Supporting Information

Benzene-Fused BODIPY and Fully-Fused BODIPY Dimer: Impacts of the Ring-Fusing at the *b* Bond in the BODIPY Skeleton

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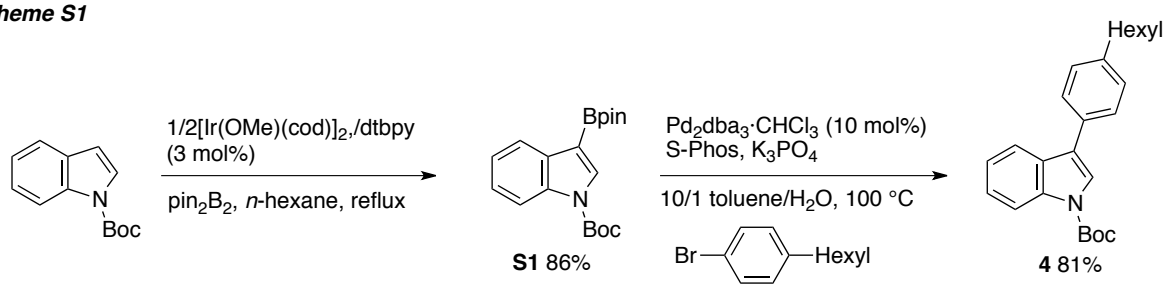
General. Melting points (mp) were measured on a Stanford Research System OptiMelt MPA100 instrument. ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded with a JEOL AL-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 128 MHz for ^{11}B, 376 MHz for ^{19}F). Chemical shifts are reported in δ ppm using residual protons in the deuterated solvents for ^{1}H NMR and using solvent peak for ^{13}C NMR as an internal standard, whereas those in ^{11}B and ^{19}F NMR spectra were relative to $BF_3 \cdot OEt_2$ (0.00 ppm) and CF_3COOH (–78.5 ppm), respectively. UV-vis-NIR absorption spectra measurement was performed with a Shimadzu UV-3150 spectrometer, in degassed spectral grade solvents. Fluorescence spectra measurement was performed with a HORIBA FluoroMax 4P for compound **1** and **3**, and Fluorolon-NIR for compound **2**, respectively. Quantum yields were determined with a Hamamatsu Quantaurus QY C11347 calibrated integrating sphere system. Cyclic voltammetry (CV) was performed on an ALS/chi-617A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ reference electrode. The measurement was carried out under an argon atmosphere using CH_2Cl_2 solutions of samples (1 mM) with 0.1 M tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 60B (Fuji Silysia). 2-Mesitylpyrrole[1] and 1,7-dihydrobenzo[1,2-*b*:5,4-*b'*]dipyrrole[2] were synthesized according to the literature. All reactions were carried out under an argon atmosphere.

Computation Method. All calculations were conducted using the Gaussian 09 program.[3]

Scheme S1

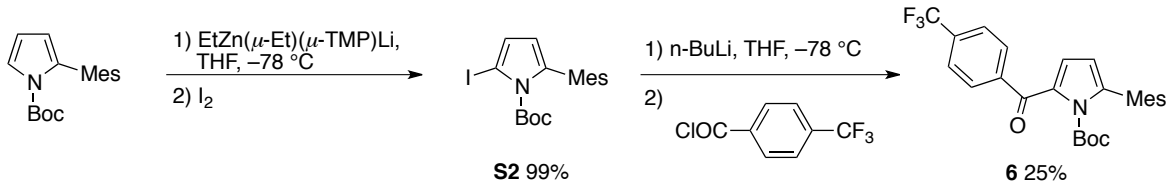


***N*-(*tert*-Butoxycarbonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indole (S1).** In a 100 mL flask equipped with a reflux condenser, *N*-(*tert*-butoxycarbonyl)indole (6.51 g, 30.0 mmol), $[Ir(OMe)(cod)]_2$ (291 mg, 0.45 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridine (241 mg, 0.90 mmol), and bis(pinacolato)diboron (5.69 g, 22.5 mmol) were dissolved in *n*-hexane (60 mL).[4] The mixture was refluxed for 58 h. After being cooled to room temperature and addition of water, the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was purified by silica gel column chromatography ($CHCl_3$, R_f = 0.45) to give 8.83 g (25.8 mmol) of **S1** in 86% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 12H), 1.66 (s, 9H), 7.24–7.31(m, 2H), (d, J_{HH} = 8.0 Hz, 1H), 8.00 (s, 1H), 8.16 (t, J_{HH} = 8.0 Hz, 1H).

***N*-(*tert*-Butoxycarbonyl)-3-(4-hexylphenyl)indole (4)**. In a 100 mL flask equipped with a reflux condenser, **S1** (2.29 g, 10 mmol), *p*-bromohexylbenzene (2.04 mL, 10.0 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (258 mg, 0.50 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (S-Phos)[5] (820 mg, 2.00 mmol), and K_3PO_4 (8.49 g, 40.0 mmol) were dissolved in a mixed solvent of toluene (50 mL) and water (5 mL). The mixture was stirred at 100 °C for 6 h. After being cooled to room temperature, the mixture was passed through a pad of Celite. After addition of water, the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (1/2 $CHCl_3$/*n*-hexane, R_f = 0.48) to give 3.06 g (8.09 mmol) of **4** in 81% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J_{HH} = 6.8 Hz, 3H), 1.31–1.38 (m, 6H), 1.63–1.69 (m, 2H), 1.69 (s, 9H), 2.67 (t, J_{HH} = 7.5 Hz, 2H), 7.26–7.30 (m, 3H), 7.36 (t, J_{HH} = 8.0 Hz, 1H), 7.55(d, J_{HH} = 8.0 Hz, 2H), 7.68 (s, 1H), 7.82 (d, J_{HH} = 8.0 Hz, 1H), 8.21 (d, J_{HH} = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 28.1,

28.2, 29.1, 31.5, 35.8, 83.7, 115.4, 120.0, 122.1, 122.5, 122.8, 124.5, 127.8, 128.8, 129.1, 131.1, 135. 9, 142.0, 149.8; HRMS (APCI) Calcd for $C_{25}H_{32}NO_2$: 378.2433 [(*M*+H)$^+$]. Found: 378.2428 [(*M*+H)$^+$].

Scheme S2



***N*-(*tert*-Butoxycarbonyl)-2-iodo-5-mesitylpyrrole (S2).** To a solution of 2,2,6,6-tetramethylpiperidine (TMP) (10.3 mL, 61.6 mmol) in THF (60 mL), *n*-BuLi (1.60 M in hexane, 35.0 mL, 56.0 mmol) was added dropwise at –78 °C. The mixture was stirred at –78 °C for 10 min and then at 0 °C for further 30 min. Et_2Zn (1.0 M in hexane, 67.2 mL, 67.2 mmol) was added to the mixture at –78 °C.[6] After being stirred at –78 °C for 15 min, the mixture was allowed to warm to room temperature followed by stirring for 1 h. A solution of *N*-(*tert*-butoxycalbonyl)-2-mesitylpyrrole (8.00 g, 28.0 mmol) in THF (20 mL) was added to the solution dropwise at –78 °C. After being stirred for 15 min at –78 °C, the mixture was allowed to warm to room temperature and stirred for further 1 h. Iodine (56.0 g, 224 mmol) was added to the resulting solution at –78 °C. The mixture was gradually warmed to room temperature over 2 h. After addition of a saturated aqueous Na_2SO_3 solution (200 mL), the mixture was extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (1/2 $CHCl_3$/hexane, R_f = 0.30) to give 11.1 g (27.0 mmol) of **S2** in 99% yield as colorless solids: mp 77.7–78.4 °C; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 9H), 2.02 (s, 6H), 2.30 (s, 3H), 5.98 (d, J_{HH} = 3.4 Hz, 1H), 6.58 (d, J_{HH} = 3.4 Hz, 1H), 6.87 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 20.2, 21.1, 27.1, 63.6, 84.1, 114.5, 123.9, 127.6, 131.6, 136.2, 137.6, 138.0, 148.9; HRMS (FAB) Calcd for $C_{18}H_{22}INO_2$: 411.0695 [M^+]. Found: 411.0691 [M^+].

***N*-(*tert*-Butoxycalbonyl)-2-mesityl-5-[4-(trifluoromethyl)benzoyl]pyrrole (6).** To a solution of **S2** (8.22 mg, 20 mmol) in THF (40 mL) was added dropwise *n*-BuLi (1.60 M in hexane,

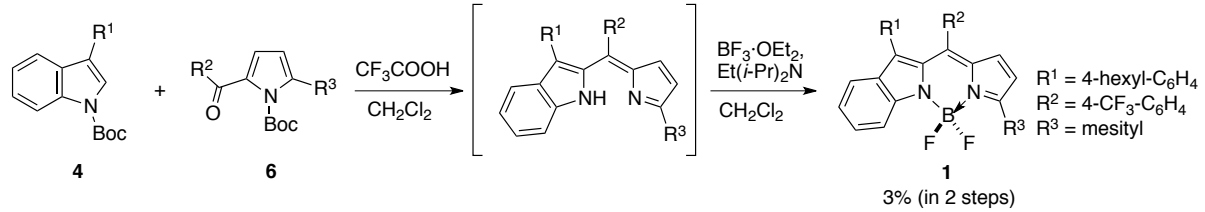
13.1 mL, 21.0 mmol) at –78 °C. After the mixture was stirred for 30 min at –78 °C, 4-(trifluoromethyl)benzoyl chloride (3.1 mL, 21 mmol) was added dropwise to the solution at –78 °C. The mixture was allowed to warm to room temperature and stirred for further 30 min. After addition of water, the mixture was extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was purified by silica gel column chromatography (2/3 $CHCl_3$/hexane, R_f = 0.14) to give 2.35 g (5.14 mmol) of **6** in 25% yield as colorless solids: mp 101.0–102.3 °C; ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 9H), 2.10 (s, 6H), 2.33 (s, 3H), 6.08 (d, J_{HH} = 3.6 Hz, 1H), 6.80 (d, J_{HH} = 3.6 Hz, 1H), 6.93 (s, 2H), 7.75 (d, J_{HH} = 8.5 Hz, 2H), 8.06 (d, J_{HH} = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.1, 21.2, 26.8. 84.7, 110.9, 122.5, 123.7 (q, $^1J_{CF}$ = 271 Hz), 125,3 (q, $^3J_{CF}$ = 3.3 Hz), 127.8, 129.7, 131.8, 133.5 (q, $^2J_{CF}$ = 31 Hz), 138.4, 138.7, 140.5, 141.0, 149.0, 183.0; ^{19}F NMR ($CDCl_3$) δ –62.6 (s, 3F); HRMS (APCI) Calcd for $C_{26}H_{27}F_3NO_3$: 458.1943 [(M+H)$^+$]. Found: 458.1938 [(M+H)$^+$].

***N*-(*tert*-Butoxycarbonyl)-3-(4-hexylphenyl)-2-iodoindole (5).** To a solution of 2,2,6,6-tetramethylpiperidine (TMP, 3.70 mL, 21.9 mmol) in THF (40 mL), *n*-BuLi (1.60 M in hexane, 12.5 mL, 20.0 mmol) was added dropwise at –78 °C. The mixture was stirred at –78 °C for 10 min and then at 0 °C for 30 min. Et_2Zn (1.0 M in hexane, 24.0 mL, 24.0 mmol) was added to the mixture at –78 °C.[6] After the mixture was stirred at –78 °C for 15 min and then at room temperature for 30 min, a solution of **4** (3.77 g, 10.0 mmol) in THF (20 mL) was added dropwise at –78 °C. The mixture was gradually warmed to room temperature followed by stirring for 1h. Iodine (20.3 g, 80.0 mmol) was added to the solution at –78 °C. The mixture was allowed to warm to room temperature over 2 h. After addition of a saturated aqueous Na_2SO_3 solution (100 mL), the mixture was extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (1/2 $CHCl_3$/hexane, R_f = 0.25) to give 4.97 g (9.87 mmol) of **5** in 99% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J_{HH} = 7.3 Hz, 3H), 1.32–1.42 (m, 6H), 1.67–1.74 (m, 2H), 1.75 (s, 9H), 2.69 (t, J_{HH} = 7.8 Hz, 2H), 7.17 (t, J_{HH} = 7.2 Hz, 1H), 7.26 (t, J_{HH} = 7.2 Hz, 1H), 7.30 (d, J_{HH} = 8.0 Hz, 2H),

7.38–7.42 (m, 3H), 8.11 (d, J_{HH} = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 28.3, 29.1, 31.3, 31.8, 35.9, 77.9, 85.2, 115.3, 119.4, 122.8, 124.5, 128.4, 130.0, 130.1, 131.4, 131.8, 138.1, 142.6, 149.5; HRMS (FAB) Calcd for $C_{25}H_{30}INO_2$: 503.1321 [M^+]. Found: 503.1322 [M^+].

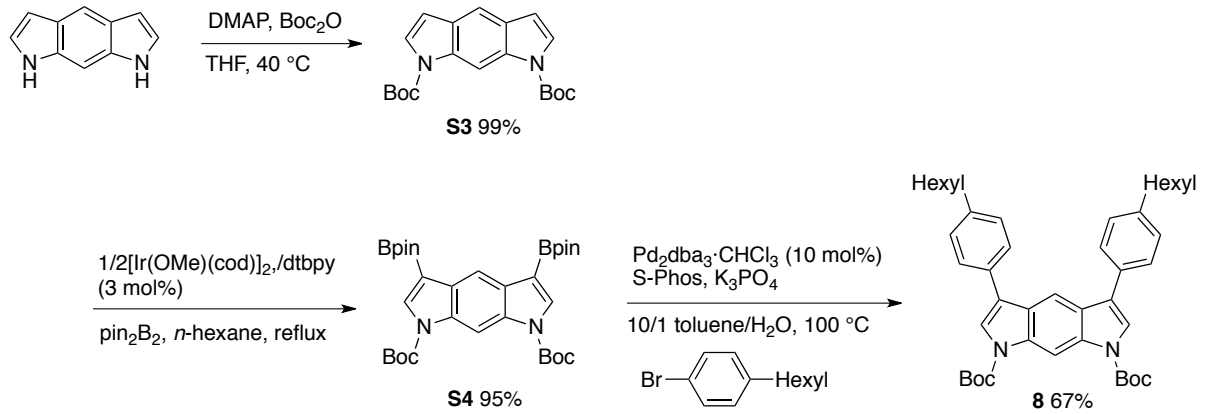
Compound 1. To a solution of **5** (251 mg, 0.50 mmol) in THF (2 mL), *tert*-BuLi (1.60 M in pentane, 0.62 mL, 1.0 mmol) was added dropwise at –78 °C. The mixture was stirred at –78 °C for 30 min. A solution of **6** (228 mg, 0.50 mmol) in THF (5 mL) was added to the resulting solution dropwise at –78 °C. After being stirred at –78 °C for 30 min, the resulting solution was allowed to warm to room temperature followed by stirring for another 2 h. After addition of water, the mixture was extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resultant mixture was dissolved in CH_2Cl_2 (5 mL). CF_3COOH (0.18 mL, 2.0 mmol) was added to the solution and the mixture was stirred for 1 h. After evaporation of the solvent under reduced pressure, the mixture was dissolved in toluene (10 mL) and triethylamine (0.69 mL, 5.0 mmol) and $BF_3{\cdot}OEt_2$ (0.75 mL, 6.0 mmol) were successively added. The mixture was stirred at 100 °C for 10 h. After addition of water, the mixture was extracted with toluene. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (1/1 toluene/hexane, R_f = 0.25) to give 117 mg (0.17 mmol) of **1** in 34% yield as dark purple-red solids with gold luster: mp 229.8–231.4 °C; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J_{HH} = 6.6 Hz, 3H), 1.31–1.38 (m, 6H), 1.50–1.58 (m, 2H), 2.22 (s, 6H), 2.38 (s, 3H), 2.47 (t, J_{HH} = 8.0 Hz, 2H), 6.52 (d, J_{HH} = 4.3 Hz, 1H), 6.78–6.84 (m, 4H), 6.92–6.96 (m, 2H), 7.01 (s, 2H), 7.31–7.34 (m, 4H), 7.37 (d, J_{HH} = 8.0 Hz, 2H), 7.70 (d, J_{HH} = 8.0 Hz, 1H); ^{13}C NMR (CD_2Cl_2) δ 14.2, 20.2, 21.4, 23.0, 29.6, 31.5, 32.0, 35.8, 115.6, 122.2, 123.3, 124.2 (q, $^1J_{CF}$ = 271 Hz), 124.6 (q, $^3J_{CF}$ = 4.1 Hz), 124.8, 128.0, 128.1, 129.2, 130.4, 130.7, 131.1 (q, $^2J_{CF}$ = 34 Hz), 131.4 131.7, 132.9, 134.3, 137.1, 137.3, 139.6, 139.8, 140.4, 142.7, 145.9, 147.1, 170.0; ^{11}B NMR (CD_2Cl_2) δ 0.40 (t, J_{B-F} = 30 Hz); ^{19}F NMR (CD_2Cl_2) δ –62.8 (s, 3F), –145.8 (m, 2F); HRMS (APCI) Calcd for $C_{41}H_{39}BF_5N_2$: 665.3126 [(M+H)$^+$]. Found: 645.3121 [(M+H)$^+$].

Scheme S3



Synthesis of compound 1 under acidic condition. To a solution of **4** (146 mg, 0.39 mmol) and **6** (179 mg, 0.39 mmol) in CH_2Cl_2 (10 mL), CF_3COOH (0.23 mL, 3.1 mmol) was added at room temperature. After the mixture was stirred for 24 h, diisopropylethylamine (2.0 mL, 1.5 g, 11 mmol)) and $BF_3{\cdot}OEt_2$ (3.0 mL, 3.5 g, 24 mmol) were added. After the mixture was stirred for 1 h, 30 mL of water was added. The water layer was extracted with CH_2Cl_2 three times, and the combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was purified by silica gel column chromatography (1/1 toluene/hexane, R_f = 0.25) to give 6.6 mg (0.01 mmol) of **1** in 3% yield as dark purple-red solids.

Scheme S4



***N*-(*tert*-Butoxycarbonyl)benzo[1,2-*b*:5,4-*b*′]dipyrrole (S3).** A solution of 4-dimethylaminopyridine (0.327 g, 2.68 mmol), 1,7-dihydrobenzo[1,2-*b*:5,4-*b*′]dipyrrole, and di-*tert*-butyl dicarbonate (6.7 mL, 29.5 mL) in THF (200 mL) was stirred at 40 °C for 5 h. After addition of water at room temperature, the mixture was extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was dissolved in CH_2Cl_2, which was passed through a pad of silica gel with CH_2Cl_2 as an eluent to give 4.70 g (1.31 mmol) of **S3** in 99% as colorless solids: mp 118.7–121.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.69 (s, 18H), 6.59 (d, J_{HH} = 2.7

Hz, 2H), 7.59 (d, J_{HH} = 2.7 Hz, 2H), 7.64 (s, 1H), 9.11 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 28.2, 83.2, 102.2, 107.0, 111.5, 126.2, 127.2, 133.8, 149.7; HRMS (APCI) Calcd for $C_{20}H_{25}N_2O_4$: 357.1804 [(*M*+H)$^+$]. Found: 357.1809 [(*M*+H)$^+$].

***N*-(*tert*-Butoxycarbonyl)-3,5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[1,2-*b*:5,4-*b*′]dipyrrole (S4).** A solution of **S3**, $[Ir(OMe)(cod)]_2$ (0.18 mmol, 116 mg), 4,4′-di(*tert*-butyl)-2,2′-bipyridyl (96 mg, 0.36 mmol), and bis(pinacolato)diboron (4.54 g, 18.0 mmol) in *n*-hexane (60 mL) was stirred at 80 °C for 41 h.[4] After being cooled to room temperature, water was added to the mixture. The water layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (9/1 CH_2Cl_2/EtOH, R_f = 0.70) to give 6.97 g (11.4 mmol) of **S4** in 95% as a colorless solids: mp 202.7–204.8 °C; ^{1}H NMR ($CDCl_3$) 1.41 (s, 24H), 1.67 (s, 18H), 8.01 (s, 2H), 8.57 (s, 1H), 9.07 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.0, 28.2, 83.2, 83.4, 101.5, 115.3, 130.5, 134.5, 135.1, 149.4; ^{11}B NMR ($CDCl_3$) δ 29.8; HRMS (APCI) Calcd for $C_{32}H_{47}B_2N_2O_8$: 609.3518 [(*M*+H)$^+$]. Found: 609.3513 [(*M*+H)$^+$].

***N*-(*tert*-Butoxycarbonyl)-3,5-(4-hexylphenyl)benzo[1,2-*b*:5,4-*b*′]dipyrrole (8).** A solution of **S4** (6.38 g, 10.5 mmol), *p*-bromohexylbenzene (4.2 mL, 21 mmol), $Pd_2(dba)_3$·$CHCl_3$ (270 mg, 0.52 mmol), S-Phos (861 mg, 2.1 mmol),[5] and K_3PO_4 (8.91 g, 42 mmol) in a mixed solvent of toluene (60 mL) and water (6 mL) was stirred at 100 °C for 6 h. After being cooled to room temperature, the resulting mixture was passed through a pad of Celite. After addition of water, the resulting mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (1/1 CH_2Cl_2/hexane, R_f = 0.48) to give 4.81 g (7.10 mmol) of **8** in 67% as colorless solids: mp 125.2–126.7 °C; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J_{HH} = 6.8 Hz, 6H), 1.32–1.42 (m, 12H), 1.63–1.67 (m, 4H), 1.77 (s, 18H), 2.66 (t, J_{HH} = 7.8 Hz, 4H), 7.28 (d, J_{HH} = 8.0 Hz, 4H), 7. 58 (d, J_{HH} = 8.0 Hz, 4H), 7.69 (s, 2H), 8.14 (s, 1H), 9.23 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 28.2, 29.1, 31.5, 31.8, 35.8, 83.3,

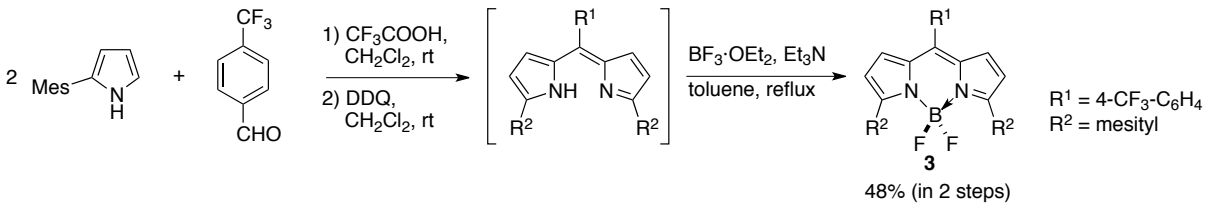
102.5, 109.9, 122.0, 123.1, 126.0, 127.8, 128.9, 131.4, 134.6, 141.9, 149.7; HRMS (APCI) Calcd for $C_{44}H_{57}N_2O_4$: 677.4318 [(*M*+H)$^+$]. Found: 677.4313 [(*M*+H)$^+$].

