

## ELECTRONIC SUPPORTING INFORMATION

### A waste-minimized approach for the synthesis of iodinated organic borazines

Dario Marchionni<sup>1</sup>, Daniele Gernini<sup>1</sup>, Alireza Nazari Khodadadi<sup>1</sup>, Ejdi Cela<sup>1</sup>, Fan Huang<sup>1</sup>, Luigi Vaccaro<sup>1\*</sup>

<sup>1</sup>Laboratory of Green Synthetic Organic Chemistry. – Dipartimento di Chimica, biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto 8, 06123 – Perugia – I;

\*E-mail: [luigi.vaccaro@unipg.it](mailto:luigi.vaccaro@unipg.it)

#### Table of content:

1. General Remarks .....	1
2. Solubility data .....	2
3. Green Metrics .....	3
4. General procedures .....	7
5. Characterization Data .....	9
5. NMR Spectral Data .....	30

### 1. General Remarks

Unless otherwise stated, all chemicals were purchased and used without any further purification. Melting points were measured on a Büchi 510 apparatus. <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F and <sup>11</sup>B NMR spectra were recorded on a Bruker DRX-ADVANCE 400 MHz (<sup>1</sup>H at 400 MHz, NS = 4, d1 = 5s, SW = 20.0254 ppm., <sup>13</sup>C at 100.6 MHz, NS = 2000, d1 = 1s, SW = 238.8967 ppm., <sup>11</sup>B at 128.4 MHz, NS = 1024, d1 = 1s, SW = 397.4245 ppm., <sup>19</sup>F at 376.5 MHz, NS = 30, d1 = 2s, SW = 249,0300 ppm.). Chemical shifts are reported in ppm ( $\delta$ ), coupling constant (J) in hertz and multiplicity are reported as follows: s = singlet, bs = broad singlet, d = doublet, dd = double doublet, td = double triplet, t = triplet, m = multiplet. HPLC optimization was done using an Agilent 1100 series HPLC system equipped with Agilent Zorbax Eclipse XDB-C8 4.6x150mm or ACE 5 C8 4.6x150mm, UV-Vis detector set at 254 nm with acetonitrile as solvent, 1 to 2 mL/min as flow rate. Elemental analysis was performed using Elementar UNICUBE<sup>®</sup> elemental analyzer. Mechanochemical reactions were performed on a Retsch MM200 vibratory ball-mill equipped with a zirconium oxide jar and ball. Unless otherwise stated, no precautions were taken to exclude air or moisture from reaction environment.

## 2. Solubility data

**Table S1.** Solubility screening for borazine **11** at 25 °C.

< 0.5g/100mL	Between 0.5g/100mL and 1g/100mL	> 1g/100mL
MTBE CPME 2Me2BuOH Acetone MeCN DMC GVL DMF Toluene Anisole	2MeTHF EtOAc	DCM CHCl <sub>3</sub> PhCl

Screening performed by dissolving 50 mg of borazine **11** in 10 mL of solvent at 25 °C under strong stirring, if a transparent solution was obtained after 30 min stirring borazine was considered having a solubility higher than 0.5g/100mL and further 50 mg of borazine were added and stirred for 30 minutes, again if a transparent solution was obtained the borazine was then considered having a solubility higher than 1g/100mL.

**Table S2.** Qualitative solubility data for borazine **11** in hot or boiling solvents.

Solvent	Temperature (°C)	Solubility (g/100mL)
MTBE	55 <sup>a</sup>	<0.95
CPME	106 <sup>a</sup>	>0.95 <sup>b</sup>
2MeTHF	50	>0.95
2MeTHF	78 <sup>a</sup>	>0.95 <sup>b</sup>
2Me2BuOH	102 <sup>a</sup>	<0.95 <sup>b</sup>
Acetone	56 <sup>a</sup>	<0.95
MeCN	82 <sup>a</sup>	<0.95
EtOAc	77 <sup>a</sup>	>1.9
Anisole	120	>0.95 <sup>b</sup>
DMC	90 <sup>a</sup>	<0.95
Toluene	100	>1.9 <sup>b</sup>
Mesitylene	100	>1.9 <sup>b</sup>
GVL	150	<0.95
DMF dry	140	>9.5
PhCl	100	>4.75 <sup>b</sup>

<sup>a</sup>Boiling, <sup>b</sup>Partial degradation observed by HPLC analysis of the resulting solution.

Data obtained by stirring 95 mg of iodoborazine **11** with preheated solvent for 20 minutes, borazine was assumed to be soluble upon complete homogenization of the mixture to a transparent solution.

**Table S3.** Quantitative solubility data for solvents in which borazine **11** has a solubility higher than 0.5g/100mL at 25 °C.

Solvent	Solubility of 11 (g/100mL)	Solubility of 1 (g/100mL)
2MeTHF	0.7	3.5
EtOAc	0.9	4.1
PhCl	3.3	5.9
DCM	17.4	25.7
CHCl <sub>3</sub>	15.8	22.2

Solubility determined through gravimetric analysis. Starting material and iodination intermediates were generally found to be more soluble than the final product.

### 3. Green Metrics

#### - Large-scale procedure using I<sub>2</sub>, AgNO<sub>3</sub> (solution)

**Reactants:**

Borazine **1**: 0.874 g, 873.74 g/mol, 1 mmol

I<sub>2</sub>: 0.787 g, 253.81 g/mol, 3.1 mmol

AgNO<sub>3</sub>: 0.510 g, 169.87 g/mol, 3 mmol

**Reaction Medium:**

DCM: 16 mL, 21.28 g

MeCN: 4 mL, 3.13 g

**Catalysts:** None.

**Workup Materials:** None.

**Purification:**

MeOH: 20 mL, 15.84 g

DCM: 20 mL, 26.6 g

Celite: 1g

**Recycling-Recovery of Materials:** None.

**Product:** Borazine **11** 1.198 g, 1251.42 g/mol

E-Factor:  $\frac{((2.171 \text{ g})_{\text{reactants}} + (24.41 \text{ g})_{\text{reaction medium}} + (43,44 \text{ g})_{\text{purification materials}} - (1.198 \text{ g})_{\text{product}})}{(1.198 \text{ g})_{\text{product}}} = 57.45$

- **Large-scale procedure using I<sub>2</sub>, AgNO<sub>3</sub>, MeCN (LAG) (ball-milling)**

**Reactants:**

Borazine **1**: 0.874 g, 873.74 g/mol, 1 mmol

I<sub>2</sub>: 0.685 g, 253.81 g/mol, 2.7 mmol

AgNO<sub>3</sub>: 0.408 g, 169.87 g/mol, 2.4 mmol

**Reaction Medium:**

MeCN: 0.5 mL, 0.392 g

**Catalysts:** None.

**Workup Materials:** None.

**Purification:**

MeOH: 20 mL, 15.84 g

DCM: 20 mL, 26.6 g

Celite: 1g

**Recycling-Recovery of Materials:** None.

**Product:** Borazine **11** 1.105 g, 1251.42 g/mol

E-Factor:  $((1.967 \text{ g})_{\text{reactants}} + (0.392 \text{ g})_{\text{reaction medium}} + (43,44 \text{ g})_{\text{purification materials}} - (1.105 \text{ g})_{\text{product}}) / (1.105 \text{ g})_{\text{product}} = 40.45$

- **Large-scale procedure using I<sub>2</sub>, NaNO<sub>3</sub>, TsOH (ball-milling)**

**Reactants:**

Borazine **1**: 0.874 g, 873.74 g/mol, 1 mmol

I<sub>2</sub>: 0.381 g, 253.81 g/mol, 1.5 mmol

NaNO<sub>3</sub>: 0.255 g, 85 g/mol, 3 mmol

**Reaction Medium:** None.

**Catalysts:**

TsOH: 0.571 g, 190.22 g/mol, 3 mmol

**Workup Materials:** None.

**Purification:**

MeOH: 12 mL, 9.504 g

Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5 H<sub>2</sub>O: 0.1g

**Recycling-Recovery of Materials:**

MeOH: 7.68 g

**Product:** Borazine **11** 1.146 g, 1251.42 g/mol

E-Factor:  $((1.51 \text{ g})_{\text{reactants}} + (0.571 \text{ g})_{\text{catalyst}} + (9.604 \text{ g})_{\text{purification materials}} - (7.68 \text{ g})_{\text{recovered materials}} - (1.146 \text{ g})_{\text{product}}) / (1.146 \text{ g})_{\text{product}} = 2.49$

## - Large-scale procedure using NIS, TsOH (ball-milling)

### Reactants:

Borazine **1**: 0.874 g, 873.74 g/mol, 1 mmol

NIS: 0.675 g, 224.99 g/mol, 3 mmol

**Reaction Medium:** None.

### Catalysts:

TsOH: 0.571 g, 190.22 g/mol, 3 mmol

**Workup Materials:** None.

### Purification:

MeOH: 12 mL, 9.504 g

Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5 H<sub>2</sub>O: 0.1g

### Recycling-Recovery of Materials:

MeOH: 7.23 g

**Product:** Borazine **11** 1.146 g, 1251.42 g/mol

E-Factor:  $((1.549 \text{ g})_{\text{reactants}} + (0.571 \text{ g})_{\text{catalyst}} + (9.604 \text{ g})_{\text{purification materials}} - (7.23)_{\text{recovered materials}} - (1.186 \text{ g})_{\text{product}}) / (1.186 \text{ g})_{\text{product}} = 2.79$

**Table S4.** Comparison of different mass based green metrics for the four iodination processes.

Method	E-factor	AE	RME	MRP	1/SF	Rxn Yield	VMR
I <sub>2</sub> /AgNO <sub>3</sub> /DCM/MeCN	57.45	0.583	0.017	0.031	0.988	0.957	0.668
I <sub>2</sub> /AgNO <sub>3</sub> /MeCN(LAG)	40.45	0.736	0.024	0.043	0.864	0.883	0.644
I <sub>2</sub> /NaNO <sub>3</sub> /TsOH	2.49	0.906	0.286	0.377	0.915	0.915	0.738
NIS/TsOH	2.79	0.808	0.264	0.345	1.000	0.947	0.740

## 4. General procedures

### **Optimization of mechanochemical iodination of borazine using iodine and silver nitrate**

**(Table 1):** Milling jar was filled with Borazine, I<sub>2</sub>, AgNO<sub>3</sub>, LAG additive when used and the zirconium oxide ball. The jar was closed, and the content was milled at 30 Hz for the indicated time. The resulting powder was scraped from the jar, the jar was washed thoroughly with DCM and the resulting suspension was added to the scraped powder. After complete dissolution of the borazine the suspension was filtered over celite to remove AgI byproduct, the solvent was concentrated under vacuum and the product crystallized with MeOH.

### **Optimization of iodinating systems (Table 2):**

**Small-scale procedure entry 1:** Borazine 0.08 mmol 1 eq, and I<sub>2</sub> 3.1 eq were added to a 4 mL vial containing DCM 1280 uL, upon complete dissolution and under strong stirring a solution of 3 eq AgNO<sub>3</sub> in 320 uL of MeCN was dropwised into the vial, the vial was capped and left stirring for 1h at room temperature. The solution was subsequently concentrated to dryness, dissolved in dichloromethane, filtered over celite to remove AgI byproduct and the product crystallized with methanol.

**Small-scale procedure entry 2:** Milling jar was filled with Borazine 0.08 mmol 1 eq, 2.7 eq I<sub>2</sub>, 2.4 eq AgNO<sub>3</sub>, 40 uL MeCN and the zirconium oxide ball. The jar was closed, and the content was milled at 30 Hz for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with DCM and the resulting suspension was added to the scraped powder. After complete dissolution of the borazine the suspension was filtered over celite to remove AgI byproduct, the solvent was concentrated under vacuum and the product crystallized with MeOH.

**Small-scale procedure entry 3:** Milling jar was filled with Borazine 0.08 mmol 1 eq, 3 eq KI, 3 eq Oxone, and the zirconium oxide ball. The jar was closed, and the content was milled at 30 Hz for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover the borazine product.

**Small-scale procedure entry 4:** Milling jar was filled with Borazine 0.08 mmol 1 eq, 1.5 eq I<sub>2</sub>, 3 eq NaNO<sub>3</sub>, 3 eq TsOH and the zirconium oxide ball. The jar was closed, and the content was milled at 30 Hz for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover the borazine product.

**Small-scale procedure entry 5:** Milling jar was filled with Borazine 0.08 mmol 1 eq, NaI 3 eq, H<sub>2</sub>O<sub>2</sub> 30% aq. 6 eq, TsOH 3 eq and the zirconium oxide ball. The jar was closed, and the content was milled at 30 Hz for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover the borazine product

**Small-scale procedure entry 6:** Milling jar was filled with Borazine 0.08 mmol 1 eq, 3 eq NIS, 3 eq TsOH and the zirconium oxide ball. The jar was closed, and the content was milled at 30 Hz for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover the borazine product.

### **Large-scale procedures (Table 3):**

**Large-scale procedure using I<sub>2</sub>, AgNO<sub>3</sub>, DCM/MeCN in solution:** Borazine 1 mmol 1 eq, I<sub>2</sub> 3.1 eq., were added to a round-bottom flask containing DCM 16 mL, upon complete dissolution and

under strong stirring a solution of 3 eq  $\text{AgNO}_3$  in 4 mL of MeCN was dropwised into the flask, the flask was capped and left stirring for 1h at room temperature. The solution was subsequently concentrated to dryness, dissolved in 20 mL dichloromethane, filtered over celite to remove AgI byproduct, concentrated under vacuum and the product crystallized with 20 mL methanol.

**Large-scale procedure using  $\text{I}_2$ ,  $\text{AgNO}_3$ , MeCN Liquid Assisted Grinding:** Milling jar was filled with Borazine 1 mmol 1 eq, 2.7 eq  $\text{I}_2$ , 2.4 eq  $\text{AgNO}_3$ , 500  $\mu\text{L}$  MeCN and the zirconium oxide ball. The jar was closed, and the content was milled at 30 Hz for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with 20 mL DCM and the resulting suspension was added to the scraped powder. After complete dissolution of the borazine the suspension was filtered over celite to remove AgI byproduct, the solvent was concentrated under vacuum and the product crystallized with 20 mL MeOH.

**Large-scale procedure using  $\text{I}_2$ ,  $\text{NaNO}_3$ , TsOH grinding:** Milling jar was filled with Borazine 1 mmol 1 eq, 1.5 eq  $\text{I}_2$ , 3 eq  $\text{NaNO}_3$ , 3 eq TsOH and the zirconium oxide ball. The jar was closed, and the content was milled at 30 Hz for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with 12 mL MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover the borazine product.

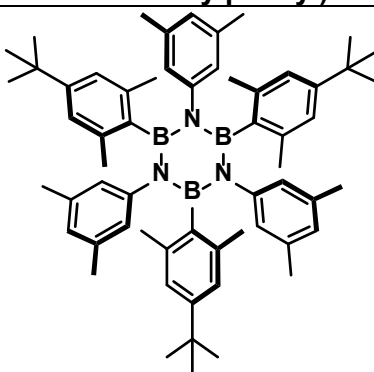
Solvent was scrubbed of residual iodine by addition of 100 mg of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ , then distilled to afford 7.68 g of clean MeOH

**Large-scale procedure using NIS, TsOH grinding:** Milling jar was filled with Borazine 1 mmol 1 eq, 3 eq NIS, 3 eq TsOH and the zirconium oxide ball. The jar was closed, and the content was milled at 30 Hz for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with 12 mL MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover the borazine product.

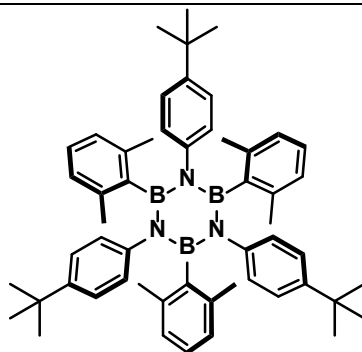
Solvent was scrubbed of residual iodine by addition of 100 mg of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ , then distilled to afford 7.23 g of clean MeOH



## 5. Characterization Data

Chem. Name	<b>B,B',B''-Tris(4-(tertbutyl)-2,6-dimethylphenyl)-N,N',N''-tris(3,5-dimethylphenyl)borazine (1)</b>			
 <p>Molecular Weight: 873,73</p>				
<b>METHOD:</b>				
<p>To an oven-dried 50 mL Schlenk tube under dry argon atmosphere were added 6 mmol (748 <math>\mu</math>L) of dry 3,5-dimethylaniline (distilled under vacuum from calcium hydride) followed by addition of 14 mL dry toluene. 1.25 eq (7.5 mL) of <math>\text{BCl}_3</math> 1 M in heptane were dropwisely slowly in this solution at <math>0^\circ\text{C}</math> under strong stirring. After 1h stirring the Schlenk was equipped with a condenser and a calcium chloride drying tube, the resulting solution was refluxed at <math>110^\circ\text{C}</math> for 20h, the Schlenk was then cooled to room temperature and subjected to 5 freeze-pump-thaw cycles to remove excess of HCl. The thus obtained chloroborazole intermediate was diluted with 8 mL of dry THF and 6 mL of dry toluene as cosolvent, then cannulated slowly in a stirred solution of aryllithium at <math>0^\circ\text{C}</math> and left to react for 20h. Aryllithium was prepared treating 4-tertbutyl-2,6-dimethylbromobenzene 1.8 eq (10.8 mmol, 2.6 g) dissolved in dry THF 24 mL with n-butyl lithium 3.1 eq (11.5 mL) 1.6 M in hexanes at <math>-78^\circ\text{C}</math> then gradually warming up to <math>0^\circ\text{C}</math>, the solution was kept stirring for 10 minutes before cannulating. The final product was added to a separatory funnel together with 50 mL DCM and extracted twice with 50 mL water then with 50 mL brine. Organic phase was dried over sodium sulfate then stripped of solvent under vacuum, dispersed in chloroform and crystallized with MeOH, product was filtered under vacuum and left to dry for 30 minutes affording pure product as a white solid <b>1.3g 74%</b>.</p>				
<b>Mol Formula</b>		$\text{C}_{60}\text{H}_{78}\text{B}_3\text{N}_3$	<b>m. p.</b>	
			$> 300^\circ\text{C}$	
<b><math>^1\text{H}</math> NMR (400 MHz, <math>\text{CDCl}_3</math>)</b>	<b><math>\delta</math> Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>
	1.08	27	s	
	1.86	18	s	
	2.19	18	s	
	6.27	3	s	
	6.32	6	s	
	6.51	6	s	
<b><math>^{13}\text{C}</math> NMR (100.6 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math>:</b> 149.2, 146.0, 137.2, 135.3, 125.6, 125.2, 122.1, 34.0, 31.3, 23.4, 20.9. (One peak is missing due to boron quadrupolar relaxation)				
<b><math>^{11}\text{B}</math> NMR (128.4 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math>:</b> 37.1				
<b>Anal. Calcd.:</b> C, 82.48; H, 9.00; N, 4.81; <b>Found:</b> C, 82.23; 9.29; 4.86;				

