Supporting Information for

Negishi cross-coupling is compatible with a reactive *B*-Cl bond: Development of a versatile late stage functionalization of 1,2-azaborines and its application to the synthesis of new BN isosteres of naphthalene and indenyl

Alec N. Brown, Bo Li, and Shih-Yuan Liu*

Department of Chemistry, Boston College, Chestnut Hill, MA 02467, United States

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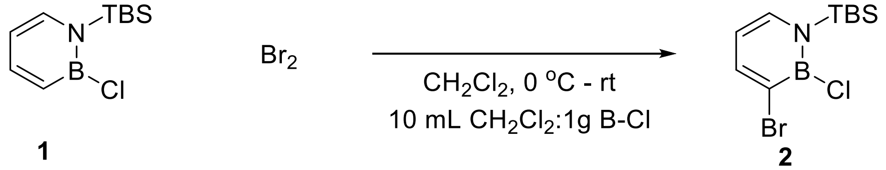
General

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere (N_2) using either standard Schlenk techniques or a glove box. THF, Et_2O, CH_2Cl_2, and pentane were purified by passing through a neutral alumina column under argon. Commercially available zinc reagents were purchased from Sigma-Aldrich: 0.5 M (THF) propylzinc bromide solution-499374, 0.5 M (THF) (1-phenylvinyl)zinc bromide solution-499390, 0.5 M (THF) (4-chloro)phenylzinc iodide solution-497835, 1 M (hexanes) diethyl zinc solution-296112; or Alfa Aesar: 0.5M (THF) (2-(1,3-dioxan-2-yl)ethyl)zinc bromide solution-H58912 or 0.5 M (THF) (3,4,5-trifluorophenyl)zinc bromide solution-H58581; and used without further purification. All other chemicals were purchased (Sigma-Aldrich or TCI) and used as received. Silica and alumina were dried overnight at 120 ^{o}C under high vacuum. NMR spectra were recorded on a Varian VNMRS 600 MHz, VNMRS 500 MHz, INOVA 500 MHz, or VNMRS 400 MHz spectrometer. ^{11}B NMR spectra were externally referenced to $BF_3{\bullet}Et_2O$ (δ 0). Fluorescence emission spectra were collected on Photon Technology International spectrometer in dry, distilled, and degassed (by 4 freeze-pump-thaw cycles) HPLC grade cyclohexane (Sigma-Aldrich CHROMASOLV$^{®}$ plus-650455). Photoluminescence quantum yields were calculated using anthracene and 9,10–diphenylanthracene as external reference standards by literature procedure.[1] 9,10-diphenylanthracene was recrystallized from hot ethanol with a hot polish filtration to remove impurities before measurement. UV-Vis spectra were collected on an Agilent Cary 100 spectrophotometer. High resolution mass spectroscopy was carried out on a JEOL AccuTOF instrument (JEOL USA, Peabody, MA), equipped with a DART ion source (IonSense, Inc., Danvers, MA) in positive ion mode.

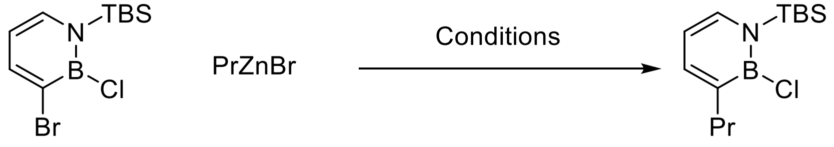
Synthesis of Azaborine 2 (Scheme 2)



1 **2**

A 100 mL round bottom flask was charged with 1 equiv of *B*–Cl azaborine **1** (5.000 g, 21.97 mmol), a bar of stirring, and 50 mL of CH_2Cl_2. This mixture was cooled to 0 °C in an ice/water bath. In a separate vessel, 1.05 equiv Br_2 (3.58g, 23.1 mmol) was diluted in 2 parts methylene chloride: 1 part Br_2. This mixture was added dropwise to the azaborine solution over 15 minutes. The reaction was stirred for 15 additional minutes at 0 °C and was allowed to warm to room temperature and continued until 1H NMR analysis indicated completion (30 min to 2 h). Solvent was removed under reduced pressure, and 30 mL pentane was added. Solids were removed by filtration and the filtrate was concentrated. Vacuum distillation (62-65 °C, 120 mT) provided product **2** as a clear, colorless liquid (18.8 g, 70%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.89 (d, *J* = 7.0 Hz, 1H), 7.28 (d, *J* = 6.7 Hz, 1H), 6.23 (app t, *J* = 6.7 Hz, 1H), 0.95 (s, 9H), 0.55 (s, 6H). ^{11}B NMR (192.5 MHz, CD_2Cl_2): δ 37.4. ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 147.0, 139.0, 111.8, 26.8, 19.7, −1.3. The quaternary carbon adjacent to boron was not observed. HRMS (EI) calcd for $C_{10}H_{18}BNSiCl^{81}Br(M+)$ 307.01530, found 307.01500.

Conditions Screening for Optimization of Negishi Coupling for B-Cl (Table 1)



2 **3a**

General Procedure: In a nitrogen glovebox, a 1 dram scintillation vial was charged with 100 μL of a stock solution in THF containing both: 1) internal standard hexamethylbenzene (28.8 mg : 3 mL; 0.96 mg, 0.0059 mmol) and 2) azaborine **2** (902.5 mg : 3 mL; 30.1 mg, 0.0981 mmol). This was mixed with 1 mL of THF and additives and catalysts (0.05 equiv. as noted below) followed by 0.3 mL of a 0.5 M solution of PrZnBr (1.5 equiv., 0.15 mmol) and stirred for 24 hours upon which solvent was removed under reduced pressure. ^{1}H NMR analysis of the crude reaction mixtures was carried out in dry deuterated benzene. Yields were determined by the internal standard method with a calibration to the measured NMR ratio of the starting material and hexamethylbenzene in the prepared stock solution. Since the reactions were run in duplicate, the reported NMR yields are the average of two yields and as such, the yields reported in Table 1 will not necessarily match the individual yields reported below.

Entry 1: The general procedure was followed with the following modifications: 0.05 equiv. $Pd(P^tBu_3)_2$ (2.3 mg, 0.0049 mmol) was used as the catalyst. NMR analysis of the crude reaction mixture indicated 89% yield (a second run indicated 86% yield).

Entry 2: The general procedure was followed with the following modifications: no catalyst was added. NMR analysis of the crude reaction mixture indicated no reaction.

Entry 3: The general procedure was followed with the following modifications: 0.05 equiv. $Pd(P^otol_3)_2Cl_2$ (3.5 mg, 0.0045 mmol) was used as the catalyst. NMR analysis of the crude reaction mixture indicated 74% yield (a second run indicated 76% yield).

Entry 4: The general procedure was followed with the following modifications: 0.05 equiv. Xphos Pd G2 catalyst (3.5 mg, 0.0044 mmol) was used as the catalyst. NMR analysis of the crude reaction mixture indicated 88% yield (a second run indicated 71% yield). This catalyst system gives inconsistent results, potentially due to incomplete activation of the catalyst under room temperature conditions.

Entry 5: The general procedure was followed with the following modifications: 0.05 equiv. Pcy_3 Pd G2 (2.9 mg, 0.0049 mmol) and additive Pcy_3 (1.6 mg, 0.0057 mmol) was used as the catalyst. NMR analysis of the crude reaction mixture indicated 64% yield (a second run indicated 62% yield).

Entry 6: The general procedure was followed with the following modifications: 0.05 equiv. $NiCl_2(Pcy_3)_2$ (3.6 mg, 0.0052 mmol) was used as the catalyst. NMR analysis of the crude reaction mixture indicated 37% yield (a second run indicated 34% yield).

Entry 7: The general procedure was followed with the following modifications: 0.05 equiv. $Ni(cod)_2$ (2.1 mg, 0.0076 mmol) was used as the catalyst with 0.1 equiv. of terpyridine (3.0 mg, .0128 mmol) as added ligand. NMR analysis of the crude reaction mixture indicated 30% yield (a second run indicated 31% yield).

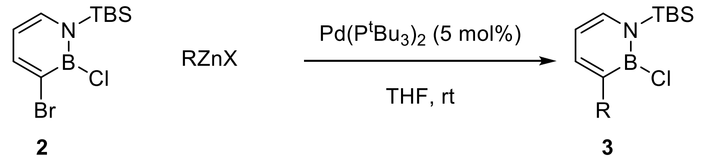
Entry 8: The general procedure was followed with the following modifications: 0.05 equiv. $Pd(P\text{-}t\text{-}Bu_3)_2$ (2.3 mg, 0.0049 mmol) was used as the catalyst. Before addition of the zinc reagent the THF solvent was removed under high vacuum from both the stock solution of azaborine and hexamethylbenzene and *n*-PrZnBr and replaced with Et_2O. NMR analysis of the crude reaction mixture indicated 81% yield (a second run indicated 78% yield).

Entry 9: The general procedure was followed with the following modifications: 0.05 equiv. $Pd(P\text{-}t\text{-}Bu_3)_2$ (2.3 mg, 0.0049 mmol). Before addition of the zinc reagent the THF solvent was removed from both the stock solution of azaborine and hexamethylbenzene and replaced with toluene. NMR analysis of the crude reaction mixture indicated 42% yield (a second run indicated 44% yield).

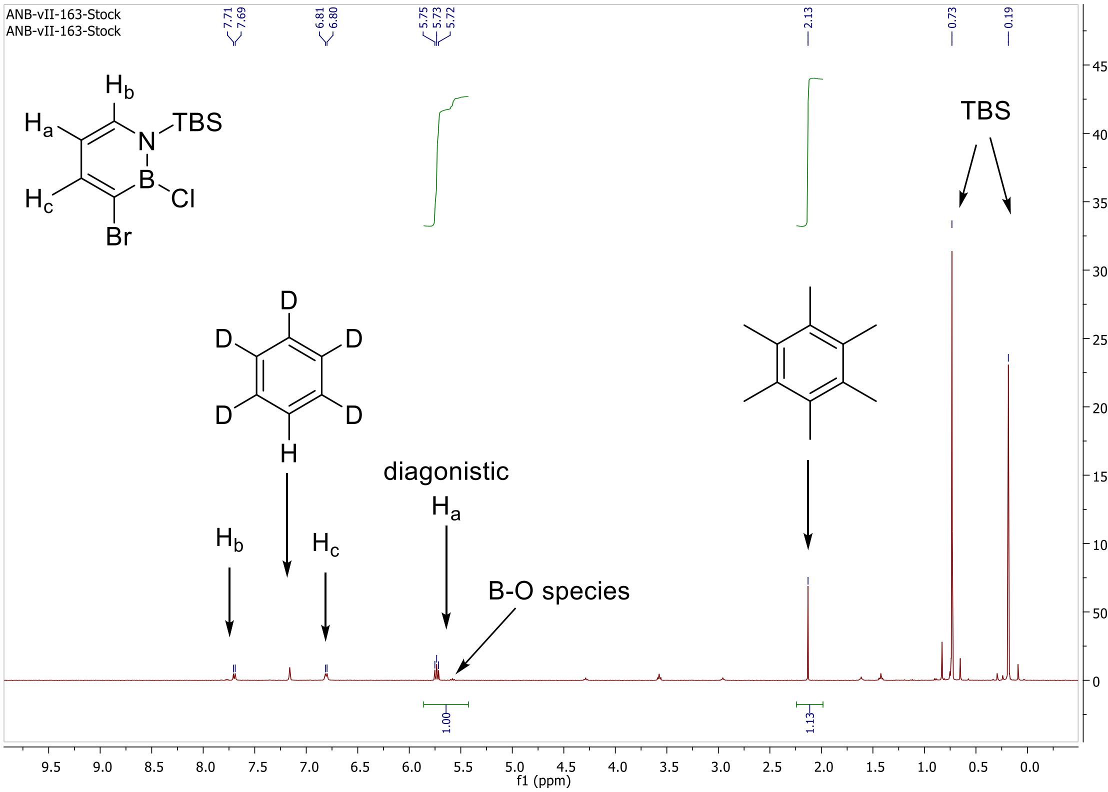
Entry 10: The general procedure was followed with the following modifications: 0.05 equiv. Pd(P-*t*-Bu$_3$)$_2$ (2.4 mg, 0.0049 mmol) was used as the catalyst and 1.2 equivalents of *N*-methyl- 2-pyrrolidone (12 μL, 12 mg, 0.12 mmol) was added. NMR analysis of the crude reaction mixture indicated 84% yield (a second run indicated 79% yield).

Entry 11: see Table 2, entry 1.

NMR Yields of B-Cl Azaborines 3a-3f (Table 2)



Each stock solution was prepared and calibrated by removing the solvent under a stream of nitrogen followed by NMR analysis to obtain an initial integrative ratio of the starting azaborine **2** versus the internal standard. This ratio was used to determine the NMR yield of the products by comparing the initial ratio of azaborine **2** to internal standard to the final ratio of the C3 functionalized azaborine to internal standard. We also checked the ^{11}B NMR of each sample to verify the major product was not alkylation or B–O bond formation, which are diagnostic in the ^{11}B NMR ($\delta_{\text{B-alkyl}}$~40, $\delta_{\text{B-aryl}}$~38, $\delta_{\text{B-OR}}$~29, $\delta_{\text{B-Cl}}$~35). The NMR signal for H$_a$ consistently shifts downfield to ~6.1 upon C3 substitution.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7.69
6.81
6.80
5.75
5.73
5.72
2.13
0.73
0.19
H
b
H
a
N
TBS
B
Cl
H
c
Br
D
D
D
D
D
H
diagonistic
H
a
H
b
H
c
B-O species
TBS
1.00
1.13
4500
4000
3500
3000
2500
2000
1500
1000
500
0
9.5
9.0
8.5
8.0
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6.5
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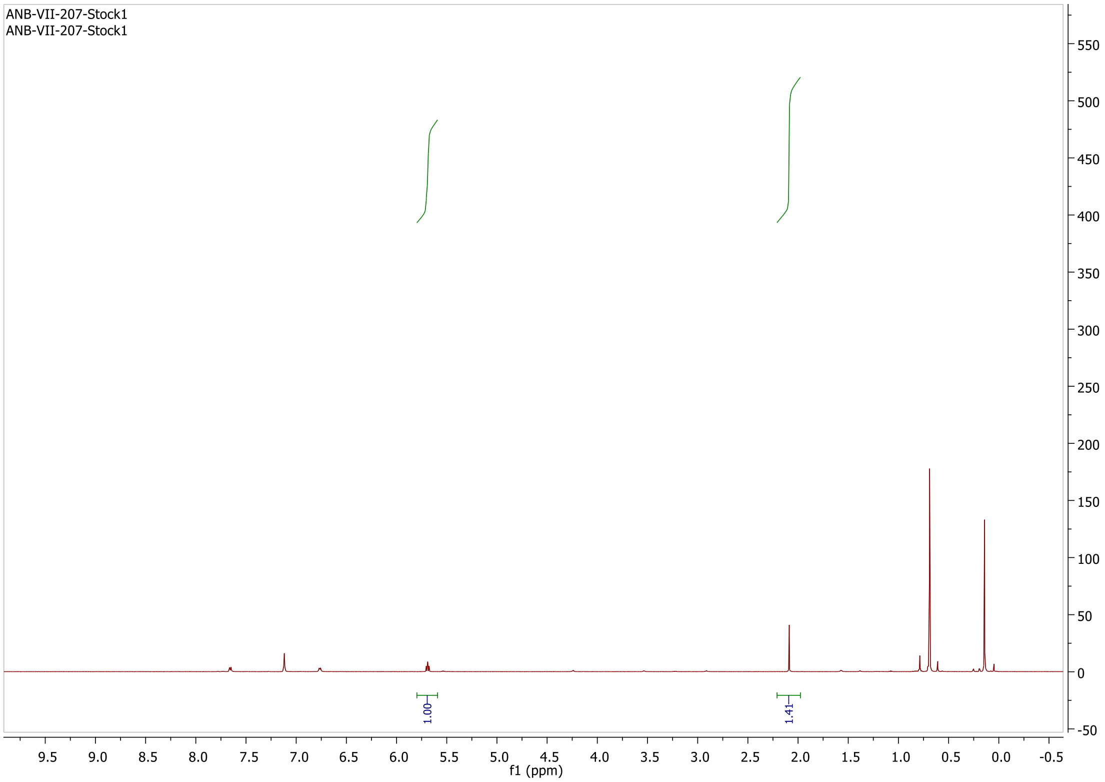
f1 (ppm)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ANB-VII-207-Stock1
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500
450
400
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300
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100
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0
-50
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
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1.5
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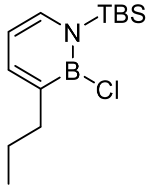
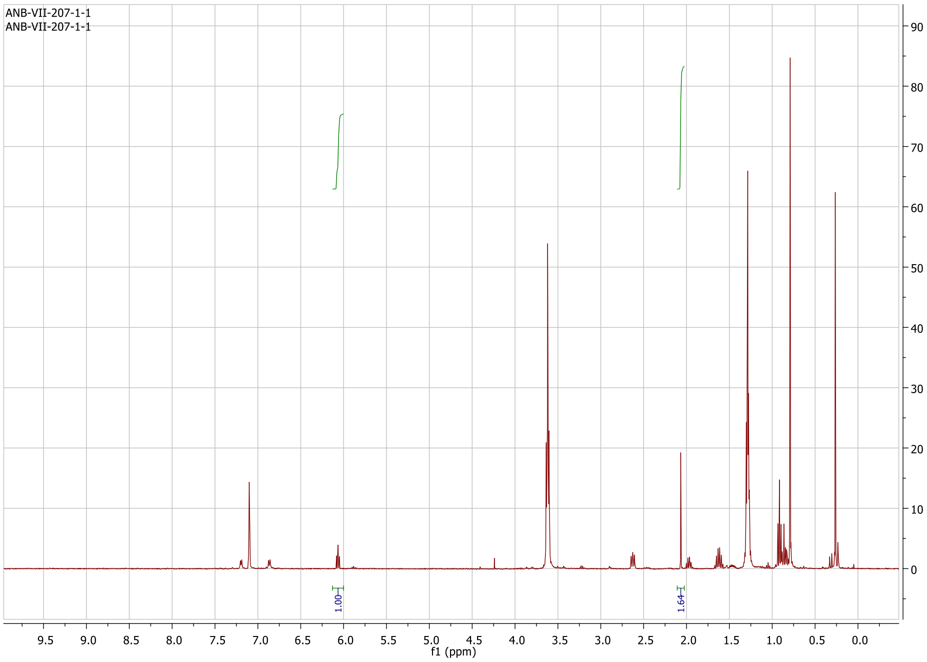
0.0
-0.5
f1 (ppm)

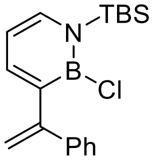
Compound 3a:



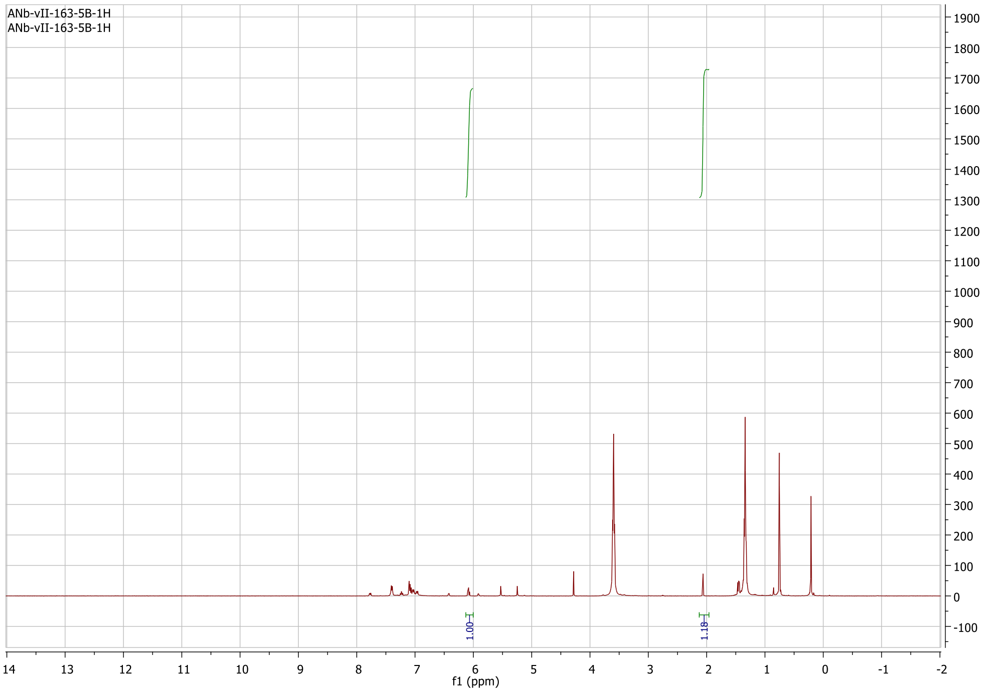
A vial was charged with 1.0 mL of THF and 300 μL of a stock solution of both azaborine **2** (302.5 mg : 3.0 mL; 30.3 mg, 0.099 mmol) and hexamethylbenzene (11.1 mg : 3.0 mL; 1.1 mg, 0.0068 mmol). Then, 0.05 equiv. of Pd(P-*t*-Bu$_3$)$_2$ (2.5 mg, 0.0050 mmol) in 0.5 mL of THF was added to this mixture followed by 1.5 equiv. propylzinc bromide (0.5 M solution, 0.30 mL, 0.15 mmol). The reaction was stirred for 3 hours, and an aliquot was quenched with ~0.1 mL CH$_2$Cl$_2$. The solvent was removed under a stream of nitrogen and NMR analysis of the crude reaction mixture indicated 86% yield (a second run gave 88% yield). The calibrated initial integrative ratio of **2** : internal standard = 1.00 : 1.41.



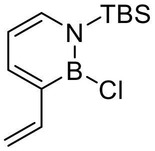
Compound 3b:



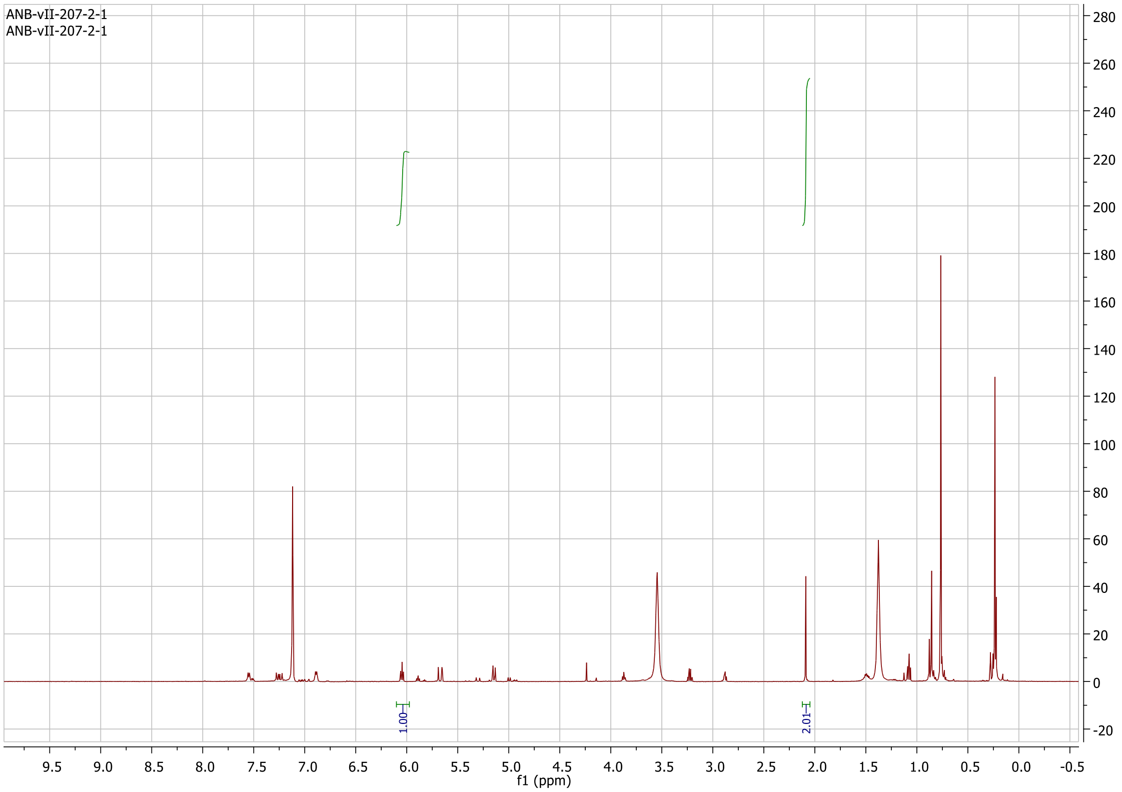
A vial was charged with 1.0 mL of THF and 200 µL of a stock solution of azaborine **2** (299.2 mg : 2.0 mL; 29.9 mg, 0.098 mmol) and hexamethylbenzene (10.4 mg : 2.0 mL; 1.0 mg, 0.0062 mmol). Then, 0.05 equiv. of Pd(P-*t*-Bu_3)$_2$ (2.5 mg, 0.0050 mmole) in 0.5 mL of THF was added to this mixture followed by 1.5 equiv. (1-phenylvinyl)zinc bromide (0.5 M solution, 0.3 mL, 0.15 mmol). The reaction was stirred for 3 hours, and an aliquot was quenched with ~0.1 mL CH_2Cl_2. The solvent was removed under a stream of nitrogen and NMR analysis of the crude reaction mixture indicated 97% yield (a second run gave 96% yield). The calibrated initial integrative ratio of **2** : internal standard = 1.00 : 1.13.



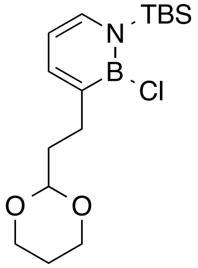
Compound 3c:



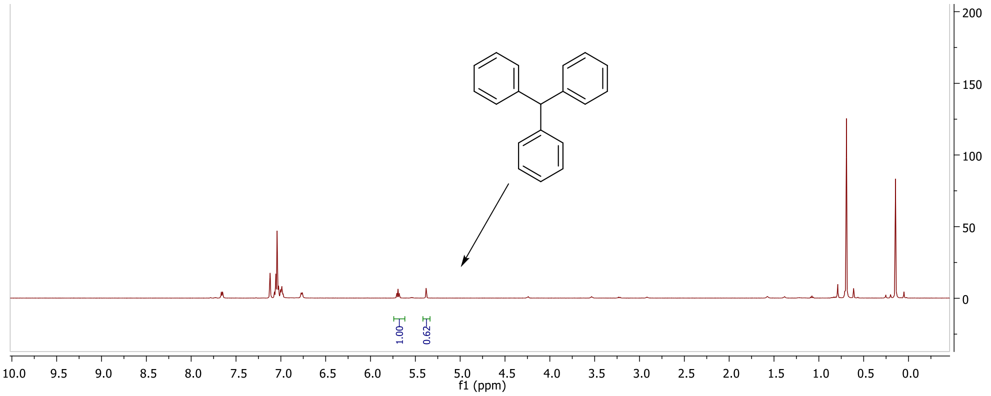
Vinylzinc bromide was prepared by stirring a solution of 1.2 equiv. of vinylmagnesium bromide (117 µL of 1.0 M solution, 0.117 mmol) with 2 equiv. of zinc bromide (51 mg, 0.23 mmol) for 2 hours in 1.0 mL THF. A vial was charged with 300 µL of a stock solution of azaborine **2** (302.5 mg : 3.0 mL; 30.3 mg, 0.099 mmol) and hexamethylbenzene (11.1 mg : 3.0 mL; 1.1 mg, 0.0068 mmol). Then, 0.05 equiv. of Pd(P-*t*-Bu$_3$)$_2$ (2.5 mg, 0.0050 mmol) in 0.5 mL of THF was added to the mixture, and the resulting solution was rinsed into the vinylzinc bromide slurry (total volume ~2.5 mL) with THF. The reaction was allowed to stir for 24 hours, and an aliquot was quenched with ~0.1 mL of CH$_2$Cl$_2$. The solvent was removed under a stream of nitrogen, and NMR analysis of the crude reaction mixture indicated 70% yield of the desired product (a second run gave 67% yield). The calibrated initial integrative ratio of **2** : internal standard = 1.00 : 1.41. This crude reaction mixture also contained ~20% of the *B*-vinyl species.

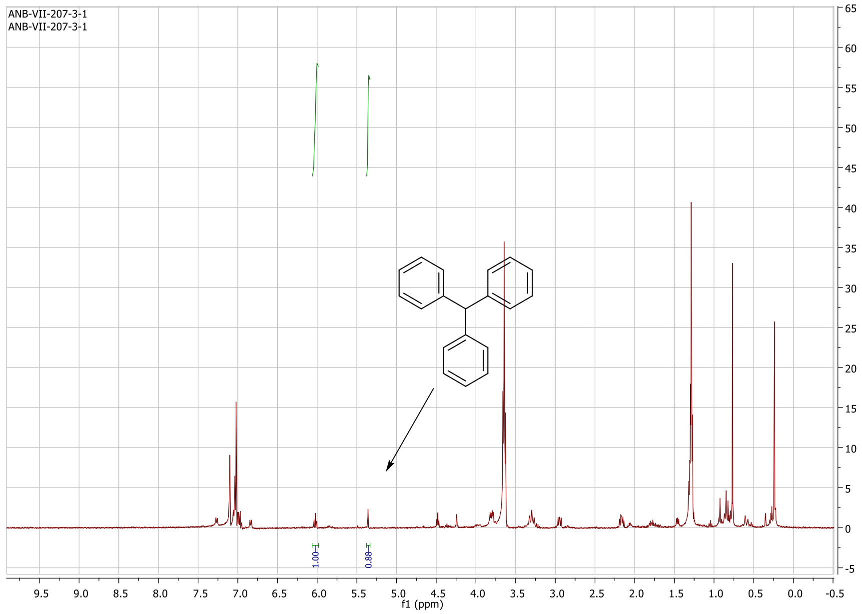


Compound 3d:

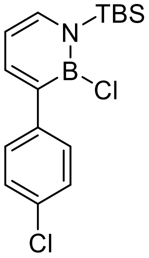


A vial was charged with 1.0 mL of THF and 300 µL of a stock solution of azaborine **2** (302.3 mg : 3.0 mL; 30.2 mg, 0.099 mmol) and triphenylmethane (121.1 mg : 3 mL; 12.1 mg, 0.0491 mmol). Then, 0.05 equiv. of Pd(P-*t*-Bu$_3$)$_2$ (2.5 mg, 0.0050 mmol) in 0.5 mL of THF was added to this mixture followed by 1.5 equiv. (2-(1,3-dioxan-2-yl)ethyl)zinc bromide (0.5 M solution, 0.3 mL, 0.15 mmol). The reaction was stirred for 3 hours and an aliquot was quenched with ~0.1 mL CH_2Cl_2. The solvent was removed under a stream of nitrogen and NMR analysis of the crude reaction mixture indicated 71% yield (a second run gave 67% yield). Note: triphenylmethane was used due to overlap of signals with hexamethylbenzene. The calibrated initial integrative ratio of **2** : internal standard = 1.00 : 0.62.

