Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Catalyst-Free and Solvent-Free Hydroboration of Aldehydes

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Content

1. Experimental Section

General Information

The reagents used for experiments were purchased from Sigma-Aldrich Co. and ABCR GmbH & Co. KG. and used purified by distillation. The progress of reactions (the conversion of aldehyde) was monitored by GC chromatography using Bruker Scion 460-GC. The structures of products were determined by NMR spectroscopy. The spectra ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) were recorded on Bruker ASCEND 400 (400 MHz), Bruker ASCEND 600 (600 MHz) spectrometers using C_6D_6 and $CDCl_3$ as the solvents. In situ FT-IR measurements were conducted with a Mettler–Toledo ReactIR 15 equipped with a DS 6.3 mm AgX DiCompFiber Probe with a diamond sensor and a Hg–Cd telluride detector.

Synthetic procedures

General procedure for the synthesis of compounds (3a-3r)

Aldehyde (**1a-1r**, 1.0 mmol, 1.0 eq.) and pinacolborane (**2a**, 1.4 mmol, 1.4 eq.) were added to a 25 ml one-necked round-bottom flask equipped with a magnetic stir bar. The reaction mixture was stirred at 60°C (or at room temperature, according to the reaction conditions mentioned in Table 2) for definite time. The progress of reaction was monitored by GC chromatography. After the reaction was completed the excess of pinacolborane (**2a**) was evaporated under reduced pressure (10^{-2} Torr). Next, the potassium carbonate (0.15 mmol, 0.15 eq.) and 1 mL of CH_2Cl_2 were added and stirred with the crude product for 25 minutes. After that, the solution was filtrated (through Celite) to give the corresponding compounds **3a-3r**.

General procedure for the inter- and intramolecular competition experiments (Scheme 2)

Pinacolborane (**2a**, 1.4 mmol, 1.4 eq.) and the equimolar mixture of benzaldehyde (**1a**, 1.0 mmol, 1.0 eq.) with acetophenone (**4a**, 1.0 mmol, 1.0 eq.) were added to a 25 ml one-necked round-bottom flask equipped with a magnetic stirrer. The reaction mixture was stirred at room temperature for 3 hours. After the reaction was completed the excess of pinacolborane (**2a**) was evaporated under reduced pressure to give the mixture of products: the main product **3a** in 99% yield and the by-product **5a** in 1% yield.

Pinacolborane (**2a**, 1.4 mmol, 1.4 eq.) and 4-acetylbenzaldehyde (**1s**, 1.0 mmol, 1.0 eq.) were added to a 25 ml one-necked round-bottom flask equipped with a magnetic stirrer. The reaction mixture was stirred at room temperature for 1 hour. After the reaction was completed the excess of pinacolborane (**2a**) was evaporated under reduced pressure (10^{-2} Torr). Next, potassium carbonate (0.15 mmol, 0.15 eq.) and 1 mL of CH_2Cl_2 were added and stirred with the crude product for 25 minutes. After that, the solution was filtrated (through Celite) to give the product **3s** in 99% yield.

The hydrolysis of boronic ester 3a

4,4,5,5-tetramethyl-2-(benzyloxy)-1,3,2-dioxaborolane (**3a**, 0.3 g, 1.28 mmol) was passed through a silica plug using ethyl acetate/hexane (1:10, v/v) as eluent. A clear colorless solution was collected and excess solvents were removed via distillation. The benzyl alcohol was obtained as colorless liquid in 82% yield (**6a**, 0.113 g, 1.05 mmol).

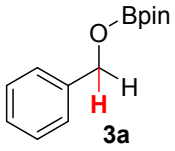
Gram-Scale Synthesis of 4,4,5,5-tetramethyl-2-(benzyloxy)-1,3,2-dioxaborolane

Benzaldehyde (**1a**, 1.0 g, 9.4 mmol, 1.0 eq.) and pinacolborane (**2a**, 1.80 g, 14.1 mmol, 1.4 eq.) were added to a 50 ml one-necked round-bottom flask equipped with a magnetic stir bar. The reaction mixture was stirred at 60°C for 30 minutes. The progress of reaction was monitored by GC chromatography. After the reaction was completed the excess of pinacolborane (**2a**) was evaporated under reduced pressure. Next, potassium carbonate (1.35 mmol, 0.15 eq.) and 5 mL of CH_2Cl_2 were added and stirred with the crude product for 25

minutes. After that, the solution was filtrated (through Celite) to give the corresponding 4,4,5,5-tetramethyl-2-(benzyloxy)-1,3,2-dioxaborolane (3a, 2.14 g, 9.15 mmol) in 97% yield.

2. Characterization data

4,4,5,5-tetramethyl-2-(benzyloxy)-1,3,2-dioxaborolane (**3a**)[1]



3a

4,4,5,5-tetramethyl-2-(benzyloxy)-1,3,2-dioxaborolane was obtained as colorless oil in 99% yield.

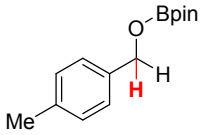
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.18 (s, 12H), 4.84 (s, 2H), 7.15-7.19 (m, 1H), 7.22-7.27 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.5, 66.6, 82.9, 126.6, 127.3, 128.2, 139.1.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.5.

EA: $C_{13}H_{19}BO_3$ (234.14): calcd.C 66.70; H 8.18; found C 66.76; H 8.07.

4,4,5,5-tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane (**3b**)[1]



3b

4,4,5,5-tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane was obtained as colorless oil in 97% yield.

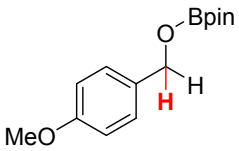
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.29 (s, 12H), 2.36 (s, 3H), 4.91 (s, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.27-7.30 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 21.3, 24.7, 66.7, 83.0, 127.0, 127.2, 129.1, 129.3, 136.4, 137.1.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.5.

EA: $C_{14}H_{21}BO_3$ (248.16): calcd.C 67.77; H 8.53; found C 67.66; H 8.47.

4,4,5,5-tetramethyl-2-((4-methoxybenzyl)oxy)-1,3,2-dioxaborolane (**3c**)[1]



3c

4,4,5,5-tetramethyl-2-((4-methoxybenzyl)oxy)-1,3,2-dioxaborolane was obtained as colorless oil in 99% yield.

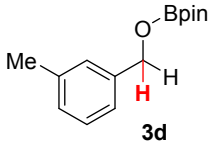
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.26 (s, 12H), 3.79 (s, 3H), 4.85 (s, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.6, 55.4, 66.6, 83.0, 113.8, 113.9, 128.6, 129.5, 131.6, 159.1.

^{11}B NMR (128 MHz $CDCl_3$) δ (ppm) = 22.3.

EA: $C_{14}H_{21}BO_4$ (264.15): calcd.C 63.66; H 8.01; found C 63.73; H 7.97.

4,4,5,5-tetramethyl-2-((3-methylbenzyl)oxy)-1,3,2-dioxaborolane (*novel product*) (**3d**)



3d

4,4,5,5-tetramethyl-2-((3-methylbenzyl)oxy)-1,3,2-dioxaborolane was obtained as colorless oil in 99% yield.

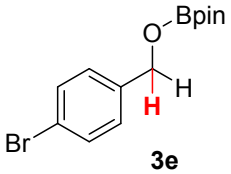
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.30 (s, 12H), 2.37 (s, 3H), 4.93 (s, 2H), 7.11 (d, *J* = 7.6 Hz, 1H) 7.17 (d, *J* = 7.7 Hz, 1H), 7.21-7.28 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 21.5, 24.7, 66.8, 83.1, 123.8, 127.5, 128.2, 128.3, 138.0, 139.2.

^{11}B NMR (128 MHz $CDCl_3$) δ (ppm) = 22.5.

EA: $C_{14}H_{21}BO_3$ (248.16): calcd.C 67.77; H 8.53; found C 67.69; H 8.58.

4,4,5,5-tetramethyl-2-((4-bromobenzyl)oxy)-1,3,2-dioxaborolane (**3e**)[1]



3e

4,4,5,5-tetramethyl-2-((4-bromobenzyl)oxy)-1,3,2-dioxaborolane was obtained as colorless oil in 98% yield.

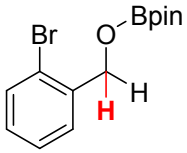
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.26 (s, 12H), 4.86 (s, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.7, 66.1, 83.2, 121.3, 128.5, 128.7, 131.5, 131.7, 138.3.

^{11}B NMR (128 MHz $CDCl_3$) δ (ppm) = 22.5.

EA: $C_{13}H_{18}BBrO_3$ (312.05): calcd.C 49.89; H 5.80; found C 50.03; H 5.88.

4,4,5,5-tetramethyl-2-((2-bromobenzyl)oxy)-1,3,2-dioxaborolane (**3f**)[2]



3f

4,4,5,5-tetramethyl-2-((2-bromobenzyl)oxy)-1,3,2-dioxaborolane was obtained as colorless oil in 90% yield.

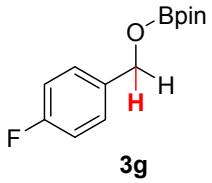
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.27 (s, 12H), 4.97 (s, 2H), 7.09-7.16 (m, 1H), 7.26-7.35 (m, 1H), 7.47-7.54 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.7, 66.4, 83.3, 121.6, 127.4, 127.9, 128.7, 132.3, 138.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.4.

EA: $C_{13}H_{18}BBrO_3$ (312.05): calcd.C 49.89; H 5.80; found C 50.00; H 5.91.

4,4,5,5-tetramethyl-2-((4-fluorobenzyl)oxy)-1,3,2-dioxaborolane (**3g**)[3]



3g

4,4,5,5-tetramethyl-2-((4-fluorobenzyl)oxy)-1,3,2-dioxaborolane was obtained as colorless oil in 97% yield.

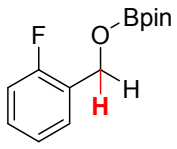
^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 1.25 (s, 12H), 4.87 (s, 2H), 6.97-7.03 (m, 2H), 7.27-7.35 (m, 2H).

^{13}C NMR (101 MHz, C_6D_6) δ (ppm) = 24.7, 66.2, 83.2, 115.2 (d, *J* = 21.4 Hz), 128.7 (d, *J* = 8.1 Hz), 135.1 (d, *J* = 3.1 Hz), 162.3 (d, *J* = 245.2 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.4.

EA: $C_{13}H_{18}BFO_3$ (252.13): calcd.C 61.94; H 7.20; found C 61.88; H 7.18.

4,4,5,5-tetramethyl-2-((2-fluorobenzyl)oxy)-1,3,2-dioxaborolane (**3h**)[4]



3h

4,4,5,5-tetramethyl-2-((2-fluorobenzyl)oxy)-1,3,2-dioxaborolane was obtained as colorless oil in 83% yield.

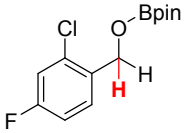
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.27 (s, 12H), 5.00 (s, 2H), 6.97-7.05 (m, 1H), 7.07-7.16 (m, 1H), 7.19-7.27 (m, 1H), 7.41-7.48 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.7, 60.9, 83.2, 115.9 (d, *J* = 21.1 Hz), 124.1 (d, *J* = 3.6 Hz), 126.5 (d, *J* = 14.4 Hz), 128.9 (d, *J* = 4.3 Hz), 129.1 (d, *J* = 8.1 Hz), 160.3 (d, *J* = 246.6 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.5.

EA: $C_{13}H_{18}BFO_3$ (252.13): calcd.C 61.94; H 7.20; found C 62.05; H 7.27.

4,4,5,5-tetramethyl-2-((2-chloro-4-fluorobenzyl)oxy)-1,3,2-dioxaborolane (*novel product*) (**3i**)



3i

4,4,5,5-tetramethyl-2-((2-chloro-4-fluorobenzyl)oxy)-1,3,2-dioxaborolane was obtained as oil in 97% yield.

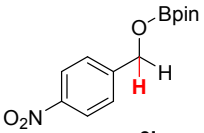
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.27 (s, 12H), 5.08 (s, 2H), 6.89-7.06 (m, 1H), 7.11-7.25 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.7, 58.0, 83.2, 114.2 (d, *J* = 22.8 Hz), 124.5 (d, *J* = 17.7 Hz), 130.2 (d, *J* = 9.6 Hz), 136.2 (d, *J* = 5.4 Hz), 162.0 (d, *J* = 251.3 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.3.

EA: $C_{13}H_{17}BClFO_3$ (286.09): calcd.C 54.49; H 5.98; found C 54.47; H 6.07.

4,4,5,5-tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (**3j**)[1]



3j

4,4,5,5-tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane was obtained as a yellow solid in 99% yield. Melting point: 62-64°C.

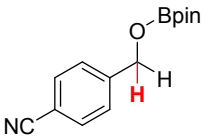
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.24 (s, 12H), 5.00 (s, 2H), 7.47 (d, *J* = 8.9 Hz, 2H), 8.17 (d, *J* = 8.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.6, 65.5, 83.4, 123.5, 126.8, 146.5, 147.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.5.

EA: $C_{13}H_{18}BNO_5$ (279.13): calcd.C 55.95; H 6.50; found C 54.87; H 6.59.

4,4,5,5-tetramethyl-2-((4-cyanobenzyl)oxy)-1,3,2-dioxaborolane (**3k**)[1]



3k

4,4,5,5-tetramethyl-2-((4-cyanobenzyl)oxy)-1,3,2-dioxaborolane was obtained as a white solid in 94% yield. Melting point: 93-95°C (in accordance with the literature[5]).

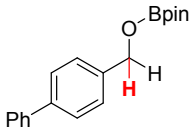
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.24 (s, 12H), 4.95 (s, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.6, 65.7, 83.3, 111.1, 118.8, 126.8, 132.1, 144.6.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.5.

EA: $C_{14}H_{18}BNO_3$ (259.14): calcd.C 64.90; H 7.00; found C 64.96; H 7.10.

4,4,5,5-tetramethyl-2-((4-phenylbenzyl)oxy)-1,3,2-dioxaborolane (**3l**)[6]



3l

4,4,5,5-tetramethyl-2-((4-phenylbenzyl)oxy)-1,3,2-dioxaborolane was obtained as oil in 97% yield.

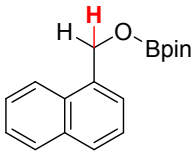
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.29 (s, 12H), 4.99 (s, 2H), 7.32-7.38 (m, 1H), 7.40-7.49 (m, 4H), 7.55-7.64 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.8, 66.6, 83.1, 127.2, 127.2, 127.3, 127.3, 128.8, 138.4, 140.4, 141.1.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.4.

EA: $C_{19}H_{23}BO_3$ (310.17): calcd.C 73.57; H 7.47; found C 73.66; H 7.50.

4,4,5,5-tetramethyl-2-((1-naphthylmethoxy)-1,3,2-dioxaborolane (**3m**)[1]



3m

4,4,5,5-tetramethyl-2-((1-naphthylmethoxy)-1,3,2-dioxaborolane was obtained as oil in 99% yield.

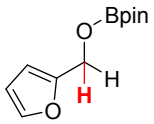
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.29 (s, 12H), 5.42 (s, 2H), 7.42-7.55 (m, 3H), 7.59 (dd, *J* = 7.1 Hz, 1.2 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.84-7.89 (m, 1H), 8.01-8.08 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.8, 65.1, 83.2, 123.6, 125.0, 125.5, 125.8, 126.2, 128.3, 128.7, 131.1, 133.7, 134.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.7.

EA: $C_{17}H_{21}BO_3$ (284.16): calcd.C 71.86; H 7.45; found C 71.79; H 7.39.

4,4,5,5-tetramethyl-2-(furan-2-ylmethoxy)-1,3,2-dioxaborolane (**3n**)[3]



3n

4,4,5,5-tetramethyl-2-(furan-2-ylmethoxy)-1,3,2-dioxaborolanewas obtained as yellow oil in 76% yield.

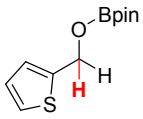
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.25 (s, 12H), 4.81 (s, 2H), 6.21-6.36 (m, 2H), 7.32-7.40 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.7, 59.3, 83.2, 108.4, 110.4, 142.6, 152.6.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.3.

EA: $C_{11}H_{17}BO_4$ (224.12): calcd.C 58.97; H 7.65; found C 59.08; H 7.59.

4,4,5,5-tetramethyl-2-(thiophen-2-ylmethoxy)-1,3,2-dioxaborolane (**3o**)[1]



3o

4,4,5,5-tetramethyl-2-(thiophen-2-ylmethoxy)-1,3,2-dioxaborolane was obtained as oil in 70% yield.

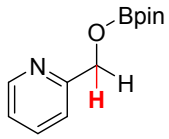
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.29 (s, 12H), 5.07 (s, 2H), 6.94-7.01 (m, 1H), 7.01-7.07 (m, 1H), 7.24-7.31 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.7, 61.7, 83.2, 125.6, 126.0, 126.7, 142.1.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.5.

EA: $C_{11}H_{17}BO_3S$ (240.10): calcd.C 55.02; H 7.14; found C 54.98; H 7.10.

4,4,5,5-tetramethyl-2-(pyridine-2ylmethoxy)-1,3,2-dioxaborolane (**3p**)[7]



3p

4,4,5,5-tetramethyl-2-(pyridine-2ylmethoxy)-1,3,2-dioxaborolane was obtained as yellow oil in 99% yield.

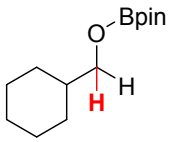
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.25 (s, 12H), 5.04 (s, 2H), 7.34-7.50 (m, 2H), 7.88 (t, *J* = 7.7 Hz, 1H), 8.54 (t, *J* = 4.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 25.4, 66.3, 81.0, 120.2, 123.5, 139.9, 143.4, 159.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 15.1.

EA: $C_{12}H_{18}BNO_3$ (235.14): calcd.C 61.31; H 7.72; found C 61.42; H 7.81.

4,4,5,5-tetramethyl-2-(cyclohexylmethoxy)-1,3,2-dioxaborolane (**3q**)[1]



3q

4,4,5,5-tetramethyl-2-(cyclohexylmethoxy)-1,3,2-dioxaborolane was obtained as colorless oil in 99% yield.

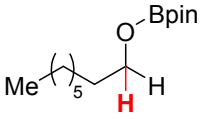
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 0.84-1.00 (m, 2H), 1.05-1.23 (m, 3H), 1.24 (s, 12H), 1.43-1.57 (m, 1H), 1.63-1.76 (m, 5H), 3.63 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.7, 25.9, 26.7, 29.5, 39.4, 70.5, 82.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.1.

EA: $C_{13}H_{25}BO_3$ (240.20): calcd.C 65.02; H 10.49; found C 64.89; H 10.41.

4,4,5,5-tetramethyl-2-(octoxy)-1,3,2-dioxaborolane (*novel product*) (**3r**)



3r

4,4,5,5-tetramethyl-2-(octoxy)-1,3,2-dioxaborolane was obtained as colorless oil in 98 % yield.

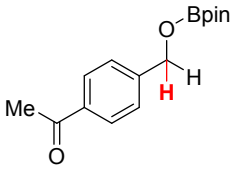
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.83-0.89 (m, 3H), 1.24 (s, 12H), 1.26 (s, 10H), 1.52-1.59 (m, 2H), 3.82 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 14.1, 22.6, 24.6, 25.6, 29.3, 31.5, 31.8, 65.0, 82.6.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.4.

EA: $C_{14}H_{29}BO_3$ (256.22): calcd.C 65.64; H 11.41; found C 65.70; H 11.49.

4,4,5,5-tetramethyl-2-((4-acetylbenzyl)oxy)-1,3,2-dioxaborolane (**3s**)[8]



3s

4,4,5,5-tetramethyl-2-((4-acetylbenzyl)oxy)-1,3,2-dioxaborolane was obtained as colorless oil in 99% yield.

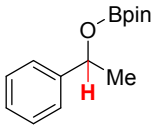
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.26 (s, 12H), 2.59 (s, 3H), 4.98 (s, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.92 (d, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.7, 26.7, 66.2, 83.3, 126.5, 128.6, 136.3, 144.7, 198.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 22.4.

EA: $C_{15}H_{21}BO_4$ (256.22): calcd.C 65.24; H 7.67; found C 65.33; H 7.64.

4,4,5,5-tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (**5a**)[1]



5a

4,4,5,5-tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane was obtained as colorless oil in 35% yield.

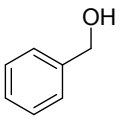
^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 0.97-1.04 (m, 12H), 1.40-1.48 (m, 3H), 5.39 (s, 1H), 7.00-7.07 (m, 1H), 7.10-7.17 (m, 2H), 7.31-7.38 (m, 2H).

^{13}C NMR (101 MHz, C_6D_6) δ (ppm) = 24.3, 25.4, 72.6, 82.2, 125.3, 127.0, 128.2, 145.0.

^{11}B NMR (128 MHz, C_6D_6) δ (ppm) = 22.6.

EA: $C_{14}H_{21}BO_3$ (248.16): calcd.C 67.77; H 8.53; found C 67.83; H 8.64.

Phenylmethanol (**6a**)



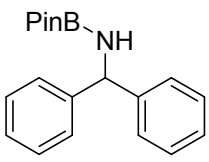
6a

Phenylmethanol (**6a**) was obtained as colorless oil in 82% yield.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 2.11 (s, 1H), 4.32 (s, 2H), 7.03-7.20 (m, 5H).

^{13}C NMR (101 MHz, C_6D_6) δ (ppm) = 64.6, 126.7, 127.1, 128.2, 141.4.

N-benzhydryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**7a**)



7a

N-benzhydryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine was obtained as white solid in 93% yield. Melting point: 73-75^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.27 (s, 12H), 2.93 (s, 1H), 5.23 (s, 2H), 7.17-7.34 (m, 7H), 7.35-7.44 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.7, 59.8, 83.2, 127.1, 127.2, 127.3, 127.7, 128.4, 128.4, 128.6, 128.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 21.2.

EA: $C_{19}H_{24}BNO_2$ (309.19): calcd.C 73.80; H 7.82; found C 73.73; H 7.79.

4. FT-IR measurements and kinetic analysis

Influence of borane concentration for the rate of benzaldehyde conversion: The reactions between benzaldehyde (1.0 eq.) and pinacolborane (1.0, 1.5 and 3.0 eq.) were monitored using a real-time FT-IR spectroscopy. The kinetic plots obtained for the hydroboration of benzaldehyde (at rt) confirmed a disappearance of the distinguishing band of the carbonyl group (Fig. 1-4).

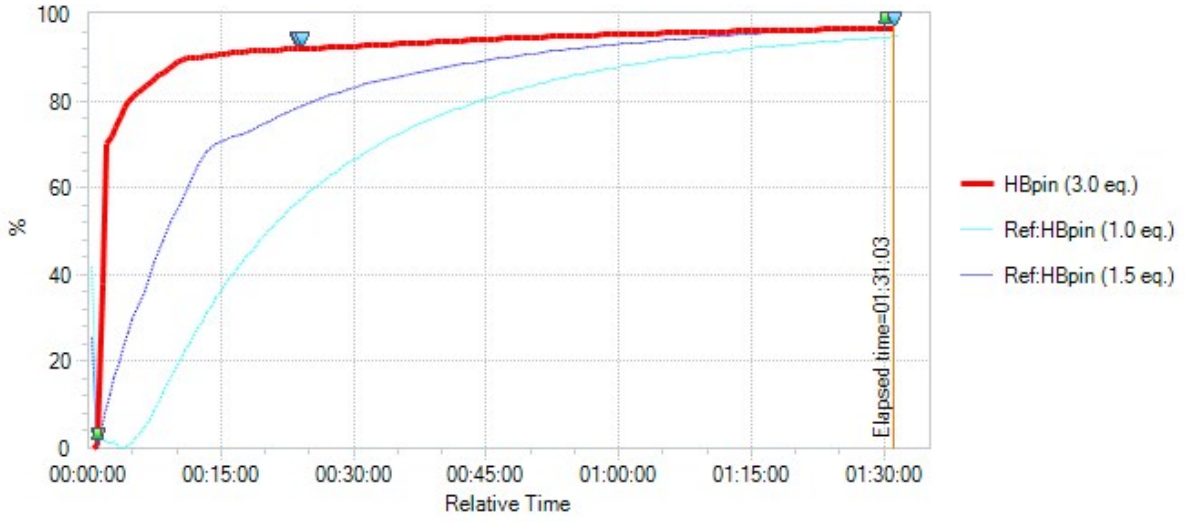


Fig. 1. Plot of the conversion of aldehyde (%) against time (h) for varying concentration of HBpin.

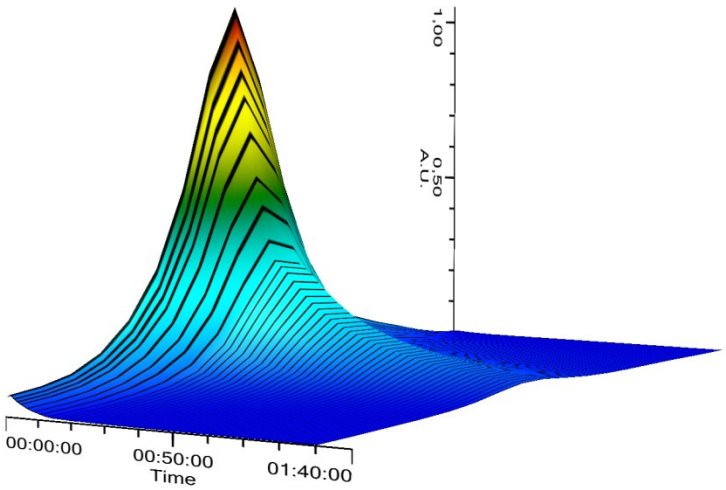


Fig. 2. Illustration of C=O band disappearance recorded in real time FT-IR during the hydroboration of benzaldehyde (1.0 eq.) with pinacolborane (1.0 eq.).

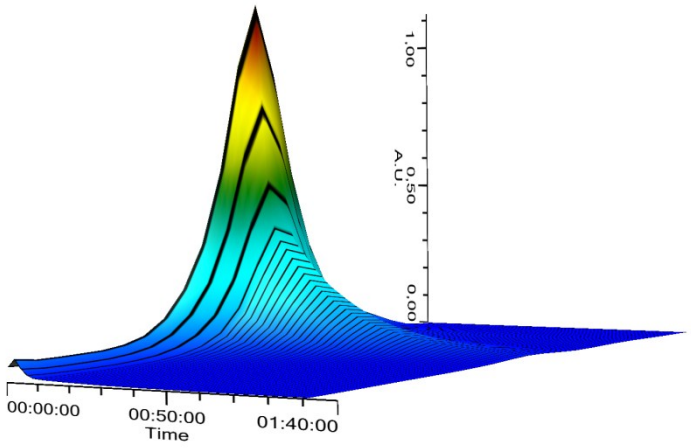


Fig. 3. Illustration of C=O band disappearance recorded in real time FT-IR during the hydroboration of benzaldehyde (1.0 eq.) with pinacolborane (1.5 eq.).

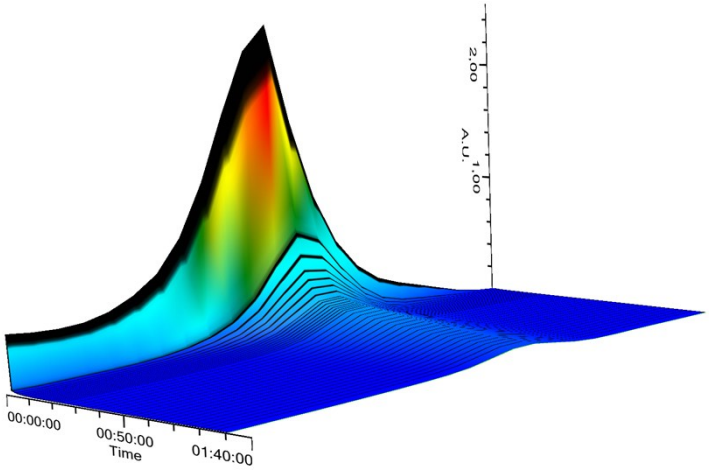
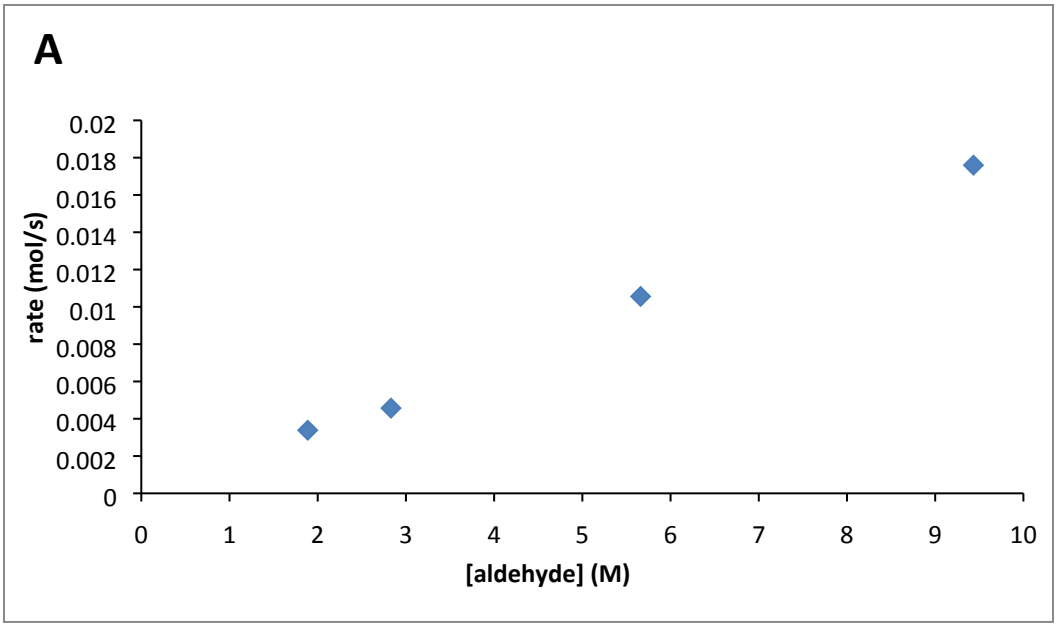


Fig. 4. Illustration of C=O band disappearance recorded in real time FT-IR during the hydroboration of benzaldehyde (1.0 eq.) with pinacolborane (3.0 eq.).

Kinetic Analysis: Kinetic analysis was carried out using a real-time FT-IR spectroscopy by collecting conversion data early in the reaction. The product concentration was measured from the area of carbonyl peak in first 60 seconds to get the most appropriate data. Orders for each reactant (pinacolborane and benzaldehyde) were determined from the rates (according to Equation 1) at varying concentrations of both reactants (we used following molar ratios: 1:1, 1.5:1, 3:1 and 5:1, in case of both substrates).These results were then plotted (Fig. 5 and 6) as rate vs. [borane (B)/aldehyde (A)], as well as ln(rate) vs. ln[borane (B1)/aldehyde (A1)]. Therefore, the order and the slope (α) of the plot (ln(rate) vs. ln[borane/aldehyde]) are equal ($R^2 > 0.98$).

$$rate = \frac{[p]}{t}; \quad \textit{where } t \textit{ is time, } [p] \textit{is the concentration of product at time } t; \quad (\textit{Equation } 1)$$



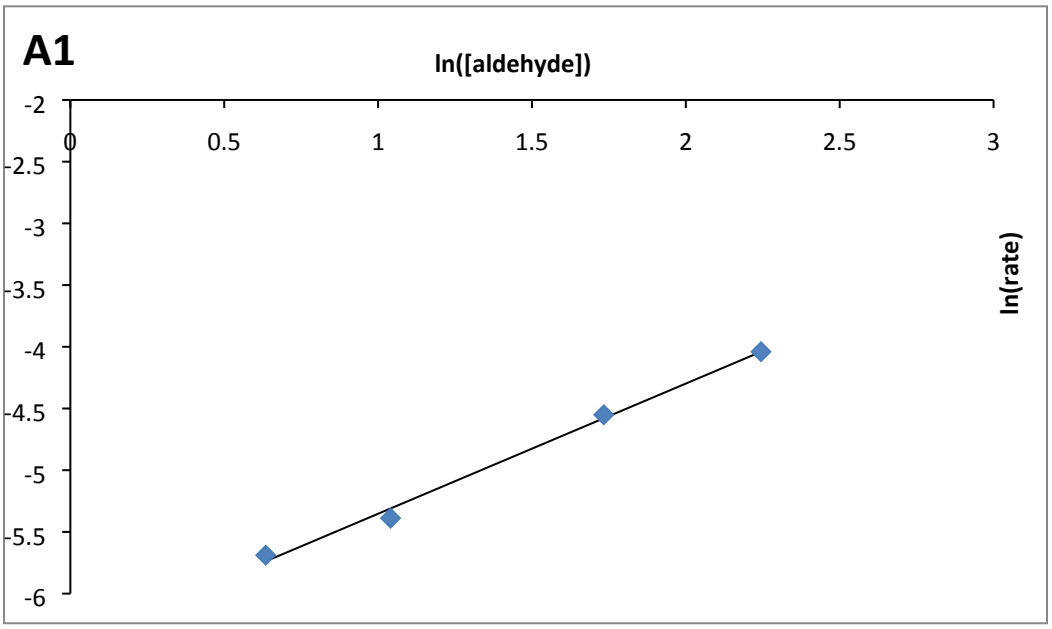


Fig. 5. (A) Plot of aldehyde concentration vs. rate (mol/s); (A1) Plot of ln([aldehyde]) vs. ln(rate).

