SUPPORTING INFORMATION

1,3,2-Dioxaborine-Based Mero-Polyanionic Dyes: High-Extinction NIR-Absorbing Polymethines

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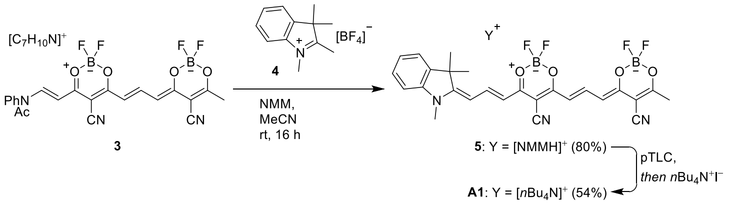
Experimental Procedures and Characterization Data

Anionic dyes **3** and **6**,[1] 5-cyano-2,2-difluoro-4,6-dimethyl-1,3,2-dioxaborine **7**,[2] merocyanine **1**,[2] were prepared according to published methods. Anionic dye **11** was prepared as a complex with acetanilide according to the reported procedure.[2] Hemicyanine **9**, 1,2,3,3-tetramethyl-3H-indolium tetrafluoroborate **4** and other reagents were purchased from commercial sources.



Anionic dye 5. A solution of **3** (0.8 g, 1.31 mmol, 1.0 eq.), compound **4** (0.48 g, 1.82 mmol, 1.4 eq.), and *N*-methylmorpholine (0.38 g, 3.94 mmol, 3.0 eq.) in MeCN (13 mL) was stirred at r. t. for 16 h. Then the reaction mixture was concentrated under reduced pressure and the residue was triturated with *i*PrOH (40 mL) until fine solid was precipitated. The solid was collected by filtration and rinsed by *i*PrOH (30 mL) to give **5** (0.67 g, 1.05 mmol, 47%) as a dark blue solid. The obtained compound was put into further transformations without additional purification.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ_H 9.59 (br s, 1H), 8.26 (t, *J* = 13.2 Hz, 1H), 8.06 (t, *J* = 13.2 Hz, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.43–7.28 (m, 2H), 7.20 (t, *J* = 7.1 Hz, 1H), 6.32 (d, *J* = 13.2 Hz, 1H), 6.16 (d, *J* = 13.2 Hz, 1H), 6.15 (d, *J* = 12.2 Hz, 1H), 5.65 (d, *J* = 12.2 Hz, 1H), 3.96 (br s, 2H), 3.66–3.49 (m, 5H), 3.34 (br s, 2H; *overlaid with water residue*), 3.07 (br s, 2H), 2.81 (s, 3H), 2.24 (s, 3H), 1.60 (s, 6H) ppm.

^{13}C NMR (76 MHz, DMSO-d$_6$): δ_C 179.5, 174.1, 172.96, 172.3, 164.1, 146.8, 143.9, 142.9, 140.4, 128.3, 124.3, 122.2, 116.8, 116.5, 110.6, 109.0, 107.0, 100.2, 99.7, 85.3, 82.8, 63.4, 52.6, 48.4, 42.5, 30.8, 27.8, 22.2 ppm.

^{19}F NMR (188 MHz, DMSO-d$_6$): δ_F –143.13 (^{10}B, 0.2F), –143.19 (^{11}B, 0.8F), –143.35 (^{10}B, 0.2F), –143.40 (^{11}B, 0.8F) ppm.

Elemental analysis calcd. (%) for $C_{31}H_{34}B_2F_4N_4O_5$: C 58.16, H 5.35, N 8.75; found: C 58.33, H 5.31, N 8.94.

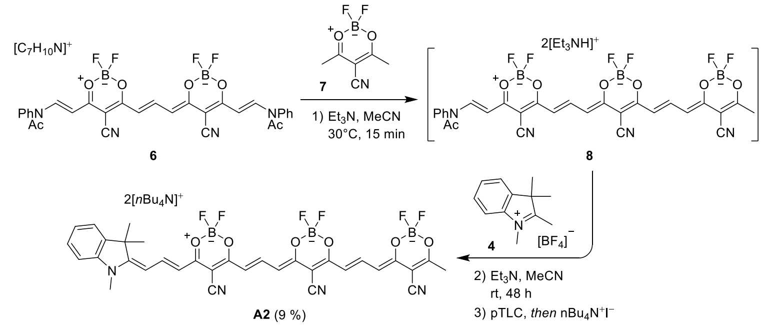
Anionic dye A1. Dye **5** (0.23 g, 0.36 mmol) was purified by preparative thin layer chromatography on silica gel (DCM/acetone = 17:3 (v/v)). The solid (0.15 g), which was isolated after pTLC, was dissolved in an aq. 50% MeCN (6 mL) and freshly prepared solution of tetra-*n*-butylammonium iodide (0.42 g, 1.14 mmol) in an aq. 50% MeCN (1.5 mL) was added to the dye's solution. Immediately after the addition slurry residue was precipitated. *i*PrOH (0.5 mL) was added to the mixture and the slurry residue was triturated upon the precipitation into fine solid. The solid was collected by filtration, washed with aq. 50% MeCN (3 mL) and aq. 50% EtOH (6 mL) to yield **A1** (0.15 g, 0.19 mmol, 54%) as a blue solid.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ_H 8.25 (t, *J* = 13.4 Hz, 1H), 8.07 (t, *J* = 13.4 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.42–7.28 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.33 (d, *J* = 13.3 Hz, 1H), 6.33 (d, *J* = 13.4 Hz, 1H), 6.16 (d, *J* = 13.4 Hz, 1H), 6.15 (d, *J* = 12.8 Hz, 1H), 5.65 (d, *J* = 12.8 Hz, 1H), 3.55 (s, 3H), 3.15 (br. t, *J* = 7.8 Hz, 8H), 2.24 (s, 3H), 1.64–1.49 (m, 14H), 1.30 (sxt, *J* = 7.4 Hz, 9H), 0.93 (t, *J* = 7.4 Hz, 12H) ppm.

^{13}C NMR (76 MHz, DMSO-d$_6$): δ$_C$ 179.5, 174.1, 172.9, 172.3, 164.1, 146.8, 143.9, 142.9, 140.4, 128.4, 124.3, 122.2, 116.7, 116.5, 110.6, 108.9, 107.0, 100.2, 99.7, 85.3, 82.8, 57.5, 48.4, 30.8, 27.8, 23.0, 22.2, 19.2, 13.5 ppm.

^{19}F NMR (188 MHz, DMSO-d$_6$): δ$_F$ –142.95 (^{10}B, 0.2F), –143.01 (^{11}B, 0.8F), –143.14 (^{10}B, 0.2F), –143.20 (^{11}B, 0.8F).

Elemental analysis calcd. (%) for $C_{42}H_{58}B_2F_4N_4O_4$: C 64.63, H 7.49, N 7.18; found: C 64.80, H 7.59, N 7.24.



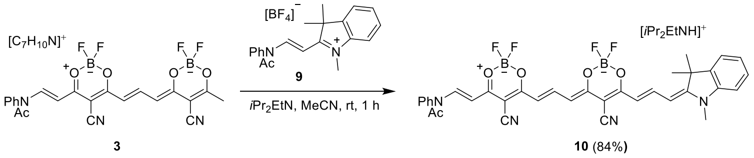
Dianionic dye A2. A mixture of compound **6** (0.50 g, 0.66 mmol, 1.0 eq.), dioxaborine **7** (0.16 g, 0.92 mmol, 1.4 eq.) and triethylamine (0.20 g, 1.98 mmol, 3.0 eq.) in MeCN (7 mL) was stirred at 30°C for 15 min, then compound **4** (0.29 g, 1.12 mmol, 1.7 eq.) and triethylamine (0.20 g, 1.98 mmol, 3.0 eq.) were added, and the resulting mixture was stirred at r. t. for 24 h. Additional portions of **4** (0.09 g, 0.33 mmol, 0.5 eq.) and triethylamine (0.13 g, 1.32 mmol, 2.0 eq.) were added and the mixture was stirred at r. t. for another 24 h. The reaction mixture was concentrated under reduced pressure, the residue was triturated with methanol (10 mL) and the precipitated solid was collected by filtration. The solid was suspended in DCM (15 mL), stirred at r. t. for 15 min, filtrated, and purified by preparative thin layer chromatography on silica gel (DCM/acetone = 1:1 (v/v)). The solid (0.092 g), which was isolated after pTLC, was dissolved in an aq. 50% MeCN (4 mL) and freshly prepared solution of tetra-*n*-butylammonium iodide (0.23 g, 0.62 mmol) in an aq. 50% MeCN (1.5 mL) was added to the dye's solution. Immediately after the addition fine solid was precipitated. The solid was collected by filtration and rinsed by aq. 50% MeCN (7 mL), aq. 50% EtOH (10 mL), and MTBE (5 mL) to yield **A2** (0.07 g, 0.058 mmol, 9 %) as a black solid.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ$_H$ 8.19–8.06 (m, 2H), 7.92 (t, *J* = 13.4 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.15 (d, *J* = 13.4 Hz, 1H), 6.14 (d, *J* = 13.4 Hz, 1H), 6.11 (d, *J* = 13.4 Hz, 1H), 5.96 (d, *J* = 13.4 Hz, 1H), 5.83 (d, *J* = 13.4 Hz, 1H), 5.53 (d, *J* = 12.8 Hz, 1H), 3.46 (s, 3H), 3.15 (br. t, *J* = 7.8 Hz, 16H), 2.20 (s, 3H), 1.62 – 1.47 (m, 22H), 1.30 (sxt, *J* = 7.4 Hz, 45H), 0.93 (t, *J* = 7.4 Hz, 24H) ppm.

^{13}C NMR (76 MHz, DMSO-d$_6$): δ$_C$ 177.8, 172.8, 172.3, 171.7, 170.1, 169.3, 161.7, 144.3, 144.3, 143.3, 141.4, 139.9, 128.2, 123.2, 122.1, 117.1, 117.0, 116.9, 110.0, 109.7, 108.5, 105.1, 102.8, 98.9, 98.5, 85.0, 82.6, 82.10, 58.0, 57.5, 47.6, 30.3, 28.0, 23.0, 22.0, 19.2, 13.5 ppm.

^{19}F NMR (376 MHz, DMSO-d$_6$): δ$_F$ –142.57 (^{10}B, 0.2F), –143.63 (^{11}B, 0.8F), –143.89 (^{10}B, 0.2F), –143.95 (^{11}B, 0.8F), –144.01 (^{10}B, 0.2F), –144.07 (^{11}B, 0.8F).

Elemental analysis calcd. (%) for $C_{65}H_{97}B_3F_6N_6O_6$: C 64.79, H 8.11, N 6.97; found: C 64.93, H 8.18, N 7.10.



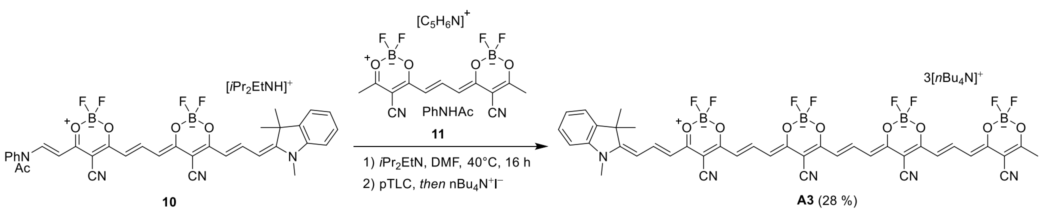
Intermediate 10. A solution of **3** (0.80 g, 1.31 mmol, 1.0 eq.), hemicyanine **9** (0.56 g, 1.38 mmol, 1.05 eq.), and *N,N*-diisopropylethylamine (0.51 g, 3.93 mmol, 3.0 eq.) in MeCN (7 mL) was stirred at r. t. for 1 h. Then the reaction mixture was concentrated under reduced pressure, the residue was triturated with hot MeOH/MeCN 30:1 mixture and the precipitated solid collected by filtration. The solid was rinsed by MeOH (10 mL) and MTBE (20 mL) to give **10** (0.90 g, 1.11 mmol, 84 %) as a blue solid. The compound was put into further transformations without additional purification.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ_H 8.56 (d, *J* = 13.5 Hz, 1H), 8.26 (t, *J* = 13.2 Hz, 1H), 8.10 (t, *J* = 12.8 Hz, 1H), 8.10 (br s, 1H; *this [iPr$_2$EtN–H]$^+$ peak overlapped with triplet at 8.10 ppm*), 7.66–7.54 (m, 3H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.20 (d, *J* = 13.5 Hz, 1H), 6.16 (d, *J* = 13.2 Hz, 1H), 6.10 (d, *J* = 13.5 Hz, 1H), 5.66 (d, *J* = 12.8 Hz, 1H), 5.19 (d, *J* = 13.2 Hz, 1H), 3.63 (br s, 3H), 3.51 (s, 3H), 3.15 (s, 2H; *overlapped with water residue*), 1.98 (s, 3H), 1.61 (s, 6H), 1.28 (s, 15H) ppm.

^{13}C NMR (76 MHz, DMSO-d$_6$): δ_C 173.6, 172.3, 171.8, 169.5, 165.5, 146.2, 143.9, 143.0, 140.3, 140.1, 137.9, 130.4, 129.7, 128.3, 124.1, 122.2, 116.6, 116.2, 110.4, 108.3, 107.4, 101.9, 101.4, 99.8, 83.9, 82.8, 53.6, 48.2, 41.9, 27.9, 23.2, 18.1, 16.7, 12.5 ppm.

^{19}F NMR (188 MHz, DMSO-d$_6$): δ_F −143.30 (^{11}B, 0.8F), −143.21 (^{11}B, 0.8F) ppm; *coupling to ^{10}B was not clearly resolved.*

Elemental analysis calcd. (%) for $C_{43}H_{49}B_2F_4N_5O_5$: C 63.49, H 6.07, N 8.61; found: C 63.62, H 6.18, N 8.78.



Trianionic dye A3. A mixture of **10** (0.28 g, 0.35 mmol, 1.0 eq.), anionic dye **11** (0.28 g, 0.49 mmol, 1.4 eq.), and *N,N*-diisopropylethylamine (0.63 g, 4.9 mmol, 14.0 eq.) in DMF (3 mL) was stirred at 40 °C for 16 h. Then MTBE (40 mL) was added to the solution, resulting mixture was kept at −10 °C for 1 h and the MTBE solution was decanted. Water (40 mL) was added to the slurry residue and the mixture was triturated until fine solid was precipitated, which was then collected by filtration. The isolated solid (0.29 g) was purified by preparative thin layer chromatography on silica gel (DCM/acetone = 2:3 (v/v)). The solid (0.17 g), which was isolated after pTLC, was dissolved in an aq. 50 % MeCN (5 mL) and freshly prepared solution of tetra-*n*-butylammonium iodide (0.41 g, 1.11 mmol) in an aq. 50 % MeCN (2 mL) was added to the dye's solution. Immediately after the addition fine solid was precipitated. The solid was collected by filtration and rinsed by aq. 50 % MeCN (10 mL), aq. 50 % EtOH (10 mL), and MTBE (5 mL) to yield **A3** (0.16 g, 0.098 mmol, 28 %) as a black solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ_H 8.07 (t, *J* = 14.0 Hz, 1H), 8.04 (t, *J* = 13.8 Hz, 1H), 8.02 (t, *J* = 13.2 Hz, 1H), 7.84 (dd, *J* = 14.0, 12.8 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.14 (d, *J* = 13.2 Hz, 1H), 6.09 (d, *J* = 14.0 Hz, 1H), 6.02 (d, *J* = 13.8 Hz, 1H), 5.97 (d, *J* = 14.0 Hz, 1H), 5.89 (d, *J* = 13.2 Hz, 1H), 5.81 (d, *J* = 13.8 Hz, 1H), 5.71 (d, *J* = 12.8 Hz, 1H), 5.47 (d, *J* = 12.2 Hz, 1H), 3.39 (s, 3H), 3.14 (br. t, *J* = 8.2 Hz, 24H), 2.18 (s, 3H), 1.63–1.49 (m, 30H), 1.30 (sxt, *J* = 7.4 Hz, 24H), 0.93 (t, *J* = 7.4 Hz, 36H) ppm.

^{13}C NMR (76 MHz, DMSO-d_6): δ_C 176.9, 176.0, 171.8, 171.7, 170.8, 169.2, 168.3, 166.9, 160.3, 143.5, 142.7, 142.3, 139.9, 139.5, 128.1, 122.5, 121.9, 117.3, 117.2, 110.6, 109.6, 109.0, 106.5, 104.5, 102.9, 101.5, 98.4, 97.5, 84.8, 82.4, 81.9, 81.8, 57.5, 47.1, 29.9, 28.0, 23.0, 21.9, 19.2, 13.4 ppm.

^{19}F NMR (376 MHz, DMSO-d_6): δ_F –143.60 (^{10}B, 0.2F), –143.66 (^{11}B, 0.8F), –143.86 (^{10}B, 0.2F), –143.91 (^{11}B, 0.8F), –143.97 (^{11}B, 0.8F), –144.08 (^{10}B, 0.2F), –144.14 (^{11}B, 0.8F) ppm.

Elemental analysis calcd. (%) for $C_{88}H_{136}B_4F_8N_8O_8$: C 64.87, H 8.41, N 6.88; found: C 65.01, H 8.55, N 6.99.

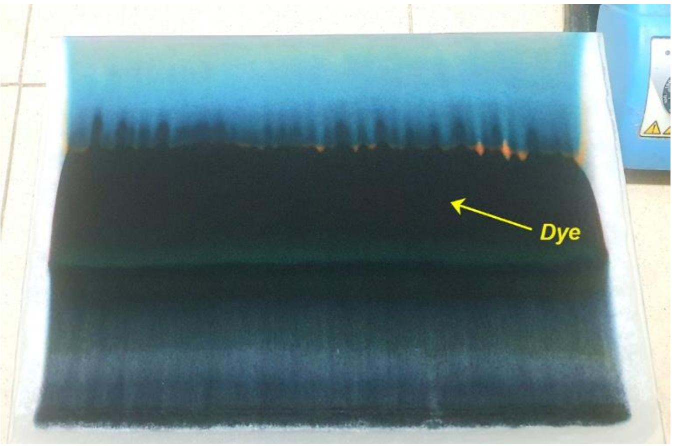
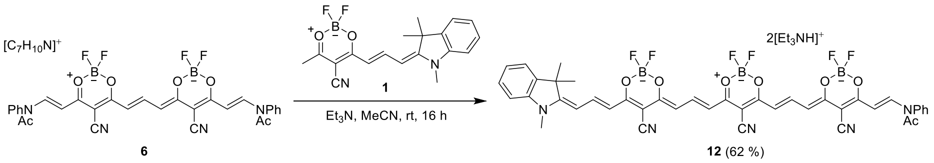


Figure S1. Developed preparative TLC plate of dye **A3** (with *N,N*-diisopropylethylammonium counterions)



Intermediate 12. A mixture of **6** (0.50 g, 0.66 mmol, 1.0 eq.), merocyanine **1** (0.25 g, 0.69 mmol, 1.05 eq.), and triethylamine (0.47 g, 4.62 mmol, 7.0 eq.) in MeCN (6 mL) was stirred at r. t. for 16 h. Then warm MTBE (18 mL) was added to the reaction mixture, the precipitate was collected by filtration and rinsed with MeCN/MTBE 1:3 (v/v) mixture (10 mL) to give **12** (0.44 g, 0.41 mmol,

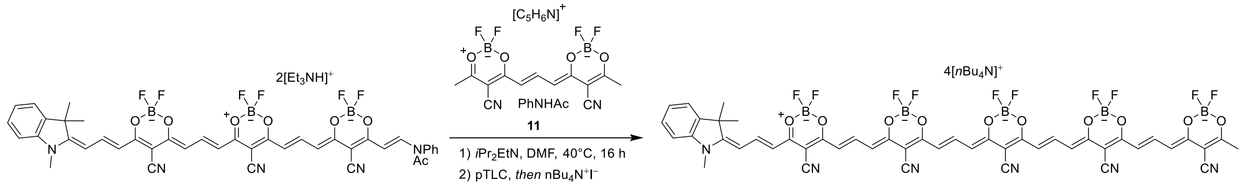
62 %) as a dark blue solid. The compound was put into further transformations without additional purification.

^{1}H NMR (300 MHz, DMSO-d$_6$): δ_H 8.86 (br s, 2H), 8.50 (d, J = 13.6 Hz, 1H), 8.11 (t, J = 13.2 Hz, 1H), 8.11 (t, J = 13.2 Hz, 1H), 7.90 (dd, J = 13.2, 12.4 Hz, 1H), 7.67–7.55 (m, 3H), 7.51–7.40 (m, 3H), 7.32 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.15 (d, J = 13.2 Hz, 1H), 6.11 (d, J = 13.2 Hz, 1H), 6.08 (d, J = 12.8 Hz, 1H), 5.93 (d, J = 13.2 Hz, 1H), 5.84 (d, J = 13.2 Hz, 1H), 5.55 (d, J = 12.4 Hz, 1H), 5.10 (d, J = 13.6 Hz, 1H), 3.44 (s, 3H), 3.15–3.03 (m, 12H), 1.95 (s, 3H), 1.57 (s, 6H), 1.17 (t, J = 7.3 Hz, 18H) ppm.

^{13}C NMR (76 MHz, DMSO-d$_6$): δ_C 172.5, 172.1, 171.2, 170.4, 169.8, 169.6, 169.4, 162.9, 144.2, 143.9, 143.3, 141.5, 139.8, 139.2, 138.0, 130.4, 129.6, 128.3, 128.2, 123.1, 122.0, 118.9, 117.1, 117.0, 116.5, 109.5, 108.8, 104.8, 103.3, 102.3, 100.4, 98.3, 83.8, 82.6, 82.1, 47.5, 45.8, 28.0, 23.2, 8.6 ppm.

^{19}F NMR (188 MHz, DMSO-d$_6$): δ_F –143.44 (^{10}B, 0.2F), –143.51 (^{11}B, 0.8F), –143.87 (^{10}B, 0.2F), –143.94 (^{11}B, 0.8F), –144.43 (^{10}B, 0.2F), –144.49 (^{11}B, 0.8F) ppm.

Elemental analysis calcd. (%) for $C_{54}H_{64}B_3F_6N_7O_7$: C 60.64, H 6.03, N 9.17; found: C 60.77, H 6.20, N 9.03.



