

Electronic Supplementary Information

Boron-dibenzopyrromethene-based organic dyes for application in dye-sensitized solar cells

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1. Synthesis of intermediates

Difluoro[5-(3-hexyl-5-(5,5-dimethyl-[1,3]dioxane-2-yl)thiophen-2-yl)-1-[[5-(3-hexyl-5-(5,5-dimethyl-[1,3]dioxane)thiophene-2-yl)-3-(2-methoxyphenyl)-2*H*-isoindole-1-yl]methylene]-3-(2-methoxyphenyl)-1*H*-isoindolate-*N*¹,*N*²]boron (6)

To a solution of **4** (1.50 g, 2.27 mmol), **5** (2.78 g, 6.81 mmol), and K₂CO₃ (6.28 g, 45.4 mmol) in THF (75 mL)/H₂O (10 mL) was added Pd(PPh₃)₄ (0.80 g, 0.69 mmol). The resulting solution was refluxed overnight under a N₂ atmosphere. After evaporation of THF, the subsequent solution was extracted with CH₂Cl₂ (150 mL). And the organic layer was then washed with water (150 mL) and dried with Na₂SO₄. After the removal of solvent *in vacuo*, the residue was chromatographed on silica gel (Wacogel C-300) using CH₂Cl₂/hexane (1:1 v/v) as an eluent. In this way, 984 mg of **6** was obtained (41% yield). ¹H NMR (500 MHz, CDCl₃) δ (ppm) 0.79 (s, 6H), 0.83 (t, 6H, *J* = 6.92 Hz), 1.18–1.22 (m, 12H), 1.28 (s, 6H), 1.47–1.53 (m, 4H), 2.56 (t, 4H, *J* = 7.82 Hz), 3.63 (d, 4H, *J* = 10.95 Hz), 3.69 (s, 3H), 3.75 (d, 4H, *J* = 9.75 Hz), 3.76 (s, 3H), 5.59 (s, 2H), 6.95 (d, 1H, *J* = 8.35 Hz), 6.99 (s, 2H), 6.99–7.01 (m, 2H), 7.06 (t, 1H, *J* = 7.33 Hz), 7.36 (s, 1H), 7.37 (s, 1H), 7.38–7.42 (m, 2H), 7.49 (d, 2H, *J* = 8.35 Hz), 7.54 (d, 1H, *J* = 7.55 Hz), 7.66 (d, 1H, *J* = 7.30 Hz), 7.81 and 7.82 (s, 1H), 7.89 (d, 1H, *J* = 8.45 Hz), 7.90 (d, 1H, *J* = 8.55 Hz); FAB MS : *m/z* 1064 [M]⁺.

Difluoro[5-(3-hexyl-5-formylthiophene-2-yl)-1-[[5-(3-hexyl-5-formylthiophene-2-yl)-3-(2-methoxyphenyl)-2*H*-isoindole-1-yl]methylene]-3-(2-methoxyphenyl)-1*H*-isoindolate-*N*¹,*N*²]boron (7)

To a solution of **6** (980 mg, 0.920 mmol) in THF (120 mL) was added a solution of *p*-toluene sulfonic acid monohydrate (270 mg, 1.42 mmol) in water (20 mL). The resulting solution was stirred at 40°C overnight under dark conditions. After evaporation of THF, the subsequent solution was extracted with CH₂Cl₂ (100 mL). And the organic layer was then washed with water (100 mL × 2) and dried with Na₂SO₄. After the removal of solvent *in vacuo*, the residue was reprecipitated from CH₂Cl₂/hexane to give **7** as a deep-blue solid (723 mg, 88%). ¹H NMR (500 MHz, CDCl₃) δ (ppm) 0.84 (t, 6H, *J* = 6.95 Hz), 1.21–1.25 (m, 12H), 1.57–1.64 (m, 4H), 2.66 (t, 4H, *J* = 7.80 Hz), 3.72 (s, 3H), 3.80 (s, 3H), 6.99 (d, 1H, *J* = 8.65 Hz), 7.03 (t, 1H, *J* = 8.00 Hz), 7.08 (t, 1H, *J* = 7.15 Hz), 7.41–7.43 (m, 3H), 7.45 (s, 1H), 7.46 (s, 1H), 7.52–7.54 (m, 2H), 7.56 (d, 1H, *J* = 7.65 Hz), 7.63 (s, 2H), 7.69 (d, 1H, *J* = 7.55 Hz), 7.88 and 7.89 (s, 1H), 7.96 (d, 1H, *J* = 8.45 Hz), 7.97 (d, 1H, *J* = 8.05 Hz), 9.84 (s, 2H); FAB MS: *m/z* 892 [M]⁺; Elemental analysis: Calcd for C₅₃H₅₁BF₂N₄O₆S₂: C, 71.29; H, 5.76; N, 3.14, found: C, 71.39; H, 6.12; N, 2.98.

(Z)-N'-(1-(5-Bromo-2-hydroxyphenyl)ethylidene)-2-methoxybenzohydrazide (9)

2-Acetyl-4-bromophenol **8** (4.87 g, 22.6 mmol) and 2-methoxybenzohydrazine (3.76 g, 22.6 mmol) were dissolved in dry EtOH (46 mL). The resulting mixture was stirred for 4 days at 85 °C to give 7.81 g of **9** as a light yellow solid in 95% yield. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 2.35 (s, 3H), 4.10 (s, 3H), 6.94 (d, 1H, *J* = 8.75 Hz), 7.05 (d, 1H, *J* = 8.10 Hz), 7.17 (td, 1H, *J* = 7.57 and 0.95 Hz), 7.35 (dd, 1H, *J* = 2.43 and 8.80 Hz), 7.52–7.55 (m, 2H), 8.35 (dd, 1H, *J* = 1.80 and 7.85 Hz), 11.03 (s, 1H), 12.93 (s, 1H); FAB MS : *m/z* 363 [M]⁺.

1-(5-Bromo-2-(2-methoxybenzoyl)phenyl)ethanone (10)

To a solution of compound **9** (4.00 g, 11.0 mmol) in THF (200 mL) was dropwisely added Pb(OAc)₄ (5.99 g, 13.5 mmol) under an icy condition and then the mixture was stirred for 6 h at room temperature to give **10** as a brown solid with quantitative yield (3.97 g). ¹H NMR (500 MHz, CDCl₃) δ (ppm) 2.47 (s, 3H), 3.65 (s, 3H), 6.94 (d, 1H, *J* = 8.40 Hz), 7.05 (td, 1H, *J* = 7.50 and 0.85 Hz), 7.25 (d, 1H, *J* = 8.30 Hz), 7.51 (ddd, 1H, *J* = 8.35, 7.40 and 1.80 Hz), 7.61 (dd, 1H, *J* = 1.90 and 8.20 Hz), 7.66 (dd, 1H, *J* = 1.80 and 7.70 Hz), 7.74 (d, 1H, *J* = 1.90); FAB MS : *m/z* 333 [M]⁺.

