Blending materials composed of Boron, Nitrogen and Carbon to transform approaches to Liquid Hydrogen Stores

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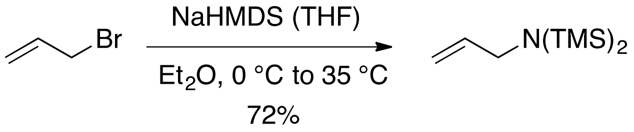
Supplementary Information

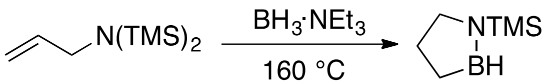
Synthesis of compounds A and D

Allyl hexamethyldisilazane



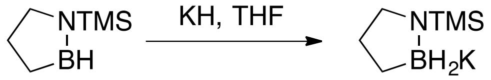
Allyl bromide (12.1 g, 100 mmol) in ether (80 mL) was cooled to 0 °C in a 250 mL round-bottomed flask. NaHMDS solution (52.6 mL, ca. 100 mmol in THF, 1.0 equiv.) was added carefully *via* syringe. The reaction mixture was refluxed for 18 hours then cooled to room temperature, and solid was filtered off with Celite. The solvents were removed with a rotary evaporator, and the remaining liquid was vacuum distilled (28 °C, 350 mTorr). Yielded 28.8 g (72%). ^{1}H NMR (300 MHz, C_6D_6) 5.74-5.88 (m, 1H), 5.13 (d, *J* = 18 Hz, 1H), 4.98 (d, *J* = 9 Hz, 1H), 3.37 (d, *J* = 3 Hz, 2H), 0.14 (s, 18H).

Cyclized Product NTMSBH



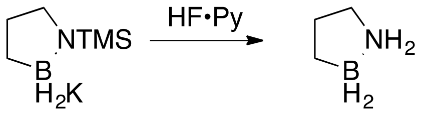
Allyl hexamethyldisilazane (10.0 g, 50 mmol) and borane-triethylamine complex (8.25 mL, 55 mmol, 1.1 equiv.) were added neat into a 100 mL pressure vessel. The pressure vessels were sealed with Viton o-rings and heated to 160 °C for 14 hours. The product was distilled using attenuated vacuum (53 torr) to provide the crude product (3.6 g, 51% crude, ~78% purity), which contains small amounts of triethylamine, can be carried on to the next step because the purification there will eliminate those impurities. ^{1}H NMR (300 MHz, C_6D_6) 3.05 (t, *J* = 6 Hz, 2H), 1.72-1.67 (m, 2H), 1.19 (t, *J* = 6 Hz, 2H), 0.13 (s, 9H). B–H proton not observed. ^{11}B NMR (96 MHz, C_6D_6) δ 48.3 (d, *J* = 130.6 Hz).

Potassium salt



Potassium hydride (73.8 mg, 18.4 mmol) was added in portions to the distillate from the last step (3.35 g, ~78% purity, 18.4 mmol) in THF (20 mL) in the drybox at room temperature. The reaction was then stirred for 14 hours under inert atmosphere. The solids were filtered off in the drybox, and the solvent was removed *via* high-vacuum with slight heat (30 °C). Remaining volatiles, which may include residual THF, triethylamine, and borane-triethylamine, can be removed with the high-vacuum and more applied heat (70 °C). The residue was rinsed with a minimal amount of pentane and filtered in the drybox to provide the product which was directly used in the next step. ^{11}B NMR (96 MHz, C_6D_6) δ −16.4 (t, *J* = 77.8 Hz).

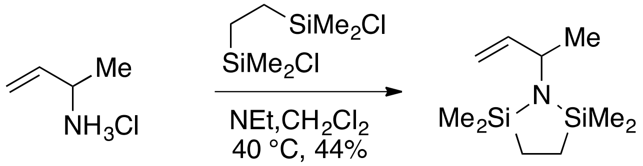
BN-cyclopentane (Compound A)



The potassium salt (~18.4 mmol) was taken into 40 mL THF and cooled to –78 °C in a plastic vessel. Hydrogen fluoride pyridine (1.05 g, 36.8 mmol of ca. 70 wt.% HF, 2 equiv.) diluted with 40 mL THF was added slowly *via* Teflon tubing cannula from another plastic vessel and stirred for 2 hours. The solid was filtered off through a plug of celite, and the solvent was removed *via* rotary evaporator. (Care must be taken to apply as little heat as possible. The bath may be maintained at ~35 °C for the duration of the solvent removal.) Residual solvent was removed with a high-vacuum at room temperature. Additional purification can be achieved using silica gel chromatography (gradient from 10% v/v THF in hexane as the mobile phase) to provide the product as white solid (1.06 g, 81% for two steps) ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.81-3.54 (m, 2H), 2.88 (t, *J* = 6 Hz, 2H), 1.81 (q, *J* = 96Hz, 2H), 1.66 (br s, 2H), 0.61 (br s, 2H). -^{13}C NMR (150 MHz, C_6D_6) δ 45.7, 26,2, 13.5 (br). ^{11}B NMR (96 MHz, C_6D_6) δ – 13.2 (t, *J* = 96.9 Hz). WARNING:

Hydrogen fluoride is corrosive and toxic. Take extra care with addition, since it has been dissolved in polar aprotic solvent. Keep calcium gluconate HF treatment on hand.

