# Electronic Supplementary Information

## Acetoxymethyl-BODIPYs: A Universal Platform for the Fluorescence Labeling of Nucleophiles

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## Synthesis and characterization of compounds

### General methods

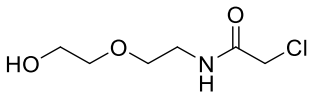
Proton and carbon-13 nuclear magnetic resonance ($^{1}$H NMR or $^{13}$C NMR) spectra were recorded on a Bruker Avance III-400 (400 and 100 MHz, respectively) or a Varian System 500 (500 and 125 MHz, respectively) spectrometers. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual peaks of the deuterated NMR solvent used. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m= multiplet and/or multiple resonances, b = broad), integration, coupling constants in hertz (Hz), and assignment. Proton and carbon-13 assignments are based on gCOSY, gHSQC, and gHMBC correlation experiments. Thin layer chromatography (TLC) was performed with Merck Silica Gel 60 F254 plates. Chromatograms were visualized using UV light (254 nm or 365 nm). Column chromatography was performed on a 971-FP Flash Purification System from Agilent Technologies using SF Si35 silica cartridges. High-resolution mass spectra (HRMS) were recorded on an Agilent 6520 Q-TOF instrument with an ESI source. Anhydrous solvents were prepared according to standard methods by distillation over drying agents or via elution through a PureSolv™ column drying system from Innovative Technology, Inc. All other solvents were of HPLC grade and were used as provided. Microwave irradiation experiments were performed under magnetic stirring with a single-mode Anton Parr Monowave 300 reactor, using standard Pyrex tubes (10 mL capacity) sealed with a PTFE-lined rubber septum. BODIPYs **2** and **4** were purchased from Exciton and Merck, respectively, and used as received. BODIPY **3** was synthesized by a previously described method.[1]

### Initial qualitative screening of acid catalysts for the substitution reaction

The screening experiments were carried out in parallel, distributing aliquots of a stoichiometric mixture of 3-acetoxymethyl-CN-BODIPY **9** and isobutanol in different reaction vials to which the corresponding acid catalyst (2.5 mol%) was added at room temperature. Thin-layer chromatography was used as a rapid naked-eye inspection method for parallel qualitative reaction analysis (UV). This study helped us classify the screened catalysts into three main groups based on their efficiency. The first group comprised the most active catalysts, which achieved >50% product formation in <1 h

reaction time, included the following in decreasing order of activity: $Et_3SiOTf$ > $Cu(OTf)_2$ > $Sc(OTf)_3$ ~ $In(OTf)_3$ ~ $Ga(OTf)_3$ ~ $Bi(OTf)_3$ > $Hf(OTf)_4$. The second group included the catalysts with medium activity, which required a reaction time of >4 h to achieve a 50% product formation, was made up by the only Brønsted acid tested: *p*-toluenesulfonic acid. Finally, the less efficient catalysts, with product yields ≤10% after a 4 h reaction time, included the following: $Zn(OTf)_2$ > AgOTf > $Yb(OTf)_3$ >> $Sm(OTf)_3$ (inactive). This fast and very convenient study showed that the most suitable catalyst in terms of reaction rate, total transformation of the starting BODIPY and generation of the substitution product was $Sc(OTf)_3$.

**2-Chloro-*N*-(2-(2-hydroxyethoxy)ethyl)acetamide**

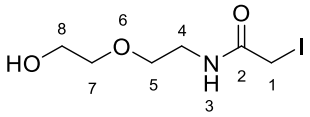



To a stirred solution of 2-(2aminoethoxy)ethanol (473 µL, 4.66 mmol) and triehylamine (1.3 mL, 9.32 mmol) in anhydrous $CH_2Cl_2$ (5 mL) was added dropwise chloroacetyl chloride (370 µL, 4.66 mmol) at 0 °C, under an argon atmosphere. The resulting mixture was stirred 1 h at 0 °C and 4 h more at room temperature. Then, chloroacetyl chloride (185 µL, 2.33 mmol) was added to the mixture again, at 0 °C for 30 min. The mixture reaction was diluted with $CH_2Cl_2$ (20 mL) and saturated $NaHCO_3$ (20 mL) solution. The organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was diluted with MeOH (3 mL) and $K_2CO_3$ (small amount) was added. After stirring for 1.5 h at room temperature, the solvent was removed at reduced pressure and the crude was purified by silica gel flash column chromatography ($CH_2Cl_2$/MeOH, 90:10 to 60:40) to afford 2-chloro-*N*-(2-(2-(2-hydroxyethoxy)ethyl)acetamide (257 mg, 30% yield; non-optimized procedure) as a yellow oil.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 7.14 (1H, br s, H3), 4.01 (2H, s, H1), 3.70 (2H, t, *J* = 4.4 Hz, H8), 3.56 (4H, q, *J* = 5.3 Hz, H5 and H7), 3.47 (2H, q, *J* = 5.3 Hz, H4), 2.80 (1H, br s, OH8). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 166.5 (C2), 72.4 (H5/H7), 69.5 (H7/H5), 61.7 (C1), 42.7 (C1), 39.7 (C4).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_6H_{12}ClNNaO_3$ $[M+Na]^+$ 204.0398 ($^{35}Cl$), 206.0370 ($^{37}Cl$); found 204.0401 ($^{35}Cl$), 206.0372 ($^{37}Cl$). Calcd. for $C_6H_{13}ClNO_3$ $[M+H]^+$ 182.0578 ($^{35}Cl$), 184.0551 ($^{37}Cl$); found 182.0577 ($^{35}Cl$), 184.0551 ($^{37}Cl$).

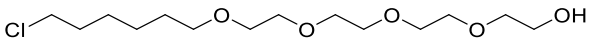
**2-Iodo-*N*-(2-(2-hydroxyethoxy)ethyl)acetamide**




To a stirred solution of 2-chloro-*N*-(2-(2-(2-hydroxyethoxy)ethyl)acetamide (90 mg, 0.495 mmol) in acetone ( 2 mL) was added KI (123.4 mg, 0.743 mmol) at 70 °C, under argon. After stirring for 4 h at 70 °C, the solvent was removed at reduced pressure and the crude was purified by silica gel flash column chromatography ($CH_2Cl_2$/MeOH, 100:0 to 90:10) to afford 2-iodo-*N*-(2-(2-hydroxyethoxy)ethyl)acetamide (127 mg, 88% yield) as colorless oil.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 7.05 (1H, br s, H3), 3.75 (2H, t, *J* = 4.7 Hz, H8), 3.71 (2H, s, H1), 3.58 (4H, m, H5 and H7), 3.47 (2H, q, *J* = 5.0 Hz, H4), 2.83 (1H, br s, OH8).
**$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 168.0 (C2), 72.4 (C5), 69.5 (C7), 61.8 (C8), 40.3 (C4), -0.46 (C1).
**HRMS** (API-ES$^+$) *m/z* calcd. for $C_6H_{12}INNaO_3$ $[M+Na]^+$ 295.9754; found 295.9755. Calcd. for $C_6H_{13}INO_3$ $[M+H]^+$ 273.9934; found 273.9930.

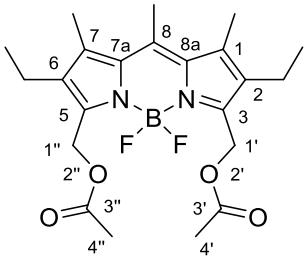
**18-Chloro-3,6,9,12-tetraoxaoctadecan-1-ol**[2]




Tetraethylene glycol (1.7 mL, 9.88 mmol) was added dropwise to a mixture of NaH 60% (316 mg, 7.9 mmol) in DMF (2 mL, 1 M) and THF (2 mL, 1 M) at 0 °C under argon. After 50 minutes, 1-chloro-6-iodohexane (300 µL, 1.98 mmol) was added, and the mixture was warmed to room temperature and stirred for 4 h. The reaction was diluted with MeOH (1 mL), quenched with 1 M HCl, and extracted with chloroform. The combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered, and concentrated at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 0:100) to afford 18-chloro-3,6,9,12-tetraoxaoctadecan-1-ol (273 mg, 44% yield) as a colorless oil.

**$^1$H NMR** ($CDCl_3$, 300 MHz): δ = 3.67 – 3.62 (m, 2H), 3.59 – 3.49 (m, 14H), 3.46 (t, J = 6.7 Hz, 2H), 3.38 (t, J = 6.6 Hz, 2H), 2.96 (br s, 1H), 1.74 – 1.65 (m, 2H), 1.57 – 1.47 (m, 2H), 1.41 – 1.27 (m, 4H).

**Compound 1**




A suspension of $Pb(OAc)_4$ (48 mg, 0.102 mmol) in $AcOH/Ac_2O$ (20:1, 1 mL) and $CH_2Cl_2$ (0.2 mL) was added dropwise to a stirred solution of *F*-BODIPY **1** (15.5 mg, 0.048 mmol) in $AcOH/Ac_2O$ (20:1, 1 mL) and $CH_2Cl_2$ (0.3 mL) at 0 °C under argon atmosphere. After stirring at 0 °C for 3 h, the reaction mixture was warmed to room temperature and stirred for an additional 90 minutes. Cold water (20 mL) was added and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 40 mL). The combined organic layers were washed with 0.1 M aq. $NaHCO_3$, brine and dried ($Na_2SO_4$). After solvent evaporation at reduced pressure, the residue was purified by column chromatography (hexane/AcOEt, 100:0 to 48:52) to afford compound **2** (14 mg, 66%) as an orange solid.

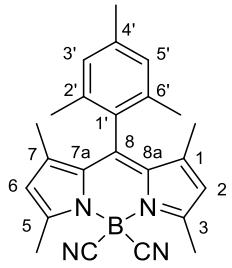
**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 5.34 (4H, s, H1' and H1"), 2.70 (3H, s, $CH_3$8), 2.46 (4H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 2.38 (6H, s, $CH_3$1 and $CH_3$7), 2.10 (6H, s, H4' and H4"), 1.07 (6H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 170.6 (C3' and C3"), 148.2 (C3 and C5), 145.3 (C8), 138.5 (C1 and C7), 134.6 (C2 and C6), 133.3 (C7a and C8a), 57.2 (C1' and C1"), 21.0 (C4' and C4"), 17.9 ($CH_3$8), 17.2 ($CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 15.3 ($\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6), 14.7 ($CH_3$1 and $CH_3$7). **HRMS** (API-ES$^+$) *m/z* calcd. for $C_{22}H_{29}BF_2N_2NaO_4$ $[M+Na]^+$ 457.2085; found 457.2068. calcd. for $C_{22}H_{33}BF_2N_3O_4$ $[M+NH_4]^+$ 452.2531; found 52.2505.

**Compound 5**[3]


To a stirred solution of *F*-BODIPY **1** (300 mg, 0.94 mmol) in anhydrous $CH_2Cl_2$ (3 mL) was added TMSCN (0.84 mL, 6.6 mmol) and $SnCl_4$ (0.056 mL, 0.47 mmol) at room temperature under an argon atmosphere. After stirring for 30 minutes at room temperature, the reaction mixture was diluted with $H_2O$ (30 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 50 mL). The combined organic phases were washed with 0.1 M aqueous $NaHCO_3$ solution, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure to afford pure compound **5** (313 mg, 100% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 300 MHz): δ = 2.66 (9H, s), 2.46 (4H, q, *J* = 7.5 Hz), 2.38 (6H, s), 1.07 (6H, t, *J* = 7.5 Hz).

**Compound 6**

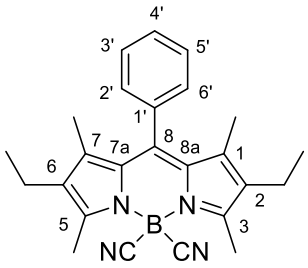



To a stirred solution of *F*-BODIPY **3** (200 mg, 0.546 mmol) in anhydrous $CH_2Cl_2$ (16 mL) were added TMSCN (478 µL, 3.82 mmol) and $SnCl_4$ (32 µL, 0.273 mmol) at room temperature under an argon atmosphere. After stirring for 40 minutes at room temperature, the reaction mixture was diluted with $CH_2Cl_2$ (20 mL) and $H_2O$ (30 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 50 mL). The combined organic phases were washed with 0.1 M aqueous $NaHCO_3$ solution, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 80:20) to afford compound **6** (199 mg, 96% yield), as an orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 6.97 (2H, s, H3' and H5'), 6.14 (2H, s, H2 and H6), 2.73 (6H, s, $CH_3$3 and $CH_3$5), 2.34 (3H, s, $CH_3$4'), 2.07 (6H, s, $CH_3$2' and $CH_3$6'), 1.42

(6H, s, $CH_3$1 and $CH_3$7). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 155.8 (C3 and C5), 143.8 (C7/C1/C7a/C8a), 143.0 8 (C8), 139.4 (C4'), 134.8 (C2' and C6'), 130.3 (C1'), 129.4 (C3' and C5'), 129.03 (C7a/C8a/C7/C1), 126.4 (q, $J_{CB}$ = 74 Hz, 2 x CN), 122.4 (C2 and C6), 21.3 ($CH_3$4'), 19.6 ($CH_3$2' and $CH_3$6'), 15.6 ($CH_3$3 and $CH_3$5), 13.8 ($CH_3$1 and $CH_3$7).
**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{24}H_{26}BN_4$ $[M+H]^+$ 381.2249; found 381.2250. calcd. for $C_{24}H_{25}BN_4Na$ $[M+Na]^+$ 403.2069; found 403.2060.

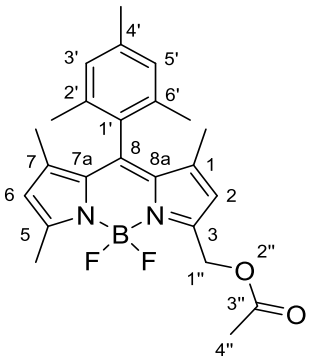
**Compound 7**




To a stirred solution of *F*-BODIPY **4** (204 mg, 0.563 mmol) in anhydrous $CH_2Cl_2$ (2 mL) were added TMSCN (479.4 µL, 3.76 mmol) and $SnCl_4$ (31.7 µL, 0.268 mmol) at room temperature under an argon atmosphere. After stirring for 30 minutes at room temperature, the reaction mixture was diluted with $H_2O$ (30 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 50 mL). The combined organic phases were washed with 0.1 M aqueous $NaHCO_3$ solution, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure to afford pure compound **7** (210 mg, 99% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 7.58-7.47 (3H, m, H3', H4' and H5'), 7.31-7.22 (2H, m, H2' and H6'), 2.70 (6H, s, $CH_3$3 and $CH_3$5), 2.36 (4H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 1.33 (6H, s, $CH_3$1 and $CH_3$7), 1.01 (6H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 154.0 (C3 and C5), 141.1 (C8), 139.9 (C1 and C7), 134.8 (C2 and C6), 134.3 (C1'), 129.4 (C3'/C5'/C4'), 129.4 (C4'/C5'/C3'), 129.3 (C7a and C8a), 128.1 (C2' and C6'), 127.0 (q, $J_{CB}$ = 73.4 Hz, 2 × CN), 17.3 ($CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 14.6 ($\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6) , 13.4 ($CH_3$3 and $CH_3$5), 11.9 ($CH_3$1 and $CH_3$7).
**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{25}H_{28}BN_4$ $[M+H]^+$ 395.2406; found 395.2412. Calcd. for $C_{25}H_{27}BN_4Na$ $[M+Na]^+$ 417.2226; found 417.2221.

**Compound 8**

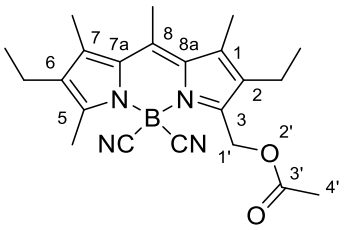



A suspension of $Pb(OAc)_4$ (68 mg, 0.144mmol) in $AcOH/Ac_2O$ (20:1, 0.5 mL) and $CH_2Cl_2$ (0.2 mL) was added dropwise to a stirred solution of *F*-BODIPY **3** (25.1 mg, 0.068 mmol) in $AcOH/Ac_2O$ (20:1, 1 mL) and $CH_2Cl_2$ (0.3mL) at 0 °C under argon atmosphere. After stirring at 0 °C for 90 minutes, the reaction mixture was warmed to room temperature and stirred for an additional 90 minutes. Cold water (20 mL) was added and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 40 mL). The combined organic layers were washed with 0.1 M aq. $NaHCO_3$, brine and dried ($Na_2SO_4$). After solvent evaporation at reduced pressure, the residue was purified by column chromatography (hexane/AcOEt, 100:0 to 75:25) to afford compound **8** (18 mg, 62%) as an orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 6.96 (2H, s, H3' and H5'), 6.16 (1H, s, H2), 6.03 (1H, s, H6), 5.42 (2H, s, H1''), 2.57 (3H, s, $CH_3$5), 2.34 (3H, s, $CH_3$4'), 2.15 (3H, s, H4''), 2.09 (6H, s, $CH_3$2' and $CH_3$6'), 1.41 (6H, s, $CH_3$1 and $CH_3$7). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 170.7 (C3''), 158.8 (C5), 149.4 (C3), 145.1 (C7/C7a), 143.5 (C8), 140.9 (C1/C8a), 139.0 (C4'), 134.9 (C2' and C6'), 132.1 (C7a/C7), 130.9 (C1'), 130.4 (C8a/C1), 129.3 (C3' and C5'), 122.3 (C6), 118.8 (C2), 59.6 (C1''), 21.3 ($CH_3$4'), 21.1 (C4''), 19.7 ($CH_3$2' and $CH_3$6'), 15.0 ($CH_3$5), 13.8 ($CH_3$1/$CH_3$7), 13.5 ($CH_3$7/$CH_3$1).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{24}H_{27}BF_2N_2NaO_2$ $[M+Na]^+$ 447.2030; found 447.2048. Calcd. for $C_{24}H_{31}BF_2N_3O_2$ $[M+NH_4]^+$ 442.2476; found 442.2491. Calcd. for $C_{24}H_{28}BF_2N_2O_2$ $[M+H]^+$ 425.2211; found 425.2207.

**Compound 9**

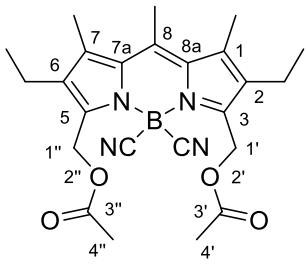


A solution of $Pb(OAc)_4$ (1.25 g, 2.81 mmol) in $CH_2Cl_2$ (5 mL) was added dropwise to a stirred solution of *CN*-BODIPY **5** (390 mg, 1.17 mmol) in an AcOH/$Ac_2O$ (20:1) mixture (20 mL) at 0 °C. After addition, the reaction mixture was stirred at room temperature until completion of the reaction (TLC monitoring, *ca.* 2.5h). Water (50 mL) was added and the aqueous phase was extracted with $CH_2Cl_2$ (2 x 50 mL). The combined organic layers were washed with 0.1 M aq. $NaHCO_3$, brine and dried ($Na_2SO_4$). After solvent evaporation at reduced pressure, the residue was purified by column chromatography (hexane/AcOEt, 50:50 to 20:80) to afford compound **9** (330 mg, 72%) as an orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 5.43 (2H, s, H1'), 2.70 (6H, s, $CH_3$5 and $CH_3$8), 2.52 (2H, q, *J* = 7.4 Hz, $CH_3\underline{CH_2}$2), 2.48 (2H, q, *J* = 7.4 Hz, $CH_3\underline{CH_2}$6), 2.41 (3H, s, $CH_3$1), 2.40 (3H, s, $CH_3$7), 2.16 (3H, s, H4'), 1.10 (3H, t, *J* = 7.4 Hz, $\underline{CH_3}CH_2$2), 1.09 (3H, t, *J* = 7.4 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 170.9 (C3'), 157.8 (C5), 143.7 (C3), 142.9 (C8), 140.8 (C7), 136.3 (C1), 136.2 (C6), 135.0 (C2), 132.3 (C7a), 130.6 (C8a), 127.1 (q, $J_{CB}$ = 74 Hz, 2 x CN), 56.5 (C1'), 21.0 (C4'), 17.8 ($CH_3\underline{CH_2}$6), 17.4 ($CH_3\underline{CH_2}$2/$CH_3$8), 17.4 ($CH_3$8/$CH_3\underline{CH_2}$2), 15.5 ($\underline{CH_3}CH_2$2), 15.1 ($\underline{CH_3}CH_2$6), 14.7 ($CH_3$7), 14.6 ($CH_3$1), 14.1 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{22}H_{27}BN_4NaO_2$ $[M+Na]^+$ 413.2123; found 413.2138. Calcd. for $C_{22}H_{31}BN_5O_2$ $[M+NH_4]^+$ 408.2569; found 408.2587.

**Compound 10**



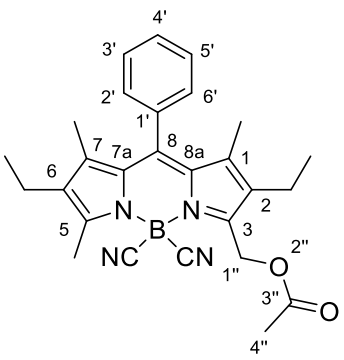
A solution of $Pb(OAc)_4$ (717.3 mg, 1.55 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise to a stirred solution of *CN*-BODIPY **5** (172 mg, 0.517 mmol) in AcOH/$Ac_2O$ (20:1, 5 mL) at room temperature. After stirring at 50 °C for 5.5 h, water (40 mL) was added and

the aqueous phase was extracted with $CH_2Cl_2$ (3 x 50 mL). The combined organic layers were washed with 0.1 M aq. $NaHCO_3$, brine and dried ($Na_2SO_4$). After the solvent was removed at reduced pressure, the crude solid was recrystalized from hexane/$CH_2Cl_2$ (5:1) to afford compound **10** (201 mg, 87%) as an orange solid.

**$^1$H NMR** ($CDCl_3$, 500 MHz): δ = 5.45 (4H, s, H1' and H1"), 2.76 (3H, s, $CH_3$8), 2.53 (4H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 2.43 (6H, s, $CH_3$1 and $CH_3$7), 2.18 (6H, s, H4' and H4"), 1.10 (6H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 125 MHz): δ = 170.7 (C3' and C3"), 148.7 (C3 and C5), 146.4 (C8), 139.9 (C1 and C7), 136.4 (C2 and C6), 132.3 (C7a and C8a), 127.4 (q, $J_{CB}$ = 76.5 Hz, 2 × CN), 56.4 (C1' and C1"), 20.9 (C4' and C4"), 18.5 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 15.3 ($\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6), 15.0 ($CH_3$1 and $CH_3$7).
**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{24}H_{33}BN_5O_4$ $[M+NH_4]^+$ 466.2625; found 466.2612. calcd. for $C_{24}H_{29}BN_4NaO_4$ $[M+Na]^+$ 471.2178; found 471.2165.

**Compounds 11, 12 and 13**

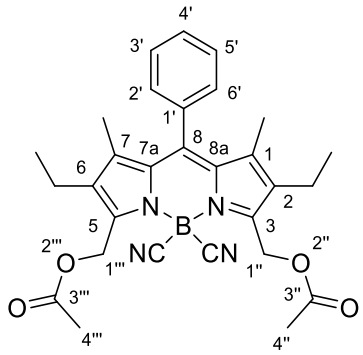
A solution of $Pb(OAc)_4$ (1.92 g, 4.34 mmol) in a $CH_2Cl_2$ (6 mL) and AcOH/$Ac_2O$ (20:1, 6 mL) was added dropwise to a stirred solution of compound **7** (428 mg, 1.09 mmol) in $CH_2Cl_2$ (6 mL) at room temperature, under argon. After addition, the reaction mixture was heated at 40 °C for 6 hours. Water (50 mL) was added and the aqueous phase was extracted with $CH_2Cl_2$ (2 x 50 mL). The combined organic layers were washed with 0.1 M aq. $NaHCO_3$, brine and dried ($Na_2SO_4$). After solvent evaporation at reduced pressure, the residue was purified by column chromatography (hexane/AcOEt, 95:5 to 70:30) to afford compound **11** (119 mg, 24% yield), compound **12** (244 mg, 44% yield), and compound **13** (33 mg, 5% yield), as orange solids.




**11**

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 7.56-7.51 (3H, m, H3', H4' and H5'), 7.31-7.24 (2H, m, H2' and H6'), 5.45 (2H, s, H1''), 2.73 (3H, s, $CH_3$5), 2.40 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.37 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.19 (3H, s, H4''), 1.35 (3H, s, $CH_3$7), 1.32 (3H, s, $CH_3$1), 1.02 (6H, t, *J* = 7.5Hz, $\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 170.9 (C3''), 159.7 (C5), 145.2 (C3), 142.9 (C7/C8), 142.8 (C8/C7), 138.9 (C1), 136.5 (C6), 135.3 (C2), 134.5 (C1'), 131.3 (C7a), 129.7 (C4'/C3'/C5'), 129.7 (C3'/C5'/C4'), 129.5 (C8a), 127.8 (C2' and C6'), 127.2 (q, $J_{CB}$ = 76.4 Hz, 2 × CN), 56.4 (C1''), 21.0 (C4''), 17.4 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 17.3 ($CH_3\underline{CH_2}$6/$CH_3\underline{CH_2}$2), 15.2 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 14.4 ($\underline{CH_3}CH_2$6/$\underline{CH_3}CH_2$2), 14.2 ($CH_3$5), 12.3 ($CH_3$7), 11.8 ($CH_3$1).

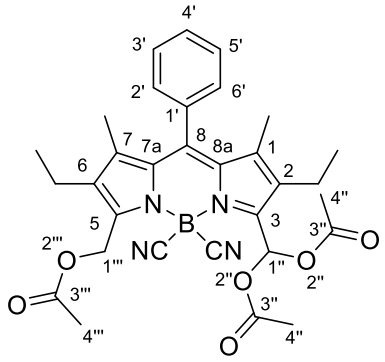
**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{27}H_{33}BN_5O_2$ $[M+NH_4]^+$ 470.2727; found 470.2730. Calcd. for $C_{27}H_{29}BN_4NaO_2$ $[M+Na]^+$ 475.2281; found 475.2279.




**12**

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 7.59-7.54 (3H, m, H3', H4' and H5'), 7.31-7.24 (2H, m, H2' and H6'), 5.47 (4H, s, H1'' and H1'''), 2.41 (4H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 2.19 (6H, s, H4'' and H4'''), 1.35 (6H, s, $CH_3$1 and $CH_3$7), 1.02 (6H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 170.6 (C3'' and C3'''), 150.4 (C3 and C5), 145.8 (C8), 142.4 (C1 and C7), 136.7 (C2 and C6), 134.2 (C1'), 131.1 (C7a and C8a), 130.0 (C4'/C3'/C5'), 129.9 (C3'/C5'/4'), 127.5 (C2' and C6'), 127.4 (q, $J_{CB}$ = 76.6 Hz, 2 × CN), 56.4 (C1'' and C1'''), 20.9 (C4'' and C4'''), 17.3 ($CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 15.0 ($\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6), 12.2 ($CH_3$1 and $CH_3$7).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{29}H_{35}BN_5O_4$ $[M+NH_4]^+$ 528.2782; found 528.2766. Calcd. for $C_{29}H_{31}BN_4NaO_4$ $[M+Na]^+$ 533.2336; found 533.2311.

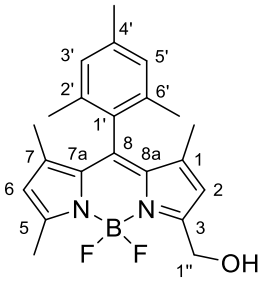


**13**

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 8.17 (1H, s, H1''), 7.68-7.42 (3H, m, H3', H4' and H5'), 7.30-7.27 (2H, m, H2' and H6'), 5.51 (2H, s, H1'''), 2.58 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}2$), 2.42 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}6$), 2.21 (6H, s, H4''), 2.19 (3H, s, H4'''), 1.37 (3H, s, $CH_3$7), 1.35 (3H, s, $CH_3$1), 1.05 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.03 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 170.4 (C3'''), 168.2 (C3''), 152.4 (C5), 146.6 (C3/C8), 146.5 (C8/C3), 143.3 (C7), 142.5 (C1), 137.3 (C6), 135.7 (C2), 134.1 (C1'), 131.6 (C7a), 130.6 (C8a), 130.0 (C4'), 129.8 (C3' and C5'), 127.3 (C2' and C6'), 127.2 (q, $J_{CB}$ = 76.5 Hz, 2 × CN), 83.3 (C1''), 56.5 (C1'''), 20.8 (C4''), 20.7 (C4'''), 17.4 ($CH_3\underline{CH_2}2$/$CH_3\underline{CH_2}6$), 17.2 ($CH_3\underline{CH_2}6$/$CH_3\underline{CH_2}2$), 14.7 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 14.6 ($\underline{CH_3}CH_2$6/$\underline{CH_3}CH_2$2), 12.2 ($CH_3$1/$CH_3$7), 12.0 ($CH_3$7/$CH_3$1).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{31}H_{37}BN_5O_6$ $[M+NH_4]^+$ 586.2837; found 586.2843. Calcd. for $C_{31}H_{33}BN_4NaO_6$ $[M+Na]^+$ 591.2391; found 591.2379.

**Compound 14**

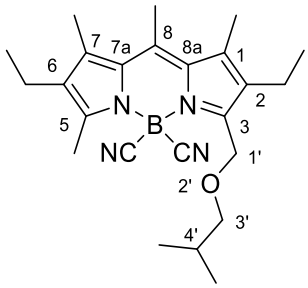


To a stirred solution of compound **8** (9 mg, 0.021 mmol) in $CH_2Cl_2$ (0.3 mL) and MeOH (0.8 mL) was added magnesium (2 grains) at room temperature. After stirring for 4 h at room temperature, the reaction mixture was diluted with $CH_2Cl_2$ (10 mL) and $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous

$Na_2SO_4$, and the solvent was removed at reduced pressure to afford pure compound **14** (7 mg, 90%), as an orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 6.96 (2H, s, H3' and H5'), 6.19 (1H, s, H2), 6.04 (1H, s, H6), 4.82 (2H, s, H1''), 2.69 (1H, br s, OH1''), 2.57 (3H, s, $CH_3$5), 2.34 (3H, s, $CH_3$4'), 2.09 (6H, s, $CH_3$2' and $CH_3$6'), 1.42 (6H, s, $CH_3$1 and $CH_3$7). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 158.3 (C5), 154.1 (C3), 145.0 (C7/C7a), 143.6 (C8), 141.5, (C1/C8a) 139.0 (C4'), 134.9 (C2' and C6'), 132.0 (C7a/C7), 130.9 (C1'), 130.8 (C8a/C1), 129.3 (C3' and C5'), 122.2 (C6), 119.3 (C2), 58.1 (C1''), 21.3 ($CH_3$4'), 19.6 ($CH_3$2' and $CH_3$6'), 15.0 ($CH_3$5), 13.7 ($CH_3$1/$CH_3$7), 13.5 ($CH_3$7/$CH_3$1).
**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{22}H_{25}BF_2N_2NaO$ $[M+Na]^+$ 405.1924; found 405.1935.

**Compound 15**



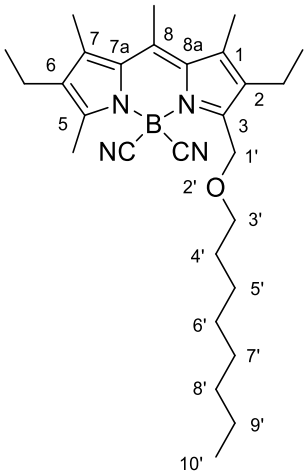

To a stirred solution of compound **9** (10 mg, 0.025 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added isobutyl alcohol (4.74 µL, 0.051 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (64 µL of a 0.01 M solution, 0.025 equiv). After stirring for 3.5 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 65:35) to afford compound **15** (9 mg, 86% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.83 (2H, s, H1'), 3.44 (2H, d, *J* = 6.6 Hz, H3'), 2.67 (6H, s, $CH_3$5 and $CH_3$8), 2.57 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2), 2.46 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.39 (3H, s, $CH_3$7), 2.38 (3H, s, $CH_3$1), 2.07-1.88 (1H, m, H4'), 1.12 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2), 1.08 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6), 0.97 (3H, s, $CH_3$4'), 0.95 (3H, s, $CH_3$4'). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 155.3 (C5), 148.8 (C3), 142.5 (C8), 139.5

(C7), 137.9 (C1), 135.2 (C6), 135.0 (C2), 131.4 (C7a), 130.2 (C8a), 127.3 (q, $J_{CB}$ = 74.5 Hz, 2 × CN), 78.7 (C3'), 64.5 (C1'), 28.6 (C4'), 19.6 (2 × $CH_3$4'), 17.6 ($CH_3$8), 17.5 ($CH_3\underline{CH_2}$2), 17.4 ($CH_3\underline{CH_2}$6), 15.2 ($\underline{CH_3}CH_2$2), 15.0 ($CH_3$1/$CH_3$7), 14.8 ($CH_3$7/$CH_3$1), 14.6 ($\underline{CH_3}CH_2$6), 13.9 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{24}H_{37}BN_5O$ $[M+NH_4]^+$ 422.3090; found 422.3086. Calcd. for $C_{24}H_{33}BN_4NaO$ $[M+Na]^+$ 427.2644; found 427.2633.

**Compound 16**



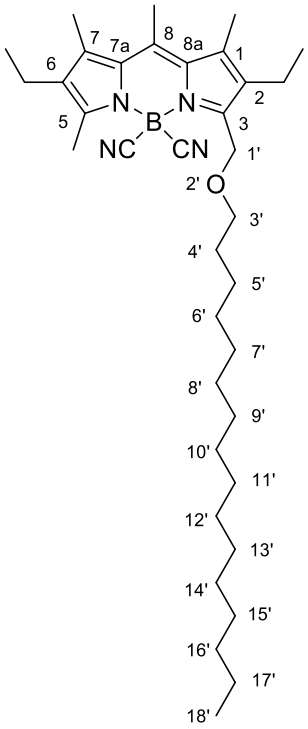

To a stirred solution of compound **9** (10 mg, 0.026 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added 1-octanol (8.15 µL, 0.051 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (64 µL of a 0.01 M solution, 0.025 equiv). After stirring for 3.5 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 65:35) to afford compound **16** (10.1 mg, 85% yield) as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.83 (2H, s, H1'), 3.65 (2H, t, *J* = 6.7 Hz, H3'), 2.67 (6H, s, $CH_3$5 and $CH_3$8), 2.56 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2), 2.46 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.39 (3H, s, $CH_3$7), 2.38 (3H, s, $CH_3$1), 1.67 (2H, q, *J* = 6.7 Hz, H4'), 1.43-1.35 (2H, m, H5'), 1.35-1.20 (8H, m, H6', H7', H8' and H9'), 1.11 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2), 1.07 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6), 0.87 (3H, t, *J* = 6.7 Hz, H10'). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 155.4 (C5), 148.7 (C3), 142.4 (C8), 139.5 (C7), 137.5 (C1), 135.2 (C6), 135.0 (C2), 131.4 (C7a), 130.2 (C8a), 127.8 (q, $J_{CB}$ = 74.8 Hz, 2 × CN), 71.9 (C3'),

64.2 (C1'), 32.0 (C8'), 29.8 (C4'), 29.6 (C6'/C7'), 29.4 (C7'/C6'), 26.3 (C5'), 22.8 (C9'), 17.6 ($CH_3$8), 17.5 ($CH_3\underline{CH_2}$2), 17.4 ($CH_3\underline{CH_2}$6), 15.2 ($\underline{CH_3}CH_2$2), 15.0 ($CH_3$7), 14.8, ($\underline{CH_3}CH_2$6) 14.6 ($CH_3$1), 14.3 (C10'), 13.9 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{28}H_{45}BN_5O$ $[M+NH_4]^+$ 478.3717; found 478.3735. Calcd. for $C_{28}H_{41}BN_4NaO$ $[M+Na]^+$ 483.3271; found 483.3287. Calcd. for $C_{28}H_{42}BN_4O$ $(M+H)^+$ 461.3451; found 461.3477.

**Compound 17**



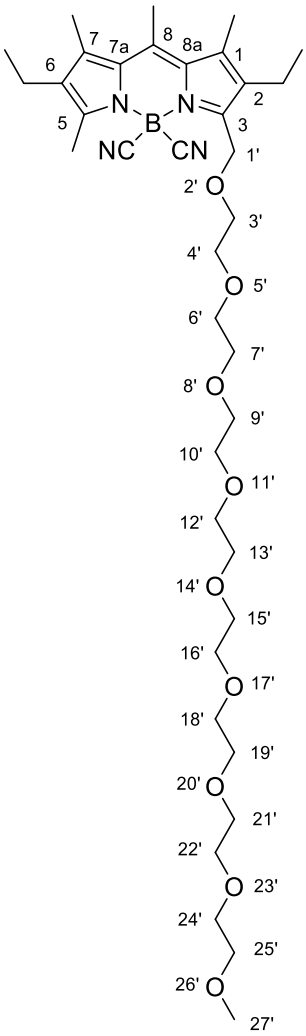

To a stirred solution of compound **9** (10.8 mg, 0.028 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added 1-hexadecanol (17.5 mg, 0.055 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (64 µL of a 0.01 M solution, 0.025 equiv). After stirring for 1 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (toluene/MeOH, 98:2) to afford compound **17** (13 mg, 82% yield) as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.83 (2H, s, H1'), 3.65 (2H, t, *J* = 6.7 Hz, H3'), 2.67 (6H, s, $CH_3$5 and $CH_3$8), 2.56 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2), 2.46 (2H, q, *J* = 7.6 Hz,

$CH_3\underline{CH_2}6$), 2.39 (3H, s, $CH_3$7), 2.38 (3H, s, $CH_3$1), 1.67 (2H, p, $J$ = 6.7 Hz, H4'), 1.45-1.21 (26 H, br m, H5'-H17'), 1.11 (3H, t, $J$ = 7.6 Hz, $\underline{CH_3}CH_2$2), 1.07 (3H, t, $J$ = 7.6 Hz, $\underline{CH_3}CH_2$6), 0.88 (3H, t, $J$ = 6.7 Hz, H18'). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 155.4 (C5), 148.7 (C3), 142.4 (C8), 139.5 (C7), 137.5 (C1), 135.2 (C6), 135.0 (C2), 131.4 (C7a), 130.2 (C8a), 127.4 (q, $J_{CB}$ = 74.5 Hz, 2 × CN), 71.9 (C3'), 64.2 (C1'), 32.1, 29.9, 29.8, 29.8, 29.7, 29.5, 26.4, 22.9 (from 32.1 to 22.9: C4'-C17'), 17.6 ($CH_3$8), 17.5 ($CH_3\underline{CH_2}$2), 17.4 ($CH_3\underline{CH_2}$6), 15.2 ($\underline{CH_3}CH_2$2), 15.0 ($CH_3$7) , 14.8 ($CH_3$1), 14.6 ($\underline{CH_3}CH_2$6), 14.3 (C18'), 13.9 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{36}H_{61}BN_5O$ $[M+NH_4]^+$ 590.4970; found 590.4969. Calcd. for $C_{36}H_{57}BN_4NaO$ $(M+Na)^+$ 595.4524; found 595.4517.

**Compound 18**

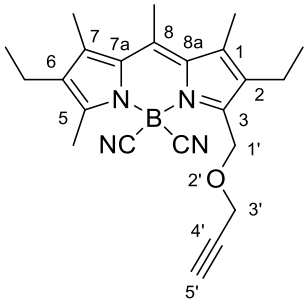


To a stirred solution of compound **9** (19.8 mg, 0.051 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added octaethylene glycol monomethyl ether (15.5 µL, 0.042 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (506 µL of a 0.01 M solution, 0.1 equiv). After stirring for 24 h at 40 °C, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (AcOEt/MeOH, 100:0 to 85:15) to afford compound **18** (10.8 mg, 36% yield, 40% yield considering recovered **9**: 2 mg), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.91 (2H, s, H1'), 3.84-3.81 (2H, m, H3'), 3.75-3.73 (2H, m, H4'), 3.67-3.63 (26, m, H6', H7', H9', H10', H12', H13',H15', H16', H18', H19', H21', H22' and H24'), 3.56-3.53 (2H, m, H25'), 3.37 (3H, s, H27'), 2.68 (3H, s, $CH_3$8), 2.67 (3H, s, $CH_3$5), 2.56 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.46 (2H. q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.40 (3H, s, $CH_3$7), 2.38 (3H, s, $CH_3$1), 1.11 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.07 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 155.7 (C5), 148.1 (C3), 142.5 (C8), 139.7 (C7), 137.4 (C1), 135.3 (C6), 135.0 (C2), 131.5 (C7a), 130.2 (C8a), 127.4 (q, $J_{CB}$ = 74.3 Hz, 2 × CN), 72.1 (C25'), 70.7 (C6', C7', C9', C10', C12', C13', C15', C16', C18', C19', C21', C22' and C24'), 70.7 (C4'), 70.5 (C3'), 64.4 (C1'), 59.2 (27'), 17.7 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 17.4 ($CH_3\underline{CH_2}$6/$CH_3\underline{CH_2}$2), 15.2 ($CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7), 15.0 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1), 14.8 ($\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2), 14.6 ($CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 13.9 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{37}H_{63}BN_5O_9$ $[M+NH_4]^+$ 732.4720; found 732.4731.

**Compound 19**



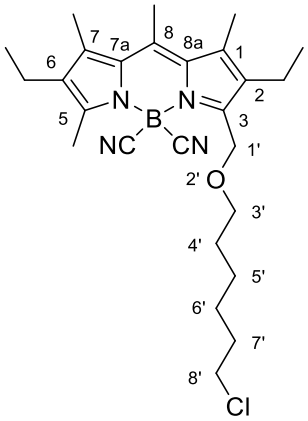

To a stirred solution of compound **9** (15.9 mg, 0.041 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added propargyl alcohol (4.8 µL, 0.081 mmol) and a solution of $Sc(OTf)_3$ in

anhydrous $CH_2Cl_2$ (96 µL of a 0.01 M solution, 0.025 equiv). After stirring for 90 min at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt mixtures, 93:7 to 70:30) to afford compound **9** (14.2 mg, 90% yield) as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.93 (2H, s H1'), 4.36 (2H, d, *J* = 2.3 Hz, H3'), 2.68 (6H, s, $CH_3$5 and $CH_3$8), 2.55 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2), 2.52 (1H, t, *J* = 2.3 Hz, H5'), 2.47 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.40 (3H, s, $CH_3$7), 2.39 (3H, s, $CH_3$1), 1.13 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2), 1.08 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 156.3 (C5), 146.8 (C3), 142.7 (C8), 140.1 (C7), 137.1 (C1), 135.6 (C6), 135.2 (C2), 131.8 (C7a), 130.7 (C8a), 127.4 (q, $J_{CB}$ = 74.8 Hz, 2 × CN), 79.5 (C4'), 75.4 (C5'), 62.5 (C1'), 58.4 (C3'), 17.7 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 15.3 ($\underline{CH_3}CH_2$2), 15.0 ($CH_3$7), 14.7 ($\underline{CH_3}CH_2$6), 14.6 ($CH_3$1), 14.0 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{23}H_{31}BN_5O$ $[M+NH_4]^+$ 404.2620; found 404.2635. Calcd. for $C_{23}H_{27}BN_4NaO$ $[M+Na]^+$ 409.2174; found 409.2190. Calcd. for $C_{23}H_{28}BN_4O$ $[M+H]^+$ 387.2355; found 387.2352.

**Compound 20**



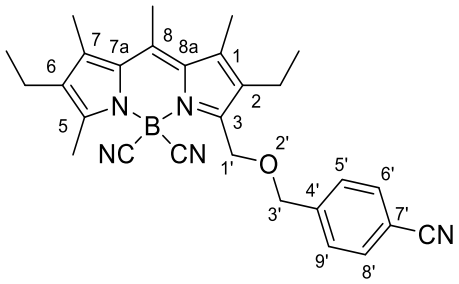

To a stirred solution of compound **9** (12 mg, 0.031 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added 6-chlorohexanol (8.5 µL, 0.061 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (76 µL of a 0.01 M solution, 0.025 equiv). After stirring for 1 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined

organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (toluene/MeOH, 99:1) to afford compound **20** (12.7 mg, 88% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 500 MHz): δ = 4.83 (2H, s, H1'), 3.66 (2H, t, *J* = 6.7 Hz, H3'), 3.52 (2H, t, *J* = 6.7 Hz, H8'), 2.67 (6H, s, $CH_3$5 and $CH_3$8), 2.55 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2), 2.46 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.39 (3H, s, $CH_3$7), 2.38 (3H, s, $CH_3$1), 1.78 (2H, p, *J* = 6.7 Hz, H7'), 1.69 (2H, p, *J* = 6.7 Hz, H4'), 1.52-1.38 (4H, m, H5' and H6'), 1.11 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2), 1.08 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 125 MHz): δ = 155.5 (C5), 148.4 (C3), 142.5 (C8), 139.6 (C7), 137.5 (C1), 135.3 (C6), 134.9 (C2), 131.5 (C7a), 130.2 (C8a), 127.4 (q, $J_{CB}$ = 74.6 Hz, 2 × CN), 71.5 (C3'), 64.2 (C1'), 45.3 (C8'), 32.7 (C7'), 29.7 (C4'), 26.8 (C6'), 25.6 (C5'), 17.7 ($CH_3$8), 17.5 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 17.4 ($CH_3\underline{CH_2}$6/$CH_3\underline{CH_2}$2), 15.3 ($\underline{CH_3}CH_2$6), 15.0 ($CH_3$7), 14.8 ($\underline{CH_3}CH_2$2), 14.6 ($CH_3$1), 13.9 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{26}H_{40}BClN_5O$ $[M+NH_4]^+$ 484.3014 ($^{35}$Cl), 486.2995 ($^{37}$Cl); found 484.3015 $^{35}$(Cl), 486.2995 ($^{37}$Cl). Calcd. for $C_{26}H_{36}BClN_4NaO$ $[M+Na]^+$ 489.2568 ($^{35}$Cl), 491.2548 ($^{37}$Cl); found 489.2578 ($^{35}$Cl), 491.2547 ($^{37}$Cl).

**Compound 21**



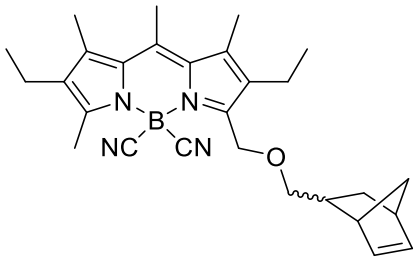

To a stirred solution of compound **9** (10 mg, 0.026 mmol) in anhydrous $CH_2Cl_2$ (5 mL) was added 4-(hydroxymethyl)benzonitrile (5.1 mg, 0.038 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (64 µL of a 0.01 M solution, 0.025 equiv). After stirring for 8 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by

silica gel flash column chromatography (hexane/AcOEt, 100:0 to 75:25) to afford compound **21** (10 mg, 88% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 7.63 (2H, d, *J* = 8.2 Hz, H6' and H8'), 7.55 (2H, d, *J* = 8.2 Hz, H5' and H9'), 4.93 (2H, s, H3'), 4.78 (2H, s, H1'), 2.69 (6H, s, $CH_3$5 and $CH_3$8), 2.52 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.47 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.41 (3H, s, $CH_3$7), 2.38 (3H, s, $CH_3$1), 1.08 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 1.08 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6/$\underline{CH_3}CH_2$2). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 156.5 (C5), 146.6 (C3), 143.5 (C4'), 142.8 (C8), 140.3 (C7a), 137.1 (C8a), 135.7 (C7), 134.9 (C1), 132.3 (C6' and C8'), 131.8 (C6), 130.2 (C2), 128.4 (C5' and C9'), 127.4 (q, $J_{CB}$ = 74 Hz, 2 x BCN), 119.0 (CN7'), 111.5 (C7'), 72.5 (C3'), 63.8 (C1'), 17.7 ($CH_3$8) , 17.5 ($CH_3\underline{CH_2}$6), 17.4 ($CH_3\underline{CH_2}$2), 15.3 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 15.0 ($CH_3$7), 14.7 ($CH_3$1), 14.6 ($\underline{CH_3}CH_2$6/$\underline{CH_3}CH_2$2), 14.0 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{28}H_{34}BN_6O$ $[M+NH_4]^+$ 481.2887; found 481.2885. Calcd. for $C_{28}H_{30}BN_5NaO$ $[M+Na]^+$ 486.2441; found 486.2451.

**Compound 22**



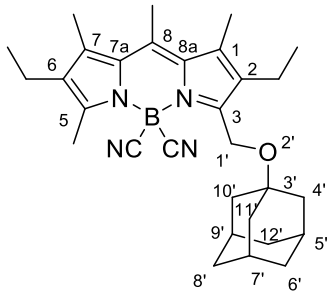

To a stirred solution of compound **9** (16 mg, 0.041 mmol) in anhydrous $CH_2Cl_2$ (1.5 mL) was added 5-norbornene-2-methanol (6.44 µL, 0.053 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (102 µL of a 0.01 M solution, 0.025 equiv). After stirring for 1 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 70:30) to afford compound **22** (15.7 mg, 84% yield), as a red-orange solid (2:1 mixture of *endo*/*exo*-isomers).

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 6.14 (dd, *J* = 5.5, 2.9 Hz, 1H *endo*), 6.10 (dd, *J* = 5.5, 3.0 Hz, 1H *exo*), 6.04 (dd, *J* = 5.5, 2.8 Hz, 1H *exo*), 6.00 (dd, *J* = 5.5, 2.8 Hz, 1H *endo*), 4.85 (s, 2H *exo*), 4.81 (d, *J* = 12.7 Hz, 1H *endo*), 4.76 (d, *J* = 12.7 Hz, 1H *endo*), 3.72 (dd,

*J* = 9.0, 6.5 Hz, 1H *exo*), 3.60 (t, *J* = 9.0 Hz, 1H *exo*), 3.40 (dd, *J* = 9.0, 6.7 Hz, 1H *endo*), 3.28 (t, *J* = 9.0 Hz, 1H *endo*), 2.98 (br s, 1H *endo*), 2.81-2.79 (m, 2H *exo*), 2.79 (s, 1H *endo*), 2.67 (s, 6H *endo*+*exo*), 2.57 (q, *J* = 7.5 Hz, 2H *endo*+*exo*), 2.52-2.44 (m, 1H *endo*), 2.46 (q, *J* = 7.5 Hz, 2H *endo*+*exo*), 2.39 (s, 3H *endo*+*exo*), 2.38 (s, 3H *endo*+*exo*), 1.85 (m, 1H *endo*) 1.80 (m, 1H *exo*), 1.41 (m, 1H *endo*), 1.36-1.17 (m, 4H *exo* + 1H *endo*), 1.14 (t, *J* = 7.5 Hz, 3H *endo*), 1.13 (t, *J* = 7.5 Hz, 3H *endo*), 1.07 (t, *J* = 7.5 Hz, 3H *endo*+*exo*), 0.61- 0.53 (m, 1H *endo*). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.5, 155.3, 148.7, 148.5, 142.5, 139.6, 139.5, 137.5, 137.2, 136.8, 136.7, 135.2, 135.0, 132.8, 131.4, 130.2, 127.3 (q, $J_{CB}$ = 74.5 Hz, 2 × CN), 76.4, 75.5, 64.3, 49.5, 45.3, 44.2, 44.0, 42.4, 41.7, 38.9, 38.8, 30.0, 29.4, 17.6, 17.5, 17.4, 15.2, 15.2, 15.0, 14.8, 14.6, 14.6, 13.8.

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{28}H_{39}BN_5$ $[M+NH_4]^+$ 472.3248; found 472.3251.

**Compound 23**



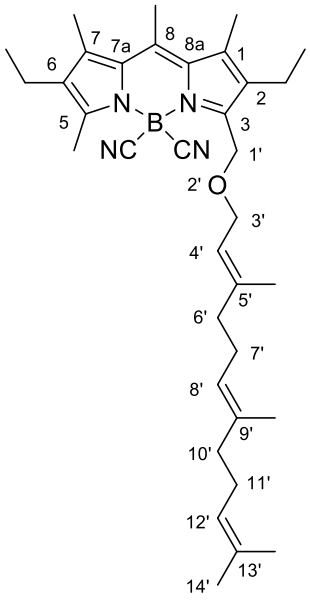

To a stirred solution of compound **9** (20 mg, 0.038 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added 1-adamantanol (10.1 mg, 0.067 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (256 µL of a 0.01 M solution, 0.05 equiv). After stirring for 5 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography ($CH_2Cl_2$/AcOEt, 100:0 to 92:8) to afford compound **23** (6.8 mg, 27% yield; 46% yield considering recovered **9**: 8.1 mg), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.85 (2H, s, H1'), 2.67 (3H, s, $CH_3$5), 2.66 (3H, s, $CH_3$8), 2.57 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.46 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.38 (3H, s, $CH_3$7), 2.37 (3H, s, $CH_3$1), 2.23-2.19 (3H, br m, H5', H7' and H9'), 1.97 (6H, d, *J* = 3.1 Hz, H4', H10' and H11'), 1.67 (6H, t, *J* = 2.1 Hz, H6', H8' and H12'), 1.14 (3H, t, *J* = 7.5

Hz, $\underline{CH_3}CH_2$2), 1.08 (3H, t, $J$ = 7.5 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 154.7 (C5), 150.1 (C3), 142.1 (C8), 139.1 (C7), 137.9 (C1), 135.3 (C2), 134.9 (C6), 131.1 (C7a), 130.2 (C8a), 127.7 (q, $J_{CB}$ = 74.7 Hz, 2 × CN), 73.9 (C3'), 54.4 (C1'), 41.3 (C4', C10' and C11'), 36.6 (C6', C8' and C12'), 30.9 (C5', C7' and C9'), 17.6 ($CH_3\underline{CH_2}$2/$CH_3$8), 17.6 ($CH_3$8/$CH_3\underline{CH_2}$2), 17.4 ($CH_3\underline{CH_2}$6), 15.2 ($\underline{CH_3}CH_2$2), 14.9 ($CH_3$1/$CH_3$7), 14.8 ($\underline{CH_3}CH_2$6), 14.6 ($CH_3$7/$CH_3$1), 13.8 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{30}H_{39}BN_4NaO$ $[M+Na]^+$ 505.3115; found 505.3120.

**Compound 24**



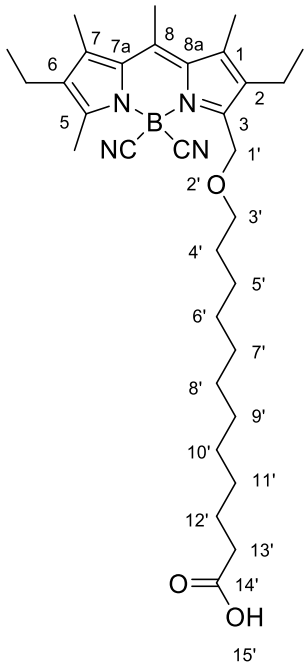

To a stirred solution of compound **9** (23.3 mg, 0.06 mmol) in anhydrous $CH_2Cl_2$ (1.5 mL) was added farnesol (5 μL, 0.05 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (150 μL of a 0.01 M solution, 0.025 equiv). After stirring for 4 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 70:30) to afford compound **24** (5.7 mg, 21% yield, 96% yield considering recovered **24**: 18.3 mg), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 500 MHz): δ = 5.48 (1H, m, H4'), 5.13 (1H, m, H8'), 5.09 (1H, m, H12'), 4.83 (2H, s, H1'), 4.22 (2H, d, $J$ = 6.9 Hz, H3'), 2.68 (3H, s, $CH_3$5), 2.67 (3H, s,

$CH_3$8), 2.55 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2), 2.46 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.39 (3H, s, $CH_3$7), 2.38 (3H, s, $CH_3$1), 2.17-2.10 (2H, m, H7'), 2.09-2.02 (4H, m, H6' and H11'), 2.00-1.94 (2H, m, H10'), 1.73 (3H, s, $CH_3$5'), 1.68 (3H, s, $CH_3$13'/H14'), 1.60 (6H, s, $CH_3$9' and H14'/$CH_3$13'), 1.11 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2), 1.08 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 125 MHz): δ = 155.4 (C5), 148.7 (C3), 142.4 (C8), 141.4 (C5'), 139.5 (C7), 137.5 (C1), 135.3 (C9'), 135.2 (C6), 135.0 (C2), 131.4 (C13'), 130.2 (C7a and C8a), 128.1 (q, $J_{CB}$ = 74.6 Hz, 2 × CN), 124.5 (C12'), 124.2 (C8'), 120.5 (C4'), 67.8 (C3'), 63.1 (C1'), 39.9 (C6'/C10'), 39.8 (C10'/C6'), 26.9 (C11'), 26.6 (C7'), 25.8 ($CH_3$13'/H14'), 17.8 (H14'/$CH_3$13'), 17.6 ($CH_3$8), 17.5 ($CH_3\underline{CH_2}$2), 17.4 ($CH_3\underline{CH_2}$6), 16.7 ($CH_3$5'), 16.1 ($CH_3$9'), 15.2 ($\underline{CH_3}CH_2$2), 15.0 ($CH_3$7), 14.8 ($\underline{CH_3}CH_2$6), 14.6 ($CH_3$1), 13.9 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{35}H_{49}BN_4NaO$ $[M+Na]^+$ 575.3898; found 575.3873. Calcd. for $C_{35}H_{53}BN_5O$ $[M+NH_4]^+$ 570.4344; found 570.4344.

**Compound 25**



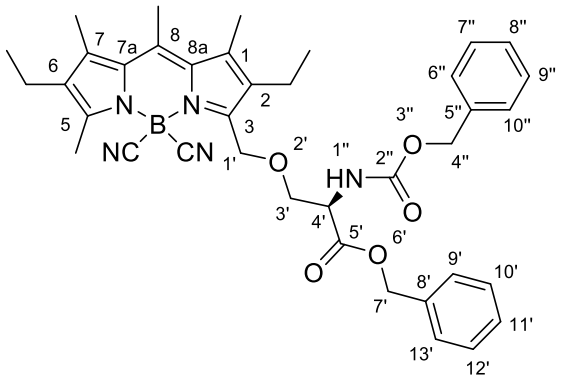

To a stirred solution of compound **9** (15 mg, 0.038 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added 12-hydroxydodecanoic acid (8.6 mg, 0.038 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (96 µL of a 0.01 M solution, 0.025 equiv). After stirring for 6 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the

solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography ($CH_2Cl_2$/AcOEt, 100:0 to 80:20) to afford compound **25** (11.8 mg, 56% yield) as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.83 (2H, s, H1'), 3.65 (2H, t, *J* = 6.7 Hz, H3'), 2.67 (6H, s, $CH_3$5 and $CH_3$8), 2.56 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.46 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.39 (3H, s, $CH_3$7), 2.38 (3H, s, $CH_3$1), 2.34 (2H, t, *J* = 7.5 Hz, H13'), 1.74 - 1.53 (4H, m, H4' and H12'), 1.45-1.19 (14H, m, H5', H6', H7', H8', H9', H10' and H11'), 1.11 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.07 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 178.5 (C14'), 155.4 (C5), 148.7 (C3), 142.4 (C8), 139.5 (C7), 137.6 (C1), 135.2 (C2), 134.9 (C6), 131.4 (C7a), 130.2 (C8a), 127.4 (q, $J_{CB}$ = 74.2 Hz, 2 × CN), 71.8 (C3'), 64.2 (C1'), 33.9 (C13'), 29.8 (C4'), 29.7 – 29.2 (C6' - C11'), 26.3 (C5'), 24.8 (C12'), 17.6 ($CH_3$8), 17.5 ($CH_3\underline{CH_2}$2), 17.4 ($CH_3\underline{CH_2}$6), 15.2 ($CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7), 15.0 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1), 14.8 ($\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2), 14.6 ($CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 13.9 ($CH_3$9).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{32}H_{51}BN_5O_3$ $[M+NH_4]^+$ 564.4085; found 564.4103. Calcd. for $C_{32}H_{47}BN_4NaO_3$ $[M+Na]^+$ 569.3639; found 569.3673.

**Compound 26**




To a stirred solution of compound **9** (15 mg, 0.038 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added *N*-Cbz-L-serine benzyl ester (15.1 mg, 0.038 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (192 µL of a 0.01 M solution, 0.05 equiv). After stirring for 30 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The

combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (cyclohexane/AcOEt, 95:5 to 80:20) to afford compound **26** (17.12 mg, 67% yield; 83% yield considering recovered **9**: 2.8 mg ), as a red-orange solid.

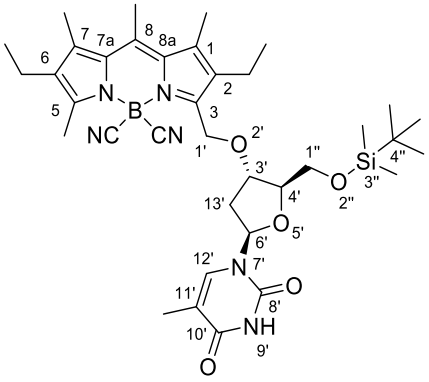
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ = 7.38-7.27 (10H, m, H9', H10', H11', H12', H13', H6", H7", H8", H9" and H10"), 6.18 (1H, d, *J* = 8.3 Hz, H1"), 5.20 (1H, d, *J* = 12.4 Hz, H7'), 5.16 (1H, d, *J* = 12.4 Hz, H7'), 5.14 (1H, d, *J* = 12.6 Hz, H4"), 5.09 (1H, d, *J* = 12.6 Hz, H4"), 4.83(1H, d, *J* = 12.1 Hz, H1'), 4.73(1H, d, *J* = 12.1 Hz, H1'), 4.59 (1H, ddd, *J* = 8.3, 3.5, 2.8 Hz, H4'), 4.17 (1H, dd, *J* = 9.2, 3.5 Hz, H3'), 3.97 (1H, dd, *J* = 9.2, 2.8 Hz, H3'), 2.68 (3H, s, $CH_3$8), 2.66 (3H, s, $CH_3$5), 2.46 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.41 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.40 (3H, s, $CH_3$7), 2.36 (3H, s, $CH_3$1), 1.08 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6), 1.02 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2). **$^{13}$C NMR** ($CDCl_3$, 125 MHz): δ = 170.1 (C5'), 156.7 (C5/C2"), 156.5 (C2"/C5), 146.0 (C3), 142.9 (C8), 140.3 (C7), 136.9 (C1/C5"), 136.9 (C5"/C1), 135.7 (C6 and C8"), 135.0 (C2), 131.9 (C7a), 130.2 (C8a), 128.7 – 127.9 (C9'/C10'/C11'/C12'/C13'/C6"/C7"/C8"/C9"/C10"), 70.9 (C3'), 67.3 (C7'), 66.8 (C4"), 63.8 (C1'), 54.9 (C4'), 17.7 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 17.4 ($CH_3\underline{CH_2}$6/$CH_3\underline{CH_2}$2), 15.4 ($\underline{CH_3}CH_2$2), 15.1 ($CH_3$7), 14.7 ($\underline{CH_3}CH_2$6), 14.6 ($CH_3$1), 14.0 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{38}H_{43}BN_5O_5$ $[M+H]^+$ 660.3358; found 660.3358. Calcd. for $C_{38}H_{46}BN_6O_5$ $[M+NH_4]^+$ 677.3624; found 677.3625. Calcd. for $C_{38}H_{42}BN_5NaO_5$ $[M+Na]^+$ 682.3178; found 682.3176.

**Compounds 27 and 28**

To a stirred solution of compound **9** (20 mg, 0.051 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added 5'-*O*-(*tert*-butyldimethylsilyl)thymidine (18.3 mg, 0.051 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (128 µL of a 0.01 M solution, 0.025 equiv) at room temperature. The reaction mixture was then heated at 40 °C for 5 h. After cooling to room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography ($CH_2Cl_2$/AcOEt, 85:15 to 50:50) to afford compounds **27** (6.2 mg, 17%

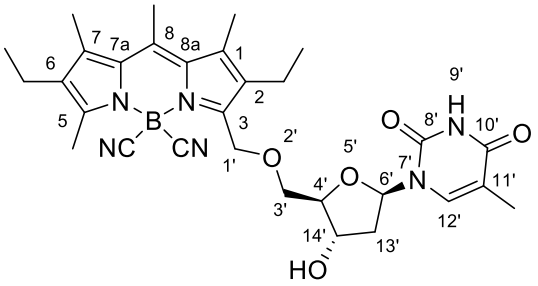
yield; 27% yield considering recovered **9**: 7.2 mg) and compound **28** (5.3 mg, 18% yield; 28% yield considering recovered **9**), as red-orange solids.



**27**

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 8.05 (1H, s, H9'), 7.55 (1H, s, H12'), 6.33 (1H, dd, *J* = 8.6, 5.6 Hz, H6'), 4.84 (2H, m, H1'), 4.40-4.35 (1H, m, H3'), 4.30-4.25 (1H, m, H4'), 3.98-3.84 (2H, m, H1''), 2.70 (3H, s, $CH_3$8), 2.68 (3H, s, $CH_3$5), 2.63 (1H, ddd, *J* = 14.0, 5.6, 1.2 Hz, H13'), 2.55 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2), 2.47 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.41 (3H, s, $CH_3$7), 2.40 (3H, s, $CH_3$1), 2.07 (1H, ddd, *J* = 14.0, 8.4, 5.6 Hz, H13'), 1.91 (3H, s, $CH_3$11'), 1.14 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2), 1.08 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6), 0.94 (9H, s, $(CH_3)_3$4''), 0.14 (3H, s, $(CH_3)_2$3''), 0.13 (3H, s, $(CH_3)_2$3''). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 163.6 (C10'), 156.6 (C5), 150.1 (C8'), 146.2 (C3), 142.9 (C8), 140.3 (C7), 137.2 (C1), 135.9 (C12'), 135.7 (C6), 134.9 (C2), 131.9 (C7a), 130.3 (C8a), 110.8 (C11'), 85.3 (C4'/C6'), 85.3 (C6'/C4'), 81.0 (C3'), 63.9 (C1''), 62.4 (C1'), 37.7 (C13'), 26.1 ($(CH_3)_3$4''), 18.5 (C4''), 17.7 ($CH_3$8), 17.6 ($CH_3\underline{CH_2}$2), 17.4 ($CH_3\underline{CH_2}$6), 15.4 ($\underline{CH_3}CH_2$2), 15.1 ($CH_3$1/$CH_3$7), 14.7 ($\underline{CH_3}CH_2$6), 14.6 ($CH_3$7/$CH_3$1), 14.0 ($CH_3$5), 12.6 ($CH_3$11'), -5.2 ($(CH_3)_2$3'').

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{36}H_{55}BN_7O_5Si$ $[M+NH_4]^+$ 704.4128; found 704.4147. Calcd. for $C_{36}H_{52}BN_6O_5Si$ $[M+H]^+$ 687.3863; found 687.3876.

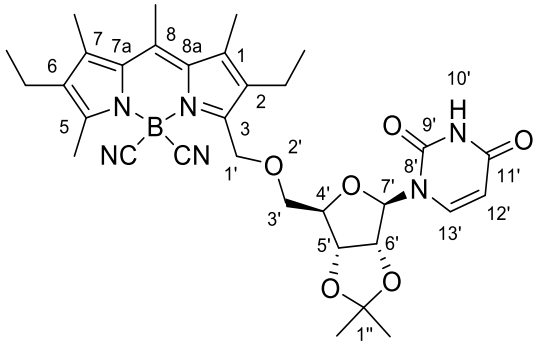


**28**

**$^1$H NMR** ($CDCl_3$, 500 MHz): δ = 8.11 (1H, s, H9'), 7.41 (1H, s, H12'), 6.24 (1H, dd, *J* = 7.3, 3.3 Hz, H6'), 4.84 (2H, s, H1'), 4.74-4.63 (1H, m, H14'), 4.01-3.92 (2H, m, H3'), 3.93-3.86 (1H, m, H4'), 2.72 (3H, s, $CH_3$8), 2.69 (3H, s, $CH_3$5), 2.49 (4H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 2.43 (3H, s, $CH_3$7), 2.41-2.36 (1H, m, H13'), 2.39 (3H, s, $CH_3$1), 2.12 (1H, ddd, *J* = 13.8, 7.5, 3.4 Hz, H13'), 1.64 (3H, s, $CH_3$11'), 1.09 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 1.08 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6/ $\underline{CH_3}CH_2$2). **$^{13}$C NMR** ($CDCl_3$, 125 MHz): δ = 163.6 (C10'), 157.4 (C5), 150.1 (C8'), 145.7 (C3), 143.2 (C8), 141.1 (C7), 136.9 (C1), 136.2 (C6/C12'), 136.2 (C12'/C6) 135.0 (C2), 132.3 (C7a), 130.4 (C8a), 110.5 (C11'), 84.6 (C4'), 83.7 (C6'), 68.6 (C3'), 67.6 (C14'), 63.3 (C1'), 39.7 (C13'), 17.8 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 17.4 ($CH_3\underline{CH_2}$6/$CH_3\underline{CH_2}$2), 15.6 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 15.1 ($CH_3$7), 14.7 ($\underline{CH_3}CH_2$6/$\underline{CH_3}CH_2$2), 14.6 ($CH_3$1) , 14.1 ($CH_3$5), 12.2 ($CH_3$11').

