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Supporting Information

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Palladium-Catalyzed Addition of Cyanoborane to Alkynes, Leading to Regio- and Stereoselective Synthesis of β-Boryl-α,β-unsaturated Nitriles

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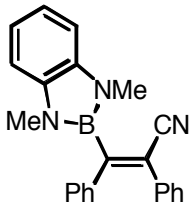
Experimental procedures and characterization data for the new compounds

General. All reactions were performed under a nitrogen atmosphere with magnetic stirring. ^{1}H and ^{11}B NMR spectra were recorded on a Mercury-400 spectrometer at 400 MHz and 128.3 MHz at ambient temperature, ^{13}C NMR spectra were recorded on a Varian GEMINI-2000 spectrometer at 75.45 MHz. ^{1}H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, and m = multiplet), coupling constant (Hz), and integration. ^{13}C and ^{11}B NMR data are reported in ppm downfield from tetramethylsilane (δ scale) and $BF_3{\cdot}OEt_2$, respectively. High resolution mass spectra were recorded on a JEOL JMS-SX102A (EI) spectrometer. Infrared spectra were recorded on a FTIR SHIMADZU DR-8000 spectrometer.

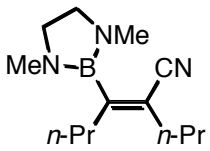
Anhydrous THF (Kanto) was purchased from the commercial sources. Dioxane was distilled from sodium/benzophenone ketyl. Cp(η^3-allyl)Pd was prepared according to the literature method.[1] Trimethyphosphine (Aldrich), tricyclohexylphosphine (Aldrich), dimethylphenylphosphine (Aldrich), tri(*t*-butyl)phosphine (Kanto), *p*-chloroiodobenzene (TCI), pinacol (TCI), borontrichloride methylsulfide complex (Aldrich), triethylamine (Wako), *p*-toluenesulfonic acid monohydrate (Nacalai), and KF (spray dried, Wako) were used as received from the commercial sources.

Preparation of 1d To a suspension of borontrichloride methylsulfide complex (18.6 g, 104 mmol) in triethylamine (26.6 mL, 191 mmol) and hexane (300 mL) was slowly added *N,N'*-

diisopropylethylenediamine (12.5 g, 86.6 mmol) at room temperature. The mixture was stirred at room temperature for 1 h and at 80 °C (bath temp.) for 4 h. After the reaction mixture was cooled to room temperature, hexane (200 mL) was added. The ammonium salt was removed by filtration. Evaporation of the filtrate followed by distillation (85-87 °C / 20 mmHg) gave 2-chloro-1,3-diisopropyl-1,3,2-diazaborolidine (14.0 g, 86%). Trimethylsilylcyanide (6.79 mL, 50.9 mmol) and 2-chloro-1,3-diisopropyl-1,3,2-diazaborolidine (8.73 g, 46.3 mmol) were mixed at room temperature. The mixture was stirred for 24 h at 50 °C. Removal of volatile materials in vacuo followed by distillation (59-61°C / 6.0 mmHg) afforded **1d** as colorless liquid (7.93 g, 96%). Other cyanoboranes could also be prepared according to this method.



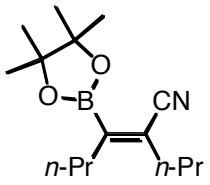
3-(1,3-Dimethyl-1,3-dihydrobenzo-1,3,2-diazaborol-2-yl)-2,3-diphenylacrylonitrile (Table 1, entry 9): To a solution of Cp(η^3-C_3H_5)Pd (5.3 mg, 0.025 mmol) and trimethylphosphine (10.4 μL, 0.10 mmol) in dioxane (0.2 mL) were added diphenylacetylene (107 mg, 0.6 mmol) and a solution of cyanoborane **1f** (85.5 mg, 0.50 mmol) in dioxane (0.3 mL). The reaction mixture was heated to 130 °C (bath temp.) for 10 h. Bulb-to-bulb distillation (250-300 °C/1.0 mmHg) afforded the cyanoboration product **3fb** as white solid (149 mg, 82%). 3fb: mp 176-177 °C; ^{1}H NMR (C_6D_6) δ 3.04 (s, 6H), 6.83-6.98 (m, 9H), 7.15-7.20 (m, 3H), 7.28-7.35 (m, 2H), ^{13}C NMR ($CDCl_3$) δ 29.9, 108.8, 119.4, 119.9, 121.3, 128.2, 128.5, 128.8, 129.2, 129.5, 134.1, 137.9, 139.1 ^{11}B NMR (C_6D_6) δ 26.9, IR (nujol) 2220 cm^{-1}. Anal. calcd. for $C_{23}H_{20}BN_3$: C, 79.10; H, 5.77; N, 12.03. Found: C, 78.82; H, 5.79; N, 12.00.



(*E*)-2-Propyl-3-(1,3-dimethyl-1,3,2-diazaborolidin-2-yl)hex-2-enenitrile (Table 1, entry 1): ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.2 Hz, 3H), 0.97 (t, J = 7.2 Hz, 3H), 1.32-1.41 (m, 2H),

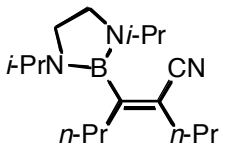
[1] Shriver, D. F.; *Inorg. Synth.* **1979**, *19*, 220.

1.61 (sext, J = 7.2 Hz, 2H), 2.18-2.24 (m, 2H), 2.27 (t, J = 7.2 Hz, 2H), 2.58 (s, 6H), 3.20-3.25 (m, 4H), ^{13}C NMR ($CDCl_3$) δ 13.4, 14.4, 21.6, 21.8, 31.4, 34.0, 34.2, 51.7, 118.1, 120.2, ^{11}B NMR ($CDCl_3$) δ 30.4, IR (neat) 2207 cm^{-1}. HRMS calcd. for $C_{13}H_{24}BN_3$ (M^+): 233.2063. Found: 233.2061. Since the compound was not stable enough for further purification, the coumound was identified by converting to the corresponding pinacol ester **(10)**. The pinacol derivative **10** was obtained with the same procedure as the preparation of **8** (vide infra).

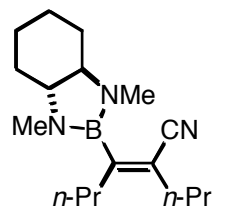


10

2-Propyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-2-enenitrile (10): ^{1}H NMR ($CDCl_3$) δ 0.95-1.00, (m 6H), 1.41 (sext, J = 7.6 Hz, 2H), 1.60 (sext, J = 7.6Hz, 2H), 2.26 (dt, J = 1.2, 7.6 Hz, 4H), ^{13}C NMR ($CDCl_3$) δ 13.6, 14.1, 21.4, 22.3, 24.7, 32.6, 33.0, 84.5, 119.4, 122.9, ^{11}B NMR ($CDCl_3$) δ 29.8, IR (neat) 2213 cm^{-1}. HRMS calcd. for $C_{15}H_{26}BNO_2$ (M^+): 263.2057. Found: 263.2054. See below for the ^{1}H and ^{13}C NMR charts.

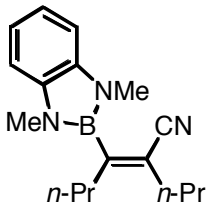


(*E*)-2-Propyl-3-(1,3-diisopropyl-1,3,2-diazaborolidin-2-yl)hex-2-enenitrile (Table 1, entry 2): ^{1}H NMR ($CDCl_3$) δ 0.92-0.98 (m, 6H), 1.34-1.44 (m, 2H), 1.60 (sext, J = 7.2 Hz, 2H), 2.15-2.21 (m, 2H), 2.25 (t, J = 7.2 Hz, 2H), 3.16-3.22 (m, 2H), 3.23-3.36 (m, 4H), ^{13}C NMR ($CDCl_3$) δ 13.4, 14.6, 21.6, 21.9, 31.4, 34.7, 41.5, 45.4, 117.5, 120.6, ^{11}B NMR ($CDCl_3$) δ 29.7, IR (neat) 2207 cm^{-1}. Anal. calcd. for $C_{17}H_{32}BN_3$: C, 70.59; H, 11.15; N, 14.53. Found: C, 70.48; H, 11.34; N, 14.48.