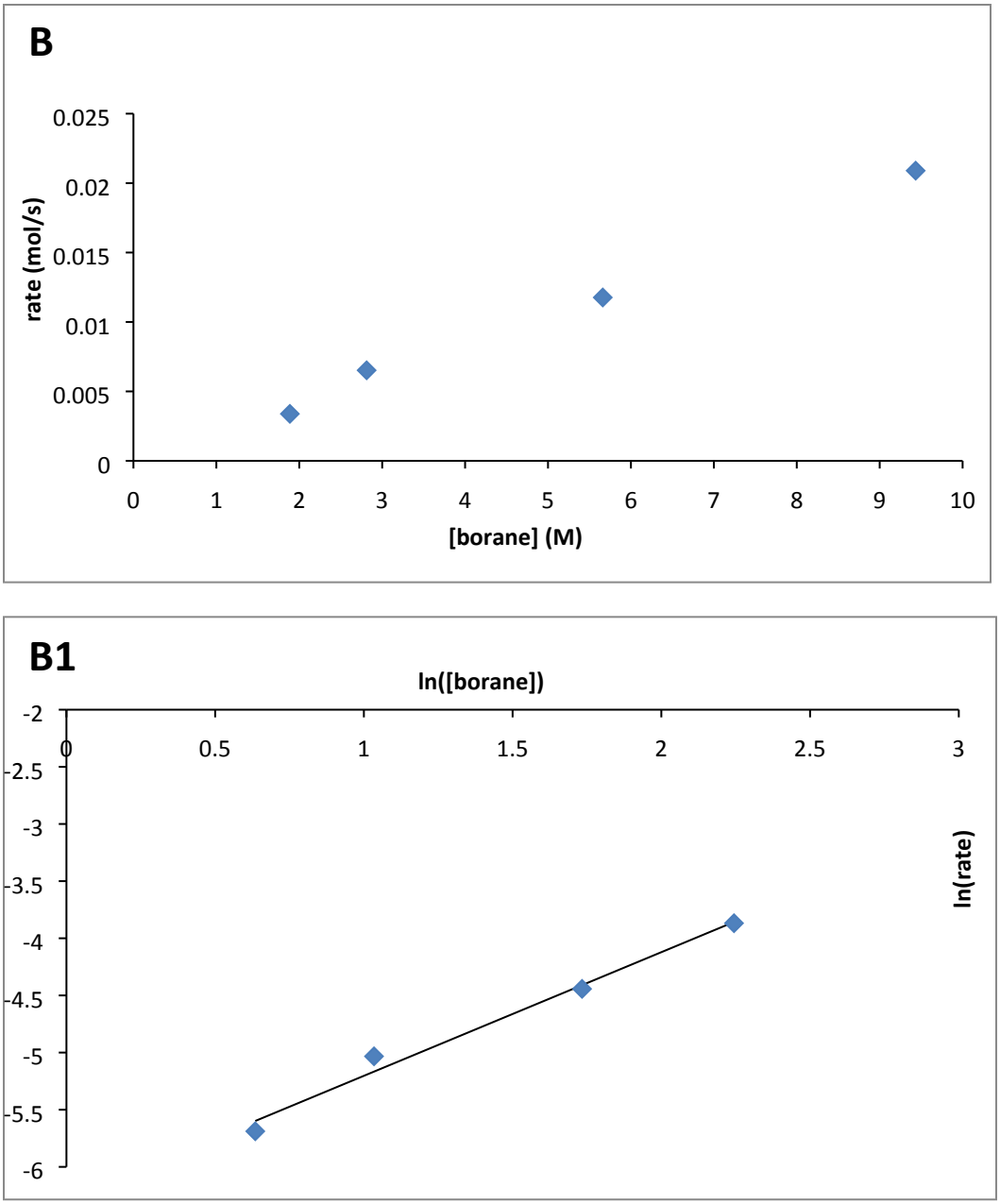
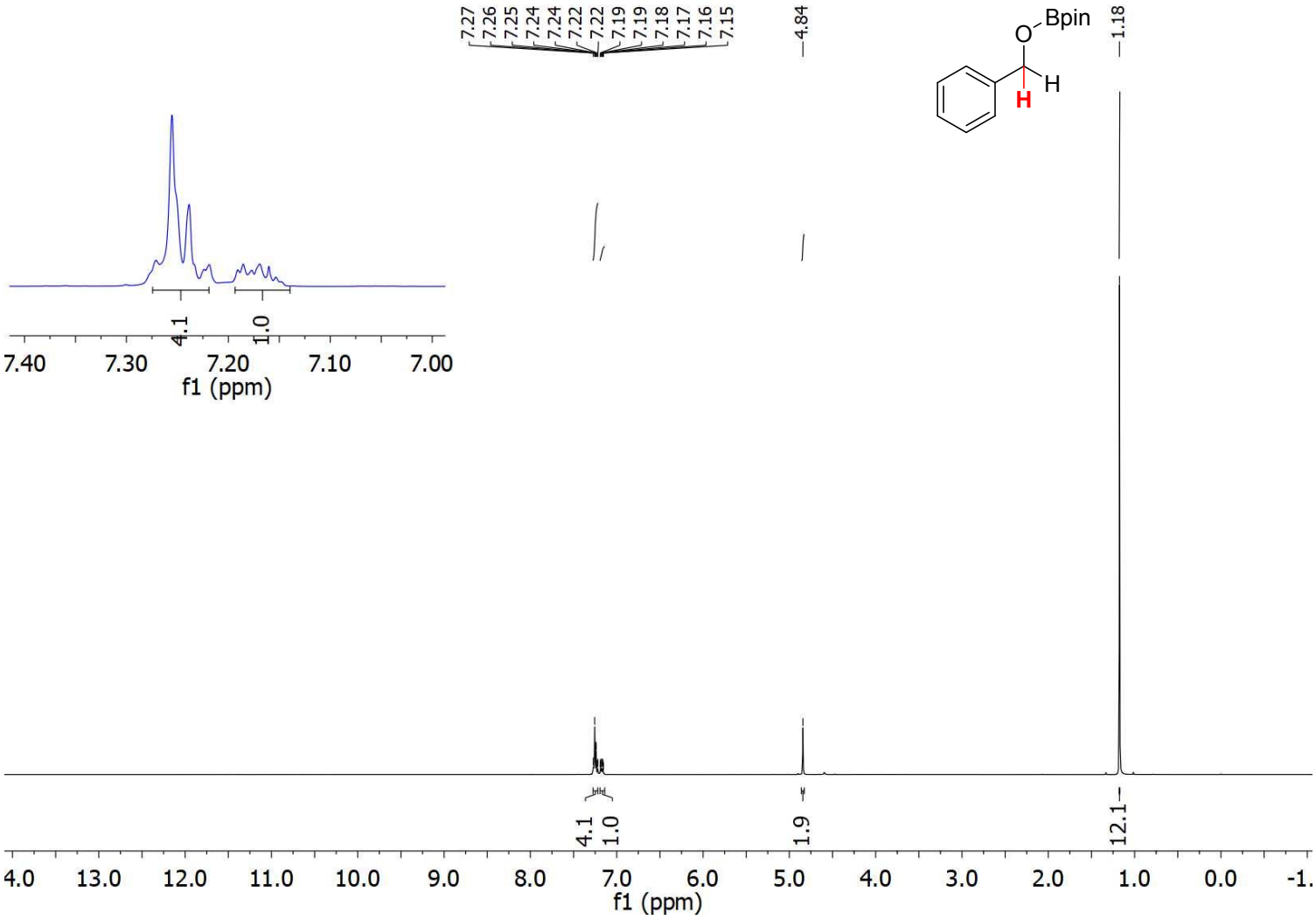


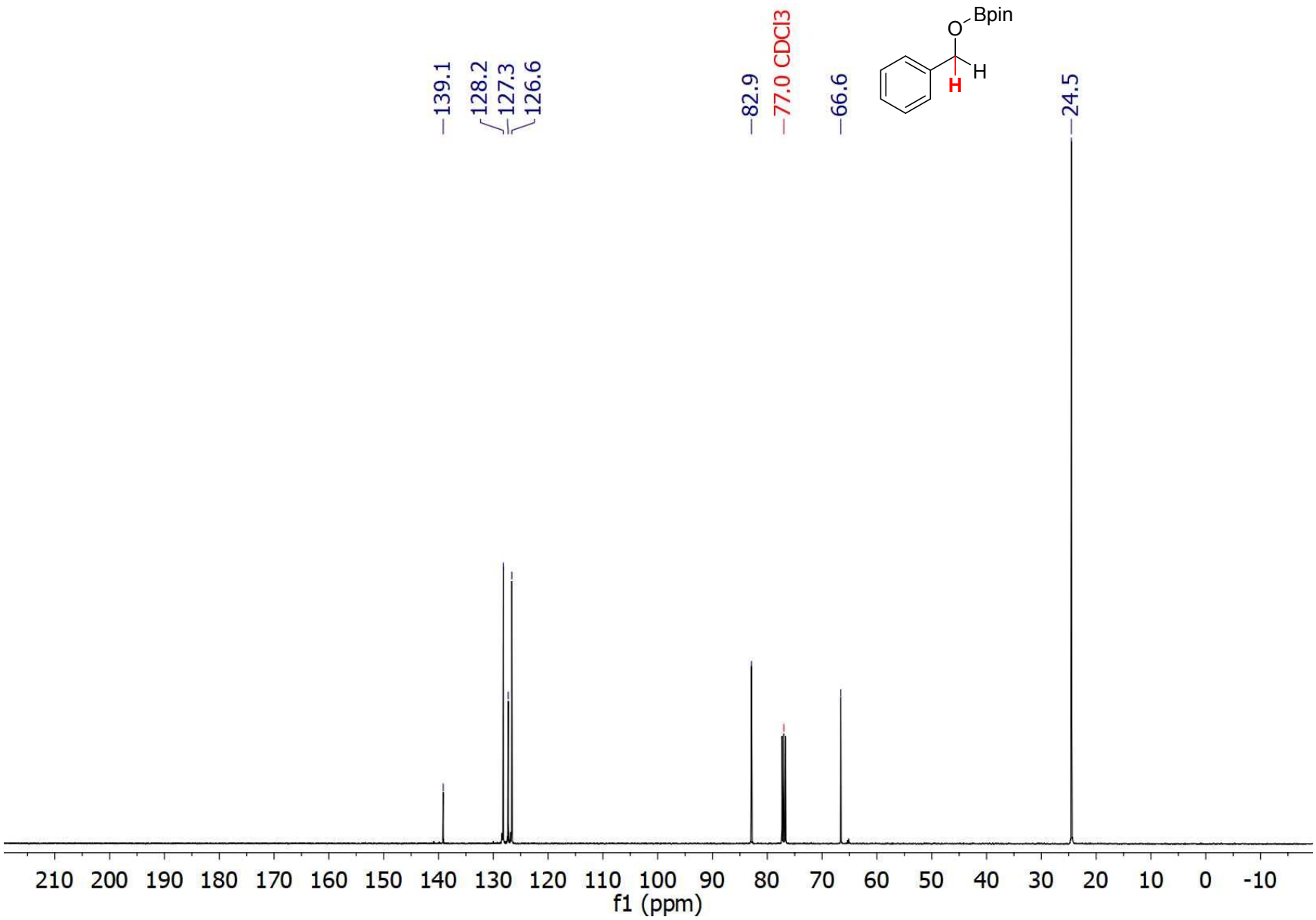
Fig. 6. (B) Plot of borane concentration vs. rate (mol/s); (B1) Plot of ln([borane]) vs. ln(rate).

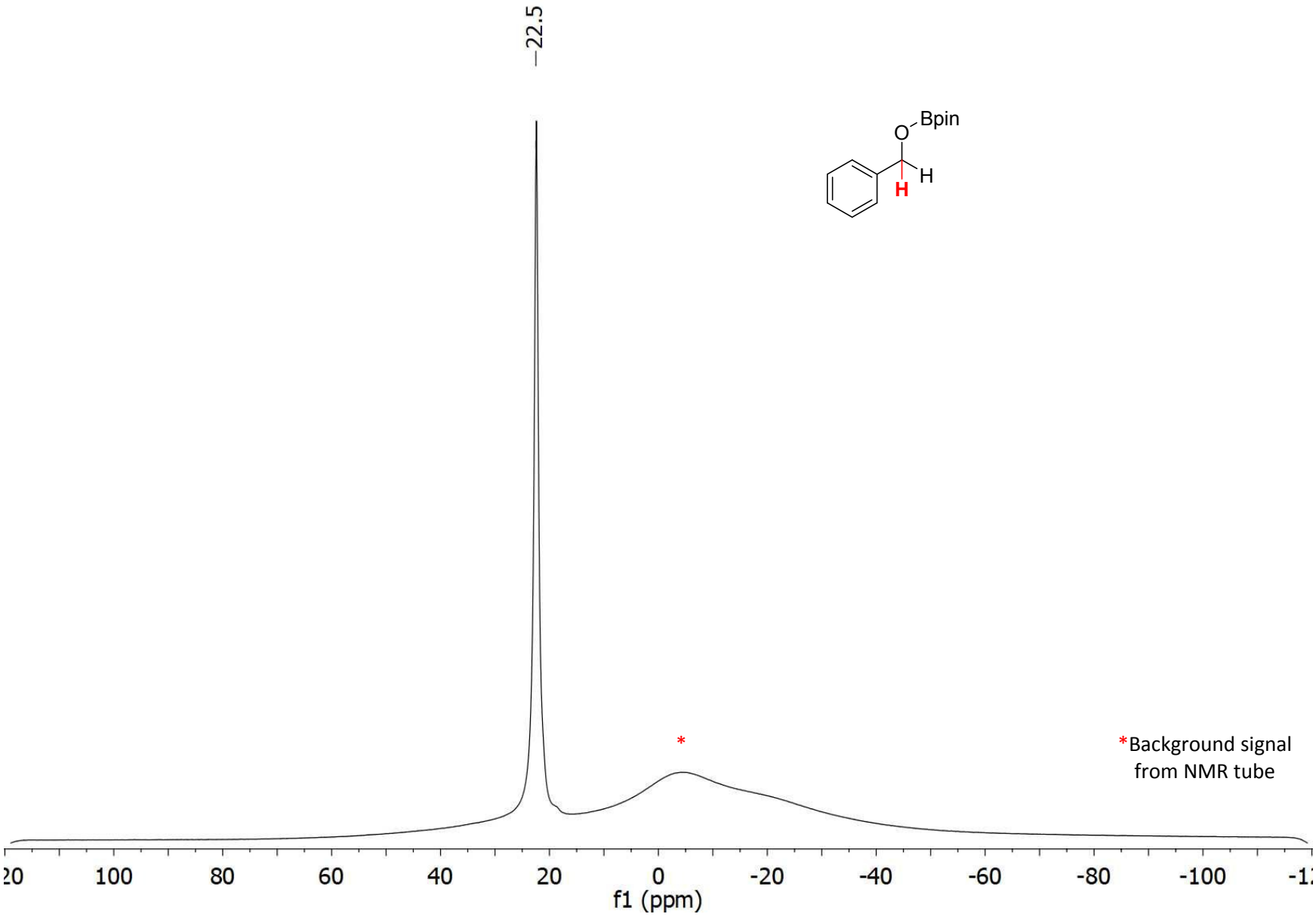
Under the reaction conditions, the rate is found to be first-order in [aldehyde] and [HBpin]. Based on these results and due to fact that borane's adducts with nucleophiles weaken the B-H bond, what facilitate and accelerate further reduction of C=O moiety,[1] the hydroboration is proposed to occur intramolecularly.

4. Copies of ^{1}H, ^{11}B and ^{13}C NMR spectra

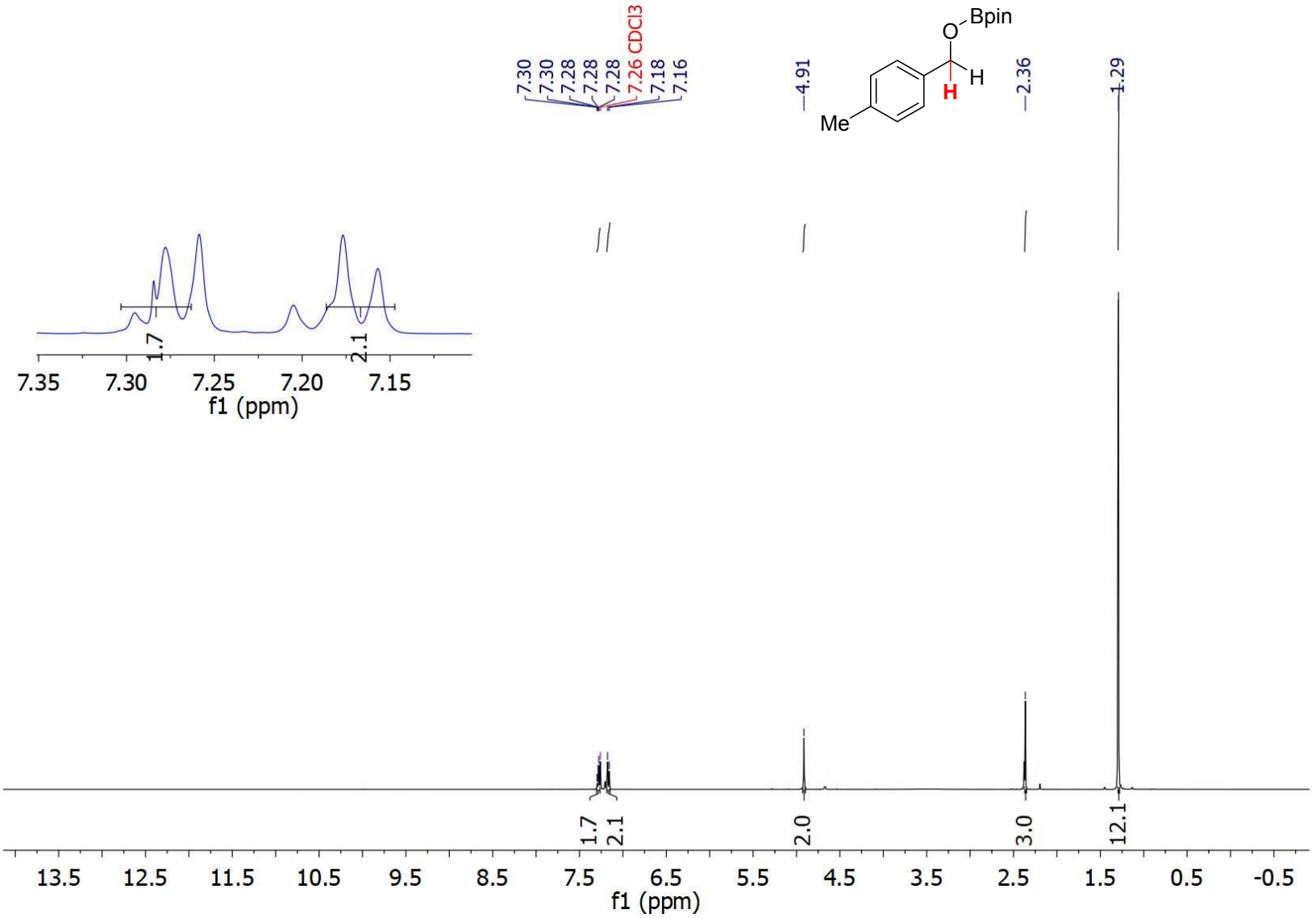
4,4,5,5-tetramethyl-2-(benzyloxy)-1,3,2-dioxaborolane (**3a**)

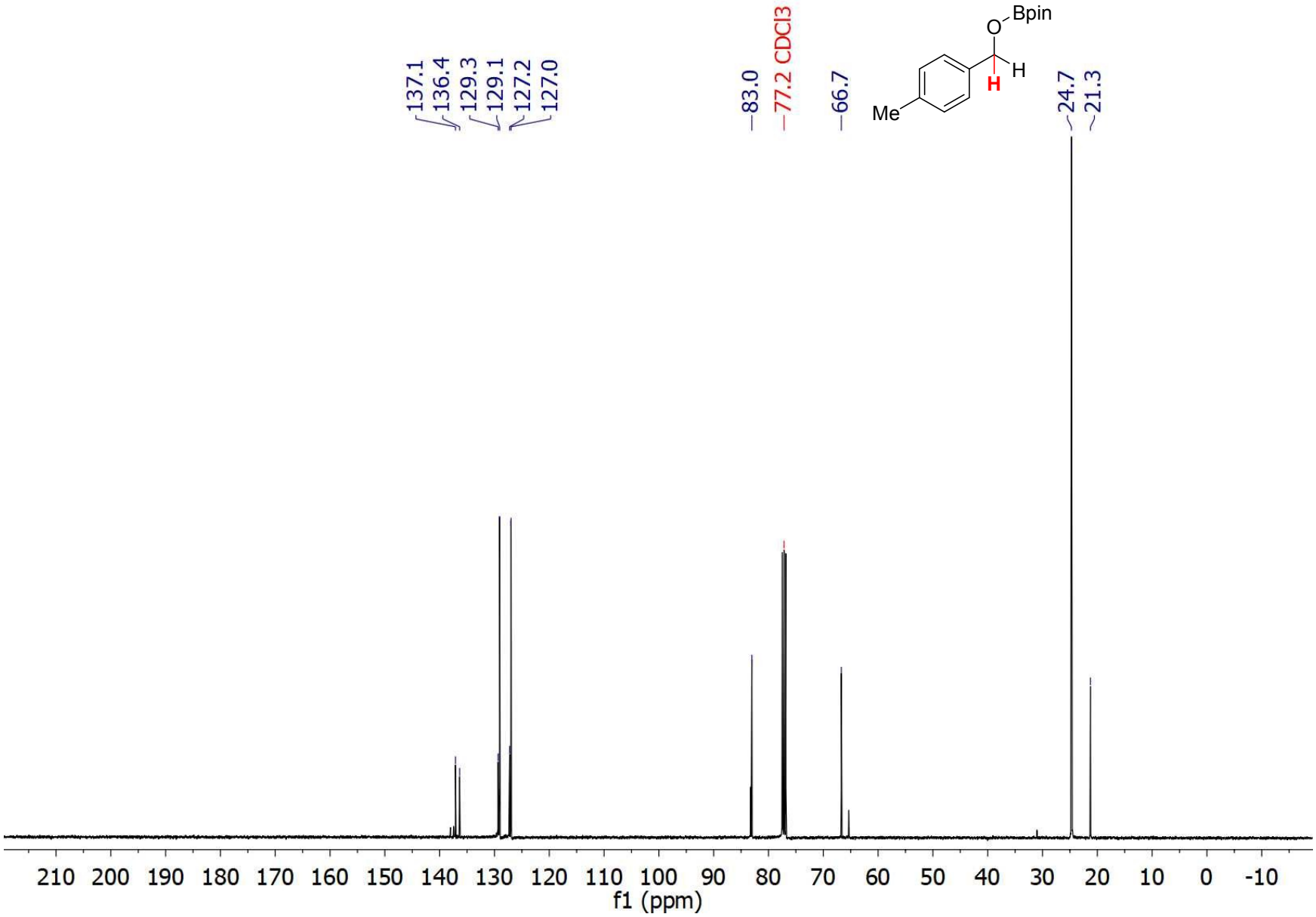


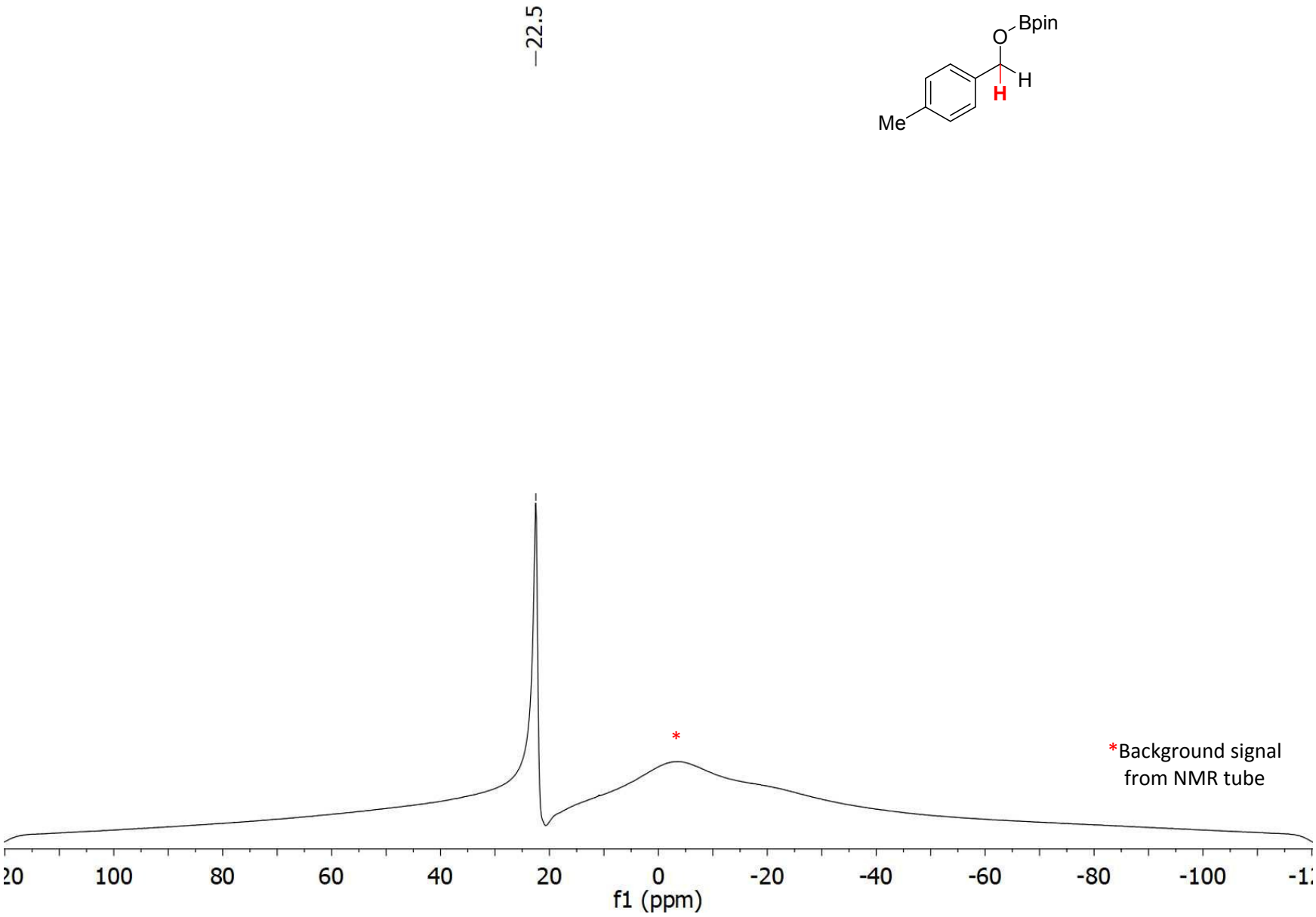

139.1
128.2
127.3
126.6
82.9
77.0 CDCl3
66.6
24.5
Bpin
O
H
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


22.5
Bpin
O
H
H
*
*Background signal
from NMR tube
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

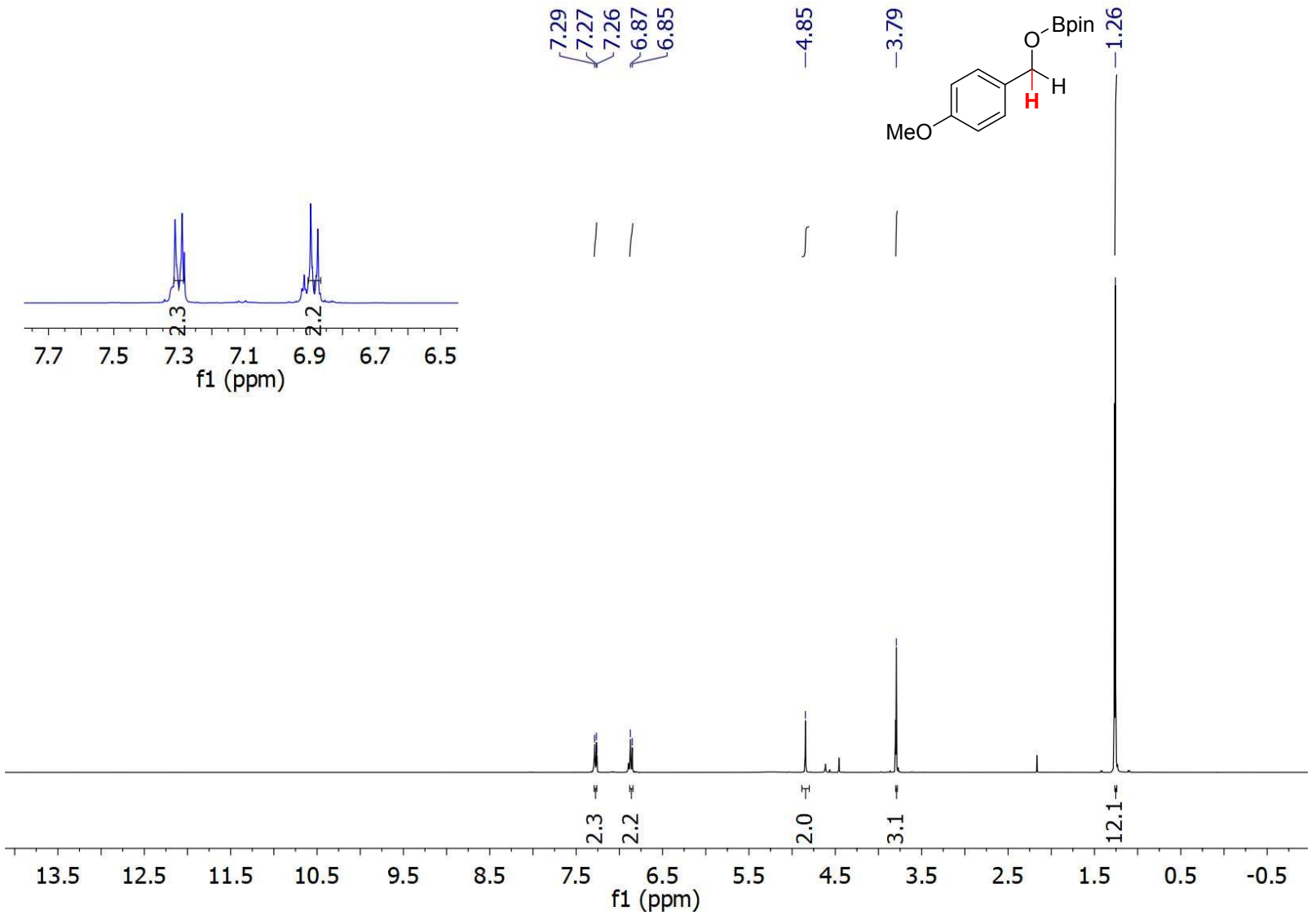
4,4,5,5-tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane (**3b**)

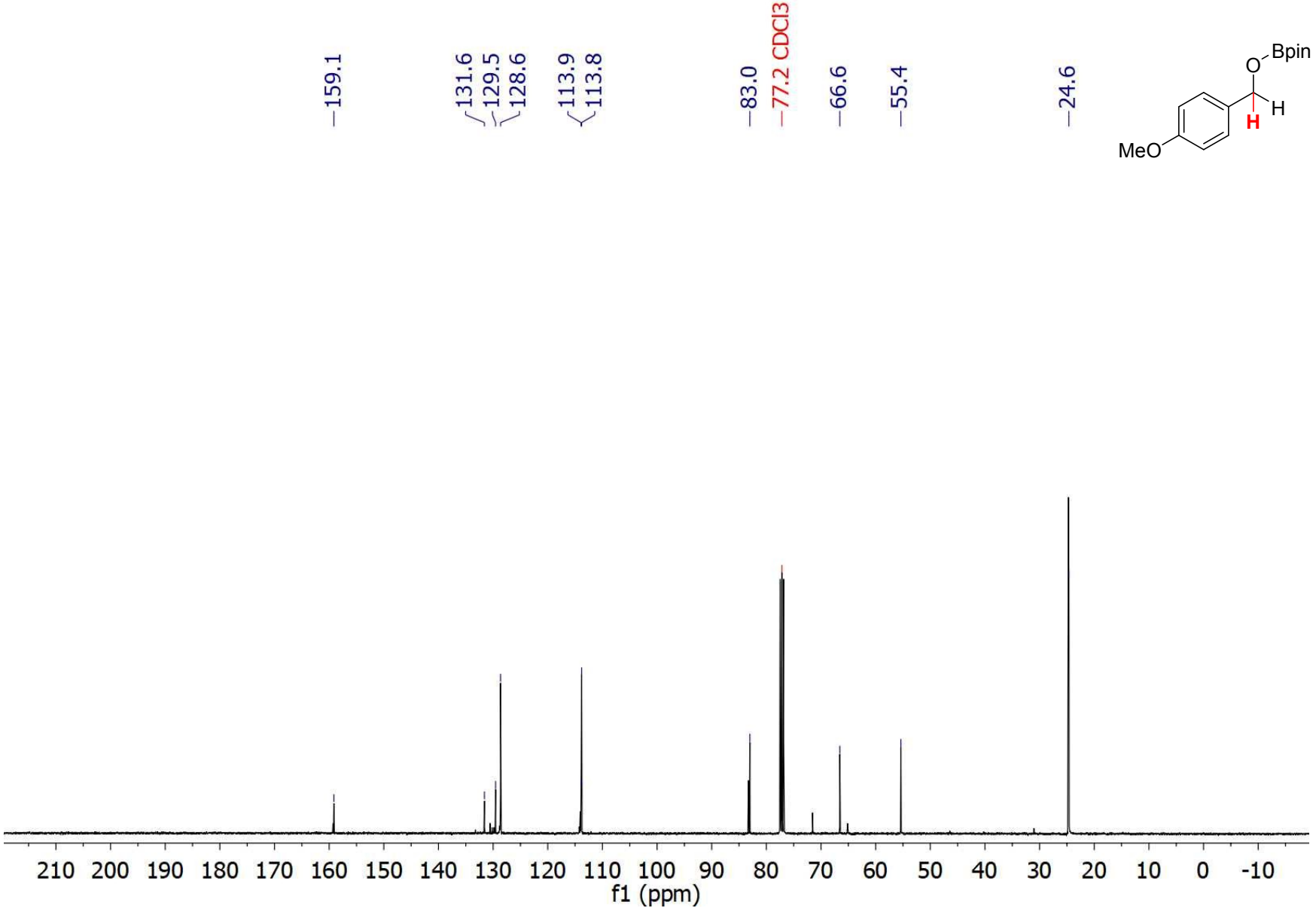


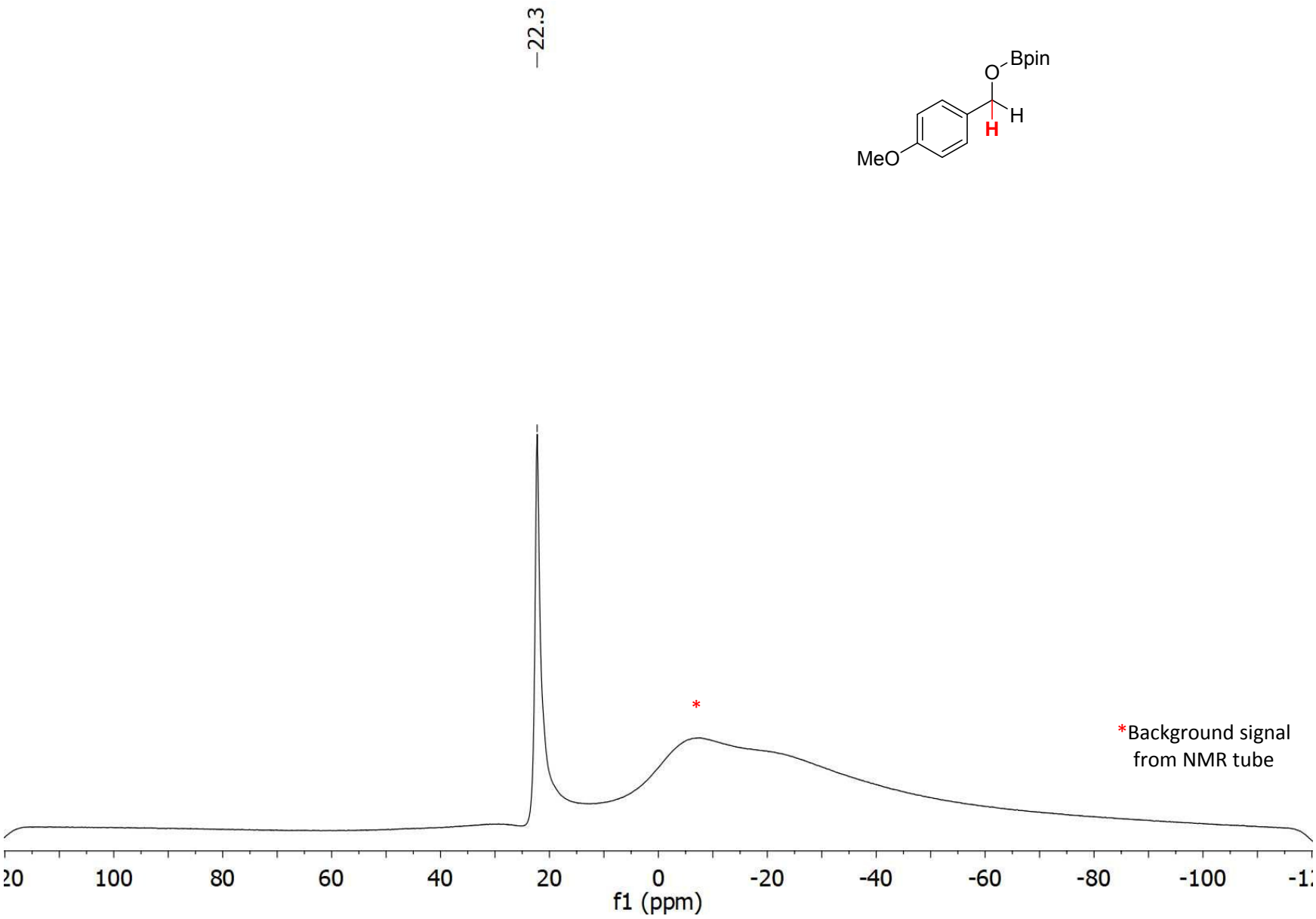

137.1
136.4
129.3
129.1
127.2
127.0
83.0
77.2 CDCl3
66.7
24.7
21.3
Bpin
O
H
H
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


−22.5
Bpin
O
H
H
Me
*
*Background signal
from NMR tube
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