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{30}H_{37}BN_6NaO_5$ $[M+Na]^+$ 595.2816; found 595.2824.

**Compound 29**

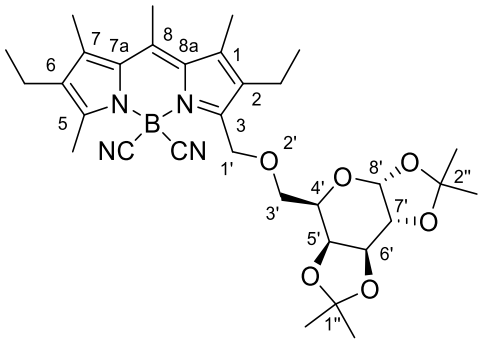



To a stirred solution of compound **9** (20.3 mg, 0.052 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added 2',3'-*O*-isopropylideneuridine (16.3 mg, 0.057 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (128 μL of a 0.01 M solution, 0.025 equiv). After stirring for 23 h at room temperature, a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (128 μL of a 0.01 M solution, 0.025 equiv) was added again, followed by stirring the reaction mixture at room temperature for 4 h and at 40 °C for 3 h. The reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography ($CH_2Cl_2$/AcOEt, 90:10 to 50:50) to afford compound **29** (8.9 mg, 28% yield; 48% yield considering recovered **9**: 8.5 mg), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 8.16 (1H, s, NH10'), 7.59 (1H, d, *J* = 8.1 Hz, H13'), 5.97 (1H, d, *J* = 2.9 Hz, H7'), 5.25 (1H, dd, *J* = 8.1, 2.2 Hz, H12'), 5.05 (1H, dd, *J* = 6.3, 2.6 Hz, H5'), 4.94 (1H, d, *J* = 12.1 Hz, H1'), 4.76 (1H, d, *J* = 12.1 Hz, H1'), 4.71 (1H, dd, *J* = 6.3, 2.9 Hz, H6'), 4.46 (1H, m, H4'), 4.02 (1H, dd, *J* = 10.3, 2.6 Hz, H3'), 3.88 (1H, dd, *J* = 10.3, 2.6 Hz, H3'), 2.73 (3H, s, $CH_3$8), 2.69 (3H, s, $CH_3$5), 2.47 (4H, m, $CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 2.43 (3H, s, $CH_3$7), 2.39 (3H, s, $CH_3$1), 1.56 (3H, s, $CH_3$1"), 1.33 (3H, s, $CH_3$1"), 1.09 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2), 1.09 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 162.9 (C11'), 157.2 (C5), 150.2 (C9'), 145.2 (C3), 143.4 (C8), 141.5 (C13'), 141.0 (C7), 136.8 (C1), 136.1 (C6), 134.6 (C2) , 132.1 (C7a), 130.1 (C8a), 114.1 (C1"), 101.5 (C12'), 92.3 (C7'), 85.8 (C4'), 85.2 (C6'), 81.4 (C5'), 71.3 (C3'), 63.7 (C1'), 27.2 ($CH_3$1"), 25.4 ($CH_3$1"), 17.8 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 15.4 ($CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7), 15.1 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1), 14.7 ($\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2), 14.6 ($CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 14.0 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{32}H_{39}BN_6NaO_6$ $[M+Na]^+$ 637.2922; found 637.2912. Calcd. for $C_{32}H_{43}BN_7O_6$ $[M+NH_4]^+$ 632.3368; found 632.3348.

**Compound 30**



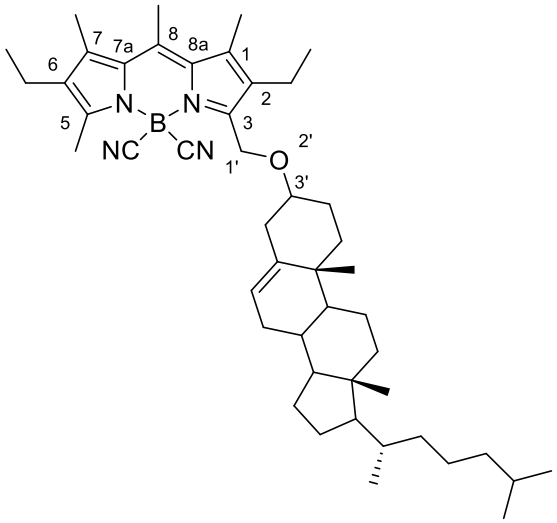

To a stirred solution of compound **9** (16 mg, 0.041 mmol) in chloroform (1 mL) was added 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (16.5 mg, 0.061 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (409 µL of a 0.01 M solution, 0.1 equiv). After stirring for 1 day at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by

silica gel flash column chromatography (hexane/AcOEt, 100:0 to 80:20) to afford compound **30** (12.6 mg, 52% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 5.55 (1H, d, *J* = 5.0 Hz, H8'), 4.95 (1H, d, *J* = 12.8 Hz, H1'), 4.90 (1H, d, *J* = 12.8 Hz, H1'), 4.59 (1H, dd, *J* = 8.0, 2.1 Hz, H6'), 4.34 (dd, *J* = 8.0, 1.2 Hz, H5'), 4.30 (1H, ddd, *J* = 5.0, 2.1, 0.5 Hz, H7'), 4.15-4.10 (1H, m, H4'), 3.88 (1H, dd, *J* = 10.1, 5.6 Hz, H3'), 3.83 (1H, dd, *J* = 10.1, 6.9 Hz, H3'), 2.67 (6H, s, $CH_3$5 and $CH_3$8), 2.56 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.45 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.39 (3H, s, $CH_3$7), 2.38 (3H, s, $CH_3$1), 1.54 (3H, s, $CH_3$2"), 1.47 (3H, s, $CH_3$1"), 1.33 (3H, s, $CH_3$1"), 1.32 (3H, s, $CH_3$2"), 1.11 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.06 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 155.7 (C5), 148.1 (C3), 142.5 (C8), 139.6 (C7), 137.3 (C1), 135.3 (C2/C6), 135.2 (C6/C2), 131.5 (C7a), 130.3 (C8a), 127.3 (q, $J_{CB}$ = 76.9 Hz, 2 × CN), 109.3 (C1"), 108.7 (C2"), 96.5 (C8'), 71.2 (C5'), 70.8 (C6' and C7'), 70.0 (C3'), 67.0 (C4'), 64.4 (C1'), 26.2 ($CH_3$1"/$CH_3$2"), 26.2 ($CH_3$2"/$CH_3$1"), 25.1 ($CH_3$2"), 24.5 ($CH_3$1"), 17.7 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 17.4 ($CH_3\underline{CH_2}$6/$CH_3\underline{CH_2}$2), 15.4 ($CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7), 15.0 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1), 14.8 ($\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2), 14.6 ($CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 13.9 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{32}H_{47}BN_5O_6$ $[M+NH_4]^+$ 608.3620; found 608.3606. Calcd. for $C_{32}H_{43}BN_4O_6$ $[M+Na]^+$ 613.3174; found 613.3157.

**Compound 31**

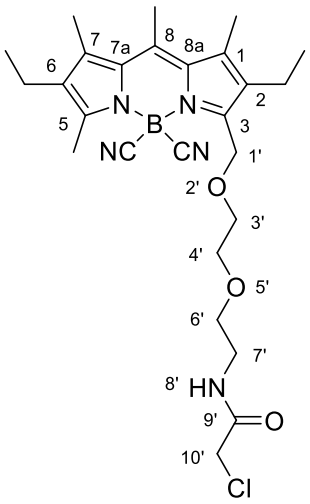


To a stirred solution of compound **9** (11 mg, 0.028 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added cholesterol (16.5 mg, 0.042 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (70 µL of a 0.01 M solution, 0.025 equiv). After stirring for 90 min at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 75:25) to afford compound **31** (12.5 mg, 80% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 5.40 (br s, 1H), 4.87 (2H, s, H1'), 3.48 (1H, m, H3'), 2.67 (6H, s, $CH_3$5 and $CH_3$8), 2.56 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.55-2.52 (m, 1H), 2.46 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.39 (3H, s, $CH_3$7), 2.38 (3H, s, $CH_3$1), 2.36-2.30 (m, 1H), 2.16-2.08 (m, 1H), 2.07-1.73 (m, 5H), 1.64-1.06 (m, 20H), 1.13 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.08 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.02 (s, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 1.5 Hz, 6H), 0.68 (s, 3H). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 155.3 (C5), 148.9 (C3), 142.4 (C8), 140.9, 139.4 (C7), 137.6 (C1), 135.1 (C2/C6), 135.1 (C6/C2), 131.4 (C7a), 130.2 (C8a), 127.4 (q, $J_{CB}$ = 74.5 Hz, 2 × CN), 121.9, 80.2 (C3'), 61.5 (C1'), 56.9, 56.3, 50.3, 42.5, 40.0, 39.7, 39.0, 37.4, 37.0, 36.4, 35.9, 32.1, 32.1, 28.4, 28.3, 28.2, 24.5, 24.0, 23.0, 22.7, 21.2, 19.6, 18.9, 17.6 ($CH_3\underline{CH_2}$2/$CH_3$8), 17.6 ($CH_3$8/$CH_3\underline{CH_2}$2), 17.4 ($CH_3\underline{CH_2}$6), 15.2 ($\underline{CH_3}CH_2$2), 15.0 ($CH_3$7), 14.8 ($\underline{CH_3}CH_2$6), 14.6 ($CH_3$1), 13.9 ($CH_3$5), 12.0.

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{47}H_{73}BN_5O$ $[M+NH_4]^+$ 734.5911; found 734.5908. Calcd. for $C_{47}H_{69}BN_4NaO$ $[M+Na]^+$ 739.5465; found 739.5457.

**Compound 32**

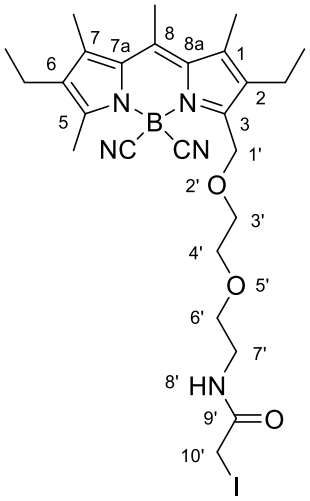


To a stirred solution of compound **9** (25 mg, 0.064 mmol) in anhydrous $CH_2Cl_2$ (1.2 mL) was added 2-chloro-*N*-(2-(2-hydroxyethoxy)ethyl)acetamide (17.5 mg, 0.096 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (320 µL of a 0.01 M solution, 0.05 equiv). After stirring for 24 h at 45 °C, a solution of $Sc(OTf)_3$ (160 µL of a 0.01 M solution, 0.025 equiv) was added to the mixture again. After stirring for an additional 6 h at 50 °C, the reaction mixture was then quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 80:20 to 25:75) to afford compound **32** (23.4 mg, 71% yield; 95% yield considering recovered **9**: 6.3 mg), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 500 MHz): δ = 7.09 (1H, br s, H8'), 4.89 (2H, s, H1'), 3.97 (2H, s, H10'), 3.83 (2H, t, *J* = 5.1 Hz, H3'), 3.74 (2H, t, *J* = 5.1 Hz, H4'), 3.60 (2H, t, *J* = 5.1 Hz, H6'), 3.49 (2H, q, *J* = 5.1 Hz, H7'), 2.68 (3H, s, $CH_3$5/$CH_3$8), 2.68 (3H, s, $CH_3$8/$CH_3$5), 2.54 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.47 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.40 (3H, s, $CH_3$7), 2.38 (3H, s, $CH_3$1), 1.11 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2) , 1.08 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 125 MHz): δ = 166.3 (C9'), 156.0 (C5), 147.4 (C3), 142.7 (C8), 140.0 (C7), 137.3 (C1), 135.5 (C6), 134.8 (C2), 131.7 (C7a), 130.3 (C8a), 127.4 (q, $J_{CB}$ = 74.7 Hz, 2 × CN), 70.6 (C3'/C4'), 70.5 (C4'/C3'), 69.5 (C6'), 64.2 (C1'), 42.8 (C10'), 39.8 (C7'), 17.7 ($CH_3$8), 17.5 ($CH_3\underline{CH_2}$6), 17.4 ($CH_3\underline{CH_2}$2), 15.3 ($CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7), 15.0 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1), 14.8 ($\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2), 14.6 ($CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 13.9 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{26}H_{35}BClN_5NaO_3$ $[M+Na]^+$ 534.2418 ($^{35}Cl$), 536.2400 ($^{37}Cl$); found 534.2440 ($^{35}Cl$), 536.2414 ($^{37}Cl$).

**Compound 33**

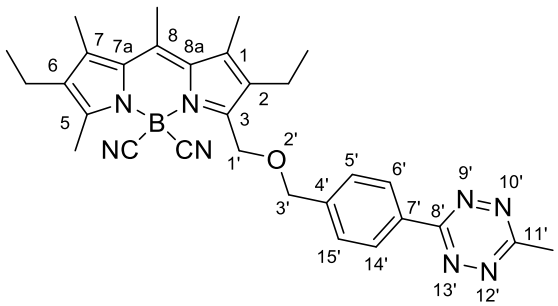



To a stirred solution of compound **9** (25 mg, 0.064 mmol) in anhydrous $CH_2Cl_2$ (1.2 mL) was added 2-iodo-*N*-(2-(2-hydroxyethoxy)ethyl)acetamide (26.2 mg, 0.096 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (320 µL of a 0.01 M solution, 0.05 equiv). After stirring for 8 h at 60 °C, the reaction mixture was cooled to room temperature and stirred for an additional 22 h. The reaction mixture was then quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 80:20 to 30:70) to afford compound **33** (34 mg, 88% yield; 95% yield considering recovered **9**: 2 mg), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): 7.03 (1H, br s, H8'), 4.86 (2H, s, H1'), 3.86-3.83 (2H, m, H3'), 3.76-3.72 (2H, m, H4'), 3.58 (2H, s, H10'), 3.56 (2H, t, *J* = 5.1 Hz, H6'), 3.43 (2H, q, *J* = 5.1 Hz, H7'), 2.69 (3H, s, $CH_3$5/$CH_3$8), 2.69 (3H, s, $CH_3$8/$CH_3$5), 2.53 (2H, q, *J* = 7.4 Hz, $CH_3\underline{CH_2}$2), 2.47 (2H, q, *J* = 7.4 Hz, $CH_3\underline{CH_2}$6), 2.41 (3H, s, $CH_3$7), 2.39 (3H, s, $CH_3$1), 1.11 (3H, t, *J* = 7.4 Hz, $\underline{CH_3}CH_2$2), 1.09 (3H, t, *J* = 7.4 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 167.8 (C9'), 156.1 (C5), 147.2 (C3), 142.8 (C8), 140.2 (C7), 137.2 (C1), 135.6 (C6), 134.8 (C2), 131.8 (C7a), 130.3 (C8a), 127.4 (q, $J_{CB}$ = 74.8 Hz, 2 × CN), 70.9 (C3'), 70.5 (C4'), 69.6 (C6'), 64.1 (C1'), 40.2 (C7'), 17.7 ($CH_3$8), 17.5

($CH_3\underline{CH_2}2$/$CH_3\underline{CH_2}6$), 17.4 ($CH_3\underline{CH_2}6$/$CH_3\underline{CH_2}2$), 15.3 ($\underline{CH_3}CH_22$/$\underline{CH_3}CH_26$), 15.0 ($\underline{CH_3}CH_26$/$\underline{CH_3}CH_22$), 14.7 ($CH_31$/$CH_37$), 14.6 ($CH_37$/$CH_31$), 14.0 ($CH_35$), -0.2 (C10'). **HRMS** (API-ES$^+$) *m/z* calcd. for $C_{26}H_{35}BIN_5NaO_3$ $[M+Na]^+$ 626.1775; found 626.1797. calcd. for $C_{26}H_{36}BIN_5O_3$ $[M+H]^+$ 604.1955; found 604.1946. calcd. for $C_{26}H_{39}BIN_6O_3$ $[M+NH_4]^+$ 621.2221; found 621.2209.

**Compound 34**

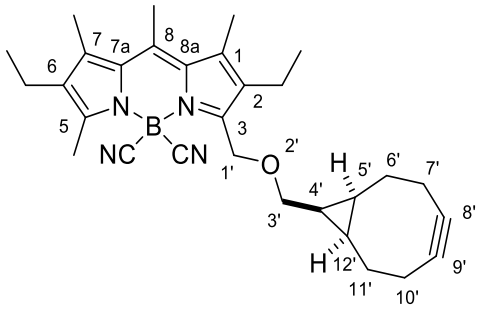



To a stirred solution of compound **9** (10 mg, 0.026 mmol) in anhydrous $CH_2Cl_2$ (4 mL) was added (4-(6-methyl-1,2,4,5-tetrazin-3-yl)phenyl)methanol (7.7 mg, 0.038 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (64 µL of a 0.01 M solution, 0.025 equiv). After stirring for 1 day at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 65:35) to afford compound **34** (7 mg, 51% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 8.58 (2H, d, *J* = 8.2 Hz, H6' and H14'), 7.66 (2H, d, *J* = 8.2 Hz, H5' and H15'), 4.96 (2H, s, H3'), 4.86 (2H, s, H1'), 3.09 (3H, s, $CH_311$'), 2.70 (3H, s, $CH_35$), 2.69 (3H, s, $CH_38$), 2.54 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}6$), 2.47 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}2$), 2.41 (3H, s, $CH_37$), 2.39 (3H, s, $CH_31$), 1.10 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_22$/$\underline{CH_3}CH_26$), 1.09 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_26$/$\underline{CH_3}CH_22$). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 167.3 (C11'), 164.2 (C8'), 156.2 (C5), 147.2 (C3), 143.0 (C4'), 142.7 (C8), 140.0 (C7a), 137.2 (C8a), 135.6 (C7), 135.0 (C1), 131.7 (C6), 131.2 (C7'), 130.3 (C2), 128.8 (C5' and C15'), 128.1 (C6' and C14'), 127.4 (q, $J_{CB}$ = 74 Hz, 2 x CN), 73.0 (C3'), 63.7 (C1'), 21.3 ($CH_311$'), 17.7 ($CH_38$), 17.5 ($CH_3\underline{CH_2}6$), 17.4 ($CH_3\underline{CH_2}2$), 15.3 ($\underline{CH_3}CH_22$/$\underline{CH_3}CH_26$), 15.0 ($CH_37$), 14.7 ($CH_31$), 14.6 ($\underline{CH_3}CH_26$/$\underline{CH_3}CH_22$), 14.0 ($CH_35$).

**HRMS** (API-ES$^+$) *m/z* calcd for $C_{30}H_{33}BN_8NaO$ $[M+Na]^+$ 555.2768; found 555.2753. Calcd for $C_{30}H_{37}BN_9O$ $[M+NH_4]^+$ 550.3214; found 550.3203.

**Compound 35**



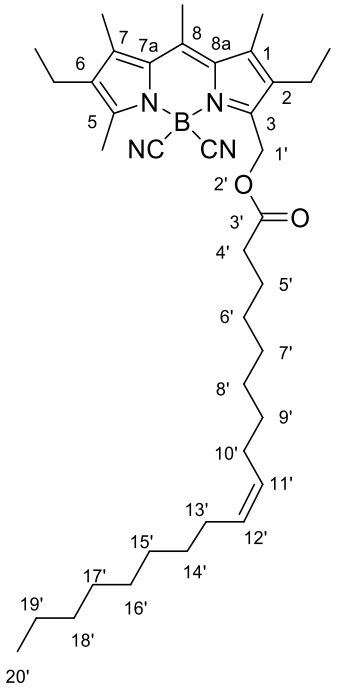

To a stirred solution of (1*R*,8*S*,9*s*)-bicyclo[6.1.0]non-4-yn-9-ylmethanol (5.7 mg, 0.038 mmol) in anhydrous $CH_2Cl_2$ (0.5 mL) was added tetrakis(acetonitrile)copper(I) tetrafluoroborate (12.3 mg, 0.038 mmol) at room temperature. After stirring the mixture for 1 h at the room temperature, complexation of the alkyne with copper was completed (as judged from TLC analysis). To this mixture was added compound **9** (14 mg, 0.036 mmol) in anhydrous $CH_2Cl_2$ (0.5 mL) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (90 µL of a 0.01 M solution, 0.025 equiv) at room temperature. After stirring for 22 h at room temperature, an aqueous ammonia solution (30%, 0.3 mL) and $H_2O$ (0.1 mL) were added at room temperature. After stirring for 5 minutes at room temperature, the mixture was diluted with $CH_2Cl_2$ (15 mL) and the mixture was extracted with water (15 mL) and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 70:30) to afford compound **35** (9.1 mg, 53% yield; 60% yield considering recovered **9**: 1.8 mg), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.84 (2H, s, H1'), 3.75 (2H, d, *J* = 7.5 Hz, H3'), 2.68 (6H, s, $CH_3$5 and $CH_3$8), 2.57 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.46 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.40 (3H, s, $CH_3$7), 2.38 (3H, s, $CH_3$1), 2.37-2.15 (6H, m, H6', H7', H10' and H11'), 1.70-1.58 (2H, m, H6' and H11'), 1.51-1.41 (1H, m, H4'), 1.13 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.08 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6), 0.99-0.90 (2H, m, H5' and H12'). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ =155.6 (C5), 148.3 (C3), 142.5 (C8), 139.7 (C7), 137.5 (C1), 135.3 (C6), 135.0 (C2), 131.5 (C7a), 130.2 (C8a), 127.5 (q, $J_{CB}$ = 74.5 Hz, 2 × CN), 99.1 (C8' and C9'), 68.6 (C3'), 63.9 (C1'), 29.3 (C6' and C11'), 21.7 (C7' and C10'), 20.1 (C5'

and C12'), 18.8 (C4'), 17.6 ($CH_3$8), 17.5 ($CH_3\underline{CH_2}$2), 17.4 ($CH_3\underline{CH_2}$6), 15.2 ($CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7), 15.0 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1), 14.8 ($\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2), 14.6 ($CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 13.9 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{30}H_{41}BN_5O$ $[M+NH_4]^+$ 498.3404; found 498.3403. Calcd. for $C_{30}H_{37}BN_4NaO$ $[M+Na]^+$ 503.2958; found 503.2954. Calcd. for $C_{30}H_{38}BN_4O$ $[M+H]^+$ 481.3139; found 481.3128.

**Compound 36**



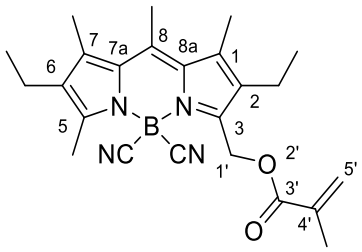

To a stirred solution of compound **9** (10 mg, 0.026 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added oleic acid (16.77 µL, 0.051 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (64 µL of a 0.01 M solution, 0.025 equiv). After stirring for 1 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 93:7 to 70:30) to afford compound **36** (12.5 mg, 80% yield; 86% considering recoverd **9**: 1.8 mg), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 5.36 (2H, s, H1'), 5.27 (2H, m, H11' and H12'), 2.63 (3H, s, $CH_3$8), 2.62 (3H, s, $CH_3$5), 2.41 (4H, m, $CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 2.34 (3H, s,

$CH_3$7), 2.33 (s, $CH_3$1), 2.28 (2H, t, $J$ = 7.2 Hz, H4'), 1.98-1.89 (4H, br m, H10' and H13'), 1.58 (2H, m, H5'), 1.30-1.16 (20H, br m, H6', H7',H8', H9'and H14', H15', H16', H17', H18' and H19'), 1.02 (3H, t, $J$ = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.01 (3H, t, $J$ = 7.5 Hz, $\underline{CH_3}CH_2$6), 0.81 (3H, t, $J$ = 6.7 Hz, H20'). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ = 173.6 (C3'), 157.6 (C5), 143.9 (C3), 142.9 (C8), 140.7 (C7), 136.4 (C1), 136.1 (C6), 135.0 (C2), 132.3 (C7a), 130.6 (C8a), 130.2, 130.0, 130.0, 129.9 (from 130.2 to 129.9: C11' and C12'), 127.1 (q, $J_{CB}$ = 74.2 Hz, 2 × CN), 56.3 (C1'), 34.2 (C4'), 32.0, 29.9, 29.9, 29.8, 29.7, 29.5, 29.5, 29.3, 29.3, 29.2, 29.2 (from 32.0 to 29.2: C6'-C9'/C14'-C19'), 27.4 (C10' and C13'), 24.9 (C5'), 22.8 (C14'-C19'/C6'-C9'), 17.8 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 17.4 ($CH_3\underline{CH_2}$6/ $CH_3\underline{CH_2}$2), 15.5($\underline{CH_3}CH_2$6), 15.1 ($\underline{CH_3}CH_2$2), 14.7 ($CH_3$7), 14.6 ($CH_3$1), 14.3 (C20'), 14.1 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{38}H_{61}BN_5O_2$ $[M+NH_4]^+$ 630.4920; found 630.4931. Calcd. for $C_{38}H_{57}BN_4NaO_2$ $[M+Na]^+$ 635.4473; found 635.4492.

**Compound 37**

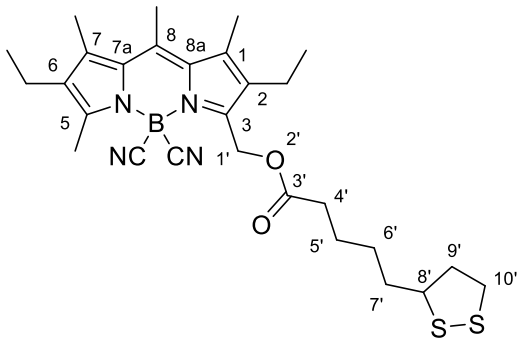



To a stirred solution of compound **9** (20.3 mg, 0.052 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added methacrylic acid (4.41 µL, 0.052 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (192 µL of a 0.01 M solution, 0.025 equiv). After stirring for 3.5 h at room temperature, additional methacrylic acid (4.41 µL, 0.052 mmol) and a solution of $Sc(OTf)_3$ (192 µL of a 0.01 M solution, 0.025 equiv) were added to the mixture again. After stirring for an additional 2 h at room temperature, the reaction mixture was then quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 80:20) to afford compound **37** (7.2 mg, 33% yield; 46% yield considering recoverd **9**: 5.7 mg), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 6.23 (1H, br s, H5'), 5.59 (1H, br s, H5'), 5.53 (2H, s, H1'), 2.71 (3H, s, $CH_3$8), 2.69 (3H, s, $CH_3$5), 2.55-2.45 (4H, m, $CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 2.42 (3H, s, $CH_3$7), 2.41 (3H, s, $CH_3$1), 1.97 (3H, s, $CH_3$4'), 1.08 (6H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 167.1 (C3'), 157.7 (C5), 143.8 (C3), 143.0 (C8), 140.7 (C7), 136.5 (C1), 136.2 (C6), 135.9 (C4'), 135.3 (C2), 132.3 (C7a), 130.5 (C8a), 127.1 (q, $J_{CB}$ = 74.9 Hz, 2 × CN), 126.7 (C5'), 56.55 (C1'), 18.6 ($CH_3$4'), 17.8 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 17.3 ($CH_3\underline{CH_2}$6/$CH_3\underline{CH_2}$2), 15.5 ($CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7), 15.1 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1), 14.7 ($\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2), 14.7 ($CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 14.1 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{24}H_{33}BN_5O_2$ $[M+NH_4]^+$ 434.2727; found 434.2730.

**Compound 38**



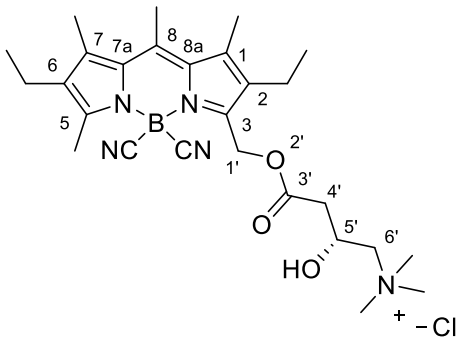

To a stirred solution of compound **9** (20 mg, 0.051 mmol) in anhydrous $CH_2Cl_2$ (2 mL) was added DL-α-lipoic acid (53.4 mg, 0.256 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (130 μL of a 0.01 M solution, 0.025 equiv). After stirring for 5 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography ($CH_2Cl_2$/AcOEt, 100:0 to 94:6) to afford compound **38** (15.6 mg, 57% yield, 98% yield considering recovered **9**: 8.4 mg), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 5.43 (2H, s, H1'), 3.55 (1H, q, *J* = 6.5 Hz, H8'), 3.24-3.00 (2H, m, H10'), 2.70 (3H, s, $CH_3$8), 2.69 (3H, s, $CH_3$5), 2.54-2.42 (7H, m, $CH_3\underline{CH_2}$2, $CH_3\underline{CH_2}$6, H4' and H9'), 2.41 (3H, s, $CH_3$7), 2.40 (3H, s, $CH_3$1), 1.95-1.83 (1H, m, H9'), 1.76-1.60 (4H, m, H5' and H7'), 1.54-1.41 (2H, m, H6'), 1.09 (3H, t, *J* =

7.5 Hz, $\underline{CH_3}CH_23$), 1.08 (3H, t, $J$ = 7.5 Hz, $\underline{CH_3}CH_26$). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 173.3 (C3'), 157.7 (C5), 143.7 (C3), 142.9 (C8), 140.8 (C7), 136.4 (C1), 136.2 (C6), 135.0 (C2), 132.3 (C7a), 130.6 (C8a), 127.1 (q, $J_{CB}$ = 74.4 Hz, 2 × CN), 56.5 (C8'), 56.3 (C1'), 40.3 (C9'), 38.6 (C10'), 34.7 (C7'), 33.9 (C4'), 28.8 (C6'), 24.6 (C5'), 17.8 ($CH_38$), 17.4 ($CH_3\underline{CH_2}2$/$CH_3\underline{CH_2}6$), 17.4 ($CH_3\underline{CH_2}6$/$CH_3\underline{CH_2}2$), 15.6 ($CH_31$/$\underline{CH_3}CH_22$/$\underline{CH_3}CH_26$/$CH_37$), 15.1 ($\underline{CH_3}CH_22$/$\underline{CH_3}CH_26$/$CH_37$/$CH_31$), 14.7 ($\underline{CH_3}CH_26$/$CH_37$/$CH_31$/$\underline{CH_3}CH_22$), 14.6 ($CH_37$/$CH_31$/$\underline{CH_3}CH_22$/$\underline{CH_3}CH_26$), 14.1 ($CH_35$).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{28}H_{41}BN_5O_2S_2$ $[M+NH_4]^+$ 554.2794; found 554.2798. calcd. for $C_{28}H_{37}BN_4NaO_2S_2$ $[M+Na]^+$ 559.2348; found 559.2343.

**Compound 39**




Chloride to tetrafluorborate exchange

To a stirred solution of L-carnitine chloride (25 mg, 0.126 mmol) in EtOH (2 mL) was added $AgBF_4$ (24.6 mg, 0.126 mmol) at room temperature in the dark. After stirring the mixture at room temperature in the dark for 1 h, it was filtered through cotton. The filtrate was evaporated under vacuum to afford L-carnitine tetrafluoroborate (30.5 mg, 97% yield), as a white solid.

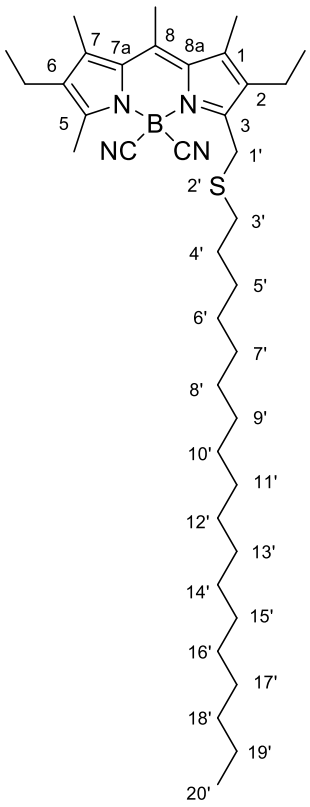
To a stirred solution of compound **9** (15 mg, 0.038 mmol) in anhydrous MeCN (2 mL) was added L-carnitine tetrafluoroborate (19.1 mg, 0.077 mmol) (the mixture was treated in an ultrasound bath to dissolve the carnitine salt). A solution of $Sc(OTf)_3$ in anhydrous MeCN (192 µL of a 0.01 M solution, 0.05 equiv) was then added dropwise at room temperature. The stirred reaction mixture was heated at 60 °C under microwave irradiation for 8 h. Aqueous HCl (4 mL, 0.01 M) and $H_2O$ (4 mL) were added to the reaction mixture and stirred for 5 minutes at room temperature ($BF_4^-$ to $Cl^-$ exchange). The organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 ×

20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography ($CH_2Cl_2$/MeOH, 100:0 to 70:30) to afford compound **39** (3.8 mg, 20% yield; 38% yield considering recovered **9**:7.1 mg), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 500 MHz): δ = 5.48-5.36 (2H, m, H1'), 4.71-4.61 (1H, br m, H5'), 4.25 (1H, d, *J* = 5.3 Hz, OH5'), 3.54 (1H, d, *J* = 13.5 Hz, H6'), 3.39 (1H, dd, *J* = 13.5, 10.2 Hz, H6'), 3.22 (9H, s, $(CH_3)_3$N6'), 2.73 (3H, s, $CH_3$8), 2.71-2.60 (2H, m, H4'), 2.66 (3H, s, $CH_3$5), 2.55-2.45 (4H, m, $CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 2.43 (3H, s, $CH_3$7), 2.42 (3H, s, $CH_3$1), 1.13-1.05 (6H, m, $\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6). $^{13}$C NMR ($CDCl_3$, 125 MHz): δ = 170.0 (C3'), 157.9 (C5), 143.6 (C8), 142.2 (C3), 141.5 (C7), 136.9 (C1), 136.4 (C6), 135.9 (C2), 132.5 (C7a), 130.7 (C8a), 126.1 (q, $J_{CB}$ = 76.4 Hz, 2 × CN), 69.6 (C6'), 63.5 (C5'), 56.9 (C1'), 54.8 ($(CH_3)_3$N6'), 40.3 (C4'), 17.9 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 17.4 ($CH_3\underline{CH_2}$6/$CH_3\underline{CH_2}$2), 15.5 ($CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7), 15.2 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1), 14.7 ($\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2), 14.7 ($CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 14.1 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{27}H_{39}BN_5O_3$ $[M]^+$ 492.3145; found 492.3144.

**Compound 41**



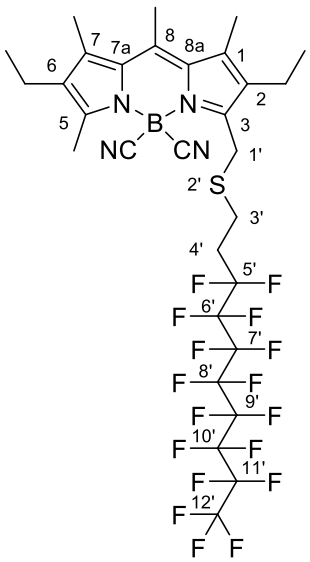

To a stirred solution of compound **9** (15.1 mg, 0.039 mmol) in anhydrous $CH_2Cl_2$ (1.2 mL) was added 1-octadecanethiol (13.6 mg, 0.046 mmol) at room temperature. A solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (96 μL of a 0.01 M solution, 0.025 equiv) was then added dropwise. After stirring for 20 min at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 97:3) to afford compound **41** (22.1 mg, 93% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.13 (2H, s, H1'), 2.78 (2H, t, *J* = 7.4 Hz, H3'), 2.68 (3H, s, $CH_3$5), 2.66 (3H, s, $CH_3$8), 2.58 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.46 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.39 (3H, s, $CH_3$7), 2.37 (3H, s, $CH_3$1), 1.68 (2H, p, *J* = 7.4 Hz, H4'), 1.45-1.37 (2H, m, H5'), 1.26 (28H, br s, H6', H7', H8', H9', H10', H11', H12', H13', H14', H15', H16', H17', H18' and H19'), 1.16 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.07 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6), 0.88 (3H, t, *J* = 6.7 Hz, H20'). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 154.6 (C5), 149.5 (C3), 141.7 (C8), 139.1 (C7), 138.1 (C1), 135.0 (C6), 134.7 (C2), 131.1 (C7a), 130.3 (C8a), 127.4 (q, $J_{CB}$ = 74.3 Hz, 2 × CN), 34.3 (C3'), 32.1

(C18'/C19'), 29.9 - 29.8 (C6'-C17'), 29.7 (C4'), 29.1 (C5'), 28.4 (C1'), 22.4 (C19'/C18'), 17.6 ($CH_3\underline{CH_2}2$), 17.5 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}6$), 15.1 ($\underline{CH_3}CH_2$2), 14.9 ($\underline{CH_3}CH_2$6), 14.8 ($CH_3$1/$CH_3$7), 14.8 ($CH_3$7/$CH_3$1), 14.3 (C20'), 13.8 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{38}H_{65}BN_5S$ $[M+NH_4]^+$ 634.5055; found 634.5069. Calcd. for $C_{38}H_{61}BN_4NaS$ $[M+Na]^+$ 639.4609 found; 639.4622.

**Compound 42**



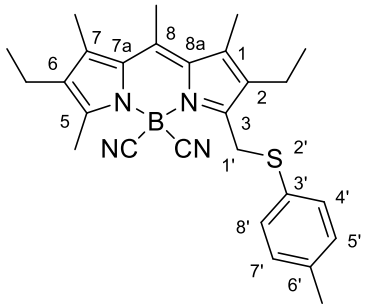

To a stirred solution of compound **9** (12.4 mg, 0.032 mmol) in anhydrous $CH_2Cl_2$ (1.2 mL) was added 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanethiol (11.1 µL, 0.038 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (70 µL of a 0.01 M solution, 0.025 equiv). After stirring for 30 min at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 80:20) to afford compound **42** (24.8 mg, 96% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.20 (2H, s, H1'), 3.00 (2H, t, *J* = 7.9 Hz, H3'), 2.69 (3H, s, $CH_3$5), 2.67 (3H, s, $CH_3$8), 2.57 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}2$), 2.53-2.50 (2H, m, H4'), 2.47 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}6$), 2.40 (3H, s, $CH_3$7), 2.38 (3H, s, $CH_3$1), 1.16 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.08 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 155.8 (C5), 147.0 (C3), 142.1 (C8), 139.8 (C6), 137.8 (C1), 135.5 (C7), 134.5 (C2), 131.5 (C7a), 130.3 (C8a), 127.4 (q, $J_{CB}$ = 74.2 Hz, 2 × CN), 118.7-108.3 (m, 8$CF_n$

n = 2, 3; C5', C6', C7', C8', C9', C10', C11' C12'), 32.0 (t, $J_{CF}$ = 22.1 Hz, C4'), 28.5 (C1'), 24.5 (t, $J_{CF}$ = 4.1 Hz, C3'), 17.6 ($CH_3\underline{CH_2}2$ and $CH_3\underline{CH_2}6$), 17.4 ($CH_38$), 15.1 ($\underline{CH_3}CH_26$), 15.0 ($\underline{CH_3}CH_22$), 14.7 ($CH_31$ and $CH_37$), 13.9 ($CH_35$).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{30}H_{32}BF_{17}N_5S$ $(M+NH_4)^+$ 828.2200; found 828.2239.

**Compound 43**

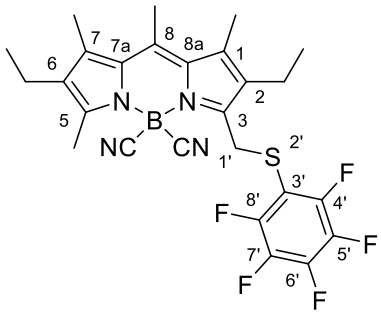



To a stirred solution of compound **9** (20 mg, 0.051 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added 4-methylbenzenethiol (6.49 mg, 0.051 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (128 µL of a 0.01 M solution, 0.025 equiv. After stirring for 1 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The resultant crude was washed with hexane to afford compound **43** (23 mg, 98% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 7.49 (2H, d, *J* = 8.0 Hz, H4' and H8'), 7.15 (2H, d, *J* = 8.0 Hz, H5' and H7'), 4.50 (2H, s, H1'), 2.69 (3H, s, $CH_35$), 2.67 (3H, s, $CH_38$), 2.51 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}2$), 2.49 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}6$), 2.39 (3H, s, $CH_37$), 2.38 (3H, s, $CH_31$), 2.35 (3H, s, $CH_36'$), 1.12 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_22$), 1.08 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_26$). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 155.3 (C5), 147.4 (C3), 141.9 (C8), 139.5 (C7), 137.8 (C1), 137.5 (C6'), 135.2 (C6), 134.9 (C2), 132.4 (C3'), 132.0 (C4' and C8'), 131.4 (C7a), 130.4 (C8a), 130.0 (C5' and C7'), 127.4 (q, $J_{CB}$ = 74.2 Hz, 2 × CN), 32.5 (C1'), 21.3 ($CH_36'$), 17.6 ($CH_38$), 17.5 ($CH_3\underline{CH_2}2$), 17.4 ($CH_3\underline{CH_2}6$), 15.1 ($\underline{CH_3}CH_22$), 14.9 ($\underline{CH_3}CH_26$), 14.8 ($CH_31$/$CH_37$) 14.8 ($CH_37$/$CH_31$), 13.9 ($CH_35$).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{27}H_{35}BN_5S$ $[M+NH_4]^+$ 472.2706; found 472.2734.

**Compound 44**

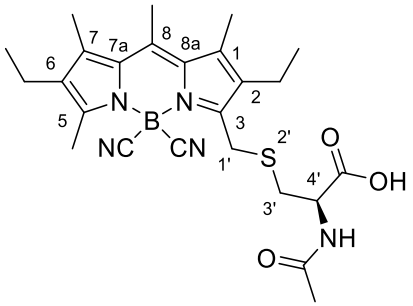



To a stirred solution of compound **9** (14.9 mg, 0.038 mmol) in anhydrous $CH_2Cl_2$ (1.2 mL) was added 2,3,4,5,6-pentafluorothiophenol (6.3 μL, 0.046 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (96 μL of a 0.01 M solution, 0.025 equiv). After stirring for 5 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 68:32) to afford compound **44** (14.8 mg, 73% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.53 (2H, s, H1'), 2.69 (3H, s, $CH_3$8), 2.68 (3H, s, $CH_3$5), 2.58 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.47 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.41 (3H, s, $CH_3$7), 2.40 (3H, s, $CH_3$1), 1.19 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.08 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 157.0 (C5), 147.5 (m, C4'/C5'/C6'/C7'/C8'), 144.4 (C3), 142.4 (C8), 141.9 (m, C5'/C6'/C7'/C8'/C4'), 140.4 (C7), 138.0 (m, C6'/C7'/C8'/C4'/C5') 137.3 (C1), 136.0 (C6), 134.9 (C2), 132.0 (C7a), 130.5 (C8a), 127.2 (q, $J_{CB}$ = 74.1 Hz, 2 × CN), 109.1 (m, C3'), 31.0 (C1'), 17.7 ($CH_3$8), 17.6 ($CH_3\underline{CH_2}$2), 17.4 ($CH_3\underline{CH_2}$6), 15.1 ($CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7), 15.1 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1), 14.7 ($\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2), 14.7 ($CH_3$7/$CH_3$1/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 14.0 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{26}H_{28}BF_5N_5S$ $[M+NH_4]^+$ 548.2078; found 548.2061.

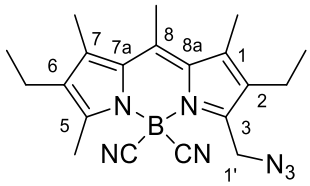
**Compound 45**




To a stirred solution of compound **9** (15 mg, 0.038 mmol) in anhydrous $CH_2Cl_2$ (1.5 mL) was added *N*-acetyl-L-cysteine (7.53 mg, 0.046 mmol) (treated in an ultrasounds bath to dissolve the amino acid) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (192 µL of a 0.01 M solution, 0.05 equiv). After stirring for 2.5 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 70:30) to afford compound **45** (18 mg, 94% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 7.31 (1H, s, $CH_3CO\underline{NH}$4'/COOH4'), 5.70 (1H, br s, COOH4'/$CH_3CO\underline{NH}$4'), 4.76-4.67 (1H, br m, H4'), 4.22 (1H, d, $J_{AB}$= 12.5 Hz, H1'), 4.14 (1H, d, $J_{AB}$ = 12.5 Hz, H1'), 3.32 (1H, dd, $J_{AB}$ = 13.2, 6.4 Hz, H3'), 3.22 (1H, dd, $J_{AB}$ 13.2, 3.3 Hz, H3'), 2.67 (6H, s, $CH_3$5/$CH_3$8), 2.55 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.47 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.40 (3H, s, $CH_3$7), 2.37 (3H, s, $CH_3$1), 2.05 (3H, s, $\underline{CH_3}CONH$4), 1.14 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.08 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 172.6 ($CH_3\underline{CO}NH$4'/COOH4'), 172.4 (COOH4'/$CH_3\underline{CO}NH$4'), 155.5 (C5), 146.9 (C3), 142.3 (C8), 140.0 (C7), 138.1 (C1), 135.5 (C6), 134.9 (C2), 131.5 (C7a), 130.4 (C8a), 127.5 (q, $J_{CB}$ = 72.5 Hz, 2 × CN), 52.7 (C4'), 34.9 (C3'), 28.8 (C1'), 22.7 ($\underline{CH_3}CONH$4'), 17.6 ($CH_3$8), 17.5 ($CH_3\underline{CH_2}$2), 17.4 ($CH_3\underline{CH_2}$6), 15.3 ($\underline{CH_3}CH_2$2), 15.0 ($CH_3$1/$CH_3$7), 14.8 ($\underline{CH_3}CH_2$6), 14.7 ($CH_3$7/$CH_3$1), 13.9 ($CH_3$5).
**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{25}H_{32}BN_5NaO_3S$ $[M+Na]^+$ 516.2216; found 516.2229. Calcd. for $C_{25}H_{33}BN_5O_3S$ $[M+H]^+$ 494.2396; found 494.2415.

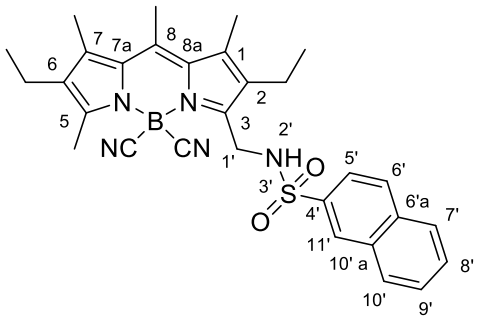
**Compound 46**




To a stirred solution of compound **9** (14.6 mg, 0.037 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added trimethylsilyl azide (10.5 µL, 0.075 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (96 µL of a 0.01 M solution, 0.025 equiv). After stirring for 1 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 90:10 to 50:50) to afford compound **46** (11.5 mg, 82% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.81 (2H, s, H1'), 2.70 (3H, s, $CH_3$5/$CH_3$8), 2.70 (3H, s, $CH_3$8/$CH_3$5), 2.55 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2), 2.48 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.42 (3H, s, $CH_3$1/$CH_3$7), 2.41 (3H, s, $CH_3$7/$CH_3$1), 1.15 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2), 1.09 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 157.5 (C5), 143.5 (C3), 143.0 (C8), 140.9 (C1), 136.9 (C7), 136.1 (C6), 134.7 (C2), 132.2 (C7a), 130.2 (C8a), 127.2 (q, $J_{CB}$ = 74.4 Hz, 2 × CN), 45.2 (C1'), 17.8 ($CH_3$8), 17.5 ($CH_3\underline{CH_2}$2), 17.4 ($CH_3\underline{CH_2}$6), 15.2 ($\underline{CH_3}CH_2$6), 15.1 ($\underline{CH_3}CH_2$2), 14.7 ($CH_3$1 and $CH_3$7), 14.1 ($CH_3$5). **HRMS** (API-ES$^+$) *m/z* calcd. for $C_{20}H_{24}BN_7Na$ $[M+Na]^+$ 396.2084; found 396.2073.

**Compound 47**



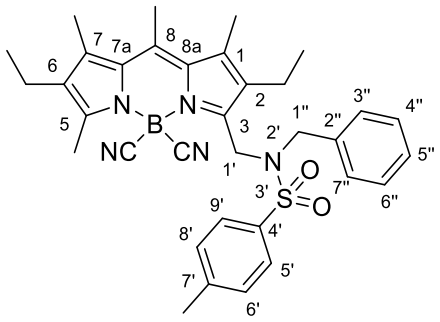

To a stirred solution of compound **9** (15 mg, 0.038 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added naphthalene-2-sulfonamide (9.9 mg, 0.046 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (96 µL of a 0.01 M solution, 0.025 equiv). After stirring for 5 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic

layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 95:5 to 84:16) to afford compound **47** (15.3 mg, 74% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 8.52 (1H, s, H11'), 8.02 (2H, t, *J* = 9.3 Hz, H7'/H10'/H6'), 7.95-7.87 (2H, m, H5' and H6'/H7'/H10'), 7.70-7.56 (2H, m, H8' and H9'), 5.55 (1H, t, *J* = 7.1 Hz, H2'), 4.46 (2H, d, *J* = 7.1 Hz, H1'), 2.65 (3H, s, $CH_3$8), 2.64 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2), 2.53 (3H, s, $CH_3$5), 2.44 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.39 (3H, s, $CH_3$7), 2.34 (3H, s, $CH_3$1), 1.17 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2), 1.05 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 156.3 (C5), 144.7 (C3), 142.3 (C8), 140.7 (C7), 137.7 (C1), 136.4 (C4'), 135.7 (C6), 135.4 (C2), 135.2 (C6'a/C10'a), 132.4 (C10'a/C6'a), 131.7 (C7a), 130.2 (C8a), 129.9 (C7'/10'/C6'), 129.5 (C10'/C7'/C6'), 128.9 (C11'/C8'/C9'), 128.7 (C8'/C11'/C9'), 128.4 (q, $J_{CB}$ = 74.1 Hz, 2 × CN), 128.1 (C6'/C7'/C10'), 127.6 (C9'/C8'), 122.4 (C5') 38.2 (C1'), 17.7 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$6), 17.0 ($CH_3\underline{CH_2}$2), 15.2 ($\underline{CH_3}CH_2$2), 15.0 ($CH_3$7), 14.7 ($\underline{CH_3}CH_2$6), 14.6 ($CH_3$1), 13.8 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{30}H_{36}BN_6O_2S$ $[M+NH_4]^+$ 555.2713; found 555.2739.

**Compound 48**



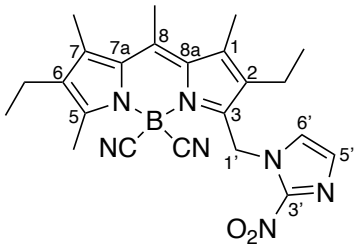

To a stirred solution of compound **9** (15 mg, 0.038 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added *N*-benzyl-p-toluenesulfonamide (12.1 mg, 0.046 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (192 μL of a 0.01 M solution, 0.05 equiv). After stirring for 7 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous

$Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 70:30) to afford compound **48** (11.1 mg, 49% yield; 68% yield considering recovered **9**: 4.3 mg), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 7.82 (2H, d, *J* = 8.2 Hz, H5' and H9'), 7.42 (2H, d, *J* = 8.2 Hz, H6' and H8'), 7.23-7.16 (2H, m, H3" and H7"), 7.09-6.96 (3H, m, H4", H5" and H6"), 4.83 (2H, s, H1'), 4.41 (2H, s, H1"), 2.61 (3H, s, $CH_3$5), 2.59 (3H, s, $CH_3$8), 2.49 (3H, s, $CH_3$7'), 2.46 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.40 (3H, s, $CH_3$7), 2.34 (2H, br q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2), 1.97 (3H, s, $CH_3$1), 1.07 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6), 0.93 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 154.9 (C5), 145.4 (C3), 144.1 (C7'), 142.2 (C8), 139.6 (C7), 138.1 (C1), 136.7 (C2), 136.5 (C2"), 135.2 (C6), 135.0 (C4'), 131.0 (C7a), 130.3 (C6' and C8'), 130.2 (C8a), 128.9 (C3" and C7"), 127.8 (q, $J_{CB}$ = 74.1 Hz, 2 × CN), 127.5 (C5'/C9'/C4"/C5"/C6"), 127.4 (C9'/C4"/C5"/C6"/C5'), 127.0 (C4"/C5"/C6"/C5'/C9'), 52.9 (C1"), 46.8 (C1'), 21.8 ($CH_3$7'), 17.6 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$6), 17.0 ($CH_3\underline{CH_2}$2), 15.0 ($CH_3$7), 14.8 ($\underline{CH_3}CH_2$6), 14.7 ($\underline{CH_3}CH_2$2), 14.0 ($CH_3$1), 13.8 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{34}H_{42}BN_6O_2S$ $[M+NH_4]^+$ 609.3184; found 609.3166.

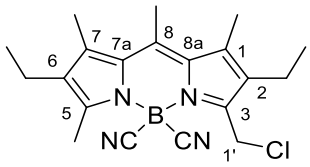
**Compound 49**




To a solution of compound **9** (25.0 mg, 0.064 mmol) in $CH_2Cl_2$ (2.0 mL), 2-nitroimidazole (7.2 mg, 0.064 mmol) and $Sc(OTf)_3$ (3.1 mg, 0.0064 mmol) were added and the mixture was stirred at room temperature. After stirring for 25 hours at room temperature, another equal portion of $Sc(OTf)_3$ was added and the reaction was stirred for another 28 hours before quenching with $H_2O$ (10 mL) followed by extraction with $CH_2Cl_2$ (4 x 15 mL). The combined organic phases were dried over $Na_2SO_4$ and concentrated at reduced pressure. The resulting crude was purified by flash chromatography (hexane/AcOEt, 100:0 to 30:70), to afford compound **49** (20.1 mg, 71%), as a red solid.

**$^1$H RMN** ($CDCl_3$, 400 MHz); δ (ppm) = 7.09 (1H, d, *J* = 1.1 Hz, H5'), 6.90 (1H, d, *J* = 1.1 Hz, H6'), 6.05 (2H, s, H1'), 2.76 (3H, s, $CH_3$8), 2.68 (3H, s, $CH_3$5), 2.49 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.45 (3H, s, $CH_3$7), 2.42 (3H, s, $CH_3$1), 2.31 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2), 1.09 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6), 0.88 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2).
**$^{13}$C RMN (**$CDCl_3$, 100 MHz); δ (ppm) = 159.8 (C5), 145.1 (C3'), 143.2 (C8), 142.1 (C7), 139.5 (C2), 137.2 (C6), 136.5 (C1), 134.4 (C3), 132.9 (C7a), 130.3 (C8a), 128.4 (C5'), 126.6 (2 x CN q, *J* = 74.0 Hz), 125.1 (C6'), 44.6 (C10), 17.9 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$6), 17.3 ($CH_3\underline{CH_2}$2), 15.3 ($CH_3$7), 14.6 ($\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6), 14.6 ($CH_3$1), 14.3 ($CH_3$5).
**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{23}H_{26}BN_7O_2$ [M+Na] 466.2137; found 466.2139.

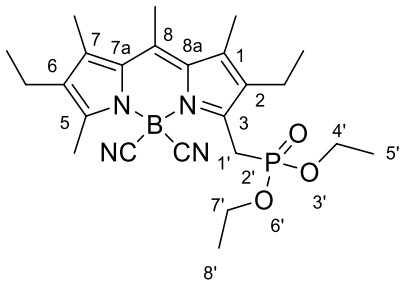
**Compound 50**




To a stirred solution of compound **9** (23. mg, 0.059 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added chlorotrimethylsilane (150 µL, 1.18 mmol) at room temperature. After stirring for 24 h at room temperature, the solvent was removed at reduced pressure to afford compound **50** (21.6 mg, 100% yield), as an orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.95 (2H, s, H1'), 2.71 (3H, s, $CH_3$5), 2.70 (3H, s, $CH_3$8), 2.57 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2), 2.48 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.42 (3H, s, $CH_3$7), 2.40 (3H, s, $CH_3$1), 1.17 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2), 1.09 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 157.7 (C5), 144.8 (C3), 142.9 (C8), 140.8 (C7), 136.9 (C1), 136.2 (C6), 134.9 (C2), 132.2 (C7a), 130.3 (C8a), 127.0 (q, $J_{CB}$ = 74.3 Hz, 2 × CN), 35.6 (C1'), 17.8 (C8), 17.4 ($CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 15.1 ($CH_3$7), 15.0 ($\underline{CH_3}CH_2$2), 14.7 ($CH_3$1 and $\underline{CH_3}CH_2$6), 14.1 ($CH_3$5).
**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{20}H_{24}BN_4$ $[M–Cl]^+$ 331.2092; found 331.2101.

**Compound 51**

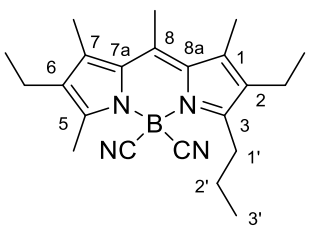


To a stirred solution of compound **50** (9.4 mg, 0.026 mmol) in anhydrous $CH_2Cl_2$ (2 mL) were added triethylphosphite (5.9 µL, 0.033 mmol) at room temperature. The stirred reaction mixture was heated at 80 °C for 30 min and at 120 °C for 4.5 h, under microwave irradiation. The reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 70:30 to 30:70) to afford compound **51** (10.2 mg, 85% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.19-4.10 (4H, m, H4' and H7'), 3.70 (2H, d, $J_{HP}$ = 27.8 Hz, H1'), 2.73 (2H, q, $J$ = 7.6 Hz, $CH_3\underline{CH_2}2$), 2.68 (6H, br s, $CH_35$ and $CH_38$), 2.46 (2H, q, $J$ = 7.6 Hz, $CH_3\underline{CH_2}6$), 2.40 (6H, s, $CH_31$ and $CH_37$), 1.30 (6H, t, $J$ = 7.1 Hz, H5' and H8'), 1.11 (3H, t, $J$ = 7.6 Hz, $\underline{CH_3}CH_22$), 1.06 (3H, t, $J$ = 7.6 Hz, $\underline{CH_3}CH_26$). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 154.8 (C5), 144.1 (d, $J_{CP}$ = 10.0 Hz, C3), 141.8 (C8), 139.1 (C1), 138.3 (C7), 135.1 (C2 and C6), 131.2 (C7a/C8a), 130.9 (C8a/C7a), 127.1 (q, $J_{CB}$ = 74.1 Hz, 2 × CN), 62.7 (d, $J_{CP}$ = 7.0 Hz, C4' and C7'), 27.7 (d, $J_{CP}$ = 140.8 Hz, C1'), 17.7 ($CH_38$), 17.4 ($CH_3\underline{CH_2}6$), 17.3 ($CH_3\underline{CH_2}2$), 16.5 (d, $J_{CP}$ = 6.0 Hz, C5' and C8') 15.0 ($CH_31$/$\underline{CH_3}CH_22$/$\underline{CH_3}CH_26$/$CH_37$), 14.9 ($\underline{CH_3}CH_22$/$\underline{CH_3}CH_26$/$CH_37$/$CH_31$), 14.8 ($\underline{CH_3}CH_26$/$CH_37$/$CH_31$/$\underline{CH_3}CH_22$), 14.6 ($CH_37$/$CH_31$/$\underline{CH_3}CH_22$/ $\underline{CH_3}CH_26$), 13.9 (C5). **$^{31}$P-NMR** ($CDCl_3$, 162 MHz): δ = 22.1

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{24}H_{34}BN_4NaO_3P$ $[M+Na]^+$ 491.2358; found 491.2357.

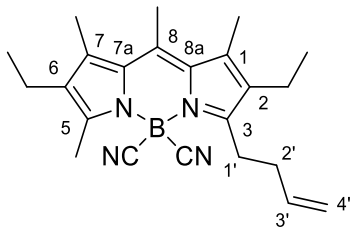
**Compound 52**



To a stirred solution of compound **9** (16 mg, 0.041 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added diethylzinc (140 µL, 15% w/w in hexane, 0.129 mmol) and TMSOTf (11.1 µL, 0.062 mmol) at room temperature and under argon (glovebox). After stirring for 90 min at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 95:5 to 60:40) to afford compound **52** (7.3 mg, 49% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 3.00-2.90 (2H, m, H1'), 2.66 (3H, s, $CH_3$5), 2.65 (3H, s, $CH_3$8), 2.45 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6), 2.46 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2), 2.38 (6H, s, $CH_3$1 and $CH_3$7), 1.86-1.72 (2H, m, H2'), 1.16 (3H, t, *J* = 7.3 Hz, H3'), 1.11 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.07 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 156.3 (C3), 152.5 (C5), 141.0 (C8), 138.7 (C1/C7), 137.8 (C7/C1), 134.1 (C6), 133.8 (C2), 130.4 (C7a/C8a), 130.2 (C8a/C7a), 127.8 (q, $J_{CB}$ = 74.8 Hz, 2 × CN), 29.8 (C1'), 22.3 (C2'), 17.4 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6/$CH_3$8), 17.4 ($CH_3\underline{CH_2}$6/$CH_3$8/$CH_3\underline{CH_2}$2), 15.2 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1/C3'), 14.9 ($\underline{CH_3}CH_2$6/$CH_3$7/$CH_3$1/C3'/$\underline{CH_3}CH_2$2), 14.9 ($CH_3$7/$CH_3$1/C3'/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 14.8 ($CH_3$1/C3'/$\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6/$CH_3$7), 13.6 ($CH_3$5).
**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{22}H_{30}BN_4$ $[M+H]^+$ 361.2562; found 361.2573. Calcd. for $C_{22}H_{29}BN_4Na$ $[M+Na]^+$ 383.2382; found 383.2391.

**Compound 53**



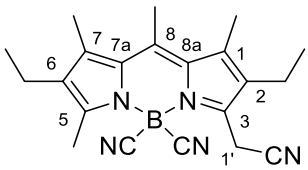

To a stirred solution of compound **9** (15 mg, 0.038 mmol) in anhydrous $CH_2Cl_2$ (2 mL) was added allyltrimethylsilane (9.2 µL, 0.058 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (96 µL of a 0.01 M solution, 0.025 equiv). After stirring for 2 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined

organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 80:20) to afford compound **53** (12 mg, 84% yield), as a red solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 6.07-5.91 (1H, m, H3'), 5.22 (1H, dd, *J* = 1.2, 17.2 Hz, H4'$_{trans}$), 5.09 (1H, d, *J* = 10.2 Hz, H4'$_{cis}$), 3.09 (2H, m, H1'), 2.66 (6H, s, $CH_3$5 and $CH_3$8), 2.52 (2H, m, H2'), 2.46 (4H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2 and $CH_3\underline{CH_2}$6), 2.39 (6H, s, $CH_3$1 and $CH_3$7), 1.12 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2), 1.07 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 154.9 (C5), 153.0 (C3), 141.2 (C8), 138.5 (C7a), 138.2 (C8a), 137.2 (C3'), 134.3 (C7), 133.7 (C1), 130.5 (C6), 130.2 (C2), 127.7 (q, $J_{CB}$ = 74 Hz, 2 x CN), 115.9 (C4'), 32.5 (C2'), 27.1 (C1'), 17.4 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6/$CH_3$8), 17.4 ($CH_3$8/$CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 15.2 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 14.9 ($\underline{CH_3}CH_2$6/$\underline{CH_3}CH_2$2), 14.9 ($CH_3$7), 14.8 ($CH_3$1), 13.7 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{23}H_{30}BN_4$ $[M+H]^+$ 373.2562; found 373.2556. Calcd. for $C_{23}H_{33}BN_5$ $[M+NH_4]^+$ 390.2828; found 390.2826. Calcd. for $C_{23}H_{29}BN_4Na$ $[M+Na]^+$ 395.2382; found 395.2367.

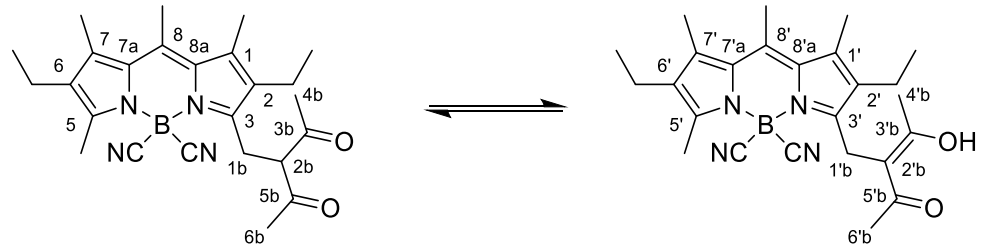
**Compound 54**




To a stirred solution of compound **9** (20 mg, 0.051 mmol) in anhydrous $CH_2Cl_2$ (2 mL) was added TMSCN (9.6 µL, 0.077 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (128 µL of a 0.01 M solution, 0.025 equiv). After stirring for 3 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 80:20) to afford compound **54** (17 mg, 92% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.14 (2H, s, H1'), 2.71 (3H, s, $CH_3$5), 2.69 (3H, s, $CH_3$8), 2.60 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$2), 2.48 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.42 (3H, s, $CH_3$7), 2.41 (3H, s, $CH_3$1), 1.19 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2), 1.09 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 157.8 (C5), 142.9 (C3), 141.2 (C8), 137.3 (C7a), 136.9 (C8a), 136.3 (C7), 133.5 (C1), 132.0 (C6), 129.9 (C2), 126.3 (q, $J_{CB}$ = 74 Hz, 2 x BCN), 114.5 (CN1'), 17.6 ($CH_3$8), 17.3 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 17.3 ($CH_3\underline{CH_2}$6/$CH_3\underline{CH_2}$2), 16.3 (C1'), 15.0 ($\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 14.5 ($\underline{CH_3}CH_2$6/$\underline{CH_3}CH_2$2), 14.4 ($CH_3$1/$CH_3$7), 14.4 ($CH_3$7/$CH_3$1), 13.9 ($CH_3$5).
**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{21}H_{28}BN_6$ $[M+NH_4]^+$ 375.2467; found 375.2479.

**Compound 55**

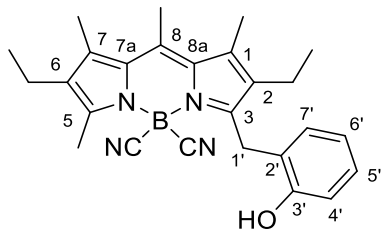



To a stirred solution of compound **9** (10 mg, 0.026 mmol) in anhydrous $CH_2Cl_2$ (2 mL) was added acetylacetone (3.8 mg, 0.038 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (64 µL of a 0.01 M solution, 0.025 equiv). After stirring for 1 day at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 80:20) to afford compound **55** (10 mg, 90% yield), as a red-orange solid, almost equimolar mixture of the two tautomers in $CDCl_3$ at 25 ºC.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 4.82 (1H, t, *J* = 7.2 Hz, H2b), 4.20 (2H, s, H1'b), 3.56 (2H, d, *J* = 7.2 Hz, H1b), 2.70 (3H, s, $CH_3$5'/$CH_3$8'), 2.70 (3H, s, $CH_3$8'/$CH_3$5'), 2.68 (6H, s, $CH_3$5 and $CH_3$8), 2.47 (4H, m, $CH_3\underline{CH_2}$6 and $CH_3\underline{CH_2}$6'), 2.41 (3H, s, $CH_3$1/$CH_3$1'), 2.40 (3H, s, $CH_3$1'/$CH_3$1), 2.38 (2H, m, $CH_3\underline{CH_2}$2), 2.37 (3H, s, $CH_3$7/$CH_3$7'), 2.36 (3H, s, $CH_3$7'/$CH_3$7), 2.33 (2H, m, $CH_3\underline{CH_2}$2'), 2.25 (6H, s, $CH_3$4b and $CH_3$6b), 2.19 (6H, s, 6H, s, $CH_3$4'b and $CH_3$6'b), 1.08 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6'), 1.06 (3H, t, *J* = 7.5 Hz,

$\underline{CH_3}CH_26$), 1.01 (3H, t, $J$ = 7.5 Hz, $\underline{CH_3}CH_22'$), 0.91 (3H, t, $J$ = 7.5 Hz, $\underline{CH_3}CH_22$). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 202.9 (C3b and C5b), 192.1 (C3'b and C5'b), 155.0 (C5), 154.6 (C5'), 150.2 (C3'), 149.9 (C3), 141.9 (C8), 141.6 (C8'), 139.5 (C1'b), 139.2 (C7), 139.1 (C7'), 138.0 (C1), 135.4 (C6), 135.2 (C6'), 134.9 (C2), 133.3 (C2'), 131.3 (C8a), 131.1 (C7a), 131.0 (C7'a), 130.2 (C8'a), 128.3 (q, $J_{CB}$ = 73.9 Hz, 2 x CN), 126.8 (q, $J_{CB}$ = 73.9 Hz, 2 x CN'), 106.3 (C2'b), 65.1 (C2b), 30.7 (C4b and C6b), 28.6 (C1'b), 24.7 (C1b), 24.2 (C4'b and C6'b), 17.8 ($CH_38$), 17.7 ($CH_38'$), 17.7 ($CH_3\underline{CH_2}2'$), 17.4 ($CH_3\underline{CH_2}6$ and $CH_3\underline{CH_2}6'$), 17.2 ($CH_3\underline{CH_2}2$), 15.1 ($CH_37$), 15.0 ($\underline{CH_3}CH_22$), 14.9 ($CH_31$ and $CH_31'$), 14.8 ($\underline{CH_3}CH_22'$), 14.7 ($\underline{CH_3}CH_26$ and $\underline{CH_3}CH_26'$), 14.5 ($CH_37'$), 13.9 ($CH_35$), 13.7 ($CH_35'$). **HRMS** (API-ES$^+$) *m/z* calcd for $C_{25}H_{35}BN_5O_2$ $[M+NH_4]^+$ 448.2883; found 448.2868. Calcd for $C_{25}H_{31}BN_4NaO_2$ $[M+Na]^+$ 453.2437; found 453.2418. Calcd for $C_{25}H_{32}BN_4O_2$ $[M+H]^+$ 431.2617; found 431.2621.

