Supporting Information for:

Cobalt-catalyzed ammonia borane dehydrocoupling and transfer hydrogenation under aerobic conditions

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Experimental Considerations

General Considerations

All manipulations were performed under an inert atmosphere of N_2 using Schlenk line or glovebox techniques using oxygen-free, anhydrous solvents unless otherwise specified. NMR spectra were recorded using a Bruker AXR 500 MHz spectrometer, using an external reference of 10 % BF_3•Et_2O in $CDCl_3$ for ^{11}B NMR experiments and residual solvent resonances for ^{1}H and $^{13}C\{^{1}H\}$ experiments (δ 3.58 and δ 67.31, respectively). GC spectra were collected using a Varian Saturn 2100T gas chromatograph. Ammonia borane was purchased from Sigma Aldrich and opened August 2014, after which it was stored at –35 °C under an inert atmosphere of N_2. THF-d_8 was purchased from Cambridge Isotopes and was stored over Na at –35 °C in the dark under an inert atmosphere of N_2. All other reagents were obtained from commercial suppliers and dried by conventional means as necessary. Stock solutions of $CpCo(CO)I_2$ (1.0 mM, 2.0 mM, 4.0 mM), $Cp^*Co(CO)I_2$ (1.0 mM, 2.0 mM, 4.0 mM), and NH_3BH_3 (1.0 M, 2.0 M, 4.0 M) were prepared in a glovebox using anhydrous THF, volumetric glassware, and were stored at –30 °C in the dark prior to use. $CpCo(CO)I_2$,[1] $Cp^*Co(CO)I_2$,[1] and $[Cp^*Co(CO)I][PF_6]$[2] were prepared according to literature procedures. Borazine,[3] borazane,[3] cyclodiborazane,[3] *B*-(cyclodiborazanyl)aminoborohydride,[4] polyborazylene,[3] and polyaminoborane[5] were identified by their reported ^{11}B NMR chemical shifts as compared to the unreacted ammonia borane as an internal reference.

Safety note: Handling amine boranes represents a series of potential hazards. A resource to help identify potential safety issues is http://h2bestpractices.org/docs/nbh_h2_storage_survey.pdf

(1) Typical procedure for dehydrocoupling reactions

Stock solutions of $Cp^*Co(CO)I_2$ (0.20 mL, 2.0 mM) in THF and NH_3BH_3 (0.20 mL, 2.0 M) in THF were added to a PTFE-sealed NMR tube (quartz or borosilicate) in an N_2-filled glovebox, whereupon immediate gas evolution and a color change from dark red to light green occurred. After two freeze-pump-thaw cycles, an initial $^{11}B\{^{1}H\}$ NMR spectrum was collected. The solution was then heated to 65 °C, and $^{11}B\{^{1}H\}$ NMR spectra were collected at 2 h, 4 h, 6 h, 8 h, and 24 h intervals. After each NMR experiment, an additional freeze-pump-thaw cycle was performed to remove H_2.

(2) Typical procedure for aerobic dehydrocoupling reactions

A mixture of solutions of $Cp^*Co(CO)I_2$ (0.40 mL, 2.0 mM) in THF and NH_3BH_3 (0.40 mL, 2.0 M) in THF were measured in an N_2 filled glovebox, then transferred in air and thoroughly mixed before being added to a Schlenk flask fitted with a condenser, septum, and venting needle. An initial aliquot of the reaction mixture was analyzed by $^{11}B\{^{1}H\}$ NMR, and the reaction mixture was heated to 65 °C. Additional $^{11}B\{^{1}H\}$ NMR spectra were collected using a quartz NMR tube at 1 h, 1.5 h, 2 h, and 3 h intervals.

(3) Typical procedure for transfer hydrogenation reactions

A stock solution of Cp*Co(CO)I_2 (0.20 mL, 2.0 mM) in THF was added to the unsaturated organic (0.0690 mmol) followed by addition of a stock solution of NH_3BH_3 (0.20 mL, 2.0 M). This solution was quickly transferred to a PTFE-sealed NMR tube (quartz or borosilicate) in an N_2-filled glovebox, whereupon immediate gas evolution and a color change from dark red to light green occurred. Initial $^{11}B\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were collected, then the solution was heated to 65 °C. Additional NMR spectra were collected after 3 h, 6 h, and 24 h intervals.

(4) Typical procedure for aerobic transfer hydrogenation reactions

A stock solution of Cp*Co(CO)I_2 (0.40 mL, 2.0 mM) in THF was added to the unsaturated organic (0.138 mmol) which was then added to a stock solution of NH_3BH_3 (0.40 mL, 2.0 M) in air before being thoroughly mixed and transferred to a Schlenk flask fitted with a condenser, septum, and venting needle. Initial $^{11}B\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were collected, then the solution was heated to 65 °C. Additional NMR spectra were collected using a quartz NMR tube after 3 h, 6 h, and 24 h intervals.

Determination of H_2 volume produced

A mixture of solutions of Cp*Co(CO)I_2 (0.40 mL, 2.0 mM) in THF and NH_3BH_3 (0.40 mL, 2.0 M) in THF were measured in an N_2 filled glovebox, then transferred in air and thoroughly mixed before being added to a Schlenk flask fitted with a condenser that was connected to a gas burette (Figure S.1). The reaction was then heated to 65 °C and allowed to run for 4 h, whereupon there was no further visible gas evolution. The actual pressure of H_2 gas evolved was determined as follows:

$$P_{H_2} = P_{atm} - P_{THF} - P_{column} - P_{H_2O}$$

Where P_{H_2} is the actual pressure of H_2 gas, P_{atm} is the atmospheric pressure, P_{THF} is the vapor pressure of THF at the measured ambient temperature (20–22 °C), P_{column} is the pressure caused by the weight of water in the gas burette, and P_{H_2O} is the vapor pressure of H_2O measured at ambient temperature. The moles of H_2 produced were calculated using the ideal gas law. Turnover number (TON) was determined by the following equation.[6]

$$TON = n_{H2}/n_{cat}$$

Turnover frequency (TOF) is defined as the TON for the first hour of the reaction.

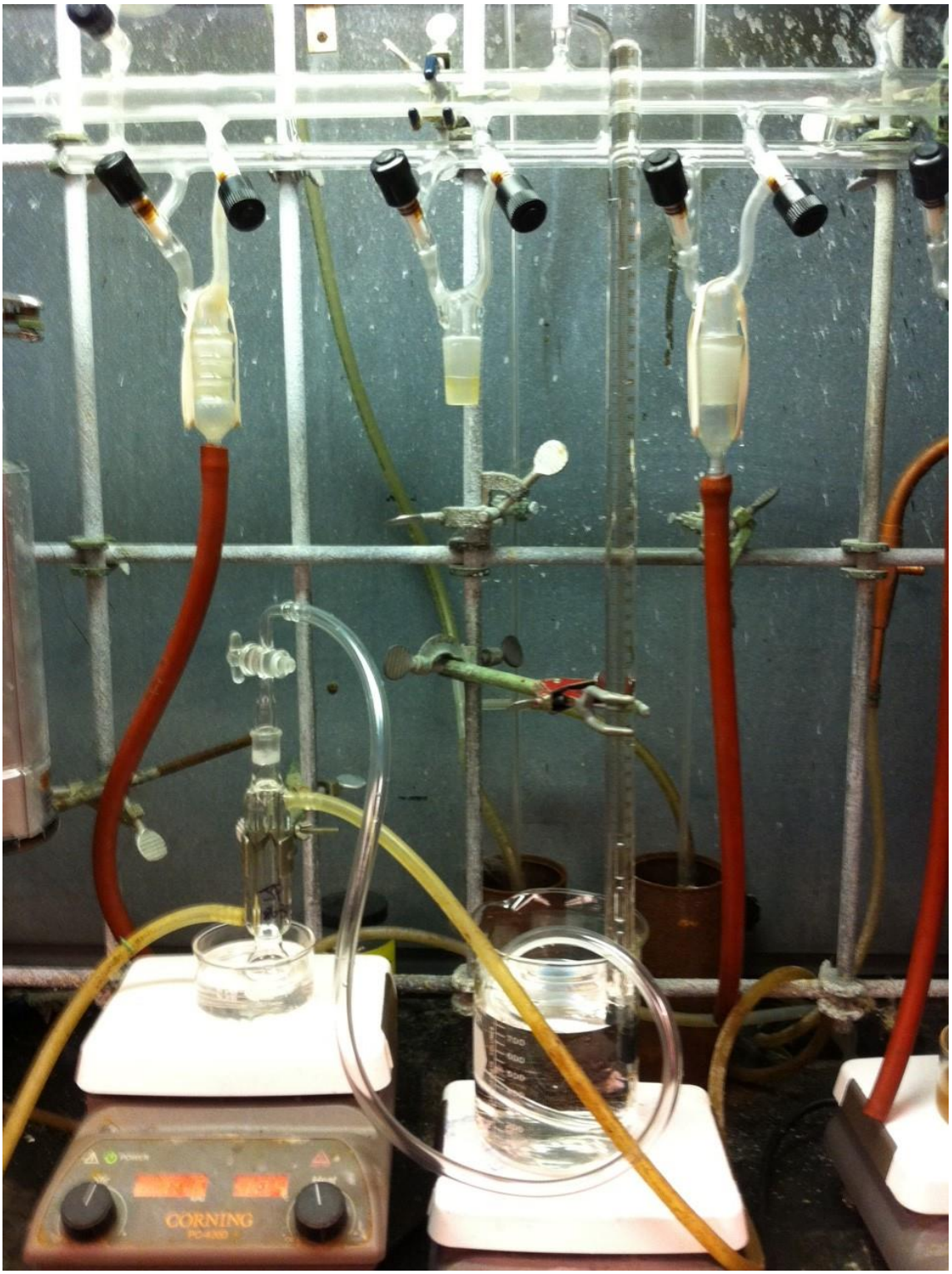


Figure S-1: Experimental setup for determination of moles of H_2 gas produced

Table S-1: Concentration controlled amine borane dehydrocoupling by **1**

Catalyst Concentration (mM)	1.0	1.0	1.0	2.0	2.0	2.0	4.0	4.0	4.0
NH_3BH_3 Concentration (M)	1.0	2.0	4.0	1.0	2.0	4.0	1.0	2.0	4.0
Conversion (%)	98	97	97	99	98	96	99	98	98

Reaction conditions: 0.20 mL **1** in THF, 0.20 mL NH_3BH_3 in THF, 65 °C, 2 freeze-pump-thaw cycles performed before heating and every 2 h thereafter, 24 h

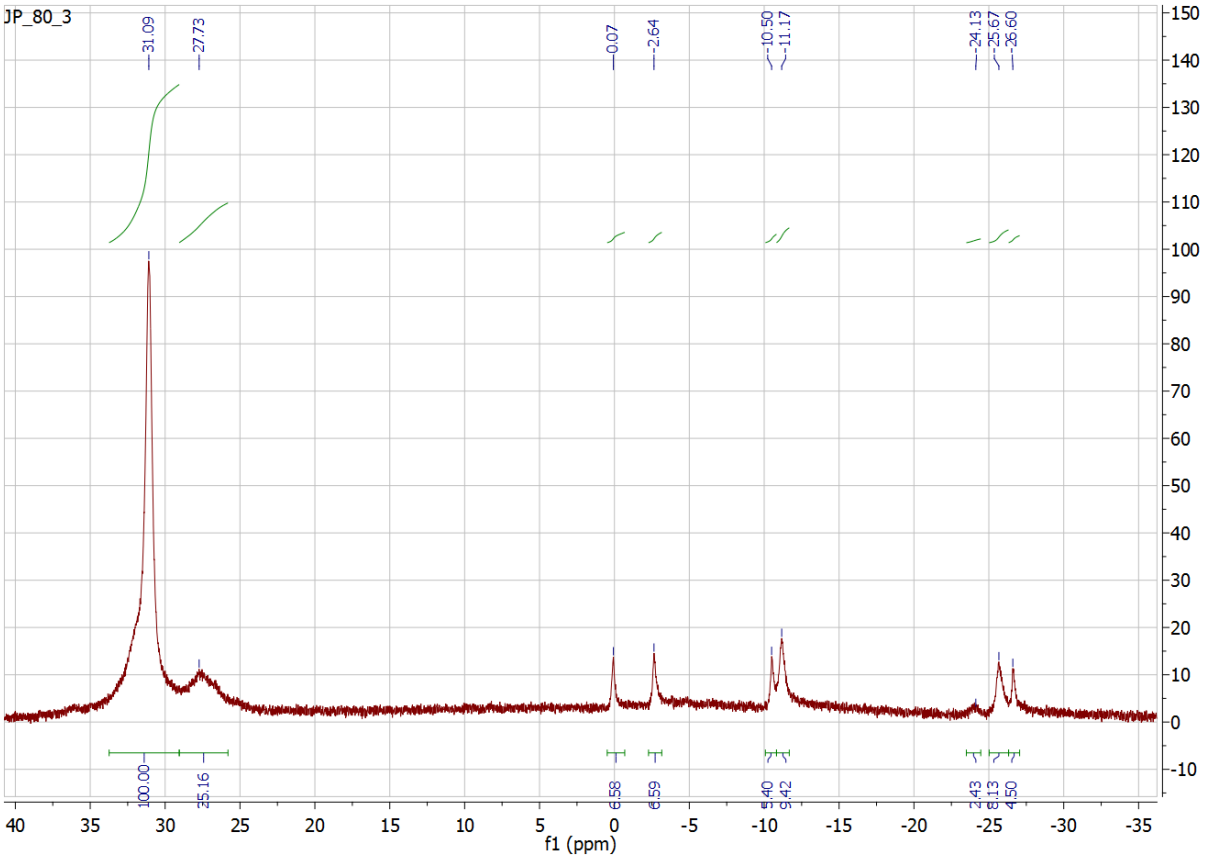
Table S-2: Concentration controlled amine borane dehydrocoupling by **2**

Catalyst Concentration (mM)	1.0	1.0	1.0	2.0	2.0	2.0	4.0	4.0	4.0
NH_3BH_3 Concentration (M)	1.0	2.0	4.0	1.0	2.0	4.0	1.0	2.0	4.0
Conversion (%)	99	96	98	99	97	97	98	98	98

Reaction conditions: 0.20 mL **2** in THF, 0.20 mL NH_3BH_3 in THF, 65 °C, 2 freeze-pump-thaw cycles performed before heating and every 2 h thereafter, 24 h

