Extremely Efficient Hydroboration of Ketones and Aldehydes by Copper Carbene Catalysis

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Electronic Supplementary Information

General considerations: All reactions were conducted under purified N_2 using in a glovebox and a Schlenk line. Deuterated benzene (C_6D_6) was degased by repeated freeze-pump-thaw cycles and stored over activated 3-Å molecular sieves prior to use. ^1H and ^{11}B NMR spectra were recorded using Bruker Avance 400-MHz NMR spectrometer. NMR spectra were recorded at room temperature, and chemical shifts were referenced to residual solvent peak. ^{11}B NMR chemical shifts were referenced to external pinacolborane (29.01 and 27.6 ppm). Literature methods was used to synthesize (IPr)CuOtBu.[1] All other reagents were purchased from commercial vendors and used without further purification.

General catalytic procedure: In the glovebox, a scintillation vial was charged with (IPr)CuOtBu (1.5 mg, 0.00285 mmol), and C_6D_6 (6 mL) was added. Another 20-mL scintillation vial was charged with a stirbar and substrate (0.952 mmol). The substrate was dissolved in C_6D_6 (5 mL), and then pinacolborane (138 µL, 0.952 mmol), mesitylene (132.6 µL, 0.952 mmol) and in some cases additive (0.952 mmol) were added to this solution. Then an aliquot of the (IPr)CuOtBu stock solution (2 mL) was added to the reaction vial, and the resulting mixture was stirred at room temperature for 10 min and 1 h (as indicated in the manuscript). Aliquots of the reaction solution was transferred to NMR tubes, and ^1H and ^{11}B NMR spectra (see below) were taken to monitor reaction progress. Separate catalytic runs performed by multiple researchers were reproduced to within ±2%.

Isolation of 2-(1-(4-iodophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: In the glovebox, a scintillation vial was charged with (IPr)CuOtBu (1 mg, 0.002 mmol), and was dissolved in C_6D_6 (2 mL). Another 20-mL scintillation vial was charged with a stirbar and 4-iodoacetophenone (0.234 g, 0.952 mmol). The substrate was dissolved in C_6D_6 (2 mL), and then pinacolborane (138 µL, 0.952 mmol) was added to this solution. Then an aliquote of the catalyst stock solution (1 mL) was added to the solution to the reaction vial, and the resulting mixture

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[1] N. P. Mankad, D. S. Laitar, & J. P. Sadighi, *Organometallics*, 2004, **23**, 3369-3371.

was stirred at room temperature for 1 h. The volatiles were removed to afford the product: 0.25 g, 70%.

Isolation of 2-(benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: In the glovebox, a scintillation vial was charged with (IPr)CuOtBu (1 mg, 0.002 mmol), and was dissolved in C_6D_6 (2 mL). Another 20-mL scintillation vial was charged with a stirbar and benzophenone (0.173 g, 0.952 mmol). The substrate was dissolved in C_6D_6 (2 mL), and then pinacolborane (138 µL, 0.952 mmol) was added to this solution. An aliquot of the catalyst stock solution (1 mL) was added to the solution to the reaction vial, and the resulting mixture was stirred at room temperature for 1 h. The volatiles were removed to afford the product: 0.20 g, yield: 68%.

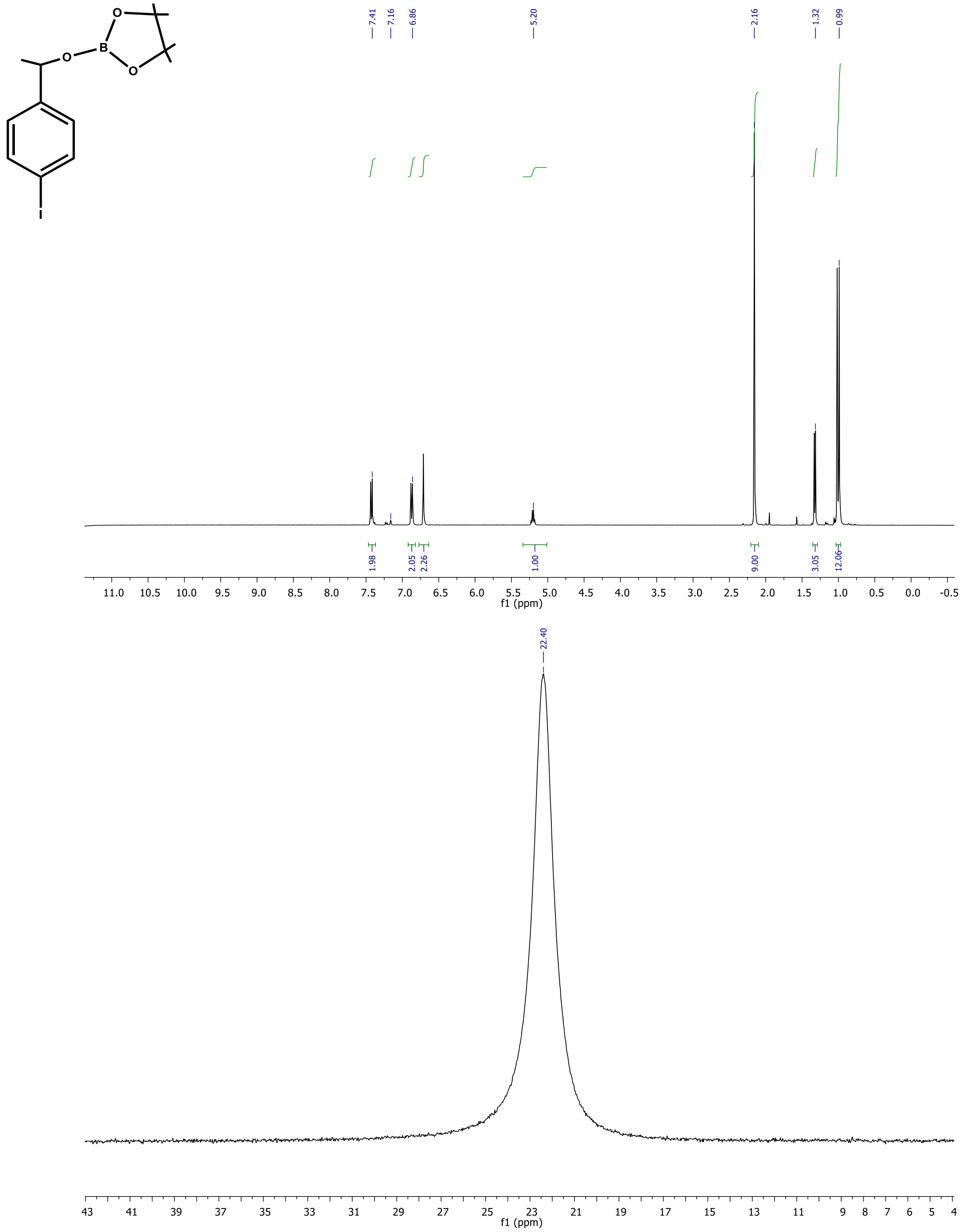


Figure S1. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-iodoacetophenone at 10min.

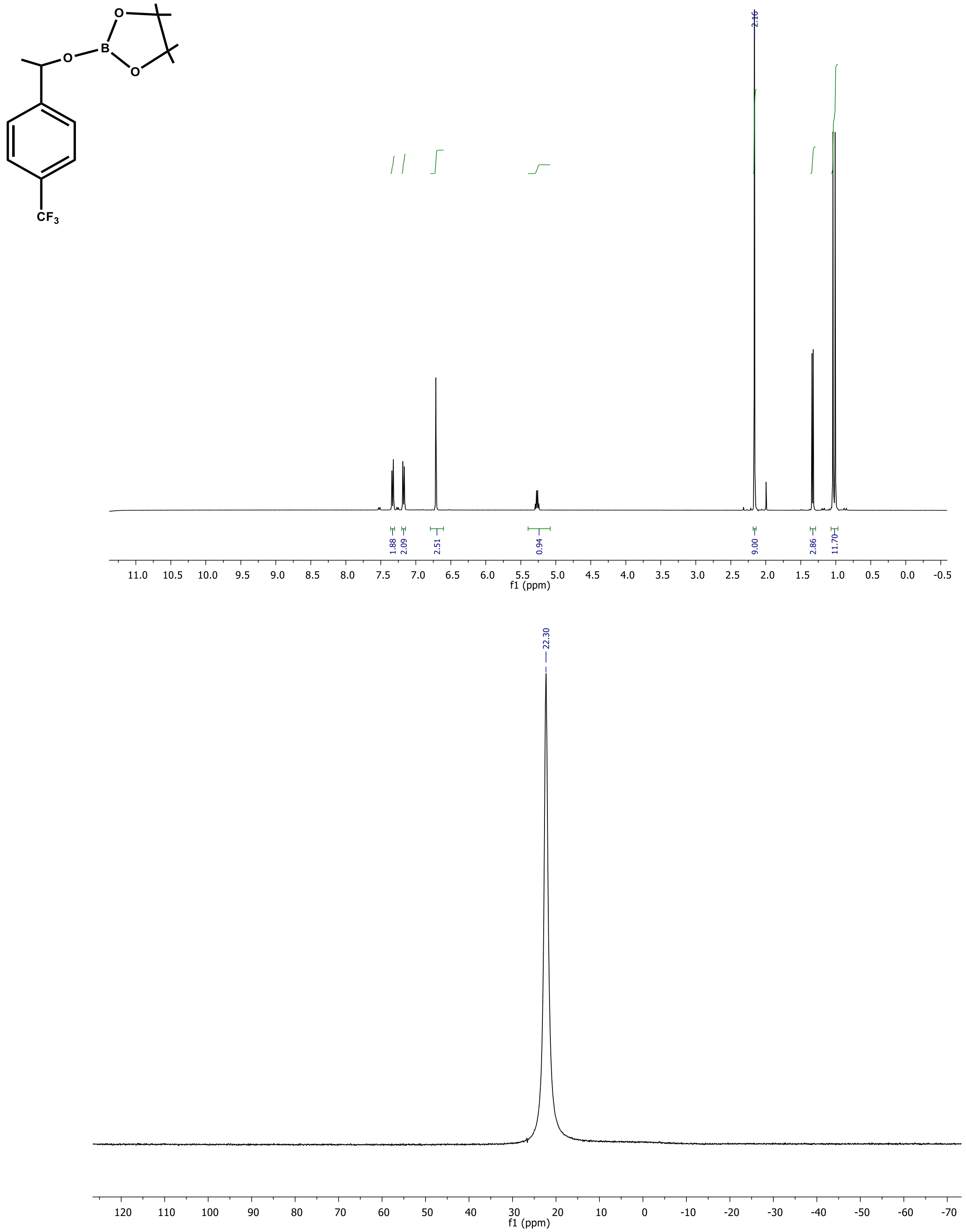


Figure S2. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4'- (trifluoromethyl)acetophenone at 10min.

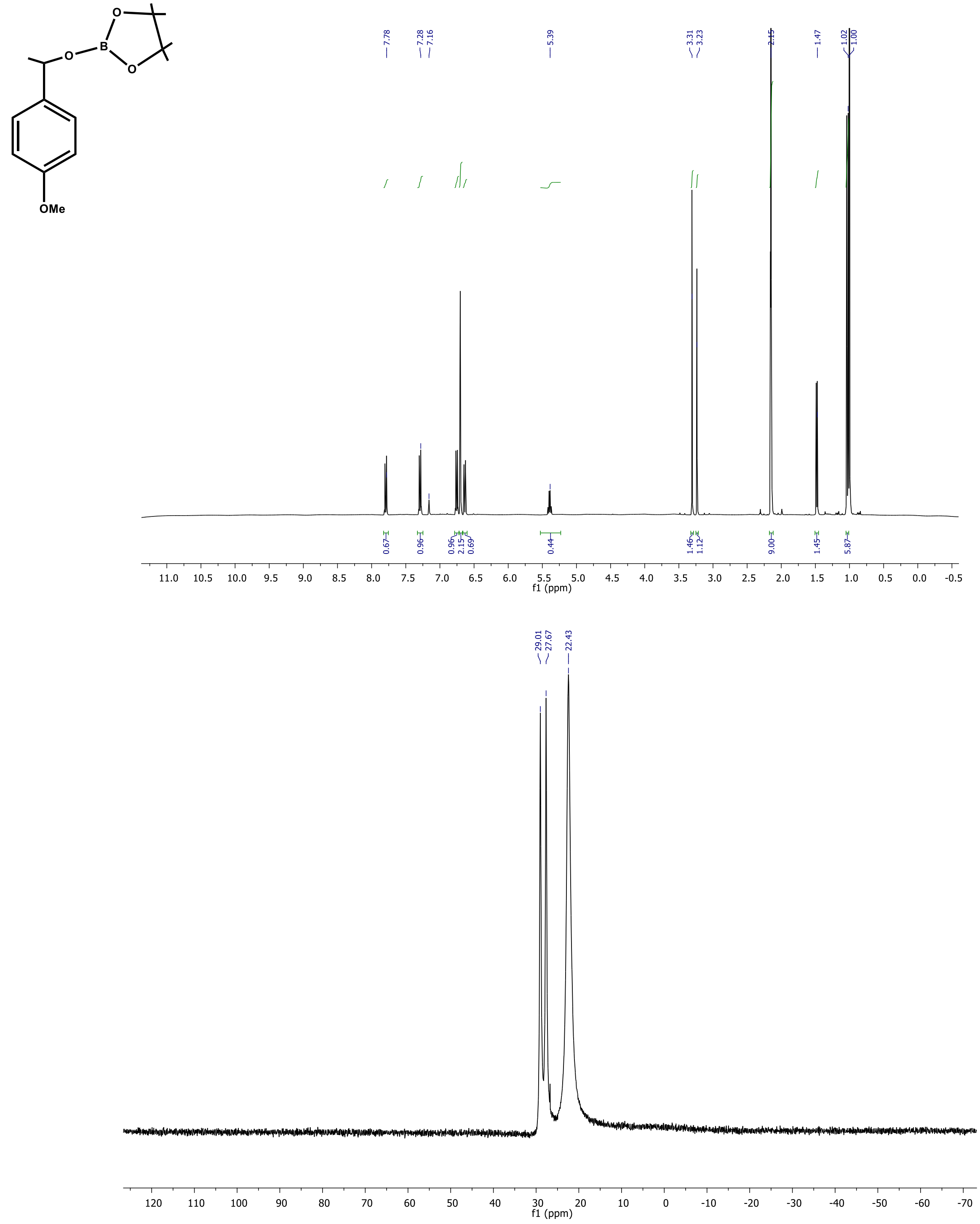


Figure S3. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-methoxyacetophenone at 10min.