**Compound 56**

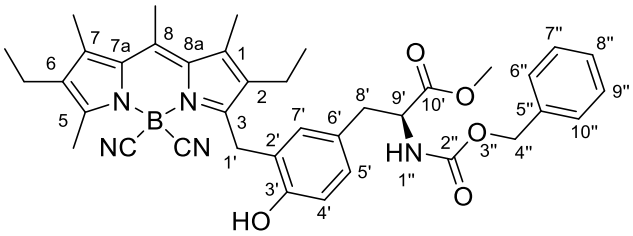



To a stirred solution of compound **9** (15 mg, 0.038 mmol) in anhydrous $CH_2Cl_2$ (2 mL) was added phenol (5.4 mg, 0.058 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (96 µL of a 0.01 M solution, 0.025 equiv). After stirring for 3 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 75:25) to afford compound **56** (11 mg, 80% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 7.09 (1H, br t, $J$ = 7.5 Hz, H5'), 6.97 (1H, d, $J$ = 7.5 Hz, H7'), 6.82 (1H, t, $J$ = 7.5 Hz, H6'), 6.78 (1H, d, $J$ = 7.5 Hz, H4'), 5.20 (1H, s, OH3'), 4.46 (2H, s, H1'), 2.69 (3H, s, $CH_38$), 2.65 (3H, s, $CH_35$), 2.46 (2H, q, $J$ = 7.6 Hz, $CH_3\underline{CH_2}6$), 2.40 (3H, s, $CH_37$), 2.38 (3H, s, $CH_31$), 2.20 (2H, q, $J$ = 7.6 Hz, $CH_3\underline{CH_2}2$), 1.07 (3H, t, $J$ = 7.6 Hz, $\underline{CH_3}CH_26$), 0.73 (3H, t, $J$ = 7.6 Hz, $\underline{CH_3}CH_22$). **$^{13}$C NMR** ($CDCl_3$, 100 MHz):

δ = 153.6 (C3'), 153.3 (C3 and C5), 141.3 (C8), 138.7 (C7a), 138.3 (C8a), 134.7 (C7), 134.4 (C1), 130.7 (C6), 130.5 (C7'), 130.3 (C2), 128.5 (C5'), 127.3 (q, $J_{CB}$ = 74 Hz, 2 x CN), 123.8 (C2'), 121.0 (C6'), 115.7 (C4'), 28.0 (C1'), 17.5 ($CH_3$8), 17.4 8 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 17.3 ($CH_3\underline{CH_2}$6/$CH_3\underline{CH_2}$2), 14.9 ($CH_3$1/$CH_3$7/$\underline{CH_3}CH_2$6), 14.9 ($CH_3$7/$\underline{CH_3}CH_2$6/$CH_3$1), 14.8 ($\underline{CH_3}CH_2$6/$CH_3$1/$CH_3$7), 14.1 ($\underline{CH_3}CH_2$2), 13.7 ($CH_3$5).
**HRMS** (API-ES$^+$) *m/z* calcd for $C_{26}H_{33}BN_5O$ $[M+NH_4]^+$ 442.2777; found 442.2768. Calcd. for $C_{26}H_{29}BN_4NaO$ $[M+Na]^+$ 447.2331; found 447.2322

**Compound 57**



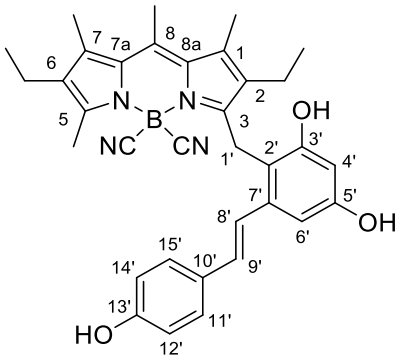

To a stirred solution of compound **9** (15 mg, 0.038 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added *N*-benzyloxycarbonyl-L-tyrosine methyl ester (15.5 mg, 0.046 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (96 µL of a 0.01 M solution, 0.025 equiv). After stirring for 5 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography ($CH_2Cl_2$/MeOH, 100:0 to 90:10) to afford compound **57** (19 mg, 75% yield), as a red-orange solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 7.34-7.24 (5H, m, H6", H7", H8", H9" and H10"), 6.82 (1H, br d, H5'), 6.68 (1H, br d, H4'), 6.67 (1H, br s, H7'), 5.38 (1H, d, *J* = 9.2 Hz, H1"), 5.05 (1H, d, *J* = 12.4 Hz, H4"), 4.97 (1H, d, *J* = 12.4 Hz, H4"), 4.53-4.46 (1H, m, H9'), 4.40 (2H, m, H1'), 3.62 (3H, s, $OCH_3$10'), 2.95 (2H, d, *J* = 4.8 Hz, H8'), 2.67 (3H, s, $CH_3$8), 2.63 (3H, s, $CH_3$5), 2.45 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 2.39 (3H, s, $CH_3$1/$CH_3$7), 2.35 (3H, s, $CH_3$7/$CH_3$1), 2.18 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}$6/$CH_3\underline{CH_2}$2), 1.06 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2/$\underline{CH_3}CH_2$6), 0.74 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$6/$\underline{CH_3}CH_2$2). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 172.3 (C10'), 156.1 (C2"), 153.4 (C3/C5), 152.9 (C5/C3), 152.8 (C3'), 141.3 (C8), 138.6 (C1/C7), 138.5 (C7/C1), 136.7 (C5"), 134.7 (C2/C6), 134.5 (C6/C2), 131.1 (C7'), 130.7 (C7a/C8a), 130.4

(C8a/C7a), 128.8 (C5'), 128.5 (C6'/C6"/C7"/C8"/C9"/C10"), 128.0 (C6"/C7"/C8"/C9"/C10"/C6'), 127.8 (C7"/C8"/C9"/C10"/C6'/C6"), 123.9 (C2'), 115.9 (C4'), 66.7 (C4"), 55.1 (C9'), 52.3 ($OCH_3$10'), 37.1 (C8'), 27.6 (C1'), 17.5 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 17.3 ($CH_3\underline{CH_2}$6/$CH_3\underline{CH_2}$2), 14.9 ($CH_3$1/$CH_3$7/$\underline{CH_3}CH_2$6/$\underline{CH_3}CH_2$2), 14.9 ($CH_3$7/$\underline{CH_3}CH_2$6/$\underline{CH_3}CH_2$2/$CH_3$1), 14.8 ($\underline{CH_3}CH_2$6/$\underline{CH_3}CH_2$2/$CH_3$1/$CH_3$7), 14.2 ($\underline{CH_3}CH_2$6/$\underline{CH_3}CH_2$2), 13.7 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{38}H_{42}BN_5NaO_5$ $[M+Na]^+$ 682.3178; found 682.3175. Calcd. for $C_{38}H_{43}BN_5O_5$ $[M+H]^+$ 660.3350; found 660.3358.

**Compound 58**



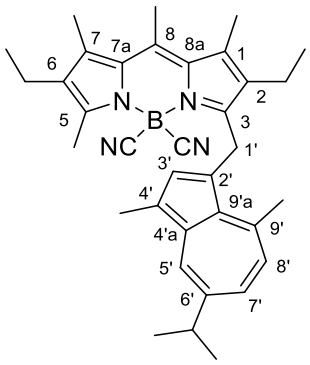

To a stirred solution of compound **9** (15 mg, 0.038 mmol) in anhydrous MeCN (1 mL) was added resveratrol (8.8 mg, 0.038 mmol) and a solution of $Sc(OTf)_3$ in anhydrous MeCN (96 µL of a 0.01 M solution, 0.025 equiv). After stirring for 2 h at room temperature, a solution of $Sc(OTf)_3$ in anhydrous MeCN (96 µL of a 0.01 M solution, 0.025 equiv) was added again. After stirring for 3 h at 50 °C and for 12 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography ($CHCl_3$/MeOH, 100:0 to 94:6) to afford a mixture of 3 regioisomers (12.5 mg, 58% yield), as a red-orange solid. The major regioisomer **58** was isolated by crystallization from hexane/AcOEt.

**$^1$H NMR** ($CD_3CN$/$CD_3COCD_3$ mixtures, 6:1, 500 MHz): δ = 8.04 (1H, s, OH3'), 7.76 (1H, s, OH13'), 7.67 (1H, s, OH5'), 7.20 (2H, d, *J* = 8.6 Hz, H11' and H15'), 6.99 (1H, d, *J* = 16.0 Hz, H8'), 6.76 (1H, d, *J* = 16.0 Hz, H9'), 6.63 (1H, d, *J* = 2.4 Hz, H6'), 6.61 (2H, d, *J* = 8.6 Hz, H12' and H14'), 6.38 (1H, d, *J* = 2.4 Hz, H4'), 4.57 (2H, br s, H1'), 2.67

(3H, s, $CH_3$5), 2.62 (3H, s, $CH_3$8), 2.54 (2H, m, $CH_3\underline{CH_2}$2) 2.44 (3H, s, $CH_3$7), 2.23 (3H, s, $CH_3$1), 1.96 (2H, m, $CH_3\underline{CH_2}$6)1.09 (3H, m, $\underline{CH_3}CH_2$6), 0.64 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2). **$^{13}$C NMR** ($CD_3CN/CD_3COCD_3$ mixtures, 6:1, 125 MHz): δ = 158.1 (C13'), 158.0 (C5'), 157.3 (C3'), 155.2 (C3), 152.8 (C5), 143.4 (C8), 141.4 (C1), 141.2 (C7'), 139.9 (C7), 135.5 (C2), 135.3 (C6), 131.6 (C9'), 131.3 (C7a and C8a), 130.4 (C10'), 129.2 (C11' and C15'), 124.8 (C8'), 116.3 (C12' and C14'), 113.6 (C2'), 105.3 (C6'), 102.6 (C4'), 26.8 (C1'), 18.2 ($CH_3$8), 17.9 ($CH_3\underline{CH_2}$6), 17.7 ($CH_3\underline{CH_2}$2), 15.3 ($\underline{CH_3}CH_2$6), 15.0 ($CH_3$7), 14.7 ($CH_3$1), 14.3 ($\underline{CH_3}CH_2$2), 13.9 ($CH_3$5).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{34}H_{35}BN_4NaO_3$ $[M+Na]^+$ 581.2700; found 581.2701.

**Compound 59**



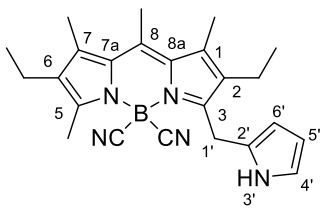

To a stirred solution of compound **9** (16 mg, 0.041 mmol) in anhydrous $CH_2Cl_2$ (1 mL) was added guaiazulene (8.9 mg, 0.057 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (103 µL of a 0.01 M solution, 0.025 equiv). After stirring for 1 day at room temperature, a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (103 µL of a 0.01 M solution, 0.025 equiv) was added again, following by stirring the reaction mixture at room temperature for 3 days. The reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 70:30) to afford compound **59** (16.2 mg, 75% yield), as a purple solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 8.03 (1H, d, *J* = 2.0 Hz, H5'), 7.26 (1H, dd, *J* = 10.7, 2.0 Hz, H7'), 7.11 (1H, s, H3'), 6.87 (1H, d, *J* = 10.7 Hz, H8'), 5.14 (2H, s, H1'), 3.11 (3H, s, $CH_3$9'), 3.06-2.94 (1H, m, $C_2H_6\underline{CH}$6'), 2.72 (3H, s, $CH_3$8), 2.64 (3H, s, $CH_3$5), 2.51 (3H, s, $CH_3$4'), 2.46 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.41 (6H, s, $CH_3$1 and $CH_3$7), 2.09

(2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}2$), 1.34 (6H, d, *J* = 6.9 Hz, $\underline{C_2H_6}CH6'$), 1.07 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_26$), 0.76 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_22$). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 155.3 (C3), 152.9 (C5), 145.2 (C9'), 141.1 (C8), 139.2 (C3'), 139.1 (C6'), 138.8 (C1), 138.0 (C4'), 137.9 (C7), 134.9 (C7'), 134.7 (C2), 134.2 (C6), 133.7 (C5'), 133.3 (C9'a), 130.6 (C7a/C8a), 130.4 (C8a/C7a), 126.7 (C8'), 124.0 (C4'a), 121.3 (C2'), 37.8 ($C_2H_6\underline{CH}6'$), 30.7 (C1'), 27.8 ($CH_39'$), 24.7 ($\underline{C_2H_6}CH6'$), 17.5 ($CH_38$), 17.4 ($CH_3\underline{CH_2}6$), 17.3 ($CH_3\underline{CH_2}2$), 14.9 ($CH_31$ and $CH_37$), 14.8 ($\underline{CH_3}CH_26$), 14.5 ($\underline{CH_3}CH_22$), 13.7 ($CH_35$), 13.0 ($CH_34'$).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{35}H_{42}BN_4$ $[M+H]^+$ 529.3503; found 529.3506. Calcd. for $C_{34}H_{35}BN_4NaO_3$ $[M+Na]^+$ 581.2700; found 581.2701.

**Compound 60**



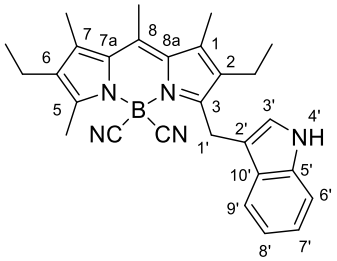

To a stirred solution of compound **9** (10 mg, 0.026 mmol) in anhydrous $CH_2Cl_2$ (2 mL) was added pyrrole (2.6 mg, 0.038 mmol) and asolution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (96 μL of a 0.01 M solution, 0.025 equiv). After stirring for 1.5 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 75:25) to afford compound **60** (7 mg, 69% yield), as a red solid.

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 8.78 (1H, br s, H3'), 6.69 (1H, s, 1H, H4'), 6.13 (2H, m, H5' and H6'), 4.45 (2H, s, H1'), 2.68 (3H, s, $CH_35$), 2.66 (3H, s, $CH_38$), 2.48 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}6$), 2.42 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}2$), 2.41 (3H, s, $CH_37$), 2.36 (3H, s, $CH_31$), 1.09 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_26$), 0.73 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_22$). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 153.3 (C5), 151.4 (C3), 141.7 (C8), 138.9 (C7a), 138.7 (C8a), 135.0 (C7), 134.6 (C1), 130.6 (C6), 130.0 (C2), 127.6 (q, $J_{CB}$ = 73.9 Hz, 2 × CN), 125.8 (C2'), 118.2 (C4'), 108.6 (C5'), 108.3 (C6'), 26.7 (C1'), 17.5 ($CH_35$), 17.4

($CH_3\underline{CH_2}6$), 17.3 ($CH_3\underline{CH_2}2$), 14.9 ($CH_3C7$ and $\underline{CH_3}CH_26$), 14.6 ($CH_31$), 14.1 ($\underline{CH_3}CH_22$), 13.7 ($CH_38$).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{28}H_{34}BN_6$ $C_{24}H_{29}BN_5$ $[M+H]^+$ 398.2515; found 398.2526. Calcd. for $C_{24}H_{28}BN_5Na$ $[M+Na]^+$ 420.2334; found 420.2353.

**Compound 61**




To a stirred solution of compound **9** (15 mg, 0.038 mmol) in anhydrous $CH_2Cl_2$ (2 mL) was added indole (6.7 mg, 0.058 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (96 µL of a 0.01 M solution, 0.025 equiv). After stirring for 1.5 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 80:20) to afford compound **61** (15 mg, 88% yield), as a red solid.

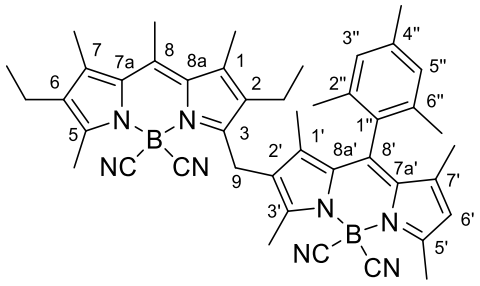
**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 8.08 (1H, s, H4'), 7.66 (1H, d, *J* = 7.3 Hz, H9'), 7.32 (1H, d, *J* = 7.3 Hz, H6'), 7.18 (1H, t, *J* = 7.3 Hz, H7'), ), 7.14 (1H, t, *J* = 7.3 Hz, H8'), 6.97 (1H, s, H3'), 4.55 (2H, s, H1'), 2.70 (3H, s, $CH_35$), 2.65 (3H, s, $CH_38$), 2.47 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}6$), 2.41 (3H, s, $CH_37$), 2.36 (3H, s, $CH_31$), 2.20 (2H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}2$), 1.08 (3H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_26$), 0.70 (3H, t, *J* = 7.5 Hz, 3H, $\underline{CH_3}CH_22$).

**$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 154.4 (C5), 152.8 (C3), 141.2 (C8), 138.6 (C8a), 138.0 (C7a), 134.6 (C7), 134.3 (C1), 130.5 (C6), 130.2 (C2), 127.6 (q, $J_{CB}$ = 74 Hz, 2 × CN), 127.5 (C10'), 123.3 (C3'), 122.1 (C7'), 119.7 (C8'), 118.7 (C9'), 111.3 (C6'), 111.1 (C2'), 24.1 (C1'), 17.5 ($CH_35$), 17.4 ($CH_3\underline{CH_2}6$), 17.3 ($CH_3\underline{CH_2}2$), 14.9 ($\underline{CH_3}CH_26$), 14.8 ($CH_37$), 14.8 ($CH_31$), 14.3 ($CH_3\underline{CH_2}2$), 13.7 ($CH_38$).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{28}H_{34}BN_6$ $[M+NH_4]^+$ 465.2938; found 465.2953. Calcd. for $C_{28}H_{30}BN_5Na$ $[M+Na]^+$ 470.2491; found 470.2494.

**Compounds 62 and 63**

To a stirred solution of compound **9** (11 mg, 0.028 mmol) in anhydrous $CH_2Cl_2$ (2 mL) was added compound **6** (10.7 mg, 0.028 mmol) and a solution of $Sc(OTf)_3$ in anhydrous $CH_2Cl_2$ (64 μL of a 0.01 M solution, 0.025 equiv). After stirring for 5.5 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 100:0 to 70:20) to afford **62** (9.3 mg, 47% yield) and **63** (4.5 mg, 15%), as red solids. Compound **6** (4.0 mg, 37%) was also recovered.

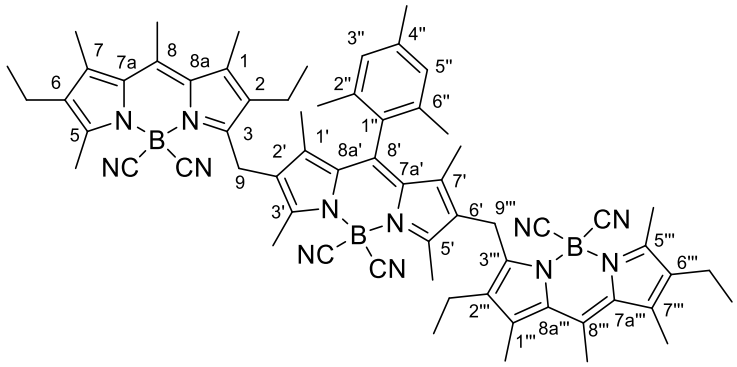



**62**

**$^1$H NMR** ($CDCl_3$, 500 MHz): δ = 6.97 (2H, s, H3" and H5"), 6.14 (1H, s, H6'), 4.23 (2H, br d, H9), 2.72 (3H, s, $CH_3$5'), 2.68 (3H, s, $CH_3$5/$CH_3$8), 2.68 (3H, s, $CH_3$8/$CH_3$5), 2.66 (3H, s, $CH_3$3'), 2.47 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}$6), 2.41 (3H, s, $CH_3$7), 2.33 (3H, s, $CH_3$4"), 2.32 (3H, s, $CH_3$1), 2.06 (8H, m, $CH_3\underline{CH_2}$2, $CH_3$2" and $CH_3$6"), 1.42 (6H, s, $CH_3$1' and $CH_3$7'), 1.08 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6), 0.69 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$6).

**$^{13}$C NMR** ($CDCl_3$, 125 MHz): δ = 156.0 (C5'), 155.1 (C3'), 154.5 (C5), 150.0 (C3), 144.0 (C7'/C7a'), 142.9 (C8'), 141.6 (C8), 141.0 (C1'/C8a'), 139.4 (C4"), 139.1 (C7), 138.9 (C1), 135.0 (C6), 134.4(C2" and C6"), 133.6 (C2), 131.0 (C7a), 130.4 (C1"), 130.0 (C8a), 129.6 (C3" and C5"), 129.3 (C7a'/C7'), 128.4 (C8a'/C1'), 127.5 (C2'), 126.9 (q, $J_{CB}$ = 74.0 Hz, 4 × CN), 122.5 (C6'), 24.7 (C9), 21.3 ($CH_3$8"), 19.7 ($CH_3$2"/$CH_3$6"), 19.5 ($CH_3$6"/$CH_3$2"), 17.7 ($CH_3$8), 17.4 ($CH_3\underline{CH_2}$2/$CH_3\underline{CH_2}$6), 17.4 ($CH_3\underline{CH_2}$6/$CH_3\underline{CH_2}$2), 15.6 ($CH_3$5'), 15.0 ($CH_3$7), 14.8 ($\underline{CH_3}CH_2$6), 14.6 ($CH_3$1), 14.4 ($CH_3$3'), 14.2 ($\underline{CH_3}CH_2$2), 13.9 ($CH_3$7'), 13.8 ($CH_3$5), 11.8 ($CH_3$1').

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{44}H_{52}B_2N_9$ $[M+NH_4]^+$ 728.4541; found 728.4512. calcd. for $C_{44}H_{48}B_2N_8Na$ $[M+Na]^+$ 733.4095; found 733.4052.

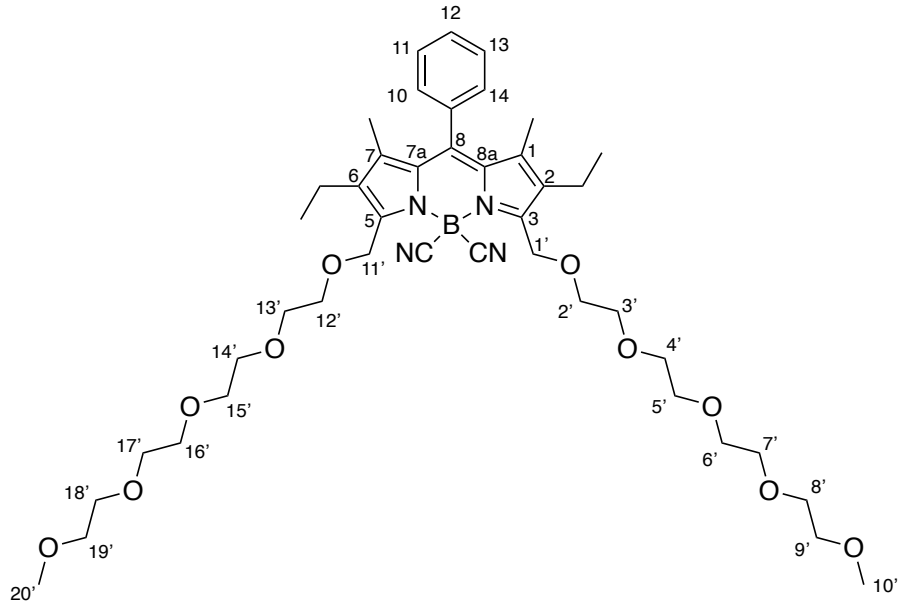


**63**

**$^1$H NMR** ($CDCl_3$, 500 MHz): δ = 6.97 (2H, s, H3" and H5"), 4.23 (4H, br d, H9 and H9'"), 2.68 (9H, s), 2.68 (3H, s), 2.66 (6H, s), 2.47 (4H, q, *J* = 7.6 Hz), 2.41 (6H, s), 2.32 (9H, s, $CH_3$2", $CH_3$6"), 2.15–2.01 (10H, m), 1.41 (6H, s, $CH_3$1' and $CH_3$7'), 1.08 (6H, t, *J* = 7.6 Hz), 0.69 (6H, t, *J* = 7.5 Hz).**$^{13}$C NMR** ($CDCl_3$, 125 MHz): δ = 155.4, 154.4, 150.0, 142.8, 141.6, 141.1, 139.5, 139.1, 135.1, 133.7, 131.1, 130.6, 130.0, 129.6, 128.7, 127.7, 29.9, 24.7, 21.4, 19.5, 17.7, 17.4, 14.9, 14.8, 14.6, 14.5, 14.2, 13.8, 11.9.

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{64}H_{75}B_3N_{13}$ $[M+NH_4]^+$ 1058.6569; found 1058.6567. Calcd. for $C_{64}H_{71}B_3N_{12}Na$ $[M+Na]^+$ 1063.6123; found 1063.6106.

**Compound 64**

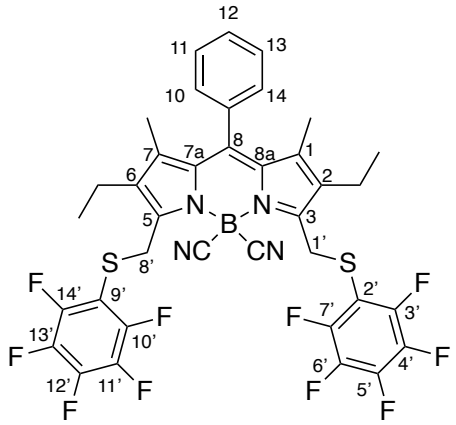


To a solution of compound **12** (10.2 mg, 0.020 mmol) in $CH_2Cl_2$ (1.0 mL), tetraethyleneglycol monomethyl ether (0.013 mL, 0.067 mmol), and a solution of bis(trifluoromethane)sulfonimide (bistriflimide) in $CH_3CN$ (0.01 M, 0.33 mL, 0.0033

mmol) were added and the mixture was heated to 60 °C. After 5 hours, an equal portion of the bistriflimide solution was added and the mixture was heated for 2 more hours before being concentrated at reduced pressure. The crude product was submitted to flash chromatography (hexane/AcOEt, 100:0 to 10:90) to afford compound **64** (5.31 mg, 39%), as a red oil.

**$^1$H RMN** ($CDCl_3$, 400 MHz); δ (ppm) = 7.54 – 7.53 (3H, m, H11, H12 and H13), 7.26 – 7.24 (2H, m, H10 and H14), 4.95 (4H, s, H1' and H11'), 3.86 – 3.84 (4H, m, H2' and H12'), 3.76 - 3.63 (24H, m, C3' - C8' and C13' - C18'), 3.55 – 3.53 (4H, m, H9' and H19'), 3.37 (6H, s, H10' and H20'), 2.46 (4H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}2$ and $CH_3\underline{CH_2}6$), 1.31 (6H, s, $CH_3$1 and $CH_3$7), 1.03 (6H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6).
**$^{13}$C RMN** ($CDCl_3$, 100 MHz); δ (ppm) = 153.0 (C3 and C5), 144.4 (C8), 141.9 (C1 and C7), 136.4 (C2 and C6), 134.6 (C9), 130.2 (C7a and C8a), 129.7 (C11, C12 and C13), 127.7 (C10 and C14), 72.1 (C9' and C19'), 70.8 - 70.6 (C2' - C8' and C12' - C18'), 64.6 (C1' and C11'), 59.2 (C10' and C20'), 17.4 ($CH_3\underline{CH_2}2$ and $CH_3\underline{CH_2}6$), 14.8 ($\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6), 12.0 ($CH_3$1 and $CH_3$7).
**HRMS** (API-ES+) *m/z* calcd. for $C_{43}H_{63}BN_4NaO_{10}$ [M+Na] 829.4537; found 829.4550. Calcd. for $C_{43}H_{67}BN_5O_{10}$ $[M+NH_4]^+$ 824.4983; found 824.4972.

**Compound 65**

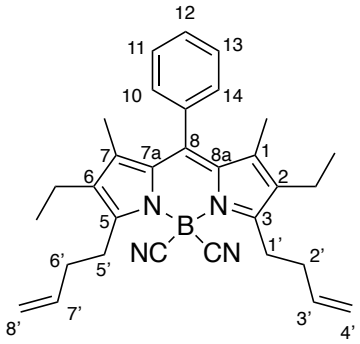



To a solution of compound **12** (19.6 mg, 0.039 mmol) in dry $CH_2Cl_2$ (1.5 mL), pentafluorothiophenol (0.015 mL, 0.12 mmol) and a solution bistriflimide in $CH_3CN$ (0.01 M, 0.58 mL, 0.0058 mmol) were added and the mixture was heated to 60 °C for 1.5 hours before being concentrated at reduced pressure. The crude product was submitted to flash chromatography (hexane/AcOEt, 100:0 to 10:90) to afford compound **65** (16.4 mg, 54 %), as a pink solid.

**$^1$H RMN** ($CDCl_3$, 400 MHz); δ (ppm) = 7.59 – 7.56 (3H, m, H11, H12 and H13), 7.32 – 7.30 (2H, m, H10 and H14), 4.53 (4H, s, H1' and H8'), 2.46 (4H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}2$ and $CH_3\underline{CH_2}6$), 1.35 (6H, s, $CH_3$1 and $CH_3$7), 1.10 (6H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6). **$^{13}$C RMN** ($CDCl_3$, 100 MHz); δ (ppm) = 150.7 (C3 and C5), 144.5 (C8), 142.7 (C1 and C7), 136.6 (C2 and C6), 134.2 (C9), 130.8 (C7a and C8a), 130.0 (C12), 129.8 (C11 and C13), 127.7 (C10 and C14), 108.5 (t, $J_{S,C}$ = 21.7 Hz, C2' and C9'), 31.1 (C1' and C8'), 17.6 ($CH_3\underline{CH_2}2$ and $CH_3\underline{CH_2}6$), 14.6 ($\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6), 12.3 ($CH_3$1 and $CH_3$7).

**HRMS** (API-ES+) *m/z* calcd. for $C_{37}H_{25}BF_{10}N_4NaS_2$ $[M+Na]^+$ 813.1353; found 813.1360. Calcd. for $C_{37}H_{29}BF_{10}N_5S_2$ $[M+NH_4]^+$ 808.1799; found 808.1806.

**Compound 66**




To a solution of compound **12** (20.7 mg, 0.041 mmol) in $CH_2Cl_2$ (1.5 mL), allyltrimethylsilane (0.033 mL, 0.20 mmol) and a $Sc(OTf)_3$ solution in $CH_3CN$ (0.01 M, 0.406 mL, 0.0041 mmol) were added. After stirring at 60 °C for 2 hours, the reaction mixture was quenched with $H_2O$ (5 mL) and extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic phases were dried over $Na_2SO_4$ and the solvent was removed at reduced pressure. The resulting crude product was submitted to flash chromatography (hexane/AcOEt, 100:0 to 30:70) to afford **66** (10.5 mg, 55%), as an orange powder.

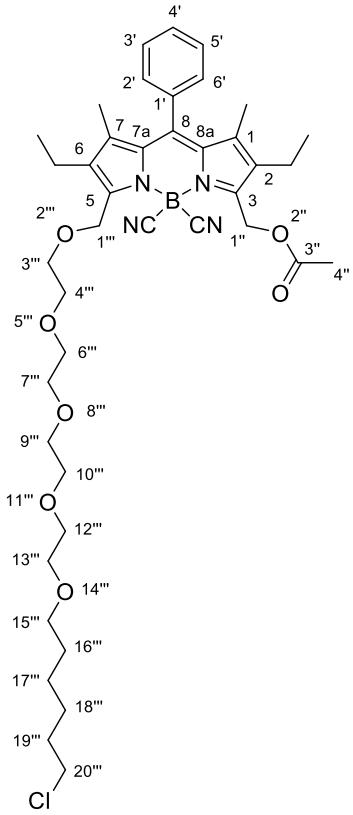
**$^1$H RMN** ($CDCl_3$, 400 MHz); δ (ppm) = 7.54 - 7.51 (3H, m, H11, H12 and H13), 7.31 - 7.28 (2H, m, H10 and H14), 6.02 (2H, ddt, *J* = 6.5, 10.2, 16.8 Hz, H3' and H7'), 5.24 (2H, dq, *J* = 1.6, 17.1 Hz, H4' and H8'), 5.11 (2H, dd, *J* = 1.6, 10.2 Hz, H4' and H8'), 3.14 – 3.10 (4H, m, H1' and H5'), 2.59 – 2.53 (4H, m, H2' and H6'), 2.36 (4H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}2$ and $CH_3\underline{CH_2}6$), 1.31 (6H, s, $CH_3$1 and $CH_3$7), 1.04 (6H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6).

**$^{13}$C RMN** ($CDCl_3$, 100 MHz); δ (ppm) = 157.3 (C3 and C5), 141.7 (C8), 141.1 (C1 and C7), 137.2 (C3' and C7'), 135.0 (C9), 134.4 (C2 and C6), 129.5 (C11 and C13), 129.4 (C12), 129.3 (C7a and C8a), 128.5 (q, $J_{B,C}$ = 74.0 Hz, 2xCN), 128.1 (C10 and C14), 116.0 (C4' and C8'), 32.1 (C2' and C6'), 27.4 (C1' and C5'), 17.4 ($CH_3\underline{CH_2}2$ and $CH_3\underline{CH_2}6$), 14.8 ($\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6), 12.2 ($CH_3$1 and $CH_3$7).

**HRMS (ESI$^+$):** *m/z* calcd. for $C_{31}H_{35}BN_4$ $[M+H]^+$ 475.3033; found 475.3053.

**Compounds 67 and 69**

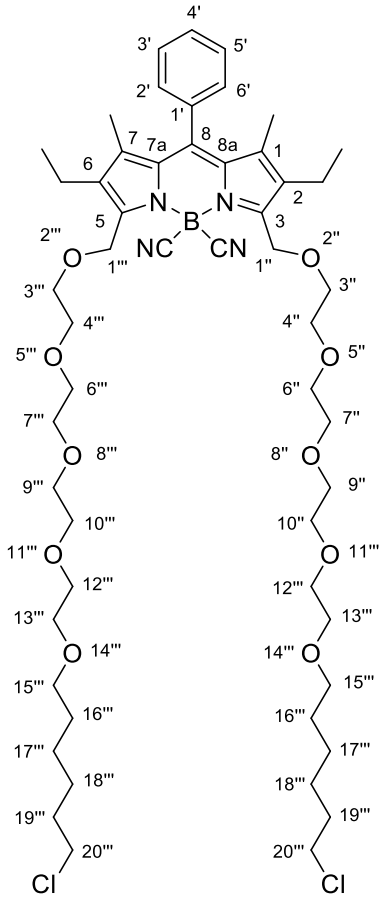
To a stirred solution of compound **12** (52.5 mg, 0.103 mmol) in anhydrous $CH_2Cl_2$ (1.5 mL) were added 2-(2-(2-((6-chlorohexyl)oxy)ethoxy)ethoxy)ethanol (16.1 mg, 0.051 mmol) and $Sc(OTf)_3$ (7.1 mg, 0.014 mmol) at room temperature. After stirring for 1 day at 50 °C in a closed vial, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 85:15 to 30:70) to afford **67** (16.4 mg, 42% yield, based on starting limiting alcohol) and **69** (3.1 mg, 6% yield), as red-orange solids, and unreacted compound **12** (21 mg, 40% recovery).



**67**

**$^{1}$H NMR** ($CDCl_3$, 500 MHz): δ = 7.58-7.52 (3H, m, H3', H4' and H5'), 7.29-7.26 (2H, m, H2' and H6'), 5.45 (2H, s, H1'''), 4.97 (2H, s, H1''), 3.86 (2H, dd, *J* = 5.6, 3.9 Hz, H3'''), 3.75 (2H, dd, *J* = 5.6, 3.9 Hz, H4''), 3.69-3.65 (8H, m, H6''', H7''', H9''' and H10'''), 3.65-3.62 (2H, m, H12''') 3.57 (2H, dd, *J* = 6.1, 3.9 Hz, H13'''), 3.53 (2H, t, *J* = 6.7 Hz, H20'''), 3.45 (2H, t, *J* = 6.7 Hz, H15'''), 2.47 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}6$), 2.40 (2H, q, *J* = 7.6 Hz, $CH_3\underline{CH_2}2$), 2.19 (3H, s, H4''), 1.77 (2H, q, *J* = 6.7 Hz, H19'''), 1.62-1-56 (2H.s, H16'''), 1.50-1.40 (2H, m, H18'''), 1.40-1.34 (2H, m, H17'''), 1.34 ($CH_31/CH_37$), 1.33 ($CH_37/CH_31$),1.04 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_26$) 1.02 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_22$). **$^{13}$C NMR** ($CDCl_3$, 125 MHz): δ = 170.7 (C3''), 155.2 (C5), 148.2 (C3), 145.0 (C8), 143.2 (C7), 141.0 (C1), 137.2 (C6), 136.1 (C2), 134.4 (C1'), 131.0 (C7a/C8a), 130.4 (C8a/C7a), 129.9 (C4'), 129.8 (C3' and C5'), 127.6 (C1' and C6'), 71.4 (C15'''), 70.9 (C3'''), 70.7 (C4'''), 70.8, 70.7 (*from* 70.7 *to* 70.7: C6''', C7''', C9''', C10''' and C12'''), 70.3 (C13'''), 64.7 (C1'''), 56.5 (C1''), 45.2 (C20'''), 32.7 (C19'''), 29.6 (C16'''), 26.9 (C18'''), 25.6 (C17'''), 20.96 (C4''), 17.5 ($CH_3\underline{CH_2}2/CH_3\underline{CH_2}6$), 17.3 ($CH_3\underline{CH_2}6/CH_3\underline{CH_2}2$), 15.1 ($\underline{CH_3}CH_22/\underline{CH_3}CH_26$), 14.7 ($\underline{CH_3}CH_26/\underline{CH_3}CH_22$), 12.2 ($CH_31/CH_37$), 12.1 ($CH_37/CH_31$).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{41}H_{60}BClN_5O_7$ $[M+NH_4]^+$ 780.4276 ($^{35}Cl$), 782.4269 ($3^7Cl$); found 780.4294 ($^{35}Cl$), 782.4286 ($^{37}Cl$). Calcd for $C_{41}H_{56}BClN_4NaO_7$ $[M+Na]^+$ 785.3830 ($^{35}Cl$), 787.3823 ($^{37}Cl$); found 785.3859 ($^{35}Cl$), 787.3820 ($^{37}Cl$).




**69**

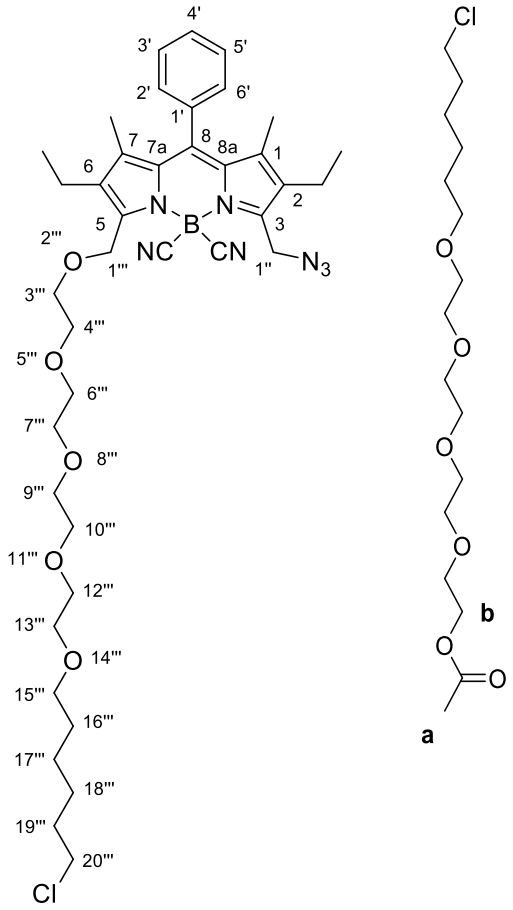
**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 7.54 (3H, m, H3', H4 and H5'), 7.24 (2H, m, H2' and H6'), 4.95 (4H, s, H1" and H1'"), 3.85 (4H, dd, *J* = 5.8, 3.7 Hz, H3" and H3'"), 3.75 (4H, dd, *J* = 5.8, 3.7 Hz, H4" and H4'"), 3.68-3.64 (16H, m, H6", H6'", H7", H7'", H9", H9'" H10" and H10'"), 3.63 (4H, dd, *J* = 4.7, 1.8 Hz, H12" and H12'"), 3.58 (4H, dd, *J* = 4.7, 1.8 Hz, H13" and H13'"), 3.53 (4H, t, *J* = 6.7 Hz, H20" and H20'"), 3.45 (4H, t, *J* = 6.7 Hz, H15" and H15'"), 2.46 (4H, q, *J* = 7.5 Hz, $CH_3\underline{CH_2}2$ and $CH_3\underline{CH_2}6$), 1.83-1.71 (4H, m, H19" and H19'"), 1.63-1.55 (4H, m, H16" and H16'"), 1.48-1.40 (4H, m, H18" and H18'"), 1.39-1.32 (4H, m, H17" and H17'"), 1.31 (6H, s, $CH_3$1 and $CH_3$7), 1.03 (6H, t, *J* = 7.5 Hz, $\underline{CH_3}CH_2$2 and $\underline{CH_3}CH_2$6). **$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 153.0 (C3 and C5), 144.4 (C8), 141.9 (C1 and C7), 136.4 (C2 and C6), 134.6 (C1'), 130.2 (C7a and C8a), 129.7 (C3'/C4'/C5'), 129.7 (C4'/C5'/C3'), 127.7 (C2' and C6'), 71.4 (C15" and

C15'"), 70.8, 70.7, 70.7, 70.7 (from 70.8 to 70.7: C3", C3'", C4", C4'", C6", C6'", C7", C7'", C9", C9'", C10", C10'", C12" and C12'"), 70.3 (C13" and C13'"), 64.7 (C1" and C1'"), 45.2 (C20" and C20'"), 32.7 (C19" and C19'"), 29.6 (C16" and C16'"), 26.9 (C18" and C18'"), 25.6 (C17" and C17'"), 17.4 ($CH_3\underline{CH_2}2$ and $CH_3\underline{CH_2}6$), 14.8 ($\underline{CH_3}CH_2 2$ and $\underline{CH_3}CH_2 6$), 12.0 ($CH_3 1$ and $CH_3 7$).

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{53}H_{85}BCl_2N_5O_{10}$ $[M+NH_4]^+$ 1032.5770 ($^{35}Cl$); found 1032.5790 ($^{35}Cl$).

**Compound 68**

To a stirred solution of compound **67** (15 mg, 0.019 mmol) in anhydrous $CH_2Cl_2$ (1.5 mL) were added trimethylsilyl azide (4.1 μl, 0.029 mmol) and $Sc(OTf)_3$ (1.1 mg, 0.002 mmol) at room temperature. After stirring for 6 h at 50 °C in a closed vial and for 18 h at room temperature, the reaction mixture was quenched with $H_2O$ (10 mL), the organic layer was separated and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, and the solvent was removed at reduced pressure. The crude was purified by silica gel flash column chromatography (hexane/AcOEt, 80:20 to 10:90) to afford **68** (3.8 mg, 25% yield), as a red-orange solid. Compound **68** was accompanied by a small impurity that was tentatively assigned, from $^1H$ NMR and HRMS data, to 18-chloro-3,6,9,12-tetraoxaoctadecyl acetate, formed by trans-esterification with **67** under the reaction conditions (see copies of NMR spectra in the accompanying Supporting Information document).



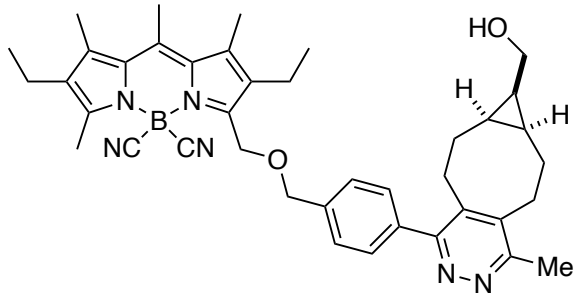

**68** Impurity

**$^{1}$H NMR** ($CDCl_3$, 500 MHz): δ = 7.58–7.53 (3H, m, H3', H4 and H5'), 7.29-7.26 (2H, m, H2' and H6'), 4.97 (2H, s, H1'''), 4.86 (2H, s, H1''), 4.24-4.20 (2H, m, $CH_2$b: **impurity**), 3.87 (4H, dd, *J* = 5.6, 3.9 Hz), 3.76 (4H, dd, *J* = 5.6, 3.9 Hz), 3.71-3.67 (20H, m), 3.64–3.62 (4H, m), 3.59-3.56 (4H, m), 3.53 (2H, t, *J* = 6.7 Hz), 3.54 (2H, t, *J* = 6.7 Hz), 3.46 (2H, t, *J* = 6.7 Hz), ), 3.47 (2H, t, *J* = 6.7 Hz), 2.50-2.45 (4H, m, $CH_3\underline{CH_2}2$ and $CH_3\underline{CH_2}6$), 2.08 (3H, s, $CH_3$a: **impurity**), 1.80-1.73 (4H, m), 1.62–1.56 (4H, m), 1.50-1.41 (4H, m), 1.40-1.36 (4H, m), 1.07 (3H, t, *J* = 7.6 Hz, $CH_3\underline{CH_2}2$/$CH_3\underline{CH_2}6$), 1.03 (3H, t, *J* = 7.6 Hz, $\underline{CH_3}CH_26$/$\underline{CH_3}CH_22$).

**$^{13}$C NMR** ($CDCl_3$, 100 MHz): δ = 171.2 (COO), 154.9 (C5), 148.3 (C8), 145.0 (C3), 143.1(C1/C7), 141.6 (C7/C1), 137.0 (C2/C6), 135.9 (C6/C2), 134.3(C1'), 130.8 (C7a/C8a), 130.0 (C8a/C7a), 129.9 (C4'), 129.8 (C3' and C5'), 127.6 (C1' and C6'), 71.4, 70.4, 70.8, 70.8, 70.8, 70.7, 70.7, 70.6, 70.3, 69.3 (C1'''), 64.7(Cb: **impurity**), 45.4 (C1''), 45.2, 45.2, 32.7, 29.9, 29.6, 26.9, 25.6, 21.1 (Ca: **impurity**) 17.5($CH_3\underline{CH_2}2$/$CH_3\underline{CH_2}6$), 17.4 ($CH_3\underline{CH_2}6$/$CH_3\underline{CH_2}2$), 14.7 ($\underline{CH_3}CH_22$/$\underline{CH_3}CH_26$), 14.7 ($\underline{CH_3}CH_26$/$\underline{CH_3}CH_22$), 12.2, 12.1.

**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{39}H_{57}BClN_8O_5$ $[M+NH_4]^+$ 763.4235 ($^{35}Cl$), 765.4226 ($^{37}Cl$); found 763.4214 ($^{35}Cl$), 765.4208 ($^{37}Cl$). Calcd for $C_{39}H_{53}BClN_7NaO_5$ $[M+Na]^+$ 768.3789 ($^{35}Cl$), 770.3780 ($^{37}Cl$); found 768.3766 ($^{35}Cl$), 770.3817 ($^{37}Cl$).
**HRMS** (API-ES$^+$) **impurity** *m/z* calcd. for $C_{16}H_{35}ClNO_6$ $[M+NH_4]^+$ 372.2153; found 372.2152.

**Compound 70**




To a stirred solution of tetrazine **34** (1.0 mg, 0.0018 mmol) in AcOEt (0.5 mL), was added cyclooctyne **40** (4.0 mg, 0.026 mmol) in AcOEt (1.0 mL). After stirring for 5 min at room temperature, the reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (AcOEt) to afford compound **70** (1.1 mg, 94%), as a red solid.

**$^1$H NMR** (400 MHz, $CDCl_3$); δ = 7.56 (m, 2H), 7.44 (m, 2H), 4.93 (s, 2H), 4.81 (s, 2H), 3.72 (m, 2H), 3'02 (m, 1H), 2.86 (m, 3H), 2.79 (s, 3H), 2.70 (s, 3H), 2.69 (s, 3H), 2,52 (q, J = 7.4 Hz, 2H), 2.45 (q, J = 7.4 Hz, 2H), 2.41 (s, 3H), 2.39 (s, 3H), 1.56 (m, 4H), 1.27 (m, 1H), 1.10 (t, J = 7.4 Hz, 3H), 1.08 (t, J = 7.4 Hz, 3H), 0.91 (m, 2H). **$^{13}$C NMR** (100 MHz, $CDCl_3$); δ = 161.1, 157.5, 155.9, 147.6, 142.7, 139.9, 138.4, 137.5, 137.4, 135.5, 135.1, 131.6, 130.3, 129.5, 128.3, 73.3, 63.5, 59.5, 32.1, 29.8, 28.2, 27.3, 22.8, 22.5, 20.5, 17.7, 17.5, 17.4, 15.3, 15.0, 14.8, 14.6, 14.3, 13.9.
**HRMS** (API-ES$^+$) *m/z* calcd. for $C_{40}H_{47}BN_6O_2$ $[M+H]^+$ 655.3926; found 655.3917.

**Photophysical characterization**

The UV/Vis absorption spectra were recorded by UV–Vis–NIR Spectroscopy (Cary 7000) equipped with two lamps (halogen lamp for Vis-IR region and deuterium lamp for UV region), a double monochromator (Littrow) and double diffraction grating of 1200 lines/mm. The fluorescence measurements were recorded with an Edinburgh Instruments Spectrofluorimeter (FLSP920 model) equipped with a xenon flash lamp 450 W as the excitation source. The fluorescence spectra were corrected from the wavelength dependence on the detector sensibility. The fluorescence quantum yield ($\Phi_{fl}$) was calculated using as reference commercial BODIPY **3** in MeOH ($\Phi_{fl}^{ref} = 0.91$),[4] using an excitation wavelength of 490 nm for all measurements.

Radiative decay curves were recorded with a time-correlated single-photon counting technique (Edinburgh Instruments, model FL920) using a microchannel plate detector (Hamamatsu C4878) with picosecond time resolution. The fluorescence lifetimes ($\tau_{fl}$) were obtained after deconvolution of the instrumental response signal from the recorded decay curves by means of an iterative method. The goodness of the exponential fit was controlled by statistical parameters (chi-square, $\chi^2$, and analysis of the residuals). The estimated errors in the photophysical parameters are estimated to be around 10%. Fluorescence emission curves were monitored upon excitation by means of a continuous laser (Fianium) with 150 ps full-width at half maximum (FWHM) pulses.

**Live-cell imaging studies**

*Cell culture.* The established human squamous cell carcinoma (SCC38)-derived cell line was kindly provided by Dr R Grenman (University Central Hospital, Turku, Finland). SCC38 and HeLa cells were grown in DMEM supplemented with 10% fetal bovine serum, 100 units per mL penicillin, 200 μg $mL^{-1}$ streptomycin, 2 mmol $L^{-1}$-glutamine and 100 μmol $L^{-1}$ nonessential amino acids. Cell lines were periodically tested for human pathogens and mycoplasma infection. All methods were carried out in accordance with the approved guidelines of our institution.

*Fluorescent cell labeling.* Cells ($50 \times 10^3$) were plated on black 24 well plates with flat and clear bottom suitable for fluorescence-based imaging of living cells (Ibidi GmbH) 24 hours before labeling. BODIPY probes were diluted in $H_2O$ or DMSO to a stock

concentration of 500 μM, 50 μM or 20 μM. Adhered living cells were incubated with probes at 500 nM, 100 nM, or 50 nM, as indicated in figure legends, in DMEM without supplements for 30 minutes at 37 °C. Subsequently, the probes were removed and the cells were washed with PBS (3 × 5 min). Supplemented DMEM was then added to cells prior to microscopy analysis.

*Live-cell microscopy.* Microscopy imaging was performed on a Cell Observer equipment composed of a Zeiss AxioObserver Z1 wide field inverted fluorescence microscope (Carl Zeiss, Germany) with a Plan-Apochromat 40X/1.3 (NA = 1.3, working distance = 0.21 mm) or Plan-Apochromat 63X/1.4 (NA = 1.4, working distance = 0.19 mm) oil lens objective, a camera (AxioCam MRm; Carl Zeiss), a $CO_2$ incubator, and a ZEISS ApoTome.2 structured illumination system. ApoTome.2 allows acquisition of optical sections of the fluorescent sample by moving the appropriate grid into the beam path and calculating the optical section from three images with different grid positions without time lag. Acquisition and processing of images were conducted using the Zen (Carl Zeiss) software.

**X-Ray diffraction**

*Experimental*

Single crystals of compound **9** $C_{22}H_{27}BN_4O_2$ **[CCDC 2177585]**. A suitable crystal was selected and mounted on a **SuperNova, Single source at offset/far, Atlas** diffractometer. The crystal was kept at 150.00(10) K during data collection. Using Olex2,[5] the structure was solved with the ShelXS[6] structure solution program using Direct Methods and refined with the ShelXL[7] refinement package using Least Squares minimization.

*Crystal structure determination of **9** [CCDC 2177585]*

Crystal Data for $C_{22}H_{27}BN_4O_2$ ($M$ =390.28 g/mol): triclinic, space group P-1 (no. 2), $a$ = 9.5191(6) Å, $b$ = 10.8959(7) Å, $c$ = 11.6708(6) Å, $\alpha$ = 114.490(5)°, $\beta$ = 96.844(5)°, $\gamma$ = 101.099(5)°, $V$ = 1053.80(10) Å$^3$, $Z$ = 2, $T$ = 150.00(10) K, μ(CuKα) = 0.634 mm$^{-1}$, *Dcalc* = 1.230 g/cm$^3$, 6898 reflections measured (8.54° ≤ 2Θ ≤ 137.94°), 3908 unique ($R_{int}$ = 0.0396, $R_{sigma}$ = 0.0664) which were used in all calculations. The final $R_1$ was 0.0490 (I > 2σ(I)) and $wR_2$ was 0.1292 (all data).

**Table 1 Crystal data and structure refinement for 9 (CCDC 2177585).**

| | |
|---|---|
| Identification code | a20190212_BODIPV |
| Empirical formula | $C_{22}H_{27}BN_4O_2$ |
| Formula weight | 390.28 |
| Temperature/K | 150.00(10) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.5191(6) |
| b/Å | 10.8959(7) |
| c/Å | 11.6708(6) |
| α/° | 114.490(5) |
| β/° | 96.844(5) |
| γ/° | 101.099(5) |
| Volume/Å$^3$ | 1053.80(10) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.230 |
| μ/mm$^{-1}$ | 0.634 |
| F(000) | 416.0 |
| Crystal size/mm$^3$ | 0.299 × 0.053 × 0.043 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.54 to 137.94 |
| Index ranges | -11 ≤ h ≤ 11, -13 ≤ k ≤ 11, -11 ≤ l ≤ 14 |
| Reflections collected | 6898 |
| Independent reflections | 3908 [$R_{int}$ = 0.0396, $R_{sigma}$ = 0.0664] |
| Data/restraints/parameters | 3908/0/269 |
| Goodness-of-fit on F$^2$ | 1.002 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0490, $wR_2$ = 0.1179 |
| Final R indexes [all data] | $R_1$ = 0.0702, $wR_2$ = 0.1292 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.31/-0.22 |

[a] Weighting scheme: $1/[\sigma^2(F^2)+(0.0586P)^2]$ donde $P = [Max(F^2,0)+2F^2]/3$.
[b] Secondary extinction expression type SHELXL: $F_c^* = kF_c[1+0.001F_c^2\lambda^3/sen(2\theta)]^{-1/4}$

## Quantum mechanics calculations

Ground state geometries of compounds **59-61** were optimized at Density Functional Theory (DFT) using the hybrid B3LYP method and the basis set function 6-311+G*. The energy minimization was carried out without any geometrical constraints and an energy minimum was reached when the corresponding frequency analysis did not give any negative value. Absorption energies and probability were simulated with the time-dependent (TD DFT) method using the same basis set. All calculations were performed

using the Gaussian 16 program suite, implemented in the computational cluster provided by the SGIker resources of UPV-EHU.

**Atom coordinates and total energy (in Hartrees) of the ground state (B3LYP/6-311+G*) of compounds 59-61.**

**Compound 59**

| | | | |
|---|---|---|---|
| C | -3.12573800 | -2.35132700 | 0.57073000 |
| N | -2.80219900 | -1.07094200 | 0.28786600 |
| C | -3.78965500 | -0.53174400 | -0.54429900 |
| C | -4.78803600 | -1.53832400 | -0.73549300 |
| C | -4.36795400 | -2.66599600 | -0.02944900 |
| B | -1.47152300 | -0.34331600 | 0.64547500 |
| N | -1.63649600 | 1.15994700 | 0.27743400 |
| C | -2.66103600 | 1.63452400 | -0.55530800 |
| C | -3.68529200 | 0.78548700 | -1.01111200 |
| C | -0.83896300 | 2.20349100 | 0.61500700 |
| C | -1.34347600 | 3.38680300 | 0.02563800 |
| C | -2.47612300 | 3.04104500 | -0.71206100 |
| C | -1.21549400 | -0.48664900 | 2.21606900 |
| C | -0.31200200 | -1.03089100 | -0.21401800 |
| C | -4.68207600 | 1.29735900 | -2.01987000 |
| C | -5.07143000 | -3.99202600 | 0.07403000 |
| C | -4.73953900 | -4.95702700 | -1.07718500 |
| C | -0.78103900 | 4.77125300 | 0.21326400 |
| C | -1.36077200 | 5.51370800 | 1.42967500 |
| C | 0.35241900 | 2.12951700 | 1.53293100 |
| C | -3.33312900 | 4.02610800 | -1.45429700 |
| C | -2.25525500 | -3.26306300 | 1.36974000 |
| C | -6.08396600 | -1.44276900 | -1.48658100 |
| N | -1.07397800 | -0.58661800 | 3.35783800 |
| N | 0.43845500 | -1.58727200 | -0.89349500 |
| C | 2.28437500 | 1.36192300 | -0.07315400 |
| C | 1.99020900 | 2.20946900 | -1.27678000 |
| C | 1.54826300 | 1.29322500 | 1.12441400 |
| C | 2.13939000 | 0.35431200 | 1.99321500 |
| C | 3.25966800 | -0.20505300 | 1.37377600 |
| C | 4.10473400 | -1.18030400 | 1.91885000 |
| C | 3.78532100 | -1.68316100 | 3.31082300 |
| C | 5.22232600 | -1.73671500 | 1.28429900 |
| C | 5.76804400 | -1.50878700 | 0.02076900 |
| C | 5.38453700 | -0.65523000 | -1.01720600 |
| C | 6.21830000 | -0.67329200 | -2.30284900 |
| C | 7.67292600 | -0.23130200 | -2.06584500 |
| C | 6.15994500 | -2.03690200 | -3.01356600 |
| C | 4.28569000 | 0.21261800 | -0.97350300 |
| C | 3.35497100 | 0.44207900 | 0.03011100 |

| | | | |
|---|---|---|---|
| H | -4.23639600 | 2.04183100 | -2.67271800 |
| H | -5.04983900 | 0.49434800 | -2.65134700 |
| H | -5.54914300 | 1.75898900 | -1.53487100 |
| H | -4.82308400 | -4.46741000 | 1.02737500 |
| H | -6.15408900 | -3.83340600 | 0.10849000 |
| H | -5.26860300 | -5.90699800 | -0.95833800 |
| H | -5.02407800 | -4.53274400 | -2.04374500 |
| H | -3.66851300 | -5.17144800 | -1.11899400 |
| H | 0.30737000 | 4.72198000 | 0.31037000 |
| H | -0.95704500 | 5.36349100 | -0.68969900 |
| H | -0.92749700 | 6.51374900 | 1.52227800 |
| H | -2.44556600 | 5.62336900 | 1.34858300 |
| H | -1.15782300 | 4.97336500 | 2.35796400 |
| H | 0.68972900 | 3.15739600 | 1.69538800 |
| H | 0.01343400 | 1.77795200 | 2.51128300 |
| H | -3.05165800 | 5.04706400 | -1.19658500 |
| H | -3.23018800 | 3.93401400 | -2.54084300 |
| H | -4.39397700 | 3.91786000 | -1.21984000 |
| H | -2.19932300 | -2.95559500 | 2.41700000 |
| H | -2.63650700 | -4.28288300 | 1.33339700 |
| H | -1.23265900 | -3.27276500 | 0.98399200 |
| H | -6.63544300 | -0.52904400 | -1.25636700 |
| H | -5.94003600 | -1.47098500 | -2.57221500 |
| H | -6.73218000 | -2.28321800 | -1.23558600 |
| H | 2.86873600 | 2.77221200 | -1.61031800 |
| H | 1.65306800 | 1.60363200 | -2.12590600 |
| H | 1.20282300 | 2.93657900 | -1.07682500 |
| H | 1.75620100 | 0.10298400 | 2.97141500 |
| H | 4.49463200 | -2.44508300 | 3.63628900 |
| H | 3.80830300 | -0.86767100 | 4.03982900 |
| H | 2.78159800 | -2.11537900 | 3.35134500 |
| H | 5.75687500 | -2.48047700 | 1.87005100 |
| H | 6.64842800 | -2.11445800 | -0.18333100 |
| H | 5.76868300 | 0.05975400 | -2.98193300 |
| H | 8.22018800 | -0.17788900 | -3.01215600 |
| H | 7.71632900 | 0.75410800 | -1.59468300 |
| H | 8.20907800 | -0.93106300 | -1.41788000 |
| H | 6.69354900 | -1.99913600 | -3.96849500 |
| H | 5.12768500 | -2.33448300 | -3.21332400 |
| H | 6.62069500 | -2.82616700 | -2.41200300 |
| H | 4.13253200 | 0.80024600 | -1.87652200 |

TOTAL ENERGY (Hartrees) = –1602.677713

**Compound 60**

| | | | |
|---|---|---|---|
| C | -2.333372 | 0.846136 | -0.116749 |
| N | -1.976620 | -0.458180 | 0.247894 |

| | | | |
|---|---|---|---|
| B | -0.522531 | -0.956154 | 0.431950 |
| N | 0.433132 | 0.248862 | 0.221690 |
| C | 0.010020 | 1.543486 | -0.109158 |
| C | -1.349041 | 1.826235 | -0.326533 |
| C | 1.778092 | 0.254286 | 0.361792 |
| C | 2.269379 | 1.564287 | 0.155096 |
| C | 1.173668 | 2.376191 | -0.140168 |
| C | -3.761491 | 0.894799 | -0.181940 |
| C | -4.229814 | -0.383210 | 0.135595 |
| C | -3.101720 | -1.196681 | 0.385273 |
| C | -0.208776 | -2.102673 | -0.641525 |
| C | -0.336971 | -1.519532 | 1.922175 |
| C | 1.266232 | 3.855333 | -0.383745 |
| C | 3.706606 | 1.990936 | 0.289509 |
| C | -1.755908 | 3.196777 | -0.804297 |
| C | 2.576259 | -0.974035 | 0.708750 |
| C | 4.096505 | 2.389041 | 1.725436 |
| C | -4.650535 | 2.066810 | -0.481898 |
| C | -5.661206 | -0.843835 | 0.188493 |
| C | -3.086966 | -2.644625 | 0.743457 |
| C | -6.203460 | -1.335021 | -1.166110 |
| C | 3.694998 | -1.276813 | -0.250961 |
| N | 4.961486 | -1.582394 | 0.199796 |
| C | 5.789981 | -1.857344 | -0.864591 |
| C | 5.045683 | -1.719692 | -2.013704 |
| C | 3.724159 | -1.355920 | -1.627403 |
| N | -0.200118 | -1.894708 | 3.006644 |
| N | -0.003882 | -2.912879 | -1.439590 |
| H | 0.547807 | 4.419049 | 0.214946 |
| H | 2.260909 | 4.217659 | -0.123736 |
| H | 1.096378 | 4.115063 | -1.434179 |
| H | 3.902502 | 2.831551 | -0.382126 |
| H | 4.354981 | 1.182645 | -0.054687 |
| H | -0.969462 | 3.659508 | -1.391704 |
| H | -2.642982 | 3.146948 | -1.428145 |
| H | -1.978544 | 3.860619 | 0.038489 |
| H | 2.992672 | -0.835384 | 1.714648 |
| H | 1.917828 | -1.839679 | 0.787823 |
| H | 5.149256 | 2.681572 | 1.774941 |
| H | 3.944539 | 1.560797 | 2.423221 |
| H | 3.494662 | 3.229082 | 2.083046 |
| H | -5.687997 | 1.819973 | -0.253988 |
| H | -4.387763 | 2.949394 | 0.104917 |
| H | -4.617256 | 2.352470 | -1.538799 |
| H | -6.294618 | -0.030853 | 0.555920 |
| H | -5.759843 | -1.644259 | 0.927223 |
| H | -2.511070 | -3.225508 | 0.017610 |
| H | -2.629952 | -2.808986 | 1.723466 |
| H | -4.101039 | -3.041159 | 0.767887 |
| H | -7.242810 | -1.663143 | -1.074476 |

| | | | |
|---|---|---|---|
| H | -5.615042 | -2.175059 | -1.544237 |
| H | -6.163917 | -0.541559 | -1.917250 |
| H | 5.230748 | -1.629853 | 1.169006 |
| H | 6.822791 | -2.126251 | -0.714443 |
| H | 5.405413 | -1.869932 | -3.019660 |
| H | 2.882542 | -1.188457 | -2.281262 |

TOTAL ENERGY (Hartrees) = –1230.422291

**Compound 61**

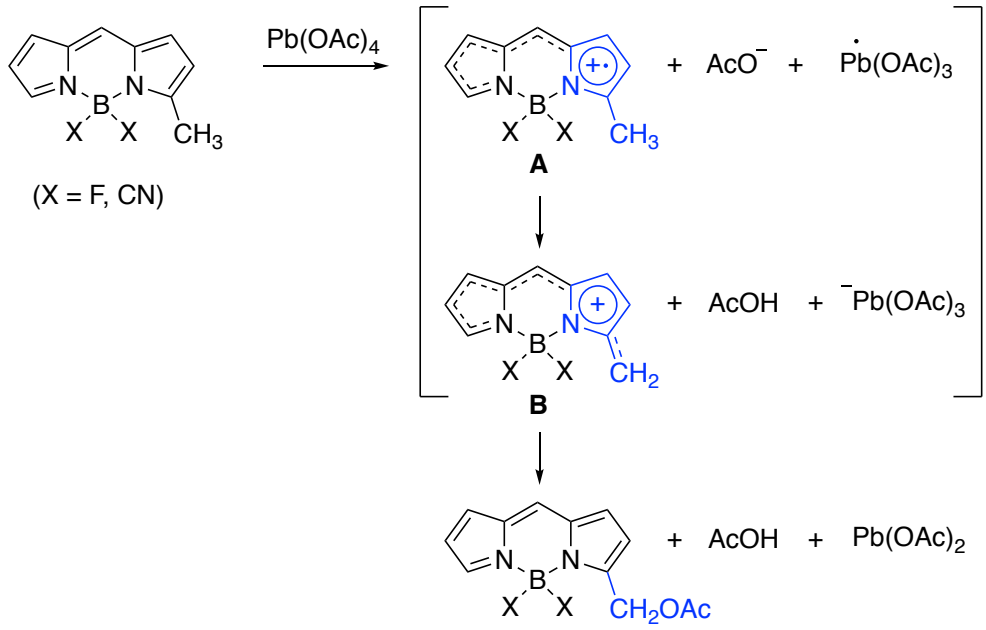
| | | | |
|---|---|---|---|
| C | -2.970182 | 0.736849 | -0.300398 |
| N | -2.571315 | -0.441142 | 0.342732 |
| B | -1.109540 | -0.785633 | 0.720535 |
| N | -0.220996 | 0.447151 | 0.405651 |
| C | -0.694855 | 1.622282 | -0.192463 |
| C | -2.034675 | 1.741731 | -0.597506 |
| C | 1.098110 | 0.595539 | 0.681799 |
| C | 1.511237 | 1.896182 | 0.298896 |
| C | 0.399186 | 2.540184 | -0.248815 |
| C | -4.382636 | 0.652678 | -0.508031 |
| C | -4.799213 | -0.578091 | 0.007250 |
| C | -3.654466 | -1.233364 | 0.513732 |
| C | -0.630522 | -2.049349 | -0.142751 |
| C | -1.026911 | -1.111015 | 2.287677 |
| C | 0.401928 | 3.961534 | -0.734615 |
| C | 2.874179 | 2.503395 | 0.503277 |
| C | -2.472395 | 2.955408 | -1.377294 |
| C | 1.894677 | -0.505093 | 1.340423 |
| C | 3.073066 | 3.098114 | 1.908883 |
| C | -5.307044 | 1.669541 | -1.112504 |
| C | -6.194957 | -1.140032 | 0.015448 |
| C | -3.587614 | -2.584927 | 1.142226 |
| C | -6.545639 | -1.941980 | -1.251223 |
| C | 3.321390 | -0.670314 | 0.893618 |
| C | 4.425286 | -0.610210 | 1.702882 |
| N | 5.568138 | -0.847864 | 0.961854 |
| C | 5.214616 | -1.085915 | -0.351186 |
| C | 3.800031 | -0.986179 | -0.430991 |
| N | -0.971327 | -1.311774 | 3.424221 |
| N | -0.308352 | -2.944875 | -0.798459 |
| H | -0.445169 | 4.531881 | -0.349020 |
| H | 1.309192 | 4.470641 | -0.410024 |
| H | 0.373177 | 4.026377 | -1.827869 |
| H | 3.037436 | 3.283911 | -0.244607 |
| H | 3.641044 | 1.750774 | 0.321290 |
| H | -1.654676 | 3.362603 | -1.963338 |
| H | -3.275452 | 2.708296 | -2.064957 |

| | | | |
|---|---|---|---|
| H | -2.835420 | 3.747417 | -0.712931 |
| H | 1.876256 | -0.337927 | 2.424311 |
| H | 1.373515 | -1.452907 | 1.190043 |
| H | 4.071791 | 3.533322 | 2.008006 |
| H | 2.963226 | 2.331289 | 2.680315 |
| H | 2.339338 | 3.881750 | 2.117883 |
| H | -6.345017 | 1.380684 | -0.944238 |
| H | -5.170589 | 2.664120 | -0.682729 |
| H | -5.173920 | 1.758036 | -2.196015 |
| H | -6.916864 | -0.326807 | 0.137197 |
| H | -6.326446 | -1.778428 | 0.893834 |
| H | -2.875715 | -3.230251 | 0.620280 |
| H | -3.263949 | -2.524099 | 2.185064 |
| H | -4.564650 | -3.065224 | 1.113136 |
| H | -7.566970 | -2.329719 | -1.197403 |
| H | -5.867846 | -2.789804 | -1.380619 |
| H | -6.466317 | -1.318859 | -2.146076 |
| H | 4.488708 | -0.411358 | 2.761945 |
| H | 6.501804 | -0.890725 | 1.333550 |
| C | 6.006366 | -1.383270 | -1.463201 |
| H | 7.085759 | -1.456694 | -1.385774 |
| C | 5.358728 | -1.587769 | -2.673575 |
| C | 3.956257 | -1.503769 | -2.774259 |
| C | 3.173283 | -1.206173 | -1.669040 |
| H | 5.942598 | -1.823763 | -3.556060 |
| H | 3.482454 | -1.684814 | -3.732203 |
| H | 2.093990 | -1.167956 | -1.757212 |

TOTAL ENERGY (Hartrees) = –1384.104609

## Plausible mechanistic proposal for the acetoxylation of 3/5-methyl-BODIPYs with $Pb(OAc)_4$

As explained in the main text, in the absence of conclusive mechanistic studies on the C–H acyloxylation reaction of alkyl-substituted aromatic and heteroaromatic compounds with $Pb(OAc)_4$,[8] the substituents effects observed in this work for the reaction of BODIPYs point to a rate determining step with partial development of positive charge. A plausible mechanistic proposal is the following. Single-electron oxidation of the BODIPY π-system by the $Pb^{+4}$ reagent leads to a delocalized radical-cation **A**, which evolves via deprotonation and reoxidation of the resulting radical to the corresponding carbocation **B** by the unstable $Pb^{+3}$-radical intermediate.[9] Subsequent nucleophilic attack by acetate anion affords the final acetoxylated product (Scheme 1). Methyl groups at C3/5 in the intermediate radical-cation **A** should have a considerably higher acidity than on the neutral molecule, thus facilitating their ionization and the ensuing second single-electron oxidation step.