(Z)-6-Bromo-1-((6-bromo-3-(2-methoxyphenyl)-2H-isoindol-1-yl)methylene)-3-(2-methoxyphenyl)-1H-isoindole (11)

To a solution of **10** (301 mg, 0.902 mmol) in EtOH (10 mL) and AcOH (2 mL) was added NH₄OAc (459 mg, 5.96 mmol) and NH₄Cl (50.5 mg, 0.945 mmol) at 65 °C. The resulting mixture was stirred overnight at 90 °C. The resulting solution was poured into water (50 mL) and then was extracted with AcOEt (160 mL). The organic layer was dried with Na₂SO₄. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel (Wacogel C-300) using CH₂Cl₂/hexane (1:1 v/v) as an eluent to give 149 mg of **11** as a purple solid in 54% yield. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 3.75 (s, 6H), 7.04 (d, 2H, *J* = 8.20 Hz), 7.11 (td, 2H, *J* = 7.57 and 0.95 Hz), 7.32 (dd, 2H, *J* = 1.75 and 8.60 Hz), 7.40 (ddd, 2H, *J* = 8.25, 7.43 and 1.54 Hz), 7.49 (s, 1H), 7.69 (d, 2H, *J* = 8.50 Hz), 7.88 (dd, 2H, *J* = 1.70 and 7.70 Hz), 8.06 (d, 2H, *J* = 1.40 Hz); FAB MS : *m/z* 614 [M]⁺.

Difluoro[6-bromo-1-[[6-bromo-3-(2-methoxyphenyl)-2H-isoindole-1-yl]methylene]-3-(2-methoxyphenyl)-1H-isoindolate-N¹,N²]boron (12)

Triethylamine (0.6 mL, 7.27 mmol) was added to a solution of **11** (1.00 g, 1.63 mmol) in dry toluene (130 mL), followed by the addition of BF₃·Et₂O (2 mL, 16.3 mmol) at 80 °C. The mixture was stirred for 18 h at 100 °C. After cooling, the solution was poured into water (100 mL) and extracted with AcOEt (200 mL), the organic layer

was washed with water (400 mL) and dried with Na₂SO₄. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel (Wacogel C-300) using CHCl₃/hexane (1:1 v/v) as an eluent. In this way, 960 mg of **12** was obtained in 89% yield. ¹H NMR (500 MHz, DMSO-*d*₆) δ (ppm) 3.66 (s, 3H), 3.72 (s, 3H), 7.01 (td, 1H, *J* = 7.53 and 0.68 Hz), 7.07 (td, 1H, *J* = 7.48 and 0.80 Hz), 7.17 (d, 1H, *J* = 8.15 Hz), 7.21 (d, 1H, *J* = 8.20 Hz), 7.27 (d, 2H, *J* = 8.75 Hz), 7.37–7.40 (m, 3H), 7.45 (d, 1H, *J* = 7.60 Hz), 7.50 (td, 2H, *J* = 7.87 and 1.13 Hz), 8.36–8.37 (m, 2H), 8.82 (s, 1H); FAB MS : *m/z* 662 [M]⁺; Elemental analysis: Calcd for C₃₁H₂₁BBr₂F₂N₂O₂ · H₂O: C, 54.74; H, 3.41; N, 4.12, found: C, 54.59; H, 3.22; N, 3.98

Difluoro[6-(3-hexyl-5-(5,5-dimethyl-[1,3]dioxane-2-yl)thiophen-2-yl)-1-[[6-(3-hexyl-5-(5,5-dimethyl-[1,3]dioxane)thiophene-2-yl)-3-(2-methoxyphenyl)-2*H*-isoindole-1-yl]methylene]-3-(2-methoxyphenyl)-1*H*-isoindolate-*N*¹,*N*²]boron (13)

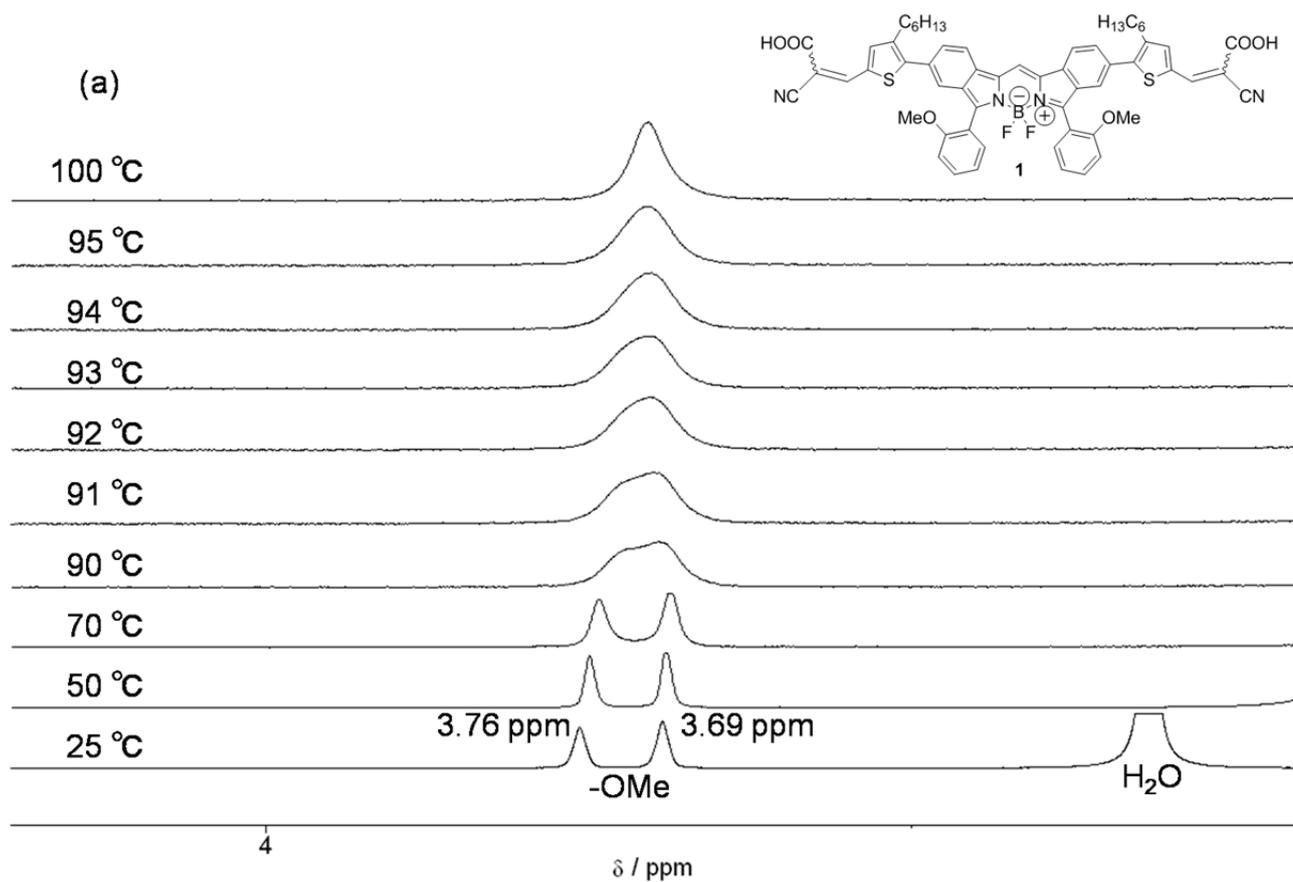
To a solution of **12** (425 mg, 0.427 mmol) and **5** (655 mg, 1.60 mmol) in THF (33 mL), 2 M K₂CO₃ aq. (6.5 mL) was added and the resulting solution was degassed by freeze-pump-thaw cycles. After adding Pd(PPh₃)₄ (0.16 g, 0.139 mmol) into the frozen flask under a N₂ atmosphere, the reaction mixture was stirred at 70 °C overnight, poured into water (20 mL), and then extracted with AcOEt (100 mL). The organic layer was washed with water (230 mL) and dried with Na₂SO₄. After the removal of solvent *in vacuo*, the residue was chromatographed on silica gel (Wacogel C-300) using CH₂Cl₂/hexane (3:2 v/v) as an eluent. In this way, 446 mg of **13** was obtained (65% yield). ¹H NMR (500 MHz, DMSO-*d*₆) δ (ppm) 0.77 (t, 6H, *J* = 6.93 Hz), 1.19 (s, 12H), 1.20–1.25 (m, 12H), 1.57 (quint, 4H, *J* = 7.31 Hz), 2.70 (t, 4H, *J* = 7.70 Hz), 3.67 (s, 8H), 3.69 (s, 3H), 3.75 (s, 3H), 5.70 (s, 2H), 7.02 (td, 1H, *J* = 7.50 and 0.63 Hz), 7.08 (td, 1H, *J* = 7.58 and 0.73 Hz), 7.10 (s, 2H), 7.19 (d, 1H, *J* = 8.35 Hz), 7.22 (d, 1H, *J* = 8.10 Hz), 7.31 (d, 1H, *J* = 8.50 Hz), 7.31 (d, 1H, *J* = 8.35 Hz), 7.37 (d, 2H, *J* = 8.45 Hz), 7.41 (d, 1H, *J* = 7.50 Hz), 7.47 (dd, 1H, *J* = 1.48 and 8.15 Hz), 7.50 (td, 2H, *J* = 7.98 and 1.42 Hz), 8.20 (s, 2H), 8.78 (s, 1H); FAB MS : *m/z* 1065 [M+1]⁺.