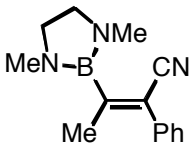


(*E*)-2-Propyl-3-(1,3-dimethyloctahydrobenzo-1,3,2-diazaborol-2-yl)hex-2-enenitrile (Table 1, entries 3-6): ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.2 Hz, 3H), 0.97 (t, J = 7.2 Hz, 3H),

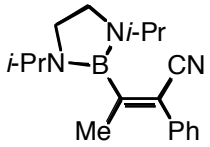
1.10-1.41 (m, 6H), 1.61 (sext, J = 7.2 Hz, 2H), 1.75-1.87 (m, 2H), 1.88-2.08 (m, 2H), 2.19-2.25 (m, 2H), 2.27 (t, J = 7.2 Hz, 2H), 2.49-2.62 (m, 8H), ^{13}C NMR ($CDCl_3$) δ 13.4, 14.4, 21.6, 21.8, 25.00, 25.05, 29.2, 29.4, 30.9, 31.3, 31.4, 34.2, 67.9, 68.8. 117.7, 120.2, ^{11}B NMR ($CDCl_3$) δ 28.0, IR (neat) 2207 cm^{-1}. Anal. calcd. for $C_{17}H_{30}BN_3$: C, 71.08; H, 10.53; N, 14.63. Found: C, 70.98; H, 10.51; N, 14.54.



(*E*)-2-Propyl-3-(1,3-dimethyl-1,3-dihydrobenzo-1,3,2-diazaborol-2-yl)hex-2-enenitrile (Table 1, entry 7): ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H), 1.35-1.45 (m, 2H), 1.73 (sext, J = 7.2 Hz, 2H), 2.44 (q, J = 7.2 Hz, 4H), 3.35 (s, 6H), 7.09 (s, 4H), ^{13}C NMR ($CDCl_3$) δ 13.5, 14.2, 21.6, 22.1, 29.8, 31.9, 34.9, 108.4, 119.1, 119.8, 121.4, 137.9, ^{11}B NMR ($CDCl_3$) δ 27.8, IR (neat) 2207 cm^{-1}. HRMS calcd. for $C_{17}H_{24}BN_3$ (M^+): 281.2063. Found: 281.2057. The title compound was converted to pinacol ester **10** for assignment by the same procedures as that for **8**.

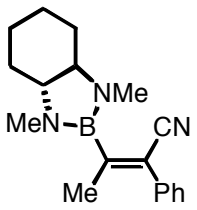


(*E*)-2-Phenyl-3-(1,3-dimethyl-1,3,2-diazaborolidin-2-yl)but-2-enenitrile (Table 2, entry 1): ^{1}H NMR (C_6D_6) δ 1.70 (s, 3H), 2.57 (s, 6H), 2.89-3.09 (m, 4H), 6.95-7.10 (m, 3H), 7.22-7.28 (m, 2H), ^{13}C NMR ($CDCl_3$) δ 19.3, 33.9, 51.7, 118.9, 119.7, 128.2, 128.5, 128.9, 134.1, ^{11}B NMR (C_6D_6) δ 29.6, IR (neat) 2207 cm^{-1}. Anal. calcd. for $C_{14}H_{18}BN_3$: C, 70.32; H, 7.59; N, 17.57. Found: C, 70.46; H, 7.60; N, 17.46.

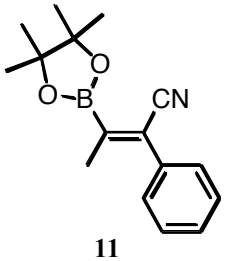


(*E*)-2-Phenyl-3-(1,3-diisopropyl-1,3,2-diazaborolidin-2-yl)but-2-enenitrile (Table 2, entry 2): ^{1}H NMR ($CDCl_3$) δ 1.12 (d, J = 6.4 Hz, 6H), 1.19 (d, J = 6.4 Hz, 6H), 1.97 (s, 3H), 3.18-3.47 (m, 6H), 7.31-7.44 (m, 5H), ^{13}C NMR ($CDCl_3$) δ 19.9, 21.9, 22.2, 42.4, 45.9, 117.9,

120.0, 128.2, 128.5, 128.9, 134.2, ^{11}B NMR ($CDCl_3$) δ 29.7, IR (nujol) 2209 cm^{-1}. Anal. calcd. for $C_{18}H_{26}BN_3$: C, 73.23; H, 8.88; N, 14.23. Found: C, 73.06; H, 9.07; N, 14.42.

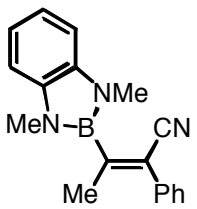


(*E*)-2-Phenyl-3-(1,3-dimethyloctahydrobenzo-1,3,2-diazaborol-2-yl)but-2-enenitrile (Table 2, entry 3): ^{1}H NMR ($CDCl_3$) δ 1.15-1.42 (m, 4H), 1.78-1.88 (m, 2H), 1.98 (s, 3H), 2.03-2.13 (m, 2H), 2.56-2.70 (m, 8H), 7.25-7.45 (m, 5H), ^{13}C NMR ($CDCl_3$) δ 19.2, 25.0, 29.2, 29.3, 30.9, 31.3, 68.3, 68.7, 118.6, 119.6, 128.2, 128.5, 128.9, 134.0, ^{11}B NMR ($CDCl_3$) δ 32.7, IR (nujol) 2203 cm^{-1}. HRMS Calcd. for $C_{18}H_{24}BN_3$ (M^+): 293.2063. Found: 293.2063. The title compound was converted to pinacol ester **11** by the method as that for **8**.



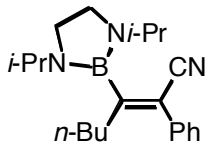
11

(*E*)-2-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enenitrile (11): ^{1}H NMR ($CDCl_3$) δ 1.38, (s, 12H), 1.96 (s, 3H), 7.30-7.43 (m, 5H) ^{13}C NMR ($CDCl_3$) δ 18.6, 24.7, 84.8, 118.9, 122.9, 128.5, 128.6, 128.7, 134.3, ^{11}B NMR ($CDCl_3$) δ 29.7, IR (nujol) 2215 cm^{-1}. HRMS calcd. for $C_{16}H_{20}BNO_2$ (M^+): 269.1578. Found: 269.1582. See below for the ^{1}H and ^{13}C NMR charts.

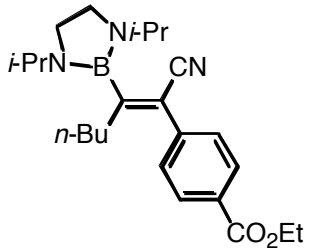


(*E*)-2-Phenyl-3-(1,3-dimethyl-1,3-dihydrobenzo-1,3,2-diazaborol-2-yl)but-2-enenitrile (Table 2, entry 4): ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3H), 3.47 (s, 6H), 7.16 (s, 4H), 7.40-7.56 (m, 5H), ^{13}C NMR ($CDCl_3$) δ 20.5, 29.9, 108.6, 118.4, 119.3, 121.8, 128.61, 128.65, 128.9, 133.9, 137.9, ^{11}B NMR ($CDCl_3$) δ 27.8, IR (neat) 2224 cm^{-1}. HRMS calcd. for $C_{18}H_{18}BN_3$ (M^+):

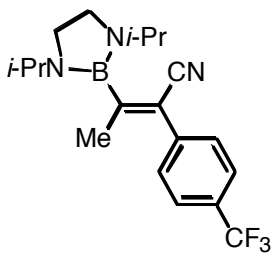
287.1594. Found: 287.1592. The title compound was converted to **11** by the same method as that for **8.**



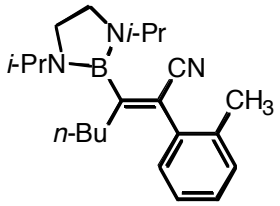
(*E*)-2-Phenyl-3-(1,3-diisopropyl-1,3,2-diazaborolidin-2-yl)hept-2-enenitrile (Table 2, entry 5): ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.2 Hz, 3H), 1.10 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.8 Hz, 6H), 1.28 (sext, J = 7.2 Hz, 2H), 1.36-1.46 (m, 2H), 3.22-3.29 (m, 2H), 3.29-3.36 (m, 2H) 3.44 (sept, J = 6.4 Hz, 2H), 7.31-7.36 (m 3H), 7.36-7.43 (m, 2H), ^{13}C NMR ($CDCl_3$) δ 13.8, 21.7, 21.9, 31.0, 33.6, 41.7, 45.6, 117.6, 120.1, 128.1, 128.5, 128.9, 134.6, ^{11}B NMR ($CDCl_3$) δ 29.6, IR (nujol) 2209 cm^{-1} Anal. calcd. for $C_{21}H_{32}BN_3$: C, 74.78; H, 9.56; N, 12.46. Found: C, 74.67; H, 9.53; N, 12.43.