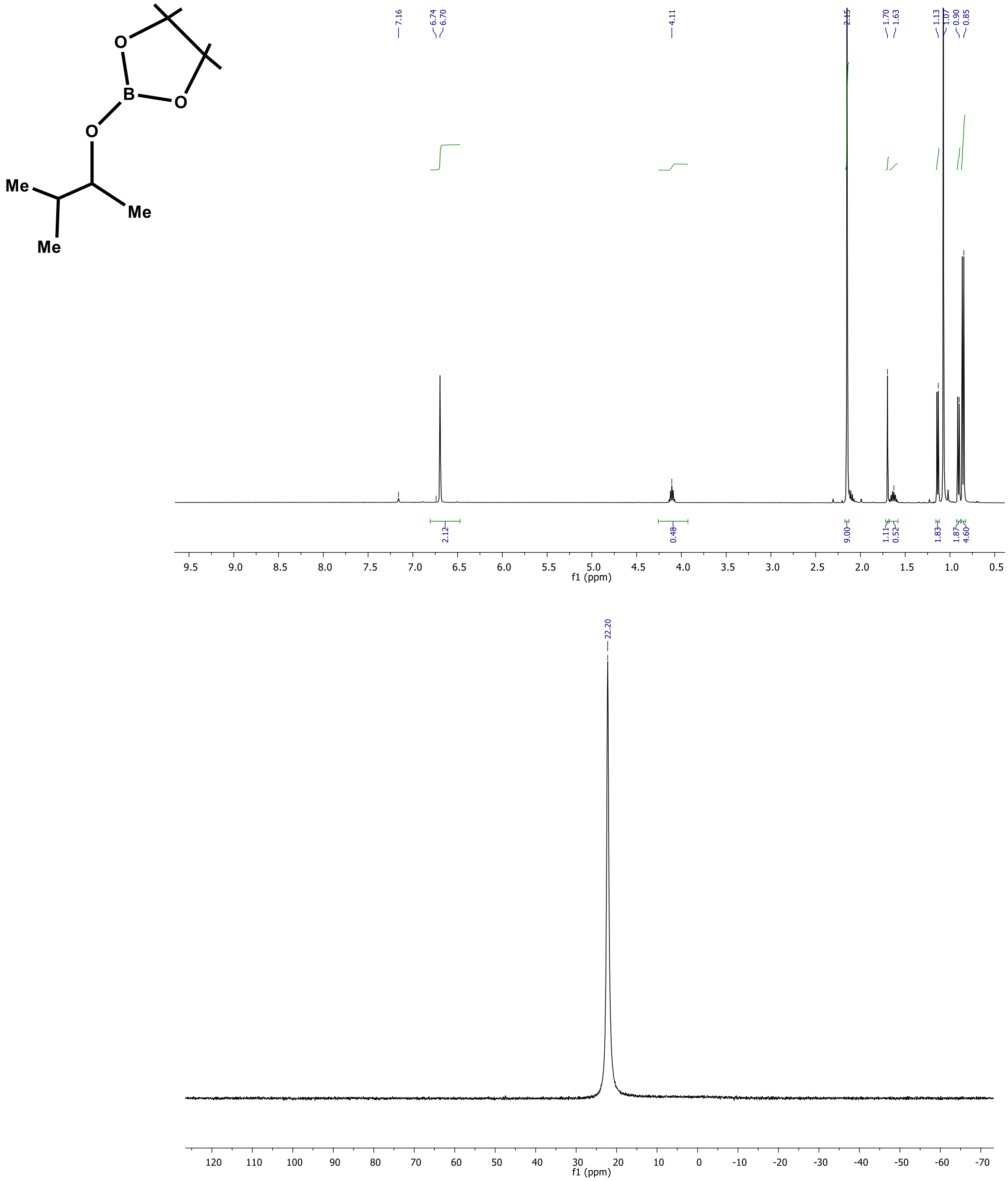


Figure S4. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 3-methyl 2-butanone at 10min.

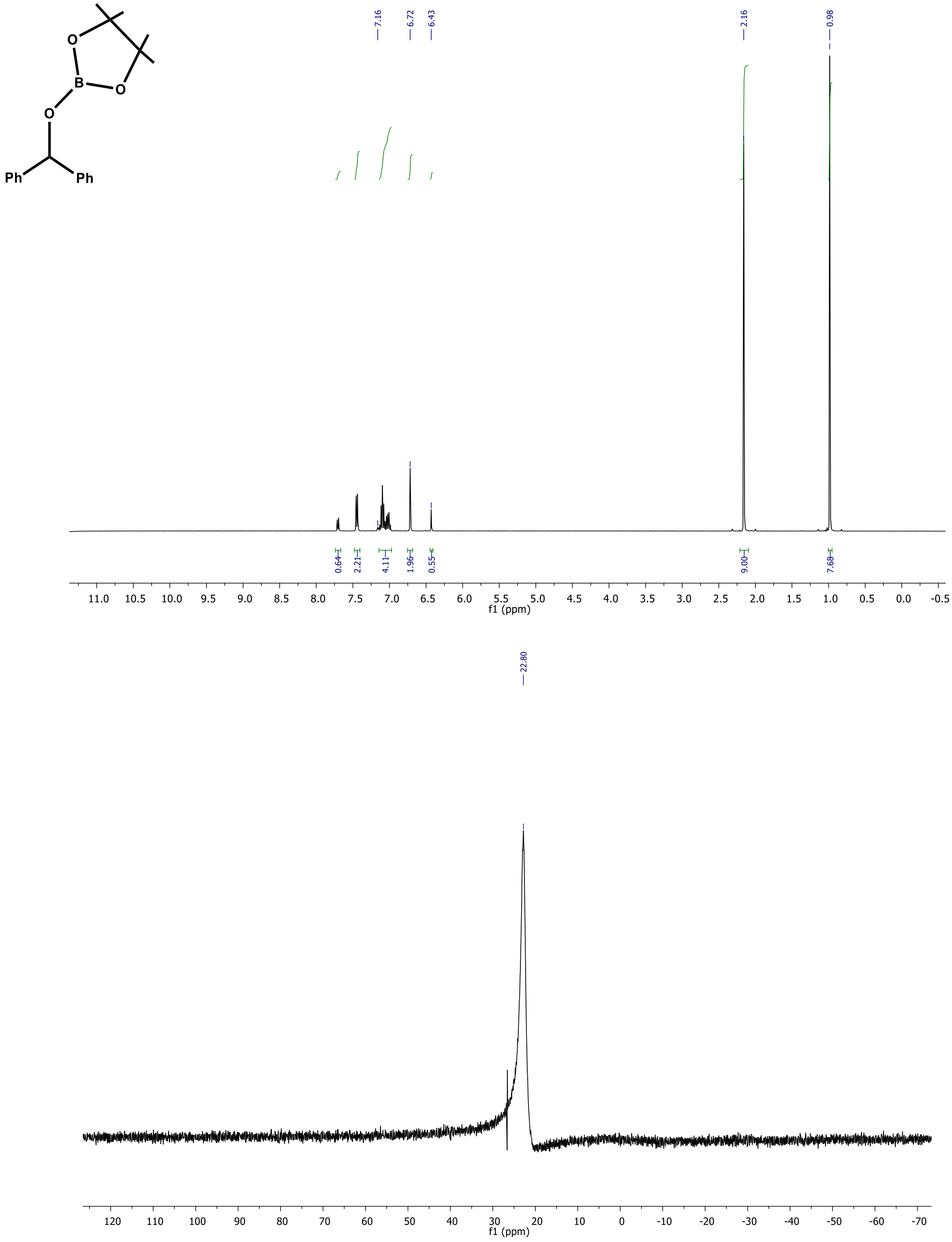


Figure S5. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of benzophenone at 10min.

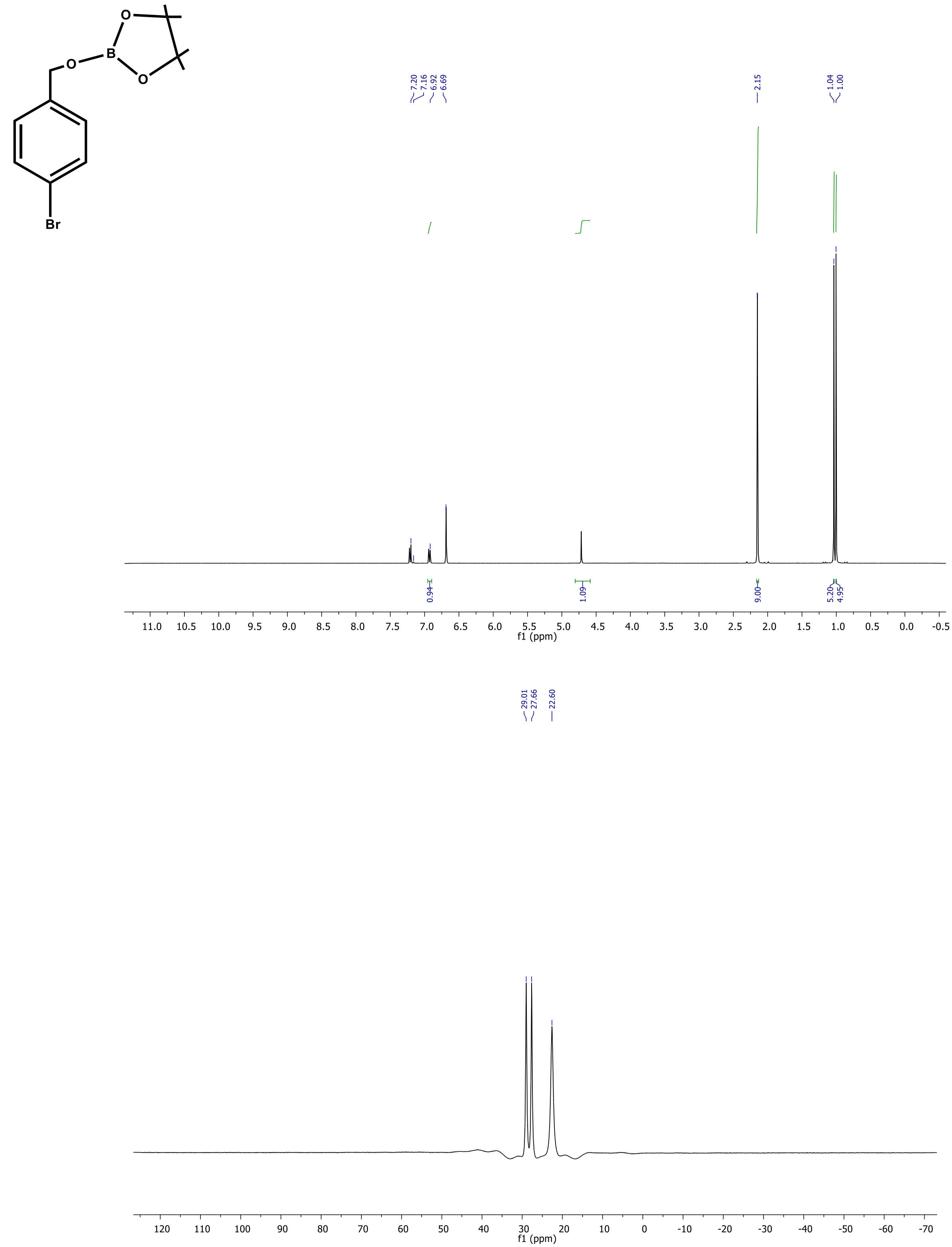


Figure S**6.** ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4- bromobenzaldehyde at 10min.

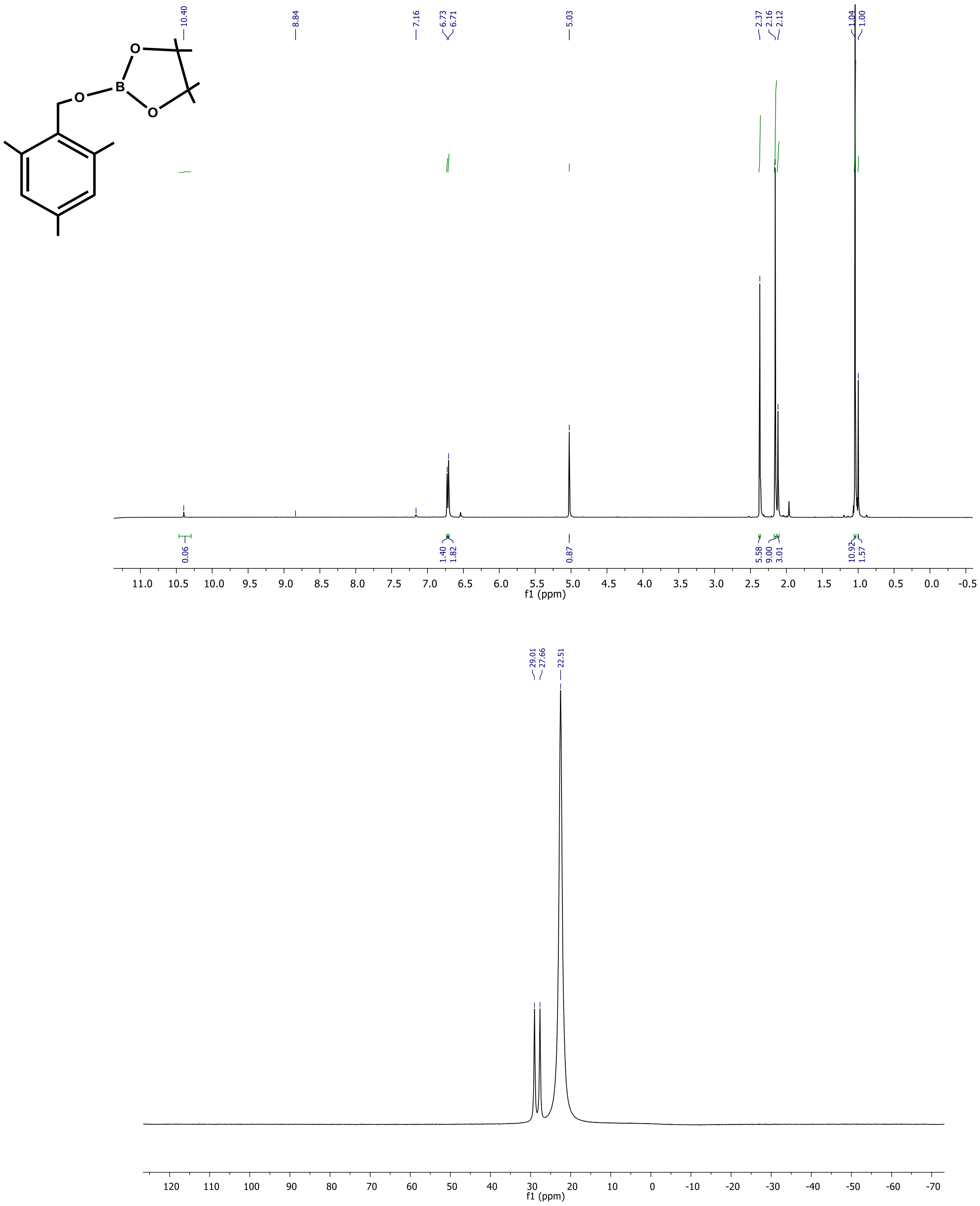


Figure S7. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 2,4,6- trimethylbenzaldehyde at 10min.

