Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information for

Organic and Biomolecular Chemistry

Manipulating *Non-Innocent* π-Spacers: The Challenges of Using 2,6-Disubstituted BODIPY Cores Within Donor-Acceptor Light-harvesting Motifs

by

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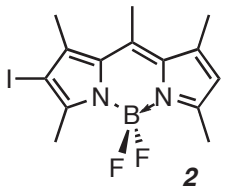
General Considerations

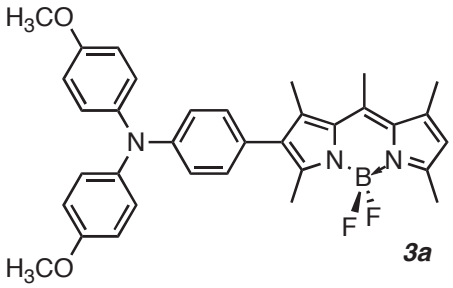
All reagents were purchased from Aldrich except $Pd(PPh_3)_4$ (Pressure Chemical Co., Pittsburg, PA). Purification by column chromatography was carried out using silica (Silicycle: ultrapure flash silica). Analytical thin-layer chromatography was performed on aluminum-backed sheets precoated with silica 60 F254 adsorbent (0.25 mm thick; Silicycle) and visualized under UV light. IR data was collected in KBr using a Perkin Elmer Spectrum 1 Fourier Transform Infrared spectrophotometer. Melting points were determined using a Perkin Elmer Diamond Differential Scanning Calorimeter. Routine ^{1}H, $^{13}C\{^{1}H\}$, $^{11}B\{^{1}H\}$ and ^{19}F NMR spectra were recorded at 400, 100, 128 and 376 MHz, respectively, on a Bruker AV 400 instrument at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to a residual nondeuterated solvent ($CHCl_3$) for ^{1}H and ^{13}C nuclei and $BF_3{\bullet}OEt_2$ (^{11}B nucleus; δ = 0 ppm) C_6F_6 (^{19}F nucleus; δ = 0 ppm). Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; m = multiplet; br = broad. 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (***A***)[1], 4-hexyloxy-*N*-(4-hexyloxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (***B***)[2], 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (***C***)[3] and compound ***1***[4] were prepared as previously reported.

Experimental Procedures



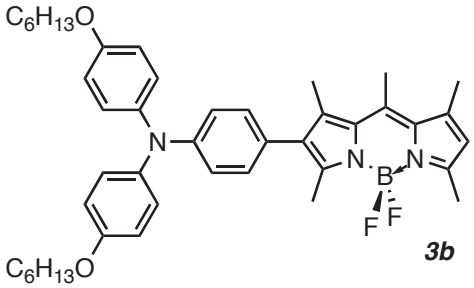
2

Synthesis of 2*: *1 (1.0 g, 3.8 mmol) was dissolved in a minimum amount of CH_2Cl_2 and NIS (0.86 g, 3.8 mmol) was added in one portion. The mixture was stirred 12 h with the flask covered with Al foil. Volatiles were removed *in vacuo* and the crude material was purified via column chromatography using hexanes:CH_2Cl_2 1:1 as the eluent, affording 1.13 g of desired compound as an orange solid (77%), 52 mg of starting material ***1*** and 112 mg of the corresponding *di*iodo derivative ***11***. The spectroscopic data of ***2*** agreed with the literature.[5] ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.10 (s, 1H), 2.59 (s, 3H), 2.57 (s, 3H), 2.52 (s, 3H), 2.42 (s, 3H), 2.40 s, 3H).



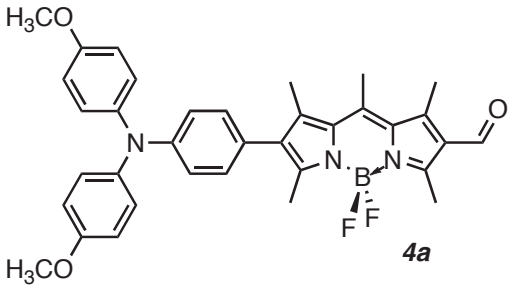
3a

Synthesis of *3a*: *2* (110 mg, 0.28 mmol) and ***A*** (182 mg, 0.42 mmol) were solubilized in 110 mL of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (196 mg, 1.4 mmol) and $Pd(PPh_3)_4$ (32 mg, 0.028 mmol) were added and the mixture was refluxed 12 h under an atmosphere of N_2. After being cooled to room temperature, 50 mL of H_2O were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using hexanes:CH_2Cl_2 1:1 as the eluent, affording the desired product as a pink solid (108 mg, 68 %). Mp 213 - 215 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.11 (d, 4H, $^3J_{HH}$ = 8.9 Hz), 6.97 (m, 4H), 6.85 (d, 4H), 6.06 (s, 1H), 3.80 (s, 6H), 2.64 (s, 3H), 2.53 (s, 3H), 2.49 (s, 3H), 2.43 (s, 3H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 156.2, 153.4, 153.2, 147.9, 141.4, 141.0, 140.7, 137.3, 133.7, 132.4, 132.2, 131.0, 127.0, 125.3, 121.3, 119.9, 114.9, 55.6, 17.5, 17.0, 15.7, 14.6 (t, J_{CF} = 2.6 Hz), 13.5 (t, J_{CF} = 2.7 Hz). ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ = 0.72 (t, $^1J_{BF}$ = 32 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -146.6 (q). HRMS (DART): *m/z* 566.2793 ([M+H]$^+$), calcd for $^{12}C_{34}{}^1H_{35}{}^{11}B^{19}F_2{}^{14}N_3{}^{16}O_2{}^+$: *m/z* 566.2790.



3b

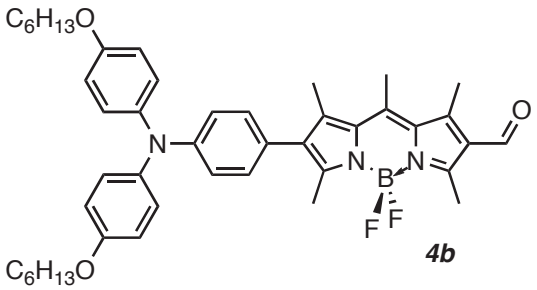
Synthesis of *3b*: *2* (55 mg, 0.14 mmol) and ***B*** (121 mg, 0.0.21 mmol) were solubilized in 55 mL of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (97 mg, 0.71 mmol) and $Pd(PPh_3)_4$ (16 mg, 0.014 mmol) were added and the mixture was refluxed 12 h under an atmosphere of N_2. After being cooled to room temperature, 25 mL of H_2O were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using hexanes:CH_2Cl_2 1:1 as the eluent, affording the desired product as a pink solid (61 mg, 62 %). Mp 76-78 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.09 (d, 4H, $^3J_{HH}$ = 8.8 Hz), 6.96 (m, 4H), 6.84 (d, 4H), 6.06 (s, 1H), 3.94 (t, 4H, $^3J_{HH}$ = 6.6 Hz), 2.64 (s, 3H), 2.53 (s, 3H), 2.50 (s, 3H), 2.43 (s, 3H), 2.34 (s, 3H), 1.77 (m, 4H), 1.46, (m, 4H), 1.35 (m, 8H), 0.91 (t, 4H, $^3J_{HH}$ = 7.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 155.7, 153.3, 153.2, 148.0, 141.3, 140.8, 140.6, 137.3, 133.8, 132.4, 132.2, 130.9, 127.0, 125.1, 121.2, 119.8, 115.5, 68.4, 31.8, 29.5, 25.9, 22.8, 17.5, 17.0, 15.7, 14.6 (t, J_{CF} = 2.4 Hz), 14.2, 13.6 (t, J_{CF} = 2.7 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.72 (t, $^1J_{BF}$ = 30 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -146.6 (q). HRMS (DART): *m/z* 706.4357 ($[M+H]^+$), calcd for $^{12}C_{44}{}^1H_{55}{}^{11}B^{19}F_2{}^{14}N_3{}^{16}O_2{}^+$: *m/z* 706.4355.



4a

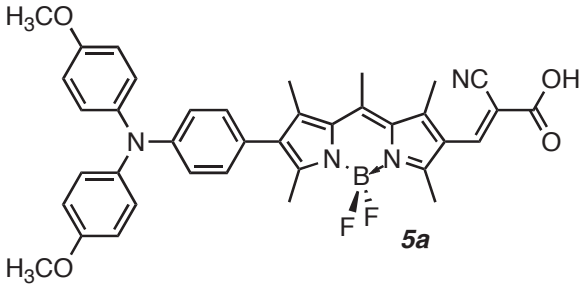
Synthesis of *4a*: A solution of 0.5 mL of dry DMF in 5 mL of dry 1,2-dichloroethane was cooled in an ice bath and 0.6 mL of $POCl_3$ was added dropwise. The mixture was warmed to room temperature and stirred 30 min. ***3a*** (26 mg, 0.05 mmol) dissolved in 6 mL of dry 1,2-dichloroethane was added in one portion and the mixture was stirred 2 h. The mixture was neutralized in 30 mL of saturated aqueous $NaHCO_3$ cooled to 0°C and the mixture was stirred 30 min. at room temperature. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using CH_2Cl_2 as the eluent, affording the desired product as a purple solid (21 mg, 77%). Mp 119 - 121 °C; IR (KBr, cm^{-1}) 1663. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.11 (s, 1H), 7.12 (d, 4H, $^3J_{HH}$ = 8.9 Hz), 6.96 (m, 4H), 6.87 (d, 4H), 3.81 (s, 6H), 2.79 (s, 3H), 2.75 (s, 3H), 2.74 (s, 3H), 2.55 (s, 3H), 2.39

(s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ = 186.3, 160.0, 156.4, 155.1, 148.6, 143.1, 140.7, 140.6, 139.4, 136.9, 2135.1, 131.2, 130.8, 127.2, 125.8, 123.5, 119.5, 115.0, 55.7, 17.8, 16.2, 14.2, 14.1 (t, J_{CF} = 2.6 Hz), 12.7. $^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.62 (t, $^{1}J_{BF}$ = 32 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -145.1 (q). HRMS (DART): *m/z* 594.2746 ($[M+H]^+$), calcd for $^{12}C_{35}{}^{1}H_{35}{}^{11}B^{19}F_2{}^{14}N_3{}^{16}O_3{}^{+}$: *m/z* 594.2740.



4b

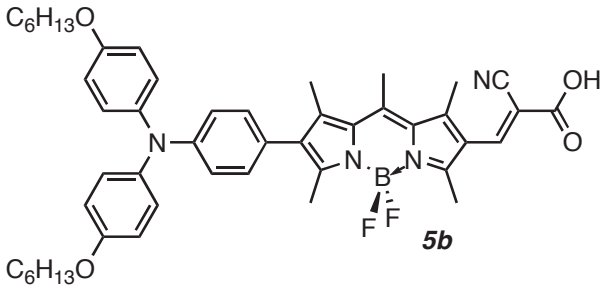
Synthesis of *4b*: A solution of 1.0 mL of dry DMF in 10 mL of dry 1,2-dichloroethane was cooled in an ice bath and 1.2 mL of $POCl_3$ was added dropwise. The mixture was warmed to room temperature and stirred 30 min. ***3b*** (61 mg, 0.09 mmol) dissolved in 12 mL of dry 1,2-dichloroethane was added in one portion and the mixture was stirred 2 hr. The mixture was neutralized in 30 mL of saturated aqueous $NaHCO_3$ cooled to 0°C and the mixture was stirred 30 min. at room temperature. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using CH_2Cl_2 as the eluent, affording the desired product as a purple solid (54 mg, 86%). Mp 94 - 95 °C; IR (KBr, cm^{-1}) 1671. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.11 (s, 1H), 7.10 (d, 4H, $^{3}J_{HH}$ = 8.9 Hz), 6.95 (m, 4H), 6.85 (d, 4H), 3.94 (t, 4H, $^{3}J_{HH}$ = 6.6 Hz), 2.79 (s, 3H), 2.75 (s, 3H), 2.74 (s, 3H), 2.54 (s, 3H), 2.39 (s, 3H), 1.78 (m, 4H), 1.46 (m, 4H), 1.35 (m, 8H), 0.91 (t, 6H, $^{3}J_{HH}$ = 7.0 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ = 186.3, 160.1, 156.0, 155.0, 148.7, 143.1, 140.7, 140.4, 139.3, 136.9, 135.1, 131.1, 130.7, 127.2, 125.8, 123.3, 119.3, 115.5, 68.4, 31.8, 29.5, 25.9, 22.8, 17.8, 16.2, 14.3, 14.2, 14.1 (t, J_{CF} = 3.0 Hz), 12.7 (t, J_{CF} = 3.1 Hz). $^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.63 (t, $^{1}J_{BF}$ = 31 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -145.1 (q). HRMS (DART): *m/z* 734.4276 ($[M+H]^+$), calcd for $^{12}C_{45}{}^{1}H_{55}{}^{11}B^{19}F_2{}^{14}N_3{}^{16}O_3{}^{+}$: *m/z* 734.4305.



5a

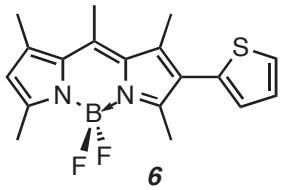
Synthesis of *5a*: *4a* (48 mg, 0.081 mmol) was dissolved in 25 mL of MeCN:$CHCl_3$ 1:1 and cyanoacetic acid (14 mg, 0.17 mmol) was added, followed by piperidine (2 μL, 0.02 mmol). The mixture was refluxed 24 h and after being cooled at room temperature, the

organic layer was washed with HCl 1N (3 × 25 mL). The organic layer was dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was recrystallized from hexanes:CH_2Cl_2 3:1, affording a dark purple solid (48 mg, 90 %). Mp 175 (decomp.) °C; IR (KBr, cm^{-1}) 1671, 2217, 2947. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.33 (s, 1H), 7.12 (d, 4H, $^3J_{HH}$ = 9.0 Hz), 6.97 (s, 4H), 6.86 (d, 4H), 3.81 (s, 6H), 2.74 (s, 3H), 2.63 (s, 3H), 2.55 (s, 3H), 2.53 (s, 3H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 165.8, 159.7, 156.3, 151.9, 150.1, 148.5, 142.3, 140.6, 137.0, 136.7, 134.9, 132.7, 130.8, 127.3, 127.2, 123.6, 123.4, 119.5, 116.0, 115.0, 55.7, 17.8, 17.5, 16.2, 14.1, 14.0, *C*=O signal not observed. $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.61 (t, $^1J_{BF}$ = 30 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -145.8 (q). HRMS (ESI): *m/z* 659.2626 ($[M-H]^-$), calcd for $^{12}C_{38}{}^1H_{34}{}^{11}B^{19}F_2{}^{14}N_4{}^{16}O_4^-$: *m/z* 659.2646.



5b

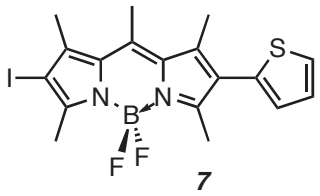
Synthesis of *5b*: *4b* (50 mg, 0.07 mmol) was dissolved in 25 mL of MeCN:$CHCl_3$ 1:1 and cyanoacetic acid (12 mg, 0.14 mmol) was added, followed by piperidine (2 μL, 0.02 mmol). The mixture was refluxed 24 hr and after being cooled at room temperature, the organic layer was washed with HCl 1N (3 × 25 mL). The organic layer was dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was recrystallized from hexanes:MeOH 3:1, affording a dark purple solid (55 mg, quantitative). Mp 114 (decomp.) °C; IR (KBr, cm^{-1}) 1691, 2213, 2929. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.34 (s, 1H), 7.10 (d, 4H, $^3J_{HH}$ = 9.0 Hz), 6.96 (m, 4H), 6.85 (d, 4H), 3.94 (t, 4H, $^3J_{HH}$ = 6.6 Hz), 2.74 (s, 3H), 2.64 (s, 3H), 2.55 (s, 3H), 2.53 (s, 3H), 2.39 (s, 3H), 1.78 (m, 4H), 1.45 (m, 4H), 1.35 (m, 8H), 0.91 (t, 6H, $^3J_{HH}$ = 7.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 165.7, 159.9, 156.0, 152.0, 150.4, 148.6, 142.2, 140.7, 140.4, 137.0, 136.9, 135.0, 132.7, 130.7, 127.2, 123.4, 123.3, 119.4, 115.9, 115.5, 68.4, 31.8, 29.5, 25.9, 22.8, 17.8, 17.6, 16.2, 14.2, 14.1, 14.0, *C*=O signal not observed. $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.61 (t, $^1J_{BF}$ = 31 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -145.8 (q). HRMS (ESI): *m/z* 799.4264 ($[M-H]^-$), calcd for $^{12}C_{48}{}^1H_{54}{}^{11}B^{19}F_2{}^{14}N_4{}^{16}O_4^-$: *m/z* 799.4211.



6

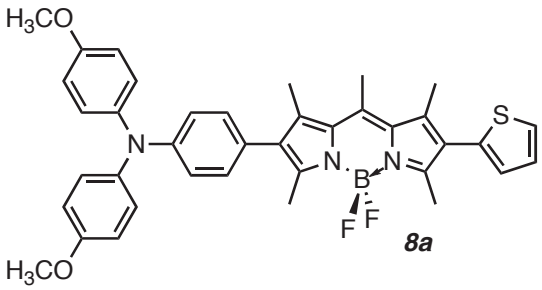
Synthesis of *6*: *2* (450 mg, 1.17 mmol) and ***C*** (488 mg, 1.74 mmol) were solubilized in 330 mL of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (807 mg,

5.85 mmol) and $Pd(PPh_3)_4$ (135 mg, 0.12 mmol) were added and the mixture was refluxed 12 h under an atmosphere of N_2. After being cooled to room temperature, 100 mL of H_2O were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 75 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using hexanes:CH_2Cl_2 1:1 as the eluent, affording the desired product as an orange solid (372 mg, 92 %). Mp 181 - 183 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.39 (d, 1H, $^3J_{HH}$ = 5.0 Hz), 7.12 (dd, 1H), 6.90 (d, 1H, $^3J_{HH}$ = 3.0 Hz), 6.10 (s, 1H), 2.64 (s, 3H), 2.54 (s, 3H), 2.53 (s, 3H), 2.44 (s, 3H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 154.0, 152.5, 142.0, 141.9, 138.2, 134.8, 132.9, 131.8, 128.1, 127.4, 126.2, 125.7, 122.0, 17.6, 17.0, 15.5, 14.7, (t, J_{CF} = 2.5 Hz), 13.4 (t, J_{CF} = 2.9 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.67 (t, $^1J_{BF}$ = 32 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -146.3 (q). HRMS (DART): *m/z* 345.1416 ($[M+H]^+$), calcd for $^{12}C_{18}{}^1H_{20}{}^{11}B^{19}F_2{}^{14}N_3{}^{32}S^+$: *m/z* 345.1408.



7

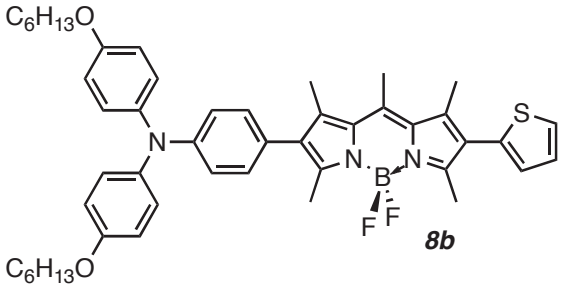
Synthesis of *7*: *6* (200 mg, 0.58 mmol) was dissolved in a minimum amount of CH_2Cl_2 and NIS (150 mg, 0.67 mmol) was added in one portion. The mixture was stirred 12 h with the flask covered with Al foil. Volatiles were removed *in vacuo* and the crude material was purified via column chromatography using hexanes:CH_2Cl_2 1:1 as the eluent, affording the desired product as an orange solid (253 mg, 93 %). Mp 222-225 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.41 (d, 1H, $^3J_{HH}$ = 5.0 Hz), 7.13 (dd, 1H), 6.91 (d, 1H, $^3J_{HH}$ = 3.0 Hz), 2.68 (s, 3H), 2.63 (s, 3H), 2.54 (s, 3H), 2.49 (s, 3H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 155.0, 154.0, 141.8, 141.7, 140.2, 134.1, 132.5, 132.3, 128.3, 127.5, 127.1, 127.0, 126.5, 19.8, 17.8, 16.1 (t, J_{CF} = 2.9 Hz), 15.9, 13.6 (t, J_{CF} = 2.7 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.55 (t, $^1J_{BF}$ = 31 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -146.0 (q). HRMS (DART): *m/z* 471.0369 ($[M+H]^+$), calcd for $^{12}C_{18}{}^1H_{19}{}^{11}B^{19}F_2{}^{127}I^{14}N_2{}^{32}S^+$: *m/z* 471.0375.



8a

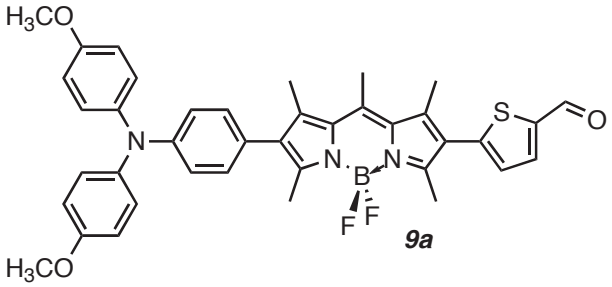
Synthesis of *8a*: *7* (96 mg, 0.20 mmol) and ***A*** (129 mg, 0.30 mmol) were solubilized in 110 mL of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (138 mg, 1.0 mmol) and $Pd(PPh_3)_4$ (23 mg, 0.020 mmol) were added and the mixture was refluxed

12 h under an atmosphere of N_2. After being cooled to room temperature, 50 mL of H_2O were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 50 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using hexanes:CH_2Cl_2 1:1 as the eluent, affording the desired product as a purple solid (97 mg, 75 %). Mp 135 - 137 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.39 (d, 1H, $^3J_{HH}$ = 5.0 Hz), 7.12 (m, 5H), 6.98 (m, 4H), 6.91 (d, 1H, $^3J_{HH}$ = 2.9 Hz), 6.86 (d, 4H, $^3J_{HH}$ = 8.7 Hz), 3.81 (s, 6H), 2.70 (s, 3H), 2.54 (s, 3H), 2.52 (s, 3H), 2.41 (s, 3H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 156.2, 154.4, 152.0, 148.0, 141.7, 140.9, 137.9, 137.7, 135.0, 134.3, 132.8, 131.9, 131.0, 128.1, 127.4, 127.0, 126.1, 125.5, 125.0, 119.8, 114.9, 55.7, 17.4, 15.9, 15.6, 13.7 (t, J_{CF} = 2.4 Hz), 13.4 (t, J_{CF} = 2.6 Hz). ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ = 0.77 (t, $^1J_{BF}$ = 30 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -146.3 (q). HRMS (DART): *m/z* 648.2660 ([M+H]$^+$), calcd for $^{12}C_{38}{}^1H_{37}{}^{11}B^{19}F_2{}^{14}N_3{}^{16}O_2{}^{32}S^+$: *m/z* 648.2668.



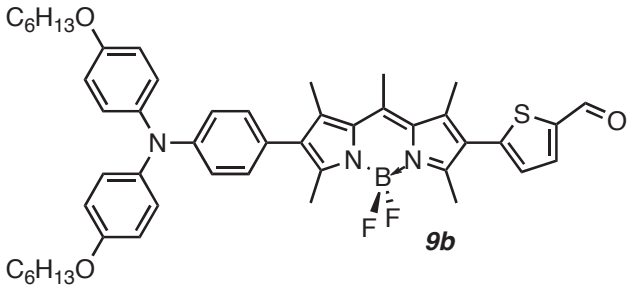
8b

Synthesis of *8b*: *7* (51 mg, 0.11 mmol) and ***B*** (94 mg, 0.17 mmol) were solubilized in 55 mL of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (76 mg, 0.55 mmol) and $Pd(PPh_3)_4$ (13 mg, 0.011 mmol) were added and the mixture was refluxed 12 h under an atmosphere of N_2. After being cooled to room temperature, 25 mL of H_2O were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using hexanes:CH_2Cl_2 1:1 as the eluent, affording the desired product as a purple solid (69 mg, 80 %). Mp 82 - 83 °C;. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.39 (d, 1H, $^3J_{HH}$ = 5.0 Hz), 7.12 (m, 5H), 6.97 (m, 4H), 6.91 (d, 1H, $^3J_{HH}$ = 3.0 Hz), 6.85 (d, 4H, $^3J_{HH}$ = 8.8 Hz), 3.94 (t, 4H, $^3J_{HH}$ = 6.5 Hz), 2.70 (s, 3H), 2.54 (s, 3H). 2.52 (s, 3H), 2.41 (s, 3H). 2.37 (s, 3H), 1.78 (m, 4H), 1.46 (m, 4H), 1.35 (m, 8H), 0.91 (t, 6H, $^3J_{HH}$ = 6.6 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 155.6, 154.3, 151.8, 148.0, 141.5, 140.5, 137.7, 137.5, 134.8, 134.2, 132.7, 131.7, 130.8, 127.9, 127.2, 126.9, 126.0, 125.4, 124.7, 119.6, 115.4, 68.3, 31.6, 29.3, 25.8, 22.6, 17.3, 15.7, 15.4, 14.0, 13.5 (t, J_{CF} = 2.6 Hz), 13.2 (t, J_{CF} = 2.2 Hz). ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ = 0.78 (t, $^1J_{BF}$ = 30 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -146.3 (q). HRMS (DART): *m/z* 788.4231 ([M+H]$^+$), calcd for $^{12}C_{48}{}^1H_{57}{}^{11}B^{19}F_2{}^{14}N_3{}^{16}O_2{}^{32}S^+$: *m/z* 788.4233.



