

Copper-Catalyzed Dehydrogenative Borylation of Alkynes Terminal Alkynes with Pinacolborane

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A. General Considerations	2
B. Optimization Tables for the Dehydroborylation Reaction.....	2
C. Catalytic procedure for the Dehydroborylation Reaction	3
D. Compounds B ₁ -B ₁₅	4
E. Preliminary mechanistic studies	6
F. Spectra.....	13

A. General Considerations

All reactions were performed under an atmosphere of argon using standard Schlenk or dry box techniques; solvents were dried over Na metal, or CaH₂. Reagents of analytical grade were obtained from commercial suppliers, dried over 4Å molecular sieves and degassed before use. ¹H, ¹³C, and ¹⁹F NMR spectra were obtained with a Bruker Advance 300 MHz, and a Varian INOVA 500 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS, and were referenced to the residual solvent peak. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex sextet, m = multiplet, br = broad signal. Complexes (Et₂CAAC)CuOTf (**L₁CuOTf**),ⁱ(MenthylCAAC)CuOTf (**L₂CuOTf**),ⁱ(IPr)CuOTf (**L₃CuOTf**)ⁱⁱ were prepared following literature procedures.

B. Optimization Tables for the Dehydroborylation Reaction

Table S1. In a culture tube were added equipped with a magnetic stir bar **cat.** (x mol%) and 4-tolylacetylene (0.087 ml, 0.69 mmol) were combined in a culture tube. y μL (determined according to the named concentration **M**) of **Solvent** was added followed immediately by appropriate amount of base additive (z mol%). After 1 minute stirring, HBPIn (0.100 ml, 0.69 mmol) was added in a single portion and the resulting solution was allowed to stir for 2 hours at room temperature. NMR yields based on 1 equivalent addition of 1,4-dioxane after the 2 hour stirring period.

Entry	Cat. (mol%)	Base (mol%)	Solvent	Conc. (M)	1a (%) ^b	B ₁ (%) ^b	D ₁ (%) ^b	E ₁ (%) ^b
1	-	-	C ₆ D ₆	1.4	100	0	0	0
2	L ₁ CuOTf (1)	-	C ₆ D ₆	1.4	86	0	6	6
3	L ₁ CuOTf (1)	Et ₃ N (1)	C ₆ D ₆	1.4	14	48	11	7
4	CuOTf	Et ₃ N (1)	C ₆ D ₆	1.4	100	0	0	0
5	L ₁ CuOTf (1)	Et ₃ N (2)	C ₆ D ₆	1.4	1	70	14	12
6	L ₁ CuOTf (1)	Et ₃ N (2)	CD ₂ Cl ₂	1.4	12	42	6	26
7	L ₁ CuOTf (1)	Et ₃ N (2)	THF-d ₈	1.4	5	64	12	17
8	L ₁ CuOTf (1)	Et ₃ N (2)	CD ₃ CN	1.4	18	38	0	6
9	L ₁ CuOTf (1)	ⁱ PrNH ₂ (2)	C ₆ D ₆	1.4	67	5	12	10
10	L ₁ CuOTf (1)	ⁱ Pr ₂ NH (2)	C ₆ D ₆	1.4	47	11	13	7
11	L ₁ CuOTf (1)	ⁱ Pr ₂ NEt (2)	C ₆ D ₆	1.4	10	28	45	3
12	L ₁ CuOTf (1)	BnNEt ₂ (2)	C ₆ D ₆	1.4	14	53	8	7
13	L ₁ CuOTf (1)	DABCO (2)	C ₆ D ₆	1.4	18	60	1	7
14	L ₁ CuOTf (0.25)	Et ₃ N (0.5)	C ₆ D ₆	1.4	37	36	15	6
15	L ₁ CuOTf (0.5)	Et ₃ N (1)	C ₆ D ₆	1.4	20	54	15	9
16	L ₁ CuOTf (2.5)	Et ₃ N (5)	C ₆ D ₆	1.4	4	83	4	7
17	L₁CuOTf (2.5)	Et₃N (5)	C₆D₆	0.1	1	98	0	1
18	L ₂ CuOTf (2.5)	Et ₃ N (5)	C ₆ D ₆	0.1	0	96	0	4
19	L ₃ CuOTf (2.5)	Et ₃ N (5)	C ₆ D ₆	0.1	0	92	0	8

C. Catalytic procedure for the Dehydroborylation Reaction

A General Protocol.

In a schlenk tube under an argon atmosphere were added C_6H_6 (17 mL), the alkyne (1.82 mmol), pinacol borane (0.264 mL, 1.82 mmol), and triethylamine (0.012 mL, 0.091 mmol). Then, $Et_2CAACCuOTf$ (0.024 g, 0.045 mmol%) was added to the mixture and the reaction was left stirring at room temperature until the reaction had completed. After completion, all the volatiles were evaporated under vacuum and 5 mL of pentane was added. The mixture was passed, under argon, through a short column packed with dry neutral alumina (3 cm diameter x 5 cm high) using 30 mL of pentane as eluent. Evaporation of the volatiles under vacuum afforded the corresponding product.

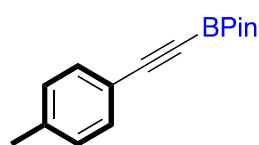
B. Gram Scale Reaction.

In a schlenk tube under an argon atmosphere were added C_6H_6 (17 mL, 18.2 mmol), pinacol borane (2.64 mL, 18.2 mmol), and triethylamine (0.12 mL, 0.91 mmol). Then, $Et_2CAACCuOTf$ (0.24 g, 0.45 mmol%) was added to the mixture and the reaction was left stirring at room temperature until the reaction had completed (as confirmed by NMR). After completion, all the volatiles were evaporated under vacuum and 50 mL of pentane was added. The mixture was passed under argon through a short column packed with of dry neutral alumina (3 cm diameter x 5 cm high) using 2 x 25 mL of pentane as eluent. Evaporation of the volatiles under vacuum afforded an analytically pure product as a deliquescent solid in 3.952 g (95 %).ⁱⁱⁱ

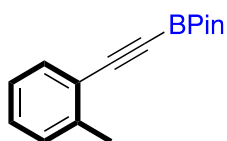


D. Compounds B₁-B₁₅

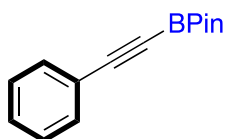
*NMR spectra of these substrates are in accordance with literature reports (see references accordingly). As noted by others, we were unable to observe the quaternary alkyne carbon (R-CBPIn).



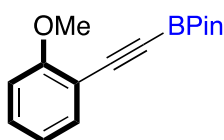
B₁^{iii,iv}: White solid (m.p. 103-105 °C) 0.437 g (99% yield). ¹H NMR (CDCl₃, 500 MHz) δ = 1.27 (s, 12H), 2.29 (s, 3H), 7.07 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H) ppm. ¹³C NMR (CDCl₃, 125.7 MHz) δ = 21.5, 24.6, 84.2, 102.0 (br), 118.6, 129.0, 132.5, 139.7 ppm.



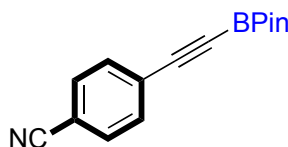
B₂ⁱⁱⁱ: Deliquescent solid 0.432 g (98% yield). ¹H NMR (CDCl₃, 500 MHz) δ = 1.03 (s, 12H), 2.35 (s, 3H), 6.75 (t, J = 8.0 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.89 (t, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H) ppm. ¹³C NMR (CDCl₃, 125.7 MHz) δ = 20.7, 24.7, 84.1, 101.0 (br), 122.6, 125.9, 129.4, 129.7, 133.3, 141.6 ppm.



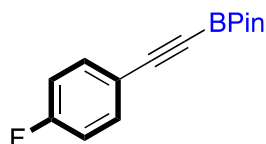
B₃^v: Deliquescent solid 0.411 g (99% yield). ¹H NMR (CDCl₃, 500 MHz) δ = 1.22 (s, 12H), 7.23 (m, 3H), 7.41 (m, 2H) ppm. ¹³C NMR (CDCl₃, 125.7 MHz) δ = 24.8, 84.6, 101.9 (br), 121.9, 128.4, 129.5, 132.7 ppm.



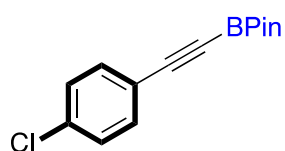
B₄: Deliquescent solid 0.413 g (88% yield). ¹H NMR (C₆H₆, 500 MHz) δ = 1.00 (s, 12H), 3.19 (s, 3H), 6.31 (d, J = 8.0 Hz, 1H), 6.55 (t, J = 8.0 Hz, 1H), 6.91 (t, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H) ppm. ¹³C NMR (C₆H₆, 125.7 MHz) δ = 24.7, 55.1, 83.9, 98.5 (br), 110.9, 112.3, 120.4, 130.7, 134.7, 160.6 ppm. HRMS analysis was unsuccessful.



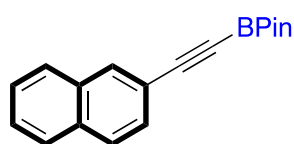
B₅: Deliquescent solid 0.392 g (85% yield). ¹H NMR (C₆D₆, 300 MHz) δ = 1.23 (s, 12H), 7.51 (s, 4H) ppm. ¹³C NMR (CDCl₃, 125.7 MHz) δ = 24.7, 84.5, 99.5, 113.1, 118.2, 126.4, 131.9, 132.6 ppm.



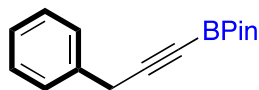
B₆^{iii,v}: Deliquescent solid 0.367 g (85% yield). ¹H NMR (CDCl₃, 500 MHz) δ = 1.31 (s, 12H), 7.0 (t, J = 8.7 Hz, 2H), 7.51 (m, 2H) ppm. ¹³C NMR (CDCl₃, 125.7 MHz) δ = 24.7, 84.2, 100.7 (br), 115.5 (d, J = 22.1 Hz), 117.9 (d = 3.5 Hz), 134.7 (J = 8.5 Hz), 163.3 (J = 250.4 Hz) ppm.



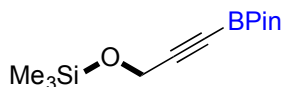
B₇^{iii,iv}: Deliquescent solid 0.392 g (82% yield). ¹H NMR (C₆D₆, 500 MHz) δ = 1.02 (s, 12H), 6.75 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H) ppm. ¹³C NMR (C₆D₆, 125.7 MHz) δ = 24.7, 84.2, 100.6 (br), 121.0, 129.0, 133.9, 135.5 ppm.



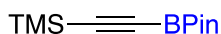
B₈ⁱⁱⁱ: Deliquescent solid 0.407 g (81% yield). ¹H NMR (C₆D₆, 500 MHz) δ = 1.06 (s, 12H), 7.12 (m, 2H), 7.32 (m, 1H), 7.34 (m, 1H), 7.40 (m, 1H), 7.43 (m, 1H), 7.85 (s, 1H) ppm. ¹³C NMR (C₆D₆, 125.7 MHz) δ = 23.4, 82.8, 101.0 (br), 118.5, 125.4, 125.9, 127.2, 127.4, 131.8, 132.1, 132.3 ppm.



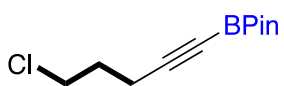
B₉: Deliquescent solid 0.374 g (85% yield). ¹H NMR (C₆D₆, 500 MHz) δ = 1.03 (s, 12H), 3.32 (s, 2H) 7.00-7.20 (m, 5H) ppm. ¹³C NMR (C₆D₆, 125.7 MHz) δ = 24.7, 25.9, 83.8, 101.6 (br), 126.9, 128.2, 128.7, 135.9 ppm.



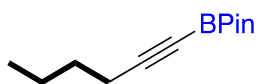
B₁₀^v: Colorless oil 0.250 g (89% yield). ¹H NMR (CDCl₃, 300 MHz) δ = 0.07 (s, 9H), 1.17 (s, 12H), 4.12 (s, 2H) ppm. ¹³C NMR (C₆D₆, 125.7 MHz) δ = 0.3, 24.7, 51.3, 84.3, 101.2 (br) ppm.



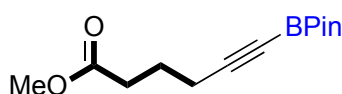
B₁₁^{v,vi}: Colorless oil 0.404 g (99% yield). ¹H NMR (C₆D₆, 500 MHz) δ = 0.05 (s, 9H), 0.93 ppm. ¹³C NMR (C₆D₆, 125.7 MHz) δ = 0.51, 24.6, 84.0, 110.1 (br) ppm.



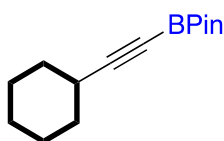
B₁₂^v: Colorless oil 0.437 g (99% yield). ¹H NMR (C₆D₆, 500 MHz) δ = 1.01, 1.410 (quint, J = 7.0 Hz, 2H), 1.99 (t, J = 7.0 Hz, 2H), 3.09 (t, J = 7.0 Hz, 2H) ppm. ¹³C NMR (C₆D₆, 125.7 MHz) δ = 16.9, 24.7, 31.0, 43.3, 83.8, 102.3 (br) ppm.



B₁₃^{viii}: Colorless oil 0.400 g (99% yield). ¹H NMR (C₆D₆, 500 MHz) δ = 0.67 (t, J = 7.5 Hz, 3H), 1.01 (s, 12H), 1.23 (septet, J = 7.5 Hz, 2H), 1.96 (t, J = 7.5 Hz, 2H) ppm. ¹³C NMR (C₆D₆, 125.7 MHz) δ = 13.2, 19.0, 21.6, 24.3, 30.0, 83.2, 104.0 (br) ppm.



B₁₄: Colorless oil 0.441 g (96% yield). ¹H NMR (C₆D₆, 300 MHz) δ = 1.31 (s, 12H), 1.80 (quint, J = 6.0 Hz, 2H), 2.29 (t, J = 6.0 Hz, 2H), 2.40 (t, J = 6.0 Hz, 2H), 3.61 (s, 3H) ppm. ¹³C NMR (C₆D₆, 125.7 MHz) δ = 18.9, 23.6, 24.7, 32.5, 51.0, 83.7, 103.2, 172.6 ppm.



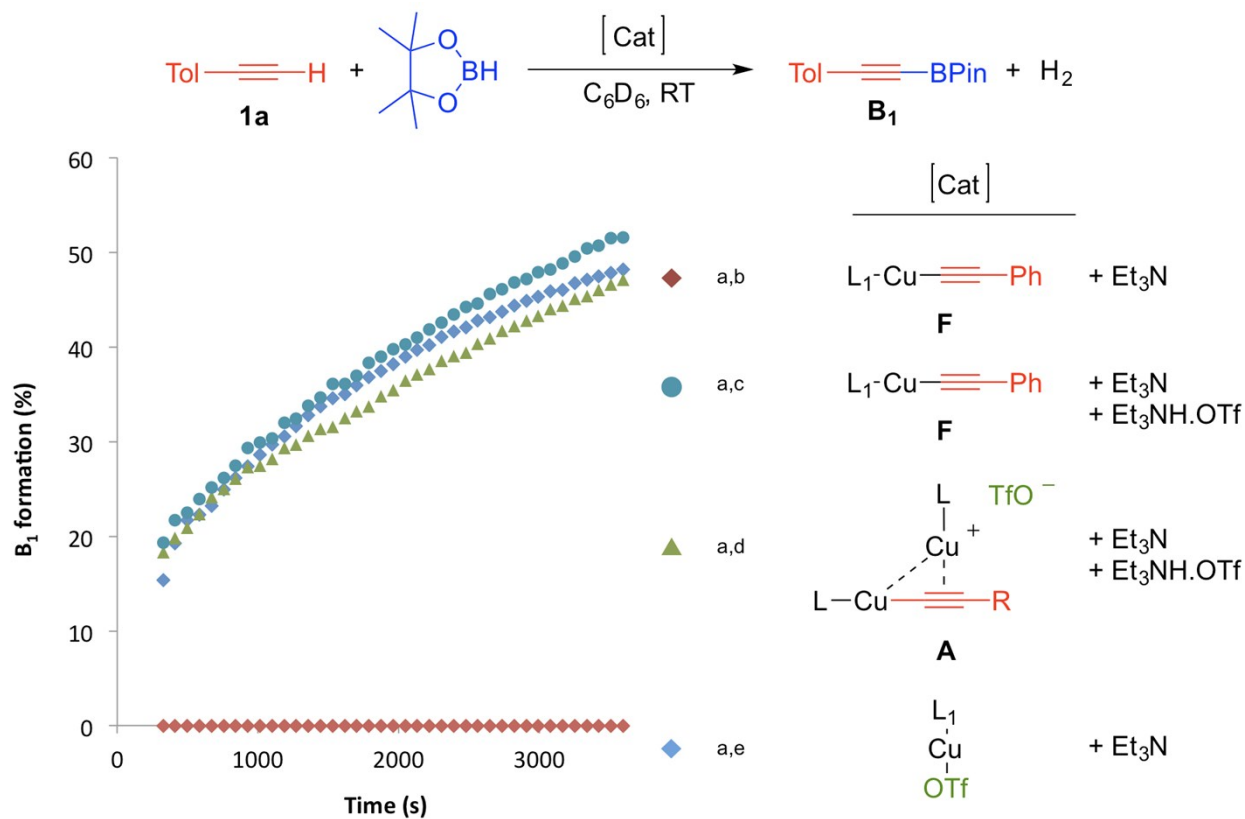
B₁₅^{iii,v}: Deliquescent solid 0.405 g (95% yield). ¹H NMR (C₆D₆, 500 MHz) δ = 1.26 (m, 16H), 1.00 (m, 13H), 1.19 (m, 1H) 1.38-1.64 (m, 8H), 2.25 (m, 1H) ppm. ¹³C NMR (C₆D₆, 125.7 MHz) δ = 24.5, 24.6, 25.7, 29.7, 32.1, 83.5, 108.3 (br) ppm.