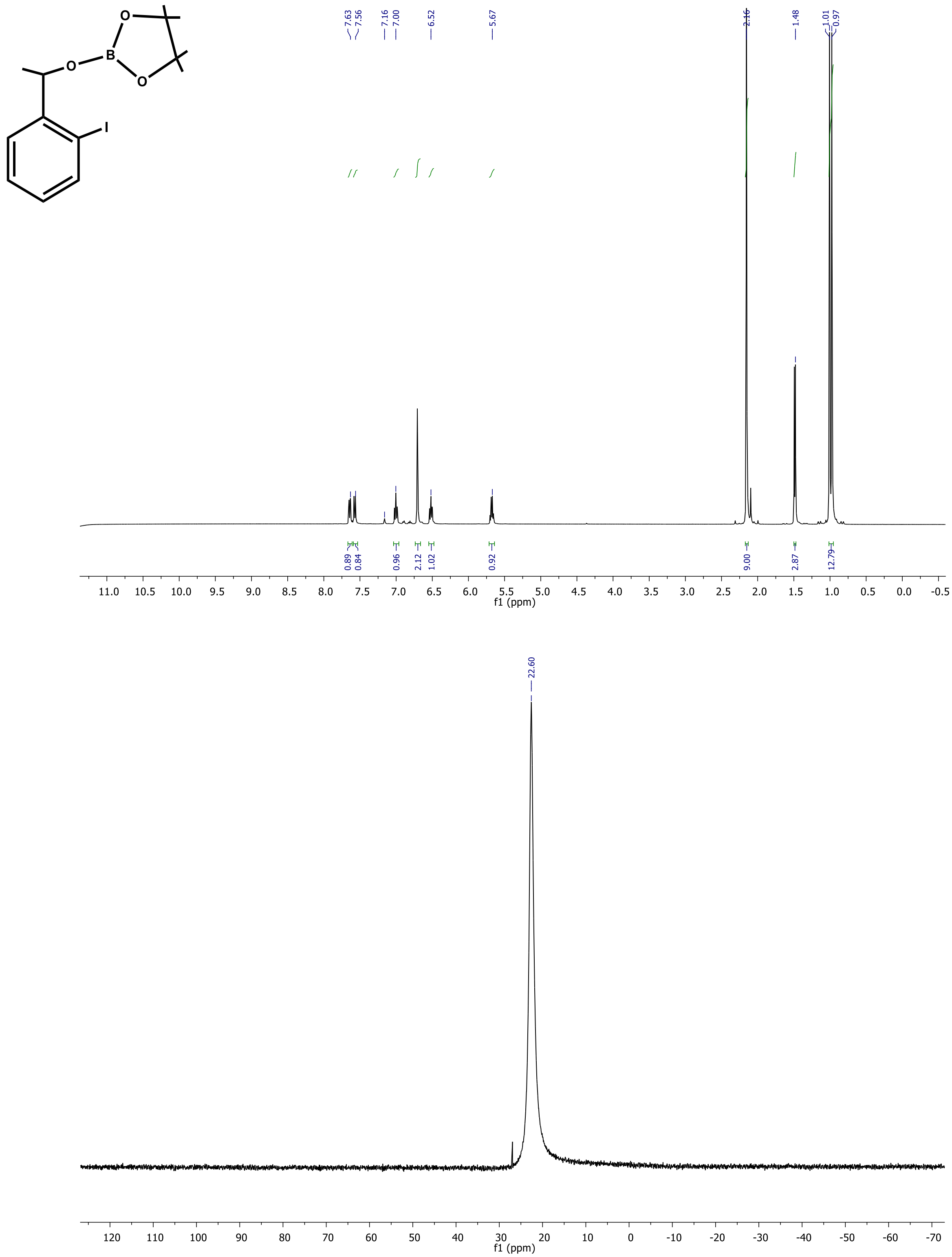
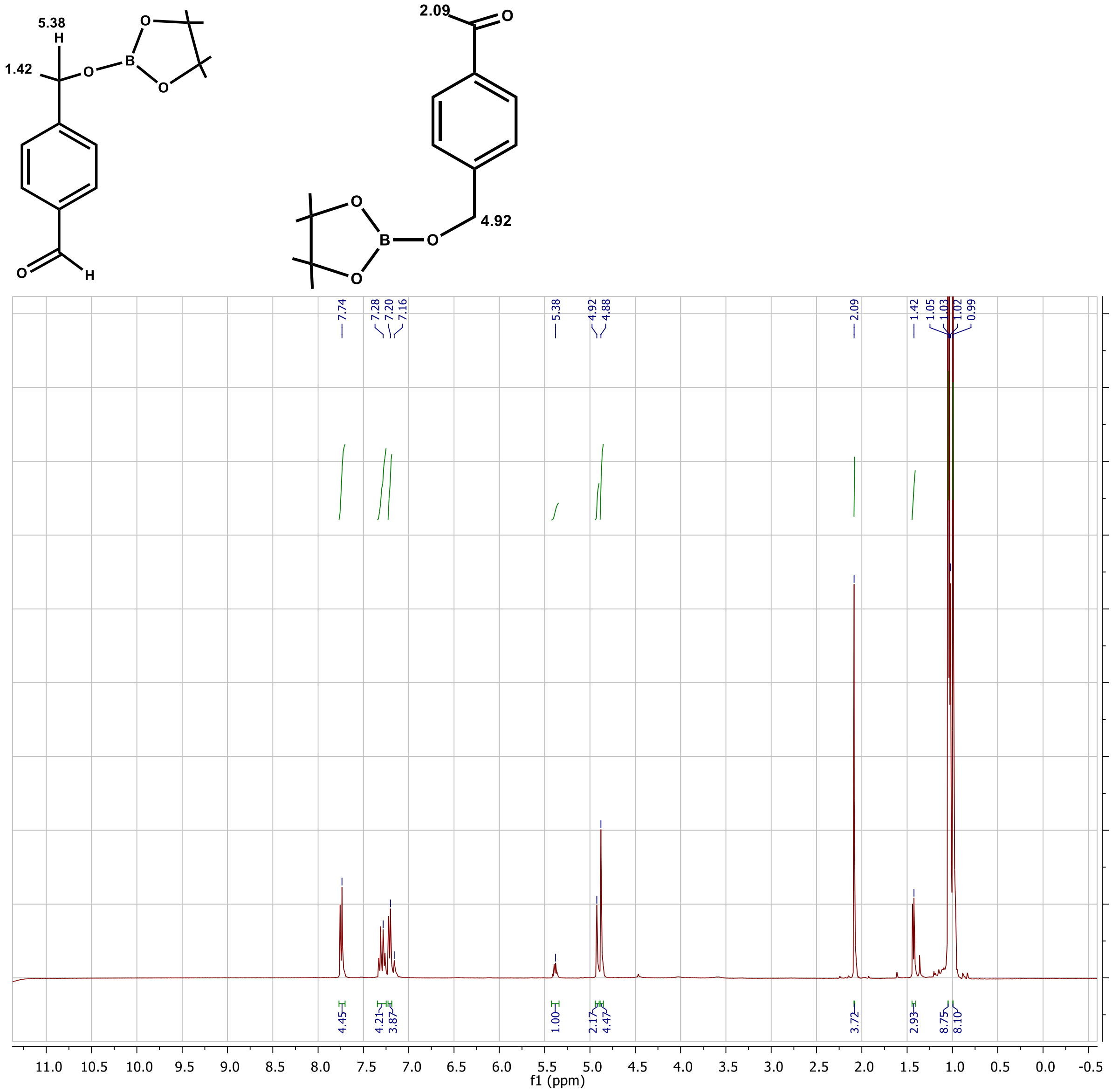


Figure S8. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 2- iodoacetophenone at 10min.


5.38
H
1.42
O
B
O
O
2.09
O
O
O
B
O
4.92
7.74
7.28
7.20
7.16
5.38
4.92
4.88
2.09
1.42
1.05
1.03
1.02
0.99
4.45
4.21
3.87
1.00
2.17
4.47
3.72
2.93
8.75
8.10
900
800
700
600
500
400
300
200
100
0
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
5.0
4.5
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2.5
2.0
1.5
1.0
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0.0
-0.5
f1 (ppm)

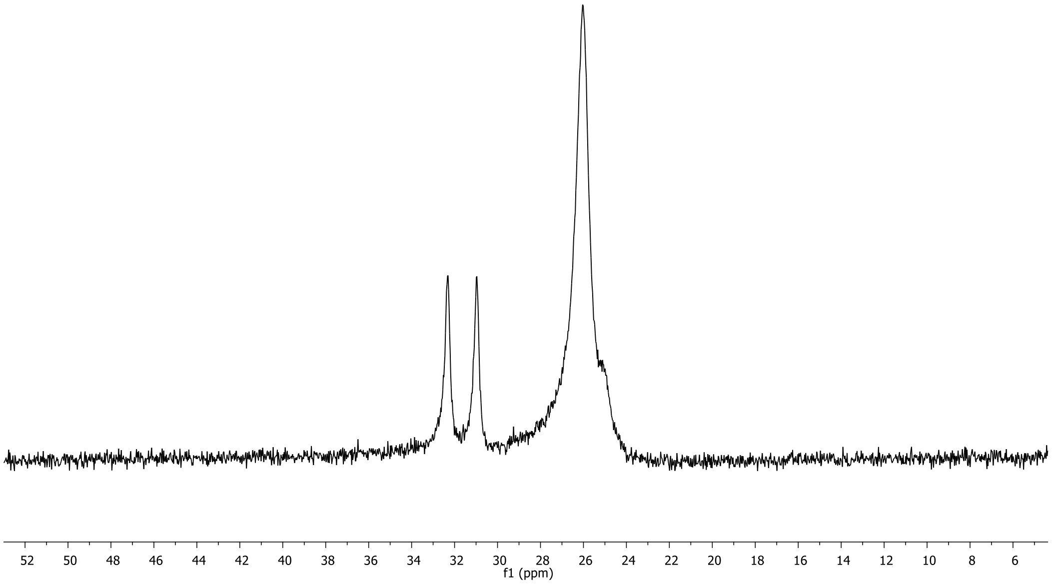


Figure S9. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-acetylbenzaldehyde at 10min.

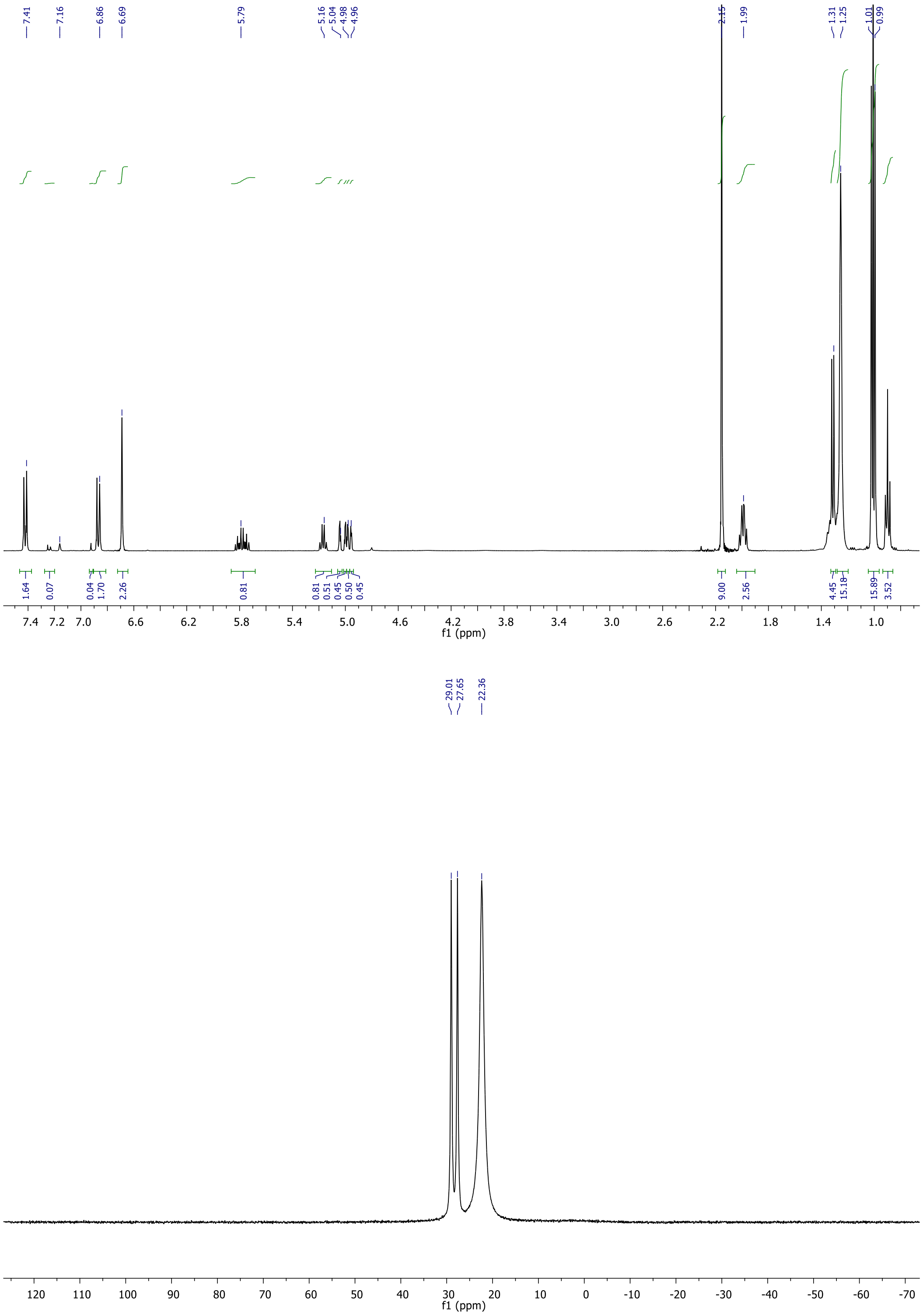
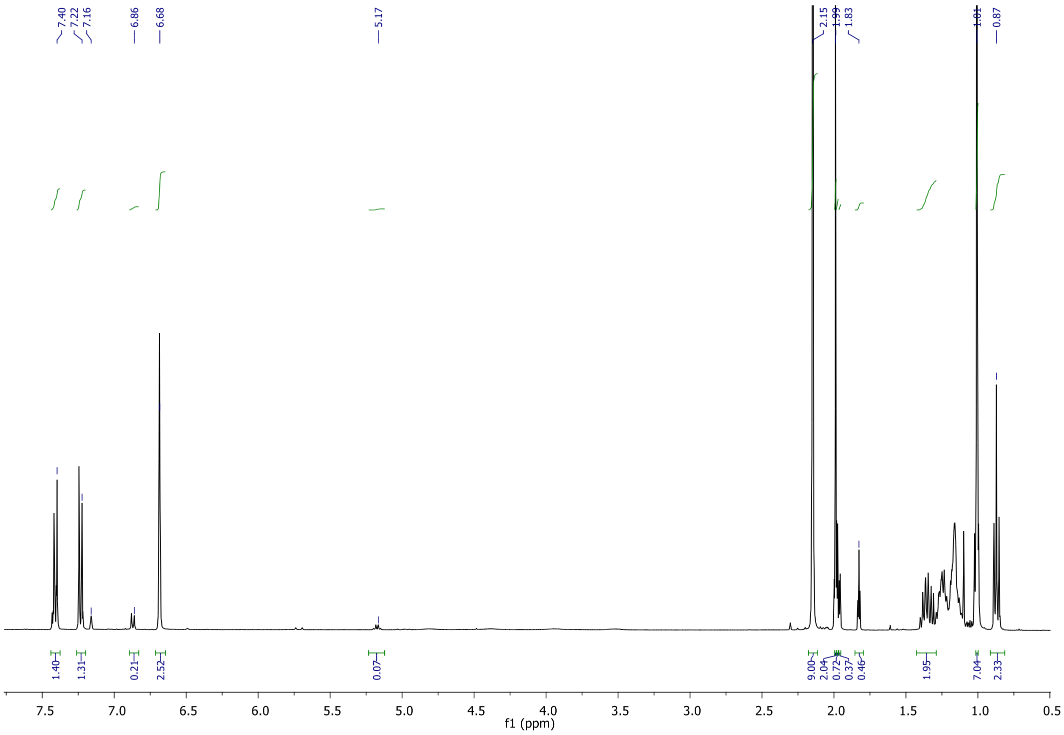


Figure S10. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-iodoacetophenone in the presence of 1-dodecene at 10min.



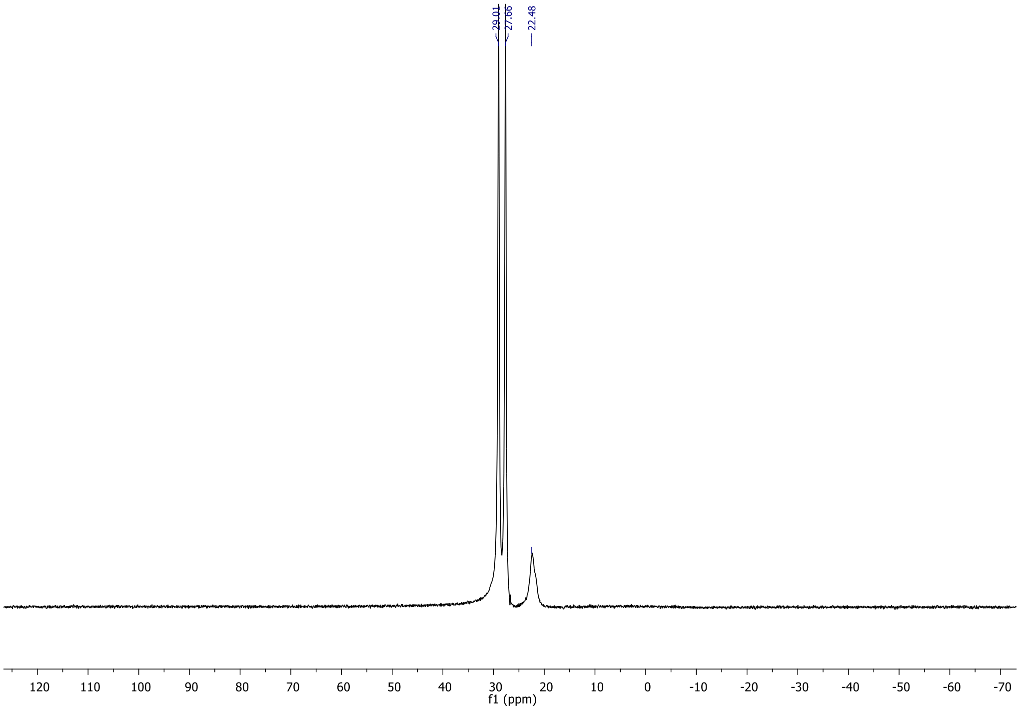


Figure S11. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-iodoacetophenone additive 1-decyne at 10min.