Chem. Name	<b>B,B',B''-Tris(2,6-dimethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine (2)</b>
------------	---

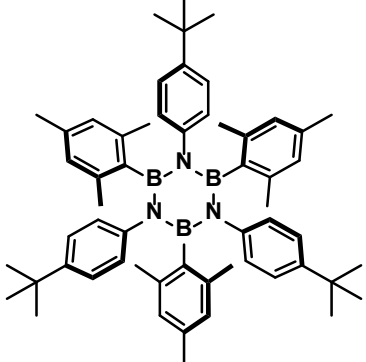


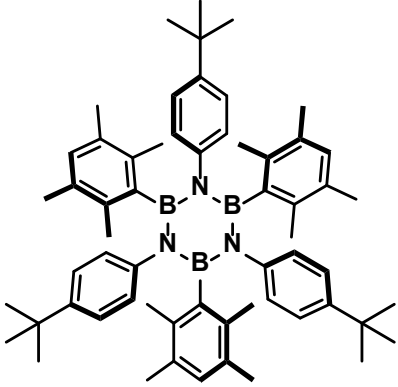
Molecular Weight: 789,57

**METHOD:**

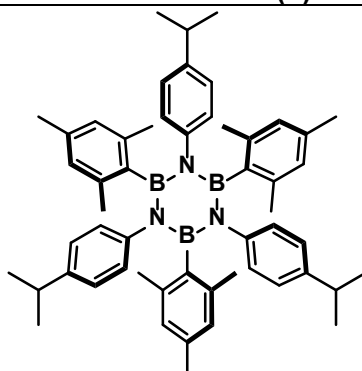
To an oven-dried 50 mL Schlenk tube under dry argon atmosphere were added 6 mmol (956  $\mu$ L) of dry 4-tertbutylaniline (distilled under vacuum from calcium hydride) followed by addition of 9 mL dry toluene. 1.25 eq (7.5 mL) of  $\text{BCl}_3$  1 M in heptane were dropwisely slowly in this solution at  $0^\circ\text{C}$  under strong stirring. After 1h stirring the Schlenk was equipped with a condenser and a calcium chloride drying tube, the resulting solution was refluxed at  $110^\circ\text{C}$  for 20h, the Schlenk was then cooled to room temperature and subjected to 5 freeze-pump-thaw cycles to remove excess of HCl. The thus obtained chloroborazole intermediate was then cannulated slowly in a stirred solution of aryllithium at  $0^\circ\text{C}$  and left to react for 20h. Aryllithium was prepared treating 2-bromoxylene 1.8 eq (10.8 mmol, 1.44 mL) dissolved in dry THF 20 mL with n-butyl lithium 3.1 eq (11.5 mL) 1.6 M in hexanes at  $-78^\circ\text{C}$  then gradually warming up to  $0^\circ\text{C}$ , the solution was kept stirring for 10 minutes before cannulating. The final product was added to a separatory funnel together with 50 mL DCM and extracted twice with 50 mL water then with 50 mL brine. Organic phase was dried over sodium sulfate then stripped of solvent under vacuum, dispersed in chloroform and crystallized with MeOH, product was filtered under vacuum and left to dry for 30 minutes affording pure product as a white solid **59% 926 mg**.

Mol Formula		$\text{C}_{54}\text{H}_{66}\text{B}_3\text{N}_3$	m. p.		$> 300^\circ\text{C}$
<b><math>^1\text{H}</math> NMR (400 MHz, <math>\text{CDCl}_3</math>)</b>	<b><math>\delta</math> Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	1.02	27	s		
	2.25	18	s		
	6.50-6.48	6	d	7.56	
	6.69-6.65	15	m		
<b><math>^{13}\text{C}</math> NMR (100.6 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math>: 146.7, 143.4, 137.6, 126.7, 126.4, 125.2, 123.4, 34.0, 31.3, 23.3. (One peak is missing due to boron quadrupolar relaxation)</b>					
<b><math>^{11}\text{B}</math> NMR (128.4 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math>: 36.4</b>					
<b>Anal. Calcd.:</b> C, 82.14; H, 8.43; N, 5.32; <b>Found:</b> C, 82.25; H, 8.64; N, 5.37					

Chem. Name	B,B',B''-Tris(2,4,6-trimethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine (3)			
				
Molecular Weight: 831,65				
<b>METHOD:</b>				
<p>To an oven-dried 50 mL Schlenk tube under dry argon atmosphere were added 6 mmol (956 uL) of dry 4-tertbutylaniline (distilled under vacuum from calcium hydride) followed by addition of 9 mL dry toluene. 1.25 eq (7.5 mL) of BCl<sub>3</sub> 1 M in heptane were dropwised slowly in this solution at 0°C under strong stirring. After 1h stirring the Schlenk was equipped with a condenser and a calcium chloride drying tube, the resulting solution was refluxed at 110°C for 20h, the Schlenk was then cooled to room temperature and subjected to 5 freeze-pump-thaw cycles to remove excess of HCl. The thus obtained chloroborazole intermediate was cannulated slowly in a stirred solution of aryllithium at 0°C and left to react for 20h. Aryllithium was prepared treating mesitylbromide 1.8 eq (10.8 mmol, 1.65 mL) dissolved in dry THF 18 mL with n-butyl lithium 3.1 eq (11.5 mL) 1.6 M in hexanes at -78°C then gradually warming up to 0°C, the solution was kept stirring for 10 minutes before cannulating. The final product was added to a separatory funnel together with 50 mL DCM and extracted twice with 50 mL water then with 50 mL brine. Organic phase was dried over sodium sulfate then stripped of solvent under vacuum, dispersed in chloroform and crystallized with MeOH, product was filtered under vacuum and left to dry for 30 minutes affording pure product as a white solid <b>1.08 g 65%</b>.</p>				
<b>Mol Formula</b>		C <sub>57</sub> H <sub>72</sub> B <sub>3</sub> N <sub>3</sub>		<b>m. p.</b>
				225 °C
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b>δ Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>
	1.03	27	s	
	1.96	9	s	
	2.19	18	s	
	6.30	6	s	
	6.70-6.64	12	m	
<b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 146.4, 143.7, 137.6, 135.7, 126.5, 126.0, 123.3, 34.0, 31.3, 23.1, 21.0. (One peak is missing due to boron quadrupolar relaxation)				
<b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) δ:</b> 36.6				
<b>Anal. Calcd.:</b> C, 82.32; H, 8.73; N, 5.05; <b>Found:</b> C, 82.02; H, 8.52; N, 5.18				

Chem. Name	<b>B,B',B''-Tris(2,3,5,6-tetramethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine (4)</b>				
 <p data-bbox="646 660 949 694">Molecular Weight: 873,73</p>					
<p><b>METHOD:</b>            To an oven-dried 50 mL Schlenk tube under dry argon atmosphere were added 6 mmol (956 uL) of dry 4-tertbutylaniline (distilled under vacuum from calcium hydride) followed by addition of 9 mL dry toluene. 1.25 eq (7.5 mL) of BCl<sub>3</sub> 1 M in heptane were dropwisely slowly in this solution at 0°C under strong stirring. After 1h stirring the Schlenk was equipped with a condenser and a calcium chloride drying tube, the resulting solution was refluxed at 110°C for 20h, the Schlenk was then cooled to room temperature and subjected to 5 freeze-pump-thaw cycles to remove excess of HCl. The thus obtained chloroborazole intermediate was cannulated slowly in a stirred solution of aryllithium at 0°C and left to react for 20h. Aryllithium was prepared treating Bromodurene 1 eq (6 mmol, 1.28 g) dissolved in dry THF 20 mL with t-butyl lithium 2 eq (7.1 mL) 1.7 M in pentane at -78°C then gradually warming up to 0°C, the solution was kept stirring for 10 minutes before cannulating. The final product was quenched by addition of a small volume of water, added to a separatory funnel together with 100 mL DCM and extracted twice with 50 mL water then with 50 mL brine. Carefully extracting a second time each water fraction with more DCM. Organic phase was dried over sodium sulfate then stripped of solvent under vacuum, dispersed in chloroform and crystallized with MeOH, product was filtered under vacuum and left to dry for 30 minutes affording pure product as a white solid <b>934 mg 53%</b>.</p>					
<b>Mol Formula</b>		C <sub>60</sub> H <sub>78</sub> B <sub>3</sub> N <sub>3</sub>		<b>m. p.</b>	> 300 °C
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b>δ Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	1.02	27	s		
	1.85	18	s		
	2.12	18	s		
	6.39	3	s		
6.64-6.59	12	m			
<p><b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 146.1, 143.8, 133.3, 131.7, 129.6, 126.5, 123.1, 34.0, 31.3, 21.0, 19.4. (One peak is missing due to boron quadrupolar relaxation)</p>					
<p><b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) δ:</b> 36.5</p>					
<p><b>Anal. Calcd.:</b> C, 82.48; H, 9.00; N, 4.81; <b>Found:</b> C, 82.31; H, 9.30; N, 4.76</p>					

Chem. Name	<b>B,B',B''-Tris(2,4,6-trimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine (5)</b>
------------	--

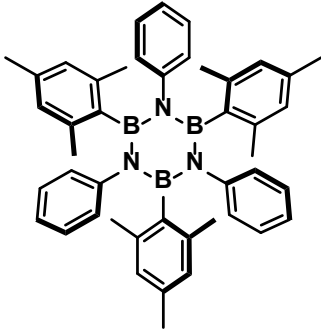


Molecular Weight: 789,57

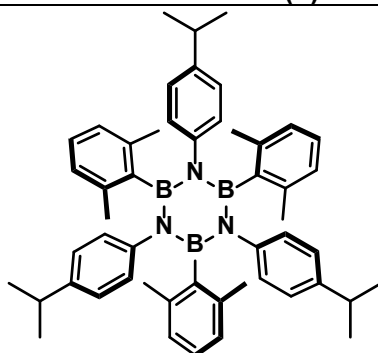
**METHOD:**

To an oven-dried 50 mL Schlenk tube under dry argon atmosphere were added 6 mmol (820  $\mu$ L) of dry 4-isopropylaniline (distilled under vacuum from calcium hydride) followed by addition of 9 mL dry toluene. 1.25 eq (7.5 mL) of  $\text{BCl}_3$  1 M in heptane were dropwised slowly in this solution at  $0^\circ\text{C}$  under strong stirring. After 1h stirring the Schlenk was equipped with a condenser and a calcium chloride drying tube, the resulting solution was refluxed at  $110^\circ\text{C}$  for 20h, the Schlenk was then cooled to room temperature and subjected to 5 freeze-pump-thaw cycles to remove excess of HCl. The thus obtained chloroborazole intermediate was cannulated slowly in a stirred solution of aryllithium at  $0^\circ\text{C}$  and left to react for 20h. Aryllithium was prepared treating mesitylbromide 1.8 eq (10.8 mmol, 1.65 mL) dissolved in dry THF 18 mL with n-butyl lithium 3.1 eq (11.5 mL) 1.6 M in hexanes at  $-78^\circ\text{C}$  then gradually warming up to  $0^\circ\text{C}$ , the solution was kept stirring for 10 minutes before cannulating. The final product was added to a separatory funnel together with 50 mL DCM and extracted twice with 50 mL water then with 50 mL brine. Organic phase was dried over sodium sulfate then stripped of solvent under vacuum, dispersed in chloroform and crystallized with MeOH, product was filtered under vacuum and left to dry for 30 minutes affording pure product as a white solid **1.040 g 66%**.

Mol Formula	$\text{C}_{54}\text{H}_{68}\text{B}_3\text{N}_3$			m. p.	289 $^\circ\text{C}$
<b><math>^1\text{H}</math> NMR (400 MHz, <math>\text{CDCl}_3</math>)</b>	$\delta$ Value	No. H	Mult.	J Value/Hz	
	0.97-0.95	18	d	6.84	
	1.97	9	s		
	2.20	18	s		
	2.61-2.51	3	m		
	6.31	6	s		
	6.56-6.54	6	d	8.40	
6.69-6.67	6	d	8.44		
<b><math>^{13}\text{C}</math> NMR (100.6 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math>:</b> 144.2, 144.1, 137.5, 135.7, 126.8, 126.0, 124.5, 33.3, 23.9, 23.1, 21.0. (One peak is missing due to boron quadrupolar relaxation)					
<b><math>^{11}\text{B}</math> NMR (128.4 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math>:</b> 37.2					
<b>Anal. Calcd.:</b> C, 82.14; H, 8.43; N, 5.32; <b>Found:</b> C, 82.31; H, 8.33; N, 5.28					

Chem. Name	B,B',B''-Tris(2,4,6-trimethylphenyl)-N,N',N''-tris(phenyl)borazine (6)				
 <p>Molecular Weight: 663,33</p>					
<b>METHOD:</b>					
<p>To an oven-dried 50 mL Schlenk tube under dry argon atmosphere were added 6 mmol (542 <math>\mu</math>L) of dry aniline (distilled under vacuum from calcium hydride) followed by addition of 10 mL dry toluene. 1.25 eq (7.5 mL) of BCl<sub>3</sub> 1 M in heptane were dropwisely slowly in this solution at 0°C under strong stirring. After 1h stirring the Schlenk was equipped with a condenser and a calcium chloride drying tube, the resulting solution was refluxed at 110°C for 20h, the Schlenk was then cooled to room temperature and subjected to 5 freeze-pump-thaw cycles to remove excess of HCl. The thus obtained chloroborazole intermediate was cannulated slowly in a stirred solution of aryllithium at 0°C and left to react for 20h. Aryllithium was prepared treating mesitylbromide 1.8 eq (10.8 mmol, 1.65 mL) dissolved in dry THF 18 mL with n-butyl lithium 3.1 eq (11.5 mL) 1.6 M in hexanes at -78°C then gradually warming up to 0°C, the solution was kept stirring for 10 minutes before cannulating. The final product was added to a separatory funnel together with 50 mL DCM and extracted twice with 50 mL water then with 50 mL brine. Organic phase was dried over sodium sulfate then stripped of solvent under vacuum, dispersed in chloroform and crystallized with MeOH, product was filtered under vacuum and left to dry for 30 minutes affording pure product as a white solid <b>572 mg 43%</b>.</p>					
<b>Mol Formula</b>		C <sub>45</sub> H <sub>48</sub> B <sub>3</sub> N <sub>3</sub>		<b>m. p.</b>	288 °C
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b><math>\delta</math> Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	1.97	9	s		
	2.23	18	s		
	6.33	6	s		
	6.70-6.83	15	m		
<p><b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) <math>\delta</math>:</b> 146.4, 137.4, 136.2, 127.1, 126.8, 126.3, 124.3, 23.1, 21.2. (One peak is missing due to boron quadrupolar relaxation)</p>					
<p><b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) <math>\delta</math>:</b> 36.9</p>					
<p><b>Anal. Calcd.:</b> C, 81.48; H, 7.29; N, 6.33; <b>Found:</b> C, 81.32; H, 7.42; N, 6.44</p>					

Chem. Name	<b>B,B',B''-Tris(2,6-dimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine</b> (7)
------------	--

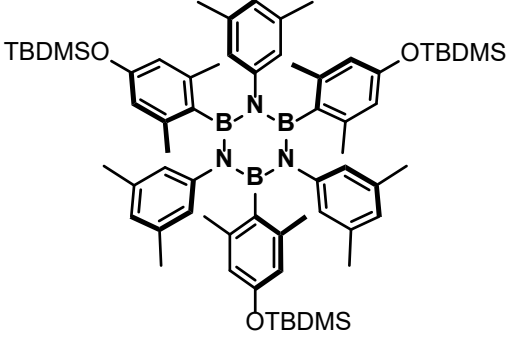


Molecular Weight: 747,49

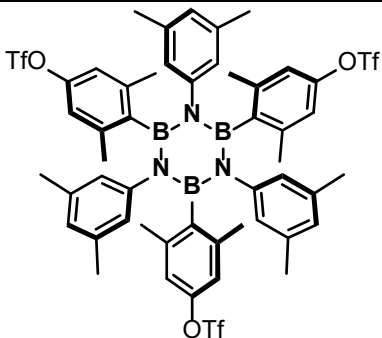
**METHOD:**

To an oven-dried 50 mL Schlenk tube under dry argon atmosphere were added 6 mmol (820  $\mu$ L) of dry 4-isopropylaniline (distilled under vacuum from calcium hydride) followed by addition of 9 mL dry toluene. 1.25 eq (7.5 mL) of  $\text{BCl}_3$  1 M in heptane were dropwised slowly in this solution at  $0^\circ\text{C}$  under strong stirring. After 1h stirring the Schlenk was equipped with a condenser and a calcium chloride drying tube, the resulting solution was refluxed at  $110^\circ\text{C}$  for 20h, the Schlenk was then cooled to room temperature and subjected to 5 freeze-pump-thaw cycles to remove excess of HCl. The thus obtained chloroborazole intermediate was cannulated slowly in a stirred solution of aryllithium at  $0^\circ\text{C}$  and left to react for 20h. Aryllithium was prepared treating Bromoxylene 1.8 eq (10.8 mmol, 1.44 mL) dissolved in dry THF 18 mL with n-butyl lithium 3.1 eq (11.5 mL) 1.6 M in hexanes at  $-78^\circ\text{C}$  then gradually warming up to  $0^\circ\text{C}$ , the solution was kept stirring for 10 minutes before cannulating. The final product was added to a separatory funnel together with 50 mL DCM and extracted twice with 50 mL water then with 50 mL brine. Organic phase was dried over sodium sulfate then stripped of solvent under vacuum, dispersed in 2 mL chloroform and crystallized with MeOH, product was filtered under vacuum and left to dry for 30 minutes affording pure product as a white solid **1.078 g 72%**.