E. Preliminary Mechanistic Studies

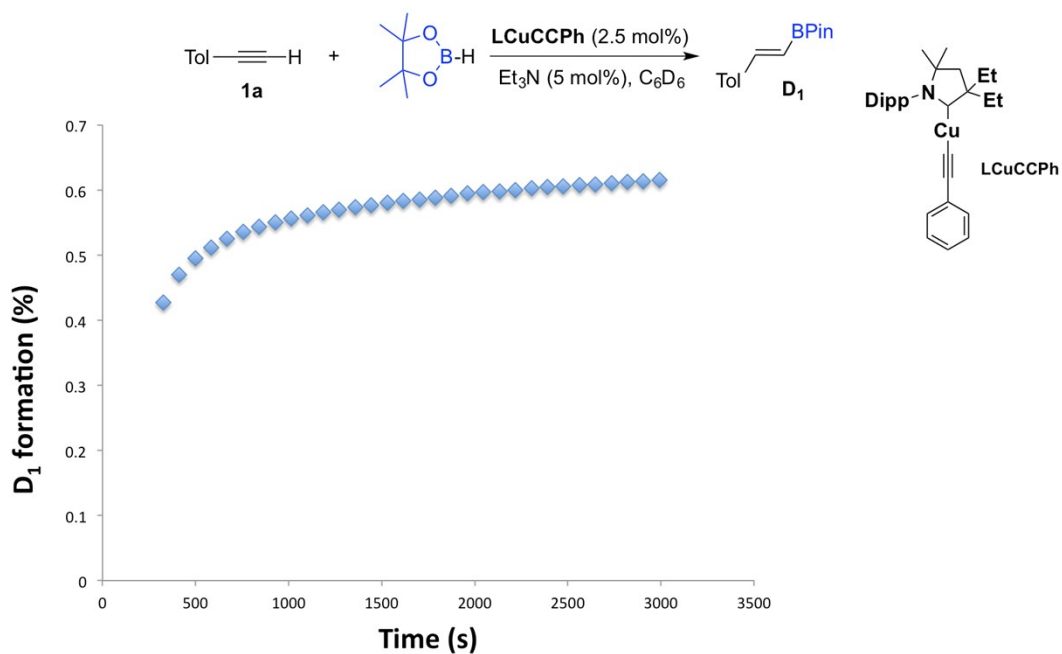
A. Kinetic measurements.

All the kinetic measurements were performed in a J-Young NMR tube at room temperature on a Bruker 300MHz NMR machine using the multi_zgvd command. Conversions were measured by following the growth of the characteristic signals for **B**₁ or **D**₁ with respect to the depleting signals for **1a**. In each kinetic run, 0.45 mmol (0.057 mL) of **1a** and 0.45 mmol (0.066 mL) of PinBH were used in combination with 2.5 mol% of the catalyst (either L₁CuOTf: 6.8 mg or L₁CuCCPh: 5.4 mg), the corresponding amount of Et₃N (either 5 mol%: 0.0032 mL or 2.5 mol%: 0.0016 mL) and Et₃NH.OTf (1.4 mg, 2.5 mol%) when needed. At the end of these experiments, the resulting mixture was transferred to a schlenk tube, the volatiles were evaporated under vacuum and 5 mL of pentane was added. The mixture was passed, through a short column packed with dry neutral alumina (3 cm diameter x 5 cm high) under an argon atmosphere using pentane as eluent. Evaporation of the volatiles under vacuum afforded the corresponding product as white solids.

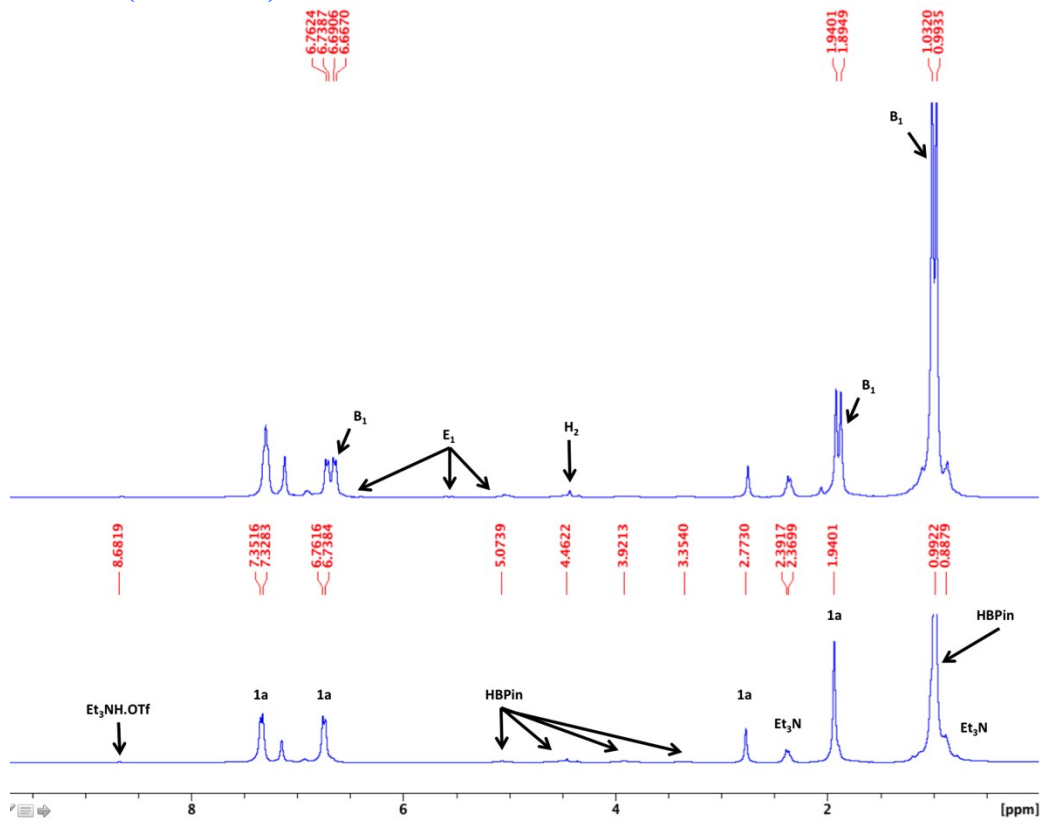
- Kinetic plots with respect to the formation of **B₁**



- Kinetic plot with respect to the formation of **D₁**

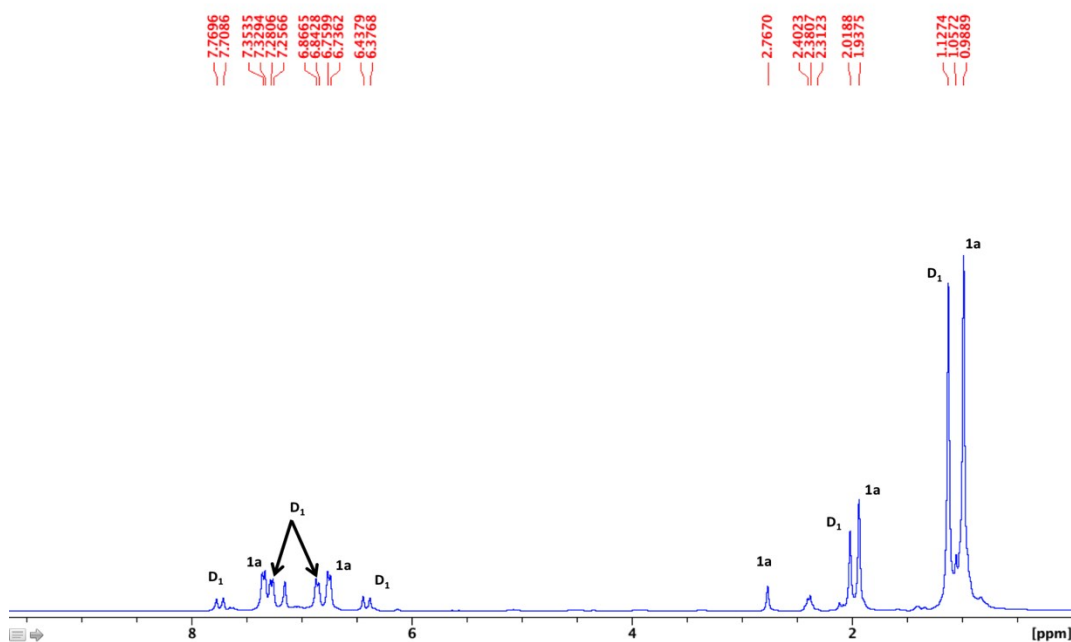


a) Selected spectra from the kinetic run using Cat: $L_1CuCCPh + HBPiN + Et_3N$ (2.5 mol%) and $Et_3NH.OTf$ (2.5 mol%)



1H NMR spectra after 5 minutes bottom. 1H spectra after 45 min top.

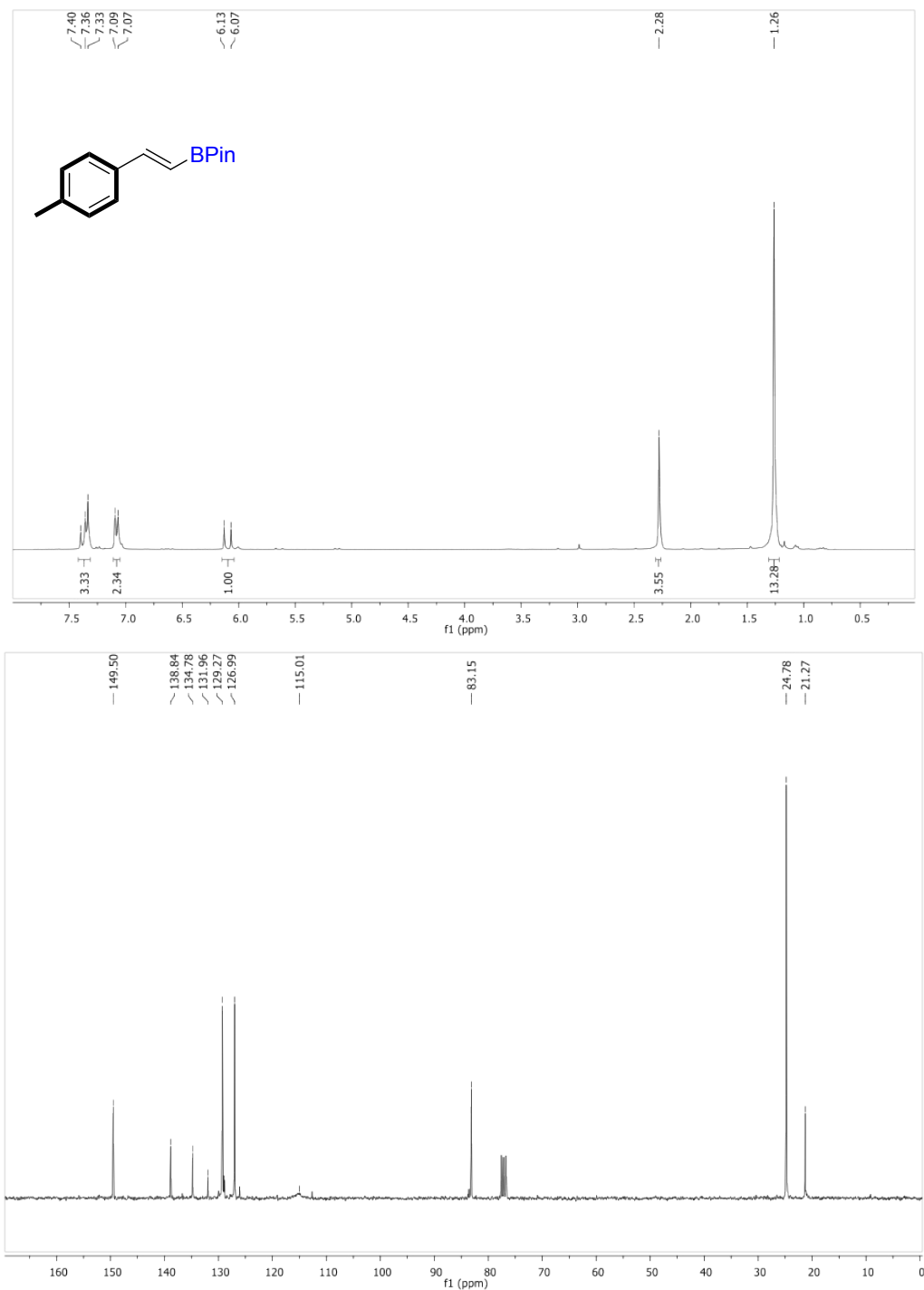
b) Selected spectra from the kinetic run using Cat: $L_1CuCCPh + HBPiN + Et_3N$ (5 mol%).



1H NMR spectra after 5 minutes.

NMR of the isolated D_1 isolated at the end of the kinetic run using **Cat:** $L_1CuCCPh + HBPin + Et_3N$ (5 mol%). The reaction was complete within 30 minutes.

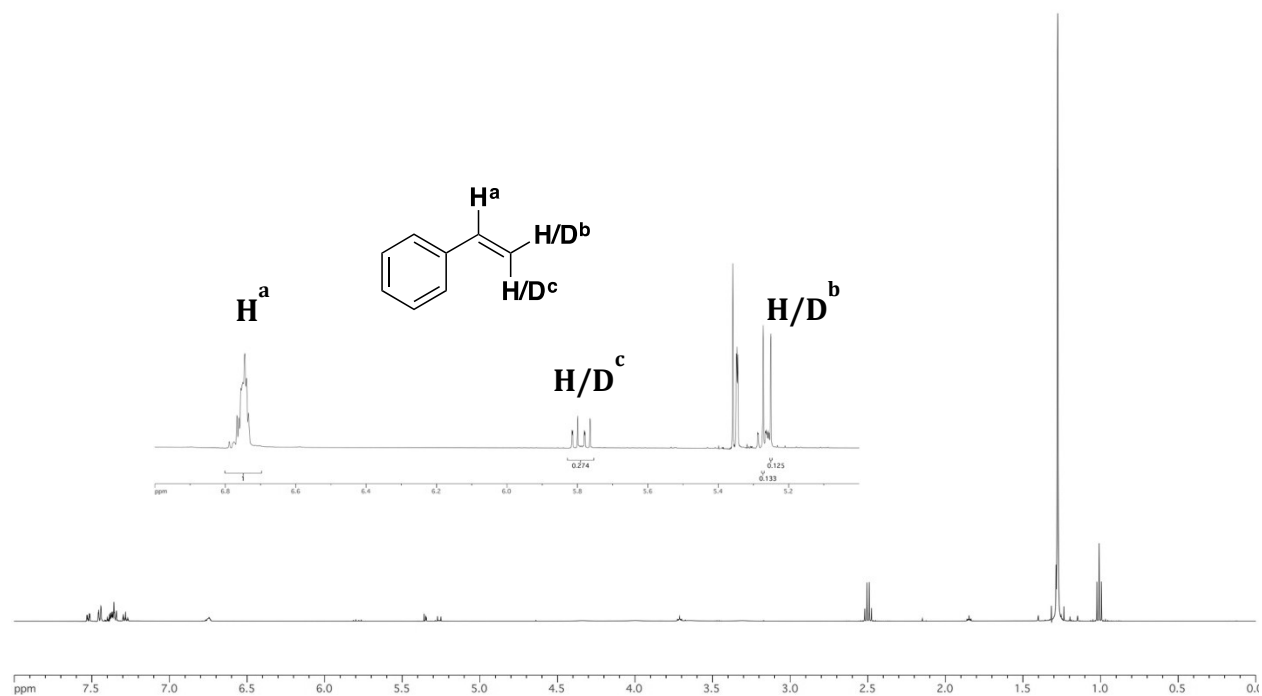
Colorless oil : 95% yield. 1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.26$ (s, 12H), 2.28 (s, 3H), 6.11 (d, $J = 18.6$ Hz, 1H), 7.10 (d, $J = 7.9$ Hz, 2H), 7.34 (d, $J = 7.6$ Hz, 2H), 7.38 (d, $J = 19.5$ Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 21.3, 24.8, 83.2, 115.0$ (br), 127.0, 129.3, 134.8, 138.8, 149.5 ppm.