Scheme 1. Plausive mechanism of the acetoxylation reaction of 3/5-methyl-BODIPYs with $Pb(OAc)_4$

**Table S1.** Photophysical properties of starting 3-acetoxymethyl-CN-BODIPY **9** and the resultant BODIPY-derivatives from the reaction with oxygen nucleophiles, in diluted solutions in different solvents. Absorption ($\lambda_{ab}$) and fluorescence ($\lambda_{fl}$) wavelengths (±1 nm), molar absorption coefficients ($\varepsilon_{max}$), fluorescence quantum yields ($\varphi$) and excited-state lifetimes ($\tau$) at room temperature.

| **Compound** | **Solvent** | $\boldsymbol{\lambda_{ab}}$ (nm) | $\boldsymbol{\varepsilon_{max}}$ ($10^4 M^{-1}cm^{-1}$) | $\boldsymbol{\lambda_{fl}}$ (nm) | $\boldsymbol{\phi}$ | $\boldsymbol{\tau}$ (ns) |
|---|---|---|---|---|---|---|
| **9** | AcOEt | 515.0 | 4.3 | 538.0 | 0.64 | 6.7 |
| | MeOH | 514.0 | 4.4 | 534.0 | 0.61 | 6.9 |
| | PBS | 538.0 | 1.1 | 538.0 | 0.01 | 3.0 (43%), 6.2(57%) |
| **15** | AcOEt | 516.0 | 5.8 | 536.0 | 0.85 | 6.6 |
| | MeOH | 516.0 | 5.5 | 537.0 | 0.79 | 7.0 |
| | PBS | 522.0 | 1.4 | 554.0 | 0.10 | 6.4 |
| **16** | AcOEt | 517.0 | 4.7 | 537.5 | 0.99 | 6.6 |
| | MeOH | 516.0 | 4.1 | 536.0 | 0.98 | 6.9 |
| | PBS | 523.0 | 1.3 | - | - | - |
| **17** | AcOEt | 523.0 | 2.9 | 535.0 | 0.39 | 2.8(48%),6.2(52%) |
| | MeOH | 522.0 | 2.8 | 538.0 | 0.28 | 6.8[b] |
| | PBS | 535.0 | 0.7 | 543.0 | 0.01 | 2.8 (31%), 6.6(69%) |
| **18** | AcOEt | 516.5 | 6.1 | 537.0 | 0.83 | 6.8 |
| | MeOH | 515.5 | 6.1 | 536.5 | 0.81 | 7.1 |
| | PBS | 513.5 | 3.4 | 534.5 | 0.78 | 7.1 |
| **19** | AcOEt | 516.0 | 5.6 | 535.0 | 0.98 | 6.6 |
| | MeOH | 515.0 | 4.9 | 535.0 | 0.99 | 6.9 |
| | PBS | 514.0 | 1.8 | 535.0 | 0.34 | 6.7 |
| **20** | AcOEt | 516.0 | 8.8 | 537.5 | 0.99 | 6.7 |
| | MeOH | 516.0 | 7.7 | 535.0 | 0.98 | 7.1 |
| | PBS | 522.0 | 3.1 | 537.0 | 0.01 | - |
| **21** | AcOEt | 516.0 | 5.0 | 538.0 | 0.89 | 6.5 |
| | MeOH | 516.0 | 5.0 | 534.0 | 0.79 | 6.8 |
| | PBS | 527.0 | 1.3 | 544.0 | 0.06 | 6.5[b] |
| **22** | AcOEt | 517.5 | 6.5 | 535.5 | 0.87 | 6.5 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | MeOH | 517.0 | 6.0 | 535.0 | 0.86 | 6.9 |
| | PBS | 521.5 | 1.8 | 546.5 | 0.01 | - |
| **23** | AcOEt | 516.0 | 6.4 | 535.5 | 0.99 | 6.6 |
| | MeOH | 516.0 | 5.8 | 536.5 | 0.93 | 7.0 |
| | PBS | 521.0 | 1.3 | 542.0 | 0.03 | 6.5[b] |
| **24** | AcOEt | 518.0 | 9.2 | 537.0 | 0.83 | 6.6 |
| | MeOH | 515.0 | 5.3 | 538.0 | 0.70 | 7.0 |
| | PBS | 521.0 | 1.4 | 536.0 | 0.02 | 0.5 (24%), 6.2(76%) |
| **25** | AcOEt | 516.5 | 6.8 | 535.0 | 0.83 | 6.7 |
| | MeOH | 515.5 | 6.0 | 535.5 | 0.83 | 7.0 |
| | PBS | 517.5 | 0.9 | 536.5 | 0.15 | 6.7 |
| **26** | AcOEt | 516.0 | 7.6 | 536.0 | 0.85 | 6.8 |
| | MeOH | 515.0 | 7.2 | 536.5 | 0.83 | 7.2 |
| | PBS | 525.0 | 3.0 | 547.0 | 0.01 | - |
| **27** | AcOEt | 516.0 | 4.8 | 534.5 | 0.87 | 6.7 |
| | MeOH | 515.0 | 4.6 | 535.5 | 0.82 | 7.0 |
| | PBS | 525.0 | 1.9 | 544.0 | 0.01 | - |
| **28** | AcOEt | 515.5 | 3.3 | 534.0 | 0.84 | 6.6 |
| | MeOH | 515.0 | 3.1 | 535.0 | 0.81 | 6.7 |
| | PBS | 514.0 | 1.9 | 534.0 | 0.67 | 6.9 |
| **29** | AcOEt | 515.5 | 4.5 | 534.5 | 0.85 | 6.6 |
| | MeOH | 514.5 | 4.7 | 534.0 | 0.82 | 6.9 |
| | PBS | 514.0 | 1.9 | 532.5 | 0.67 | 6.9 |
| **30** | AcOEt | 516.0 | 5.9 | 535.0 | 0.83 | 6.6 |
| | MeOH | 515.5 | 5.7 | 535.0 | 0.84 | 7.0 |
| | PBS | 515.5 | 1.8 | 534.5 | 0.26 | 6.7 |
| **31** | AcOEt | 517.0 | 6.5 | 535.0 | 0.84 | 6.5 |
| | MeOH | 516.0 | 5.6 | 536.0 | 0.78 | 6.9 |
| | PBS | 524.0 | 1.4 | - | - | - |
| **32** | AcOEt | 516.0 | 6.3 | 536.5 | 0.90 | 6.7 |
| | MeOH | 516.0 | 5.5 | 535.0 | 0.76 | 6.2 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | PBS | 513.0 | 1.8 | 534.0 | 0.71 | 6.8 |
| **34** | AcOEt | 516.0 | 7.5 | 535.5 | 0.04 | 0.1[b] |
| | MeOH | 516.0 | 3.8 | 533.0 | 0.05 | 0.1[b] |
| | PBS | 522.0 | 1.8 | 539.5 | 0.01 | - |
| **35** | AcOEt | 517.0 | 3.3 | 534.5 | 0.94 | 6.4 |
| | MeOH | 516.0 | 2.8 | 535.0 | 0.76 | 6.8[b] |
| | PBS | 520.0 | 0.6 | 536.5 | 0.18 | 6.6[b] |
| **36** | AcOEt | 515.0 | 4.5 | 536.0 | 0.88 | 6.5 |
| | MeOH | 514.0 | 3.9 | 534.0 | 0.93 | 6.9 |
| | PBS | 521.0 | 1.4 | 535.0 | 0.01 | - |
| **37** | AcOEt | 515.0 | 3.8 | 539.0 | 0.75 | 6.3 |
| | MeOH | 514.0 | 3.5 | 533.5 | 0.68 | 6.8 |
| | PBS[a] | - | - | - | - | - |
| **38** | AcOEt | 514.0 | 3.1 | 533.5 | 0.80 | 6.5 |
| | MeOH | 513.0 | 1.7 | 534.0 | 0.74 | 6.8 |
| | PBS | 514.0 | 1.6 | 534.0 | 0.17 | 6.8 |
| **39** | AcOEt | 538.0 | 2.0 | 557.0 | 0.35 | 2.2 (43%), 5.1(57%) |
| | MeOH | 537.0 | 2.9 | 550.0 | 0.06 | 0.1 (74%), 0.6(26%) |
| | PBS | 541.0 | 0.3 | 534.0 | 0.01 | - |

[a] Not soluble in PBS. [b] Contribution ≥ 90%

**Table S2.** Photophysical properties of the new BODIPYs from the reaction with sulfur (**41**-**45**), nitrogen (**46**, **49)**, halogen (**50**), and phosphorous (**51**) nucleophiles, in diluted solutions different solvents. Absorption ($\lambda_{ab}$) and fluorescence ($\lambda_{fl}$) wavelengths (±1 nm), molar absorption coefficients ($\varepsilon_{max}$), fluorescence quantum yields ($\varphi$) and excited-state lifetimes ($\tau$) at room temperature.

| **Compound** | **Solvent** | $\lambda_{ab}$ (nm) | $\varepsilon$ ($10^4$ $M^{-1}$ $cm^{-1}$) | $\lambda_{fl}$ (nm) | $\phi$ | $\tau$ (ns) |
|---|---|---|---|---|---|---|
| **41** | AcOEt | 522.0 | 6.9 | 542.0 | 0.79 | 6.3 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | MeOH | 522.0 | 6.3 | 540.5 | 0.94 | 6.6 |
| | PBS | 520.0 | 1.9 | 535.0 | 0.04 | 6.7[a] |
| **42** | AcOEt | 521.0 | 6.8 | 541.5 | 0.94 | 6.4 |
| | MeOH | 520.0 | 6.7 | 542.0 | 0.82 | 6.7 |
| | PBS | 520.0 | 1.6 | 536.5 | 0.03 | 6.6[a] |
| **43** | AcOEt | 517.0 | 2.9 | 539.0 | 0.68 | 3.5 (35%), 6.2 (65%) |
| | MeOH | 516.0 | 2.6 | 538.0 | 0.51 | 1.1 (31%), 6.6 (69%) |
| | PBS | 515.0 | 0.8 | 531.0 | 0.34 | 6.7 |
| **44** | AcOEt | 518.0 | 3.5 | 539.0 | 0.86 | 6.2[a] |
| | MeOH | 516.0 | 2.5 | 535.5 | 0.53 | 0.9 (17%), 6.6 (83%) |
| | PBS | 516.0 | 0.6 | - | - | - |
| **45** | AcOEt | 522.0 | 4.0 | 539.5 | 0.86 | 6.2 |
| | MeOH | 522.0 | 4.3 | 540.0 | 0.77 | 6.4 |
| | PBS | 520.0 | 1.3 | 540.5 | 0.44 | 6.3 |
| **46** | AcOEt | 517.0 | 5.0 | 535.0 | 0.95 | 6.6 |
| | MeOH | 516.0 | 4.7 | 536.0 | 0.88 | 6.9 |
| | PBS | 521.0 | 1.6 | 539.0 | - | - |
| **47** | AcOEt | 517.5 | 5.3 | 537.0 | 0.84 | 6.8 |
| | MeOH | 516.5 | 5.2 | 537.5 | 0.84 | 7.2 |
| | PBS | 528.0 | 0.6 | - | - | - |
| **48** | AcOEt | 523.0 | 5.5 | 544.5 | 0.84 | 6.9 |
| | MeOH | 521.5 | 5.2 | 544.5 | 0.84 | 7.3 |
| | PBS | 530.5 | 0.7 | - | - | - |
| **49** | AcOEt | 512.0 | 4.0 | 536.0 | 0.33 | 2.4[a] |
| | MeOH | 509.0 | 3.5 | 534.0 | 0.15 | 0.06 (83%), 6.6(17%) |
| | PBS | 510.0 | 1.4 | 530.0 | 0.03 | 1.0[a] |
| **50** | AcOEt | 517.0 | 4.8 | 538.0 | 0.78 | 6.7 |
| | MeOH | 515.0 | 5.1 | 534.0 | 0.73 | 6.8 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | PBS | 516.0 | 0.8 | 534.0 | 0.41 | 6.7 |
| **51** | AcOEt | 519.5 | 6.1 | 538.0 | 0.82 | 6.3 |
| | MeOH | 518.0 | 5.8 | 537.0 | 0.82 | 6.5 |
| | PBS | 516.0 | 3.3 | 537.0 | 0.28 | 5.7 |

[a] Contribution ≥ 90%.

**Table S3.** Photophysical properties of the new BODIPYs from the reaction with carbon nucleophiles, in diluted solutions different solvents. Absorption ($\lambda_{ab}$) and fluorescence ($\lambda_{fl}$) wavelengths (±1 nm), molar absorption coefficients ($\varepsilon_{max}$), fluorescence quantum yields (φ) and excited-state lifetimes (τ) at room temperature.

| **Compound** | **Solvent** | $\lambda_{ab}$ (nm) | $\varepsilon$ ($10^4 M^{-1}$ $cm^{-1}$) | $\lambda_{fl}$ (nm) | $\phi$ | $\tau$ (ns) |
|---|---|---|---|---|---|---|
| **52** | AcOEt | 517.5 | 6.6 | 536.0 | 0.83 | 6.4 |
| | MeOH | 517.5 | 6.5 | 535.5 | 0.84 | 6.8 |
| | PBS | 521.0 | 0.3 | 534.5 | 0.01 | - |
| **53** | AcOEt | 518.0 | 7.6 | 536.0 | 0.89 | 6.4 |
| | MeOH | 518.0 | 7.4 | 536.0 | 0.91 | 6.7 |
| | PBS | 524.0 | 1.5 | 546.0 | 0.06 | 6.3 |
| **54**[a] | AcOEt | 511.0 | 5.3 | 532.0 | 0.84 | 6.4 |
| | MeOH | 510.0 | 4.9 | 529.0 | 0.79 | 6.5 |
| | PBS | - | - | - | - | - |
| **55** | AcOEt | 518.0 | 6.9 | 538.0 | 0.84 | 6.5 |
| | MeOH | 517.0 | 6.8 | 538.0 | 0.83 | 6.8 |
| | PBS | - | - | - | - | - |
| **56** | AcOEt | 520.0 | 7.4 | 538.0 | 0.87 | 6.1 |
| | MeOH | 520.0 | 7.3 | 538.0 | 0.87 | 6.4 |
| | PBS | 532.0 | 1.3 | 540.0 | 0.01 | 1.3 (42%), 5.0 (58%) |

| | | | | | | |
|---|---|---|---|---|---|---|
| **57** | AcOEt | 520.5 | 4.5 | 538.0 | 0.83 | 6.2 |
| | MeOH | 520.0 | 4.3 | 538.0 | 0.67 | 5.4 |
| | PBS | 528.5 | 1.4 | 542.0 | - | - |
| **59** | AcOEt | 522.0 | 5.1 | 537.0 | 0.02 | 5.9 |
| | MeOH | 521.0 | 4.9 | 533.0 | 0.02 | 6.2 |
| | PBS | 527.0 | 1.8 | 529.5 | - | - |
| **60** | AcOEt | 521.0 | 3.6 | 537.0 | 0.16 | 0.4 (37%), 5.2 (63%) |
| | MeOH | 520.0 | 3.4 | 536.0 | 0.19 | 1.8 (27%), 5.6 (73%) |
| | PBS | 520.0 | 1.0 | 535.0[b] | 0.12 | 1.8 (37%), 5.6 (63%) |
| **61** | AcOEt | 523.0 | 7.3 | 549.0 | 0.01 | - |
| | MeOH | 522.0 | 7.2 | 540.0 | 0.01 | - |
| | PBS | 532.0 | 1.7 | 538.0 | 0.01 | - |
| **62** | AcOEt | 533.0 | 14.53 | 547.7 | 0.69 | 3.9 |
| | MeOH | 532.0 | 12.9 | 545.5 | 0.05 | 0.06 (89%), 0.3(8%),6.2(3%) |
| | PBS | 536.6 | 3.8 | - | - | - |
| **63** | AcOEt | 549.5 | 18.8 | 562.0 | 0.67 | 3.0 |
| | MeOH | 549.0 | 18.1 | 560.5 | 0.03 | 0.1 (93%), 0.7 (6%),5.8(1%) |
| | PBS | 552.5 | 5.2 | - | - | - |

**Table S4.** Photophysical properties of the homo- and heterobifunctional BODIPYs. Absorption ($\lambda_{ab}$) and fluorescence ($\lambda_{fl}$) wavelengths (±1 nm), molar absorption coefficients ($\varepsilon_{max}$), fluorescence quantum yields ($\varphi$) and excited-state lifetimes ($\tau$) at room temperature.

| **Comp.** | **Disolv.** | $\lambda_{ab}$ (nm) | $\varepsilon$ ($10^4 M^{-1}cm^{-1}$) | $\lambda_{fl}$ (nm) | $\phi$ | $\tau$ (ns) |
|---|---|---|---|---|---|---|
| **12** | AcOEt | 525.0 | 4.8 | 539.0 | 0.62 | 4.75 |
| | MeOH | 550.0 | 3.9 | 540.0 | 0.57 | 5.12 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | PBS | 554.0 | 1.5 | 541.0 | 0.11 | 1.0 (7%), 4.2 (93%) |
| **64** | AcOEt | 527.0 | 5.8 | 541.0 | 0.79 | 5.9 |
| | MeOH | 526.0 | 7.8 | 541.0 | 0.61 | 5.5 |
| | PBS | 531.0 | 4.4 | 541.0 | 0.45 | 5.0 |
| **66** | AcOEt | 527.0 | 8.1 | 539.0 | 0.93 | 5.9 |
| | MeOH | 527.0 | 7.8 | 540.0 | 0.88 | 6.2 |
| | PBS | 531.0 | 0.7 | 540.0 | 0.05 | 0.02 (99%) |

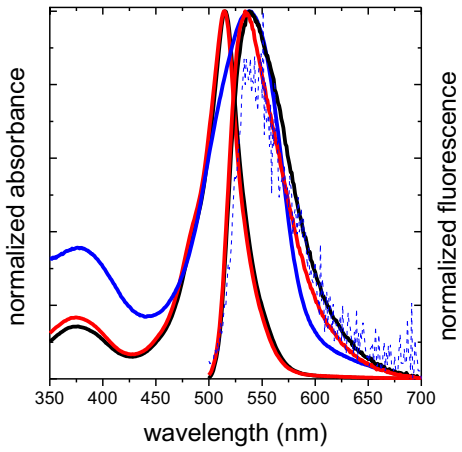



**Figure S1.** Normalized fluorescence absorption and emission spectrum of starting acetoximethyl-BODIPY **9** in different solvents: AcOEt (black), MeOH (red) and PBS (blue).

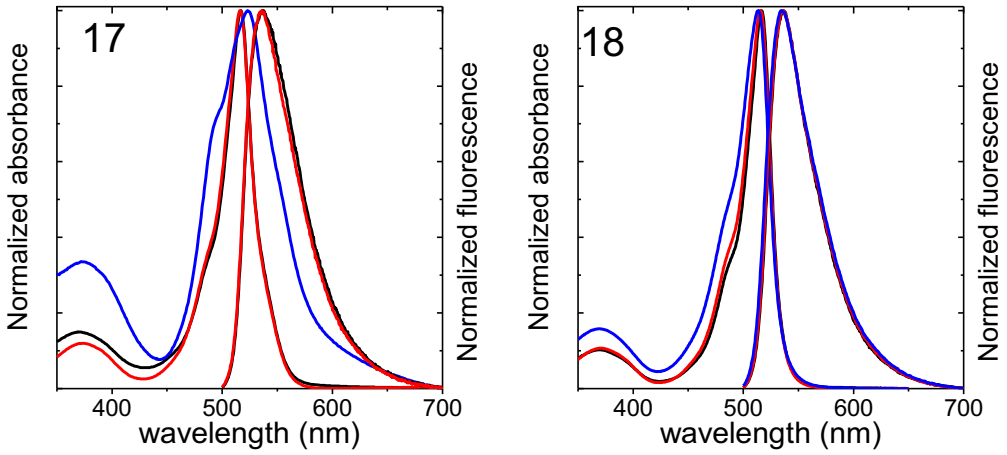



**Figure S2.** Normalized fluorescence absorption and emission spectra for compounds derived from O-nucleophiles with a lipophilic chain of C16 (**17**) and octaethylene glycol (**18**) in different solvents: AcOEt (black), MeOH (red) and PBS (blue).

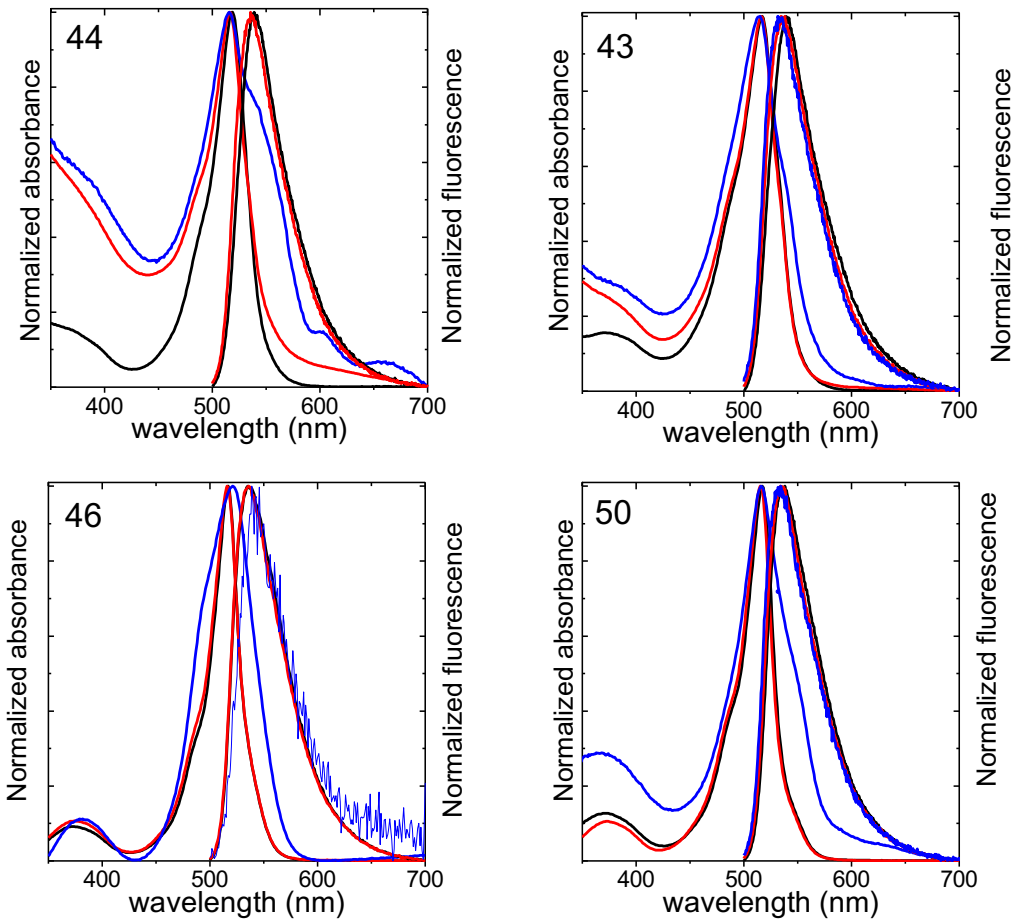



**Figure S3.** Normalized fluorescence absorption and emission spectra of the S-derivatives **44** (pentafluoreophenyl substituent) and **43** (*p*-tolyl substituent), the N-derivative with azide substituent **46** and the chlorine-derivative **50** in different solvents: AcOEt (black), MeOH (red), and PBS (blue).

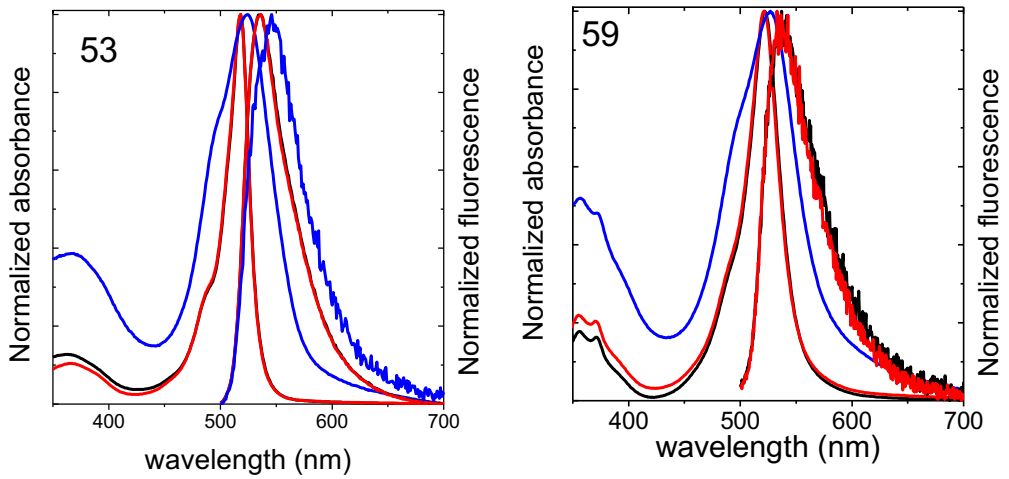



**Figure S4.** Normalized fluorescence absorption and emission spectra of the C-nucleophilic derivatives **53** (allyl substituent) and **59** (guaiazulene substituent) in different solvents: AcOEt (black), MeOH (red) and PBS (blue).

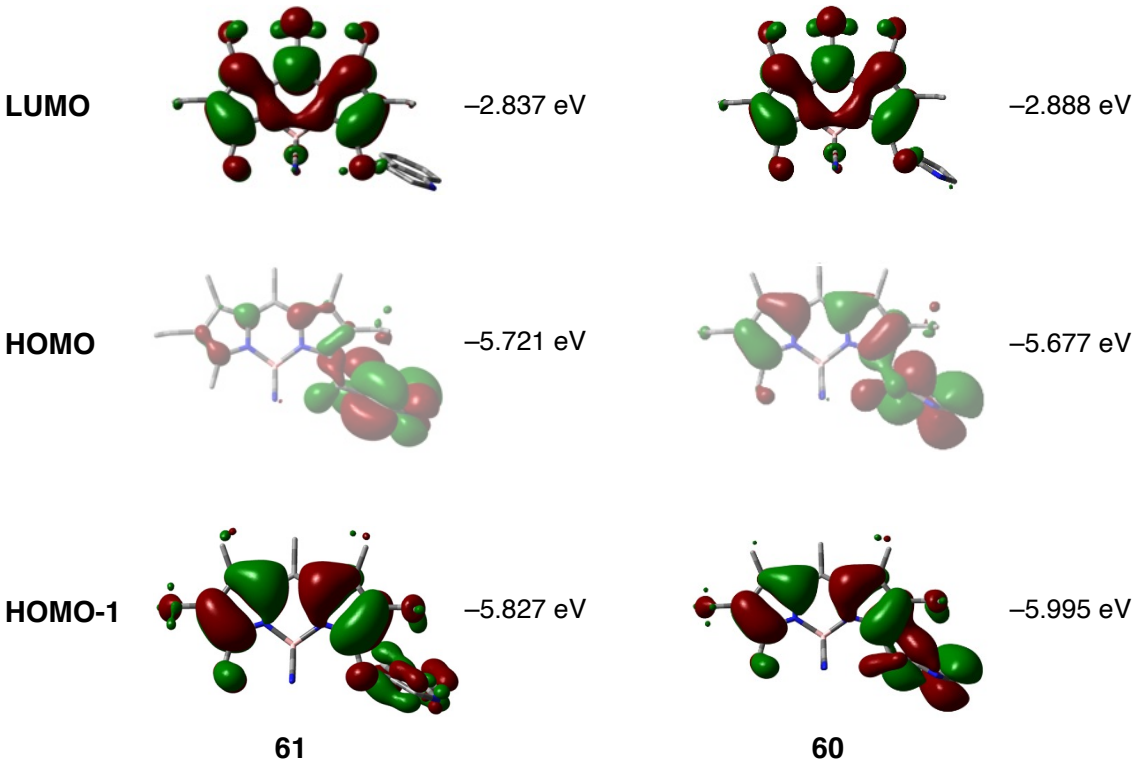



**Figure S5.** Frontier orbitals of **60** and **61** computed at B3LYP/6-311+G* level. The simulation of the absorption probabilities indicates that the first transition involves HOMO-1/LUMO molecular orbitals.

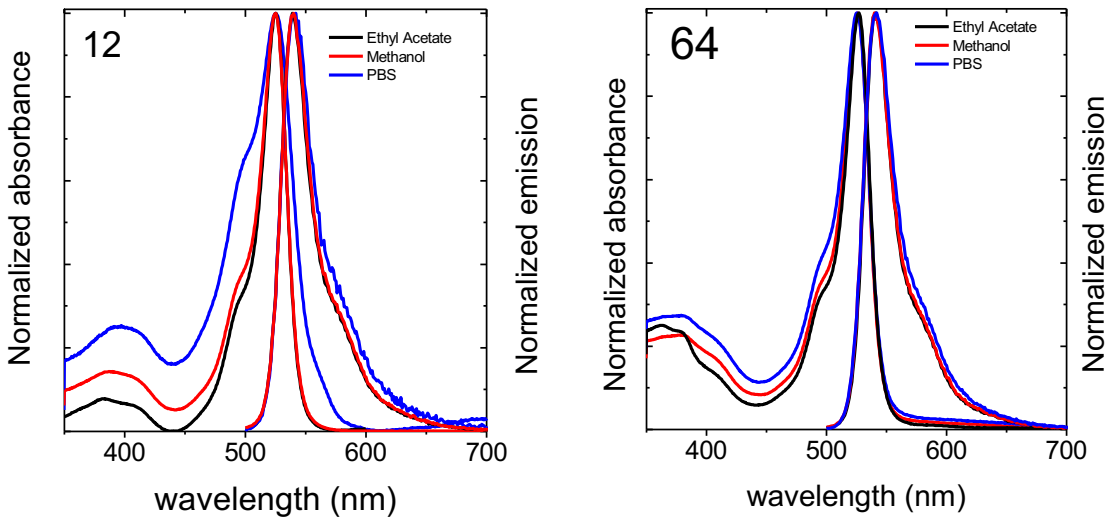



**Figure S6.** Normalized fluorescence absorption and emission spectra of homo-disubstituted compounds **12** (with acetate groups) and **64** (with *O*-methyltetraethylene groups) in different solvents: AcOEt (black), MeOH (red) and PBS (blue).

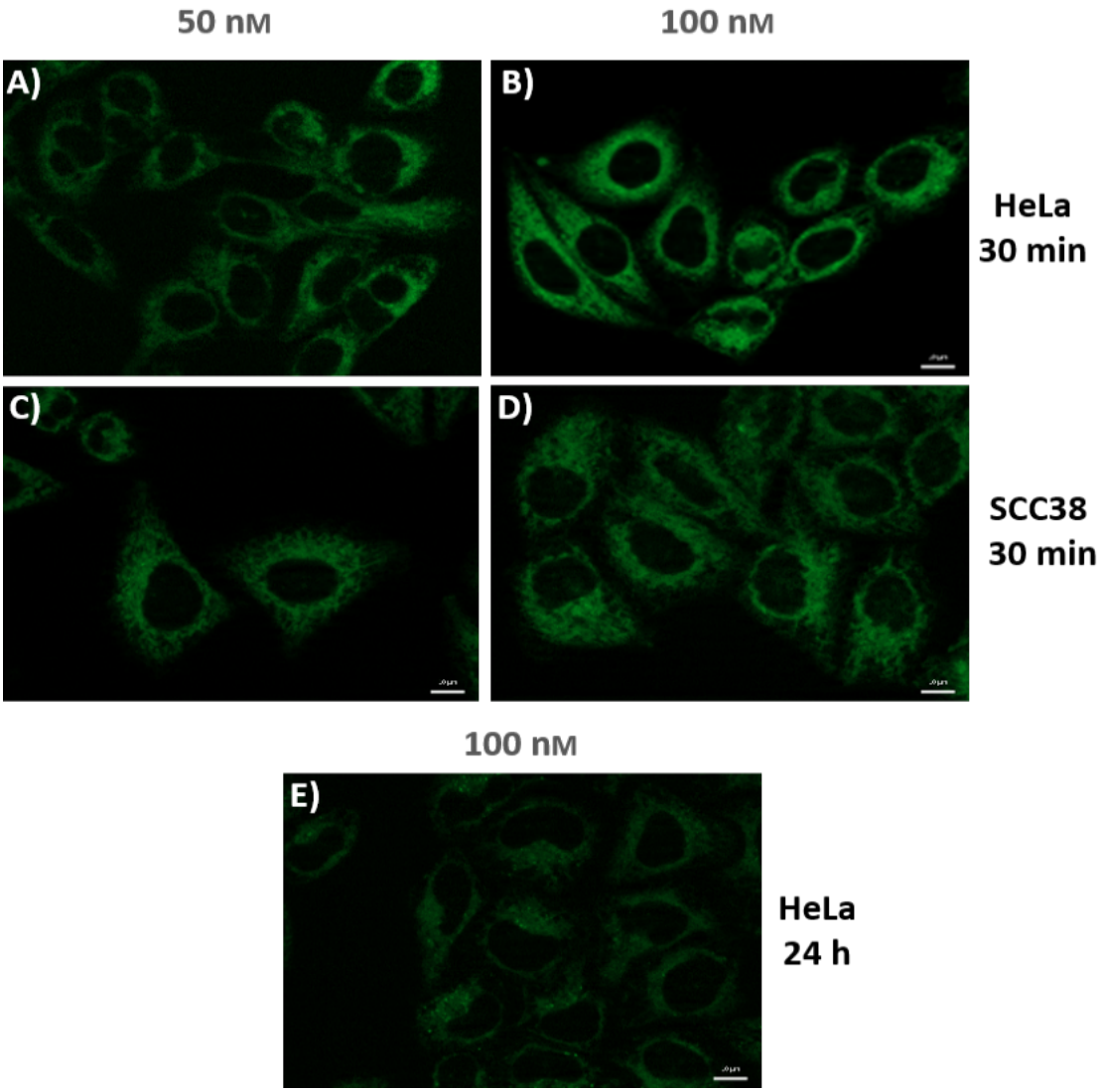



**Figure S7.** Representative fluorescence microscopy images of Hela (A/B) and SCC38 (C/D) cells stained with 50 nM (A/C) or 100 nM (B, D, E) of dye **33** after 30 min (A-D) or 24 h (E) incubation. As shown, only partial loss of fluorescent emission was observed after 24 h, while retaining the same initial subcellular specificity. Scale bars: 10 μm.

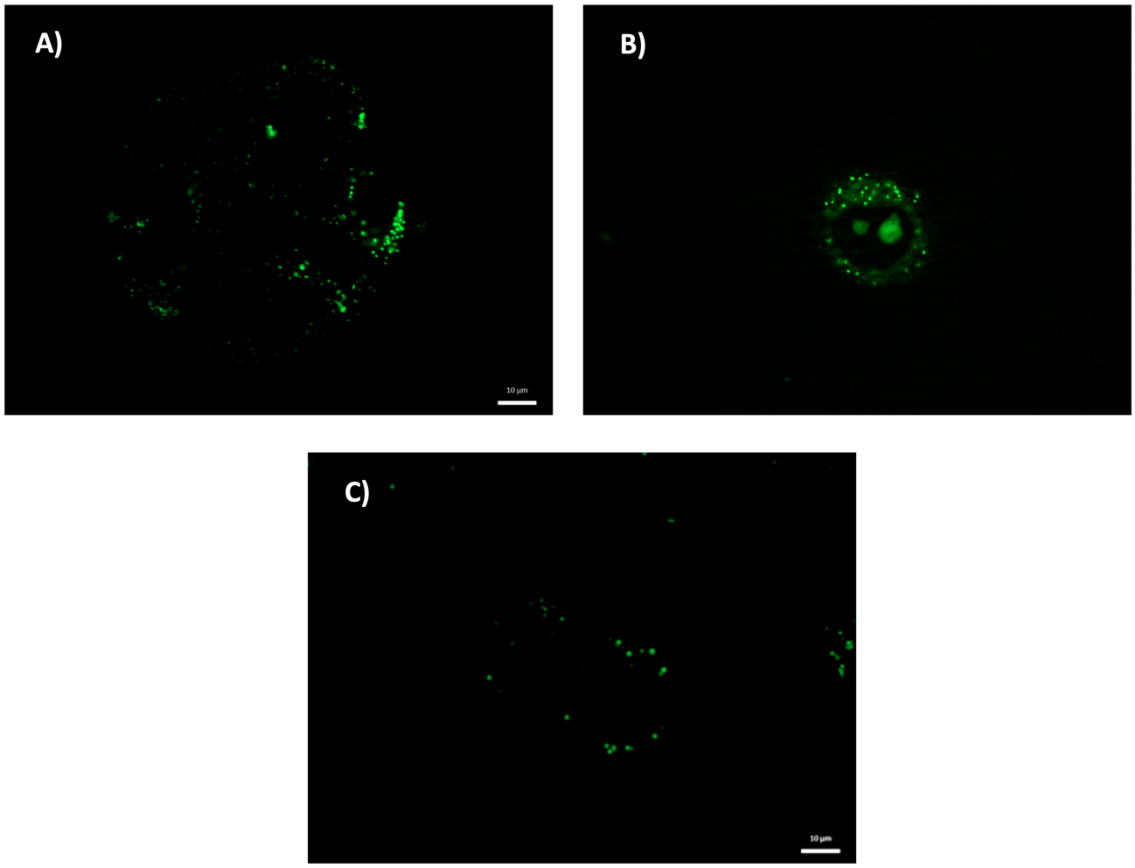



**Figure S8.** Representative examples of compounds that presumably exhibit specific subcellular staining. HeLa cells were stained with 100 nM of: A) **26** (serine); B) **22** (norbornene); and C) **52** (prepared from diethylzinc). Scale bars: 10 μm.

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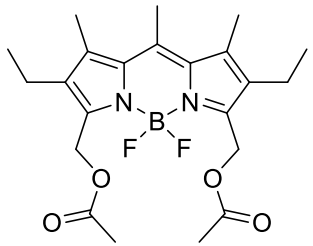
# Copies of $^{1}H$ and $^{13}C$ NMR of the new compounds

**Compound 1**

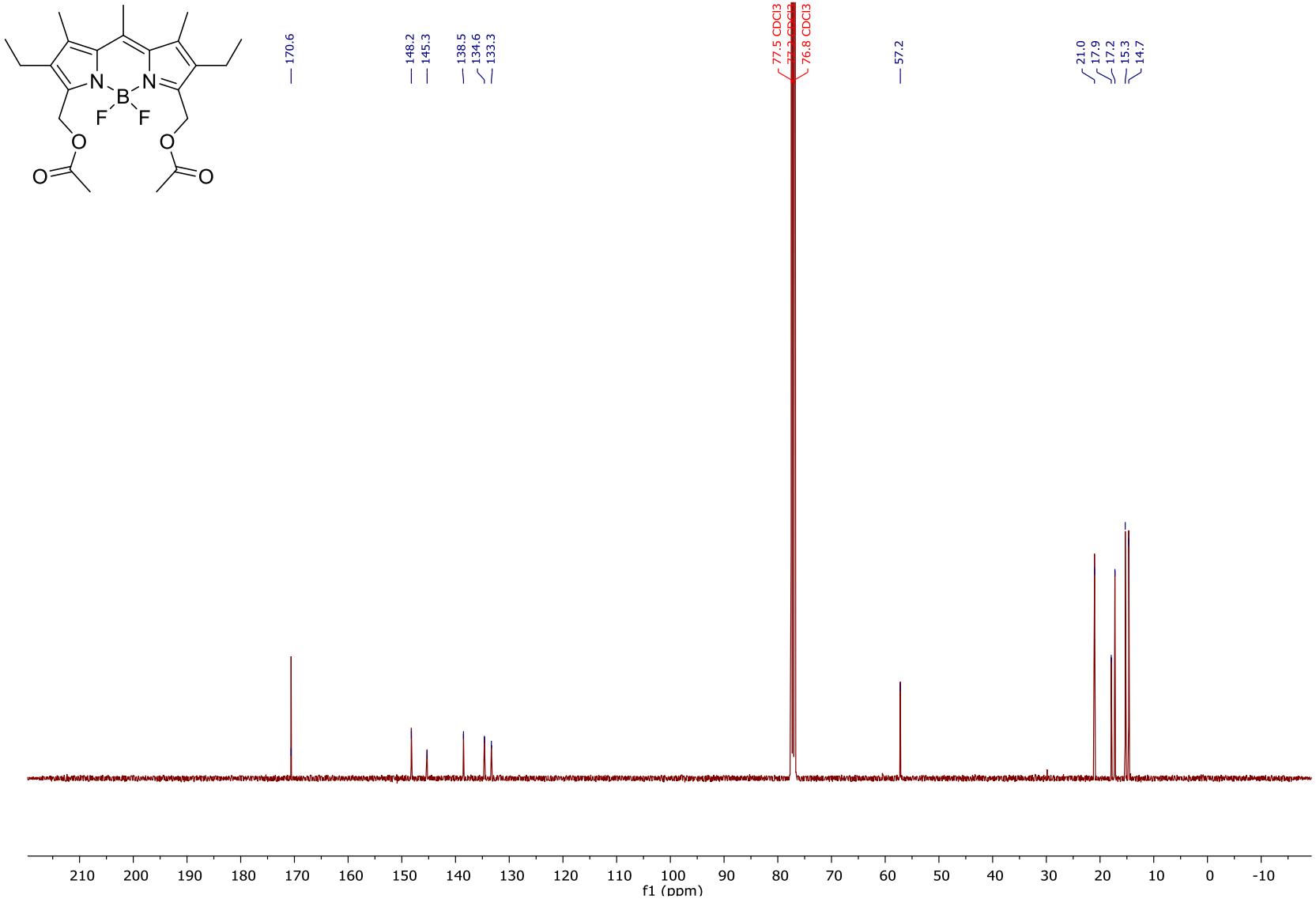






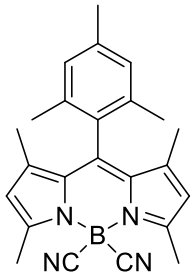
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **1**

**Compound 1**




**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **1**

**Compound 6**

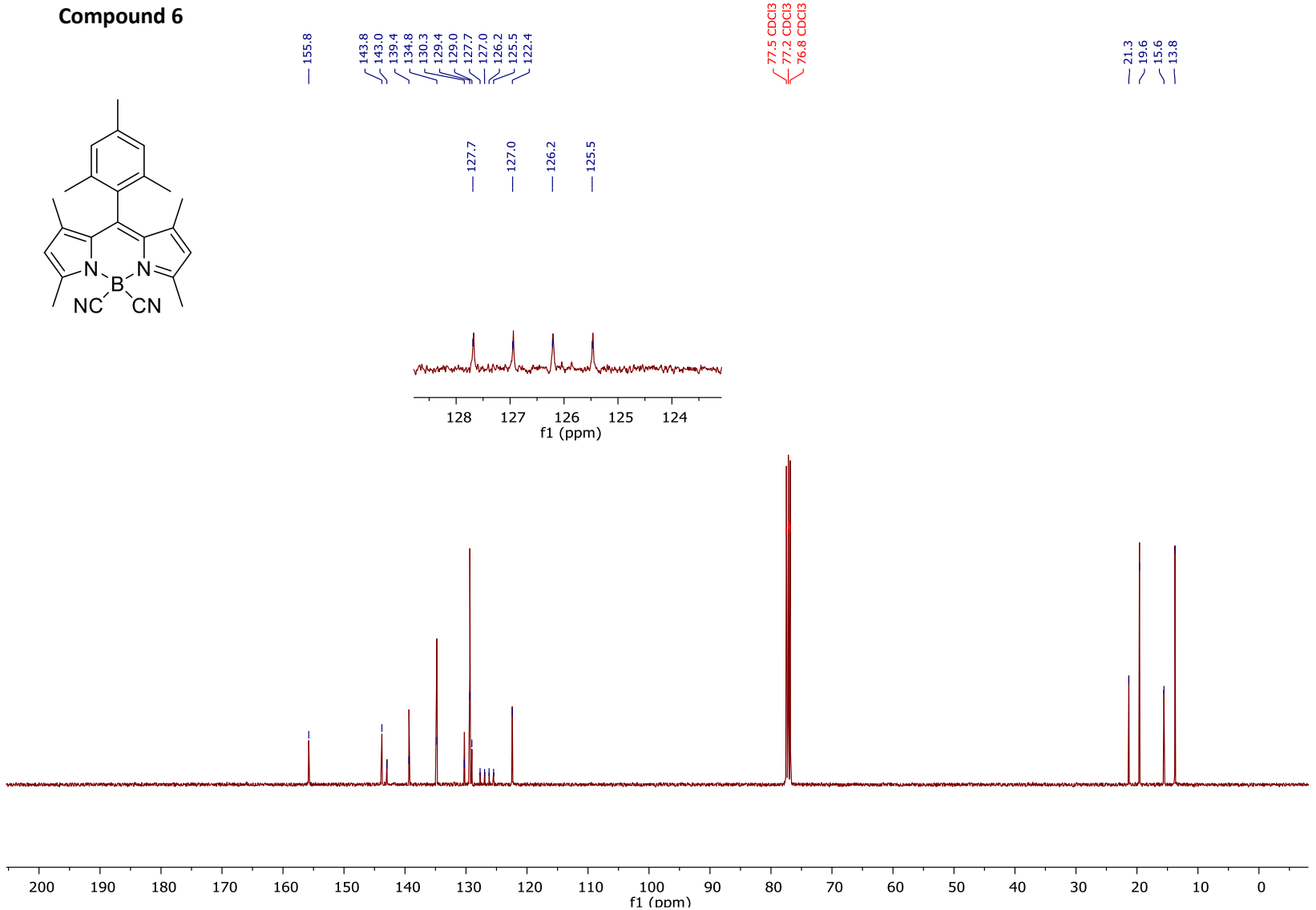






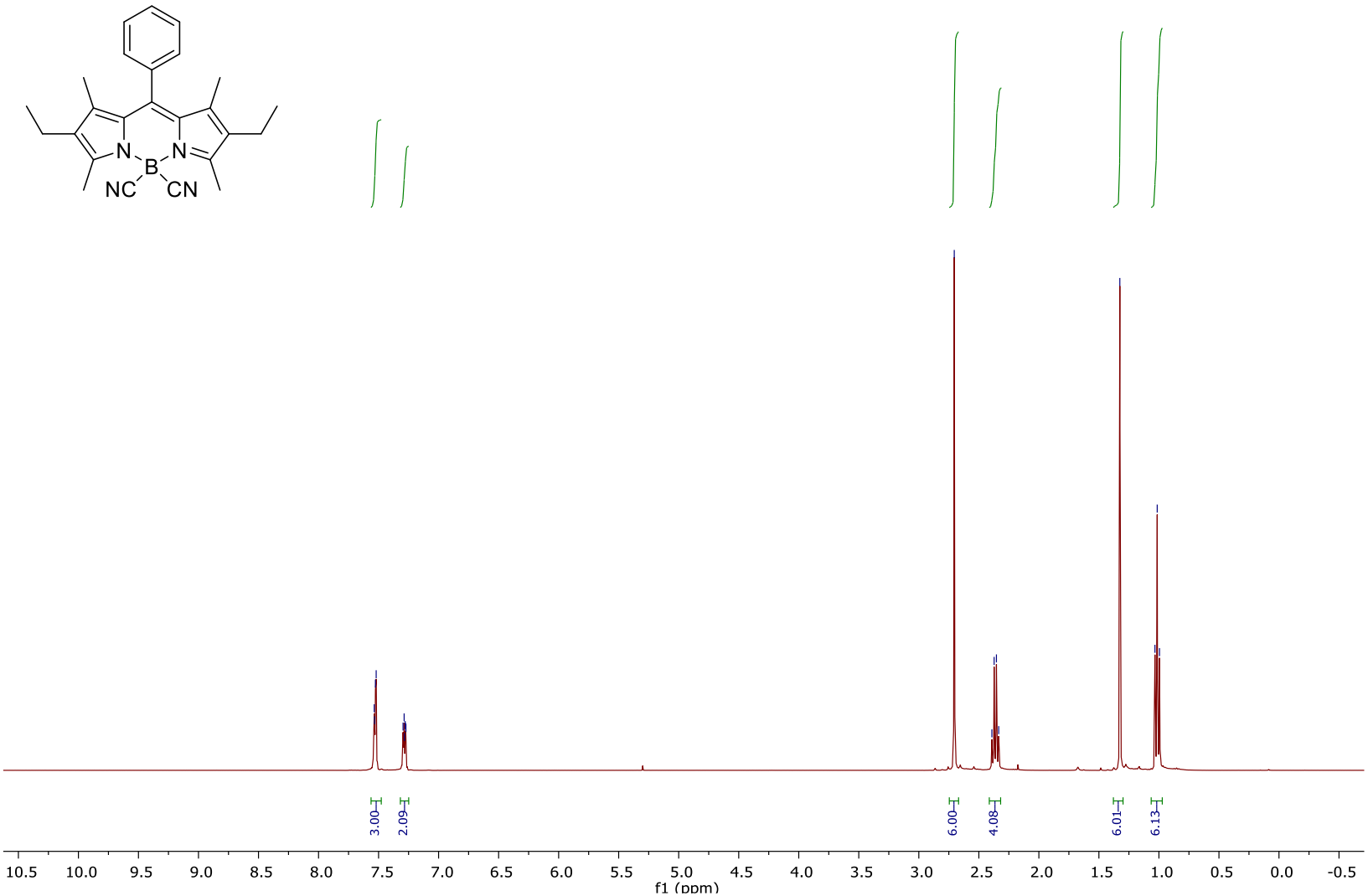
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **6**

**Compound 6**



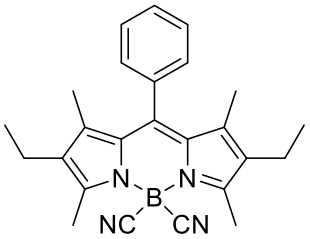

**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **6**

**Compound 7**




**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **7**

**Compound 7**

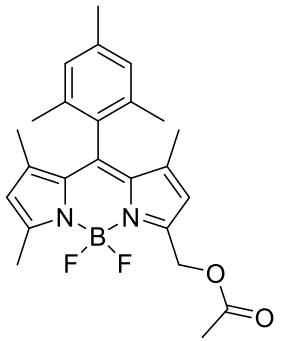






**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **7**

**Compound 8**

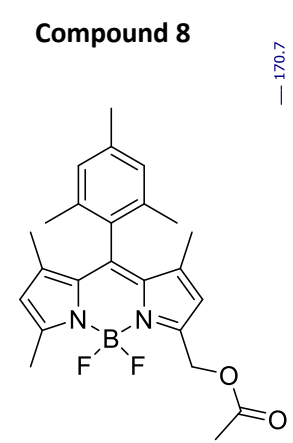






**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **8**

**Compound 8**

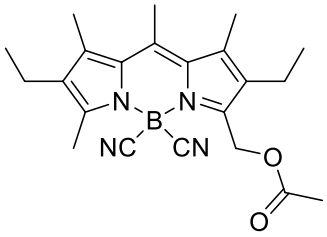






**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **8**

**Compound 9**

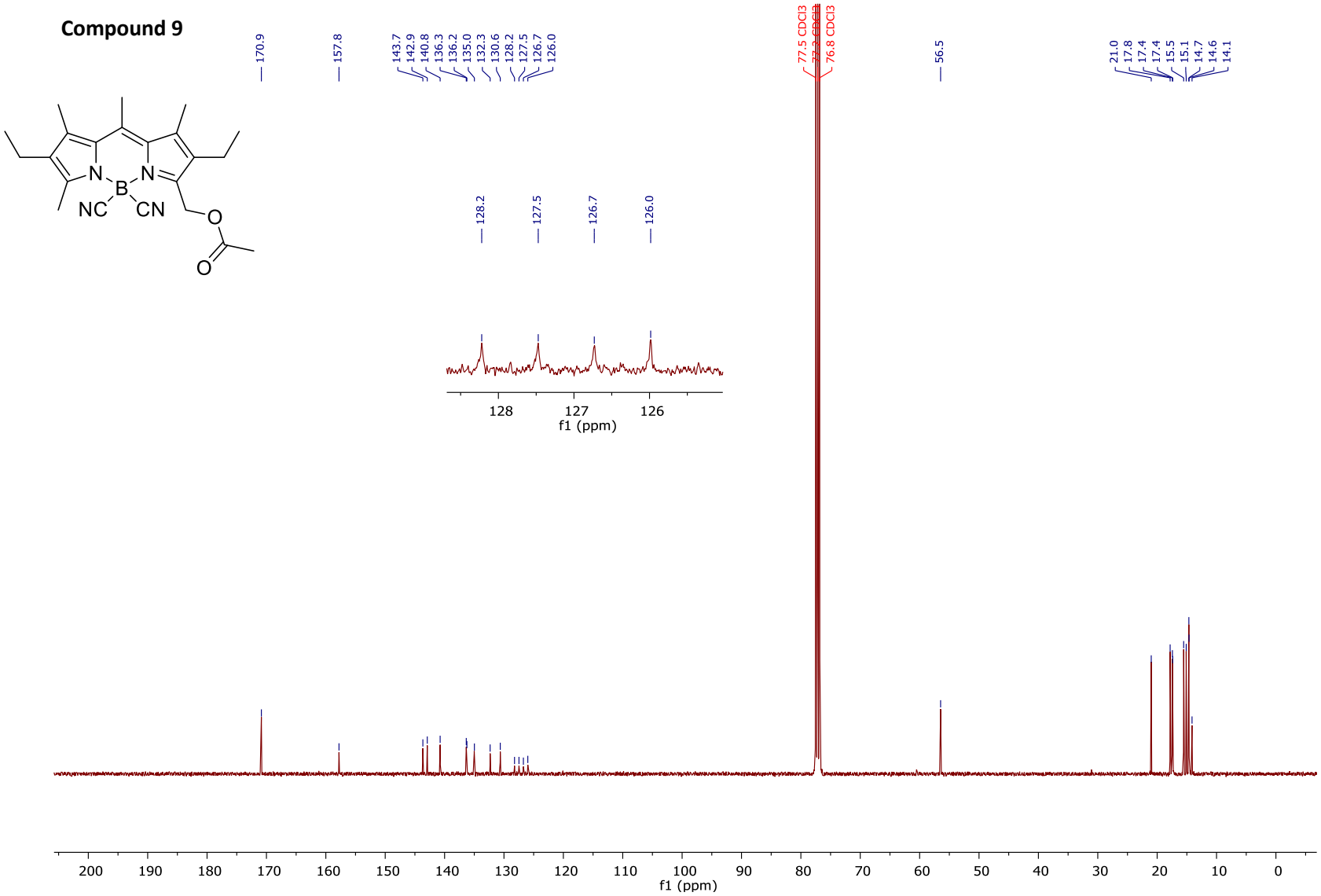






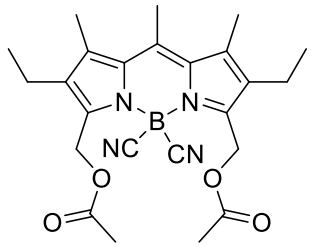
**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **9**

**Compound 9**




**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **9**

**Compound 10**

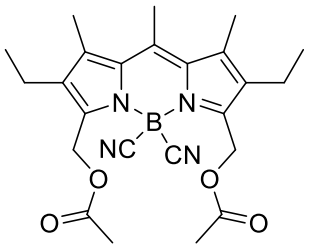






**$^{1}$H NMR** (500 MHz, $CDCl_3$) spectrum of compound **10**

**Compound 10**

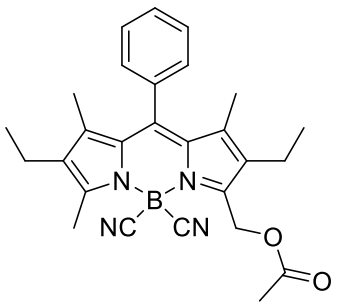






**$^{13}$C NMR** (125 MHz, $CDCl_3$) spectrum of compound **10**

**Compound 11**

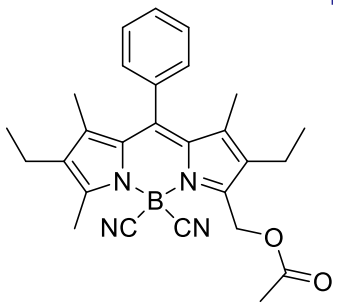






**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **11**

**Compound 11**

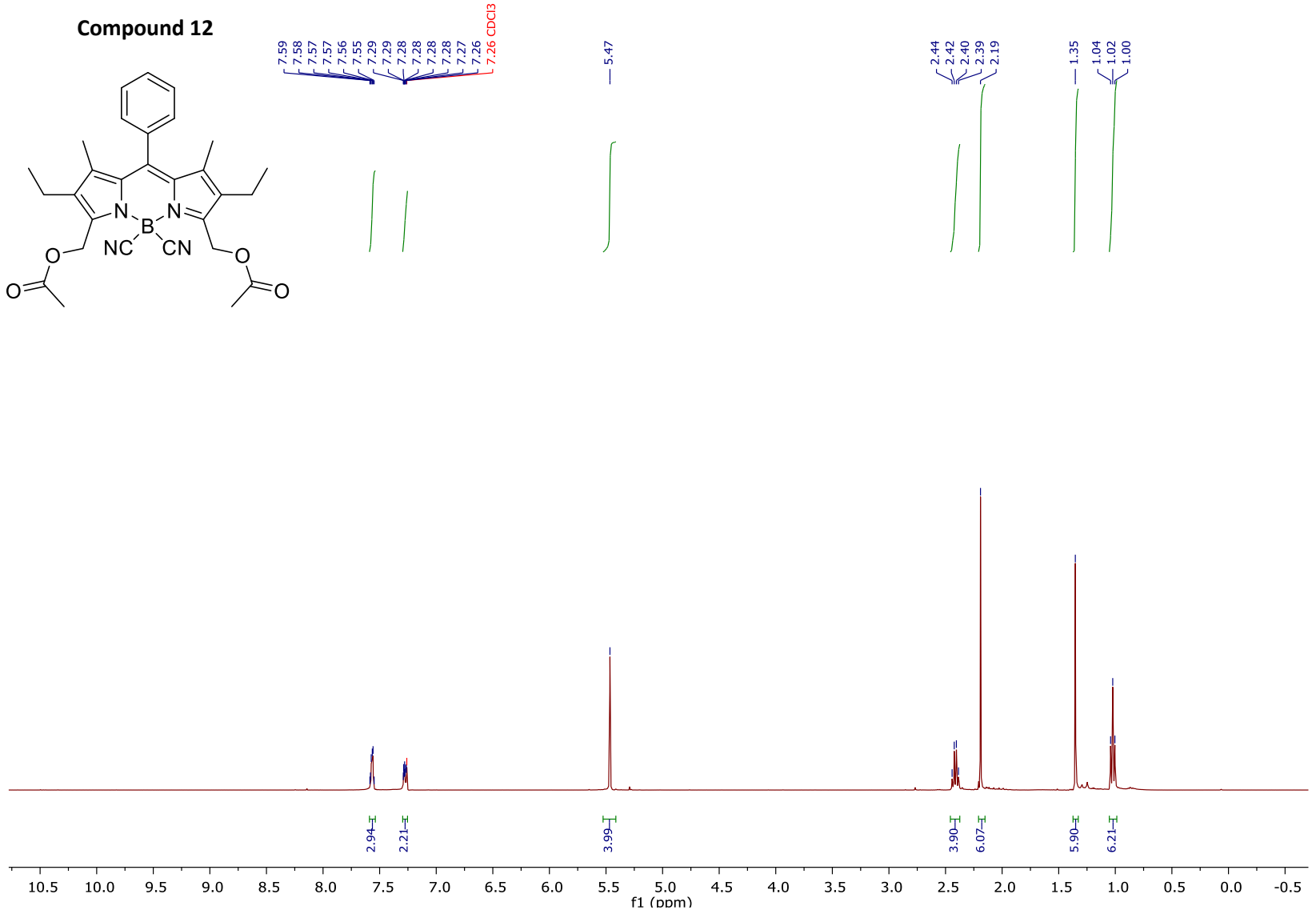






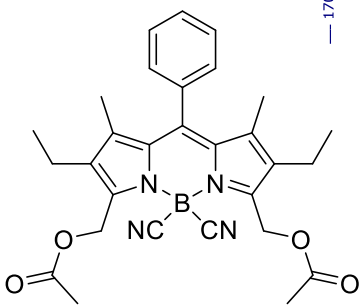
**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **11**

**Compound 12**




**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **12**

**Compound 12**

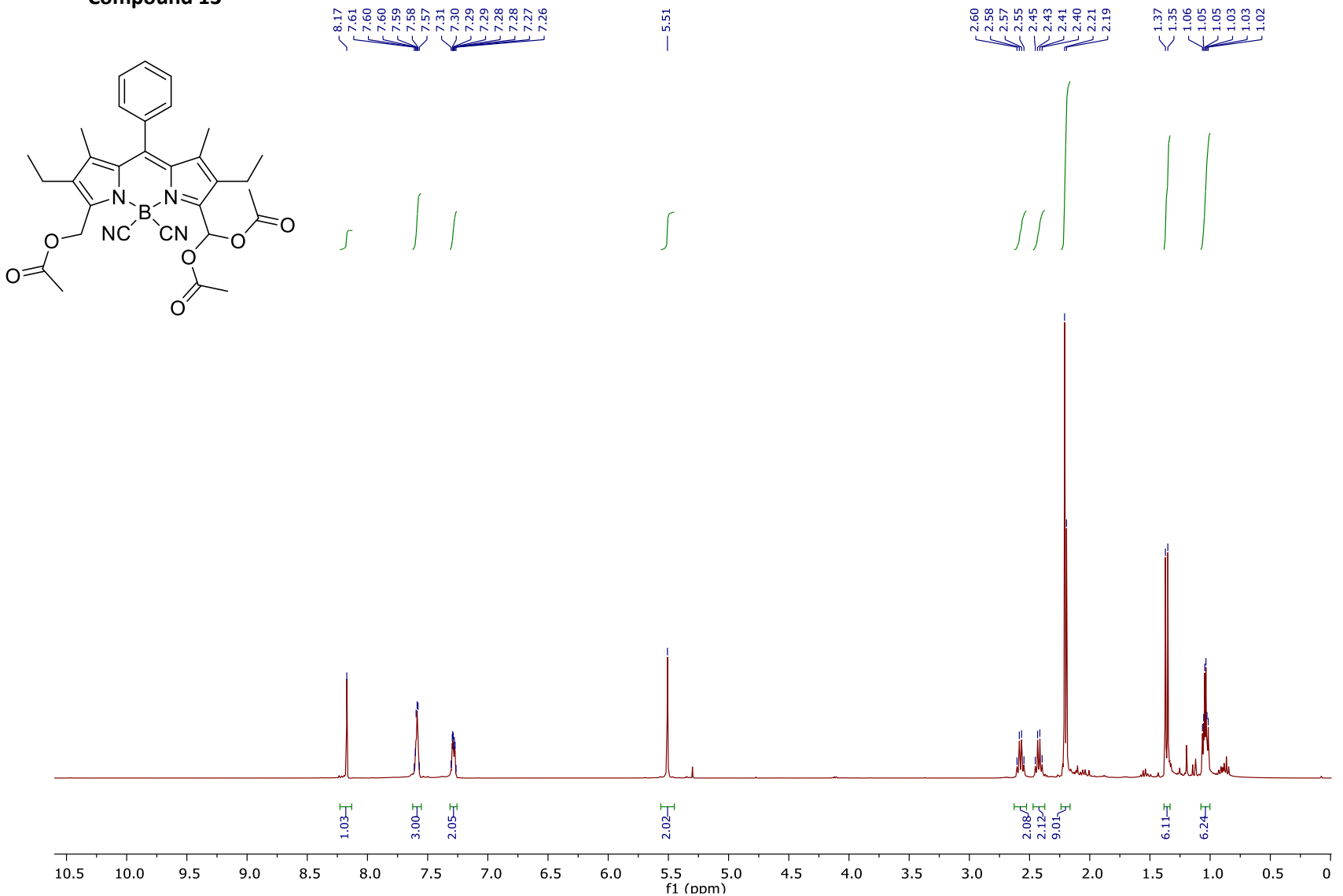






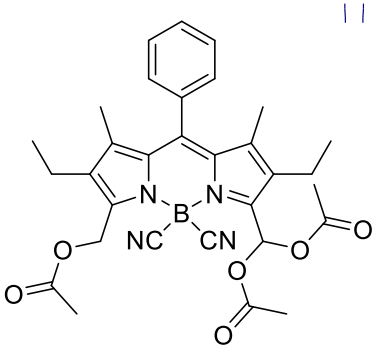
**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **12**

