Supporting Information

General Reagent Information

All reactions were carried out under an argon atmosphere. THF was purchased from J.T. Baker in CYCLE-TAINER® solvent delivery kegs and vigorously purged with argon for 2 h. The solvent was further purified by passing it under argon pressure through two packed columns of neutral alumina and copper (II) oxide. Copper(I)triflate benzene complex, bis(diisopropylphosphino)ferrocene and 1,2-bis(diphenylphosphino)benzene were purchased from Strem and was used as received. CyJohnPhos and BINAP were purchased from Aldrich and were used as received. DTBM-Segphos was purchased from Takasago and was used as received. Bis(pinacolato)diboron (B_2Pin_2) was purchased from Frontier Scientific and was used as received. Li*O*t*Bu was purchased from Strem or Aldrich and was stored in a nitrogen-filled glove box. 3,3-Disubstituted allylvinylnaphthalenes were prepared from the corresponding *ortho*-bromovinylnaphthalenes and allylboronates using regioselective Suzuki-Miyaura cross-couplings described by Miyaura or Organ.[1] 2-Substituted allylvinylnaphthalenes were prepared from the corresponding arylcuprates and 2-substituted allyl bromides using the procedure described by Snyder. [2] *N*-Cyano-4-methyl-*N*-phenylbenzenesulfonamide (NCTS) was synthesized according to Kurzer's procedure modified by Beller.[3] *m*-CPBA, 3-bromoaniole, sodium perborate tetrahydrate were purchased from Aldrich and were used as received. *N*-bromosuccinimide was recrystallized from hot water prior to use. $[(allyl)PdCl]_2$ was purchased from Johnson-Matthey and was used as received. NaO*t*Bu was purchased from Aldrich and was stored in a nitrogen-filled glove box. A small portion of NaO*t*Bu was removed from the glove box and stored in a desiccator for use. Flash chromatography was performed using a Biotage Isolera instrument with prepacked silica cartridges (10-100 g).

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[1] (a) J. L. Farmer, H. N. Hunter, M. G. Organ, *J. Am. Chem. Soc.* **2012**, *134*, 17470. (b) Y. Yamamoto, Y. Takada, N. Miyaura, *Organometallics* **2009**, *28*, 152.

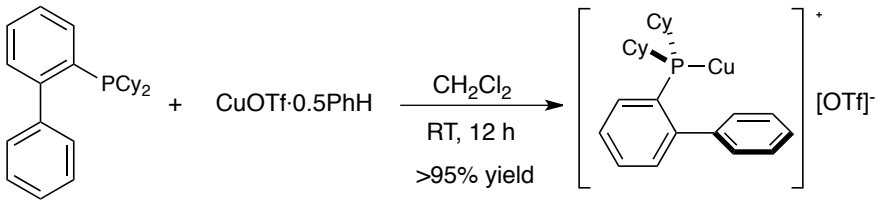
[2] S. A. Snyder, D. S. Treitler, A. P. Brucks, *J. Am. Chem. Soc.* **2010**, *132*, 14303.

[3] P. Anbarasan, H. Neumann, M. Beller, *Angew. Chem., Int. Ed.* **2011**, *50*, 519.

General Analytical Information

All compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR (where applicable). New compounds were also characterized by IR spectroscopy, high-resolution mass spectroscopy and melting point (if solids). Copies of the ^{1}H and ^{13}C NMR spectra can be found at the end of the Supporting Information. Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 MHz instrument. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent. All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.16 ppm) and all were obtained with ^{1}H decoupling. All ^{19}F NMR spectra are reported in ppm relative to $CFCl_3$ (0.00 ppm). All ^{11}B NMR spectra are reported in ppm relative to $BF_3 \cdot OEt_2$ (0.00 ppm). All IR spectra were taken on a Thermo Scientific Nicolet iS5 spectrometer (iD5 ATR, diamond). Melting points (m.p.) were obtained on a Mel-Temp capillary melting point apparatus. ESI-MS spectra were recorded on a Bruker Daltonics APEXIV 4.7 Tesla Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS).

Preparation of [(CyJohnPhos)Cu][OTf]



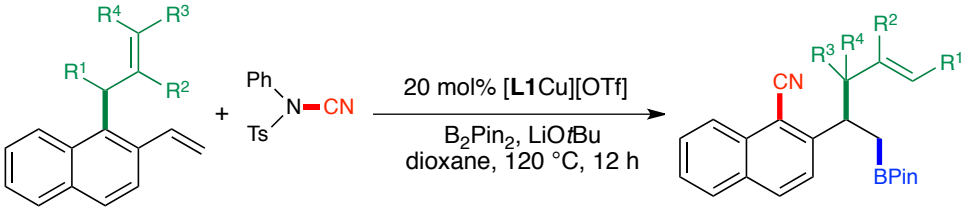
[(CyJohnPhos)Cu][OTf]

Procedure: In a nitrogen-filled glove box, Cu(OTf)·½PhH (251 mg, 1.0 mmol, 1.0 equiv) and CyJohnPhos (350 mg, 1.0 mmol, 1.0 equiv) were charged to a round bottom flask equipped with a magnetic stir bar. CH_2Cl_2 (4.0 mL) was added and the reaction mixture was stirred at room temperature for 12 h, during which time all the solid reagents dissolved to give a clear yellowish solution. The solvents were then carefully removed *in*

vacuo to afford the title compound as a white powder (550 mg, >95% yield). The catalyst was stored in a nitrogen-filled glove box.

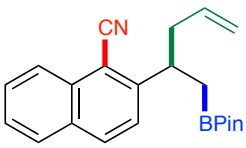
^{1}H NMR (400 HMz, CD_2Cl_2) δ: 7.63-7.52 (m, 6H), 7.38-7.35 (m, 2H), 7.27-7.25 (m, 1H), 2.11-2.09 (m, 2H), 1.82-1.65 (m, 10H), 1.34-1.15 (m, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.8 (d, *J* = 18 Hz), 142.0 (d, *J* = 9 Hz), 132.7, 131.3 (d, *J* = 6 Hz), 131.0 (d, *J* = 1 Hz), 130.5, 128.9, 128.4 (d, *J* = 6 Hz), 127.6, 126.0 (d, *J* = 40 Hz), 34.3 (d, *J* = 25 Hz), 30.8 (d, *J* = 7 Hz), 29.5, 27.1 (d, *J* = 3 Hz), 27.0 (d, *J* = 7 Hz), 26.1 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2) δ: -78.0 ppm. ^{31}P NMR (162 MHz, CD_2Cl_2) δ: 9.5 ppm.

Experimental Procedures for Examples Described in Scheme 2 and 3



General Procedure: To an oven-dried screw-cap test tube equipped with a magnetic stir bar were charged with NCTS (1.20 equiv), allylvinylnaphthalene (1.00 equiv) and B_2Pin_2 (1.1 equiv). The test tube was then transferred to a nitrogen-filled glove box, where [(CyJohnPhos)Cu][OTf] (20 mol %) and Li*O*t*Bu* (1.2 equiv) were added. Dioxane (0.40 M) was then added via syringe. The test tube was capped with a teflon-fitted septum and removed from the glove box. The reaction mixture was allowed to stir at 120 °C for 12 h, during which time significant amount of white/grey precipitation formed and vigorous stirring (ca. 1150 rpm) was critical to achieving reproducible yields. After cooling to room temperature, the reaction mixture was diluted with EtOAc and passed through a short plug of silica gel (1.5 cm) eluting with EtOAc (50-70 mL/0.20 mmol). The filtrate was concentrated *in vacuo* and rapidly purified with the aid of a Biotage Isolera instrument. The yield of product was also determined by ^{1}H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard prior to purification. Isolated yields were typically 5%-20% lower than yields estimated by ^{1}H NMR because of product decomposition on silica gel.

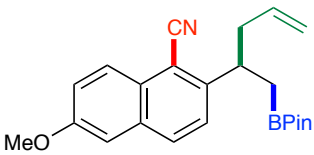
2-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-1-naphthonitrile



According to the General Procedure, 1-allyl-2-vinylnaphthalene (38.8 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), Li*O*t*Bu* (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (45 mg, 65%. ^{1}H NMR yield: 75%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.23 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.65 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.55 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 5.76-5.65 (m, 1H), 4.95-4.90 (m, 2H), 3.77-3.69 (m, 1H), 2.58-2.51 (m, 1H), 2.50-2.42 (m, 1H), 1.39 (dd, *J* = 15.6, 6.8 Hz, 1H), 1.21 (dd, *J* = 15.6, 8.8 Hz, 1H), 1.08 (s, 6H), 1.03 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.3, 135.9, 132.9, 132.8, 131.6, 128.5, 126.8, 125.5, 124.2, 117.2, 117.1, 109.4, 83.3, 43.0, 40.2, 24.8, 24.7 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 33.4 ppm. IR: 2977, 2930, 2216, 1366, 1142, 752 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{22}H_{26}BNO_2$, 348.2144; found, 348.2145.

6-Methoxy-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-1-naphthonitrile

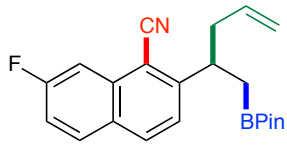


According to the General Procedure, 1-allyl-7-methoxy-2-vinylnaphthalene (44.8 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), Li*O*t*Bu* (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 1% EtOAc/DCM) to afford the title compound as a colorless solid (41.0 mg, 56%. ^{1}H NMR yield: 72%). m.p. = 119-120 °C.

^{1}H NMR (400 HMz, CD_2Cl_2) δ: 8.09 (d, *J* = 9.2 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.31 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 5.74-5.65 (m,

1H), 4.96-4.88 (m, 2H), 3.92 (s, 3H), 3.64-3.56 (m, 1H), 2.56-2.48 (m, 1H), 2.46-2.40 (m, 1H), 1.35 (dd, *J* = 15.6, 6.8 Hz, 1H), 1.20 (dd, *J* = 15.6, 8.4 Hz, 1H), 1.07 (s, 6H), 1.03 (s, 6H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2) δ: 158.7, 148.9, 136.6, 133.2, 132.0, 128.2, 127.0, 125.0, 121.3, 117.4, 116.9, 109.4, 106.9, 83.5, 55.8, 43.3, 40.4, 24.9, 24.8 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.7 ppm. IR: 2977, 2935, 2218, 1506, 1143, 846 cm^{-1}. HRMS-ESI (*m/z*) $[M + NH_4]^+$ calcd for $C_{23}H_{28}BNO_3$, 395.2516; found, 395.2537.

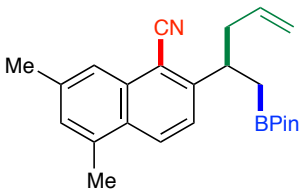
7-Fluoro-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-1-naphthonitrile



According to the General Procedure, 1-allyl-7-fluoro-2-vinylnaphthalene (42.4 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), LiO*t*Bu (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless solid (41.0 mg, 56%. ^{1}H NMR yield: 72%). m.p. = 99-100 °C. ^{1}H NMR (400 HMz, $CDCl_3$) δ: 7.97 (d, *J* = 8.8 Hz, 1H), 7.87-7.83 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.32 (ddd, *J* = 8.4, 8.4, 2.4 Hz, 1H), 5.72-5.64 (m, 1H), 4.95-4.90 (m, 2H), 3.74-3.67 (m, 1H), 2.57-2.50 (m, 1H), 2.48-2.41 (m, 1H), 1.38 (dd, *J* = 15.6, 6.8 Hz, 1H), 1.21 (dd, *J* = 15.6, 4.4 Hz, 1H), 1.08 (s, 6H), 1.02 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.3 (d, *J* = 249 Hz), 152.3, 135.6, 134.0 (d, *J* = 10 Hz), 132.6, 130.9 (d, *J* = 9 Hz), 128.4, 123.5, 117.2 (d, *J* = 3 Hz), 117.0, 116.7, 109.3 (d, *J* = 23 Hz), 108.9 (d, *J* = 5 Hz), 83.2, 42.9, 40.2, 24.7, 24.5 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -109.9 ppm. IR: 2978, 2932, 2218, 1371, 1144, 845 cm^{-1}. HRMS-ESI (*m/z*) $[M + NH_4]^+$ calcd for $C_{22}H_{25}BFNO_2$, 383.2316; found, 383.2316.

5,7-Dimethyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-1-naphthonitrile

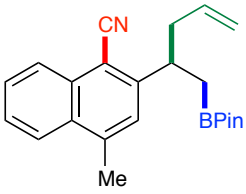
According to the General Procedure, 1-allyl-5,7-dimethyl-2-vinylnaphthalene (44.4 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), LiO*t*Bu (19.2 mg, 0.24 mmol) and



dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (48 mg, 64%. ^{1}H NMR yield: 75%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.10 (d, *J* = 8.8 Hz, 1H), 7.89 (s, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.21 (s, 1H), 5.75-5.65 (m, 1H), 4.95-4.89 (m, 2H), 3.72-3.68 (m, 1H), 2.65 (s, 3H), 2.57-2.48 (m, 1H), 2.52 (s, 3H), 2.47-2.41 (m, 1H), 1.38 (dd, *J* = 15.6, 6.8 Hz, 1H), 1.25 (dd, *J* = 15.6, 8.4 Hz, 1H), 1.09 (s, 6H), 1.05 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.8, 138.5, 136.0, 134.8, 133.4, 129.9, 129.1, 129.0, 123.0, 122.9, 117.6, 117.1, 109.1, 83.3, 43.1, 40.1, 24.8, 24.7, 22.0, 19.3 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.6 ppm. IR: 2977, 2929, 2216, 1365, 1143, 856 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{24}H_{30}BNO_2$, 376.2458; found, 376.2462.

4-Methyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-1-naphthonitrile

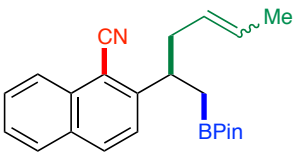


According to the General Procedure, 1-allyl-4-methyl-2-vinylnaphthalene (41.6 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), LiO*t*Bu (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (53.0 mg, 73%. ^{1}H NMR yield: 89%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.25 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.54 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.31 (s, 1H), 5.74-5.66 (m, 1H), 4.98-4.90 (m, 2H), 3.71-3.67 (m, 1H), 2.72 (s, 3H), 2.53-2.47 (m, 2H), 1.38 (dd, *J* = 16.0, 6.8 Hz, 1H), 1.25 (dd, *J* = 16.0, 8.4 Hz, 1H), 1.08 (s, 6H), 1.04 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.0, 140.3, 136.0, 132.7, 131.0, 128.1, 126.6, 125.1, 124.6, 117.4, 117.1, 107.6, 83.3, 42.9, 40.1, 24.8, 24.7, 20.2 ppm. ^{11}B NMR (128 MHz, $CDCl_3$)

δ: 32.6 ppm. IR: 2977, 2928, 2217, 1366, 1144, 760 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{23}H_{28}BNO_2$, 362.2301; found, 362.2316.

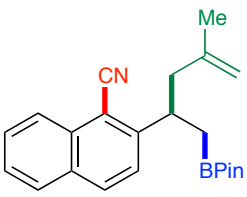
2-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-en-2-yl)-1-naphthonitrile



According to the General Procedure, 1-(but-3-en-2-yl)-2-vinylnaphthalene (41.6 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), Li*O*t*Bu* (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (23.0 mg, 32%, *E*/*Z* = 75:25. ^{1}H NMR yield: 31%).

Major stereoisomer (*trans*): ^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.24 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.65 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.55 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 5.43-5.33 (m, 2H), 3.72-3.63 (m, 1H), 2.44-2.34 (m, 2H), 1.54 (d, *J* = 4.8 Hz, 3H), 1.37 (dd, *J* = 15.6, 6.8 Hz, 1H), 1.21 (dd, *J* = 15.6, 8.8 Hz, 1H), 1.09 (s, 6H), 1.03 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.7, 144.4, 132.8, 131.5, 128.5, 128.3, 127.8, 126.7, 125.4, 124.3, 122.5, 117.1, 109.4, 83.3, 41.9, 40.5, 24.8, 24.7, 18.0 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 33.7 ppm. IR: 2976, 2214, 1370, 1143, 967, 847 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{23}H_{28}BNO_2$, 362.2301; found, 362.2303.

2-(4-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-1-naphthonitrile

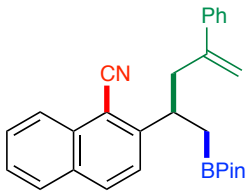


According to the General Procedure, 1-(2-methylallyl)-2-vinylnaphthalene (41.6 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), Li*O*t*Bu* (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8%

EtOAc/hexanes) to afford the title compound as a colorless oil (45.0 mg, 62%. ^{1}H NMR yield: 71%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.23 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.54 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 4.62 (d, *J* = 0.8 Hz, 1H), 4.52 (d, *J* = 0.8 Hz, 1H), 3.88-3.80 (m, 1H), 2.47-2.43 (m, 2H), 1.78 (s, 3H), 1.37 (dd, *J* = 15.6, 6.8 Hz, 1H), 1.21 (dd, *J* = 15.6, 8.8 Hz, 1H), 1.07 (s, 6H), 1.02 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.6, 143.2, 132.8, 132.7, 131.5, 128.5, 128.4, 126.7, 125.4, 124.1, 117.1, 113.1, 109.4, 83.3, 47.4, 38.6, 24.8, 24.6, 22.4 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.5 ppm. IR: 2977, 2933, 2216, 1365, 1142, 845 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{23}H_{28}BNO_2$, 362.2301; found, 362.2286.

2-(4-Phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-1-naphthonitrile

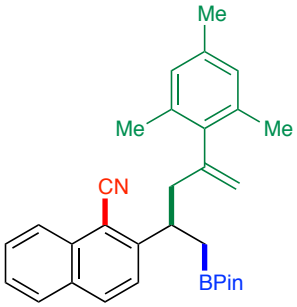


According to the General Procedure, 1-(2-phenylallyl)-2-vinylnaphthalene (54.0 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), Li*O*t*Bu* (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (64.0 mg, 76%. ^{1}H NMR yield: 77%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.18 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.56 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.52 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.30-7.28 (m, 2H), 7.27-7.22 (m, 3H), 5.17 (d, *J* = 0.8 Hz, 1H), 4.86 (d, *J* = 0.8 Hz, 1H), 3.82-3.76 (m, 1H), 3.08 (dd, *J* = 13.6, 5.6 Hz, 1H), 2.93 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.42 (dd, *J* = 15.6, 6.8 Hz, 1H), 1.21 (dd, *J* = 15.6, 8.4 Hz, 1H), 1.07 (s, 6H), 1.02 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.1, 146.1, 140.5, 132.70, 132.66, 131.5, 128.4, 128.3, 127.6, 126.7, 126.4, 125.4, 124.5, 116.6, 114.9, 109.5, 83.3, 44.1, 39.3, 24.8, 24.6 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.5 ppm. IR: 2977, 2217,

1367, 1324, 1143, 754 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{28}H_{30}BNO_2$, 424.2459; found, 424.2446.

2-(4-Mesityl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-1-naphthonitrile

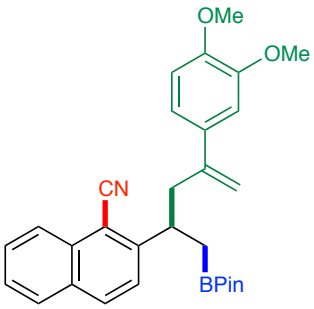


According to the General Procedure, 1-(2-mesitylallyl)-2-vinylnaphthalene (62.4 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), Li*O*tBu (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (43.2 mg, 46%. ^{1}H NMR yield: 53%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.26 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.55 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 6.83 (s, 1H), 6.79 (s, 1H), 5.41 (d, *J* = 0.8 Hz, 1H), 4.86 (d, *J* = 0.8 Hz, 1H), 4.05-3.98 (m, 1H), 2.79-2.67 (m, 2H), 2.25 (s, 3H), 2.19 (s, 3H), 2.00 (s, 3H), 1.48 (dd, *J* = 16.0, 6.8 Hz, 1H), 1.21 (dd, *J* = 16.0, 9.2 Hz, 1H), 1.09 (s, 6H), 1.08 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.7, 145.9, 140.1, 136.1, 135.0, 134.9, 132.9, 131.5, 128.5, 128.4, 128.2, 126.8, 125.4, 124.1, 117.1, 114.9, 109.5, 83.3, 44.0, 37.7, 24.8, 24.7, 21.0, 19.9, 19.8 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.3 ppm. IR: 2978, 2216, 1366, 1142, 847, 753 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{31}H_{36}BNO_2$, 466.2929; found, 466.2918.

2-(4-(3,4-Dimethoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-1-naphthonitrile

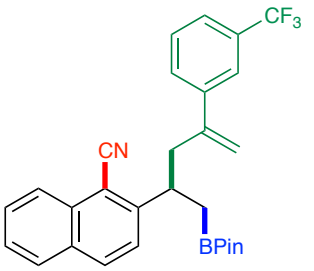
According to the General Procedure, 1-(2-(3,4-dimethoxyphenyl)allyl)-2-vinylnaphthalene (66.0 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), Li*O*tBu (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP



cartridge, 0-10-30% EtOAc/hexanes) to afford the title compound as a colorless oil (74.1 mg, 77%. ^{1}H NMR yield: 86%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.17 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.60 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.53 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 6.91 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.79 (d, *J* = 2.0 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.10 (d, *J* = 1.2 Hz, 1H), 4.88 (d, *J* = 1.2 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 2.97-2.88 (m, 2H), 1.38 (dd, *J* = 15.2, 6.8 Hz, 1H), 1.21 (dd, *J* = 15.2, 7.6 Hz, 1H), 1.04 (s, 6H), 0.99 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.1, 148.73, 148.70, 145.8, 133.6, 132.6, 132.5, 131.4, 128.4, 128.3, 126.7, 125.3, 124.5, 118.9, 116.8, 113.8, 111.0, 109.9, 109.4, 83.2, 55.94, 55.91, 44.3, 39.5, 24.7, 24.6 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.3 ppm. IR: 2980, 2216, 1516, 1371, 1254, 1143 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{30}H_{34}BNO_4$, 484.2671; found, 484.2683.

2-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(3-(trifluoromethyl)phenyl)pent-4-en-2-yl)-1-naphthonitrile

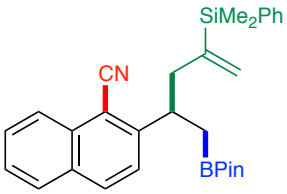


According to the General Procedure, 1-(2-(3-trifluoromethylphenyl)allyl)-2-vinylnaphthalene (67.6 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), Li*O*t*Bu* (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (67.0 mg, 68%. ^{1}H NMR yield: 86%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.14 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.63 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.53 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.52-7.49 (m, 2H), 7.45-7.40 (m, 2H), 7.37-7.34 (m, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 5.18 (d, *J* = 0.8 Hz, 1H), 5.00 (d, *J* = 0.8 Hz, 1H), 3.79-3.71 (m, 1H), 3.13 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.92 (dd, *J* = 14.4, 9.2 Hz, 1H), 1.42 (dd, *J* = 16.0, 7.6 Hz, 1H), 1.21 (dd, *J* =

16.0, 8.0 Hz, 1H), 1.10 (s, 6H), 1.06 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.5, 145.3, 141.5, 132.8, 132.6, 131.5, 130.5 (q, J = 32 Hz), 129.8, 128.8, 128.5, 128.3, 126.8, 125.4, 124.3 (q, J = 271 Hz), 124.2, 124.1 (q, J = 4 Hz), 123.2 (q, J = 4 Hz), 116.63, 116.55, 109.5, 83.2, 43.9, 39.5, 24.8, 24.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.5 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.6 ppm. IR: 2978, 2216, 1333, 1125, 847, 752 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{29}H_{29}BF_2NO_2$, 492.2333; found, 492.2343.

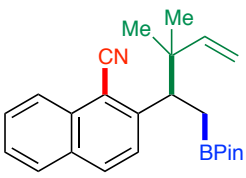
2-(4-(Dimethyl(phenyl)silyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-1-naphthonitrile



According to the General Procedure, dimethyl(phenyl)(3-(2-vinylnaphthalen-1-yl)prop-1-en-2-yl)silane (65.6 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), LiO*t*Bu (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (66.0 mg, 69%. ^{1}H NMR yield: 76%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.24 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.65 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.54 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.50-7.48 (m, 2H), 7.38 (d, J = 8.8 Hz, 1H), 7.37-7.28 (m, 3H), 5.60 (d, J = 2.4 Hz, 1H), 5.41 (d, J = 2.4 Hz, 1H), 3.85-3.77 (m, 1H), 2.59 (d, J = 7.2 Hz, 2H), 1.33 (dd, J = 15.6, 6.0 Hz, 1H), 1.21 (dd, J = 15.6, 8.8 Hz, 1H), 1.06 (s, 6H), 1.02 (s, 6H), 0.46 (s, 3H), 0.39 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.7, 147.3, 138.1, 134.1, 132.71, 132.69, 131.5, 129.0, 129.0, 128.4, 128.3, 127.8, 126.7, 125.4, 124.3, 117.2, 109.6, 83.2, 43.8, 39.4, 24.8, 24.6, -2.9, -3.0 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.3 ppm. IR: 2976, 2216, 1366, 1143, 818, 701 cm^{-1}. HRMS-ESI (*m/z*) $[M + NH_4]^+$ calcd for $C_{30}H_{36}B_2O_4Si$, 499.2962; found, 499.2961.

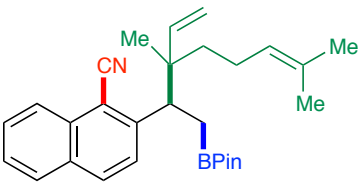
2-(3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-1-naphthonitrile



According to the General Procedure, 1-(3-methylbut-2-en-1-yl)-2-vinylnaphthalene (44.4 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), LiO*t*Bu (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (45 mg, 60%. ^{1}H NMR yield: 69%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.26 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.65 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.54 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 5.96 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.04 (dd, *J* = 10.8, 1.2 Hz, 1H), 4.91 (dd, *J* = 17.6, 1.2 Hz, 1H), 3.62 (dd, *J* = 12.0, 4.4 Hz, 1H), 1.40 (dd, *J* = 15.6, 4.4 Hz, 1H), 1.28 (dd, *J* = 15.6, 12.0 Hz, 1H), 1.11 (s, 3H), 1.03 (s, 3H), 0.90 (s, 6H), 0.78 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.0, 145.6, 132.6, 131.7, 131.5, 128.4, 128.3, 126.8, 125.9, 125.6, 117.7, 113.0, 111.6, 83.1, 49.5, 41.5, 26.2, 24.8, 24.2, 24.1 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 33.7 ppm. IR: 2965, 2219, 1367, 1144, 847, 763 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{24}H_{30}BNO_2$, 376.2458; found, 376.2443.

2-(3,7-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-vinyloct-6-en-2-yl)-1-naphthonitrile

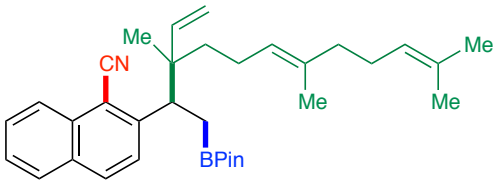


According to the General Procedure, (*E*)-1-(3,7-dimethylocta-2,6-dien-1-yl)-2-vinylnaphthalene (58.0 mg, 0.20 mmol, *E*/*Z* > 95:5), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), LiO*t*Bu (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (66.0 mg, 74%, d.r. > 95:5. ^{1}H NMR yield: 75%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.25 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.65 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.54 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 5.84 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.19 (dd, *J* = 10.8, 1.2 Hz, 1H),

5.01-4.97 (m, 1H), 4.84 (dd, J = 17.6, 1.2 Hz, 1H), 3.62 (dd, J = 12.0, 4.8 Hz, 1H), 1.94-1.86 (m, 1H), 1.84-1.75 (m, 1H), 1.76-1.51 (m, 7H), 1.41 (dd, J = 15.2, 4.4 Hz, 1H), 1.32-1.24 (m, 2H), 1.14 (s, 3H), 0.89 (s, 6H), 0.76 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.0, 143.5, 132.6, 131.6, 131.4, 131.2, 128.4, 128.3, 126.8, 126.1, 125.6, 124.9, 117.8, 114.5, 111.8, 83.1, 49.6, 44.7, 39.2, 25.8, 24.7, 24.2, 23.4, 19.5, 17.7 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.7 ppm. IR: 2976, 2925, 2219, 1362, 1143, 847 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{29}H_{38}BNO_2$, 444.3085; found, 444.3074.

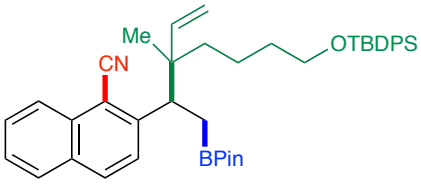
2-((*E*)-3,7,11-trimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-vinyldodeca-6,10-dien-2-yl)-1-naphthonitrile



According to the General Procedure, 1-((*2E,6E*)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl)-2-vinylnaphthalene (71.8 mg, 0.20 mmol, *E*/*Z* > 95:5), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), LiO*t*Bu (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (54.0 mg, 53%, d.r. > 95:5. ^{1}H NMR yield: 55%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.25 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.65 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.54 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.42 (d, J = 8.8 Hz, 1H), 5.85 (dd, J = 17.6, 10.8 Hz, 1H), 5.07 (dd, J = 10.8, 1.2 Hz, 1H), 5.05-4.99 (m, 2H), 4.83 (dd, J = 17.6, 1.2 Hz, 1H), 3.63 (dd, J = 11.6, 4.8 Hz, 1H), 2.04-1.81 (m, 7H), 1.65-1.61 (m, 4H), 1.57-1.55 (m, 4H), 1.52 (s, 3H), 1.40 (dd, J = 14.8, 4.4 Hz, 1H), 1.32-1.25 (m, 2H), 1.14 (s, 3H), 0.89 (s, 6H), 0.77 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.0, 143.5, 134.8, 132.6, 131.6, 131.4, 131.3, 128.4, 128.3, 126.7, 126.1, 125.6, 124.8, 124.5, 117.8, 114.5, 111.8, 83.1, 49.6, 44.8, 39.8, 39.2, 26.8, 25.8, 24.7, 24.2, 23.3, 18.4, 17.8, 16.1 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 34.0 ppm. IR: 2977, 2928, 2218, 1362, 1143, 732 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{34}H_{46}BNO_2$, 512.3712; found, 512.3734.

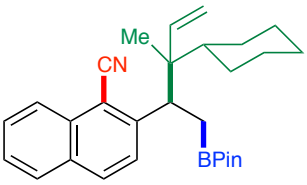
2-(7-((*Tert*-butyldiphenylsilyl)oxy)-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-vinylheptan-2-yl)-1-naphthonitrile



According to the General Procedure, (*E*)-*tert*-butyl((5-methyl-7-(2-vinylnaphthalen-1-yl)hept-5-en-1-yl)oxy)diphenylsilane (100.8 mg, 0.20 mmol, *E*/*Z* > 95:5), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), Li*O*t*Bu* (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (69.0 mg, 51%, d.r. > 95:5. ^{1}H NMR yield: 50%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.27 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.69-7.63 (m, 5H), 7.56 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.41-7.35 (m, 6H), 5.82 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.06 (dd, *J* = 10.8, 1.2 Hz, 1H), 4.82 (dd, *J* = 17.6, 1.2 Hz, 1H), 3.66-3.59 (m, 3H), 1.55-1.39 (m, 4H), 1.34-1.02 (m, 5H), 1.12 (s, 3H), 1.02 (s, 9H), 0.91 (s, 6H), 0.78 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.0, 143.6, 135.7, 134.3, 132.5, 131.6, 131.4, 129.6, 128.4, 128.3, 127.7, 126.8, 126.1, 125.6, 117.8, 114.4, 111.8, 83.1, 63.9, 49.6, 44.8, 39.0, 33.4, 27.0, 24.7, 24.2, 20.9, 19.5, 19.3 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 35.6 ppm. IR: 2932, 2856, 2217, 1361, 1111, 702 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{43}H_{54}BNO_3Si$, 694.3858; found, 694.3927.

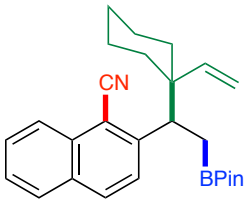
2-(3-cyclohexyl-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-1-naphthonitrile



Major diastereomer: ^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.25 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.64 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.53 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 5.96 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.04 (dd, *J* = 10.8, 1.2 Hz, 1H), 4.91 (dd, *J* = 17.6, 1.2 Hz, 1H), 3.94 (dd, *J* = 10.4, 6.4 Hz, 1H), 2.01-1.97 (m, 1H), 1.86-1.84 (m, 1H), 1.80-1.77 (m, 2H), 1.64-1.61 (m, 1H), 1.30-1.13 (m, 8H), 1.03 (s, 3H), 0.98-0.89 (m, 1H), 0.87 (s, 6H), 0.73 (s, 6H)

ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.2, 142.9, 132.6, 131.4, 131.2, 128.3, 128.2, 126.9, 126.7, 125.6, 117.7, 113.5, 112.0, 81.3, 47.4, 45.0, 44.2, 28.5, 27.7, 27.4, 27.2, 26.9, 24.7, 24.2, 15.6 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 33.9 ppm. IR: 2925, 2851, 2218, 1360, 1143, 732 cm^{-1}. HRMS-ESI (*m/z*) $[M + NH_4]^+$ calcd for $C_{29}H_{38}BNO_2$, 461.3350; found, 461.3348.

