

# Supplementary Information

## Supplementary Methods

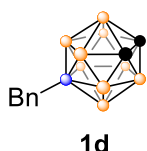
**General Procedures.** All reactions were carried out in oven-dried glassware under an atmosphere of dry N<sub>2</sub> with the rigid exclusion of air and moisture using standard Schlenk techniques or in a glovebox. Organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Compounds **1b**,<sup>1</sup> **1c**,<sup>2,3</sup> **1e**,<sup>2,3,4</sup> **1g**,<sup>4</sup> **1i**,<sup>4</sup> **1j**,<sup>4</sup> **1k**,<sup>5</sup> **1l**,<sup>2</sup> **1m**,<sup>2,3</sup> **1n**,<sup>6</sup> **1o**,<sup>2,3</sup> **1p**,<sup>7</sup> **1q**,<sup>6</sup> **1r**,<sup>8</sup> **6a**,<sup>9</sup> and ( $\eta^6$ -MesH)Ir(Bpin)<sub>3</sub><sup>10</sup> were prepared according to literature procedures. All other chemicals were purchased from either Aldrich or J&K Chemical Co. and used as received unless otherwise specified. <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on a Varian Inova 300 spectrometer at 300 MHz and 282 MHz, respectively. <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on either a Varian Inova 300 spectrometer at 75 Hz or a Bruker 400 spectrometer at 100 Hz. <sup>11</sup>B{<sup>1</sup>H} NMR spectra were recorded on a Bruker 400 spectrometer at 128 MHz. All signals were reported in ppm unit with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external BF<sub>3</sub> OEt<sub>2</sub> (0.00) for boron chemical shifts and to external CFC<sub>3</sub> (0.00) for fluorine chemical shifts. Mass spectra were obtained on a Thermo Finnigan MAT 95 XL spectrometer. Elemental analyses were performed with an elementary VARIO EL III elemental analyzer, Shanghai Institute of Organic Chemistry, CAS.

## Preparation of Starting Materials.

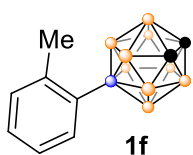
### (1) Preparation of **1d**, **1f**, **1h**. A representative procedure.

To a THF (15 mL) solution of 9-iodo-*o*-carborane (2.700 g, 10.0 mmol) and [(PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>] (280 mg,

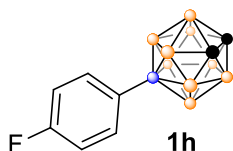
0.4 mmol) was added RMgBr (1.0 M in THF, 50.0 mL, 50.0 mmol) and CuI (76 mg, 0.4 mmol), respectively, under an atmosphere of dry nitrogen at 0 °C. The resulting mixture was stirred at 45 °C till the completion of the reaction as monitored by GC-MS. The reaction was slowly quenched with water at 0 °C and extracted with diethyl ether (20 mL x 3). The ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give product **1**.



**1d**: Yield: 81%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.21 (m, 2H), 7.04 (m, 3H) (aromatic CH), 3.44 (s, 1H), 3.39 (s, 1H) (cage CH), 3.21 (s, 2H) ( $\text{B}_{\text{cage}}\text{-CH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  144.7, 128.5, 128.0, 124.1 (aromatic C), 53.3, 48.5 (cage CH), the  $\text{B}_{\text{cage}}\text{-CH}_2$  was not observed;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  8.4 (s, 1B) ( $\text{B}_{\text{cage}}\text{-CH}_2$ ), -1.9 (d,  $J_{\text{BH}} = 148$  Hz, 2B), -8.7 (d,  $J_{\text{BH}} = 149$  Hz, 2B), -13.7 (d,  $J_{\text{BH}} = 76$  Hz, 2B), -14.3 (m, 2B), -15.4 (d,  $J_{\text{BH}} = 163$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ); analysis (calcd., found for  $\text{C}_9\text{H}_{18}\text{B}_{10}$ ): C (46.13, 46.37), H (7.74, 7.69).



**1f**: Yield: 70%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.50 (m, 1H), 7.08 (m, 3H) (aromatic CH), 3.58 (s, 1H), 3.55 (s, 1H) (cage CH), 2.49 (s, 3H) ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  141.7, 136.0, 130.4, 127.5, 125.0 (aromatic C), 53.1, 50.5 (cage CH), 24.1 ( $\text{CH}_3$ ), the  $\text{B}_{\text{cage}}\text{-C}$  was not observed.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  7.7 (s, 1B) ( $\text{B}_{\text{cage}}\text{-C}$ ), -1.7 (d,  $J_{\text{BH}} = 149$  Hz, 2B), -8.4 (d,  $J_{\text{BH}} = 149$  Hz, 2B), -13.5 (d,  $J_{\text{BH}} = 91$  Hz, 2B), -14.2 (d,  $J_{\text{BH}} = 75$  Hz, 2B), -15.4 (d,  $J_{\text{BH}} = 163$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ); analysis (calcd., found for  $\text{C}_9\text{H}_{18}\text{B}_{10}$ ): C (46.13, 46.25), H (7.74, 7.46).



**1h**: White solid, Yield: 83%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.33 (m, 2H), 6.92

(m, 2H) (aromatic CH), 3.64 (s, 1H), 3.53 (s, 1H) (cage CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR

( $\text{CDCl}_3$ , 75 MHz):  $\delta$  162.9 (d,  $^1J_{\text{CF}} = 244$  Hz), 134.1 (d,  $^3J_{\text{CF}} = 7.4$  Hz), 114.4 (d,  $^2J_{\text{CF}} = 19.7$  Hz)

(aromatic C) 53.3, 50.0 (cage CH), the  $\text{B}_{\text{cage}}\text{-C}$  was not observed.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  7.6

(s, 1B) ( $\text{B}_{\text{cage}}\text{-C}$ ), -1.9 (d,  $J_{\text{BH}} = 149$  Hz, 2B), -8.4 (d,  $J_{\text{BH}} = 149$  Hz, 2B), -13.5 (d,  $J_{\text{BH}} = 52$  Hz, 2B),

-14.0 (m, 2B), -15.1 (d,  $J_{\text{BH}} = 174$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ); analysis (calcd., found for  $\text{C}_8\text{H}_{15}\text{FB}_{10}$ ): C (40.32,

40.16), H (6.34, 6.20).

## (2) Preparation of 1-Silyl-*o*-carboranes (**6b**, **6c**). A Representative Procedure.

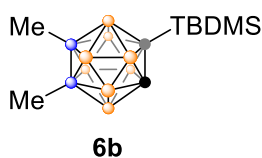
To a diethyl ether solution (8 mL) of *o*-carborane (2.0 mmol) was added  $^n\text{BuLi}$  (1.6 M in ether, 1.3 mL) under an atmosphere of dry nitrogen at  $0^\circ\text{C}$ . After stirring for 2 h at  $0^\circ\text{C}$ , TBDMSCl (452 mg,

3.0 mmol) was added at  $0^\circ\text{C}$  and the resulting mixture was stirred overnight at room temperature.

After hydrolysis with water (10 mL) and extraction with diethyl ether (10 mL x 3), the ether

solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash

column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give the product **6**.



**6b**: Yield 81%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.24 (s, 1H)

(cage CH), 1.01 (s, 9H) ( $\text{C}(\text{CH}_3)_3$ ), 0.21 (s, 6H) ( $\text{SiCH}_3$ ), 0.18 (s, 6H) ( $\text{B}_{\text{cage}}\text{-}$

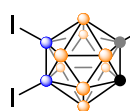
$\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  57.1 (cage C), 53.6 (cage CH),

27.2 ( $\text{C}(\text{CH}_3)_3$ ), 19.5 ( $\text{C}(\text{CH}_3)_3$ ), -4.3 ( $\text{SiCH}_3$ ), the two  $\text{B}_{\text{cage}}\text{-CH}_3$  were not observed.  $^{11}\text{B}$  NMR

( $\text{CDCl}_3$ , 128 MHz):  $\delta$  9.9 (s, 1B), 7.9 (s, 1B) ( $\text{B}_{\text{cage}}\text{-CH}_3$ ), -5.2 (d,  $J_{\text{BH}} = 145$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -10.7

(d,  $J_{\text{BH}} = 177$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -12.4 (d,  $J_{\text{BH}} = 195$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -14.7 (d,  $J_{\text{BH}} = 172$  Hz, 2B)

( $B_{\text{cageH}}$ ); analysis (calcd., found for  $C_{10}H_{30}B_{10}Si$ ): C (41.92, 42.32), H (10.55, 10.56).

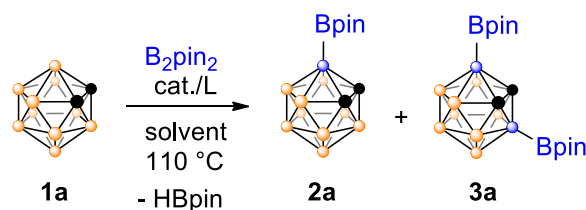


**6c**

**6c:** Yield 81%. White solid.  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  3.83 (s, 1H) (cage CH), 1.03 (s, 9H) ( $C(CH_3)_3$ ), 0.25 (s, 6H) ( $SiCH_3$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 75 MHz):  $\delta$  62.2 (cage C), 57.3 (cage CH), 27.0 ( $C(CH_3)_3$ ), 19.4 ( $C(CH_3)_3$ ), -4.3 ( $SiCH_3$ ).  $^{11}B$  NMR ( $CDCl_3$ , 128 MHz):  $\delta$  -2.7 (d,  $J_{BH} = 156$  Hz, 2B), -9.0 (m, 2B), -10.6 (m, 2B), -11.6 (m, 2B) ( $B_{\text{cageH}}$ ), -12.4 (s, 2B) ( $B_{\text{cage-I}}$ ); analysis (calcd., found for  $C_8H_{24}B_{10}I_2Si$ ): C (18.83, 19.07), H (4.74, 4.74).

### B(3,6)- or B(3)-borylation of *o*-carboranes.

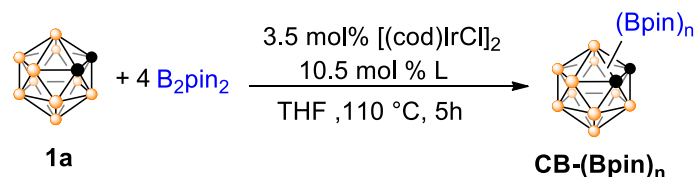
Supplementary Table 1. Optimization of reaction conditions.\*



entry	cat. (mol%)	L (mol%)	B <sub>2</sub> pin <sub>2</sub> (eq.)	solvent	yield (%) <sup>†</sup>		
					1a	2a	3a
1	[(cod)IrCl] <sub>2</sub> (3.5)	-	4	THF	40	60	-
2	[(cod)IrCl] <sub>2</sub> (3.5)	Py (21)	4	THF	10	23	67
3	[(cod)IrCl] <sub>2</sub> (5.0)	2-MePy (20)	4	THF	-	10	90
4	[(cod)IrCl] <sub>2</sub> (3.5)	2-MePy (14)	4	THF	-	10	90
5	[(cod)IrCl] <sub>2</sub> (2.5)	2-MePy (10)	4	THF	-	20	80
6	[(cod)IrCl] <sub>2</sub> (3.5)	2-MePy (21)	4	THF	-	2	98
7	[(cod)IrCl] <sub>2</sub> (3.5)	2-MePy (21)	2	THF	3	35	62
8	[(cod)IrCl] <sub>2</sub> (3.5)	2-MePy (21)	1	THF	12	65	23
9 <sup>‡</sup>	[(cod)IrCl] <sub>2</sub> (3.5)	2-MePy (21)	4	THF	-	9	91
10	[(cod)IrCl] <sub>2</sub> (3.5)	2-MePy (32)	4	THF	-	2	98
11	[(cod)IrCl] <sub>2</sub> (3.5)	2-MePy (21)	4	toluene	63	37	-
12	[(cod)IrCl] <sub>2</sub> (3.5)	2-MePy (21)	4	DME	9	58	33
13	[(cod)IrCl] <sub>2</sub> (3.5)	2-MePy (21)	4	1,4-dioxane	-	33	67
14	[(cod)IrCl] <sub>2</sub> (3.5)	4-MePy (21)	4	THF	-	5	95
15	[(cod)IrCl] <sub>2</sub> (3.5)	4- <sup>t</sup> BuPy (21)	4	THF	6	54	40
16	[(cod)IrCl] <sub>2</sub> (3.5)	2,6-Me <sub>2</sub> Py (21)	4	THF	18	68	14
17	[(cod)IrCl] <sub>2</sub> (3.5)	2,4,6-Me <sub>3</sub> Py (21)	4	THF	32	61	7
18	[(cod)IrCl] <sub>2</sub> (3.5)	2-PhPy (21)	4	THF	8	63	29
19	[(cod)IrCl] <sub>2</sub> (3.5)	4-CF <sub>3</sub> Py (21)	4	THF	81	9	-
20	[(cod)IrCl] <sub>2</sub> (3.5)	2,6-F <sub>2</sub> Py (21)	4	THF	71	29	-
21	[(cod)Ir(OMe)] <sub>2</sub> (3.5)	2-MePy (21)	4	THF	-	14	86
22	(cod)Ir(acac) (7.0)	2-MePy (21)	4	THF	-	3	97
23	(cod) <sub>2</sub> IrBF <sub>4</sub> (7.0)	2-MePy (21)	4	THF	-	2	98
24	(cod) <sub>2</sub> IrB <sub>ArF</sub> (7.0)	2-MePy (21)	4	THF	-	14	86
25	[Cp*IrCl <sub>2</sub> ] <sub>2</sub> (3.5)	2-MePy (21)	4	THF	100	-	-
26	IrCl <sub>3</sub> (7.0)	2-MePy (21)	4	THF	100	-	-
27	[(cod)RhCl] <sub>2</sub> (3.5)	2-MePy (21)	4	THF	60	40	-
28	Pd(OAc) <sub>2</sub> (7.0)	2-MePy (21)	4	THF	100	-	-

\*Reaction conditions: **1a** (0.2 mmol), B<sub>2</sub>pin<sub>2</sub>, [M] catalyst, L, 110 °C (bath), 5 h; B<sub>2</sub>pin<sub>2</sub> = [B(OCMe<sub>2</sub>CMe<sub>2</sub>O)]<sub>2</sub>, Bpin = B(OCMe<sub>2</sub>CMe<sub>2</sub>O), cod = 1,5-cyclooctadiene, acac = acetylacetonato, B<sub>ArF</sub> = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, Py = pyridine. <sup>†</sup>GC yield. <sup>‡</sup>80 °C (bath).

**Supplementary Table 2. Optimization of reaction conditions with bipyridine ligands.\***

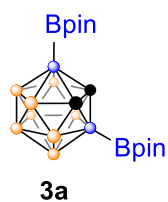


entry	L	yield (%) <sup>†</sup>			
		<b>1a</b>	<b>n = 1</b>	<b>n = 2</b>	<b>n = 3</b>
1	2,2'-bipy	2	3( <b>2a</b> ) + 1	73( <b>3a</b> ) + 5 + 4	8 + 4
2	4,4'-Me <sub>2</sub> bipy	2	4( <b>2a</b> ) + 2	62( <b>3a</b> ) + 7 + 1	17 + 5
3	4,4'- <sup>t</sup> Bu <sub>2</sub> bipy	3	3( <b>2a</b> ) + 3	27( <b>3a</b> ) + 5 + 2	42 + 12 + 3
4	1,10-Phen	4	7( <b>2a</b> ) + 4	57( <b>3a</b> ) + 8 + 2	8 + 10
5	3,4,7,8-Me <sub>4</sub> -1,10-Phen	9	8( <b>2a</b> ) + 4	35( <b>3a</b> ) + 11 + 2	18 + 13
6 <sup>‡</sup>	Py	10	23( <b>2a</b> )	67( <b>3a</b> )	-
7 <sup>‡</sup>	2-MePy	-	2( <b>2a</b> )	98( <b>3a</b> )	-

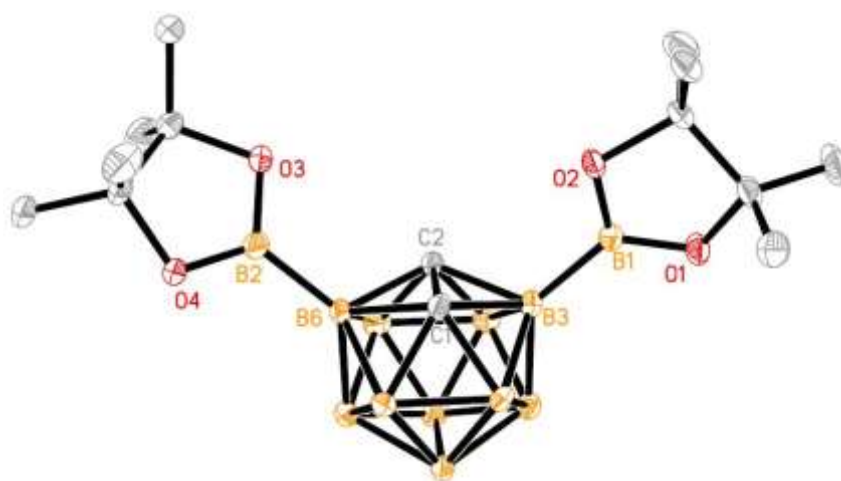
\*Reaction condition: **1a** (0.1 mmol), 3.5 mol% [(cod)IrCl]<sub>2</sub>, 10.5 mol% L. <sup>†</sup>The ratio and selectivity of borylation products were determined by GC-MS. Noted that there were several geometrical isomers of borylated species with the same MS using bipyridine ligands. <sup>‡</sup>21 mol% L.

### Preparation of B(3,6)-diborylated- or B(3)-borylated-*o*-carboranes (3 or 2). A Representative

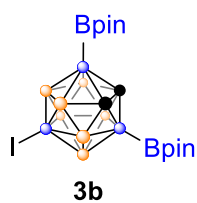
**Procedure.** An oven-dried Schlenk flask equipped with a stir bar was charged with *o*-carborane (**1**) (0.5 mmol), B<sub>2</sub>pin<sub>2</sub> (508 mg, 2.0 mmol), [(cod)IrCl]<sub>2</sub> (11.8 mg, 0.0175 mmol), and 2-methylpyridine (9.8 mg, 0.105 mmol), followed by dry THF (5 mL). The flask was closed under an atmosphere of nitrogen and stirred at 110 °C (bath temperature) for 5 h. After hydrolysis with water (10 mL) and extraction with diethyl ether (10 mL x 3), the ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane and ethyl acetate (10/1 in v/v) as eluent to give a mixture of product and B<sub>2</sub>pin<sub>2</sub>. Removal of B<sub>2</sub>pin<sub>2</sub> via sublimation at 90 °C under vacuum (0.1 torr) afforded a pure product **2o-r** or **3a-n**.



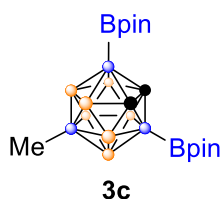
**3a:** Yield 83%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.53 (s, 2H) (cage CH), 1.24 (s, 24H) ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  84.2 (OC), 57.6 (cage CH), 24.9 ( $\text{CH}_3$ );  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  32.7 (s, 2B) ( $\text{B}-\text{B}_{\text{cage}}$ ), -0.9 (d,  $J_{\text{BH}} = 151$  Hz, 2B), -6.7 (d,  $J_{\text{BH}} = 156$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -11.8 (m, 6B) ( $\text{B}_{\text{cage}}\text{H}$  &  $\text{B}-\text{B}_{\text{cage}}$ ); analysis (calcd., found for  $\text{C}_{14}\text{H}_{34}\text{B}_{12}\text{O}_4$ ): C (42.45, 42.46), H (8.65, 8.71).



**Supplementary Figure 1.** Molecular structure of **3a** drawn with 30% probability ellipsoids.

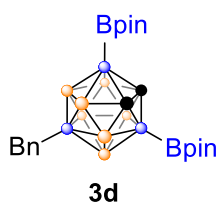


**3b:** Yield 84%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.86 (s, 1H), 3.64 (s, 1H) (cage CH), 1.26 (s, 24H) ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  84.6 (OC), 58.0, 53.8 (cage CH), 25.0 ( $\text{CH}_3$ );  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  32.4 (s, 2B) ( $\text{B}-\text{B}_{\text{cage}}$ ), 0.8 (d,  $J_{\text{BH}} = 144$  Hz, 1B), -4.9 (d,  $J_{\text{BH}} = 156$  Hz, 2B), -11.2 (m, 5B) ( $\text{B}_{\text{cage}}\text{H}$ ), -14.8 (s, 2B) ( $\text{B}_{\text{cage}}-\text{I}$  &  $\text{B}-\text{B}_{\text{cage}}$ ); analysis (calcd., found for  $\text{C}_{14}\text{H}_{33}\text{B}_{12}\text{O}_4\text{I}$ ): C (32.21, 32.48), H (6.37, 6.34).



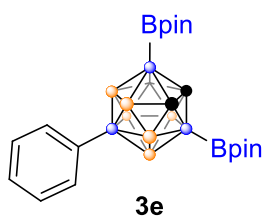
**3c:** Yield 78%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.47 (s, 1H), 3.39 (s, 1H) (cage CH), 1.25 (s, 27H) ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  84.2

(OC), 56.6, 50.4 (cage CH), 25.0 (CCH<sub>3</sub>), the B<sub>cage</sub>-CH<sub>3</sub> was not observed; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128 MHz): δ 32.9 (s, 2B) (B-B<sub>cage</sub>), 9.1 (s, 1B) (B<sub>cage</sub>Me), 0.6 (d, J<sub>BH</sub> = 42 Hz, 1B) (B<sub>cage</sub>H), -5.5 (d, J<sub>BH</sub> = 132 Hz, 2B) (B<sub>cage</sub>H), -11.8 (m, 6B) (B<sub>cage</sub>H & B-B<sub>cage</sub>); analysis (calcd., found for C<sub>15</sub>H<sub>36</sub>B<sub>12</sub>O<sub>4</sub>): C (43.92, 43.93), H (8.85, 8.91).



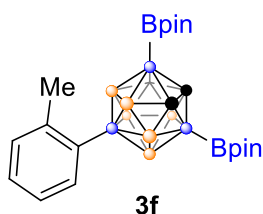
**3d:** Yield 82%. White solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.19 (m, 2H), 7.04 (m, 3H) (aromatic CH), 3.47 (s, 1H), 3.45 (s, 1H) (cage CH), 2.22 (s, 2H) (CH<sub>2</sub>), 1.29 (s, 24H) (CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz): δ 144.8, 128.5, 127.8,

123.8 (aromatic C), 84.1 (OC), 56.4, 51.7 (cage CH), 24.9(CH<sub>3</sub>), the B<sub>cage</sub>-CH<sub>2</sub> was not observed; <sup>11</sup>B{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 128 MHz): δ 33.1 (s, 2B) (B-B<sub>cage</sub>), 10.0 (s, 1B) (B<sub>cage</sub>-Bn), -0.2 (d, J<sub>BH</sub> = 61 Hz, 1B) (BH), -5.9 (d, J<sub>BH</sub> = 113 Hz, 2B) (B<sub>cage</sub>H), -11.9 (m, 6B) (B<sub>cage</sub>H & B-B<sub>cage</sub>); analysis (calcd., found for C<sub>21</sub>H<sub>40</sub>B<sub>12</sub>O<sub>4</sub>): C (51.87, 51.50), H (8.29, 8.34).



**3e:** Yield 83%. White solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.40 (m, 2H) 7.20 (m, 3H) (aromatic CH), 3.66 (s, 1H), 3.57 (s, 1H) (cage CH), 1.29 (s, 24H) (CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz): δ 132.5, 127.3, 127.0 (aromatic C),

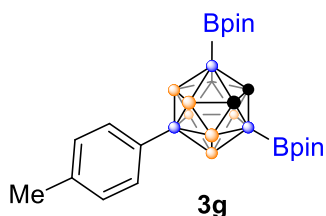
84.3 (OC), 56.4, 52.1 (cage CH), 25.0 (CH<sub>3</sub>), the B<sub>cage</sub>-C was not observed; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128 MHz): δ 33.1 (s, 2B) (B-B<sub>cage</sub>), 9.4 (s, 1B) (B<sub>cage</sub>-Ph), 0.2 (d, J<sub>BH</sub> = 50 Hz, 1B) (B<sub>cage</sub>H), -6.1 (d, J<sub>BH</sub> = 148 Hz, 2B) (B<sub>cage</sub>H), -11.9 (m, 6B) (B<sub>cage</sub>H & B-B<sub>cage</sub>); analysis (calcd., found for C<sub>20</sub>H<sub>38</sub>B<sub>12</sub>O<sub>4</sub>): C (50.87, 51.22), H (8.11, 8.13).



**3f:** Yield 95%. White solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.52 (m, 1H), 7.03

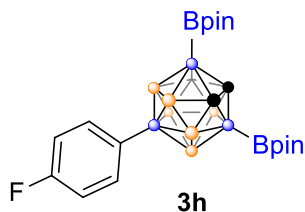


(m, 3H) (aromatic *CH*), 3.63 (s, 1H), 3.59 (s, 1H) (cage *CH*), 2.48 (s, 3H) ( $C_6H_4-CH_3$ ), 1.28 (s, 24H) ( $OC-CH_3$ );  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 75 MHz):  $\delta$  141.6, 136.0, 130.1, 127.2, 124.7 (aromatic C), 84.3 (OC), 56.1, 53.6 (cage CH), 25.0 ( $OC-CH_3$ ), 24.0 ( $C_6H_4-CH_3$ ), the  $B_{cage}-C$  was not observed;  $^{11}B$  NMR ( $CDCl_3$ , 128 MHz):  $\delta$  33.1 (s, 2B) ( $B-B_{cage}$ ), 9.0 (s, 1B) ( $B_{cage}-C$ ), -0.1 (d,  $J_{BH} = 121$  Hz, 1B) ( $B_{cage}H$ ), -6.0 (d,  $J_{BH} = 118$  Hz, 2B) ( $B_{cage}H$ ), -12.2 (m, 6B) ( $B_{cage}H$  &  $B-B_{cage}$ ); analysis (calcd., found for  $C_{21}H_{40}B_{12}O_4$ ): C (51.87, 51.68), H (8.29, 8.29).



**3g:** Yield 88%. White solid.  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  7.30 (d,  $J = 8.0$  Hz, 2H), 7.03 (d,  $J = 8.0$  Hz, 2H) (aromatic *CH*), 3.64 (s, 1H), 3.54 (s, 1H) (cage *CH*), 2.28 (s, 3H) ( $C_6H_4-CH_3$ ), 1.28 (s, 24H) ( $OC-CH_3$ );

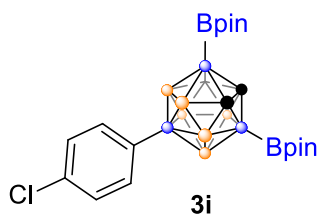
$^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 75 MHz):  $\delta$  136.5, 132.5, 128.1 (aromatic C), 84.3 (OC), 56.4, 51.9 (cage CH), 24.9, 21.3 ( $CH_3$ ), the  $B_{cage}-C$  was not observed;  $^{11}B$  NMR ( $CDCl_3$ , 128 MHz):  $\delta$  36.3 (s, 2B) ( $B-B_{cage}$ ), 12.5 (s, 1B) ( $B_{cage}-C$ ), 2.8 (d,  $J_{BH} = 110$  Hz, 1B) ( $B_{cage}H$ ), -2.9 (d,  $J_{BH} = 113$  Hz, 2B) ( $B_{cage}H$ ), -8.1 (m, 6B) ( $B_{cage}H$  &  $B-B_{cage}$ ); analysis (calcd., found for  $C_{21}H_{40}B_{12}O_4$ ): C (51.87, 51.76), H (8.29, 8.41).



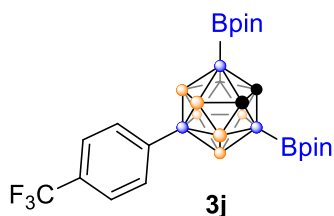
**3h:** Yield 94%. White solid.  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  7.33 (m, 2H), 6.88 (m, 2H) (aromatic *CH*), 3.65 (s, 1H), 3.55 (s, 1H) (cage *CH*), 1.28 (s, 24H) ( $CH_3$ );  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 75 MHz):  $\delta$  162.7 (d,  $^1J_{CF} = 263$  Hz),

134.1 (d,  $^3J_{CF} = 7.3$  Hz), 114.1 (d,  $^2J_{CF} = 19.6$  Hz) (aromatic C), 84.3 (OC), 56.5, 52.1 (cage CH), 25.0 ( $CH_3$ ), the  $B_{cage}-C$  was not observed;  $^{11}B$  NMR ( $CDCl_3$ , 128 MHz):  $\delta$  32.5 (s, 2B) ( $B-B_{cage}$ ), 8.9 (s, 1B) ( $B_{cage}-C$ ), -0.3 (d,  $J_{BH} = 116$  Hz, 1B) ( $B_{cage}H$ ), -6.0 (d,  $J_{BH} = 108$  Hz, 2B) ( $B_{cage}H$ ), -11.9 (m,

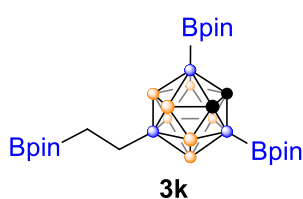
6B) ( $B_{\text{cage}}\text{H}$  &  $\text{B}-B_{\text{cage}}$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -116.7 (m, 1F); analysis (calcd., found for  $\text{C}_{20}\text{H}_{37}\text{B}_{12}\text{O}_4\text{F}$ ): C (49.00, 48.98), H (7.61, 7.50).



**3i:** Yield 89%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.30 (d,  $J$  = 7.8 Hz, 2H), 7.15 (d,  $J$  = 7.8 Hz, 2H) (aromatic  $\text{CH}$ ), 3.65 (s, 1H), 3.55 (s, 1H) (cage  $\text{CH}$ ), 1.28 (s, 24H) ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  133.9, 133.2, 127.4 (aromatic C), 84.4 (OC), 56.6, 52.4 (cage  $\text{CH}$ ), 25.0 ( $\text{CH}_3$ ), the  $\text{B}_{\text{cage}}-\text{C}$  was not observed;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  33.1 (s, 2B) ( $\text{B}-\text{B}_{\text{cage}}$ ), 8.8 (s, 1B) ( $\text{B}_{\text{cage}}-\text{C}$ ), -0.3 (d,  $J_{\text{BH}}$  = 137 Hz, 1B) ( $\text{B}_{\text{cage}}\text{H}$ ), -6.0 (d,  $J_{\text{BH}}$  = 133 Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -12.0 (m, 6B) ( $\text{B}_{\text{cage}}\text{H}$  &  $\text{B}-\text{B}_{\text{cage}}$ ); analysis (calcd., found for  $\text{C}_{20}\text{H}_{37}\text{B}_{12}\text{O}_4\text{Cl}$ ): C (47.41, 47.15), H (7.36, 7.24).

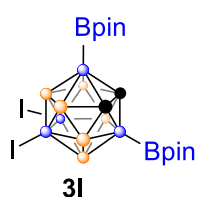


**3j:** Yield 89%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.49 (d,  $J$  = 7.5 Hz, 2H), 7.42 (d,  $J$  = 7.5 Hz, 2H) (aromatic  $\text{CH}$ ), 3.68 (s, 1H), 3.58 (s, 1H) (cage  $\text{CH}$ ), 1.28 (s, 24H) ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  132.8, 124.0, 107.8 (aromatic C), 84.5 (OC), 56.7, 52.9 (cage  $\text{CH}$ ), 25.0 ( $\text{CH}_3$ ), the  $\text{B}_{\text{cage}}-\text{C}$  was not observed; and the  $\text{CF}_3$  was not observed due to the poor solubility of **3j**;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  32.4 (s, 2B) ( $\text{B}-\text{B}_{\text{cage}}$ ), 8.4 (s, 1B) ( $\text{B}_{\text{cage}}-\text{C}$ ), -0.6 (d,  $J_{\text{BH}}$  = 131 Hz, 1B) ( $\text{B}_{\text{cage}}\text{H}$ ), -6.1 (d,  $J_{\text{BH}}$  = 115 Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -12.1 (m, 6B) ( $\text{B}_{\text{cage}}\text{H}$  &  $\text{B}-\text{B}_{\text{cage}}$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -62.5 (s, 3F); analysis (calcd., found for  $\text{C}_{21}\text{H}_{37}\text{B}_{12}\text{O}_4\text{F}_3$ ): C (46.69, 46.67), H (6.90, 6.79).

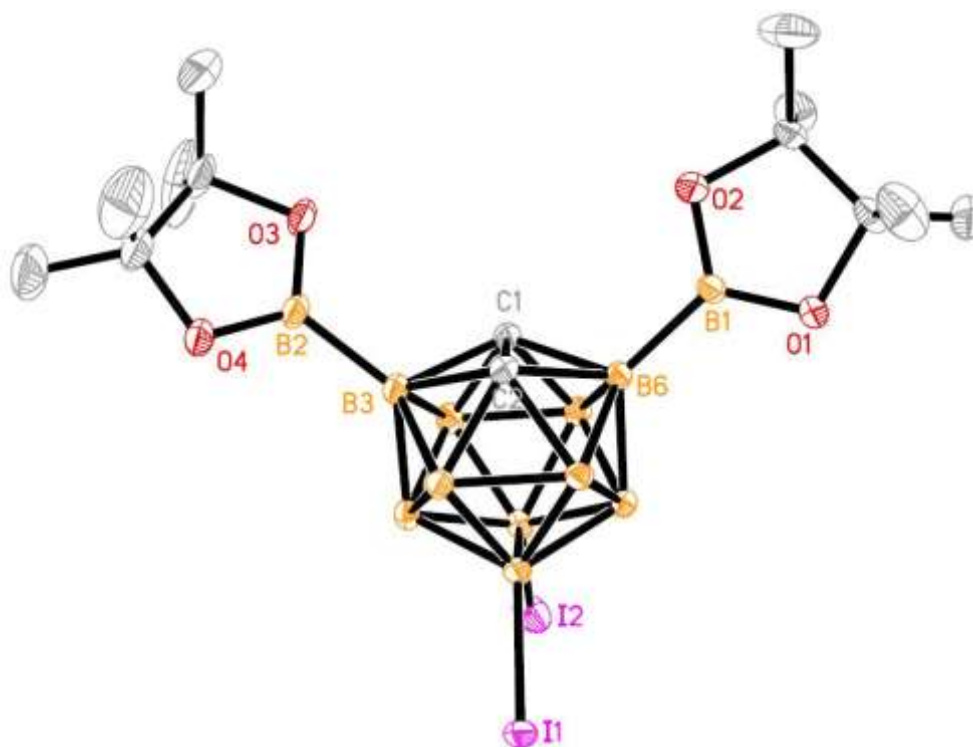


**3k:** Yield 91%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.48 (s, 1H), 3.41 (s, 1H) (cage  $\text{CH}$ ), 1.25 (s, 24H), 1.22 (s, 12H) ( $\text{CH}_3$ ), 0.78 (m, 2H),

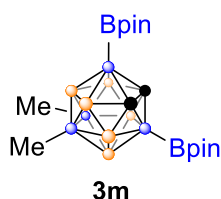
0.75 (m, 2H) ( $CH_2$ );  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 75 MHz):  $\delta$  84.1, 82.7 (OC), 56.2, 50.9 (cage CH), 24.9 ( $CH_3$ ), the two B- $CH_2$  was not observed;  $^{11}B$  NMR ( $CDCl_3$ , 128 MHz):  $\delta$  33.0 (s, 3B) (*B*pin), 11.5 (s, 1B) ( $B_{cage-CH_2}$ ), -0.6 (d,  $J_{BH}$  = 125 Hz, 1B) ( $B_{cageH}$ ), -6.3 (d,  $J_{BH}$  = 134 Hz, 2B) ( $B_{cageH}$ ), -12.3 (m, 6B) ( $B_{cageH}$  & B- $B_{cage}$ ); analysis (calcd., found for  $C_{22}H_{49}B_{13}O_6$ ): C (48.03, 48.01), H (8.98, 8.94).



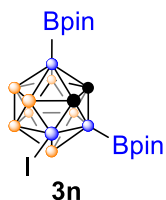
**31:** Yield 88%. White solid.  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  3.96 (s, 2H) (cage CH), 1.25 (s, 24H) ( $CH_3$ );  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 75 MHz):  $\delta$  84.8 (OC), 54.6 (cage CH), 25.0 ( $CH_3$ );  $^{11}B$  NMR ( $CDCl_3$ , 128 MHz):  $\delta$  32.4 (s, 2B) (B- $B_{cage}$ ), -3.3 (d,  $J_{BH}$  = 152 Hz, 2B) ( $B_{cageH}$ ), -11.0 (m, 4B) ( $B_{cageH}$ ), -12.6 (s, 4B) ( $B_{cage-I}$  & B- $B_{cage}$ ); analysis (calcd., found for  $C_{14}H_{32}B_{12}O_4I_2$ ): C (25.95, 26.07), H (4.98, 4.79).



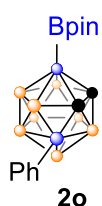
**Supplementary Figure 2.** Molecular structure of **31** drawn with 30% probability ellipsoids.



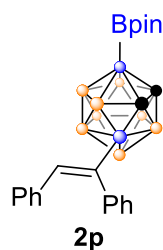
**3m:** Yield 85%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.37 (s, 2H) (cage CH), 1.26 (s, 30H) ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  84.1 (OC), 50.5 (cage CH), 25.0 ( $\text{CCH}_3$ ), the two  $\text{B}_{\text{cage}}\text{-CH}_3$  were not observed;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  33.0 (s, 2B) ( $\text{B-B}_{\text{cage}}$ ), 9.0 (s, 2B) ( $\text{B}_{\text{cage}}\text{-CH}_3$ ), -4.6 (d,  $J_{\text{BH}} = 131$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -11.8 (d,  $J_{\text{BH}} = 138$  Hz, 4B) ( $\text{B}_{\text{cage}}\text{H}$ ), -15.1 (s, 2B) ( $\text{B-B}_{\text{cage}}$ ); analysis (calcd., found for  $\text{C}_{16}\text{H}_{38}\text{B}_{12}\text{O}_4$ ): C (45.30, 45.02), H (9.03, 8.70).



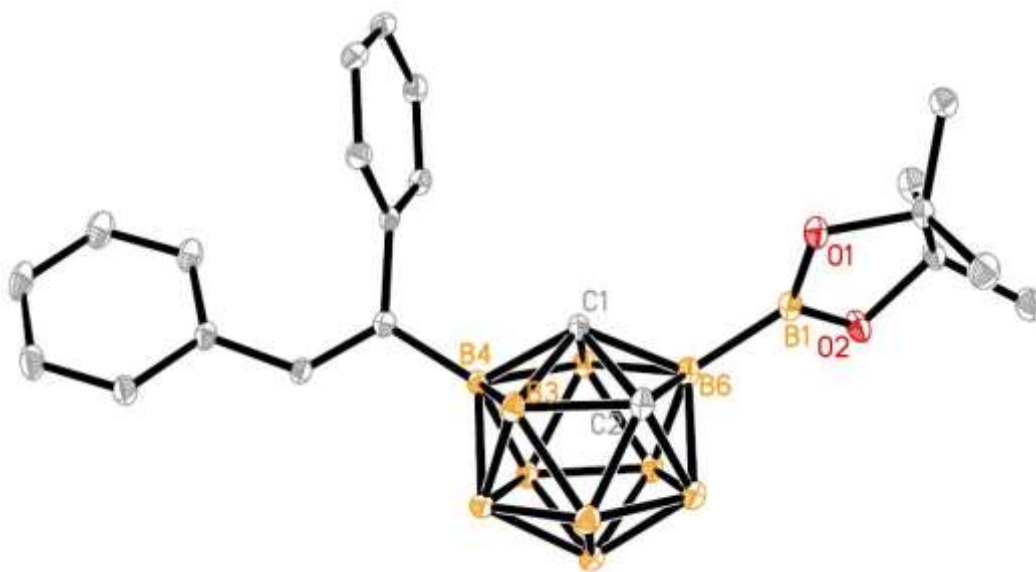
**3n:** Yield 63%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.96 (s, 1H), 3.72 (s, 1H) (cage CH), 1.30 (s, 12H), 1.28 (s, 12H) ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  84.7, 84.5 (OC), 59.8 (cage CH), 25.1, 25.0 ( $\text{CH}_3$ );  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  32.9 (s, 2B) ( $\text{B-B}_{\text{cage}}$ ), 1.1 (d,  $J_{\text{BH}} = 123$  Hz, 1B), 0.4 (d,  $J_{\text{BH}} = 96$  Hz, 1B), -4.6 (d,  $J_{\text{BH}} = 179$  Hz, 1B), -5.9 (d,  $J_{\text{BH}} = 148$  Hz, 1B), -8.9 (d,  $J_{\text{BH}} = 161$  Hz, 1B) ( $\text{B}_{\text{cage}}\text{H}$ ), -11.6 (m, 3B) ( $\text{B}_{\text{cage}}\text{H}$  &  $\text{B-B}_{\text{cage}}$ ), -25.1 (s, 2B) ( $\text{B}_{\text{cage}}\text{-I}$  &  $\text{B-B}_{\text{cage}}$ ); analysis (calcd., found for  $\text{C}_{14}\text{H}_{33}\text{B}_{12}\text{O}_4\text{I}$ ): C (32.21, 32.13), H (6.37, 6.40).



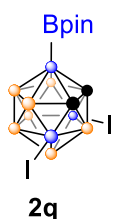
**2o:** Yield 76%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.57 (m, 2H) 7.32 (m, 3H) (aromatic CH), 3.80 (s, 1H), 3.72 (s, 1H) (cage CH), 1.26 (s, 12H) ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  133.4, 128.6, 127.9 (aromatic C), 84.4 (OC), 57.0, 56.6 (cage CH), 25.0 ( $\text{CH}_3$ ), the  $\text{B}_{\text{cage}}\text{-C}$  were not observed;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  32.9 (s, 1B) ( $\text{B-B}_{\text{cage}}$ ), -1.4 (m, 4B) ( $\text{B}_{\text{cage}}\text{H}$  &  $\text{B}_{\text{cage}}\text{-Ph}$ ), -6.8 (d,  $J_{\text{BH}} = 168$  Hz, 1B) ( $\text{B}_{\text{cage}}\text{H}$ ), -8.4 (d,  $J_{\text{BH}} = 154$  Hz, 1B) ( $\text{B}_{\text{cage}}\text{H}$ ), -11.6 (d,  $J_{\text{BH}} = 158$  Hz, 1B) ( $\text{B}_{\text{cage}}\text{H}$ ), -13.7 (m, 3B) ( $\text{B}_{\text{cage}}\text{H}$  &  $\text{B-B}_{\text{cage}}$ ); analysis (calcd., found for  $\text{C}_{14}\text{H}_{27}\text{B}_{11}\text{O}_2$ ): C (48.56, 48.37), H (7.86, 7.82).



**2p**: Yield 89%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.37 (m, 2H), 7.27 (m, 1H), 7.10 (m, 5H), 6.93 (m, 3H) (aromatic *CH* & olefinic *CH*), 3.53 (s, 1H), 3.36 (s, 1H) (cage *CH*), 1.26 (s, 12H) ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  142.9, 138.0, 137.4, 129.4, 129.0, 128.0, 127.8, 127.0, 126.4 (aromatic and olefinic *C*), 84.3 (OC), 55.8, 55.5 (cage *CH*), 24.9 ( $\text{CH}_3$ ), the  $\text{B}_{\text{cage}}\text{-C}$  was not observed;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  32.9 (s, 1B) ( $\text{B-B}_{\text{cage}}$ ), -1.6 (m, 3B) ( $\text{B}_{\text{cage}}\text{H}$  &  $\text{B}_{\text{cage}}\text{-C}$ ), -6.7 (d,  $J_{\text{BH}} = 190$  Hz, 1B), -8.3 (d,  $J_{\text{BH}} = 152$  Hz, 1B) ( $\text{B}_{\text{cage}}\text{H}$ ), -11.6 (m, 5B) ( $\text{B}_{\text{cage}}\text{H}$  &  $\text{B-B}_{\text{cage}}$ ); analysis (calcd., found for  $\text{C}_{22}\text{H}_{33}\text{B}_{11}\text{O}_2$ ): C (58.93, 59.05), H (7.42, 7.38).

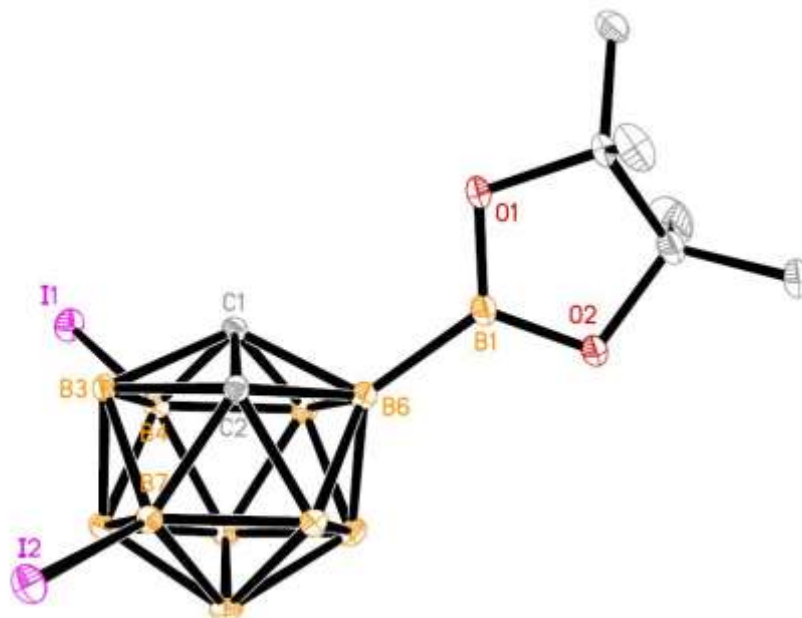


**Supplementary Figure 3.** Molecular structure of **2p** drawn with 30% probability ellipsoids.

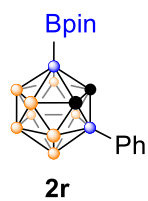


**2q**: Yield 83%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  4.11 (s, 2H), (cage *CH*), 1.27 (s, 12H) ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  84.9 (OC), 60.6 (cage *CH*), 25.0 ( $\text{CH}_3$ );  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  32.6 (s, 1B) ( $\text{B-B}_{\text{cage}}$ ), 1.3 (d,  $J_{\text{BH}} = 149$  Hz, 2B), -3.7 (d,  $J_{\text{BH}} = 124$  Hz, 1B), -6.7 (d,  $J_{\text{BH}} = 151$  Hz, 1B), -10.4 (d,  $J_{\text{BH}} = 169$  Hz, 1B), -11.8 (d,  $J_{\text{BH}} =$

161 Hz, 2B) ( $B_{\text{cageH}}$ ), -26.0 (s, 3B) ( $B_{\text{cage-I}}$  &  $B-B_{\text{cage}}$ ); analysis (calcd., found for  $\text{C}_8\text{H}_{21}\text{B}_{11}\text{O}_2\text{I}_2$ ): C (18.41, 18.64), H (4.06, 4.04).

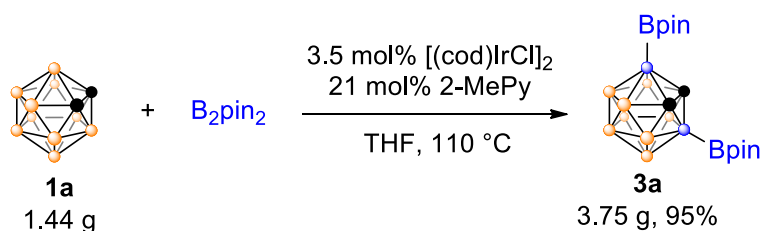


**Supplementary Figure 4.** Molecular structure of **2q** drawn with 30% probability ellipsoids.



**2r:** Yield 89%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.65 (m, 2H), 7.41 (m, 3H) (aromatic CH), 3.71 (s, 2H) (cage CH), 1.27 (s, 12H) ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  133.4, 129.8, 128.3 (aromatic C), 84.4 (OC), 58.5 (cage CH), 25.0 ( $\text{CH}_3$ ), the  $B_{\text{cage-C}}$  was not observed;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  32.8 (s, 1B) ( $B-B_{\text{cage}}$ ), -1.4 (d,  $J_{\text{BH}} = 145$  Hz, 2B) ( $B_{\text{cageH}}$ ), -4.5 (s, 1B) ( $B_{\text{cage-Ph}}$ ), -6.7 (d,  $J_{\text{BH}} = 142$  Hz, 1B) ( $B_{\text{cageH}}$ ), -12.3 (m, 6B) ( $B_{\text{cageH}}$  &  $B-B_{\text{cage}}$ ); analysis (calcd., found for  $\text{C}_{14}\text{H}_{27}\text{B}_{11}\text{O}_2$ ): C (48.56, 48.93), H (7.86, 8.00).

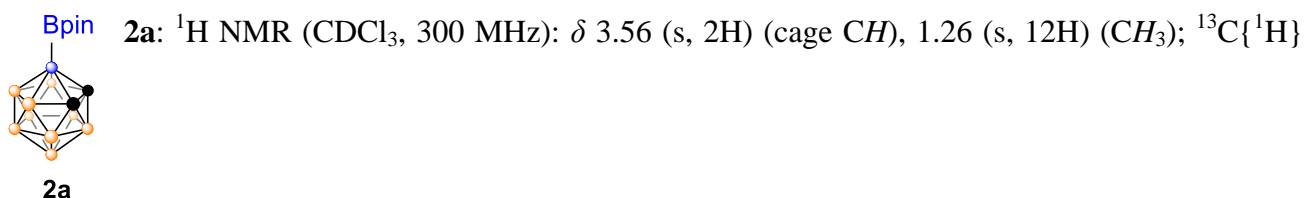
### Gram scale synthesis of **3a**.



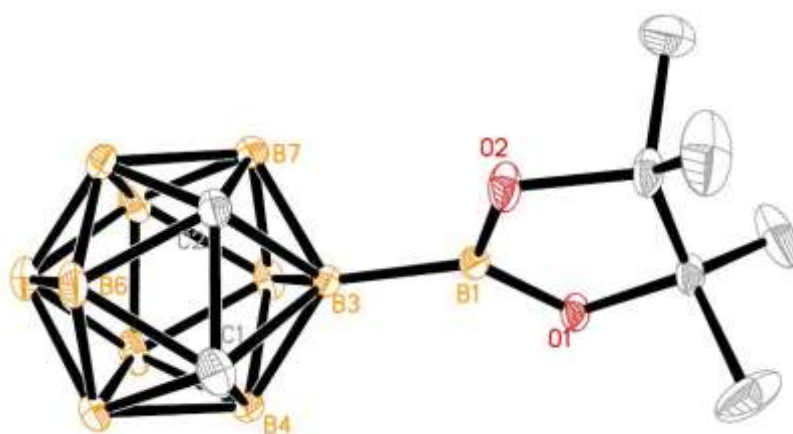
An oven-dried Schlenk flask equipped with a stir bar was charged with *o*-carborane (**1**) (1.44 g, 10 mmol),  $B_2pin_2$  (10.16 g, 40 mmol), [(cod)IrCl]<sub>2</sub> (236 mg, 0.35 mmol), and 2-methylpyridine (195 mg, 2.1 mmol), followed by dry THF (80 mL). The flask was closed under an atmosphere of nitrogen and stirred at 110 °C (bath temperature) for 5 h. After hydrolysis with water (80 mL) and extraction with diethyl ether (80 mL x 3), the ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane and ethyl acetate (10/1 in v/v) as eluent to give a mixture of product and  $B_2pin_2$ . Removal of  $B_2pin_2$  via sublimation at 90 °C under vacuum (0.1 torr) afforded a pure product **3a** (3.75 g, 95%).

### Preparation of 3-Bpin-*o*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (**2a**).

An oven-dried Schlenk flask equipped with a stir bar was charged with *o*-carborane (**1**) (72 mg, 0.50 mmol),  $B_2pin_2$  (152 mg, 0.60 mmol), [(cod)IrCl]<sub>2</sub> (11.8 mg, 0.0175 mmol), and 2,6-dimethylpyridine (9.8 mg, 0.105 mmol), followed by dry THF (5 mL). The flask was closed under an atmosphere of nitrogen and stirred at 80 °C for 12 h. After hydrolysis with water (10 mL) and extraction with diethyl ether (10 mL x 3), the ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane and ethyl acetate (10/1 in v/v) as eluent to give **2a** as a white solid (60 mg, 44%).



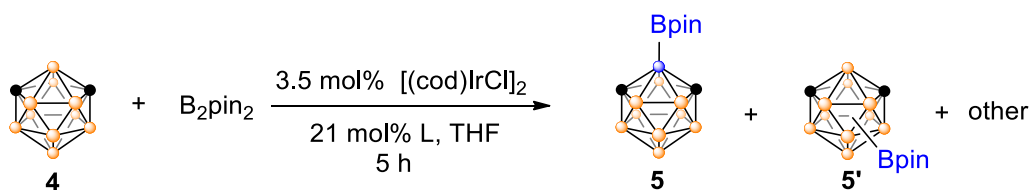
NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  84.4 (OC), 56.3 (cage CH), 25.0 (CH<sub>3</sub>); <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128 MHz):  $\delta$  32.9 (s, 1B) (*B*-B<sub>cage</sub>), -1.4 (d, *J*<sub>BH</sub> = 147 Hz, 2B), -7.5 (d, *J*<sub>BH</sub> = 157 Hz, 1B), -8.0 (d, *J*<sub>BH</sub> = 80 Hz, 1B) (*B*<sub>cage</sub>H), -12.5 (d, *J*<sub>BH</sub> = 164 Hz, 5B) (*B*<sub>cage</sub>H & *B*-B<sub>cage</sub>), -11.8 (d, *J*<sub>BH</sub> = 173 Hz, 1B) (*B*<sub>cage</sub>H); analysis (calcd., found for C<sub>8</sub>H<sub>23</sub>B<sub>11</sub>O<sub>2</sub>): C (35.56, 35.41), H (8.58, 8.55).



**Supplementary Figure 5.** Molecular structure of **2a** drawn with 30% probability ellipsoids.

### B(2)-borylation of *m*-carborane.

**Supplementary Table 3.** Optimization of conditions for B(2)-borylation of *m*-carborane <sup>a</sup>

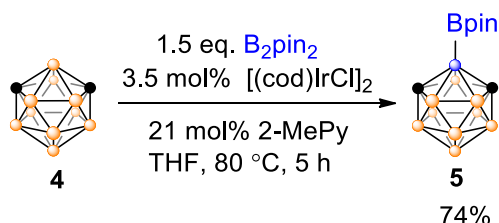


Entry	L (mol %)	T / °C	B <sub>2</sub> pin <sub>2</sub> (equiv)	Yield (%) <sup>b</sup>			
				4	5	5'	other <sup>c</sup>
1	2-MePy	110	4	-	77	-	23
2	2-MePy	110	10	-	63	-	37
3	2-MePy	80	4	-	70	-	30
4	2-MePy	80	2	5	84	4	7
5	2-MePy	80	1.5	6	85	4	5
6	2,6-Me <sub>2</sub> Py	80	2	6	85	4	5
7	4- <i>t</i> BuPy	80	2	25	63	8	3



8	2-PhPy	80	2	46	50	4	-
9	2,6-F <sub>2</sub> Py	80	2	39	60	1	-
10 <sup>d</sup>	2,2'-bipy	80	2	20	29	31	20
11 <sup>d</sup>	4,4'-Me <sub>2</sub> bipy	80	2	10	47	19	24

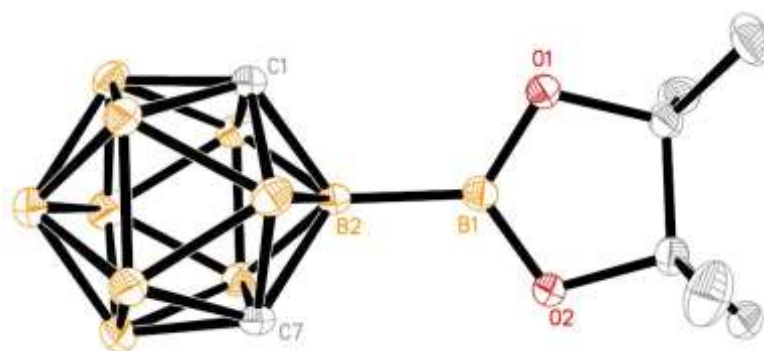
<sup>a</sup>Reaction condition: **4** (0.2 mmol), 3.5 mol% [(cod)IrCl]<sub>2</sub>, 21 mol% L. <sup>b</sup>GC yield. <sup>c</sup>Other: geometrical isomers of diborylated *o*-carboranes. <sup>d</sup>14 mol% L.



**Supplementary Figure 6.** Regioselective synthesis of 2-Bpin-*m*-carborane.

**Preparation of 2-Bpin-*m*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (**5**).** An oven-dried Schlenk flask equipped with a stir bar was charged with *m*-carborane (72 mg, 0.50 mmol), B<sub>2</sub>pin<sub>2</sub> (191 mg, 0.75 mmol), [(cod)IrCl]<sub>2</sub> (11.8 mg, 0.0175 mmol), and 2-methylpyridine (9.8 mg, 0.105 mmol), followed by dry THF (5 mL). The flask was closed under an atmosphere of nitrogen and stirred at 80 °C for 5 h. After hydrolysis with water (10 mL) and extraction with diethyl ether (10 mL x 3), the ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane and ethyl acetate (30/1 in v/v) as eluent to give **5** as a white solid (100 mg, 74%).

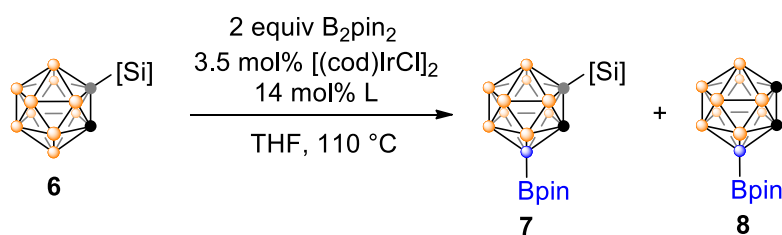
**5**: Yield 74%. White solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 2.92 (s, 2H) (cage CH), 1.27 (s, 12H) (CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz): δ 84.2 (OC), 57.0 (cage CH), 24.9 (CH<sub>3</sub>); <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128 MHz): δ 34.8 (s, 1B) (B-B<sub>cage</sub>), -5.0 (d, J<sub>BH</sub> = 162 Hz, 2B) (B<sub>cage</sub>H), -8.0 (m, 2B) (B<sub>cage</sub>H), -11.1 (d, J<sub>BH</sub> = 163 Hz, 4B) (B<sub>cage</sub>H), -15.2 (m, 2B) (B<sub>cage</sub>H & B-B<sub>cage</sub>); analysis (calcd., found for C<sub>8</sub>H<sub>23</sub>B<sub>11</sub>O<sub>2</sub>): C (35.56, 35.43), H (8.58, 8.74).



**Supplementary Figure 7.** Molecular structure of **5** drawn with 30% probability ellipsoids.

### B(4)-borylation of *o*-carboranes.

**Supplementary Table 4.** Optimization of B(4)-H borylation reaction.\*



Entry	[Si]	L	Time (h)	Yield (%) <sup>†</sup>			
				<b>6</b>	<b>7</b>	<b>8</b>	other <sup>‡</sup>
1	TMS	4,4'-Me <sub>2</sub> bipy	1	5	54	5	36
2	TMS	4,4'-dtbpy	1	4	43	12	41
3	TMS	2,2'-bipy	1	8	69	8	15
4	TES	2,2'-bipy	1	5	80	1	11
5	TBDMS	2,2'-bipy	1	10	86	-	4
6	TBDMS	2,2'-bipy	3	4	90	-	6
7	TBDMS	2,2'-bipy	5	-	88	-	12

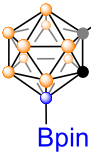
\*Reactions were conducted on 0.2 mmol scale in a closed flask. TMS = trimethylsilyl, TES = triethylsilyl, TBDMS = tert-butyldimethylsilyl; 4,4'-Me<sub>2</sub>bipy = 4,4'-dimethyl-2,2'-bipyridine, 4,4'-dtbpy = 4,4'-di-tert-butyl-2,2'-bipyridine, 2,2'-bipy = 2,2'-bipyridine. <sup>†</sup>GC yield. <sup>‡</sup>Other: geometrical isomers of diborylated *o*-carboranes.

### Preparation of B(4)-borylated *o*-Carboranes (**8**). A Representative Procedure.

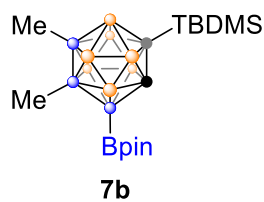
An oven-dried Schlenk flask equipped with a stir bar was charged with 1-TBDMS-*o*-carboranes (0.5

mmol), B<sub>2</sub>pin<sub>2</sub> (254 mg, 1.0 mmol), [(cod)IrCl]<sub>2</sub> (11.8 mg, 0.0175 mmol), and 2,2'-bipyridine (10.9 mg, 0.07 mmol), followed by dry THF (5 mL). The flask was closed under an atmosphere of nitrogen and stirred at 110 °C (bath temperature) for 3 h. After hydrolysis with water (10 mL) and extraction with diethyl ether (10 mL x 3), the ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane and ethyl acetate (10/1 in v/v) as eluent to give a mixture of product and B<sub>2</sub>pin<sub>2</sub>. Removal of B<sub>2</sub>pin<sub>2</sub> by sublimation at 90 °C under vacuum (0.1 torr) afforded the pure product **7**.

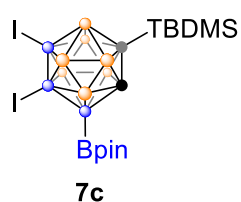
To a solution (2 mL) of **7** (0.3 mmol) (acetone for **7a** and **7b**; MeOH/DCM (2/1 in v/v) for **7c**) was added CsF (182 mg, 1.2 mmol). The mixture was stirred at room temperature for 1 h for **7a,7b** and 20 min for **7c**. After filtration, the filtrate was concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230–400 mesh) using *n*-hexane and ethyl acetate (10/1 in v/v) as eluent to give product **8**.


**7a**

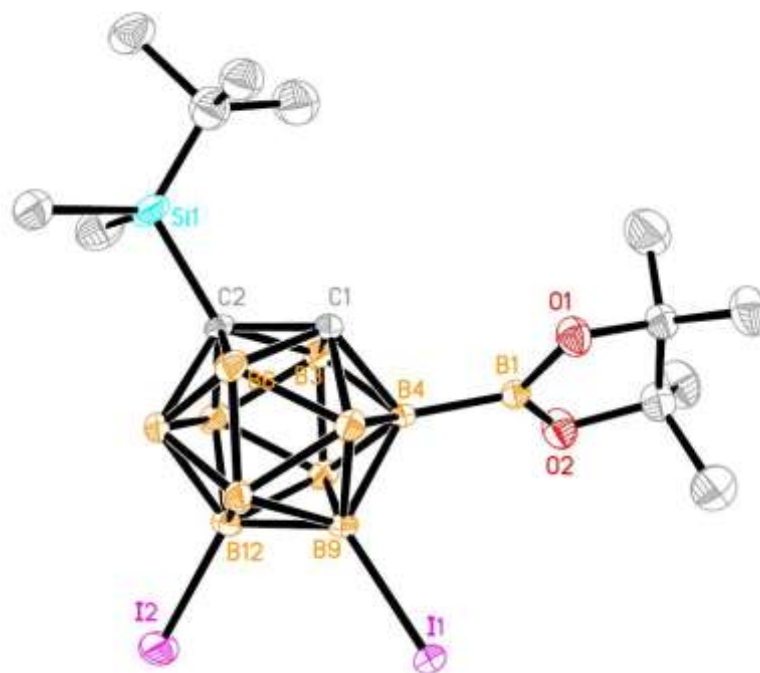
**7a**: Yield 92%. White solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.46 (s, 1H) (cage CH), 1.24 (s, 6H), 1.23 (s, 6H) (OC(CH<sub>3</sub>)<sub>2</sub>), 1.01 (s, 9H) (C(CH<sub>3</sub>)<sub>3</sub>), 0.23 (s, 3H), 0.22 (s, 3H) (SiCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz): δ 83.6 (OC), 67.6 (cage C), 61.9 (cage CH), 27.1 (C(CH<sub>3</sub>)<sub>3</sub>), 25.0, 24.8 (OC(CH<sub>3</sub>)<sub>2</sub>), 19.4 (SiC(CH<sub>3</sub>)<sub>3</sub>), -4.2 (SiCH<sub>3</sub>); <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128 MHz): δ 34.3 (s, 1B) (B–B<sub>cage</sub>), -0.7 (d, J<sub>BH</sub> = 152 Hz, 1B), -1.0 (d, J<sub>BH</sub> = 143 Hz, 1B), -5.9 (d, J<sub>BH</sub> = 144 Hz, 2B), -9.8 (m, 2B), -10.9 (m, 2B) (B<sub>cage</sub>H), -12.4 (m, 2B) (B<sub>cage</sub>H & B–B<sub>cage</sub>); analysis (calcd., found for C<sub>14</sub>H<sub>37</sub>B<sub>11</sub>O<sub>2</sub>Si): C (43.74, 43.73), H (9.70, 9.73).



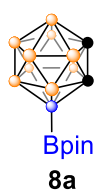
**7b:** Yield 92%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.27 (s, 1H) (cage CH), 1.24 (s, 6H), 1.23 (s, 6H) ( $\text{OC}(\text{CH}_3)_2$ ), 1.0 (s, 9H) ( $\text{C}(\text{CH}_3)_3$ ), 0.21 (s, 3H), 0.20 (s, 3H) ( $\text{SiCH}_3$ ), 0.20 (s, 3H), 0.16 (s, 3H) ( $\text{B}_{\text{cage}}\text{-CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  83.3 (OC), 58.9 (cage C), 55.1 (cage CH), 27.1 ( $\text{C}(\text{CH}_3)_3$ ), 25.2, 24.7 ( $\text{OC}(\text{CH}_3)_2$ ), 19.4 ( $\text{SiC}(\text{CH}_3)_3$ ), -4.3 ( $\text{SiCH}_3$ ), the two  $\text{B}_{\text{cage}}\text{-CH}_3$  were not observed;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  33.8 (s, 1B) ( $\text{B-B}_{\text{cage}}$ ), 10.9 (s, 1B), 8.6 (s, 1B) ( $\text{B}_{\text{cage}}\text{-C}$ ), -4.1 (d,  $J_{\text{BH}} = 134$  Hz, 2B), -9.8 (d,  $J_{\text{BH}} = 143$  Hz, 2B), -11.1 (d,  $J_{\text{BH}} = 179$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -14.0 (m, 2B) ( $\text{B}_{\text{cage}}\text{H}$  &  $\text{B-B}_{\text{cage}}$ ); analysis (calcd., found for  $\text{C}_{16}\text{H}_{41}\text{B}_{11}\text{O}_2\text{Si}$ ): C (46.59, 47.11), H (10.02, 10.02).



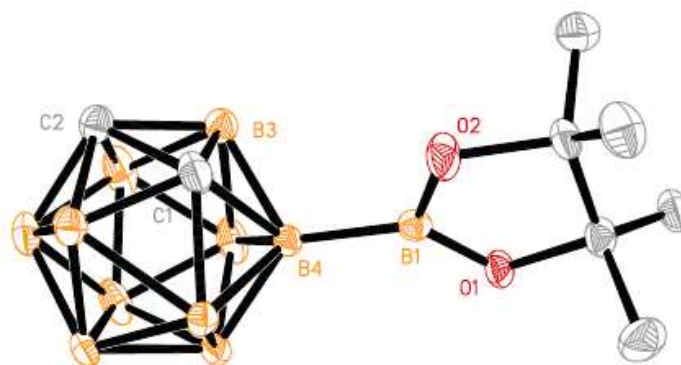
**7c:** Yield 89%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.84 (s, 1H) (cage CH), 1.27 (s, 6H), 1.26 (s, 6H) ( $\text{OC}(\text{CH}_3)_2$ ), 1.01 (s, 9H) ( $\text{C}(\text{CH}_3)_3$ ), 0.24 (s, 6H) ( $\text{SiCH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  84.2 (OC), 63.9 (cage C), 58.6 (cage CH), 27.0 ( $\text{C}(\text{CH}_3)_3$ ), 25.2, 24.7 ( $\text{OC}(\text{CH}_3)_2$ ), 19.4 ( $\text{SiC}(\text{CH}_3)_3$ ), -4.4 ( $\text{SiCH}_3$ );  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  33.4 (s, 1B) ( $\text{B-B}_{\text{cage}}$ ), -2.8 (d,  $J_{\text{BH}} = 163$  Hz, 2B), -9.1 (m, 2B), -10.5 (m, 1B) ( $\text{B}_{\text{cage}}\text{H}$ ), -11.6 (m, 3B) ( $\text{B}_{\text{cage}}\text{H}$  &  $\text{B-B}_{\text{cage}}$ ), -12.9 (s, 2B) ( $\text{B}_{\text{cage}}\text{-I}$ ); analysis (calcd., found for  $\text{C}_{14}\text{H}_{35}\text{B}_{11}\text{I}_2\text{O}_2\text{Si}$ ): C (26.43, 26.47), H (5.54, 5.82).



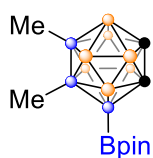
**Supplementary Figure 8.** Molecular structure of **7c** drawn with 30% probability ellipsoids.



**8a:** Yield 95%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.60 (s, 2H) (cage CH), 1.24 (s, 12H) ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  83.7 (OC), 56.1, 55.9 (cage CH), 24.9 ( $\text{CH}_3$ );  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  33.9 (s, 1B) ( $\text{B}-\text{B}_{\text{cage}}$ ), -1.5 (d,  $J_{\text{BH}} = 168$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -8.1 (d,  $J_{\text{BH}} = 137$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -12.1 (m, 3B) ( $\text{B}_{\text{cage}}\text{H}$  &  $\text{B}-\text{B}_{\text{cage}}$ ), -13.9 (d,  $J_{\text{BH}} = 182$  Hz, 3B) ( $\text{B}_{\text{cage}}\text{H}$ ); analysis (calcd., found for  $\text{C}_8\text{H}_{23}\text{B}_{11}\text{O}_2$ ): C (35.56, 35.65), H (8.58, 8.62).

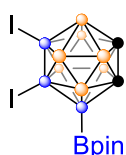


**Supplementary Figure 9.** Molecular structure of **8a** drawn with 30% probability ellipsoids.



**8b**: Yield 94%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.40 (s, 2H) (cage CH), 1.24 (s, 6H), 1.22 (s, 6H) ( $\text{OC}(\text{CH}_3)_2$ ), 0.21 (s, 3H), 0.19 (s, 3H) ( $\text{BCH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  83.4 (OC), 49.2, 49.0 (cage CH), 25.1, 24.8 ( $\text{OC}(\text{CH}_3)_2$ ),

the two  $\text{B}_{\text{cage}}\text{-CH}_3$  were not observed;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  35.1 (s, 1B) ( $\text{B-B}_{\text{cage}}$ ), 9.6 (s, 2B) ( $\text{B}_{\text{cage}}\text{-CH}_3$ ), -5.0 (d,  $J_{\text{BH}} = 145$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -11.5 (m, 4B) ( $\text{B}_{\text{cage}}\text{H}$  &  $\text{B-B}_{\text{cage}}$ ), -14.3 (d,  $J_{\text{BH}} = 169$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ); analysis (calcd., found for  $\text{C}_{10}\text{H}_{27}\text{B}_{11}\text{O}_2$ ): C (40.27, 40.58), H (9.12, 9.19).



**8c**: Yield 95%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  4.06 (s, 2H) (cage CH), 1.32 (s, 12H) ( $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  84.4 (OC), 53.4, 53.1 (cage CH), 25.2, 24.8 ( $\text{CH}_3$ );  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  35.1 (s, 1B) ( $\text{B-B}_{\text{cage}}$ ), -4.6 (d,  $J_{\text{BH}} =$

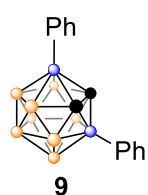
161 Hz, 2B), -11.7 (m, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -13.1 (m, 6B) ( $\text{B}_{\text{cage}}\text{H}$ ,  $\text{B}_{\text{cage}}\text{-I}$  &  $\text{B-B}_{\text{cage}}$ ); analysis (calcd., found for  $\text{C}_8\text{H}_{21}\text{B}_{11}\text{I}_2\text{O}_2$ ): C (18.41, 18.33), H (4.06, 3.94).

### Transformation of 3,6-(Bpin) $_2$ -*o*-carborane (3a)

#### Preparation of 3,6-Diphenyl-*o*-carborane (9)

An oven-dried Schlenk flask equipped with a stir bar was charged with **3a** (198 mg, 0.5 mmol), bromobenzene (236 mg, 1.5 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (115 mg, 0.1 mmol) and  $\text{Cs}_2\text{CO}_3$  (490 mg, 1.5 mmol), followed by dry cyclohexane (5 mL). The flask was closed under an atmosphere of nitrogen and stirred at 150 °C (bath temperature) for 8 h. After cooled to room temperature, water (10 mL) and 30%  $\text{H}_2\text{O}_2$  (5 mL) aqueous solution were successively added and the mixture was stirred at room temperature for 15 min. After extraction with diethyl ether (10 mL x 3), the ether solutions were

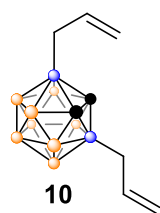
combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane and ethyl acetate (100/1 in v/v) as eluent to give a white solid. Removal of biphenyl byproduct via sublimation at 90 °C under vacuum (0.1 torr) gave the pure 3,6-diphenyl-*o*-carborane (**9**) as a white solid (120 mg, 81%).



**9**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.62 (m, 4H) 7.40 (m, 6H) (aromatic CH), 3.85 (s, 2H) (cage CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  133.3, 130.0, 128.4 (aromatic C), 59.2 (cage CH), the two  $\text{B}_{\text{cage}}\text{-C}$  were not observed;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  -2.2 (d,  $J_{\text{BH}} = 149$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -3.7 (s, 2B) ( $\text{B}_{\text{cage}}\text{-Ph}$ ), -11.2 (d,  $J_{\text{BH}} = 182$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -12.8 (d,  $J_{\text{BH}} = 173$  Hz, 4B) ( $\text{B}_{\text{cage}}\text{H}$ ); analysis (calcd., found for  $\text{C}_{14}\text{H}_{20}\text{B}_{10}$ ): C (56.73, 56.18), H (6.80, 6.71).

### Preparation of 3,6-Diallyl-*o*-carborane (**10**)

Compound **3a** (198 mg, 0.5 mmol), allyl chloride (230 mg, 3.0 mmol),  $\text{Pd}(\text{dba})_2$  (58 mg, 0.1 mmol) and  $\text{Cs}_2\text{CO}_3$  (490 mg, 1.5 mmol) were mixed in toluene (6 mL). The resulting mixture was stirred at room temperature under nitrogen atmosphere for 8 h. After hydrolysis with water (10 mL) and extraction with diethyl ether (10 mL x 3), the ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give **10** as a colorless liquid (97 mg, 87%).

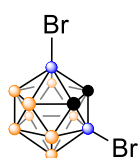


**10**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  5.80 (m, 2H) ( $\text{CH}=\text{CH}_2$ ), 4.96 (m, 4H) ( $\text{CH}_2=\text{CH}$ ), 3.25 (s, 2H) (cage CH), 2.01 (d,  $J = 6.9$ , 4H) ( $\text{B}_{\text{cage}}\text{-CH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  135.9, 115.7 (olefinic C), 57.6 (cage CH), the two  $\text{B}_{\text{cage}}\text{-CH}_2$  were not observed;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  -2.3 (d,  $J_{\text{BH}} = 145$  Hz, 2B) ( $\text{B}_{\text{cage}}\text{H}$ ), -4.0 (s, 2B) ( $\text{B}_{\text{cage}}\text{-C}$ ),

-12.4 (m, 6B) ( $B_{\text{cageH}}$ ); analysis (calcd., found for  $\text{C}_8\text{H}_{20}\text{B}_{10}$ ): C (42.83, 43.31), H (8.99, 8.94).

### Preparation of 3,6-Dihalogen-*o*-carborane (**11**). A Representative Procedure.

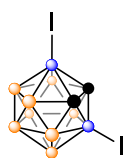
An oven-dried Schlenk flask equipped with a stir bar was charged with **3a** (198 mg, 0.5 mmol), PhX (X = Br or I; 1.5 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (58 mg, 0.05 mmol) and  $t\text{BuOK}$  (168 mg, 1.5 mmol), followed by dry THF (7 mL). The flask was closed under an atmosphere of nitrogen and stirred at 80 °C for 24 h. After cooling to room temperature, water (10 mL) and 30%  $\text{H}_2\text{O}_2$  (5 mL) aqueous solution were successively added and the mixture was stirred at room temperature for 15 min.. After extraction with diethyl ether (10 mL x 3), the ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane as eluent to give **11**.



**11a**

**11a**: Yield 73%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  4.14 (s, 2H) (cage CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  63.4 (cage CH);  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  -1.8 (d,  $J_{\text{BH}} = 145$  Hz, 2B) ( $B_{\text{cageH}}$ ), -11.4 (m, 6B) ( $B_{\text{cage-Br}}$  &  $B_{\text{cageH}}$ ), 12.3 (d,  $J_{\text{BH}} =$

96 Hz, 2B) ( $B_{\text{cageH}}$ ); analysis (calcd., found for  $\text{C}_2\text{H}_{10}\text{B}_{10}\text{Br}_2$ ): C (7.95, 8.21), H (3.34, 3.33).



**11b**

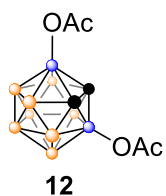
**11b**: Yield 78%. White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  4.13 (s, 2H) (cage CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  64.3 (cage CH);  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  -0.1 (d,  $J_{\text{BH}} = 151$  Hz, 2B), -8.7 (d,  $J_{\text{BH}} = 134$  Hz, 2B), -9.9 (d,  $J_{\text{BH}} = 162$  Hz, 4B)

( $B_{\text{cageH}}$ ), -27.8 (s, 2B) ( $B_{\text{cage-I}}$ ); analysis (calcd., found for  $\text{C}_2\text{H}_{10}\text{B}_{10}\text{I}_2$ ): C (6.07, 6.10), H (2.55, 2.53).



### Preparation of 3,6-Diacetoxy-*o*-carborane (**12**).

Compound **3a** (198 mg, 0.5 mmol), Cu(OAc)<sub>2</sub> (545 mg, 3 mmol), KF (175 mg, 3 mmol) and 4 Å molecular sieve (150 mg) were mixed in CH<sub>3</sub>CN (2.5 mL) in a 25 mL Schlenk flask. The mixture was heated at 80 °C under O<sub>2</sub> atmosphere (1 atm) for 12 h. After hydrolysis with water (10 mL) and extraction with diethyl ether (10 mL x 3), the ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane/ethyl acetate (10/1 in v/v) as eluent to give **12** as a white solid (104 mg, 80%).



**12**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 4.79 (s, 2H) (cage CH), 2.17 (s, 6H) (COCH<sub>3</sub>);

<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 170.0 (C=O), 55.7 (cage CH), 22.5 (CH<sub>3</sub>); <sup>11</sup>B

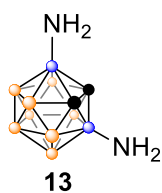
NMR (CDCl<sub>3</sub>, 128 MHz): δ -4.3 (s, 2B) (*B*<sub>cage</sub>-O), -7.4 (d, *J*<sub>BH</sub> = 150 Hz, 2B) (*B*<sub>cage</sub>H),

-15.7 (d, *J*<sub>BH</sub> = 164 Hz, 4B) (*B*<sub>cage</sub>H), -18.1 (d, *J*<sub>BH</sub> = 156 Hz, 2B) (*B*<sub>cage</sub>H); analysis (calcd., found for C<sub>6</sub>H<sub>16</sub>B<sub>10</sub>O<sub>4</sub>): C (27.69, 27.66), H (6.20, 6.15).

### Preparation of 3,6-Diamino-*o*-carborane (**13**).

To a THF solution of MeONH<sub>2</sub> (6.0 mL, 3.0 mmol), prepared in situ from the reaction of MeONH<sub>2</sub> HCl (251 mg, 3.0 mmol) with NaH (85 mg, 3.5 mmol) at room temperature for 12 h, was slowly added <sup>n</sup>BuLi (1.6 M, 1.9 mL, 3.0 mmol) at -78 °C under an atmosphere of dry nitrogen. After stirring at room temperature for 30 min, a THF solution (4 mL) of **3a** (198 mg, 0.5 mmol) was added. The resulting mixture was heated in a closed flask at 80 °C for 8 h. After hydrolysis with water (10 mL) and extraction with diethyl ether (10 mL x 3), the ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on

silica gel (230-400 mesh) using *n*-hexane/ethyl acetate (4/1 in v/v) as eluent to give **13** as a white solid (78 mg, 90%).



**13:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  3.58 (s, 2H) (cage CH), 1.45 (s, 4H) ( $\text{NH}_2$ );

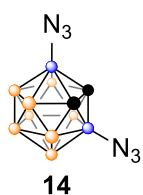
$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  62.5 (cage CH);  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$

1.1 (s, 2B) ( $B_{\text{cage-N}}$ ), -6.4 (d,  $J_{\text{BH}} = 147$  Hz, 2B) ( $B_{\text{cageH}}$ ), -16.3 (d,  $J_{\text{BH}} = 158$  Hz, 4B)

( $B_{\text{cageH}}$ ), -19.1 (d,  $J_{\text{BH}} = 150$  Hz, 2B) ( $B_{\text{cageH}}$ ); analysis (calcd., found for  $\text{C}_2\text{H}_{14}\text{B}_{10}\text{N}_2$ ): C (13.79, 13.98), H (8.10, 8.07), N (16.08, 15.77).

#### Preparation of 3,6-Diazido-*o*-carborane (**14**).

To a THF suspension (3 mL) of **3a** (198 mg, 0.5 mmol), CuCl (104 mg, 1.05 mmol) and KF (70 mg, 1.2 mmol) was added  $\text{TMSN}_3$  (138 mg, 1.2 mmol). The resulting mixture was stirred at 60 °C for 24 h. After hydrolysis with water (10 mL) and extraction with diethyl ether (10 mL x 3), the ether solutions were combined and concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using *n*-hexane/ethyl acetate (100/1 in v/v) as eluent to give the product **14** as a white solid (94 mg, 83%).



**14:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.67 (s, 2H) (cage CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75

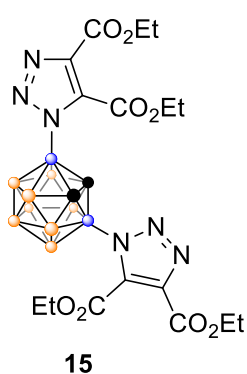
MHz):  $\delta$  57.2 (cage CH);  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  -4.2 (s, 2B) ( $B_{\text{cage-N}}$ ), -4.6 (d,

$J_{\text{BH}} = 117$  Hz, 2B) ( $B_{\text{cageH}}$ ), -14.6 (d,  $J_{\text{BH}} = 166$  Hz, 4B) ( $B_{\text{cageH}}$ ), -17.0 (d,  $J_{\text{BH}} = 153$  Hz,

2B) ( $B_{\text{cageH}}$ ); analysis (calcd., found for  $\text{C}_2\text{H}_{10}\text{B}_{10}\text{N}_6$ ): C (10.62, 10.46), H (4.45, 4.45), N (37.14, 37.05).

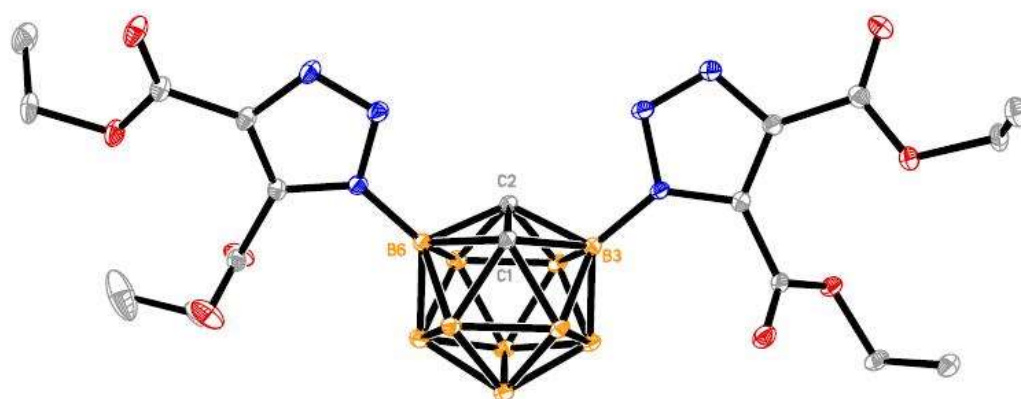
### Preparation of 3,6-Ditriazolyl-*o*-carborane by Click Reaction.