12

A4 (10 %)

Tetraanionic dye A4. A mixture of **12** (0.37 g, 0.35 mmol, 1.0 eq.), anionic dye **11** (0.32 g, 0.56 mmol, 1.6 eq.), and *N,N*-diisopropylethylamine (0.68 g, 5.25 mmol, 15.0 eq.) in DMF (4 mL) was stirred at 40 °C for 16 h. Then MTBE (40 mL) was added to the solution, resulting mixture was kept at −10 °C for 1 h and the MTBE solution was decanted. Water (40 mL) was added to the slurry residue and the mixture was triturated until fine solid was precipitated, which was then collected by filtration. The isolated solid (0.54 g) was purified by preparative thin layer chromatography on silica gel (DCM/acetone = 2:3 (v/v)). The solid (0.165 g), which was isolated after pTLC, was dissolved in an aq. 50 % MeCN (4.5 mL) and freshly prepared solution of tetra-*n*-butylammonium iodide (0.46 g, 1.26 mmol) in an aq. 50 % MeCN (2.5 mL) was added to the dye's solution. Immediately after the addition fine solid was precipitated. The solid was collected by filtration and rinsed by aq. 50 % MeCN (10 mL), aq. 50 % EtOH (10 mL), and MTBE (5 mL) to yield **A4** (0.16 g, 0.078 mmol, 22 %) as a black solid.

^{1}H NMR (300 MHz, DMSO-d$_6$): δ_H 8.10–7.89 (m, 4H), 7.79 (t, J = 13.1 Hz, 1H), 7.42 (d, J = 7.3 Hz, 1H), 7.28 (t, J = 7.7 Hz, 1H), 7.09 (d, J = 7.7 Hz, 1H), 7.03 (t, J = 7.3 Hz, 1H), 6.14 (d, J = 13.7 Hz, 1H), 6.08 (d, J = 14.2 Hz, 1H), 6.03–5.60 (m, 7H), 5.43 (d, J = 12.2 Hz, 1H), 3.36 (s, 3H; *overlapped with water residue*), 3.14 (br. t, J = 7.3 Hz, 32H), 2.17 (s, 3H), 1.63–1.49 (m, 38H), 1.30 (sxt, J = 7.3 Hz, 32H), 0.93 (t, J = 7.3 Hz, 48H) ppm.

^{13}C NMR (76 MHz, DMSO-d$_6$): δ_C 176.3, 171.5, 171.1, 170.2, 168.9, 167.2, 167.2, 167.1, 165.2, 159.4, 143.6, 142.7, 142.3, 141.5, 141.0, 139.3, 139.0, 128.1, 122.1, 121.9, 117.6, 117.5, 117.3, 111.0, 110.3, 108.7, 107.5, 105.7, 104.4, 102.9, 101.6, 100.7, 98.2, 97.0, 84.8, 82.4, 81.7, 81.7, 81.6, 57.6, 46.9, 29.7, 28.1, 23.0, 21.8, 19.2, 13.4 ppm.

^{19}F NMR (376 MHz, DMSO-d$_6$): δ_F –143.73 (^{10}B, 0.2F), –143.79 (^{11}B, 0.8F), –143.93 (^{10}B, 0.2F), –144.0 (^{11}B, 0.8F), –144.04 (^{11}B, 0.8F), –144.05 (^{11}B, 0.8F), –144.21 (^{10}B, 0.2F), –144.28 (^{11}B, 0.8F) ppm. *coupling to ^{10}B was not clearly resolved*.

Elemental analysis calcd. (%) for $C_{111}H_{175}B_5F_{10}N_{10}O_{10}$: C 64.92, H 8.59, N 6.82; found: C 65.04, H 8.73, N 6.97.

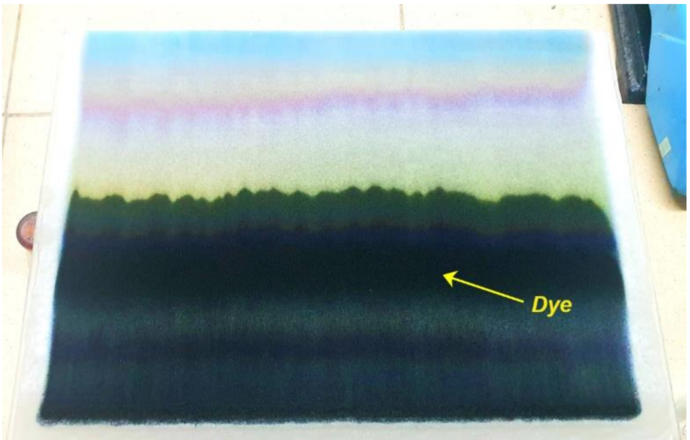
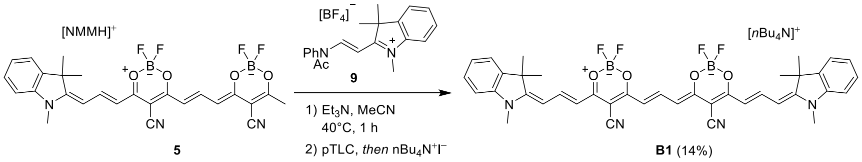


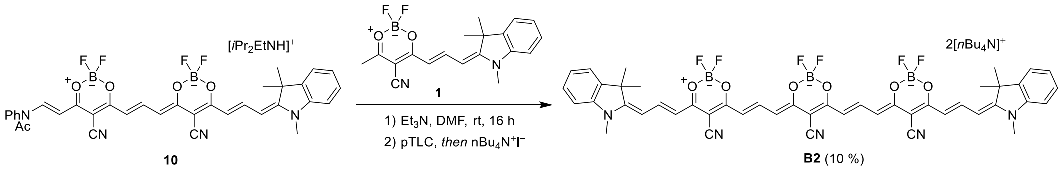
Figure S2. Developed preparative TLC plate of dye **A4** (with *N,N*-diisopropylethylammonium counterions)



Anionic dye B1. A solution of **5** (0.23 g, 0.36 mmol, 1.0 eq.), hemicyanine **9** (0.18 g, 0.43 mmol, 1.2 eq.), and triethylamine (0.18 g, 1.80 mmol, 5.0 eq.) in MeCN (3 mL) was stirred at r. t. for 16 h. Then the reaction mixture was concentrated under reduced pressure and the residue was triturated with *i*PrOH (10 mL) until fine solid was precipitated, which then was collected by filtration. The obtained solid was purified by preparative thin layer chromatography on silica gel (DCM/acetone = 11:4 (v/v)). The solid (0.065 g), which was isolated after pTLC, was dissolved in a MeCN/H$_2$O 3:2 mixture (10 mL) and freshly prepared solution of tetra-*n*-butylammonium iodide (0.12 g, 0.31 mmol) in an aq. 50% MeCN (0.5 mL) was added to the dye's solution. Immediately after the addition fine solid was precipitated. The solid was collected by filtration and washed with aq. 50% MeCN (3 mL) and MTBE (5 mL) to yield **B1** (0.05 g, 0.052 mmol, 14 %) as a black solid.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ_H 8.11 (t, *J* = 13.4 Hz, 1H), 8.08 (t, *J* = 13.4 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 2H), 6.15 (d, *J* = 13.4 Hz, 2H), 6.06 (d, *J* = 13.4 Hz, 2H), 5.88 (d, *J* = 13.4 Hz, 2H), 3.42 (s, 6H), 3.15 (br. t, *J* = 8.3 Hz, 8H), 1.60–1.51 (m, 20H), 1.30 (sxt, *J* = 7.4 Hz, 8H), 0.93 (t, *J* = 7.4 Hz, 12H) ppm.

^{13}C NMR (76 MHz, DMSO-d$_6$): δ_C 172.0, 170.3, 169.0, 144.0, 143.4, 143.1, 139.7, 128.1, 122.7, 122.0, 117.2, 103.7, 97.8, 81.9, 57.5, 47.3, 30.0, 28.0, 23.0, 19.2, 13.4 ppm.
^{19}F NMR (376 MHz, DMSO-d$_6$): δ_F –143.37 (^{10}B, 0.2F), –143.43 (^{11}B, 0.8F) ppm.
Elemental analysis calcd. (%) for $C_{55}H_{71}B_2F_4N_5O_4$: C 68.54, H 7.43, N 7.27; found: C 68.69, H 7.57, N 7.18.



10

1

B2 (10 %)

Dianionic dye B2. A mixture of **10** (0.41 g, 0.50 mmol, 1.0 eq.), merocyanine **2** (0.21 g, 0.6 mmol, 1.2 eq.), and triethylamine (0.40 g, 4.00 mmol, 8.0 eq.) in DMF (2 mL) was stirred at r. t. for 16 h. Then MTBE (40 mL) was added to the solution, resulting mixture was kept at −10 °C for 1 h and the MTBE solution was decanted. Water (40 mL) was added to the slurry residue and the mixture was triturated until fine solid was precipitated, which was then collected by filtration. The isolated solid (0.46 g) was purified by preparative thin layer chromatography on silica gel (DCM/acetone = 3:2 (v/v)). The solid (0.13 g), which was isolated after pTLC, was dissolved in an aq. 50 % MeCN (4.5 mL) and freshly prepared solution of tetra-*n*-butylammonium iodide (0.22 g, 0.60 mmol) in an aq. 50% MeCN (1.2 mL) was added to the dye's solution. Immediately after the addition fine solid was precipitated. The solid was collected by filtration and washed with aq. 50 % MeCN (mL), aq. 50 % EtOH (10 mL), and MTBE (5 mL) to yield **B2** (0.07 g, 0.050 mmol, 10 %) as a black solid.
^{1}H NMR (400 MHz, DMSO-d$_6$): δ_H 8.04 (t, J = 13.4 Hz, 2H), 8.00 (t, J = 13.4 Hz, 2H), 7.43 (d, J = 7.4 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 7.10 (d, J = 7.4 Hz, 2H), 7.04 (t, J = 7.4 Hz, 2H), 6.14 (d, J = 13.4 Hz, 2H), 5.97 (d, J = 13.4 Hz, 2H), 5.91 (d, J = 13.4 Hz, 2H), 5.76 (d, J = 13.4 Hz, 2H), 3.37 (s, 6H), 3.14 (br. t, J = 8.3 Hz, 16H), 1.63–1.50 (m, 28H), 1.30 (sxt, J = 7.4 Hz, 16H), 0.92 (t, J = 7.4 Hz, 24H) ppm.
^{13}C NMR (76 MHz, DMSO-d$_6$): δ_C 171.3, 171.0, 168.1, 167.5, 143.6, 142.9, 141.5, 139.4, 128.1, 122.2, 121.9, 117.4, 117.4, 110.0, 108.8, 105.2, 102.1, 97.2, 81.7, 57.5, 47.0, 29.7, 28.1, 23.0, 19.2, 13.4 ppm
^{19}F NMR (376 MHz, DMSO-d$_6$): δ_F –143.55 (^{10}B, 0.4F), –143.61 (^{11}B, 1.6F), –143.78 (^{10}B, 0.2F), –143.84 (^{11}B, 0.8F) ppm.
Elemental analysis calcd. (%) for $C_{78}H_{110}B_3F_6N_7O_6$: C 67.49, H 7.99, N 7.06; found: C 67.62, H 7.91, N 6.96.

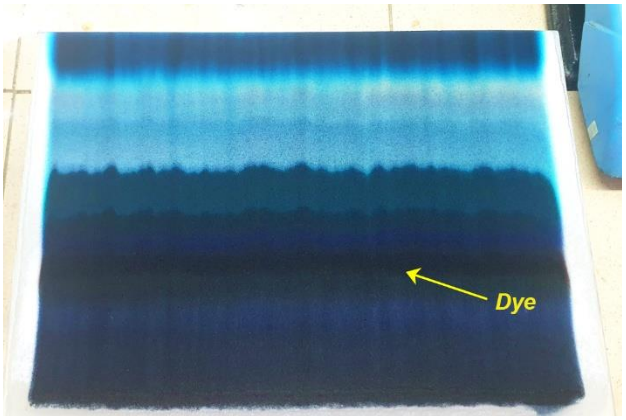
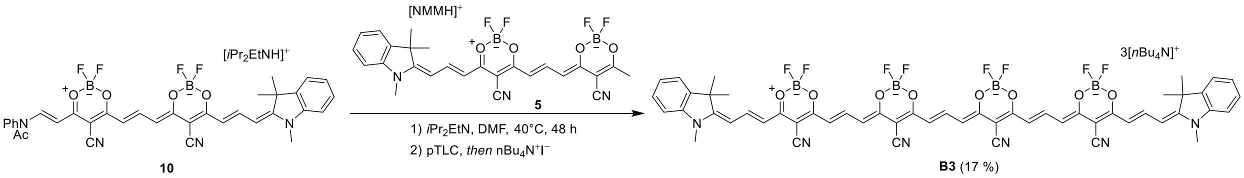


Figure S3. Developed preparative TLC plate of dye **B2** (with triethylammonium counterions)



Trianionic dye B3. A mixture of **10** (0.41 g, 0.50 mmol, 1.0 eq.), anionic dye **5** (0.35 g, 0.55 mmol, 1.1 eq.), and *N,N*-diisopropylethylamine (0.97 g, 7.50 mmol, 15.0 eq.) in DMF (4 mL) was stirred at 40 °C for 24 h. Then additional portion of *N,N*-diisopropylethylamine (0.34 g, 2.63 mmol, 5.25 eq.) was added and the reaction mixture was left stirring at 40 °C for another 24 h. Then MTBE (40 mL) was added to the solution, resulting mixture was kept at −10 °C for 1 h and the MTBE solution was decanted. Water (50 mL) was added to the slurry residue and the mixture was triturated until fine solid was precipitated, which was then collected by filtration. The isolated solid (0.68 g) was purified by preparative thin layer chromatography on silica gel (DCM/acetone = 3:2 (v/v)). The solid (0.23 g), which was isolated after pTLC, was dissolved in an aq. 50 % MeCN (10 mL) and freshly prepared solution of tetra-*n*-butylammonium iodide (0.65 g, 1.76 mmol) in an aq. 50 % MeCN (2.5 mL) was added to the dye's solution. Immediately after the addition fine solid was precipitated. The solid was collected by filtration and washed with aq. 50 % MeCN (12 mL), aq. 50 % EtOH (15 mL), and MTBE (10 mL) to yield **B1** (0.15 g, 0.083 mmol, 17 %) as a black solid.

^{1}H NMR (400 MHz, DMSO-d$_6$): δ_H 8.08–7.88 (m, 5H), 7.40 (d, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 7.4 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 2H), 6.14 (d, *J* = 13.4 Hz, 2H), 5.92 (d, *J* = 13.4, 2H), 5.91 (d, *J* = 13.4, 2H), 5.80 (d, *J* = 12.7 Hz, 2H), 5.68 (d, *J* = 12.7 Hz, 2H), 3.34 (s, 6H), 3.14 (br. t, *J* = 7.7 Hz, 24H), 1.67–1.45 (m, 36H), 1.30 (sxt, *J* = 7.3 Hz, 24H), 0.93 (t, *J* = 7.3 Hz, 36H) ppm.

^{13}C NMR (76 MHz, DMSO-d$_6$): δ_C 171.0, 170.8, 169.4, 166.6, 166.4, 143.7, 142.5, 141.8, 140.5, 139.3, 128.1, 121.9, 121.9, 117.7, 117.6, 110.6, 108.5, 106.2, 103.5, 101.2, 96.8, 81.6, 81.5, 57.5, 46.8, 29.6, 28.1, 23.0, 19.2, 13.4 ppm.

^{19}F NMR (188 MHz, DMSO-d_6): δ_F –144.09 (^{11}B, 0.8F), –144.25 (^{11}B, 0.8F). *coupling to ^{10}B was not clearly resolved*.

Elemental analysis calcd. (%) for $C_{101}H_{149}B_4F_8N_9O_8$: C 66.93, H 8.29, N 6.95; found: C 67.07, H 8.16, N 6.88.

X-Ray Diffraction Data

Table S1. Crystal data and structure refinement parameters.

	A1	**B1**
Formula	$C_{26}H_{22}B_2F_4N_3O_4^-$, $C_{16}H_{36}N^+$	$C_{39}H_{35}B_2F_4N_4O_4^-$, $C_{16}H_{36}N^+$
Unit cell a, Å	17.7626(12)	12.4841(4)
b, Å	9.5986(5)	19.6198(5)
c, Å	24.9869(15)	23.1211(7)
α, deg	90.0	90.0
β, deg	98.100(5)	98.004(2)
γ, deg	90.0	90.0
V, $Å^3$	4217.7(4)	5608.0(3)
F(000)	1664	2056
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Z	4	4
T, K	173(2)	173(2)
μ, mm^{-1}	0.090	0.080
D_{calc}, g/cm^3	1.229	1.142
$2\Theta_{max}$, grad	50.0	50.0
Measured reflections	57065	81354
Independent reflections	7423	9869
R_{int}	0.1133	0.0465
Reflections with F>4σ(F)	2946	6660
Parameters	513	641
R_1 [I>2σ(I)]	0.0979	0.0566
wR_2 [I>2σ(I)]	0.1362	0.1361
R_1 [all data]	0.2536	0.0903
wR_2 [all data]	0.1846	0.1619
S	1.008	1.040
CCDC number	2548387	2548388

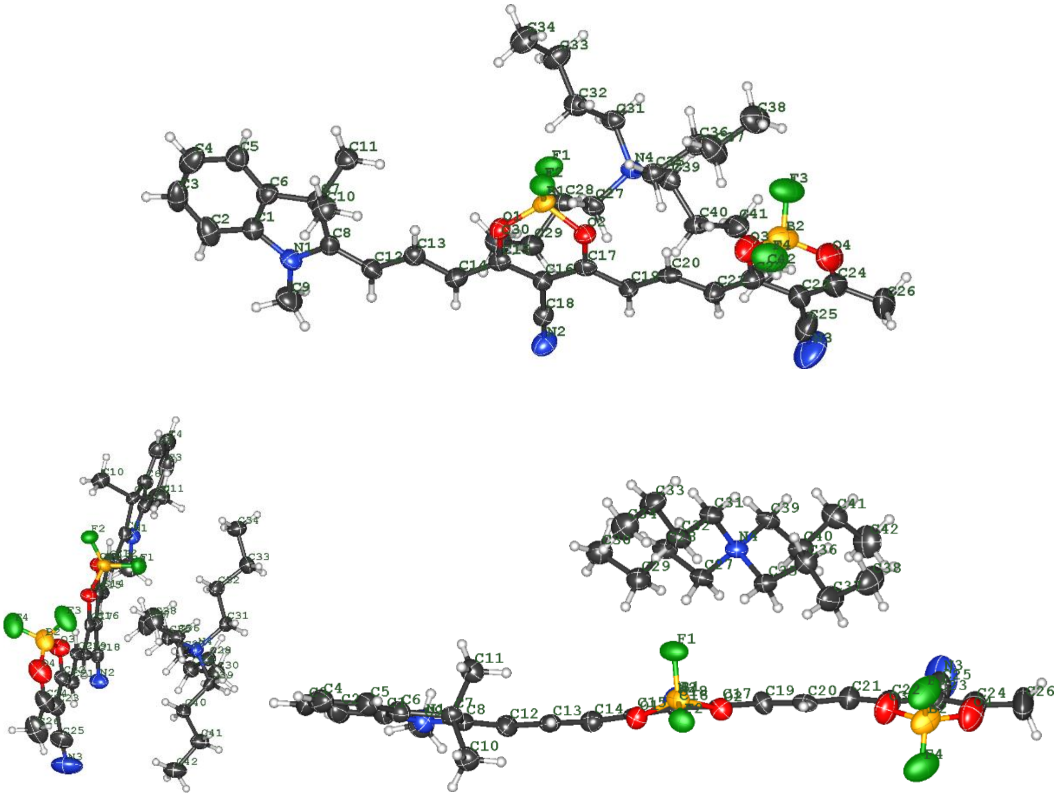


Figure S4. Molecular structure of **A1**. ORTEP probability level 50%.

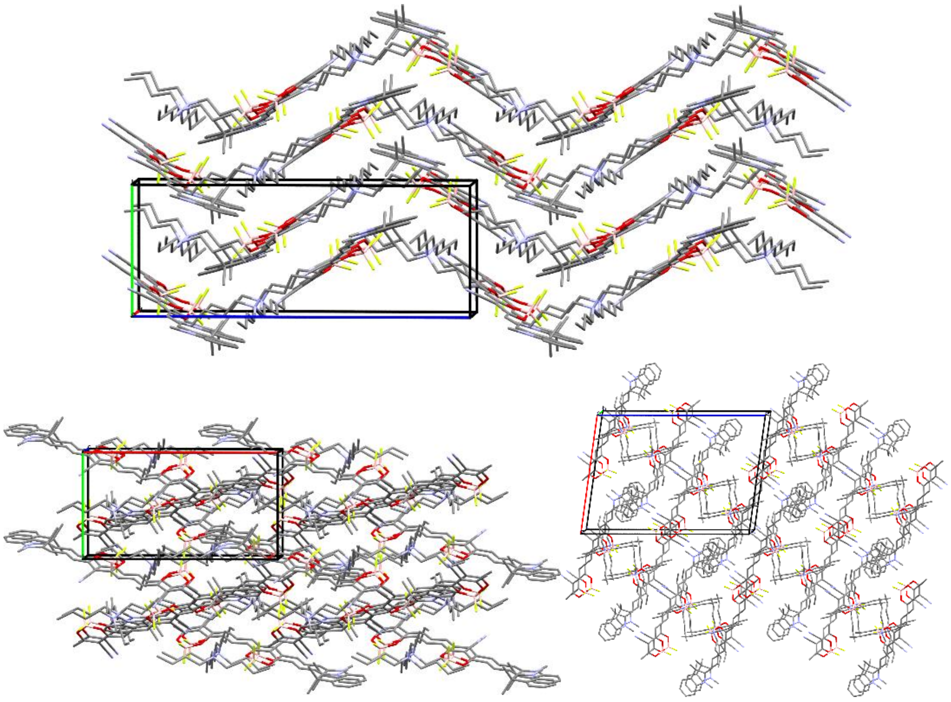


Figure S5. Molecular packing of **A1**

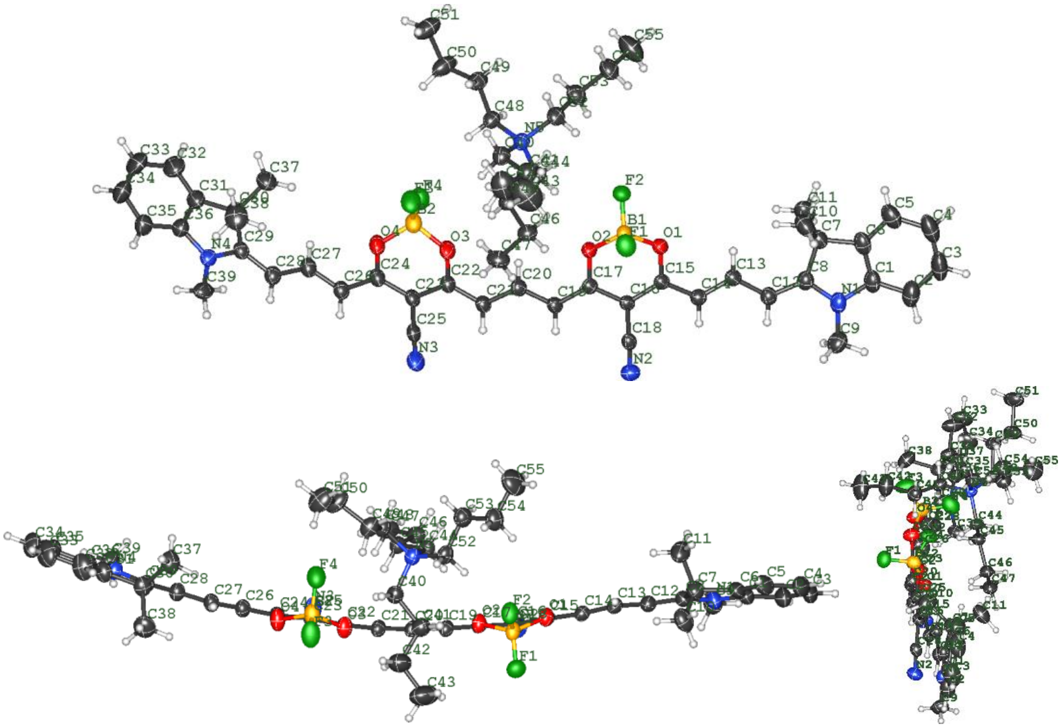


Figure S6. Molecular structure of **B1**. ORTEP probability level 50%.