Difluoro[6-(3-hexyl-5-formylthiophene-2-yl)-1-[[6-(3-hexyl-5-formylthiophene-2-yl)-3-(2-methoxyphenyl)-2*H*-isoindole-1-yl]methylene]-3-(2-methoxyphenyl)-1*H*-isoindolate-*N*¹,*N*²]boron (14)

To a solution of **13** (445 mg, 0.426 mmol) in THF (54 mL) was added a solution of *p*-toluene sulfonic acid monohydrate (122 mg, 0.639 mmol) in water (8.5 mL) at room temperature. The resulting solution was stirred at 40°C, and then partitioned using water (50 mL) and AcOEt (50 mL). The organic layer was washed with water (100 mL) and dried with Na₂SO₄. After the removal of solvent *in vacuo*, the residue was chromatographed on silica gel (Wacogel C-300) using CH₂Cl₂/hexane (2:1 v/v) as an eluent. In this way, 283 mg of **14** was obtained

(61% yield). ^1H NMR (500MHz, $\text{DMSO-}d_6$) δ (ppm) 0.76 (t, 6H, $J = 7.00$ Hz), 1.19–1.27 (m, 12H), 1.62 (quint, 4H, $J = 7.37$ Hz), 2.78 (t, 4H, $J = 7.68$ Hz), 3.70 (s, 3H), 3.75 (s, 3H), 7.03 (t, 1H, $J = 7.78$ Hz), 7.09 (t, 1H, $J = 7.48$ Hz), 7.20 (d, 1H, $J = 8.20$ Hz), 7.23 (d, 1H, $J = 8.05$ Hz), 7.38–7.45 (m, 5H), 7.49 (d, 1H, $J = 8.25$ Hz), 7.51 (t, 2H, $J = 8.00$ Hz), 8.06 (s, 2H), 8.29 (s, 1H), 8.30 (s, 1H), 8.84 and 8.85 (s, 1H), 9.93 (s, 2H); FAB MS : m/z 892 $[\text{M}]^+$.

2. Variable temperature ^1H NMR measurements



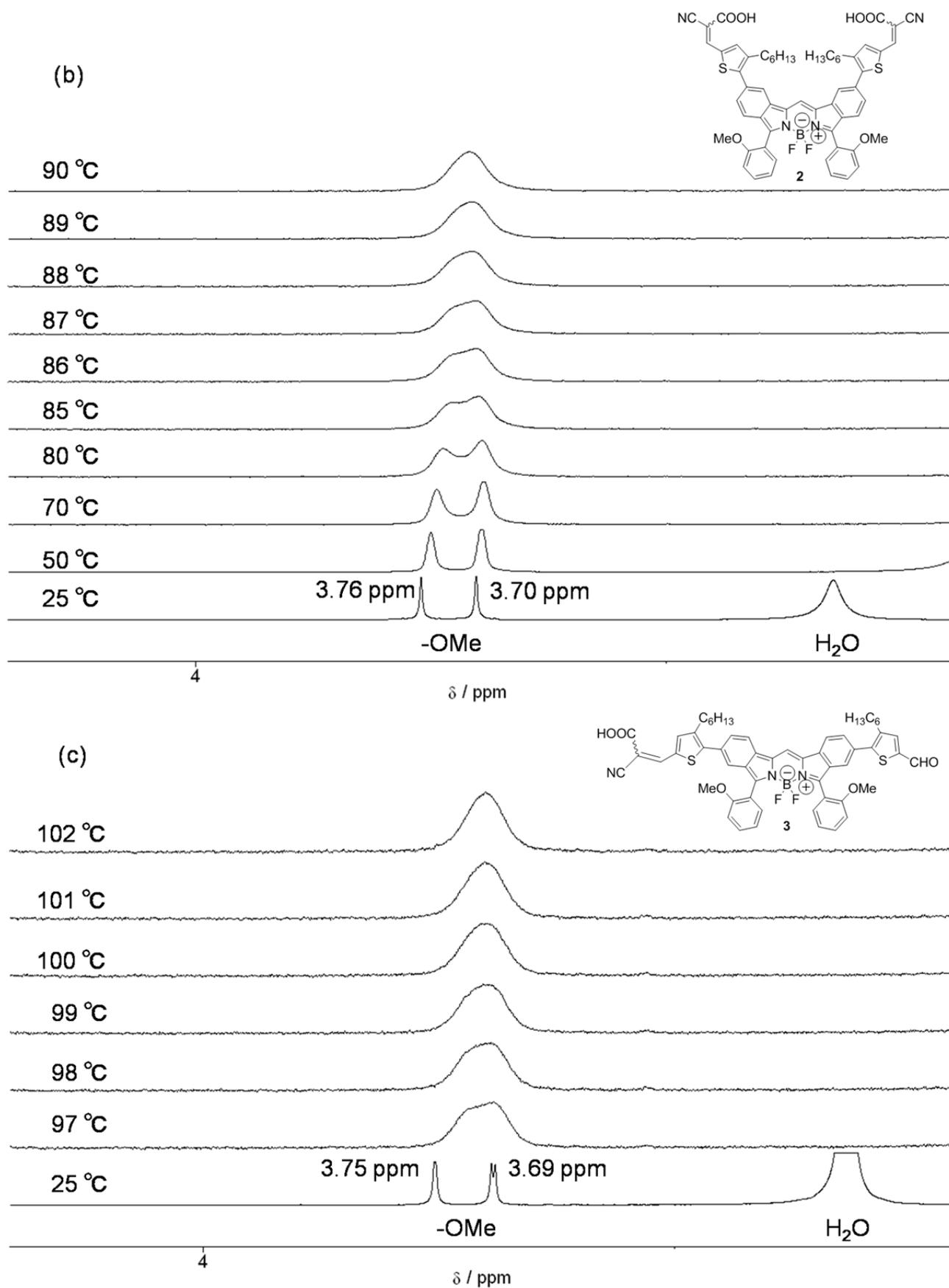


Fig. S1 Variable temperature ¹H NMR spectra of **1** (a), **2** (b), and **3** (c) in DMSO-*d*₆.