Compound **14** (68 mg, 0.3 mmol) and diethyl but-2-ynedioate (123 mg, 0.72 mmol) were dissolved in toluene (1 mL). The resulting mixture was stirred at 95 °C for 5 h. After removal of the solvent in vacuo, the residue recrystallized from *n*-hexane/diethyl ether (5/1 in v/v) to give **15** as a white solid (141 mg, 83%).



**15**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  5.33 (s, 2H) (cage CH), 4.52 (q,  $J = 7.2$  Hz, 4H), 4.43 (q,  $J = 6.9$  Hz, 4H) ( $\text{CH}_2$ ), 1.45 (t,  $J = 7.2$  Hz, 6H), 1.39 (t,  $J = 7.2$  Hz, 6H) ( $\text{CH}_3$ ),  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  159.6, 159.2 (C=O), 139.2, 138.8 (olefinic C), 64.0, 62.1 (OCH<sub>2</sub>), 60.6 (cage CH), 14.2, 13.9 ( $\text{CH}_3$ ),  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):  $\delta$  -2.8 (m, 2B) ( $B_{\text{cageH}}$ ), -7.1 (s, 2B) ( $B_{\text{cage-N}}$ ), -12.9

(m, 6B) ( $B_{\text{cageH}}$ ); analysis (calcd., found for  $\text{C}_{18}\text{H}_{30}\text{B}_{10}\text{N}_6\text{O}_8$ ): C (38.16, 37.95), H (5.34, 5.31), N (14.83, 14.79).

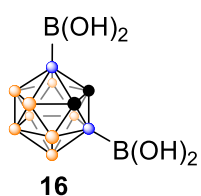


**Supplementary Figure 10.** Molecular structure of **15** drawn with 30% probability ellipsoids.

### Preparation of 3,6-[B(OH)<sub>2</sub>]<sub>2</sub>-*o*-Carborane (**16**).

To a solution of **3a** (396 mg, 1.0 mmol) in ether (15 mL) was added diethanolamine (260 mg, 2.5

mmol). After a few minutes, a white precipitate was formed, and the reaction was allowed to continue until the starting material was completely consumed as monitored by TLC (~18 h). The precipitate was then filtered off, washed with ether, and dried to afford a white solid. The solid was dispersed in ether (20 mL), to which was added HCl (0.5 M, 16 mL). The mixture was stirred till it became homogeneous. The resulting solution was extracted with ether (10 mL x 3), and the organic portions were combined and concentrated to dryness in vacuo to give the pure product **16** as a white solid (198 mg, 85%).



**16**: <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz): δ 8.11 (s, 4H) (OH), 4.32 (s, 2H) (cage CH);

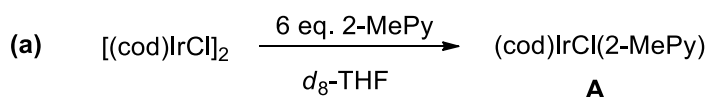
<sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub>, 100 MHz): δ 58.9 (cage CH); <sup>11</sup>B{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub>,

128 MHz): δ 31.5 (s, 2B) (B–O), -2.0 (m, 2B), -6.9 (m, 2B), -11.3 (m, 6B) (B<sub>cage</sub>H);

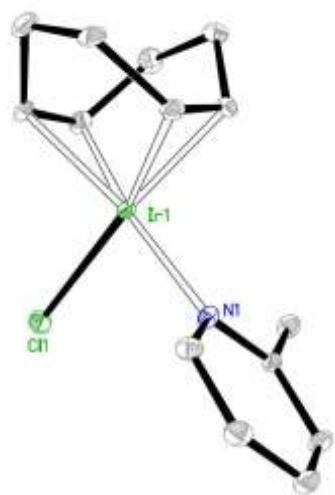
analysis (calcd., found for C<sub>2</sub>H<sub>14</sub>B<sub>12</sub>O<sub>4</sub>): C (10.36, 10.24), H (6.09, 5.89).

## Supplementary Discussion

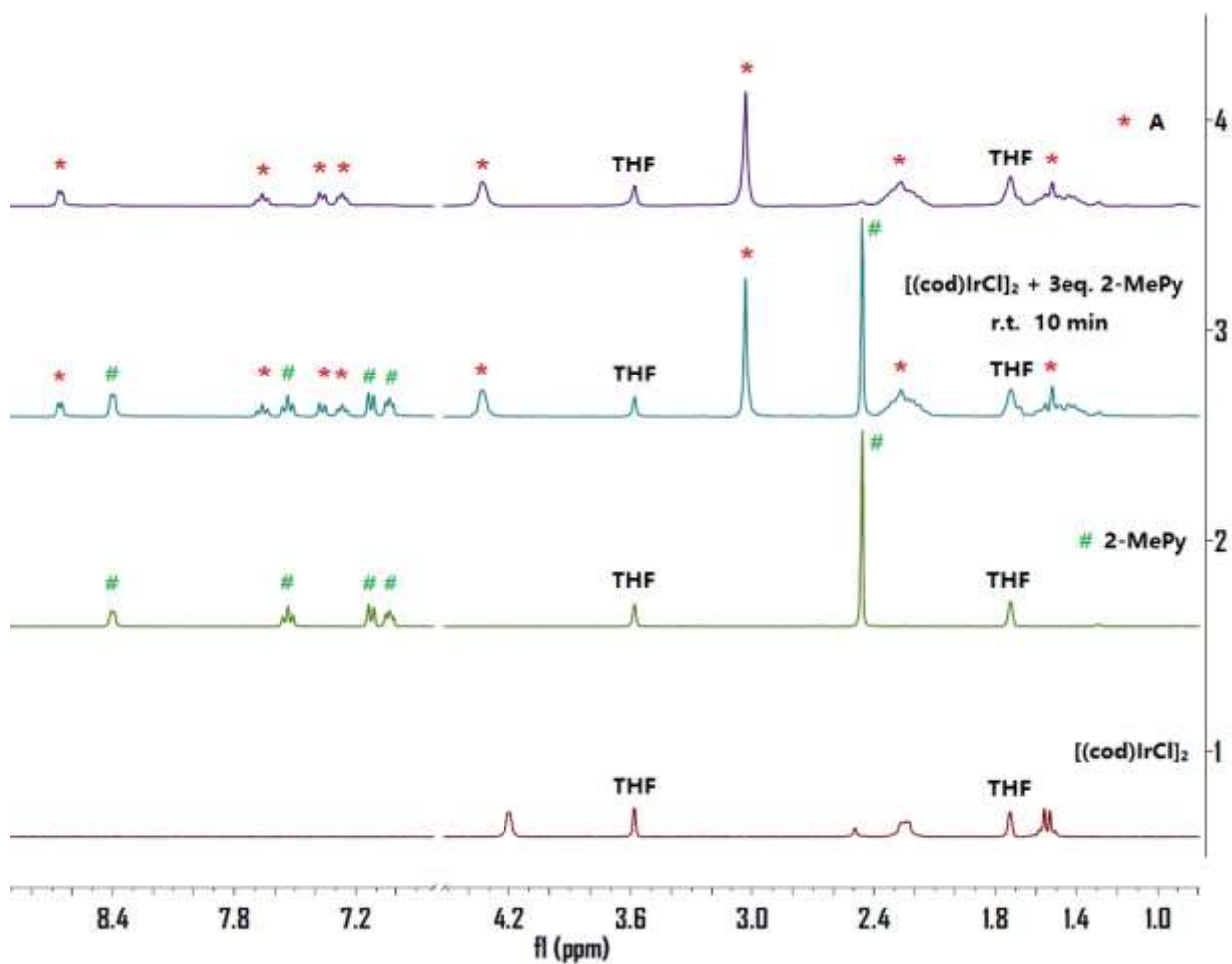
### Mechanistic Study (Control Experiments). NMR Tube Reactions



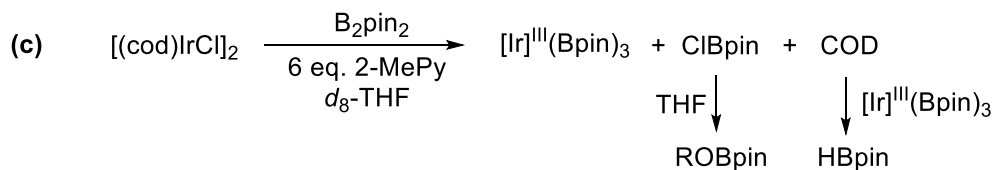
[(cod)IrCl]<sub>2</sub> (13.3 mg, 0.04 mmol) and 2-methylpyridine (2-MePy, 11.4 mg, 0.12 mmol) were mixed in *d*<sub>8</sub>-THF (0.5 mL) in a J. Young valve NMR tube in glovebox. The reaction was monitored by <sup>1</sup>H NMR at room temperature. After the solvent and excess 2-MePy were removed in vacuo, a clean <sup>1</sup>H NMR spectra of (cod)IrCl(2-MePy) (**A**) was obtained in *d*<sub>8</sub>-THF. Orange single crystals of complex **A** was obtained after this solution stood at room temperature for 1 day.



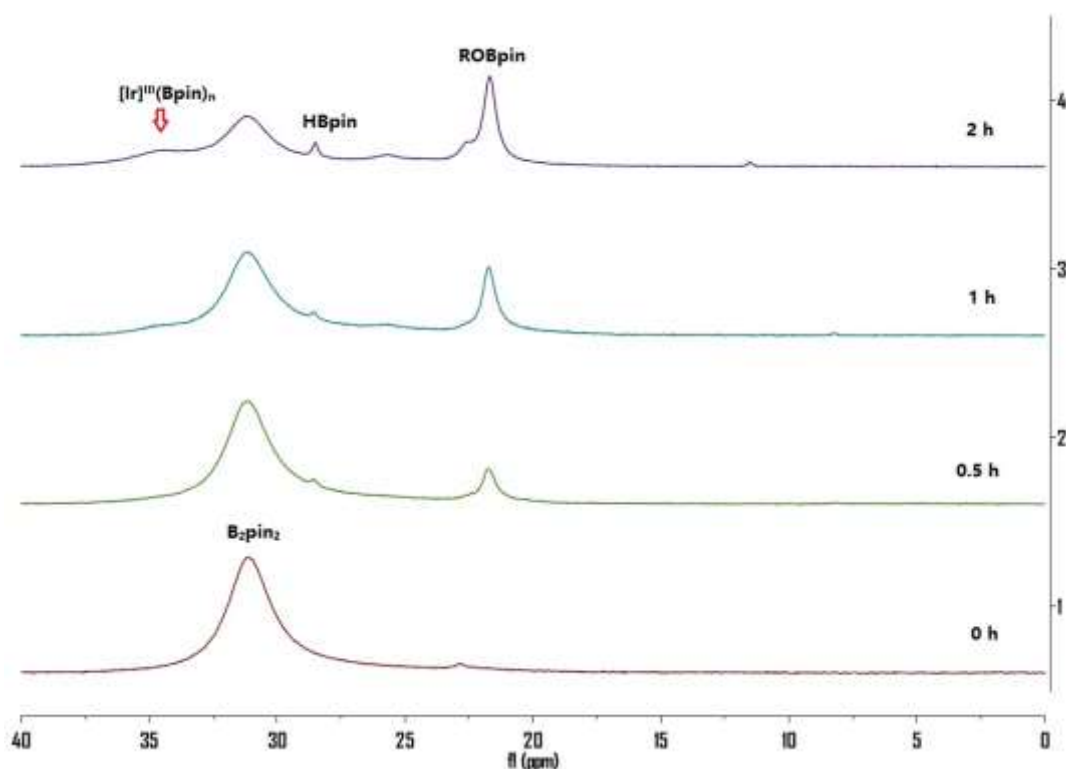
Supplementary Figure 11. Molecular structure of A drawn with 30% probability ellipsoids.



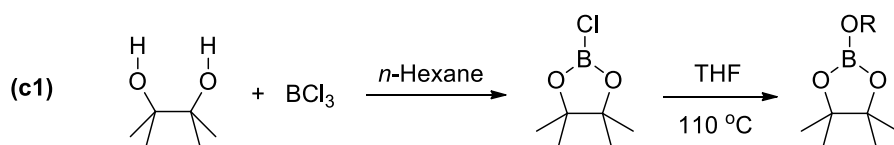
Supplementary Figure 12. <sup>1</sup>H NMR spectrum of experiment (a)



$\text{B}_2\text{pin}_2$  (10.1 mg, 0.04 mmol),  $[(\text{cod})\text{IrCl}]_2$  (13.3 mg, 0.04 mmol), and 2-methylpyridine (11.4 mg, 0.12 mmol) were mixed in  $d_8$ -THF (0.5 mL) in a J. Young valve NMR tube. The tube was closed and heated at 110 °C (bath temperature). The reaction was monitored by  $^{11}\text{B}$  NMR.

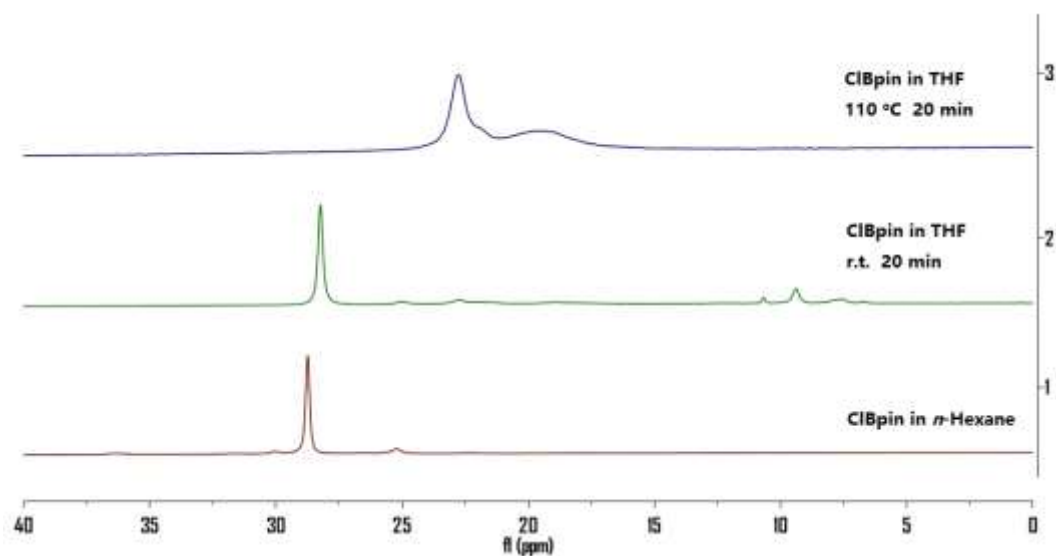


**Supplementary Figure 13.** Time-dependent  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra of experiment (c)

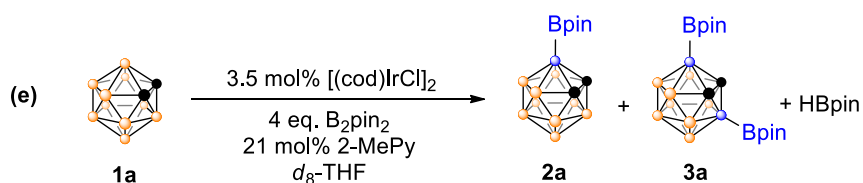


To a *n*-hexane solution (10 mL) of dry pinacol (60 mg, 0.50 mmol) was added dropwise  $\text{BCl}_3$  solution (0.75 mL, 1 M in hexane, 0.75 mmol) via syringe at 0 °C. The reaction mixture was stirred for 1 h at room temperature. The solution was condensed under vacuum to about 0.5 mL giving a

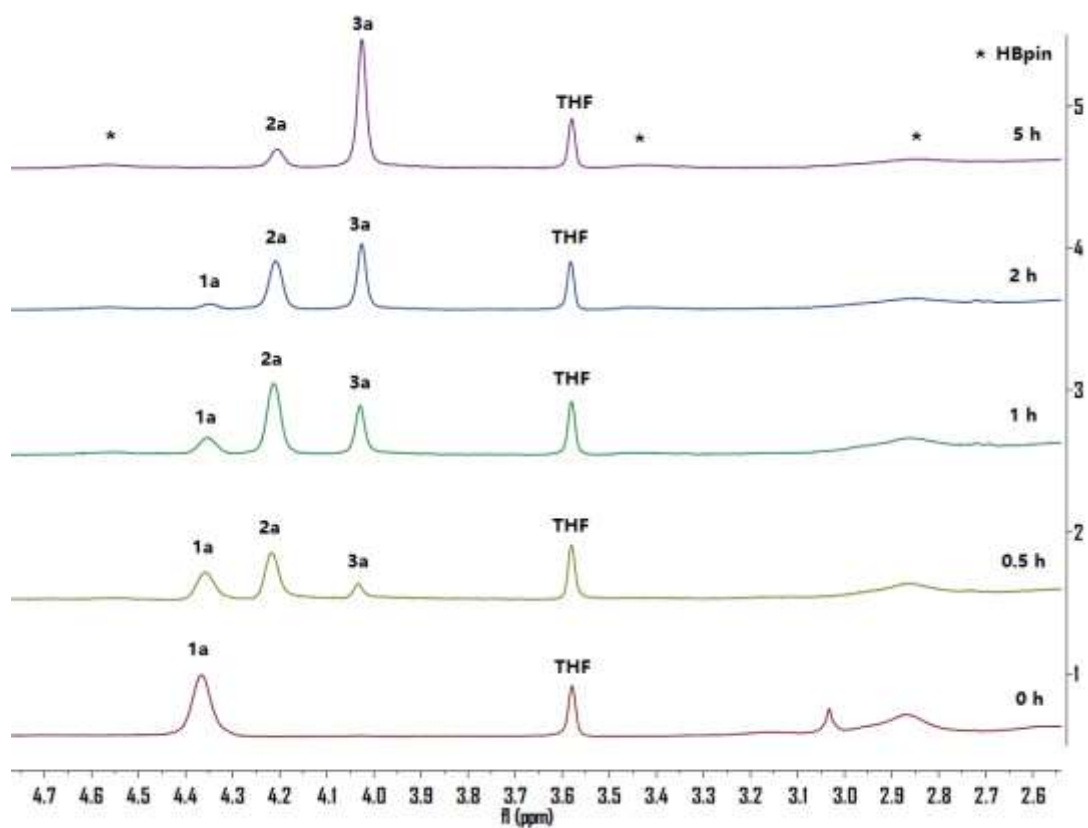
crude ClBpin solution.<sup>11</sup> The residue was dissolved in THF, which was monitored by <sup>11</sup>B NMR. The signal at 22 ppm corresponding to ROBpin resulted from the reaction of ClBpin with THF is in accordance with that observed in experiment (c).



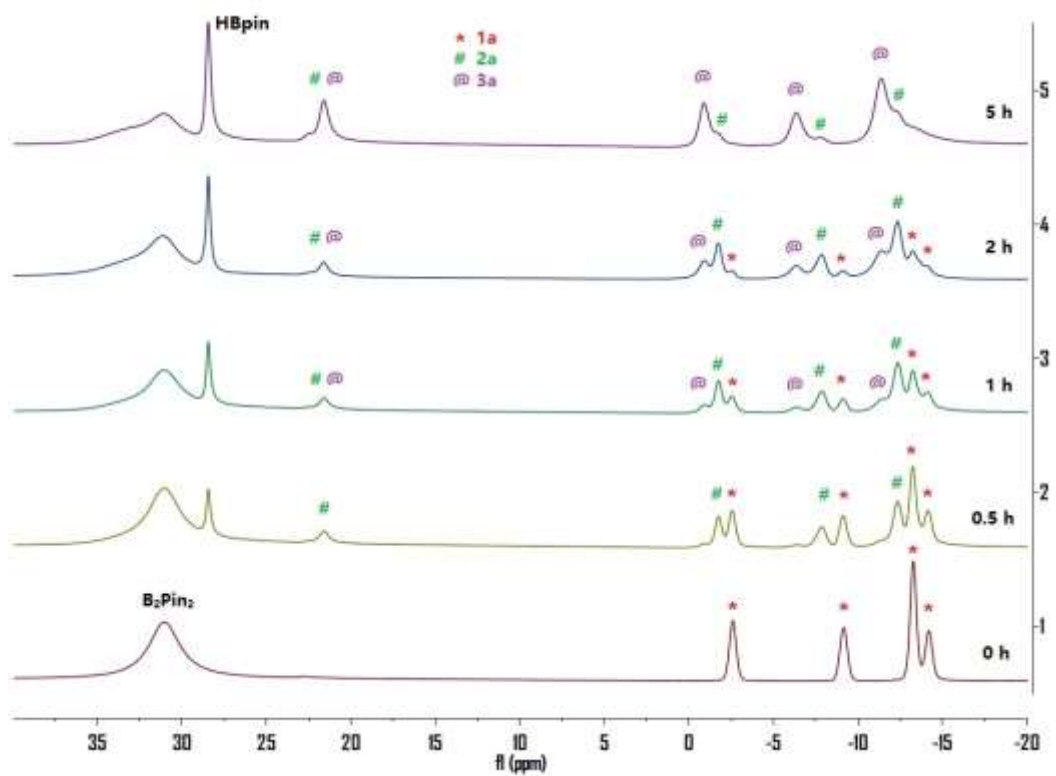
**Supplementary Figure 14.** Time-dependent <sup>11</sup>B{<sup>1</sup>H} NMR spectra of reaction (c1)



The reaction was conducted under standard conditions (4 equiv B<sub>2</sub>pin<sub>2</sub>, 3.5 mol% [(cod)IrCl]<sub>2</sub>, 21 mol% 2-methylpyridine) in d<sub>8</sub>-THF (0.5 mL) in a J. Young valve NMR tube and monitored by <sup>1</sup>H and <sup>11</sup>B NMR.



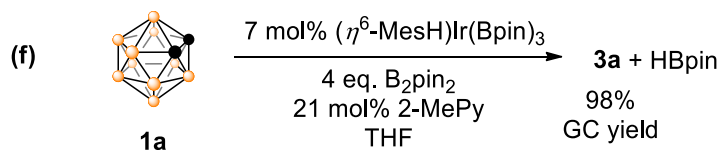
**Supplementary Figure 15.** Time-dependent  $^1\text{H}$  NMR spectra of experiment (e)



**Supplementary Figure 16.** Time-dependent  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra of experiment (e)



### Borylation Reaction of **1a** Catalyzed by ( $\eta^6$ -MesH)Ir(Bpin)<sub>3</sub>



An oven-dried Schlenk flask equipped with a stir bar was charged with *o*-carborane **1a** (14.4 mg, 0.1 mmol), B<sub>2</sub>pin<sub>2</sub> (101.6 mg, 0.4 mmol), ( $\eta^6$ -MesH)Ir(Bpin)<sub>3</sub> (4.9 mg, 0.007 mmol), and 2-methylpyridine (2.0 mg, 0.021 mmol), followed by dry THF (1 mL). The flask was closed under an atmosphere of nitrogen and stirred at 110 °C (bath temperature) for 5 h. The reaction was then quenched with wet hexane. The hexane solution was subjected to GC-MS analyses, showing that **3a** was formed in 98% GC yield.

**X-ray Structure Determination.** All data were collected at 293K on a Bruker SMART 1000 CCD diffractometer using Mo-K $\alpha$  radiation. An empirical absorption correction was applied using the SADABS program.<sup>12</sup> All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F<sup>2</sup> using the SHELXTL program package.<sup>13</sup> All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table S5.

CCDC 1500326-1500335 (**2a**, **2p**, **2q**, **3a**, **3l**, **5**, **7c**, **8a**, **15** and complexes **A**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Supplementary Table 5.** Crystal Data and Summary of Data Collection and Refinement.

compound	<b>3a</b>	<b>3l</b>	<b>2p</b>	<b>2q</b>	<b>2a</b>
formula	C <sub>14</sub> H <sub>34</sub> B <sub>12</sub> O <sub>4</sub>	C <sub>14</sub> H <sub>32</sub> B <sub>12</sub> I <sub>2</sub> O <sub>4</sub>	C <sub>22</sub> H <sub>33</sub> B <sub>11</sub> O <sub>2</sub>	C <sub>8</sub> H <sub>21</sub> B <sub>11</sub> I <sub>2</sub> O <sub>2</sub>	C <sub>8</sub> H <sub>23</sub> B <sub>11</sub> O <sub>2</sub>
crystal size (mm)	0.25x0.22x0.15	0.25x0.15x0.05	0.15x0.1x0.02	0.12x0.1x0.08	0.28x0.25x0.20
fw	396.13	647.91	448.39	521.96	270.17
crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	11.531(6)	11.871(1)	9.444(2)	11.516(1)	6.734(2)
<i>b</i> , Å	12.628(7)	13.081(1)	11.410(3)	13.637(1)	20.302(5)
<i>c</i> , Å	18.211(10)	17.992(1)	13.233(3)	12.824(1)	12.248(3)
<i>α</i> , deg	91.95(1)	90	68.38(1)	90	90
<i>β</i> , deg	91.00(1)	101.31(10)	80.64(1)	102.71(1)	93.54(1)
<i>γ</i> , deg	116.46(1)	90	73.26(1)	90	90
<i>V</i> , Å <sup>3</sup>	2371(2)	2739.6(3)	1266.8(5)	1964.6(3)	1671.4(7)
<i>Z</i>	4	4	2	4	4
<i>D</i> <sub>calcd</sub> , Mg/m <sup>3</sup>	1.110	1.571	1.176	1.765	1.074
radiation (λ) Å	0.71073	0.71073	0.71073	0.71073	0.71073
2θ range, deg	3.9 to 52.0	3.5 to 61.2	4.0 to 60.0	3.6 to 61.1	4.0 to 55.0
μ, mm <sup>-1</sup>	0.066	2.314	0.065	3.197	0.058
<i>F</i> (000)	840	1256	472	984	568
no. of obsd reflns	9252	8418	7243	6019	3709
no. of params refnd	558	297	320	212	194
goodness of fit	1.026	1.027	1.045	1.034	0.955
R1	0.0858	0.0441	0.0716	0.0249	0.0881
wR2	0.1924	0.1121	0.1691	0.0548	0.2300

compound	<b>5</b>	<b>7c</b>	<b>8a</b>	<b>15</b>	<b>A</b>
formula	C <sub>8</sub> H <sub>23</sub> B <sub>11</sub> O <sub>2</sub>	C <sub>14</sub> H <sub>35</sub> B <sub>11</sub> I <sub>2</sub> O <sub>2</sub> Si	C <sub>8</sub> H <sub>23</sub> B <sub>11</sub> O <sub>2</sub>	C <sub>18</sub> H <sub>30</sub> B <sub>10</sub> N <sub>6</sub> O <sub>8</sub>	C <sub>14</sub> H <sub>19</sub> ClIrN
crystal size (mm)	0.25x0.2x0.18	0.18x0.165x0.12	0.32x0.28x0.25	0.25 x 0.22 x 0.2	0.15x0.1x0.05
fw	270.17	636.22	270.17	566.58	428.95
crystal system	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
space group	<i>P2<sub>1</sub>/c</i>	<i>Pbca</i>	<i>P2<sub>1</sub>/n</i>	<i>P-1</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> , Å	8.374(3)	12.192(2)	6.699(1)	7.088(1)	10.507(1)
<i>b</i> , Å	18.502(7)	14.089(2)	20.308(2)	13.346(1)	10.840(1)
<i>c</i> , Å	10.724(4)	33.150(5)	12.120(1)	15.578(2)	12.435(1)
<i>α</i> , deg	90	90	90	77.22(1)	90
<i>β</i> , deg	91.29(1)	90	93.87(1)	79.09(1)	107.49(1)
<i>γ</i> , deg	90	90	90	79.59(1)	90
<i>V</i> , Å <sup>3</sup>	1661.1(11)	5694.0(15)	1645.1(3)	1396.2(3)	1350.6(2)
<i>Z</i>	4	8	4	2	4
<i>D<sub>calcd</sub></i> , Mg/m <sup>3</sup>	1.080	1.484	1.091	1.348	2.110
radiation (λ) Å	0.71073	0.71073	0.71073	0.71073	0.71073
2θ range, deg	2.2 to 55.4	4.6 to 39.2	5.2 to 58.5	3.2 to 61.2	4.1 to 613
<i>μ</i> , mm <sup>-1</sup>	0.059	2.261	0.059	0.096	10.061
<i>F</i> (000)	568	2480	568	588	816
no. of obsd reflns	3849	6601	5052	8460	4152
no. of params refnd	194	280	244	383	155
goodness of fit	1.007	1.169	1.050	1.044	1.024
R1	0.0692	0.0765	0.0770	0.0523	0.0242
wR2	0.1721	0.2001	0.2009	0.1254	0.0559

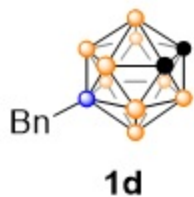
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crf-3-67-H-CDCl3

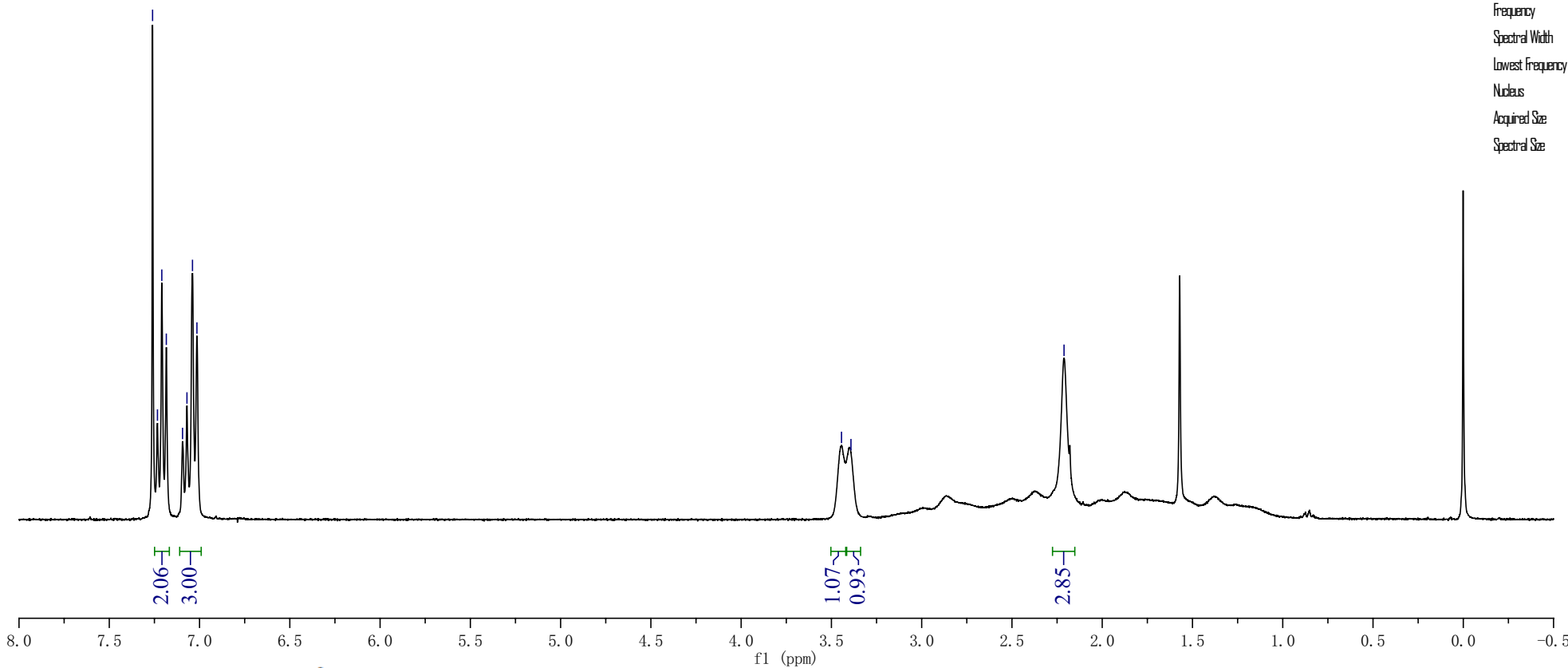
7.260  
7.233  
7.209  
7.184  
7.094  
7.070  
7.039  
7.015



3.444  
3.392

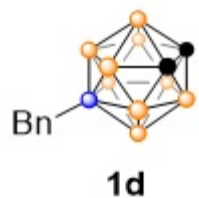
2.211

Parameter	Value
Title	crf-3-67-2
Comment	STANDARD IN CHEMIST
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	onc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	sgul
Number of Scans	8
Receiver Gain	21
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-01-28 08:16
Spectrometer	300.03
Frequency	
Spectral Width	5494.5
Lowest Frequency	-70.0
Nucleus	1H
Acquired Size	10376
Spectral Size	3268



Supplementary Figure 17. <sup>1</sup>H NMR Spectrum of 1d.

crf-3-67-C-CDCl3



144.688

128.460  
127.964

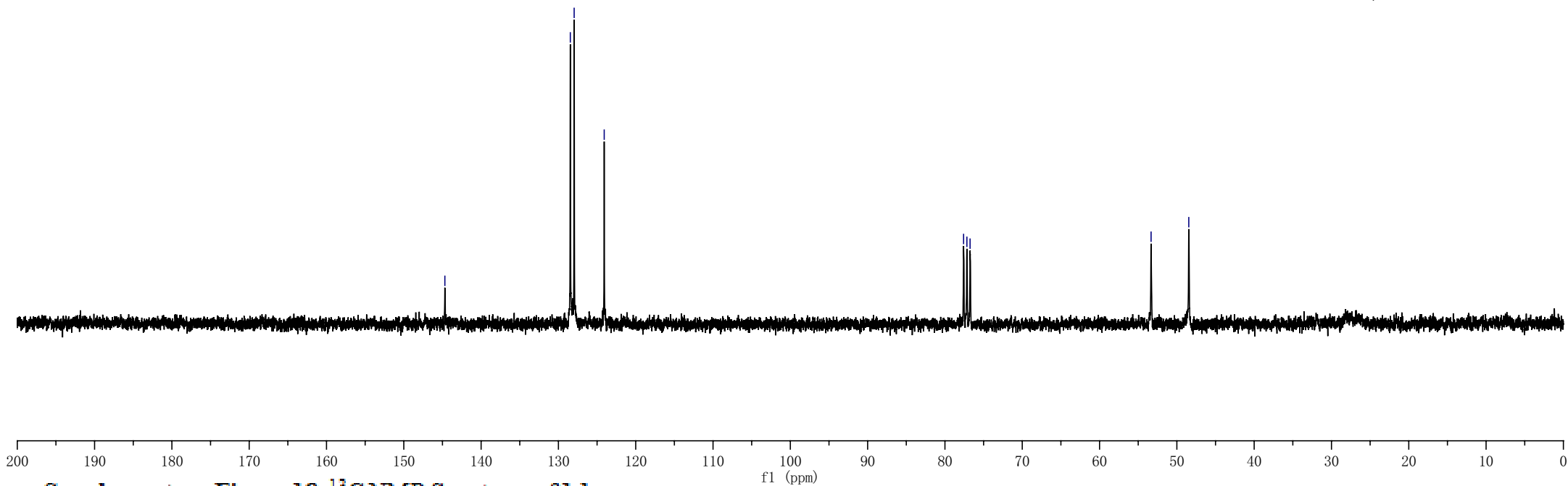
124.076

77.588  
77.160  
76.750

53.335

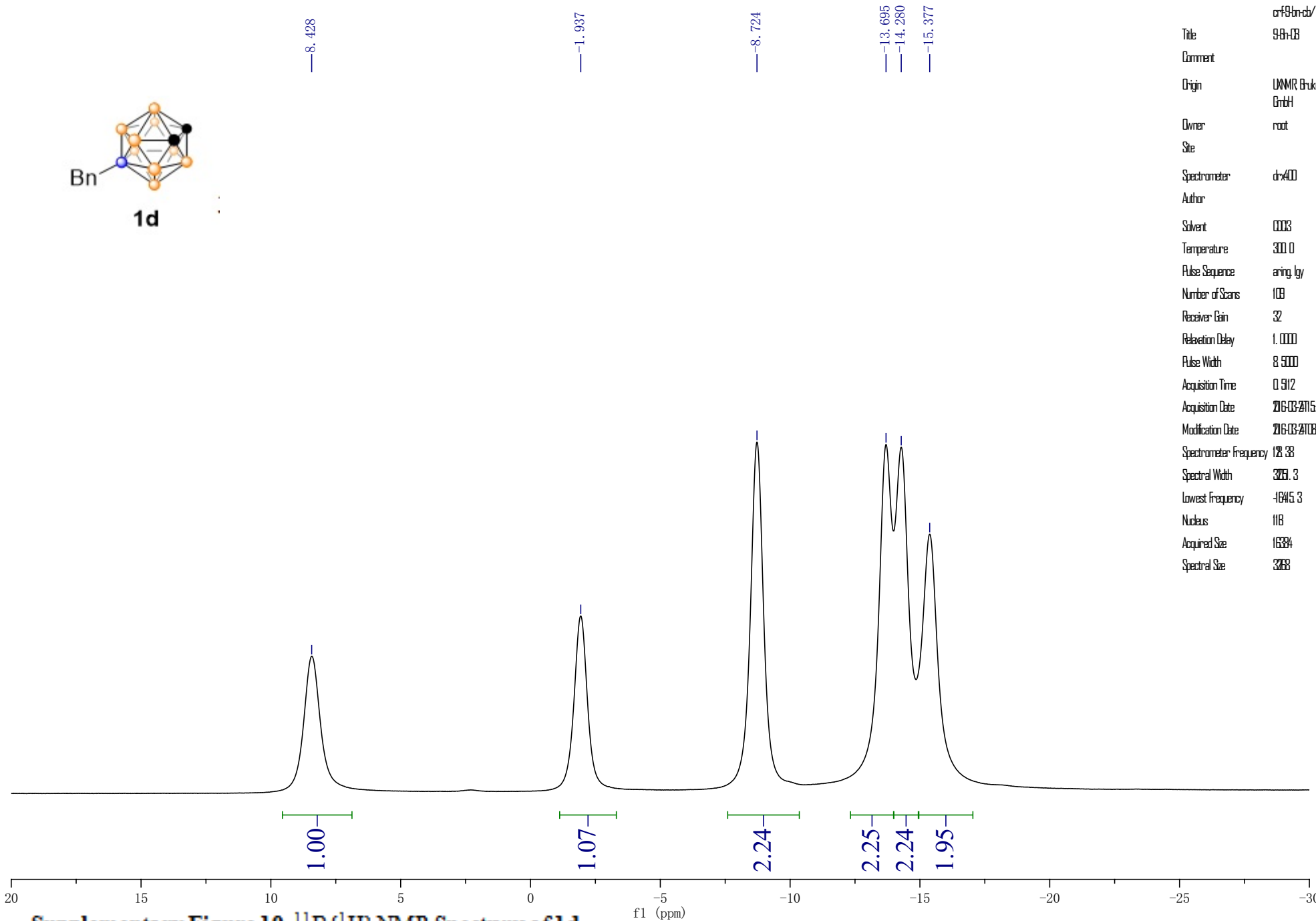
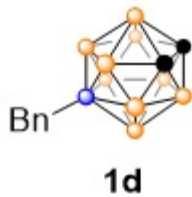
48.458

Parameter	Value
Title	crf-3-67-C-CDCl3
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	29.0
Pulse Sequence	zgpg30
Number of Scans	128
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2016-03-28T18:51:17
Spectrometer Frequency	76.46
Spectral Width	1901.4
Lowest Frequency	4735.0
Nucleus	13C
Acquired Size	2537
Spectral Size	65535



Supplementary Figure 18. <sup>13</sup>C NMR Spectrum of 1d.

crf-3-67-B-coupling-CDC13

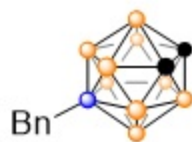


Parameter	Value
Data File Name	E:/boralation/boralation/98-08/b-crif98bn-cb/1d
Title	98-08
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dmx400
Author	
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	aning.tgy
Number of Scans	100
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	8.5000
Acquisition Time	0.512
Acquisition Date	2016-03-20 15:28:10
Modification Date	2016-03-21 08:32:00
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-1645.3
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

Supplementary Figure 19.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of **1d**.



crf-3-67-B-coupling-CDC13



**1d**

8.416

-1.359

-2.514

-8.147

-9.311

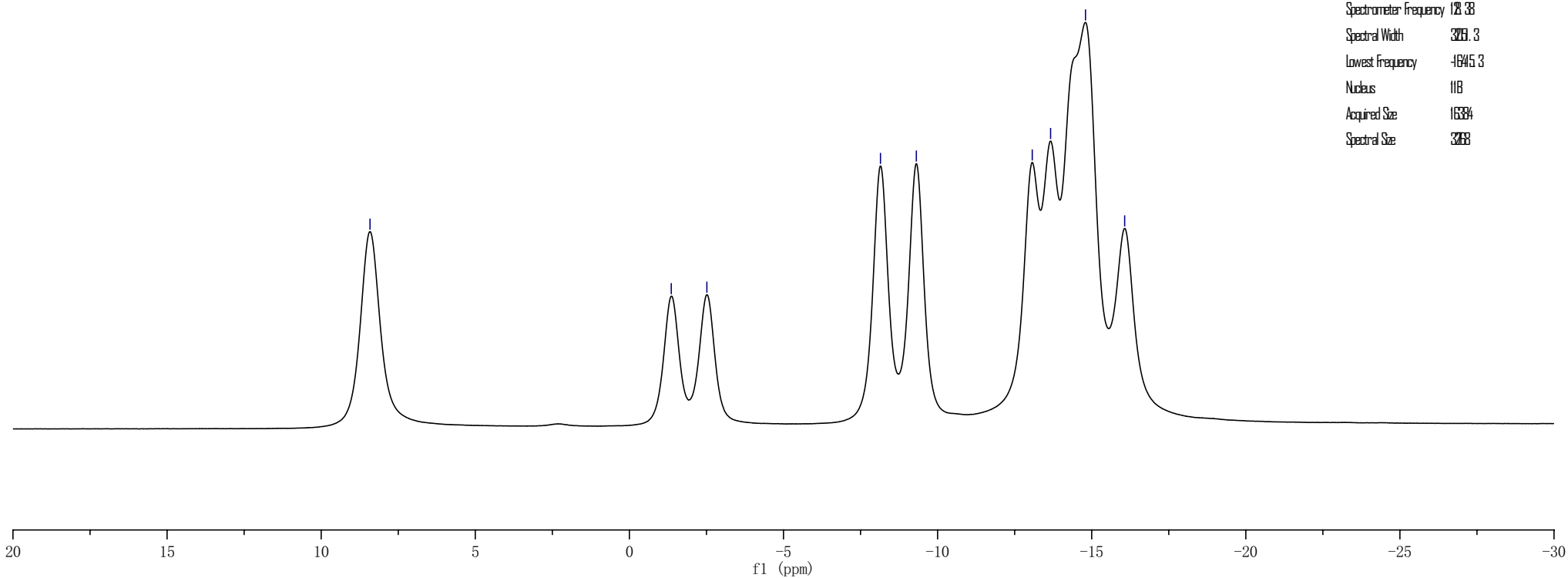
-13.071

-13.666

-14.798

-16.069

Parameter	Value
Data File Name	E:/boralation/boralation/98b-OB/b-cr-f9b-cr-cb-coupling/1d
Title	98b-OB
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dmx400
Author	
Solvent	CDCl <sub>3</sub>
Temperature	300.0
Pulse Sequence	aring-1g
Number of Scans	256
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	8.5000
Acquisition Time	0.512
Acquisition Date	2016-03-21T15:33:58
Modification Date	2016-03-21T18:38:00
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-16415.3
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

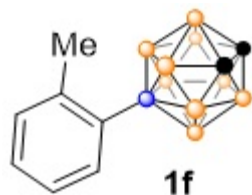


Supplementary Figure 20. <sup>11</sup>B NMR Spectrum of 1d.

crf-4-41-H-CDCl3

7.512  
7.492

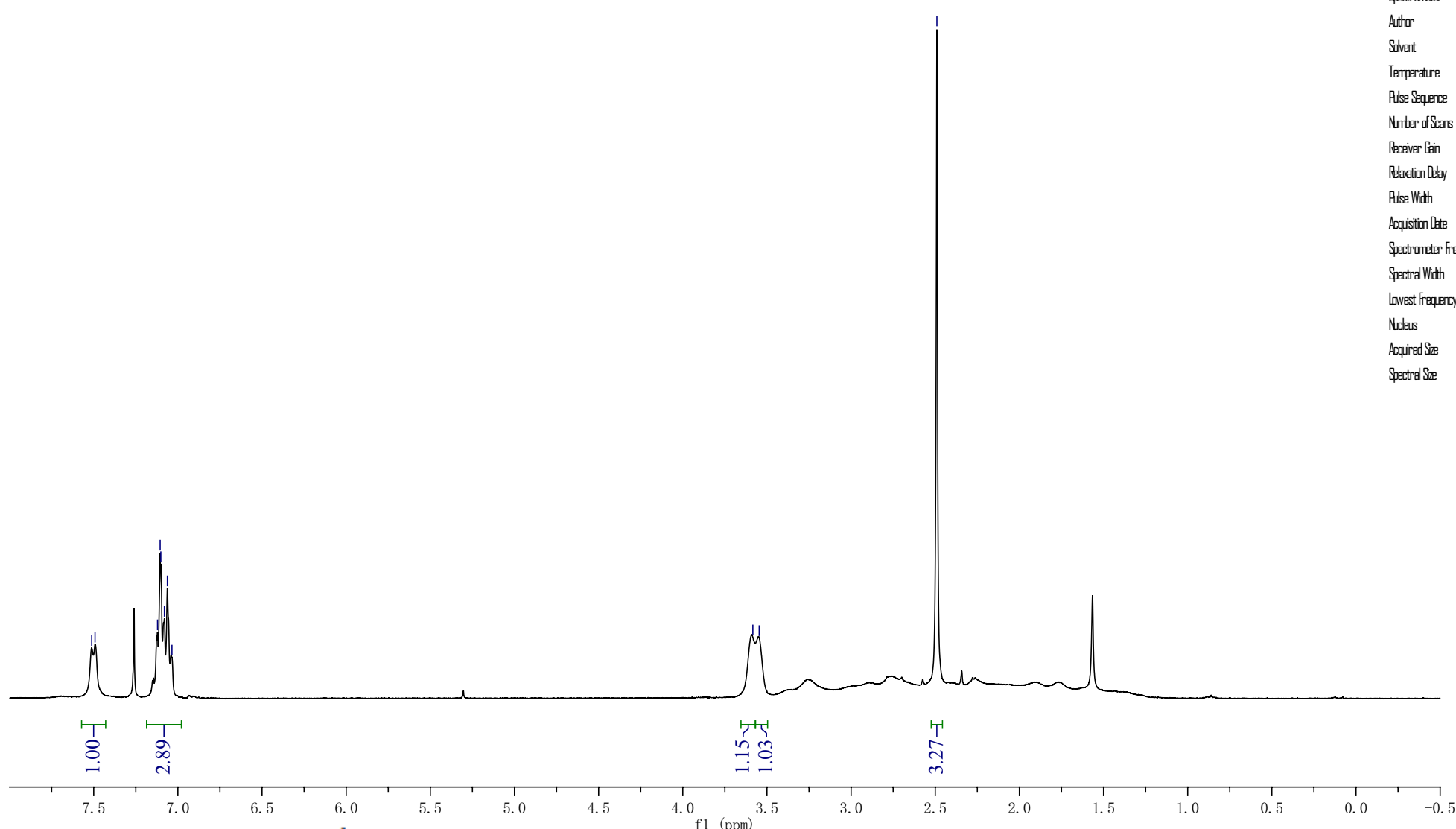
7.121  
7.105  
7.101  
7.080  
7.062  
7.035



3.584  
3.546

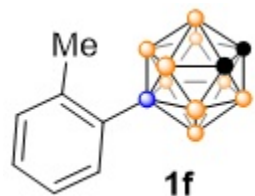
2.490

Parameter	Value
Title	crf-4-41
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	cmc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	zgpg30
Number of Scans	8
Receiver Gain	28
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-17 15:58:26
Spectrometer Frequency	300.133
Spectral Width	5464.5
Lowest Frequency	-709.9
Nucleus	1H
Acquired Size	10876
Spectral Size	3268



Supplementary Figure 21. <sup>1</sup>H NMR Spectrum of 1f.

crf-4-41-C-CDCl3



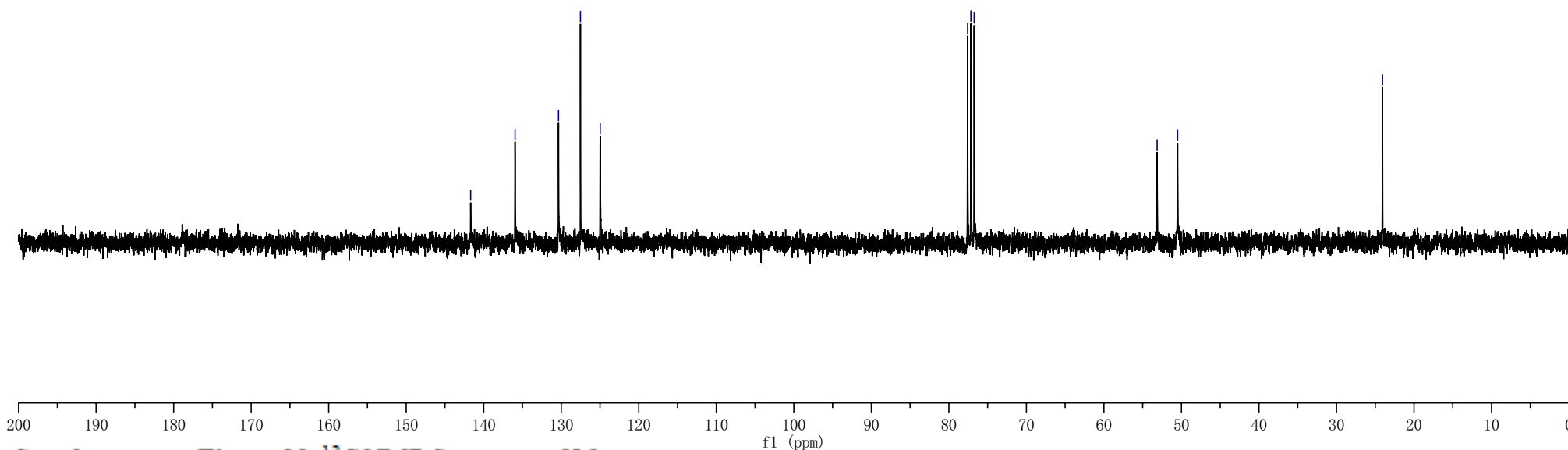
141.686  
135.958  
130.351  
127.524  
124.973

77.585  
77.160  
76.737

53.138  
50.490

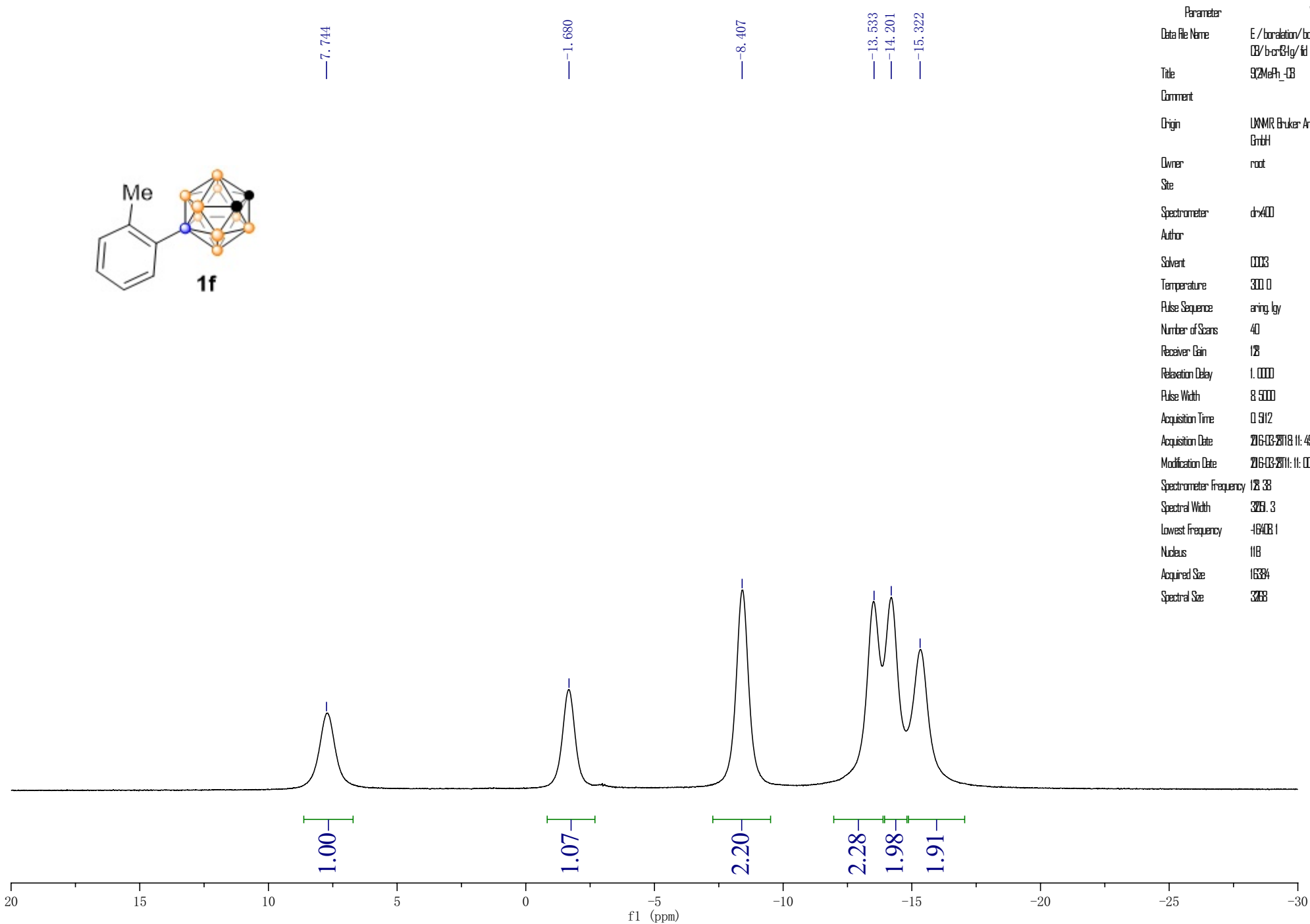
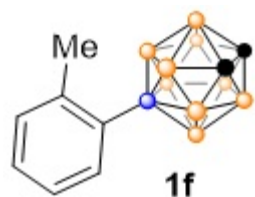
24.065

Parameter	Value
Title	crf34g-C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	zgpg30
Number of Scans	120
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2016-03-20 12:50:41
Spectrometer Frequency	76.45
Spectral Width	1901.4
Lowest Frequency	-4735.0
Nucleus	13C
Acquired Size	2617
Spectral Size	65536



Supplementary Figure 22. <sup>13</sup>C NMR Spectrum of 1f.

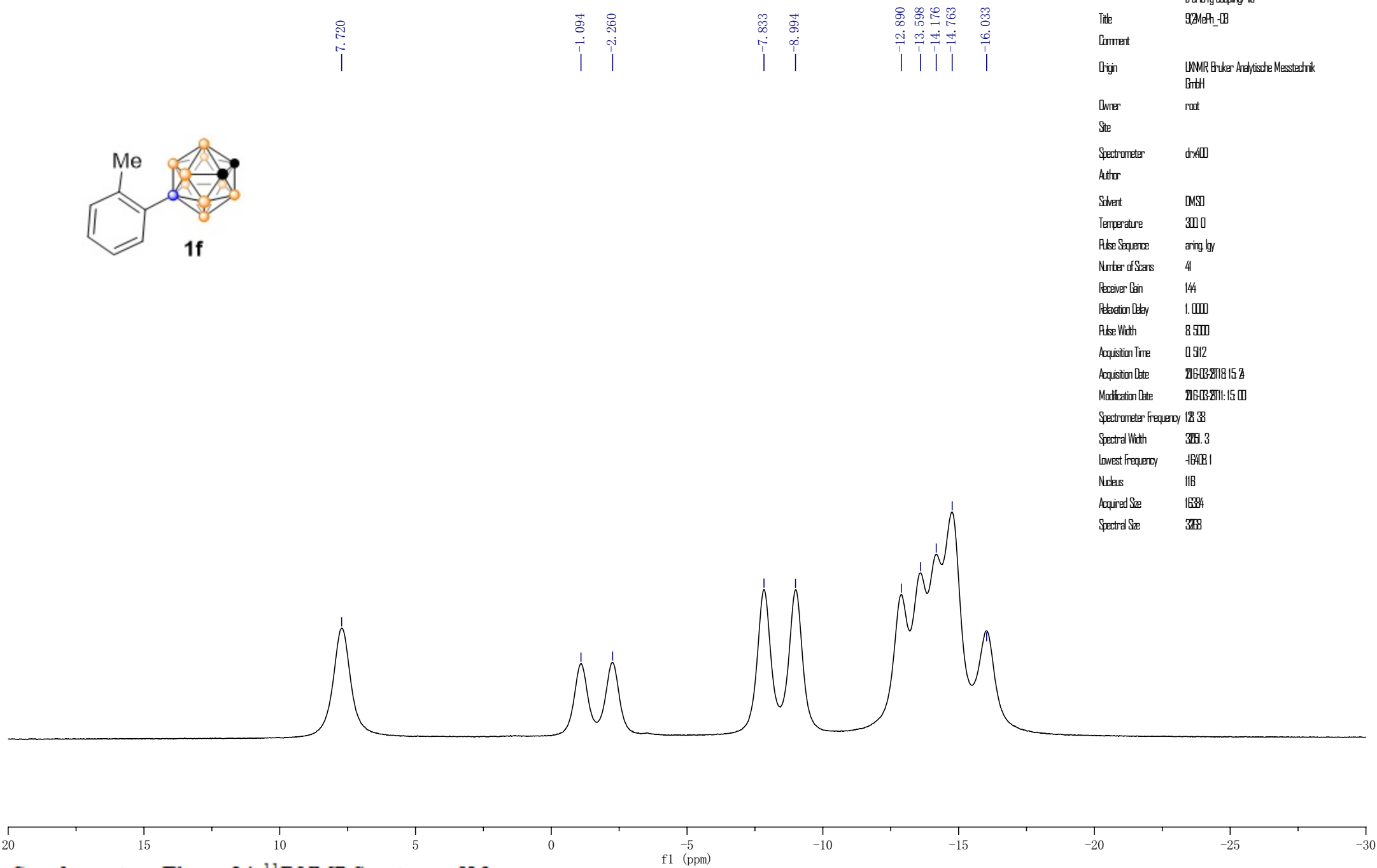
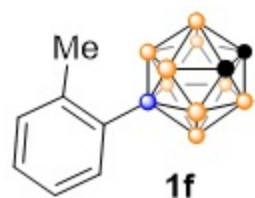
crf-4-41-B-decoupling-CDC13



Parameter	Value
Data File Name	E:/boration/boration/3(2MePh)_CB/b-cr3lg/1d
Title	3(2MePh)_CB
Comment	
Origin	LUNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	crx400
Author	
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	aning.ty
Number of Scans	40
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	8.5000
Acquisition Time	0.512
Acquisition Date	2016-03-28T18:11:49
Modification Date	2016-03-28T11:11:00
Spectrometer Frequency	128.38
Spectral Width	3259.3
Lowest Frequency	-16408.1
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

Supplementary Figure 23.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of **1f**.

crf-4-41-B-coupling-CDCl3

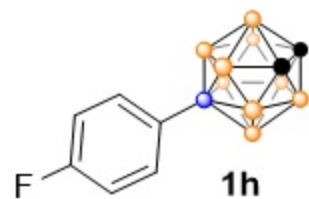


Parameter	Value
Data File Name	E:/boralation/boralation/32MePh_4B/b-cr41g-coupling/fid
Title	32MePh_4B
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dmx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1g
Number of Scans	41
Receiver Gain	144
Relaxation Delay	1.0000
Pulse Width	8.5000
Acquisition Time	0.912
Acquisition Date	2016-03-29T18:15:28
Modification Date	2016-03-29T11:15:00
Spectrometer Frequency	128.38
Spectral Width	3061.3
Lowest Frequency	-16408.1
Nucleus	11B
Acquired Size	16384
Spectral Size	3063

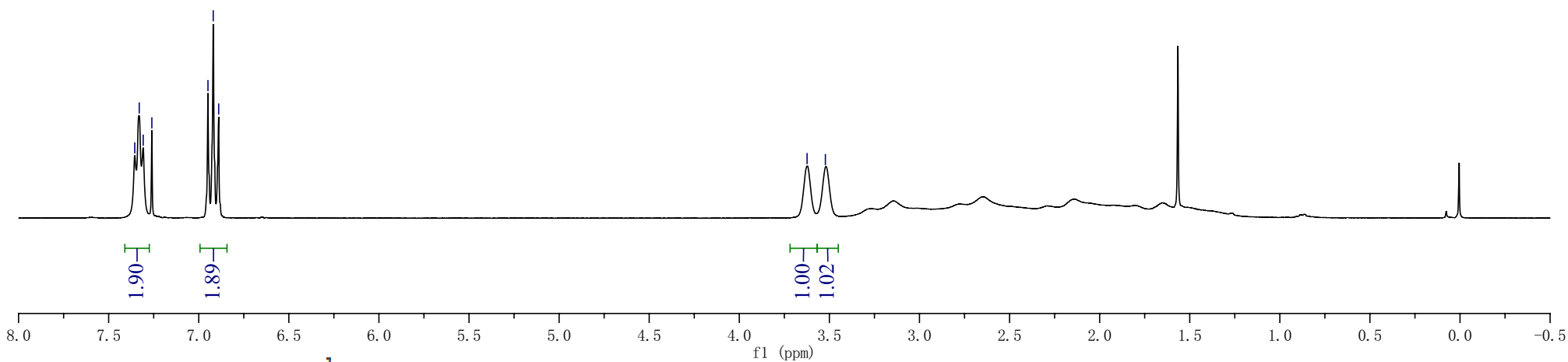
Supplementary Figure 24. <sup>11</sup>B NMR Spectrum of 1f.

crf-3-94-H-CDCl3

7.355  
7.330  
7.308  
7.260  
6.949  
6.920  
6.889



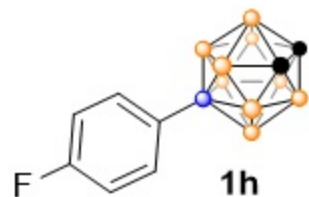
3.624  
3.522



Parameter	Value
Title	crf3-1h-HClO3
Comment	STANDARD 1H OBSERVE
Origin	Varien
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	28
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2016-04-08 12:55:05
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-708.9
Nucleus	1H
Acquired Size	10000
Spectral Size	3200

Supplementary Figure 25. <sup>1</sup>H NMR Spectrum of 1h.

crf-3-94-C-CDCl3



164.544  
161.292

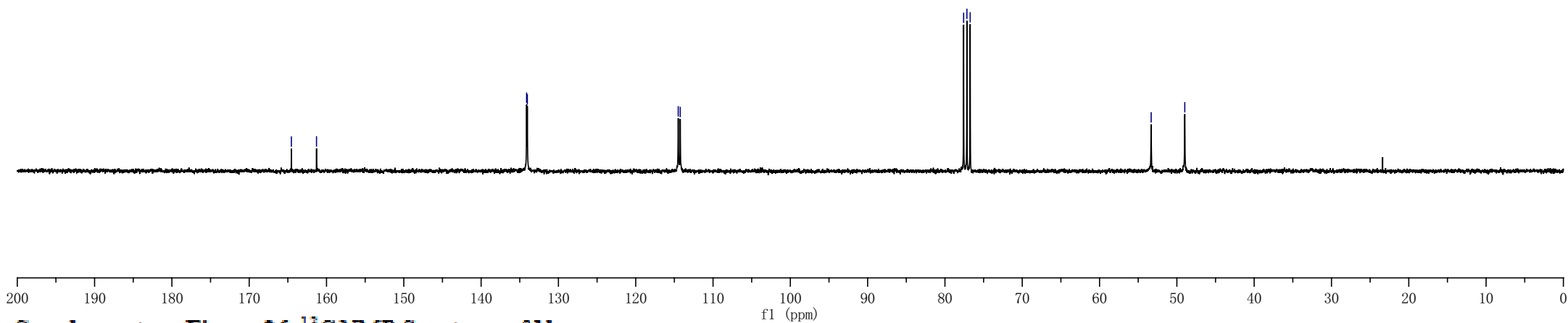
134.117  
134.019

114.503  
114.241

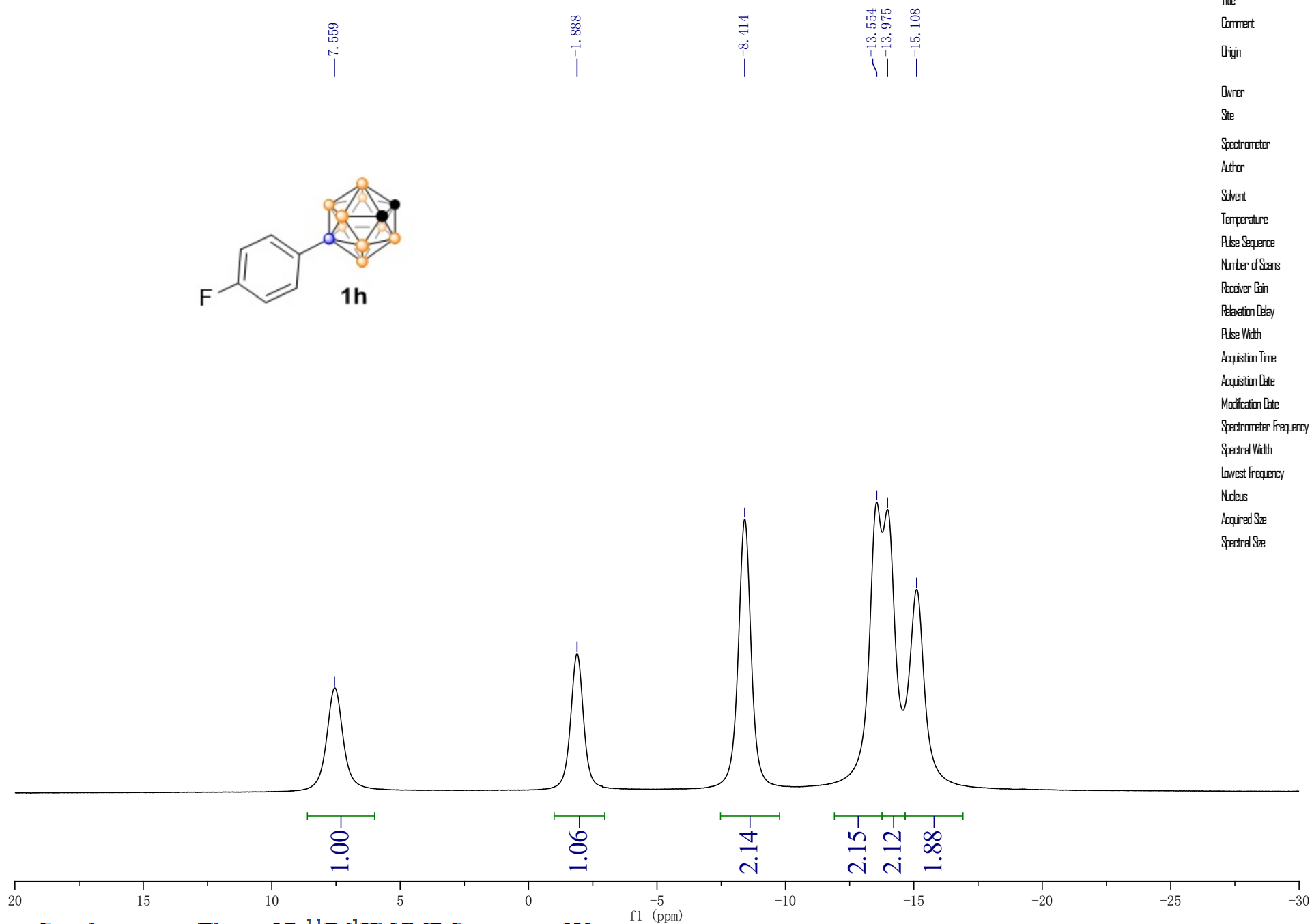
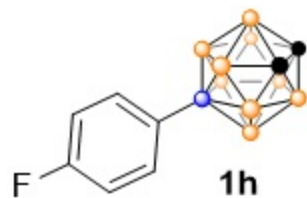
77.583  
77.160  
76.736

53.323  
48.976

Parameter	Value
Title	crf34h-0408
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	sgzb
Number of Scans	1080
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2016-04-08T2:58:44
Spectrometer Frequency	75.45
Spectral Width	1901.4
Lowest Frequency	-1743.8
Nucleus	13C
Acquired Size	2897
Spectral Size	65536



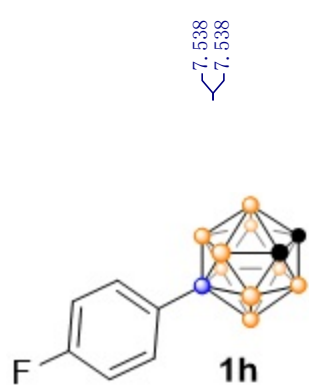
Supplementary Figure 26. <sup>13</sup>C NMR Spectrum of 1h.



Parameter	Value
Data File Name	G:/Users/Administrator/Desktop/b-cr-f34h/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dmx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aning-1g
Number of Scans	256
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	8.5000
Acquisition Time	0.512
Acquisition Date	2016-04-07 15:56:02
Modification Date	2016-04-07 09:02:00
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-16386.4
Nucleus	11B
Acquired Size	16384
Spectral Size	3288

Supplementary Figure 27.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of **1h**.





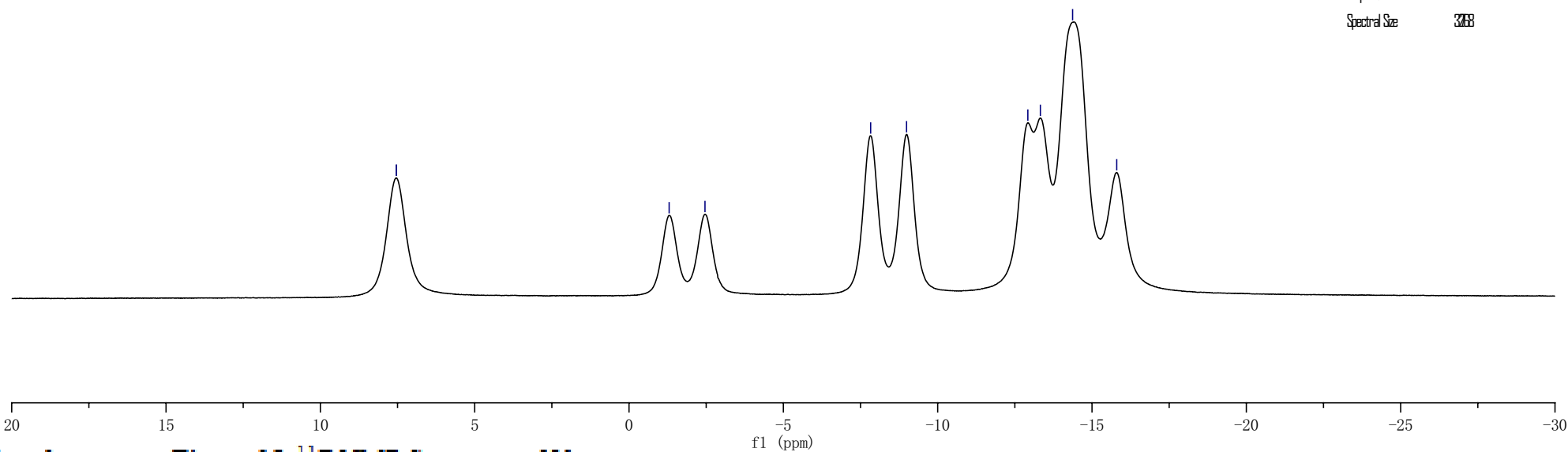
7.538  
7.538

-1.300  
-2.461

-7.828  
-8.992

-12.921  
-13.327  
-14.371  
-15.801

Parameter	Value
Data file Name	G:/Users/Administrator/Desktop/b-cr-f31h-coupling (1)/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	crx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring_1gy
Number of Scans	26
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	8.5000
Acquisition Time	0.512
Acquisition Date	2016-04-07 08:10
Modification Date	2016-04-07 09:14:00
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-16334.6
Nucleus	11B
Acquired Size	16334
Spectral Size	3268



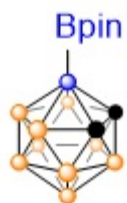
Supplementary Figure 28. <sup>11</sup>B NMR Spectrum of 1h.

crf-3-Bpin-CB-H-CDC13

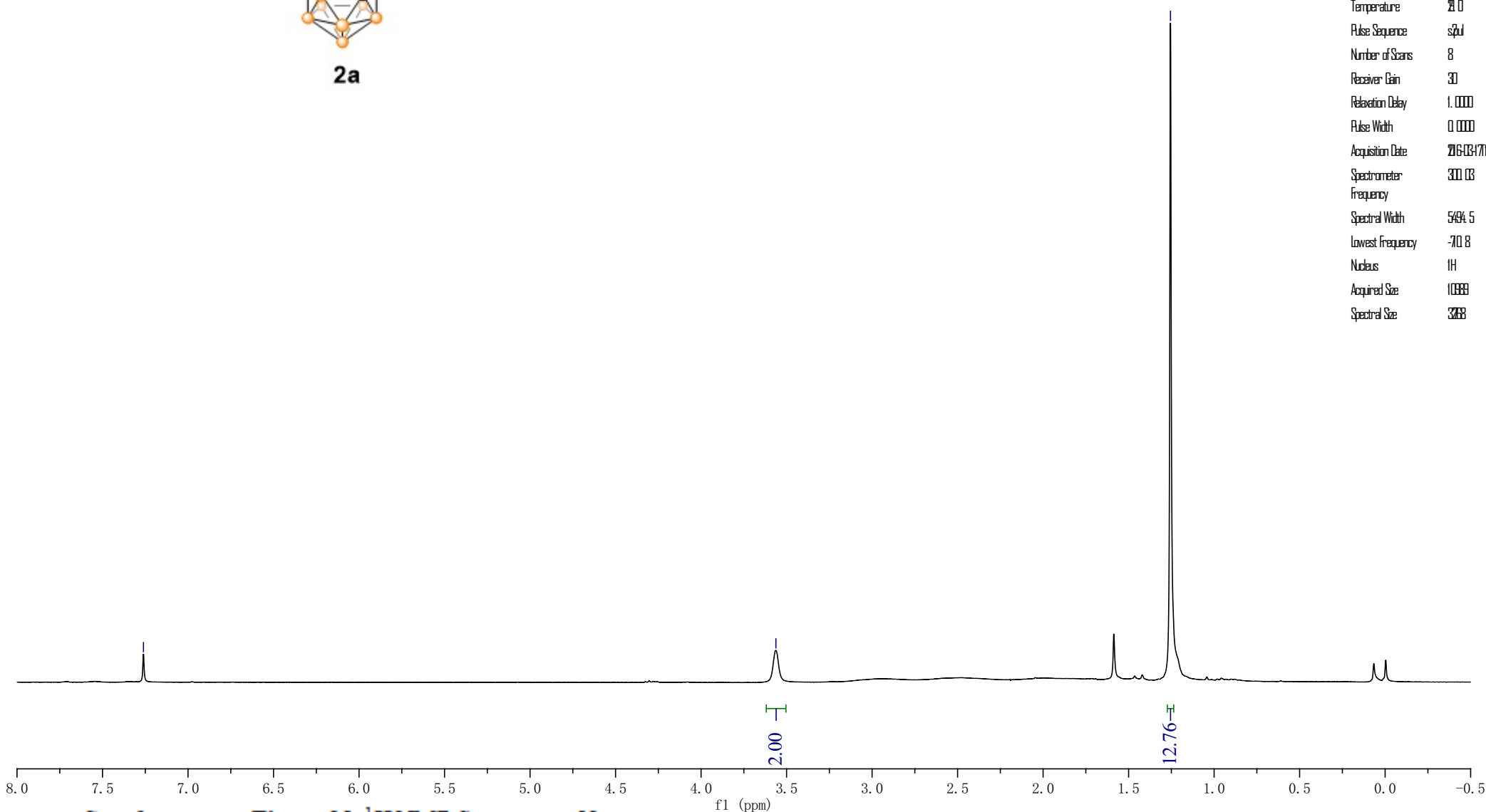
7.2

3.5

1.255



2a

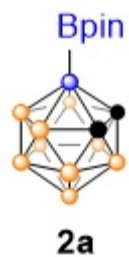


Parameter	Value
Title	crf3-Bpin-CB-H
Comment	STANDARD 1H OBSERVE
Origin	Varien
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	sgpul
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2016-03-17 19:51:47
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-70.8
Nucleus	1H
Acquired Size	10368
Spectral Size	3068

Supplementary Figure 29. <sup>1</sup>H NMR Spectrum of 2a.

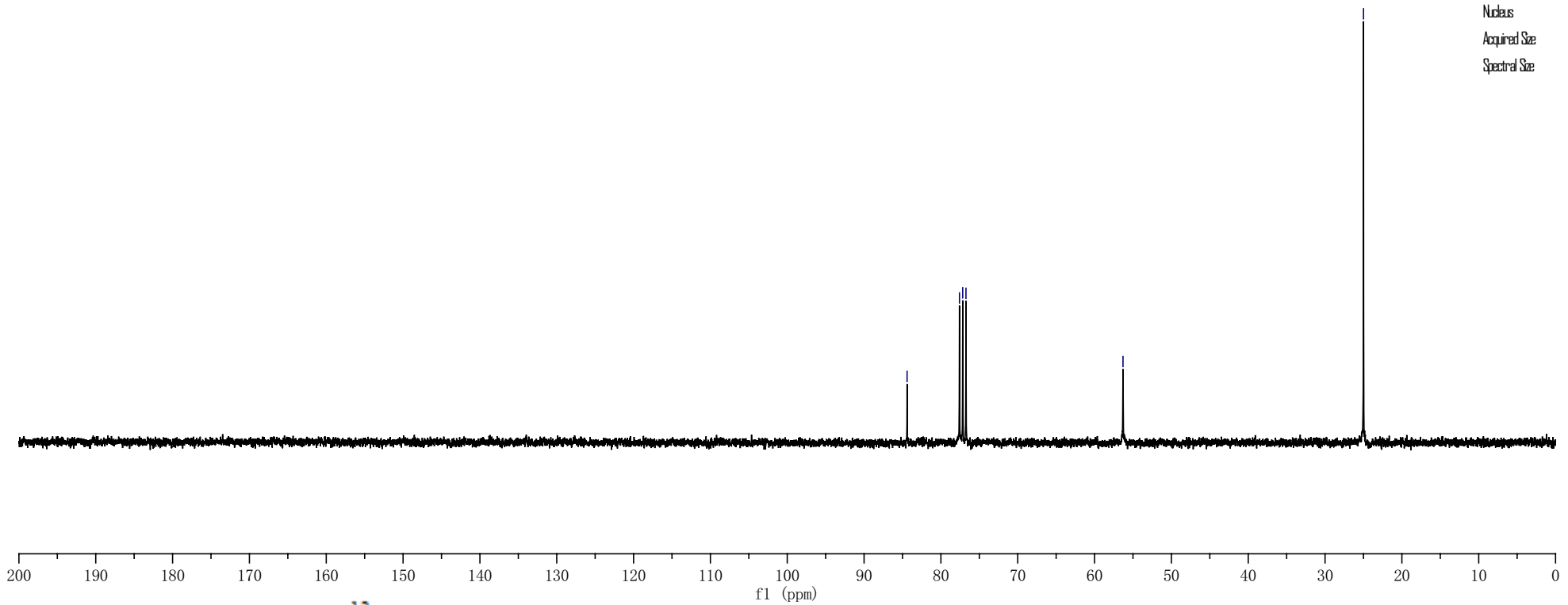
S50

crf-3-Bpin-CB-C-CDCl3



84.400  
77.583  
77.160  
76.736  
56.298  
24.995

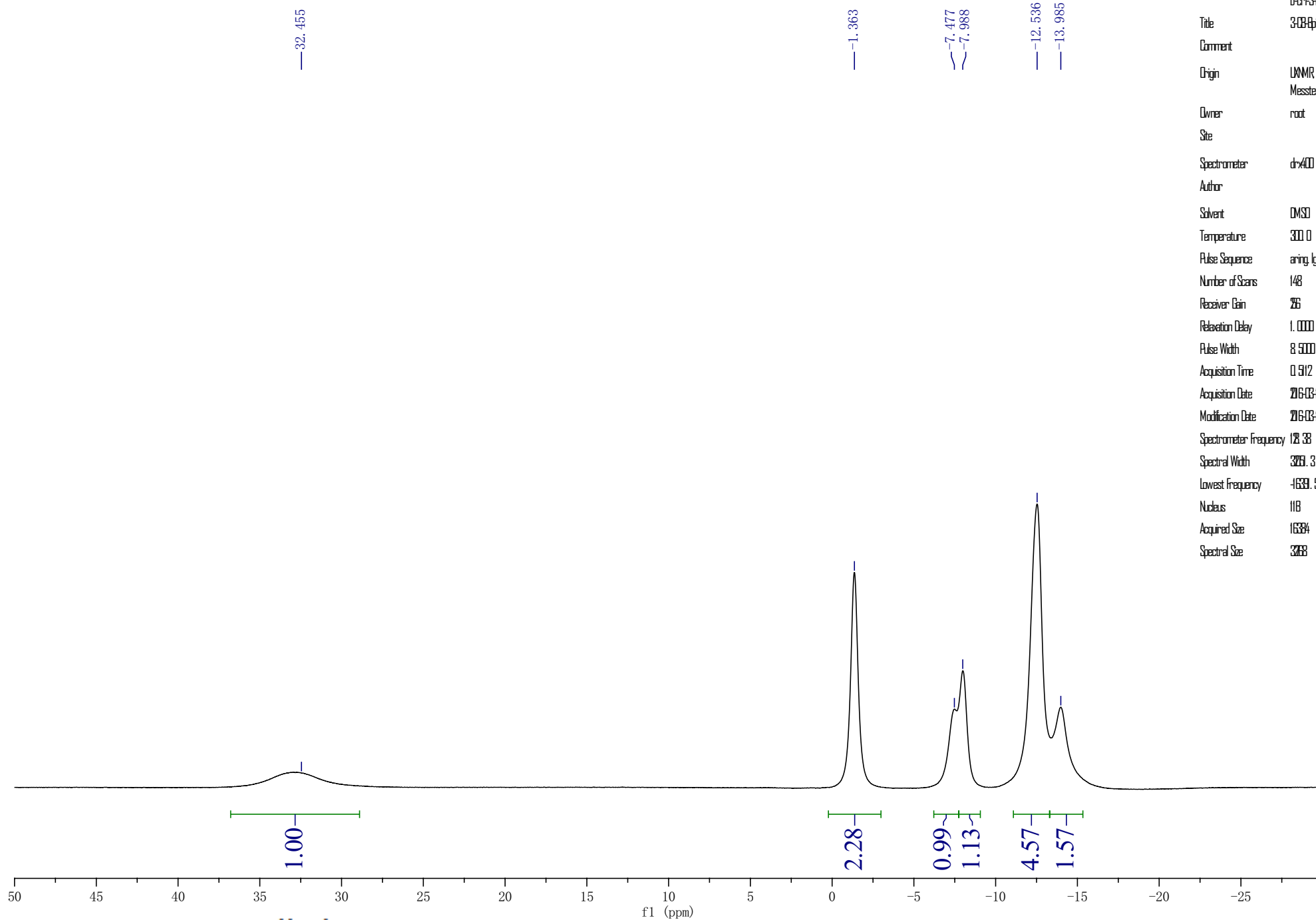
Parameter	Value
Title	crf-3-Bpin-CB-C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	zgpg30
Number of Scans	22
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2016-03-17 19:58:15
Spectrometer Frequency	76.45
Spectral Width	1901.4
Lowest Frequency	-1755.0
Nucleus	13C
Acquired Size	2937
Spectral Size	65536



Supplementary Figure 30. <sup>13</sup>C NMR Spectrum of 2a.