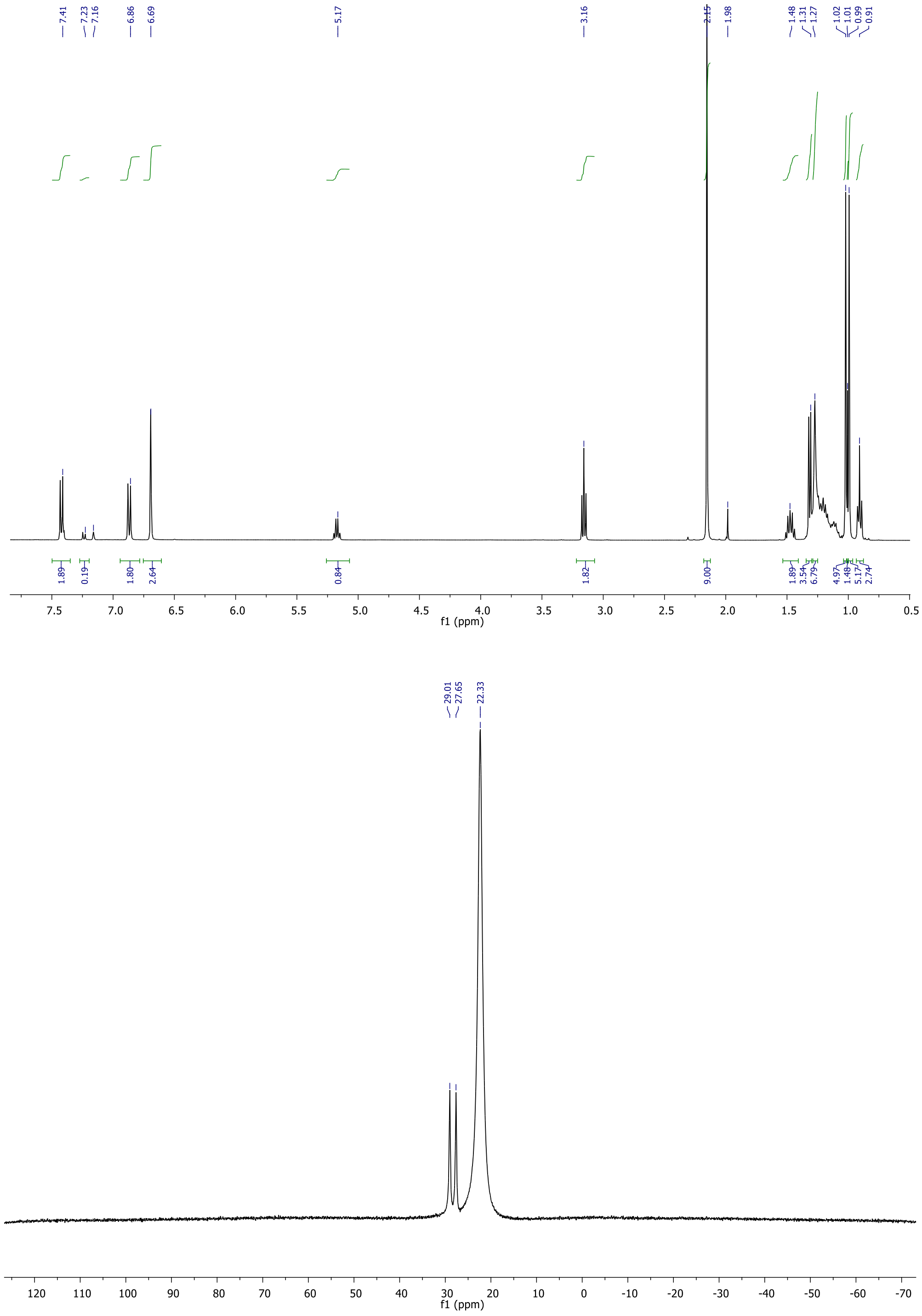


Figure S12. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-iodoacetophenone additive 1-chlorododecene at 10min.

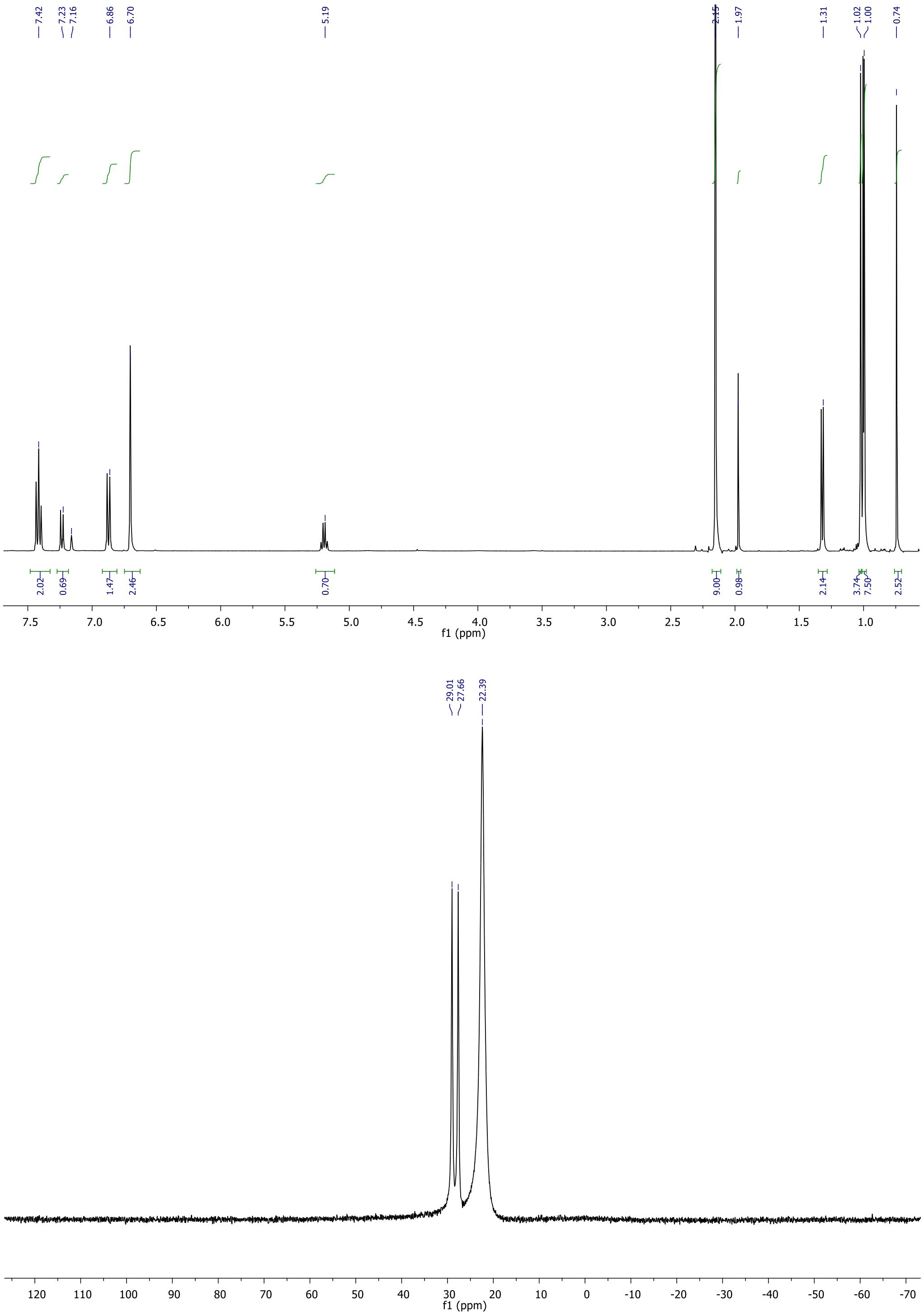


Figure S13. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-iodoacetophenone in the presence of acetonitrile at 10min.

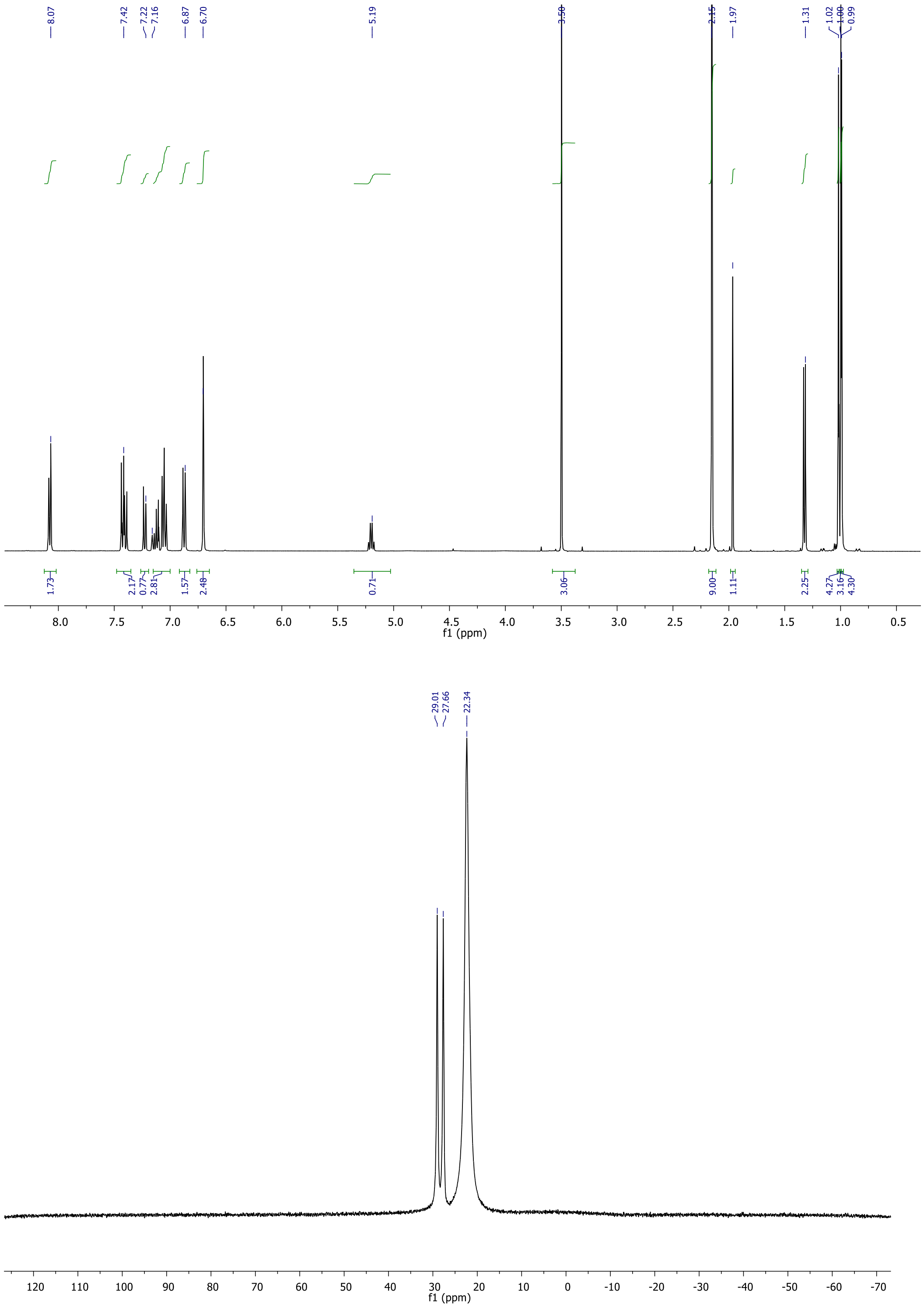


Figure S14. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-iodoacetophenone in the presence of methylbenzoate at 10min.

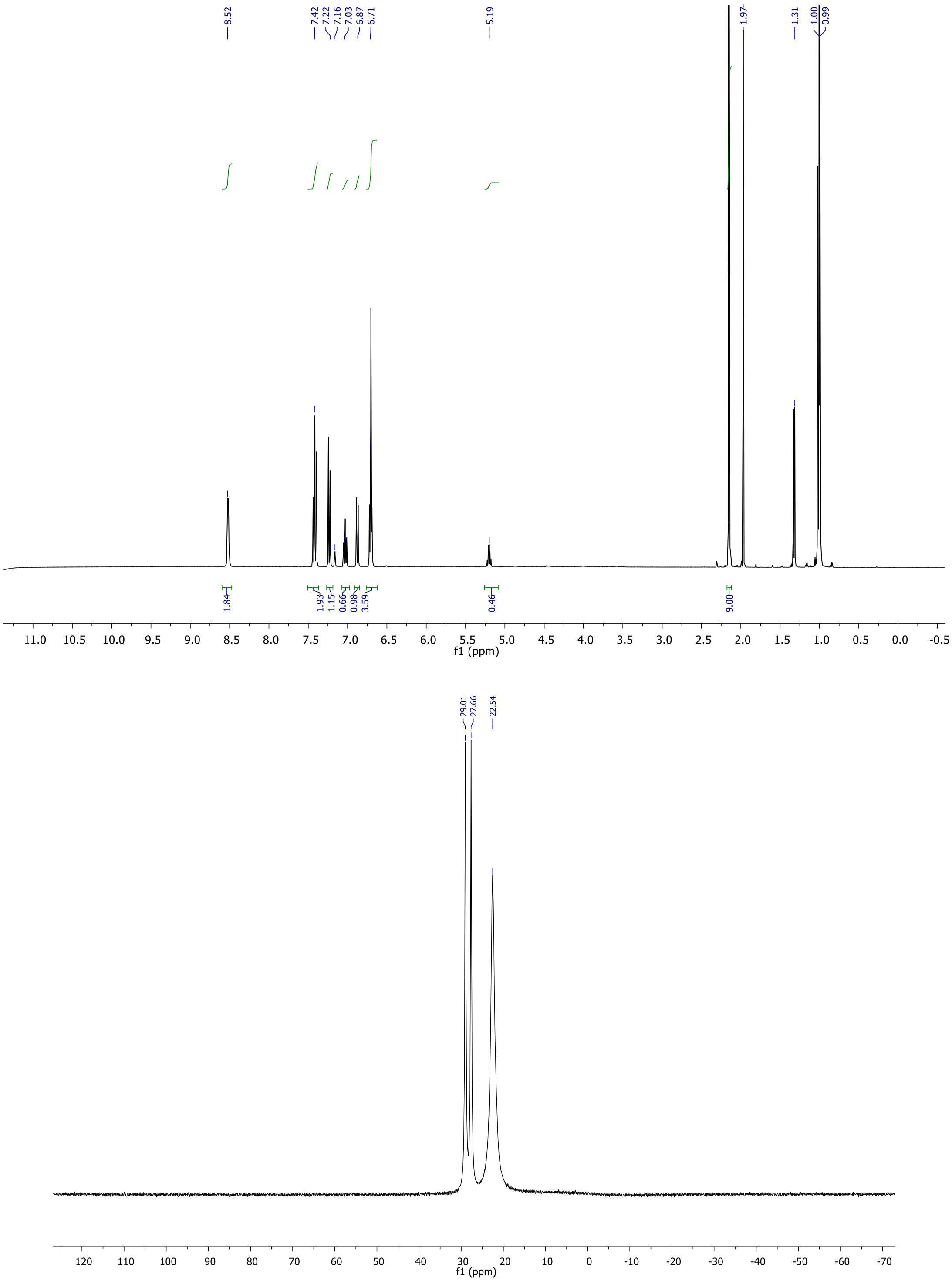


Figure S15. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-iodoacetophenone in the presence of pyridine at 10min.