Bis-Silylamine S-1



S-1

In a glovebox, 3-amino-1-butene hydrochloride[1] (8.00 g, 74.3 mmol, 1.05 equiv) was suspended in methylene chloride and cooled to –30 °C. Triethylamine (22.57 g, 223 mmol, 3.15 equiv) was added slowly along with 1,2-bis(dimethylchlorosilyl)ethane (15.24 g, 70.8 mmol, 1 equiv). The reaction was warmed to room temperature over 1 hour then refluxed at 40 °C for 18 hours. The reaction was cooled to room temperature, and the solvent was removed using a rotary evaporator. Dry ether was added to extract the product. The solids were filtered off, and the solvent was removed using a rotary evaporator. Crude ^{1}H NMR showed a 5:1 ratio of product to unreacted silyl chloride. Fractionally distilled under vacuum (35 °C, 250 mTorr) to yield 6.89 g (44%) of a clear, colorless liquid. ^{1}H NMR (300 MHz, C_6D_6) δ 5.88 (ddd, J = 17.2, 10.2, 5.9 Hz, 1H), 4.94 (dt, J = 26.4, 1.6 Hz, 1H), 4.89 (dt, J = 19.4, 1.6 Hz, 1H), 3.60 (ddt, J = 7.3, 6.1, 1.5 Hz, 1H), 1.19 (d, J = 6.8 Hz, 3H), 0.84 – 0.67 (m, 4H), 0.14 (d, J = 2.8 Hz, 12H). ^{13}C NMR (75 MHz, C_6D_6) δ 145.71, 111.96, 51.56, 24.11, 8.83, 1.84, 1.50. HRMS (EI+) $[M]^+$ calcd. for $C_{10}H_{23}NSi_2$ 214.13648, found 214.13697.

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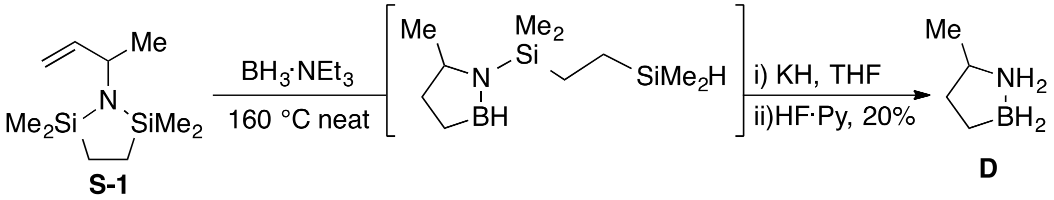
[1] This secondary amine was synthesized by the Gabriel synthesis (3-chloro-1-butene and potassium phthalimide). The exact freebased amine has been synthesized before: King, R. B.; Borodinsky, L. *Tetrahedron* **1985**, *41*, 3235–3240. A more detailed procedure: Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 2509–2520. The amine was isolated as the hydrochloride salt by bubbling anhydrous HCl through an ethanol solution of the freebased amine, then removing the ethanol. This was to ensure an anhydrous environment for future reactions.

Compound D



In a glovebox, bis-silylamine **S-1** (4.887 g, 22.9 mmol, 1 equiv) was mixed with neat borane-triethylamine (5.802 g, 50.4 mmol, 2.2 equiv) in a pressure vessel. The vessel was sealed and heated to 160 °C for 18 hours. Upon cooling, the reaction mixture was brought into the glovebox, and THF (100 mL) was added followed by careful addition of potassium hydride. This was stirred for 18 hours, and the mixture was filtered through a fritted funnel. The filtrate was treated with HF-pyridine (2M HF in THF, 22.9 mL 48.8 mmol, 2 equiv) *via* dropwise addition and stirred for two hours, keeping the temperature at room temperature through the course of the reaction to avoid thermally-induced dehydrogenation of the product. The solvent was removed using a rotary evaporator, and the residue extracted with ether. This mixture was filtered through a Whatman #5 filter paper to remove the potassium fluoride byproduct. Pure product was obtained by silica gel flash chromatography (35% v/v ether in pentane) in the air. Yield: 403 mg, 20% of an off-white solid mp 35–37 °C. ^{1}H NMR (300 MHz, C_6D_6) δ 3.12 –2.48 (m, 2H), 2.37 (h, *J* = 7.2 Hz, 2H), 2.02 (brs, 1H), 1.72 (brs, 1H), 1.25 – 0.98 (m, 3H), 0.51 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 55.1, 34.7, 19.7, 12.8 (br). ^{11}B NMR (96 MHz, C_6D_6) δ -11.7 (t, *J* = 97.6 Hz). HRMS (EI+) $[M–H]^+$ calcd. for $C_4H_{11}NB$ 84.098455, found 84.098367.