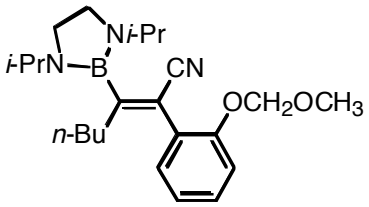
(*E*)-2-(4-Ethoxycarbonylphenyl)-3-(1,3-diisopropyl-1,3,2-diazaborolidin-2-yl)hept-2-enenitrile (Table 2, entry 6): ^{1}H NMR ($CDCl_3$) δ 0.85 (t, J = 7.2 Hz, 3H), 1.10 (d, J = 6.4 Hz, 6H), 1.20 (d, J = 6.4 Hz, 6H), 1.27 (sext, J = 7.2 Hz, 2H), 1.36-1.46 (m, 5H), 3.21-3.37 (m 4H), 3.42 (sept, J = 6.4 Hz, 2H) 4.40 (q, J = 7.2 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 8.06 (d, J = 8.4 Hz, 2H), ^{13}C NMR ($CDCl_3$) δ 13.7, 14.3, 21.7, 21.9, 23.1, 30.9, 33.7, 41.6, 45.6, 61.2, 116.7, 119.6, 128.9, 129.7, 130.2, 166.0, ^{11}B NMR ($CDCl_3$) δ 29.6, IR (neat) 2209, 1721 cm^{-1} Anal. calcd. for $C_{24}H_{36}BN_3O_2$: C, 70.41; H, 8.86; N, 10.26. Found: C, 70.43; H, 8.99; N, 10.33.



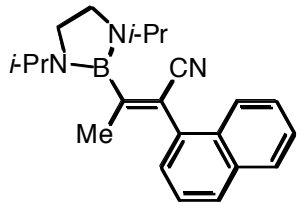
(*E*)-2-(4-Trifluoromethylphenyl)-3-(1,3-diisopropyl-1,3,2-diazaborolidin-2-yl)but-2-enenitrile (Table 2, entry 7): ^{1}H NMR ($CDCl_3$) δ 1.12 (d, J = 6.4 Hz, 6H), 1.19 (d, J = 6.4 Hz, 6H), 1.98 (s, 3H), 3.21-3.43 (m, 6H), 7.49 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), ^{13}C NMR ($CDCl_3$) δ 20.0, 21.9, 22.2, 42.5, 45.9, 116.7, 119.3, 125.5, 125.6, 128.2, 129.3, 137.8, ^{11}B NMR ($CDCl_3$) δ 29.6, IR (neat) 2213 cm^{-1}. Anal. calcd. for $C_{19}H_{25}BF_3N_3$: C, 62.83; H, 6.94; N, 11.57. Found: C, 62.97; H, 7.06; N, 11.51.



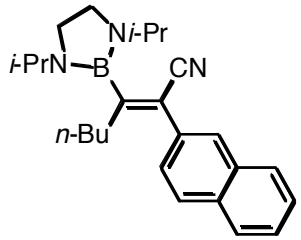
(*E*)-2-(2-Methylphenyl)-3-(1,3-diisopropyl-1,3,2-diazaborolidin-2-yl)hept-2-enenitrile (Table 2, entry 8): ^{1}H NMR ($CDCl_3$) *δ* 0.80 (t, 7.2 Hz, 3H), 1.14 (d, J = 6.4 Hz, 6H), 1.15-1.28 (m, 8H), 1.28-1.38 (m, 2H), 2.02-2.08 (m, 2H), 2.35 (s, 3H), 3.24-3.32 (m, 2H), 3.32-3.40 (m, 2H), 3.51 (sept, J = 6.4 Hz, 2H), 7.09-7.14 (m, 1H), 7.19-7.30 (m, 3H), ^{13}C NMR ($CDCl_3$) *δ* 13.7, 19.6, 21.7, 21.9, 23.0, 30.6, 33.5, 41.6, 45.7, 117.1, 119.3, 126.0, 128.5, 129.6, 130.4, 134.1, 136.2, ^{11}B NMR ($CDCl_3$) *δ* 29.8, IR (neat) 2207 cm^{-1}. Anal. calcd. for $C_{22}H_{34}BN_3$: C, 75.21; H, 9.75; N, 11.96. Found: C, 75.24; H, 9.65; N, 11.94.



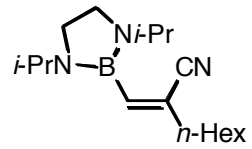
(*E*)-2-(2-Methoxymethylphenyl)-3-(1,3-diisopropyl-1,3,2-diazaborolidin-2-yl)hept-2-enenitrile (Table 2, entry 9): ^{1}H NMR ($CDCl_3$) δ 0.79 (t, J = 7.2 Hz, 3H), 1.11 (d, J = 6.8 Hz, 6H), 1.15-1.27 (m, 8H), 1.29-1.39 (m, 2H), 2.11-2.14 (m, 2H), 3.21-3.29 (m, 2H), 3.29-3.36 (m, 2H), 3.45-3.51 (m, 5H), 5.20 (s, 2H), 7.01 (dt, J = 1.2, 7.2 Hz, 1H), 7.11-7.17 (m, 2H), 7.27-7.33 (m, 1H), ^{13}C NMR ($CDCl_3$) δ 13.7, 21.7, 22.0, 23.0, 30.6, 33.7, 41.8, 45.6, 56.2, 94.2, 114.0, 114.2, 119.7, 121.5, 124.2, 129.8, 130.7, 154.3, ^{11}B NMR ($CDCl_3$) δ 30.0, IR (neat) 2208 cm^{-1}. Anal. calcd. for $C_{23}H_{36}BN_3O_2$: C, 69.52; H, 9.13; N, 10.57. Found: C, 69.40; H, 9.19; N, 10.45.



(*E*)-2-(1-Naphthyl)-3-(1,3-diisopropyl-1,3,2-diazaborolidin-2-yl)but-2-enenitrile (Table 2, entry 10): ^{1}H NMR ($CDCl_3$) δ 1.21 (d, J = 6.8 Hz, 6H), 1.32 (d, J = 6.8 Hz, 6H), 1.74 (s, 3H), 3.27-3.36 (m, 2H), 3.36-3.44 (m, 2H), 3.57 (sept. J = 6.8 Hz, 2H), 7.39 (d, J = 6.8 Hz, 1H), 7.48-7.61 (m, 3H), 7.86-7.94 (m, 3H), ^{13}C NMR ($CDCl_3$) δ 20.0, 22.0, 22.3, 42.4, 46.1, 116.2, 119.6, 124.5, 125.3, 126.2, 126.8, 127.4, 128.6, 129.0, 130.9, 131.8, 133.8, ^{11}B NMR ($CDCl_3$) δ 29.6, IR (neat) 2209 cm^{-1}. Anal. calcd. for $C_{22}H_{28}BN_3$: C, 76.53; H, 8.17; N, 12.17. Found: C, 76.55; H, 8.43; N, 12.08.