9a

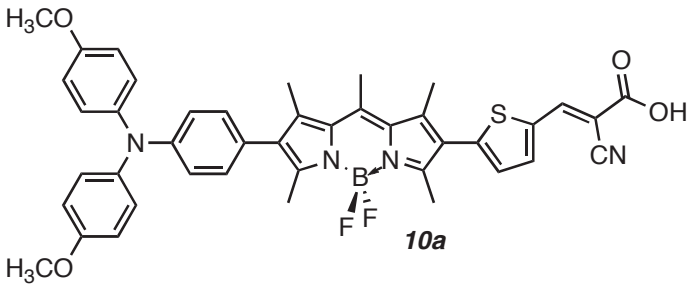
Synthesis of *9a*: A solution of 1.0 mL of dry DMF in 10 mL of dry 1,2-dichloroethane was cooled in an ice bath and 1.2 mL of $POCl_3$ was added dropwise. The mixture was warmed to room temperature and stirred 30 min. ***8a*** (70 mg, 0.11 mmol) dissolved in 12 mL of dry 1,2-dichloroethane was added in one portion and the mixture was stirred 16 hr. The mixture was neutralized in 30 mL of saturated aqueous $NaHCO_3$ cooled to 0°C and the mixture was stirred 30 min. at room temperature. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using CH_2Cl_2 as the eluent, affording the desired product as a purple solid (30 mg, 40 %). Mp 205 (decomp) °C; IR (KBr, cm^{-1}) 1660. ^1H NMR ($CDCl_3$, 400 MHz): δ = 9.91 (s, 1H), 7.79 (d, 1H, $^3J_{HH}$ = 3.6 Hz), 7.12 (d, 4H, $^3J_{HH}$ = 8.6 Hz), 7.03 (d, 1H), 6.98 (m, 4H), 6.86 (d, 4H), 3.81 (s, 6H), 2.72 (s, 3H), 2.58 (s, 3H), 2.53 (s, 3H), 2.46 (s, 3H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 182.9, 156.6, 156.3, 150.1, 148.2, 146.3, 143.7, 142.0, 140.8, 139.1, 136.9, 136.4, 135.3, 133.6, 131.8, 130.9, 129.0, 127.1, 124.4, 123.9, 119.7, 114.9, 55.7, 17.6, 16.0, 15.5, 13.8 (t, J_{CF} = 2.5 Hz), 13.4 (t, J_{CF} = 2.5 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.73 (t, $^1J_{BF}$ = 31 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -146.1 (q). HRMS (DART): *m/z* 676.2613 ($[M+H]^+$), calcd for $^{12}C_{39}{}^1H_{37}{}^{11}B^{19}F_2{}^{14}N_3{}^{16}O_3{}^{32}S^+$: *m/z* 676.2617.



9b

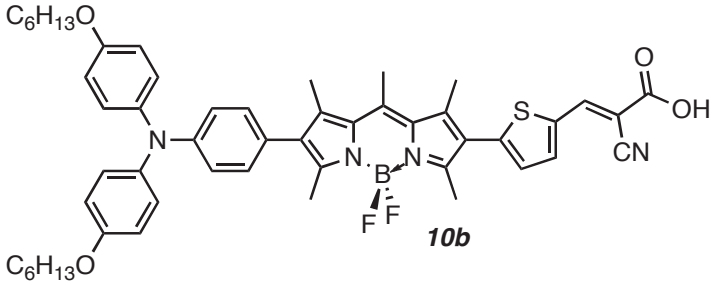
Synthesis of *9b*: A solution of 1.0 mL of dry DMF in 10 mL of dry 1,2-dichloroethane was cooled in an ice bath and 1.2 mL of $POCl_3$ was added dropwise. The mixture was warmed to room temperature and stirred 30 min. ***8b*** (70 mg, 0.089 mmol) dissolved in 12 mL of dry 1,2-dichloroethane was added in one portion and the mixture was stirred 16 hr. The mixture was neutralized in 30 mL of saturated aqueous $NaHCO_3$ cooled to 0°C and the mixture was stirred 30 min. at room temperature. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using CH_2Cl_2 as the eluent, affording the desired product as a purple solid (30 mg, 41%). Mp 95 - 100 °C; IR (KBr, cm^{-1}) 1668. ^1H NMR ($CDCl_3$, 400 MHz): δ = 9.91 (s, 1H), 7.79 (d, 1H, $^3J_{HH}$ = 3.6 Hz),

7.10 (d, 4H, $^{3}J_{HH}$ = 8.7 Hz), 7.02 (d, 1H), 6.97 (m, 4H), 6.85 (d, 4H), 3.94 (t, 4H, $^{3}J_{HH}$ = 6.4 Hz), 2.72 (s, 3H), 2.58 (s, 3H), 2.53 (s, 3H), 2.45 (s, 3H), 2.38 (s, 3H), 1.78 (m, 4H), 1.46 (m, 4H), 1.34 (m, 8H), 0.91 (t, 6H, $^{3}J_{HH}$ = 6.6 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ = 182.9, 156.6, 155.9, 150.1, 148.3, 146.3, 143.7, 142.0, 140.6, 139.1, 136.8, 136.3, 135.3, 133.6, 131.8, 130.8, 129.0, 127.1, 124.2, 123.8, 119.5, 115.5, 68.4, 31.7, 29.5, 25.9, 22.7, 17.6, 16.0, 15.5, 14.2, 13.8 (t, J_{CF} = 2.5 Hz), 13.4 (t, J_{CF} = 2.5 Hz). $^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.73 (t, $^{1}J_{BF}$ = 30 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -146.1 (q). HRMS (DART): *m/z* 816.4165 ($[M+H]^+$), calcd for $^{12}C_{49}{}^{1}H_{57}{}^{11}B^{19}F_2{}^{14}N_3{}^{16}O_3{}^{32}S^+$: *m/z* 816.4182.



10a

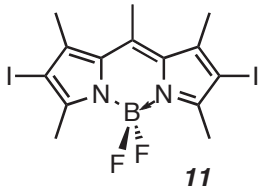
Synthesis of *10a*: *9a* (46 mg, 0.068 mmol) was dissolved in 25 mL of MeCN:$CHCl_3$ 1:1 and cyanoacetic acid (12 mg, 0.14 mmol) was added, followed by piperidine (2 μL, 0.02 mmol). The mixture was refluxed 24 hr and after being cooled at room temperature, the organic layer was washed with HCl 1N (3 × 25 mL). The organic layer was dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was recrystallized from hexanes:CH_2Cl_2 3:1, affording a dark purple solid (48 mg, 95 %). Mp 195 - 198 °C; IR (KBr, cm^{-1}) 1697, 2212, 2925. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.37 (br, 1H), 7.89 (br, 1H), 7.12 (d, 4H, $^{3}J_{HH}$ = 8.7 Hz), 7.07 (br, 1H), 6.98 (m, 4H), 6.87 (d, 4H), 3.81 (s, 6H), 2.73 (s, 3H), 2.61 (s, 3H), 2.54 (s, 3H), 2.49 (s, 3H), 2.39 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.2, 157.0, 156.2, 150.0, 148.3, 148.1, 148.0, 142.0, 140.8, 139.3, 139.1, 139.0, 136.1, 135.8, 135.4, 133.8, 131.8, 130.9, 129.4, 127.1, 124.3, 123.4, 119.5, 115.8, 114.9, 55.6, 17.7, 16.0, 15.5, 13.9, 13.5. $^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.71 (t, $^{1}J_{BF}$ = 29 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -146.1 (q). HRMS (ESI): *m/z* 741.2558 ($[M-H]^-$), calcd for $^{12}C_{42}{}^{1}H_{36}{}^{11}B^{19}F_2{}^{14}N_4{}^{16}O_4{}^{32}S^-$: *m/z* 741.2523.



10b

Synthesis of *10b*: *9b* (50 mg, 0.061 mmol) was dissolved in 25 mL of MeCN:$CHCl_3$ 1:1 and cyanoacetic acid (10 mg, 0.12 mmol) was added, followed by piperidine (2 μL, 0.02 mmol). The mixture was refluxed 24 hr and after being cooled at room temperature, the

organic layer was washed with HCl 1N (3 × 25 mL). The organic layer was dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was recrystallized from hexanes:MeOH 3:1, affording a dark purple solid (50 mg, 93 %). Mp 185 - 188 °C; IR (KBr, cm^{-1}) 1685, 2213, 2924. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.35 (s, 1H), 7.86 (d, 1H, $^3J_{HH}$ = 2.9 Hz), 7.10 (d, 4H $^3J_{HH}$ = 8.8 Hz), 7.06 (d, 1H), 6.97 (m, 4H), 6.85 (d, 4H), 3.94 (t, 4H, $^3J_{HH}$ = 6.5 Hz), 2.72 (s, 3H), 2.60 (s, 3H), 2.54 (s, 3H), 2.48 (s, 3H), 2.38 (s, 3H), 1.78 (m, 4H), 1.47 (m, 4H), 1.35 (m, 8H), 0.91 (t, 6H, $^3J_{HH}$ = 6.6 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 166.9, 157.0, 155.9, 148.3, 147.9, 147.8, 147.7, 142.0, 140.6, 139.3, 138.9, 136.1, 135.9, 135.5, 135.4, 133.8, 131.8, 130.8, 129.4, 127.1, 124.1, 123.5, 119.5, 115.9, 115.5, 68.4, 31.8, 29.5, 25.9, 22.8, 17.7, 16.1, 15.6, 14.2, 13.9 (t, J_{CF} = 2.3 Hz), 13.5 (t, J_{CF} = 2.5 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.70 (t, $^1J_{BF}$ = 31 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -146.0 (q). HRMS (ESI): *m/z* 881.4034 ([M-H]$^-$), calcd for $^{12}C_{52}{}^1H_{56}{}^{11}B{}^{19}F_2{}^{14}N_4{}^{16}O_4{}^{32}S^-$: *m/z* 881.4088.



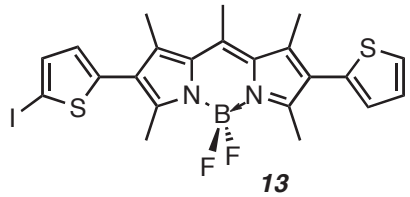
11

Synthesis of *11*: NIS (680 mg, 3.04 mmol) was added to a solution of ***1*** (199 mg, 0.76 mmol) in 35 mL of CH_2Cl_2. The mixture was stirred 12 h at room temperature and volatiles were removed *in vacuo*. The crude material was purified through column chromatography using CH_2Cl_2 as the eluent to afford the title compound as an orange solid (quantitative). The spectroscopic data agreed with the literature.[5] ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.63 (s, 3H), 2.61 (s, 6H), 2.47 (s, 6H).

12

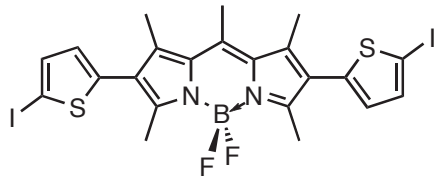
Synthesis of *12*: *11* (0.881 g, 1.76 mmol) and ***C*** (0.887 g, 4.22 mmol) were solubilized in 75 mL of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (0.822 g, 17.6 mmol) and $Pd(PPh_3)_4$ (139 mg, 0.35 mmol) were added and the mixture was refluxed 12 h under an atmosphere of N_2. After being cooled to room temperature, 25 mL of H_2O were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 50 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using hexanes:CH_2Cl_2 1:1 as the eluent, affording the desired product as a dark red solid (0.652 g, 87 %). Mp 209 - 210 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.41 (d, 2H, $^3J_{HH}$ = 4.8 Hz), 7.14 (dd, 2H), 6.93 (d, 2H, $^3J_{HH}$ = 3.0 Hz), 2.72 (s, 3H), 2.56 (s, 6H), 2.42 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 153.7, 142.4, 138.9, 134.6, 132.4, 132.3, 128.2, 127.4, 126.3, 17.5, 15.7, 13.5 (t, J_{CF} = 2.5 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.72 (t, $^1J_{BF}$ = 33 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -146.1 (q).

HRMS (DART): *m/z* 427.1286 ([M+H]$^+$), calcd for $^{12}C_{22}{}^{1}H_{22}{}^{11}B^{19}F_2{}^{14}N_2{}^{32}S_2{}^+$: *m/z* 427.1286.

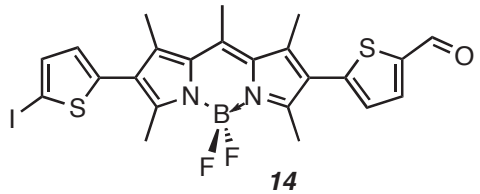


13

Synthesis of *13*: *12* (500 mg, 1.17 mmol) was dissolved in 75 mL of CH_2Cl_2 and N-iodosuccinimide (263 mg, 1.17 mmol) was added. The mixture was stirred at room temperature 12 h with the flask covered with Al foil. Volatiles were removed *in vacuo* and the crude mixture was purified through column chromatography using CH_2Cl_2:hexanes 1:1 as the eluent, affording the desired compound as a dark red solid (215 mg, 33%) and 200 mg of starting material ***12***. Mp 198 - 200 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.41 (d, 1H, $^3J_{HH}$ = 4.7 Hz), 7.27 (d, 1H, $^3J_{HH}$ = 3.6 Hz), 7.14 (dd, 1H), 6.93 (d, 1H, $^3J_{HH}$ = 3.4 Hz), 6.60 (d, 1H), 2.71 (s, 3H), 2.55 (s, 3H), 2.54 (s, 3H), 2.42 (s, 3H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 154.5, 152.9, 142.6, 141.1, 139.5, 138.6, 137.4, 134.3, 132.6, 132.2, 129.9, 128.3, 127.5, 126.7, 126.6, 126.4, 125.2, 17.5, 15.8, 15.7, 13.6 (t, J_{CF} = 2.4 Hz), 13.4 (t, J_{CF} = 2.6 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.68 (t, $^1J_{BF}$ = 32 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -146.1 (q). HRMS (DART): *m/z* 553.0265 ([M+H]$^+$), calcd for $^{12}C_{22}{}^{1}H_{21}{}^{11}B^{19}F_2{}^{127}I^{14}N_2{}^{32}S_2{}^+$: *m/z* 553.0252.



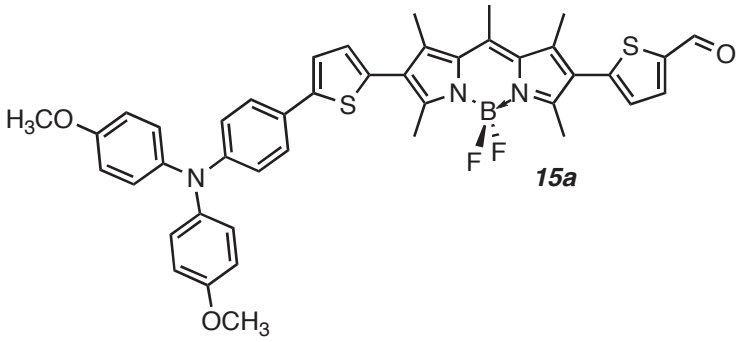
A small amount (27 mg) of the above *di*iodo derivative was also obtained: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.27 (d, 2H, $^3J_{HH}$ = 3.5 Hz), 6.60 (d, 2H), 2.70 (s, 3H), 2.54 (s, 6H), 2.41 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 153.7, 142.9, 140.8, 139.1, 137.4, 132.4, 129.9, 125.6, 125.5, 17.5, 15.7, 13.4 (t, J_{CF} = 2.8 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.64 (t, $^1J_{BF}$ = 32 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -146.1 (q). HRMS (DART): *m/z* 678.9218 ([M+H]$^+$), calcd for $^{12}C_{22}{}^{1}H_{20}{}^{11}B^{19}F_2{}^{127}I_2{}^{14}N_2{}^{32}S_2{}^+$: *m/z* 678.9218.



14

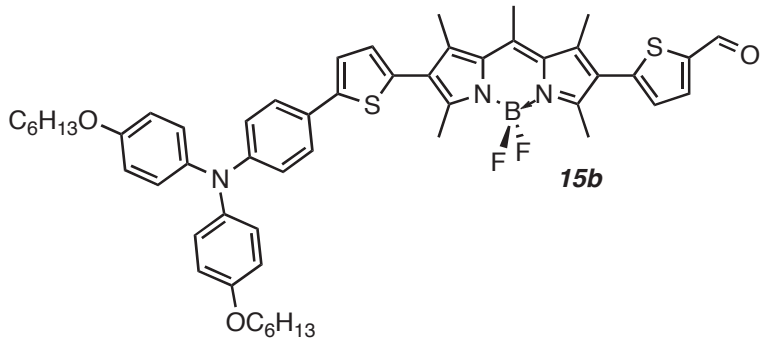
Synthesis of *14*: A solution of 2.0 mL of dry DMF in 10 mL of dry 1,2-dichloroethane was cooled in an ice bath and 2.5 mL of $POCl_3$ was added dropwise. The mixture was warmed to room temperature and stirred 30 min. ***13*** (26 mg, 0.05 mmol) dissolved in 15 mL of dry 1,2-dichloroethane was added in one portion and the mixture was stirred 16 h at room temperature. The mixture was neutralized in 60 mL of saturated aqueous

$NaHCO_3$ cooled to 0°C and the mixture was stirred 30 min. at room temperature. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using CH_2Cl_2 as the eluent, affording the desired product as a dark purple solid (60 mg, 65%). Mp 144 - 146 °C; IR (KBr, cm^{-1}) 1664. ^1H NMR ($CDCl_3$, 400 MHz): δ = 9.92 (s, 1H), 7.80 (d, 1H, $^3J_{HH}$ = 3.8 Hz), 7.28 (d, 1H, $^3J_{HH}$ = 3.6 Hz), 7.04 (d, 1H), 6.61 (d, 1H), 2.73 (s, 3H), 2.59 (s, 3H), 2.55 (s, 3H), 2.47 (s, 3H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 182.9, 154.9, 152.4, 146.5, 145.5, 144.0, 143.3, 140.5, 139.9, 138.3, 137.5, 136.8, 132.9, 132.4, 130.1, 129.2, 126.1, 125.0, 17.7, 15.8, 15.7, 13.6, 13.5. $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.64 (t, $^1J_{BF}$ = 32 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -145.9 (q). HRMS (DART): *m/z* 581.0203 ($[M+H]^+$), calcd for $^{12}C_{23}{}^1H_{21}{}^{11}B^{19}F_2{}^{127}I^{14}N_2{}^{16}O^{32}S_2{}^+$: *m/z* 581.0201.



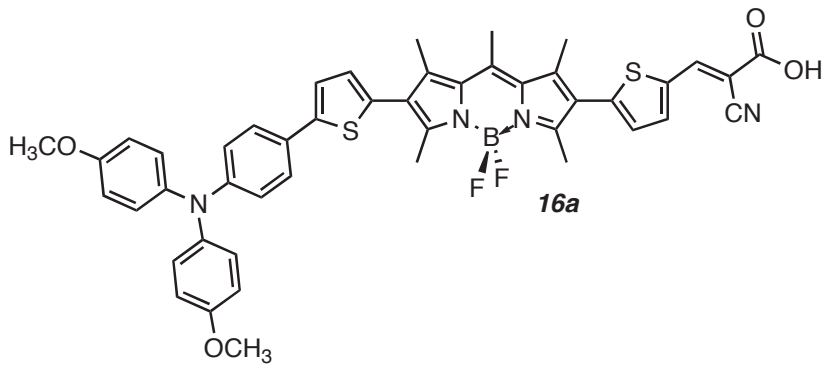
15a

Synthesis of *15a*: *14* (80 mg, 0.14 mmol) and ***A*** (80 mg, 0.18 mmol) were solubilized in 55 mL of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (100 mg, 0.70 mmol) and $Pd(PPh_3)_4$ (16 mg, 0.014 mmol) were added and the mixture was refluxed 12 h under an atmosphere of N_2. After being cooled to room temperature, 25 mL of H_2O were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using CH_2Cl_2 1 as the eluent, affording the desired product as a dark purple solid (69 mg, 65%). Mp 138 - 139 °C; IR (KBr, cm^{-1}) 1666. ^1H NMR ($CDCl_3$, 400 MHz): δ = 9.92 (s, 1H), 7.80 (d, 1H, $^3J_{HH}$ = 3.8 Hz), 7.42 (d, 2H, $^3J_{HH}$ = 8.6 Hz), 7.20 (d, 1H, $^3J_{HH}$ = 3.6 Hz), 7.08 (d, 4H, $^3J_{HH}$ = 8.9 Hz), 7.04 (d, 1H), 6.93 (d, 2H), 6.85 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 182.9, 156.2, 155.9, 151.6, 148.5, 145.8, 145.7, 143.9, 142.8, 140.8, 140.0, 137.6, 136.8, 133.2, 132.2, 131.9, 129.4, 129.2, 127.6, 126.8, 126.5, 126.3, 124.5, 122.0, 120.7, 114.9, 55.7, 17.7, 16.0, 15.7, 13.8 (t, J_{CF} = 2.9 Hz), 13.5 (t, J_{CF} = 2.5 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.69 (t, $^1J_{BF}$ = 31 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -145.9 (q). HRMS (DART): *m/z* 758.2509 ($[M+H]^+$), calcd for $^{12}C_{43}{}^1H_{39}{}^{11}B^{19}F_2{}^{14}N_3{}^{16}O_3{}^{32}S_2{}^+$: *m/z* 758.2494.



15b

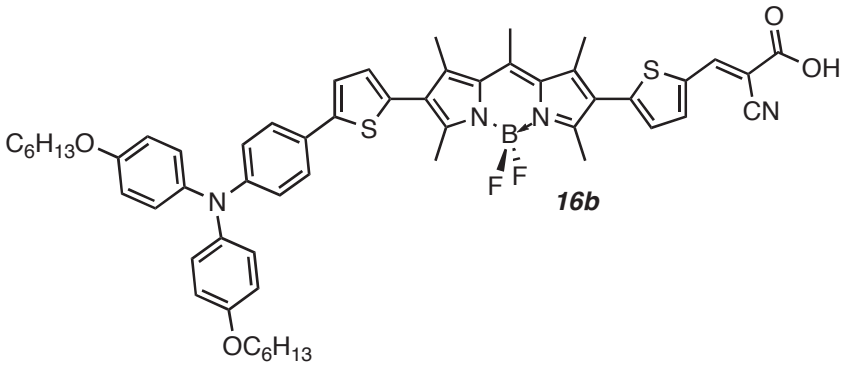
Synthesis of *15b*: *14* (80 mg, 0.14 mmol) and ***B*** (103 mg, 0.18 mmol) were solubilized in 55 mL of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (100 mg, 0.70 mmol) and $Pd(PPh_3)_4$ (16 mg, 0.014 mmol) were added and the mixture was refluxed 12 h under an atmosphere of N_2. After being cooled to room temperature, 25 mL of H_2O were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using CH_2Cl_2 1 as the eluent, affording the desired product as a dark purple solid (50 mg, 40%). Mp 123 - 125 °C; IR (KBr, cm^{-1}) 1668. ^1H NMR ($CDCl_3$, 400 MHz): δ = 9.93 (s, 1H), 7.81 (d, 1H, $^3J_{HH}$ = 3.2 Hz), 7.42 (d, 2H, $^3J_{HH}$ = 8.6 Hz), 7.20 (d, 1H), 7.07 (d, 4H, $^3J_{HH}$ = 8.5 Hz), 7.05 (d, 1H $^3J_{HH}$ = 3.5 Hz), 6.94 (d, 2H), 6.84 (m, 5H), 3.95 (t, 4H, $^3J_{HH}$ = 6.4 Hz), 2.75 (s, 3H), 2.63 (s, 3H), 2.60 (s, 3H), 2.49 (s, 3H), 2.48 (s, 3H), 1.79 (m, 4H), 1.48 (m, 4H), 1.35 (m, 8H), 0.92 (t, 6H, $^3J_{HH}$ = 6.1 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 182.9, 155.9, 155.8, 151.6, 150.6, 148.6, 145.8, 143.9, 142.8, 141.7, 140.6, 140.0, 136.8, 134.1, 133.2, 132.2, 131.9, 129.4, 129.1, 126.8, 126.5, 126.2, 124.5, 121.9, 120.6, 115.5, 68.5, 31.8, 29.5, 25.9, 22.8, 17.7, 16.0, 15.7, 14.2, 13.8 (t, J_{CF} = 2.7 Hz), 13.5 (t, J_{CF} = 3.2 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.69 (t, $^1J_{BF}$ = 31 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -145.8 (q). HRMS (DART): *m/z* 898.4045 ($[M+H]^+$), calcd for $^{12}C_{53}{}^1H_{59}{}^{11}B^{19}F_2{}^{14}N_3{}^{16}O_3{}^{32}S_2{}^+$: *m/z* 898.4059.