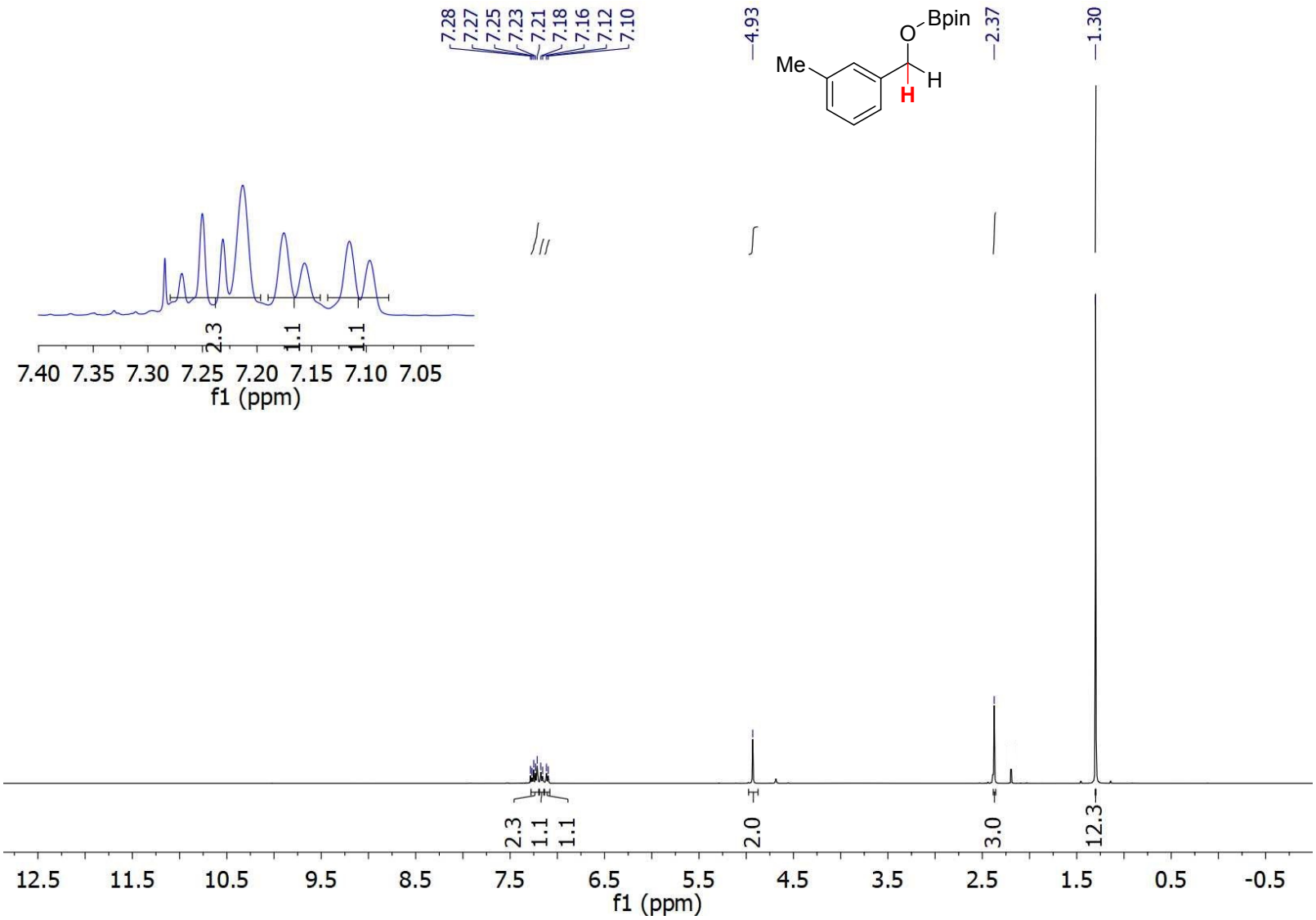
4,4,5,5-tetramethyl-2-((4-methoxybenzyl)oxy)-1,3,2-dioxaborolane (**3c**)

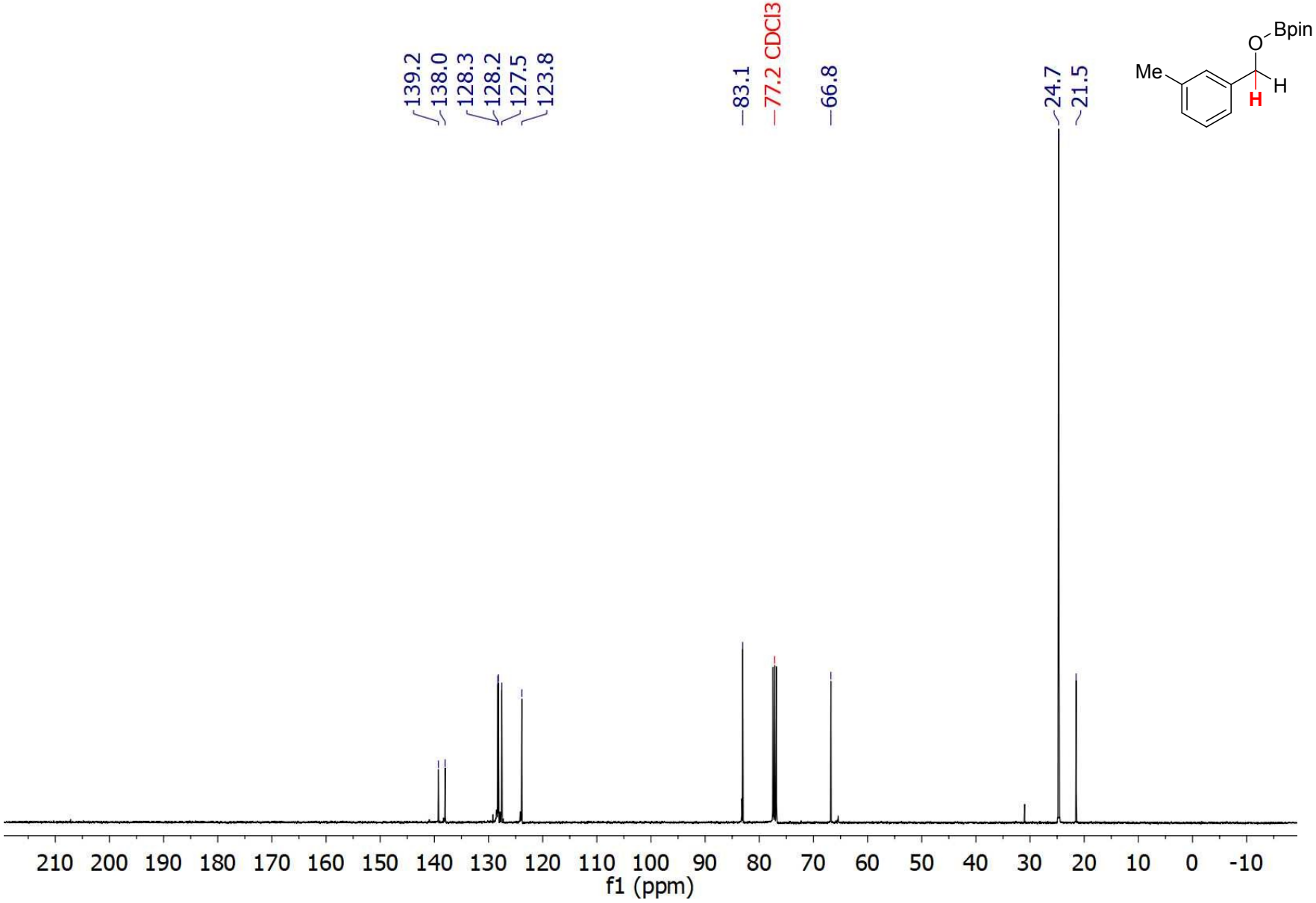


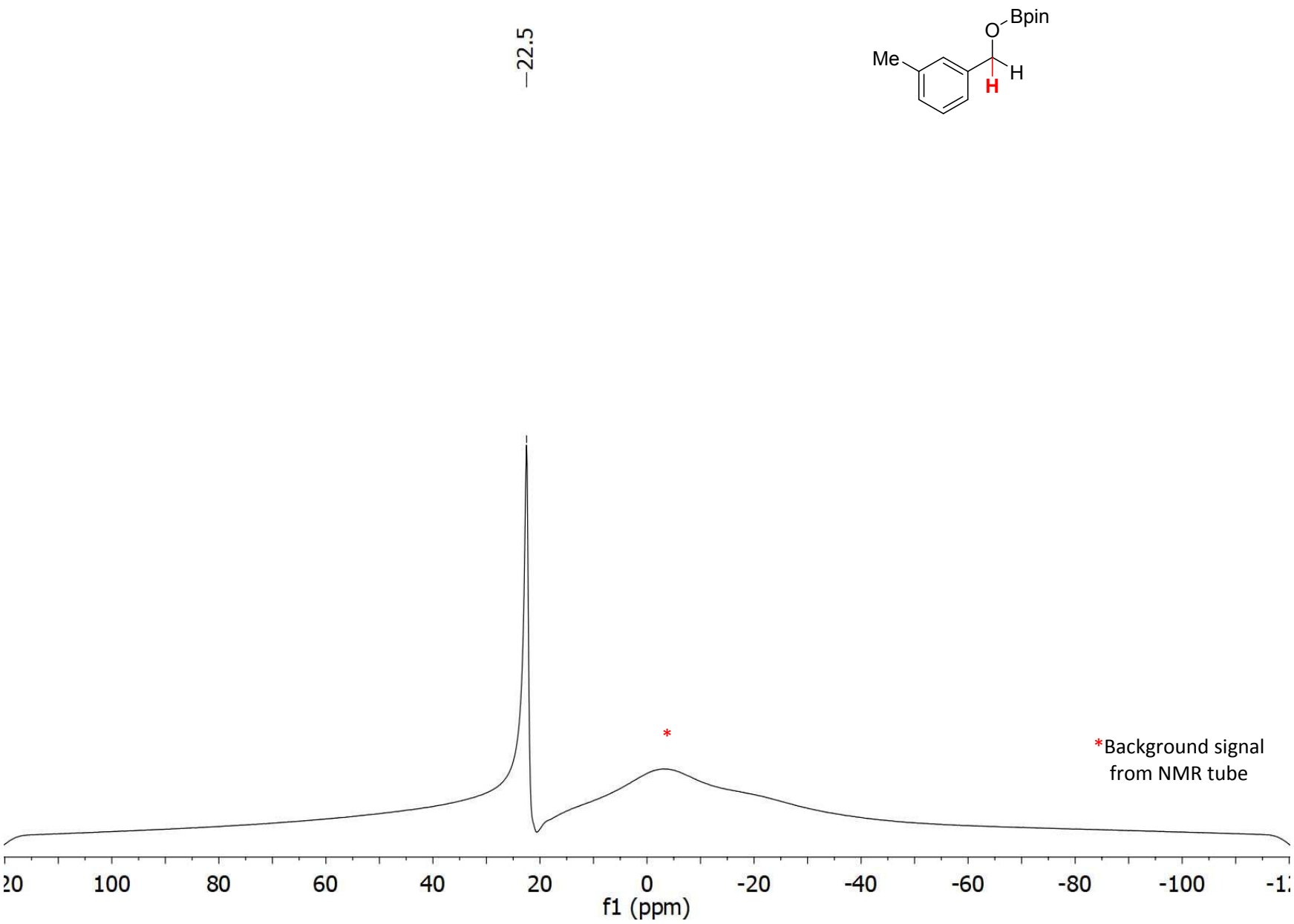

159.1
131.6
129.5
128.6
113.9
113.8
83.0
77.2 CDCl3
66.6
55.4
24.6
Bpin
O
H
H
MeO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


22.3
Bpin
O
H
H
MeO
*
*Background signal
from NMR tube
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

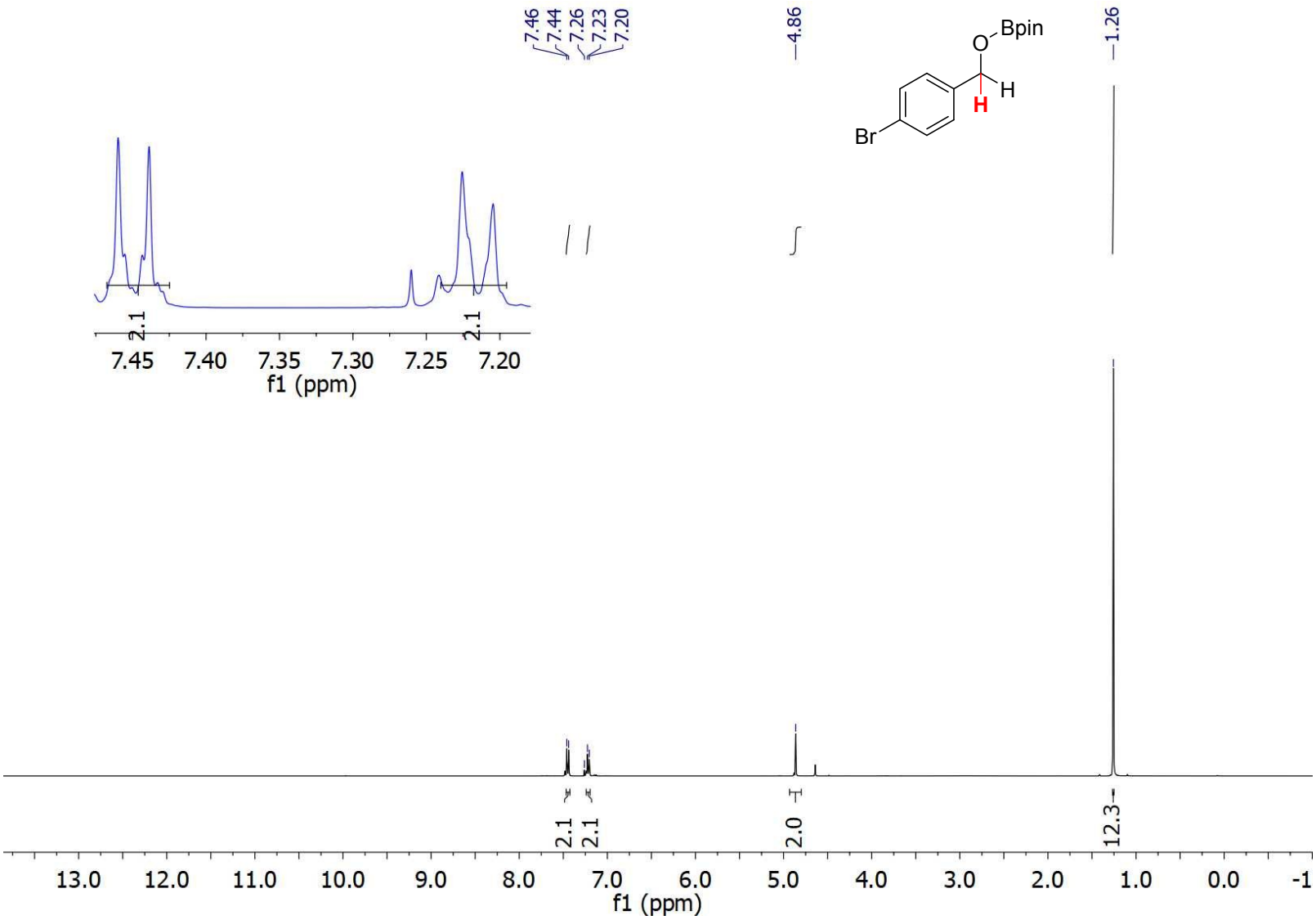
4,4,5,5-tetramethyl-2-((3-methylbenzyl)oxy)-1,3,2-dioxaborolane (**3d**)

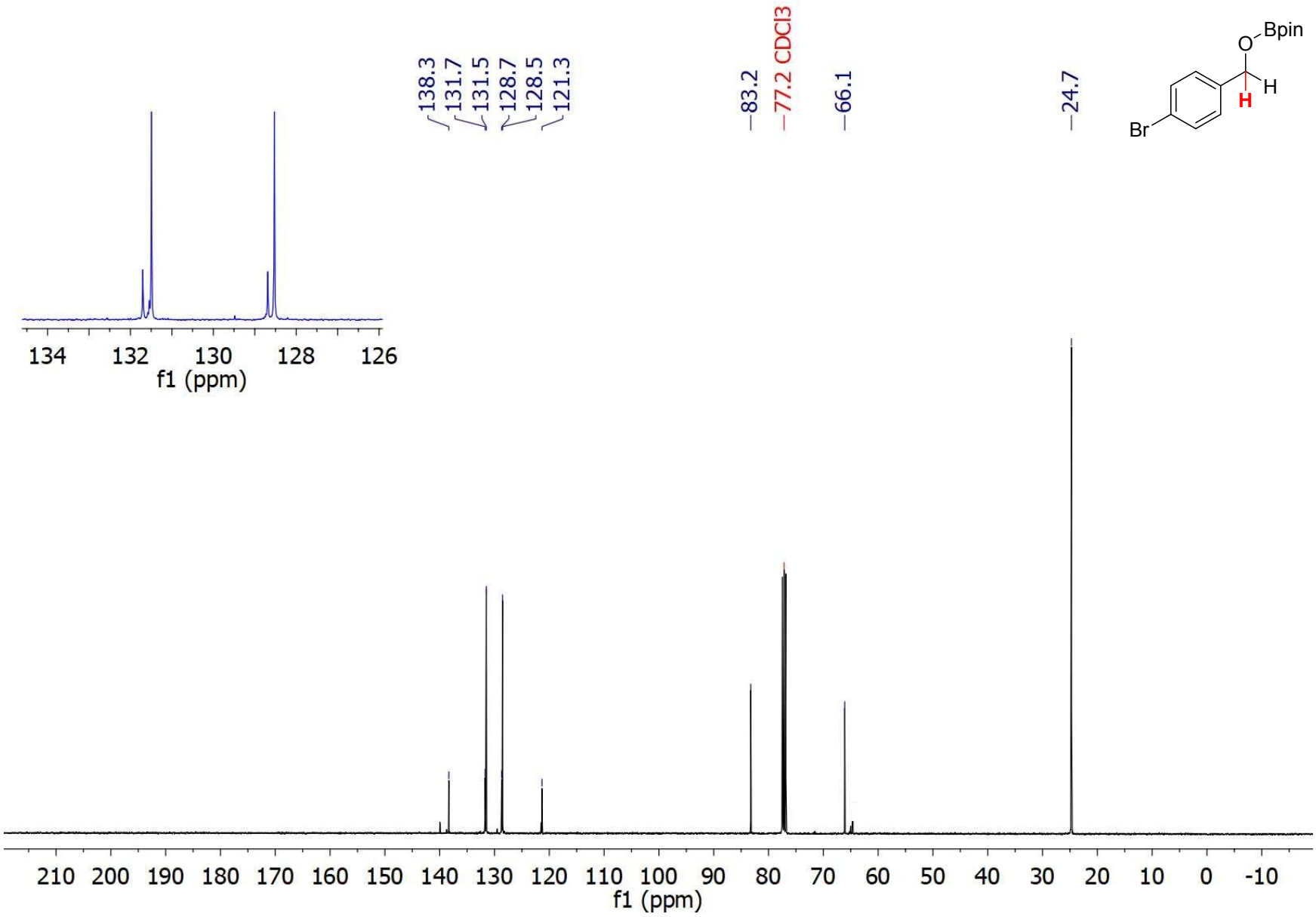


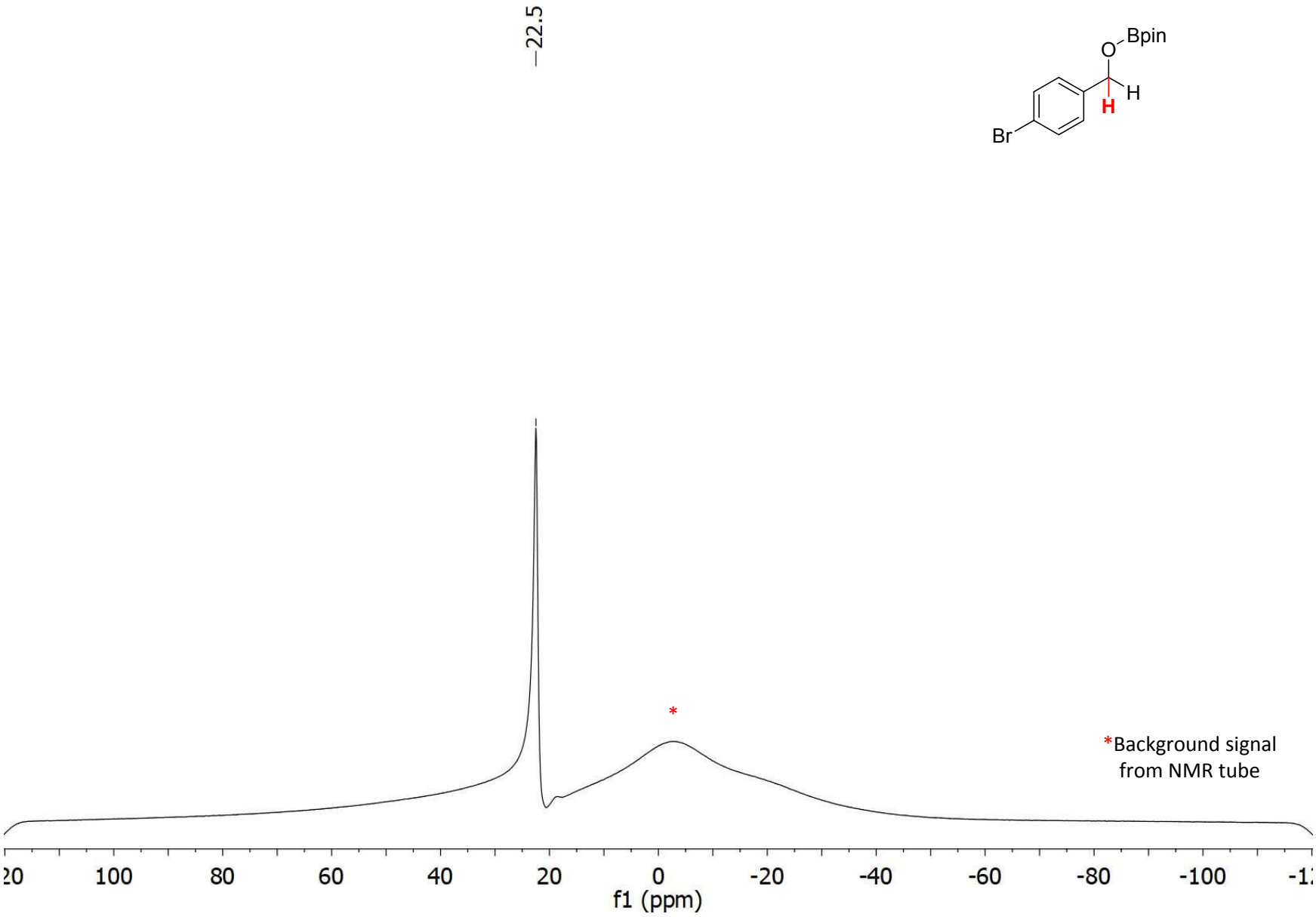

139.2
138.0
128.3
128.2
127.5
123.8
83.1
77.2 CDCl3
66.8
24.7
21.5
Bpin
O
Me
H
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


22.5
Bpin
O
Me
H
H
*
*Background signal
from NMR tube
20
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

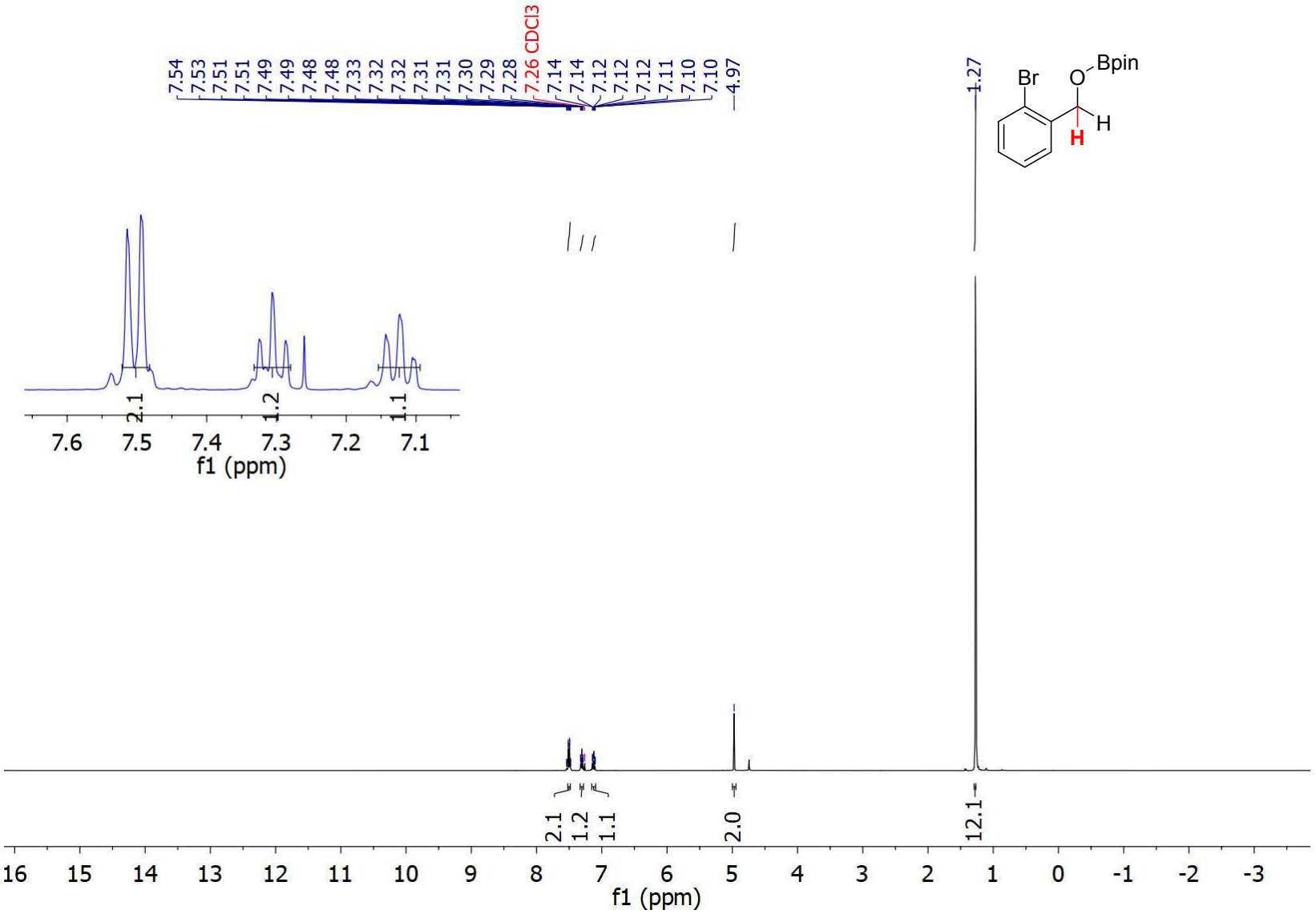
4,4,5,5-tetramethyl-2-((4-bromobenzyl)oxy)-1,3,2-dioxaborolane (**3e**)

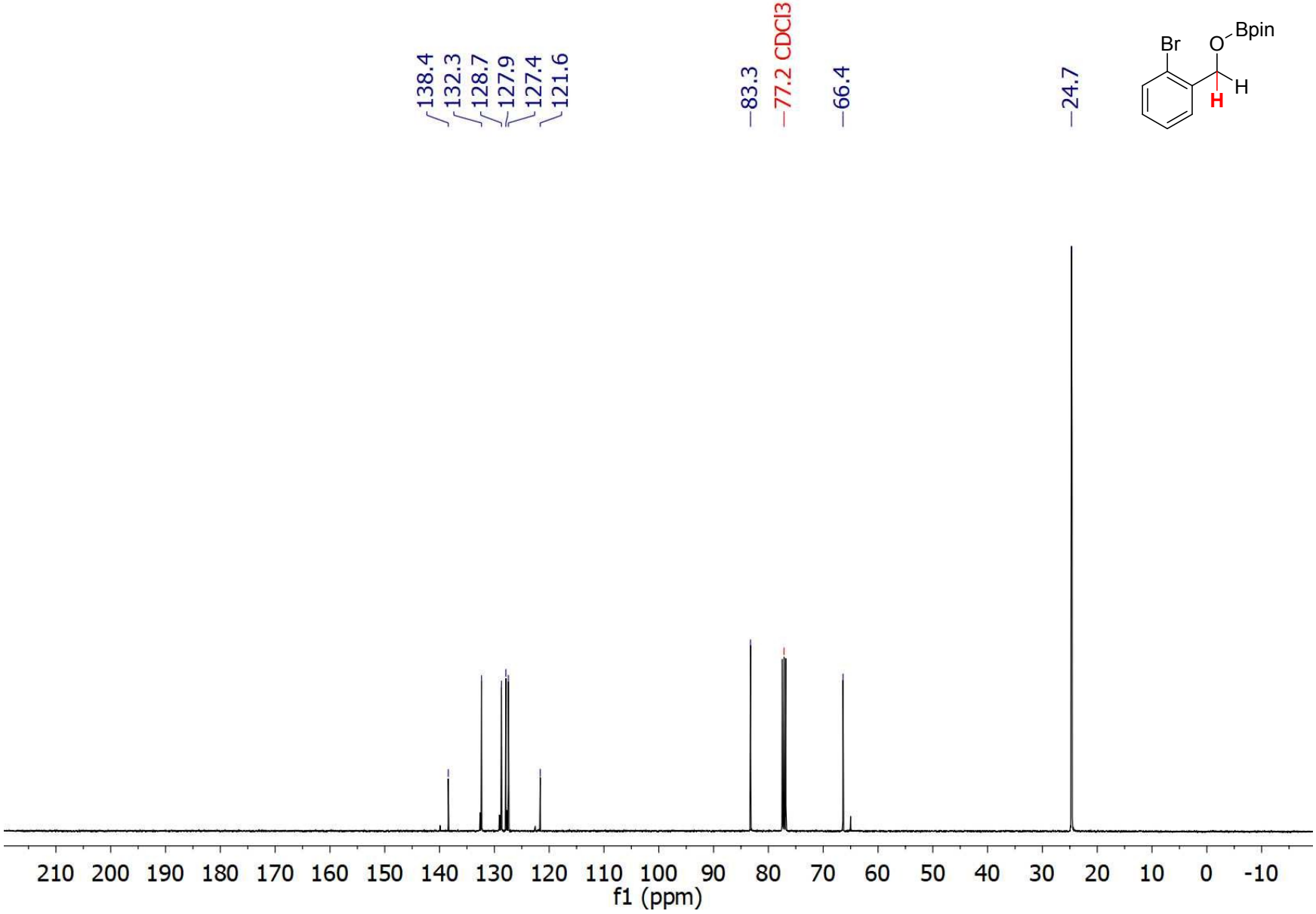


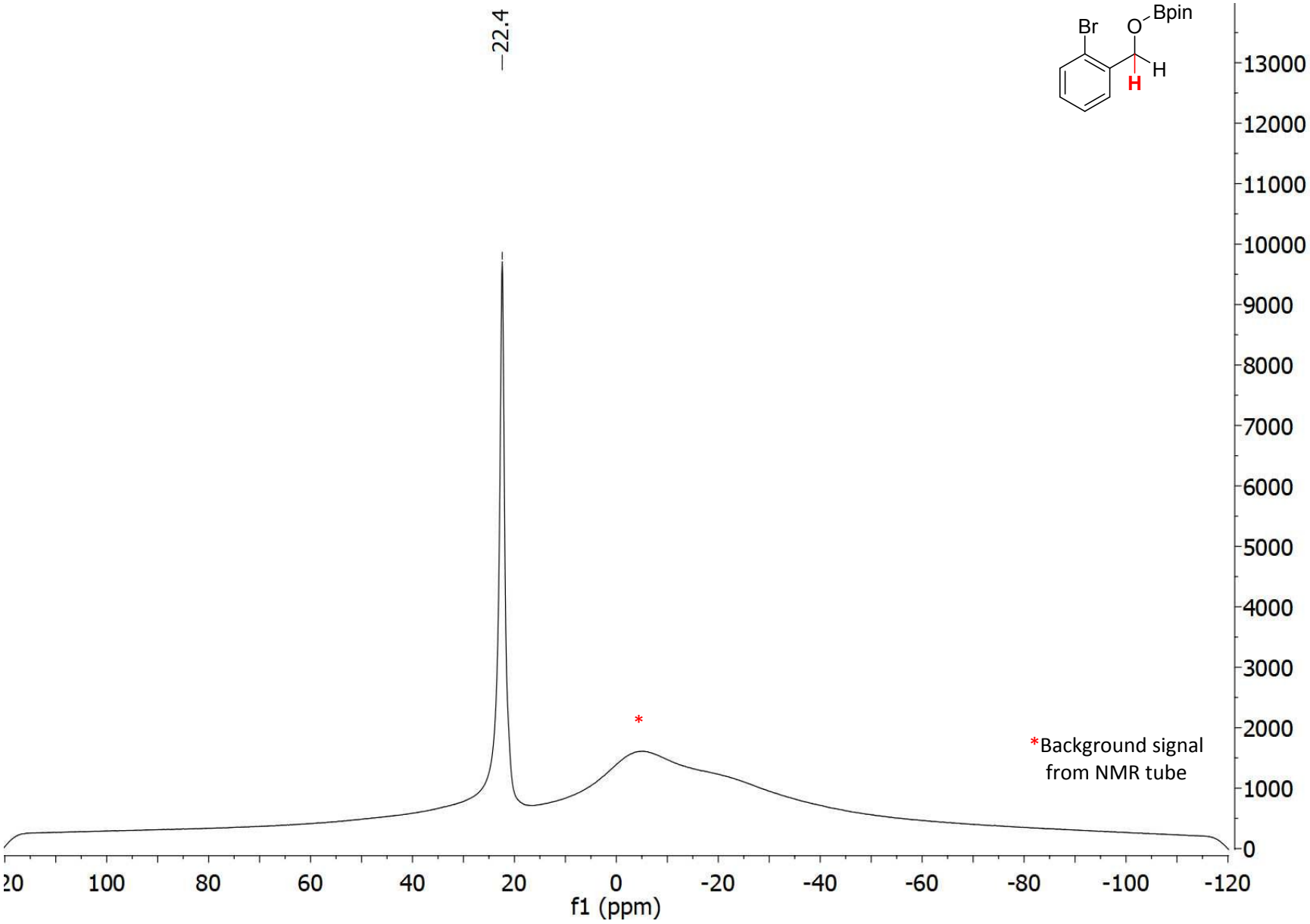

138.3
131.7
131.5
128.7
128.5
121.3
83.2
77.2 CDCl3
66.1
24.7
Bpin
O
H
H
Br
134
132
130
128
126
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