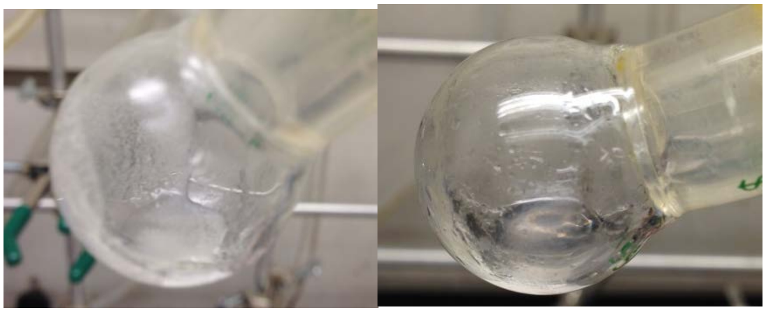
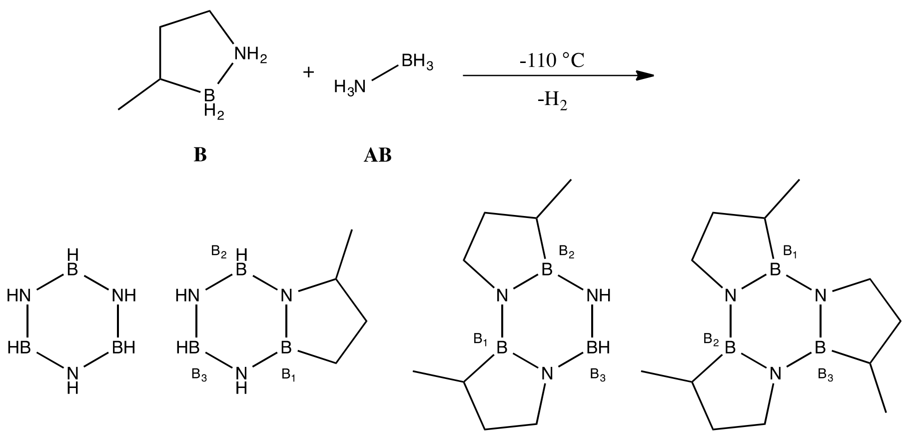


Figure S1. 2:1 **B**:**AB** mixture before (left) and after (right) hydrogen release. The initial state is a flowable slurry and the final state is a clear fluid.



B **AB**

BZ	**1**	**2**	**3**
σ = 30.8 ppm	σ	σ	σ
	B_1 = 39.9	B_1 = 42.1	B_1 = 41.7
	B_2 = 32.6	B_2 = 40.7	B_2 = 41.1
	B_3 = 31.3	B_3 = 32.0	B_3 = 40.5

Figure S2. Calculated ^{11}B NMR chemical shifts for sites in dehydrogenation products observed from **B**:**AB** blends.

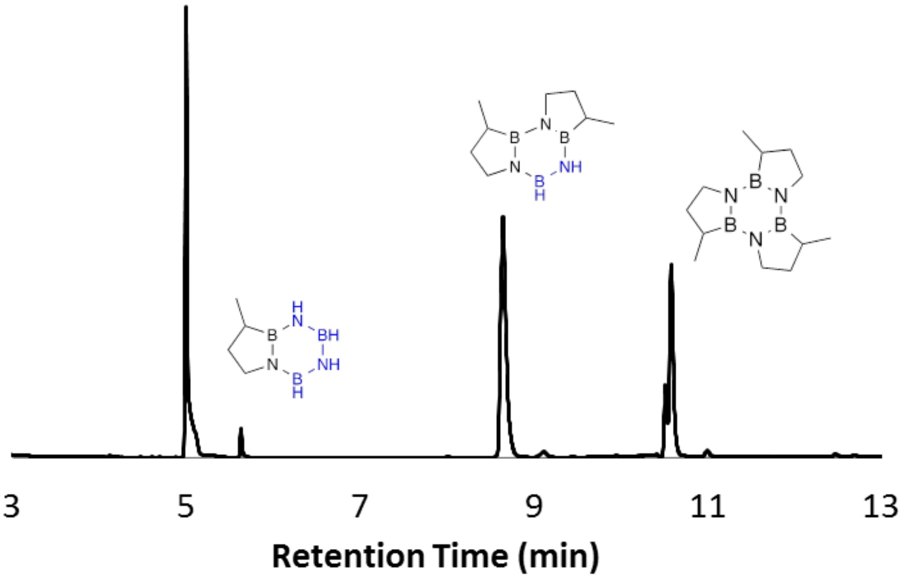


Figure S3. Gas chromatograph of spent fuel from 2:1 **B**:**AB** blend. The large peak at 5 minute is a mixture of borazine and solvent. The other peaks were identified as borazine-like compounds containing between 1 and 3 BN-methylcyclopentane residues.