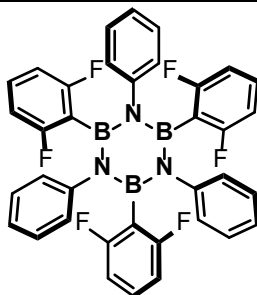
Mol Formula		$\text{C}_{51}\text{H}_{60}\text{B}_3\text{N}_3$		m. p.	272 $^\circ\text{C}$
<b><math>^1\text{H}</math> NMR</b> (400 MHz, $\text{CDCl}_3$ )	<b><math>\delta</math> Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	0.96-0.94	18	d	6.96	
	2.26	18	s		
	2.58-2.26	3	m		
	6.51-6.49	6	d	7.56	
	6.56-6.54	6	d	8.44	
	6.71-6.67	9	m		
<b><math>^{13}\text{C}</math> NMR (100.6 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math>:</b> 144.5, 143.7, 137.6, 126.7, 126.7, 125.2, 124.5, 33.2, 23.9, 23.3. (One peak is missing due to boron quadrupolar relaxation)					
<b><math>^{11}\text{B}</math> NMR (128.4 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math>:</b> 36.9					
<b>Anal. Calcd.:</b> C, 81.95; H, 8.09; N, 5.62; <b>Found:</b> C, 81.56; H, 8.30; N, 5.75					

Chem. Name	<b>B,B',B''-Tris(4-((tert-butyl)dimethylsilyloxy)-2,6-dimethylphenyl)-N,N',N''-tris(3,5-dimethylphenyl)borazine (8)</b>			
 <p data-bbox="646 667 949 698">Molecular Weight: 1096,20</p>				
<b>METHOD:</b>				
<p>To an oven-dried 50 mL Schlenk tube under dry argon atmosphere were added 6 mmol (748 <math>\mu</math>L) of dry 3,5-dimethylaniline (distilled under vacuum from calcium hydride) followed by addition of 14 mL dry toluene. 1.25 eq (7.5 mL) of <math>\text{BCl}_3</math> 1 M in heptane were dropwisely slowly in this solution at <math>0^\circ\text{C}</math> under strong stirring. After 1h stirring the Schlenk was equipped with a condenser and a calcium chloride drying tube, the resulting solution was refluxed at <math>110^\circ\text{C}</math> for 20h, the Schlenk was then cooled to room temperature and subjected to 5 freeze-pump-thaw cycles to remove excess of HCl. The thus obtained chloroborazole intermediate was diluted with 8 mL of dry THF and 6 mL of dry toluene as cosolvent then cannulated slowly in a stirred solution of aryllithium at <math>0^\circ\text{C}</math> and left to react for 20h.</p> <p>Aryllithium was prepared treating (4-bromo-3,5-dimethylphenoxy)(tert-butyl)dimethylsilane 1.2 eq (7.2 mmol, 2.15 g) dissolved in dry THF 20 mL with t-butyl lithium 2.4 eq (8.5 mL) 1.7 M in pentane at <math>-78^\circ\text{C}</math> then gradually warming up to <math>0^\circ\text{C}</math>, the solution was kept stirring for 10 minutes before cannulating. The final product was added to a separatory funnel together with 50 mL DCM and extracted twice with 50 mL water then with 50 mL brine. Organic phase was dried over sodium sulfate then stripped of solvent under vacuum and crystallized with MeOH, product was filtered under vacuum and left to dry for 30 minutes affording pure product as a white solid <b>1.293 mg 59%</b>.</p>				
<b>Mol Formula</b>		$\text{C}_{66}\text{H}_{96}\text{B}_3\text{N}_3\text{O}_3\text{Si}_3$		<b>m. p.</b>
				288 $^\circ\text{C}$
<b><math>^1\text{H}</math> NMR (400 MHz, <math>\text{CDCl}_3</math>)</b>	<b><math>\delta</math> Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>
	-0.04	18	s	
	0.84	27	s	
	1.91	18	s	
	2.20	18	s	
	6.05	6	s	
	6.27	3	s	
$^{13}\text{C}$ NMR (100.6 MHz, $\text{CDCl}_3$ ) $\delta$ : 154.3, 146.3, 138.9, 135.7, 125.7, 124.9, 117.4, 25.9, 23.3, 21.0, 18.3, -4.5. (One peak is missing due to boron quadrupolar relaxation)				
$^{11}\text{B}$ NMR (128.4 MHz, $\text{CDCl}_3$ ) $\delta$ : 37.2				
<b>Anal. Calcd.:</b> C, 72.32; H, 8.83; N, 3.83; <b>Found:</b> C, 72.41; H, 8.56; N, 3.75;				



<b>Chem. Name</b>	<b>B,B',B''-Tris(4-triflyl-2,6-dimethylphenyl)-N,N',N''-tris(3,5-dimethylphenyl)borazine (9)</b>		
 <p>Molecular Weight: 1149,58</p>			
<b>METHOD:</b>			
<p>Borazine <b>8</b> 1.146 g was dissolved in 22 mL anhydrous THF in an oven-dried argon-purged 100 mL round bottom flask. Under inert atmosphere at 0°C 3.75 mL of TBAF solution 1M in THF were dropwise added and the solution left stirring for 2h. The free OH borazine was filtered under vacuum, washed two times with 10 mL THF and left to dry under vacuum for several hours.</p> <p>In a second oven-dried flask under inert argon atmosphere the free OH borazine was added followed by 20 mL of dry pyridine and the flask cooled to 0°C, 1.64 mL of Trifluoromethanesulfonic anhydride were added dropwise and the solution was left stirring for 16h at room temperature. The mixture was then diluted with 70 mL of EtOAc and washed with HCl 0.5M 3x200 mL, 100 mL Water and 100 mL brine. Organics were dried over sodium sulphate and concentrated under vacuum, the residue was then subjected to column chromatography over silica gel (PET/EtOAc 9:1) affording borazine <b>9</b> as a white powder <b>901 mg 75%</b></p>			
<b>Mol Formula</b>		$C_{51}H_{51}B_3F_9N_3O_9S_3$	<b>m. p.</b>
			234 °C
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b>δ Value</b>	<b>No. H</b>	<b>Mult.</b>
	1.92	18	s
	2.29	18	s
	6.32	6	s
	6.40	3	s
	6.51	6	s
<b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 149.1, 144.6, 140.4, 136.7, 126.7, 120.3, 117.9, 124.5-114.0 (CF <sub>3</sub> ), 23.2, 20.8. (One peak is missing due to boron quadrupolar relaxation)			
<b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) δ:</b> 35.2			
<b><sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ:</b> -73.01			
<b>Anal. Calcd.:</b> C, 53.29; H, 4.47; N, 3.66; S, 8.37; <b>Found:</b> C, 53.16; H, 4.61; N, 3.72; S, 8.62			

Chem. Name	<b>B,B',B''-Tris(2,6-difluorophenyl)-N,N',N''-tris(phenyl)borazine (10)</b>
------------	---



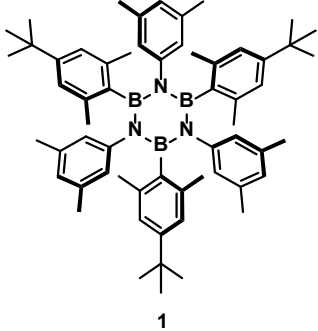
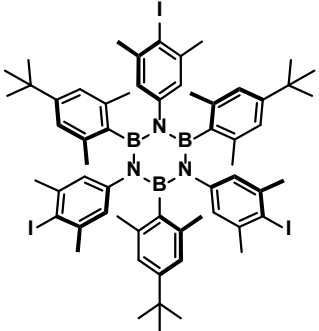
Molecular Weight: 645,03

**METHOD:**

To an oven-dried 50 mL Schlenk tube under dry argon atmosphere were added 5 mmol (452  $\mu$ L) of dry aniline (distilled under vacuum from calcium hydride) followed by addition of 9 mL dry toluene. 1.25 eq (6.25 mL) of  $\text{BCl}_3$  1 M in heptane were dropwisely slowly in this solution at  $0^\circ\text{C}$  under strong stirring. After 1h stirring the Schlenk was equipped with a condenser and a calcium chloride drying tube, the resulting solution was refluxed at  $110^\circ\text{C}$  for 20h, the Schlenk was then cooled to room temperature and subjected to 8 freeze-pump-thaw cycles to remove excess of HCl. The thus obtained chloroborazole intermediate was diluted with 8 mL of dry THF as cosolvent then cannulated slowly in a stirred solution of aryllithium and left to react for 20h.

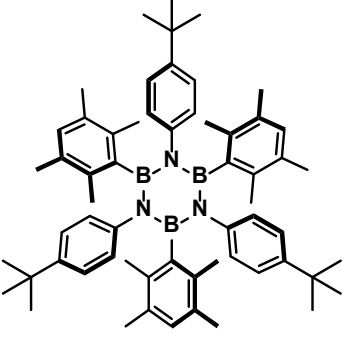
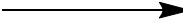
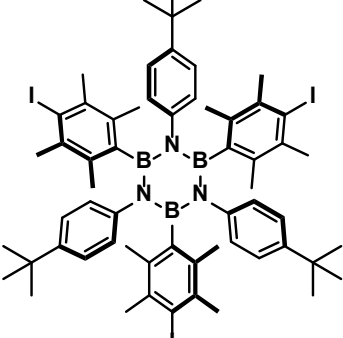
Aryllithium was prepared treating (2-Bromo-1,3-difluorobenzene 1.1 eq (5.5 mmol, 620  $\mu$ L) dissolved in dry THF 4 mL with n-butyl lithium 1.32 eq (4.13 mL) 1.6 M in hexanes at  $-84^\circ\text{C}$ , the solution was kept stirring for 10 minutes before cannulating, then left stirring at  $-84^\circ\text{C}$  for 3 hours, then warmed to  $0^\circ\text{C}$  and stirred for further 3 hours before leaving the reaction to stir overnight at room temperature. The final product was quenched by stirring with 10 mL water, added to a separatory funnel together with 80 mL DCM and extracted twice with 50 mL water then with 50 mL brine. Organic phase was dried over sodium sulfate then stripped of solvent under vacuum, dispersed in chloroform and crystallized with MeOH, product was filtered under vacuum and left to dry for 30 minutes affording pure product as a white solid **223 mg 20.7%**.

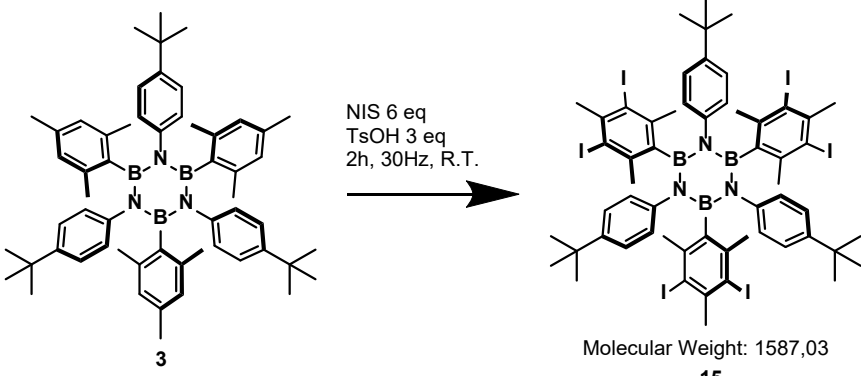
Mol Formula		$\text{C}_{36}\text{H}_{24}\text{B}_3\text{F}_6\text{N}_3$		m. p.	$>300^\circ\text{C}$
<b><math>^1\text{H}</math> NMR (400 MHz, <math>\text{CDCl}_3</math>)</b>	<b><math>\delta</math> Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	6.40-6.36	6	m		
	6.93-6.79	12	m		
	7.10-7.08	6	m		
<b><math>^{13}\text{C}</math> NMR (100.6 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math>: 163.9-161.3, 145.75, 130.7-130.5, 127.9, 127.0, 125.5, 109.9-109.7. (One peak is missing due to boron quadrupolar relaxation)</b>					
<b><math>^{11}\text{B}</math> NMR (128.4 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math>: 34.1</b>					
<b><math>^{19}\text{F}</math> NMR (376 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math>: -101.4</b>					
<b>Anal. Calcd.:</b> C, 67.04; H, 3.75; N, 6.51 <b>Found:</b> C, 66.93; H, 3.80; N, 6.41					

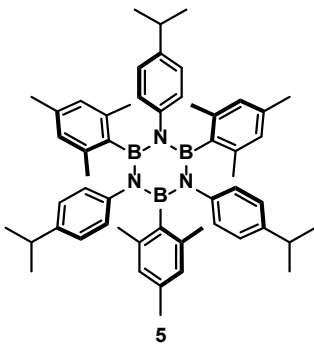
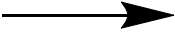
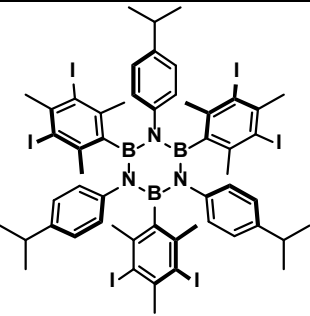
Chem. Name	B,B',B''-Tris(4-(tertbutyl)-2,6-dimethylphenyl)-N,N',N''-tris(4-iodo-3,5-dimethylphenyl)borazine ( <b>11</b> )			
<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center;">  <p><b>1</b></p> </div> <div style="margin: 0 20px; text-align: center;"> <p>NIS 3 eq TsOH 3 eq 1h, 30Hz, R.T.</p> <p>→</p> </div> <div style="text-align: center;">  <p>Molecular Weight: 1251,42 <b>11</b></p> </div> </div>				
<p><b>METHOD:</b> Ball miller jar was loaded with borazine <b>1</b> (0.08 mmol, 69.9 mg), NIS 3 eq (0.24 mmol, 54 mg), TsOH 3 eq (0.24 mmol, 45.6 mg) and a single zirconium oxide ball. The mixture was milled for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover product <b>11</b>, <b>90% 90 mg</b> as a white powder.</p>				
<b>Mol Formula</b>		C <sub>60</sub> H <sub>75</sub> B <sub>3</sub> I <sub>3</sub> N <sub>3</sub>		<b>m. p.</b>
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>		<b>δ Value</b>	<b>No. H</b>	<b>J Value/Hz</b>
		1.10	27	s
		2.02	18	s
		2.16	18	s
		6.42	6	s
6.54	6	s	> 300 °C	
<p><b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 150.0, 145.6, 139.6, 137.1, 126.2, 122.5, 102.5, 34.1, 31.3, 29.0, 23.3. (One peak is missing due to boron quadrupolar relaxation)</p>				
<p><b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) δ:</b> 36.8</p>				
<p><b>Anal. Calcd.:</b> C, 57.59; H, 6.04; N, 3.36 <b>Found:</b> C, 57.35; H, 5.97; N, 3.41</p>				

Chem. Name	<b>B,B',B''-Tris(3-iodo-2,6-dimethylphenyl)-N,N',N''-tris(4-tbutylphenyl)borazine (12)</b>			
<p style="text-align: center;">2</p> <p style="text-align: center;">cis</p> <p style="text-align: center;">trans</p> <p style="text-align: right;">Molecular Weight: 1167,26 12</p>				
<b>METHOD:</b>				
<p>Ball miller jar was loaded with borazine <b>2</b> (0.08 mmol, 63.2 mg), NIS 3 eq (0.24 mmol, 54 mg), TsOH 3 eq (0.24 mmol, 45.6 mg) and a single zirconium oxide ball. The mixture was milled for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover product <b>12</b>, <b>76% 71 mg</b> as a white powder.</p>				
<b>Mol Formula</b>		$C_{54}H_{63}B_3I_3N_3$		<b>m. p.</b>
				> 300 °C
<b><sup>1</sup>H NMR</b> <b>(400 MHz,</b> <b>CDCl<sub>3</sub>)</b>	<b>δ Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>
	1.06-1.07	27	m	
	2.21-2.25	9	m	
	2.29-2.35	9	m	
	6.22-6.27	3	m	
	6.57-6.81	12	m	
	7.21-7.24	3	m	
<p><b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 147.5, 142.6, 140.0-139.8, 138.0, 137.6, 127.8, 126.2-126.0, 123.9-123.8, 97.9, 34.2, 31.3, 30.6-30.5, 22.7. (One peak is missing due to boron quadrupolar relaxation)</p>				
<p><b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) δ:</b> 37.1</p>				
<p><b>Anal. Calcd.:</b> C, 55.57; H, 5.44; N, 3.60; <b>Found:</b> C, 55.34; H, 5.62; N, 3.43;</p>				

Chem. Name	<b>B,B',B''-Tris(3-iodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine (13)</b>				
<p style="text-align: center;">Molecular Weight: 1209,34 <b>13</b></p>					
<b>METHOD:</b>					
Ball miller jar was loaded with borazine <b>3</b> (0.08 mmol, 66.5 mg), NIS 3 eq (0.24 mmol, 54 mg), TsOH 3 eq (0.24 mmol, 45.6 mg) and a single zirconium oxide ball. The mixture was milled for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover product <b>13</b> , <b>84% 81 mg</b> as a white powder.					
<b>Mol Formula</b>		$C_{57}H_{69}B_3I_3N_3$		<b>m. p.</b>	> 300 °C
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b>δ Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	1.05	27	s		
	2.12	9	s		
	2.22-2.17	9	m		
	2.40-2.33	9	m		
	6.44-6.40	3	m		
	6.74-6.61	12	m		
<b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 147.2, 143.0, 140.8-140.6, 140.0, 137.3, 127.5, 126.1, 123.8, 105.2, 34.1, 32.2-32.1, 31.3, 29.5, 22.4. (One peak is missing due to boron quadrupolar relaxation)					
<b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) δ:</b> 36.6					
<b>Anal. Calcd.:</b> C, 56.61; H, 5.75; N, 3.47; <b>Found:</b> C, 56.92; H, 5.53; N, 3.45;					

Chem. Name	B,B',B''-Tris(4-iodo-2,3,5,6-tetramethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine ( <b>14</b> )				
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p><b>4</b></p> </div> <div style="text-align: center;"> <p>NIS 3 eq TsOH 3 eq 1h, 30Hz, R.T.</p>  </div> <div style="text-align: center;">  <p>Molecular Weight: 1251,42 <b>14</b></p> </div> </div>					
<p><b>METHOD:</b> Ball miller jar was loaded with borazine <b>4</b> (0.08 mmol, 69.9 mg), NIS 3 eq (0.24 mmol, 54 mg), TsOH 3 eq (0.24 mmol, 45.6 mg) and a single zirconium oxide ball. The mixture was milled for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover product <b>14</b>, <b>83% 83 mg</b> as a white powder.</p>					
<b>Mol Formula</b>		C <sub>60</sub> H <sub>75</sub> B <sub>3</sub> I <sub>3</sub> N <sub>3</sub>		<b>m. p.</b>	> 300 °C
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b>δ Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	1.04	27	s		
	2.14	18	s		
	2.27	18	s		
	6.60-6.58	6	d	8.56	
6.69-6.67	6	d	8.68		
<p><b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 147.1, 143.3, 135.9, 134.1, 126.0, 123.6, 110.7, 34.1, 31.4, 26.8, 23.7. (One peak is missing due to boron quadrupolar relaxation)</p>					
<p><b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) δ:</b> 36.9</p>					
<p><b>Anal. Calcd.:</b> C, 57.59; H, 6.04; N, 3.36; <b>Found:</b> C, 57.65; H, 6.00; N, 3.40;</p>					

Chem. Name	<b>B,B',B''-Tris(3,5-diiodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine (15)</b>				
<div style="display: flex; align-items: center; justify-content: center;">  </div> <p style="text-align: center; margin-top: 10px;">Molecular Weight: 1587.03 <b>15</b></p>					
<p><b>METHOD:</b> Ball miller jar was loaded with borazine <b>3</b> (0.08 mmol, 66.5 mg), NIS 6 eq (0.48 mmol, 108 mg), TsOH 3 eq (0.24 mmol, 45.6 mg) and a single zirconium oxide ball. The mixture was milled for 2h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover product <b>15</b>, <b>53% 67 mg</b> as a white powder.</p>					
<b>Mol Formula</b>		C <sub>57</sub> H <sub>66</sub> B <sub>3</sub> I <sub>6</sub> N <sub>3</sub>		<b>m. p.</b>	> 300 °C
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b>δ Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	1.07	27	s		
	2.43	18	s		
	2.65	9	s		
	6.62-6.60	6	d	8.52	
6.79-6.77	6	d	8.56		
<p><b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 147.9, 142.5, 142.0, 140.9, 125.6, 124.3, 104.3, 37.9, 34.2, 32.4, 31.3. (One peak is missing due to boron quadrupolar relaxation)</p>					
<p><b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) δ:</b> 37.3</p>					
<p><b>Anal. Calcd.:</b> C, 43.14; H, 4.19; N, 2.65; <b>Found:</b> C, 42.93; H, 4.28; N, 2.68;</p>					