22.5
Bpin
O
H
H
Br
*
*Background signal
from NMR tube
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

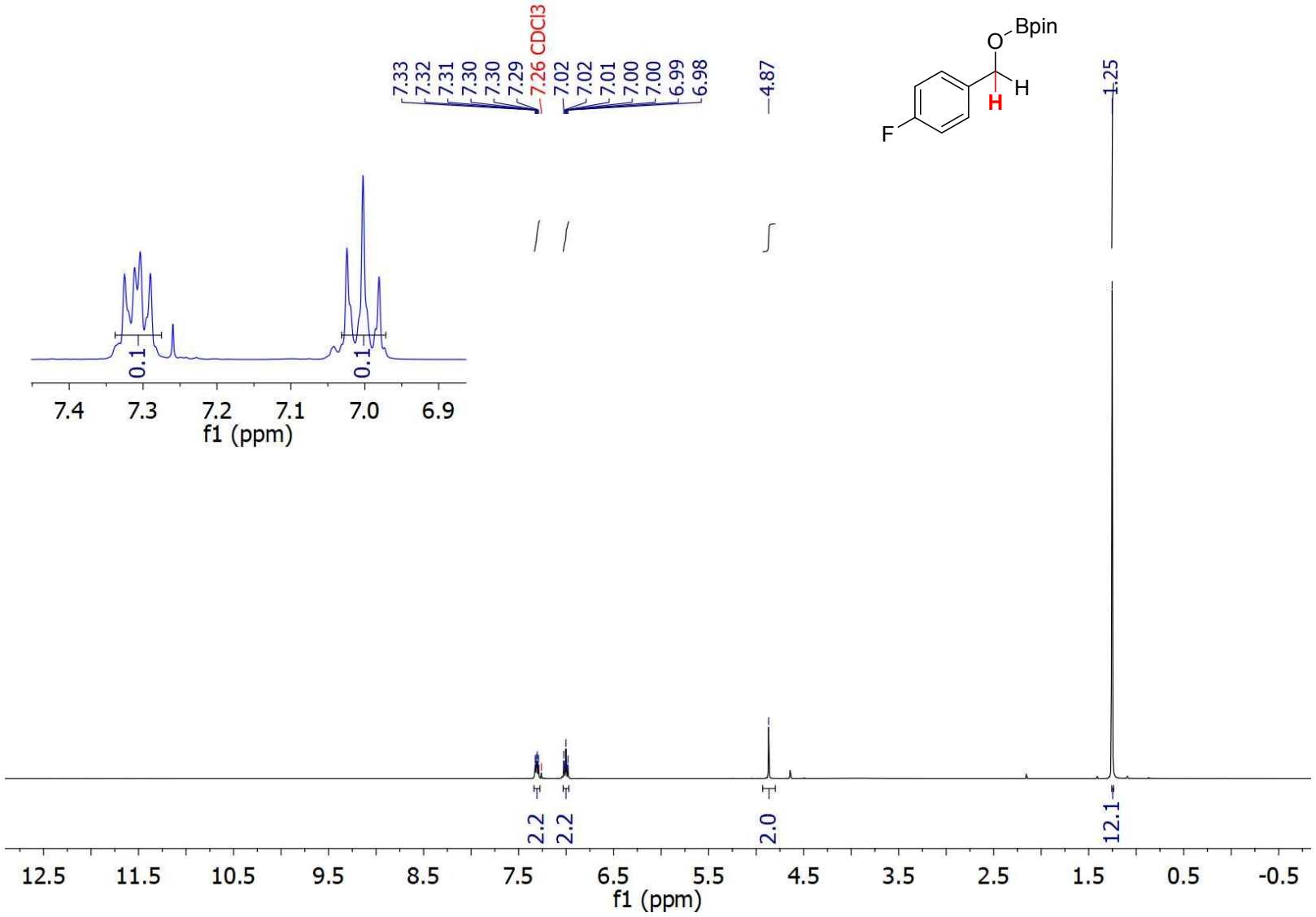
4,4,5,5-tetramethyl-2-((2-bromobenzyl)oxy)-1,3,2-dioxaborolane (**3f**)

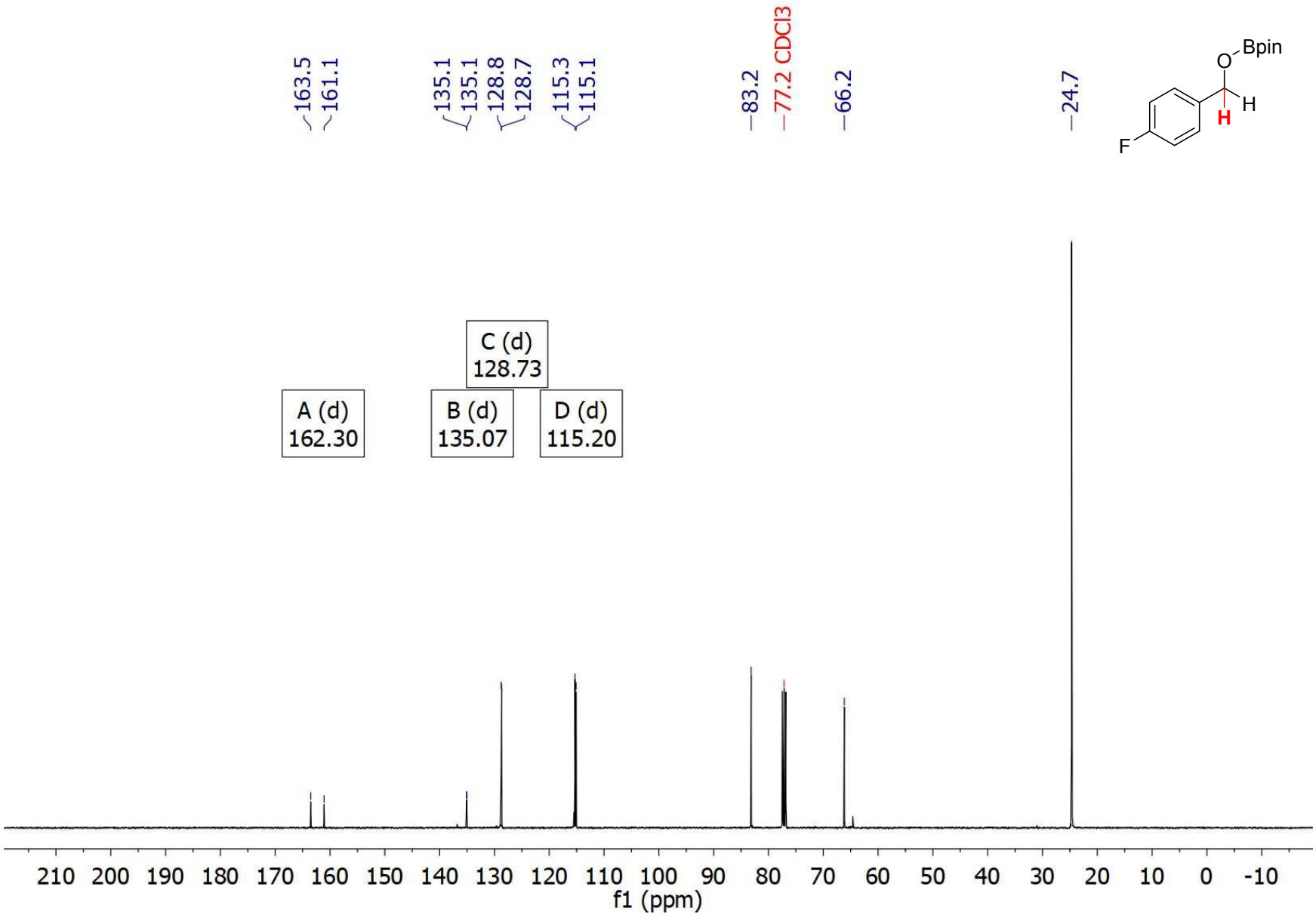


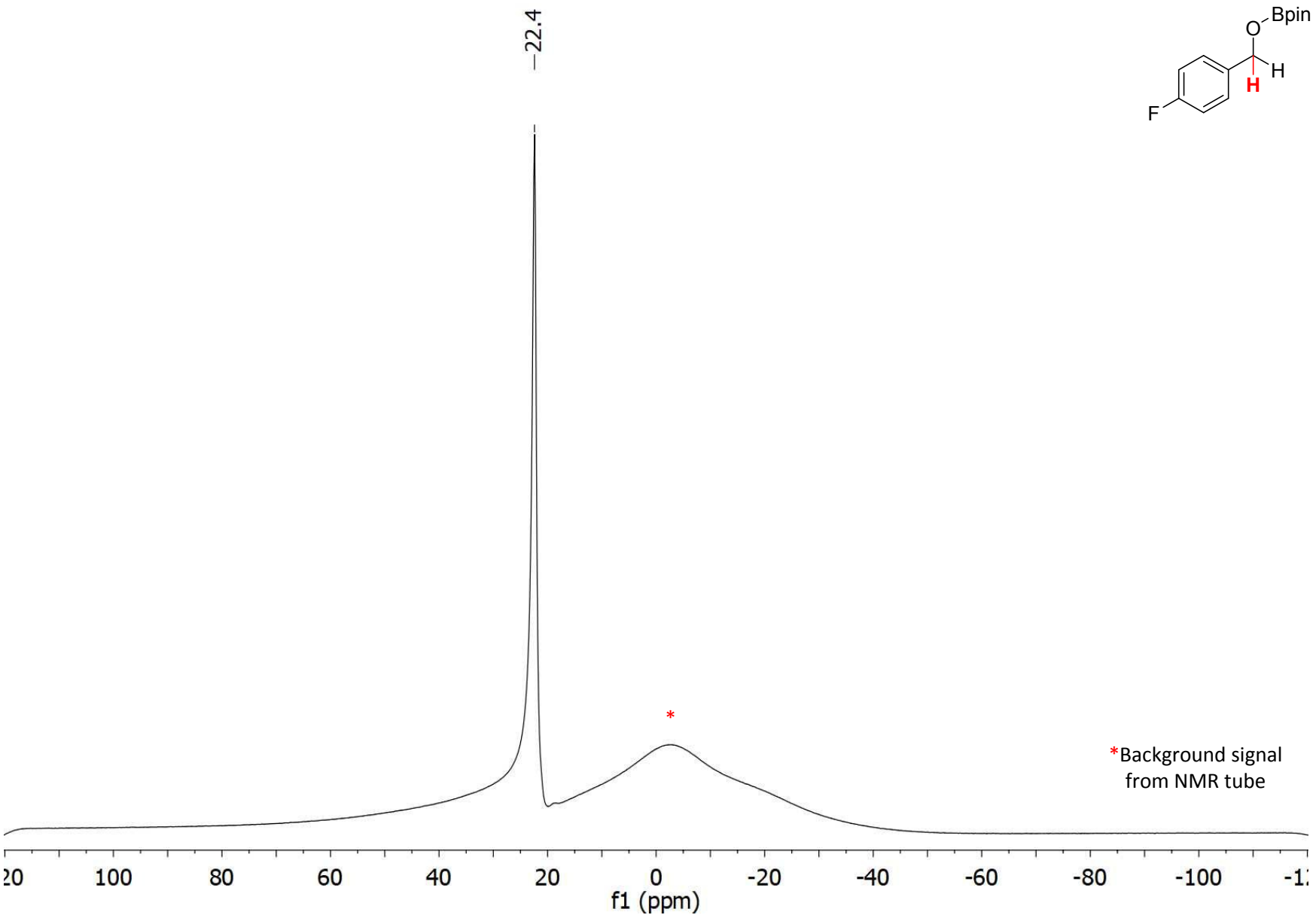

138.4
132.3
128.7
127.9
127.4
121.6
83.3
77.2 CDCl3
66.4
24.7
Br
O
Bpin
H
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


22.4
Br
O
Bpin
H
H
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
*
*Background signal
from NMR tube
20
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
f1 (ppm)

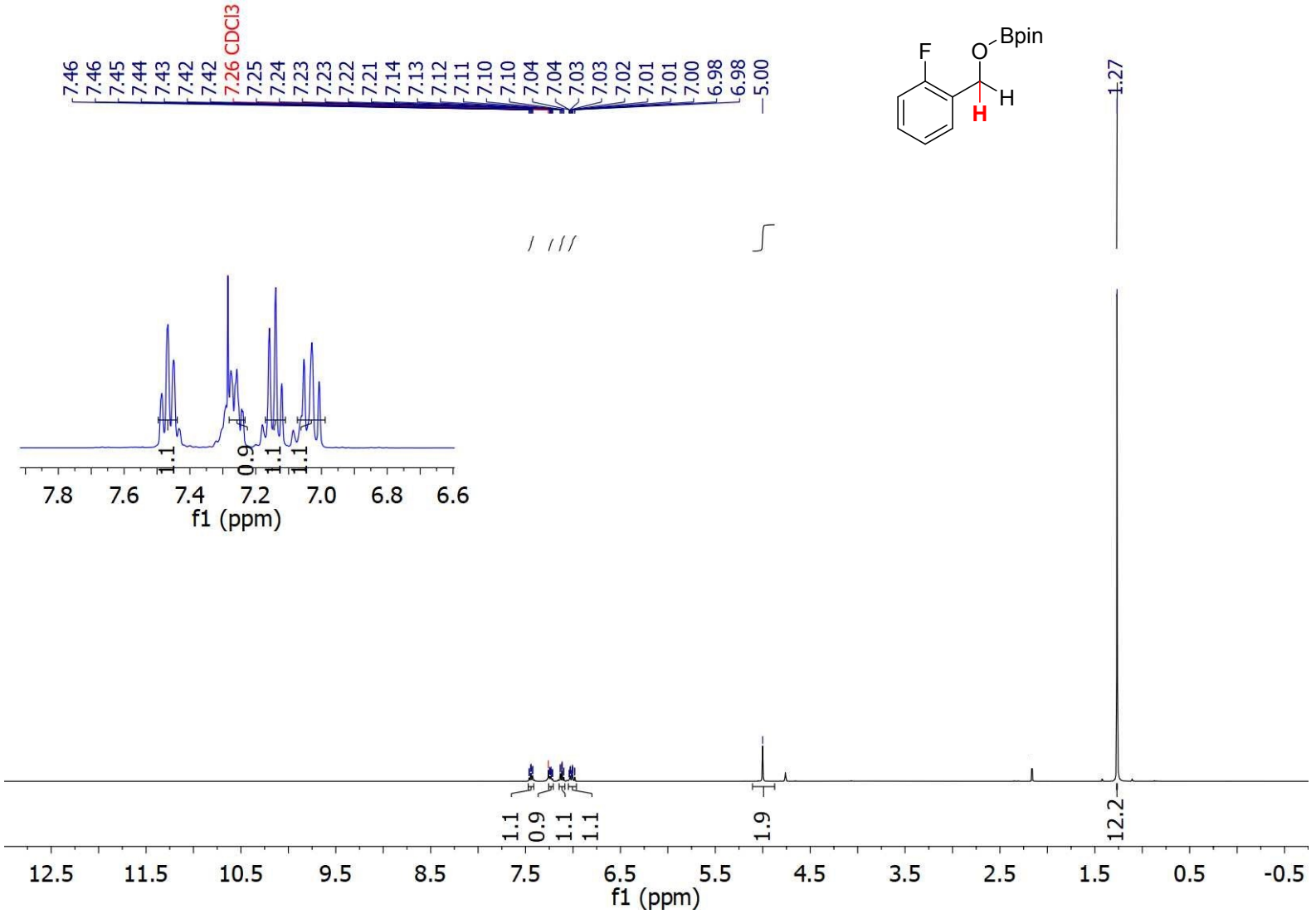
4,4,5,5-tetramethyl-2-((4-fluorobenzyl)oxy)-1,3,2-dioxaborolane (**3g**)

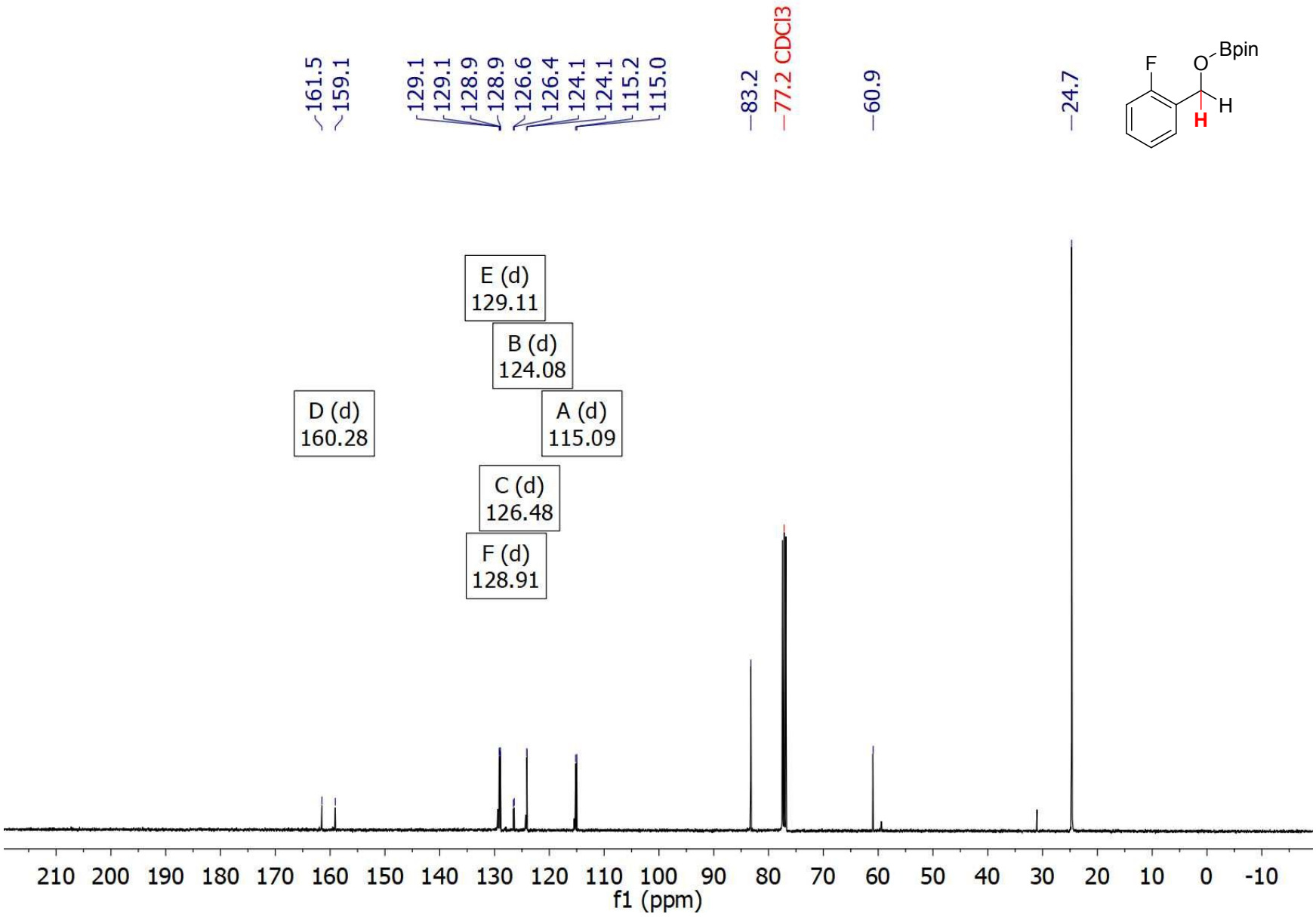


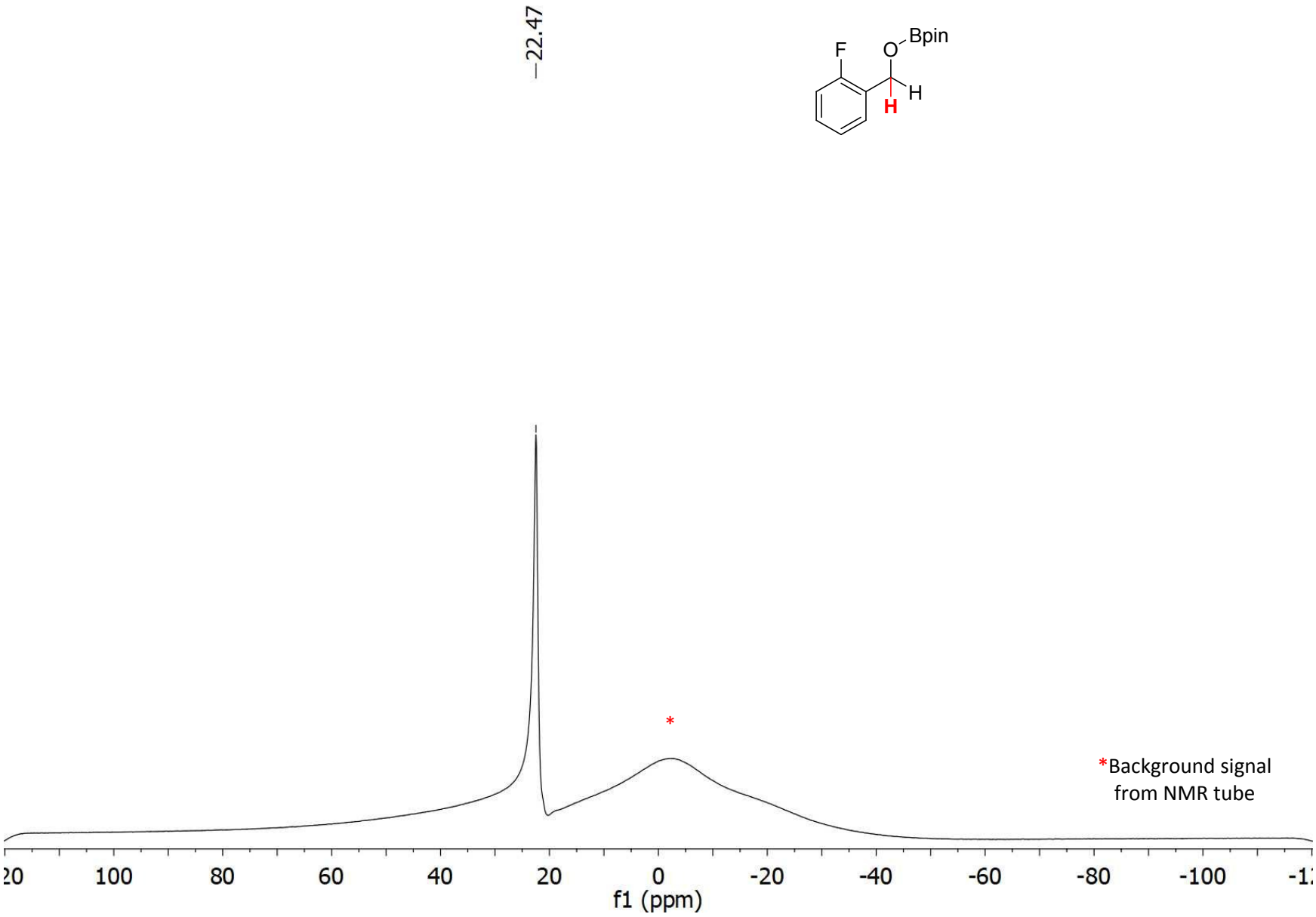

163.5
161.1
135.1
135.1
128.8
128.7
115.3
115.1
83.2
77.2 CDCl3
66.2
24.7
Bpin
O
H
H
F
A (d)
162.30
C (d)
128.73
B (d)
135.07
D (d)
115.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-22.4
Bpin
O
H
H
F
*
*Background signal
from NMR tube
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

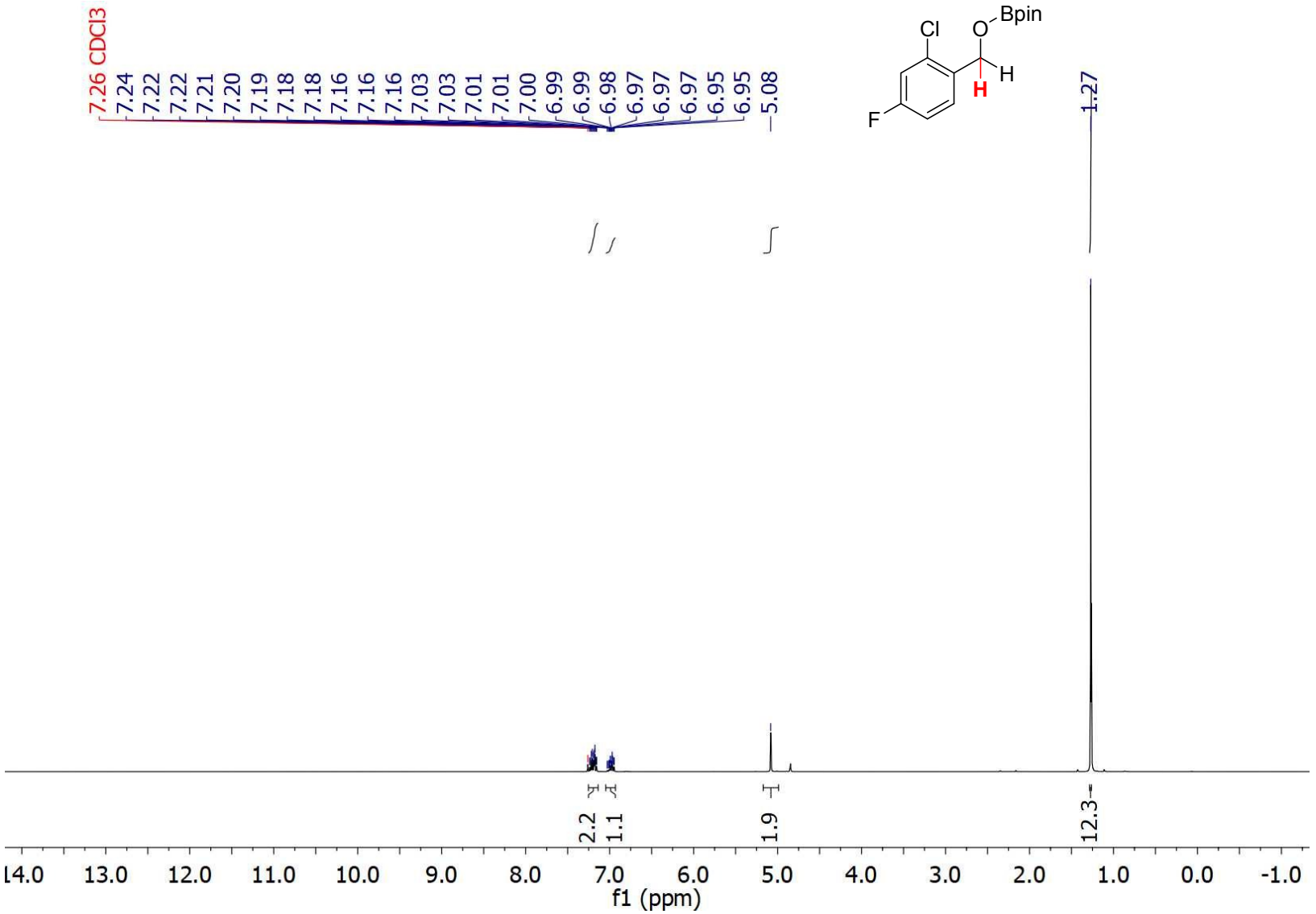
4,4,5,5-tetramethyl-2-((2-fluorobenzyl)oxy)-1,3,2-dioxaborolane (**3h**)

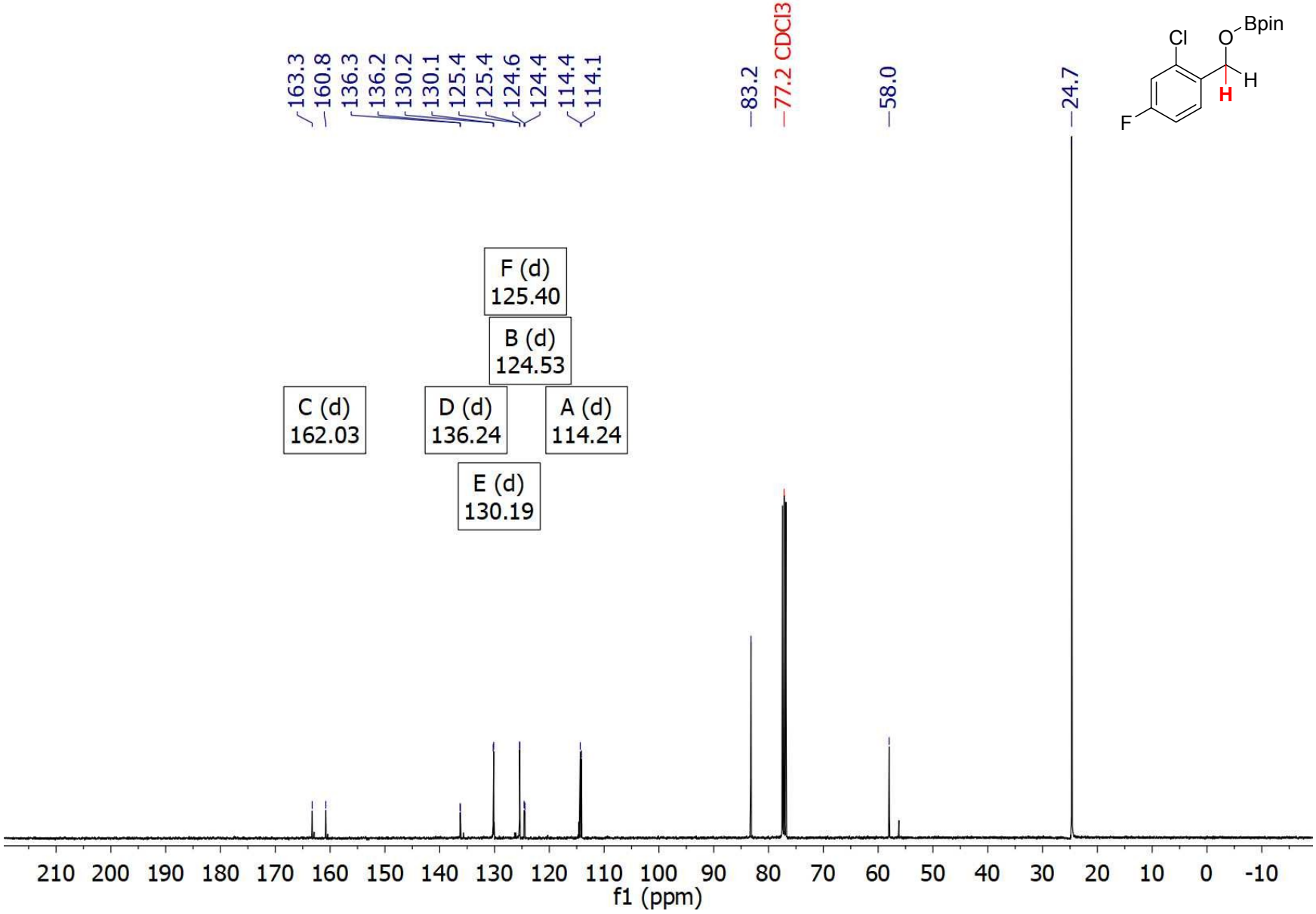


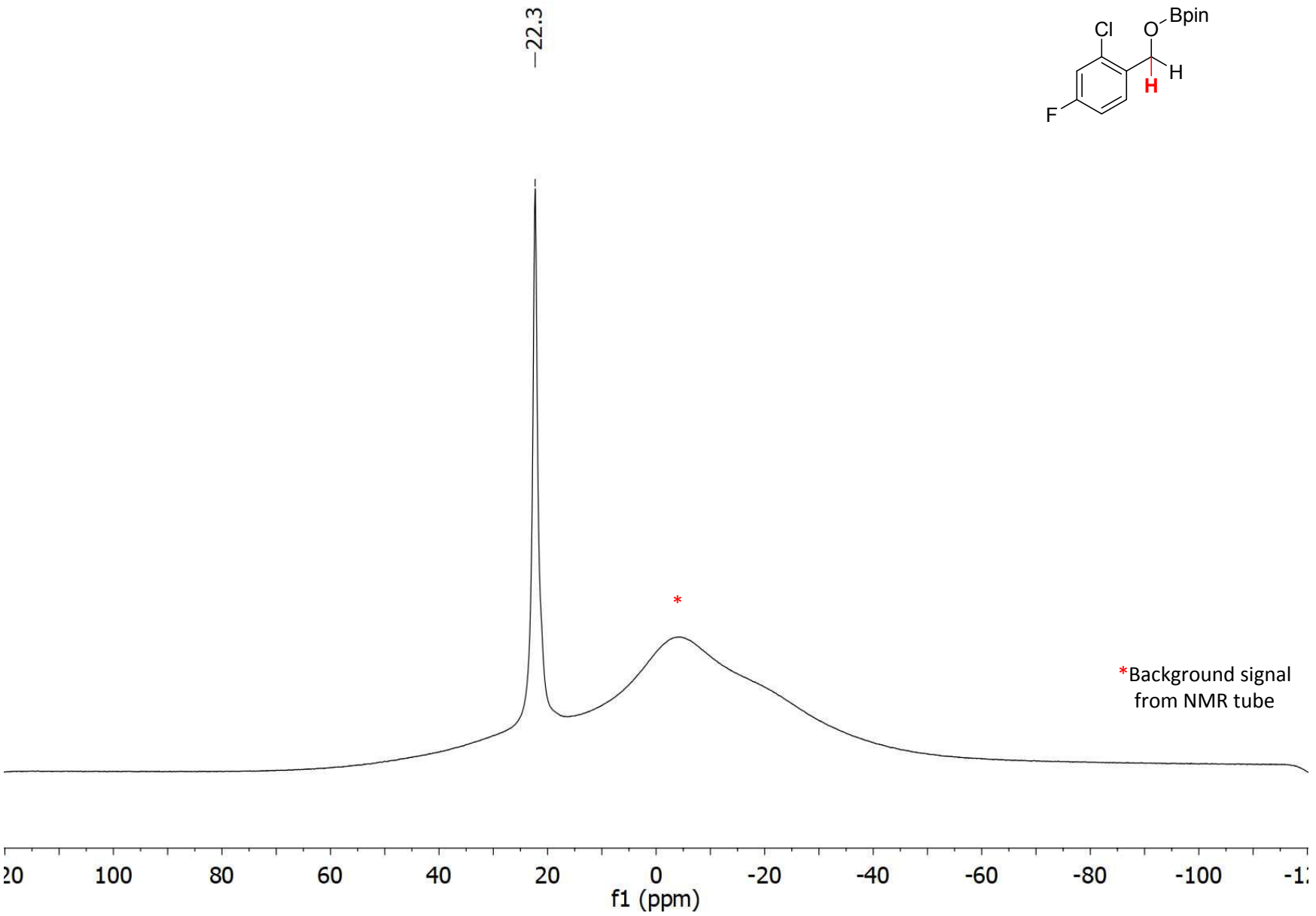

161.5
159.1
129.1
129.1
128.9
128.9
126.6
126.4
124.1
124.1
115.2
115.0
83.2
77.2 CDCl3
60.9
24.7
F
O
Bpin
H
H
E (d)
129.11
B (d)
124.08
D (d)
160.28
A (d)
115.09
C (d)
126.48
F (d)
128.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


−22.47
F
O
Bpin
H
H
*
*Background signal
from NMR tube
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

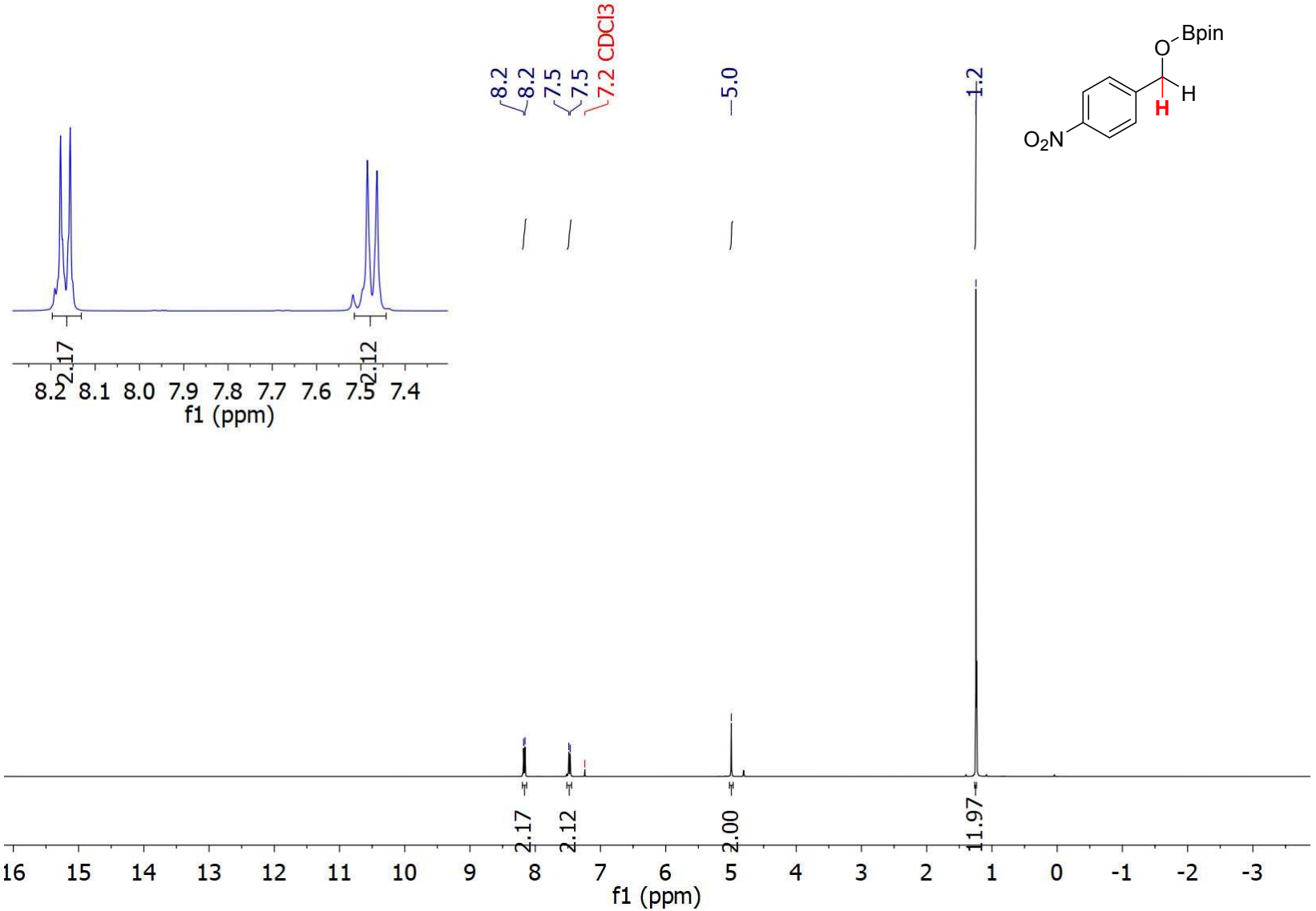
4,4,5,5-tetramethyl-2-((2-chloro-4-fluorobenzyl)oxy)-1,3,2-dioxaborolane (**3i**)

