

SUPPORTING INFORMATION

β -Borylation of Conjugated Carbonyl Compounds by Silylborane or Bis(pinacolato)diboron Catalyzed by Au Nanoparticles

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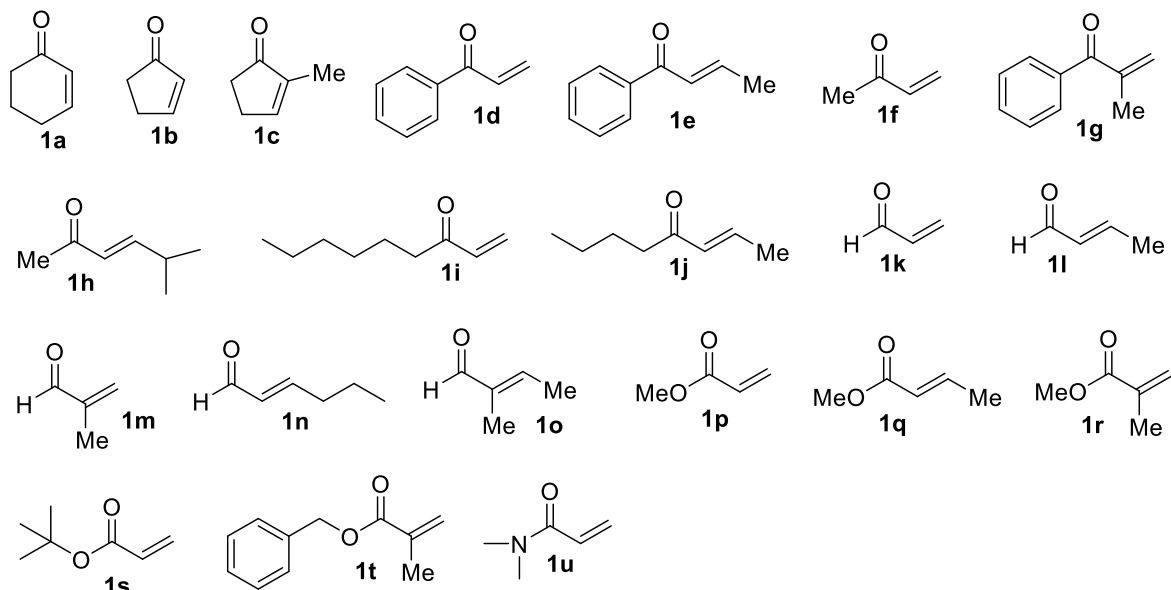
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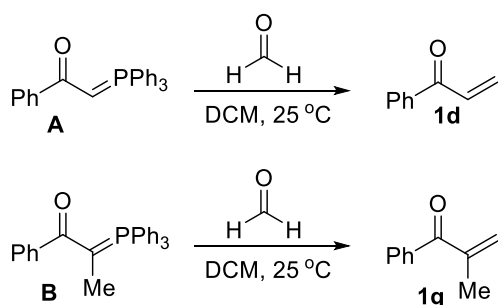
S2-S4	Substrates used in these studies
S5-S36	Copies of ^1H , ^{13}C NMR and selected MS spectra of synthesized reactants and products

Conjugated carbonyl compounds used in this studies

Below is the list of conjugated carbonyl compounds that were used in this study:



Among them, **1a-1c**, **1e-1f**, **1h**, and **1k-1u** are commercially available. Enones **1d**¹ and **1g**² were prepared from the reaction of the phosphorus stabilized ylides shown below with excess of paraformaldehyde in DCM.



To a round bottom flask were added 1 mmol of the stabilized phosphorus ylide **A** in 5 mL DCM followed by 3 mmol of paraphormaldehyde. The reaction was stirred for 12 h at room temperature. Then hexane was added for the precipitation of Ph_3PO , and enone **1d** was isolated after column chromatography (n-Hexane/EtOAc: 40/1) as a yellow oil (69% isolated yield). Enone **1g** was prepared similarly using the stabilized phosphorus ylide **B** in 66% isolated yield.

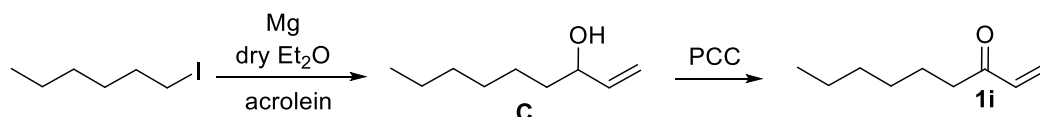
¹H NMR of **1d** (CDCl_3 , 500 MHz): 7.95 (m, 2H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.16 (dd, $J_1 = 17.0$ Hz, $J_2 = 10.5$ Hz, 1H), 6.45 (dd, $J_1 = 17.0$ Hz, $J_2 = 2.0$ Hz, 1H), 5.94 (dd, $J_1 = 10.5$ Hz, $J_2 = 2.0$ Hz, 1H).

¹³C NMR (125 MHz, CDCl_3): 191.1, 137.2, 133.0, 132.3, 130.2, 128.7, 128.6, 128.6.

^1H NMR of **1g** (CDCl_3 , 500 MHz): 7.73 (m, 2H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.43 (t, $J = 7.5$ Hz, 2H), 5.91 (m with fine splitting, 1H), 5.62 (s, 1H), 2.07 (m with fine splitting, 3H).

^{13}C NMR (125 MHz, CDCl_3): 198.4, 143.7, 137.7, 132.0, 129.4, 128.1, 127.1, 18.6.

Enone **1i**² was prepared by the reaction of hexyl magnesium iodide with acrolein followed by oxidation of the resulting alcohol with PCC.

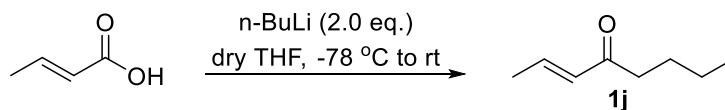


To a flame-dried two-necked round bottom flask equipped with an addition funnel and a condenser were added magnesium turnings (15.0 mmol) and 10 mL anhydrous Et_2O under an Ar atmosphere. A solution of 1-iodohexane (10.0 mmol) in 5 mL anhydrous Et_2O was added dropwise and after formation of the Grignard reagent was ensured, the mixture was cooled to 0 °C. Freshly distilled acrolein (10.0 mmol) was added dropwise and the mixture was refluxed for 2 h. The reaction was quenched with 2 mL of $\text{NH}_4\text{Cl}_{(\text{aq})}$ and the mixture was extracted with diethyl ether. The organic residue was purified by flash chromatography (n-Hexane/ EtOAc : 10/1) to afford the allylic alcohol **C** in 89% isolated yield. The alcohol (2 mmol) was oxidized with PCC (3 mmol) in DCM at room temperature for 4 h. Upon completion (TLC) the mixture was passed through Celite and the residue was purified by column chromatography (n-Hexane/ EtOAc : 20/1) to afford enone **1i** (as a yellow oil) in 71% isolated yield.

^1H NMR of **1i** (CDCl_3 , 500 MHz): 6.34 (dd, $J_1 = 18.0$ Hz, $J_2 = 11.0$ Hz, 1H), 6.21 (dd, $J_1 = 18.0$ Hz, $J_2 = 1.0$ Hz, 1H), 5.81 (dd, $J_1 = 11.0$ Hz, $J_2 = 1.0$ Hz, 1H), 2.57 (t, $J = 7.0$ Hz, 2H), 1.64-1.58 (m, 2H), 1.33-1.24 (m, 6H), 0.88 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3): 201.1, 136.6, 127.8, 39.6, 31.6, 28.9, 24.3, 22.5, 14.0.

Enone **1j**³ was prepared by treatment of crotonic acid with 2 equiv of *n*-BuLi in dry THF at -78 °C, and then warming to 0 °C.



To a flame-dried two-necked round bottom flask was added 5.81 mmol of methacrylic acid and 10 mL anhydrous THF under an Ar atmosphere. *n*-BuLi (1.6 M in hexane, 2.0 equiv) was added dropwise at -78 °C and the mixture was stirred at this temperature for 2 h. Then 0.5 mL H_2O was added dropwise and the mixture was filtered through a pad of Celite.

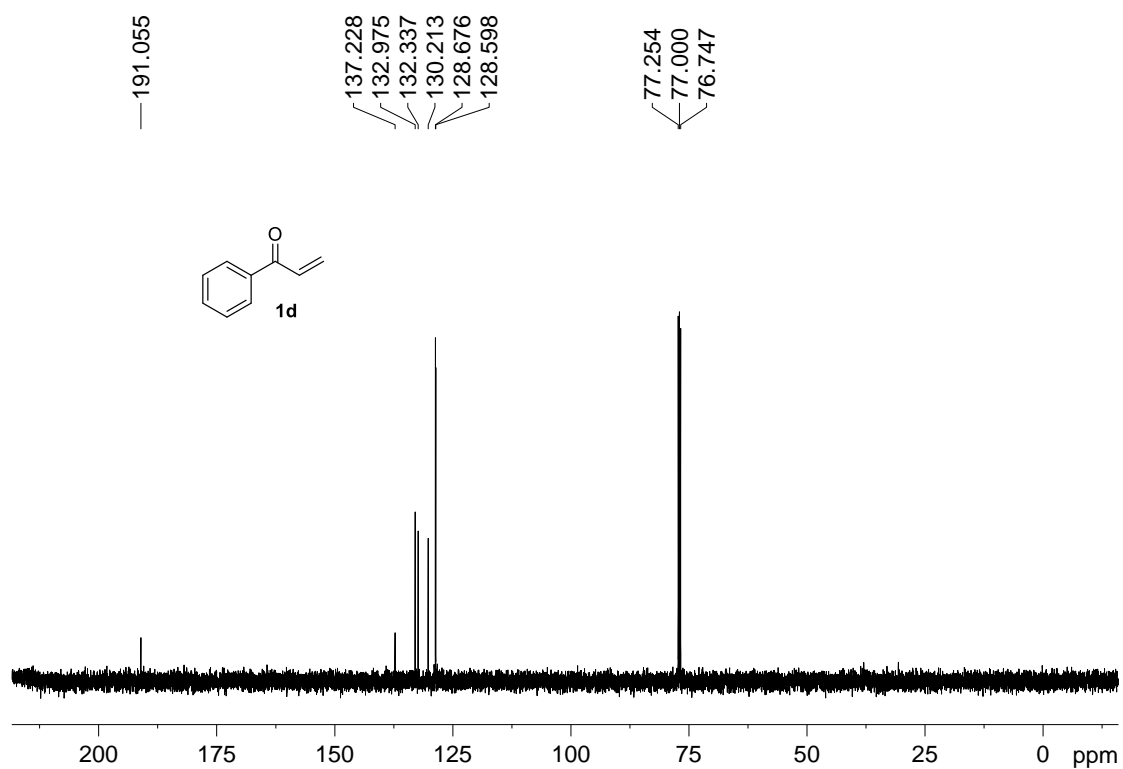
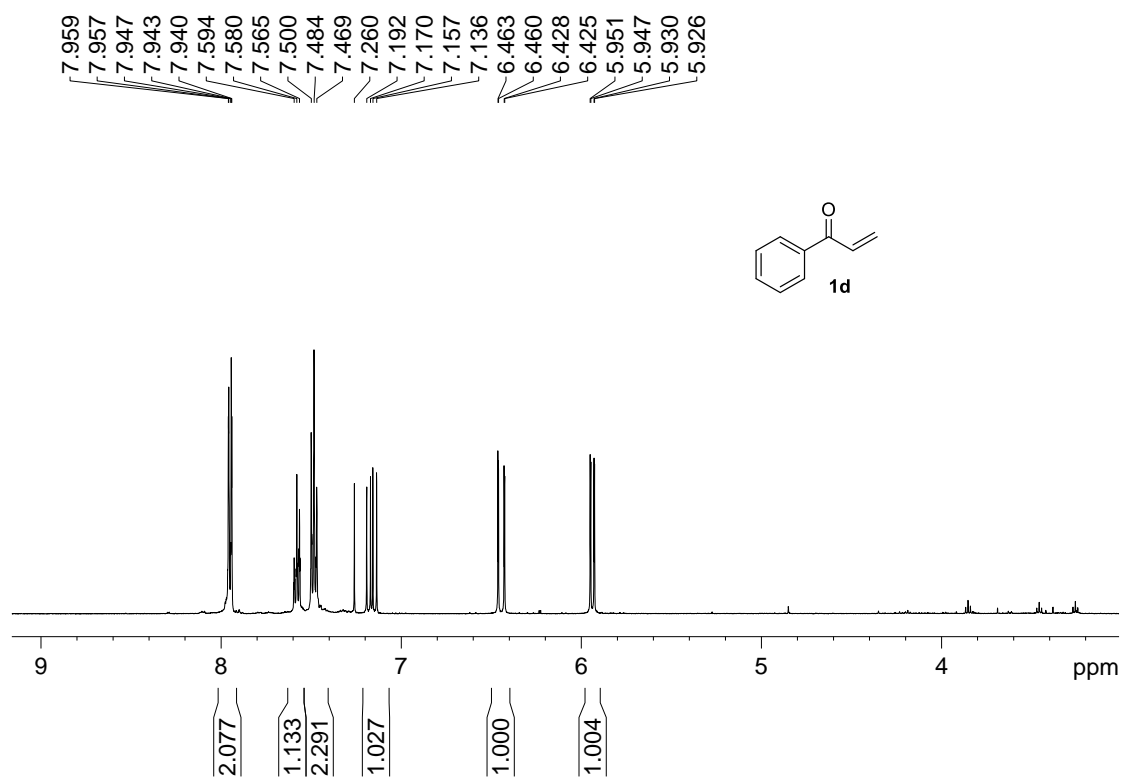
Enone **1j** was isolated upon column chromatography (*n*-Hexane/EtOAc: 30/1) as a yellow oil in 81% isolated yield.

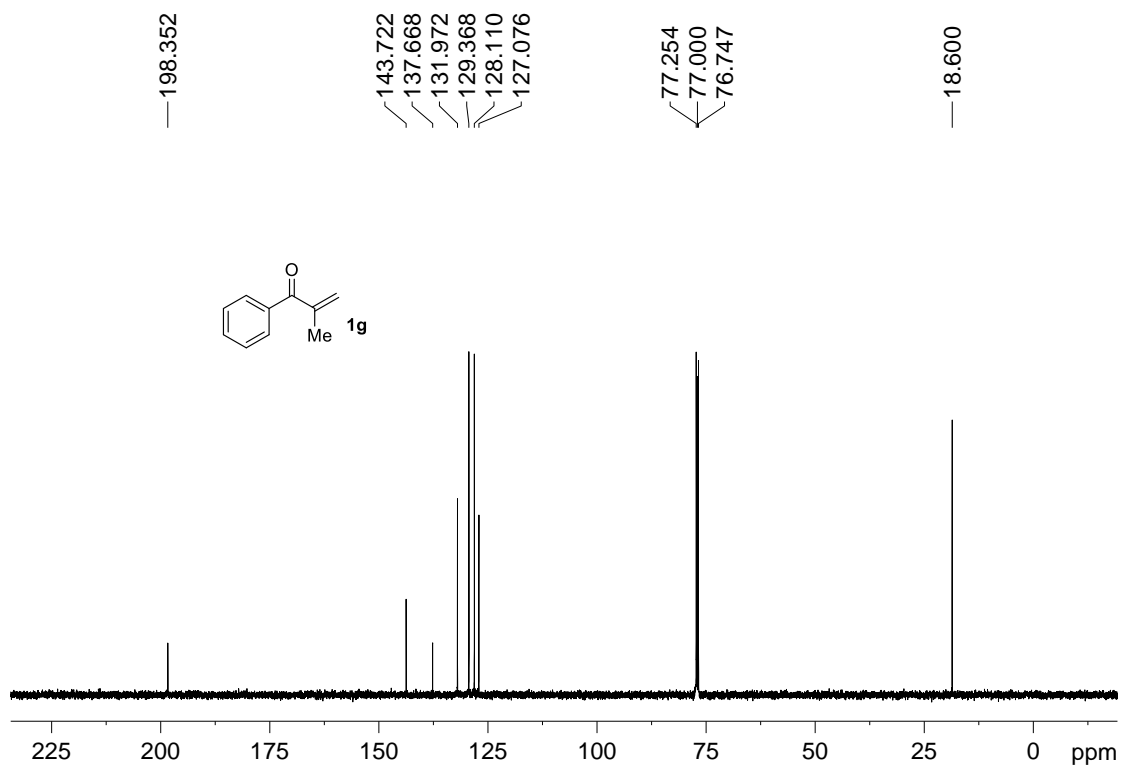
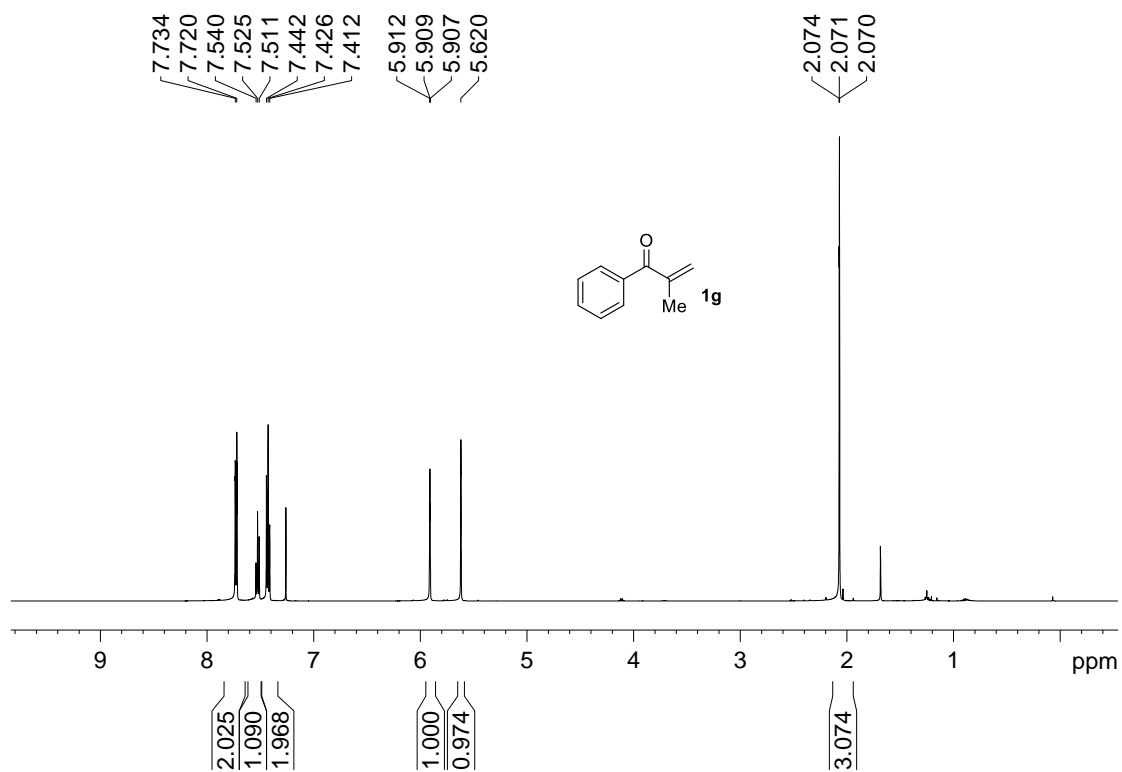
¹H NMR of **1j** (CDCl₃, 500 MHz): 6.84 (qd, $J_1 = 16.0$ Hz, $J_2 = 7.0$ Hz, 1H), 6.12 (qd, $J_1 = 16.0$ Hz, $J_2 = 1.5$ Hz, 1H), 2.51 (t, $J = 7.5$ Hz, 2H), 1.89 (m, 3H), 1.61-1.55 (m, 2H), 1.36-1.30 (m, 2H), 0.90 (t, $J = 7.0$ Hz, 3H).