16a

Synthesis of *16a*: *15a* (47 mg, 0.065 mmol) was dissolved in 25 mL of MeCN:$CHCl_3$ 1:1 and cyanoacetic acid (11 mg, 0.13 mmol) was added, followed by piperidine (2 μL, 0.02 mmol). The mixture was refluxed 24 hr and after being cooled at room temperature, the organic layer was washed with HCl 1N (3 × 25 mL). The organic layer was dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was recrystallized from hexanes:CH_2Cl_2 3:1, affording a dark purple solid (46 mg, 86 %). Mp

159 - 161°C; IR (KBr, cm^{-1}) 1675, 2216, 2924. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.35 (br, 1H), 7.87 (br, 1H), 7.41 (d, 2H, $^{3}J_{HH}$ = 8.1 Hz), 7.19 (br, 1H), 7.08 (m, 5H), 6.93 (d, 2H), 6.84 (m, 5H), 3.81 (s, 6H), 2.73 (br, 3H), 2.62 (br, 6H), 2.48 (br, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ = 179.5, 156.2, 156.1, 151.4, 148.5, 147.1, 145.8, 142.8, 140.8, 140.2, 138.8, 137.4, 136.1, 133, 3, 132.9, 132.2, 131.8, 129.5, 129.4, 127.8, 126.8, 126.5, 126.3, 124.3, 124.1, 122.0, 120.7, 116.0, 114.9, 55.7, 17.8, 16.0, 15.8, 13.8, 13.6. $^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.67 (t, $^{1}J_{BF}$ = 31 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -145.9 (q). HRMS (ESI): *m/z* 823.2356 ($[M-H]^-$), calcd for $^{12}C_{46}{}^{1}H_{38}{}^{11}B^{19}F_2{}^{14}N_4{}^{16}O_4{}^{32}S_2{}^-$: *m/z* 823.2401.



16b

Synthesis of *16b*: *15b* (50 mg, 0.056 mmol) was dissolved in 25 mL of MeCN:$CHCl_3$ 1:1 and cyanoacetic acid (10 mg, 0.11 mmol) was added, followed by piperidine (2 μL, 0.02 mmol). The mixture was refluxed 24 h and after being cooled at room temperature, the organic layer was washed with HCl 1N (3 × 25 mL). The organic layer was dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was recrystallized from hexanes:MeOH 3:1, affording a dark purple solid (43 mg, 80 %). Mp 215 (decomp.) °C; IR (KBr, cm^{-1}) 1685, 2216, 2927. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.36 (s, 1H), 7.87 (d, 1H, $^{3}J_{HH}$ = 3.1 Hz), 7.41 (d, 2H, $^{3}J_{HH}$ = 8.8 Hz), 7.19 (d, 1H, $^{3}J_{HH}$ = 3.6 Hz), 7.06 (m, 5H), 6.93 (d, 1H), 6.83 (m, 5H), 3.94 (t, 4H, $^{3}J_{HH}$ = 6.6 Hz), 2.74 (s, 3H), 2.62 (s, 3H), 2.61 (s, 3H), 2.49 (s, 3H), 2.48 (s, 3H), 1.78 (m, 4H), 1.47 (m, 4H), 1.35 (m, 8H), 0.91 (t, 6H, $^{3}J_{HH}$ = 7.0 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ = 182.3, 156.3, 155.8, 151.4, 148.6, 147.3, 145.9, 142.9, 140.6, 140.3, 138.9, 138.7, 137.4, 136.1, 133.4, 132.2, 131.8, 129.5, 129.4, 127.8, 126.8, 126.5, 126.2, 124.1, 123.9, 122.0, 120.6, 115.9, 115.5, 68.5, 31.8, 29.5, 25.9, 22.8, 17.7, 16.0, 15.8, 14.2, 13.8 (br), 13.6 (br). $^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.66 (t, $^{1}J_{BF}$ = 29 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -145.7 (q). HRMS (ESI): *m/z* 963.3974 ($[M-H]^-$), calcd for $^{12}C_{56}{}^{1}H_{58}{}^{11}B^{19}F_2{}^{14}N_4{}^{16}O_4{}^{32}S_2{}^-$: *m/z* 963.3966.

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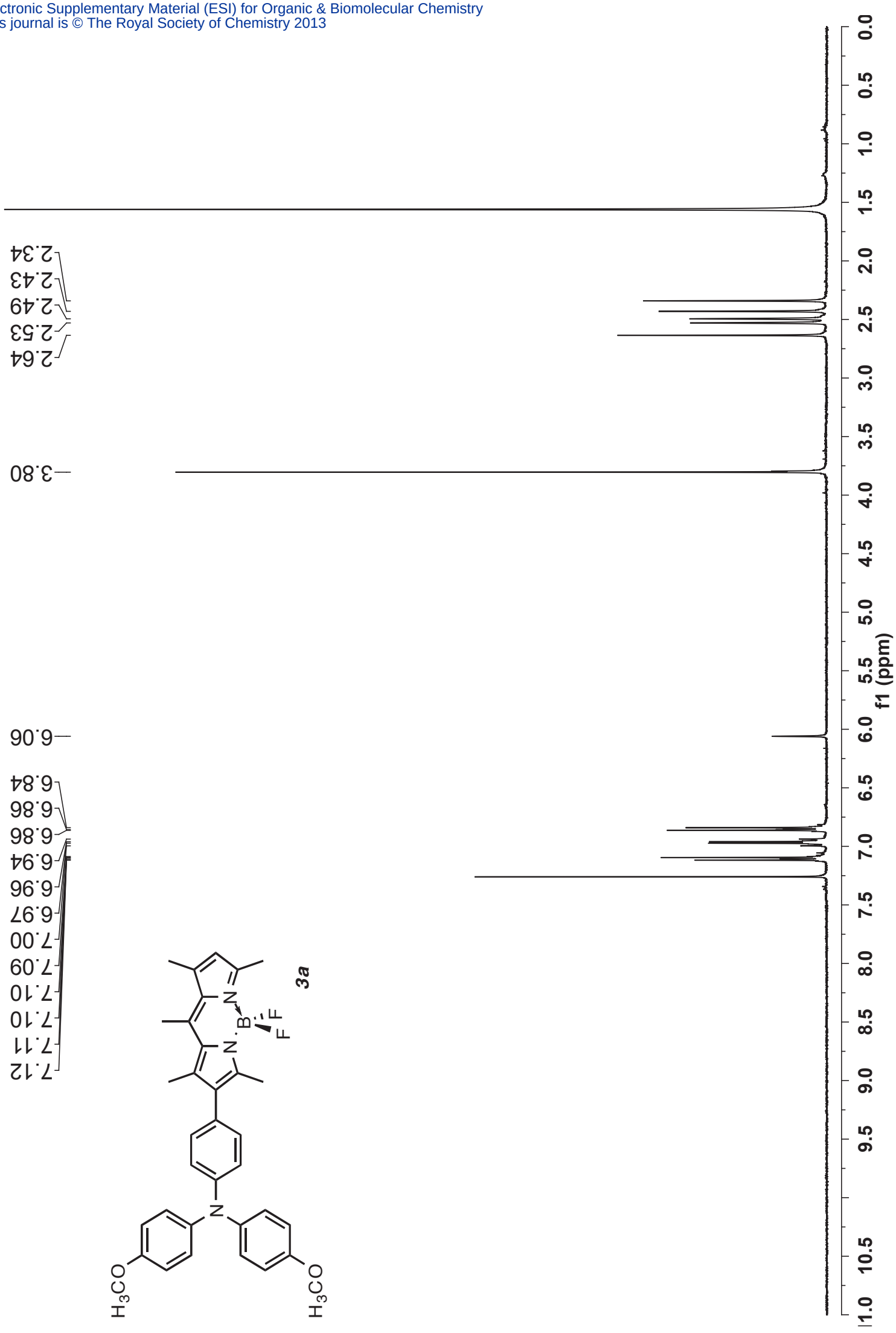

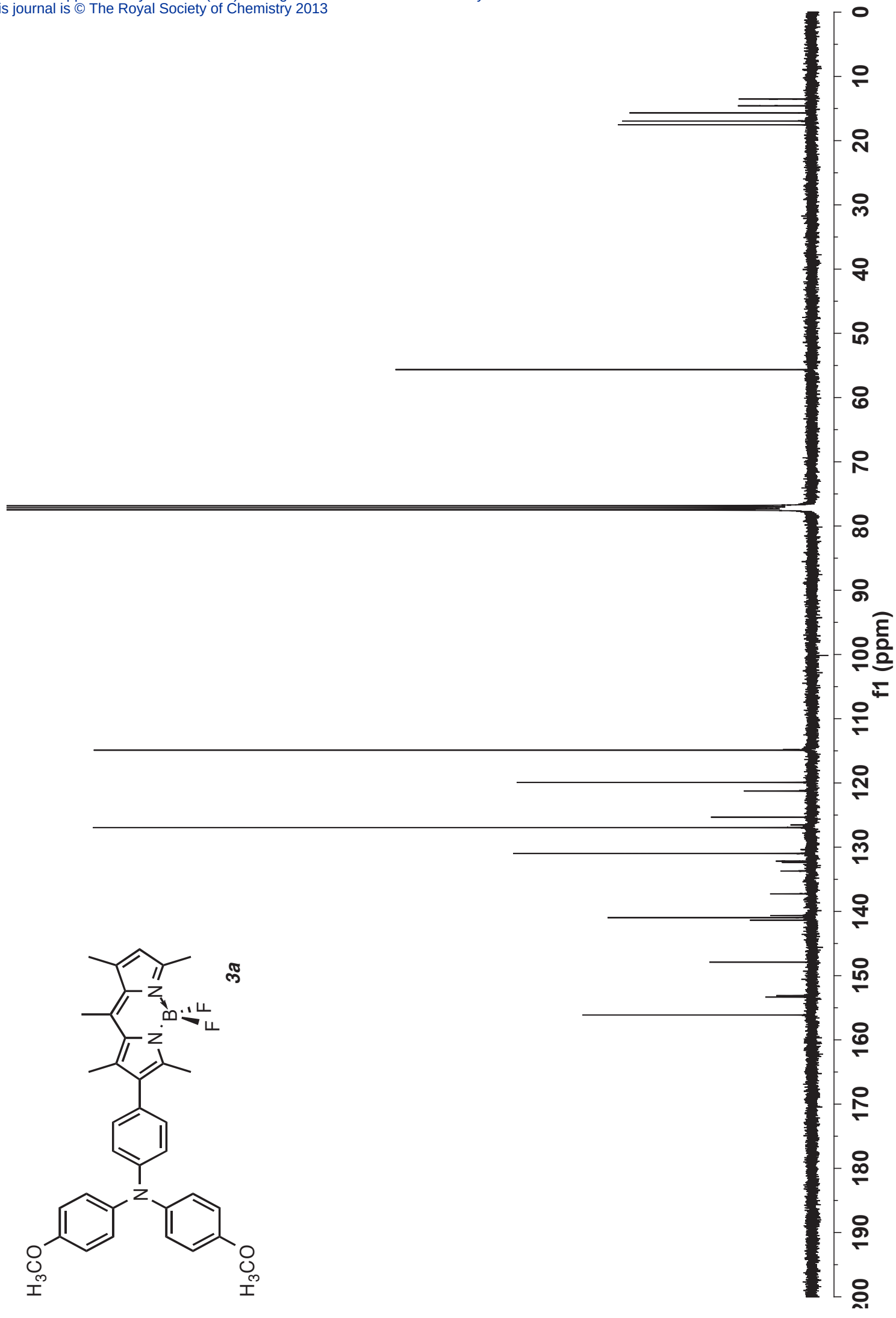

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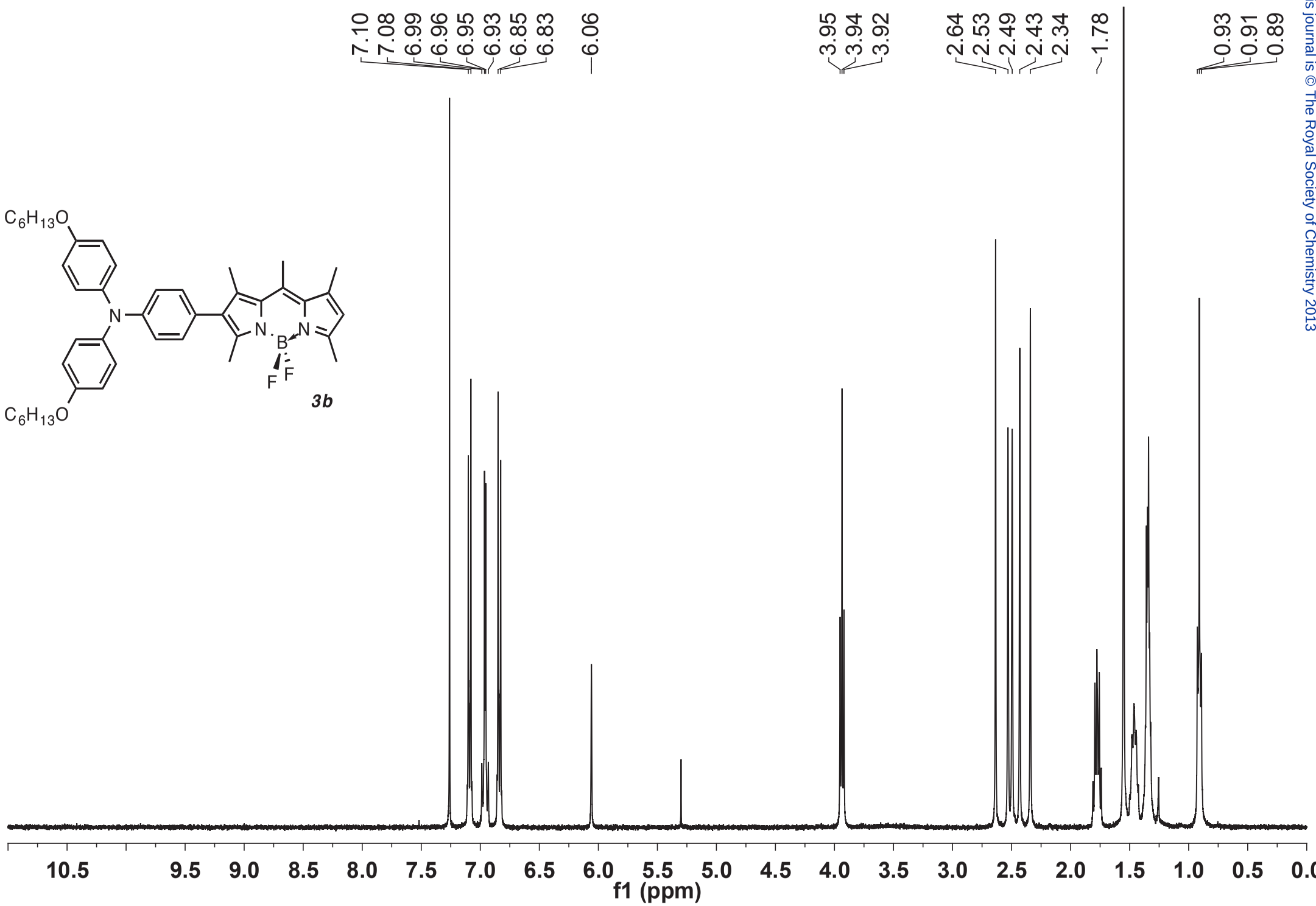

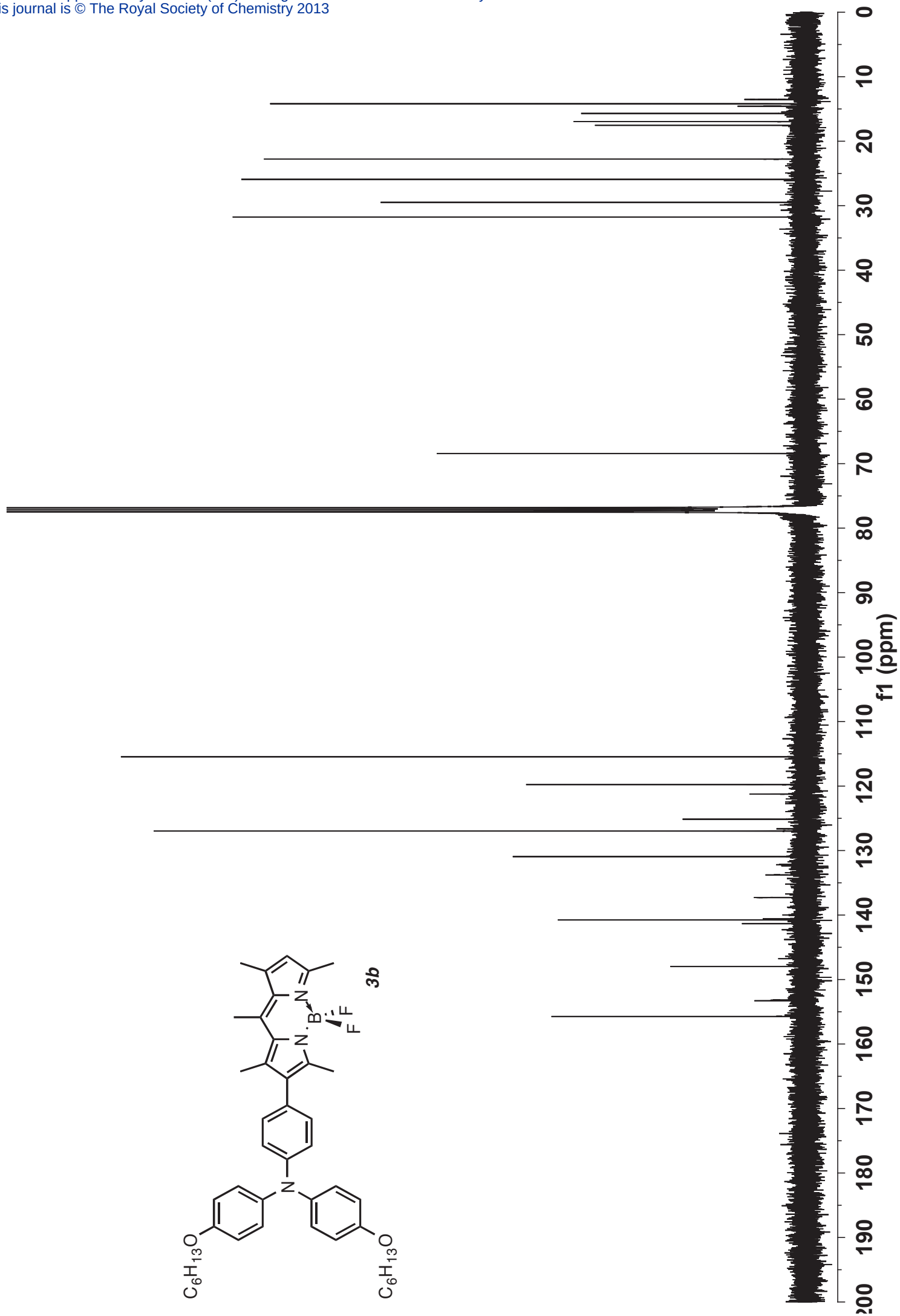

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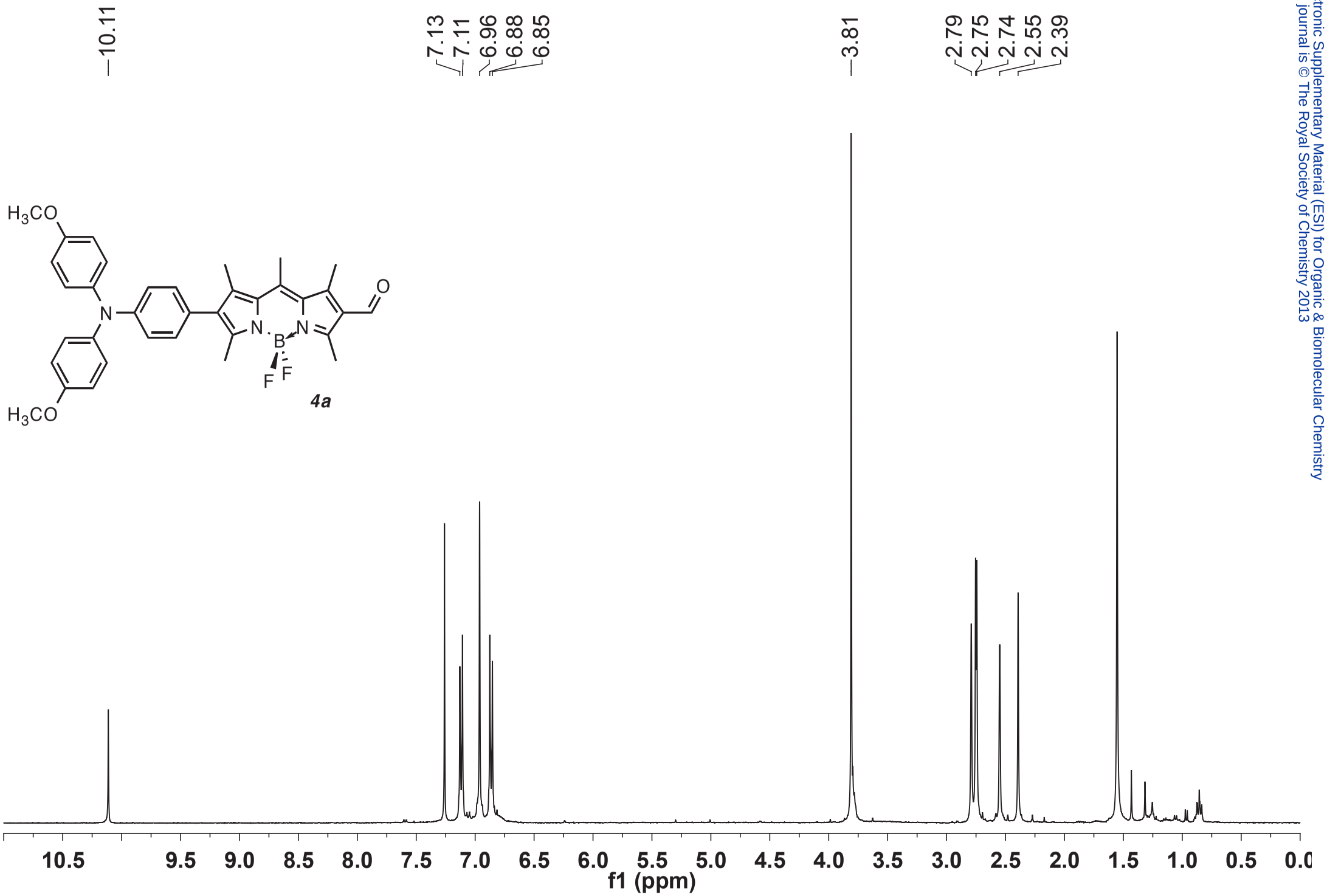