**Compound 13**




**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **13**

**Compound 13**

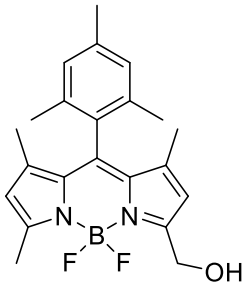






**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **13**

**Compound 14**

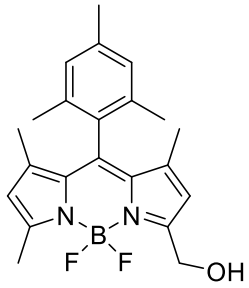






**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **14**

**Compound 14**

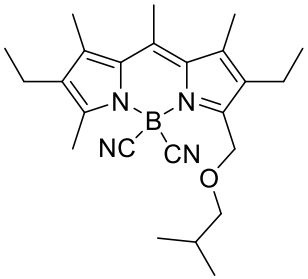






**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **14**

**Compound 15**

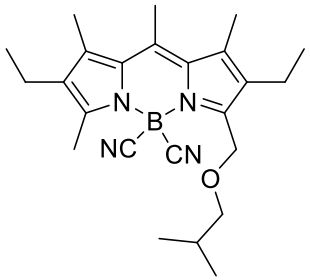






**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **15**

**Compound 15**

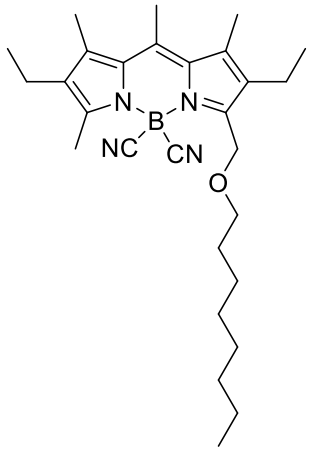






**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **15**

**Compound 16**

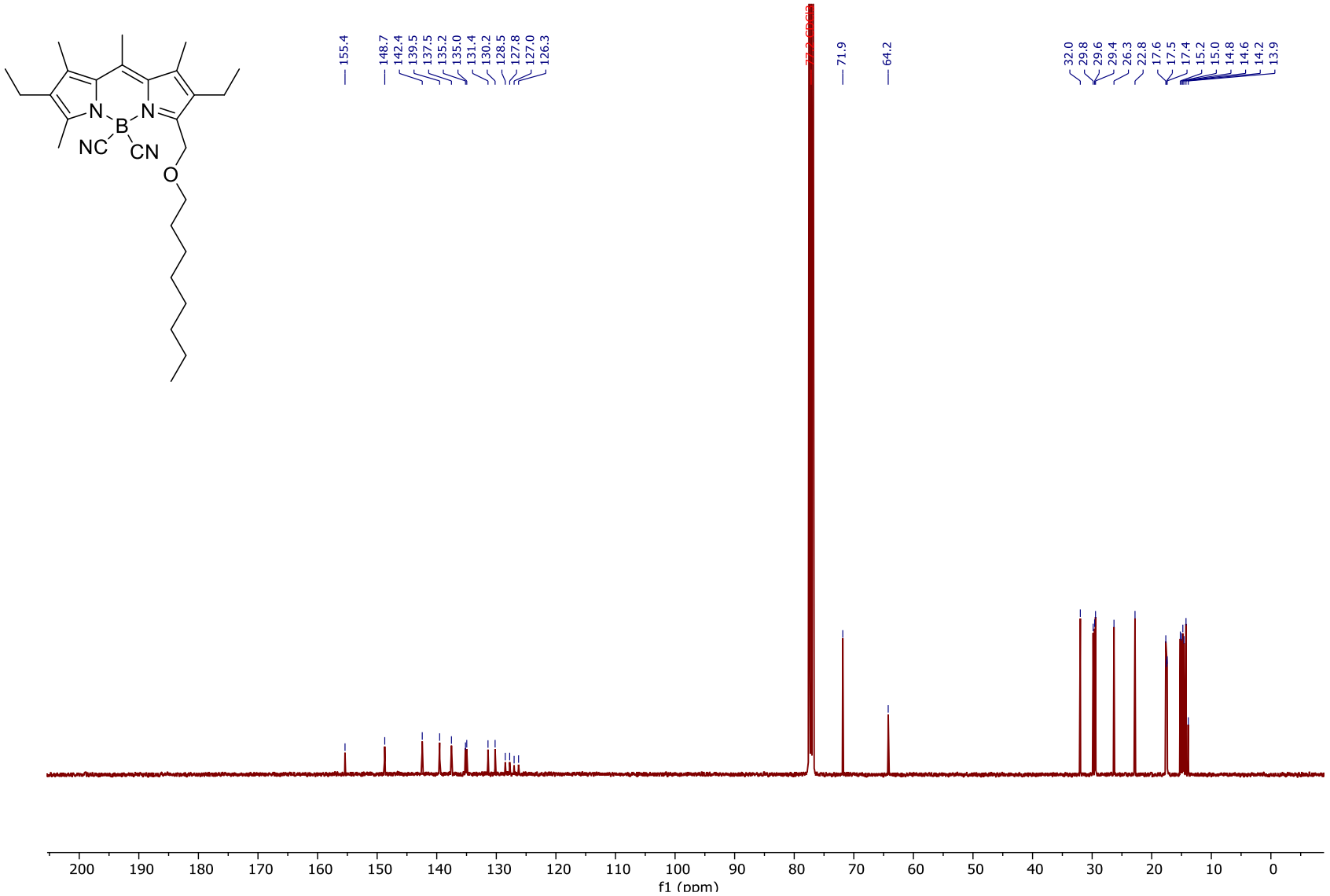






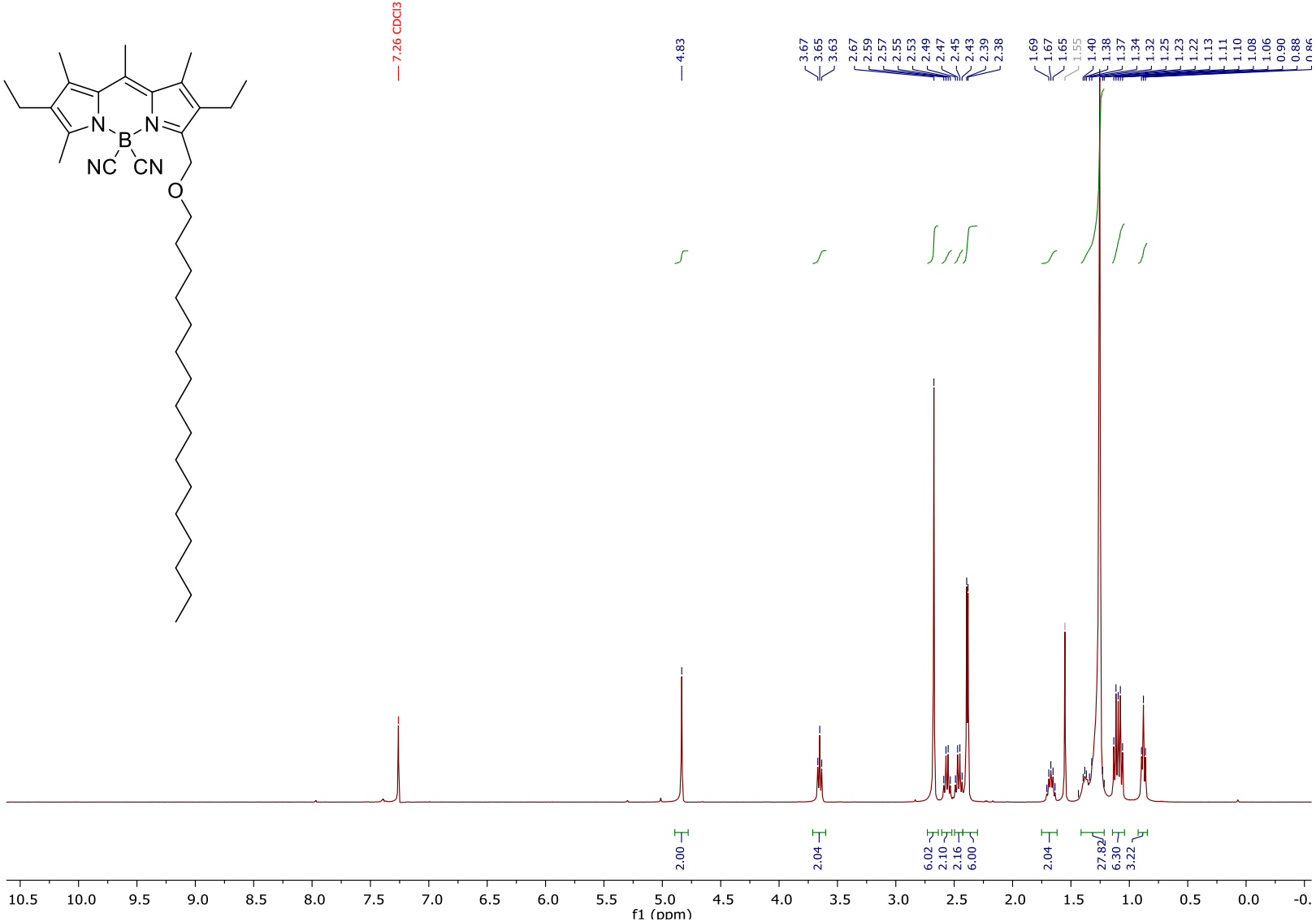
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **16**

**Compound 16**



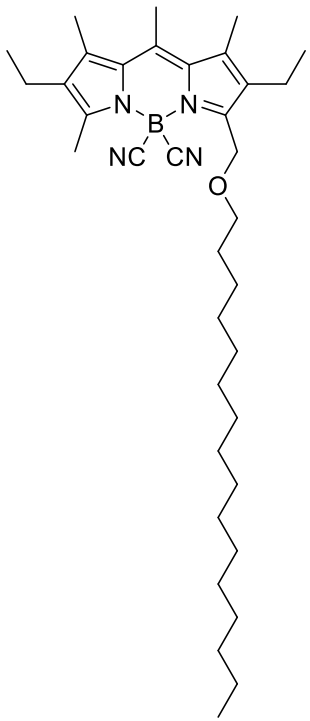

**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **16**

**Compound 17**




**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **17**

**Compound 17**

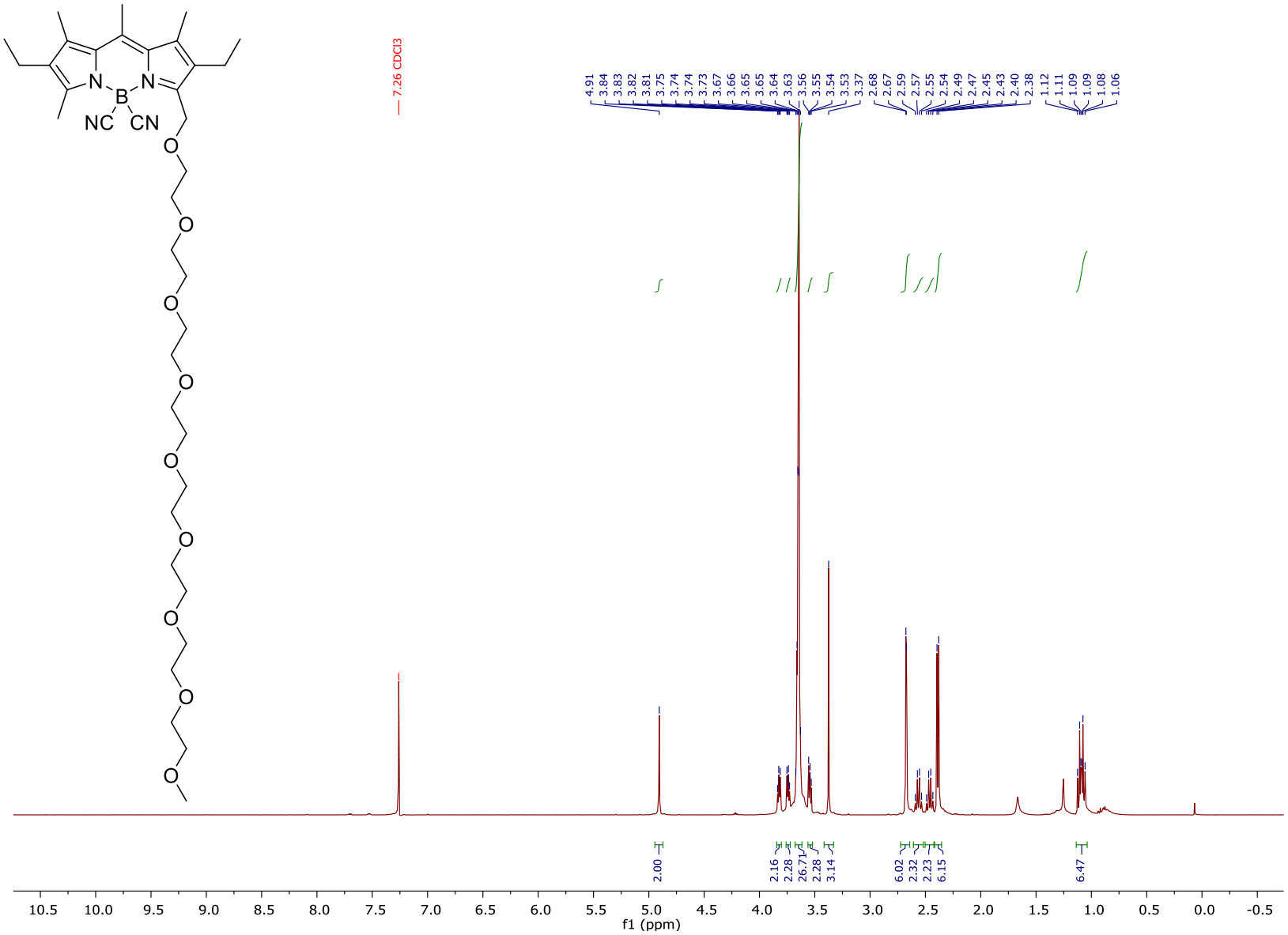






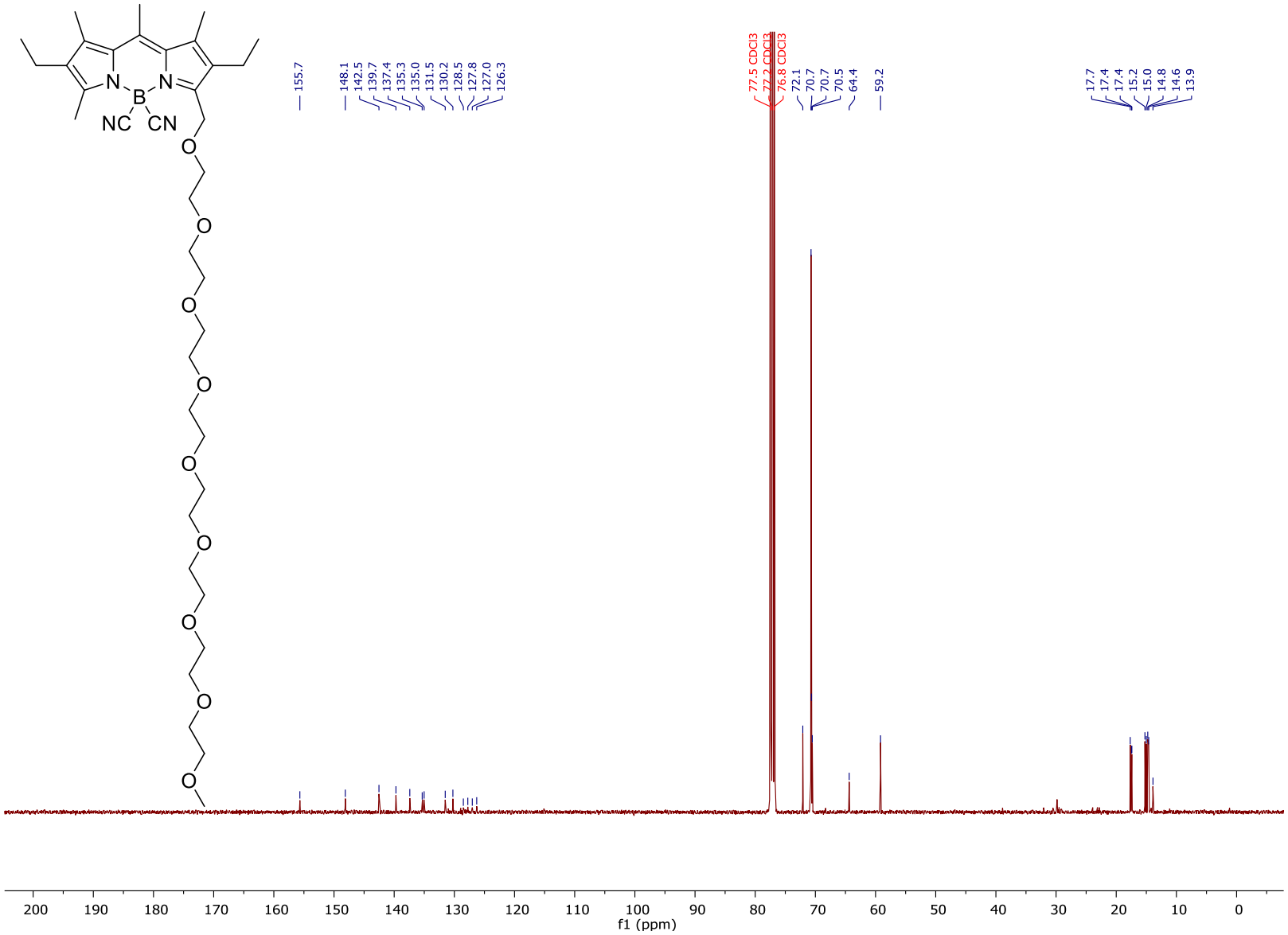
**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **17**

**Compound 18**



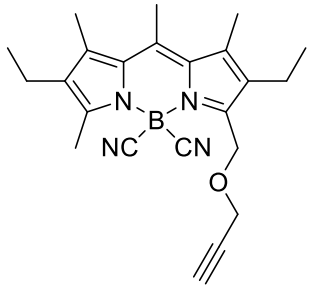

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **18**

**Compound 18**




**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **18**

**Compound 19**

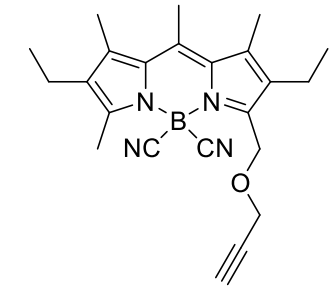






**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **19**

**Compound 19**

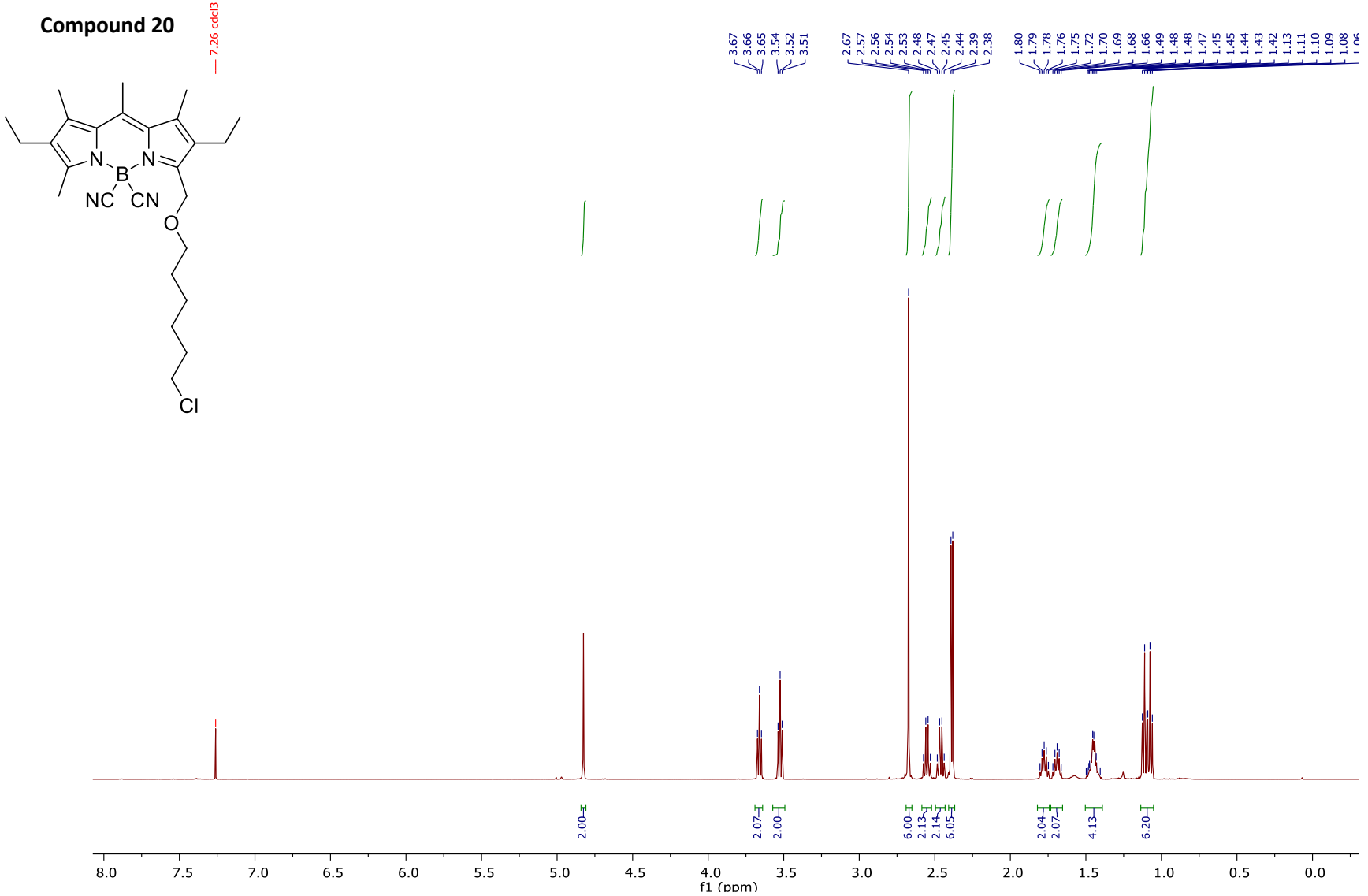






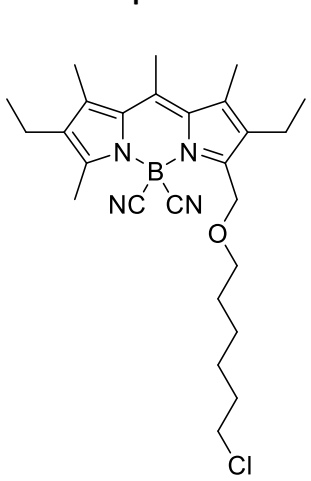
**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **19**

**Compound 20**




**$^1$H NMR** (500 MHz, $CDCl_3$) spectrum of compound **20**

**Compound 20**

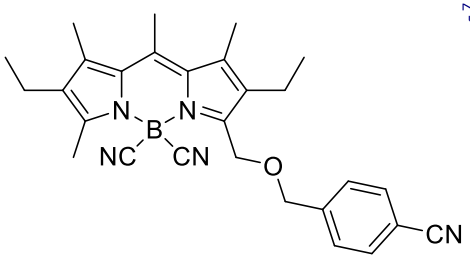






**$^{13}$C NMR** (125 MHz, $CDCl_3$) spectrum of compound **20**

**Compound 21**

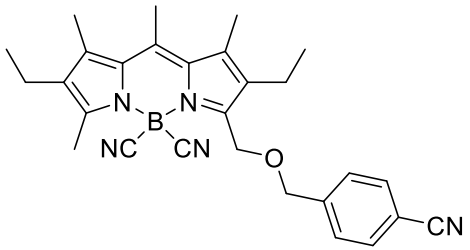






**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **21**

**Compound 21**

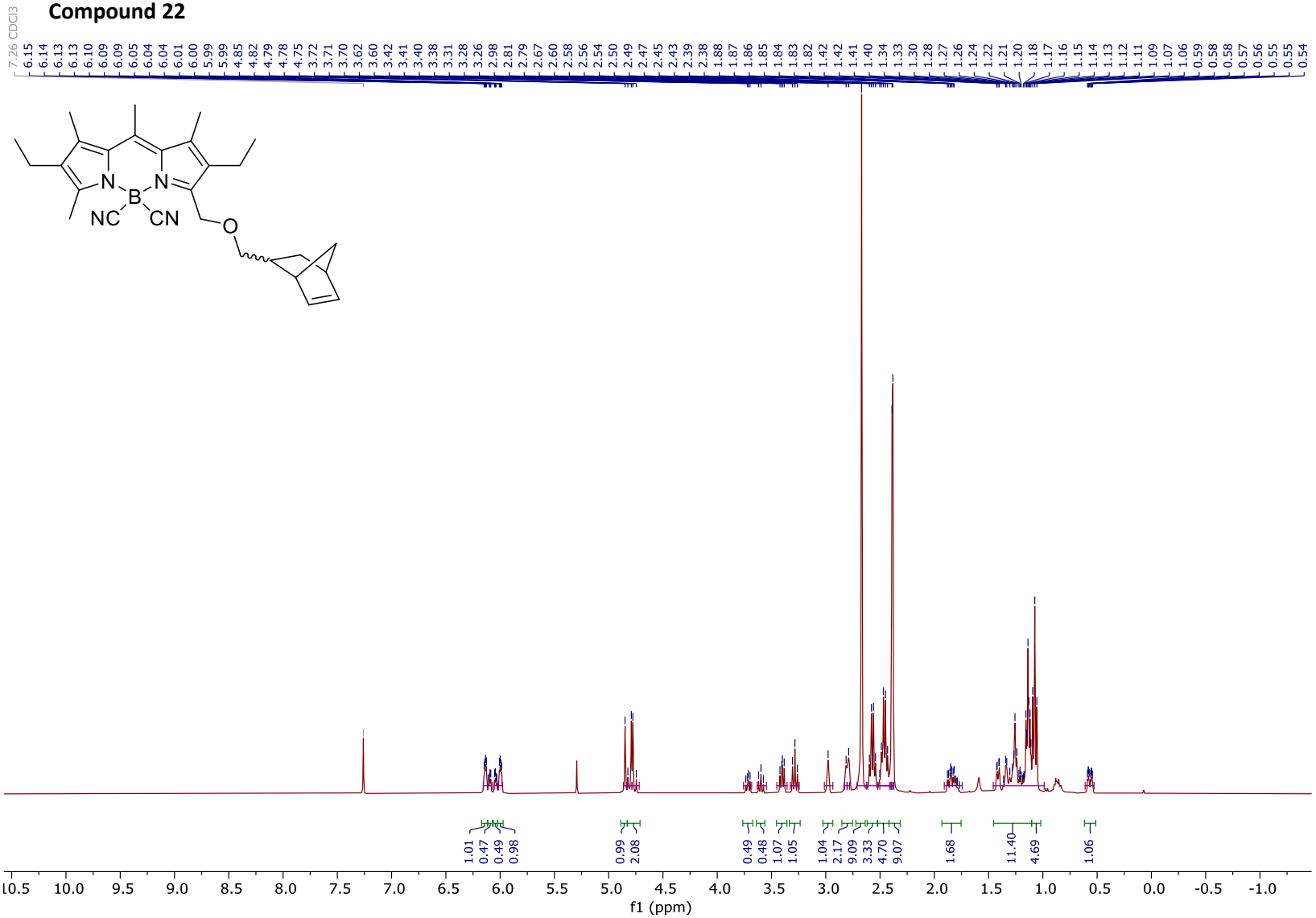






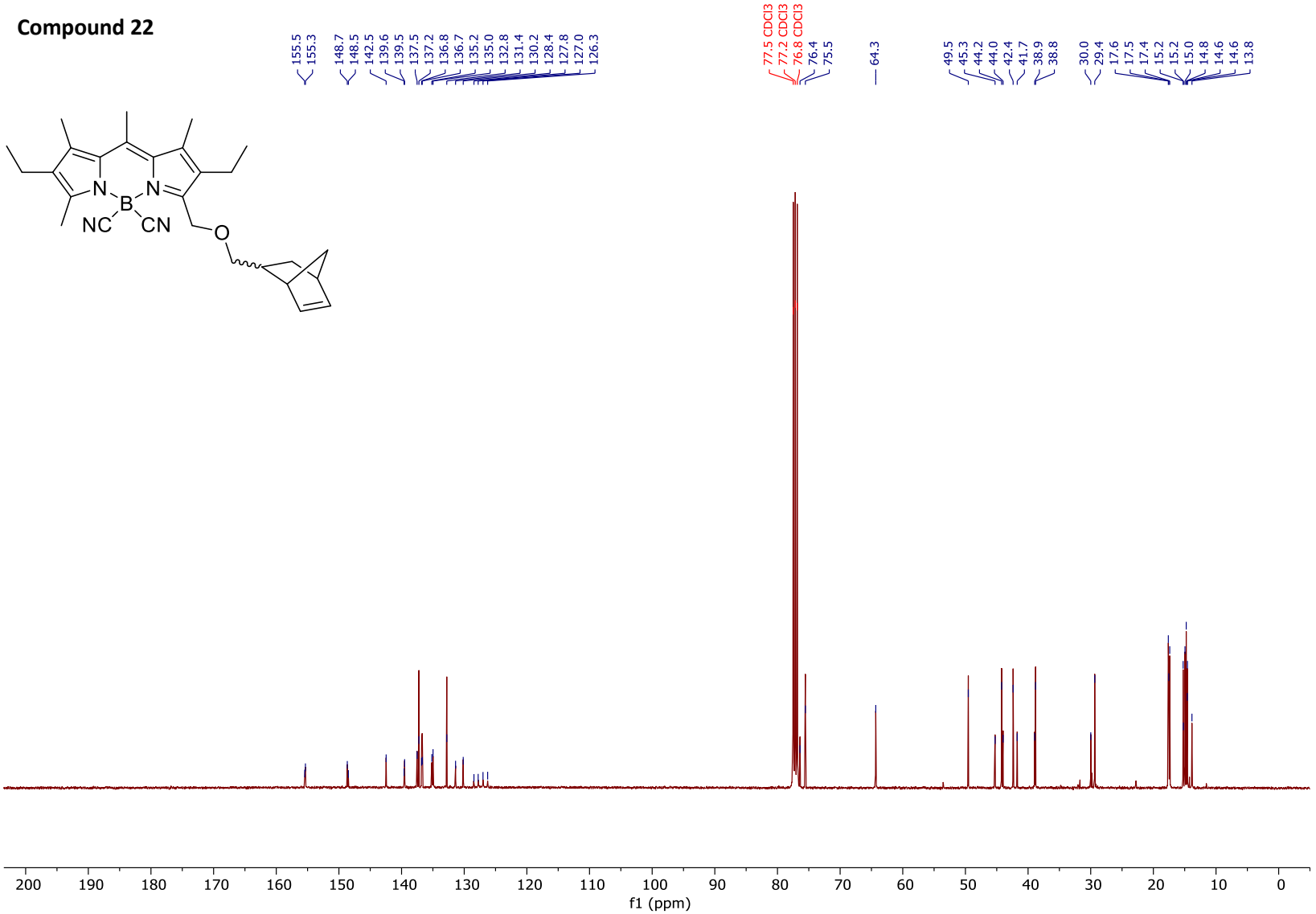
**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **21**

**Compound 22**



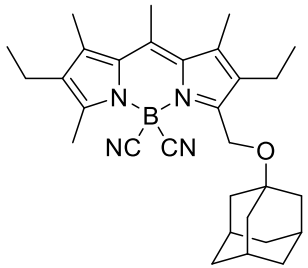

**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **22**

**Compound 22**




**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **22**

**Compound 23**

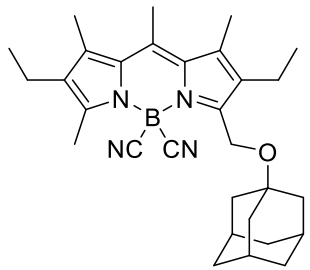






**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **23**

**Compound 23**

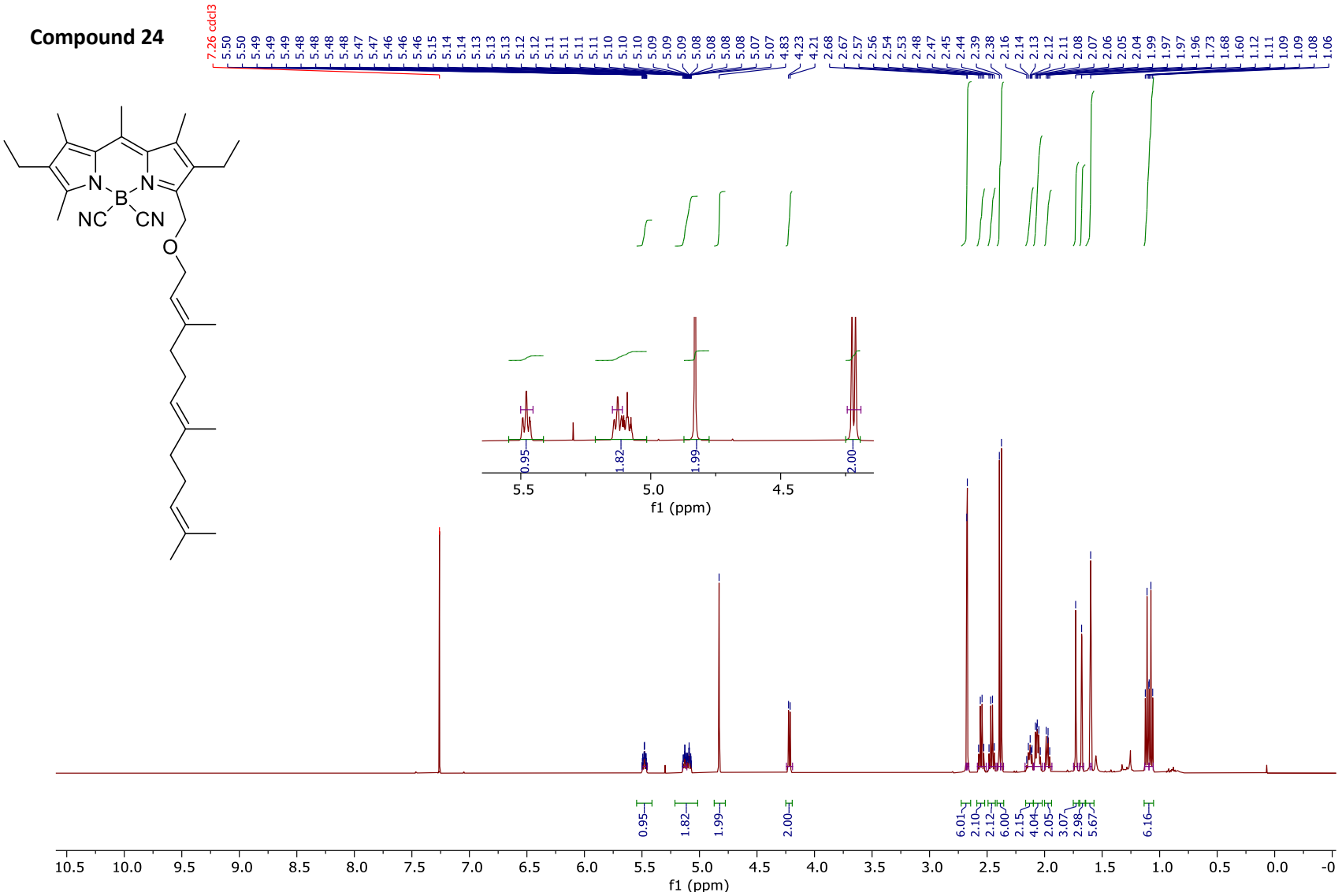






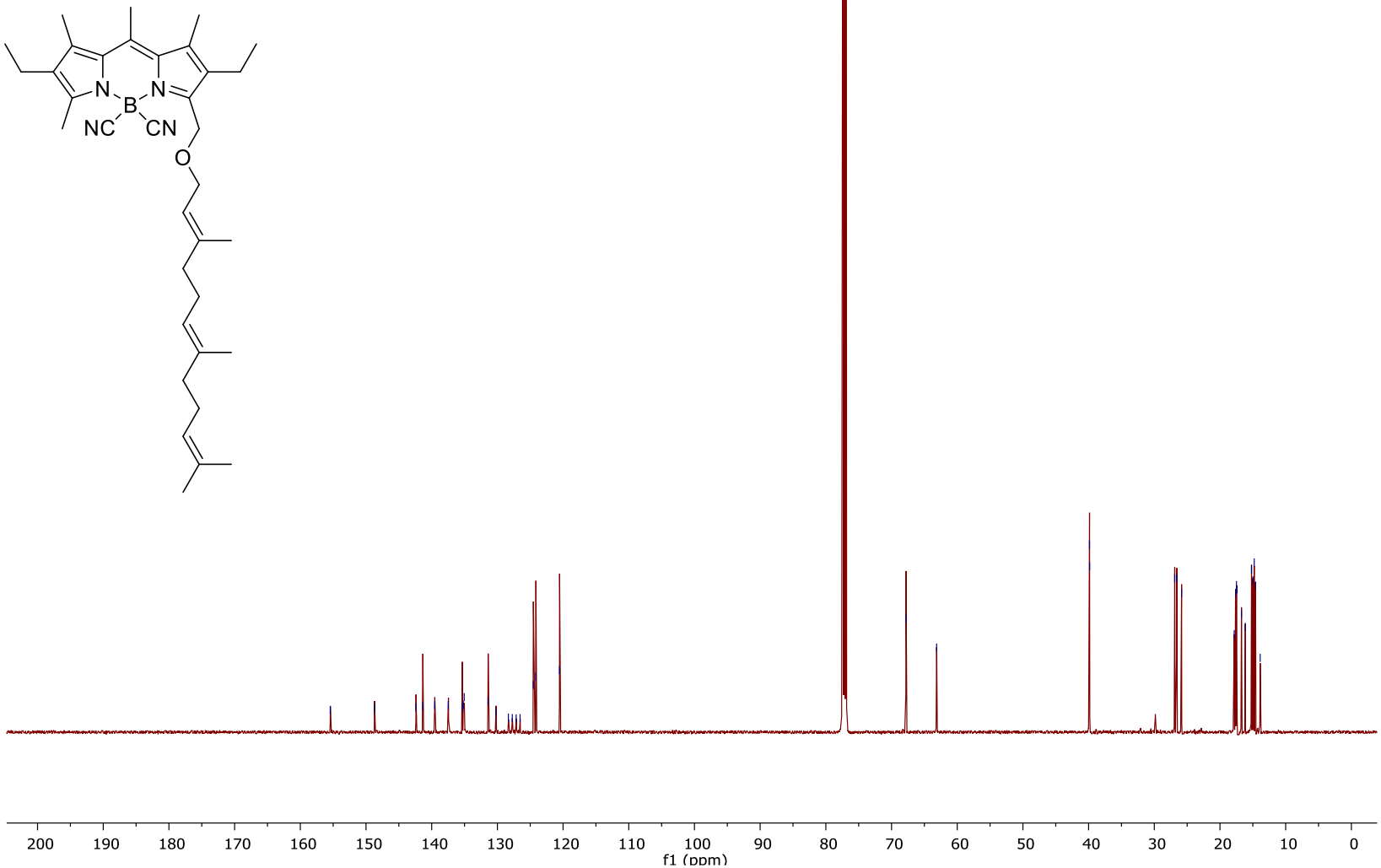
**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **23**