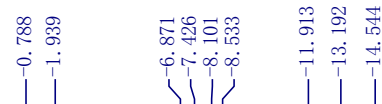
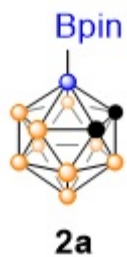
crf-3-Bpin-CB-B-decoupling-CDC13

Parameter	Value
Data File Name	E:/boralation/boralation/3-CB-Bpin/b-cr-f3-Bpin-cb/fid
Title	3-CB-Bpin
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring-1gy
Number of Scans	148
Receiver Gain	26
Relaxation Delay	1.0000
Pulse Width	8.5000
Acquisition Time	0.512
Acquisition Date	2016-03-18T16:02:19
Modification Date	2016-03-18T08:02:00
Spectrometer Frequency	128.38
Spectral Width	3269.3
Lowest Frequency	-1639.5
Nucleus	<sup>11</sup> B
Acquired Size	16384
Spectral Size	3288

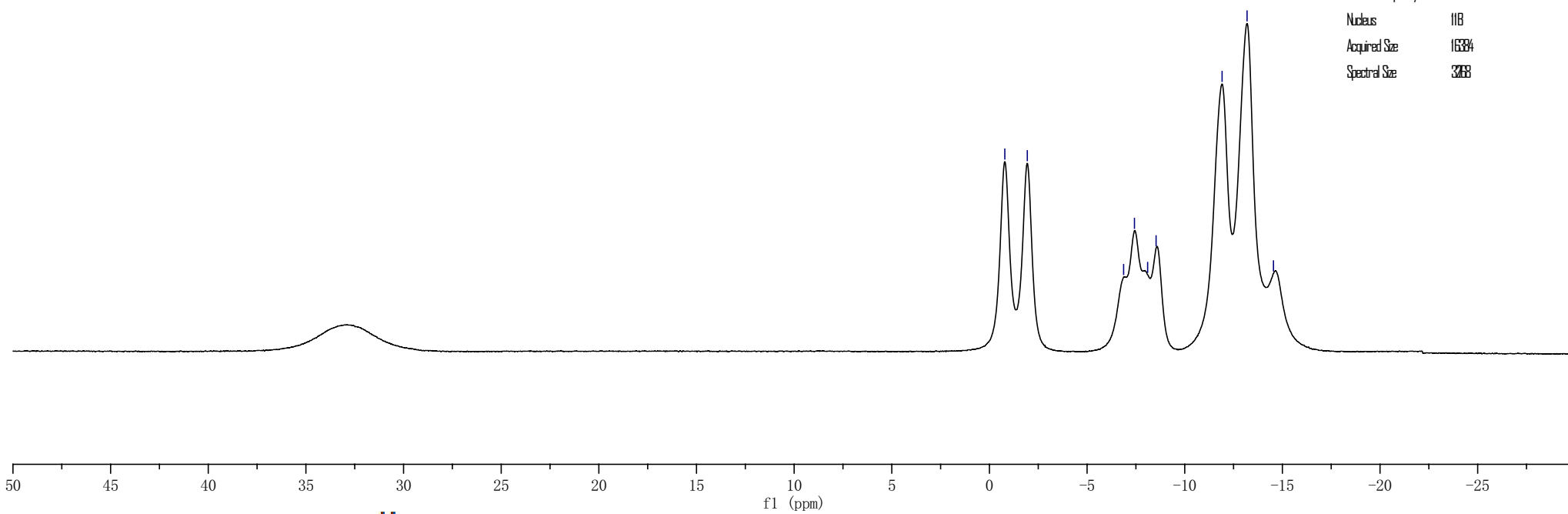


Supplementary Figure 31. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of 2a.

crf-3-Bpin-CB-B-coupling-CDC13



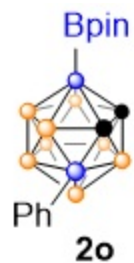
Parameter	Value
Data File Name	E:/boralation/boralation/3-CB-Bpin/b-cr3-bpin-cb-coupling/1d
Title	3-CB-Bpin
Comment	
Origin	LNMNR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	crx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.1gy
Number of Scans	128
Receiver Gain	286
Relaxation Delay	1.0000
Pulse Width	8.5000
Acquisition Time	0.512
Acquisition Date	2016-03-18 16:06:27
Modification Date	2016-03-18 16:06:00
Spectrometer Frequency	128.38
Spectral Width	3269.3
Lowest Frequency	-1639.5
Nucleus	11B
Acquired Size	16384
Spectral Size	3288



Supplementary Figure 32. <sup>11</sup>B NMR Spectrum of 2a.

crf-4-12-H-CDCl<sub>3</sub>

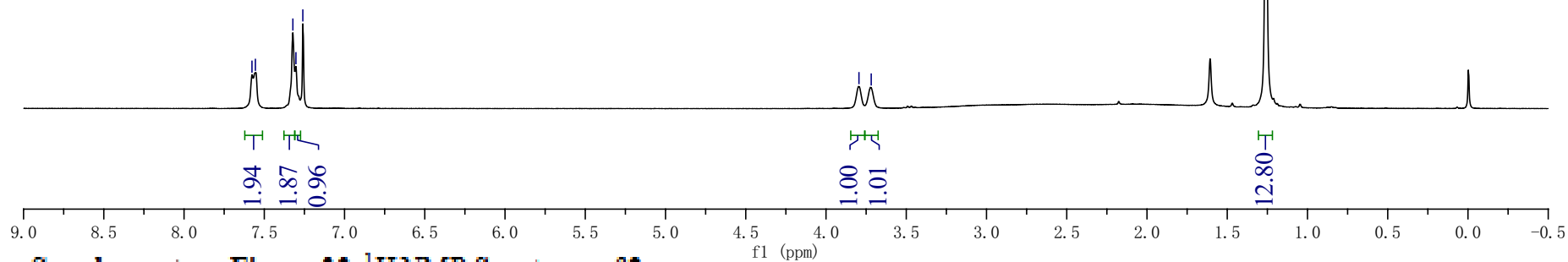
7.577  
7.555  
7.322  
7.303  
7.260



3.795  
3.718

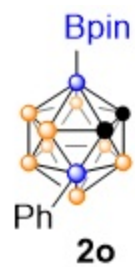
1.260

Parameter	Value
Title	crf-4-12H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	28.0
Pulse Sequence	sgpd
Number of Scans	12
Receiver Gain	30
Relaxation Delay	1.000
Pulse Width	0.000
Acquisition Date	2015-03-27 15:40:36
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-70.5
Nucleus	1H
Acquired Size	10376
Spectral Size	3268



Supplementary Figure 33. <sup>1</sup>H NMR Spectrum of 2o.

crf-4-12-C-CDCl<sub>3</sub>



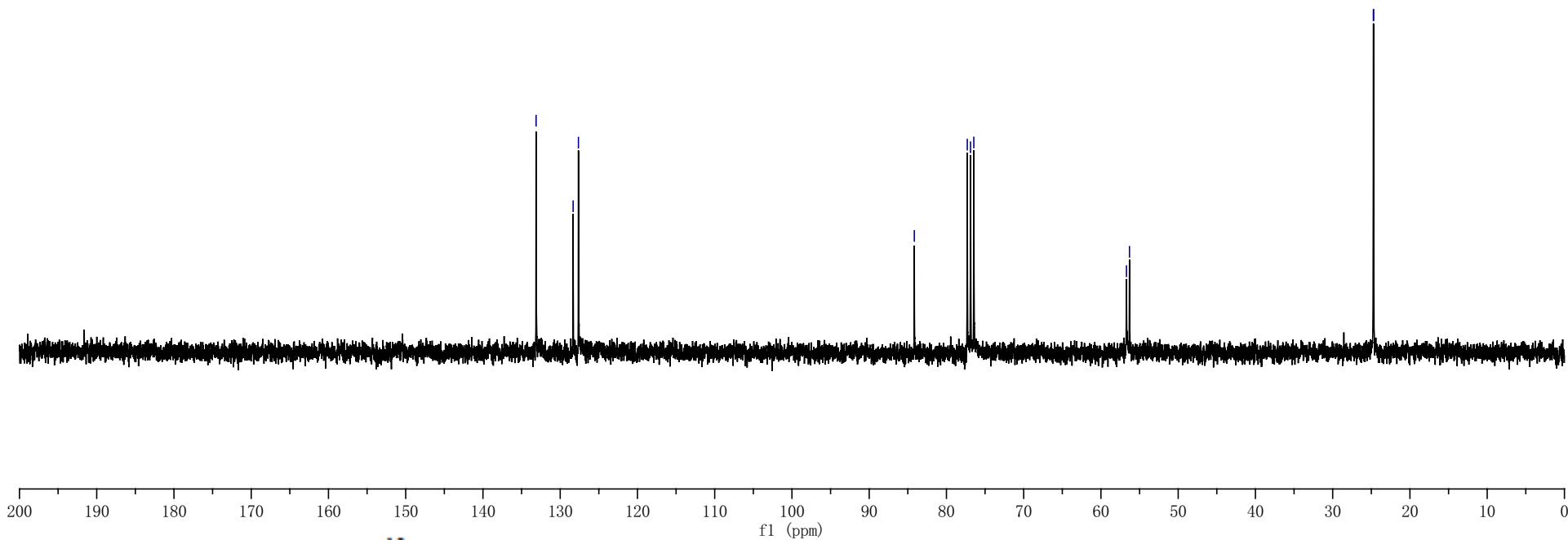
133.120  
128.327  
127.639

84.159  
77.303  
76.880  
76.456

56.698  
56.305

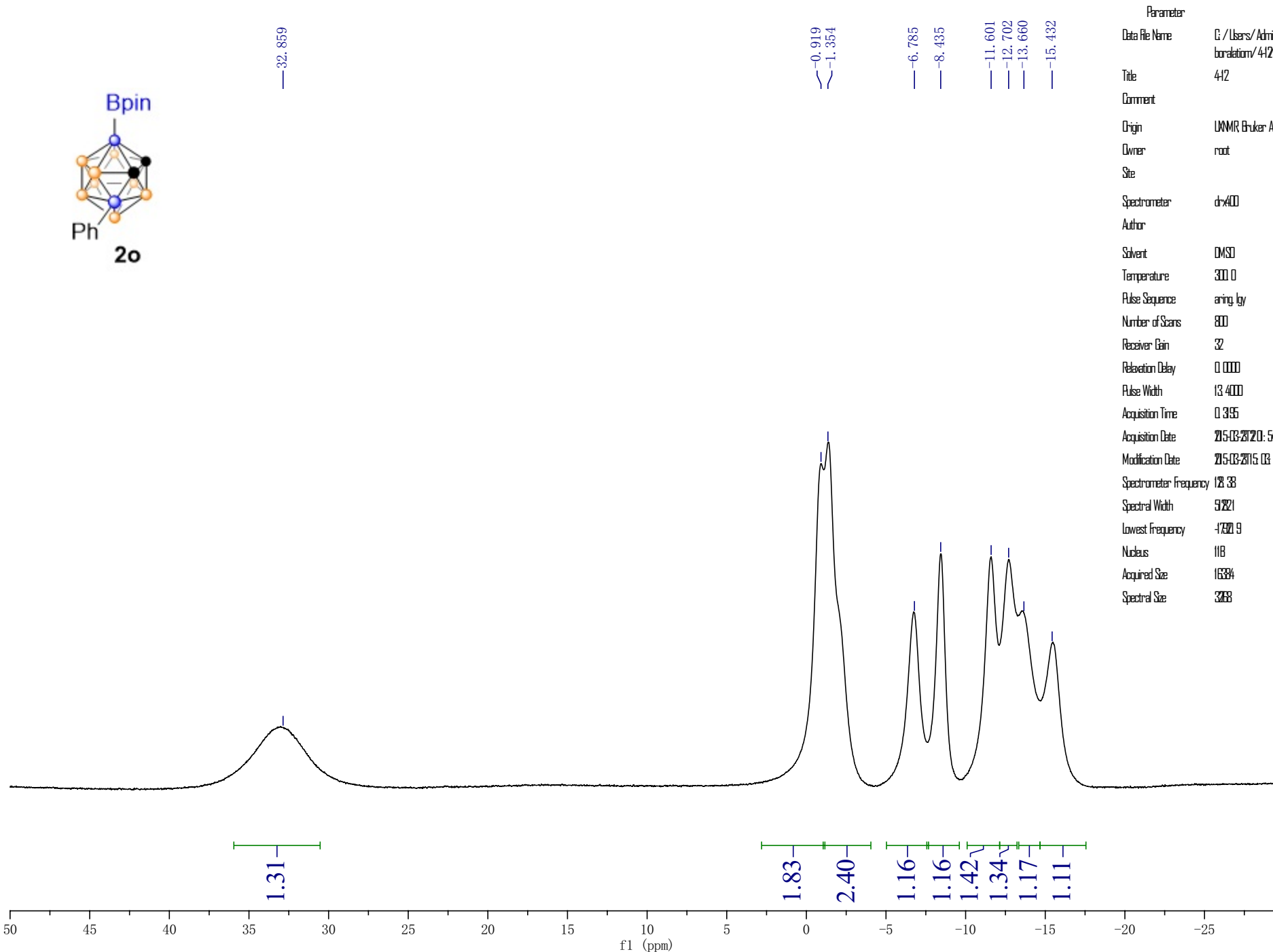
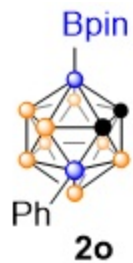
24.734  
24.699

Parameter	Value
Title	crf-4-12C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	21.0
Pulse Sequence	zgpg30
Number of Scans	52
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-03-27 16:06:26
Spectrometer Frequency	75.45
Spectral Width	1901.4
Lowest Frequency	-1766.4
Nucleus	13C
Acquired Size	2837
Spectral Size	65536



Supplementary Figure 34. <sup>13</sup>C NMR Spectrum of 2o.

crf-4-12-B-decoupling-CDCl<sub>3</sub>

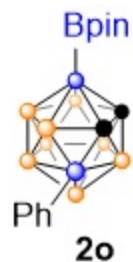


Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/work/送样NMR/borulation/412/crf-412.fid
Title	412
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1gy
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3155
Acquisition Date	2015-03-20 12:01:54
Modification Date	2015-03-20 15:03:00
Spectrometer Frequency	128.38
Spectral Width	59.821
Lowest Frequency	-17.8009
Nucleus	<sup>11</sup> B
Acquired Size	16384
Spectral Size	3288

Supplementary Figure 35. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of 2o.



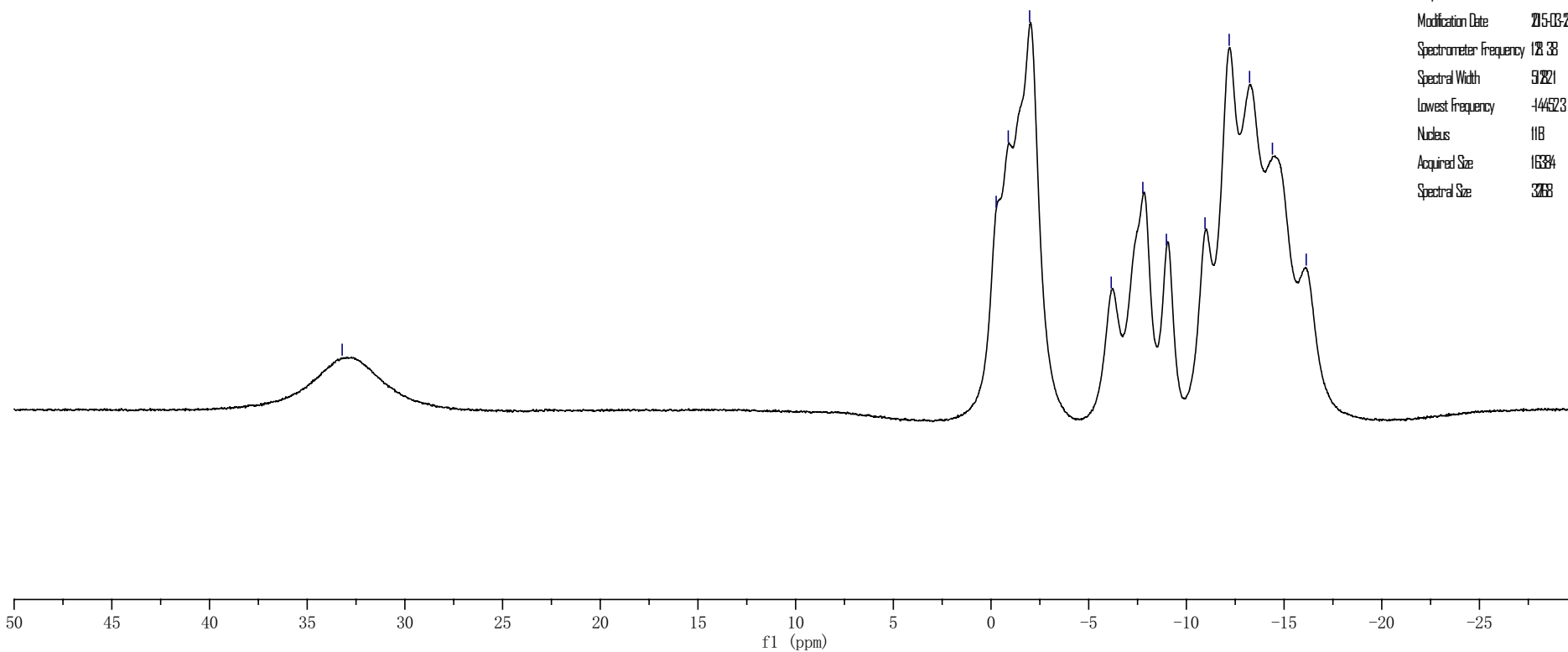
crf-4-12-B-coupling-CDCl<sub>3</sub>



33.209

-0.265  
-0.883  
-1.976  
-6.153  
-7.771  
-8.978  
-10.953  
-12.190  
-13.234  
-14.404  
-16.133

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/work/送样 NMR/borolation/412-b-cr-f412coupling/ld
Title	412
Comment	
Origin	UWMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dr400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1gy
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3155
Acquisition Date	2015-03-20 12:08:22
Modification Date	2015-03-20 15:08:00
Spectrometer Frequency	128.38
Spectral Width	51281
Lowest Frequency	-44452.3
Nucleus	11B
Acquired Size	16334
Spectral Size	3288



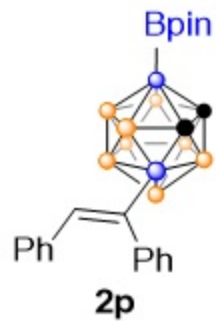
Supplementary Figure 36. <sup>11</sup>B NMR Spectrum of **2o**.

crf-3-83-H-CDCl<sub>3</sub>

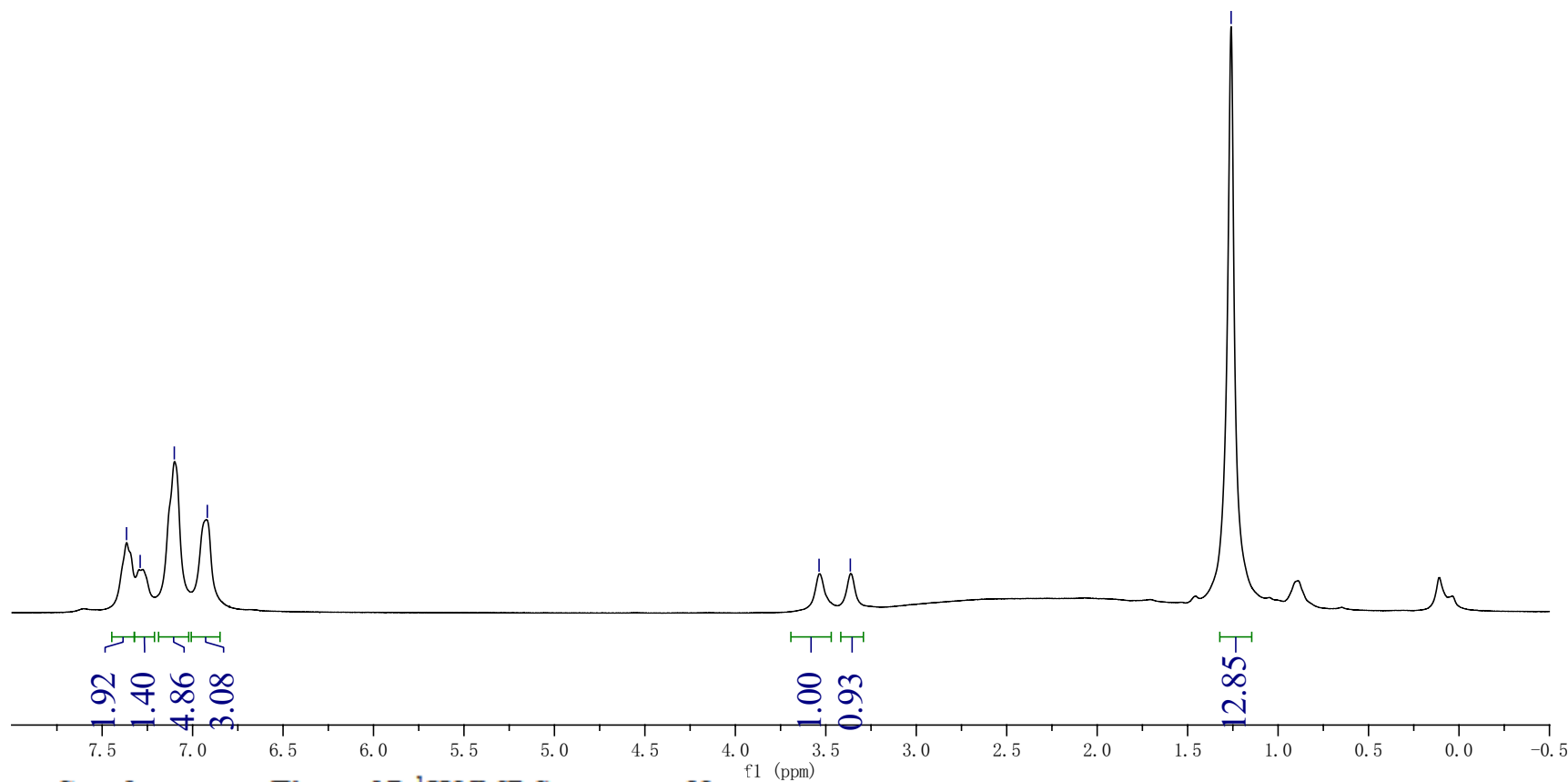
7.365  
7.290  
7.101  
6.919

3.537  
3.364

1.260

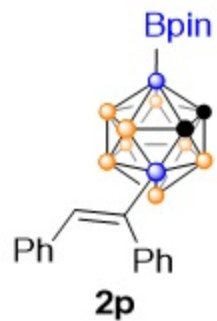


Parameter	Value
Title	crf-3-83-H-027
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	29.0
Pulse Sequence	sZul
Number of Scans	4
Receiver Gain	12
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-02-07 09:59:11
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-707.9
Nucleus	<sup>1</sup> H
Acquired Size	10376
Spectral Size	3268



Supplementary Figure 37. <sup>1</sup>H NMR Spectrum of **2p**.

crf-3-83-C-CDCl<sub>3</sub>



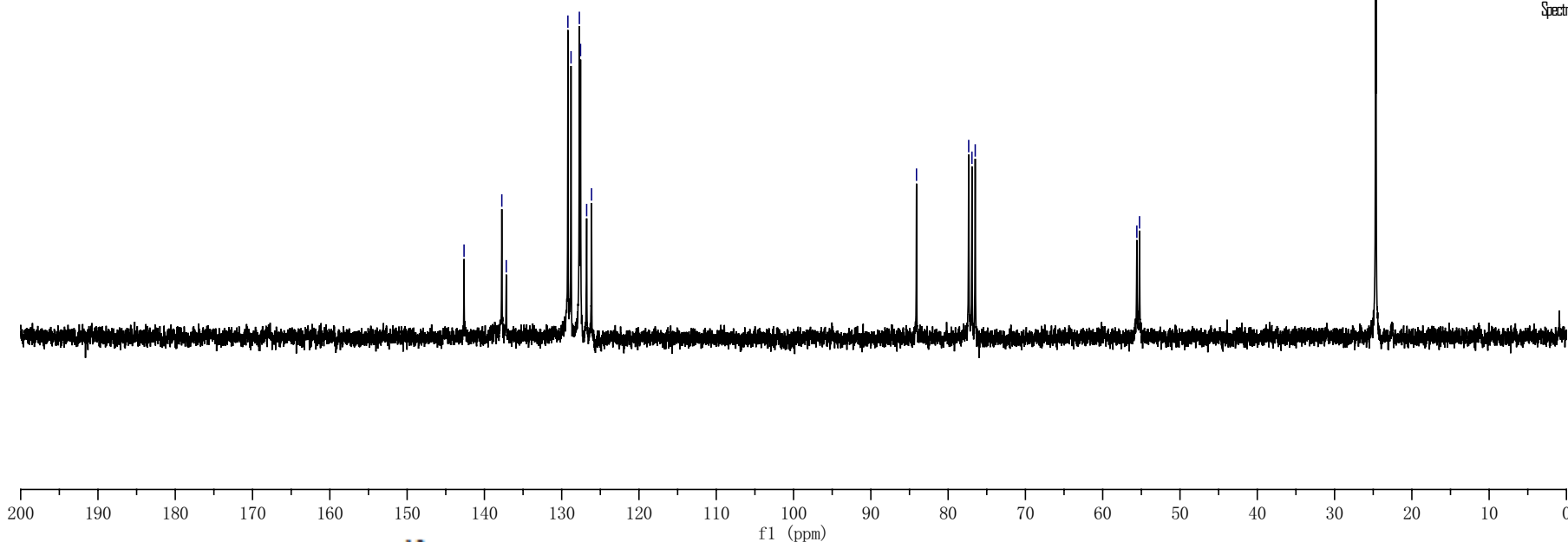
142.635  
137.746  
137.171  
129.196  
128.791  
127.712  
127.560  
126.769  
126.137

84.093  
77.340  
76.918  
76.495

55.582  
55.235

24.696  
24.633

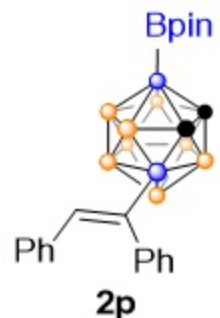
Parameter	Value
Title	crf-3-83-C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	21.0
Pulse Sequence	zg30
Number of Scans	120
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-02-07 09:59:55
Spectrometer Frequency	75.45
Spectral Width	19311.4
Lowest Frequency	4766.4
Nucleus	13C
Acquired Size	2617
Spectral Size	65536



Supplementary Figure 38. <sup>13</sup>C NMR Spectrum of **2p**.

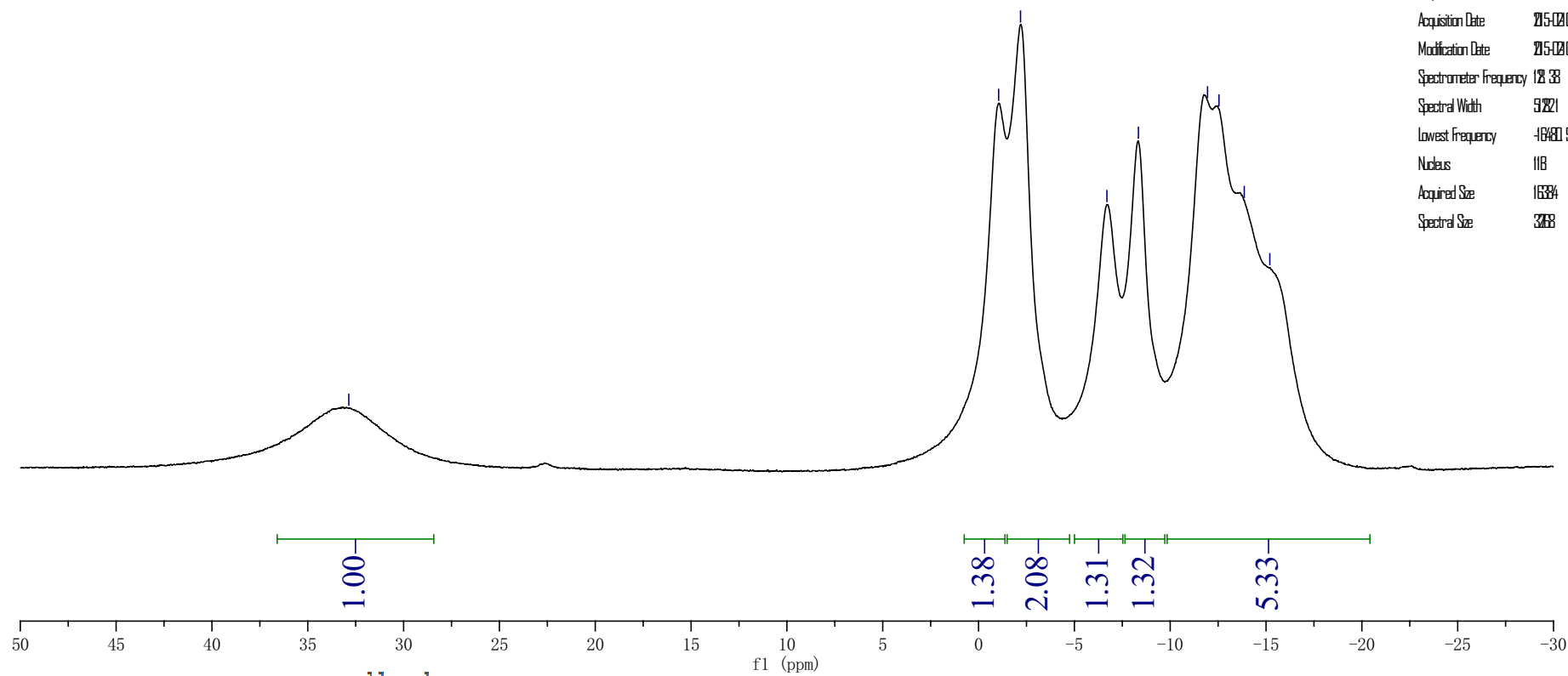
crf-3-83-B-CDCl<sub>3</sub>-decoupling

32.860



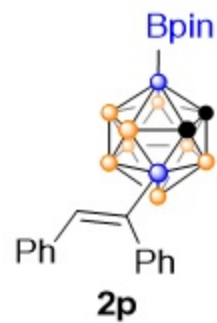
1.048  
2.190  
6.698  
8.341  
11.948  
12.544  
13.865  
15.197

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr3-83/ld
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	cr400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	zing_1g
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-02-01 19:05:10
Modification Date	2015-02-01 12:08:00
Spectrometer Frequency	128.38
Spectral Width	51281
Lowest Frequency	-16480.9
Nucleus	11B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 39. <sup>11</sup>B {<sup>1</sup>H} NMR Spectrum of **2p**.

32.757



-1.721

-6.213

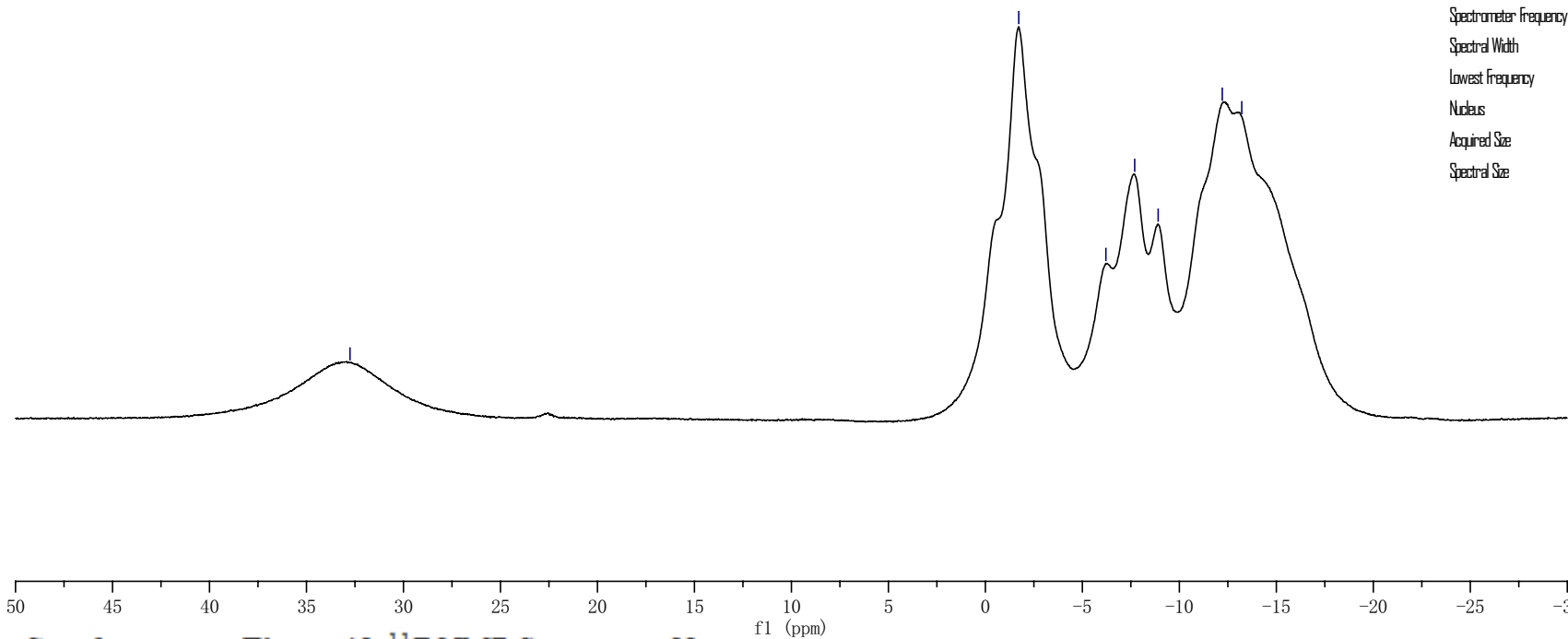
-7.697

-8.907

-12.212

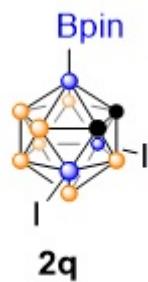
-13.216

Parameter	Value
Data File Name	E:/Users/Administrator/Desktop/b-crf3-83-withoutdecoupling/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1gy
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3155
Acquisition Date	2015-02-07 19:14:18
Modification Date	2015-02-07 12:16:00
Spectrometer Frequency	128.38
Spectral Width	51221
Lowest Frequency	-16480.9
Nucleus	11B
Acquired Size	16384
Spectral Size	32768



Supplementary Figure 40. <sup>11</sup>B NMR Spectrum of **2p**.

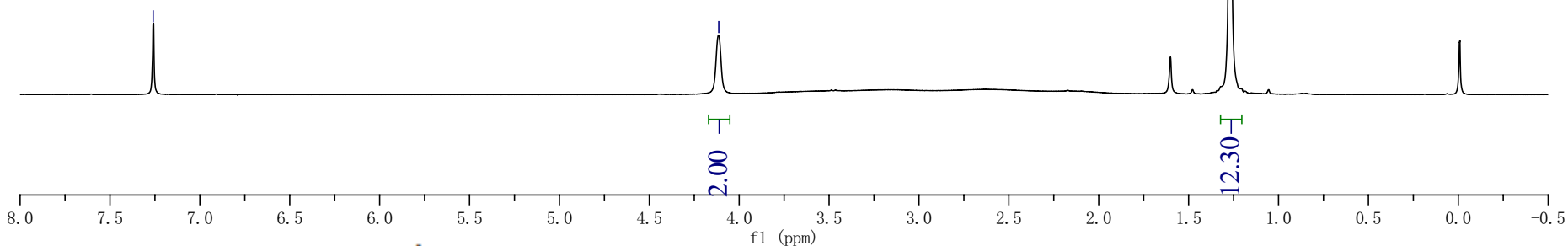
crf-3-95-H -CDCl<sub>3</sub>



7.260

4.114

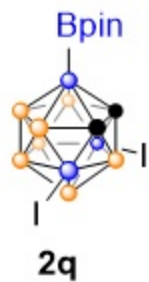
1.268



Parameter	Value
Title	crf-3-95-h
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	onc
Solvent	CDCl <sub>3</sub>
Temperature	29.0
Pulse Sequence	sgpu
Number of Scans	12
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-03-07 12:49:20
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-70.2
Nucleus	<sup>1</sup> H
Acquired Size	10976
Spectral Size	3068

Supplementary Figure 41. <sup>1</sup>H NMR Spectrum of **2q**.

crf-3-95-C-CDCl<sub>3</sub>



84.672

77.319

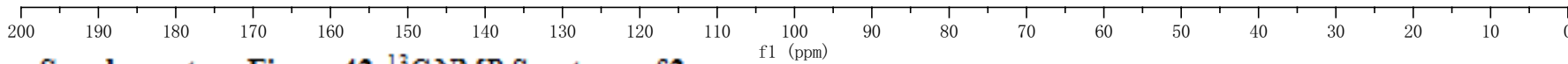
76.898

76.473

60.314

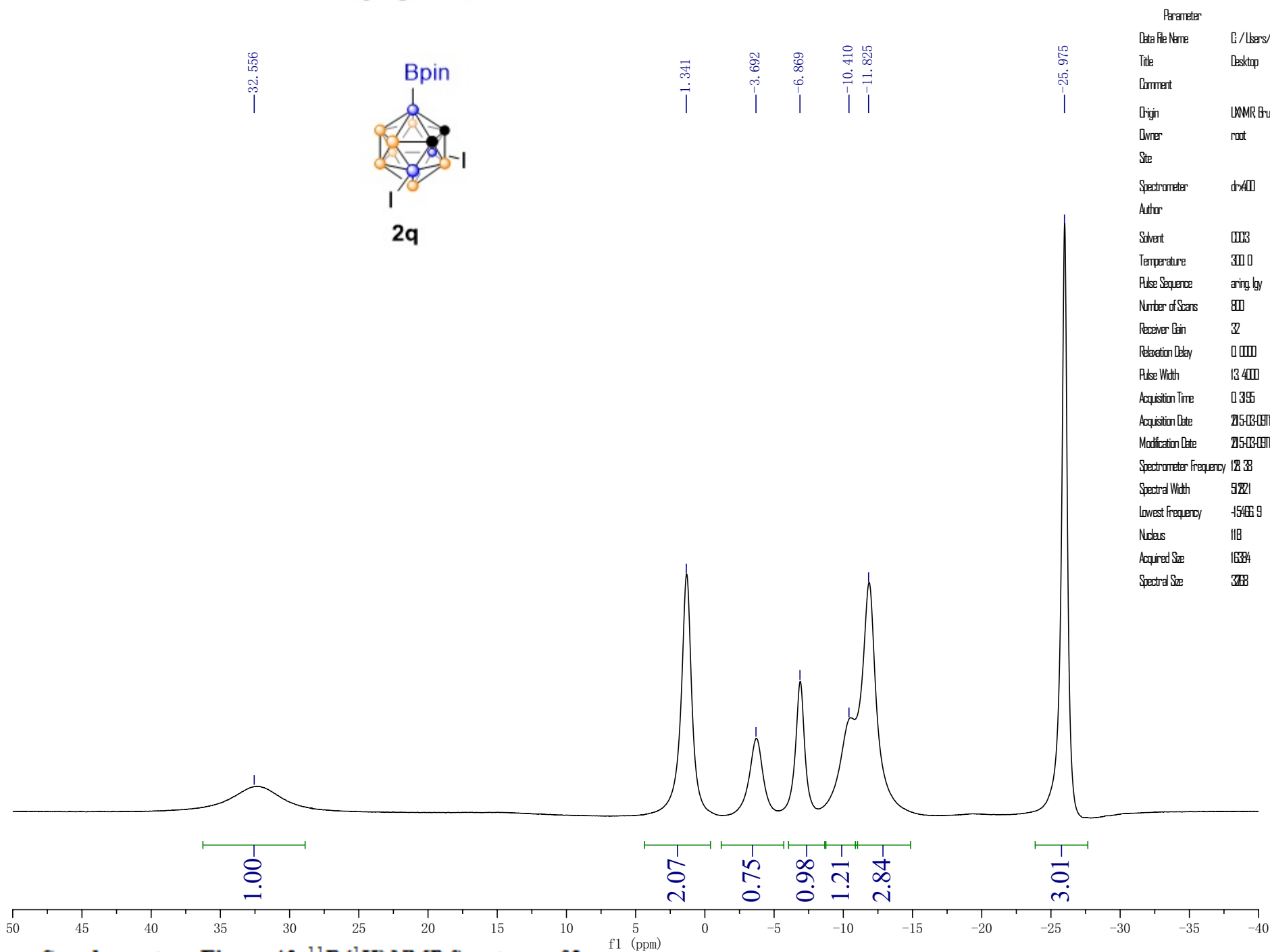
24.756

Parameter	Value
Title	crf-3-95-C
Comment	13C OBSRV
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	21.0
Pulse Sequence	sZul
Number of Scans	52
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-03-07 21:32:52
Spectrometer Frequency	75.45
Spectral Width	1901.4
Lowest Frequency	-4766.4
Nucleus	13C
Acquired Size	2817
Spectral Size	65536



Supplementary Figure 42. <sup>13</sup>C NMR Spectrum of **2q**.

crf-3-95-B-decoupling-CDCl<sub>3</sub>



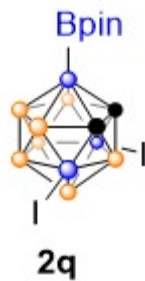
Parameter	Value
Data File Name	G:/Users/Administrator/Desktop/b-crf3-95/td
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	CDCl <sub>3</sub>
Temperature	300.0
Pulse Sequence	aring.1g
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-03-09 04: 3
Modification Date	2015-03-09 04: 00
Spectrometer Frequency	128.38
Spectral Width	91221
Lowest Frequency	-15466.9
Nucleus	<sup>11</sup> B
Acquired Size	16384
Spectral Size	3268

Supplementary Figure 43. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of **2q**.



crf-3-95-B-coupling-CDCl<sub>3</sub>

— 32.258



— 1.862  
— 0.699

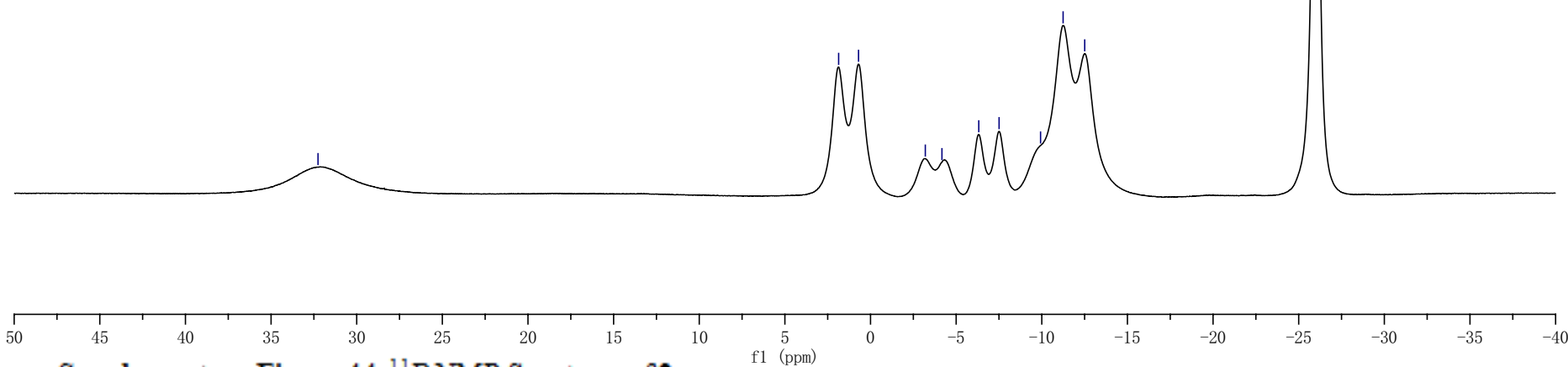
— 3.199  
— 4.170

— 6.320  
— 7.507

— 9.928  
— 11.245  
— 12.506

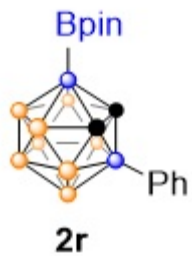
— 25.995

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr3-95-coupling/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	drx400
Author	
Solvent	CDCl <sub>3</sub>
Temperature	300.0
Pulse Sequence	aring1g
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-03-09 16:08:28
Modification Date	2015-03-09 16:08:00
Spectrometer Frequency	128.38
Spectral Width	51221
Lowest Frequency	-15466.9
Nucleus	11B
Acquired Size	16384
Spectral Size	3068



Supplementary Figure 44. <sup>11</sup>B NMR Spectrum of **2q**.

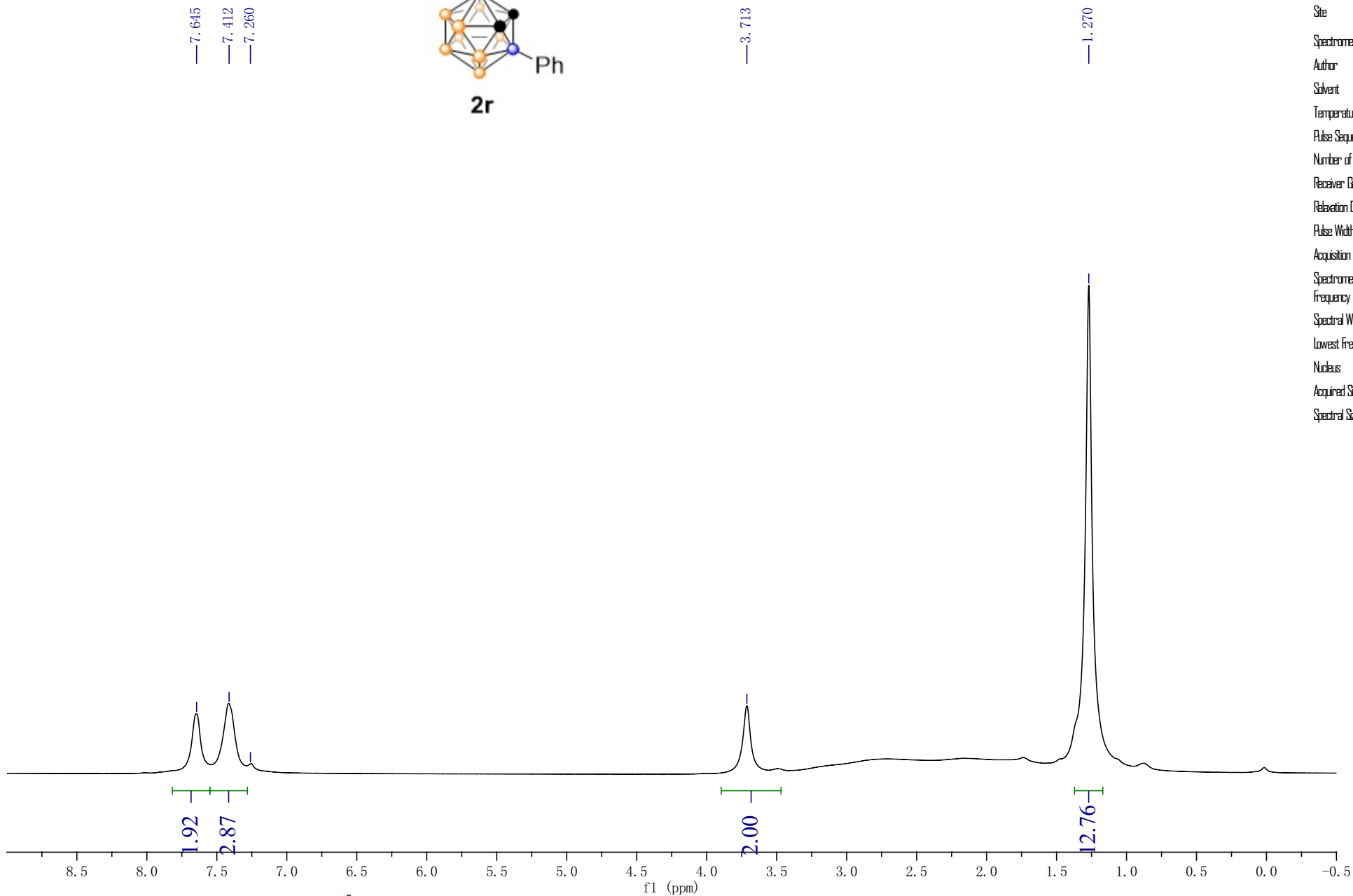
crf-3-64-H-CDCl<sub>3</sub>



7.645  
7.412  
7.260

3.713

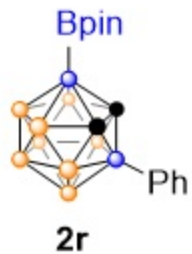
1.270



Parameter	Value
Title	crf3-64-H
Comment	STANDARD 1H CDSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	onc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	sgul
Number of Scans	12
Receiver Gain	16
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-01-28 12:03:48
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-708.1
Nucleus	1H
Acquired Size	10376
Spectral Size	3268

Supplementary Figure 45. <sup>1</sup>H NMR Spectrum of **2r**.

crf-3-64-C-CDCl<sub>3</sub>



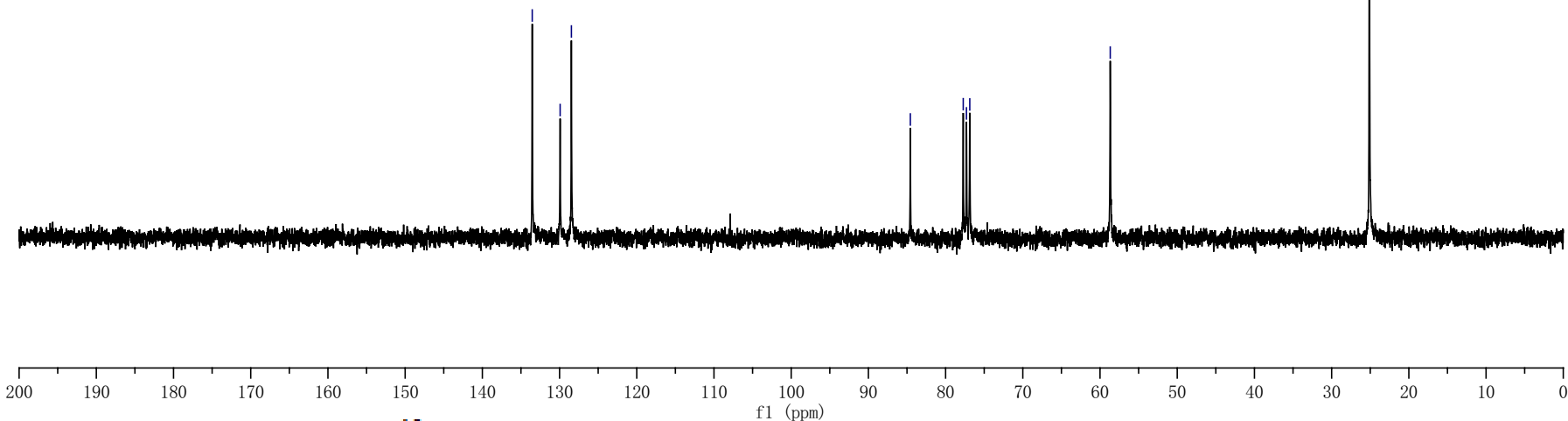
133.540  
129.926  
128.466

84.567  
77.716  
77.300  
76.870

58.676

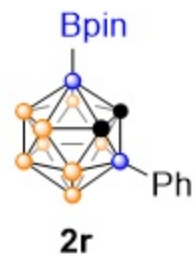
25.113

Parameter	Value
Title	crf-3-64-C
Comment	13C OBSRV
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	onc
Solvent	CDCl <sub>3</sub>
Temperature	29.0
Pulse Sequence	sgpul
Number of Scans	120
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-01-27 10:50
Spectrometer Frequency	75.45
Spectral Width	18897.0
Lowest Frequency	-162.8
Nucleus	13C
Acquired Size	2895
Spectral Size	65536



Supplementary Figure 46. <sup>13</sup>C NMR Spectrum of 2r.

crf-3-64-B- decoupling -CDCl<sub>3</sub>



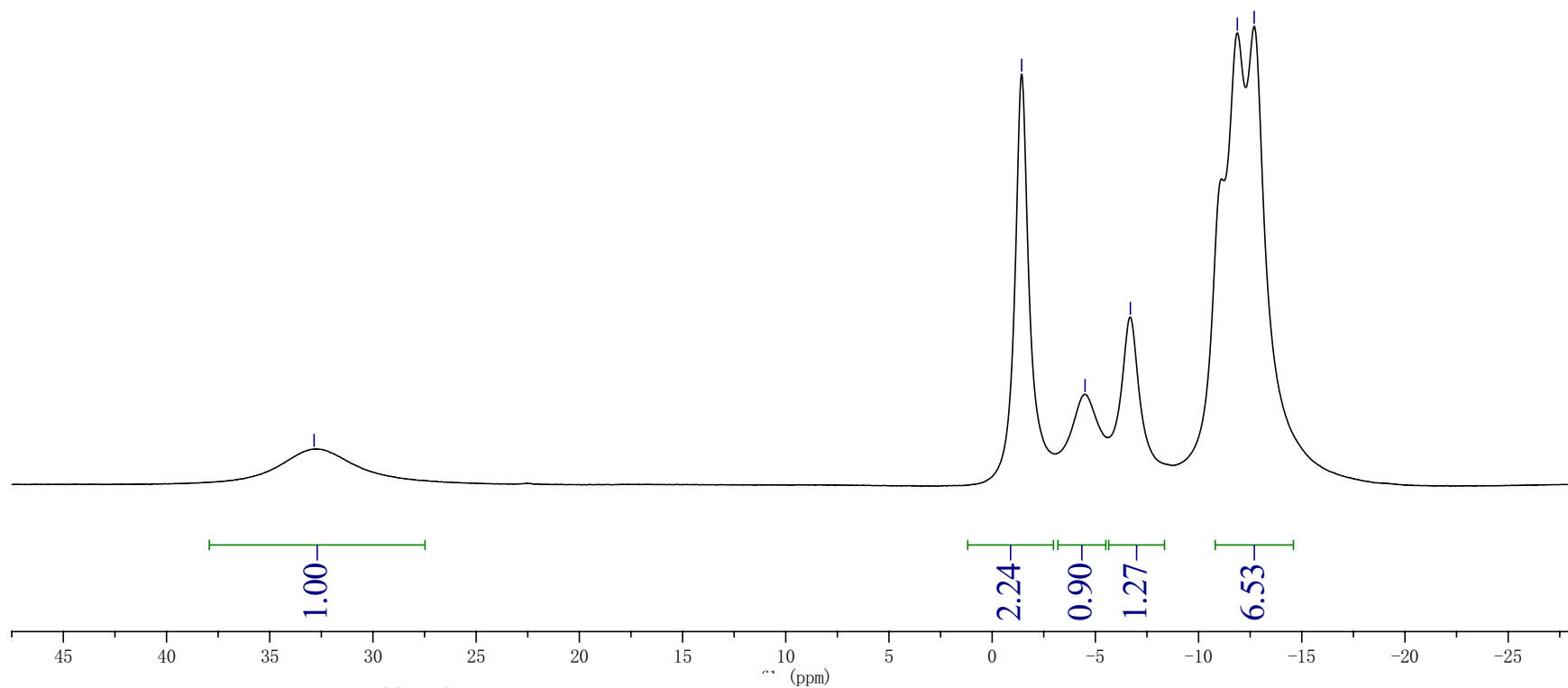
—32.849

—1.429

—4.501

—6.696

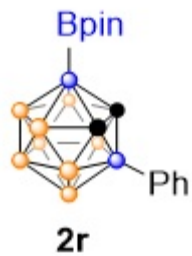
—11.878  
—12.695



Parameter	Value
Data File Name	G:/Users/Administrator/Desktop/b-crf3-64/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	chr400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.ty
Number of Scans	168
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-01-26 18:03:14
Modification Date	2015-01-26 11:11:00
Spectrometer Frequency	128.38
Spectral Width	59221
Lowest Frequency	-14649.0
Nucleus	11B
Acquired Size	16394
Spectral Size	3268

Supplementary Figure 47. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of **2r**.

— 32.854



— 0.814

— 1.976

— 4.568

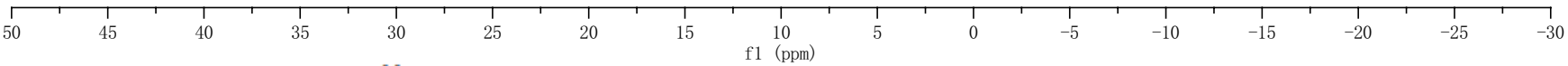
— 6.099

— 7.206

— 12.145

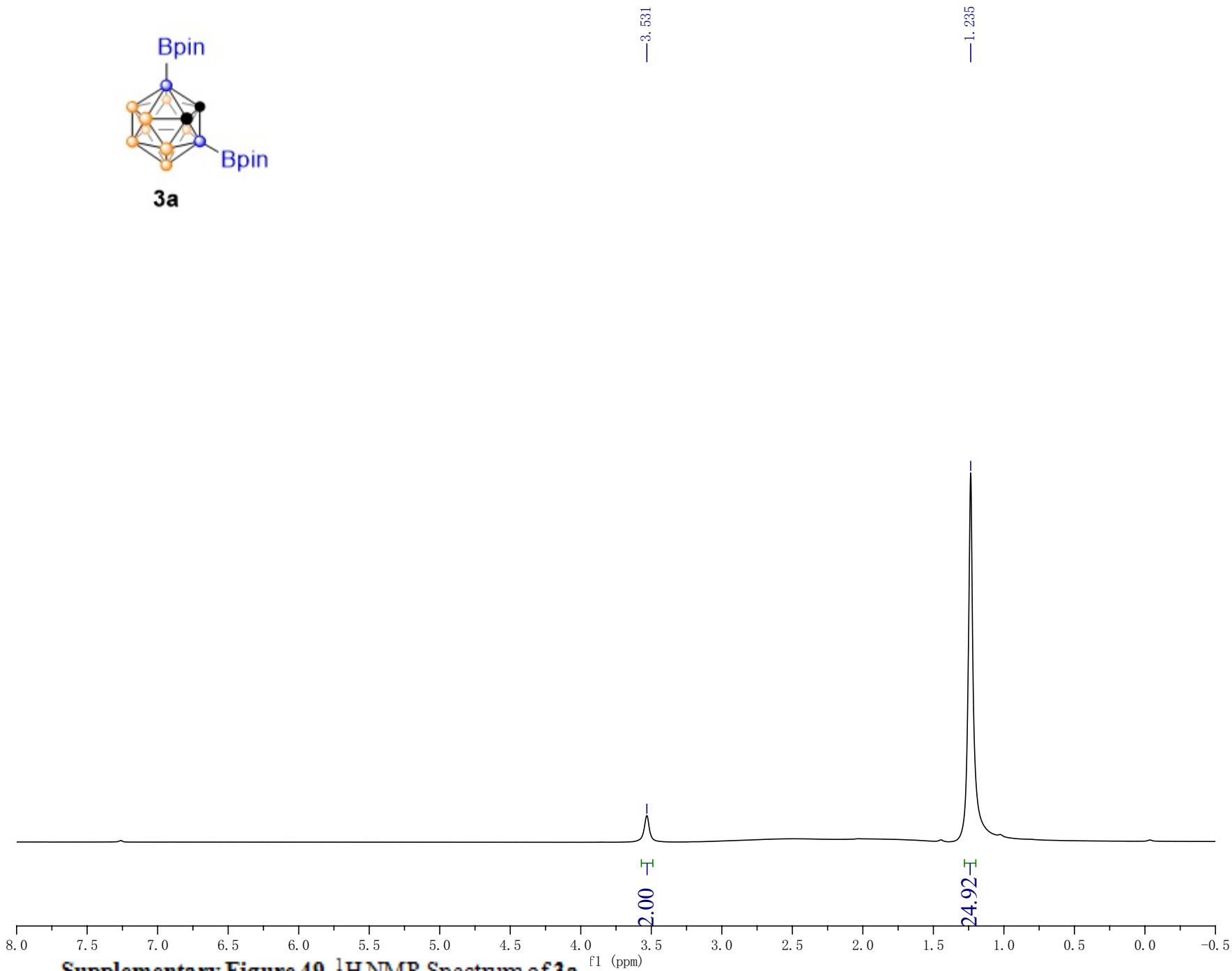
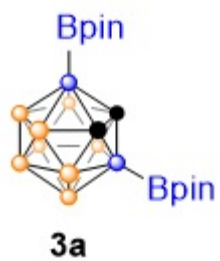
— 13.214

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr-3-64-withoutdecoupling/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	chr400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.tgy
Number of Scans	1115
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-01-26T18:17:02
Modification Date	2015-01-26T11:17:00
Spectrometer Frequency	128.38
Spectral Width	51221
Lowest Frequency	-44649.0
Nucleus	<sup>11</sup> B
Acquired Size	16394
Spectral Size	3268



Supplementary Figure 48. <sup>11</sup>B NMR Spectrum of **2r**.

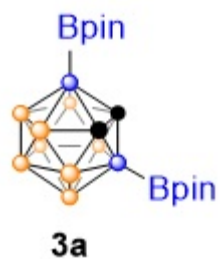
crf-CB-Bpin<sub>2</sub>-H-CDCl<sub>3</sub>



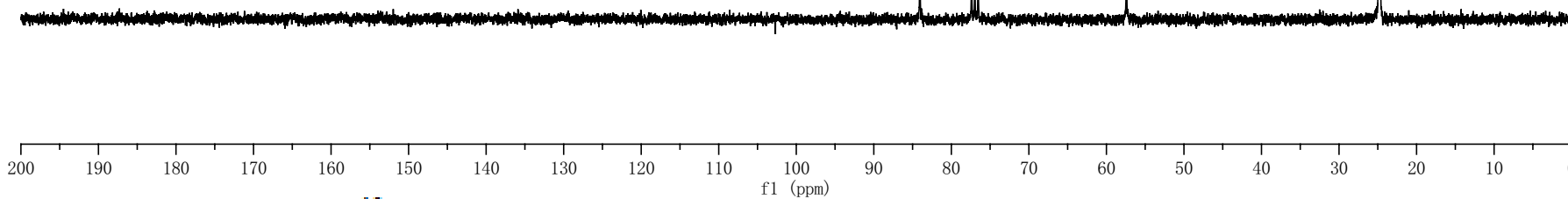
Parameter	Value
Title	crfCB@pin2
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	29.0
Pulse Sequence	sZul
Number of Scans	21
Receiver Gain	10
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-17 15:28:22
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-707.4
Nucleus	1H
Acquired Size	10976
Spectral Size	3268

Supplementary Figure 49. <sup>1</sup>H NMR Spectrum of 3a.

crf-CB-Bpin<sub>2</sub>-C-CDCl<sub>3</sub>

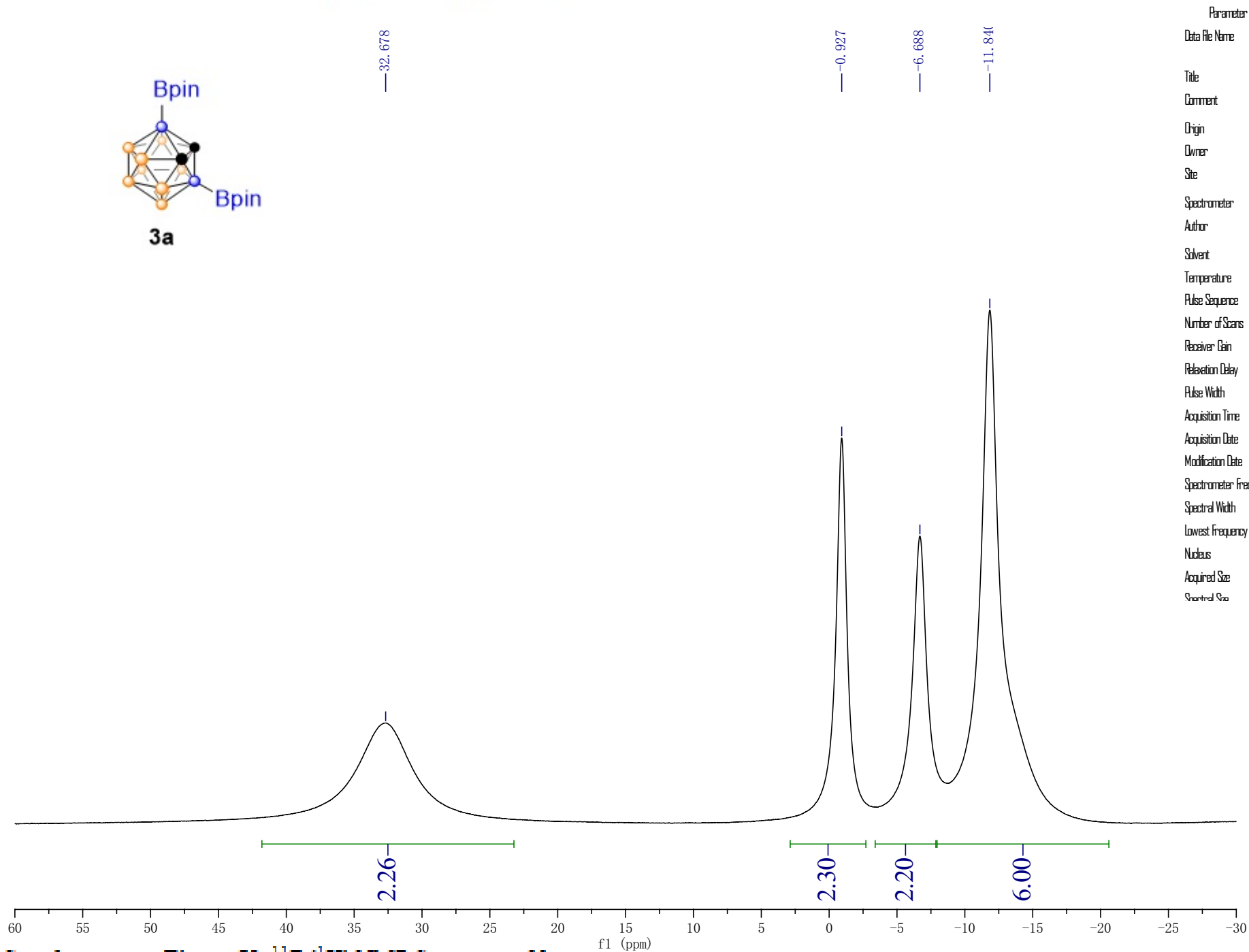
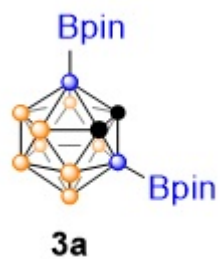


Parameter	Value
Title	crf-CB-Bpin2C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	sgpl
Number of Scans	40
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-17 15:24:47
Spectrometer Frequency	75.45
Spectral Width	18887.0
Lowest Frequency	-1681.2
Nucleus	13C
Acquired Size	3006
Spectral Size	65536



Supplementary Figure 50. <sup>13</sup>C NMR Spectrum of 3a.

crf-CB-Bpin<sub>2</sub>-B-decoupling-CDCl<sub>3</sub>



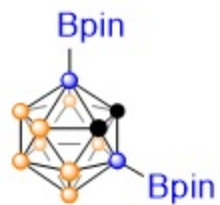
Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/work/送样NMR/b-cr/crb-bpin-2/1d
Title	送样NMR
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	CDCl <sub>3</sub>
Temperature	300.0
Pulse Sequence	aring.tgy
Number of Scans	739
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3155
Acquisition Date	215-04-30 12:00:19
Modification Date	215-04-30 13:01:00
Spectrometer Frequency	128.38
Spectral Width	9.2821
Lowest Frequency	-17849.0
Nucleus	<sup>11</sup> B
Acquired Size	16384
Scanned Size	2048

Supplementary Figure 51. <sup>11</sup>B {<sup>1</sup>H} NMR Spectrum of 3a.



crf-CB-Bpin<sub>2</sub>-B-coupling-CDCl<sub>3</sub>

33.073



3a

-0.009

-1.188

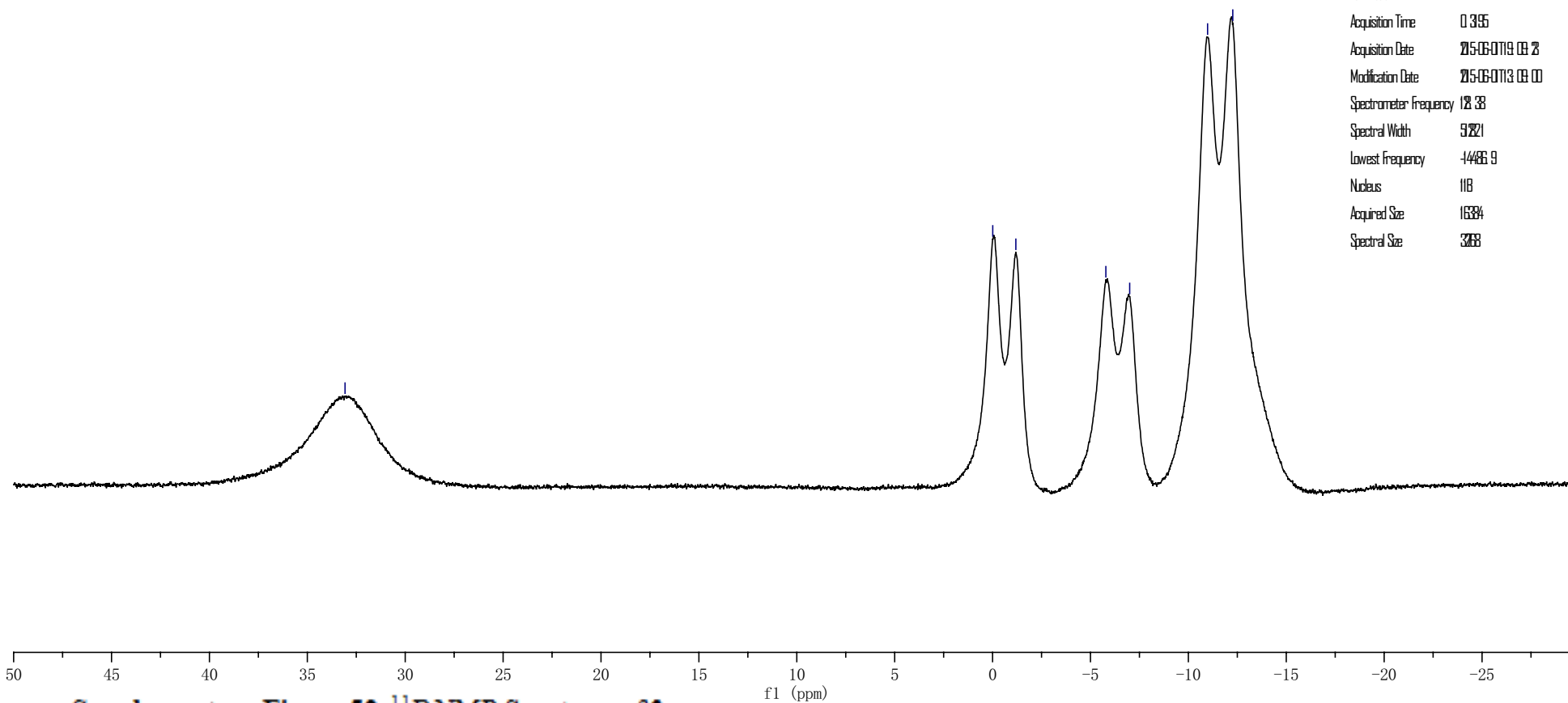
-5.785

-7.003

-10.981

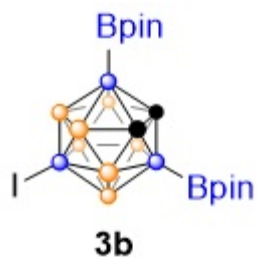
-12.268

Parameter	Value
Data File Name	G:/Users/Administrator/Desktop/work/送样NMR/loralatom/cb-Bpin2/b-crf-cb-bpin2coupling/fid
Title	cb-Bpin2
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring 1gy
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-06-01 19:08:28
Modification Date	2015-06-01 13:08:00
Spectrometer Frequency	128.38
Spectral Width	51.821
Lowest Frequency	-14486.9
Nucleus	<sup>11</sup> B
Acquired Size	16384
Spectral Size	3288



Supplementary Figure 52. <sup>11</sup>B NMR Spectrum of 3a.

crf-3-85-H-CDCl<sub>3</sub>

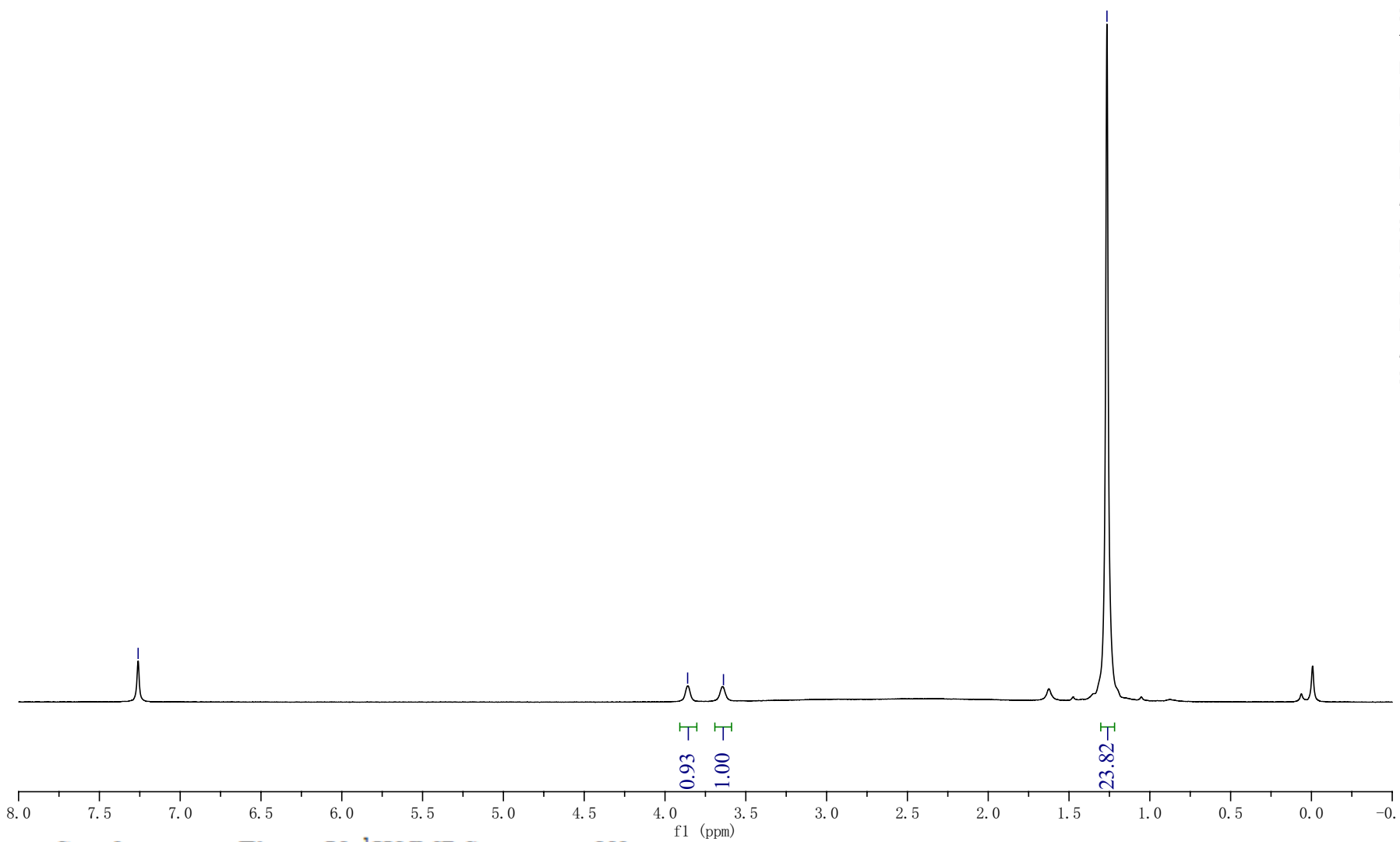


7.260

3.860

3.638

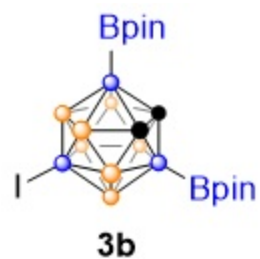
1.265



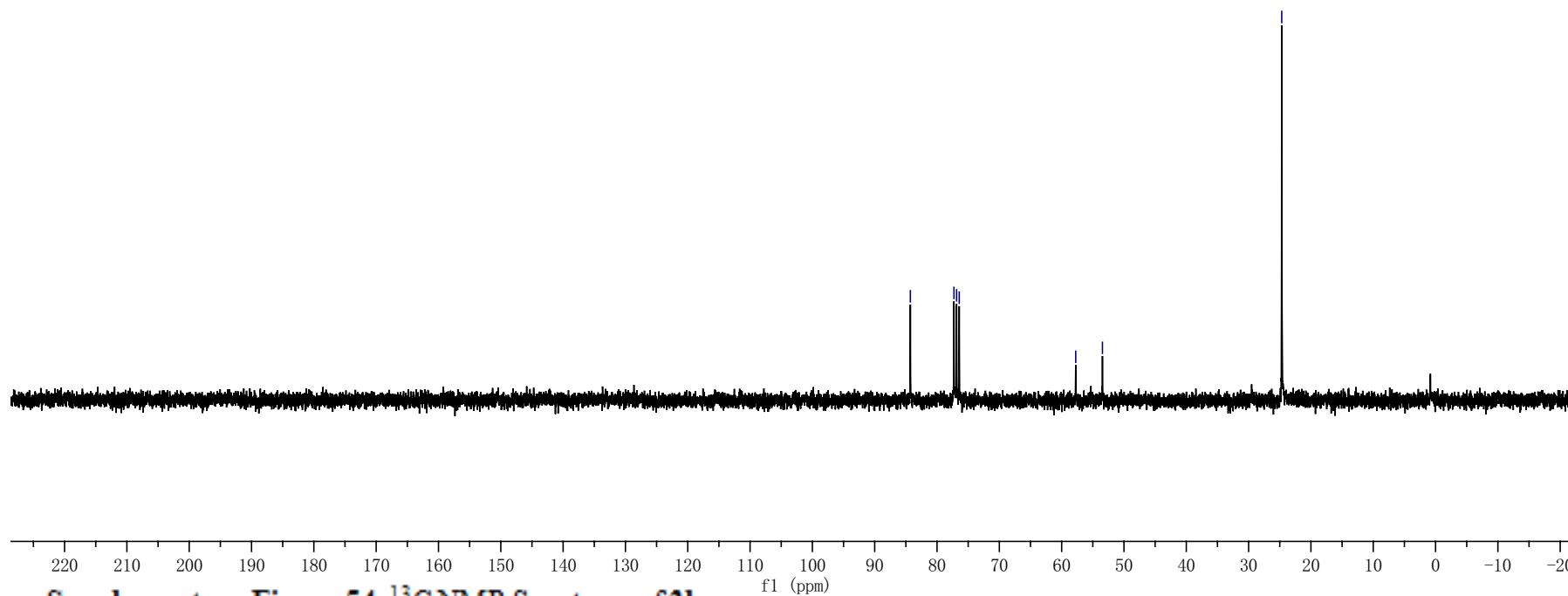
Parameter	Value
Title	crf3-85-HH
Comment	STANDARD 1H OBSERVE
Origin	Varien
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	29.0
Pulse Sequence	sZgD
Number of Scans	4
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-02-11 10:42:54
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-789.4
Nucleus	1H
Acquired Size	10376
Spectral Size	3268

Supplementary Figure 53. <sup>1</sup>H NMR Spectrum of **3b**.

crf-3-85-C-CDCl3

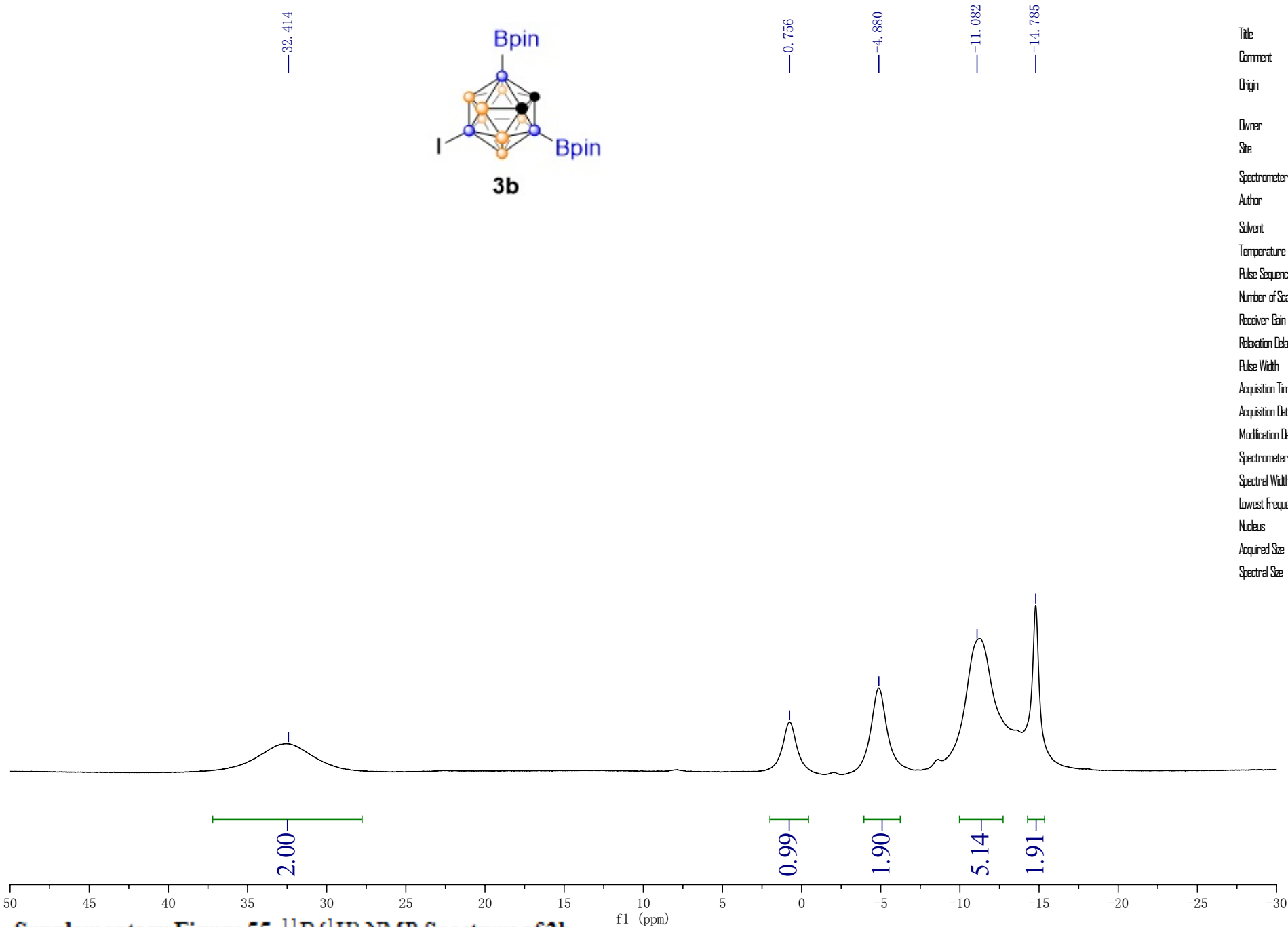


Parameter	Value
Title	crf-3-85-C-001-I
Comment	13C OBSERVE
Origin	Varien
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	zgpg30
Number of Scans	48
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-02-11 17:53
Spectrometer Frequency	75.45
Spectral Width	1901.4
Lowest Frequency	-1735.4
Nucleus	13C
Acquired Size	2817
Spectral Size	65536



Supplementary Figure 54. <sup>13</sup>C NMR Spectrum of 3b.

crf-3-85-B-decoupling-CDCl<sub>3</sub>

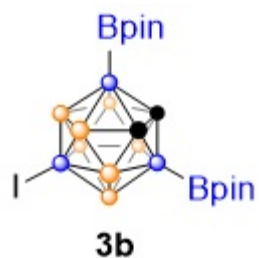


Parameter	Value
Data File Name	G:/Users/Administrator/Desktop/work/送样NMR/3-85/b-cr-f3-85/td
Title	3-85
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring-1gy
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3155
Acquisition Date	2015-02-11 21:39:13
Modification Date	2015-02-11 21:39:10
Spectrometer Frequency	128.38
Spectral Width	51821
Lowest Frequency	-16480.9
Nucleus	11B
Acquired Size	16384
Spectral Size	3288

