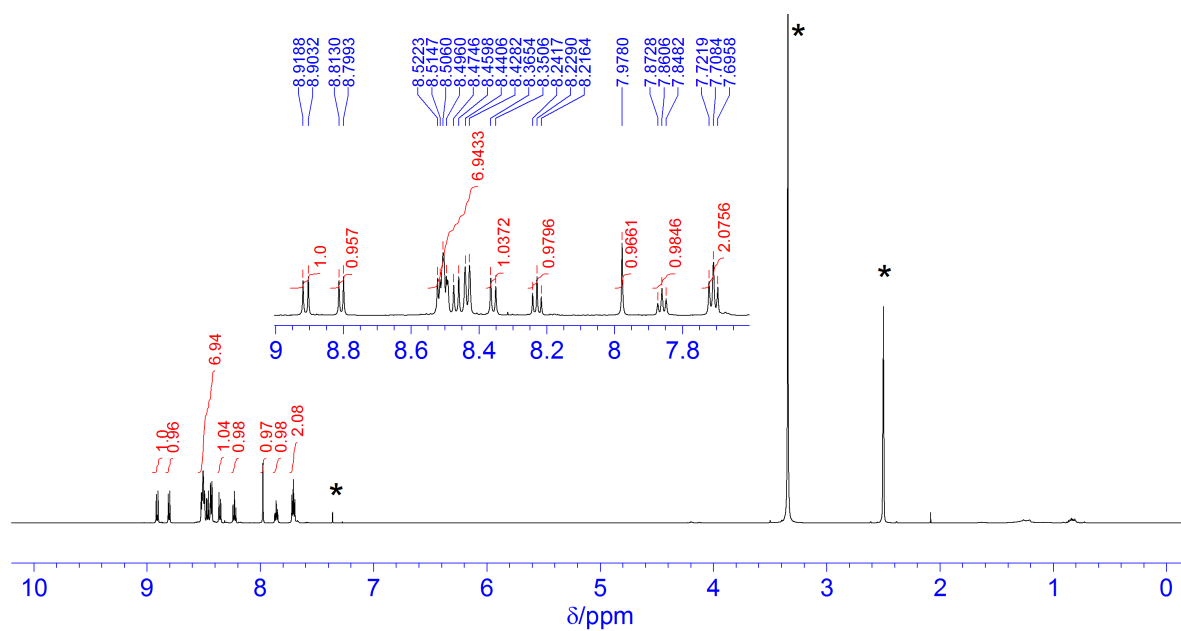
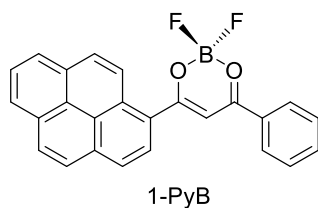


Figure S13. ^1H - (600 MHz) (upper) and ^{13}C (150 MHz) NMR spectra (lower) of 1-PyB in $\text{DMSO-}d_6$. The asterisked peaks are due to the solvent and H_2O included in the solvent.

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