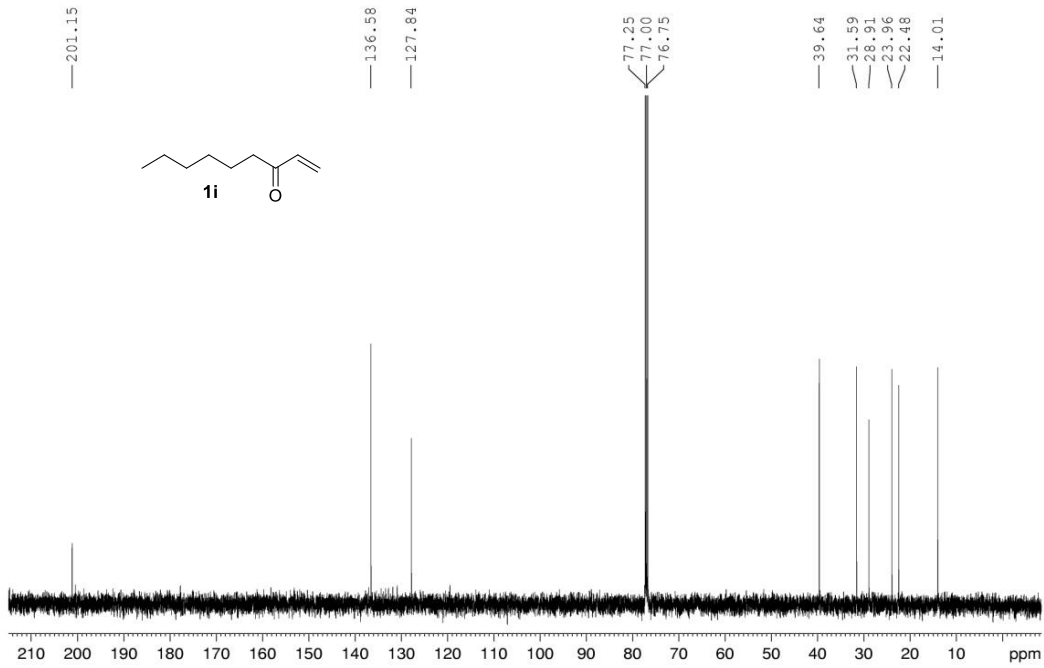
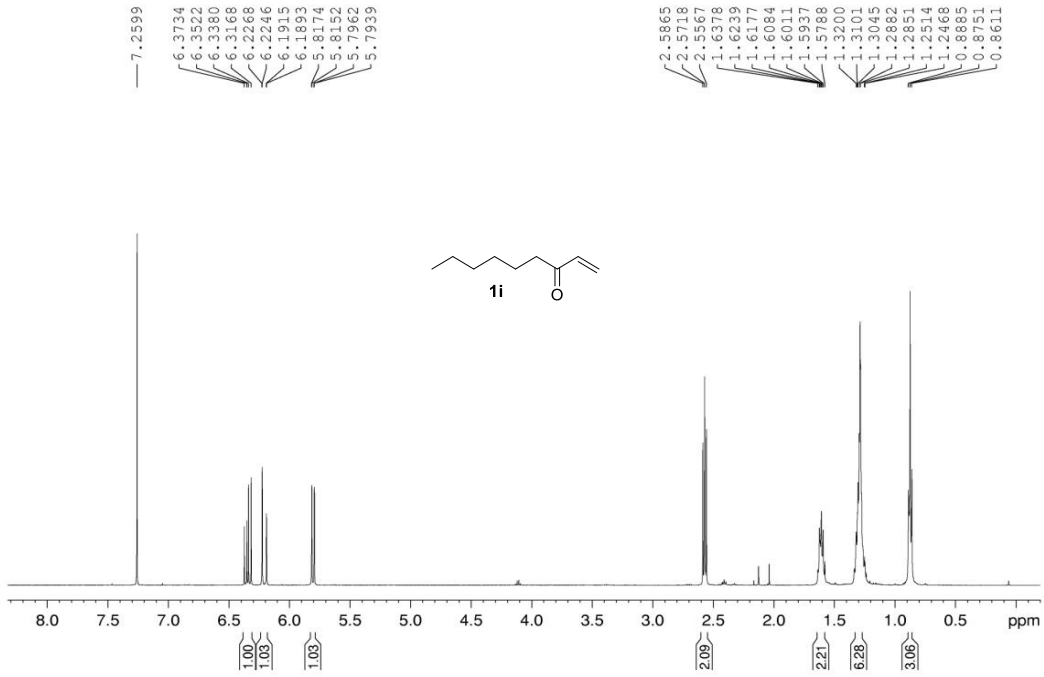
¹³C NMR (125 MHz, CDCl₃): 200.8, 142.3, 131.9, 39.7, 26.4, 22.4, 18.2, 13.9.

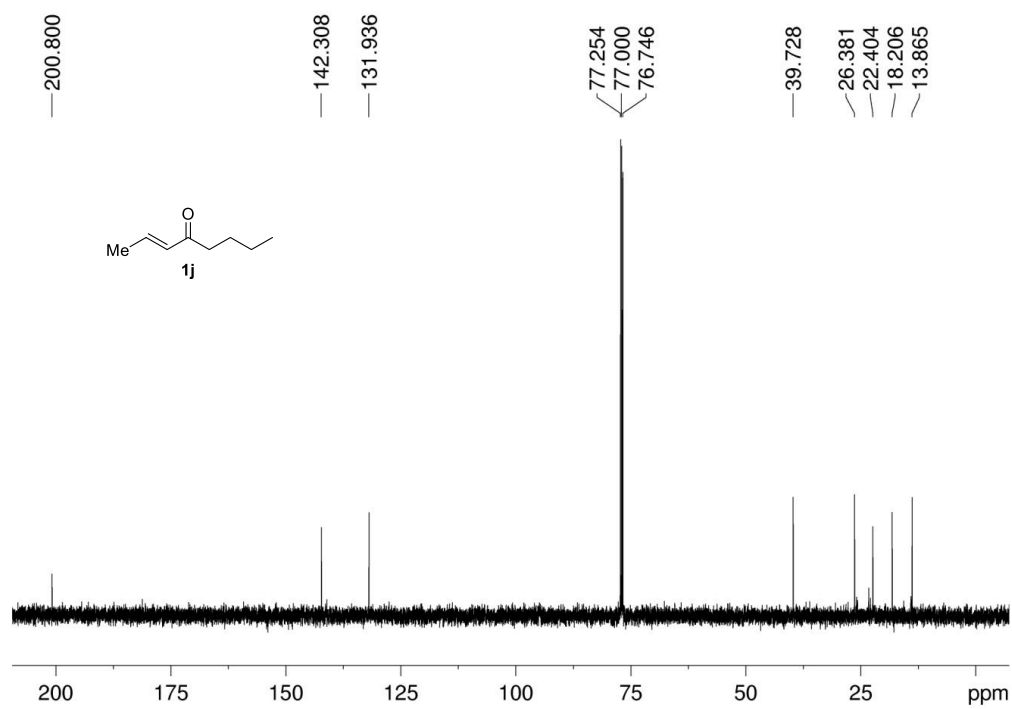
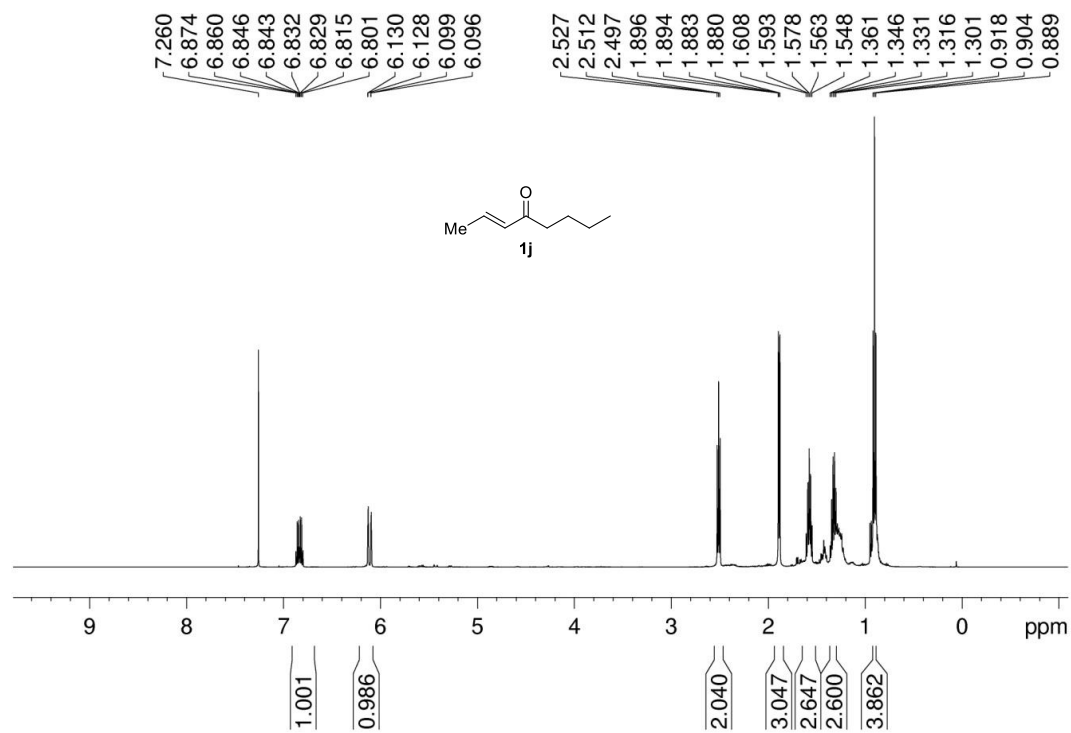
References

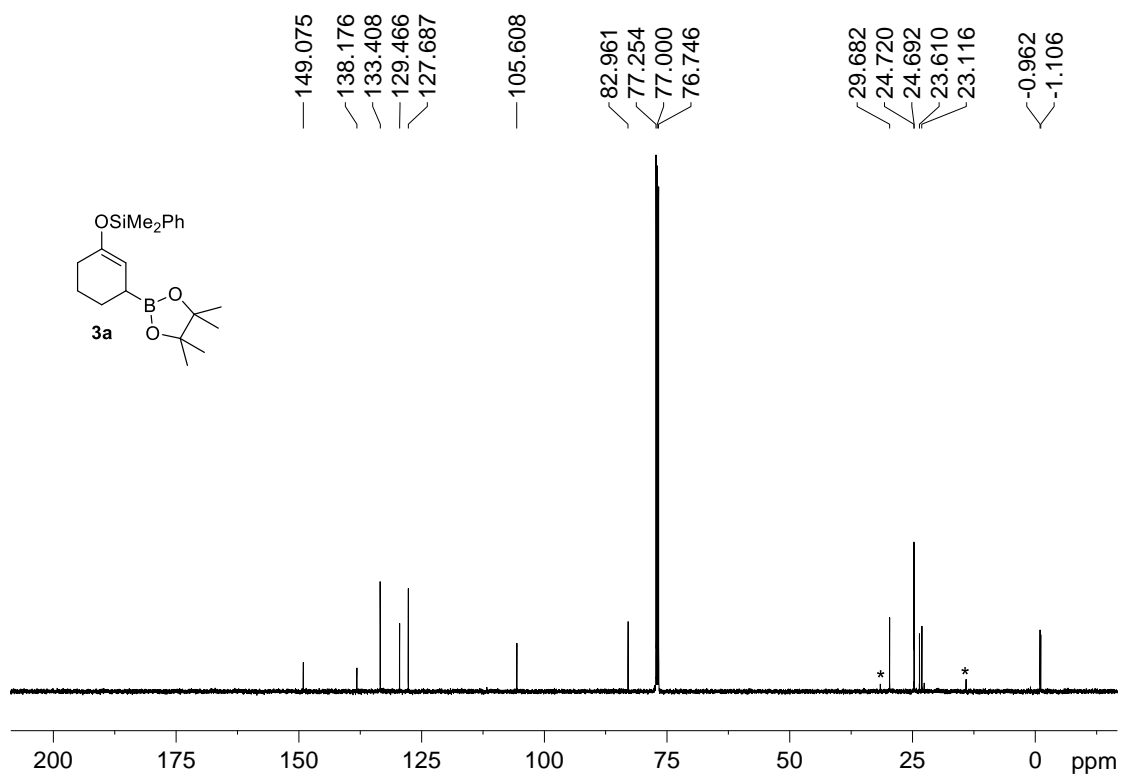
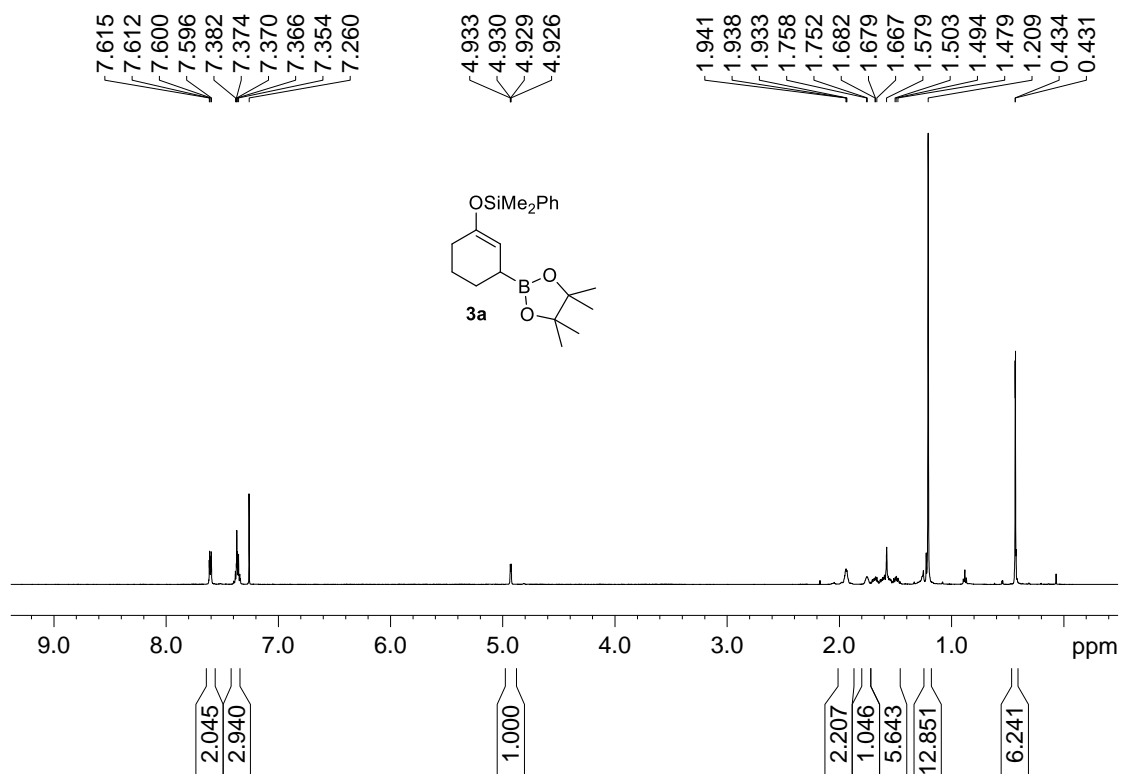
1. S. M. Hell, C. F. Meyer, G. Laudadio, A. Misale, M. C. Willis, T. Noel, A. A. Trabanco and V. Gouverneur, *J. Am. Chem. Soc.* 2020, **142**, 720.
2. J. Liu and S. Ma, *Org. Lett.* 2013, **15**, 5150.
3. A. S.-Y. Lee, M.-C. Lin, S.-H. Wang and L.-S. Lin, *J. Chin. Chem. Soc.*, 2004, **51**, 371.

^1H and ^{13}C NMR of synthesized enones

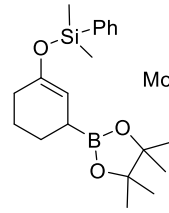




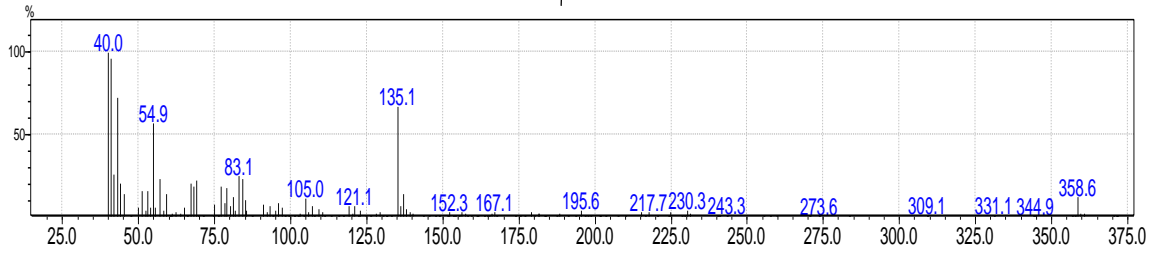


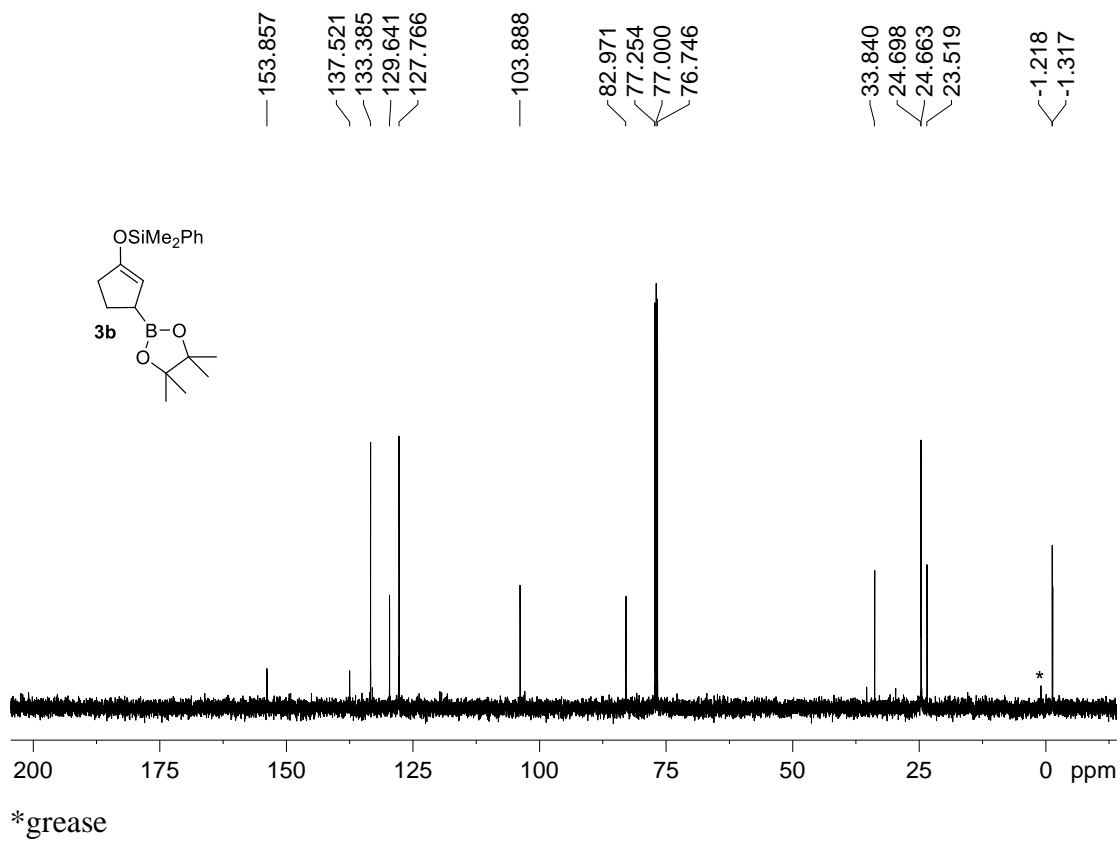
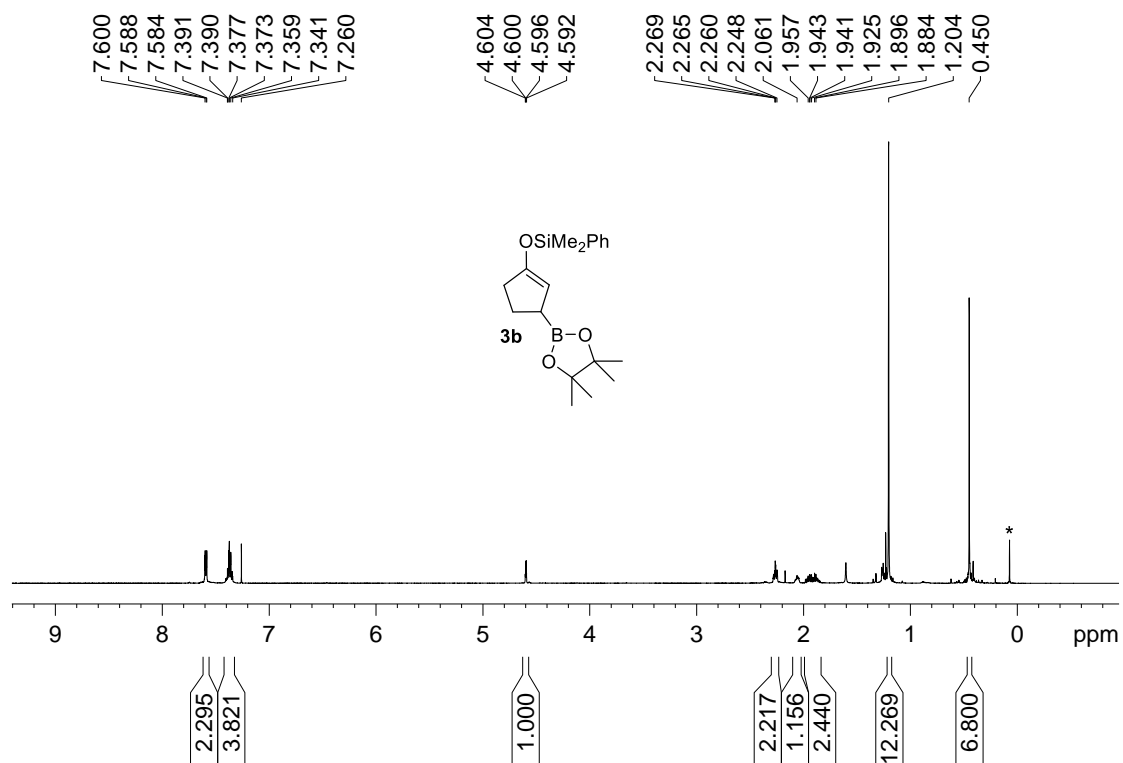
^1H , ^{13}C NMR and selected MS spectra of products