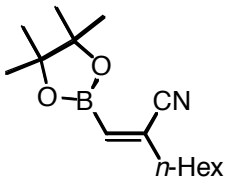


(*E*)-2-(2-Naphthyl)-3-(1,3-diisopropyl-1,3,2-diazaborolidin-2-yl)hept-2-enenitrile (Table 2, entry 11): ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.2 Hz, 3H), 1.14 (d, J = 6.4 Hz, 6H), 1.23-1.36 (m, 8H), 1.42-1.52 (m, 2H), 2.32-2.39 (m, 2H), 3.25-3.33 (m, 2H), 3.33-3.41 (m, 2H), 3.50 (sept, J = 6.4 Hz, 2H), 4.45 (dd, J = 1.6, 8.4 Hz, 1H), 7.49-7.55 (m, 2H), 7.82 (d, J = 1.6 Hz, 1H), 7.83-7.90 (m, 3H), ^{13}C NMR ($CDCl_3$) δ 13.8, 21.7, 22.0, 23.1, 31.1, 33.7, 41.7, 45.7, 117.5, 120.2, 125.9, 126.2, 126.5, 126.6, 127.7, 128.1, 128.2, 132.0, 132.8, 133.1, ^{11}B NMR ($CDCl_3$) δ 29.9, IR (neat) 2208 cm^{-1}. Anal. calcd. for $C_{25}H_{34}BN_3$: C, 77.51; H, 8.85; N, 10.85. Found: C, 77.72; H, 8.99; N, 10.76.



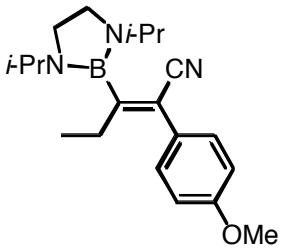
(*Z*)-2-Hexyl-3-(1,3-diisopropyl-1,3,2-diazaborolidin-2-yl)acrylonitrile (7d): To a solution of Cp(η^3-C_3H_5)Pd (5.3 mg, 0.025 mmol) and trimethylphosphine (7.8 μl, 0.075 mmol) in 1-octyne (221 μl, 1.50 mmol) was added cyanoborane**1d** (92.5 mg 0.517 mmol). The solution was stirred at 130°C for 6h. Bulb-to-bulb distillation (150-200 °C/2.0 mmHg) afforded the cyanoboration product **7d** as a colorless liquid (110 mg, 74%) in a 84:16 regioisomeric ratio.

7d: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 7.2 Hz, 3H), 1.02-1.11 (m, 10H), 1.24-1.36 (m, 8H), 1.51-1.64 (m, 2H), 2.30 (dt, J = 1.2, 7.2 Hz, 2H), 3.21 (s, 4H), 3.37 (sept, J = 6.4 Hz, 2H), 6.26 (t, J = 1.2 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ 14.0, 21.9, 22.6, 27.8, 28.2, 31.4, 37.6, 42.4, 45.8 119.3, 1249, ^{11}B NMR ($CDCl_3$) δ 28.7, IR (neat) 2215 cm^{-1}. HRMS calcd. for $C_{17}H_{32}BN_3$ (M^+): 289.2689. Found: 289.2676. The title compound was converted to pinacol ester **12** for assignment by the same procedures as that for **8**.



12

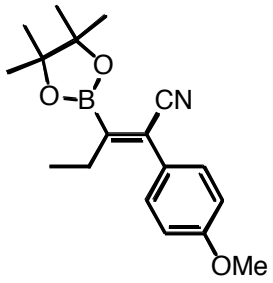
(*Z*)-2-Hexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylonitrile (12): ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.21-1.37 (m, 18H), 2.32 (dt, J = 1.6, 7,2 Hz, 2H), 6.04 (t, J = 1.6 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 24.7, 27.5, 28.3, 31.4, 38.3, 84.3, 118.0, 132.6, ^{11}B NMR ($CDCl_3$) δ 28.4, IR (neat) 2220 cm^{-1}. HRMS calcd. for $C_{15}H_{26}BNO_2$ (M^+): 263.2057. Found: 263.2063. See below for the ^{1}H and ^{13}C NMR charts.



Synthesis of a synthetic precursor of SQS inhibitor P3622 (Scheme 1)

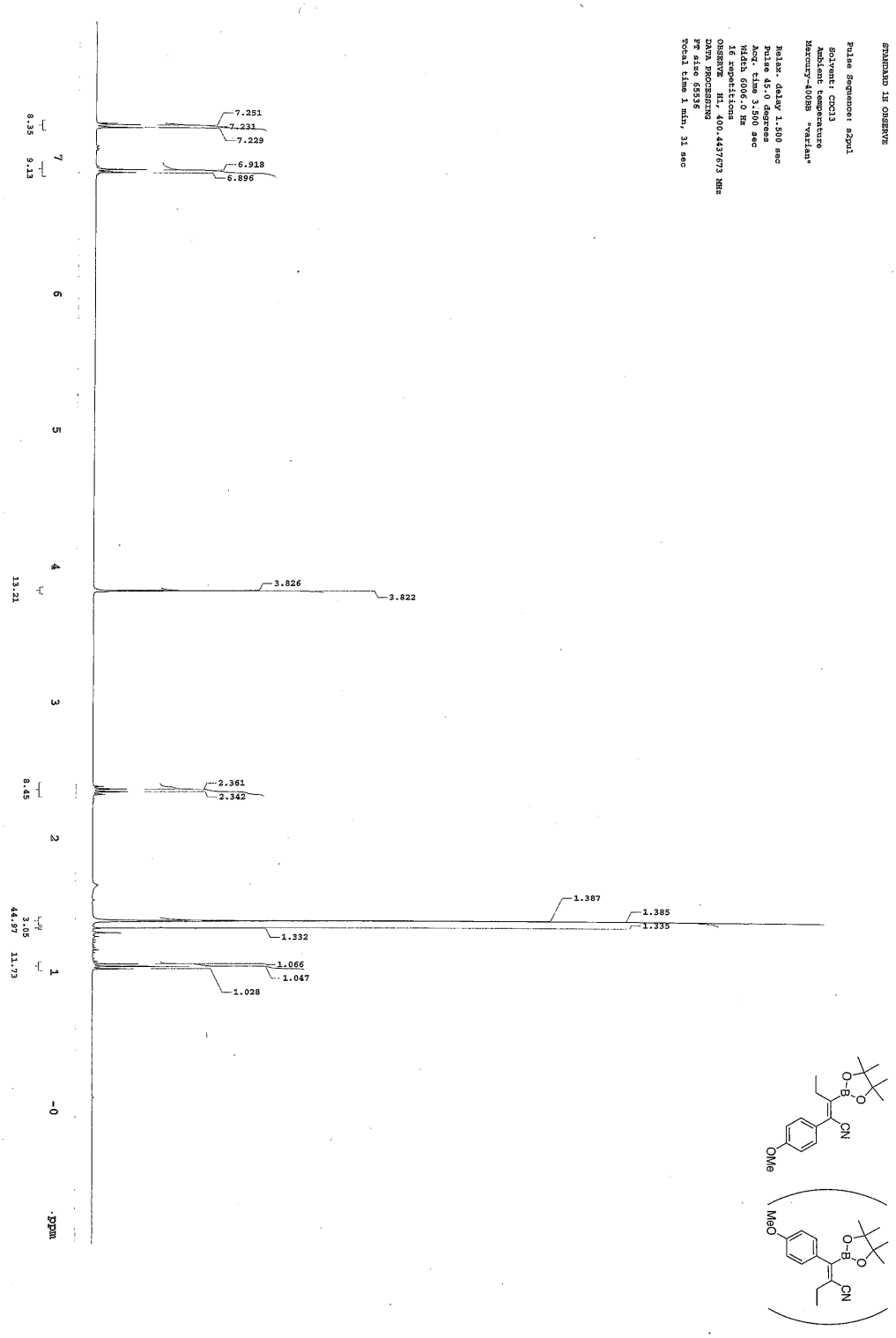
(a) Synthesis of (*E*)-2-(4-Methoxyphenyl)-3-(1,3-diisopropyl-1,3,2-diazaborolidin-2-yl)pent-2-enenitrile by cyanoboration of 1-(4-methoxyphenyl)-1-butyne: To a solution of Cp(η^3-C_3H_5)Pd (5.3 mg, 0.025 mmol) and trimethylphosphine (7.8 μl, 0.075 mmol) in dioxane (0.5 ml) were added 1-(4-methoxyphenyl)-1-butyne (96.1 mg, 0.6 mmol) and cyanoborane **1d** (89.5 mg, 0.50 mmol). The reaction mixture was heated at 130°C for 10 h. Bulb-to-bulb distillation (180-280 °C / 2.0 mmHg) afforded the cyanoboration product (155 mg, 91%) in a 94:6 regioisomeric ratio. ^{1}H NMR ($CDCl_3$) δ 1.06 (t, J = 7.6 Hz, 3H), 1.10 (d, J = 6.4 Hz, 6H), 1.20 (d, J = 6.4 Hz, 6H), 2.34 (q, J = 7.6 Hz, 2H), 3.22-3.29 (m, 2H), 3.29-3.37 (m, 2H), 3.43 (sept, J = 6.4 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), ^{13}C NMR ($CDCl_3$) δ 13.4, 21.7, 21.9, 26.7, 41.7, 45.6, 55.3, 113.8, 116.9, 120.3, 126.9, 130.1,

159.3, ^{11}B NMR ($CDCl_3$) δ 29.6, IR (neat) 2209 cm^{-1}. Anal. calcd. for $C_{20}H_{30}BN_3O$: C, 70.80; H, 8.91; N, 12.38. Found: C, 70.60; H, 8.91; N, 12.20.