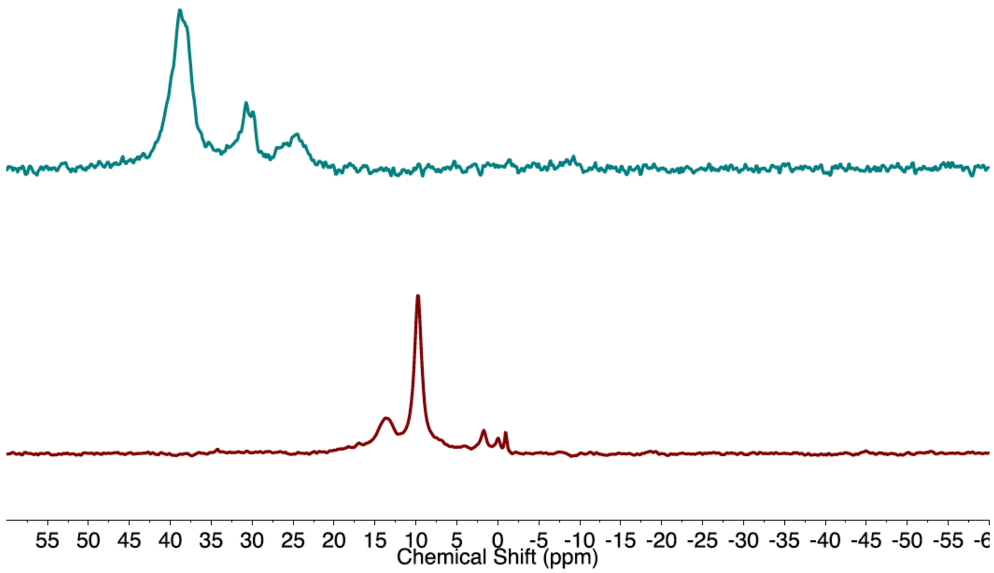


Figure S4. ^{11}B NMR spectra of spent fuel from 2:1 **B**:**AB** fuel blend before (top) and after (bottom) digestion in methanol.

