

## ELECTRONIC SUPPLEMENTARY INFORMATION

### Optimization of Distyryl-Bodipy Chromophores for Efficient Panchromatic Sensitization in Dye Sensitized Solar Cells

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## Experimental Section

### General:

All chemicals and solvents obtained from Sigma-Aldrich were used without further purification. Reactions were monitored by thin layer chromatography using Merck TLC Silica gel 60 F<sub>254</sub>. Chromatography on silica gel was performed over Merck Silica gel 60 (particle size: 0.040-0.063 mm, 230-400 mesh ASTM).

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at room temperature on Bruker DPX-400 (operating at 400 MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR) in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> with tetramethylsilane (TMS) as internal standard. Coupling constants (*J* values) are given in Hz and chemical shifts are reported in parts per million (ppm). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and p (pentet).

Absorption spectra in solution were acquired using a Varian Cary-100 spectrophotometer. Fluorescence spectra were determined on a Varian Eclipse spectrofluorometer. Excitation slit was set at 2.5 nm and emission slit was set at 5 nm. Fluorescence quantum yields of **PS-7** were measured in CHCl<sub>3</sub> vs. Rhodamine 6G ( $\Phi=0.95$  in ethanol), other reference compounds for quantum yield measurements were given in Table 1. Fluorescence life time measurements were determined on a HORIBA Jobin Yvon fluorolog, FL-1057. HORIBA Scientific NanoLEDs at 667 nm, 734 nm and 783 nm were used. Mass spectra were recorded on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS and at the Ohio State University Mass Spectrometry and Proteomics Facility, Ohio, USA. Spectrophotometric grade solvents were used for spectroscopy experiments. Compound (**5**)<sup>1</sup> and **PS-6**<sup>2</sup> were synthesized according to literature.

### Synthetic Pathways:

#### Compound (1)

To a 1 L round-bottomed flask containing 400 mL argon-degassed CH<sub>2</sub>Cl<sub>2</sub> were added 2-methyl pyrrole (12.3 mmol, 1.0 g) and 4-carboxybenzaldehyde (6.0 mmol, 0.9 g). One drop of TFA was added and the solution was stirred under N<sub>2</sub> at room temperature for 1 day. After addition of DDQ (6.0 mmol, 1.36 g) to the reaction mixture, stirring was continued for 30 min. 5 mL of Et<sub>3</sub>N and 5 mL of BF<sub>3</sub>.OEt<sub>2</sub> were successively added and after 30 min, the reaction mixture was washed three times with water (3 x 100 mL) which was then extracted into the CHCl<sub>3</sub> (3 x 100 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the residue was purified by silica gel column chromatography using (CHCl<sub>3</sub>: MeOH 95:5) as the eluant. Red solid (1.25 g, 30%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  8.25 (2H, d, *J* = 7.6 Hz, *ArH*), 7.65 (2H, d, *J* = 7.7 Hz, *ArH*), 6.70 (2H, s, *ArH*), 6.30 (2H, d, *J* = 3.4 Hz, *ArH*), 2.70 (6H, s, *CH*<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  170.5, 158.5, 140.9, 139.4, 134.5, 130.6, 130.5, 130.2, 130.0, 119.9, 15.0 ppm. MS (TOF- ESI): *m/z*: Calcd: 340.1195, Found: 340.1130 [M-H]<sup>+</sup>,  $\Delta=19.1$  ppm.

#### Compound (2)

To a 1 L round-bottomed flask containing 400 mL argon-degassed CH<sub>2</sub>Cl<sub>2</sub> were added 2,4-dimethyl pyrrole (21.9 mmol, 2.1 g) and 4-carboxybenzaldehyde (21.9 mmol, 2.1 g). One drop of TFA was added and the solution was stirred under N<sub>2</sub> at room temperature for 1 day. After addition of a solution of DDQ (9.9 mmol, 2.46 g) in 100 mL of dichloromethane to the reaction mixture, stirring was continued for 30 min. 5 mL of Et<sub>3</sub>N and 5 mL of BF<sub>3</sub>.OEt<sub>2</sub>

were successively added and after 30 min, the reaction mixture was washed three times with water (50 x 100 mL) which was then extracted into the CHCl<sub>3</sub> (3 x 100 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the residue was purified by silica gel column chromatography using (CHCl<sub>3</sub> : MeOH 97:3) as the eluant. Red solid (1.0 g, 27%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub> + CDCl<sub>3</sub>): δ<sub>H</sub> 8.07 (2H, d, *J* = 8.2 Hz, *ArH*), 7.45 (2H, d, *J* = 8.2 Hz, *ArH*), 6.10 (2H, s, *ArH*), 2.40 (6H, s, CH<sub>3</sub>), 1.30 (6H, s, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub> + CDCl<sub>3</sub>): δ<sub>C</sub> 167.2, 155.6, 143.0, 141.2, 138.9, 132.0, 130.8, 130.6, 128.6, 121.8, 14.7, 14.5 ppm. MS (TOF- ESI): *m/z*: Calcd: 368.1508, Found: 368.1432 [M-H]<sup>+</sup>, Δ=20.6 ppm.

### Compound (3)

(1) (0.44 mmol, 0.15 g) and iodine (1.10 mmol, 0.28 g) were added to a 500 mL round-bottomed flask and to this solution was added iodic acid (0.88 mmol, 0.16 g) dissolved in 2 mL of water. The reaction mixture was stirred at 60°C and was monitored by TLC (CHCl<sub>3</sub> : MeOH 93:7). When all the starting material had been consumed, saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution in water was added and the product was extracted into chloroform. The solvent was evaporated under vacuo. Red waxy solid (0.26 g, 100%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ<sub>H</sub> 8.15 (2H, d, *J* = 8.2 Hz, *ArH*), 7.65 (2H, d, *J* = 8.2 Hz, *ArH*), 7.15 (2H, s, *ArH*), 2.50 (6H, s, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ<sub>C</sub> 167.2, 160.2, 159.0, 140.4, 137.2, 136.8, 134.9, 133.1, 131.1, 130.0, 15.8 ppm. MS (TOF- ESI): *m/z*: Calcd: 591.9128, Found: 591.9031 [M-H]<sup>+</sup>, Δ=16.4 ppm.

### Compound (4)

(2) (1.41 mmol, 0.52 g) and iodine (3.53 mmol, 0.90 g) were added to a 500 mL round-bottomed flask and to this solution was added iodic acid (2.82 mmol, 0.50 g) dissolved in 2 mL of water. The reaction mixture was stirred at 60°C and was monitored by TLC (CHCl<sub>3</sub> : MeOH 97:3). When all the starting material had been consumed, saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution in water was added and the product was extracted into chloroform. The solvent was evaporated under vacuo. Red waxy solid (0.87 g, 100%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ<sub>H</sub> 7.98 (2H, d, *J* = 7.8 Hz, *ArH*), 7.38 (2H, d, *J* = 7.6 Hz, *ArH*), 2.40 (6H, s, CH<sub>3</sub>), 1.21 (6H, s, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ<sub>C</sub> 167.8, 156.7, 145.3, 141.7, 131.0, 130.7, 128.2, 17.1, 16.2 ppm. HRMS (ESI): *m/z*: Calcd: 641.9375, Found: 641.9351 [M+Na]<sup>+</sup>, Δ= 3.7 ppm.

### (PS-4)

(1) (0.44 mmol, 0.15 g) and 3,4,5-Tris(octadecyloxy)benzaldehyde (1.32 mmol, 1.26 g) were added to a 100 mL round-bottomed flask containing 50 mL benzene and to this solution was added piperidine (0.3 mL) and acetic acid (0.3 mL). The mixture was heated under reflux by using a Dean Stark trap and reaction was monitored by TLC (CHCl<sub>3</sub> : MeOH 95:5). When all the starting material had been consumed, the mixture was cooled to room temperature and solvent was evaporated. Water (100 mL) added to the residue and the product was extracted into the chloroform (3 x 100 mL). Organic phase dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated and residue was purified by silica gel column chromatography using (CHCl<sub>3</sub> : MeOH 95:5) as the eluant. Dark green solid (0.24 g, 25%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 8.28 (2H, d, *J* = 7.8 Hz, *ArH*), 7.65 (2H, d, *J* = 8.1 Hz, *ArH*), 7.60 (2H, d, *J* = 15.8 Hz, CH), 7.30 (2H, d, *J* = 16.4 Hz, CH), 6.95 (2H, d, *J* = 4.6 Hz, *ArH*), 6.85 (4H, s, *ArH*), 6.75 (2H, d, *J* = 4.3 Hz, *ArH*), 4.15-4.01 (12H, m, OCH<sub>2</sub>), 1.85-1.72 (12H, m, CH<sub>2</sub>), 1.69-1.21 (180H, m, CH<sub>2</sub>), 1.05-0.85 (18H, m, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ<sub>C</sub> 155.3, 153.4, 140.0,

139.3, 137.8, 137.0, 135.9, 131.6, 130.5, 130.0, 129.1, 118.1, 116.7, 106.6, 73.6, 69.3, 31.9, 30.4, 29.8, 29.7, 29.5, 29.4, 26.2, 26.1, 22.7, 14.1 ppm. MS (MALDI):  $m/z$ : Calcd: 2125.8418, Found: 2125.8600  $[M-H]^+$ ,  $\Delta=8.5$  ppm.

### (PS-2)

(1) (0.88 mmol, 0.30 g) and N,N-di(4-methoxyphenyl)aminobenzaldehyde (3.53 mmol, 1.18 g) were added to a 100 mL round-bottomed flask containing 50 mL benzene and to this solution was added piperidine (0.3 mL) and acetic acid (0.3 mL). The mixture was heated under reflux by using a Dean Stark trap and reaction was monitored by TLC ( $CHCl_3$ : MeOH 93:7): When all the starting material had been consumed, the mixture was cooled to room temperature and solvent was evaporated. Water (100 mL) added to the residue and the product was extracted into the chloroform (3 x 100 mL). Organic phase dried over  $Na_2SO_4$ , evaporated and residue was purified by silica gel column chromatography using ( $CHCl_3$ : MeOH 93:7) as the eluant. Black waxy solid (0.17 g, 20%).  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ):  $\delta_H$  8.25 (1H, s, COOH), 8.05 (2H, d,  $J = 8.3$  Hz, ArH), 7.64 (2H, d,  $J = 8.2$  Hz, ArH), 7.52 (2H, d,  $J = 17.2$  Hz, CH), 7.38 (4H, d,  $J = 8.7$  Hz, ArH), 7.32 (2H, d,  $J = 15.2$  Hz, CH), 7.15 (2H, d,  $J = 4.6$  Hz, ArH), 7.10-7.05 (8H, m, ArH), 6.95-6.85 (12H, m, ArH), 6.78 (2H, d,  $J = 4.6$  Hz, ArH), 6.72 (4H, d,  $J = 8.5$  Hz, ArH).  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta_C$  167.5, 156.9, 154.9, 150.2, 139.5, 138.2, 137.8, 135.4, 132.6, 131.0, 129.9, 129.8, 129.6, 129.3, 129.1, 128.0, 127.7, 120.2, 118.4, 117.6, 115.5, 55.7 ppm. MS (TOF- ESI):  $m/z$ : Calcd: 970.3713, Found: 970.3692,  $\Delta=2.2$  ppm.

### (PS-1)

(1) (0.88 mmol, 0.30 g) and N,N-diphenylaminobenzaldehyde (3.53 mmol, 0.96 g) were added to a 100 mL round-bottomed flask containing 50 mL benzene and to this solution was added piperidine (0.3 mL) and acetic acid (0.3 mL). The mixture was heated under reflux by using a Dean Stark trap and reaction was monitored by TLC ( $CHCl_3$ : MeOH 93:7). When all the starting material had been consumed, the mixture was cooled to room temperature and solvent was evaporated. Water (100 mL) added to the residue and the product was extracted into the chloroform (3 x 100 mL). Organic phase dried over  $Na_2SO_4$ , evaporated and residue was purified by silica gel column chromatography using ( $CHCl_3$ : MeOH 93:7) as the eluant. Black waxy solid (0.15 mg, 20%).  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ):  $\delta_H$  8.31 (1H, s, COOH), 8.10 (2H, d,  $J = 8.3$  Hz, ArH), 7.72 (2H, d,  $J = 8.2$  Hz, ArH), 7.62 (2H, d,  $J = 16.2$  Hz, CH), 7.51 (4H, d,  $J = 8.7$  Hz, ArH), 7.44 (2H, d,  $J = 16.2$  Hz, CH), 7.38-7.32 (8H, m, ArH), 7.23 (2H, d,  $J = 4.6$  Hz, ArH), 7.15-7.05 (12H, m, ArH), 6.95 (4H, d,  $J = 8.5$  Hz, ArH), 6.85 (2H, d,  $J = 4.6$  Hz, ArH).  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta_C$  185.7, 154.9, 149.1, 146.8, 141.5, 137.7, 136.7, 135.6, 130.9, 130.2, 129.9, 129.8, 129.1, 125.5, 124.6, 121.9, 117.8, 116.8, 116.5 ppm. MS (TOF- ESI):  $m/z$ : Calcd: 850.3291, Found: 850.3271  $[M-H]^+$ ,  $\Delta=2.3$  ppm.

### (PS-3)

(3) (0.18 mmol, 0.11 g) and N,N-diphenylaminobenzaldehyde (0.55 mmol, 0.15 g) were added to a 100 mL round-bottomed flask containing 50 mL benzene and to this solution was added piperidine (0.3 mL) and acetic acid (0.3 mL). The mixture was heated under reflux by using a Dean Stark trap and reaction was monitored by TLC ( $CHCl_3$ : MeOH 93:7): When all the starting material had been consumed, the mixture was cooled to room temperature and solvent was evaporated. Water (100 mL) added to the residue and the product was extracted

into the chloroform (3 x 100 mL). Organic phase dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated and residue was purified by silica gel column chromatography using (CHCl<sub>3</sub> : MeOH 93:7) as the eluant. Black solid (0.05g, 25%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ<sub>H</sub> 8.20 (1H, s, COOH), 8.05 (2H, d, *J* = 7.9 Hz, ArH), 8.00 (2H, d, *J* = 16.6 Hz, CH), 7.60 (2H, d, *J* = 8.2 Hz, ArH), 7.41 (4H, d, *J* = 8.6 Hz, ArH), 7.35 (2H, d, *J* = 16.4 Hz, CH), 7.30-7.21 (8H, m, ArH), 7.09-6.97 (14H, m, ArH), 6.85 (4H, d, *J* = 8.5 ArH). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ<sub>C</sub> 164.8, 162.5, 161.1, 155.7, 151.7, 149.6, 147.9, 146.8, 142.7, 139.3, 136.8, 132.7, 132.1, 130.2, 129.9, 129.3, 125.7, 125.6, 124.8, 121.9 ppm. MS (TOF- ESI): *m/z*: Calcd: 1102.1223, Found: 1102.1184 [M-H]<sup>+</sup>, Δ=3.5 ppm.

## (BOD2)

(4) (0.64 mmol, 0.40 g) and N,N-diphenylaminobenzaldehyde (2.58 mmol, 0.71 g) were added to a 100 mL round-bottomed flask containing 50 mL benzene and to this solution was added piperidine (0.3 mL) and acetic acid (0.3 mL). The mixture was heated under reflux by using a Dean Stark trap and reaction was monitored by TLC (CHCl<sub>3</sub> : MeOH 93:7): When all the starting material had been consumed, the mixture was cooled to room temperature and solvent was evaporated. Water (100 mL) added to the residue and the product was extracted into the chloroform (3 x 100 mL). Organic phase dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated and residue was purified by silica gel column chromatography using (CHCl<sub>3</sub> : MeOH 93:7) as the eluant. Purple-black solid (0.25 g, 35%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ<sub>H</sub> 8.24 (1H, s, COOH), 8.07 (2H, d, *J* = 8.3 Hz, ArH), 8.01 (2H, d, *J* = 16.4 Hz, CH), 7.53 (2H, d; *J* = 8.2 Hz, ArH), 7.44 (4H, d, *J* = 8.8 Hz, ArH), 7.36 (2H, d, *J* = 16.8 Hz, CH), 7.33-7.28 (8H, m, ArH), 7.11-7.03 (12H, m, ArH), 6.92 (4H, d, *J* = 8.7 ArH), 1.30 (6H, s, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ<sub>C</sub> 185.5, 162.3, 162.0, 146.8, 130.4, 130.3, 130.2, 129.6, 129.4, 129.2, 126.9, 125.5, 124.7, 124.6, 124.3, 124.2, 122.2, 121.7, 14.4 ppm; HRMS (ESI): *m/z* Calcd: 1152.1471, Found: 1152.1416 [M+Na]<sup>+</sup>, Δ= 4.8 ppm.

## Compound (6)

(5) (0.10 g, 0.13 mmol) was dissolved in 10 mL freshly distilled THF and 5 mL (*i*-Pr)<sub>2</sub>NH. Then the reaction was purged with argon until all the chemicals were added. After 15 minutes Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (4.71 mg, 0.0067 mmol) and CuI (2.13 mg, 0.0112 mmol) were added to the reaction mixture. Then 4-ethynyl benzoic acid (0.04 g, 0.27 mmol) was added after 10 minutes. The reaction was proceeded for 12 hours at 60°C. The reaction mixture was evaporated under reduced pressure and the compound was purified over silica gel using (CHCl<sub>3</sub> : MeOH 95:5). Red solid (76.44 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 8.05 (2H, d, *J* = 8.2 Hz, ArH), 7.55 (2H, d, *J* = 8.2 Hz, ArH), 6.60 (1H, d, *J* = 2.1 Hz, ArH), 6.41 (2H, d, *J* = 2.2 Hz, ArH), 6.05 (1H, s, ArH), 3.97 (4H, t, *J* = 6.6 Hz, OCH<sub>2</sub>), 2.72 (3H, s, CH<sub>3</sub>), 2.60 (3H, s, CH<sub>3</sub>), 1.75 (4H, p, *J* = 5.6 Hz CH<sub>2</sub>), 1.71 (3H, s, CH<sub>2</sub>), 1.62 (3H, s, CH<sub>3</sub>), 1.45 (4H, m, CH<sub>2</sub>), 1.40-1.18 (24H, m, CH<sub>2</sub>), 0.88 (6H, t, *J* = 6.7 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 171.2, 161.4, 158.4, 156.3, 145.4, 142.9, 142.3, 137.1, 136.0, 132.5, 131.1, 130.2, 129.4, 128.0, 122.3, 114.2, 106.2, 102.5, 95.3, 86.2, 68.5, 31.9, 29.5, 29.4, 29.3, 29.1, 26.0, 22.7, 14.5, 14.1, 13.1 ppm. MS (TOF- ESI): *m/z*: Calcd: 780.4849, Found: 780.4807 [M-H]<sup>+</sup>, Δ=5.4 ppm.

## (PS-5)

(6) (0.13 mmol, 0.10 g) and N,N-diphenylaminobenzaldehyde (0.51 mmol, 0.14 g) were added to a 100 mL round-bottomed flask containing 50 mL benzene and to this solution

was added piperidine (0.3 mL) and acetic acid (0.3 mL). The mixture was heated under reflux by using a Dean Stark trap and reaction was monitored by TLC (CHCl<sub>3</sub> : MeOH 93:7): When all the starting material had been consumed, the mixture was cooled to room temperature and solvent was evaporated. Water (100 mL) added to the residue and the product was extracted into the chloroform (3 x 100 mL). Organic phase dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated and residue was purified by silica gel column chromatography using (CHCl<sub>3</sub> : MeOH 93:7) as the eluant. Dark-green solid. (58.76 mg, 35%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 8.29 (1H, d, *J* = 16.1 Hz, *CH*), 8.07 (2H, d, *J* = 7.4 Hz, *ArH*), 7.72 (1H, d, *J* = 16.1 Hz, *CH*), 7.63 (1H, d, *J* = 16.1 Hz, *CH*), 7.58-7.47 (7H, m, *ArH-CH*), 7.35-7.21 (8H, m, *ArH*), 7.20-7.02 (16H, m, *ArH*), 6.67 (1H, s, *ArH*), 6.62-6.55 (1H, br s, *ArH*), 6.52-6.46 (2H, br s, *ArH*), 4.05-3.80 (4H, br s, *OCH*<sub>2</sub>), 1.85-1.67 (4H, m, *CH*<sub>2</sub>), 1.61 (3H, s, *CH*<sub>3</sub>), 1.58 (3H, s, *CH*<sub>3</sub>), 1.52-1.41 (4H, m, *CH*<sub>2</sub>), 1.38-1.15 (24H, m, *CH*<sub>2</sub>), 0.95-0.80 (6H, m, *CH*<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 161.2, 149.1, 148.7, 147.3, 147.0, 137.9, 137.0, 136.5, 134.4, 130.9, 130.7, 130.3, 129.8, 129.4, 128.9, 128.5, 125.2, 125.0, 123.8, 123.5, 122.7, 122.2, 106.9, 102.4, 96.8, 68.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 22.7, 14.7, 14.1, 12.9 ppm. MS (TOF- ESI): *m/z*: Calcd: 1290.6945, Found: 1290.6899 [M-H]<sup>+</sup>, Δ=3.6 ppm.