**Compound 24**



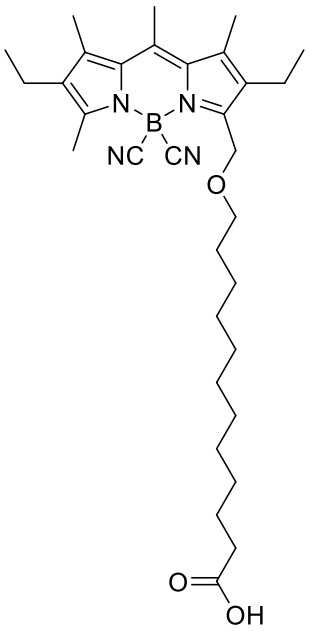

**$^1$H NMR** (500 MHz, $CDCl_3$) spectrum of compound **24**

**Compound 24**




**$^{13}$C NMR** (125 MHz, $CDCl_3$) spectrum of compound **24**

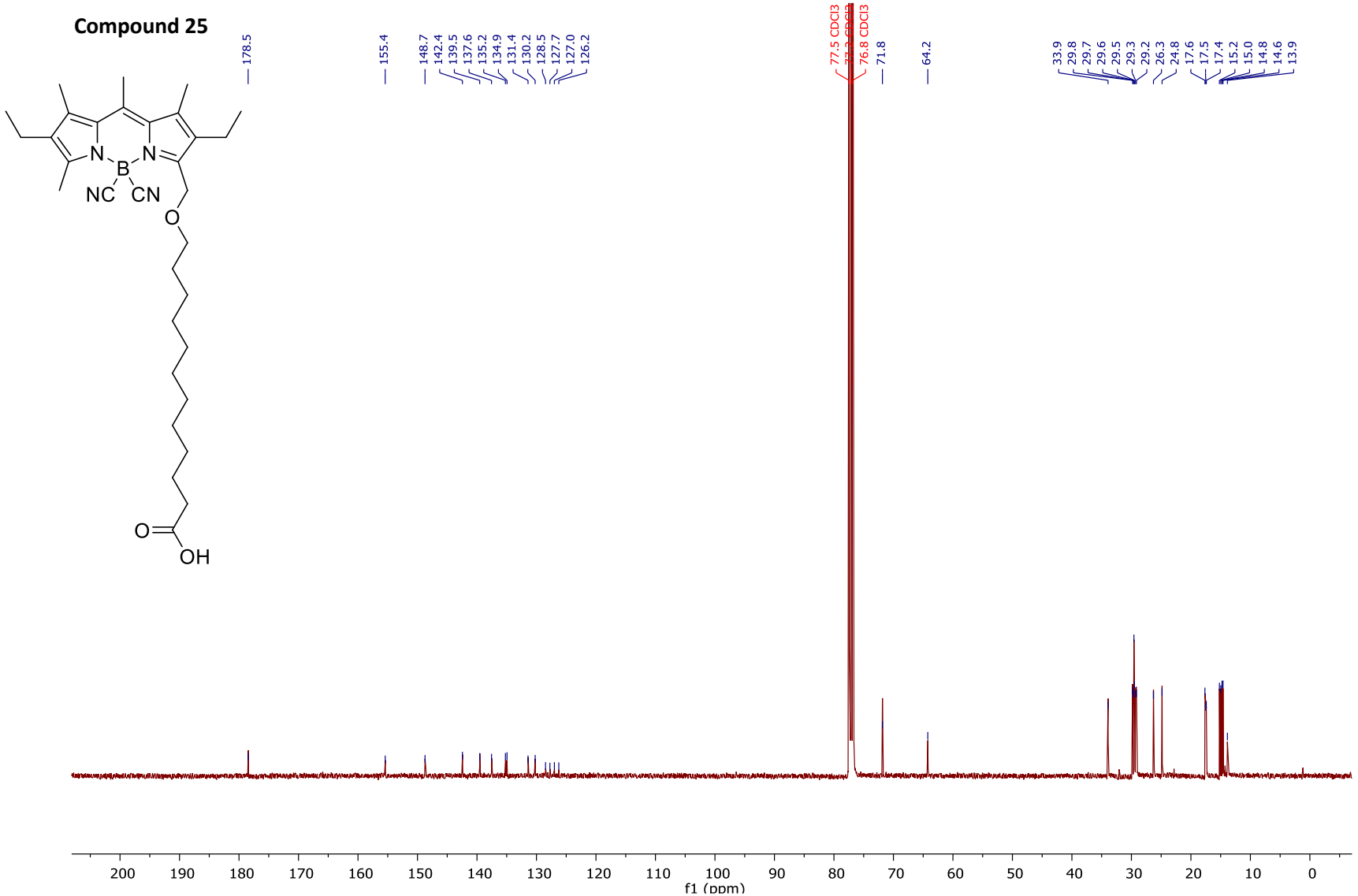
**Compound 25**





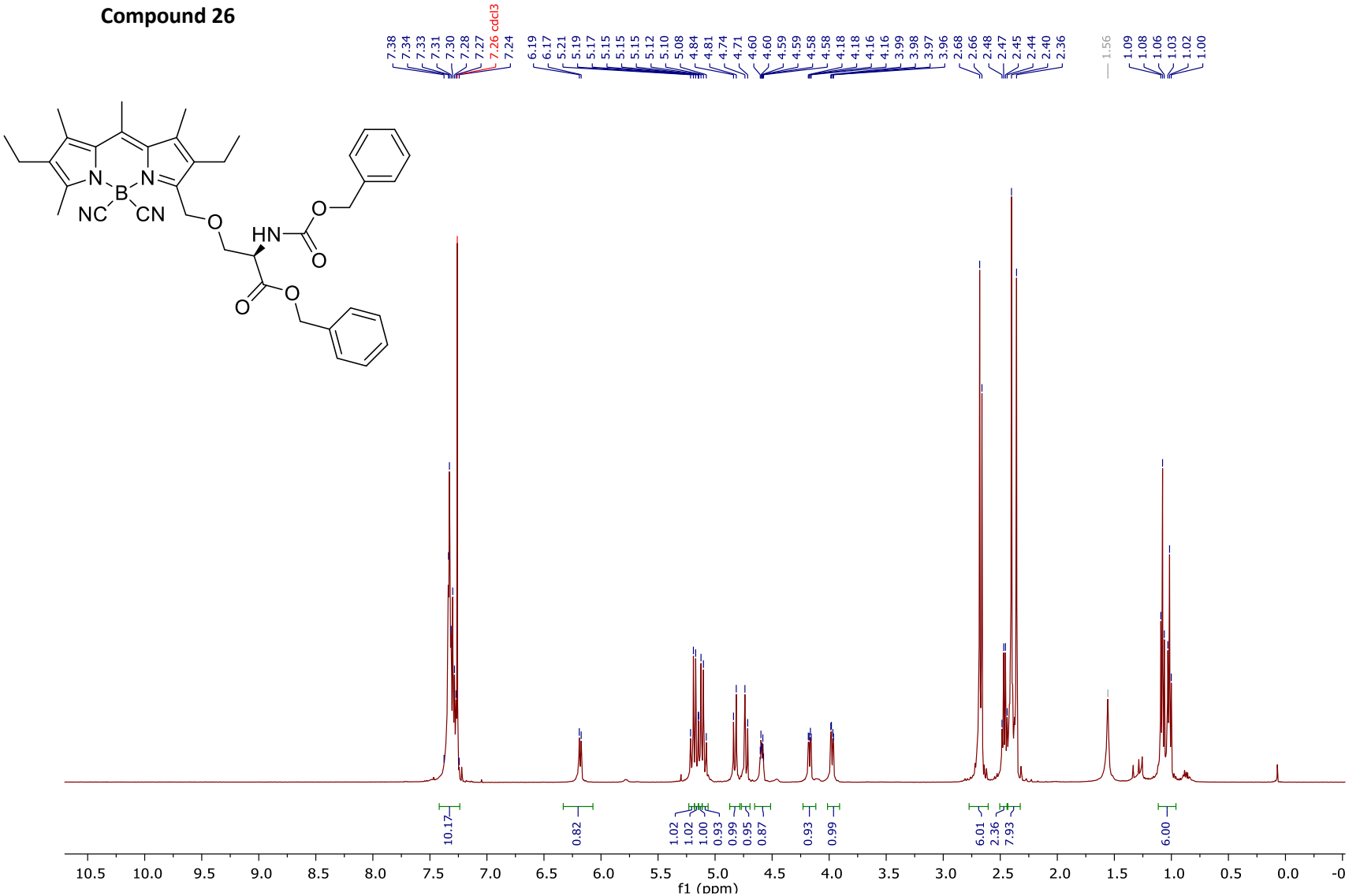


**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **25**



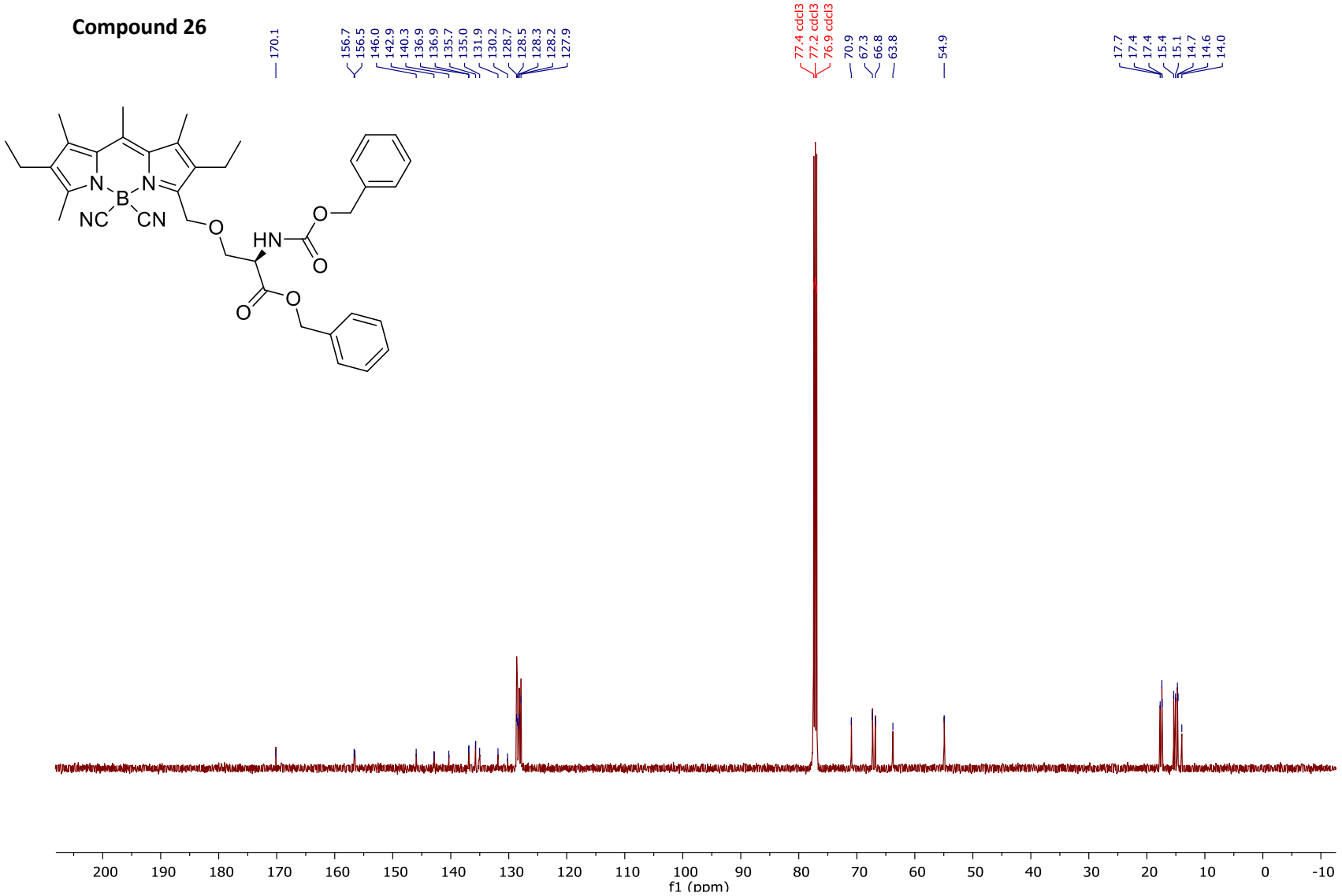

**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **25**

**Compound 26**



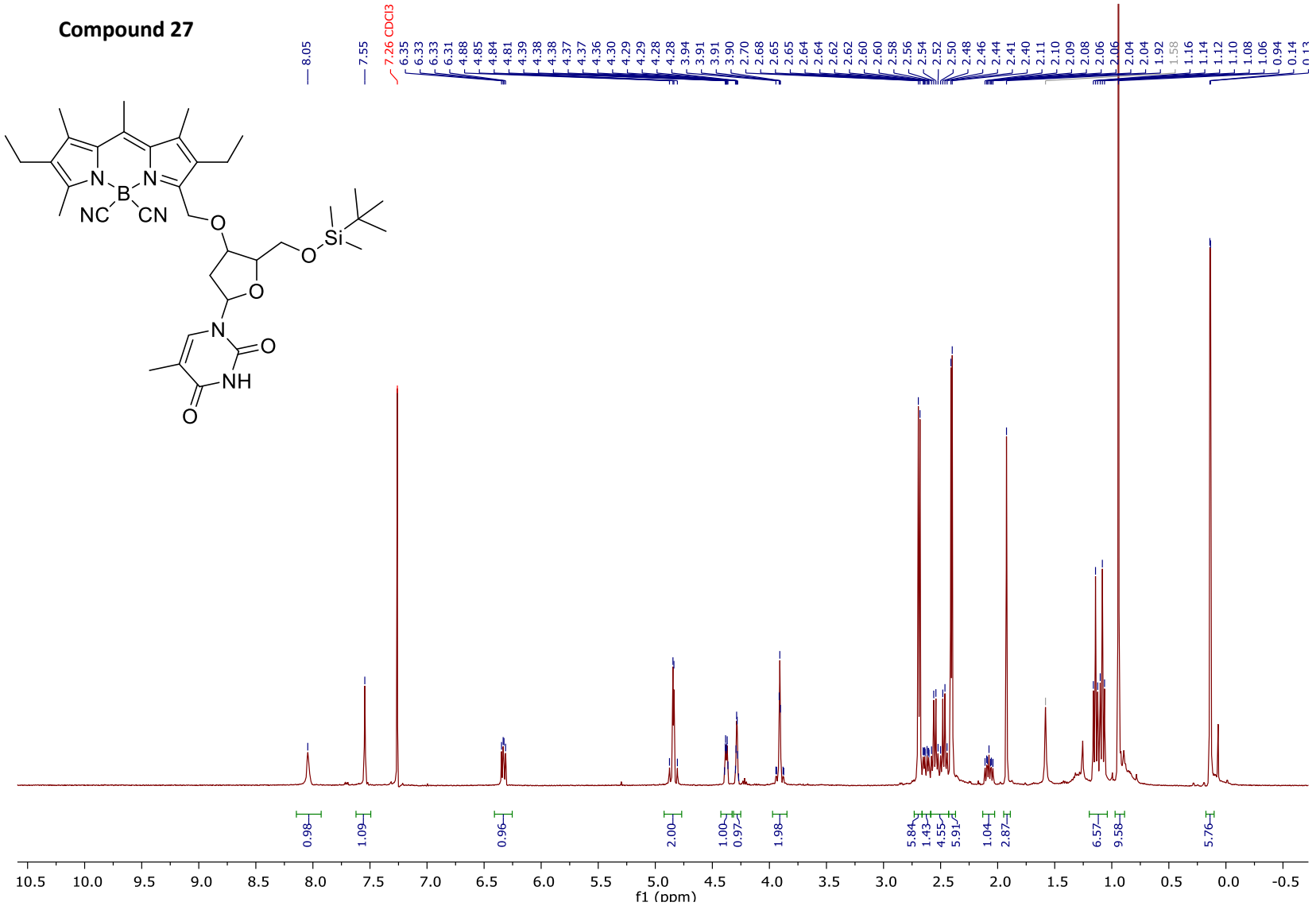

**$^1$H NMR** (500 MHz, $CDCl_3$) spectrum of compound **26**

**Compound 26**



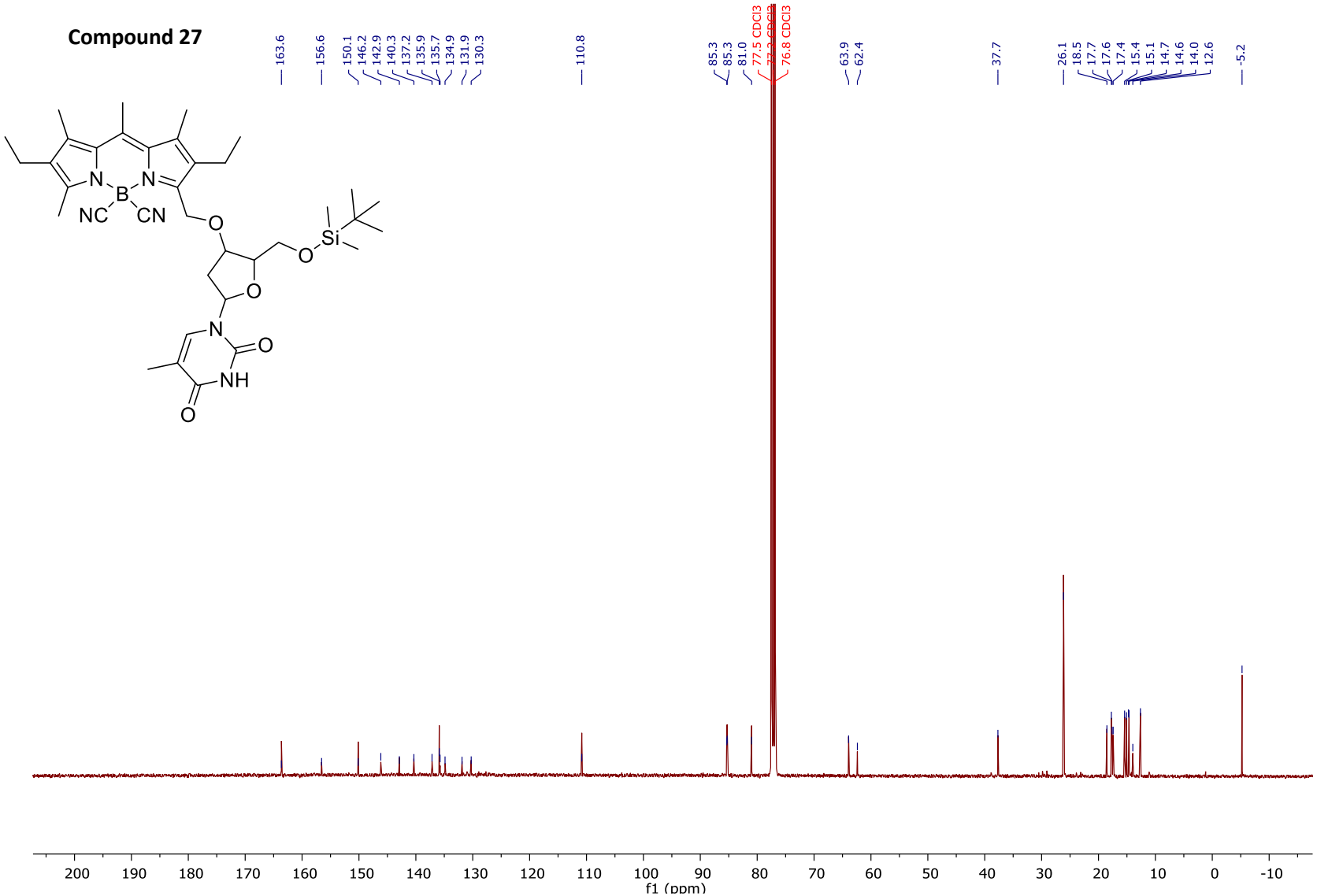

**$^{13}$C NMR** (125 MHz, $CDCl_3$) spectrum of compound **26**

**Compound 27**



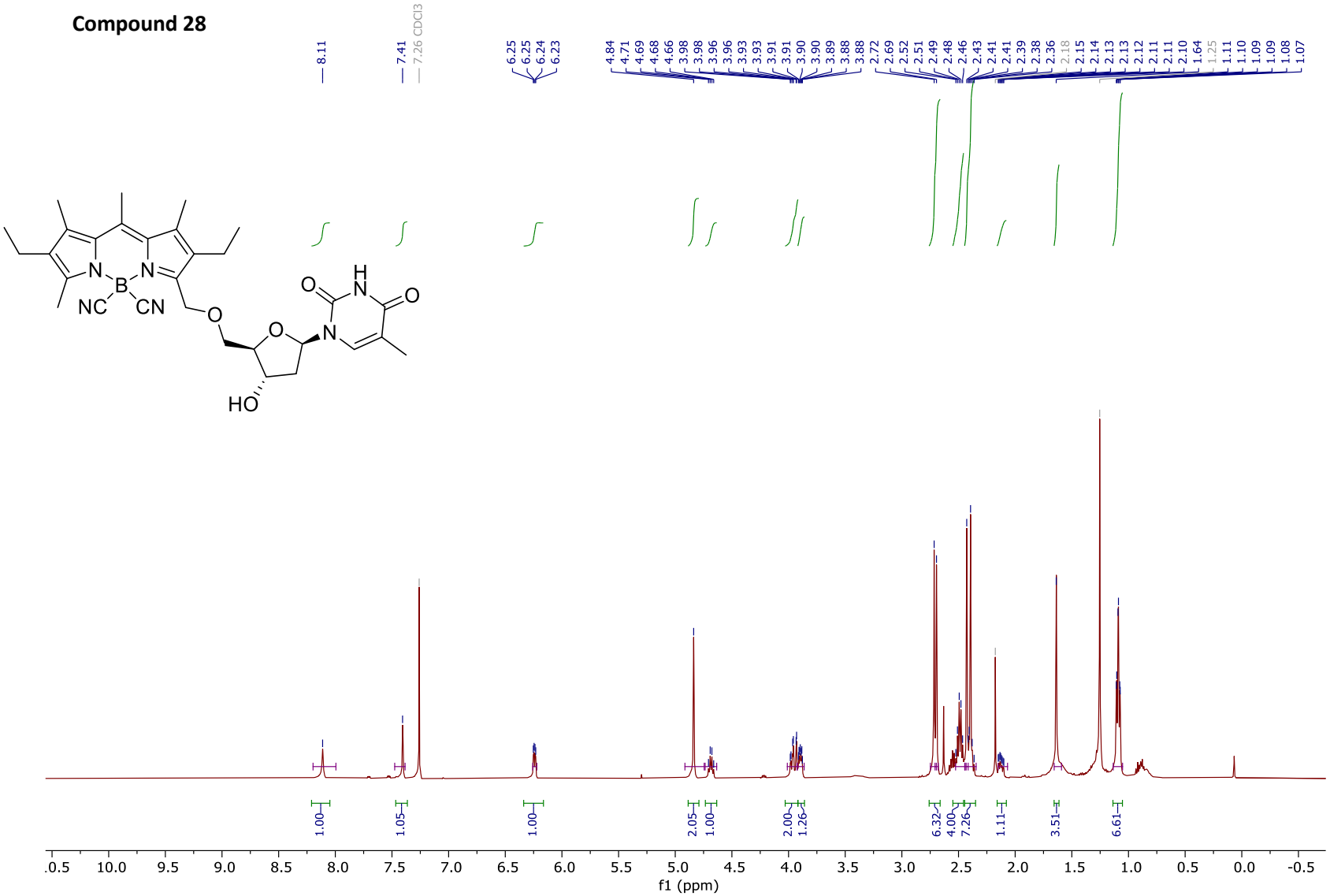

**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **27**

**Compound 27**



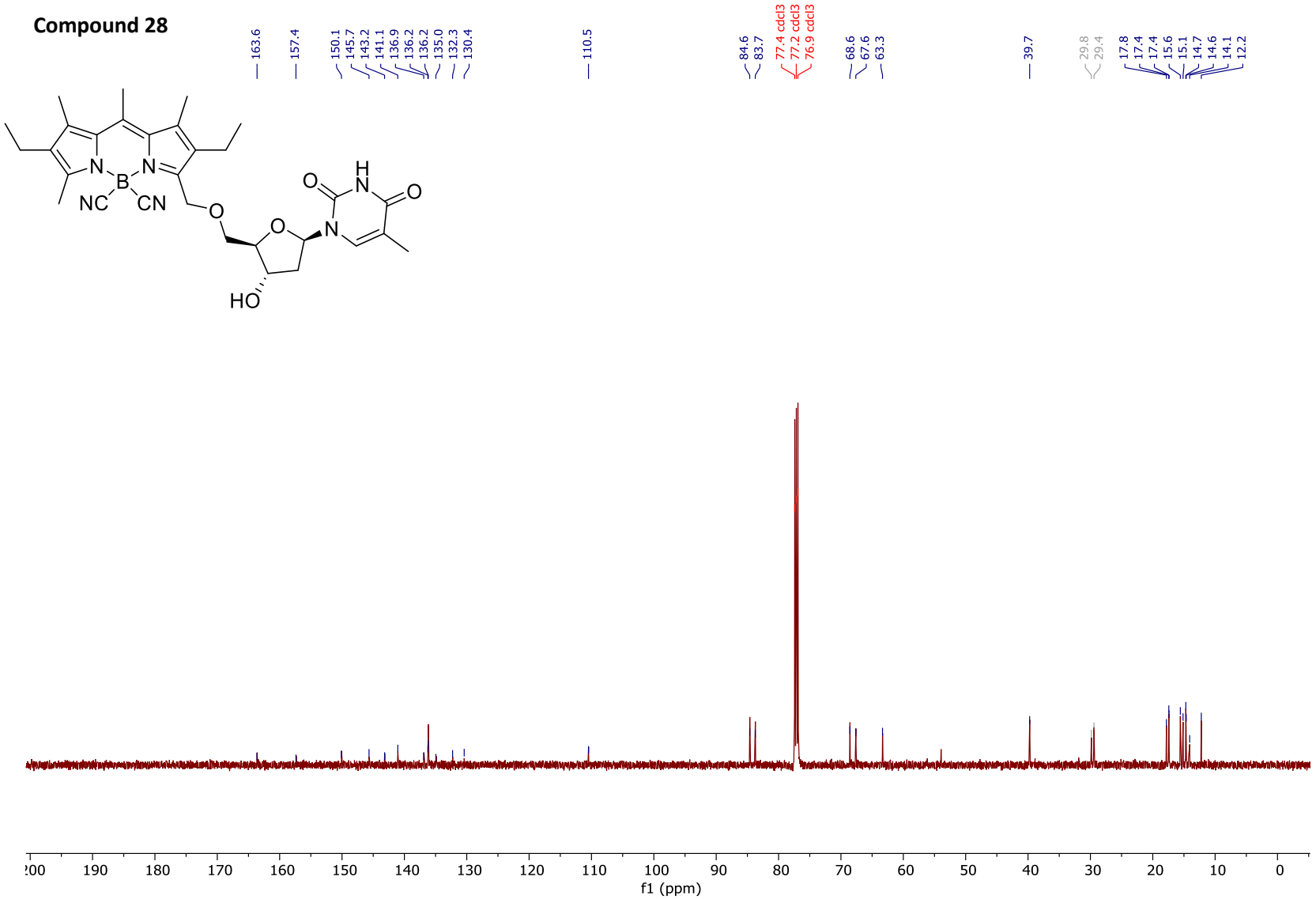

**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **27**

**Compound 28**



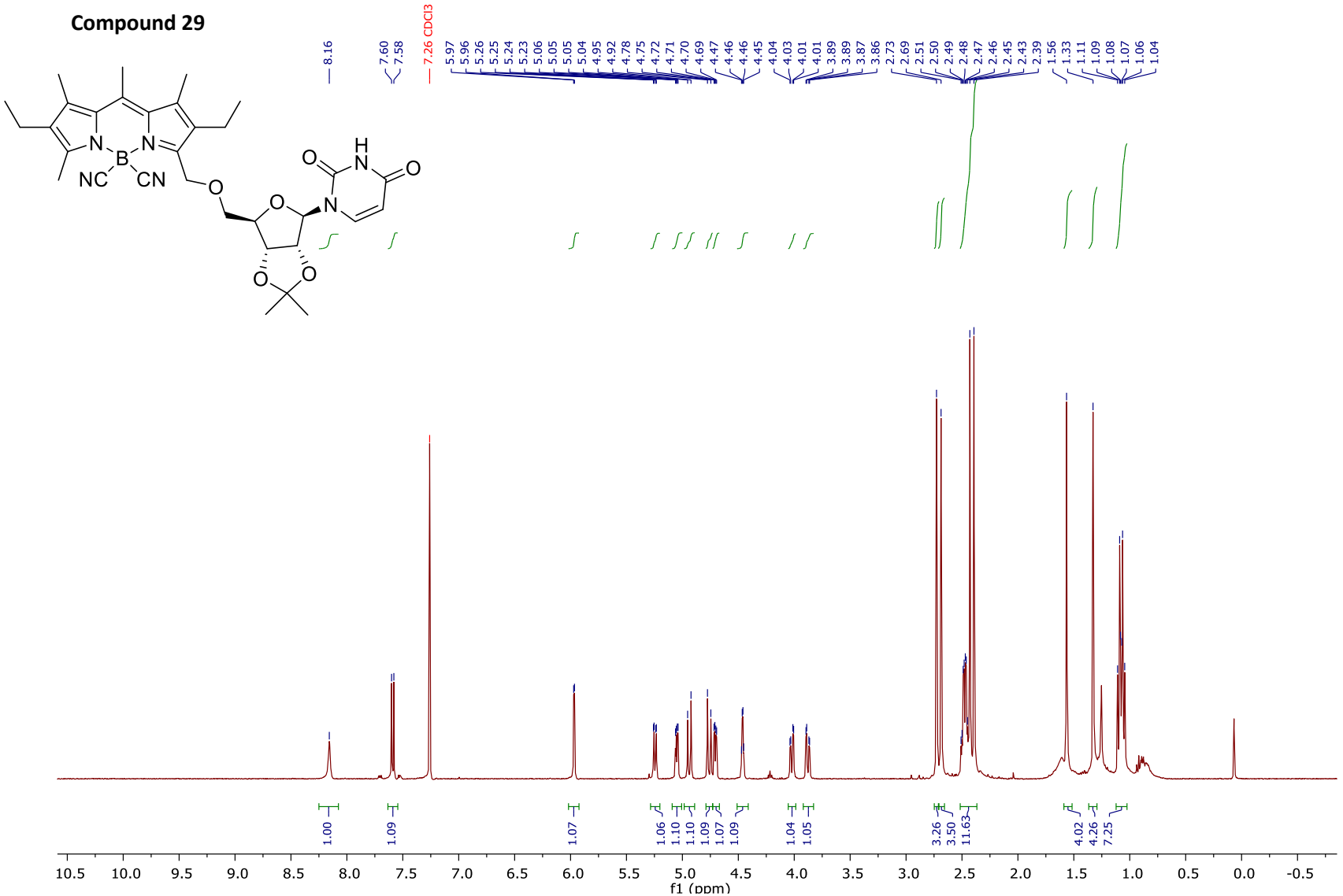

**$^1$H NMR** (500 MHz, $CDCl_3$) spectrum of compound **28**

**Compound 28**



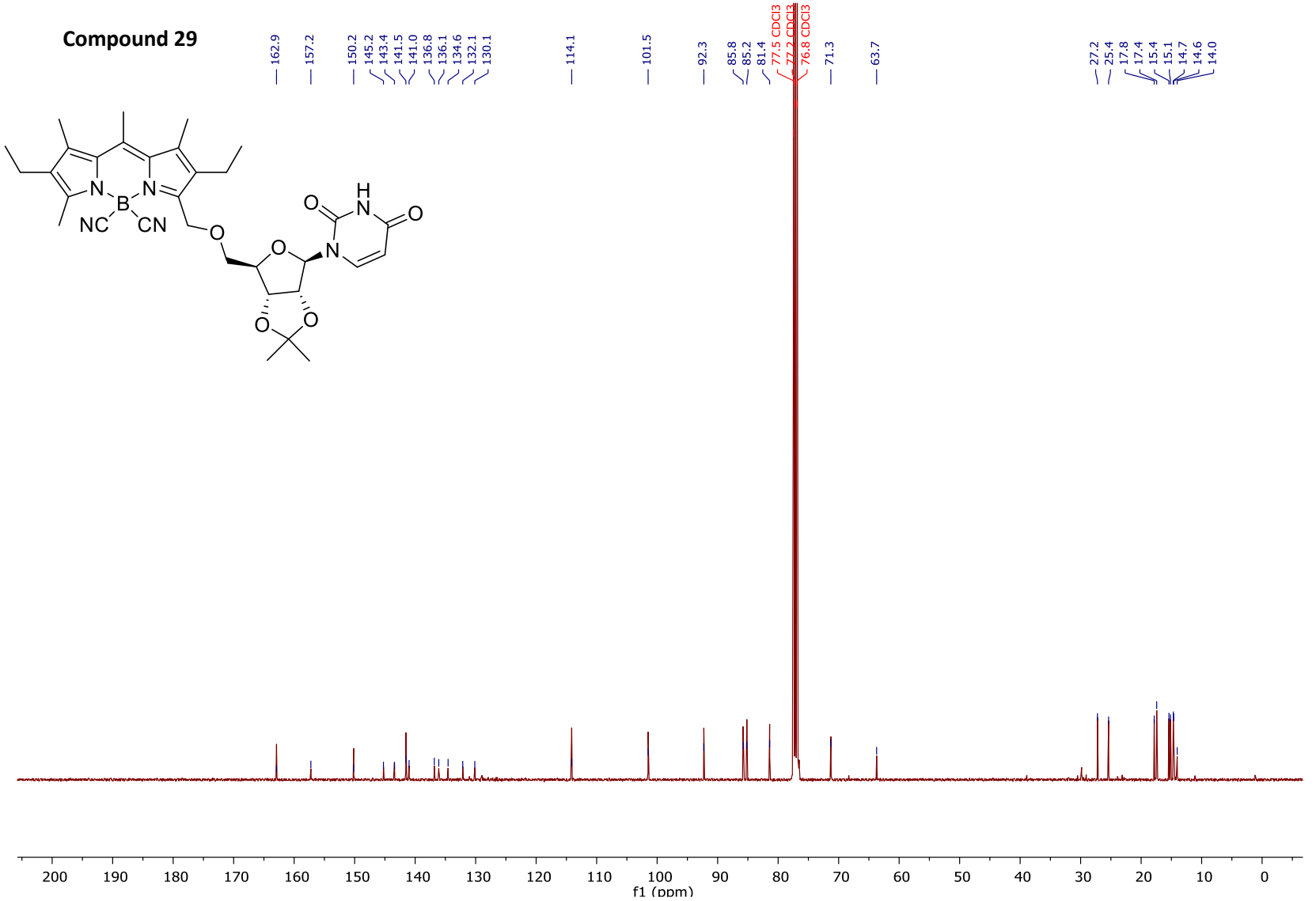

**$^{13}$C NMR** (125 MHz, $CDCl_3$) spectrum of compound **28**

**Compound 29**



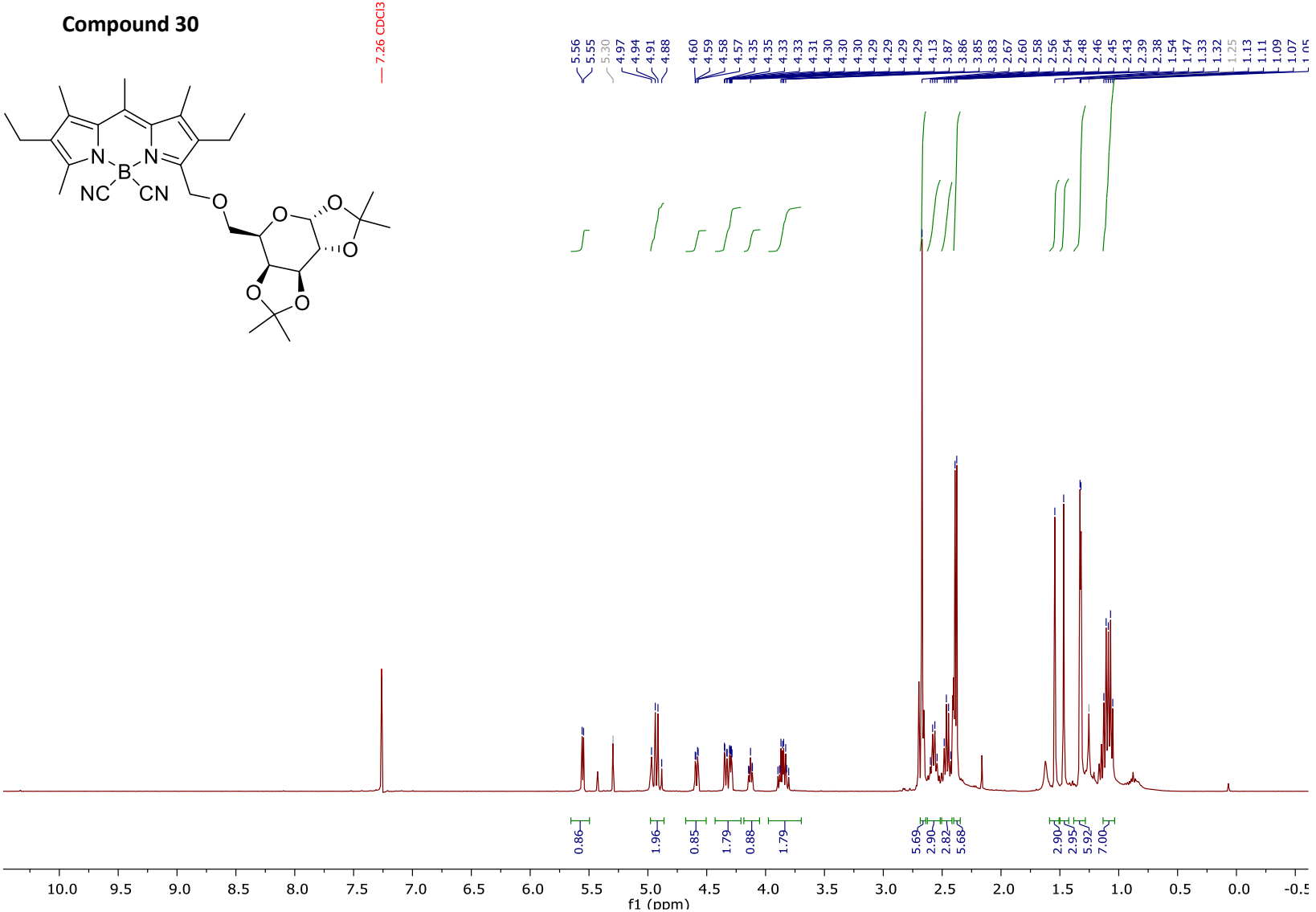

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **29**

**Compound 29**

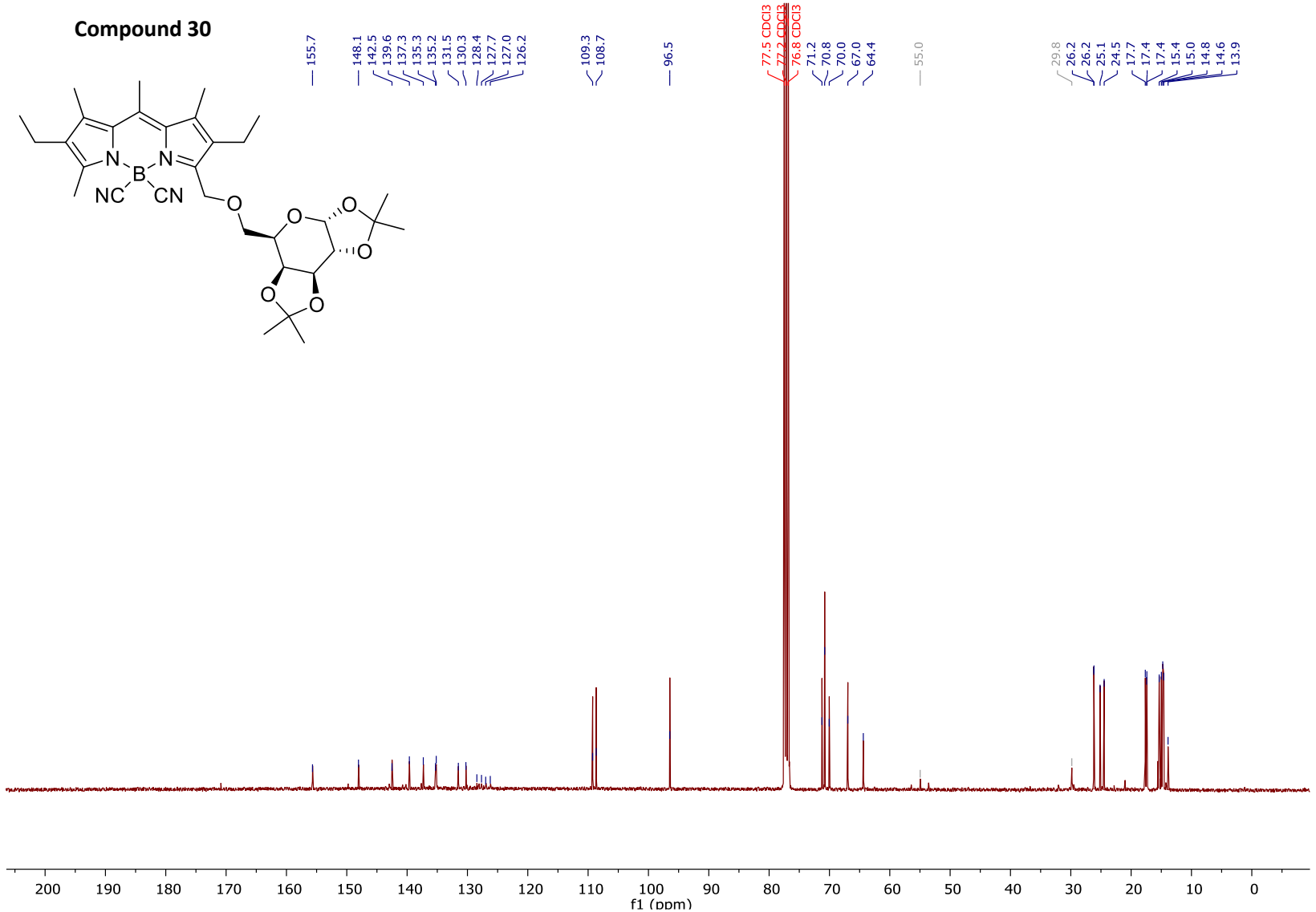



**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **29**

**Compound 30**

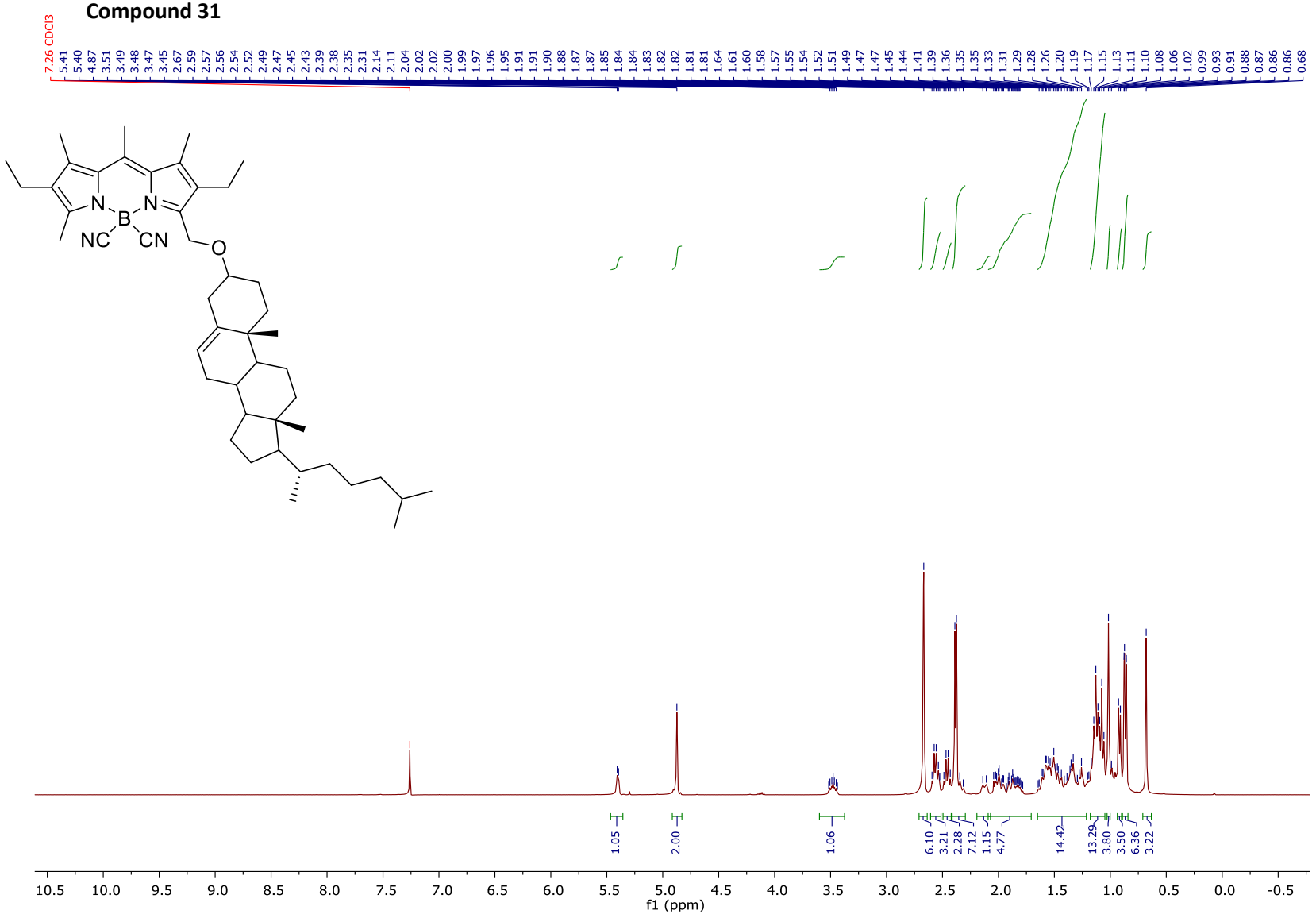



**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **30**

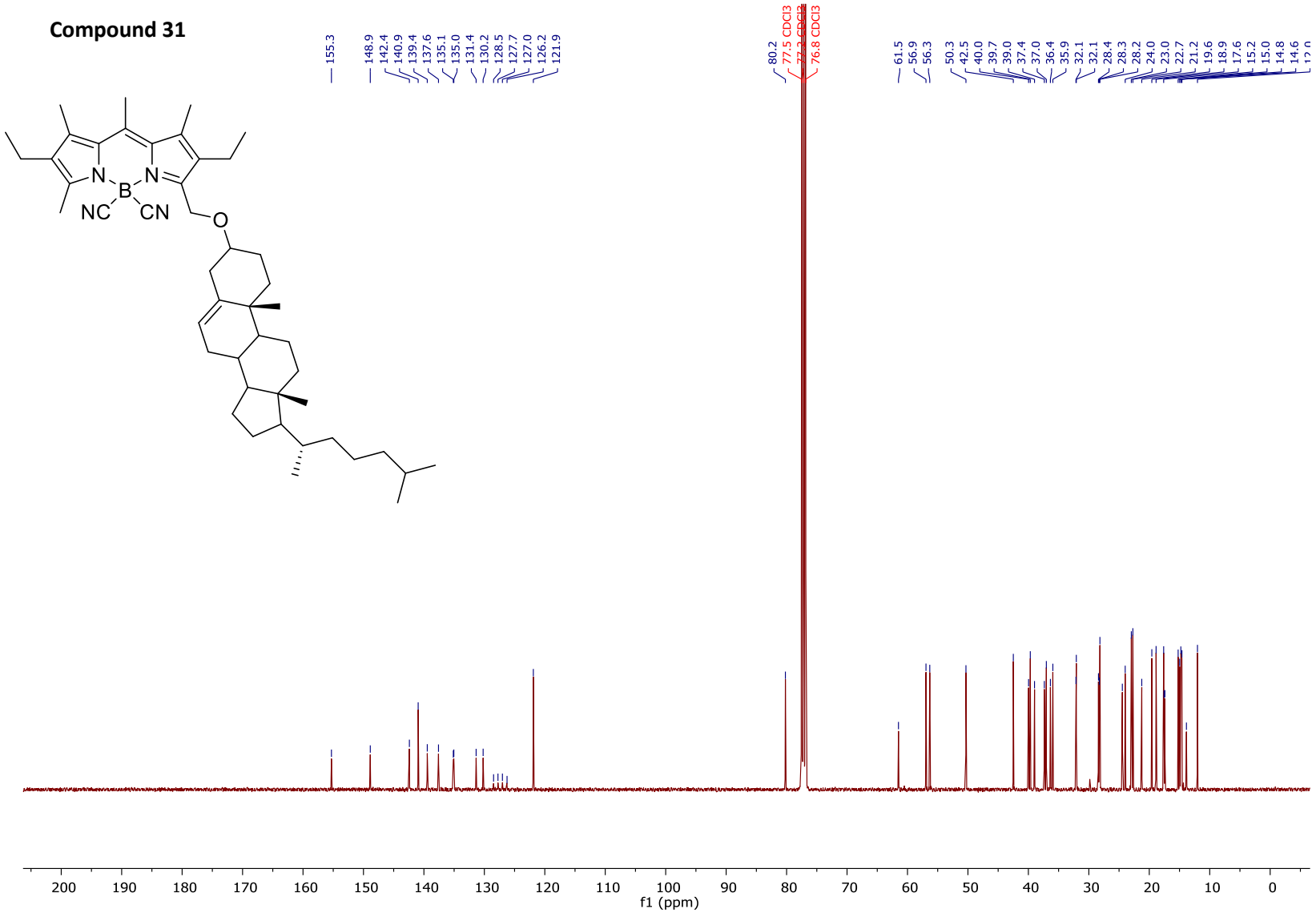



**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **30**

**Compound 31**

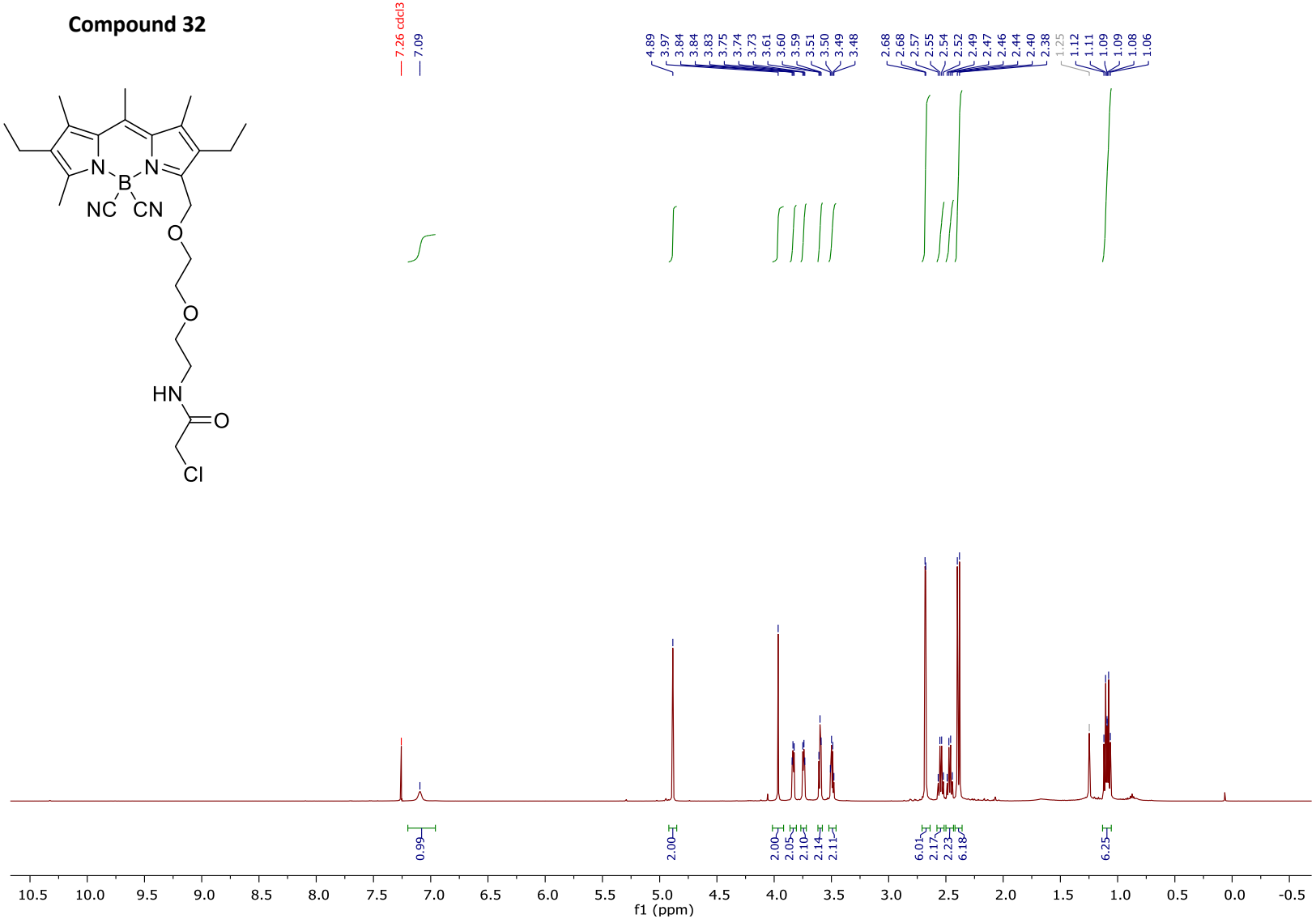



**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **31**



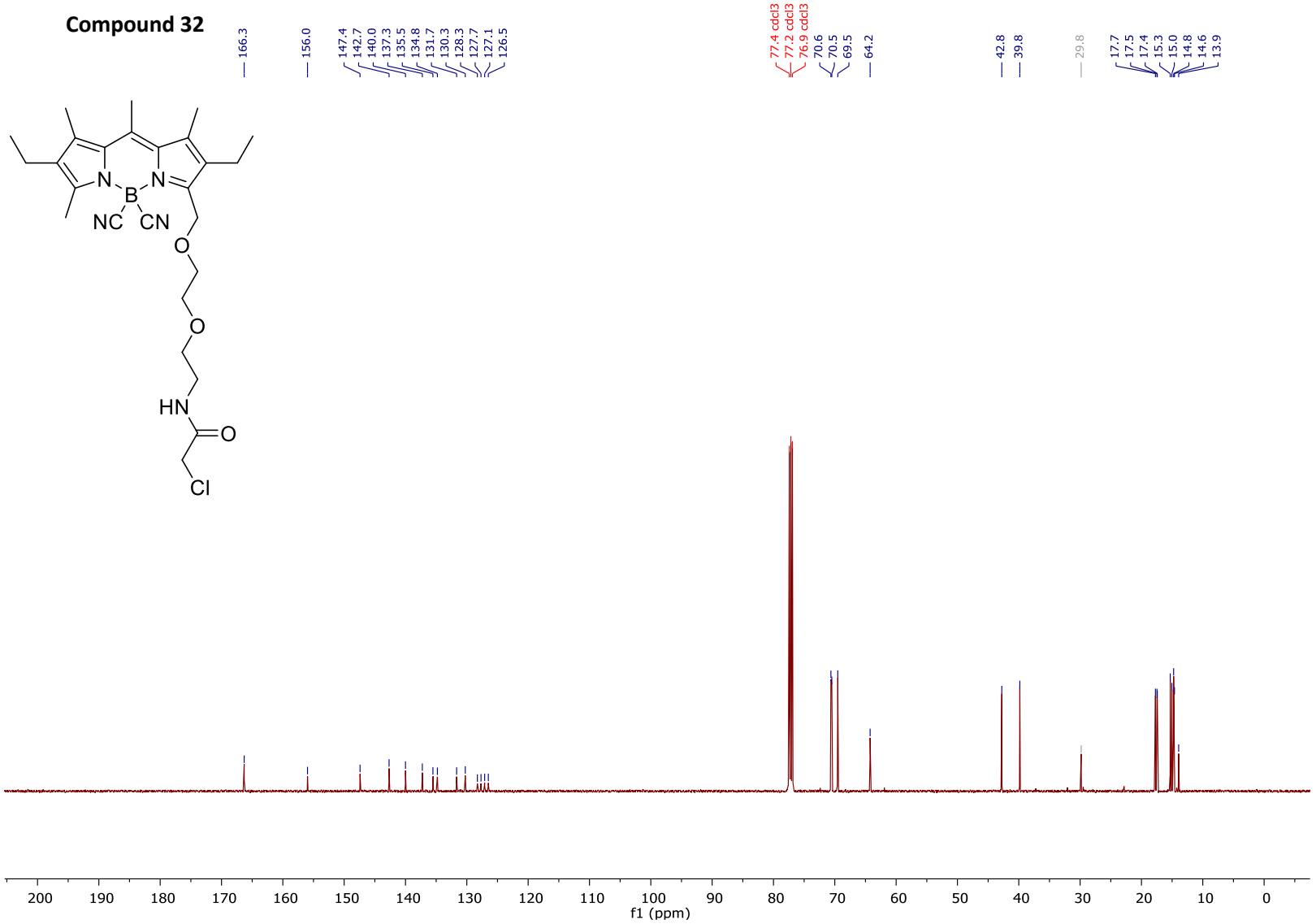

**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **31**

**Compound 32**



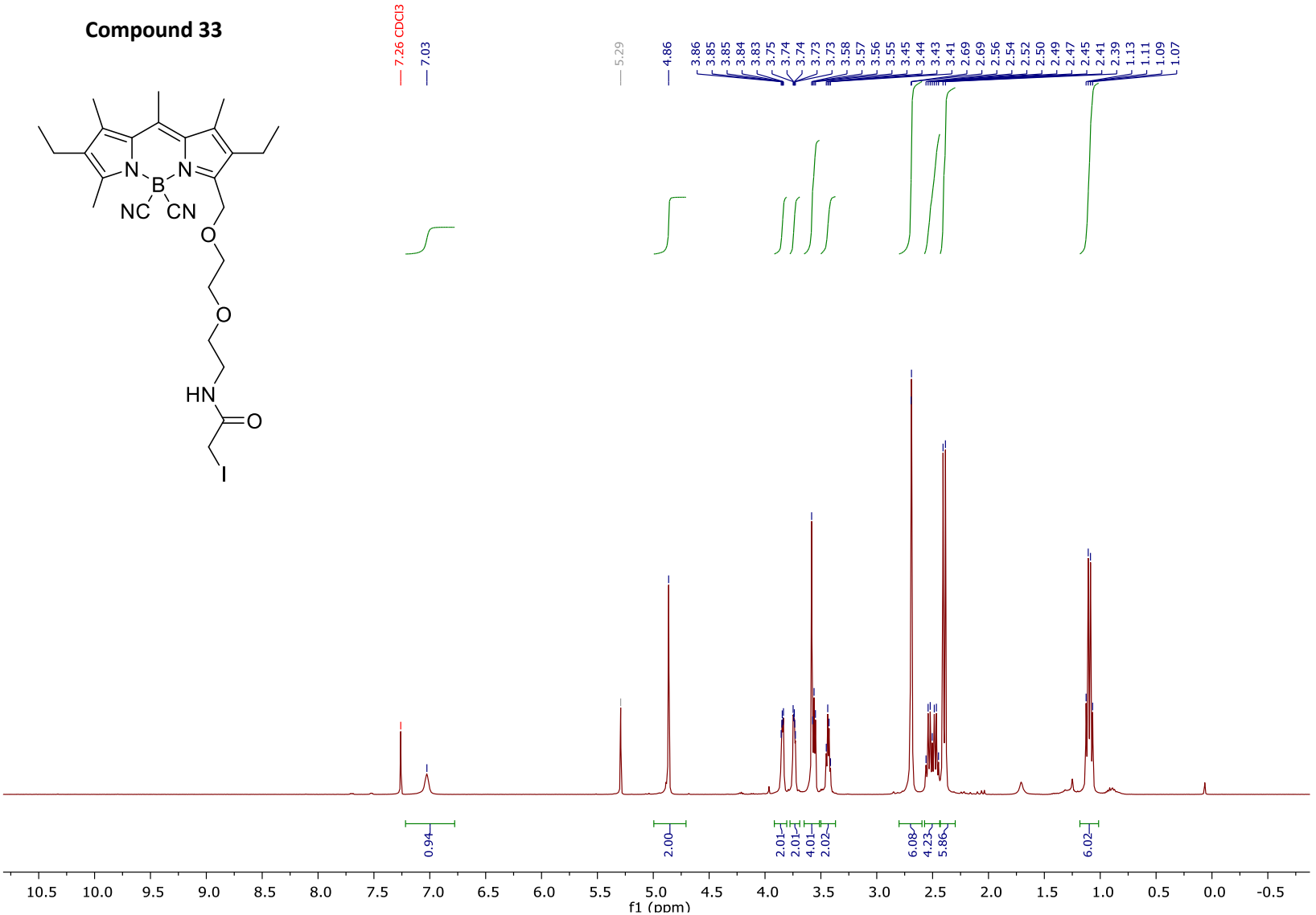

**$^1$H NMR** (500 MHz, $CDCl_3$) spectrum of compound **32**

**Compound 32**



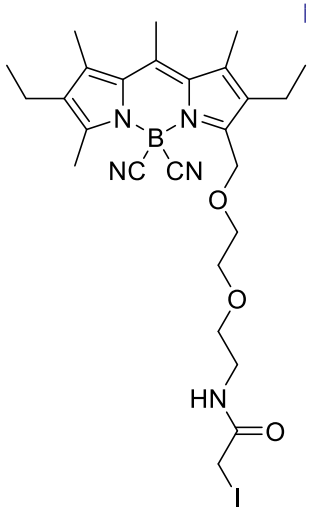

**$^{13}$C NMR** (125 MHz, $CDCl_3$) spectrum of compound **32**

**Compound 33**




**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **33**

**Compound 33**

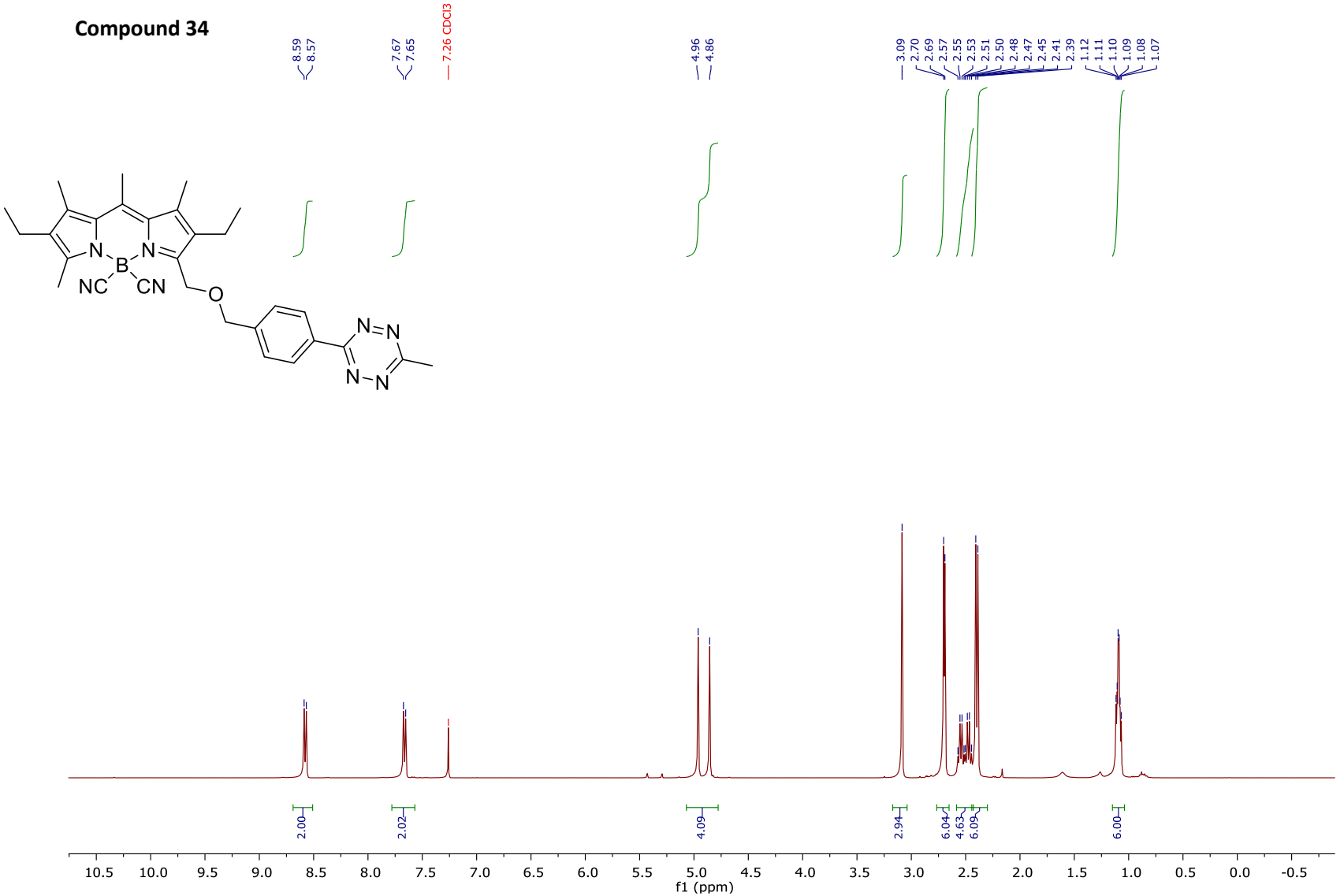






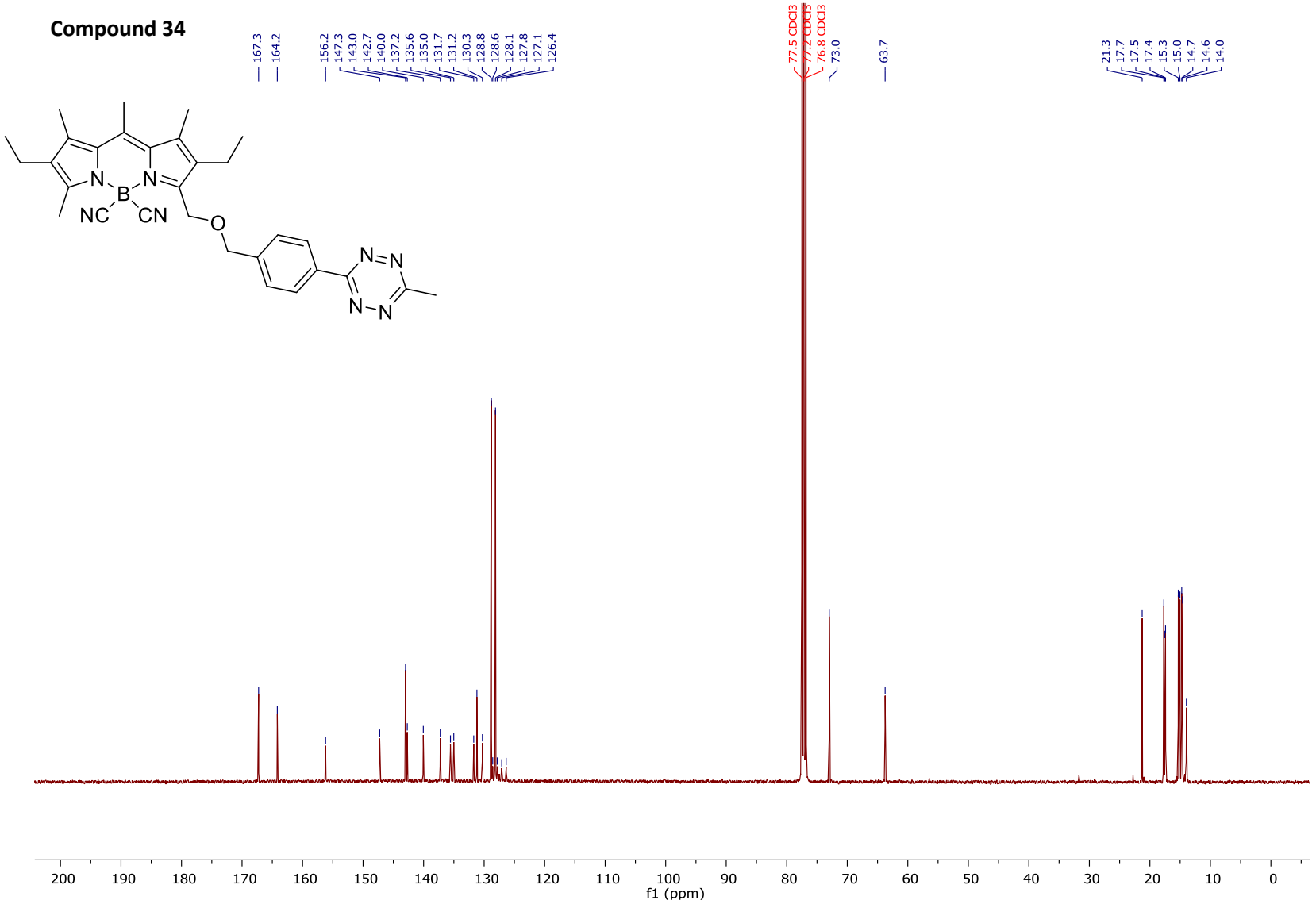
**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **33**