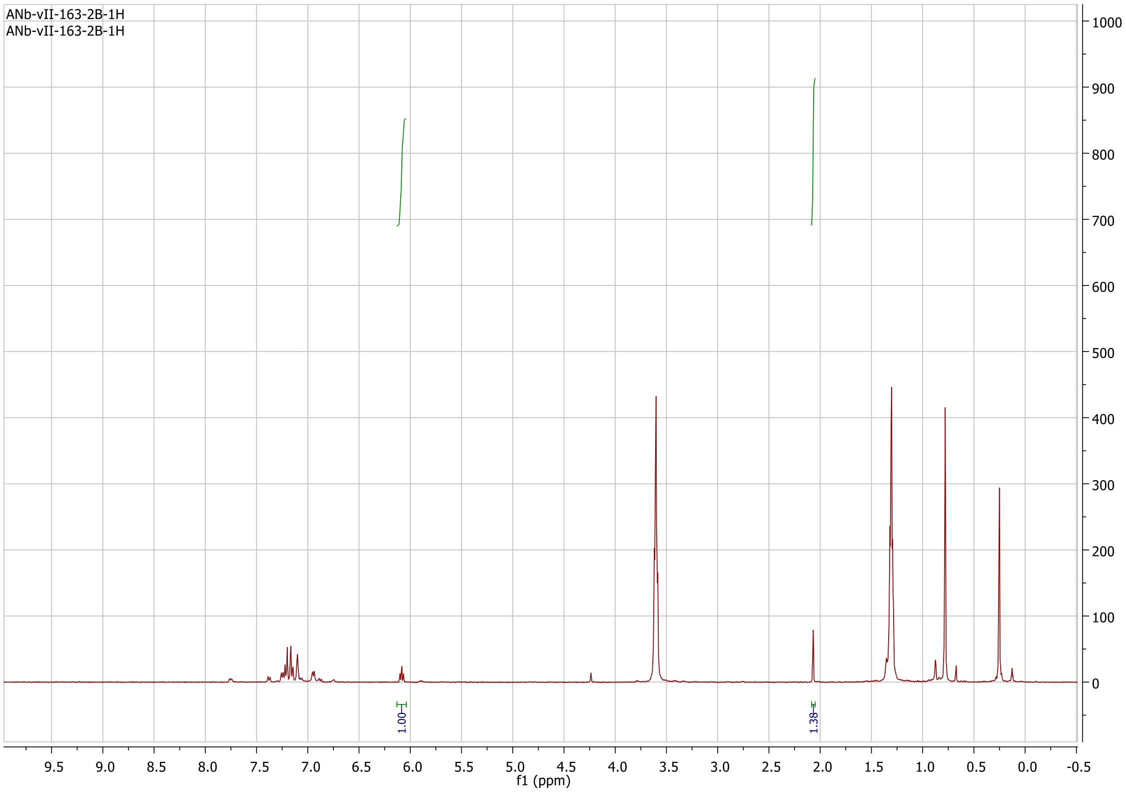




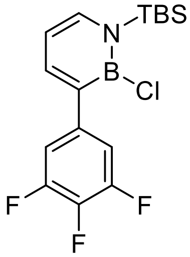
Compound 3e:



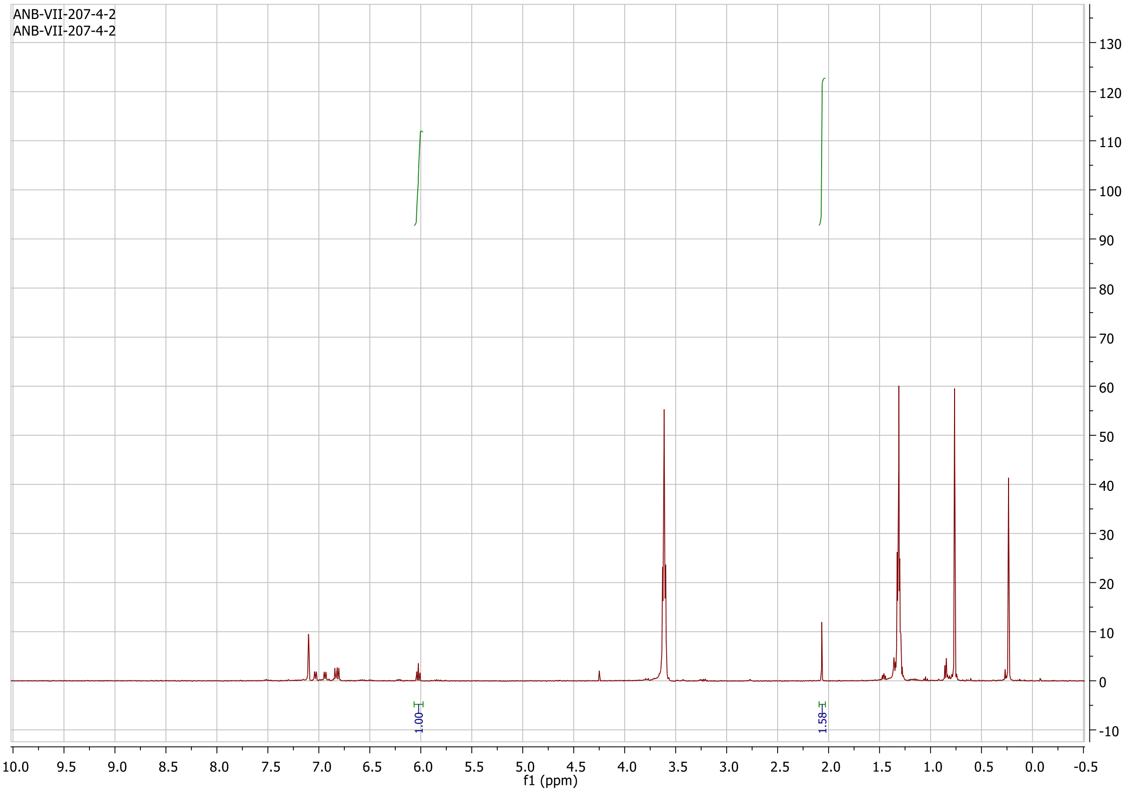
A vial was charged with 1.0 mL of THF and 200 µL of a stock solution of azaborine **2** (299.2 mg : 2.0 mL; 29.9 mg, 0.098 mmol) and hexamethylbenzene (10.4 mg : 2.0 mL; 1.0 mg, 0.0062 mmol). Then, 0.05 equiv. of Pd(P-*t*-Bu$_3$)$_2$ (2.5 mg, 0.0050 mmol) in 0.5 mL of THF was added to this followed by 1.5 equiv. (4-chloro)phenylzinc iodide (0.5 M solution, 0.3 mL, 0.15 mmol). The reaction was stirred for 3 hours and an aliquot was quenched with ~0.1 mL CH$_2$Cl$_2$. The solvent was removed under a stream of nitrogen, and NMR analysis of the crude reaction mixture indicated 83% yield (a second run gave 82% yield). The calibrated initial integrative ratio of **2** : internal standard = 1.00 : 1.13.



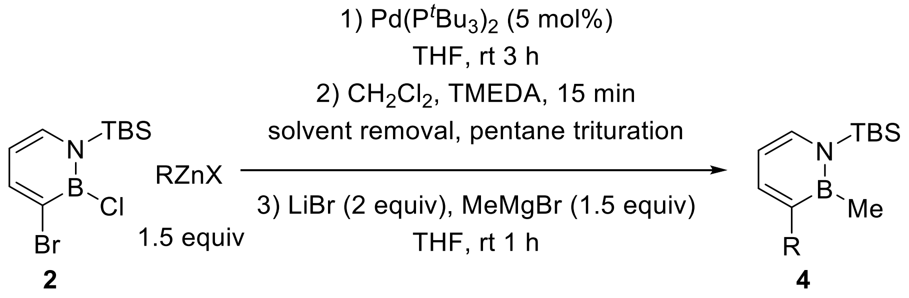
Compound 3f:



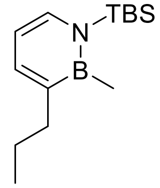
A vial was charged with 1.0 mL of THF and 300 µL of a stock solution of azaborine **2** (302.5 mg : 3.0 mL; 30.3 mg, 0.099 mmol) and hexamethylbenzene (11.1 mg : 3.0 mL; 1.1 mg, 0.0068 mmol). Then, 0.05 equiv. of Pd(P-*t*-Bu_3)$_2$ (2.5 mg, 0.0050 mmol) in 0.5 mL of THF was added to this followed by 1.5 equiv. (3,4,5-trifluorophenyl)zinc bromide (0.5 M solution, 0.3 mL, 0.15 mmol). The reaction was stirred for 3 hours and an aliquot was quenched with ~0.1 mL CH_2Cl_2. The solvent was removed under a stream of nitrogen and NMR analysis of the crude reaction mixture indicated 92% yield (a second run gave 89% yield). The calibrated initial integrative ratio of **2** : internal standard = 1.00 : 1.41.



Procedure for Isolated Yields of B-Me Azaborines 4a-4f (Table 2)

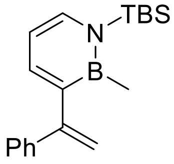


Compound 4a:



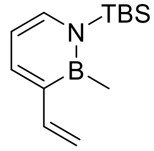
1.0 Equiv. of azaborine **2** (200 mg, 0.653 mmol) was dissolved in 3.0 mL of THF. To this mixture was added 0.05 equiv. (17.0 mg, 0.0326 mmol) of $Pd(P\text{-}t\text{-}Bu_3)_2$ in 1.0 mL THF followed by 1.5 equiv. of propylzinc bromide (2.0 mL of 0.5 M solution in THF, 1.0 mmol). The mixture was stirred for 3 hours, and then 0.5 mL of CH_2Cl_2 was added followed by 0.2 mL of TMEDA (1.3 mmol). After 15 minutes, the reaction was concentrated under reduced pressure. The remaining residue was triturated with four portions of ~2 mL of pentane and passed through an acrodisc. Upon solvent removal, NMR analysis showed clean conversion to the C3 substituted *B*-Cl compound. Then, 2 equiv. of lithium bromide (120 mg, 1.33 mmol) was added to the *B*-Cl intermediate, and the mixture was dissolved in 3.0 mL THF. Subsequently, 1.5 equiv. of methyl magnesium bromide solution (0.35 mL of 3.0 M solution in Et_2O) was added, and the mixture was stirred for 30 minutes. The reaction mixture was then passed directly through a plug of silica (~35 mL silica gel, eluent: Et_2O), and the solvents were removed under reduced pressure. The resulting oil was purified by column chromatography (~3 mL silica gel, eluent: pentane) to yield **4a** as a colorless oil: 122 mg, 75% yield (a second run gave 127 mg, 78% yield). *Note*: Compound **4a** is volatile so special care should be taken during solvent removal (significant amounts were of **4a** lost upon prolong exposure to high vacuum (75-150 mTorr)). ^1H NMR (500 MHz, CD_2Cl_2) δ 7.16 – 7.09 (m, 2H), 6.12 (t, J = 6.6 Hz, 1H), 2.47 – 2.37 (m, 2H), 1.50 – 1.41 (m, 2H), 1.05 – 0.81 (m, 12H), 0.74 (s, 3H), 0.46 (s, 6H). ^{11}B NMR (160 MHz, CD_2Cl_2) δ 40.5 (s). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 139.4, 136.5, 110.5, 38.5, 26.9, 25.2, 19.8, 14.6, -0.9. The carbons adjacent to boron were not observed. HRMS (DART+) calcd for $C_{14}H_{29}BNSi$ (M+1): 250.21623; found: 250.21640.

Compound 4b:



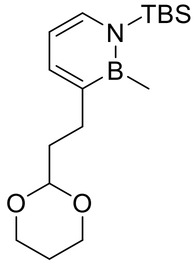
1.0 Equiv. of azaborine **2** (200 mg, 0.653 mmol) was dissolved in 3.0 mL of THF. To this mixture was added 0.05 equiv. (17.0 mg, 0.0326 mmol) of Pd(P-*t*-Bu$_3$)$_2$ in 1.0 mL THF followed by 1.5 equiv. of (1-phenylvinyl)zinc(II) bromide (2.0 mL of 0.5 M solution in THF, 1.0 mmol). The mixture was stirred for 3 hours, and then 0.5 mL of CH$_2$Cl$_2$ was added followed by 0.2 mL of TMEDA (1.3 mmol). After 15 minutes the reaction was concentrated under reduced pressure. The remaining residue was triturated with three portions of ~2 mL of pentane and passed through an acrodisc. Upon solvent removal, NMR analysis showed clean conversion to the C3 substituted *B*-Cl compound. Then, 2 equiv. of lithium bromide (120 mg, 1.33 mmol) was added to the *B*-Cl intermediate, and the mixture was dissolved in 3.0 mL THF. Subsequently, 1.5 equiv. of methyl magnesium bromide solution (0.35 mL of 3.0 M solution in Et$_2$O) was added, and the mixture was stirred for 30 minutes. The reaction mixture was passed directly through a plug of silica (~35 mL silica gel, eluent: CH$_2$Cl$_2$), and the solvents were removed under reduced pressure. The resulting oil was purified by column chromatography (silica gel, eluent: CH$_2$Cl$_2$) to yield **4b** as a yellow oil: 193.2 mg, 96% yield (a second run gave 199 mg, 98% yield). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.33 – 7.18 (m, 7H), 6.24 (t, *J* = 6.7 Hz, 1H), 5.44 (d, *J* = 1.9 Hz, 1H), 5.00 (t, *J* = 3.7 Hz, 1H), 0.90 (s, 9H), 0.44 (s, 6H), 0.41 (s, 3H). ^{11}B NMR (160 MHz, CD$_2$Cl$_2$) δ 40.2 (s). ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 155.1, 143.4, 141.4, 138.7, 128.5, 127.6, 127.4, 111.5, 110.5, 26.9, 19.8, -1.0. The carbons adjacent to boron were not observed. HRMS (DART+) calcd for $C_{19}H_{29}BNSi$ (M+1): 310.21623; found: 310.21612.

Compound 4c:



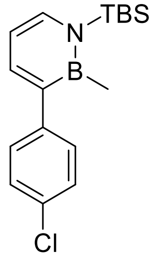
Vinylzinc bromide was generated from 1.02 equiv. vinylmagnesium bromide (660 µL of a 1.0 M solution, 0.660 mmol) and 2.04 equiv. zinc bromide (305 mg, 1.33 mmol) in 10.0 mL THF. In a separate vial 1.0 equiv. of azaborine **2** (200 mg, 0.653 mmol) was dissolved in 5.0 mL of THF. To this mixture was added 0.05 equiv. (17.0 mg, 0.0326 mmol) of Pd(P-*t*-Bu$_3$)$_2$ in 1.0 mL THF. The azaborine/catalyst mixture was rinsed into the vinylzinc bromide slurry with an additional 2.0 mL of THF (total volume 18.0 mL THF). The mixture was stirred for 20 hours. The reaction was diluted with 30 mL pentane and passed through an acrodisc. Then, 0.5 mL of CH_2Cl_2 was added to quench the remaining catalyst. After solvent removal and a second pentane "extraction", NMR analysis showed a relatively clean conversion to the C3 substituted *B*-Cl compound **3c**. 2 Equiv. of lithium bromide (120 mg, 1.33 mmol) was added to the *B*-Cl compound, and the mixture was dissolved in 3.0 mL THF. Subsequently, 1.5 equiv. of methyl magnesium bromide solution (0.25 mL of 3.0 M solution in Et_2O) was added, and the mixture was stirred for one hour. The reaction mixture was passed directly through a plug of alumina (~35 mL alumina, eluent: Et_2O), and the solvents were removed under reduced pressure. The resulting oil was purified by column chromatography (~1.5 mL alumina, eluent: pentane) to yield **4c** as a colorless oil: 74.8 mg, 48% yield (a second run gave 81.2 mg, 53% yield). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.50 (d, *J* = 6.7 Hz, 1H), 7.26 (d, *J* = 6.7 Hz, 1H), 6.91 (dd, *J* = 17.5, 10.8 Hz, 1H), 6.23 (t, *J* = 6.7 Hz, 1H), 5.37 (dd, *J* = 17.5, 2.0 Hz, 1H), 5.01 (dd, *J* = 10.8, 1.9 Hz, 1H), 0.94 (s, 9H), 0.82 (s, 3H), 0.48 (s, 6H). ^{11}B NMR (192 MHz, CD_2Cl_2) δ 40.3 (s). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 140.9, 138.9, 137.8, 111.7, 110.9, 26.9, 19.7, -0.9. The carbons adjacent to boron were not observed. HRMS (DART+) calcd for $C_{13}H_{25}BNSi$ (M+1): 234.18493; found: 234.18529.

Compound 4d:



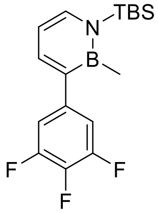
1.0 Equiv. of azaborine **2** (200 mg, 0.653 mmol) was dissolved in 3.0 mL of THF. To this mixture was added 0.05 equiv. (17.0 mg, 0.0326 mmol) of Pd(P-*t*-Bu$_3$)$_2$ in 1.0 mL THF followed by 1.5 equiv. of (2-(1,3-dioxan-2-yl)ethyl)zinc bromide (2.0 mL of 0.5 M solution in THF, 1.0 mmol). The mixture was stirred for 3 hours, and then 0.5 mL of CH_2Cl_2 was added followed by 0.2 mL of TMEDA (1.3 mmol). After 15 minutes the reaction was concentrated under reduced pressure. The resulting residue was triturated with four portions of ~2 mL of pentane and passed through an acrodisc. Upon solvent removal, NMR analysis showed clean conversion to the C3 substituted *B*-Cl compound **3d**. Then, 2 equiv. of lithium bromide (120 mg, 1.33 mmol) was added to the *B*-Cl intermediate, and the mixture was dissolved in 3.0 mL THF. Subsequently, 1.5 equiv. of methyl magnesium bromide solution (0.35 mL of 3.0 M solution in Et_2O) was added, and the mixture was stirred for 30 minutes. The reaction mixture was passed directly through a plug of silica gel (~35 mL silica gel, eluent: Et_2O), and the solvents were removed under reduced pressure. The resulting oil was purified by column chromatography (~3 mL silica gel, eluent: CH_2Cl_2) to yield **4d** as a colorless oil: 135.4 mg, 65% yield (a second run gave 140.2 mg, 67% yield). *Note*: Compound **4d** may be unstable upon extended exposure to large excess of silica gel. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.17 – 7.09 (m, 2H), 6.12 (t, *J* = 6.6 Hz, 1H), 4.50 (t, *J* = 5.2 Hz, 1H), 4.06 (dd, *J* = 10.7, 5.0 Hz, 2H), 3.73 (td, *J* = 12.3, 2.2 Hz, 2H), 2.55 – 2.43 (m, 2H), 2.11 – 1.89 (m, 1H), 1.72 – 1.58 (m, 2H), 1.32 (dd, *J* = 13.4, 1.2 Hz, 1H), 0.91 (s, 9H), 0.74 (s, 3H), 0.46 (s, 6H). ^{11}B NMR (160 MHz, CD_2Cl_2) δ 40.5 (s). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 139.5, 136.7, 110.5, 102.8, 67.4, 37.4, 30.3, 26.9, 26.6, 19.7, -0.9. The carbons adjacent to boron were not observed. HRMS (DART+) calcd for $C_{17}H_{33}BNO_2Si$ (M+1): 322.23736; found: 322.23852.

Compound 4e:



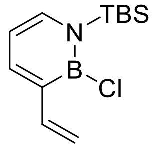
1.0 Equiv. of azaborine **2** (200 mg, 0.653 mmol) was dissolved in 3.0 mL of THF. To this mixture was added 0.05 equiv. (17.0 mg, 0.0326 mmol) of Pd(P-*t*-Bu$_3$)$_2$ in 1.0 mL THF followed by 1.5 equiv. of (4-chlorophenyl)zinc iodide (2.0 mL of 0.5 M solution in THF, 1.0 mmol). The mixture was stirred for 3 hours, and then 0.5 mL of CH_2Cl_2 was added followed by 0.2 mL of TMEDA (1.3 mmol). After 15 minutes the reaction was concentrated under reduced pressure. The resulting residue was triturated with four portions of ~2 mL of pentane and passed through an acrodisc. Upon solvent removal, NMR analysis showed clean conversion to the C3 substituted *B*-Cl compound **3e**. Then, 2 equiv. of lithium bromide (120 mg, 1.33 mmol) was added to the *B*-Cl intermediate, and the mixture was dissolved in 3.0 mL THF. Subsequently, 1.5 equiv. of methyl magnesium bromide solution (0.30 mL of 3.0 M solution in Et_2O) was added, and the mixture was stirred for one hour. The reaction mixture was passed directly through a plug of silica gel (~35 mL silica gel, eluent: Et_2O), and the solvents were removed under reduced pressure. The remaining residue was purified by column chromatography (~3 mL silica gel, eluent: pentane) to yield **4e** as a white solid: 106.0 mg, 51% yield (90% purity) (a second run gave 104.4 mg, 50% yield (90% purity). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.36 – 7.25 (m, 4H), 7.23 – 7.16 (m, 2H), 6.31 (t, *J* = 6.7 Hz, 1H), 0.95 (s, 9H), 0.74 (s, 3H), 0.51 (s, 6H). ^{11}B NMR (160 MHz, CD_2Cl_2) δ 39.9. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 145.8, 141.4, 139.0, 131.5 130.5, 128.4, 110.8, 26.9, 19.8, -0.9. The carbons adjacent to boron were not observed. HRMS (DART+) calcd for $C_{17}H_{26}BClNSi$ (M+1): 318.16161; found: 318.16265.

Compound 4f:



1.0 Equiv. of azaborine **2** (200 mg, 0.653 mmol) was dissolved in 3.0 mL of THF. To this mixture was added 0.05 equiv. (17.0 mg, 0.0326 mmol) of Pd(P-*t*-Bu$_3$)$_2$ in 1.0 mL THF followed by 1.5 equiv. of (3,4,5-trifluorophenyl)zinc bromide (2.0 mL of 0.5 M solution in THF, 1.0 mmol). The mixture was stirred for 3 hours, and then 0.5 mL of CH_2Cl_2 was added followed by 0.2 mL of TMEDA (1.3 mmol). After 15 minutes the reaction was concentrated under reduced pressure. The resulting residue was triturated with four portions of ~2 mL of pentane and passed through an acrodisc. Upon solvent removal, NMR analysis showed clean conversion to the C3 substituted *B*-Cl compound **3f**. Then, 2 equiv. of lithium bromide (120 mg, 1.33 mmol) was added to the *B*-Cl intermediate, and the mixture was dissolved in 3.0 mL THF. Subsequently, 0.92 equiv. of methyl magnesium bromide solution (0.20 mL of 3.0 M solution in Et_2O) was added, and the mixture was stirred for 30minutes. The reaction mixture was passed directly through a plug of silica gel (~35 mL silica gel, eluent: Et_2O), and the solvents were removed under reduced pressure. The resulting oil was purified by column chromatography (~3 mL silica gel, eluent: CH_2Cl_2) to yield **4f** as a colorless oil: 195.0 mg, 89% yield (a second run gave 195.1 mg, 89% yield). *Note*: This compound was especially sensitive to excess turbo Grignard reagent (when higher amounts were used, a large portion of 4-coordinate boron species was observed from overaddition) and so a limiting amount of methylmagnesium bromide was used. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.37 (dd, *J* = 6.8, 1.1 Hz, 1H), 7.32 (dd, *J* = 6.7, 1.1 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.31 (t, *J* = 6.7 Hz, 1H), 0.95 (s, 9H), 0.75 (s, 3H), 0.51 (s, 6H). ^{11}B NMR (192 MHz, CD_2Cl_2) δ 39.7 (s). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 151.9 (dd, J_{CF} = 9.9, 4.3 Hz), 150.4 (dd, J_{CF} = 9.8, 4.5 Hz), 143.7 (s), 141.9 (s), 139.8 (s), 112.9 (dd, J_{CF} = 16.3, 4.0 Hz), 110.6 (s), 26.9 (s), 19.8 (s), -0.9 (s). HRMS (DART+) calcd for $C_{17}H_{24}BF_3NSi$ (M+1): 338.17232; found: 338.17327.

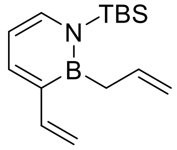
Large-Scale Isolation of Compound 3c



Vinylzinc bromide was prepared by stirring 1.2 equiv. vinylmagnesium bromide (7.8 mL of 1.0 M solution in THF, 7.8 mmol) with 2.4 equiv. zinc bromide (3.53 g, 15.7 mmol) in 125 mL THF for 2 hours at room temperature. 1.0 Equiv. of **2** (2.00 g, 6.54 mmol) and 0.05 equiv. of $Pd(P(t\text{-}Bu)_3)_2$ were combined in 20 mL of THF and added dropwise to the suspension containing the zinc reagent. The resulting mixture was allowed to stir at room temperature in a glovebox for 24 h. Then, 125 mL of pentane was added to this suspension, and this mixture was passed through an acrodisc. The solvent was removed under reduced pressure, and the resulting oil was triturated with 25 mL of pentane. The pentane suspension was passed through an acrodisc, and the solvents were removed. The resulting crude material was subjected to short-path vacuum distillation (300 mTorr, 85-100 ^{o}C) to yield **3c** as a clear colorless oil in a single fraction (870 mg, 52%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 6.7 Hz, 1H), 7.25 (d, *J* = 6.6 Hz, 1H), 6.93 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.35 (t, *J* = 6.7 Hz, 1H), 5.59 (dd, *J* = 17.6, 1.7 Hz, 1H), 5.10 (dd, *J* = 10.9, 1.7 Hz, 1H), 0.95 (s, 9H), 0.56 (s, 6H). ^{11}B NMR (160 MHz, CD_2Cl_2) δ 34.9. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.5, 139.1, 138.2, 112.9, 111.9, 27.0, 19.8, -1.1. The quaternary carbon adjacent to boron was not observed. HRMS (DART+) calcd for $C_{12}H_{22}BClNSi$ (M+1): 254.13031; found: 254.13037.

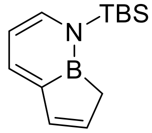
Synthesis of Compound 5 (Scheme 3)

Compound 7:



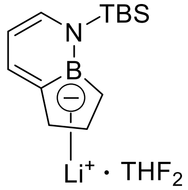
1.1 Equiv. of allylmagnesium bromide (1.0 mL of 1.0 M solution in THF, 1.0 mmol) was added dropwise to a solution of **3c** (231 mg, 0.914 mmol) in 5.0 mL THF at –20 °C. The solution was warmed to room temperature and stirred for 2 hours. Then, 200 μL of TMS-Cl was added, followed by removal of the solvent under reduced pressure. The resulting crude mixture was triturated with pentane and passed through an acrodisc. Removal of the solvents yielded **7** as a colorless oil (222.2 mg, 94% yield). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.62 (d, J = 6.7 Hz, 1H), 7.30 (d, J = 6.7 Hz, 1H), 7.01 (dd, J = 17.4, 10.7 Hz, 1H), 6.30 (t, J = 6.7 Hz, 1H), 5.96 (ddt, J = 16.1, 11.1, 6.8 Hz, 1H), 5.42 (dd, J = 17.4, 1.9 Hz, 1H), 5.00 (dd, J = 10.7, 1.8 Hz, 1H), 4.96 – 4.87 (m, 2H), 2.30 (d, J = 6.8 Hz, 2H), 0.92 (s, 9H), 0.53 (s, 6H). ^{11}B NMR (160 MHz, CD_2Cl_2) δ 39.1. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.4, 139.0, 138.3, 138.2, 115.1, 111.6, 111.8, 26.9, 19.5, -0.8. The carbons adjacent to boron were not observed. HRMS (DART+) calcd for $C_{15}H_{27}BNSi$ (M+1): 260.20058; found: 260.20166.

Compound 8:



1.0 Equiv. of compound **7** (92.5 mg, 0.357 mmol) was dissolved in 5.0 mL of CH_2Cl_2 and 0.05 equiv. of Grubbs 1st generation catalyst (15.0 mg, 0.0178 mmol) was added in one portion. The resulting purple solution was stirred at room temperature for 2 hours. Then, the solvent was removed under reduced pressure, and the product was isolated by filtration through neutral alumina (eluent: pentane). (Colorless oil, 49.5 mg, 60% yield, ~ 95% purity). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.27 (d, J = 6.1 Hz, 1H), 7.11 (d, J = 6.7 Hz, 1H), 6.93 – 6.85 (m, 1H), 6.48 – 6.40 (m, 1H), 6.32 (dd, J = 9.8, 3.6 Hz, 1H), 1.89 (s, J = 2.4 Hz, 2H), 0.89 (s, 9H), 0.48 (s, 6H). ^{11}B NMR (160 MHz, CD_2Cl_2) δ 43.8. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 138.5, 136.4, 133.6, 129.2, 112.6, 26.6, 19.2, -3.7. The carbons adjacent to boron were not observed. HRMS (DART+) calcd for $C_{19}H_{23}BNSi$ (M+1): 232.16928; found: 232.17023.

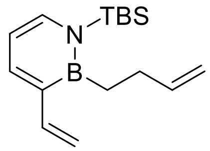
Compound 5:



Lithium tetramethylpiperidide was freshly generated by treatment of 1.2 equiv. of 2,2-6,6-tetramethylpiperidine (40.0 mg, 0.283 mmol) in 1.0 mL THF with *n*-BuLi (113 μL of 2.5 M solution in hexanes, 0.283 mmol) for 15 minutes with stirring, resulting in a blood red solution. This solution was added in one portion to a solution of **8** (54.5 mg, 0.236 mmol) in 2.0 mL THF at –20 °C. The mixture was allowed to warm to room temperature and was stirred until judged complete by ^{11}B NMR (approximately 40 minutes). The solvent was removed, and the resulting solid was washed thoroughly with a 1:1 diethyl ether : pentane mixture at room temperature. The resulting orange solid (43.5 mg, 78%) generates a red solution upon dissolution in THF for analysis. Crystals suitable for x-ray diffraction were grown in a –30 ^{o}C freezer from a THF/pentane (1:1) solution. ^{1}H NMR (600 MHz, THF) δ 7.38 – 7.36 (m, 2H), 7.03 (d, *J* = 6.3 Hz, 1H), 6.19 (t, *J* = 6.4 Hz, 1H), 5.62 (dd, *J* = 3.6, 1.1 Hz, 1H), 4.52 (d, *J* = 5.6 Hz, 1H), 0.92 (s, 9H), 0.58 (s, 6H). ^{11}B NMR (192 MHz, THF) δ 28.8. ^{13}C NMR (151 MHz, THF) δ 142.6, 126.2, 122.9, 107.3, 88.5, 26.4, 18.9, -4.1. The carbons adjacent to boron were not observed.

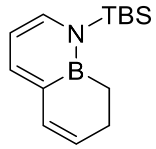
Synthesis of Compound 6 (Scheme 4)

Compound 9:



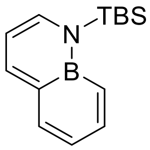
4.0 Equiv. of homoallylmagnesium bromide (3.0 mL of 0.5 M solution in Et_2O, 1.5 mmol) was added in one portion to 1.0 equiv. of **3c** (100 mg, 0.394 mmol) at room temperature. The solution was stirred for 12 h at which point approximately half of the solvent was removed and magnesium salts were precipitated with the addition of 10 mL pentane. The mixture was passed through a glass frit followed by an acrodisc, and the solvents were removed from the filtrate under reduced pressure. The resulting crude material was purified by passing through a pipette plug of silica gel (eluent: pentane) to yield **9** as a colorless oil, 65 mg (60% yield). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.58 (d, *J* = 6.7 Hz, 1H), 7.26 (d, *J* = 6.6 Hz, 1H), 6.94 (dd, *J* = 17.4, 10.8 Hz, 1H), 6.26 (t, *J* = 6.7 Hz, 1H), 5.96 (ddt, *J* = 16.6, 10.2, 6.2 Hz, 1H), 5.41 (dd, *J* = 17.3, 1.9 Hz, 1H), 5.11 – 4.95 (m, 2H), 4.91 (ddd, *J* = 10.1, 1.8, 1.1 Hz, 1H), 2.17 – 2.00 (m, 2H), 1.45 – 1.36 (m, 2H), 0.91 (s, 9H), 0.50 (s, 6H). ^{11}B NMR (160 MHz, CD_2Cl_2) δ 40.2. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 142.34, 140.4, 138.9, 138.2, 112.7, 111.4, 111.3, 31.6, 26.9, 19.4, -0.9. The carbons adjacent to boron were not observed. HRMS (DART+) calcd for $C_{16}H_{29}BNSi$ (M+1): 274.21623; found: 274,21728.

Compound 10:



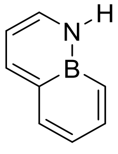
1.0 Equiv. of compound **9** (182 mg, 0.668 mmol) was dissolved in 5.0 mL of CH_2Cl_2 and 0.05 equiv. of Grubbs 1st generation catalyst (27.4 mg, .0334 mmol) was added in one portion. The resulting solution was stirred at room temperature for 25 minutes. The solvent was removed under reduced pressure, and the resulting crude mixture was purified by filtration through neutral alumina (eluent: pentane) to give **10** as a colorless oil (116.1 mg, 71% yield). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.07 (d, *J* = 6.8 Hz, 1H), 6.94 (d, *J* = 6.3 Hz, 1H), 6.46 (d, *J* = 9.6 Hz, 1H), 6.16 (t, *J* = 6.6 Hz, 1H), 5.87 – 5.75 (m, 1H), 2.32 (dt, *J* = 7.6, 6.0 Hz, 2H), 1.41 (t, *J* = 7.7 Hz, 2H), 0.94 (s, 9H), 0.44 (s, 6H). ^{11}B NMR (160 MHz, CD_2Cl_2) δ 41.5. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 137.0, 134.9, 132.7, 130.2, 111.6, 26.7, 24.9, 19.4, -1.8. The carbons adjacent to boron were not observed. HRMS (DART+) calcd for $C_{14}H_{25}BNSi$ (M+1): 246.18493; found: 246.18617.

Compound 11:



1.0 Equiv. of compound **10** (455 mg, 1.90 mmol) was mixed with 2.4 equiv. of cyclohexene (375 mg, 4.57 mmol) and 0.1 equiv. of 10 wt% palladium on carbon (200 mg, 0.187 mmol) in 30 mL of toluene, and the mixture was refluxed for 72 hours. Upon completion the reaction was passed through an acrodisc, and the solids were washed with 50 mL THF. The resulting solution was concentrated under reduced pressure. *Note:* A significant amount of reduced product (alkene to alkane) was observed (^{11}B NMR ~40, PDT:reduced = 1.0:0.8). The resulting crude mixture was purified by column chromatography (neutral alumina, ~20 mL eluent: pentane:Et$_2$O) to yield **11** as an off-white solid (190.9 mg, 41%). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 8.33 (d, *J* = 7.0 Hz, 1H), 8.00 (d, *J* = 6.2 Hz, 1H), 7.75 (dd, *J* = 11.6, 6.4 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.35 (dd, *J* = 11.7, 0.7 Hz, 1H), 6.99 – 6.90 (m, 2H), 0.94 (s, 9H), 0.71 (s, 6H). ^{11}B NMR (160 MHz, CD$_2$Cl$_2$) δ 29.5. ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 146.7, 142.9, 140.6, 132.7, 123.5, 113.2, 26.9, 19.1, -1.1. The carbons adjacent to boron were not observed. HRMS (DART+) calcd for C$_{14}$H$_{23}$BNSi (M+1): 244.16928; found: 244.16911.