### (BOD1)

To a 1 L round-bottomed flask containing 400 mL argon-degassed CH<sub>2</sub>Cl<sub>2</sub> were added 3-ethyl-2,4-dimethyl pyrrole (9.63 mmol, 1.19 g) and propargyl benzaldehyde (4.37 mmol, 0.7 g). One drop of TFA was added and the solution was stirred under N<sub>2</sub> at room temperature for 1 day. After addition of a solution of DDQ (4.37 mmol, 1.08 g) in 100 mL of dichloromethane to the reaction mixture, stirring was continued for 30 min. 5 mL of Et<sub>3</sub>N and 5 mL of BF<sub>3</sub>.OEt<sub>2</sub> were successively added and after 30 min, the reaction mixture was washed three times with water (3 x 100 mL) which was then extracted into the CHCl<sub>3</sub> (3 x 100 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the residue was purified by silica gel column chromatography using (CHCl<sub>3</sub>/Hexane (2:1)) as the eluant. Red-orange solid (0.57 g, 30%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 7.21 (2H, d, *J* = 8.8 Hz, *ArH*), 7.10 (2H, d, *J* = 8.8 Hz, *ArH*), 4.78 (2H, s, *OCH*<sub>2</sub>), 2.58 (1H, t, *J* = 2.4 Hz, *CH*) 2.55 (6H, s, *CH*<sub>3</sub>), 2.32 (4H, q, *J* = 7.50 Hz, *CH*<sub>2</sub>), 1.33 (6H, s, *CH*<sub>3</sub>), 1.00 (6H, t, *J* = 7.50 Hz, *CH*<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 157.9, 153.6, 139.9, 138.4, 132.7, 131.1, 129.5, 128.9, 115.5, 78.1, 75.8, 56.0, 17.1, 14.6, 12.5, 11.8 ppm; HRMS (ESI): *m/z*: Calcd: 456.2275, Found: 456.2246 [M+Na]<sup>+</sup>, Δ = 6.4 ppm.

### (PS-7)

(BOD1) (0.19 mmol, 0.22 g), Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol, 0.07 g) and CuI (0.01 mmol, 0.03 g) were dissolved in 5 mL of distilled THF. Then argon gas was bubbled through the mixture for 10 min which was followed by addition of P(*t*-Bu)<sub>3</sub> (0.04 mmol, 0.04 mL of a 1.0 M solution in toluene), and HN(*i*-Pr)<sub>2</sub> (0.48 mol 0.07 mL) via syringe. Finally (BOD2) (0.48 mmol, 0.21 g) was added, reaction flask was filled with argon gas and the mixture was stirred at 30°C for two days. The reaction was monitored by TLC (eluent CHCl<sub>3</sub> : MeOH 97:3). Upon the completion of reaction, THF was evaporated and crude product was purified by silica gel column chromatography (CHCl<sub>3</sub> : MeOH 97:3). Several preparative TLC purifications were applied. Red solid (0.03 g, 9%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 8.17 (2H, d, *J* = 8.0 Hz, *ArH*), 8.16 (2H, d, *J* = 16.2 Hz, *CH*), 7.53 (2H, d, *J* = 16.2 Hz, *CH*), 7.40 (4H, d, *J* = 8.6 Hz, *ArH*), 7.34 (2H, d, *J* = 8.0 Hz, *ArH*), 7.22-7.15 (8H, m, *ArH*), 7.07-6.96 (20H, m, *ArH*), 6.93 (4H, d, *J* = 8.6 Hz, *ArH*), 4.98 (4H, s, *OCH*<sub>2</sub>), 2.44 (12H, s, *CH*<sub>3</sub>), 2.19 (8H, q, *J* = 7.5 Hz, *CH*<sub>2</sub>), 1.18 (6H, s, *CH*<sub>3</sub>), 1.13 (12H, s, *CH*<sub>3</sub>), 0.98 (12H, t, *J* = 7.5 Hz, *CH*<sub>3</sub>). <sup>13</sup>C NMR (100 MHz,

$\text{CDCl}_3$ ):  $\delta_{\text{C}}$  158.0, 153.6, 152.9, 149.3, 147.0, 144.9, 139.9, 139.1, 138.4, 132.7, 131.1, 130.1, 129.5, 129.0, 128.7, 125.2, 123.8, 122.1, 115.5, 92.5, 82.1, 56.9, 17.1, 14.6, 13.3, 12.5, 11.8 ppm. MS (MALDI) Calcd: 1741.796, Found: 1741.178.

### Photophysical parameters for Energy transfer cassette:

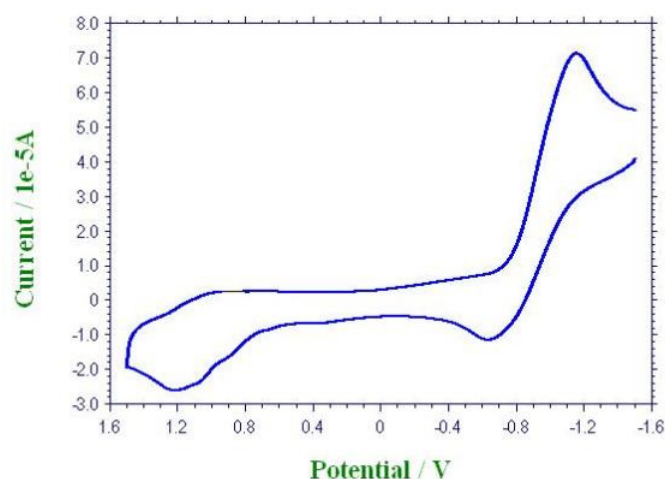
Compound	$\epsilon$ ( $\lambda_{\text{max}}$ )/ ( $\text{M}^{-1} \text{cm}^{-1}$ ). (nm)	$\lambda_{\text{em}}$ /nm	$\Phi_{\text{bodipy}}$ ( $\lambda_{\text{ex}} = 520 \text{ nm}$ )
<b>BOD2</b>	69000 (726)	785	-
<b>BOD1</b>	81000 (527)	540	0.75
<b>PS-7</b>	58000 (735), 108000 (527)	785	0.05

- The quantum yield of emission for **BOD1** was determined 0.75, whereas that of BODIPY donor units in **PS-7** was 0.05 due to the antenna effect. The efficiency of energy transfer is 96%.

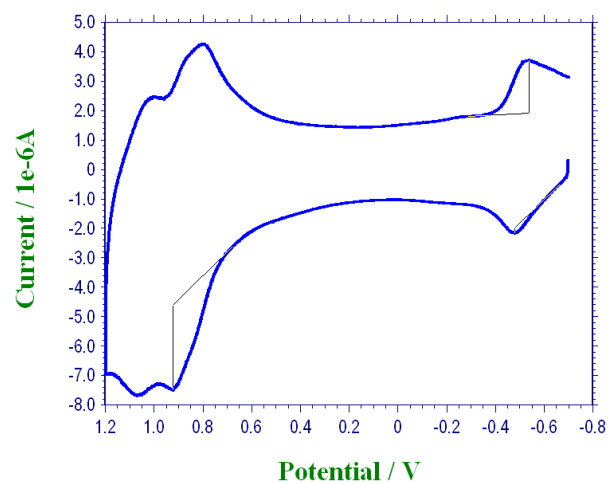
### Electrochemistry of Bodipy Dyes

CV measurement was taken by using CH-Instrument 660 B Model Potentiostat equipment. Solution was prepared in chloroform ( $10^{-3} \text{ M}$ ). A three electrode cell was used consisting of Glassy carbon working electrode, Pt wire counter electrode and Ag/AgCl reference electrode, all placed in a glass vessel. Tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ), 0.1 M, was used as supporting electrolyte. Ferrocene was used as internal reference electrode. Cyclic voltammograms of **PS-2** and **PS-6** are given in literature.<sup>2</sup>

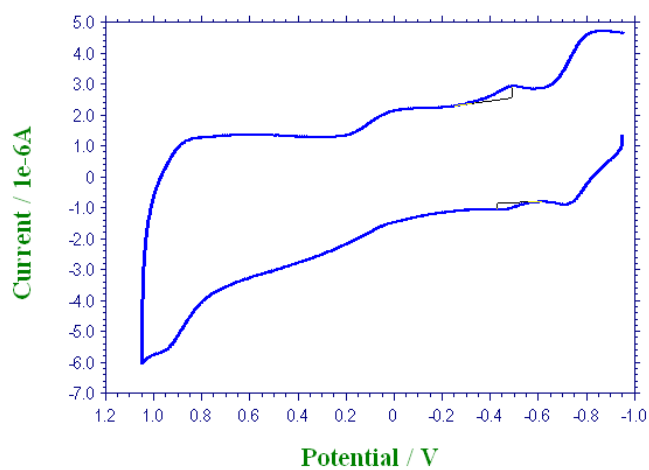
$E_{\text{LUMO}}$  level was calculated by using the formula of  $E_{\text{LUMO}} = -e(E_{1/2}(\text{red}) - E_{\text{fer.}} + 4.8)$ .  
The conduction band of  $\text{TiO}_2$  layer,  $E_{\text{TiO}_2\text{CB}} = -4.2 \text{ eV}$ .



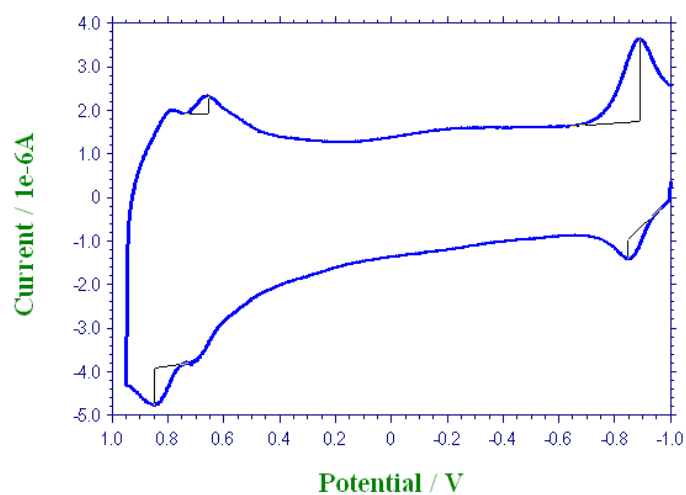
PS-1 (expanded)



(PS-3)



(PS-4)



(PS-5)

Figure S1. Cyclic voltammograms of the sensitizers PS-1 (expanded) PS-3, PS-4 and PS-5.



## Device Fabrication:

The construction of the dye sensitized solar cell device requires first cleaning of the fluorine doped tin oxide (FTO) coated glass substrates in acetone and isopropanol by using an ultrasonic bath. FTO (SnO<sub>2</sub>:F, Pilkington TEC-15; Rsheet:150/8), electrically conductive oxide-coated glasses were used as transparent electrodes. TiO<sub>2</sub> electrodes consist of an adsorbent mesoporous layer with 20 nm anatase TiO<sub>2</sub> particle size in 7 mm thicknesses and a second light scattering layer with 400 nm anatase TiO<sub>2</sub> particle size of 5 mm thicknesses. Dye solutions were prepared in chlorobenzene-methanol (1:1) mixture with a concentration of 0.5 mM BODIPY. TiO<sub>2</sub>-coated electrodes, after sintering at 450 °C for 30 min and cooling to 100 °C, were kept overnight in BODIPY solutions for adsorption. BODIPY adsorbed TiO<sub>2</sub>-coated glasses were washed with pure chlorobenzene and dried *in vacuo*. Platinized FTO glasses were used as counter electrode. Platinization of counter electrodes were done by coating of FTO glasses with 1% solution of hydrogen hexachloroplatinate (Aldrich) in 2-propanol and annealing at 400 °C for 30 min. Cells were prepared in sandwich geometry. Surlyn-1702 (DuPont) frame was used as a spacer and a thermoplastic sealant between the two electrodes. Cells prepared in this way were then sealed by heating at 100 °C. Electrolyte was filled into the space created by Surlyn-1702 between the electrodes under vacuum using a small hole pre-drilled on the counter electrode with the help of a diamond drill. After filling the electrolyte, a small hole was sealed again using a piece of Surlyn-1702 and a piece of cover glass. The electrolyte A6986 consisted of 0.6M N-methyl-N-butyl-imidazolium iodide (BMII) + 0.1 M LiI + 0.05 M I<sub>2</sub> + 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile/valeronitrile (85/15 v/v). On the other hand electrolyte Z1040 consisted of 1M LiI, 0.044M I<sub>2</sub>, 0.25M TBP in acetonitrile/valeronitrile (85/15 v/v) Active areas of the cells were adjusted to 0.159 cm<sup>2</sup> with a special mask.

Dye sensitized solar cells were characterized by current-voltage ( $I - V$ ) measurement. All current-voltage measurements ( $I - V$ ) were done under 100 mW/cm<sup>2</sup> light intensity and AM 1.5 conditions. 450 W Xenon light source (Oriel) was used to give an irradiance of various intensities. The spectral output of the lamp was matched in the region of 350–700 nm with the aid of Schott K113 Tempax sunlight filter.  $I - V$  data collection was made by using Keithley 2400 Source-Meter and LabView data acquisition software.

## References :

1. Cakmak, Y.; Akkaya, E. U. *Org. Lett.* **2009**, *11*, 85.
2. Kolemen, S.; Cakmak, Y.; Erten-Ela, S.; Altay, Y.; Brendel, J.; Thelakkat, M.; Akkaya, E. U. *Org. Lett.* **2010**, *12*, 3812.

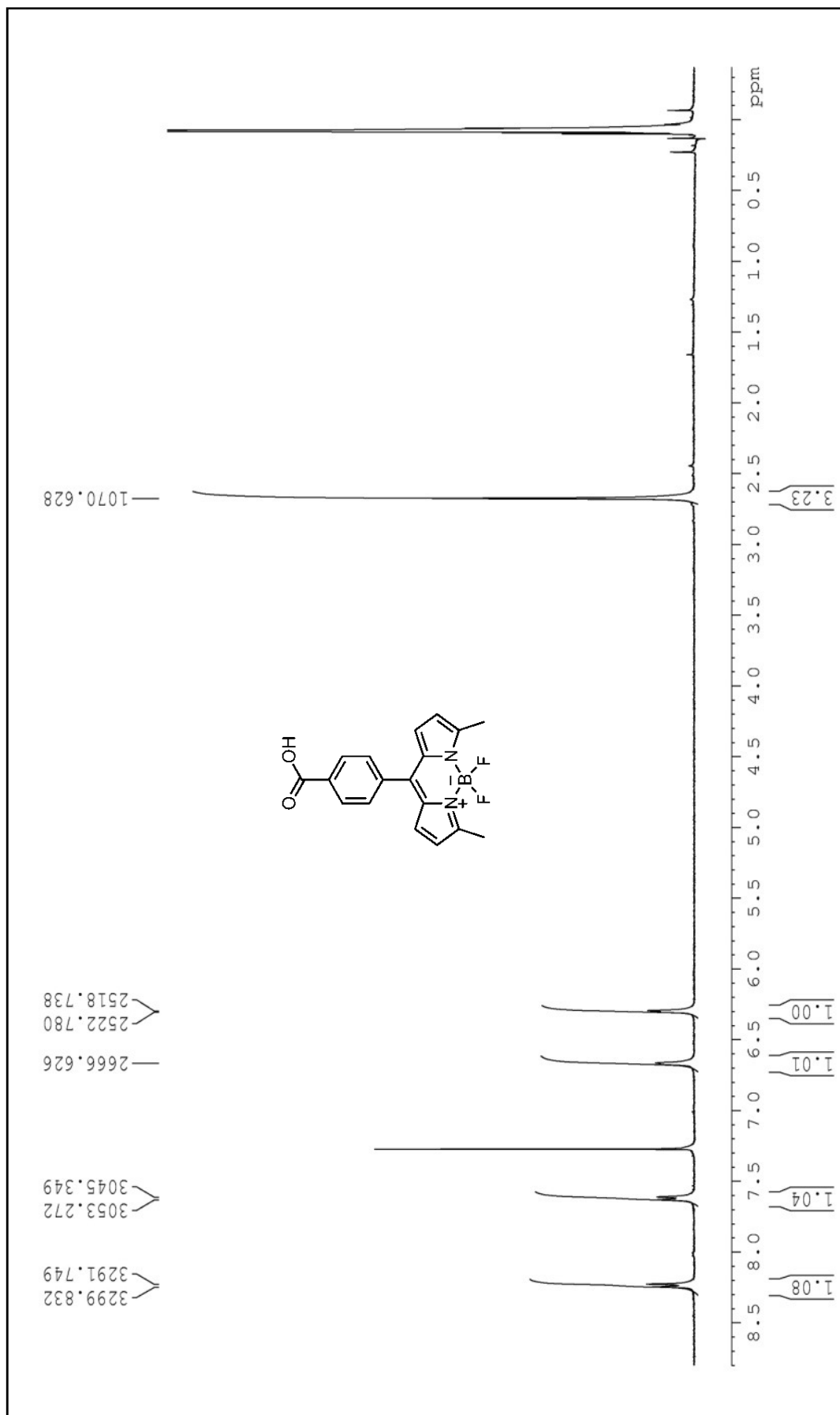


Figure S2. <sup>1</sup>H NMR spectrum of compound (1)

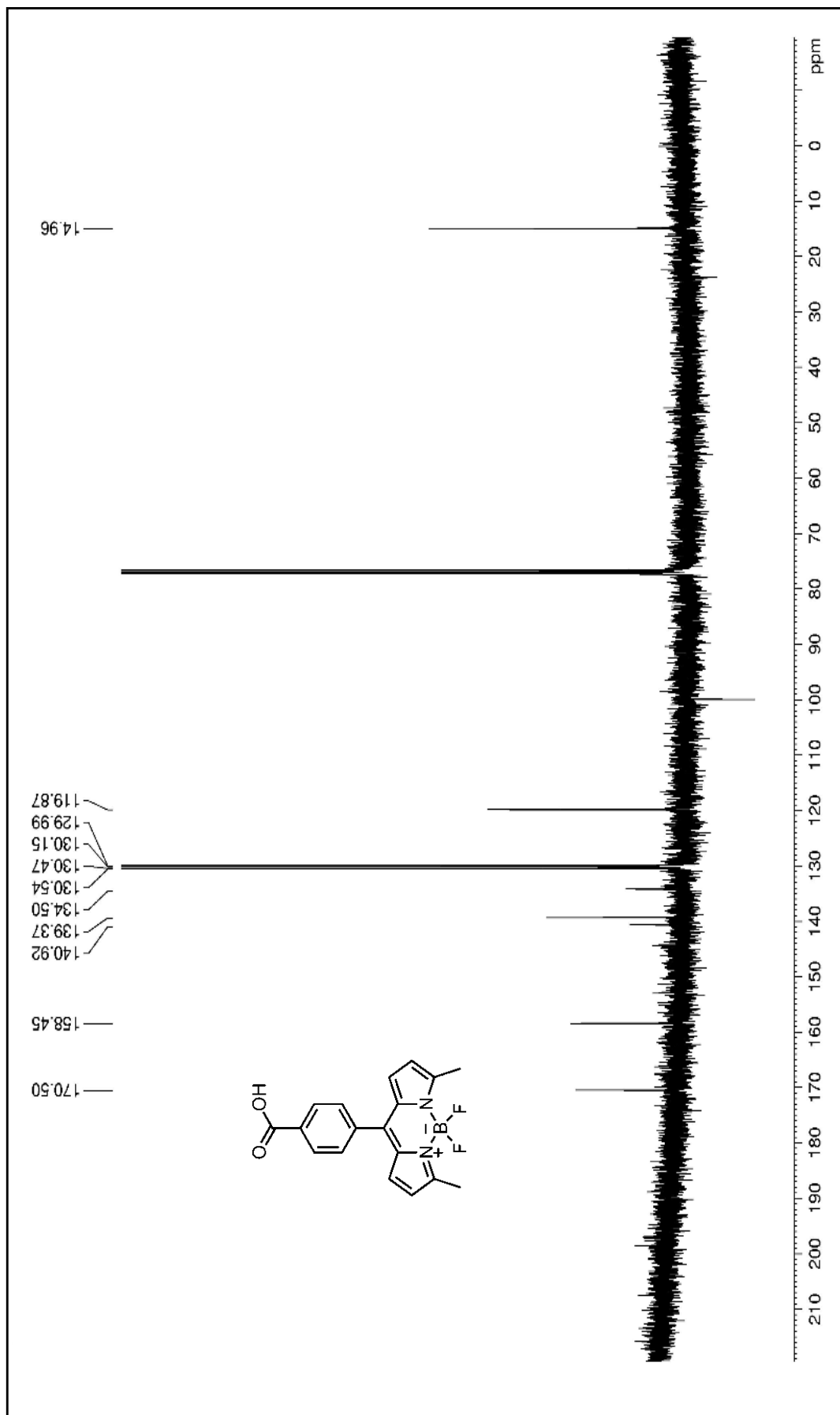


Figure S3.  $^{13}\text{C}$  NMR spectrum of compound (I)