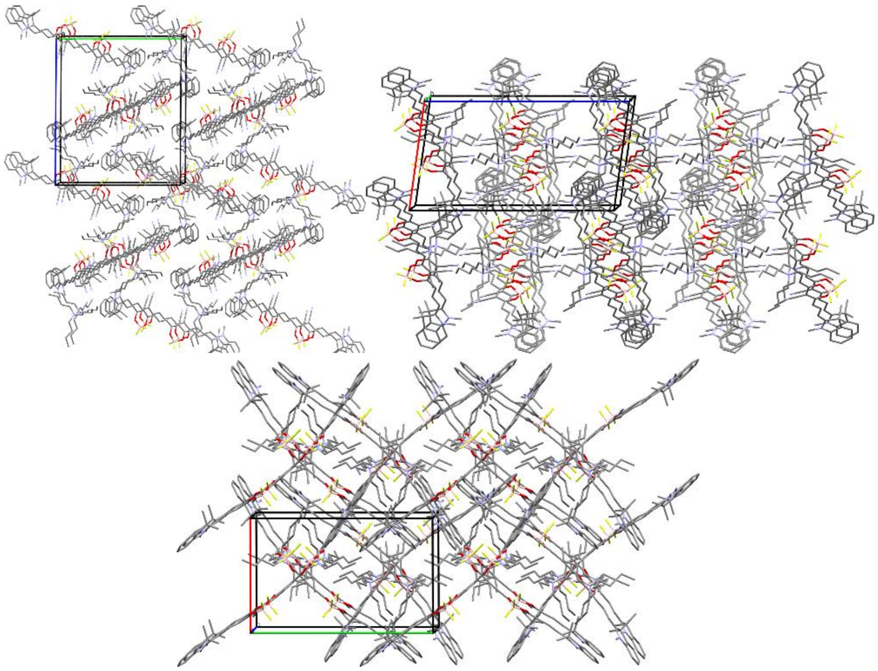


Figure S7. Molecular packing of **B1**

Additional Spectroscopic Data

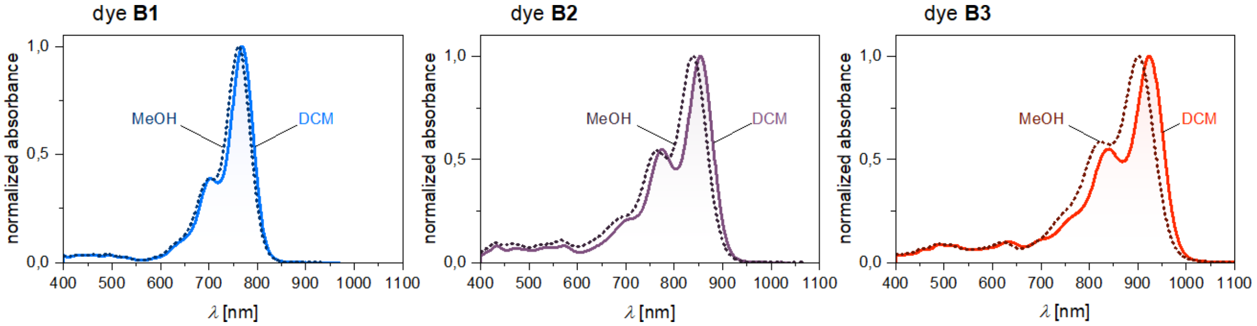


Figure S8. Absorption bands of dyes **B1**, **B2**, and **B3** in MeOH and DCM.

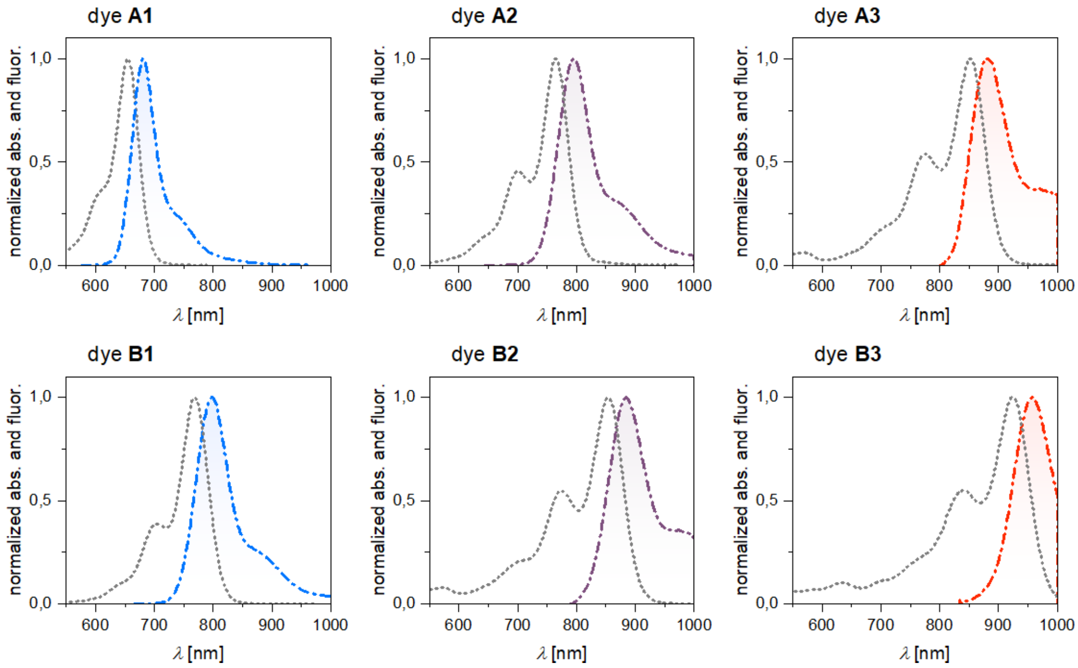


Figure S9. Absorption (grey dotted lines) and emission (colored lines) bands of the dyes **A1**–**A3** and **B1**–**B3** in DCM.

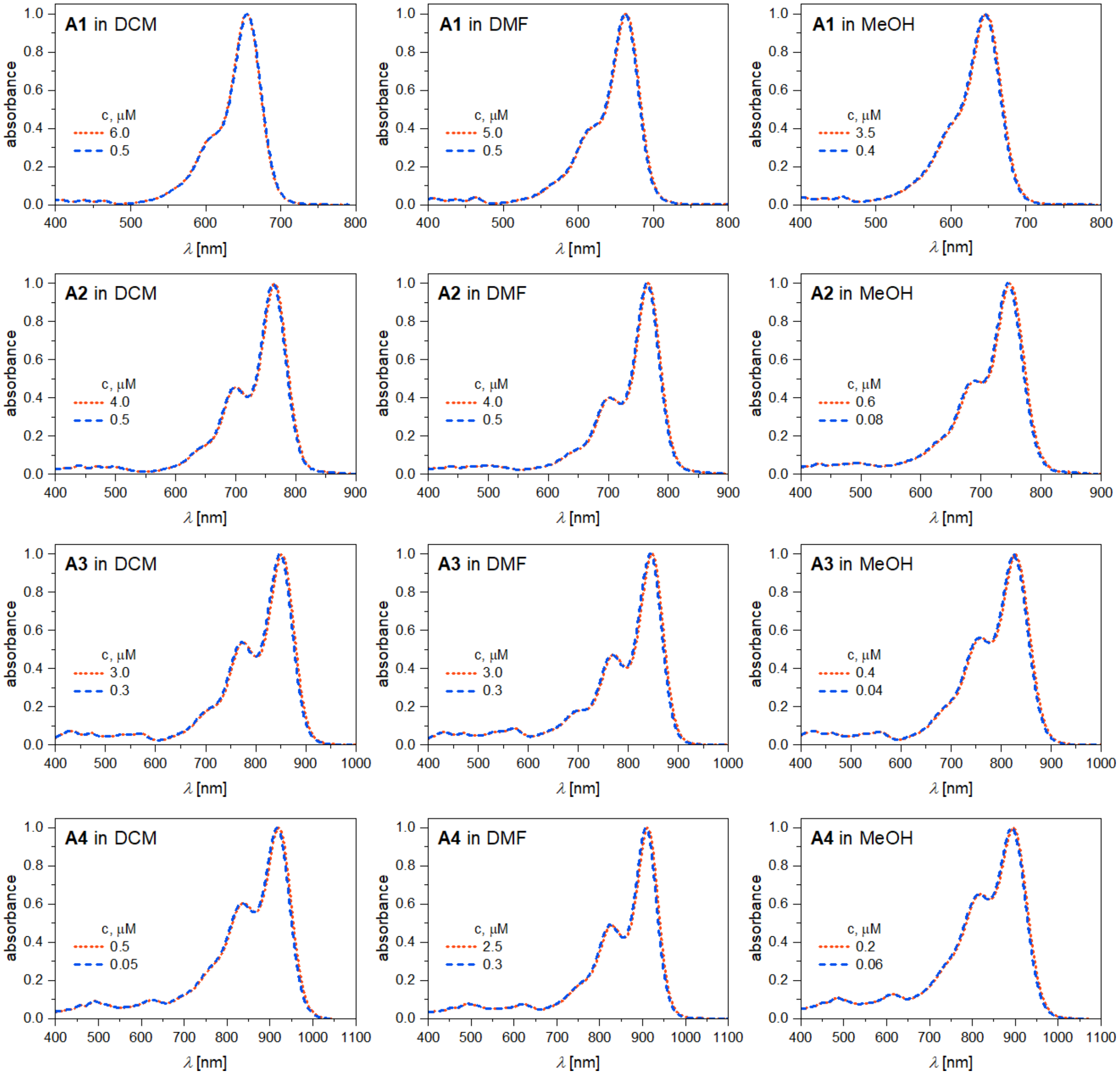


Figure S10. Normalized absorption spectra of dyes **A1**–**A4** in DCM, DMF, and MeOH at different concentrations.

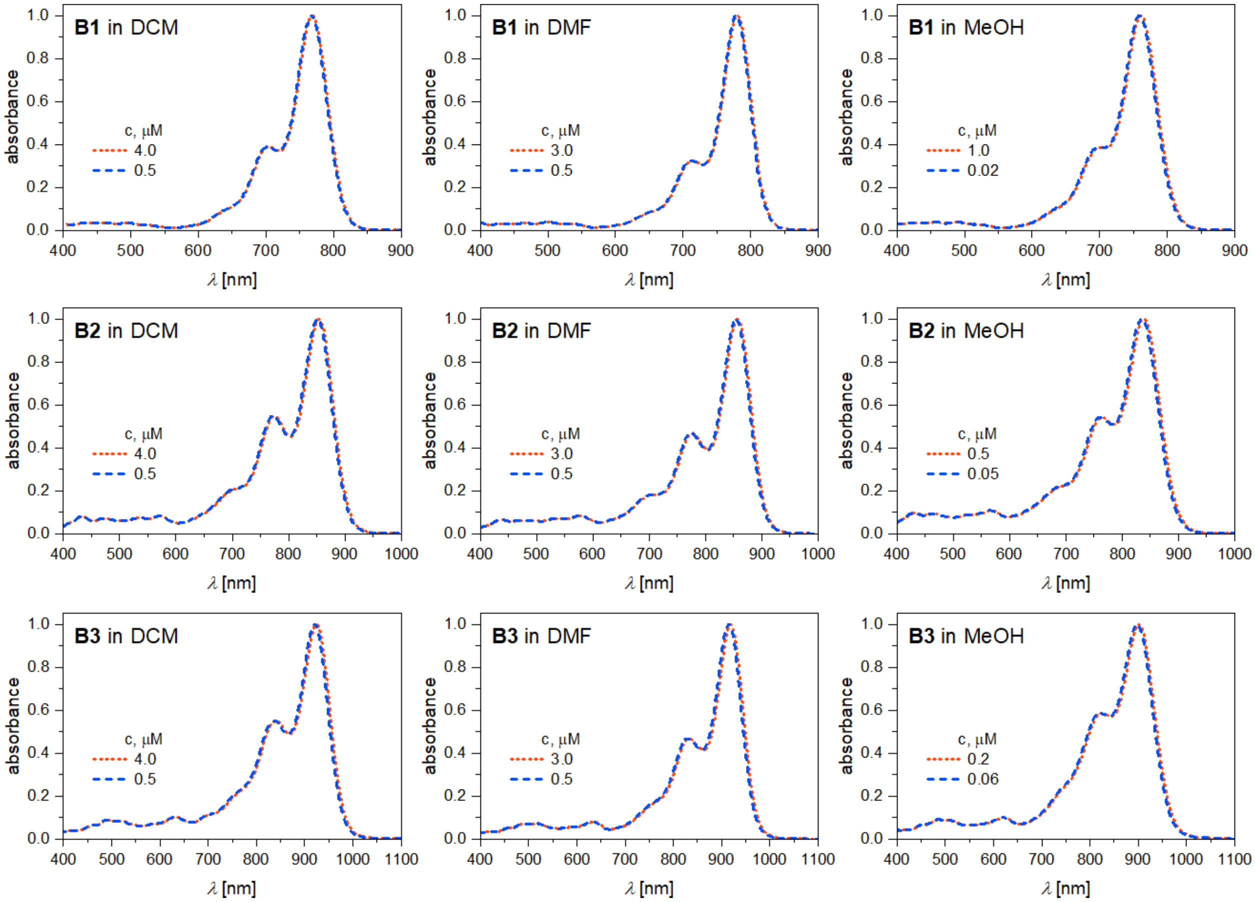


Figure S11. Normalized absorption spectra of dyes **B1**–**B3** in DCM, DMF, and MeOH at different concentrations.

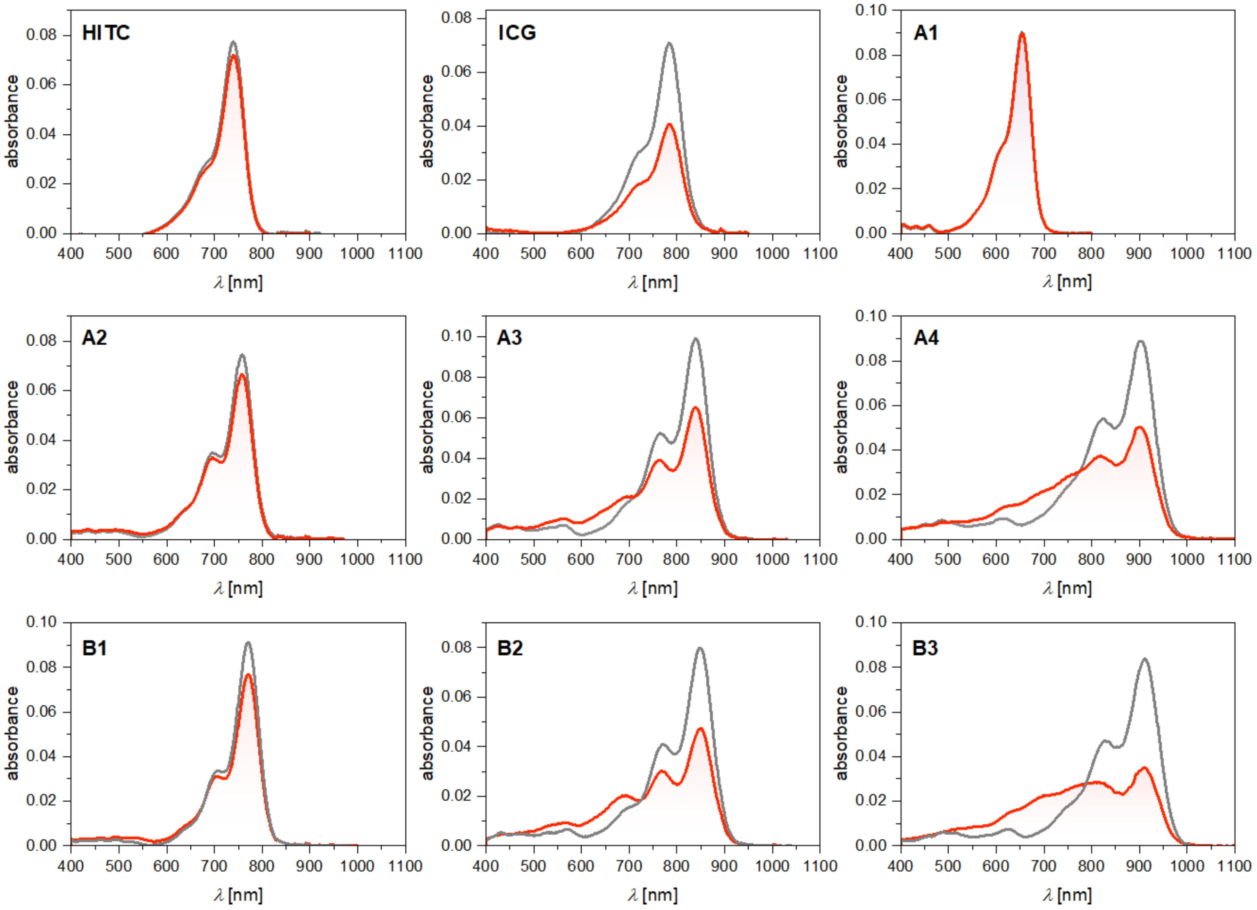


Figure S12. Absorption bands of the studied dyes in MeCN before (grey lines) after 30 min of irradiation by UV light (λ_{ex} = 300 nm; orange lines).

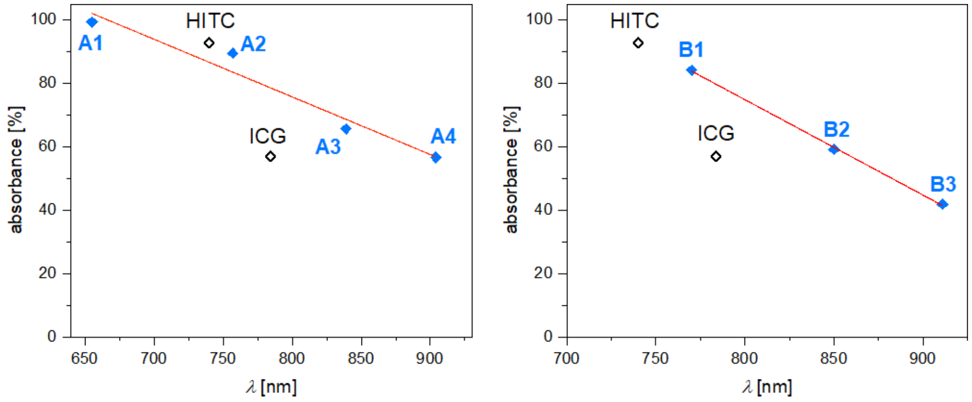


Figure S13. Absorption intensities of dyes in % after 30 min of irradiation by UV light (λ_{ex} = 300 nm) relative to 100 % (absorption intensity before irradiation).