$\underline{CpCo(CO)I_2 + AB}$

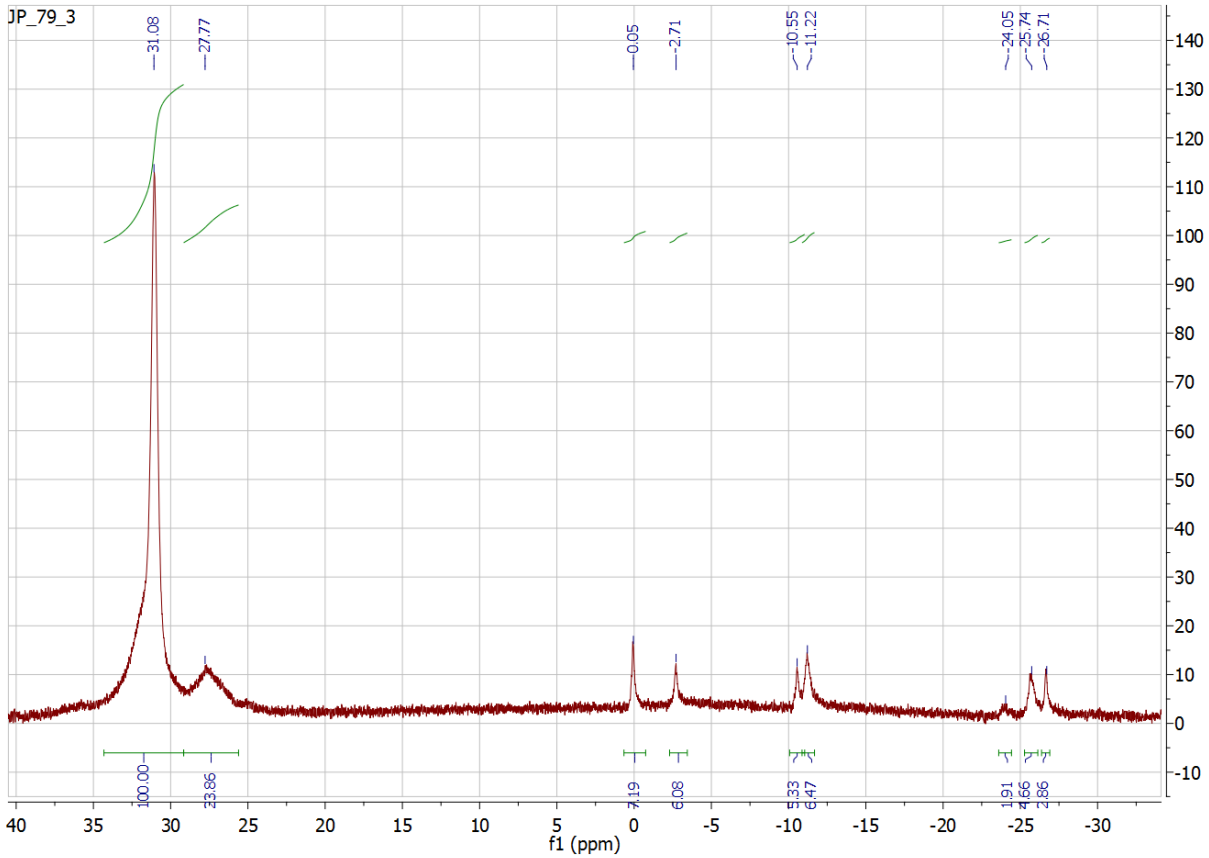
Example $^{11}B\{^1H\}$ NMR spectrum, THF, quartz PTFE-sealed NMR tube



δ (ppm)	31.1	27.7	–10.5	–11.2	0, –2.6, –24.1, –25.7, –26.6
Product	Borazine	Polyborazylene	Borazane	Cyclodiborazane	Unknown
% Conversion	60.0	21.5	5.1	2.2	11.2

Cp*Co(CO)I_2 + AB

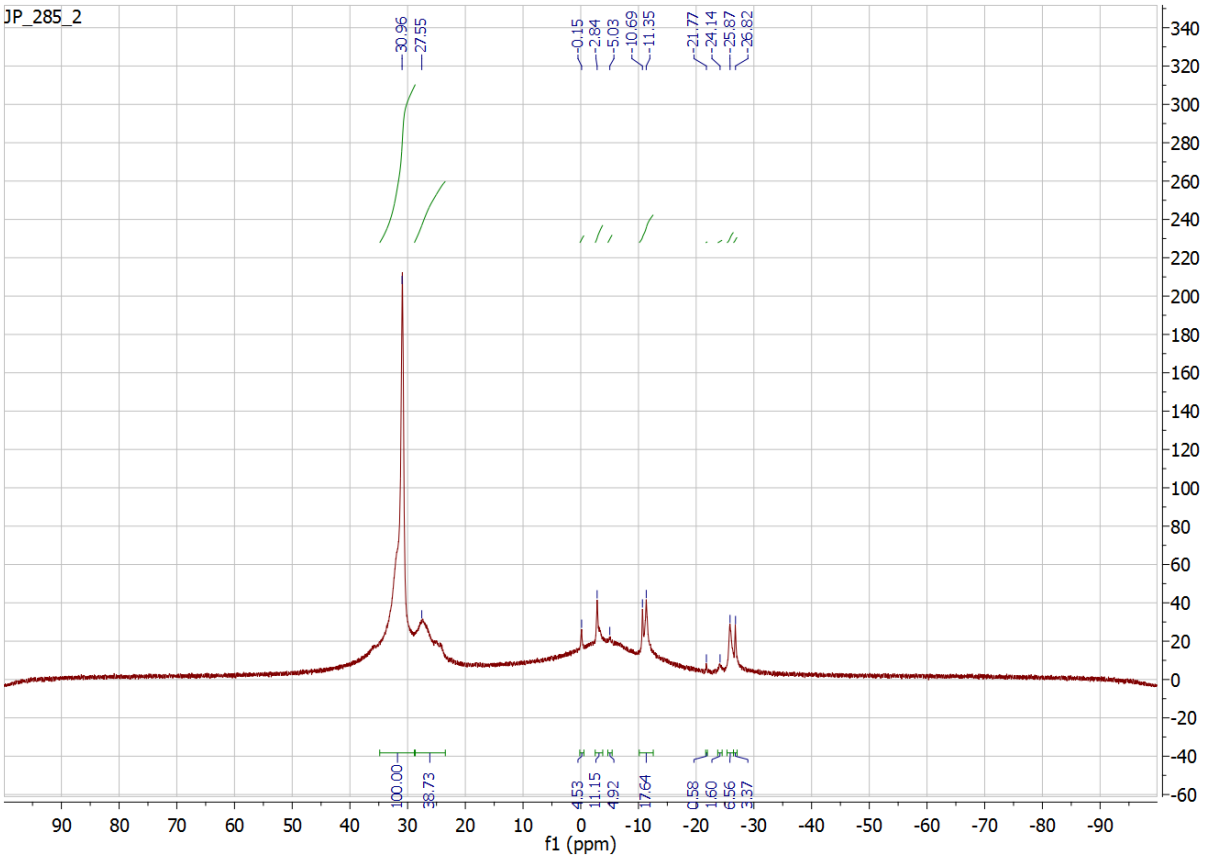
Example $^{11}B\{^1H\}$ NMR spectrum, THF, quartz PTFE-sealed NMR tube



δ (ppm)	31.1	27.8	–10.6	–11.2	0, –2.71, –24.1 –25.7, –26.7
Product	Borazine	Polyborazylene	Borazane	Cyclodiborazane	Unknown
% Conversion	59.4	20.1	3.2	3.8	13.5

Open reflux schlenk Cp*Co(CO)I_2 + AB

Example $^{11}B\{^1H\}$ NMR spectrum, THF, borosilicate NMR tube

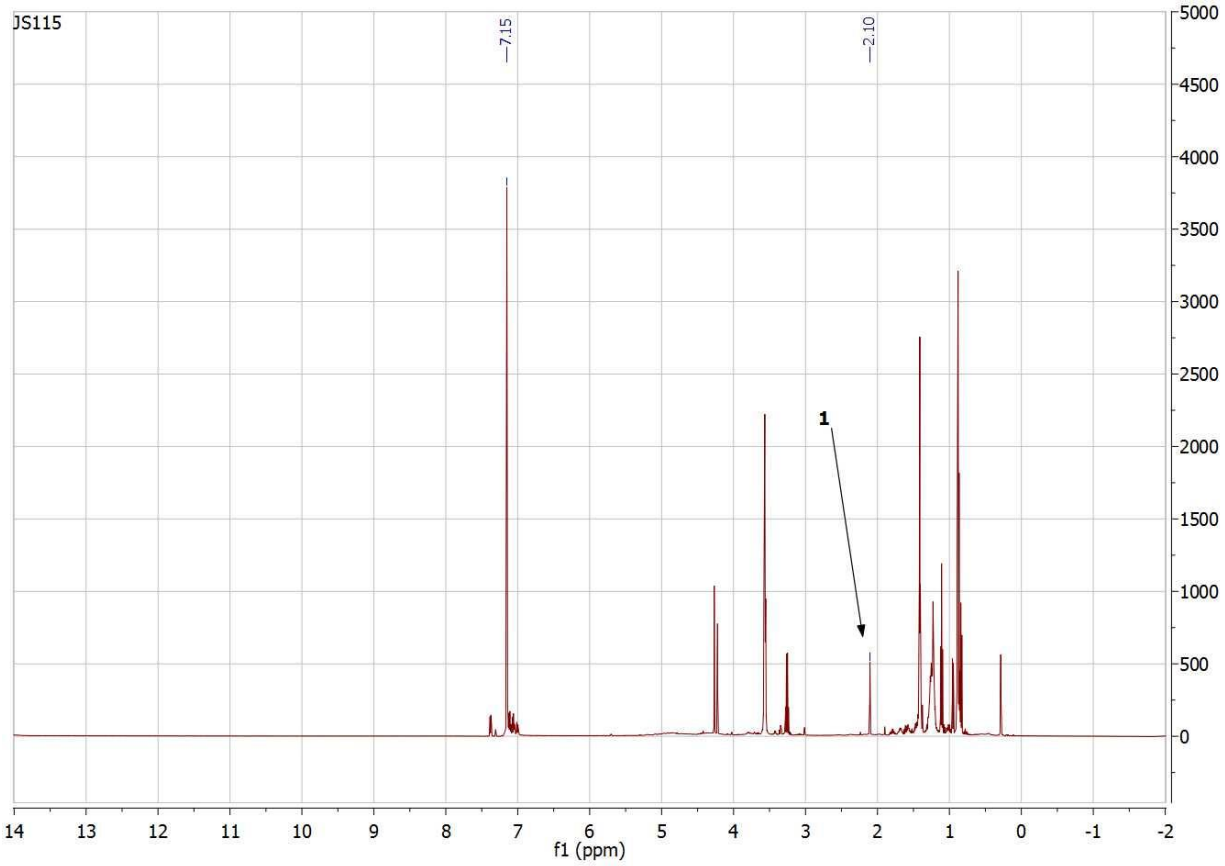


δ (ppm)	31.0	27.6	–10.6	–11.2	–21.8	–0.3, –2.8, –25.9, –26.8
Product	Borazine	Polybor azylene	Borazane	Cyclo-diborazane	NH_3BH_3	Unknown
%	50.1	30.1	~3	~4	<0.1	7.0

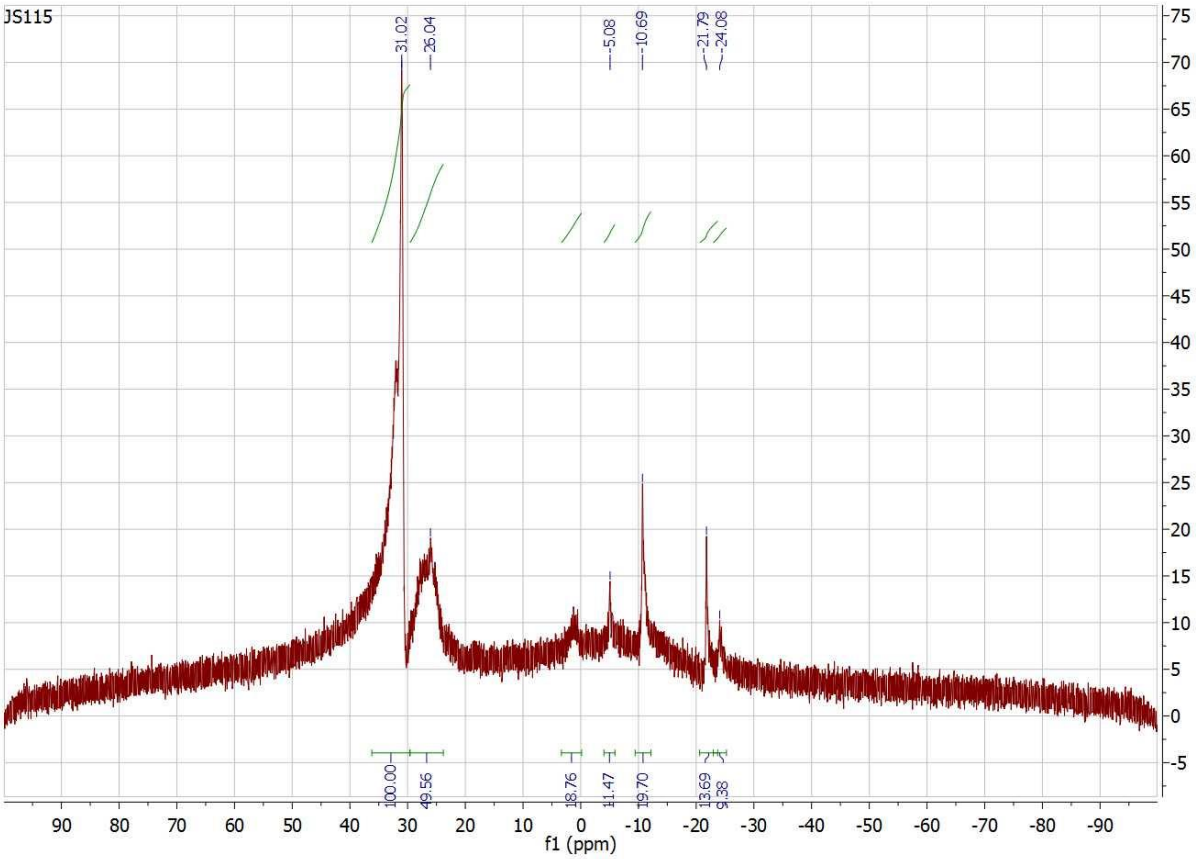
B-(cyclodiborazanyl)aminoborohydride (δ –5.0, –11.4, –24.1) appears to be present but overlapping resonance with cyclodiborazane and low intensity resonances make an assessment of concentration difficult.