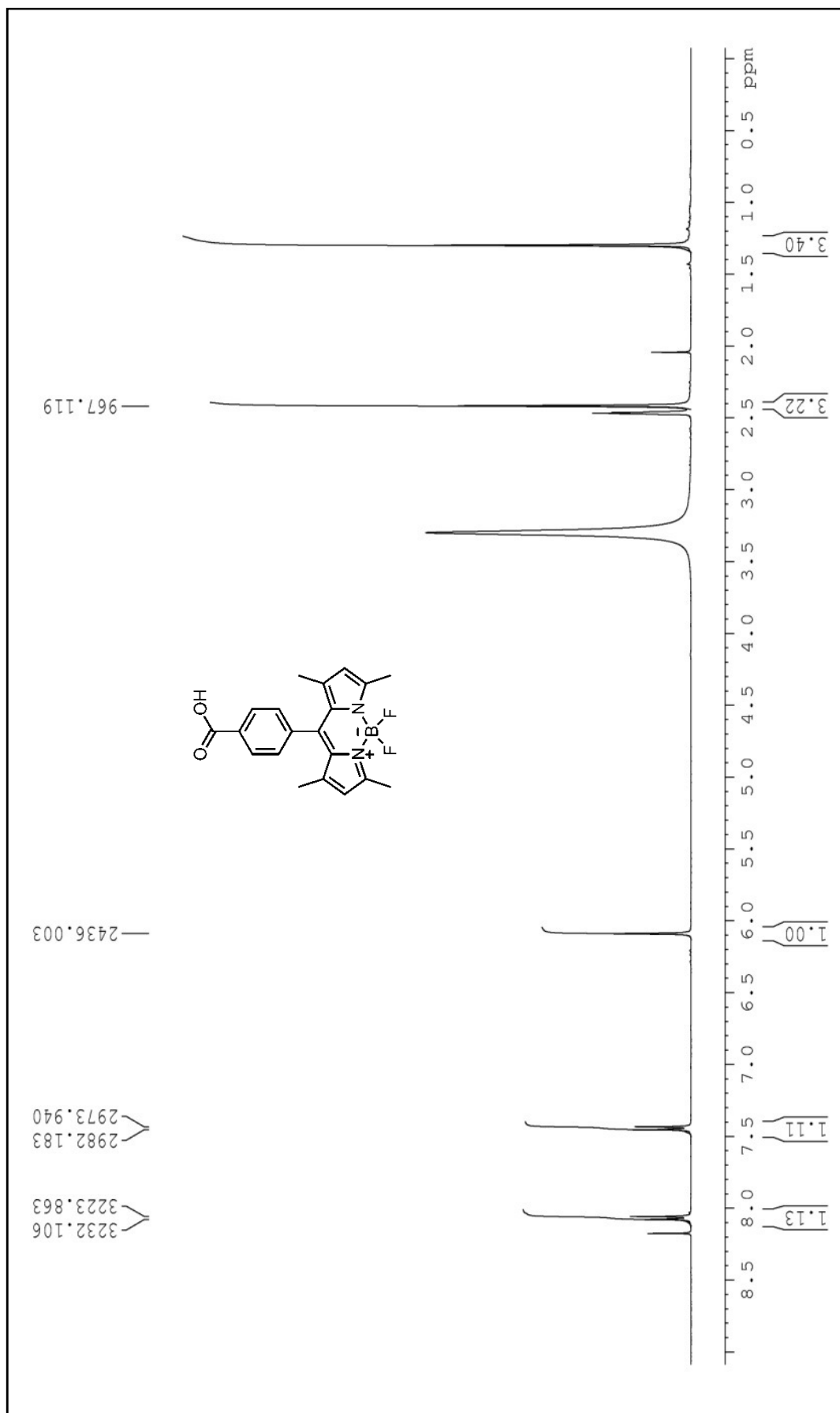


Figure S4. <sup>1</sup>H NMR spectrum of compound (2)

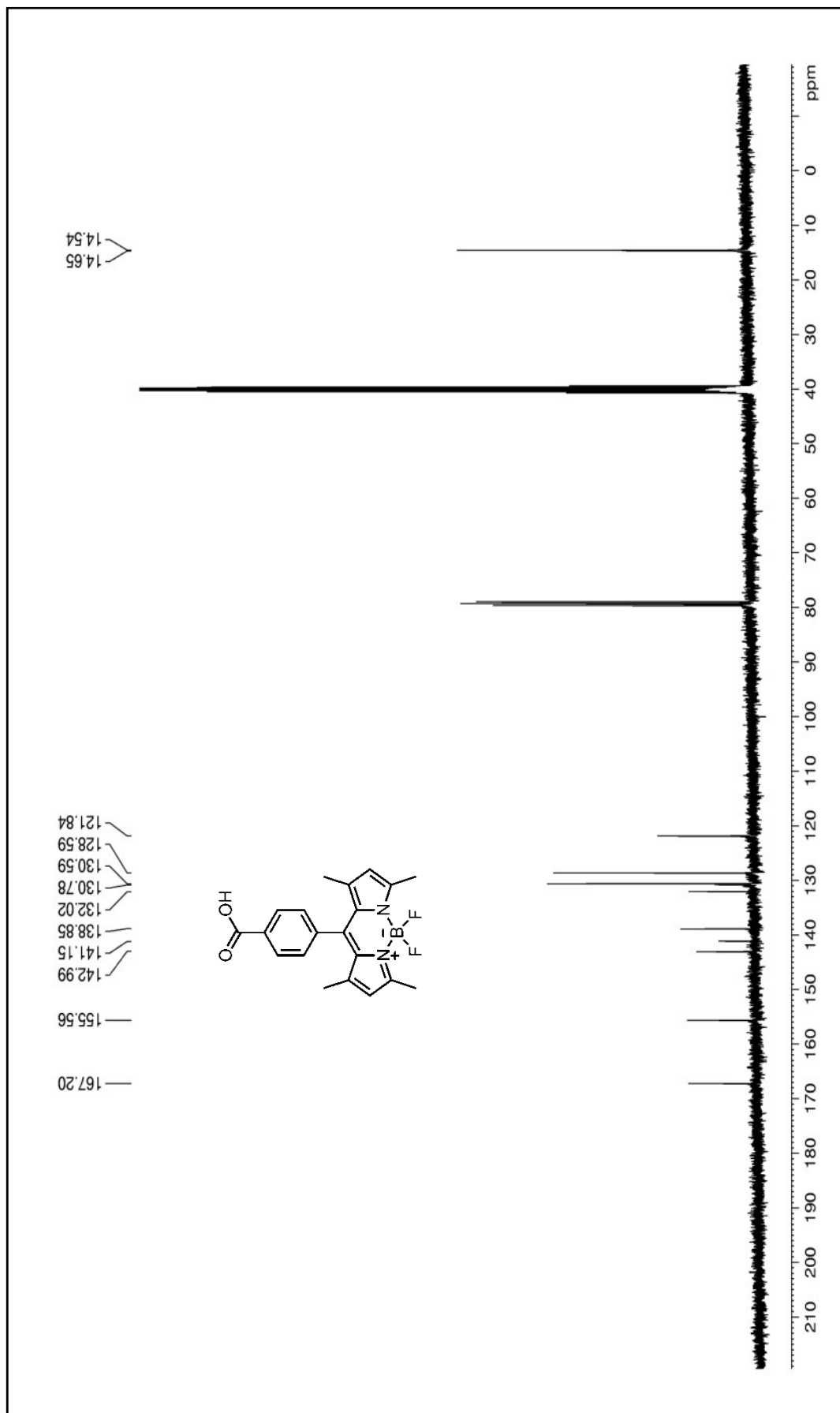


Figure S5.  $^{13}\text{C}$  NMR spectrum of compound (2)

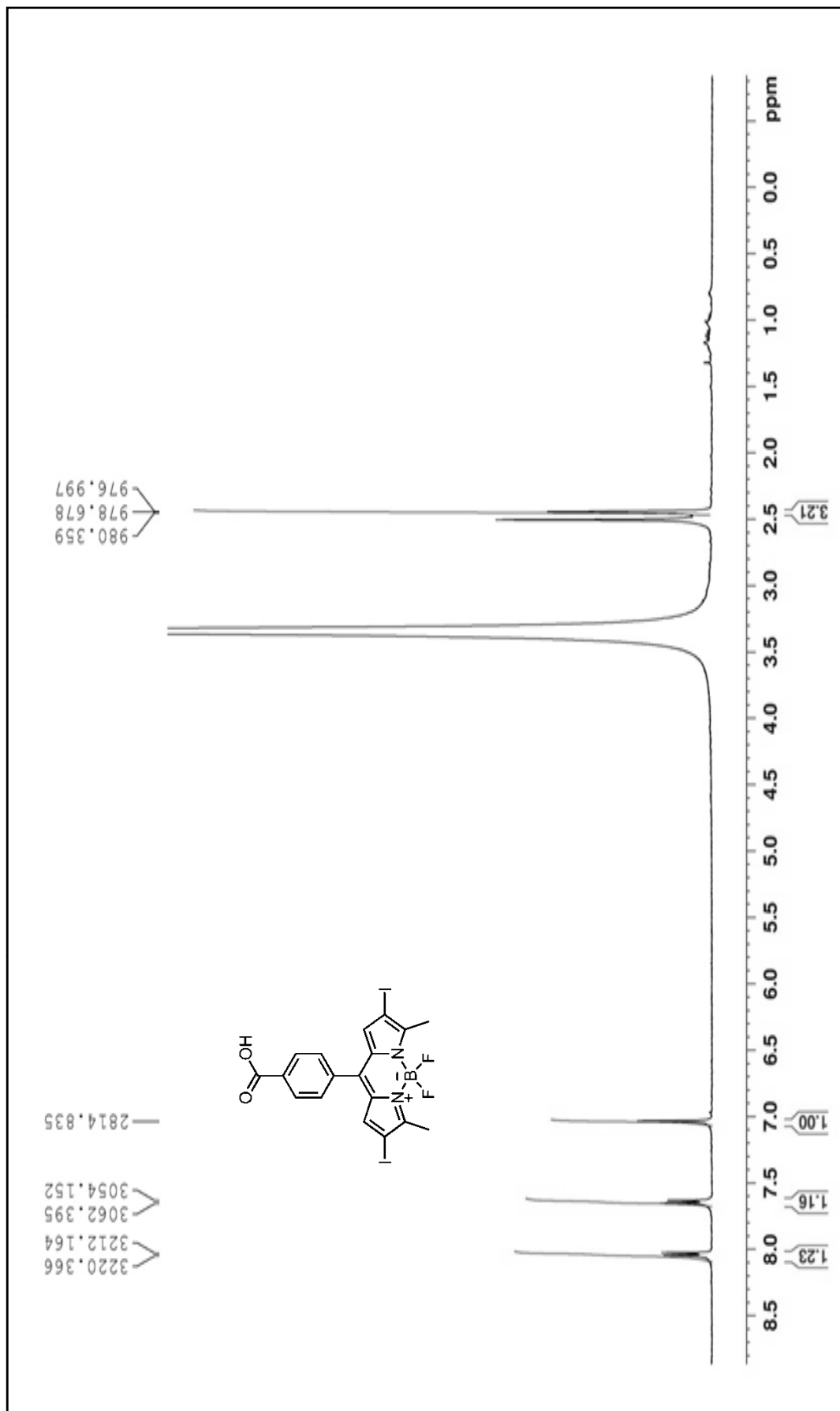


Figure S6. <sup>1</sup>H NMR spectrum of compound (3)

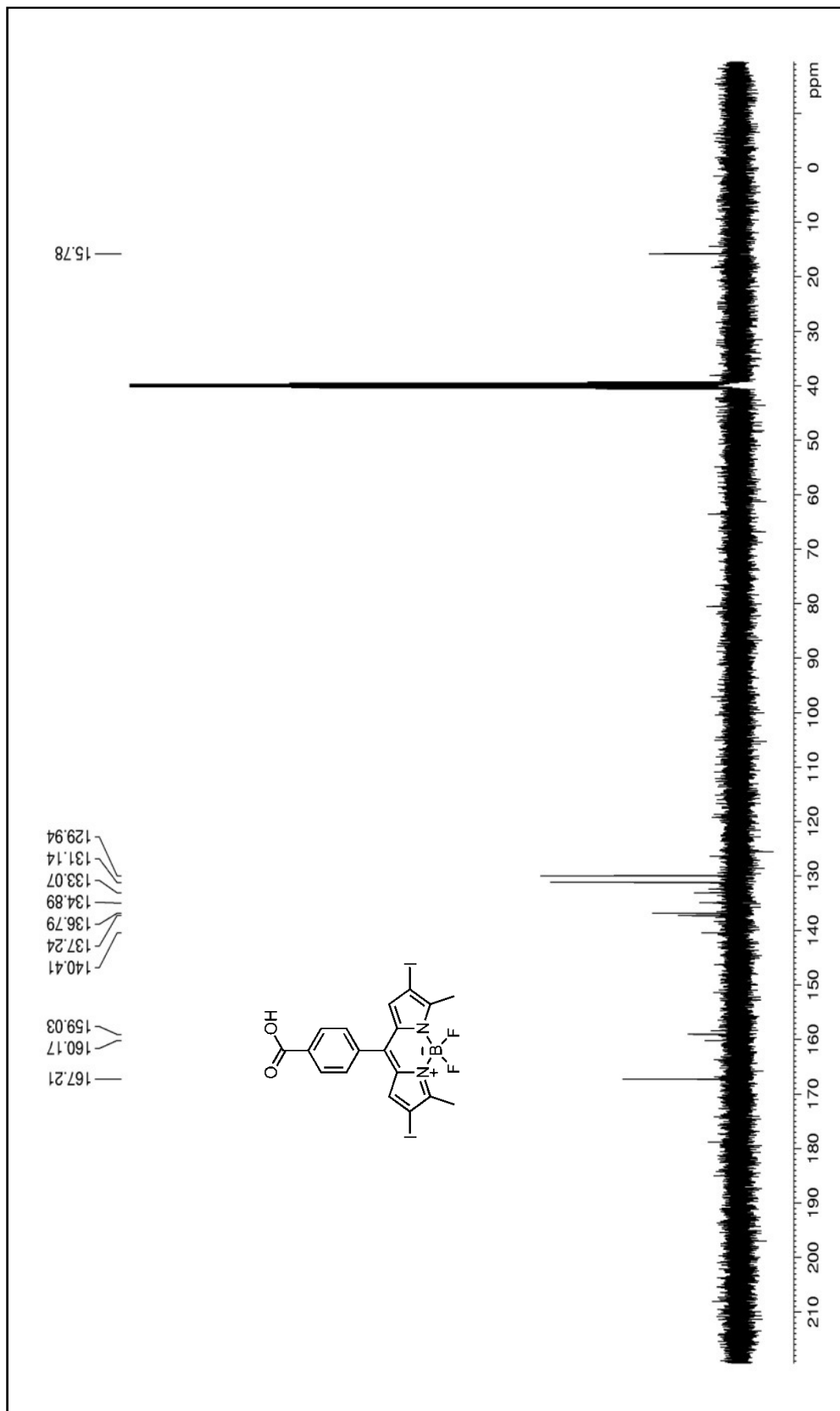


Figure S7.  $^{13}\text{C}$  NMR spectrum of compound (3)

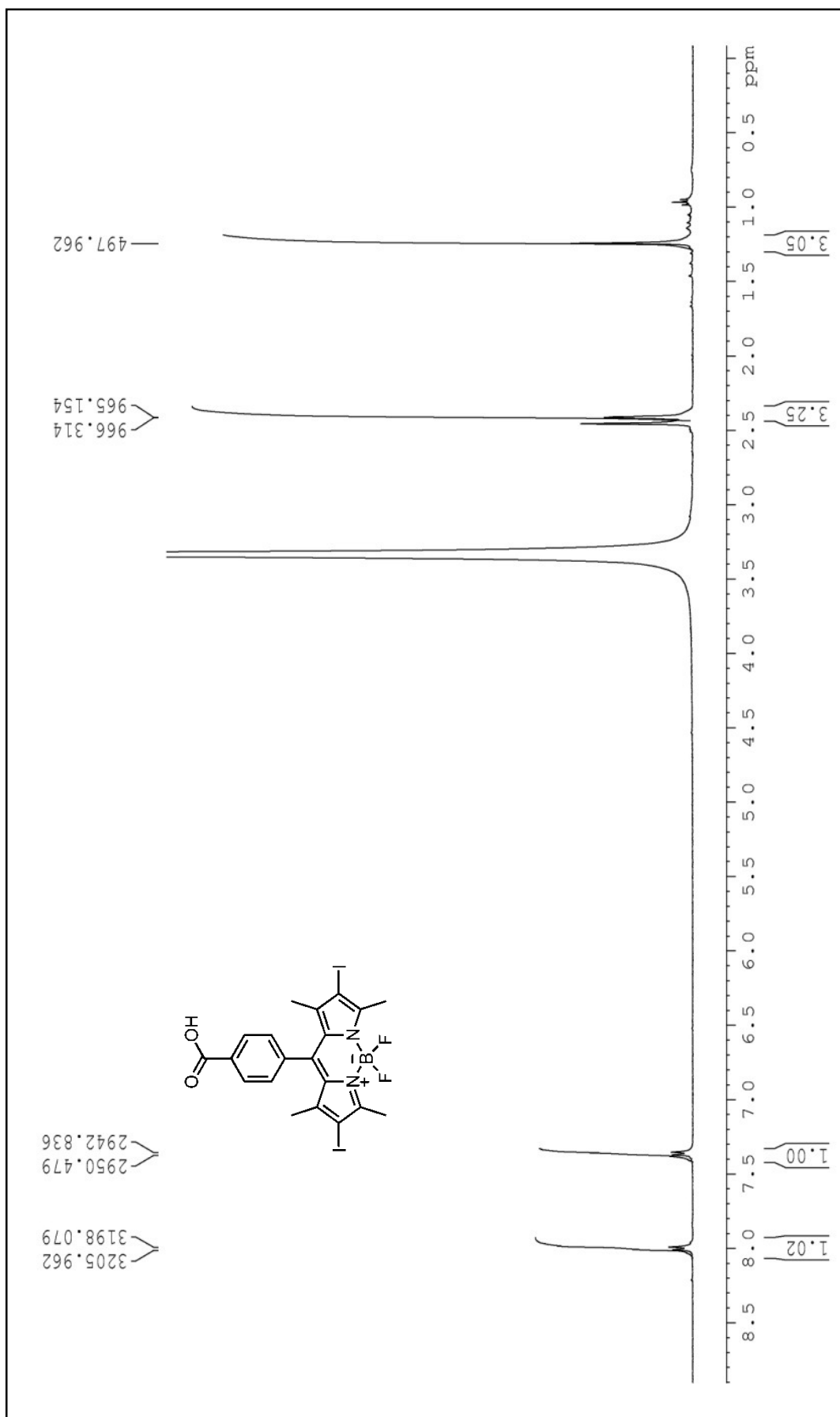


Figure S8. <sup>1</sup>H NMR spectrum of compound (4)