(b) Preparation of (*E*)-2-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-enenitrile (8). The resulting product (131.0 mg, 0.386 mmol) obtained with method (a) and pinacol (68.4 mg, 0.579 mmol) were dissolved in THF (0.4 ml). To the solution, *p*-toluenesulfonic acid monohydrate (110.1mg, 0.579mmol) was added. After stirring for 3 h, the reaction mixture was passed through florisil short column with ether. Removal of the solvent followed by bulb-to-bulb distillation (250-300 °C / 2.0 mmHg) afforded **8** (112.5 mg, 93%) **8**: ^{1}H NMR ($CDCl_3$) δ 1.05 (t, J = 7.6 Hz, 3H), 1.39 (s, 12H), 2.35 (q, J = 7.6 Hz, 2H), 3.82 (s, 3H), 6.91 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), ^{13}C NMR ($CDCl_3$) δ 13.6, 24.7, 25.5, 55.3, 84.8, 114.0, 119.2, 121.3, 129.3, 130.0, 159.7, ^{11}B NMR ($CDCl_3$) δ 30.1, IR (neat) 2208 cm^{-1}. HRMS calcd. for $C_{18}H_{24}BNO_3$ (M^+): 313.1849. Found: 313.1850. See below for the ^{1}H and ^{13}C NMR charts.

(c) Synthesis of (*Z*)-3-(4-Chlorophenyl)-2-(4-methoxyphenyl)pent-2-enenitrile by Suzuki-Miyaura coupling. To a solution of **8** (62.6 mg, 0.20 mmol) and *p*- chloroiodobenezene (71.5 mg, 0.30 mmol) in dioxane (0.3 ml) were successively added Cp(η^3-C_3H_5)Pd (4.3 mg, 0.020 mmol), tri(*t*-butyl)phosphine (8.1 mg, 0.040 mmol), potassium fluoride (38.3 mg, 0.66 mmol), and water (0.10 ml). The mixture was stirred at 60 °C for 20 h. After cooled to room temperature, water was added to the mixture, and organic materials were extracted with ether 4 times. The combined extract was dried over magnesium sulfate. After removal of the solvent, the crude material was purified by preparative TLC (Hexane / Ether = 5 / 1, two times) to give the coupling product **9** (51.7 mg, 87%).