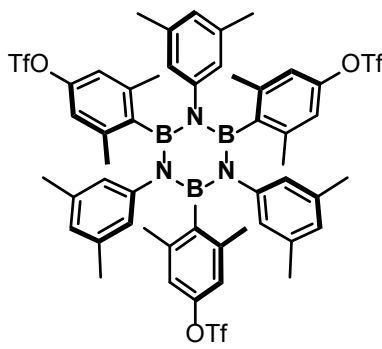
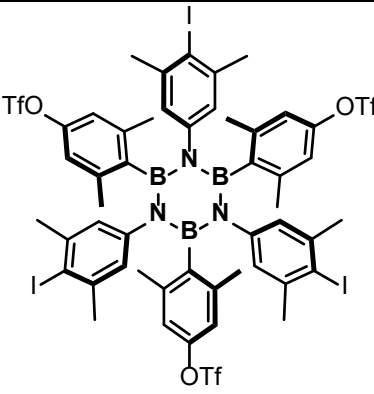
Chem. Name	<b>B,B',B''-Tris(3,5-diiodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine (16)</b>				
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p><b>5</b></p> </div> <div style="text-align: center;"> <p>NIS 6 eq TsOH 3 eq 2h, 30Hz, R.T.</p>  </div> <div style="text-align: center;">  <p>Molecular Weight: 1544,95 <b>16</b></p> </div> </div>					
<p><b>METHOD:</b> Ball miller jar was loaded with borazine <b>5</b> (0.08 mmol, 63 mg), NIS 6 eq (0.48 mmol, 108 mg), TsOH 3 eq (0.24 mmol, 45.6 mg) and a single zirconium oxide ball. The mixture was milled for 2h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover product <b>16</b>, <b>45% 56 mg</b> as a white powder.</p>					
<b>Mol Formula</b>		C <sub>54</sub> H <sub>60</sub> B <sub>3</sub> I <sub>6</sub> N <sub>3</sub>		<b>m. p.</b>	288 °C
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b>δ Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	0.99-0.98	18	d	6.84	
	2.42	18	s		
	2.63-2.56	3	m		
	2.65	8	s		
6.65-6.60	12	m			
<p><b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 145.7, 142.8, 142.1, 140.8, 125.9, 125.4, 104.3, 37.9, 33.4, 32.5, 23.9. (One peak is missing due to boron quadrupolar relaxation)</p>					
<p><b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) δ:</b> 36.6</p>					
<p><b>Anal. Calcd.:</b> C, 41.98; H, 3.91; N, 2.72; <b>Found:</b> C, 41.82; H, 3.97; N, 2.79;</p>					

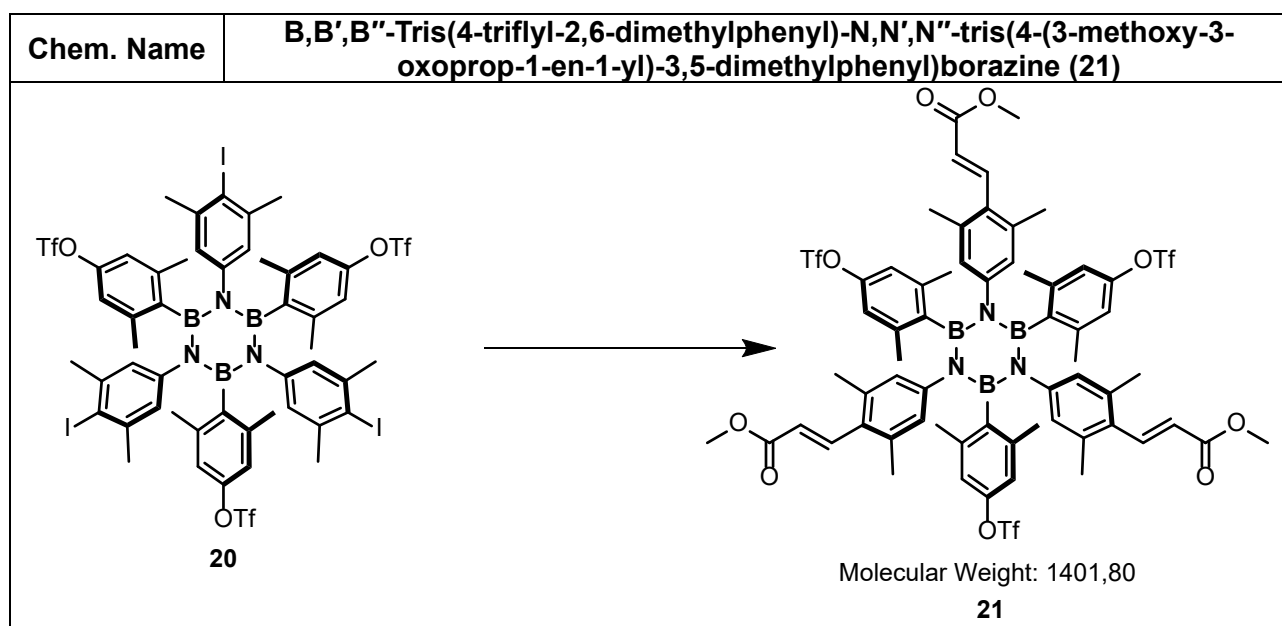


Chem. Name	B,B',B''-Tris(3-iodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine (17)			
<b>METHOD:</b>				
<p>Ball miller jar was loaded with borazine <b>5</b> (0.08 mmol, 64 mg), NIS 3 eq (0.24 mmol, 54 mg), TsOH 3 eq (0.24 mmol, 45.6 mg) and a single zirconium oxide ball. The mixture was milled for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover product <b>17</b>, <b>94% 88 mg</b> as a white powder.</p>				
<b>Mol Formula</b>	C <sub>54</sub> H <sub>63</sub> B <sub>3</sub> I <sub>3</sub> N <sub>3</sub>		<b>m. p.</b>	
	254 °C			
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b>δ Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>
	0.98-0.96	18	d	6.96
	2.13	9	s	
	2.22-2.17	9	m	
	2.40-2.34	9	m	
	2.61-2.54	3	m	
	6.43-6.40	3	m	
6.65-6.57	12	m		
<b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 145.0, 143.4, 140.7-140.6, 140.1, 137.3-137.2, 127.5, 126.5-126.2, 125.1-124.7, 105.3, 33.4-33.3, 32.1, 29.5, 24.0-23.9, 22.4. (One peak is missing due to boron quadrupolar relaxation)				
<b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) δ:</b> 36.5				
<b>Anal. Calcd.:</b> C, 55.57; H, 5.44; N, 3.60; <b>Found:</b> C, 55.43; H, 5.71; N, 3.76;				

Chem. Name		<b>B,B',B''-Tris(3-iodo-2,4,6-trimethylphenyl)-N,N',N''-tris(phenyl)borazine (18)</b>			
		<p>Molecular Weight: 1041,02 <b>18</b></p>			
<b>METHOD:</b>					
<p>Ball miller jar was loaded with borazine <b>6</b> (0.08 mmol, 53 mg), NIS 3 eq (0.24 mmol, 54 mg), TsOH 3 eq (0.24 mmol, 45.6 mg) and a single zirconium oxide ball. The mixture was milled for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover product <b>18</b>, <b>89% 74 mg</b> as a white powder.</p>					
<b>Mol Formula</b>		C <sub>45</sub> H <sub>45</sub> B <sub>3</sub> I <sub>3</sub> N <sub>3</sub>		<b>m. p.</b>	> 300 °C
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b>δ Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	2.12	9	s		
	2.24-2.19	9	m		
	2.47-2.42	9	m		
	6.41	3	m		
	6.80-6.76	15	m		
<p><b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 145.8, 140.5-140.4, 137.1-137.0, 127.7-127.6, 127.5-127.2, 126.7-126.3, 125.0, 105.4, 105.3, 32.2-32.1, 29.6, 22.5-22.4. (One peak is missing due to boron quadrupolar relaxation)</p>					
<p><b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) δ:</b> 37.2</p>					
<p><b>Anal. Calcd.:</b> C, 51.92; H, 4.36; N, 4.04; <b>Found:</b> C, 51.81; H, 4.39; N, 4.17;</p>					

Chem. Name	<b>B,B',B''-Tris(3-iodo-2,6-dimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine (19)</b>				
<p style="text-align: center;">Molecular Weight: 1125,18 <b>19</b></p>					
<b>METHOD:</b>					
<p>Ball miller jar was loaded with borazine <b>7</b> (0.08 mmol, 59.8 mg), NIS 3 eq (0.24 mmol, 54 mg), TsOH 3 eq (0.24 mmol, 45.6 mg) and a single zirconium oxide ball. The mixture was milled for 1h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover product <b>19</b>, <b>85% 76.5 mg</b> as a white powder.</p>					
<b>Mol Formula</b>		$C_{51}H_{57}B_3I_3N_3$		<b>m. p.</b>	263 °C
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b>δ Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	1.00-0.98	18	m		
	2.25-2.21	9	m		
	2.36-2.30	9	m		
	2.62-2.55	3	m		
	6.27-6.22	3	m		
	6.67-6.55	12	m		
	7.24-7.22	3	d	8.08	
<b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 145.3, 142.9, 139.9-139.8, 138.0-137.9, 137.7, 127.8, 126.5-126.1, 125.2-124.9, 97.9, 33.4-33.3, 30.6, 23.9, 22.7. (One peak is missing due to boron quadrupolar relaxation)					
<b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) δ:</b> 37.1					
<b>Anal. Calcd.:</b> C, 54.44; H, 5.11; N, 3.73; <b>Found:</b> C, 54.14; H, 5.30; N, 3.94					

Chem. Name	B,B',B''-Tris(4-triflyl-2,6-dimethylphenyl)-N,N',N''-tris(4-iodo-3,5-dimethylphenyl)borazine (20)				
<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center;">  <p><b>9</b></p> </div> <div style="margin: 0 20px; text-align: center;"> <p>NIS 3 eq TsOH 3 eq 4h, 30Hz, R.T.</p> <p>→</p> </div> <div style="text-align: center;">  <p>Molecular Weight: 1527,27 <b>20</b></p> </div> </div>					
<p><b>METHOD:</b> Ball miller jar was loaded with borazine <b>9</b> (0.08 mmol, 92 mg), NIS 3 eq (0.24 mmol, 54 mg), TsOH 3 eq (0.24 mmol, 45.6 mg) and a single zirconium oxide ball. The mixture was milled for 4h. The resulting powder was scraped from the jar, the jar was washed thoroughly with MeOH and the resulting suspension was added to the scraped powder. The suspension in MeOH was sonicated for 10 minutes then filtered to recover product <b>20</b>, <b>59% 72 mg</b> as a white powder.</p>					
<b>Mol Formula</b>		C <sub>51</sub> H <sub>48</sub> B <sub>3</sub> F <sub>9</sub> I <sub>3</sub> N <sub>3</sub> O <sub>9</sub> S <sub>3</sub>		<b>m. p.</b>	251
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b>δ Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	2.08	18	s		
	2.27	18	s		
	6.40	6	s		
6.55	6	s			
<p><b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 149.4, 144.1, 141.1, 140.2, 125.0, 118.5, 123.5-114.0 (CF<sub>3</sub>), 103.9, 29.1, 23.2. (One peak is missing due to boron quadrupolar relaxation)</p>					
<p><b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) δ:</b> 36.7</p>					
<p><b><sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ:</b> -72.8</p>					
<p><b>Anal. Calcd.:</b> C, 40.11; H, 3.17; N, 2.75; S, 6.30; <b>Found:</b> C, 40.40; H, 3.26; N, 2.57; S, 5.99;</p>					



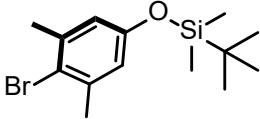
**METHOD:**

Catalyst solution: to an oven dried 10 mL Schlenk tube 5 mL of 4MeTHP was added, degassed through 3 freeze-pump-thaw cycles and backfilled with argon, under argon flow Pd(OAc)<sub>2</sub> 8.86 mg (50 mol%) and PPh<sub>3</sub> 52.45 mg (2.5 eq) were quickly added and stirred until development of a lime yellow color, indicative of the formation of the active catalyst.

To a 2 mL vial were added 0.08 mmol (122.2 mg) of borazine **20**, KOAc 6 eq, (0.48 mmol, 47 mg), methyl acrylate 9 eq (0.72 mmol, 61 mg, 65  $\mu$ L) and 1 mL of catalyst solution, the vial was rapidly capped and the solution stirred at 140 °C for 20h.

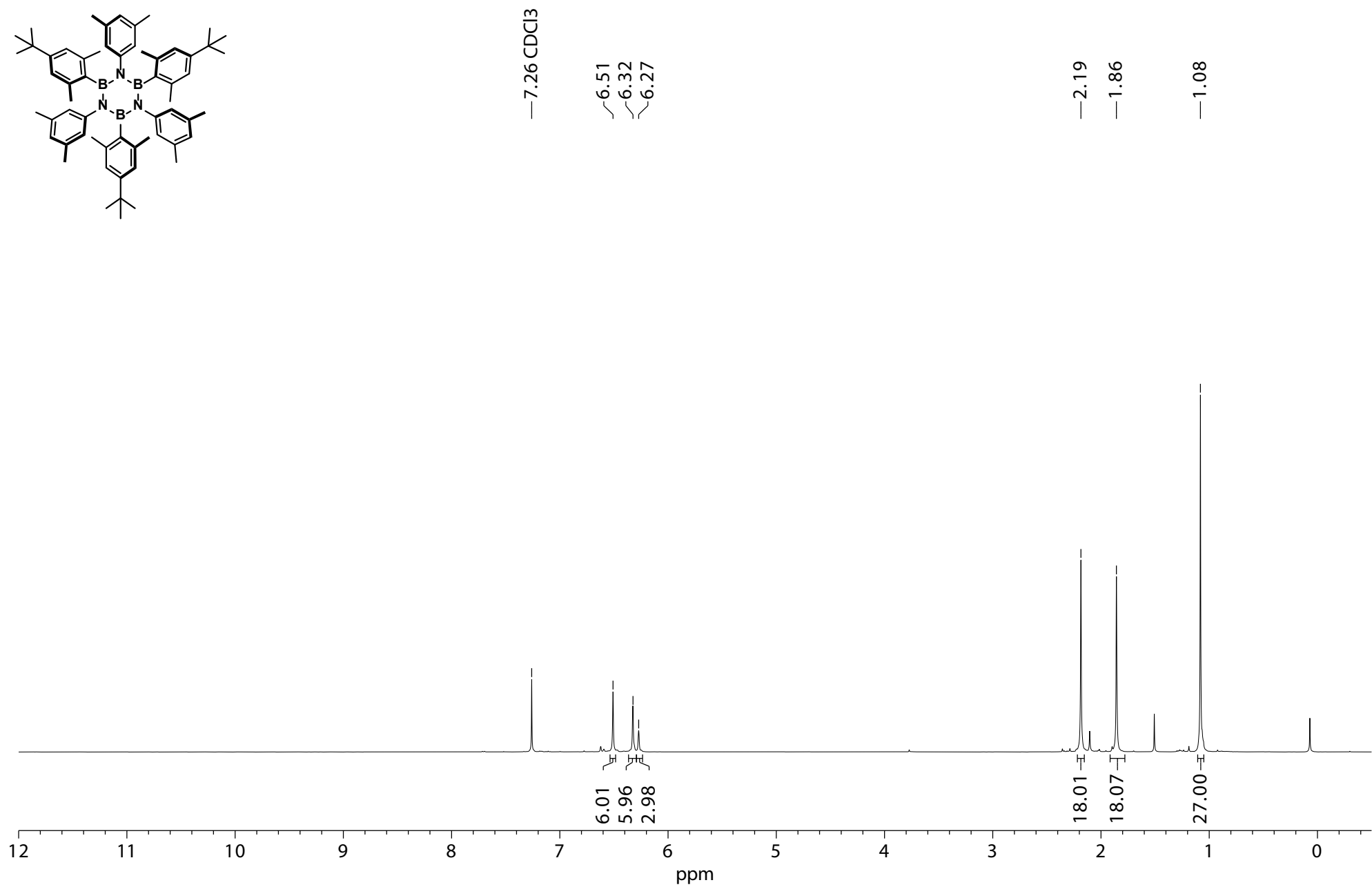
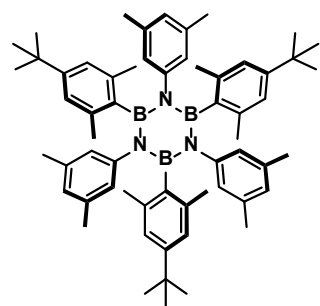
Upon reaction completion the vial was cooled to room temperature, stripped of solvent under vacuum and directly subjected to column chromatography (gradient elution ETP/EtOAc) to afford borazine **21** as an off white solid **31 mg, 28%**.

<b>Mol Formula</b>		<b>C<sub>63</sub>H<sub>63</sub>B<sub>3</sub>F<sub>9</sub>N<sub>3</sub>O<sub>15</sub>S<sub>3</sub></b>		<b>m. p.</b>	208
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b><math>\delta</math> Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	1.97	18	s		
	2.29	18	s		
	3.75	9	s		
	5.83-5.79	3	d	16.36	
	6.42	6	s		
	6.54	6	s		
	7.55-7.51	3	d	16.40	
<b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) <math>\delta</math>: 167.3, 149.2, 144.4, 142.6, 140.3, 136.2, 131.0, 126.5, 123.3, 118.4, 123.5-114.0 (CF<sub>3</sub>), 51.3, 23.2, 20.8. (One peak is missing due to boron quadrupolar relaxation).</b>					
<b><sup>11</sup>B NMR (128.4 MHz, CDCl<sub>3</sub>) <math>\delta</math>: 37.4</b>					
<b><sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) <math>\delta</math>: -73.0</b>					
<b>Anal. Calcd.: C, 53.98; H, 4.53; N, 3.00; S, 6.86; Found: C, 53.58; H, 4.64; N, 2.84; S, 6.73;</b>					

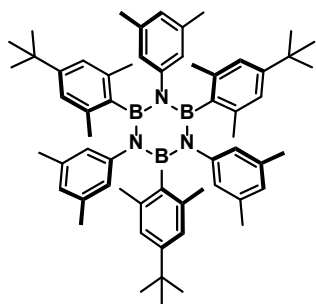
Chem. Name	(4-bromo-3,5-dimethylphenoxy)(tert-butyl)dimethylsilane (22)				
 <p>Molecular Weight: 315,33</p>					
<b>METHOD:</b>					
Product <b>22</b> was made according to a literature procedure ( <i>J. Org. Chem.</i> , 2019, <b>84</b> , 9101–9116.), yield 90% 8.85g. Characterization data is in accordance with literature reported values.					
<b>Mol Formula</b>		C <sub>14</sub> H <sub>23</sub> BrOSi		<b>m. p.</b>	oil
<b><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</b>	<b>δ Value</b>	<b>No. H</b>	<b>Mult.</b>	<b>J Value/Hz</b>	
	0.19	6	s		
	0.98	9	s		
	2.35	6	s		
	6.58	2	s		
<b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ:</b> 154.3, 139.1, 120.1, 119.1, 8.48, 77.2, 76.8, 25.8, 24.0, 18.3, -4.3.					