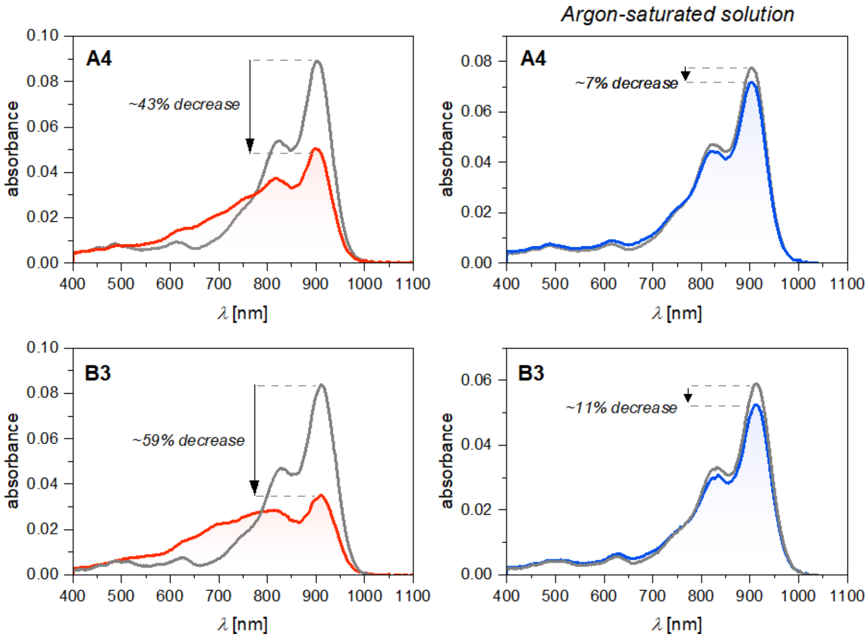
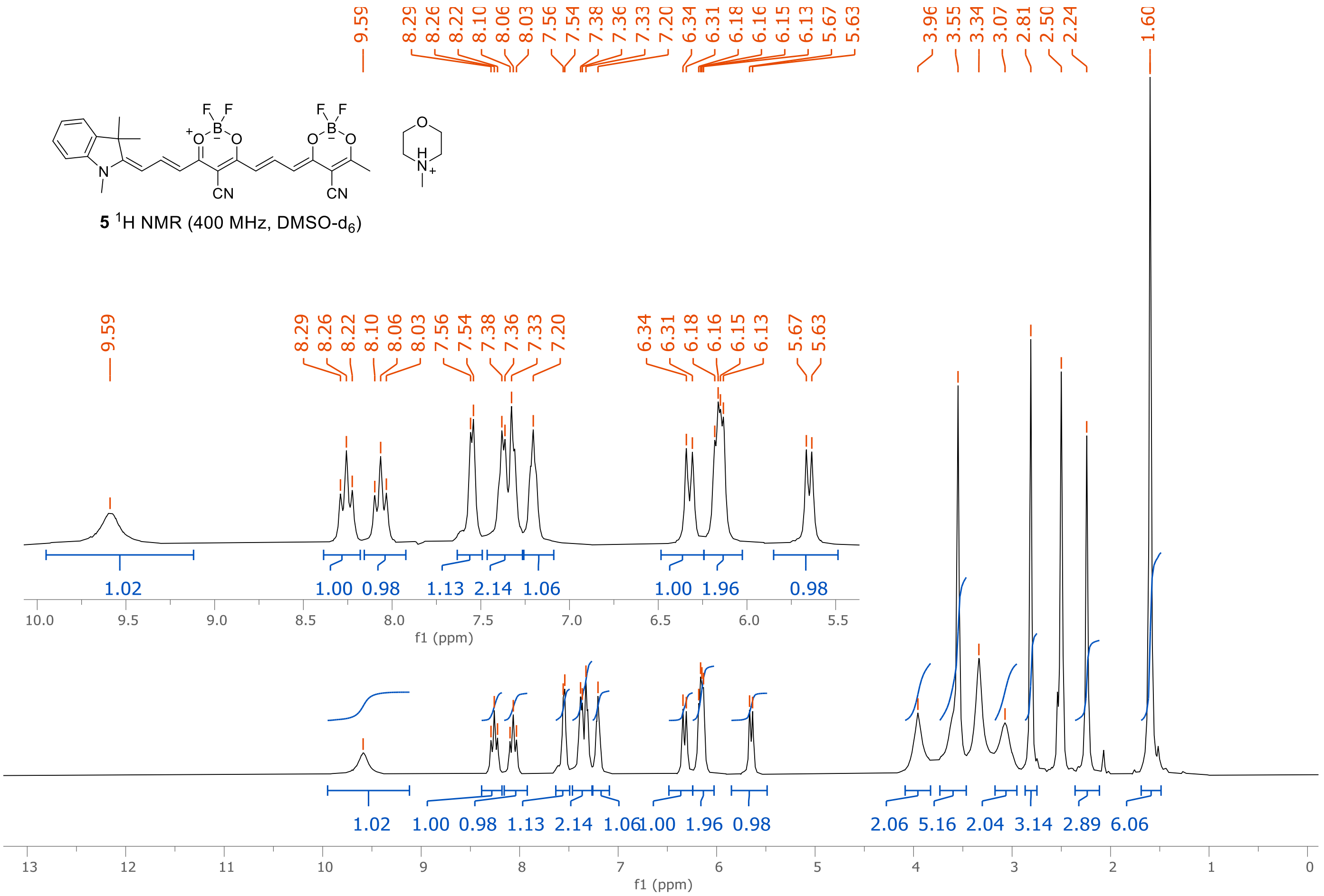
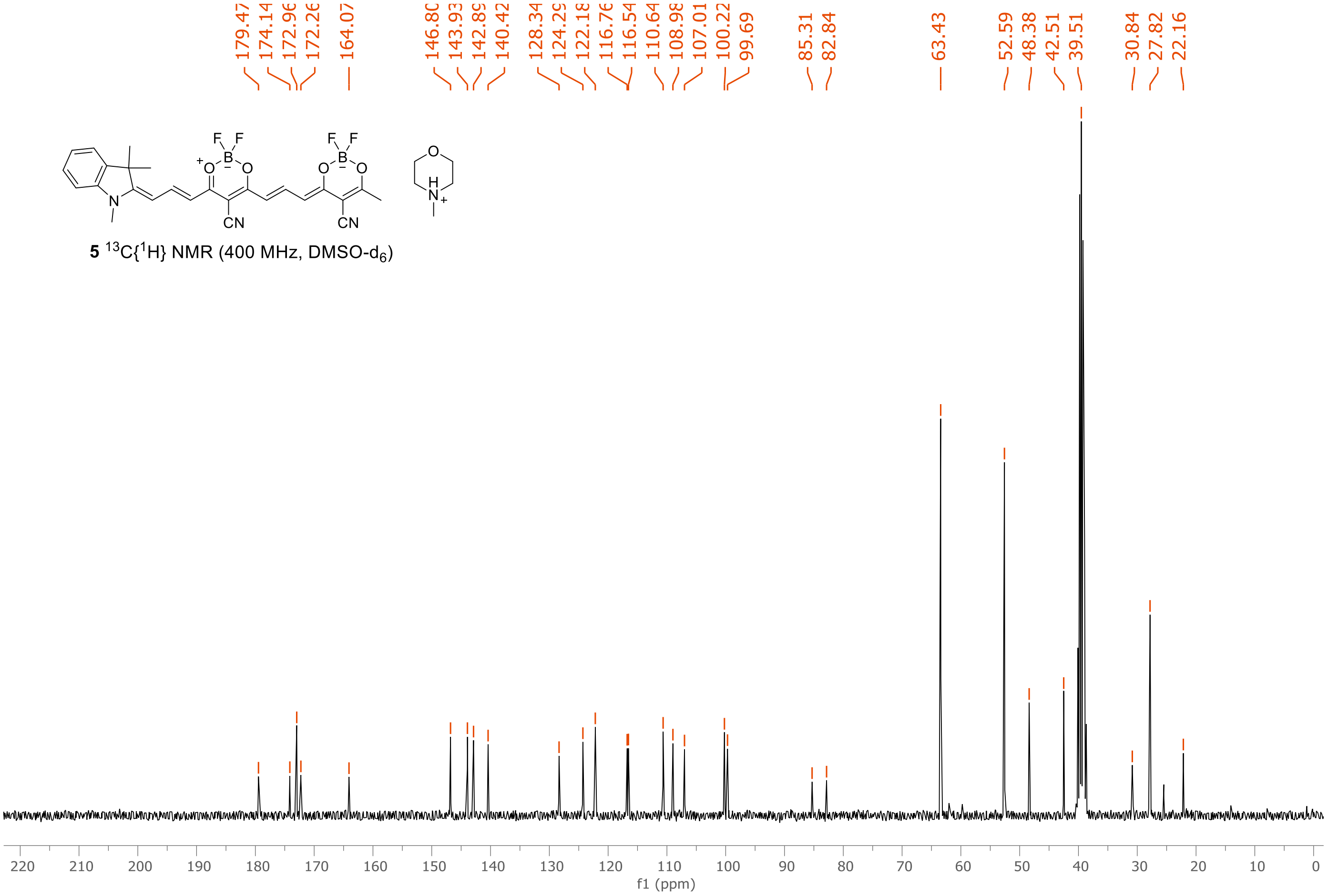


Figure S14. Absorption bands of the studied dyes in non-degassed MeCN (left graphs) and argon-saturated MeCN (right graphs) before (grey lines) after 30 min of irradiation by UV light (λ_{ex} = 300 nm; orange and blue lines).

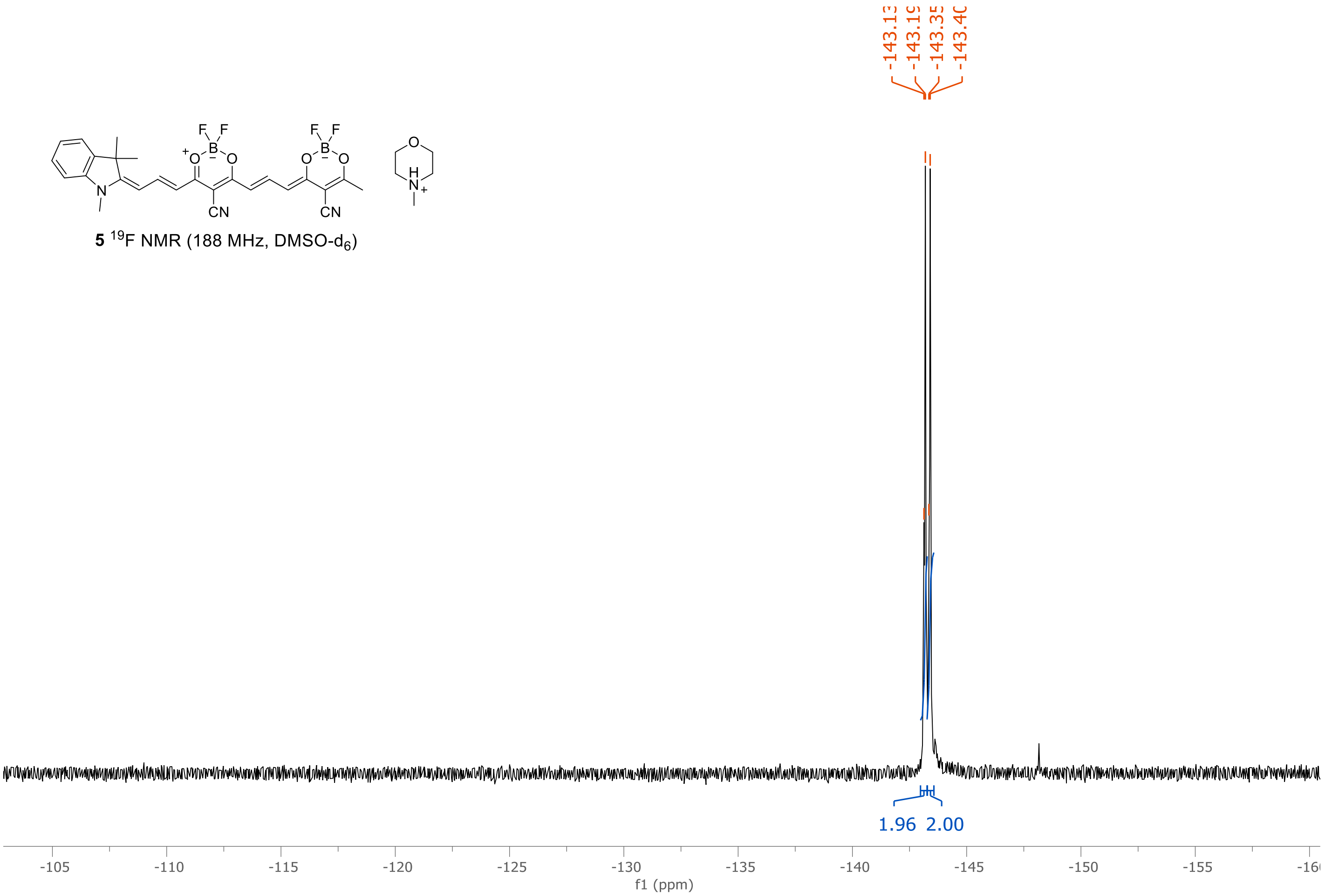
NMR Spectra



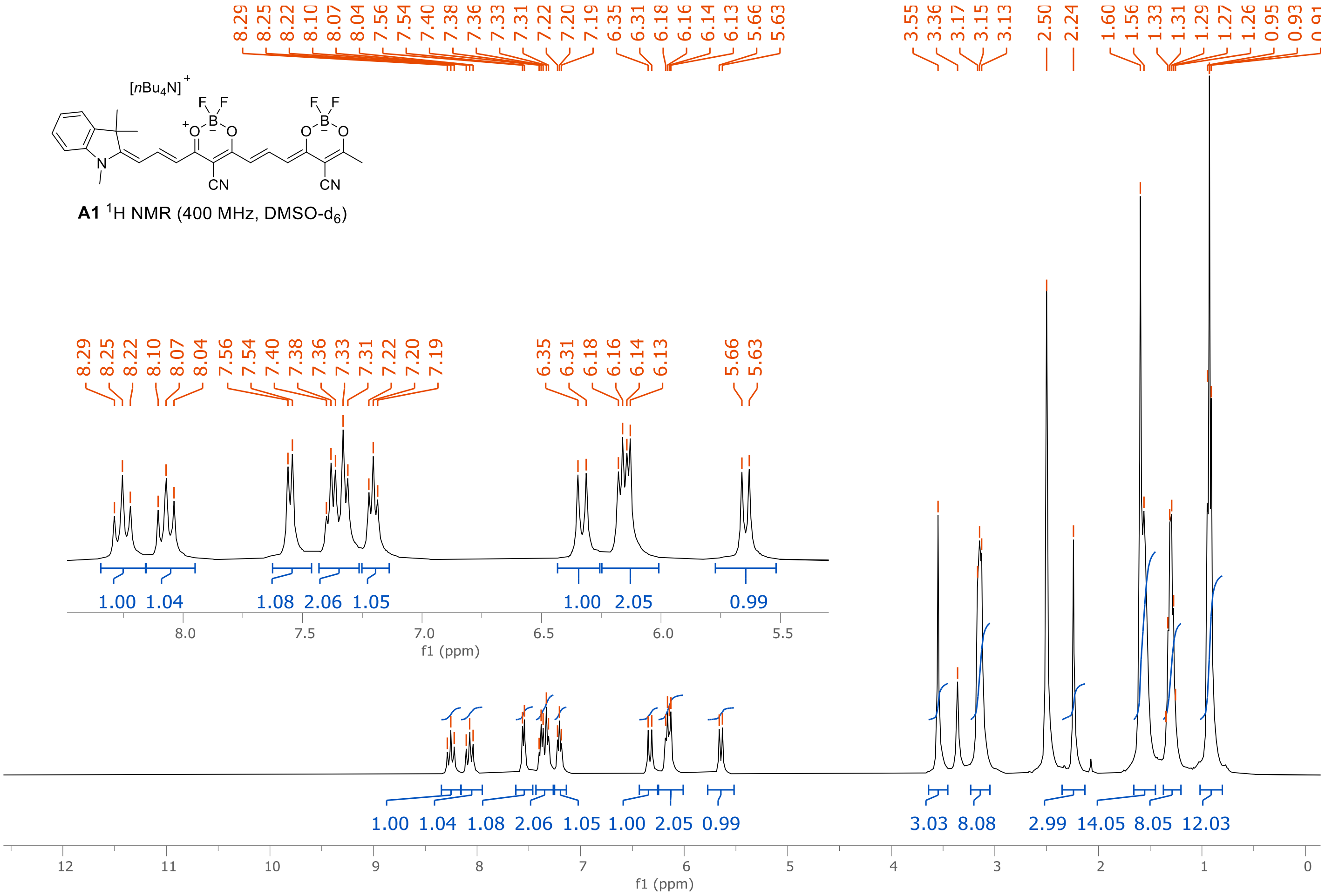
5 ^{1}H NMR (400 MHz, DMSO-d_6)



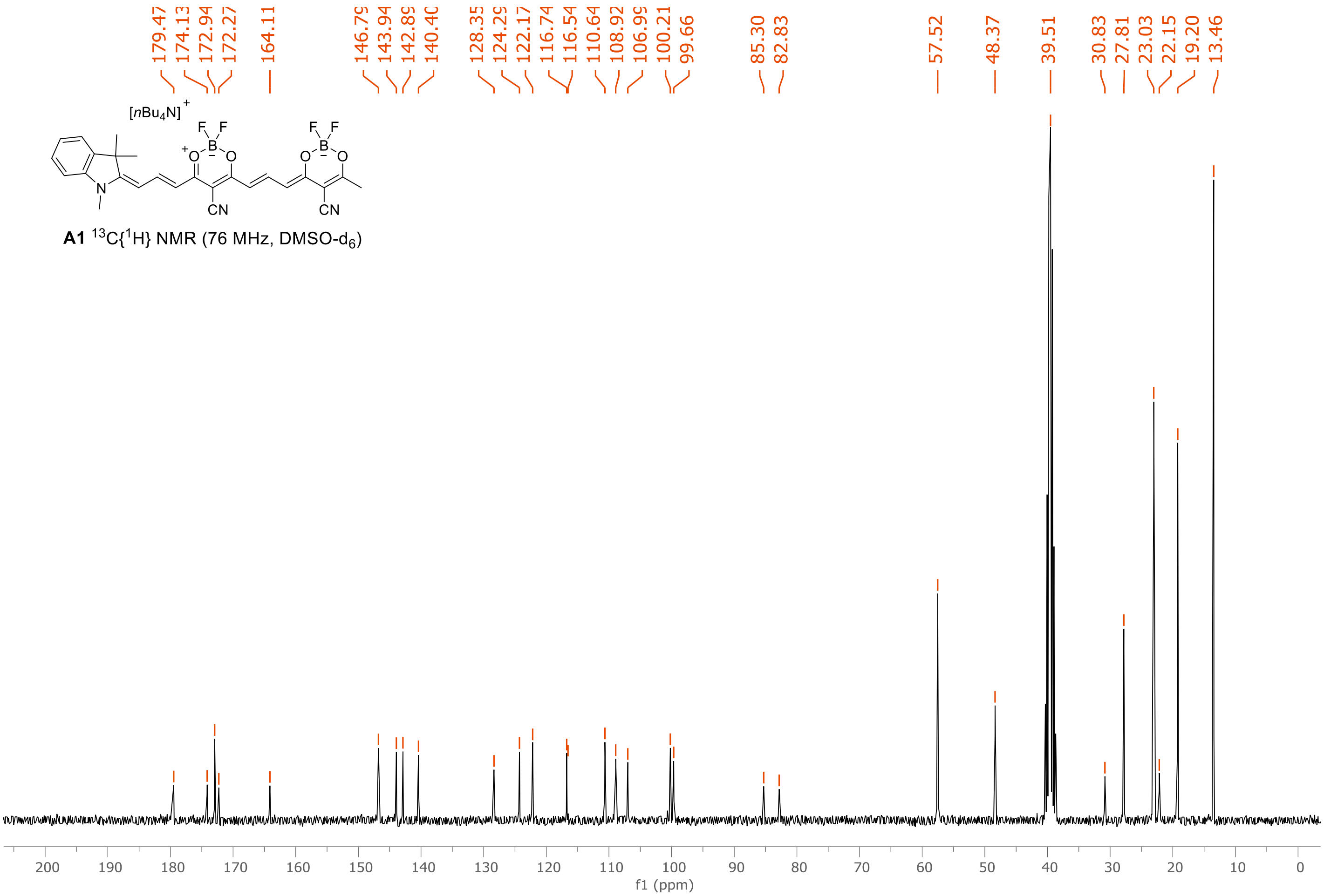
5 ^{13}C{^{1}H} NMR (400 MHz, DMSO-d_6)



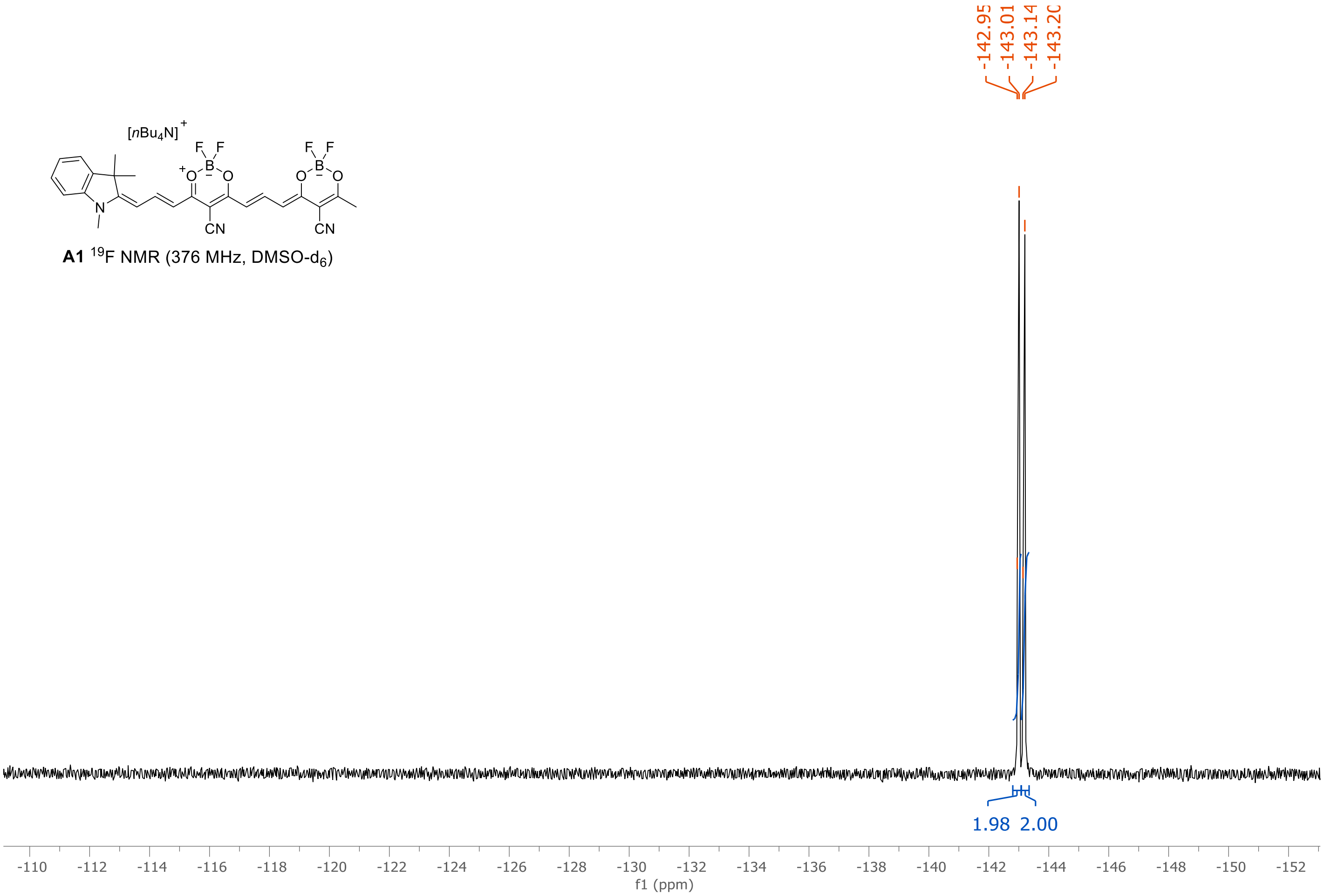
5 ^{19}F NMR (188 MHz, DMSO-d_6)