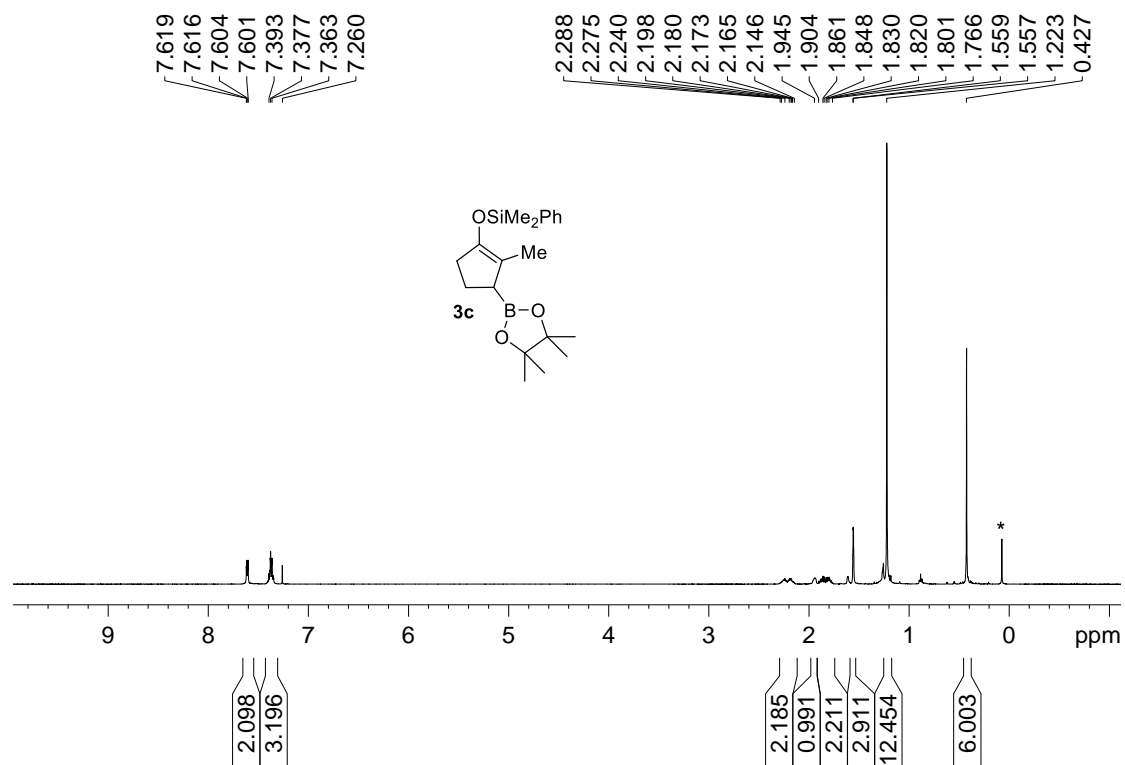
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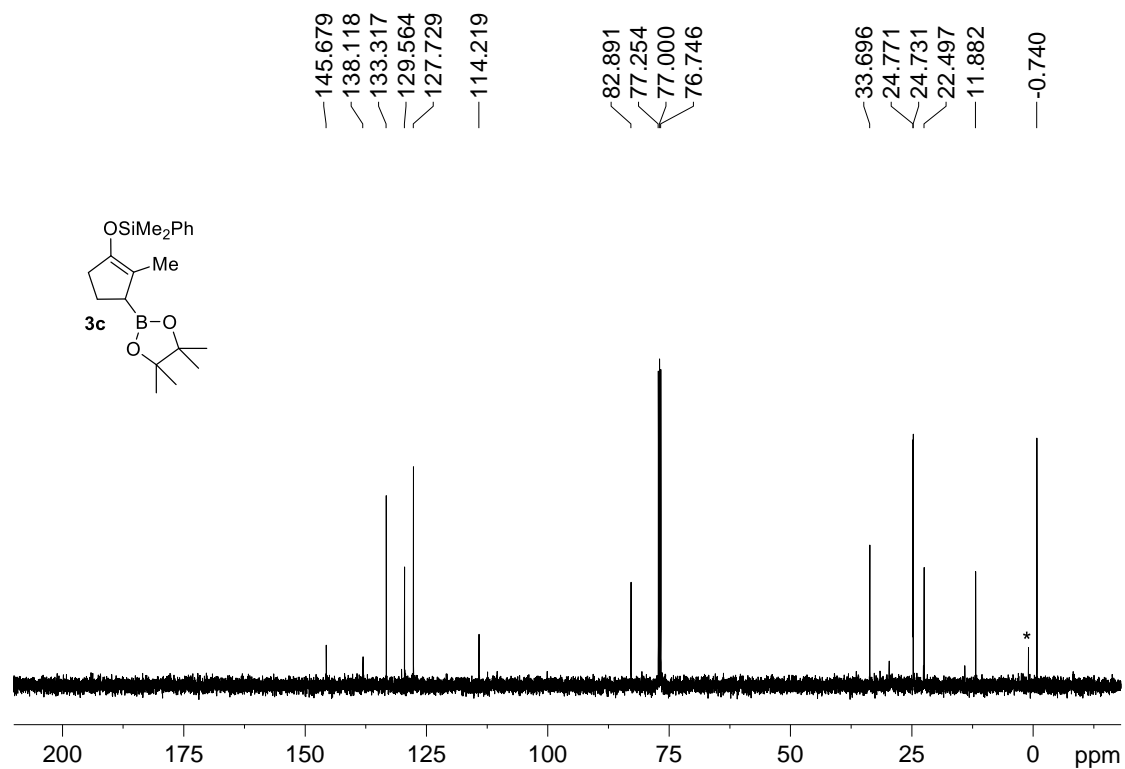
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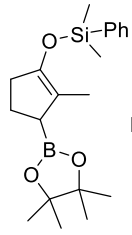


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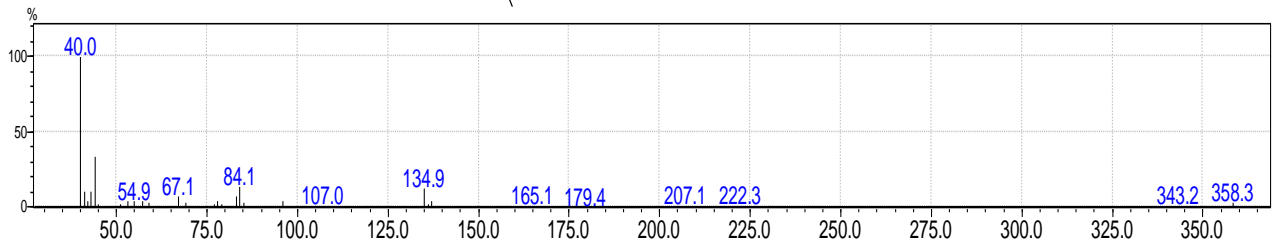


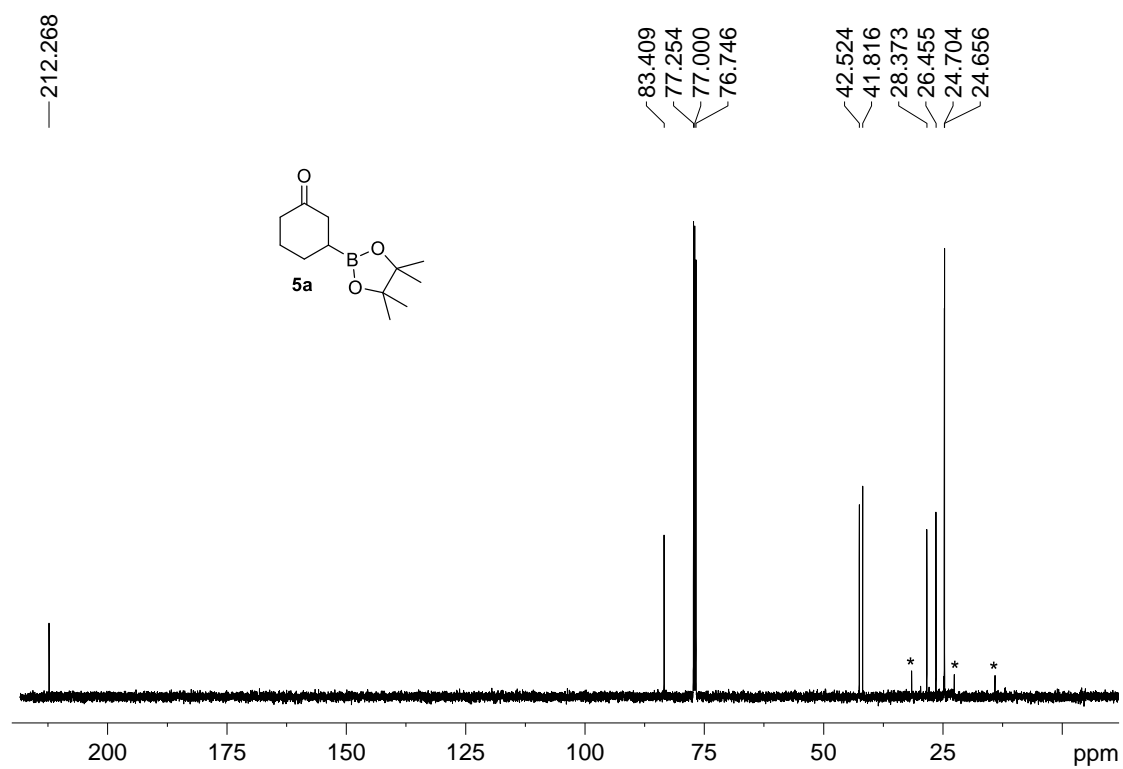
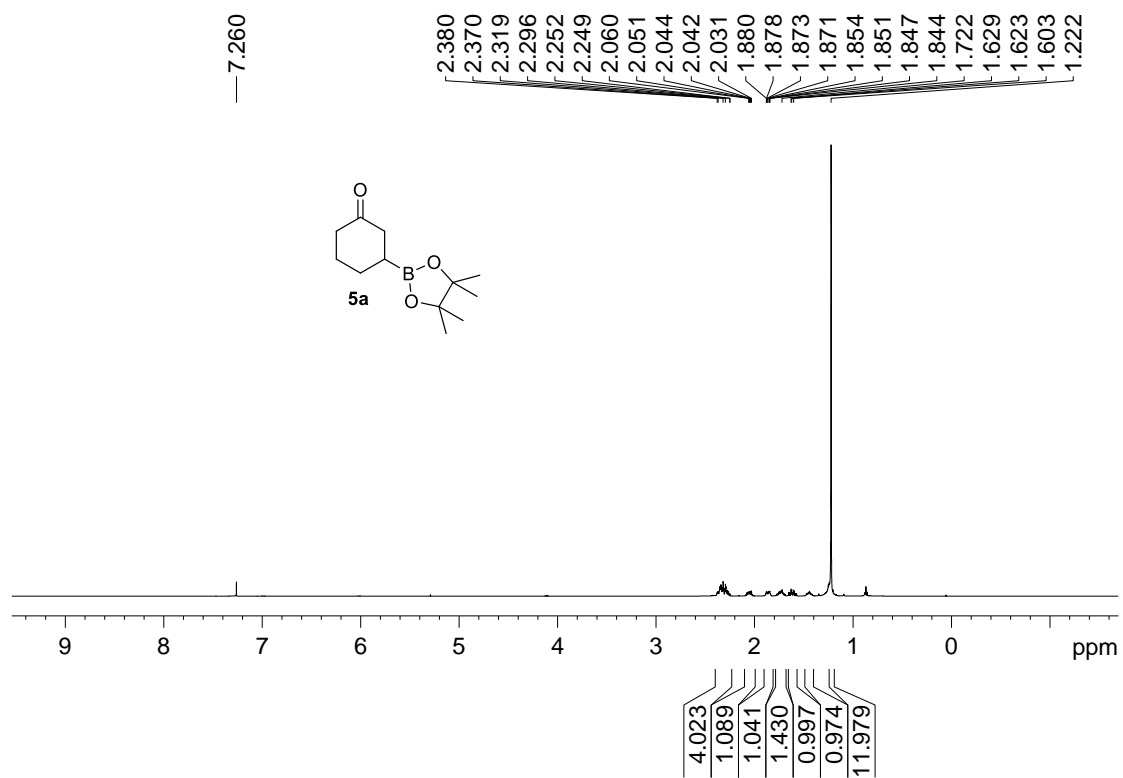
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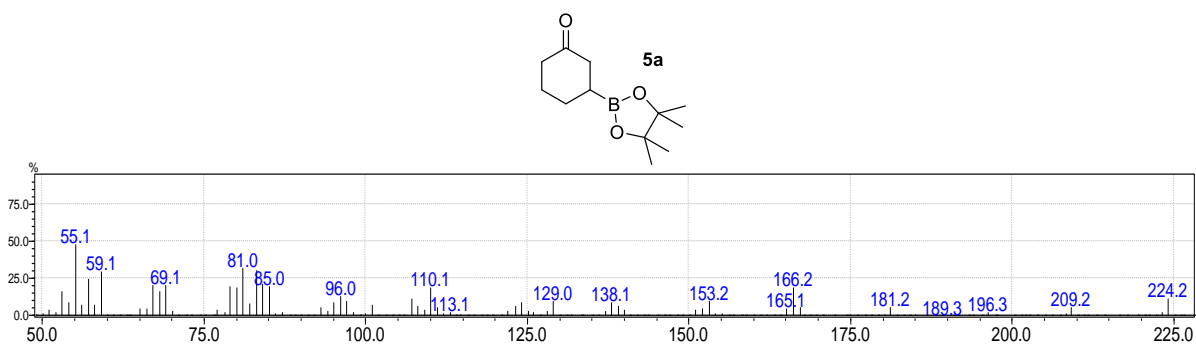
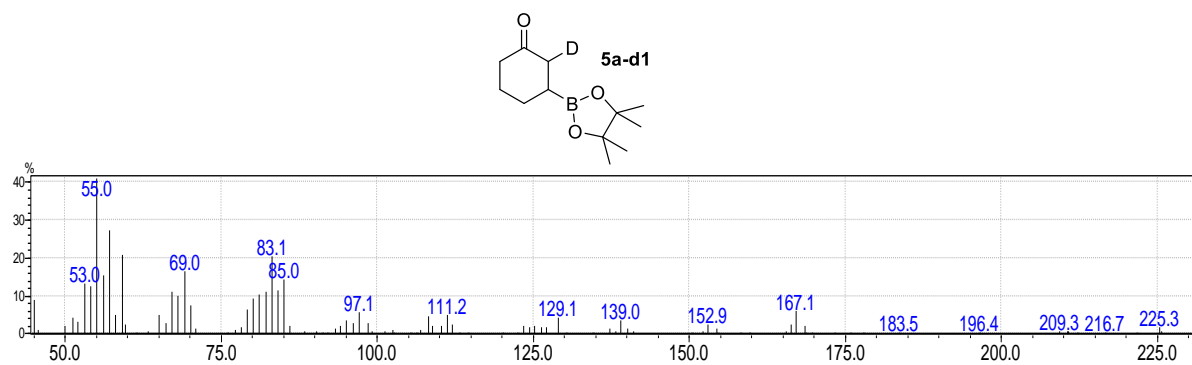
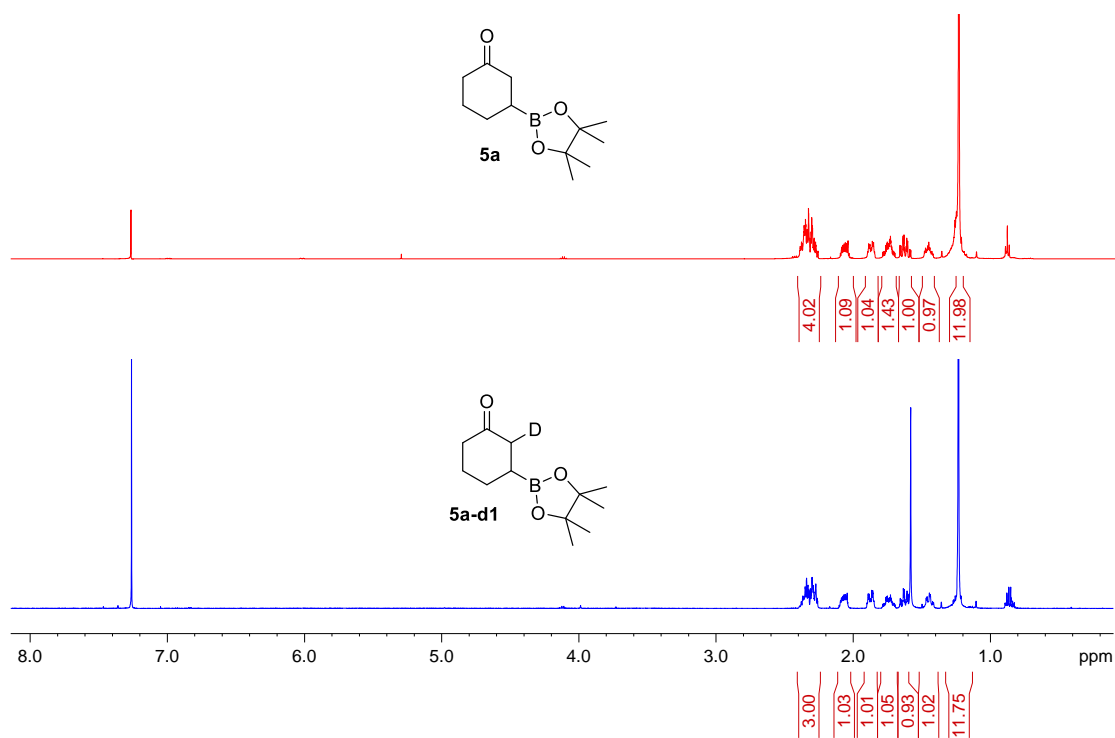


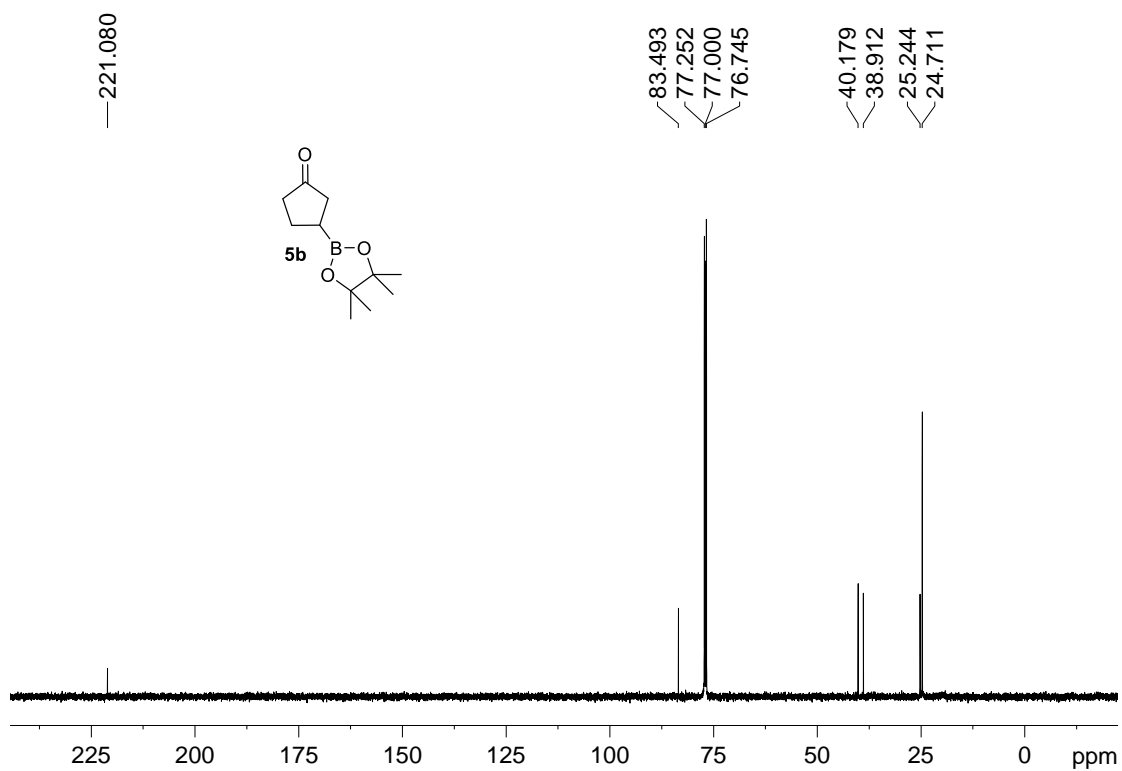
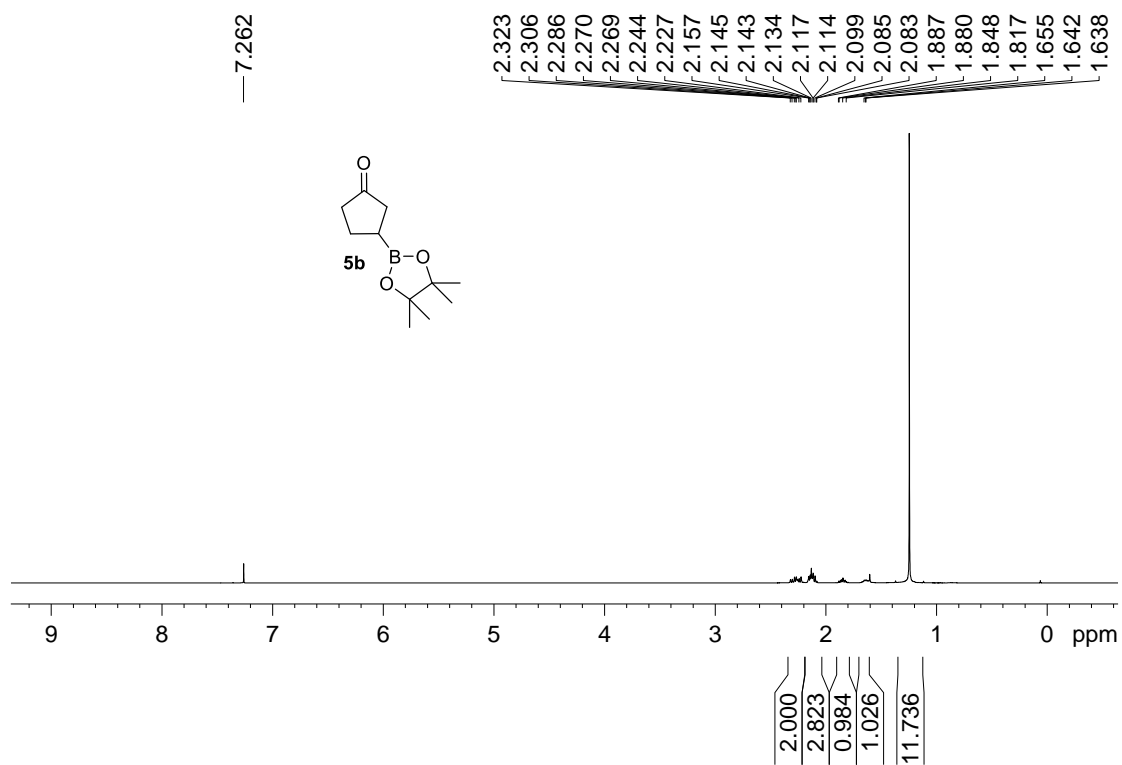
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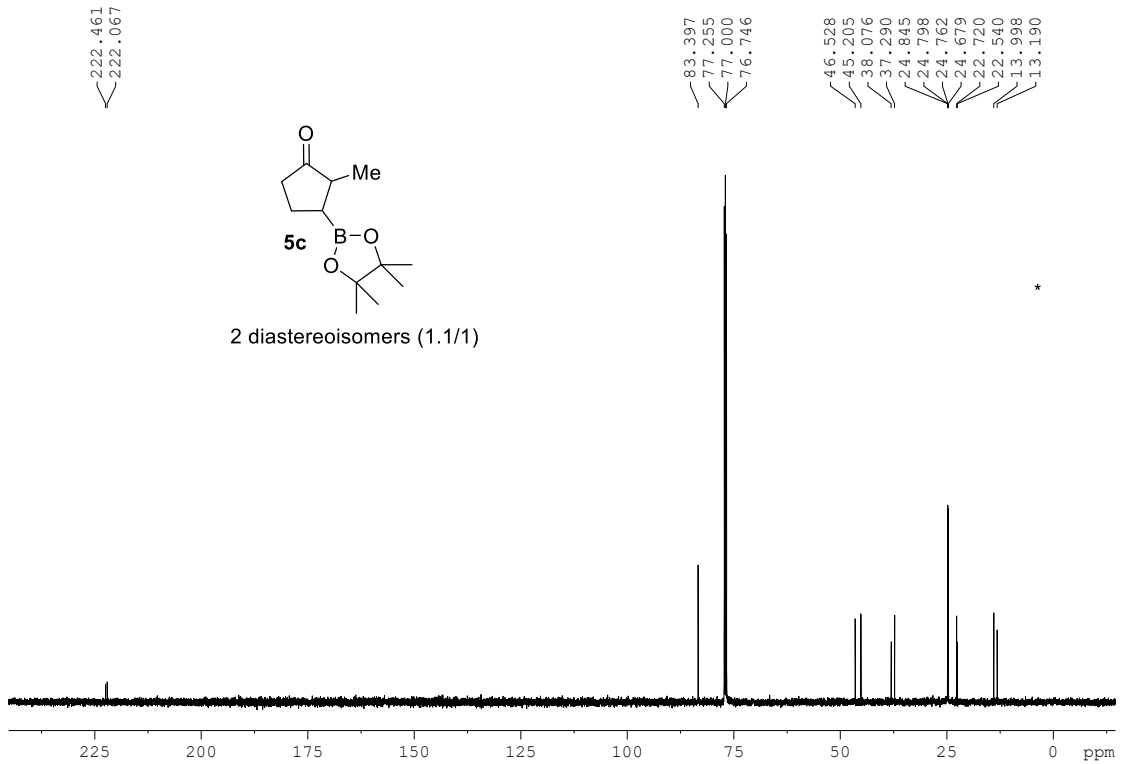
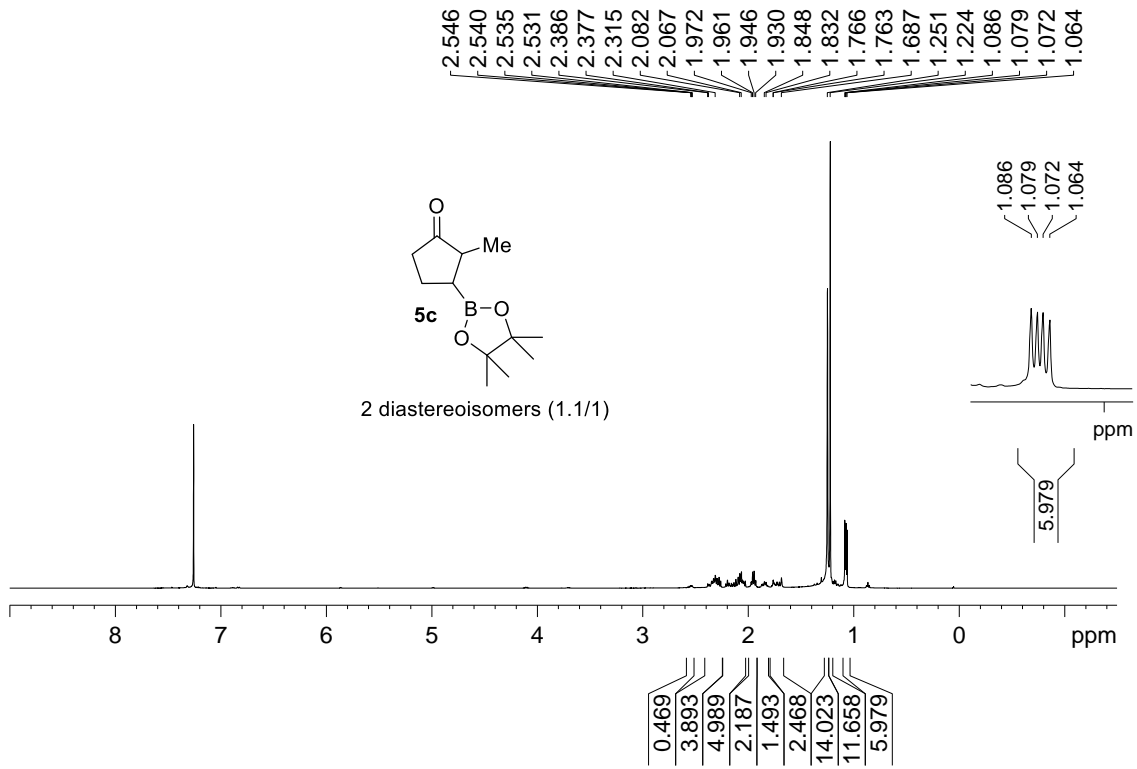