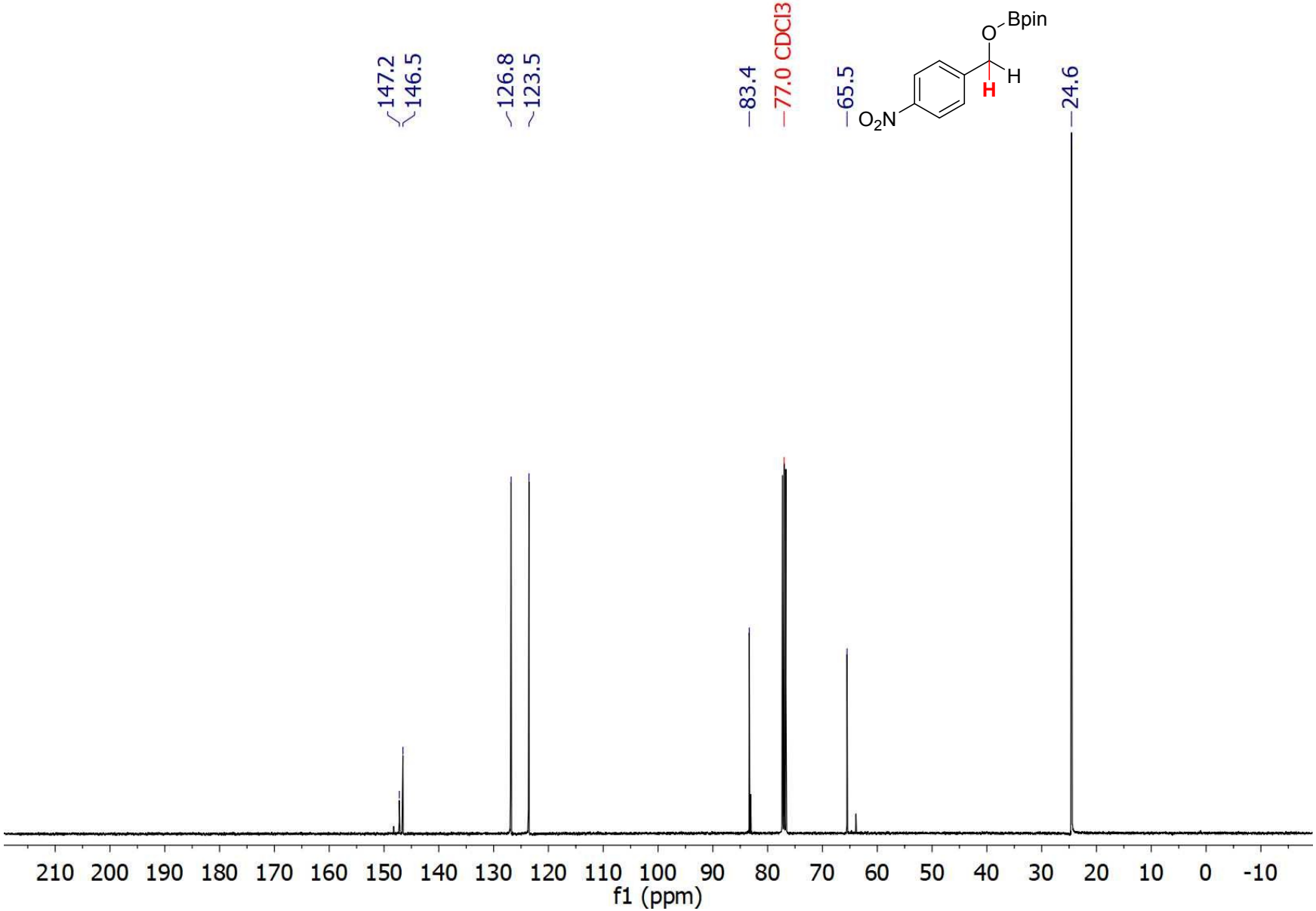


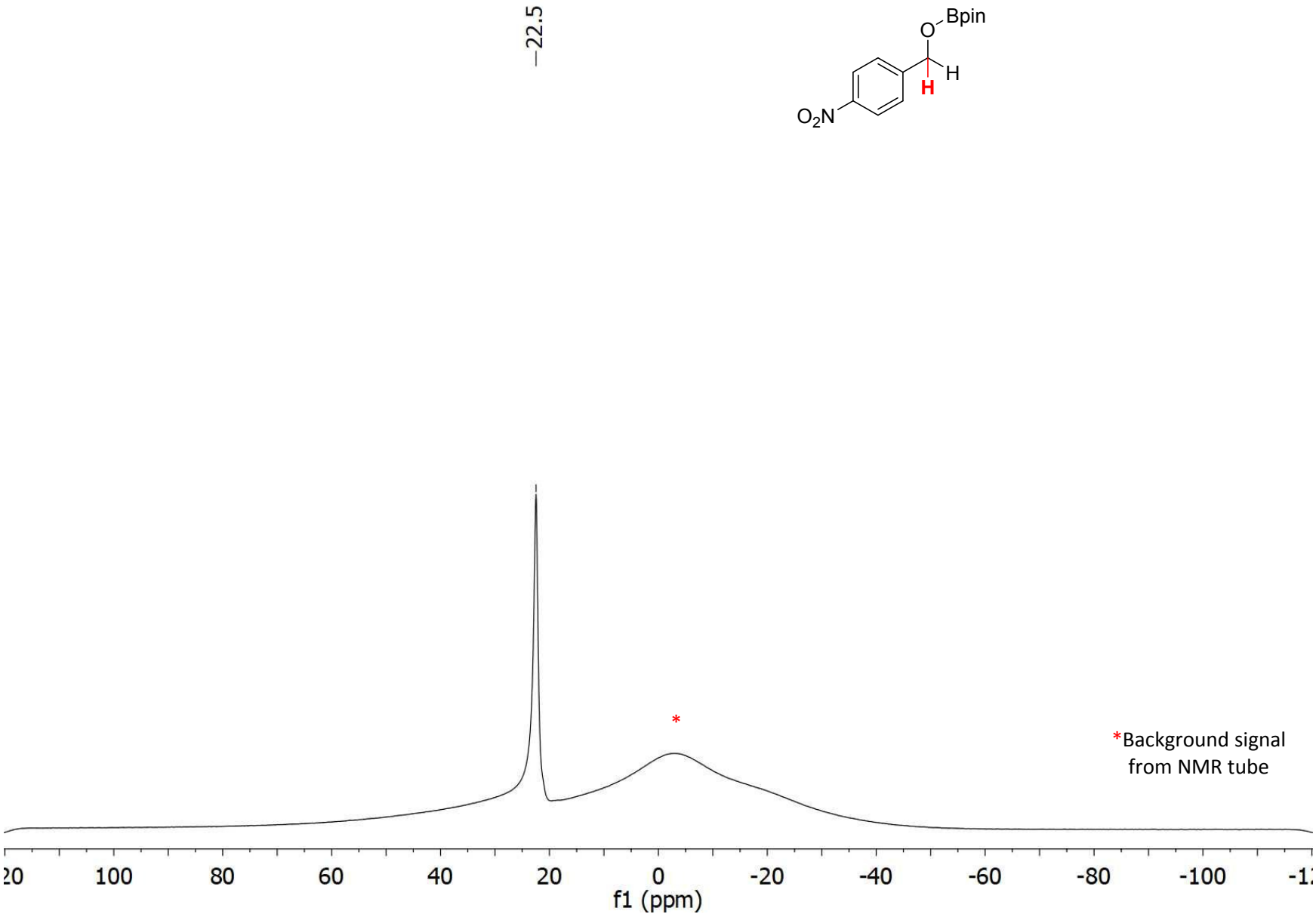

163.3
160.8
136.3
136.2
130.2
130.1
125.4
125.4
124.6
124.4
114.4
114.1
83.2
77.2 CDCl3
58.0
24.7
Cl
O
Bpin
H
H
F
F (d)
125.40
B (d)
124.53
C (d)
162.03
D (d)
136.24
A (d)
114.24
E (d)
130.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-22.3
Cl
O
Bpin
H
H
F
*
*Background signal
from NMR tube
20
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

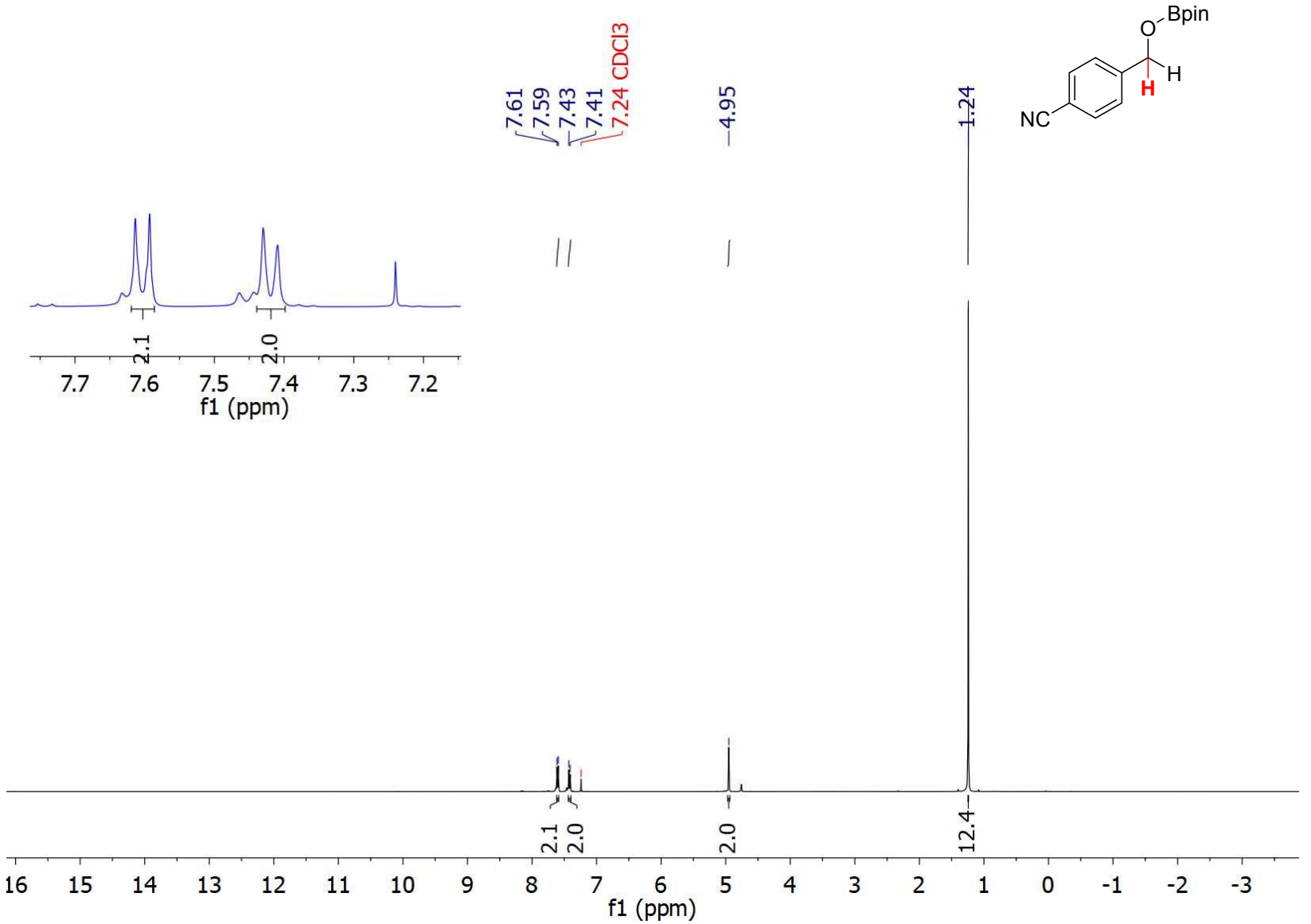
4,4,5,5-tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (**3j**)

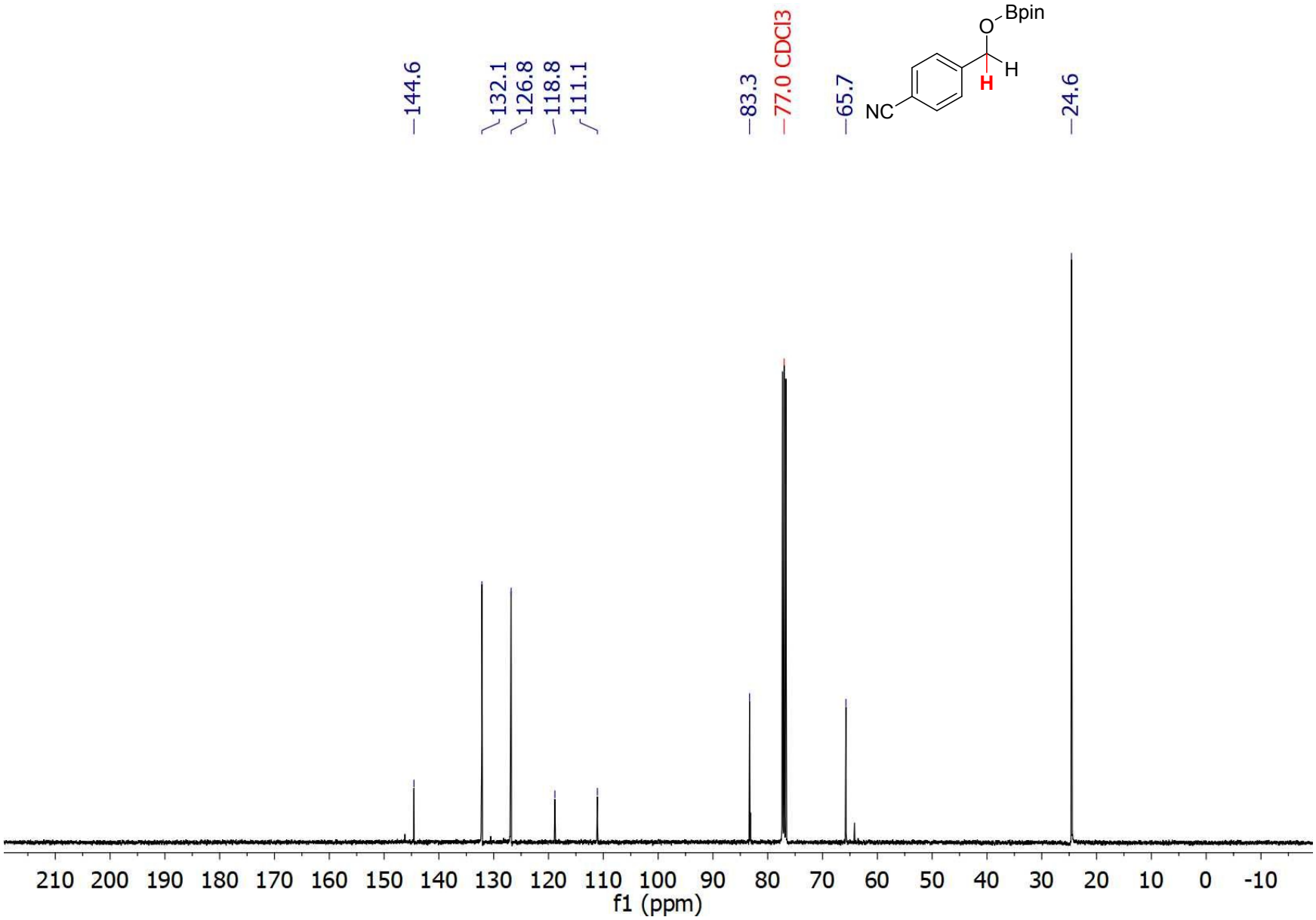


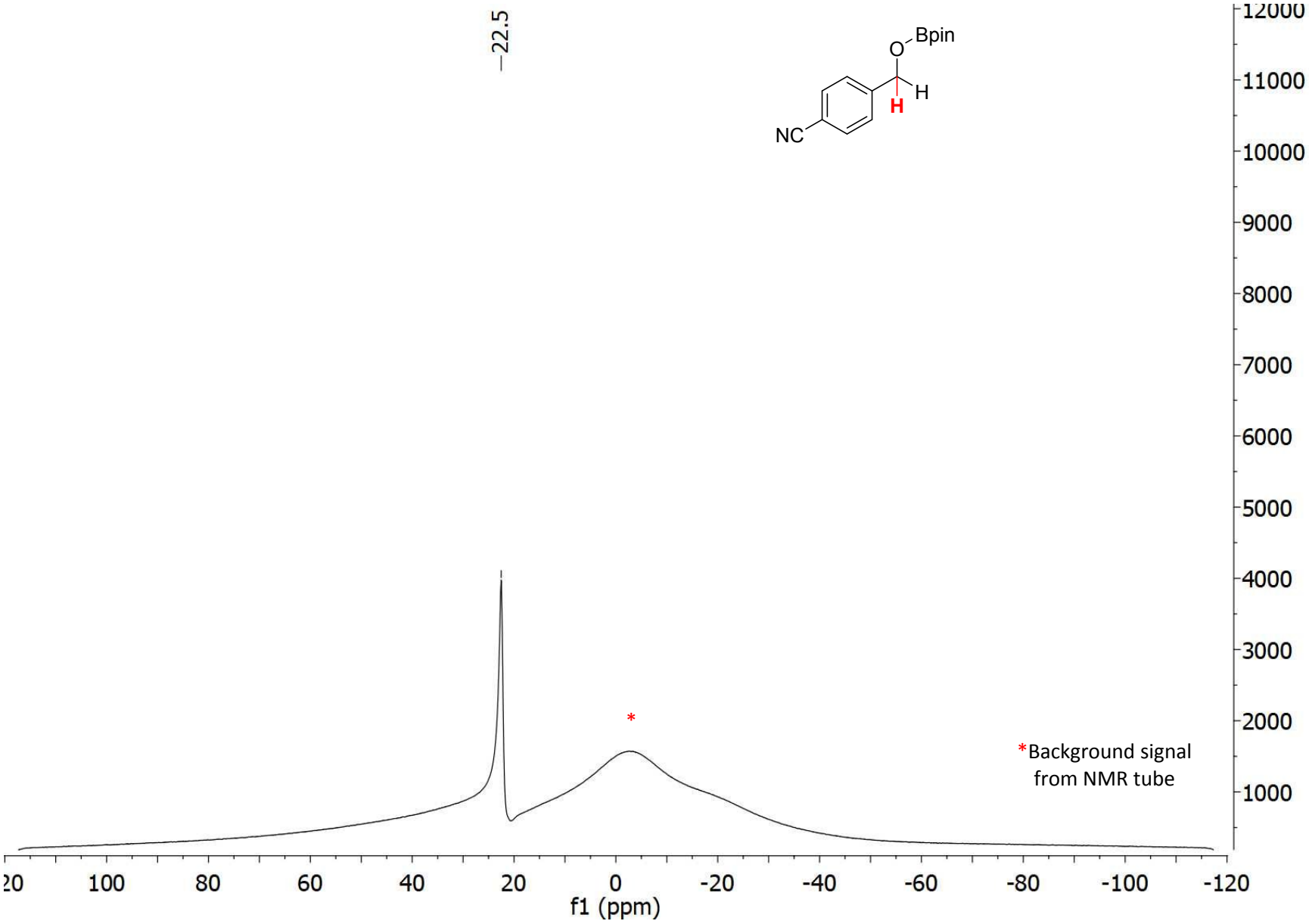

147.2
146.5
126.8
123.5
83.4
77.0 CDCl3
65.5
24.6
Bpin
O
H
H
O2N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


−22.5
Bpin
O
H
H
O_2N
*
*Background signal
from NMR tube
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

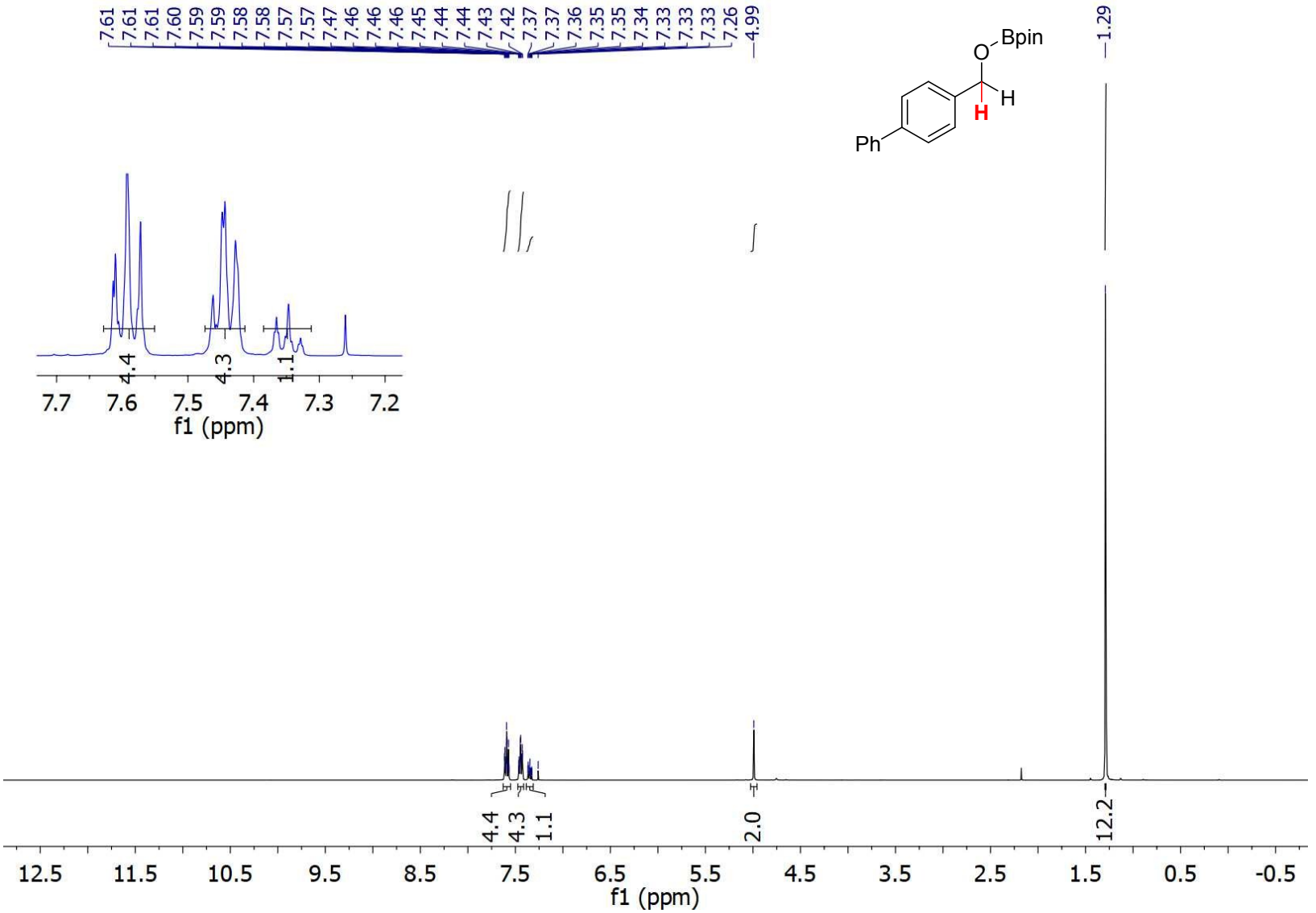
4,4,5,5-tetramethyl-2-((4-cyanobenzyl)oxy)-1,3,2-dioxaborolane (**3k**)

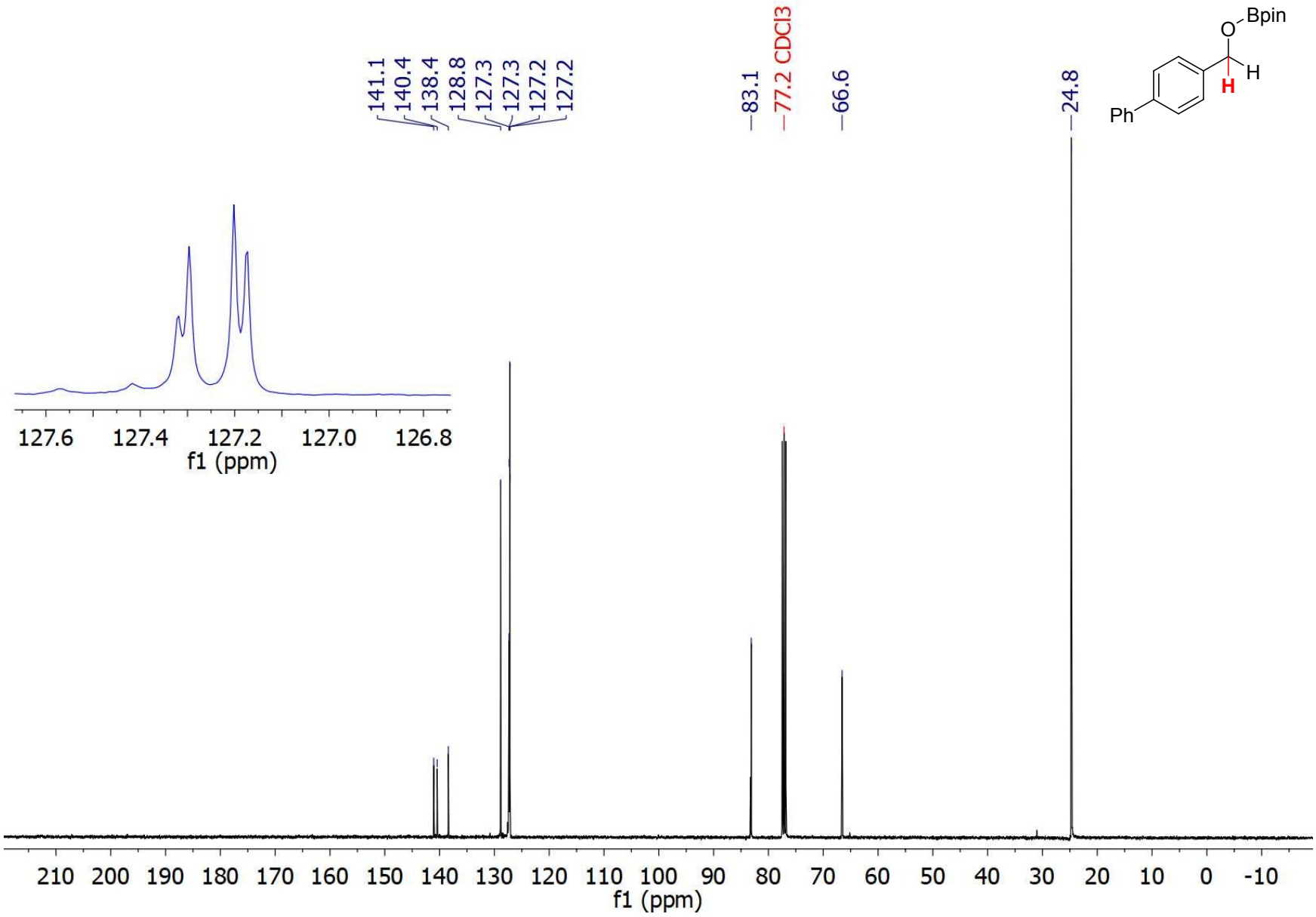


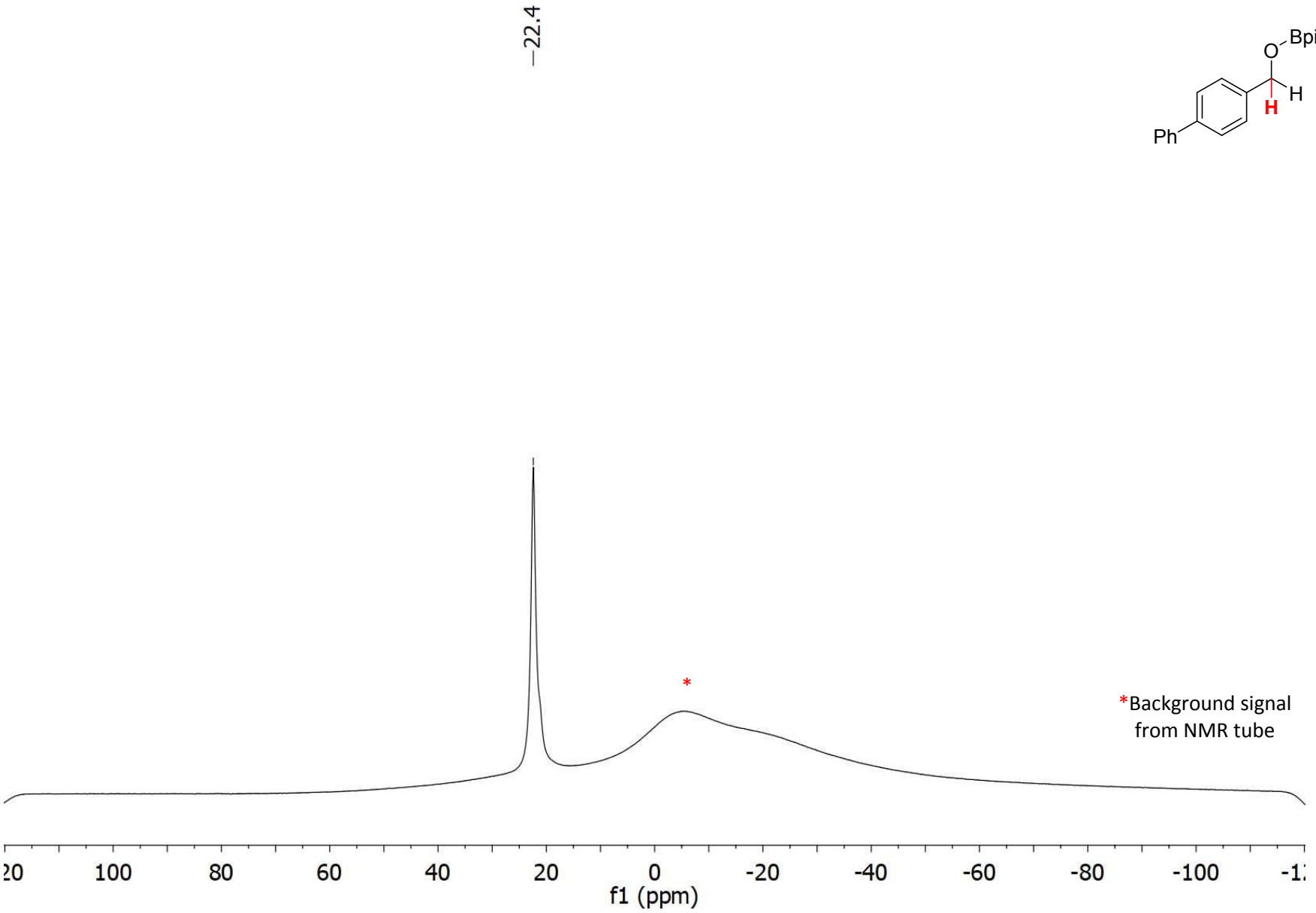

144.6
132.1
126.8
118.8
111.1
83.3
77.0 CDCl3
65.7
24.6
Bpin
O
H
H
NC
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-22.5
Bpin
O
H
H
NC
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
*
*Background signal
from NMR tube
20
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
f1 (ppm)

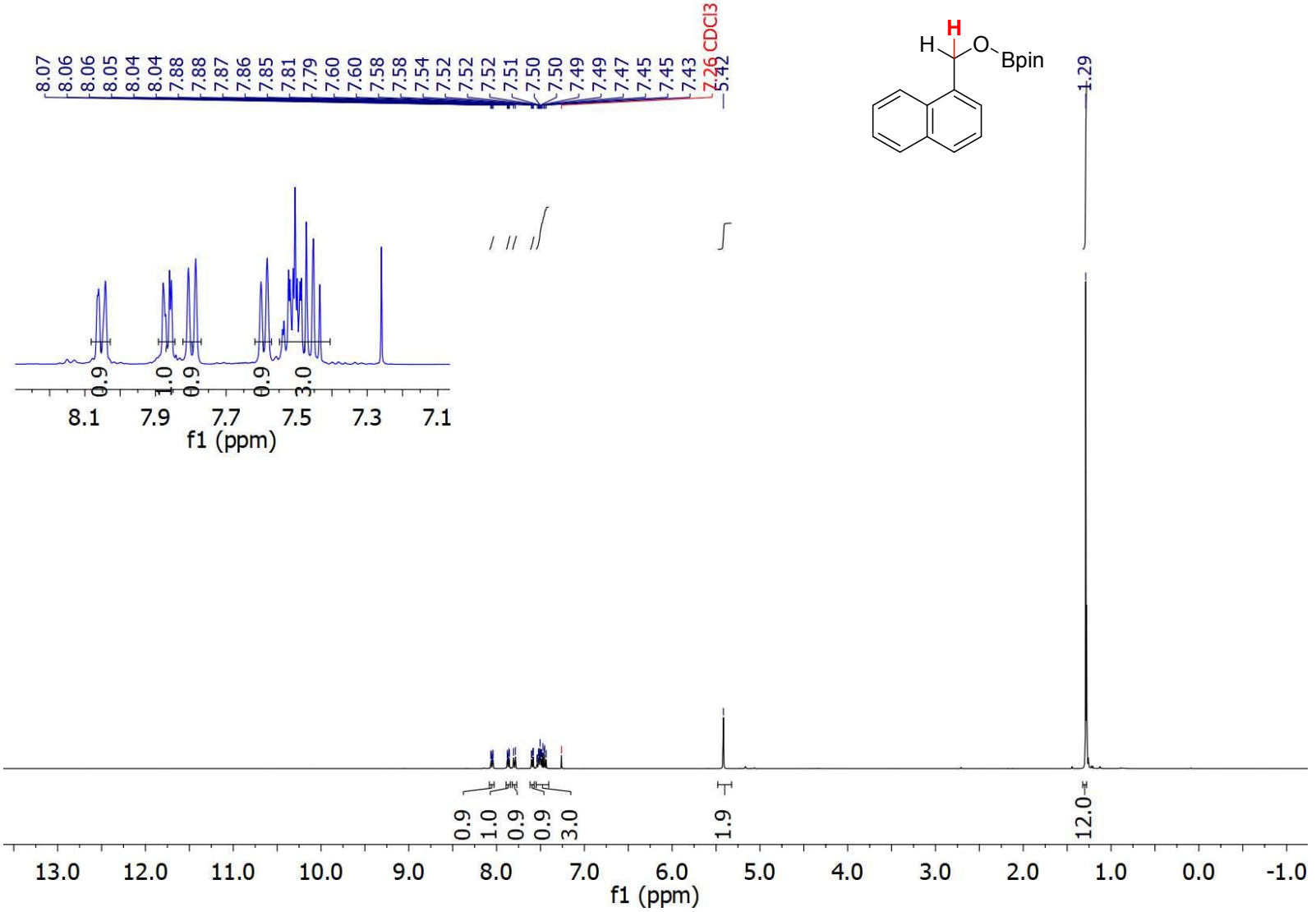
4,4,5,5-tetramethyl-2-((4-phenylbenzyl)oxy)-1,3,2-dioxaborolane (**3l**)