Compound 6:



Compound **11** (40.0 mg, 0.164 mmol) was dissolved in 3.0 mL of THF. 1.05 equiv. of a 1.0 M TBAF solution (175 μL, 0.175 mmol) was added, and the mixture was stirred for 10 minutes at room temperature. At the conclusion of the reaction, the solvent was removed under reduced pressure. The resulting crude material was purified by column chromatography (silica gel, eluent Et$_2$O) to yield **6** a sublimable white crystalline solid (21.2 mg, quantitative yield after an extended period under high vacuum). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 9.31 (t, *J* = 53.8 Hz, 1H), 8.41 (d, *J* = 7.1 Hz, 1H), 7.94 (t, *J* = 7.1 Hz, 1H), 7.82 (dd, *J* = 10.4, 6.1 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 11.3 Hz, 1H), 7.05 (dd, *J* = 8.4, 6.4 Hz, 1H), 6.93 (t, *J* = 6.6 Hz, 1H). ^{11}B NMR (160 MHz, CD$_2$Cl$_2$) δ 26.7. ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 145.7, 141.7, 136.9, 131.7, 126.7 (br), 124.8, 112.2. The quaternary carbon adjacent to boron was not observed. HRMS (DART+) calcd for C$_8$H$_9$BN (M+1): 130.08280; found: 130.08289.

Procedure for the Determination of the Quantum Yield of 6[1]:

Photoluminescence quantum yield, Φ, was measured according to the principles outlined in "*A Guide to Recording Fluorescence Quantum Yields"* from Horiba Inc. Measurements were taken in degassed cyclohexane with constant slit widths (3 nm) with an excitation wavelength of 350 nm and measurement and integration from 360-550 nm for all compounds measeured. Two compounds of known quantum yield in cyclohexane (anthracene ($\Phi = 0.36$[2]) and 9-10-diphenyl anthracene ($\Phi=0.97$[3])) were used to calibrate the measurement following the outlined procedure and equations below.

$$\boldsymbol{\Phi_{\text{standard1}}/\Phi_{\text{standard2}} \sim (\text{slope}_{\text{standard1}}/\text{slope}_{\text{standard2}})}$$

All compounds were excited at 350 nm at different concentrations to have a range of absorbance values below 0.1. A linear response ($R^2 \geq 0.95$) of absorbance vs. integrated emission over 5 points with a zero intercept indicated reliable data. The quantum yield was calculated from the following relationship

$$\boldsymbol{\Phi_{\text{azaborine}} = \Phi_{\text{standard}}(\text{slope}_{\text{azaborine}}/\text{slope}_{\text{standard}})}$$

where $\text{slope}_{\text{azaborine}}$ is the slope of the linear plot of absorbance vs. integrated emission for the azaborine sample and $\text{slope}_{\text{standard}}$ is the slope of the linear plot of absorbance vs. integrated fluorescence for calibrated 9,10 diphenylanthracene sample. Since the solvent was always the same, no correction factor for the refractive index of the solvent was necessary. For the calibration run, the slopes of the two standards (anthracene and 9,10-diphenylanthracene) were compared with the above relationship and an agreement within 10% of the published quantum yields was considered to be good data. Upon collection of reliable calibration data, the quantum yield of compound **6** was measured under identical conditions and was found to be ~0.01.

Using

$$\boldsymbol{\Phi_{\text{standard1}}/\Phi_{\text{standard2}} \sim (\text{slope}_{\text{standard1}}/\text{slope}_{\text{standard2}})}$$

(actual values) $.36/.97 = 2.235\text{E}10 / 7.767\text{E}9$

$.371 = .348$ These are within 10% of each other, so valid method.

Using

$$\boldsymbol{\Phi_{\text{azaborine}} = \Phi_{\text{standard}}(\text{slope}_{\text{azaborine}}/\text{slope}_{\text{standard}})}$$

$X = .97\ (2.47\text{E}8/2.24\text{E}10)$

$X = .011$

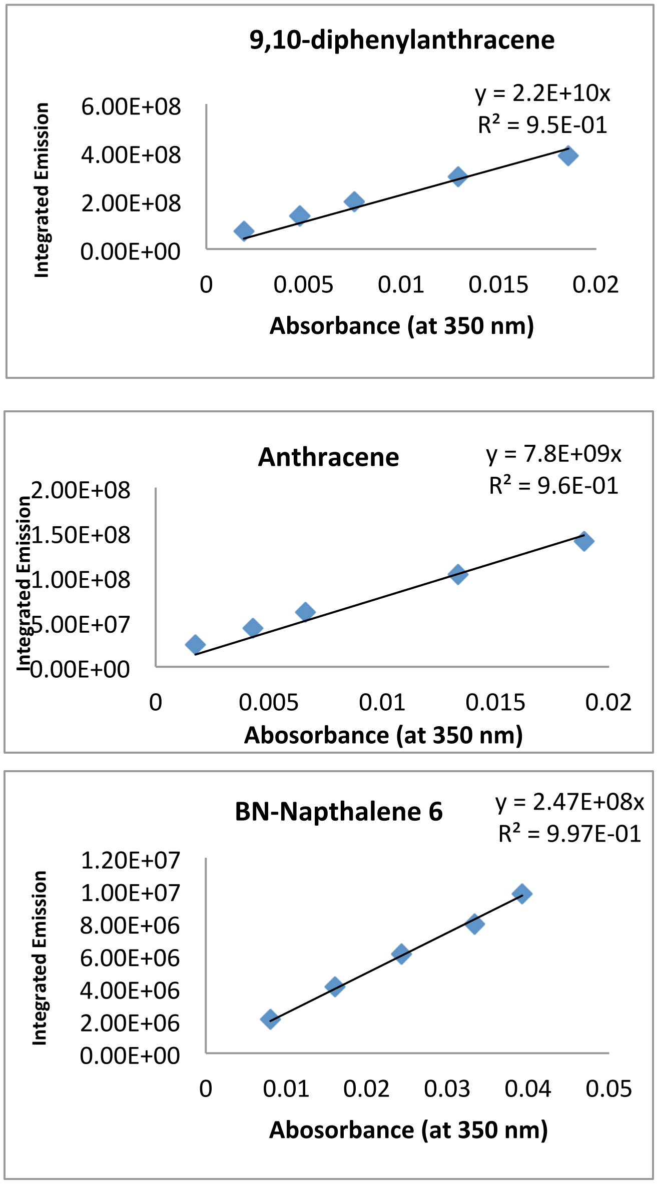
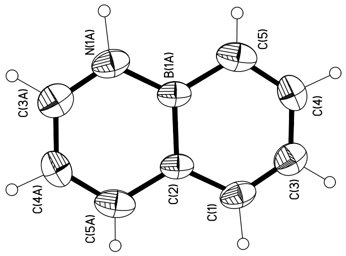


Figure SI-1: Integrated fluorescence of 9,10-diphenylanthracene, anthracene, and compound **6** taken at constant slit width in cyclohexane at various concentrations with an excitation wavelength of 350 nm and fluorescence data collected from 360-550 nm integrating over the whole spectrum.

Table SI-1 Crystal data and structure refinement for compound 5.

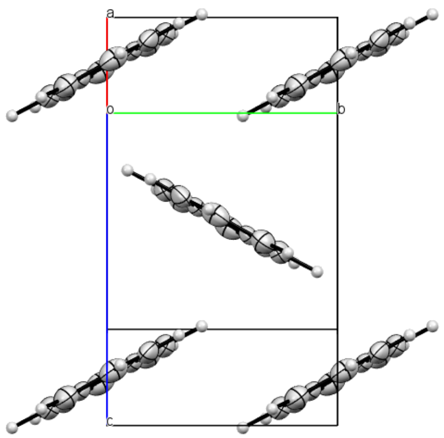
Identification code	C13H21BLiNSi(C4H8O)2	
Empirical formula	C21 H37 B Li N O2 Si	
Formula weight	381.35	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.6489(4) Å	α= 90°
	b = 17.3794(8) Å	β= 96.646(2)°
	c = 17.2195(8) Å	γ = 90°
Volume	2273.66(19) Å^3	
Z	4	
Density (calculated)	1.114 Mg/m^3	
Absorption coefficient	1.005 mm^{-1}	
F(000)	832	
Crystal size	0.480 x 0.170 x 0.060 mm^3	
Theta range for data collection	3.626 to 66.641°	
Index ranges	-8<=h<=8, 0<=k<=20, 0<=l<=20	
Reflections collected	4005	
Independent reflections	4005 [R(int) = 0.0714]	
Completeness to theta = 66.750°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.4386	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4005 / 3 / 276	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0551, wR2 = 0.1555	
R indices (all data)	R1 = 0.0616, wR2 = 0.1645	
Extinction coefficient	na	
Largest diff. peak and hole	0.480 and -0.236 e.Å^{-3}	

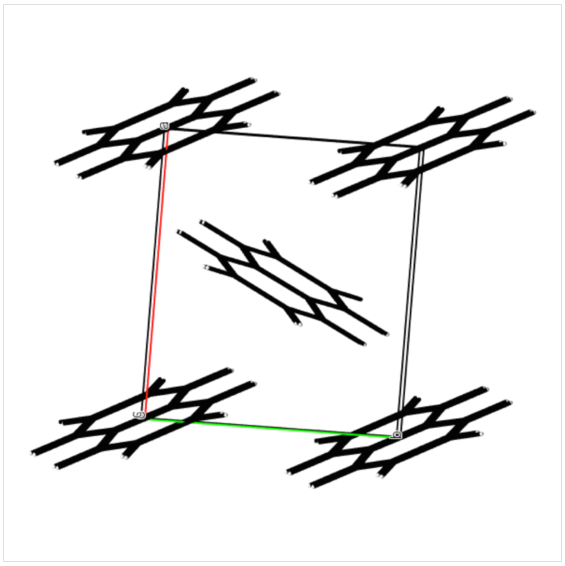
Table SI-2. Crystal data and structure refinement for Compound 6.



Identification code	C8H8BN	
Empirical formula	C8 H8 B N	
Formula weight	128.96	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.1542(6) Å	α = 90°
	b = 5.7395(4) Å	β = 107.059(6)°
	c = 7.7590(5) Å	γ = 90°
Volume	347.15(4) Å^3	
Z	2	
Density (calculated)	1.234 Mg/m^3	
Absorption coefficient	0.541 mm^{-1}	
F(000)	136	
Crystal size	0.120 x 0.040 x 0.030 mm^3	
Theta range for data collection	5.675 to 66.487°	
Index ranges	-9<=h<=9, -6<=k<=6, -9<=l<=9	
Reflections collected	3226	
Independent reflections	616 [R(int) = 0.0336]	
Completeness to theta = 67.679∞	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6336	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	616 / 0 / 62	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0566, wR2 = 0.1557	
R indices (all data)	R1 = 0.0666, wR2 = 0.1641	
Extinction coefficient	na	
Largest diff. peak and hole	0.497 and -0.186 e.Å^{-3}	

Packing Diagram for Compound 6



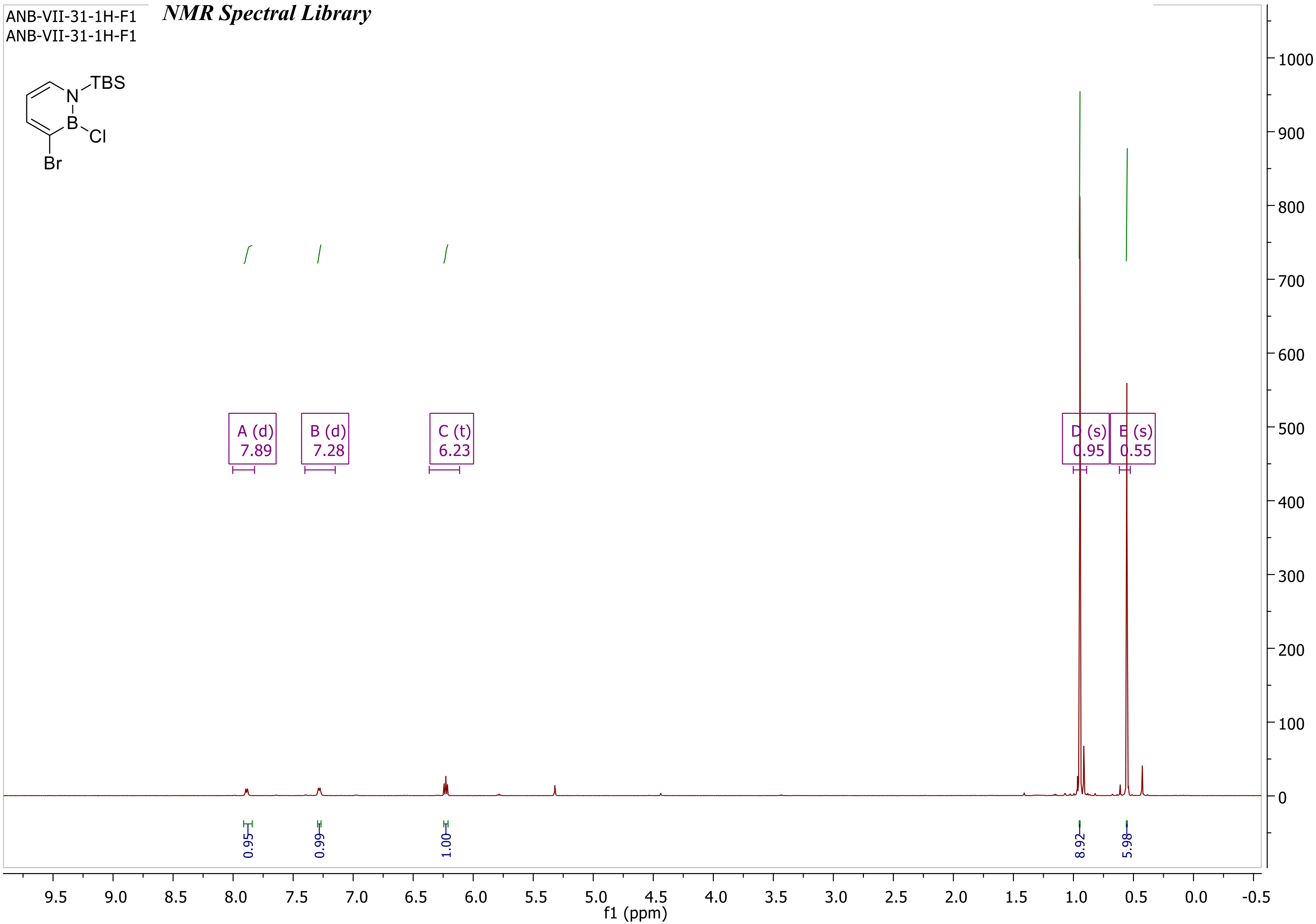


References

(1) Jobin Yvon Ltd. *A Guide to Recording Fluorescence Quantum Yields* (accessed July 2015). http://www.horiba.com/fileadmin/uploads/Scientific/Documents/Fluorescence/quantumyieldstrad.pdf

(2) Suzuki, K.; Kobayashi, A.; Kaneko, S.; Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishic, S.; Tobita, S. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9850.

(3) I. B. Berlman. *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York (1971). compiled by: Brouwer, A. M. *Pure and Applied Chemistry* **2011**, *83*, 2213-2228.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ANB-VII-31-1H-F1
NMR Spectral Library
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B
Cl
Br
A (d) 7.89
B (d) 7.28
C (t) 6.23
D (s) 0.95
E (s) 0.55
0.95
0.99
1.00
8.92
5.98
1000
900
800
700
600
500
400
300
200
100
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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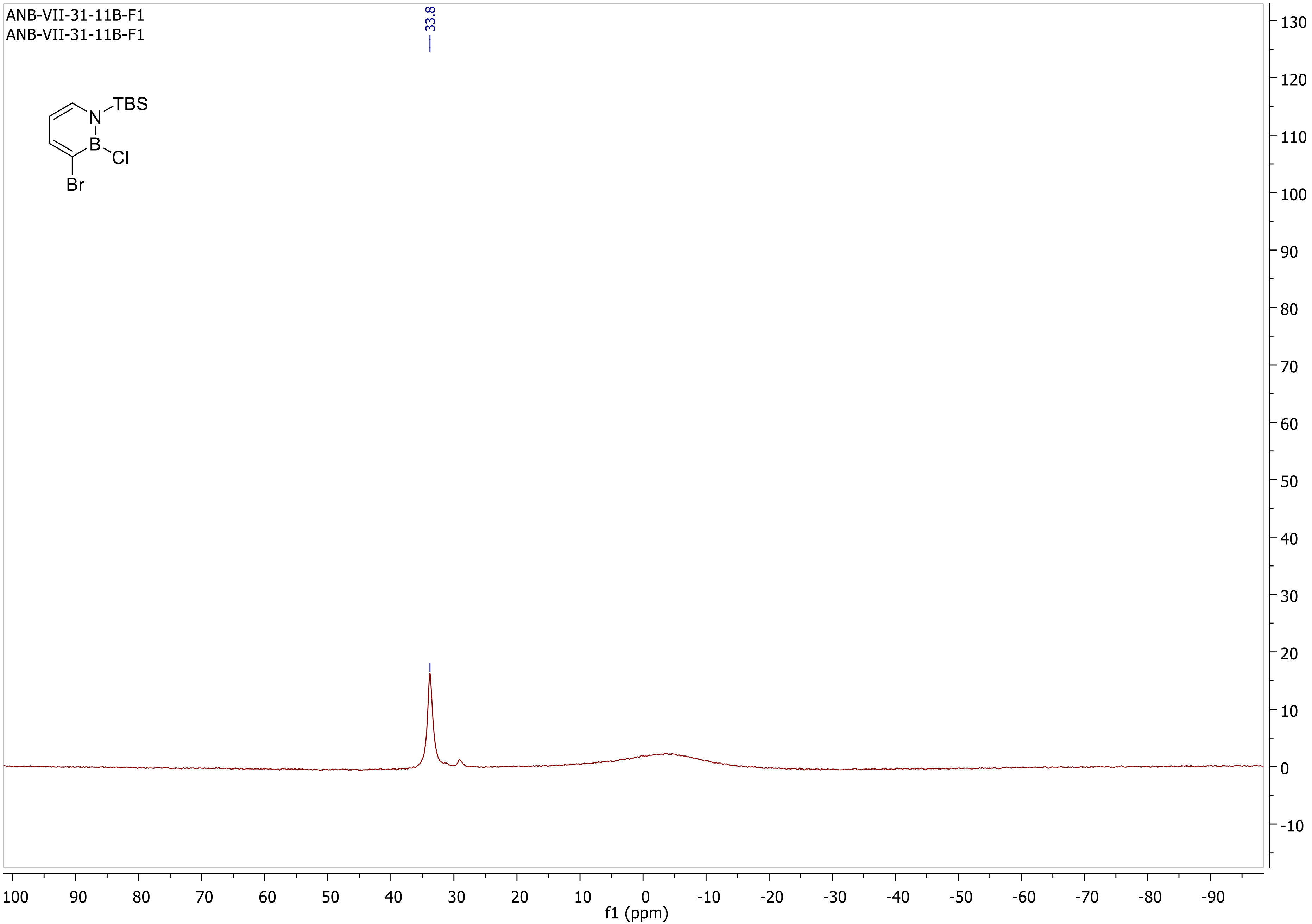
1.0
0.5
0.0
-0.5
f1 (ppm)


ANB-VII-31-11B-F1
ANB-VII-31-11B-F1
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TBS
B
Cl
Br
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100
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80
70
60
50
40
30
20
10
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90
80
70
60
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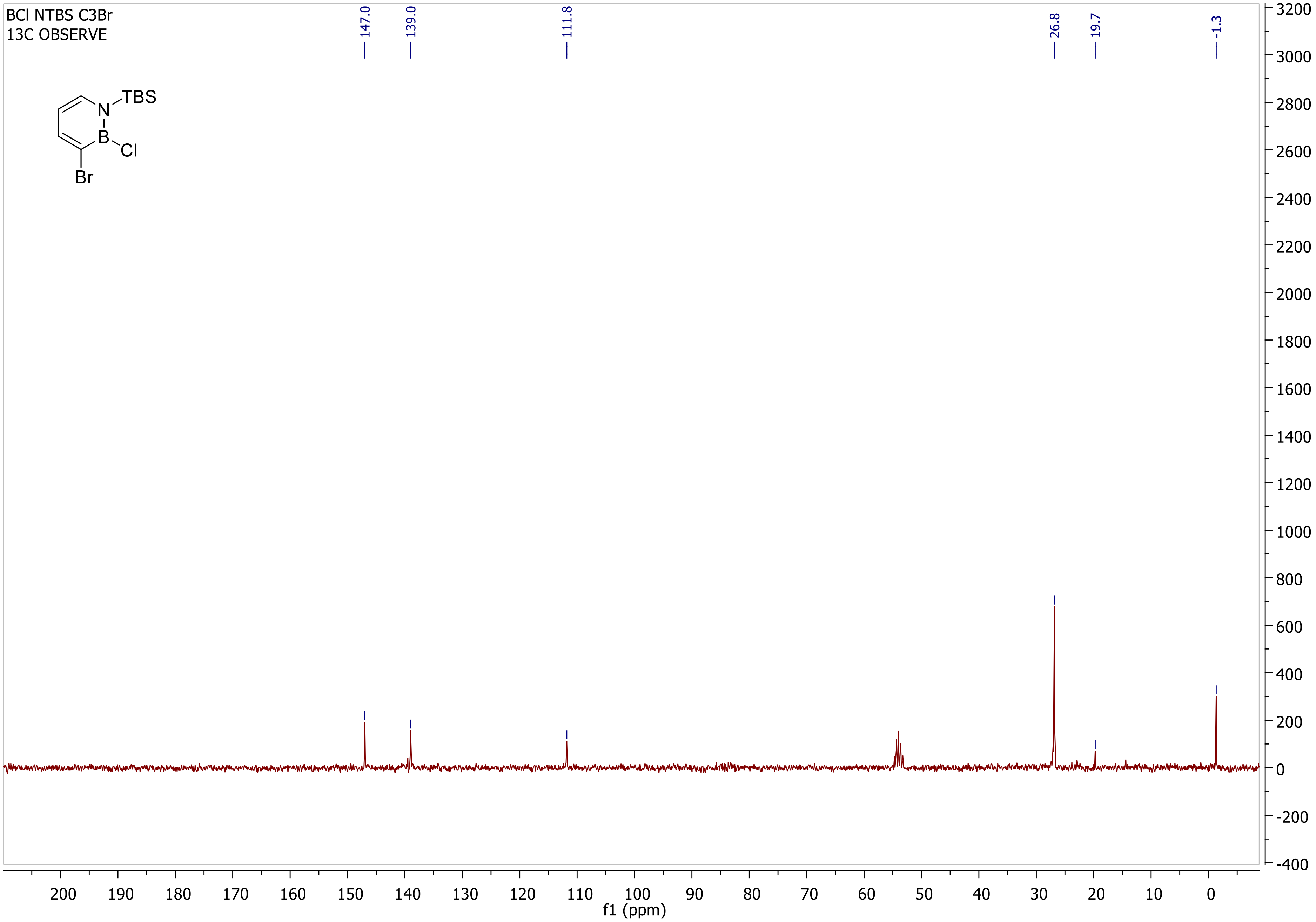
-90
f1 (ppm)



BCl NTBS C3Br
13C OBSERVE
TBS
N
B
Cl
Br
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139.0
111.8
26.8
19.7
-1.3
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
200
190
180
170
160
150
140
130
120
110
100
90
80
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60
50
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20
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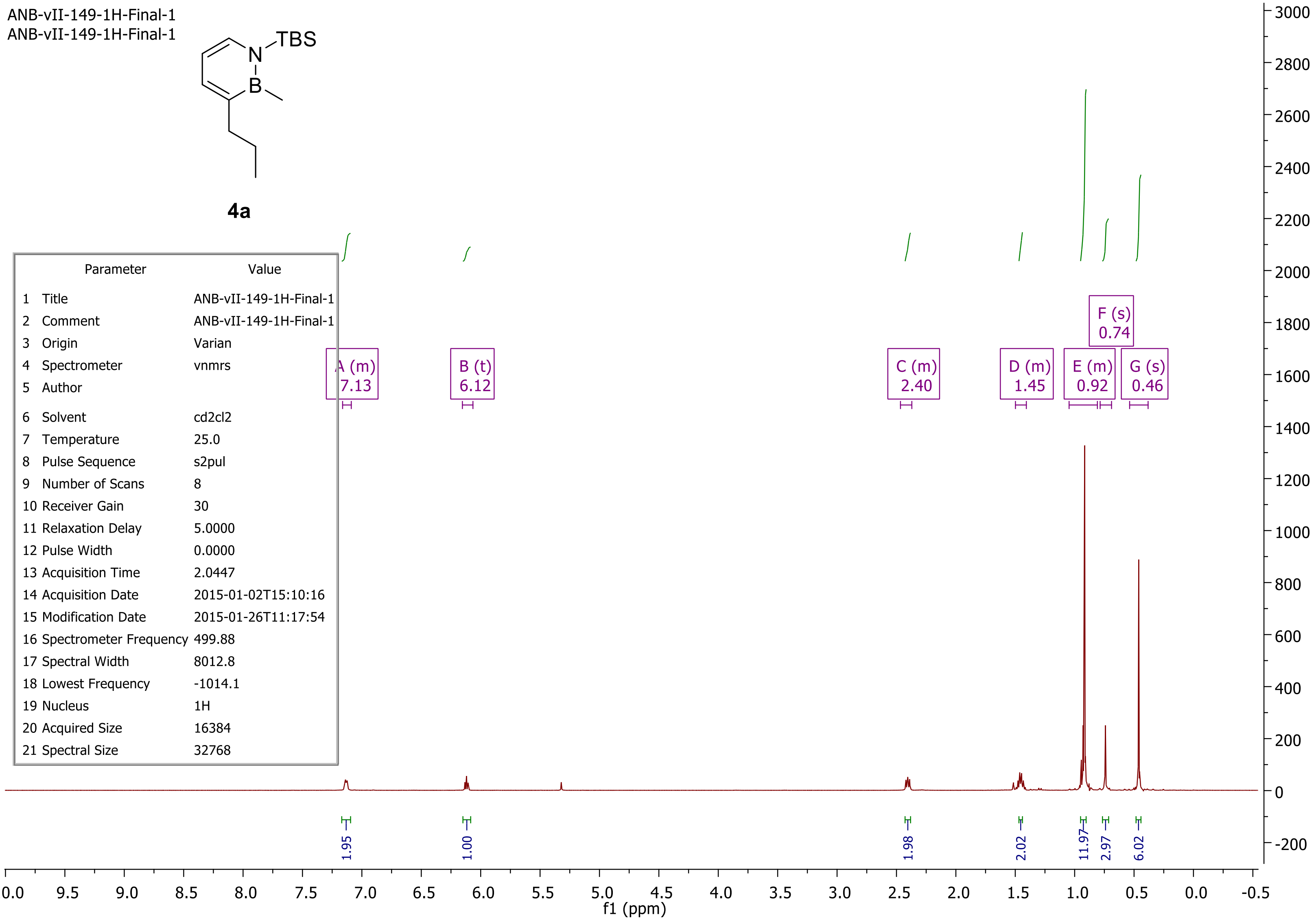
f1 (ppm)

ANB-vII-149-1H-Final-1
ANB-vII-149-1H-Final-1



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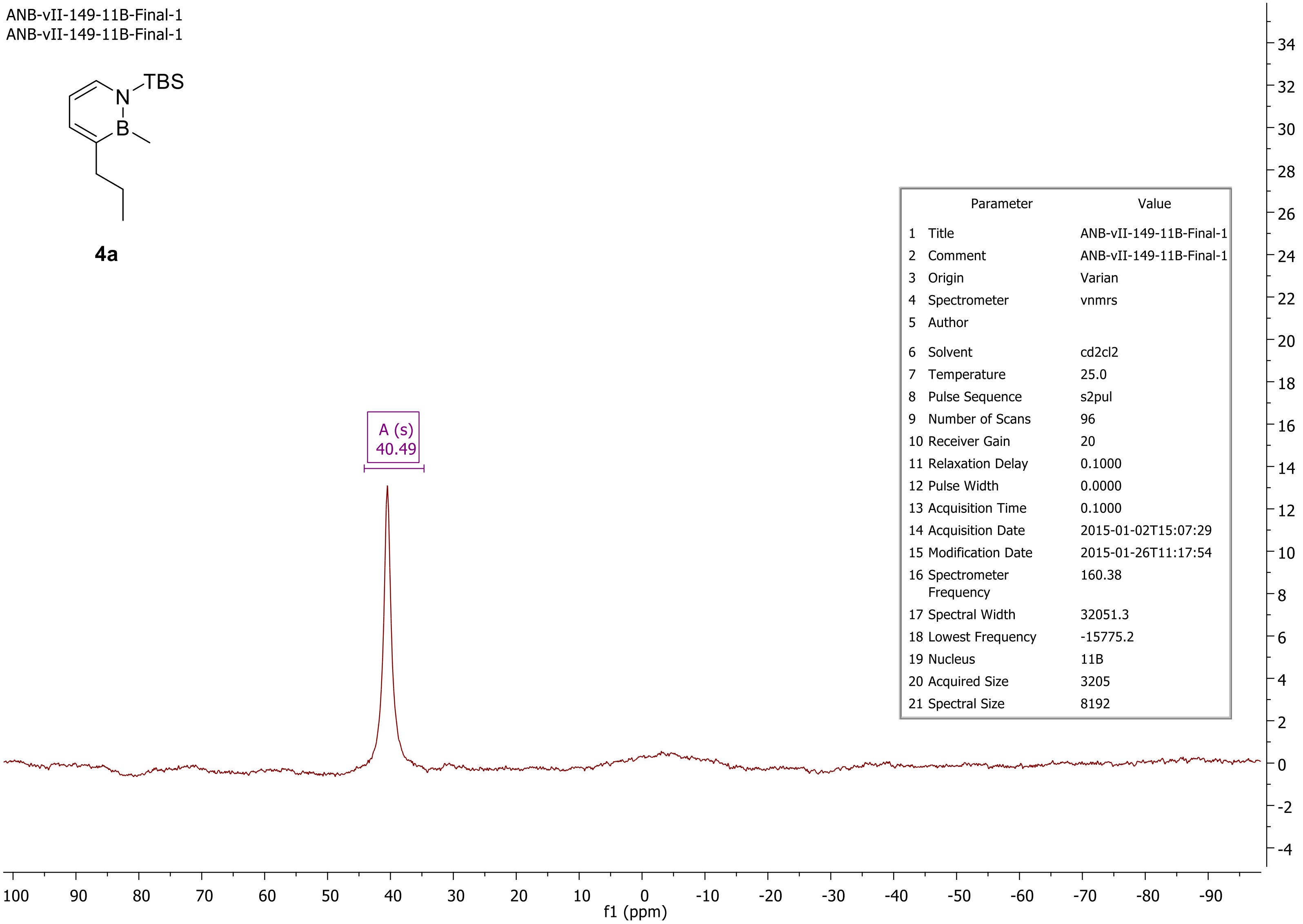
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4a

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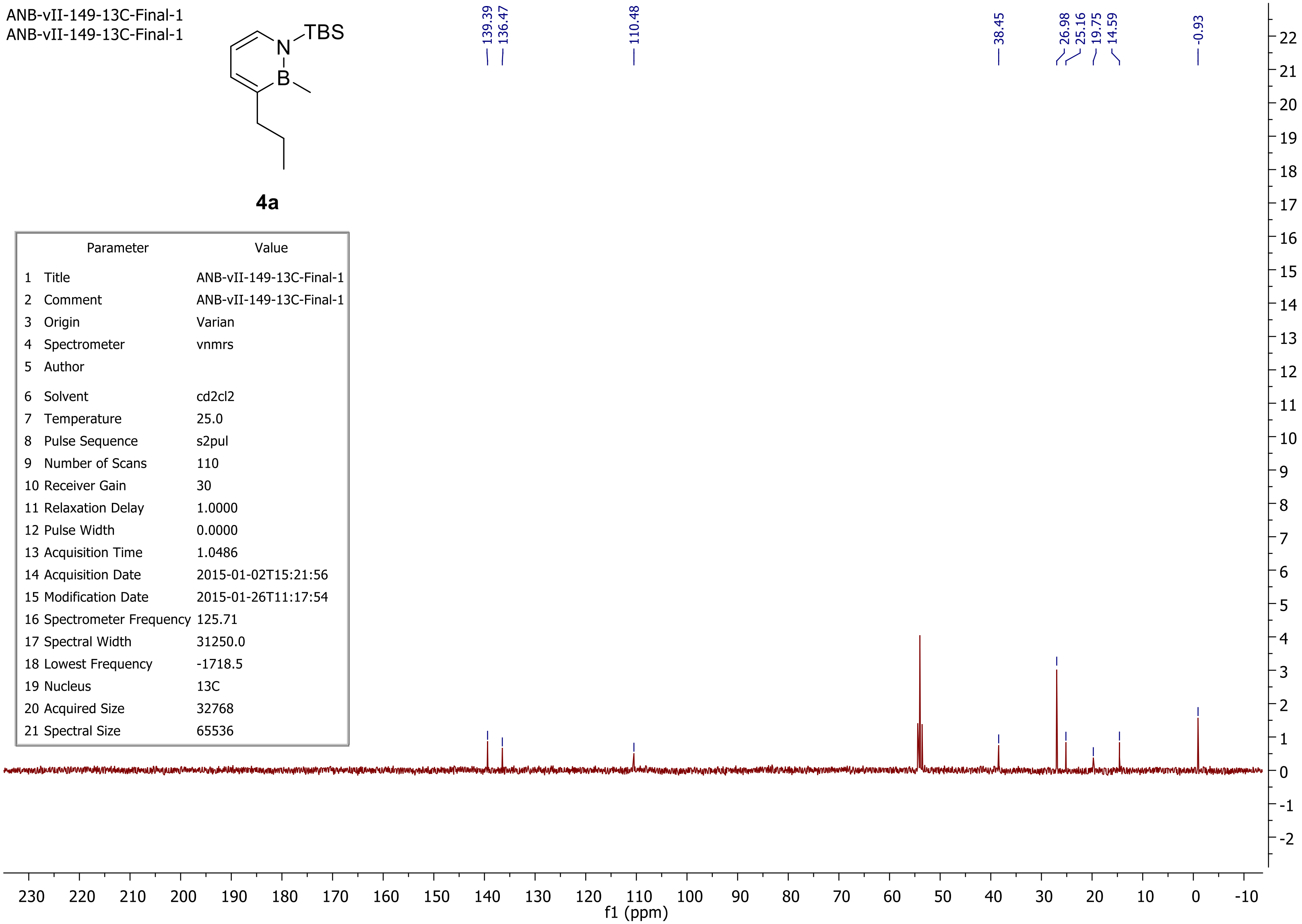