H_2 collection NMR spectra

^{1}H NMR spectrum – final, THF-d_8 quartz NMR tube

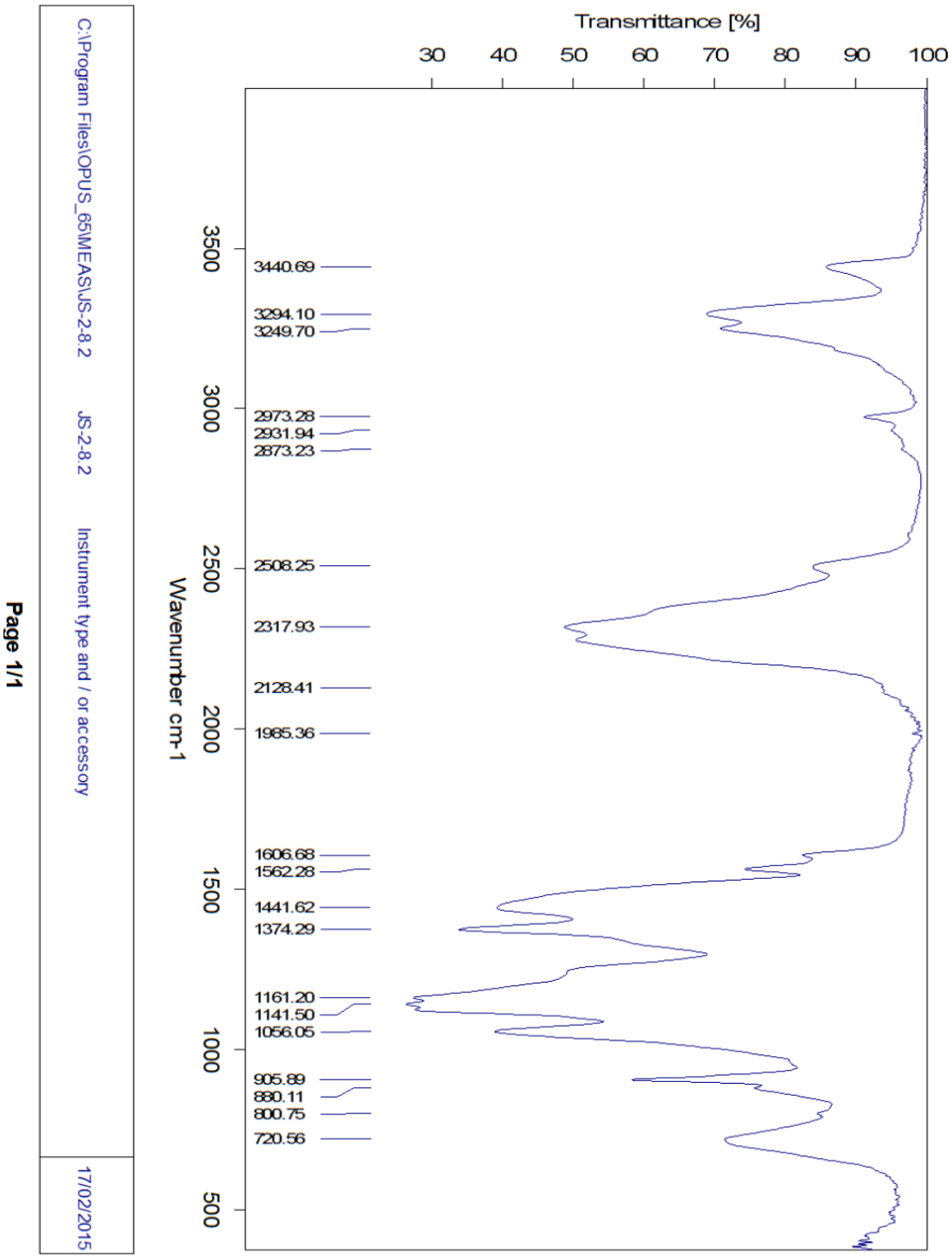


$^{11}B\{^{1}H\}$ NMR spectrum – final, THF-d_8 quartz NMR tube



δ (ppm)	31.0	26.0	–5.1, –10.7, –24.1	–21.8
Product	Borazine	Polyborazylene	*B*-(cyclodiborazanyl)aminoborohydride	NH_3BH_3
% Conversion	45.0	29.5	20.3	5.2

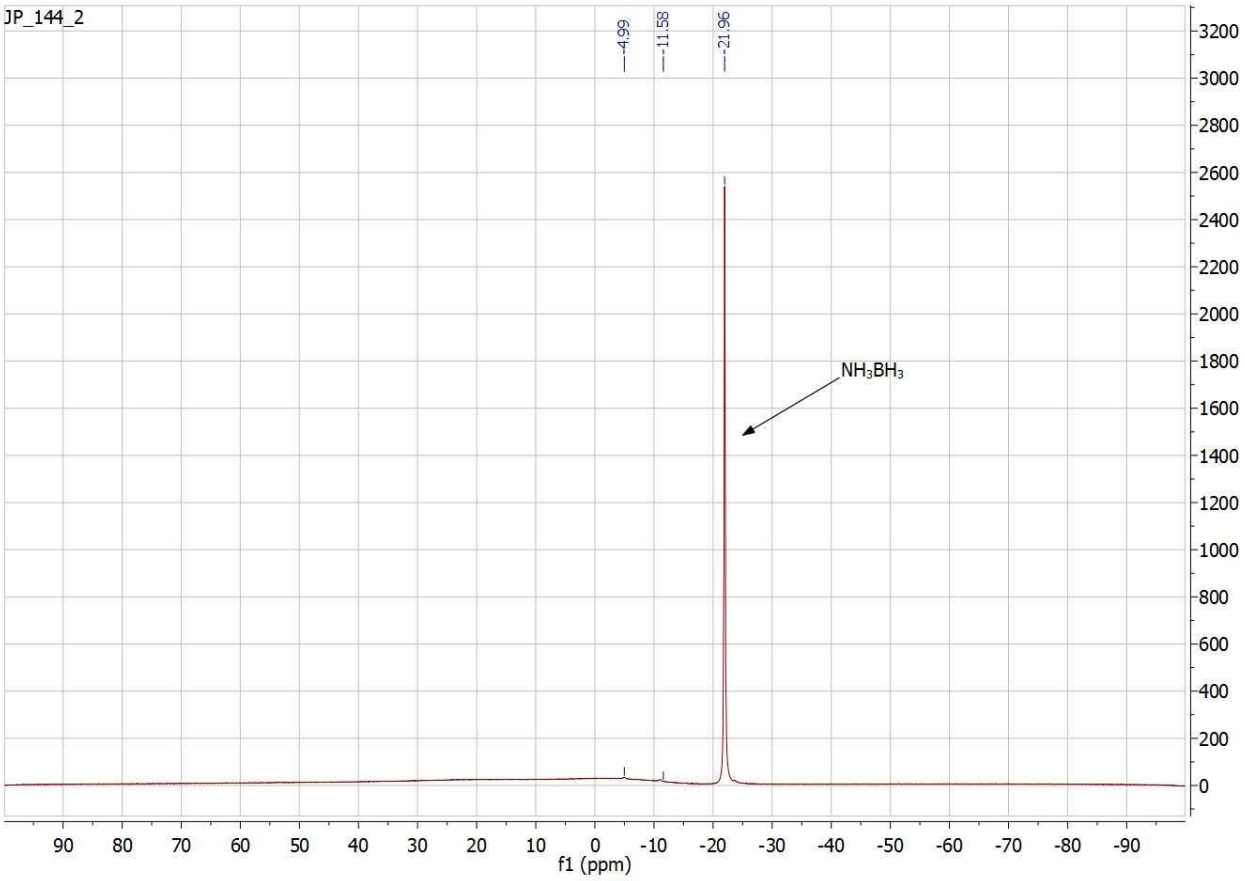
IR spectrum for H_2 collection experiment



Control reaction

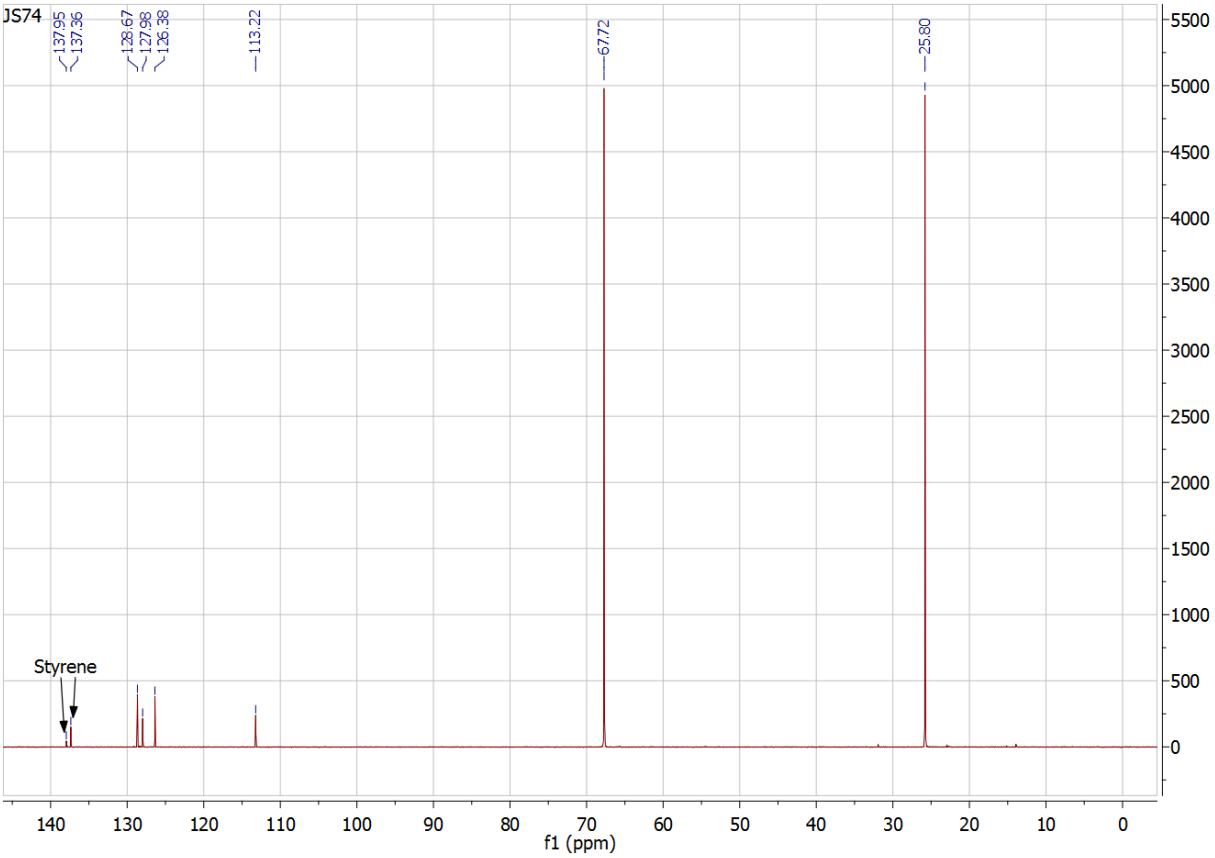
Reaction conditions: 0.40 mL NH_3BH_3 (2.0 M in THF), 65 °C, 7 d

$^{11}B\{^1H\}$ NMR spectrum, quartz tube, THF

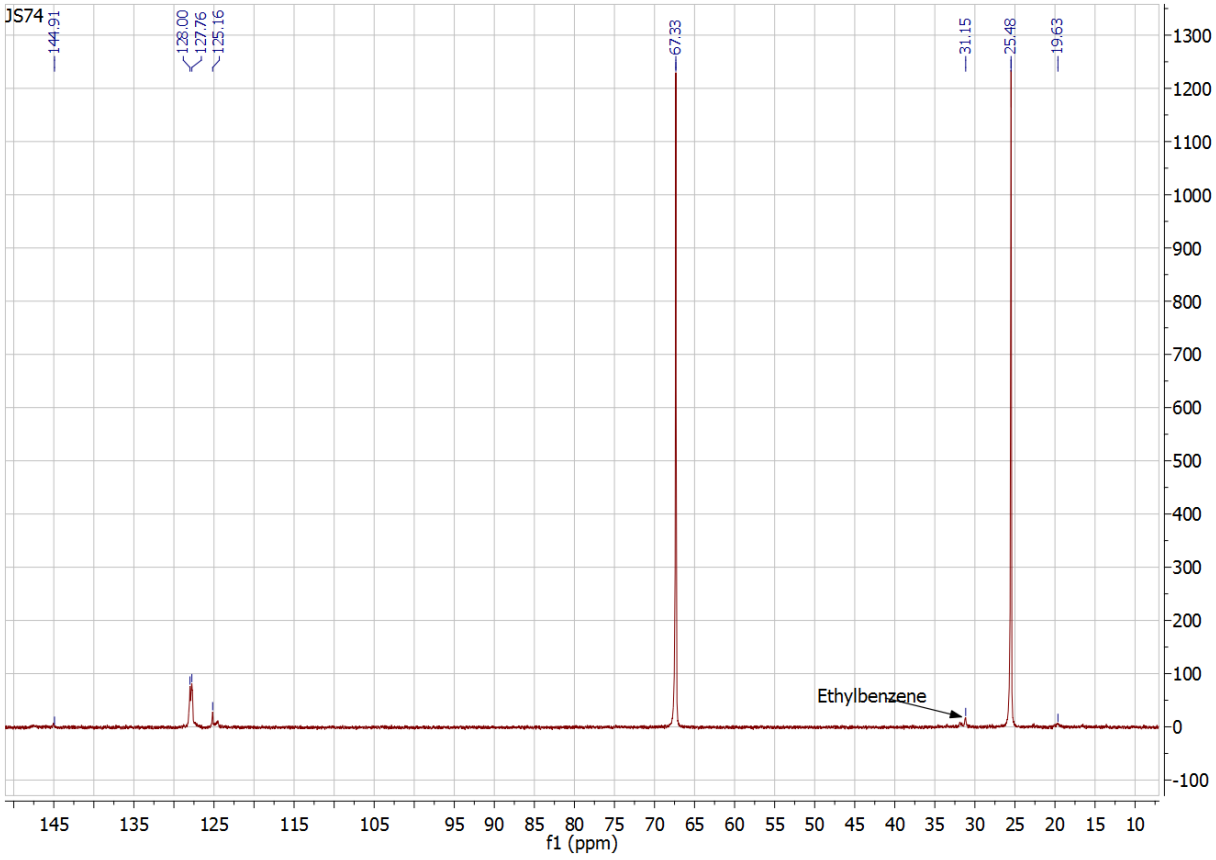


Cp*Co(CO)I_2 + AB + Styrene

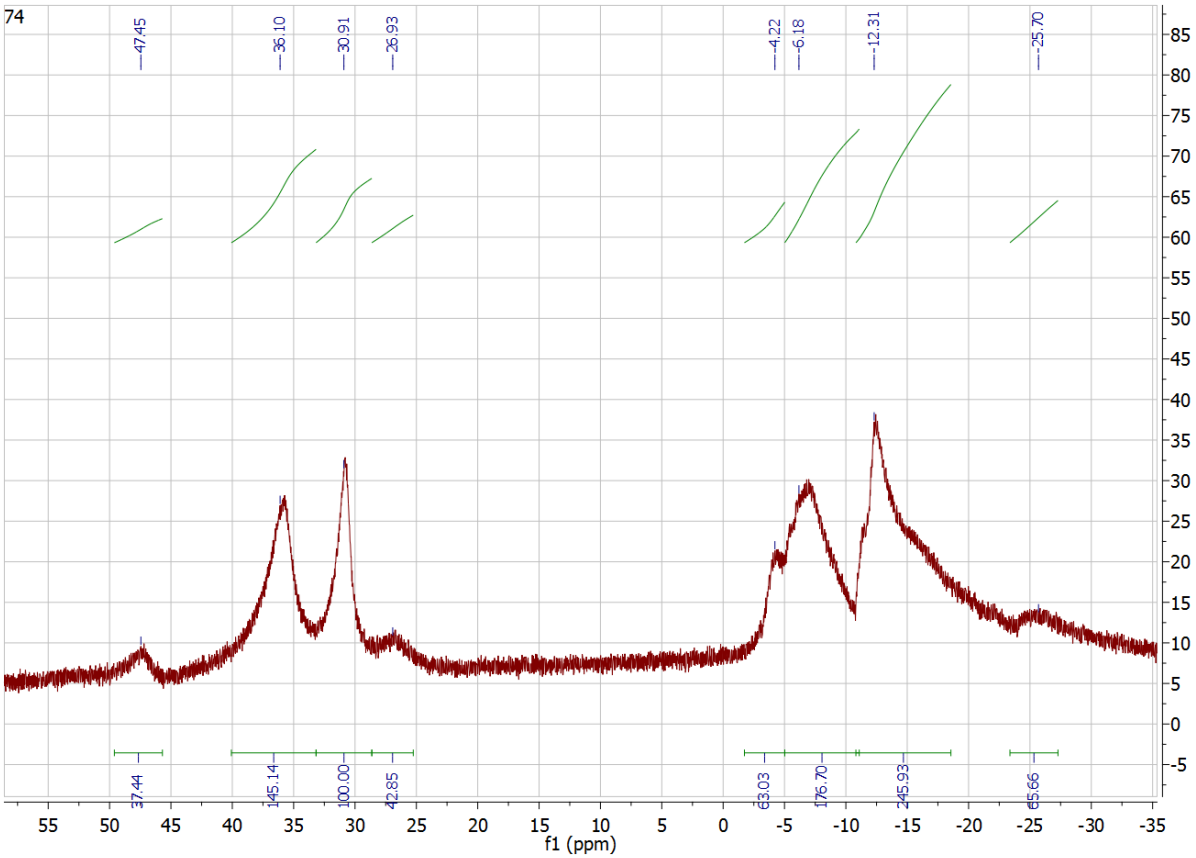
$^{13}C\{^1H\}$ NMR spectra – Initial, THF