B. Deuterium Labeling for the Dehydrogenative Transformation

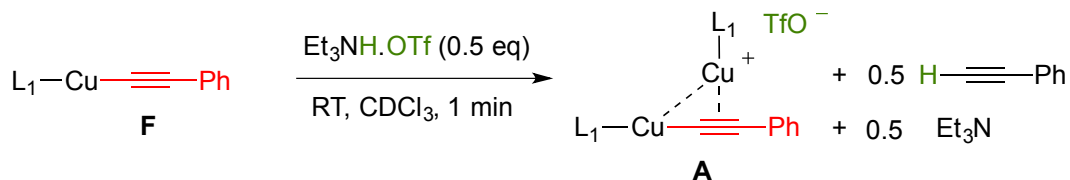
In a schlenk tube fitted with a magnetic stir bar were added under an argon atmosphere CD_2Cl_2 (17 mL), D-labeled phenyl acetylene (0.200 ml, 1.82 mmol), pinacol borane (0.264 mL, 1.82 mmol), and triethylamine (0.012 mL, 0.091 mmol). Then, $\text{Et}_2\text{CAACCuOTf}$ (0.024 g, 0.045 mmol%) was added to the mixture and the reaction was left stirring at room temperature for three hours. After this time NMR-analysis of the content showed the formation of a mixture of **B**₁ and styrene-D.^{viii}

¹H NMR of Styrene-D

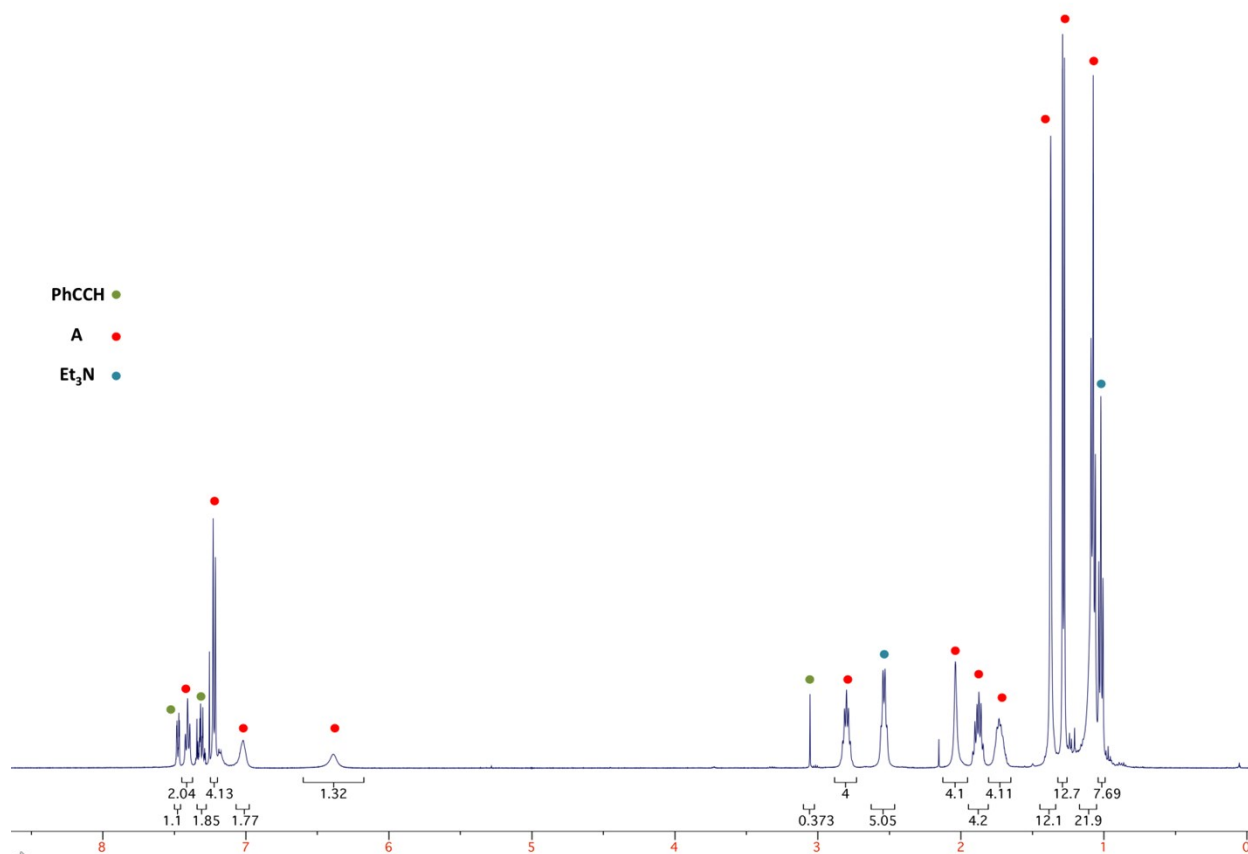


C. Evidence for the formation of A starting from F in the presence of Et₃NH.OTf.

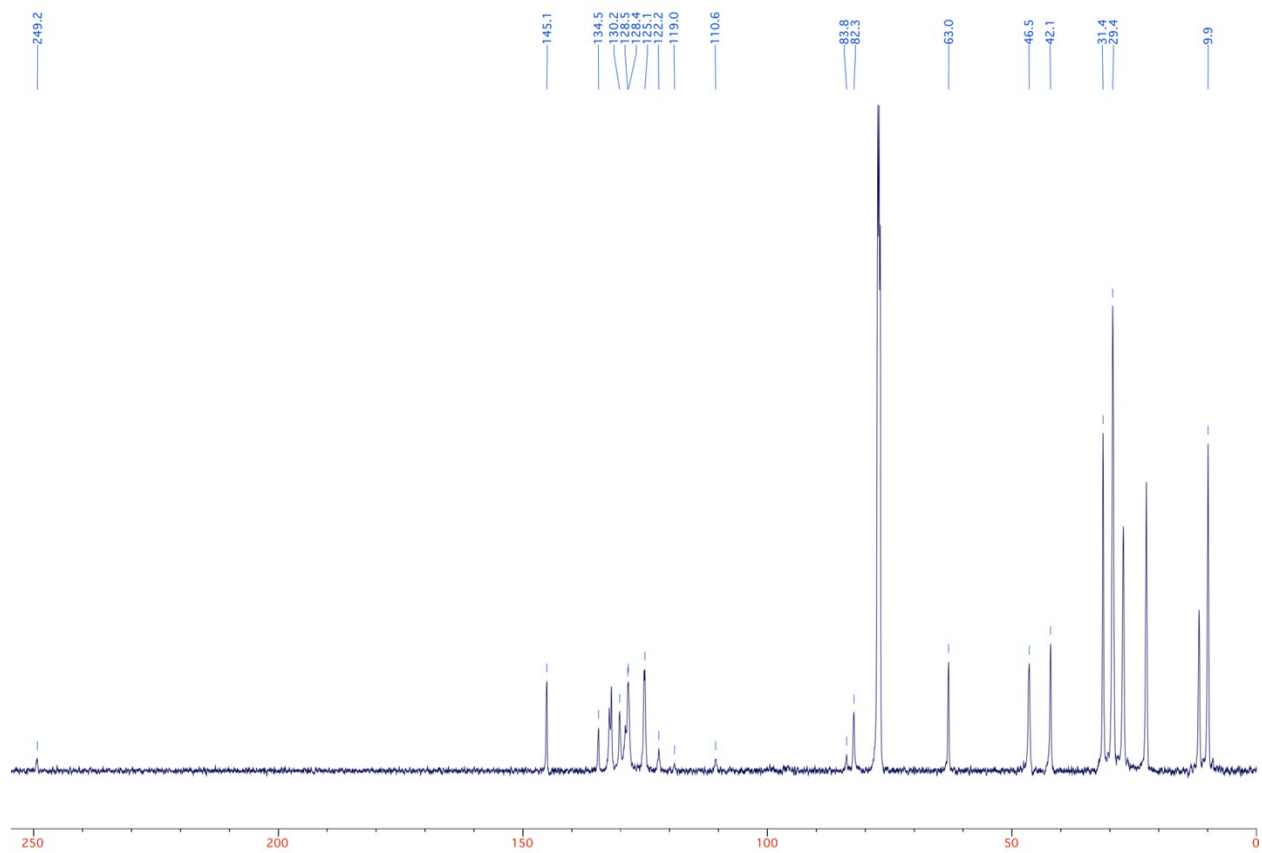
A J-Young NMR tube was charged with CDCl₃ (1 mL), **F** (20 mg), and Et₃NH.OTf (5.3 mg, 0.5 eq). The NMR taken immediately after mixing the component together show a clean formation of the *bis*-copper **A** and are in agreement with the literature.¹ See NMR spectra bellow.