***N*-(*tert*-Butoxycarbonyl)-3,5-(4-hexylphenyl)-2,6-iodo-benzo[1,2-*b*:5,4-*b'*]dipyrrole (9).** To a solution of 2,2,6,6-tetramethylpiperidine (TMP, 5.20 mL, 31.2 mmol) in THF (40 mL) was added dropwise *n*-BuLi (1.60 M in *n*-hexane, 17.7 mL, 28.4 mmoL) at –78 °C. After stirring at –78 °C for 10 min, the reaction mixture was allowed to warm to 0 °C followed by stirring for 30 min. Et_2Zn (1.0 M in *n*-hexane, 34.1 mL, 34.1 mmol) was added to the mixture at –78 °C.[6] A solution of **8** (4.80 g, 7.10 mmol) in THF was added at –78 °C, and the mixture was stirred for 15 min at the same temperature. After stirring at room temperature for 1 h, the mixture was cooled again to –78 °C and iodine (11.3 g, 28.7 mmol) was added. The resulting mixture was gradually allowed to warm to room temperature over 2 h. After addition of a saturated aqueous Na_2SO_3 solution (100 mL), the mixture was extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (1/1 CH_2Cl_2/*n*-hexane, R_f = 0.49) to give 6.28 g (6.76 mmol) of **9** in 95% as colorless solids: mp 175.1–175.9 °C; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J_{HH} = 6.8 Hz, 6H), 1.30–1.38 (m, 12H), 1.62–1.70 (m, 4H), 1.77 (s, 18H), 2.65 (t, J_{HH} = 7.6 Hz, 4H), 7.27 (d, J_{HH} = 8.0 Hz, 4H), 7. 34 (s, 1H), 7.37 (d, J_{HH} = 8.0 Hz, 4H), 9.10 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 28.3, 29.1, 31.2, 31.7, 35.8, 78.0, 85.2, 102.1, 108.4, 126.8, 128.5, 130.1, 131.6, 131.7, 136.6, 142.5, 149.6; HRMS (APCI) Calcd for $C_{44}H_{55}I_2N_2O_4$: 929.2251 [(*M*+H)$^+$]. Found: 929.2246 [(*M*+H)$^+$].

Compound 2. To a solution of **9** (464 mg, 0.50 mmol) in THF (2 mL) was added *tert*-BuLi (1.60 M in pentane, 1.37 mL, 2.2 mmol) dropwise at –78 °C. The mixture was stirred at the same temperature for 30 min and a solution of **6** (457 mg, 1.00 mmol) in THF (5 mL) was added at –78 °C. After being stirred at –78 °C for 30 min, the resulting solution was allowed to warm to room temperature followed by stirring for another 2 h. After addition of water, the mixture was extracted with ether. The combined organic layer was washed with brine, dried

over Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting solids were dissolved in CH_2Cl_2 (5 mL) and CF_3COOH (0.51 mL, 7.0 mmol) was added. The mixture was stirred for 1 h. After removal of the solvent under reduced pressure, the mixture was dissolved in toluene (10 mL) and triethylamine (1.39 mL, 10.0 mmol) and $BF_3{\cdot}OEt_2$ (2.76 mL, 22.0 mmol) were successively added. The mixture was stirred at 100 °C for 10 h. After addition of water, the resulting mixture was extracted with toluene. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (1/1 toluene/*n*-hexane, R_f = 0.30) to give 131 mg (0.10 mmol) of **2** in 20% yield as dark green solids with gold luster: mp >300 °C; ^{1}H NMR (CD_2Cl_2) δ 0.89 (t, J_{HH} = 6.6 Hz, 6H), 1.27–1.36 (m, 12H), 1.46–1.520 (m, 4H), 2.18 (s, 12H), 2.40 (s, 6H), 2.43 (t, J_{HH} = 8.3 Hz, 4H), 6.56 (d, J_{HH} = 4.3 Hz, 2H), 6.77 (d, J_{HH} = 8.0 Hz, 2H), 6.79 (d, J_{HH} = 8.0 Hz, 2H), 6.94 (d, J_{HH} = 4.3 Hz, 2H), 7.00 (s, 4H), 7.30 (d, J_{HH} = 8.0 Hz, 4H), 7.31 (s, 1H), 7.37 (d, J_{HH} = 8.0 Hz, 4H), 7.43 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 20.2, 21.4, 22.6, 29.2, 30.9, 31.6, 35.4, 96.7, 119.2, 124.1 (q, $^3J_{CF}$ = 4.1 Hz), 124.1, 124.2, 124.6, 126.4 (q, J_{CF} = 271 Hz), 127.7, 127.9, 128.7, 129.9, 130.6 (q, J_{CF} = 34 Hz), 131.3, 131.6, 132.6, 135.4, 136.8, 137.0, 139.3, 140.7, 141.1, 142.5, 149.5, 165.1; ^{11}B NMR (CD_2Cl_2) δ 0.42 (d, J_{BF} = 28.2 Hz); ^{19}F NMR ($CDCl_3$) δ –145.3 (BF_2), –62.5 (CF_3); HRMS (APCI) Calcd for $C_{76}H_{71}B_2F_{10}N_4$: 1251.5705 [(*M*+H)$^+$]. Found: 1250.5700 [(*M*+H)$^+$].

Scheme S5



Compound 3. To a solution of 2-mesitylpyrrole (1.85 g, 10.0 mmol) and 4-(trifluoromethyl)benzaldehyde (0.67 mL, 5.0 mmol) in CH_2Cl_2 (20 mL) was added CF_3COOH (0.30 mL, 4.0 mmol). The mixture was stirred at room temperature for 10 h. 2,3-Dichloro-5,6-dicyano-1,4-benoquinone (DDQ) (1.14 g, 5.0 mmol) was added to the mixture. After being stirred for 3 h, a saturated aqueous $NaHCO_3$ solution (50 mL) was added to the mixture. The resulting mixture was extracted with CH_2Cl_2. The combined organic layer

was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product of dark red solids, which was used for the next step without further purification. To a solution of the obtained solids in toluene (20 mL) was added triethylamine (2.10 mL, 15.1 mmol) and $BF_3{\cdot}OEt_2$ (6.10 mL, 48.5 mmol). The mixture was stirred at 100 °C for 21 h. After addition of a saturated aqueous $NaHCO_3$ solution (50 mL), the resulting mixture was extracted with toluene. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (1/1 toluene/*n*-hexane, R_f = 0.38) to give 1.40 g (2.45 mmol) of **3** in 49% yield as orange solids: mp 151.7–153.2 °C; ^{1}H NMR ($CDCl_3$) δ 2.11 (s, 12H), 2.26 (s, 6H), 6.29 (d, J_{HH} = 4.1 Hz, 2H), 6.84 (s, 4H), 6.87 (d, J_{HH} = 4.1 Hz, 2H), 7.83 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 20.2, 21.2, 120.8, 122.4, 125.2 (q, J_{CF} = 4.1 Hz), 126.6 (q, $^1J_{CF}$ = 271 Hz), 127.6, 129.6, 130.3, 130.9, 132.0 (q, $^2J_{CF}$ = 33 Hz), 134.9, 137.2, 137.7, 138.4, 142.1, 159.8; ^{11}B NMR ($CDCl_3$) δ –0.11 (t, J_{BF} = 29.3 Hz); ^{19}F NMR ($CDCl_3$) δ –62.4 (CF_3), –146.4 (q, J = 30.5 Hz, BF_2); HRMS (APCI) Calcd for $C_{24}H_{30}BF_5N_2$: 573.2500 [(M+H)$^+$]. Found: 573.2495 [(M+H)$^+$].

X-Ray Crystal Structure Analysis

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-899844 (**1**), CCDC-899845 (**2**), and CCDC-899846 (**3**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Compound 1. Single crystals suitable for X-ray analysis were obtained by slow diffusion of ethanol into a dichloromethane solution of **1**. Intensity data were collected at 100 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo Kα radiation (λ = 0.71070 Å) and graphite monochromator. A total of 30783 reflections were measured with a maximum 2θ angle of 50.0°, of which 6618 were independent reflections (R_{int} = 0.0404). The structure was solved by direct methods (SHELXS-97[7]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[7]). The crystal contained a disordered CH_2Cl_2 molecule *i.e.*, (C43, Cl1, and Cl2), which was solved using appropriate models. Thus, two sets of CH_2Cl_2 *i.e.*, (C43, Cl1A, and Cl2) and (C43, Cl1B, and Cl2) were placed and their occupancies were refined to be 0.89 and 0.11, respectively. The CF_3 group consisting of C29, F3, F4, and F5 was also disordered and was solved using appropriate models. Thus, two sets of CF_3 group, *i.e.*, (C29, F3A, F4A, and F5A) and (C29, F3B, F4B, and F5B), were placed and their occupancies were refined to be 0.58 and 0.42, respectively. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{42}H_{40}B_1Cl_2F_5N_2$; FW = 749.47, crystal size 0.20 × 0.18 × 0.15 mm^3, Monoclinic, $P2_1/a$, a = 12.5255(4) Å, b = 10.3779(3) Å, c = 29.0756(10) Å, β = 95.2682(14)°, V = 3763.5(2) $Å^3$, Z = 4, D_c = 1.323 g cm^{-3}. The refinement converged to R_1 = 0.0675, wR_2 = 0.1628 ($I > 2\sigma(I)$), GOF = 1.140.

Compound 2. Single crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a chloroform solution of **2**. Intensity data were collected at 123 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo Kα radiation (λ = 0.71070 Å) and graphite monochromator. A total of 44733 reflections were

measured with a maximum 2θ angle of 50.0°, of which 6277 were independent reflections (R_{int} = 0.0433). The structure was solved by direct methods (SHELXS-97[7]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[7]). The crystal contained two independent disordered $CHCl_3$ molecules *i.e.*, (C34, Cl1 Cl2, and Cl3) and (C41, Cl4, Cl5, and Cl6), which were sitting on the symmetrical axis. These $CHCl_3$ molecules (C34, Cl1 Cl2, and Cl3) and (C41, Cl4, Cl5, and Cl6) were solved by fixing their occupancies as 0.50 and 0.25, respectively. The $CHCl_3$ molecule (C41, Cl4, Cl5, and Cl6) was restrained by DFIX instruction during refinement. The hexyl group consisting of C35–C40 was also disordered and was solved using appropriate models. Thus, three sets of hexyl group, *i.e.*, (C35, C36A, C37A, C38A, C39A, and C40A), (C35, C36B, C37B, C38B, C39B, and C40B), and (C35, C36B, C37B, C38B, C39B, and C10C), were placed and solved by fixing their occupancies as 0.50, 0.25, and 0.25 respectively. These disordered hexyl moieties were restrained by DFIX, DELU, and SIMU instructions during refinement. The CF_3 group was also disordered and solved using appropriate models. Two sets of CF_3 group, *i.e.*, (C27, F3A, F4A, and F5A) and (C27, F3B, F4B, and F5B), were placed and their occupancies were refined to be 0.92 and 0.08, respectively. The minor part of CF_3 group (C27, F3B, F4B, and F5B) was restrained by DFIX instruction during refinement. All non-hydrogen atoms, except for the disordered $CHCl_3$ molecules, the disordered CF_3 moiety (F3B, F4B, and F5B) and the disordered hexyl carbon (C36A), were refined anisotropically. All hydrogen atoms, except for the disordered $CHCl_3$ molecules (C34, Cl1 Cl2, and Cl3) and (C41, Cl4, Cl5, and Cl6), and the disordered hexyl moiety (C39B, C40B, and C40C), were placed using AFIX instructions. The crystal data are as follows: $C_{77.5}H_{65}B_2Cl_{4.5}F_{10}N_4$; FW = 1423.48, crystal size 0.20 × 0.05 × 0.01 mm^3, Orthorhombic, *Pbcn*, a = 22.654(4) Å, b = 23.390(4) Å, c = 13.523(2) Å, V = 7165(2) $Å^3$, Z = 4, D_c = 1.320 g cm^{-3}. The refinement converged to R_1 = 0.0899, wR_2 = 0.2464 ($I > 2\sigma(I)$), GOF = 1.078.

Compound 3. Single crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a chloroform solution of **3**. Intensity data were collected at 123 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo Kα

radiation (λ = 0.71070 Å) and graphite monochromator. A total of 58752 reflections were measured with a maximum 2θ angle of 51.0°, of which 10608 were independent reflections (R_{int} = 0.0604). The structure was solved by direct methods (SHELXS-97[7]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[7]). The crystal contained two independent molecules. One CF_3 group of one molecule was disordered and was solved using appropriate models. Thus, two sets of CF_3 group, *i.e.*, (C68A, F8A, F9A, and F10A) and (C68B, F8B, F9B, and F10B), were placed and their occupancies were refined to be 0.52 and 0.48, respectively. The structure was solved and refined in space group $P2_1/c$, however, R_1 value was as high as 0.25. When merohedral twinning by two-fold rotation along *c*-axis was assumed (TWIN –1 0 0 0 –1 0 0 0 1, BASF 0.5), R_1 value dropped to 0.046. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{34}H_{30}BF_5N_2$; FW = 572.41, crystal size 0.20 × 0.18 × 0.15 mm^3, Monoclinic, $P2_1/c$, a = 9.2815(2) Å, b = 20.19380(10) Å, c = 30.6952(4) Å, β = 90.0000(6)°, V = 5753.16(15) $Å^3$, Z = 8, D_c = 1.322 g cm^{-3}. The refinement converged to R_1 = 0.0411, wR_2 = 0.01030 ($I > 2\sigma(I)$), GOF = 1.082.

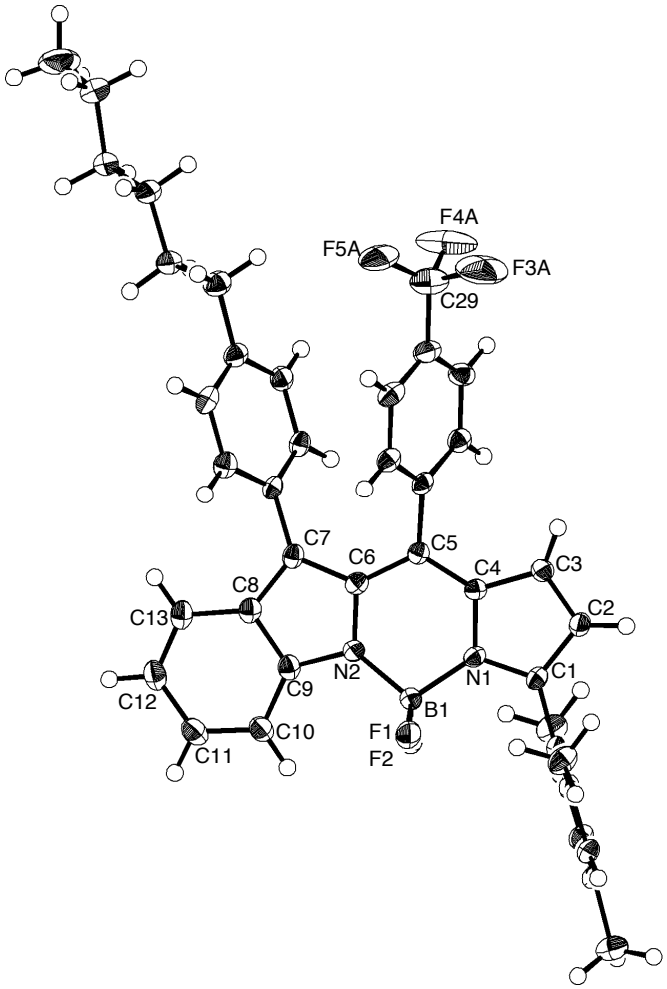


Figure S1. *ORTEP* drawing of **1** (50% probability for thermal ellipsoids). The solvent molecule of CH_2Cl_2 is omitted for clarity. Selected bond lengths (Å): N1–B1, 1.562(4); N2–B1, 1.528(4); N1–C1, 1.349(3); C1–C2, 1.425(4); C2–C3, 1.360(4); C3–C4, 1.424(4); C4–N1, 1.400(3); C4–C5, 1.388(4); C5–C6, 1.423(4); C6–N2, 1.390(3); C6–C7, 1.417(4); C7–C8, 1.425(4); C8–C9, 1.415(4); C9–N2, 1.374(3); C9–C10, 1.406(4); C10–C11, 1.377(4); C11–C12, 1.411(4); C12–C13, 1.371(4); C13–C8, 1.417(4).

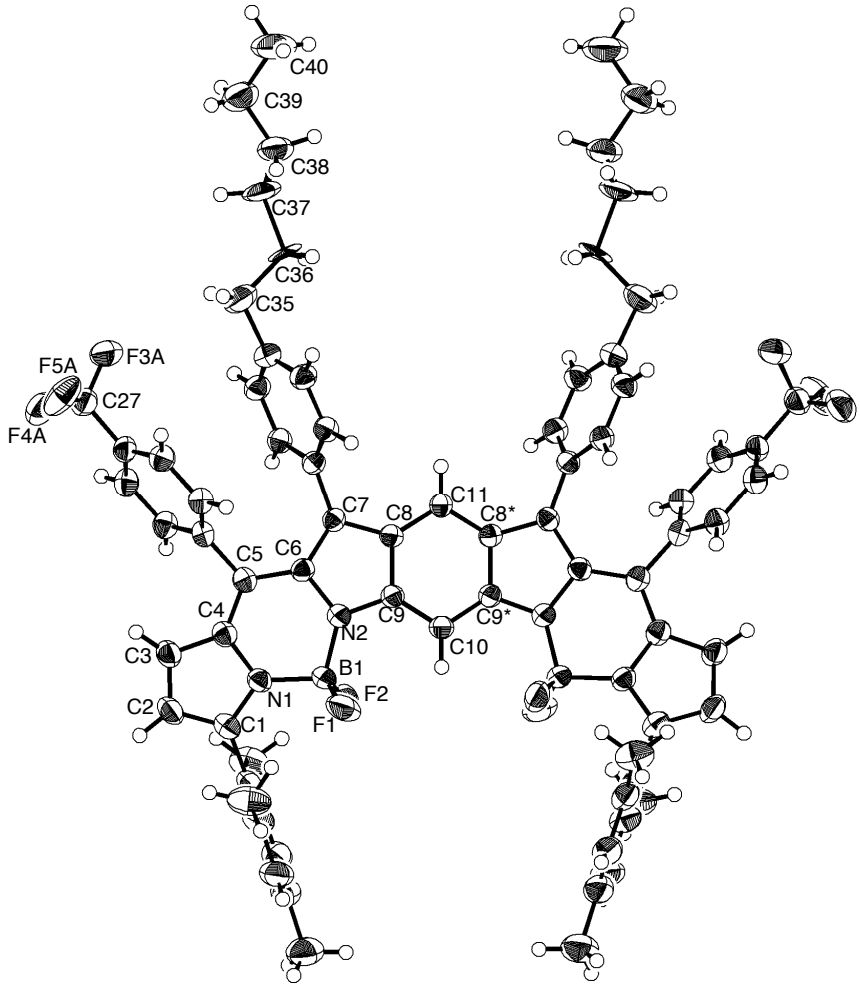


Figure S2. *ORTEP* drawing of **2** (50% probability for thermal ellipsoids). The solvent molecules of $CHCl_3$ and the minor part of the disordered hexyl groups are omitted for clarity. Selected bond lengths (Å): N1–B1, 1.548(5); N2–B1, 1.534(5); N1–C1, 1.340(4); C1–C2, 1.419(5); C2–C3, 1.367(5); C3–C4, 1.430(5); C4–C5, 1.383(5); C5–C6, 1.417(5); C6–C7, 1.415(4); C6–N2, 1.400(4); C7–C8, 1.434(4); C8–C9, 1.443(4); C9–N2, 1.368(4); C9–C10, 1.387(4); C8–C11, 1.395(4).

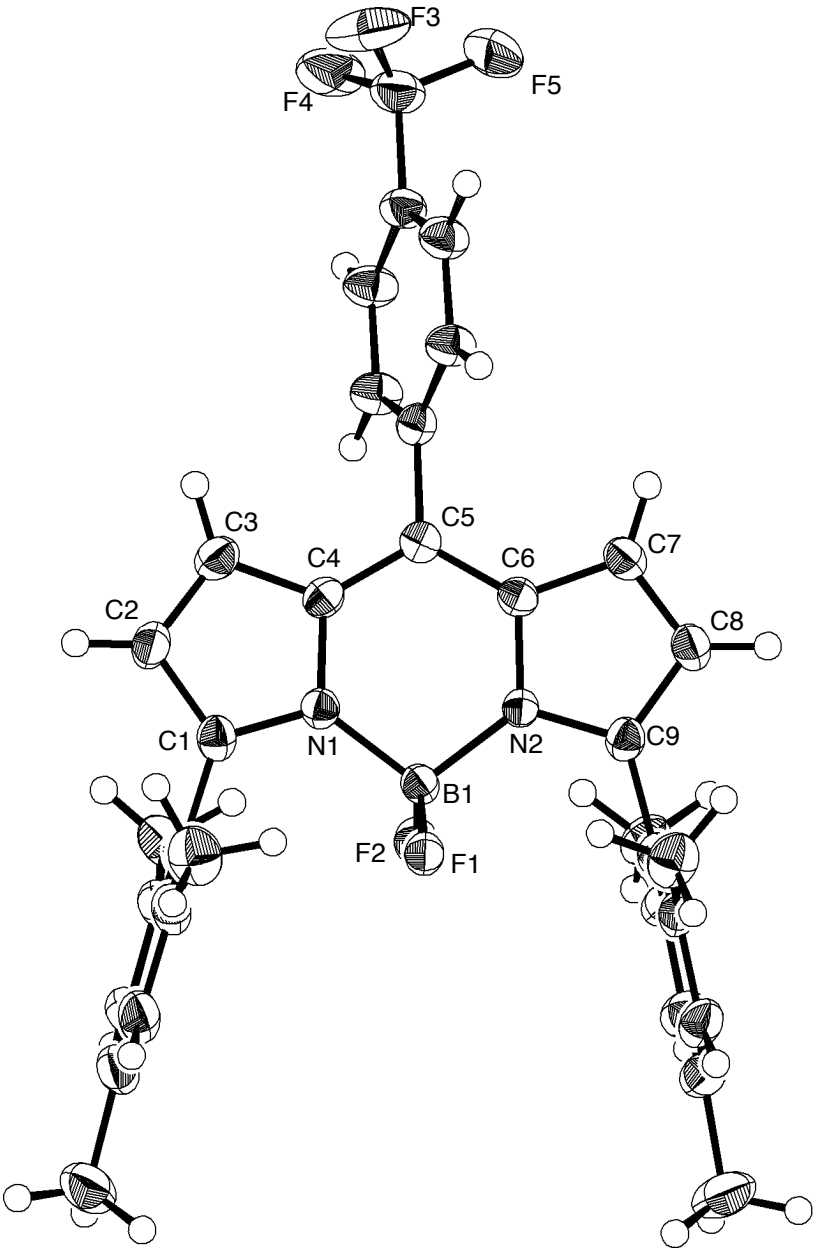
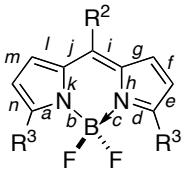


Figure S3. *ORTEP* drawing of **3** (50% probability for thermal ellipsoids). Selected bond lengths (Å): N1–B1, 1.559(3); N2–B1, 1.564(3); N1–C1, 1.353(3); C1–C2, 1.415(3); C2–C3, 1.376(3); C3–C4, 1.417(3); C4–N1, 1.392(3); C4–C5, 1.393(3); C5–C6, 1.390(3); C6–N2, 1.397(3); C6–C7, 1.410(3); C7–C8, 1.381(3); C8–C9, 1.411(3); C9–N2, 1.358(3).