Supplementary Figure 55. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of **3b**.

crf-3-85-B-coupling-CDCl<sub>3</sub>

32.666



-1.372

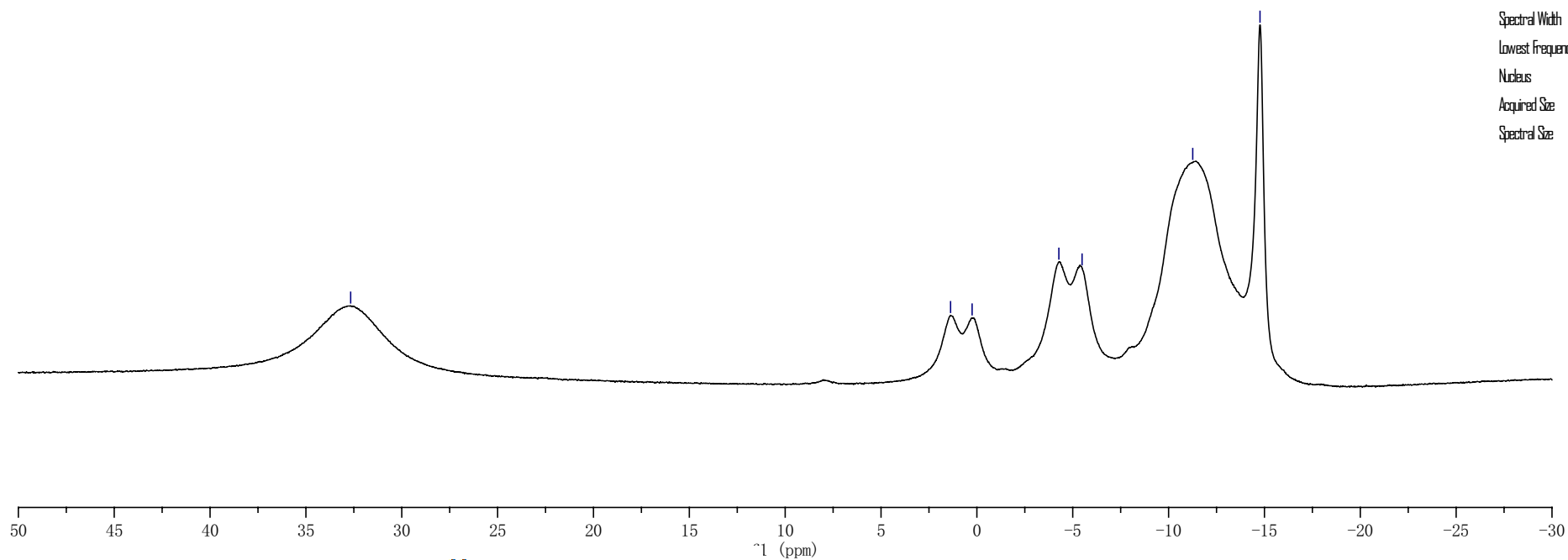
-0.249

-4.276

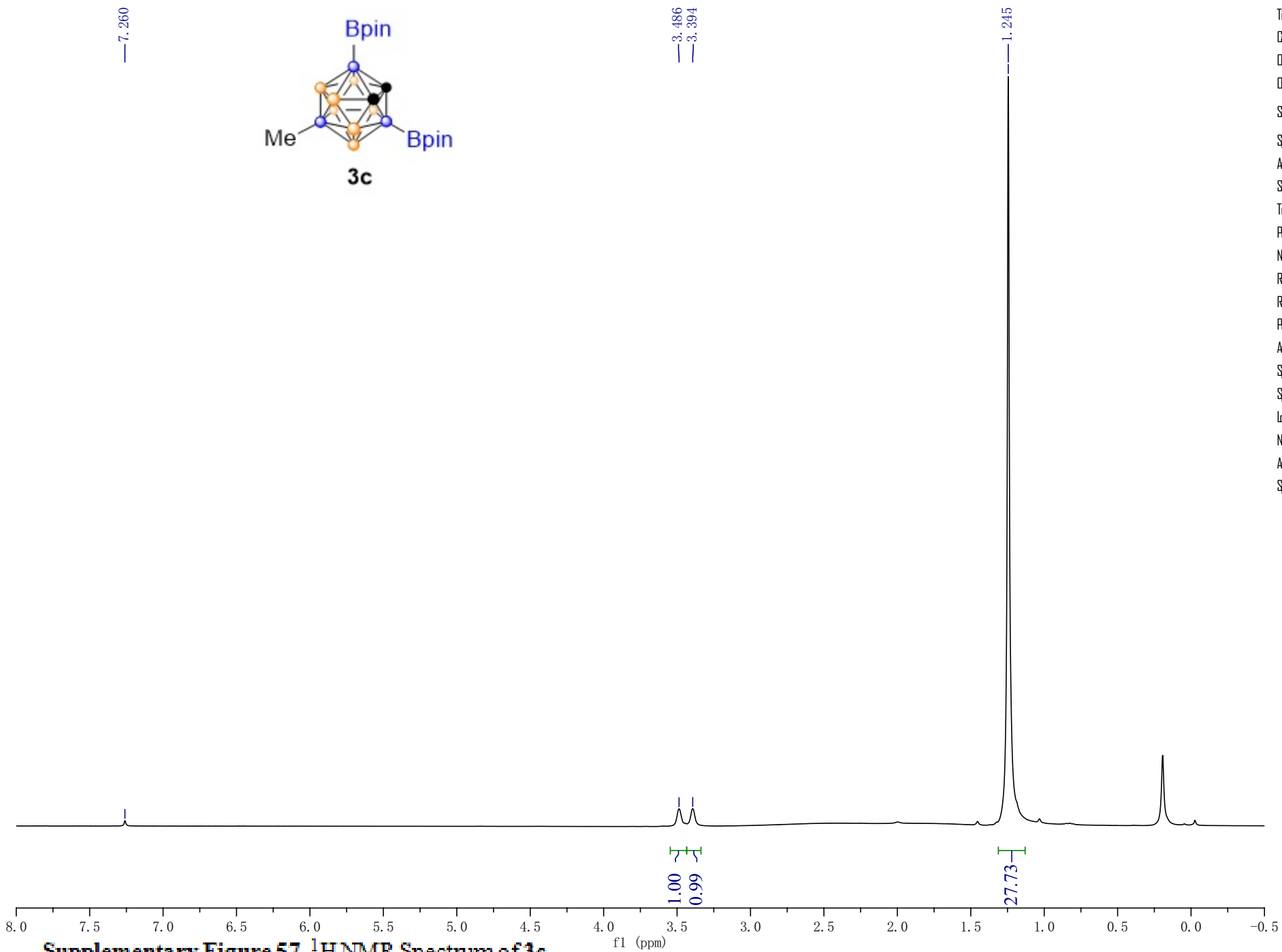
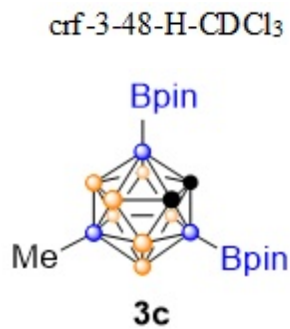
-5.487

-11.260

-14.769



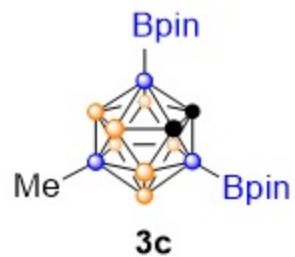
Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/work/送样NMR/borabatom/3-85/b-cr3-85-withoutdecoupling/1d
Title	3-85
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.ty
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-02-17 20:45:08
Modification Date	2015-02-17 13:47:00
Spectrometer Frequency	128.38
Spectral Width	51221
Lowest Frequency	-16480.9
Nucleus	11B
Acquired Size	16384
Spectral Size	3268



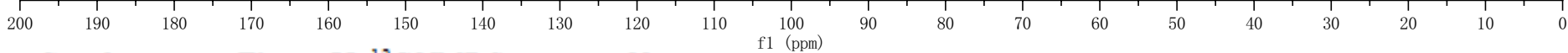
Parameter	Value
Title	crf-3-48H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	28.0
Pulse Sequence	zgpg30
Number of Scans	12
Receiver Gain	10
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-01-17 17:03:49
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-708.8
Nucleus	<sup>1</sup> H
Acquired Size	10895
Spectral Size	3268

Supplementary Figure 57. <sup>1</sup>H NMR Spectrum of 3c.

crf-3-48-C-CDCl<sub>3</sub>

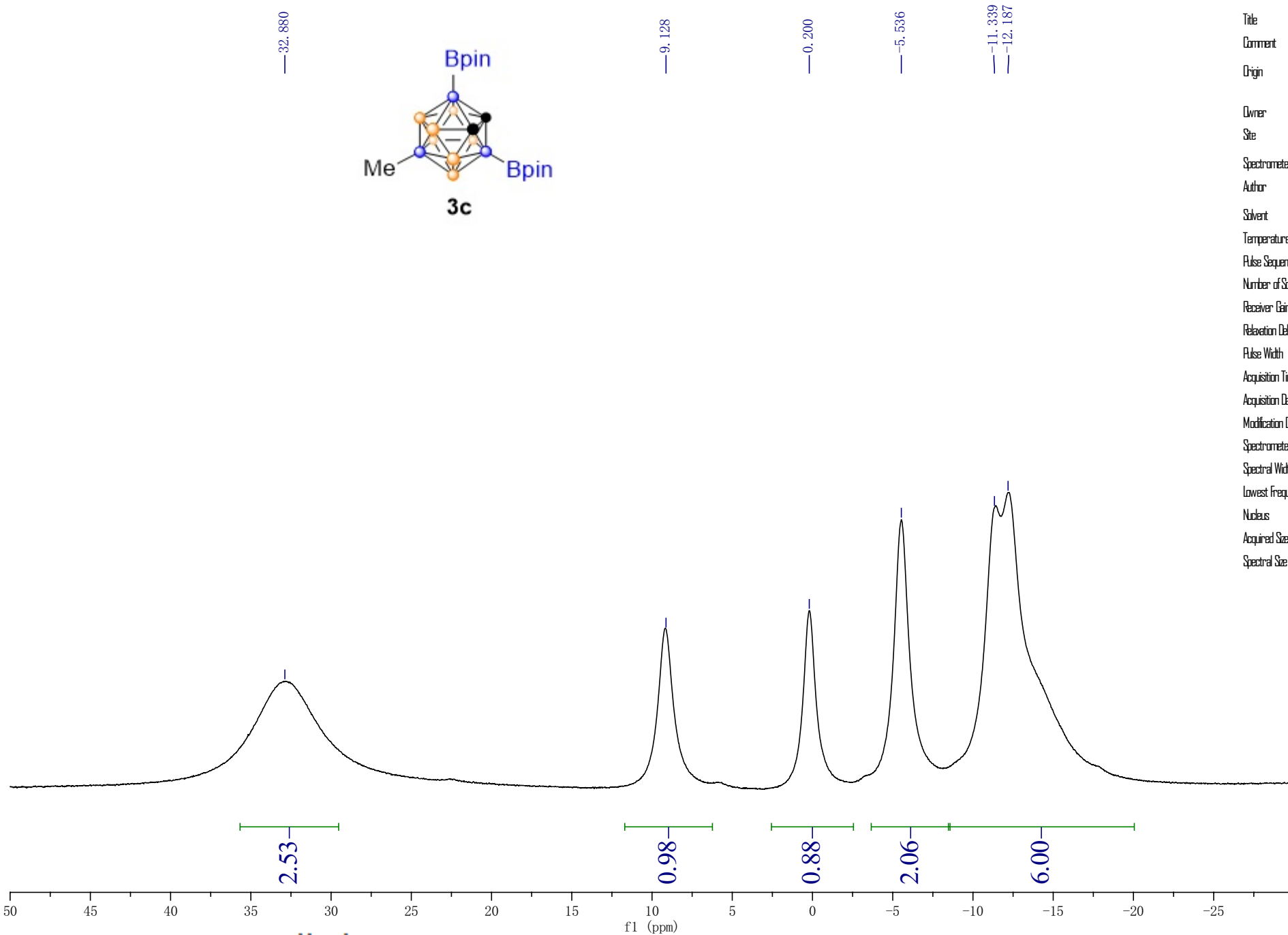
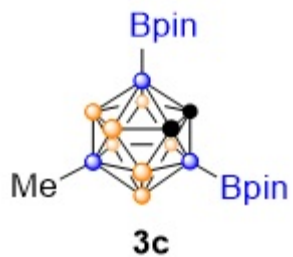


Parameter	Value
1 Title	crf-3-48-C
2 Comment	13C OBSERVE
3 Origin	Varian
4 Owner	
5 Site	
6 Spectrometer	mercury
7 Author	omc
8 Solvent	CDCl <sub>3</sub>
9 Temperature	29.0
10 Pulse Sequence	s2pul
11 Number of Scans	124
12 Receiver Gain	34
13 Relaxation Delay	1.0000
14 Pulse Width	0.0000
15 Acquisition Date	2015-01-17T17:09:5
16 Spectrometer Frequency	75.45
17 Spectral Width	18797.0
18 Lowest Frequency	-1649.4
19 Nucleus	13C
20 Acquired Size	30075
21 Spectral Size	65536



Supplementary Figure 58. <sup>13</sup>C NMR Spectrum of 3c.

crf-3-48-B-decoupling-CDCl<sub>3</sub>

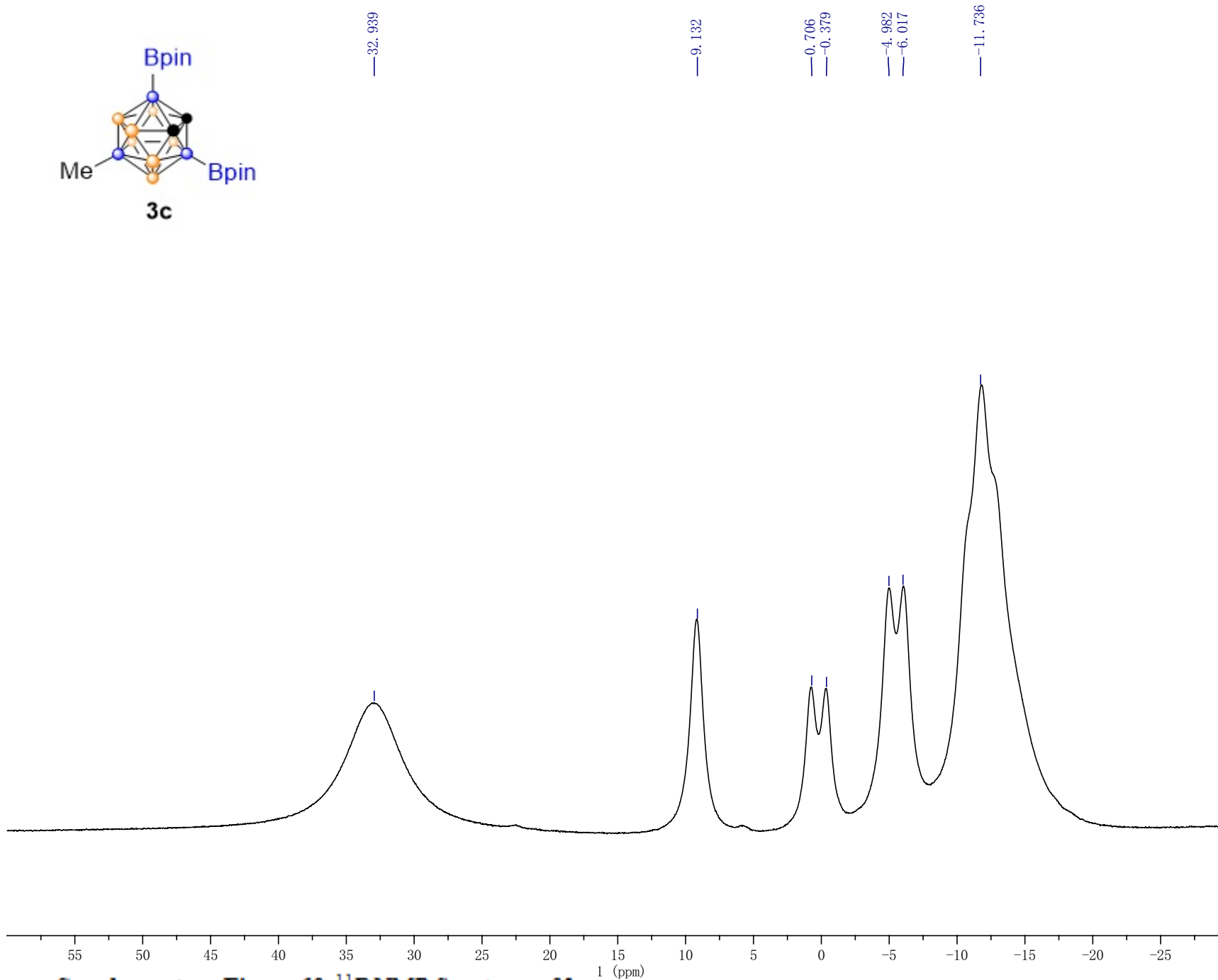
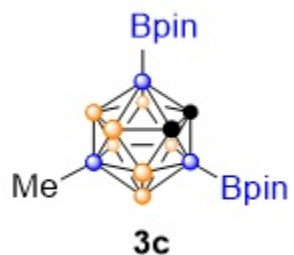


Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-crf-3-48 (1)/f1
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aning.tg
Number of Scans	364
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-01-27 19:00:31
Modification Date	2015-01-27 12:00:00
Spectrometer Frequency	128.38
Spectral Width	91821
Lowest Frequency	-17920.9
Nucleus	11B
Acquired Size	16384
Spectral Size	3068

Supplementary Figure 59. <sup>11</sup>B {<sup>1</sup>H} NMR Spectrum of **3c**.



crf-3-48-B-coupling-CDCl<sub>3</sub>

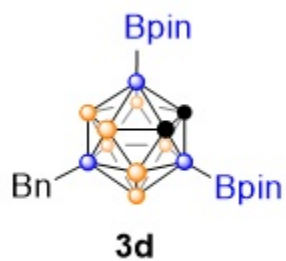


Parameter	Value
Data file Name	C:/Users/Administrator/Desktop/b-crf-3-48-withoutdecoupling/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dr400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring_tgy
Number of Scans	540
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-01-21 23:37
Modification Date	2015-01-21 15:34:00
Spectrometer Frequency	128.38
Spectral Width	51821
Lowest Frequency	-16526.9
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

Supplementary Figure 60. <sup>11</sup>B NMR Spectrum of **3c**.

crf-3-72-H-CDCl<sub>3</sub>

7.260  
7.207  
7.185  
7.162  
7.047  
7.024

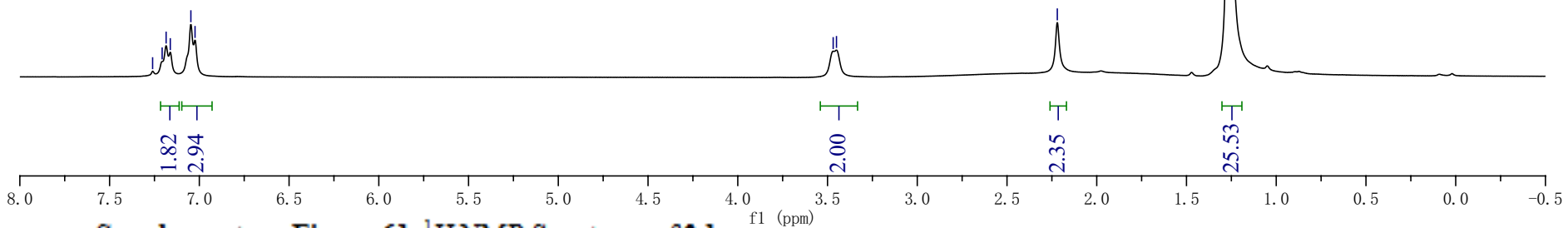


3.468  
3.450

2.220

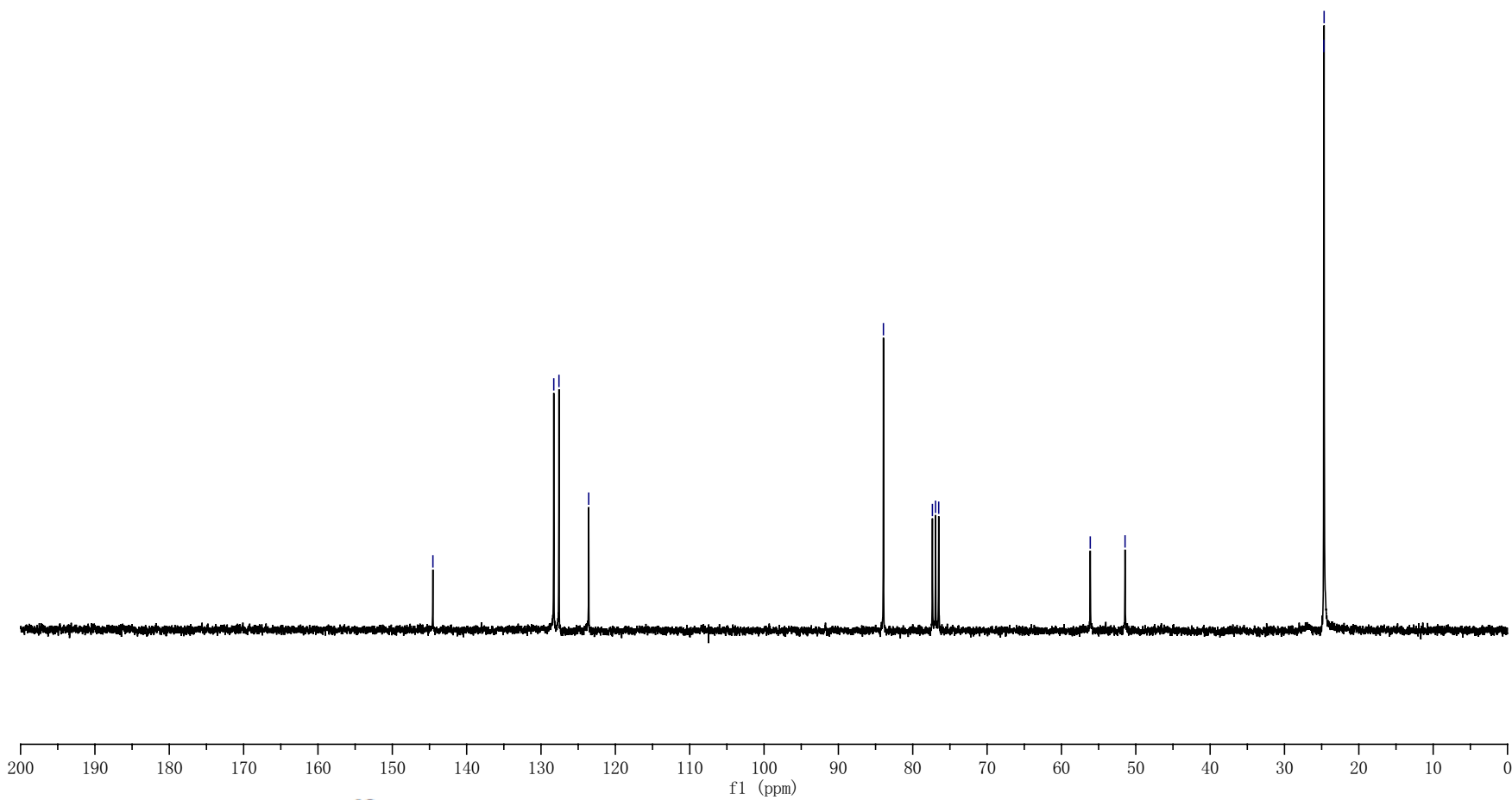
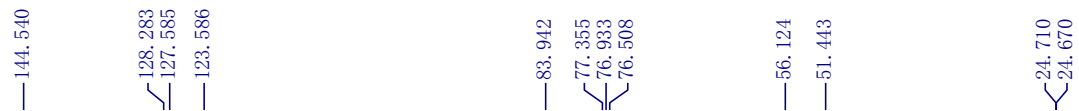
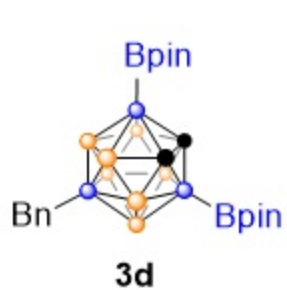
1.262

Parameter	Value
Title	crf-3-72H
Comment	STANDARD OBSERVE
Origin	Varien
Owner	
Site	
Spectrometer	mercury
Author	onc
Solvent	CDCl <sub>3</sub>
Temperature	20.0
Pulse Sequence	sgpd
Number of Scans	20
Receiver Gain	10
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-02-27 11:25:03
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-708.8
Nucleus	<sup>1</sup> H
Acquired Size	10376
Spectral Size	3268



Supplementary Figure 61. <sup>1</sup>H NMR Spectrum of 3d.

crf-3-72-C-CDCl<sub>3</sub>

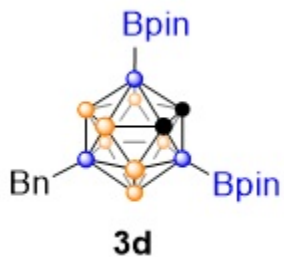


Parameter	Value
Title	crf-3-72-C
Comment	<sup>13</sup> C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	28.0
Pulse Sequence	sgpd
Number of Scans	132
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-02-27 11:28:2
Spectrometer Frequency	75.45
Spectral Width	18387.0
Lowest Frequency	-16331.2
Nucleus	<sup>13</sup> C
Acquired Size	2895
Spectral Size	65536

Supplementary Figure 62. <sup>13</sup>C NMR Spectrum of 3d.

crf-3-72-B-decoupling-CDCl<sub>3</sub>

—33.156



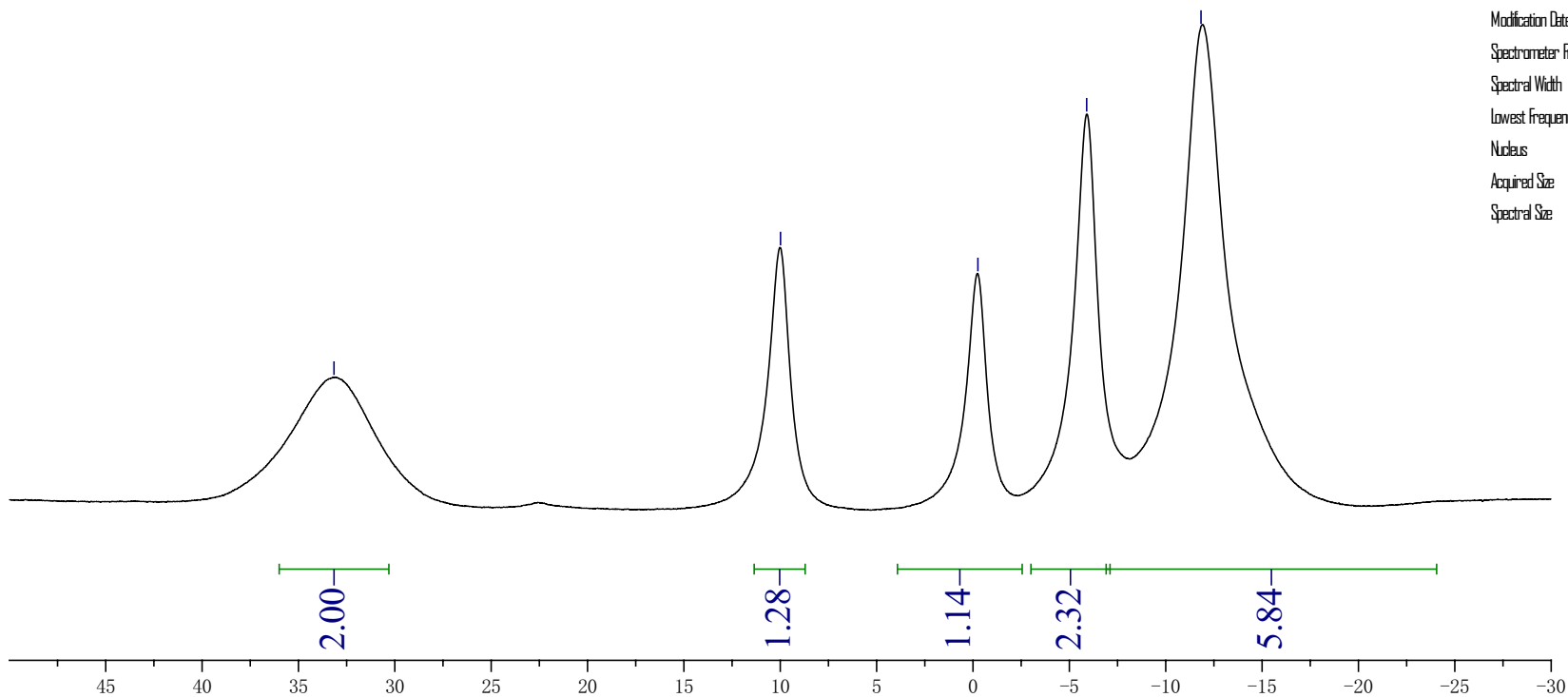
—9.987

—-0.254

—-5.898

—-11.831

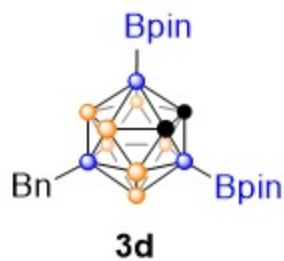
Parameter	Value
Data File Name	G:/Users/Administrator/Desktop/b-crf-3-72.fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.tgy
Number of Scans	126
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3195
Acquisition Date	215-02/07/15 12:40
Modification Date	215-02/04/08 30:00
Spectrometer Frequency	128.38
Spectral Width	5.2821
Lowest Frequency	-18555.1
Nucleus	<sup>11</sup> B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 63. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of **3d**.

crf-3-72-B-coupling-CDCl<sub>3</sub>

33.407

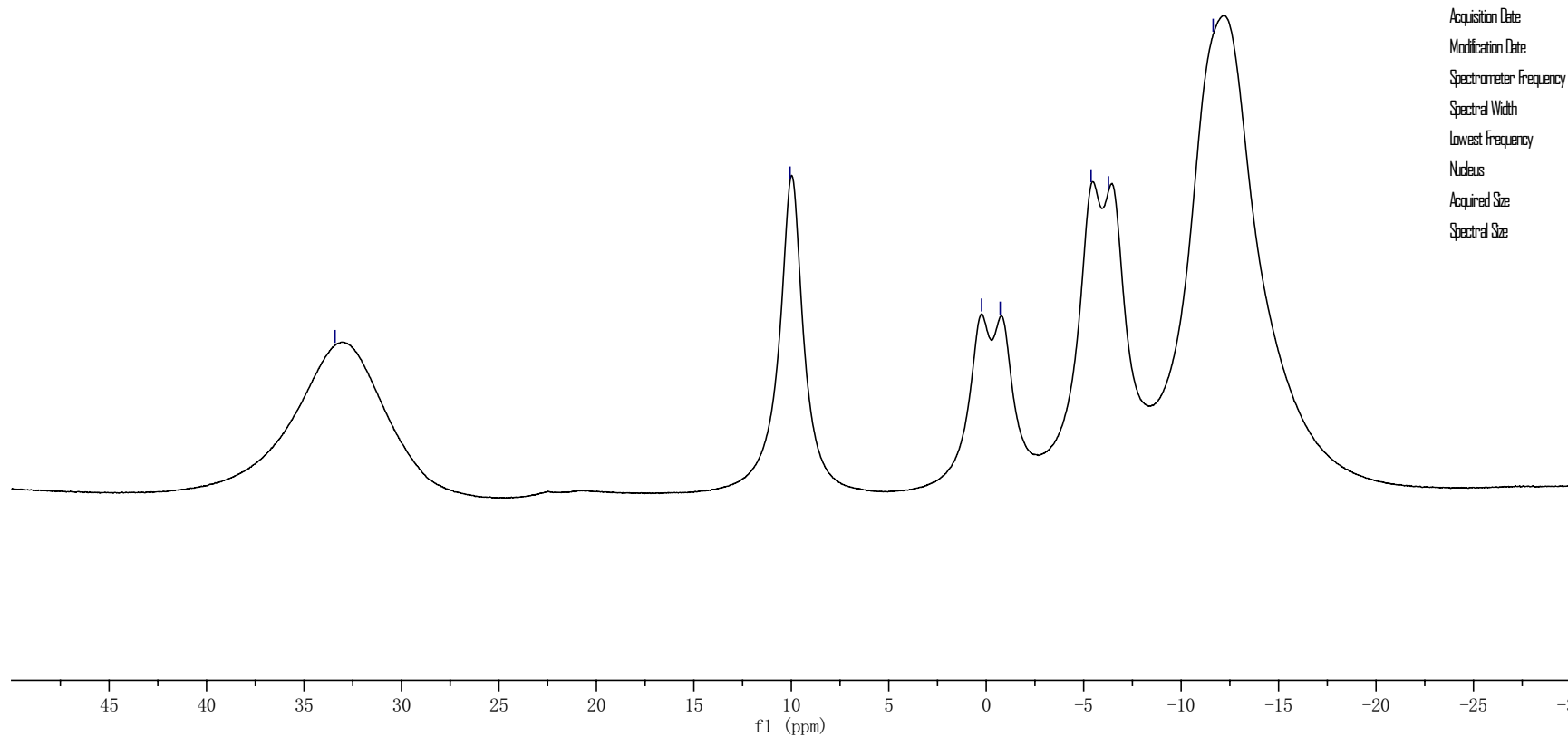


10.063

0.237  
-0.717

-5.380  
-6.272

-11.641

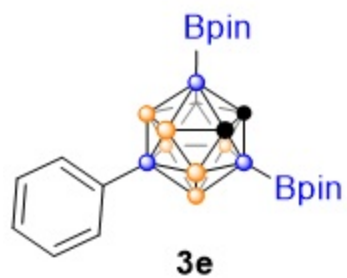


Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr-f3-72withoutdecoupling/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.ty
Number of Scans	1996
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-02-04 15:40:48
Modification Date	2015-02-04 15:40:00
Spectrometer Frequency	128.38
Spectral Width	59.821
Lowest Frequency	-18565.1
Nucleus	11B
Acquired Size	16384
Spectral Size	3888

Supplementary Figure 64. <sup>11</sup>B NMR Spectrum of 3d.

crf-3-45-H-CDCl<sub>3</sub>

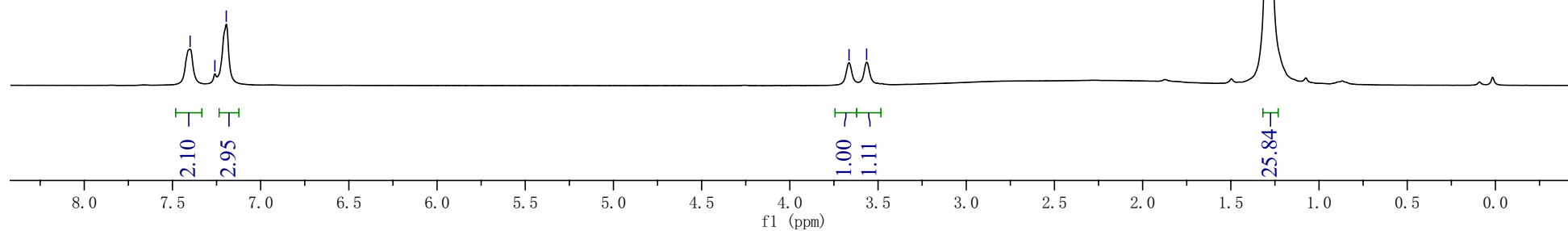
7.400  
7.260  
7.195



3.664  
3.565

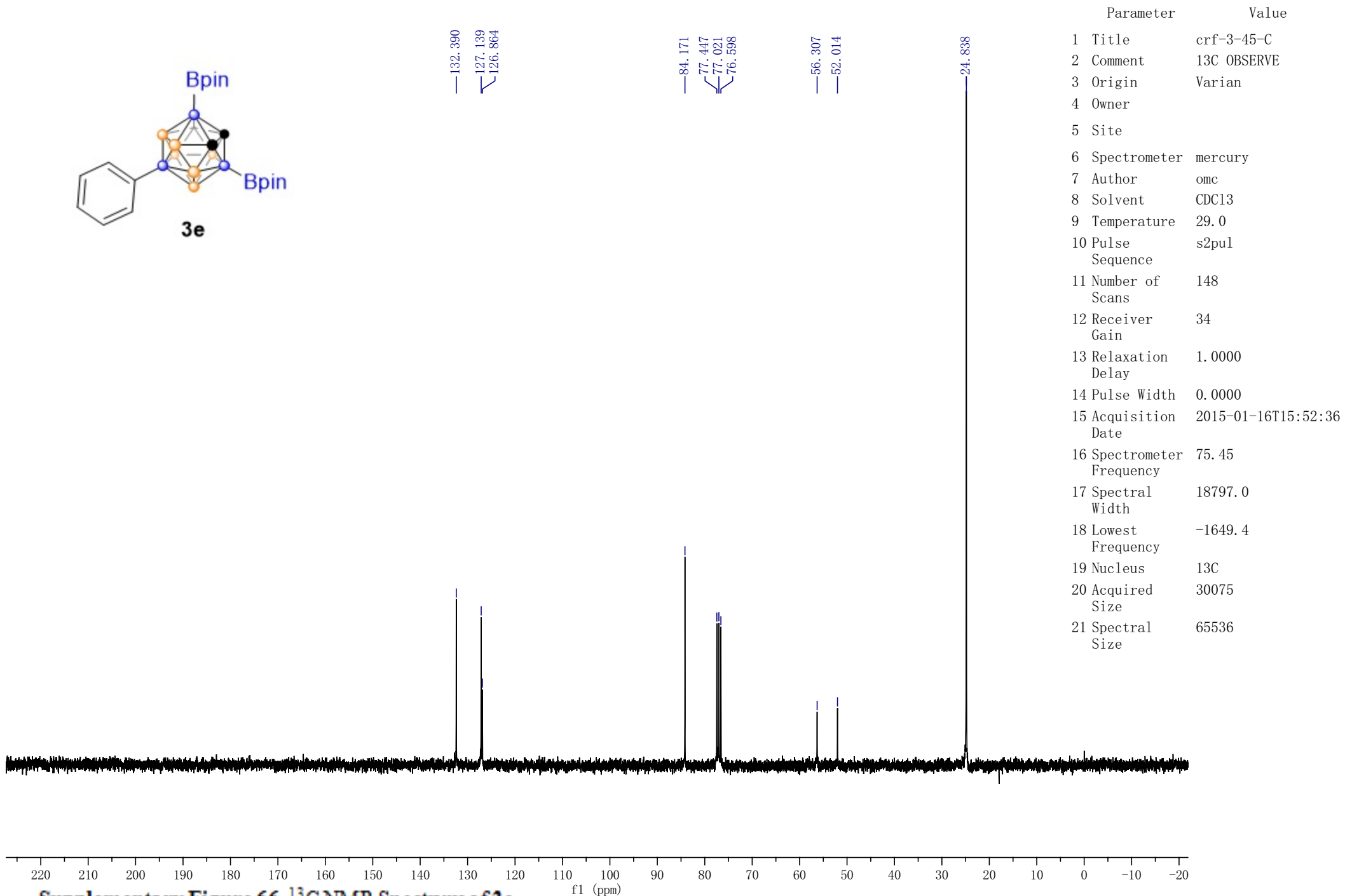
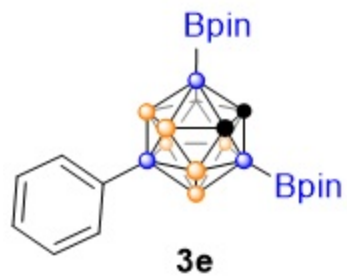
1.287

Parameter	Value
Title	crf-3-45-H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	28.0
Pulse Sequence	sgpd
Number of Scans	8
Receiver Gain	16
Relaxation Delay	1.000
Pulse Width	0.000
Acquisition Date	2015-04-01 15:51:46
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-709.8
Nucleus	<sup>1</sup> H
Acquired Size	10076
Spectral Size	3268

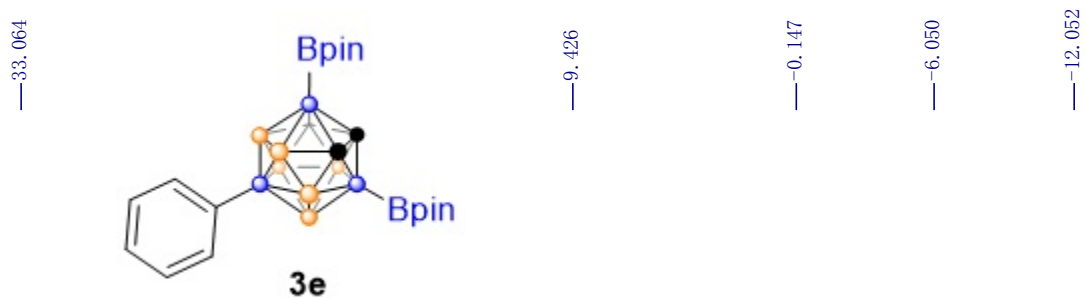


Supplementary Figure 65. <sup>1</sup>H NMR Spectrum of 3e.

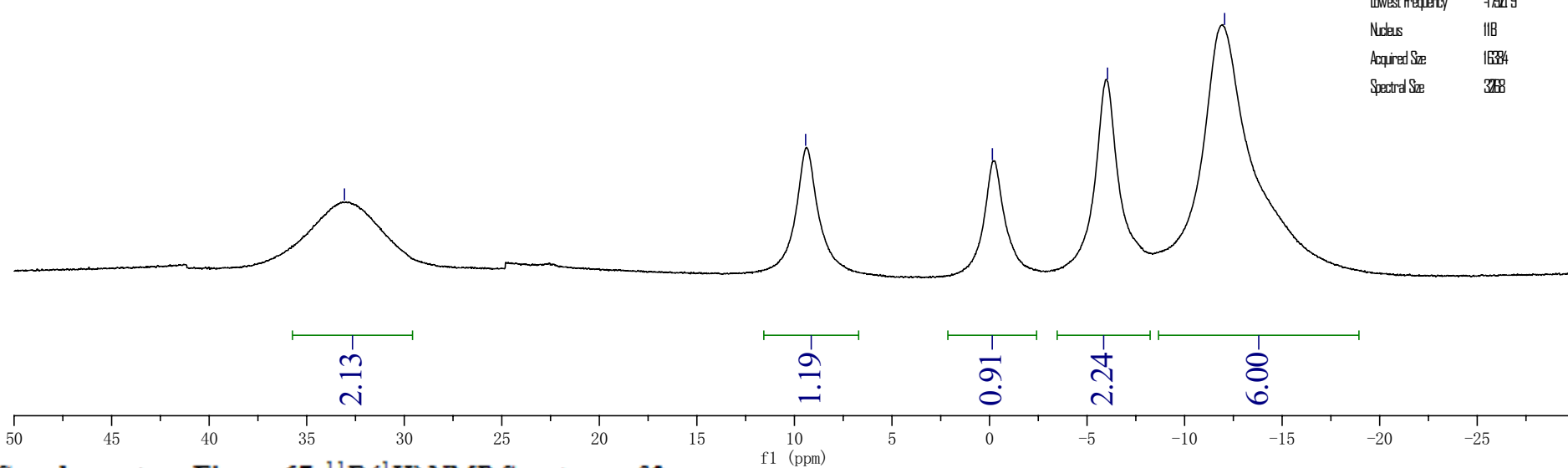
crf-3-45-C-CDCl<sub>3</sub>



Supplementary Figure 66. <sup>13</sup>C NMR Spectrum of 3e.



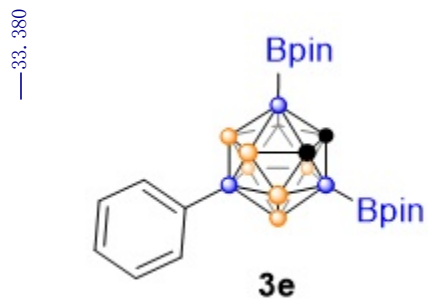
Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-crf-3-45 (1)/fid
Title	Desktop
Comment	
Origin	LWMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dmx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.1gy
Number of Scans	62
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3135
Acquisition Date	2015-01-21 18:58:06
Modification Date	2015-01-21 11:57:00
Spectrometer Frequency	128.38
Spectral Width	9.221
Lowest Frequency	-17.8019
Nucleus	<sup>11</sup> B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 67. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of **3e**.



crf-3-45-B-coupling-CDCl<sub>3</sub>



33.380

9.468

0.314

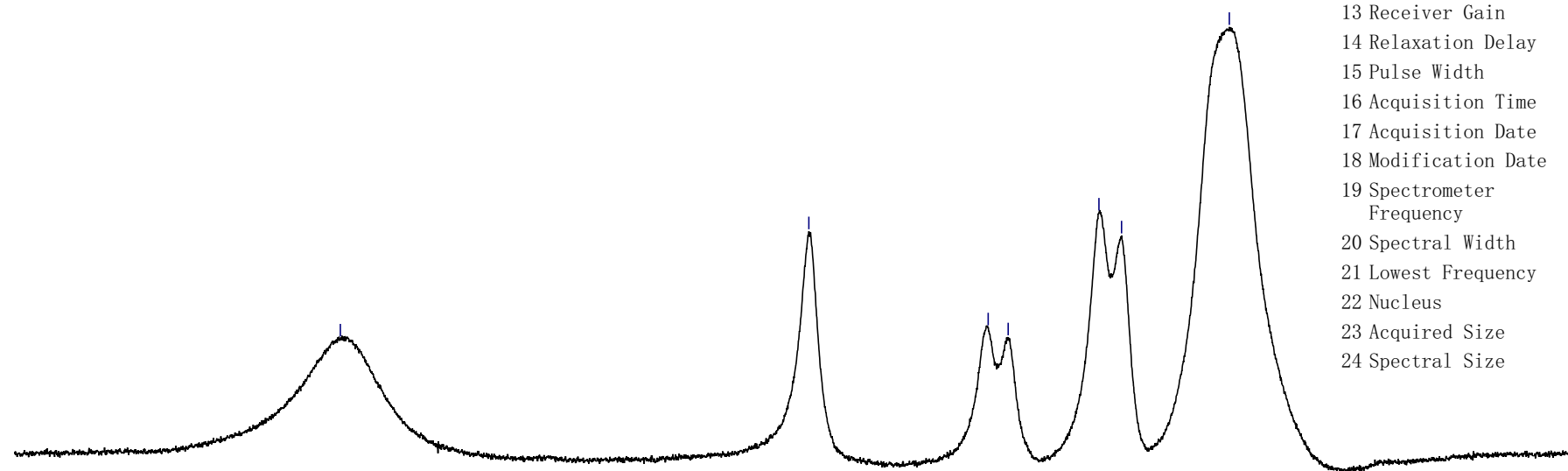
-0.706

-5.339

-6.493

-11.994

Parameter	Value
1 Data File Name	C:/Users/Administrator/Desktop/b-crf-3-45/fid
2 Title	crf-3-45-B-coupling-CDCl <sub>3</sub>
3 Comment	
4 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5 Owner	root
6 Site	
7 Spectrometer	drx400
8 Author	
9 Solvent	CDCl <sub>3</sub>
10 Temperature	300.0
11 Pulse Sequence	aring.lgy
12 Number of Scans	1600
13 Receiver Gain	32
14 Relaxation Delay	0.0000
15 Pulse Width	13.4000
16 Acquisition Time	0.3195
17 Acquisition Date	2015-03-09T15:57:45
18 Modification Date	2015-03-09T08:57:00
19 Spectrometer Frequency	128.38
20 Spectral Width	51282.1
21 Lowest Frequency	-15466.9
22 Nucleus	11B
23 Acquired Size	16384
24 Spectral Size	32768

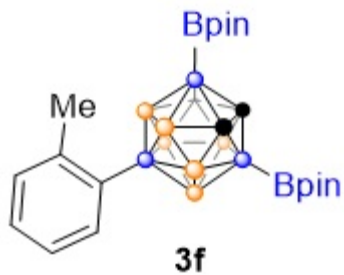


50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25

Supplementary Figure 68. <sup>11</sup>B NMR Spectrum of **3e**.

crf-4-44-H-CDCl<sub>3</sub>

7.524  
7.505  
7.260  
7.080  
7.059  
7.033  
7.021

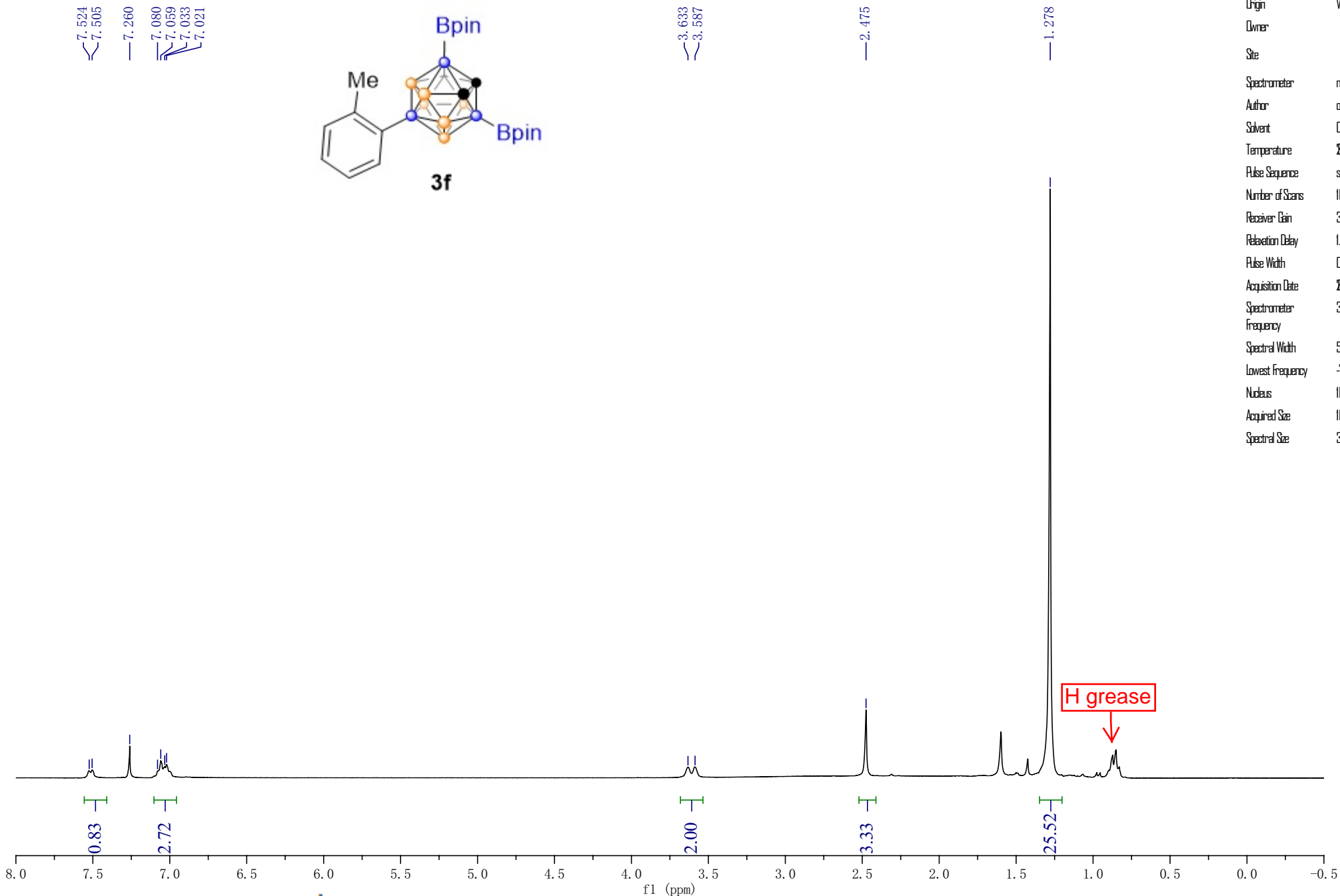


3.633  
3.587

2.475

1.278

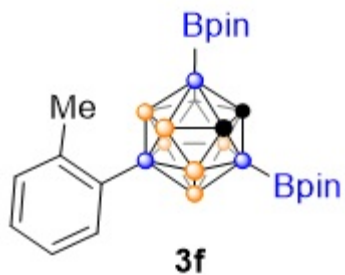
Parameter	Value
Title	crf-4-44-H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	29.0
Pulse Sequence	zgpg30
Number of Scans	16
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-20T11: 2: 35
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-703.3
Nucleus	1H
Acquired Size	10876
Spectral Size	3268



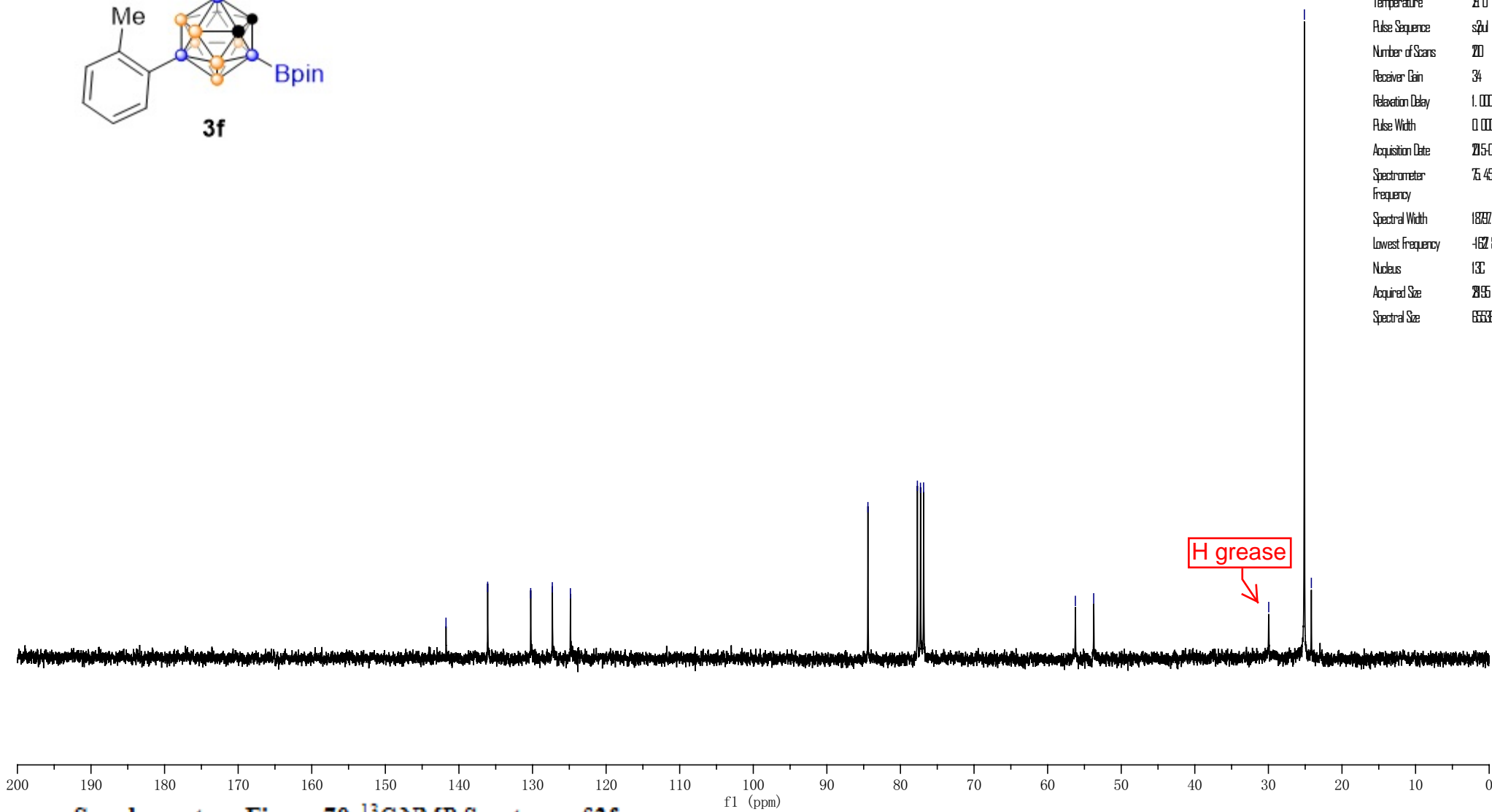
Supplementary Figure 69. <sup>1</sup>H NMR Spectrum of 3f.

S90

crf-4-44-H-CDCl<sub>3</sub>

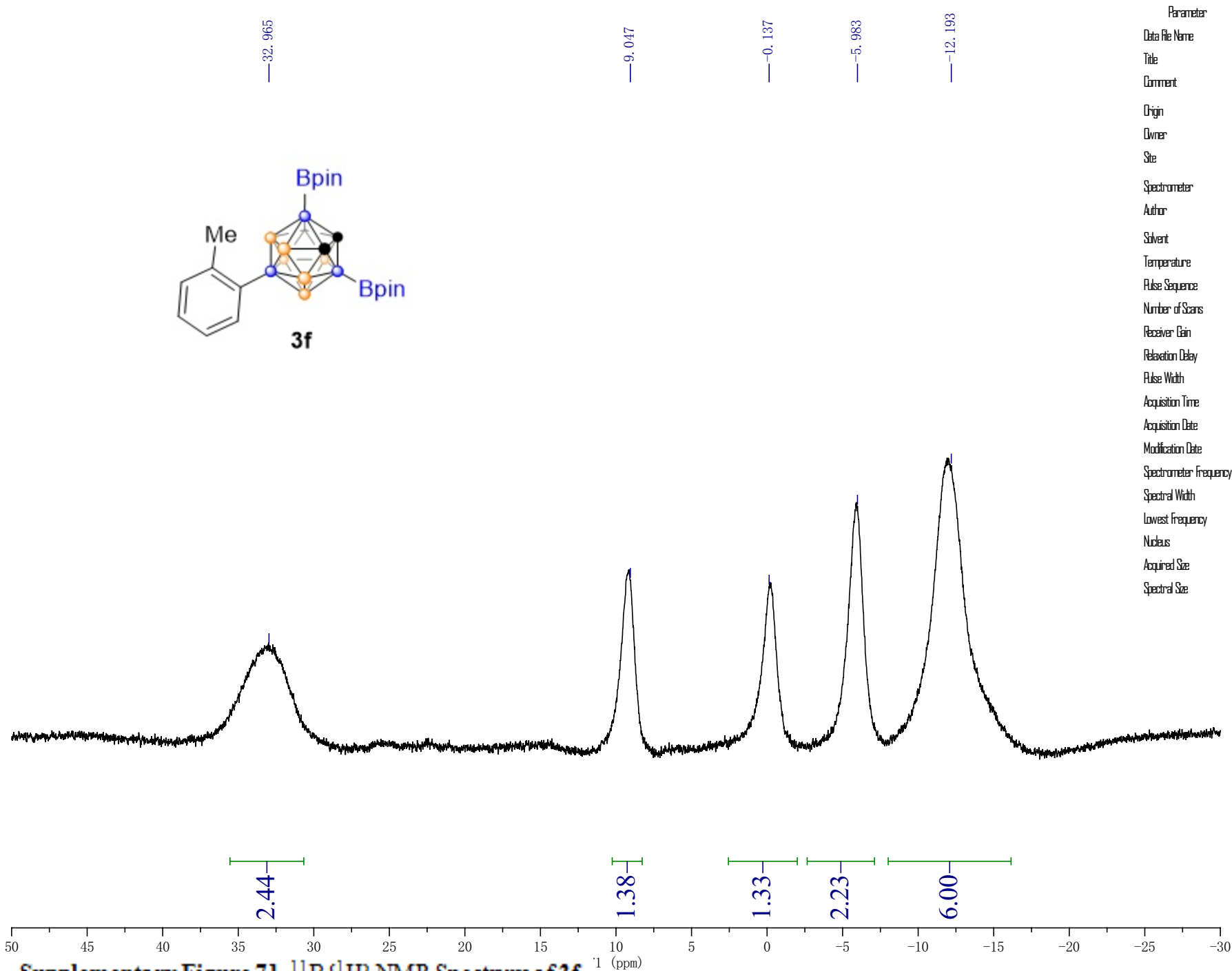
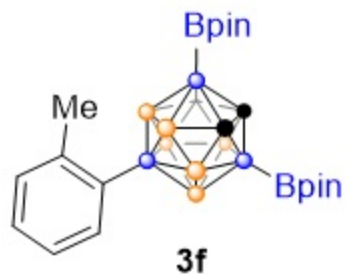


Parameter	Value
Title	crf-4-44-C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	onc
Solvent	CDCl <sub>3</sub>
Temperature	29.0
Pulse Sequence	squl
Number of Scans	20
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-27 22:41:17
Spectrometer Frequency	76.45
Spectral Width	18887.0
Lowest Frequency	-162.8
Nucleus	13C
Acquired Size	28155
Spectral Size	65536



Supplementary Figure 70. <sup>13</sup>C NMR Spectrum of **3f**.

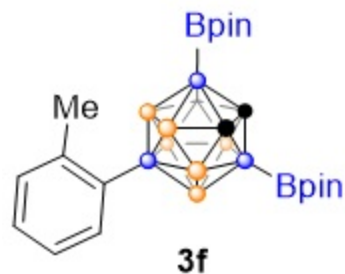
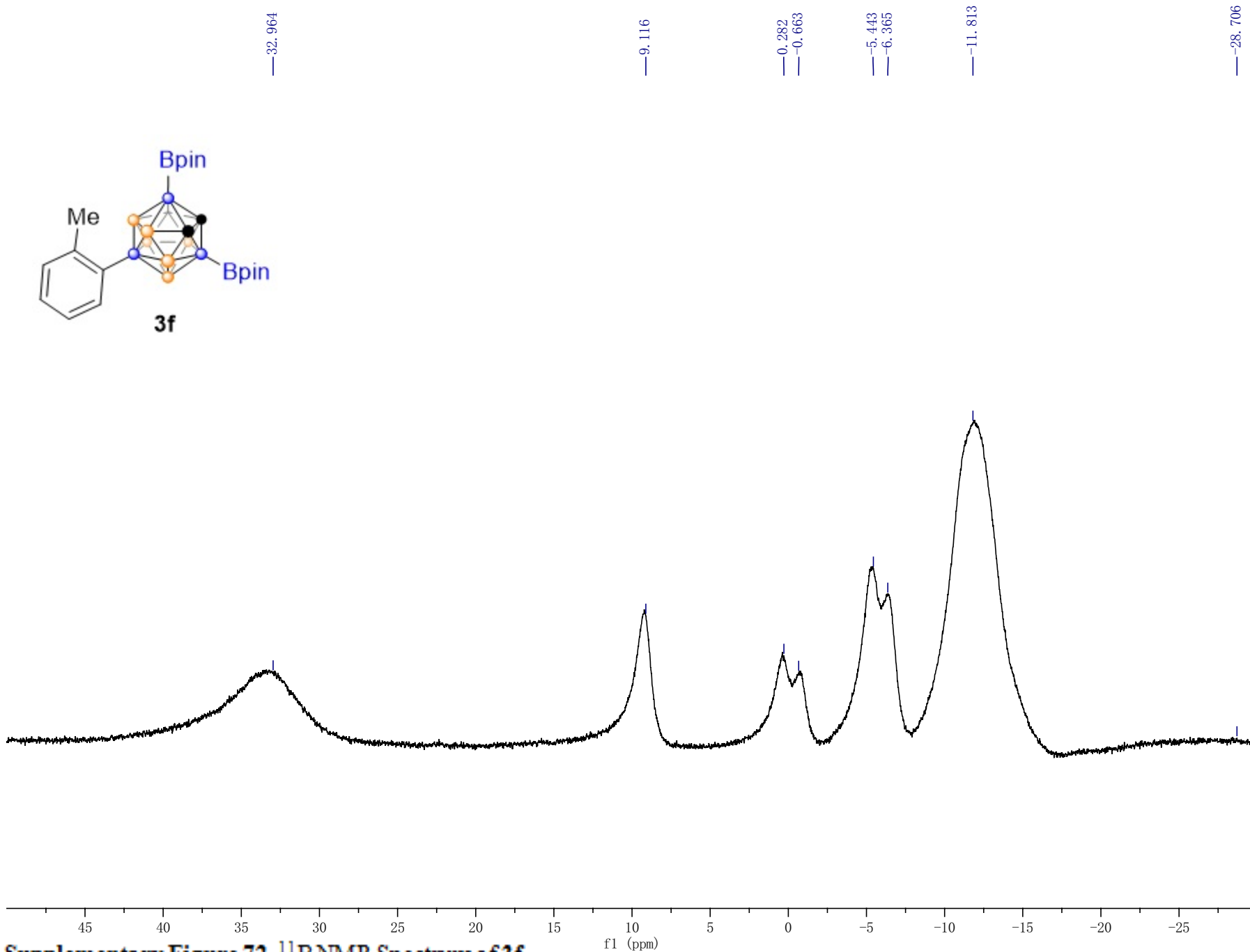
crf-444-B-decoupling-CDCl<sub>3</sub>



Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-orf444/tid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring_1g
Number of Scans	20
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3155
Acquisition Date	2015-04-20 13:01:46
Modification Date	2015-04-20 13:01:00
Spectrometer Frequency	128.38
Spectral Width	9.221
Lowest Frequency	-1789.3
Nucleus	11B
Acquired Size	16394
Spectral Size	3268

Supplementary Figure 71. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of **3f**.

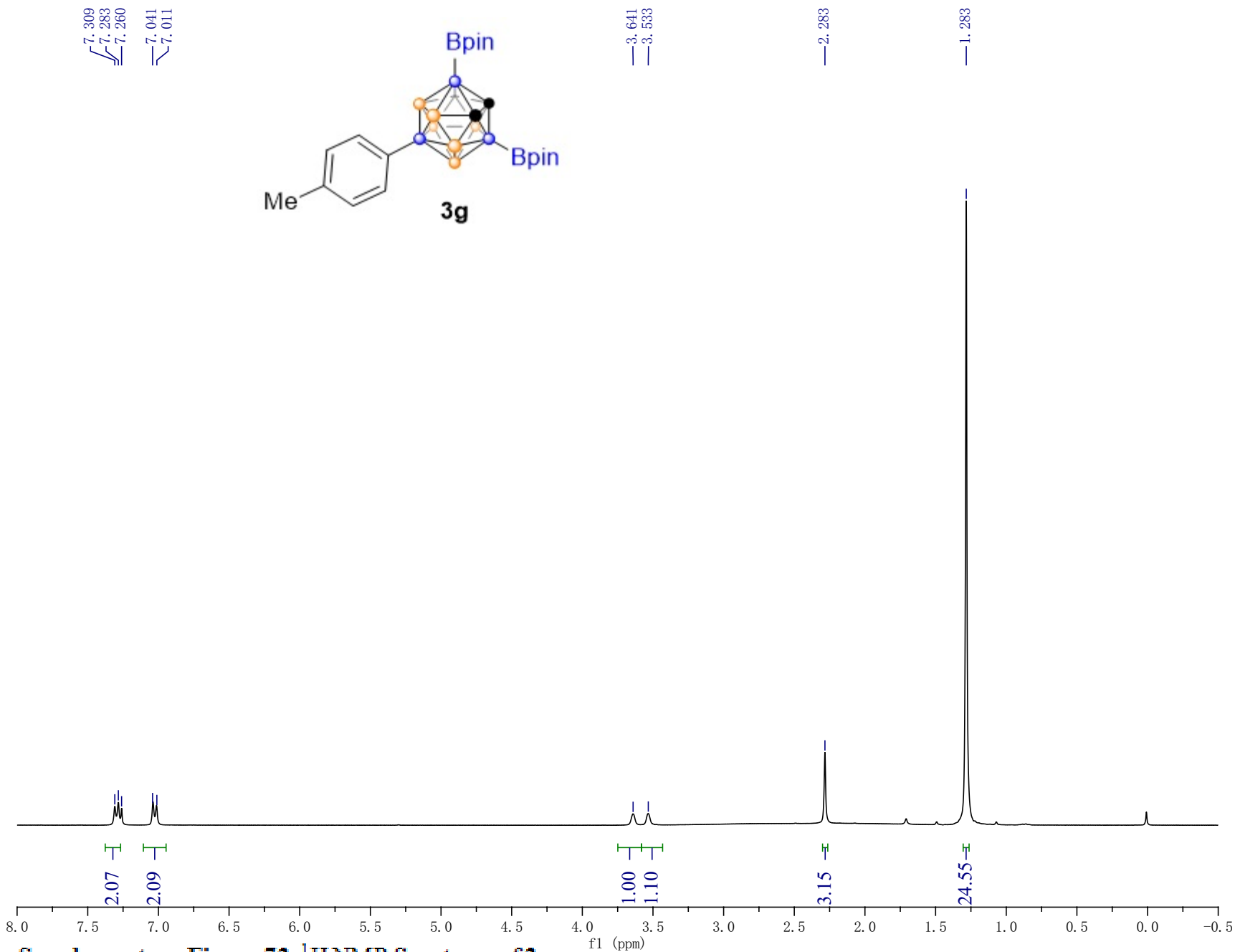
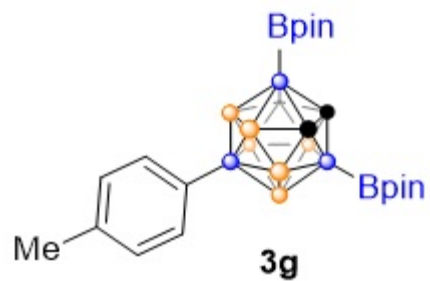
crf-444-B-decoupling-CDCl<sub>3</sub>



Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr444-coupling/1d
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dr400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1g
Number of Scans	400
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3155
Acquisition Date	2015-04-20 19:04:45
Modification Date	2015-04-20 13:04:00
Spectrometer Frequency	128.38
Spectral Width	57201
Lowest Frequency	-44628.4
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

Supplementary Figure 72. <sup>11</sup>B NMR Spectrum of **3f**.

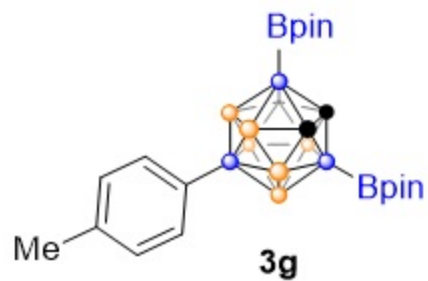
crf-3-90-H-CDCl<sub>3</sub>



Parameter	Value
Title	crf-3-90-H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	sgzg
Number of Scans	4
Receiver Gain	2
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-02-27 09:58
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-703.7
Nucleus	1H
Acquired Size	10876
Spectral Size	3268

Supplementary Figure 73. <sup>1</sup>H NMR Spectrum of **3g**.

crf-3-90-C-CDCl<sub>3</sub>



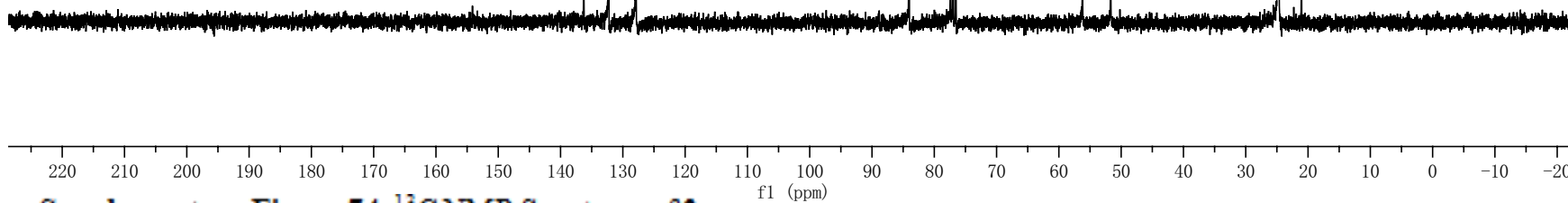
136.254  
132.261  
127.886

84.046  
77.379  
76.956  
76.534

56.219  
51.687

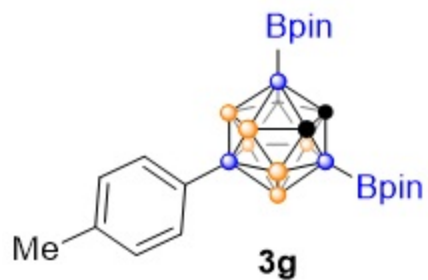
24.729  
21.055

Parameter	Value
Title	crf3-90-C
Comment	13C CESSRVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	29.0
Pulse Sequence	sZul
Number of Scans	48
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-02-22 10:55
Spectrometer Frequency	76.45
Spectral Width	1901.4
Lowest Frequency	-1766.4
Nucleus	13C
Acquired Size	2517
Spectral Size	65536

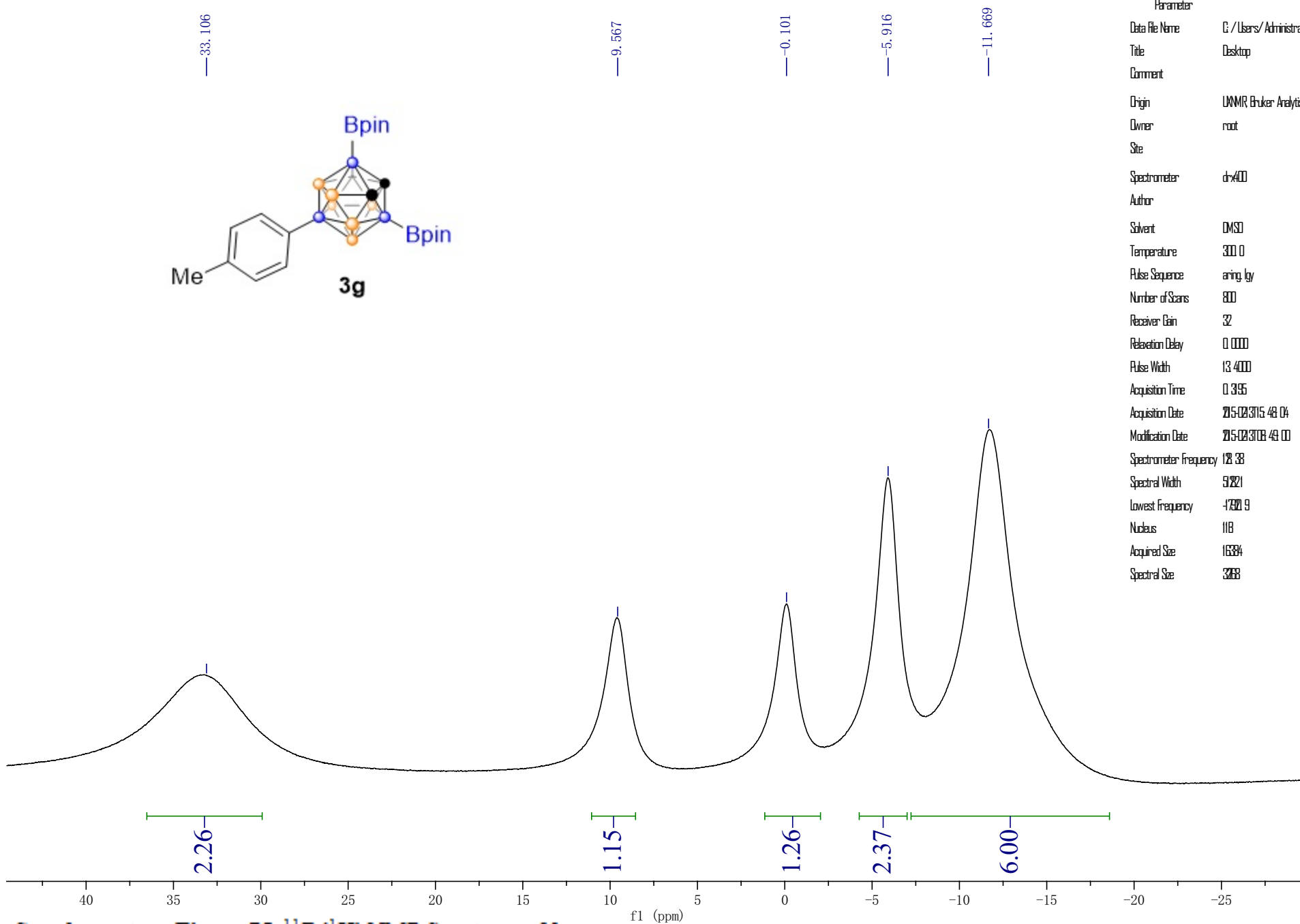


Supplementary Figure 74. <sup>13</sup>C NMR Spectrum of **3g**.

crf-3-90-B-decoupling-CDC13



Parameter	Value
Data File Name	E:/Users/Administrator/Desktop/bcrf3-90/tid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aning.ty
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3195
Acquisition Date	2015-08-31 15:48:04
Modification Date	2015-08-31 08:49:00
Spectrometer Frequency	128.38
Spectral Width	51.221
Lowest Frequency	-17320.9
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

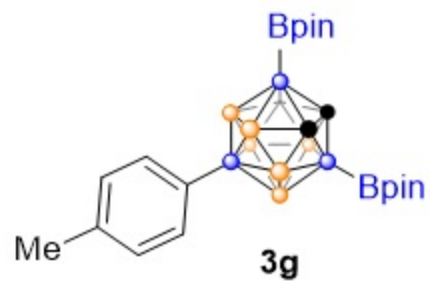


Supplementary Figure 75. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of **3g**.



crf-3-90-B-coupling-CDC13

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-crf3-90-withoutdecoupling/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dmx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.1g
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-02-31 15:54:28
Modification Date	2015-02-31 08:54:00
Spectrometer Frequency	128.39
Spectral Width	9.2821
Lowest Frequency	-16557.0
Nucleus	11B
Acquired Size	16394
Spectral Size	3268



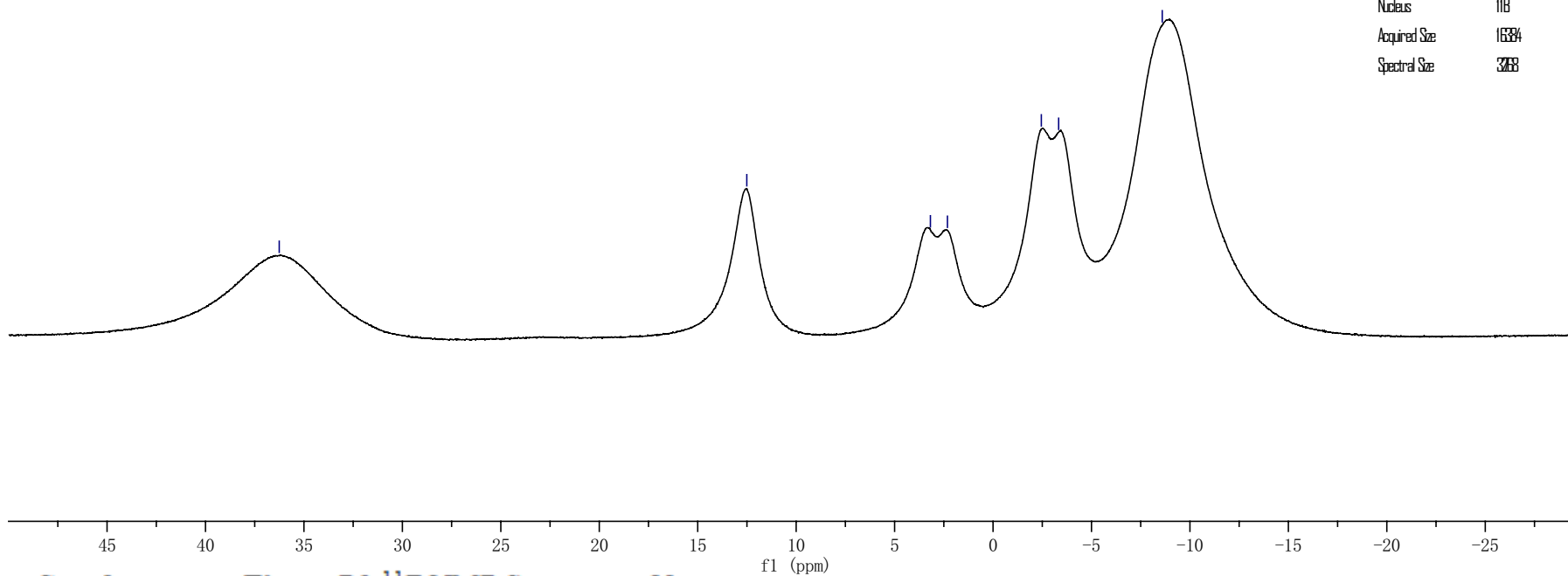
36.255

12.507

3.182  
2.316

2.452  
3.332

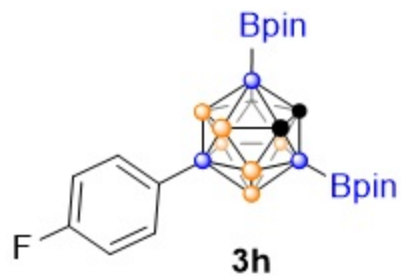
8.593



Supplementary Figure 76. <sup>11</sup>B NMR Spectrum of **3g**.