**Compound 34**



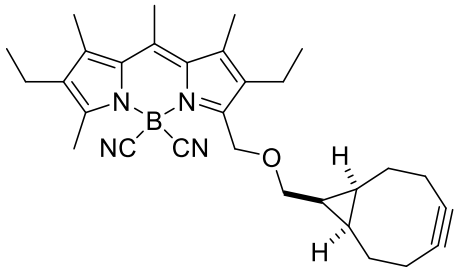

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **34**

**Compound 34**




**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **34**

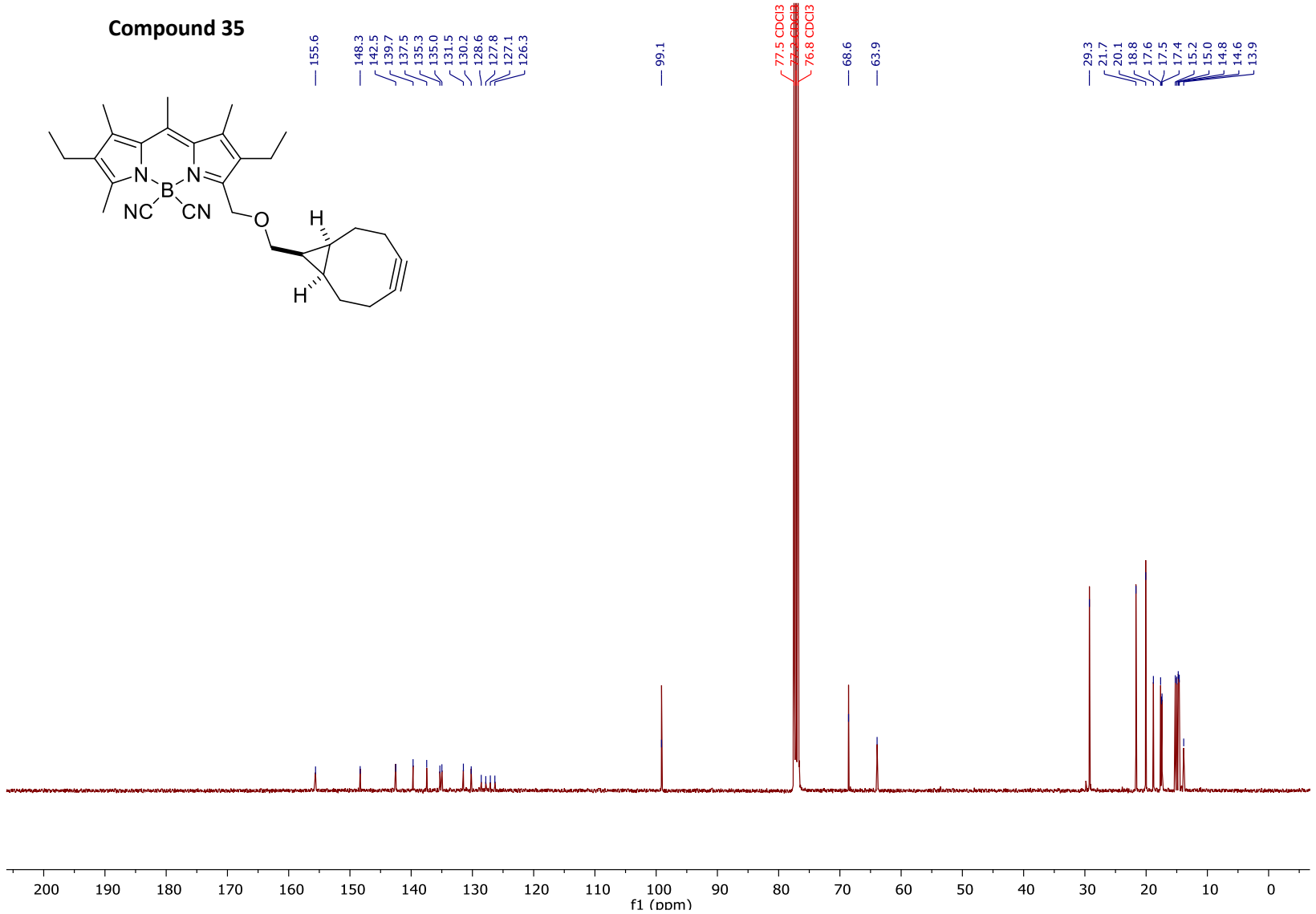
**Compound 35**





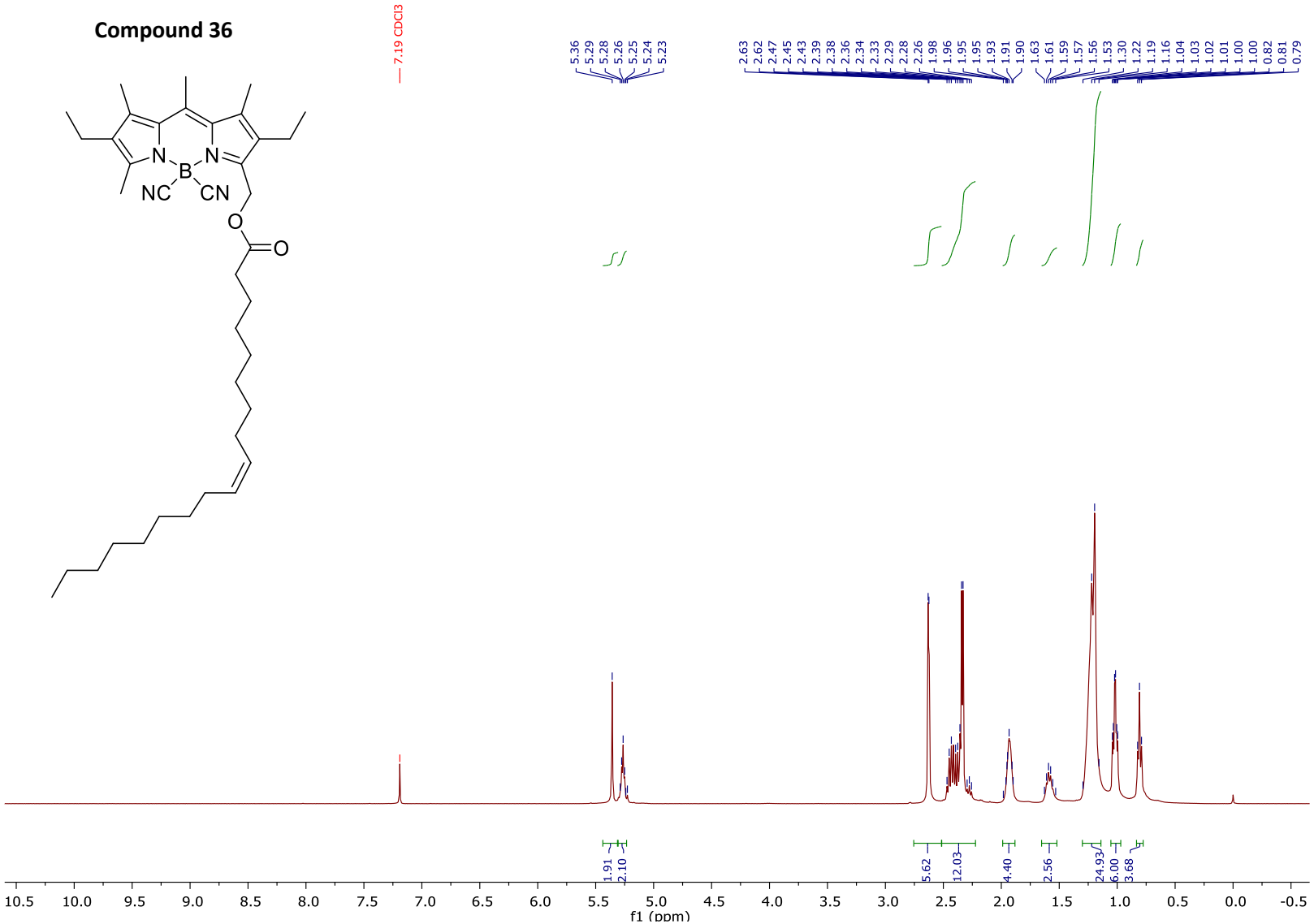


**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **35**

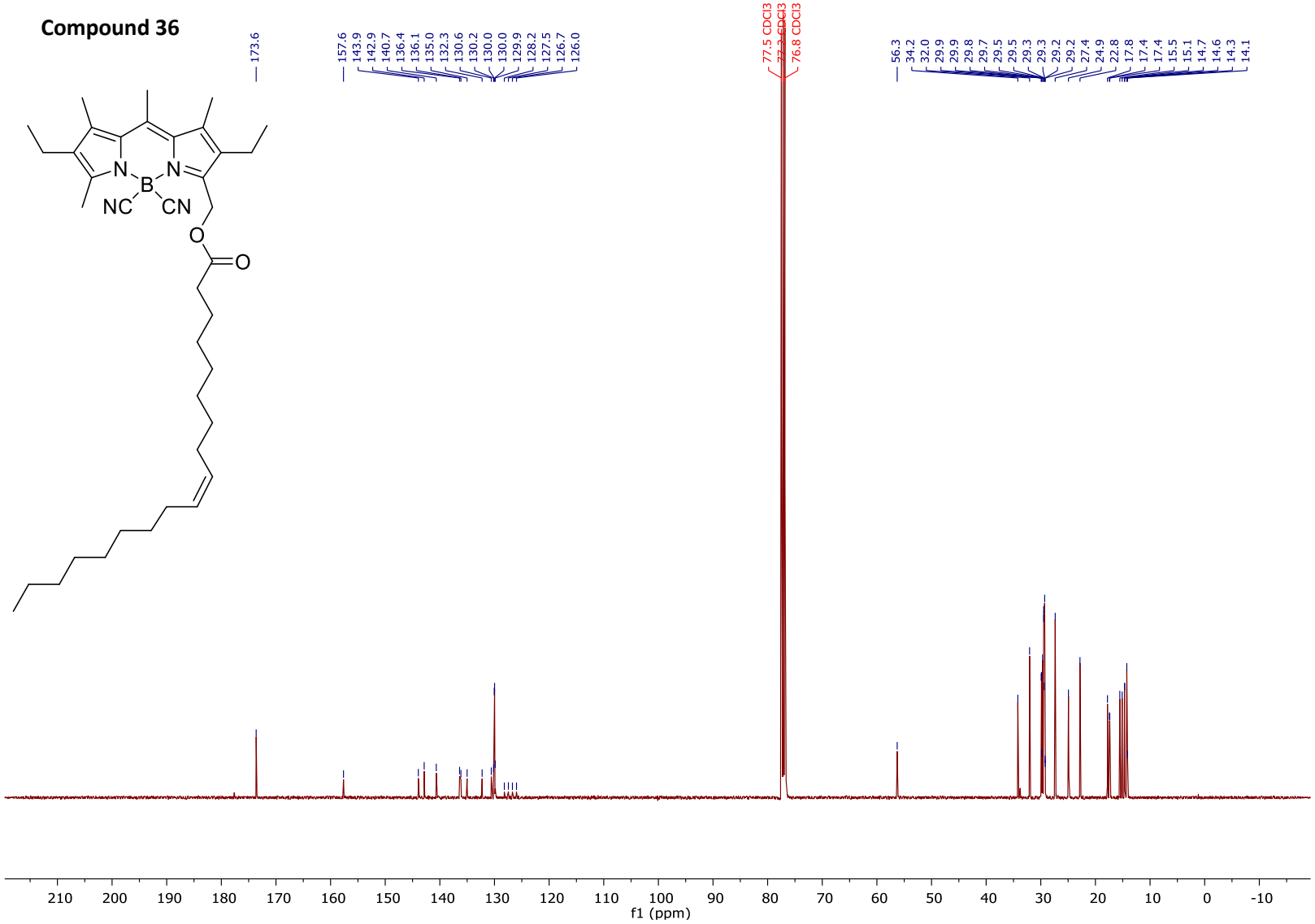



**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **35**

**Compound 36**

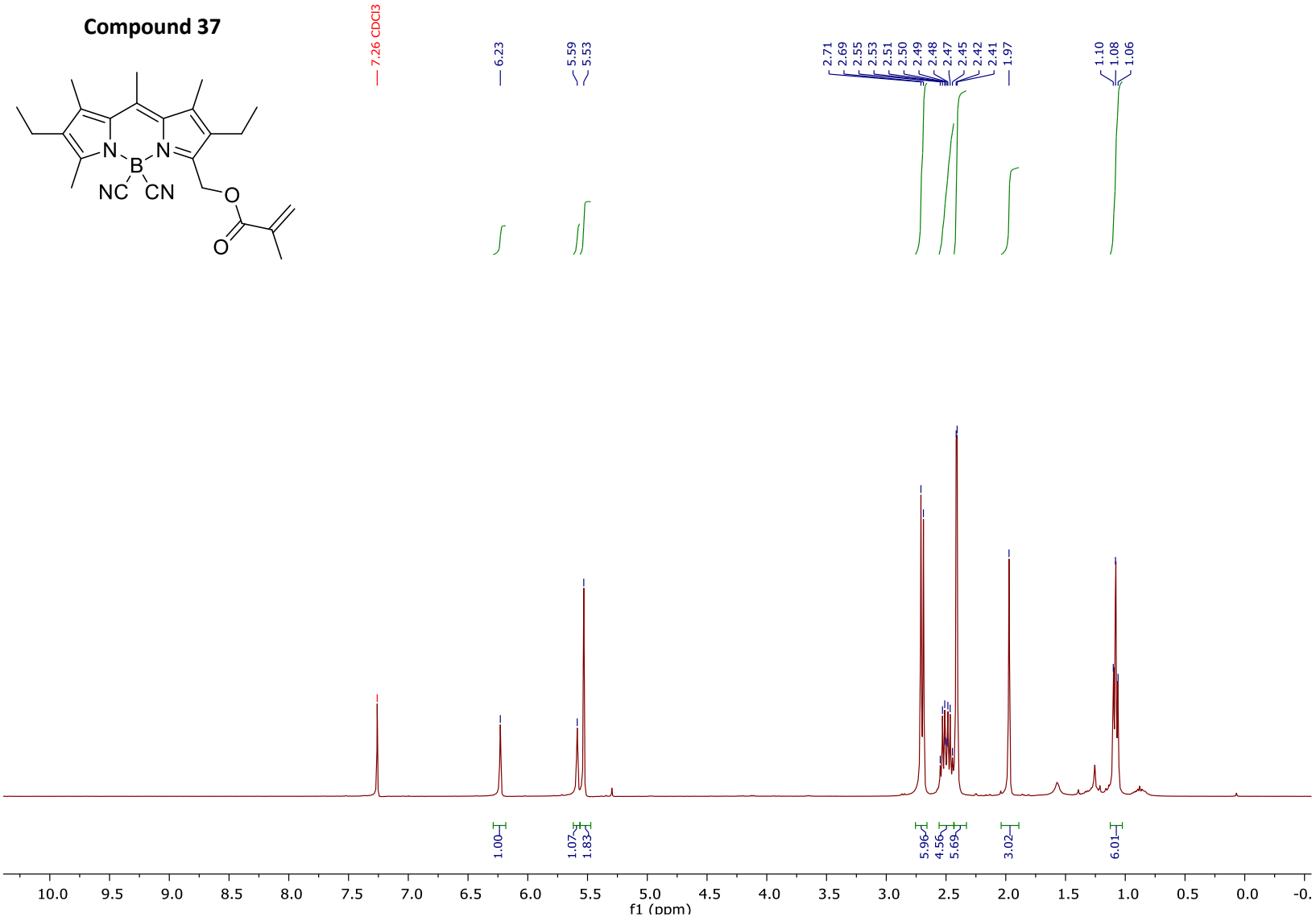



**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **36**



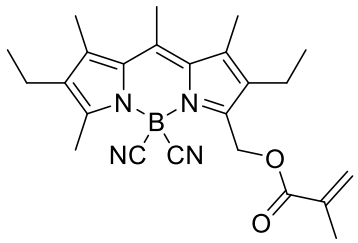

**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **36**

**Compound 37**




**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **37**

**Compound 37**

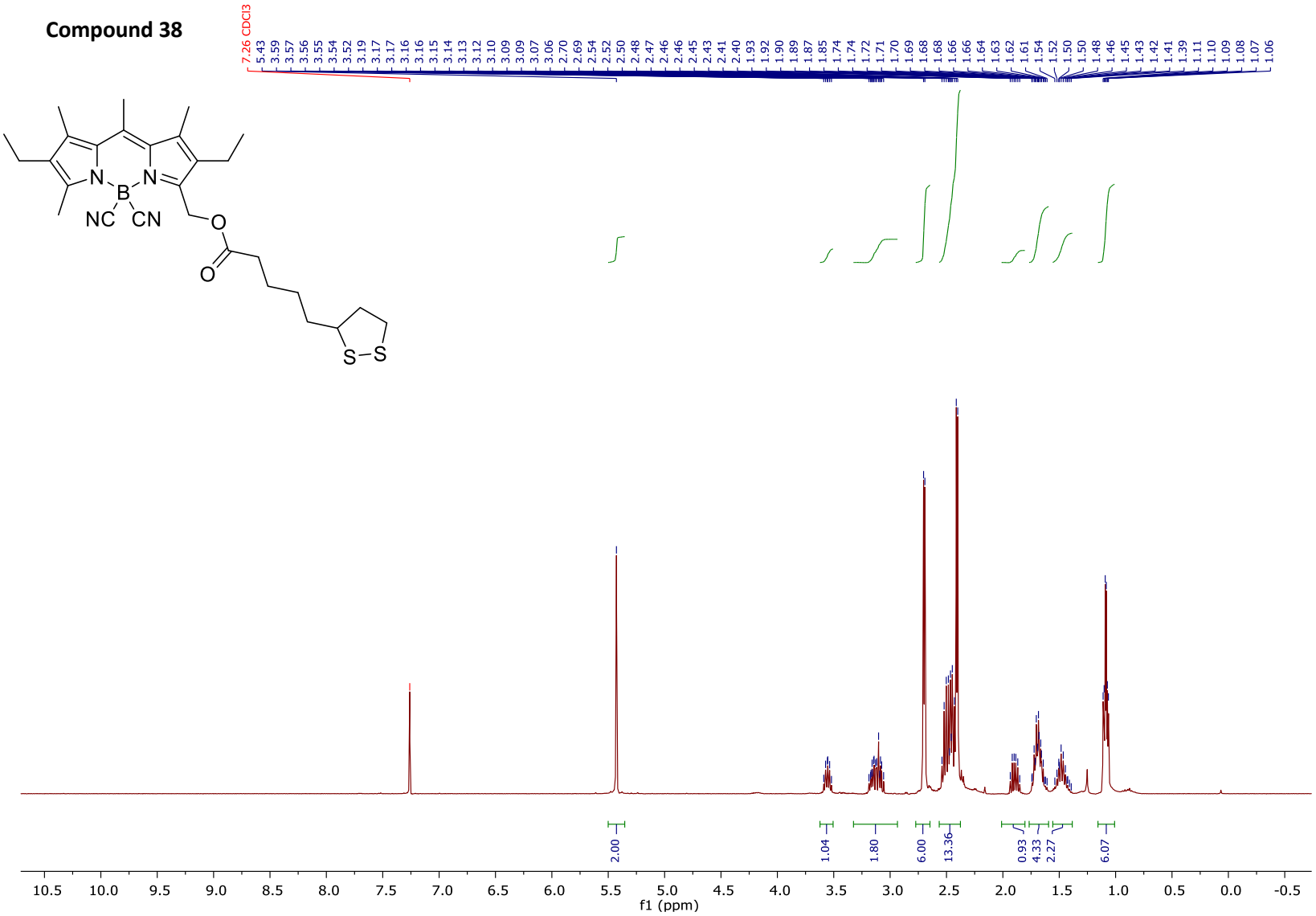




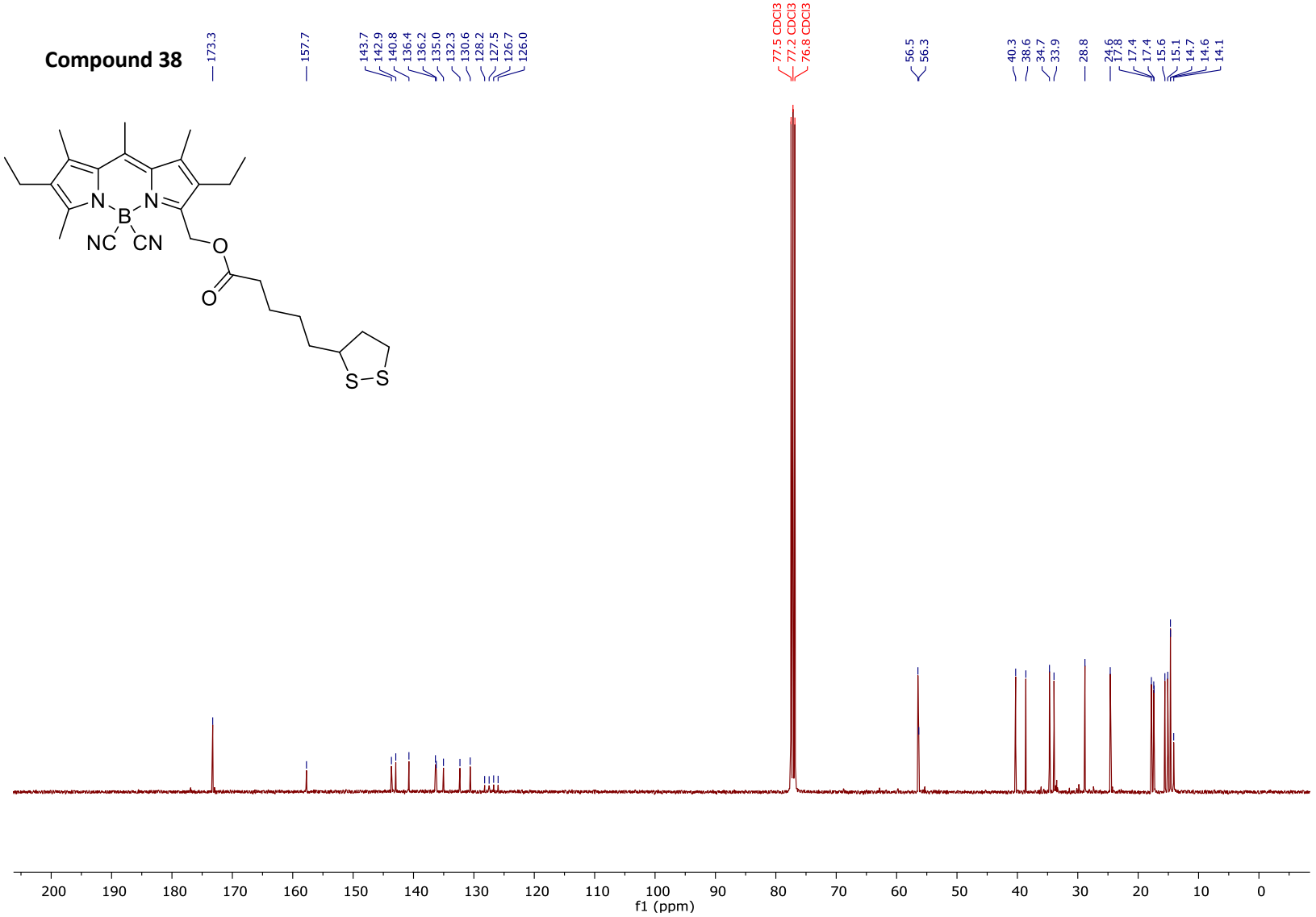


**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **37**

**Compound 38**

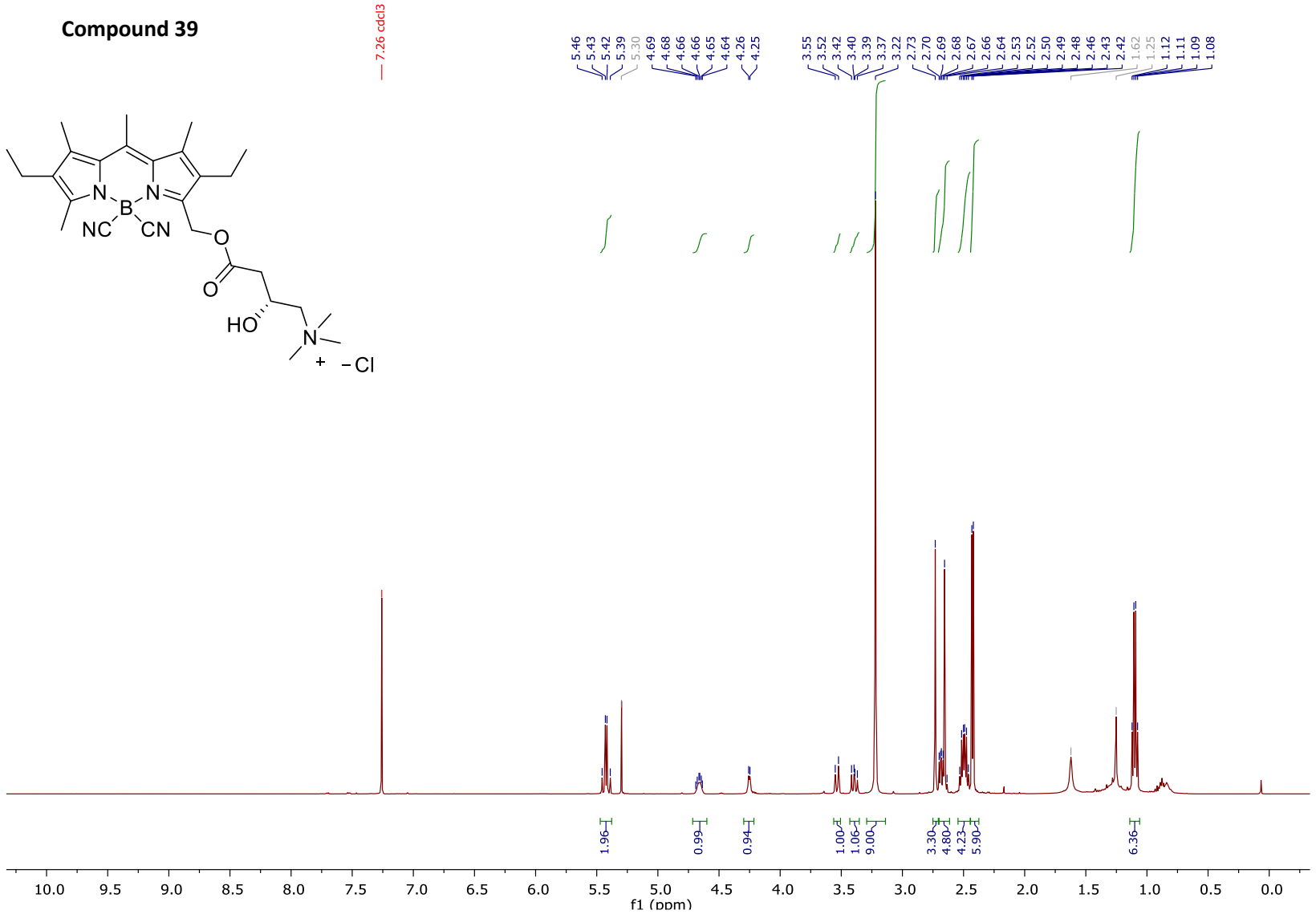



**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **38**



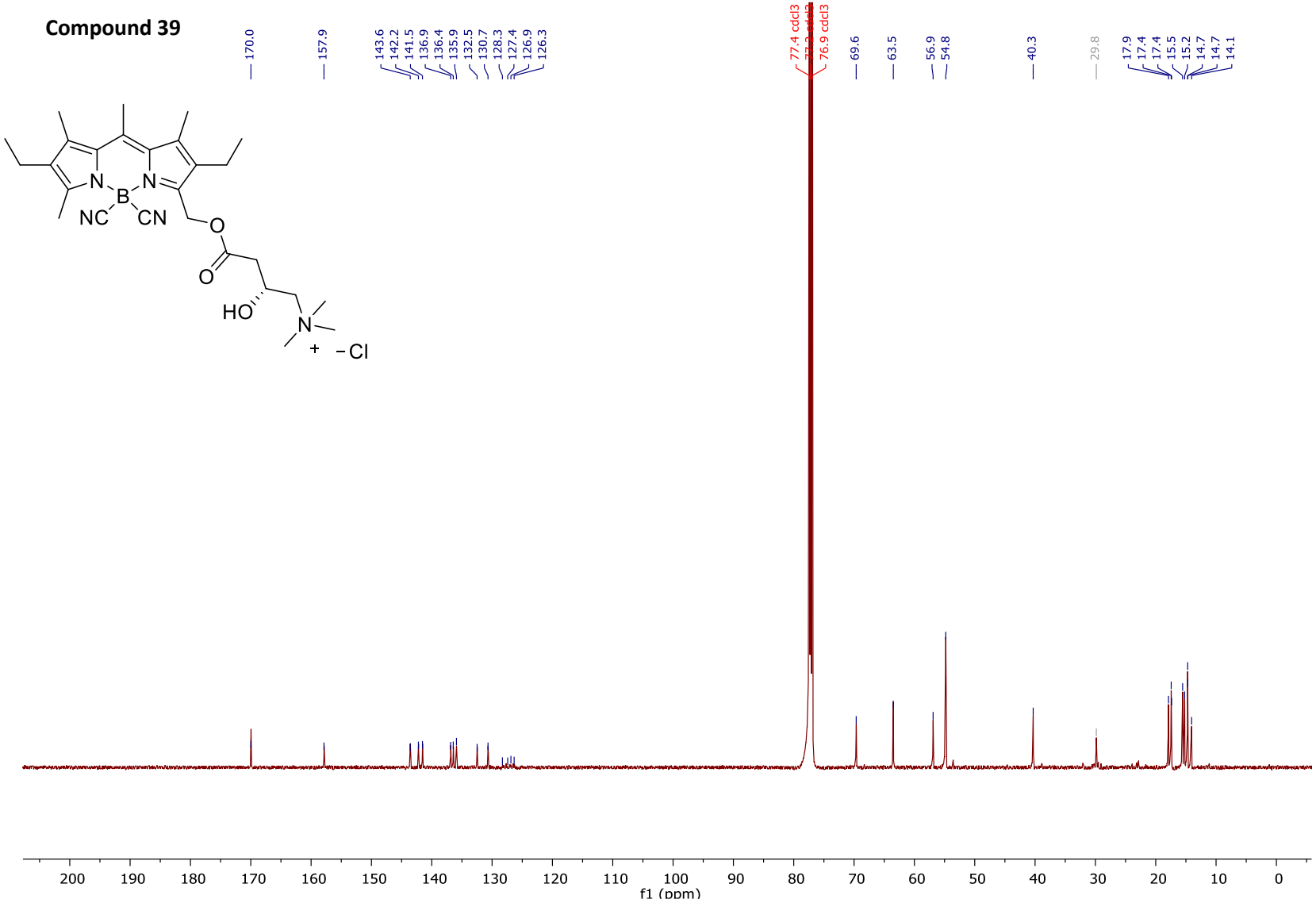

**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **38**

**Compound 39**



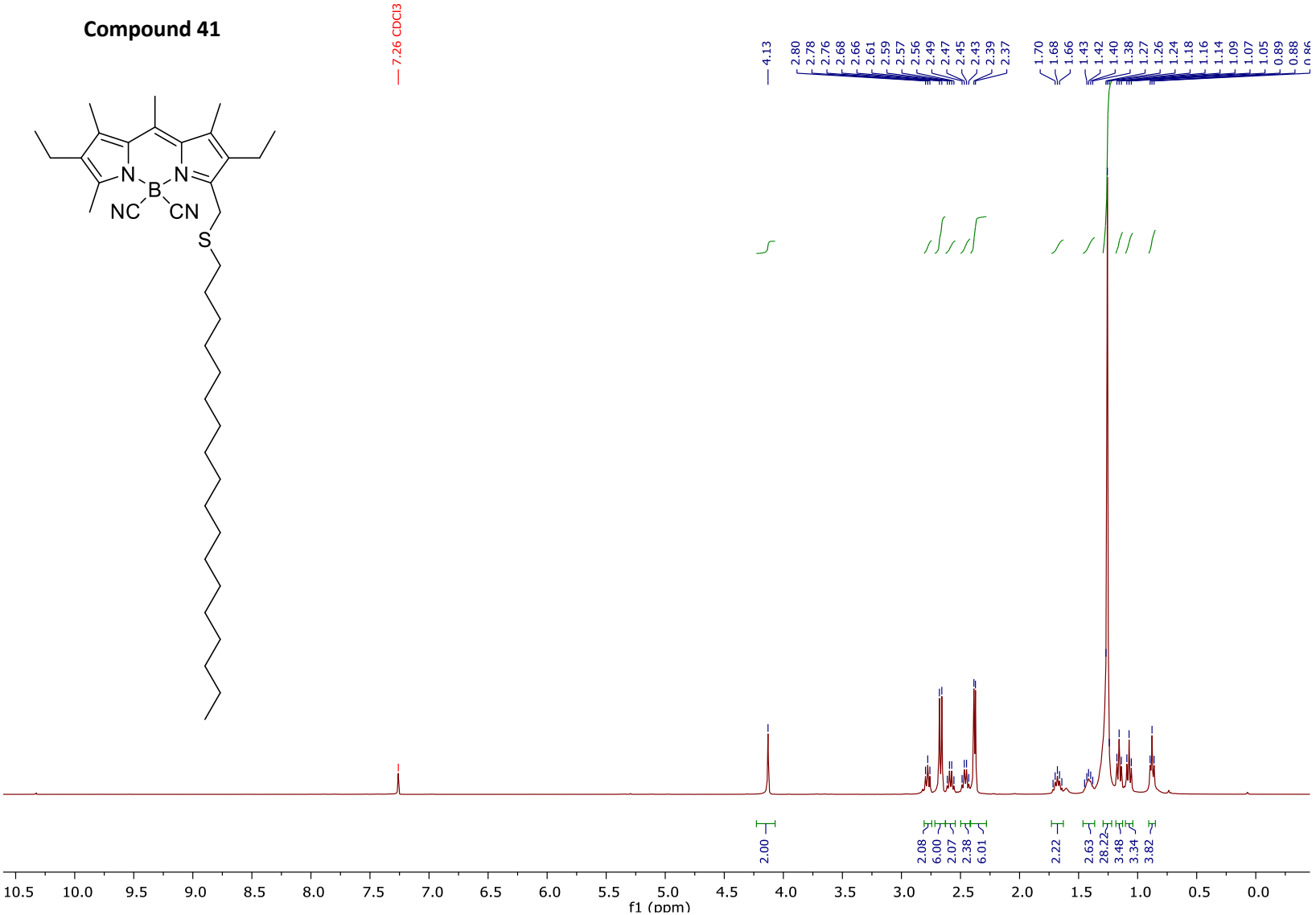

**$^1$H NMR** (500 MHz, $CDCl_3$) spectrum of compound **39**

**Compound 39**

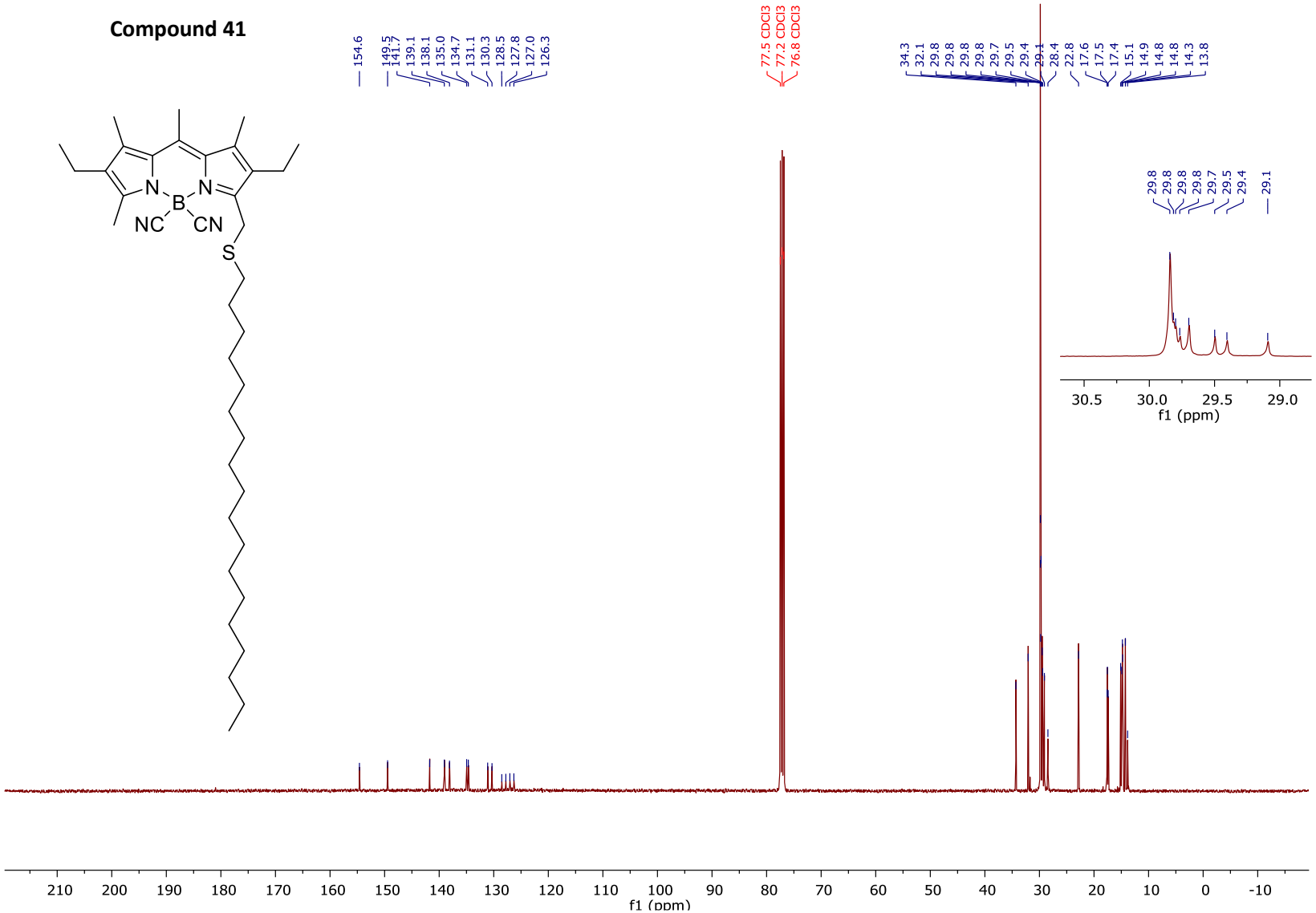



**$^{13}$C NMR** (125 MHz, $CDCl_3$) spectrum of compound 39

**Compound 41**

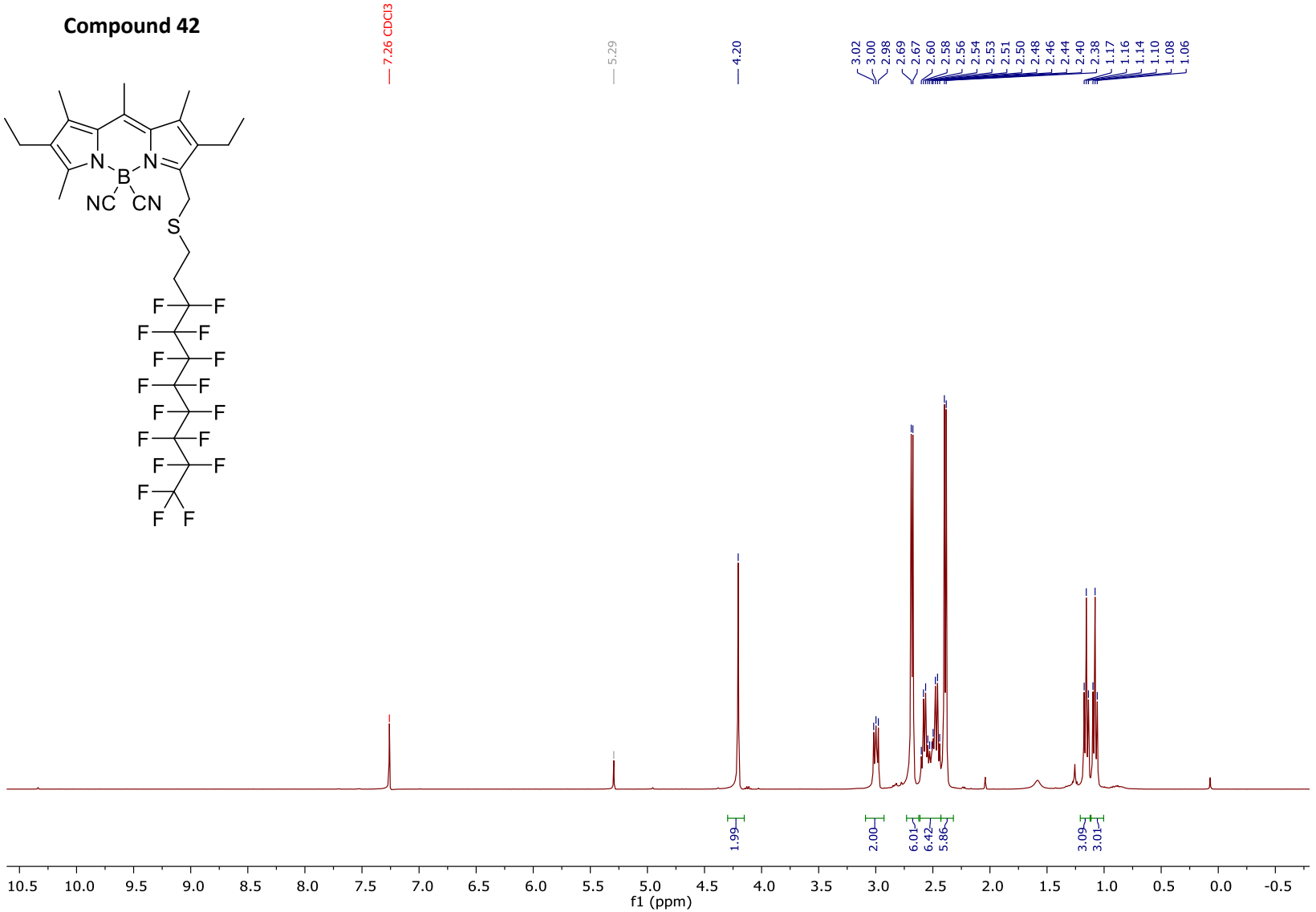



**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **41**



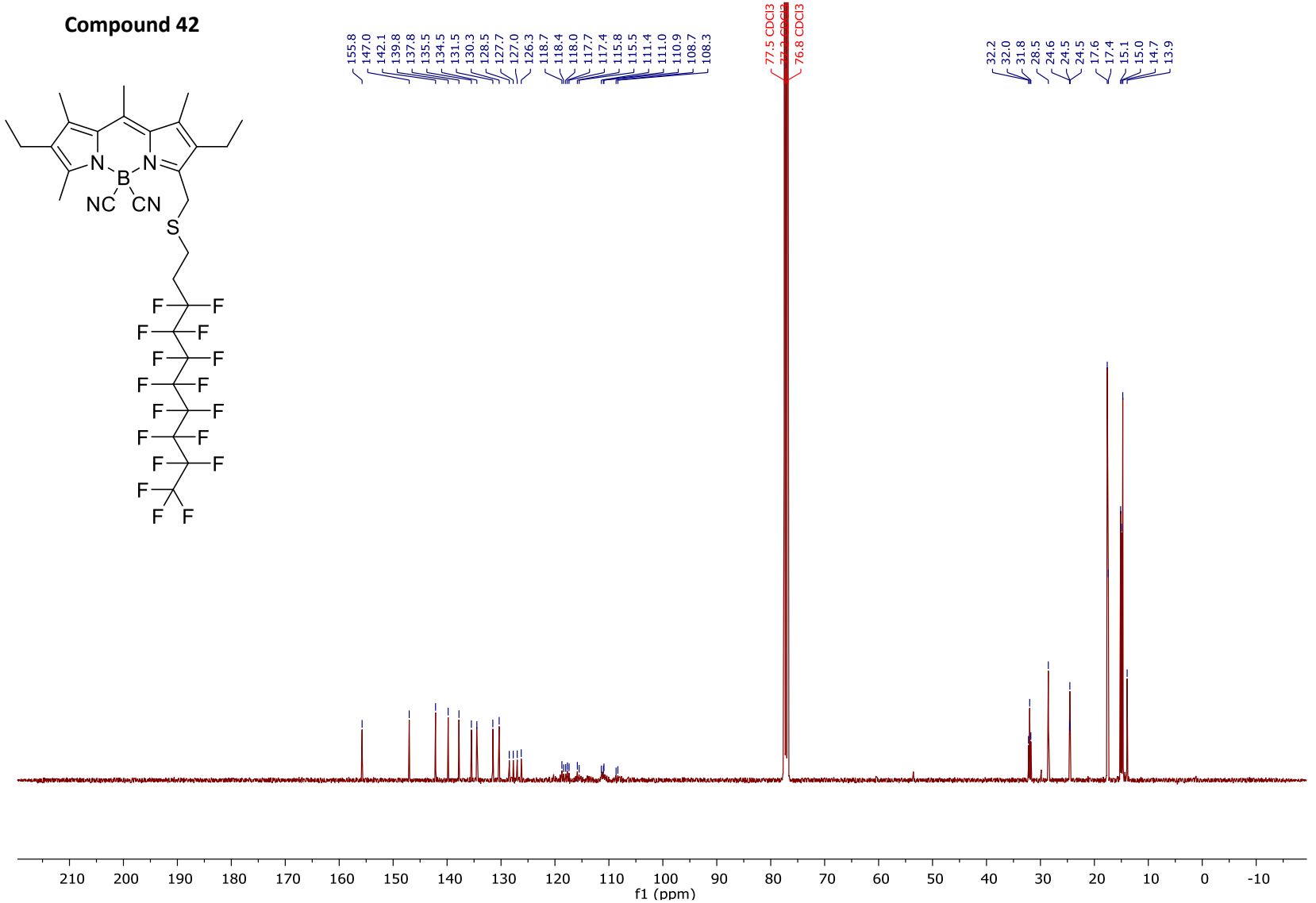

**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **41**

**Compound 42**



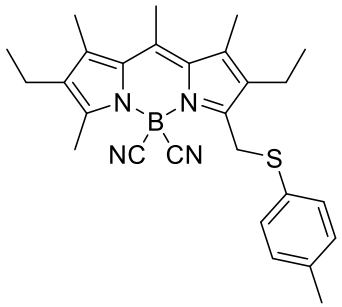

**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **42**

**Compound 42**




**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **42**

**Compound 43**

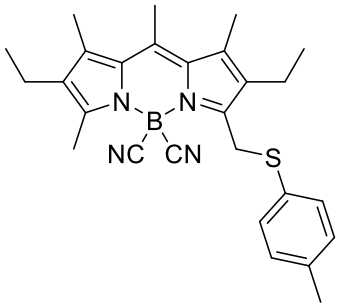






**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **43**

**Compound 43**

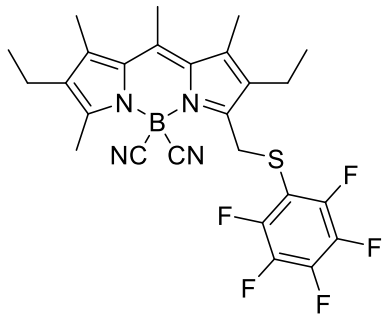






**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **43**

**Compound 44**

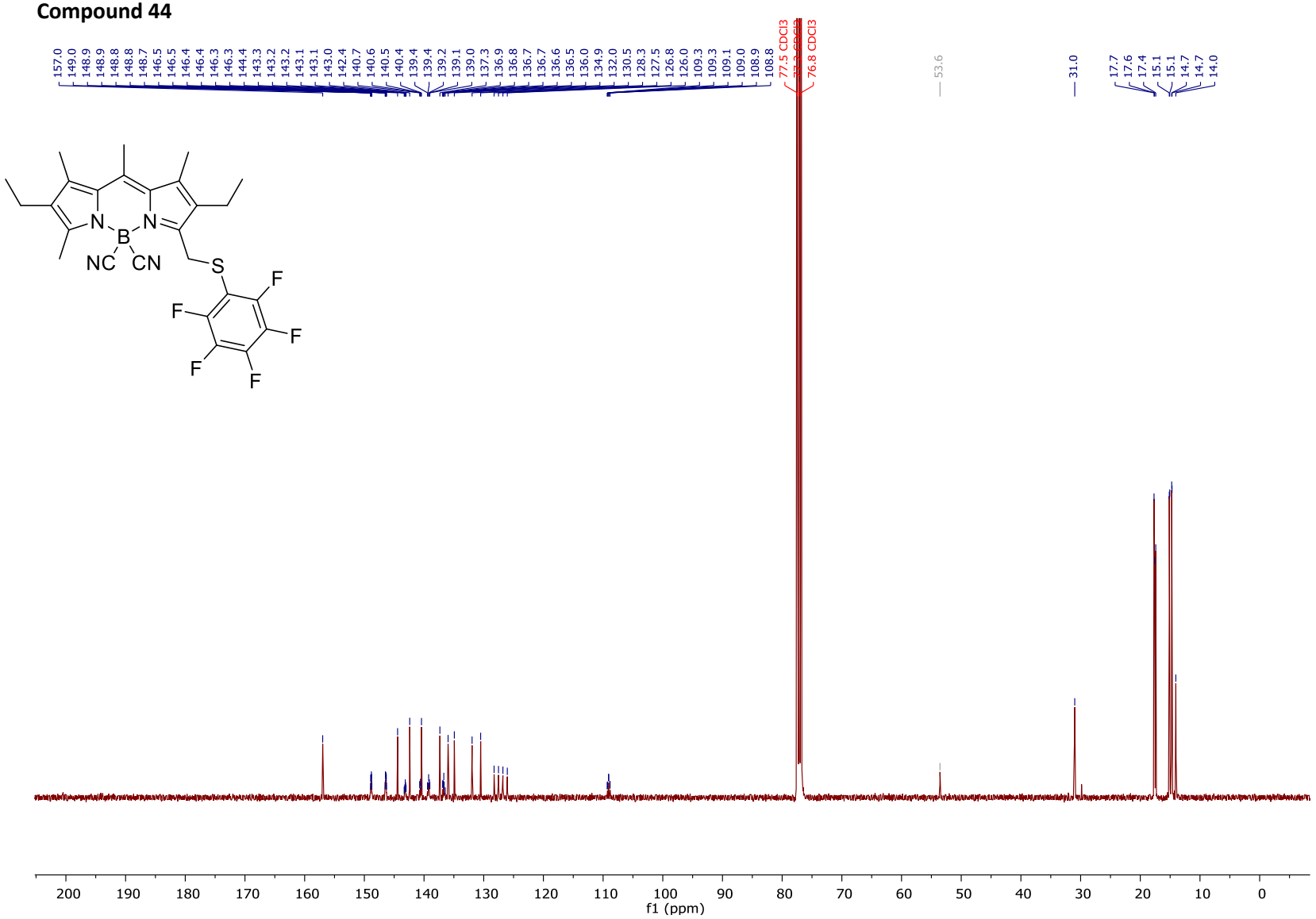






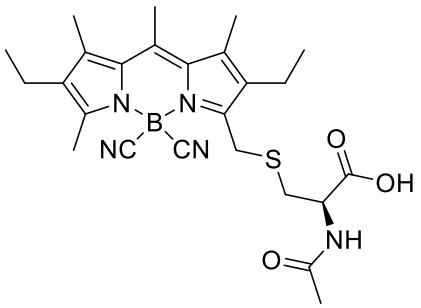
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **44**

**Compound 44**




**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **44**

**Compound 45**

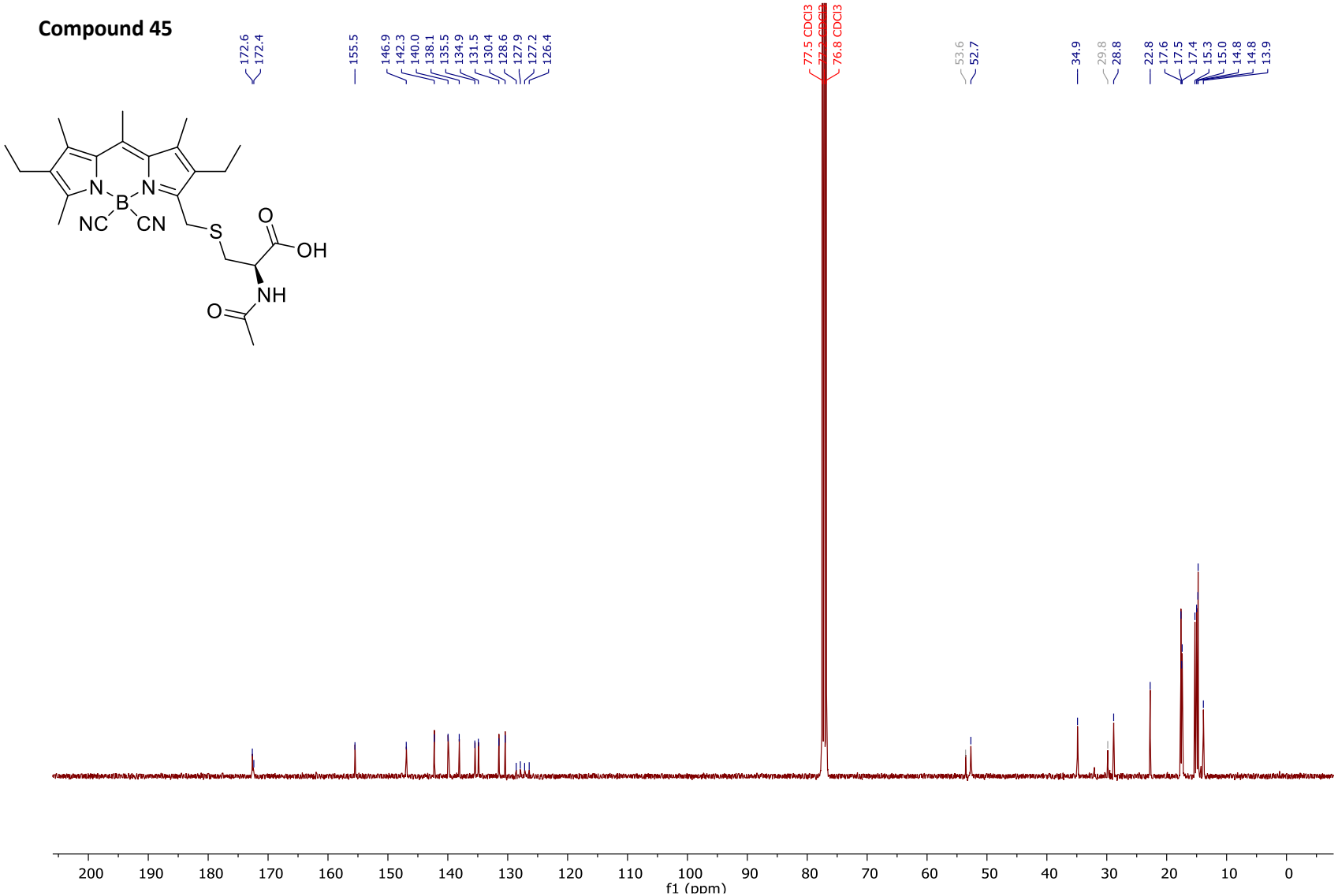






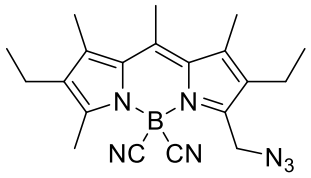
**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **45**

**Compound 45**




**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **45**

**Compound 46**







**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **46**

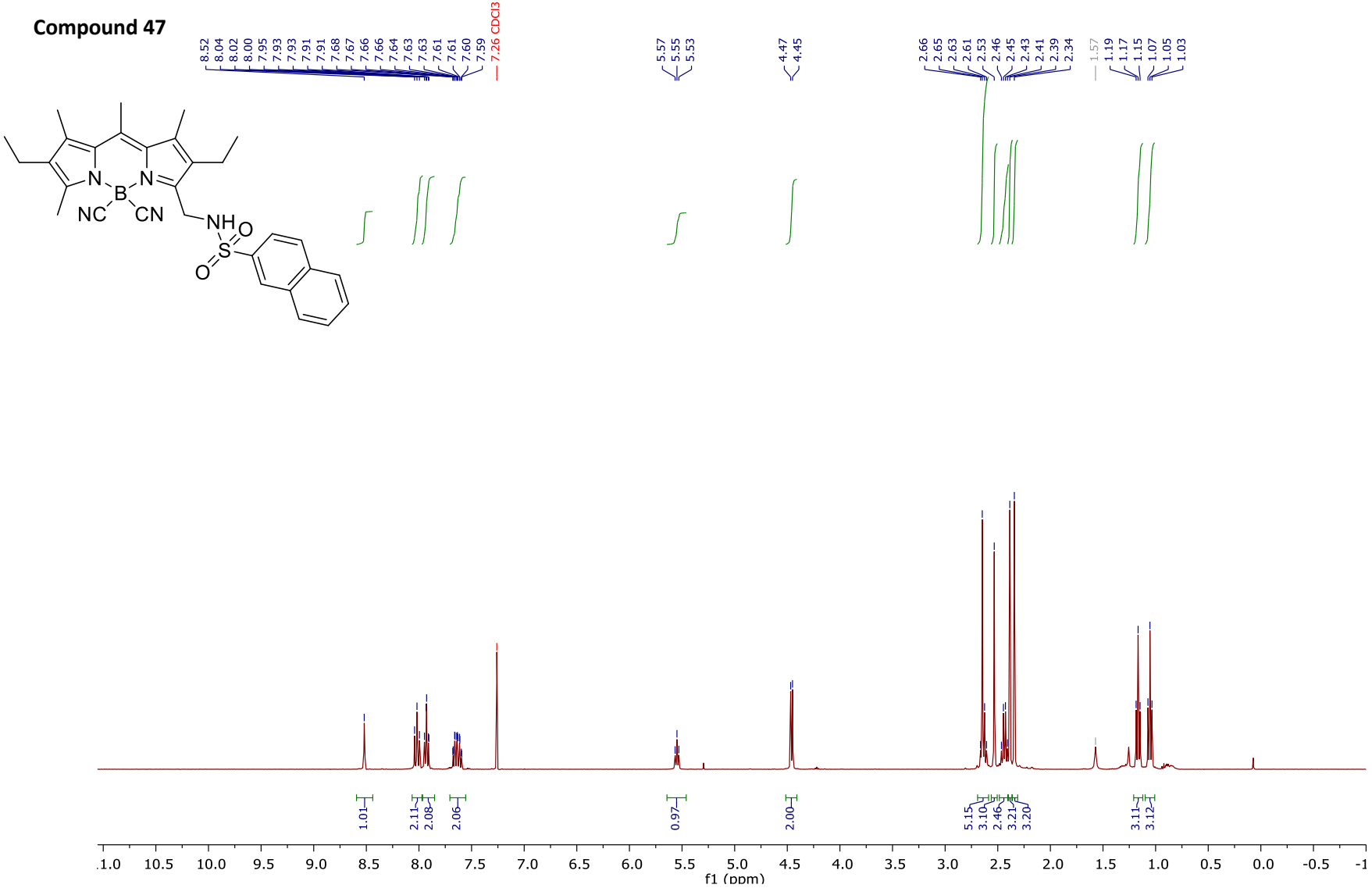
**Compound 46**





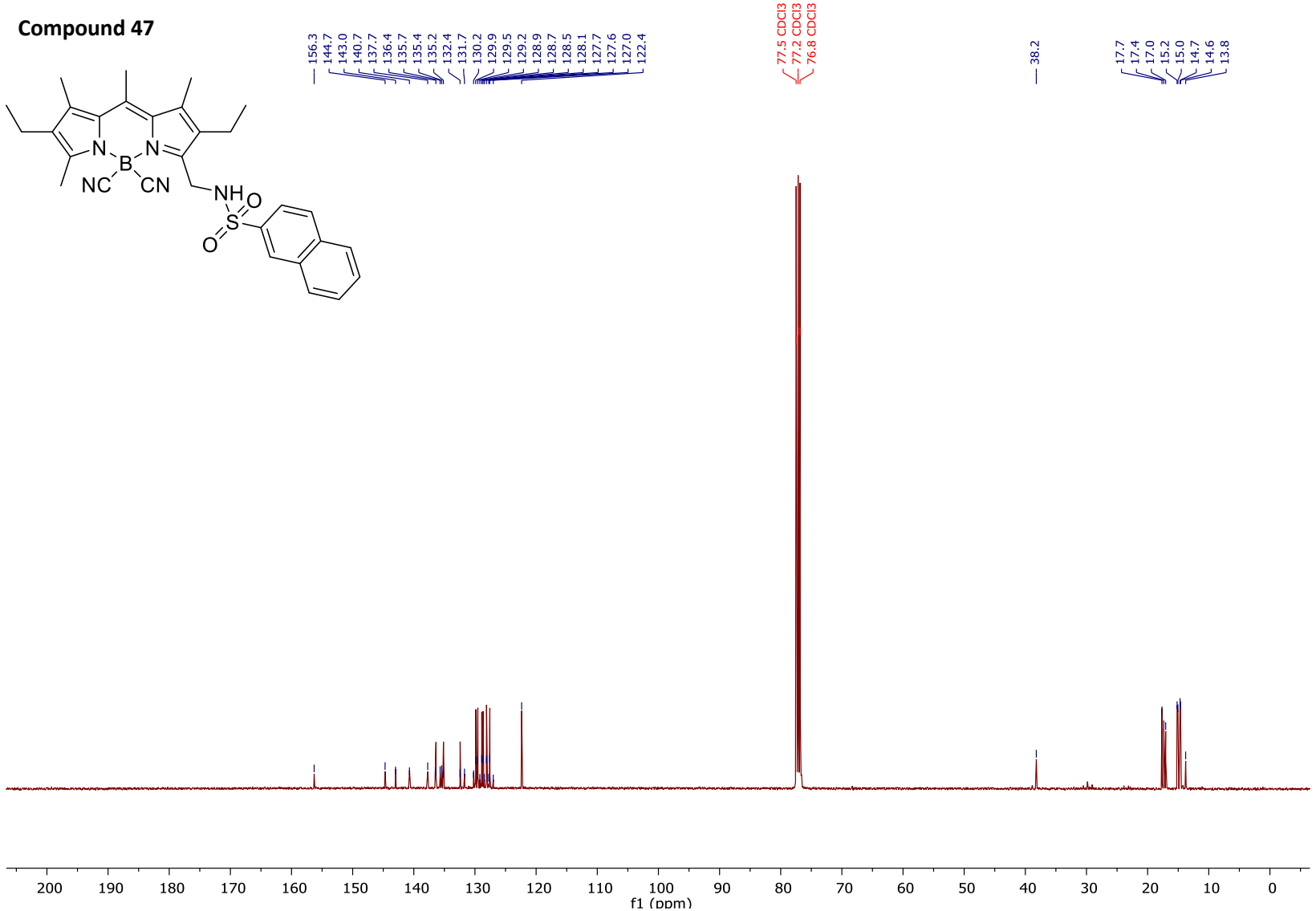
**$^{13}$C NMR** (400 MHz, $CDCl_3$) spectrum of compound **46**

**Compound 47**



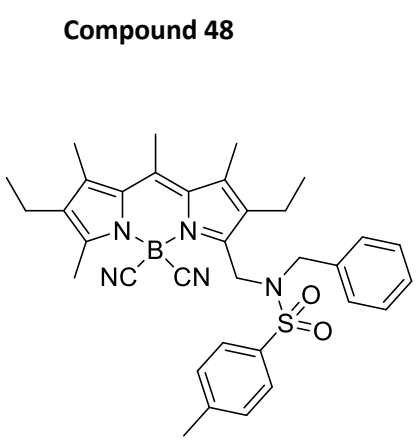

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **47**

**Compound 47**




**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **47**

**Compound 48**

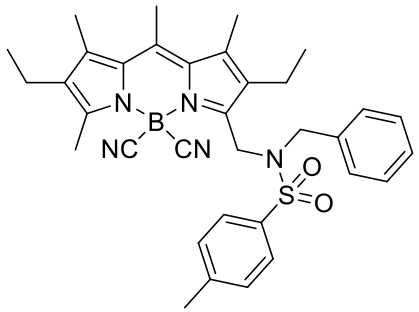






**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **48**

**Compound 48**

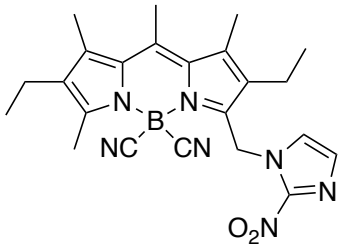






**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **48**

**Compound 49**

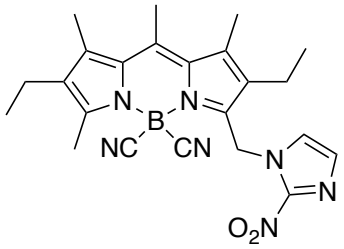






**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **49**

**Compound 49**

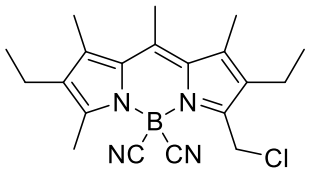






**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **49**

**Compound 50**







**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **50**

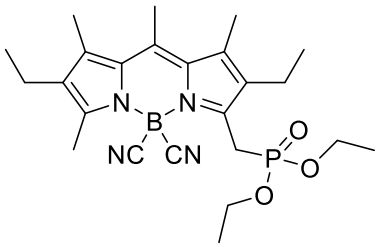
**Compound 50**





**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **50**

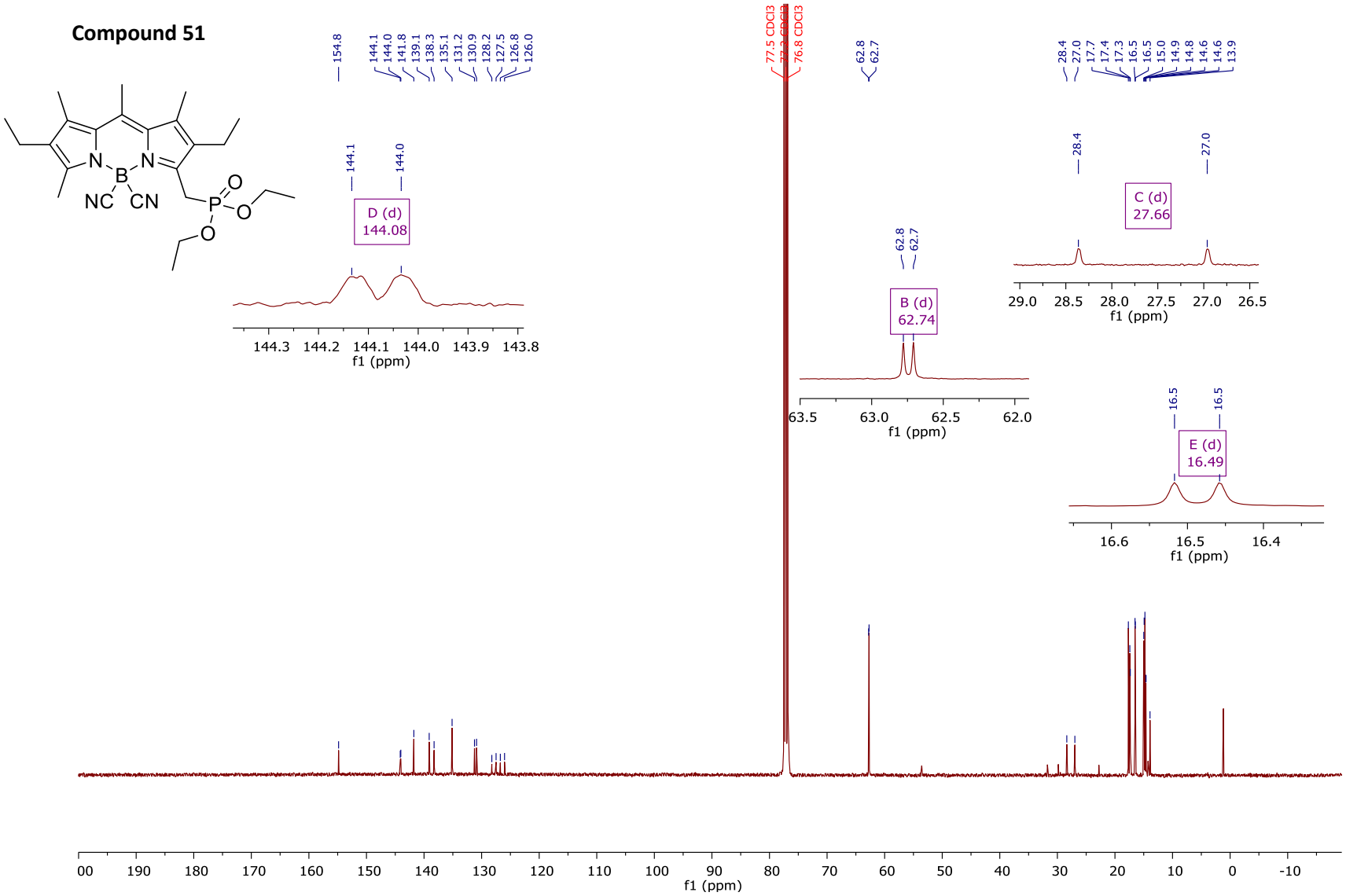
**Compound 51**





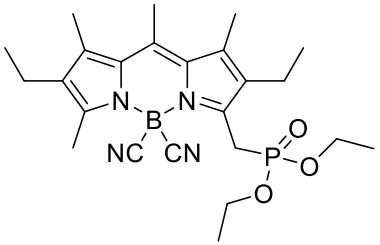


**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **51**




**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **51**

**Compound 51**

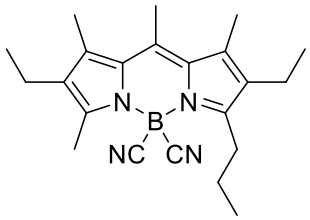






**$^{31}$P NMR** (162 MHz, $CDCl_3$) spectrum of compound **51**

**Compound 52**

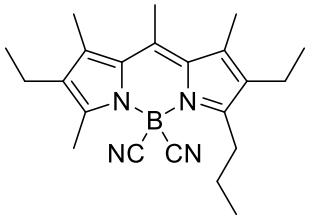






**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **52**

**Compound 52**

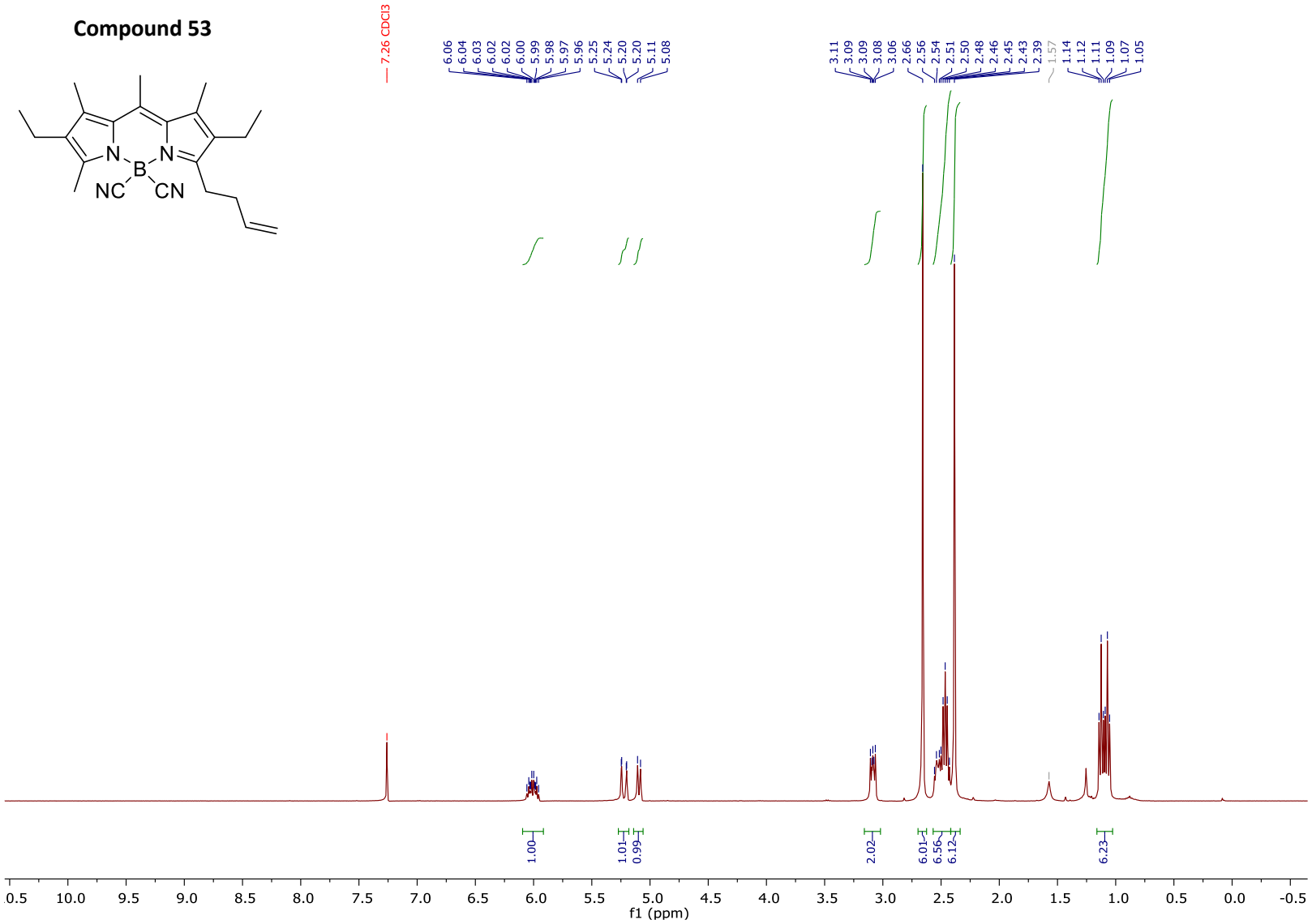






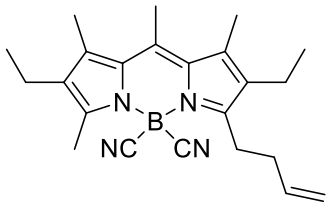
**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **52**

**Compound 53**




**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **53**

**Compound 53**

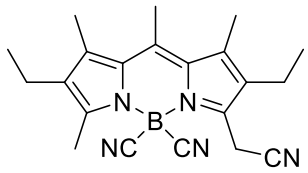






**$^{1}$H NMR** (100 MHz, $CDCl_3$) spectrum of compound **53**

**Compound 54**







**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **54**

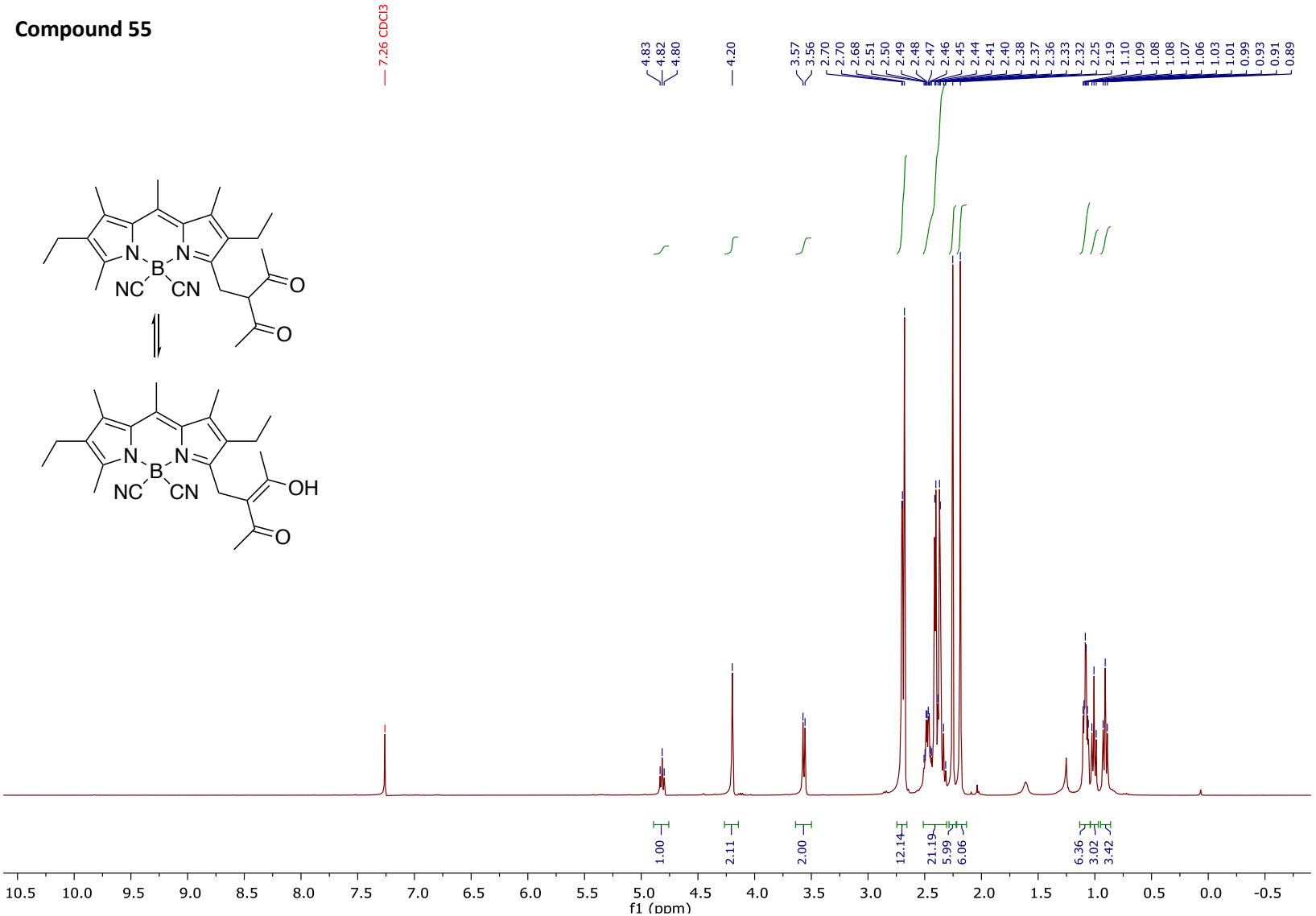
**Compound 54**





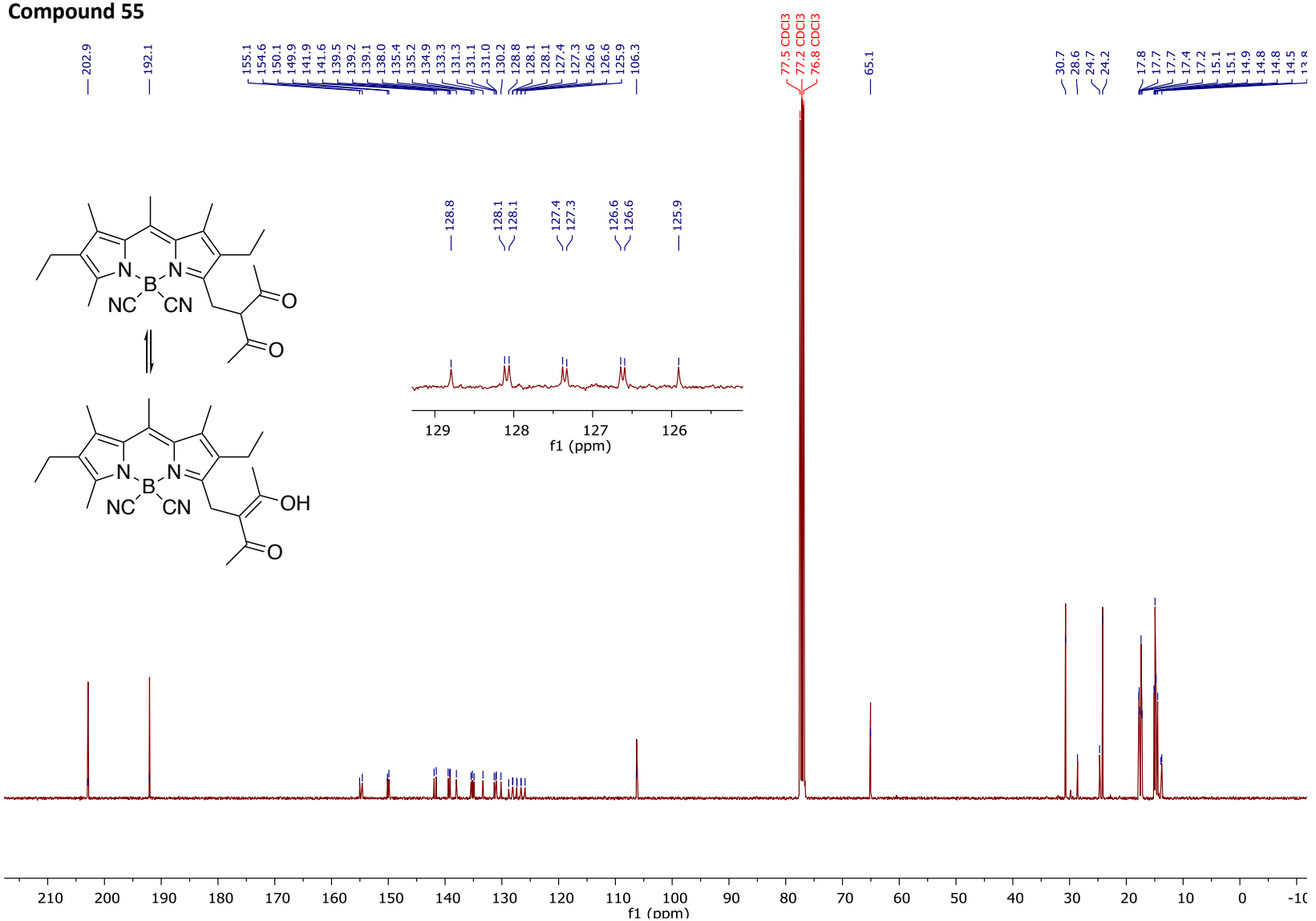
**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **54**

**Compound 55**



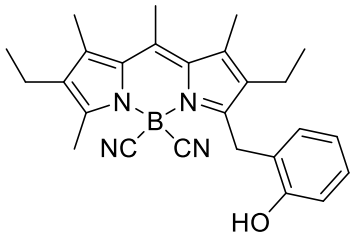

**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **55**

**Compound 55**




**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **55**

**Compound 56**

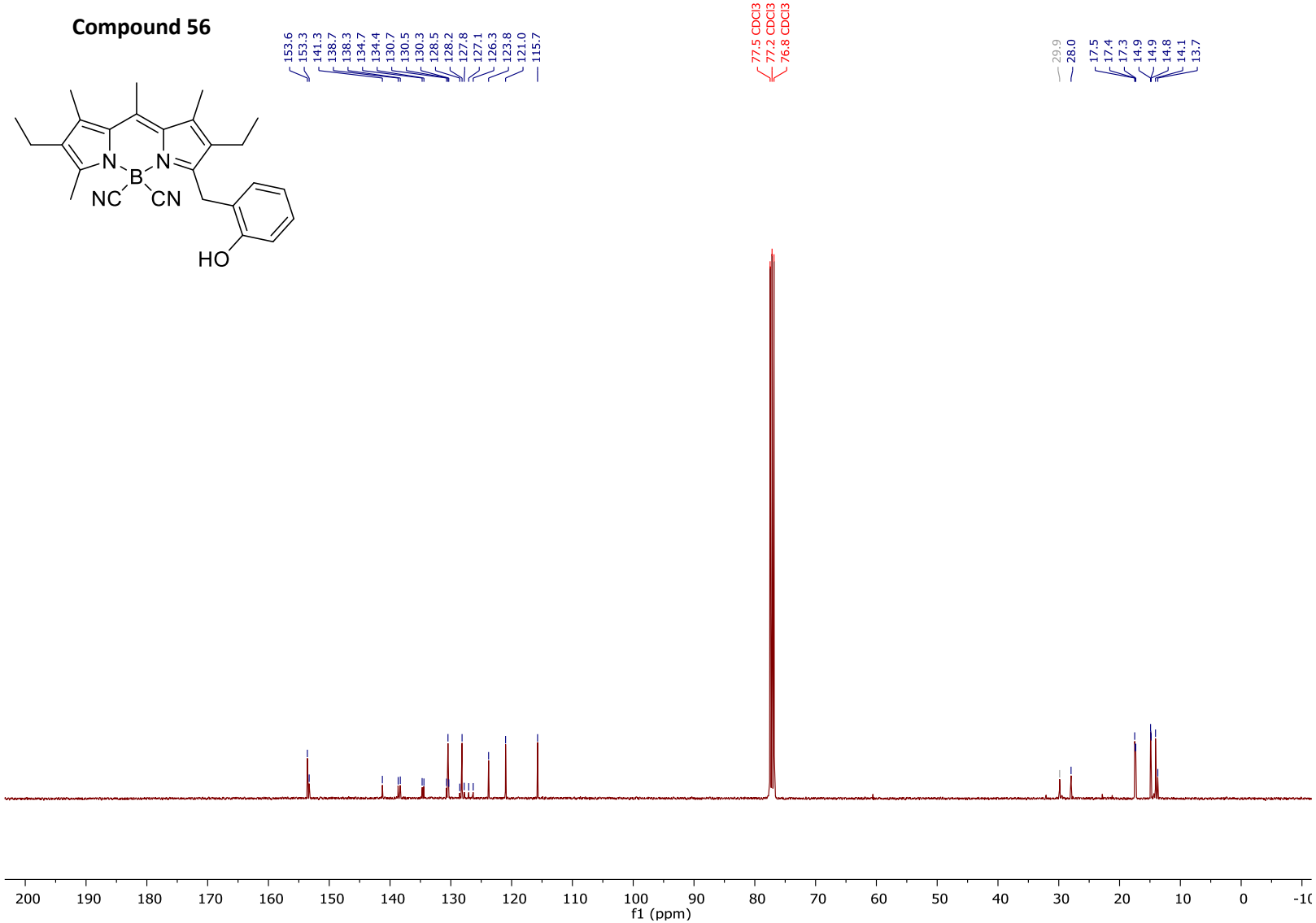






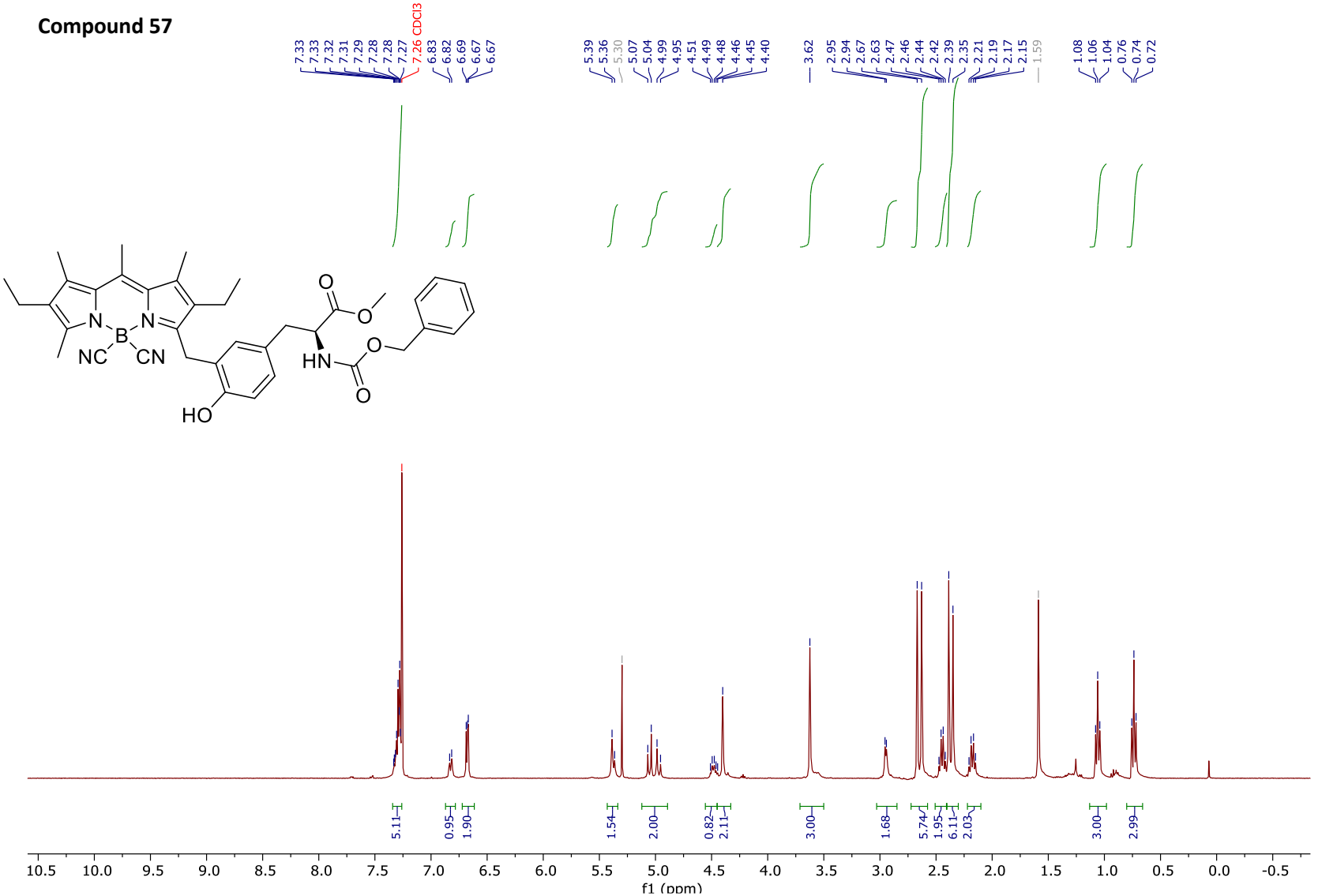
**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **56**