¹H



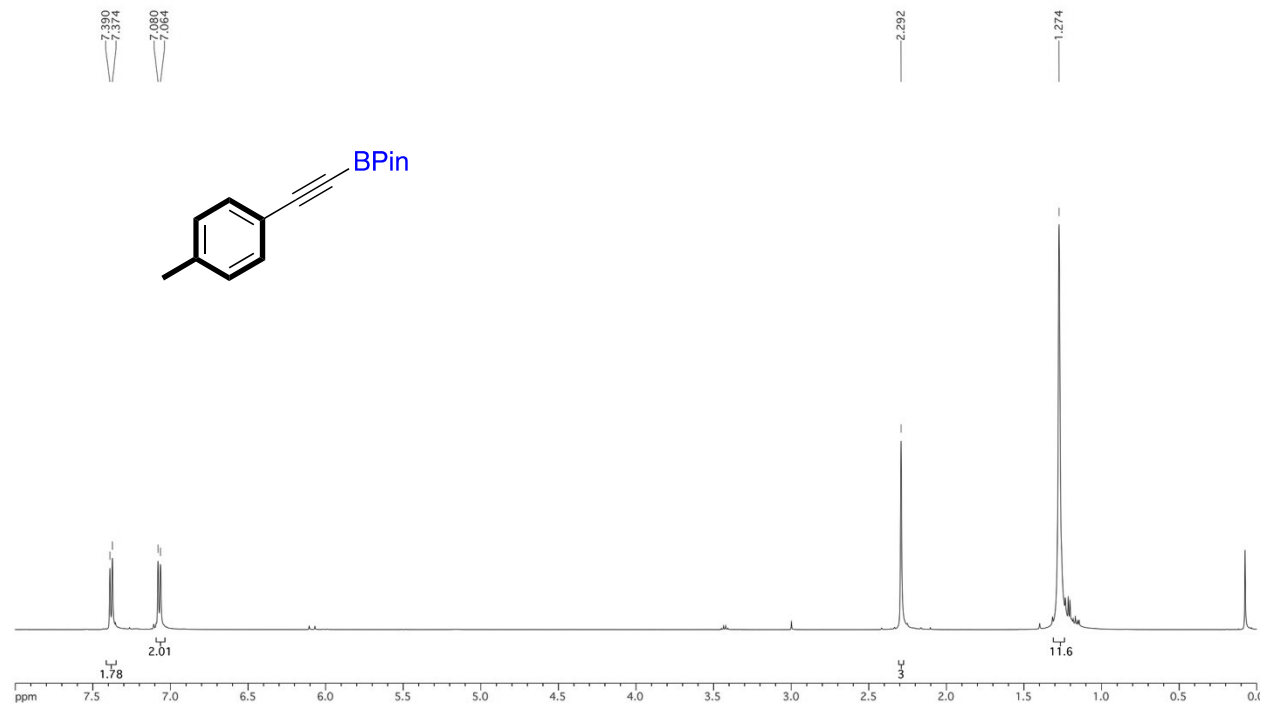
¹³C



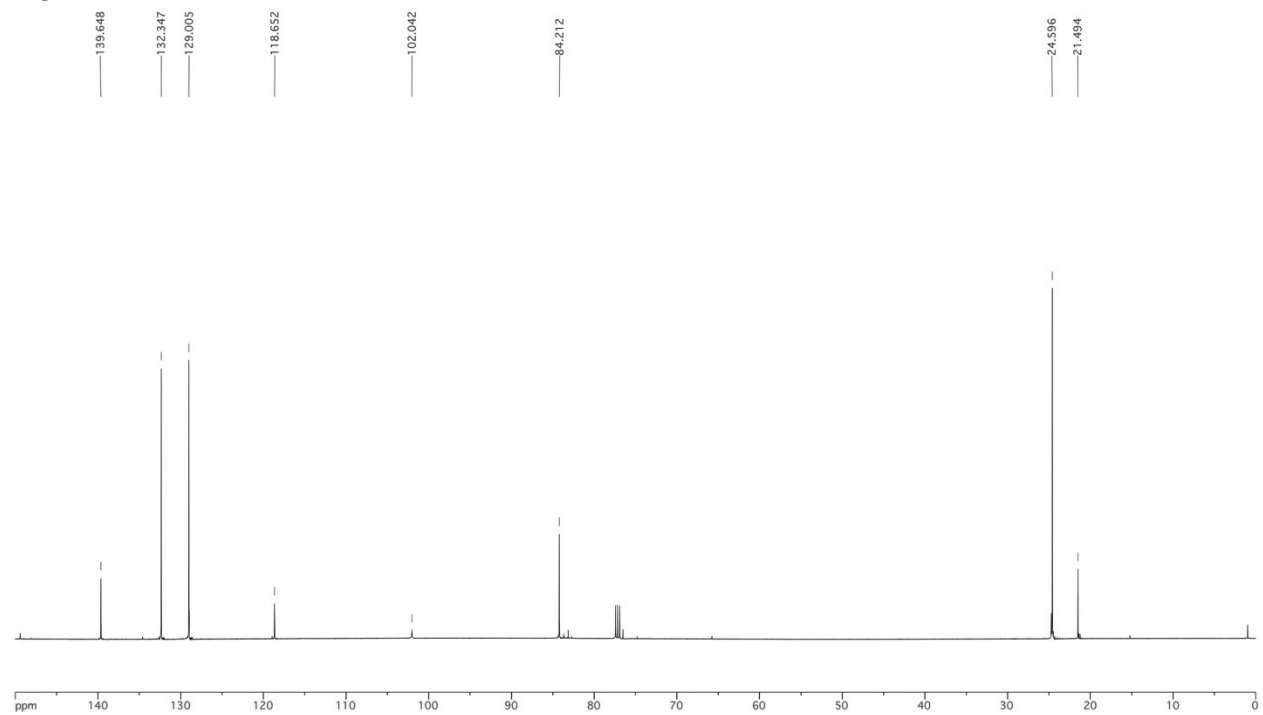
F. Spectra

B₁

¹H

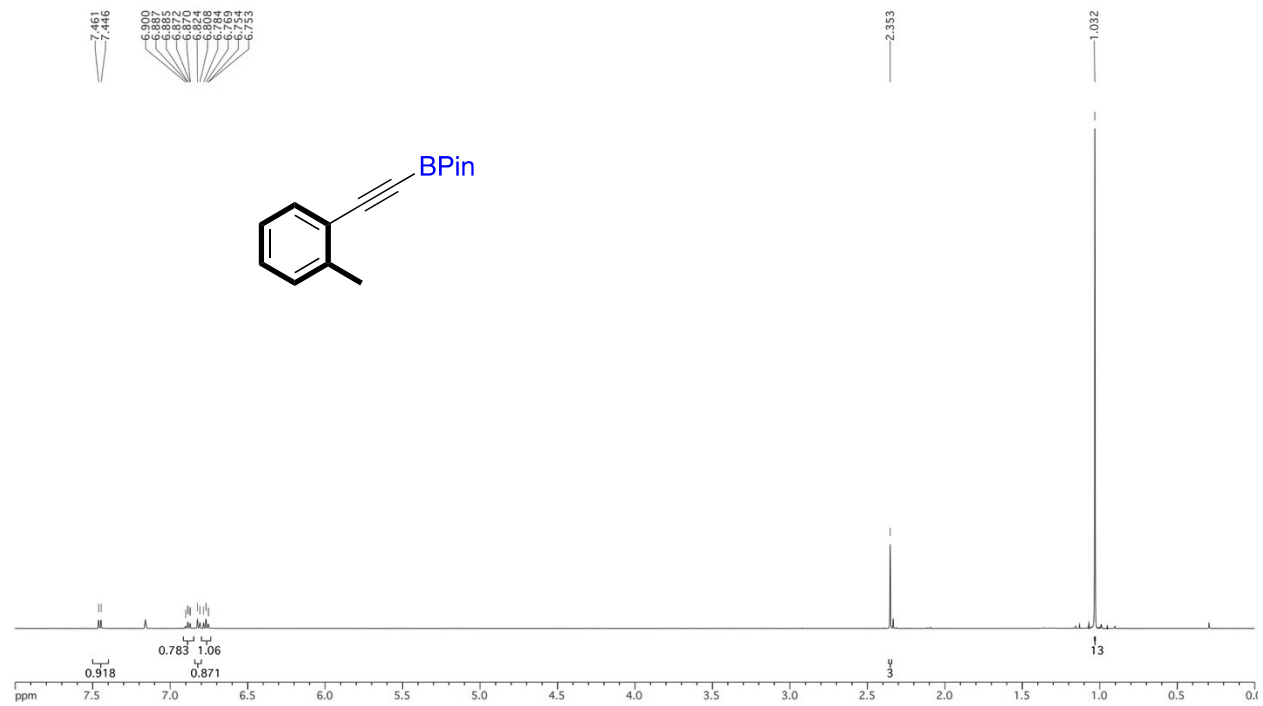


¹³C

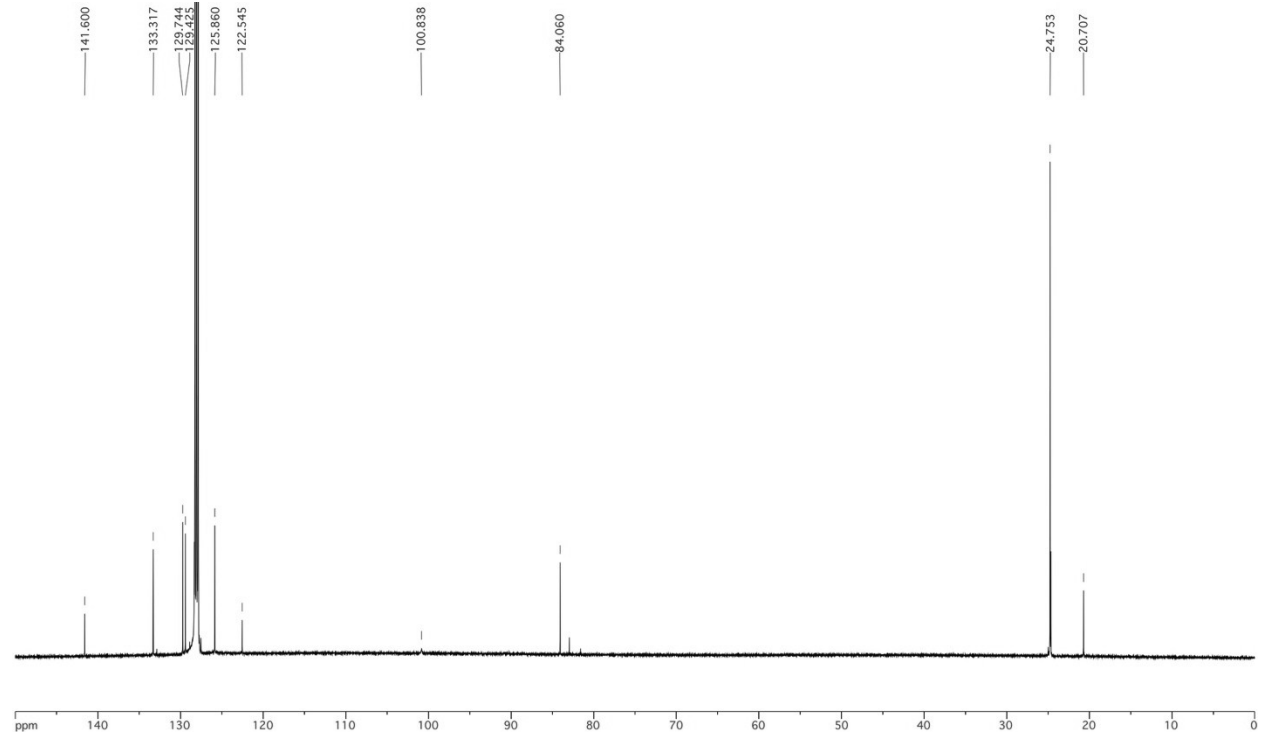


B₂

¹H

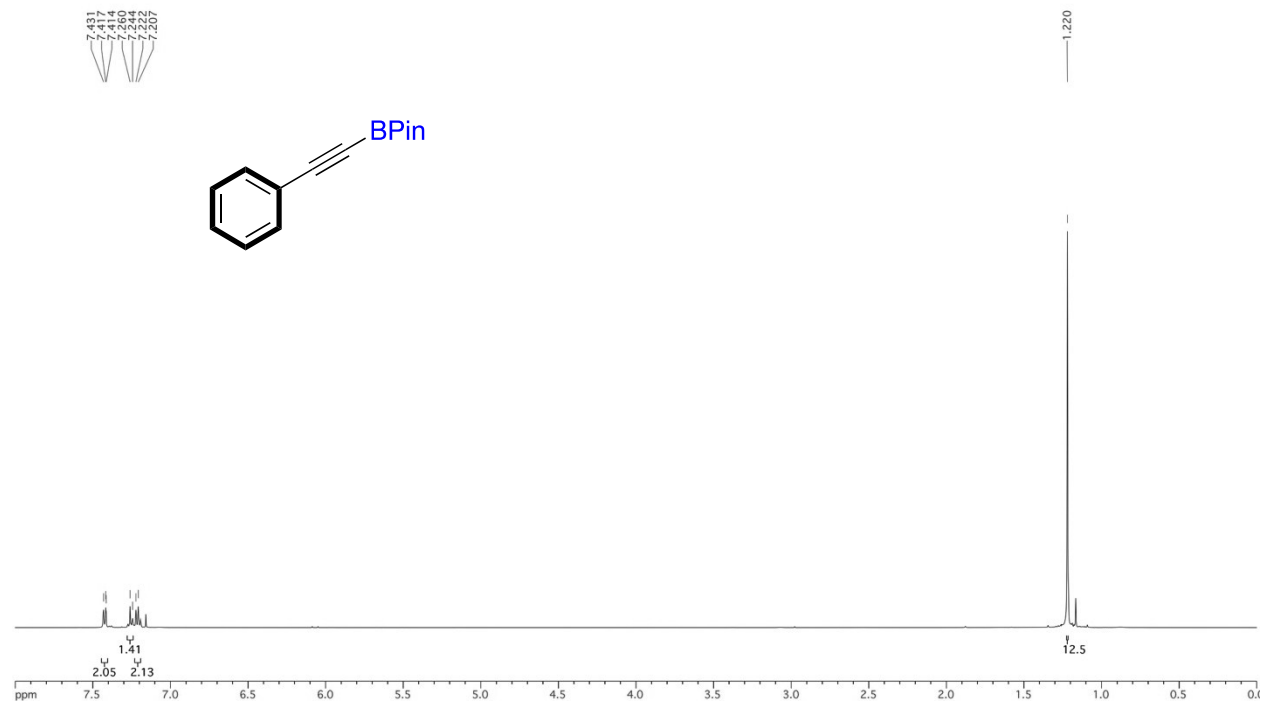


¹³C

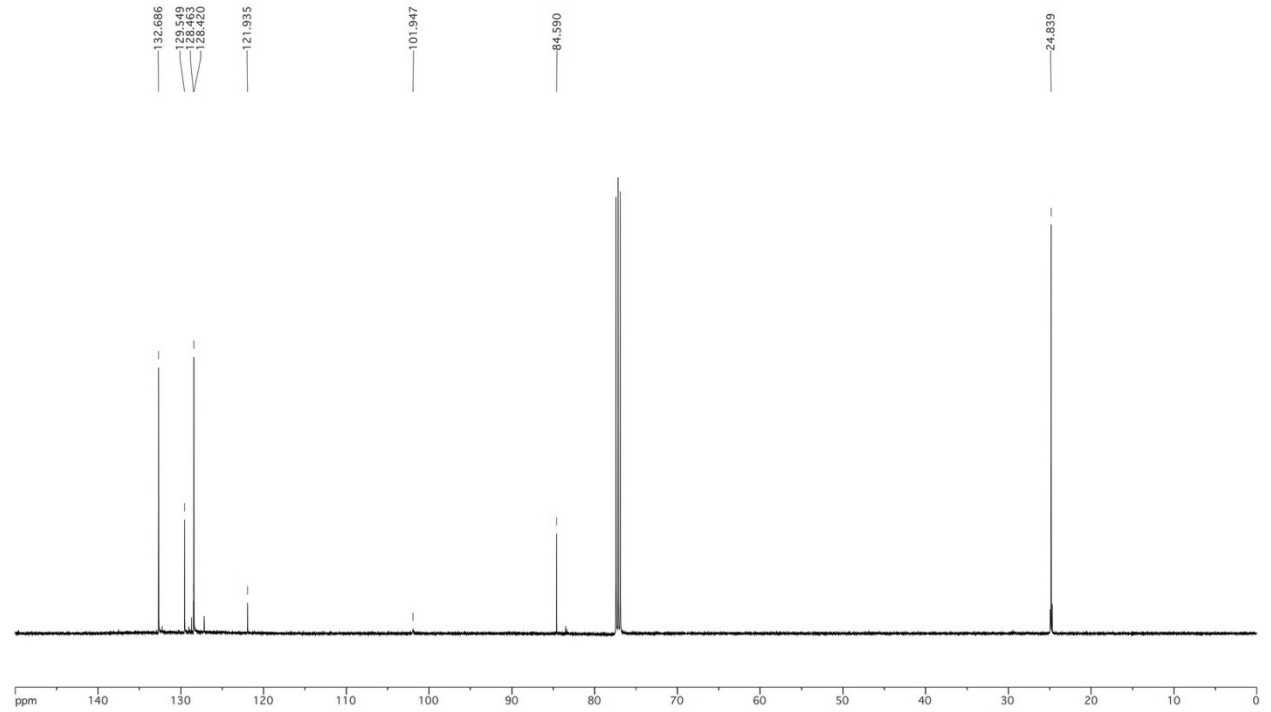


B₃

¹H