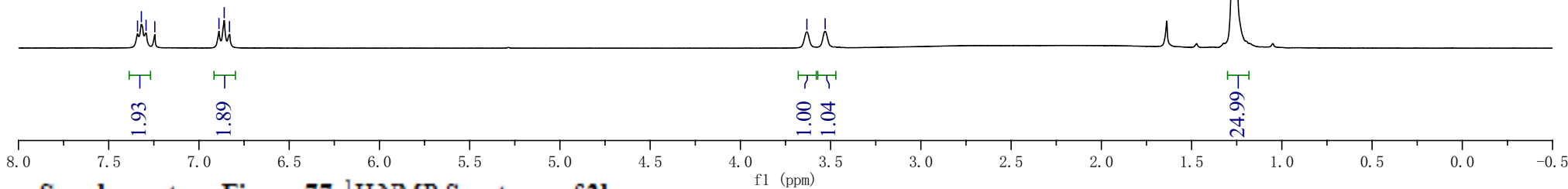
crf-4-45-H-CDCl<sub>3</sub>

7.340  
7.319  
7.293  
7.245  
6.889  
6.860  
6.831



3.632  
3.530

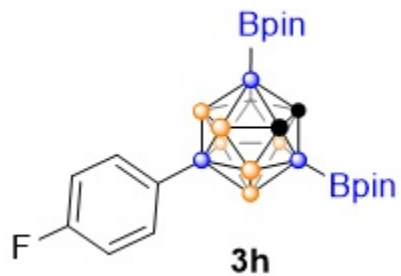
1.262



Parameter	Value
Title	crf-4-45-H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	28.0
Pulse Sequence	sgdd
Number of Scans	12
Receiver Gain	28
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-20T09:11:51
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-74.1
Nucleus	<sup>1</sup> H
Acquired Size	10365
Spectral Size	3268

Supplementary Figure 77. <sup>1</sup>H NMR Spectrum of **3h**.

crf-4-45-C-CDCl<sub>3</sub>



164.511  
161.268

134.247  
134.150

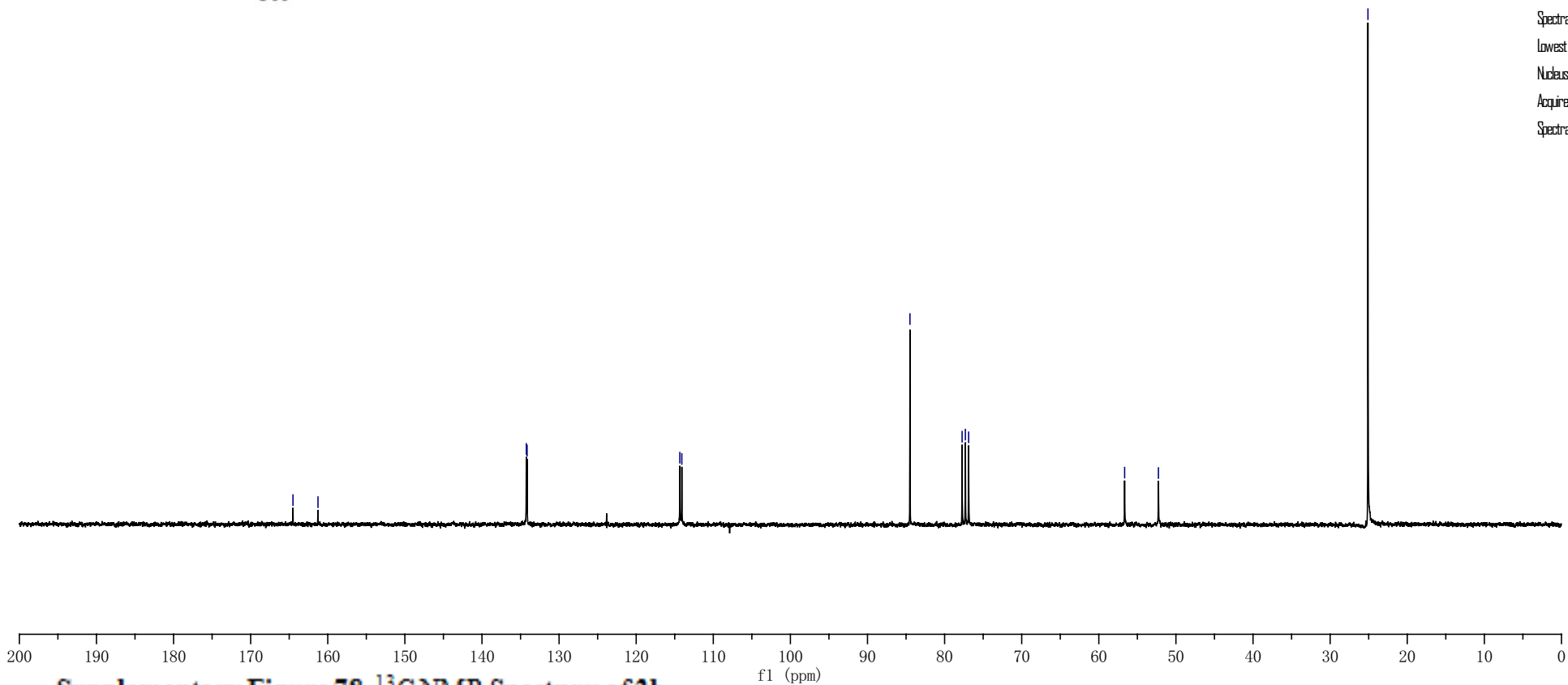
114.340  
114.079

84.494  
77.732  
77.308  
76.884

56.652  
52.267

25.096

Parameter	Value
Title	crf-4-45-C-0420
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	28.0
Pulse Sequence	zgpg30
Number of Scans	200
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-20 11: 28: 56
Spectrometer Frequency	75.45
Spectral Width	18367.0
Lowest Frequency	-1627.8
Nucleus	13C
Acquired Size	28155
Spectral Size	65536



Supplementary Figure 78. <sup>13</sup>C NMR Spectrum of **3h**.

crf-4-45-B-decoupling-CDCl<sub>3</sub>

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr-4-45/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dmx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring-1gy
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3195
Acquisition Date	2015-04-20T13:13:06
Modification Date	2015-04-20T13:13:00
Spectrometer Frequency	128.38
Spectral Width	51281
Lowest Frequency	-47300.9
Nucleus	11B
Acquired Size	16384
Spectral Size	3288

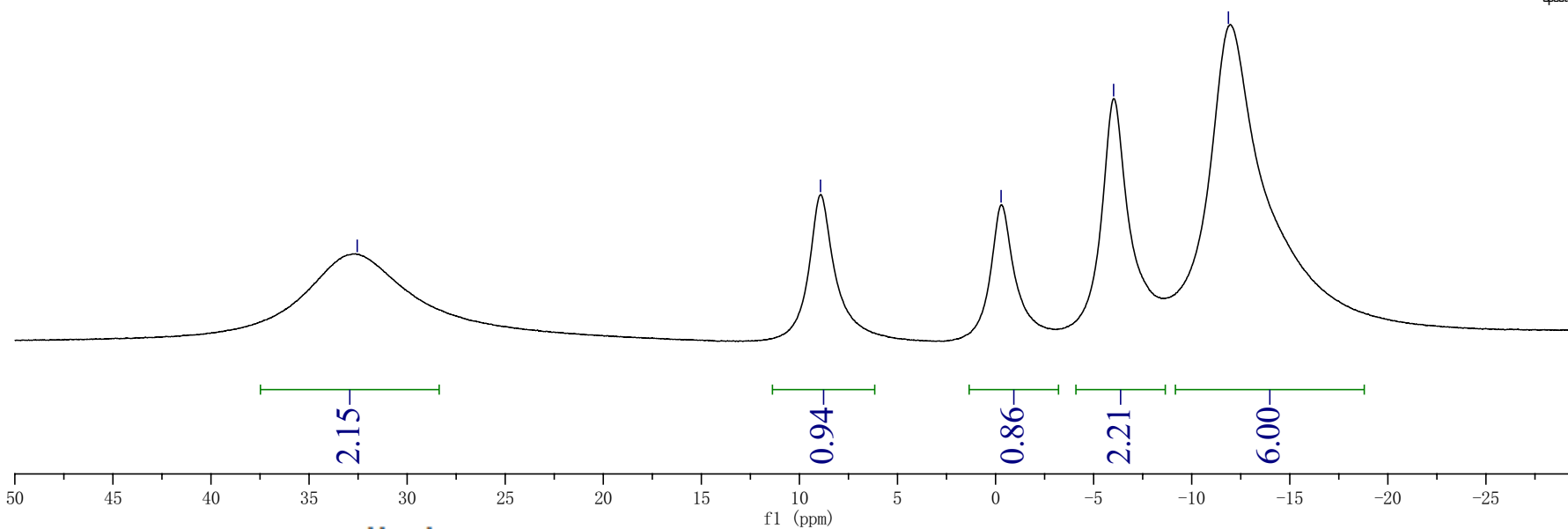
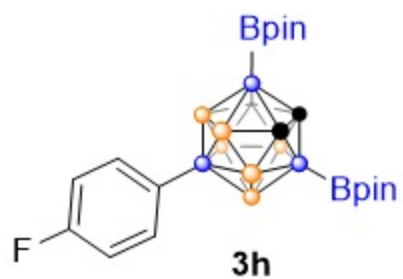
32.544

8.924

0.282

-6.018

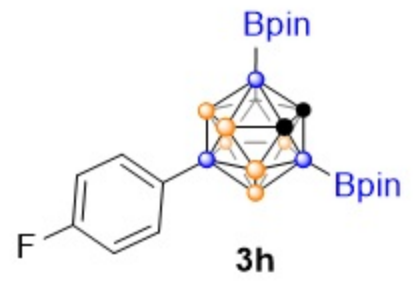
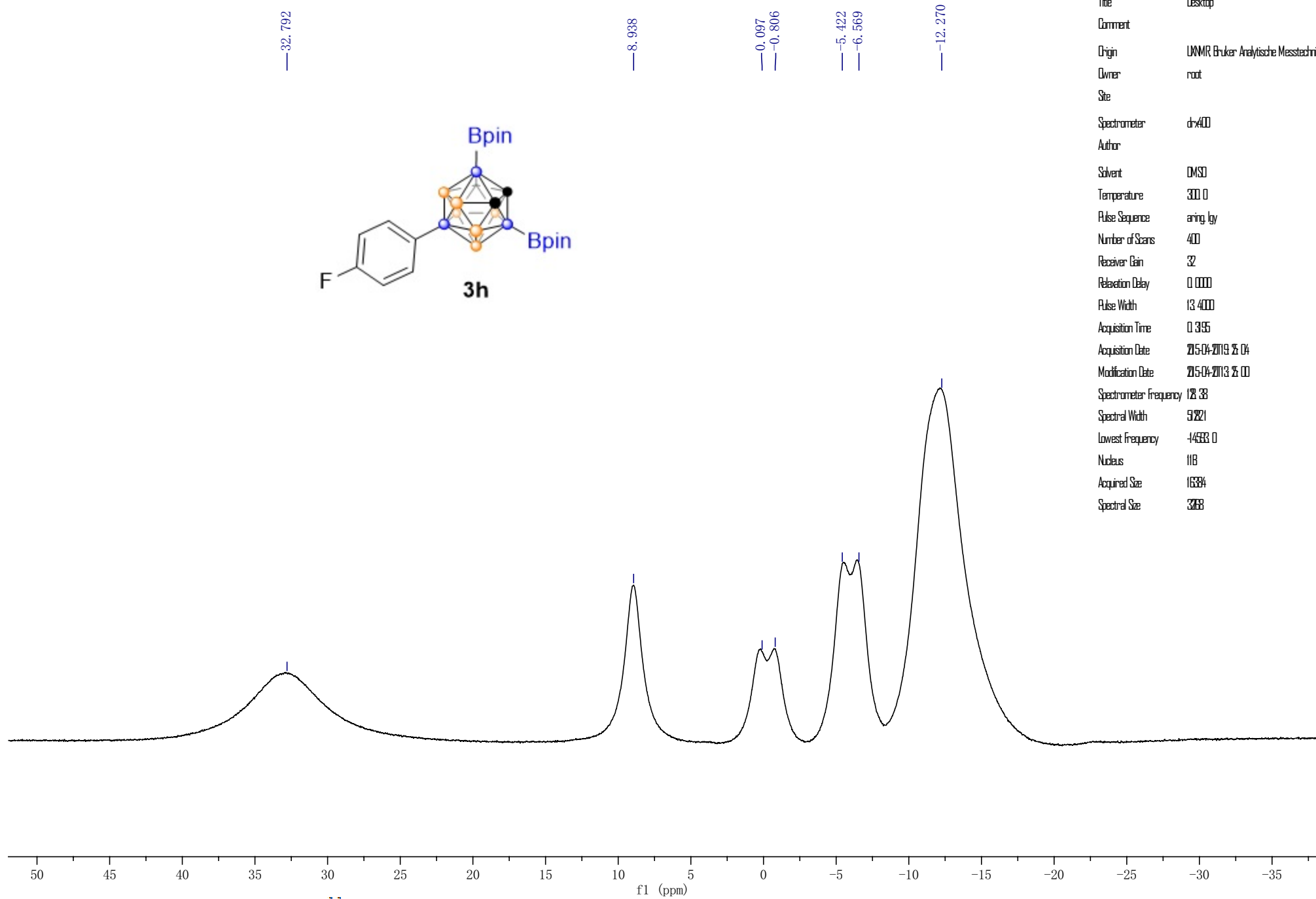
-11.871



Supplementary Figure 79. <sup>11</sup>B {<sup>1</sup>H} NMR Spectrum of 3h.

S100

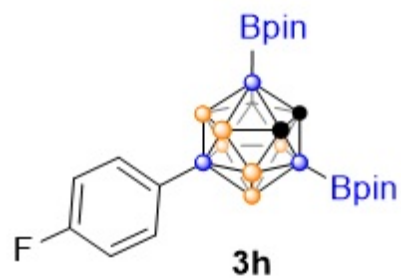
crf-4-45-B-coupling-CDCl<sub>3</sub>



Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr4-45-coupling/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dmx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.ty
Number of Scans	400
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.355
Acquisition Date	2015-04-20 19:25:04
Modification Date	2015-04-20 13:25:00
Spectrometer Frequency	128.38
Spectral Width	51.821
Lowest Frequency	-145883.0
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

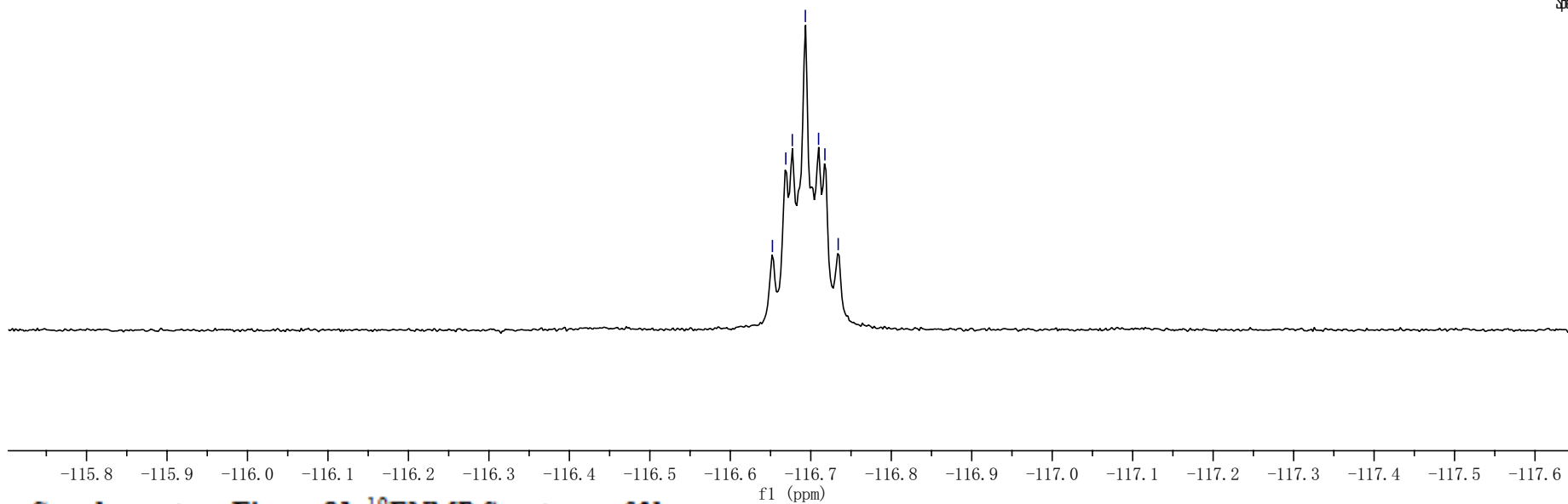
Supplementary Figure 80. <sup>11</sup>B NMR Spectrum of **3h**.

crf-4-45-F-CDCl<sub>3</sub>



-116.652  
-116.669  
-116.677  
-116.693  
-116.710  
-116.718  
-116.734

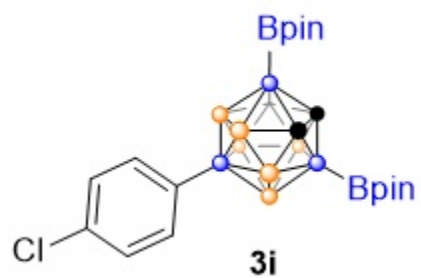
Parameter	Value
Title	21353-07-4-45_FLUORINE_0
Comment	21353-07-4-45
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	zgpg30
Number of Scans	16
Receiver Gain	56
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	21-03-2022 4: 00
Spectrometer Frequency	376.06
Spectral Width	8826.7
Lowest Frequency	-7691.4
Nucleus	19F
Acquired Size	65536
Spectral Size	13102



Supplementary Figure 81. <sup>19</sup>F NMR Spectrum of 3h.

crf-4-33-H-CDCl<sub>3</sub>

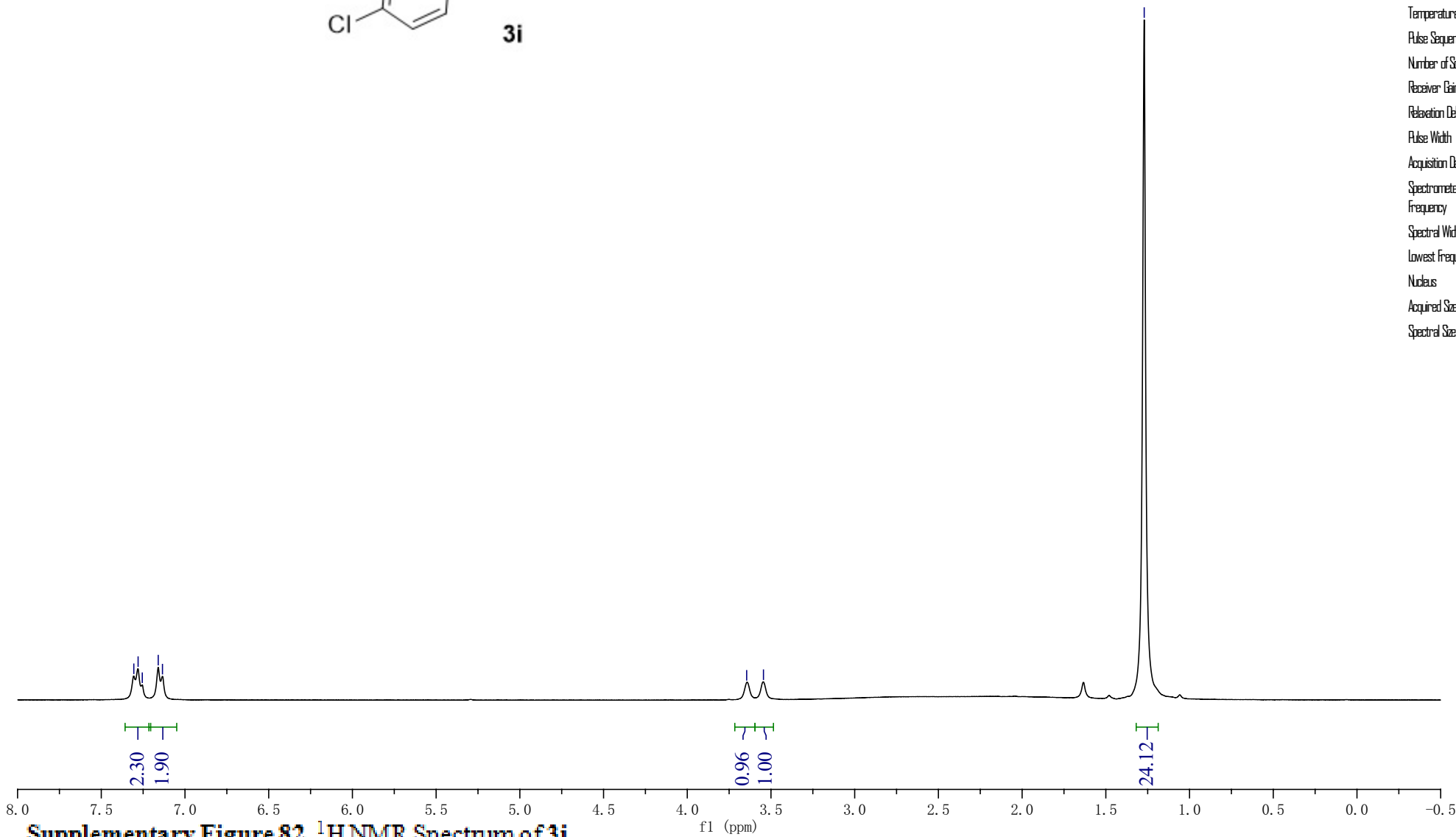
7.306  
7.280  
7.255  
7.160  
7.135



3.645  
3.545

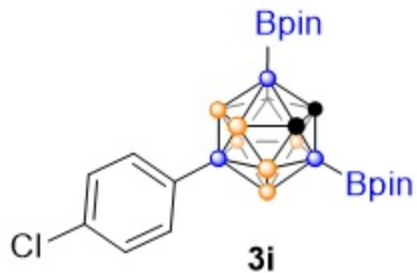
1.271

Parameter	Value
Title	crf-4-33
Comment	STANDARD OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	28.0
Pulse Sequence	sgpd
Number of Scans	8
Receiver Gain	28
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-10 09:58:28
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-71.1
Nucleus	<sup>1</sup> H
Acquired Size	10976
Spectral Size	3068



Supplementary Figure 82. <sup>1</sup>H NMR Spectrum of **3i**.

crf-4-33-H-CDCl<sub>3</sub>



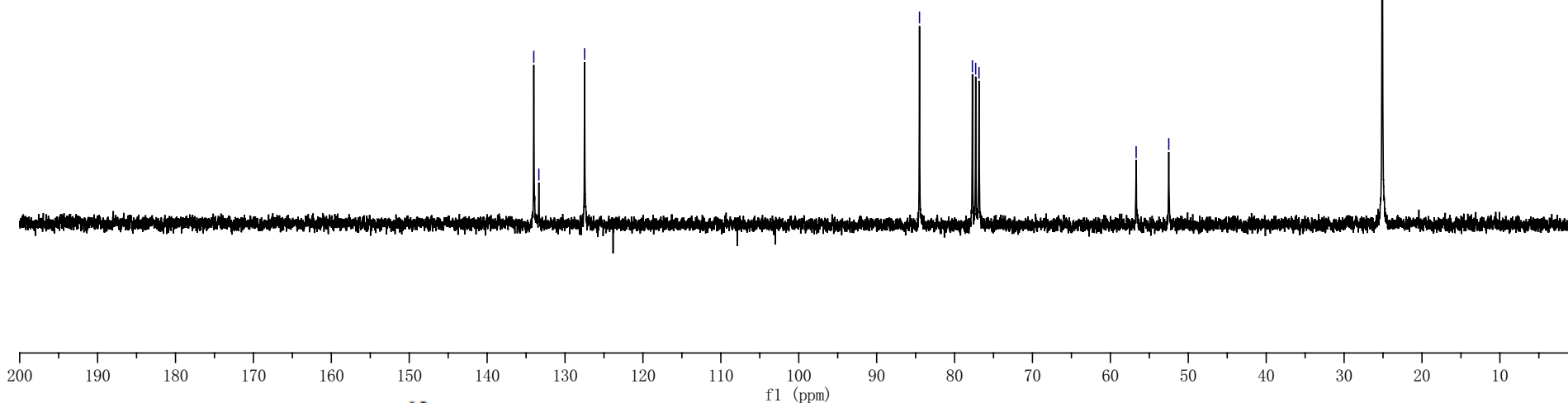
134.009  
133.362  
127.490

84.501  
77.711  
77.289  
76.864

56.692  
52.506

25.100

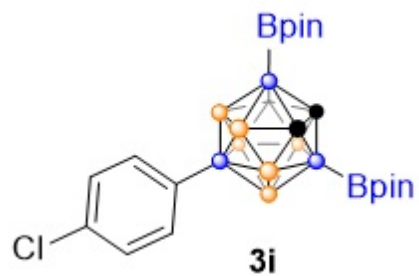
Parameter	Value
Title	crf-4-33-C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	21.0
Pulse Sequence	sgpul
Number of Scans	28
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-10T12:01:33
Spectrometer Frequency	76.45
Spectral Width	18897.0
Lowest Frequency	-462.8
Nucleus	13C
Acquired Size	2155
Spectral Size	65536



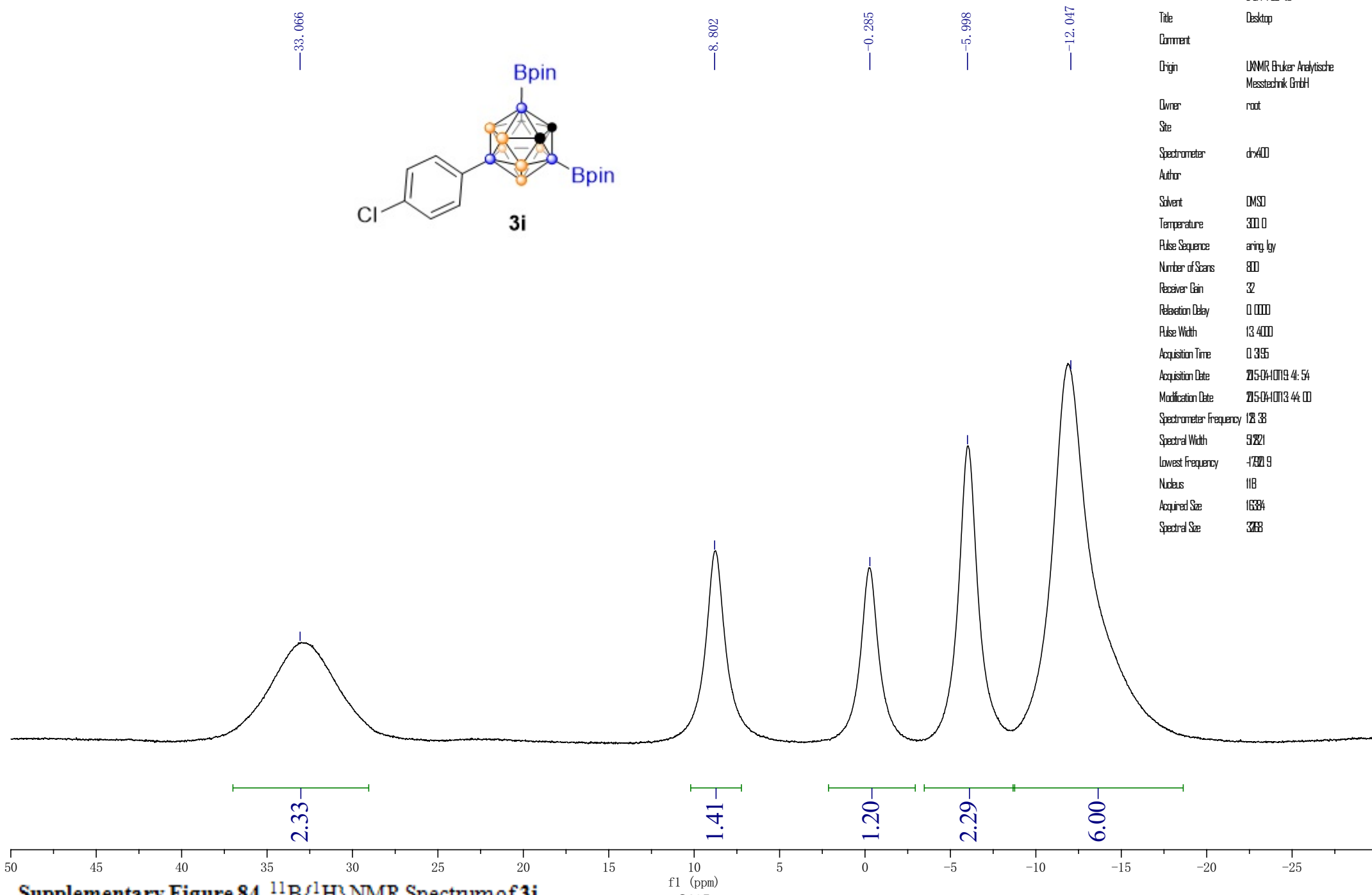
Supplementary Figure 83. <sup>13</sup>C NMR Spectrum of **3i**.



crf-4-33-B-decoupling-CDCl<sub>3</sub>



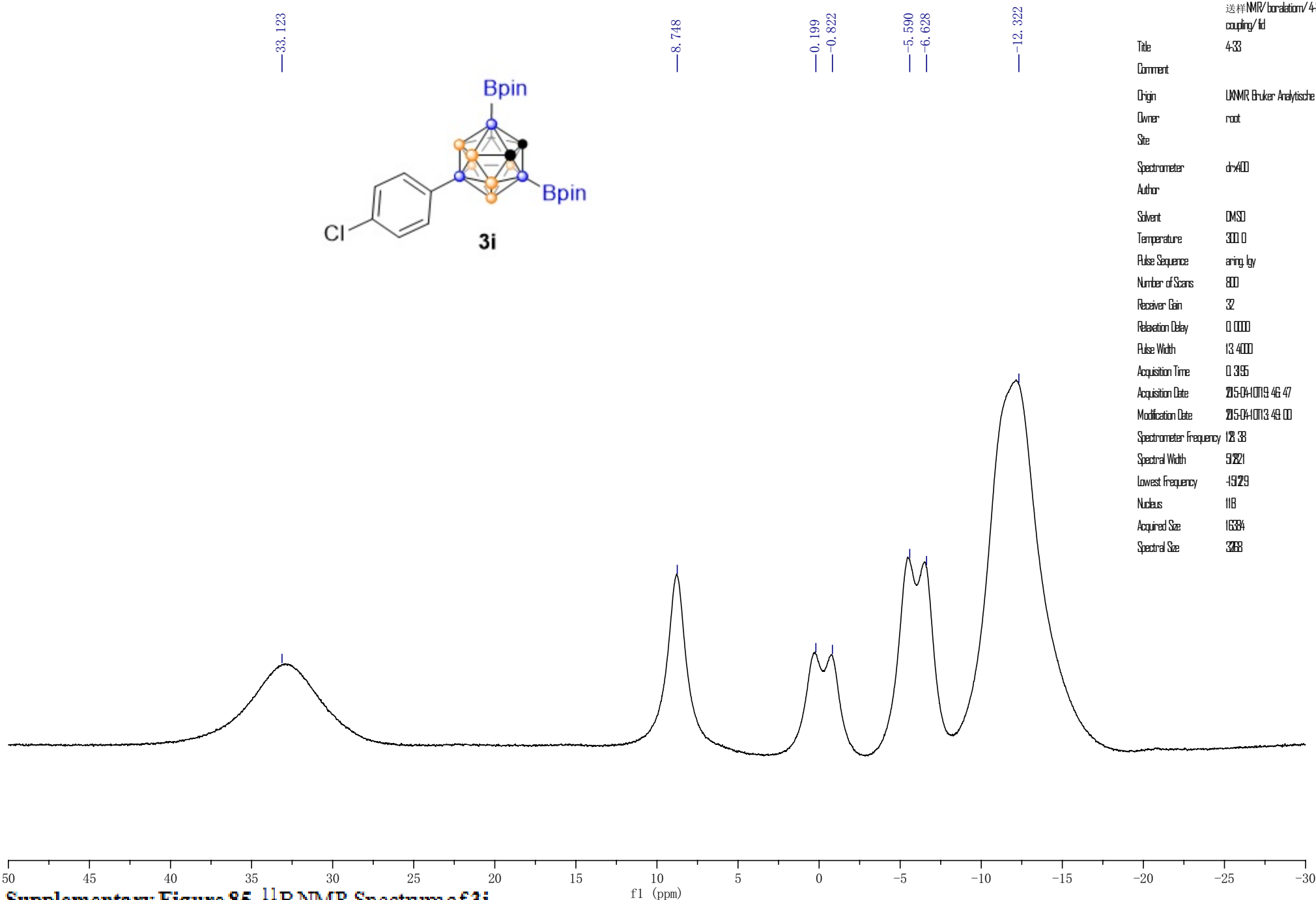
Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/bcrf4-33/td
Title	Desktop
Comment	
Origin	LNMNR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	zing1gy
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3155
Acquisition Date	2015-04-01 19:44:54
Modification Date	2015-04-01 13:44:00
Spectrometer Frequency	128.38
Spectral Width	9.821
Lowest Frequency	-1792.9
Nucleus	11B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 84. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of **3i**.

f1 (ppm)  
S105

crf-4-33-B-coupling-CDCl<sub>3</sub>

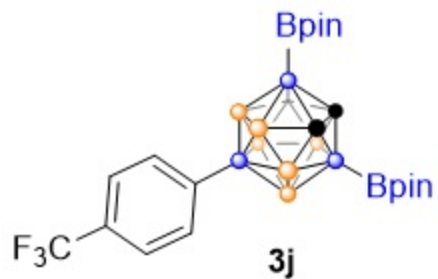


Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/work/送样NMR/correlation/4-33/b-cr4-33-coupling.fid
Title	4-33
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.ty
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3955
Acquisition Date	2015-04-01 19:46:47
Modification Date	2015-04-01 13:49:00
Spectrometer Frequency	128.38
Spectral Width	59.221
Lowest Frequency	-19.219
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

Supplementary Figure 85. <sup>11</sup>B NMR Spectrum of **3i**.

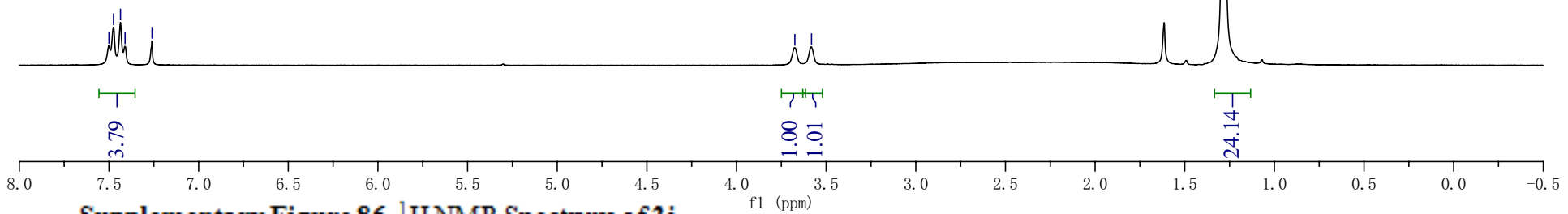
crf-4-46-H-CDCl<sub>3</sub>

7.500  
7.475  
7.436  
7.410  
7.260



3.675  
3.582

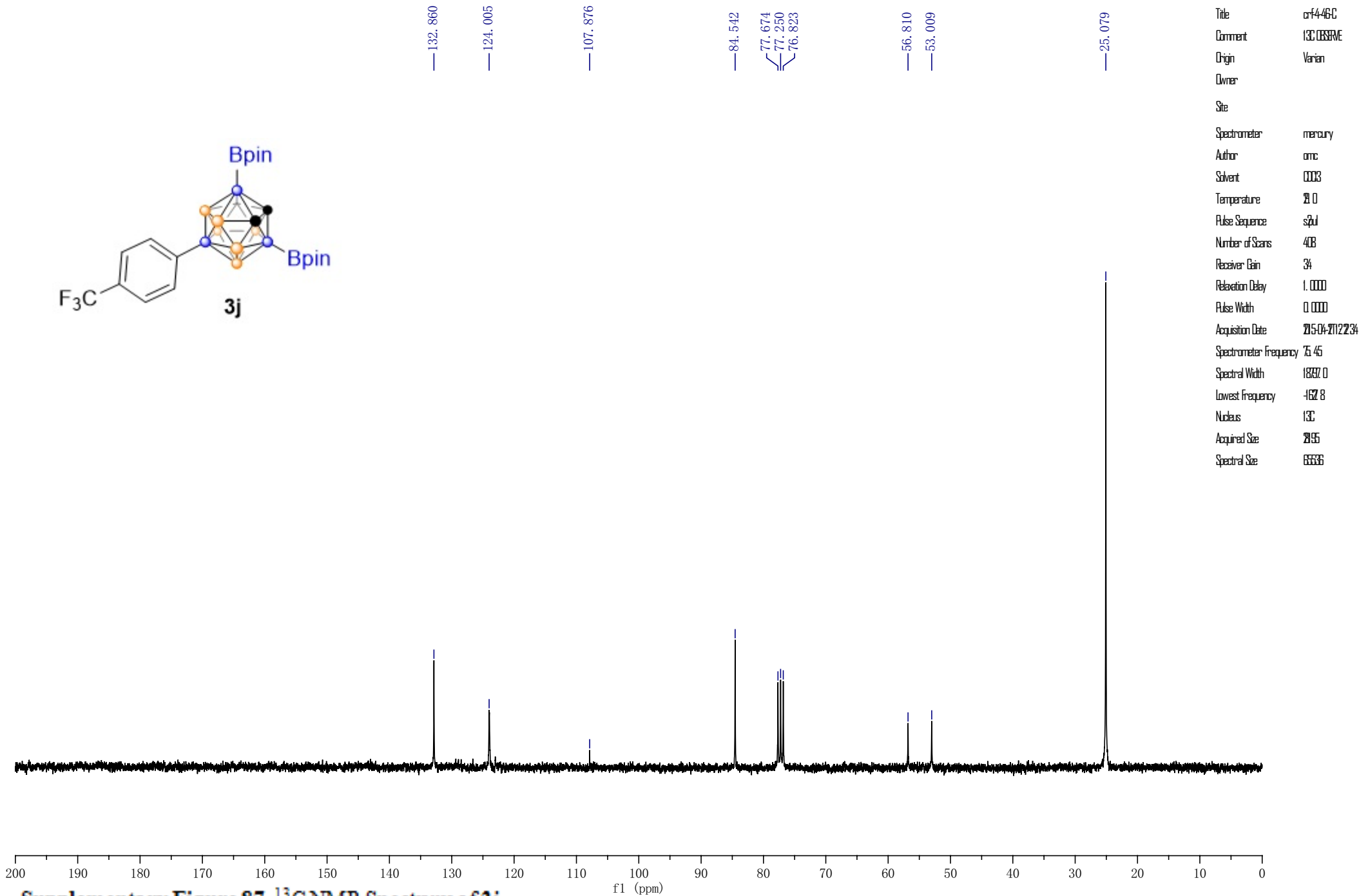
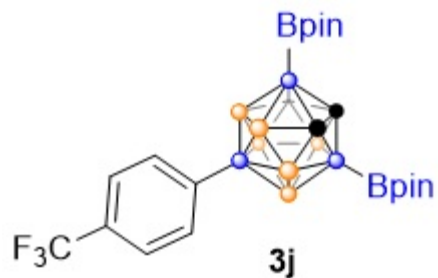
1.281



Parameter	Value
Title	crf4-46H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	20.0
Pulse Sequence	sZul
Number of Scans	12
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-27 11:25:33
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-709.3
Nucleus	1H
Acquired Size	10376
Spectral Size	3268

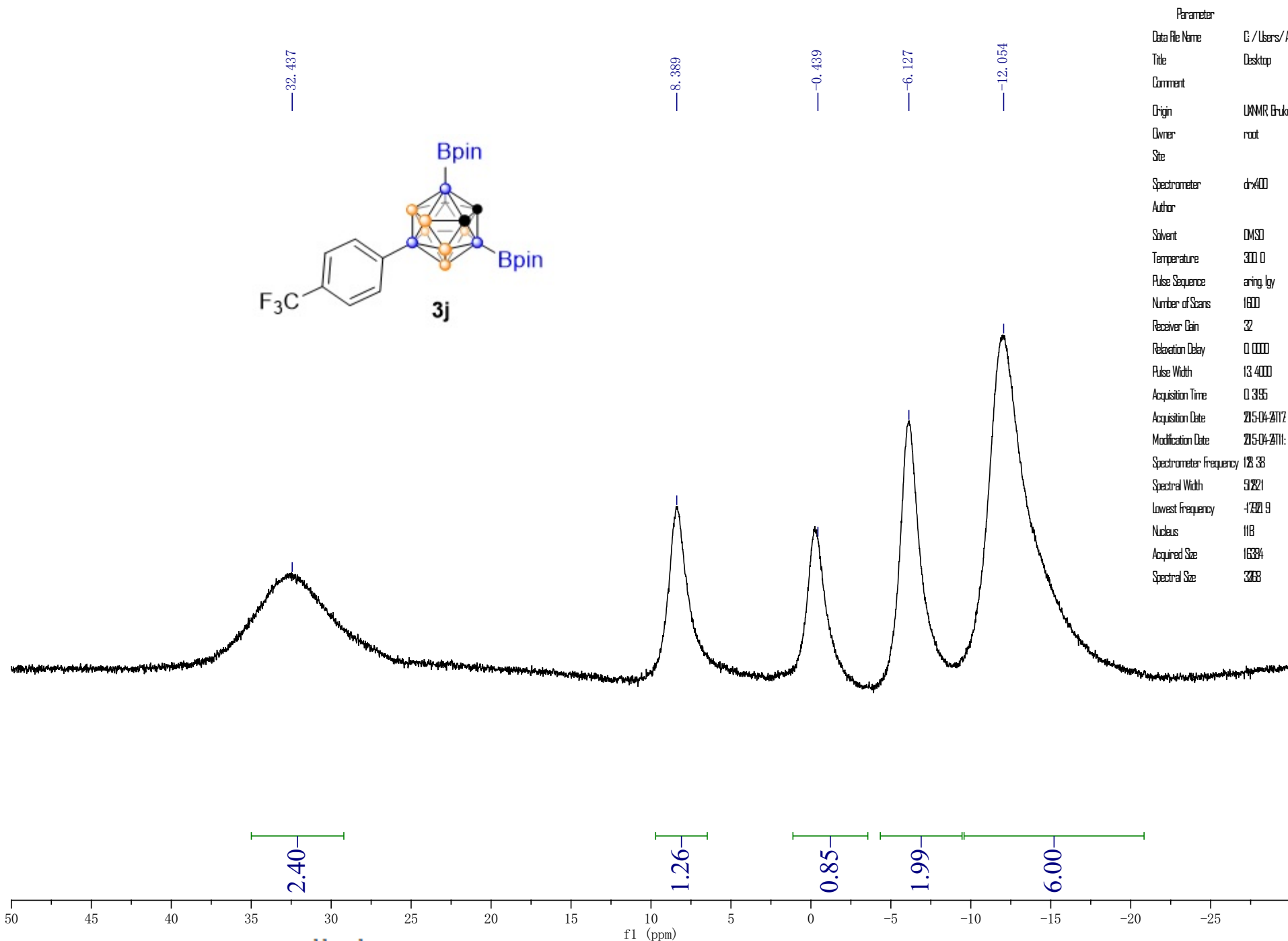
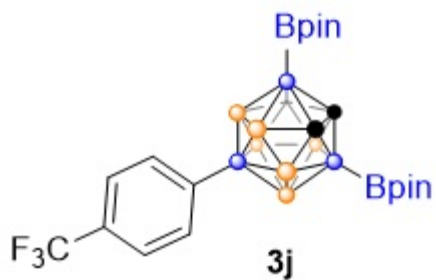
Supplementary Figure 86. <sup>1</sup>H NMR Spectrum of **3j**.

crf-4-46-C-CDCl<sub>3</sub>



Parameter	Value
Title	crf-4-46-C
Comment	13C, EBSRME
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	21.0
Pulse Sequence	sgpul
Number of Scans	408
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-20 12:23:34
Spectrometer Frequency	76.45
Spectral Width	18897.0
Lowest Frequency	-162.8
Nucleus	13C
Acquired Size	2955
Spectral Size	65536

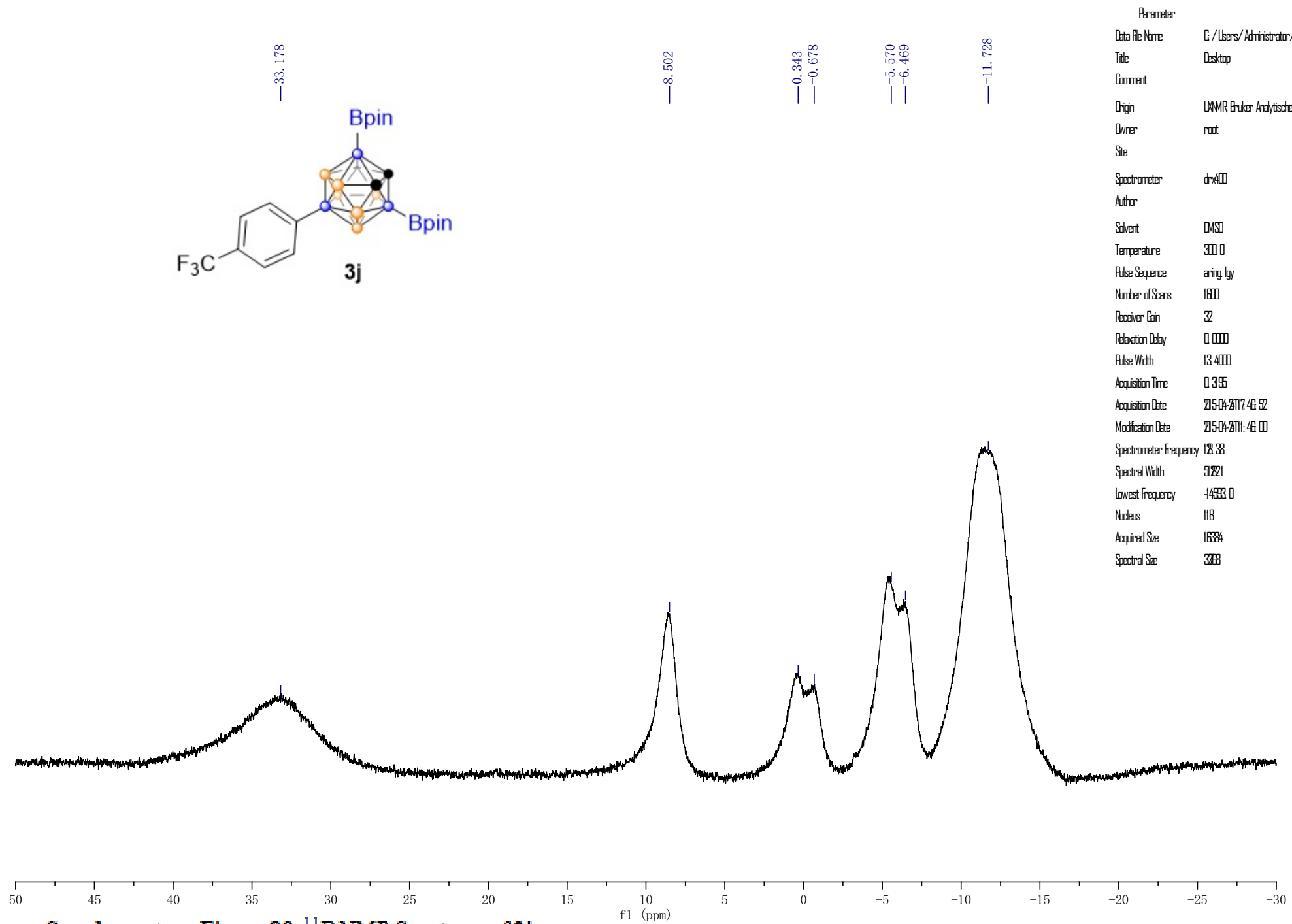
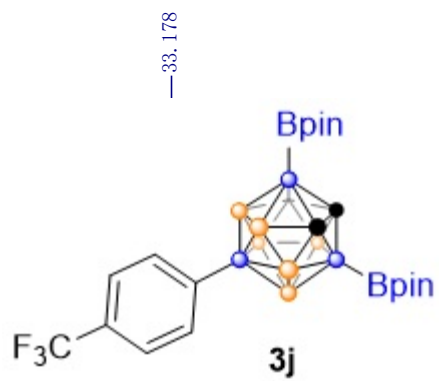
Supplementary Figure 87. <sup>13</sup>C NMR Spectrum of **3j**.



Parameter	Value
Data File Name	G:/Users/Administrator/Desktop/b-crf-4-46/td
Title	Desktop
Comment	
Origin	UNMR, Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aning_lg
Number of Scans	1600
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3155
Acquisition Date	2015-04-20T17:14:48
Modification Date	2015-04-20T11:14:00
Spectrometer Frequency	128.38
Spectral Width	51.221
Lowest Frequency	-17.0019
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

Supplementary Figure 88. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of **3j**.

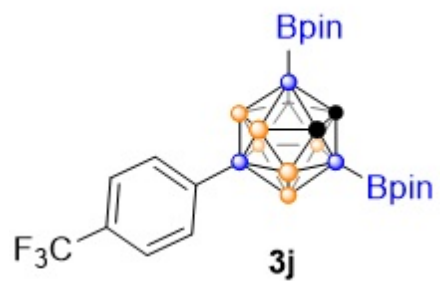
crf-4-46-B-coupling-CDCl<sub>3</sub>



Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-crf4-46-coupling/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring 1g
Number of Scans	1800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.355
Acquisition Date	2015-04-21T17:46:52
Modification Date	2015-04-21T17:46:00
Spectrometer Frequency	128.38
Spectral Width	51.821
Lowest Frequency	-44583.0
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

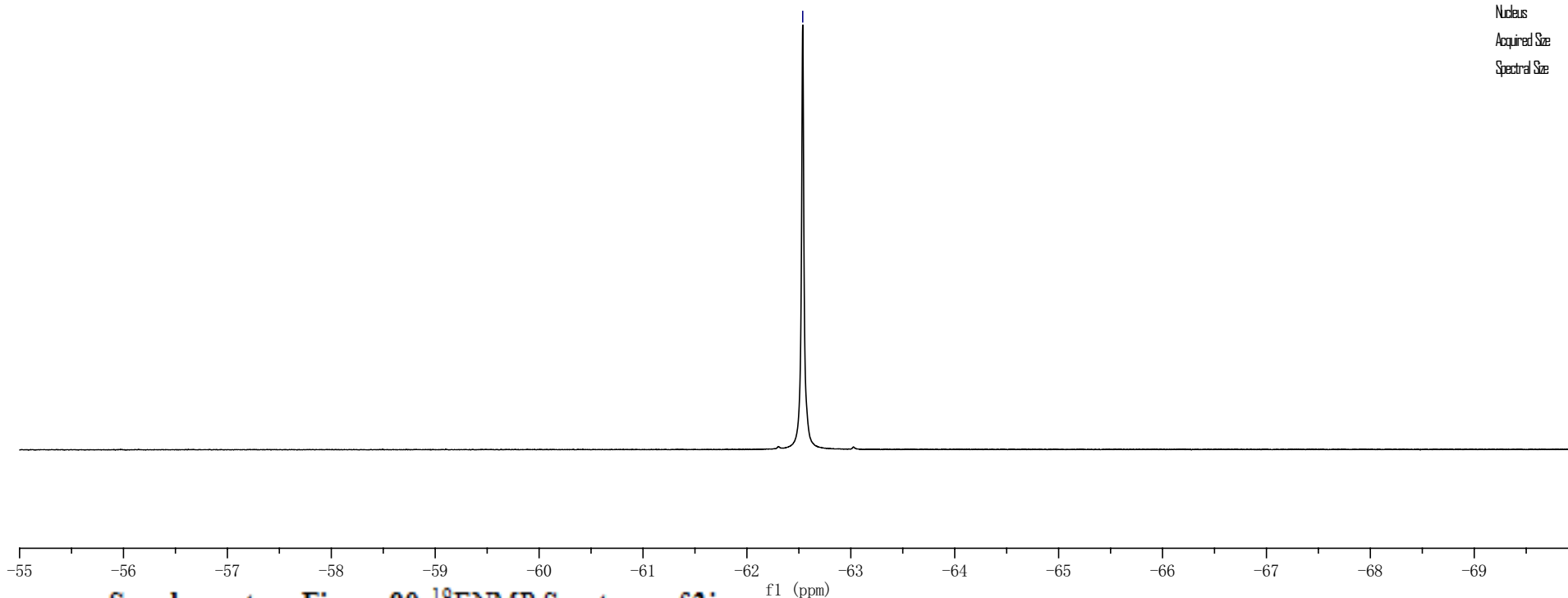
Supplementary Figure 89. <sup>11</sup>B NMR Spectrum of **3j**.

crf-4-46-F-CDCl<sub>3</sub>



62.537

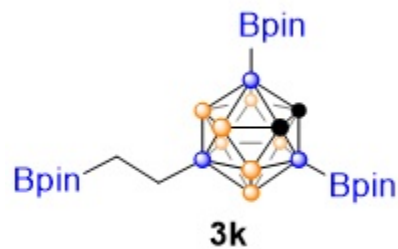
Parameter	Value
Title	21353-cr4-46_ALLONE_0
Comment	21353-cr4-46
Origin	Varian
Owner	
Site	
Spectrometer	nmr5
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	zgpg30
Number of Scans	16
Receiver Gain	56
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	21-08-04 17:08:19
Spectrometer Frequency	316.06
Spectral Width	8885.7
Lowest Frequency	-7830.4
Nucleus	19F
Acquired Size	65535
Spectral Size	13102



Supplementary Figure 90. <sup>19</sup>F NMR Spectrum of **3j**.

crf-4-21-H-CDCl<sub>3</sub>

7.260

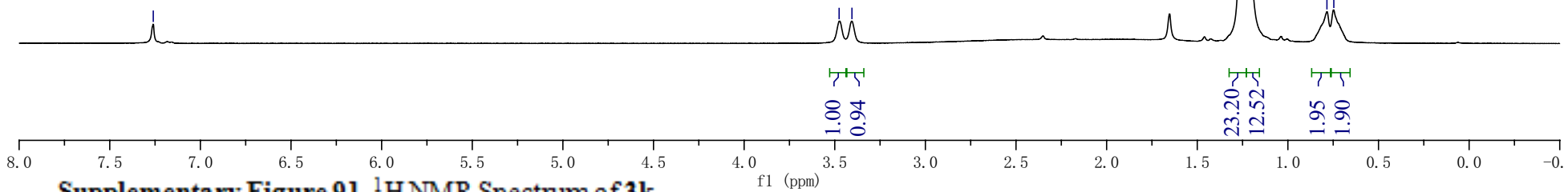


3.476  
3.405

1.250  
1.215

0.784  
0.747

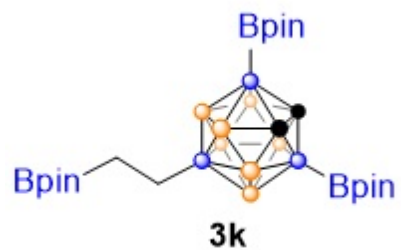
Parameter	Value
Title	crf-4-21-H-CDCl <sub>3</sub>
Comment	STANDARD 1H NMR
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	29.0
Pulse Sequence	zgpg30
Number of Scans	8
Receiver Gain	28
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-08 10:32:39
Spectrometer Frequency	300.03
Spectral Width	5464.5
Lowest Frequency	-708.6
Nucleus	1H
Acquired Size	10976
Spectral Size	3268



Supplementary Figure 91. <sup>1</sup>H NMR Spectrum of 3k.



crf-4-21-H-CDCl<sub>3</sub>

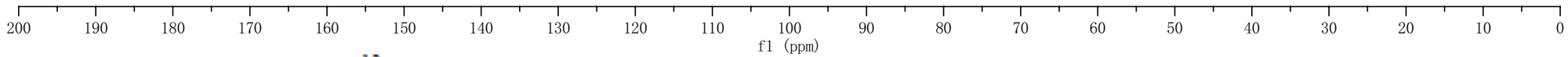


84.212  
82.783  
77.715  
77.289  
76.865

56.294  
51.010

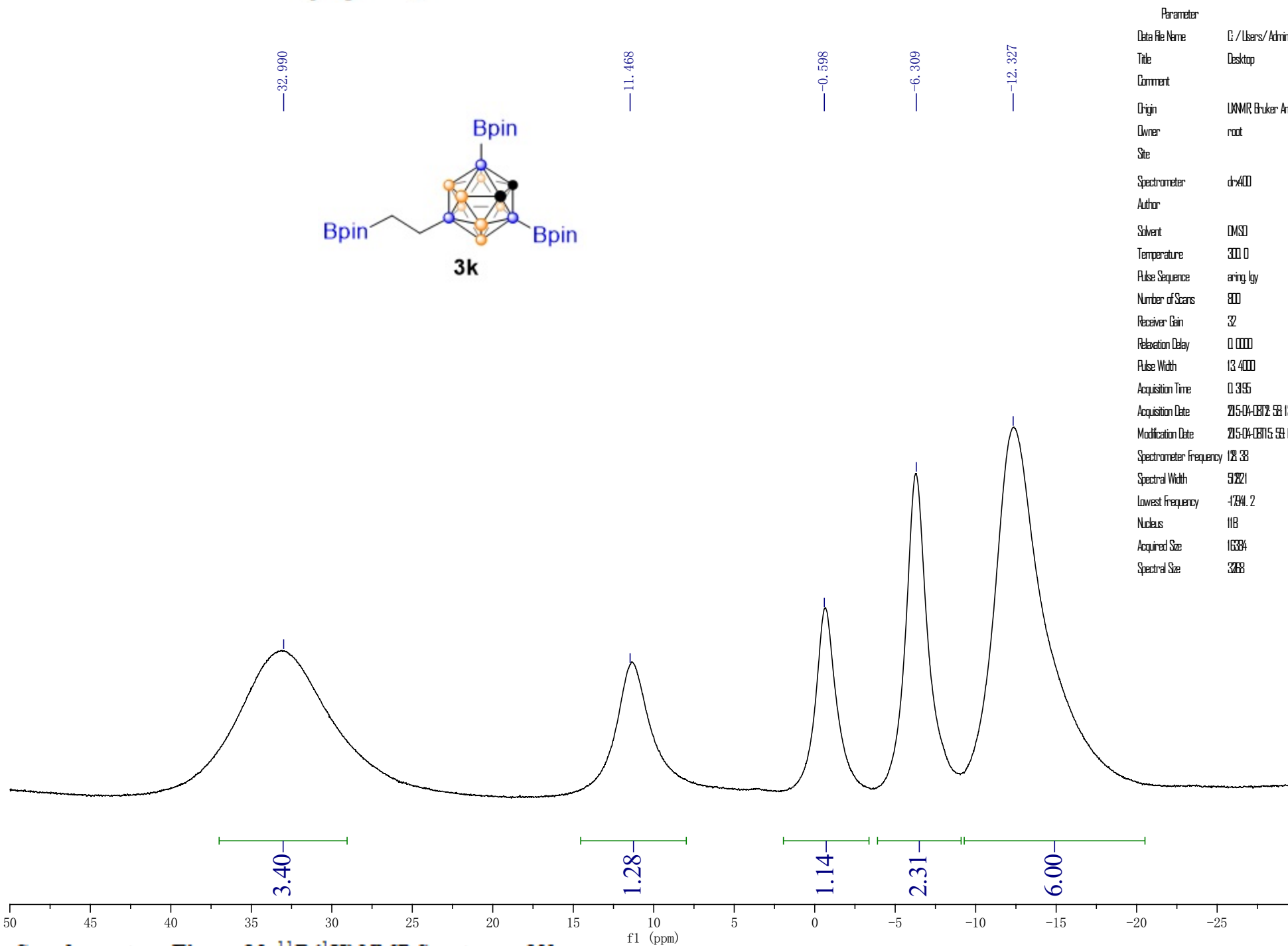
25.052

Parameter	Value
Title	crf-4-2-G-0408
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	21.0
Pulse Sequence	sZul
Number of Scans	128
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-08 11: 2: 38
Spectrometer Frequency	76.45
Spectral Width	18897.0
Lowest Frequency	-162.8
Nucleus	13C
Acquired Size	2955
Spectral Size	65536



Supplementary Figure 92. <sup>13</sup>C NMR Spectrum of 3k.

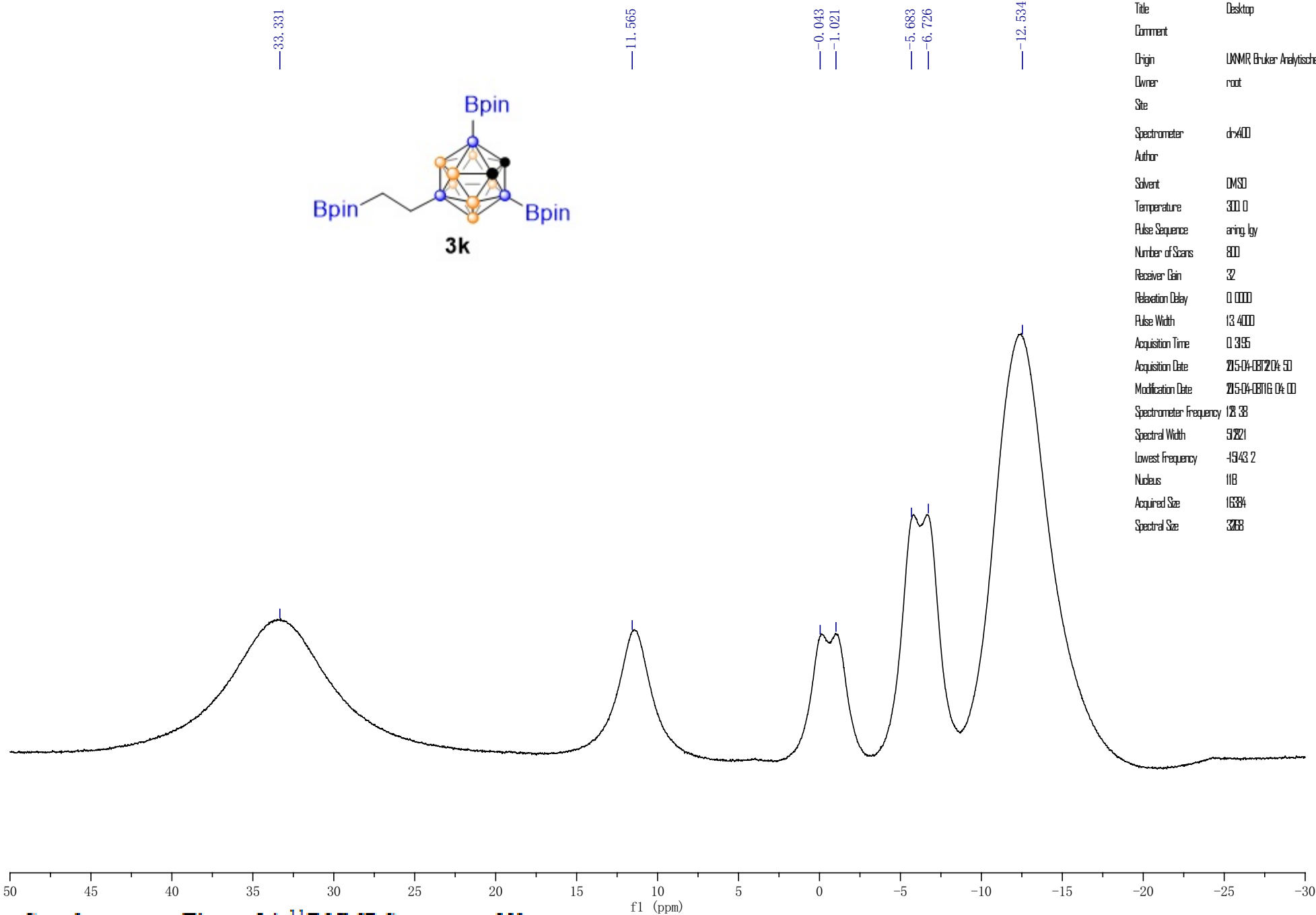
crf-4-21-B-decoupling-CDCl<sub>3</sub>



Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-crf-4-21-1d
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.1g
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-04-08 12:58:13
Modification Date	2015-04-08 15:58:00
Spectrometer Frequency	128.38
Spectral Width	51.821
Lowest Frequency	-17.894.2
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

Supplementary Figure 93. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of **3k**.

crf-4-21-B-coupling-CDCl<sub>3</sub>



Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr-4-2-coupling/fid
Title	Desktop
Comment	
Origin	LUMMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dmx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	zing_1g
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3195
Acquisition Date	2015-04-08 12:04:50
Modification Date	2015-04-08 16:04:00
Spectrometer Frequency	128.38
Spectral Width	5.2821
Lowest Frequency	-19.432
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

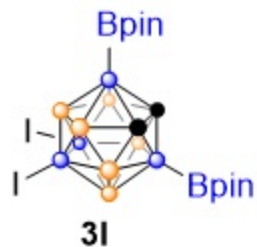
Supplementary Figure 94. <sup>11</sup>B NMR Spectrum of **3k**.

crf-3-76-H-CDCl<sub>3</sub>

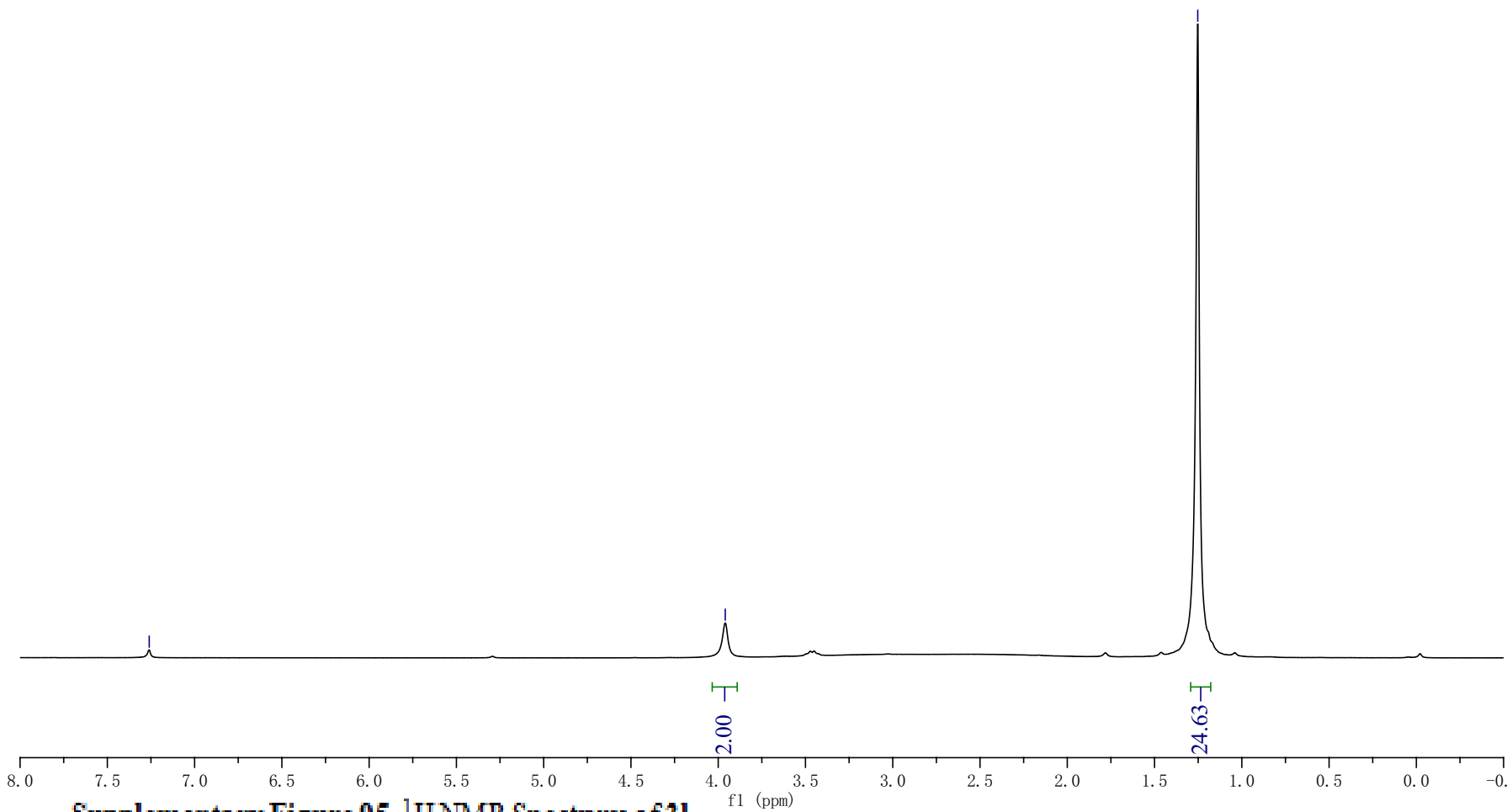
7.260

3.960

1.252

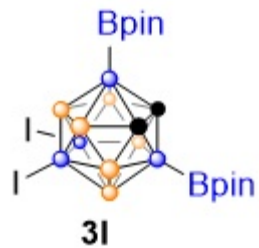


Parameter	Value
Title	crf3-76-H
Comment	STANDARD OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	21.0
Pulse Sequence	zgpg30
Number of Scans	8
Receiver Gain	21
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-02-17 24:19
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-708.5
Nucleus	<sup>1</sup> H
Acquired Size	10816
Spectral Size	3288



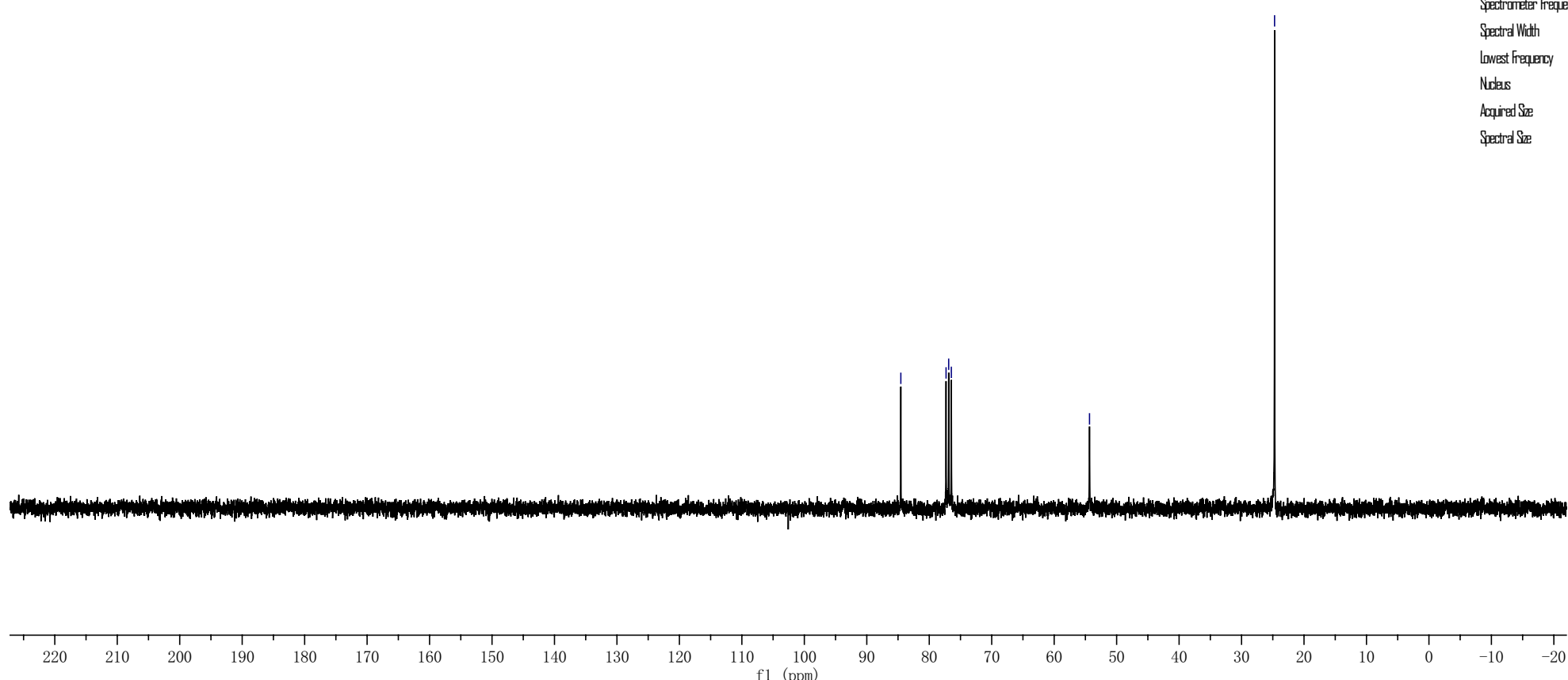
Supplementary Figure 95. <sup>1</sup>H NMR Spectrum of 31.

crf-3-76-C-CDCl<sub>3</sub>



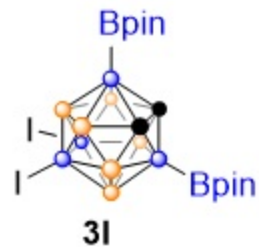
84.549  
77.311  
76.889  
76.465  
54.342  
24.714

Parameter	Value
Title	crf-3-76-C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	28.0
Pulse Sequence	sZuj
Number of Scans	40
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-02-17 2:42:05
Spectrometer Frequency	75.45
Spectral Width	18887.0
Lowest Frequency	-1658.2
Nucleus	13C
Acquired Size	2895
Spectral Size	65536



Supplementary Figure 96. <sup>13</sup>C NMR Spectrum of 31.

crf-3-76-B-decoupling-CDCl<sub>3</sub>

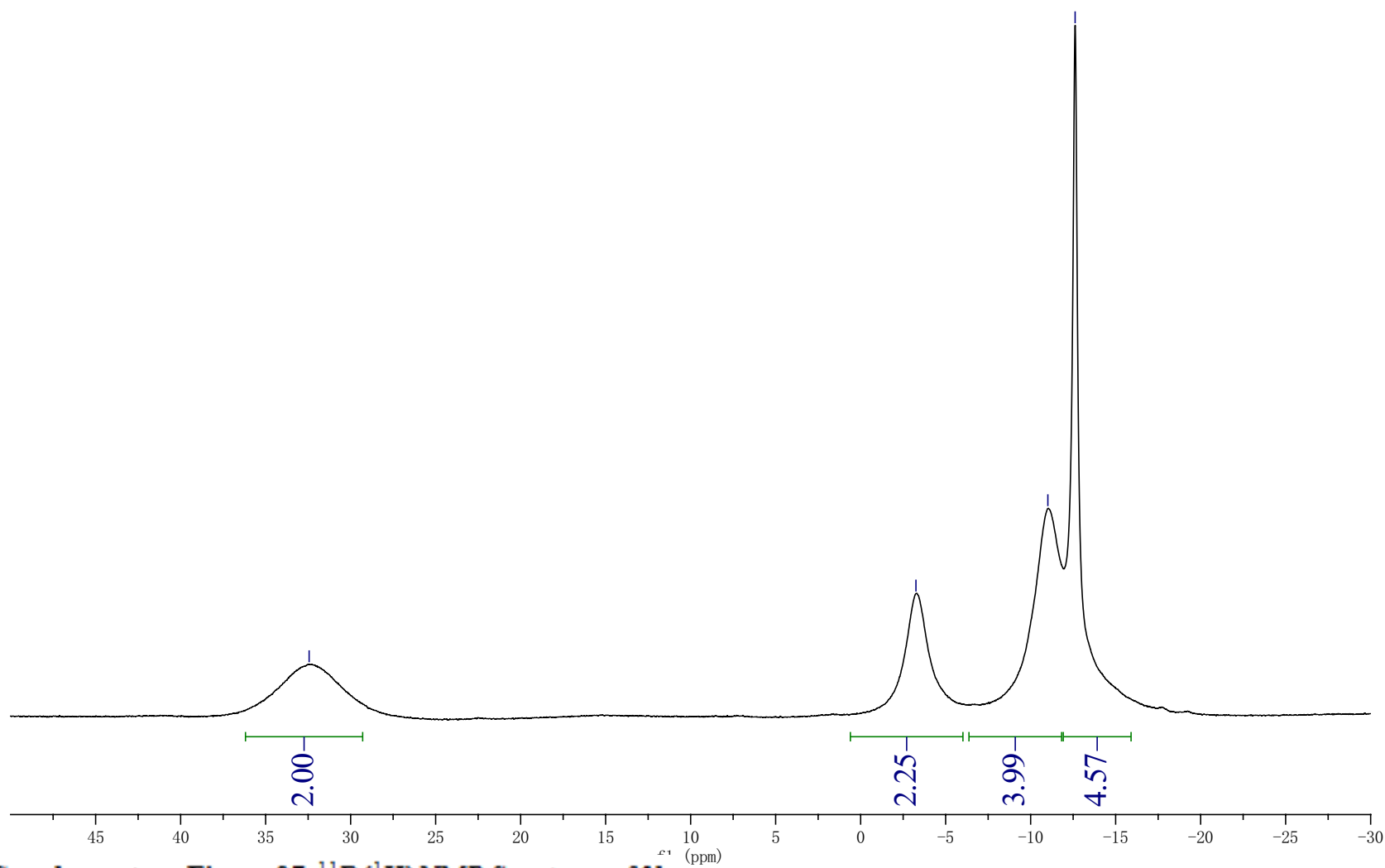


32.441

-3.253

-11.012

-12.617

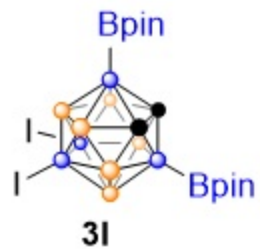


Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-crf-3-76/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dr400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.1g
Number of Scans	435
Receiver Gain	32
Relaxation Delay	0.000
Pulse Width	13.400
Acquisition Time	0.395
Acquisition Date	2015-02-04 15:59:59
Modification Date	2015-02-04 18:00:00
Spectrometer Frequency	128.38
Spectral Width	59.221
Lowest Frequency	-18565.1
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

Supplementary Figure 97. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of 31.

crf-3-76-B-coupling-CDCl<sub>3</sub>

32.661



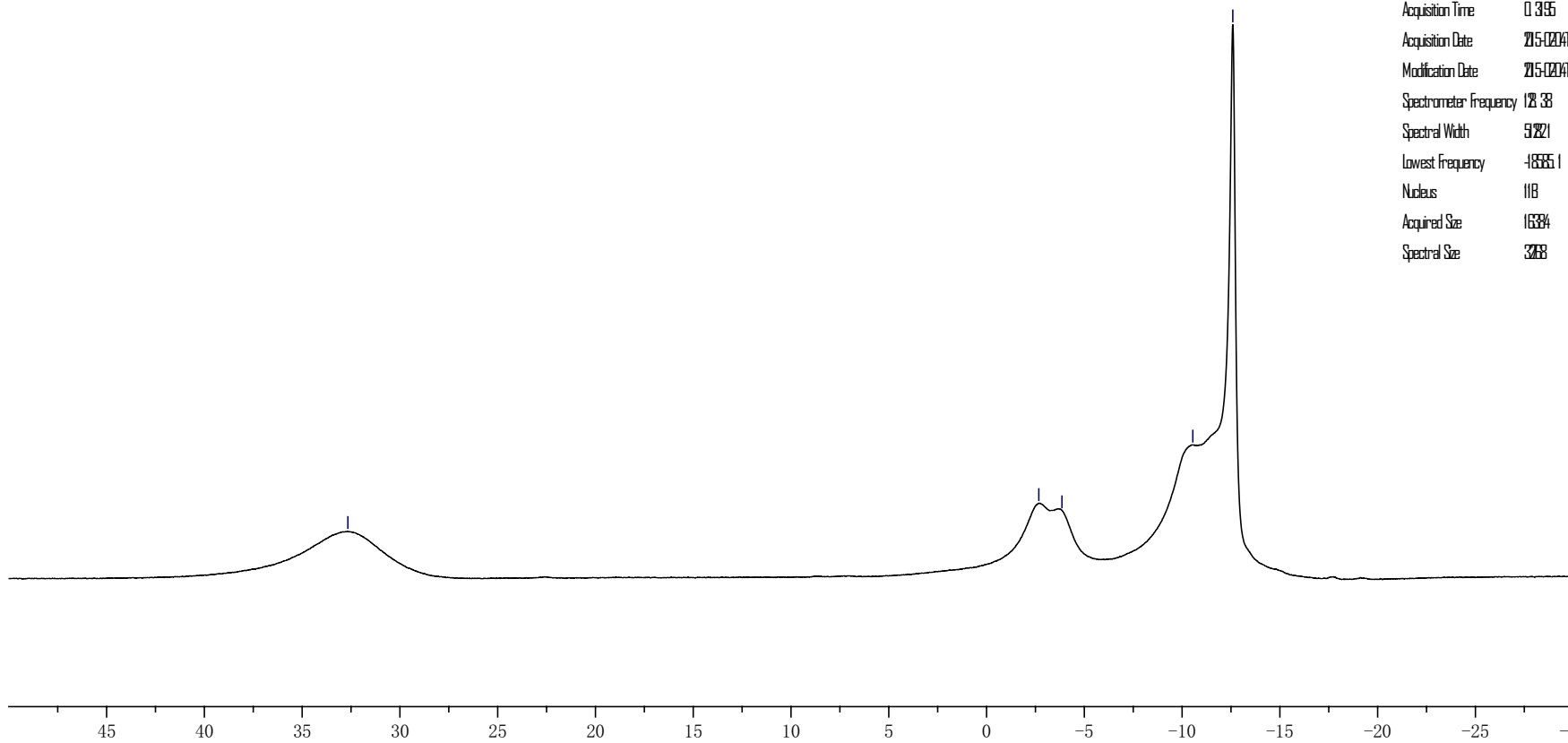
-2.672

-3.856

-10.548

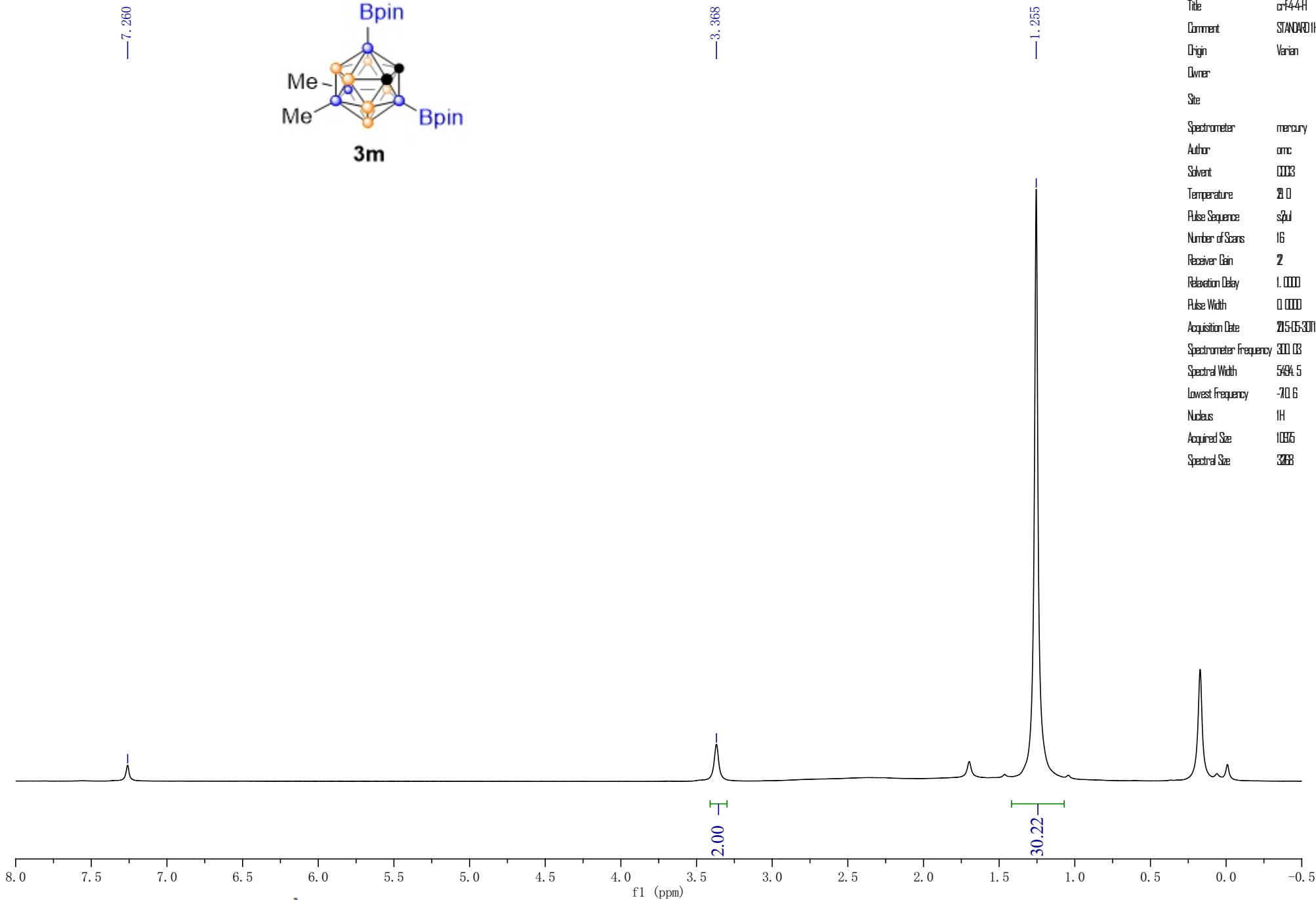
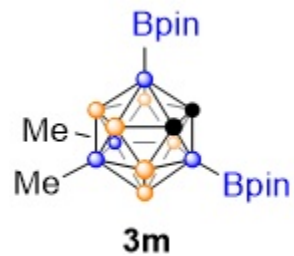
-12.592

Parameter	Value
Data File Name	G:/Users/Administrator/Desktop/b-crf-3-76-withoutdecoupling/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	drx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring-1gy
Number of Scans	666
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-02-04T16:01:17
Modification Date	2015-02-04T16:04:00
Spectrometer Frequency	128.38
Spectral Width	51921
Lowest Frequency	-18885.1
Nucleus	11B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 98. <sup>11</sup>B NMR Spectrum of 31.

crf-4-4-H-CDCl<sub>3</sub>

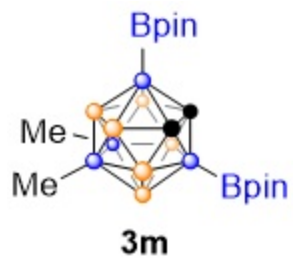


Parameter	Value
Title	crf-4-4-H
Comment	STANDARD 1H COSY
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	29.0
Pulse Sequence	sZul
Number of Scans	16
Receiver Gain	2
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-05-30T14:49:39
Spectrometer Frequency	300.03
Spectral Width	5694.5
Lowest Frequency	-70.6
Nucleus	1H
Acquired Size	10375
Spectral Size	3268

Supplementary Figure 99. <sup>1</sup>H NMR Spectrum of **3m**.