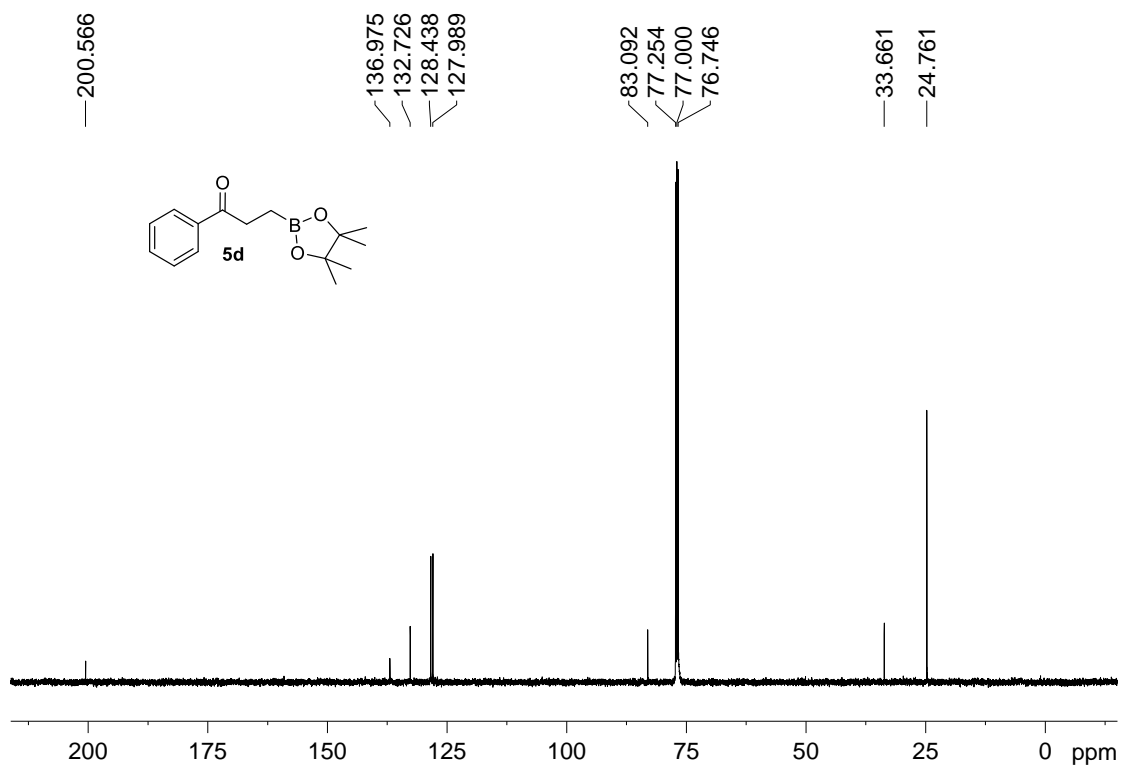
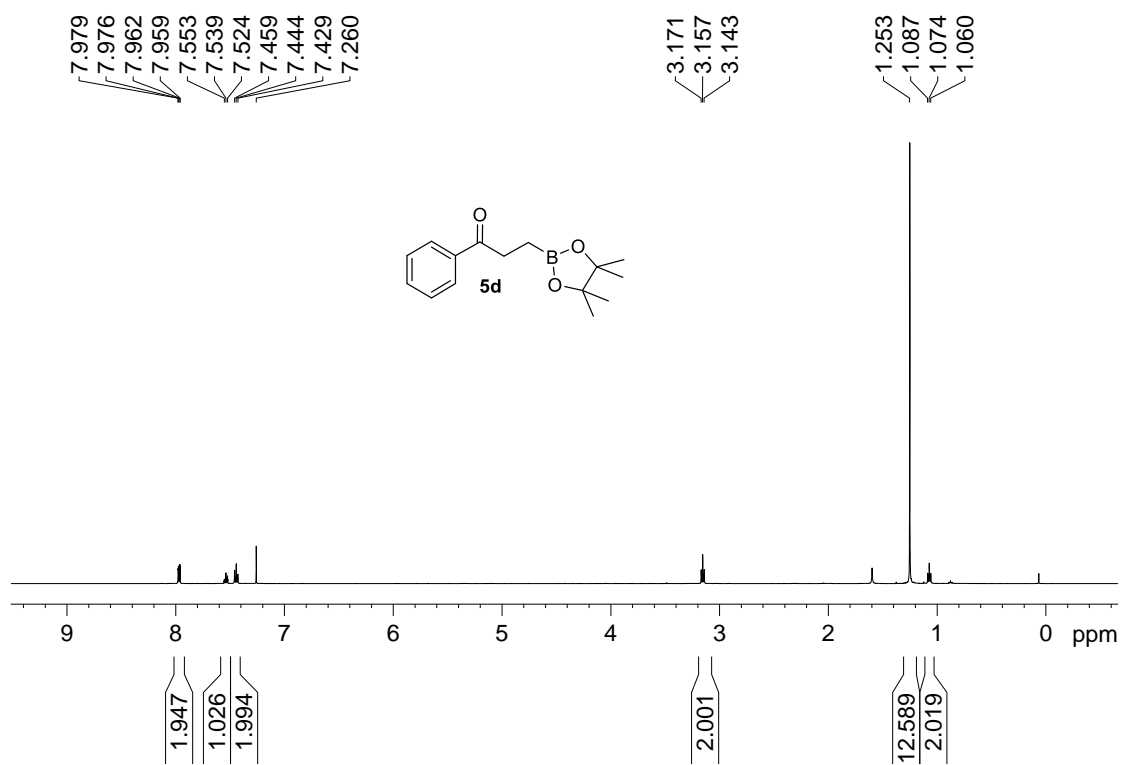


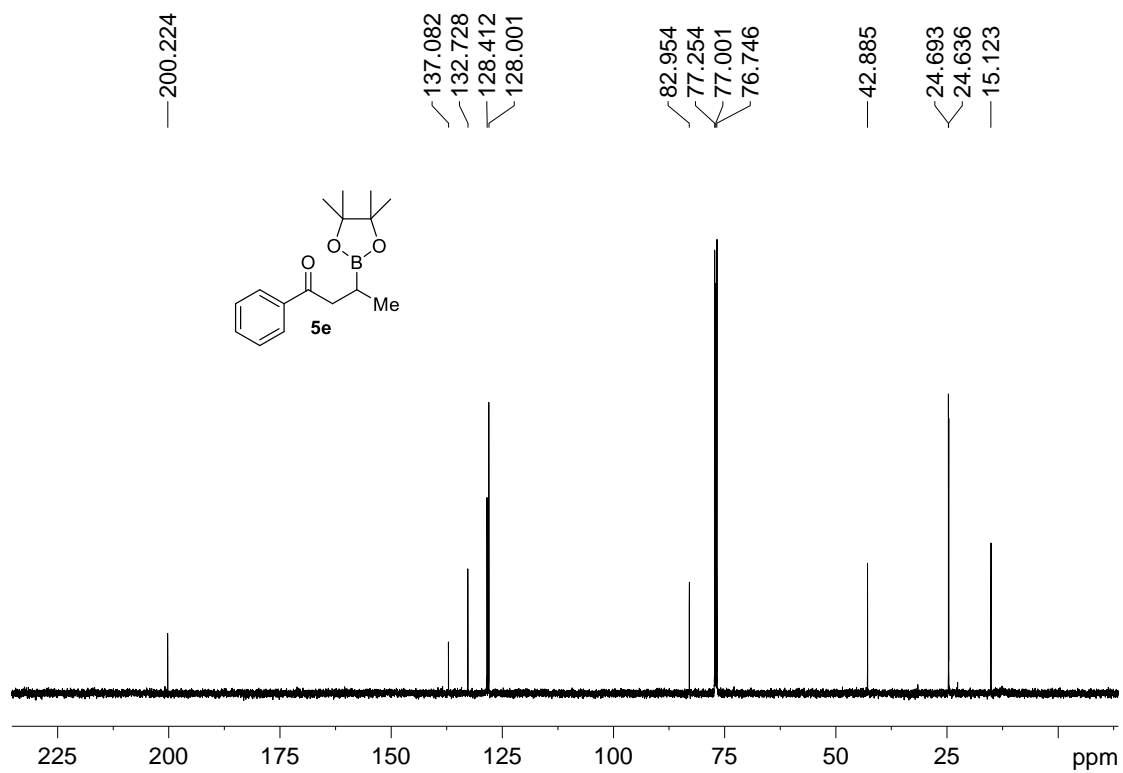
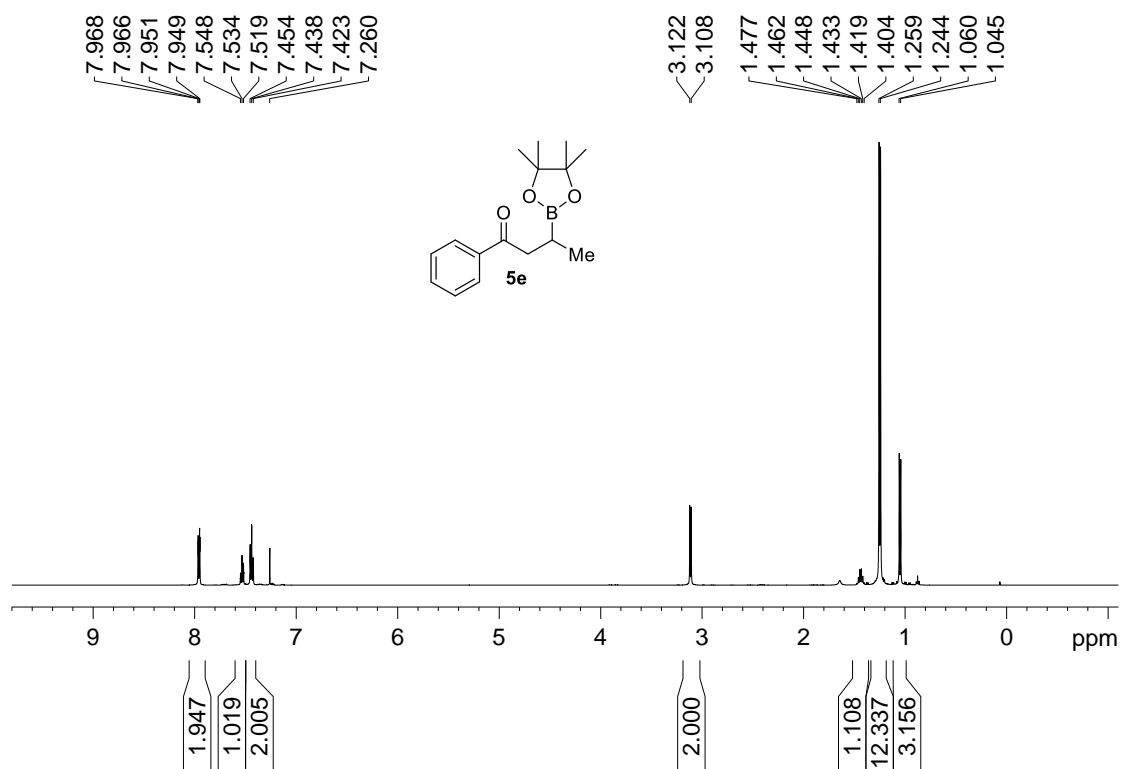
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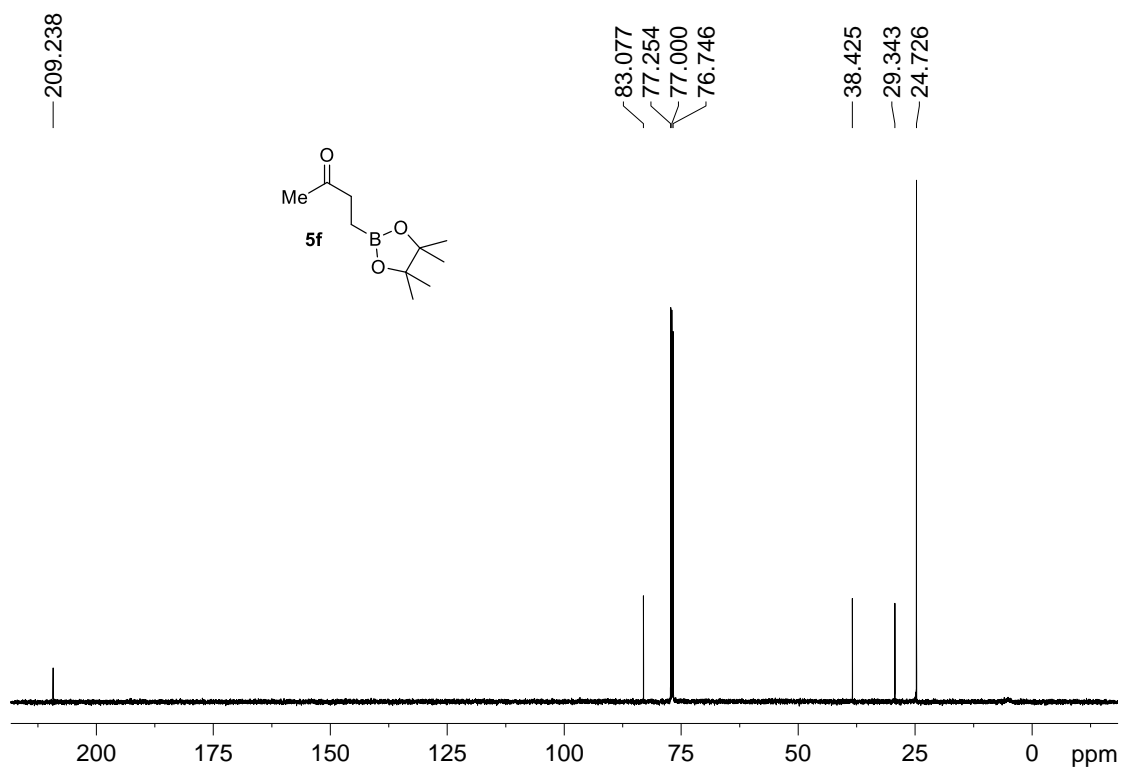
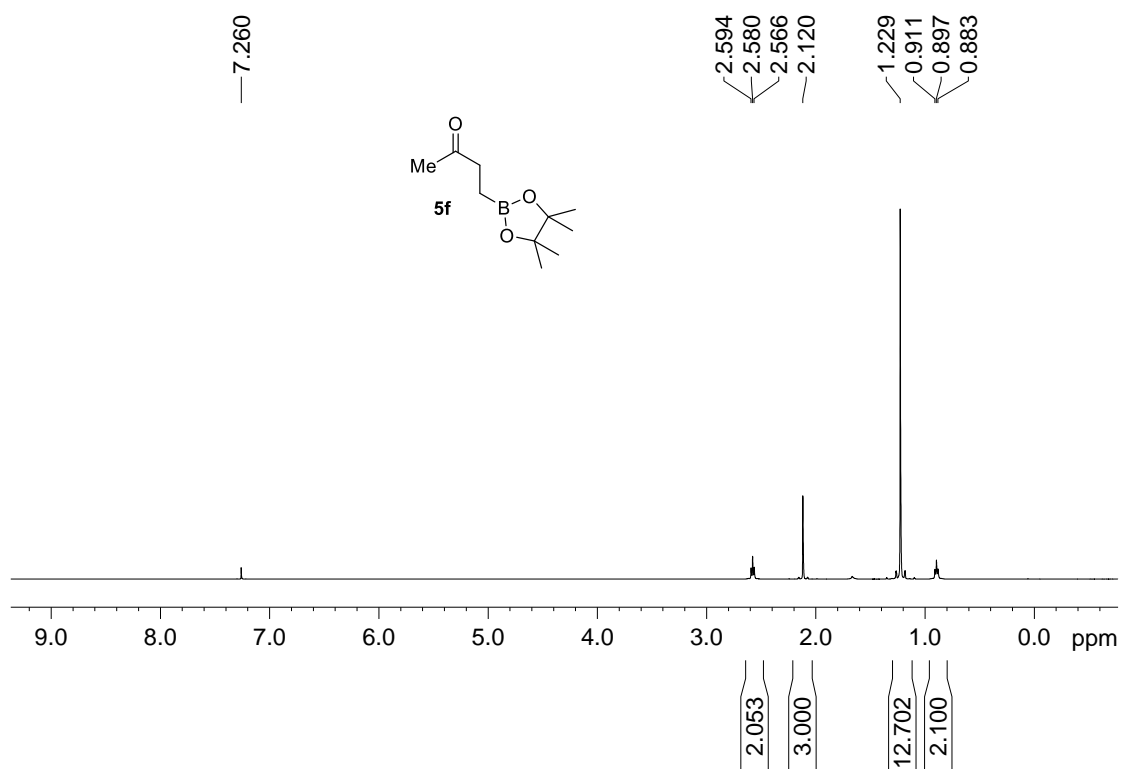