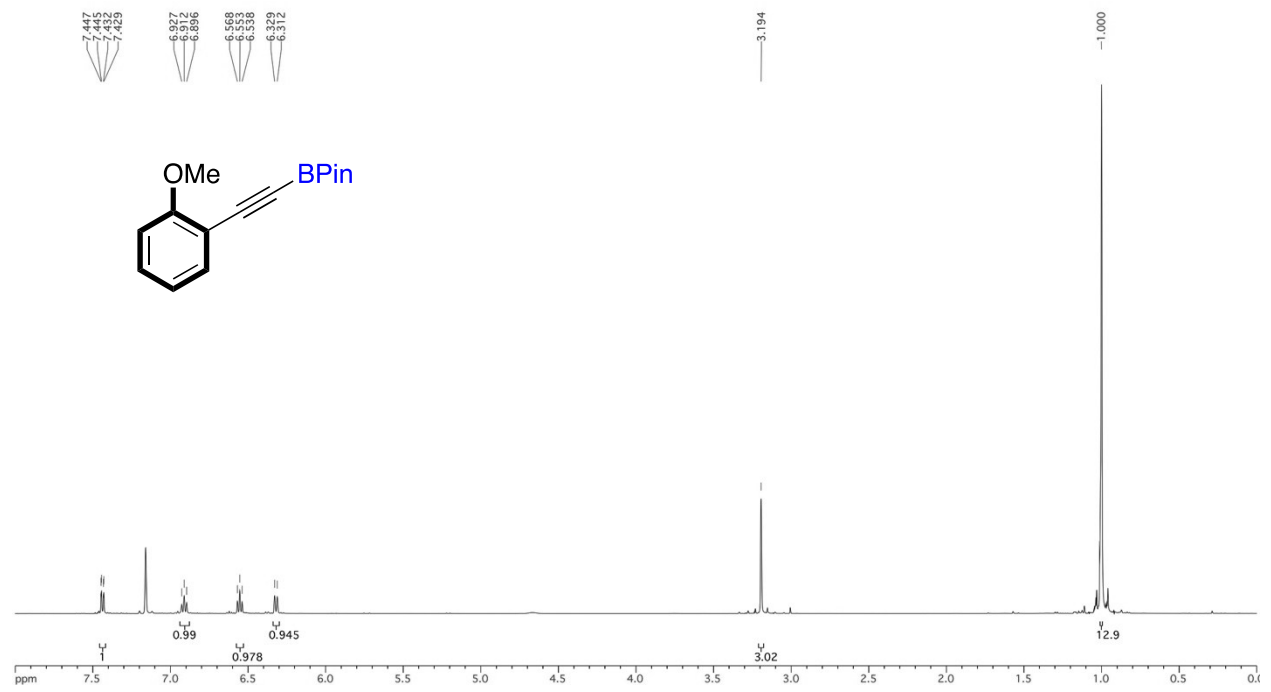


¹³C

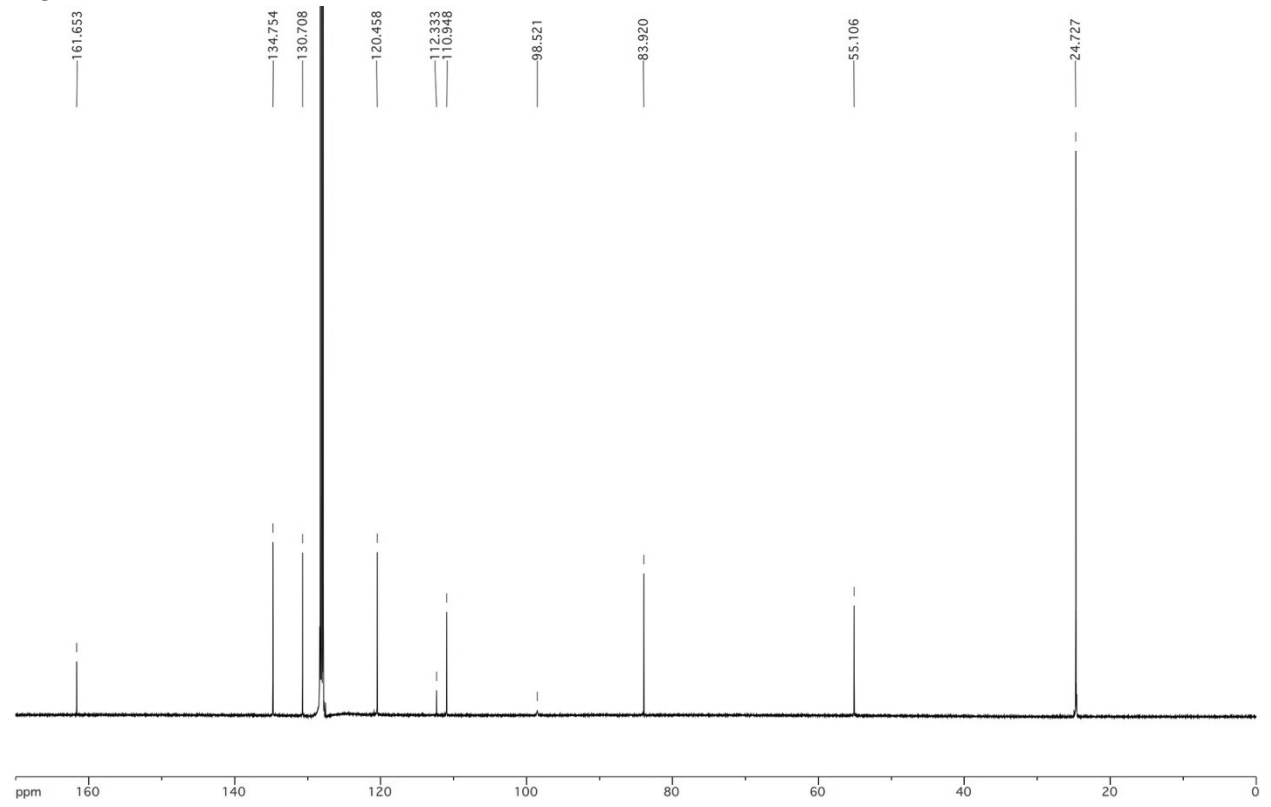


B₄

¹H

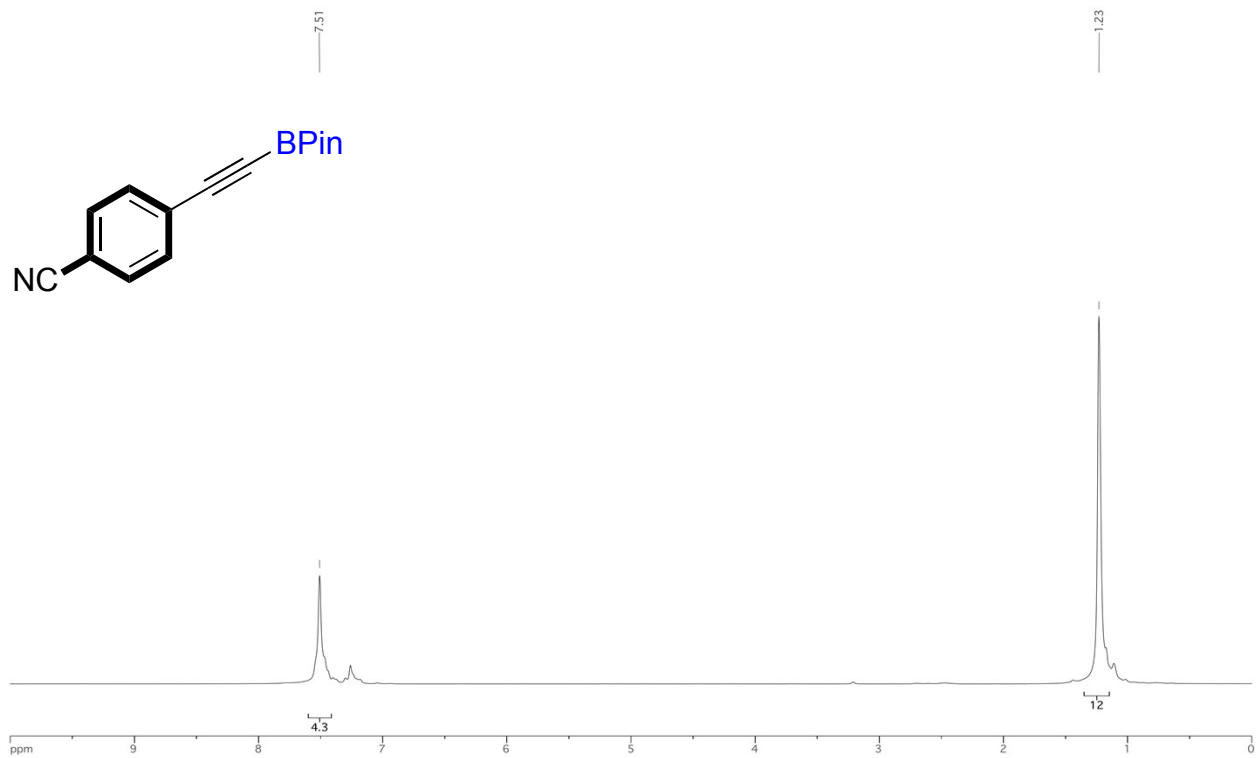


¹³C

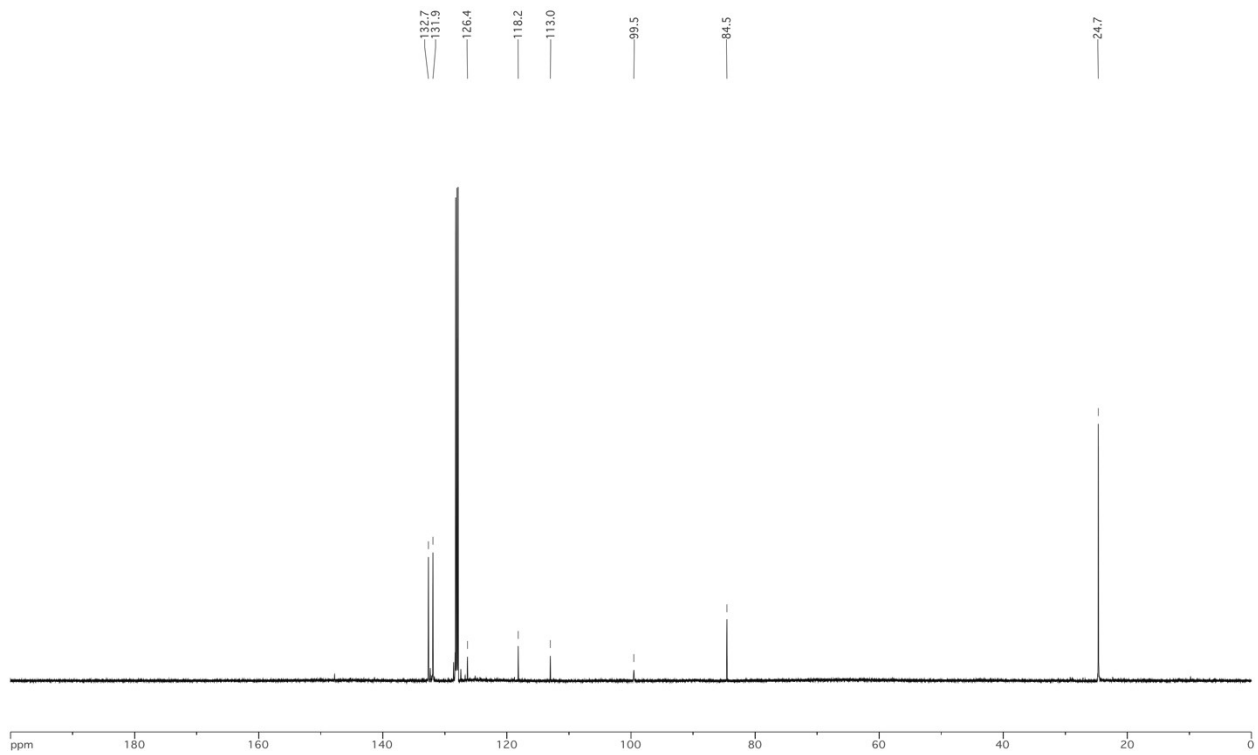


B₅

¹H

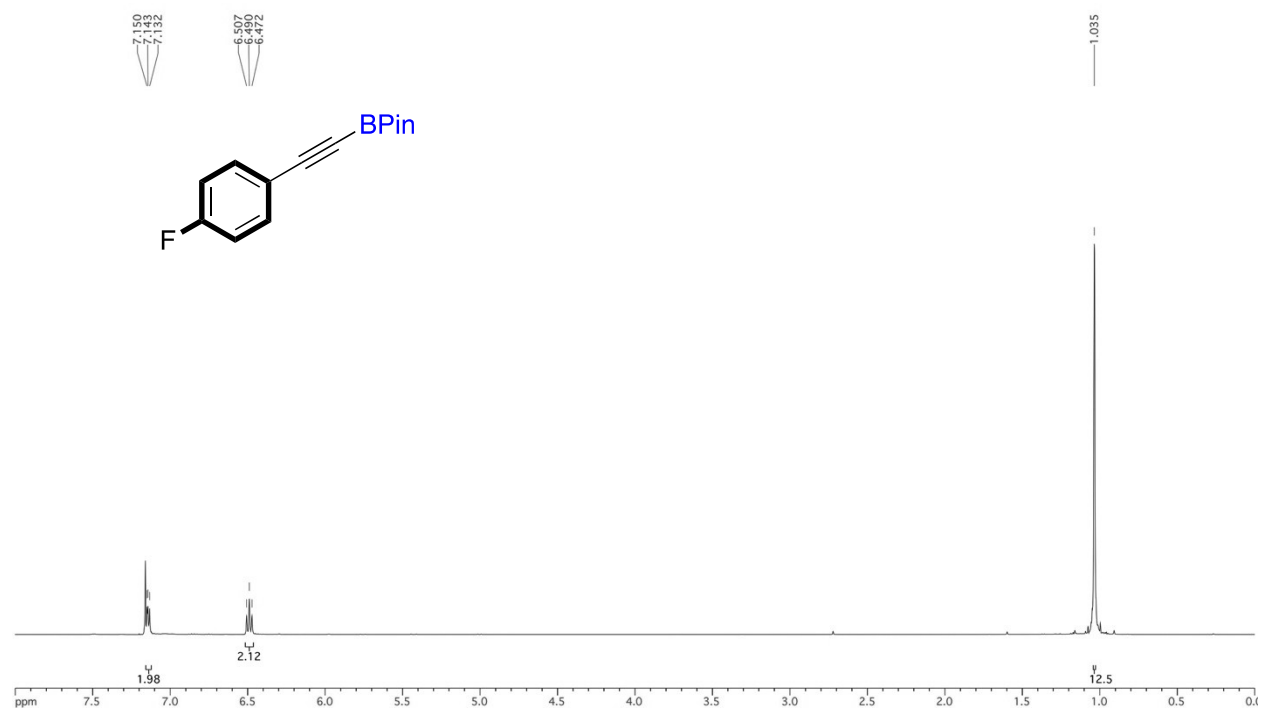


¹³C

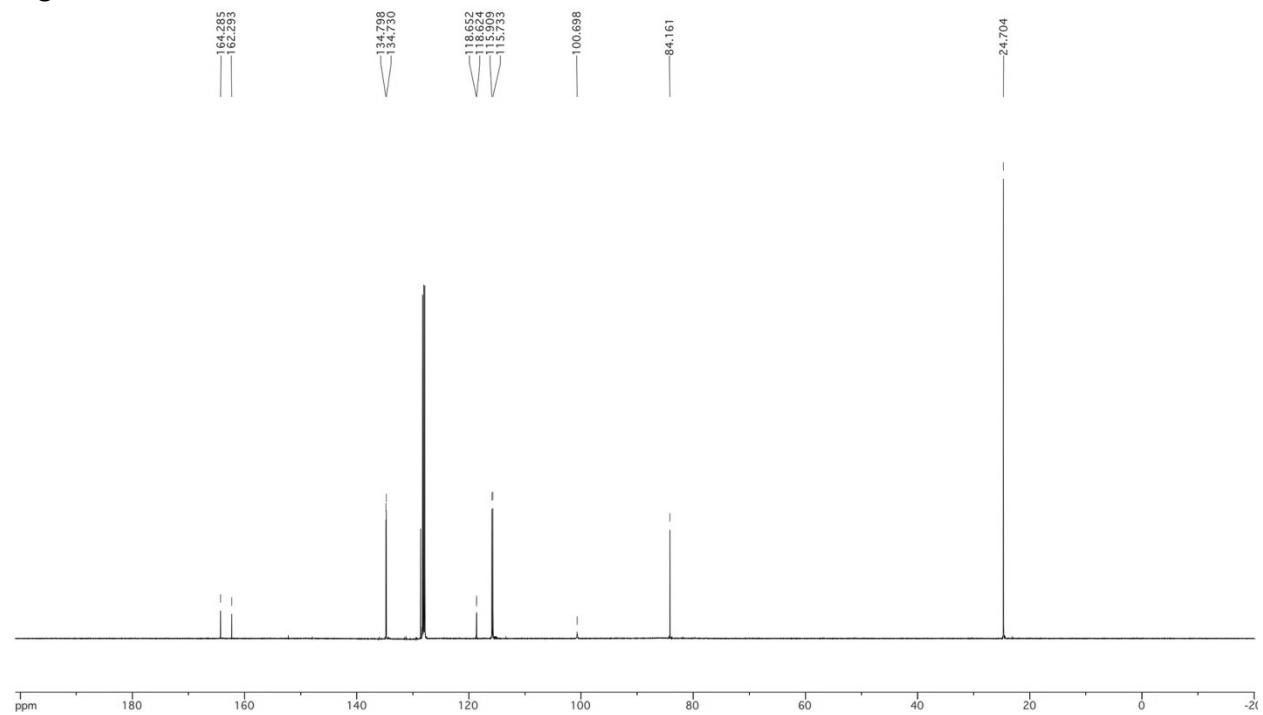


B₆

¹H