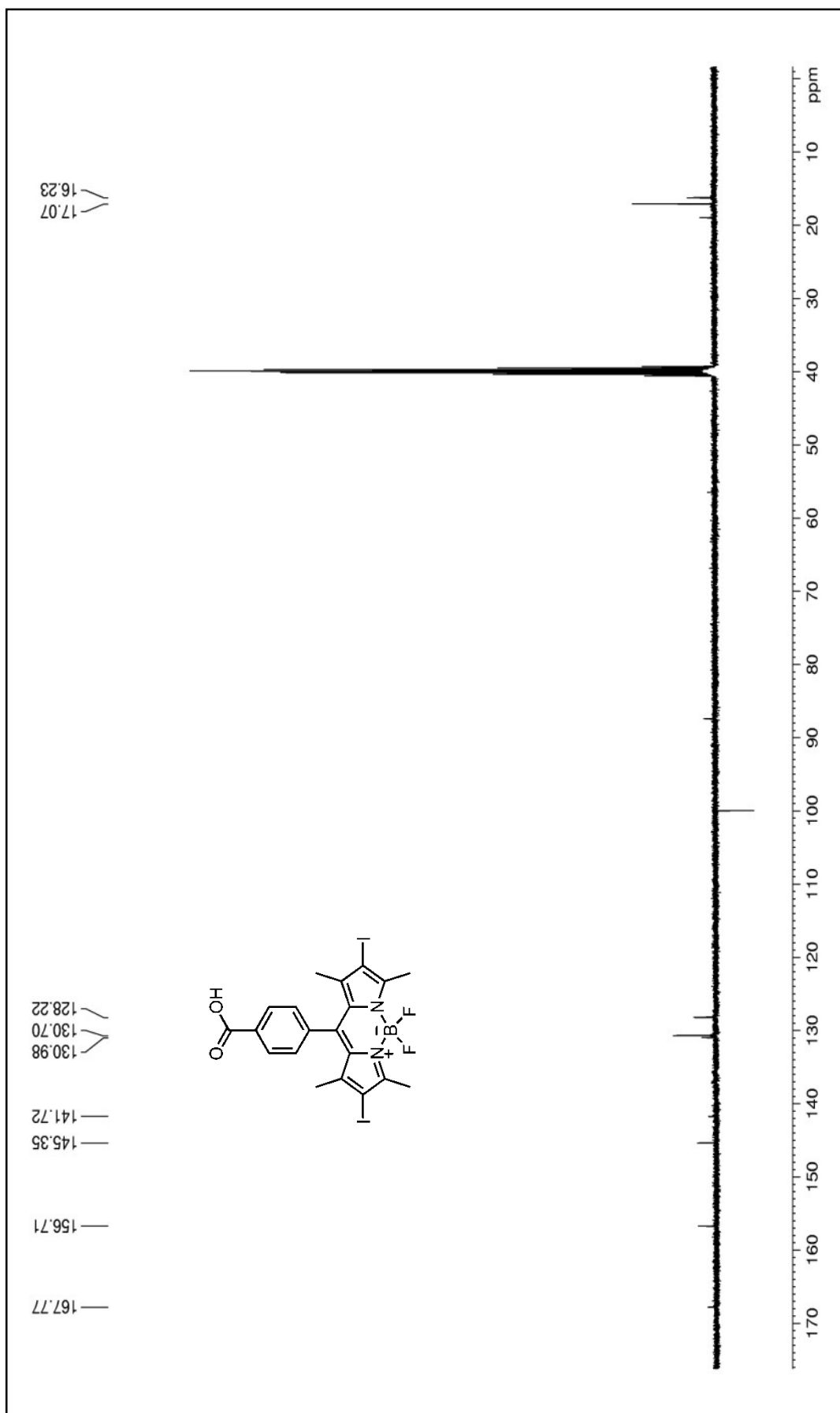


Figure S9. <sup>13</sup>C NMR spectrum of compound (4)

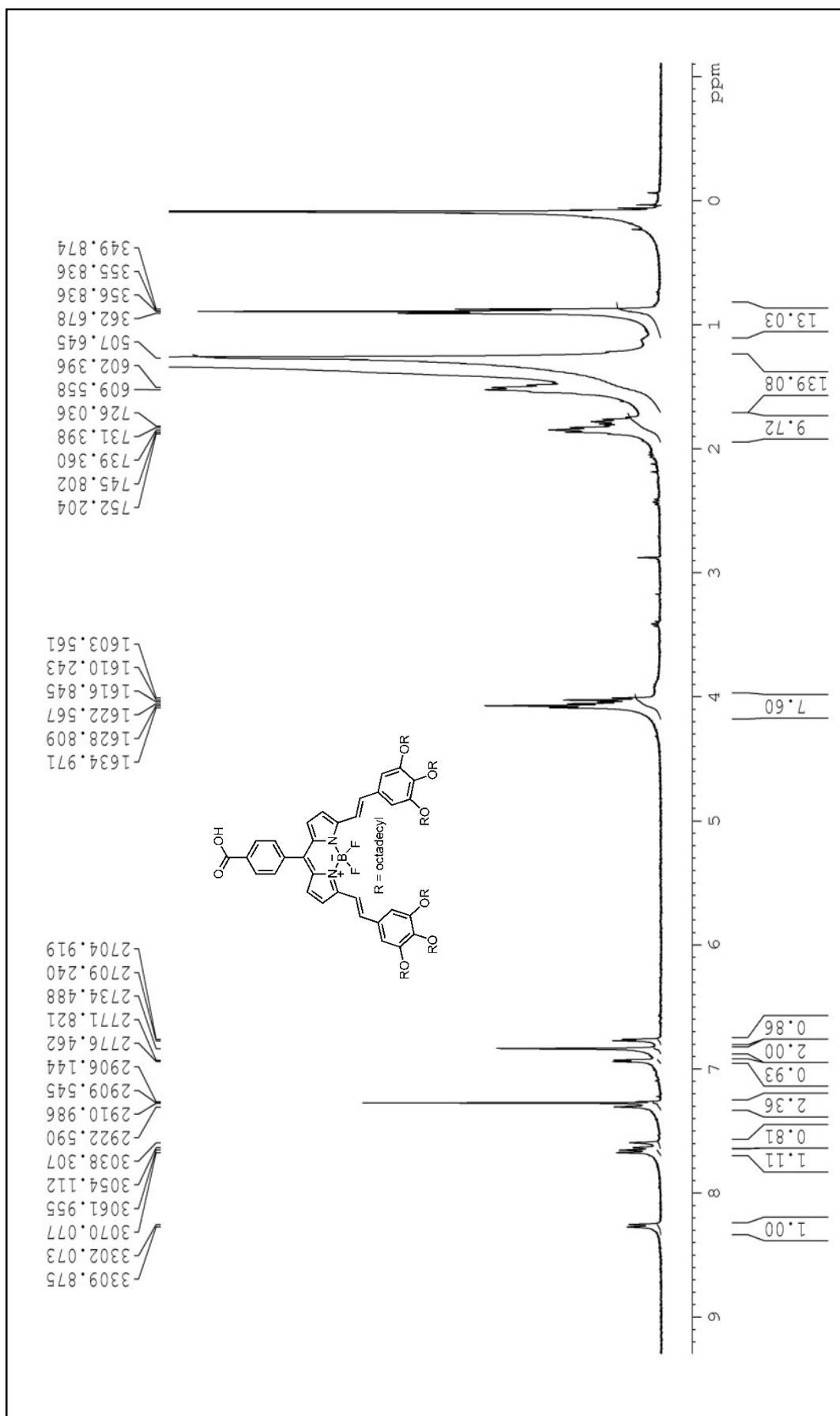


Figure S10. <sup>1</sup>H NMR spectrum of compound (PS-4)

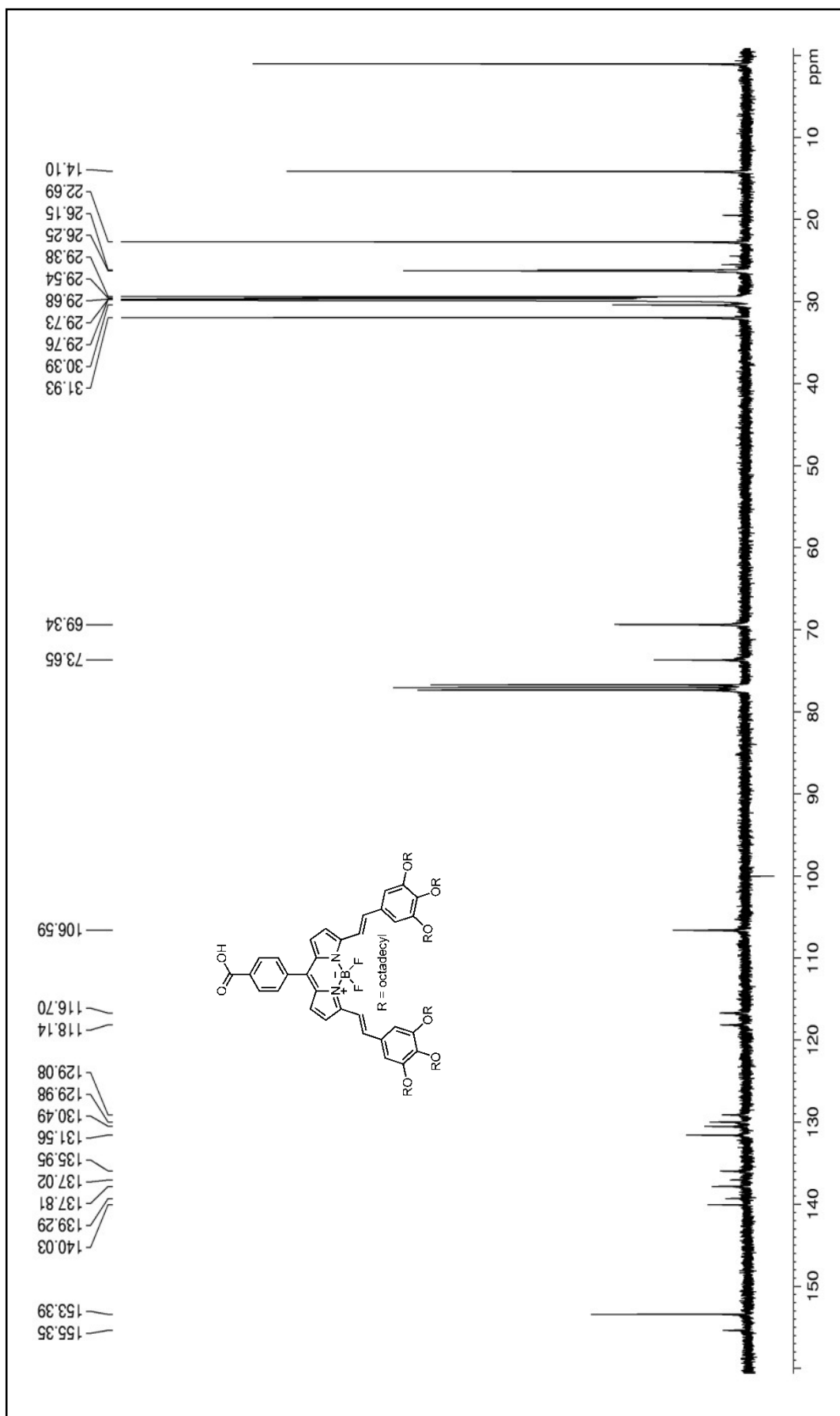
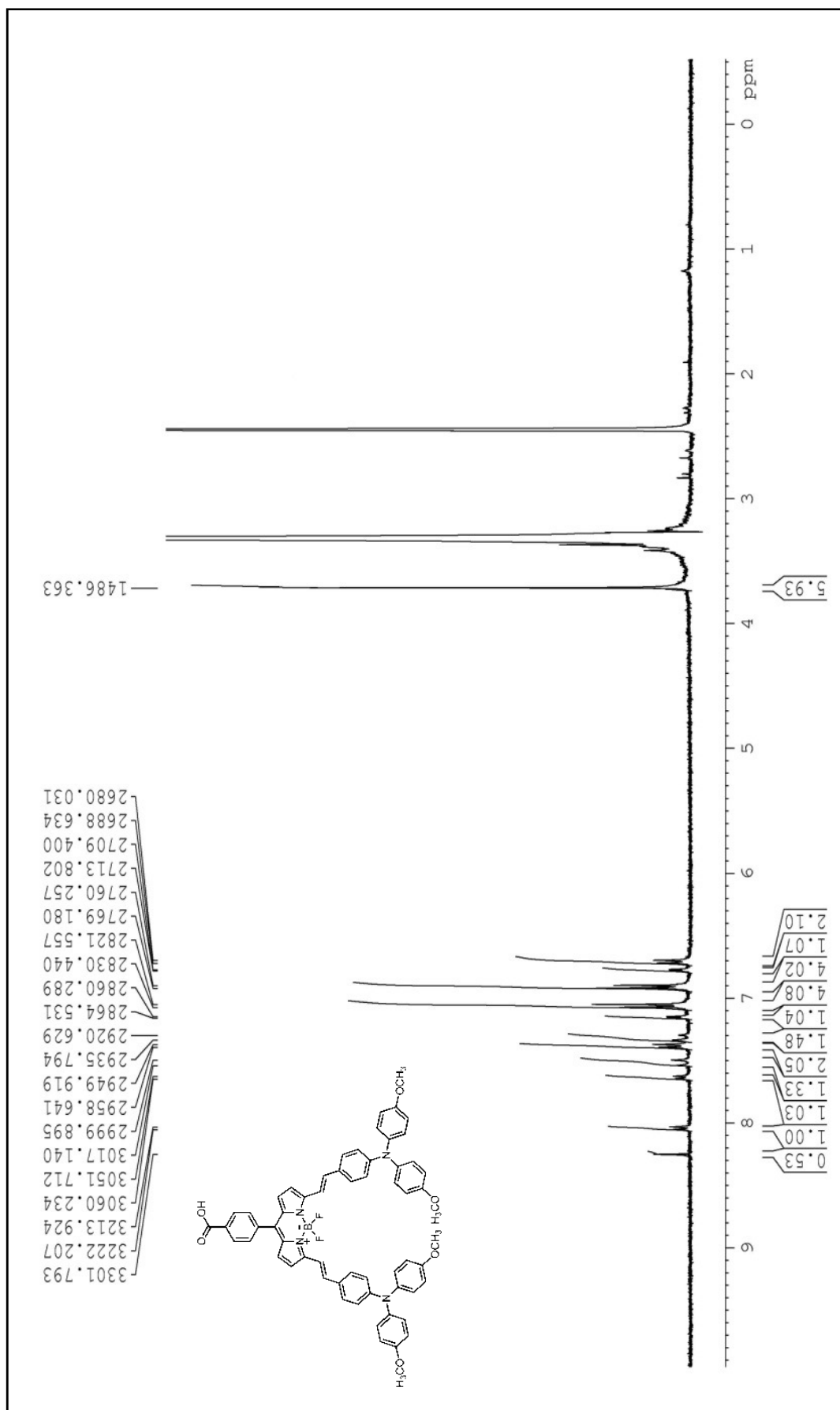


Figure S11.  $^{13}\text{C}$  NMR spectrum of compound (PS-4)



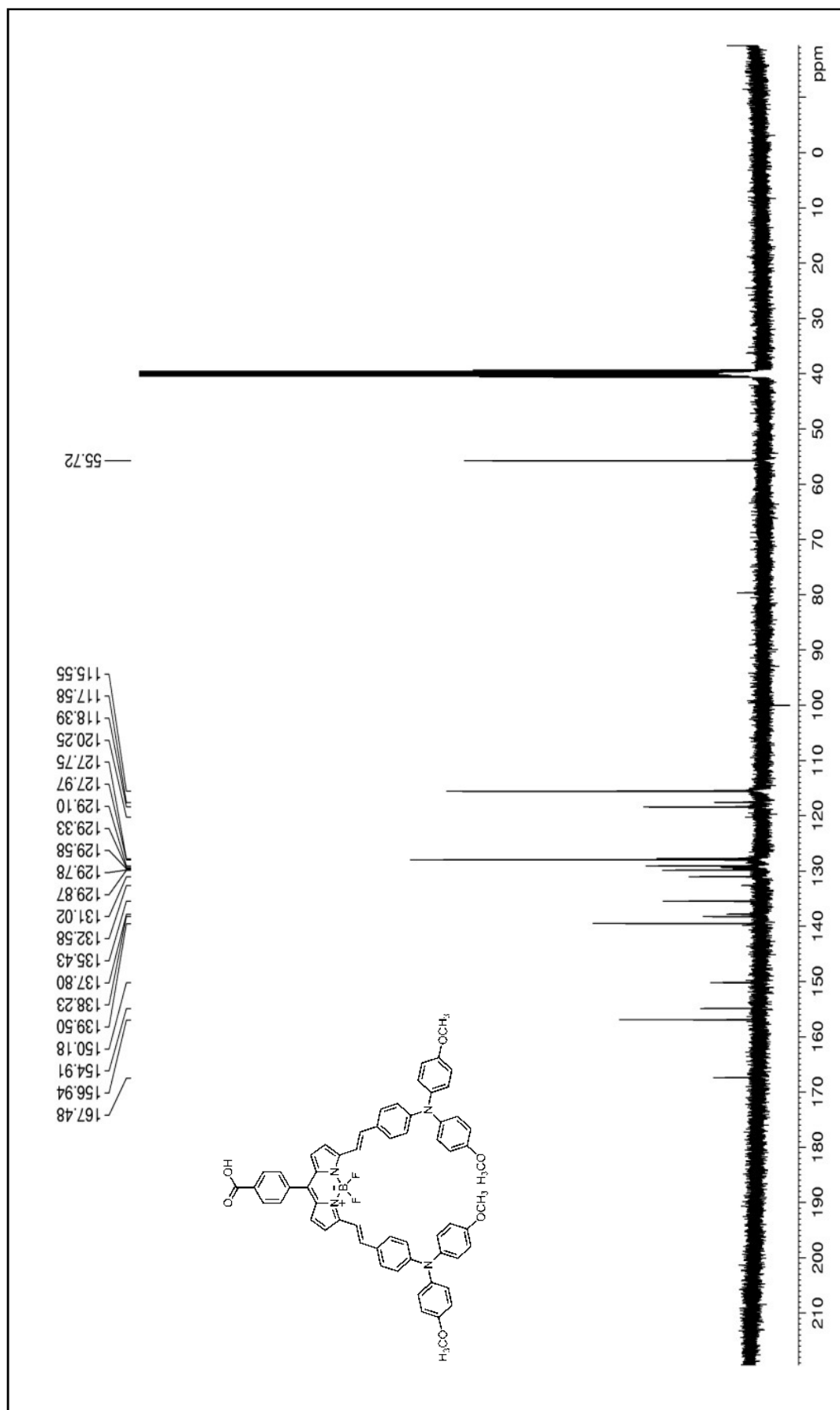


Figure S13. <sup>13</sup>C NMR spectrum of compound (PS-2)

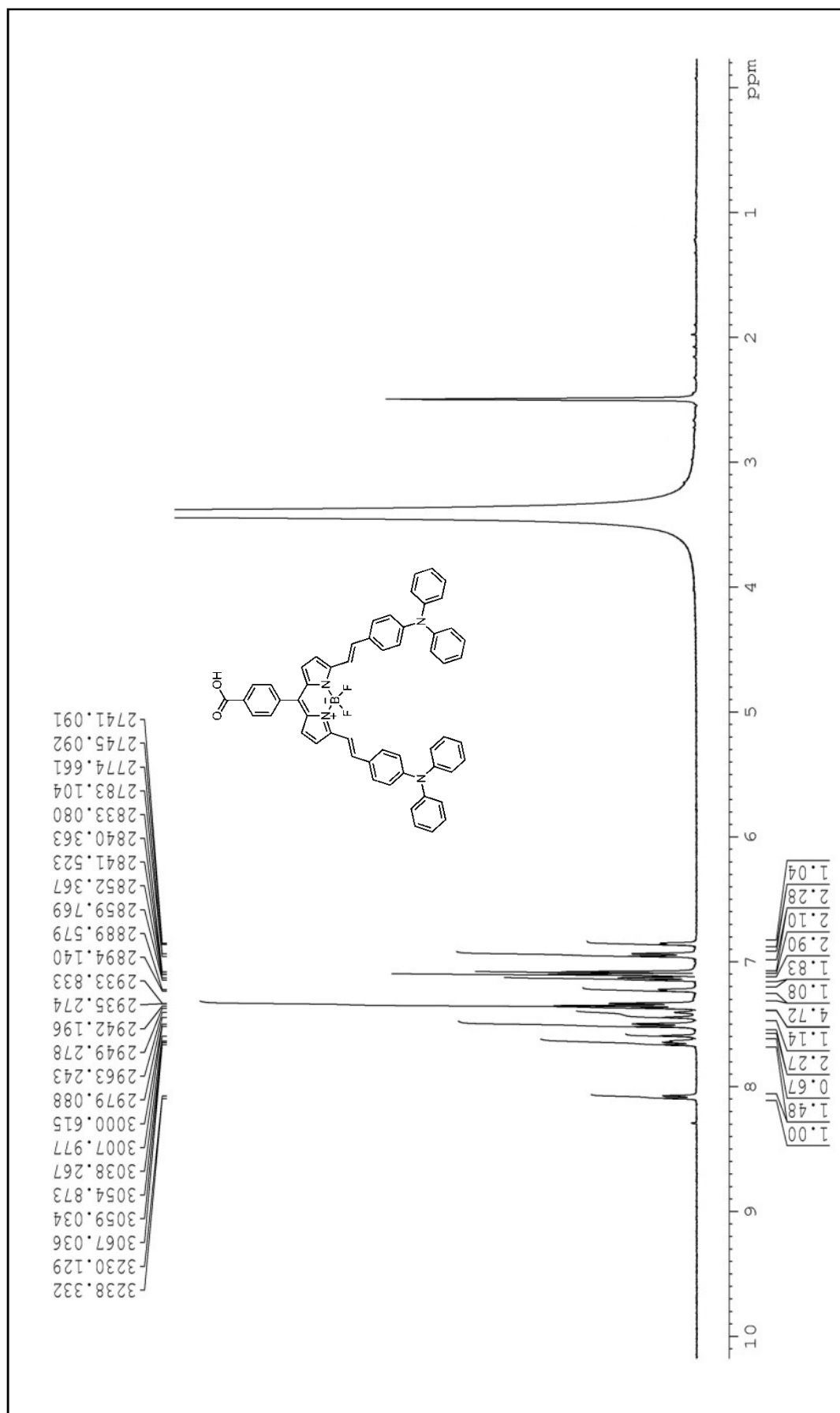


Figure S14. <sup>1</sup>H NMR spectrum of compound (PS-1)