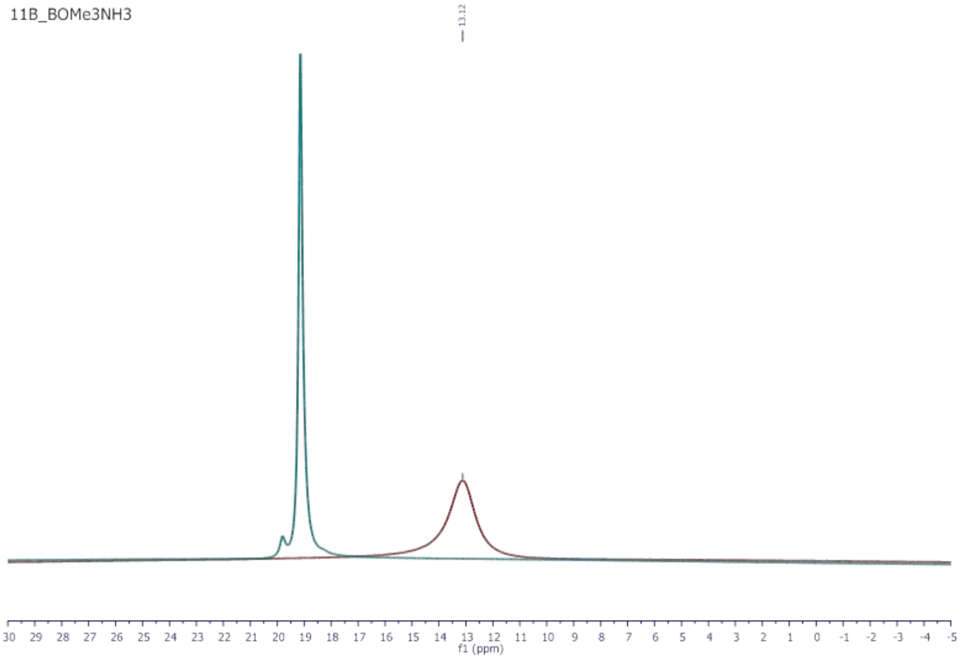


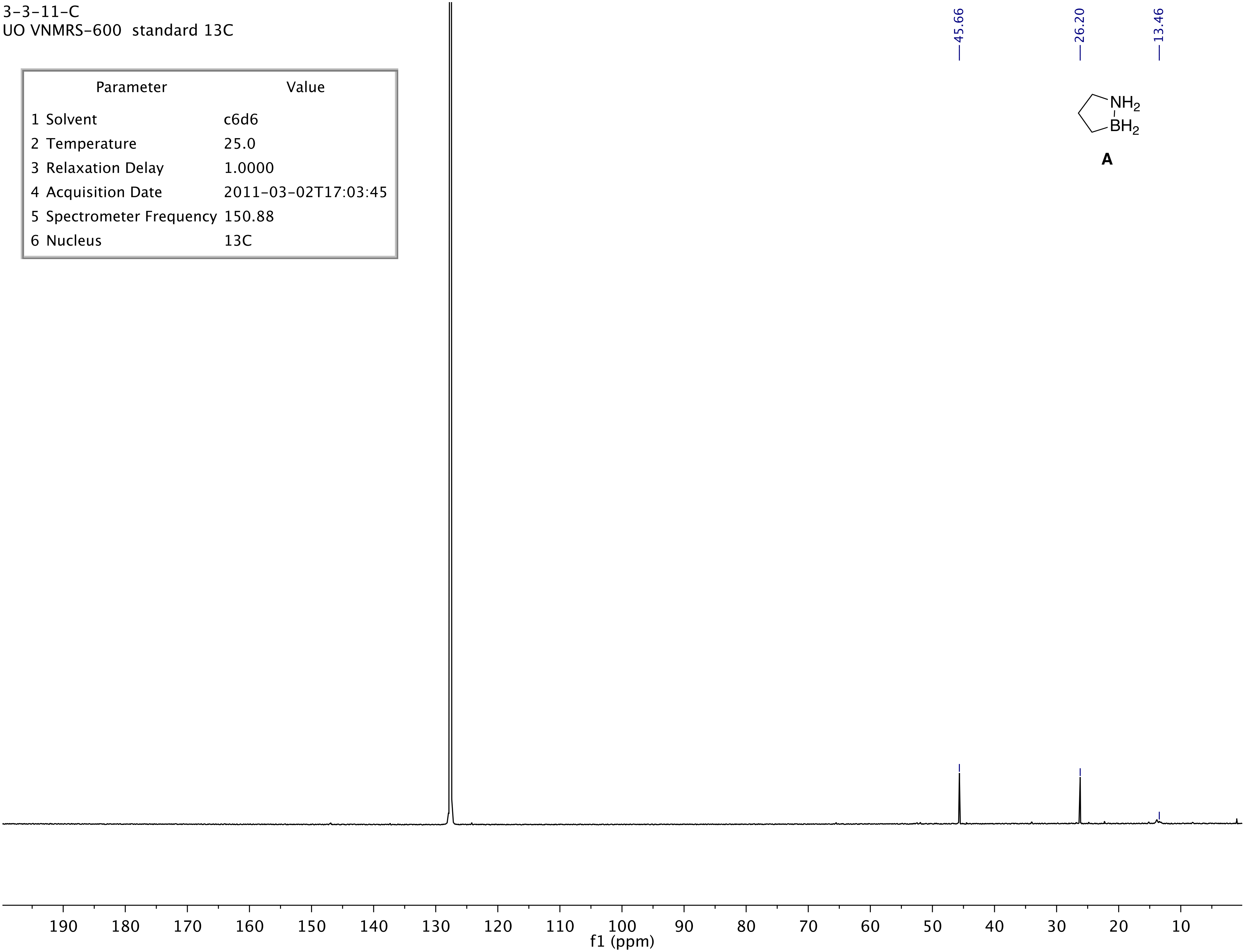
Figure S5. ^{11}B NMR spectra of (OMe)$_3$B (blue) and (OMe)$_3$B-NH$_3$ (red), recorded in CDCl$_2$ with added methanol (MeOH : (OMe)$_3$B = 20:1). The latter material was formed by bubbling NH$_3$ gas through the (OMe)$_3$B solution.

Table S1. Calculated bond dissociation energy (BDE) of B—N in CBN compounds (G3MP2) kcal/mol. Methylamine borane provides a model estimate for BDE of EDAB. Of the cyclic compounds, stability order is B > D > A. Trend follows apparent thermal stability observed in thermal decomposition experiments.

Compound	A	B	D	$H_3N\text{-}BH_3$	$CH_3NH_2\text{-}BH_3$
BDE	25.2	26.2	25.9	27.2	33.5