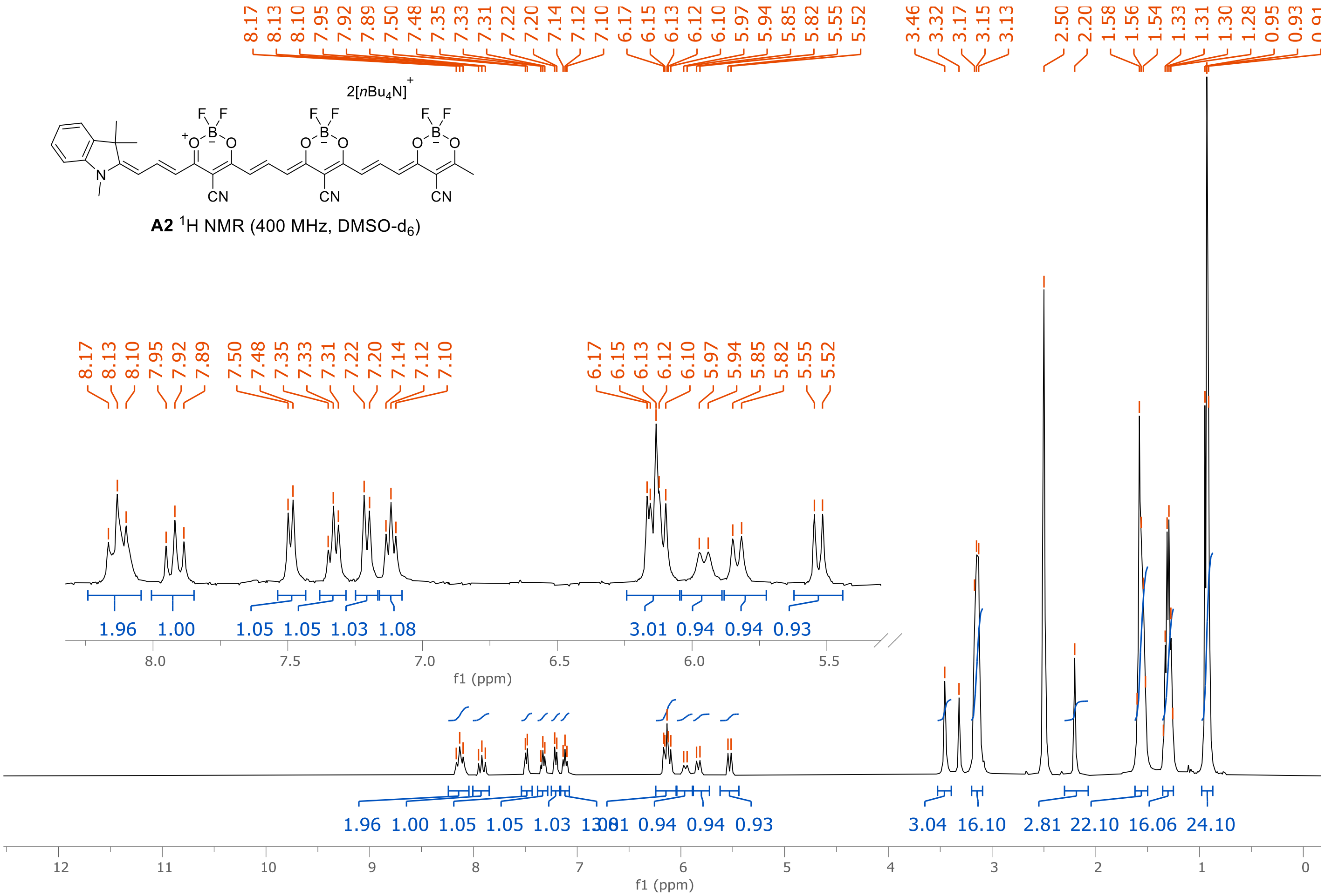
A1 ^{1}H NMR (400 MHz, DMSO-d_6)



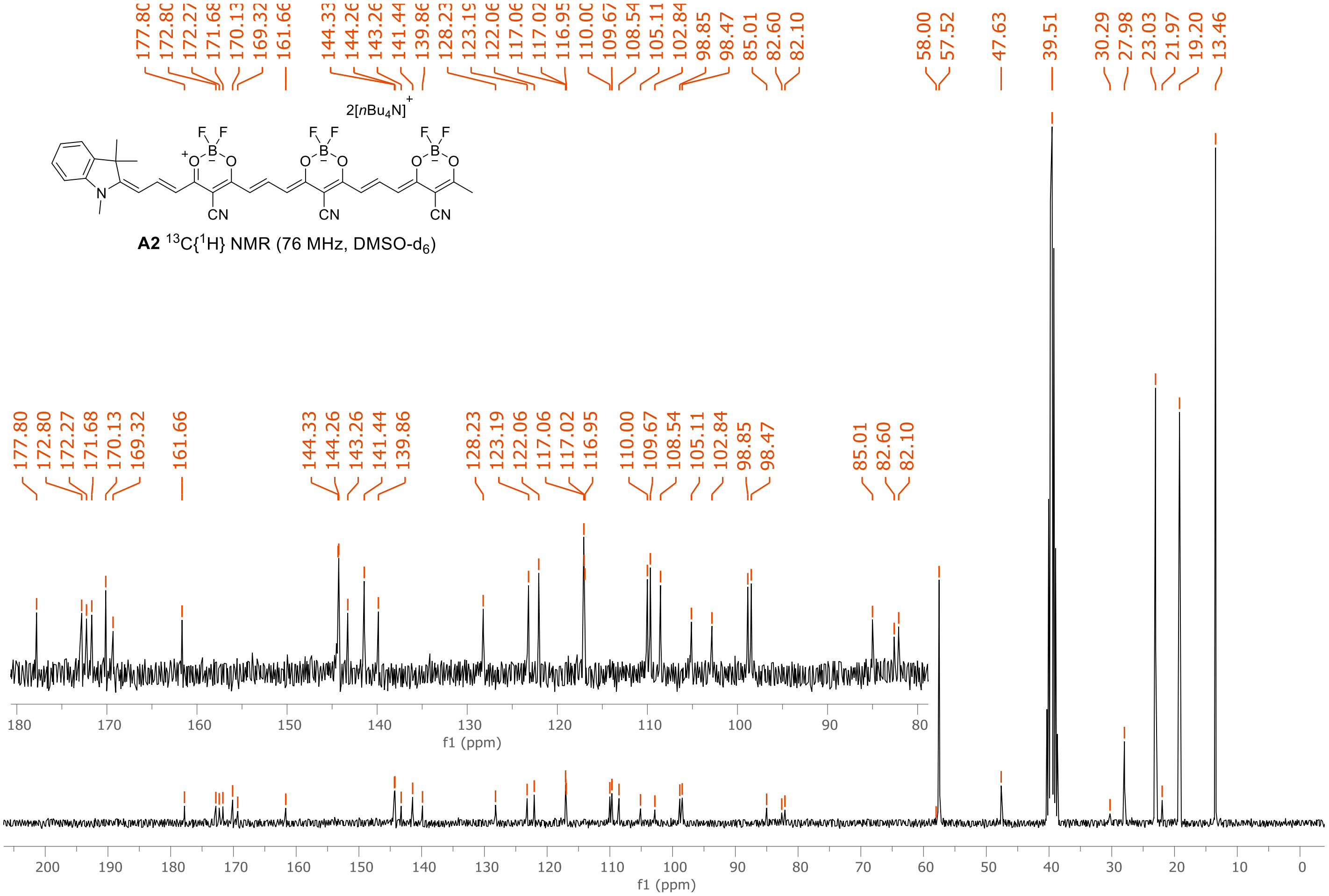
A1 $^{13}C\{^{1}H\}$ NMR (76 MHz, DMSO-d_6)



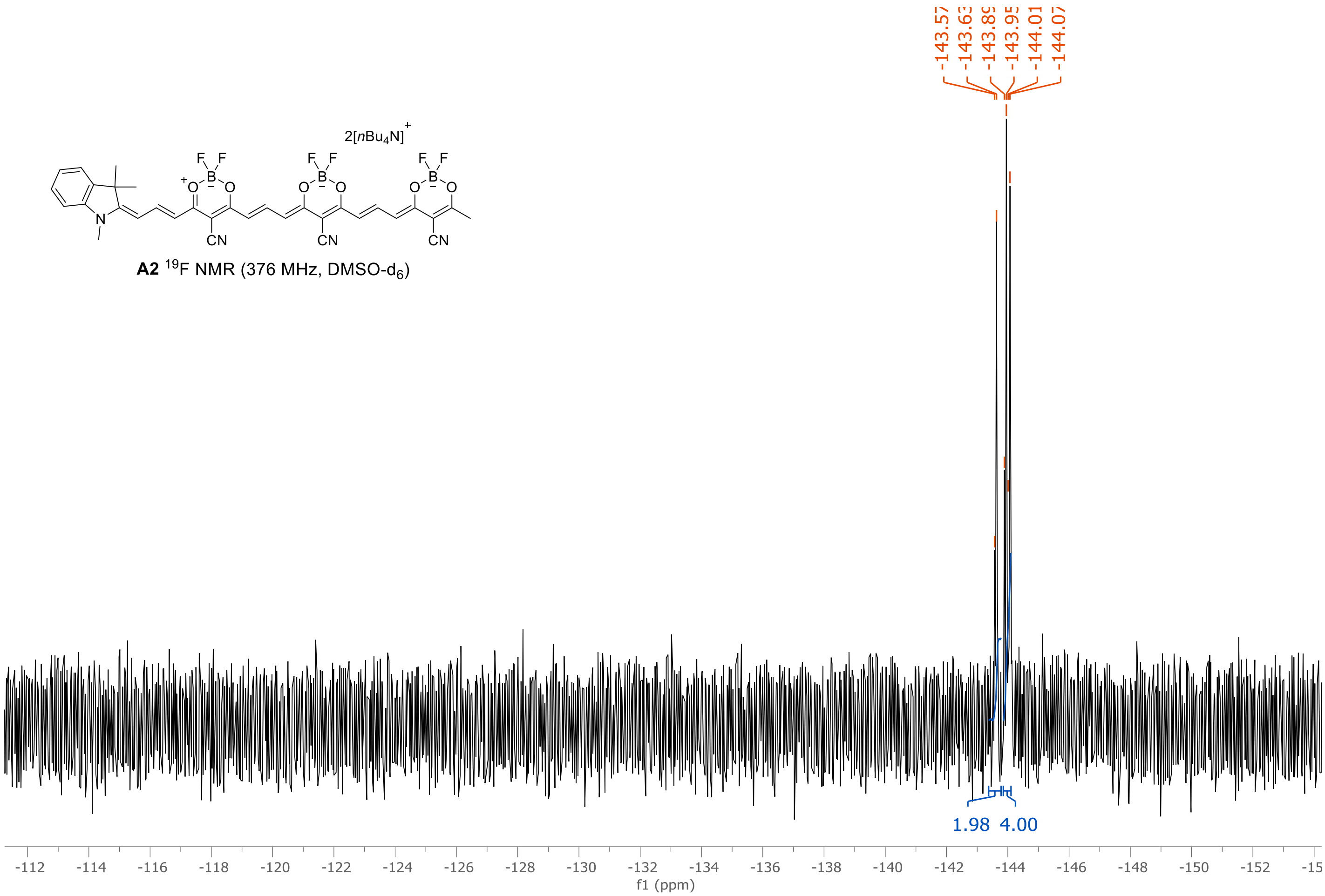
A1 ^{19}F NMR (376 MHz, DMSO-d_6)



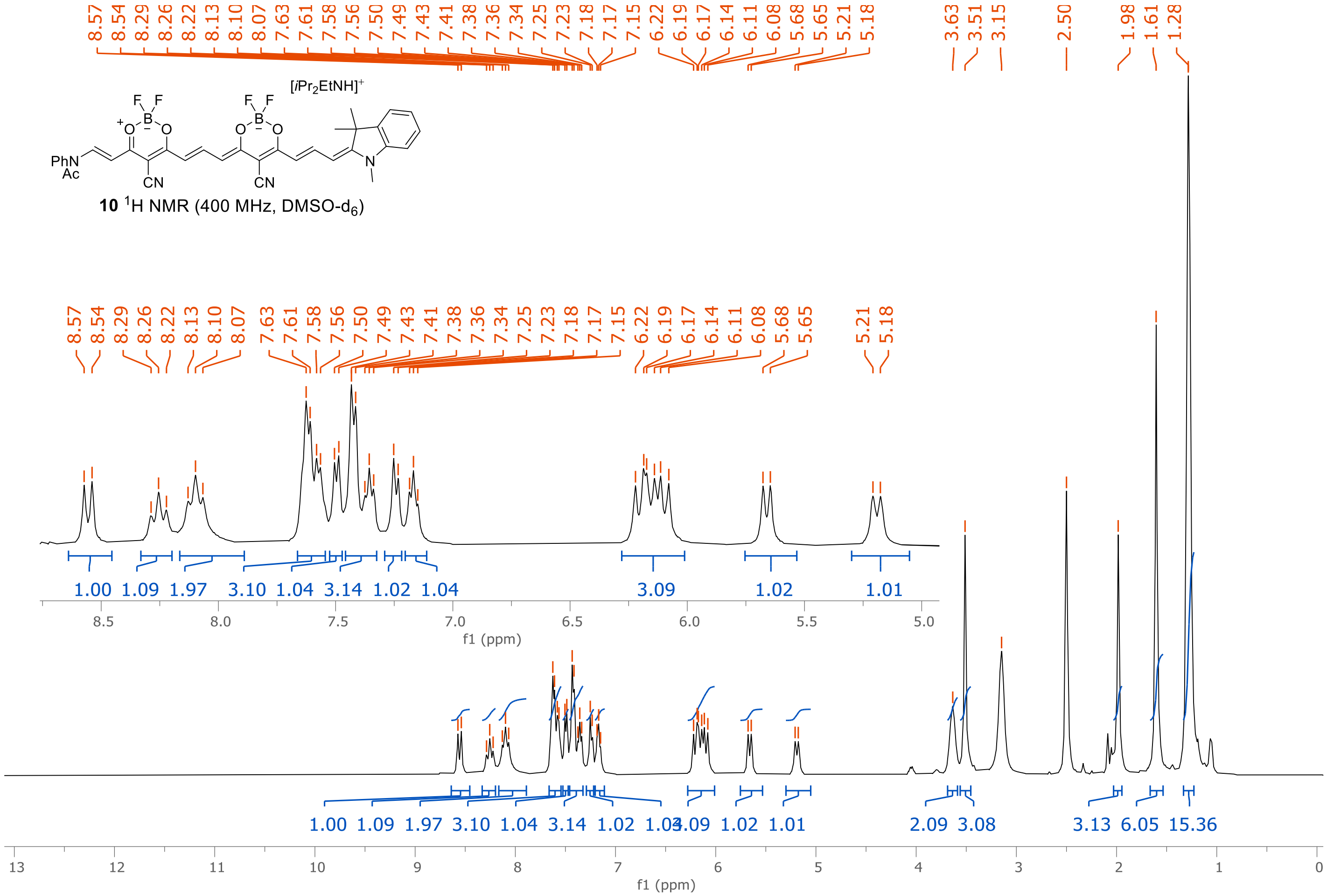
A2 ^{1}H NMR (400 MHz, DMSO-d$_6$)



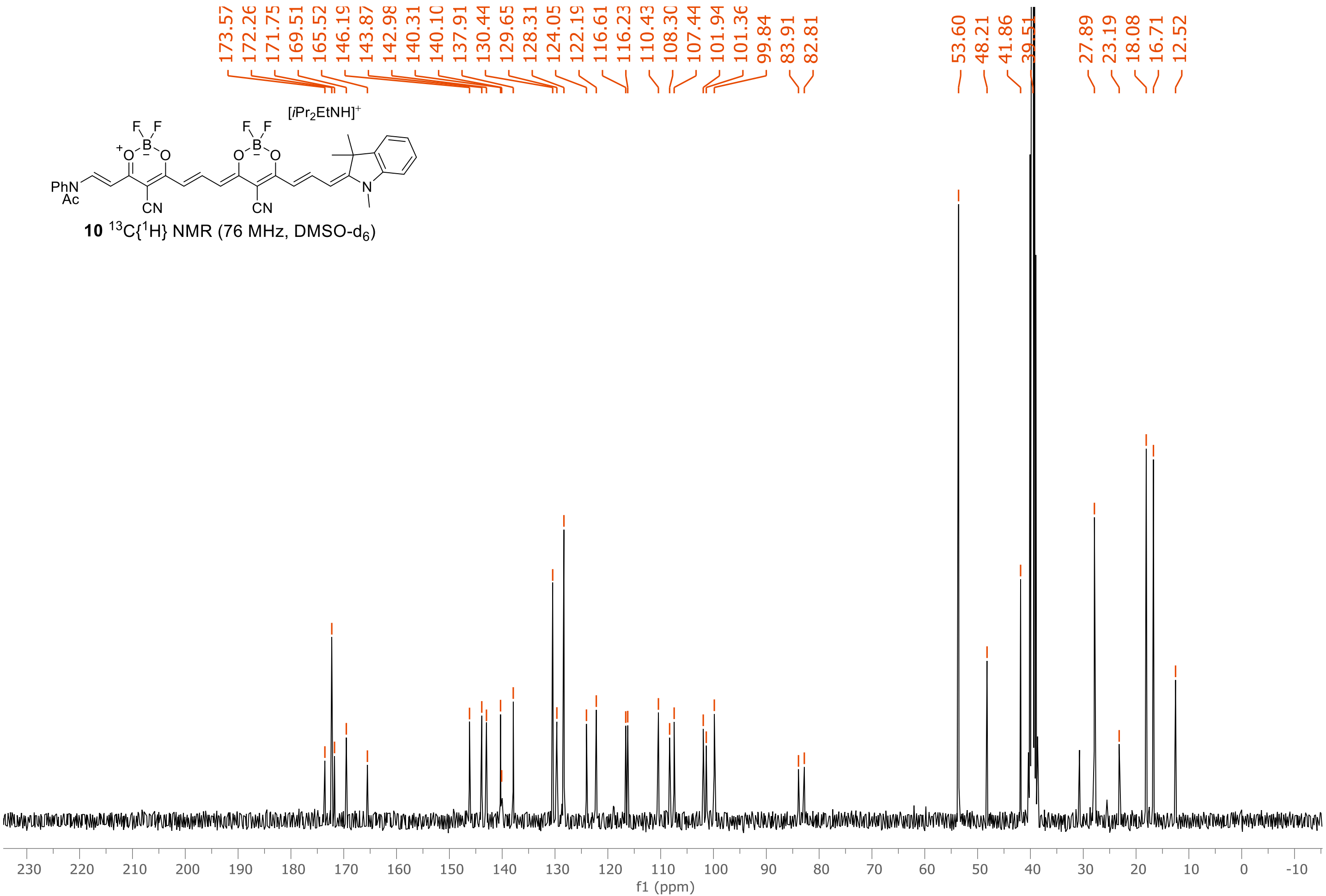
A2 ^{13}C{^{1}H} NMR (76 MHz, DMSO-d$_6$)



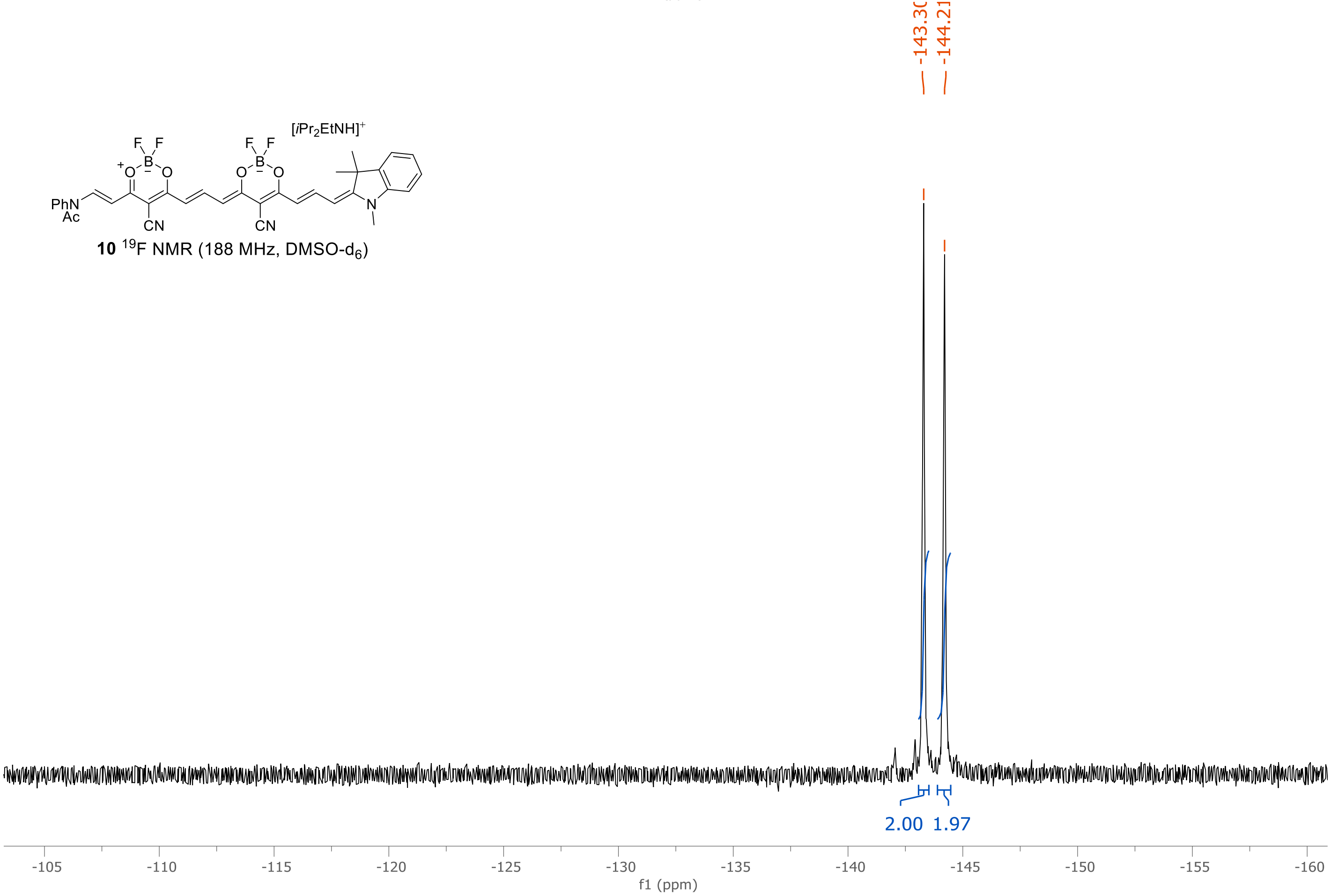
A2 ^{19}F NMR (376 MHz, DMSO-d$_6$)