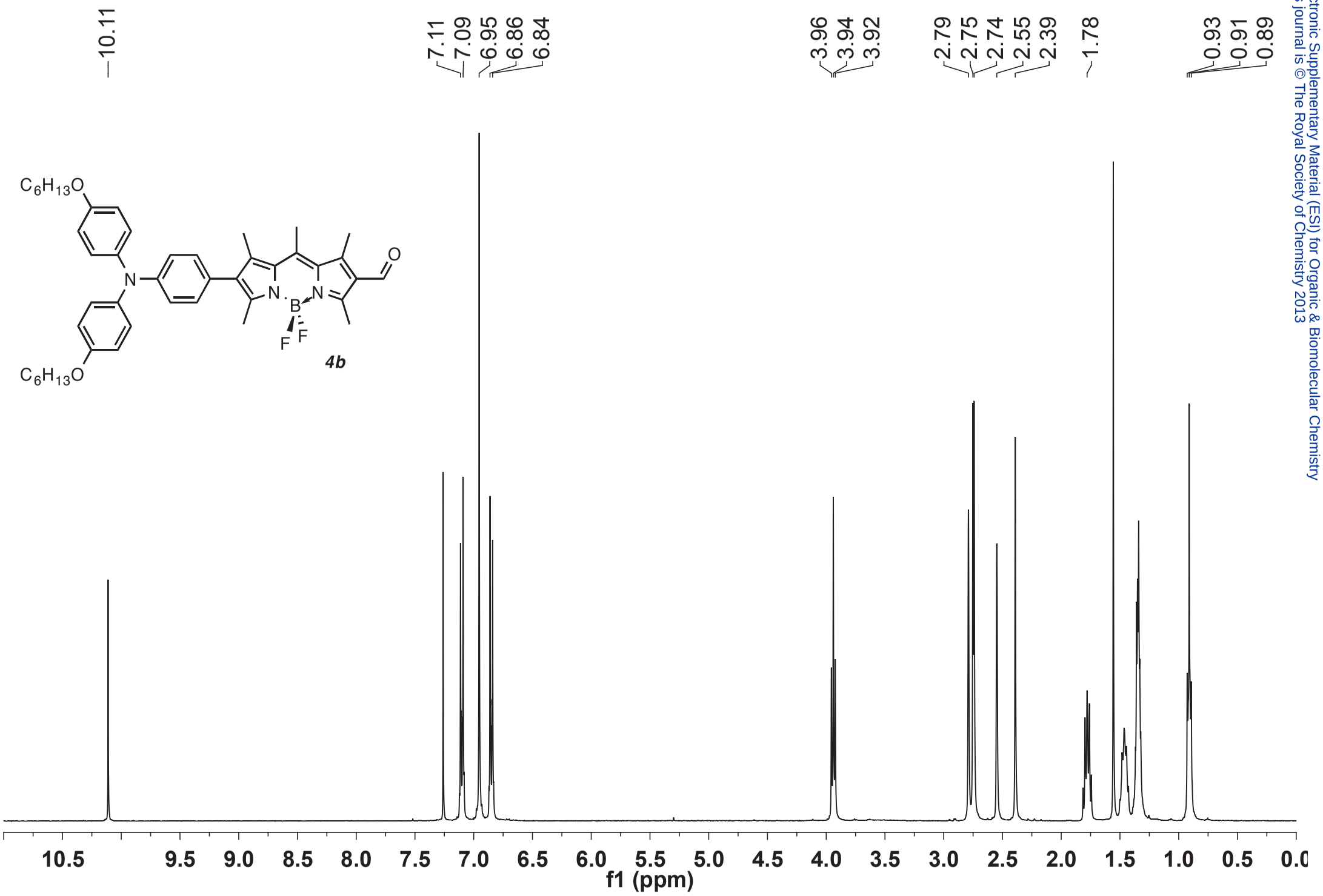

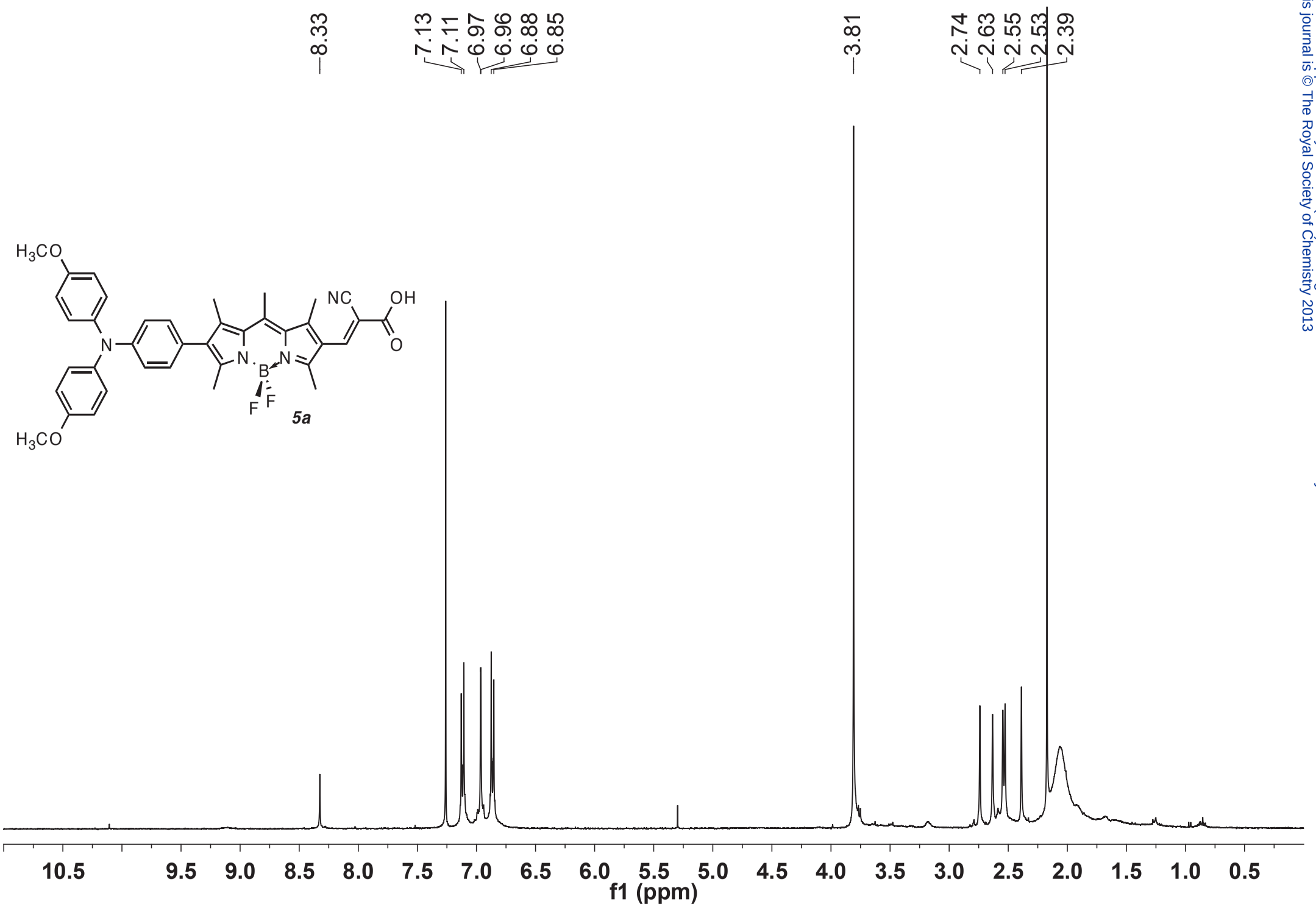

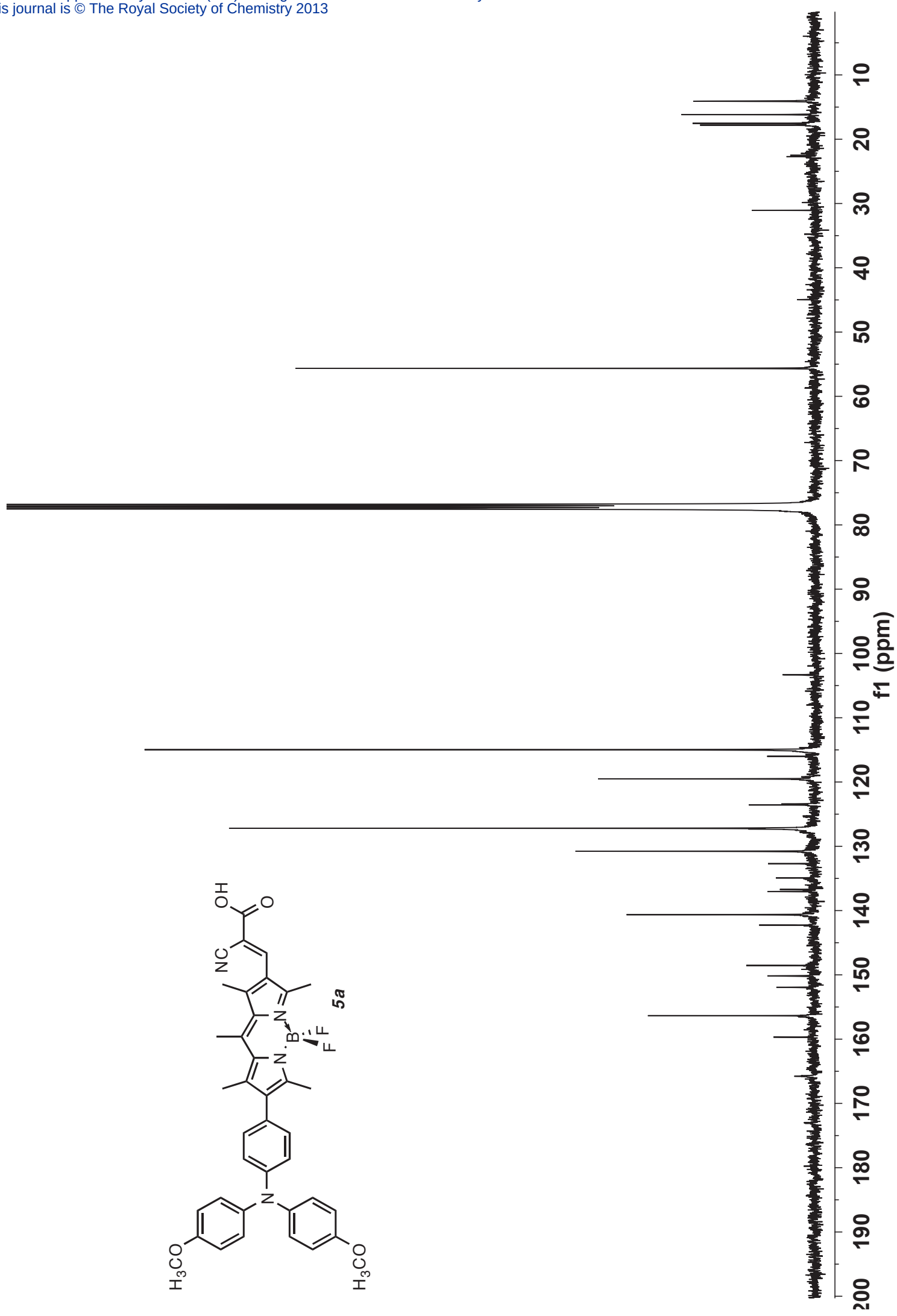

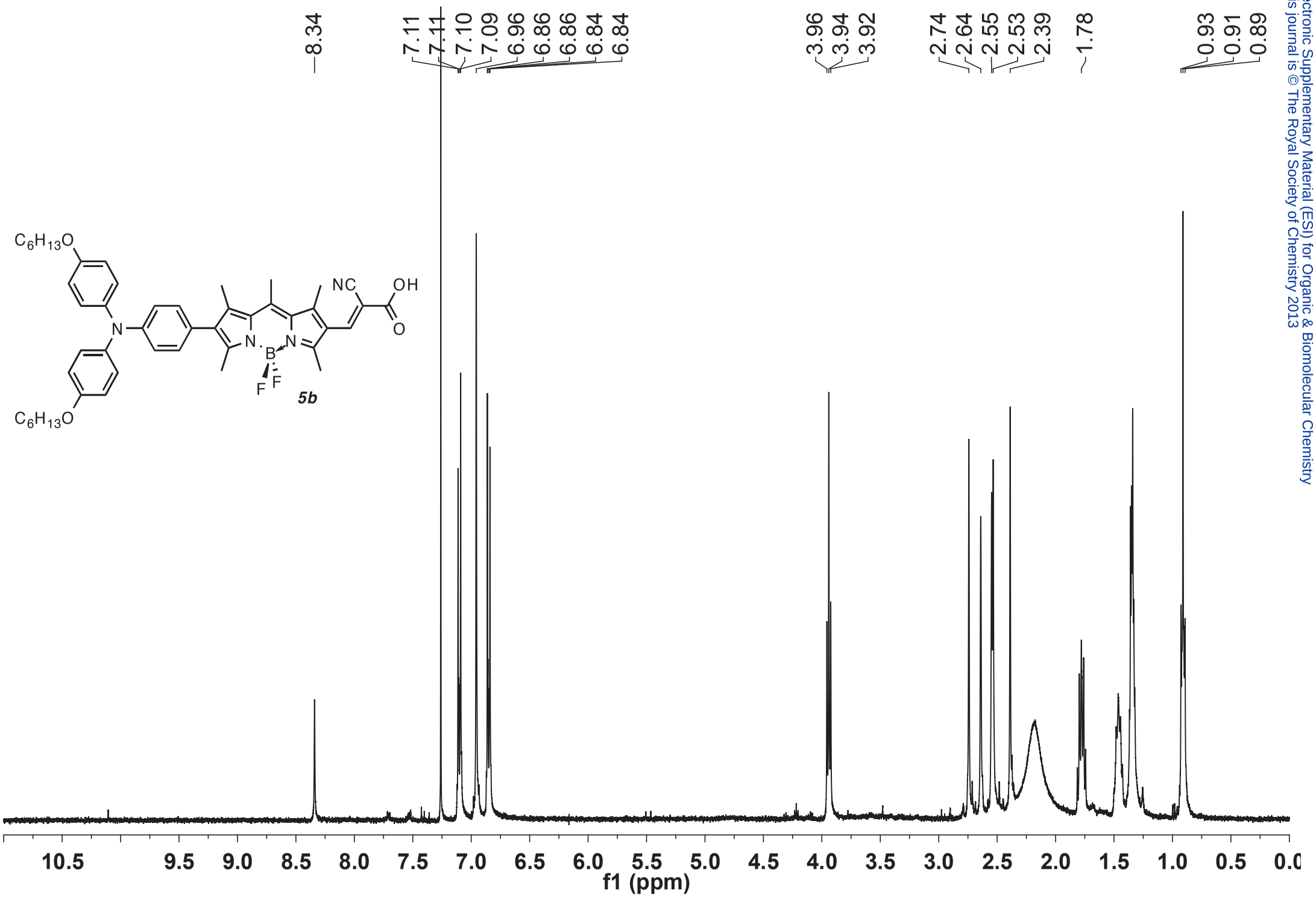

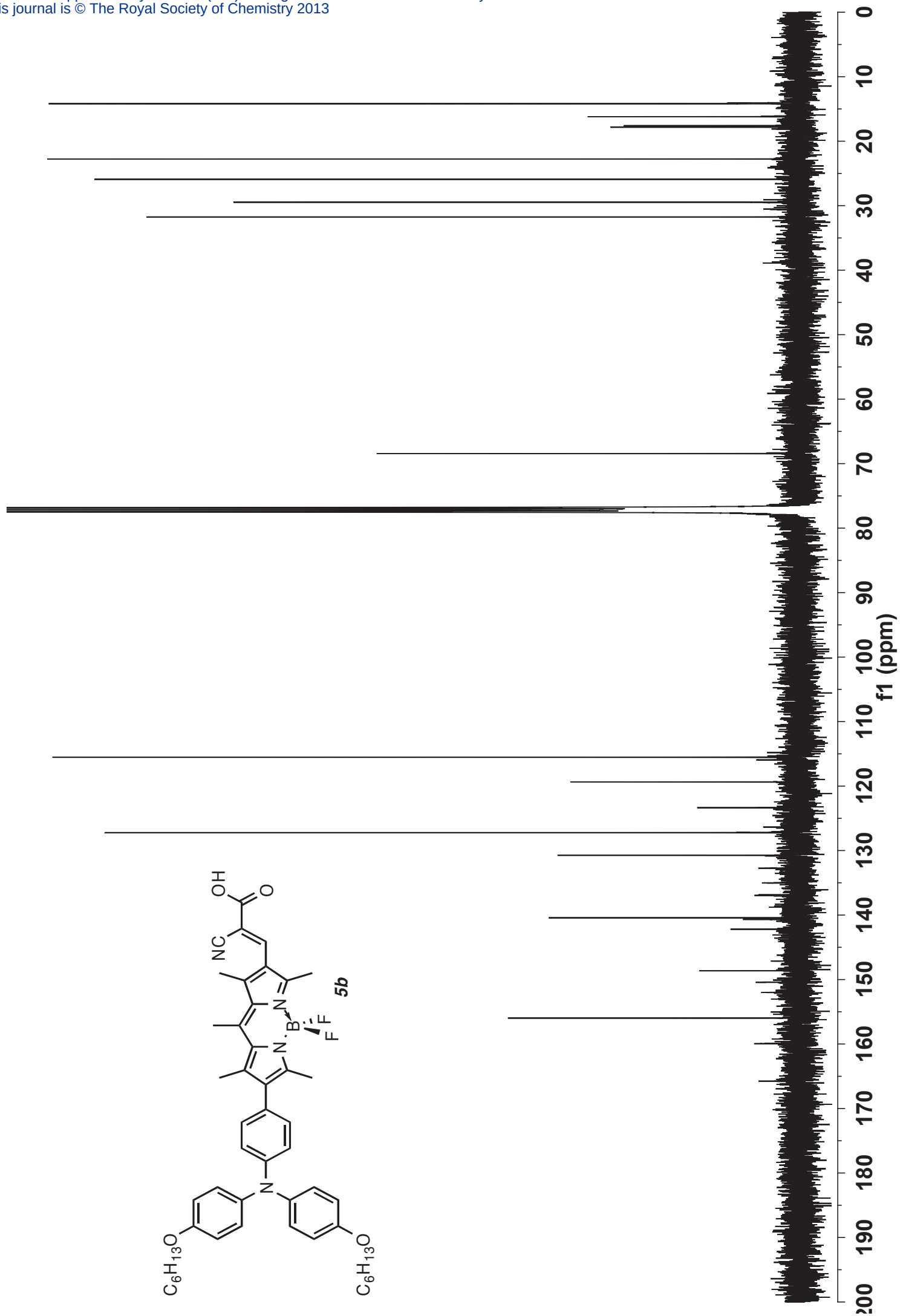

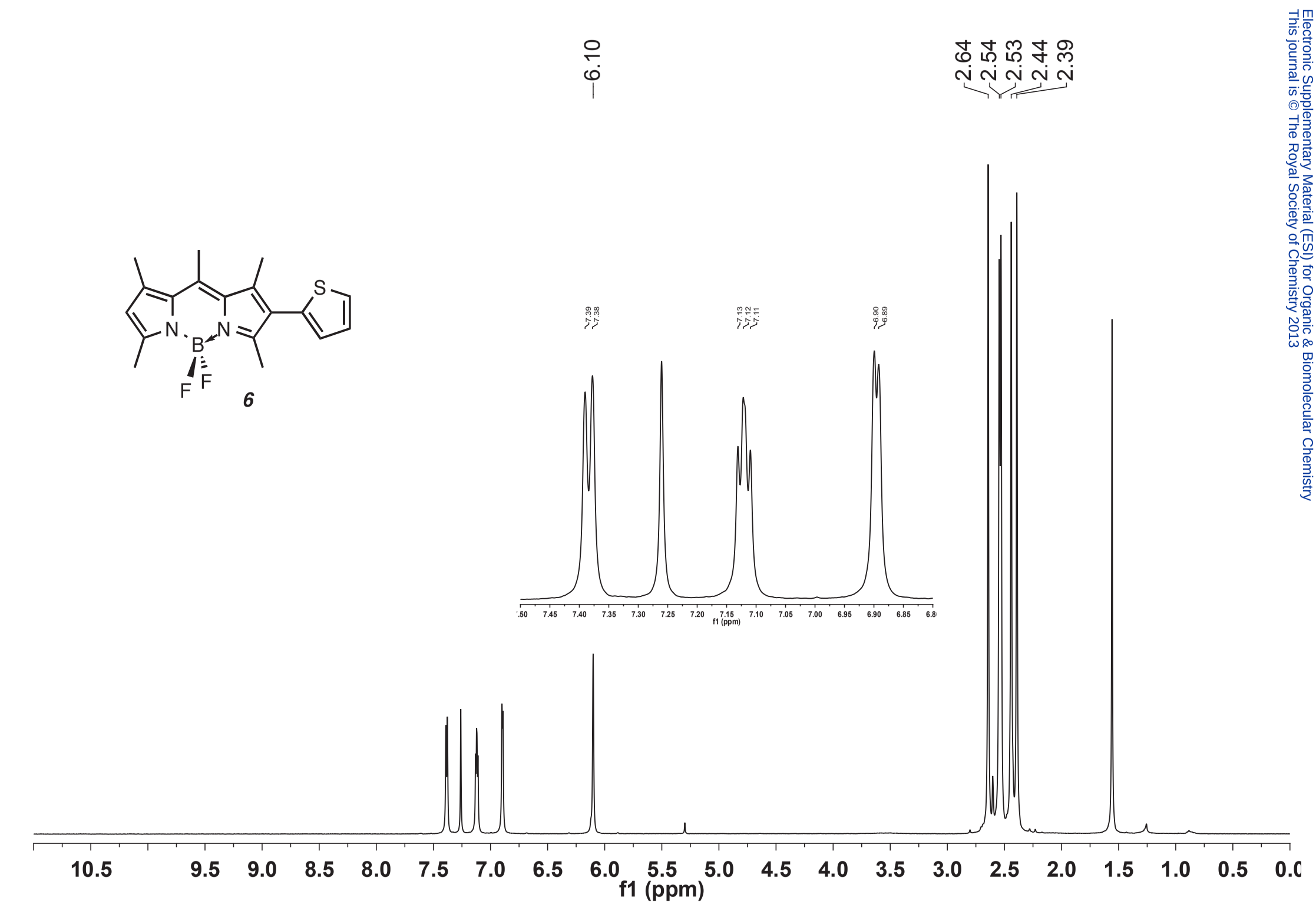

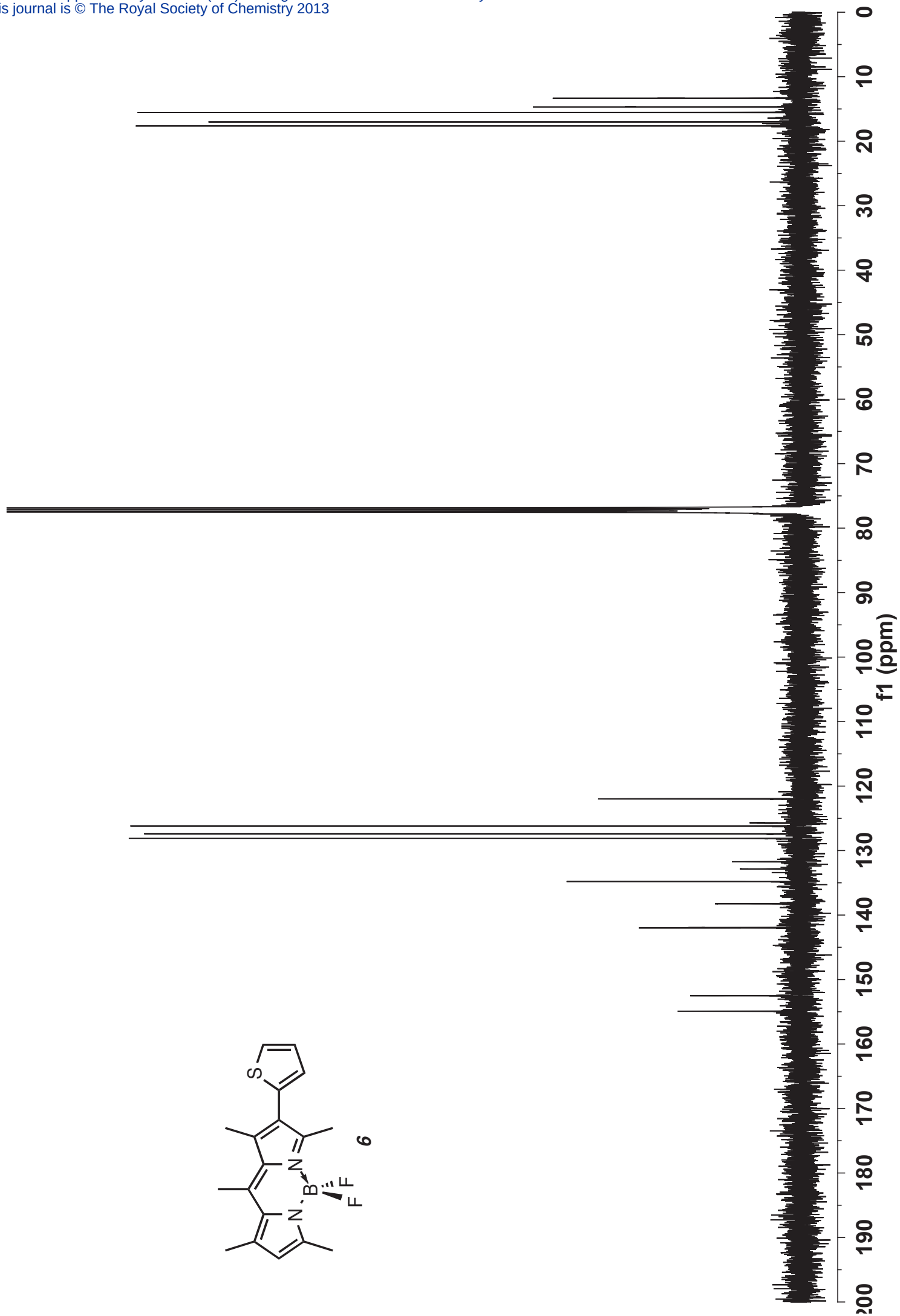