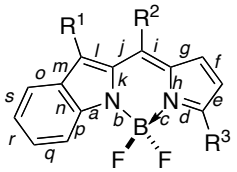
Table S1. Bond lengths for crystal structures and optimized structures for compounds **1**, **1′**, **2**, **2′**, and **3**

	3 (X-ray)	**3** (calc)[a]	**1** (X-ray)	**1′** (calc)[a]	**2** (X-ray)	**2′** (calc)[a]
a	1.353(3)	1.352	1.374(3)	1.363	1.368(4)	1.362
b	1.559(3)	1.574	1.528(4)	1.553	1.534(5)	1.553
c	1.563(3)	1.574	1.562(4)	1.571	1.548(5)	1.575
d	1.358(3)	1.352	1.349(3)	1.346	1.340(4)	1.345
e	1.411(3)	1.421	1.425(4)	1.426	1.419(5)	1.428
f	1.380(3)	1.384	1.360(4)	1.379	1.367(5)	1.377
g	1.409(3)	1.419	1.424(4)	1.428	1.430(5)	1.429
h	1.397(3)	1.396	1.400(3)	1.397	1.401(4)	1.398
i	1.390(3)	1.398	1.388(4)	1.398	1.383(5)	1.397
j	1.393(3)	1.398	1.423(4)	1.420	1.417(5)	1.422
k	1.392(3)	1.396	1.390(3)	1.394	1.400(4)	1.397
l	1.417(3)	1.419	1.417(4)	1.429	1.415(4)	1.421
m	1.376(3)	1.384	1.425(4)	1.416	1.434(4)	1.423
n	1.415(3)	1.421	1.415(4)	1.431	1.443(4)	1.451
o	–	–	1.417(4)	1.417	1.395(4)	1.398
p	–	–	1.406(4)	1.409	1.387(4)	1.395
q	–	–	1.377(4)	1.382	–	–
r	–	–	1.411(4)	1.423	–	–
s	–	–	1.371(4)	1.378	–	–

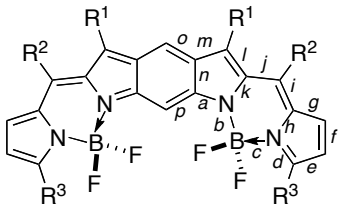
[a]Calculated at the B3LYP/6-31G(d) level of theory.



3



1 (R^1 = 4-hexyl-C_6H_5)
1' (R^1 = 4-methyl-C_6H_5)



2 (R^1 = 4-hexyl-C_6H_5)
2' (R^1 = 4-methyl-C_6H_5)

R^2 = 4-CF_3-C_6H_5
R^3 = mesityl

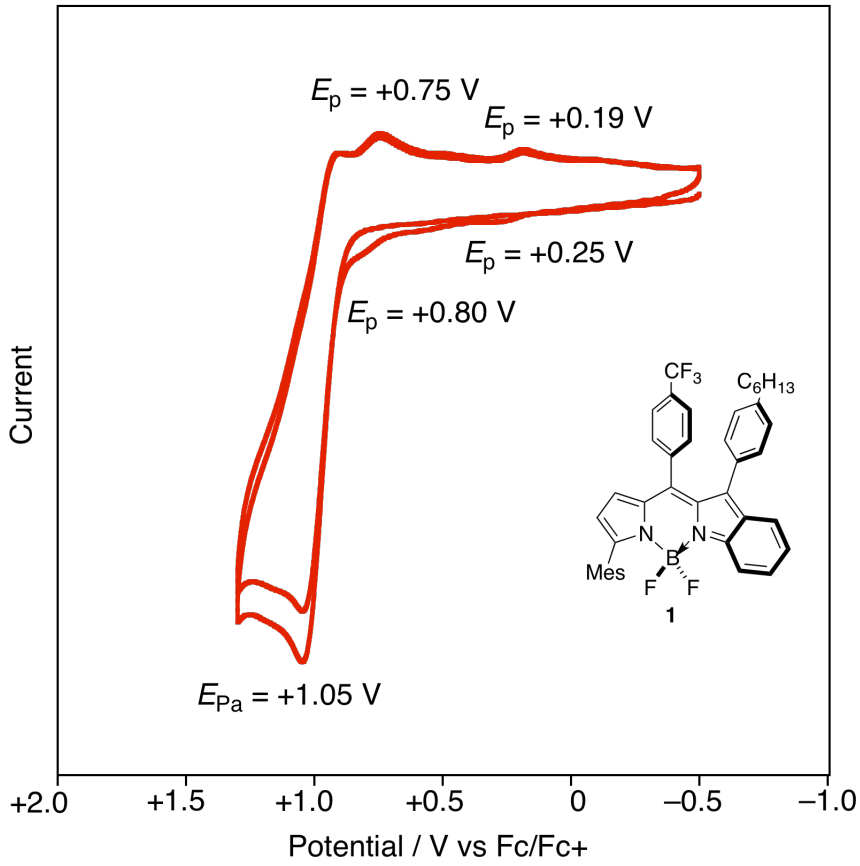


Figure S4. Cyclic voltammogram of **1** in CH_2Cl_2 (1mM), measured with $(n\text{-Bu})_4N^+PF_6^-$ as a supporting electrolyte at a scan rate of 100 mVs^{-1}.

Table S2. Photophysical data for **1**–**3** in various solvents

Compound		Absorption λ_{abs} [nm] (log ε)			
1	cyclohexane	348 (3.96)	512(sh) (4.45)	543 (4.68)	
	THF	349 (3.98)	505(sh) (4.46)	539 (4.73)	
	DMF	349 (3.92)	502(sh) (4.39)	538 (4.65)	
2	cyclohexane	493 (4.80)	637 (5.00)	789 (4.07)	868 (3.89)
	THF	489 (4.83)	629 (5.01)	753 (4.18)	
	DMF	486 (4.74)	622 (4.91)	771 (4.03)	
3	cyclohexane	326 (3.95)	493(sh) (4.22)	523 (4.78)	
	THF	328 (4.01)	488(sh) (4.26)	519 (4.80)	
	DMF	332 (3.99)	491(sh) (4.27)	520 (4.79)	

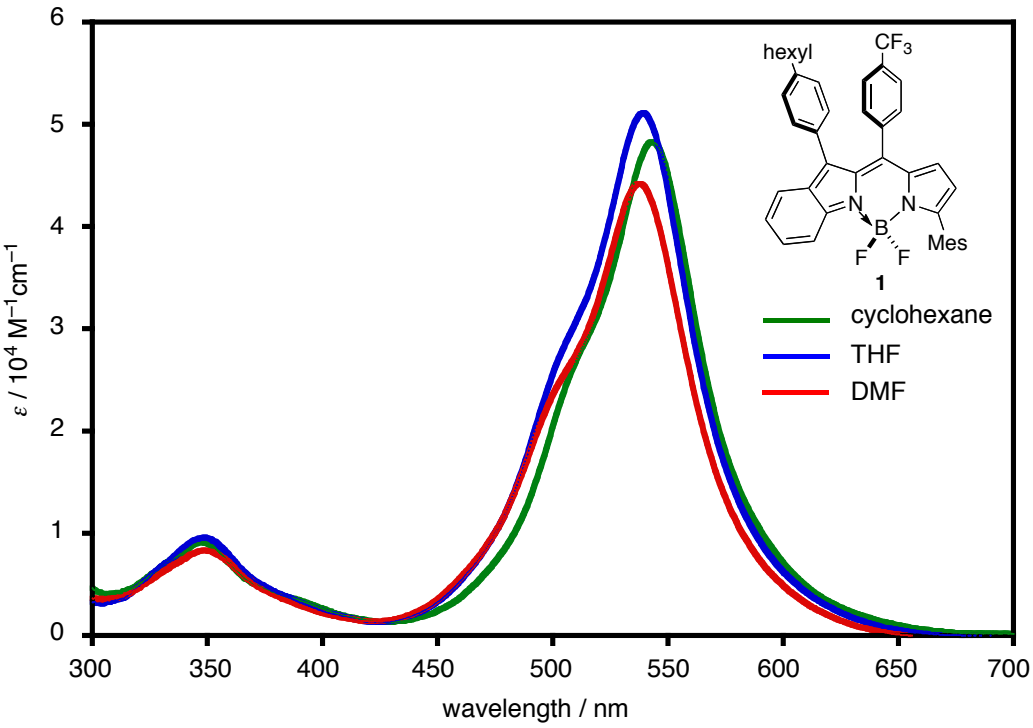


Figure S5. Absorption spectra of **1** in various solvents.

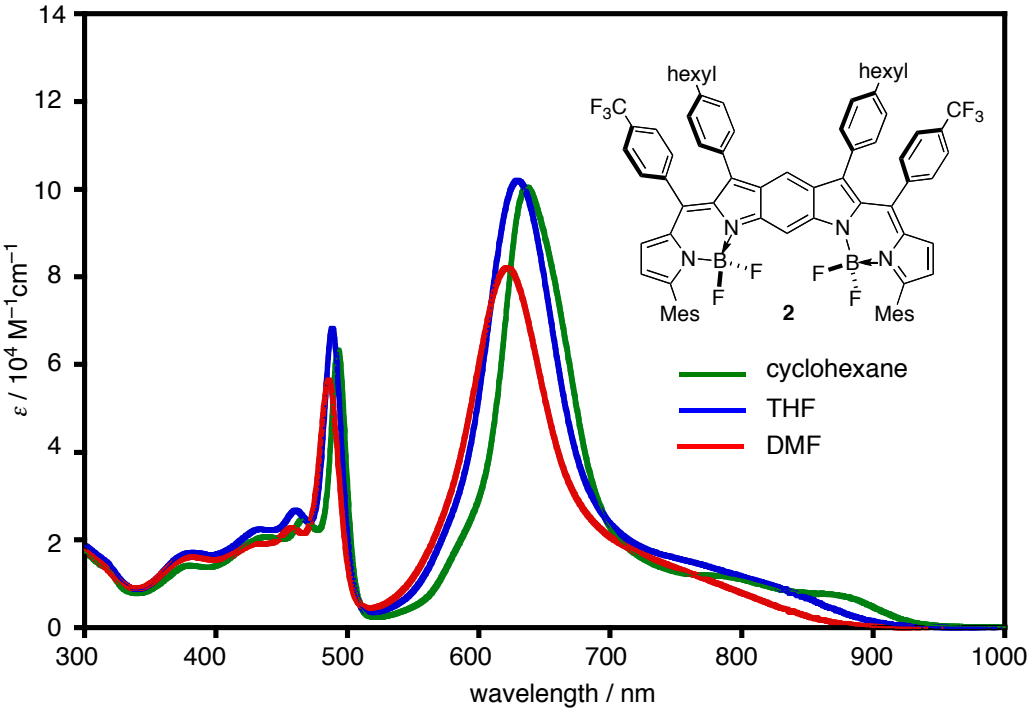


Figure S6. Absorption spectra of **2** in various solvents.

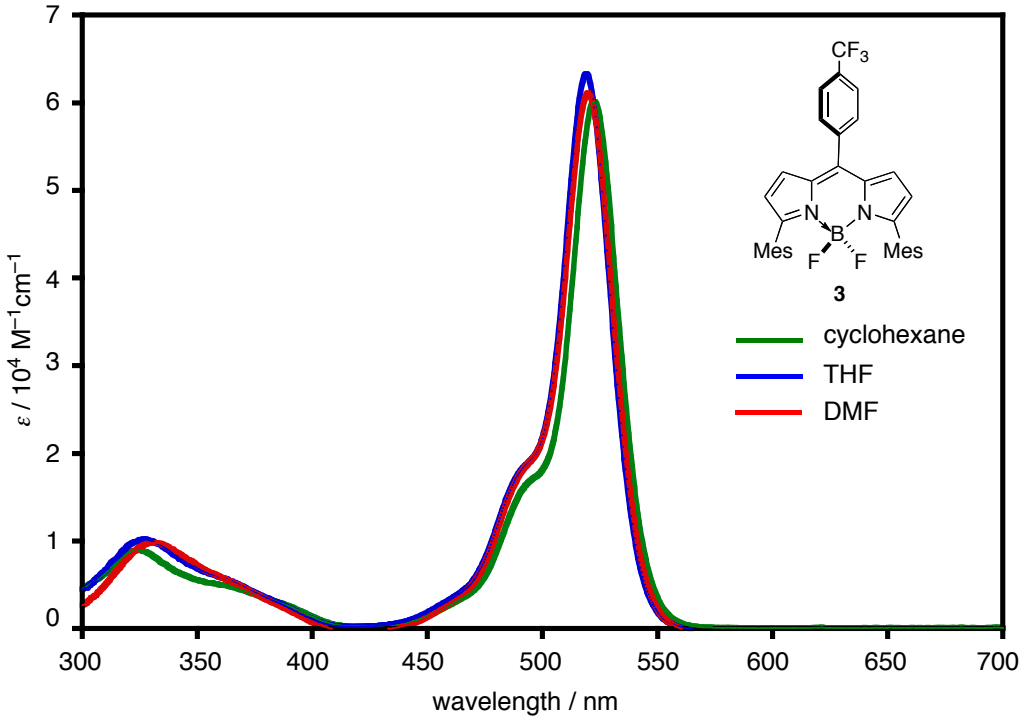
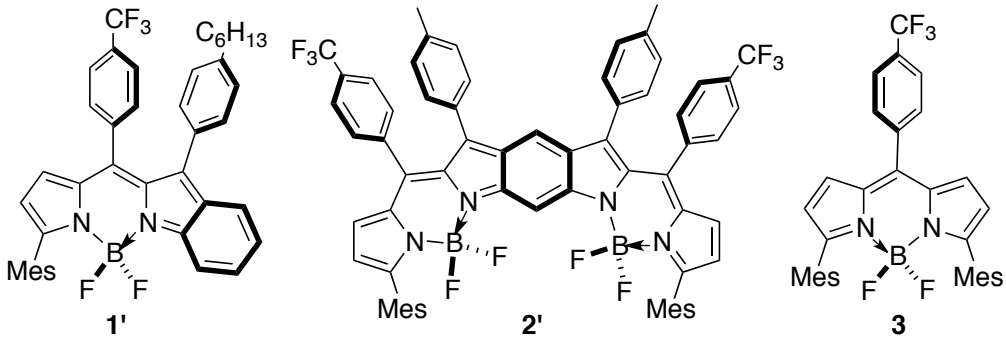


Figure S7. Absorption spectra of **3** in various solvents.

Table S3. Optical Transitions with Oscillator Strength Calculated at the TD DFT B3LYP/6-31G(d)//B3LYP/6-31G(d) Level



Compound	Calcd. [nm]	Exp. [nm][a]	Oscillator Strength *f*	composition
1'	596	539	0.0677	HOMO -> LUMO (0.56) HOMO–1 -> LUMO (0.35)
	457	505	0.5589	HOMO–1 -> LUMO (0.49) HOMO -> LUMO (0.26) HOMO-4 -> LUMO (0.24) HOMO–3 -> LUMO (0.11)
	420	349	0.0841	HOMO–4 -> LUMO (0.65) HOMO–1 -> LUMO (0.17)
2'	927	753	0.0581	HOMO -> LUMO (0.62) HOMO–1 -> LUMO+1 (0.13)
	561	629	1.1713	HOMO–1 -> LUMO (0.55) HOMO -> LUMO+1 (0.25)
	501	489	0.0873	HOMO–6 -> LUMO (0.68)
	461		0.1276	HOMO–1 -> LUMO+1 (0.61) HOMO–8 -> LUMO (0.26)
	454		0.1066	HOMO–7 -> LUMO (0.66) HOMO–8 -> LUMO (0.16) HOMO–6 -> LUMO+1 (0.13)
3	416	519	0.5160	HOMO -> LUMO (0.56) HOMO–5 -> LUMO (0.18) HOMO–3 -> LUMO (0.16)
	342	328	0.1128	HOMO–5 -> LUMO (0.65) HOMO -> LUMO (0.13)

[a]Measured in THF.

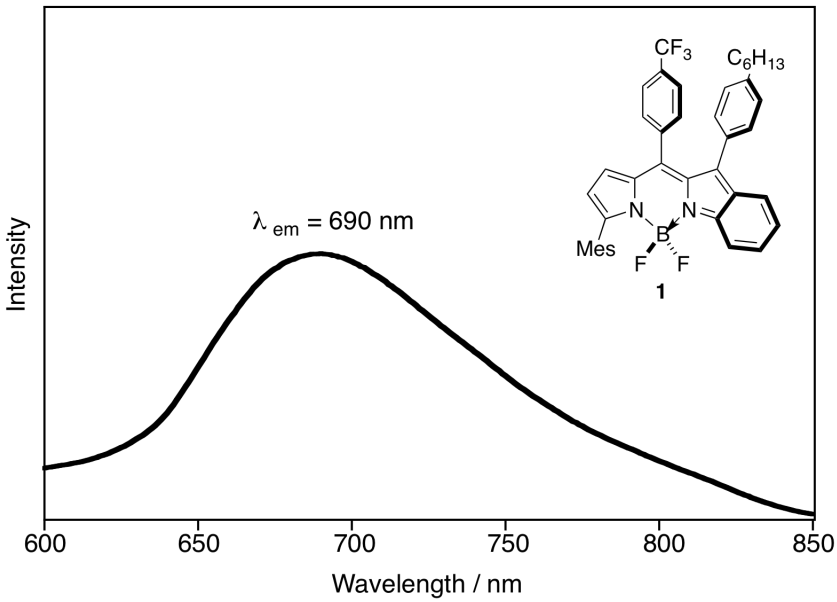


Figure S8. Fluorescence spectrum of **1** in THF.

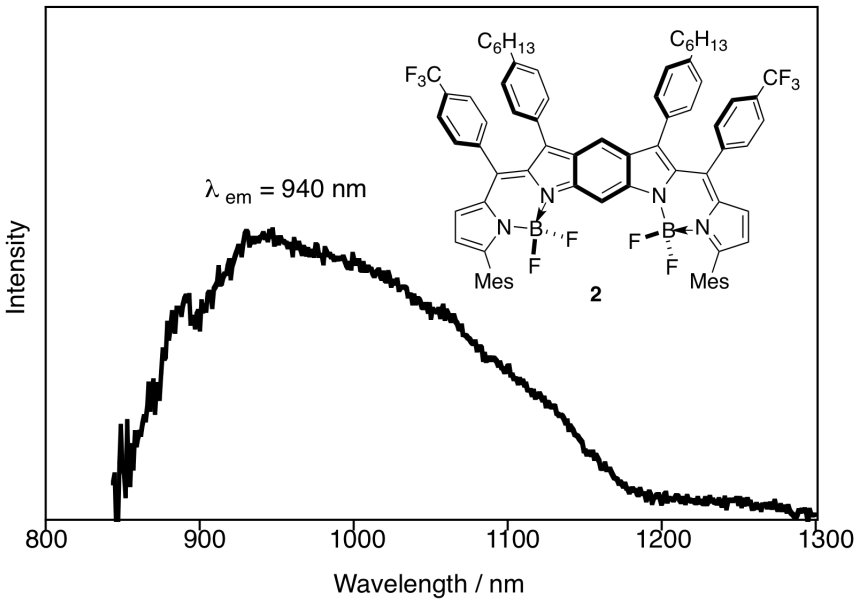


Figure S9. Fluorescence spectrum of **2** in THF.

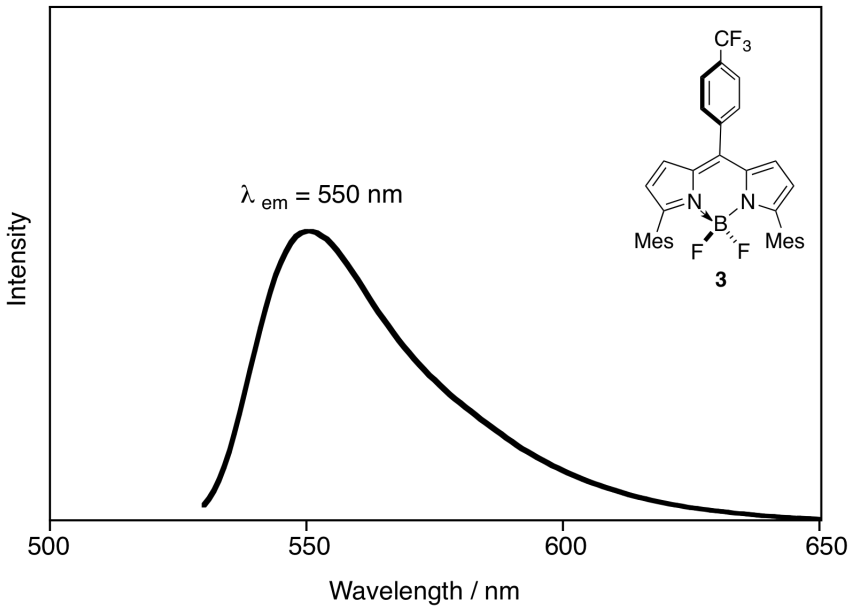


Figure S10. Fluorescence spectrum of **3** in THF.