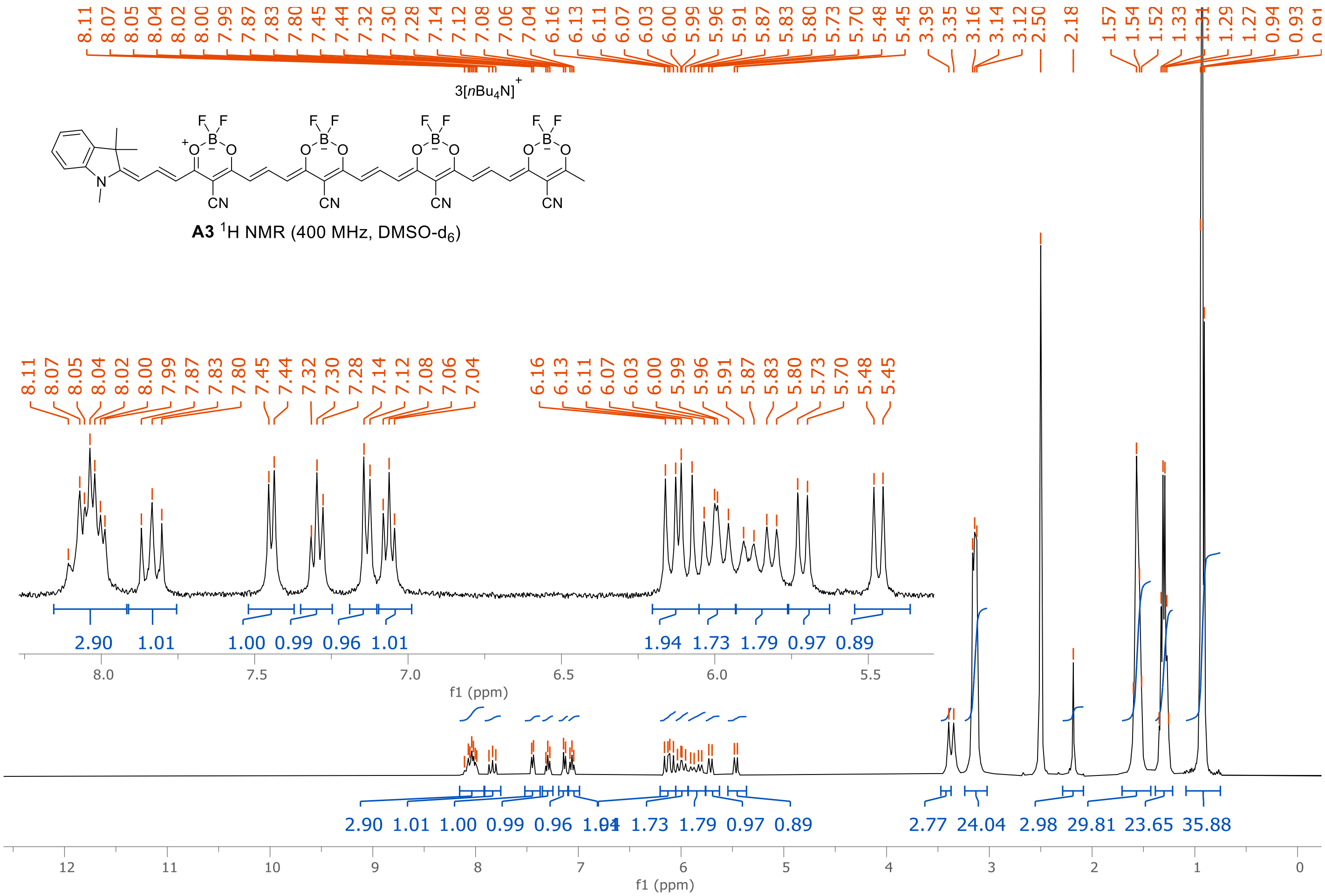
10 ^{1}H NMR (400 MHz, DMSO-d$_6$)



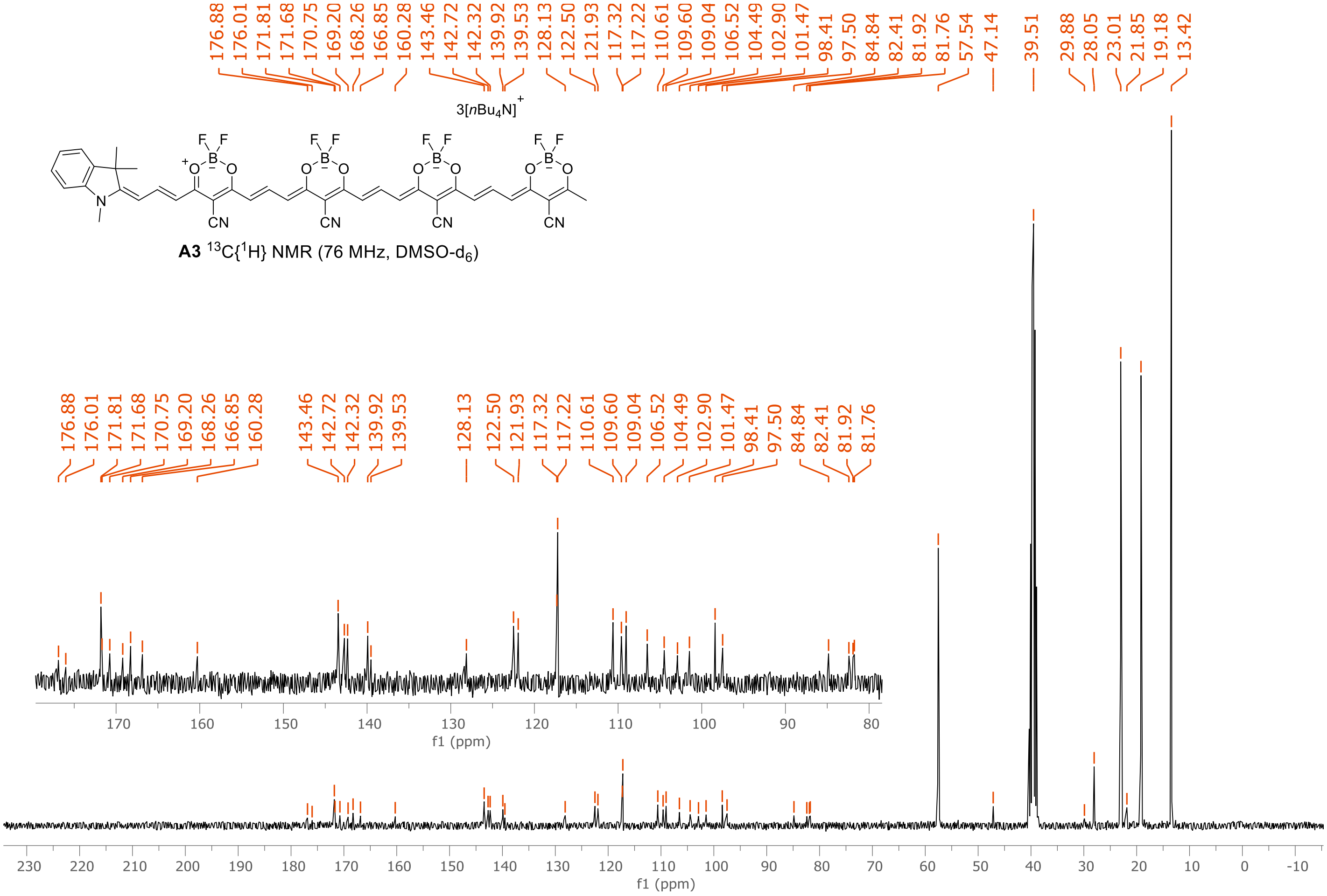
10 $^{13}C\{^1H\}$ NMR (76 MHz, DMSO-d_6)



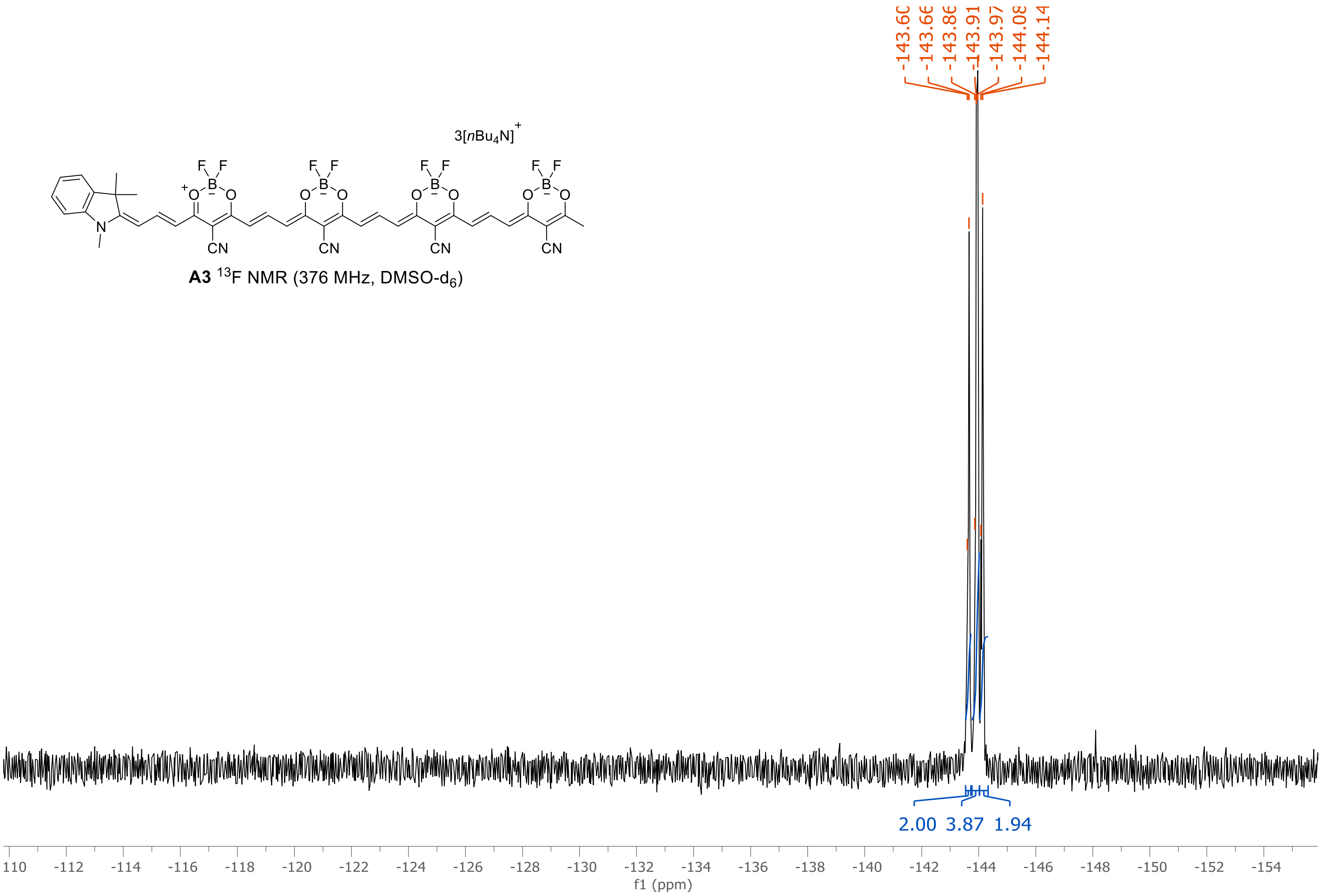
10 ^{19}F NMR (188 MHz, DMSO-d_6)



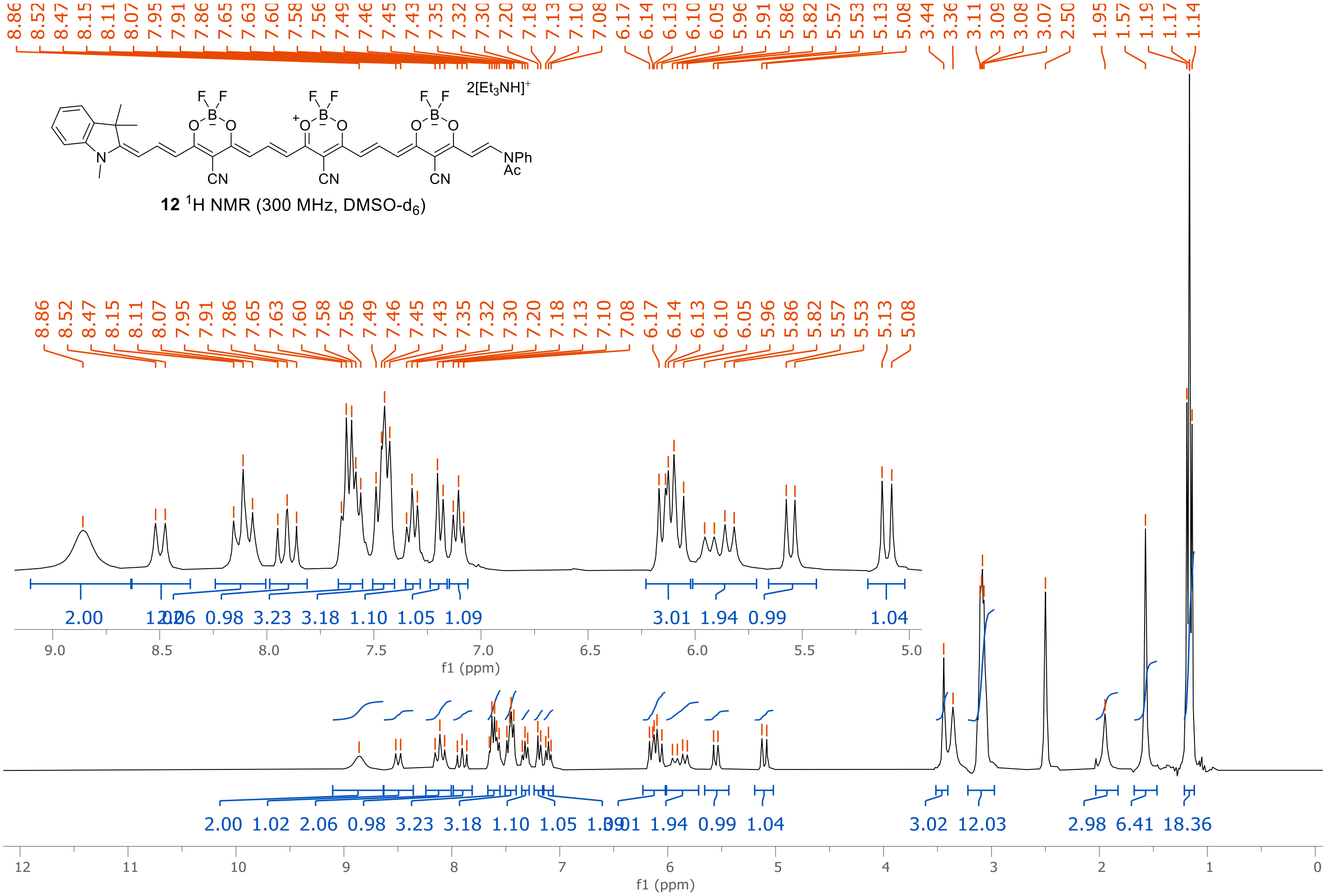
A3 ^{1}H NMR (400 MHz, DMSO-d$_6$)



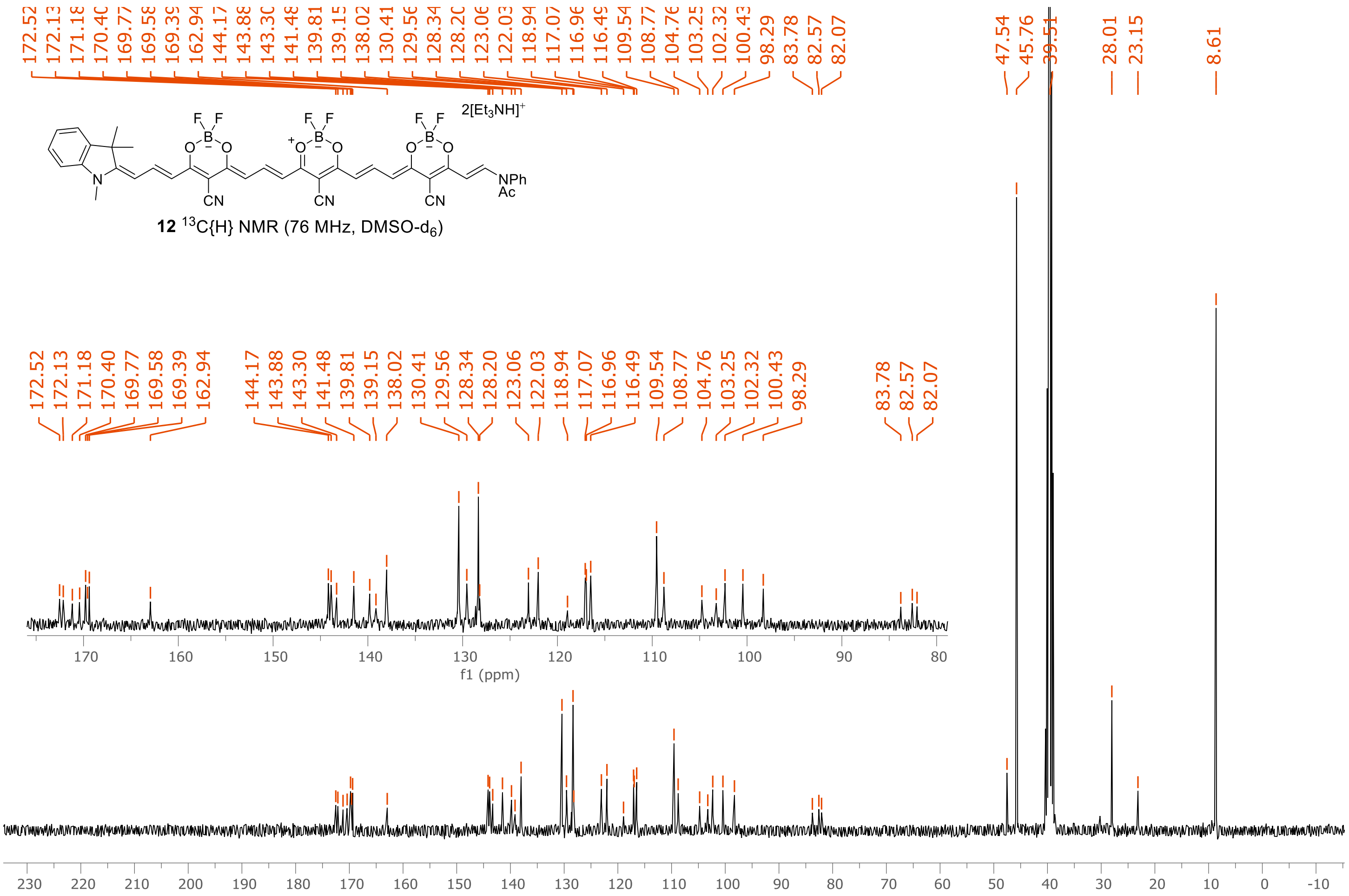
A3 ^{13}C{^{1}H} NMR (76 MHz, DMSO-d$_6$)



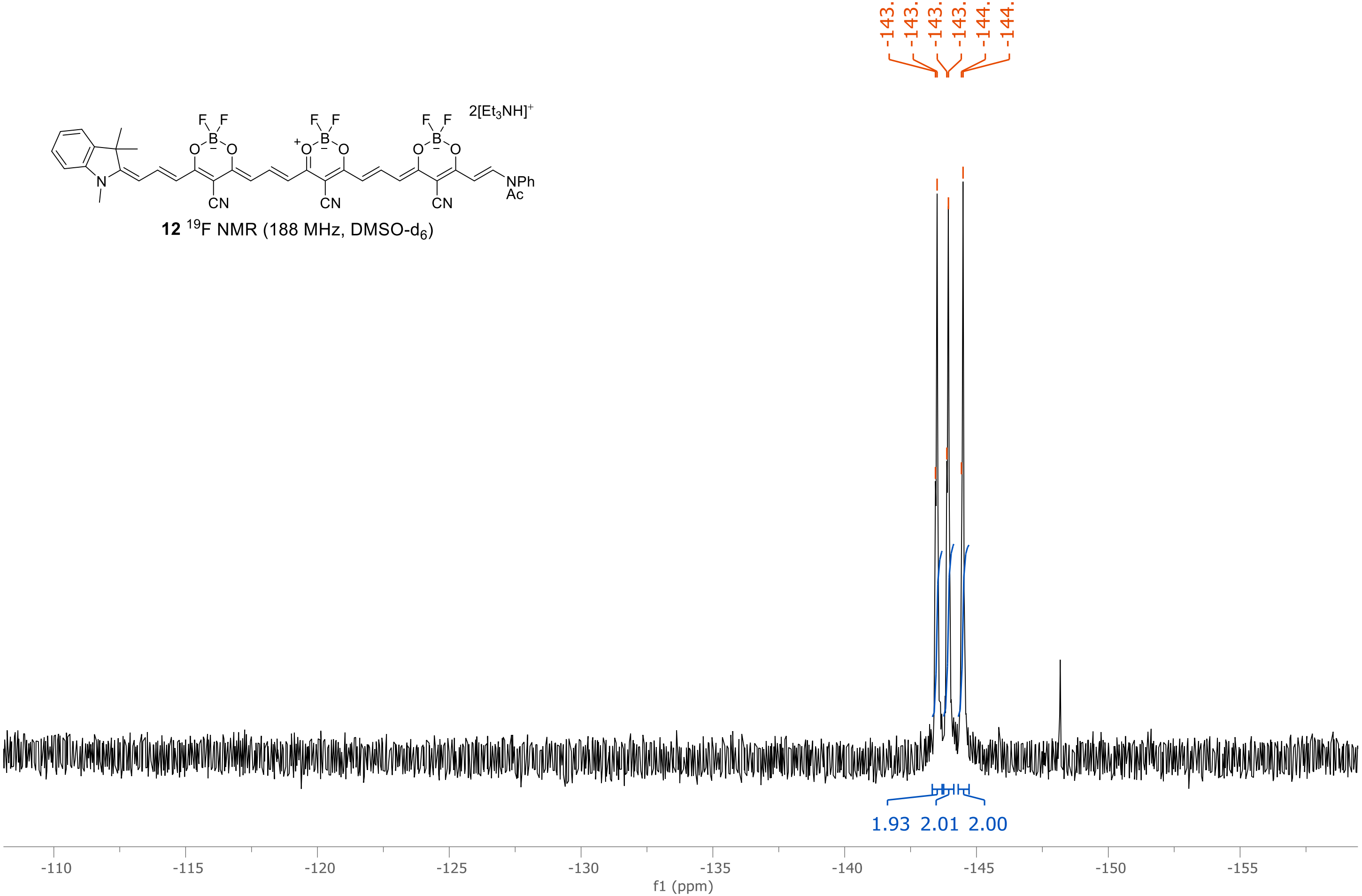
A3 ^{13}F NMR (376 MHz, DMSO-d$_6$)