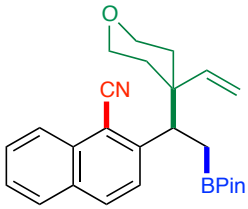
2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(1-vinylcyclohexyl)ethyl)-1-naphthonitrile



According to the General Procedure, 1-(2-cyclohexylideneethyl)-2-vinylnaphthalene (52.4 mg, 0.20 mmol), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), Li*O*t*Bu* (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (48.0 mg, 58%, d.r. > 95:5. ^{1}H NMR yield: 60%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.25 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.65 (ddd, *J* = 8.8, 6.8, 1.2 Hz, 1H), 7.54 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 5.53 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.36 (dd, *J* = 11.2, 1.2 Hz, 1H), 4.97 (dd, *J* = 17.6, 1.2 Hz, 1H), 3.53 (dd, *J* = 16.4, 4.4 Hz, 1H), 2.09 (d, *J* = 11.2 Hz, 1H), 1.56-1.20 (m, 12H), 0.88 (s, 6H), 0.76 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.9, 141.6, 132.5, 131.44, 131.39, 128.4, 128.3, 126.7, 126.4, 125.5, 117.9, 117.3, 111.6, 83.0, 51.2, 44.7, 34.6, 34.2, 26.3, 24.7, 24.2, 22.5, 22.3 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.6 ppm. IR: 2930, 2855, 2217, 1361, 1144, 847 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{27}H_{34}BNO_2$, 416.2772; found, 416.2774.

2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-vinyltetrahydro-2H-pyran-4-yl)ethyl)-1-naphthonitrile

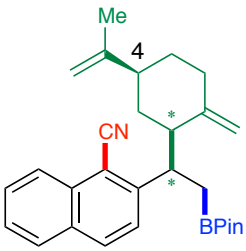


According to the General Procedure, 4-(2-(2-vinylnaphthalen-1-yl)ethylidene)tetrahydro-2*H*-pyran (52.8 mg, 0.20 mmol, *E*/*Z* > 95:5), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol),

[(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), LiO*t*Bu (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-30% EtOAc/hexanes) to afford the title compound as a yellowish oil (39.0 mg, 47%. ^{1}H NMR yield: 50%).

^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.26 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.67 (ddd, *J* = 8.8, 6.8, 1.2 Hz, 1H), 7.55 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 5.57 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.04 (dd, *J* = 11.2, 1.2 Hz, 1H), 5.00 (dd, *J* = 17.6, 1.2 Hz, 1H), 3.77 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.70 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.61-3.44 (m, 2H), 3.40 (ddd, *J* = Hz, 1H), 2.03-1.92 (m, 2H), 1.75 (ddd, *J* = 12.4, 12.4, 4.4 Hz, 1H), 1.38 (dd, *J* = 15.6, 4.8 Hz, 1H), 1.26-1.22 (m, 2H), 0.89 (s, 6H), 0.76 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 140.3, 132.5, 131.64, 131.57, 128.6, 128.3, 127.0, 126.2, 125.6, 118.6, 111.9, 83.2, 74.4, 64.3, 50.8, 42.8, 34.5, 34.4, 24.7, 24.2 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 33.7 ppm. IR: 2941, 2862, 2217, 1362, 1143, 729 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{26}H_{32}BNO_3$, 418.2564; found, 418.2573.

2-((*R*)-1-(2-methylene-5-(prop-1-en-2-yl)cyclohexyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1-naphthonitrile

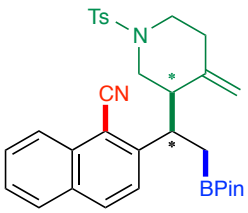


According to the General Procedure, (*S*)-1-((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)-2-vinylnaphthalene (57.6 mg, 0.20 mmol, *E*/*Z* > 95:5), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), LiO*t*Bu (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-30% EtOAc/hexanes) to afford the title compound as a yellowish oil (52.0 mg, 59%. ^{1}H NMR yield: 60%).

A mixture of two diastereomers relative to C4: ^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.24 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.66-7.61 (m, 2H), 7.55-7.51 (m, 3H), 7.45 (d, *J* = 8.8 Hz, 1H), 4.77-4.63 (m, 5H), 4.28-4.27 (m, 1H), 4.02-4.01 (m, 1H), 3.99-3.93 (m, 2H), 2.63-2.58

(m, 2H), 2.48-2.42 (m, 1H), 2.30-2.02 (m, 4H), 1.96-181 (m, 2H), 1.82 (s, 3H), 1.71 (s, 3H), 1.62-1.22 (m, 11H), 1.03 (s, 6H), 0.99 (s, 6H), 0.90 (s, 6H), 0.84 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.3, 151.2, 150.0, 149.92, 149.86, 119.2, 133.0, 132.61, 132.60, 131.4, 128.4, 128.37, 138.36, 128.33, 126.7, 125.4, 125.3, 124.5, 117.6, 117.2, 110.1, 109.7, 109.0, 108.9 107.9, 83.22, 83.18, 50.9, 48.1, 45.6, 41.1, 40.3, 38.8, 36.9, 35.7, 34.3, 33.7, 33.5, 31.8, 25.0, 24.8, 24.6, 24.3, 21.2, 20.8 ppm (some sp^2 carbon signals of these two diastereomers overlapped). ^{11}B NMR (128 MHz, $CDCl_3$) δ: 34.0 ppm. IR: 2931, 2217, 1363, 1142, 888, 751 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{29}H_{36}BNO_2$, 442.2929; found, 442.2919.

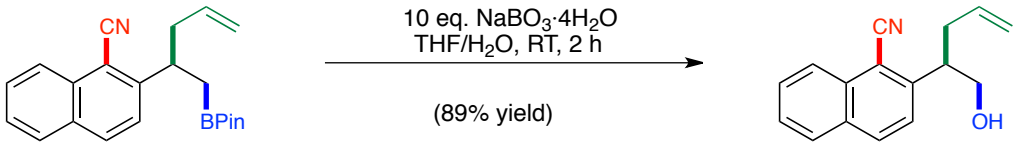
2-(1-(4-Methylene-1-tosylpiperidin-3-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1-naphthonitrile



According to the General Procedure, 1-tosyl-4-((2-vinylnaphthalen-1-yl)methyl)-1,2,3,6-tetrahydropyridine (80.6 mg, 0.20 mmol, *E*/*Z* > 95:5), NCTS (65.3 mg, 0.24 mmol), B_2Pin_2 (55.9 mg, 0.22 mmol), [(CyJohnPhos)Cu][OTf] (22.5 mg, 0.040 mmol), LiO*t*Bu (19.2 mg, 0.24 mmol) and dioxane (0.50 mL) were used. The crude reaction mixture was rapidly purified by column chromatography with the aid of Biotage Isolera (25 g SNAP cartridge, 0-30% EtOAc/hexanes) to afford the title compound as a yellowish oil (62.0 mg, 56%. ^{1}H NMR yield: 58%).

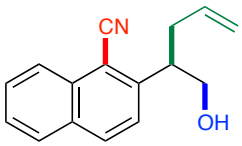
^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.14 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.63 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.53 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.68 (s, 1H), 4.37 (s, 1H), 3.74-3.66 (m, 1H), 3.59-3.55 (m, 1H), 3.40-3.35 (m, 1H), 3.07-3.01 (m, 1H), 2.58-2.56 (m, 1H), 2.44 (s, 3H), 2.01-1.90 (m, 2H), 1.38 (dd, *J* = 15.6, 5.2 Hz, 1H), 1.15 (dd, *J* = 15.6, 10.4 Hz, 1H), 0.92 (s, 6H), 0.85 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.1, 143.7, 141.3, 133.6, 132.8, 132.5, 131.4, 129.9, 128.6, 128.4, 127.8, 127.0, 125.3, 124.3, 117.0, 114.6, 109.8, 83.3, 50.7, 47.3, 42.7, 39.4, 27.4, 24.7, 24.3, 21.7 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 34.0 ppm. IR: 2976, 2215, 1346, 1163, 908, 731 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{32}H_{37}BN_2O_4S$, 557.2656; found, 557.2668.

Procedure for Derivatization Transformations



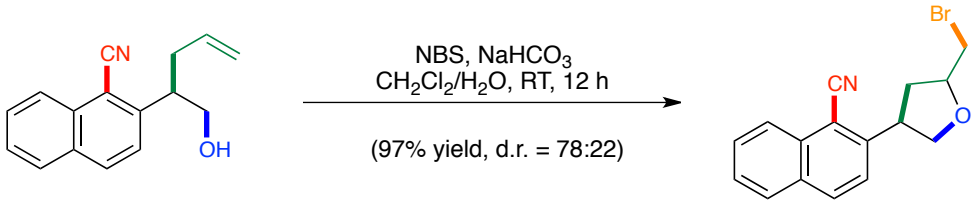
Oxidation[4]: To a round-bottom flask were added the boronate (250 mg, 0.72 mmol), THF (8.6 mL) and water (5.8 mL). $NaBO_3 \cdot 4H_2O$ (1.11 g, 7.20 mmol) was then added in one portion and the reaction mixture was allowed to stir vigorously at room temperature for 2 h. EtOAc (10 mL) was then added. The organic layer was separated and the aqueous layer was extracted with EtOAc (10 mL × 3). Combined organic layers were dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography with the aid of Biotage Isolera (10-33% EtOAc/hexanes, 25 g SNAP cartridge) to afford the alcohol as a colorless oil (150 mg, 88%). An independent experiment on 0.10 mmol scale gave 21.3 mg (90%).

2-(1-Hydroxypent-4-en-2-yl)-1-naphthonitrile



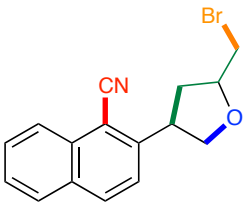
^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.23 (d, J = 8.8 Hz, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.68 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.58 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 5.77-5.68 (m, 1H), 5.03 (dd, J = 16.8, 1.2 Hz, 1H), 4.97 (d, J = 10.0 Hz, 1H), 3.98 (dd, J = 11.2, 5.6 Hz, 1H), 3.91 (dd, J = 10.8, 7.2 Hz, 1H), 3.72-3.67 (m, 1H), 2.70-2.64 (m, 1H), 2.54-2.46 (m, 1H), 1.67 (s, broad, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.0, 135.2, 133.2, 132.9, 131.9, 128.8, 128.5, 127.2, 125.5, 124.2, 117.6, 117.1, 110.6, 66.1, 47.0, 36.2 ppm. IR: 3446, 2363, 2220, 1062, 823, 748 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{16}H_{15}NO$, 238.1226; found, 238.1215.

[4] K. Kubota, E. Yamamoto, H. Ito, *J. Am. Chem. Soc.* **2013**, *135*, 2635.



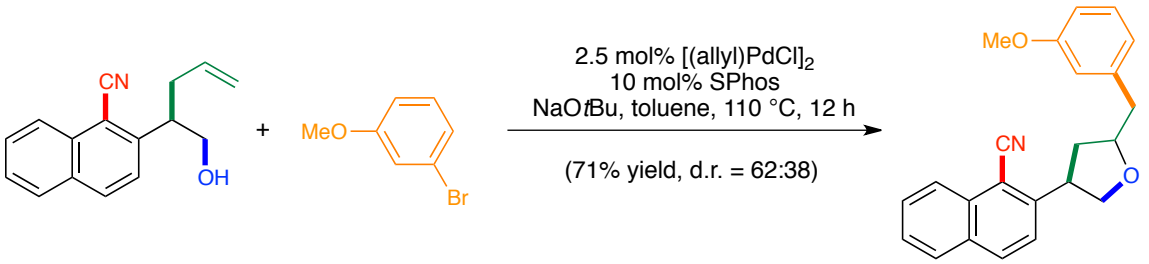
Bromoetherification[5]: $NaHCO_3$ (11.2 mg, 0.13 mmol, 1.5 eq) and NBS (19.7 mg, 0.11 mmol, 1.25 eq) were added to a CH_2Cl_2 solution (0.44 mL, 0.25 M) of the alcohol (21 mg, 0.088 mmol, 1.0 eq) in succession at room temperature in air. The reaction mixture was allowed to stir at room temperature for 12 h. Solvent was removed *in vacuo* and the crude reaction mixture was purified by column chromatography with the aid of Biotage Isolera (10 g SNAP cartridge, 0-8% EtOAc/hexanes) to afford the title compound as a colorless oil (27.0 mg, 97%, d.r. = 78:22).

2-(5-(Bromomethyl)tetrahydrofuran-3-yl)-1-naphthonitrile



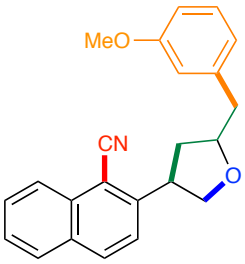
Major diastereomer: ^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.21 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.68 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.58 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 4.38-4.20 (m, 3H), 4.08 (dd, J = 8.4, 6.4 Hz, 1H), 3.63 (dd, J = 10.4, 5.2 Hz, 1H), 3.56 (ddd, J = 10.4, 10.4, 5.2 Hz, 1H), 2.71 (ddd, J = 14.4, 8.0, 6.4 Hz, 1H), 2.00 (ddd, J = 12.8, 8.8, 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.8, 133.9, 132.7, 131.8, 129.1, 128.5, 127.4, 125.4, 123.6, 116.9, 109.4, 79.1, 74.5, 44.2, 39.8, 35.3 ppm. Minor diastereomer: ^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.22 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.68 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.58 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 4.57-4.49 (m, 1H), 4.38-4.20 (m, 2H), 4.00 (dd, J = 8.8, 6.0 Hz, 1H), 3.54 (dd, J = 10.4, 5.6 Hz, 1H), 3.49 (dd, J = 10.4, 6.4 Hz, 1H), 2.48 (ddd, J = 14.8, 8.8, 6.0 Hz, 1H), 2.00 (ddd, J = 13.2, 7.6, 6.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.8, 133.8, 132.8, 131.8, 129.1, 128.5, 127.4, 125.4, 123.5, 116.8, 109.4, 78.7, 74.3, 43.7, 38.8, 35.3 ppm. IR: 2952, 2867, 2217, 1506, 1052, 751 cm^{-1}. HRMS-ESI (*m/z*) [M + H]$^+$ calcd for $C_{16}H_{14}BrNO$, 316.0332; found, 316.0333.

[5] I. D. Jurberg, Y. Odabachian, F. Gagosz, *J. Am. Chem. Soc.* **2010**, *132*, 3543.



Oxyarylation[6]: To an oven-dried screw-cap test tube equipped with a stir bar were added the alcohol (23.7 mg, 0.10 mmol, 1.0 eq), $[(allyl)PdCl]_2$ (0.9 mg, 0.0025 mmol, 2.5 mol%), SPhos (4.1 mg, 0.010 mmol, 10 mol%) and NaO*t*Bu (19.2 mg, 0.20 mmol, 2.0 eq). The test tube was evacuated and backfilled with argon and this process was repeated for a total of three times. 3-Bromoanisole (37.4 mg/25.3 μL, 0.20 mmol, 2.0 eq) and toluene (0.25 mL, 0.25 M) were then added and the reaction mixture was heated at 110 °C for 12 h, and then cooled to room temperature. The reaction mixture was allowed to pass through a short silica plug eluting with EtOAc, then concentrated *in vacuo* and purified with the aid of Biotage Isolera (0-8% EtOAc/hexanes, 10 g SNAP cartridge) to afford the title compound as a pale yellow oil (26.6 mg, 71%, d.r. = 62:38).

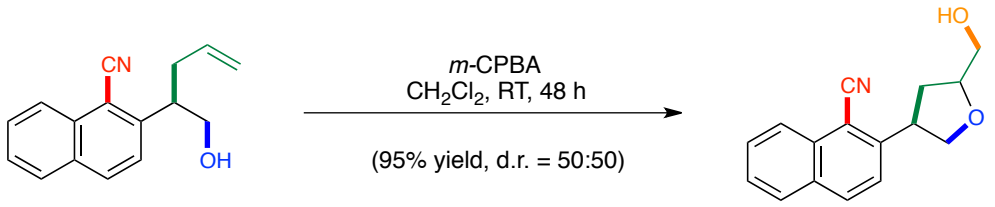
2-(5-(3-Methoxybenzyl)tetrahydrofuran-3-yl)-1-naphthonitrile



Major diastereomer: ^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.20 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.68 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.60-7.50 (m, 2H), 7.26-7.21 (m, 1H), 6.88-6.84 (m, 2H), 6.78-6.77 (m, 1H), 4.51-4.46 (m, 1H), 4.38 (dd, *J* = 8.8, 7.2 Hz, 1H), 4.24-4.18 (m, 1H), 3.92 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.82 (s, 3H), 3.03 (dd, *J* = 13.6, 8.8 Hz, 1H), 2.84 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.34 (ddd, *J* = 13.2, 8.8, 6.8 Hz, 1H), 2.16 (ddd, *J* = 13.2, 7.2, 5.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: ppm. Minor diastereomer: ^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.19 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.68 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.60-7.50 (m, 2H), 7.26-7.21 (m, 1H), 6.88-6.84 (m, 2H), 6.78-6.77 (m, 1H), 4.31-4.27 (m, 1H), 4.18-4.15 (m, 1H), 4.01 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.80 (s, 3H), 3.08 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.94 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.61 (ddd, *J* = 14.0, 8.4, 5.6 Hz, 1H), 1.76 (ddd, *J* = 12.8, 9.6, 8.4 Hz, 1H) ppm. ^{13}C NMR

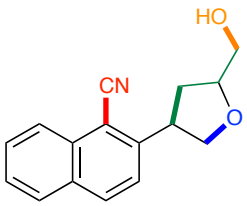
[6] J. P. Wolfe, M. A. Rossi, *J. Am. Chem. Soc.* **2004**, *126*, 1620.

(100 MHz, $CDCl_3$) δ: ppm. IR: 2934, 2217, 1594, 1259, 1051, 752 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{23}H_{21}NO_2$, 344.1645; found, 344.1661.



Dioxygenation[7]**:** *m*CPBA (29.0 mg, 0.12 mmol, 1.2 eq, <77% active content) were added to a CH_2Cl_2 solution (0.50 mL, 0.20 M) of the alcohol (23.7 mg, 0.088 mmol, 1.0 eq) in succession at room temperature in air. The reaction mixture was allowed to stir at room temperature for 48 h. Solvent was removed *in vacuo* and the crude reaction mixture was purified by column chromatography with the aid of Biotage Isolera (10 g SNAP cartridge, 10-50% EtOAc/hexanes) to afford the title compound as a colorless oil (24.0 mg, 95%, d.r. = 50:50).

2-(5-(Hydroxymethyl)tetrahydrofuran-3-yl)-1-naphthonitrile

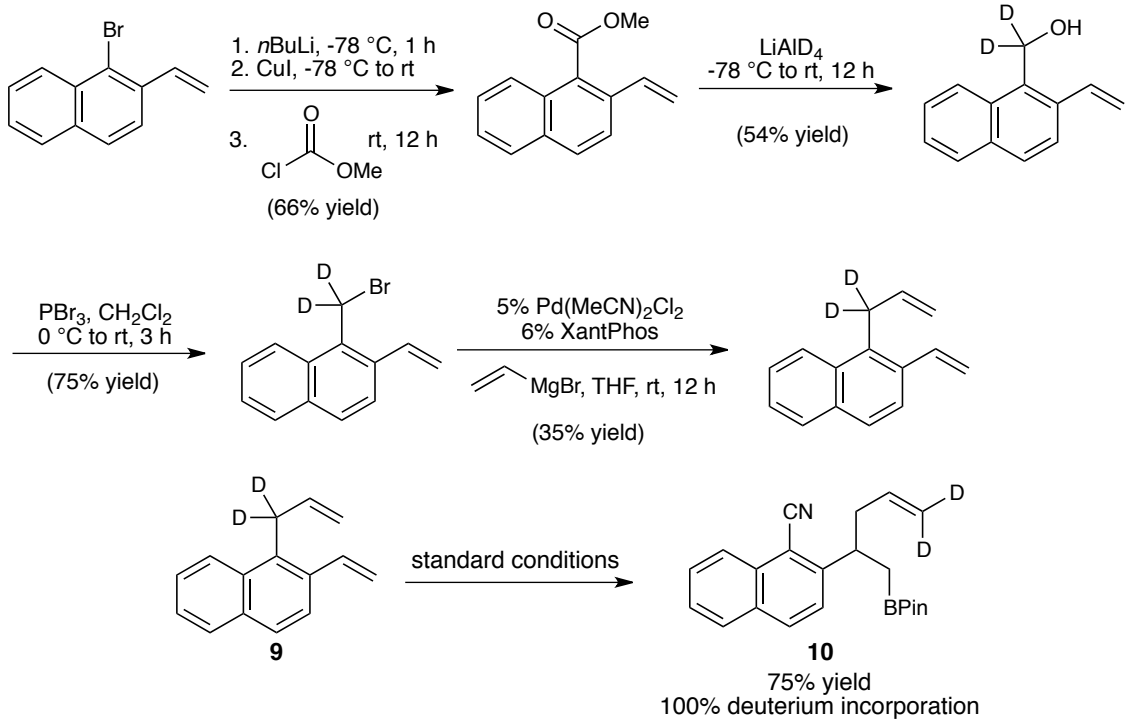


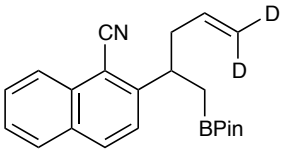
Major diastereomer: ^1H NMR (400 HMz, $CDCl_3$) δ: 8.20 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.68 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.60-7.55 (m, 3H), 4.38-4.15 (m, 2H), 3.77-3.65 (m, 2H), 2.38 (ddd, *J* = 13.2, 9.2, 6.8 Hz, 1H), 2.20 (s, broad, 1H), 2.17 (ddd, *J* = 13.2, 7.6, 6.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.3, 133.8, 132.8, 131.8, 129.0, 128.5, 127.3, 125.3, 123.7, 116.9, 109.3, 80.0, 74.0, 64.9, 44.0, 35.8 ppm. Minor diastereomer: ^1H NMR (400 HMz, $CDCl_3$) δ: 8.22 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.68 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.60-7.55 (m, 3H), 4.42-4.36 (m, 1H), 4.01-4.89 (m, 2H), 3.71-3.65 (m, 2H), 2.53 (ddd, *J* = 12.8, 9.2, 6.8 Hz, 1H), 1.99 (ddd, *J* = 12.8, 9.6, 9.6 Hz, 1H), 1.8 (s, broad, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.4, 133.7, 132.7, 131.8, 129.0, 128.5, 127.3, 125.3, 123.6, 116.9, 109.3, 80.9, 74.2, 64.3, 44.1, 36.3 ppm. IR: 3434, 2871, 2216, 1046, 824, 751 cm^{-1}. HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{16}H_{15}NO_2$, 254.1176; found, 254.1179.

[7] L. Wang, K. Thai, M. Gravel, *Org. Lett.* **2009**, *11*, 891.

Mechanistic Studies

Deuterium Incorporation Experiment: The deuterated allylvinylarene was prepared according to the procedure described by Fristrup[8] as detailed below:





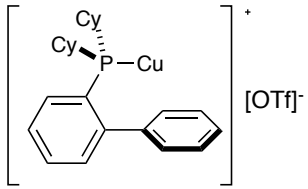
^{1}H NMR (400 HMz, $CDCl_3$) δ: 8.23 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.65 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.55 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 5.69 (t, *J* = 6.8 Hz, 1H), 3.77-3.69 (m, 1H), 2.58-2.51 (m, 1H), 2.50-2.42 (m, 1H), 1.39 (dd, *J* = 15.6, 6.8 Hz, 1H), 1.21 (dd, *J* = 15.6, 8.8 Hz, 1H), 1.08 (s, 6H), 1.03 (s, 6H) ppm.

Crossover Experiment: According to the General Procedure describe above, 1-(2-(3,4-dimethoxyphenyl)allyl)-2-vinylnaphthalene (30 mg, 0.090 mmol, 0.50 eq), 1-allyl-5,7-dimethyl-2-vinylnaphthalene (20 mg, 0.090 mmol, 0.50 eq), NCTS (59 mg, 0.216 mmol), B_2Pin_2 (50 mg, 0.198 mmol), [(CyJohnPhos)Cu][OTf] (20 mg, 0.036 mmol), LiO*t*Bu (17

[8] C. Engelin, T. Jensen, S. Rodriguez-Rodriguez, P. Fristrup, *ACS Catal.* **2013**, *3*, 294.

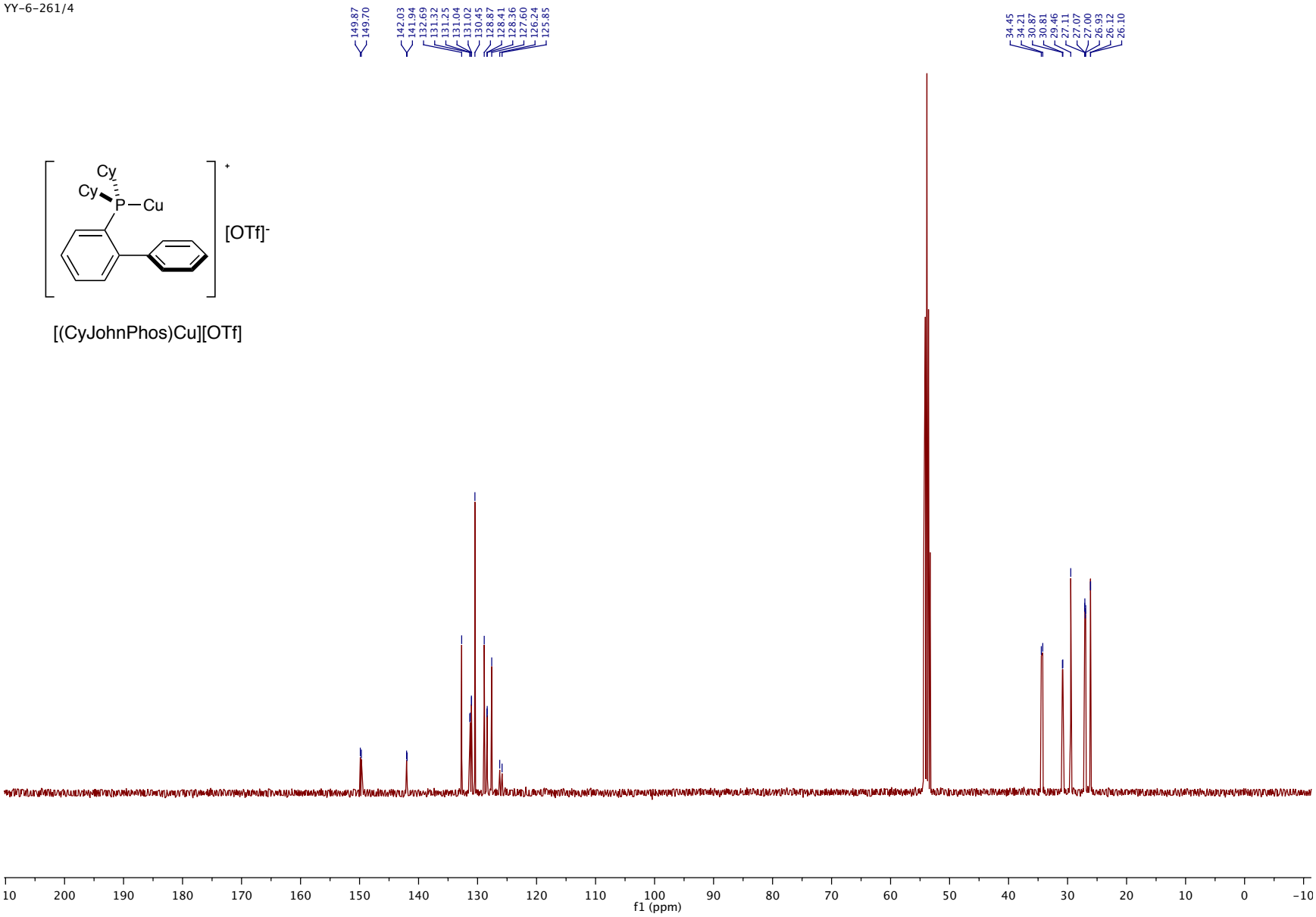
mg, 0.216 mmol) and dioxane (0.45 mL) were used. Crossover products were not observed by ^{1}H NMR analysis of the crude reaction mixture.

YY-6-261/1

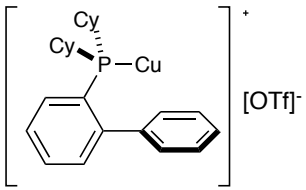


[(CyJohnPhos)Cu][OTf]

YY-6-261/4

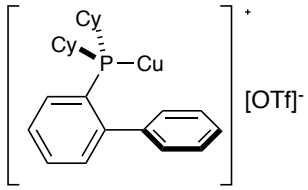

149.87
149.70
142.03
141.94
132.69
131.32
131.25
131.04
131.02
130.45
128.87
128.41
128.36
127.60
126.24
125.85
34.45
34.21
30.87
30.81
29.46
27.11
27.07
27.00
26.93
26.12
26.10
Cy
Cy
P
Cu
[OTf]-
+
[(CyJohnPhos)Cu][OTf]
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

YY-6-261/2

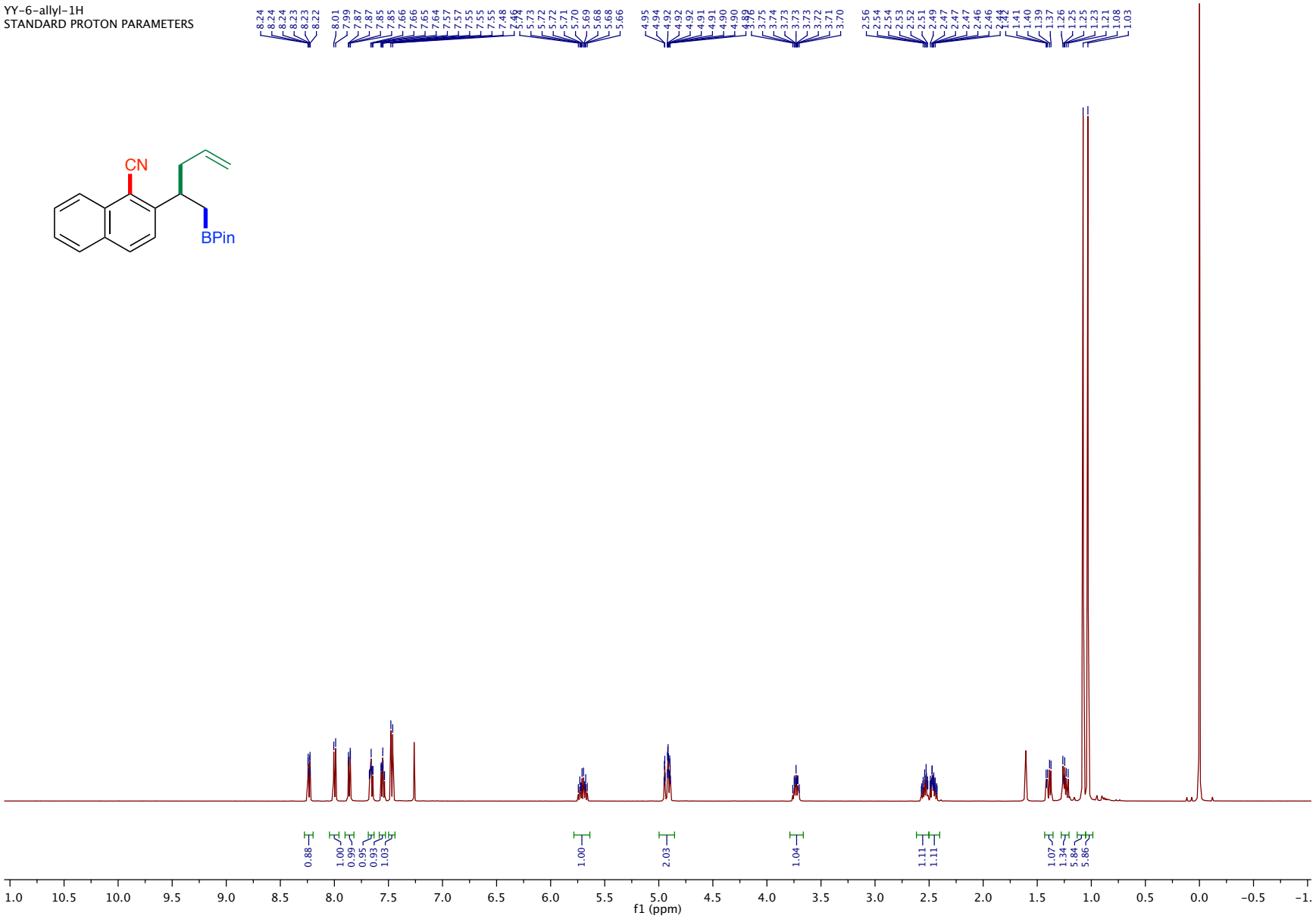


[(CyJohnPhos)Cu][OTf]