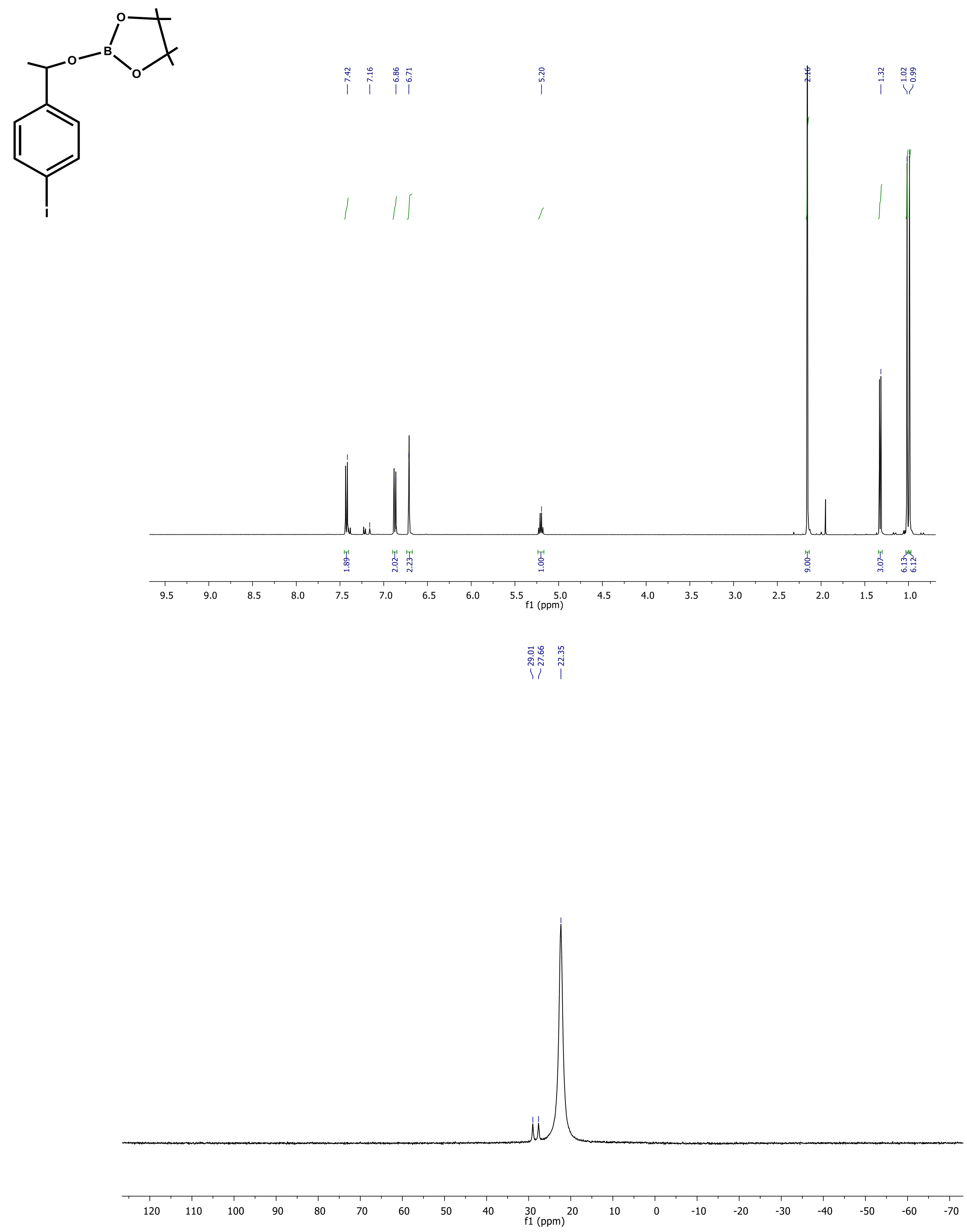


Figure S16. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-Iodoacetophenone at 1h.

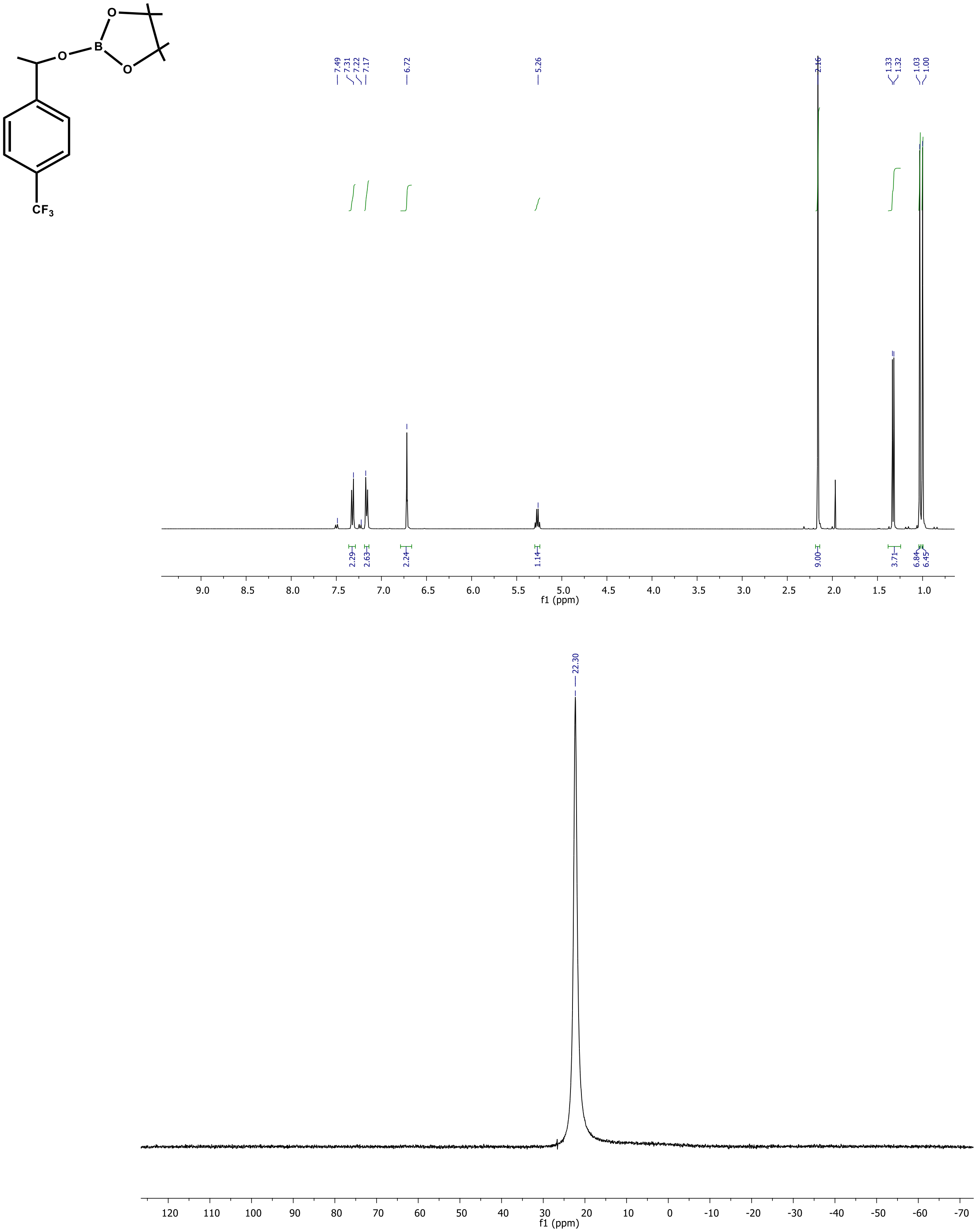


Figure S17. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4'- (trifluoromethyl)acetophenone at 1h.

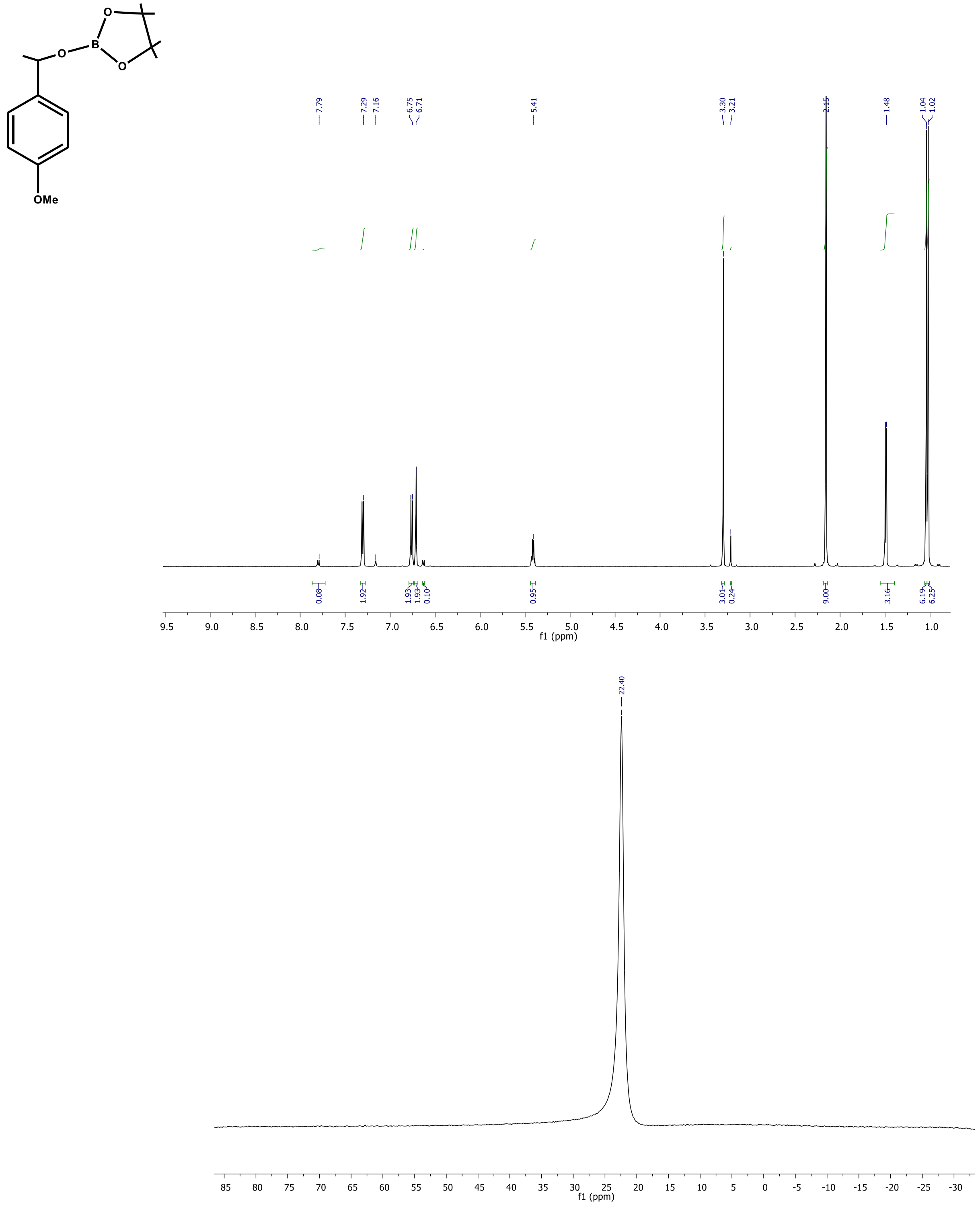


Figure S18. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-methoxyacetophenone at 1h.

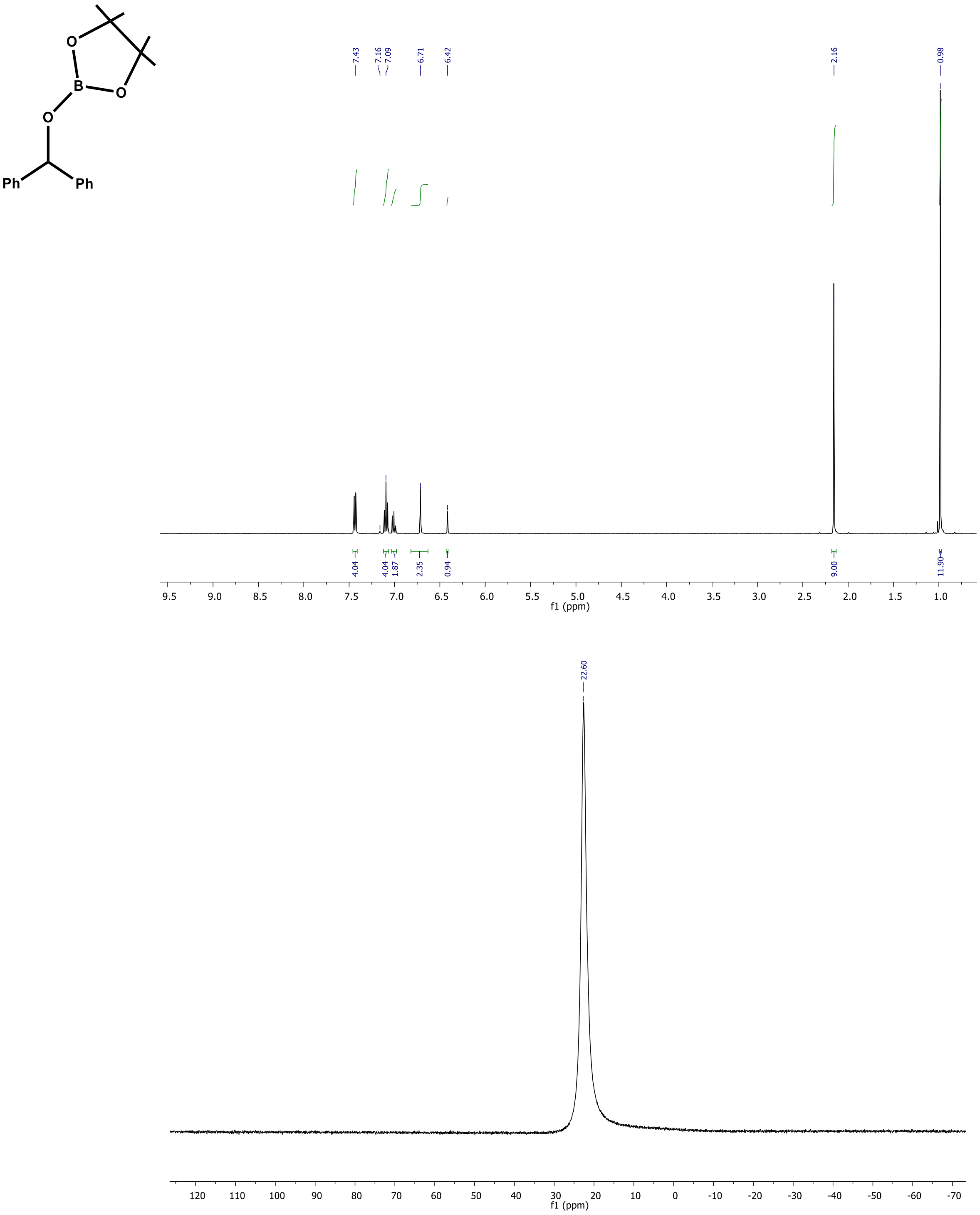


Figure S19. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of benzophenone at 1h.