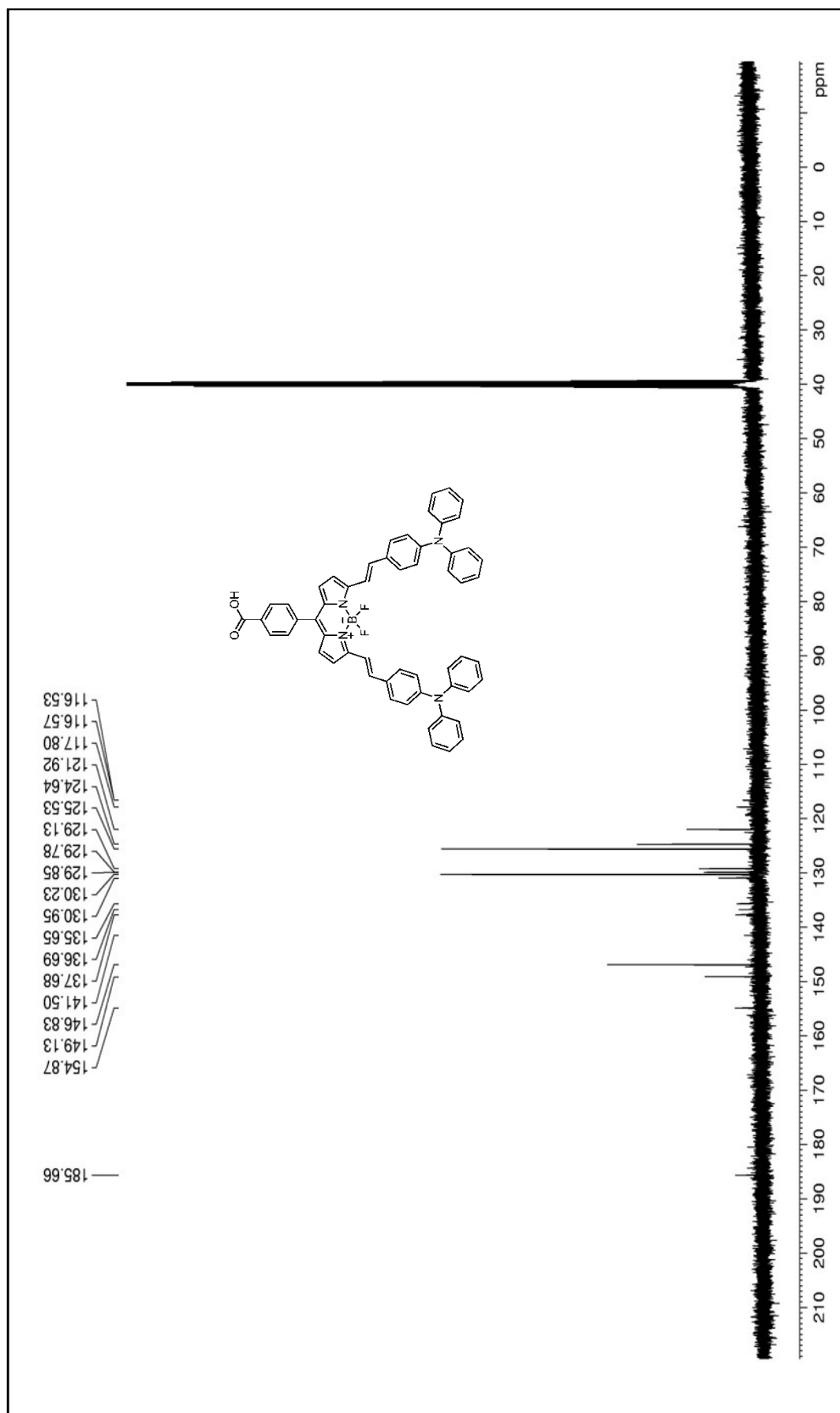
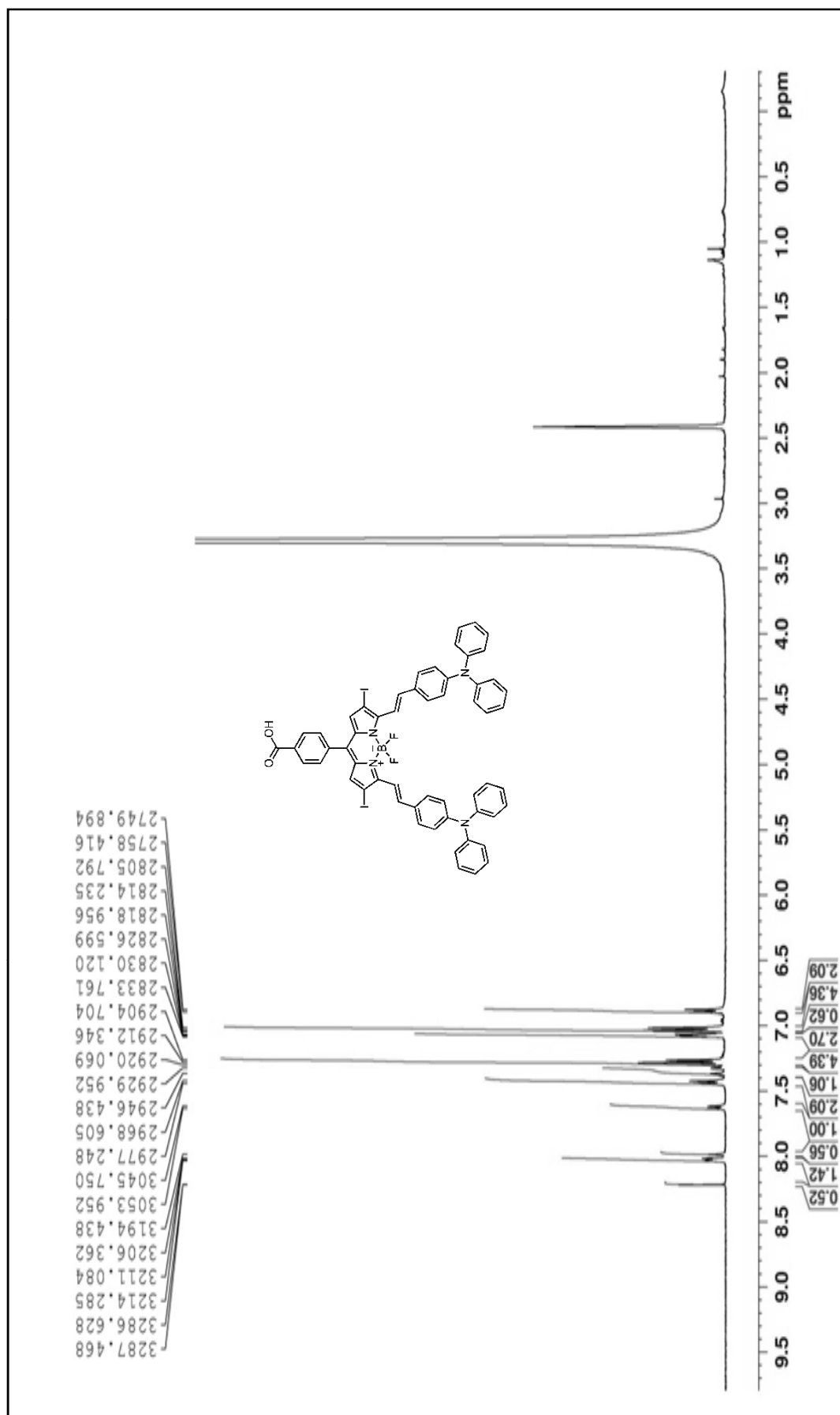


Figure S15. <sup>13</sup>C NMR spectrum of compound (PS-1)





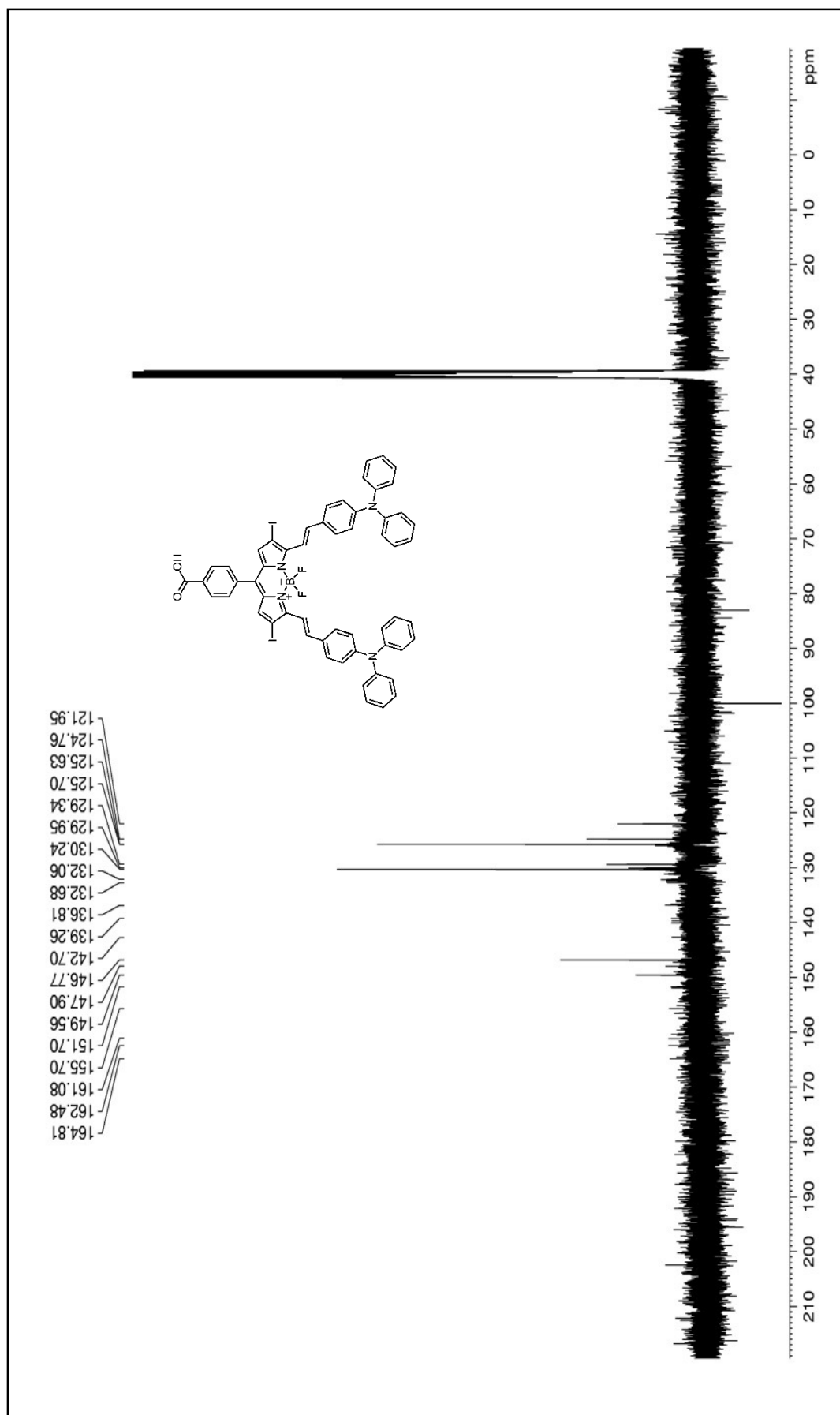


Figure S17.  $^{13}\text{C}$  NMR spectrum of compound (8), PS-3

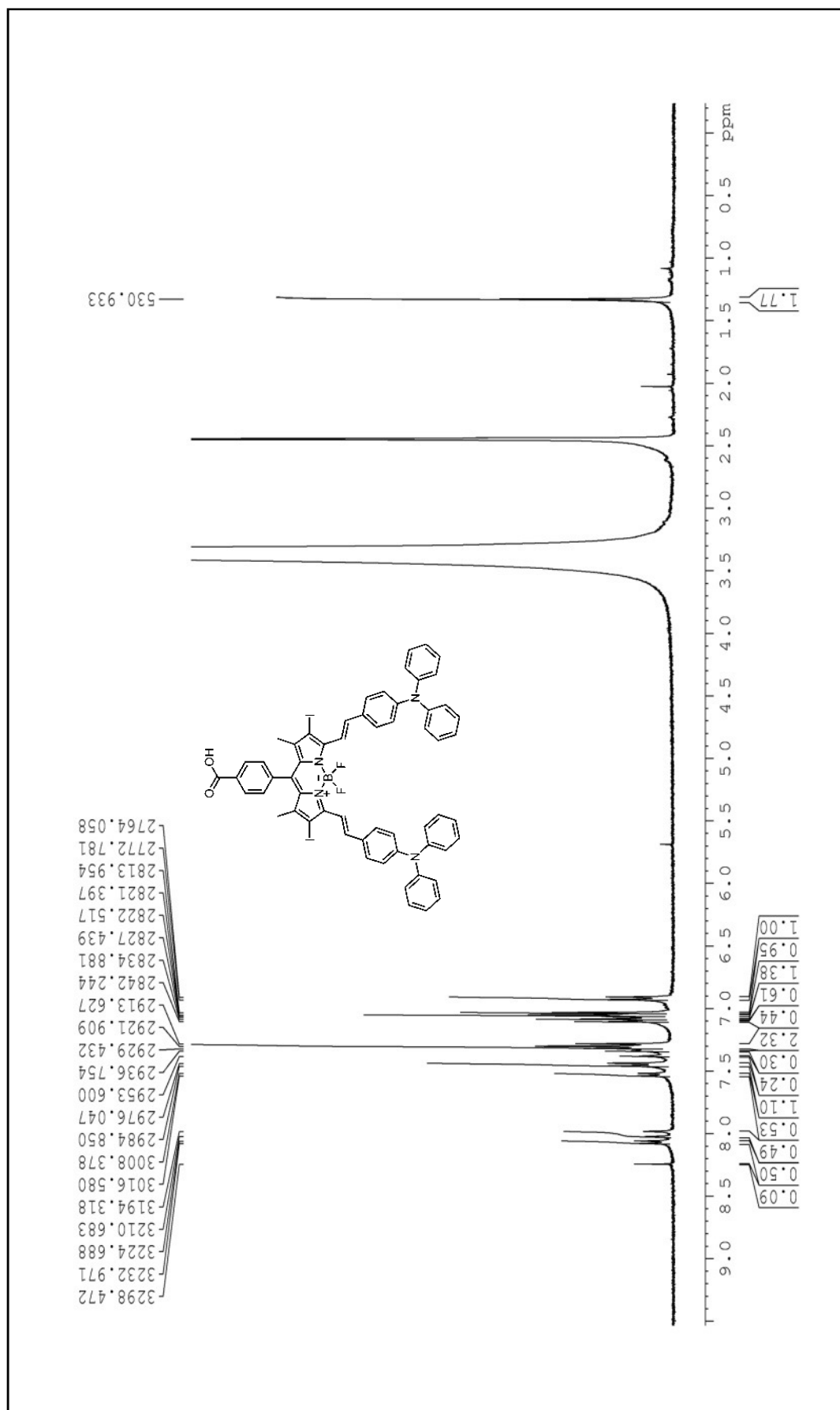


Figure S18. <sup>1</sup>H NMR spectrum of compound (BOD2)

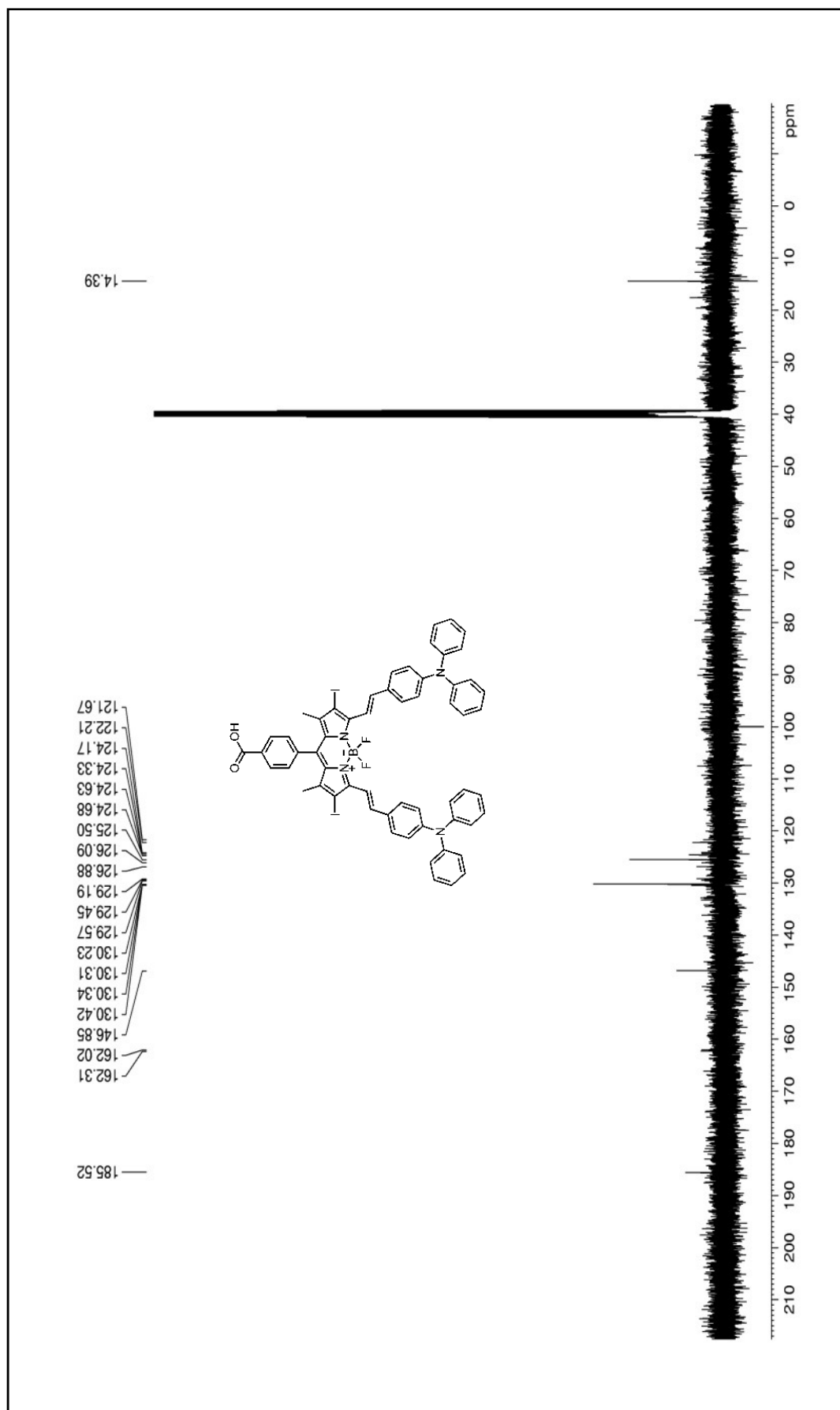


Figure S19.  $^{13}\text{C}$  NMR spectrum of compound (BOD2)