YY-6-261/3



[(CyJohnPhos)Cu][OTf]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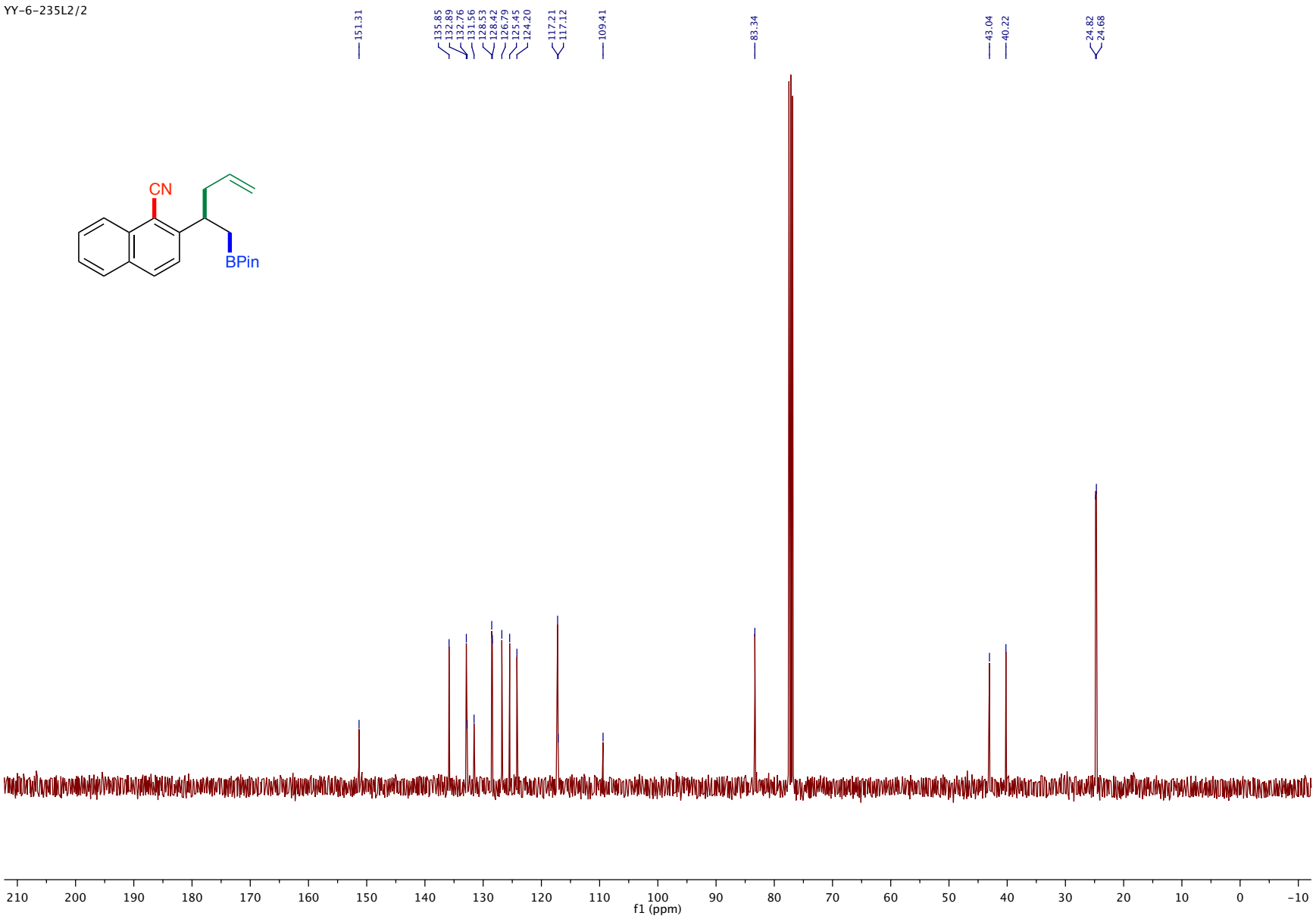
STANDARD PROTON PARAMETERS
CN
BPin
f1 (ppm)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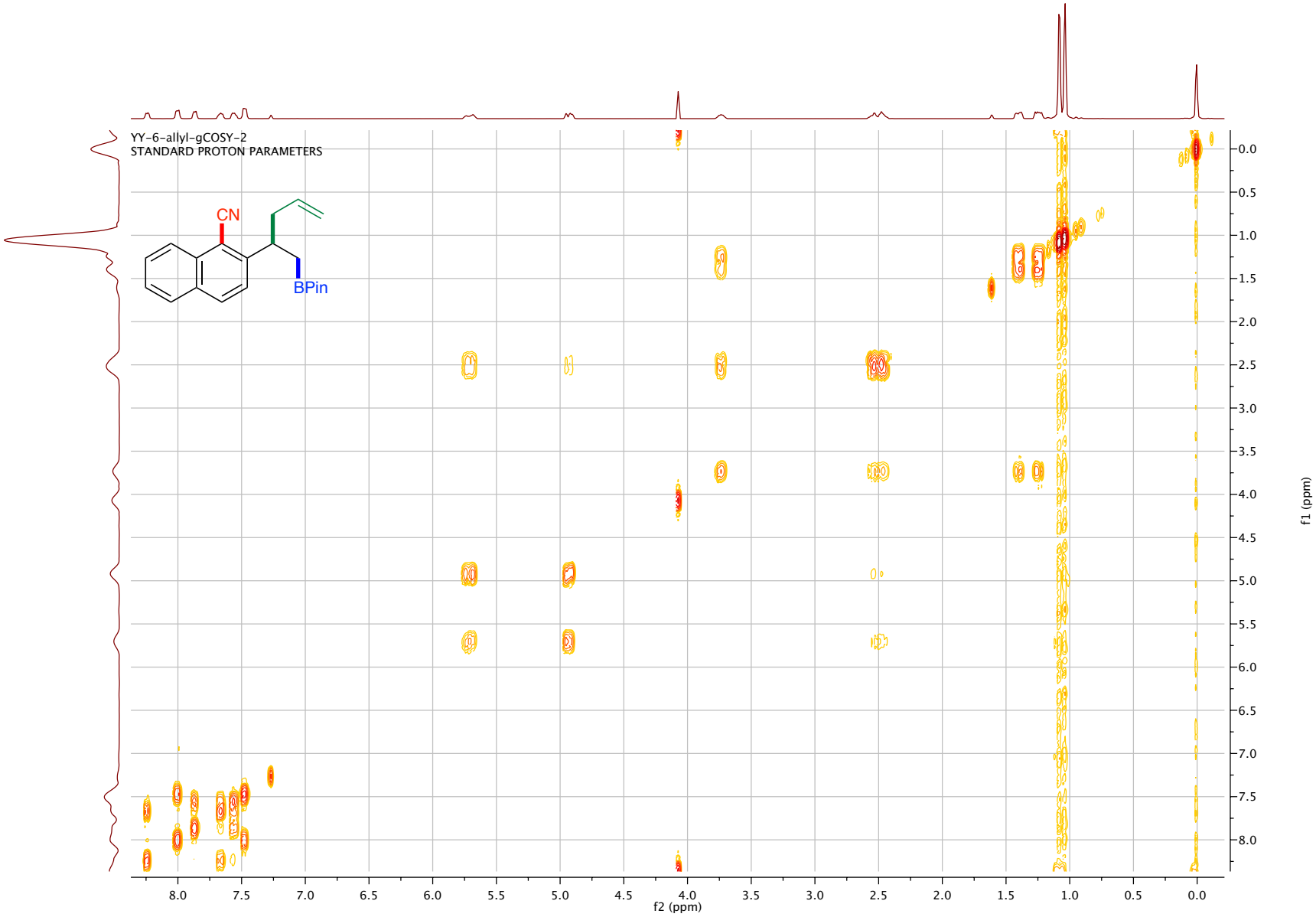
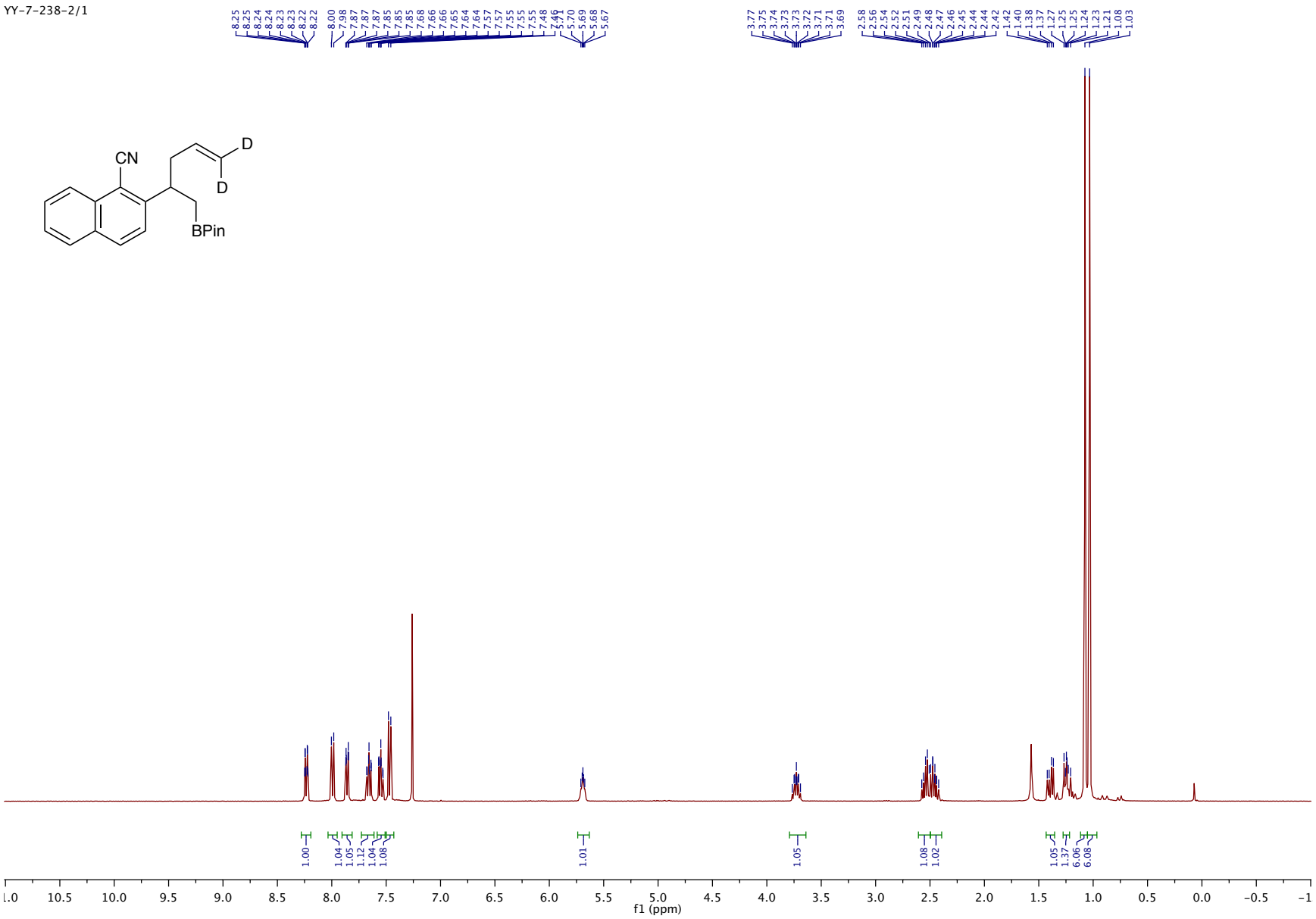
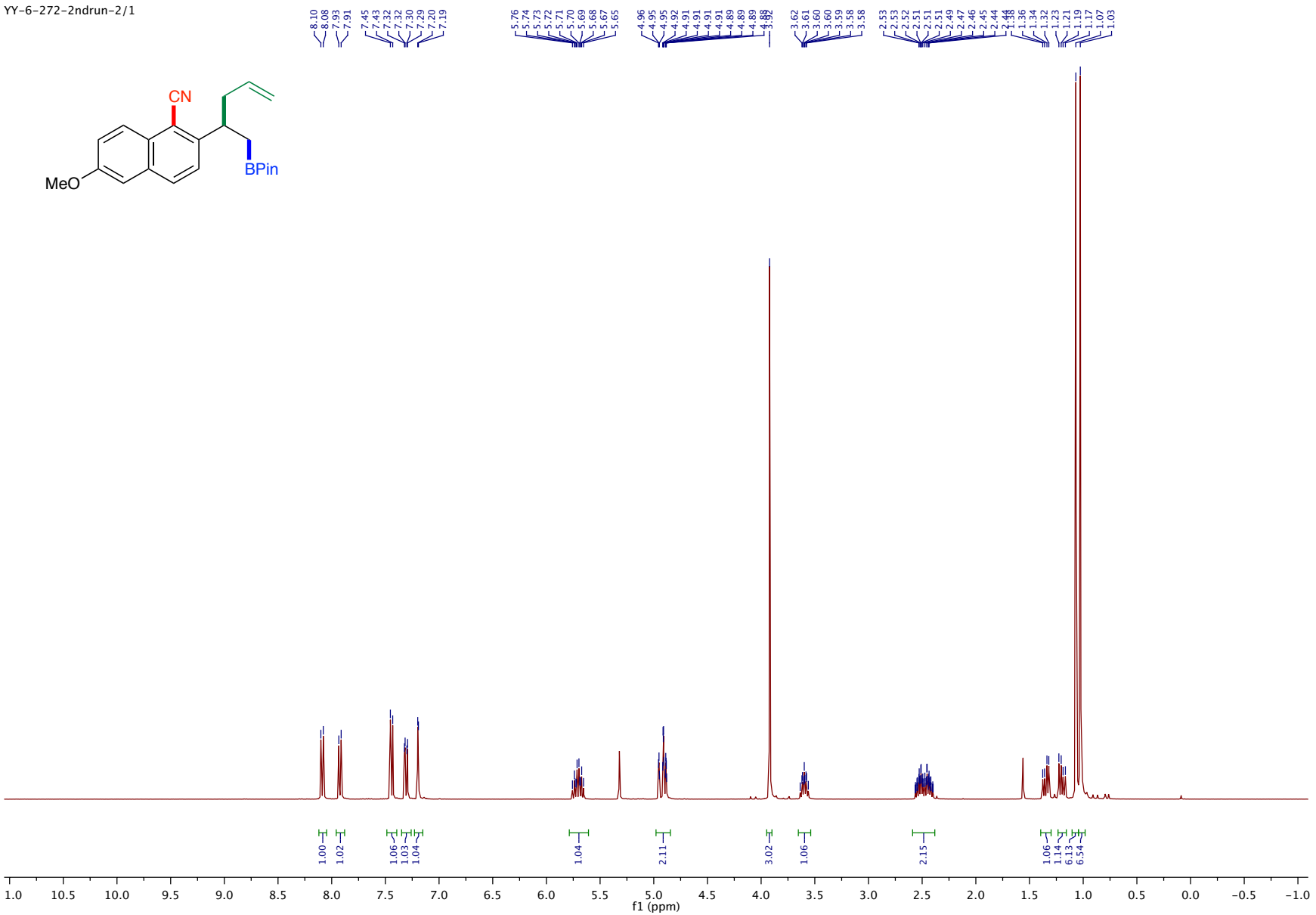
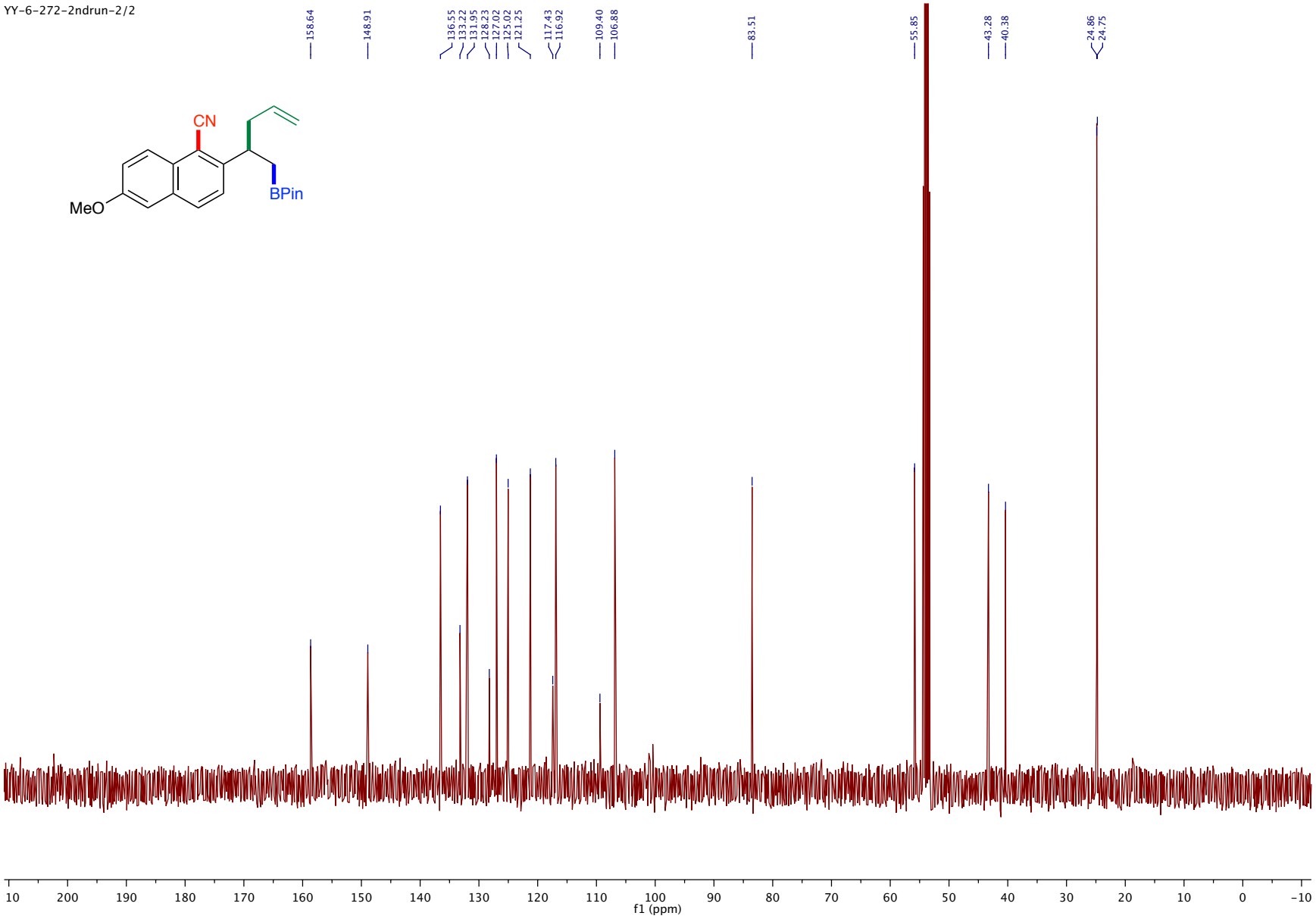
135.85
132.89
132.76
131.56
128.53
128.42
126.79
125.45
124.20
117.21
117.12
109.41
83.34
43.04
40.22
24.82
24.68
CN
BPin
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


YY-6-allyl-gCOSY-2
STANDARD PROTON PARAMETERS
CN
BPin
f2 (ppm)
f1 (ppm)


YY-7-238-2/1
CN
D
D
BPin
f1 (ppm)


YY-6-272-2ndrun-2/1
CN
BPin
MeO
f1 (ppm)


YY-6-272-2ndrun-2/2
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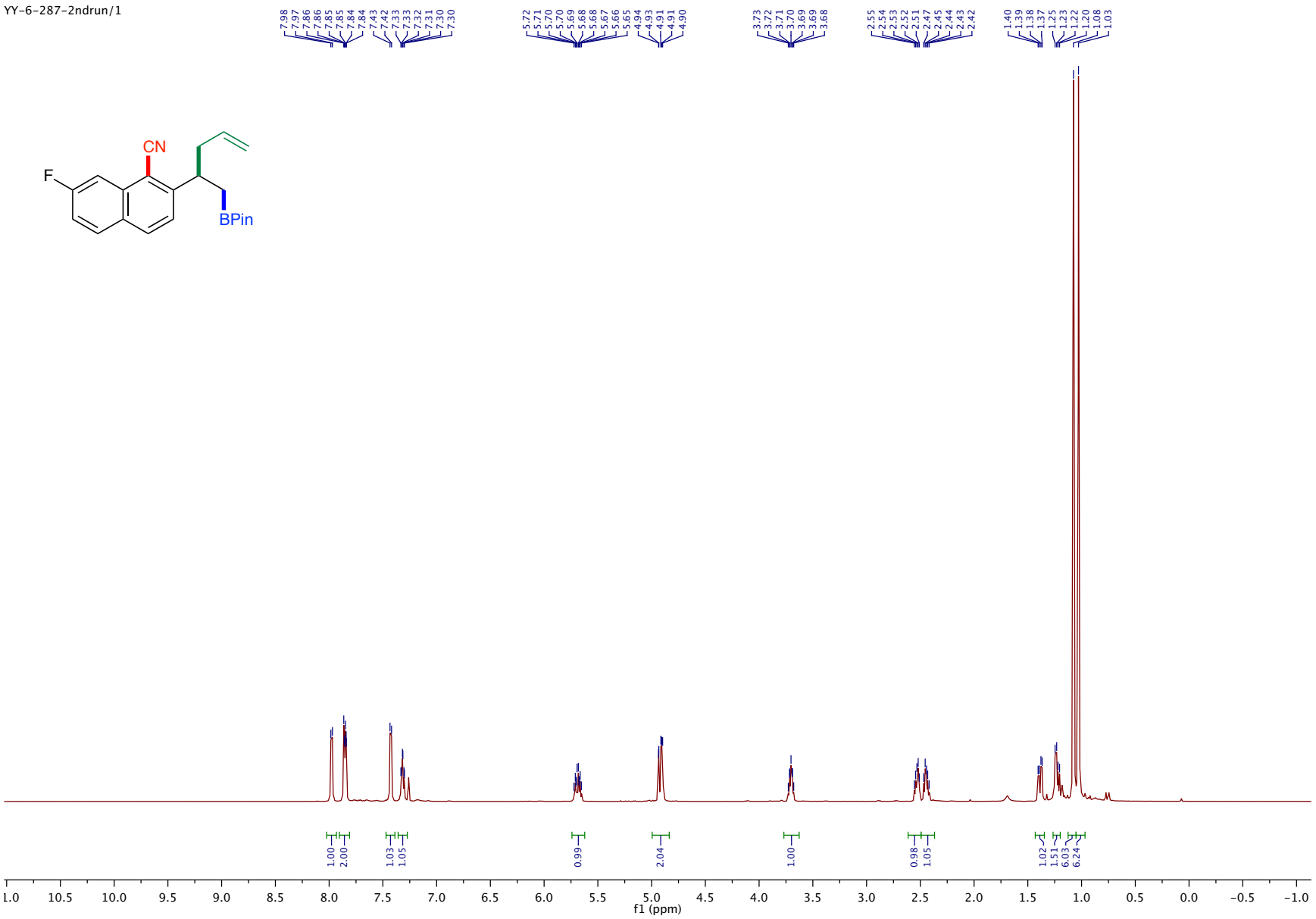
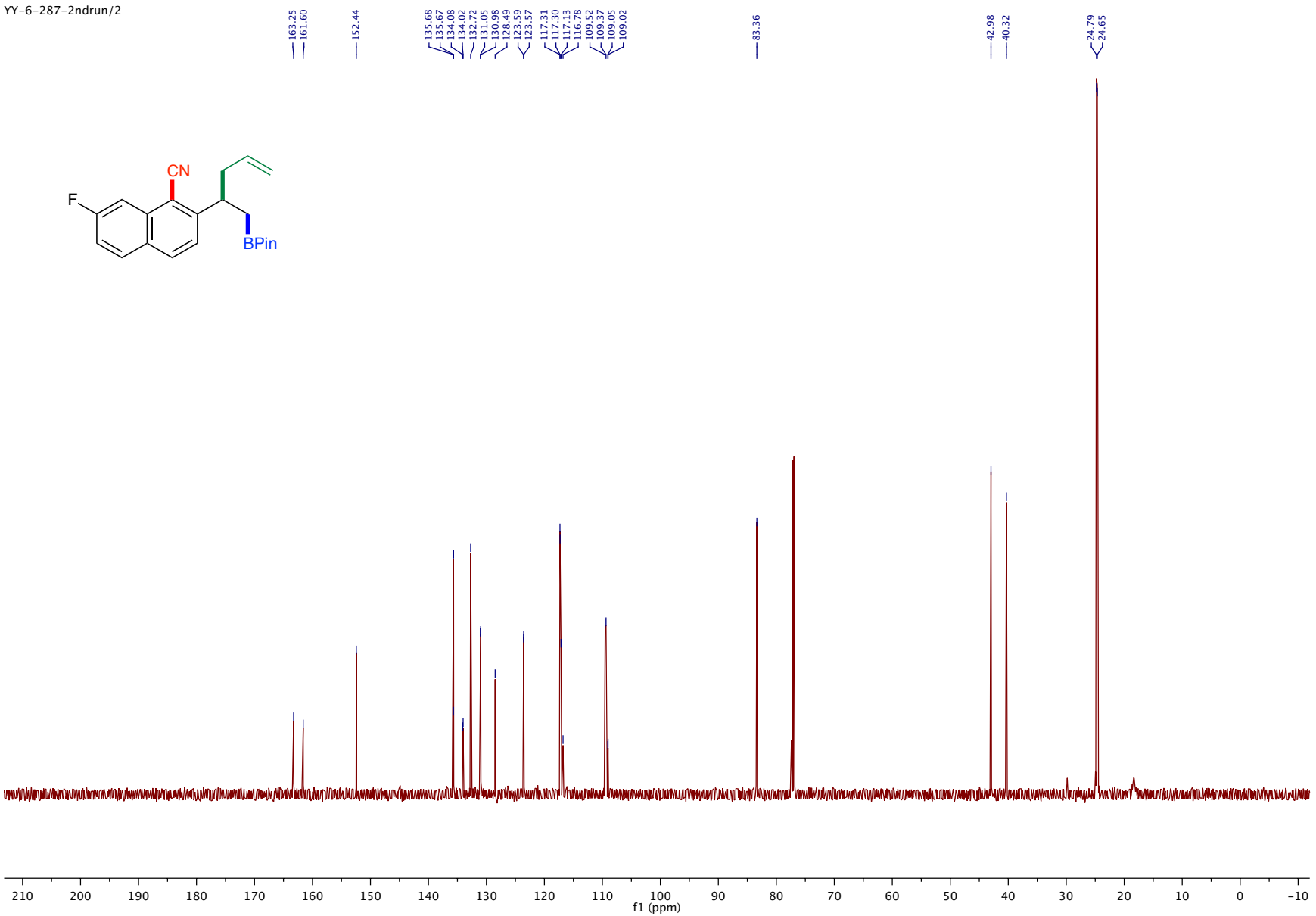
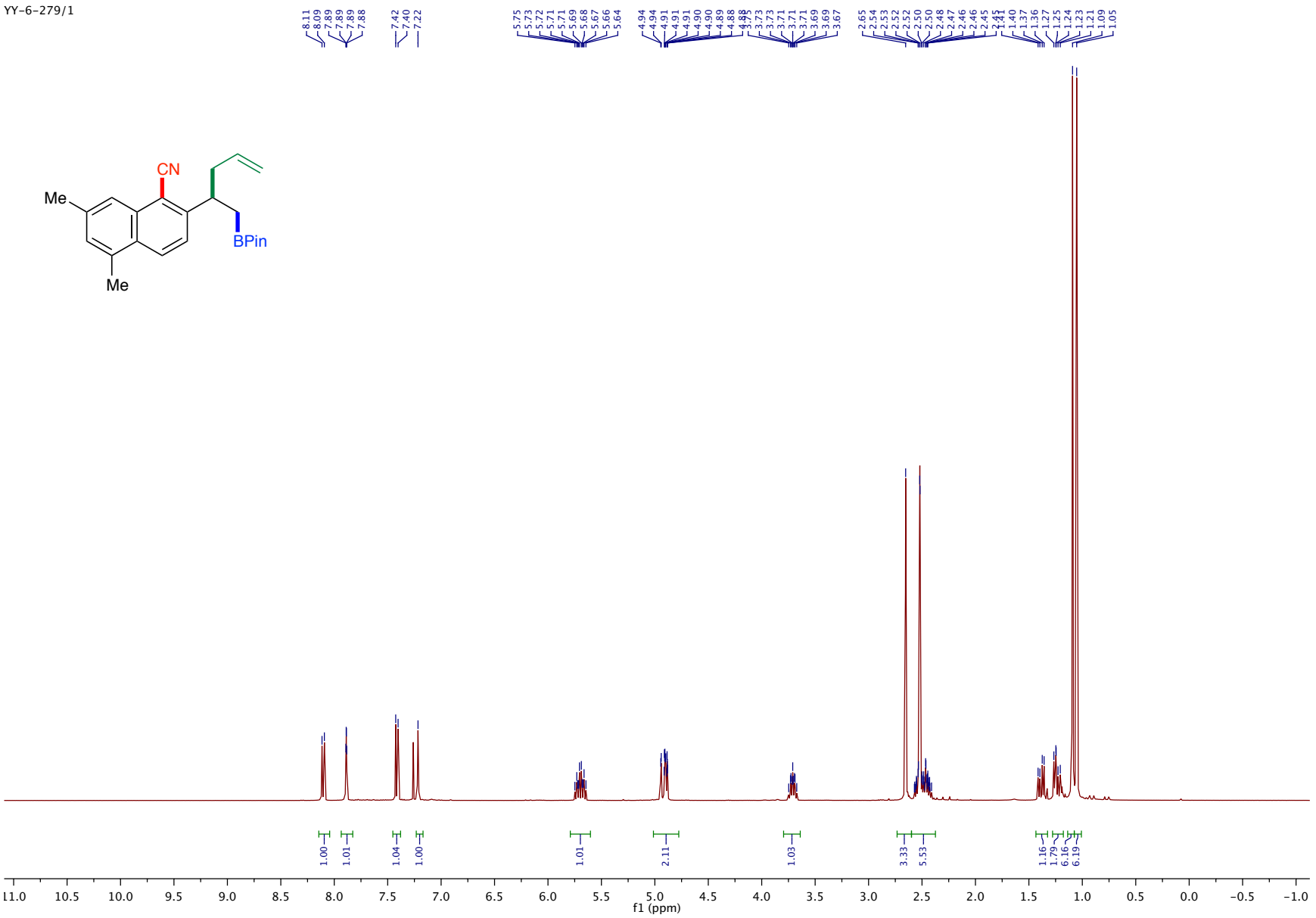
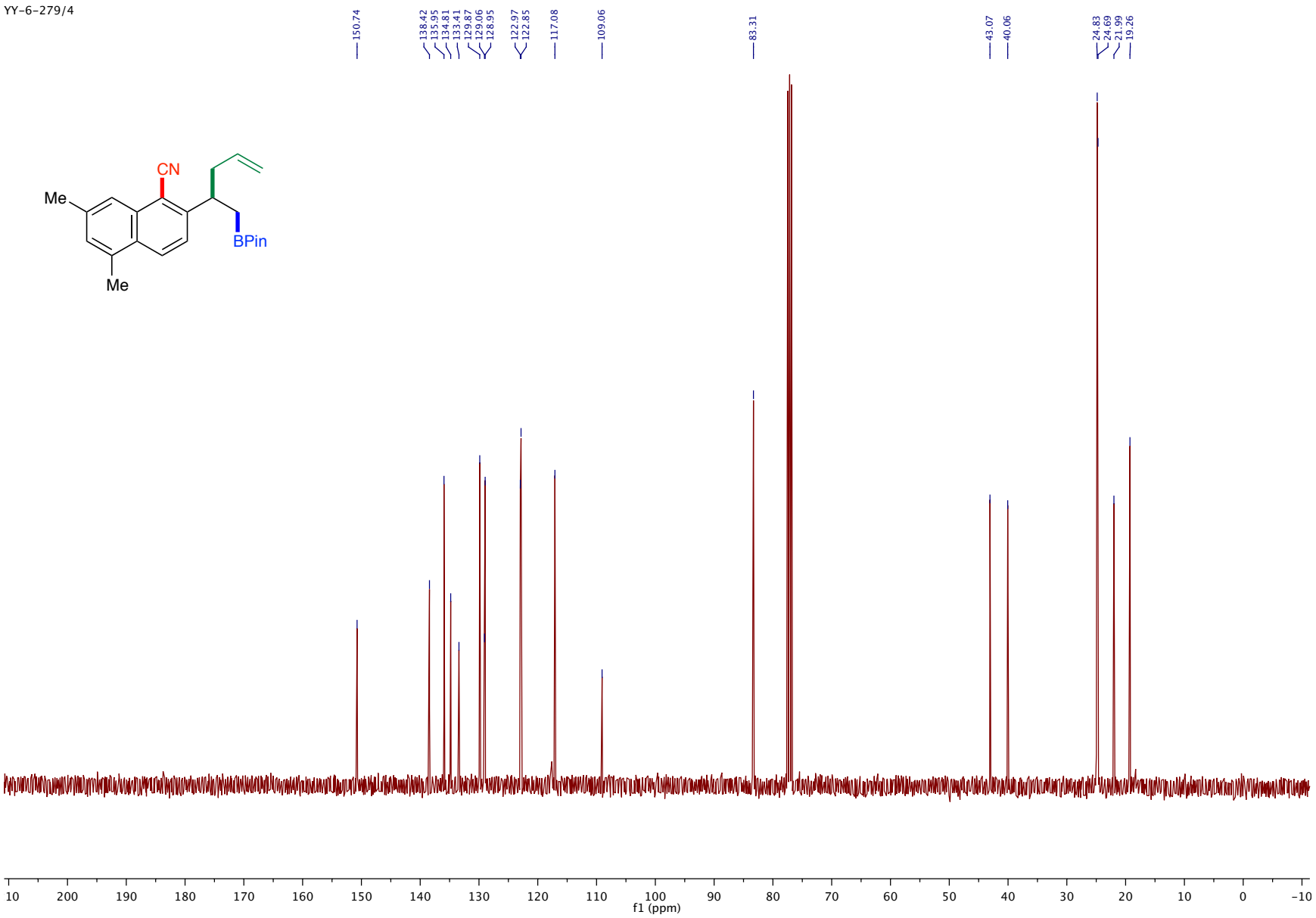
148.91
136.55
133.22
131.95
128.23
127.02
125.02
121.25
117.43
116.92
109.40
106.88
83.51
55.85
43.28
40.38
24.86
24.75
CN
BPin
MeO
f1 (ppm)