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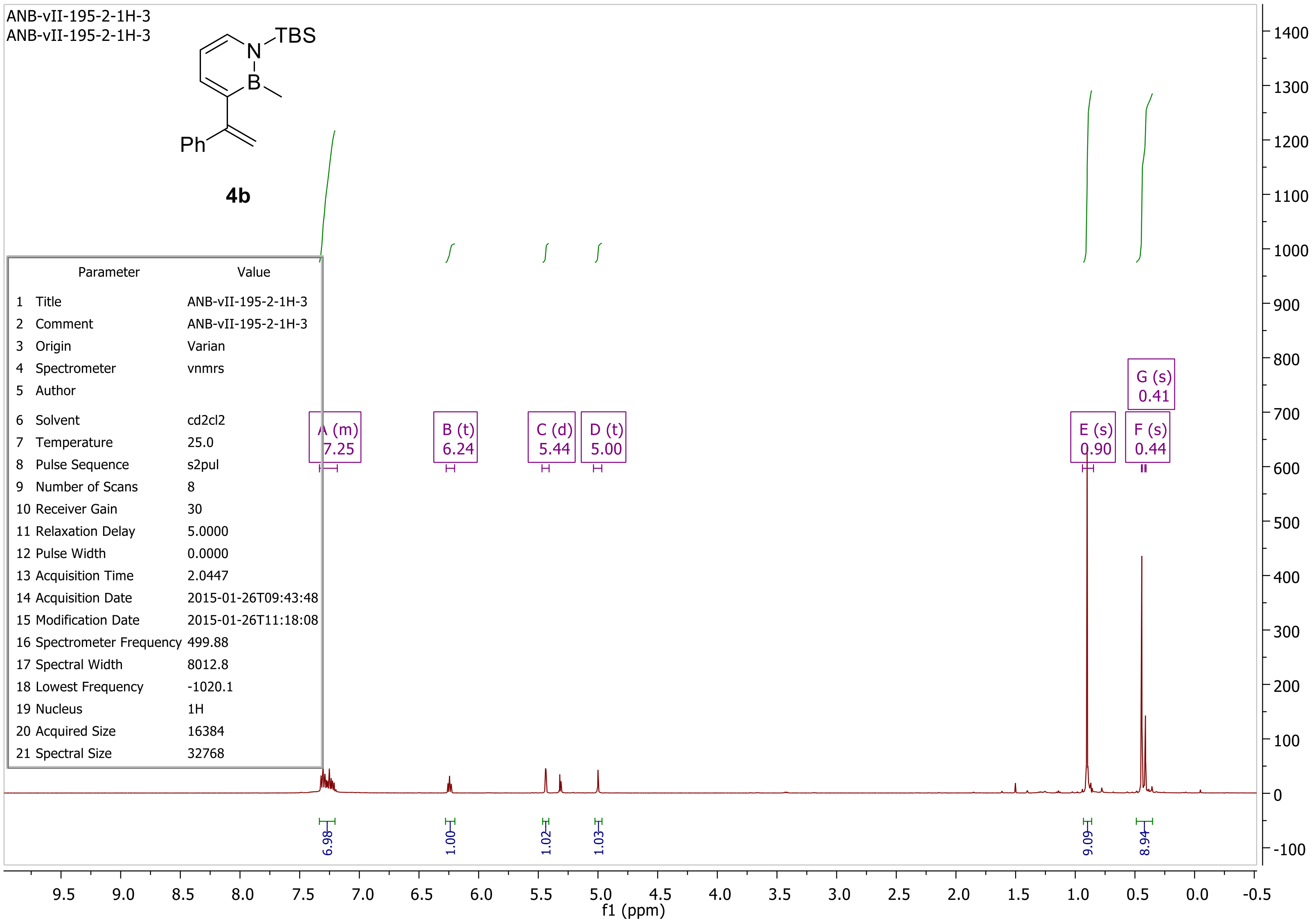

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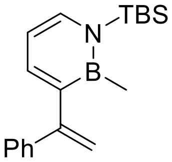
ANB-vII-195-2-11B-3
ANB-vII-195-2-11B-3



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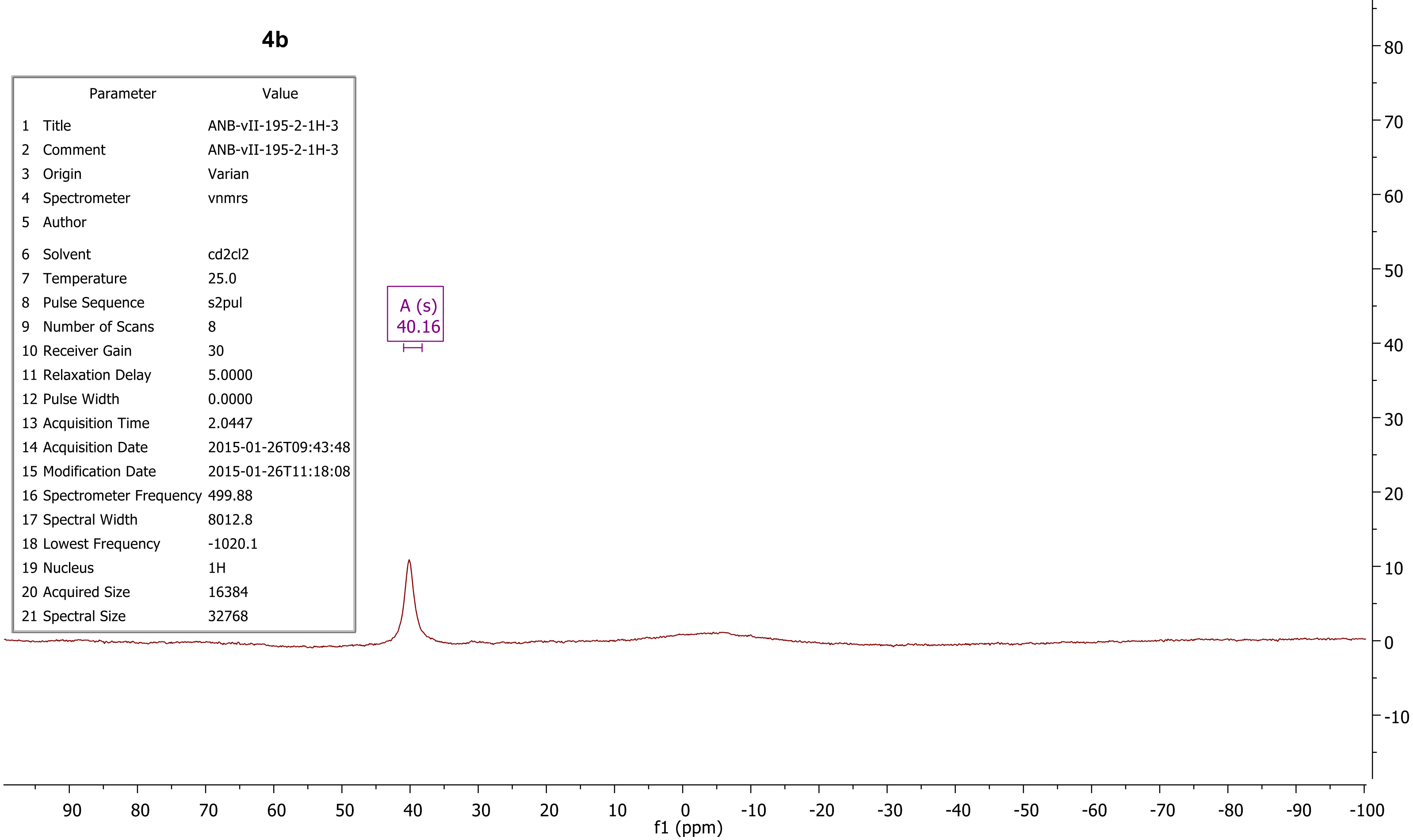
21	Spectral Size	32768



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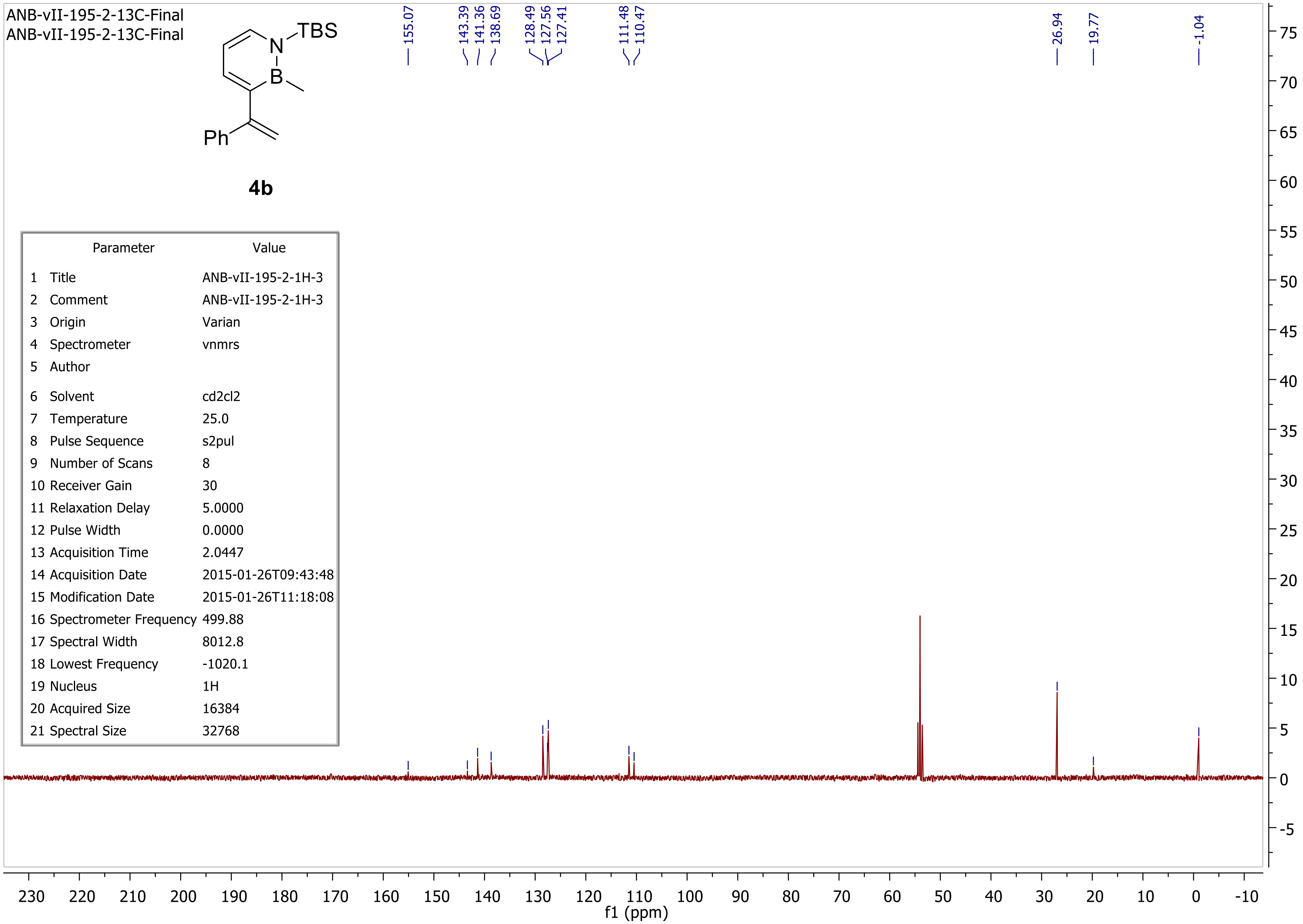

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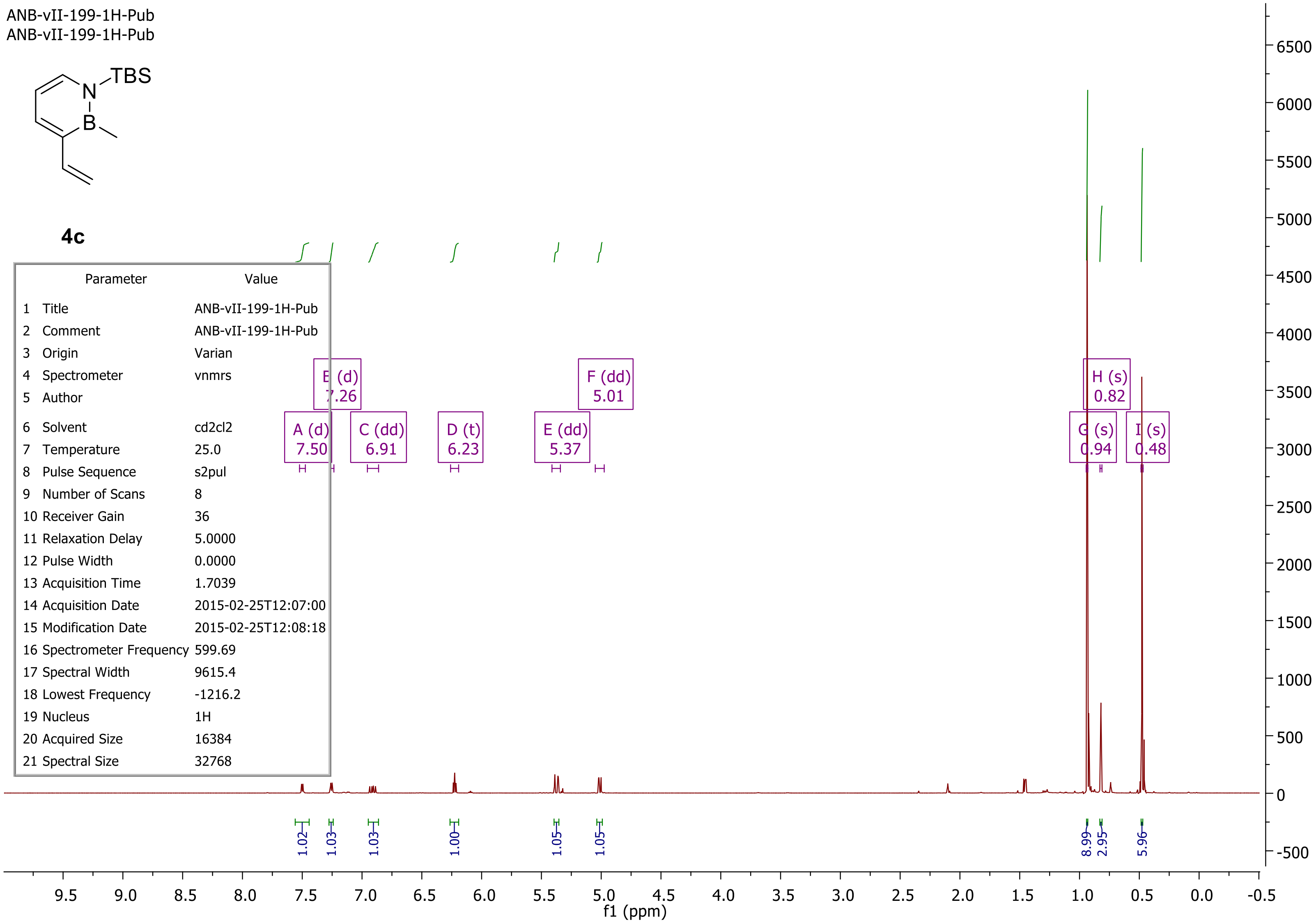

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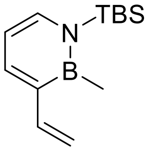

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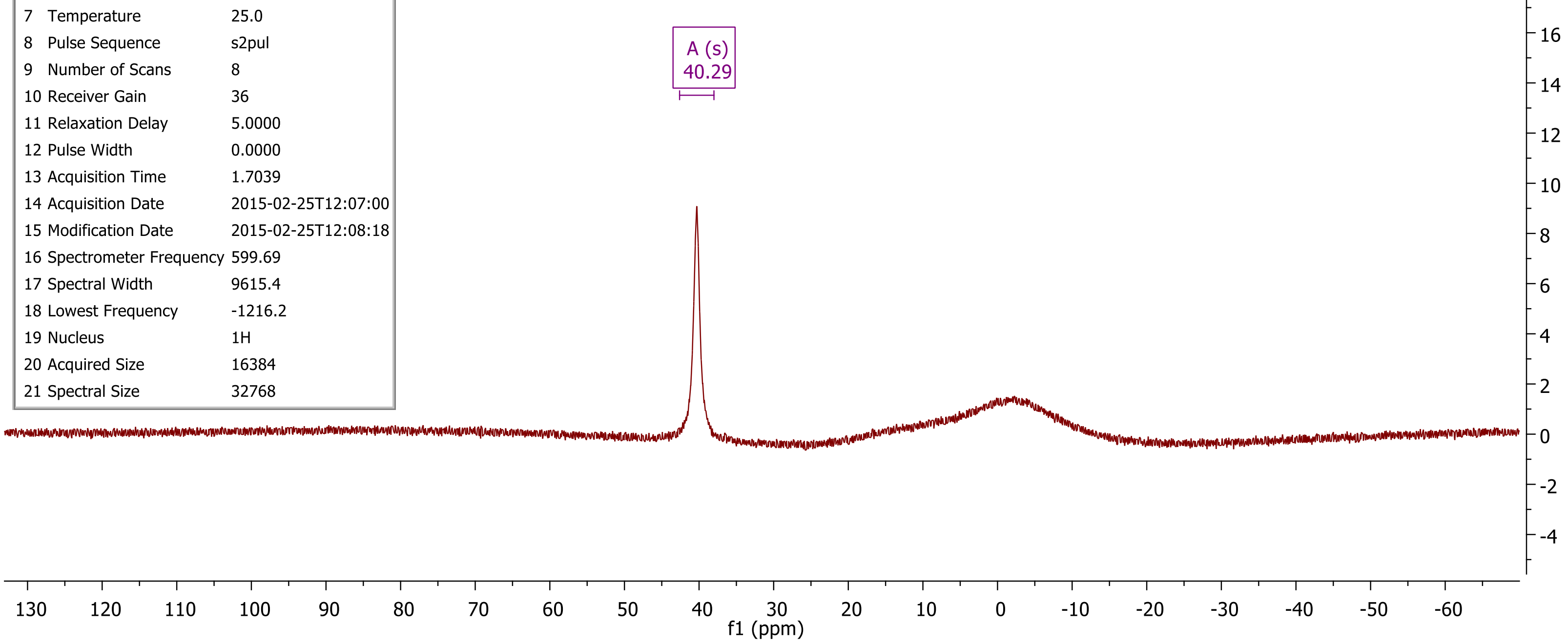

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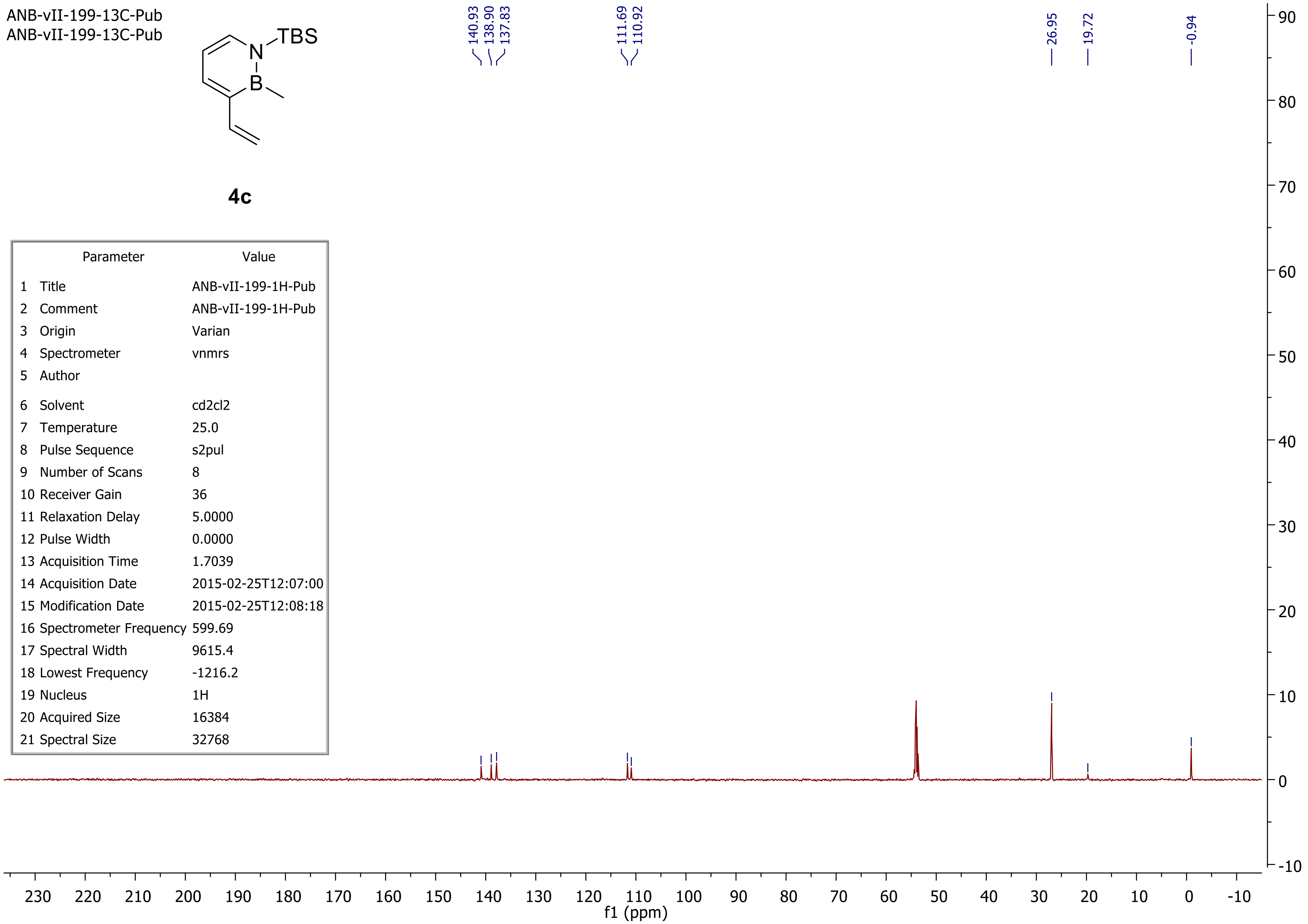

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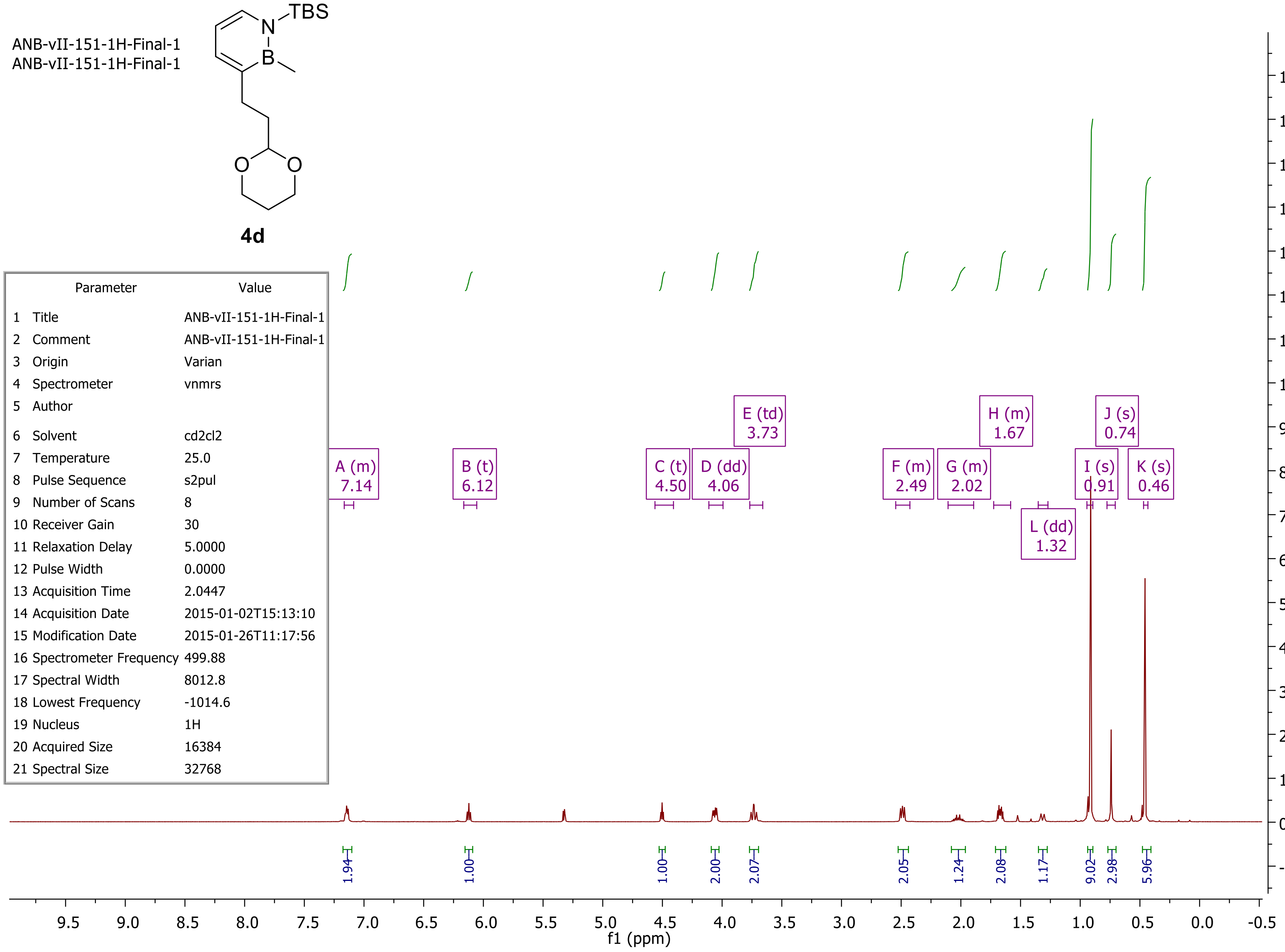
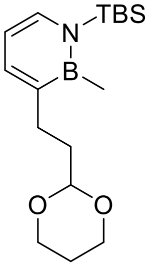
ANB-vII-151-1H-Final-1
ANB-vII-151-1H-Final-1



4d

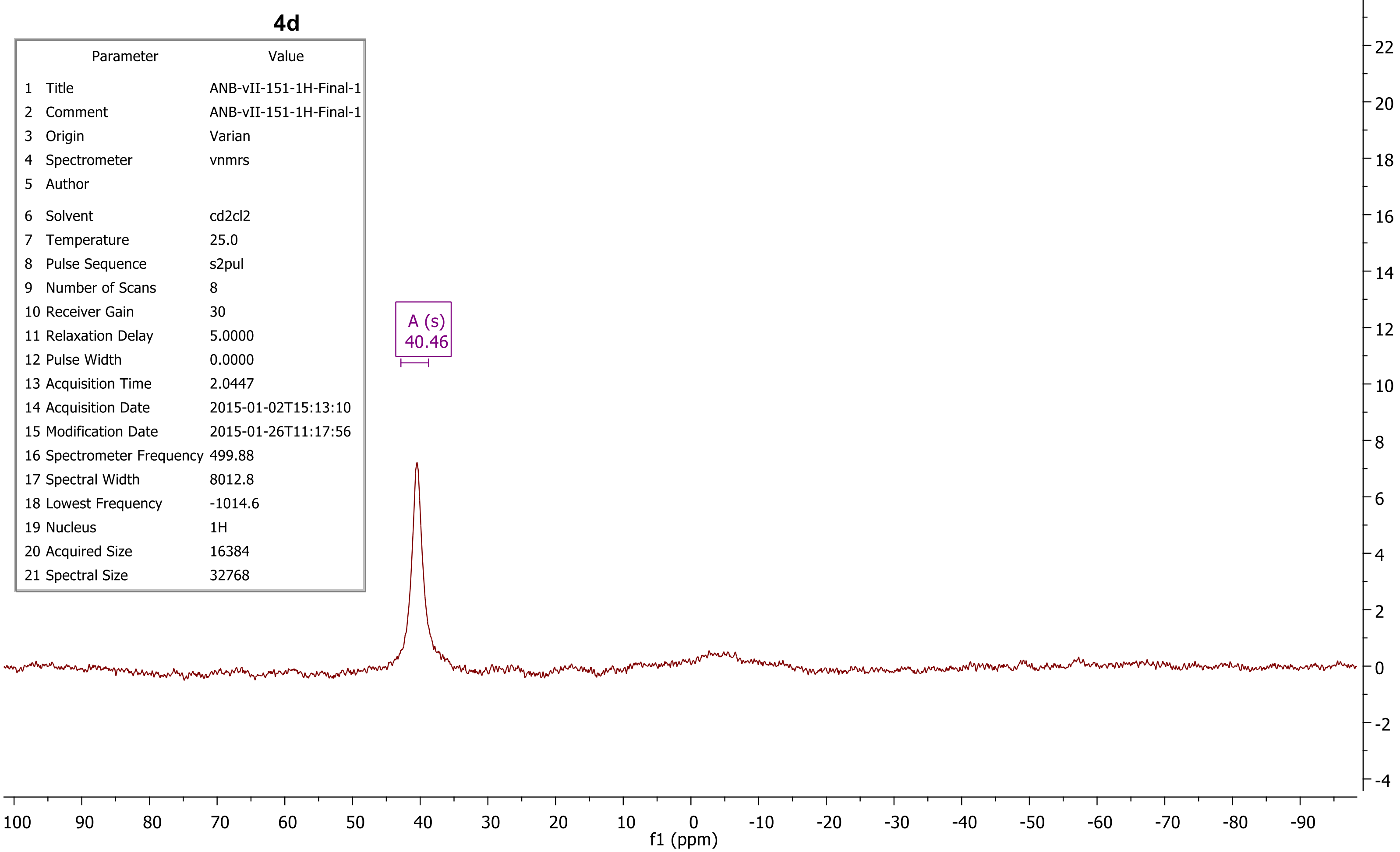
	Parameter	Value
1	Title	ANB-vII-151-1H-Final-1
2	Comment	ANB-vII-151-1H-Final-1
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	8
10	Receiver Gain	30
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0447
14	Acquisition Date	2015-01-02T15:13:10
15	Modification Date	2015-01-26T11:17:56
16	Spectrometer Frequency	499.88
17	Spectral Width	8012.8
18	Lowest Frequency	-1014.6
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

ANB-vII-151-11B-Final-1
ANB-vII-151-11B-Final-1

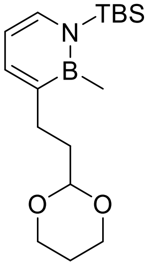


4d

	Parameter	Value
1	Title	ANB-vII-151-1H-Final-1
2	Comment	ANB-vII-151-1H-Final-1
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	8
10	Receiver Gain	30
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0447
14	Acquisition Date	2015-01-02T15:13:10
15	Modification Date	2015-01-26T11:17:56
16	Spectrometer Frequency	499.88
17	Spectral Width	8012.8
18	Lowest Frequency	-1014.6
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