## 5. NMR Spectral Data

B,B',B''-Tris(4-(tertbutyl)-2,6-dimethylphenyl)-N,N',N''-tris(3,5-dimethylphenyl)borazine-(1)



B,B',B''-Tris(4-(tertbutyl)-2,6-dimethylphenyl)-N,N',N''-tris(3,5-dimethylphenyl)borazine-(1)



— 149.18  
— 145.96

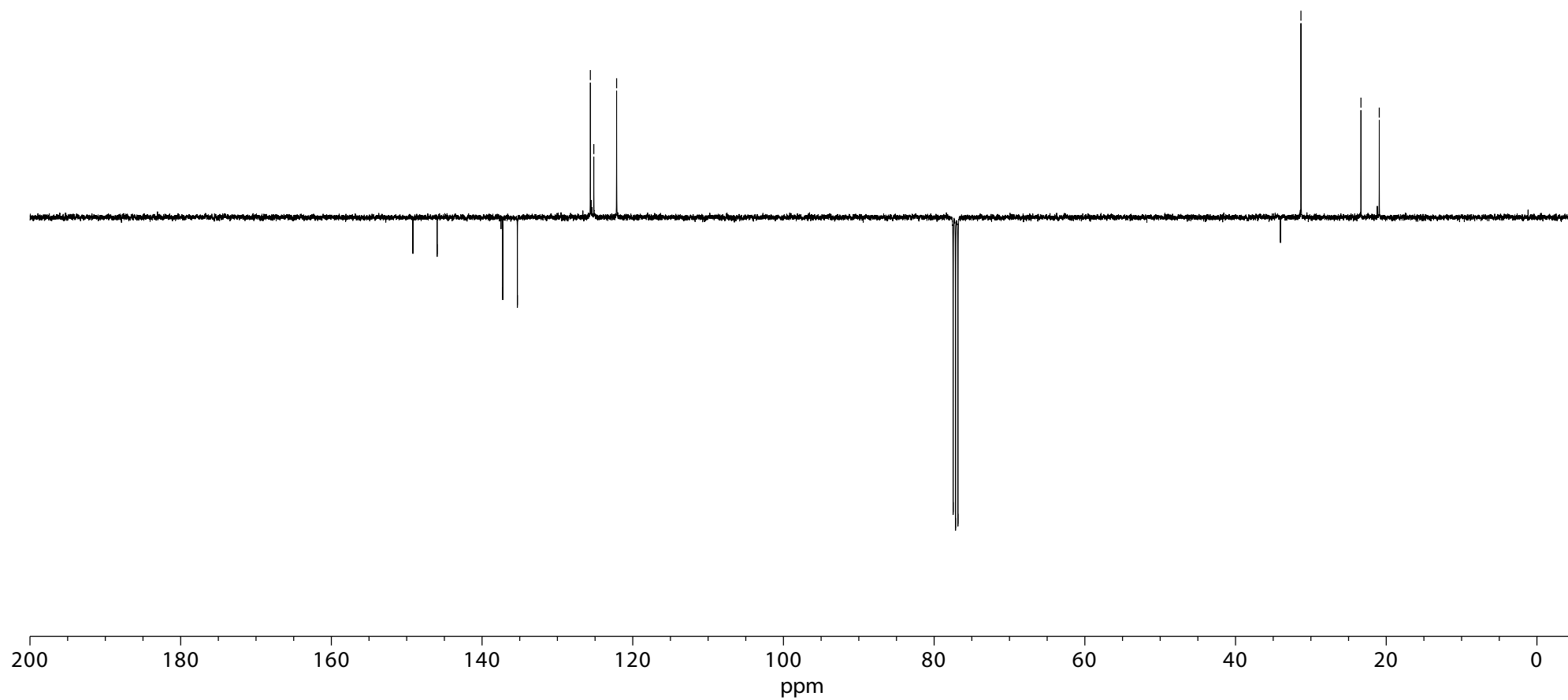
~ 137.25  
~ 135.31

~ 125.63  
~ 125.17  
~ 122.14

{ 77.48 CDCl3  
{ 77.16 CDCl3  
{ 76.84 CDCl3

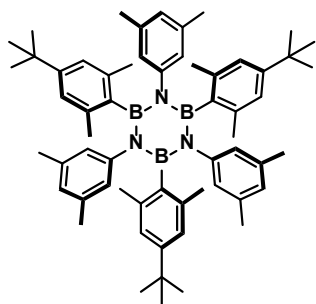
~ 34.04  
~ 31.32

~ 23.36  
~ 20.92

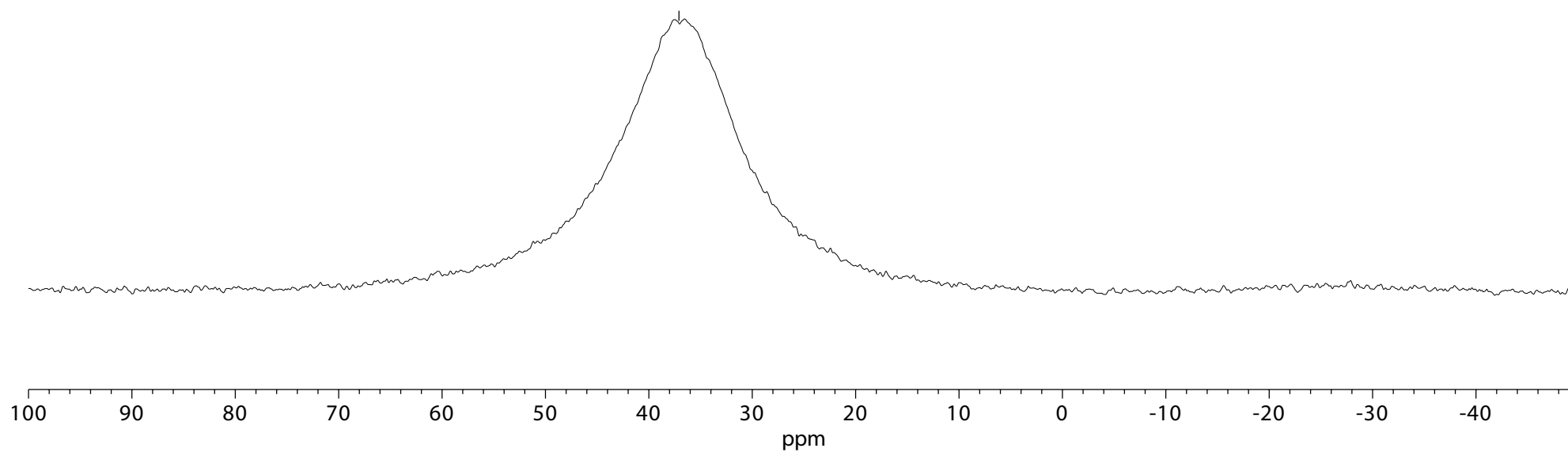




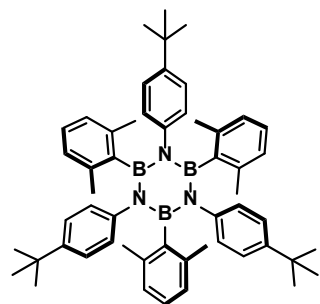
B,B',B''-Tris(4-(tertbutyl)-2,6-dimethylphenyl)-N,N',N''-tris(3,5-dimethylphenyl)borazine-(1)



—37.1



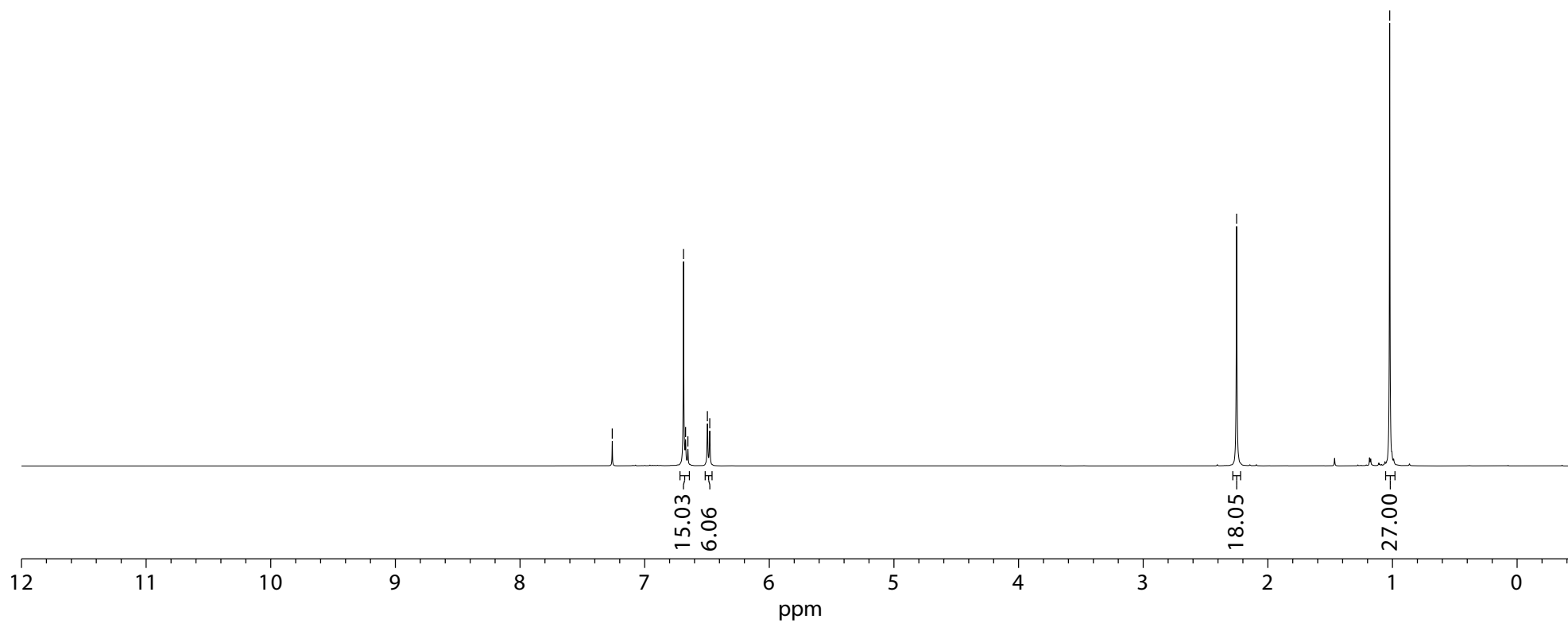
B,B',B''-Tris(2,6-dimethylphenyl)-N,N',N''-tris(4-tbutylphenyl)borazine-(2)



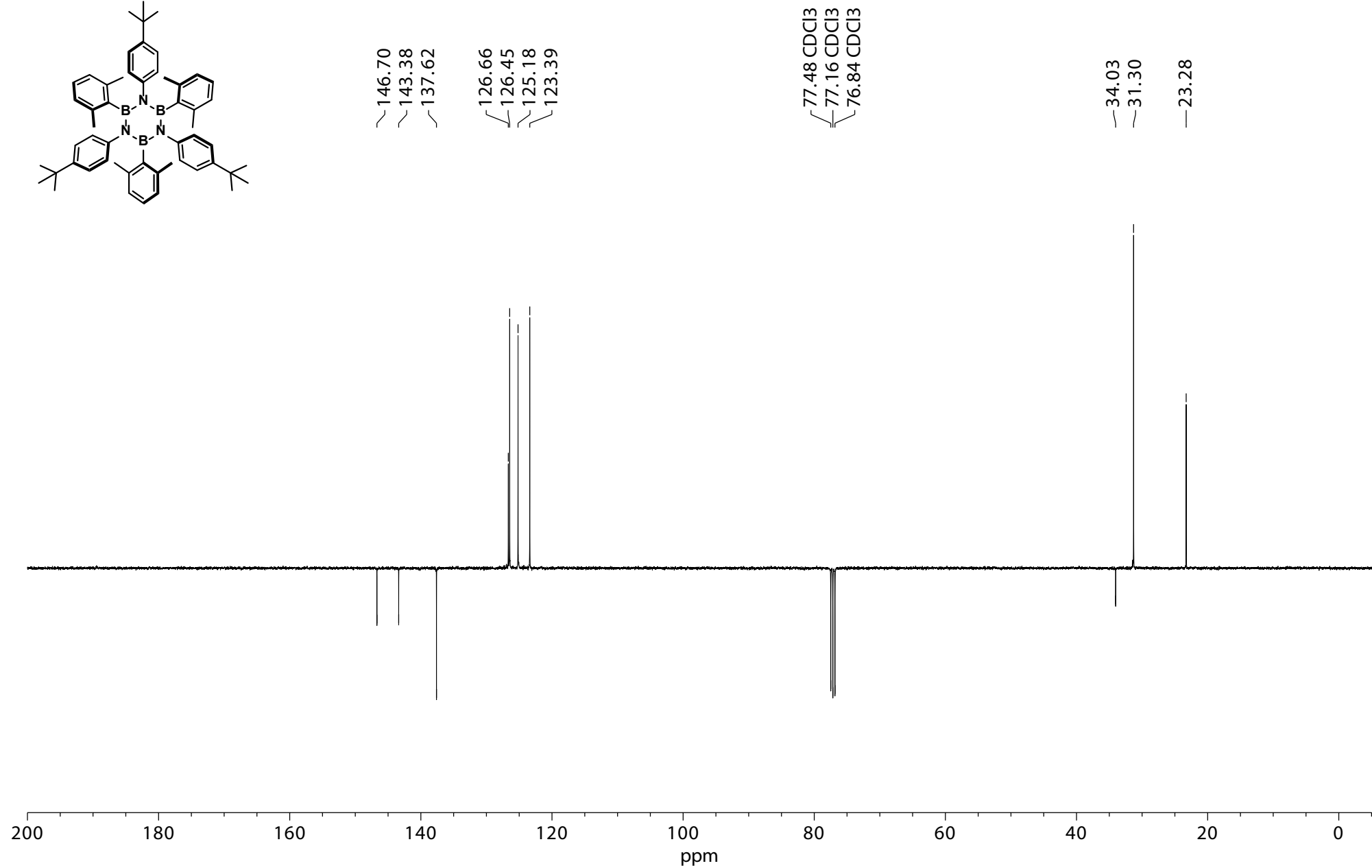
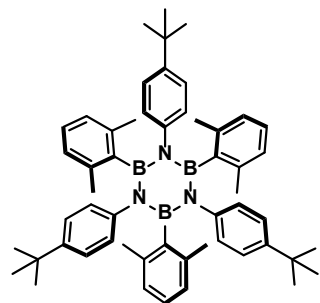
— 7.26 CDCl<sub>3</sub>  
6.69  
6.67  
6.65  
6.50  
6.48

— 2.25

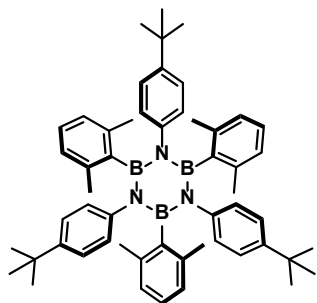
— 1.02



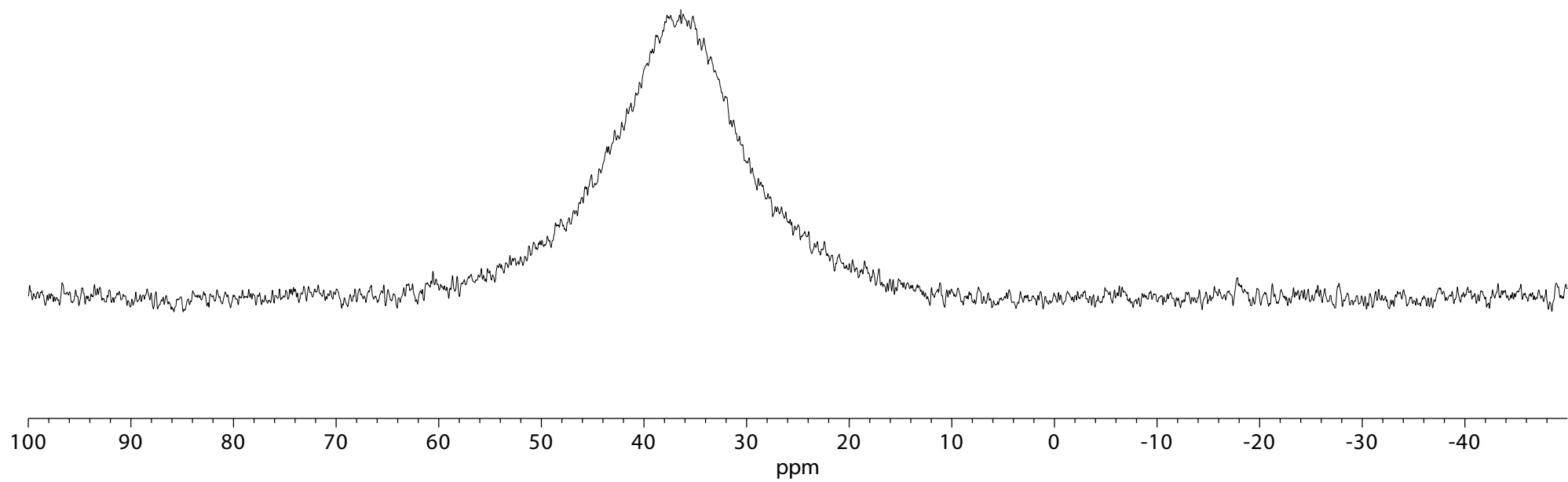
B,B',B''-Tris(2,6-dimethylphenyl)-N,N',N''-tris(4-*t*-butylphenyl)borazine-(2)