YY-6-287-2ndrun/1
7.98 7.97 7.86 7.86 7.85 7.85 7.84 7.84 7.43 7.42 7.33 7.33 7.32 7.31 7.30 7.30
5.72 5.71 5.70 5.70 5.69 5.68 5.68 5.67 5.66 5.65 4.94 4.93 4.91 4.91 4.90
3.73 3.72 3.71 3.70 3.69 3.69 3.68
2.55 2.54 2.53 2.52 2.51 2.47 2.45 2.44 2.43 2.42
1.40 1.39 1.38 1.37 1.25 1.23 1.22 1.20 1.08 1.03
CN
F
BPin
1.00 2.00 1.03 1.05 0.99 2.04 1.00 0.98 1.05 1.02 1.51 6.03 6.24
f1 (ppm)


YY-6-287-2ndrun/2
163.25
161.60
152.44
135.68
135.67
134.08
134.02
132.72
131.05
130.98
128.49
123.59
123.57
117.31
117.30
117.13
116.78
109.52
109.37
109.05
109.02
83.36
42.98
40.32
24.79
24.65
CN
F
BPin
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


YY-6-279/1
CN
Me
BPin
Me
f1 (ppm)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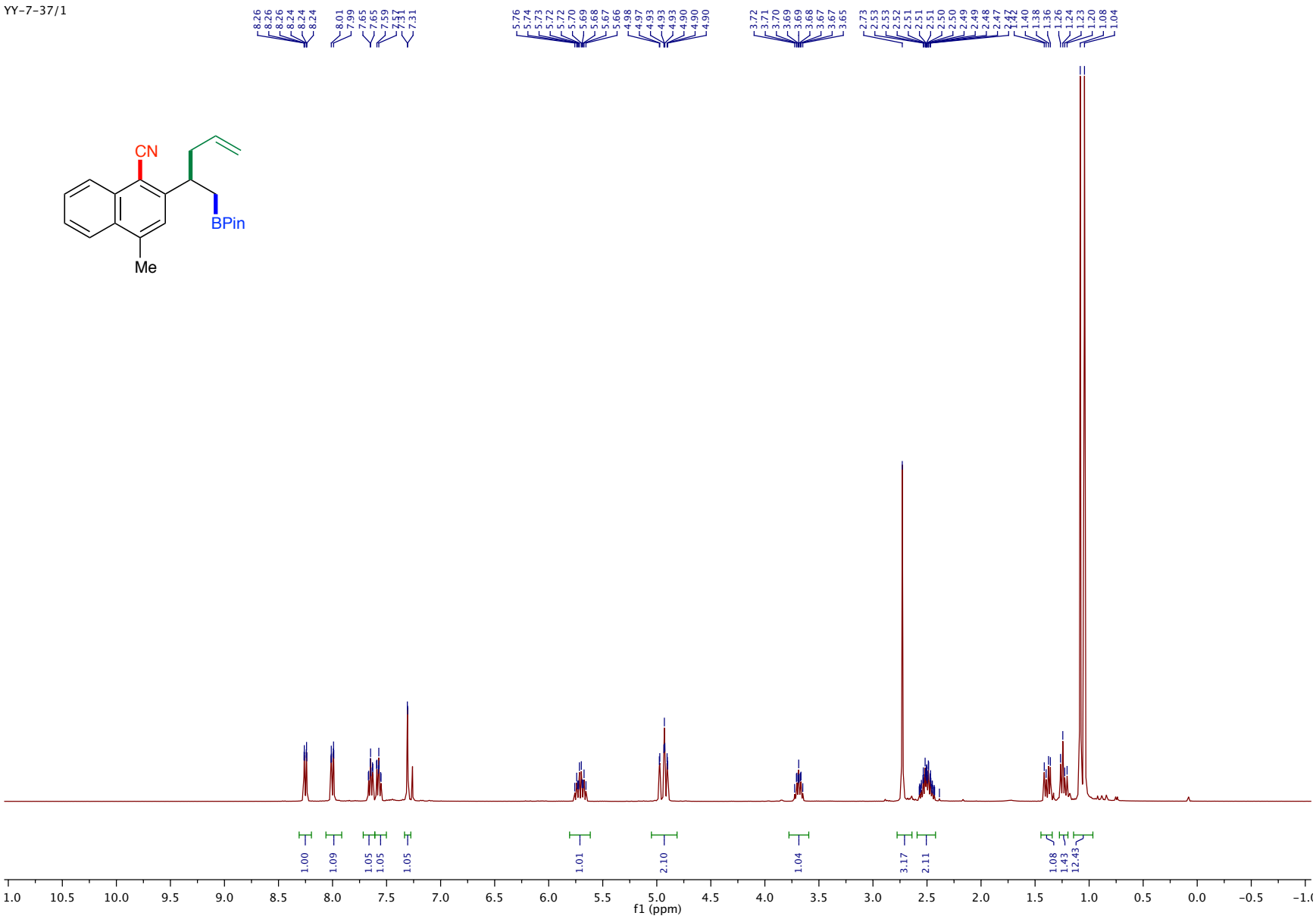
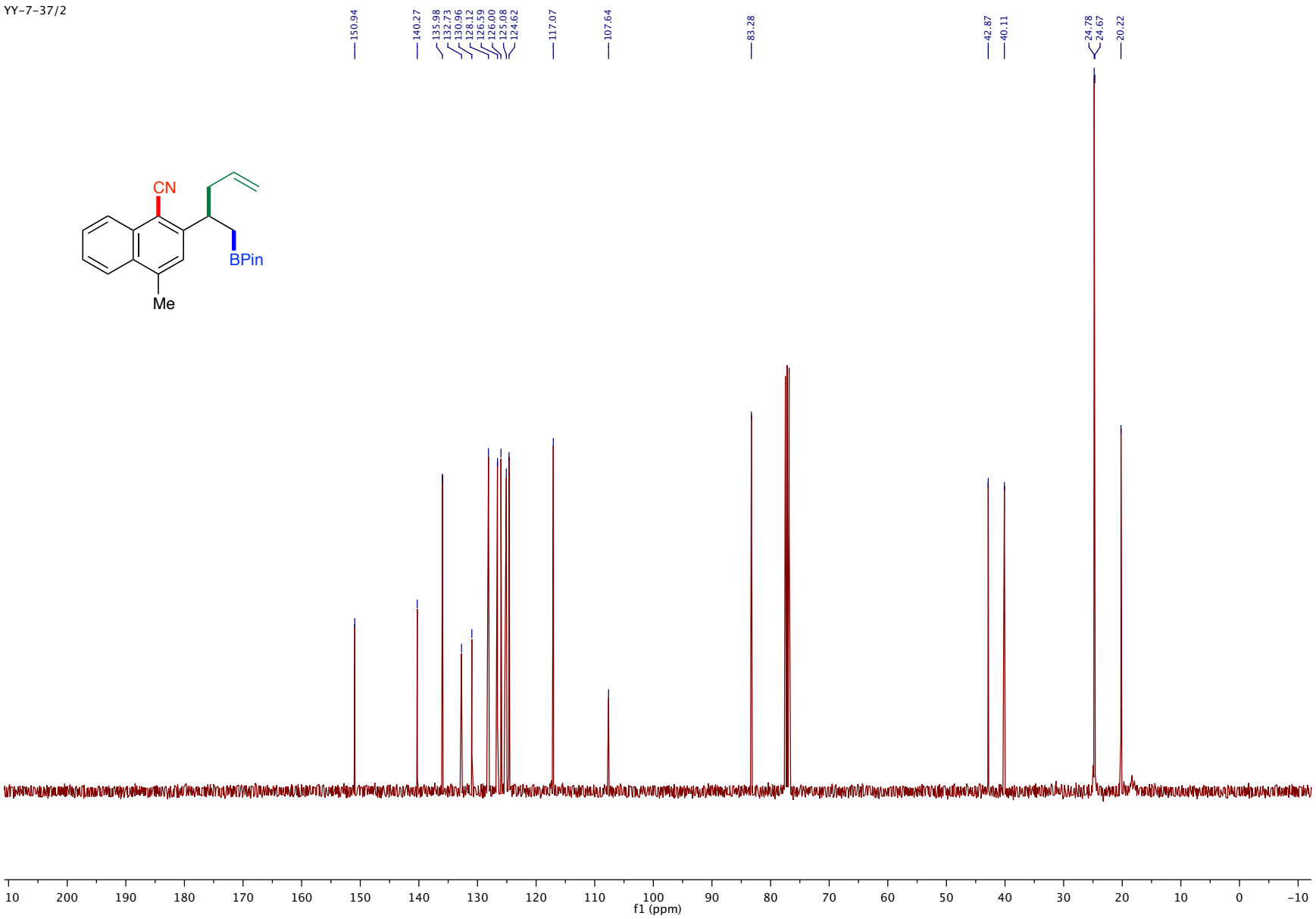
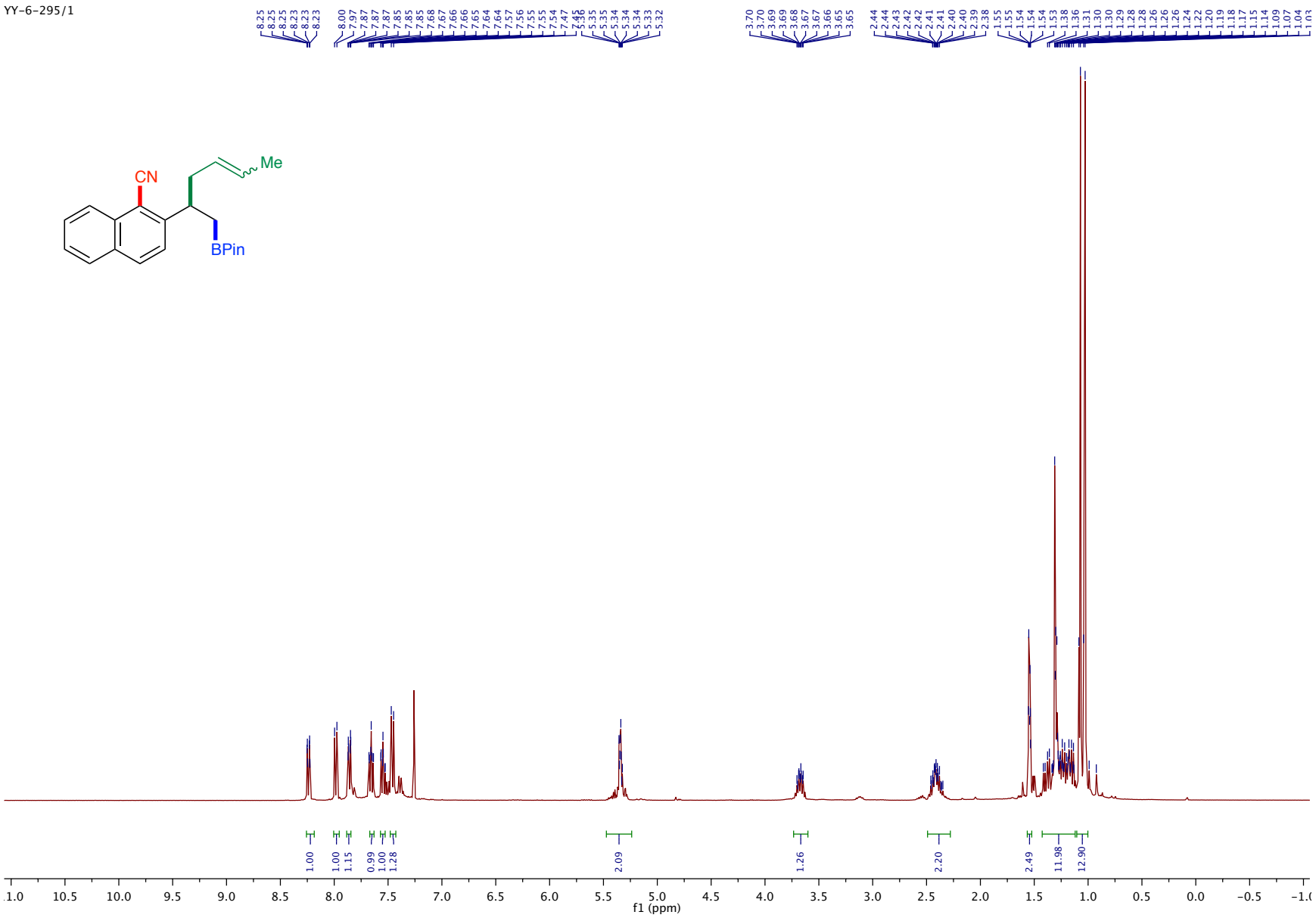
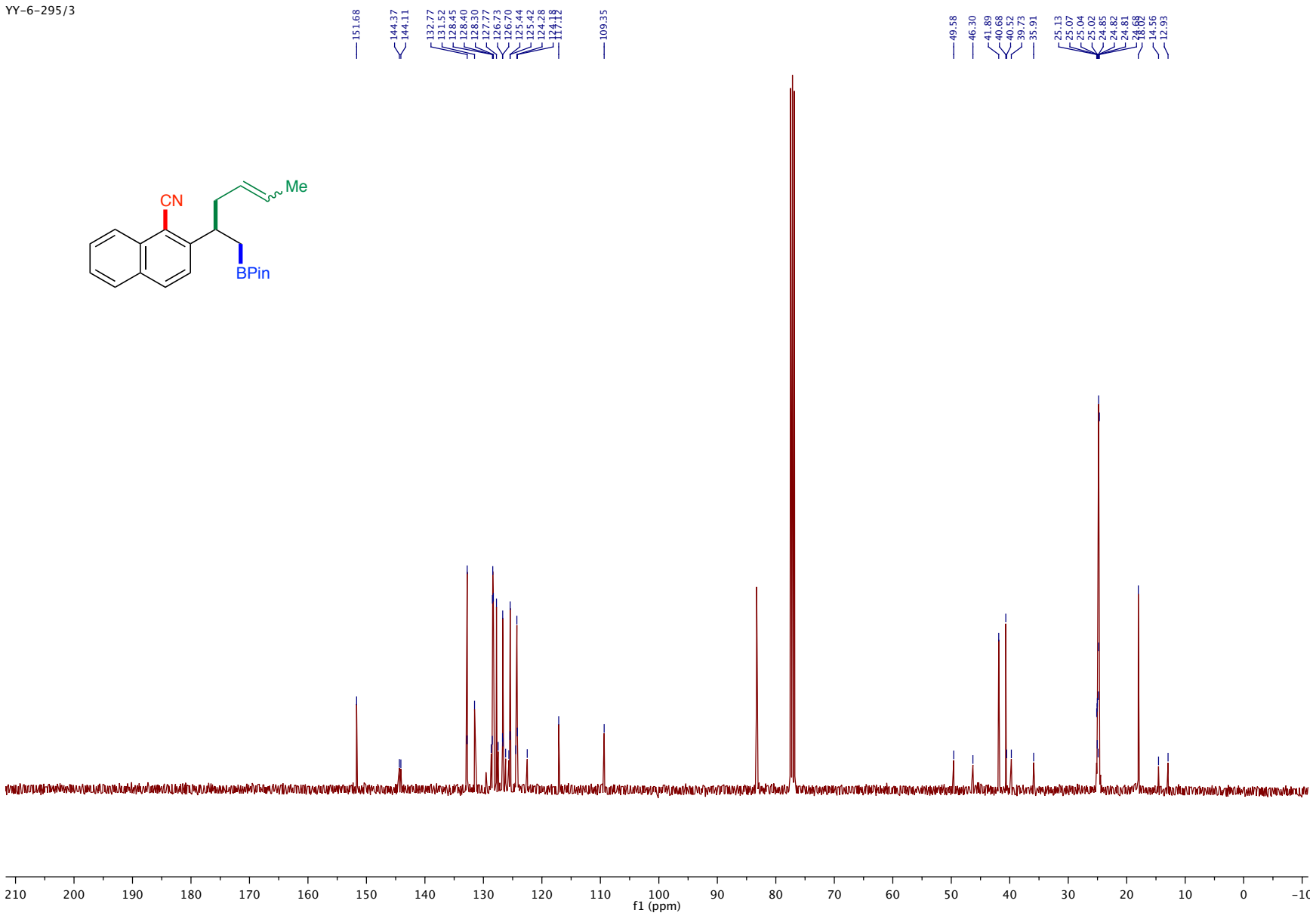
135.95
134.81
133.41
129.87
129.06
128.95
122.97
122.85
117.08
109.06
83.31
43.07
40.06
24.83
24.69
21.99
19.26
CN
Me
BPin
Me
f1 (ppm)


YY-7-37/1
CN
BPin
Me
f1 (ppm)


YY-7-37/2
150.94
140.27
135.98
132.73
130.96
128.12
126.59
126.00
125.08
124.62
117.07
107.64
83.28
42.87
40.11
24.78
24.67
20.22
CN
BPin
Me
f1 (ppm)


YY-6-295/1
CN
Me
BPin
1.00
1.00
1.15
0.99
1.00
1.28
2.09
1.26
2.20
2.49
11.98
12.90
f1 (ppm)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151.68
144.37
144.11
132.77
131.52
128.45
128.40
128.30
127.77
126.73
126.70
125.44
125.42
124.28
109.35
49.58
46.30
41.89
40.68
40.52
39.73
35.91
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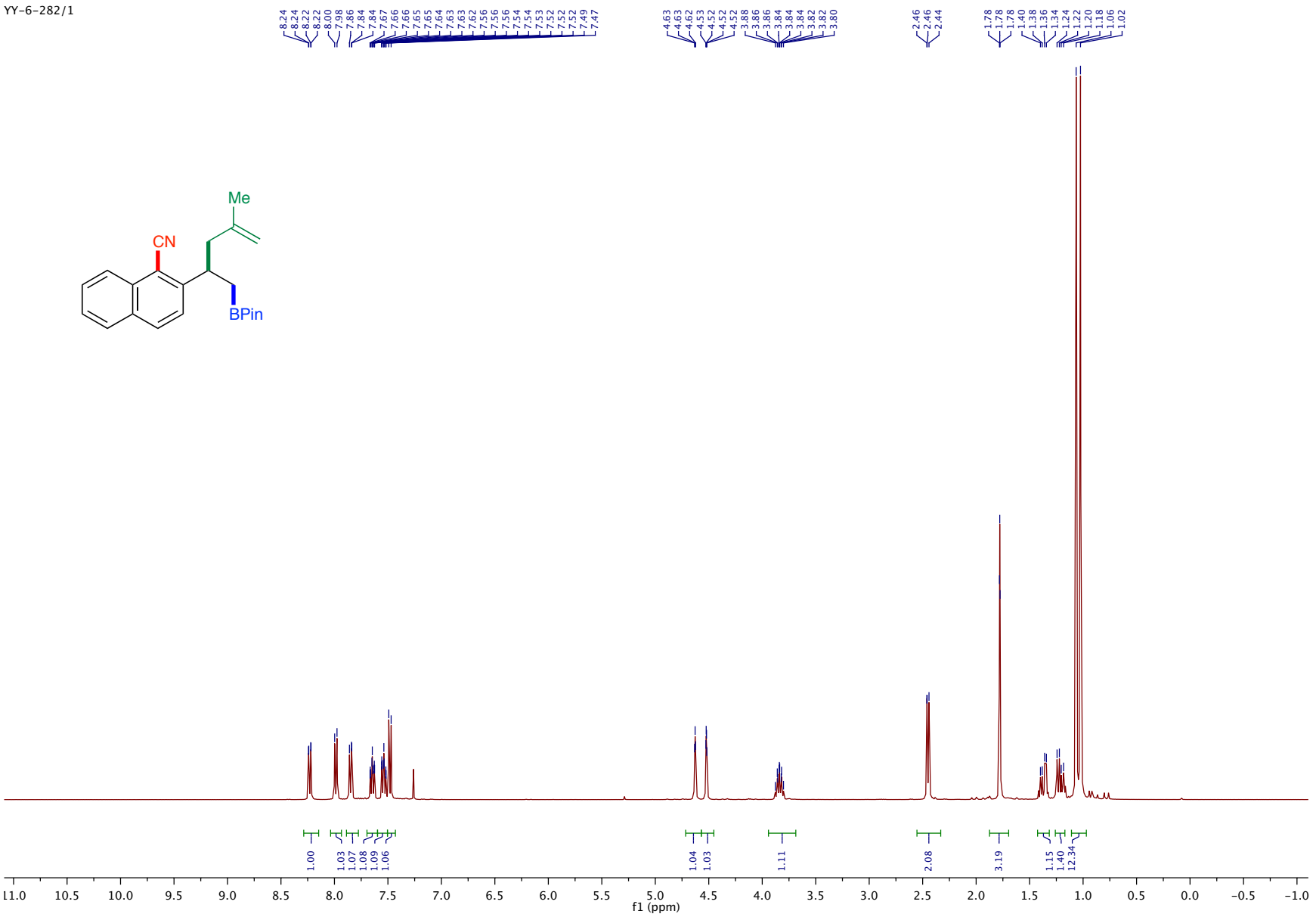
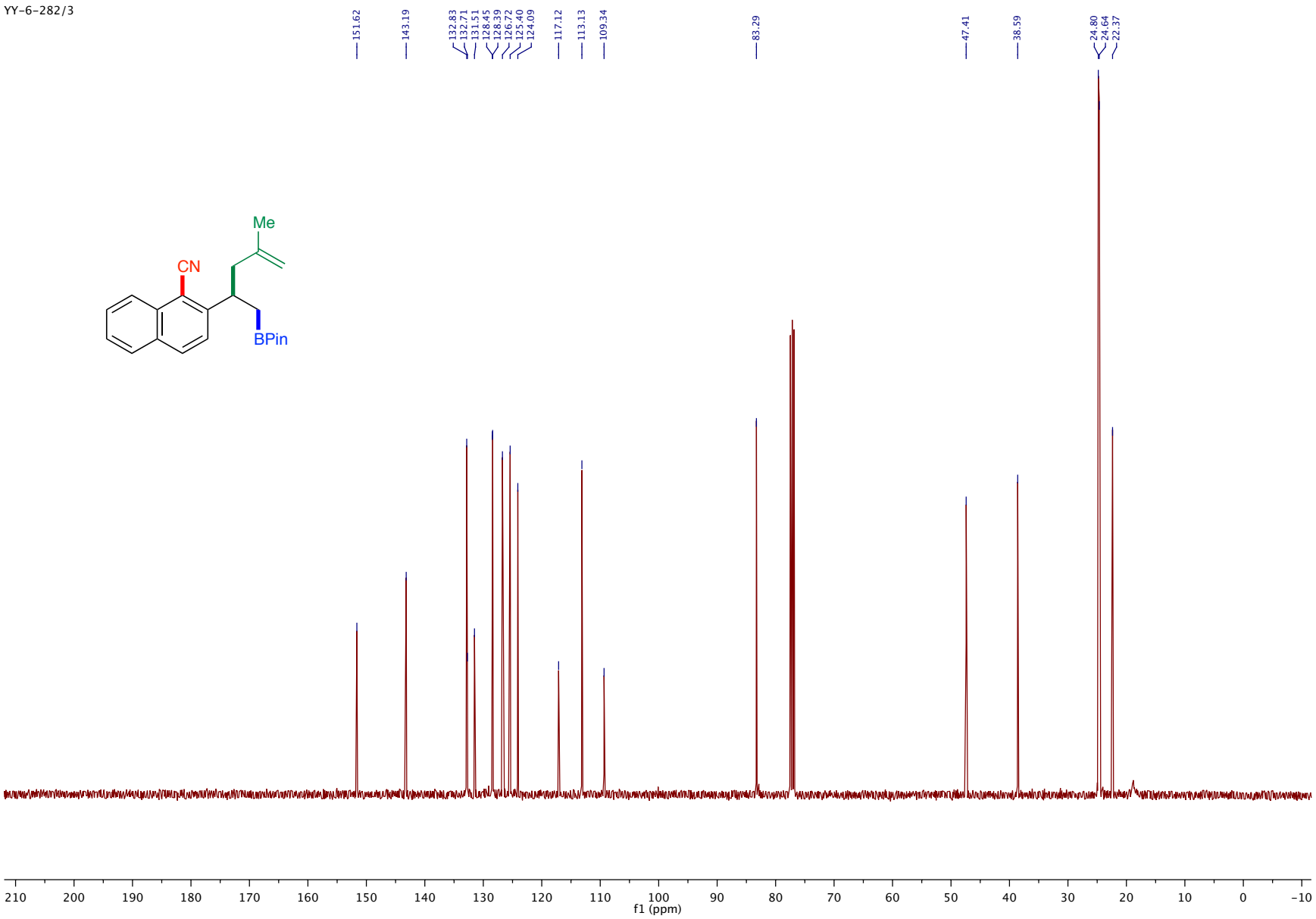
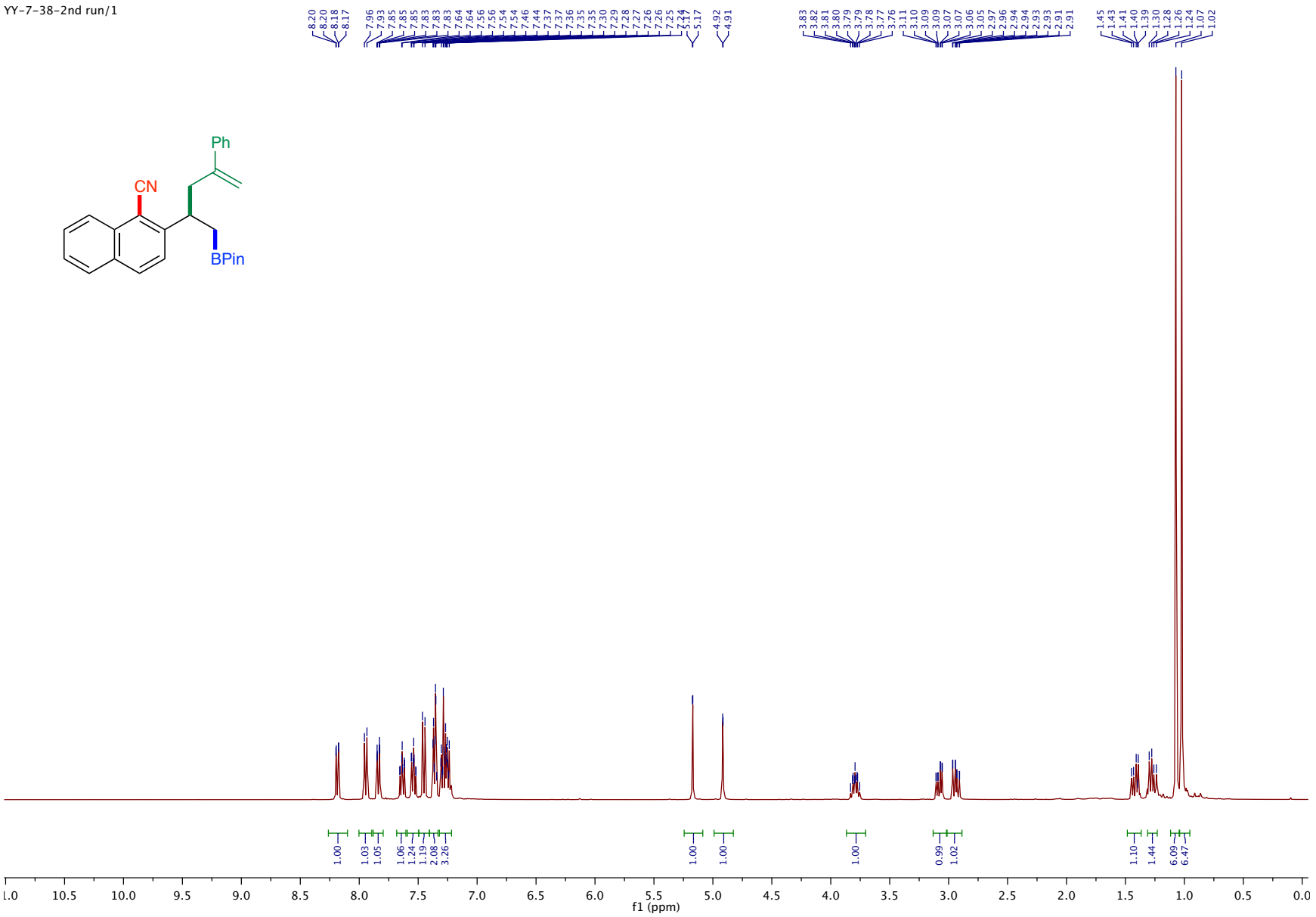
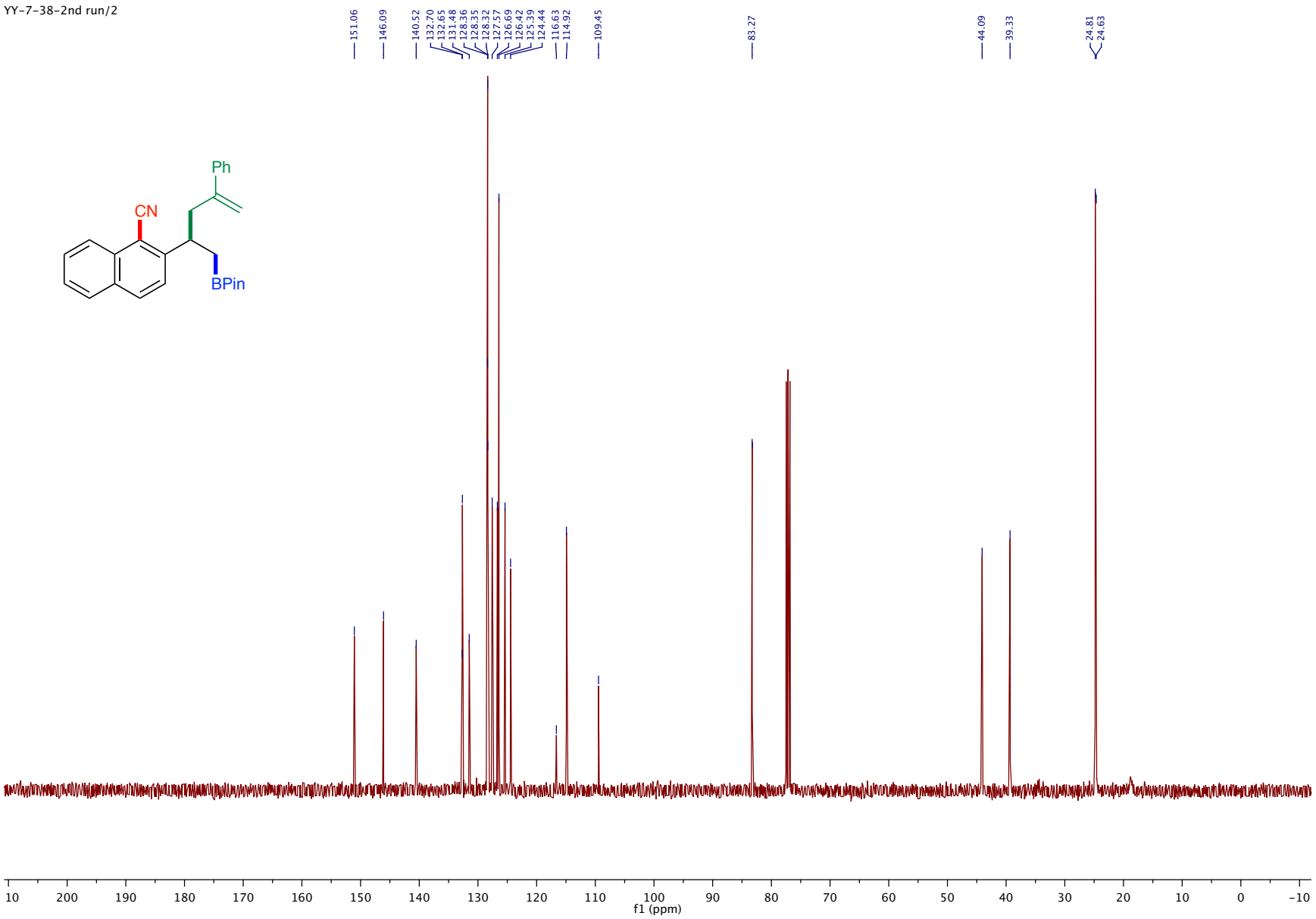
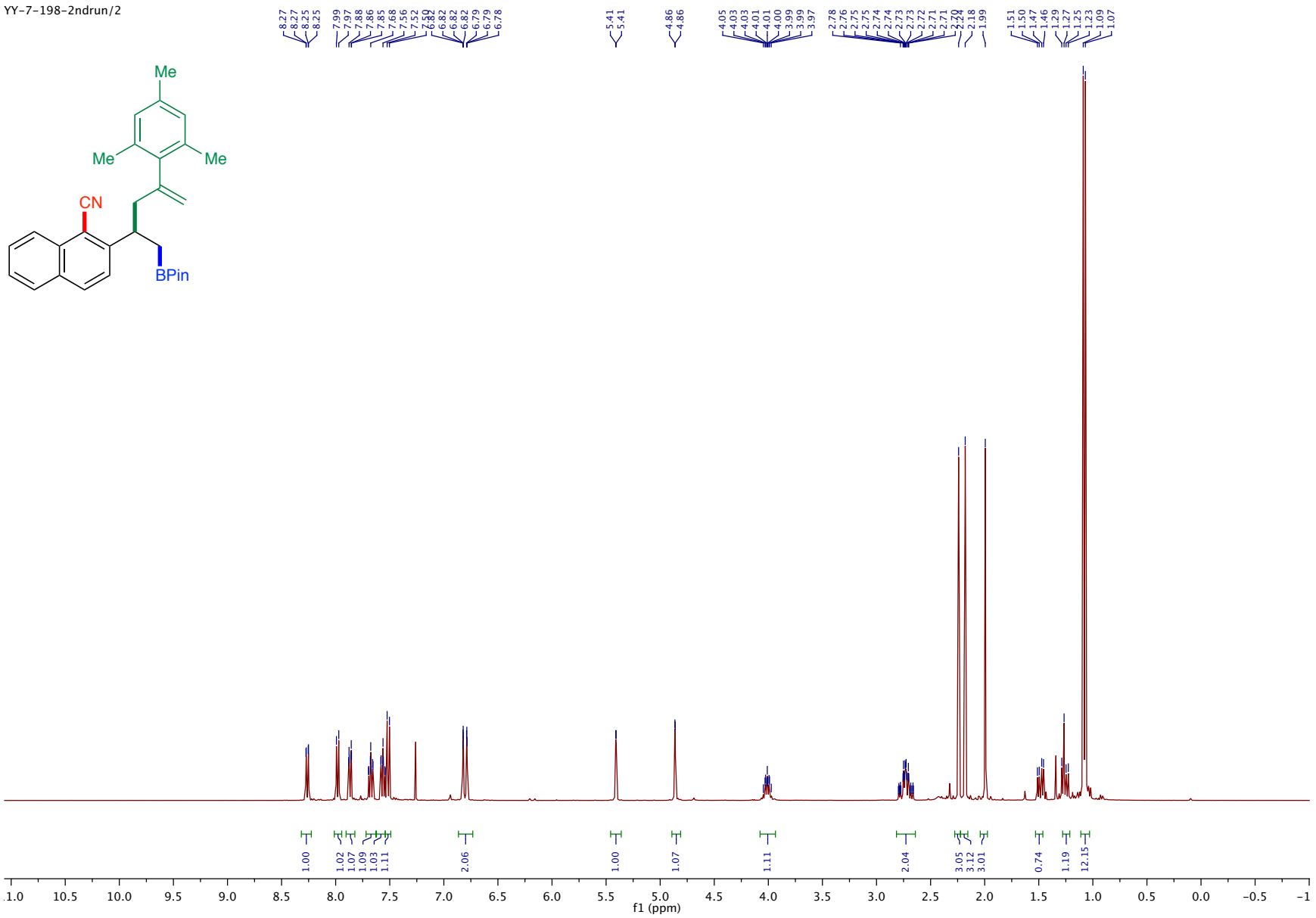
14.56
12.93
CN
Me
BPin
f1 (ppm)