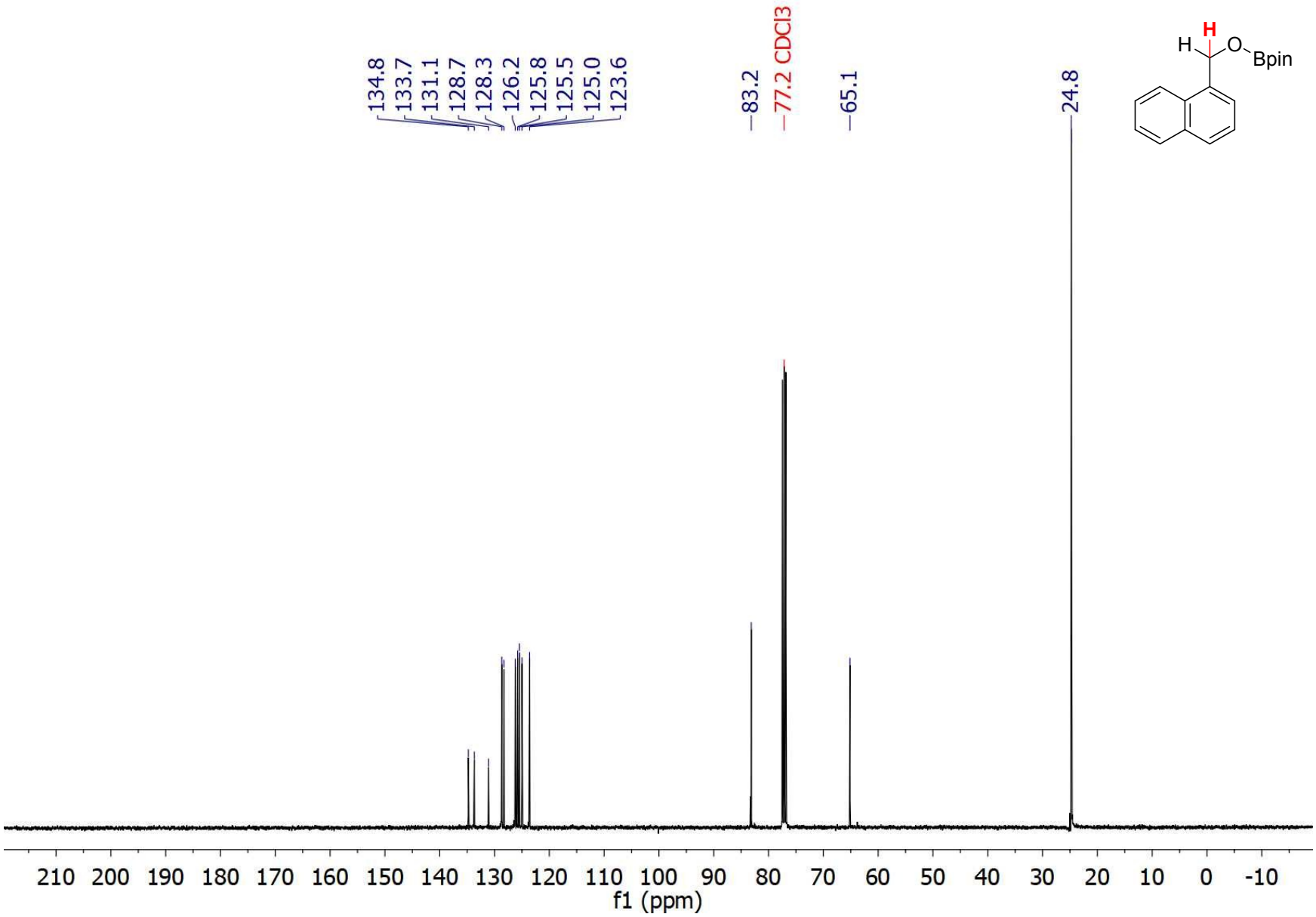


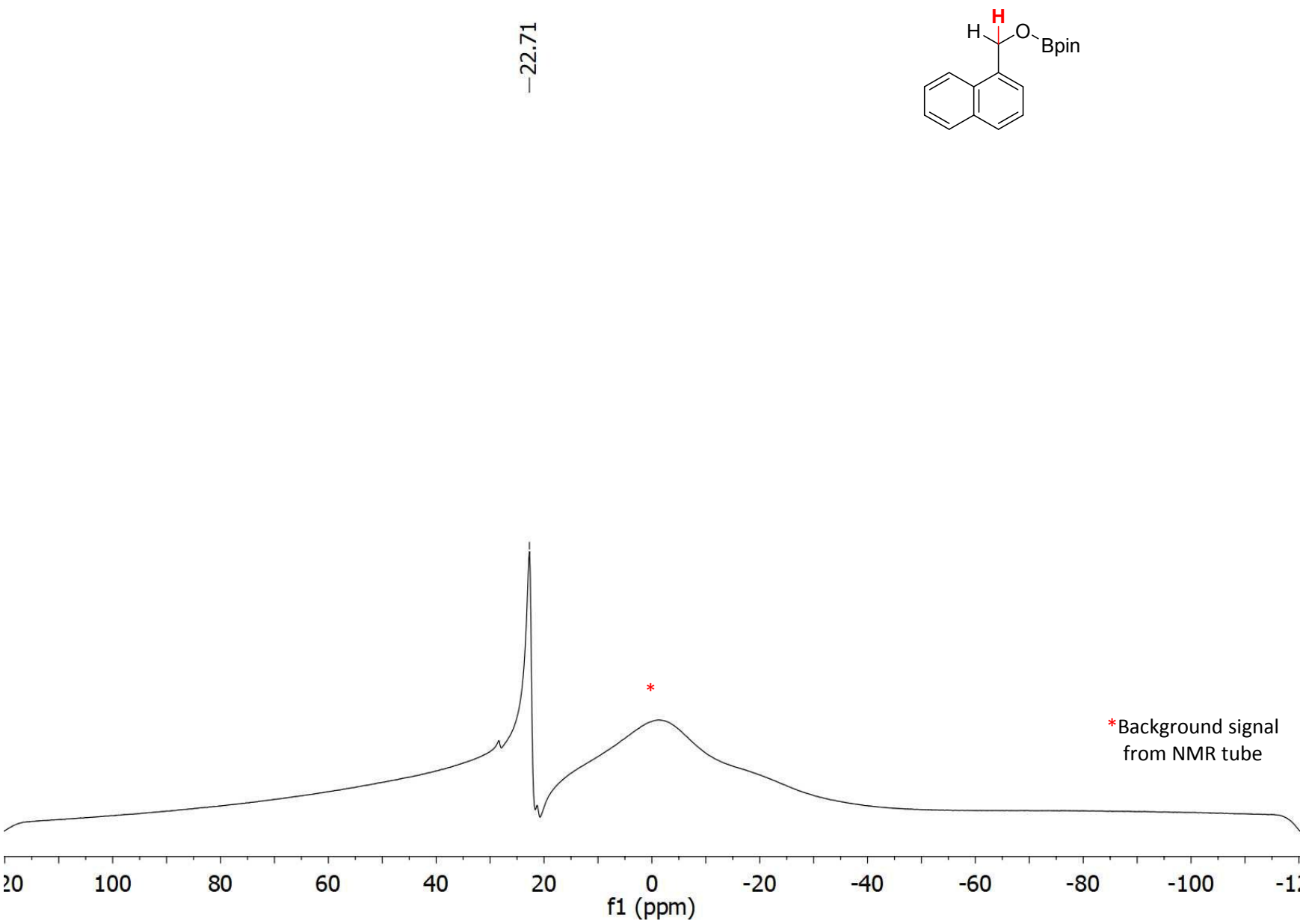

141.1
140.4
138.4
128.8
127.3
127.3
127.2
127.2
83.1
77.2 CDCl3
66.6
24.8
Bpin
O
H
H
Ph
127.6
127.4
127.2
127.0
126.8
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


22.4
Bpin
O
H
H
Ph
*
*Background signal
from NMR tube
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

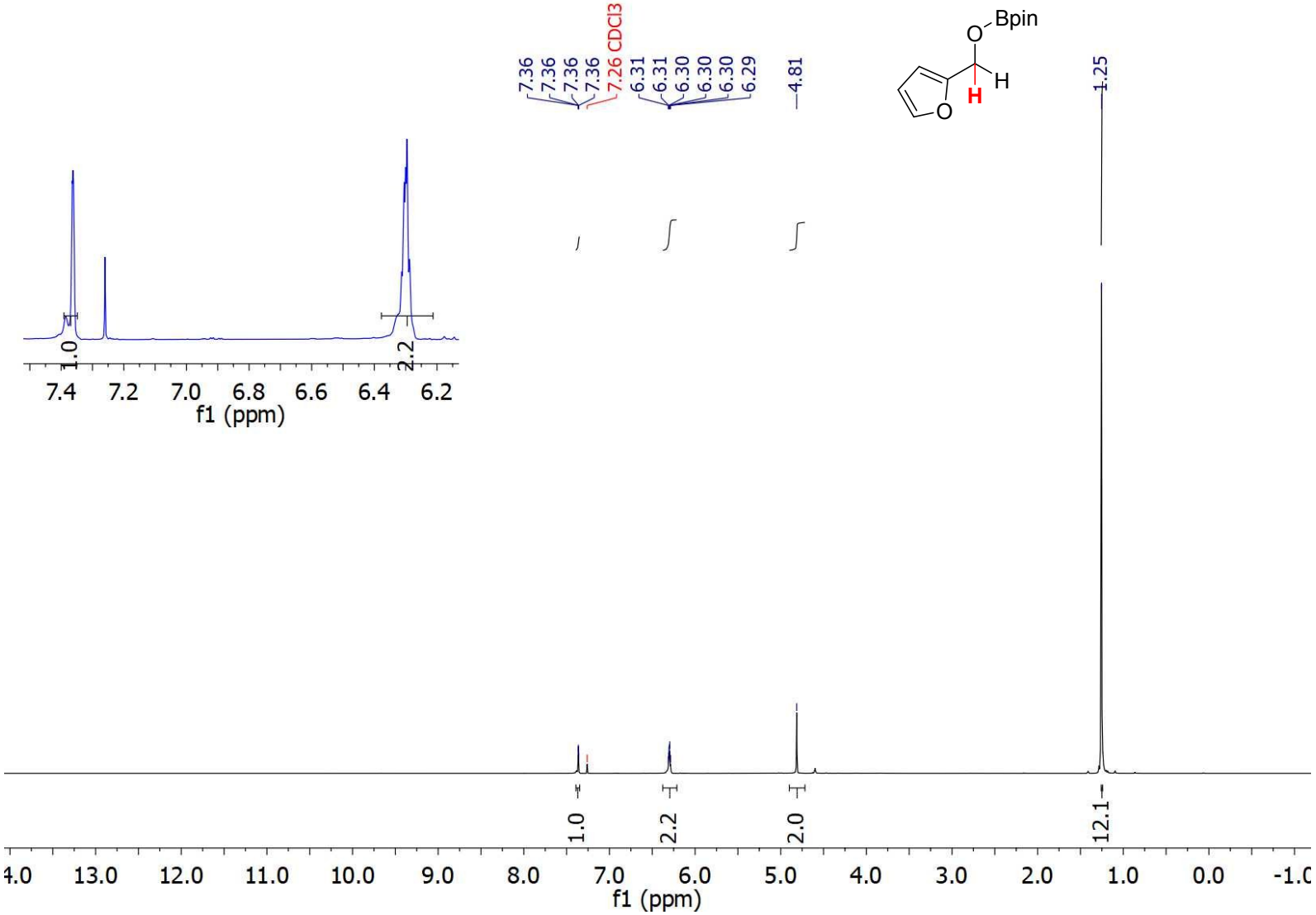
4,4,5,5-tetramethyl-2-((1-naphthylmethoxy)-1,3,2-dioxaborolane (**3m**)

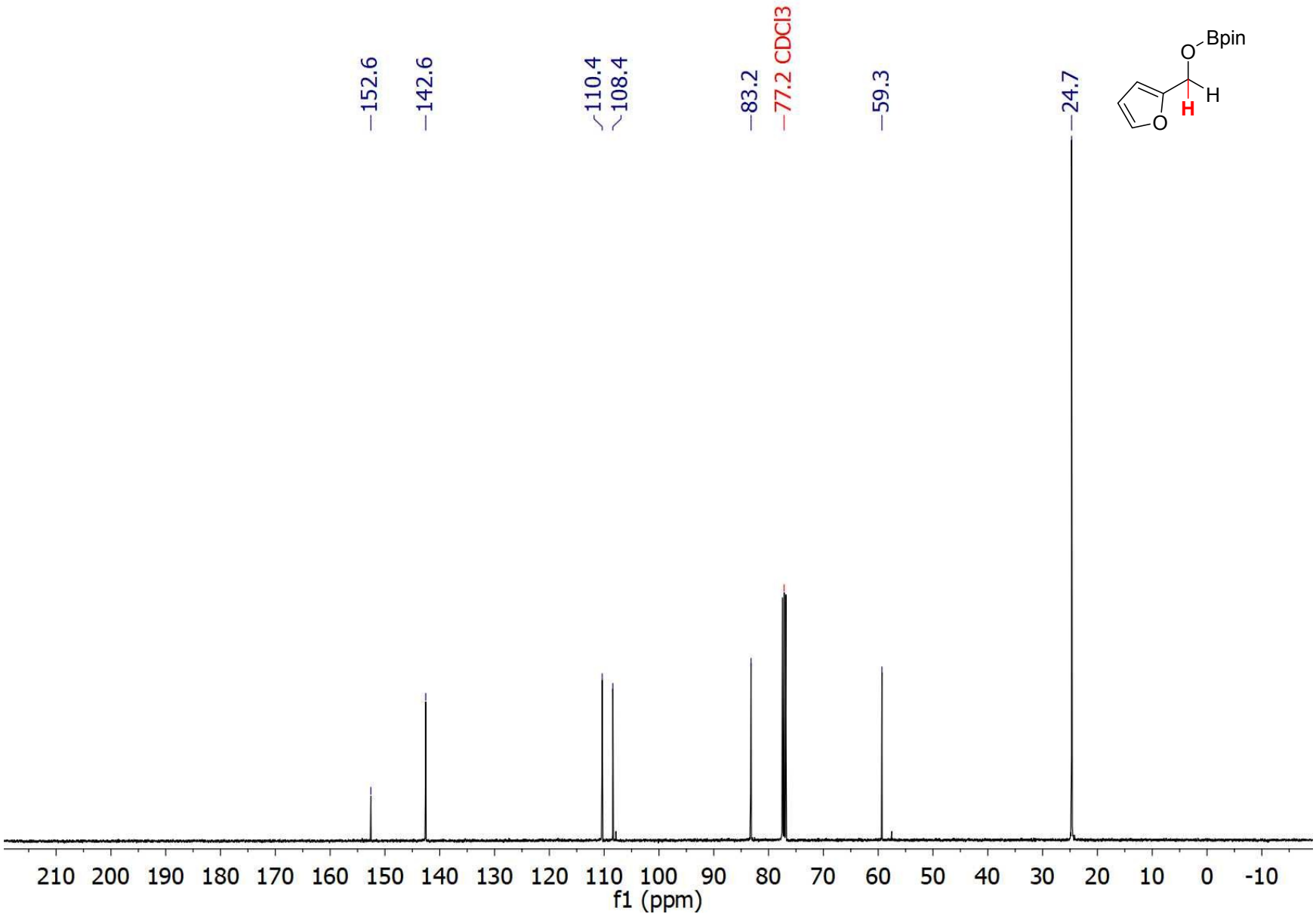


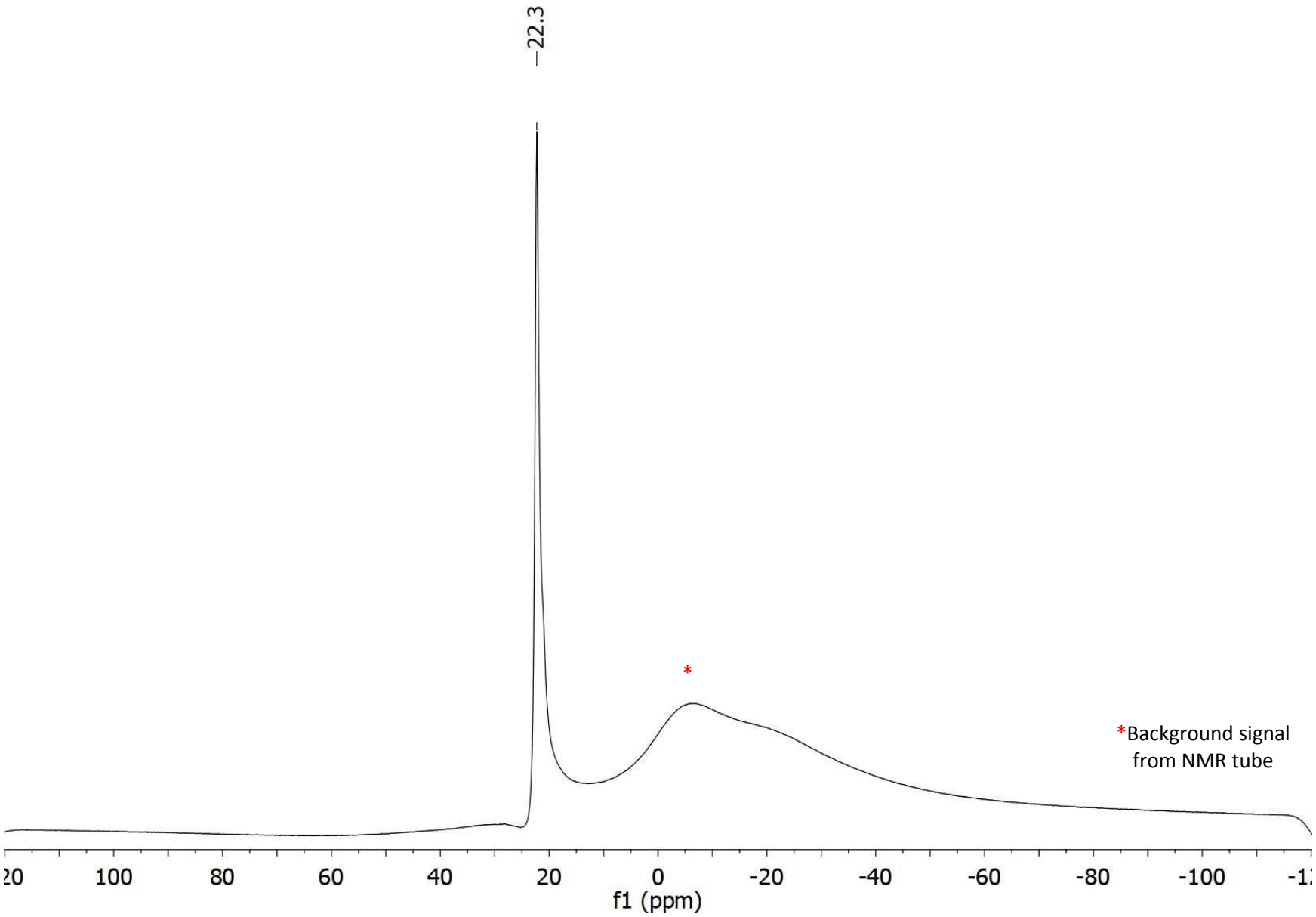

134.8
133.7
131.1
128.7
128.3
126.2
125.8
125.5
125.0
123.6
83.2
77.2 CDCl3
65.1
24.8
H
H
O
Bpin
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


22.71
H
H
O
Bpin
*
*Background signal
from NMR tube
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

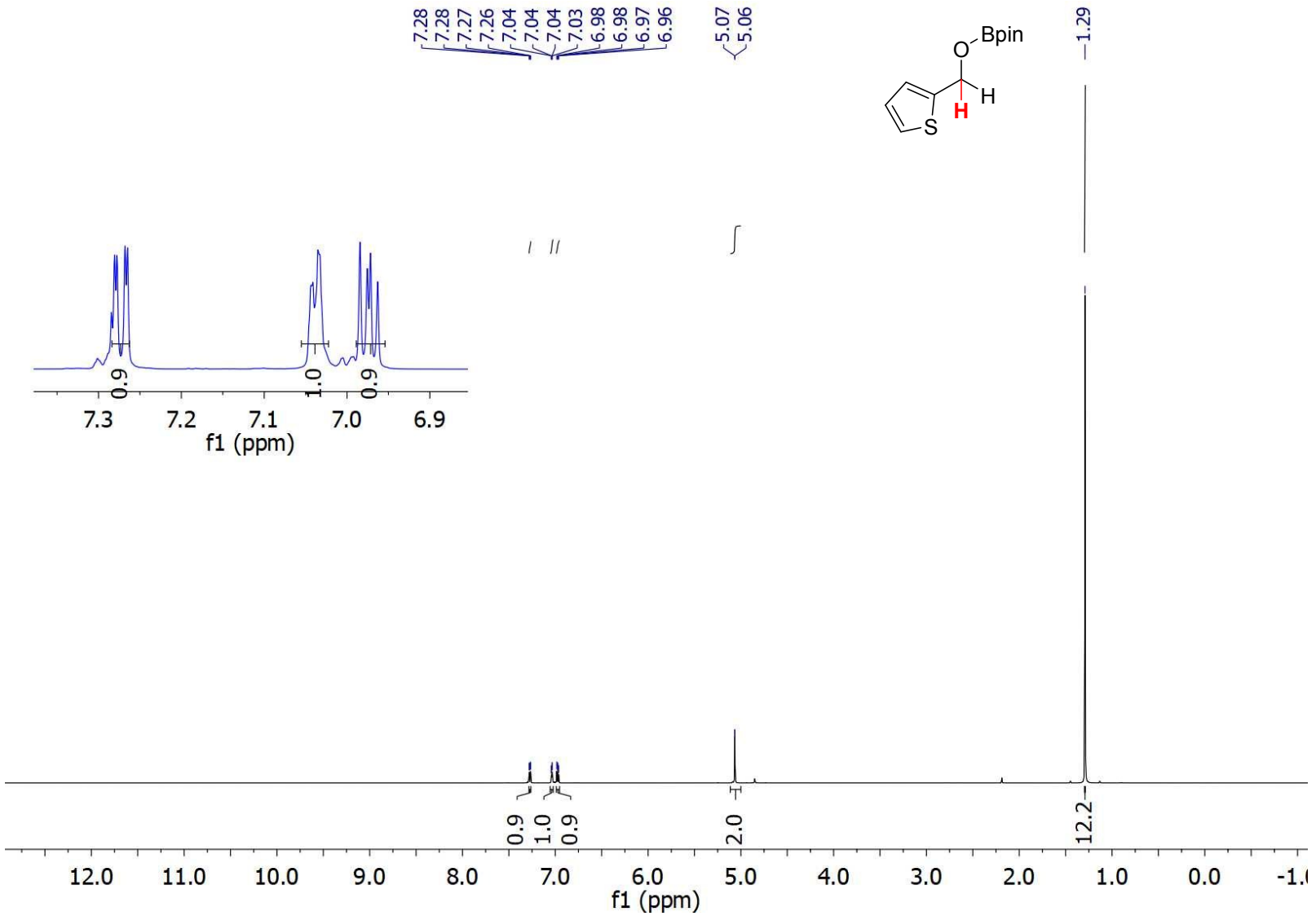
4,4,5,5-tetramethyl-2-(furan-2-ylmethoxy)-1,3,2-dioxaborolane (**3n**)

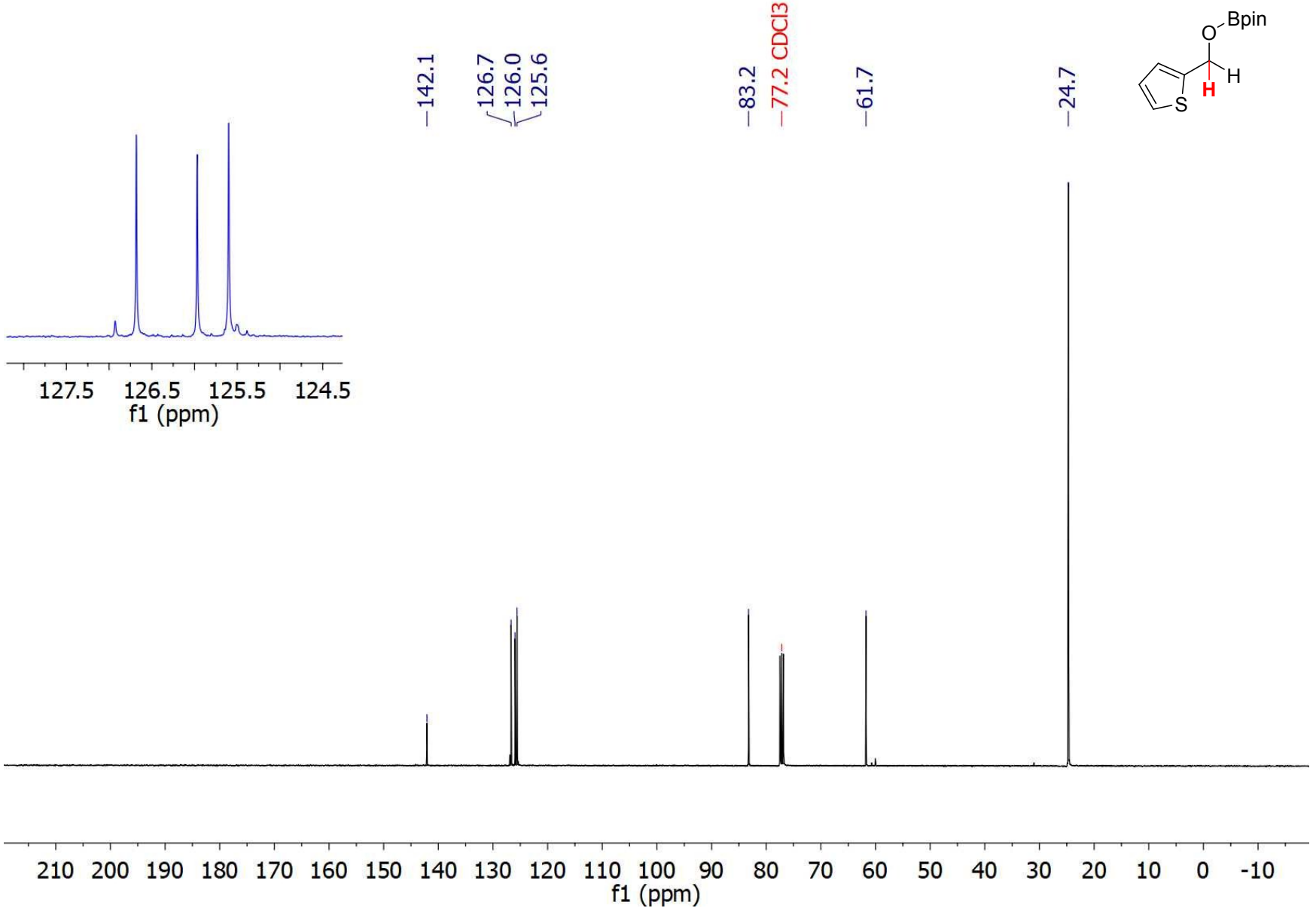


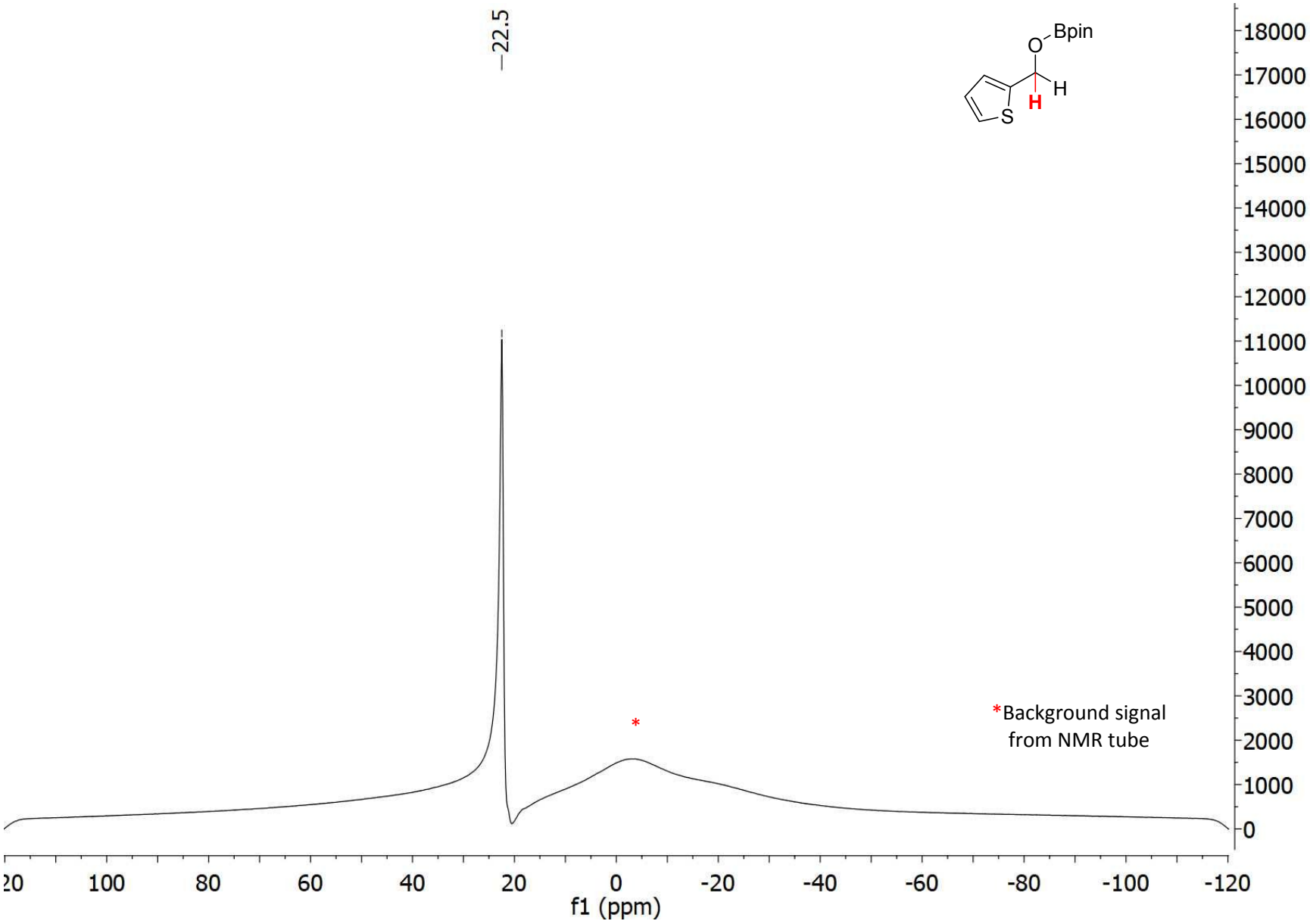

152.6
142.6
110.4
108.4
83.2
77.2 CDCl3
59.3
24.7
Bpin
O
H
H
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


22.3
*
*Background signal
from NMR tube
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

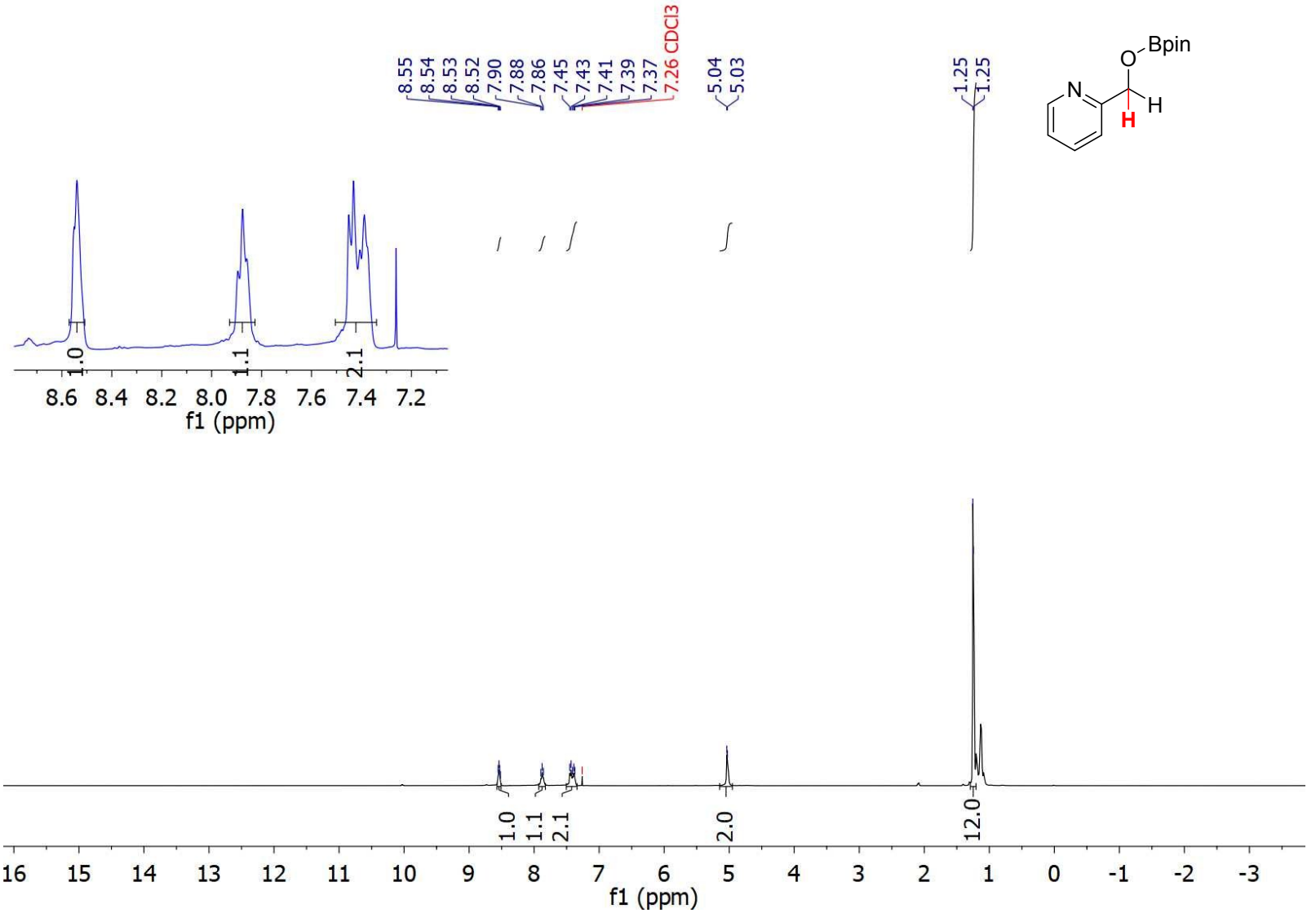
4,4,5,5-tetramethyl-2-(thiophen-2-ylmethoxy)-1,3,2-dioxaborolane (**3o**)