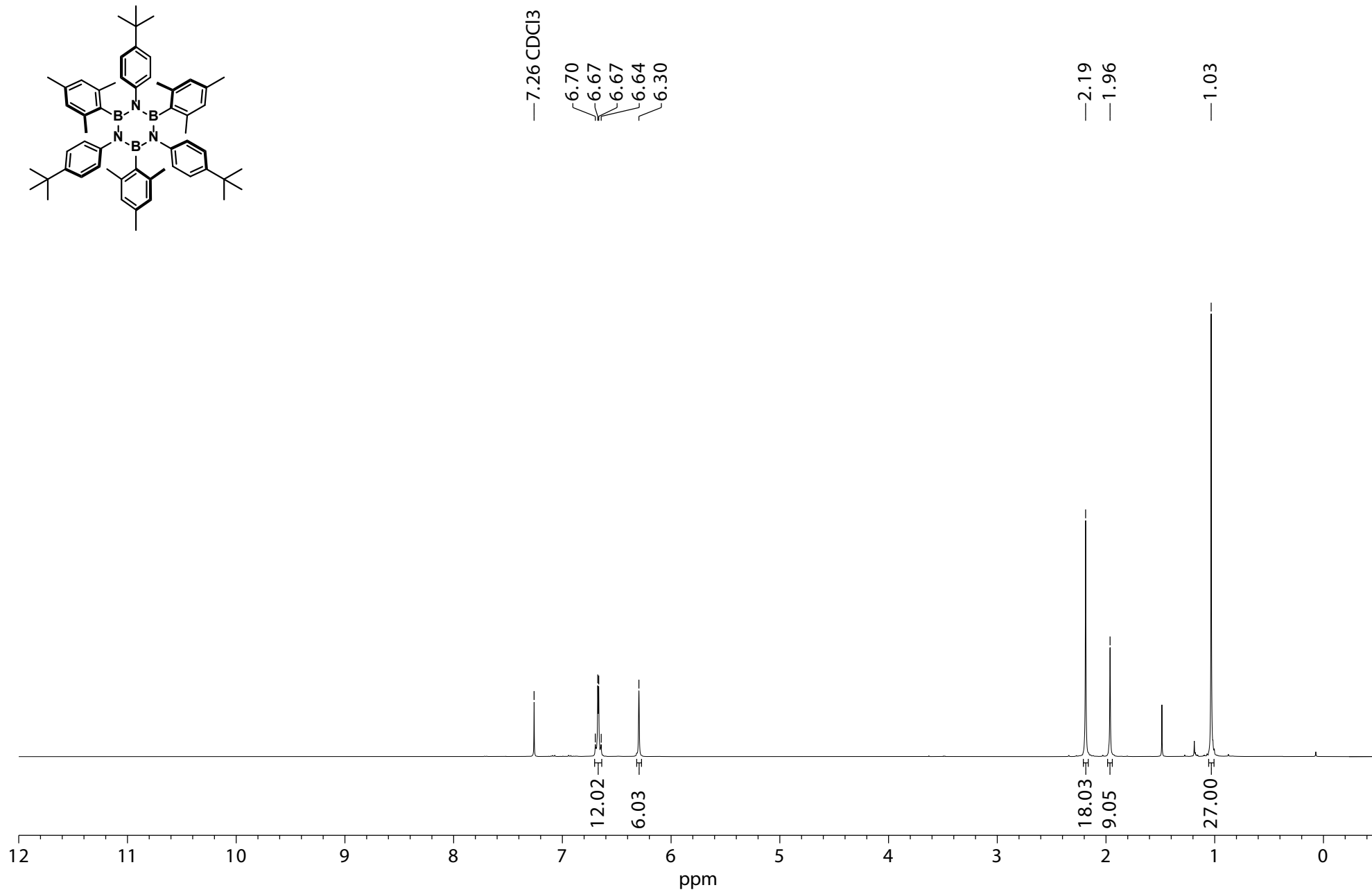
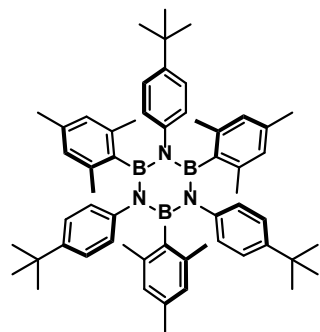
B,B',B''-Tris(2,6-dimethylphenyl)-N,N',N''-tris(4-tbutylphenyl)borazine-(2)



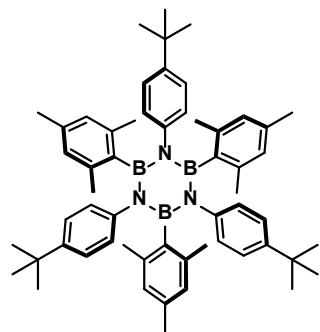
— 36.4



B,B',B''-Tris(2,4,6-trimethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(3)



B,B',B''-Tris(2,4,6-trimethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(3)



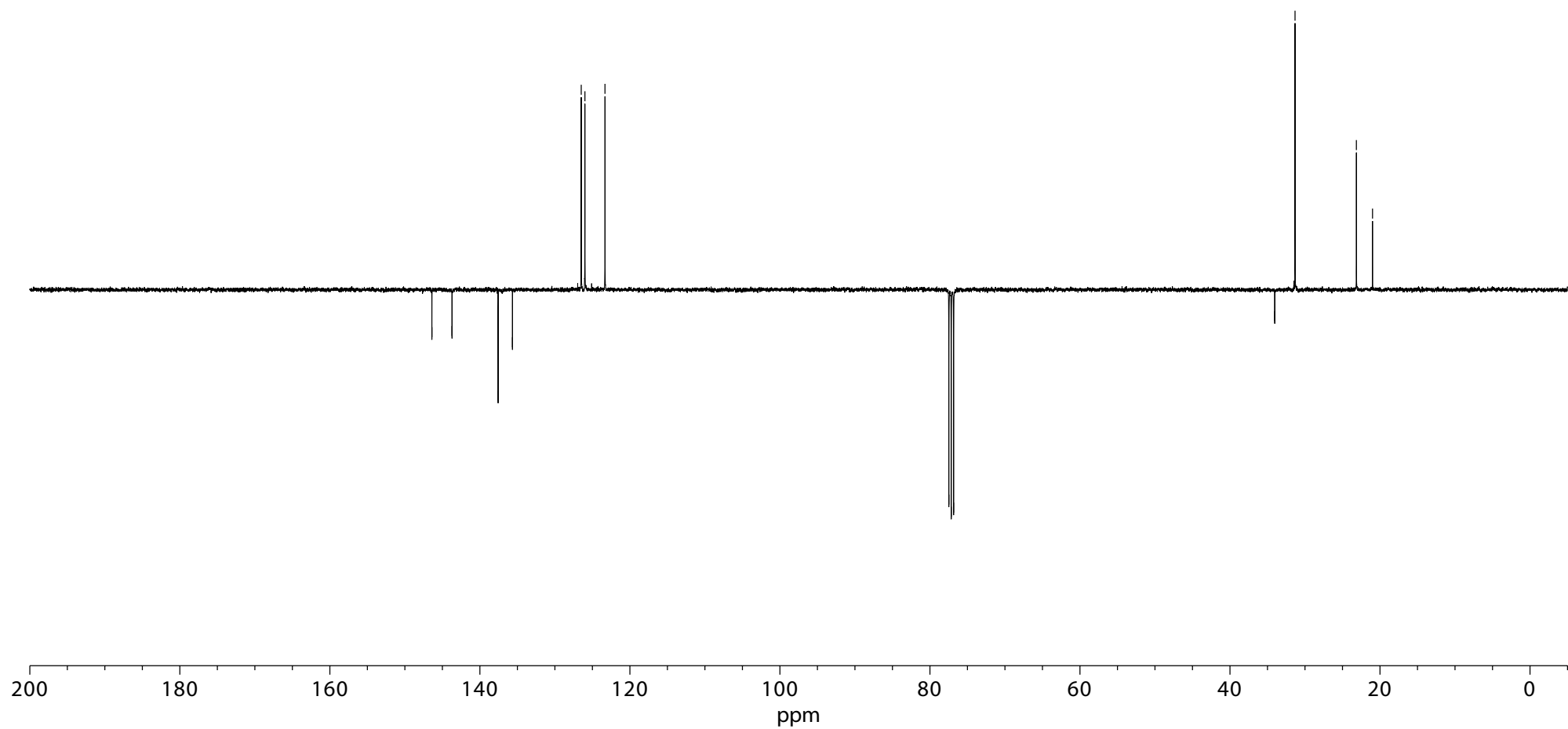
~146.40  
~143.71  
~137.57  
~135.66

~126.49  
~126.00  
~123.32

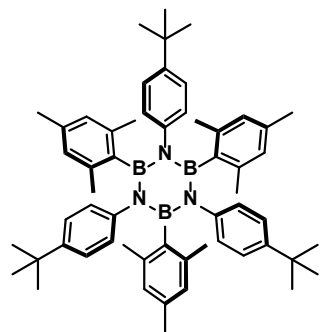
77.48 CDCl3  
77.16 CDCl3  
76.84 CDCl3

~34.03  
~31.33

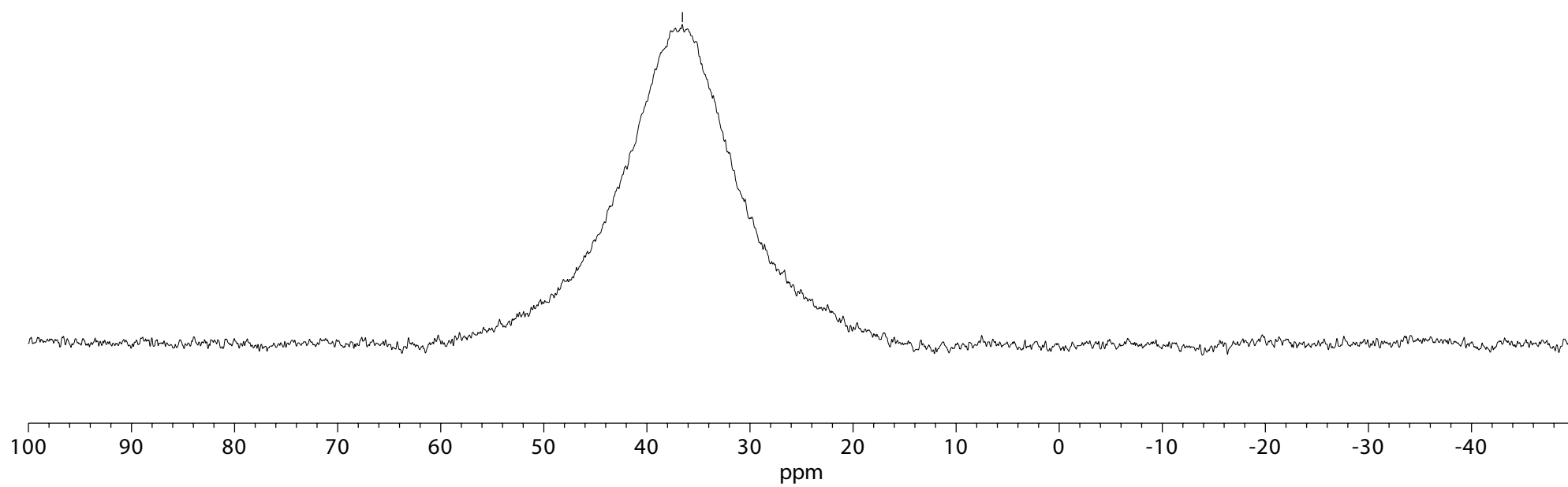
~23.15  
~21.00



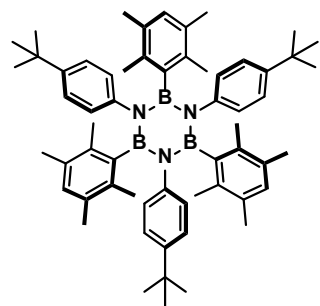
B,B',B''-Tris(2,4,6-trimethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(3)



—36.6



B,B',B''-Tris(2,3,5,6-tetramethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(4)



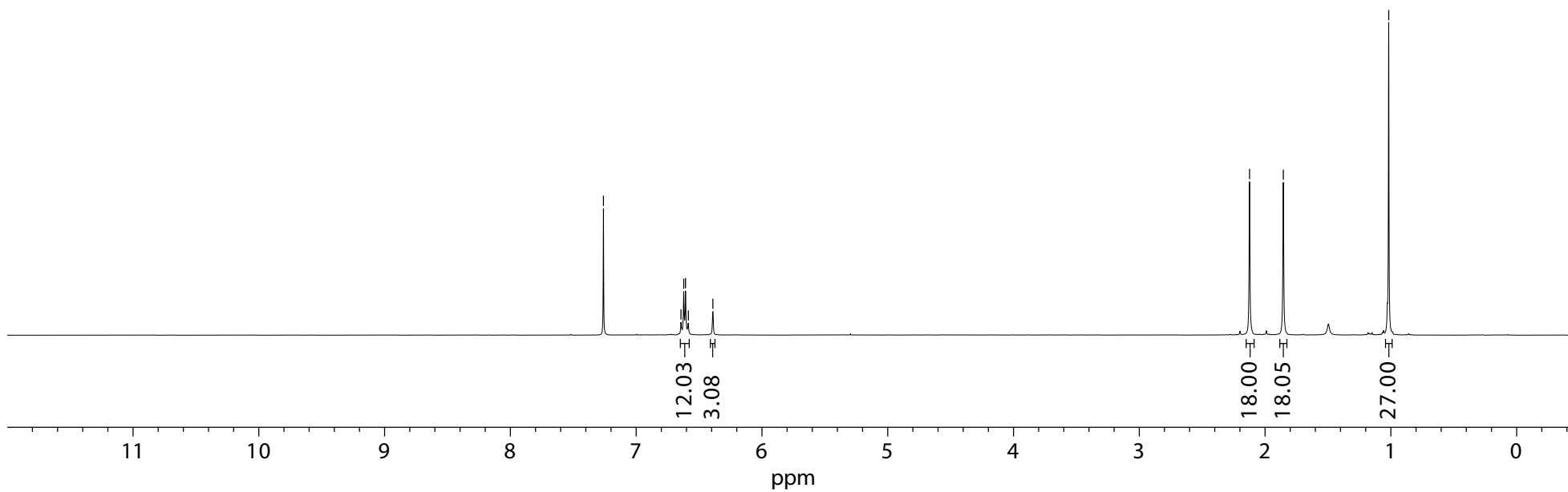
— 7.26 CDCl<sub>3</sub>

6.64  
6.62  
6.61  
6.59  
6.39

— 2.12

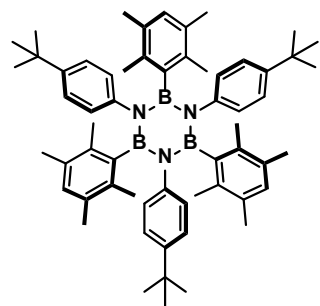
— 1.85

— 1.02





B,B',B''-Tris(2,3,5,6-tetramethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(4)



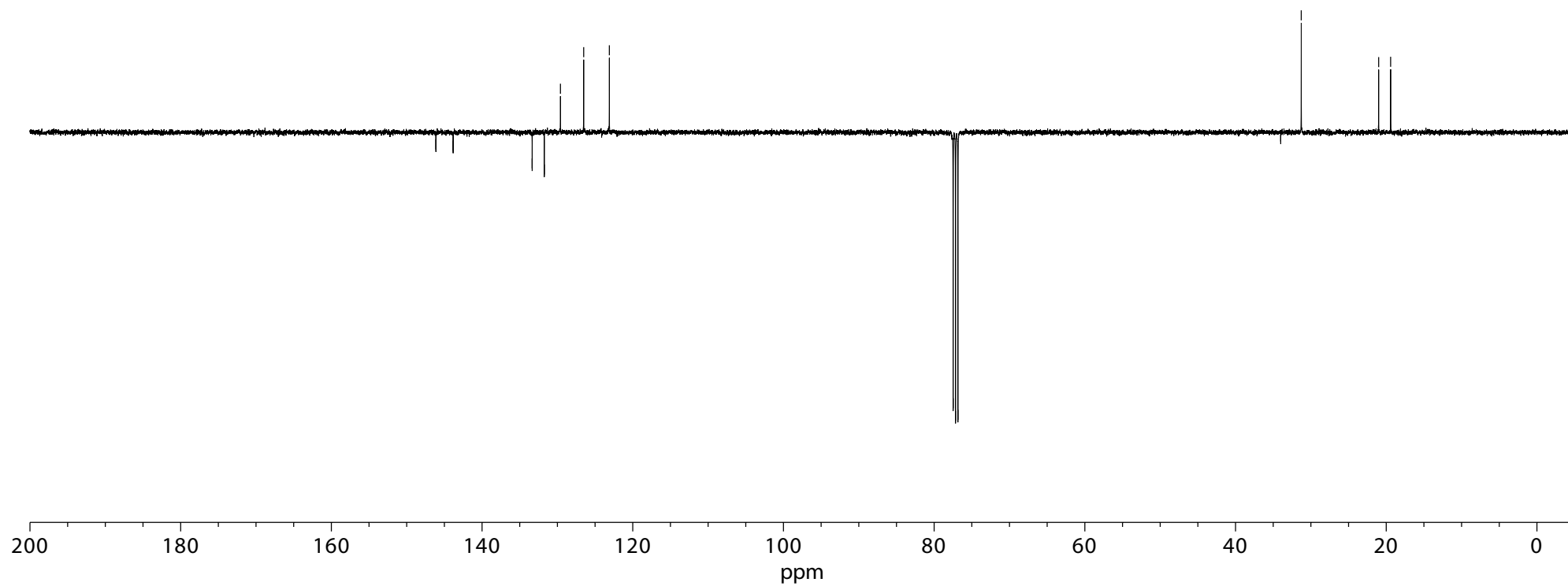
~146.13  
~143.84

~133.35  
~131.74  
~129.60  
~126.51  
~123.11

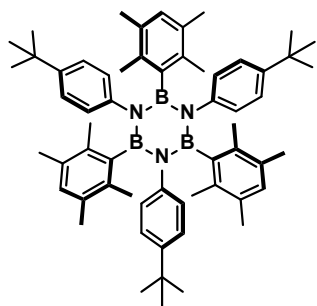
77.48 CDCl3  
77.16 CDCl3  
76.84 CDCl3

~34.01  
~31.28

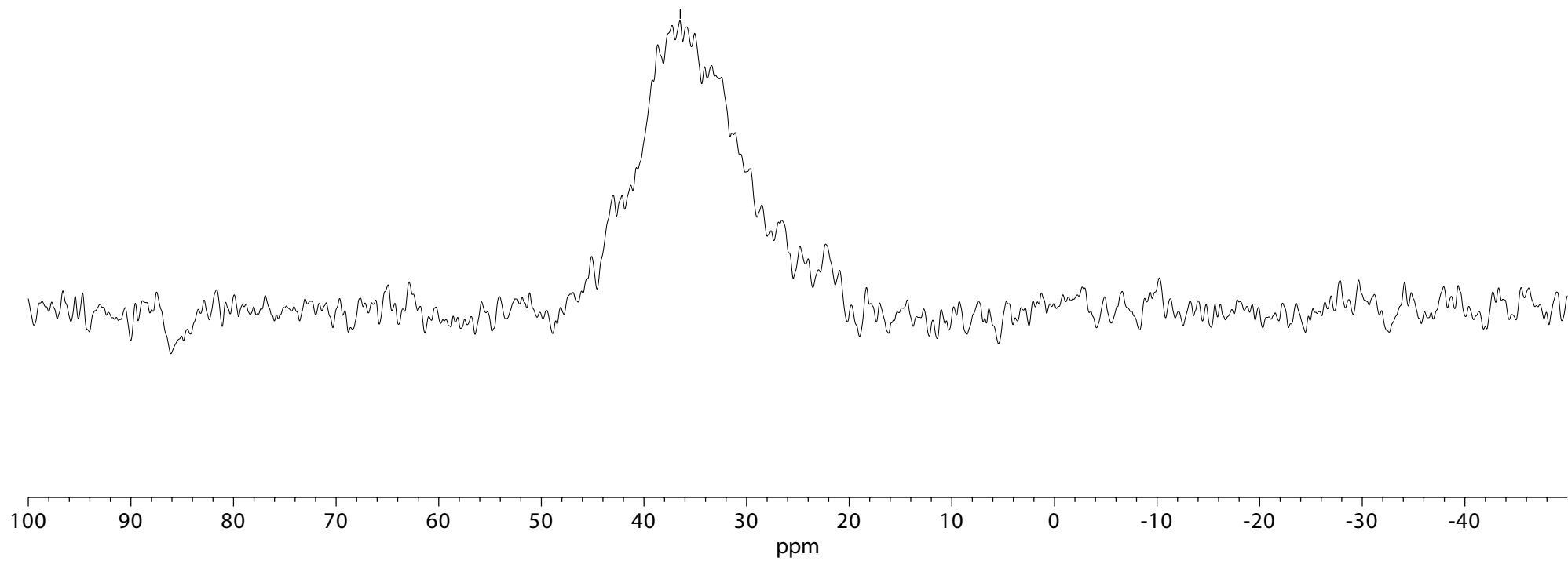
~21.00  
~19.42



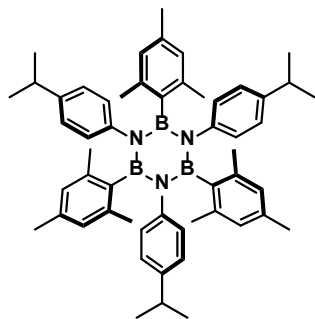
B,B',B''-Tris(2,3,5,6-tetramethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(4)