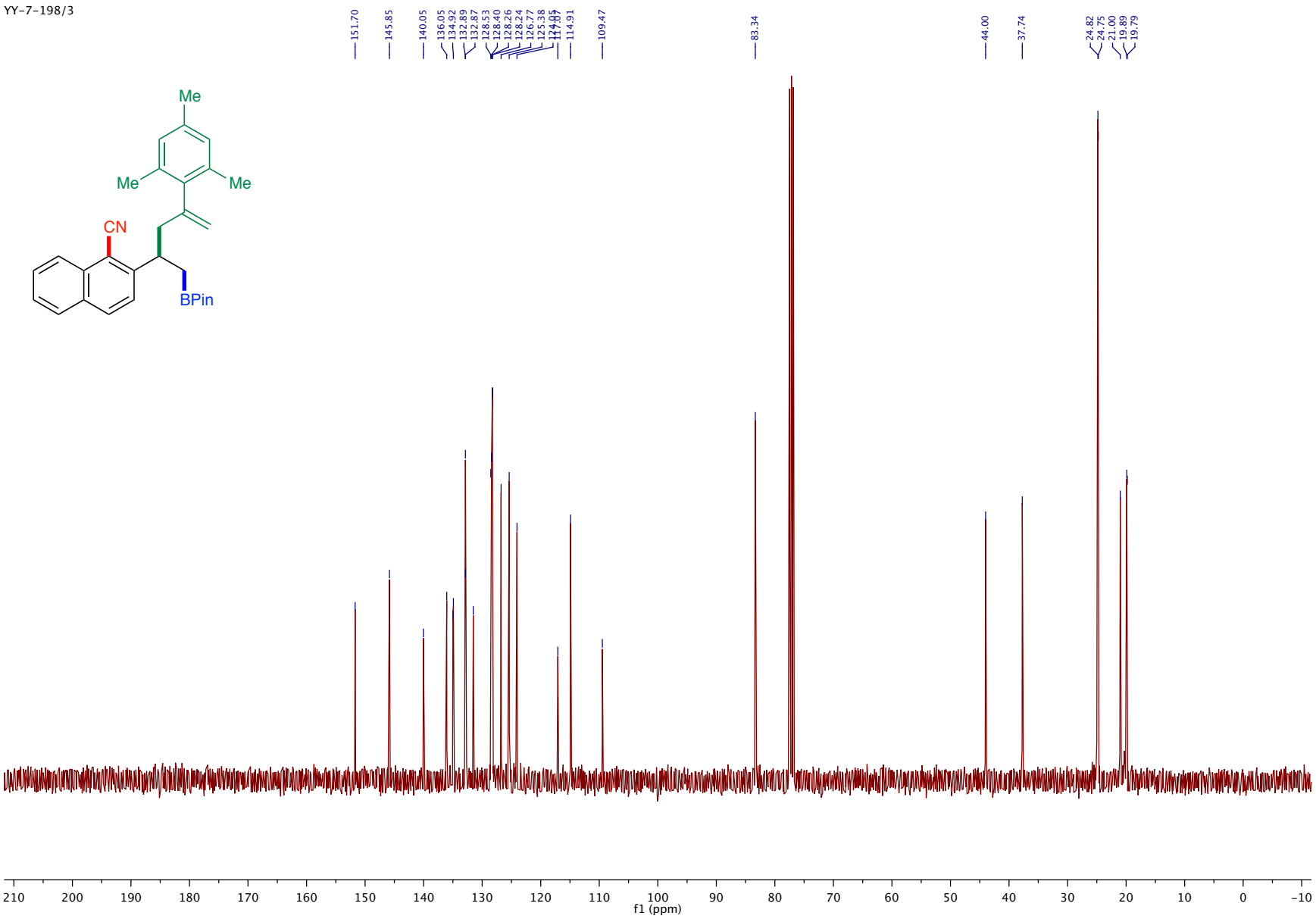

YY-6-282/1
Me
CN
BPin
f1 (ppm)

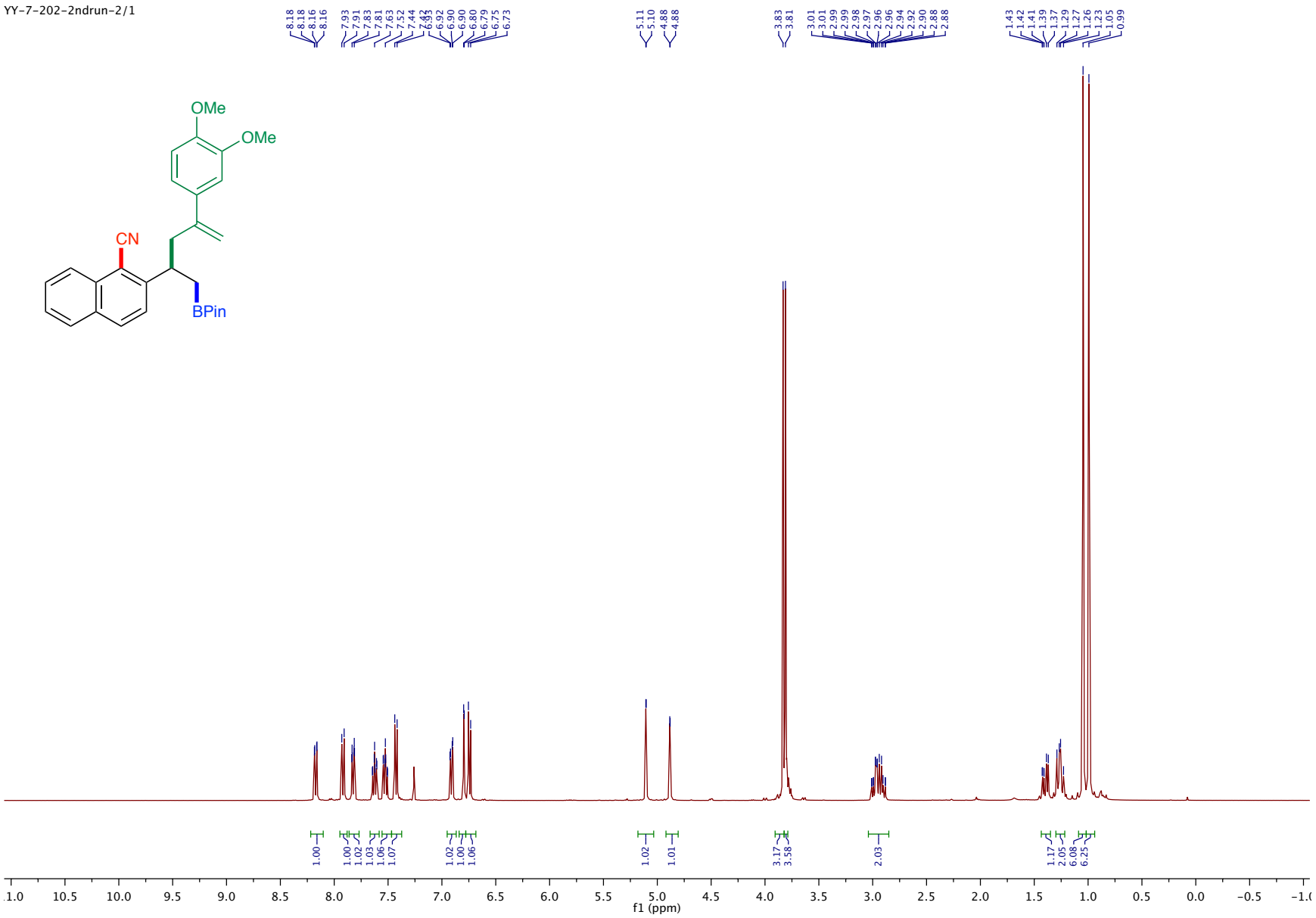

YY-6-282/3
151.62
143.19
132.83
132.71
131.51
128.45
128.39
126.72
125.40
124.09
117.12
113.13
109.34
83.29
47.41
38.59
24.80
24.64
22.37
Me
CN
BPin
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

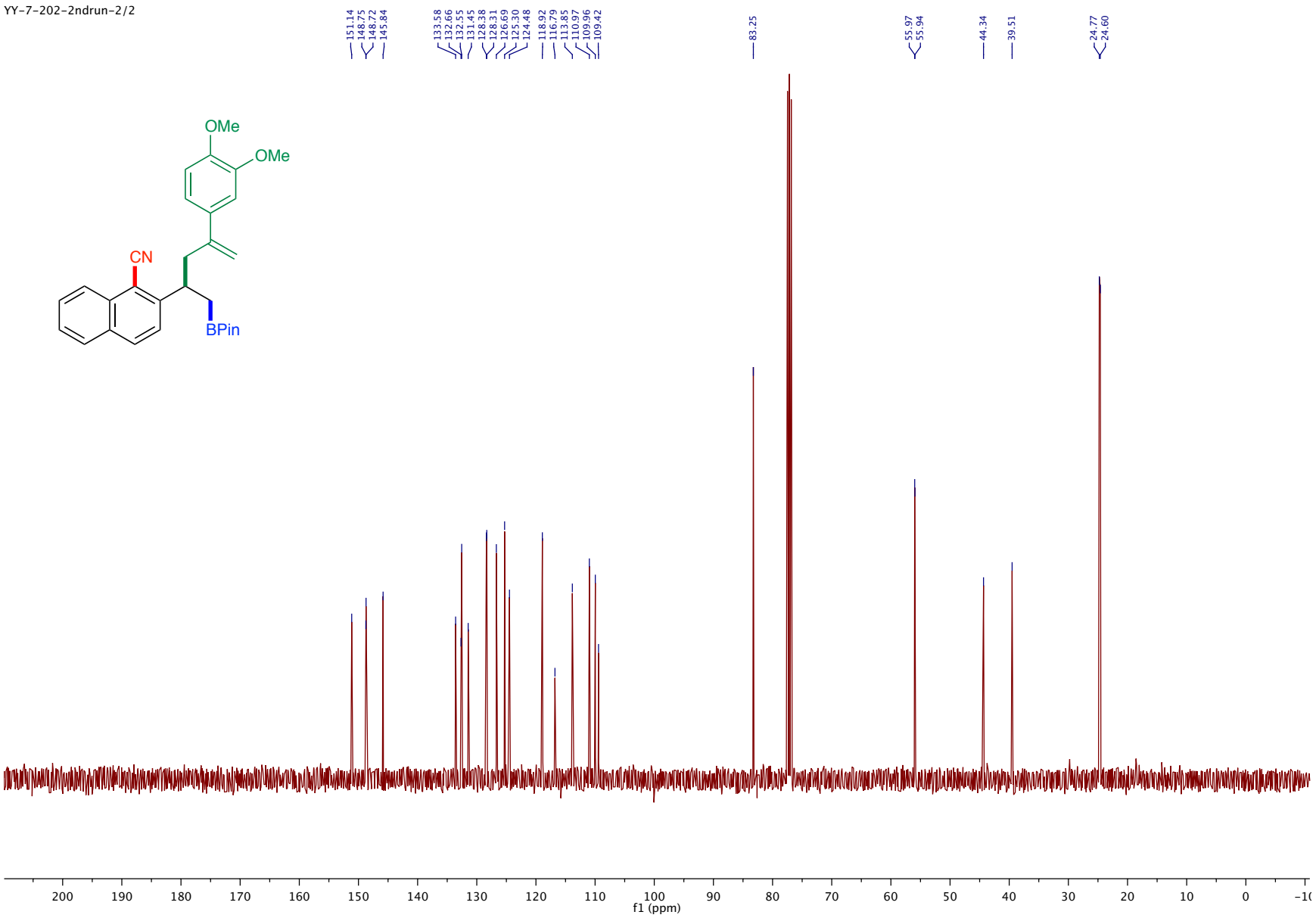

YY-7-38-2nd run/1
Ph
CN
BPin
f1 (ppm)

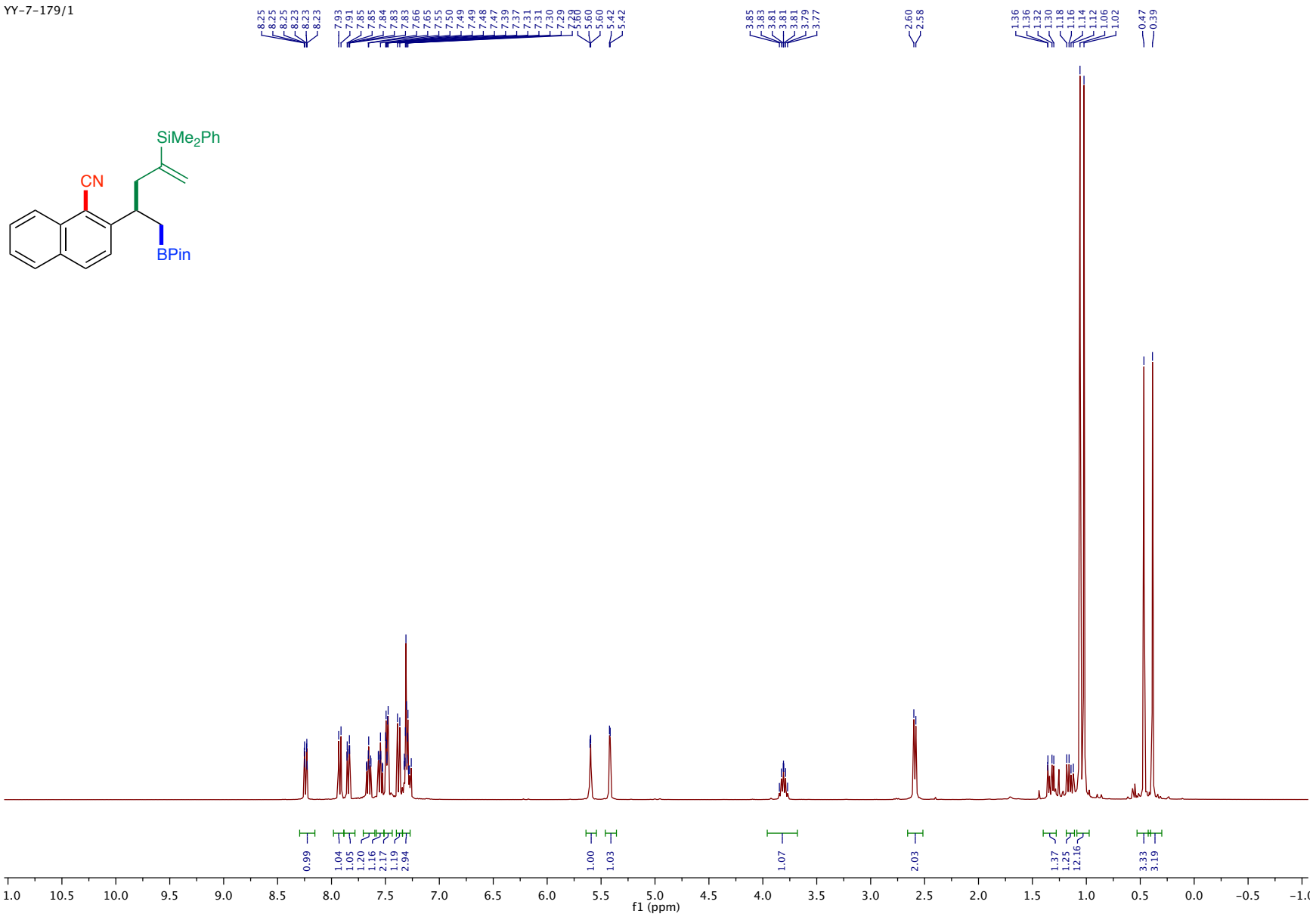

YY-7-38-2nd run/2
151.06
146.09
140.52
132.70
132.65
131.48
128.36
128.35
128.32
127.57
126.69
126.42
125.39
124.44
116.63
114.92
109.45
83.27
44.09
39.33
24.81
24.63
Ph
CN
BPin
f1 (ppm)

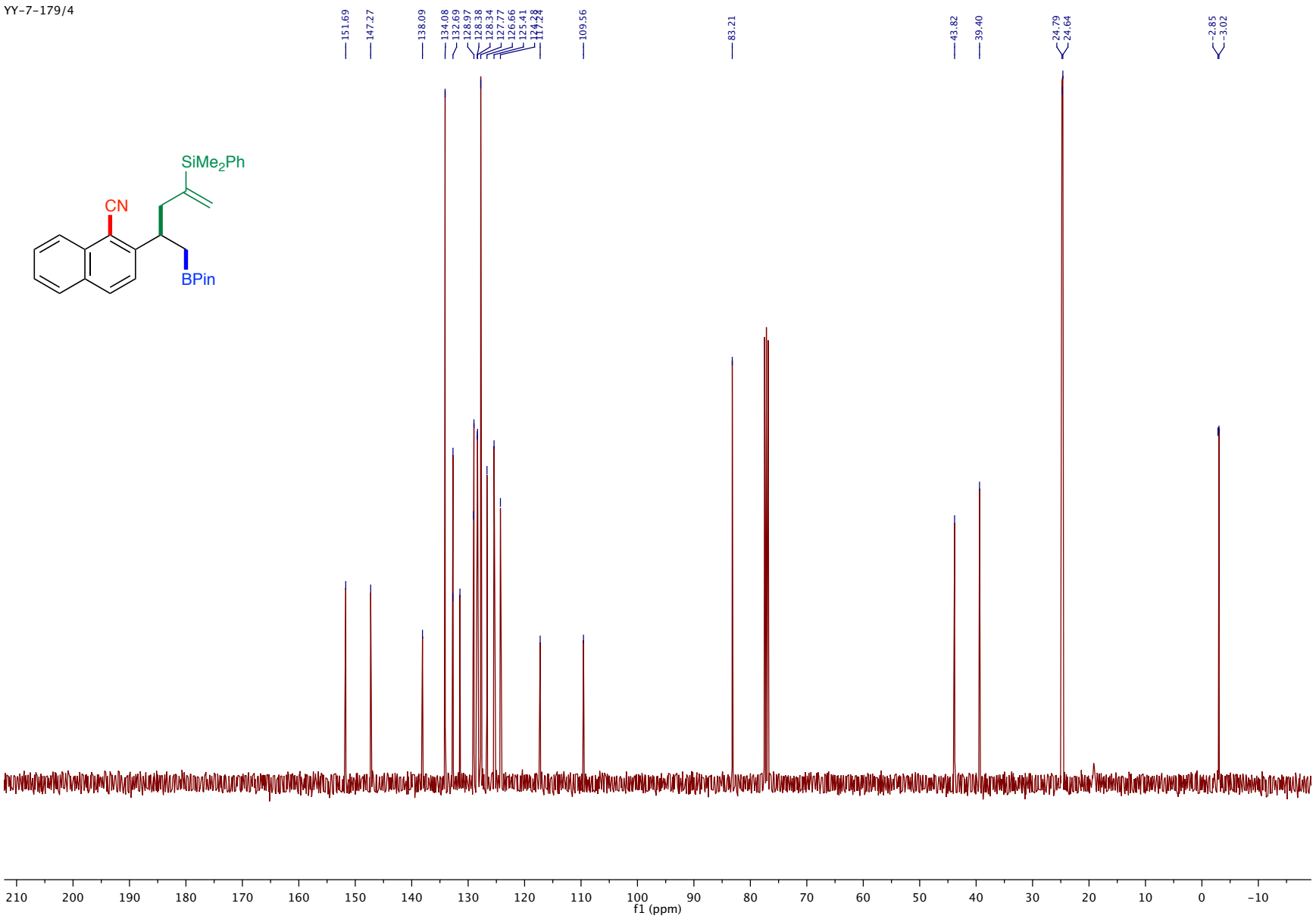

YY-7-198-2ndrun/2
Me
Me
Me
CN
BPin
f1 (ppm)

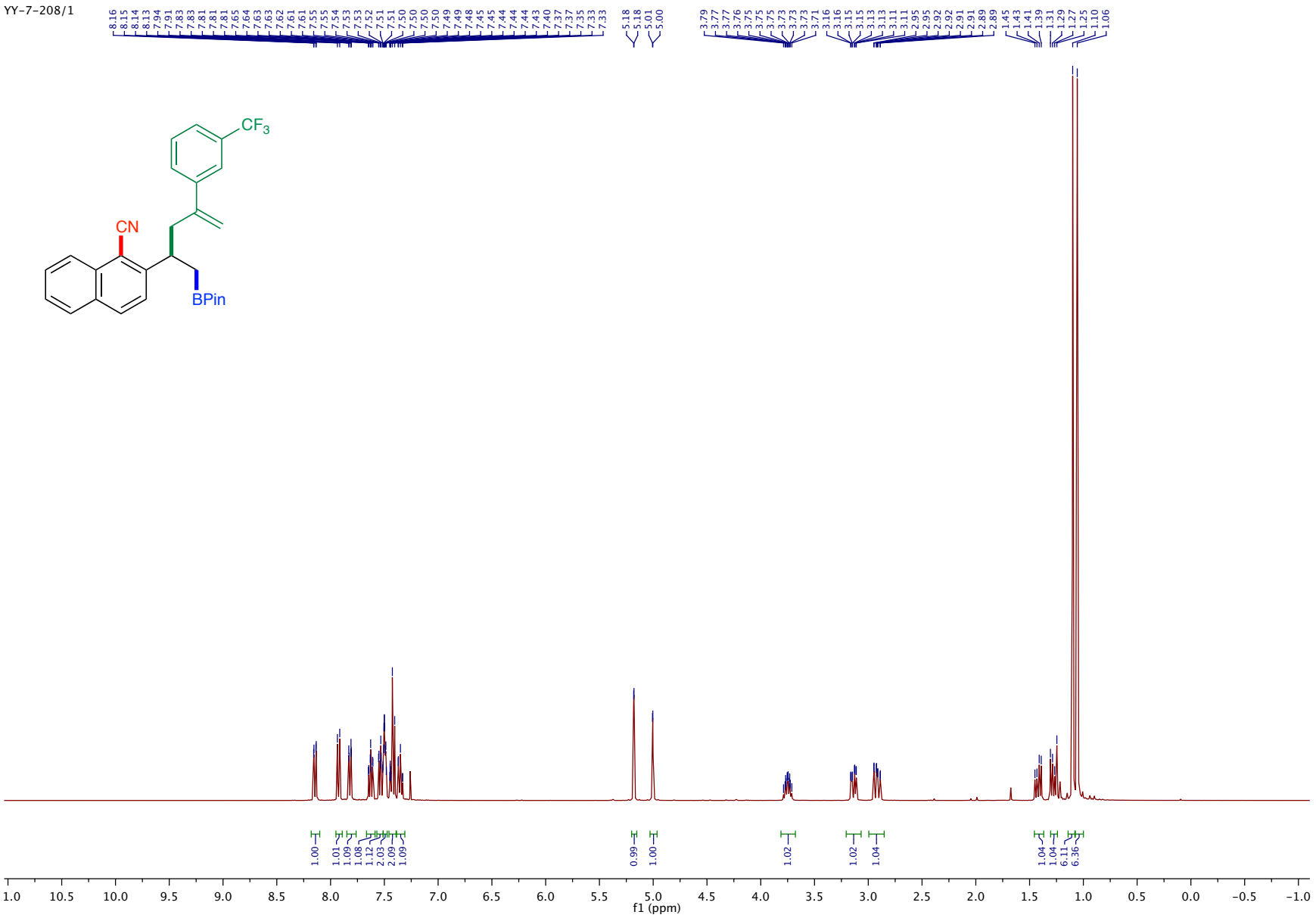

YY-7-198/3
151.70
145.85
140.05
136.05
134.92
132.89
132.87
128.53
128.40
128.26
128.24
126.77
125.38
114.91
109.47
83.34
44.00
37.74
24.82
24.75
21.00
19.89
19.79
Me
Me
Me
CN
BPin
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

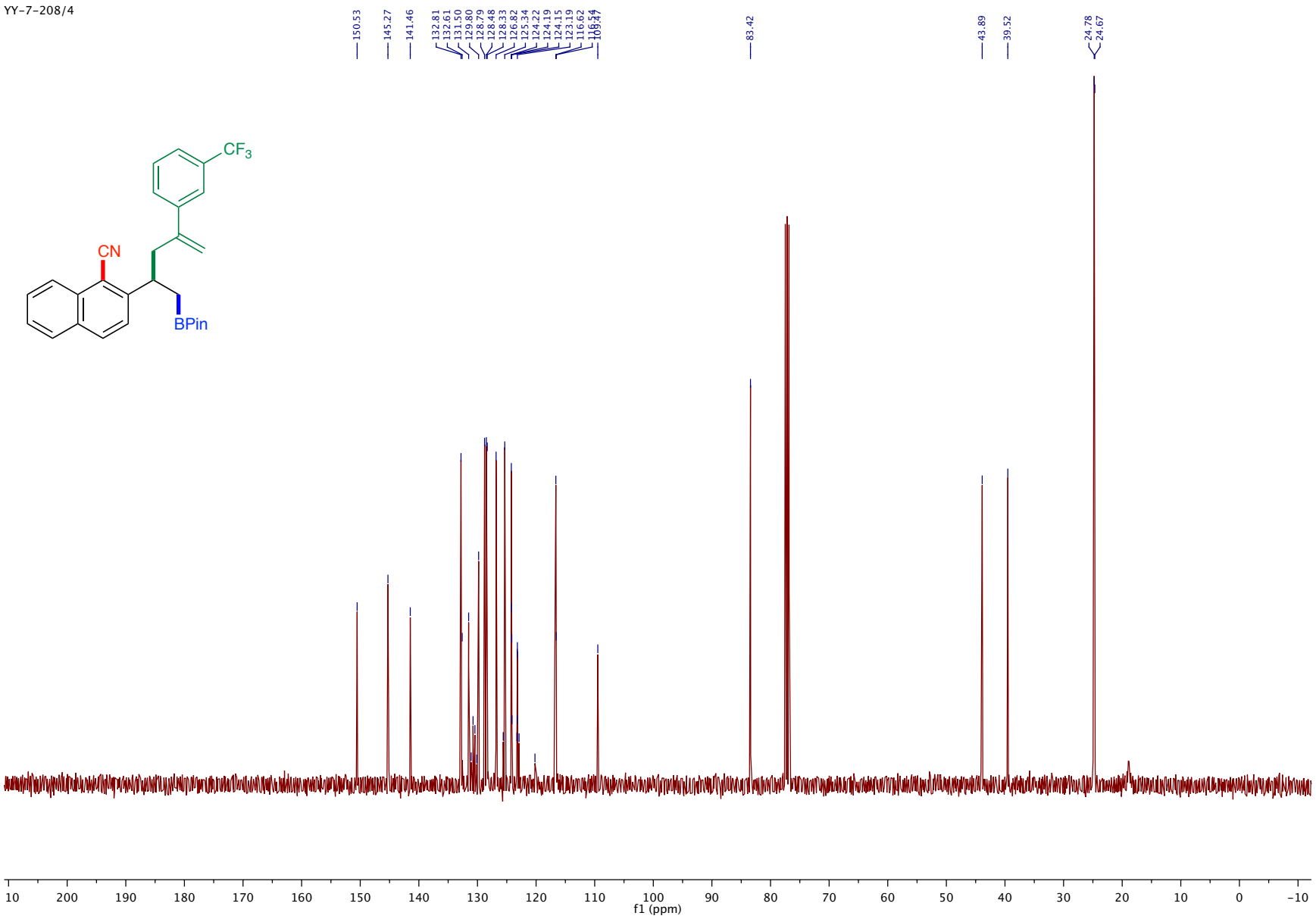

YY-7-202-2ndrun-2/1
OMe
OMe
CN
BPin
f1 (ppm)

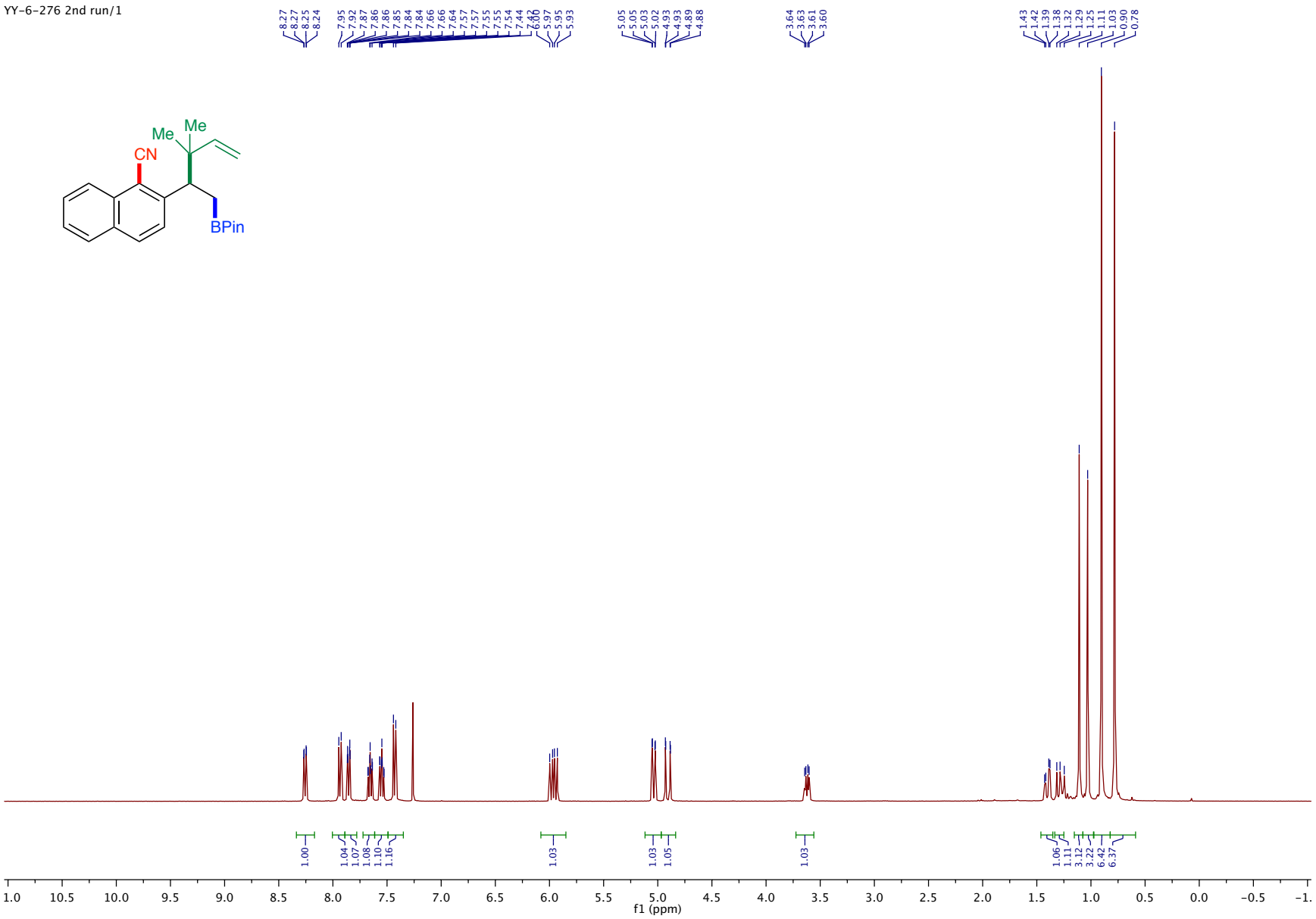

YY-7-202-2ndrun-2/2
151.14
148.75
148.72
145.84
133.58
132.66
132.55
131.45
128.38
128.31
126.69
125.30
124.48
118.92
116.79
113.85
110.97
109.96
109.42
83.25
55.97
55.94
44.34
39.51
24.77
24.60
OMe
OMe
CN
BPin
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