3. Electrochemical properties

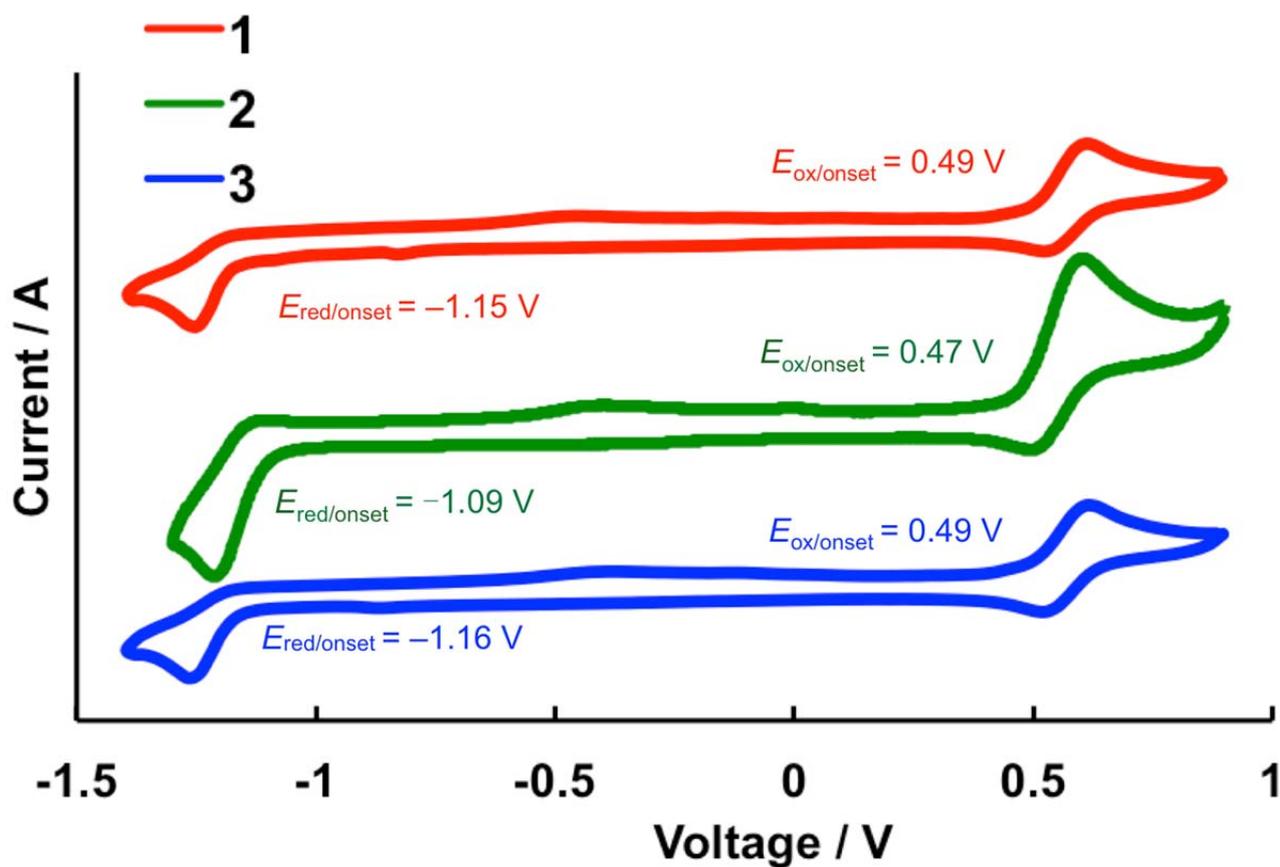


Fig. S2 (a) Cyclic voltammograms of 1, 2 and 3 measured in DMF/CH₂Cl₂ (1:4 v/v) containing 0.1 M TBAPF₆ at room temperature. Ferrocene (Fc) was used as an internal reference.

4. ATR-FT-IR spectra

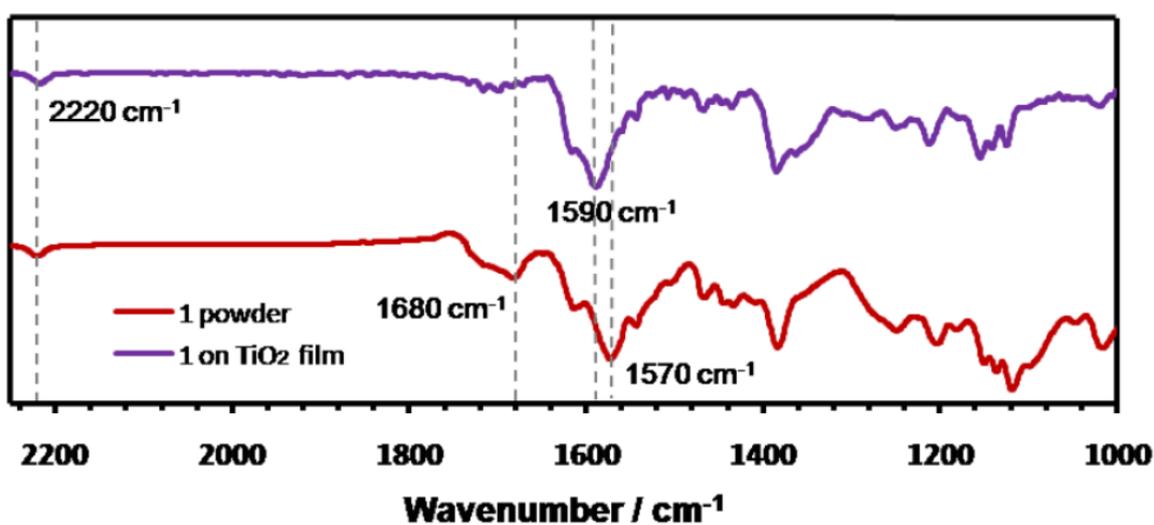


Fig. S3 ATR-FT-IR spectra of 1 and 1-loaded TiO₂ film.