crf-4-4-C-CDCl<sub>3</sub>

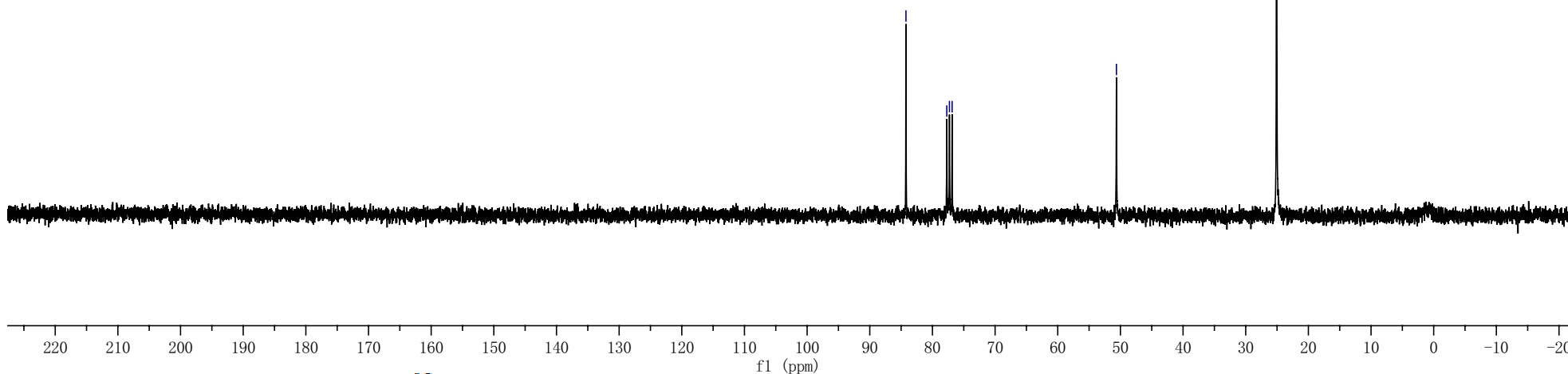


84.225  
77.708  
77.283  
76.859

50.633

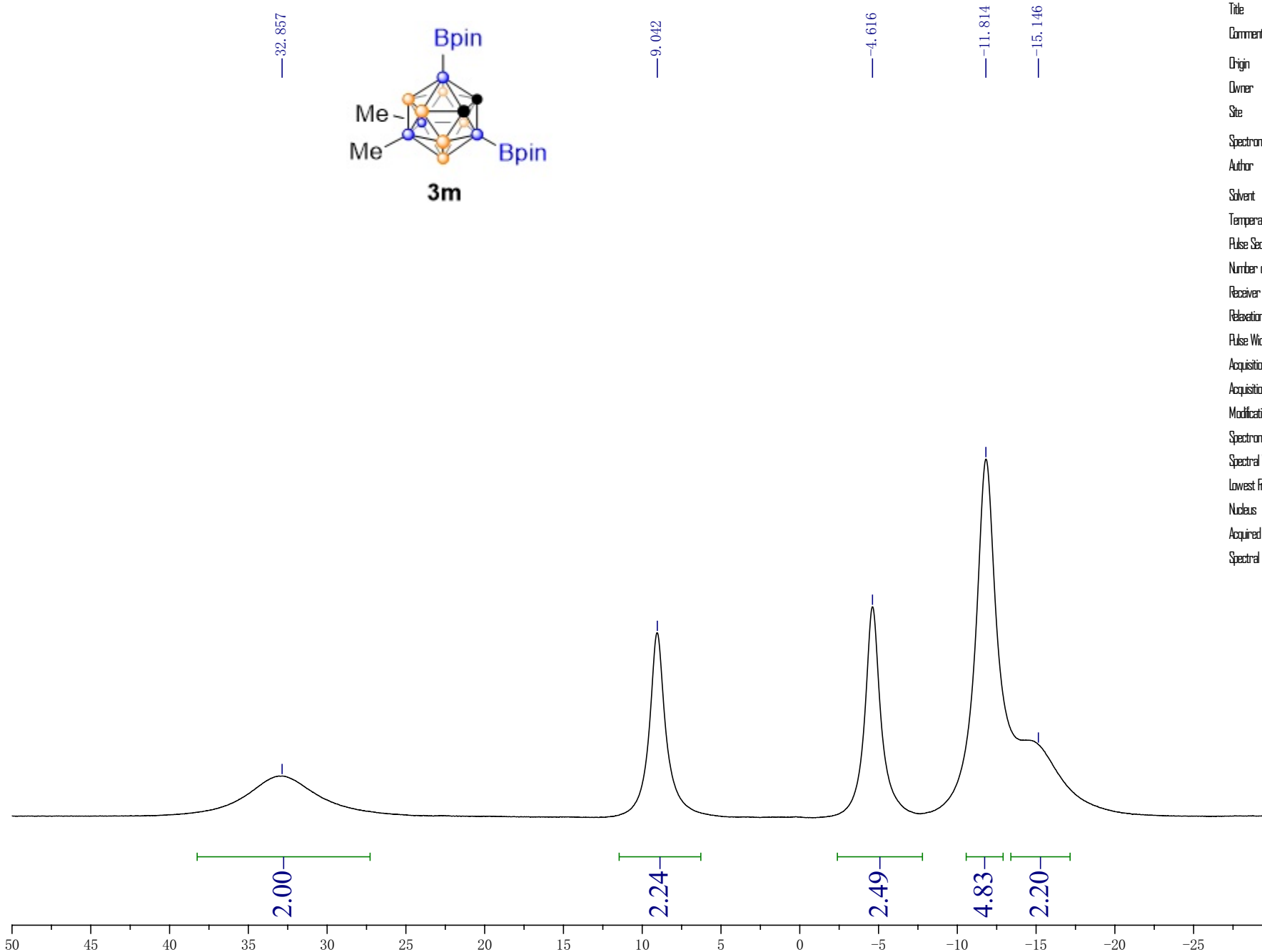
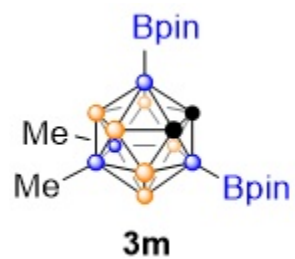
25.075

Parameter	Value
Title	crf-4-4-C-CDCl <sub>3</sub>
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	29.0
Pulse Sequence	sgul
Number of Scans	48
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-05-30 15:06:06
Spectrometer Frequency	76.45
Spectral Width	18797.0
Lowest Frequency	-162.8
Nucleus	13C
Acquired Size	2955
Spectral Size	65536



Supplementary Figure 100. <sup>13</sup>C NMR Spectrum of 3m.

crf-4-4-B-decouplinh-CDCl<sub>3</sub>



Parameter	Value
Data File Name	G:/Users/Administrator/Desktop/work/送 样NMR/borane/4-4/b-cr4-4/fid
Title	44
Comment	
Origin	UMMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dm400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.tgy
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-06-01 19:25:28
Modification Date	2015-06-01 13:25:00
Spectrometer Frequency	128.38
Spectral Width	59221
Lowest Frequency	-14466.9
Nucleus	11B
Acquired Size	16394
Spectral Size	3268

Supplementary Figure 101. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of 3m.

crf-4-4-B-coupling-CDCl<sub>3</sub>

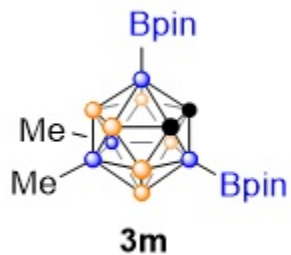
32.971

9.101

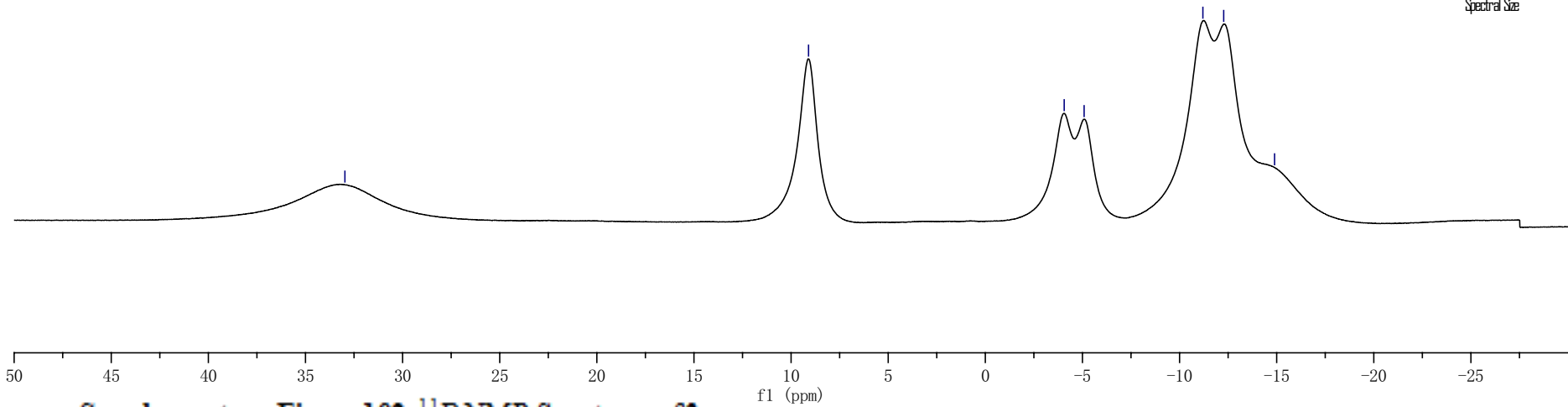
4.060  
5.087

11.201  
12.272

14.892



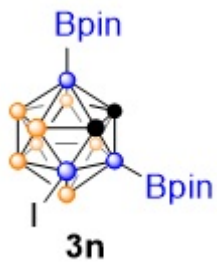
Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/work/送样NMR/borane/4-4/b-cr4-4-coupling/4d
Title	4-4
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	drx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring_1g
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.355
Acquisition Date	2015-08-07 19:18:49
Modification Date	2015-08-07 13:18:00
Spectrometer Frequency	128.38
Spectral Width	51221
Lowest Frequency	-14466.9
Nucleus	11B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 102. <sup>11</sup>B NMR Spectrum of **3m**.

crf-4-7-H-CDCl<sub>3</sub>

7.260



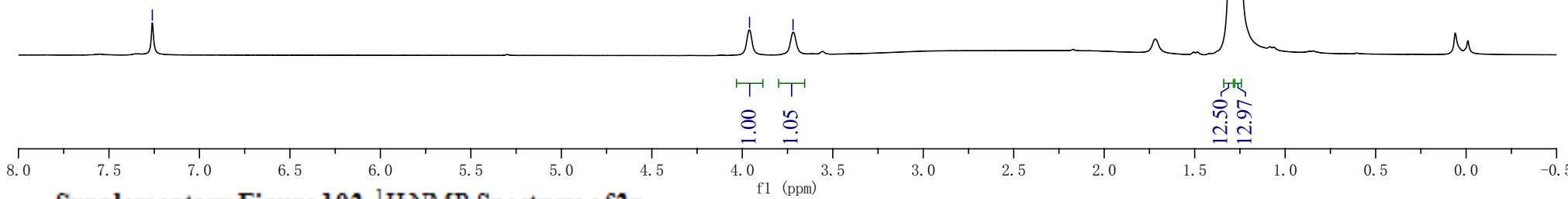
3.960

3.719

1.296

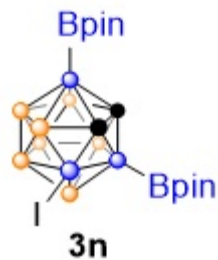
1.275

Parameter	Value
Title	crf-4-7H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	20.0
Pulse Sequence	sgpd
Number of Scans	16
Receiver Gain	2
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-03-27 15:42:42
Spectrometer	300.03
Frequency	
Spectral Width	5494.5
Lowest Frequency	-703.6
Nucleus	1H
Acquired Size	10375
Spectral Size	3268



Supplementary Figure 103. <sup>1</sup>H NMR Spectrum of **3n**.

crf-4-7-C-CDCl<sub>3</sub>

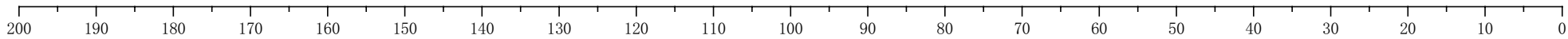


84.809  
84.651

77.689  
77.264  
76.842

59.930

25.236  
25.132  
25.091

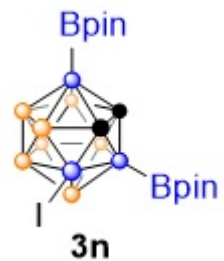


Parameter	Value
Title	crf-4-7C-0409
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	29.0
Pulse Sequence	sZul
Number of Scans	112
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-04-09 17:55:28
Spectrometer Frequency	75.45
Spectral Width	18797.0
Lowest Frequency	-1627.8
Nucleus	<sup>13</sup> C
Acquired Size	2955
Spectral Size	65536

Supplementary Figure 104. <sup>13</sup>C NMR Spectrum of 3n.

crf-4-7-B-decoupling-CDCl<sub>3</sub>

32.606



1.073  
0.433

4.589  
5.870

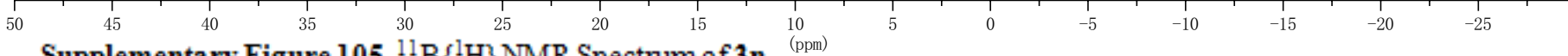
8.907

11.377

13.422

25.174

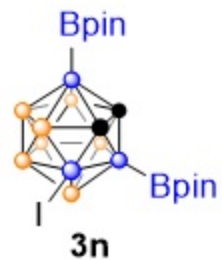
Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr4-7/td
Title	Desktop
Comment	
Origin	UMMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring 1g
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3155
Acquisition Date	2015-03-20 15:27
Modification Date	2015-03-20 15:15:00
Spectrometer Frequency	128.38
Spectral Width	59.221
Lowest Frequency	44462.3
Nucleus	<sup>11</sup> B
Acquired Size	16394
Spectral Size	3268



Supplementary Figure 105. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of 3n.

crf-4-7-B-coupling-CDCl<sub>3</sub>

32.864



1.801

0.849

0.097

3.910

5.309

6.464

8.135

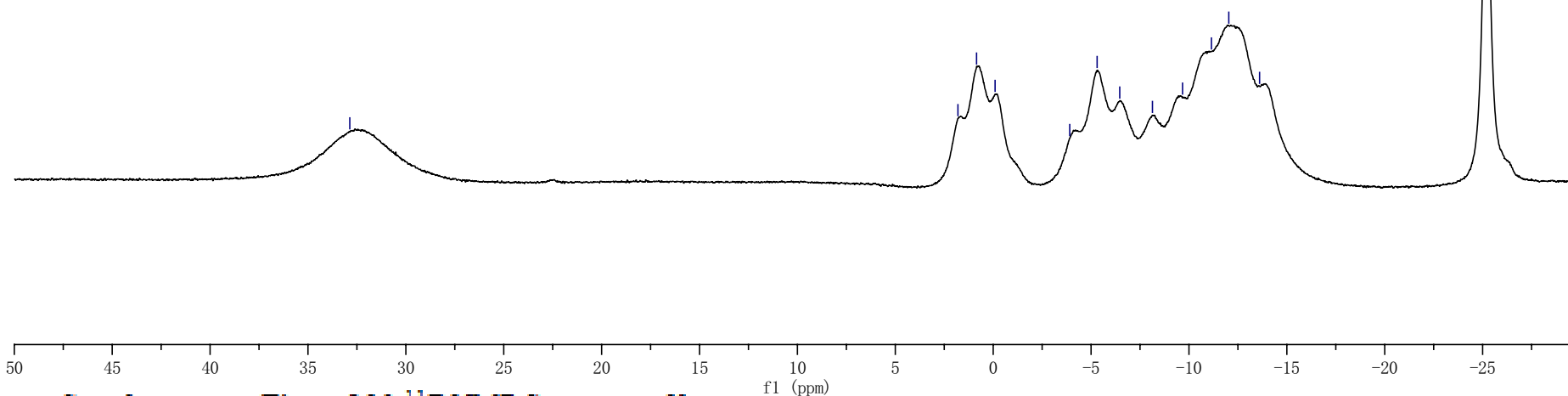
9.674

12.034

13.607

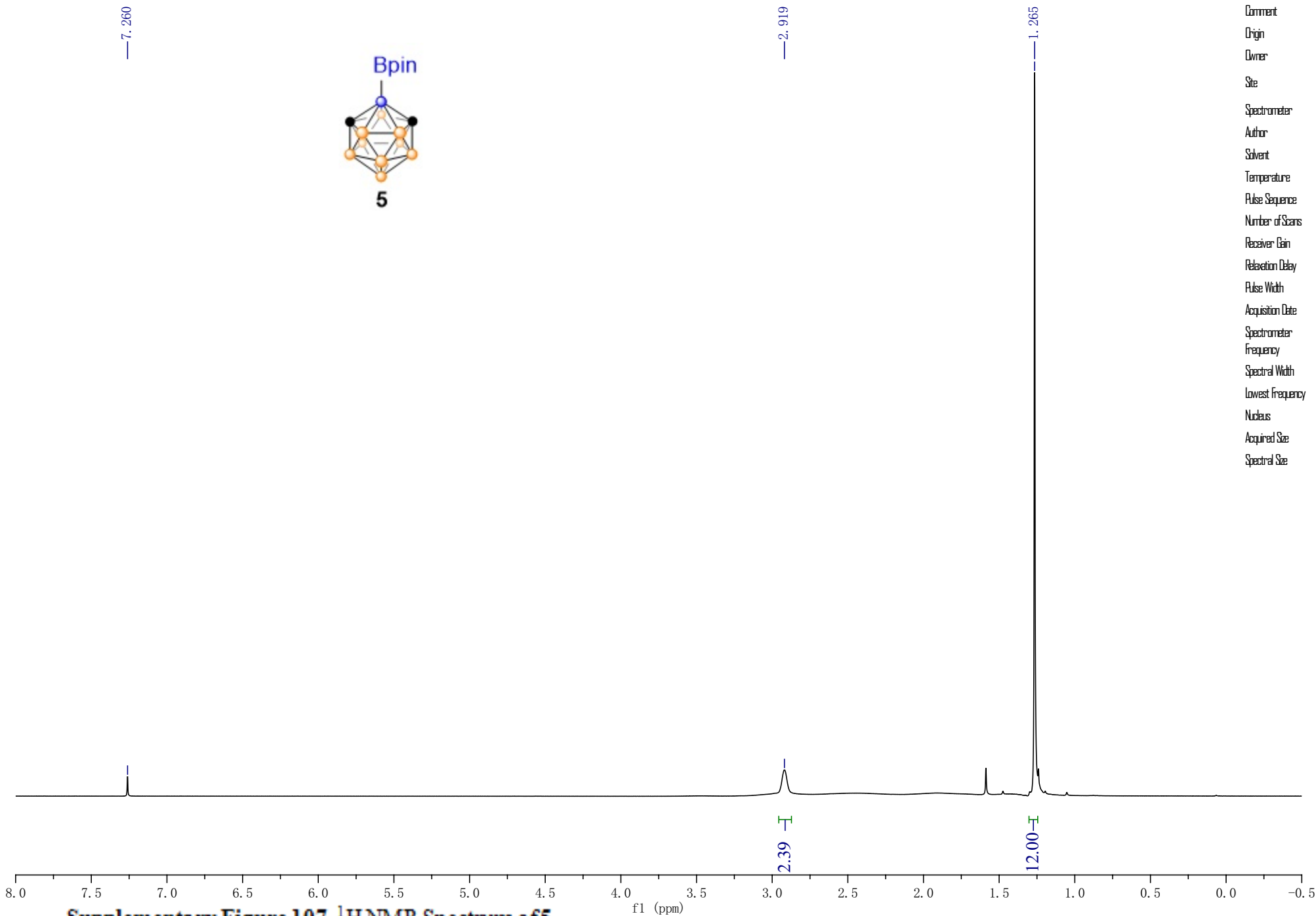
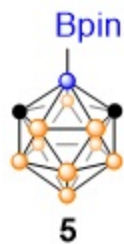
25.148

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr-f4-7-coupling/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.tgy
Number of Scans	1600
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-03-20 12:25:22
Modification Date	2015-03-20 15:25:00
Spectrometer Frequency	128.38
Spectral Width	59.221
Lowest Frequency	-444623
Nucleus	<sup>11</sup> B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 106. <sup>11</sup>B NMR Spectrum of 3n.

crf-7-79-H-CDCl3

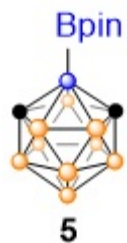


Parameter	Value
Title	crf-7-79-H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	sziul
Number of Scans	32
Receiver Gain	28
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2016-01-14 08:36
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-70.2
Nucleus	1H
Acquired Size	10888
Spectral Size	3268

Supplementary Figure 107. <sup>1</sup>H NMR Spectrum of 5.

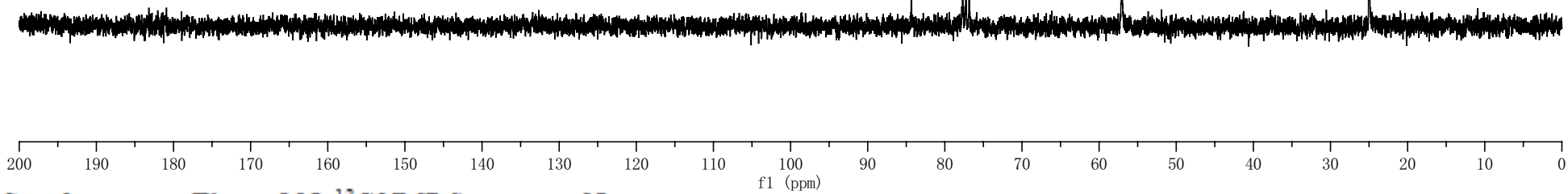


crf-7-79-C-CDCl3



84.334  
77.677  
77.253  
76.830  
57.048  
25.021

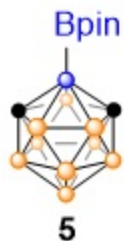
Parameter	Value
Title	crf-7-79-C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	29.0
Pulse Sequence	sZul
Number of Scans	80
Receiver Gain	38
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2016-01-07 15:04:54
Spectrometer Frequency	76.45
Spectral Width	2949.8
Lowest Frequency	-215.2
Nucleus	13C
Acquired Size	30738
Spectral Size	65536



Supplementary Figure 108. <sup>13</sup>C NMR Spectrum of 5.

crf-7-79-B-decoupling-CDC13

34.596

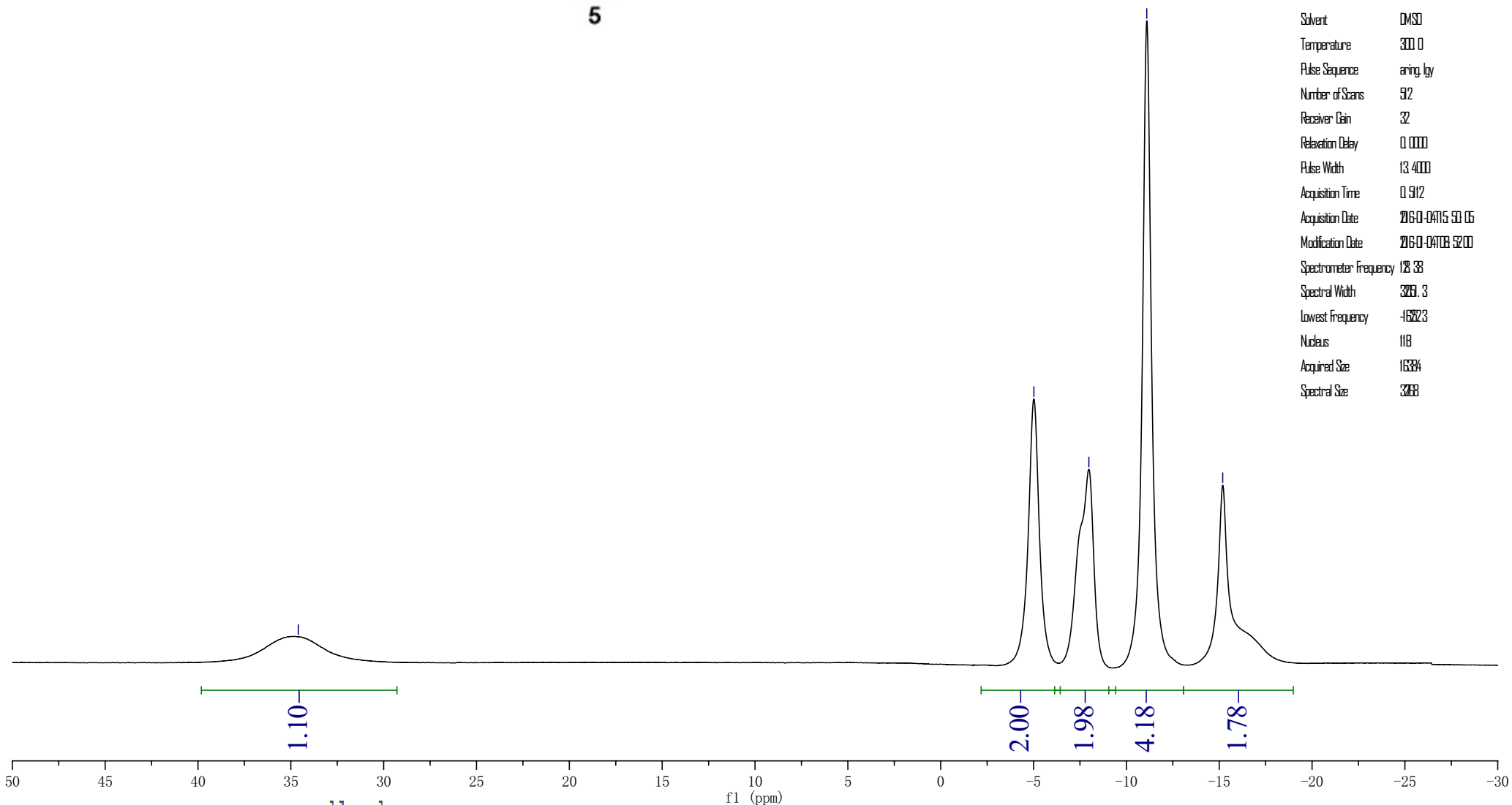


-5.018

-7.980

-11.098

-15.188

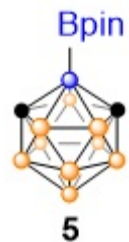


Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-crff79/ftd
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1g
Number of Scans	512
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	2016-03-04 15:50:05
Modification Date	2016-03-04 18:52:00
Spectrometer Frequency	128.38
Spectral Width	3061.3
Lowest Frequency	-1682.3
Nucleus	11B
Acquired Size	16384
Spectral Size	3263

Supplementary Figure 109.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of 5.

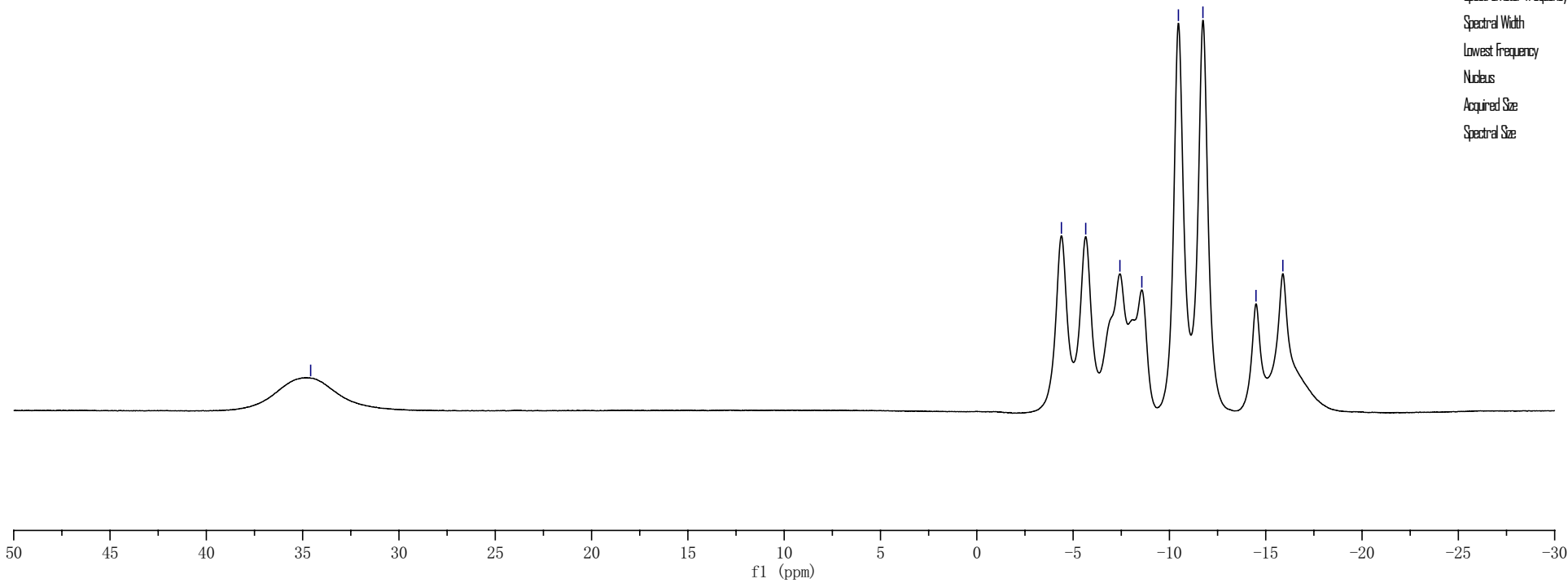
crf-7-79-B-coupling-CDC13

—34.584



—4.392  
—5.654  
—7.429  
—8.566  
—10.466  
—11.739  
—14.494  
—15.888

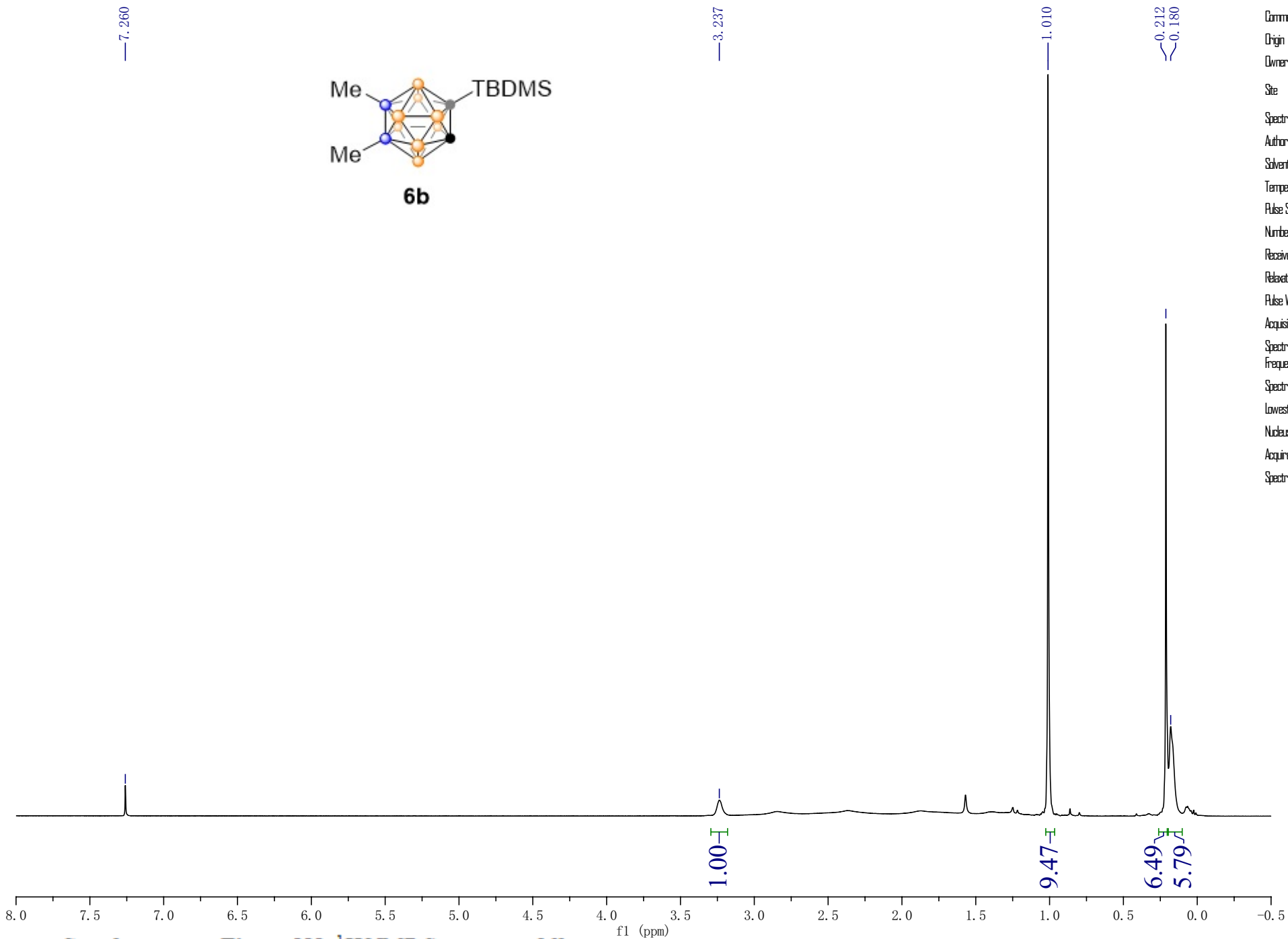
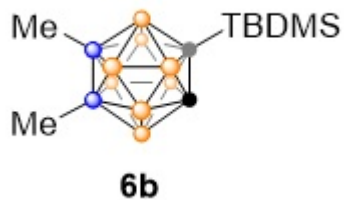
Parameter	Value
Data File Name	E:/Users/Administrator/Desktop/b-crf-7-79-coupling/1d
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1gy
Number of Scans	512
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	2016-04-15 44:53
Modification Date	2016-04-15 48:00
Spectrometer Frequency	128.33
Spectral Width	3281.3
Lowest Frequency	-16282.3
Nucleus	<sup>11</sup> B
Acquired Size	16384
Spectral Size	3288



Supplementary Figure 110. <sup>11</sup>B NMR Spectrum of 5.

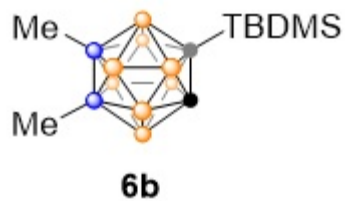
crf-7-70-1-H-CDCl3

Parameter	Value
Title	crf-7-70-1-H
Comment	STANDARD OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	cmc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	zgpg30
Number of Scans	12
Receiver Gain	24
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-12-28 22:52
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-70.8
Nucleus	1H
Acquired Size	10888
Spectral Size	3068



Supplementary Figure 111. <sup>1</sup>H NMR Spectrum of **6b**.

crf-7-70-1-C-CDCl3



77.192  
76.766  
76.340

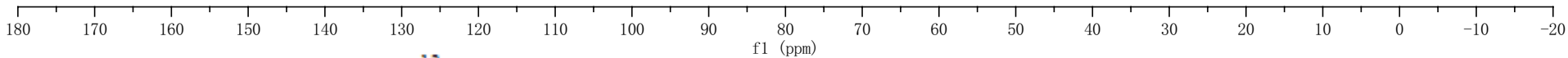
56.704  
53.199

26.776

19.060

-4.690

Parameter	Value
Title	crf7704-C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	sgpl
Number of Scans	132
Receiver Gain	38
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015/22/28 03:58
Spectrometer Frequency	75.45
Spectral Width	2749.8
Lowest Frequency	-285.2
Nucleus	13C
Acquired Size	31738
Spectral Size	65536



Supplementary Figure 112. <sup>13</sup>C NMR Spectrum of 6b.

S133

crf-7-70-1-B-decoupling-CDC13

9.961

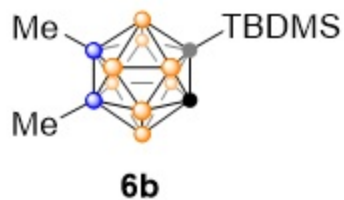
7.866

-5.190

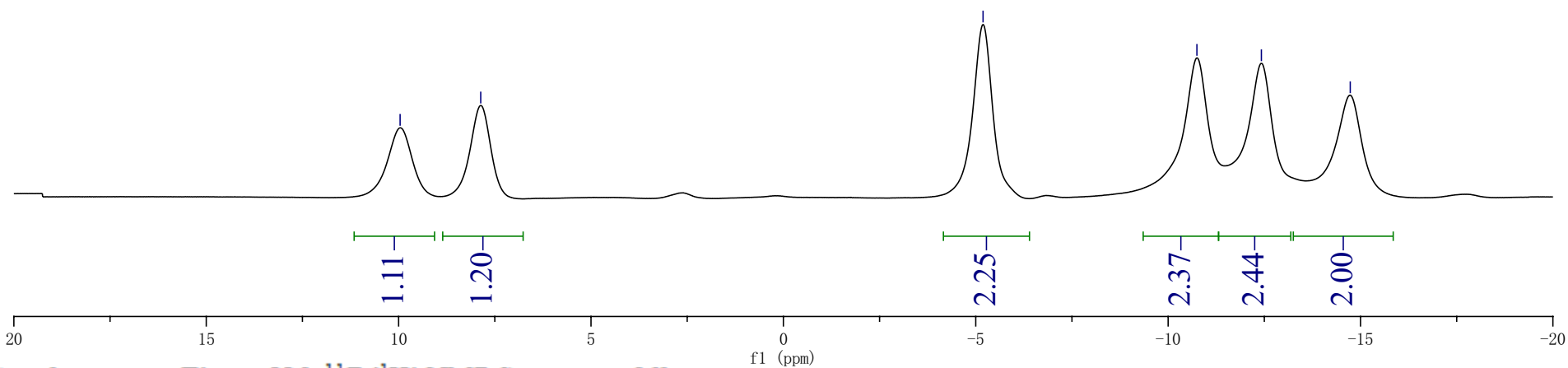
-10.748

-12.424

-14.733



Parameter	Value
Data file Name	G:/Users/Administrator/Desktop/2135b-cr7701/2135b-cr7701/1/1d
Title	2135b-cr7701
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dr400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.1g
Number of Scans	512
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	2015/28/19 07:33
Modification Date	2015/28/13 50:15
Spectrometer Frequency	128.38
Spectral Width	326.3
Lowest Frequency	-16823
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

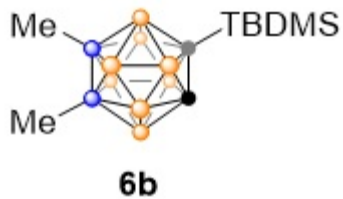


Supplementary Figure 113.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of **6b**.

crf-7-70-1-B-coupling-CDCl3

9.940

7.854



4.632

5.766

10.155

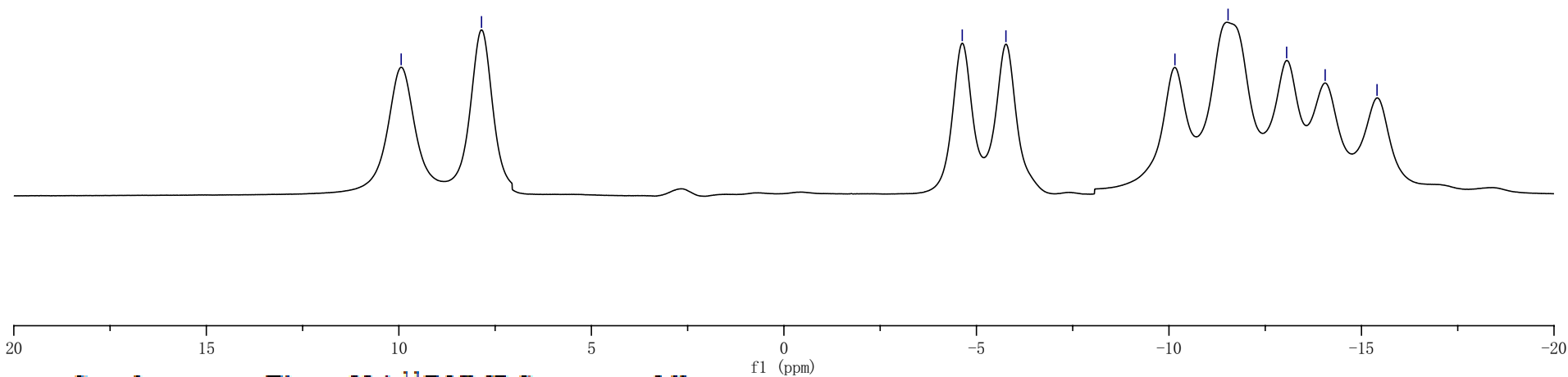
11.535

13.056

14.057

15.404

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/2135b-crf7701/2135b-crf7701-coupling/1/fid
Title	2135b-crf7701-coupling
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.1g
Number of Scans	100
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.912
Acquisition Date	2015/28/19 15:50
Modification Date	2015/28/13 50:10
Spectrometer Frequency	128.38
Spectral Width	326.3
Lowest Frequency	-16323
Nucleus	11B
Acquired Size	16394
Spectral Size	3268



Supplementary Figure 114. <sup>11</sup>B NMR Spectrum of **6b**.

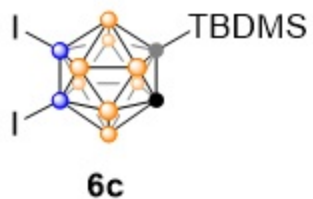
crf-7-50-2-H-CDC13

7.260

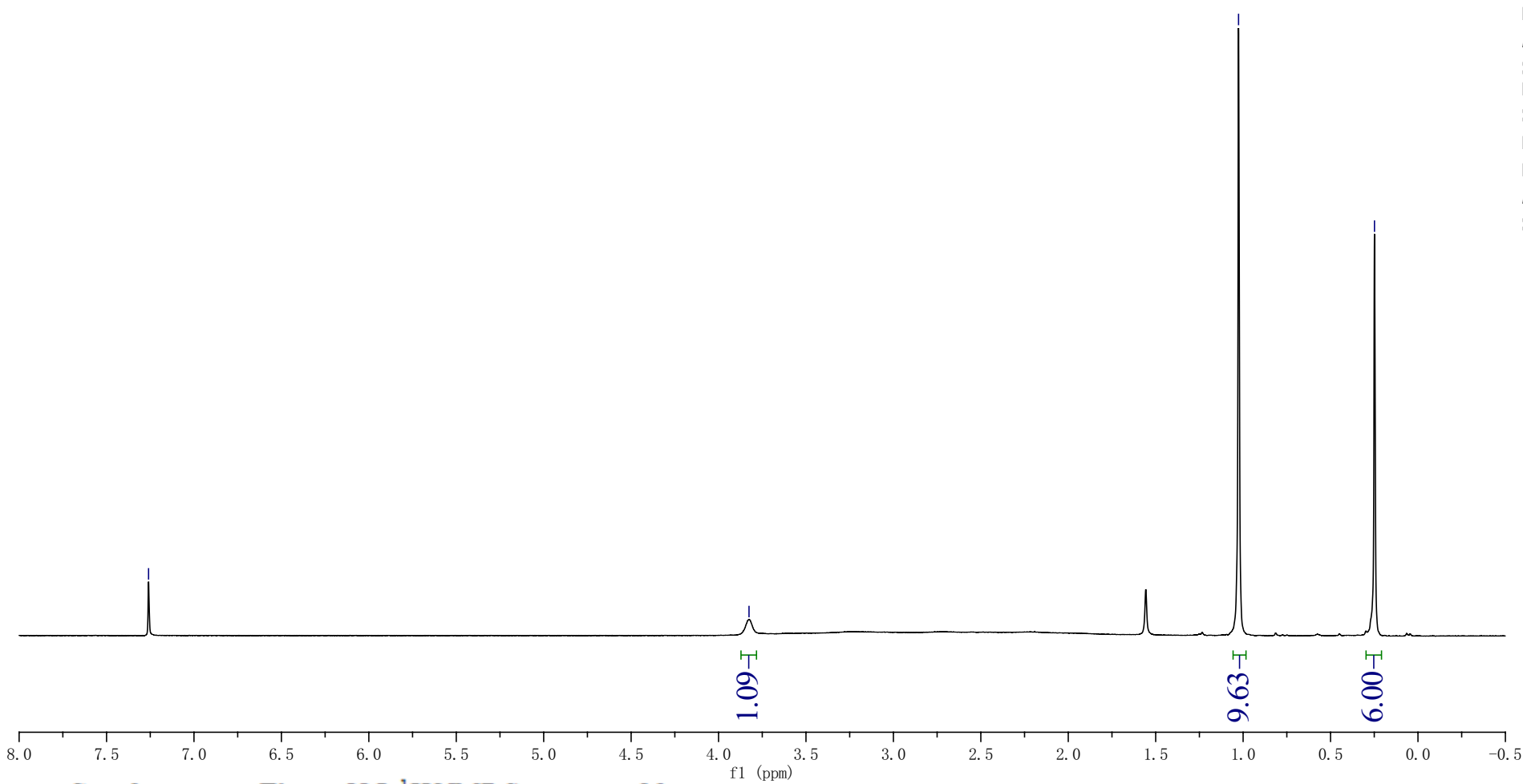
3.826

1.026

0.249



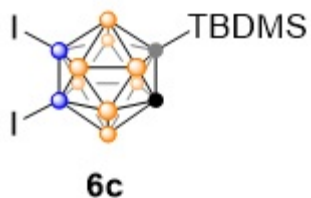
Parameter	Value
Title	crf7502
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	sgzg
Number of Scans	8
Receiver Gain	32
Relaxation Delay	1.000
Pulse Width	0.000
Acquisition Date	2015/05/16 2: 07
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-70.5
Nucleus	1H
Acquired Size	10888
Spectral Size	3268



Supplementary Figure 115. <sup>1</sup>H NMR Spectrum of 6c.



crf-7-50-2-H-CDCl3



77.761  
77.337  
76.913

62.351

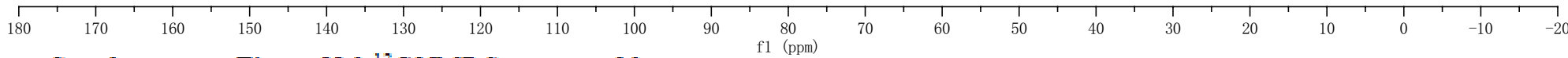
57.471

27.186

19.597

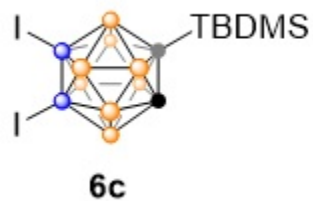
-4.140

Parameter	Value
Title	crf7-50-2c
Comment	13C OBSERVE
Origin	Varien
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	zgpg30
Number of Scans	60
Receiver Gain	38
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2014/2/16 12:55
Spectrometer Frequency	75.45
Spectral Width	299.8
Lowest Frequency	-285.2
Nucleus	13C
Acquired Size	30736
Spectral Size	65536

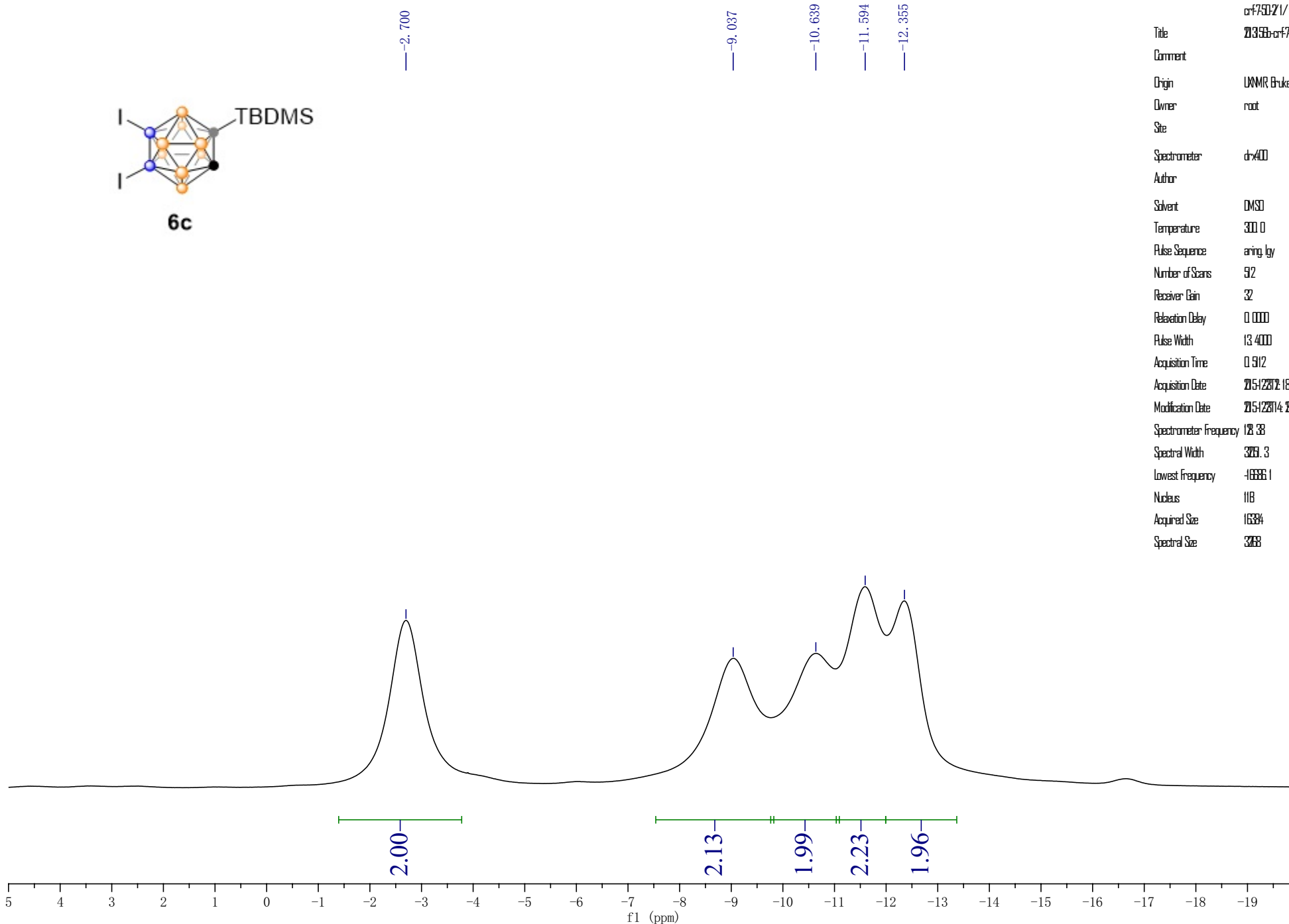


Supplementary Figure 116. <sup>13</sup>C NMR Spectrum of **6c**.

crf-7-50-2-B-decoupling-CDC13

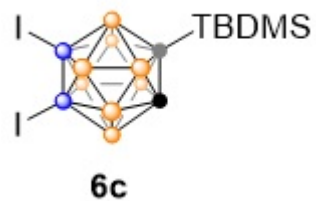


Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/2135b-crf75021/fid
Title	2135b-crf7502
Comment	
Origin	LNMNR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.tgy
Number of Scans	92
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	2015/22/12 18:54
Modification Date	2015/22/14 21:56
Spectrometer Frequency	128.38
Spectral Width	326.3
Lowest Frequency	-16666.1
Nucleus	11B
Acquired Size	16384
Spectral Size	3268



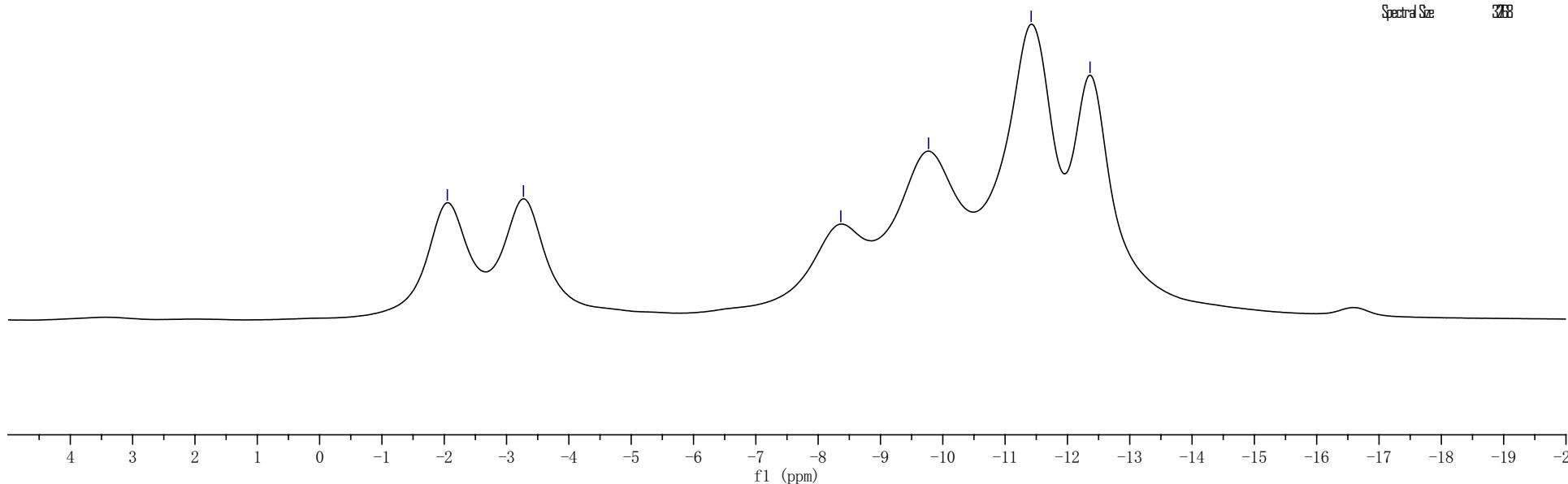
Supplementary Figure 117.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of **6c**.

crf-7-50-2-B-coupling-CDCl3



-2.050      -3.271

-8.364      -9.771      -11.418      -12.363

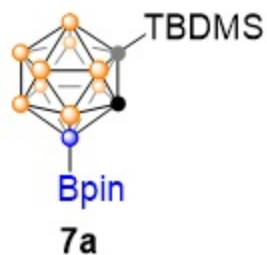


Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/work/送样 NMR/correlation/7502/b-crf7502coupling/fid
Title	7502
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1gy
Number of Scans	512
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	2016-04-11T18:00:2
Modification Date	2016-04-11T11:00:00
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-16223
Nucleus	11B
Acquired Size	16394
Spectral Size	3268

Supplementary Figure 118. <sup>11</sup>B NMR Spectrum of 6c.

crf-7-48-H-CDCl3

7.260

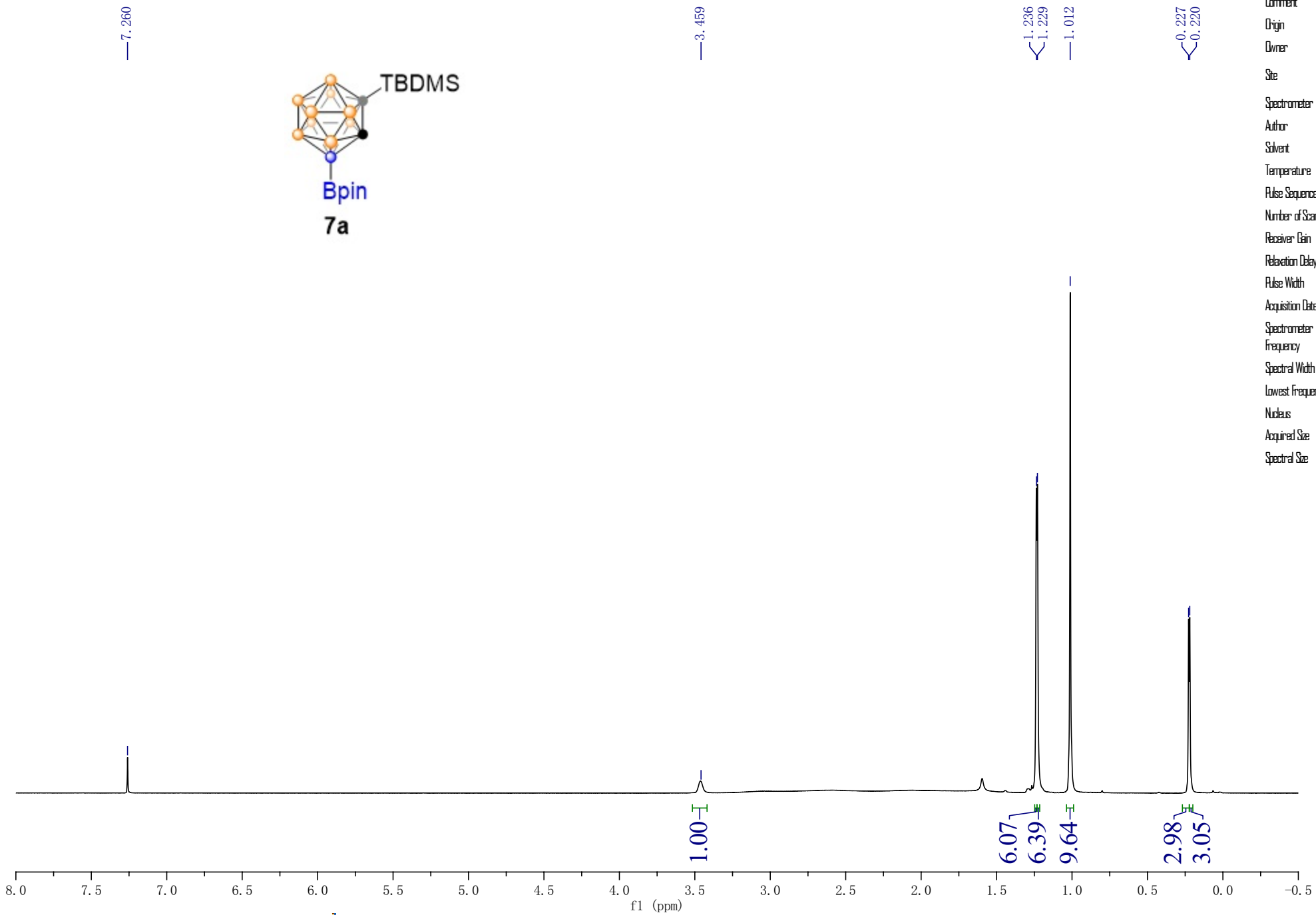


3.459

1.236  
1.229

1.012

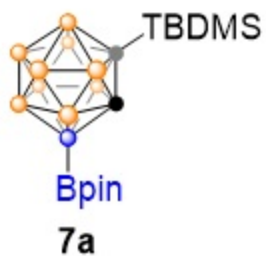
0.227  
0.220



Parameter	Value
Title	crf748H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	sgzb
Number of Scans	12
Receiver Gain	30
Relaxation Delay	1.000
Pulse Width	0.000
Acquisition Date	2015/23/08 21:2
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-71.1
Nucleus	1H
Acquired Size	10888
Spectral Size	3288

Supplementary Figure 119. <sup>1</sup>H NMR Spectrum of 7a.

crf-7-48-C-CDCl3

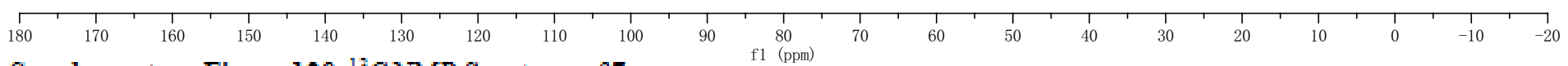


83.693  
77.692  
77.269  
76.845  
67.717  
62.006

27.177  
25.117  
24.943  
19.522

-4.315

Parameter	Value
Title	crf-7-48-C
Comment	<sup>13</sup> C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	zgpg30
Number of Scans	120
Receiver Gain	38
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015/23/10 4:43:00
Spectrometer Frequency	76.46
Spectral Width	2949.8
Lowest Frequency	-285.2
Nucleus	<sup>13</sup> C
Acquired Size	30736
Spectral Size	65536



Supplementary Figure 120. <sup>13</sup>C NMR Spectrum of 7a.

crf-7-48-B-decoupling-CDCl3

34.278

0.678

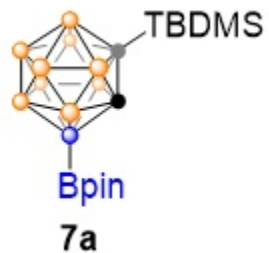
1.048

5.850

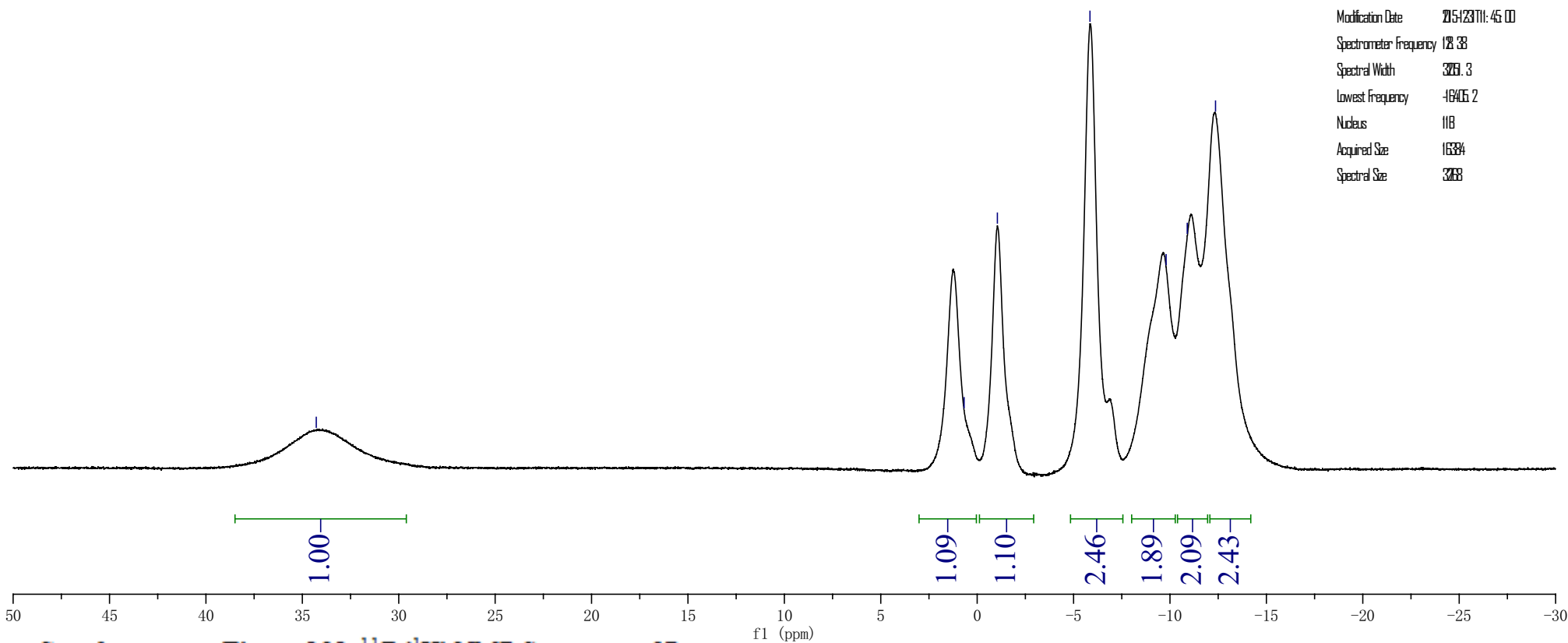
9.799

10.895

12.362



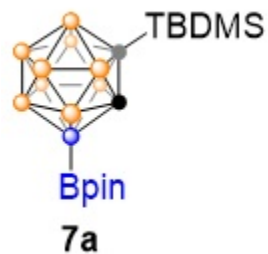
Parameter	Value
Data File Name	E:/Users/Administrator/Desktop/b-cr748/fid
Title	Desktop
Comment	
Origin	LWMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.1g
Number of Scans	26
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	2015/23/11 8:45:0
Modification Date	2015/23/11: 45:00
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-16406.2
Nucleus	11B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 121.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of **7a**.

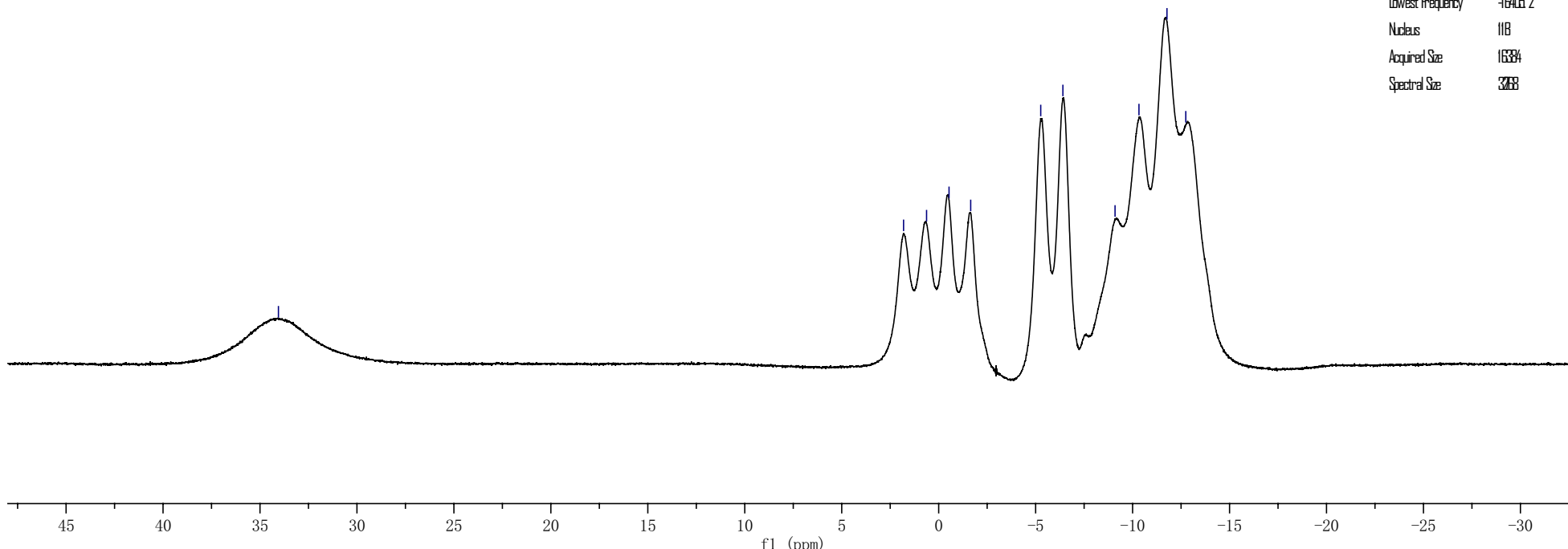
crf-7-48-B-decoupling-CDC13

34.049



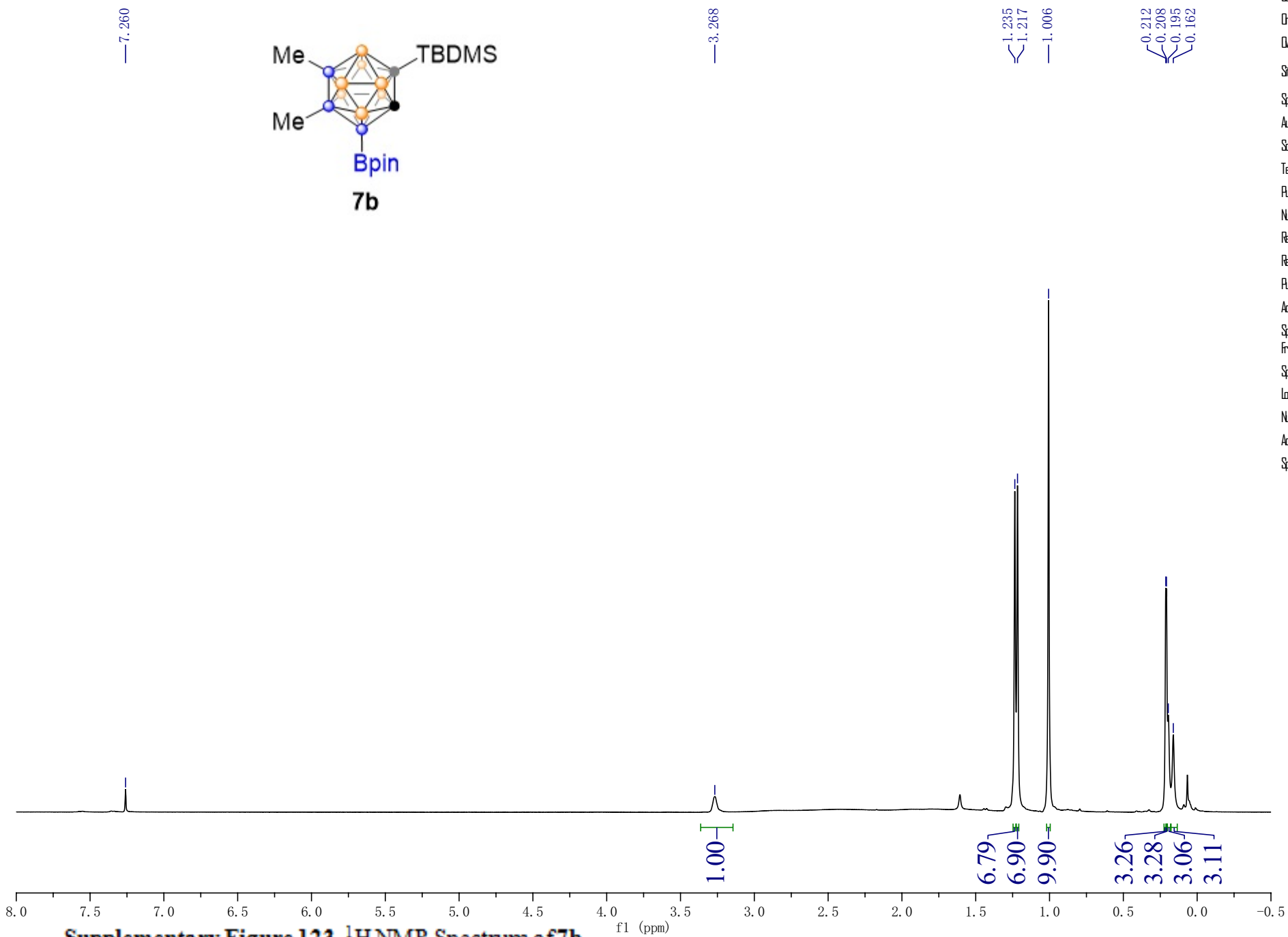
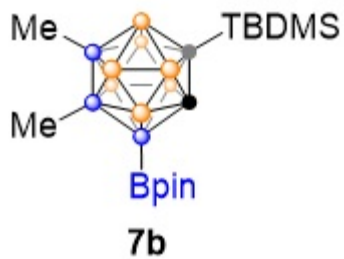
1.811  
0.625  
-0.534  
-1.651  
-5.263  
-6.406  
-9.095  
-10.328  
-11.773  
-12.743

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr7-48-coupling/fid
Title	Desktop
Comment	
Origin	LWMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	drx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1gy
Number of Scans	335
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.912
Acquisition Date	2015/23/18:48:44
Modification Date	2015/23/11:48:00
Spectrometer Frequency	128.38
Spectral Width	3263.3
Lowest Frequency	-16405.2
Nucleus	<sup>11</sup> B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 22. <sup>11</sup>B NMR Spectrum of 7a.

crf-7-74-H-CDCl3

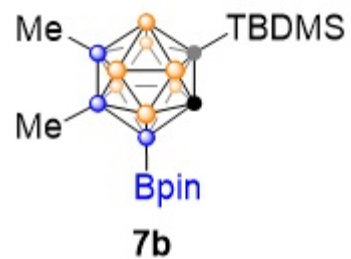


Parameter	Value
Title	crf77A-H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	squl
Number of Scans	12
Receiver Gain	2
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	20151231 09:33:45
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-71.1
Nucleus	1H
Acquired Size	10888
Spectral Size	3268

Supplementary Figure 123. <sup>1</sup>H NMR Spectrum of 7b.



crf-7-74-C-CDCl3



83.377

77.685

77.261

76.837

59.048

55.186

27.224

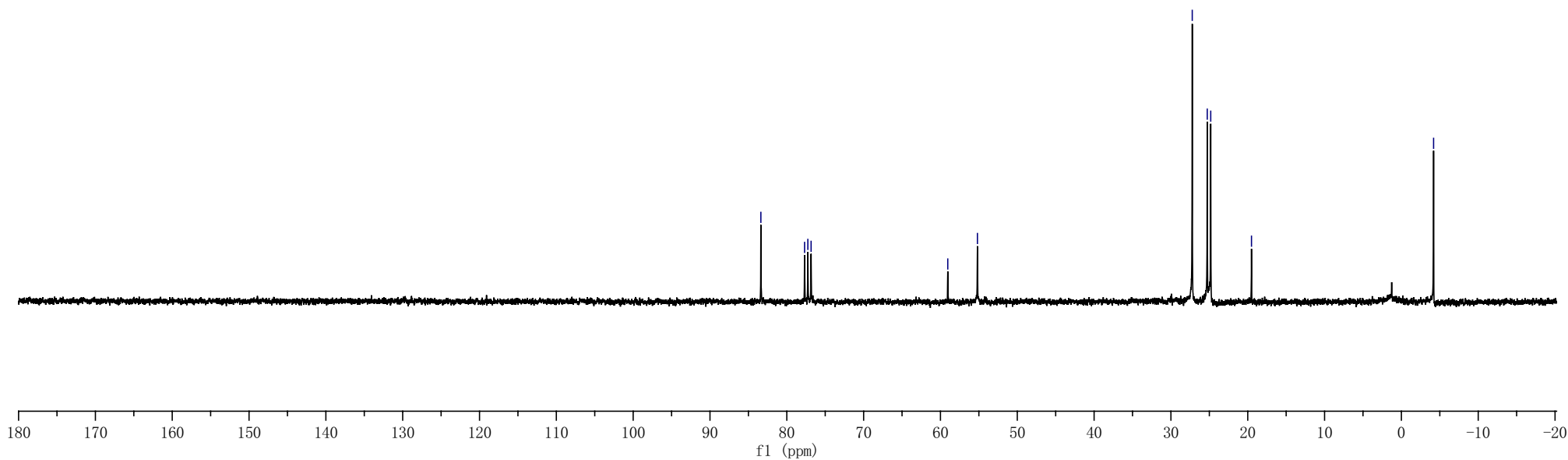
25.271

24.819

19.513

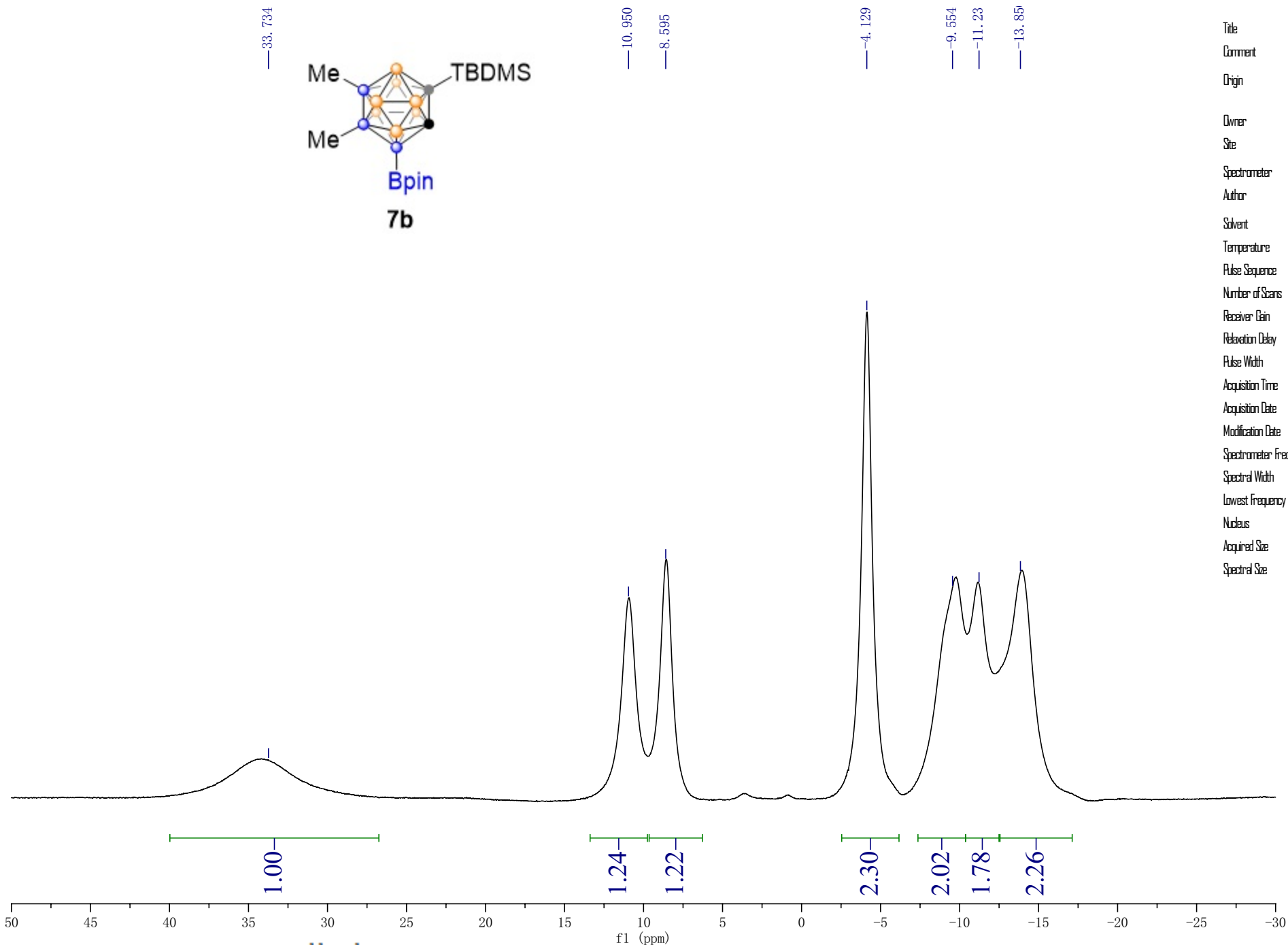
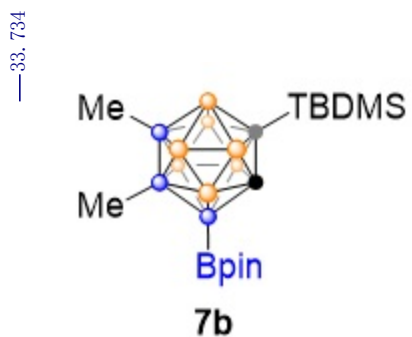
-4.191

Parameter	Value
Title	crf-774-C
Comment	<sup>13</sup> C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	zgpg30
Number of Scans	84
Receiver Gain	38
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-03-10 08:53:43
Spectrometer Frequency	76.45
Spectral Width	2991.8
Lowest Frequency	-285.2
Nucleus	<sup>13</sup> C
Acquired Size	30736
Spectral Size	65536



Supplementary Figure 124. <sup>13</sup>C NMR Spectrum of 7b.

crf-7-74-B-decoupling-CDC13

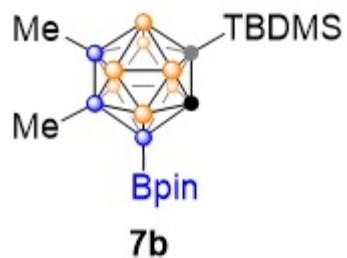


Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/crf-7-74/td
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1gy
Number of Scans	116
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	2015/23/18:37:35
Modification Date	2015/23/11:37:00
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-16406.2
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

Supplementary Figure 125.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of 7b.

crf-7-74-B-coupling-CDC13

33.807



10.841

8.502

3.657

4.703

9.617

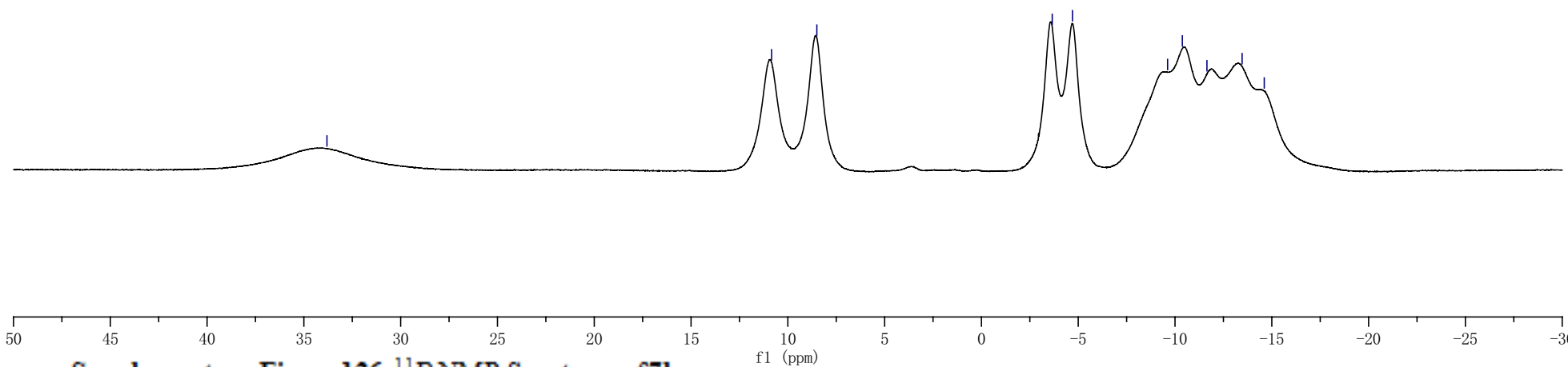
10.37

11.64

13.46

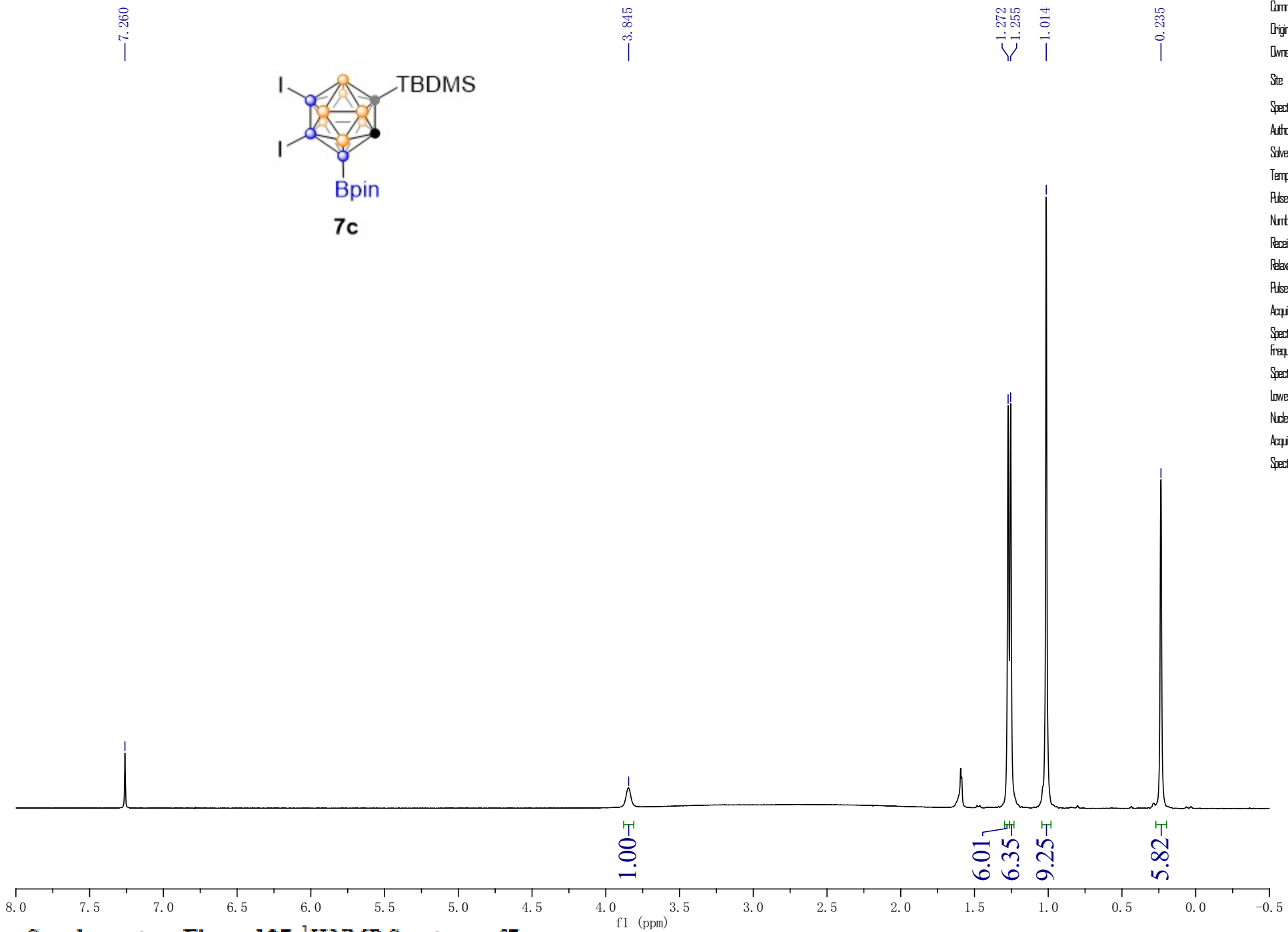
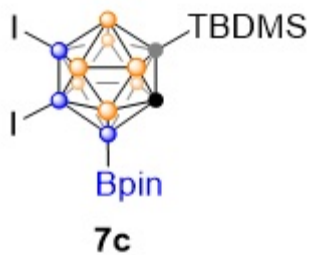
14.60

Parameter	Value
Data file Name	C:/Users/Administrator/Desktop/b-crf774-coupling (1)/fid
Title	Desktop
Comment	
Origin	UNMR, Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dmx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.ty
Number of Scans	128
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	20151231 18:39:05
Modification Date	20151231 11:39:00
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-18405.2
Nucleus	11B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 126. <sup>11</sup>B NMR Spectrum of 7b.