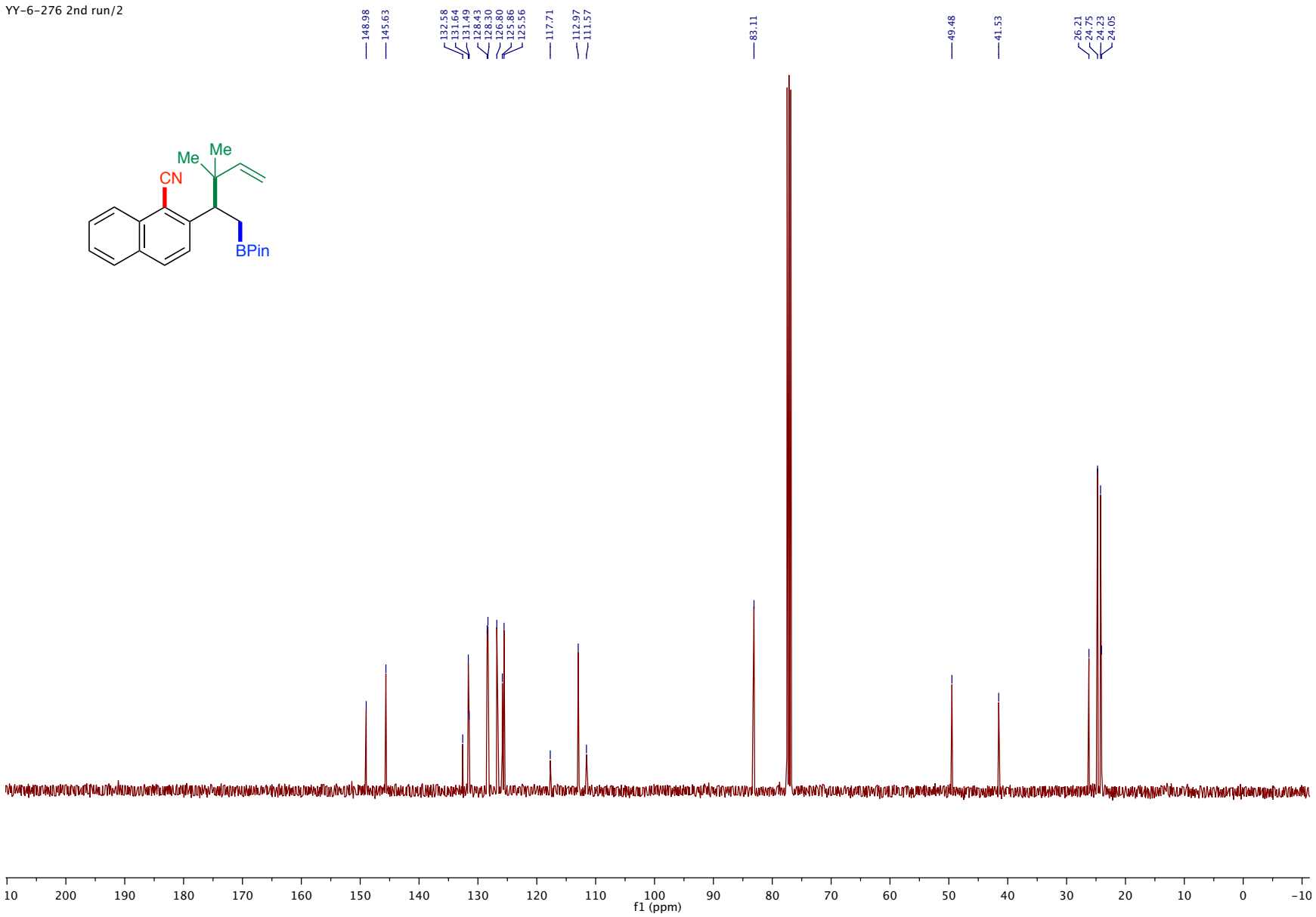

YY-7-179/1
8.25 8.25 8.23 8.23 8.23
7.93 7.91 7.85 7.85 7.84 7.83 7.83 7.66 7.65 7.55 7.50 7.49 7.49 7.48 7.47 7.39 7.37 7.31 7.31 7.30 7.29 7.26 5.60 5.42 5.42
3.85 3.83 3.81 3.81 3.79 3.77
2.60 2.58
1.36 1.36 1.32 1.30 1.18 1.16 1.14 1.12 1.06 1.02
0.47 0.39
SiMe2Ph
CN
BPin
0.99 1.04 1.05 1.20 1.16 2.17 1.19 2.94 1.00 1.03 1.07 2.03 1.37 1.25 12.16 3.33 3.19
f1 (ppm)

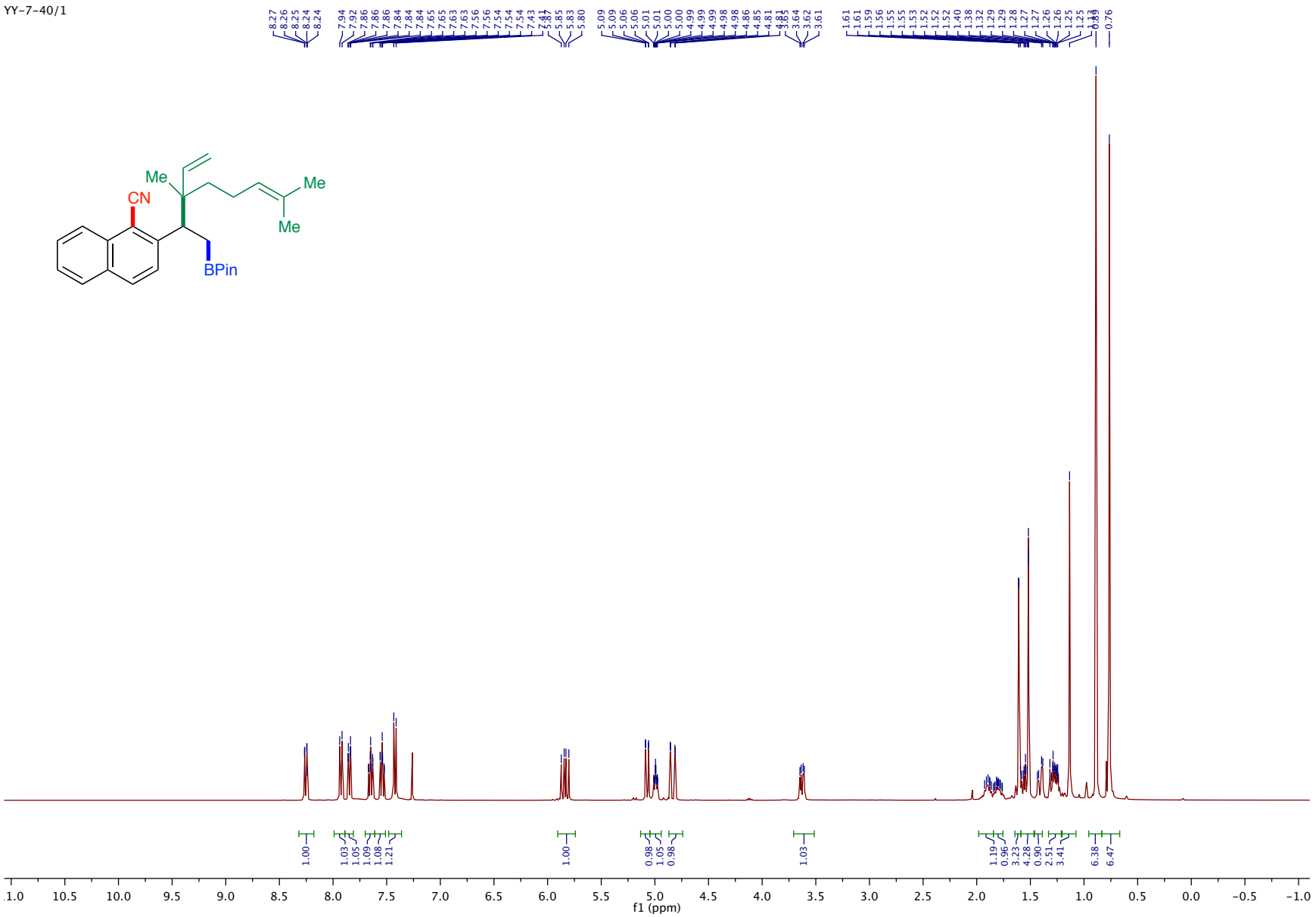

YY-7-179/4
151.69
147.27
138.09
134.08
132.69
128.97
128.38
128.34
127.77
126.66
125.41
109.56
83.21
43.82
39.40
24.79
24.64
2.85
3.02
SiMe2Ph
CN
BPin
f1 (ppm)

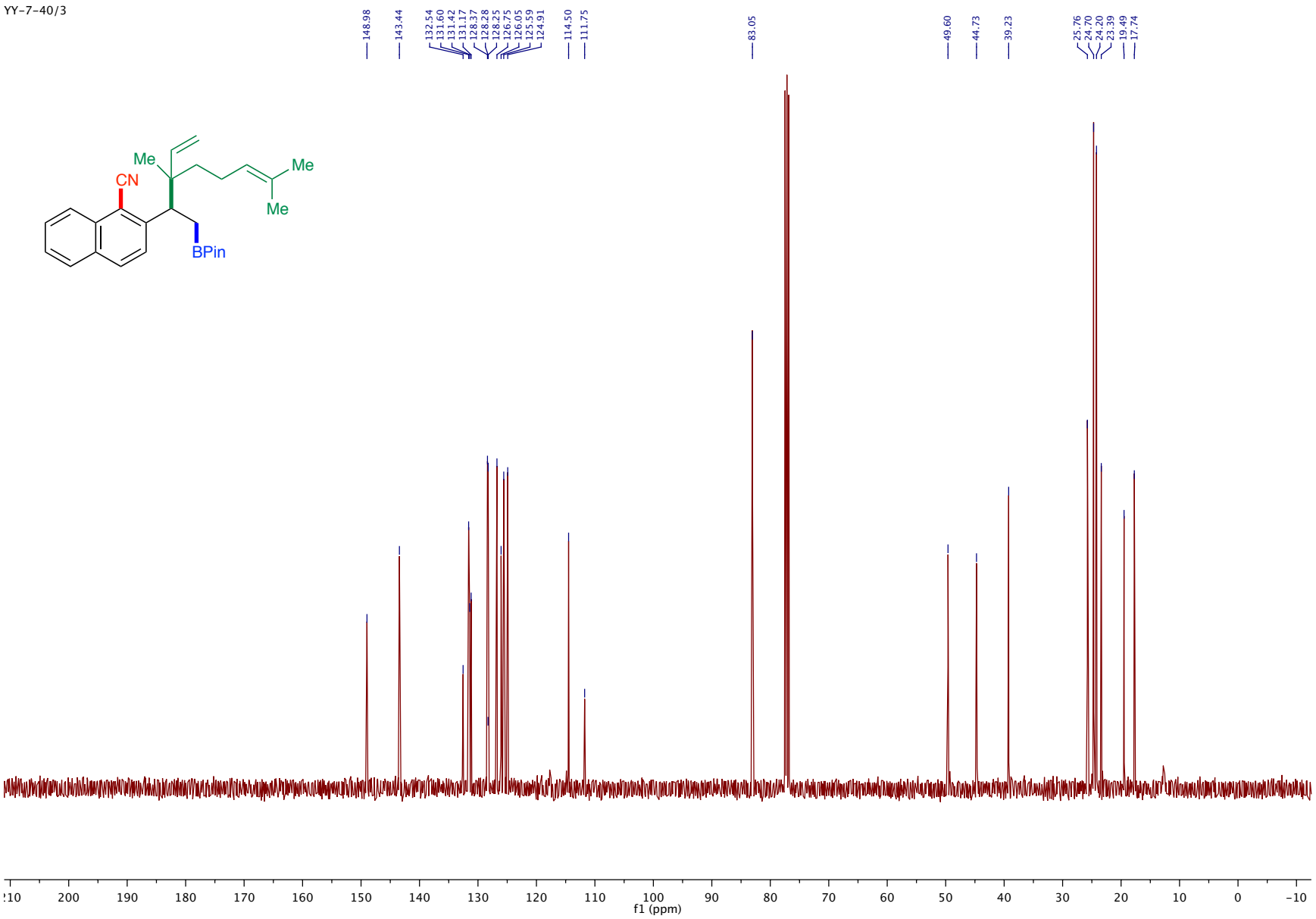

YY-7-208/1
CF3
CN
BPin
f1 (ppm)

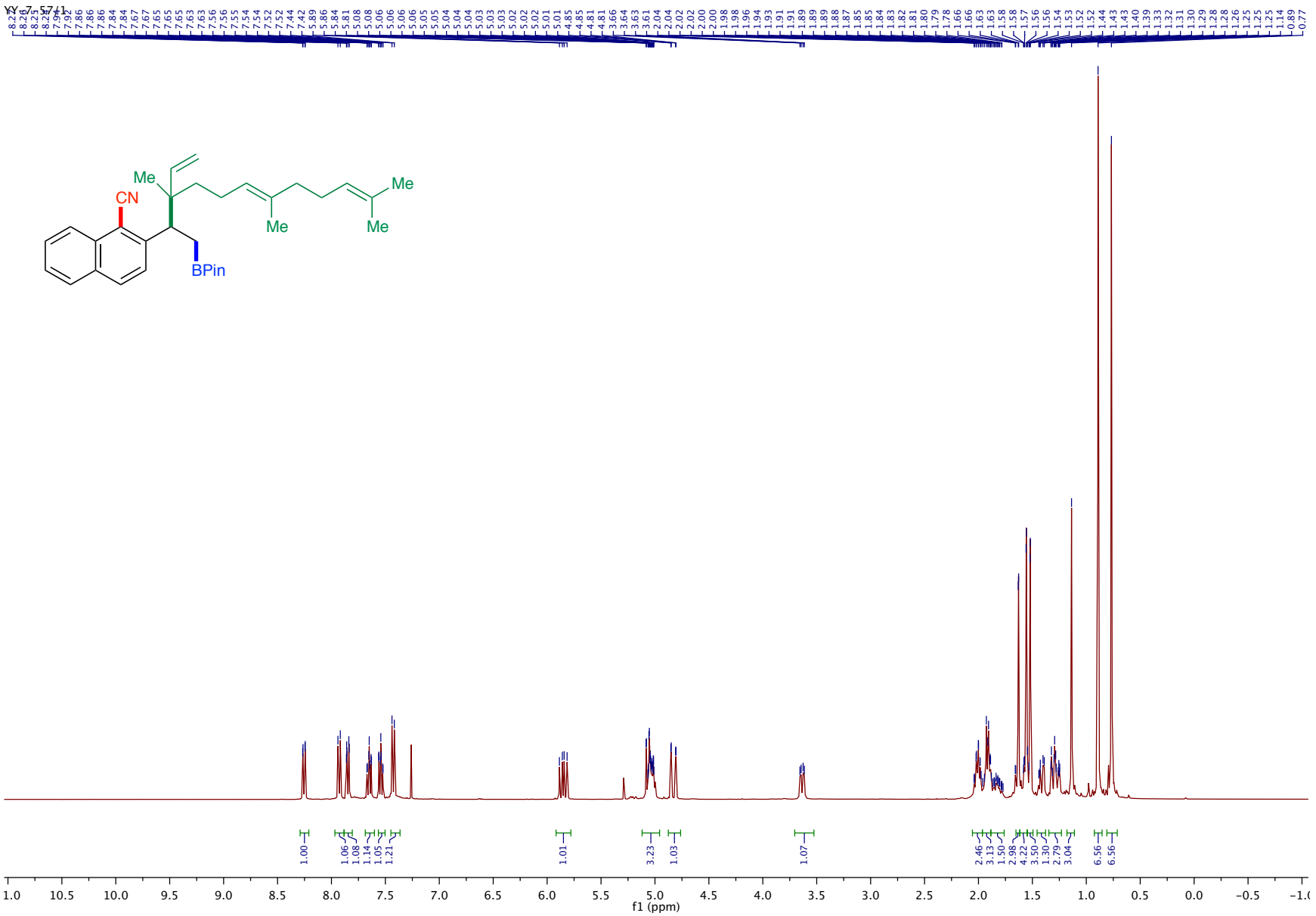

YY-7-208/4
150.53
145.27
141.46
132.81
132.61
131.50
129.80
128.79
128.48
128.33
126.82
125.34
124.22
124.19
124.15
123.19
116.62
83.42
43.89
39.52
24.78
24.67
CF3
CN
BPin
f1 (ppm)

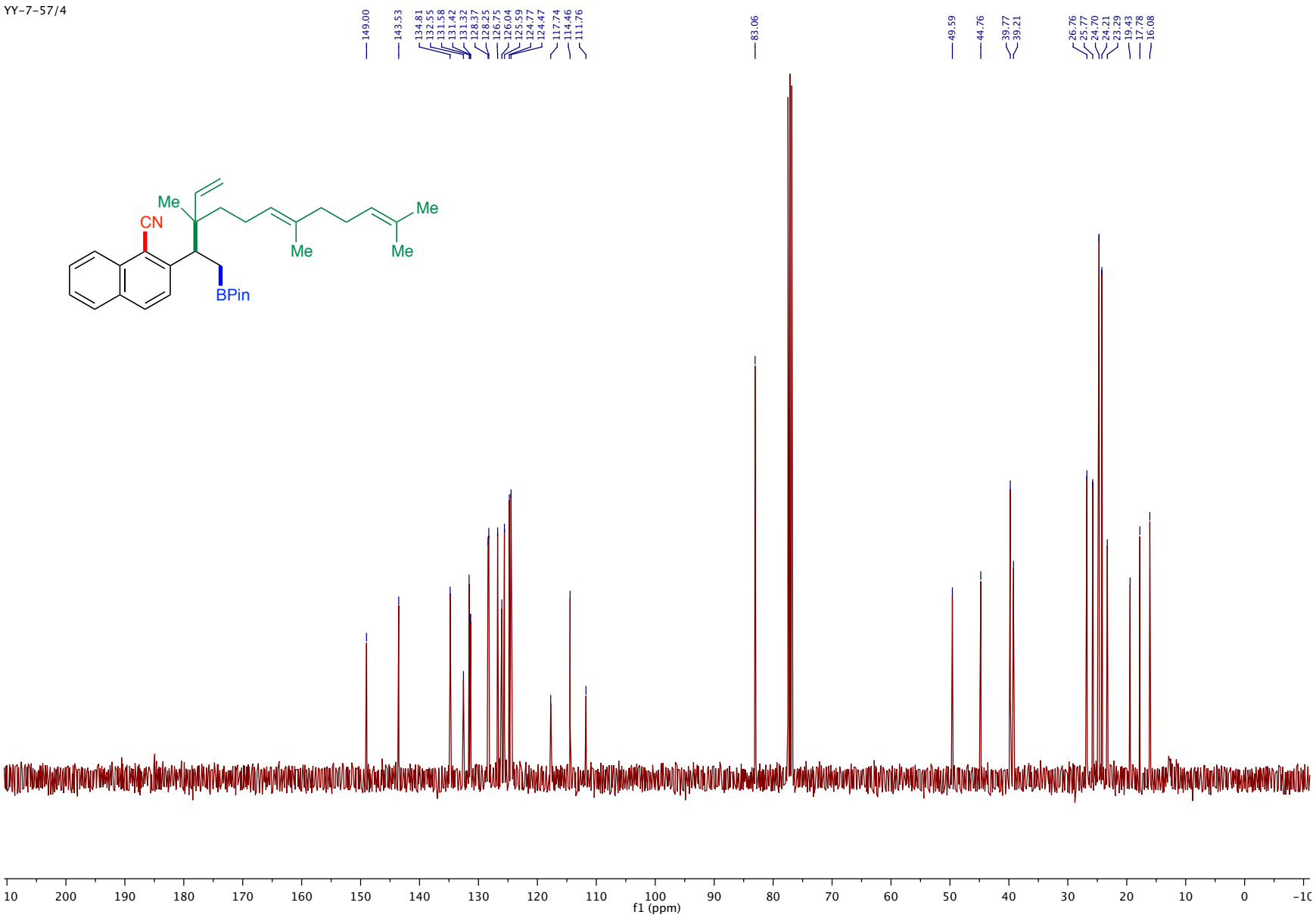

YY-6-276 2nd run/1
Me
Me
CN
BPin
f1 (ppm)

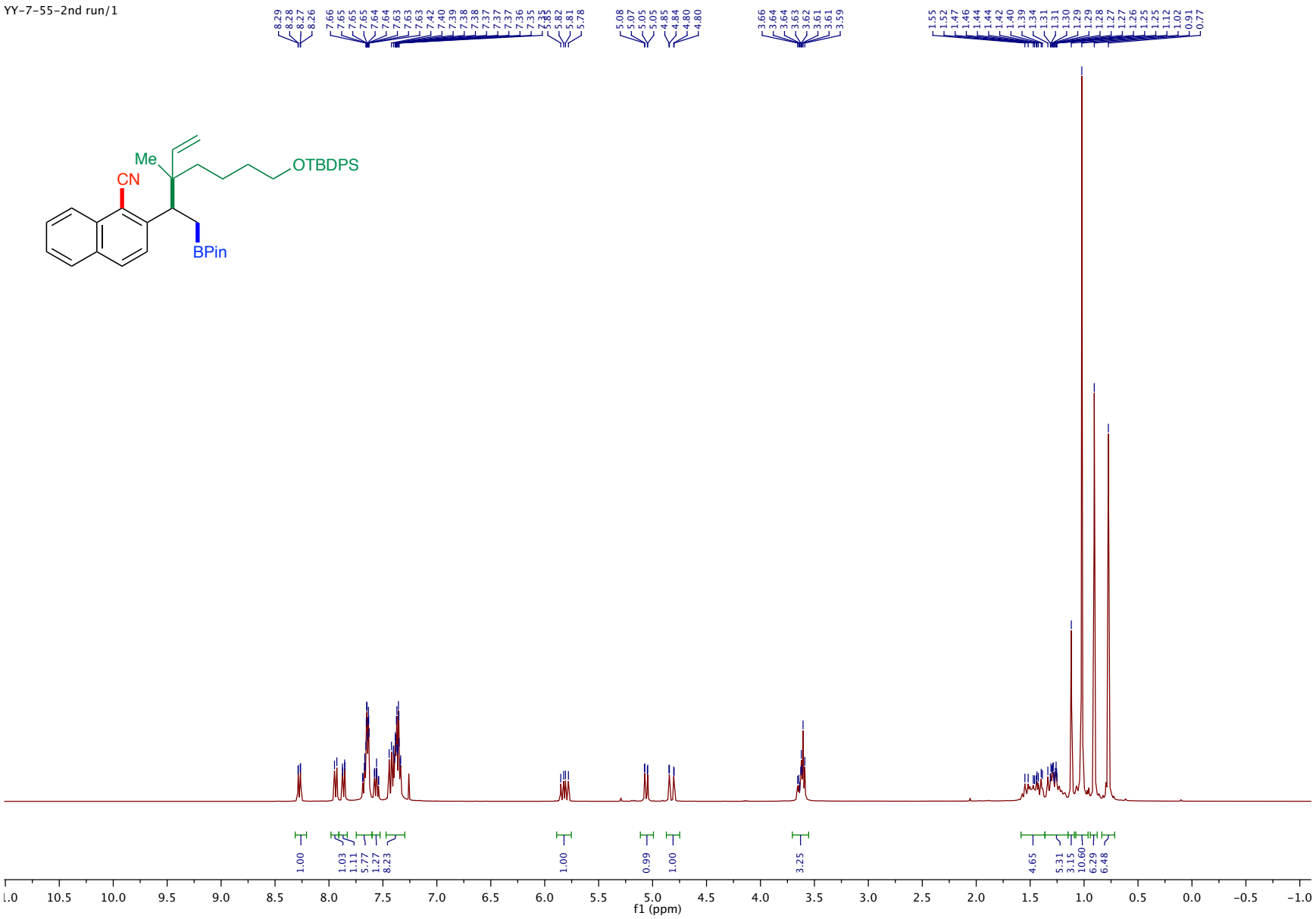

YY-6-276 2nd run/2
148.98
145.63
132.58
131.64
131.49
128.43
128.30
126.80
125.86
125.56
117.71
112.97
111.57
83.11
49.48
41.53
26.21
24.75
24.23
24.05
Me
Me
CN
BPin
f1 (ppm)

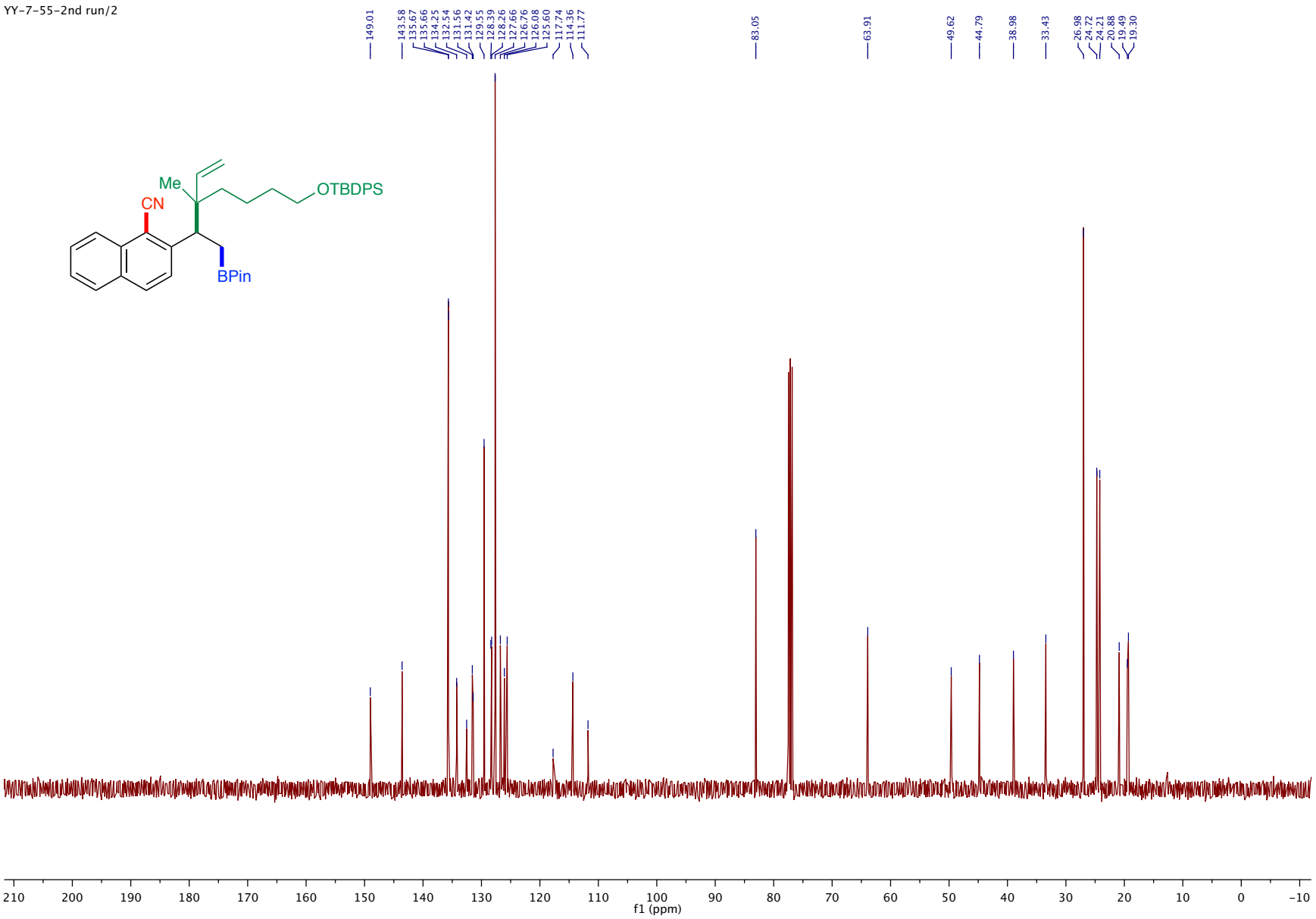

YY-7-40/1
Me
CN
Me
Me
BPin
f1 (ppm)

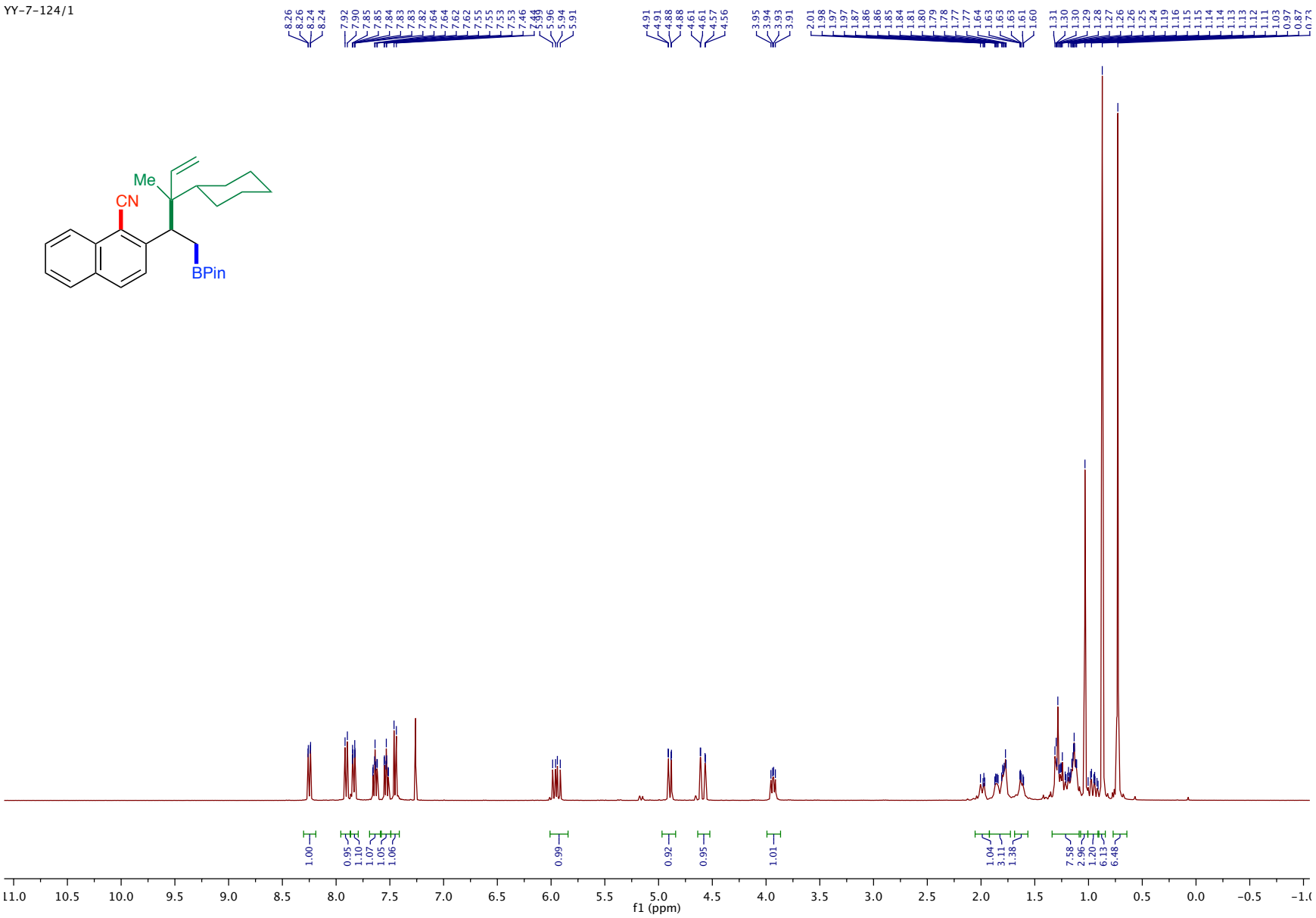

YY-7-40/3
148.98
143.44
132.54
131.60
131.42
131.17
128.37
128.28
128.25
126.75
126.05
125.59
124.91
114.50
111.75
83.05
49.60
44.73
39.23
25.76
24.70
24.20
23.39
19.49
17.74
Me
CN
Me
Me
BPin
f1 (ppm)