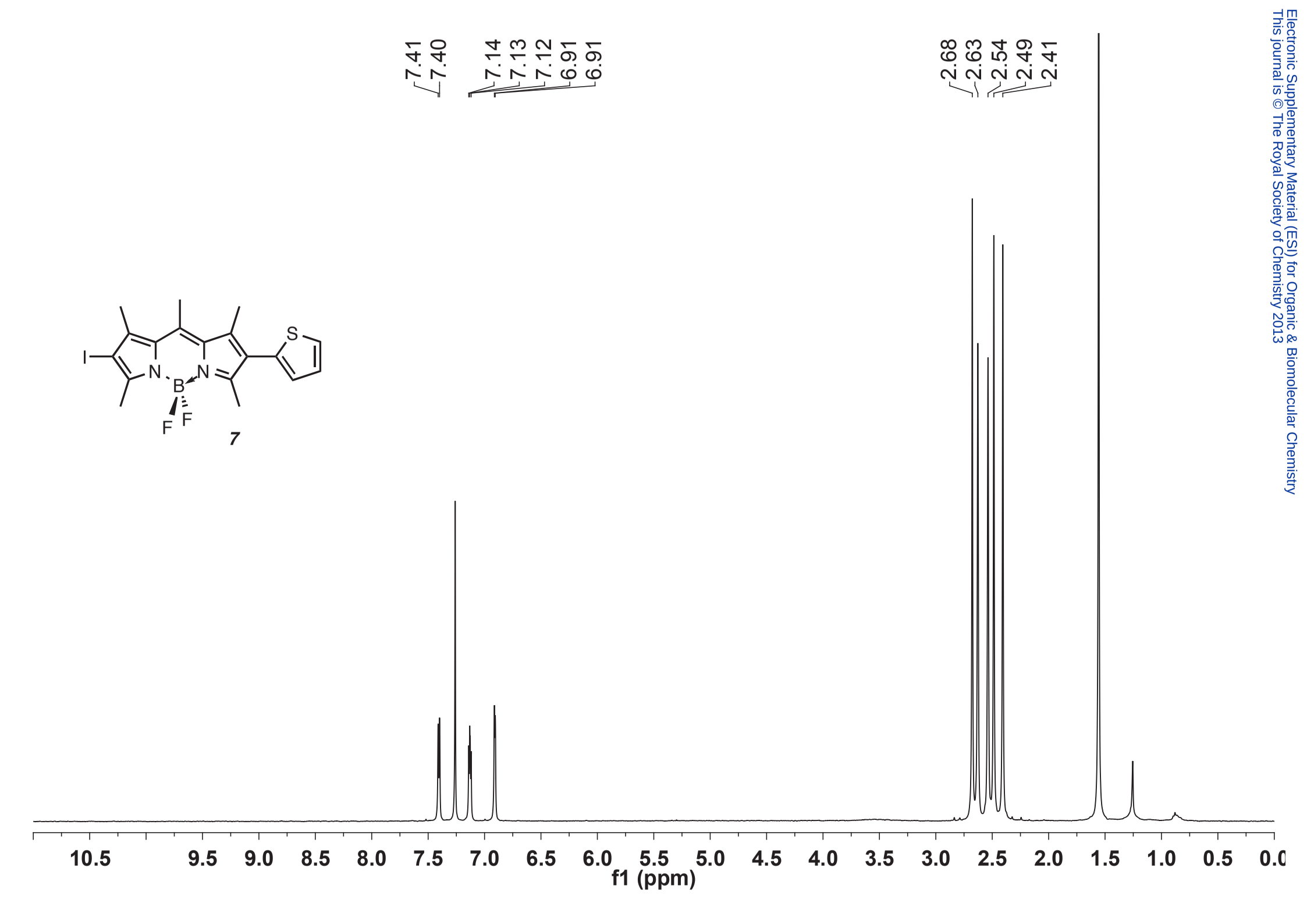

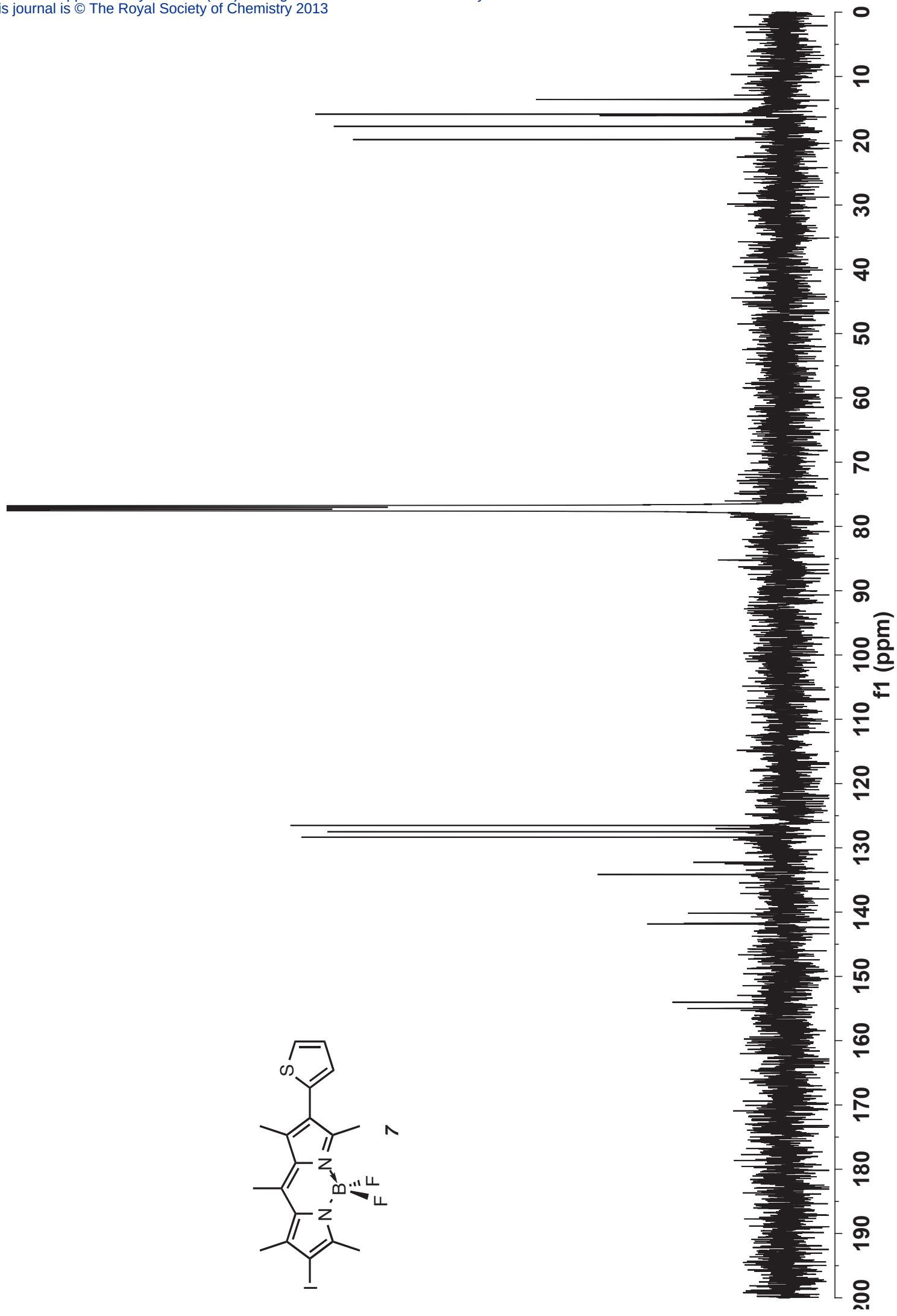

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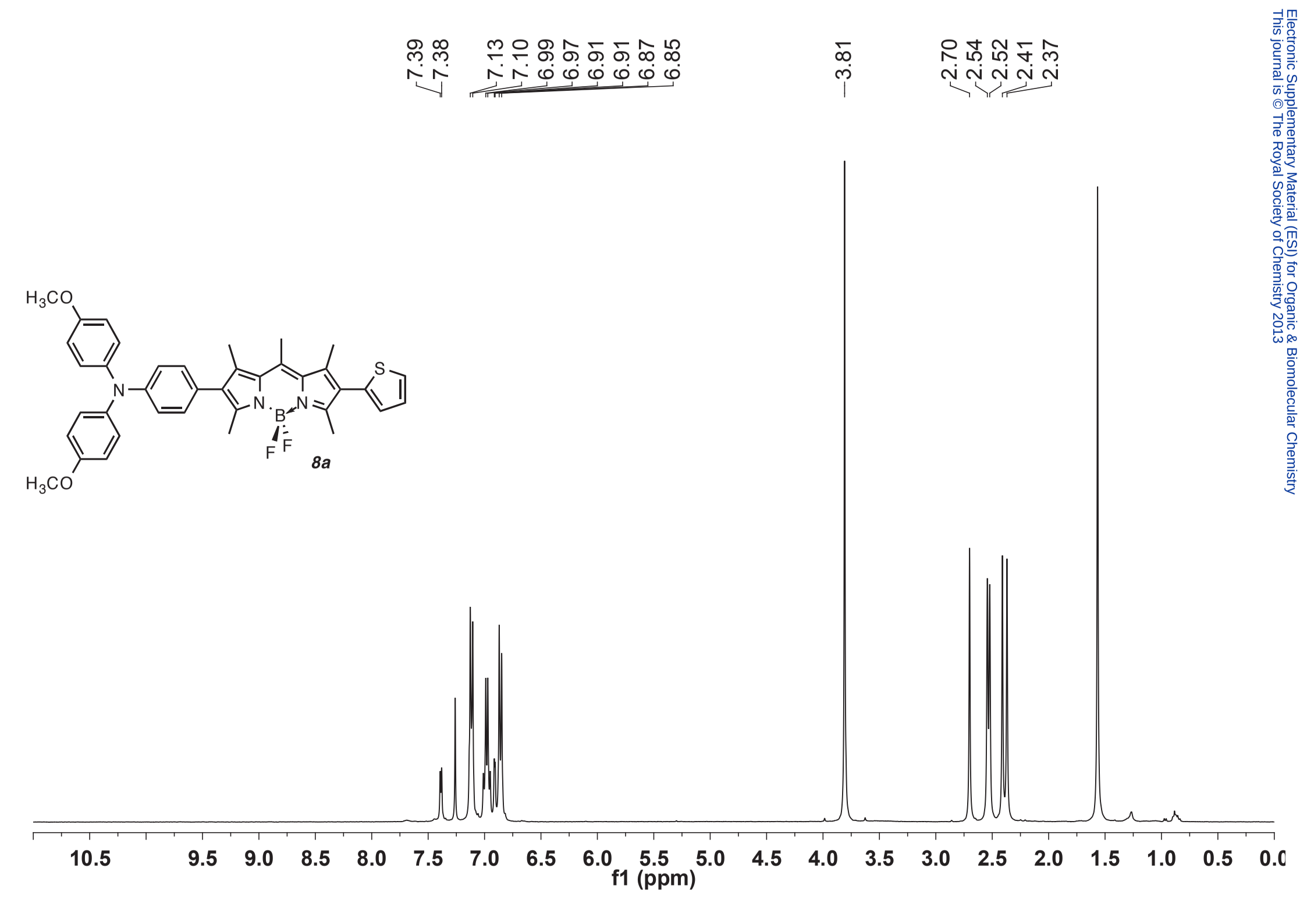

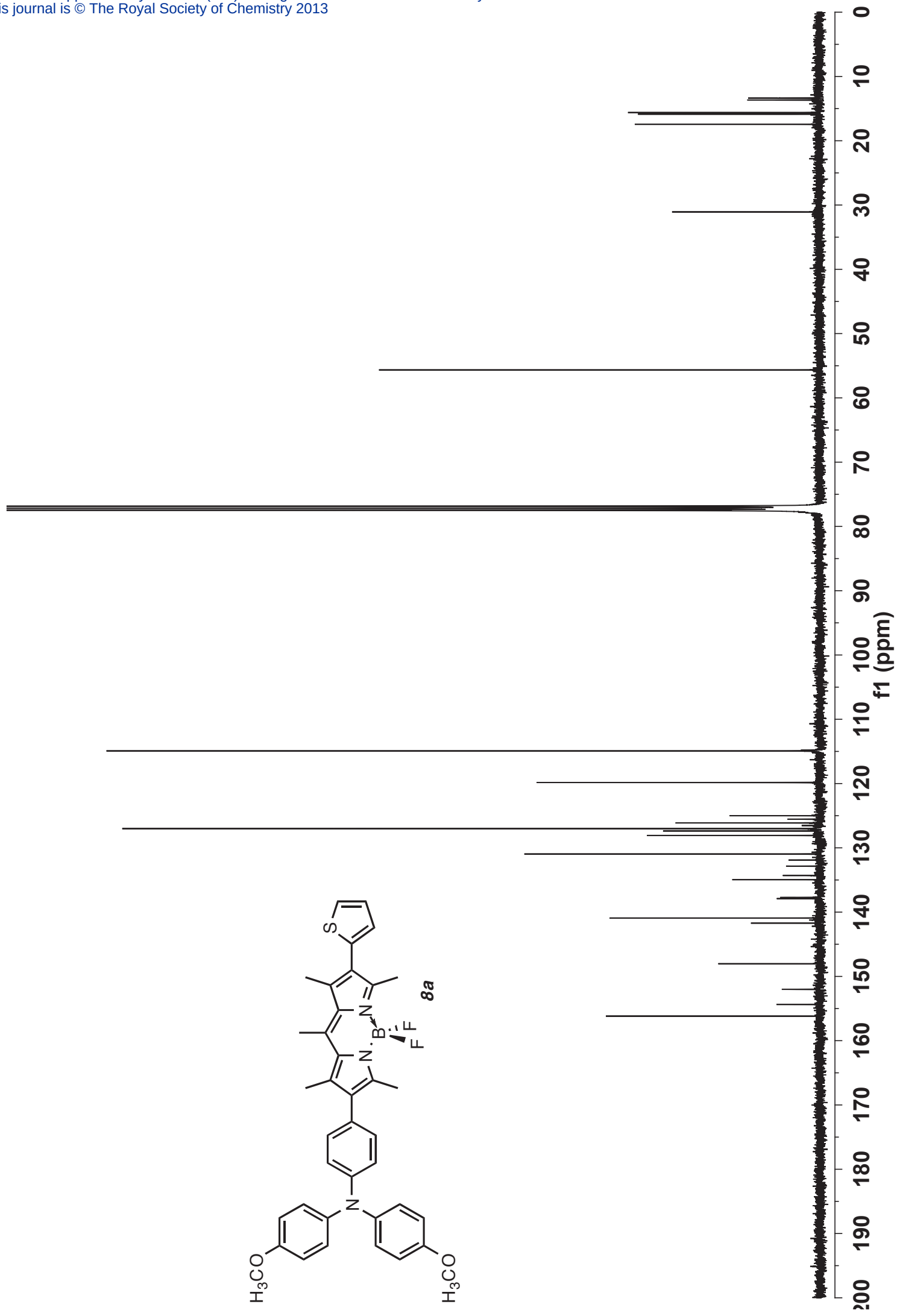

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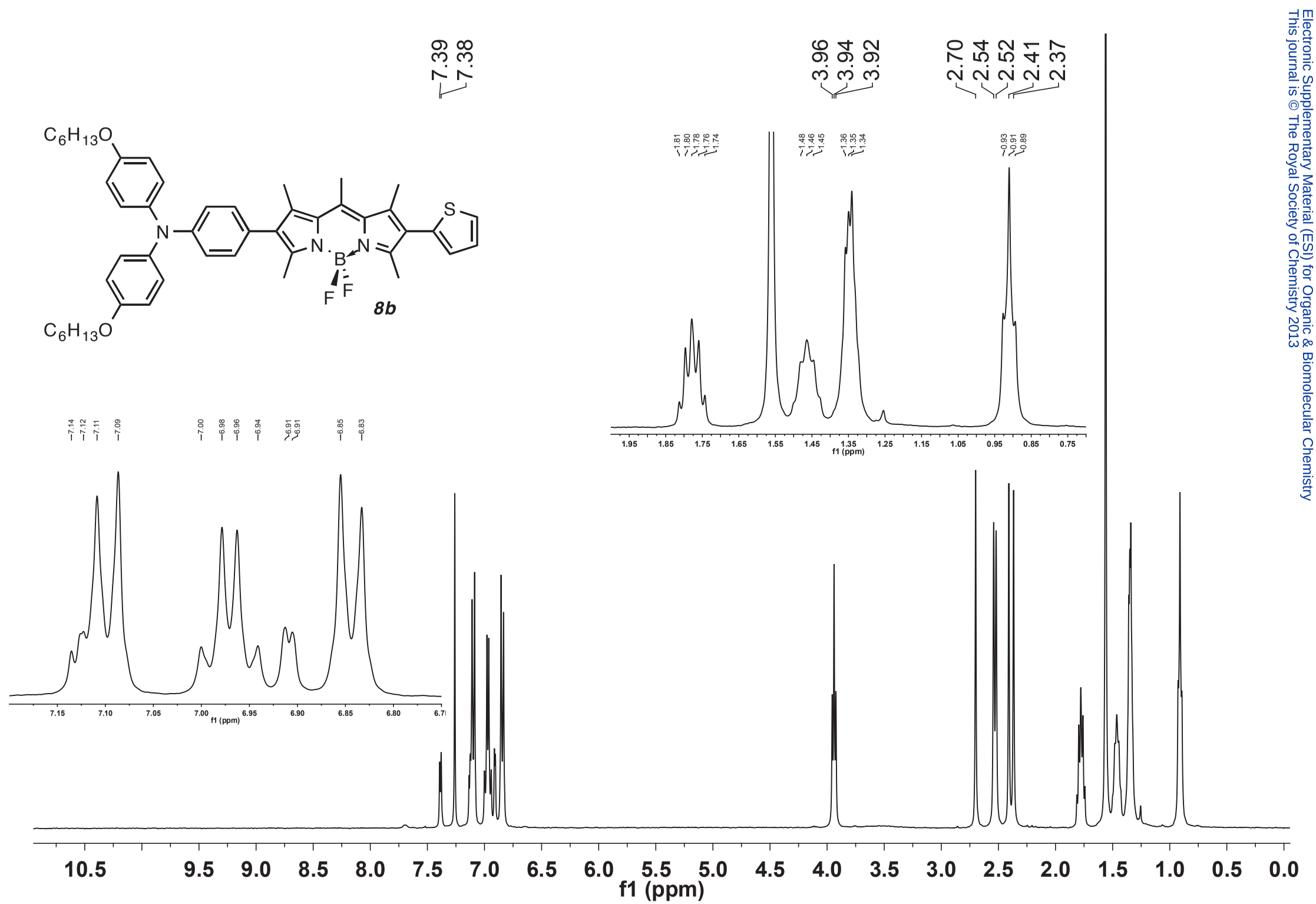