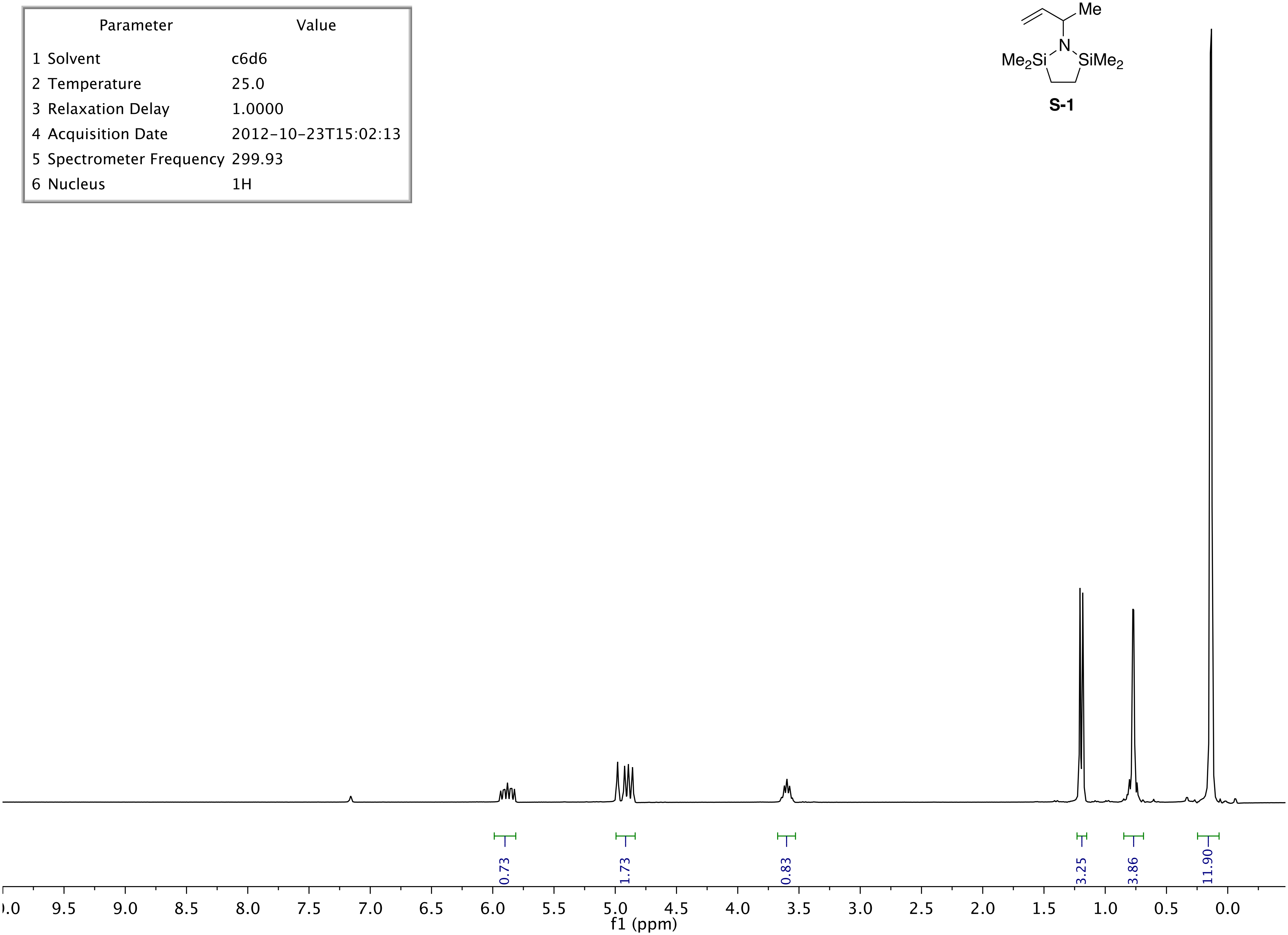
3-3-11-C
UO VNMRS-600 standard 13C

Parameter	Value
1 Solvent	c6d6
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2011-03-02T17:03:45
5 Spectrometer Frequency	150.88
6 Nucleus	13C



ji-II-H167-dist
UO Inova-300-South

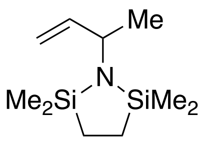
Parameter	Value
1 Solvent	c6d6
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2012-10-23T15:02:13
5 Spectrometer Frequency	299.93
6 Nucleus	1H