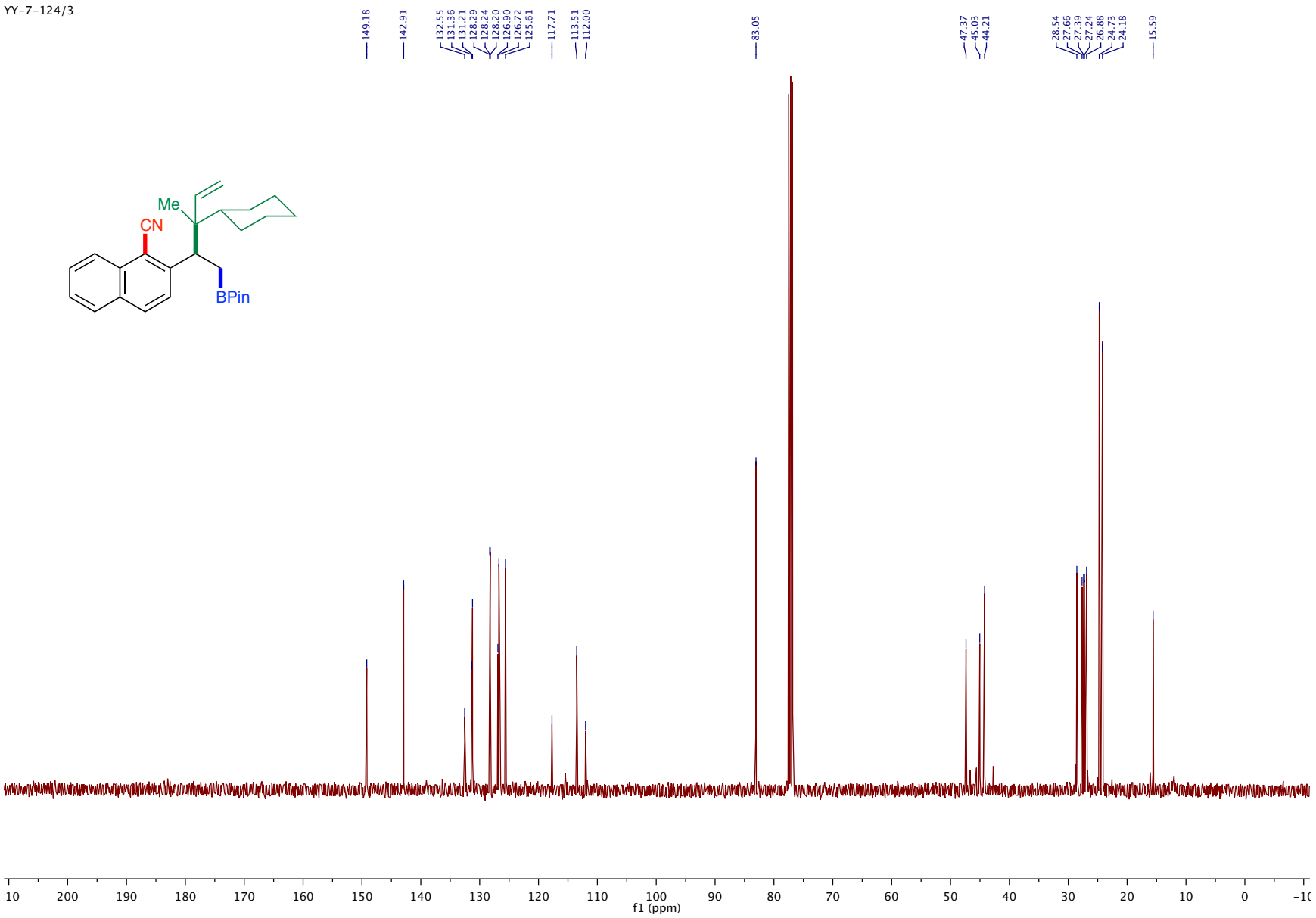

YY-7-5741
Me
CN
Me
Me
Me
BPin
1.00
1.06
1.08
1.14
1.05
1.21
1.01
3.23
1.03
1.07
2.46
3.13
1.50
2.98
4.22
3.50
1.30
2.79
3.04
6.56
6.56
f1 (ppm)

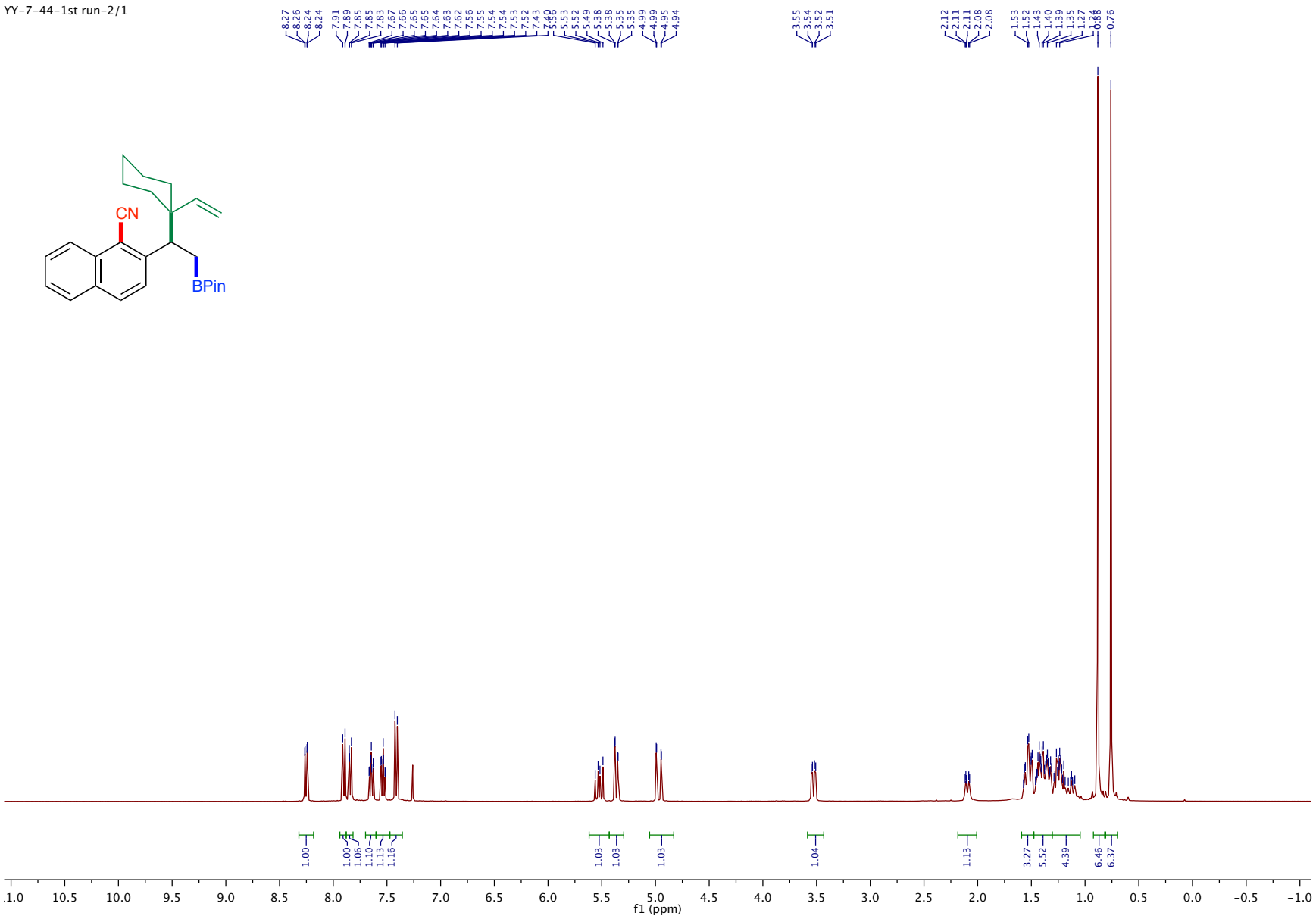

YY-7-57/4
149.00
143.53
134.81
132.55
131.58
131.42
131.32
128.37
128.25
126.75
126.04
125.59
124.77
124.47
117.74
114.46
111.76
83.06
49.59
44.76
39.77
39.21
26.76
25.77
24.70
24.21
23.29
19.43
17.78
16.08
Me
CN
Me
Me
Me
BPin
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

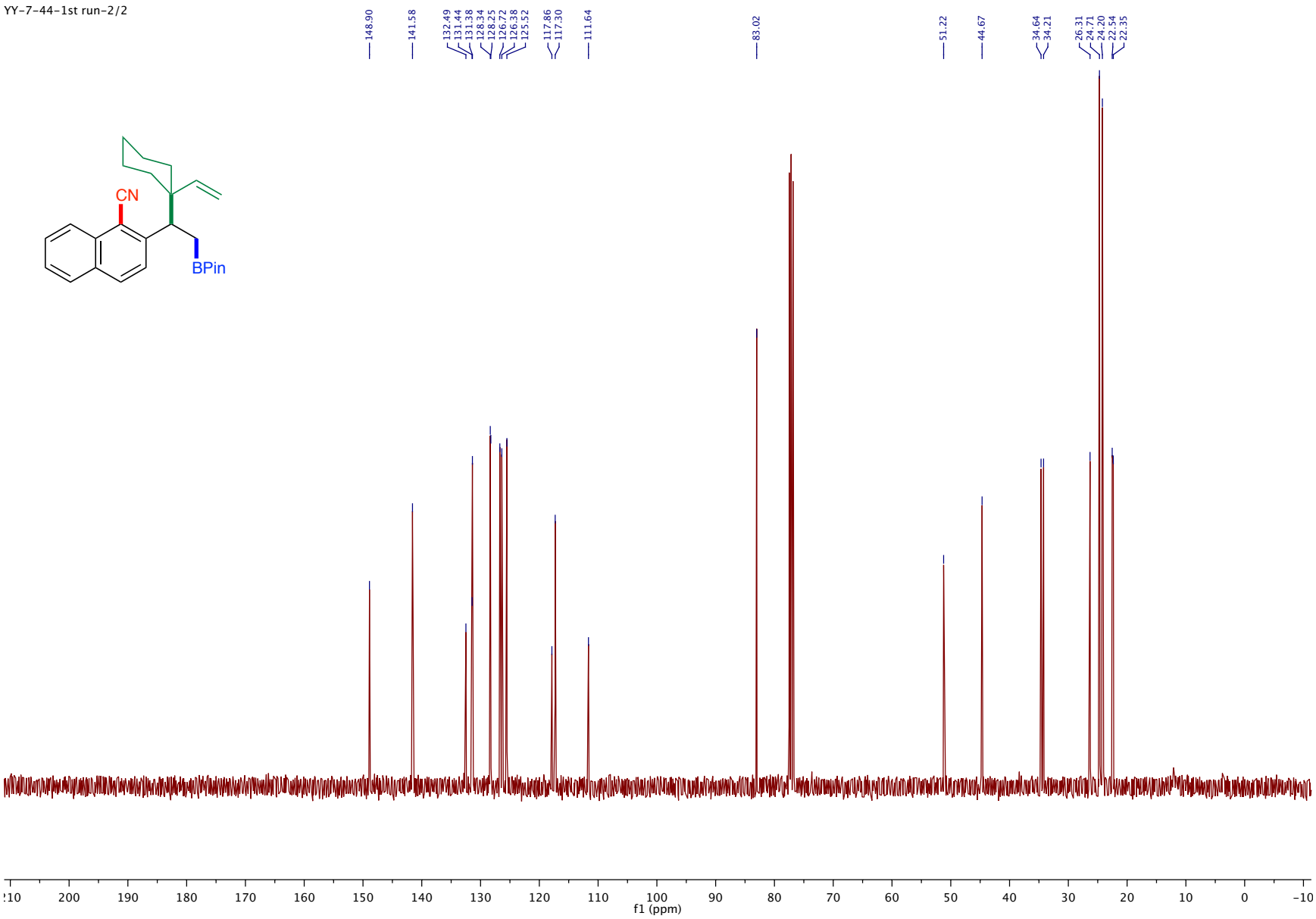

YY-7-55-2nd run/1
Me
CN
OTBDPS
BPin
f1 (ppm)

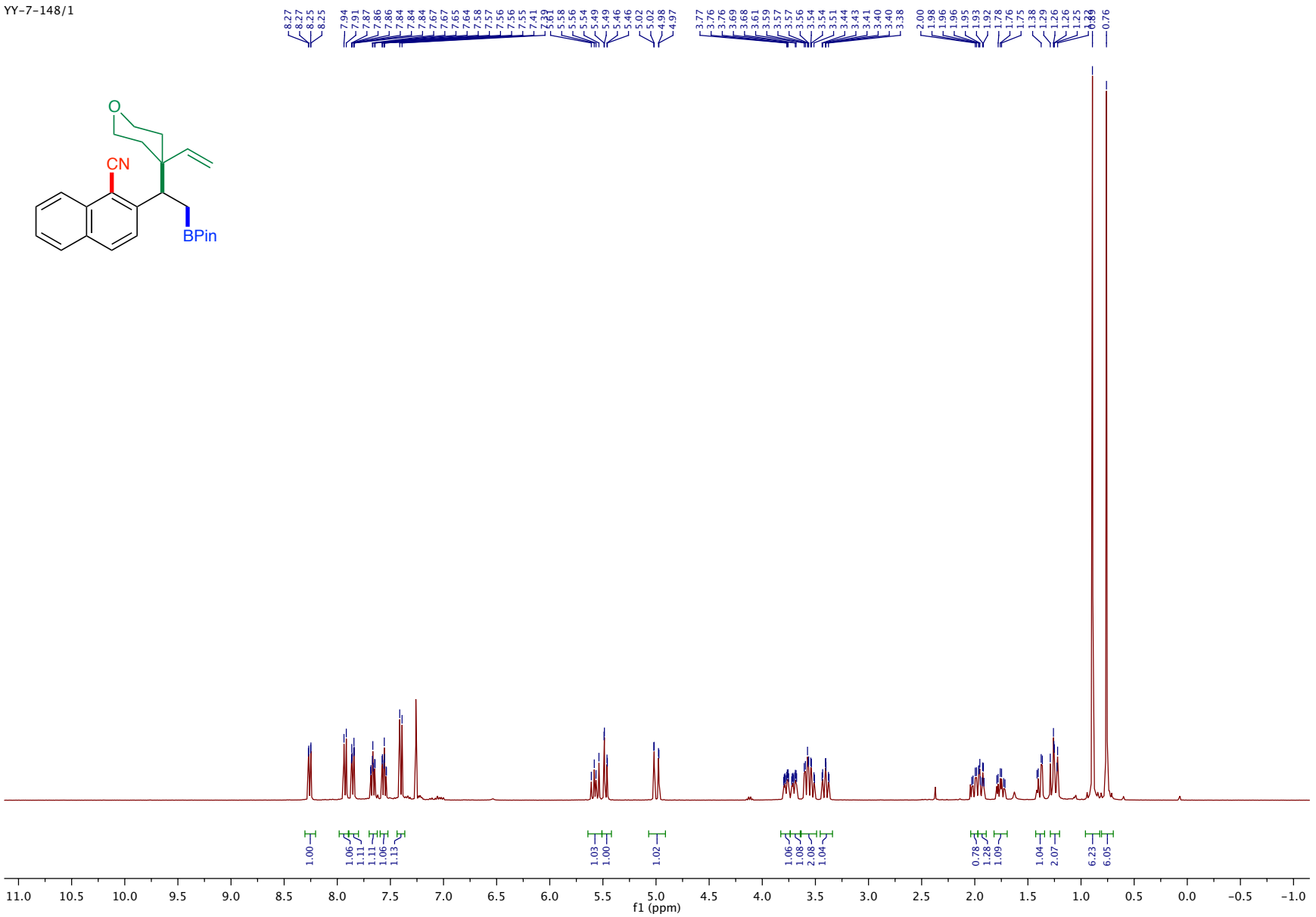

YY-7-55-2nd run/2
149.01
143.58
135.67
135.66
134.25
132.54
131.56
131.42
129.55
128.39
128.26
127.66
126.76
126.08
125.60
117.74
114.36
111.77
83.05
63.91
49.62
44.79
38.98
33.43
26.98
24.72
24.21
20.88
19.49
19.30
Me
CN
OTBDPS
BPin
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

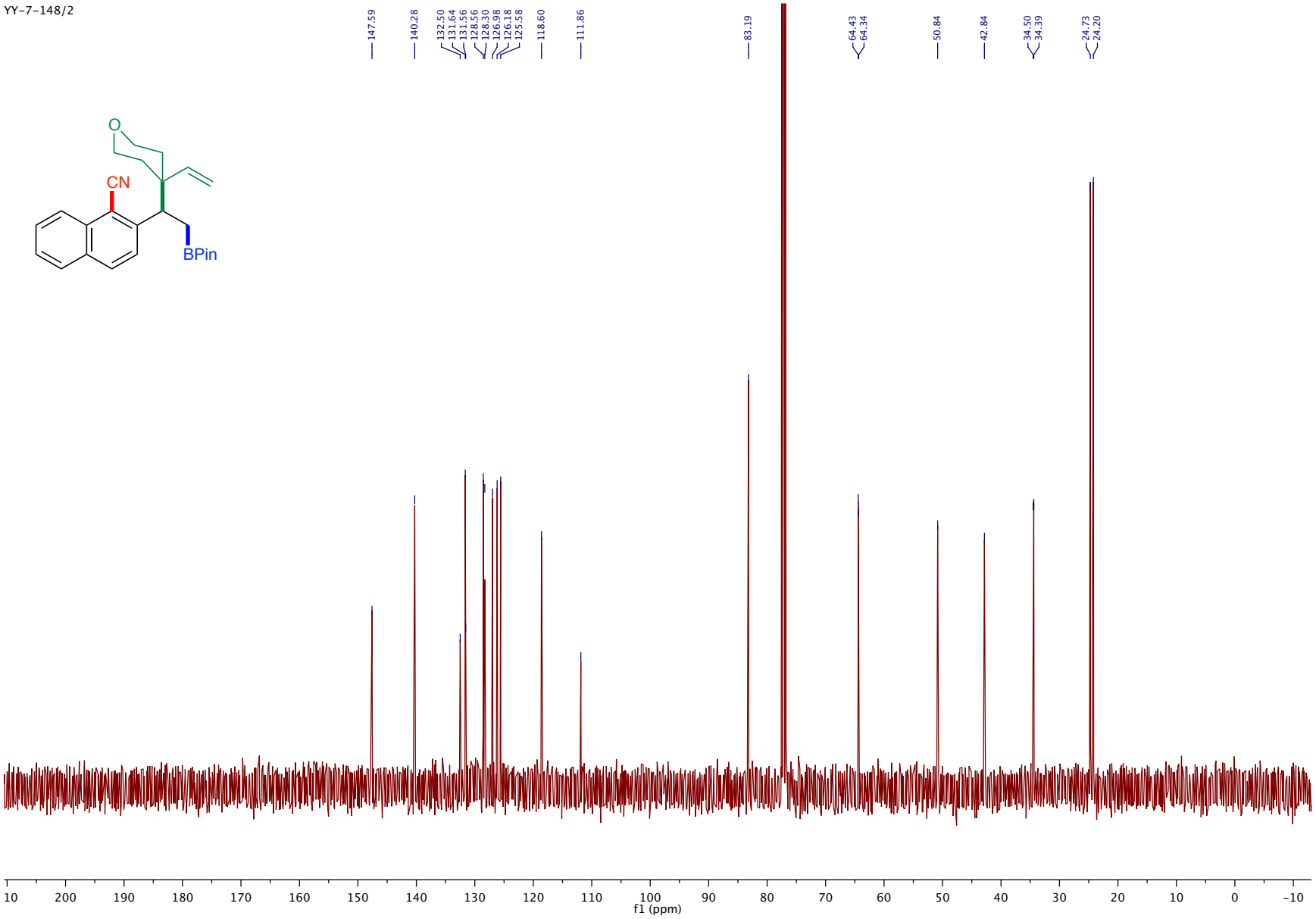

YY-7-124/1
Me
CN
BPin
f1 (ppm)

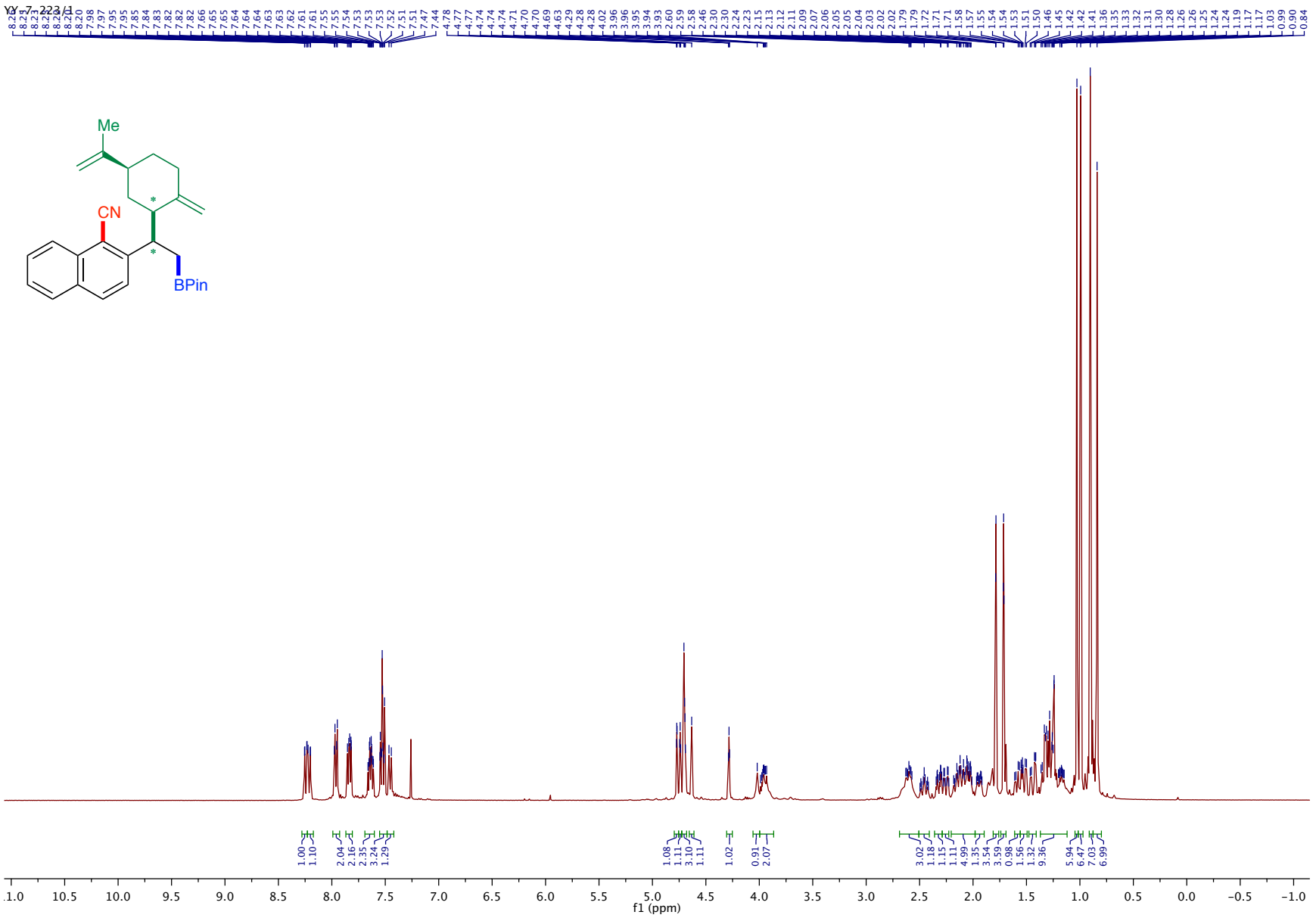

YY-7-124/3
149.18
142.91
132.55
131.36
131.21
128.29
128.24
128.20
126.90
126.72
125.61
117.71
113.51
112.00
83.05
47.37
45.03
44.21
28.54
27.66
27.39
27.24
26.88
24.73
24.18
15.59
Me
CN
BPin
f1 (ppm)

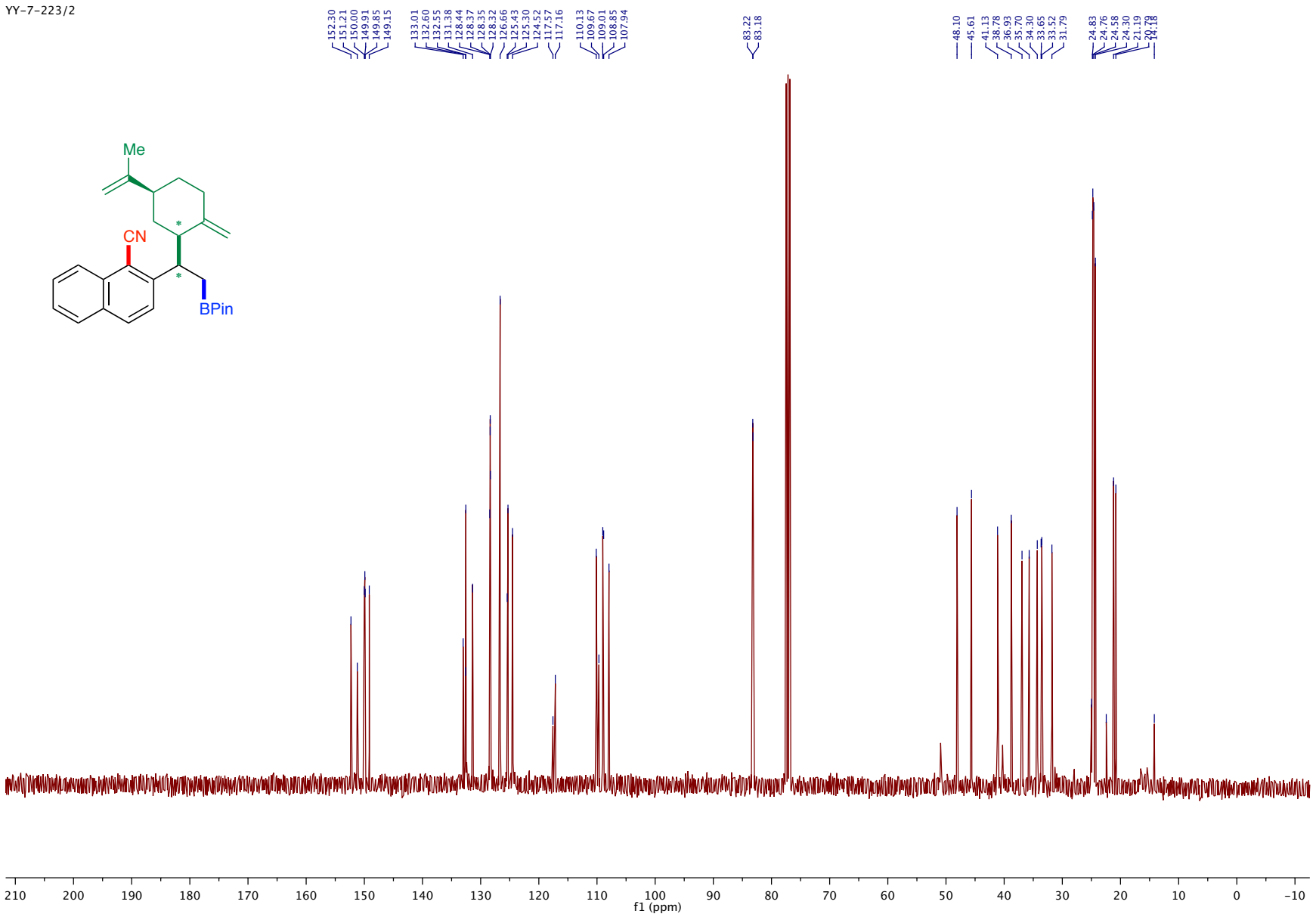

YY-7-44-1st run-2/1
CN
BPin
f1 (ppm)

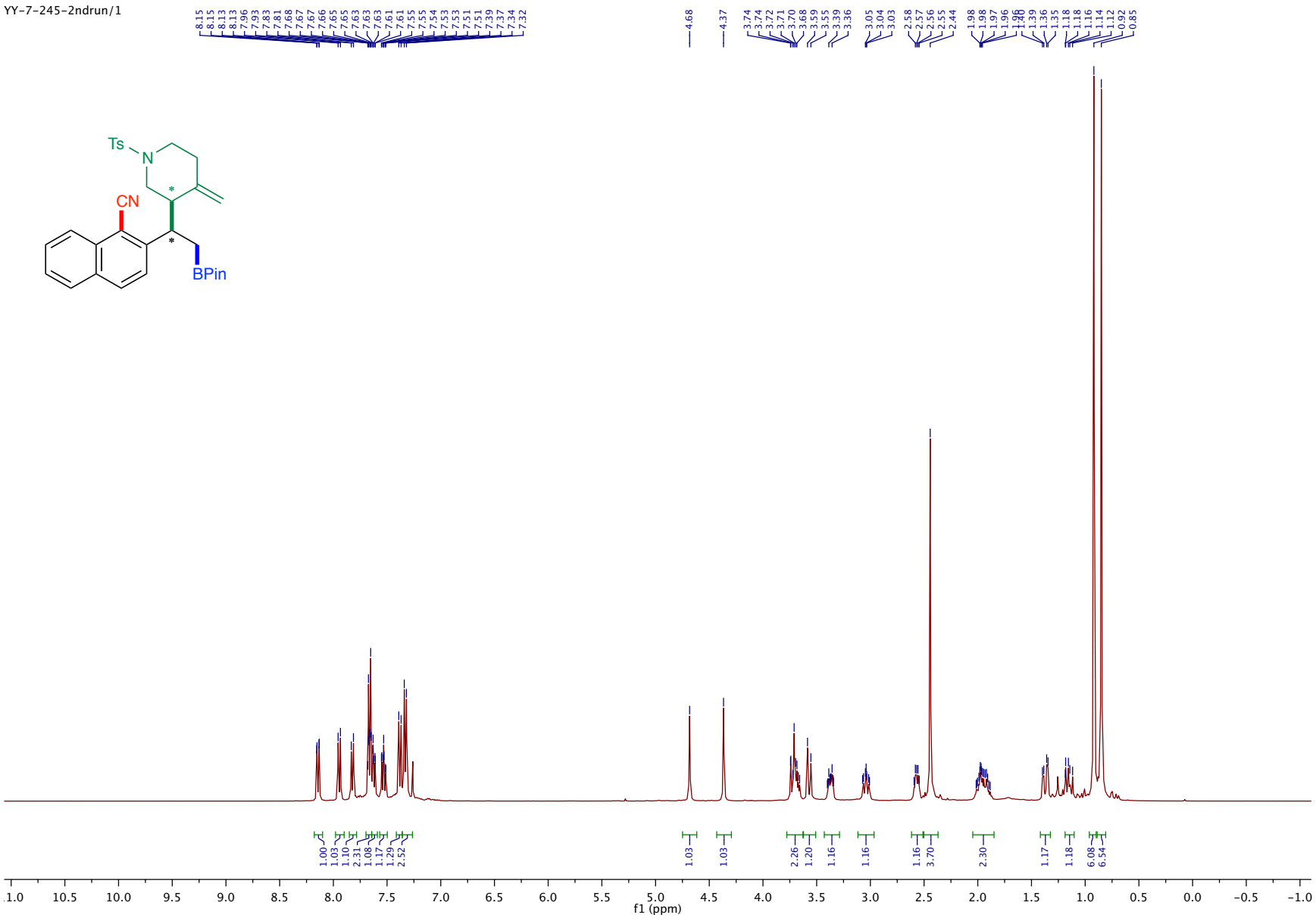

YY-7-44-1st run-2/2
148.90
141.58
132.49
131.44
131.38
128.34
128.25
126.72
126.38
125.52
117.86
117.30
111.64
83.02
51.22
44.67
34.64
34.21
26.31
24.71
24.20
22.54
22.35
CN
BPin
f1 (ppm)

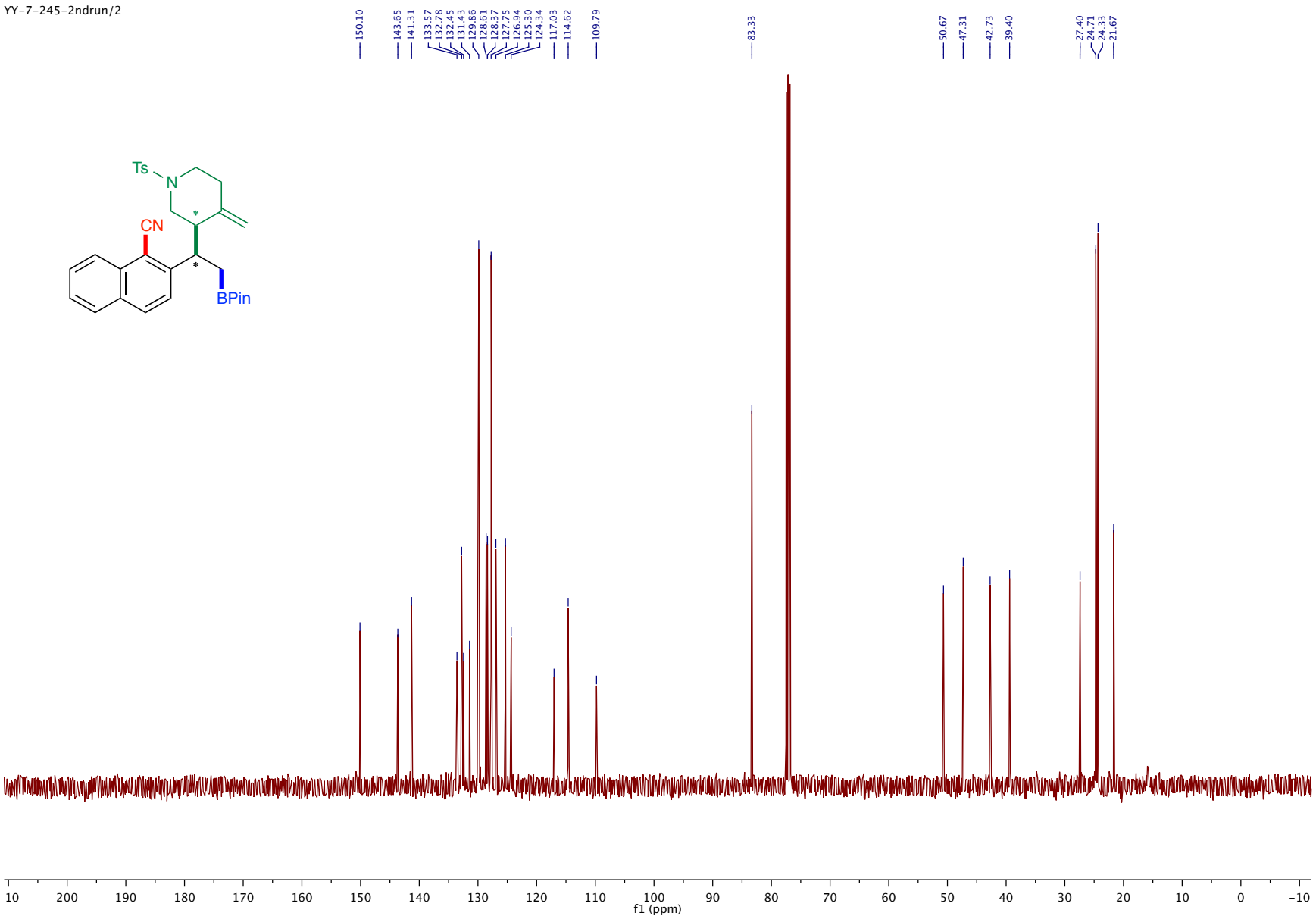

YY-7-148/1
O
CN
BPin
f1 (ppm)