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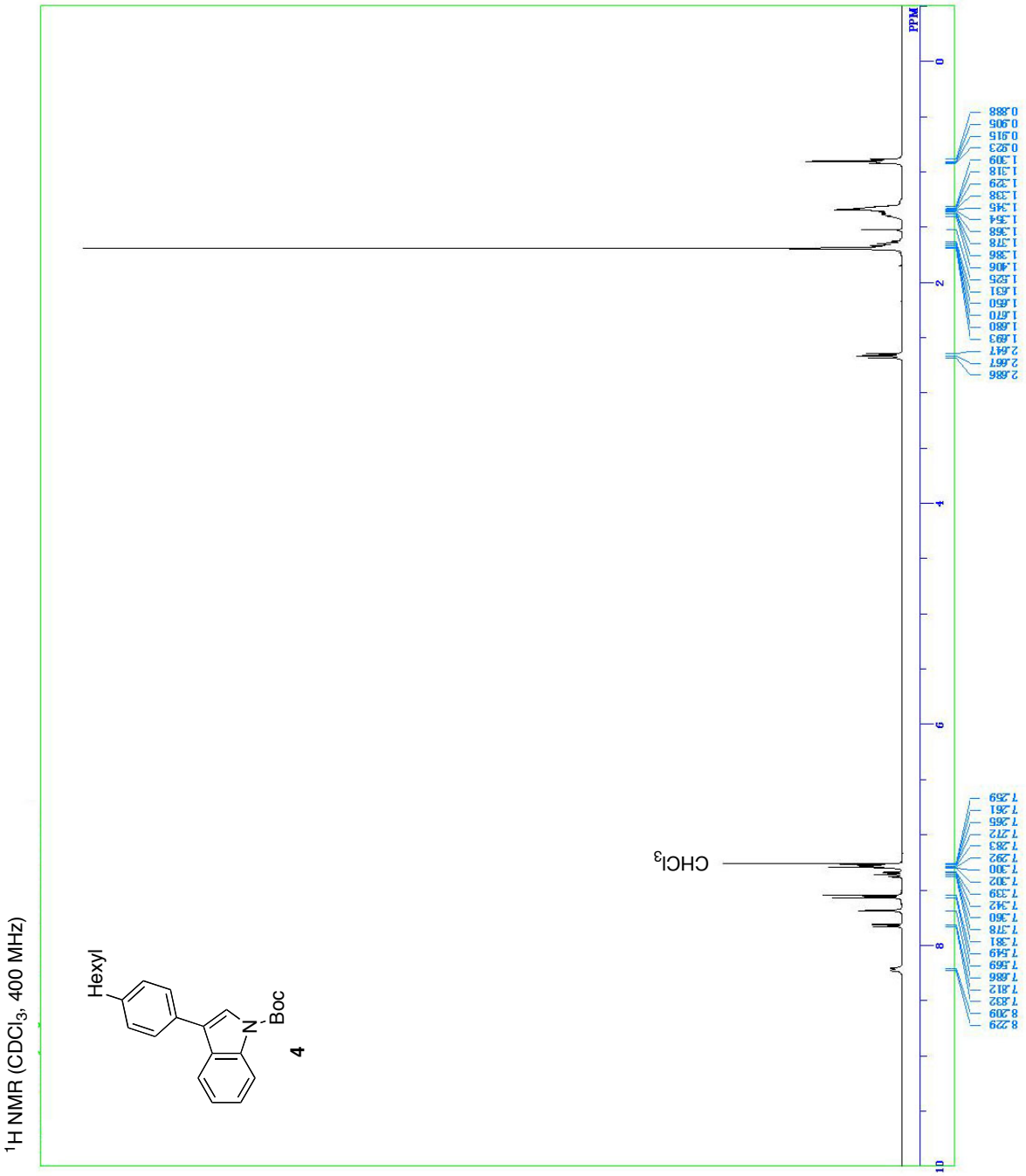
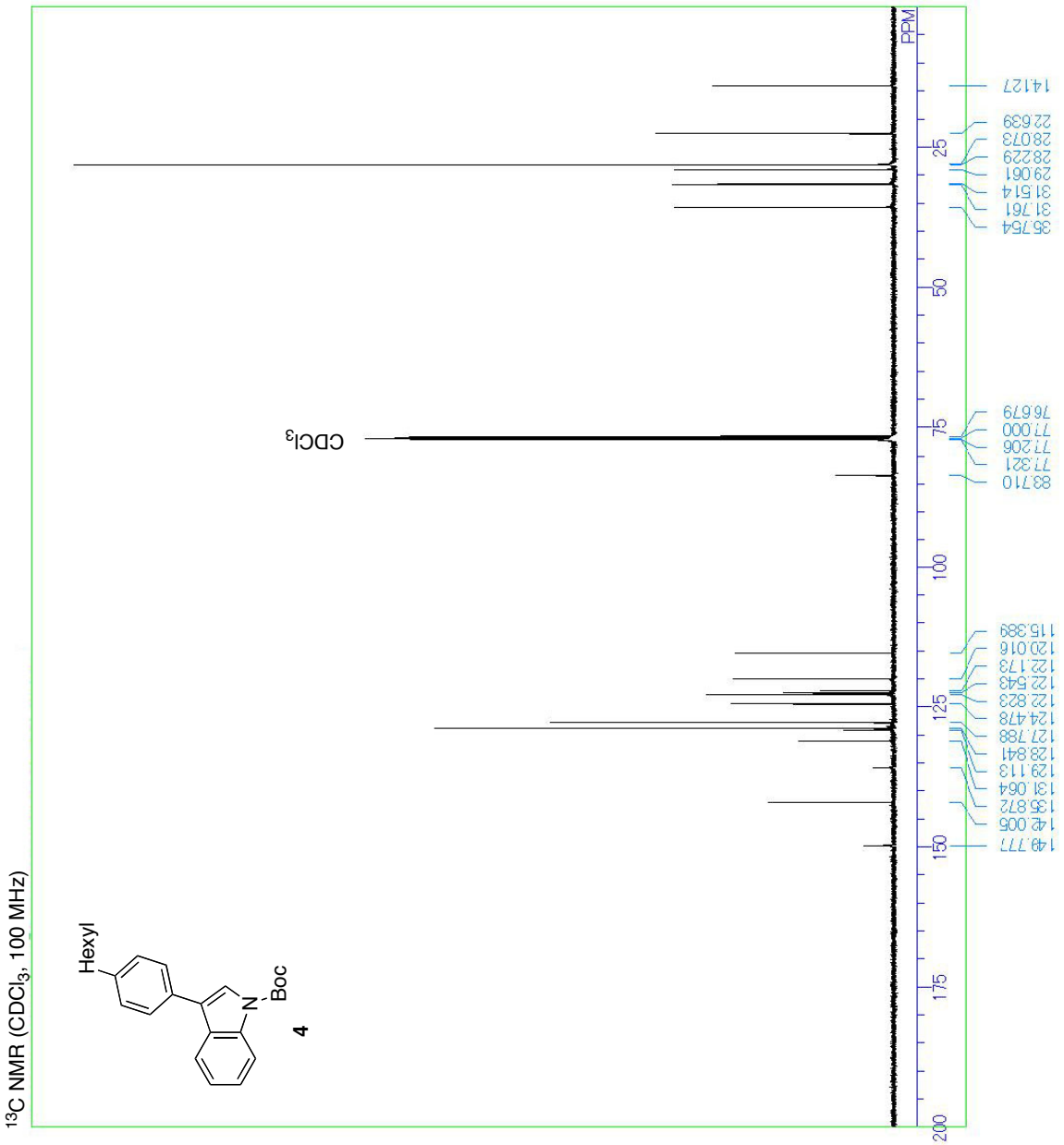
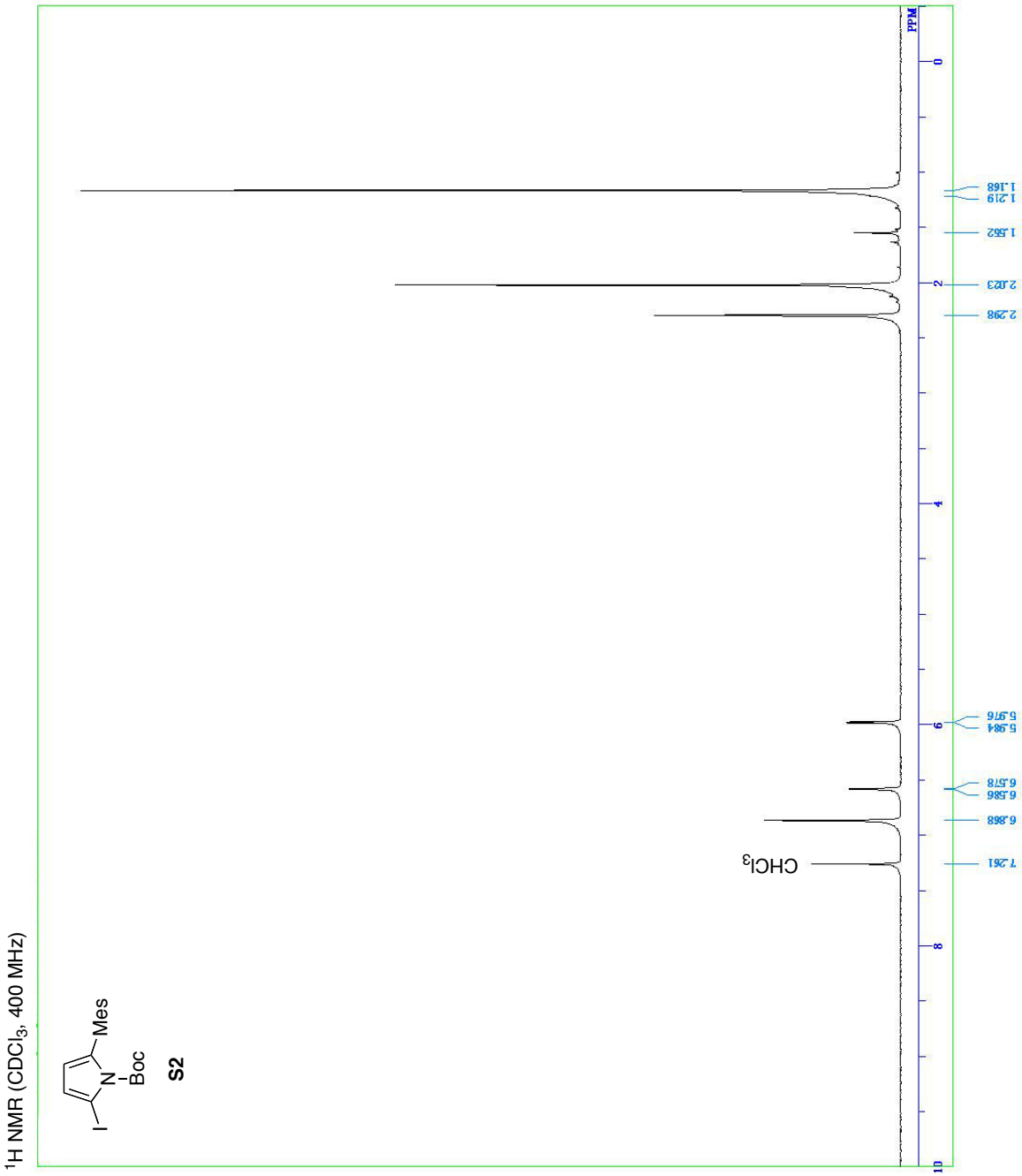
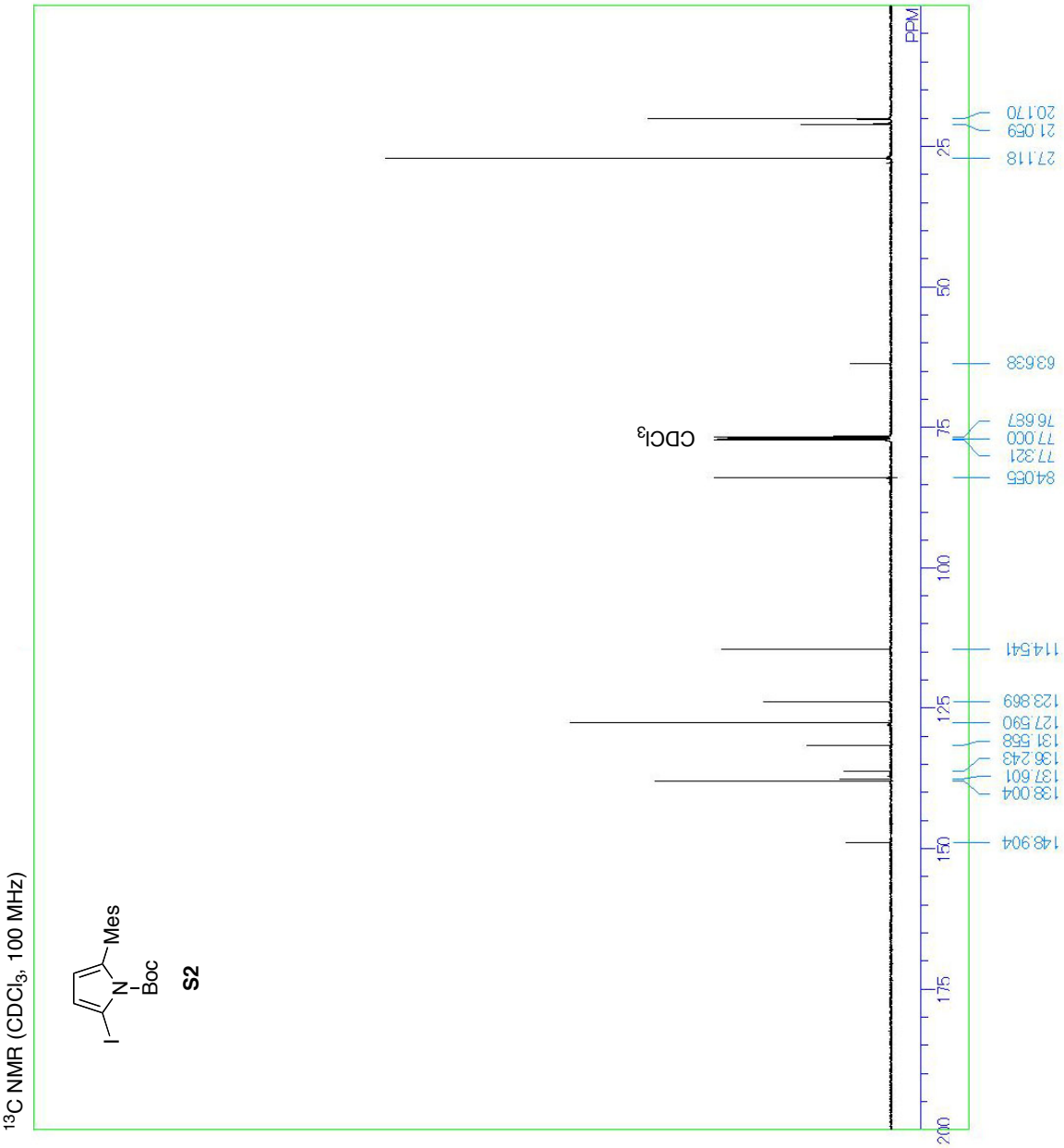
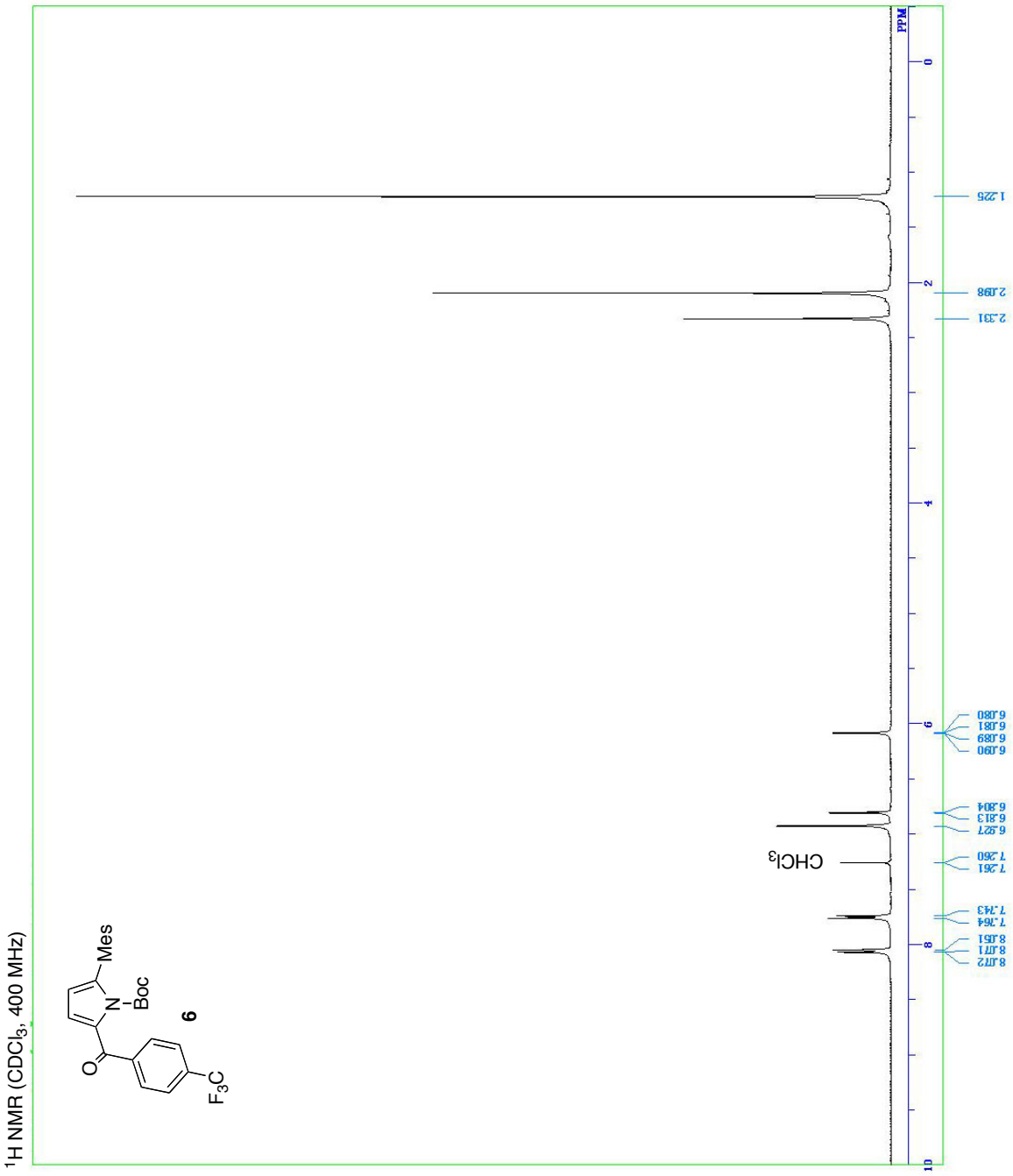
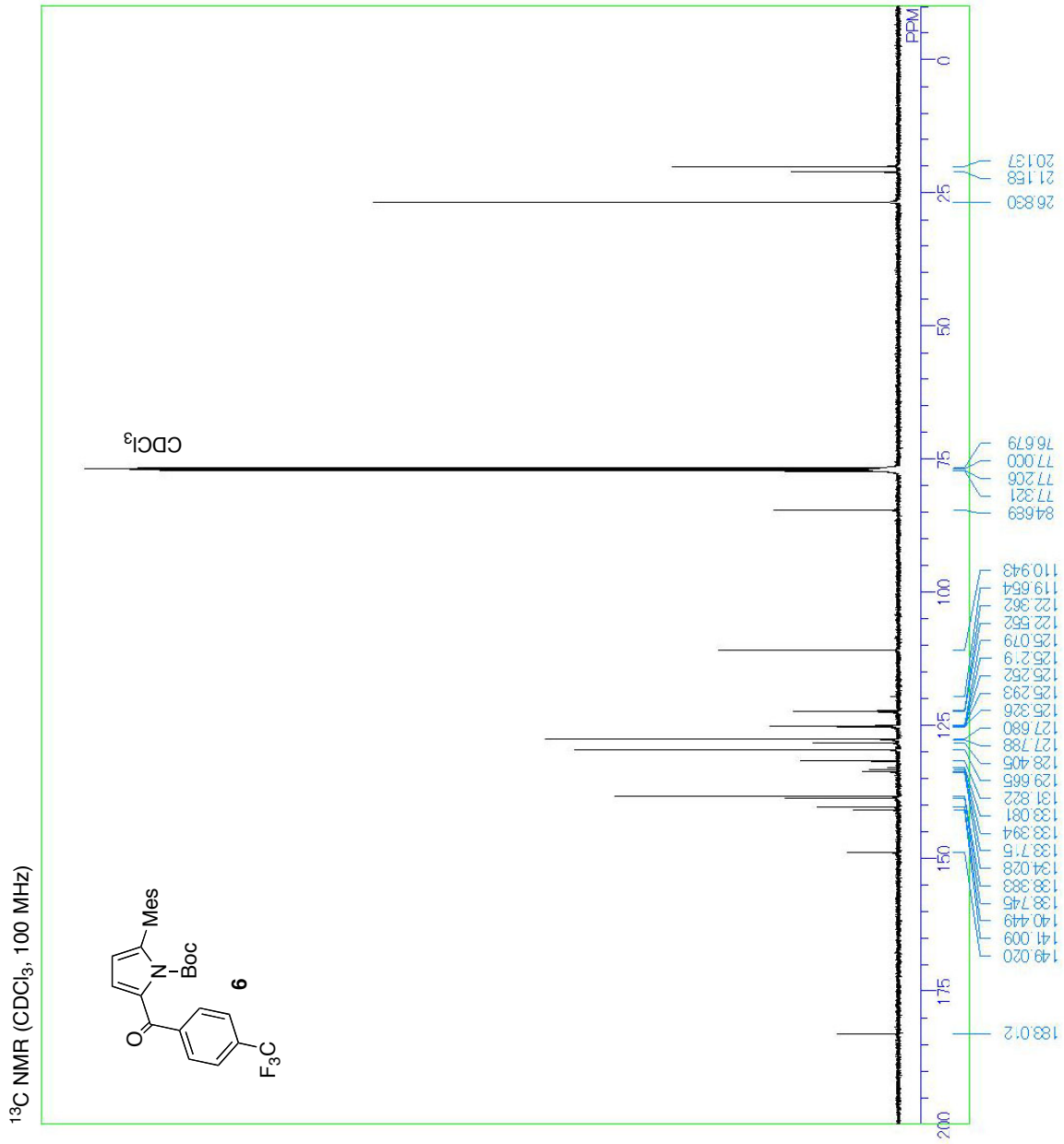