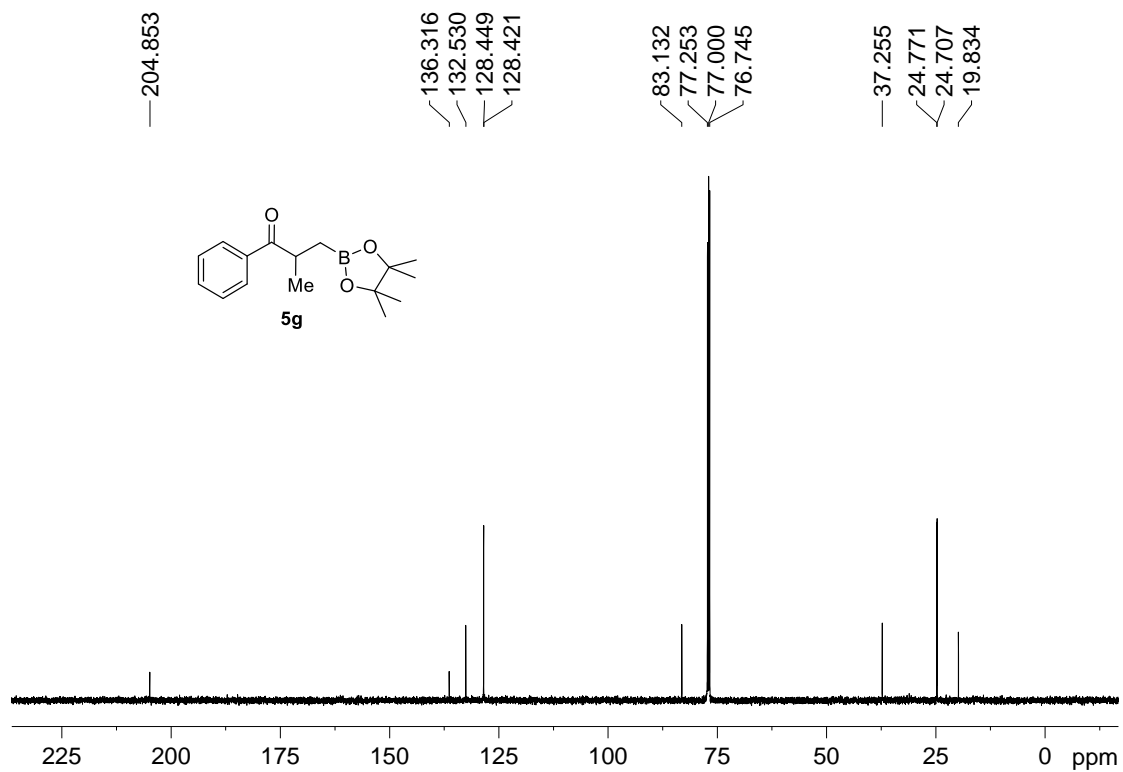
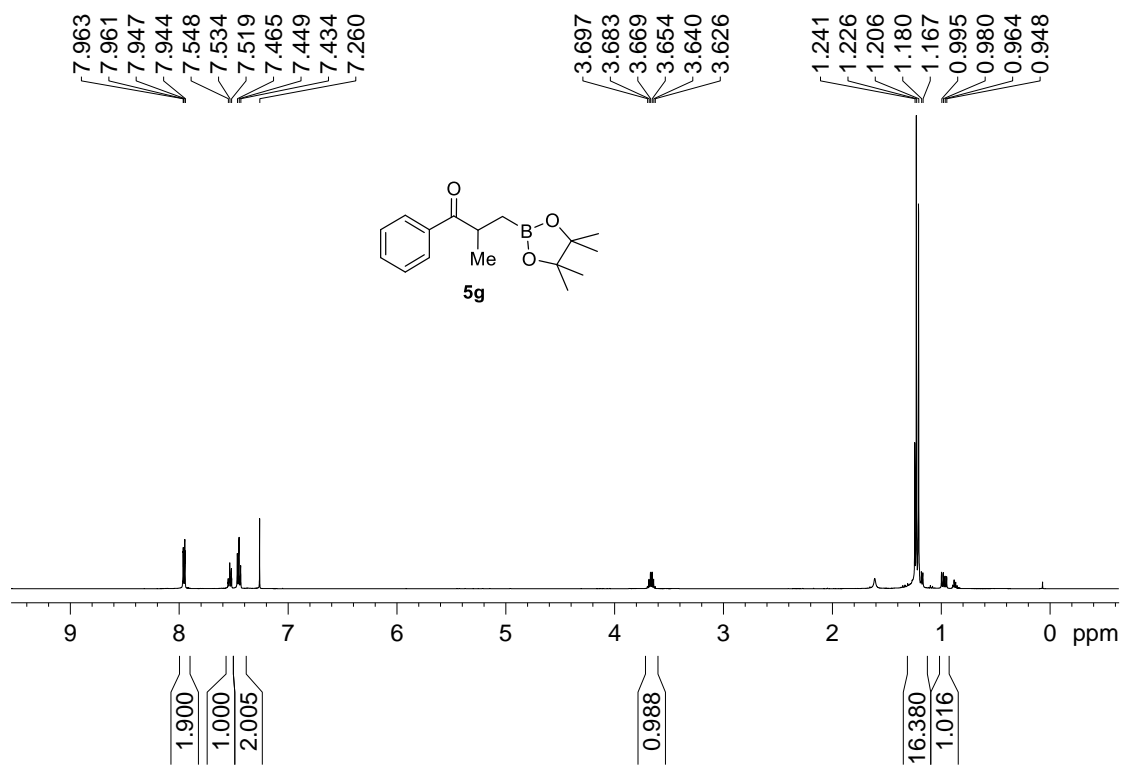


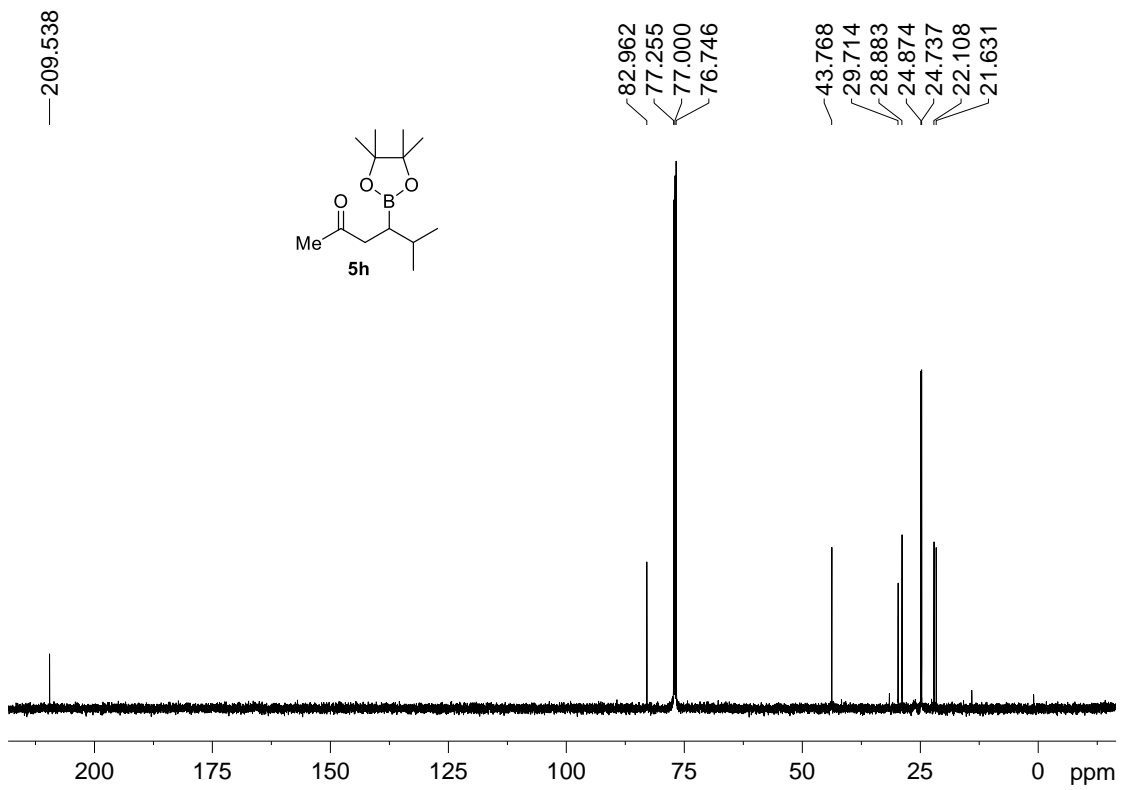
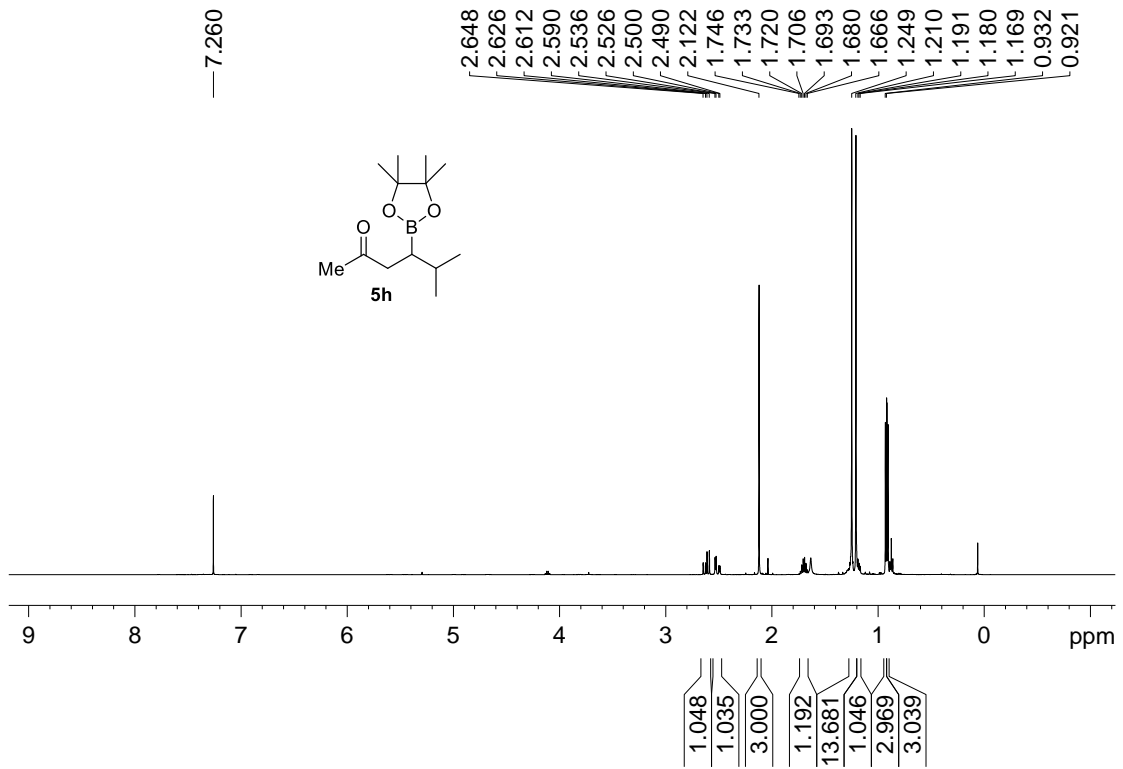


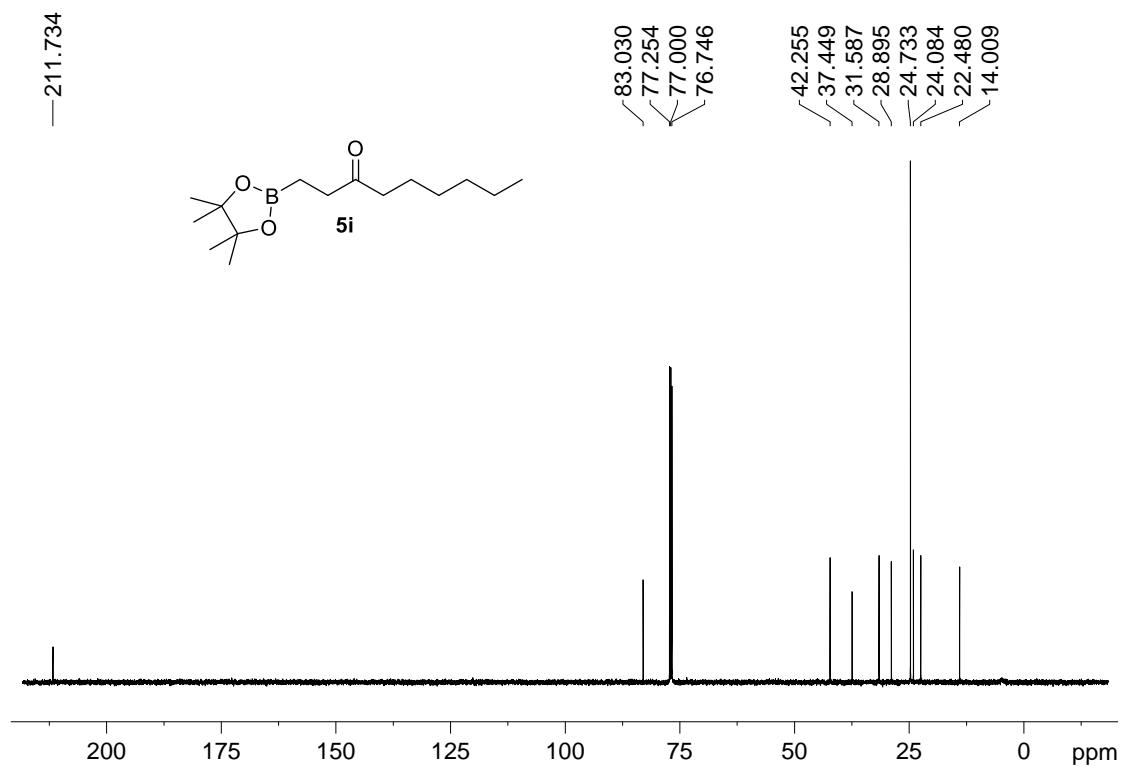
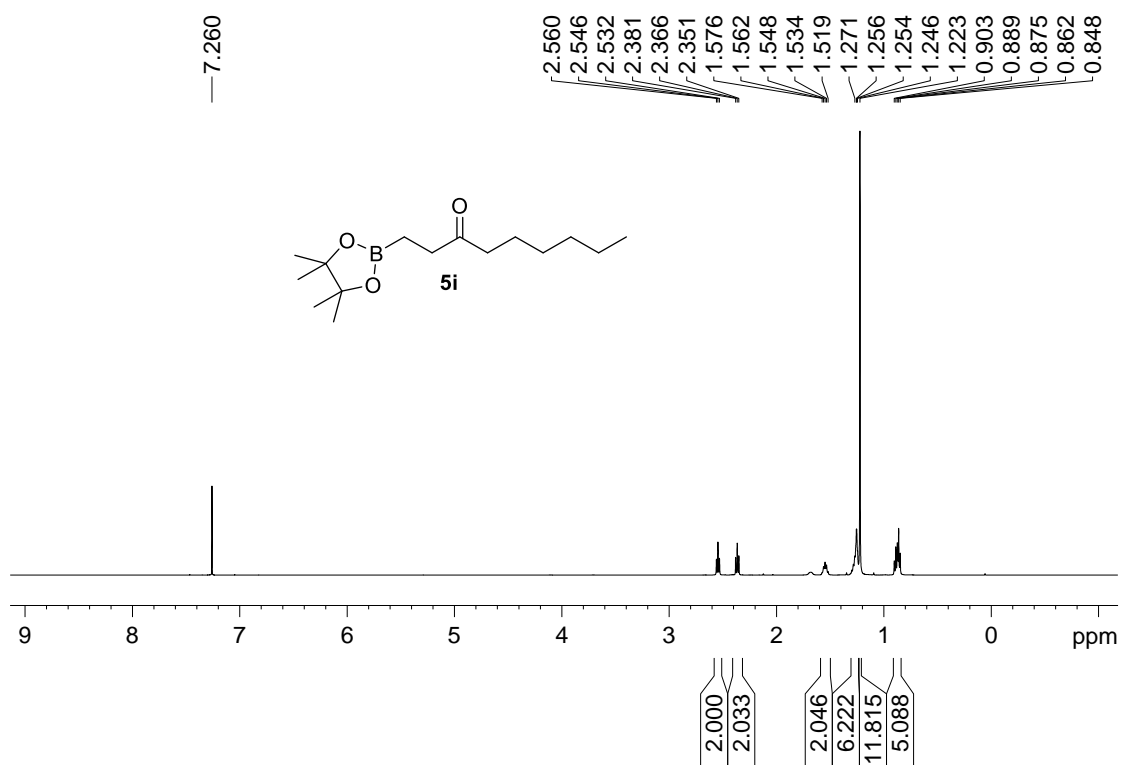