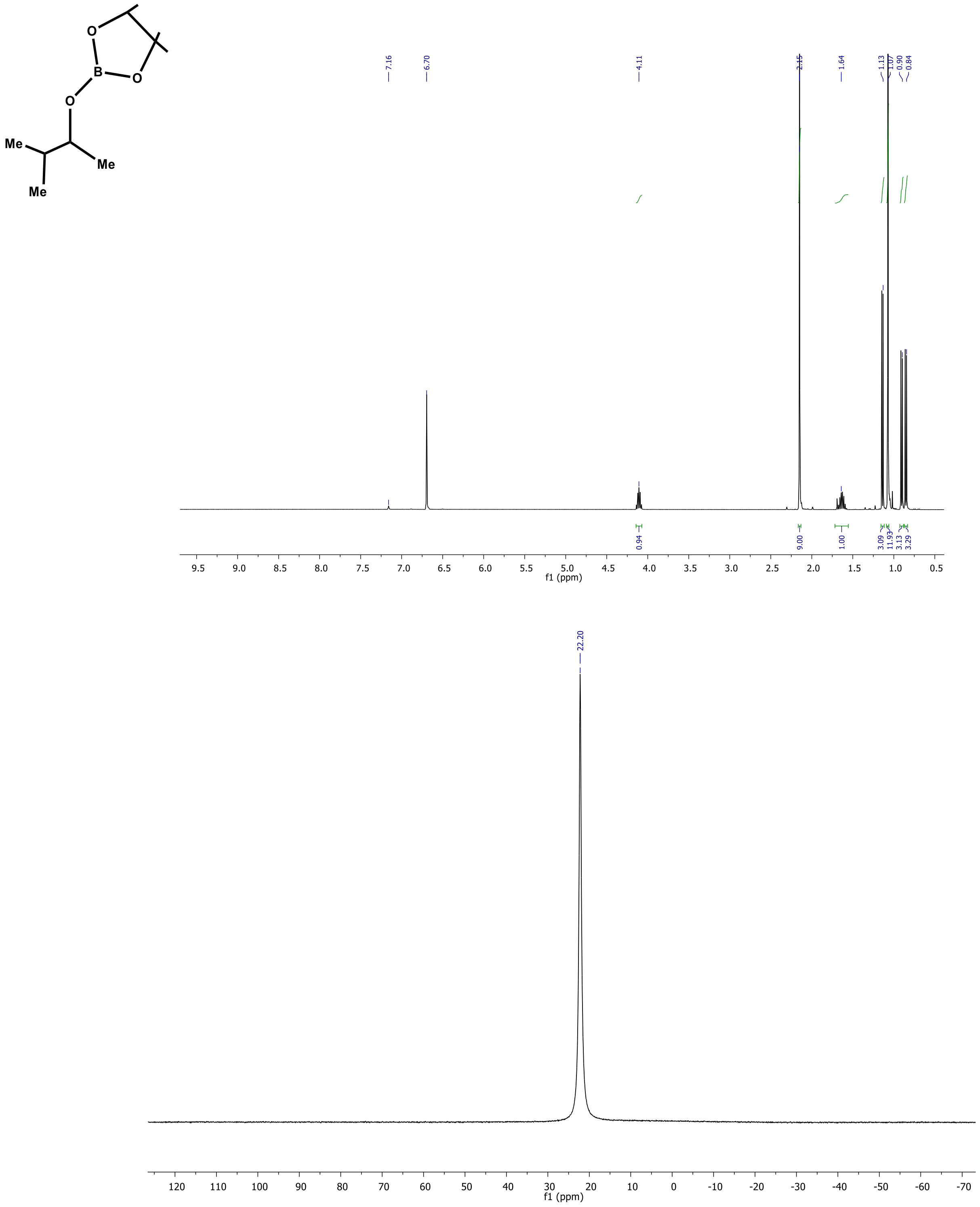


Figure S20. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 3-methyl 2-butanone at 1h.

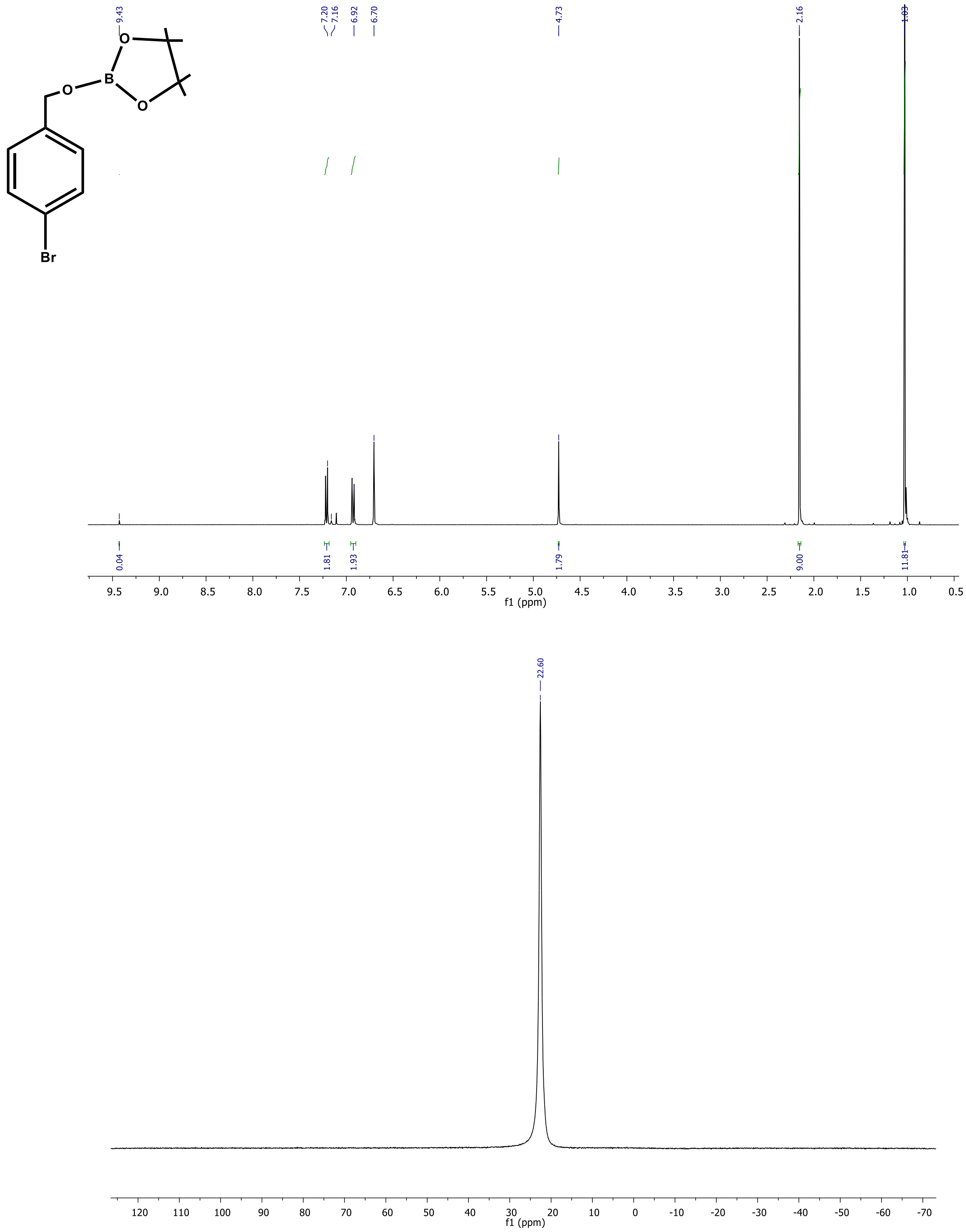


Figure S21. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-bromobenzaldehyde at 1h.

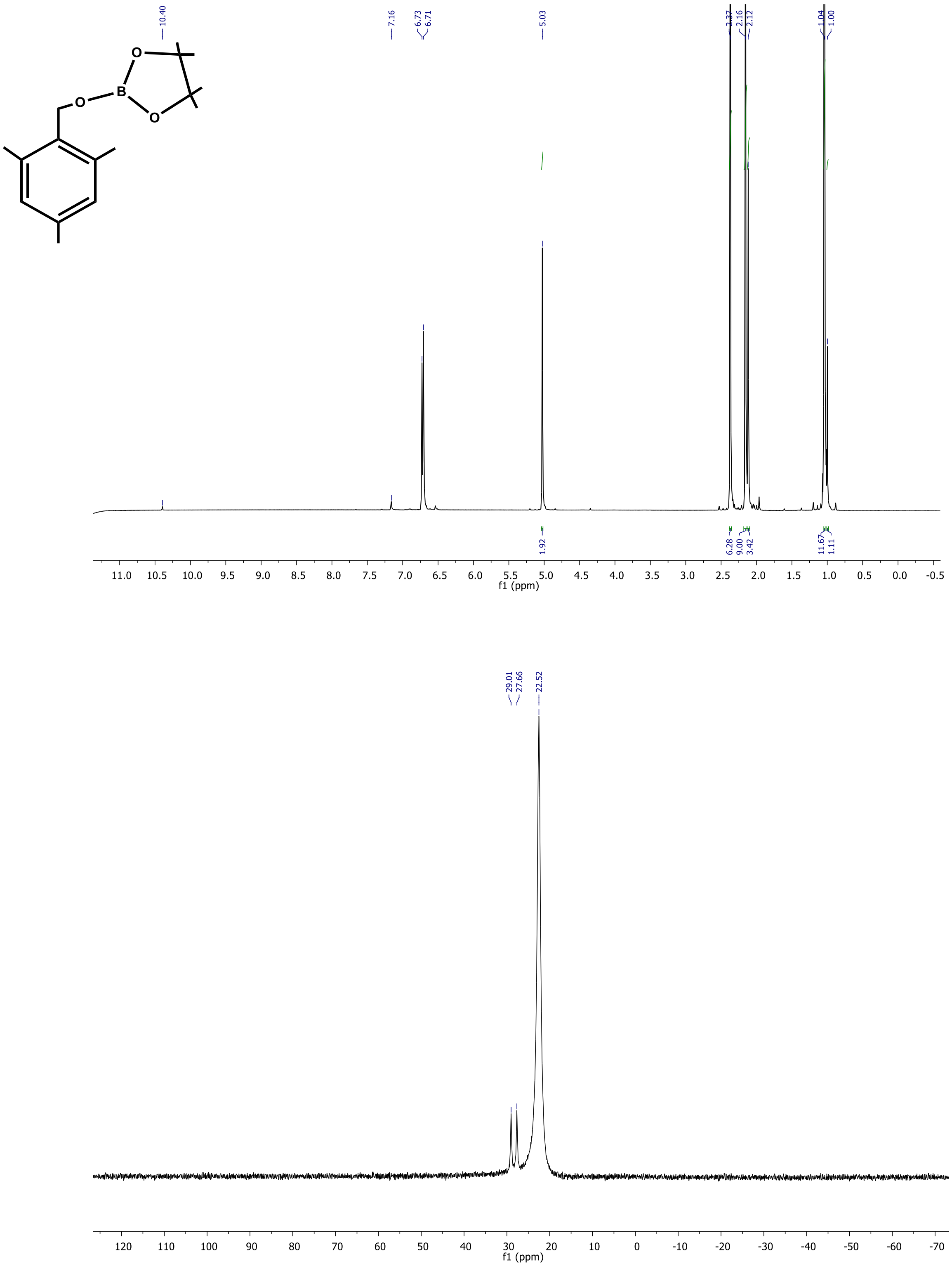


Figure S22. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 2, 4,6- trimethylbenzaldehyde at 1h.

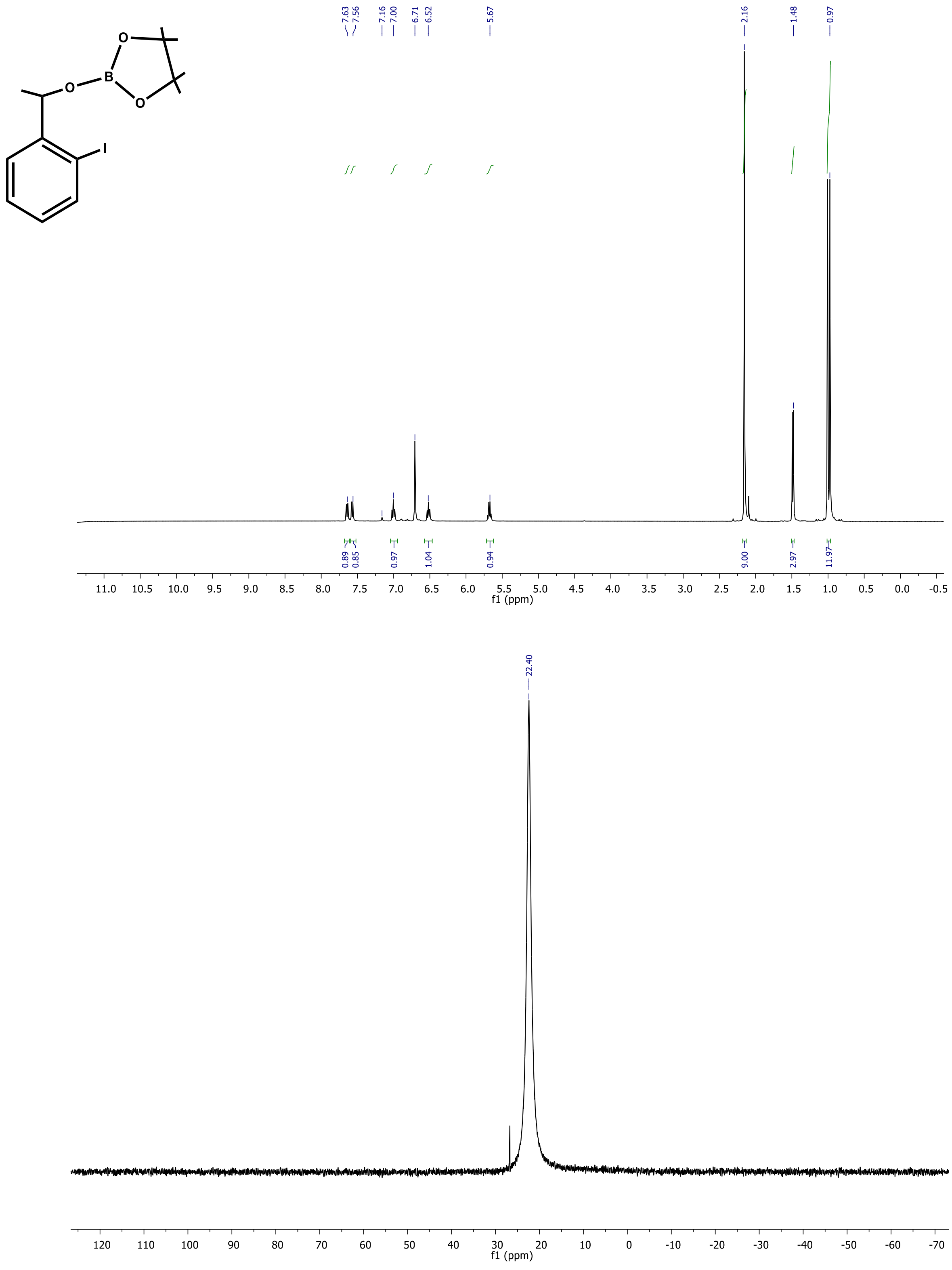


Figure S23. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 2-iodoacetophenone at 1h.