—36.5



B,B',B''-Tris(2,4,6-trimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(5)

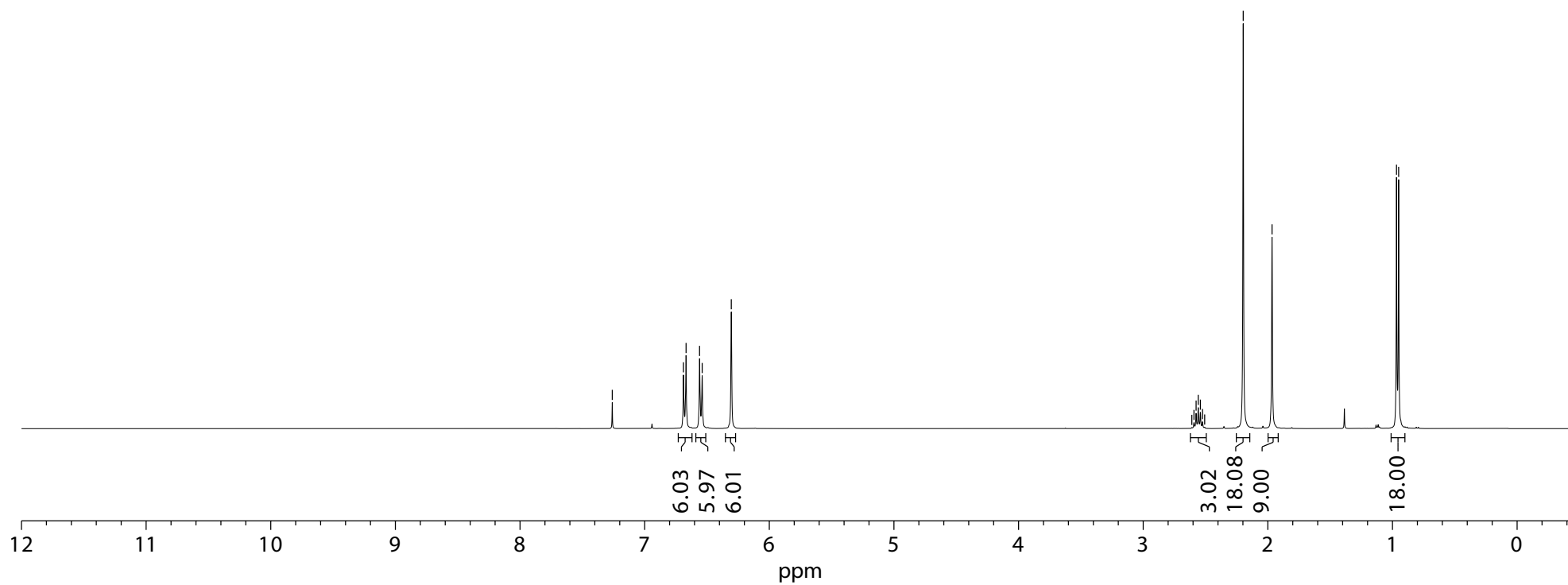


— 7.26 CDCl<sub>3</sub>

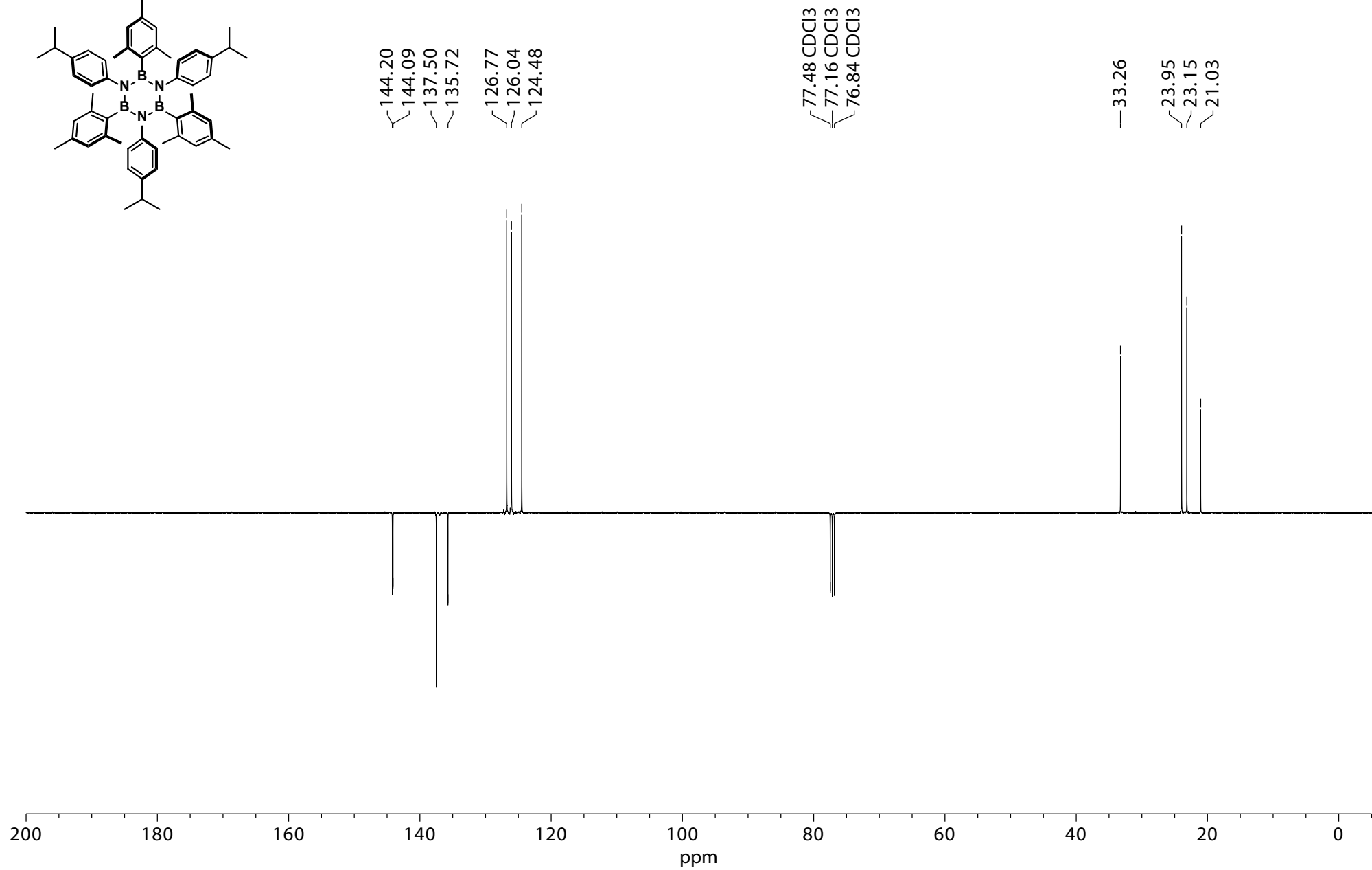
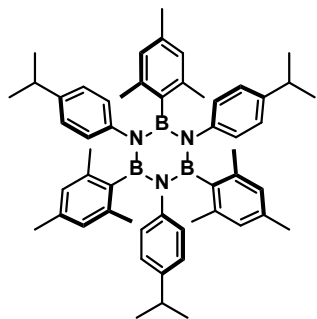
6.69  
6.67  
6.56  
6.54  
6.31

2.61  
2.59  
2.58  
2.56  
2.54  
2.52  
2.51  
2.20  
1.97

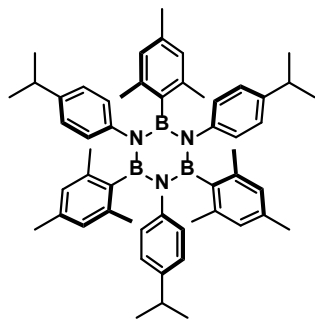
0.97  
0.95



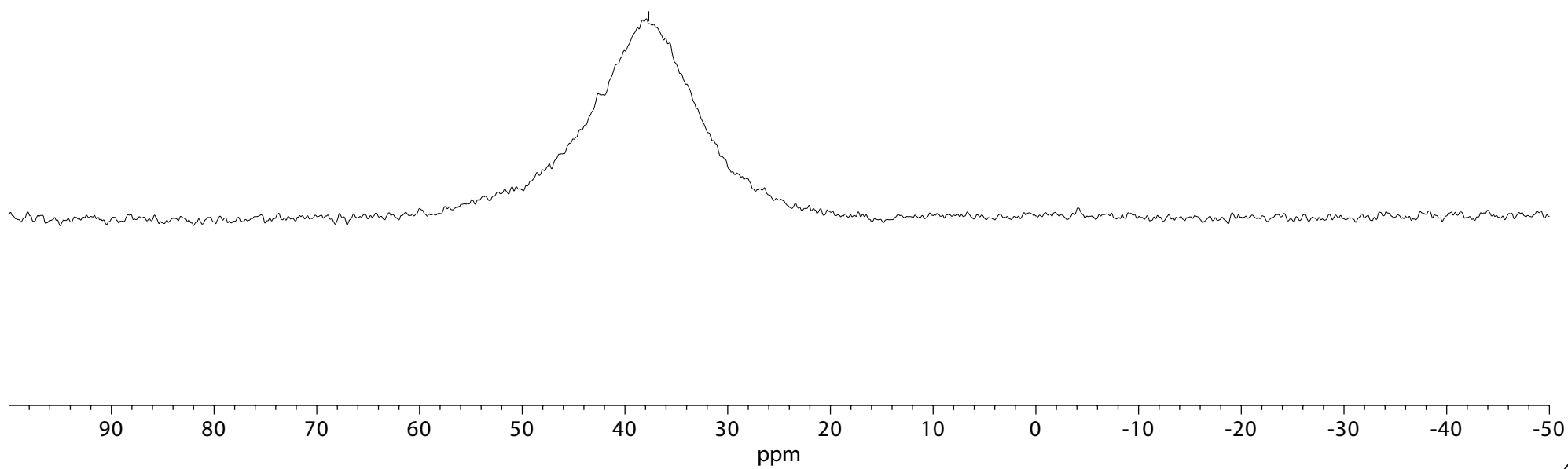
B,B',B''-Tris(2,4,6-trimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(5)



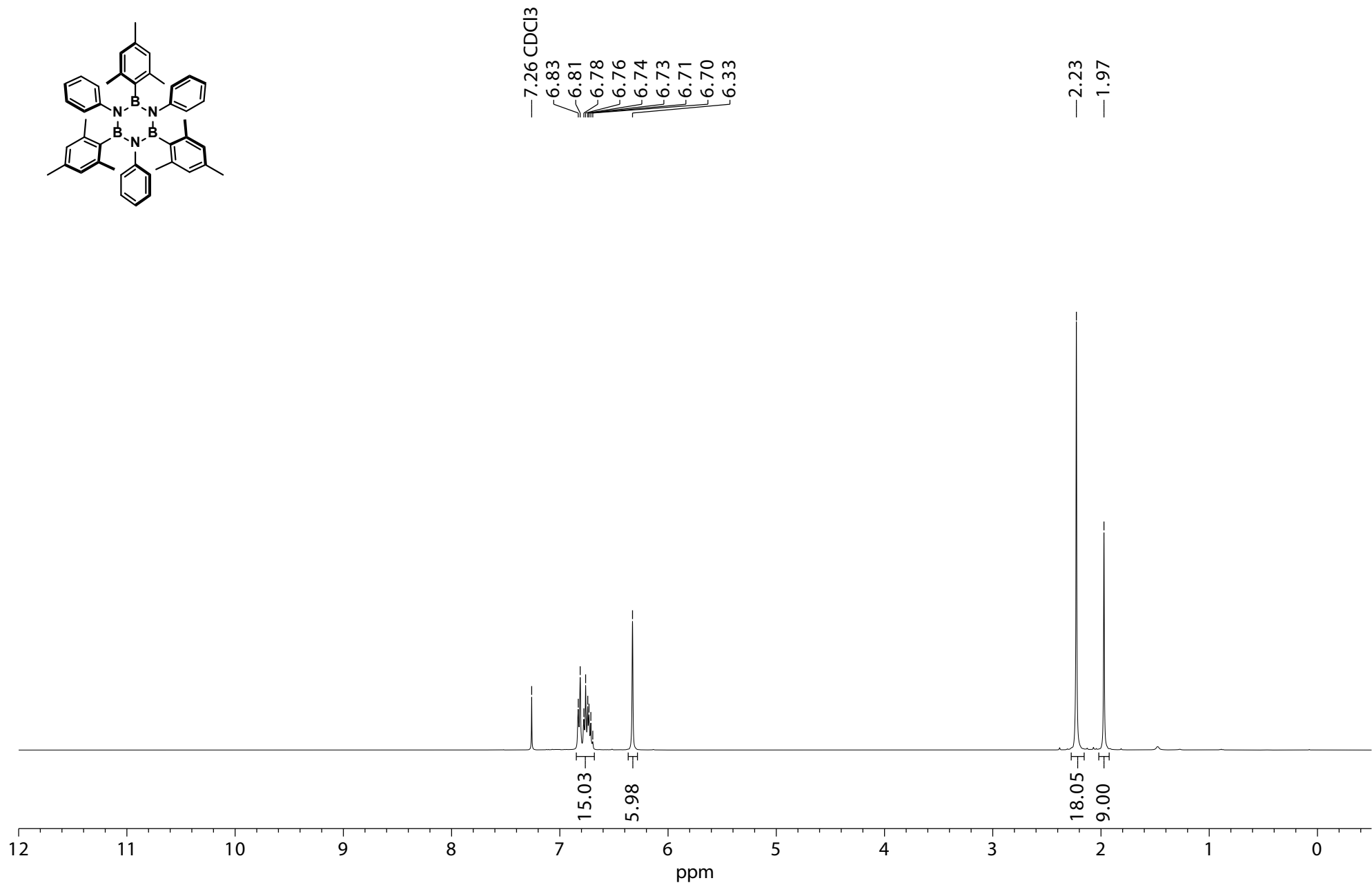
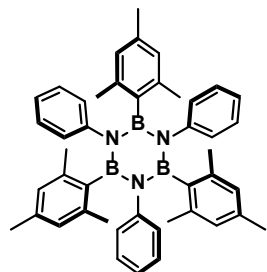
B,B',B''-Tris(2,4,6-trimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(5)



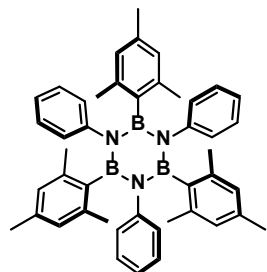
—37.2



B,B',B''-Tris(2,4,6-trimethylphenyl)-N,N',N''-tris(phenyl)borazine-(6)



B,B',B''-Tris(2,4,6-trimethylphenyl)-N,N',N''-tris(phenyl)borazine-(6)