$^{13}C\{^{1}H\}$ NMR spectrum –Final, THF

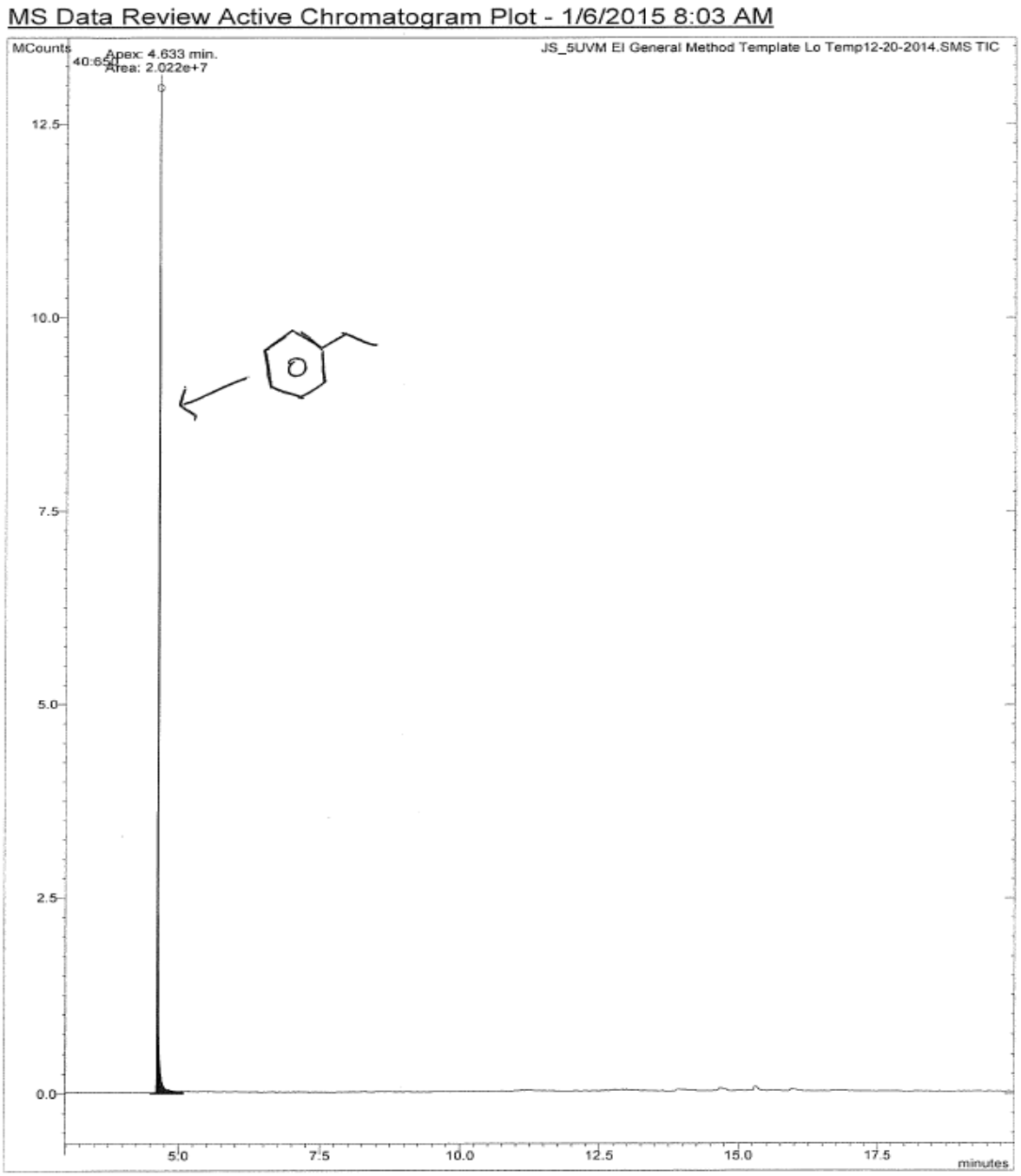


$^{11}B\{^{1}H\}$ NMR spectrum – Final, THF, borosilicate glass NMR tube



δ (ppm)	47.5	36.1, –25.7	30.9	26.9	–4.2, –6.2, –12.3
Product	Hydroborlyated species	Polyaminoborane	Borazine	Polyborazalyne	Unknown products
% Conversion	4.2	24.2	11.4	4.9	55.3

GC Spectrum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10.0
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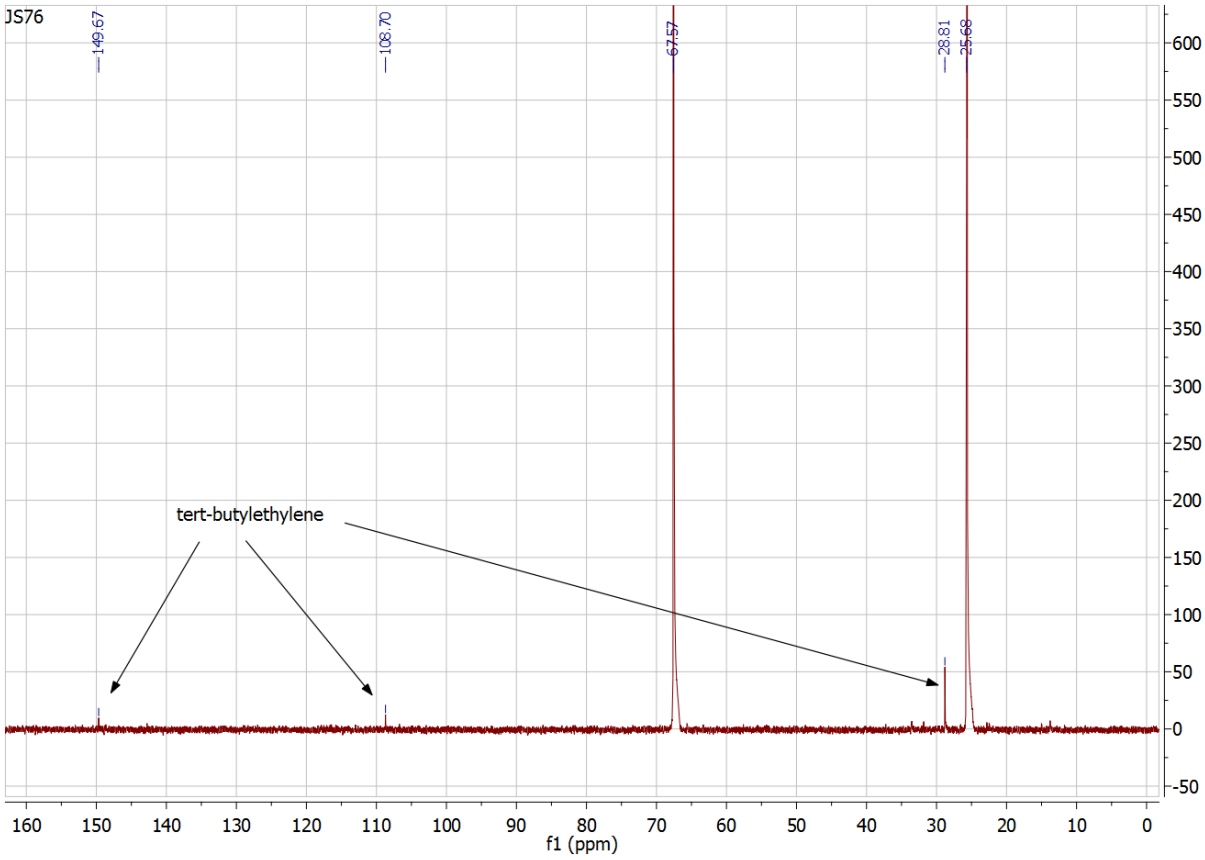
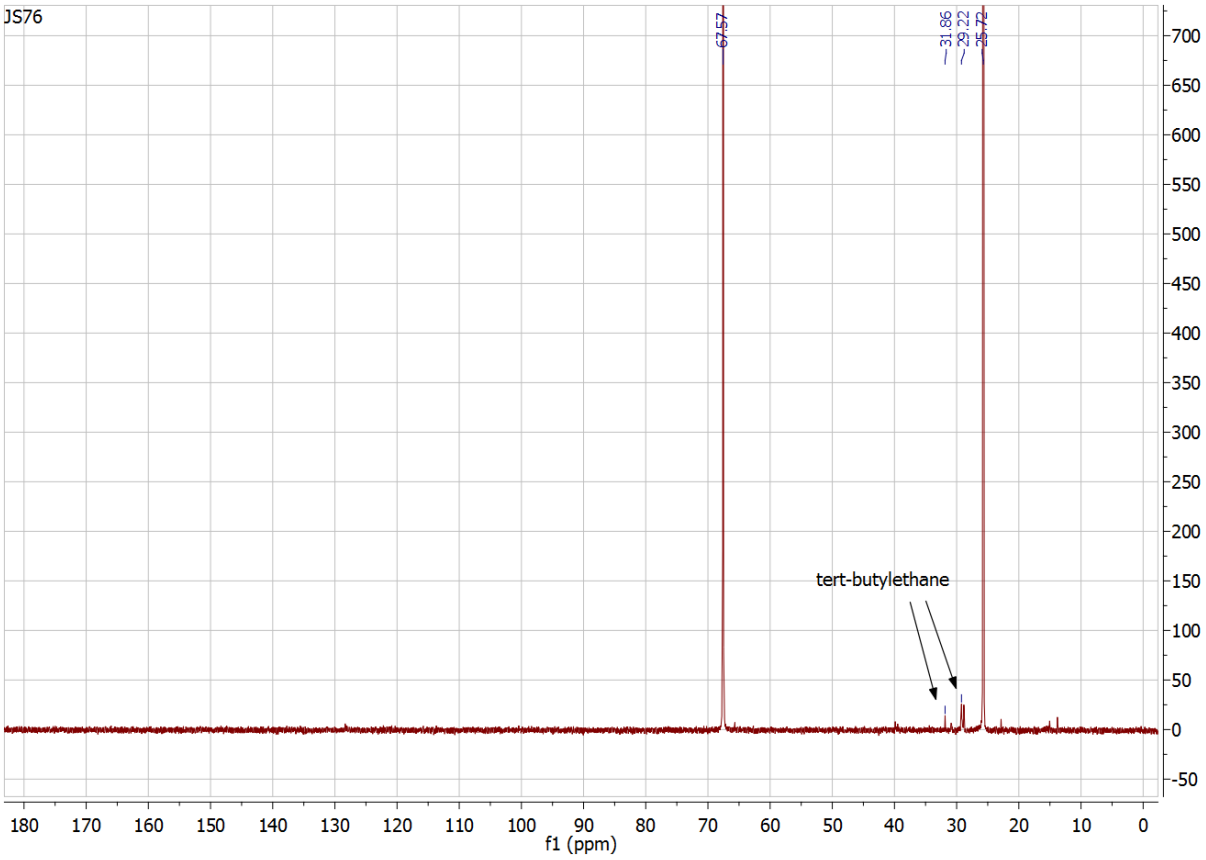
17.5
minutes

Cp*Co(CO)I_2 + AB + *tert*-butylethylene

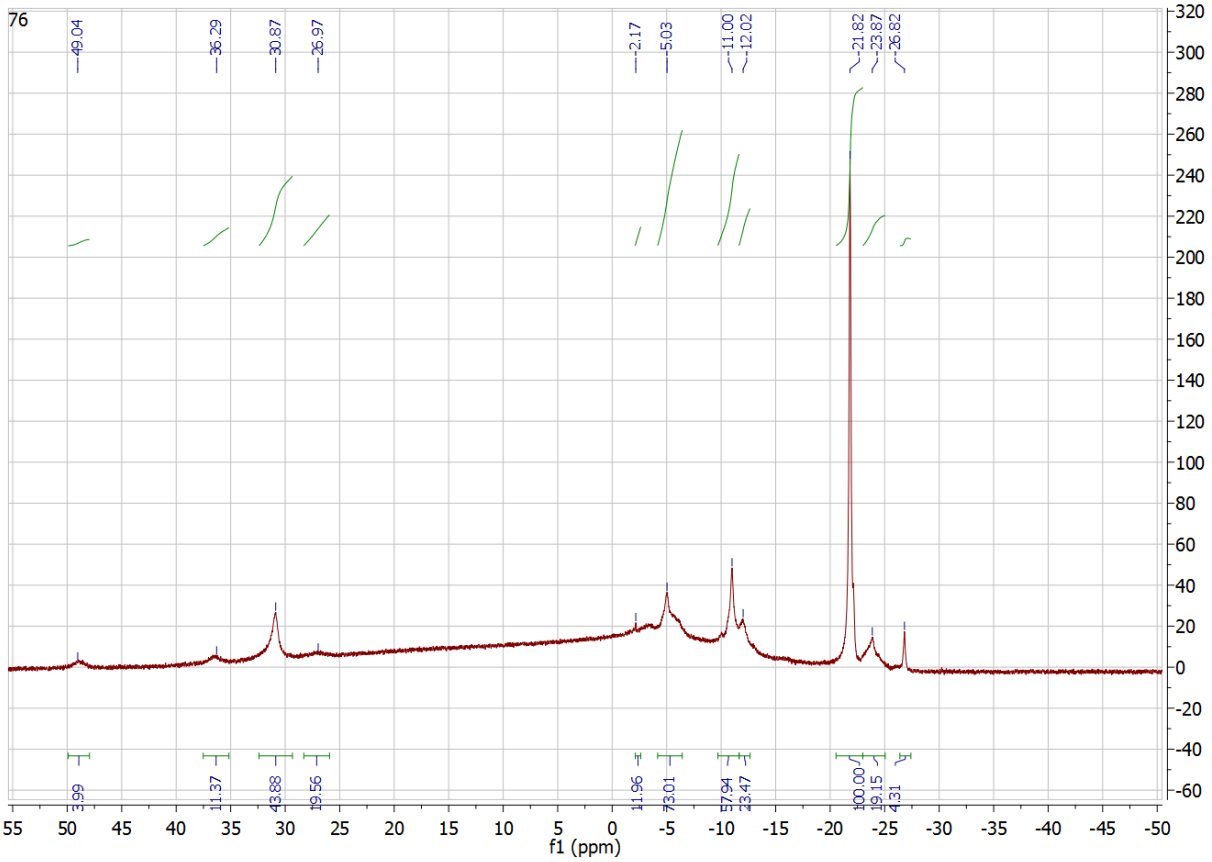
$^{13}C\{^1H\}$ NMR spectrum – initial, THF