^{1}H NMR ($CDCl_3$, 400 MHz)
Hexyl
N
Boc
4
$CHCl_3$
PPM

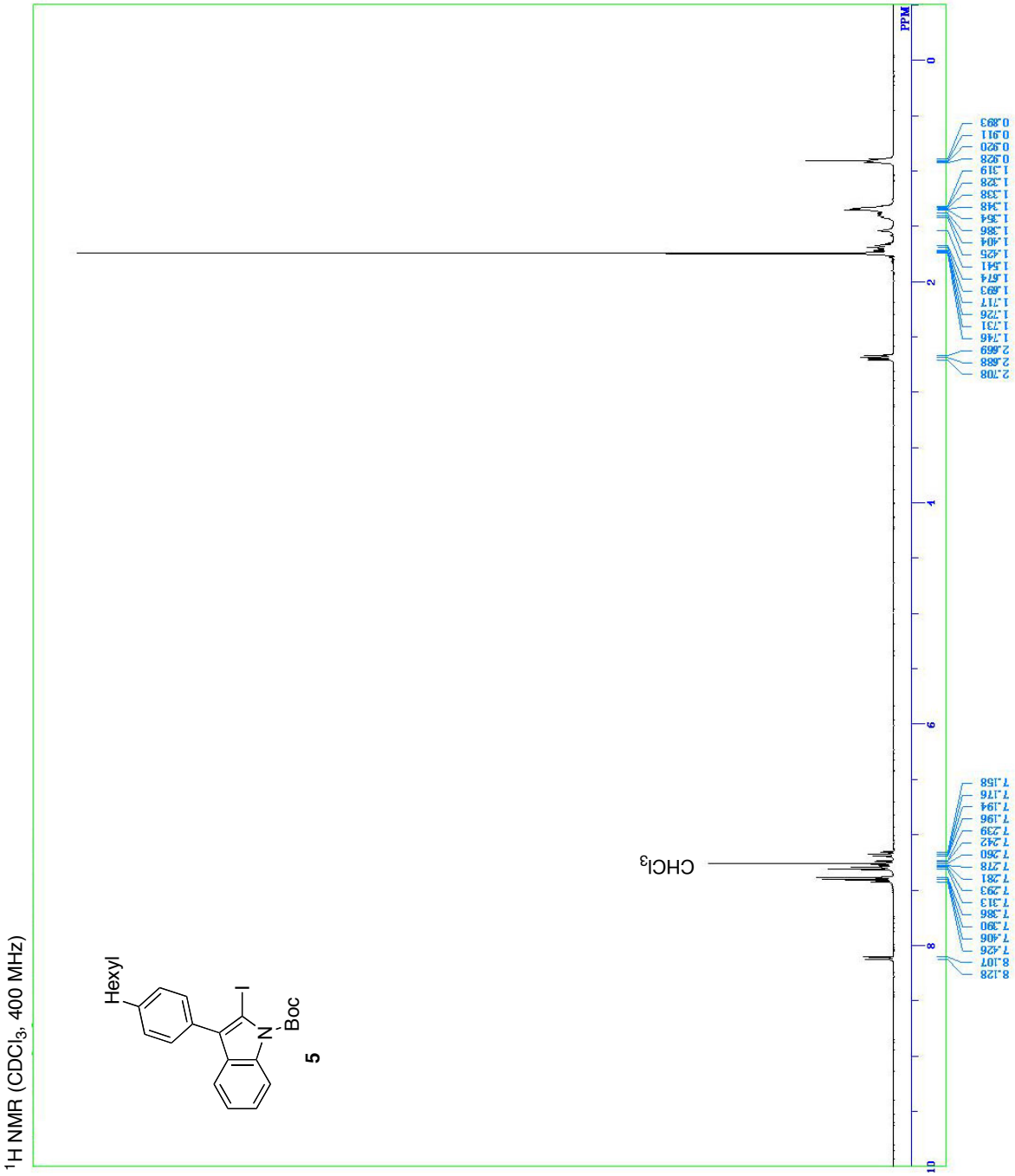

^{13}C NMR ($CDCl_3$, 100 MHz)
Hexyl
N
Boc
4
$CDCl_3$
PPM
14.127
22.639
28.073
28.229
29.061
31.514
31.761
35.754
76.679
77.000
77.206
77.321
83.710
115.389
120.016
122.173
122.543
122.823
124.478
127.788
128.841
129.113
131.064
135.872
142.005
149.777

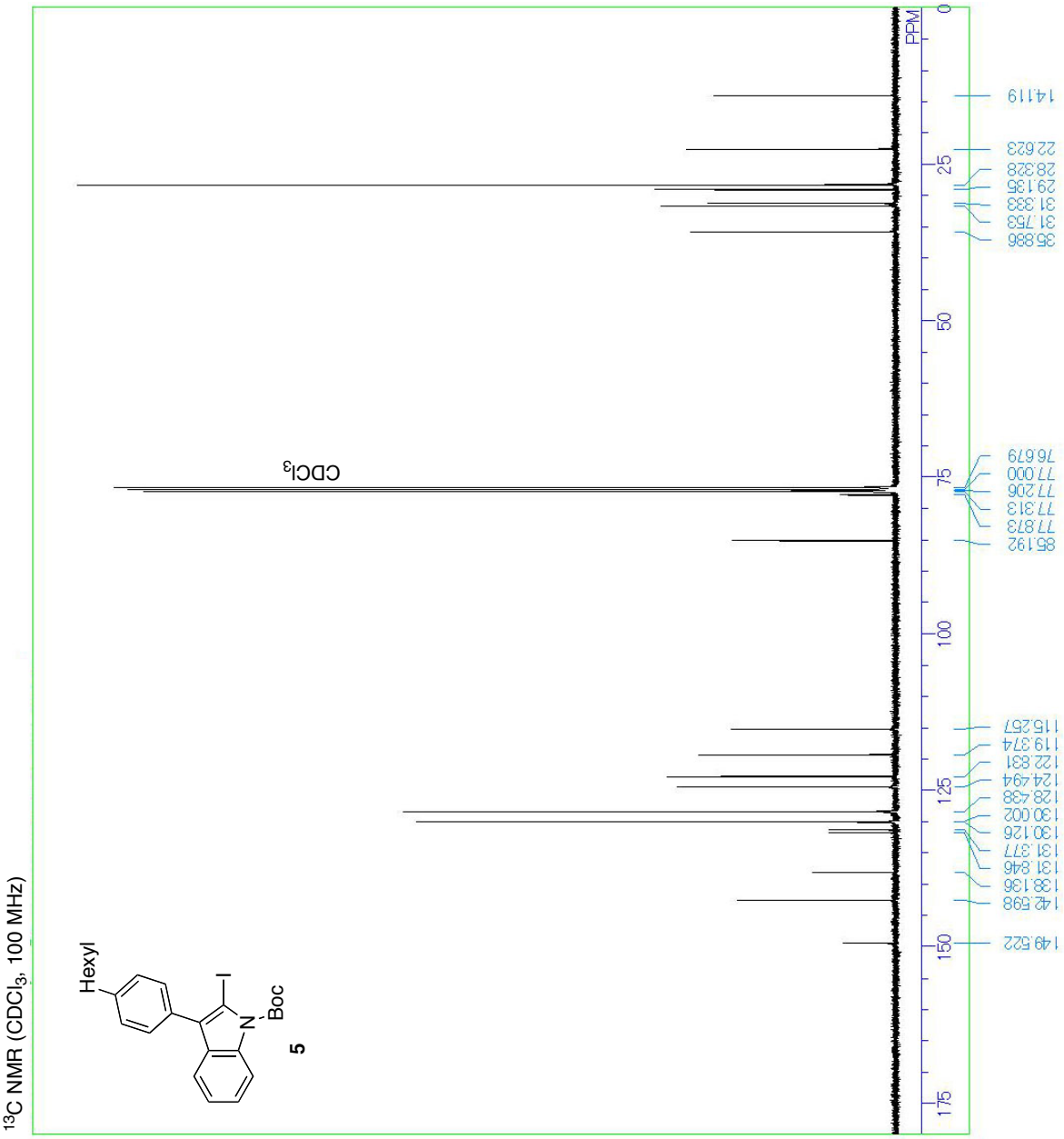

^{1}H NMR ($CDCl_3$, 400 MHz)
Mes
N
Boc
I
S2
$CHCl_3$
PPM
1.168
1.219
1.562
2.023
2.298
5.976
5.984
6.578
6.586
6.868
7.261

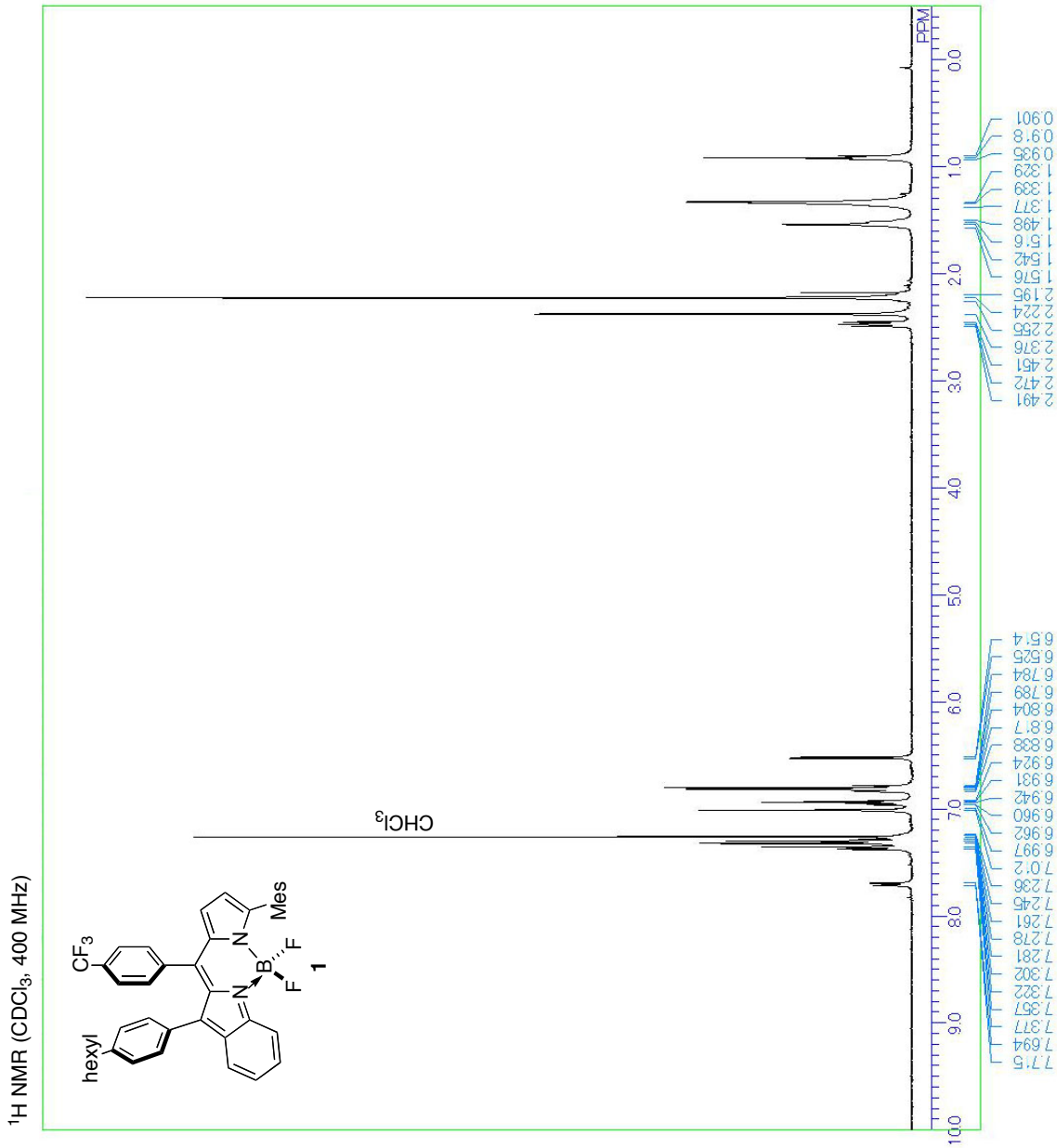

^{13}C NMR ($CDCl_3$, 100 MHz)
Mes
N
Boc
I
S2
$CDCl_3$
PPM
20.170
21.059
27.118
63.638
76.657
77.000
77.321
84.055
114.541
123.869
127.590
131.558
136.243
137.601
138.004
148.904

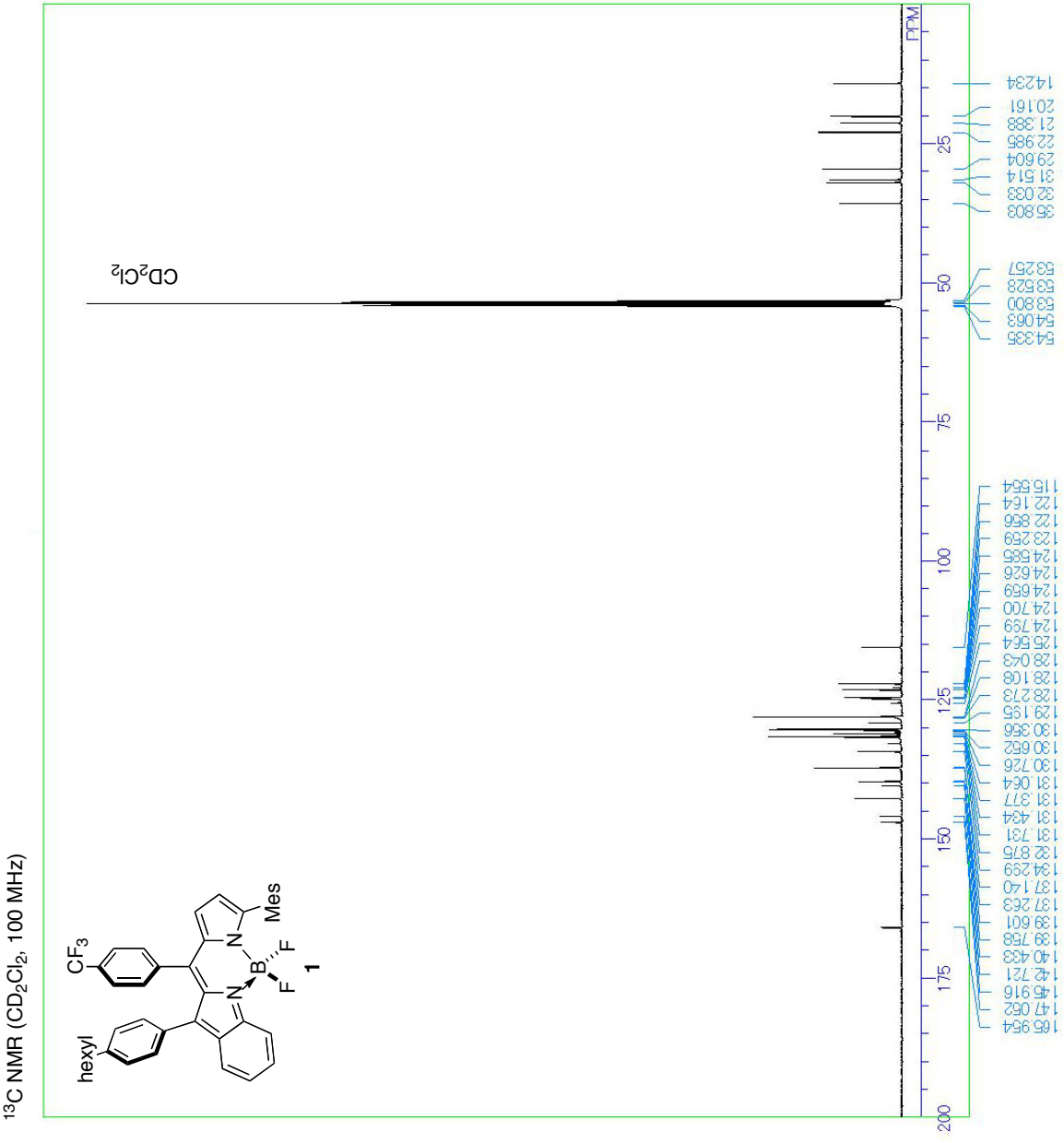

^{1}H NMR ($CDCl_3$, 400 MHz)
Mes
N
Boc
O
F_3C
6
$CHCl_3$
PPM
0
2
4
6
8
10
1.225
2.098
2.331
6.080
6.081
6.089
6.090
6.804
6.813
6.927
7.260
7.261
7.743
7.764
8.051
8.071
8.072

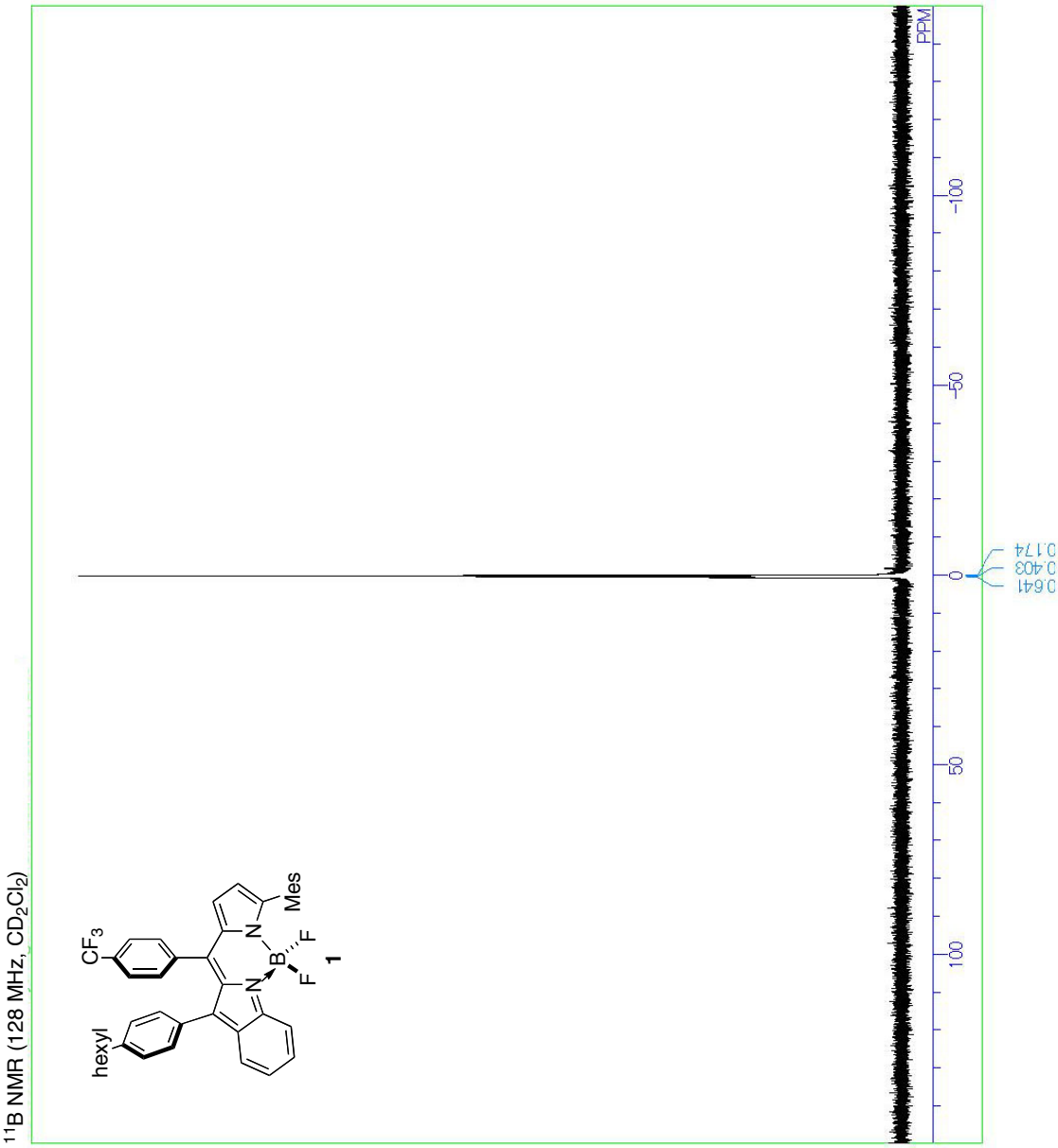

^{13}C NMR ($CDCl_3$, 100 MHz)
$CDCl_3$
Mes
N
Boc
O
F_3C
6
PPM
0
25
50
75
100
125
150
175
200
20.137
21.158
26.830
76.679
77.000
77.206
77.321
84.689
110.943
119.654
122.362
122.562
126.079
126.219
126.252
126.293
126.326
127.680
127.788
128.405
129.665
131.822
138.081
138.394
138.715
139.028
138.383
138.745
140.449
141.009
149.020
183.012

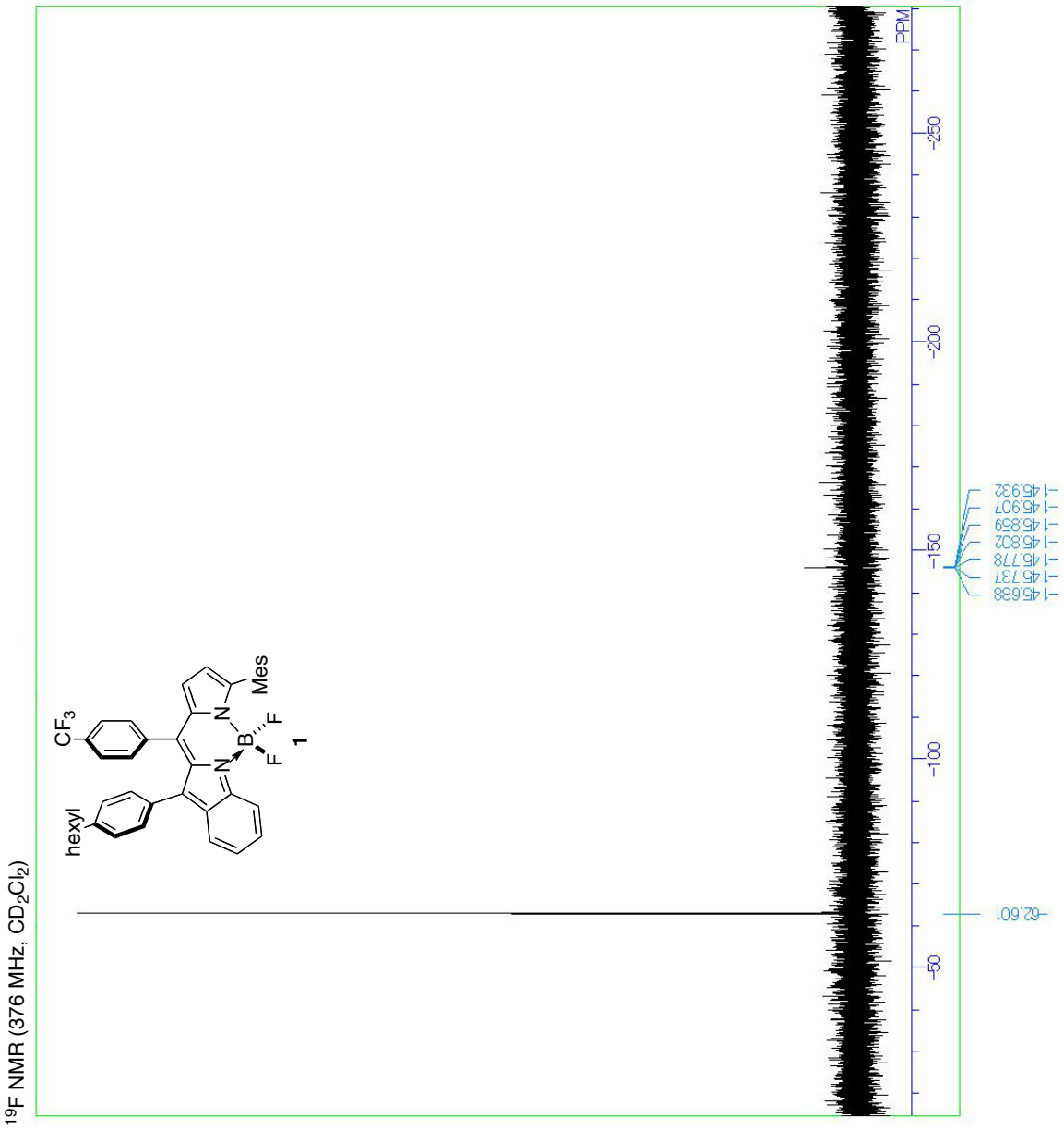

^{1}H NMR ($CDCl_3$, 400 MHz)
Hexyl
I
N
Boc
5
$CHCl_3$
PPM


^{13}C NMR (CDCl$_3$, 100 MHz)
CDCl$_3$
PPM
0
25
50
75
100
125
150
175
14.119
22.623
28.328
29.135
31.338
31.753
35.886
76.679
77.000
77.206
77.313
77.873
85.192
115.257
119.374
122.831
124.494
128.438
130.002
130.126
131.377
131.846
138.136
142.598
149.522
Hexyl
I
N
Boc
5