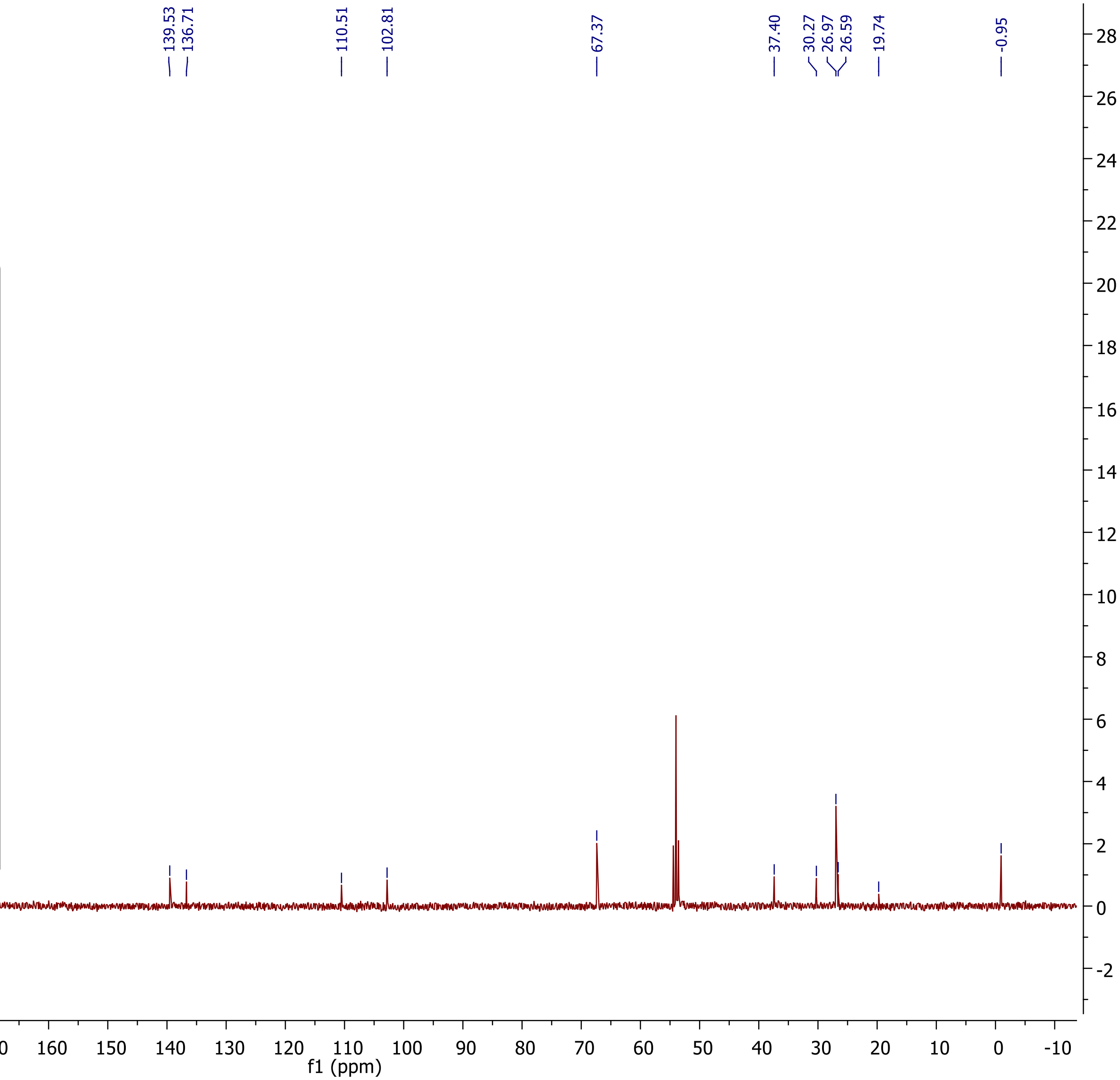


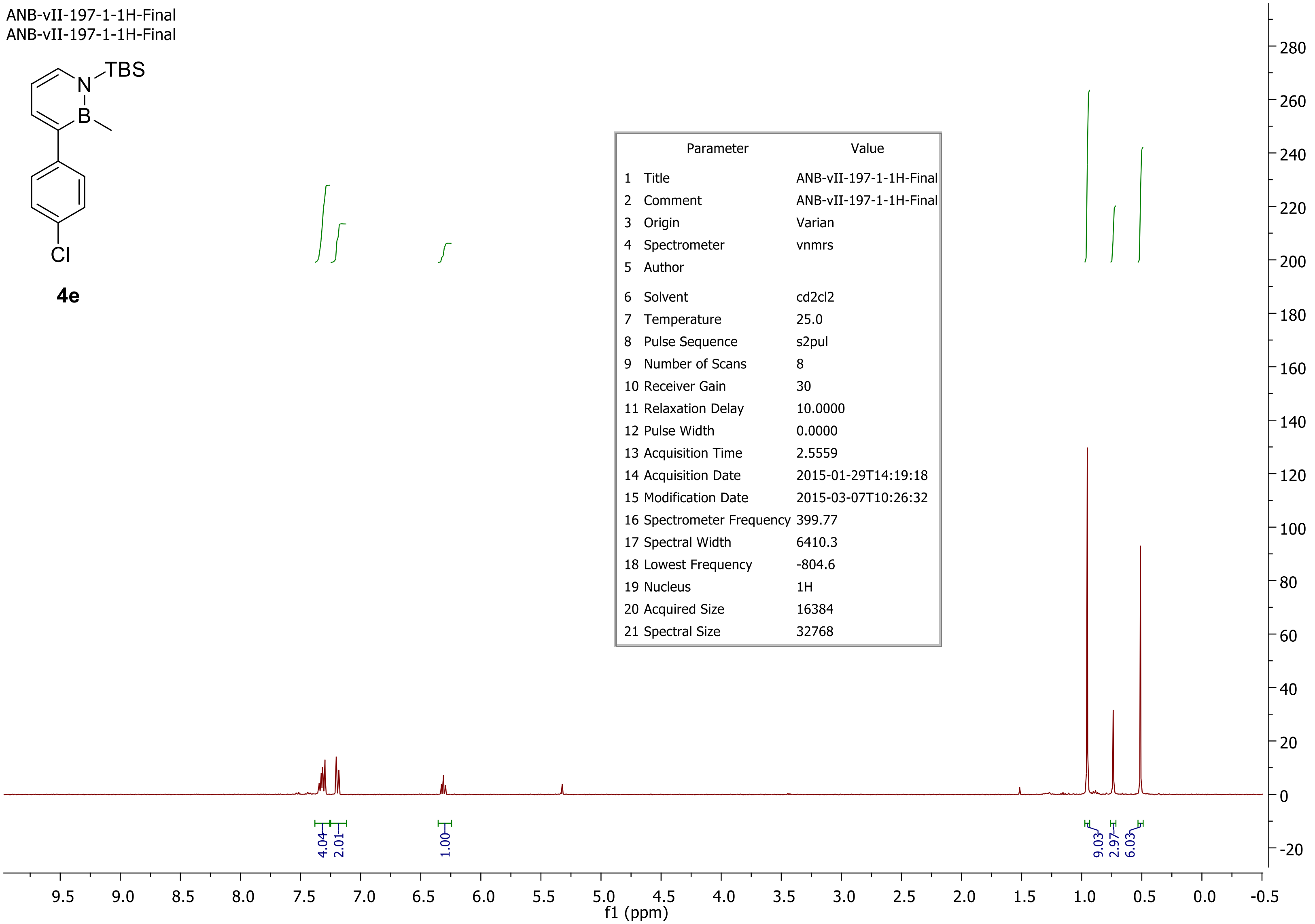
ANB-vII-151-13C-Final-1
ANB-vII-151-13C-Final-1



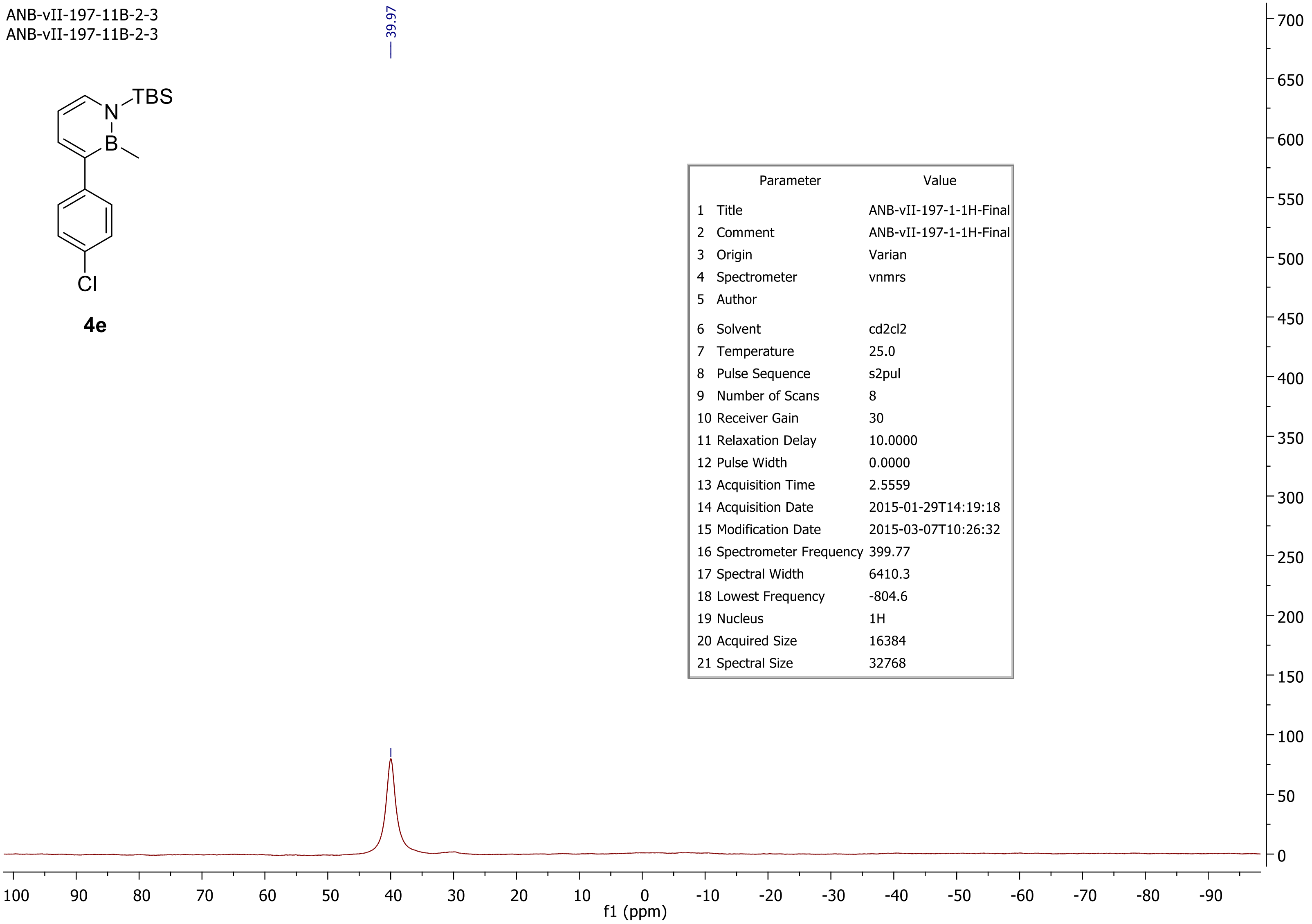
4d

Parameter		Value
1	Title	ANB-vII-151-1H-Final-1
2	Comment	ANB-vII-151-1H-Final-1
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	8
10	Receiver Gain	30
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0447
14	Acquisition Date	2015-01-02T15:13:10
15	Modification Date	2015-01-26T11:17:56
16	Spectrometer Frequency	499.88
17	Spectral Width	8012.8
18	Lowest Frequency	-1014.6
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768





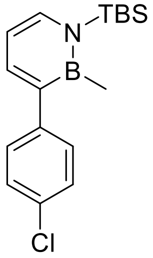
	Parameter	Value
1	Title	ANB-vII-197-1-1H-Final
2	Comment	ANB-vII-197-1-1H-Final
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	8
10	Receiver Gain	30
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.5559
14	Acquisition Date	2015-01-29T14:19:18
15	Modification Date	2015-03-07T10:26:32
16	Spectrometer Frequency	399.77
17	Spectral Width	6410.3
18	Lowest Frequency	-804.6
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768



4e

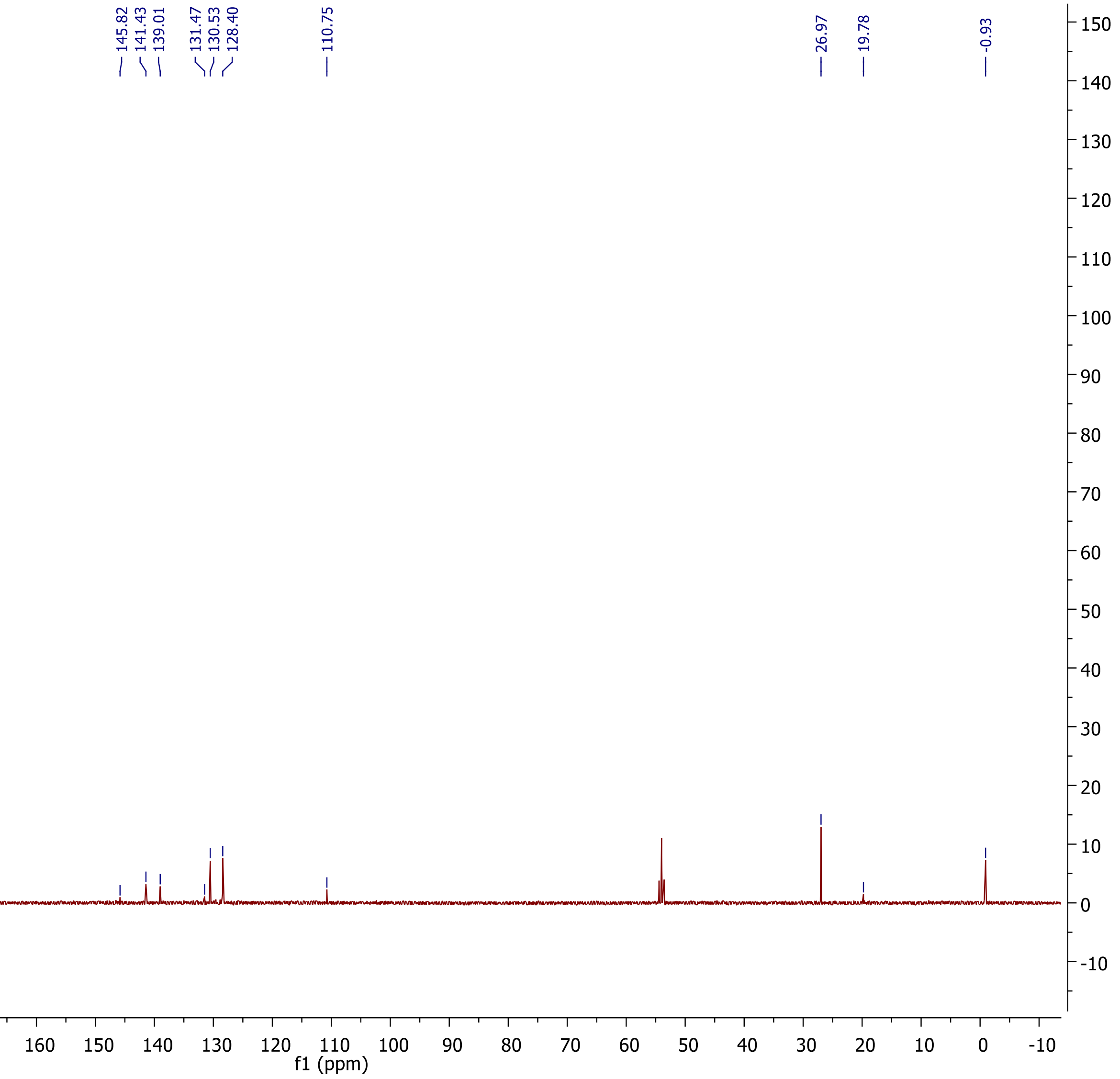
	Parameter	Value
1	Title	ANB-vII-197-1-1H-Final
2	Comment	ANB-vII-197-1-1H-Final
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	8
10	Receiver Gain	30
11	Relaxation Delay	10.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.5559
14	Acquisition Date	2015-01-29T14:19:18
15	Modification Date	2015-03-07T10:26:32
16	Spectrometer Frequency	399.77
17	Spectral Width	6410.3
18	Lowest Frequency	-804.6
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

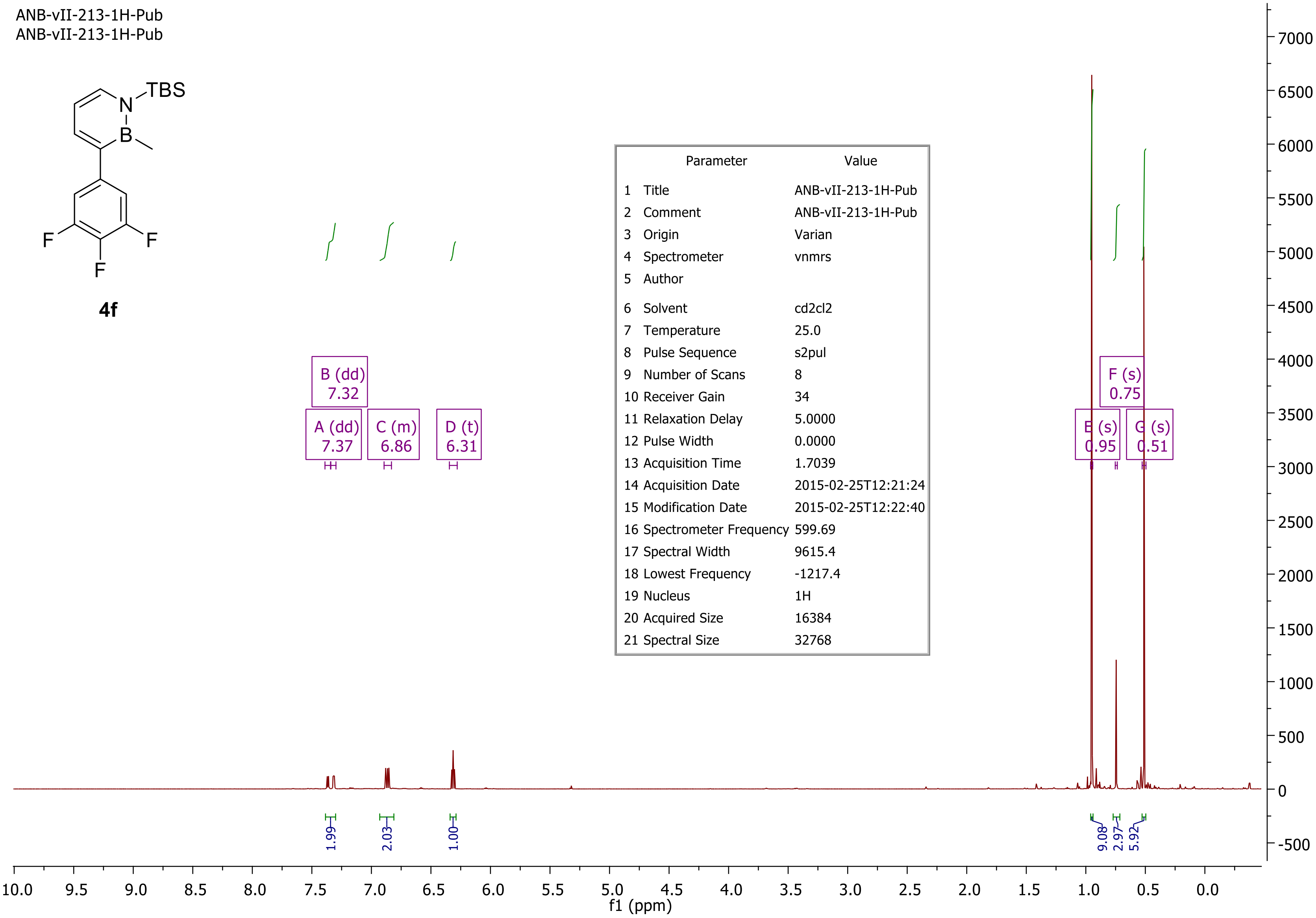
ANB-vII-197-1-13C-1
ANB-vII-197-1-13C-1



4e

Parameter	Value
1 Title	ANB-vII-197-1-1H-Final
2 Comment	ANB-vII-197-1-1H-Final
3 Origin	Varian
4 Spectrometer	vnmrs
5 Author	
6 Solvent	cd2cl2
7 Temperature	25.0
8 Pulse Sequence	s2pul
9 Number of Scans	8
10 Receiver Gain	30
11 Relaxation Delay	10.0000
12 Pulse Width	0.0000
13 Acquisition Time	2.5559
14 Acquisition Date	2015-01-29T14:19:18
15 Modification Date	2015-03-07T10:26:32
16 Spectrometer Frequency	399.77
17 Spectral Width	6410.3
18 Lowest Frequency	-804.6
19 Nucleus	1H
20 Acquired Size	16384
21 Spectral Size	32768

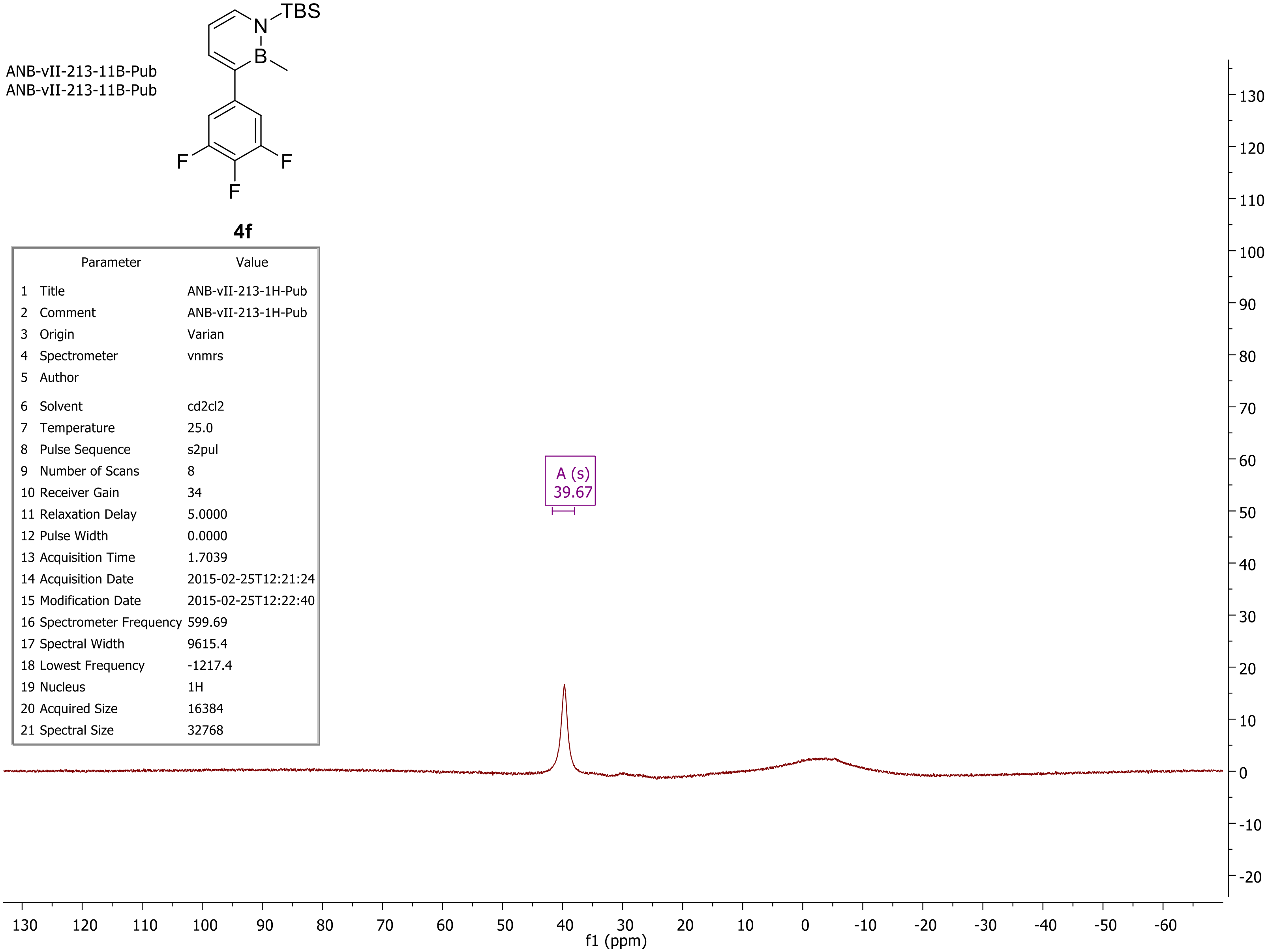




4f

	Parameter	Value
1	Title	ANB-vII-213-1H-Pub
2	Comment	ANB-vII-213-1H-Pub
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	8
10	Receiver Gain	34
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.7039
14	Acquisition Date	2015-02-25T12:21:24
15	Modification Date	2015-02-25T12:22:40
16	Spectrometer Frequency	599.69
17	Spectral Width	9615.4
18	Lowest Frequency	-1217.4
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

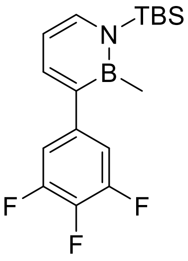
ANB-vII-213-11B-Pub
ANB-vII-213-11B-Pub



4f

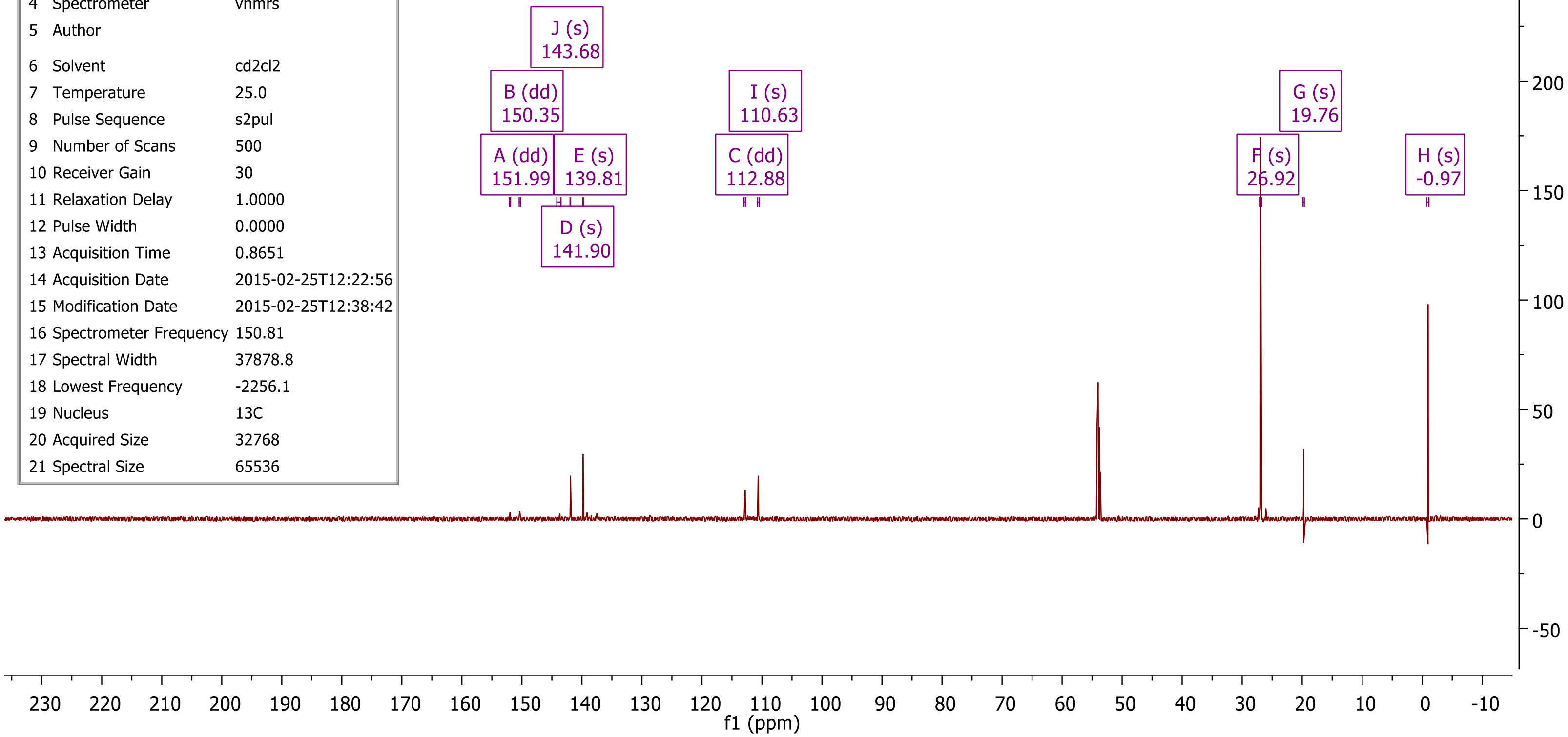
	Parameter	Value
1	Title	ANB-vII-213-1H-Pub
2	Comment	ANB-vII-213-1H-Pub
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	8
10	Receiver Gain	34
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.7039
14	Acquisition Date	2015-02-25T12:21:24
15	Modification Date	2015-02-25T12:22:40
16	Spectrometer Frequency	599.69
17	Spectral Width	9615.4
18	Lowest Frequency	-1217.4
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

ANB-vII-213-13C-Pub
ANB-vII-213-13C-Pub

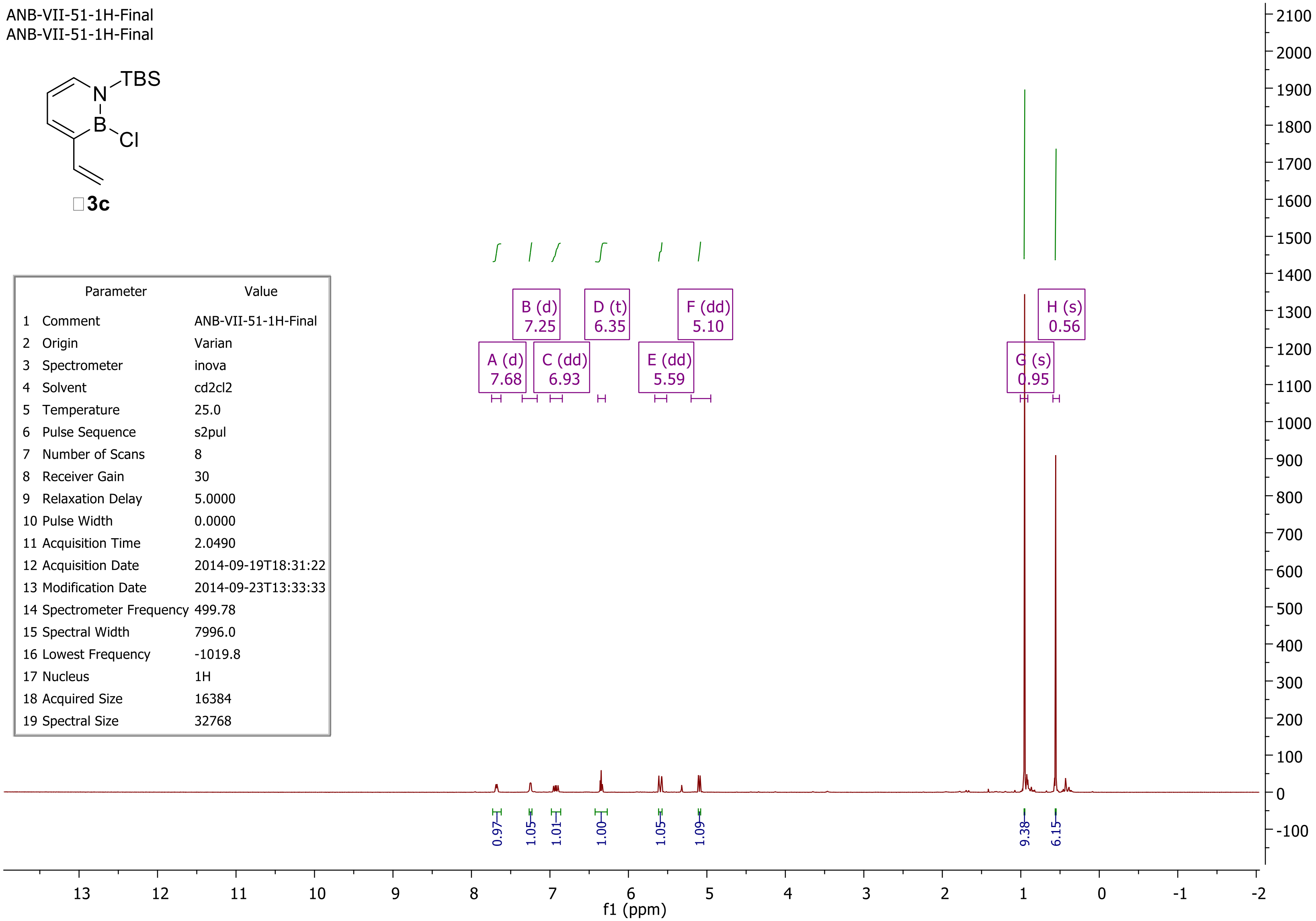


4f

Parameter	Value
1 Title	ANB-vII-213-13C-Pub
2 Comment	ANB-vII-213-13C-Pub
3 Origin	Varian
4 Spectrometer	vnmrs
5 Author	
6 Solvent	cd2cl2
7 Temperature	25.0
8 Pulse Sequence	s2pul
9 Number of Scans	500
10 Receiver Gain	30
11 Relaxation Delay	1.0000
12 Pulse Width	0.0000
13 Acquisition Time	0.8651
14 Acquisition Date	2015-02-25T12:22:56
15 Modification Date	2015-02-25T12:38:42
16 Spectrometer Frequency	150.81
17 Spectral Width	37878.8
18 Lowest Frequency	-2256.1
19 Nucleus	13C
20 Acquired Size	32768
21 Spectral Size	65536