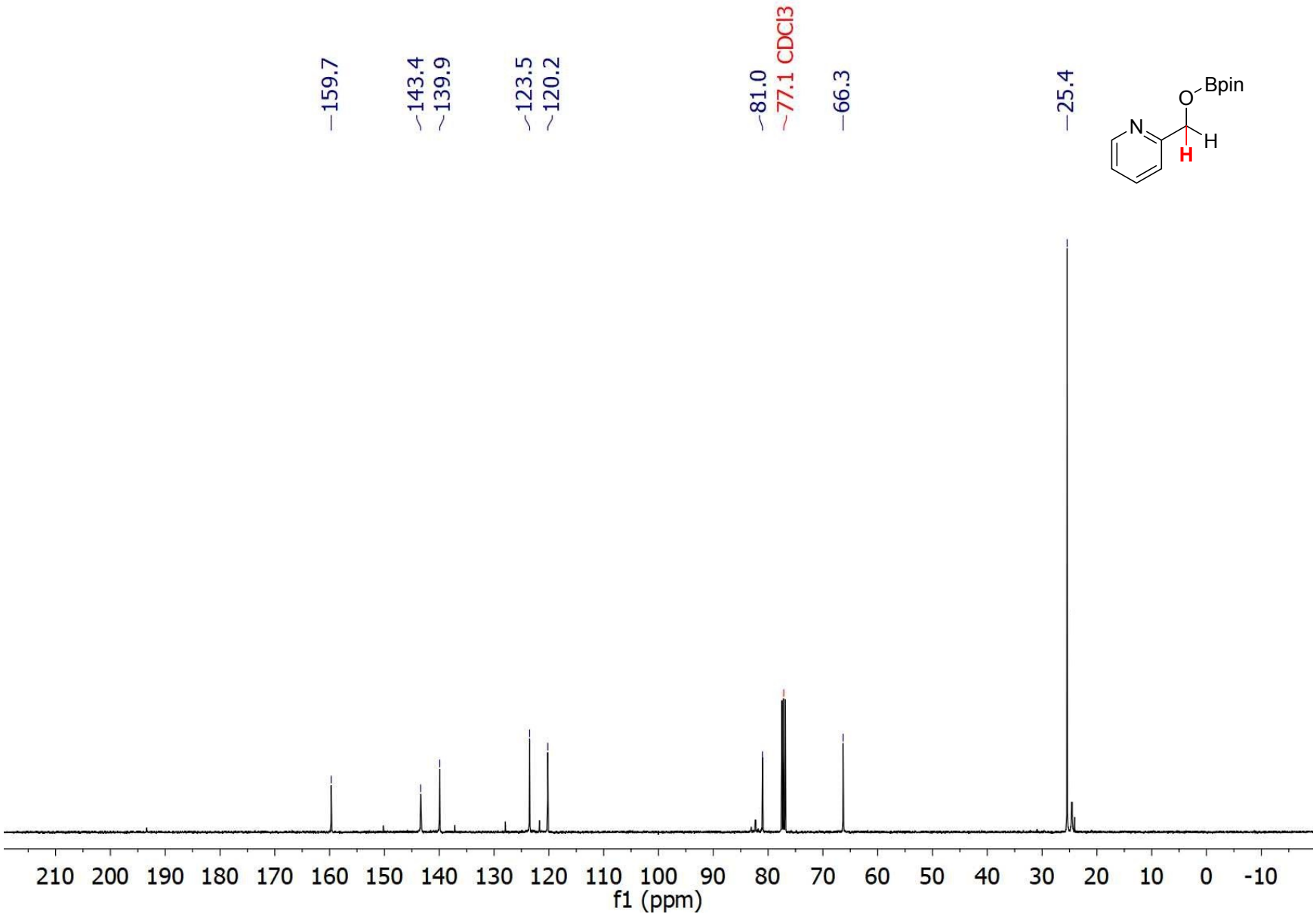


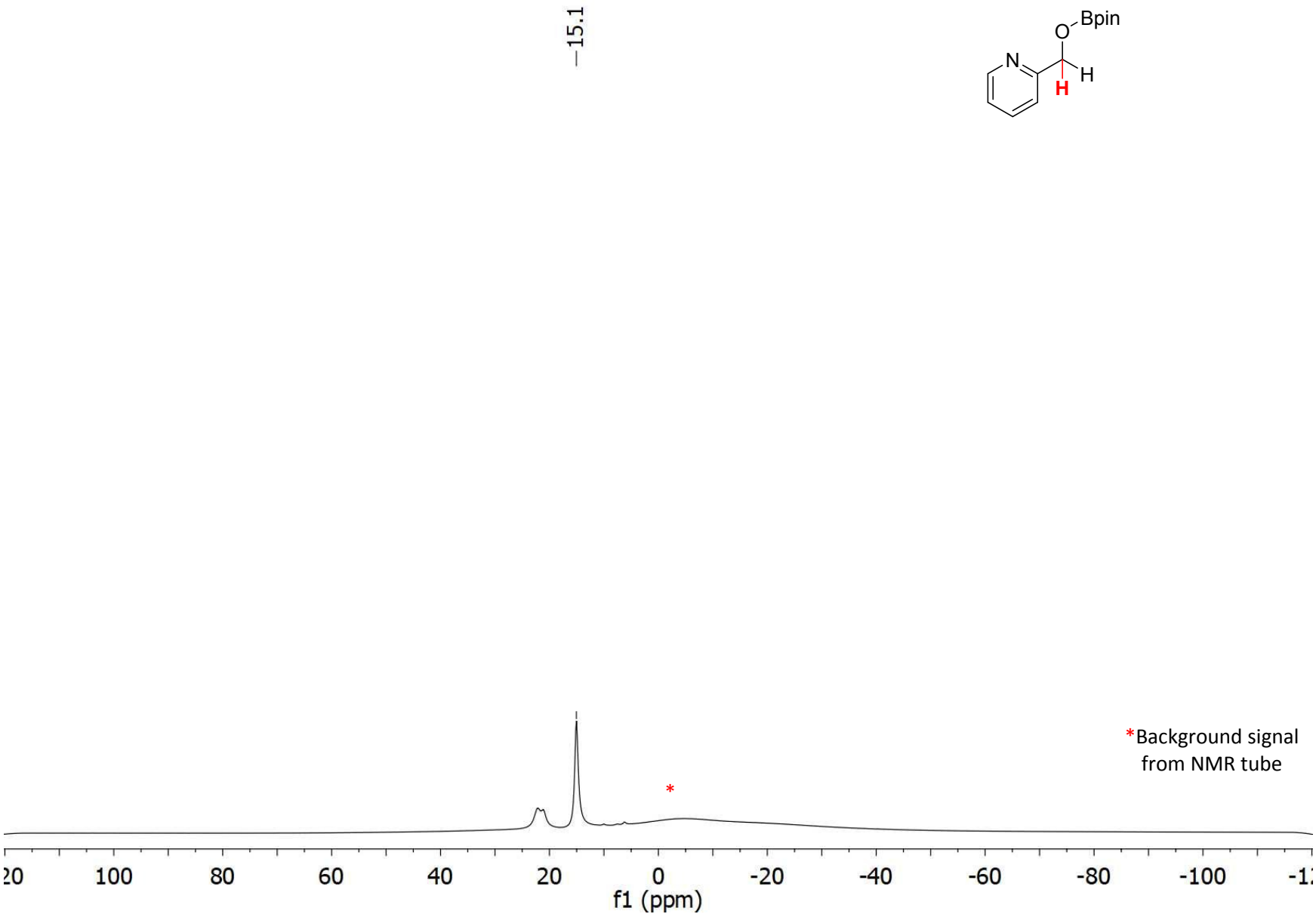

142.1
126.7
126.0
125.6
83.2
77.2 CDCl3
61.7
24.7
Bpin
O
H
H
S
127.5 126.5 125.5 124.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-22.5
Bpin
O
H
H
S
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
*
*Background signal
from NMR tube
20
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
f1 (ppm)

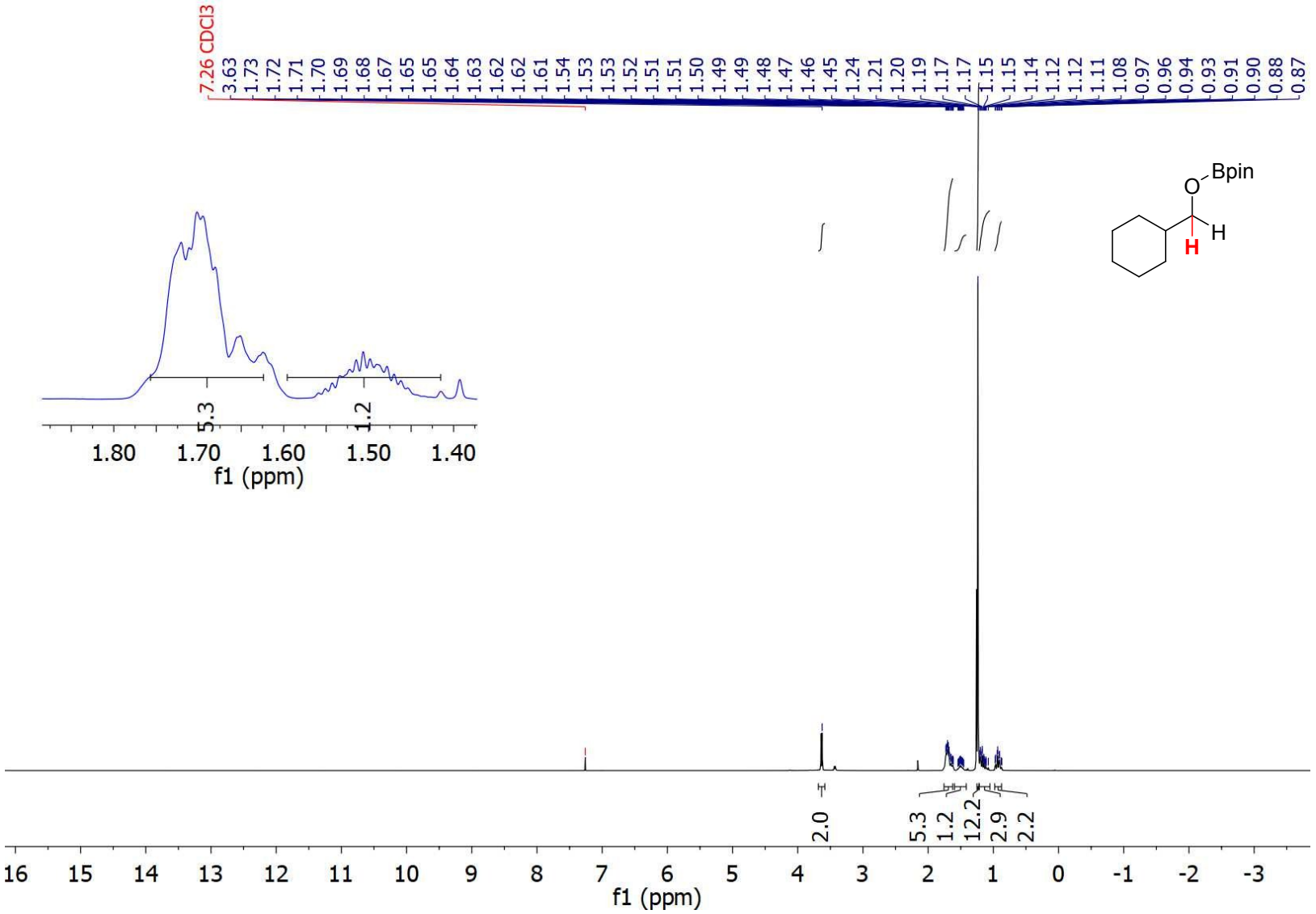
4,4,5,5-tetramethyl-2-(pyridine-2ylmethoxy)-1,3,2-dioxaborolane (**3p**)

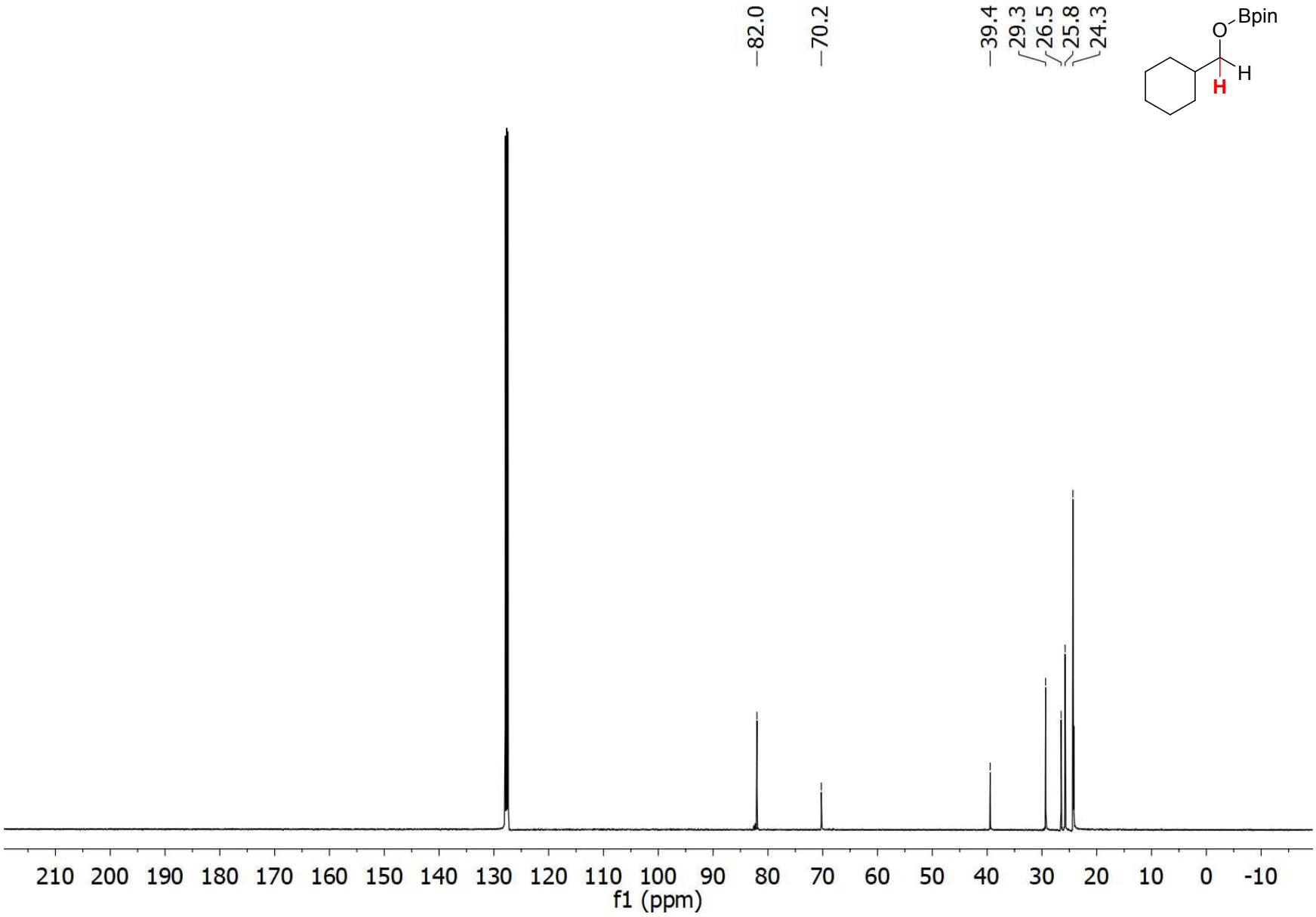


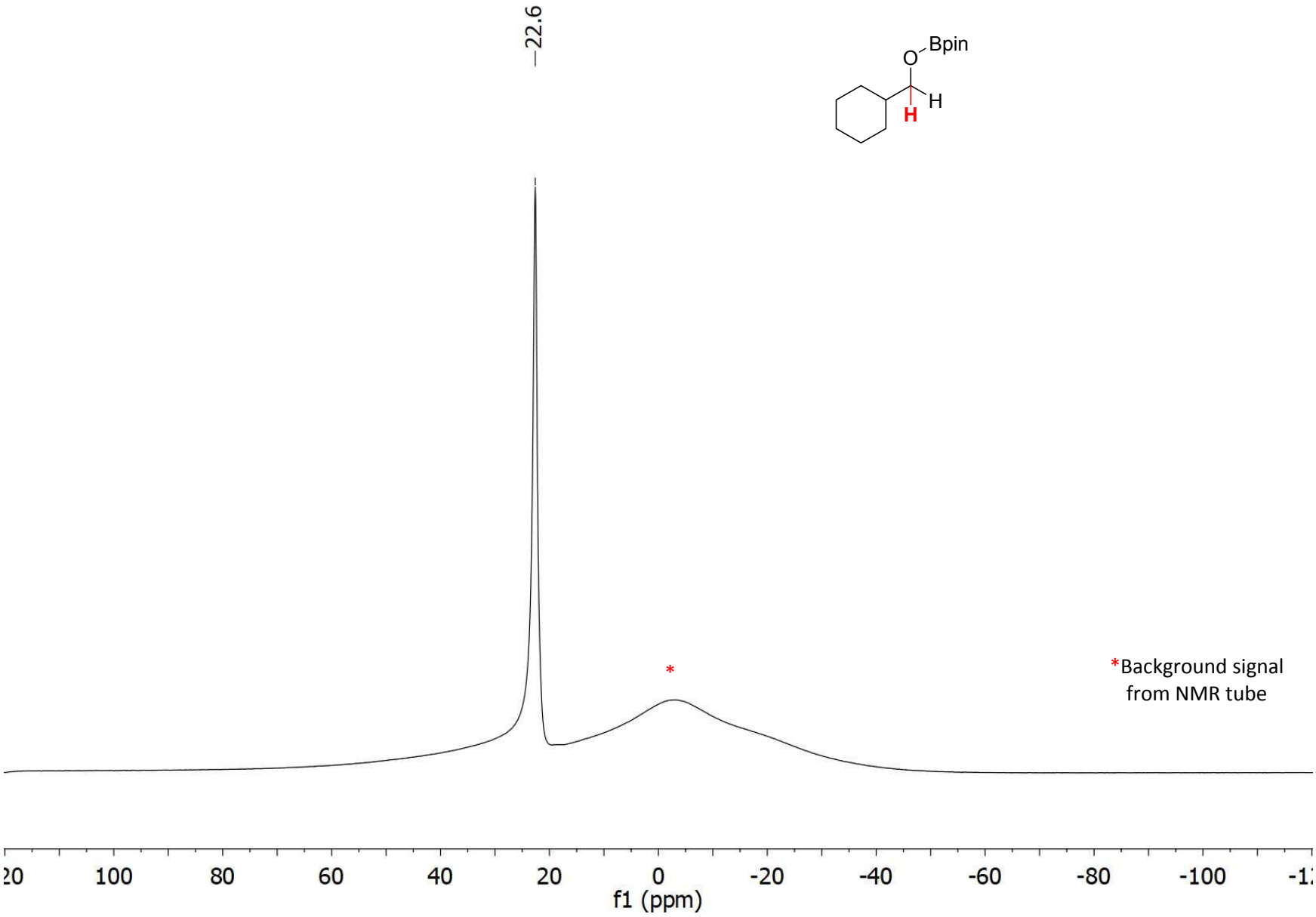

159.7
143.4
139.9
123.5
120.2
81.0
77.1 CDCl3
66.3
25.4
Bpin
O
N
H
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


−15.1
Bpin
O
N
H
H
*Background signal
from NMR tube
*
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

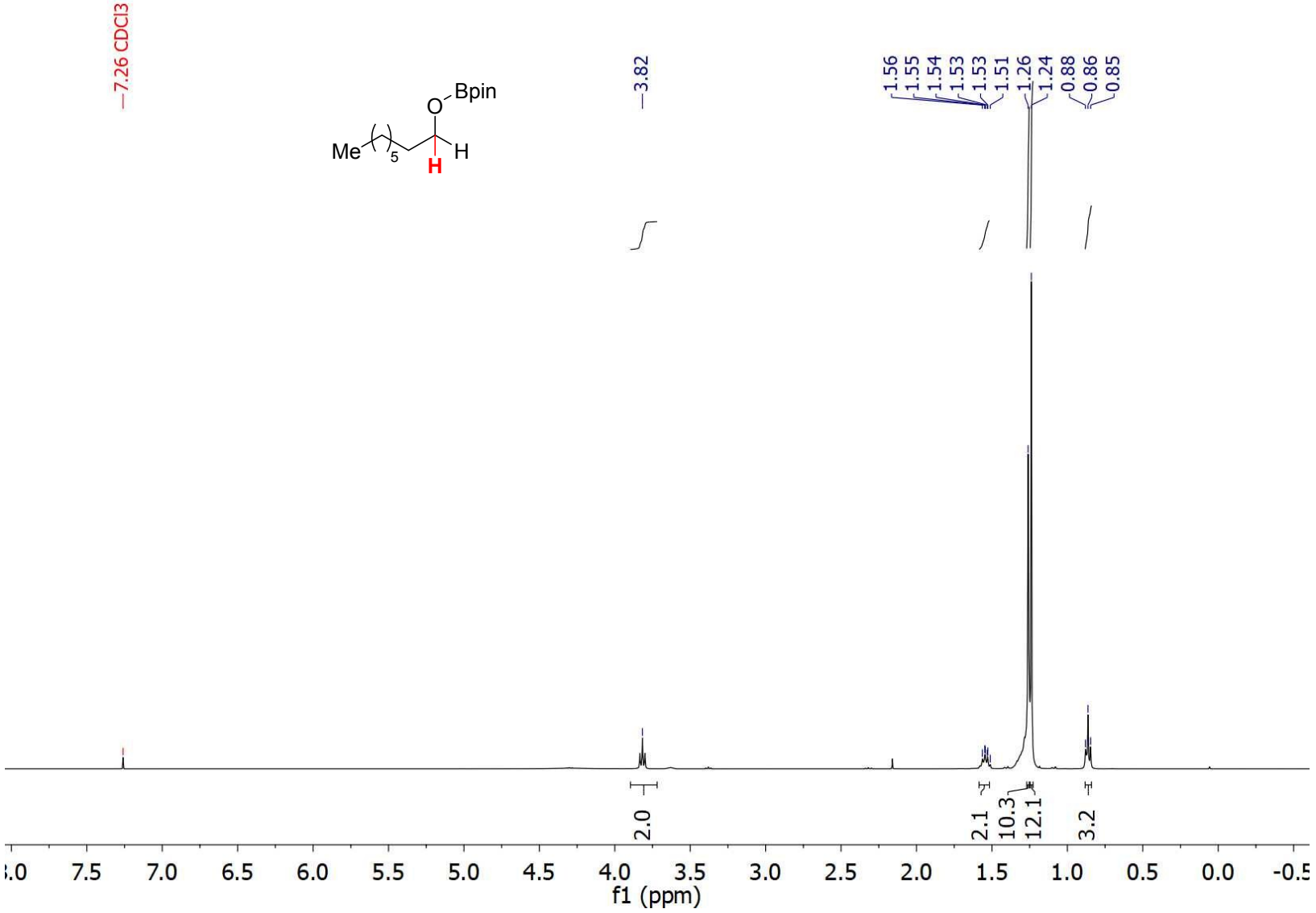
4,4,5,5-tetramethyl-2-(cyclohexylmethoxy)-1,3,2-dioxaborolane (**3q**)

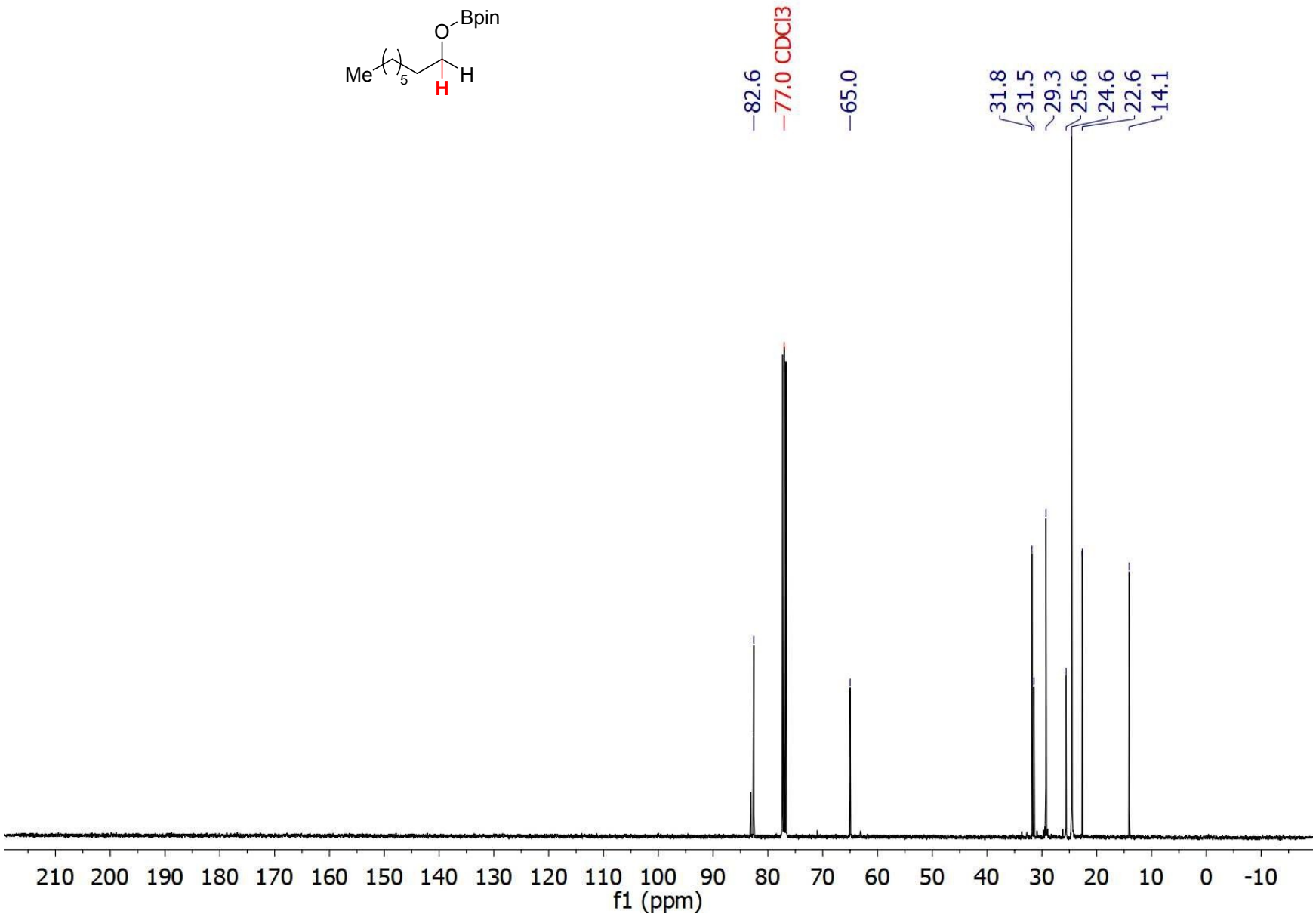


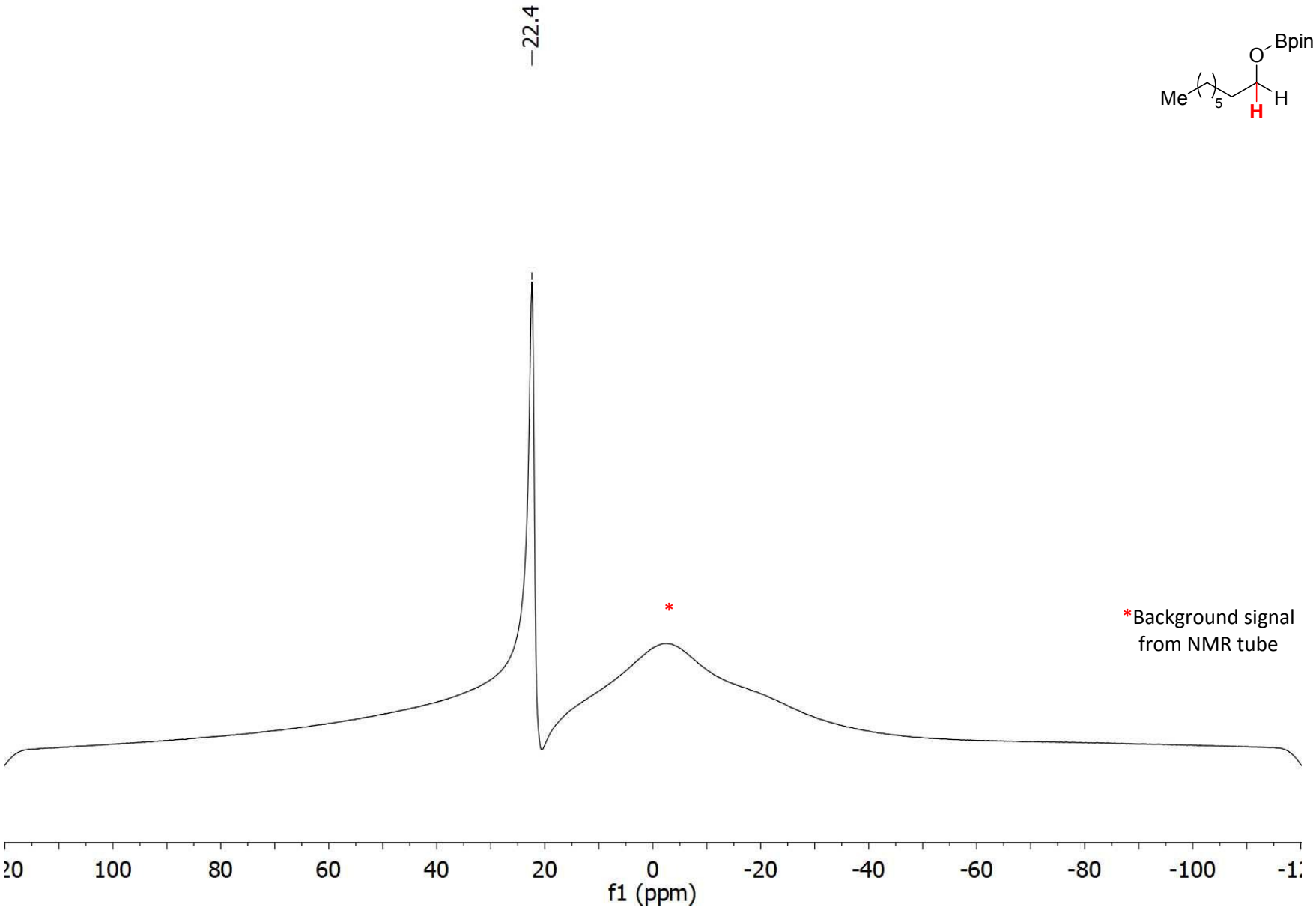

82.0
70.2
39.4
29.3
26.5
25.8
24.3
Bpin
O
H
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


22.6
Bpin
O
H
H
*
*Background signal
from NMR tube
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

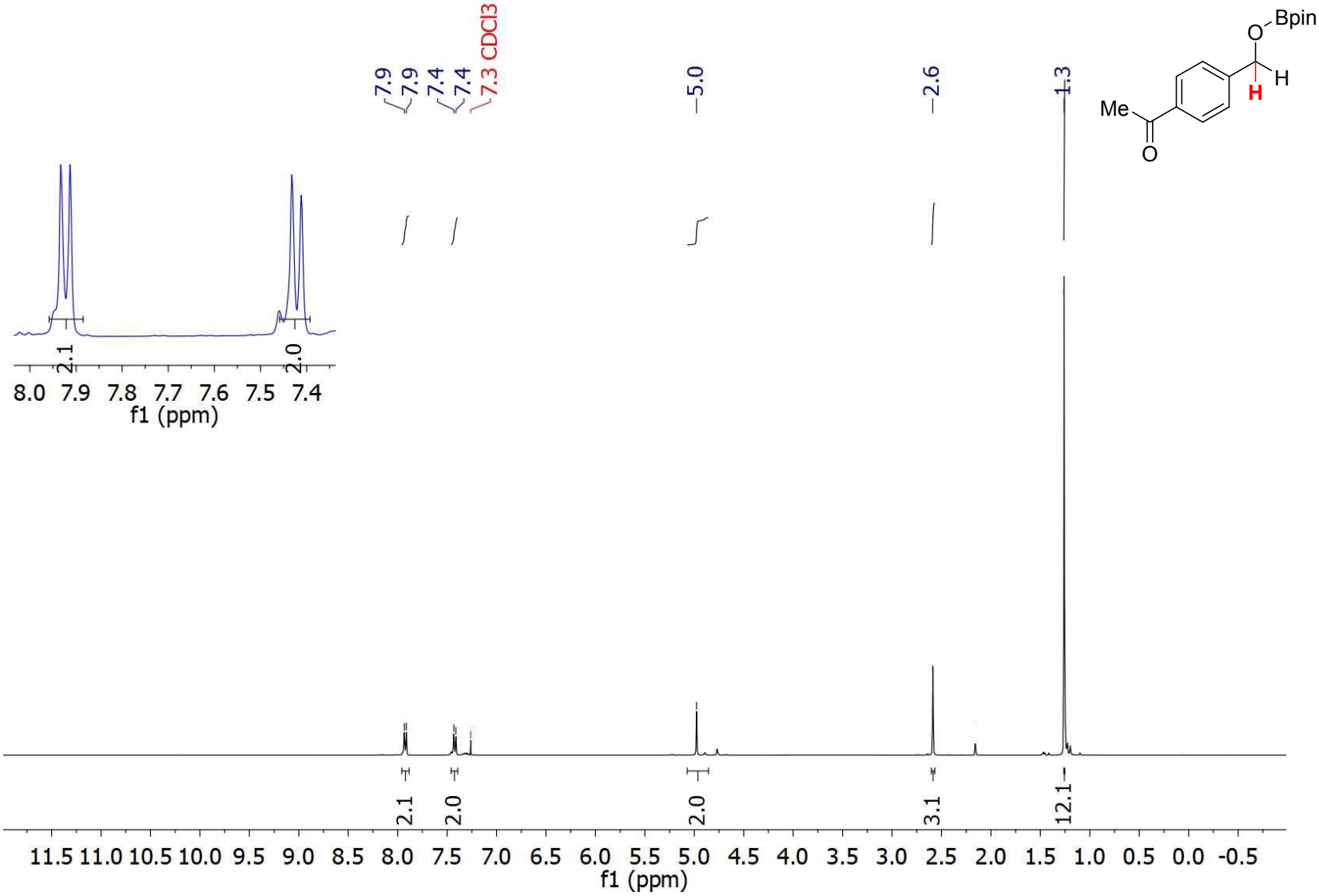
4,4,5,5-tetramethyl-2-(octanoxy)-1,3,2-dioxaborolane (**3r**)