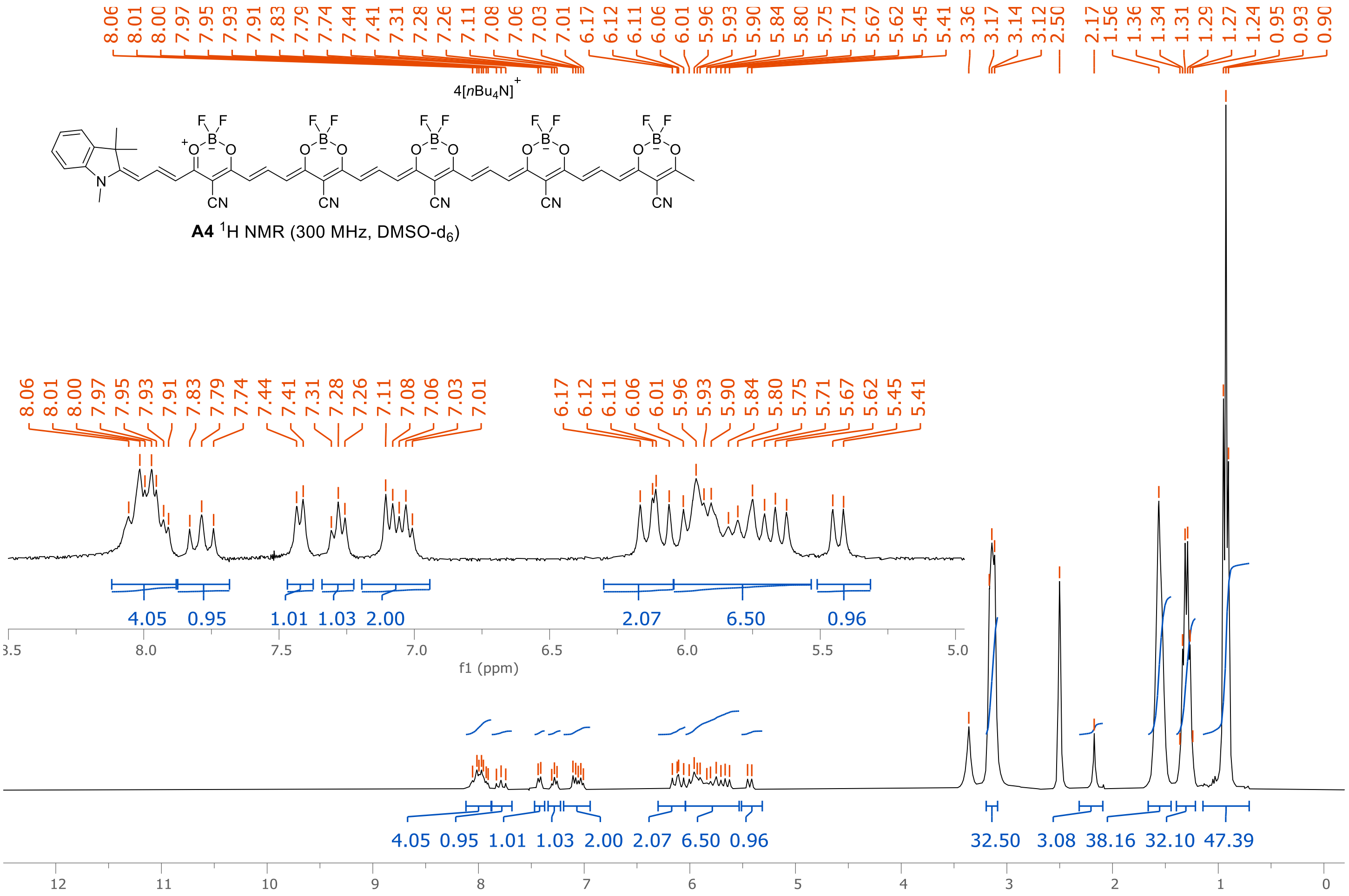
12 ^{1}H NMR (300 MHz, DMSO-d$_6$)



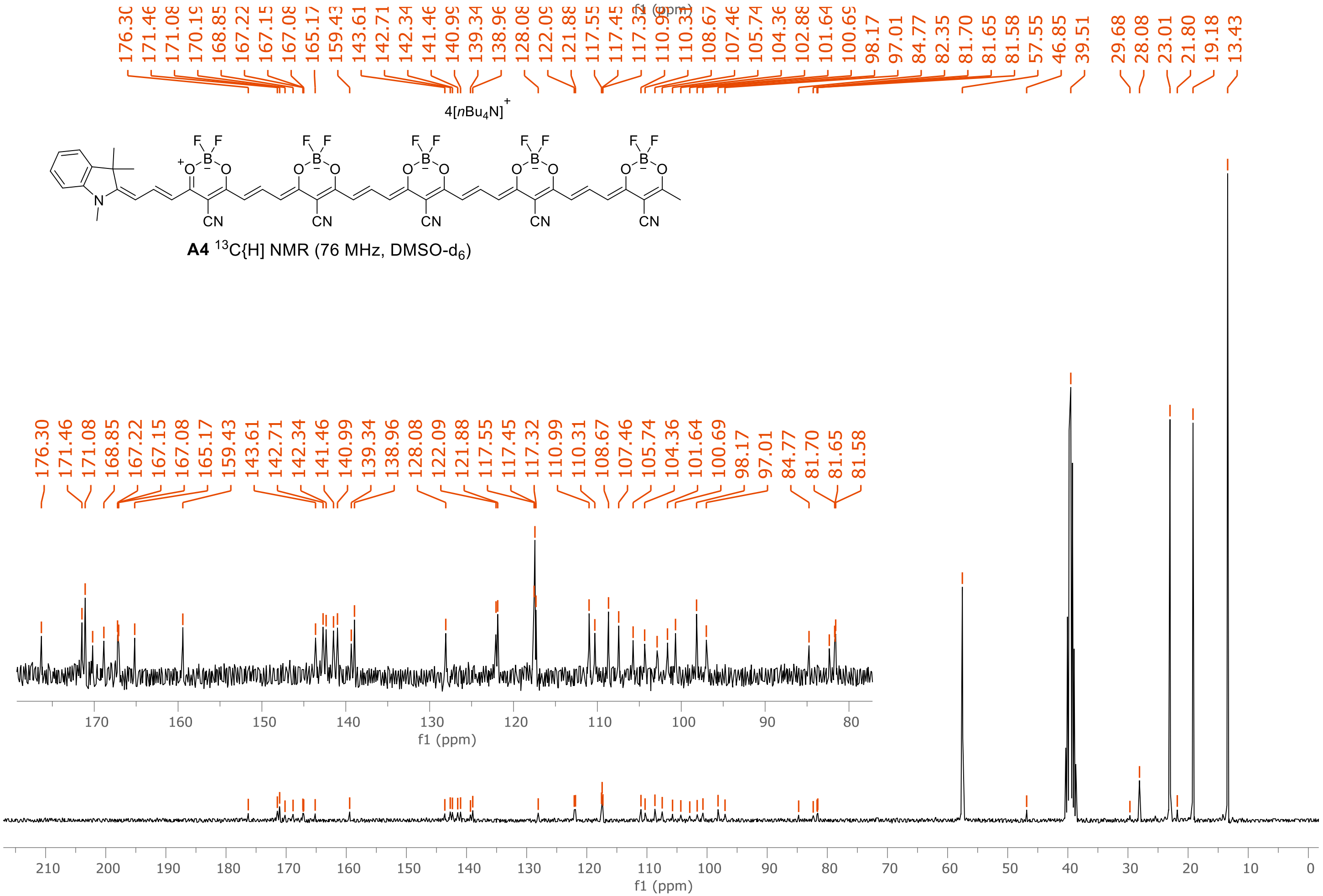
12 ^{13}C{H} NMR (76 MHz, DMSO-d$_6$)



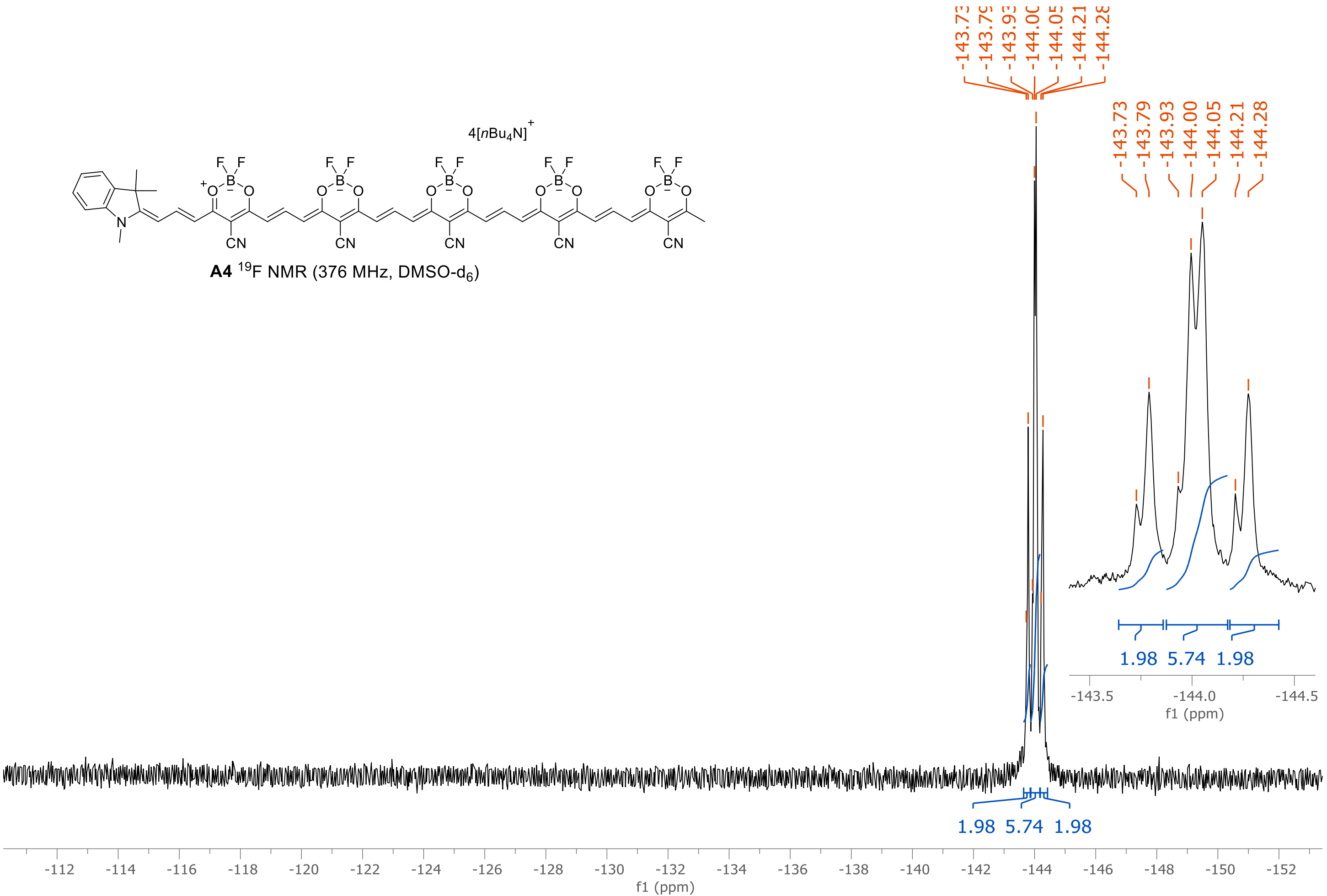
12 ^{19}F NMR (188 MHz, DMSO-d$_6$)



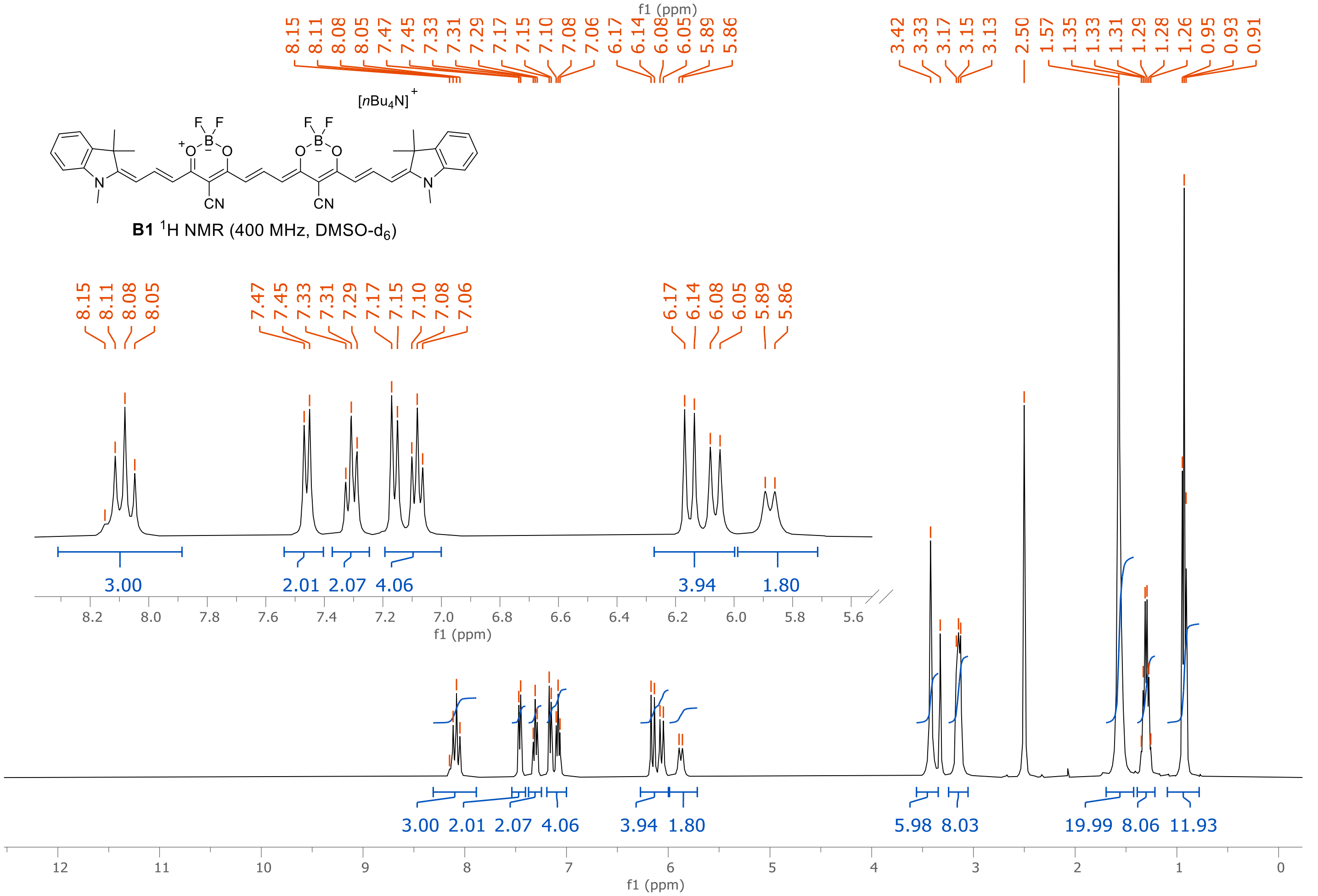
A4 ^{1}H NMR (300 MHz, DMSO-d_6)



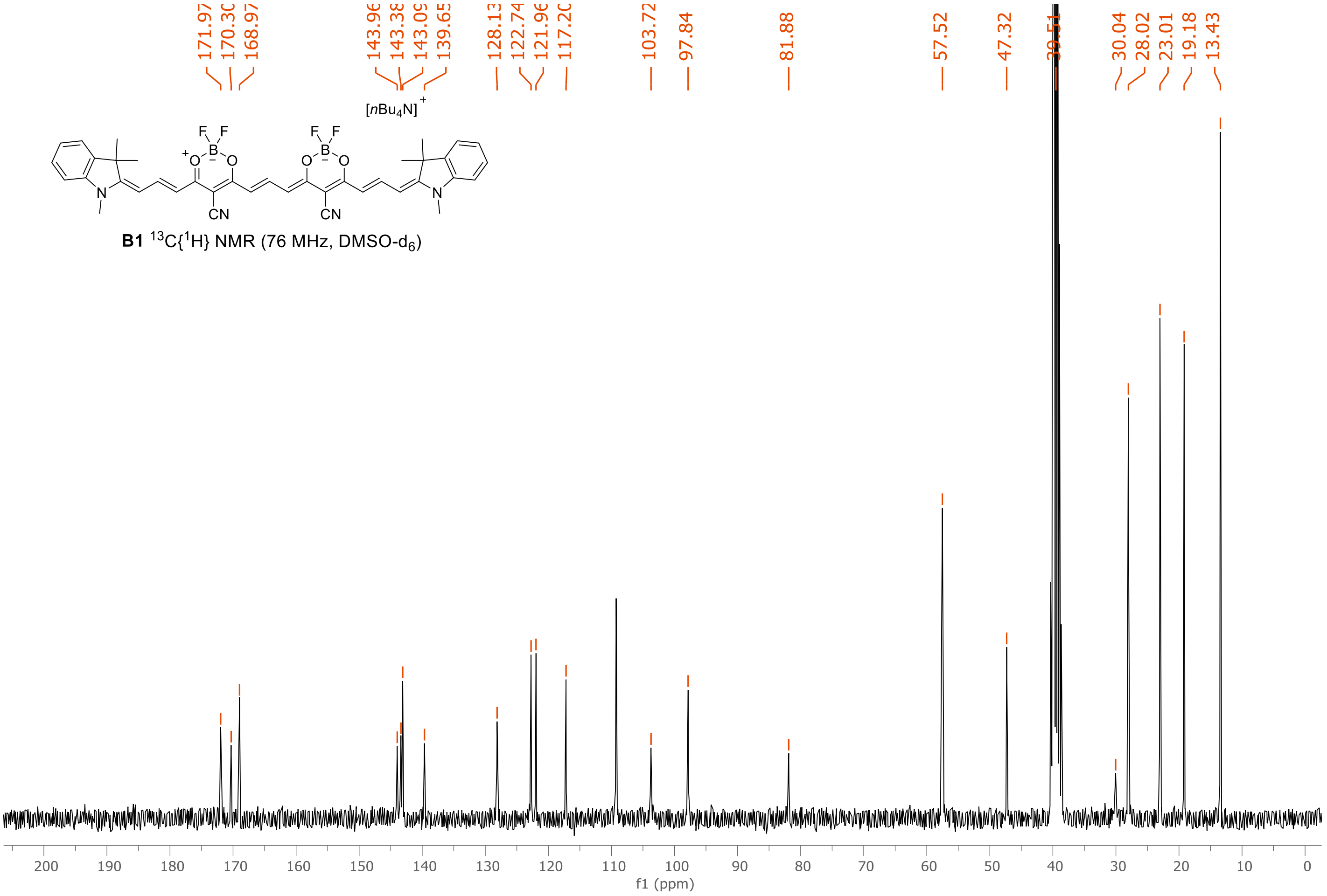
A4 ^{13}C{H} NMR (76 MHz, DMSO-d_6)



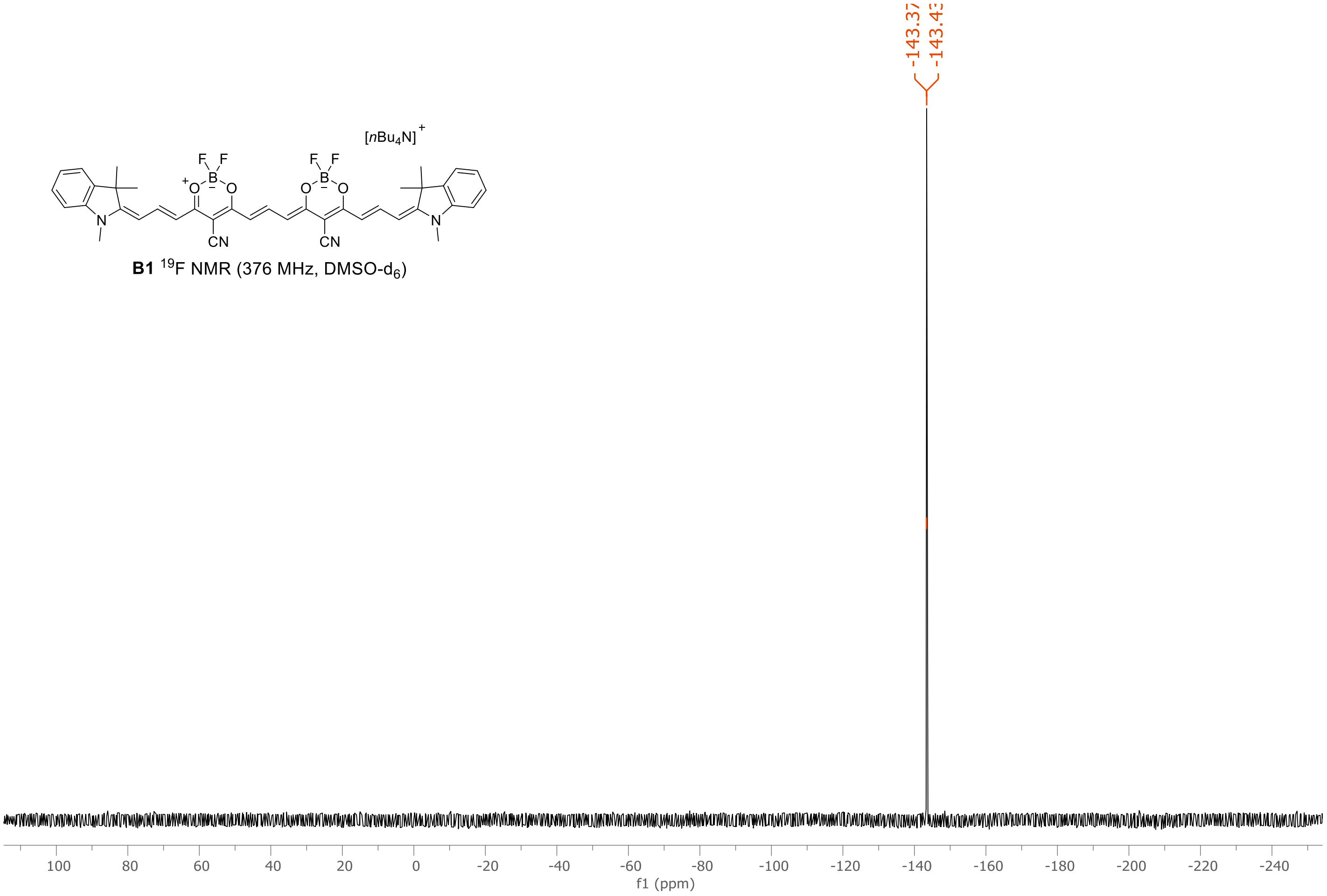
A4 ^{19}F NMR (376 MHz, DMSO-d$_6$)