ANB-VII-51-1H-Final
ANB-VII-51-1H-Final



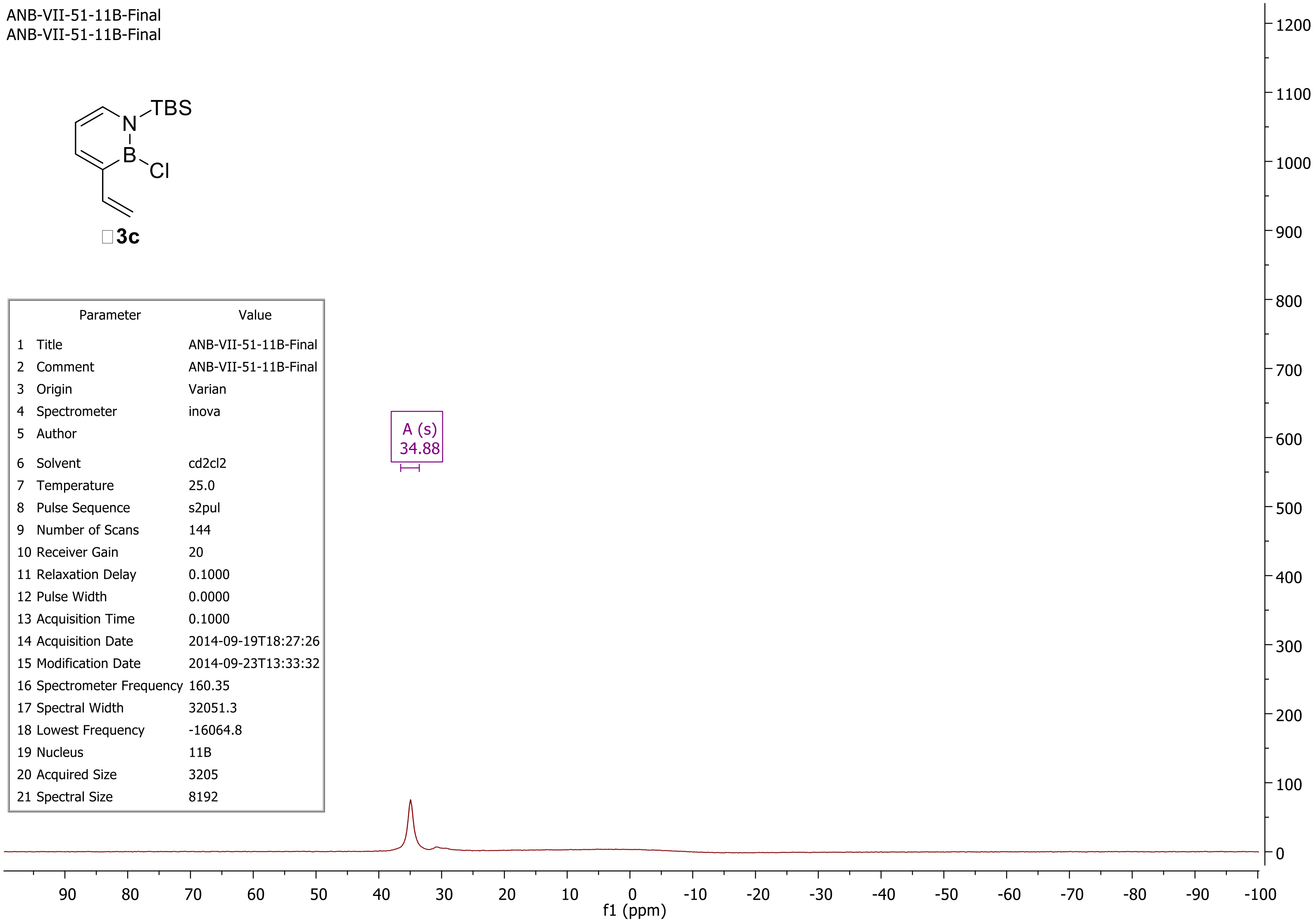
3c

	Parameter	Value
1	Comment	ANB-VII-51-1H-Final
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	cd2cl2
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Number of Scans	8
8	Receiver Gain	30
9	Relaxation Delay	5.0000
10	Pulse Width	0.0000
11	Acquisition Time	2.0490
12	Acquisition Date	2014-09-19T18:31:22
13	Modification Date	2014-09-23T13:33:33
14	Spectrometer Frequency	499.78
15	Spectral Width	7996.0
16	Lowest Frequency	-1019.8
17	Nucleus	1H
18	Acquired Size	16384
19	Spectral Size	32768

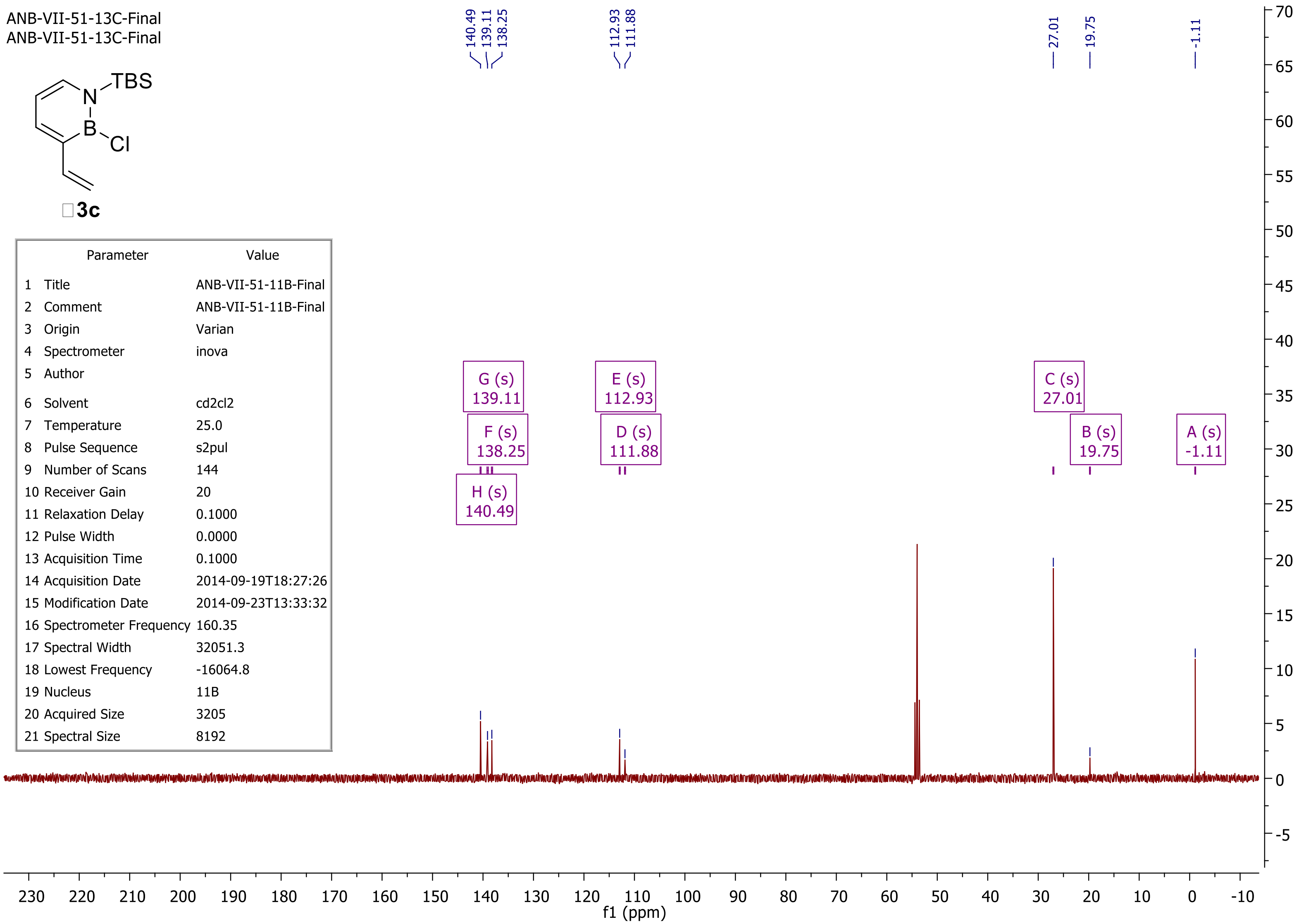
ANB-VII-51-11B-Final
ANB-VII-51-11B-Final

3c

Parameter	Value
1 Title	ANB-VII-51-11B-Final
2 Comment	ANB-VII-51-11B-Final
3 Origin	Varian
4 Spectrometer	inova
5 Author	
6 Solvent	cd2cl2
7 Temperature	25.0
8 Pulse Sequence	s2pul
9 Number of Scans	144
10 Receiver Gain	20
11 Relaxation Delay	0.1000
12 Pulse Width	0.0000
13 Acquisition Time	0.1000
14 Acquisition Date	2014-09-19T18:27:26
15 Modification Date	2014-09-23T13:33:32
16 Spectrometer Frequency	160.35
17 Spectral Width	32051.3
18 Lowest Frequency	-16064.8
19 Nucleus	11B
20 Acquired Size	3205
21 Spectral Size	8192

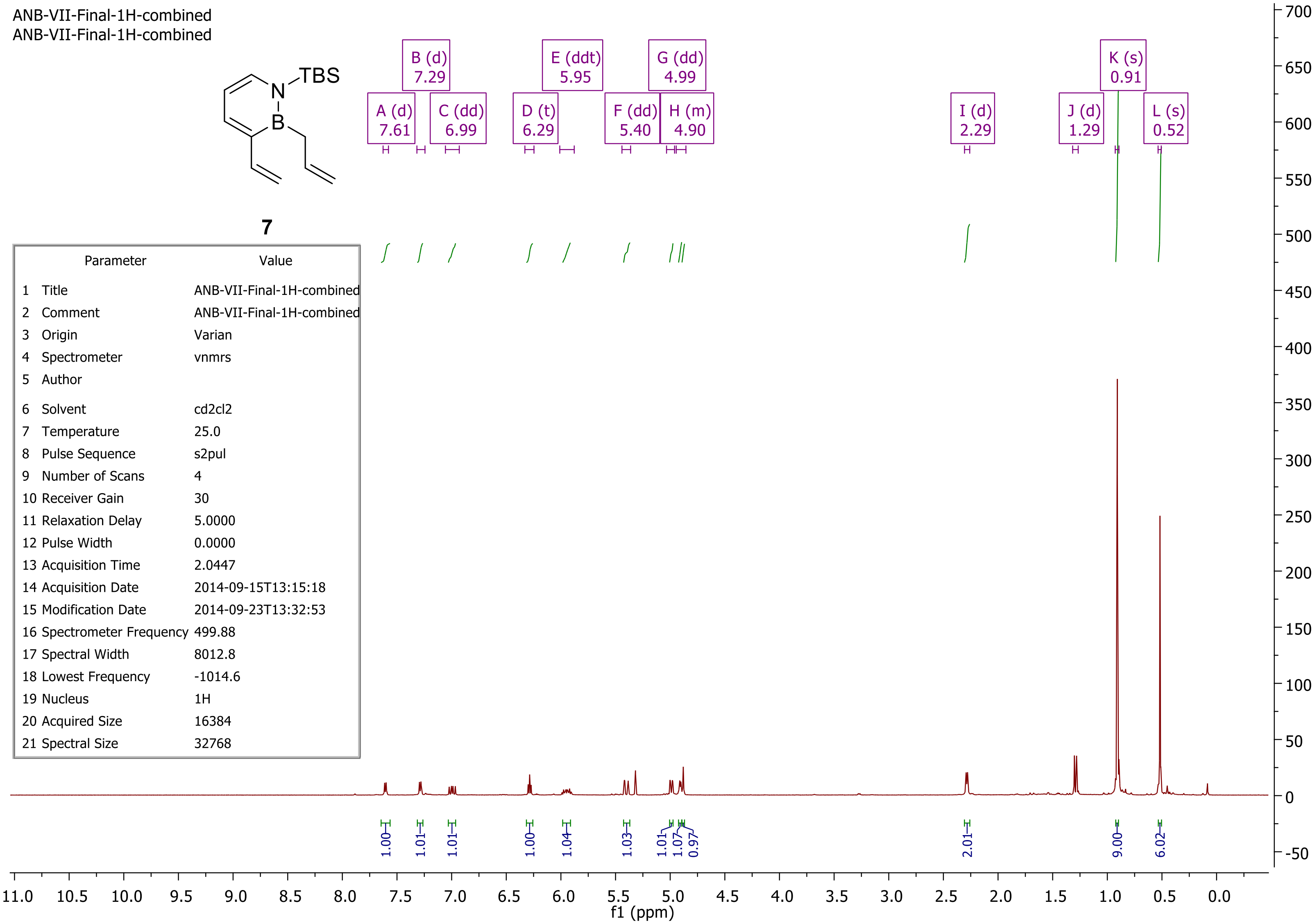


ANB-VII-51-13C-Final
ANB-VII-51-13C-Final



3c

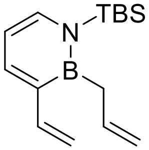
	Parameter	Value
1	Title	ANB-VII-51-11B-Final
2	Comment	ANB-VII-51-11B-Final
3	Origin	Varian
4	Spectrometer	inova
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	144
10	Receiver Gain	20
11	Relaxation Delay	0.1000
12	Pulse Width	0.0000
13	Acquisition Time	0.1000
14	Acquisition Date	2014-09-19T18:27:26
15	Modification Date	2014-09-23T13:33:32
16	Spectrometer Frequency	160.35
17	Spectral Width	32051.3
18	Lowest Frequency	-16064.8
19	Nucleus	11B
20	Acquired Size	3205
21	Spectral Size	8192



7

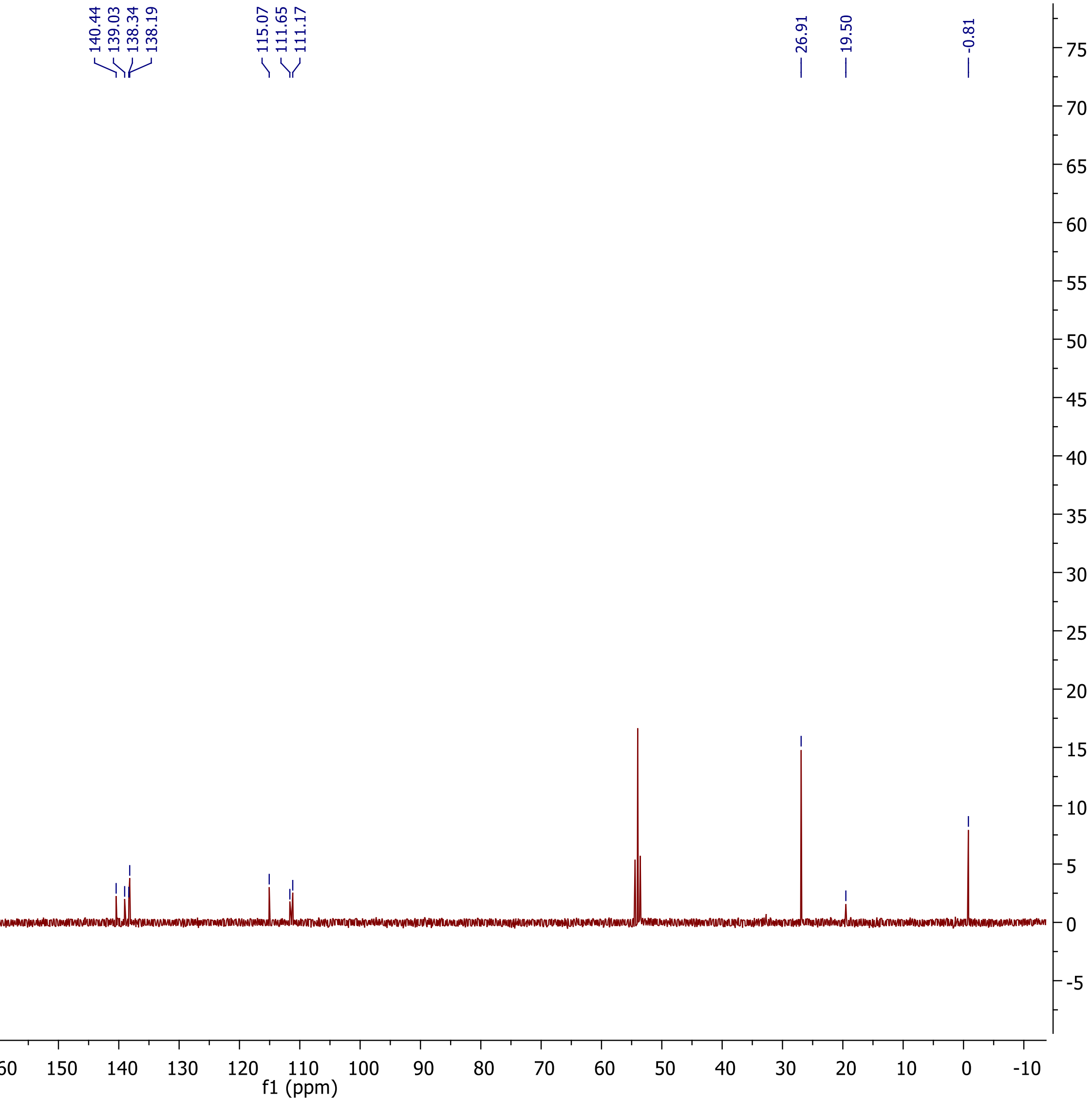
	Parameter	Value
1	Title	ANB-VII-Final-1H-combined
2	Comment	ANB-VII-Final-1H-combined
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	4
10	Receiver Gain	30
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0447
14	Acquisition Date	2014-09-15T13:15:18
15	Modification Date	2014-09-23T13:32:53
16	Spectrometer Frequency	499.88
17	Spectral Width	8012.8
18	Lowest Frequency	-1014.6
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

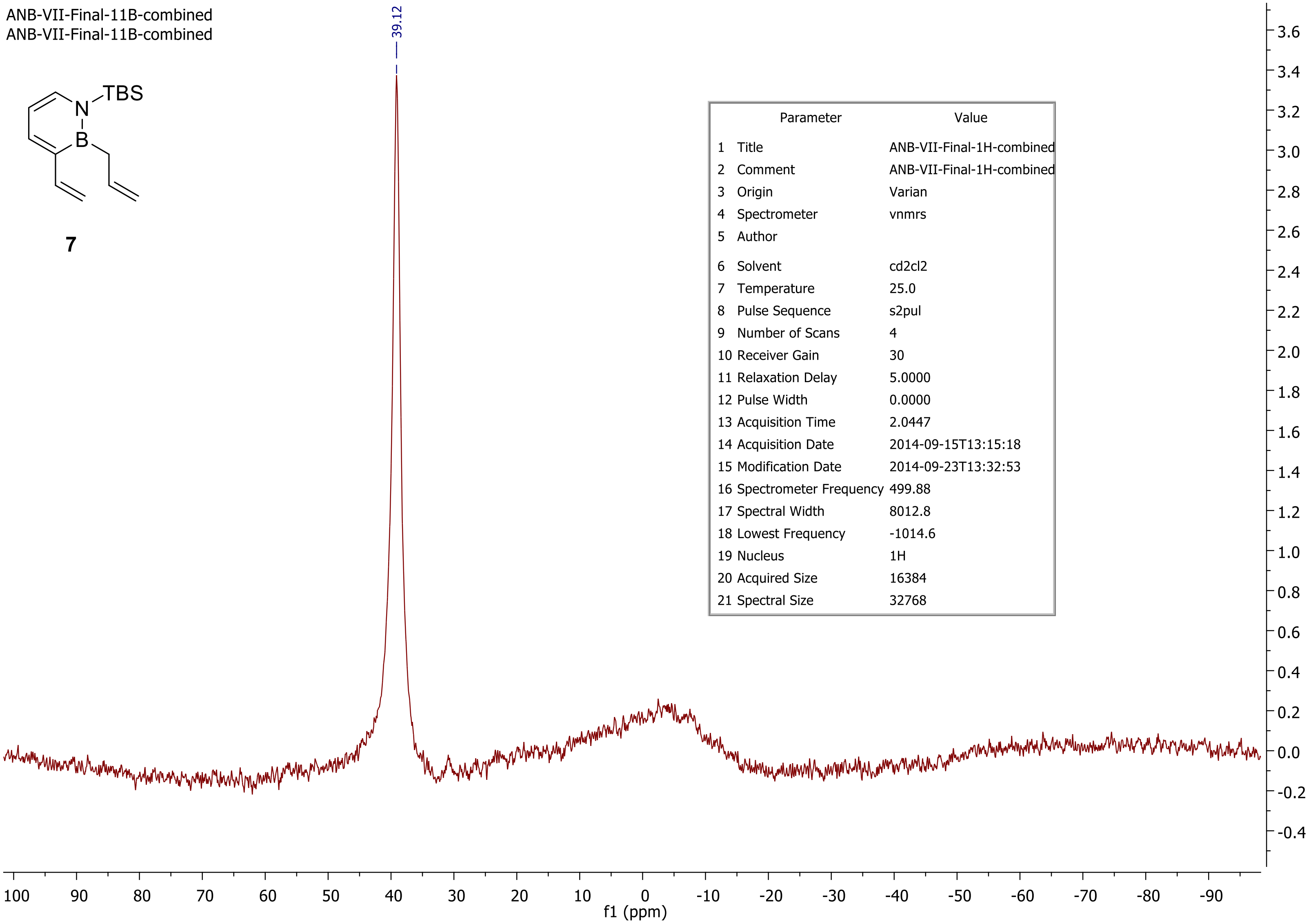
ANB-VII-Final-13C-combined
ANB-VII-Final-13C-combined



7

	Parameter	Value
1	Comment	ANB-VII-Final-11B-combined
2	Origin	Varian
3	Spectrometer	vnmrs
4	Solvent	cd2cl2
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Number of Scans	40
8	Receiver Gain	20
9	Relaxation Delay	0.1000
10	Pulse Width	0.0000
11	Acquisition Time	0.1000
12	Acquisition Date	2014-09-15T13:10:24
13	Modification Date	2014-09-23T13:32:53
14	Spectrometer Frequency	160.38
15	Spectral Width	32051.3
16	Lowest Frequency	-15759.6
17	Nucleus	11B
18	Acquired Size	3205
19	Spectral Size	8192

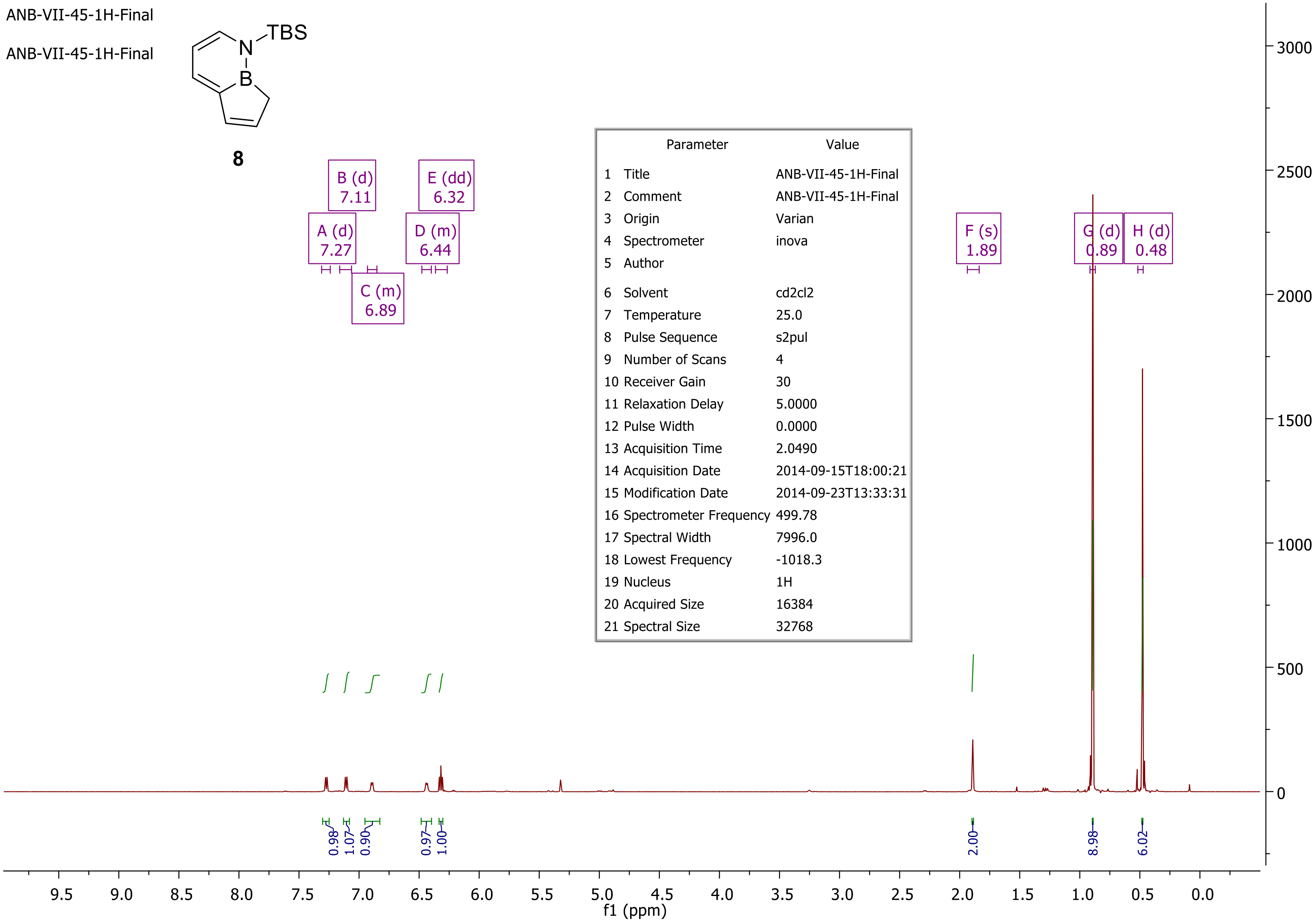




	Parameter	Value
1	Title	ANB-VII-Final-1H-combined
2	Comment	ANB-VII-Final-1H-combined
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	4
10	Receiver Gain	30
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0447
14	Acquisition Date	2014-09-15T13:15:18
15	Modification Date	2014-09-23T13:32:53
16	Spectrometer Frequency	499.88
17	Spectral Width	8012.8
18	Lowest Frequency	-1014.6
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

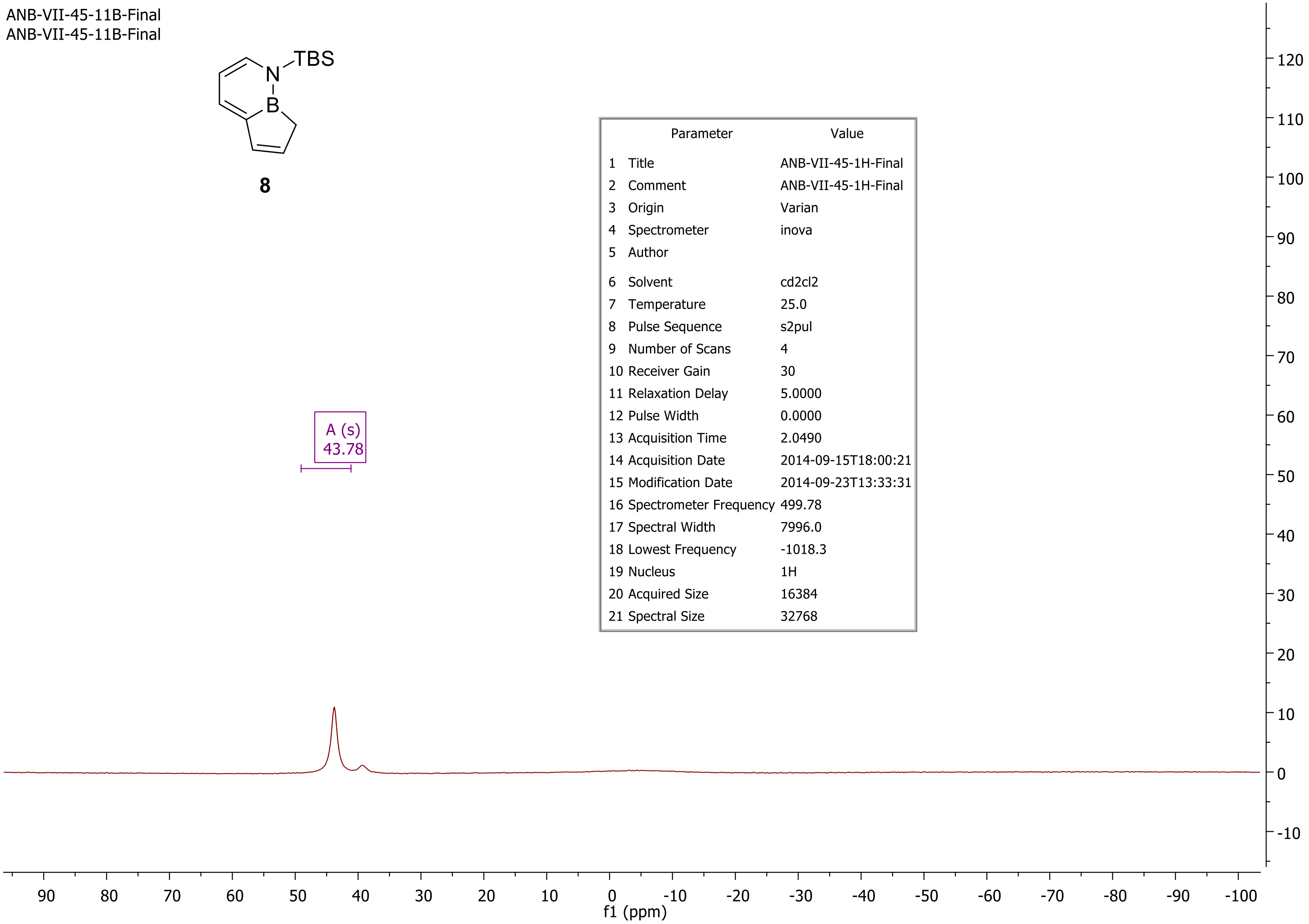
ANB-VII-45-1H-Final

ANB-VII-45-1H-Final



	Parameter	Value
1	Title	ANB-VII-45-1H-Final
2	Comment	ANB-VII-45-1H-Final
3	Origin	Varian
4	Spectrometer	inova
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	4
10	Receiver Gain	30
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0490
14	Acquisition Date	2014-09-15T18:00:21
15	Modification Date	2014-09-23T13:33:31
16	Spectrometer Frequency	499.78
17	Spectral Width	7996.0
18	Lowest Frequency	-1018.3
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

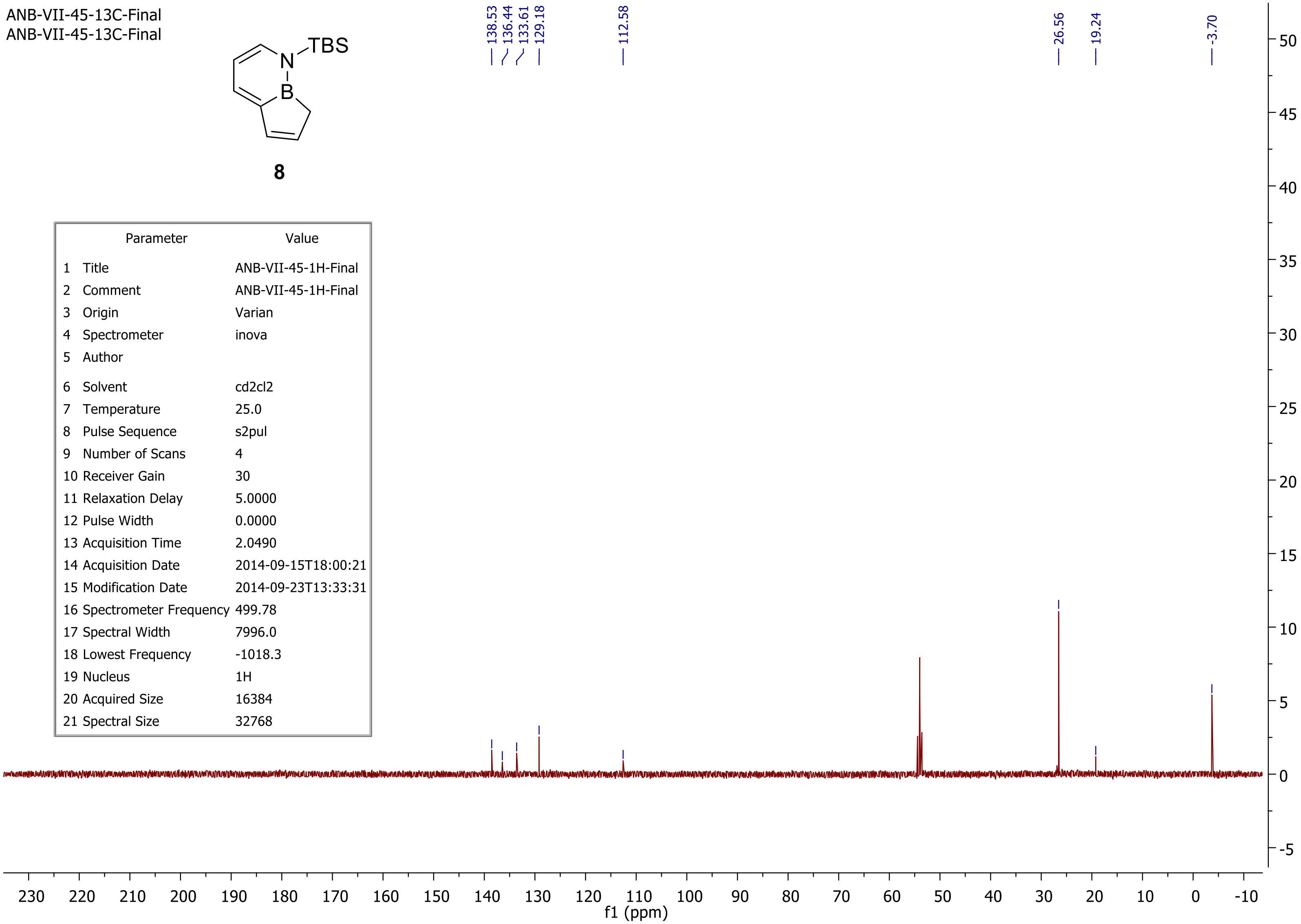
ANB-VII-45-11B-Final
ANB-VII-45-11B-Final