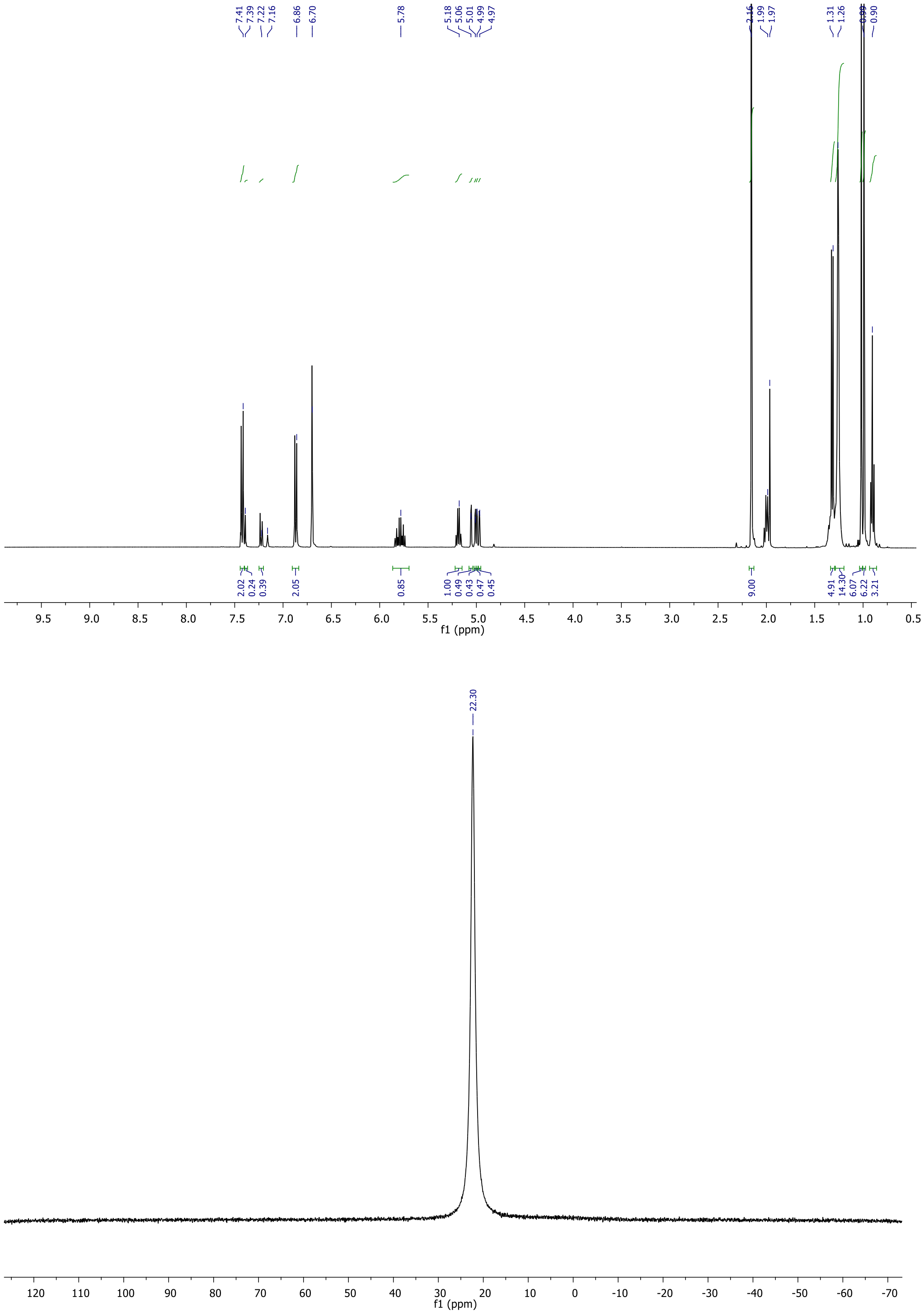
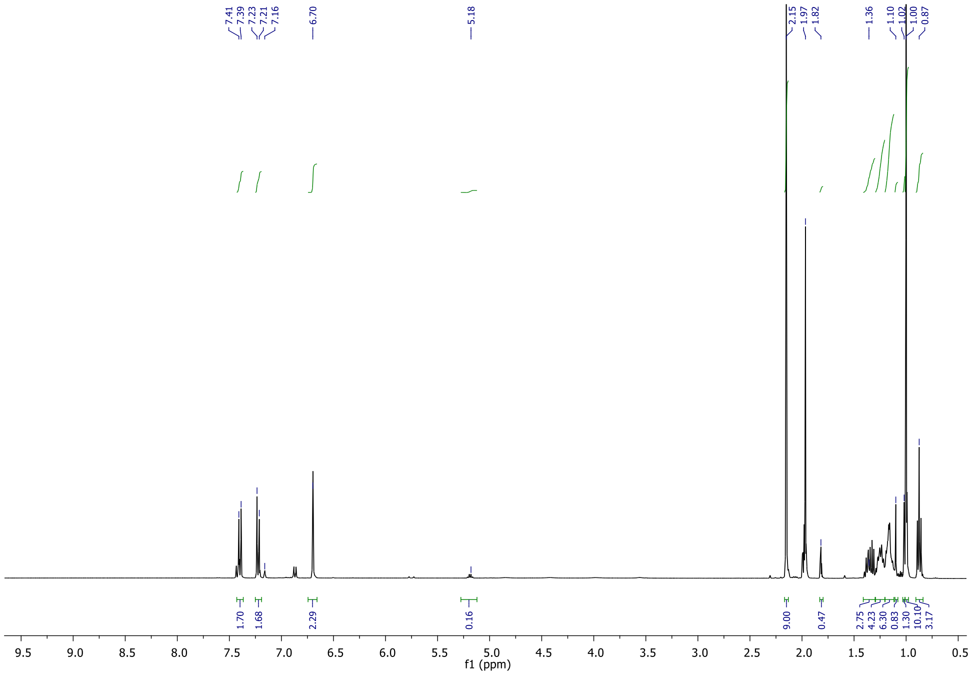


Figure S24. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-iodoacetophenone in the presence of 1-dodecene at 1h.



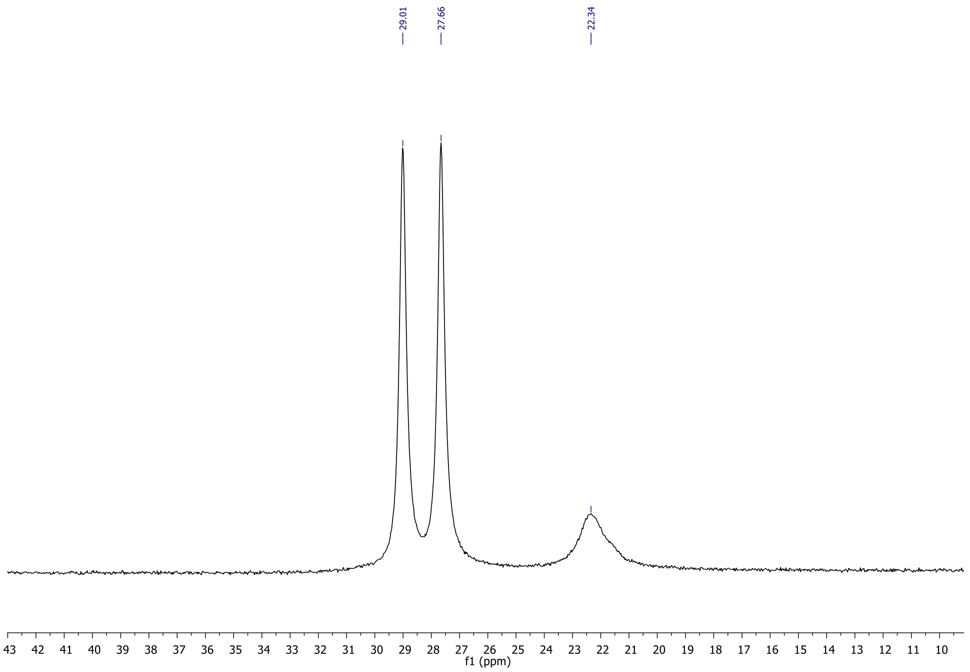
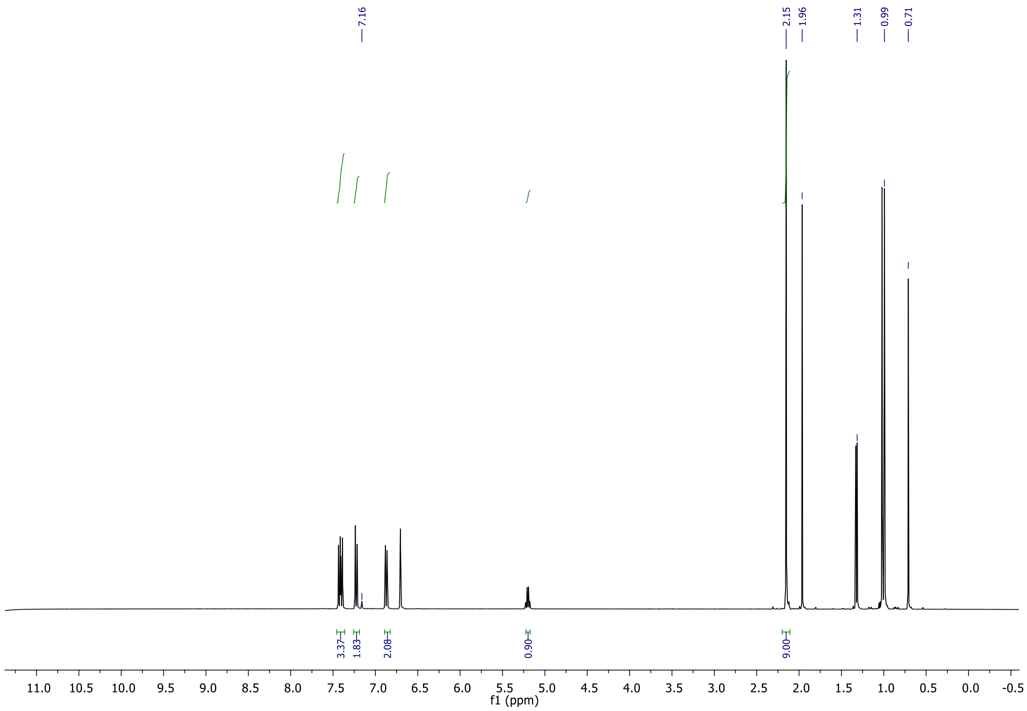


Figure S25. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-iodoacetophenone in the presence of 1-decyne at 1h.



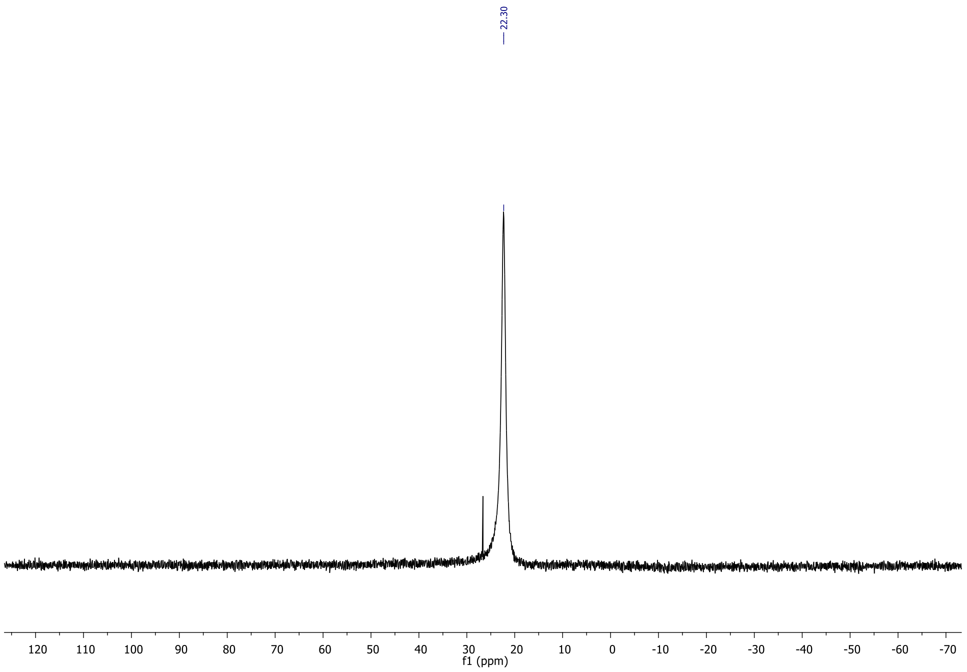


Figure S26. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-iodoacetophenone in the presence of acetonitrile at 1h.

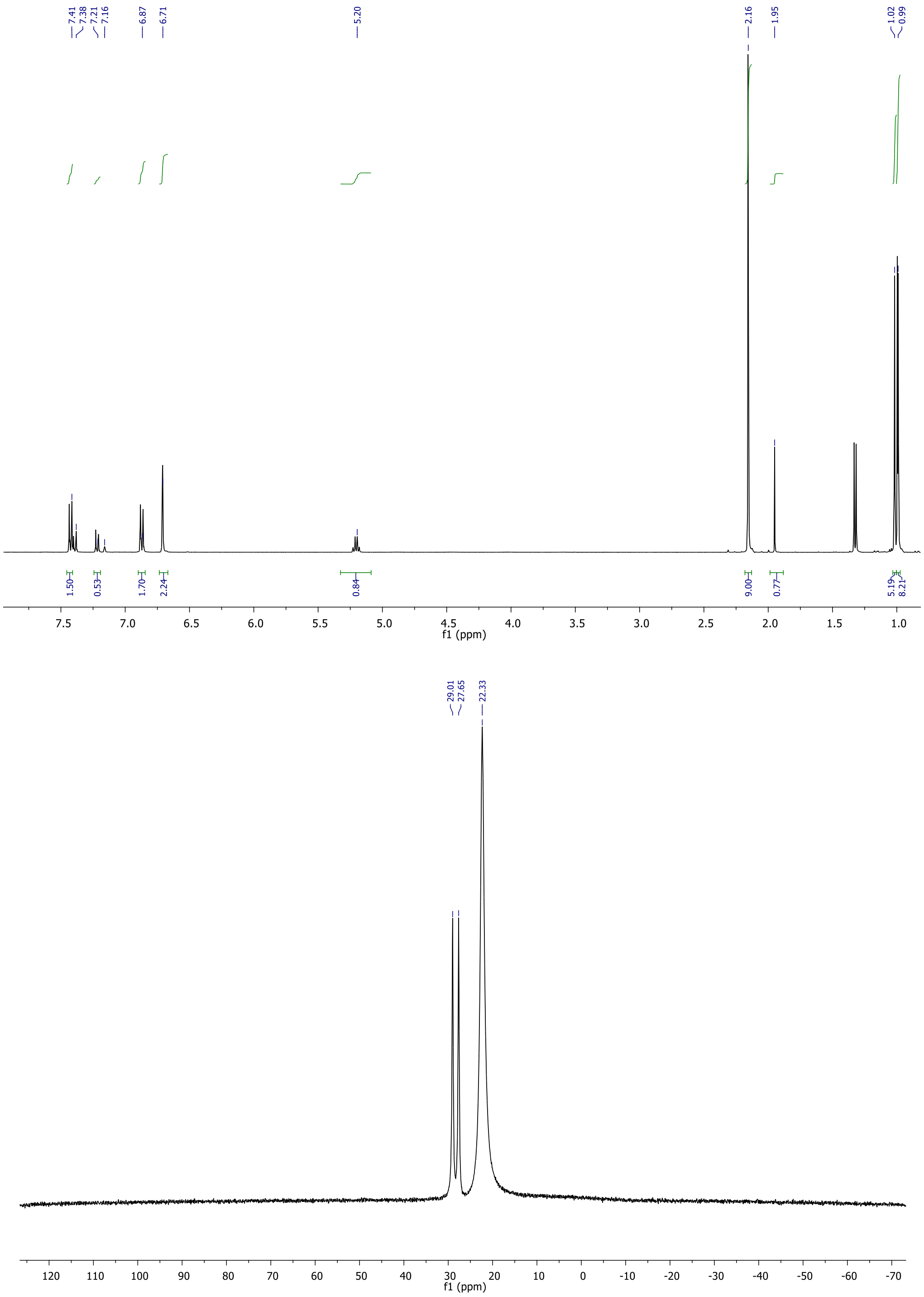


Figure S27. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-iodoacetophenone in the presence of methylbenzoate at 1h.