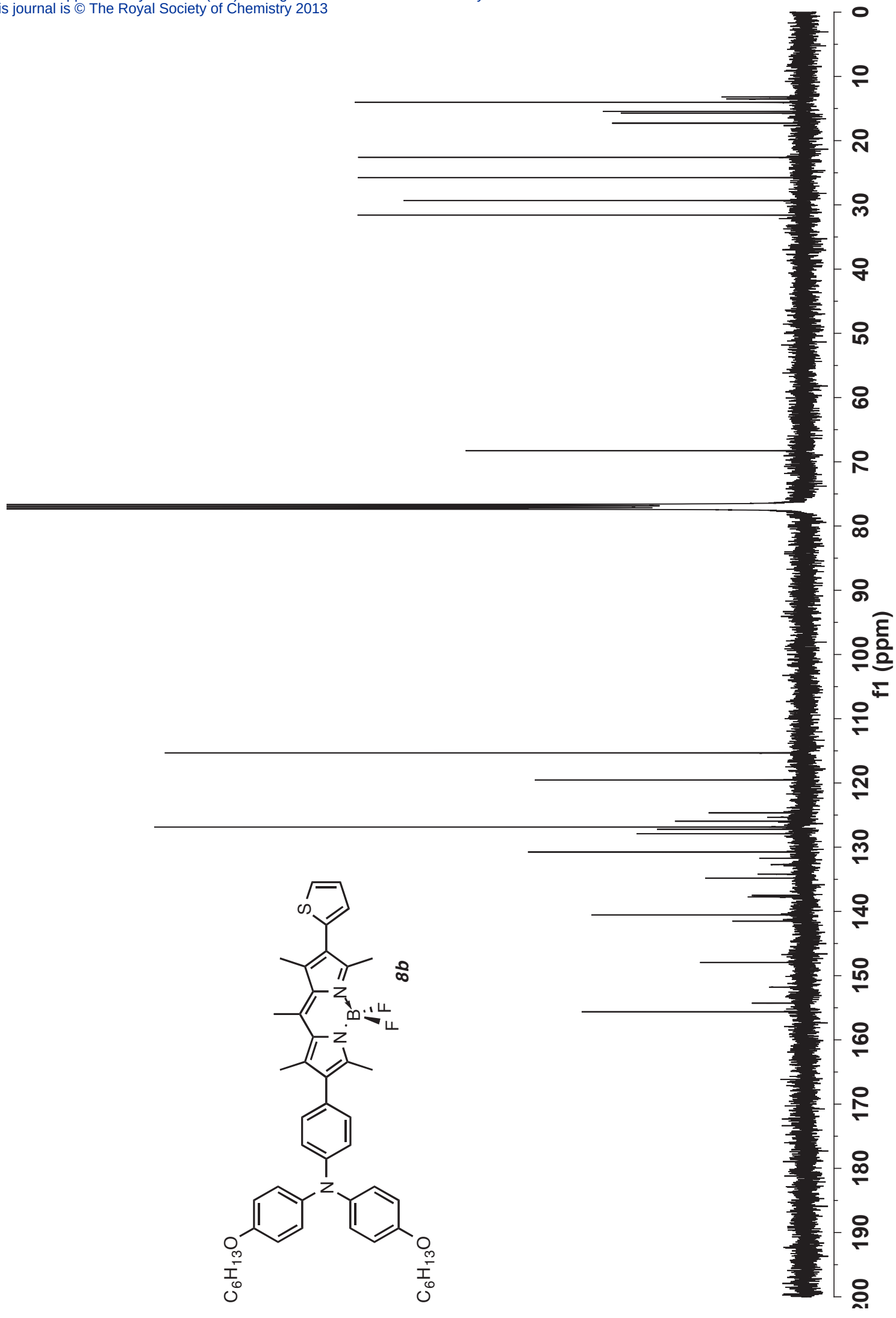

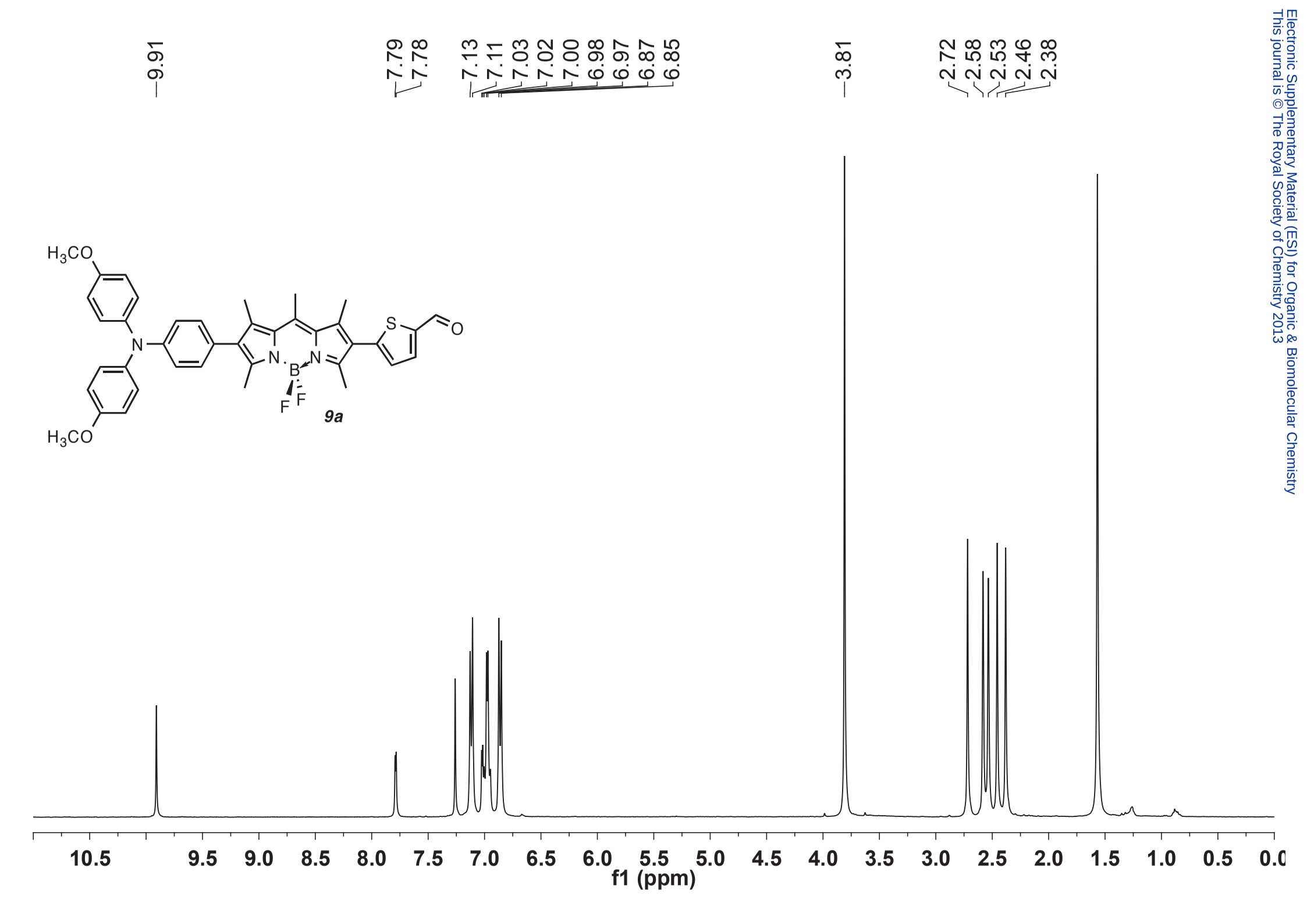

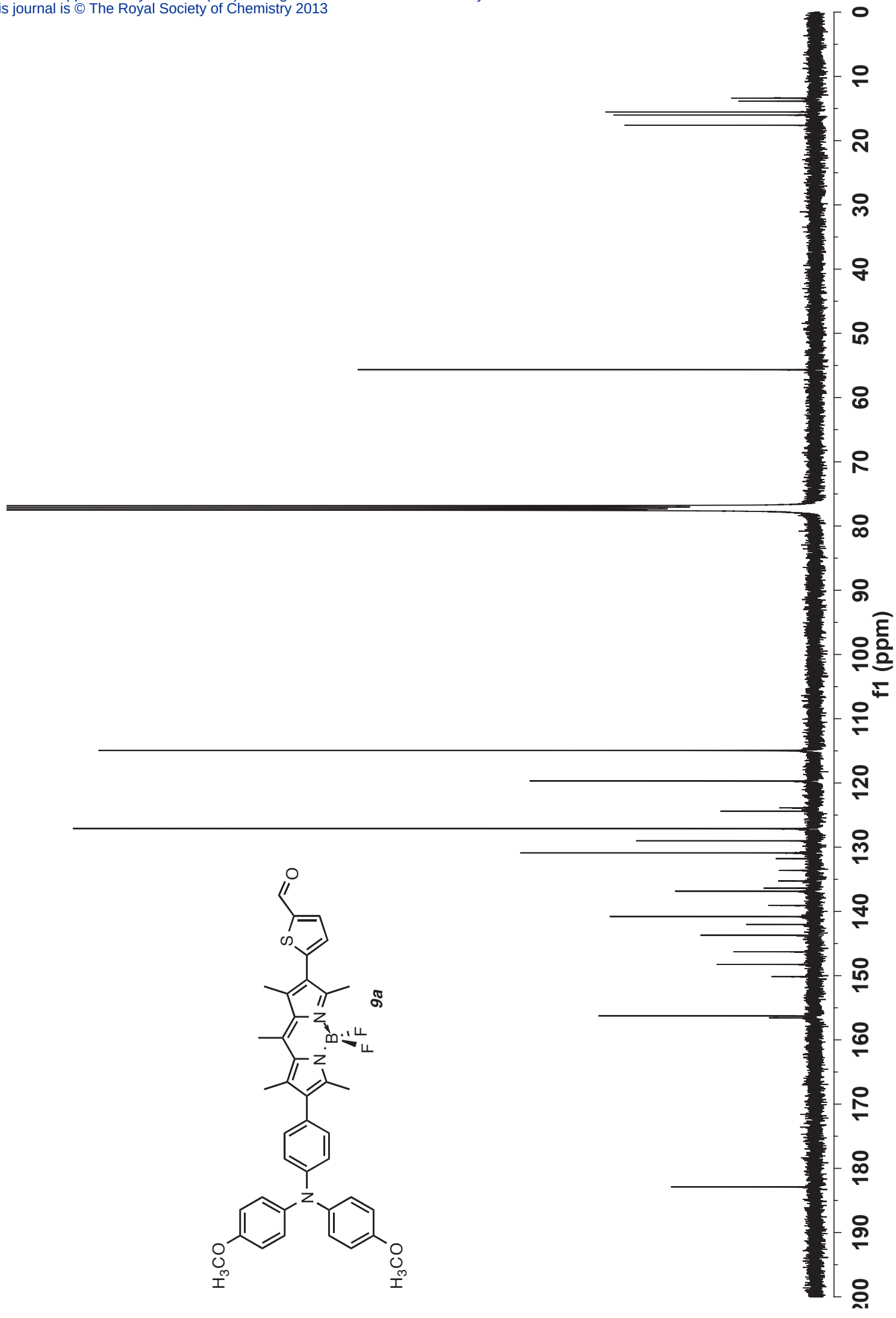

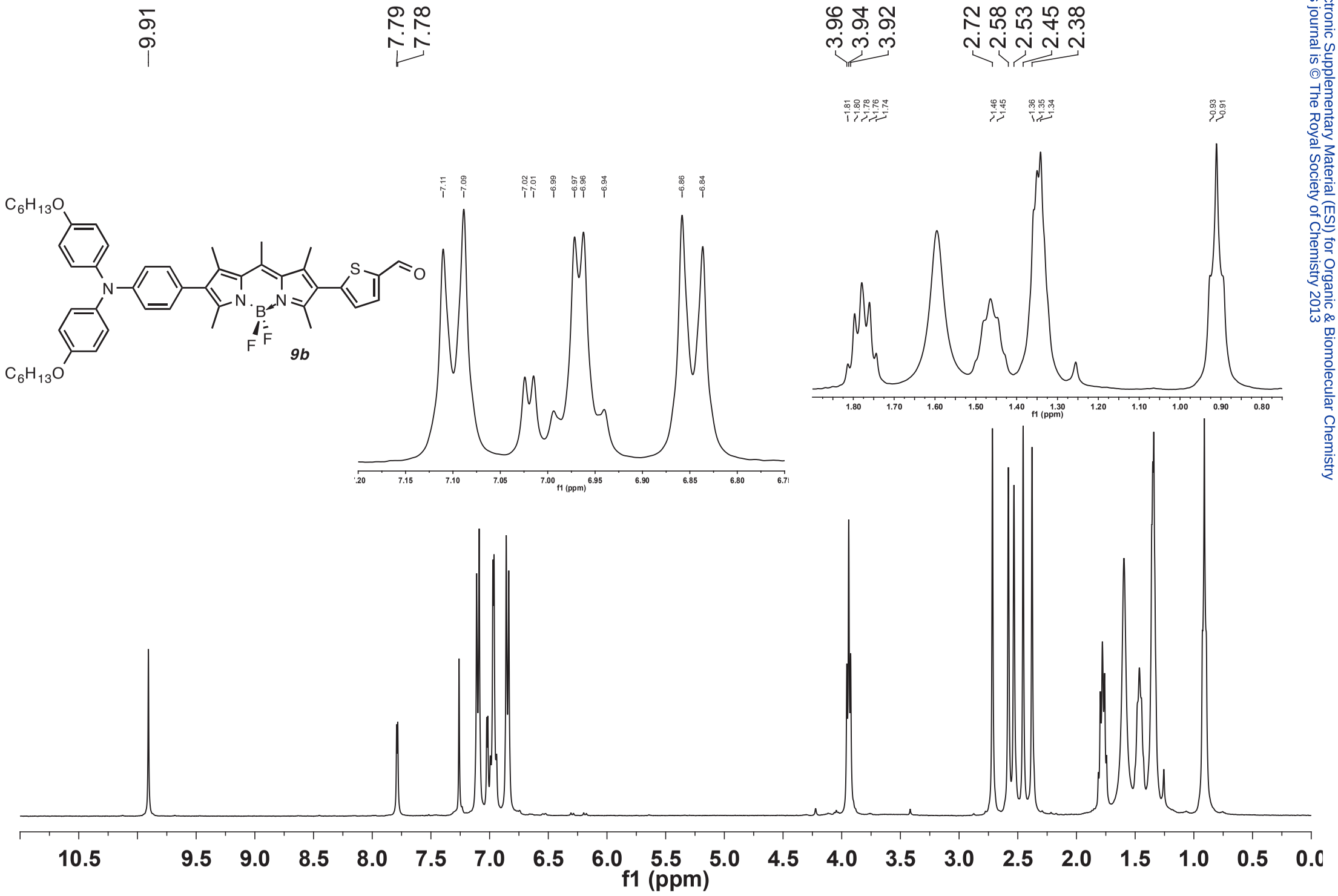

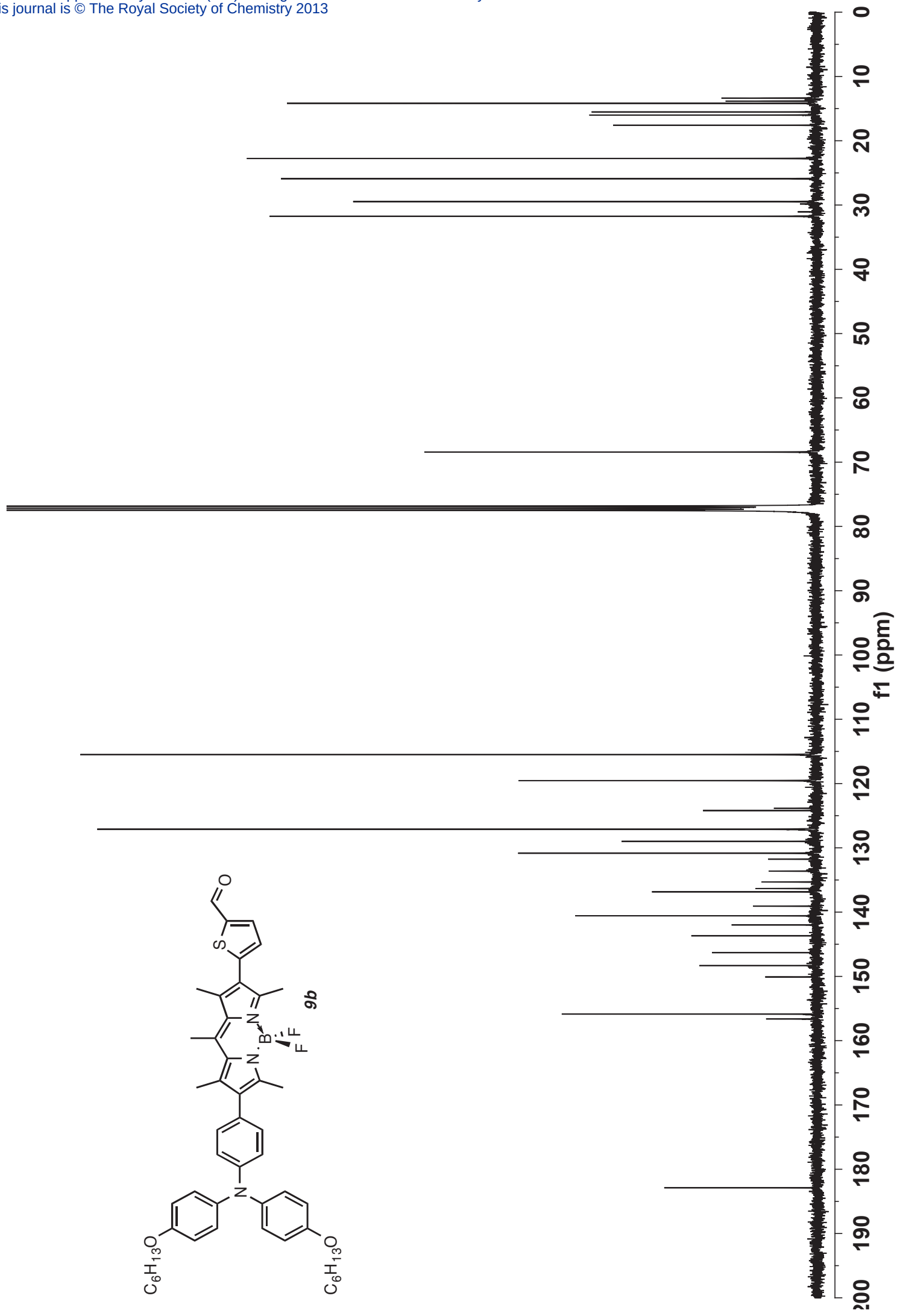

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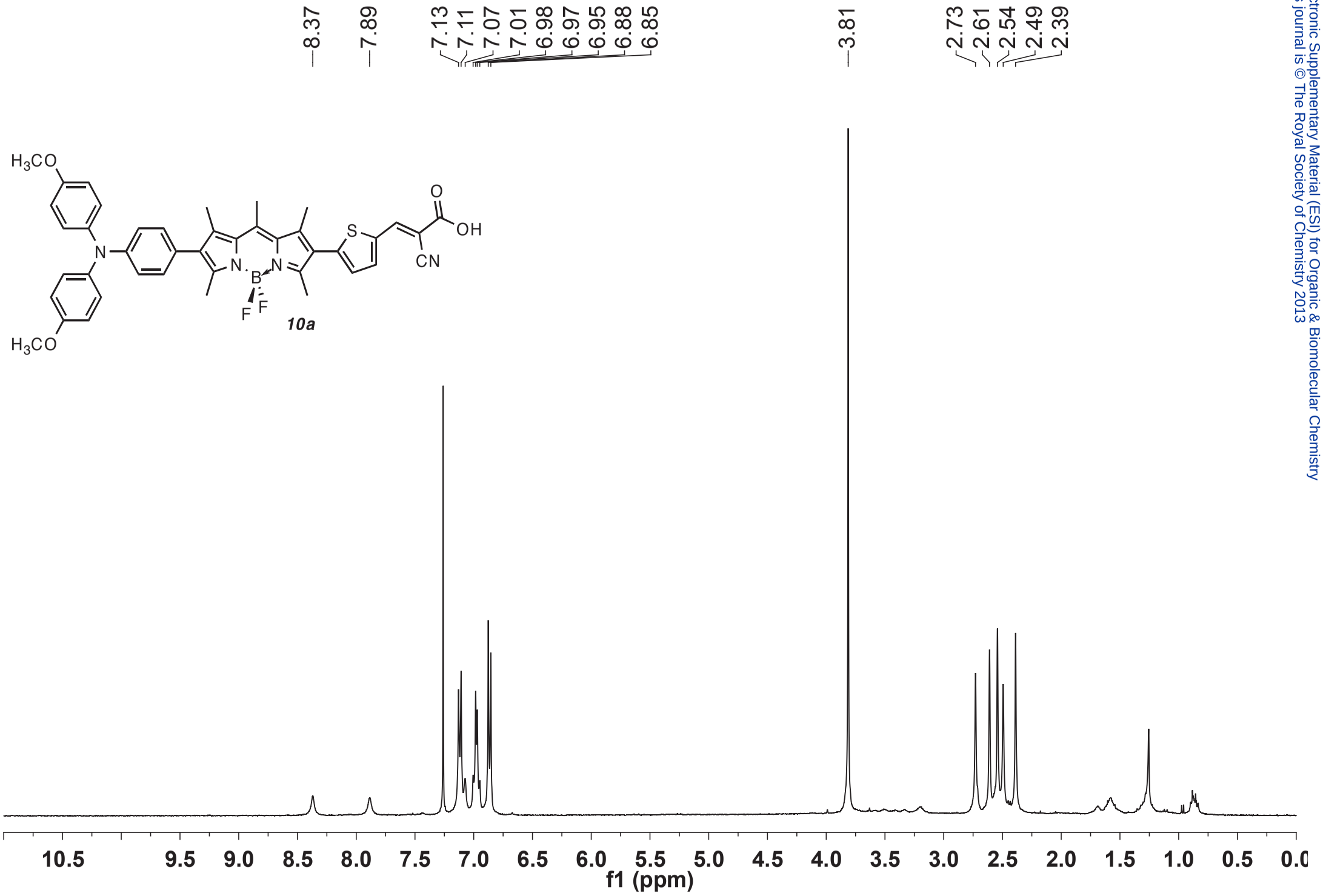

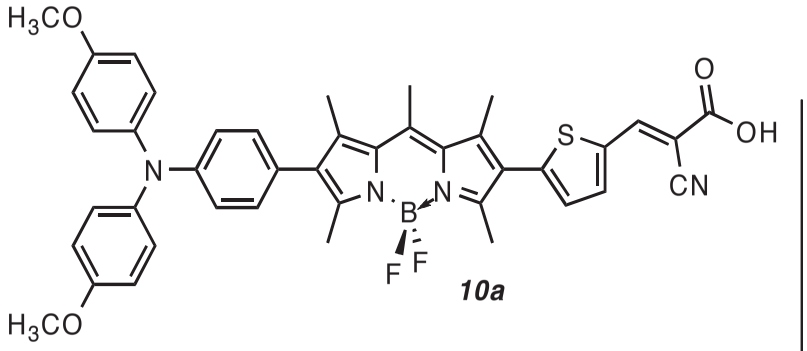

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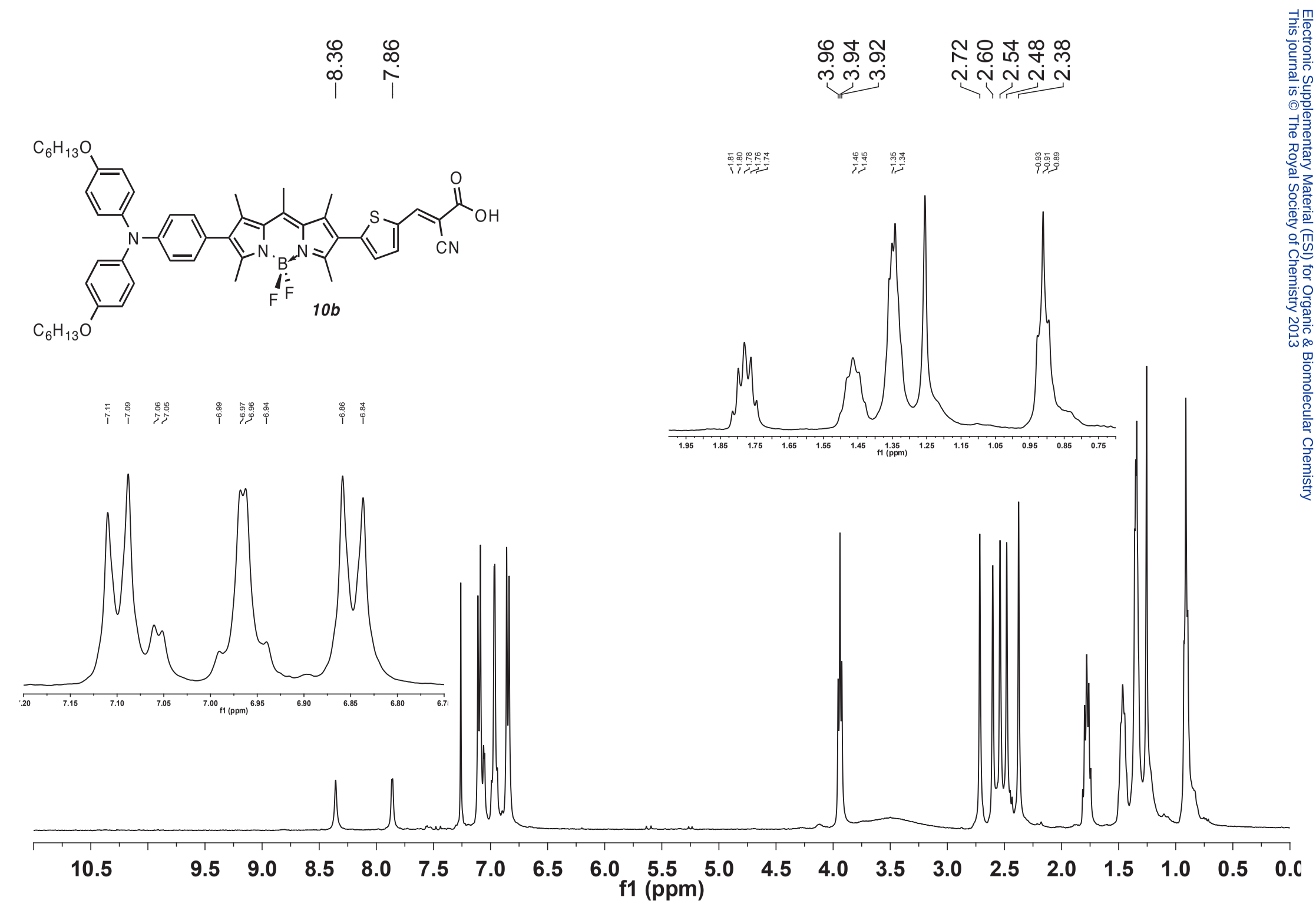

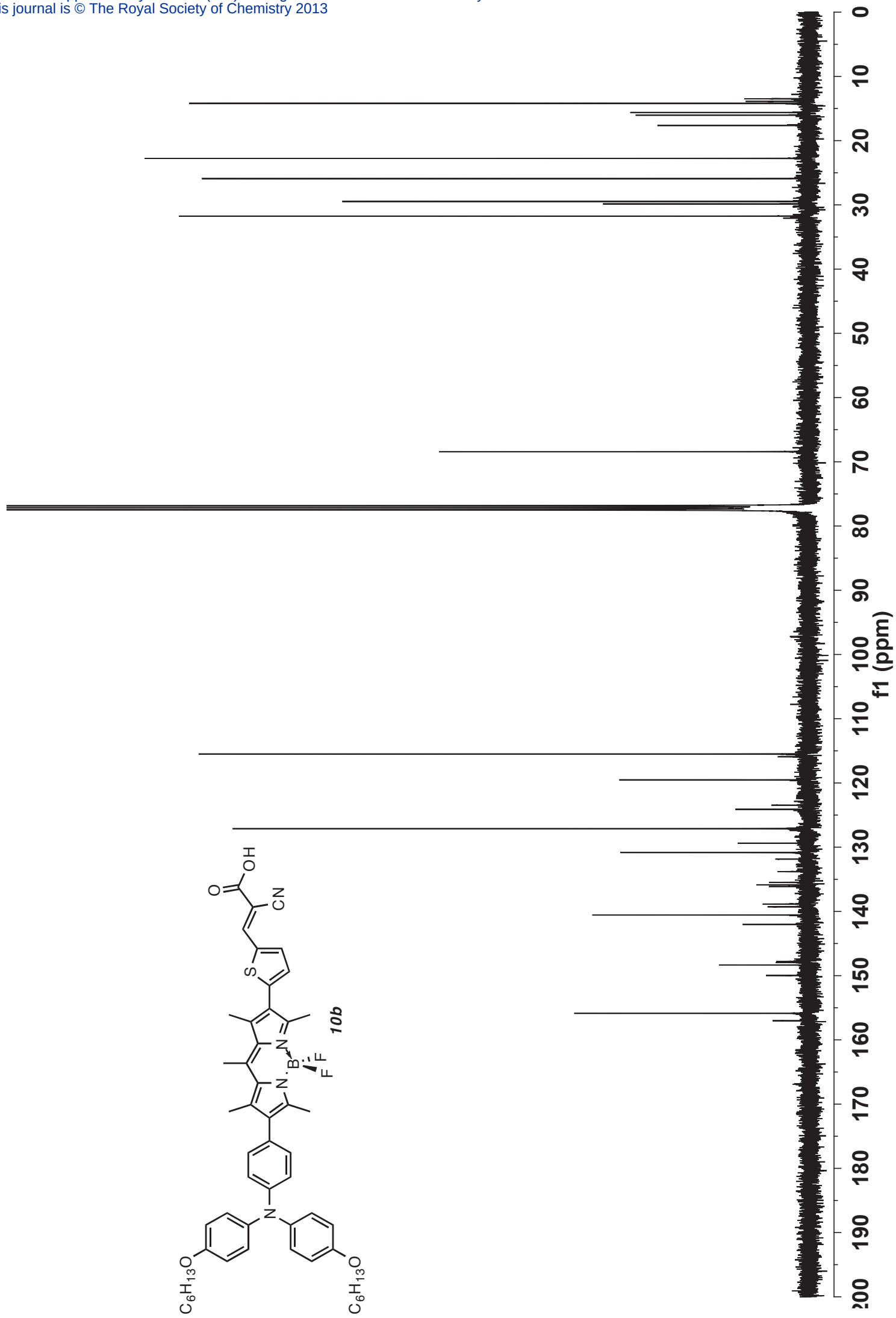

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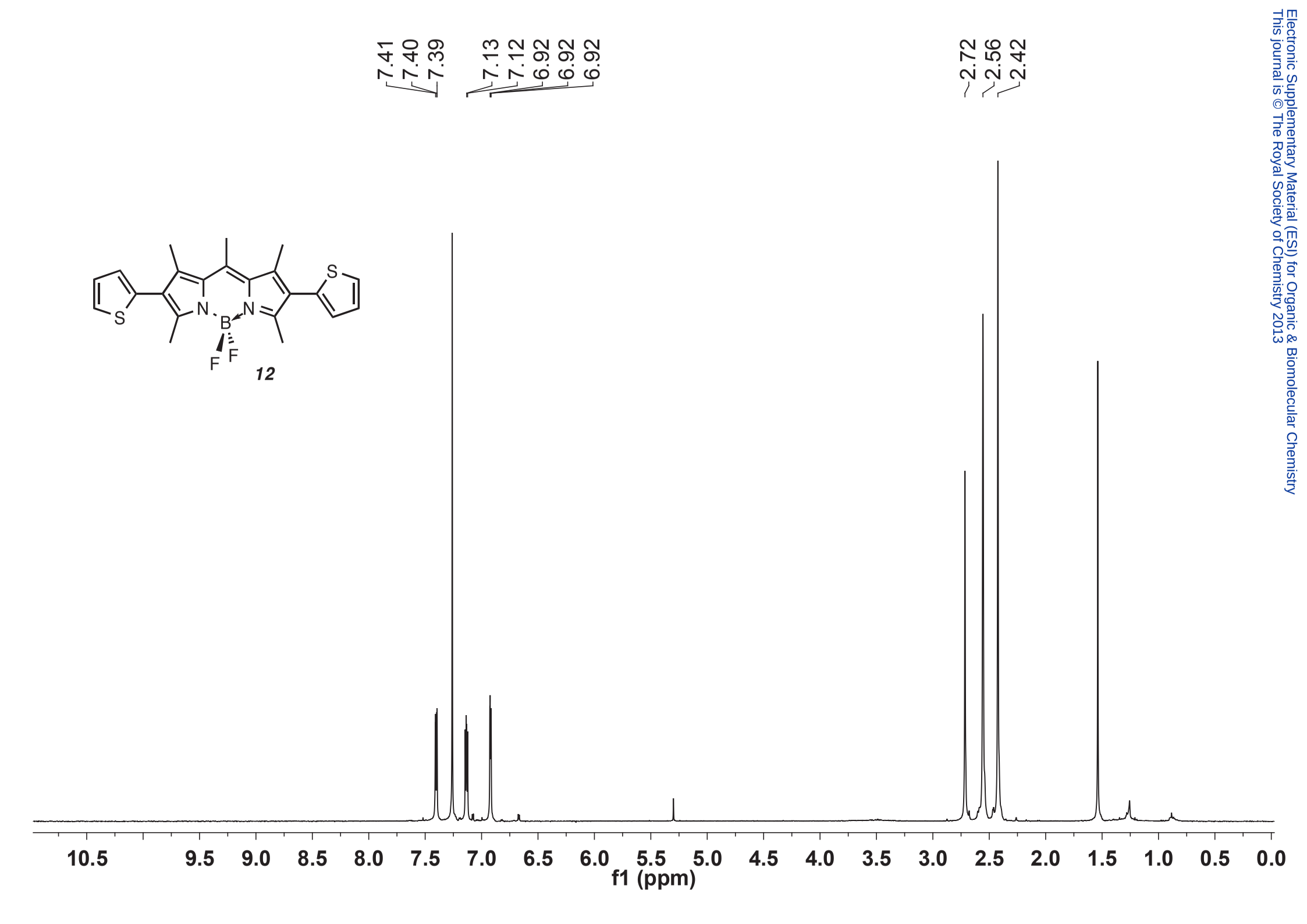