**Compound 56**



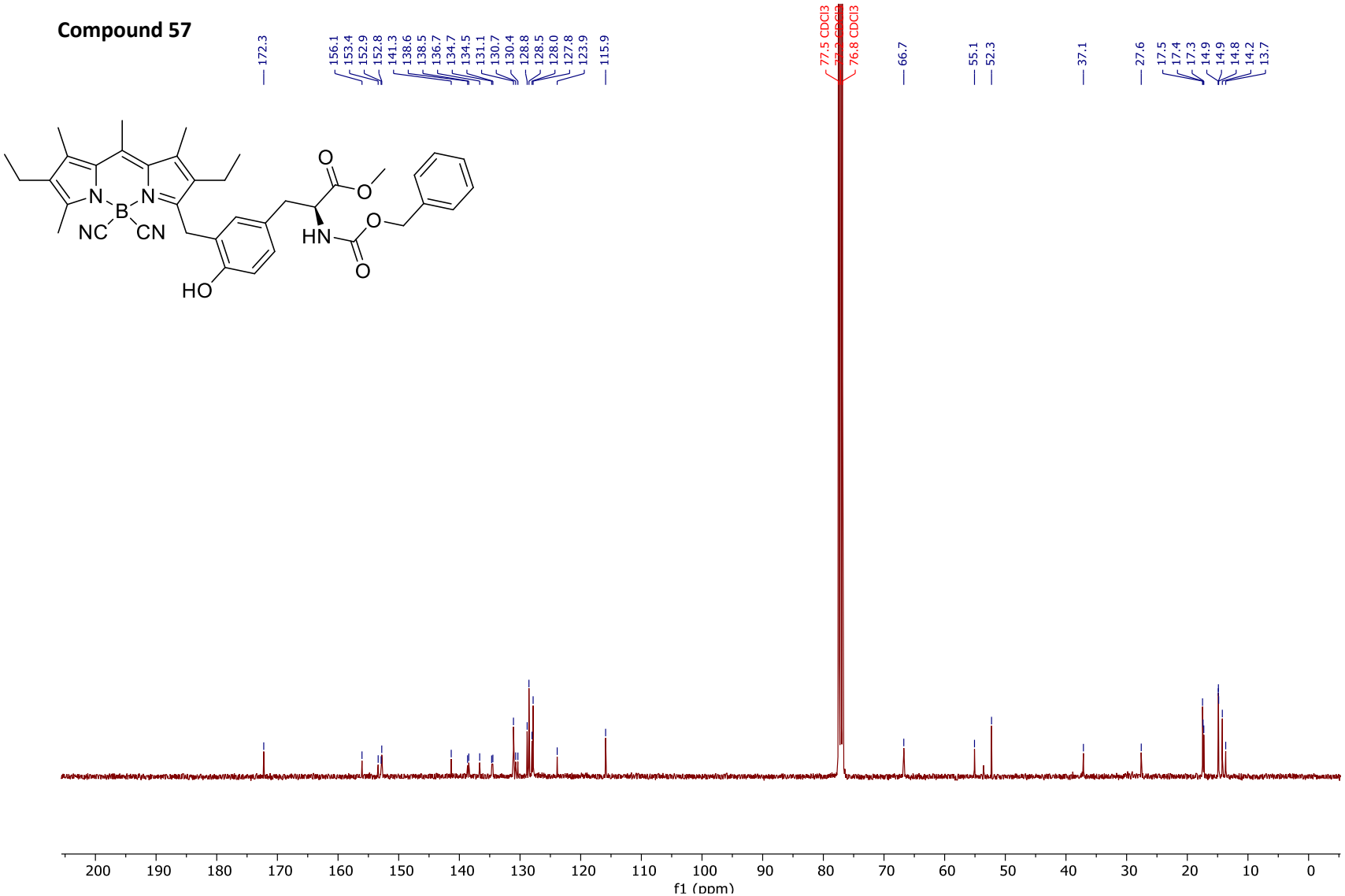

**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **56**

**Compound 57**



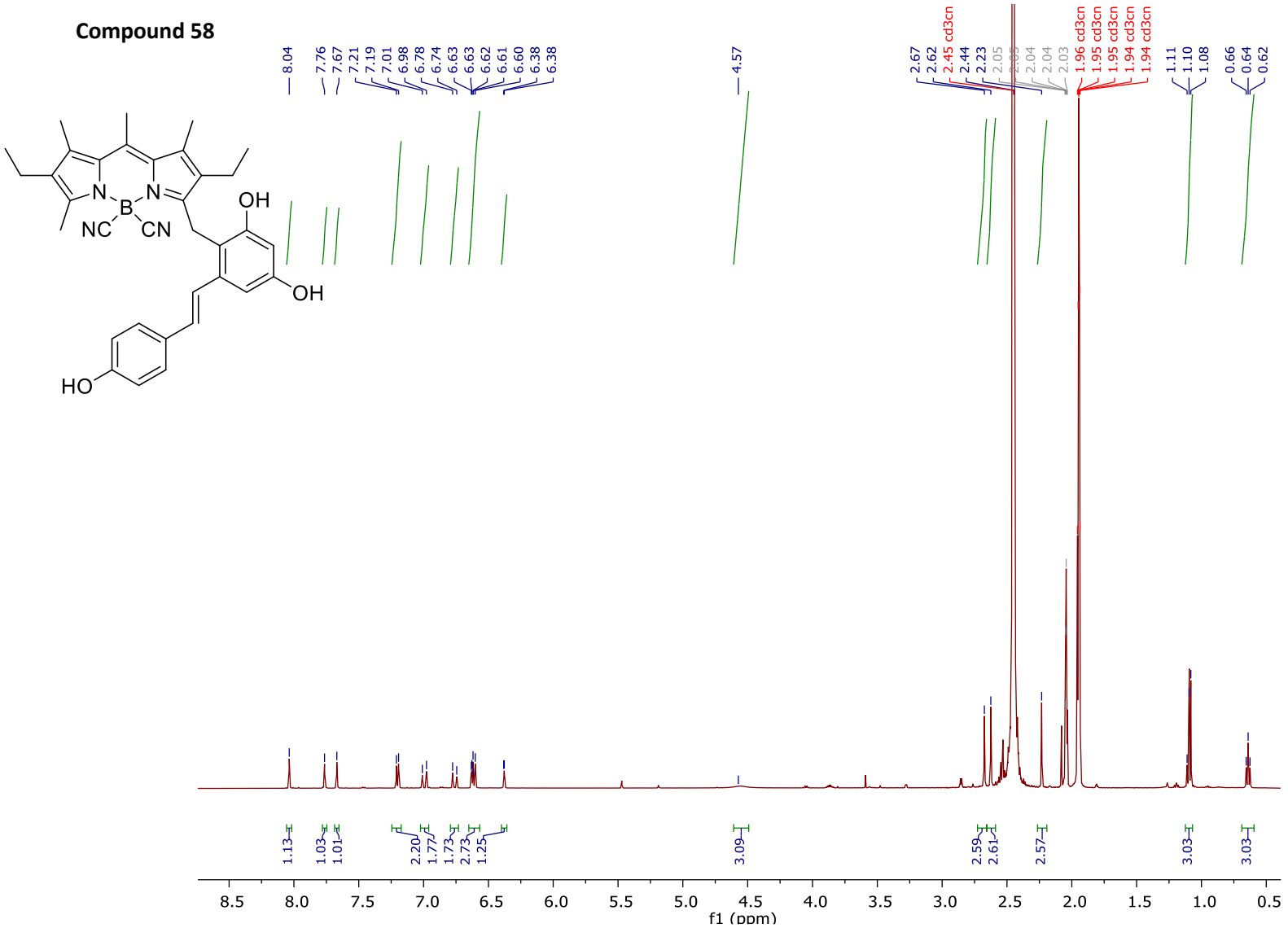

**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **57**

**Compound 57**



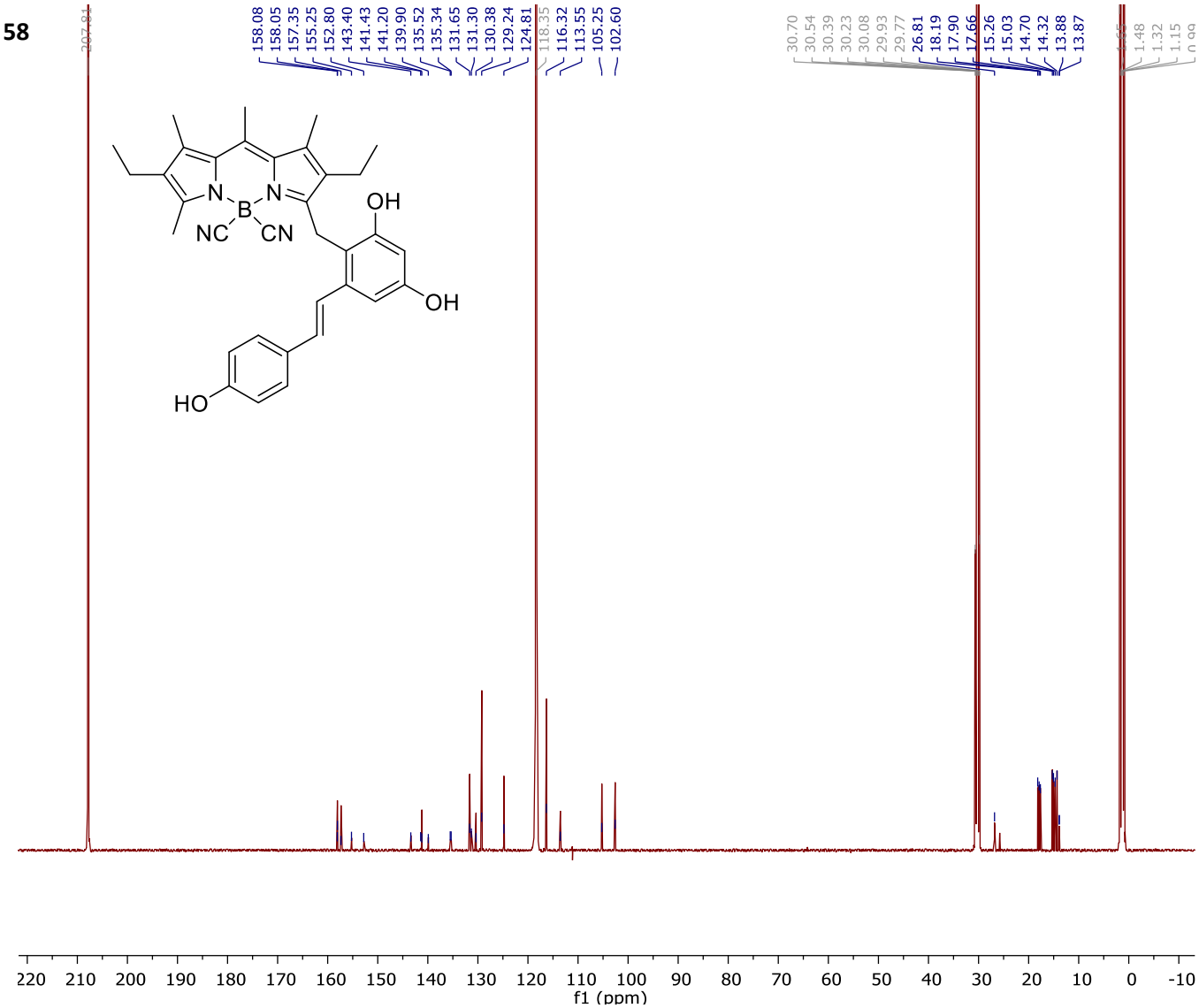

**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **57**

**Compound 58**



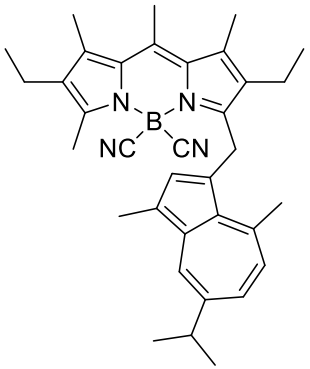

**$^{1}$H NMR** (500 MHz, $CD_3CN/CD_3COCD_3$ mixtured 6:1) spectrum of compound **58**

**Compound 58**




**$^{13}$C NMR** (125 MHz, $CD_3CN/CD_3COCD_3$ mixtured 6:1) spectrum of compound **58**

**Compound 59**

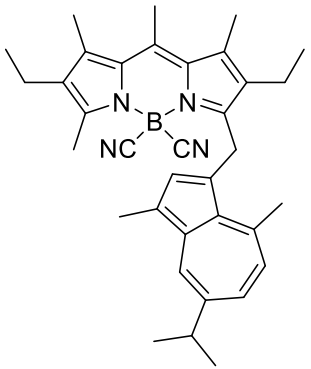






**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **59**

**Compound 59**

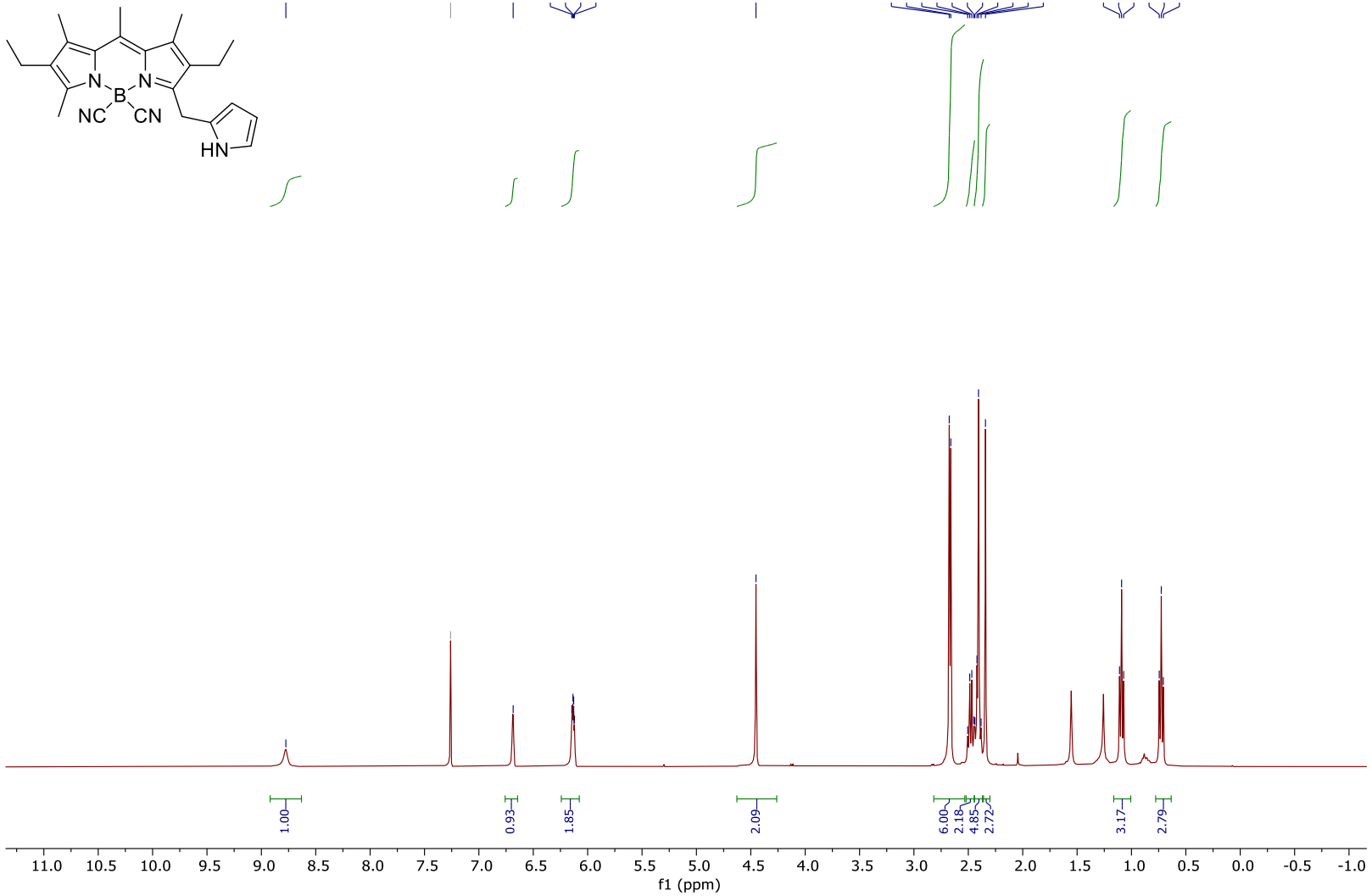






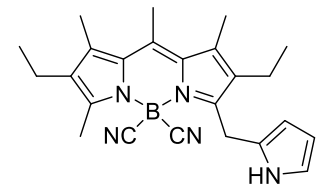
**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **59**

**Compound 60**




**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **60**

**Compound 60**

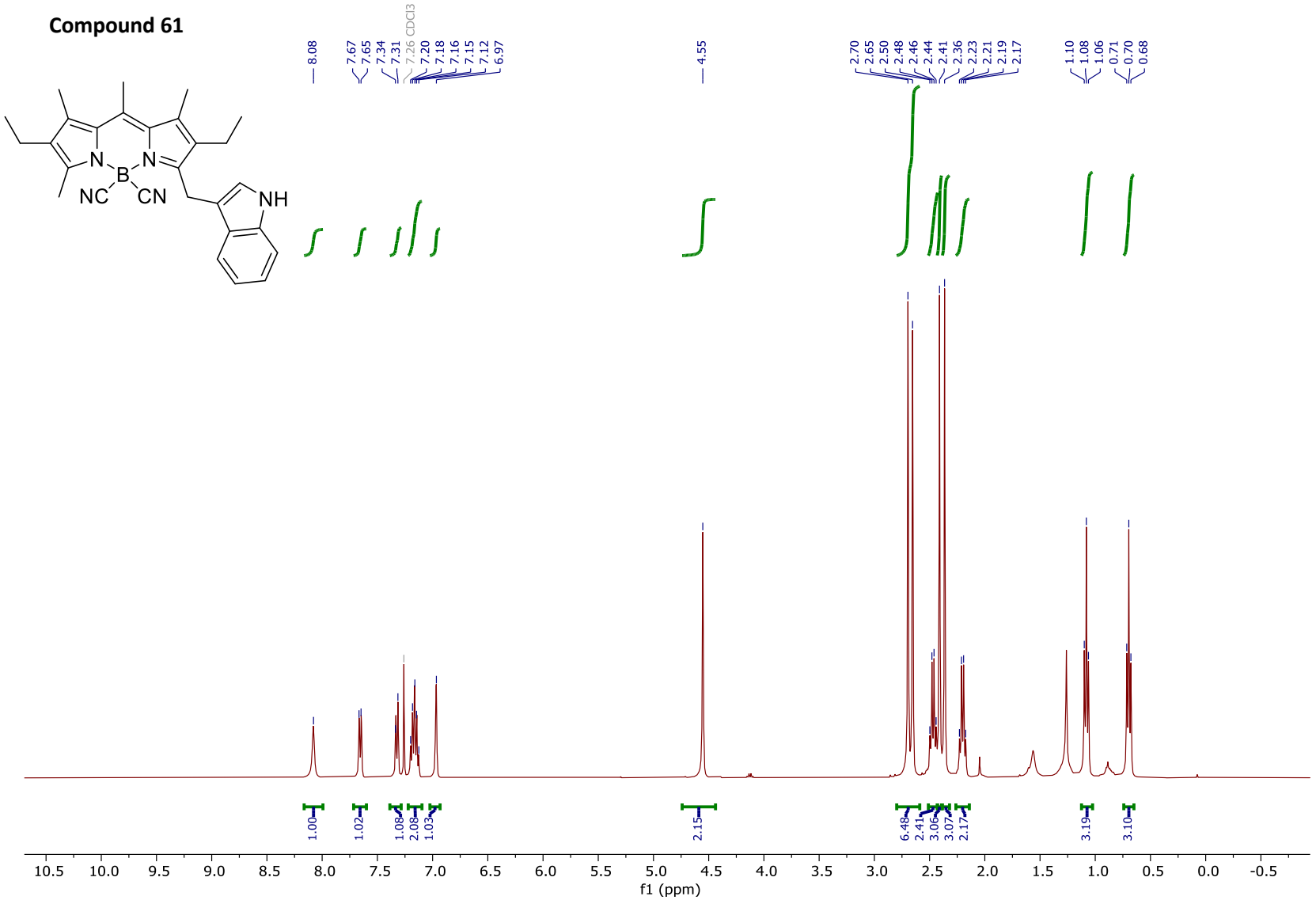






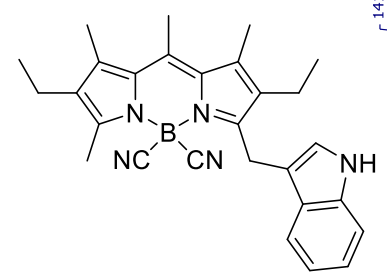
**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **60**

**Compound 61**




**$^{1}$H NMR** (100 MHz, $CDCl_3$) spectrum of compound **61**

**Compound 61**

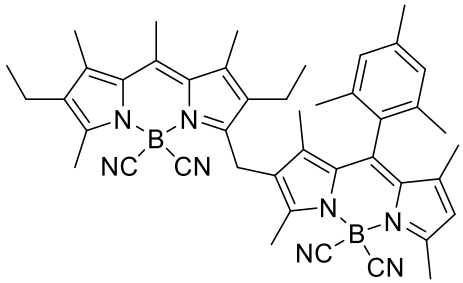






**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **61**

**Compound 62**

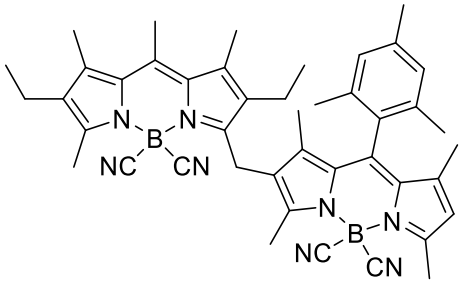






**$^1$H NMR** (500 MHz, $CDCl_3$) spectrum of compound **62**

**Compound 62**

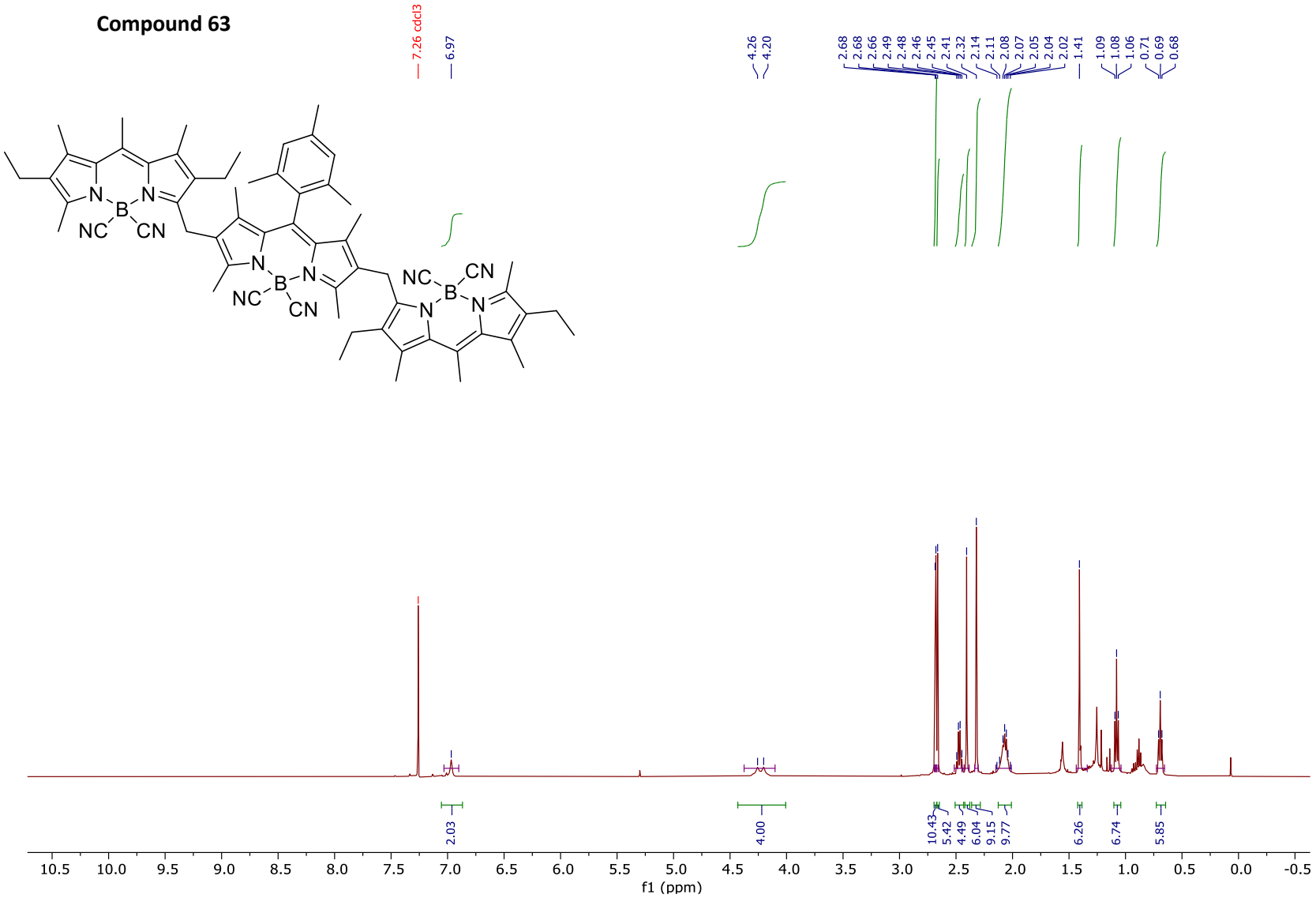






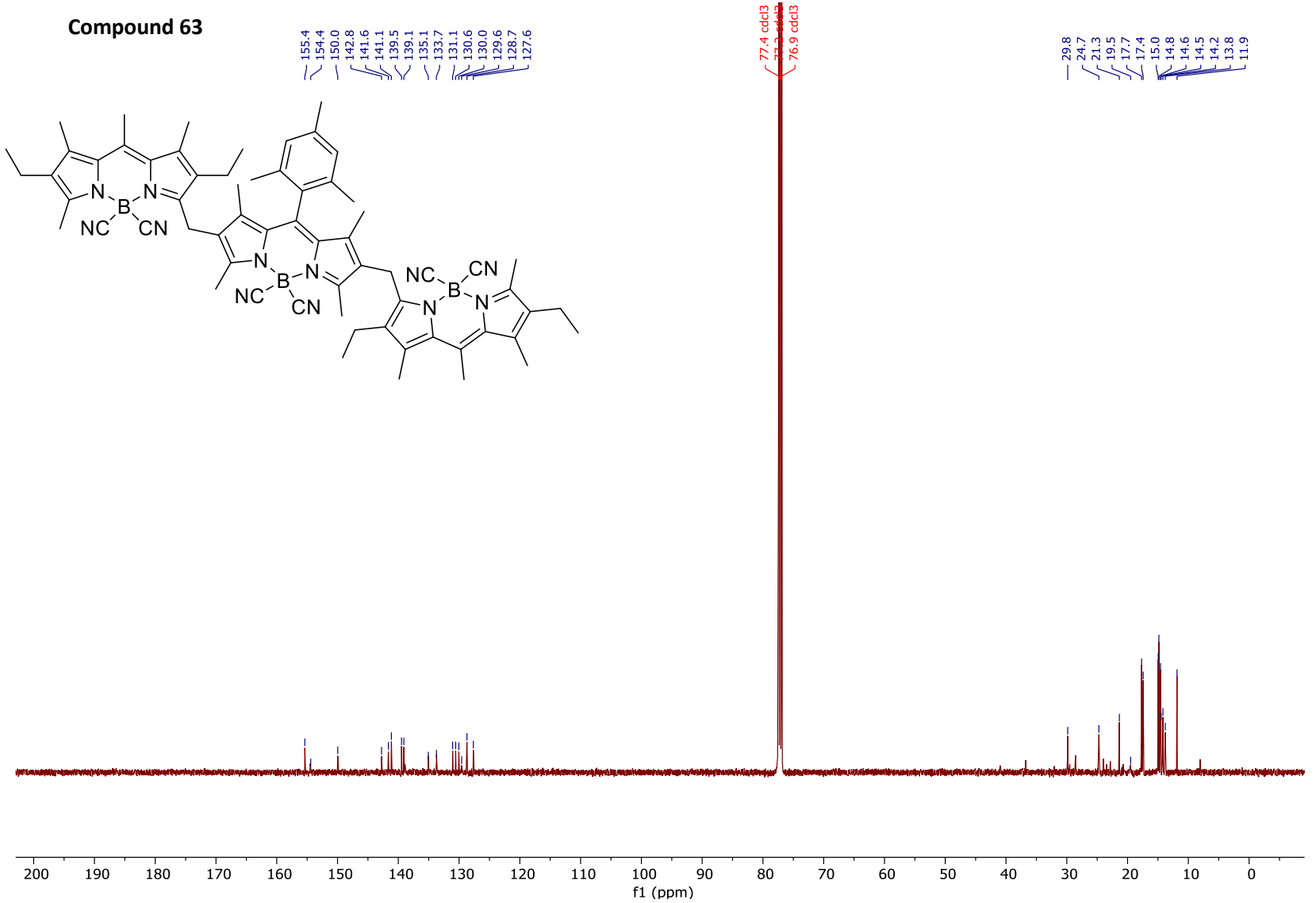
**$^{13}$C NMR** (125 MHz, $CDCl_3$) spectrum of compound **62**

**Compound 63**



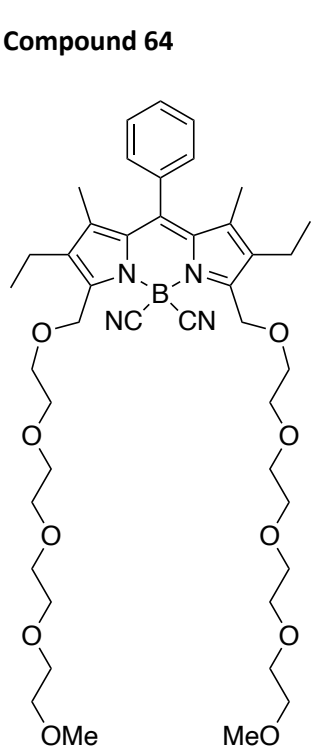

**$^{1}$H NMR** (500 MHz, $CDCl_3$) spectrum of compound **63**

**Compound 63**




**$^{13}$C NMR** (125 MHz, $CDCl_3$) spectrum of compound **63**

**Compound 64**



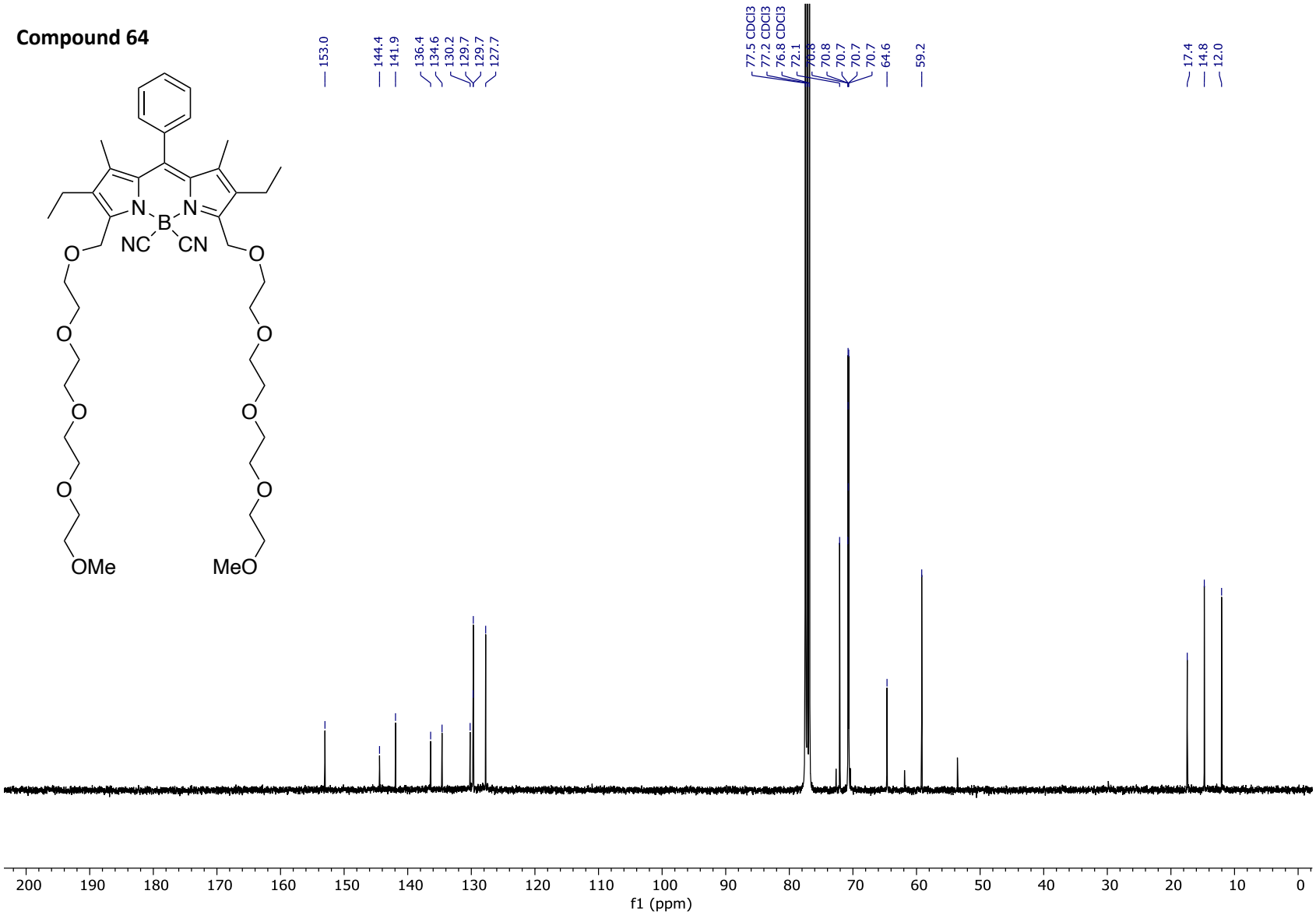






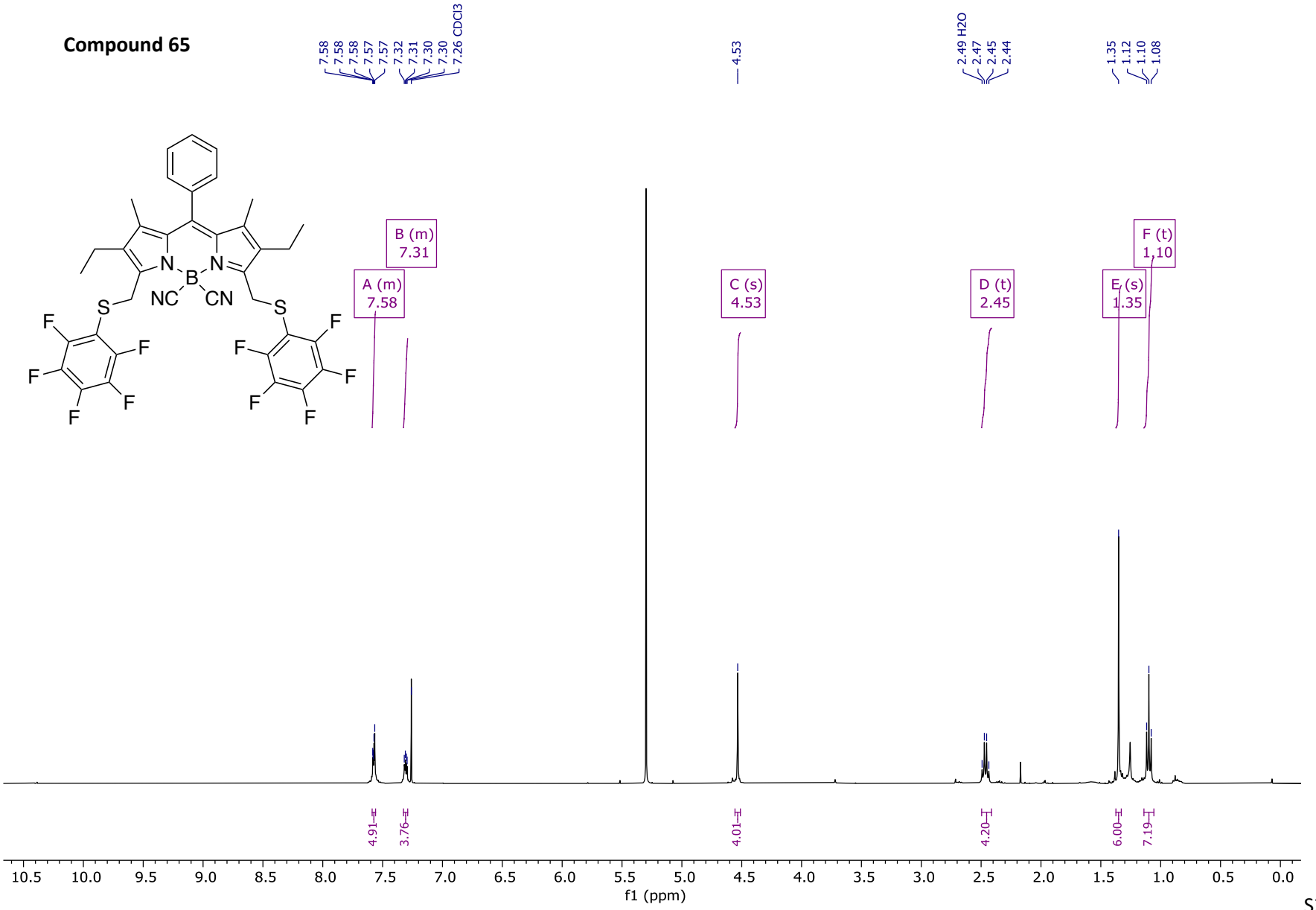
**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **64**

**Compound 64**



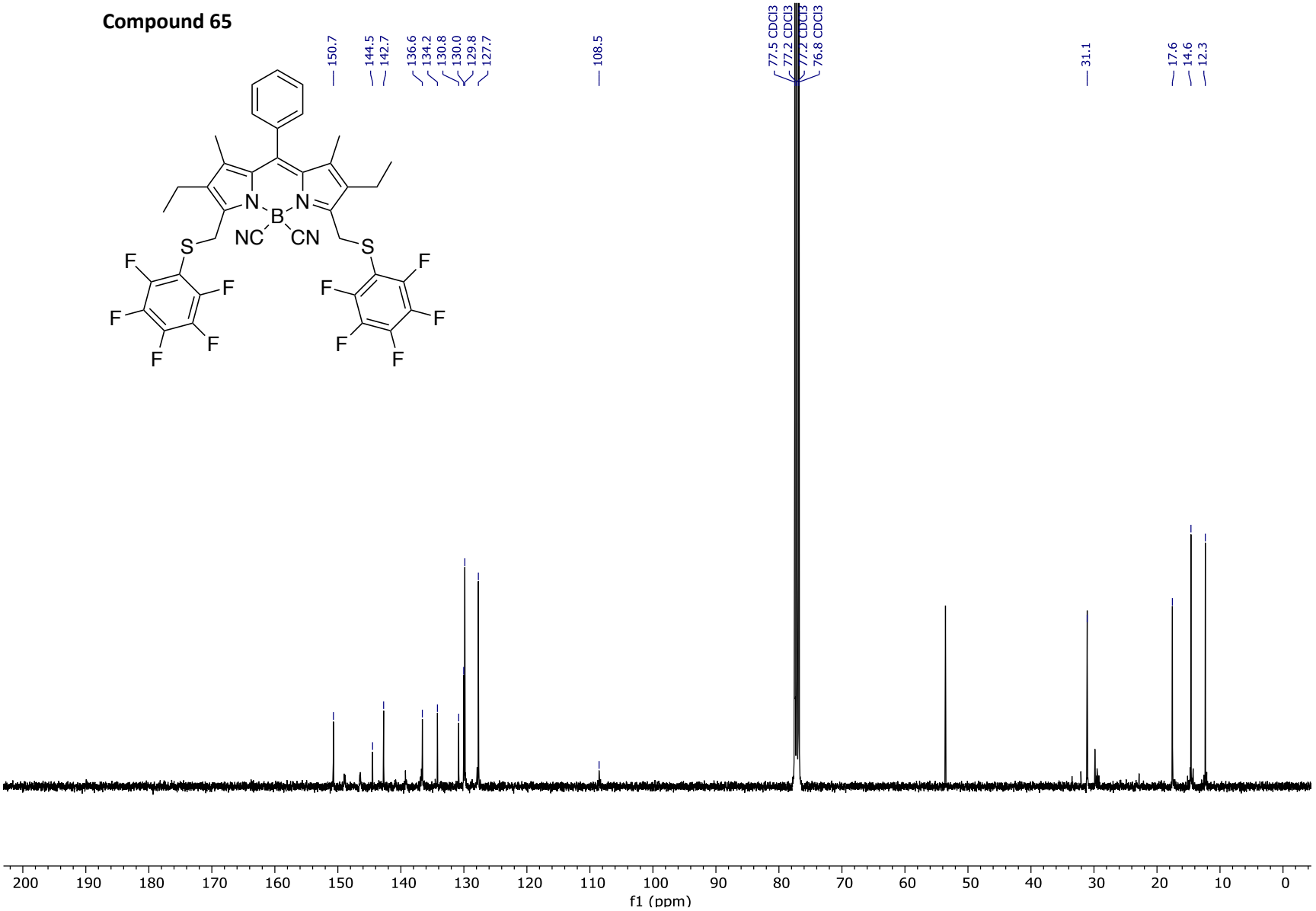

**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **64**

**Compound 65**



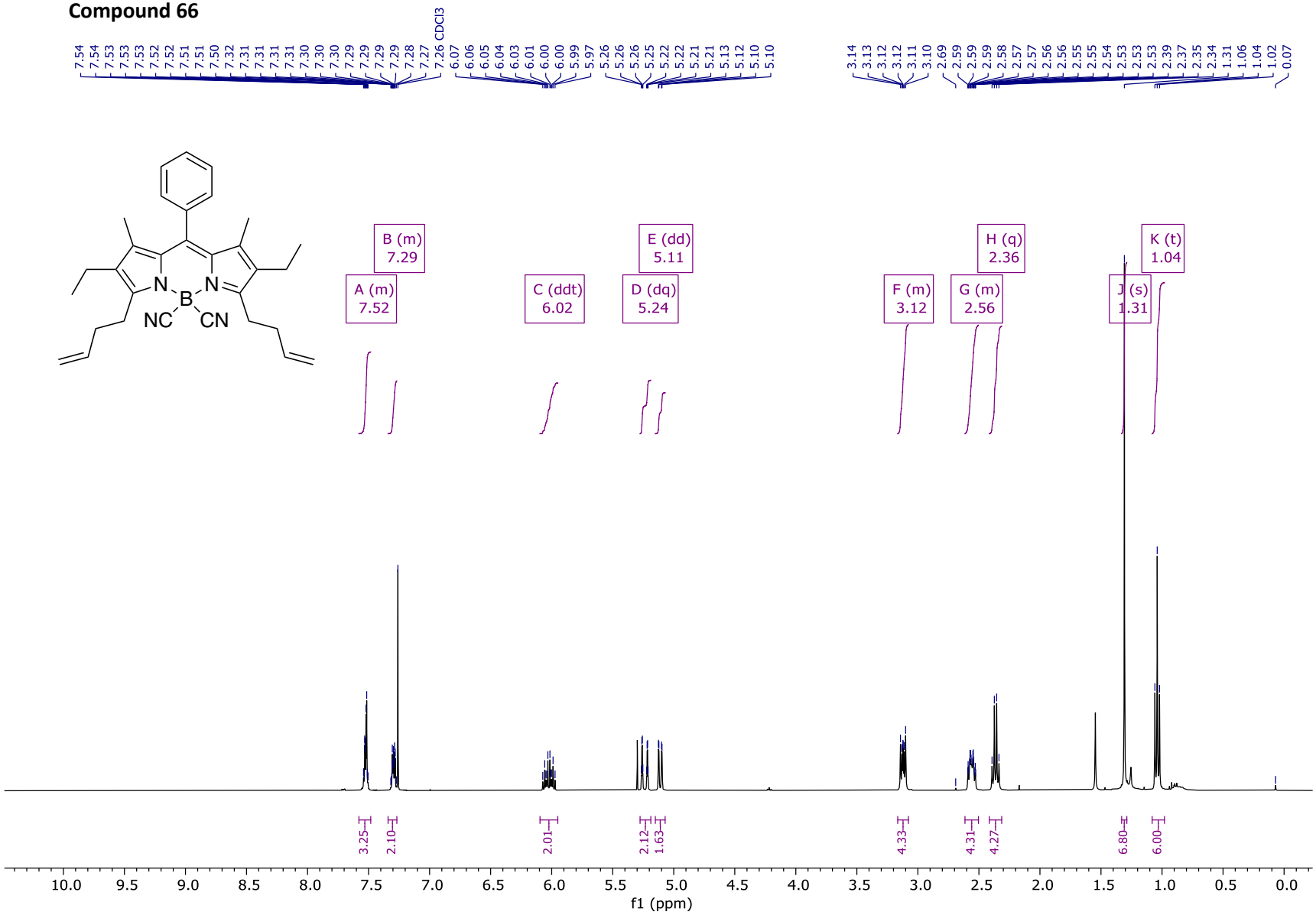

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **65**

**Compound 65**



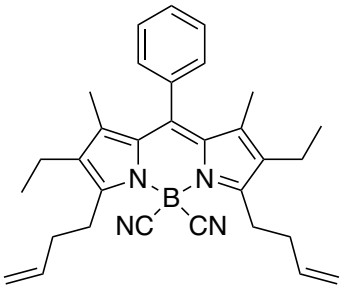

**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **65**

**Compound 66**




**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **66**

**Compound 66**

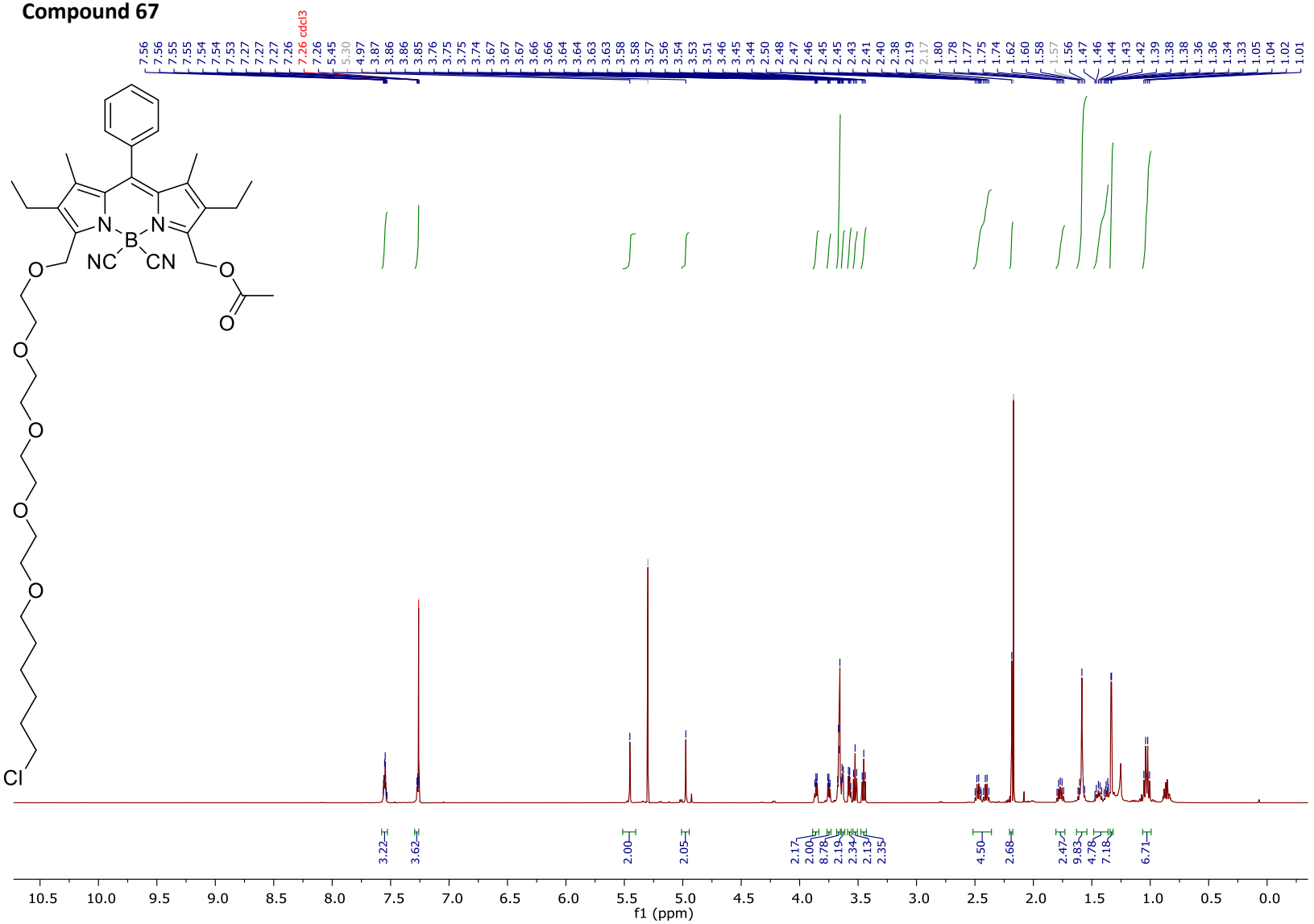






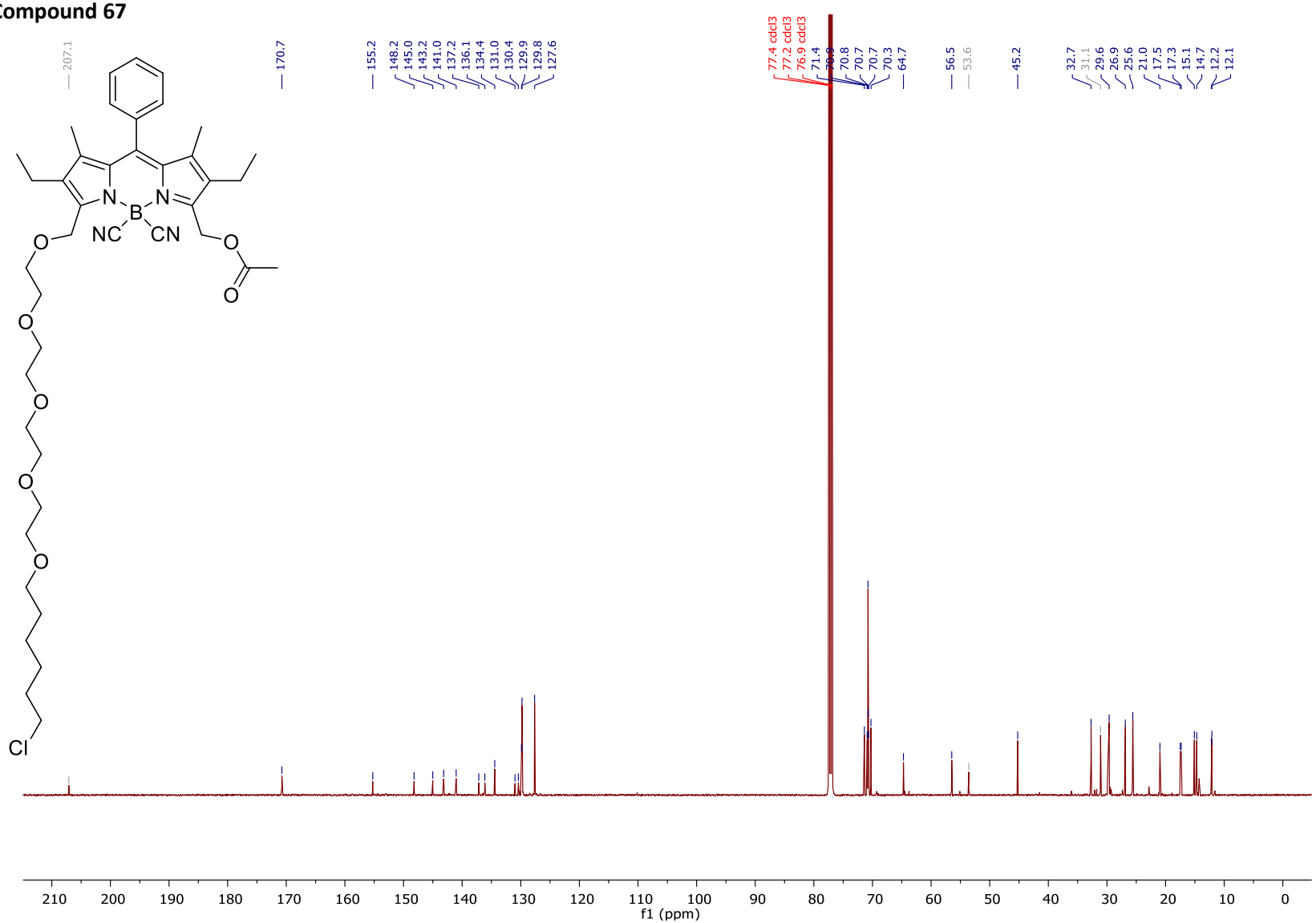
**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **66**

**Compound 67**



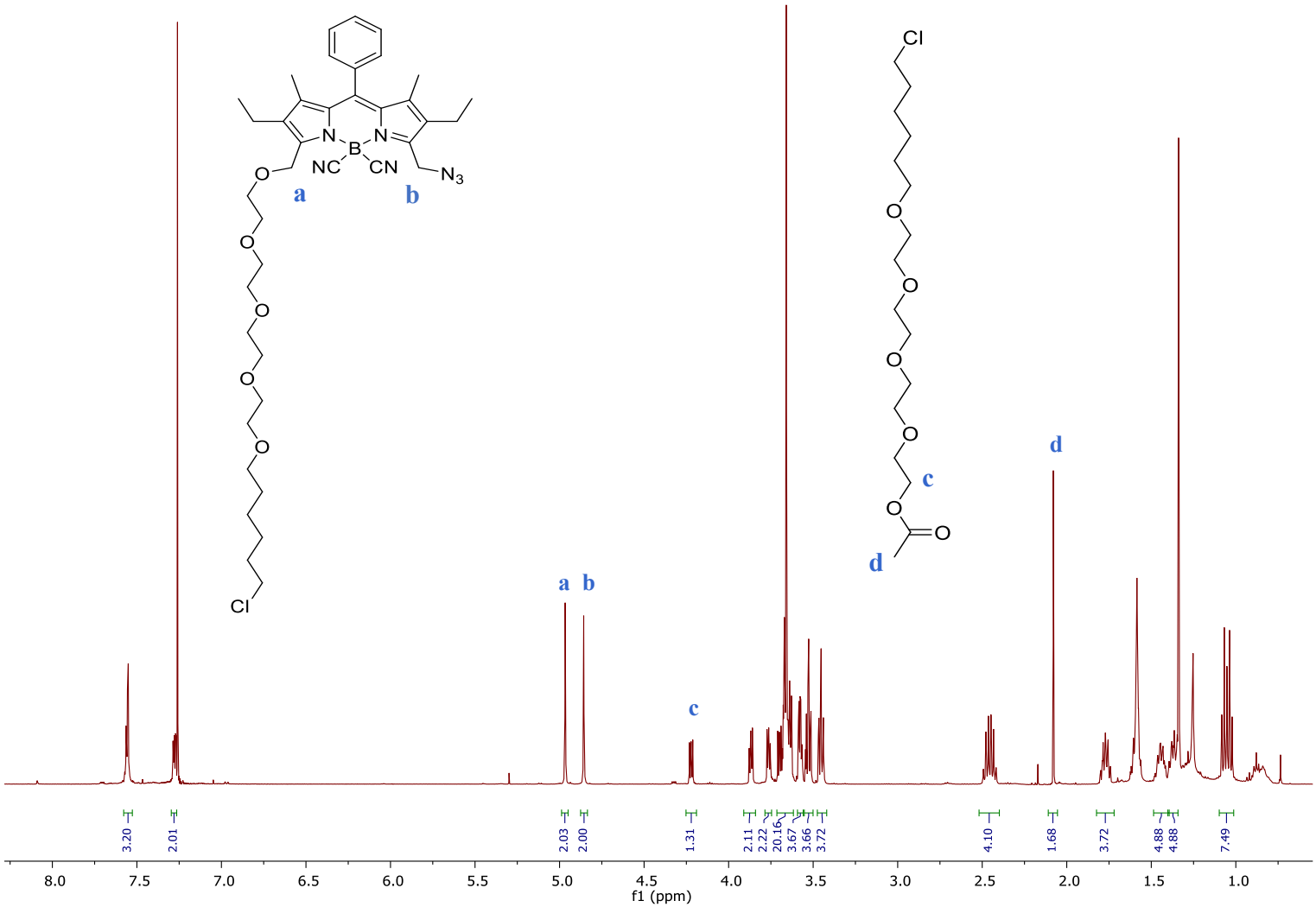

**$^1$H NMR** (500 MHz, $CDCl_3$) spectrum of compound **67**

**Compound 67**

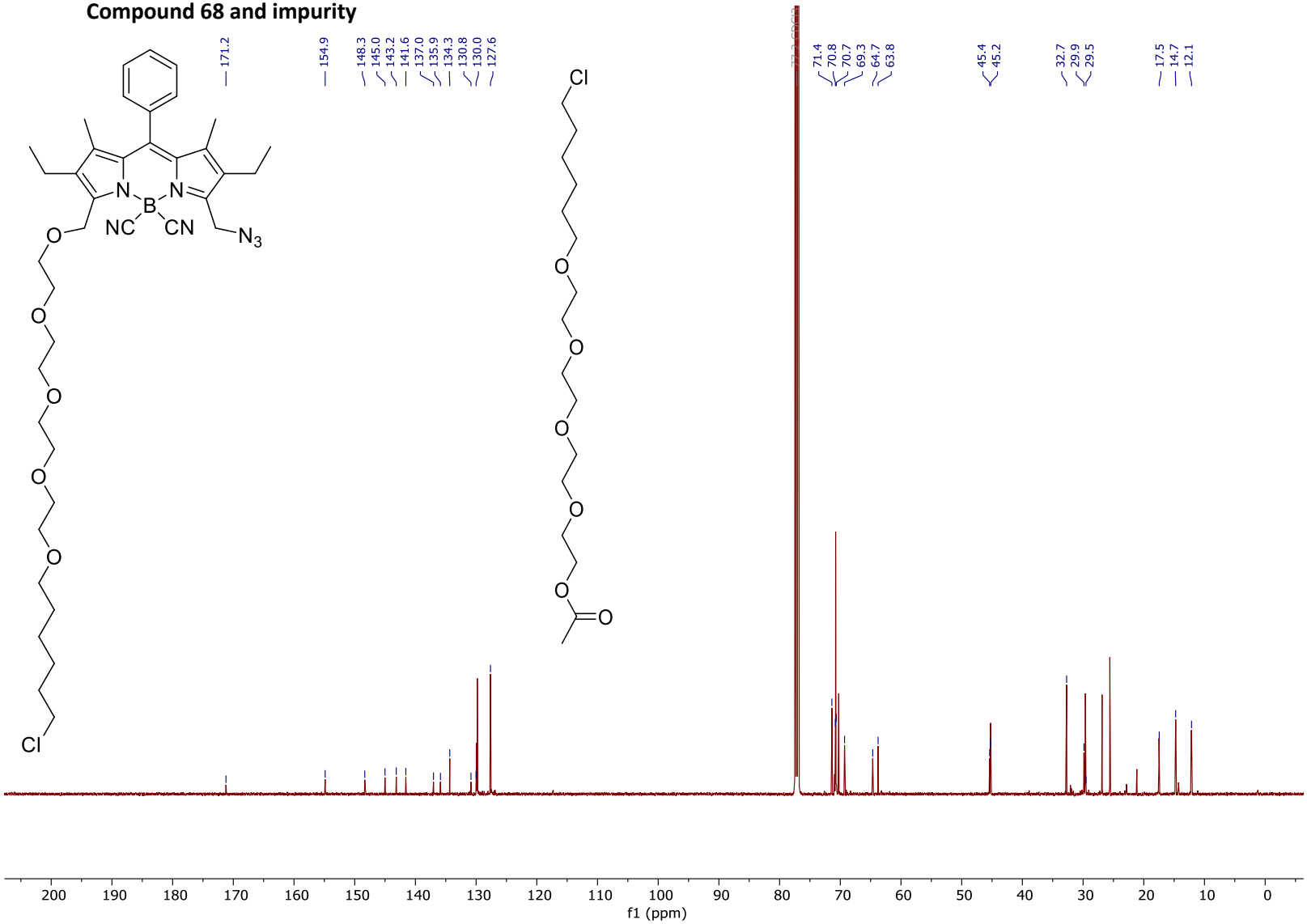



**$^{13}$C NMR** (125 MHz, $CDCl_3$) spectrum of compound **67**

**Compound 68 and impurity**

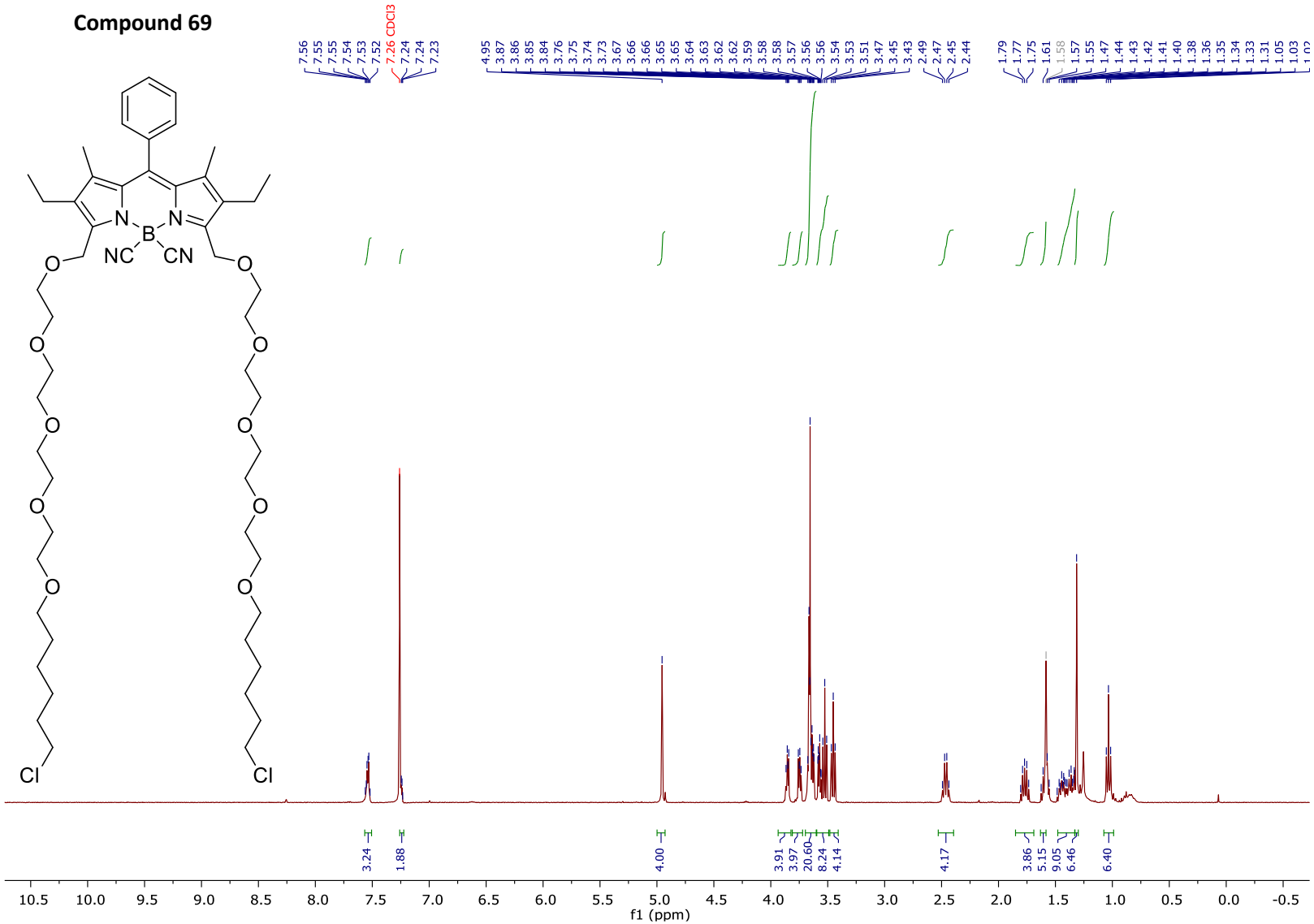



**$^1$H NMR** (500 MHz, $CDCl_3$) spectrum of compound **68** and impurity

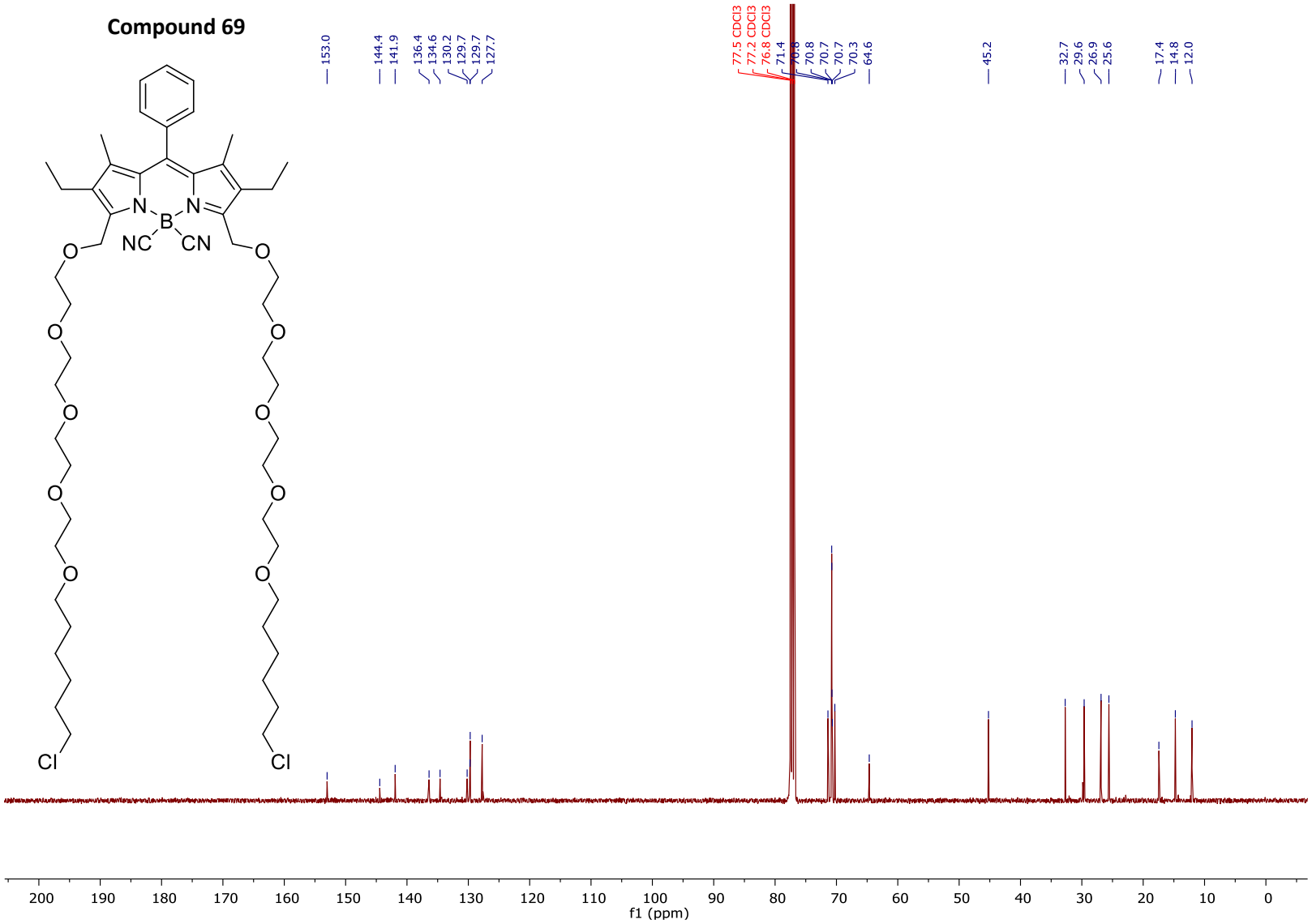



**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **68** and impurity

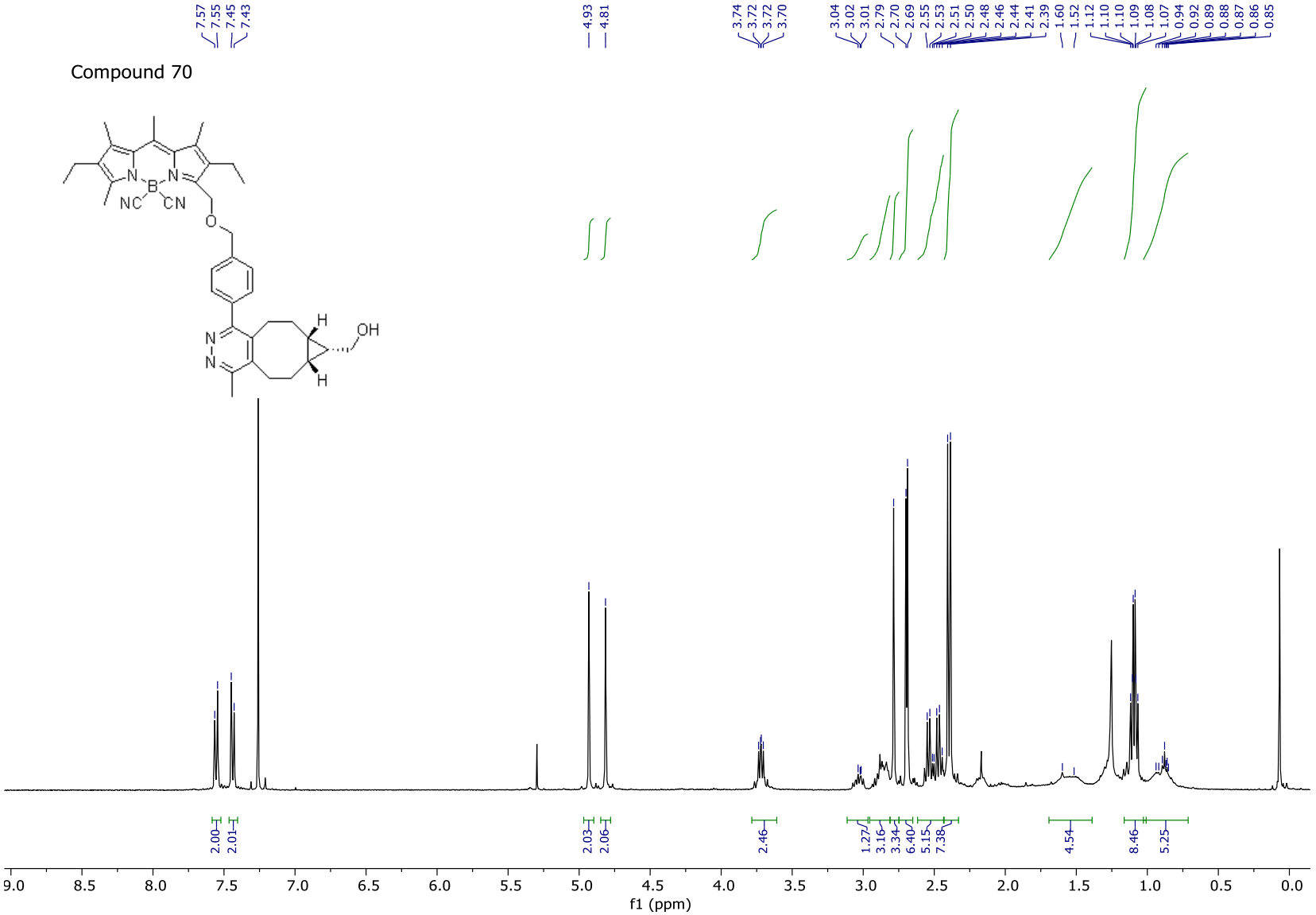
**Compound 69**



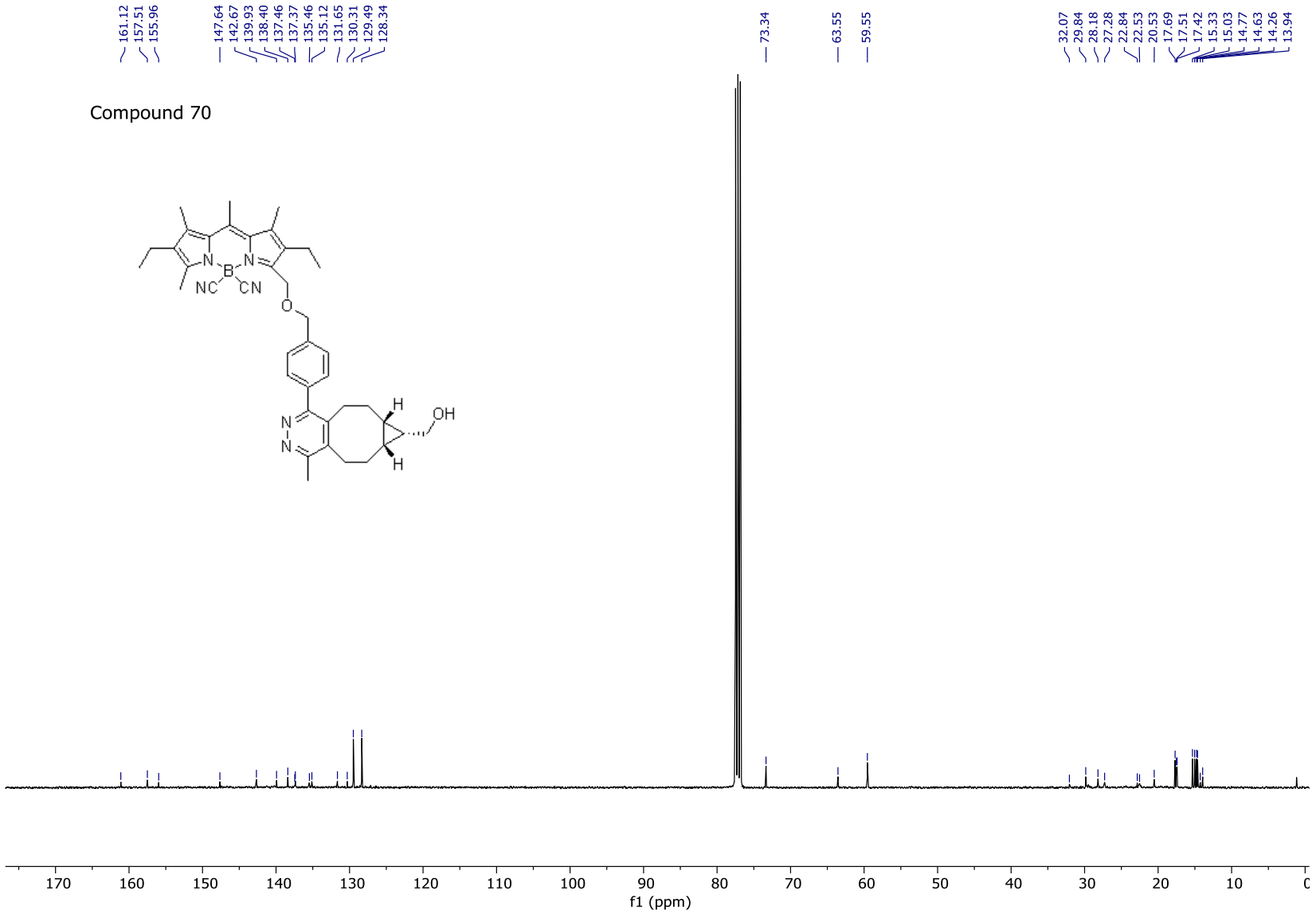

**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **69**




**$^{13}$C NMR** (100 MHz, $CDCl_3$) spectrum of compound **69**




**$^1$H NMR** (400 MHz, $CDCl_3$) spectrum of compound **70**




**$^{13}$C NMR** (400 MHz, $CDCl_3$) spectrum of compound **70**