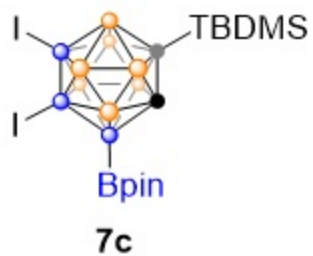
crf-7-53-H-CDCl3



Parameter	Value
Title	crf753-H-07
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	zgpg30
Number of Scans	8
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2016-01-07 11:04:04
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-71.3
Nucleus	1H
Acquired Size	10888
Spectral Size	3288

Supplementary Figure 127. <sup>1</sup>H NMR Spectrum of 7c.

crf-7-53-C-CDC13



84.009

77.381

76.957

76.526

63.733

58.396

26.783

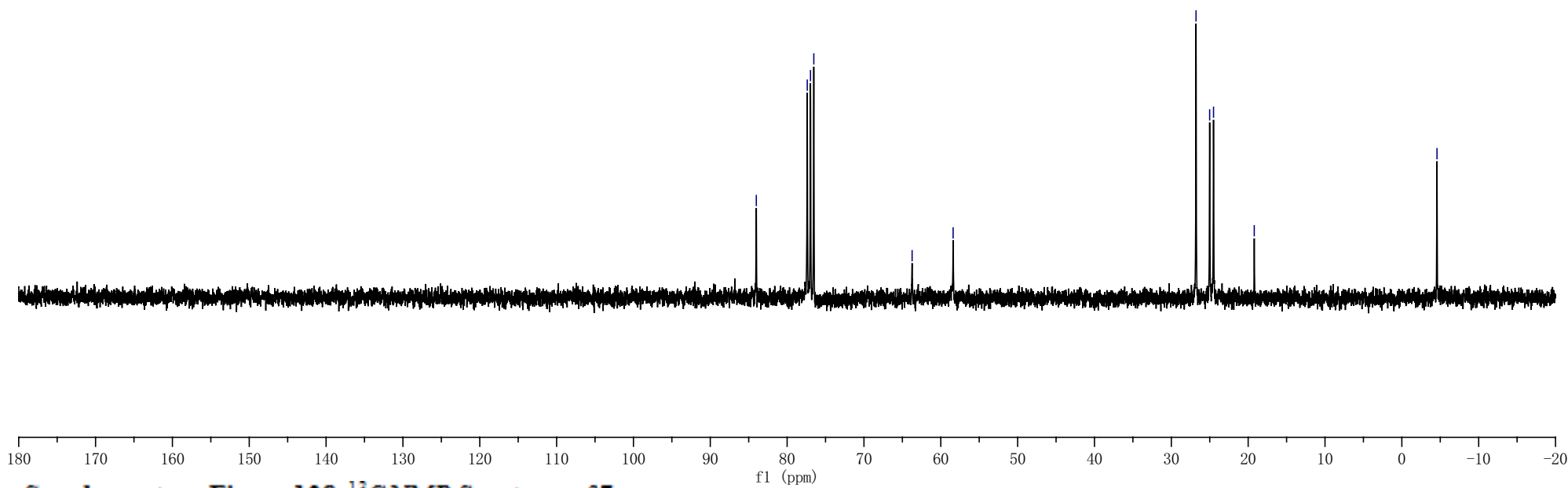
25.011

24.507

19.206

-4.575

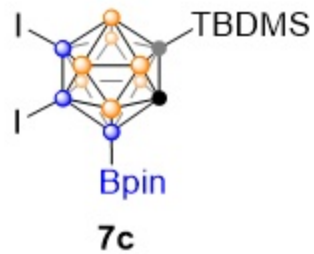
Parameter	Value
Title	crf753C
Comment	13C OBSERVE
Origin	Varien
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	zgpg30
Number of Scans	164
Receiver Gain	38
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2016-07-11: 2:53
Spectrometer Frequency	75.45
Spectral Width	2049.8
Lowest Frequency	-285.2
Nucleus	13C
Acquired Size	30736
Spectral Size	65536



Supplementary Figure 128. <sup>13</sup>C NMR Spectrum of 7c.

crf-7-53-B-decoupling-CDC13

33.421



-2.848

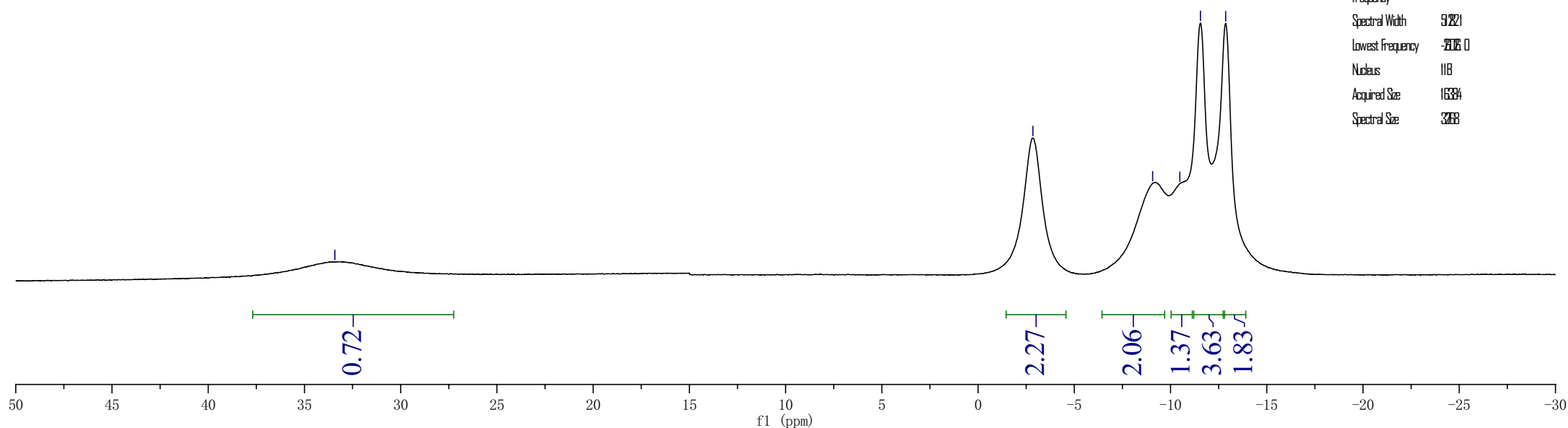
-9.069

-10.483

-11.554

-12.865

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/work/送样NMR/boradation/753/b-crf753/fid
Title	753
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring_tgy
Number of Scans	26
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2016-07-19 18:29
Modification Date	2016-07-21 18:00
Spectrometer Frequency	128.38
Spectral Width	51821
Lowest Frequency	-2006.0
Nucleus	11B
Acquired Size	16384
Spectral Size	3068

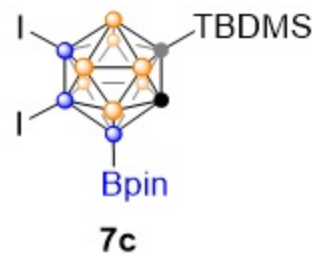


Supplementary Figure 129.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of 7c.

S150

crf-7-53-B-coupling-CDC13

—32.986



—-2.226  
—-3.501

—-10.074  
—-11.569  
—-12.880

Parameter	Value
Data file Name	C:/Users/Administrator/Desktop/work/送 样NMR/borolation/753/b-cr753-coupling/td
Title	753
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dr400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring_1gy
Number of Scans	512
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2016-01-07 19:37:59
Modification Date	2016-01-07 12:37:00
Spectrometer Frequency	128.38
Spectral Width	51.821
Lowest Frequency	-2677.1
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

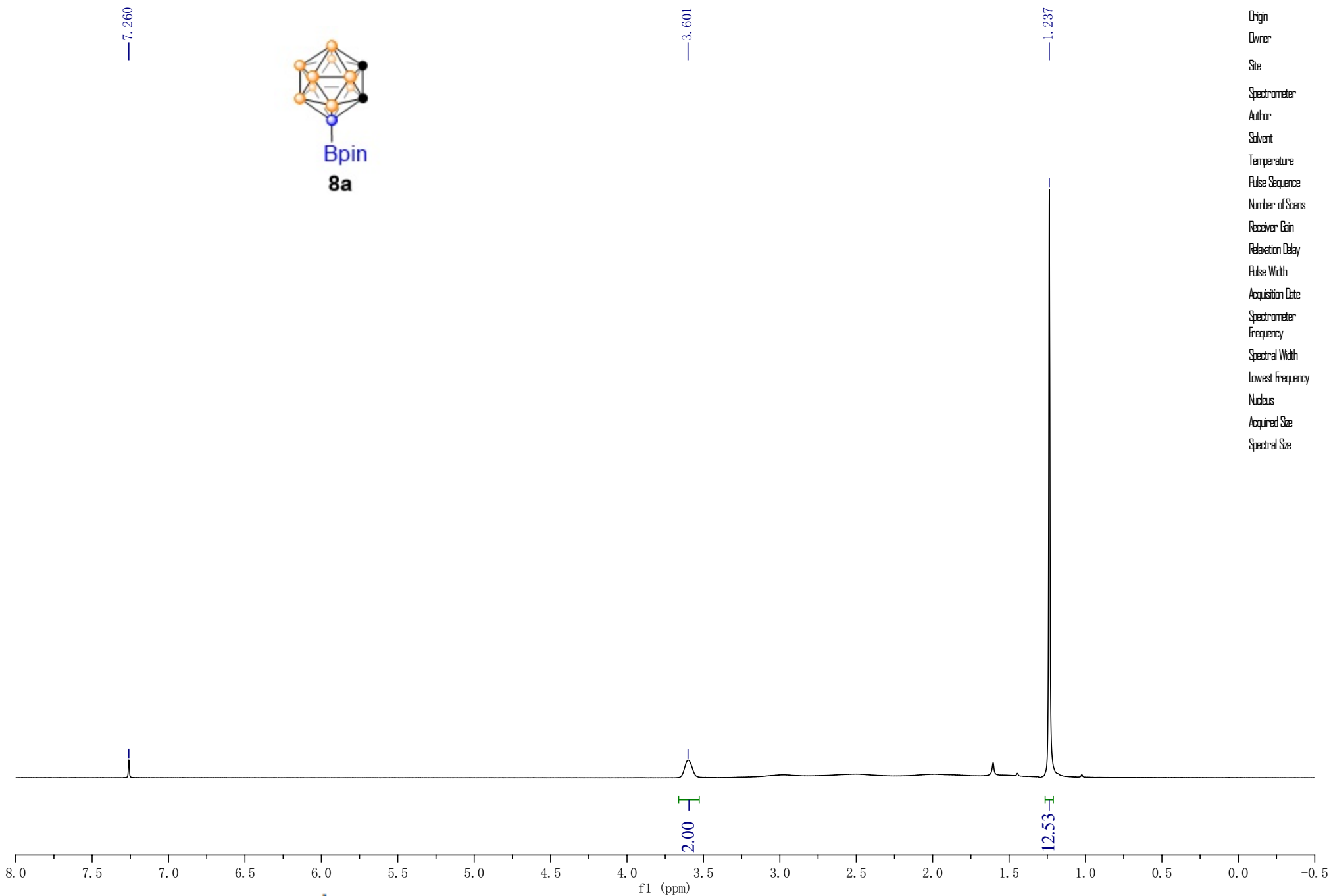
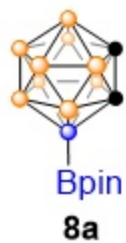


45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30

Supplementary Figure 130. <sup>11</sup>B NMR Spectrum of 7c.

f1 (ppm)  
S151

crf-7-38-H-CDCl3

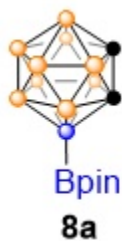


Parameter	Value
Title	crf-7-38-124
Comment	STANDARD OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	29.0
Pulse Sequence	zgpg30
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015/24/11:13:56
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-70.5
Nucleus	1H
Acquired Size	10888
Spectral Size	3268

Supplementary Figure 131. <sup>1</sup>H NMR Spectrum of 8a.



crf-7-38-C-CDCl3

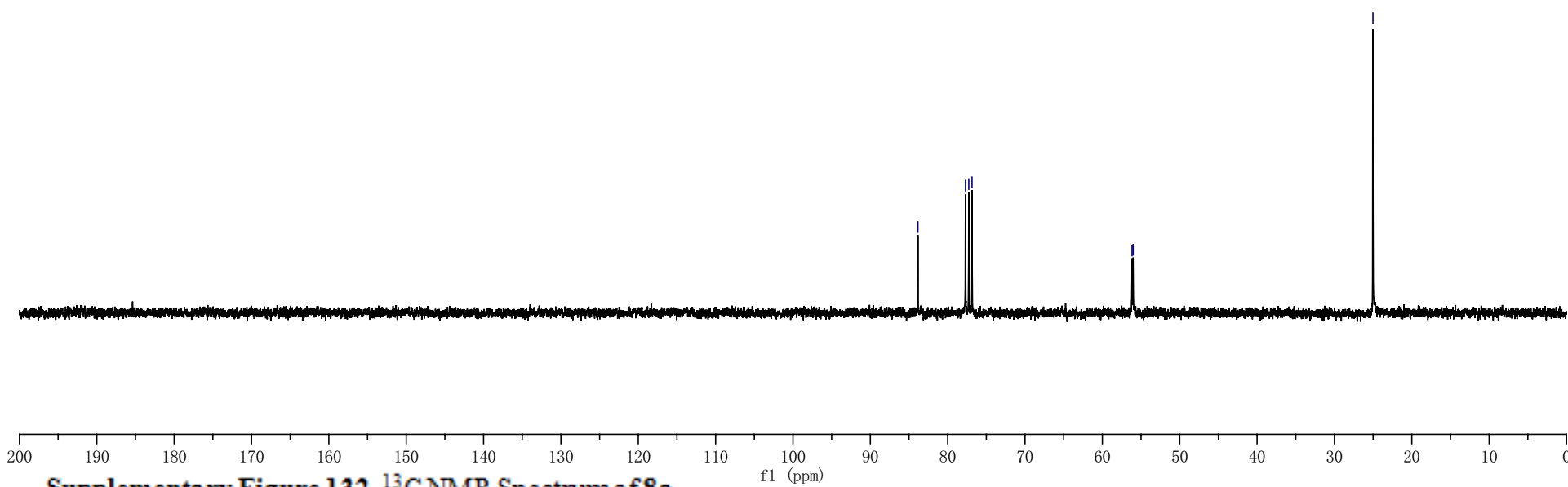


83.846  
77.694  
77.270  
76.847

56.162  
56.025

25.024

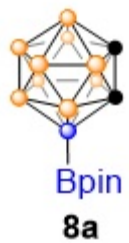
Parameter	Value
Title	crf738C124
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	sfpul
Number of Scans	120
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015124T11:17:17
Spectrometer Frequency	75.45
Spectral Width	2743.8
Lowest Frequency	-215.2
Nucleus	13C
Acquired Size	31738
Spectral Size	65536



Supplementary Figure 132. <sup>13</sup>C NMR Spectrum of 8a.

crf-7-38-B-decoupling-CDC13

33.879



-1.484

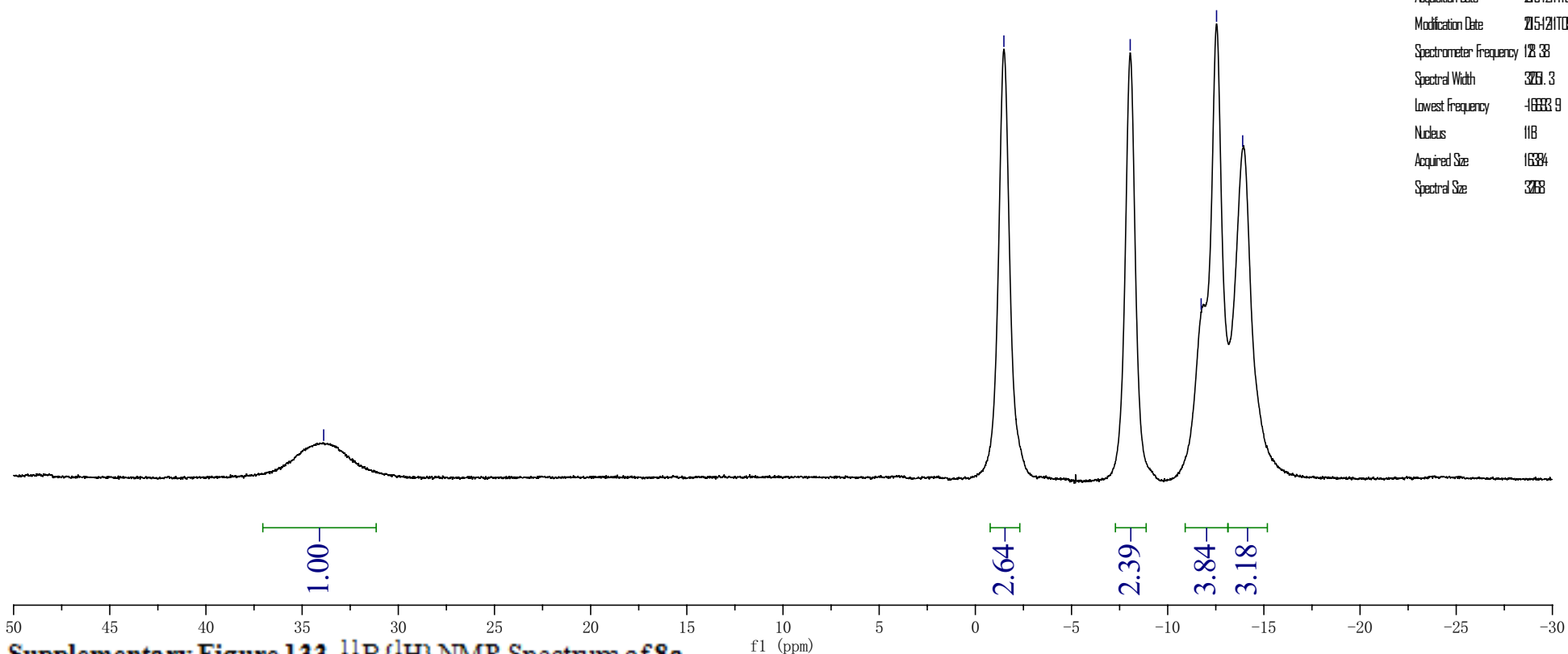
-8.051

-11.739

-12.539

-13.898

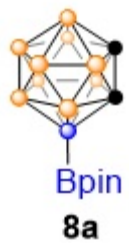
Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/work/送样NMR/b-crif-7-38/1d
Title	送样NMR
Comment	
Origin	LWMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.1gy
Number of Scans	26
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	2015/2/11/16:08:17
Modification Date	2015/2/11/16:08:00
Spectrometer Frequency	128.38
Spectral Width	3761.3
Lowest Frequency	-16668.9
Nucleus	11B
Acquired Size	16394
Spectral Size	3268



Supplementary Figure 133.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of **8a**.

crf-7-38-B-coupling-CDC13

— 34.019



— -0.830

— -2.143

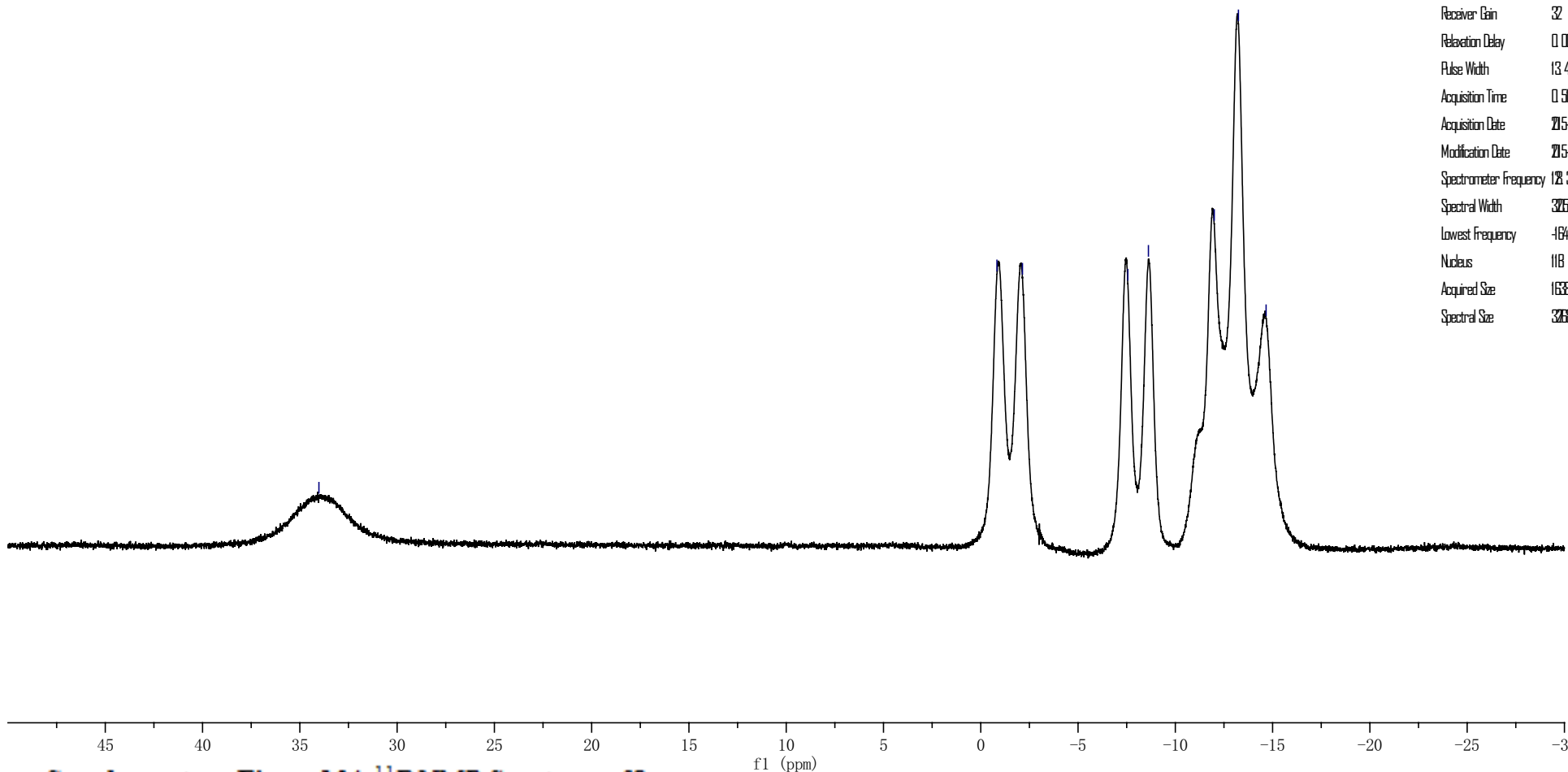
— -7.560

— -8.617

— -12.001

— -13.244

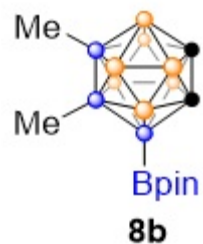
— -14.666



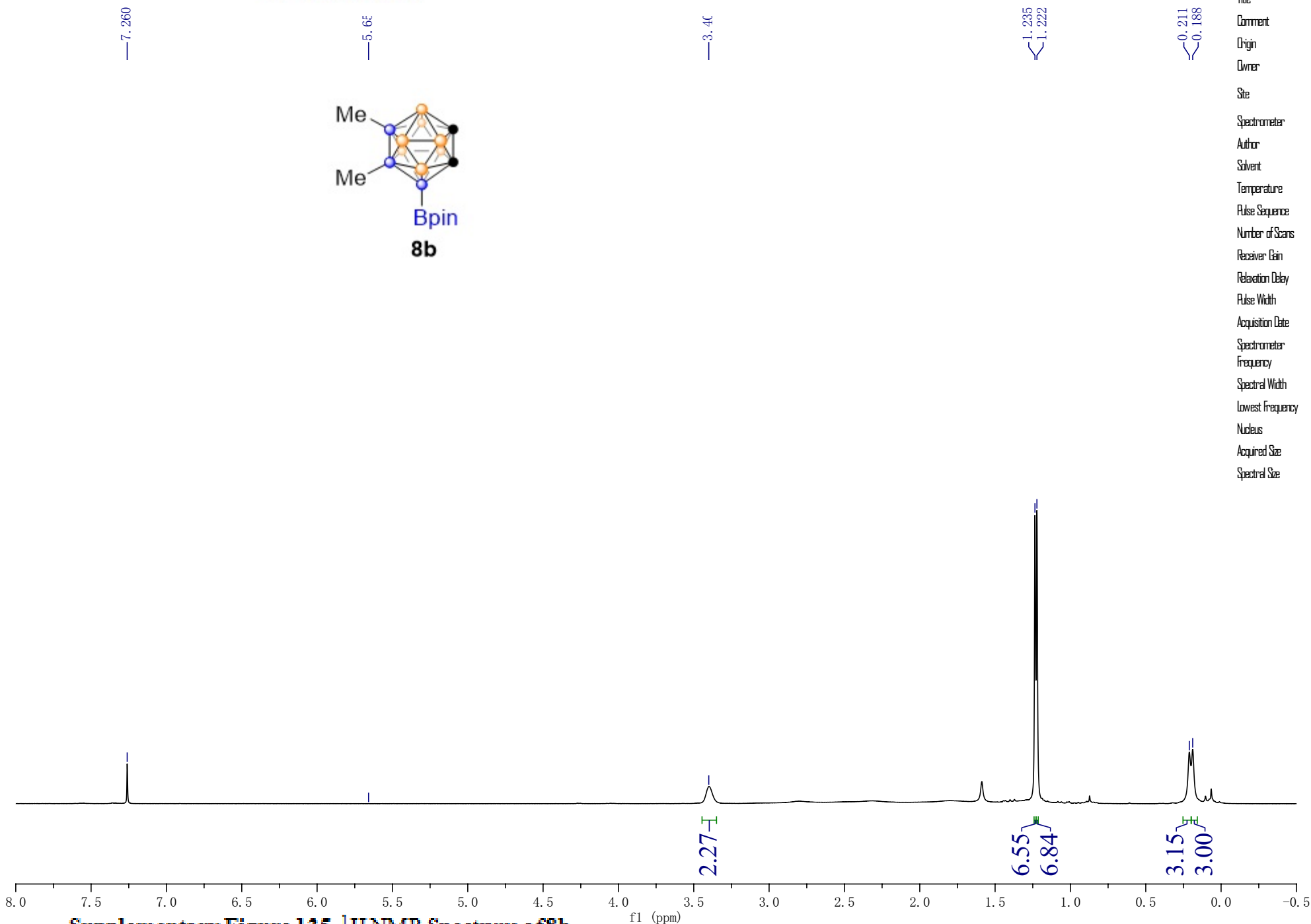
Parameter	Value
Data File Name	G:/Users/Administrator/Desktop/work/送样NMR/b-crf-7-38-coupling (1)/fid
Title	送样NMR
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dr400
Author	
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	zing1gy
Number of Scans	26
Receiver Gain	32
Relaxation Delay	0.000
Pulse Width	13.400
Acquisition Time	0.912
Acquisition Date	2015/2/11 16:10:49
Modification Date	2015/2/11 16:10:00
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-16411.0
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

Supplementary Figure 134. <sup>11</sup>B NMR Spectrum of 8a.

crf-7-82-H-CDCl3

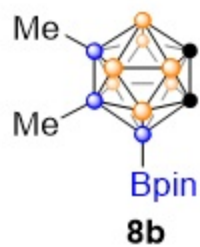


Parameter	Value
Title	crf782H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	onc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	sgul
Number of Scans	2
Receiver Gain	28
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2016-01-15 02:06
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-70.5
Nucleus	1H
Acquired Size	10000
Spectral Size	3288



Supplementary Figure 135. <sup>1</sup>H NMR Spectrum of 8b.

crf-7-82-C-CDCl3

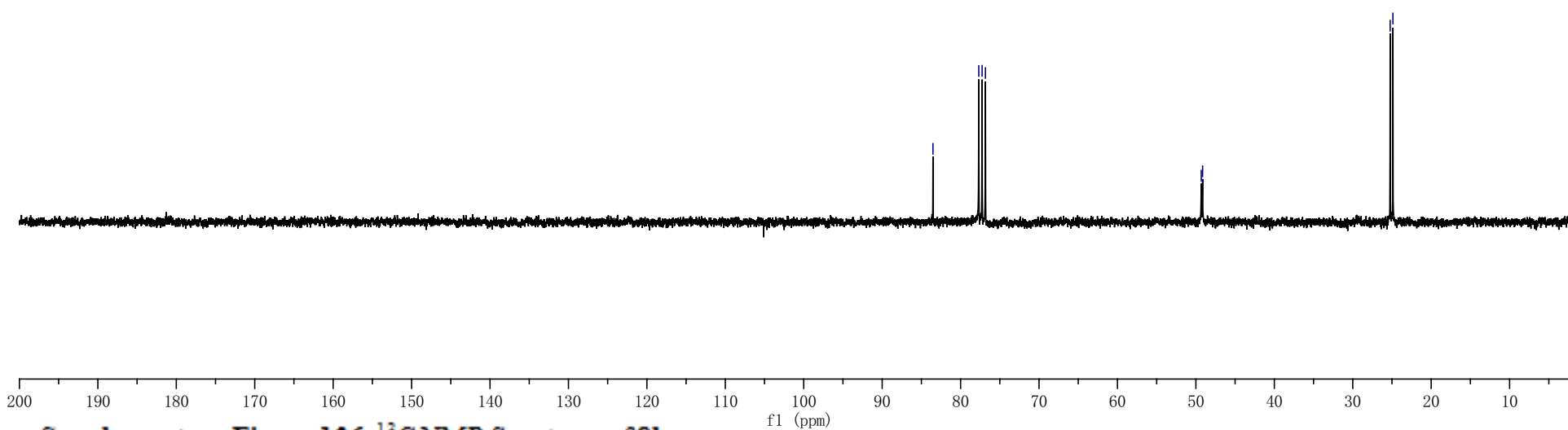


83.523  
77.682  
77.258  
76.835

49.314  
49.143

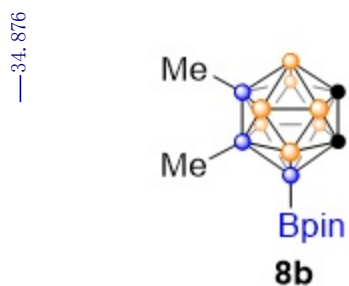
25.229  
24.878

Parameter	Value
Title	crf-782C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	29.0
Pulse Sequence	sZul
Number of Scans	168
Receiver Gain	38
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2016-01-07 15:09:14
Spectrometer Frequency	75.45
Spectral Width	2049.8
Lowest Frequency	-215.2
Nucleus	13C
Acquired Size	30738
Spectral Size	65536



Supplementary Figure 136. <sup>13</sup>C NMR Spectrum of 8b.

crf-7-82-B-decoupling-CDC13



34.876

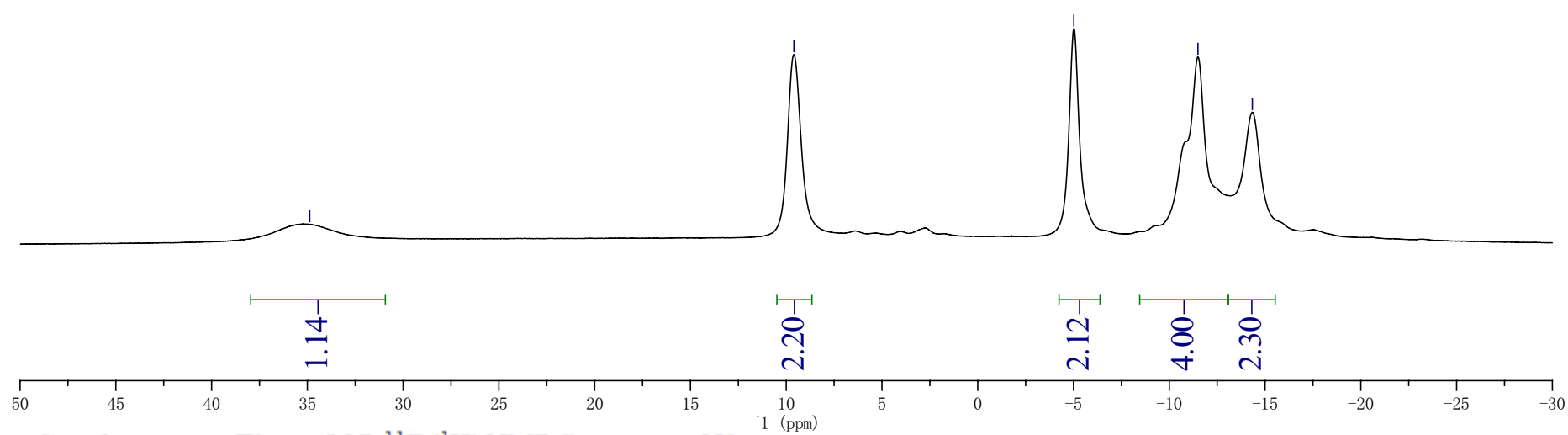
9.598

-5.017

-11.496

-14.335

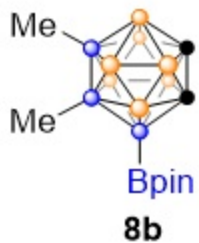
Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr7-82-1d
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring_1gy
Number of Scans	512
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	2016-01-07 15:24:45
Modification Date	2016-01-07 15:28:00
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-16282.3
Nucleus	<sup>11</sup> B
Acquired Size	16394
Spectral Size	3268



Supplementary Figure 137. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of **8b**.

crf-7-82-B-coupling-CDC13

35.119



-4.460

-5.596

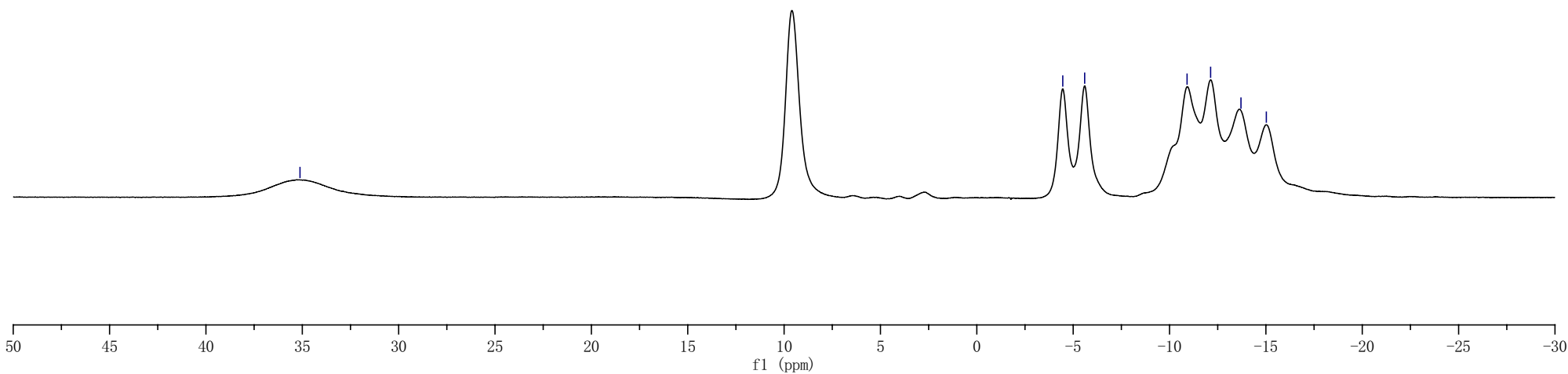
-10.910

-12.132

-13.706

-15.023

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr782coupling/td
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	chr400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1gy
Number of Scans	512
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	2016-01-04T15:31:18
Modification Date	2016-01-04T18:32:00
Spectrometer Frequency	128.38
Spectral Width	326.3
Lowest Frequency	-16323
Nucleus	11B
Acquired Size	16394
Spectral Size	3268



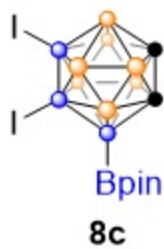
Supplementary Figure 138. <sup>11</sup>B NMR Spectrum of 8b.

crf-8-28-H-CDCl3

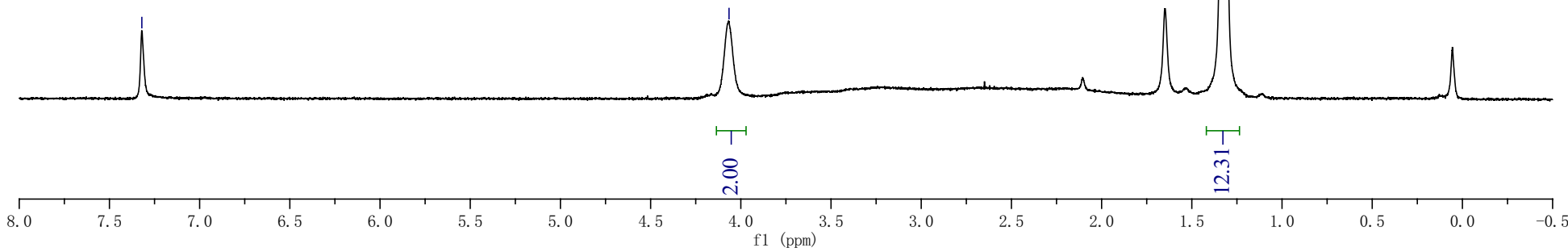
7.320

4.065

1.320



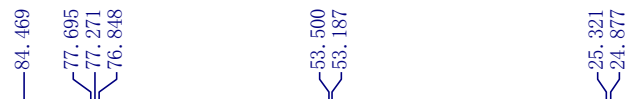
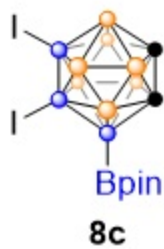
Parameter	Value
Title	crf-8-28-H-CDCl3
Comment	STANDARD 1H CDSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	zgpg30
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2016-03-14 12:25:03
Spectrometer	300 CD
Frequency	
Spectral Width	5494.5
Lowest Frequency	-53.2
Nucleus	1H
Acquired Size	10888
Spectral Size	3268



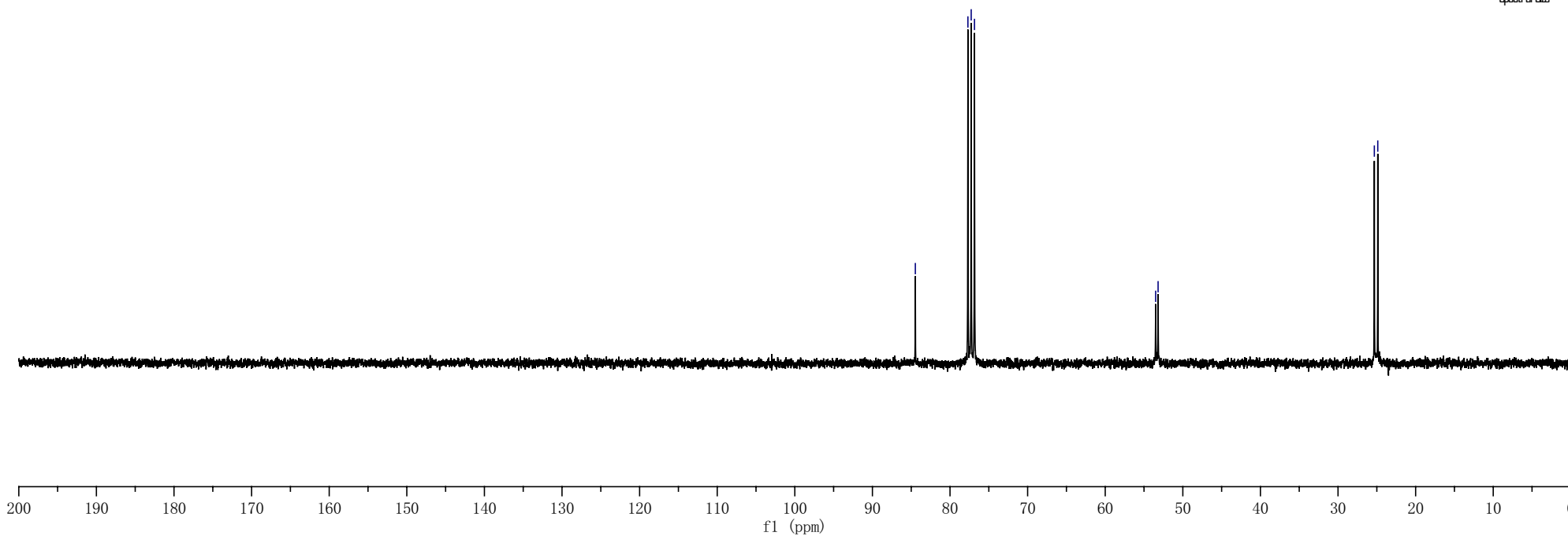
Supplementary Figure 139. <sup>1</sup>H NMR Spectrum of 8c.



crf-8-28-C-CDCl3

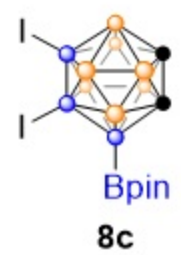


Parameter	Value
Title	crf-8-28-C-034
Comment	13C DEPT-135
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	sgzb
Number of Scans	1388
Receiver Gain	34
Relaxation Delay	1.000
Pulse Width	0.000
Acquisition Date	2016-03-14 12:30:28
Spectrometer Frequency	76.45
Spectral Width	1901.4
Lowest Frequency	-4735.0
Nucleus	13C
Acquired Size	2637
Spectral Size	65536



Supplementary Figure 140. <sup>13</sup>C NMR Spectrum of 8c.

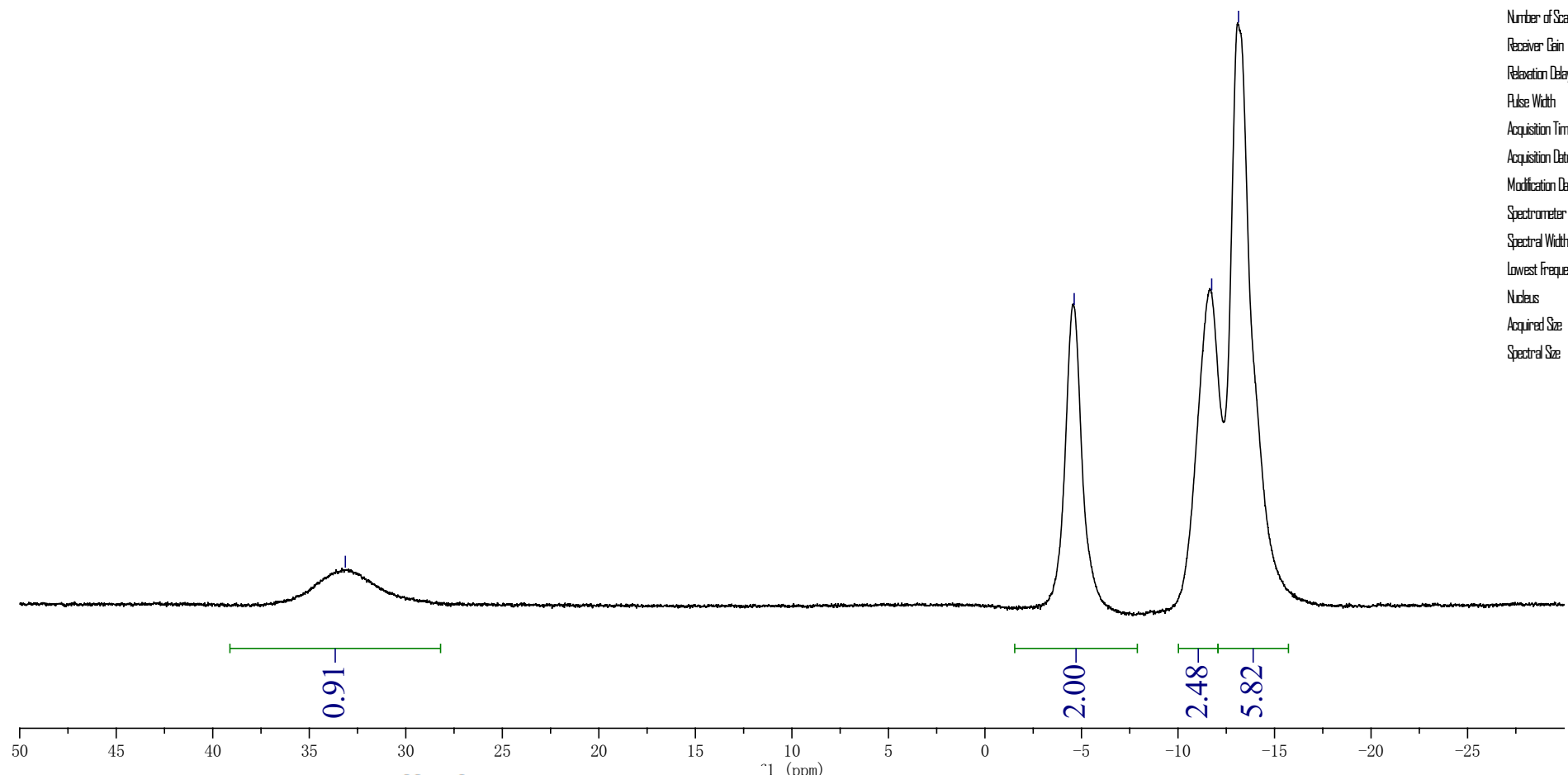
33.131



-4.623

-11.745

-13.136

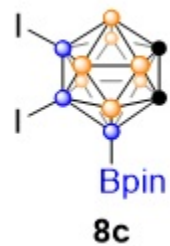


Parameter	Value
Data File Name	E:/boration/boration/8-28/ 2135b-cr8-28coupling/2135b- cr8-28/1.fid
Title	2135b-cr8-28
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.ty
Number of Scans	80
Receiver Gain	26
Relaxation Delay	1.0000
Pulse Width	8.5000
Acquisition Time	0.512
Acquisition Date	2016-03-15 15:16:04
Modification Date	2016-03-15 13:01:20
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-1639.5
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

Supplementary Figure 141. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of 8c.

crf-8-28-B-coupling-CDC13

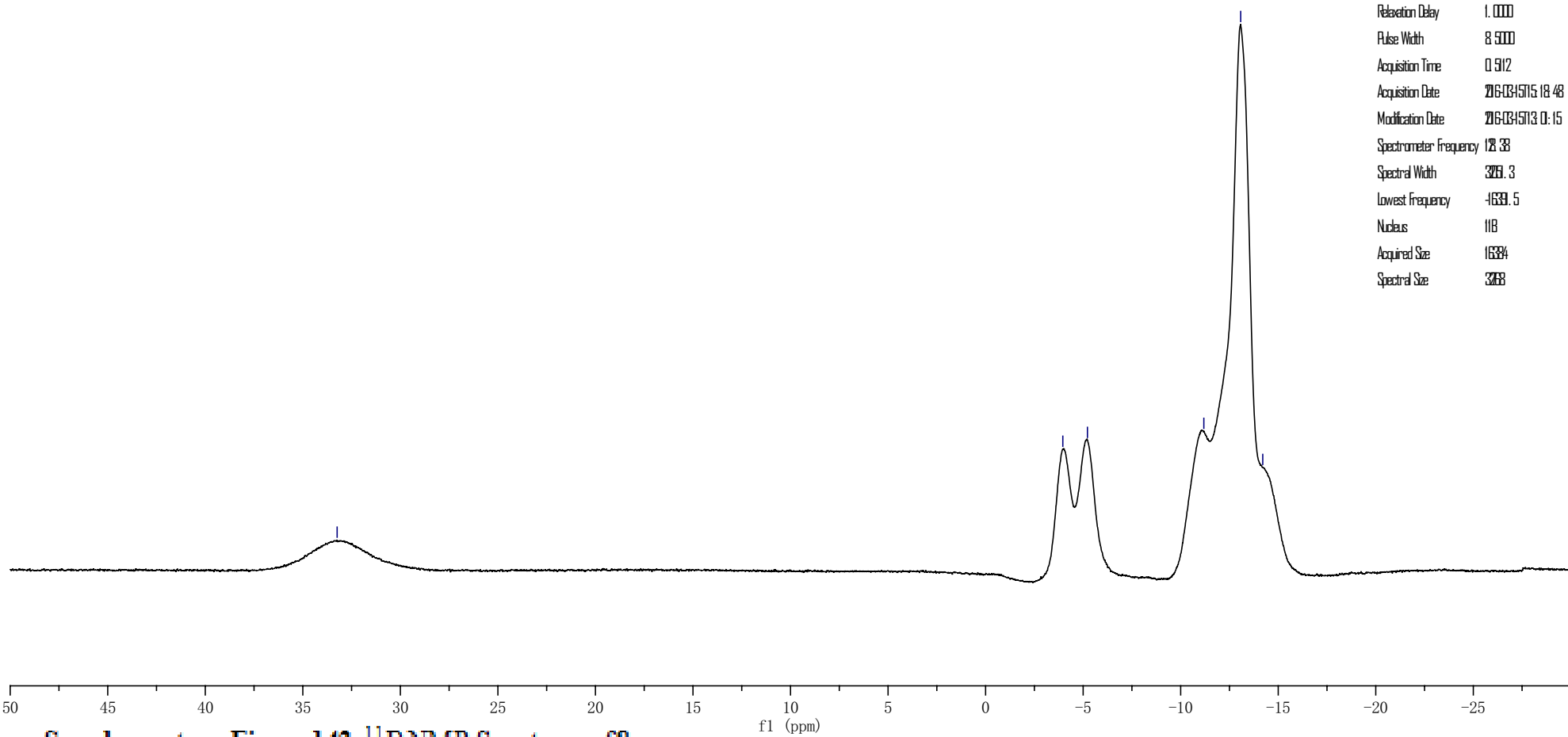
33.240



-3.959  
-5.220

-11.187  
-13.076  
-14.207

Parameter	Value
Data File Name	E:/boralation/boralation/8-28/2135b-cr8-2-coupling/2135b-cr8-2-coupling/1/fid
Title	2135b-cr8-2-coupling
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.1g
Number of Scans	172
Receiver Gain	26
Relaxation Delay	1.0000
Pulse Width	8.5000
Acquisition Time	0.912
Acquisition Date	2016-03-15 15:18:48
Modification Date	2016-03-15 13:01:15
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-1630.5
Nucleus	11B
Acquired Size	16394
Spectral Size	3268

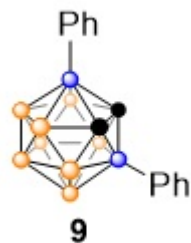


Supplementary Figure 142. <sup>11</sup>B NMR Spectrum of 8c.

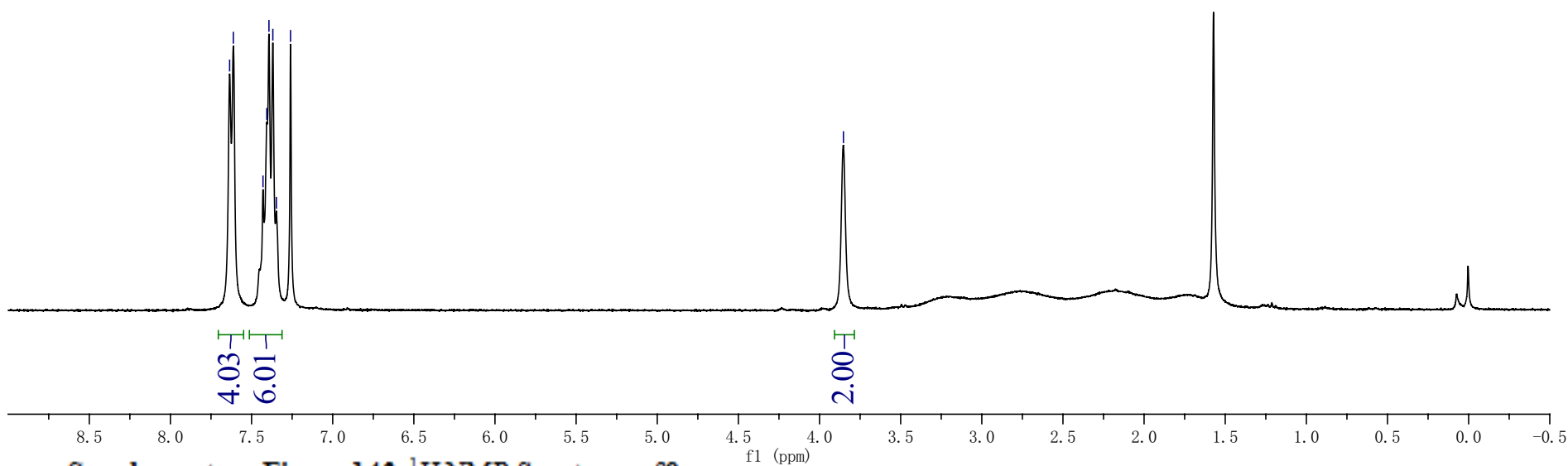
crf-5-11-H-CDCl<sub>3</sub>

7.635  
7.612  
7.430  
7.406  
7.393  
7.369  
7.347  
7.260

3.853

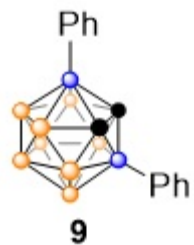


Parameter	Value
Title	crf511-H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	28.0
Pulse Sequence	sput
Number of Scans	8
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-06-20 12:03:02
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-71.0
Nucleus	<sup>1</sup> H
Acquired Size	10975
Spectral Size	3268



Supplementary Figure 143. <sup>1</sup>H NMR Spectrum of 9.

crf-5-11-C-CDCl<sub>3</sub>

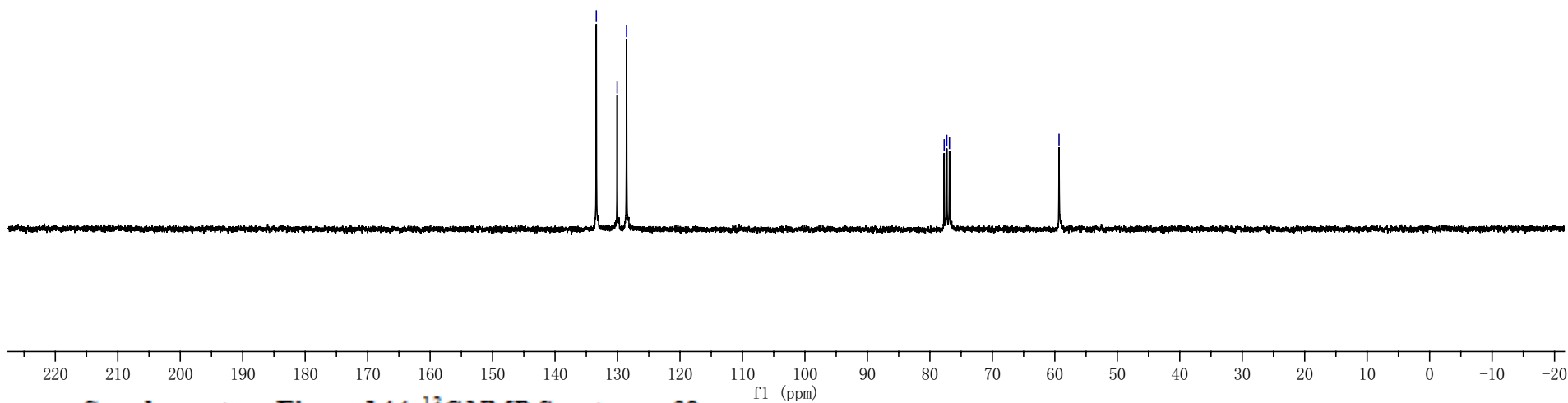


133.394  
130.060  
128.553

77.716  
77.293  
76.869

59.325

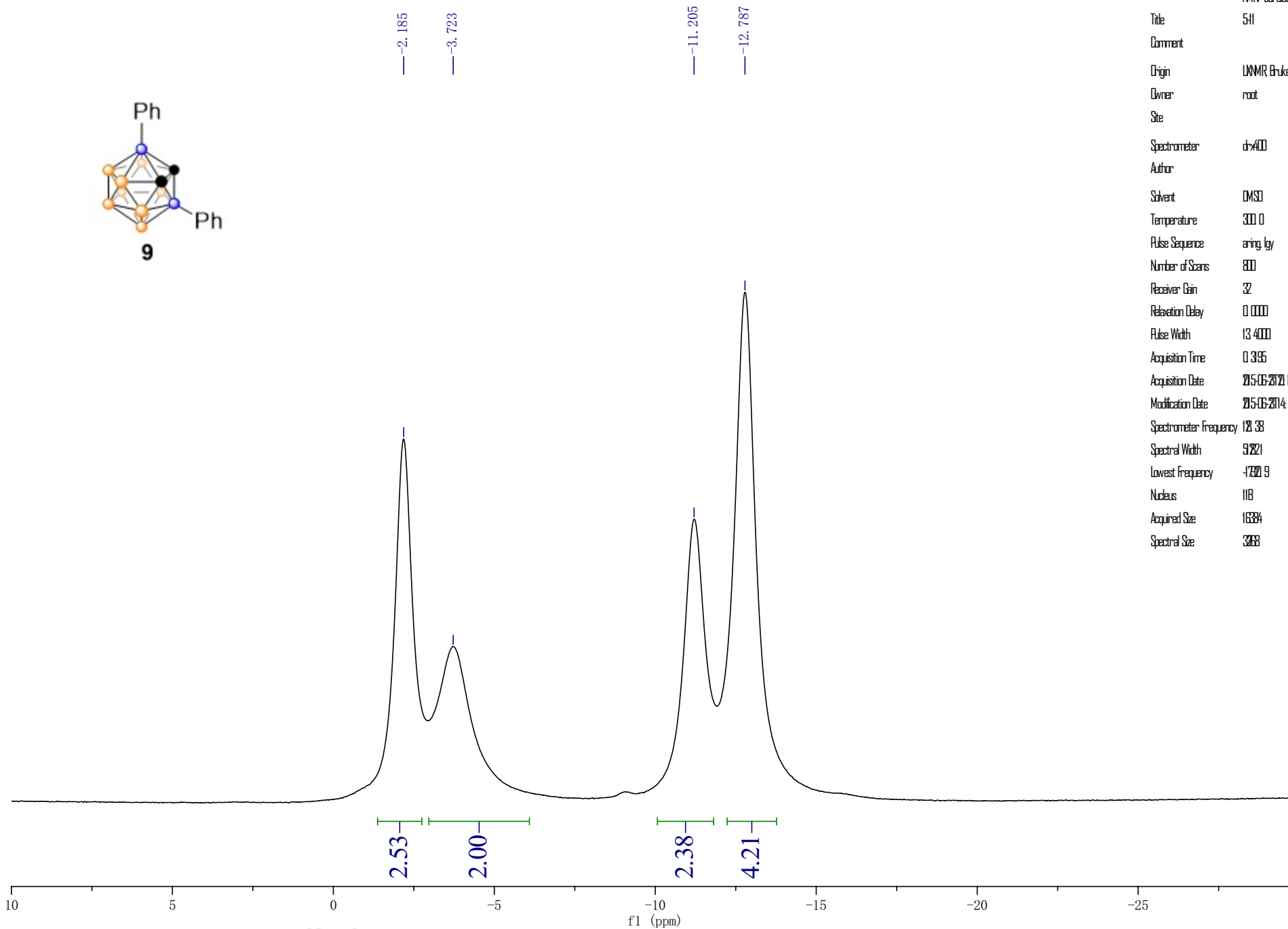
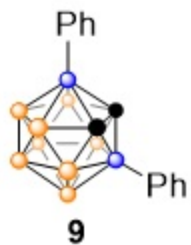
Parameter	Value
Title	crf5-11-C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl <sub>3</sub>
Temperature	28.0
Pulse Sequence	squl
Number of Scans	404
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-06-20 12:21:53
Spectrometer Frequency	75.45
Spectral Width	18887.0
Lowest Frequency	-1627.8
Nucleus	13C
Acquired Size	28155
Spectral Size	65536



Supplementary Figure 144. <sup>13</sup>C NMR Spectrum of 9.

crf-5-11-B-decoupling-CDCl<sub>3</sub>

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/work/送样 NMR/borolabium/5H/b-crfs5H/fid
Title	5H
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1gy
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-06-20 10:30
Modification Date	2015-06-20 14:03:00
Spectrometer Frequency	128.38
Spectral Width	9.2821
Lowest Frequency	-17920.9
Nucleus	<sup>11</sup> B
Acquired Size	16584
Spectral Size	3068



Supplementary Figure 145. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of **9**.

crf-5-11-B-coupling-CDCl<sub>3</sub>

—1.593

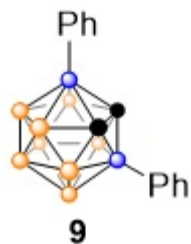
—2.760

—3.659

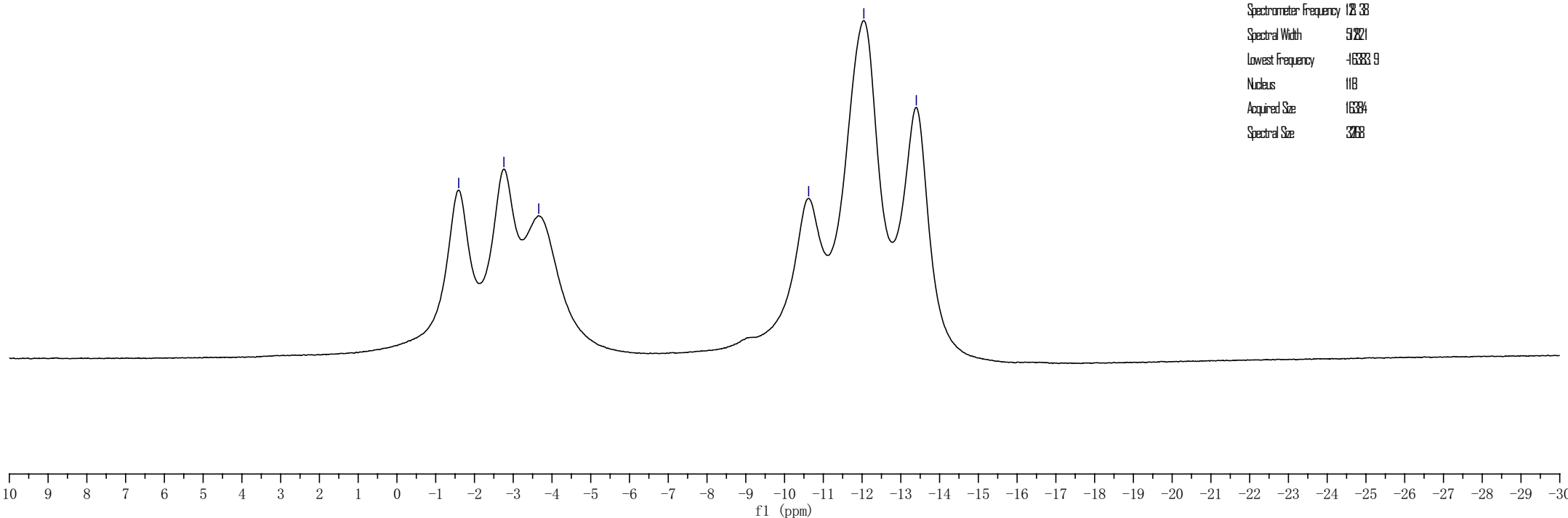
—10.622

—12.046

—13.400



Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/work/送样 NMR/borabatom/5-11/b-crf5-11/fid
Title	5-11
Comment	
Origin	LUMMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.1gy
Number of Scans	800
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3195
Acquisition Date	21-5-16-2017 14:42
Modification Date	21-5-16-2017 14:00
Spectrometer Frequency	128.38
Spectral Width	5.2821
Lowest Frequency	-16333.9
Nucleus	11B
Acquired Size	16334
Spectral Size	3268



Supplementary Figure 146. <sup>11</sup>B NMR Spectrum of 9.

S167

crf-6-58-H-CDCl3

Parameter	Value
Title	crf-6-58-H-CDCl3
Comment	STANDARD OBSERVE
Origin	Varien
Owner	
Site	
Spectrometer	mercury
Author	onc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	sgui
Number of Scans	8
Receiver Gain	24
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	20151013 16:30:13
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-71.0
Nucleus	1H
Acquired Size	10376
Spectral Size	3268

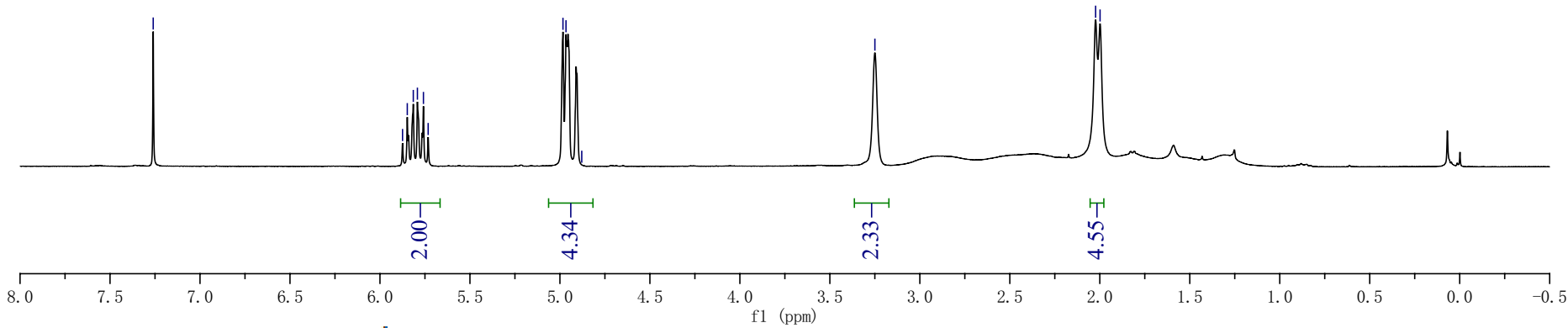
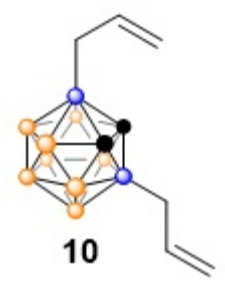
7.260

5.875  
5.848  
5.815  
5.792  
5.758  
5.732

4.983  
4.966  
4.879

3.250

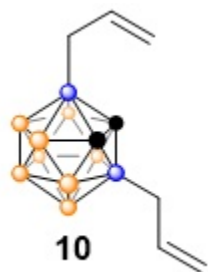
2.023  
1.998



Supplementary Figure 147. <sup>1</sup>H NMR Spectrum of 10.



crf-6-58-C-CDCl3



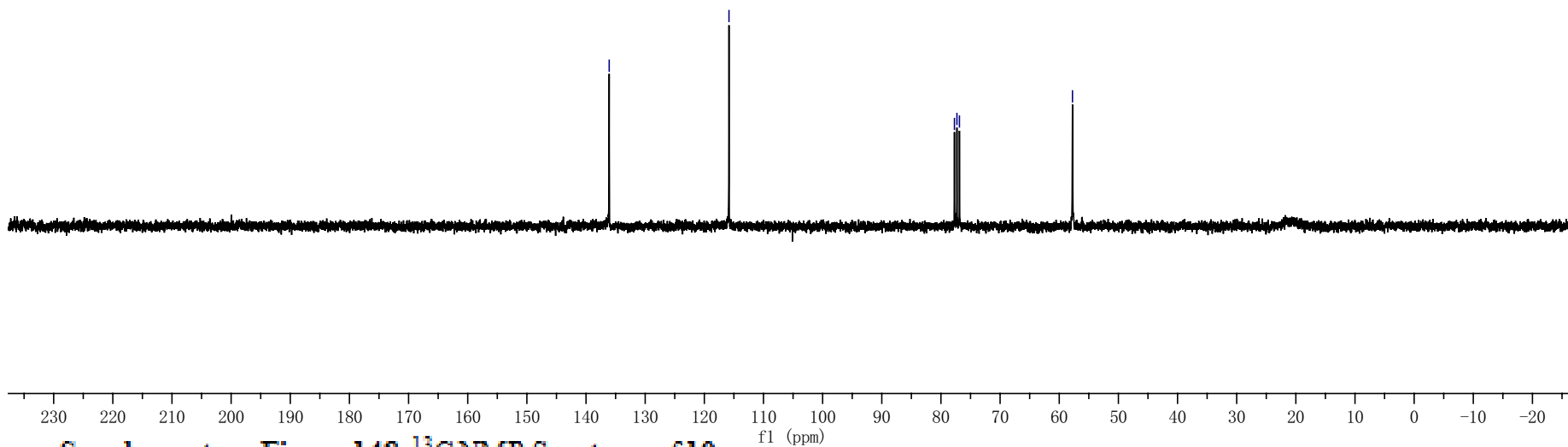
136.082

115.832

77.719  
77.296  
76.872

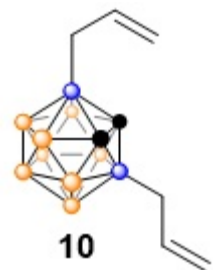
57.763

Parameter	Value
Title	crf-6-58-C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	zg31
Number of Scans	44
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-10-08 12:48:01
Spectrometer Frequency	76.45
Spectral Width	20000.0
Lowest Frequency	-288.3
Nucleus	13C
Acquired Size	2888
Spectral Size	65536



Supplementary Figure 148. <sup>13</sup>C NMR Spectrum of 10.

crf-6-58-B-decoupling-CDC13

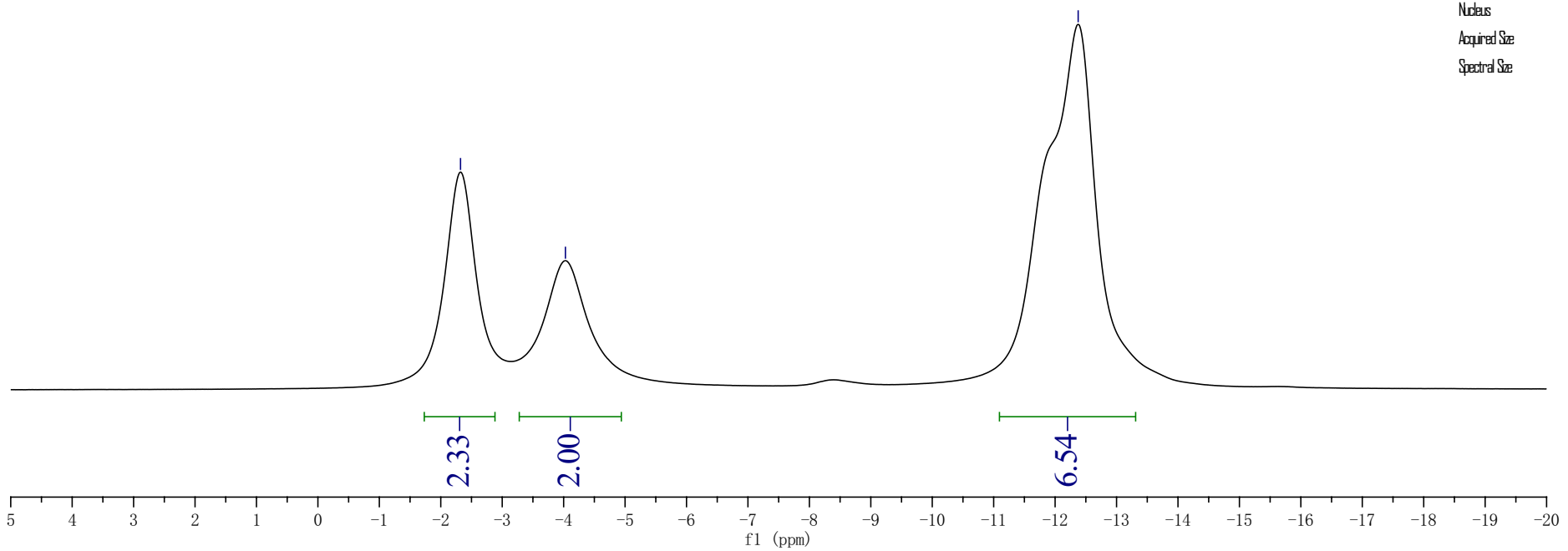


-2.322

-4.029

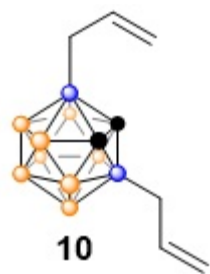
-12.375

Parameter	Value
Data File Name	E:/nmr/b-cr-f6-58/fid
Title	nmr
Comment	
Origin	LNMNR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	chr400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.tgy
Number of Scans	266
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.4260
Acquisition Date	2015-04-09T15:12:03
Modification Date	2015-04-09T08:12:00
Spectrometer Frequency	128.38
Spectral Width	38963.5
Lowest Frequency	-19333.4
Nucleus	<sup>11</sup> B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 149. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of 10.

crf-6-58-B-coupling-CDC13



-1.754

-2.909

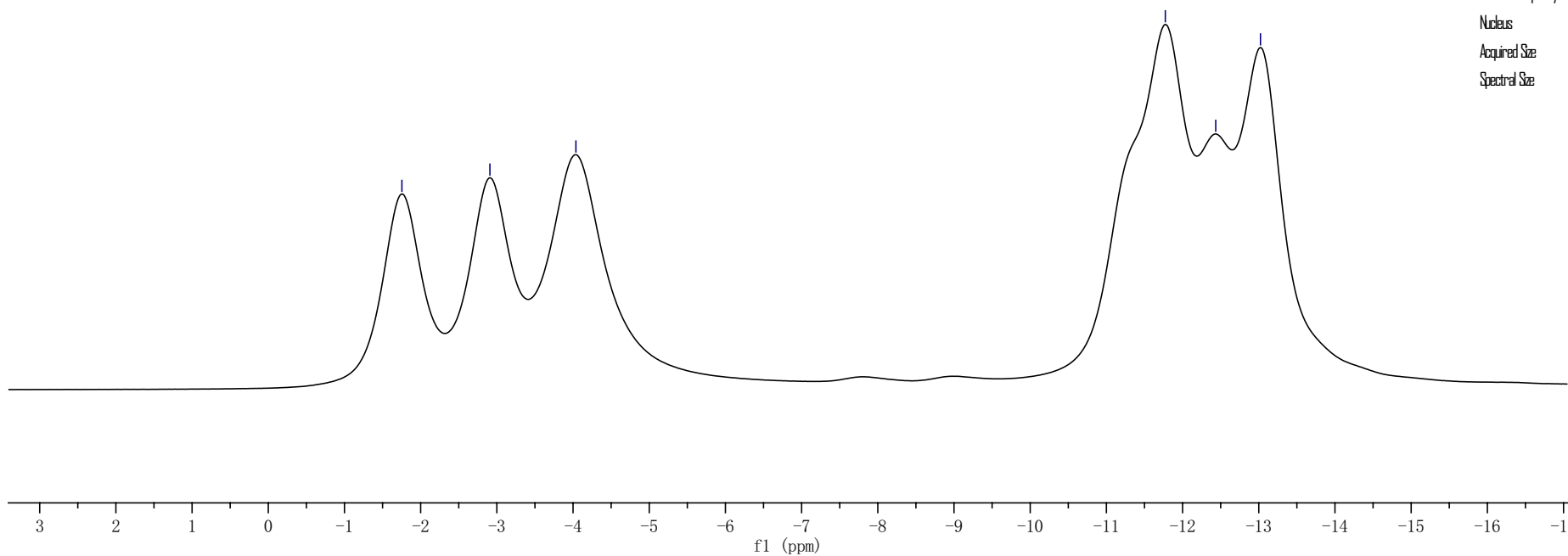
-4.038

-11.773

-12.435

-13.022

Parameter	Value
Data File Name	E:/nmr/b-cr-f6-58-coupling/1d
Title	nmr
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.tgy
Number of Scans	512
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.4260
Acquisition Date	2015-04-09T15:14:2
Modification Date	2015-04-09T08:18:00
Spectrometer Frequency	128.38
Spectral Width	3946.5
Lowest Frequency	-19810.3
Nucleus	11B
Acquired Size	16394
Spectral Size	3268

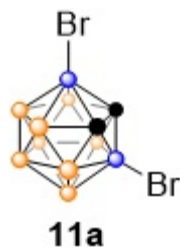


Supplementary Figure 150.  $^{11}\text{B}$  NMR Spectrum of 10.

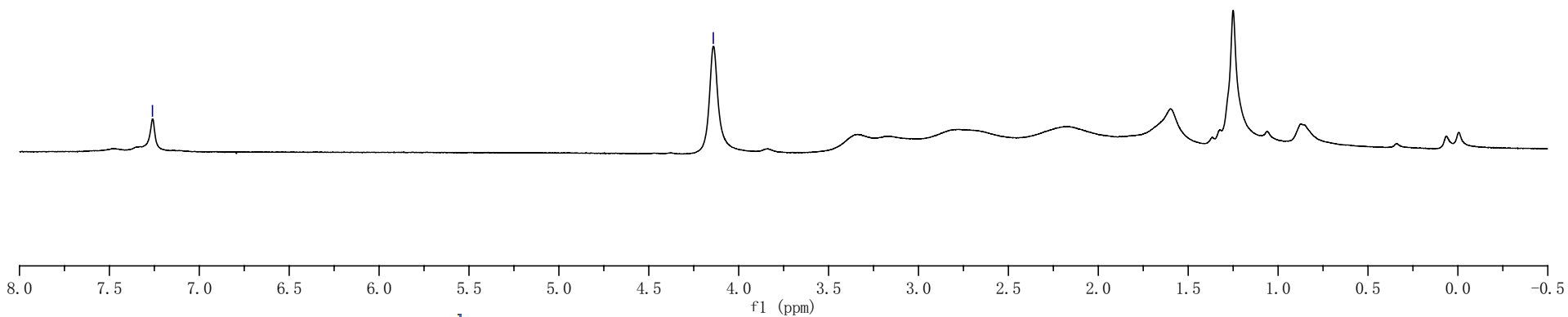
crf-6-11-H-CDC13

7.260

4.141

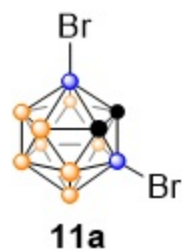


Parameter	Value
Title	crf-6-11-H-CDC13
Comment	
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	29.0
Pulse Sequence	sgdd
Number of Scans	8
Receiver Gain	2
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-09-10 17:43:10
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-708.0
Nucleus	<sup>1</sup> H
Acquired Size	10870
Spectral Size	3268



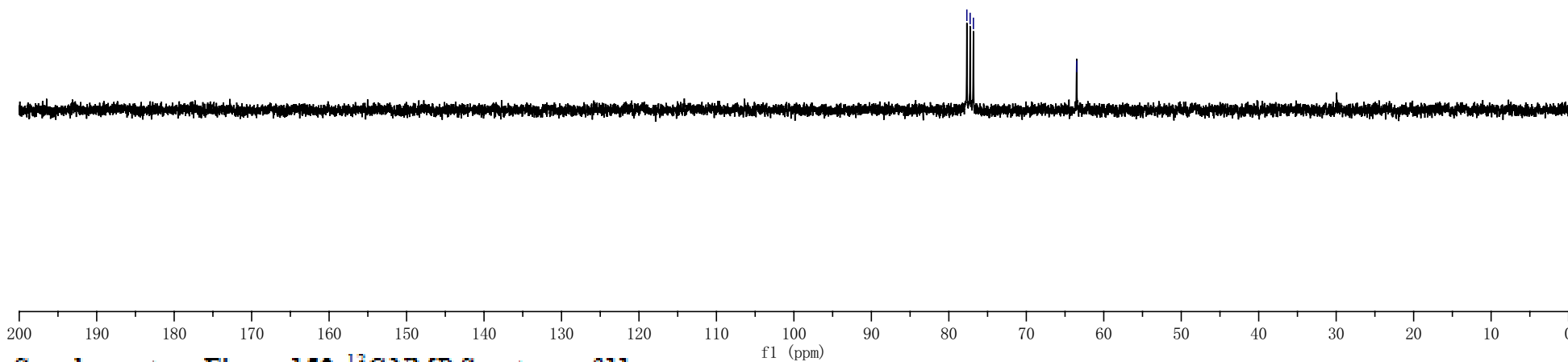
Supplementary Figure 151. <sup>1</sup>H NMR Spectrum of 11a.

crf-6-11-C-CDCl3



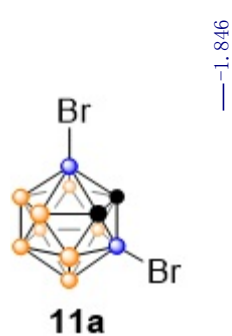
77.675  
77.250  
76.826  
— 63.498

Parameter	Value
Title	crf6-11-C-CDCl3
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	28.0
Pulse Sequence	squl
Number of Scans	68
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-09-10 17:44:11
Spectrometer Frequency	75.45
Spectral Width	2000.0
Lowest Frequency	-2183.3
Nucleus	13C
Acquired Size	28888
Spectral Size	65536



Supplementary Figure 152. <sup>13</sup>C NMR Spectrum of 11a.