^{13}C NMR (CD_2Cl_2, 100 MHz)
CD_2Cl_2
PPM
25
50
75
100
125
150
175
200
Mes
CF_3
hexyl
B
F
F
N
N
1


^{11}B NMR (128 MHz, CD_2Cl_2)
PPM
100
50
0
-50
-100
0.641
0.403
0.174
Mes
CF_3
hexyl
N
B
F
F
1


^{19}F NMR (376 MHz, CD_2Cl_2)
PPM
-250
-200
-150
-100
-50
-145.932
-145.907
-145.859
-145.802
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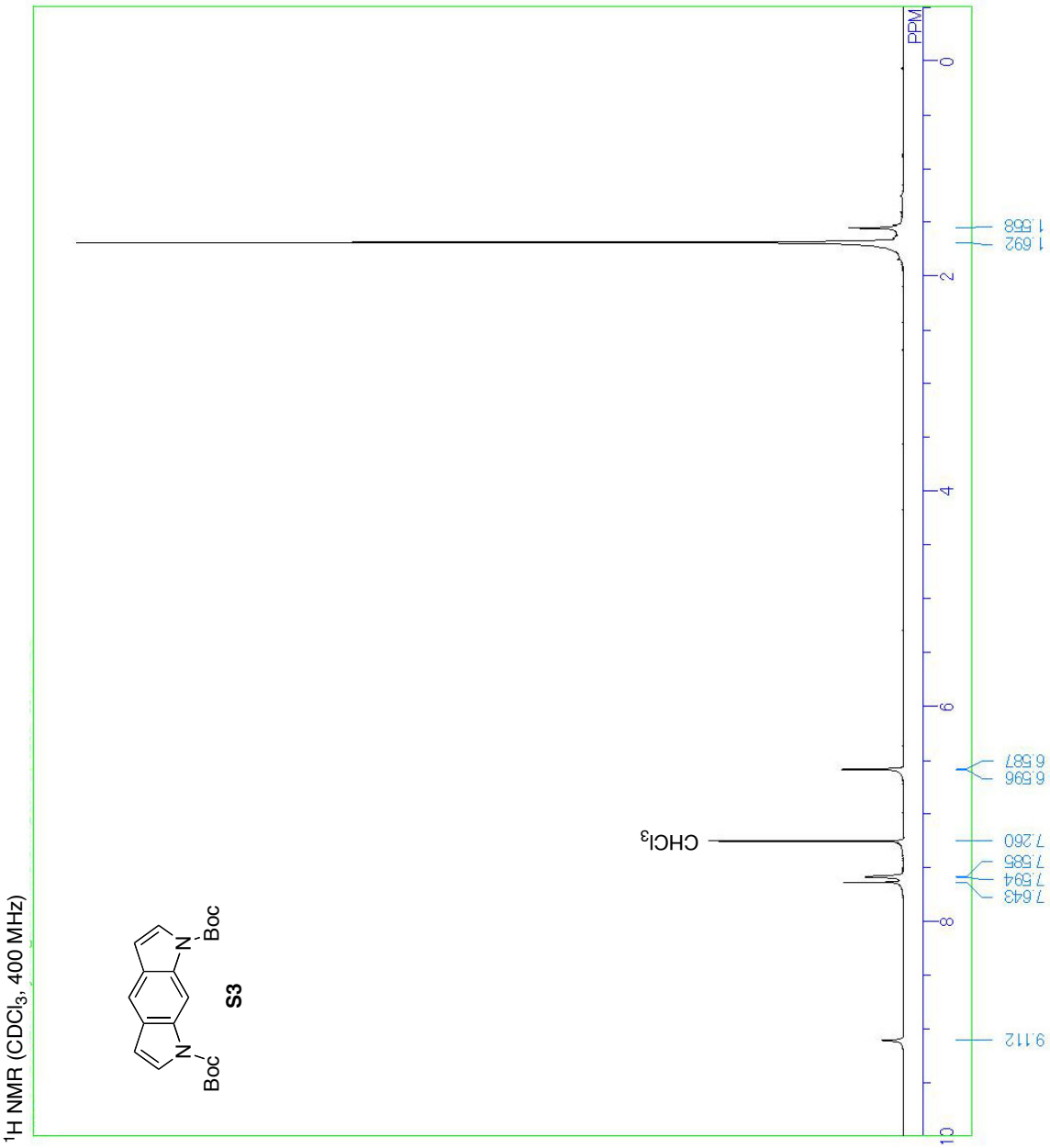
CF3
Mes
F
F
B
N
N
hexyl
1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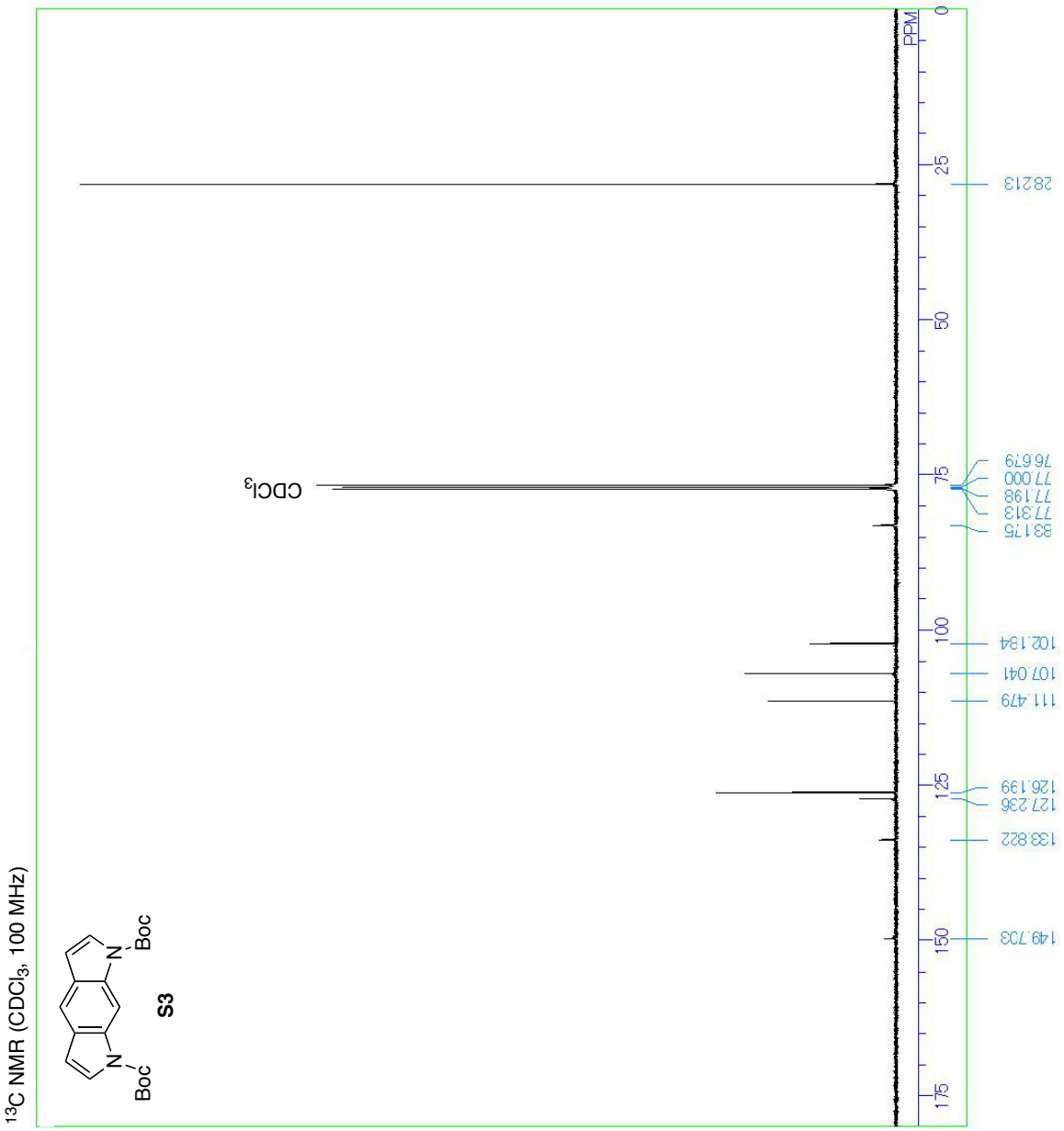
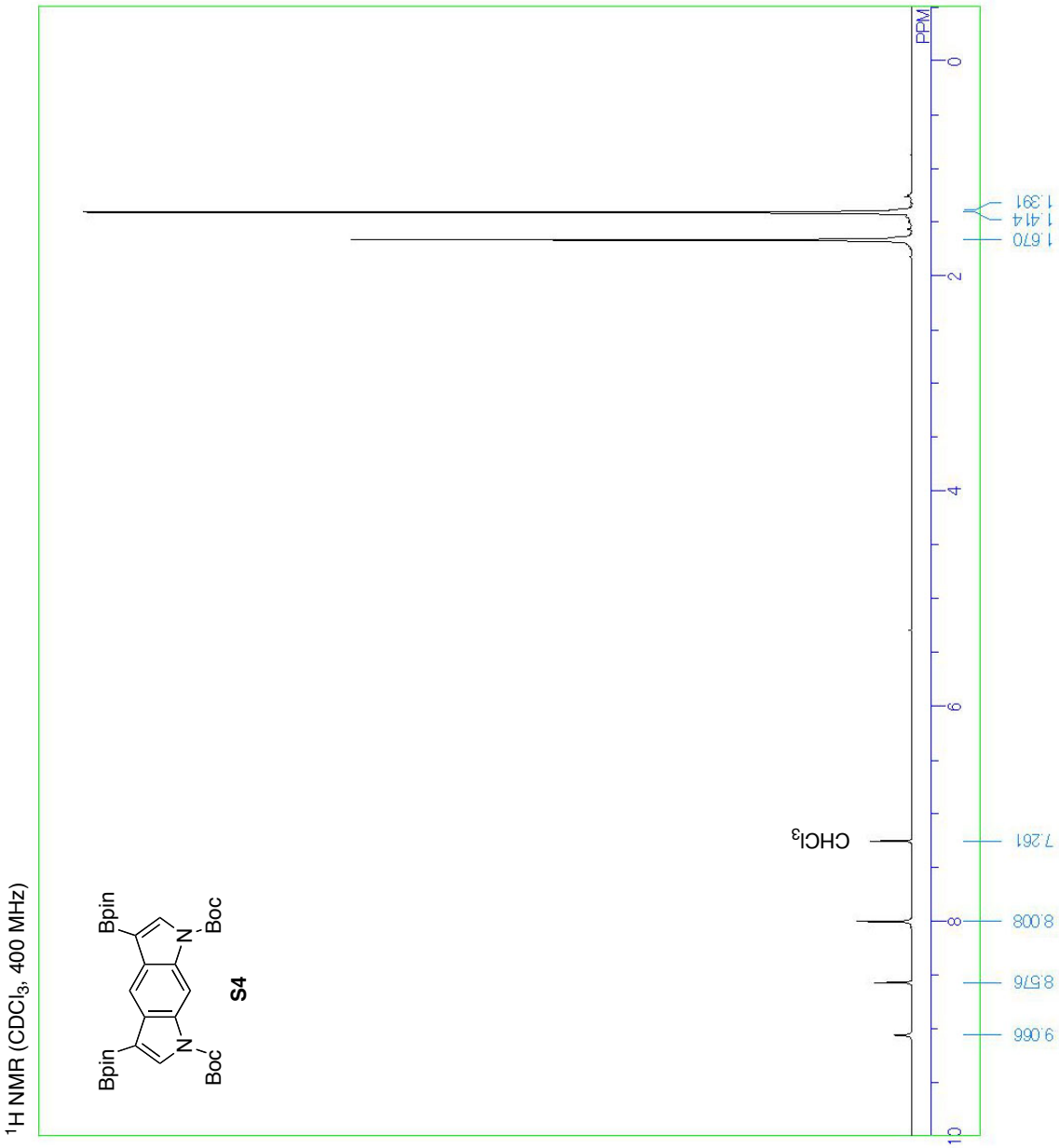
S3
Boc
Boc
$CHCl_3$
PPM
0
2
4
6
8
10
1.568
1.692
6.587
6.596
7.260
7.585
7.594
7.643
9.112


^{13}C NMR ($CDCl_3$, 100 MHz)
S3
Boc
Boc
$CDCl_3$
PPM
0
25
50
75
100
125
150
175
28.213
76.679
77.000
77.198
77.313
83.175
102.184
107.041
111.479
126.139
127.236
133.822
149.703


^{1}H NMR ($CDCl_3$, 400 MHz)
Bpin
Boc
N
Bpin
Boc
N
S4
$CHCl_3$
7.261
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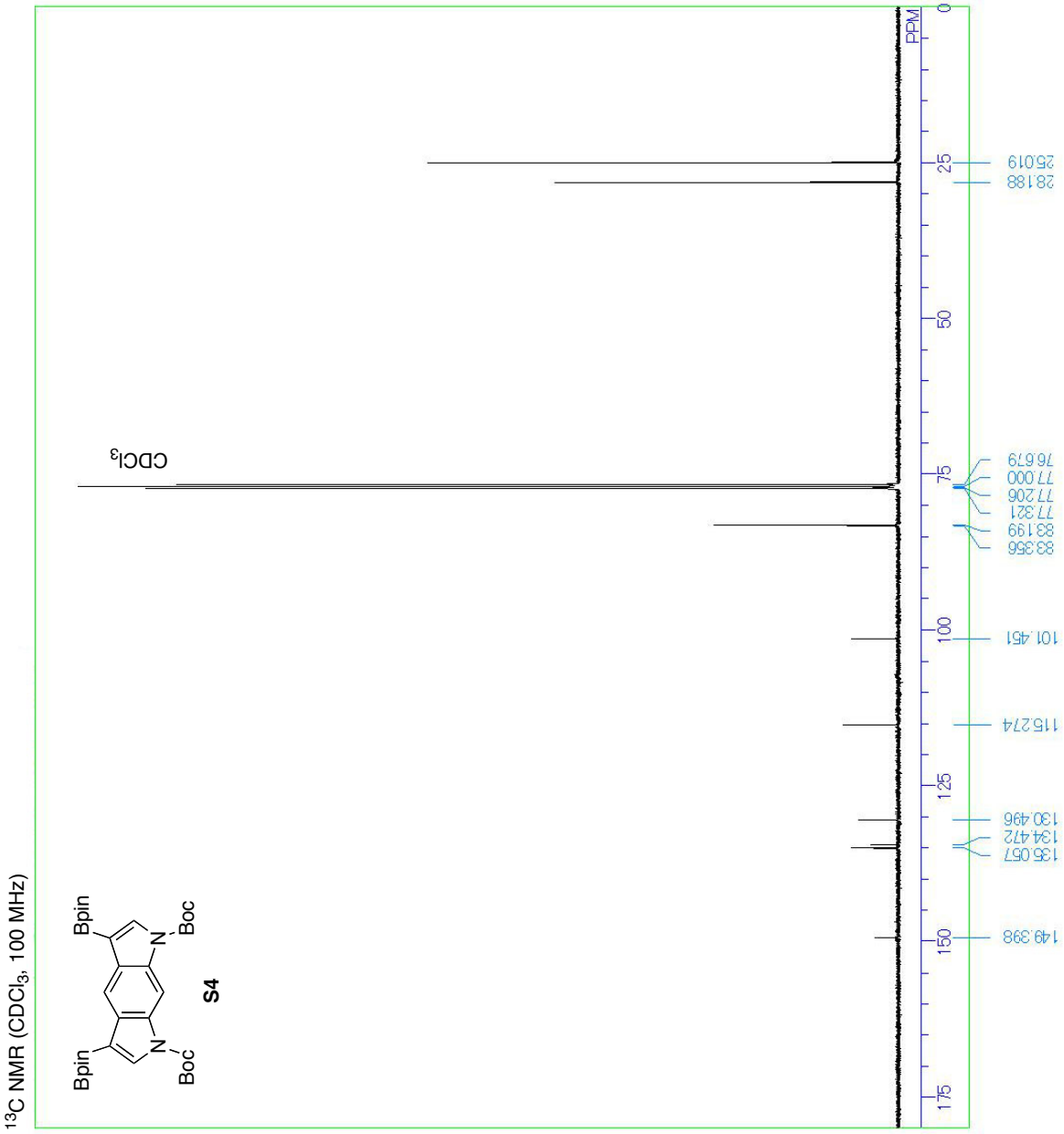
8.576
9.066
1.670
1.414
1.391
PPM
0
2
4
6
8
10


^{13}C NMR ($CDCl_3$, 100 MHz)
$CDCl_3$
Bpin
Boc
N
N
Bpin
Boc
S4
PPM
0
25
50
75
100
125
150
175
25.019
28.188
76.679
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83.199
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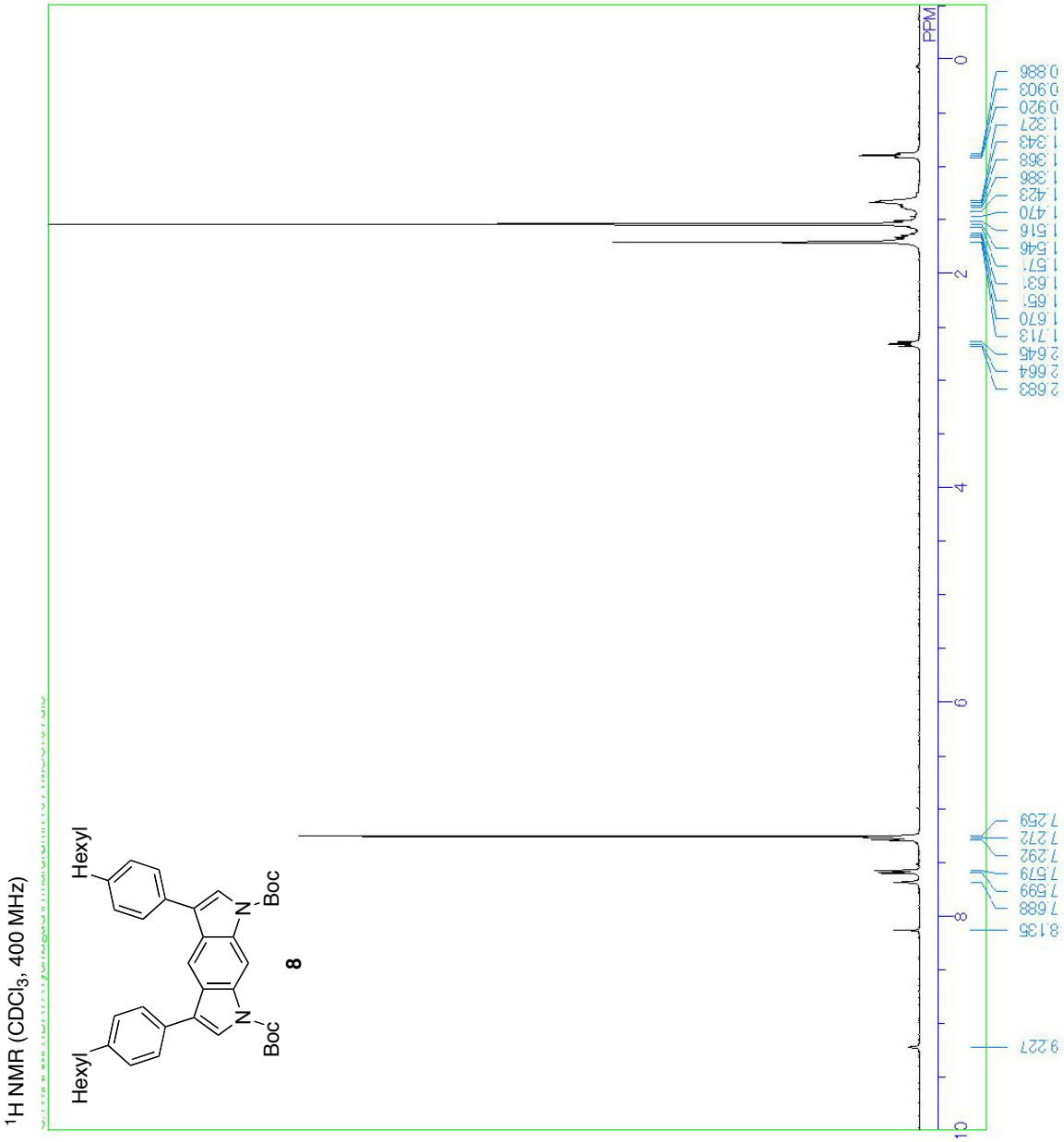
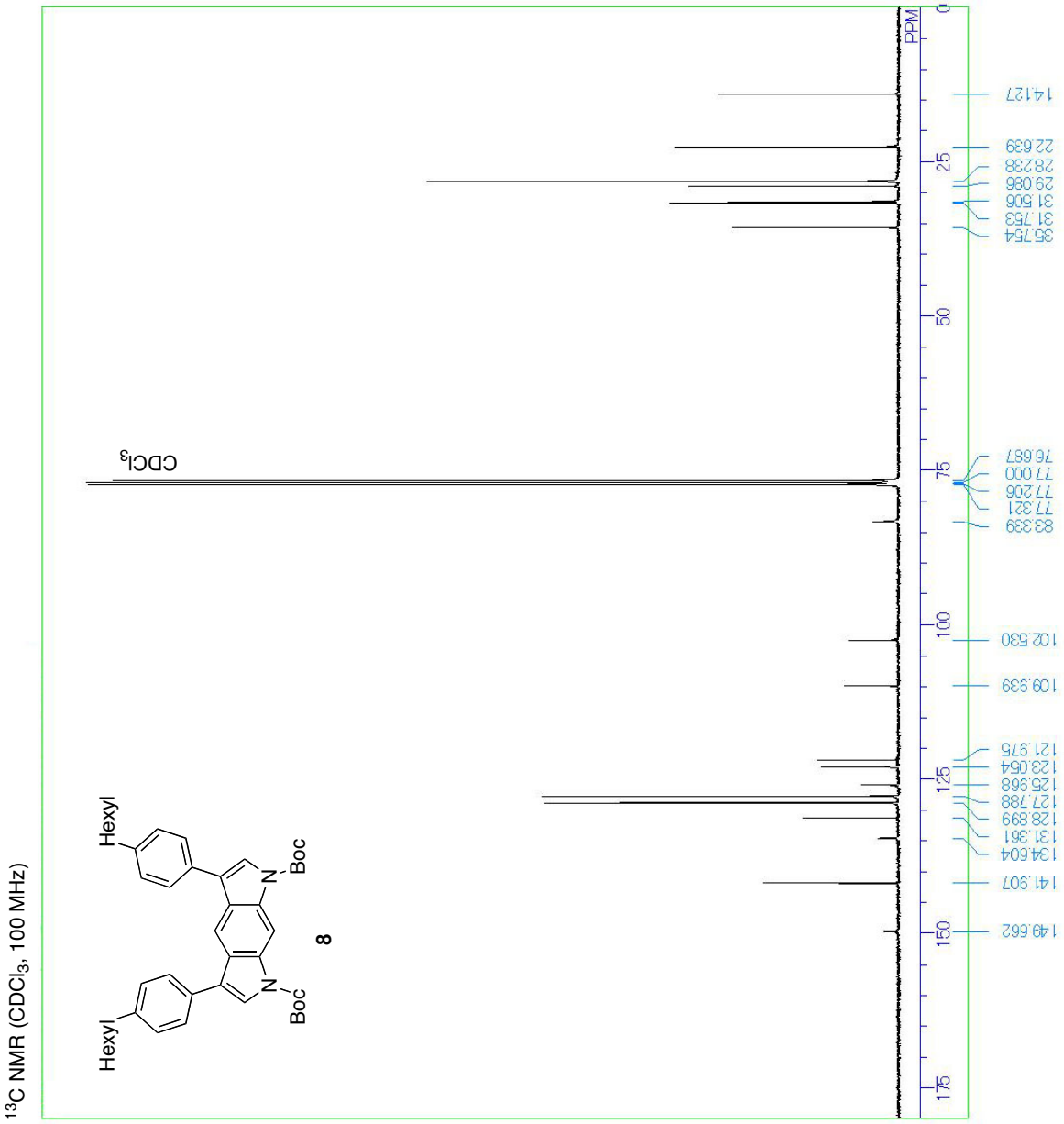
149.398