$^{13}C\{^{1}H\}$ NMR spectrum – final, THF

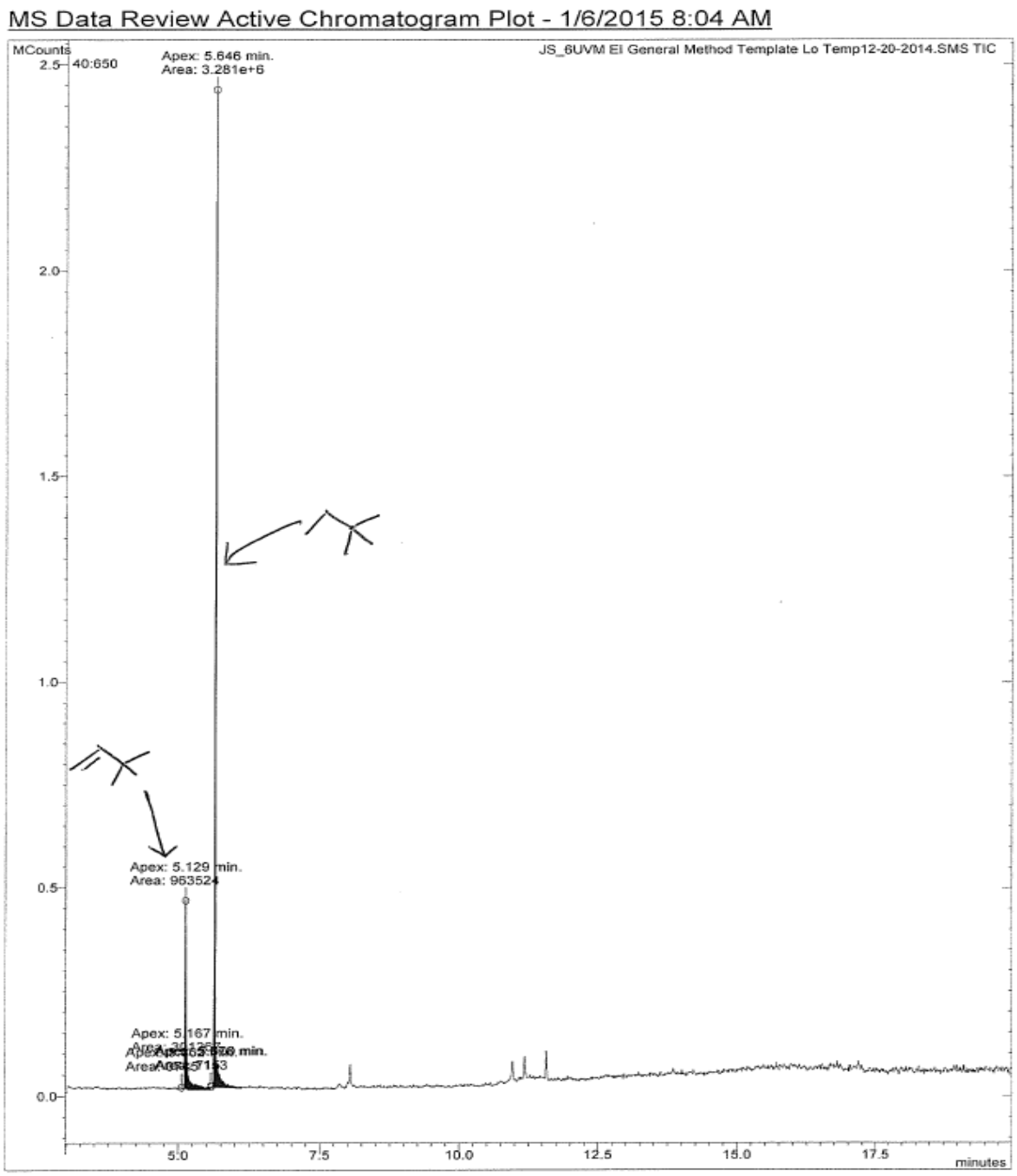


$^{11}B\{^{1}H\}$ NMR spectrum – final, THF, borosilicate glass NMR tube



δ (ppm)	49.0	36.3, –26.8	30.9	27.0	–5.0, –11.0, –23.9	–21.8	–2.2, –12.0
Product	Hydroborylated species	Polyaminoborane	Borazine	Polyborazylene	*B*-(cyclodiborazanyl)aminoborohydride	NH_3BH_3	Unknown
% Conversion	1.1	4.3	11.9	5.3	40.7	27.1	9.6

GC Spectrum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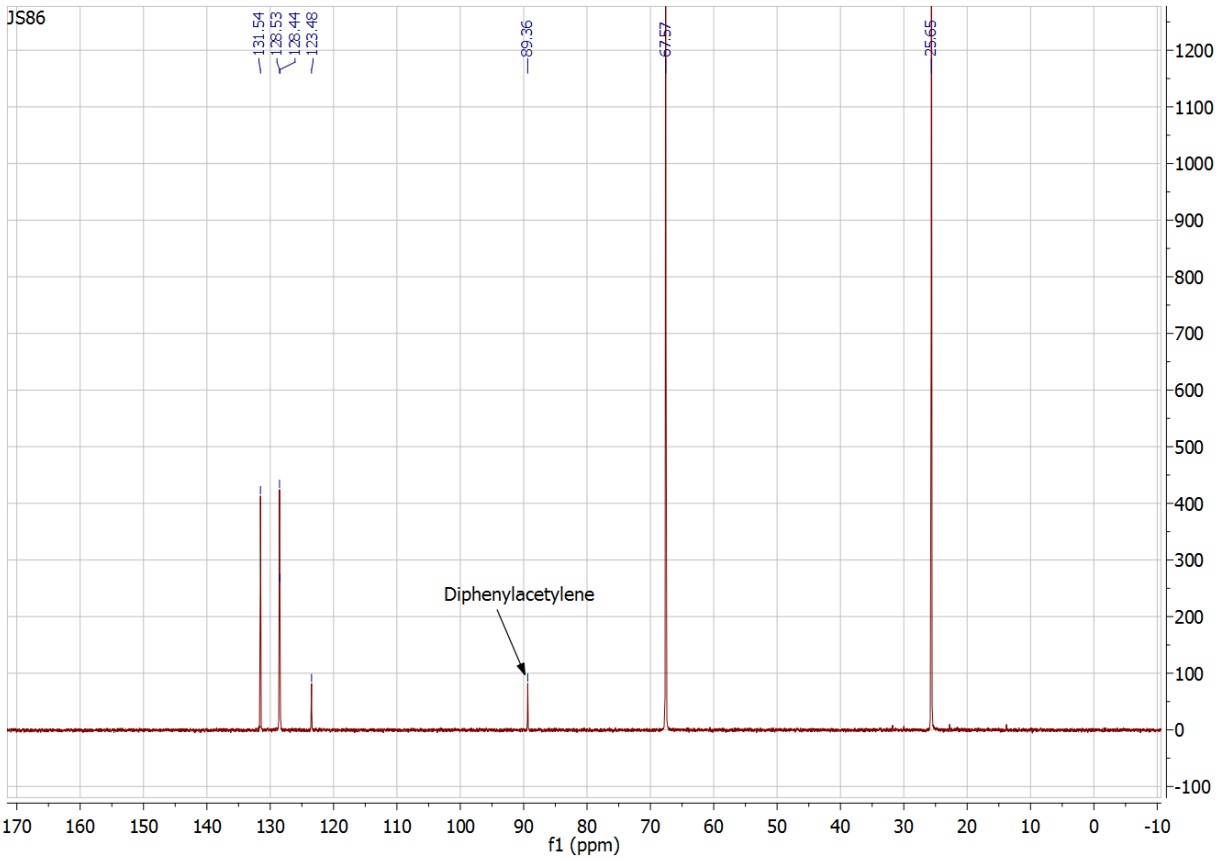
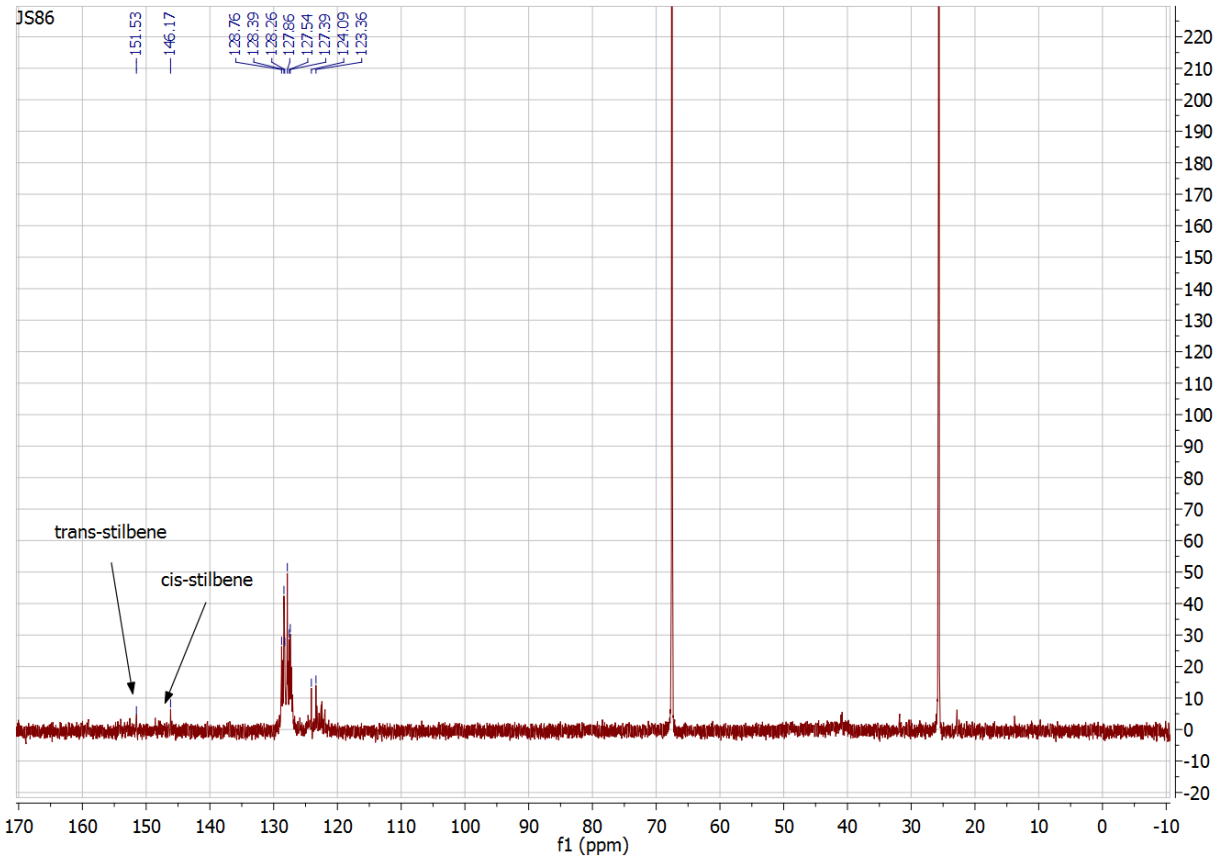
7.5
10.0
12.5
15.0
17.5
minutes

Cp*Co(CO)I_2 + AB + Diphenylacetylene

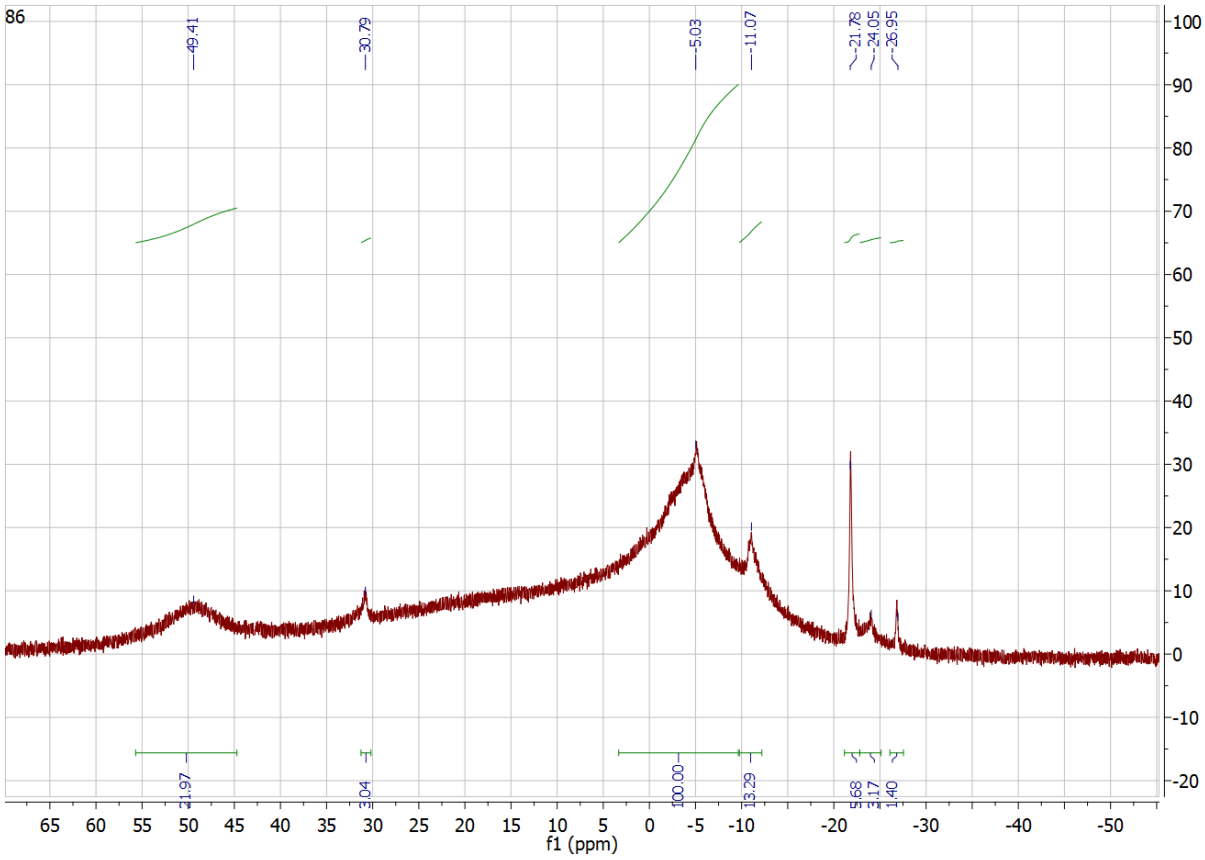
$^{13}C\{^1H\}$ NMR spectrm – initial, THF