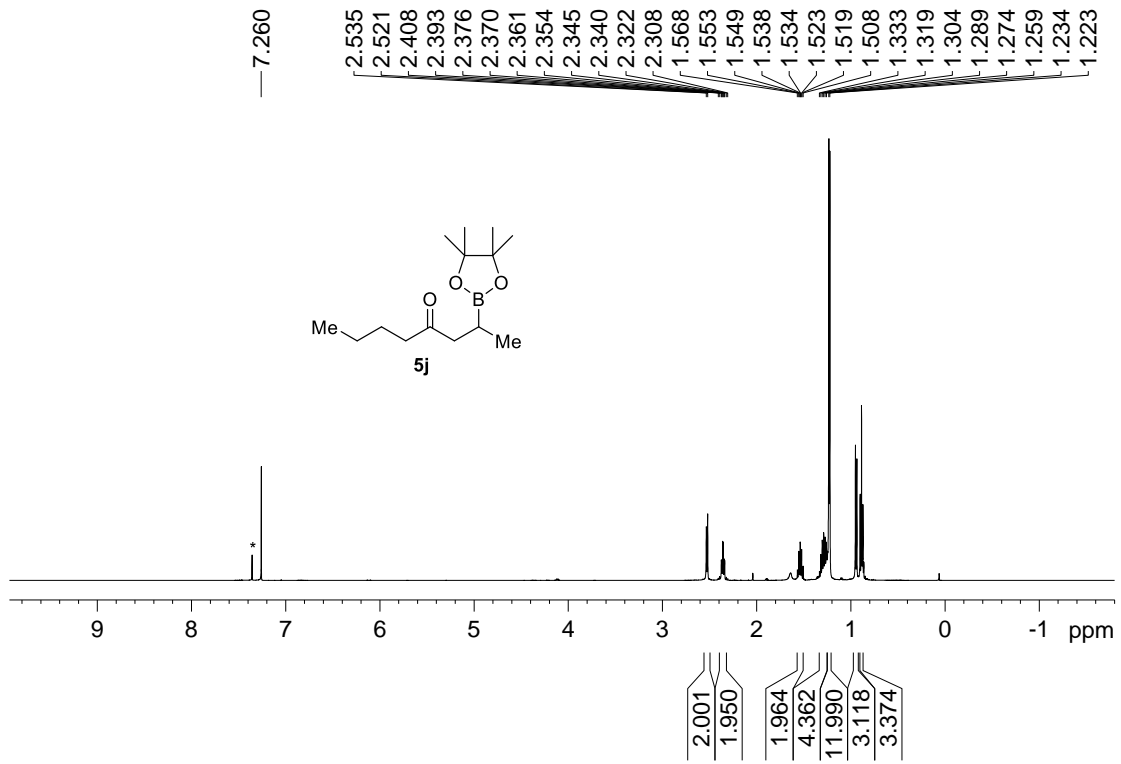




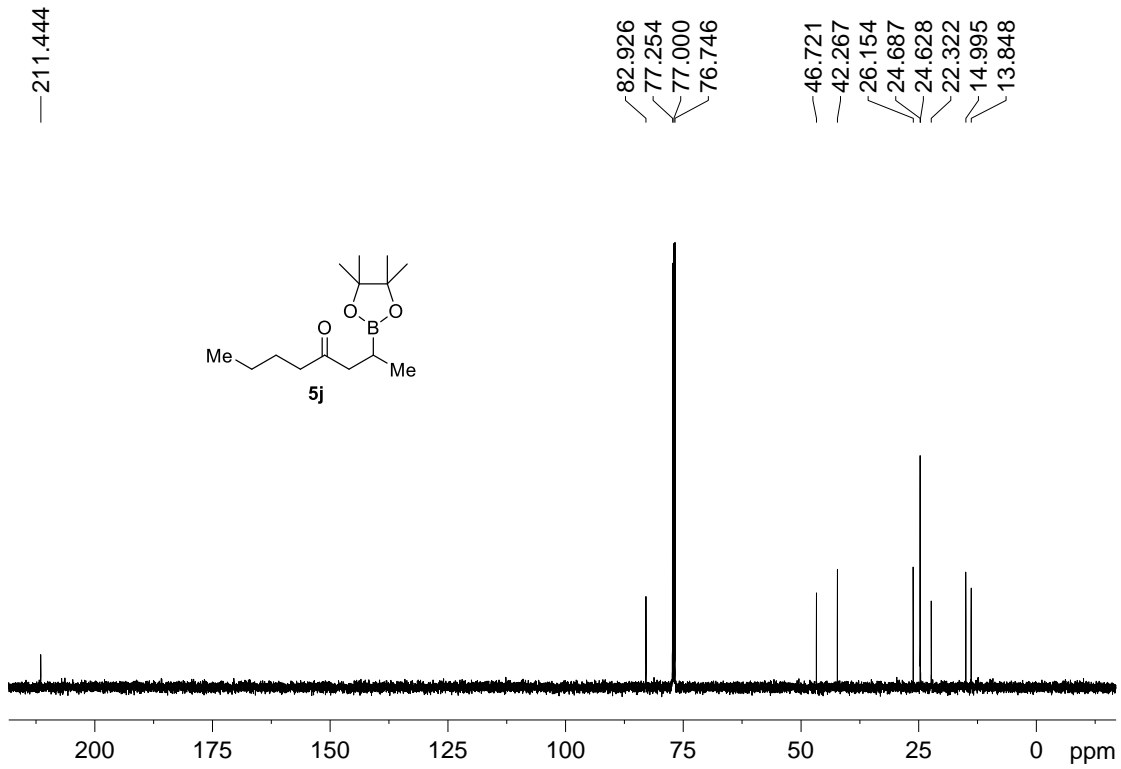


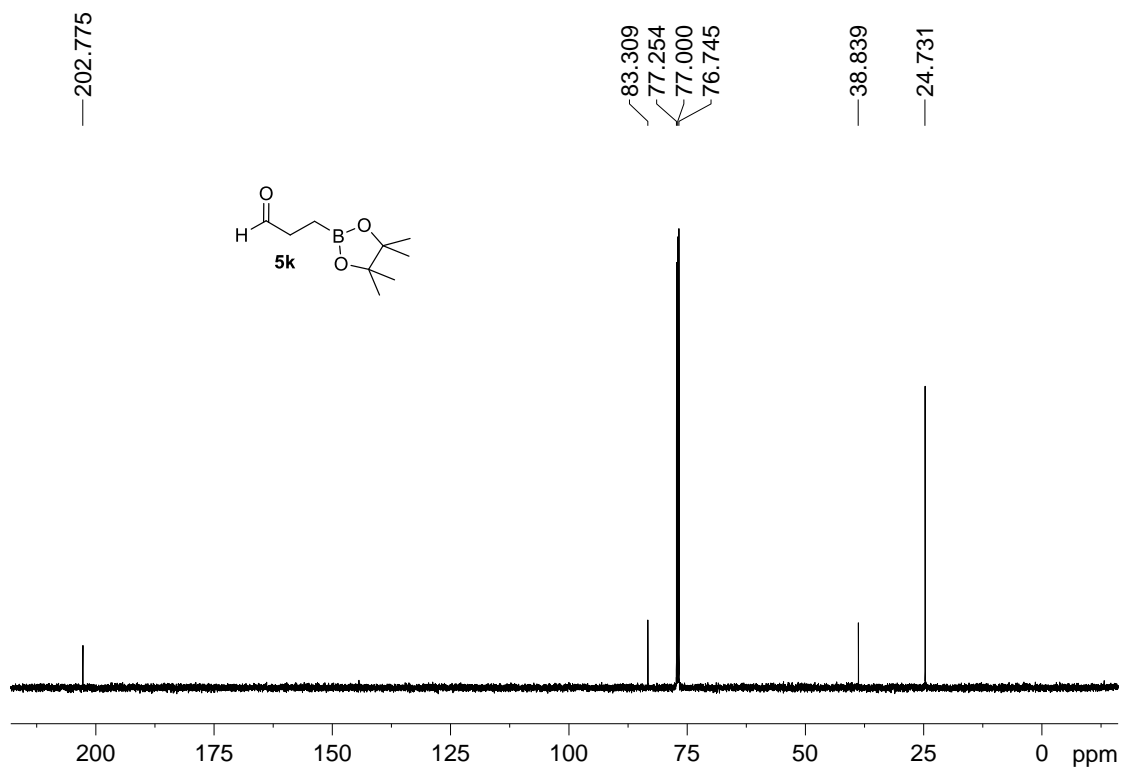
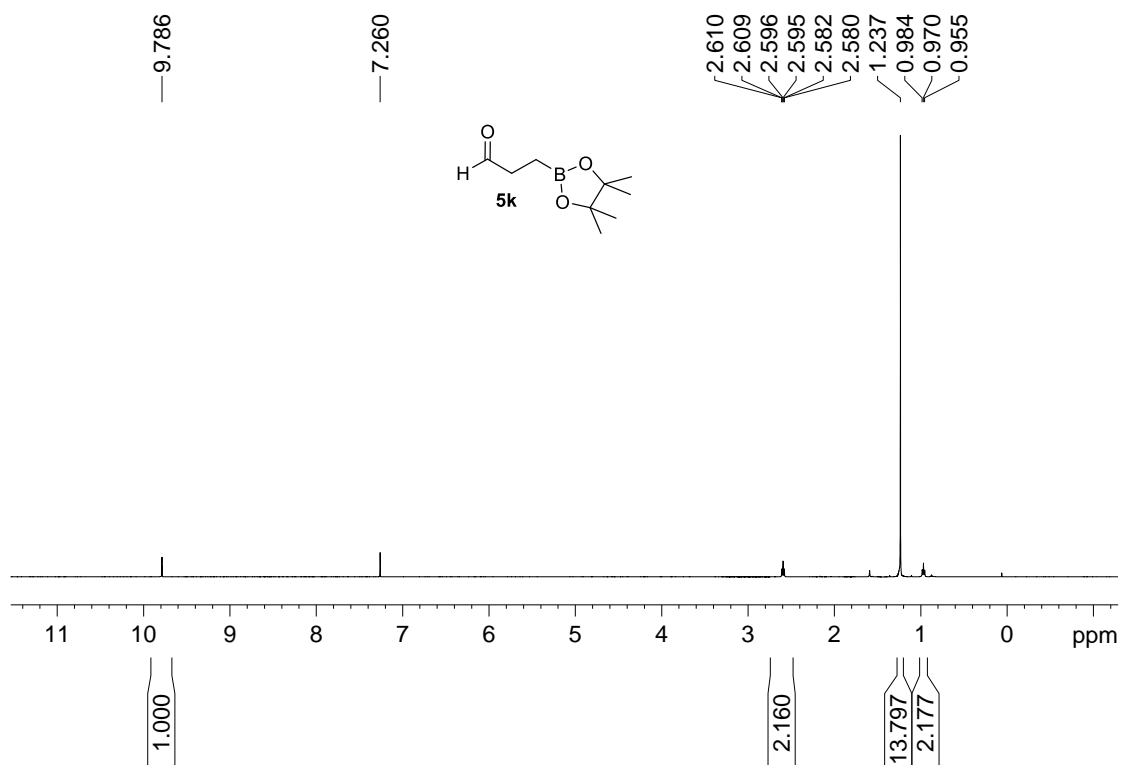


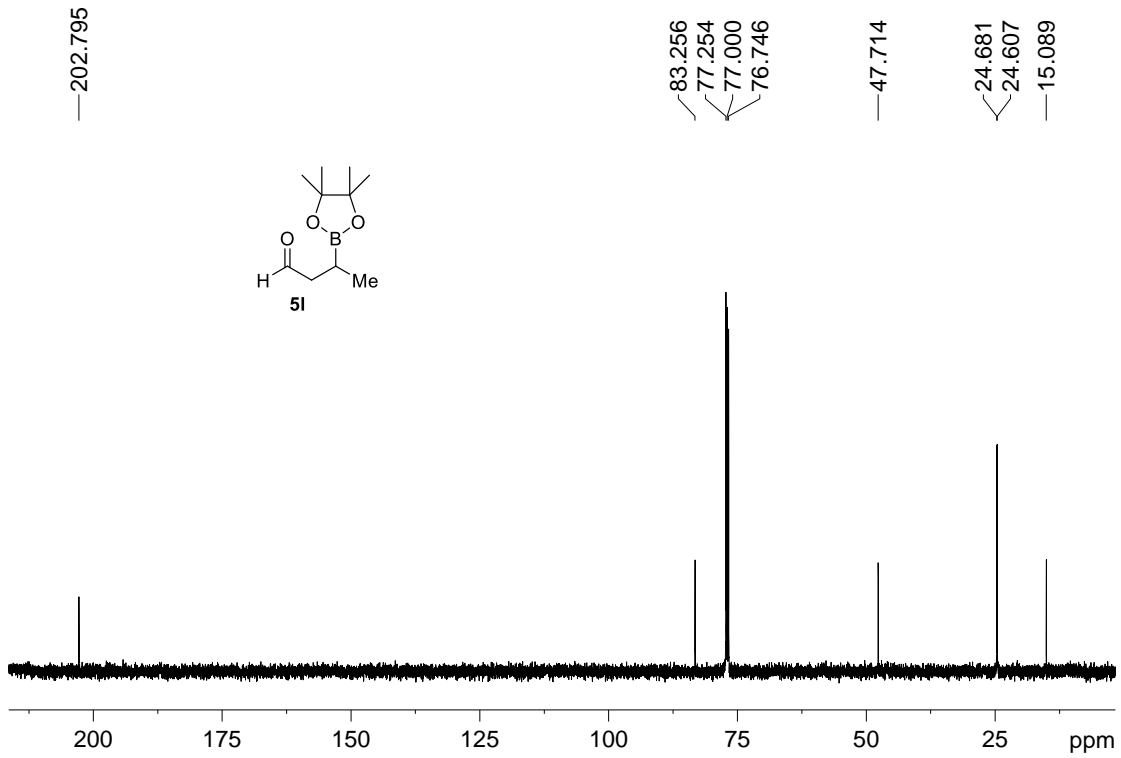
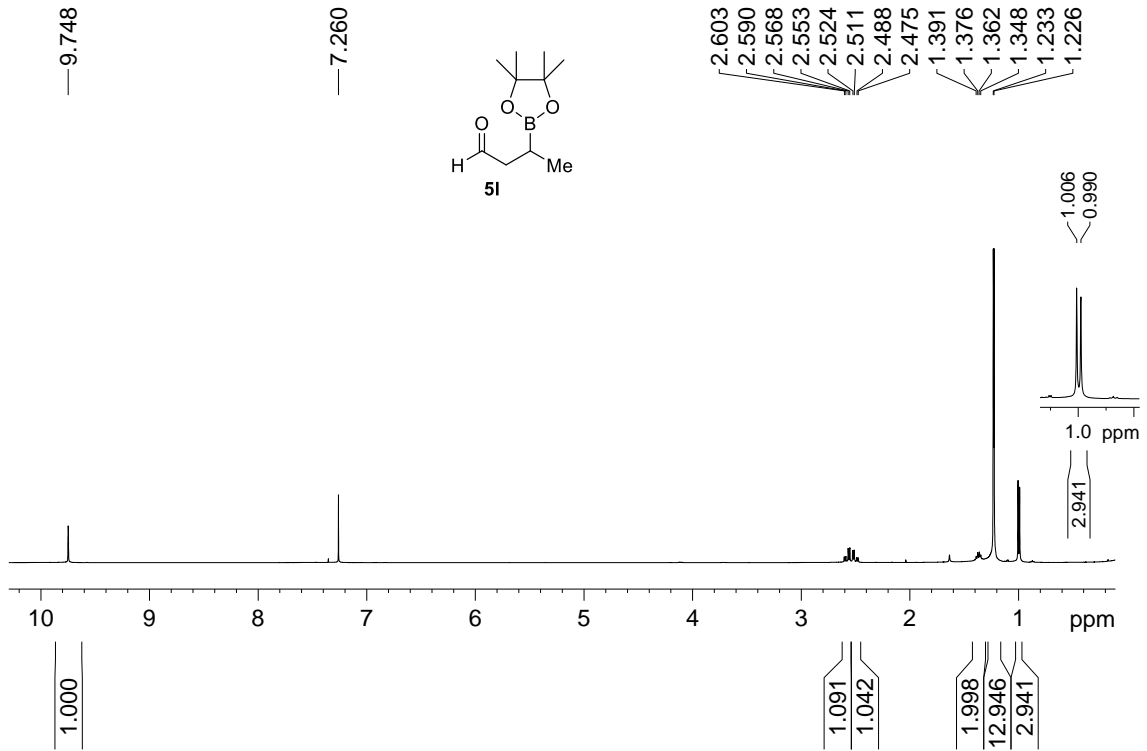




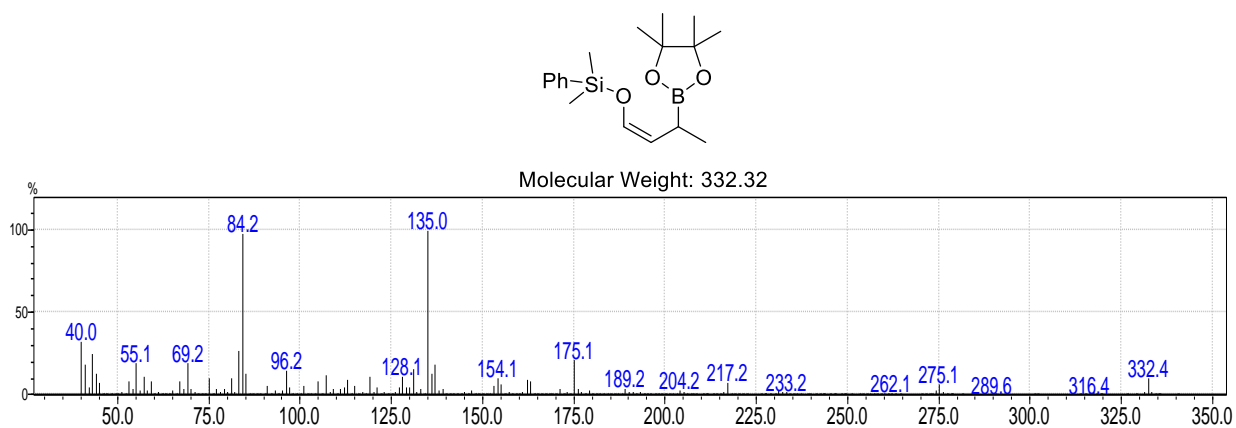
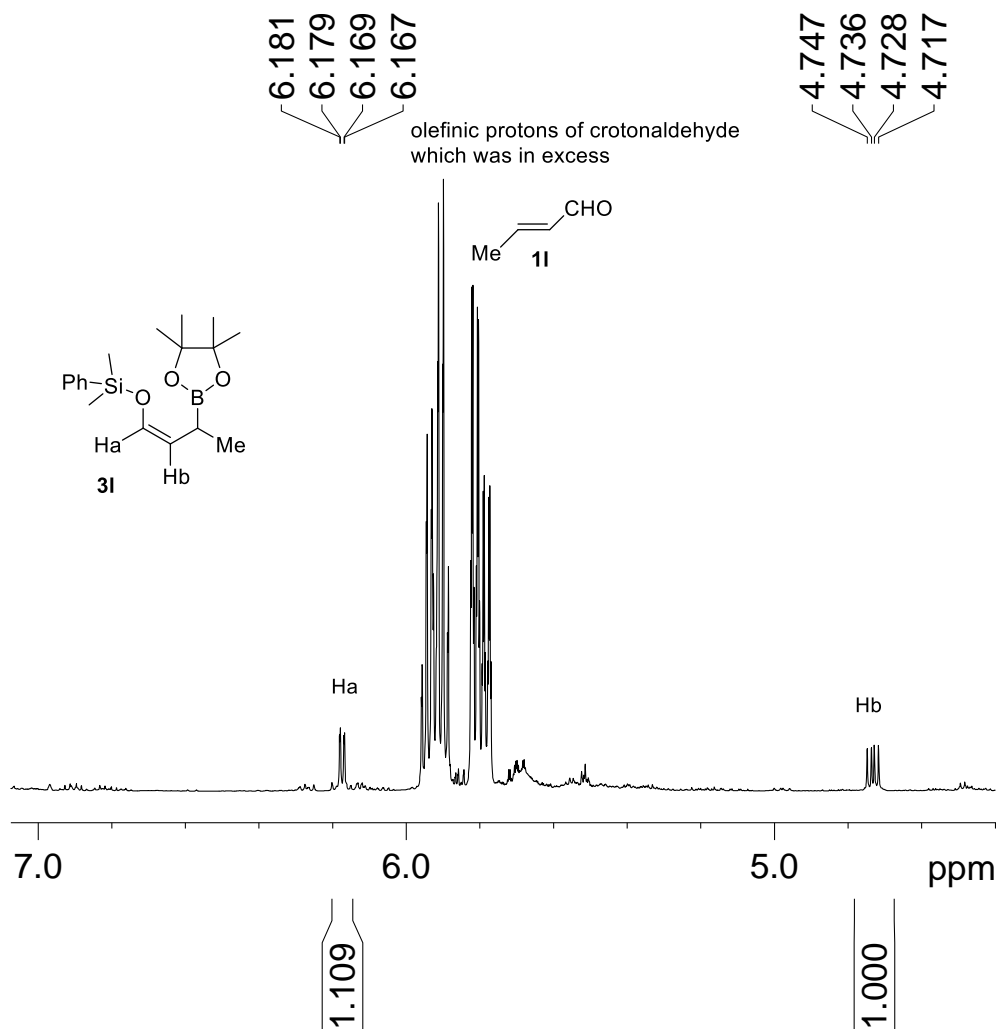
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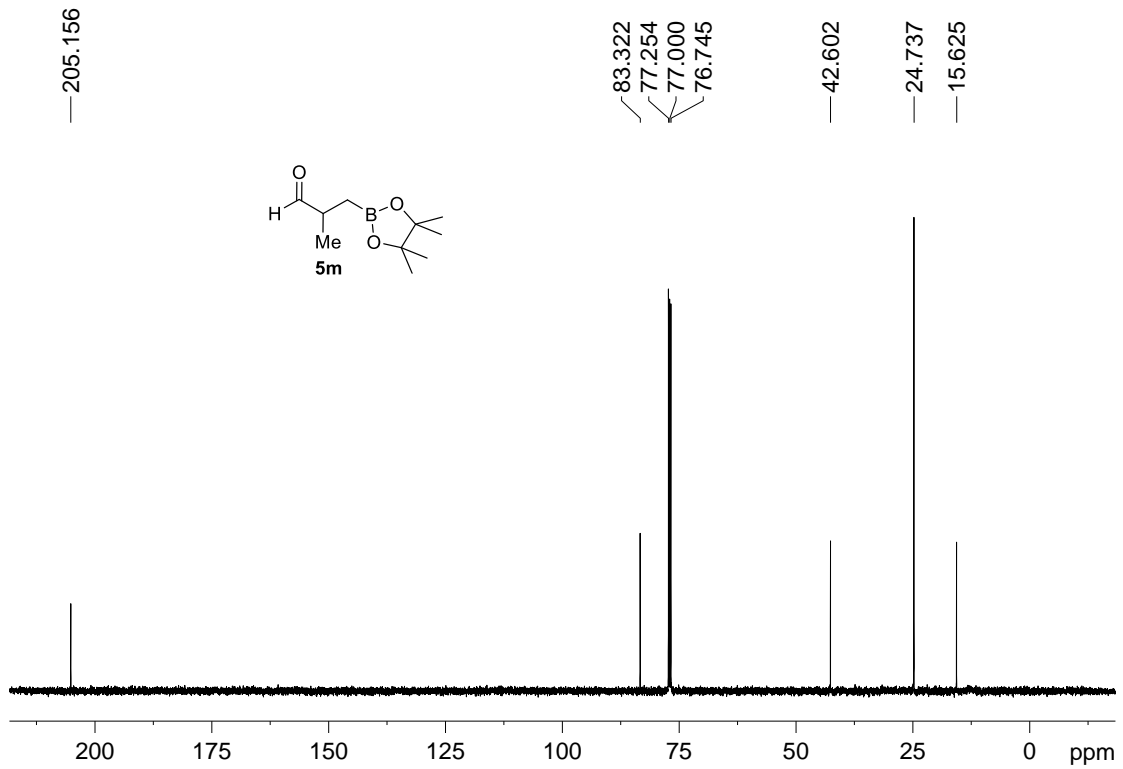
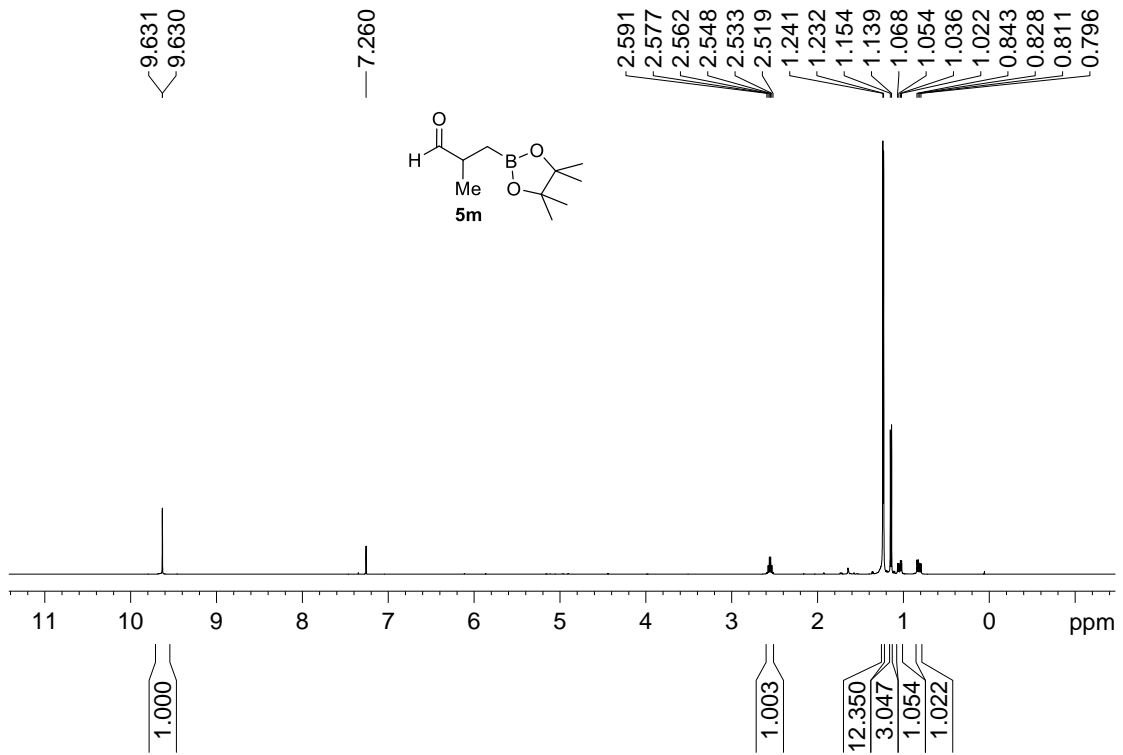