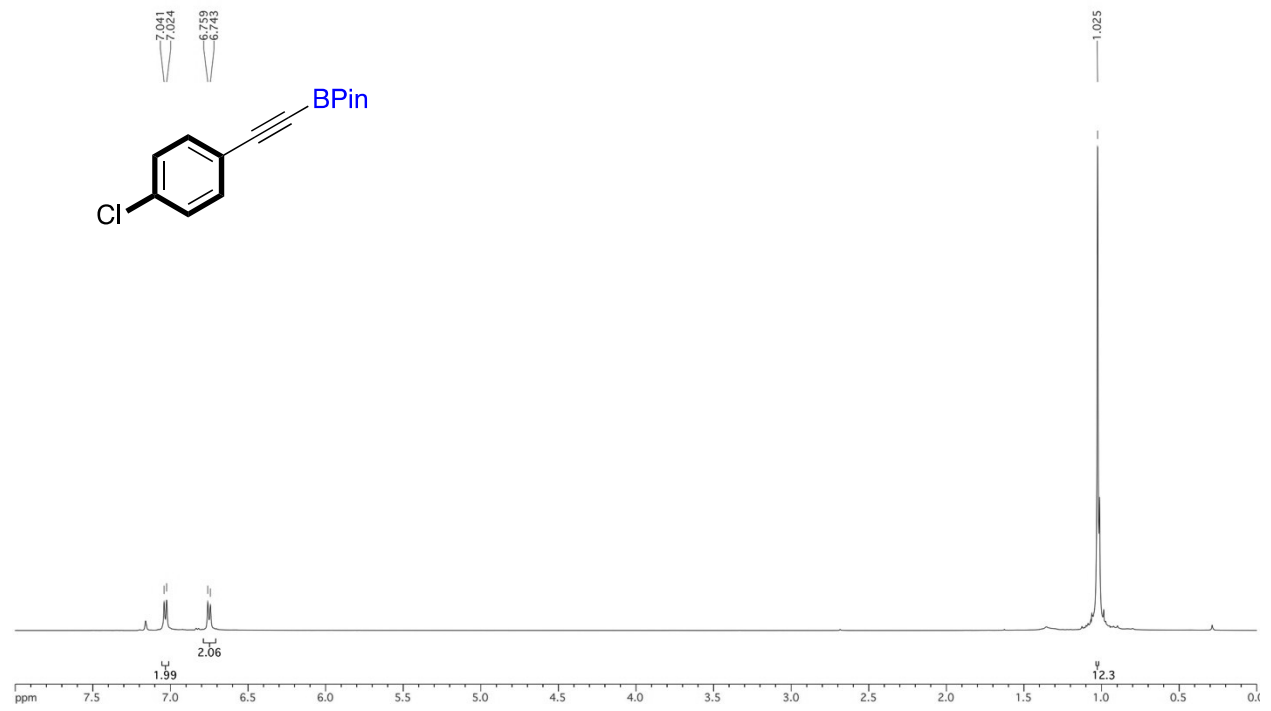


¹³C

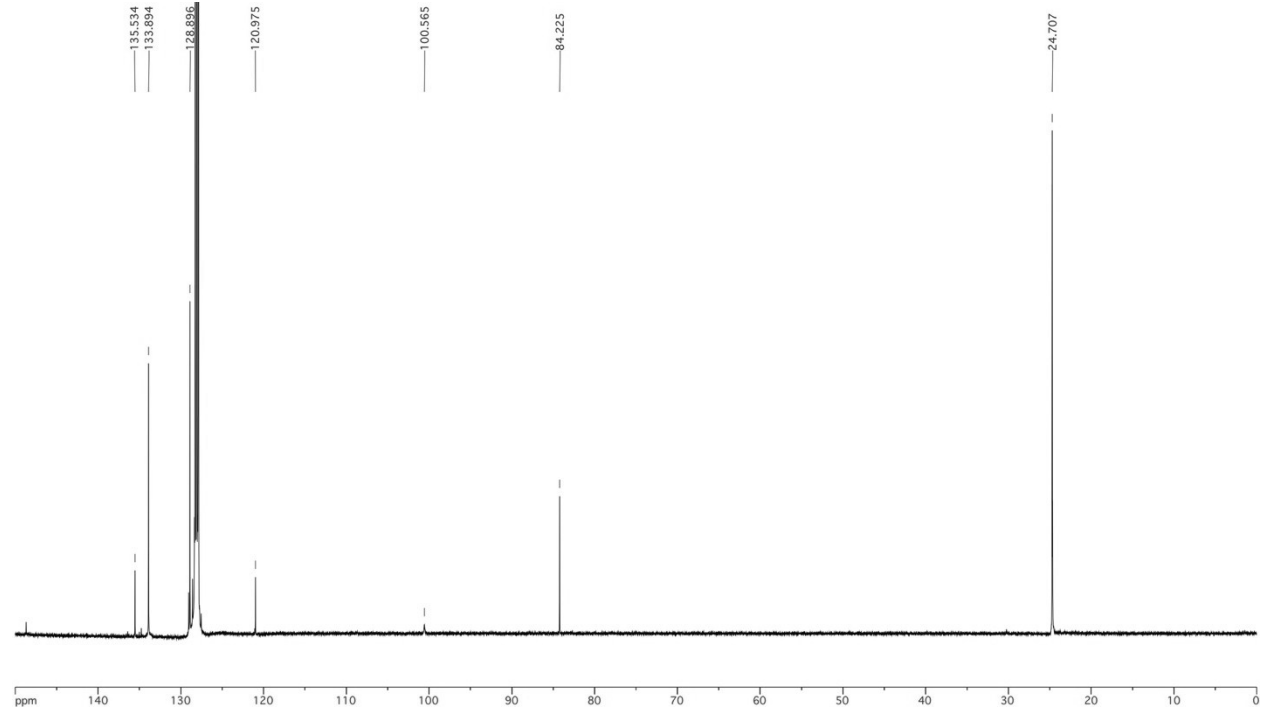


B₇

¹H

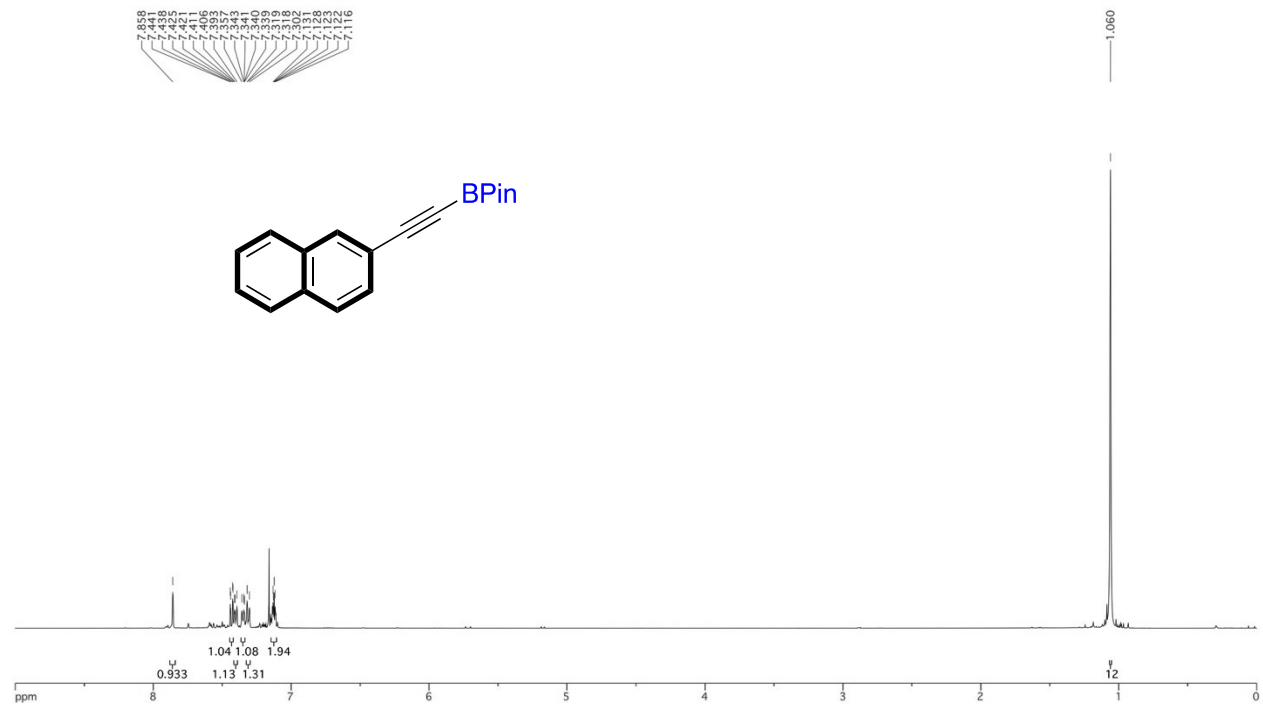


¹³C

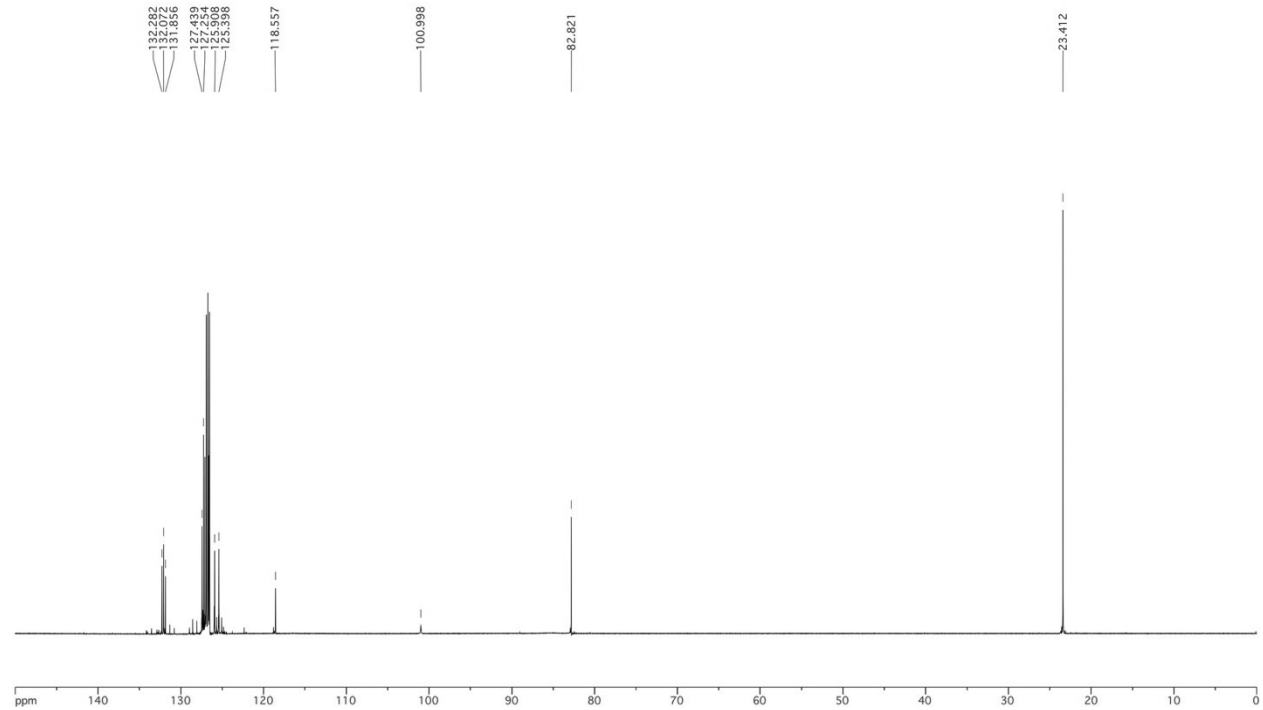


B₈

¹H

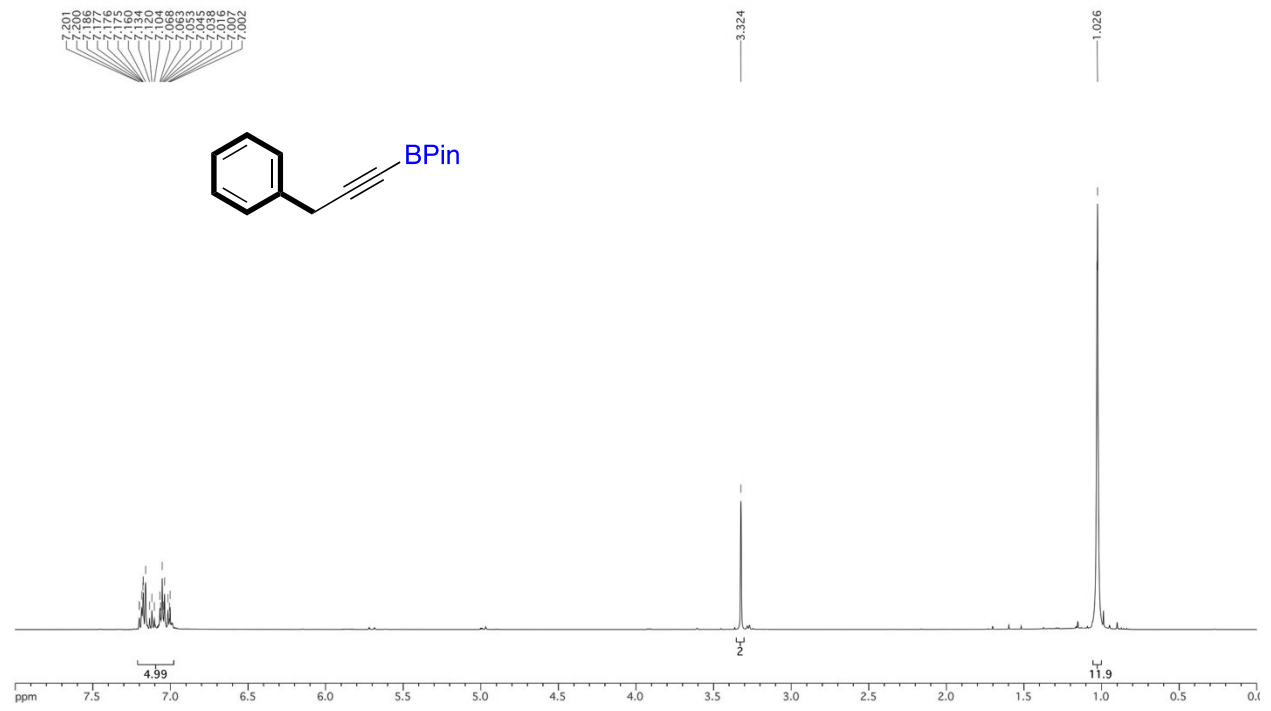


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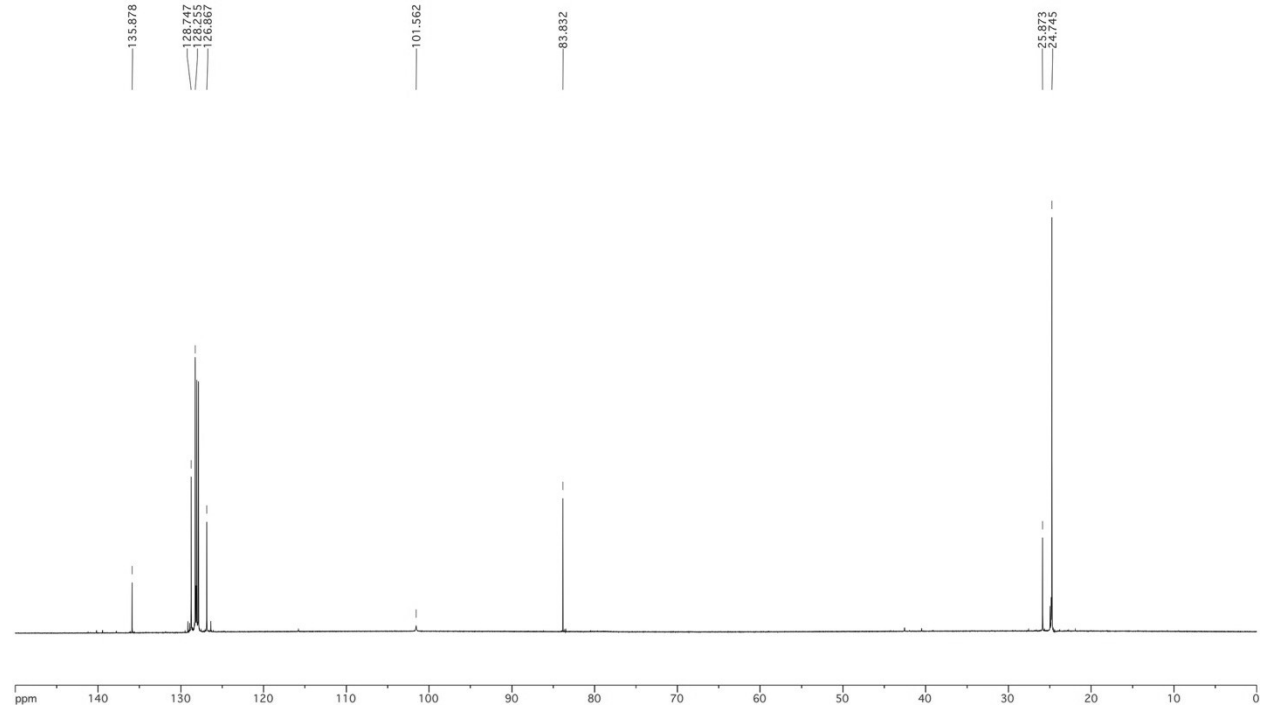