$^{13}C\{^{1}H\}$ NMR spectrum – final, THF

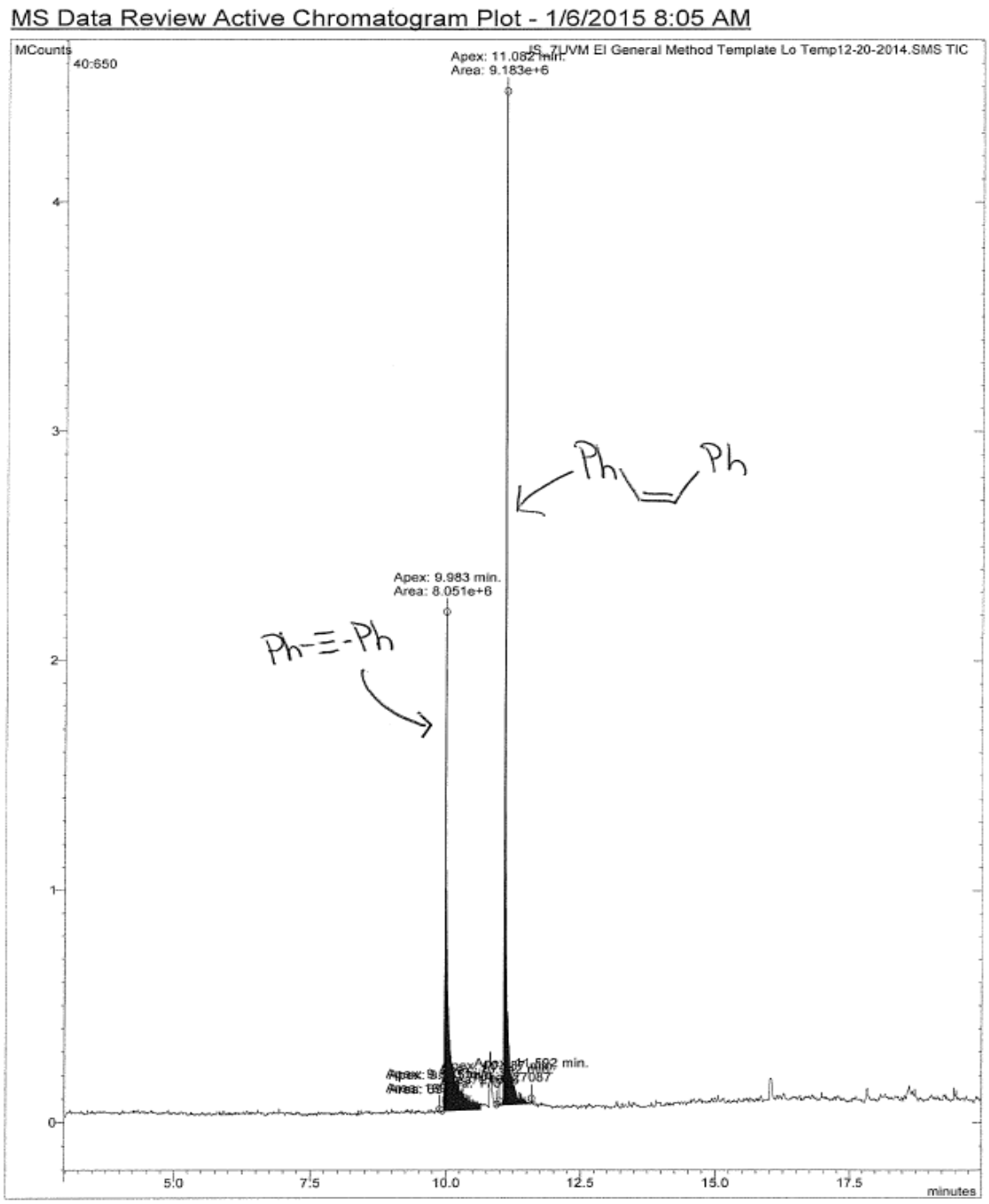


$^{11}B\{^{1}H\}$ NMR spectrum – final, THF, borosilicate NMR tube



δ (ppm)	49.4	30.8	–5.0, –11.1, –24.1	–21.8	–27.0
Product	Hydroborylated species	Polyaminoborane	*B*-(cyclodiborazanyl)aminoborohydride	NH_3BH_3	Unknown
% Conversion	14.6	2.0	78.4	3.8	1.2

GC spectrum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2
1
0
5.0
7.5
10.0
12.5
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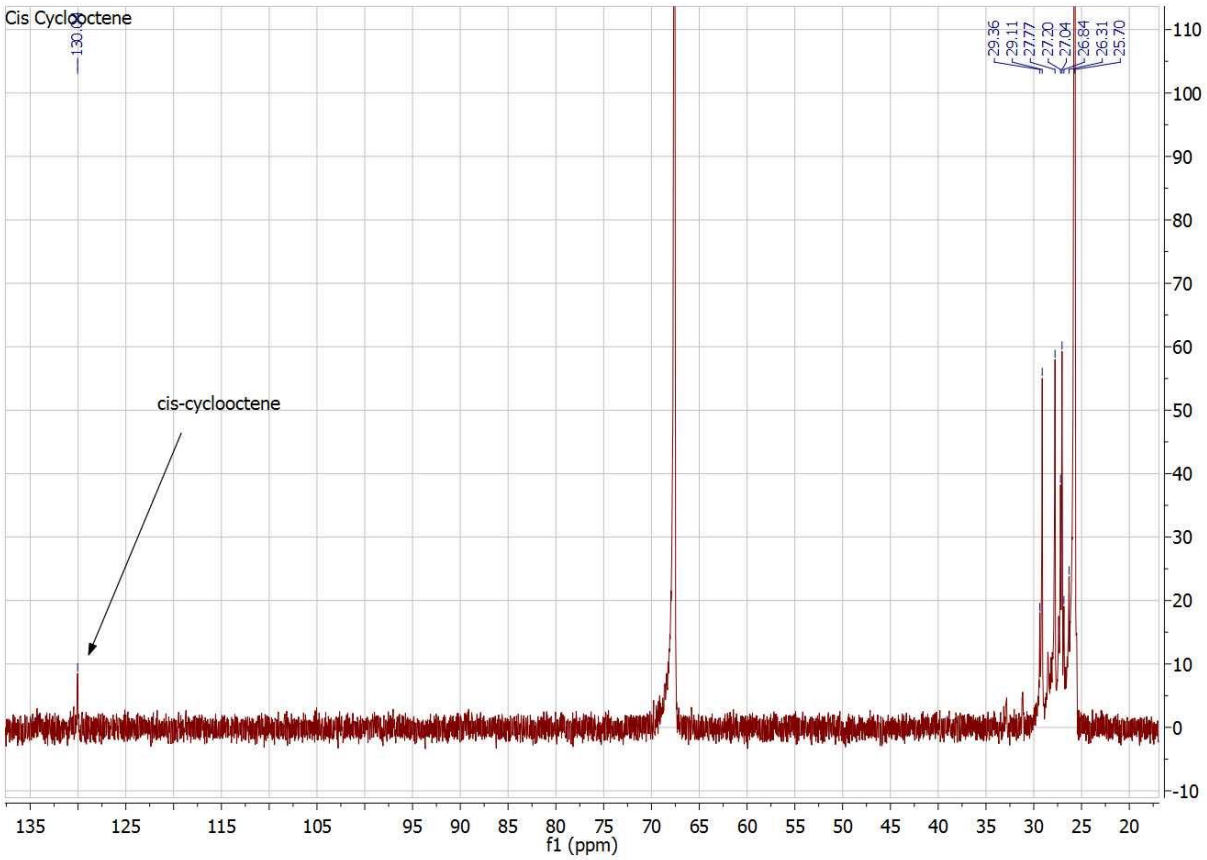
17.5
minutes

Cp*Co(CO)I_2 + AB + cis-cyclooctene

$^{13}C\{^1H\}$ NMR spectrum – initial, THF



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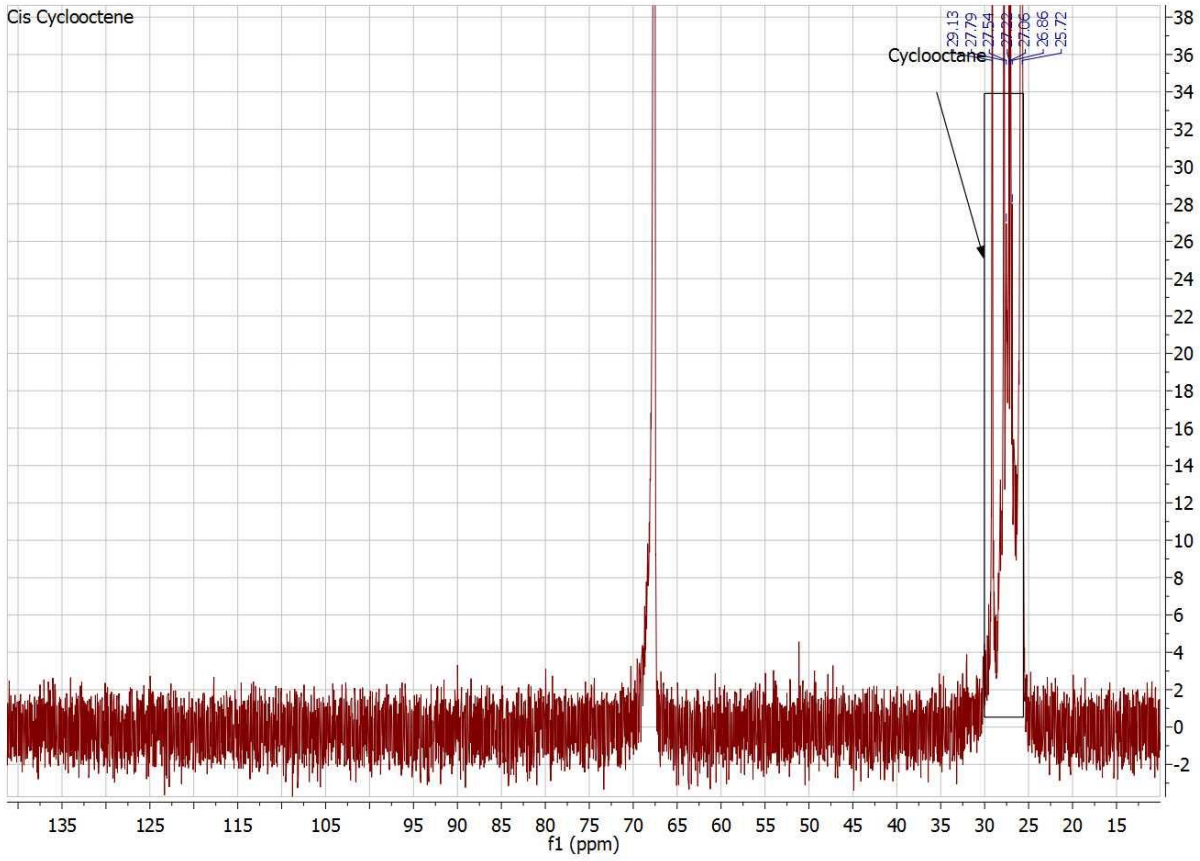
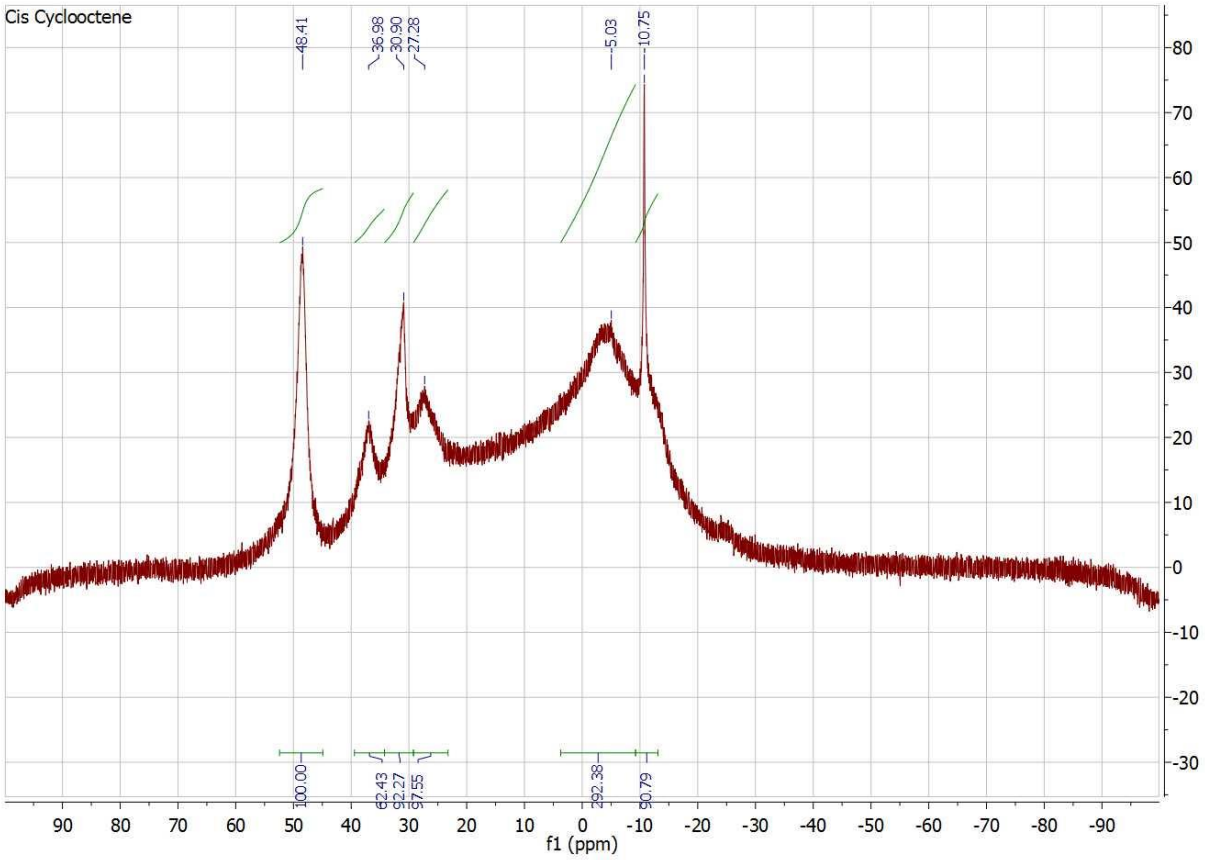
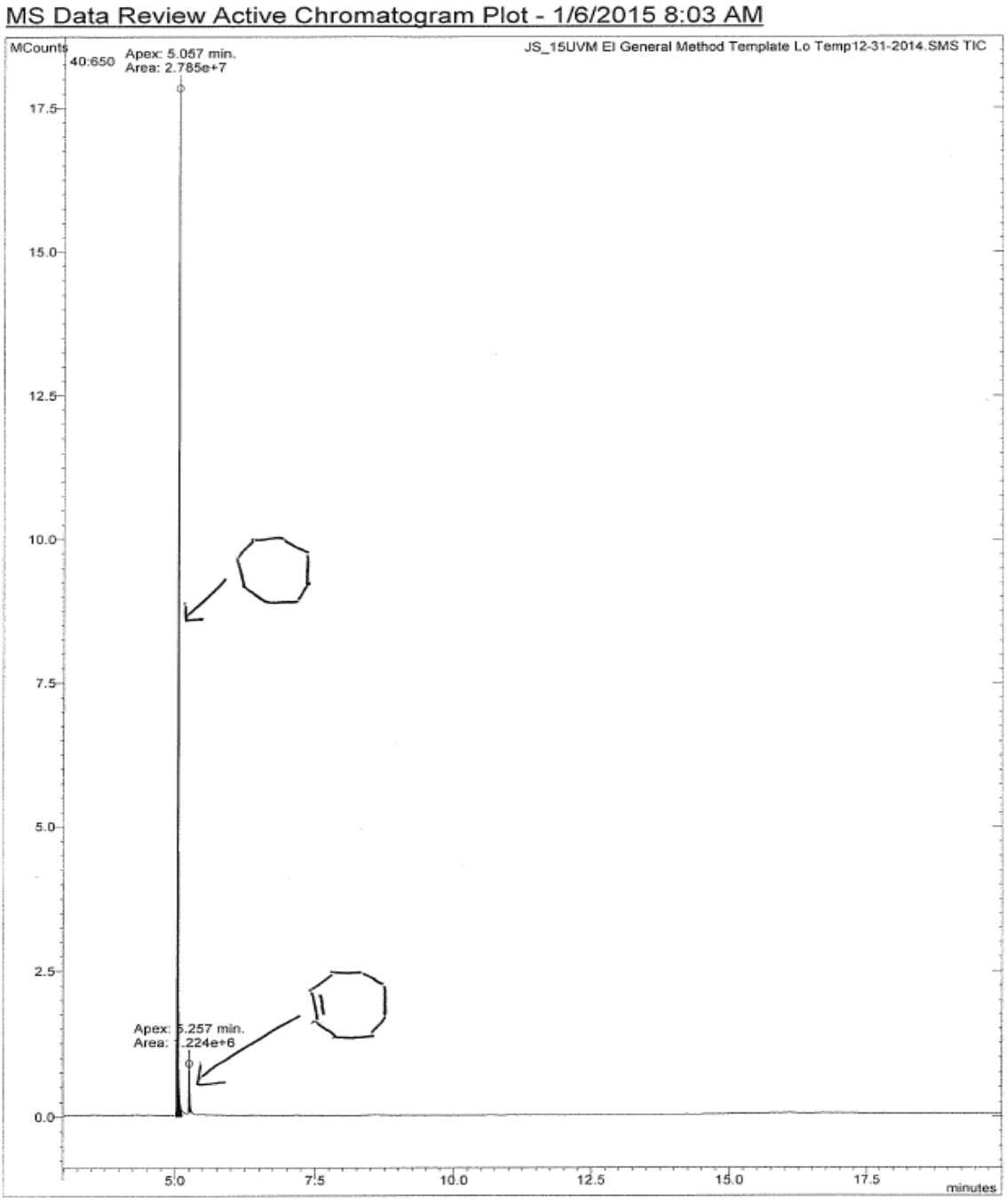