5. Characterization data of dyes

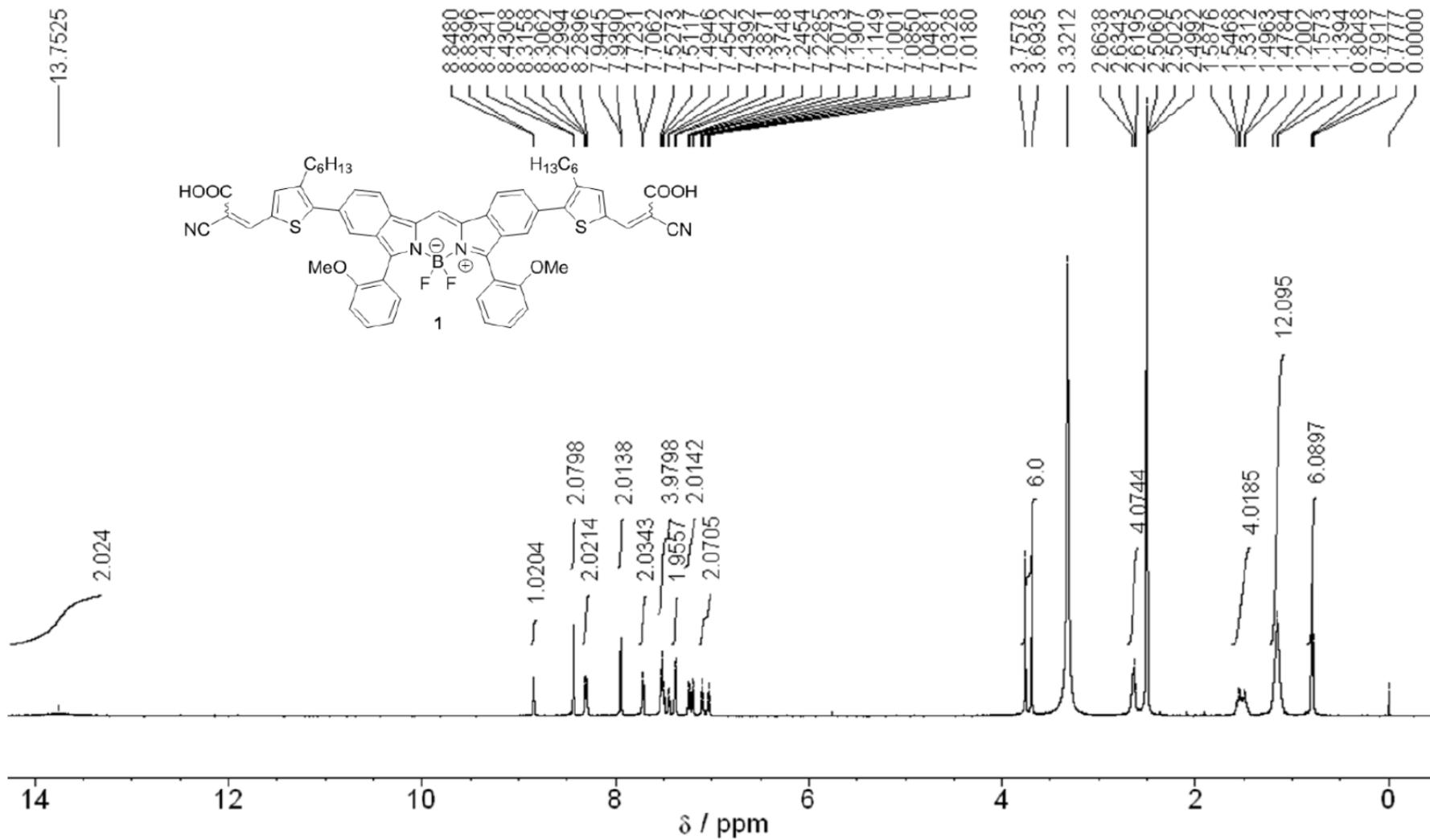


Figure S4. ^1H NMR spectrum of dye **1** in $\text{DMSO-}d_6$ at room temperature.

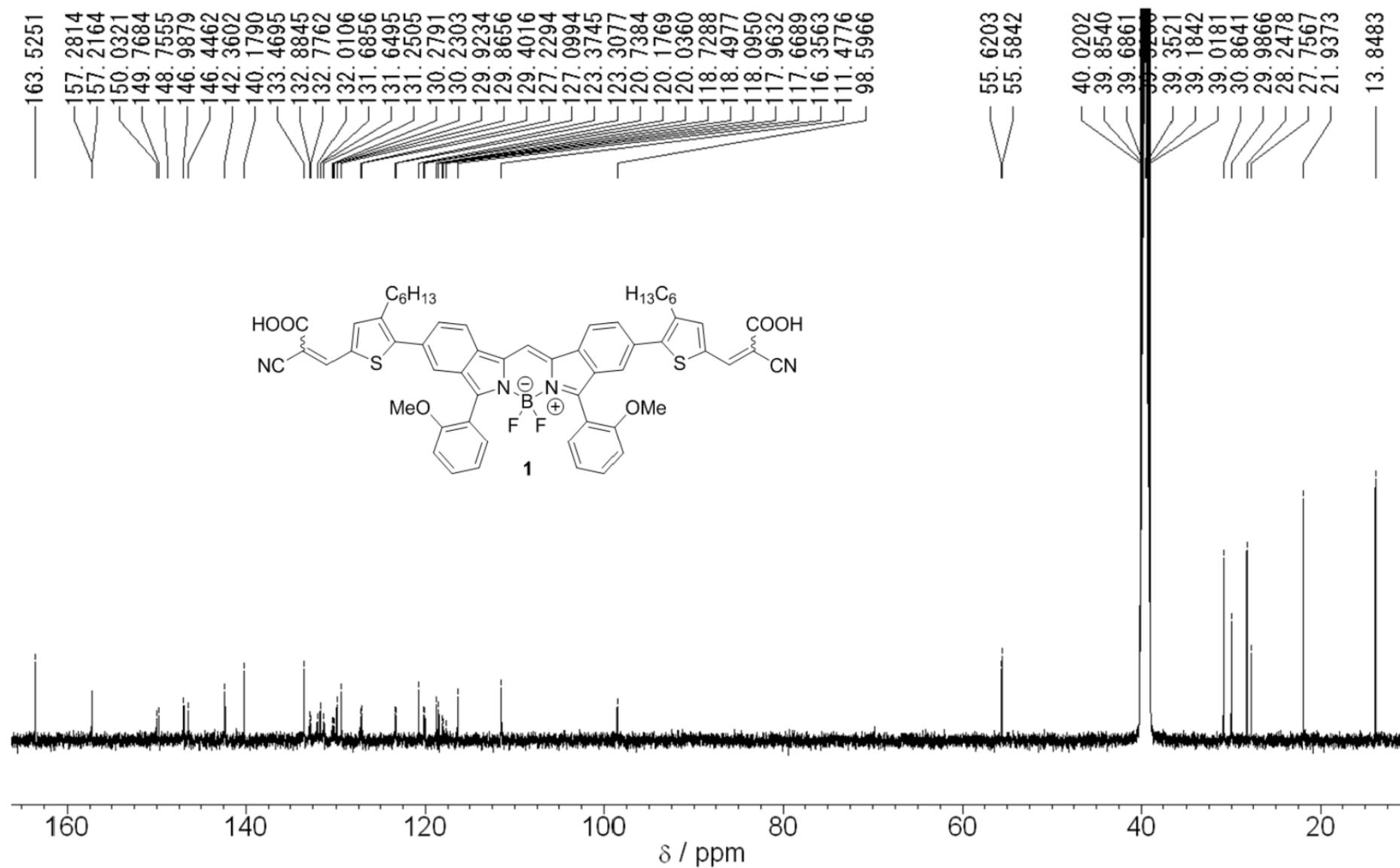


Figure S5. ^{13}C NMR spectrum of dye **1** in $\text{DMSO-}d_6$ at room temperature.