STANDARD 1H OBSERVE
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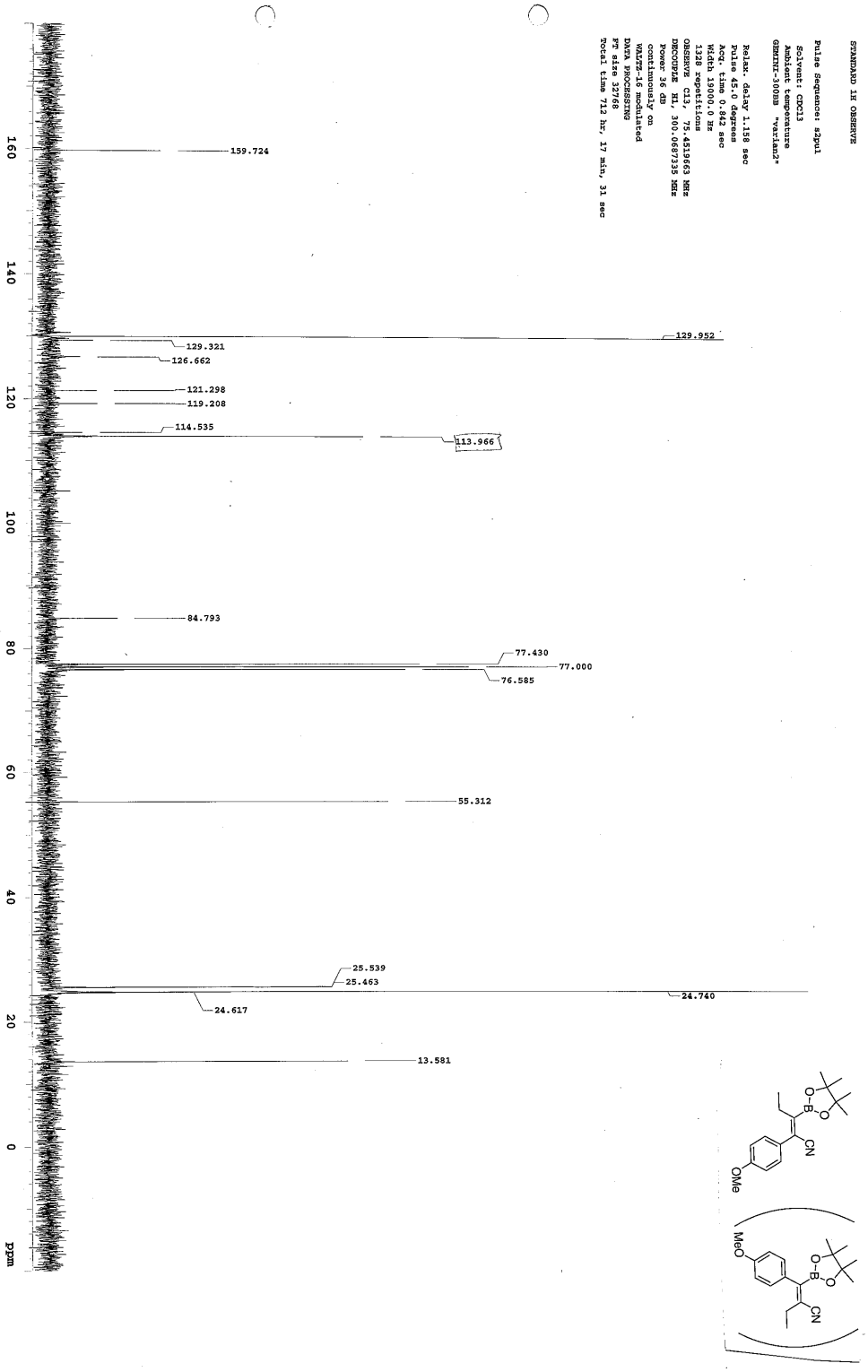
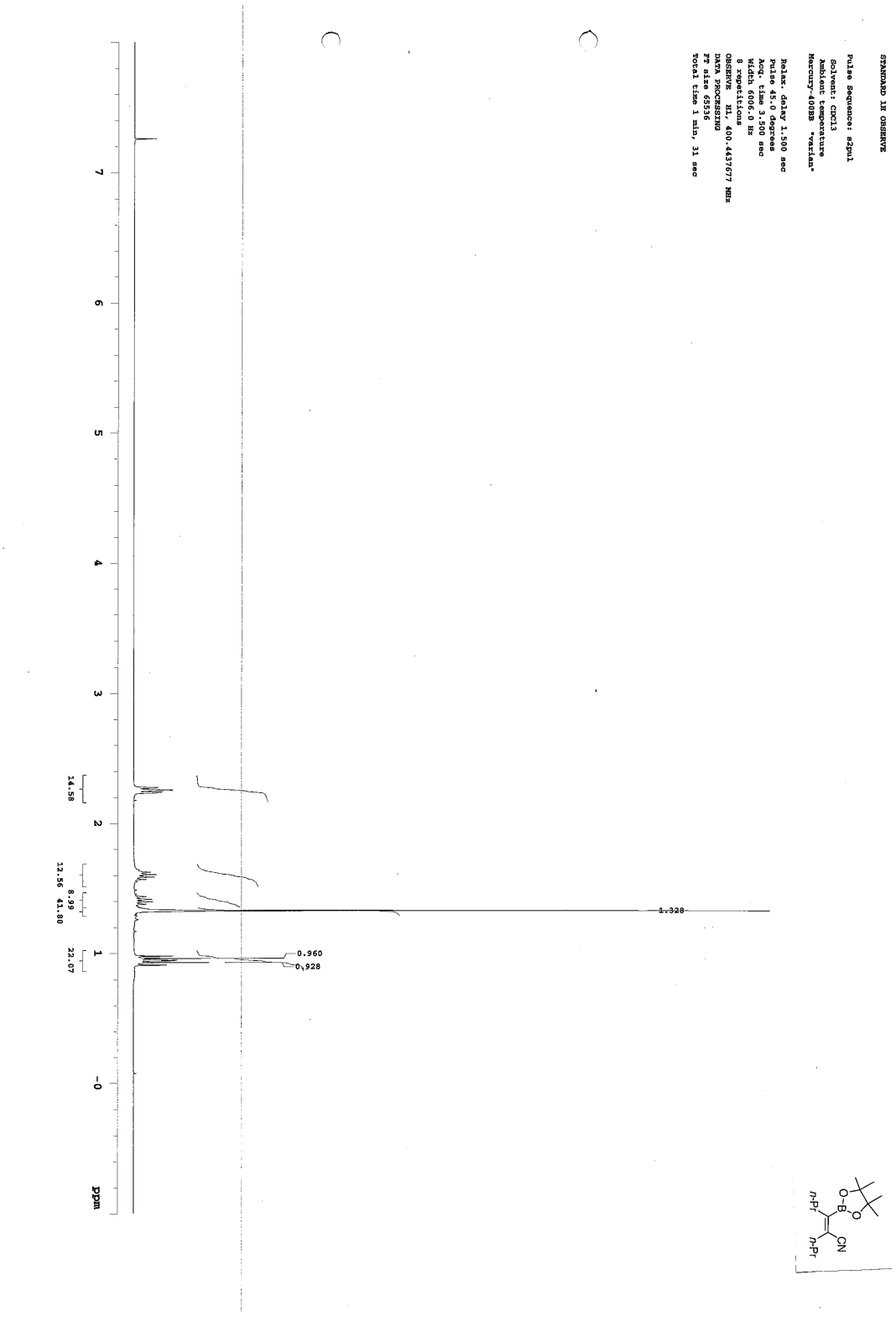
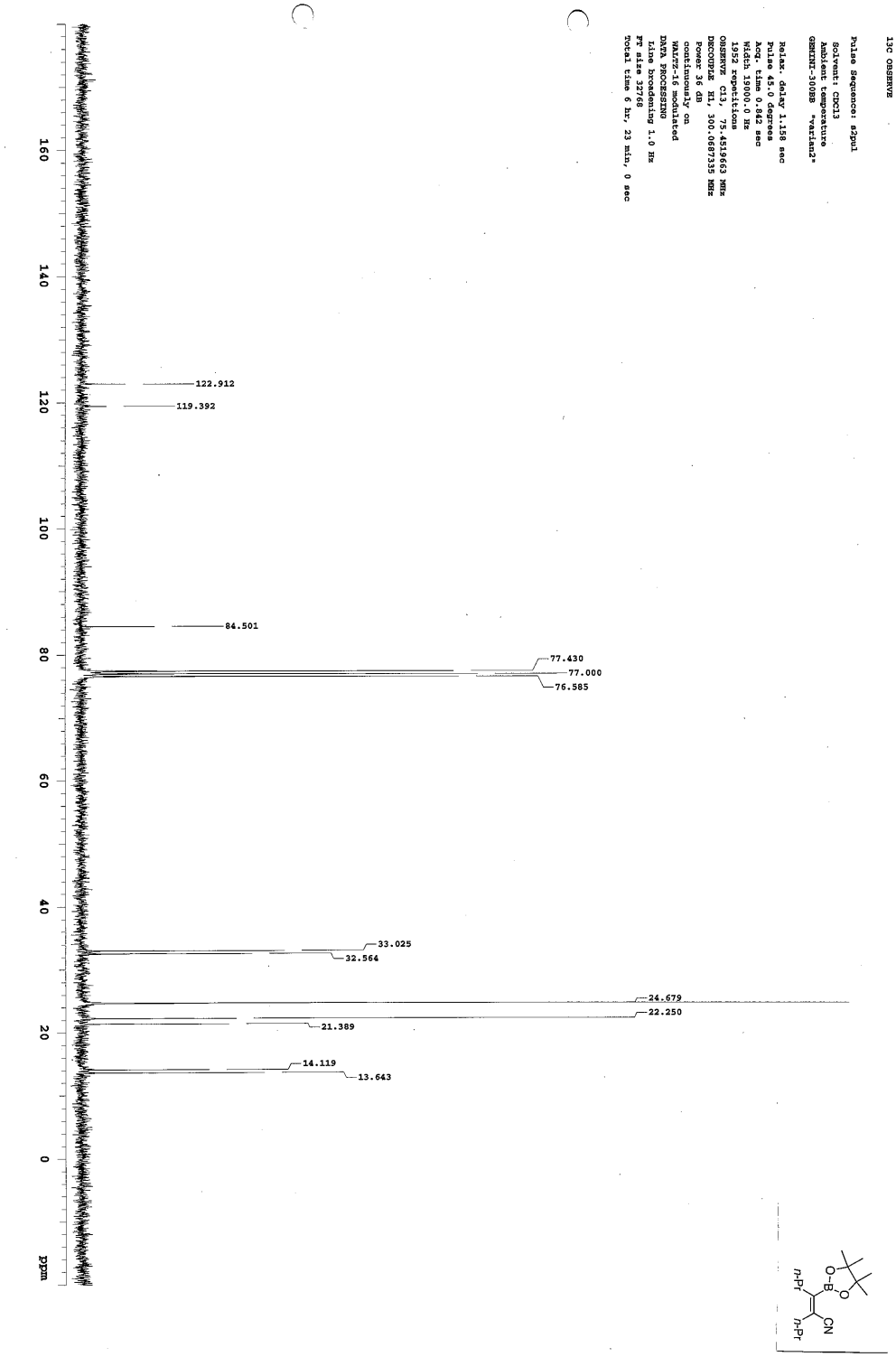
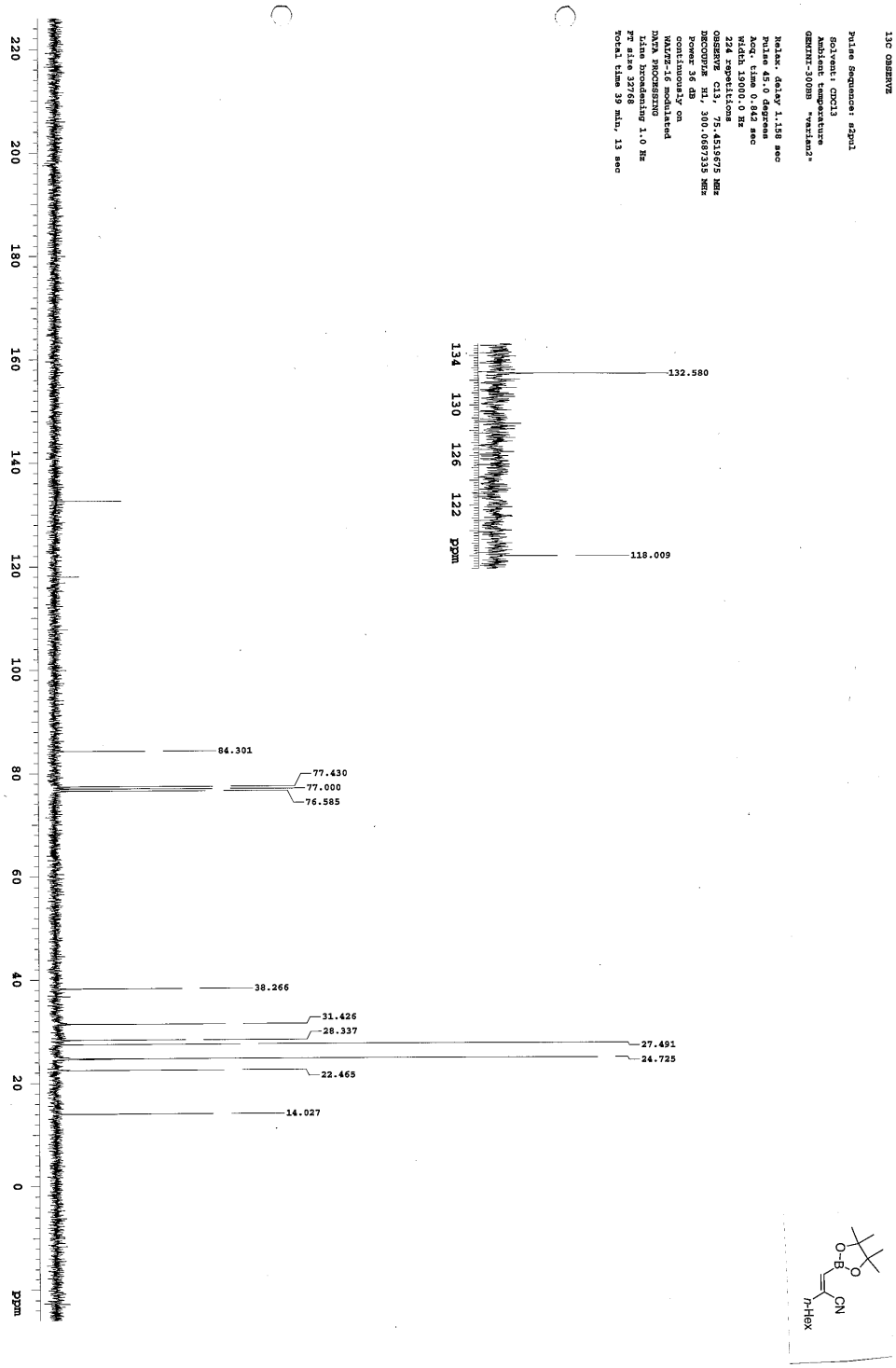
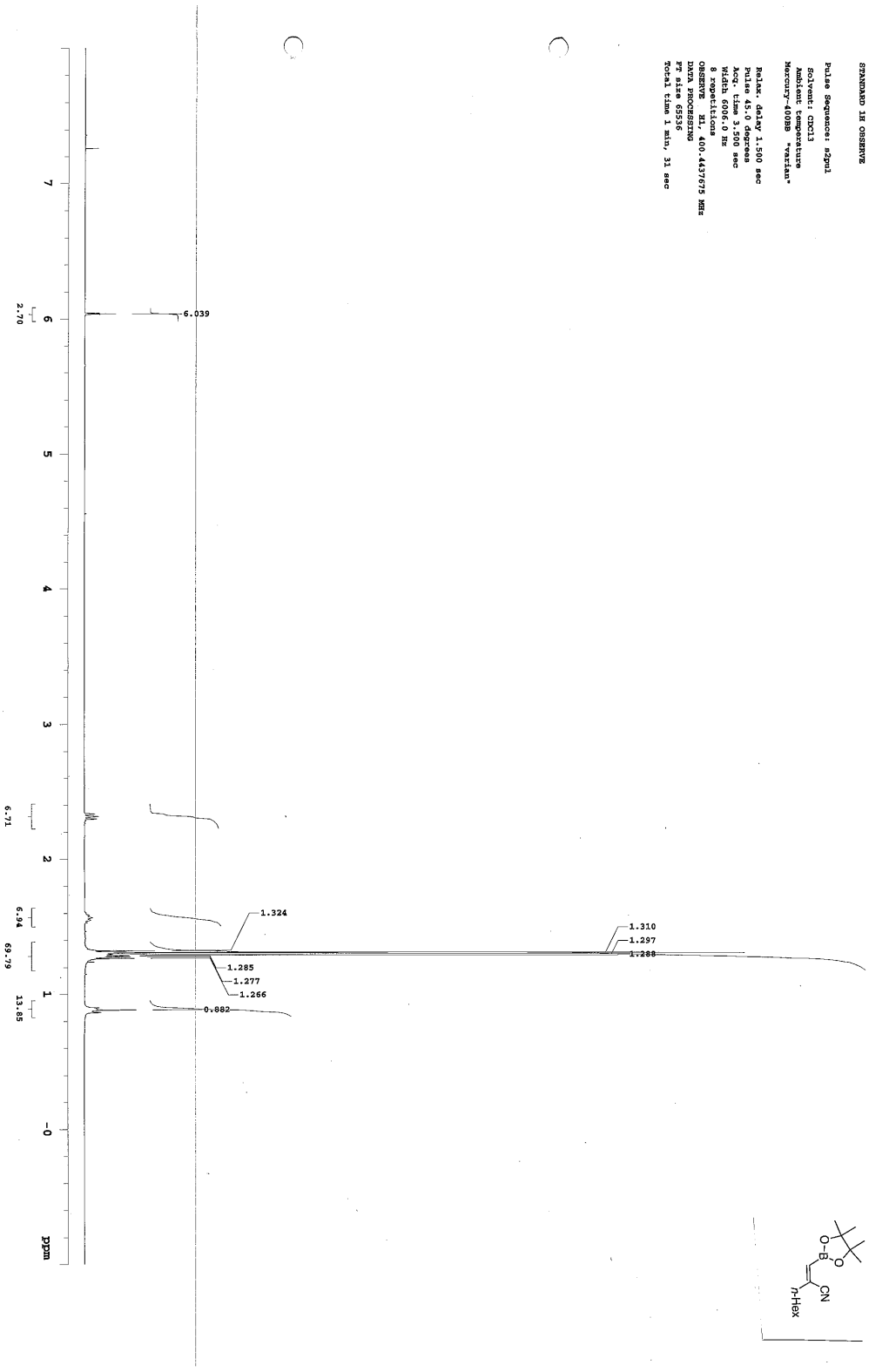
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.990 sec
Width 6006.0 Hz
16 repetitions
OBSERVE H1, 400.4437673 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec
7.251
7.231
7.229
6.918
6.896
3.826
3.822
2.361
2.342
1.387
1.385
1.335
1.332
1.066
1.047
1.028
8.35
9.13
13.21
8.45
3.05
44.97
11.73
ppm
O-B
O
CN
OMe
MeO