$^{11}B\{^{1}H\}$ NMR spectrum – final, THF, borosilicate NMR tube



δ (ppm)	48.4	37.0	30.9	27.3	–10.8	–5.0
Product	Hydroborylated species	Polyaminoborane	Borazine	Polyborazylene	Borazane	Unknown
% Conversion	15.7	9.9	14.5	15.4	14.3	30.2

GC spectrum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7.5
10.0
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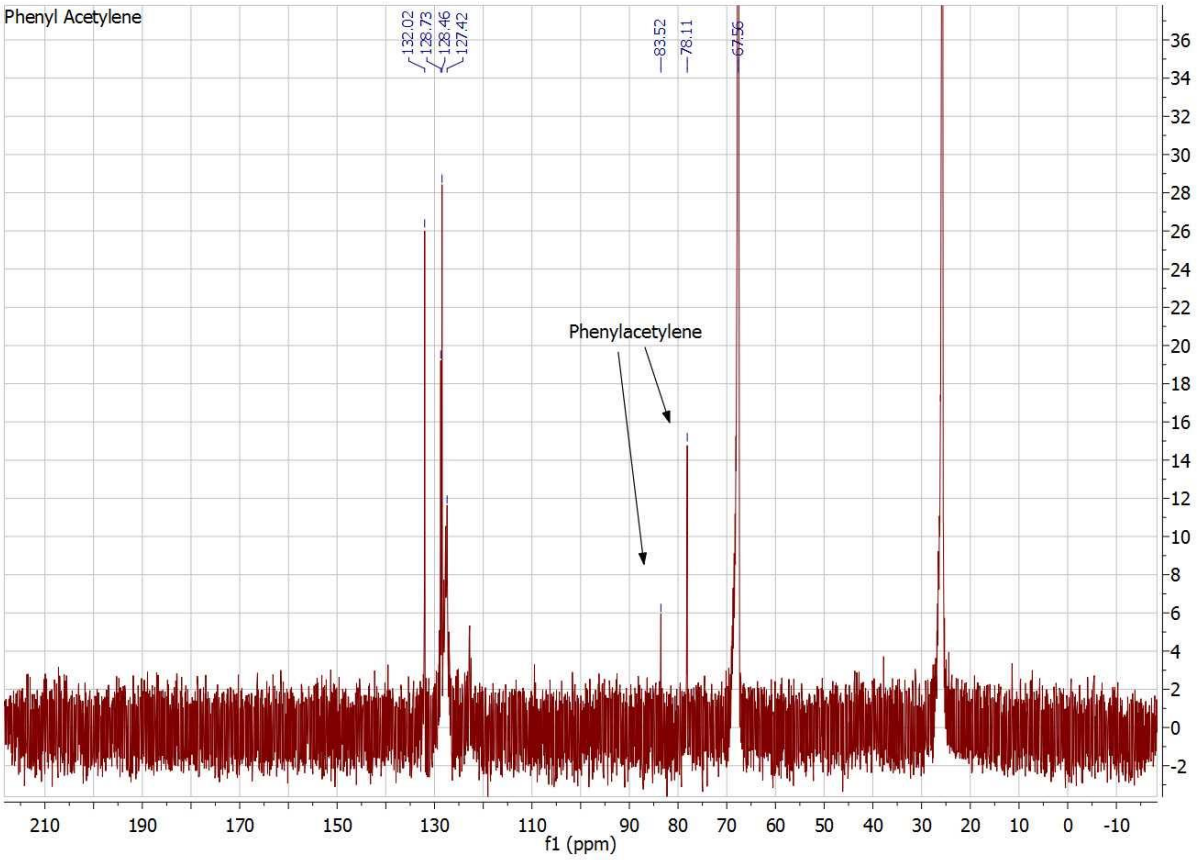
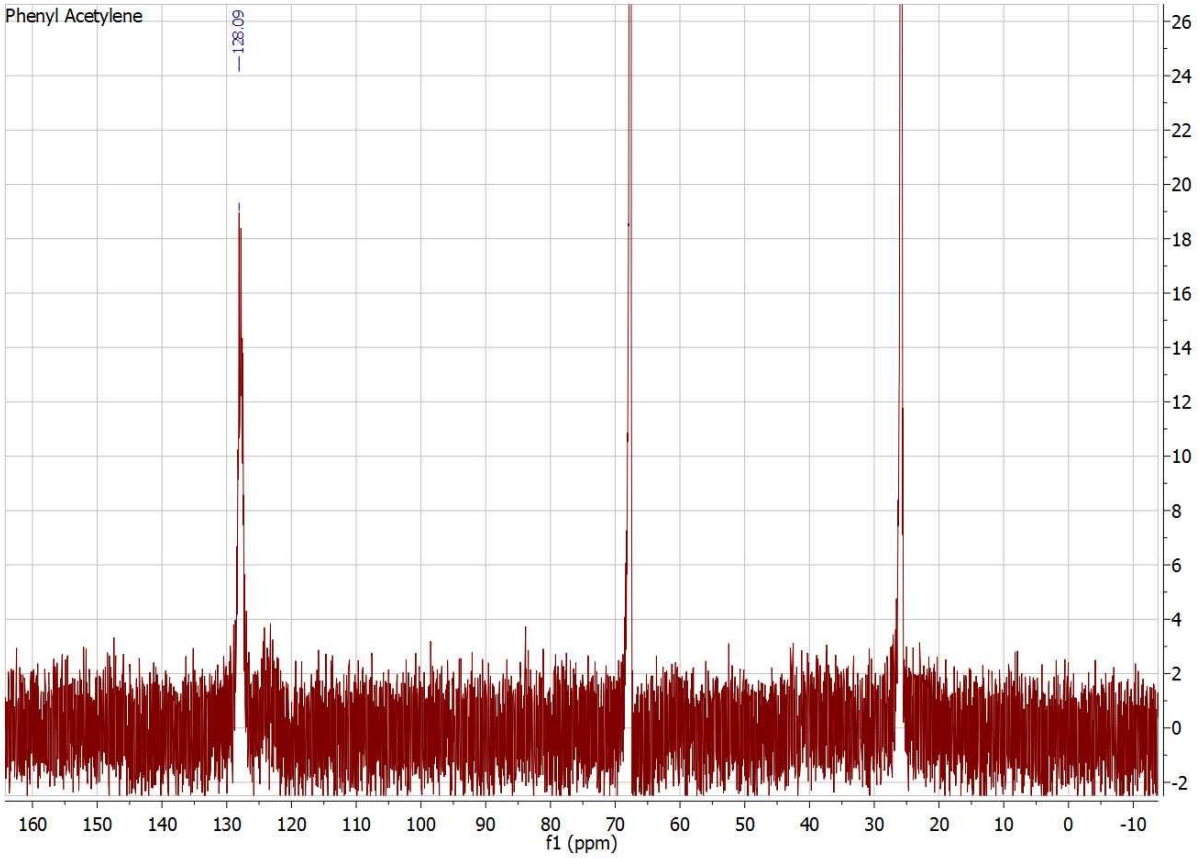
15.0
17.5
minutes

Cp*Co(CO)I_2 + AB + Phenylacetylene

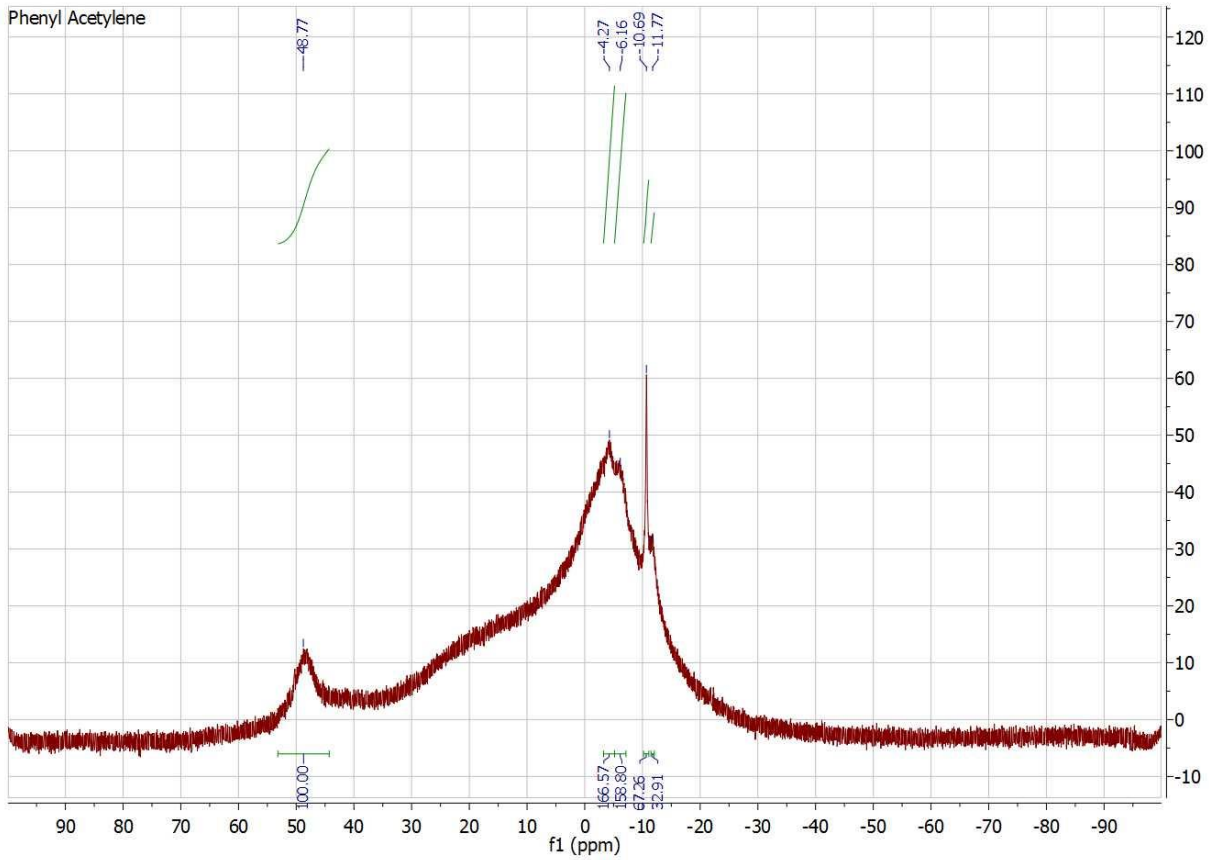
$^{13}C\{^1H\}$ NMR spectrum – final, THF



$^{13}C\{^{1}H\}$ NMR spectrum – final, THF

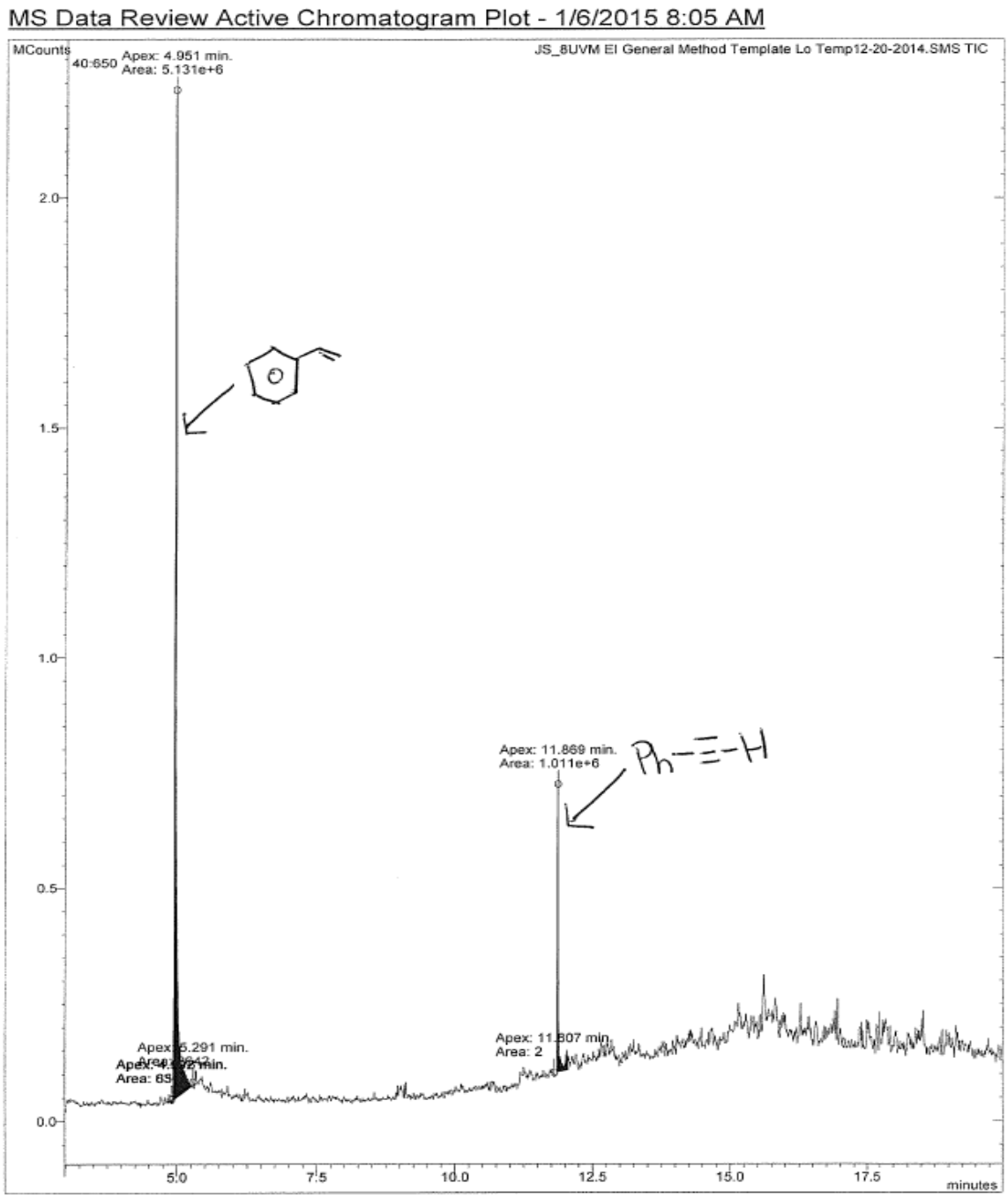


$^{11}B\{^{1}H\}$ NMR spectrum – final, THF, borosilicate NMR tube



δ (ppm)	48.8	–10.7	–11.8	–4.3, –6.2
Product	Hydroborylated Species	Borazane	Cyclodiborazane	Unknown
% Conversion	19.0	31.7	30.2	19.1