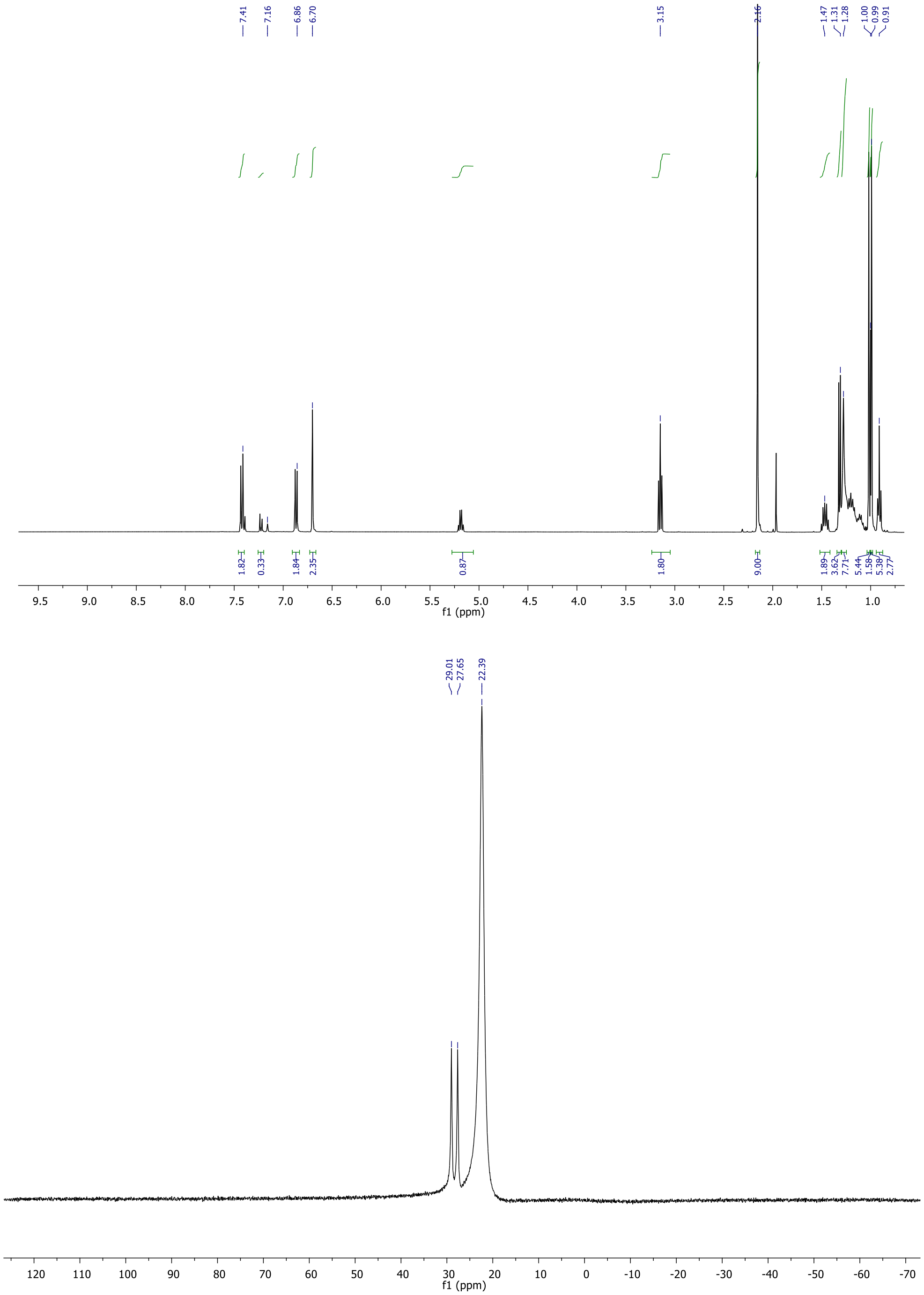


Figure S28. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-iodoacetophenone in the presence of 1-chlorododecene at 1h.

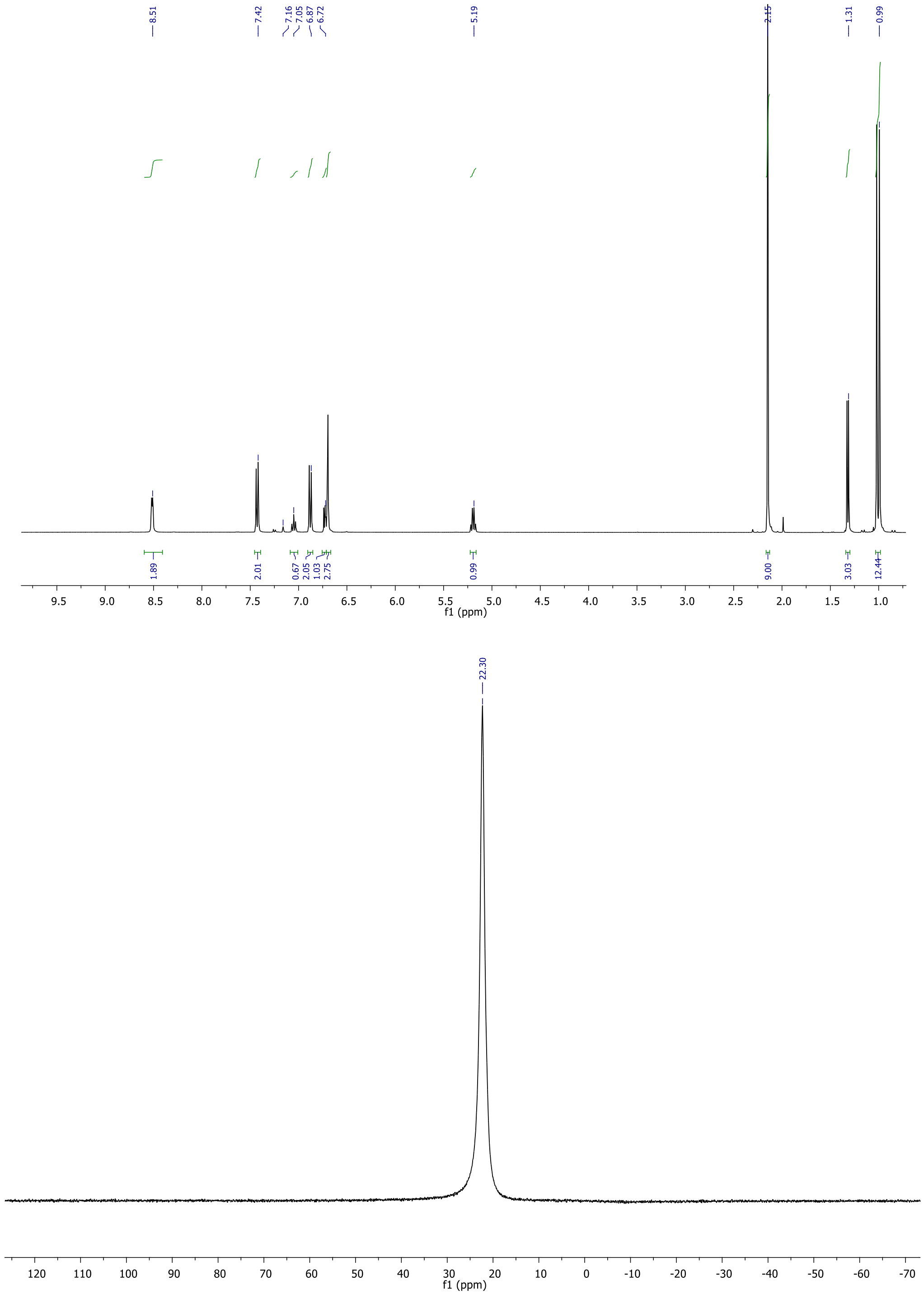
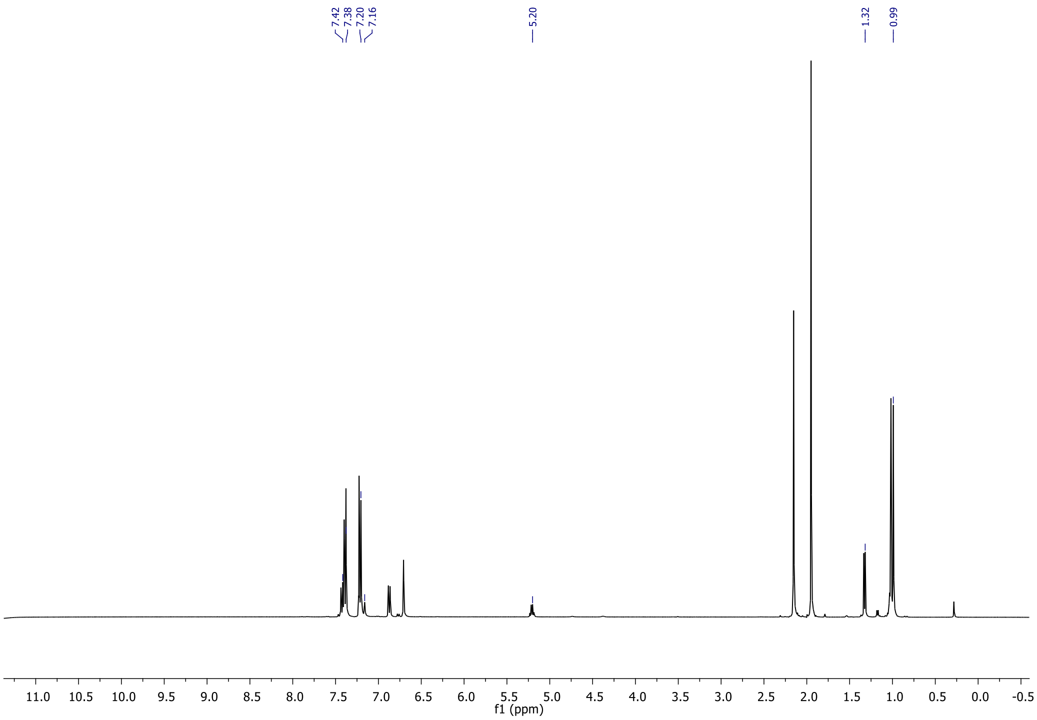


Figure S29. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra resulting from catalytic hydroboration of 4-iodoacetophenone in the presence of pyridine at 1h.



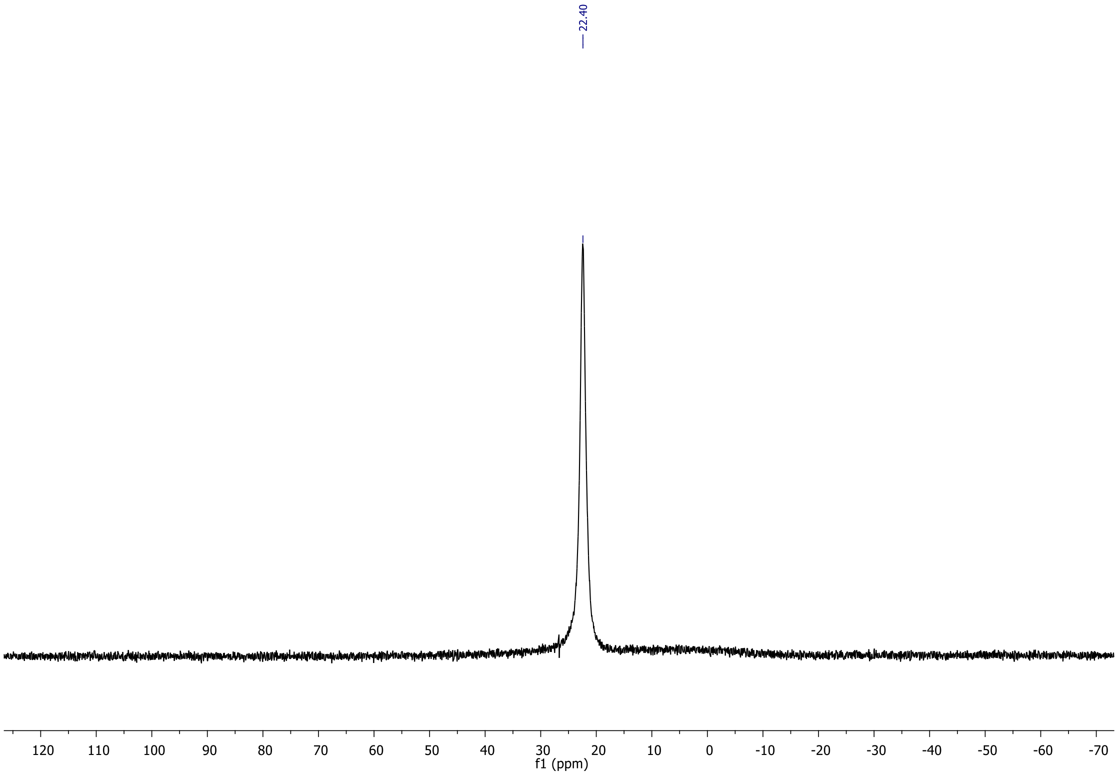


Figure S30. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra of isolated 2-(1-(4-iodophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

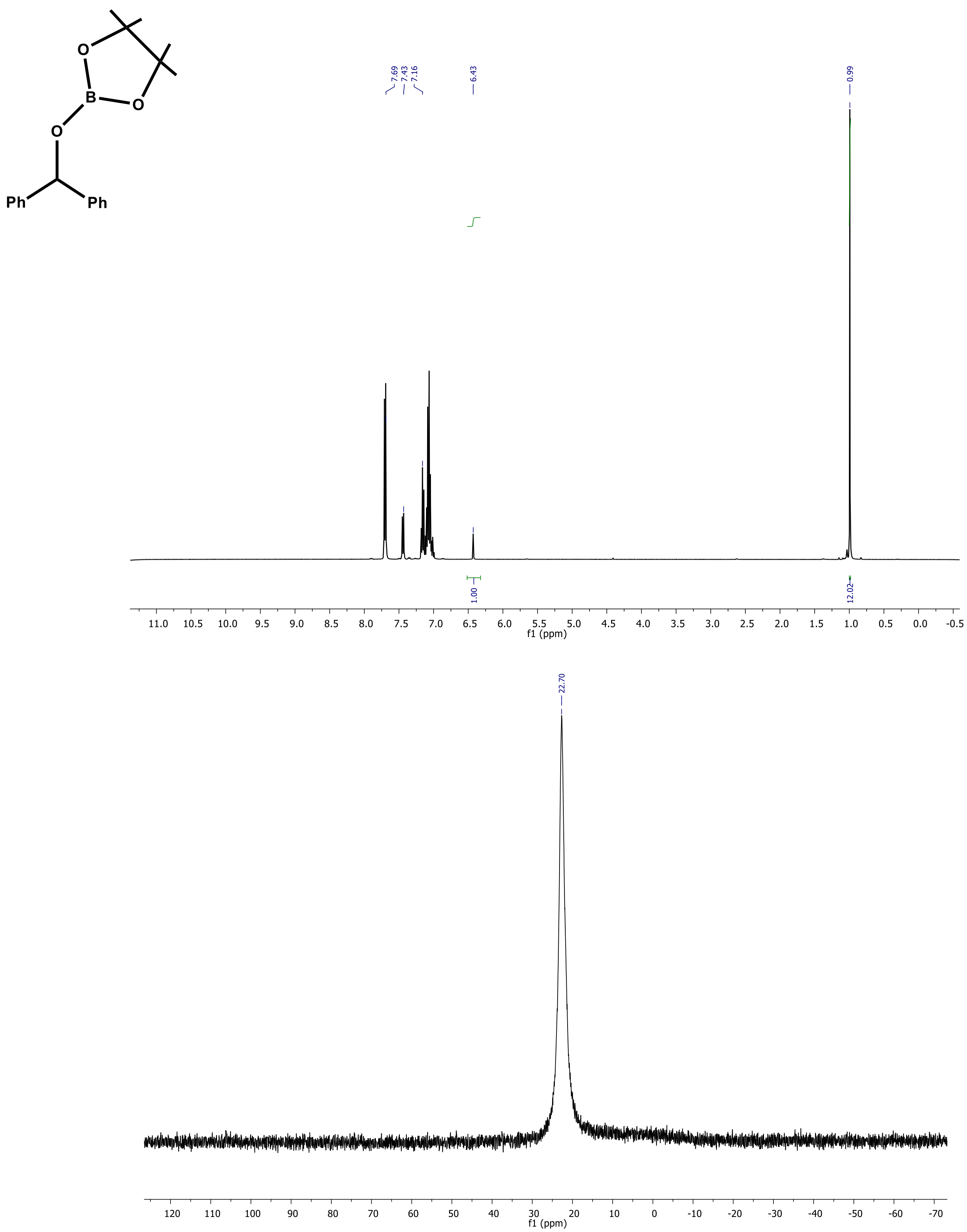


Figure S31. ^{1}H NMR (top) and ^{11}B NMR (bottom) spectra of isolated 2-(benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.