^{1}H NMR ($CDCl_3$, 400 MHz)
Hexyl
Boc
N
Boc
N
Hexyl
8
PPM
0
2
4
6
8
10
0.886
0.903
0.920
1.327
1.343
1.368
1.386
1.423
1.470
1.516
1.546
1.571
1.631
1.651
1.670
1.713
2.645
2.664
2.683
7.259
7.272
7.292
7.579
7.599
7.688
8.136
9.227


^{13}C NMR ($CDCl_3$, 100 MHz)
$CDCl_3$
Hexyl
Boc
N
Boc
N
Hexyl
8
PPM
0
25
50
75
100
125
150
175
14.127
22.639
28.238
29.086
31.506
31.753
35.754
76.687
77.000
77.206
77.321
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121.575
123.054
125.568
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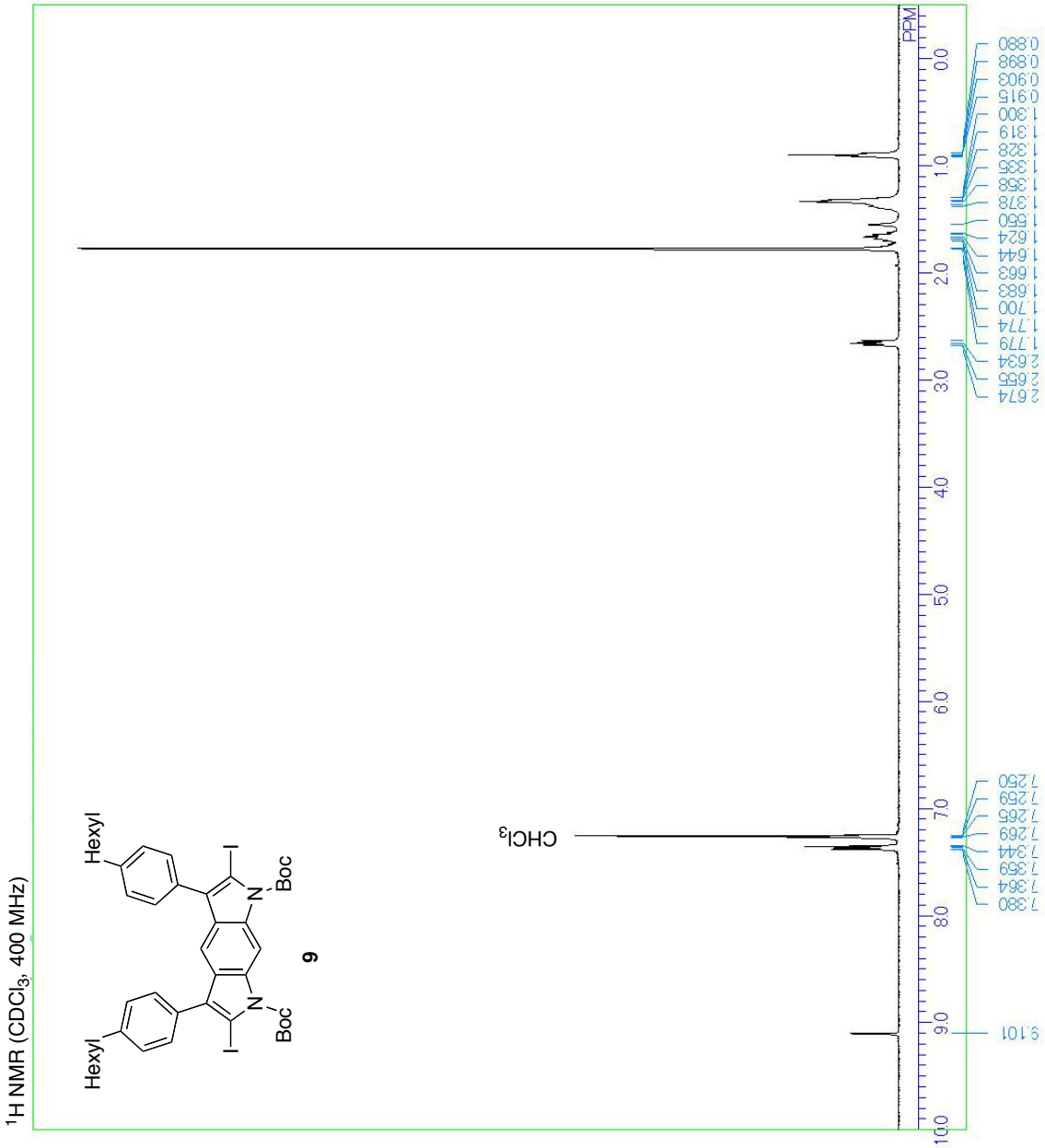
128.899
131.361
134.604
141.507
149.662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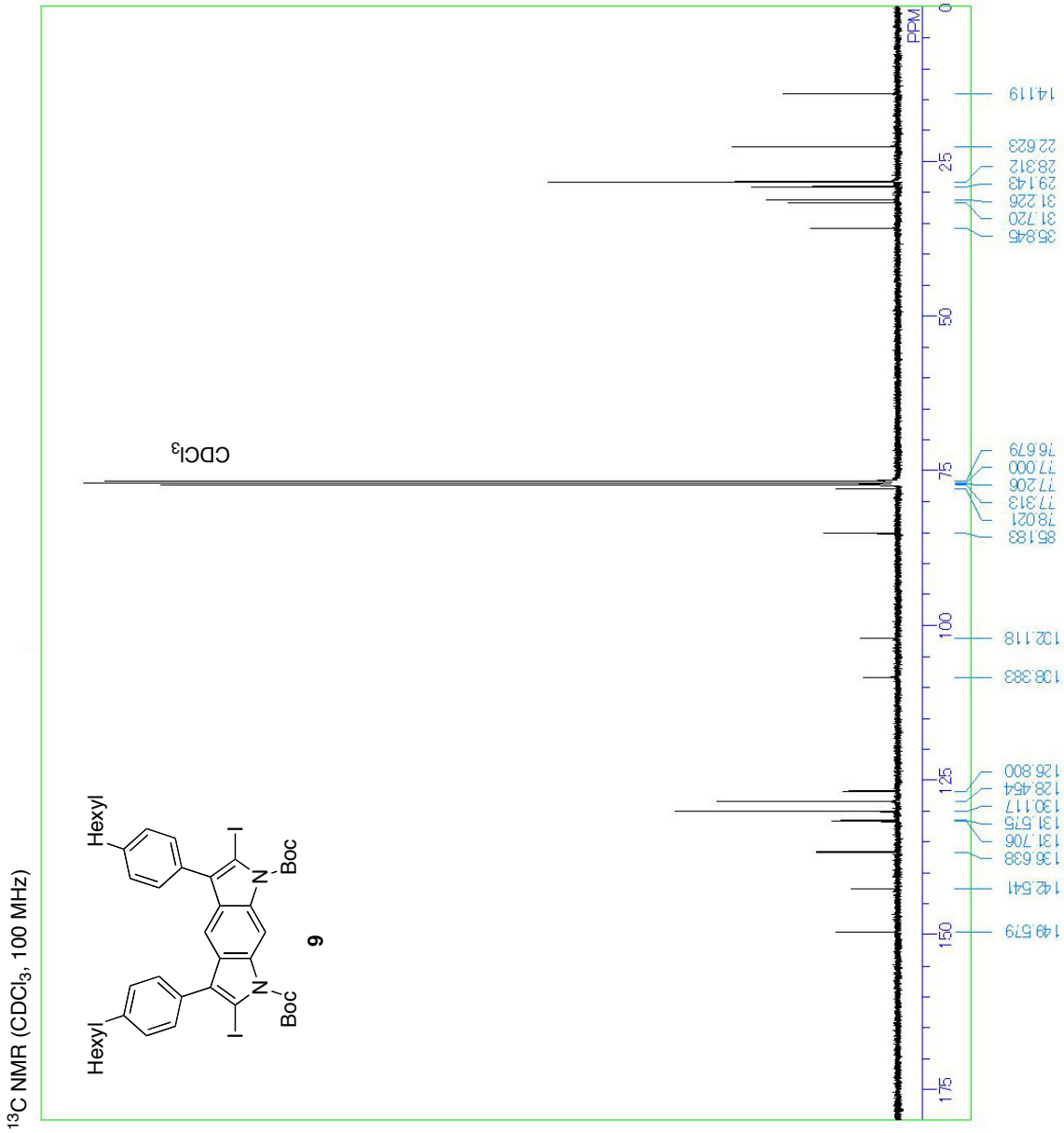
Hexyl
I
N
Boc
Hexyl
I
N
Boc
9
$CHCl_3$
PPM
0.880
0.898
0.903
0.915
1.300
1.319
1.328
1.336
1.358
1.378
1.550
1.624
1.644
1.663
1.683
1.700
1.774
1.779
2.634
2.655
2.674
7.250
7.259
7.265
7.269
7.344
7.359
7.364
7.380
9.101