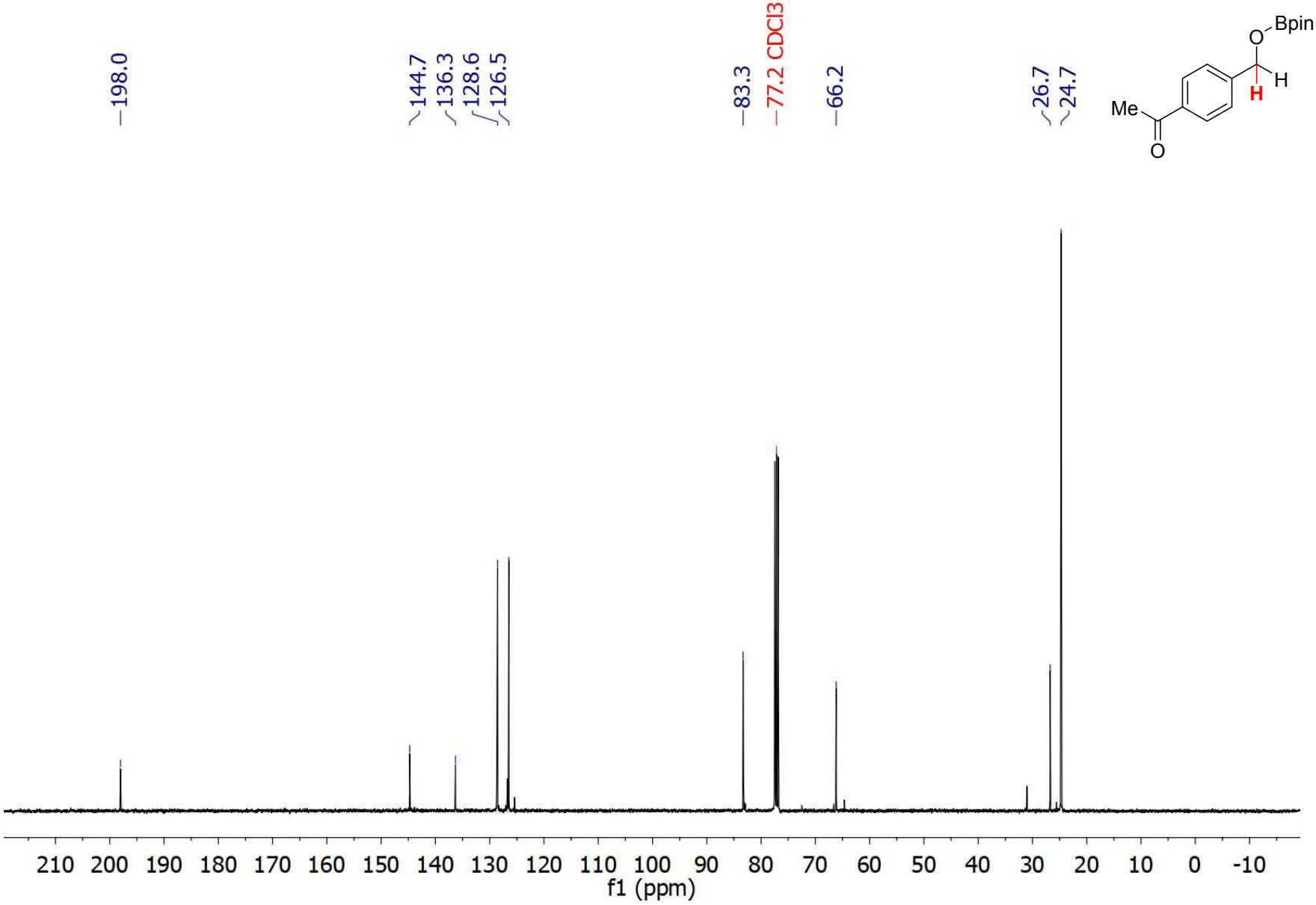


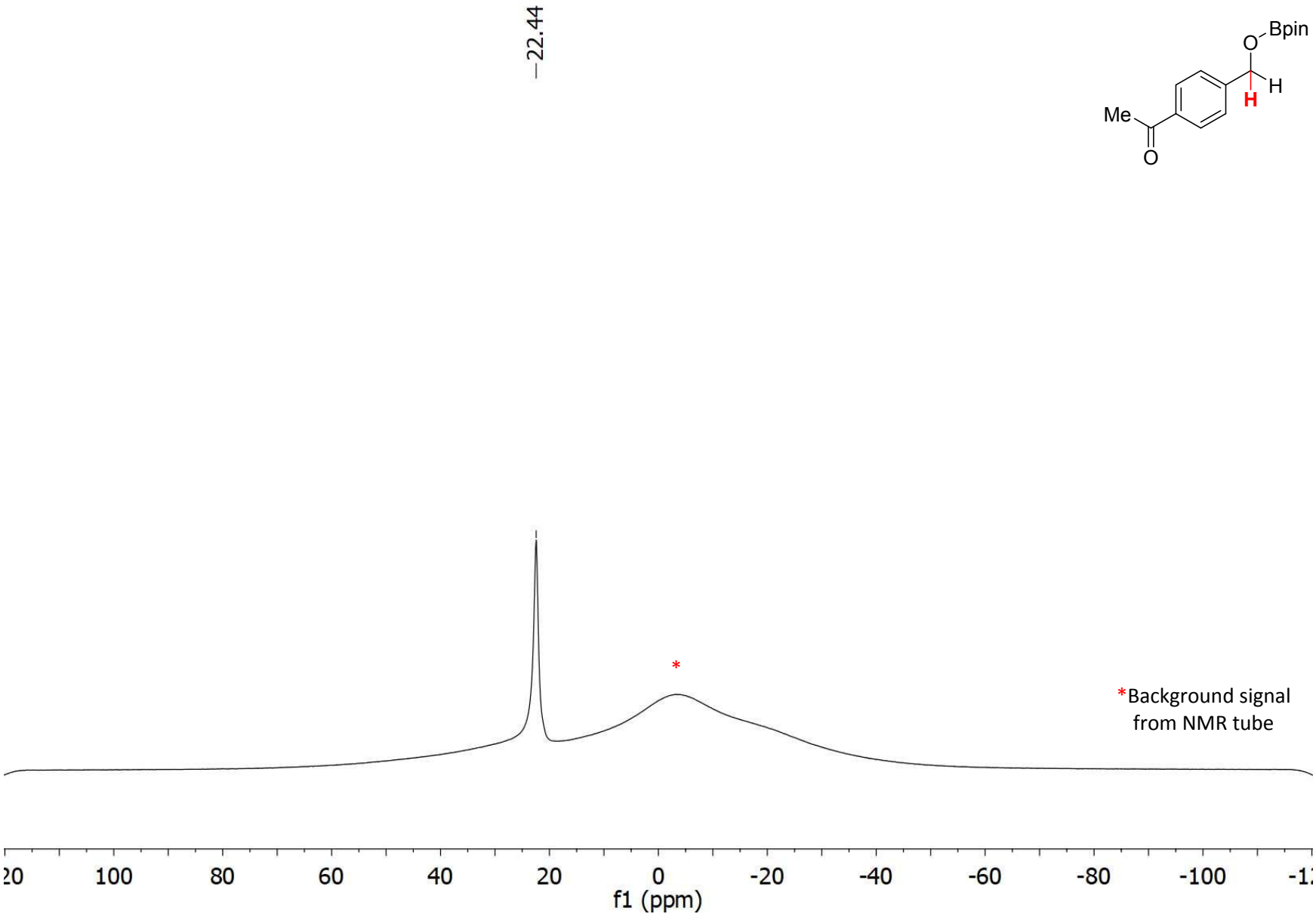

Bpin
O
Me
5
H
H
82.6
77.0 CDCl3
65.0
31.8
31.5
29.3
25.6
24.6
22.6
14.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


22.4
Bpin
O
Me
5
H
H
*
*Background signal
from NMR tube
20
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

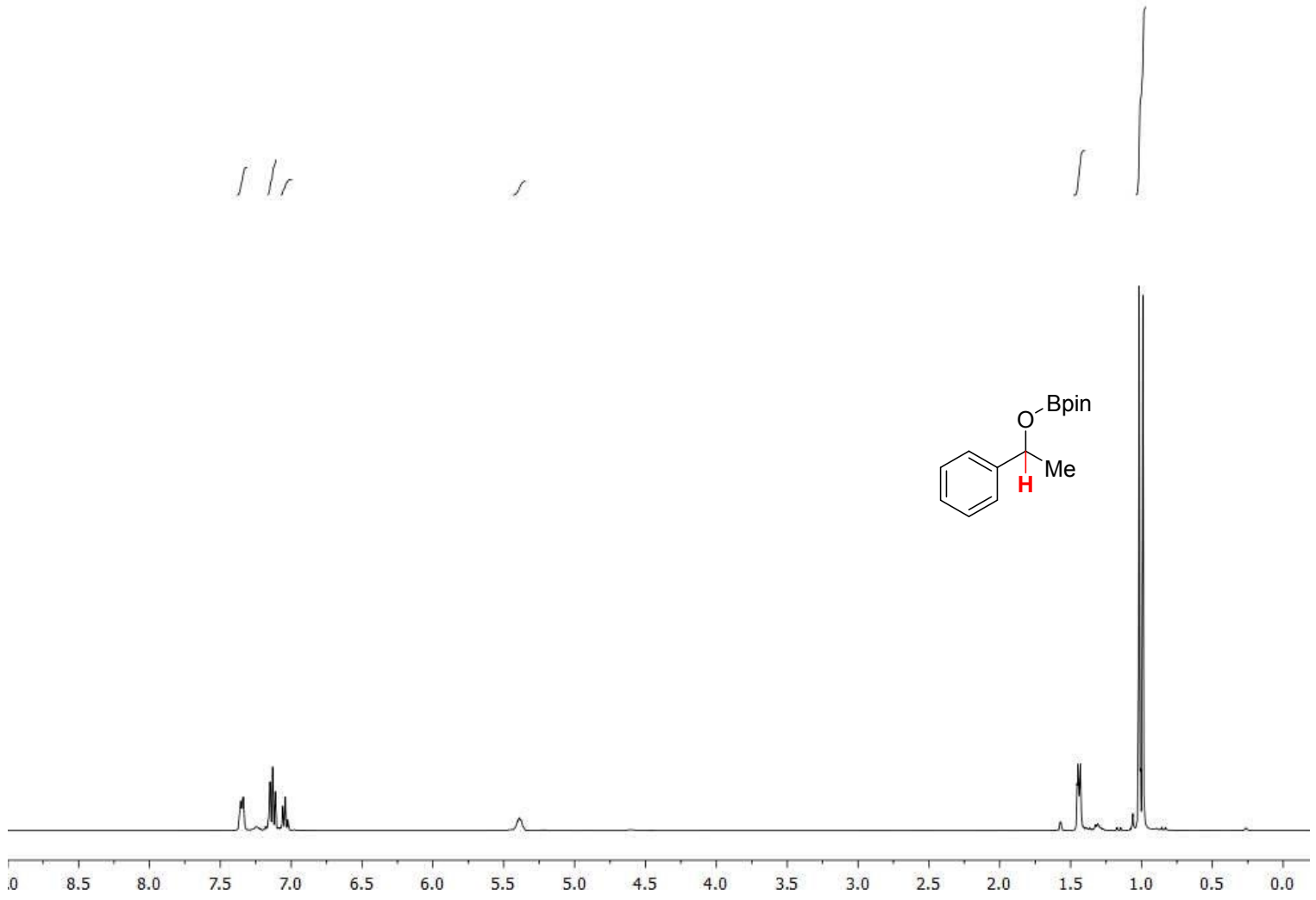
4,4,5,5-tetramethyl-2-((4-acetylbenzyl)oxy)-1,3,2-dioxaborolane (**3s**)

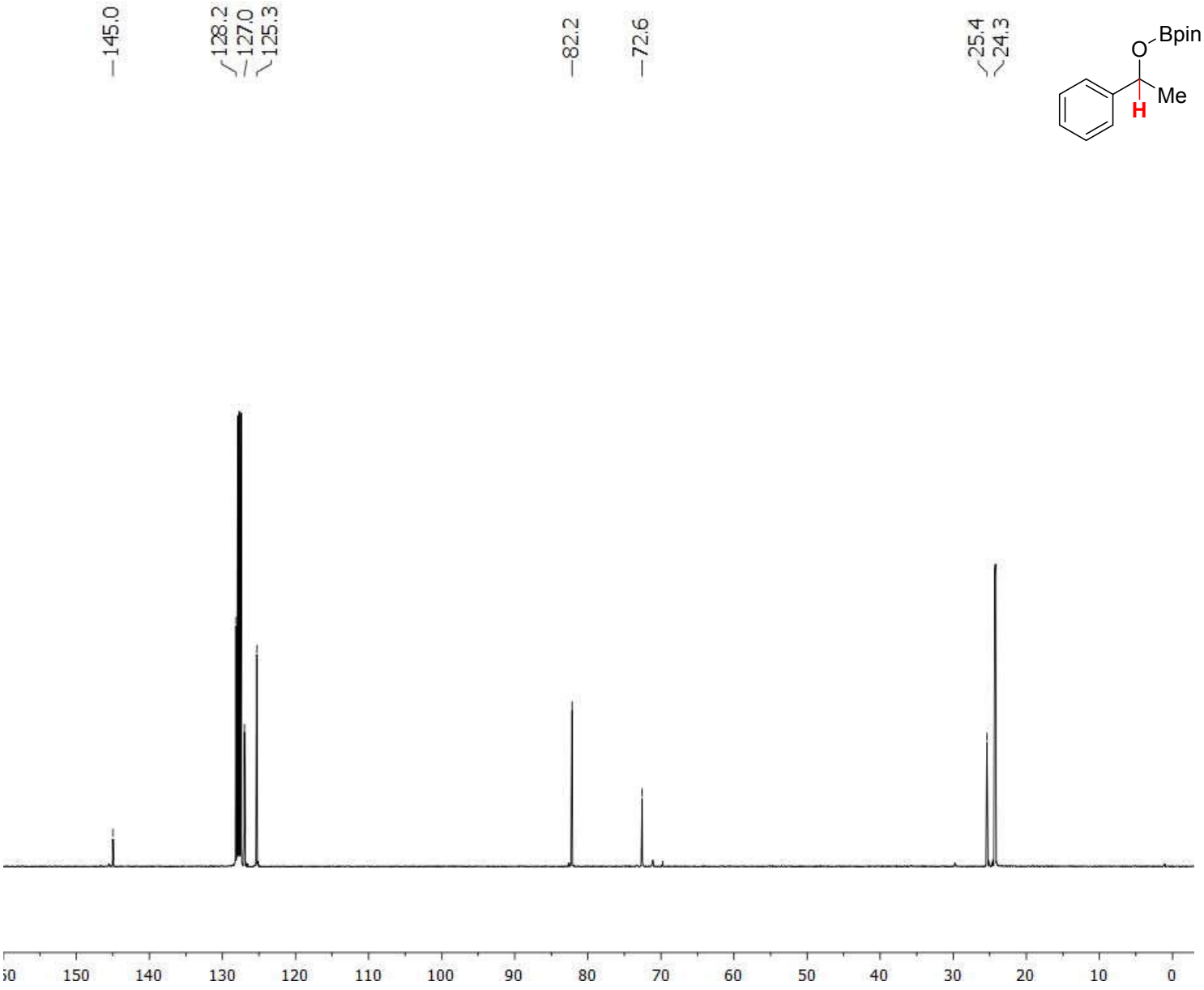


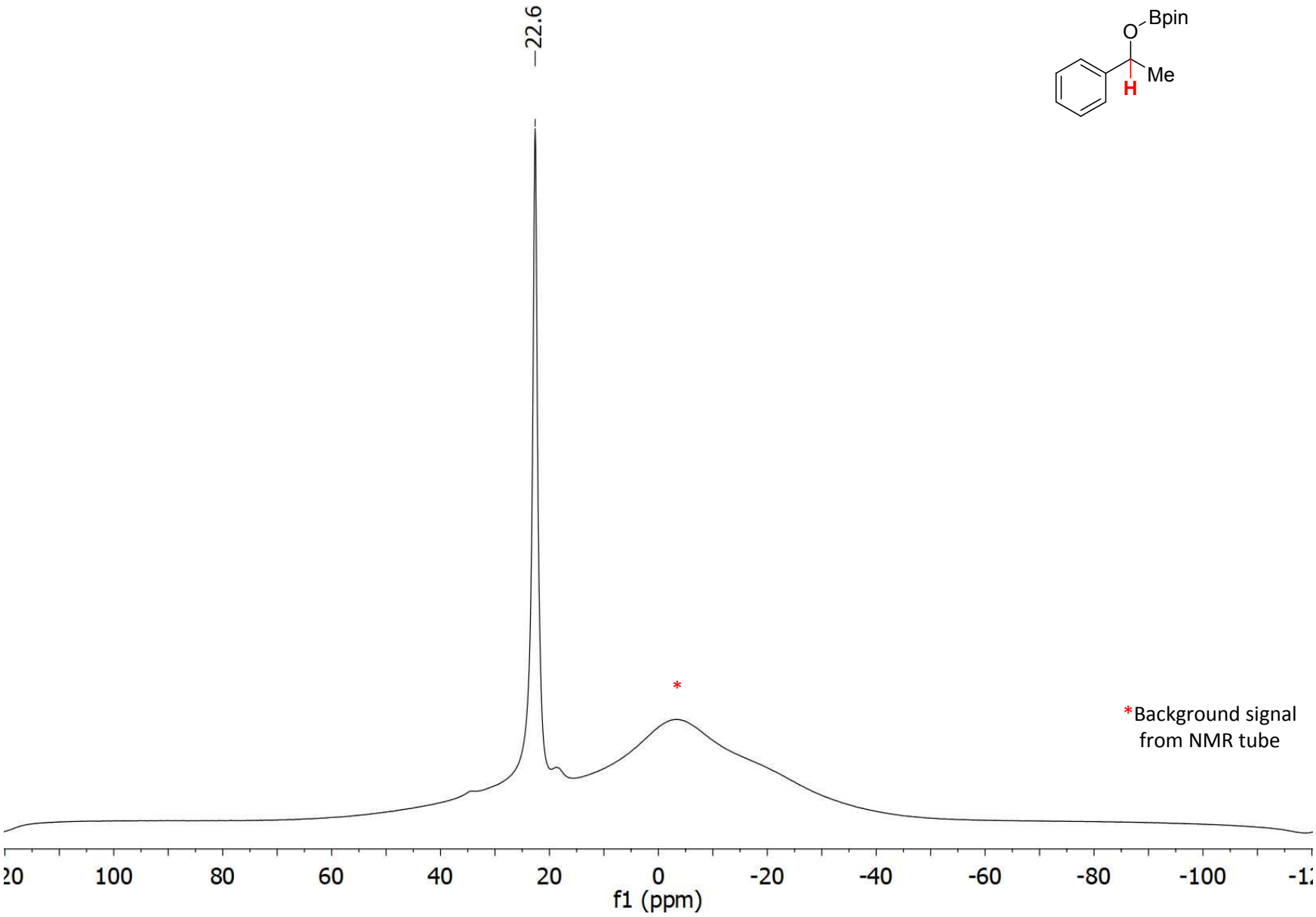

198.0
144.7
136.3
128.6
126.5
83.3
77.2 CDCl3
66.2
26.7
24.7
Bpin
O
H
H
Me
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


22.44
Bpin
O
H
H
Me
O
*
*Background signal
from NMR tube
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

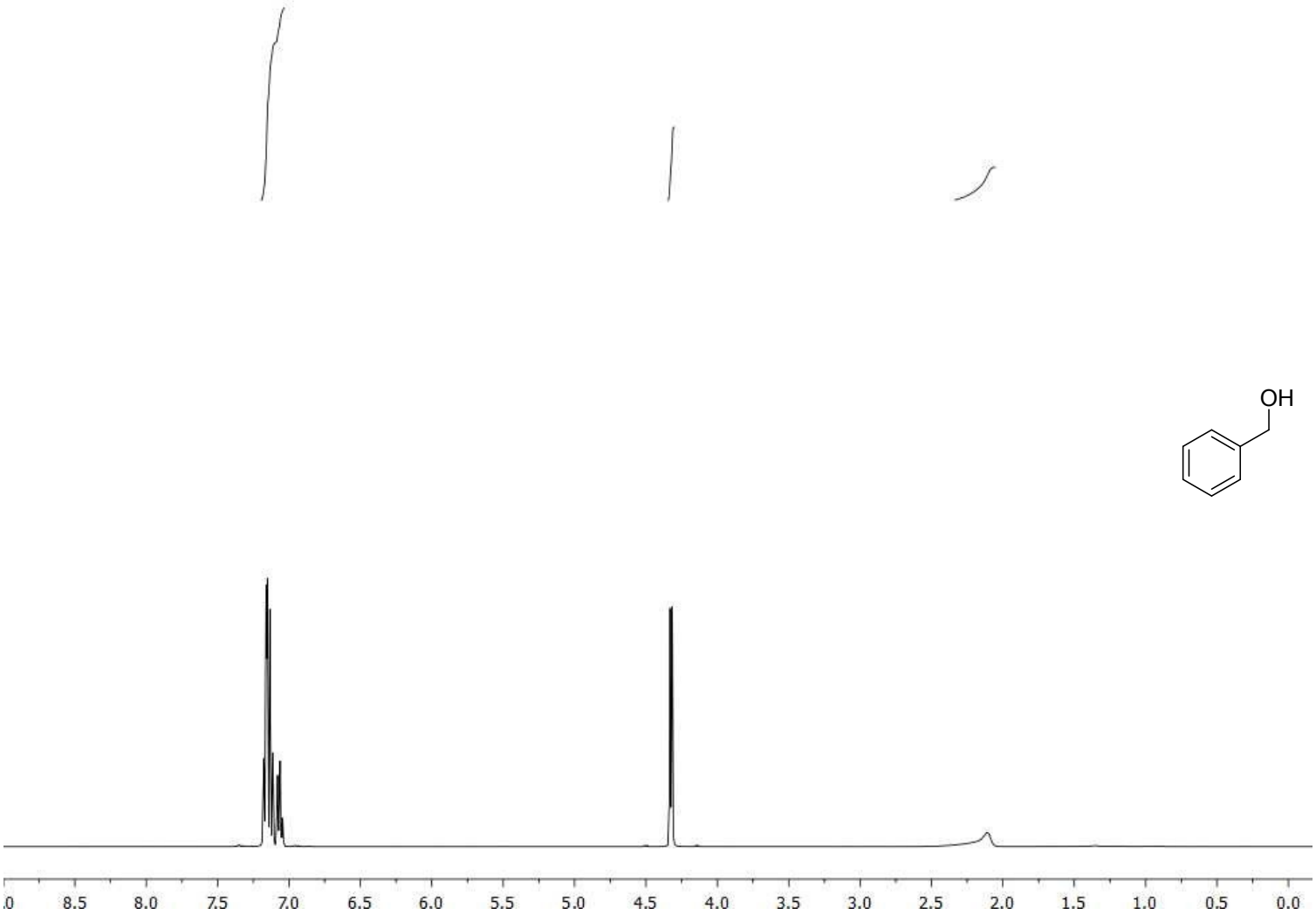
4,4,5,5-tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (**5a**)

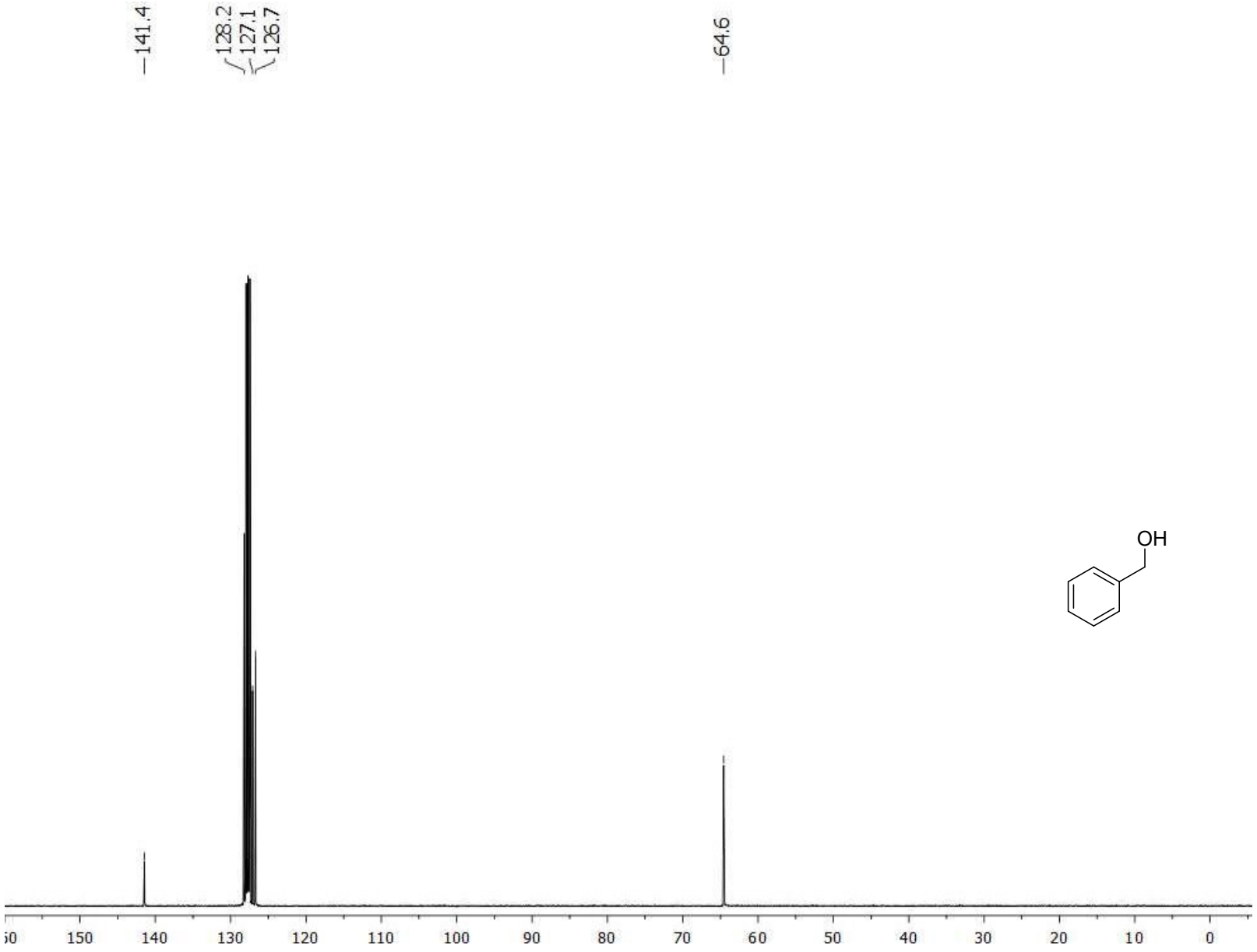



145.0
128.2
127.0
125.3
82.2
72.6
25.4
24.3
Bpin
O
Me
H
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

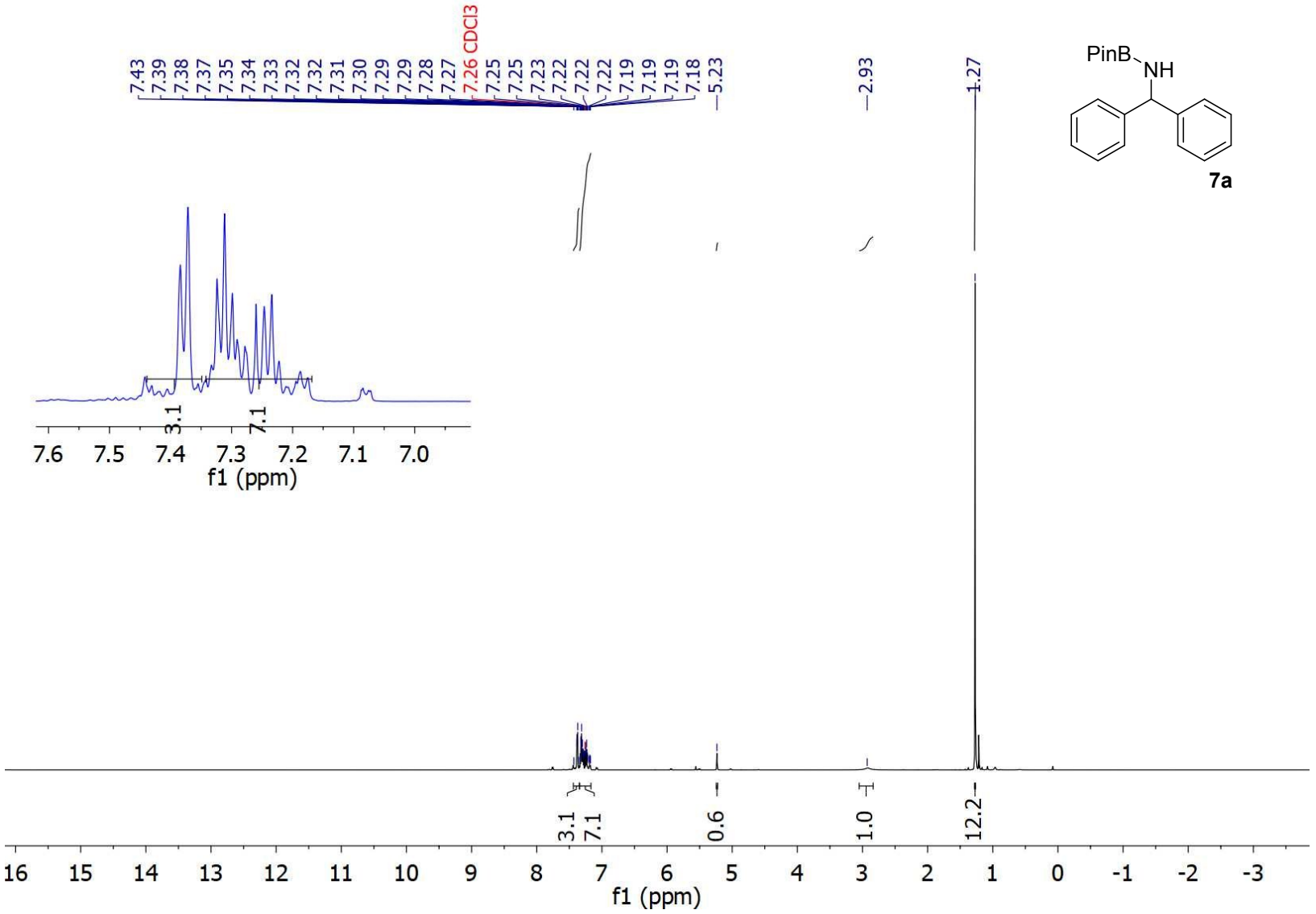

22.6
Bpin
O
Me
H
*
*Background signal
from NMR tube
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

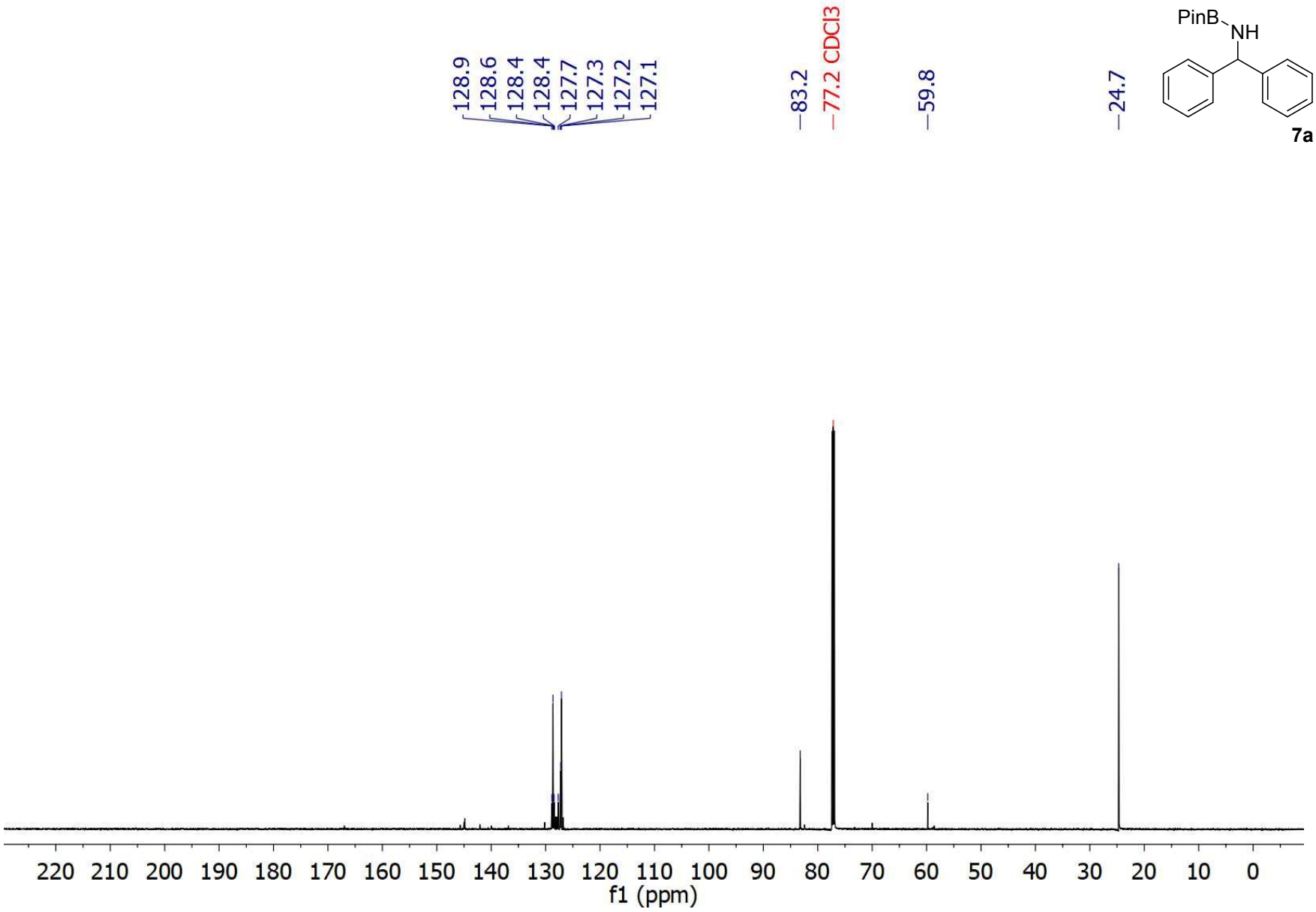
Phenylmethanol (**6a**)

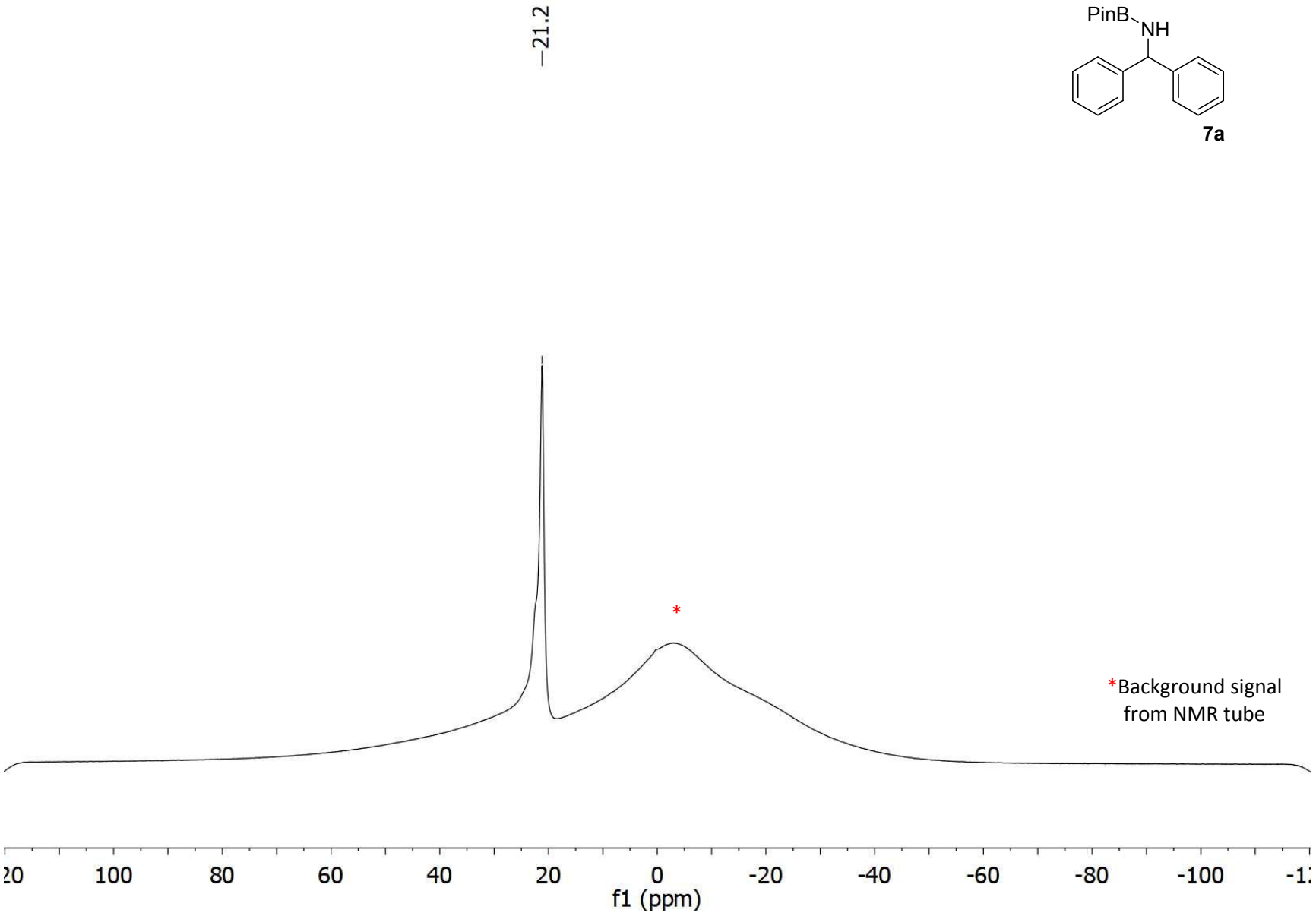



141.4
128.2
127.1
126.7
64.6
OH
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

N-benzhydryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**7a**)




128.9
128.6
128.4
128.4
127.7
127.3
127.2
127.1
83.2
77.2 CDCl3
59.8
24.7
PinB
NH
7a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


21.2
PinB
NH
7a
*
*Background signal
from NMR tube
20
100
80
60
40
20
0
-20
-40
-60
-80
-100
f1 (ppm)

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