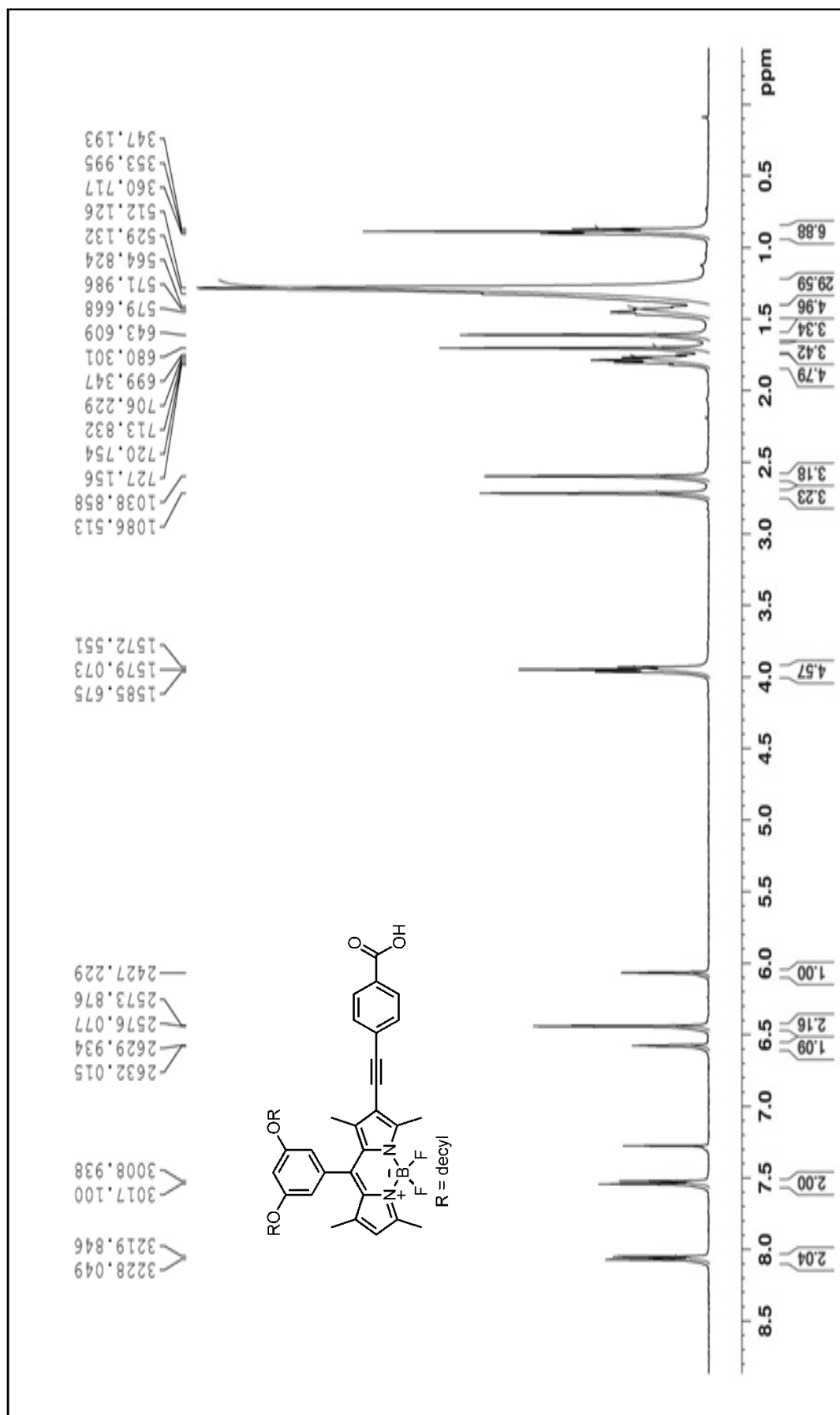


Figure S20. <sup>1</sup>H NMR spectrum of compound (6)

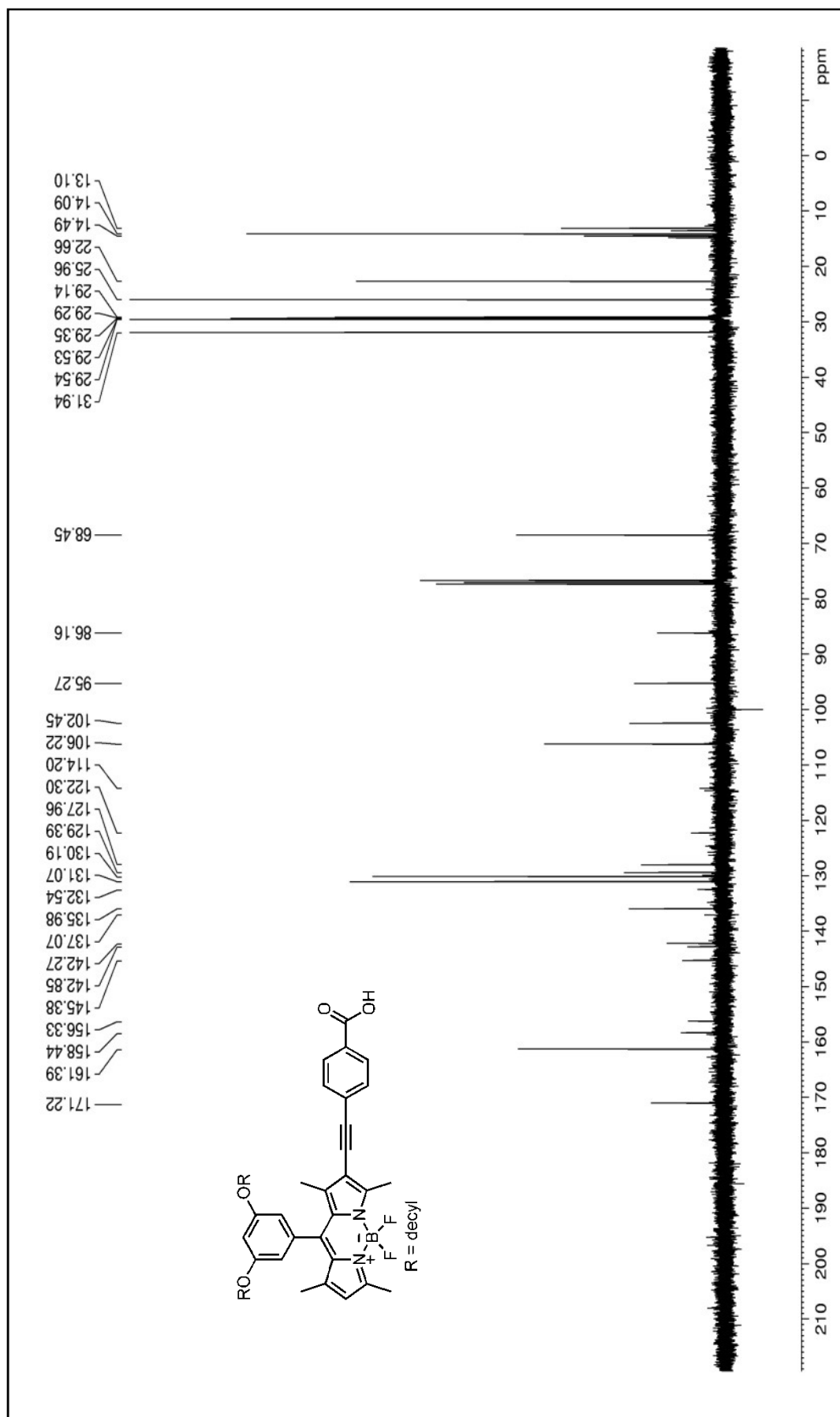


Figure S21.  $^{13}\text{C}$  NMR spectrum of compound (6)

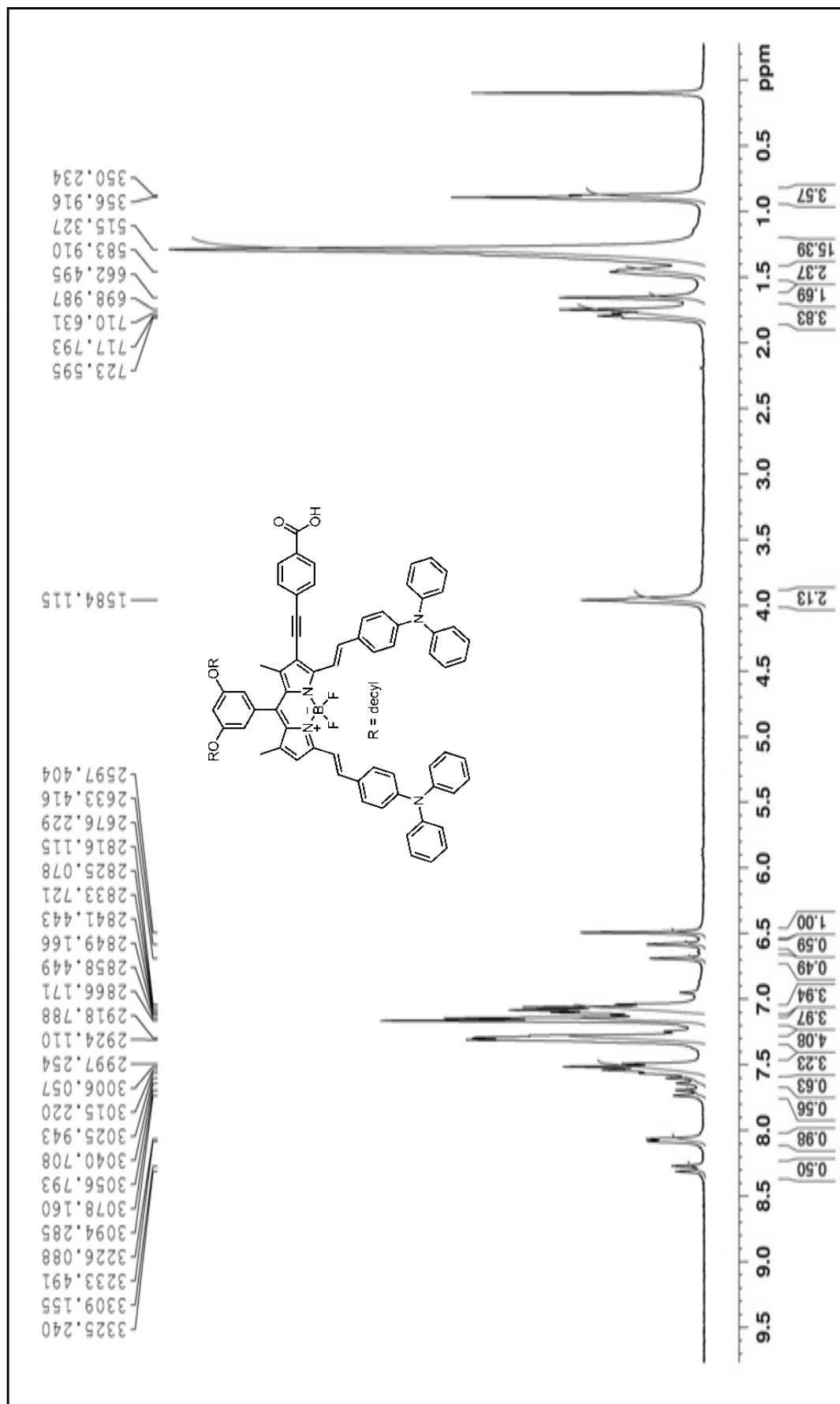


Figure S22. <sup>1</sup>H NMR spectrum of compound (PS-5)







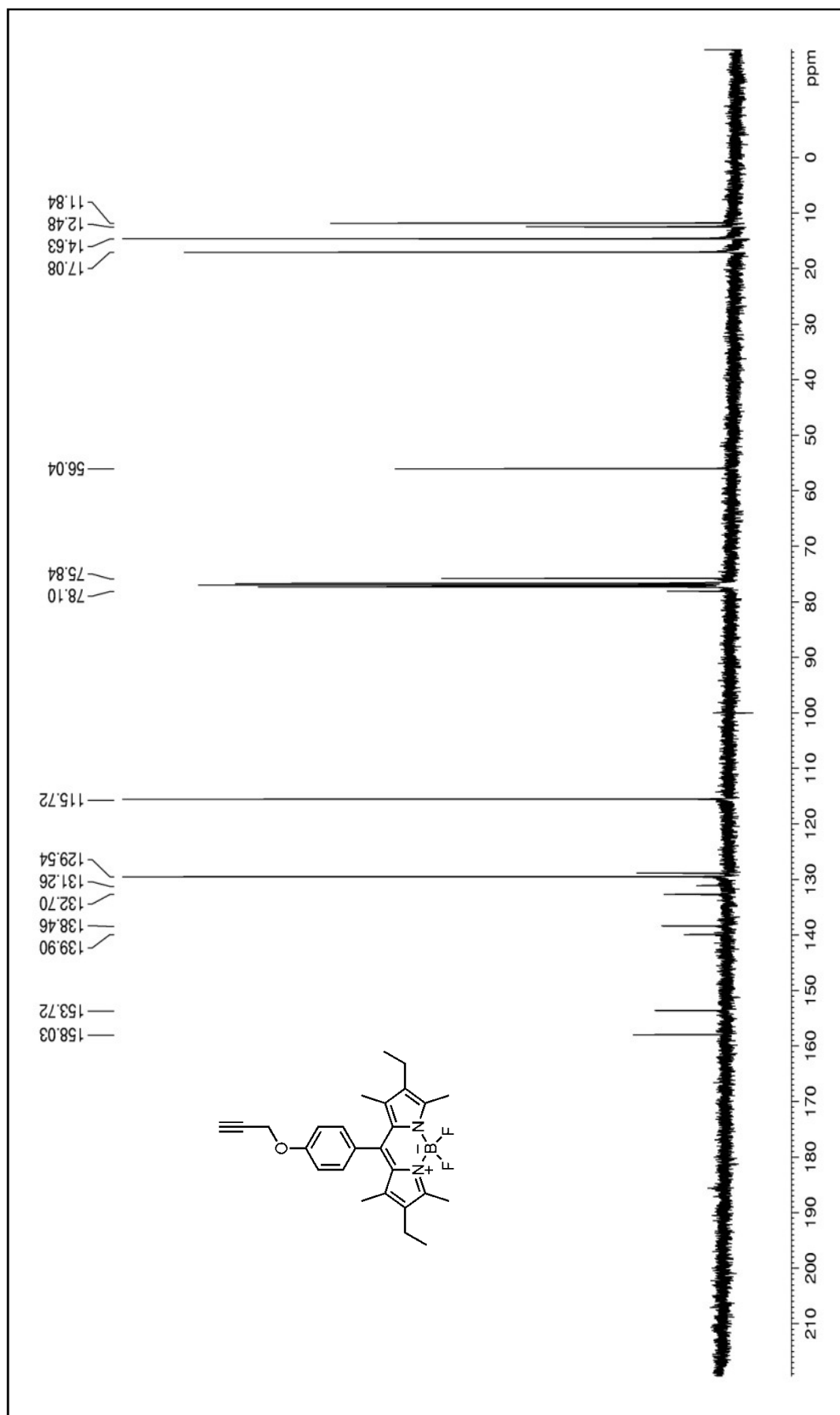


Figure S25.  $^{13}\text{C}$  NMR spectrum of compound (BOD1)

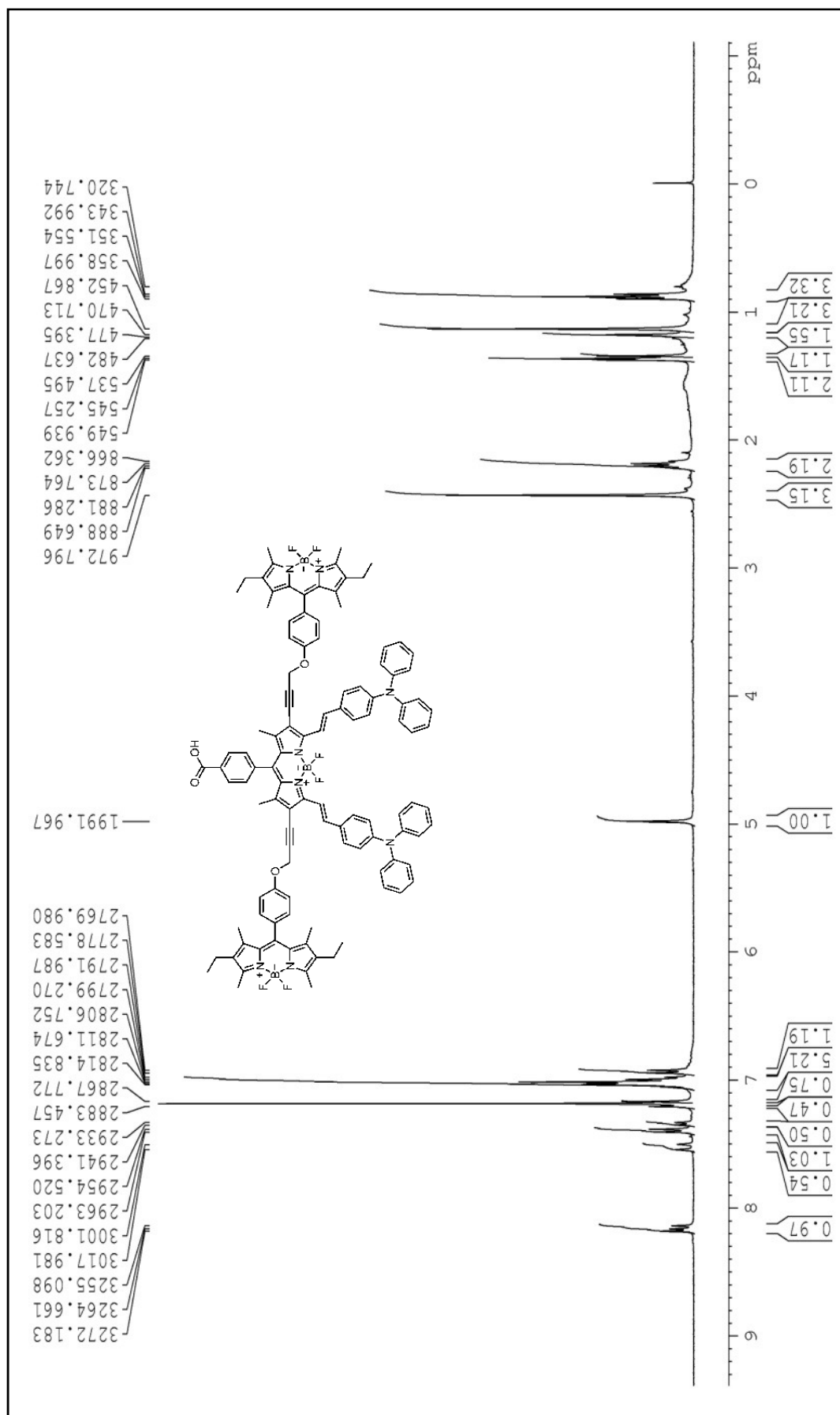


Figure S26. <sup>1</sup>H NMR spectrum of compound (PS-7)

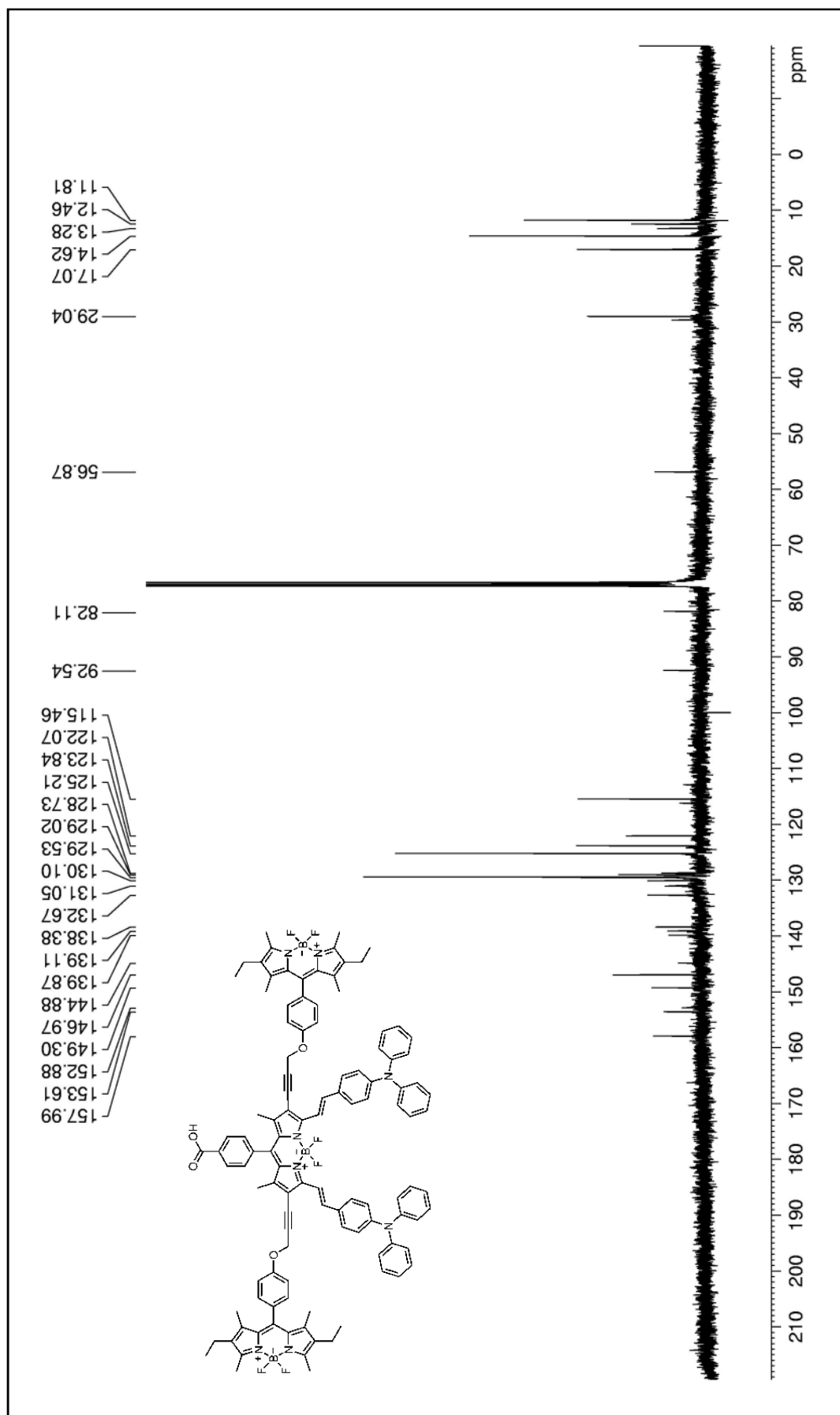


Figure S27.  $^{13}\text{C}$  NMR spectrum of compound (PS-7)