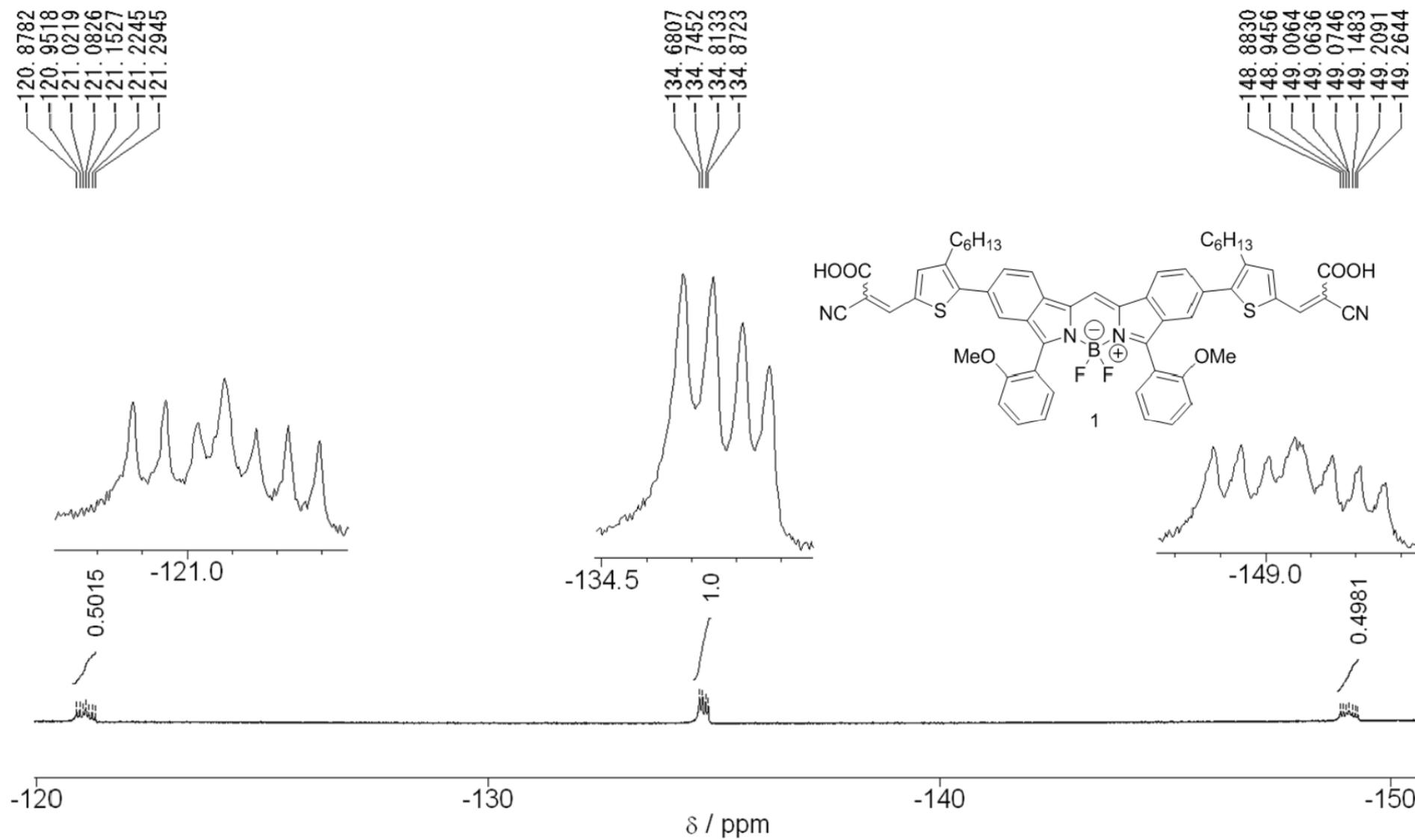


Figure S6. ^{19}F NMR spectrum of dye **1** in $\text{CDCl}_3:\text{DMSO}-d_6$ (3:7 v/v) at room temperature.

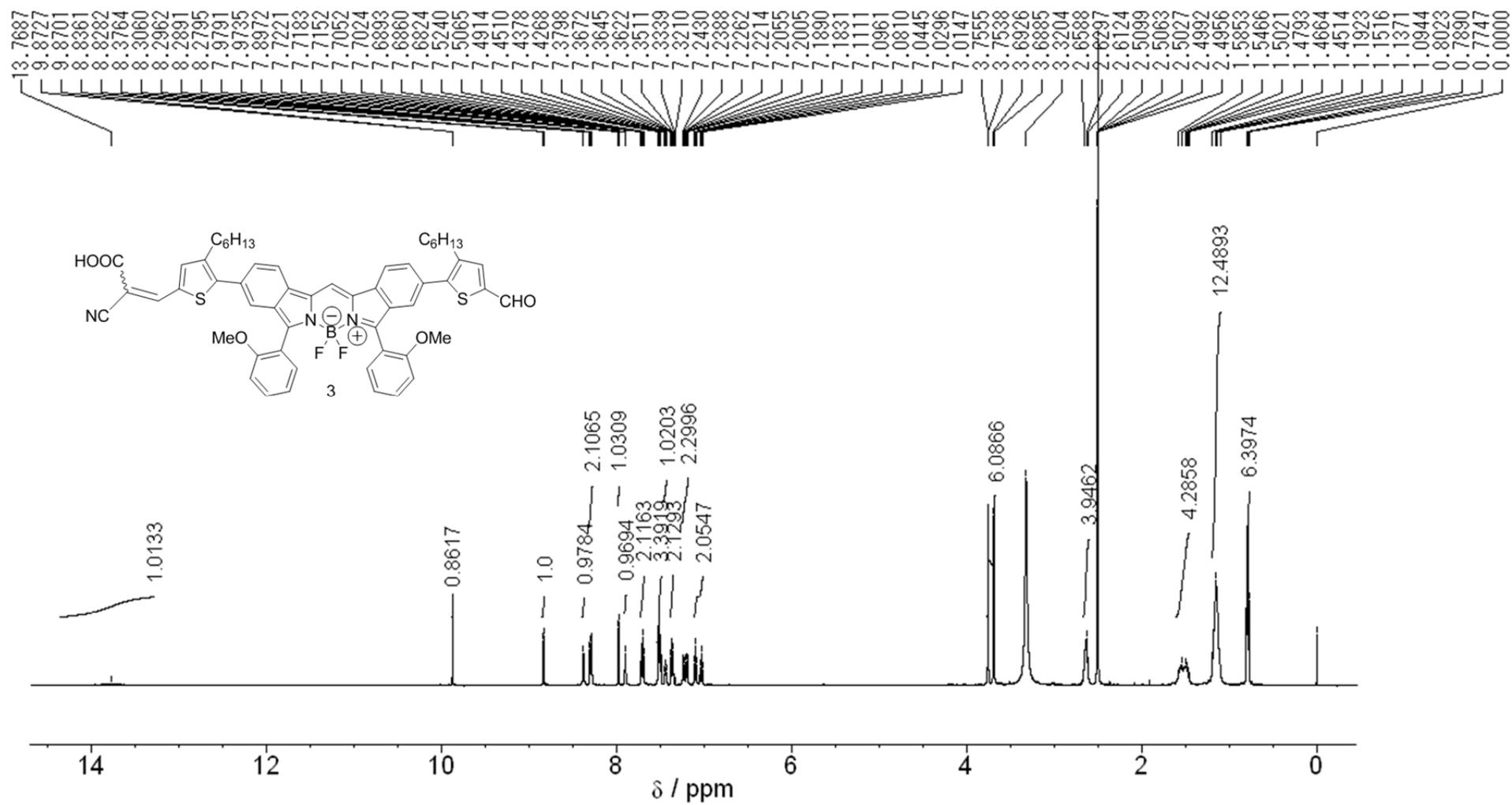


Figure S7. ¹H NMR spectrum of dye **3** in DMSO-*d*₆ at room temperature.