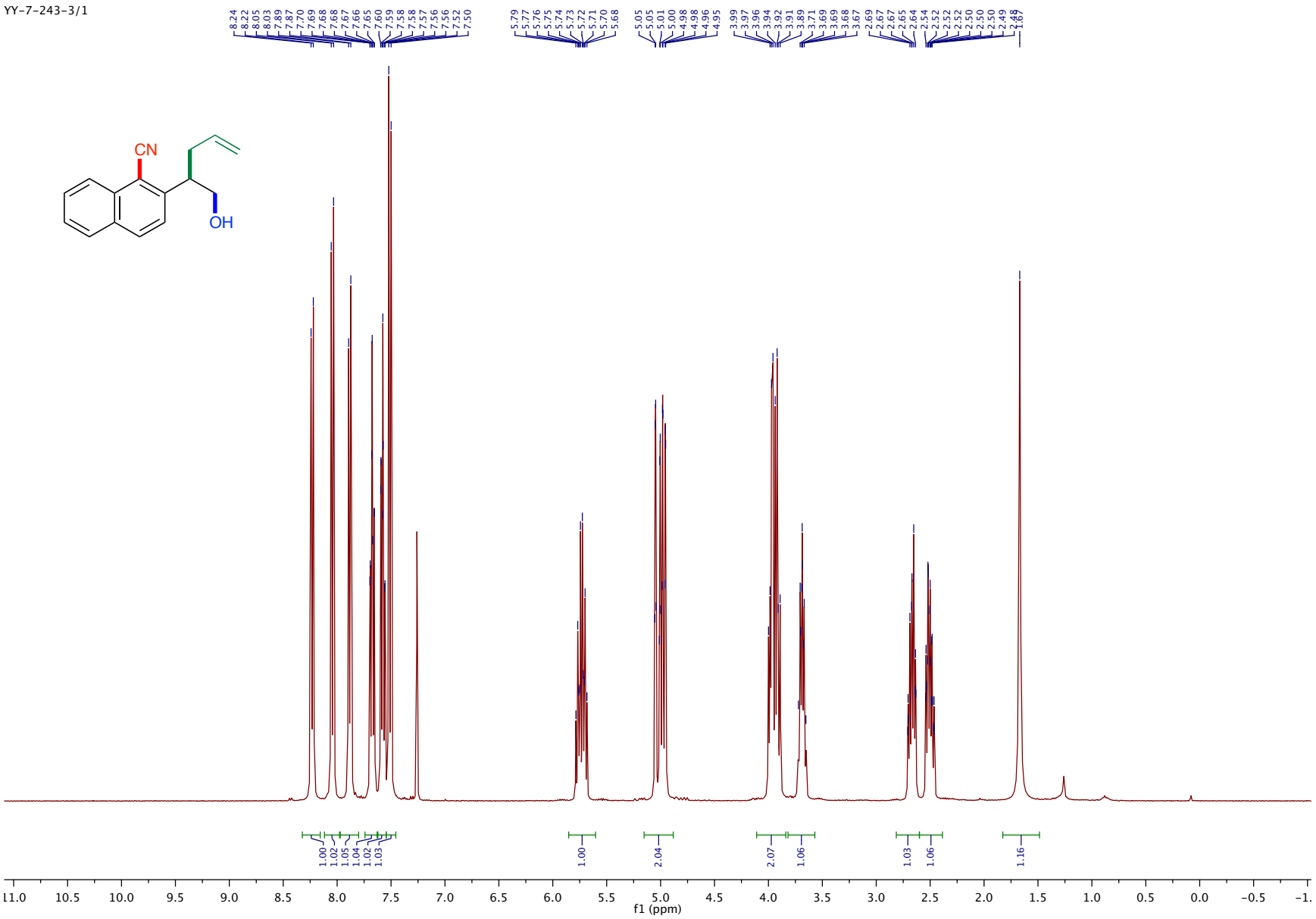

YY-7-148/2
147.59
140.28
132.50
131.64
131.56
128.56
128.30
126.98
126.18
125.58
118.60
111.86
83.19
64.43
64.34
50.84
42.84
34.50
34.39
24.73
24.20
O
CN
BPin
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

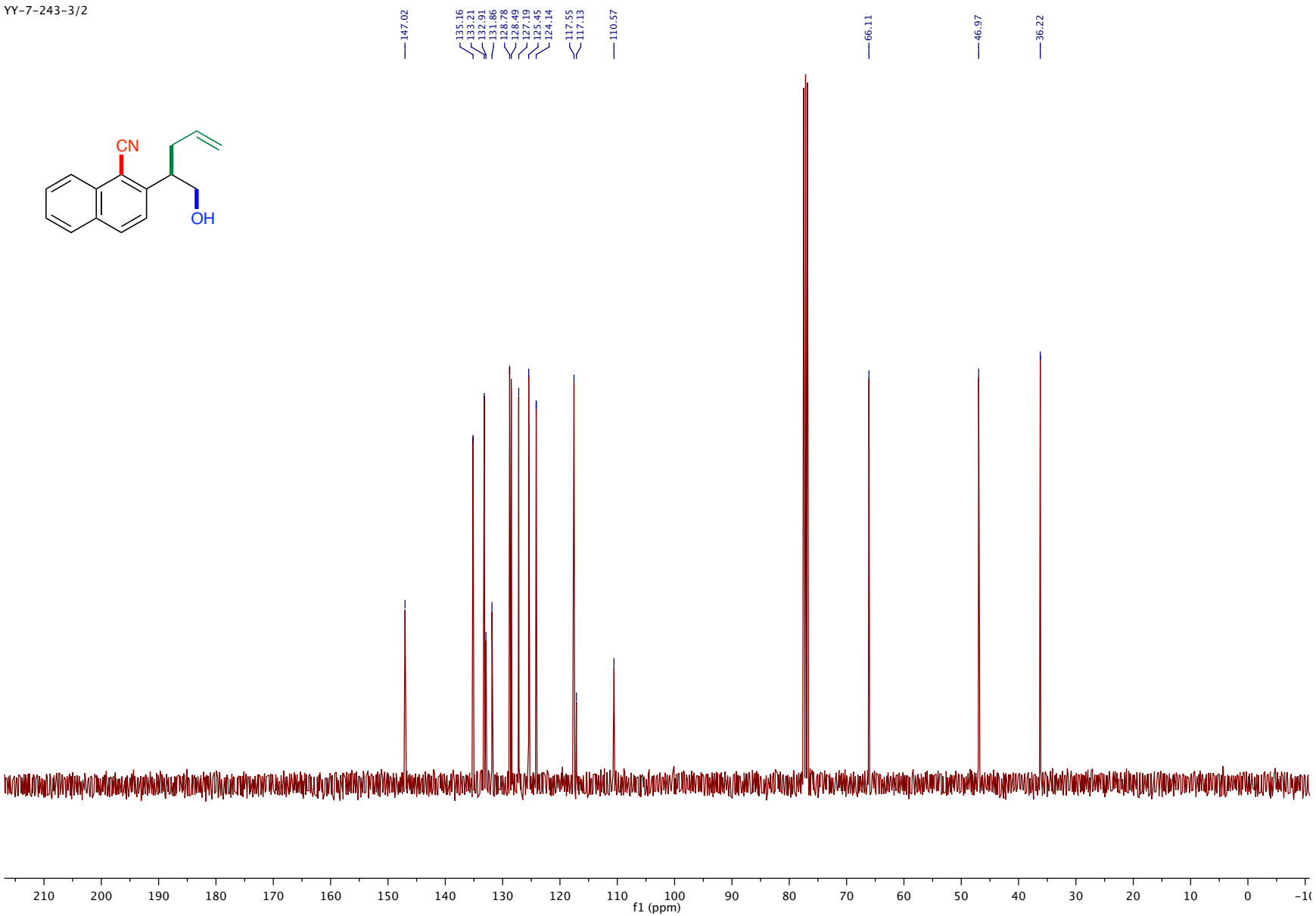

YY-7-223-1
Me
CN
BPin
f1 (ppm)

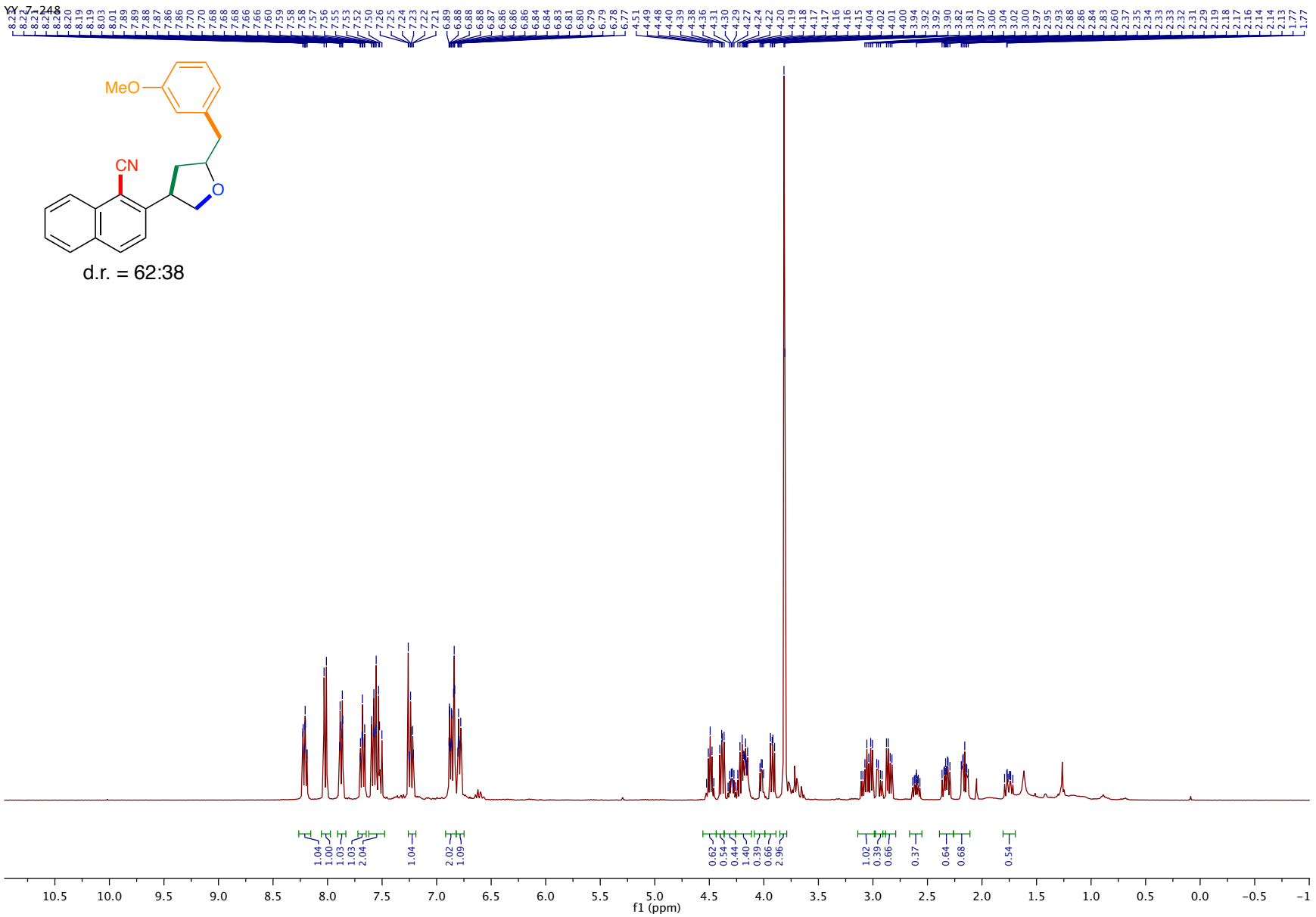

YY-7-223/2
152.30
151.21
150.00
149.91
149.85
149.15
133.01
132.60
132.55
131.38
128.44
128.37
128.35
128.32
126.66
125.43
125.30
124.52
117.57
117.16
110.13
109.67
109.01
108.85
107.94
83.22
83.18
48.10
45.61
41.13
38.78
36.93
35.70
34.30
33.65
33.52
31.79
24.83
24.76
24.58
24.30
21.19
20.79
14.18
Me
CN
BPin
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

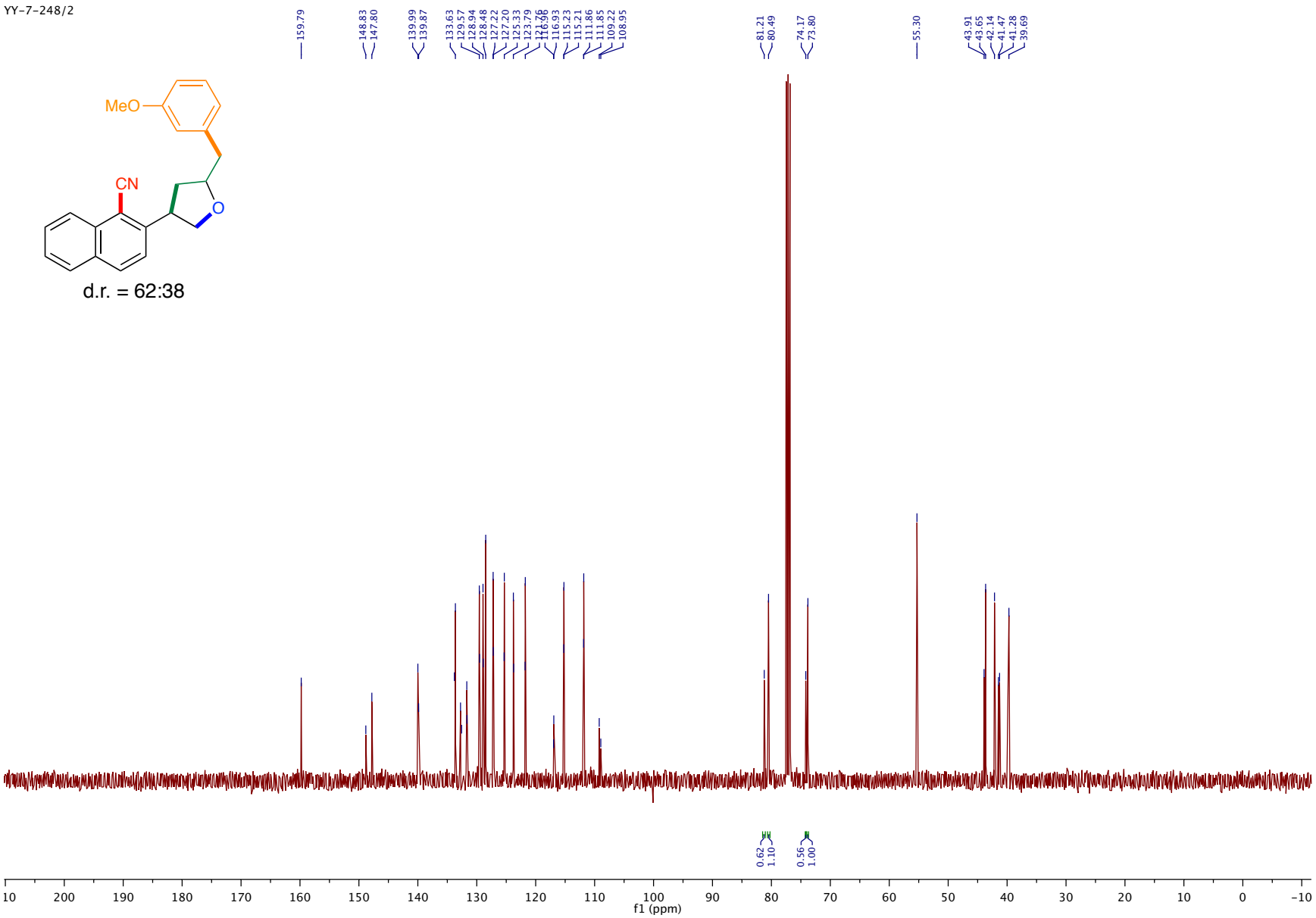

YY-7-245-2ndrun/1
Ts
N
CN
BPin
f1 (ppm)

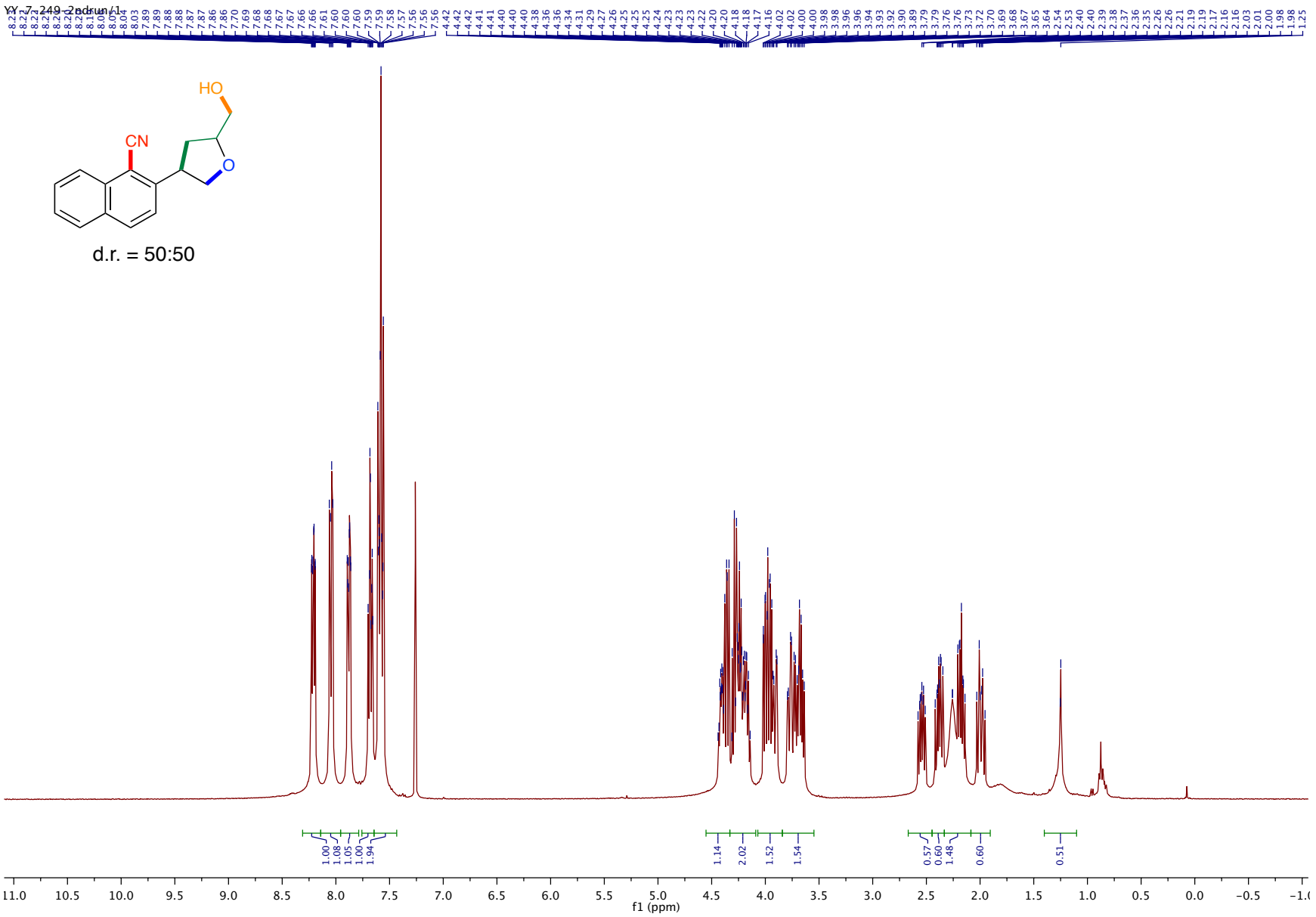

YY-7-245-2ndrun/2
150.10
143.65
141.31
133.57
132.78
132.45
131.43
129.86
128.61
128.37
127.75
126.94
125.30
124.34
117.03
114.62
109.79
83.33
50.67
47.31
42.73
39.40
27.40
24.71
24.33
21.67
Ts
N
CN
BPin
f1 (ppm)

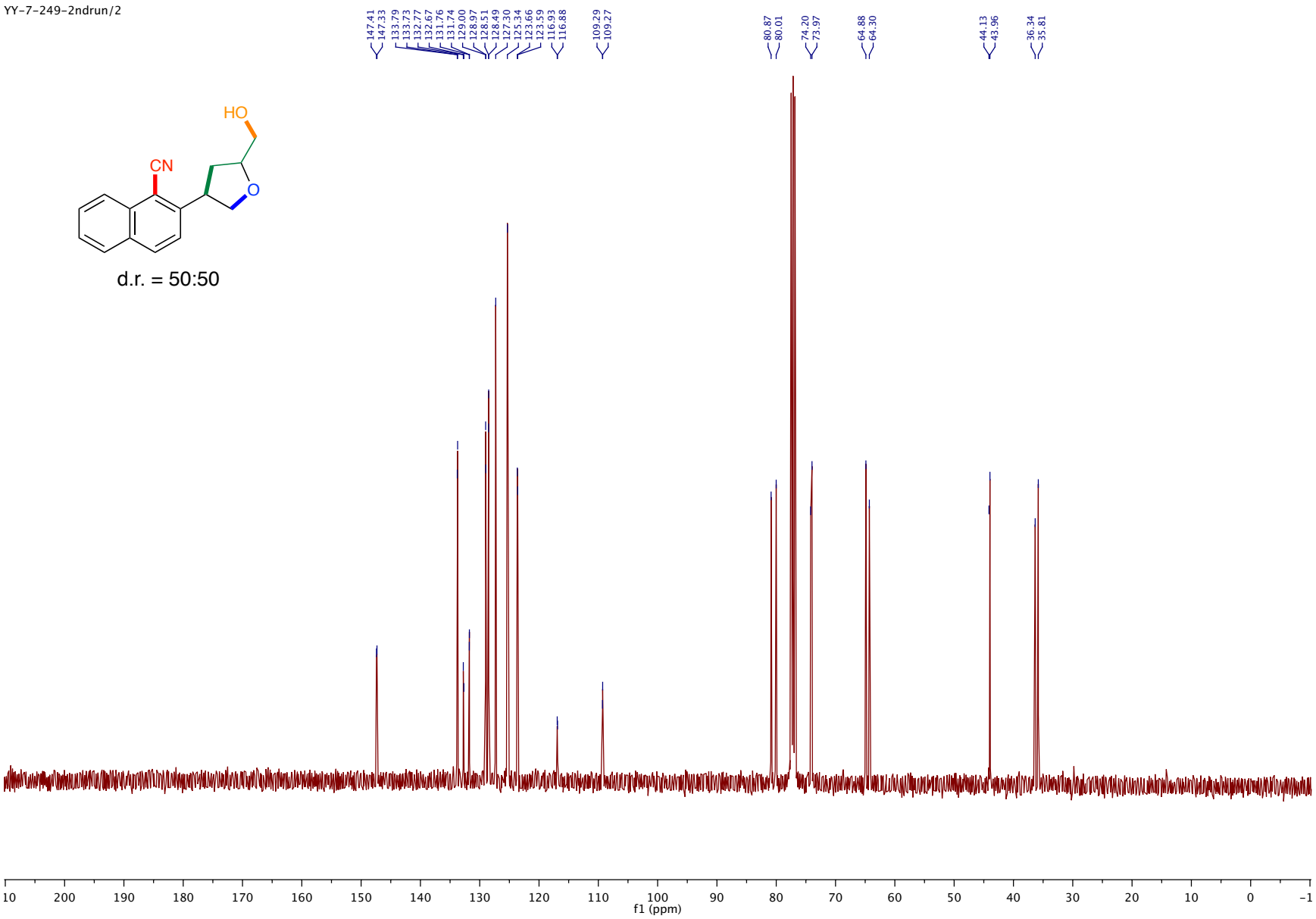

YY-7-243-3/1
CN
OH
f1 (ppm)

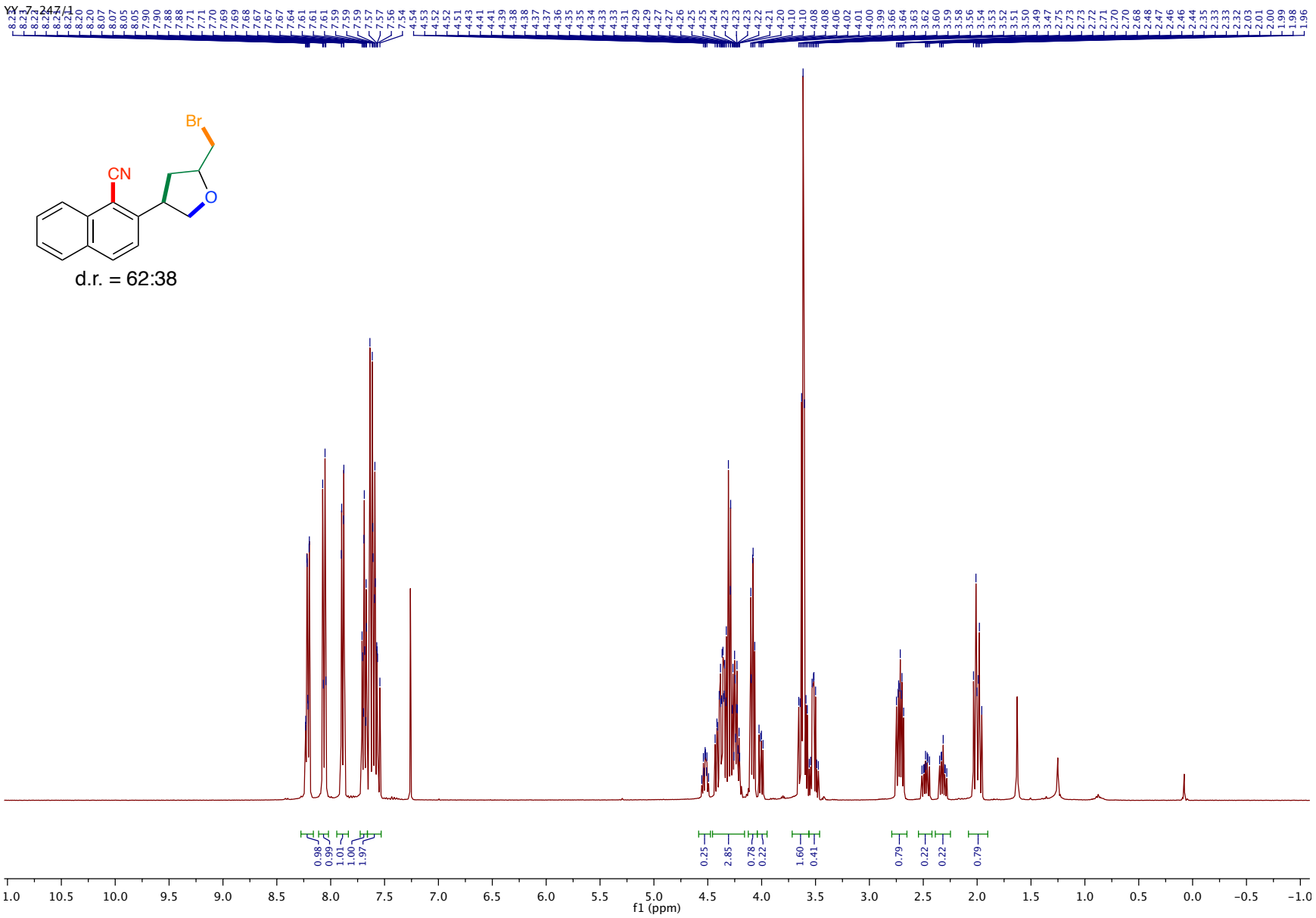

YY-7-243-3/2
147.02
135.16
133.21
132.91
131.86
128.78
128.49
127.19
125.45
124.14
117.55
117.13
110.57
66.11
46.97
36.22
CN
OH
f1 (ppm)

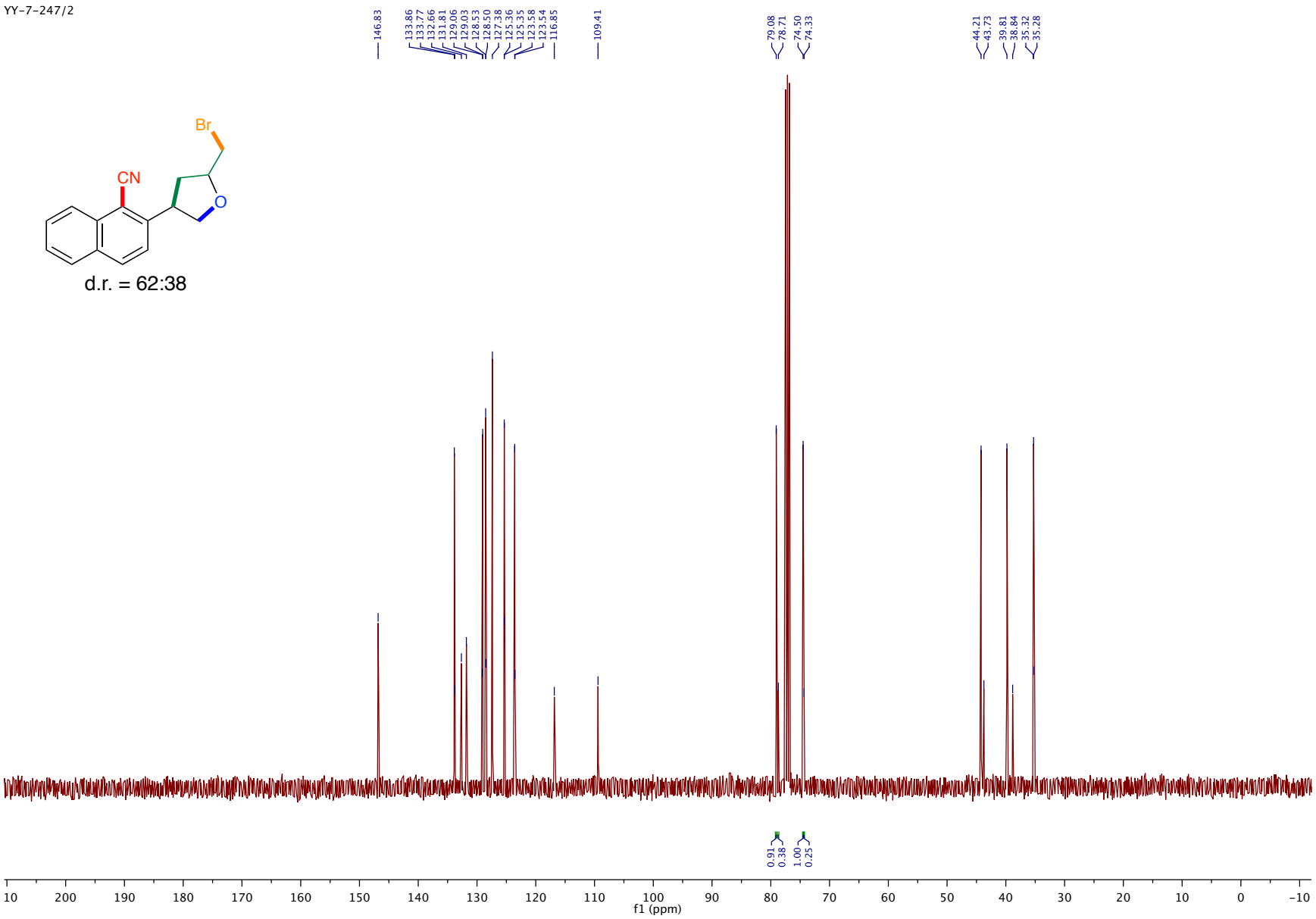

YY-7-248
MeO
CN
O
d.r. = 62:38
f1 (ppm)


YY-7-248/2
159.79
148.83
147.80
139.99
139.87
133.63
129.57
128.94
128.48
127.22
127.20
125.33
123.79
116.93
115.23
115.21
111.86
111.85
109.22
108.95
81.21
80.49
74.17
73.80
55.30
43.91
43.65
42.14
41.47
41.28
39.69
MeO
CN
O
d.r. = 62:38
0.62
1.10
0.56
1.00
f1 (ppm)


YY-7-249-2ndrun-1
HO
CN
O
d.r. = 50:50
1.00
1.08
1.05
1.00
1.94
1.14
2.02
1.52
1.54
0.57
0.60
1.48
0.60
0.51
f1 (ppm)


YY-7-249-2ndrun/2
147.41
147.33
133.79
133.73
132.77
132.67
131.76
131.74
129.00
128.97
128.51
128.49
127.30
125.34
123.66
123.59
116.93
116.88
109.29
109.27
80.87
80.01
74.20
73.97
64.88
64.30
44.13
43.96
36.34
35.81
HO
CN
O
d.r. = 50:50
f1 (ppm)


YY-7-247-1
Br
CN
O
d.r. = 62:38
0.98
0.99
1.01
1.00
1.97
0.25
2.85
0.78
0.22
1.60
0.41
0.79
0.22
0.22
0.79
f1 (ppm)


YY-7-247/2
146.83
133.86
133.77
132.66
131.81
129.06
129.03
128.53
128.50
127.38
125.36
125.35
123.58
123.54
116.85
109.41
79.08
78.71
74.50
74.33
44.21
43.73
39.81
38.84
35.32
35.28
Br
CN
O
d.r. = 62:38
0.91
0.38
1.00
0.25
f1 (ppm)