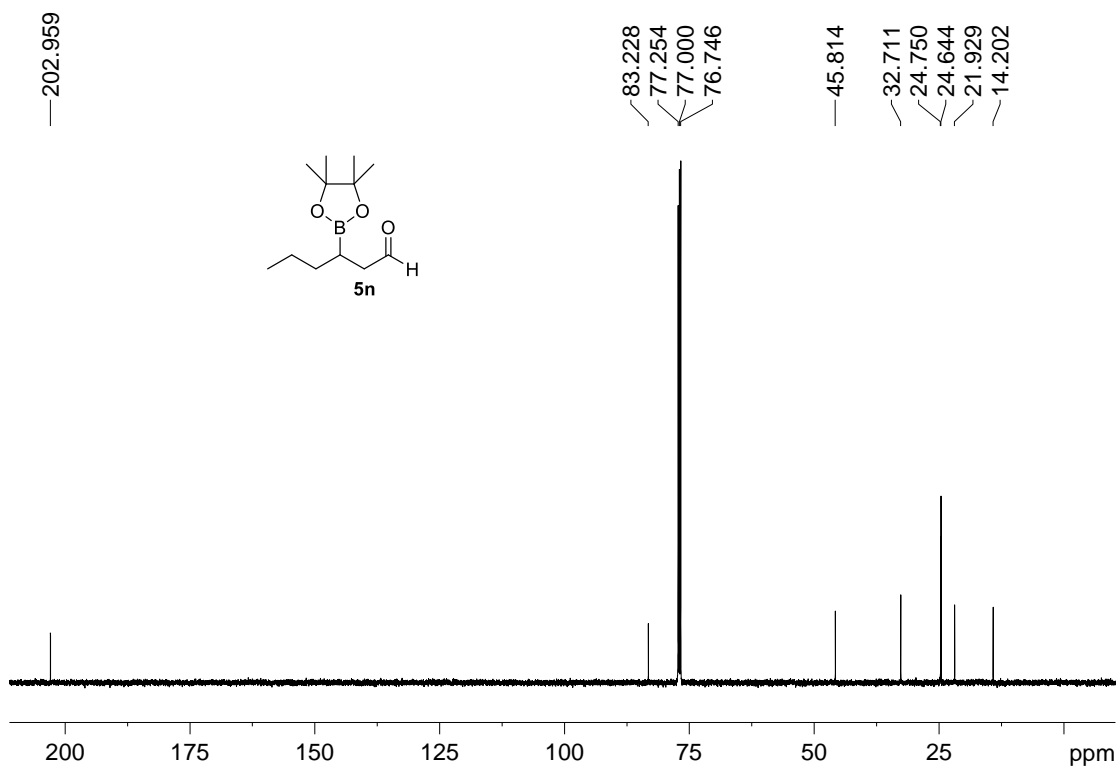
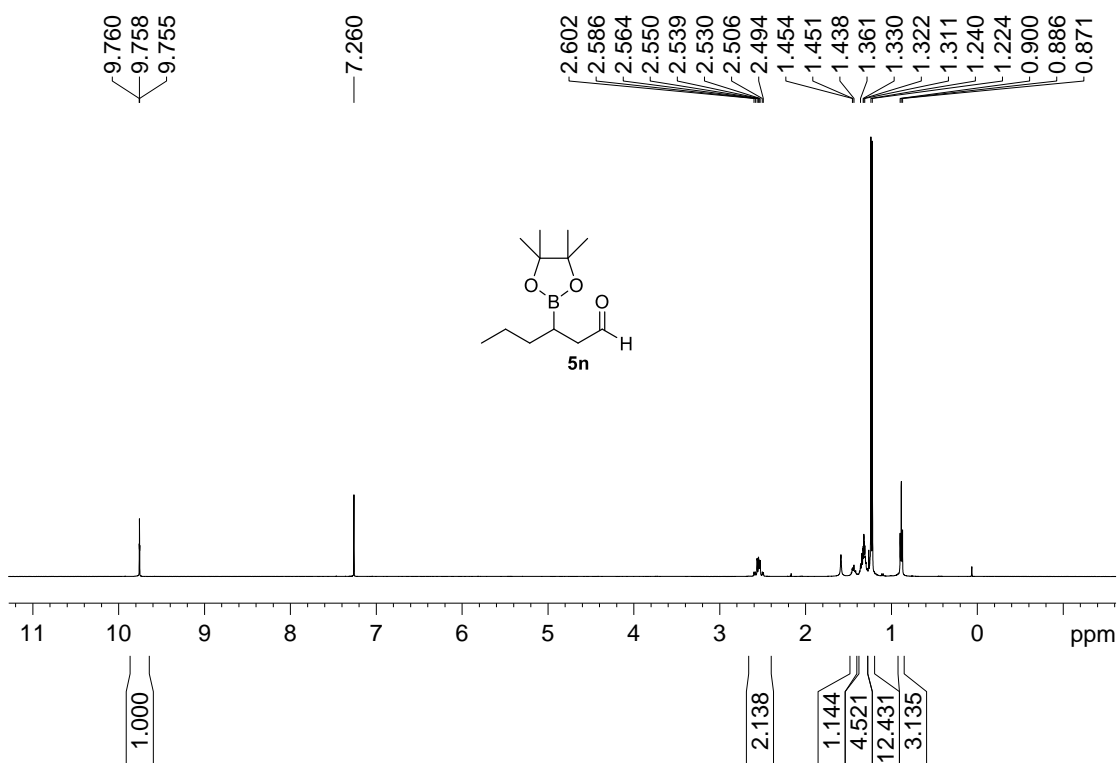


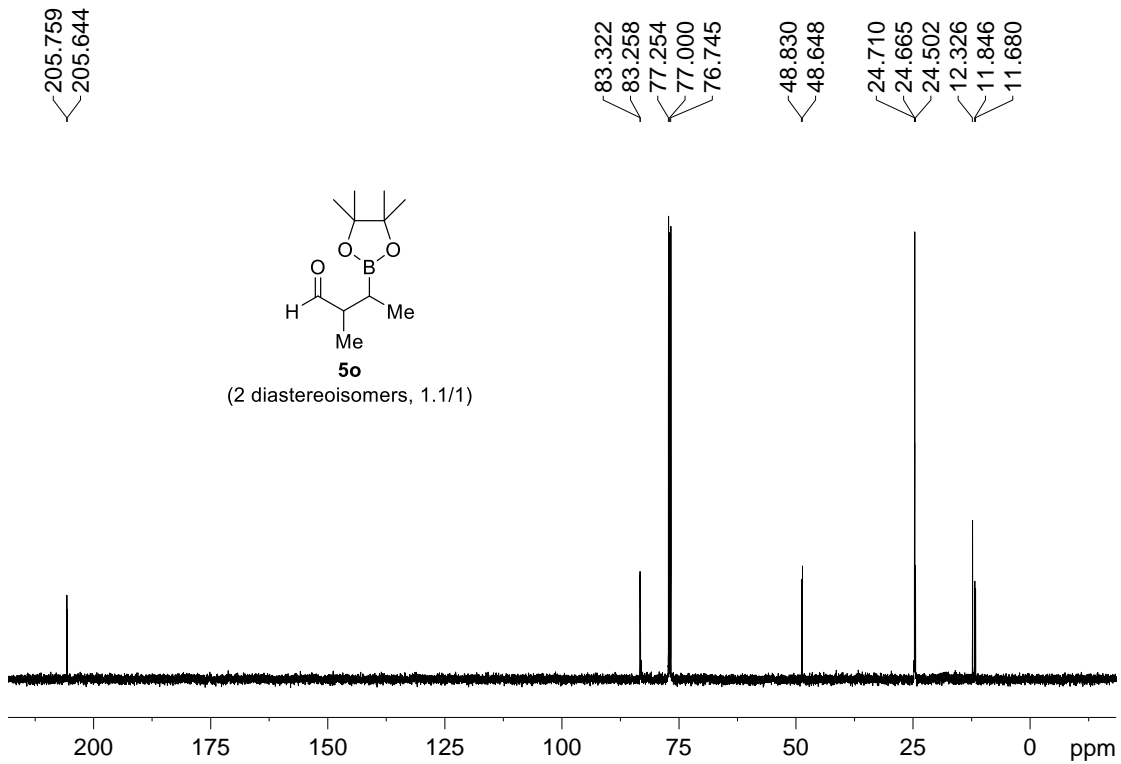
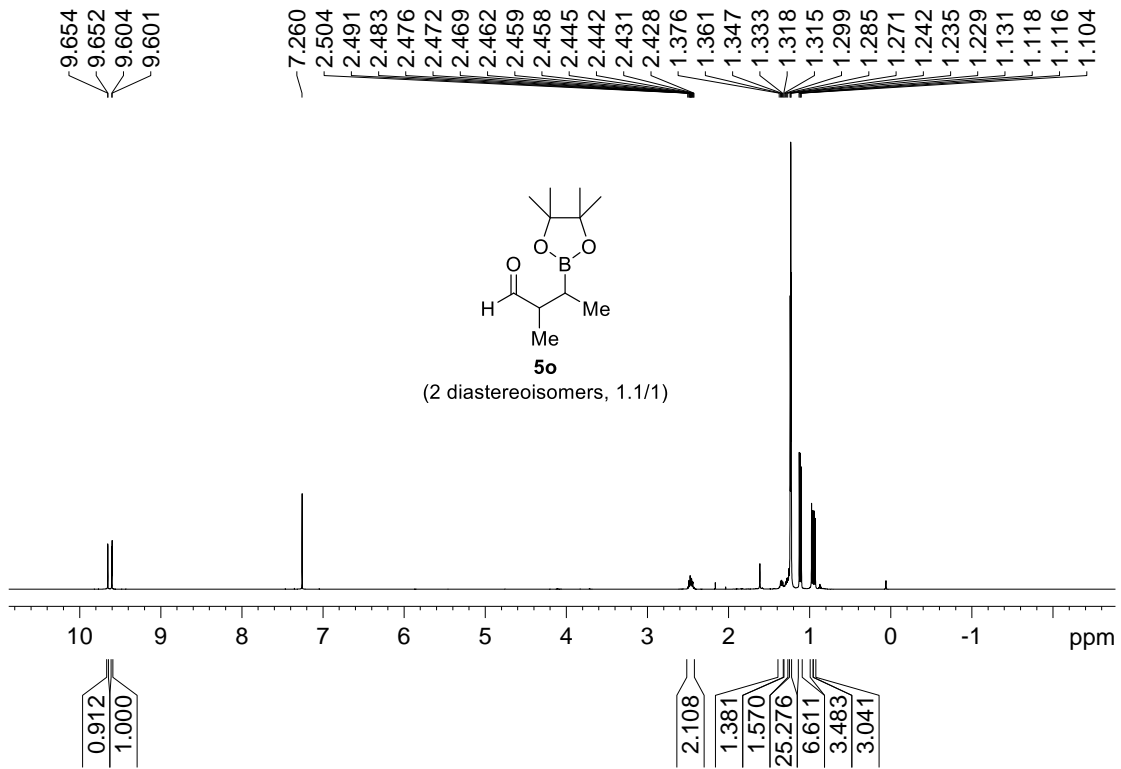


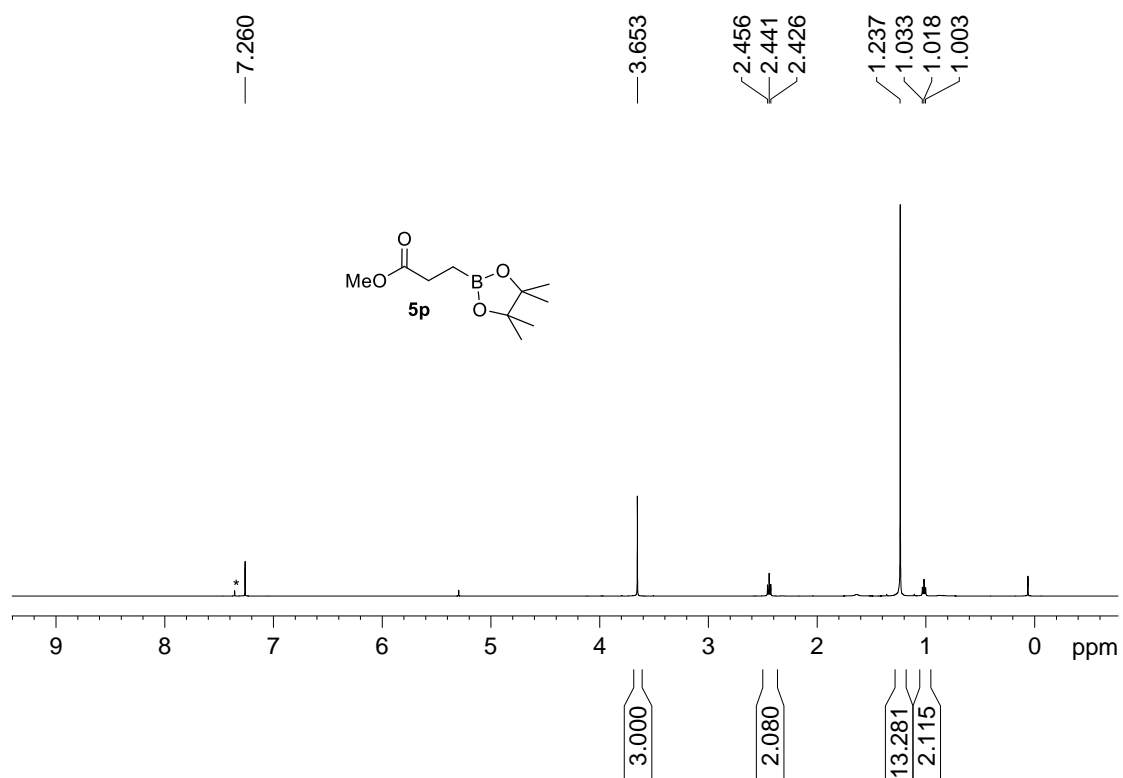
The ^1H NMR below was recorded in benzene- d_6 which was the solvent of the reaction between excess of crotonaldehyde and $\text{PhMe}_2\text{Si-Bpin}$ and shows the olefinic protons Ha and Hb of product **3I** having a $^3J_{\text{HH}} = 6.0$ Hz, indicative of a cis-configuration.



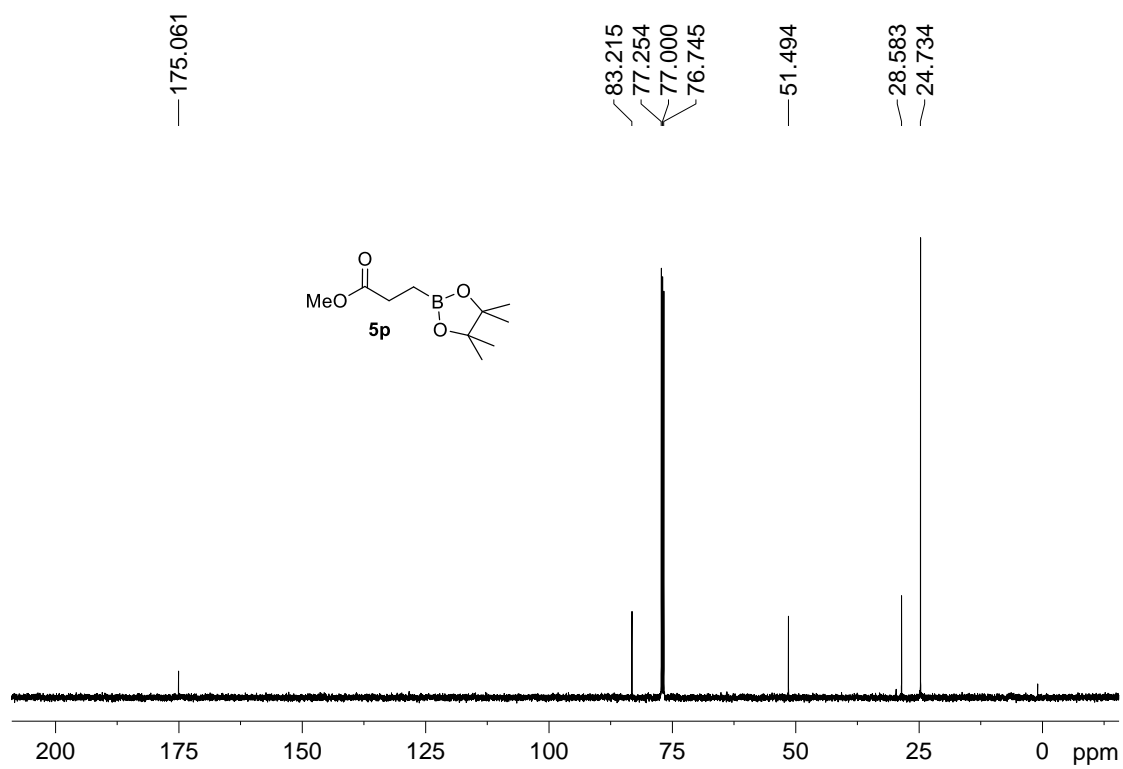


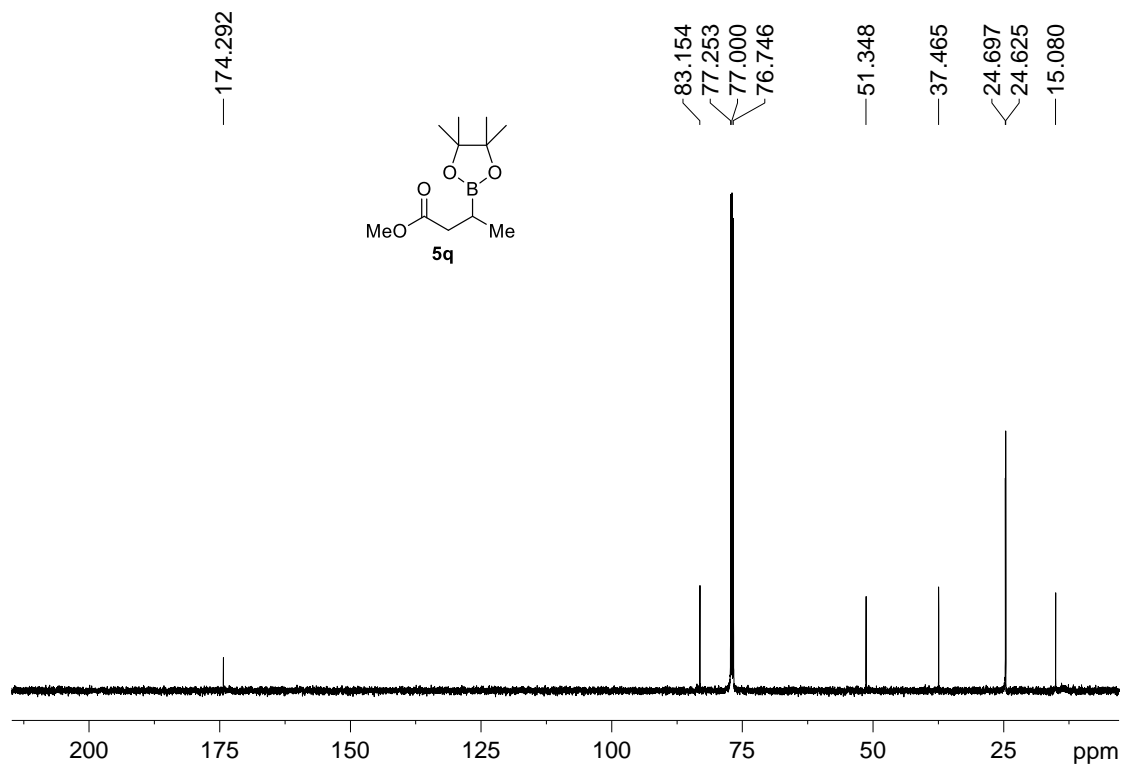
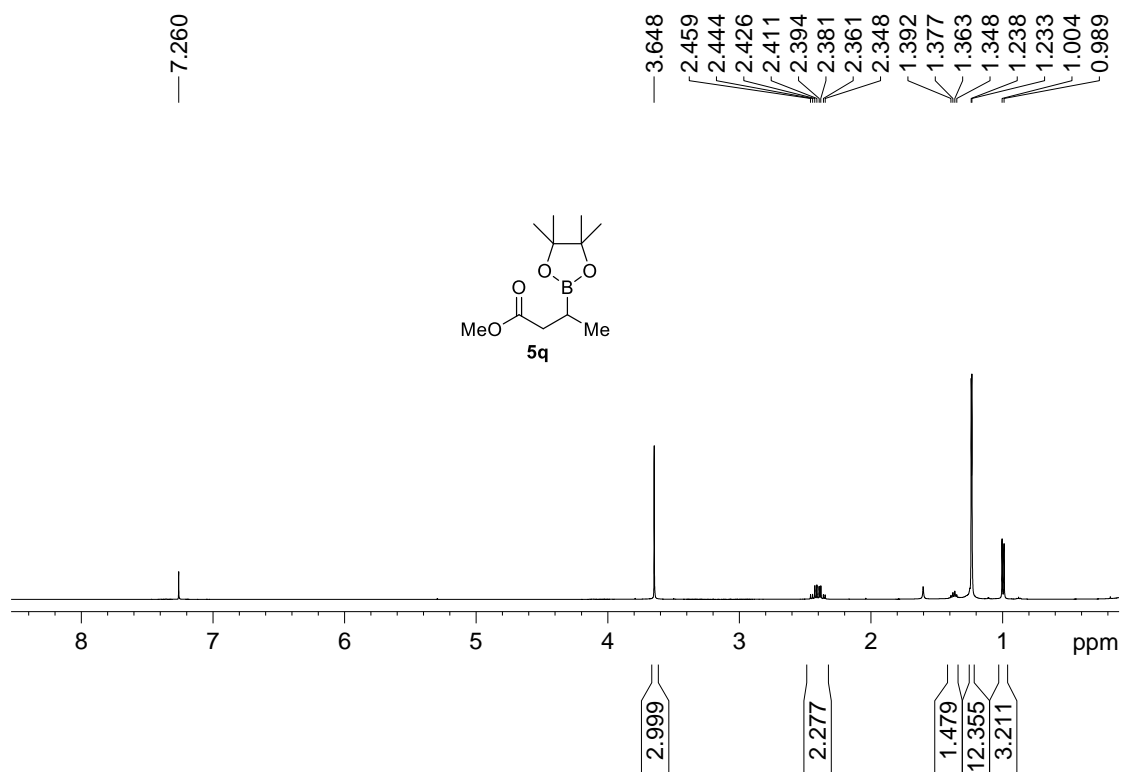