### Mass Spectra :

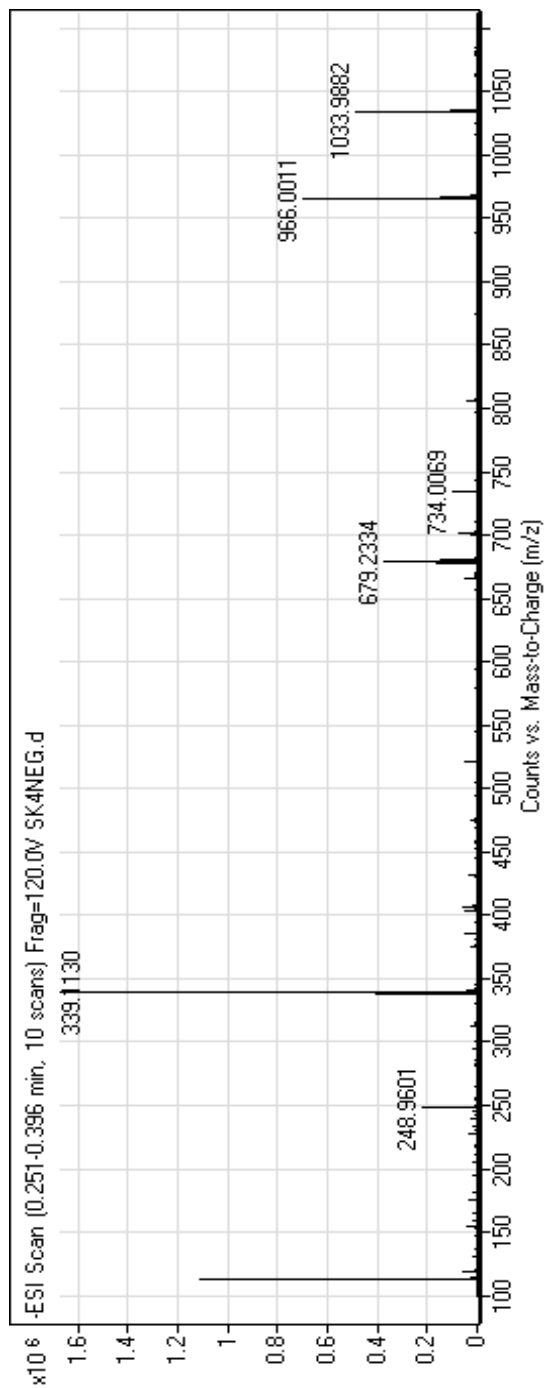


Figure S28. Mass spectrum of compound (1)

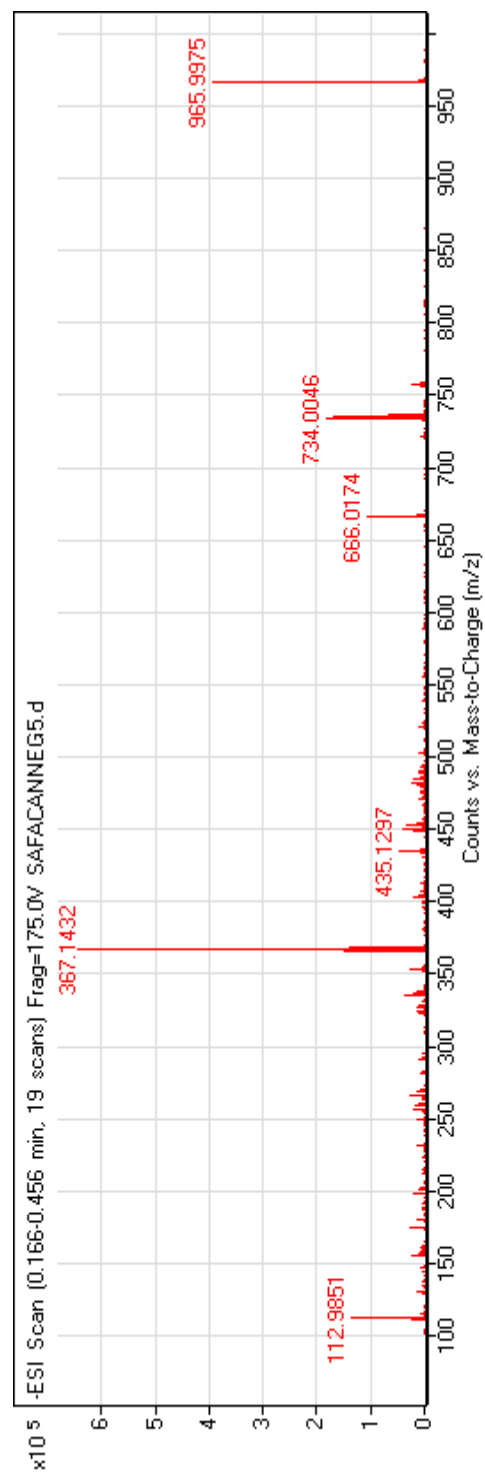
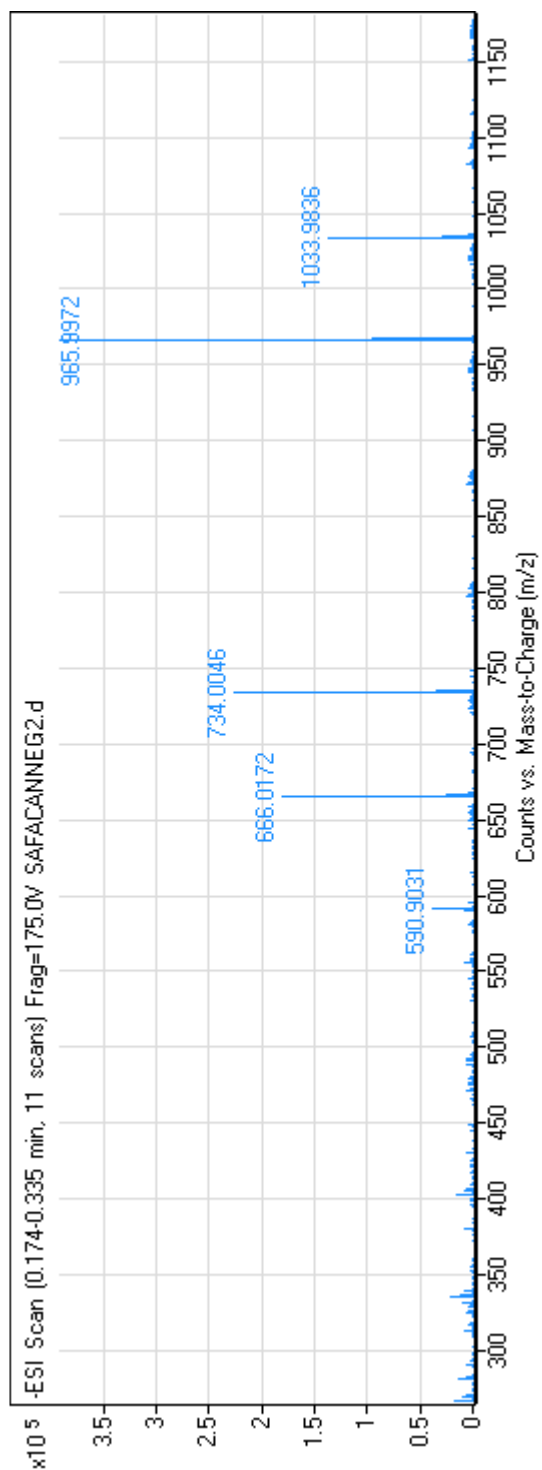


Figure S29. Mass spectrum of compound (2)



**Figure S30.** Mass spectrum of compound (3)

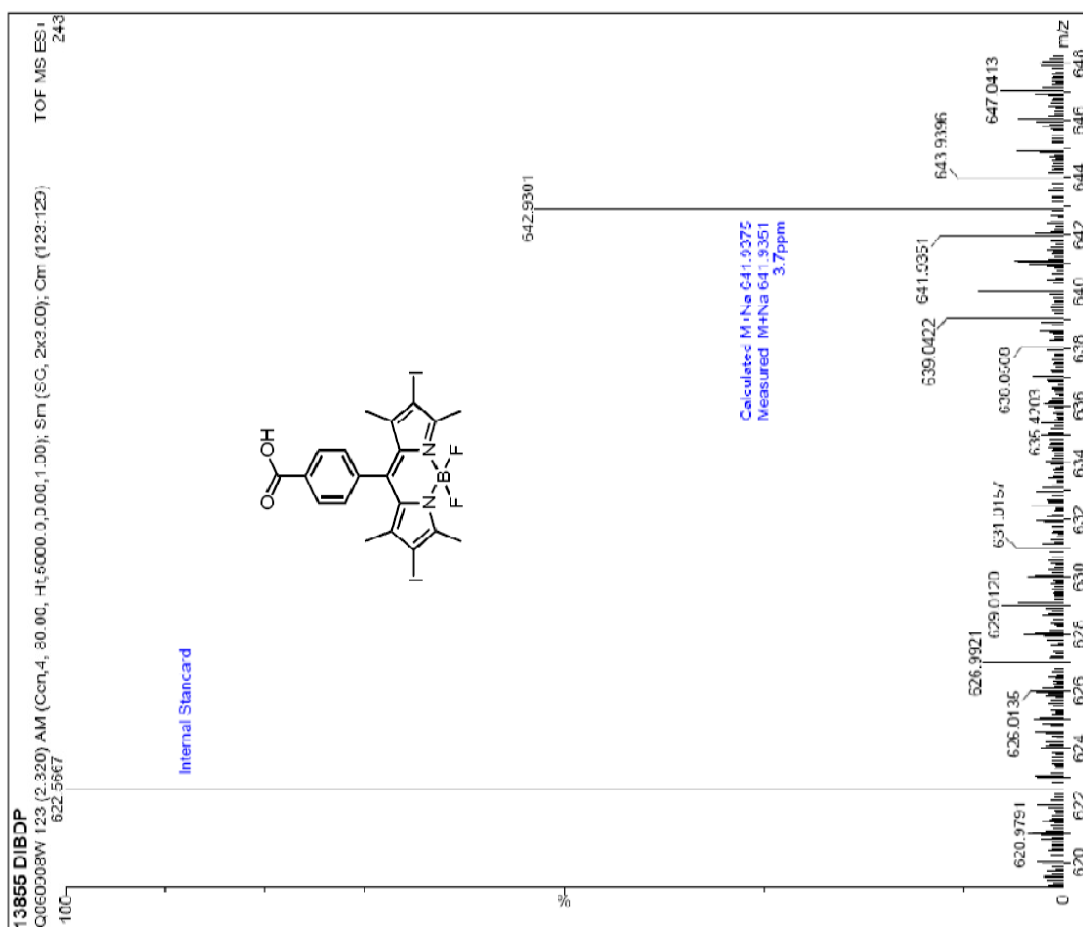
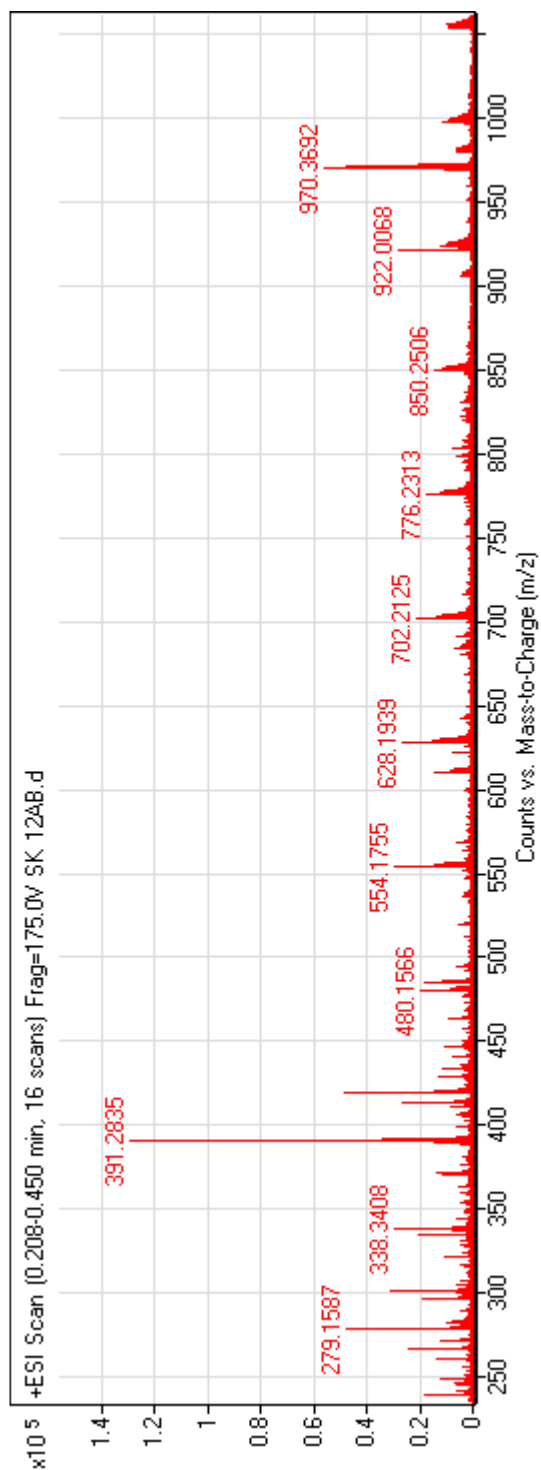
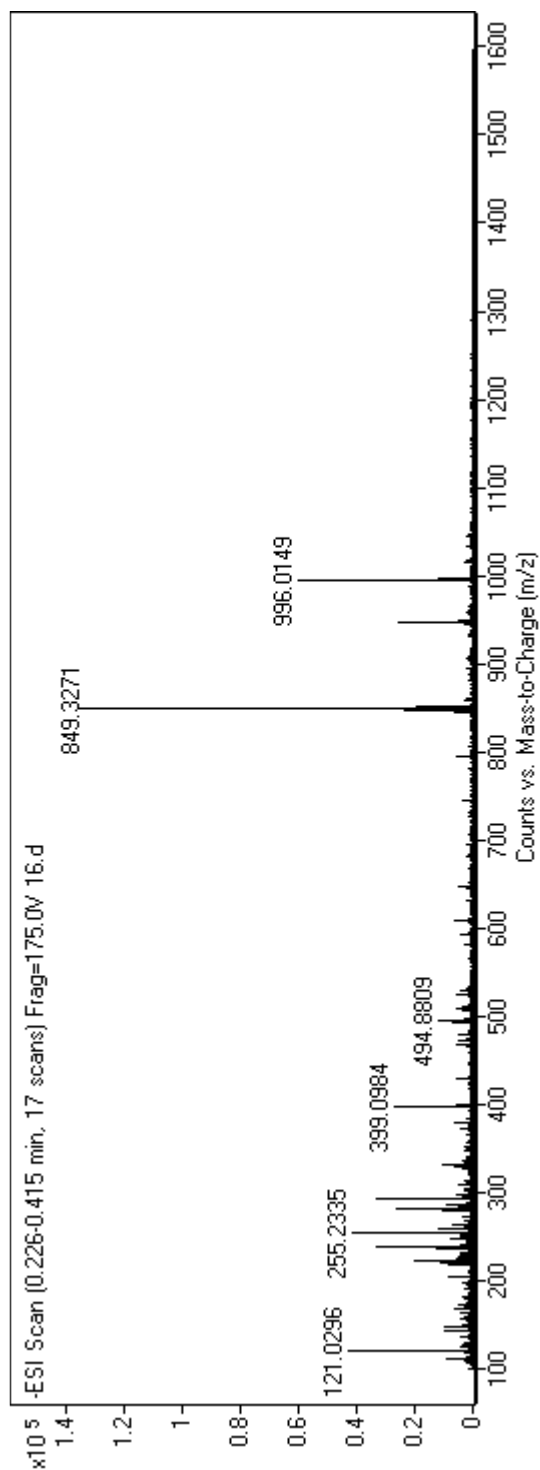


Figure S31. Mass spectrum of compound (4)



**Figure S32.** Mass spectrum of compound (PS-2)



**Figure S33.** Mass spectrum of compound (PS-1)

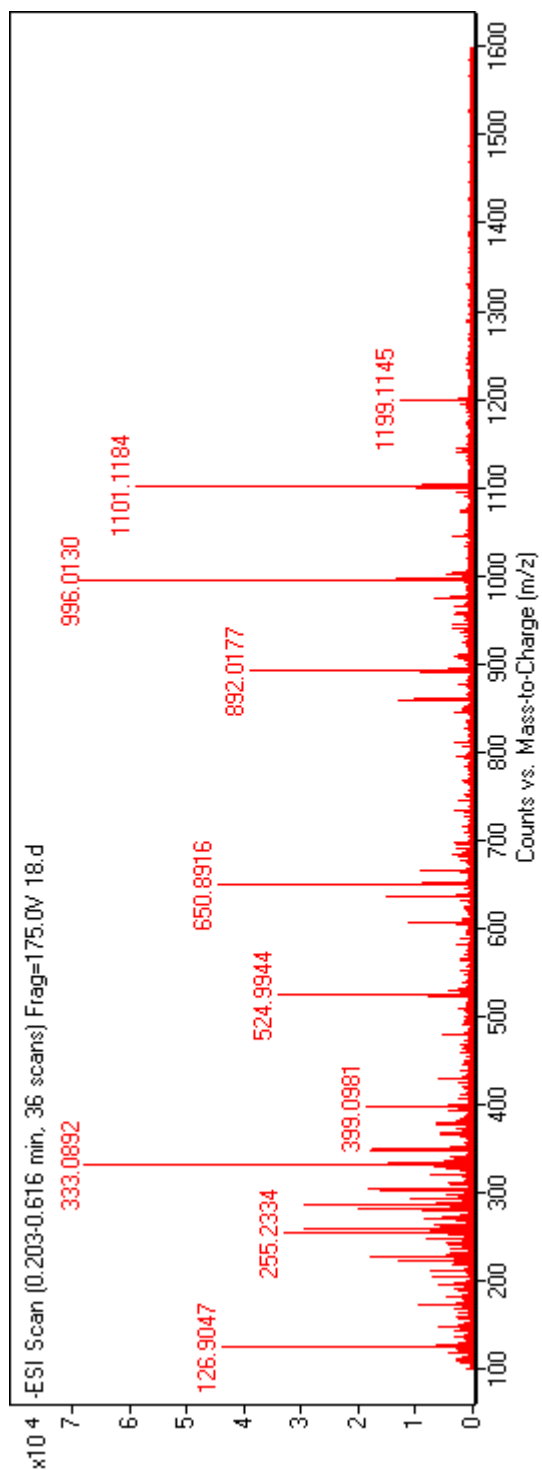


Figure S34. Mass spectrum of compound (PS-3)