8

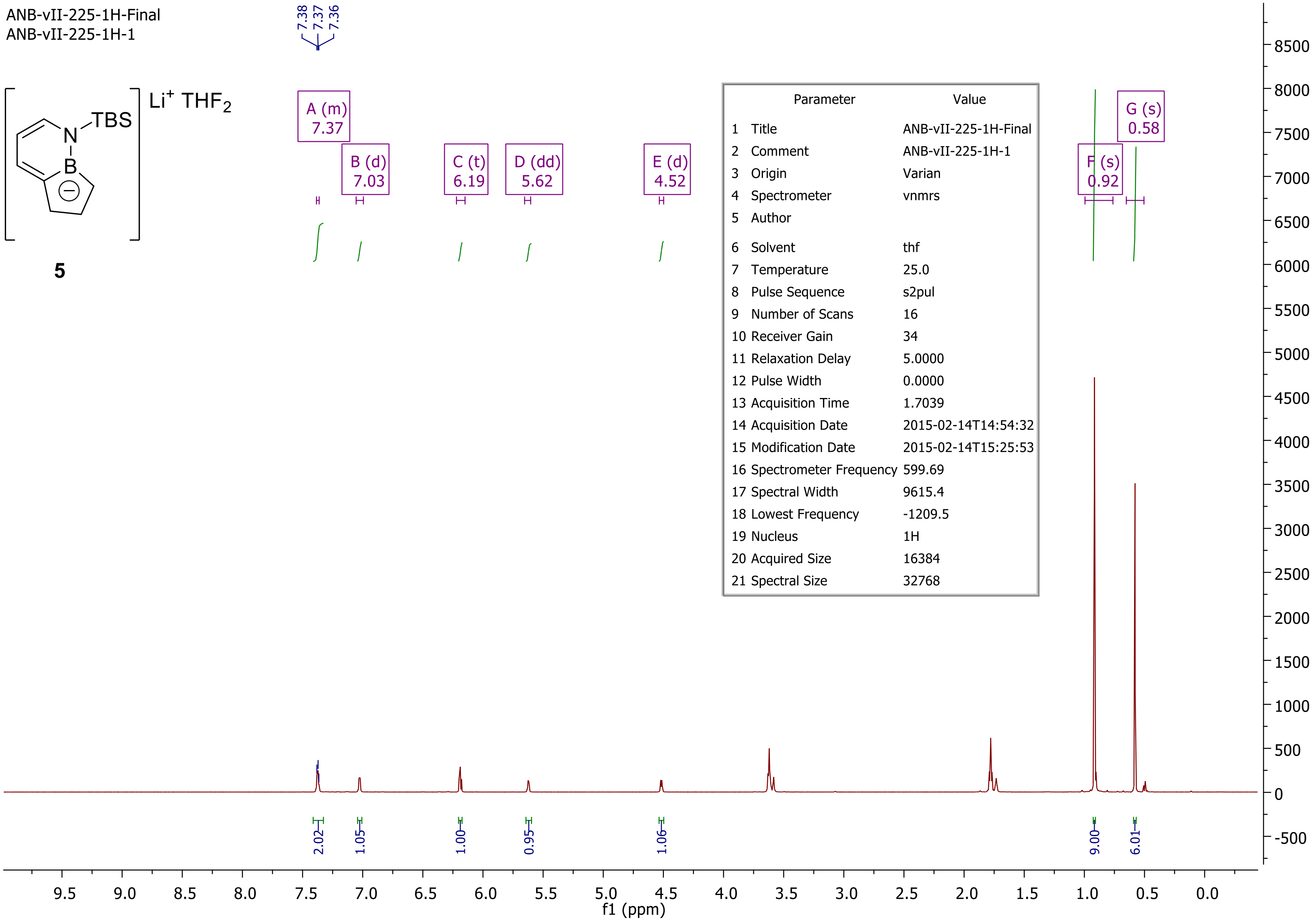
	Parameter	Value
1	Title	ANB-VII-45-1H-Final
2	Comment	ANB-VII-45-1H-Final
3	Origin	Varian
4	Spectrometer	inova
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	4
10	Receiver Gain	30
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0490
14	Acquisition Date	2014-09-15T18:00:21
15	Modification Date	2014-09-23T13:33:31
16	Spectrometer Frequency	499.78
17	Spectral Width	7996.0
18	Lowest Frequency	-1018.3
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

ANB-VII-45-13C-Final
ANB-VII-45-13C-Final



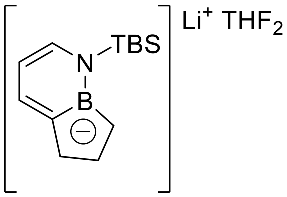
8

	Parameter	Value
1	Title	ANB-VII-45-1H-Final
2	Comment	ANB-VII-45-1H-Final
3	Origin	Varian
4	Spectrometer	inova
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	4
10	Receiver Gain	30
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0490
14	Acquisition Date	2014-09-15T18:00:21
15	Modification Date	2014-09-23T13:33:31
16	Spectrometer Frequency	499.78
17	Spectral Width	7996.0
18	Lowest Frequency	-1018.3
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768



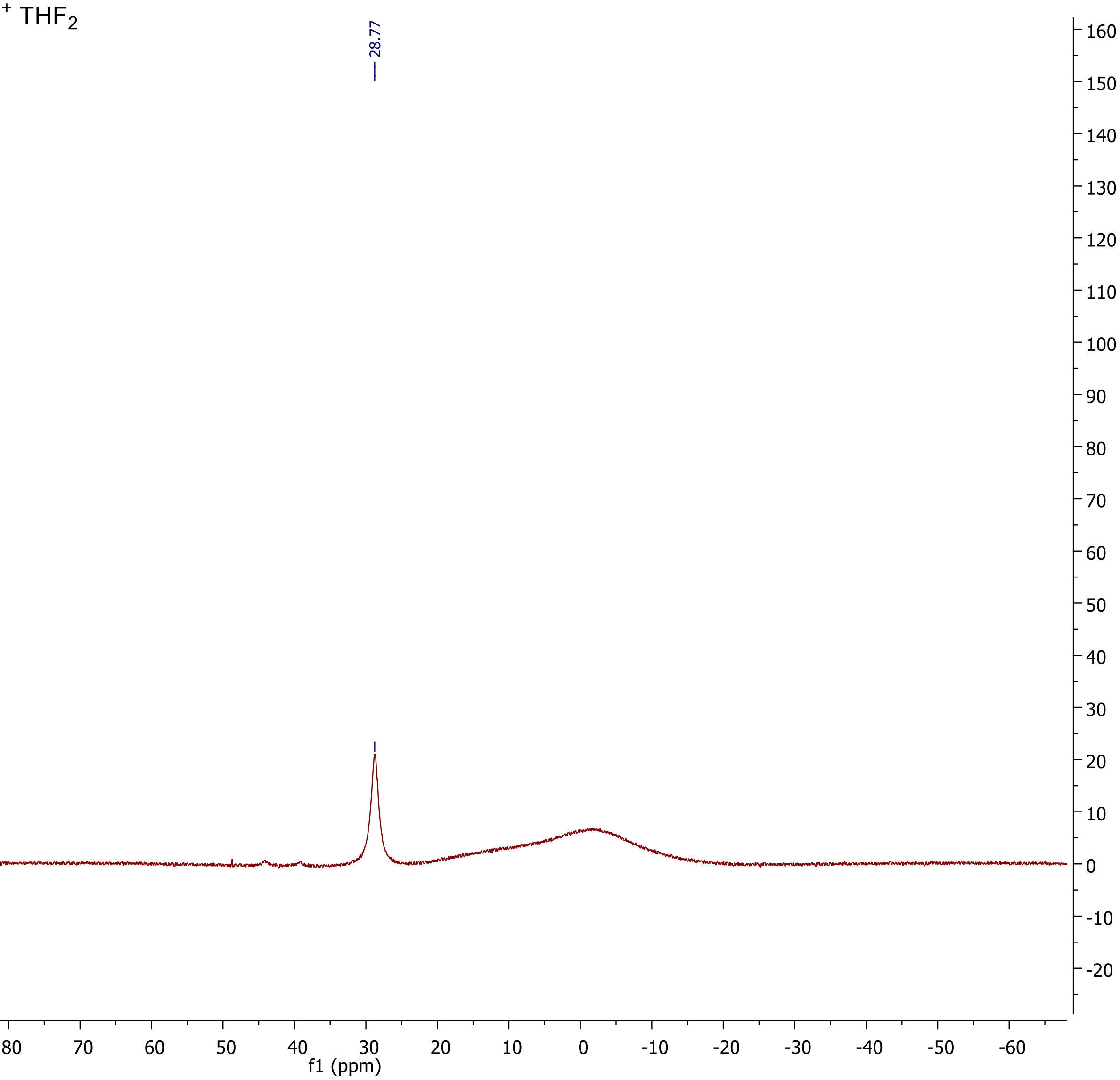
	Parameter	Value
1	Title	ANB-vII-225-1H-Final
2	Comment	ANB-vII-225-1H-1
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	thf
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	16
10	Receiver Gain	34
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.7039
14	Acquisition Date	2015-02-14T14:54:32
15	Modification Date	2015-02-14T15:25:53
16	Spectrometer Frequency	599.69
17	Spectral Width	9615.4
18	Lowest Frequency	-1209.5
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

ANB-vII-225-11B-2
ANB-vII-225-11B-2

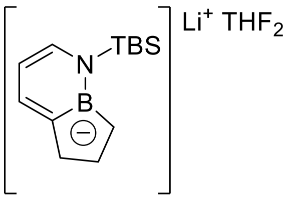


5

Parameter	Value
1 Title	ANB-vII-225-1H-Final
2 Comment	ANB-vII-225-1H-1
3 Origin	Varian
4 Spectrometer	vnmrs
5 Author	
6 Solvent	thf
7 Temperature	25.0
8 Pulse Sequence	s2pul
9 Number of Scans	16
10 Receiver Gain	34
11 Relaxation Delay	5.0000
12 Pulse Width	0.0000
13 Acquisition Time	1.7039
14 Acquisition Date	2015-02-14T14:54:32
15 Modification Date	2015-02-14T15:25:53
16 Spectrometer Frequency	599.69
17 Spectral Width	9615.4
18 Lowest Frequency	-1209.5
19 Nucleus	1H
20 Acquired Size	16384
21 Spectral Size	32768



ANB-vII-225-13C-Final
ANB-vII-225-13C-Final



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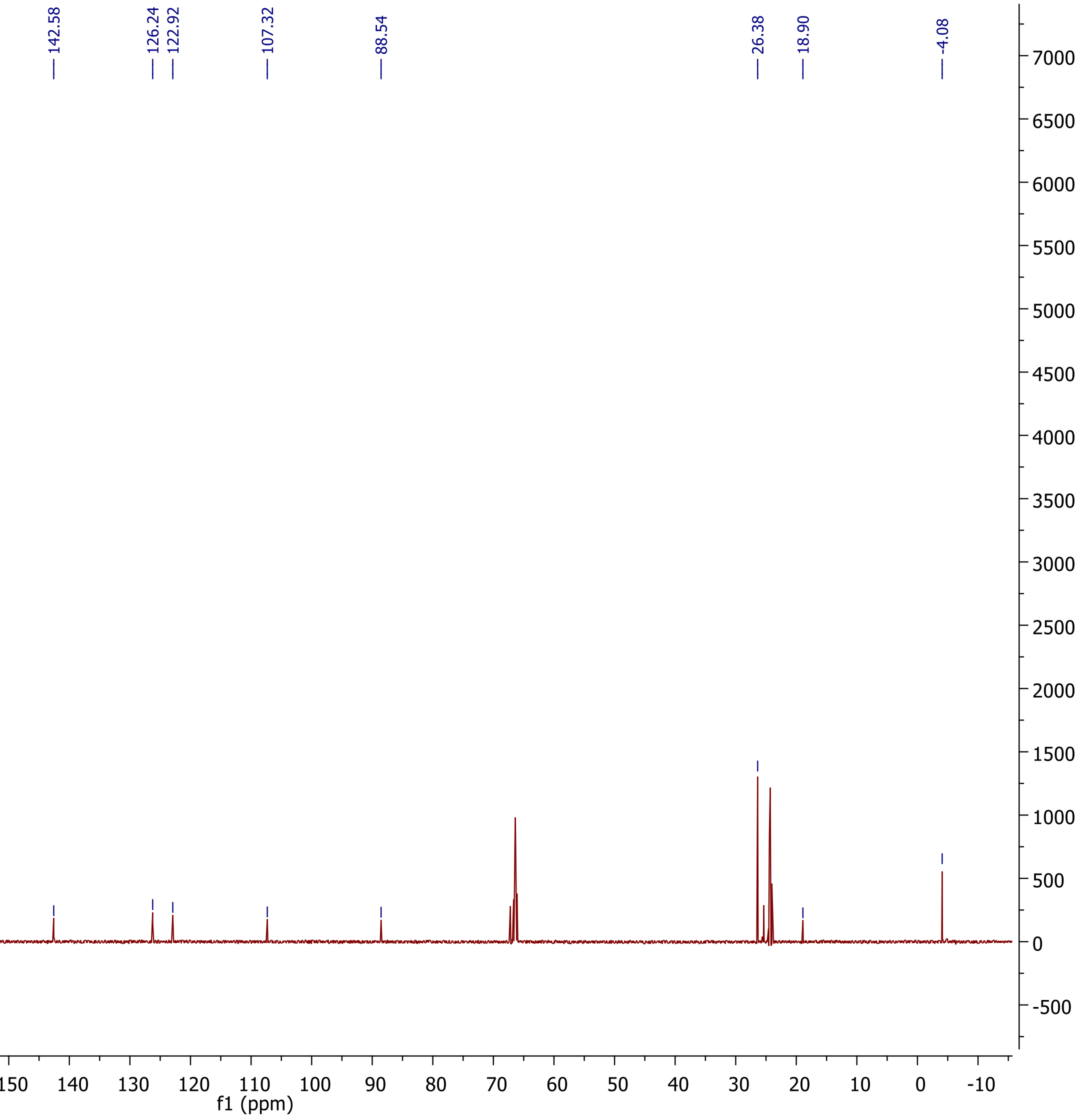
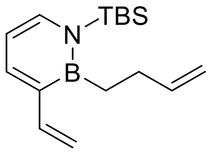
Parameter	Value
1 Title	ANB-vII-225-1H-Final
2 Comment	ANB-vII-225-1H-1
3 Origin	Varian
4 Spectrometer	vnmrs
5 Author	
6 Solvent	thf
7 Temperature	25.0
8 Pulse Sequence	s2pul
9 Number of Scans	16
10 Receiver Gain	34
11 Relaxation Delay	5.0000
12 Pulse Width	0.0000
13 Acquisition Time	1.7039
14 Acquisition Date	2015-02-14T14:54:32
15 Modification Date	2015-02-14T15:25:53
16 Spectrometer Frequency	599.69
17 Spectral Width	9615.4
18 Lowest Frequency	-1209.5
19 Nucleus	1H
20 Acquired Size	16384
21 Spectral Size	32768



ANB-VII-57-1H-Final
ANB-VII-57-1H-Final



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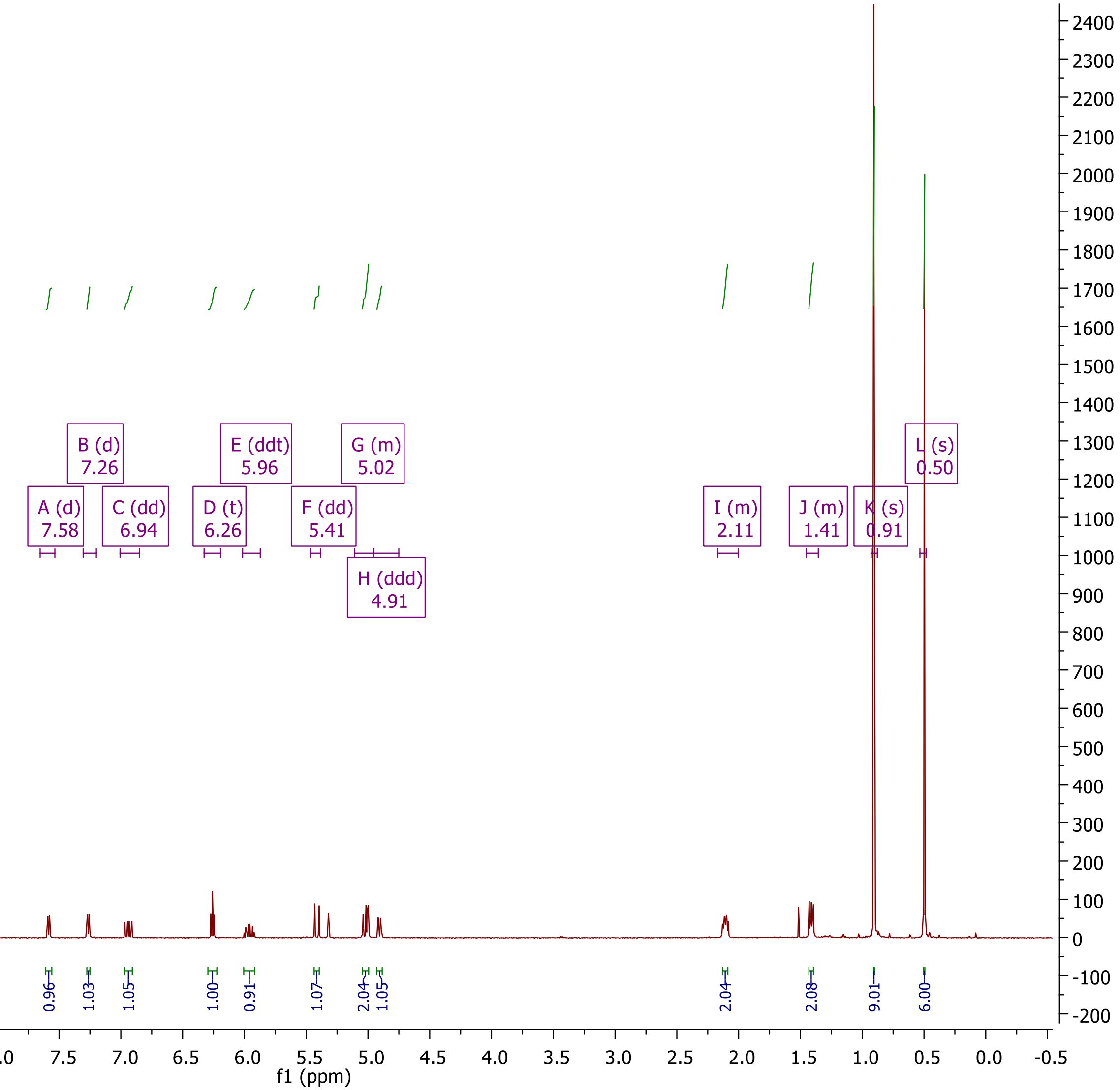
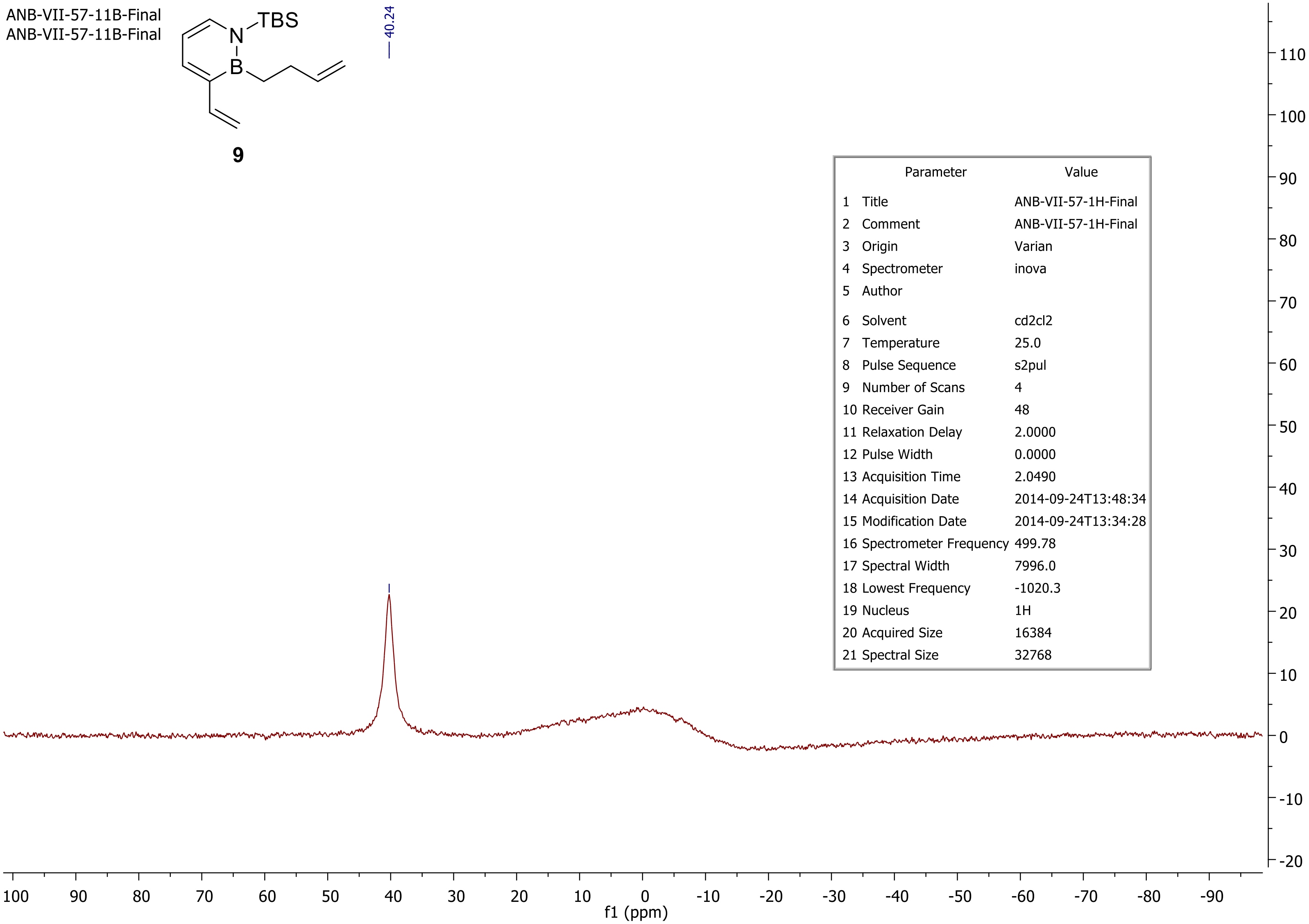


	Parameter	Value
1	Title	ANB-VII-57-1H-Final
2	Comment	ANB-VII-57-1H-Final
3	Origin	Varian
4	Spectrometer	inova
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	4
10	Receiver Gain	48
11	Relaxation Delay	2.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0490
14	Acquisition Date	2014-09-24T13:48:34
15	Modification Date	2014-09-24T13:34:28
16	Spectrometer Frequency	499.78
17	Spectral Width	7996.0
18	Lowest Frequency	-1020.3
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768



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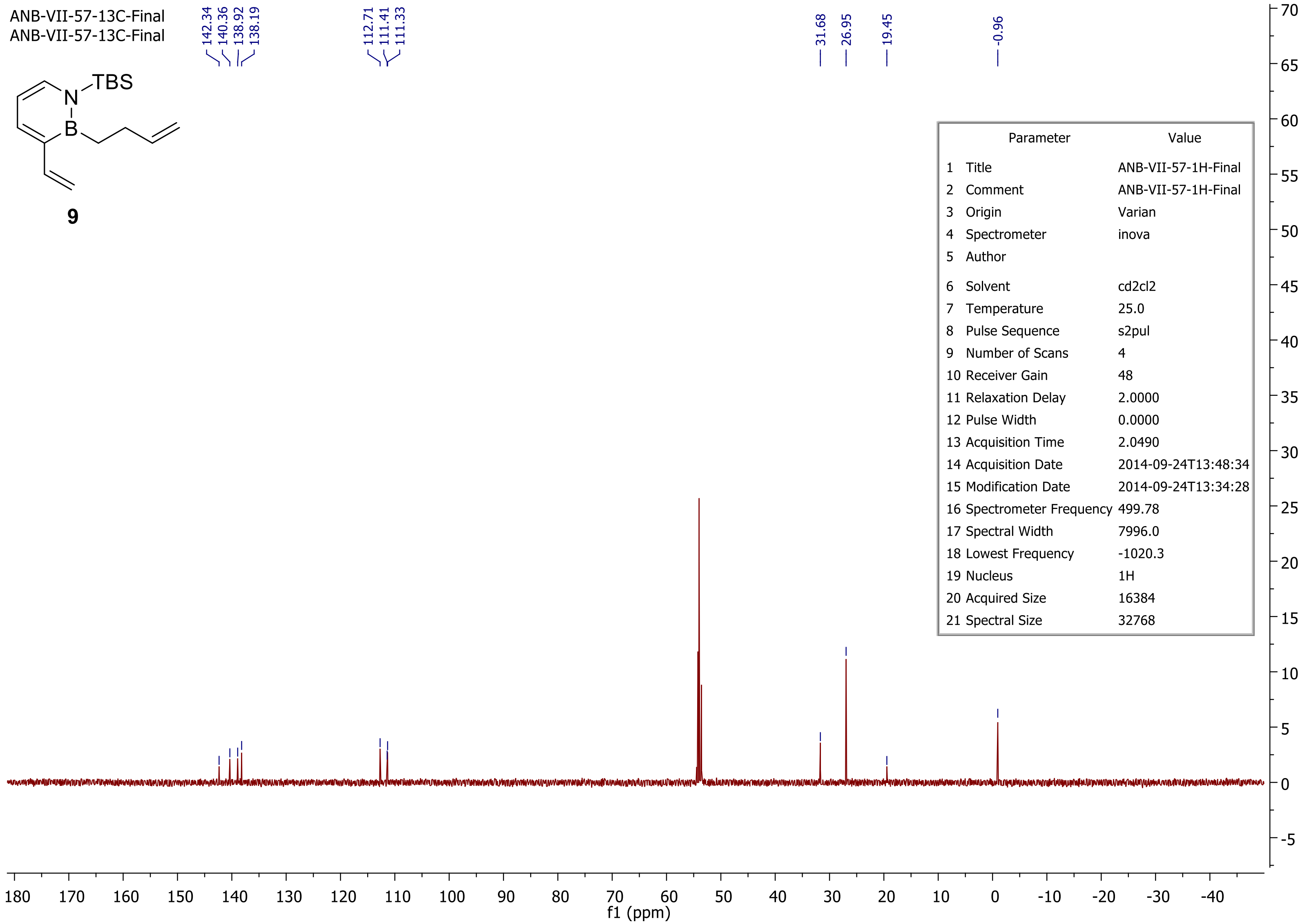
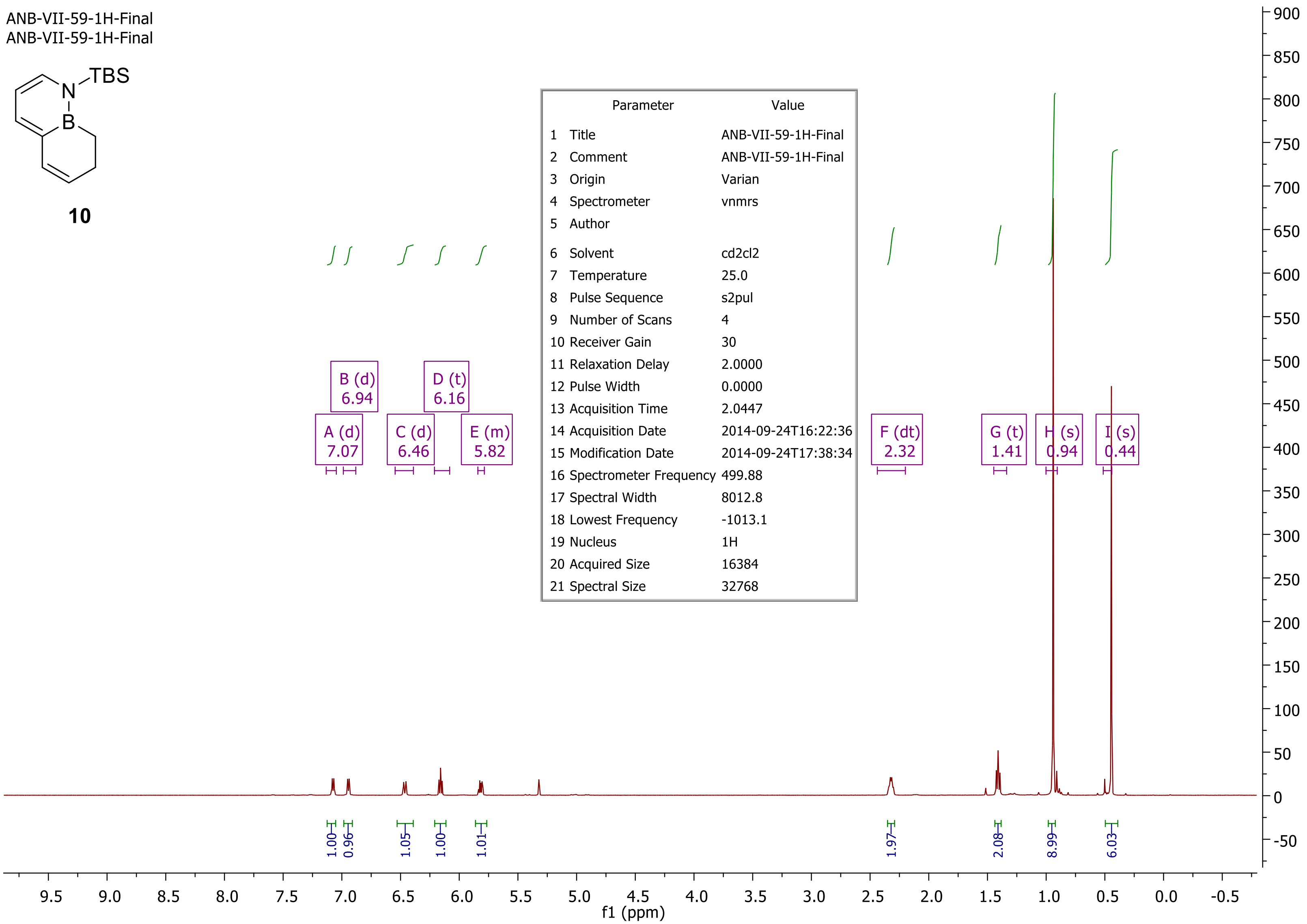
	Parameter	Value
1	Title	ANB-VII-57-1H-Final
2	Comment	ANB-VII-57-1H-Final
3	Origin	Varian
4	Spectrometer	inova
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	4
10	Receiver Gain	48
11	Relaxation Delay	2.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0490
14	Acquisition Date	2014-09-24T13:48:34
15	Modification Date	2014-09-24T13:34:28
16	Spectrometer Frequency	499.78
17	Spectral Width	7996.0
18	Lowest Frequency	-1020.3
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

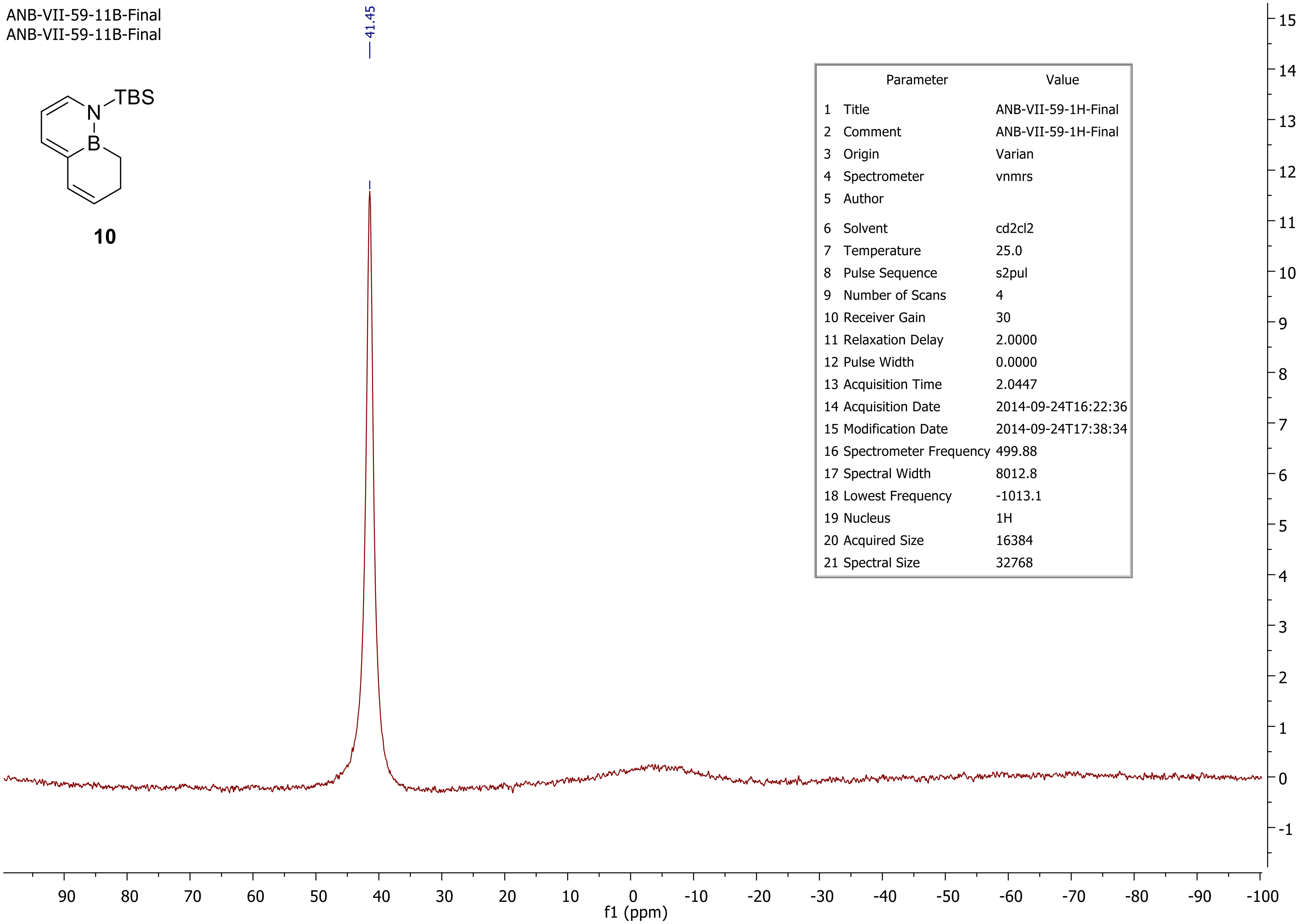


	Parameter	Value
1	Title	ANB-VII-57-1H-Final
2	Comment	ANB-VII-57-1H-Final
3	Origin	Varian
4	Spectrometer	inova
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	4
10	Receiver Gain	48
11	Relaxation Delay	2.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0490
14	Acquisition Date	2014-09-24T13:48:34
15	Modification Date	2014-09-24T13:34:28
16	Spectrometer Frequency	499.78
17	Spectral Width	7996.0
18	Lowest Frequency	-1020.3
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