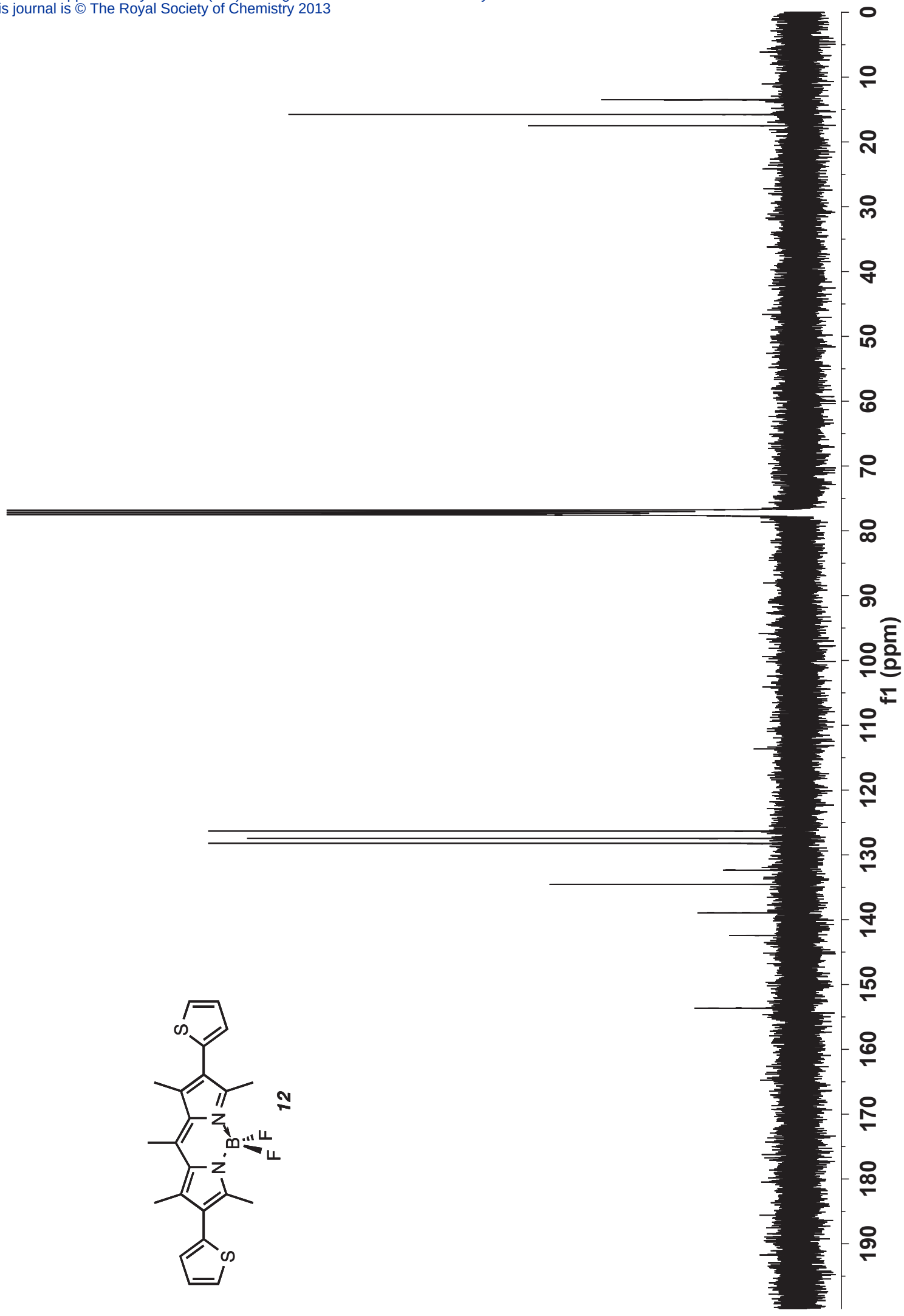

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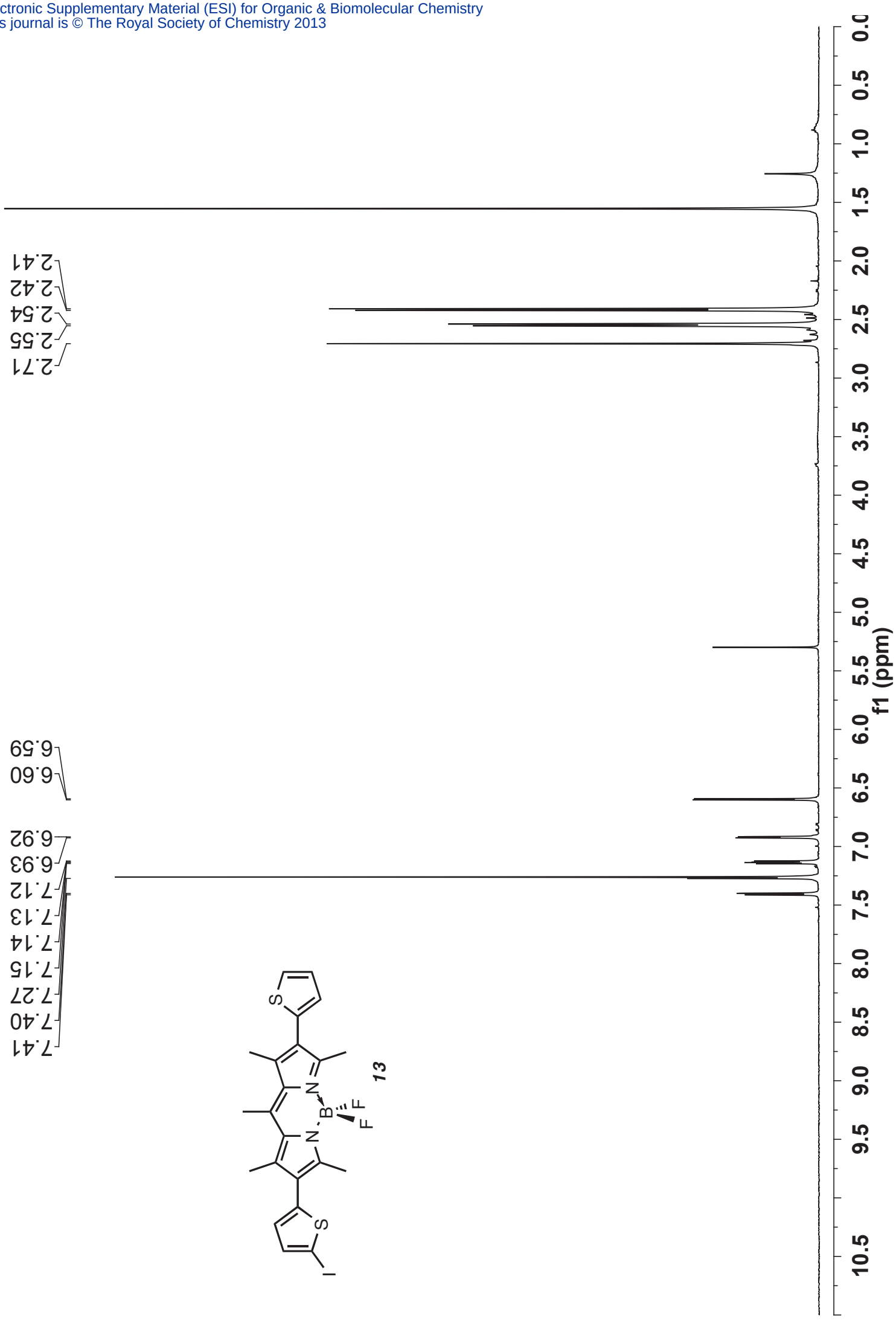

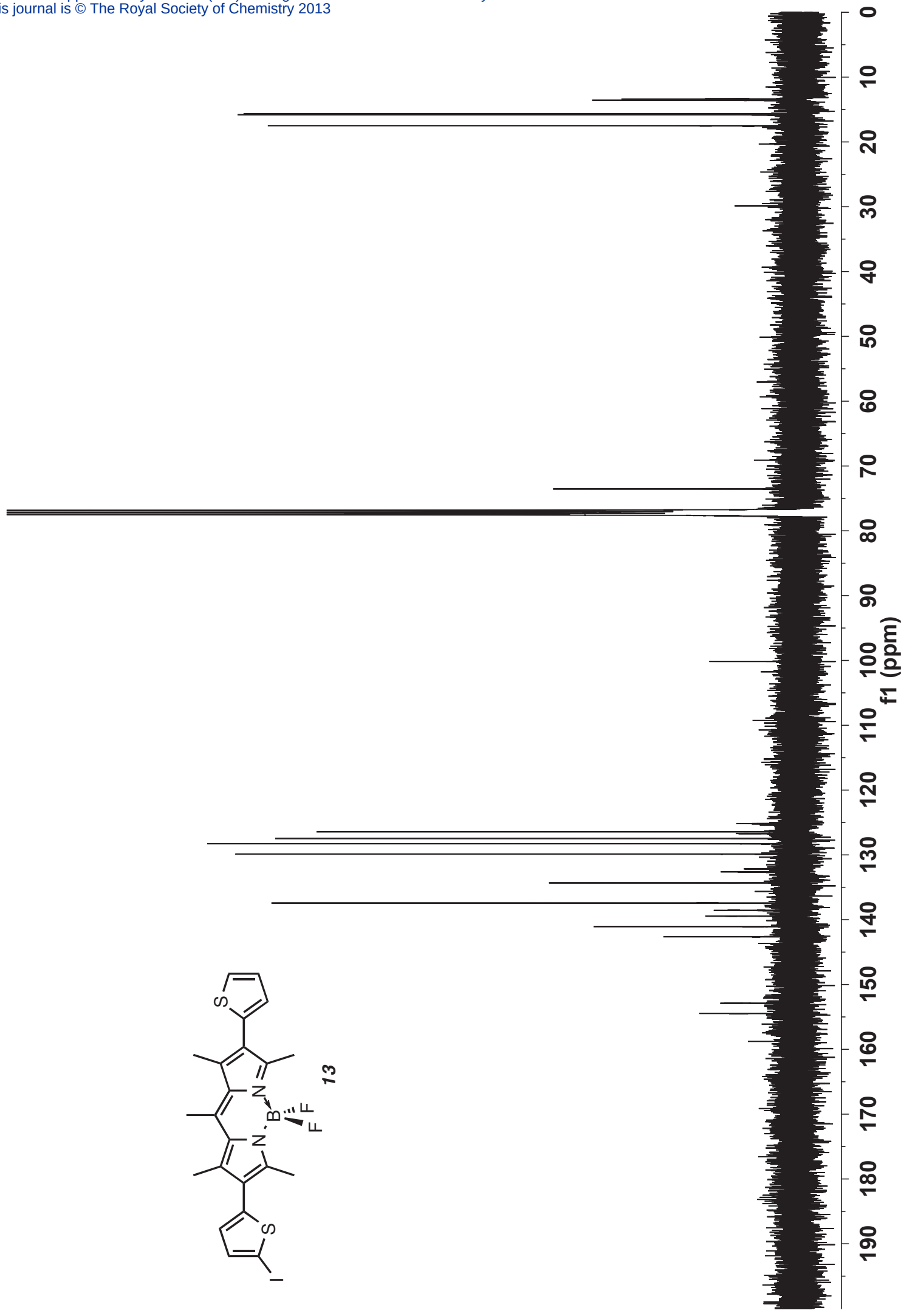

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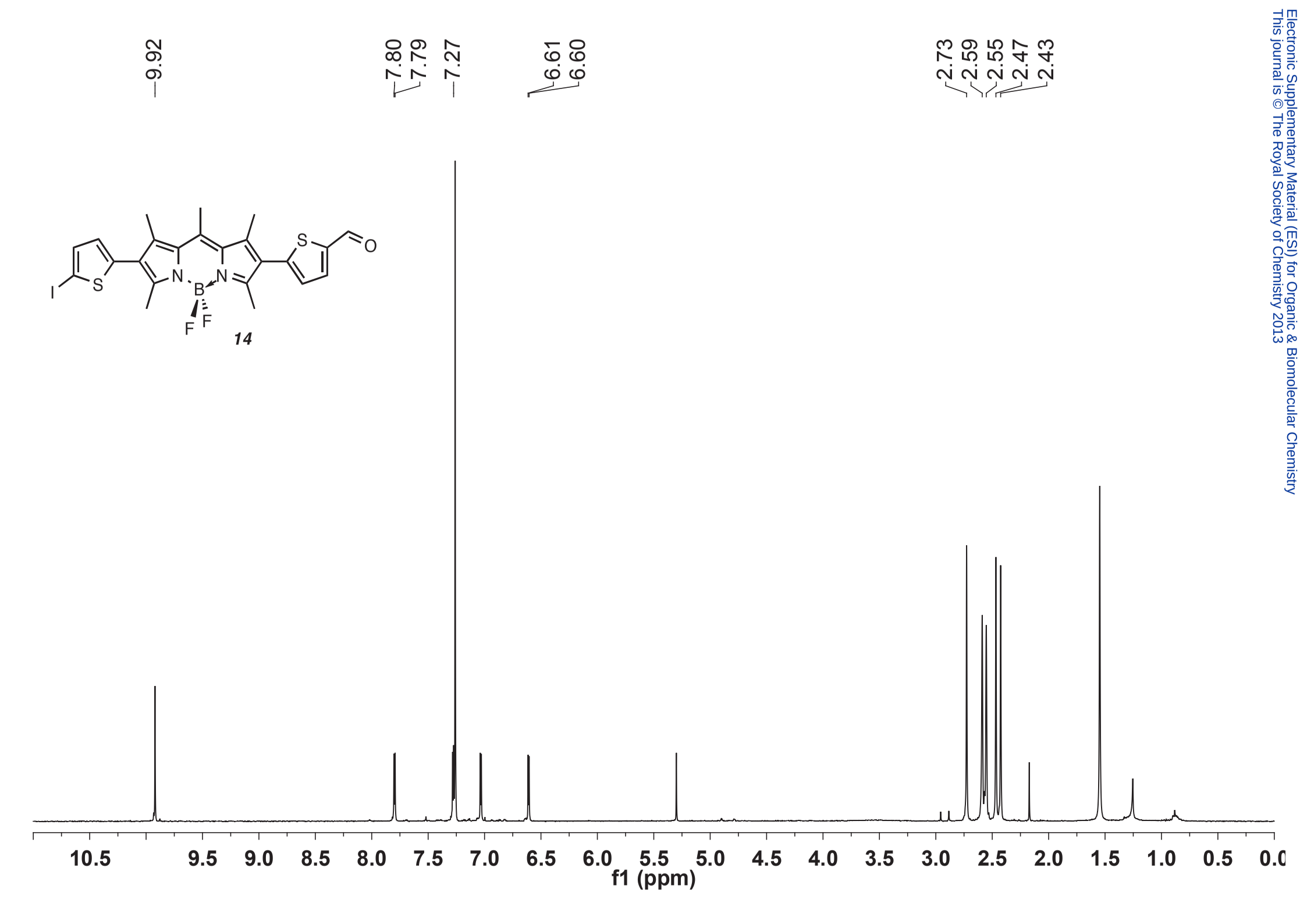

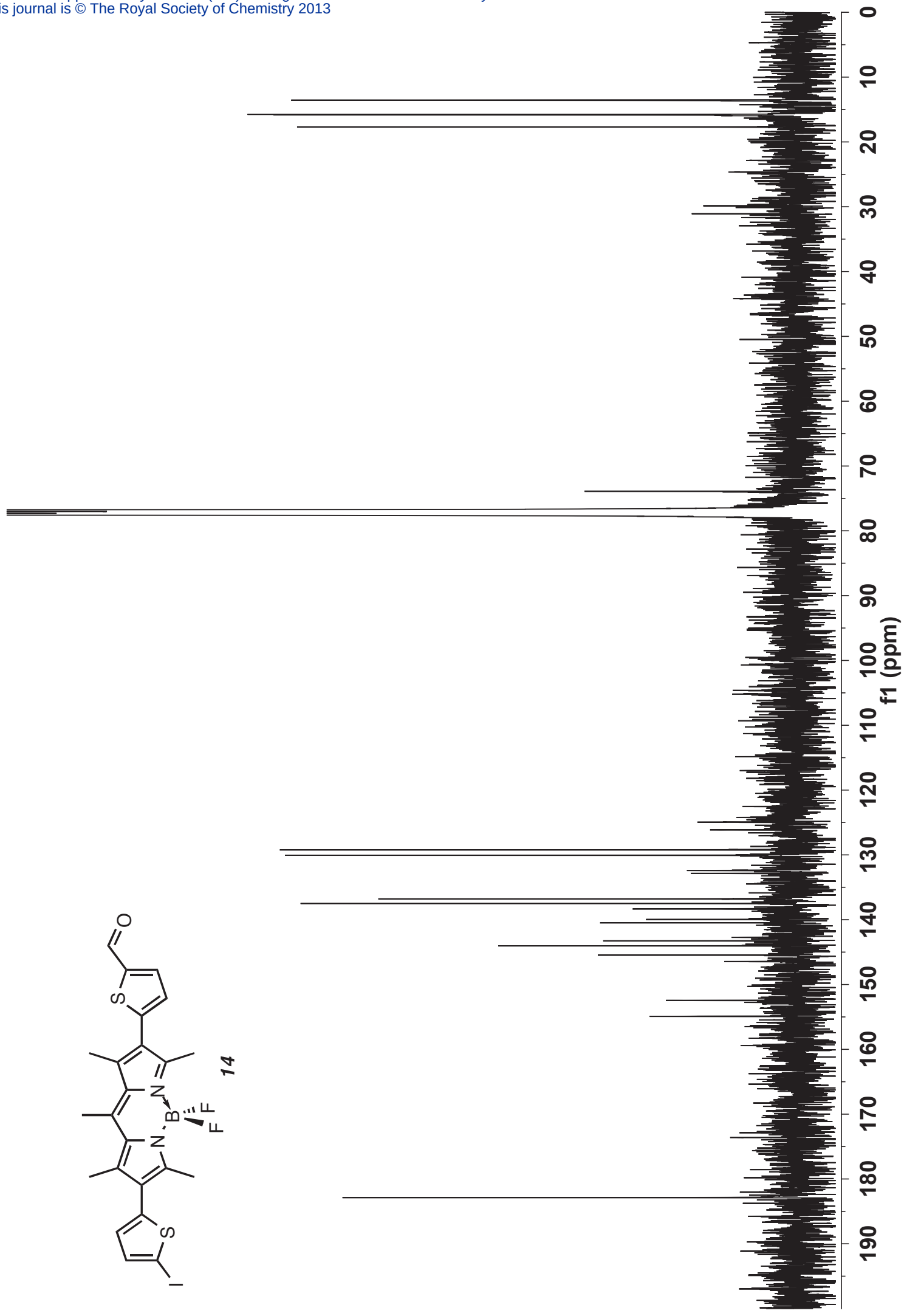

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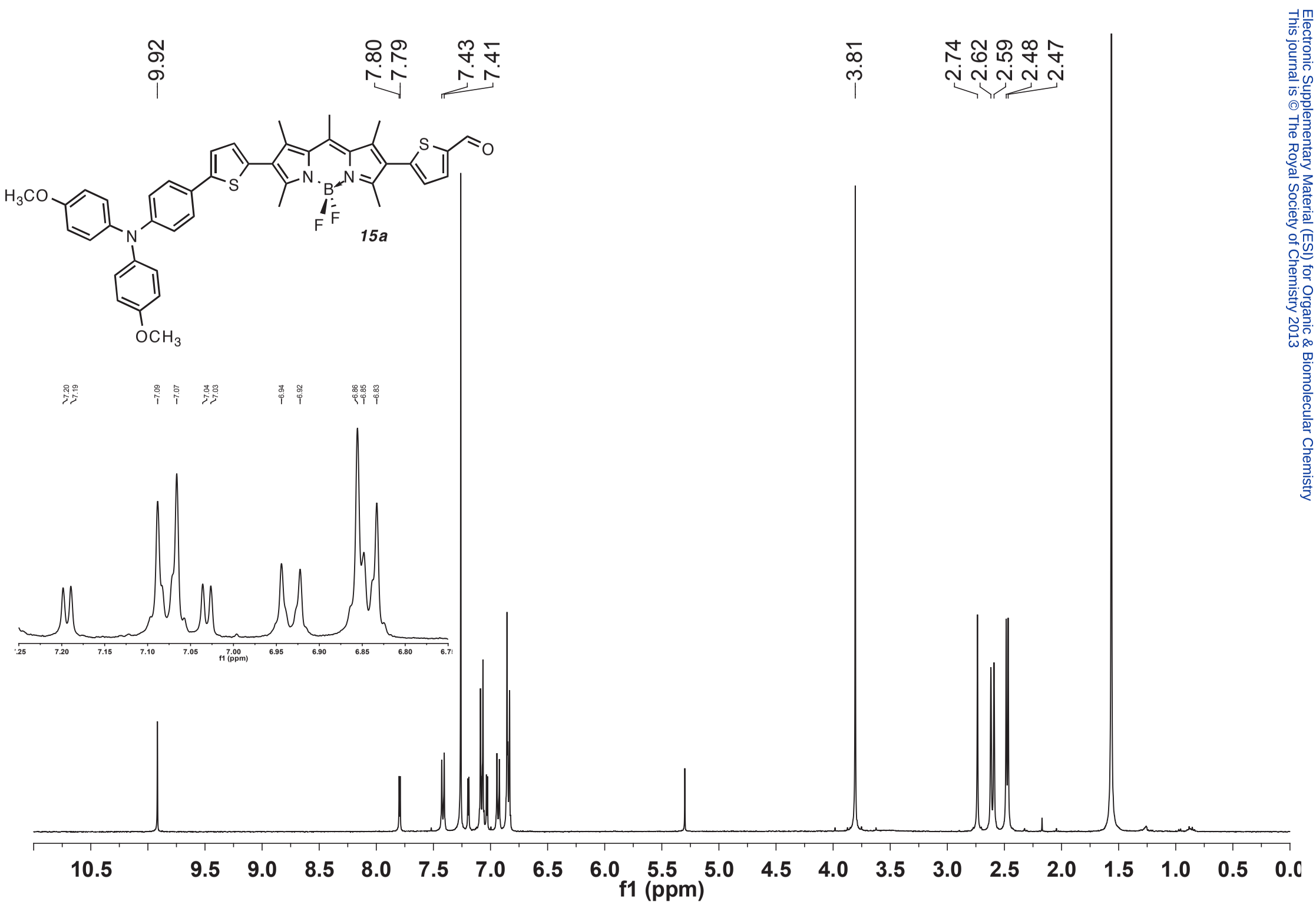