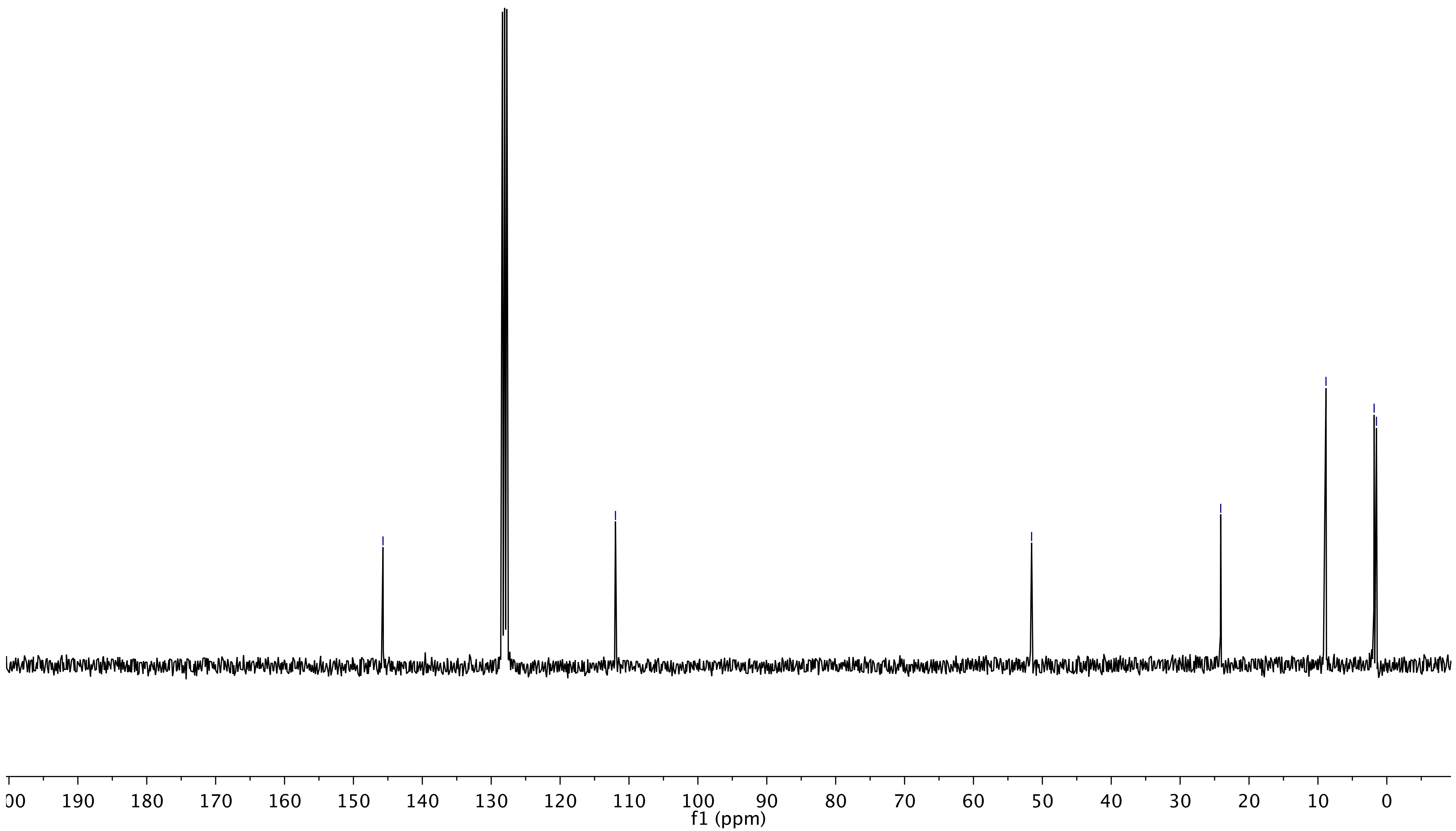
S-1

ji-II-C167-dist
UO Inova-300 Standard-1H

Parameter	Value
1 Solvent	c6d6
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2012-10-24T15:09:48
5 Spectrometer Frequency	75.43
6 Nucleus	13C