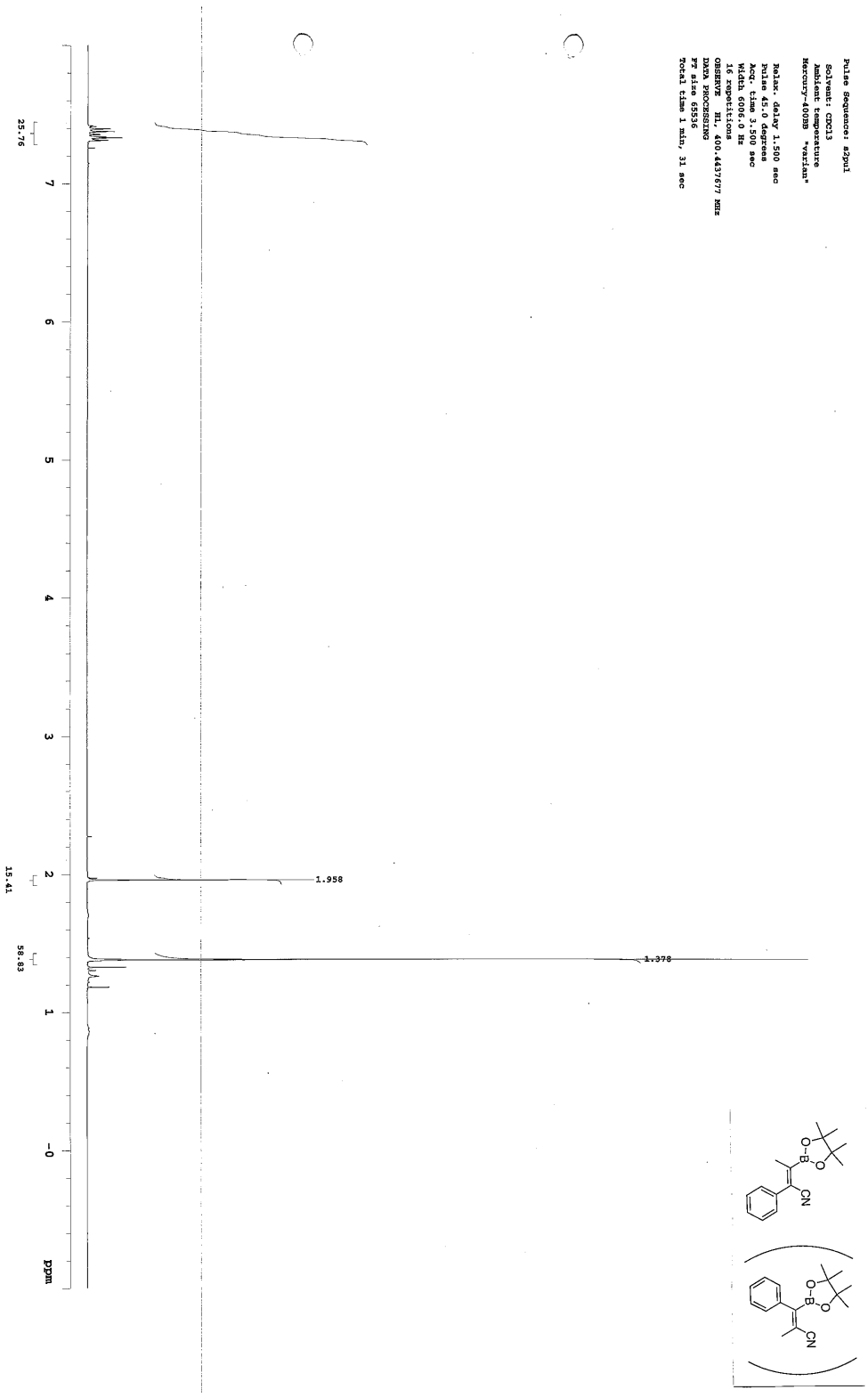

STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"
Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 19000.0 Hz
1228 repetitions
OBSERVE C13, 75.4519663 MHz
DECOUPLE H1, 300.0697335 MHz
Power 36 dB
continuously on
WALTZ16 modulated
DATA PROCESSING
FT size 32768
Total time 712 hr, 17 min, 31 sec
159.724
129.952
129.321
126.662
121.298
119.208
114.535
113.966
84.793
77.430
77.000
76.585
55.312
25.539
25.463
24.740
24.617
13.581
160
140
120
100
80
60
40
20
0
ppm
O-B
O
CN
OMe
MeO

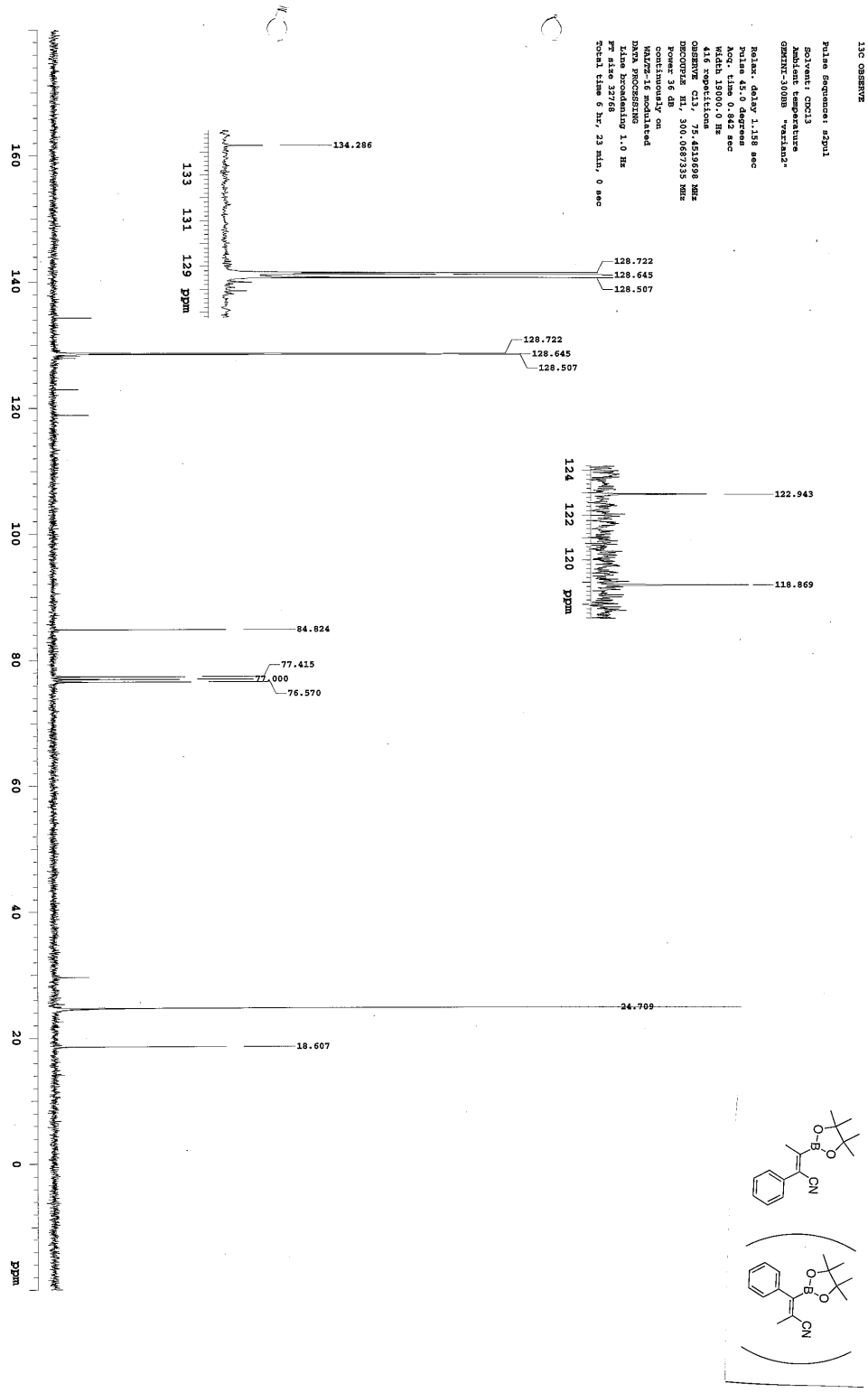

STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
8 repetitions
OBSERVE H1, 400.4437677 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec
1.328
0.960
0.928
14.58
12.56
8.99
41.80
22.07
ppm
O-B
O
CN
n-Pr
n-Pr


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"
Relax. delay 1.150 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 19000.0 Hz
1952 repetitions
OBSERVE C13, 75.4519663 MHz
DECOUPLE H1, 300.0687335 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 6 hr, 23 min, 0 sec
122.912
119.392
84.501
77.430
77.000
76.585
33.025
32.564
24.679
22.250
21.389
14.119
13.643
ppm
160
140
120
100
80
60
40
20
0
n-Pr
n-Pr
CN


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"
Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 19000.0 Hz
224 repetitions
OBSERVE C13, 75.4515675 MHz
DECOUPLE H1, 300.0687335 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 39 min, 13 sec
132.580
118.009
84.301
77.430
77.000
76.585
38.266
31.426
28.337
27.491
24.725
22.465
14.027
ppm
O-B
O
CN
n-Hex


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
8 repetitions
OBSERVE H1, 400.4437675 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec
6.039
1.324
1.310
1.297
1.288
1.285
1.277
1.256
0.882
2.70
6.71
6.94
69.79
13.85
ppm
CN
n-Hex


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
16 repetitions
OBSERVE H1, 400.4437677 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec
1.958
1.378
25.76
15.41
58.83
7
6
5
4
3
2
1
0
ppm
O
B
O
CN


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"
Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 19000.0 Hz
416 repetitions
OBSERVE C13, 75.4519698 MHz
DECOUPLE H1, 300.0687335 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 6 hr, 23 min, 0 sec
134.286
128.722
128.645
128.507
128.722
128.645
128.507
122.943
118.869
84.824
77.415
77.000
76.570
24.709
18.607
ppm
CN
CN