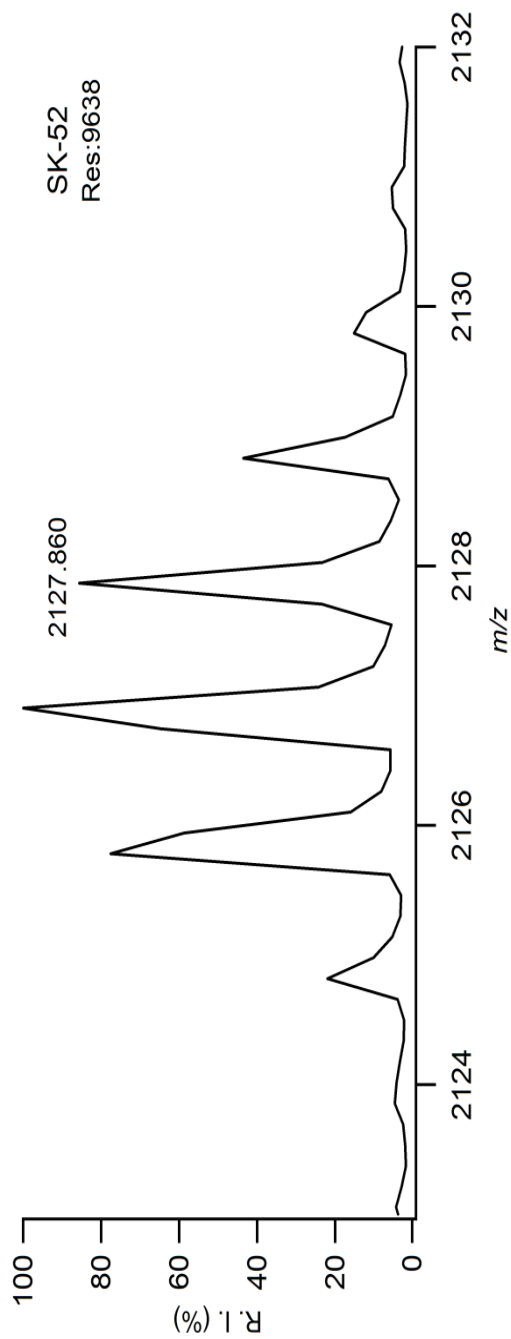


Figure S35. Mass spectrum of compound (PS-4)



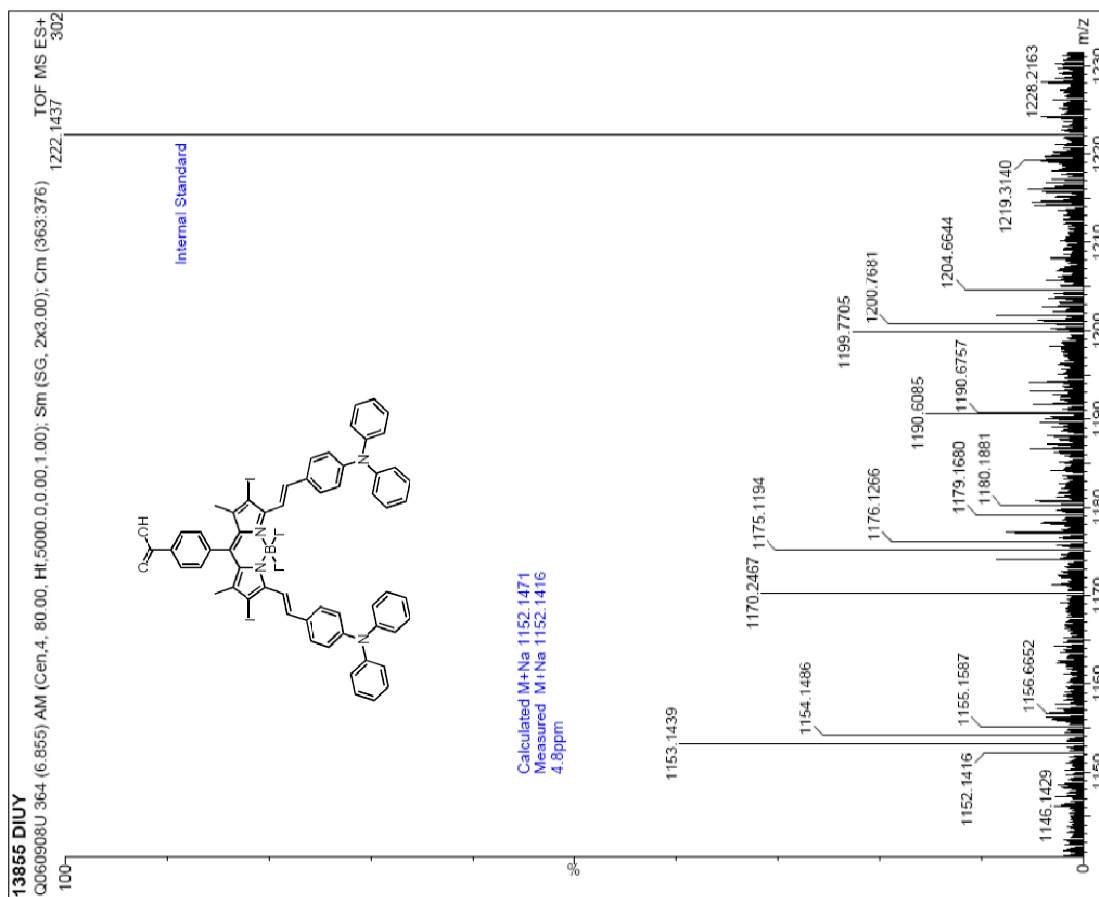
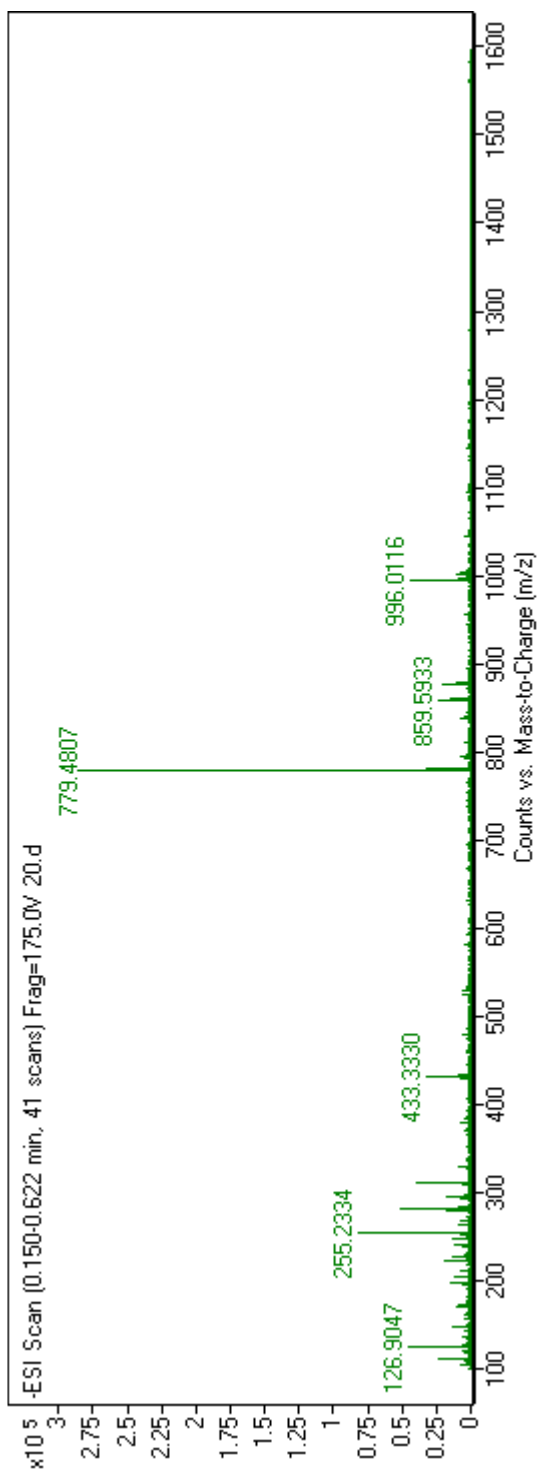
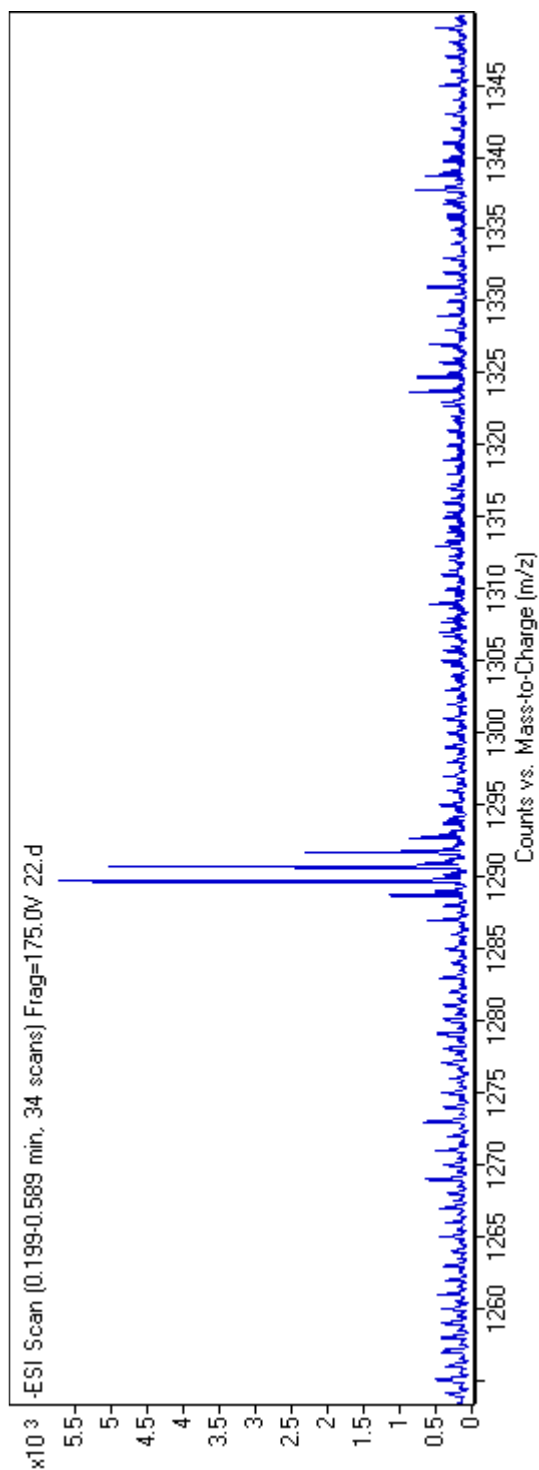


Figure S36. Mass spectrum of compound (BOD2)



**Figure S37.** Mass spectrum of compound (6)



**Figure S38.** Mass spectrum of compound (PS-5)

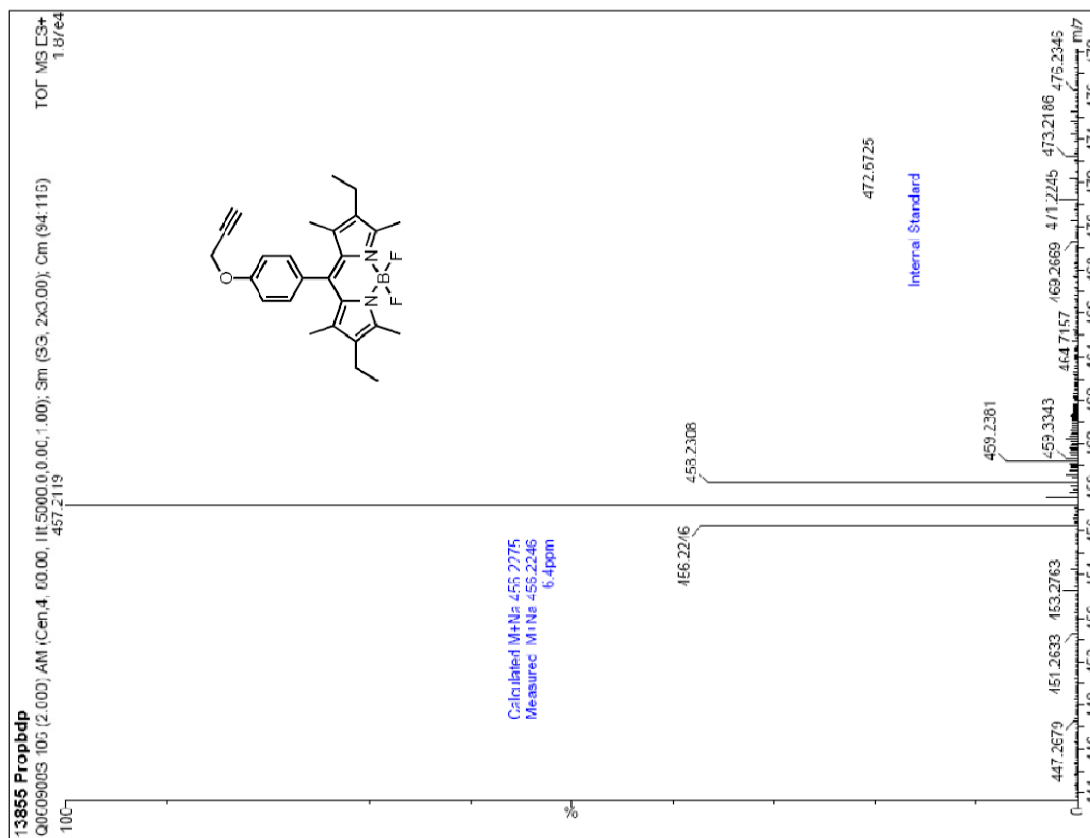
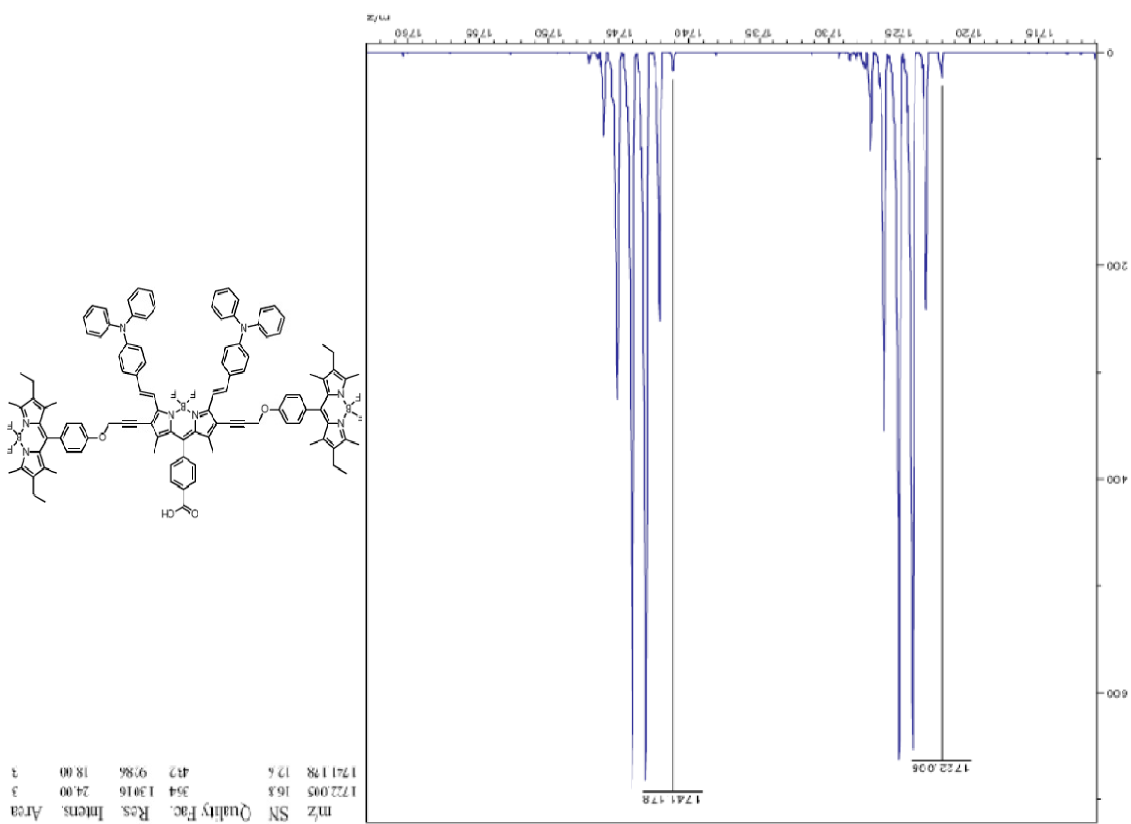
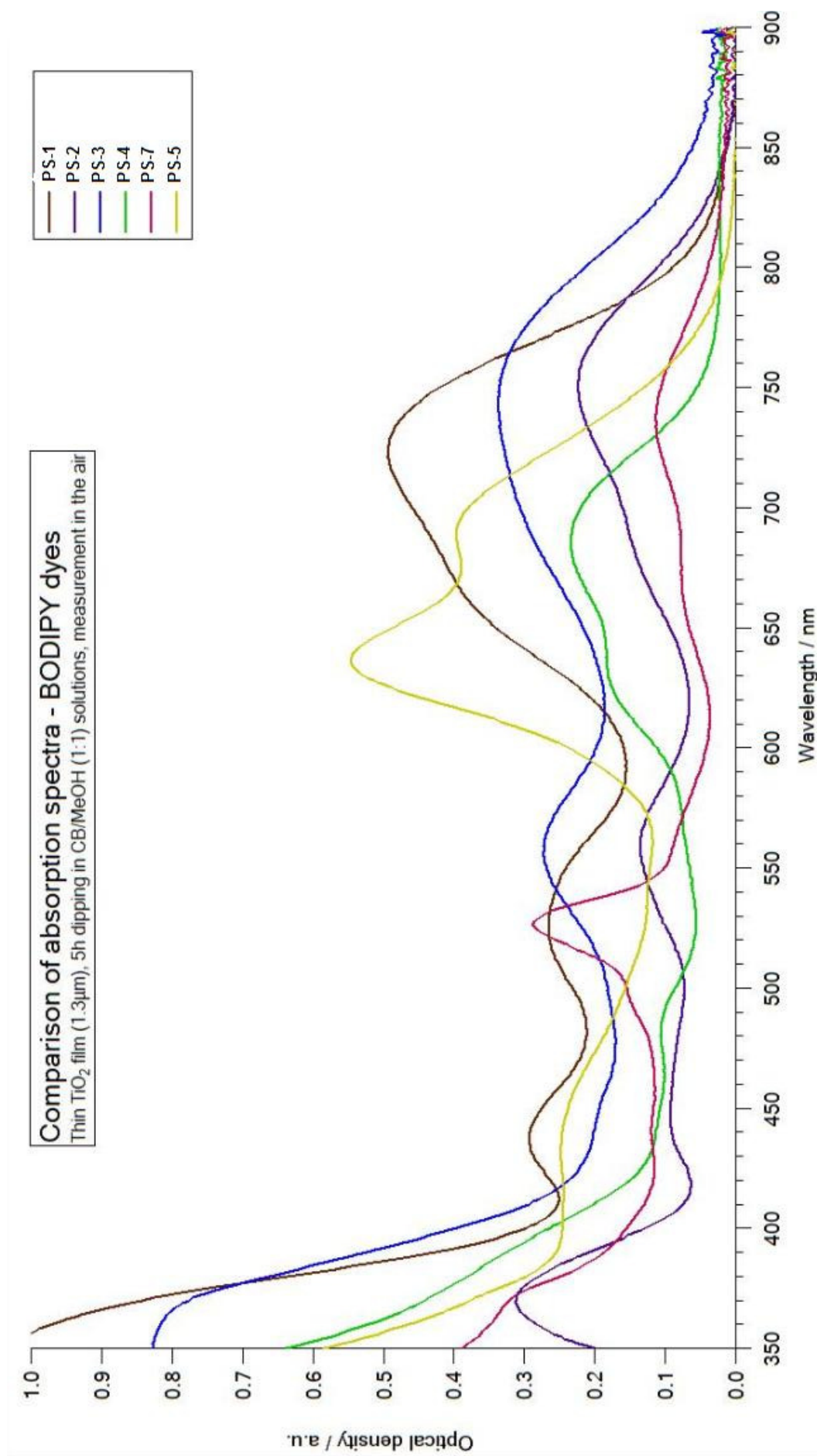


Figure S39. Mass spectrum of compound (BOD1)



**Figure S40.** Mass spectrum of compound (PS-7)

### Absorption on Titania:



**Figure S41.** Absorption spectra of sensitizers on titania. Spectrum for **PS-6** was reported in literature<sup>2</sup>.