B₉

¹H

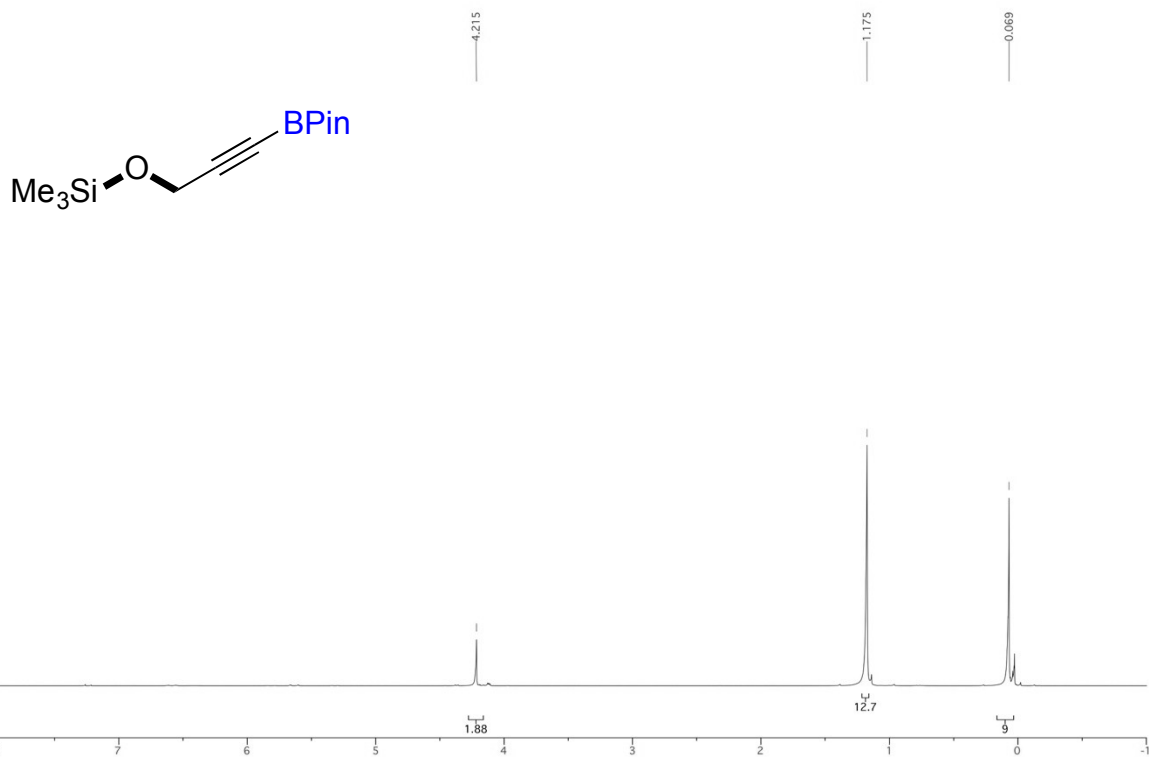


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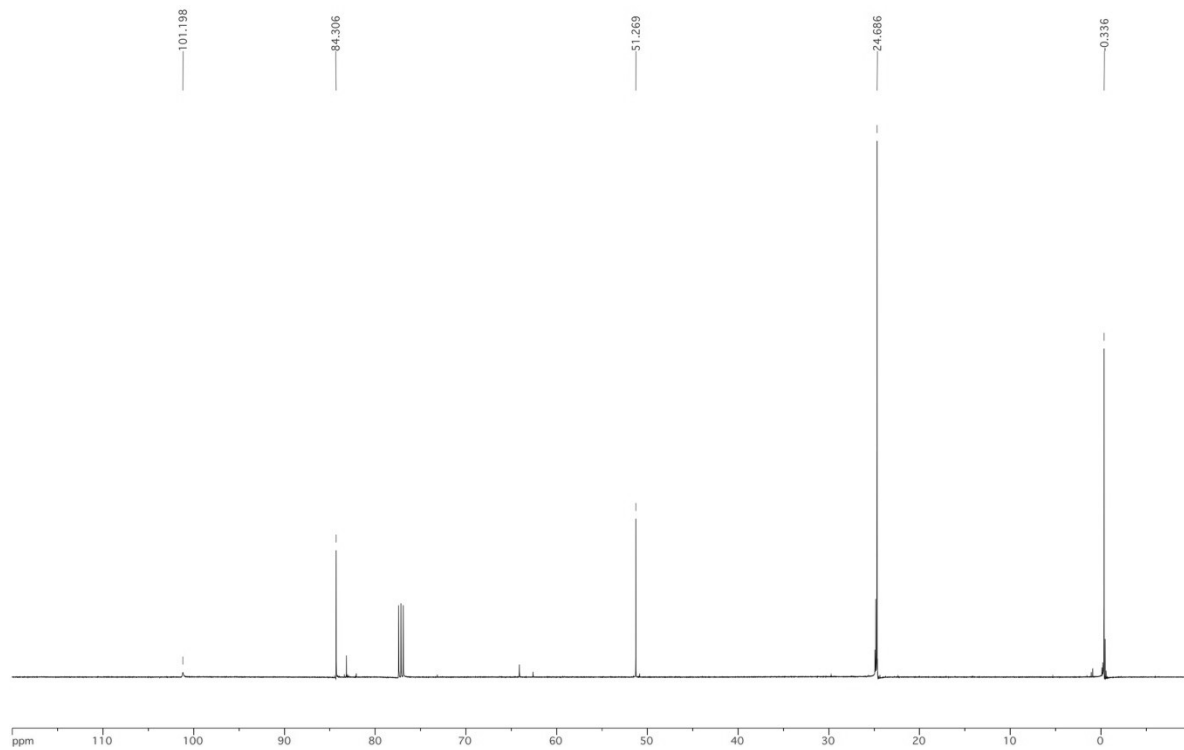


B₁₄

¹H

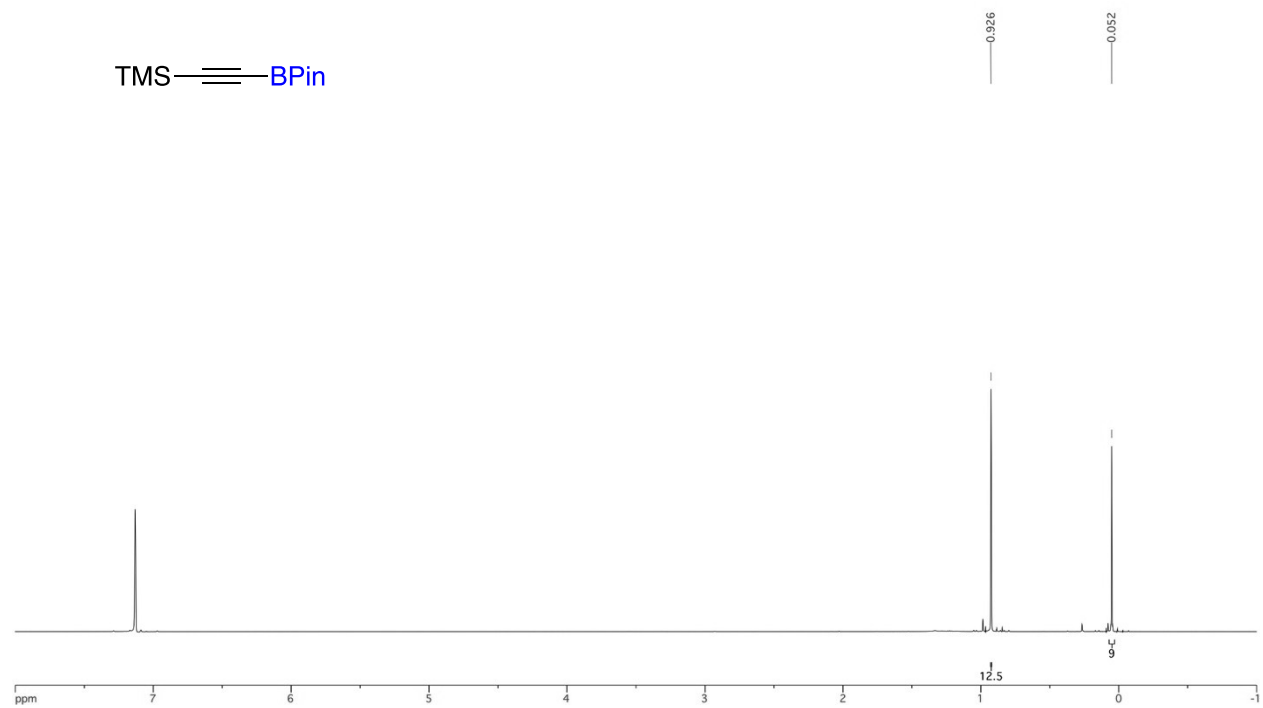


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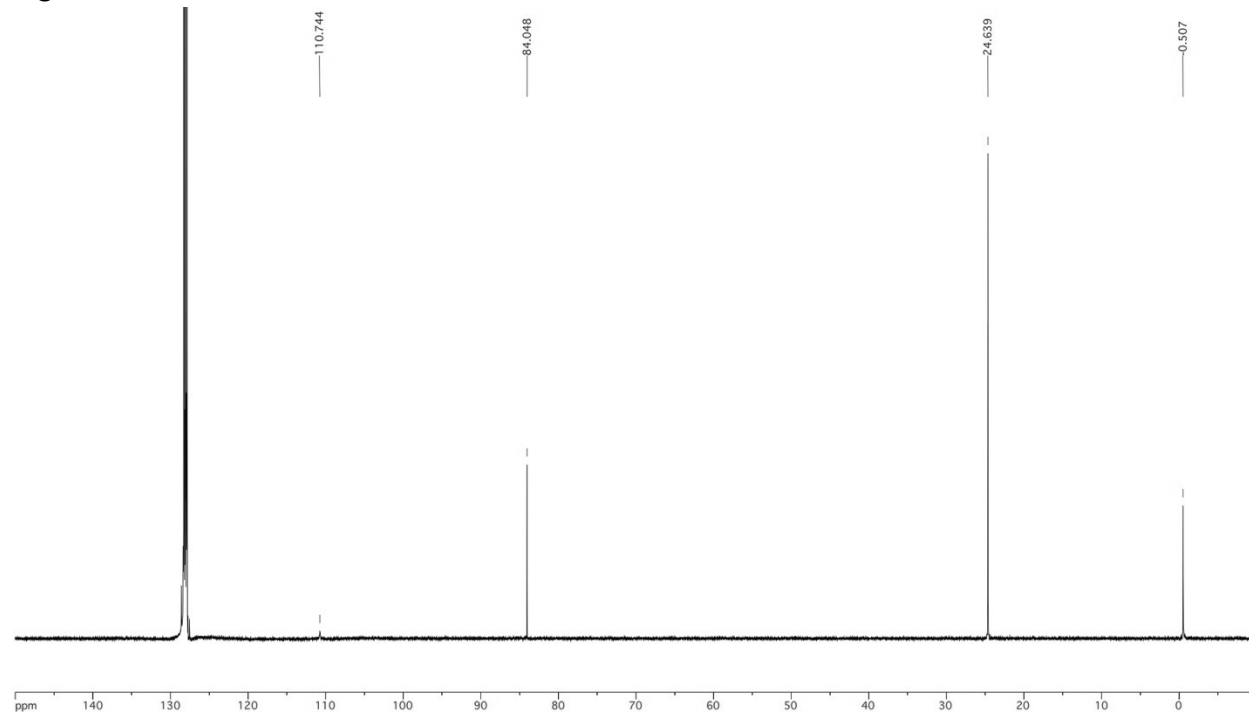