ANB-VII-59-1H-Final
ANB-VII-59-1H-Final

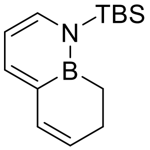


	Parameter	Value
1	Title	ANB-VII-59-1H-Final
2	Comment	ANB-VII-59-1H-Final
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	4
10	Receiver Gain	30
11	Relaxation Delay	2.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0447
14	Acquisition Date	2014-09-24T16:22:36
15	Modification Date	2014-09-24T17:38:34
16	Spectrometer Frequency	499.88
17	Spectral Width	8012.8
18	Lowest Frequency	-1013.1
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768



	Parameter	Value
1	Title	ANB-VII-59-1H-Final
2	Comment	ANB-VII-59-1H-Final
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	4
10	Receiver Gain	30
11	Relaxation Delay	2.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0447
14	Acquisition Date	2014-09-24T16:22:36
15	Modification Date	2014-09-24T17:38:34
16	Spectrometer Frequency	499.88
17	Spectral Width	8012.8
18	Lowest Frequency	-1013.1
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

ANB-VII-59-13C-Final
ANB-VII-59-13C-Final



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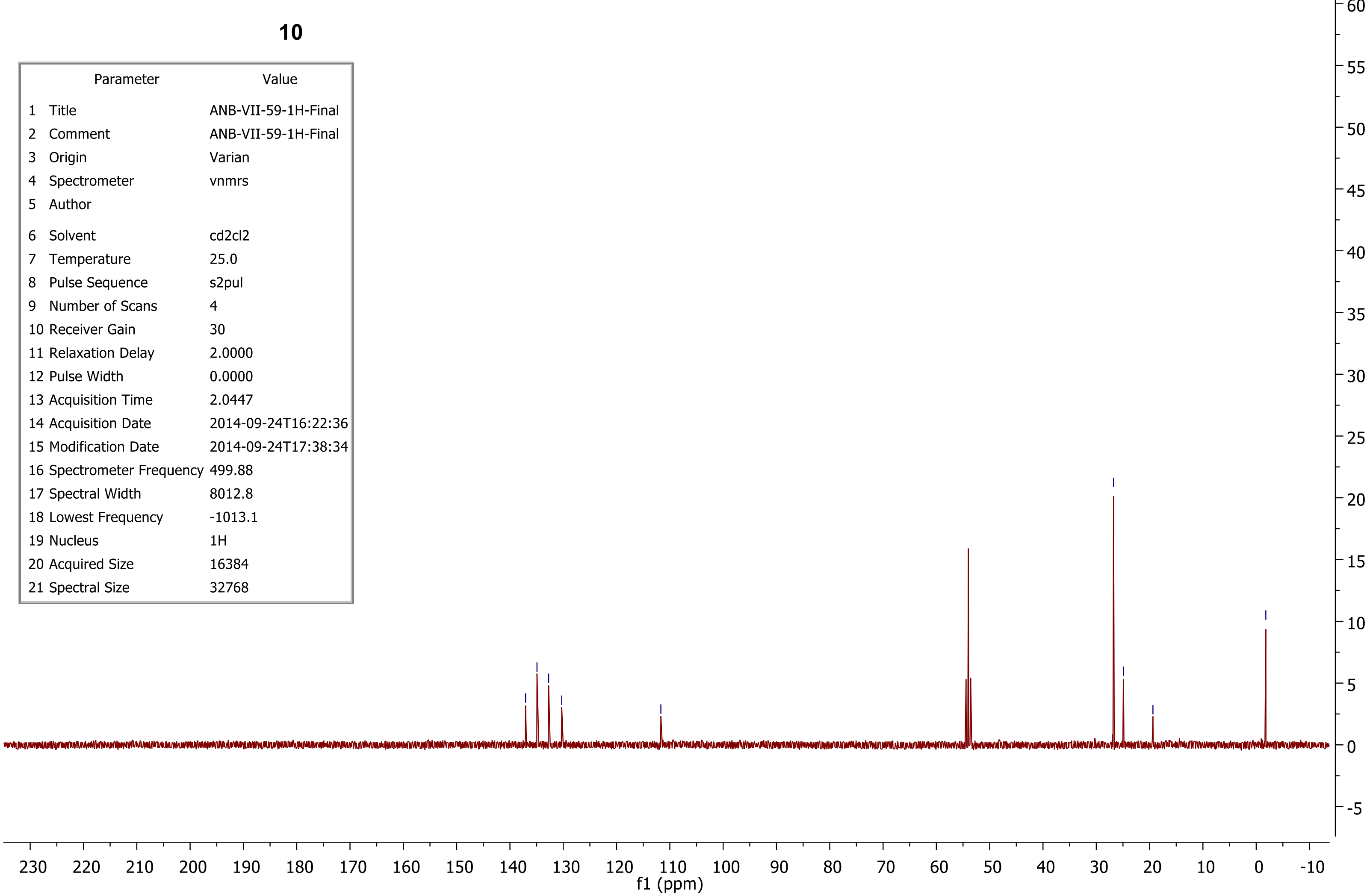
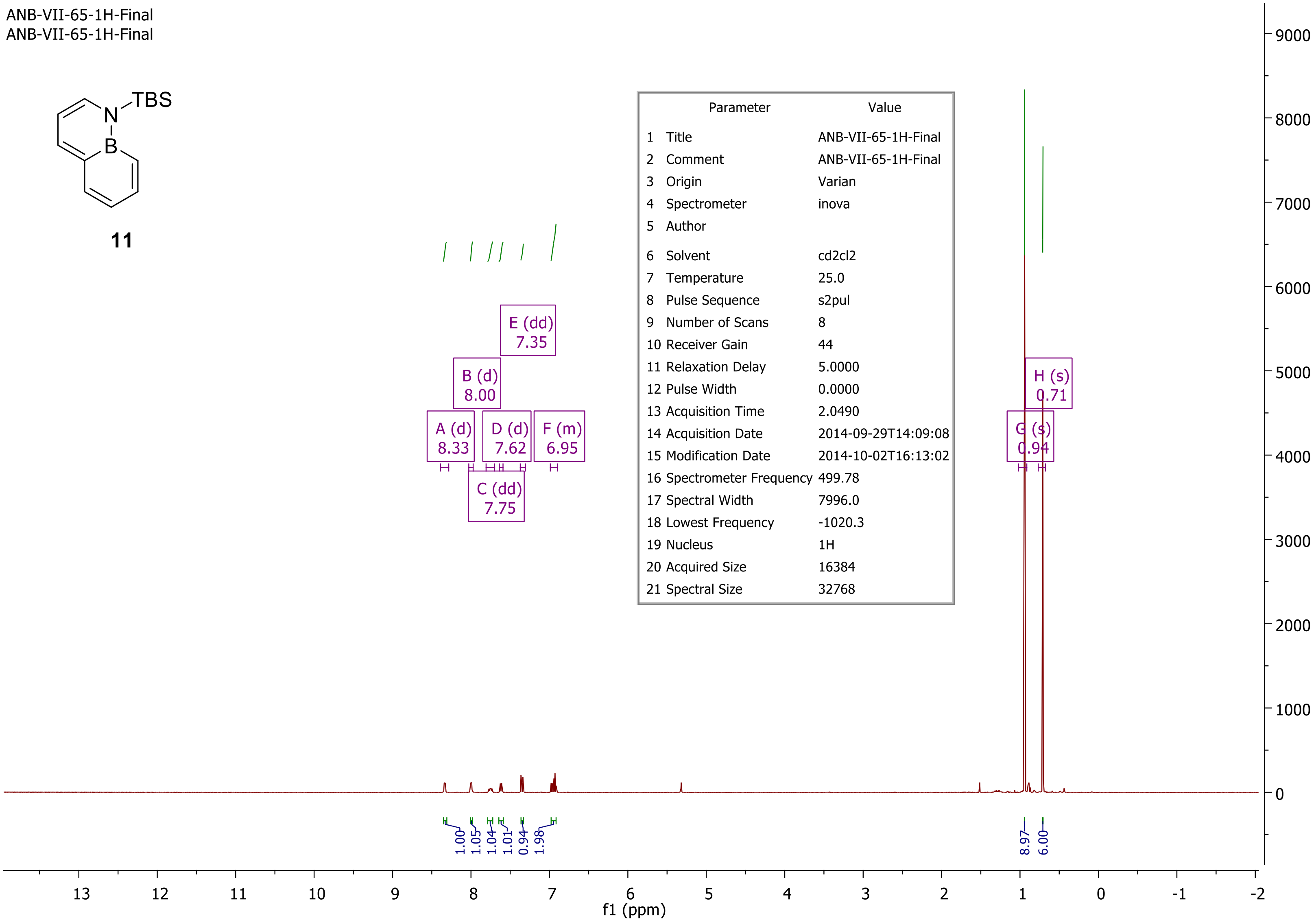
	Parameter	Value
1	Title	ANB-VII-59-1H-Final
2	Comment	ANB-VII-59-1H-Final
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	4
10	Receiver Gain	30
11	Relaxation Delay	2.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0447
14	Acquisition Date	2014-09-24T16:22:36
15	Modification Date	2014-09-24T17:38:34
16	Spectrometer Frequency	499.88
17	Spectral Width	8012.8
18	Lowest Frequency	-1013.1
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768



ANB-VII-65-1H-Final
ANB-VII-65-1H-Final



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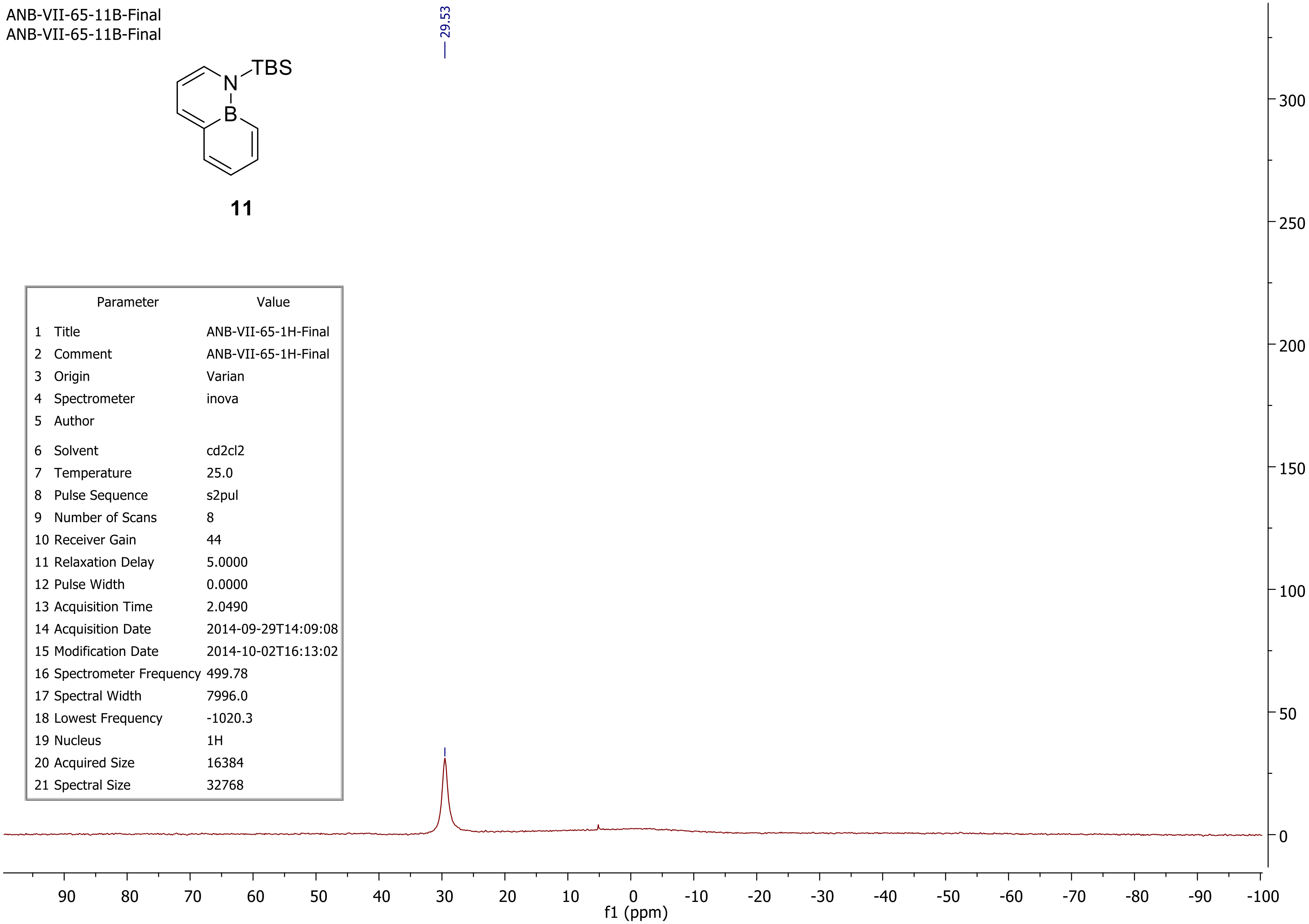
	Parameter	Value
1	Title	ANB-VII-65-1H-Final
2	Comment	ANB-VII-65-1H-Final
3	Origin	Varian
4	Spectrometer	inova
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	8
10	Receiver Gain	44
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0490
14	Acquisition Date	2014-09-29T14:09:08
15	Modification Date	2014-10-02T16:13:02
16	Spectrometer Frequency	499.78
17	Spectral Width	7996.0
18	Lowest Frequency	-1020.3
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768



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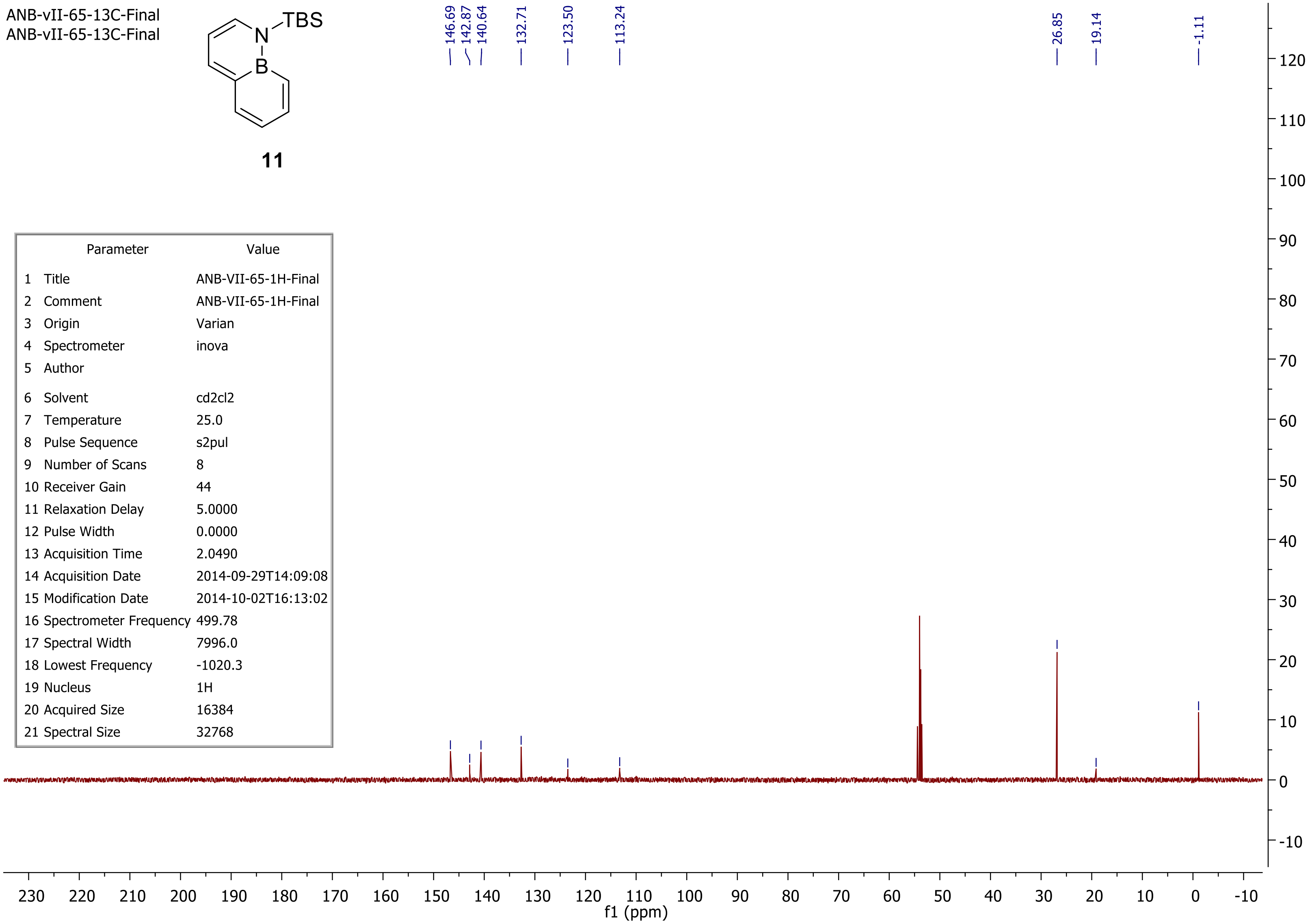
	Parameter	Value
1	Title	ANB-VII-65-1H-Final
2	Comment	ANB-VII-65-1H-Final
3	Origin	Varian
4	Spectrometer	inova
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	8
10	Receiver Gain	44
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0490
14	Acquisition Date	2014-09-29T14:09:08
15	Modification Date	2014-10-02T16:13:02
16	Spectrometer Frequency	499.78
17	Spectral Width	7996.0
18	Lowest Frequency	-1020.3
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

ANB-vII-65-13C-Final
ANB-vII-65-13C-Final



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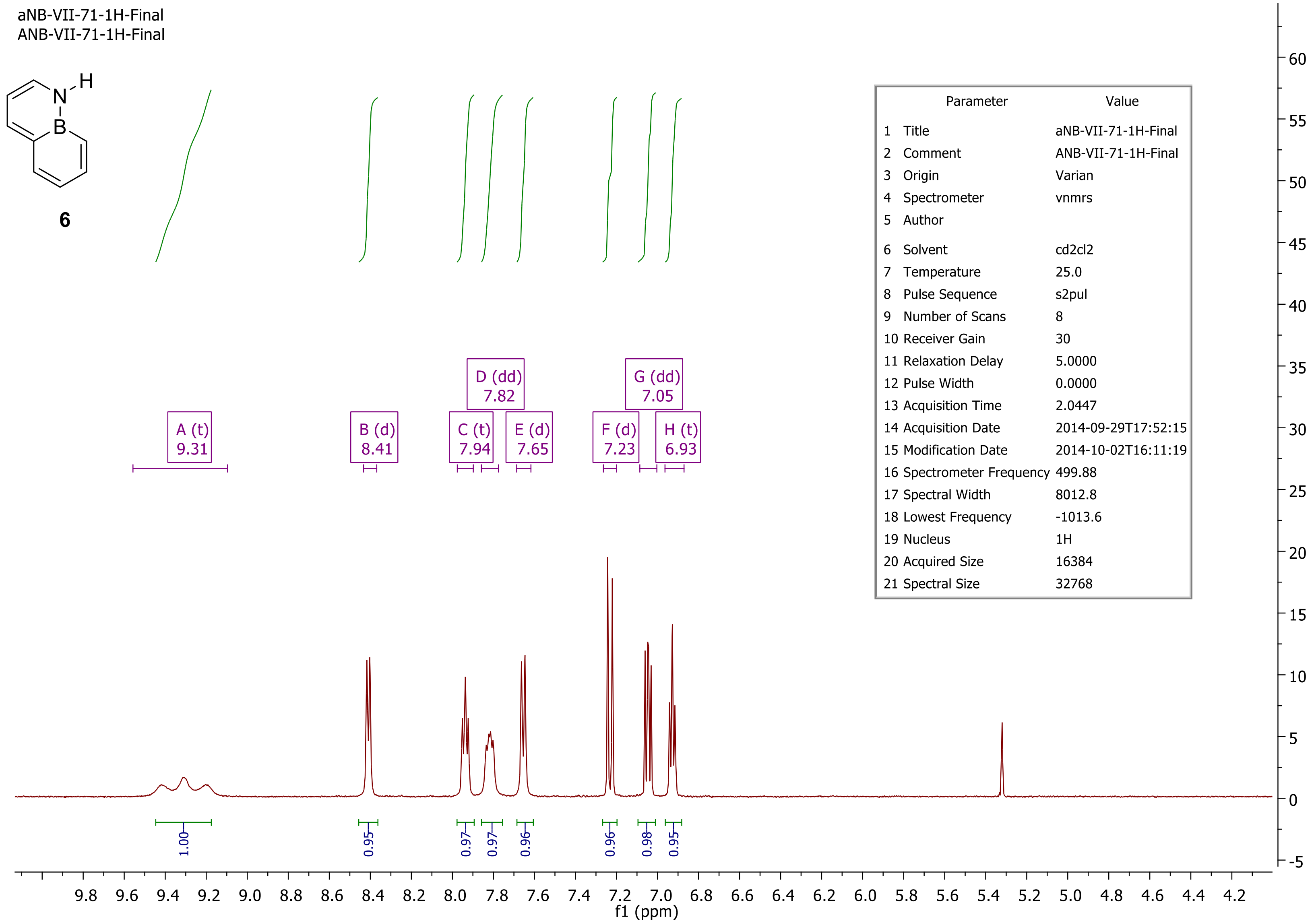
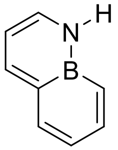
	Parameter	Value
1	Title	ANB-VII-65-1H-Final
2	Comment	ANB-VII-65-1H-Final
3	Origin	Varian
4	Spectrometer	inova
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	8
10	Receiver Gain	44
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0490
14	Acquisition Date	2014-09-29T14:09:08
15	Modification Date	2014-10-02T16:13:02
16	Spectrometer Frequency	499.78
17	Spectral Width	7996.0
18	Lowest Frequency	-1020.3
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768



	Parameter	Value
1	Title	aNB-VII-71-1H-Final
2	Comment	ANB-VII-71-1H-Final
3	Origin	Varian
4	Spectrometer	vnmrs
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	8
10	Receiver Gain	30
11	Relaxation Delay	5.0000
12	Pulse Width	0.0000
13	Acquisition Time	2.0447
14	Acquisition Date	2014-09-29T17:52:15
15	Modification Date	2014-10-02T16:11:19
16	Spectrometer Frequency	499.88
17	Spectral Width	8012.8
18	Lowest Frequency	-1013.6
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

ANB-VII-71-11B-Final
ANB-VII-71-11B-Final



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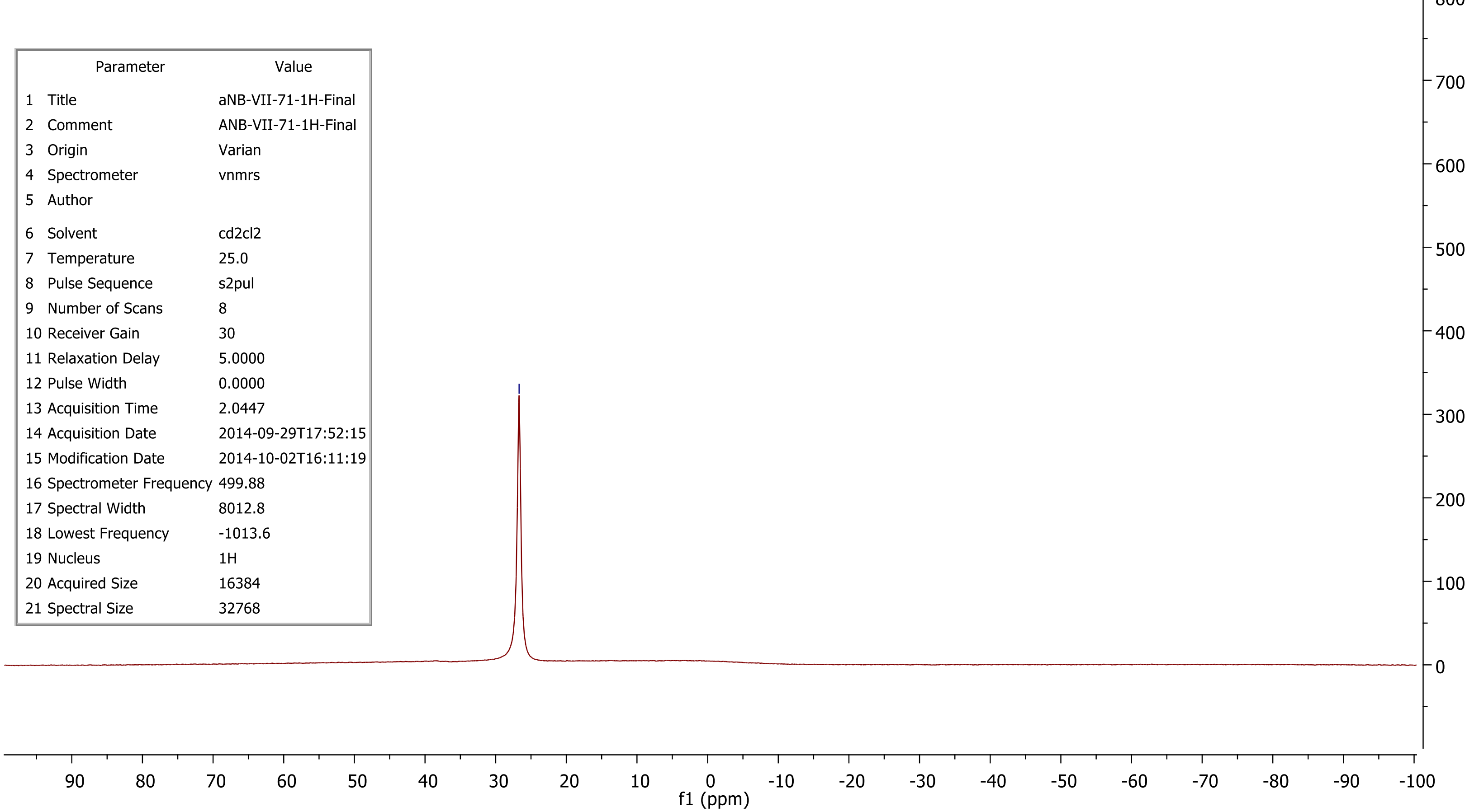
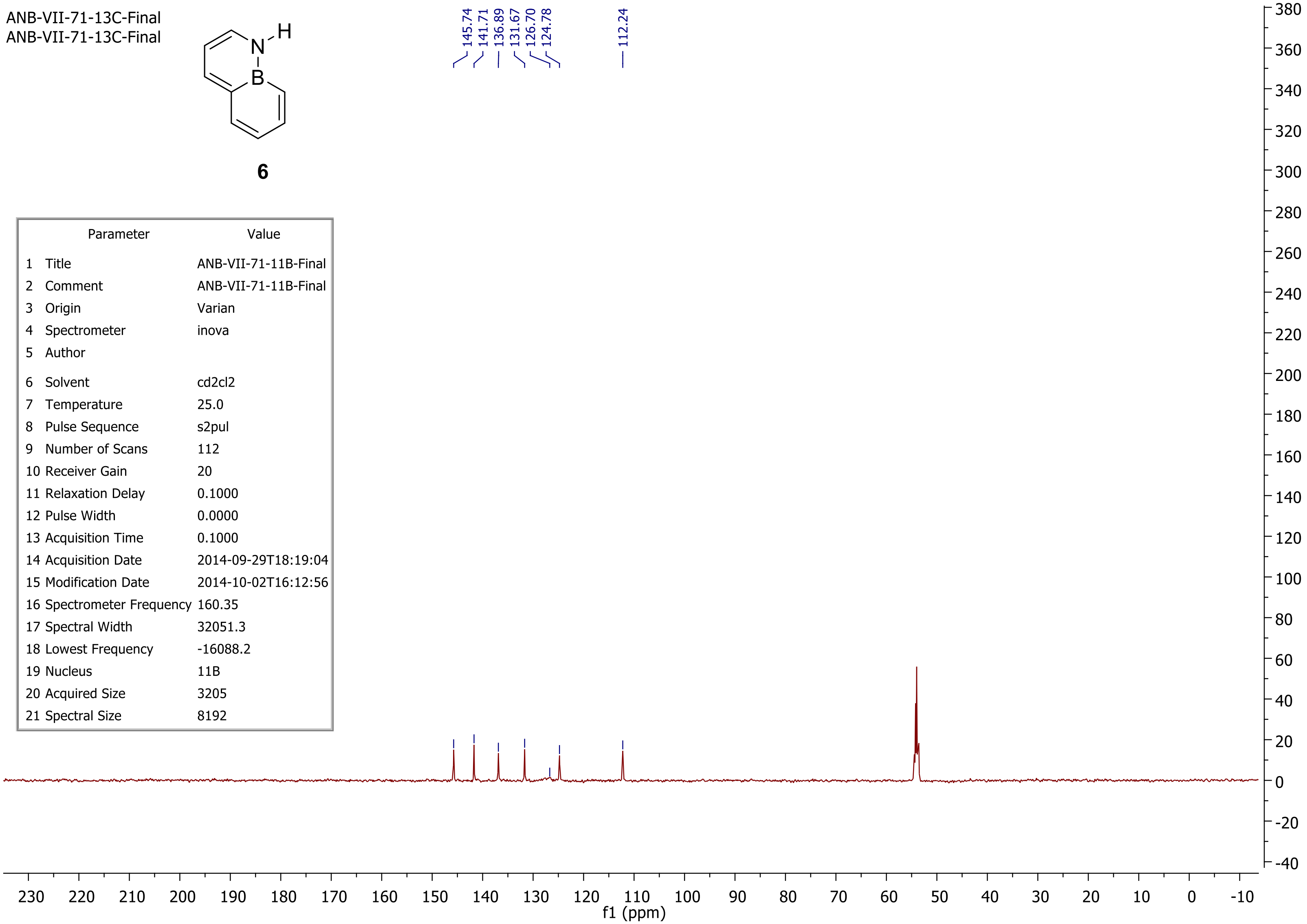
Parameter	Value
1 Title	aNB-VII-71-1H-Final
2 Comment	ANB-VII-71-1H-Final
3 Origin	Varian
4 Spectrometer	vnmrs
5 Author	
6 Solvent	cd2cl2
7 Temperature	25.0
8 Pulse Sequence	s2pul
9 Number of Scans	8
10 Receiver Gain	30
11 Relaxation Delay	5.0000
12 Pulse Width	0.0000
13 Acquisition Time	2.0447
14 Acquisition Date	2014-09-29T17:52:15
15 Modification Date	2014-10-02T16:11:19
16 Spectrometer Frequency	499.88
17 Spectral Width	8012.8
18 Lowest Frequency	-1013.6
19 Nucleus	1H
20 Acquired Size	16384
21 Spectral Size	32768



ANB-VII-71-13C-Final
ANB-VII-71-13C-Final



	Parameter	Value
1	Title	ANB-VII-71-11B-Final
2	Comment	ANB-VII-71-11B-Final
3	Origin	Varian
4	Spectrometer	inova
5	Author	
6	Solvent	cd2cl2
7	Temperature	25.0
8	Pulse Sequence	s2pul
9	Number of Scans	112
10	Receiver Gain	20
11	Relaxation Delay	0.1000
12	Pulse Width	0.0000
13	Acquisition Time	0.1000
14	Acquisition Date	2014-09-29T18:19:04
15	Modification Date	2014-10-02T16:12:56
16	Spectrometer Frequency	160.35
17	Spectral Width	32051.3
18	Lowest Frequency	-16088.2
19	Nucleus	11B
20	Acquired Size	3205
21	Spectral Size	8192