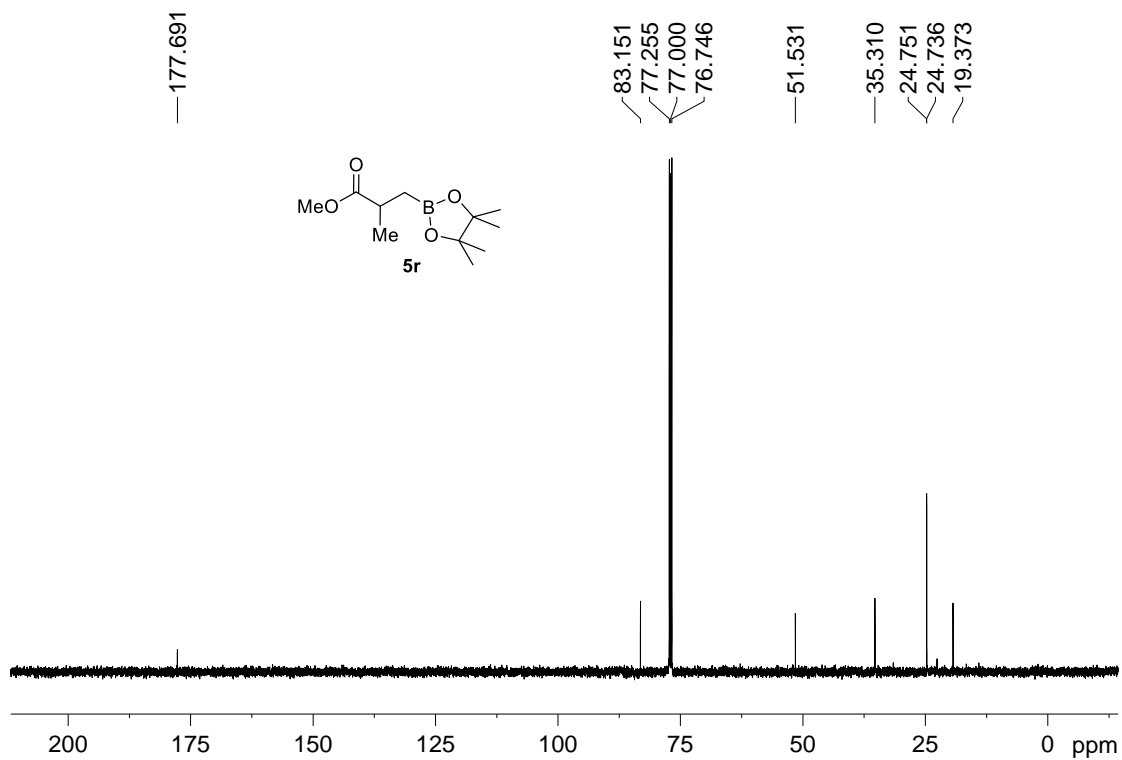
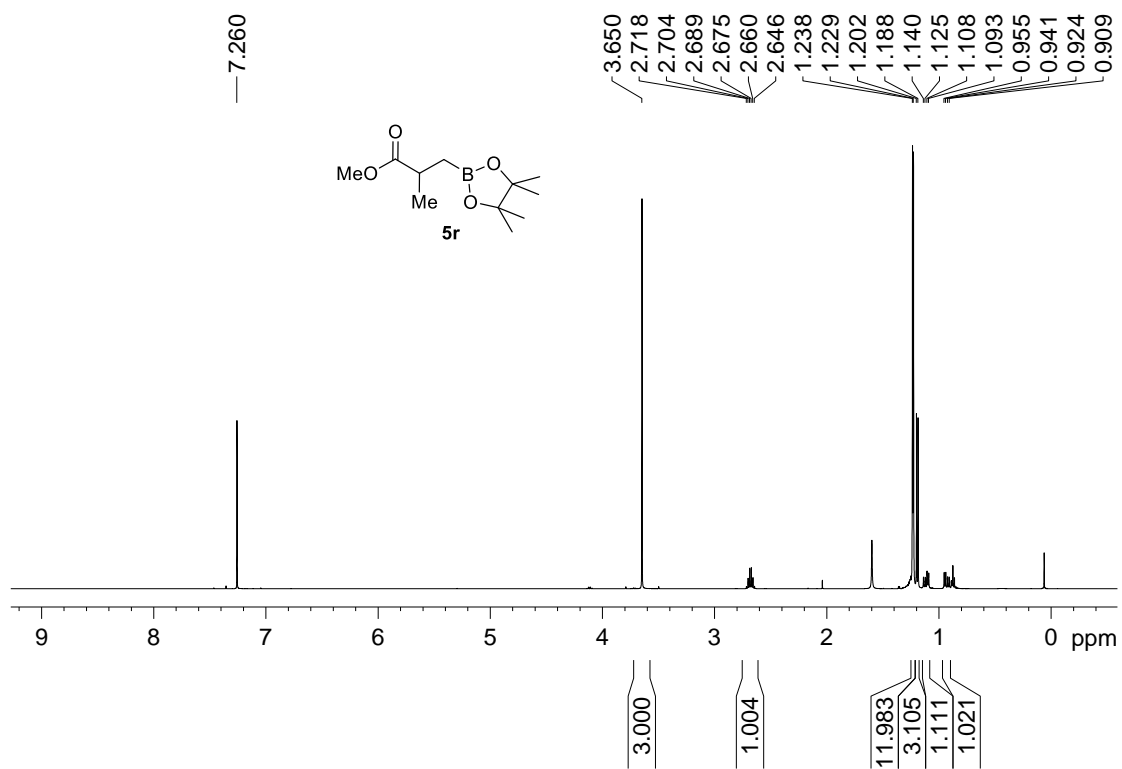


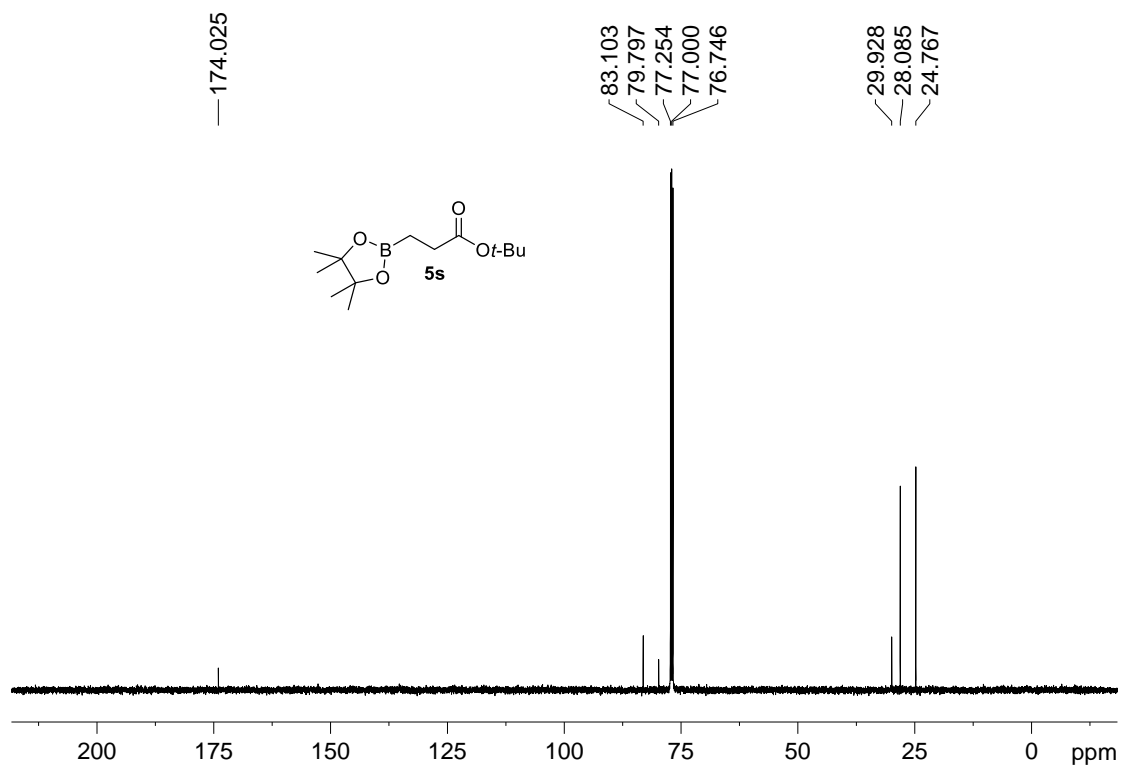
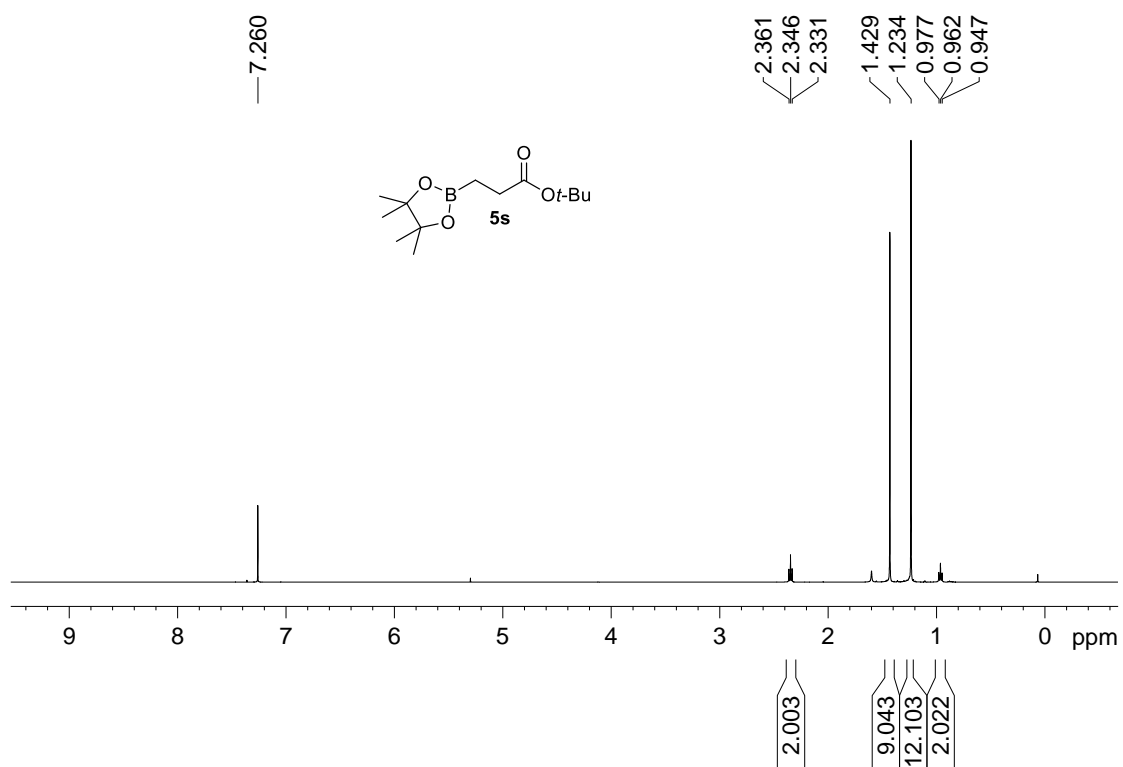


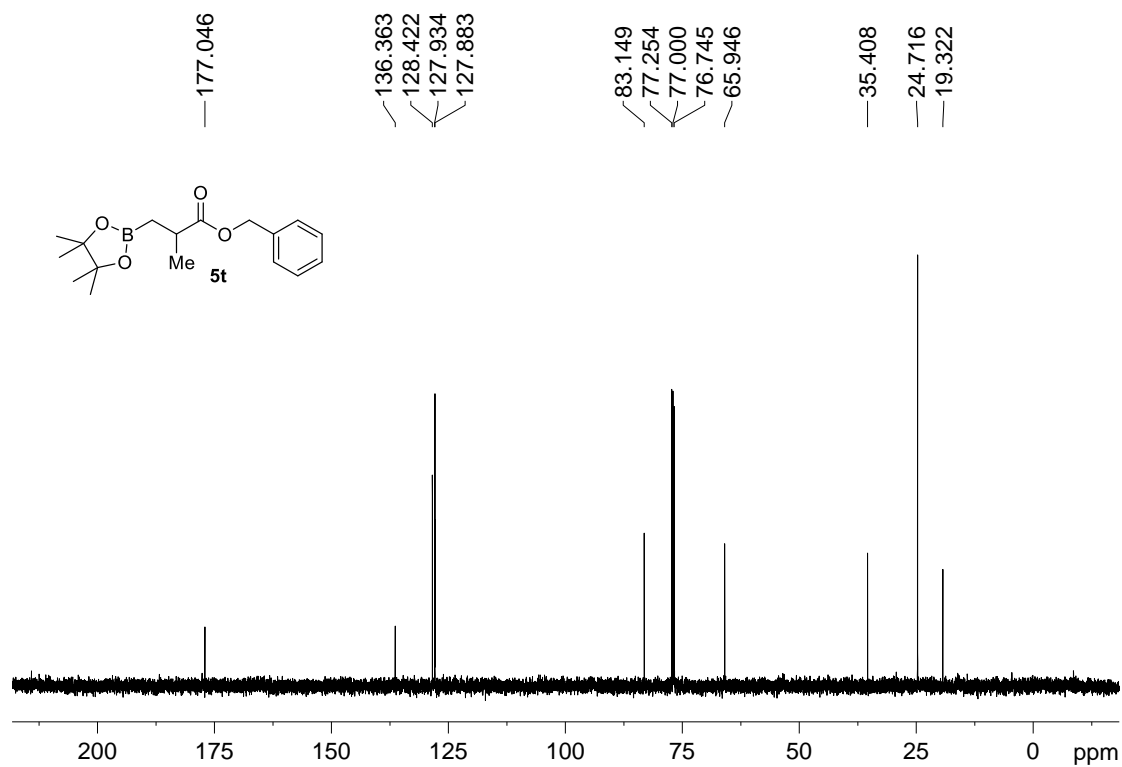
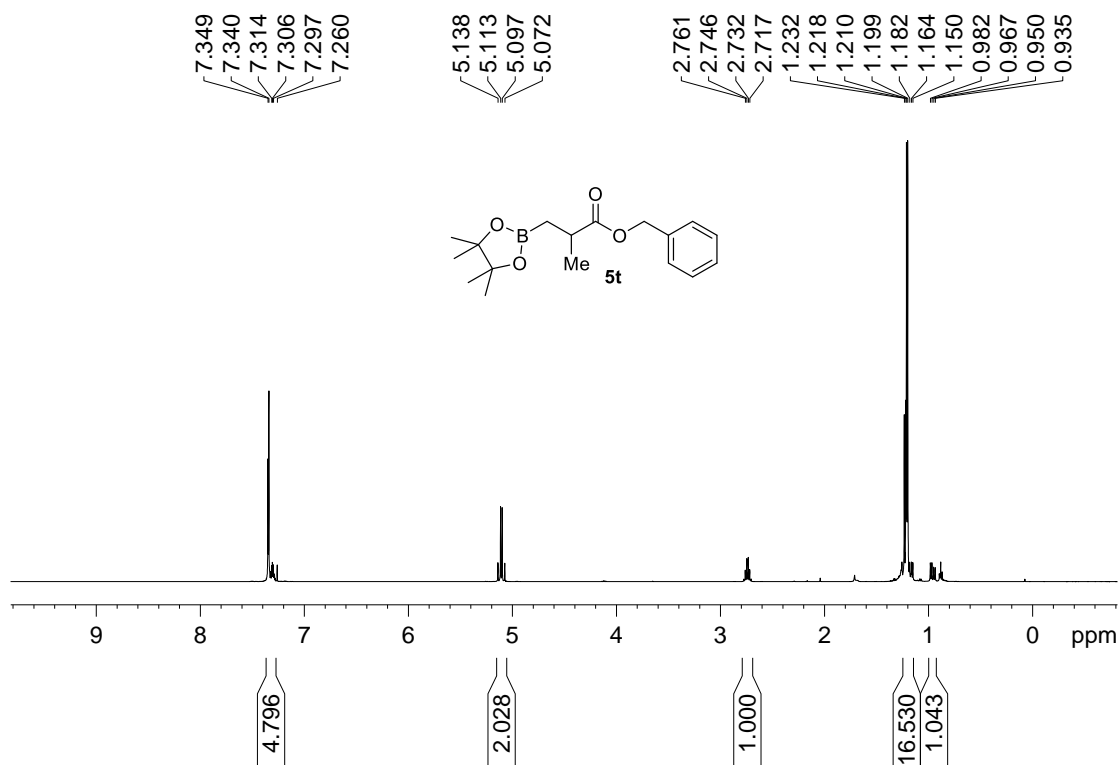
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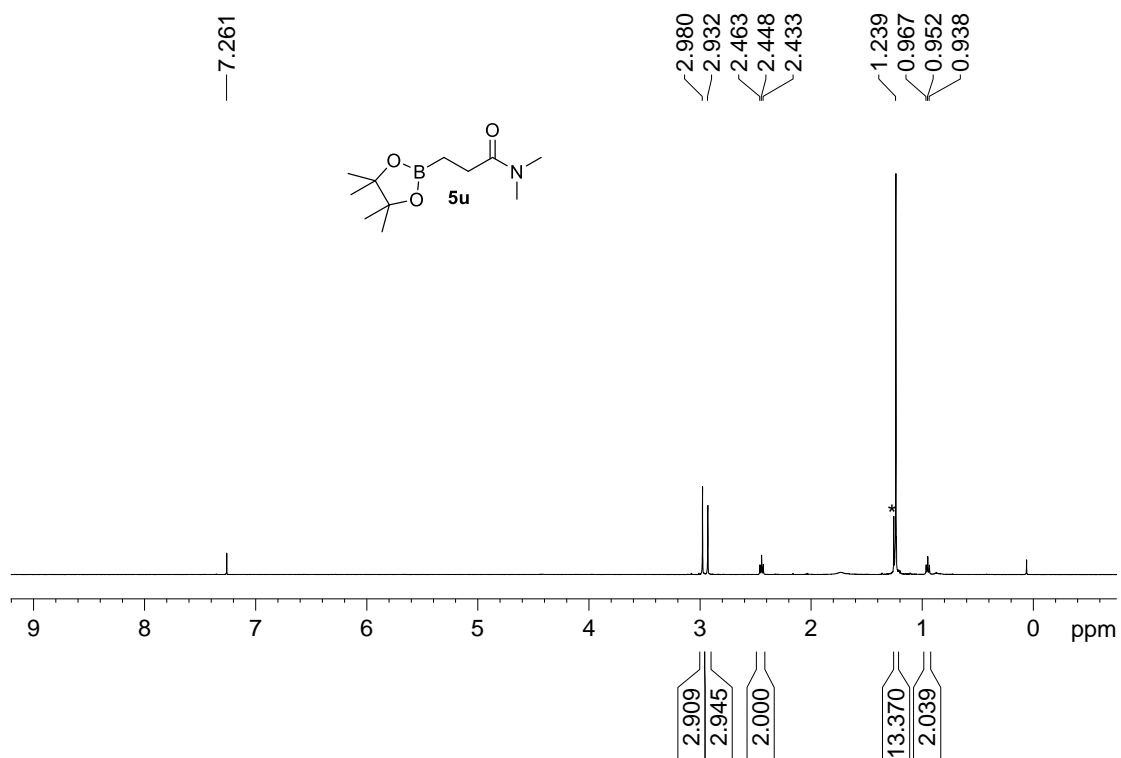




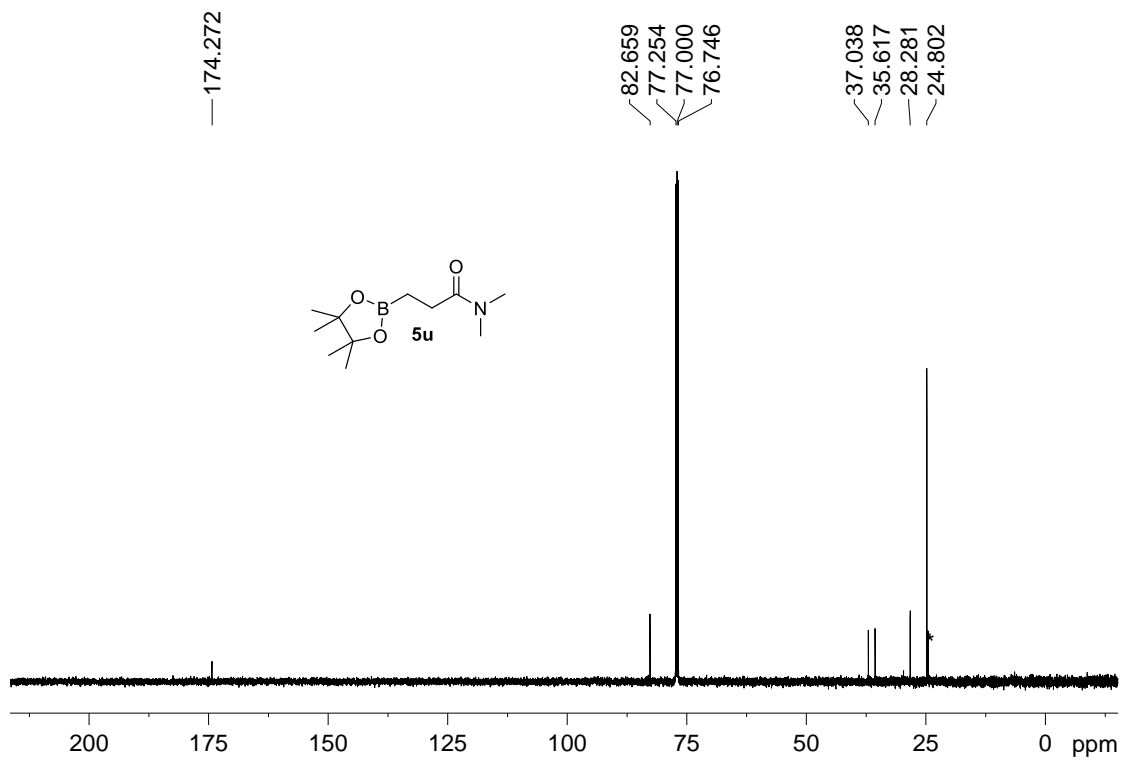








*pinBOBpin



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