GC spectrum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Apex: 11.807 min.
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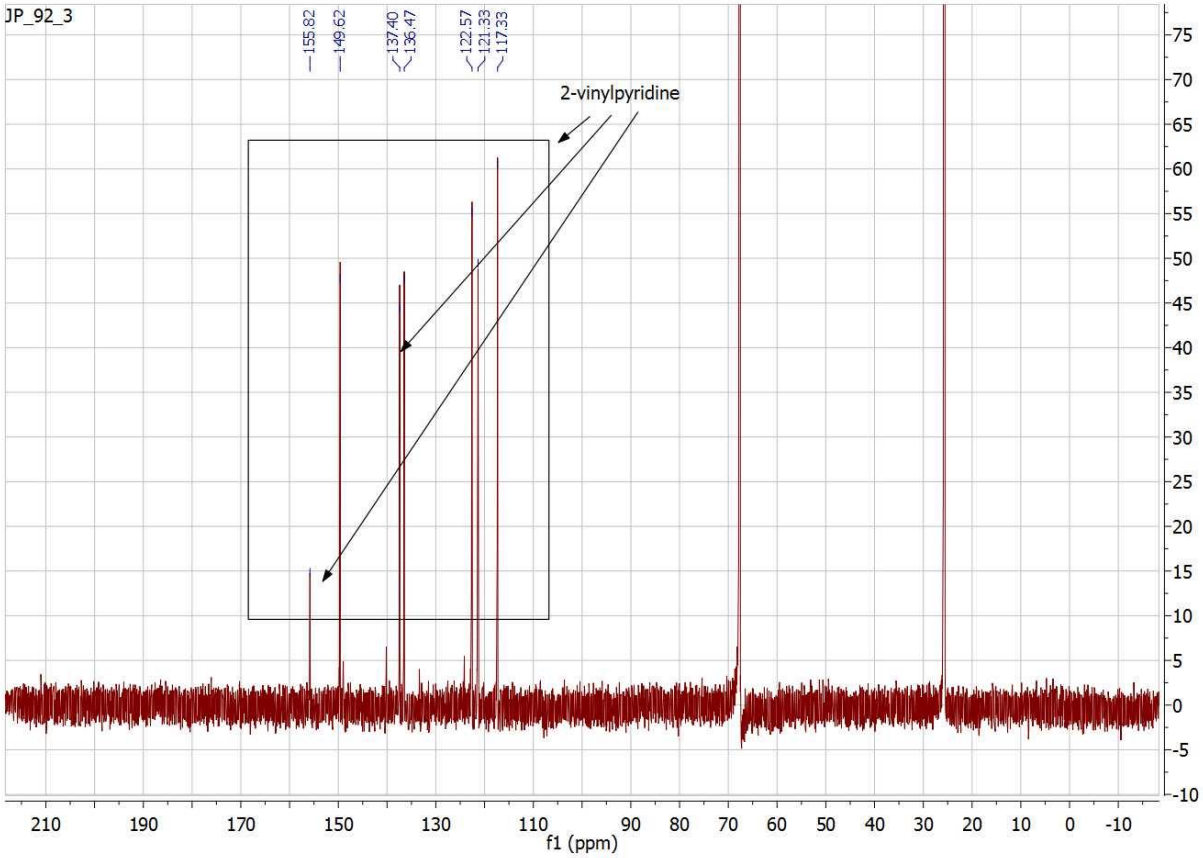
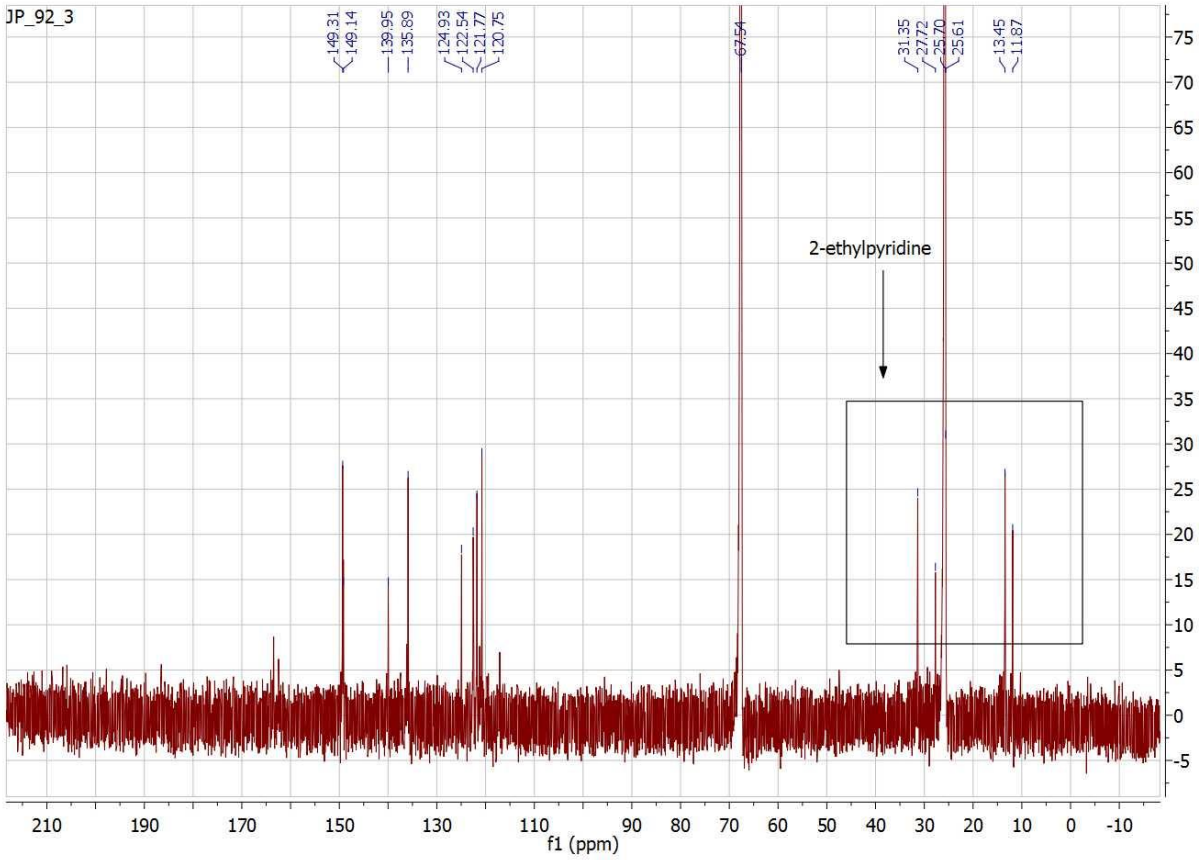
1.5
1.0
0.5
0.0
5.0
7.5
10.0
12.5
15.0
17.5
minutes

Cp*Co(CO)I_2 + AB + 2-vinylpyridine

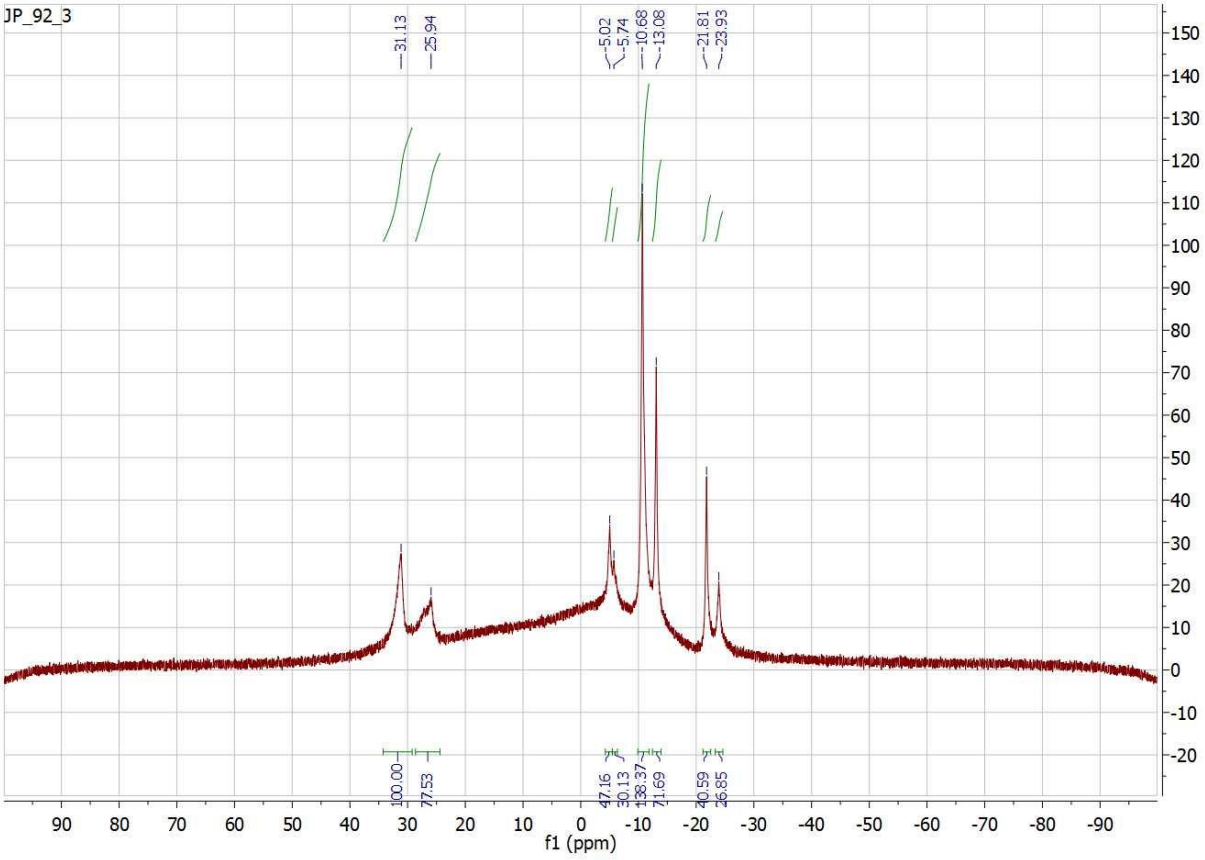
$^{13}C\{^1H\}$ NMR spectrum – initial, THF



$^{13}C\{^{1}H\}$ NMR spectrum – final, THF

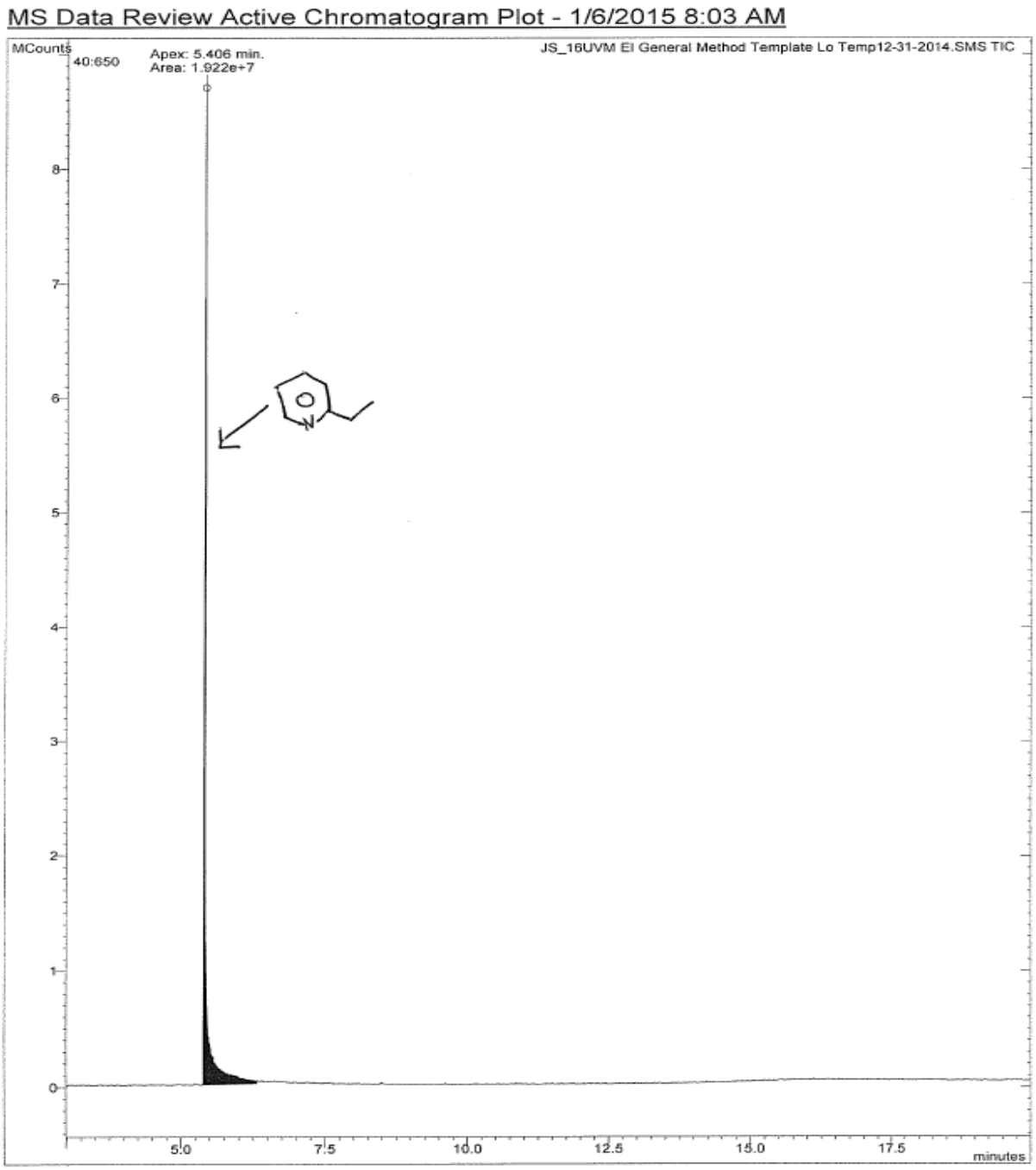


$^{11}B\{^{1}H\}$ NMR spectrum – final, THF, borosilicate NMR tube



δ (ppm)	31.1	26.0	–5.0, –10.7, –24.0	–21.8	–5.7, –13.1
Product	Borazine	Polyborazylene	*B*-(cyclodiborazanyl)aminoborohydride	NH_3BH_3	Unknown
% Conversion	19.5	15.1	41.6	4.0	19.8

GC spectrum


MS Data Review Active Chromatogram Plot - 1/6/2015 8:03 AM
MCounts
40:650
Apex: 5.406 min.
Area: 1.922e+7
JS_16UVM EI General Method Template Lo Temp12-31-2014.SMS TIC
8
7
6
5
4
3
2
1
0
5.0
7.5
10.0
12.5
15.0
17.5
minutes

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