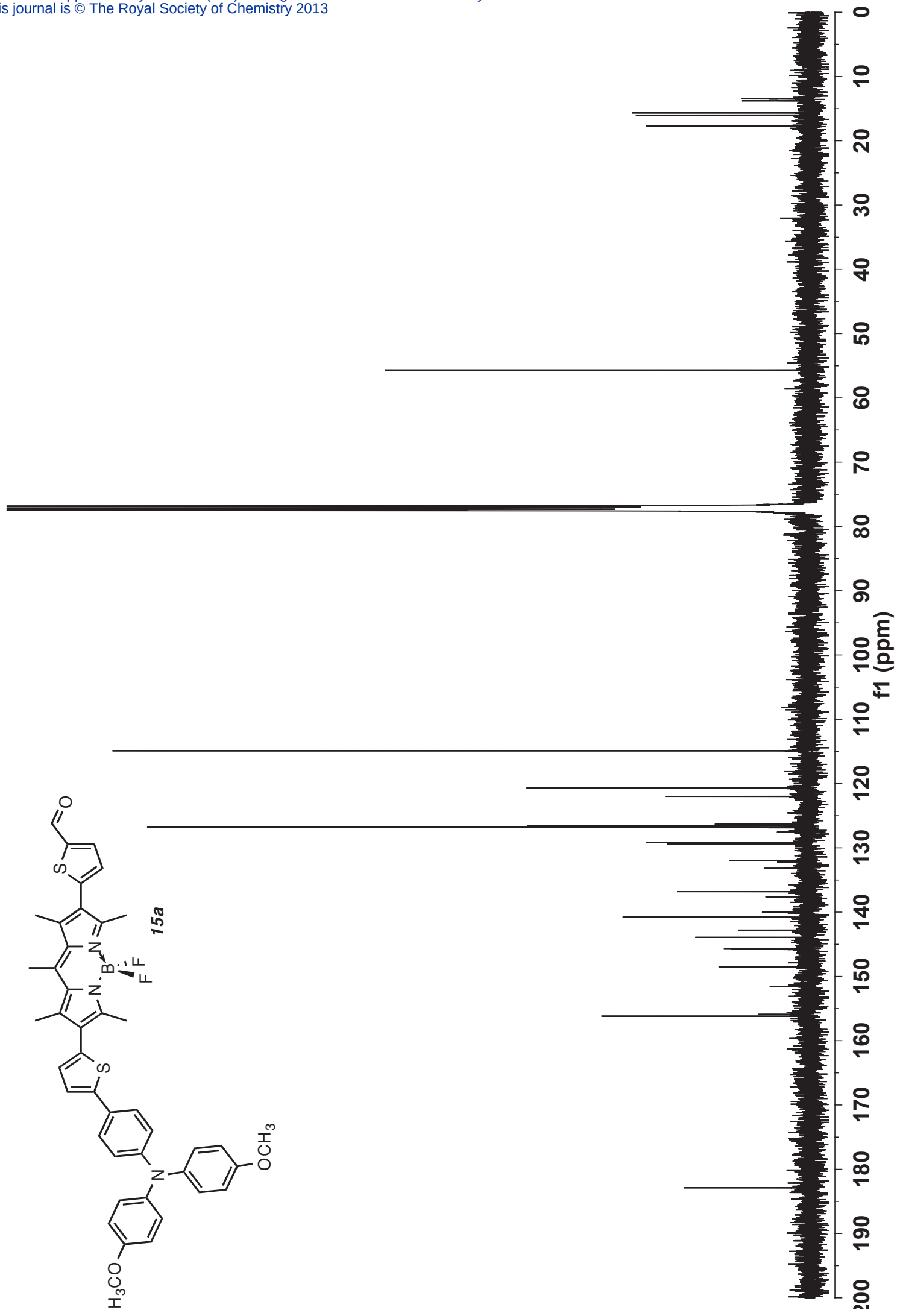

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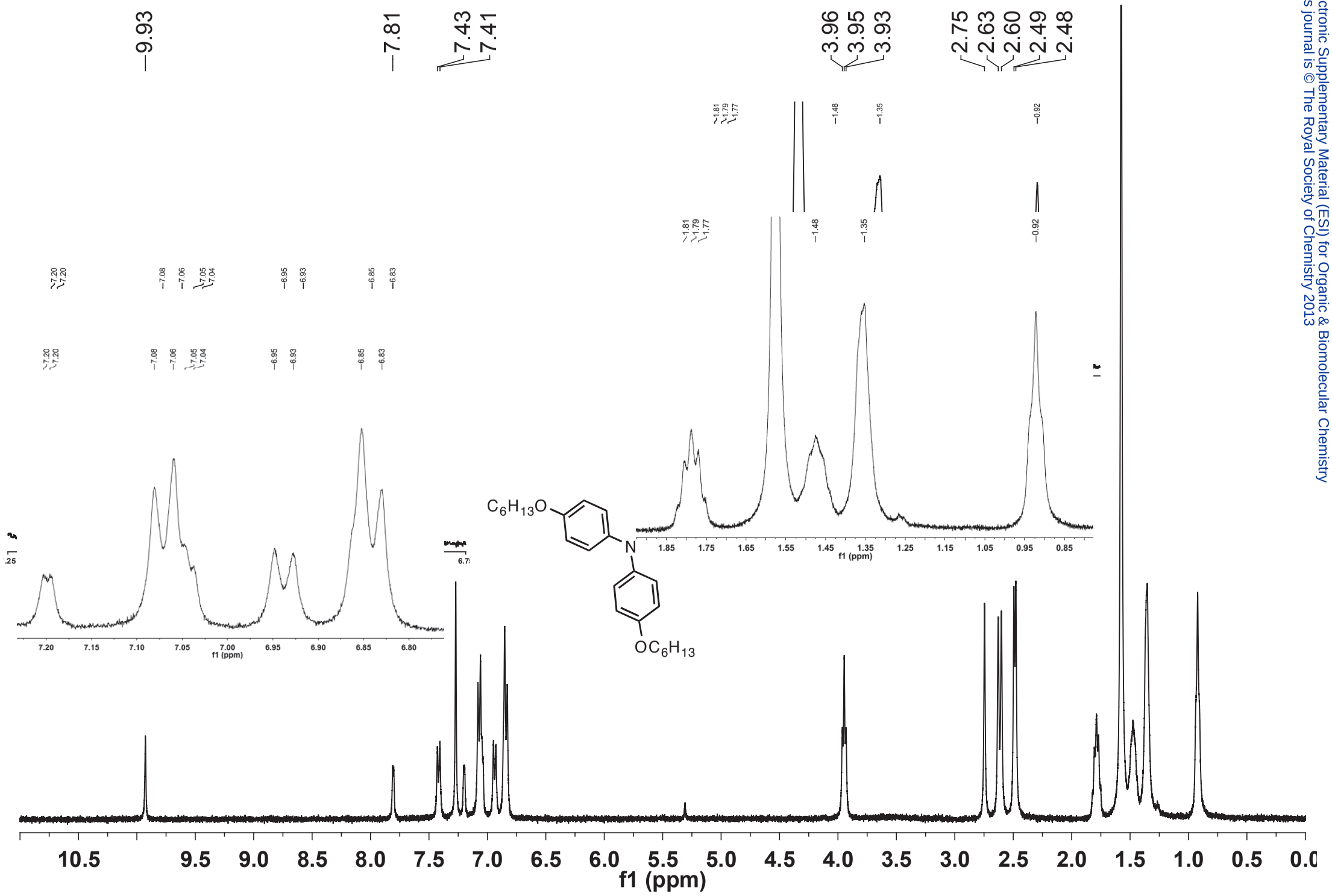

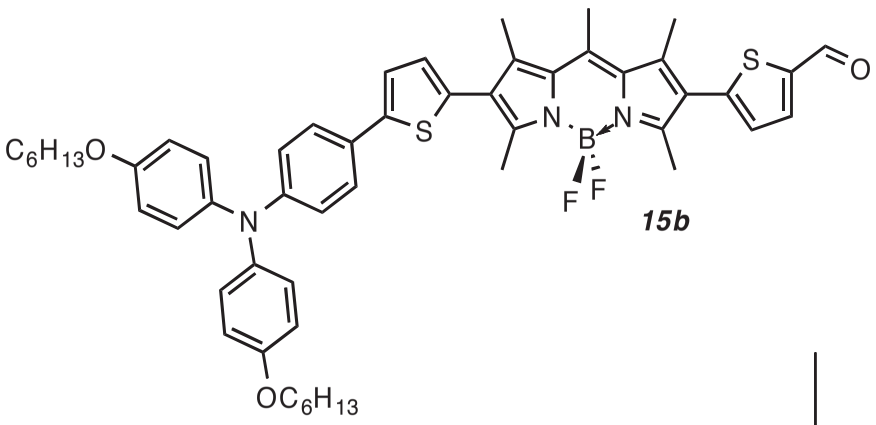

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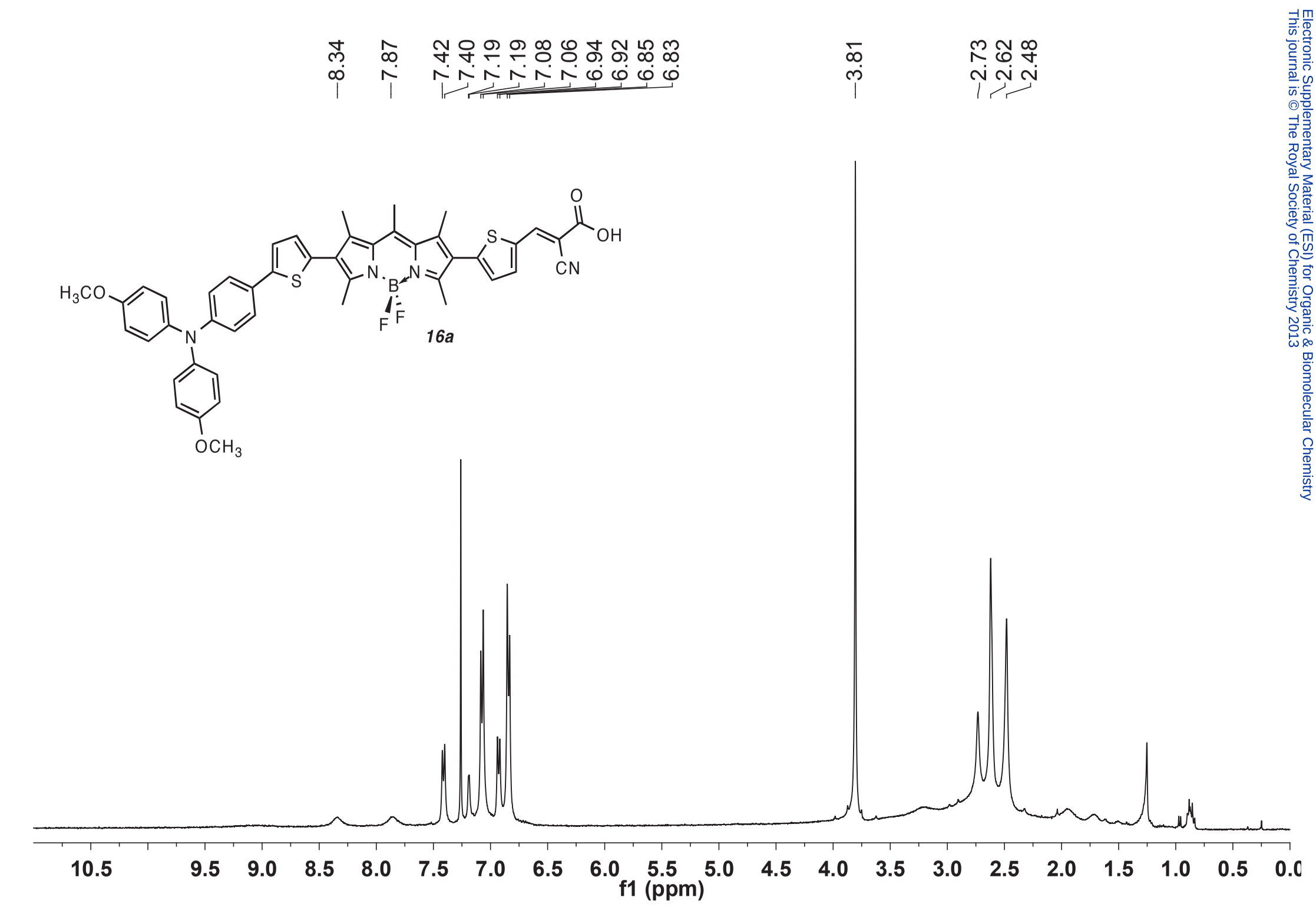

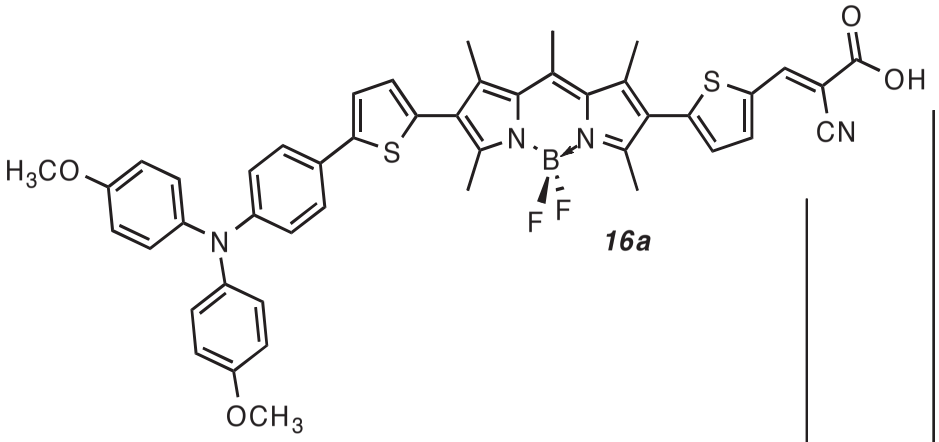

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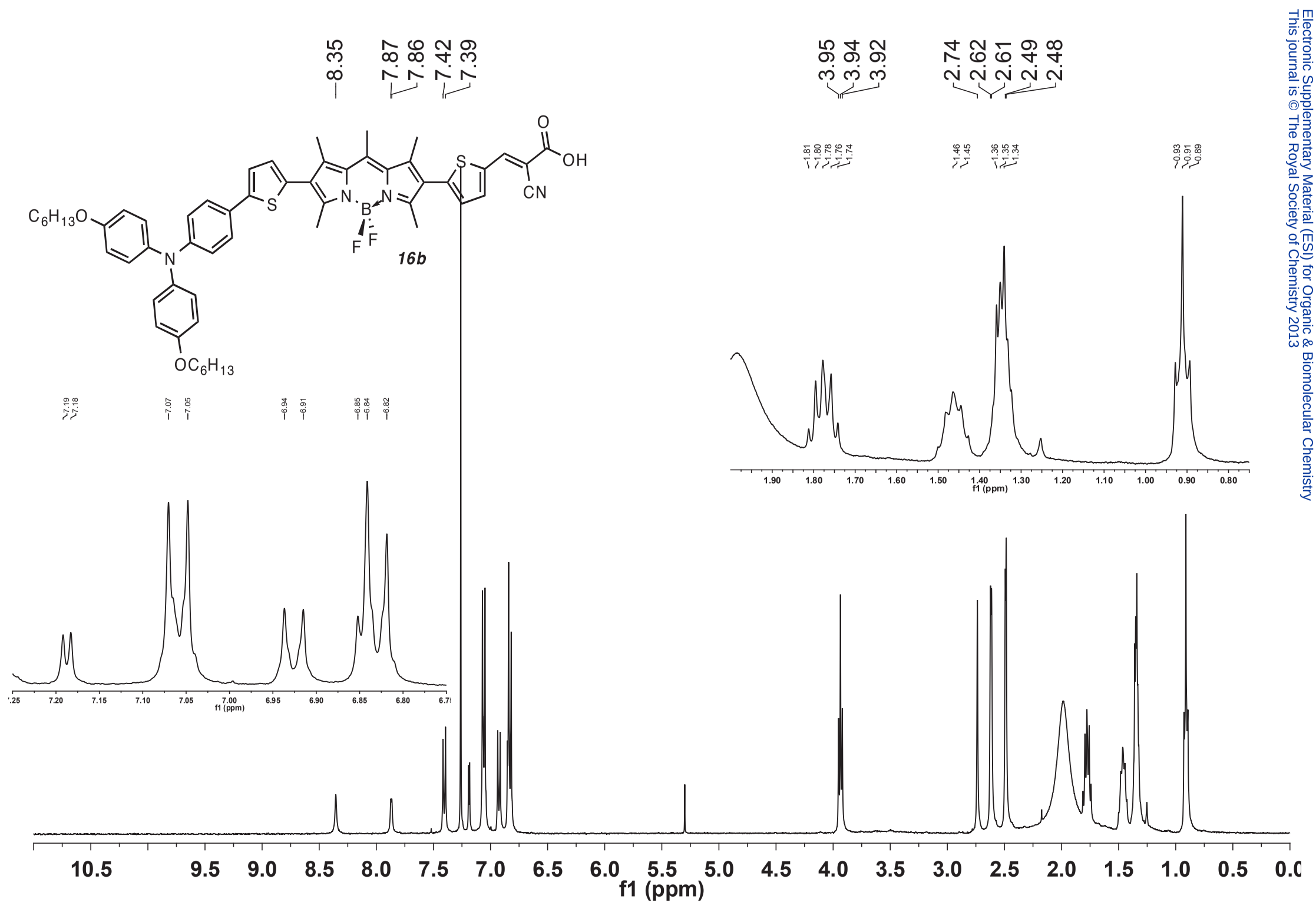
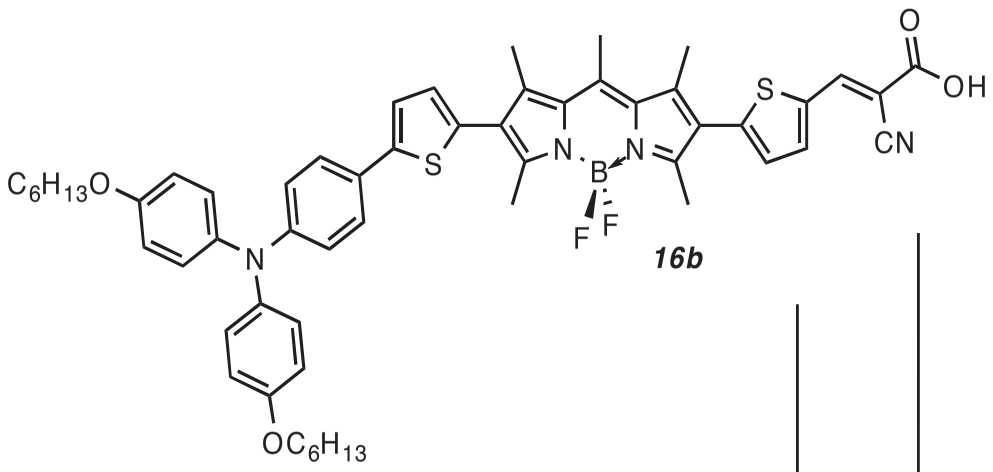




16b

Table S1. Comparison of Ground State Dihedral Angles between Neighboring Ring Systems as determined by DFT

Dye	***Dihedral angle between neighbouring planar ring systems***			
	TPA-BODIPY	*TPA-thiophene*	*proximal thiophene-BODIPY*	*distal thiophene-BODIPY*
5a	51.6	-	-	-
10a	53.4	-	-	41.8
16a	-	21.3	42.8	42.5

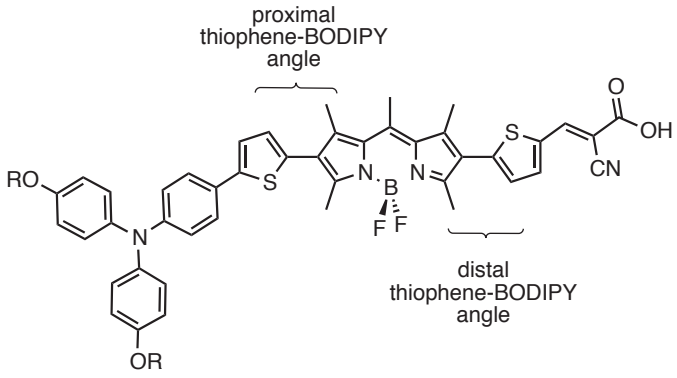
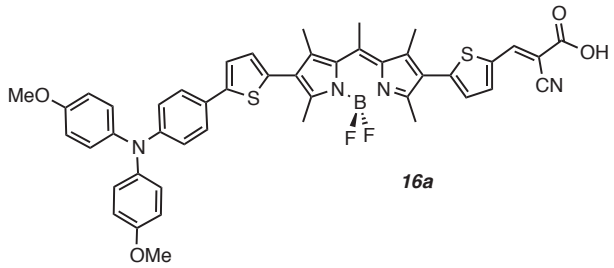


Table S2. Preliminary DSSC Cell Data for **16a**

Dye	Electrolyte	J_{sc}/mA cm^{-2}	V_{oc}/mV	FF	n (%)
16a	Z1137	1.20	0.48	0.61	0.35
16a	GI5	6.831	0.42	0.62	1.82
16a[a]	GI5	11.14	0.46	0.58	2.93

[a] The device was exposed to 1 sun for 80 minutes prior to testing.



16a

Cell Fabrication. Photoanodes were fabricated by screen-printing methods on fluorine-doped tin-oxide [FTO; Hartford Glass; TEC8 (8 Ω cm^{-2})] using 2 layers of 18NR-T (20 nm particles, 12 μm thick), and 1 layer of WER4-O (100 nm particles, 6 μm thick) for a total thickness of 18 μm. The FTO glass was cleaned by sonication in a detergent solution for 30 min followed by subsequent rinsing with deionized water and abs. EtOH and dried under a stream of air. The TiO_2 pastes were dried between layers in an oven at 120 °C for 25 min. Once the desired thickness had been achieved, the anode was fired to 450 °C for 20 min in an ambient atmosphere and left to room temperature. The TiO_2 substrates were treated with $TiCl_4$(aq) (0.05 M) at 70 °C for 30 min and subsequently rinsed with H_2O and then dried prior to heating. The electrodes were heated to 450 °C for 20 min in an ambient atmosphere and left to cool to 80 °C prior to immersing into a $CHCl_3$ solution containing the dye (0.25 mM) and chenodeoxycholic acid (2.5 mM) for 16 h. The stained films were then rinsed with copious amounts of $CHCl_3$ and dried. The cells were fabricated using Pt-coated counter-electrode [FTO TEC-15 (15 Ω cm^{-2})] and sealed with a 30 μm Surlyn (Dupont) gasket by resistive heating. The **Z1137** electrolyte used for this study was I_3^-/I^- [1.0 M 1,3- dimethylimidazolium iodide (DMII), 60 mM I_2, 0.5 M *tert*-butylpyridine, 0.05 M NaI and 0.1 M GuNCS in a mixed solvent system of acetonitrile and valeronitrile (85:15, *v/v*)]. The **GI5** electrolyte used for this study was I_3^-/I^- [0.3 M 1,3-dimethylimidazolium iodide (DMII), 60 mM I_2, 0.7 M LiI and 0.1 M GuNCS in a mixed solvent system of acetonitrile and valeronitrile (85:15, *v/v*)]. Each electrolyte was introduced into the two-sandwiched electrodes via vacuum backfilling through a hole in the counter electrode. In the cases where the I_3^-/I^- electrolyte was used, the hole was sealed with an aluminum-backed Bynel® foil (Dyesol™). The active area of the TiO_2 was 0.26 cm^2 was used. Silver bus bars were added to all cells after sealing.