B₁₁ Crude NMR

¹H

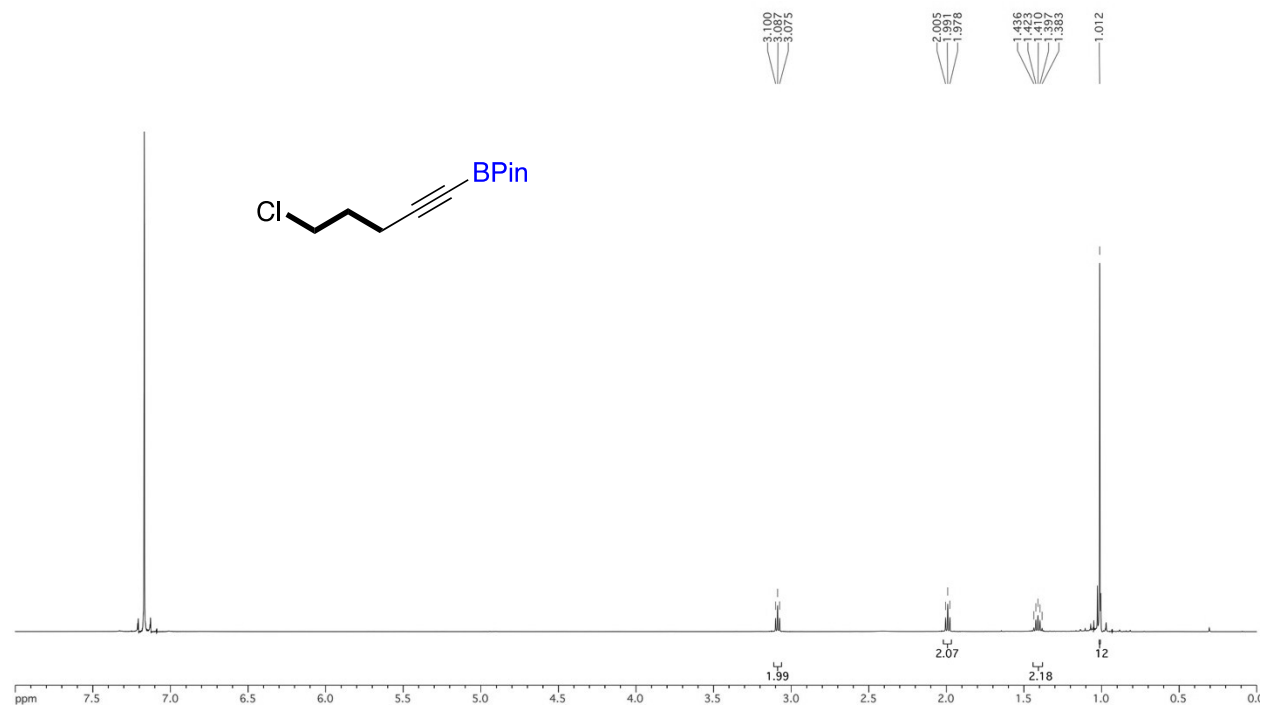


¹³C

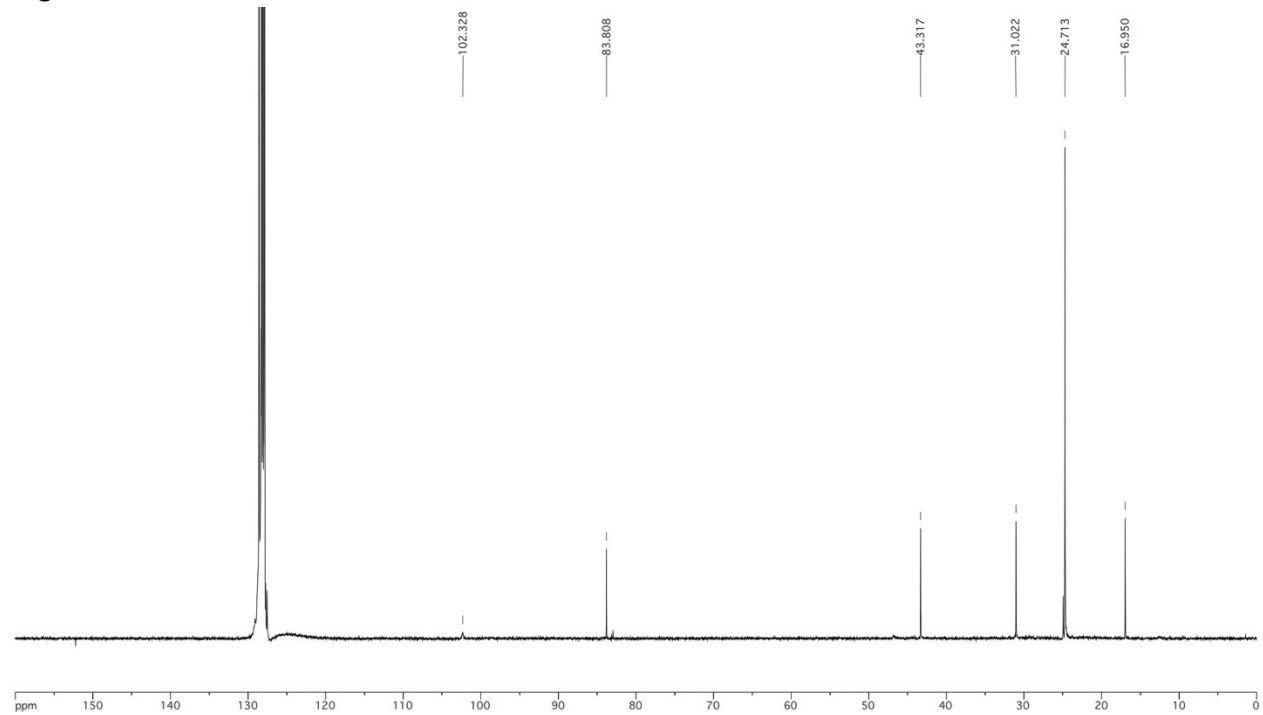


B₁₂

¹H

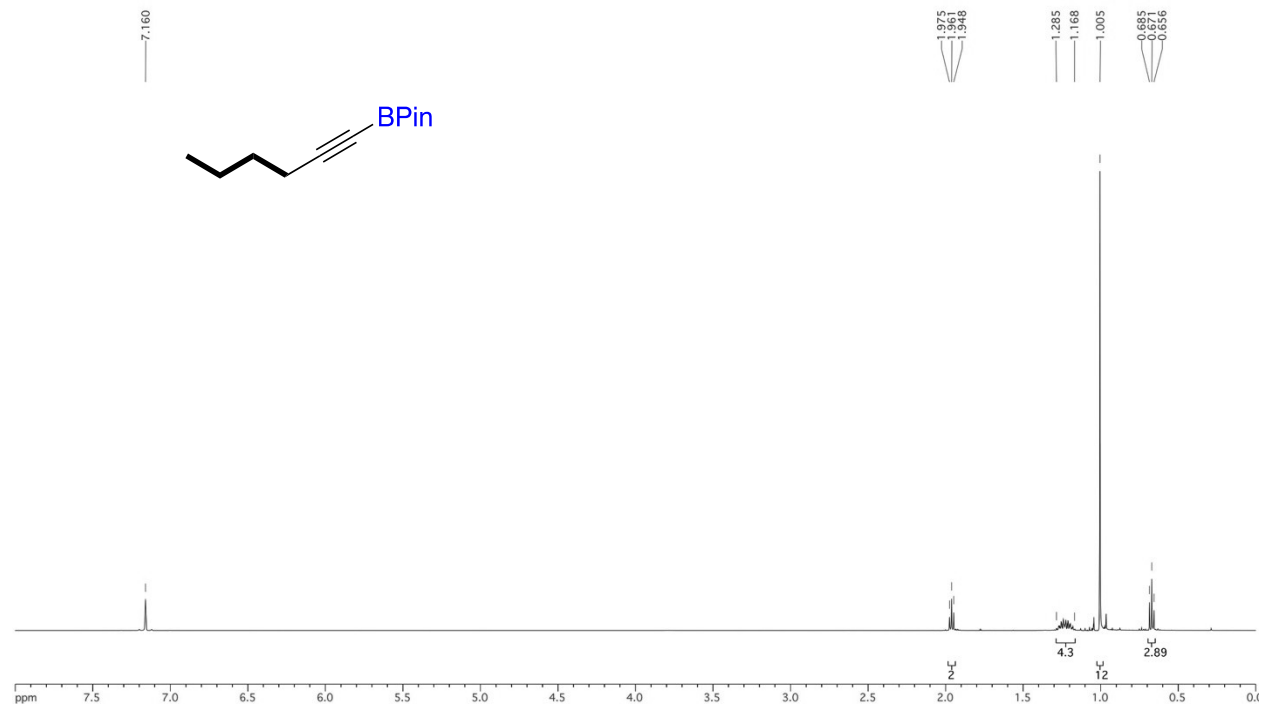


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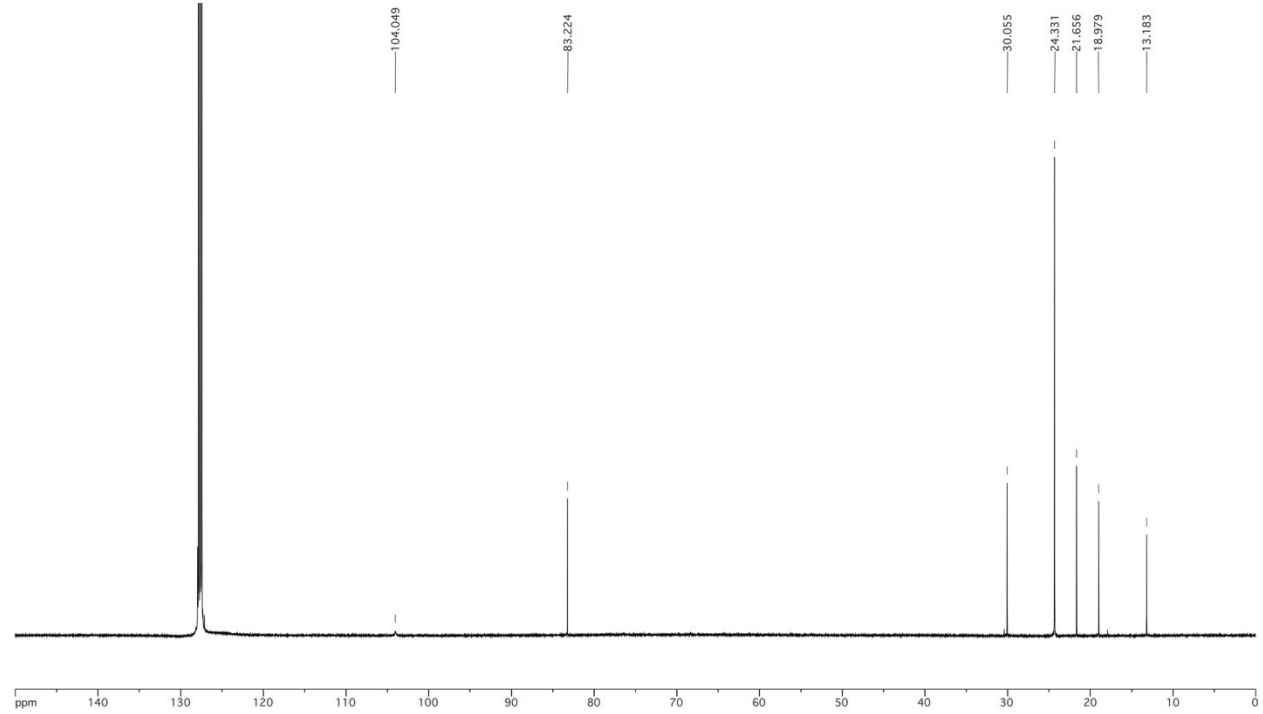


B₁₃

¹H

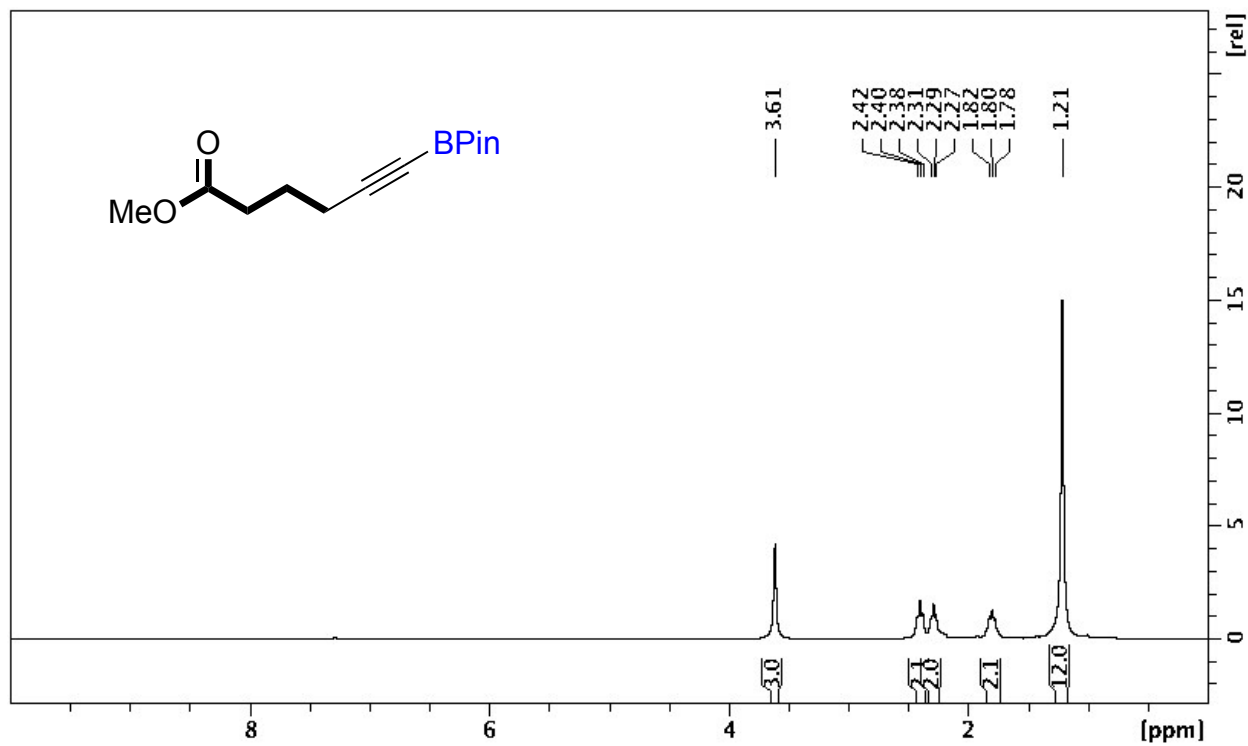


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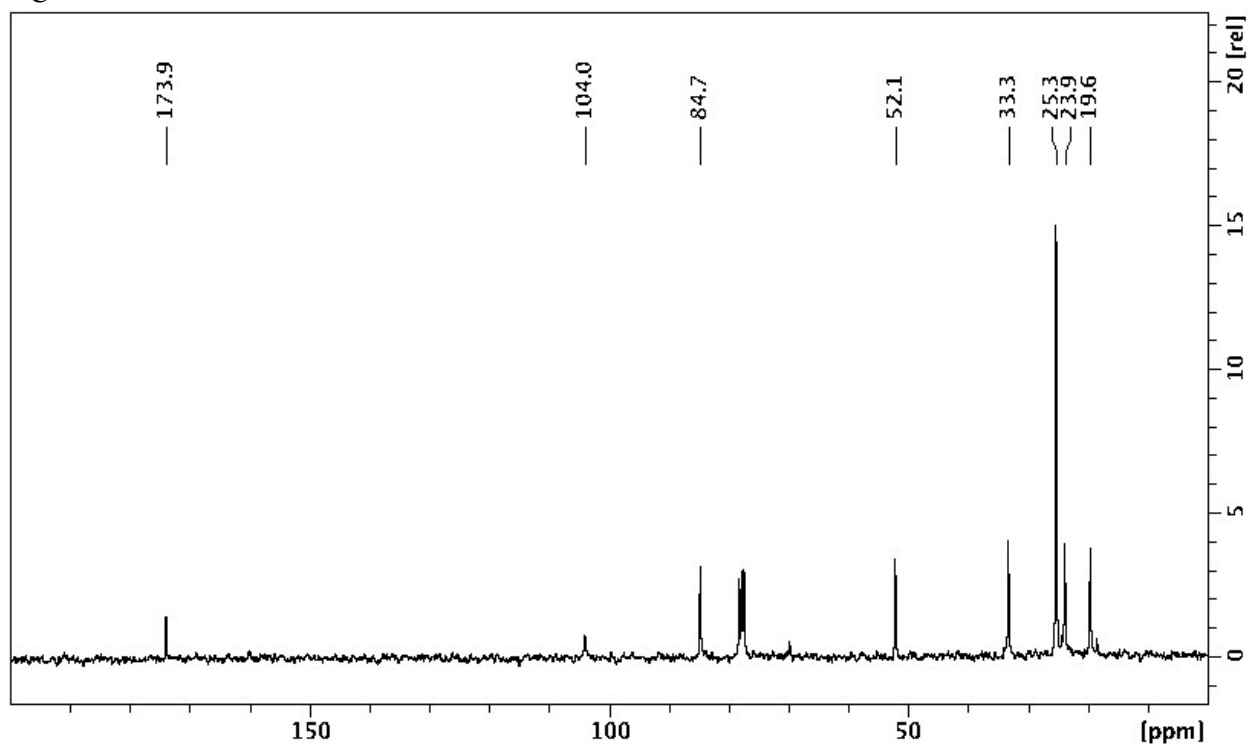


B₁₄

¹H

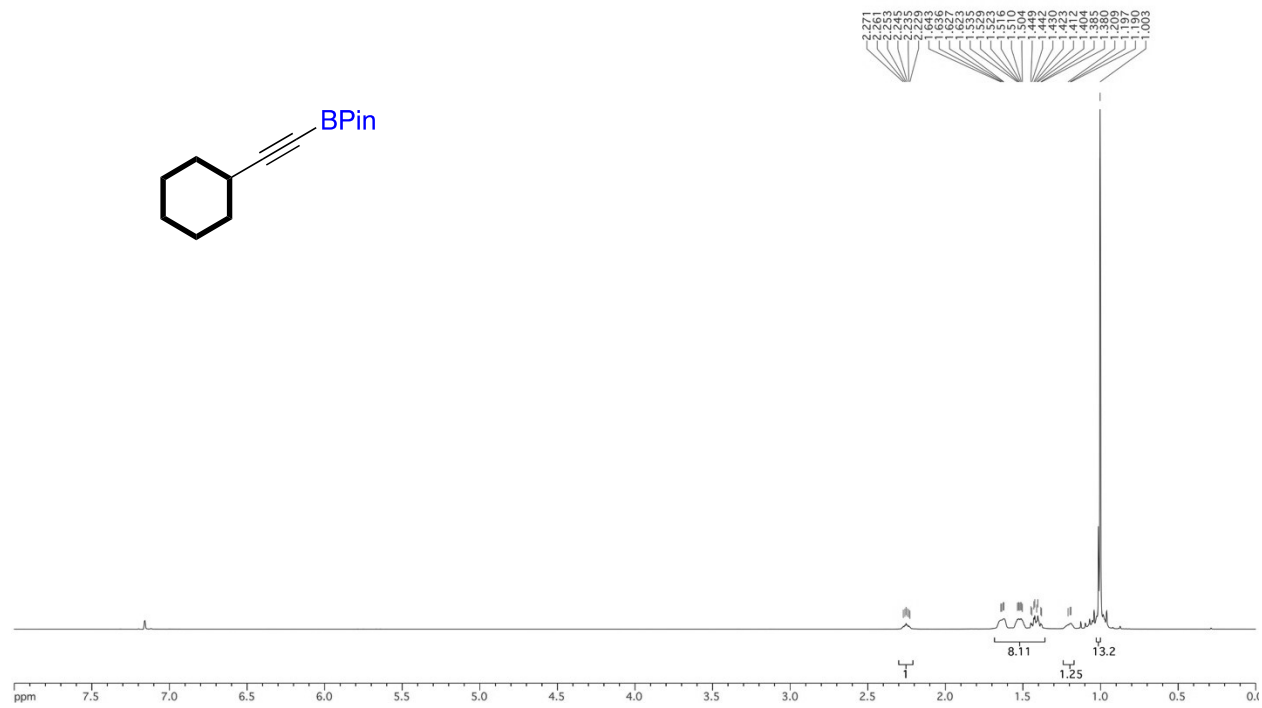
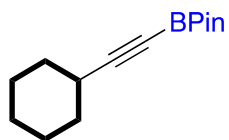


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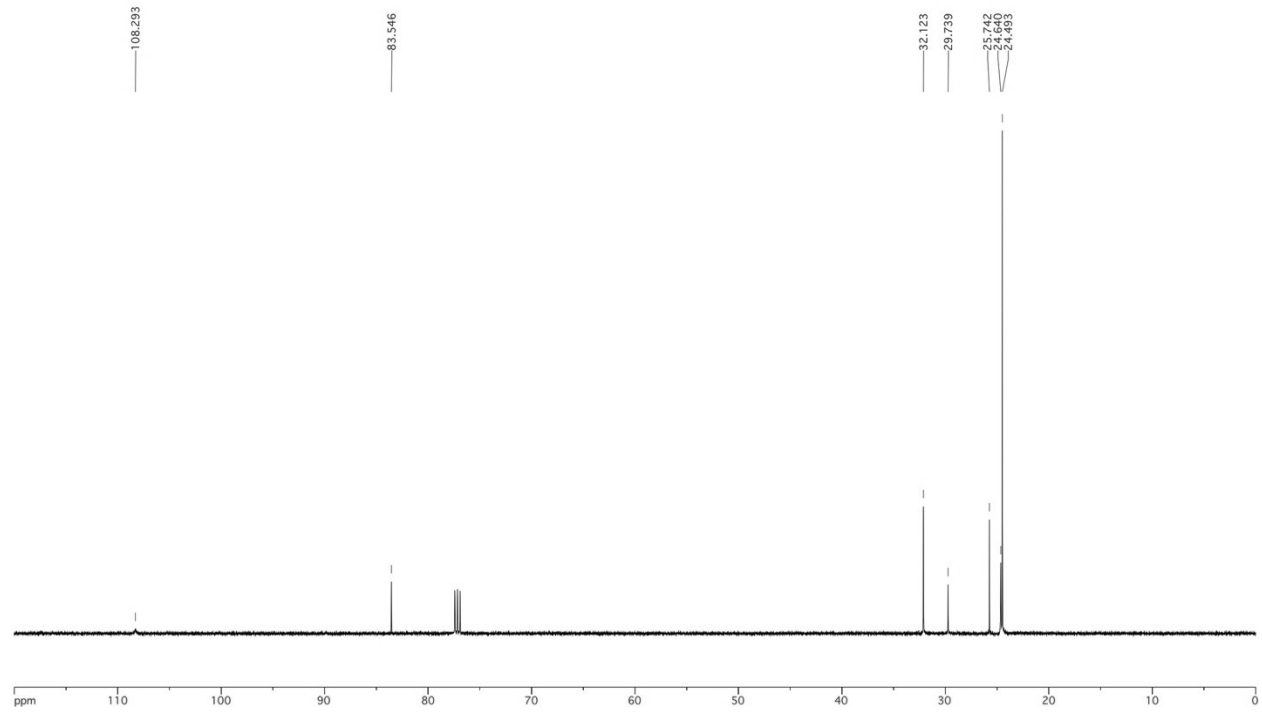


B₁₅

¹H



¹³C



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