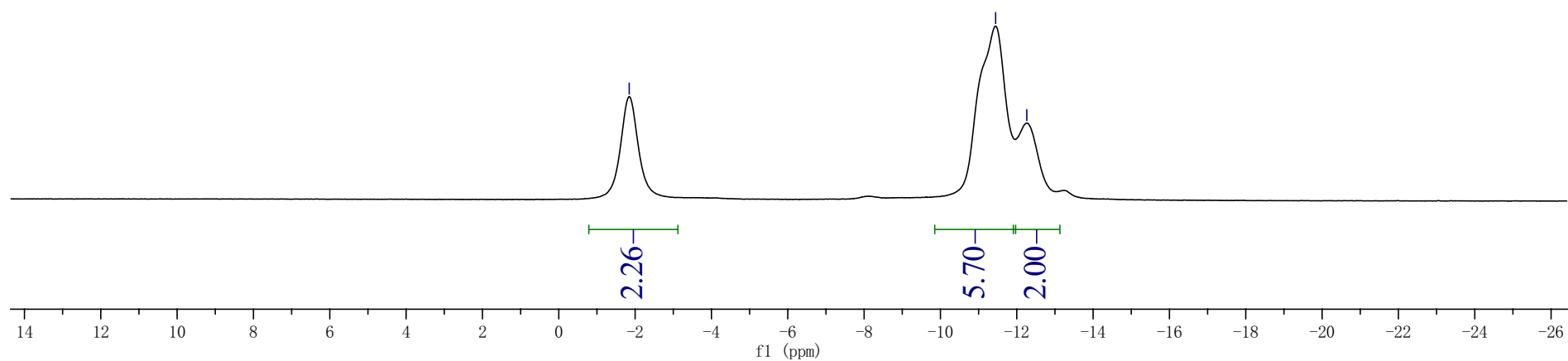
crf-6-11-B-decoupling-CDCl3



-1.846

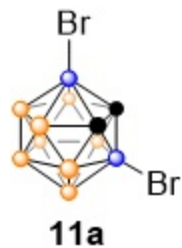
-11.446  
-12.262

Parameter	Value
Data file Name	G:/Users/Administrator/Desktop/work/送样NMR/borablation/GH/b-crF6H/fid
Title	GH
Comment	
Origin	UNMR, Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dmx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.tgy
Number of Scans	133
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.480
Acquisition Date	2015-09-11 22:00:33
Modification Date	2015-09-11 16:01:00
Spectrometer Frequency	128.38
Spectral Width	33461.5
Lowest Frequency	-15166.0
Nucleus	11B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 153.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of 11a.

crf-6-11-B-coupling-CDCl3



-1.240

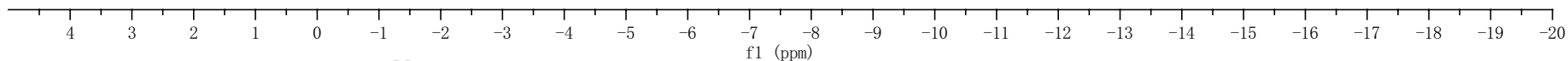
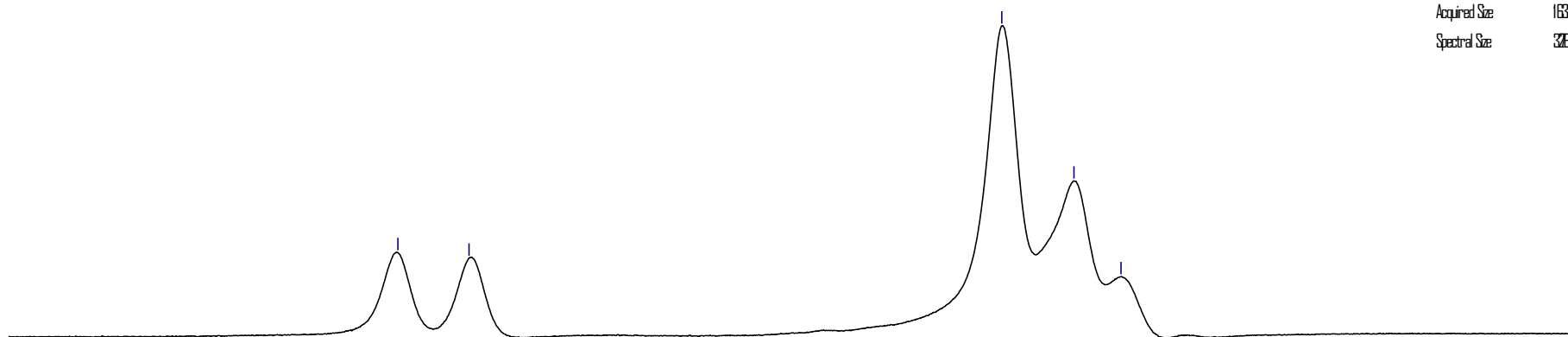
-2.380

-10.917

-12.074

-12.827

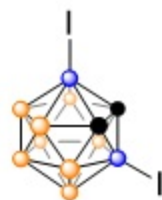
Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/work/送样NMR/borabatom/GH/b-cr6-11-coupling/fid
Title	GH
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	zing1gy
Number of Scans	400
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.4800
Acquisition Date	2015-08-17 20:04:03
Modification Date	2015-08-17 16:04:00
Spectrometer Frequency	128.38
Spectral Width	3346.5
Lowest Frequency	-11800.2
Nucleus	11B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 154. <sup>11</sup>B NMR Spectrum of 11a.

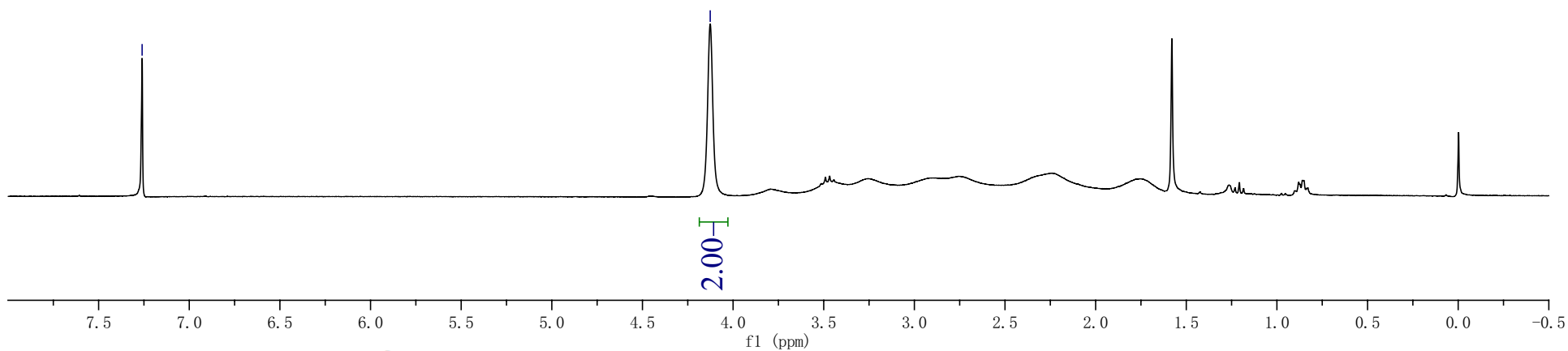
crf-6-6-H-CDCl3

7.260



11b

4.126

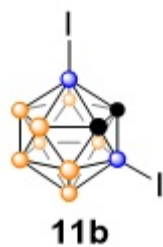


Parameter	Value
Title	crf6-6H
Comment	
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	onc
Solvent	CDCl3
Temperature	29.0
Pulse Sequence	sZgU
Number of Scans	8
Receiver Gain	28
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-09-08T12:13:35
Spectrometer Frequency	300.08
Spectral Width	5494.5
Lowest Frequency	-708.9
Nucleus	1H
Acquired Size	10970
Spectral Size	3288

Supplementary Figure 155. <sup>1</sup>H NMR Spectrum of 11b.

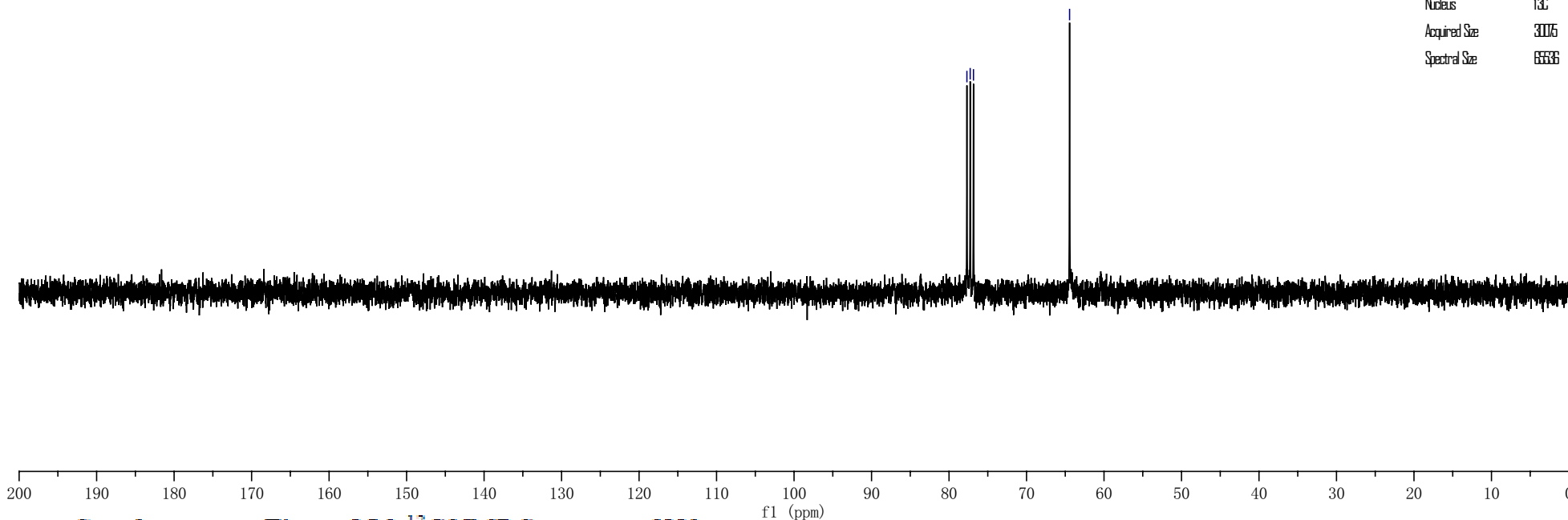


crf-6-6-C-CDCl3



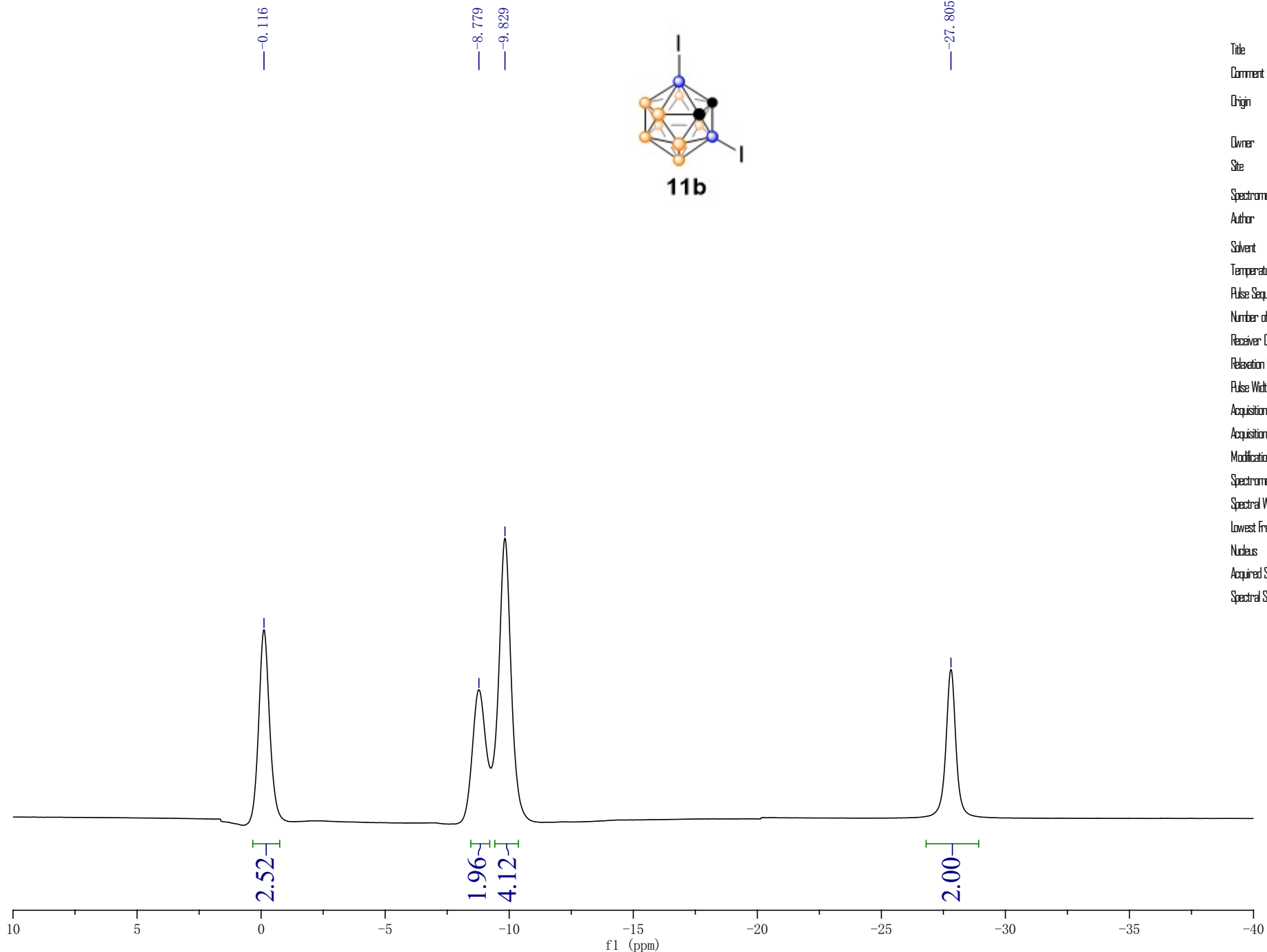
77.693  
77.269  
76.845  
64.444

Parameter	Value
Title	crf66C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	sZul
Number of Scans	52
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-09-05 12:16:47
Spectrometer Frequency	76.45
Spectral Width	18897.0
Lowest Frequency	-162.8
Nucleus	13C
Acquired Size	3006
Spectral Size	65636



Supplementary Figure 156. <sup>13</sup>C NMR Spectrum of 11b.

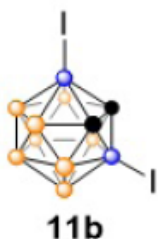
crf-6-6-B-decoupling-CDC13



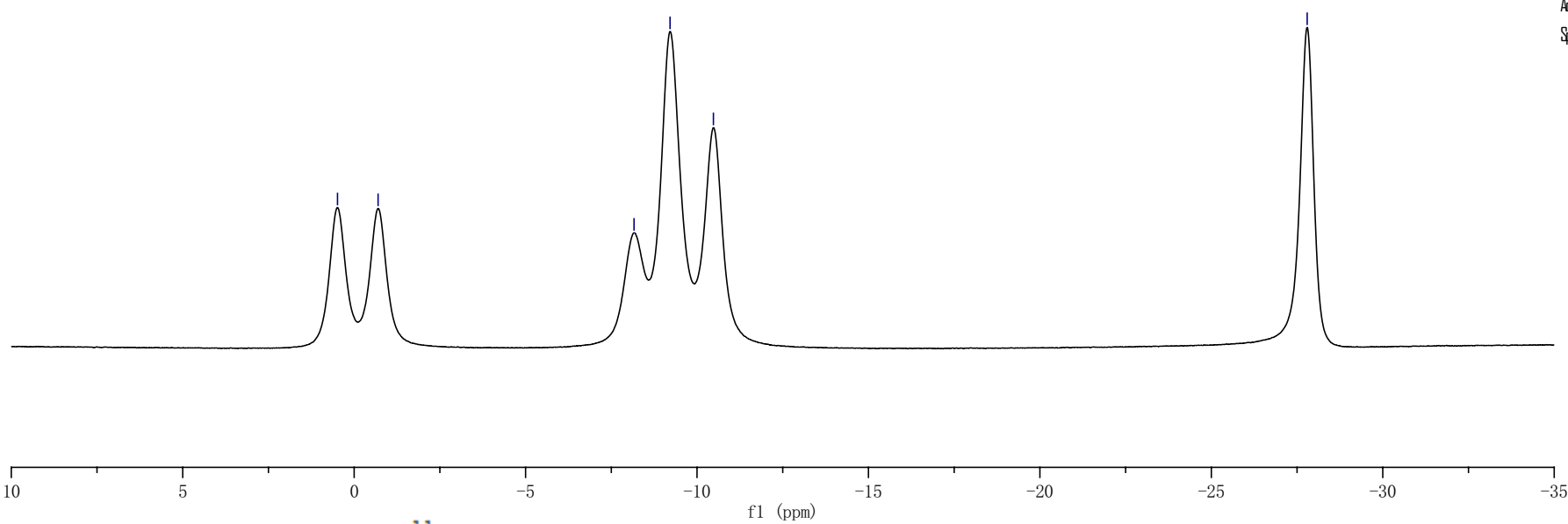
Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/2135b-cr66/2135b-cr66/1/f1
Title	2135b-cr66
Comment	
Origin	UNMR, Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	zing1gy
Number of Scans	400
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.420
Acquisition Date	21-08-07 15:50:56
Modification Date	21-08-07 10:56:15
Spectrometer Frequency	128.36
Spectral Width	3846.5
Lowest Frequency	-1566.0
Nucleus	11B
Acquired Size	16384
Spectral Size	3268

Supplementary Figure 157.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of **11b**.

crf-6-6-B-coupling-CDC13



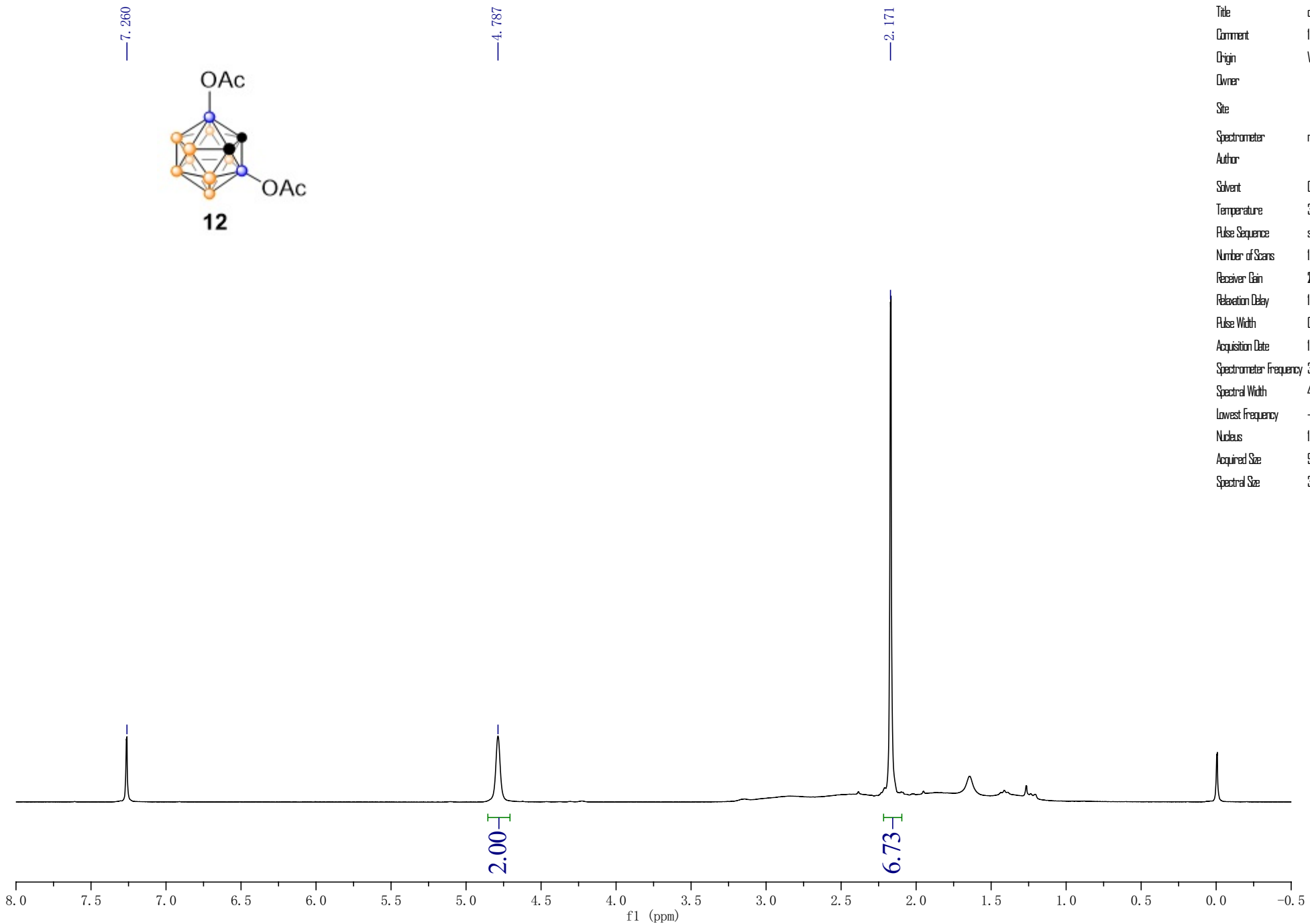
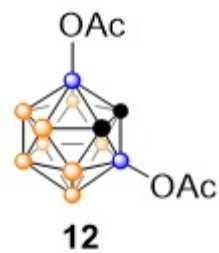
Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/21355b-crf6-6/21355b-crf6-6-coupling/1/fid
Title	21355b-crf6-6-coupling
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1gy
Number of Scans	400
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.480
Acquisition Date	21-09-07 15:54:18
Modification Date	21-09-07 10:56:10
Spectrometer Frequency	128.38
Spectral Width	3946.5
Lowest Frequency	-11870.2
Nucleus	11B
Acquired Size	16384
Spectral Size	3288



Supplementary Figure 158. <sup>11</sup>B NMR Spectrum of 11b.

crf-5-20-H-300M-CDCl3

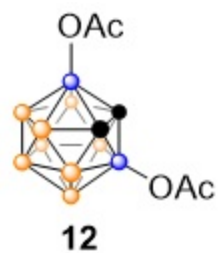
Parameter	Value
Title	crf5-20-300m205
Comment	1
Origin	Varien
Owner	
Site	
Spectrometer	mercury
Author	
Solvent	CDCl3
Temperature	3.0
Pulse Sequence	s2ul
Number of Scans	16
Receiver Gain	26
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	1999-11-13 16:21:28
Spectrometer Frequency	300.04
Spectral Width	4803.1
Lowest Frequency	-599.8
Nucleus	1H
Acquired Size	5592
Spectral Size	3268



Supplementary Figure 159. <sup>1</sup>H NMR Spectrum of 12.

crf-5-20-C-400M-CDC13

169.82

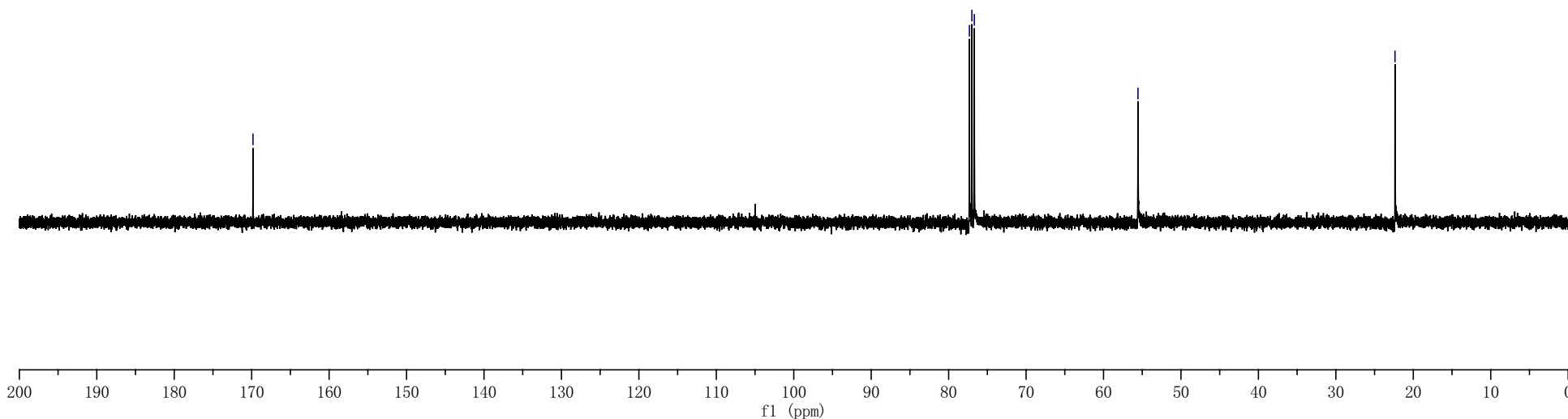


77.320  
77.003  
76.684

55.552

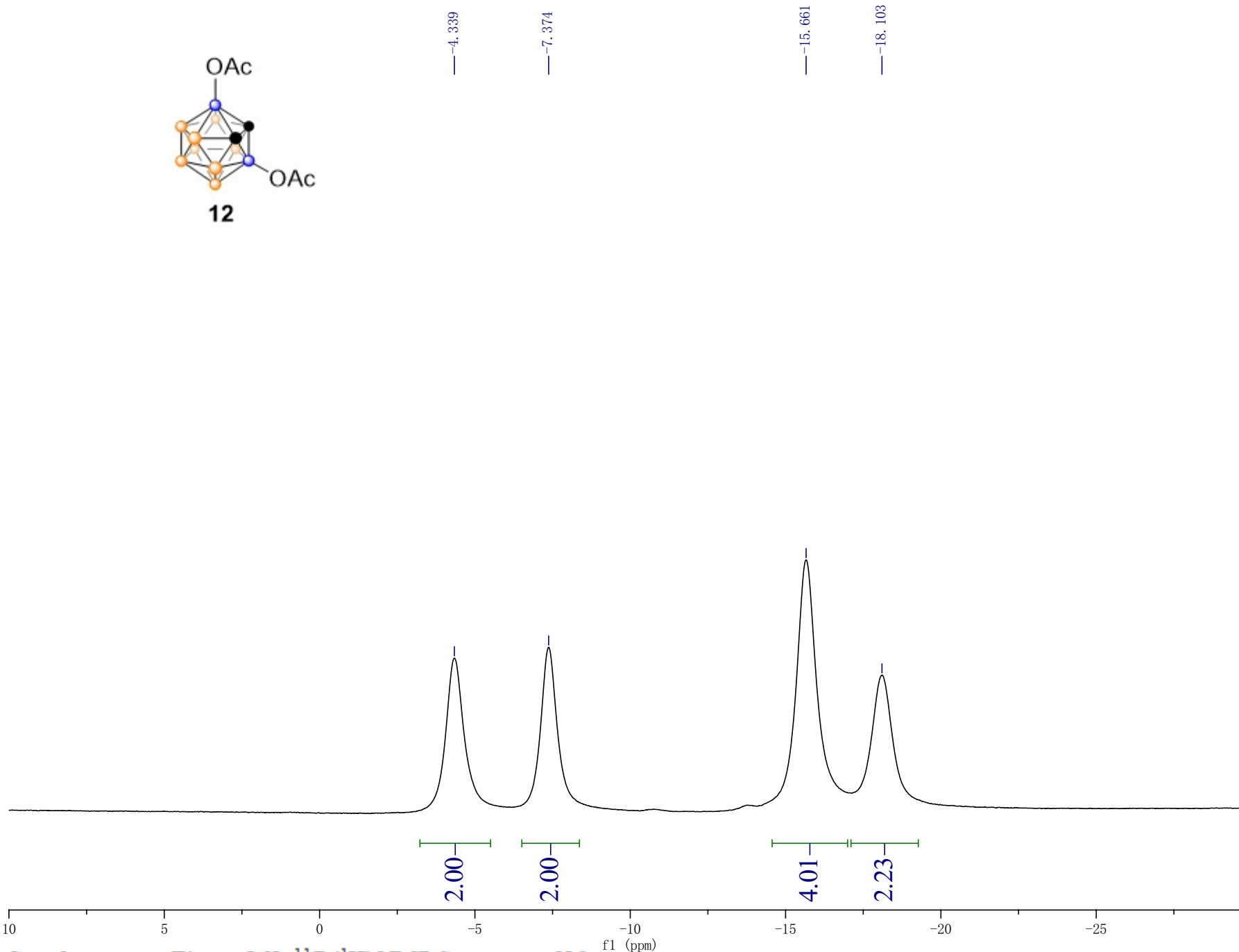
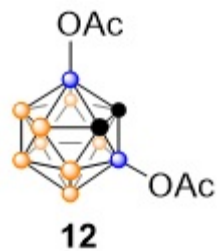
22.360

Parameter	Value
Title	crf-5-20-C-400M
Comment	Std carbon
Orign	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	omel
Solvent	cdcl3
Temperature	21.0
Pulse Sequence	sgpu
Number of Scans	112
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-05-30T12:37:28
Spectrometer Frequency	100.60
Spectral Width	2658.8
Lowest Frequency	-1688.3
Nucleus	13C
Acquired Size	3185
Spectral Size	65536



Supplementary Figure 160. <sup>13</sup>C NMR Spectrum of 12.

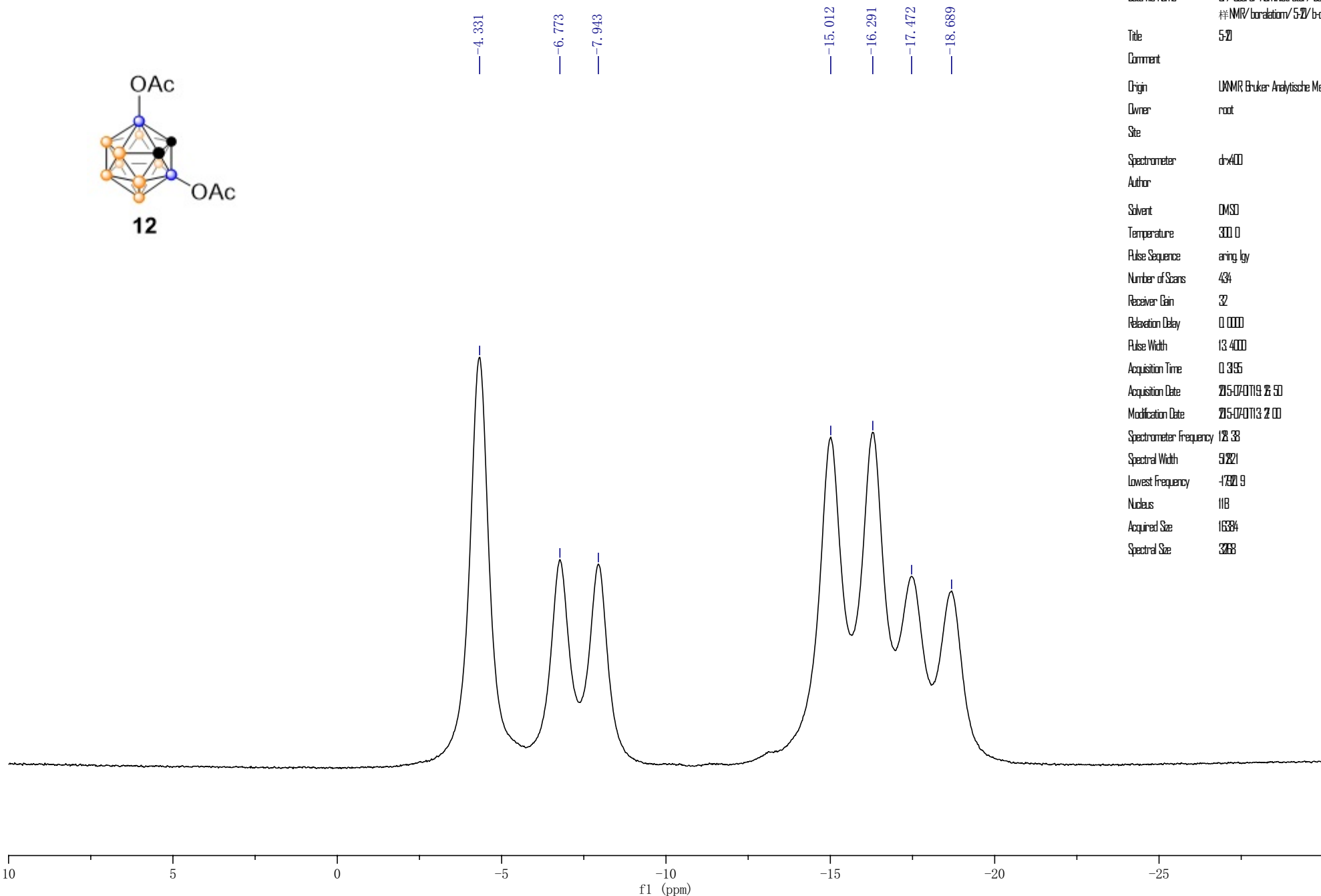
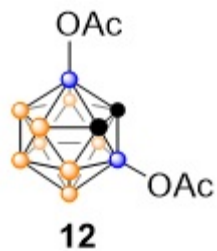
crf-5-20-B-decoupling-CDCl3



Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/work/送样NMR/borolatom/5-20/b-cr5-20.fid
Title	5-20
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1g
Number of Scans	439
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.355
Acquisition Date	2015-07-07 13:21:34
Modification Date	2015-07-07 13:24:00
Spectrometer Frequency	128.38
Spectral Width	51221
Lowest Frequency	-17321.9
Nucleus	11B
Acquired Size	16384
Spectral Size	3273

Supplementary Figure 161.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of **12**.

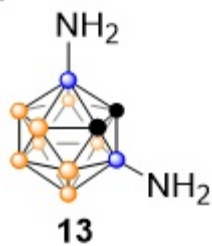
crf-5-20-B-coupling-CDC13



Parameter	Value
Data file Name	C:/Users/Administrator/Desktop/work/送 样NMR/borolab/5-20/b-cr-5-20-coupling/fid
Title	5-20
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	drx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1gy
Number of Scans	434
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-07-01 19:28:50
Modification Date	2015-07-01 19:28:00
Spectrometer Frequency	128.38
Spectral Width	51221
Lowest Frequency	-17320.9
Nucleus	11B
Acquired Size	16334
Spectral Size	3263

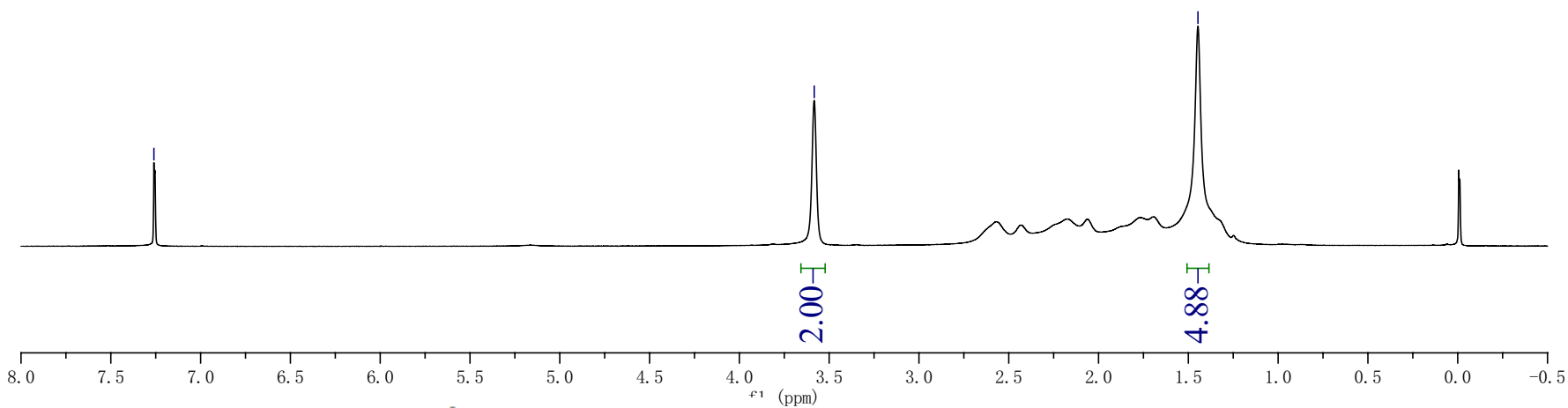
crf-5-16-H-400M-CDC13

7.260



3.583

1.447

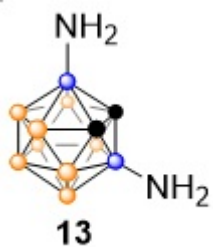


Parameter	Value
Title	crf516H400M
Comment	
Origin	Varian
Owner	
Site	
Spectrometer	nmrs
Author	
Solvent	CDCl3
Temperature	19.0
Pulse Sequence	sgpl
Number of Scans	8
Receiver Gain	36
Relaxation Delay	1.000
Pulse Width	0.000
Acquisition Date	2015-05-27 09:18:35
Spectrometer Frequency	399.72
Spectral Width	6400.3
Lowest Frequency	-808.0
Nucleus	1H
Acquired Size	1928
Spectral Size	65535

Supplementary Figure 163. <sup>1</sup>H NMR Spectrum of 13.

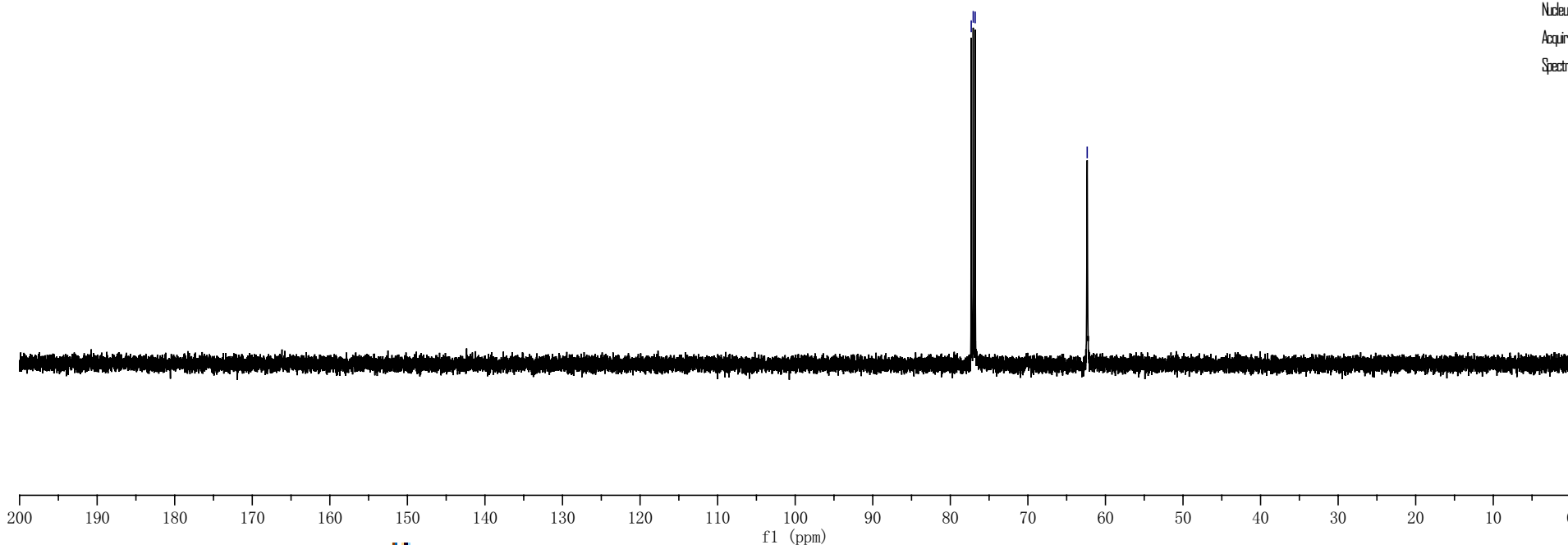


crf-5-16-C-500M-CDC13



77.303  
77.048  
76.795

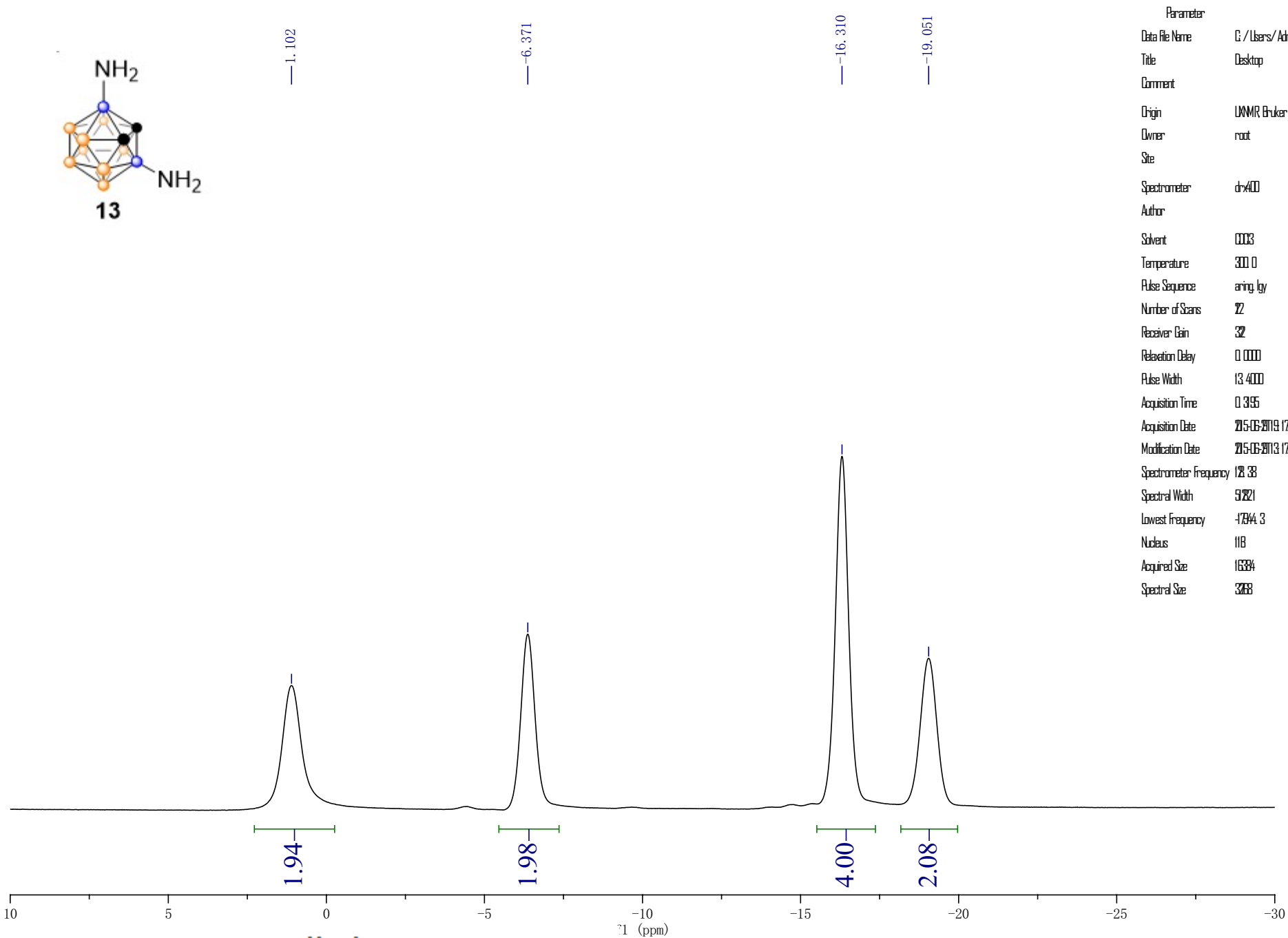
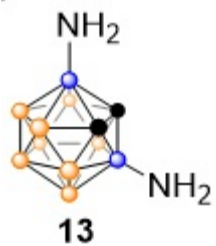
62.353



Parameter	Value
Title	21333byjc
Comment	21333byjc
Origin	Varian
Owner	
Site	
Spectrometer	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	sgpd
Number of Scans	128
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-06-20 12:43:22
Spectrometer Frequency	125.72
Spectral Width	3120.0
Lowest Frequency	-1737.9
Nucleus	13C
Acquired Size	3268
Spectral Size	65536

Supplementary Figure 164. <sup>13</sup>C NMR Spectrum of 13.

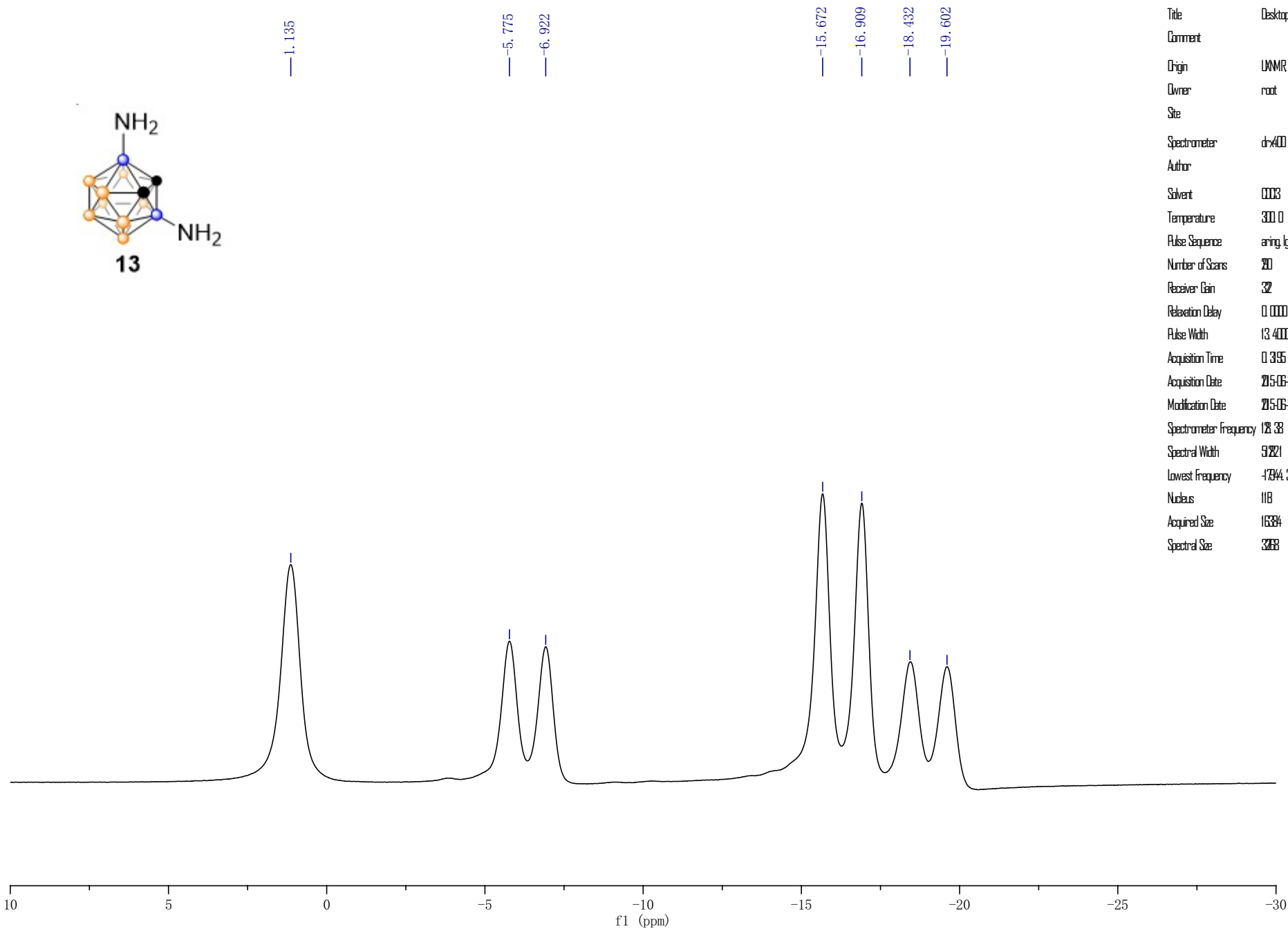
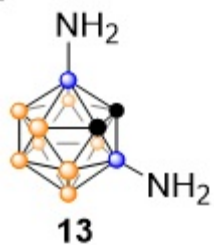
crf-5-16-B-decoupling-500M-CDCI3



Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr-f5-9/td
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	aring,lg
Number of Scans	12
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-08-20 13:17:2
Modification Date	2015-08-20 13:17:00
Spectrometer Frequency	128.38
Spectral Width	5.221
Lowest Frequency	4784.3
Nucleus	11B
Acquired Size	16394
Spectral Size	3288

Supplementary Figure 165.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of **13**.

crf-5-16-B-coupling-500M-CDC13

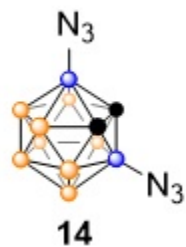


Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/b-cr-5-2-coupling/fid
Title	Desktop
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	aring1gy
Number of Scans	20
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.3155
Acquisition Date	2015-05-29 13:18:28
Modification Date	2015-05-29 13:19:00
Spectrometer Frequency	128.38
Spectral Width	5.221
Lowest Frequency	-17.844.3
Nucleus	11B
Acquired Size	16384
Spectral Size	3288

Supplementary Figure 166. <sup>11</sup>B NMR Spectrum of 13.

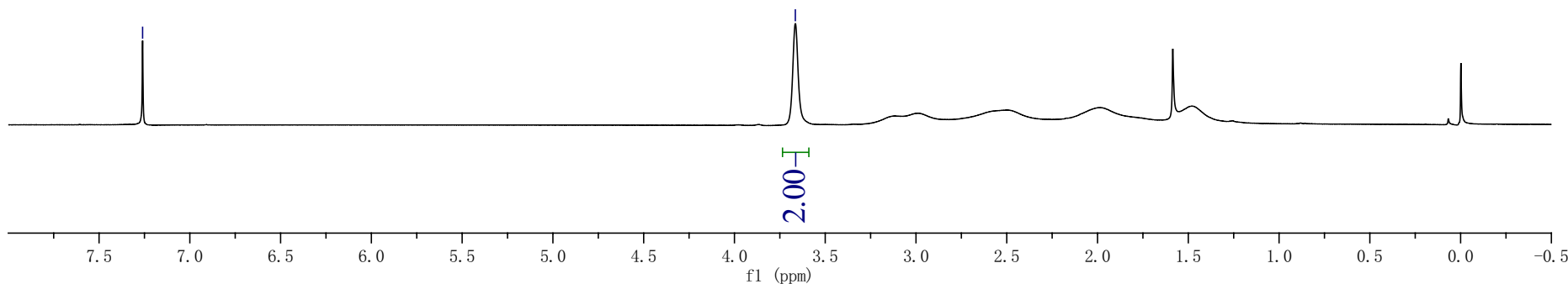
crf-4-65-H-CDCl3

7.260



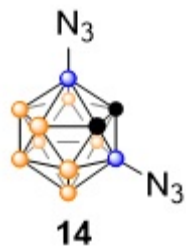
3.665

Parameter	Value
Title	crf-4-65-H-CDCl3
Comment	STANDARD 1H CDSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	sZul
Number of Scans	8
Receiver Gain	28
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-06-15 16:37:00
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-71.9
Nucleus	1H
Acquired Size	10016
Spectral Size	3288



Supplementary Figure 167. <sup>1</sup>H NMR Spectrum of 14.

crf-4-65-C-CDC13



77.702  
77.279  
76.855

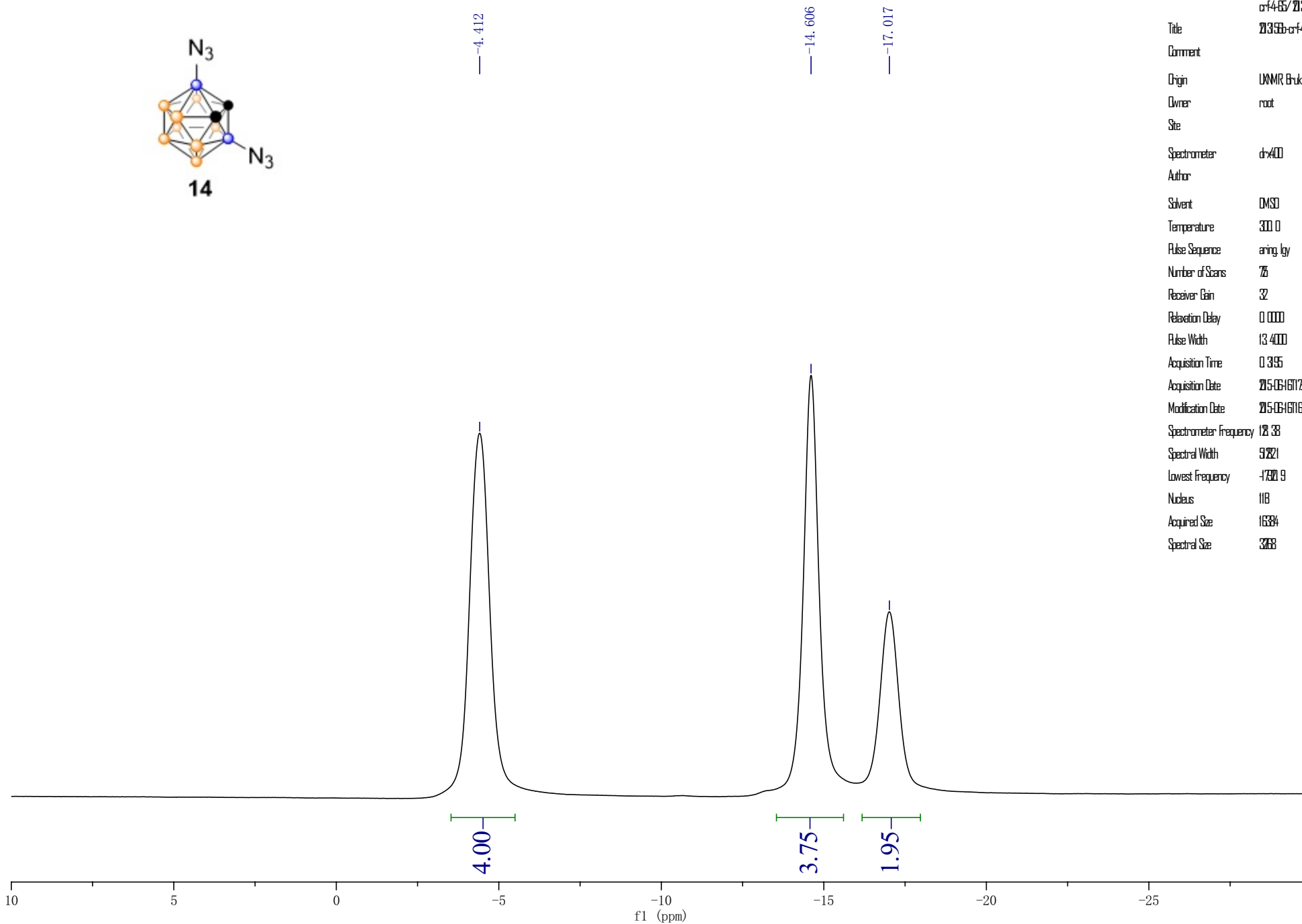
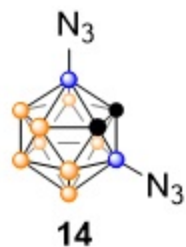
57.366

Parameter	Value
Title	crf-4-65-C
Comment	13C OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	29.0
Pulse Sequence	sZul
Number of Scans	136
Receiver Gain	28
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-08-15 17:12:51
Spectrometer Frequency	76.45
Spectral Width	18887.0
Lowest Frequency	462.8
Nucleus	13C
Acquired Size	2955
Spectral Size	65636



Supplementary Figure 168. <sup>13</sup>C NMR Spectrum of 14.

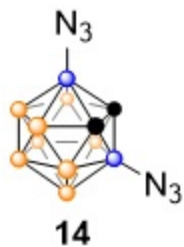
crf-4-65-B-decoupling-CDC13



Parameter	Value
Data File Name	G:/Users/Administrator/Desktop/20135B-cr4-65/20135B-cr4-65/1/f1
Title	20135B-cr4-65
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dr400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	ering_1gy
Number of Scans	78
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.355
Acquisition Date	2015-03-16 17:57:50
Modification Date	2015-03-16 16:00:25
Spectrometer Frequency	128.38
Spectral Width	9.281
Lowest Frequency	-17.929
Nucleus	11B
Acquired Size	16334
Spectral Size	3268

Supplementary Figure 169.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of 14.

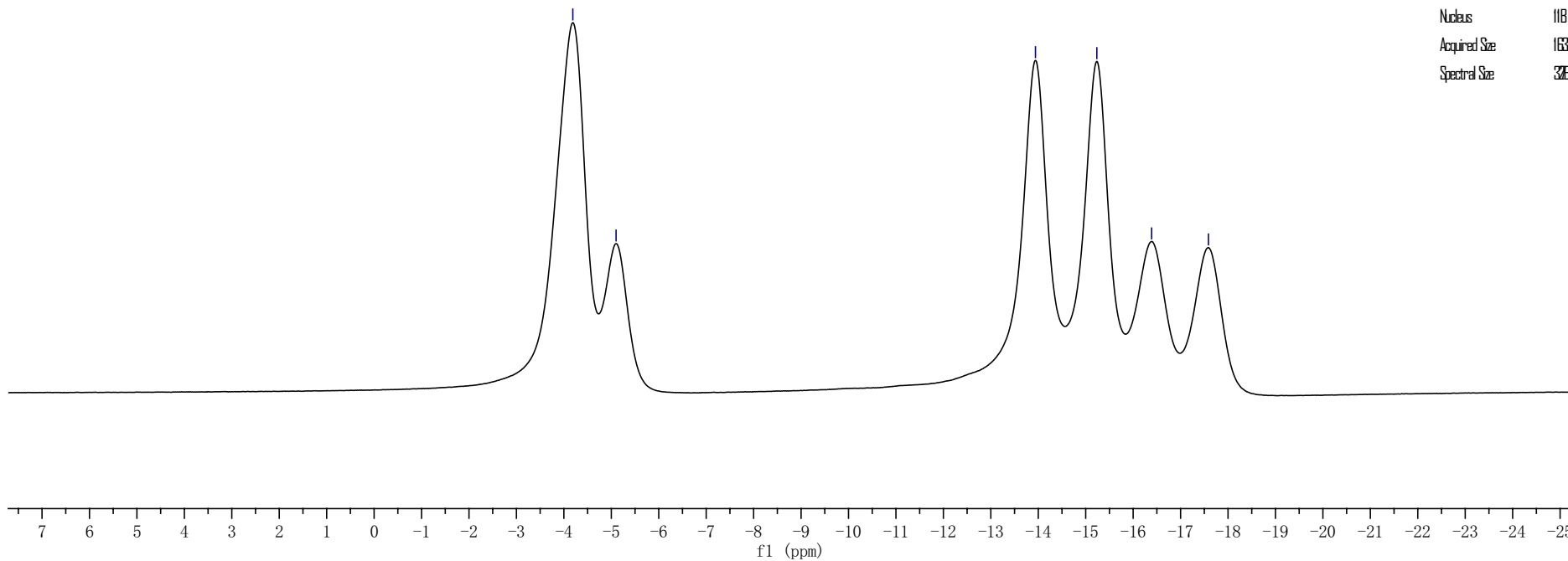
crf-4-65-B-coupling-CDCl3



-4.189  
-5.100

-13.941  
-15.235  
-16.390  
-17.587

Parameter	Value
Data file Name	C:/Users/Administrator/Desktop/201508-cr4-65/201508-cr4-65-coupling/1/fid
Title	201508-cr4-65-coupling
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dr400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	zing_1gy
Number of Scans	562
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.395
Acquisition Date	2015-08-16 18:01:48
Modification Date	2015-08-16 18:01:20
Spectrometer Frequency	128.38
Spectral Width	51221
Lowest Frequency	-14882.9
Nucleus	11B
Acquired Size	16334
Spectral Size	3268



Supplementary Figure 170. <sup>11</sup>B NMR Spectrum of 14.

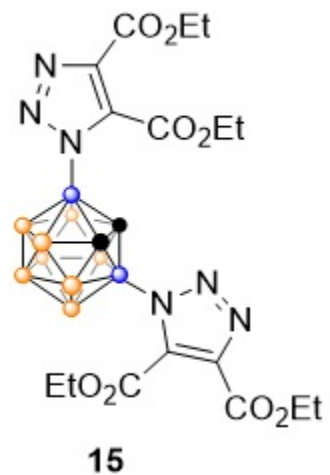
crf-7-54-H-CDCl3

7.260

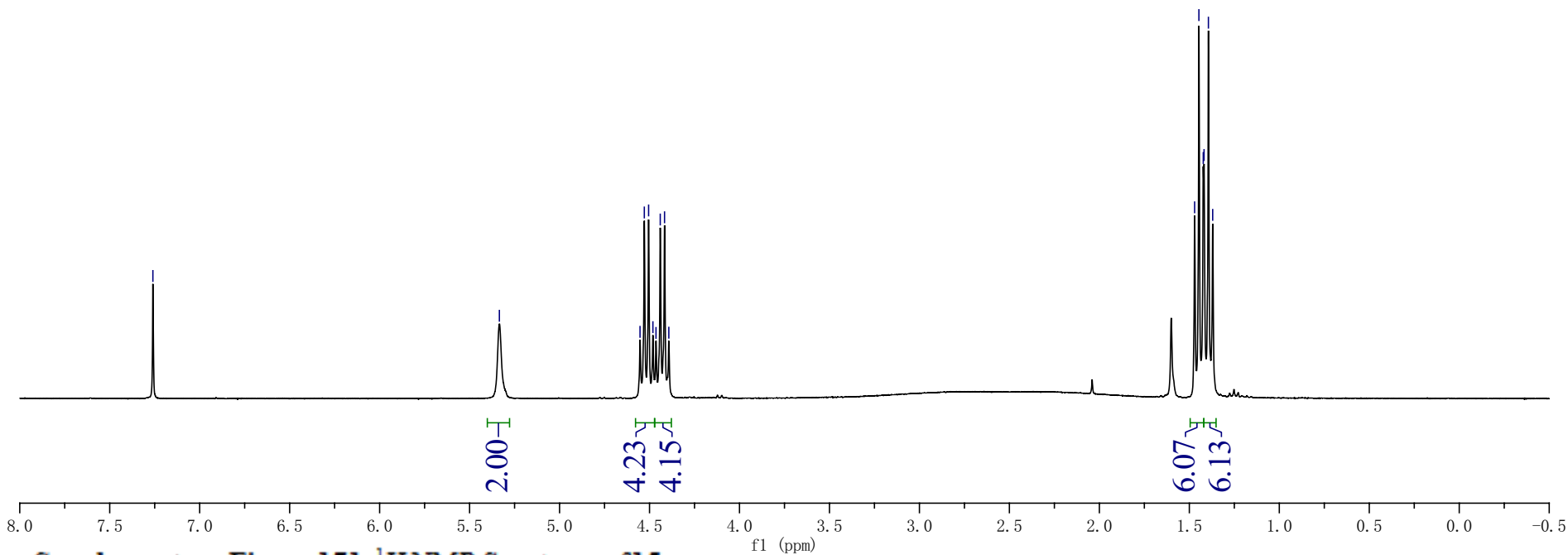
5.334

4.553  
4.529  
4.505  
4.481  
4.464  
4.440  
4.417  
4.393

1.471  
1.447  
1.423  
1.418  
1.394  
1.370



Parameter	Value
Title	crf754-H127
Comment	STANDARD OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	sgzb
Number of Scans	8
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015/28/10 3: 3
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-70.5
Nucleus	1H
Acquired Size	10333
Spectral Size	3268



Supplementary Figure 171. <sup>1</sup>H NMR Spectrum of 15.



crf-7-54-C-CDCl3

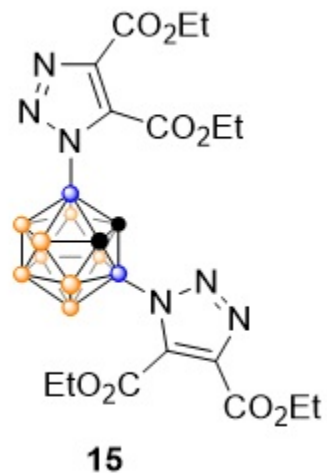
159.728  
159.381

139.293  
138.952

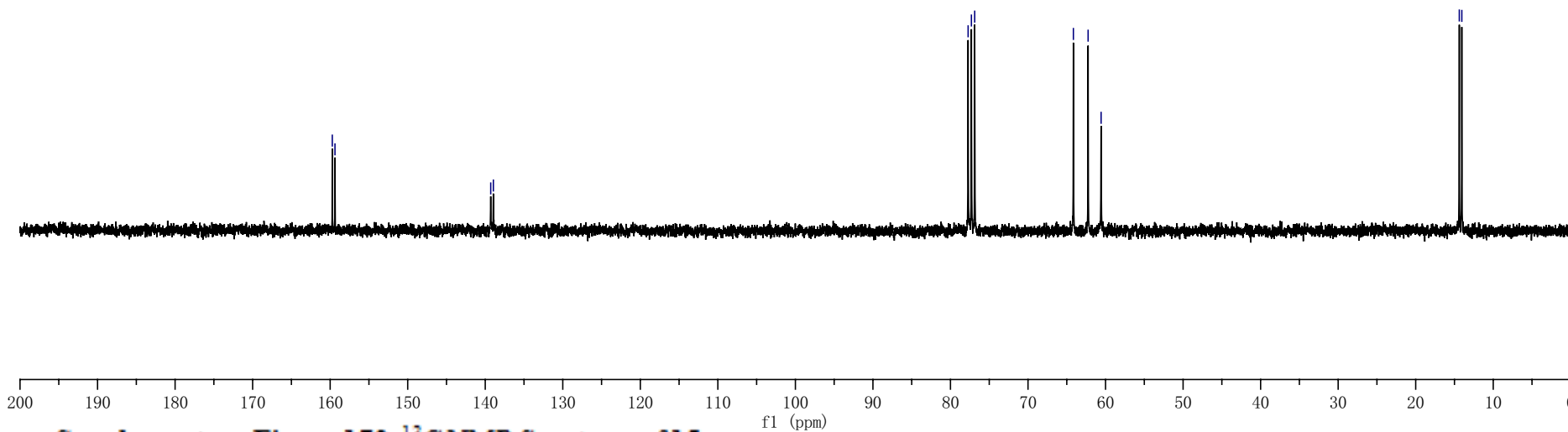
77.724  
77.300  
76.876

64.147  
62.249  
60.573

14.377  
14.050

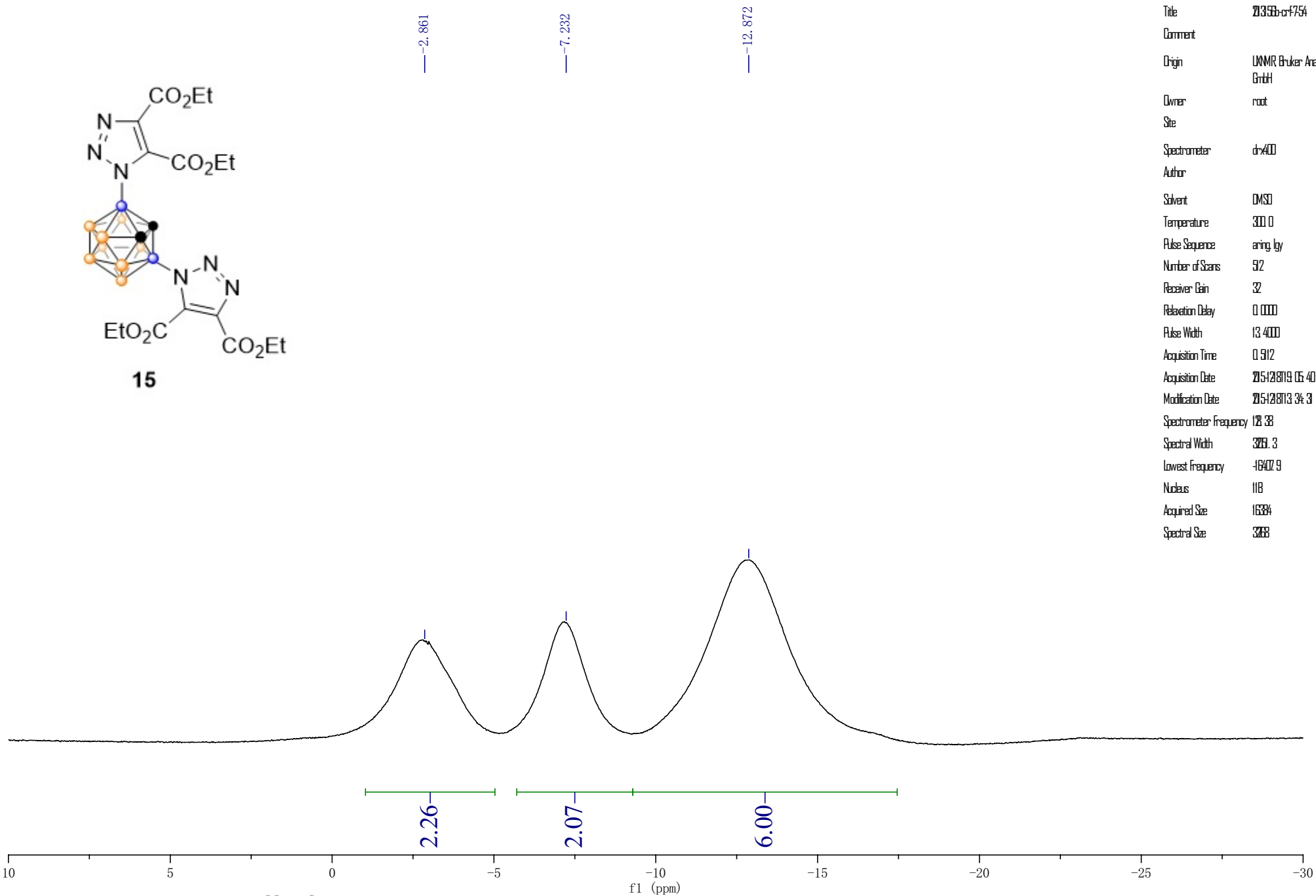
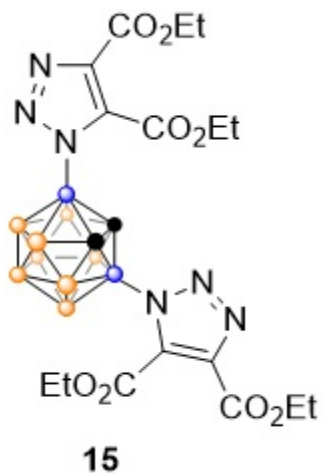


Parameter	Value
Title	crf754C
Comment	13C OBSERVE
Origin	Varien
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	CDCl3
Temperature	21.0
Pulse Sequence	zgpg30
Number of Scans	20
Receiver Gain	38
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	20151208 11:13:33
Spectrometer Frequency	75.45
Spectral Width	2949.8
Lowest Frequency	-285.2
Nucleus	13C
Acquired Size	30738
Spectral Size	65536

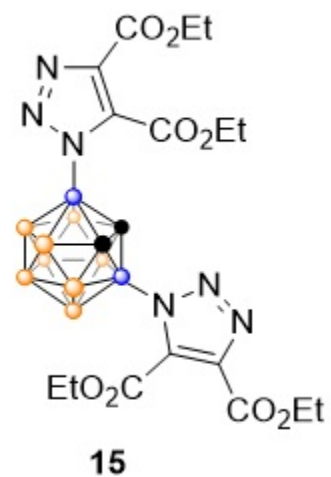


Supplementary Figure 172. <sup>13</sup>C NMR Spectrum of 15.

Parameter	Value
Data File Name	G:/Users/Administrator/Desktop/2135b-crf754/2135b-crf754/1/fid
Title	2135b-crf754
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	cry400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1g
Number of Scans	512
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	2015/2/27 19:05:40
Modification Date	2015/2/27 13:34:31
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-16407.9
Nucleus	<sup>11</sup> B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 173. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of 15.

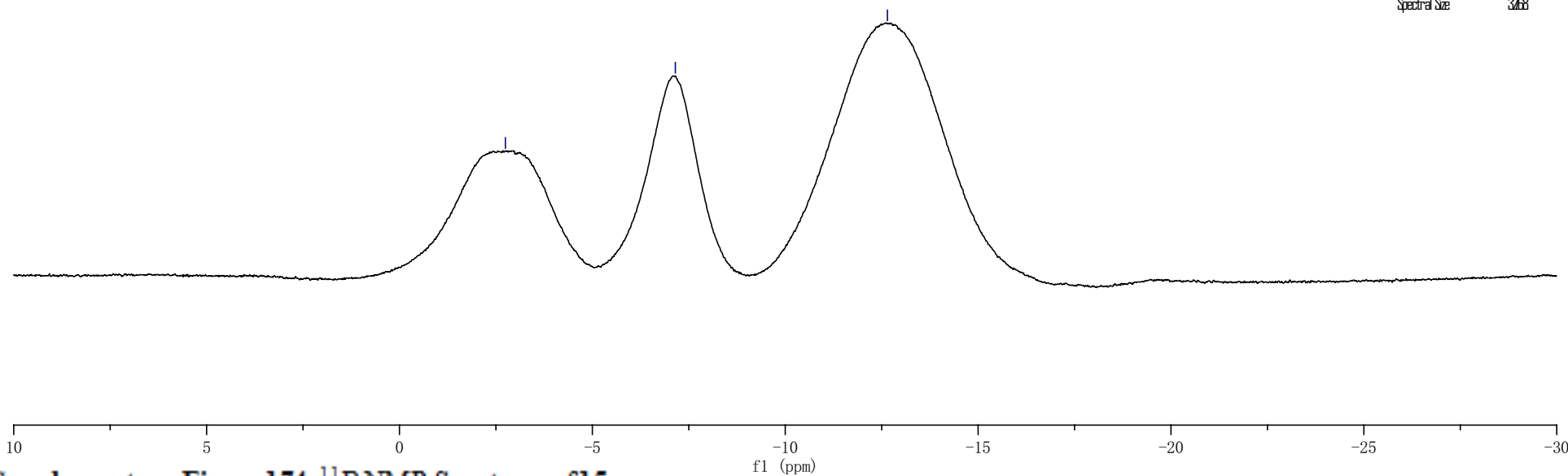


-2.745

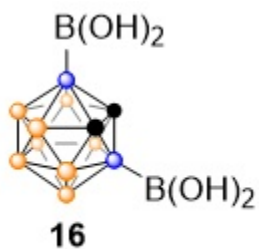
-7.151

-12.649

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/21355b-crf754/21355b-crf754-coupling/1/1d
Title	21355b-crf754-coupling
Comment	
Origin	LNMNR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring.1g
Number of Scans	512
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	2015/12/8/19:12:15
Modification Date	2015/12/8/13:34:27
Spectrometer Frequency	128.38
Spectral Width	3279.3
Lowest Frequency	-18407.9
Nucleus	11B
Acquired Size	16384
Spectral Size	3268



crf-5-93-H-DMSO



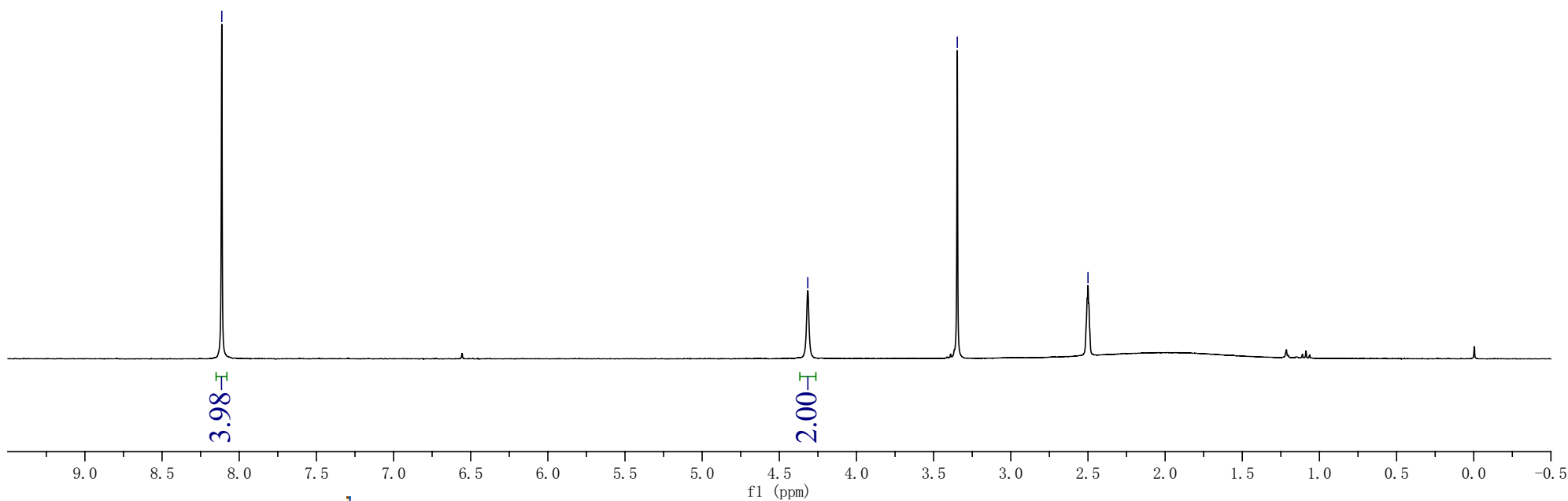
8.113

4.316

3.347

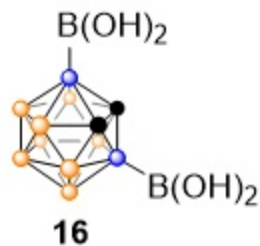
2.500

Parameter	Value
Title	crf-5-93-H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	DMSO
Temperature	29.0
Pulse Sequence	sgpd
Number of Scans	8
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-11-27 09:50:46
Spectrometer Frequency	300.03
Spectral Width	5494.5
Lowest Frequency	-706.0
Nucleus	1H
Acquired Size	10888
Spectral Size	3068



Supplementary Figure 175. <sup>1</sup>H NMR Spectrum of 16.

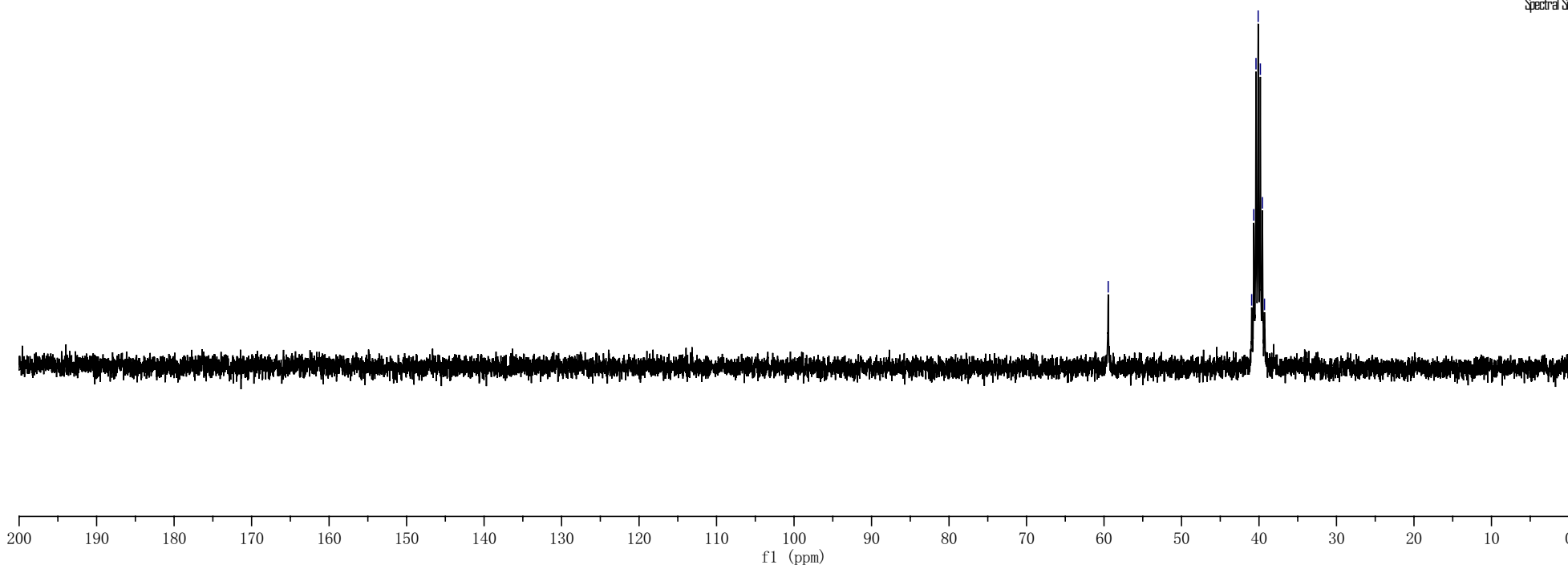
crf-5-93-C-DMSO



59.460

40.943  
40.674  
40.388  
40.106  
39.824  
39.555  
39.292

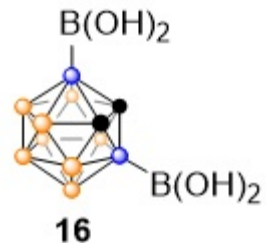
Parameter	Value
Title	crf5-93-C-DMSO12
Comment	13C OBSRV
Origin	Varian
Owner	
Site	
Spectrometer	mercury
Author	omc
Solvent	DMSO
Temperature	29.0
Pulse Sequence	sgul
Number of Scans	224
Receiver Gain	39
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Date	2015-11-27 21:58:54
Spectrometer Frequency	75.45
Spectral Width	2000.0
Lowest Frequency	-20.2
Nucleus	13C
Acquired Size	2800
Spectral Size	65536



Supplementary Figure 176. <sup>13</sup>C NMR Spectrum of 16.

crf-5-93-B-decoupling-DMSO

33.285

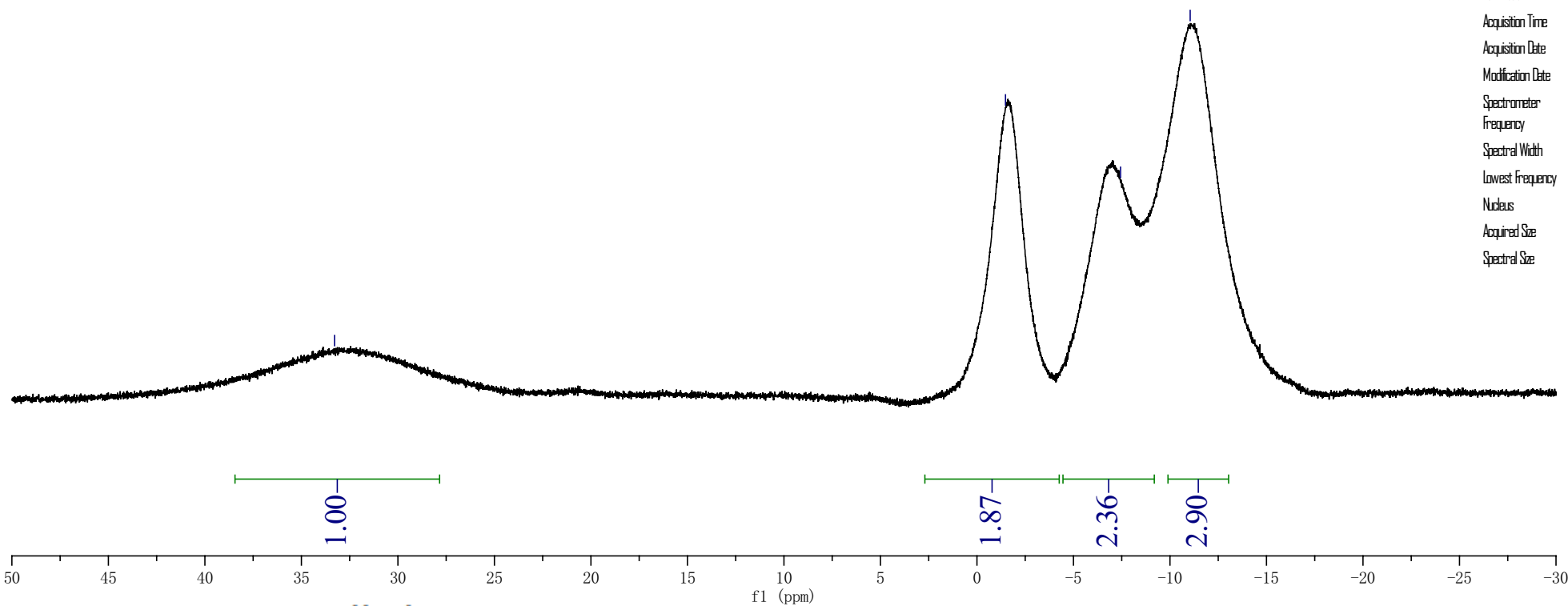


-1.479

-7.440

-11.047

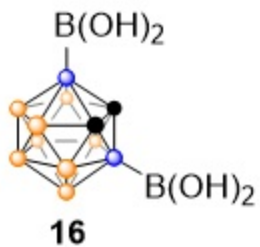
Parameter	Value
Data File Name	G:/Users/Administrator/Desktop/2015/crf-72/2135b-crf-5-93/1/fid
Title	2135b-crf-5-93
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1g
Number of Scans	26
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	2015/20/12/21 2
Modification Date	2015/20/14/33 2
Spectrometer Frequency	128.38
Spectral Width	3269.3
Lowest Frequency	-1663.3
Nucleus	11B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 177.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of 16.

crf-5-93-B-coupling-DMSO

31.489

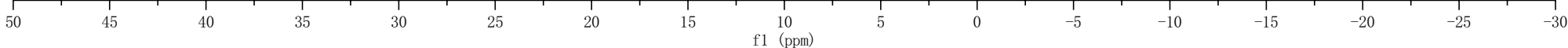


-2.001

-6.943

-11.292

Parameter	Value
Data File Name	C:/Users/Administrator/Desktop/210119-cr-f72/2135B-cr-f5-93-coupling/1/fid
Title	2135B-cr-f5-93-coupling
Comment	
Origin	UNMR Bruker Analytische Messtechnik GmbH
Owner	root
Site	
Spectrometer	dx400
Author	
Solvent	DMSO
Temperature	300.0
Pulse Sequence	aring1gy
Number of Scans	256
Receiver Gain	32
Relaxation Delay	0.0000
Pulse Width	13.4000
Acquisition Time	0.512
Acquisition Date	215420170228
Modification Date	215420171433.15
Spectrometer Frequency	128.38
Spectral Width	3261.3
Lowest Frequency	-16306.4
Nucleus	11B
Acquired Size	16384
Spectral Size	3268



Supplementary Figure 78. <sup>11</sup>B NMR Spectrum of 16.