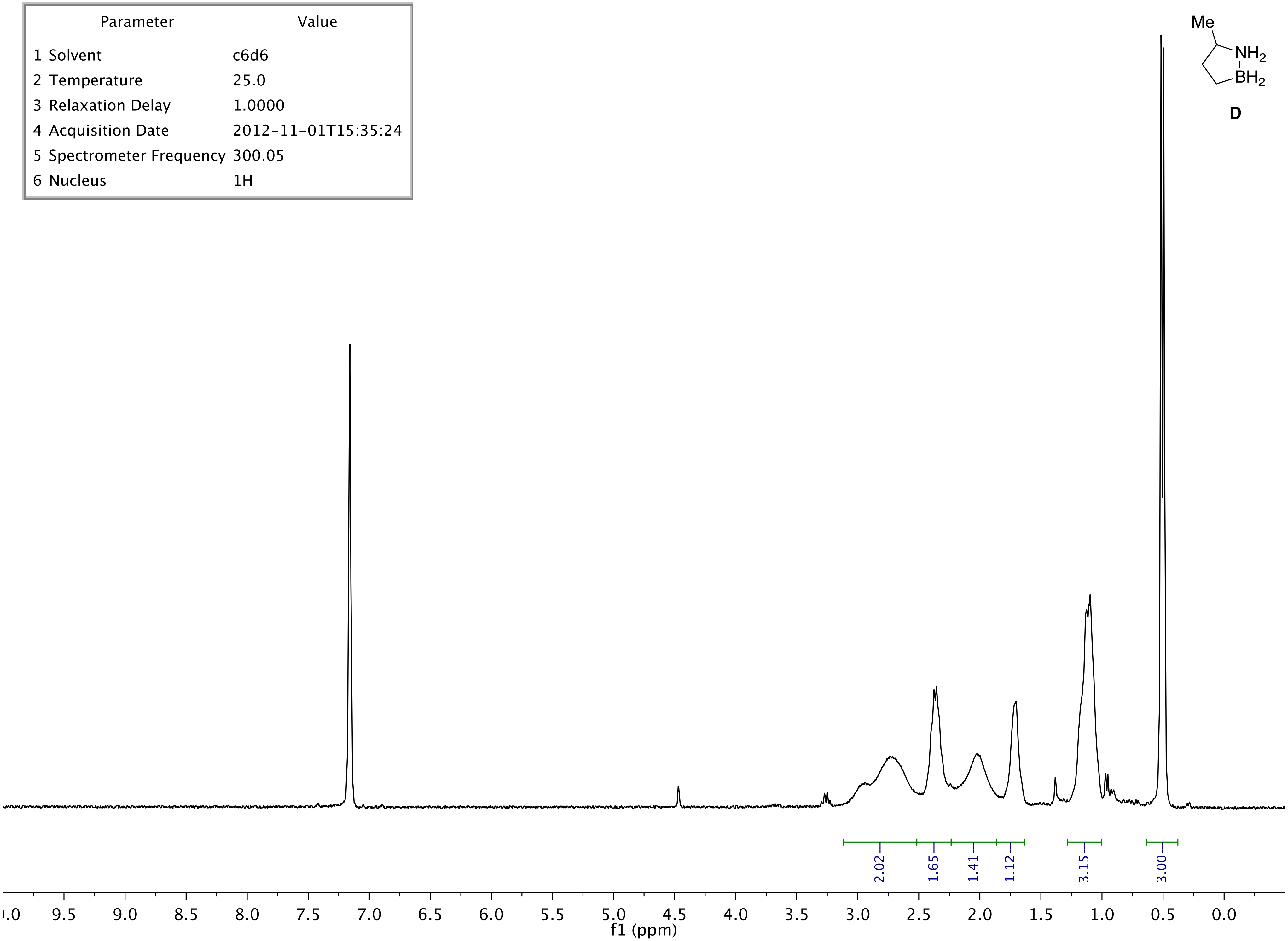
S-1



ji-II-H177-4-8
UO Inova-300-North standard 1H

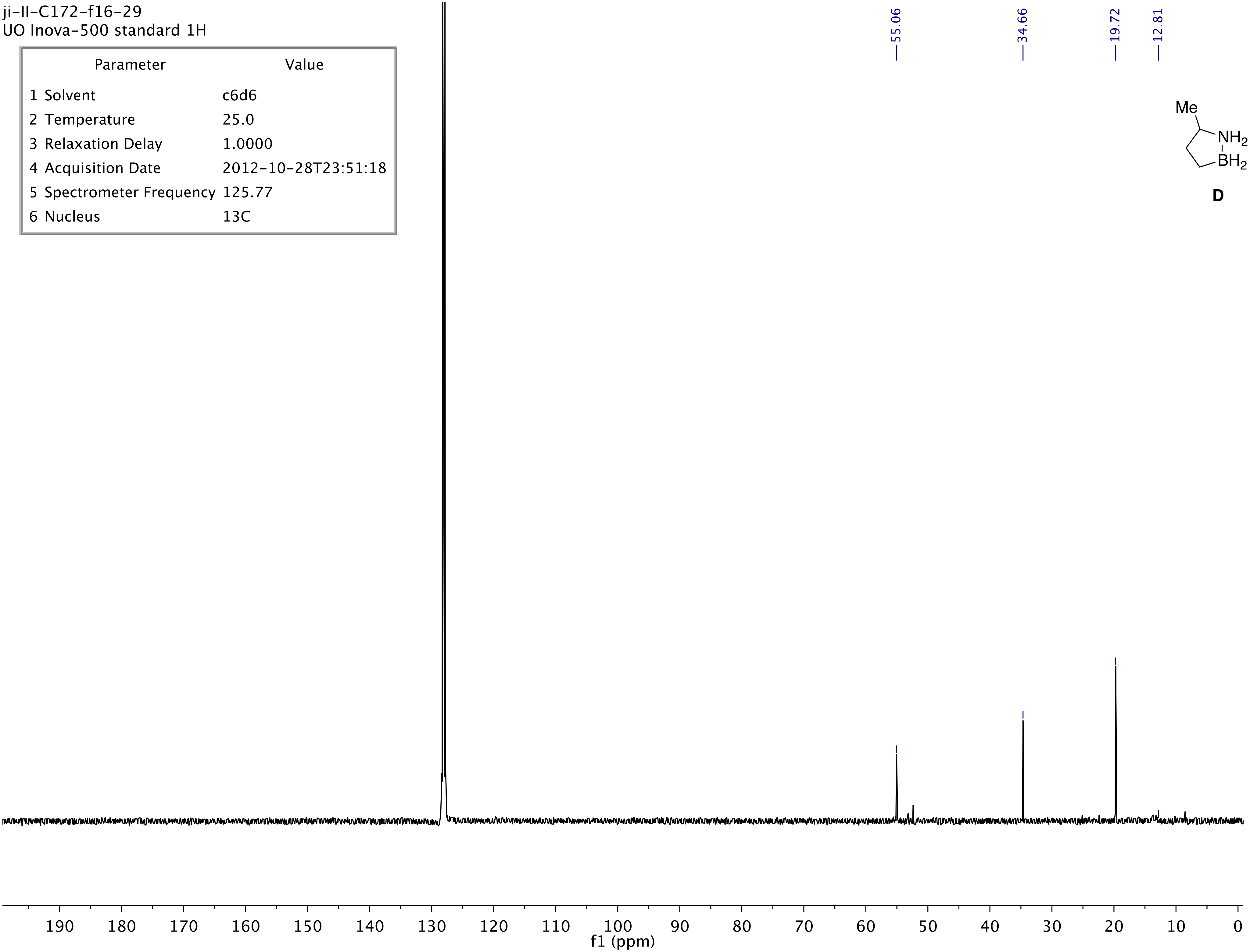
Parameter	Value
1 Solvent	c6d6
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2012-11-01T15:35:24
5 Spectrometer Frequency	300.05
6 Nucleus	1H

D



ji-II-C172-f16-29
UO Inova-500 standard 1H

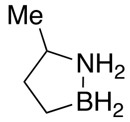
Parameter	Value
1 Solvent	c6d6
2 Temperature	25.0
3 Relaxation Delay	1.0000
4 Acquisition Date	2012-10-28T23:51:18
5 Spectrometer Frequency	125.77
6 Nucleus	13C



D

ji-II-B173-col
UO Inova-300-North Boron-11

Parameter	Value
1 Solvent	c6d6
2 Temperature	25.0
3 Relaxation Delay	0.2000
4 Acquisition Date	2012-10-29T17:54:46
5 Spectrometer Frequency	96.27
6 Nucleus	11B



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