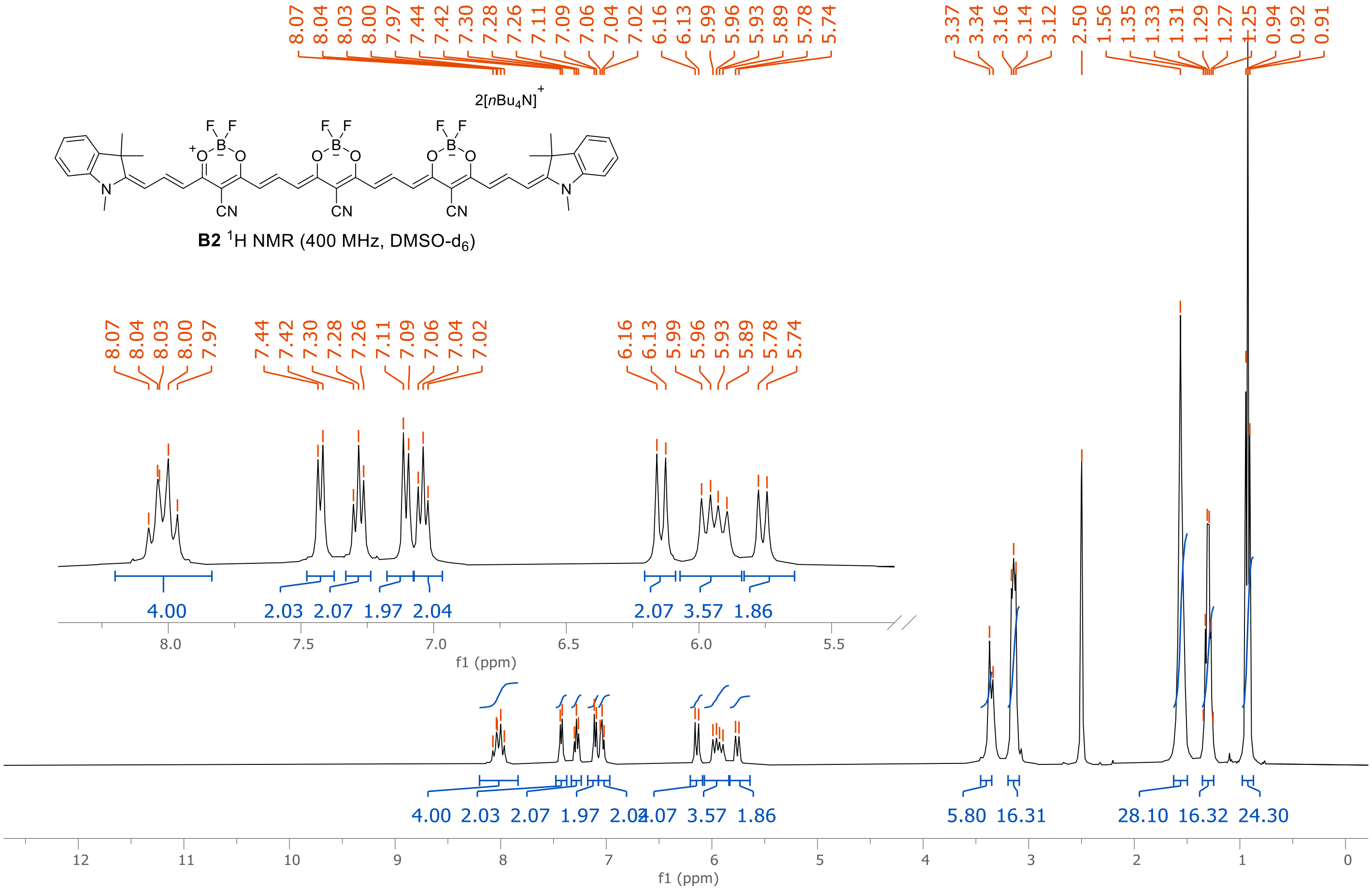
B1 ^{1}H NMR (400 MHz, DMSO-d$_6$)



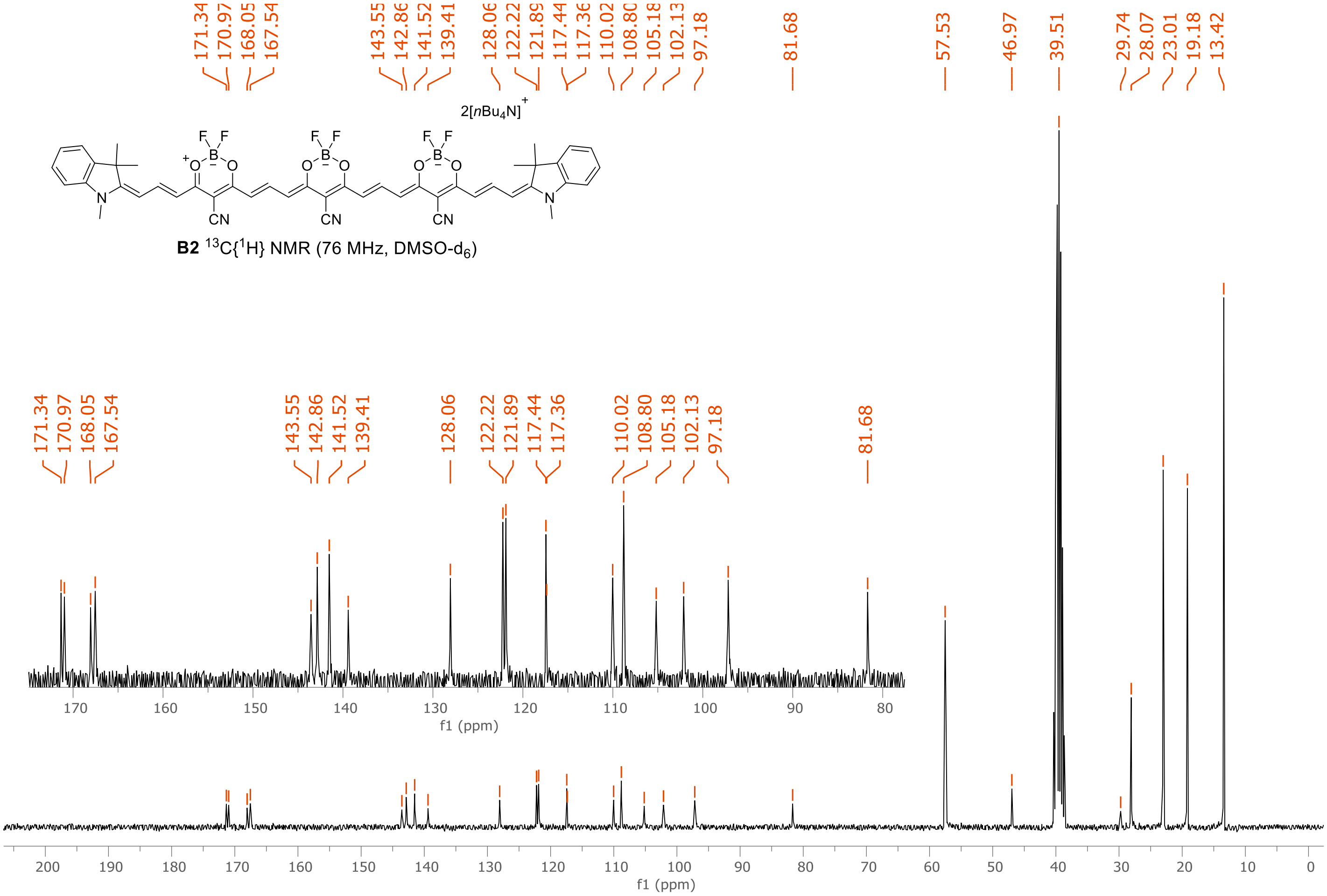
B1 ^{13}C{^{1}H} NMR (76 MHz, DMSO-d_6)



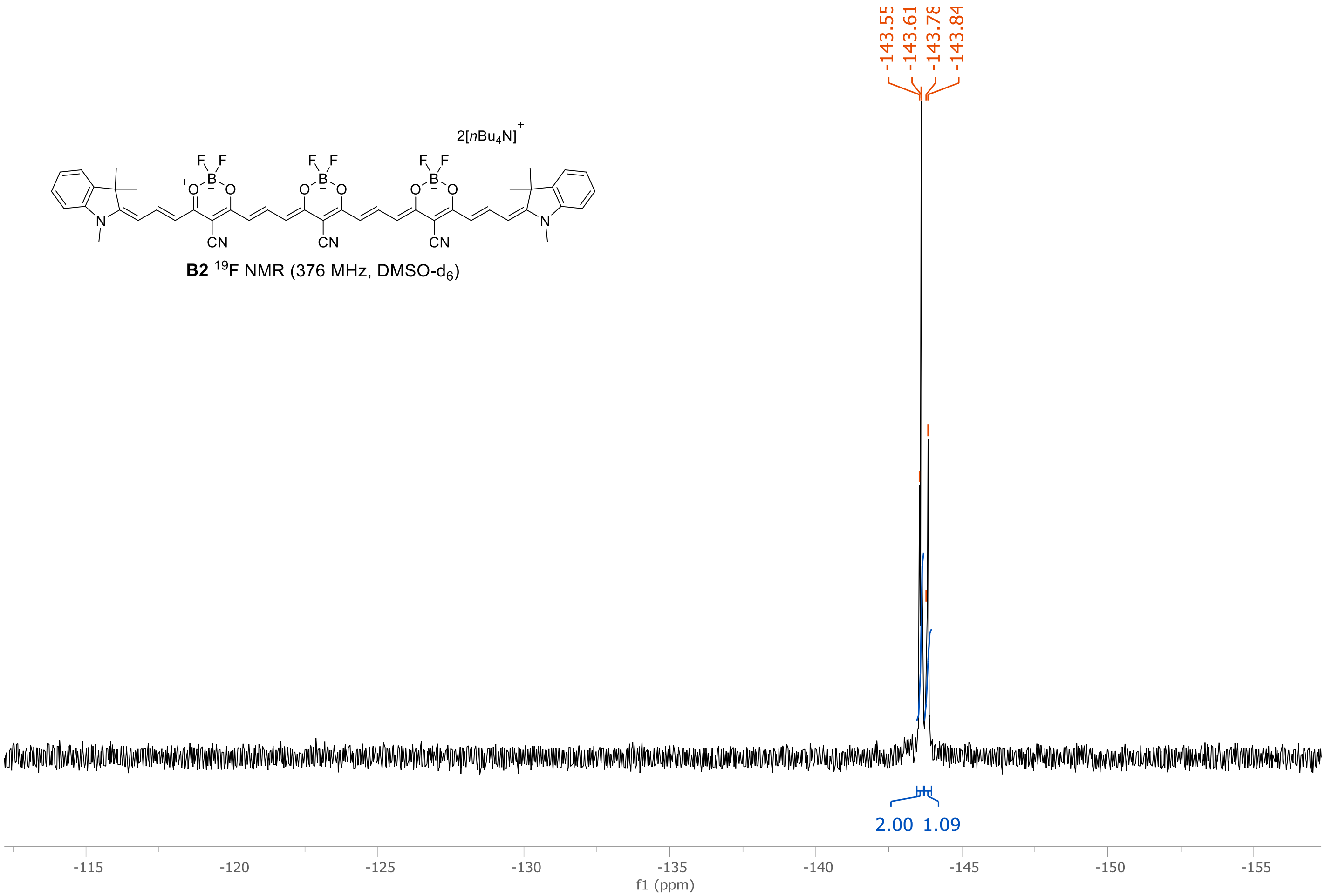
B1 ^{19}F NMR (376 MHz, DMSO-d_6)

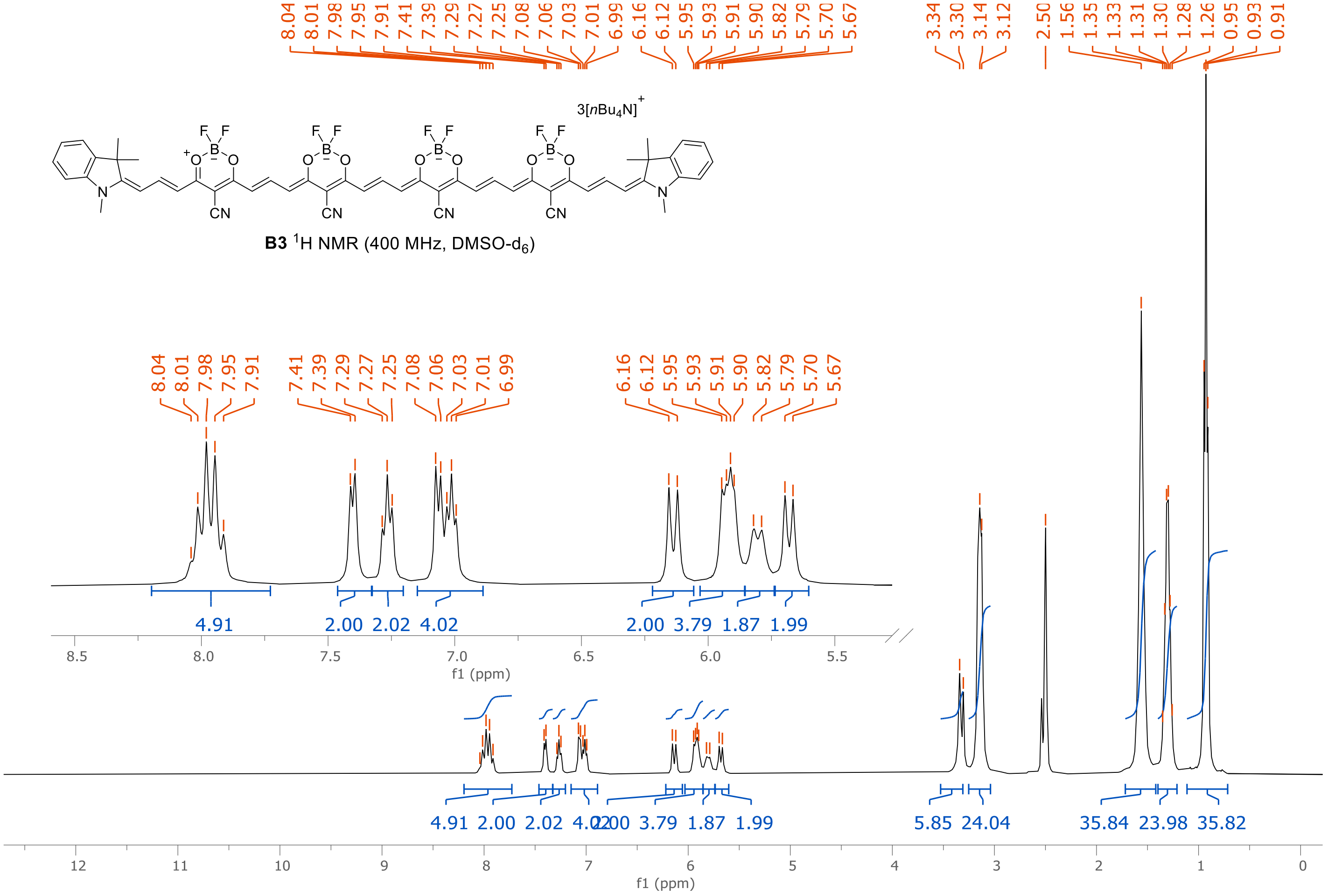


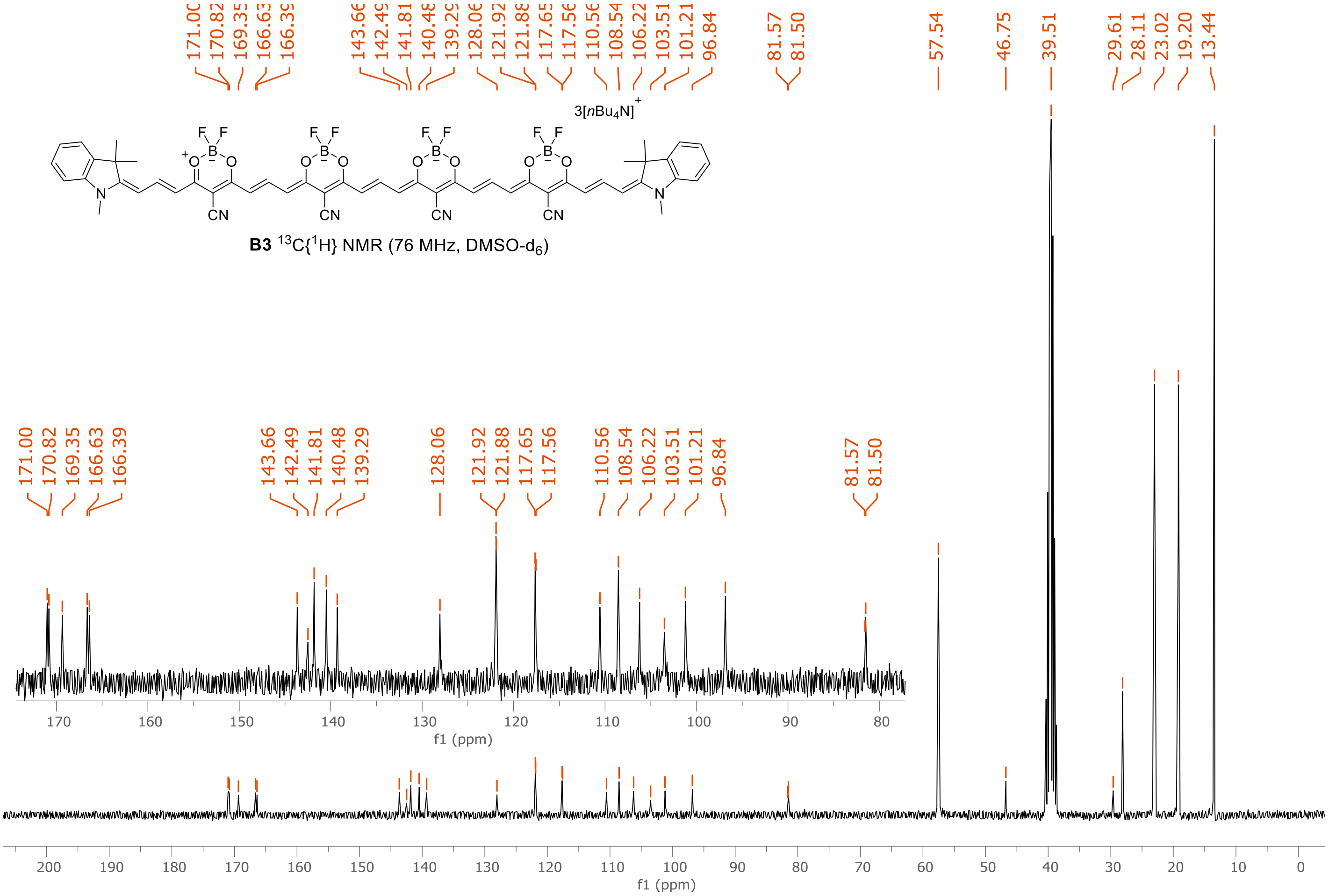
B2 ^{1}H NMR (400 MHz, DMSO-d$_6$)

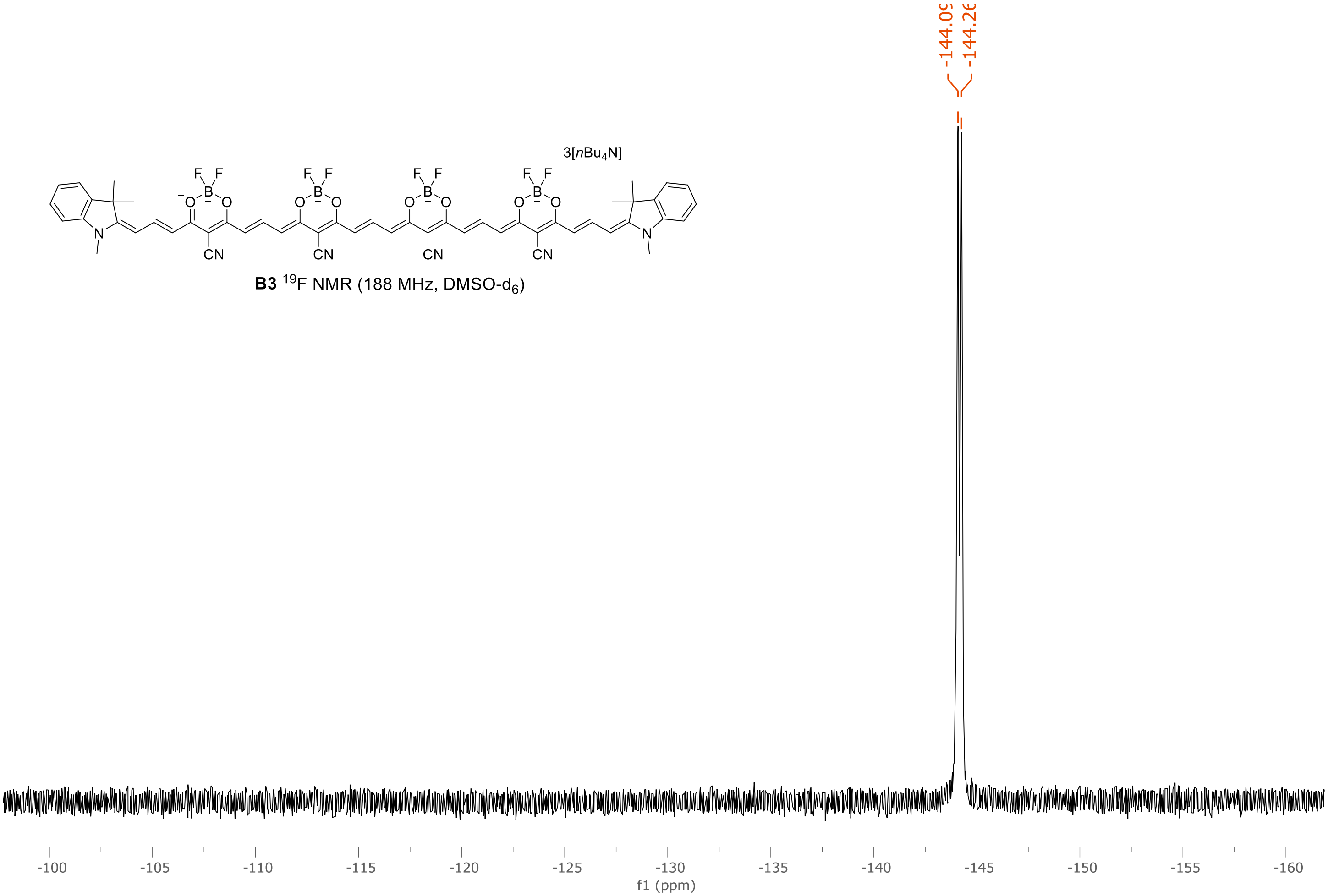


B2 ^{13}C{^{1}H} NMR (76 MHz, DMSO-d$_6$)


B2 ^{19}F NMR (376 MHz, DMSO-d_6)


B3 ^{1}H NMR (400 MHz, DMSO-d_6)


B3 $^{13}C\{^{1}H\}$ NMR (76 MHz, DMSO-d$_6$)


B3 ^{19}F NMR (188 MHz, DMSO-d$_6$)

References

1. V. Polishchuk, M. Filatova, E. Rusanov and M. Shandura, *Chem. - A Eur. J.*, 2022, **28**, e202202168.
2. V. Polishchuk, M. Stanko, A. Kulinich and M. Shandura, *Eur. J. Org. Chem.*, 2018, **2018**, 240–246.