^{13}C NMR ($CDCl_3$, 100 MHz)
$CDCl_3$
Hexyl
Boc
I
N
Boc
I
Hexyl
9
PPM
0
25
50
75
100
125
150
175
14.119
22.623
28.312
29.143
31.226
31.720
35.845
76.579
77.000
77.206
77.313
78.021
85.183
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108.383
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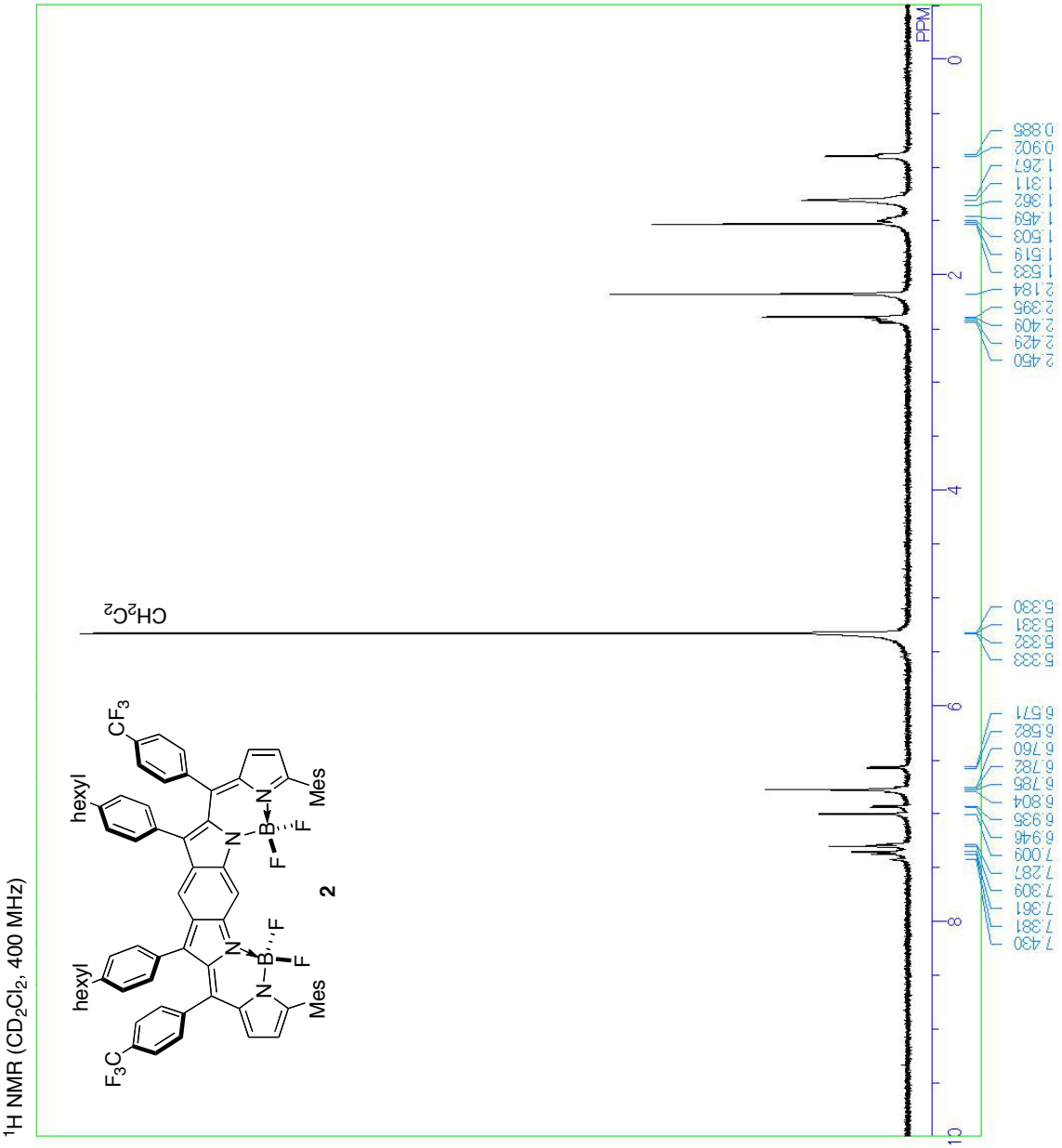
142.541
149.579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CH_2C_2
hexyl
hexyl
CF_3
F_3C
Mes
Mes
F
F
B
N
N
2
PPM
0
2
4
6
8
10
0.886
0.902
1.267
1.311
1.362
1.459
1.503
1.519
1.533
2.184
2.395
2.409
2.429
2.450
5.330
5.331
5.332
5.333
6.571
6.582
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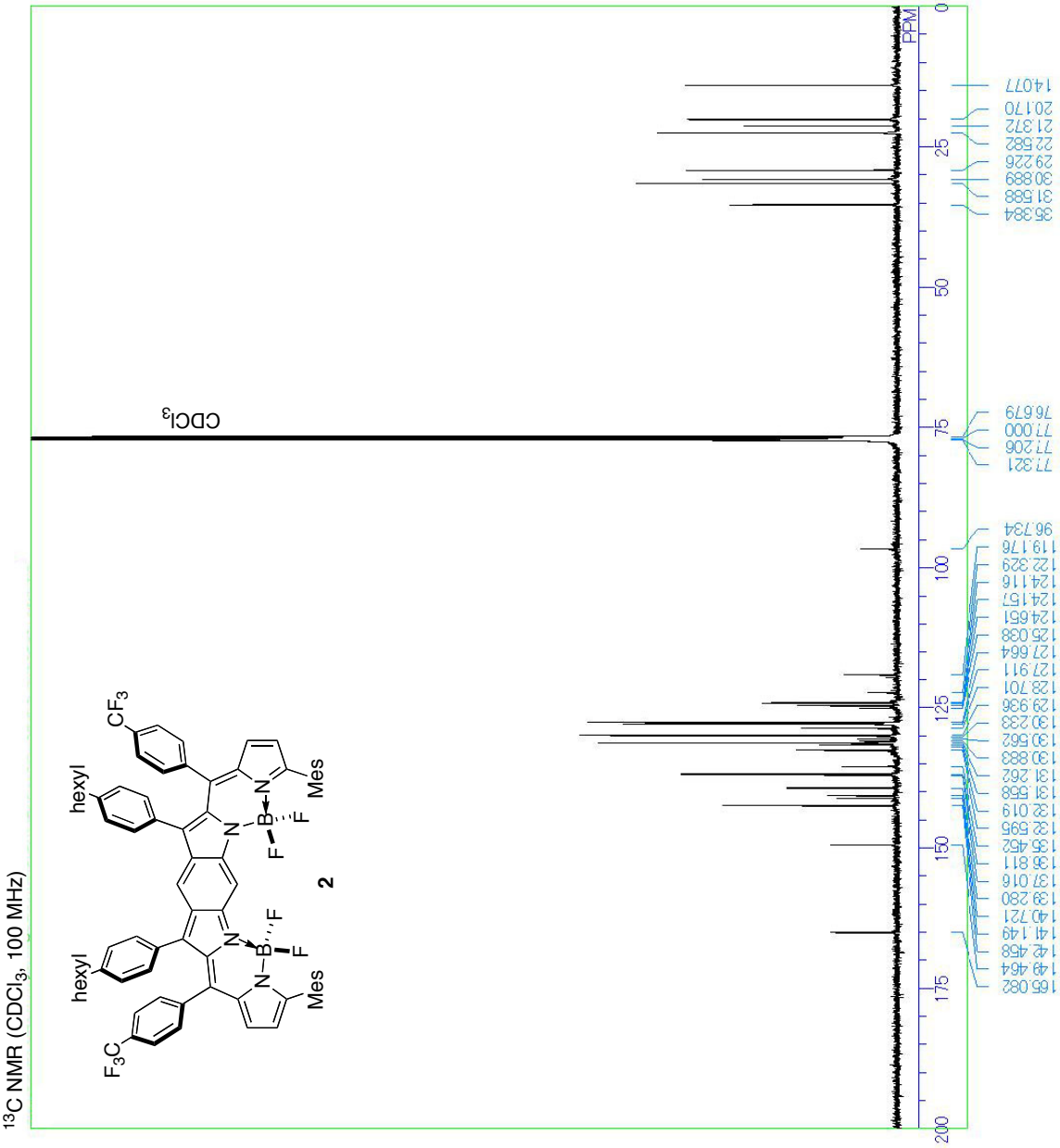
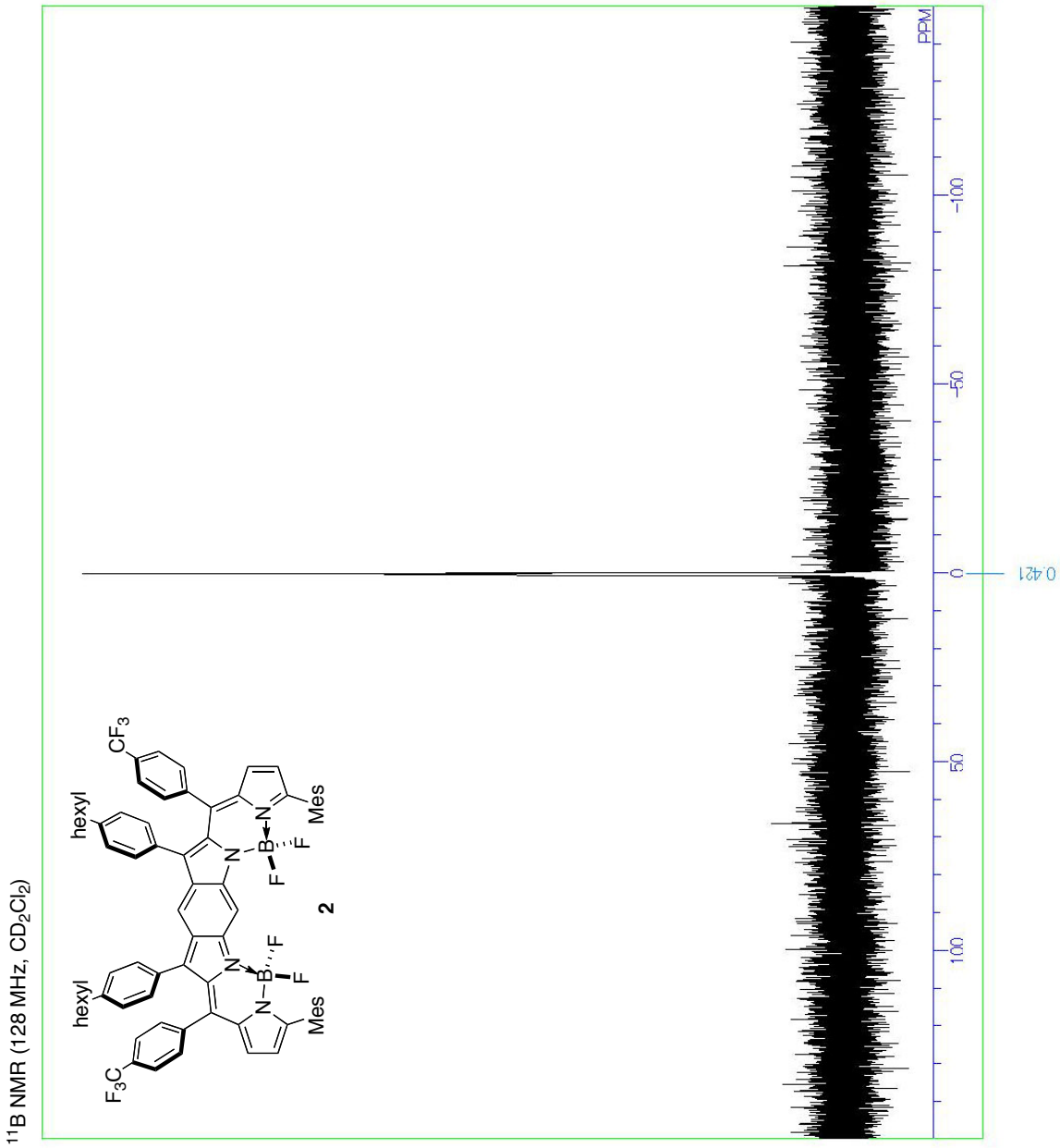
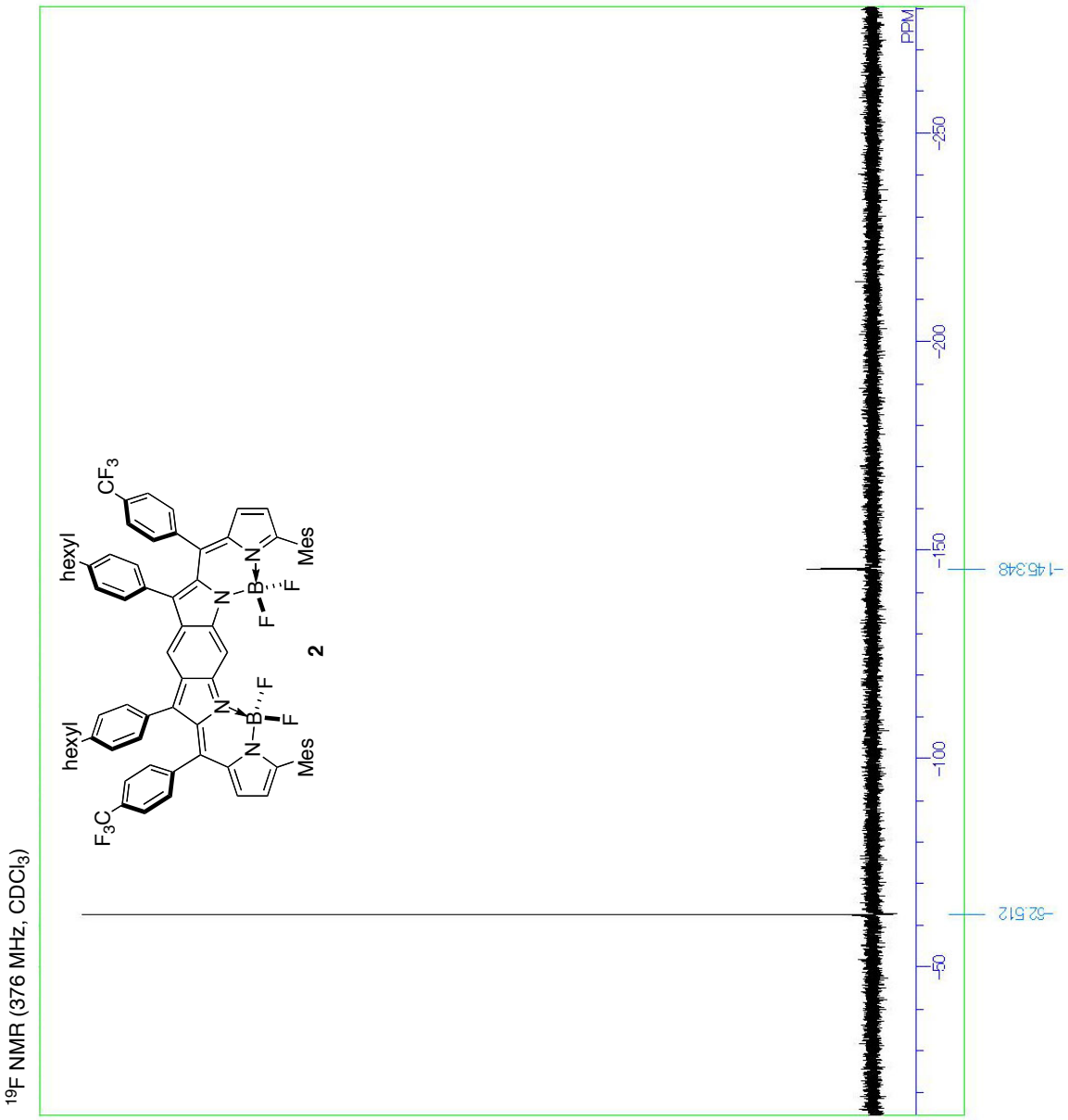
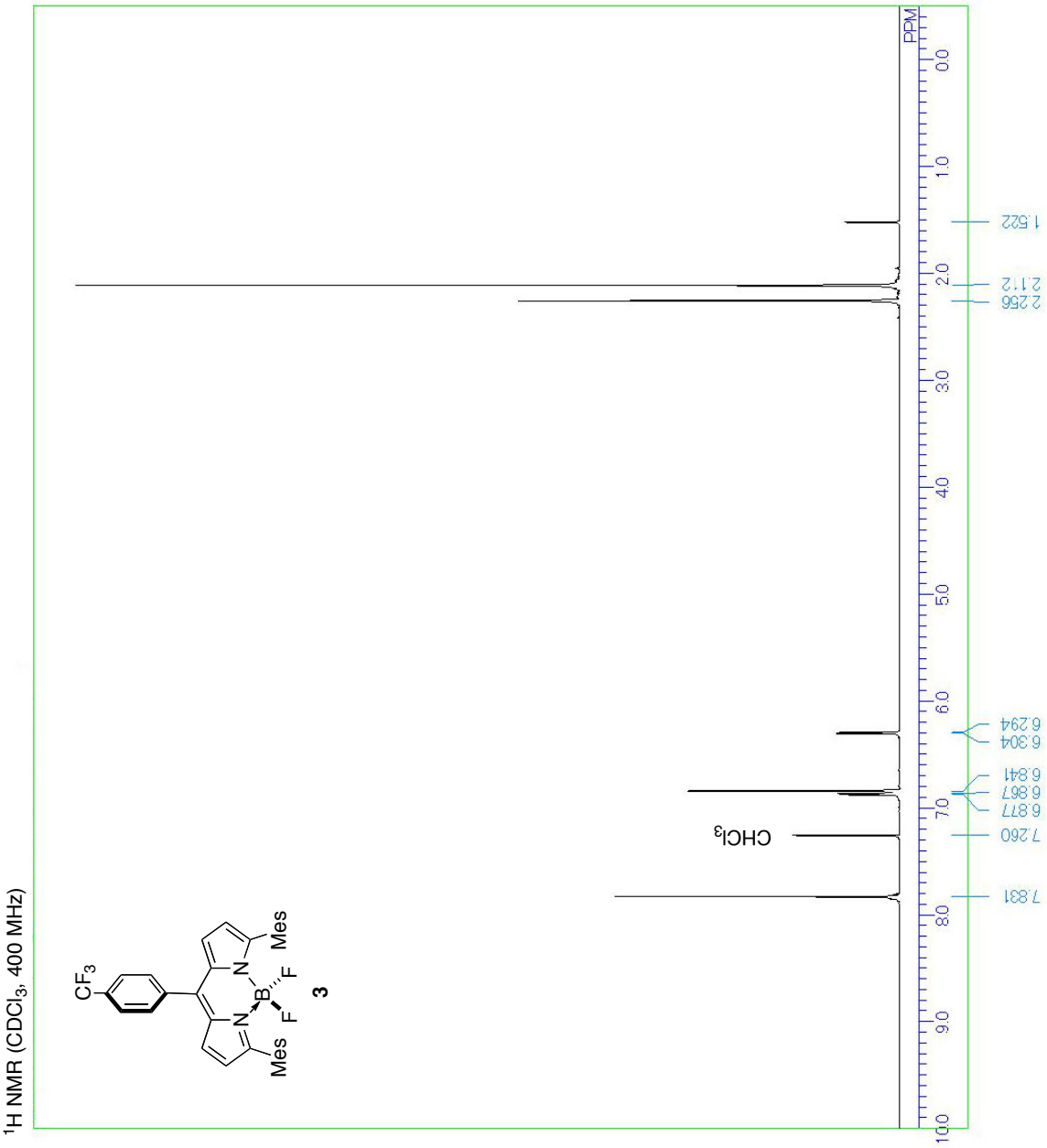
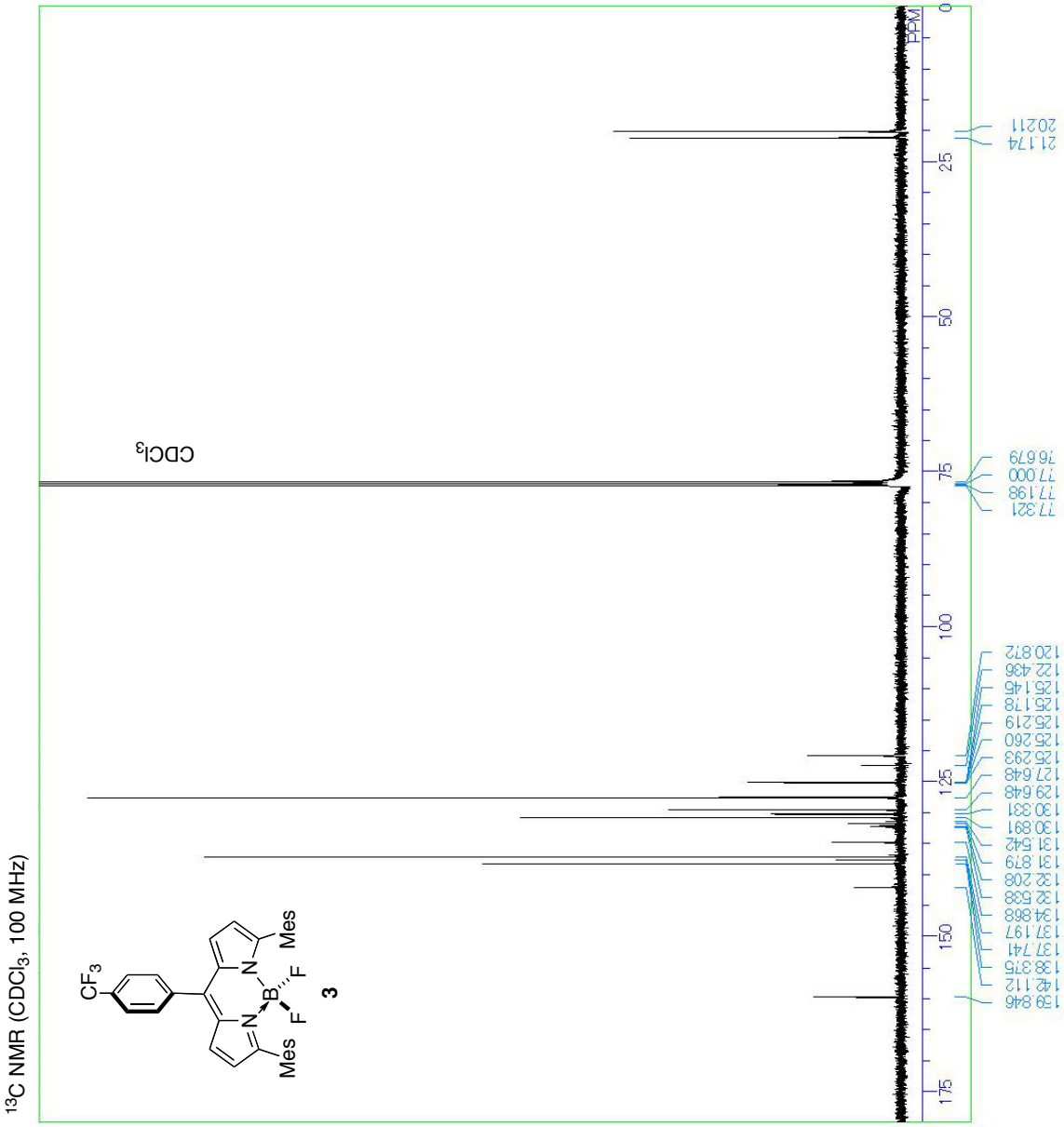
7.009
7.281
7.309
7.361
7.381
7.430

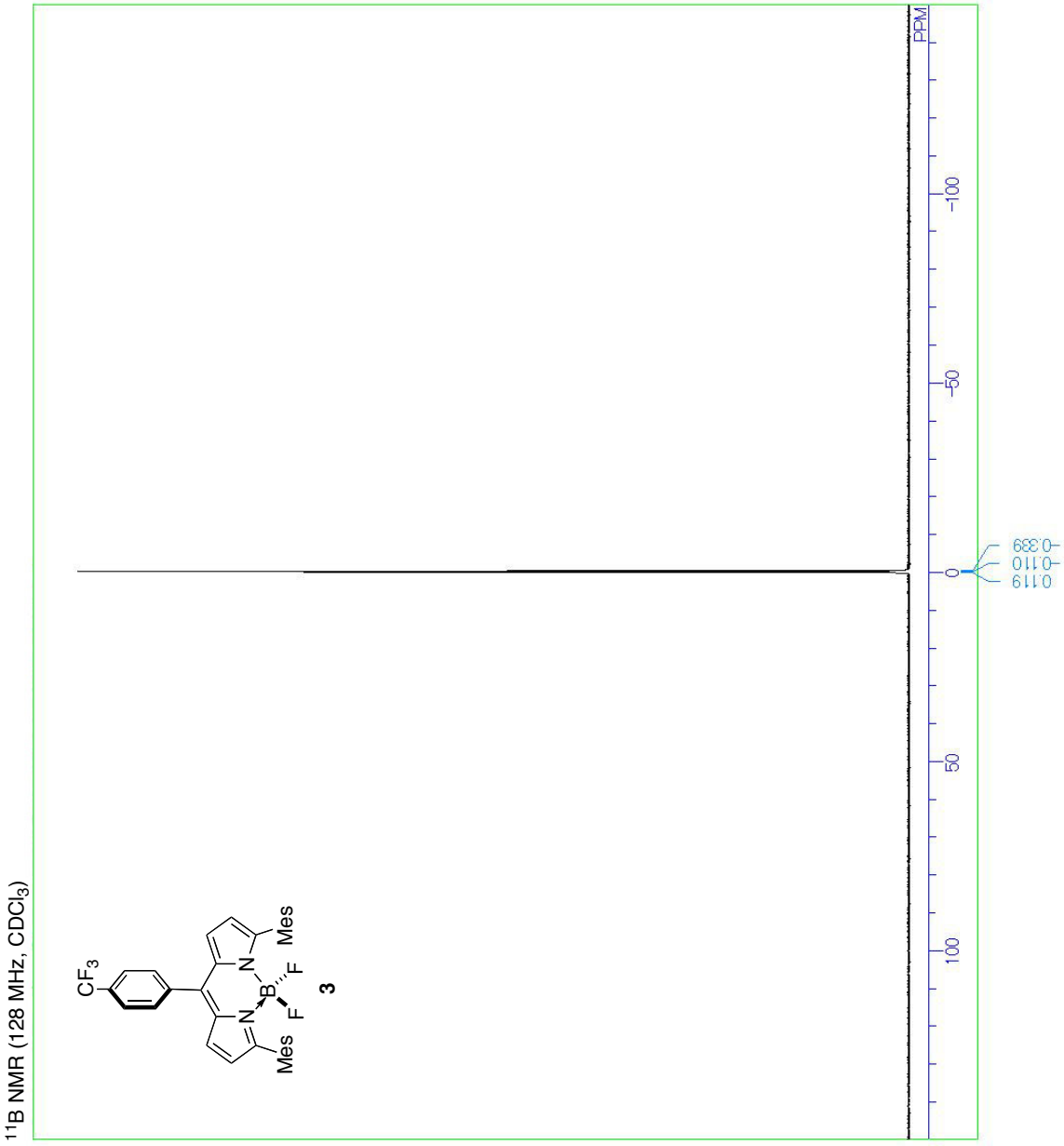

^{13}C NMR ($CDCl_3$, 100 MHz)
$CDCl_3$
PPM
0
25
50
75
100
125
150
175
200
14.077
20.170
21.372
22.582
29.226
30.889
31.588
36.384
76.679
77.000
77.321
96.734
119.176
122.329
124.116
124.157
124.651
125.038
127.664
127.911
128.701
129.936
130.233
130.562
130.883
131.262
131.558
132.019
132.595
136.462
136.811
137.016
139.280
140.721
141.149
142.464
149.464
165.082
hexyl
hexyl
CF_3
F_3C
Mes
Mes
F
F
F
F
B
B
N
N
N
N
2

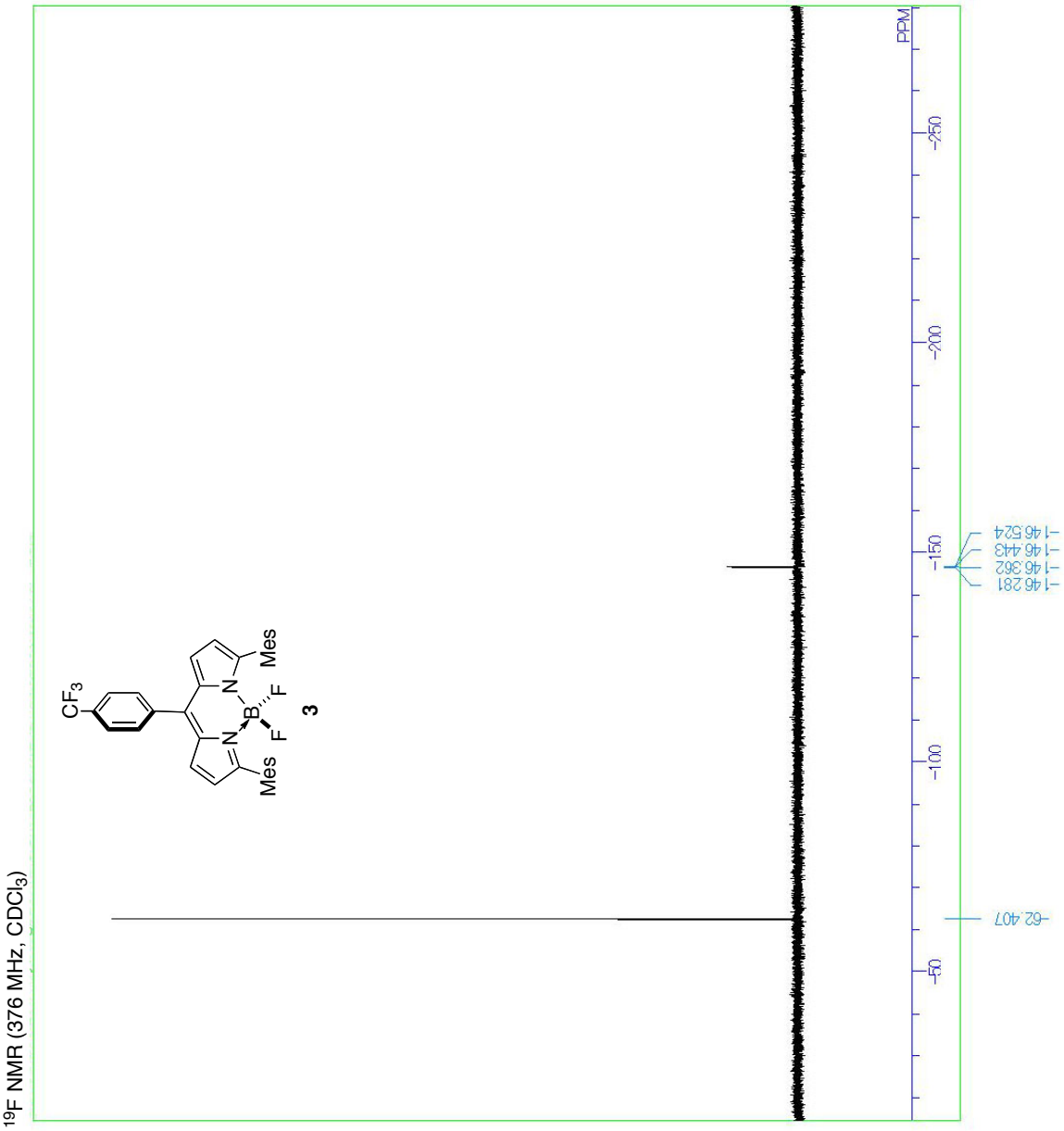

^{11}B NMR (128 MHz, CD_2Cl_2)
PPM
100
50
0
-50
-100
0.421
hexyl
hexyl
CF_3
F_3C
Mes
Mes
F
F
F
F
N
N
N
N
B
B
2


^{19}F NMR (376 MHz, $CDCl_3$)
PPM
-250
-200
-150
-100
-50
-145.348
-62.512
hexyl
hexyl
CF_3
F_3C
Mes
Mes
F
F
F
F
N
N
N
N
B
B
2


^{1}H NMR ($CDCl_3$, 400 MHz)
PPM
1.522
2.112
2.256
6.294
6.304
6.841
6.867
6.877
7.260
7.831
$CHCl_3$
CF_3
Mes
Mes
F
F
B
N
N
3


^{13}C NMR ($CDCl_3$, 100 MHz)
$CDCl_3$
PPM
0
25
50
75
100
125
150
175
21.174
20.211
76.679
77.000
77.198
77.321
120.812
122.436
125.145
125.178
125.219
125.260
125.293
127.648
129.648
130.331
130.891
131.542
131.879
132.208
132.538
134.868
137.197
137.741
138.375
142.112
139.846
CF_3
N
B
F
F
N
Mes
Mes
3


^{11}B NMR (128 MHz, $CDCl_3$)
PPM
100
50
0
-50
-100
0.119
-0.110
-0.339
CF_3
Mes
F
N
B
F
N
Mes
3


^{19}F NMR (376 MHz, $CDCl_3$)
PPM
-250
-200
-150
-100
-50
-146.524
-146.443
-146.362
-146.281
-62.407
CF_3
N
B
F
F
Mes
Mes
3