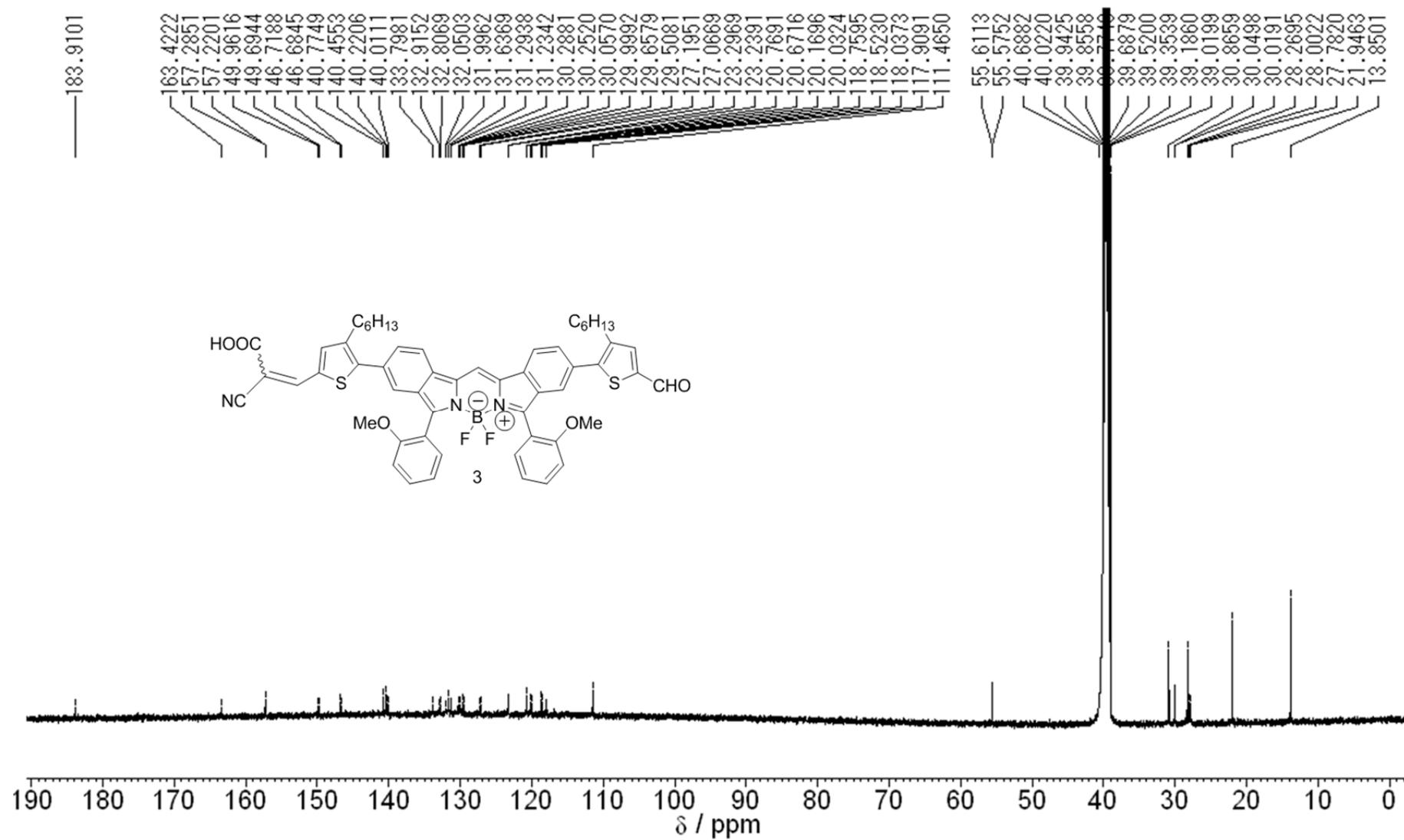


Figure S8. ¹³C NMR spectrum of dye 3 in DMSO-*d*₆ at room temperature.

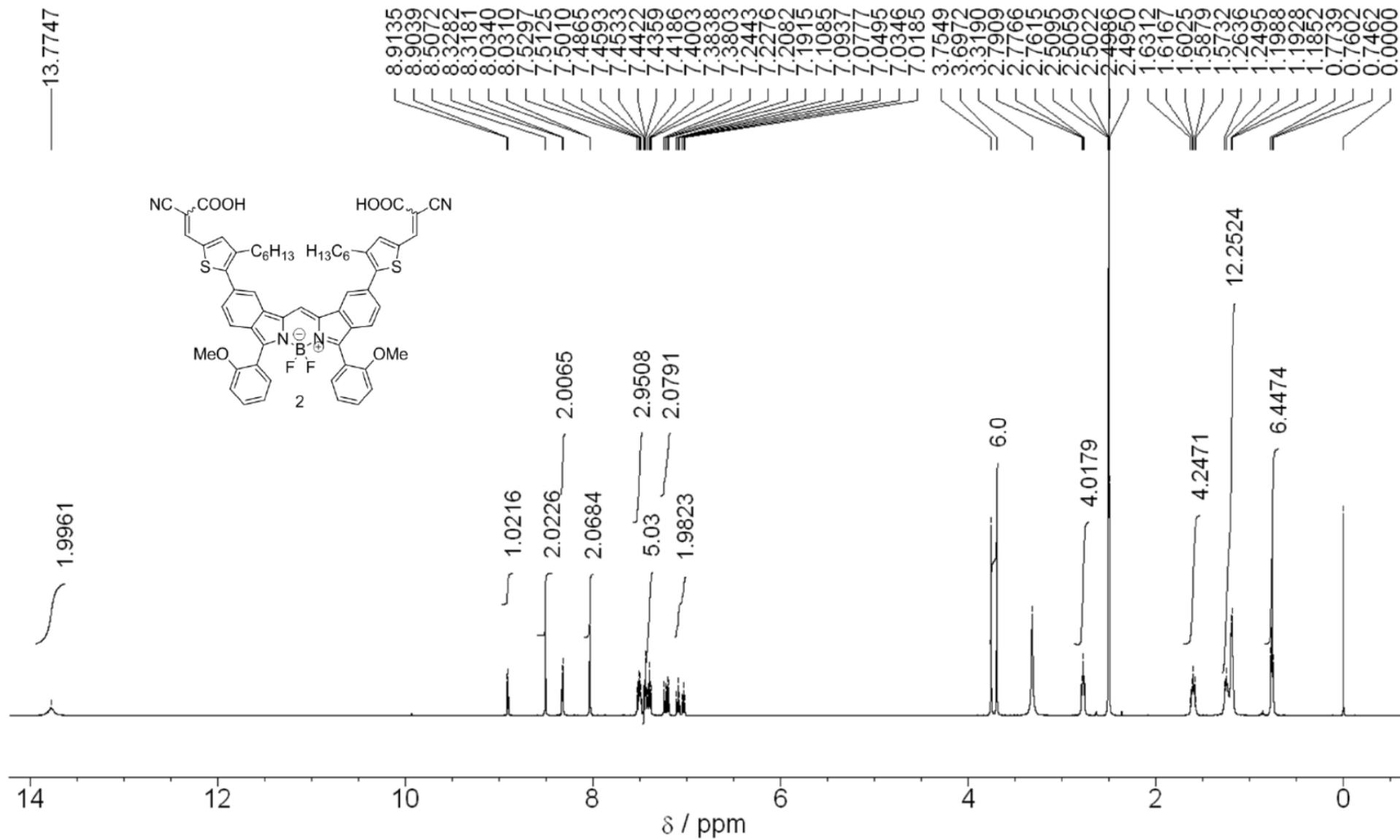


Figure S10. ¹H NMR spectrum of dye **2** in DMSO-*d*₆ at room temperature.

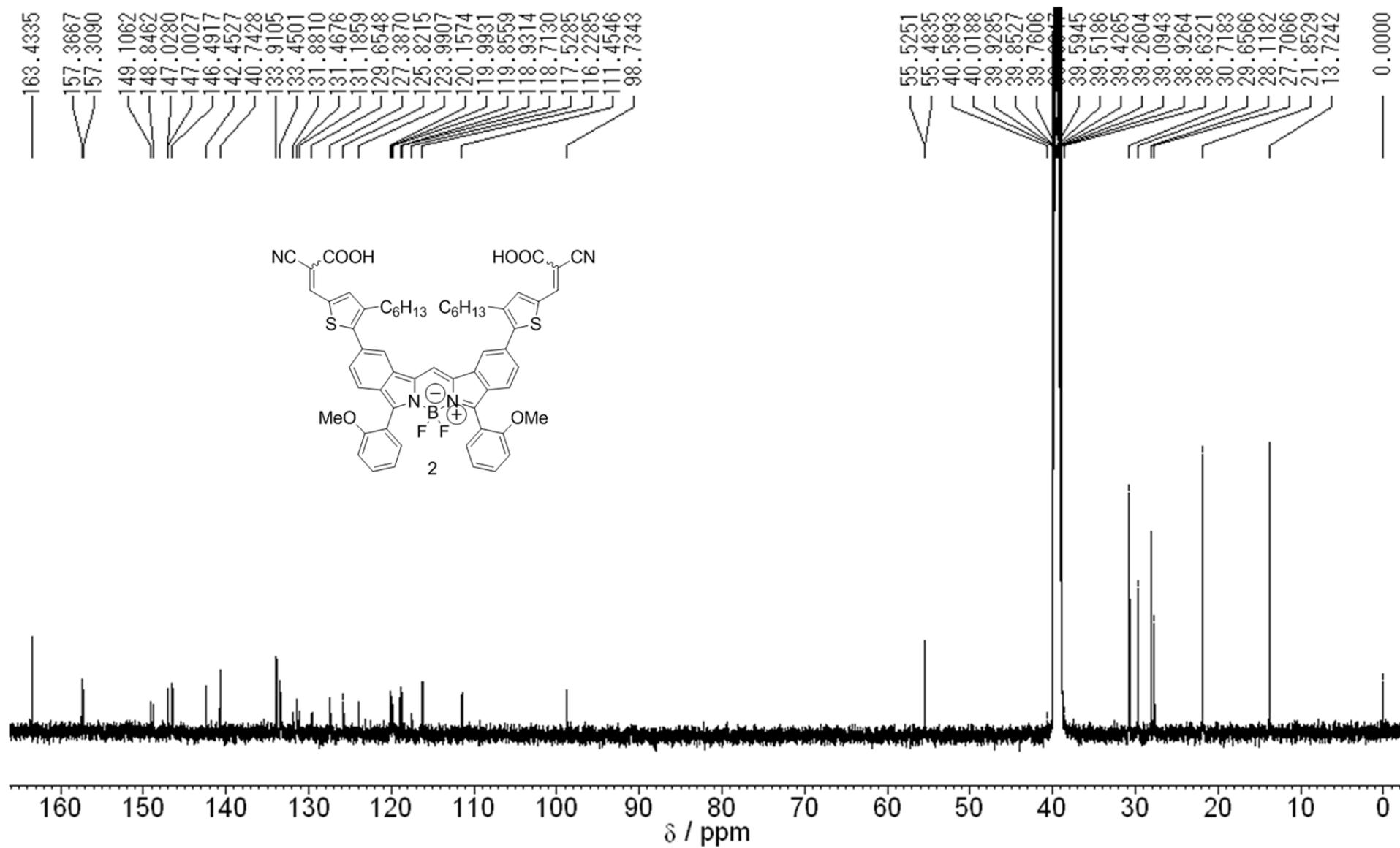


Figure S11. ^{13}C NMR spectrum of dye **2** in $\text{DMSO-}d_6$ at room temperature.

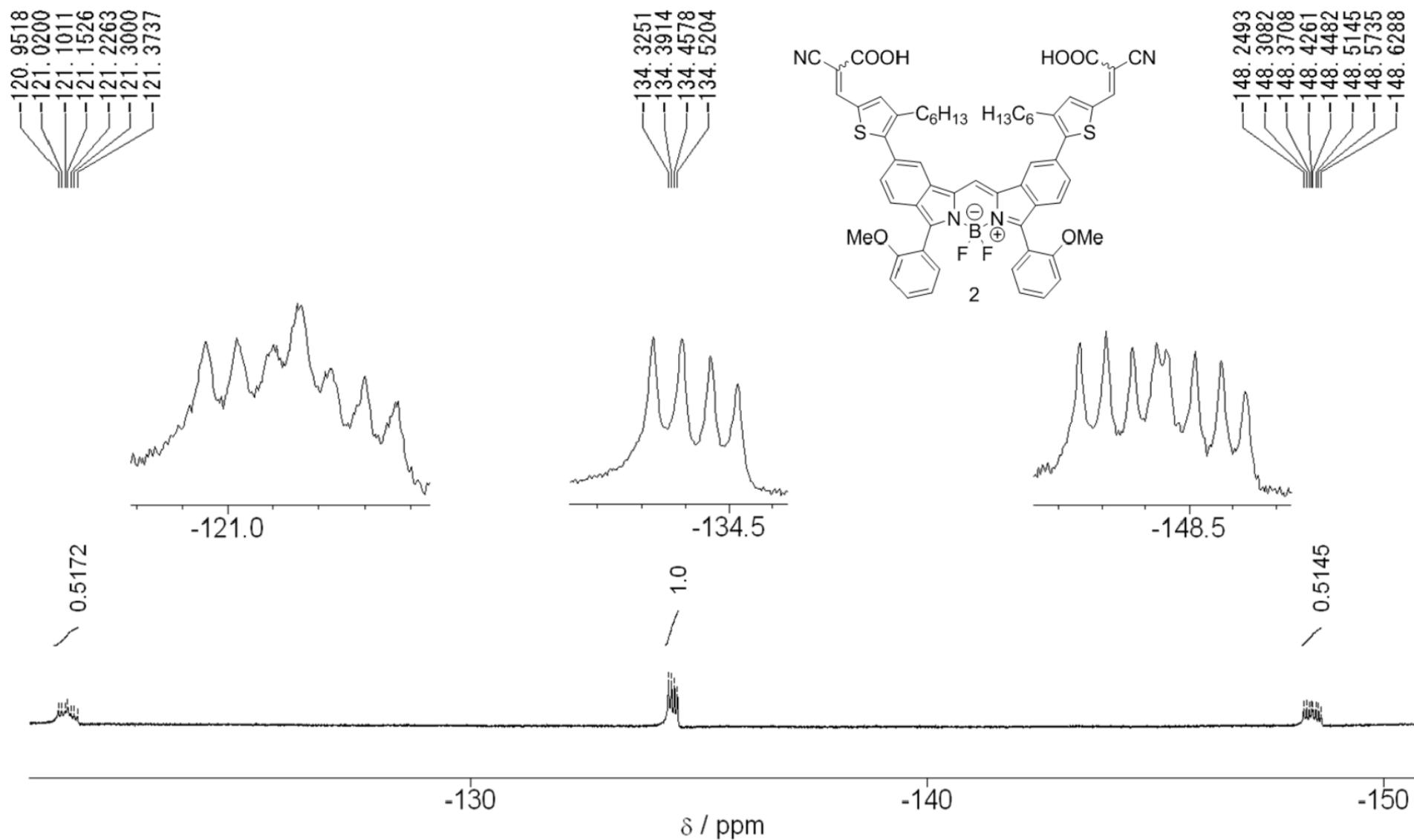


Figure S12. ^{19}F NMR spectrum of dye **2** in $\text{CDCl}_3:\text{DMSO}-d_6$ (3:7 v/v) at room temperature.