— 146.43

~ 137.37

~ 136.18

~ 127.13

~ 126.81

~ 126.29

~ 124.28

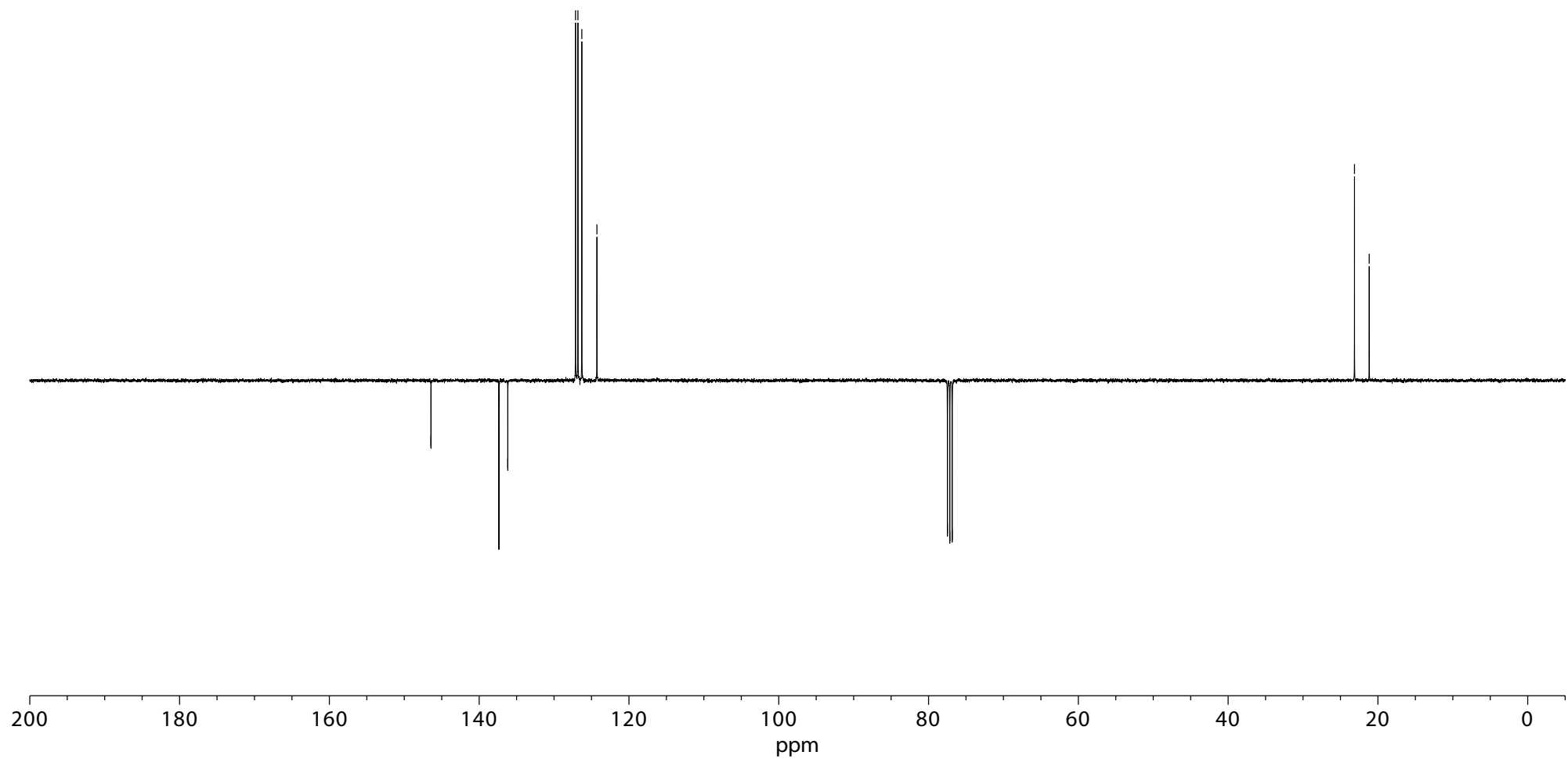
~ 77.48 CDCl<sub>3</sub>

~ 77.16 CDCl<sub>3</sub>

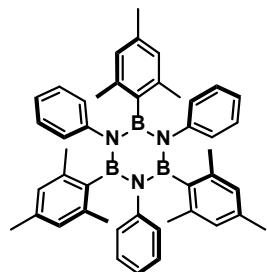
~ 76.84 CDCl<sub>3</sub>

~ 23.13

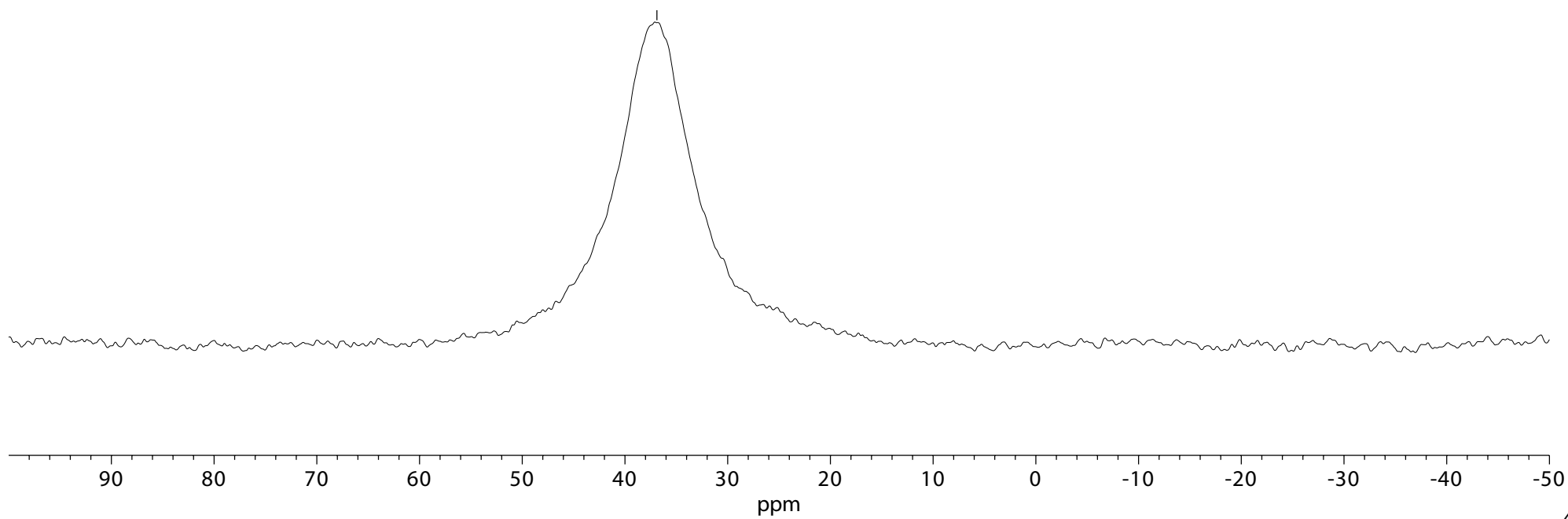
~ 21.16



B,B',B''-Tris(2,4,6-trimethylphenyl)-N,N',N''-tris(phenyl)borazine-(6)

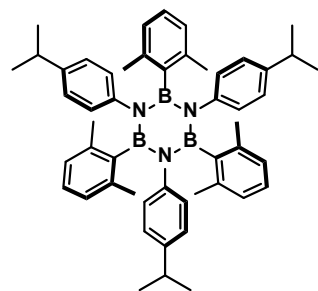


—36.9





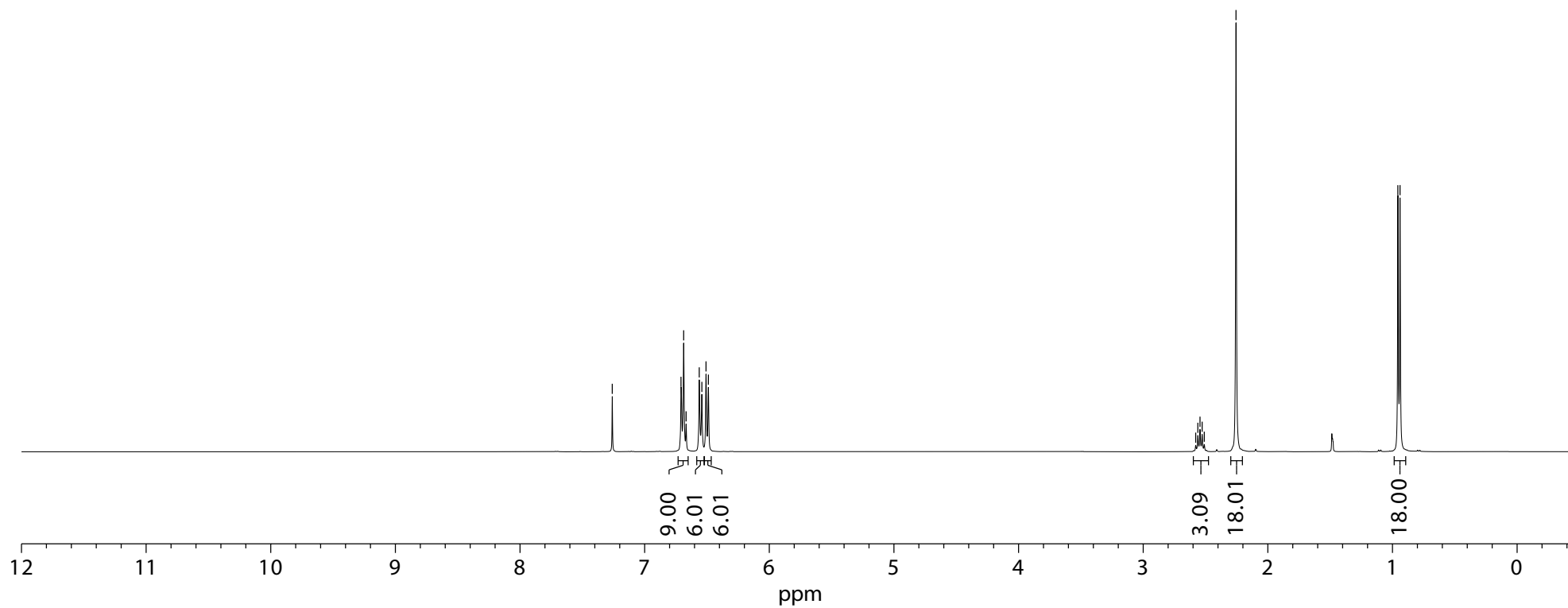
B,B',B''-Tris(2,6-dimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(7)



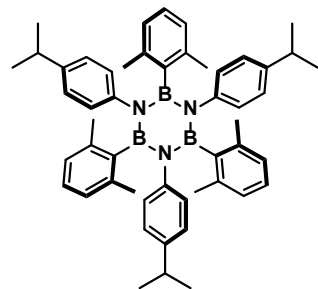
7.26 CDCl<sub>3</sub>  
6.71  
6.69  
6.67  
6.56  
6.54  
6.51  
6.49

2.58  
2.56  
2.54  
2.53  
2.51  
2.26

0.96  
0.94



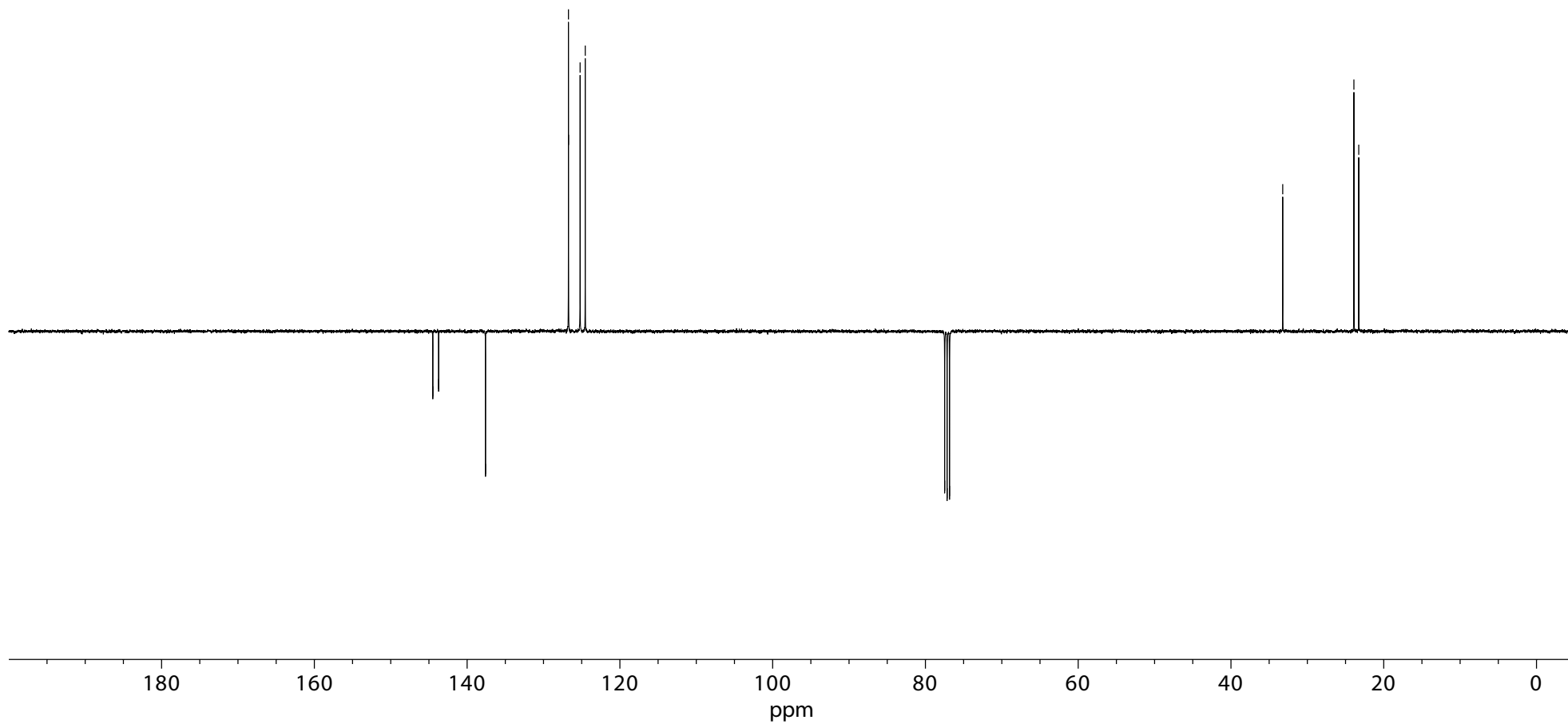
B,B',B''-Tris(2,6-dimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(7)



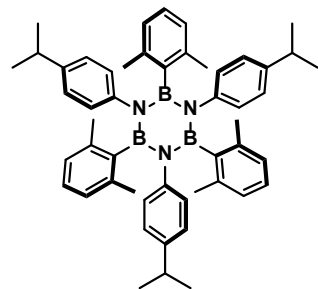
144.5  
143.7  
137.6  
126.7  
126.7  
125.2  
124.5

77.5 CDCl3  
77.2 CDCl3  
76.8 CDCl3

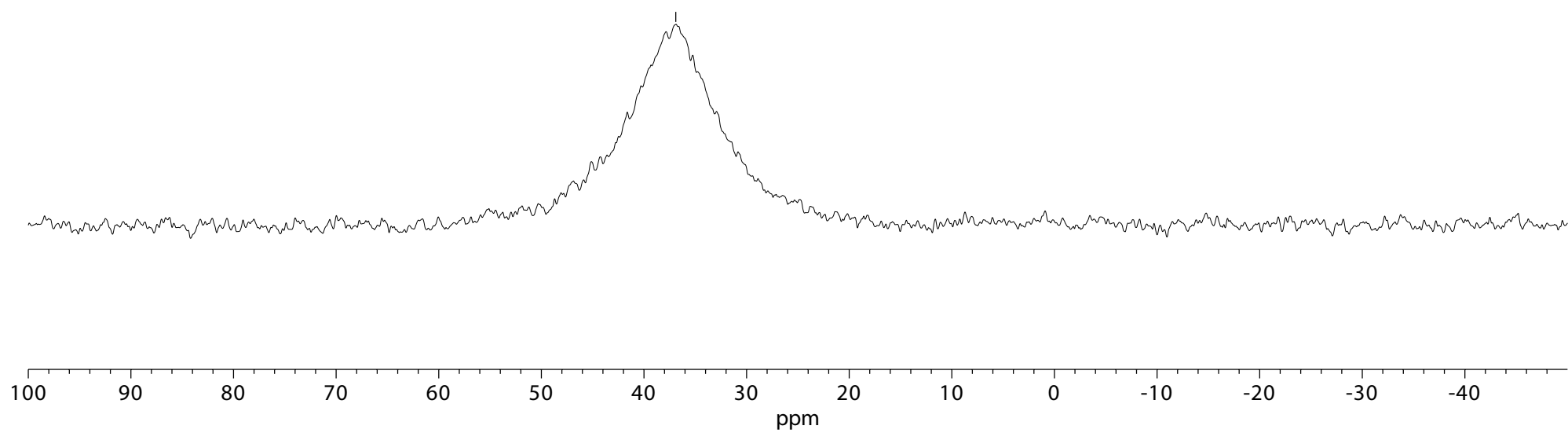
33.2  
23.9  
23.3



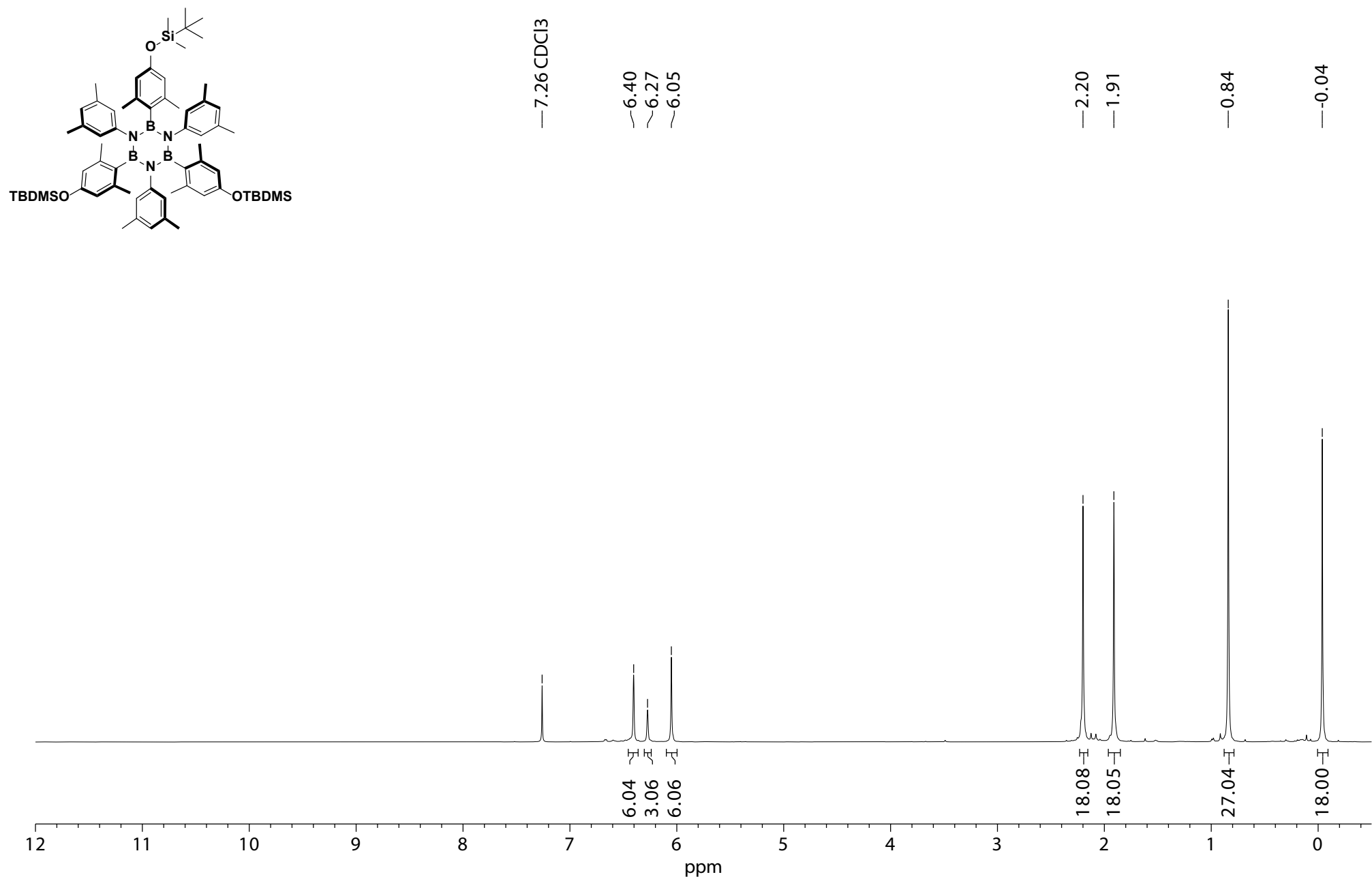
B,B',B''-Tris(2,6-dimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(7)



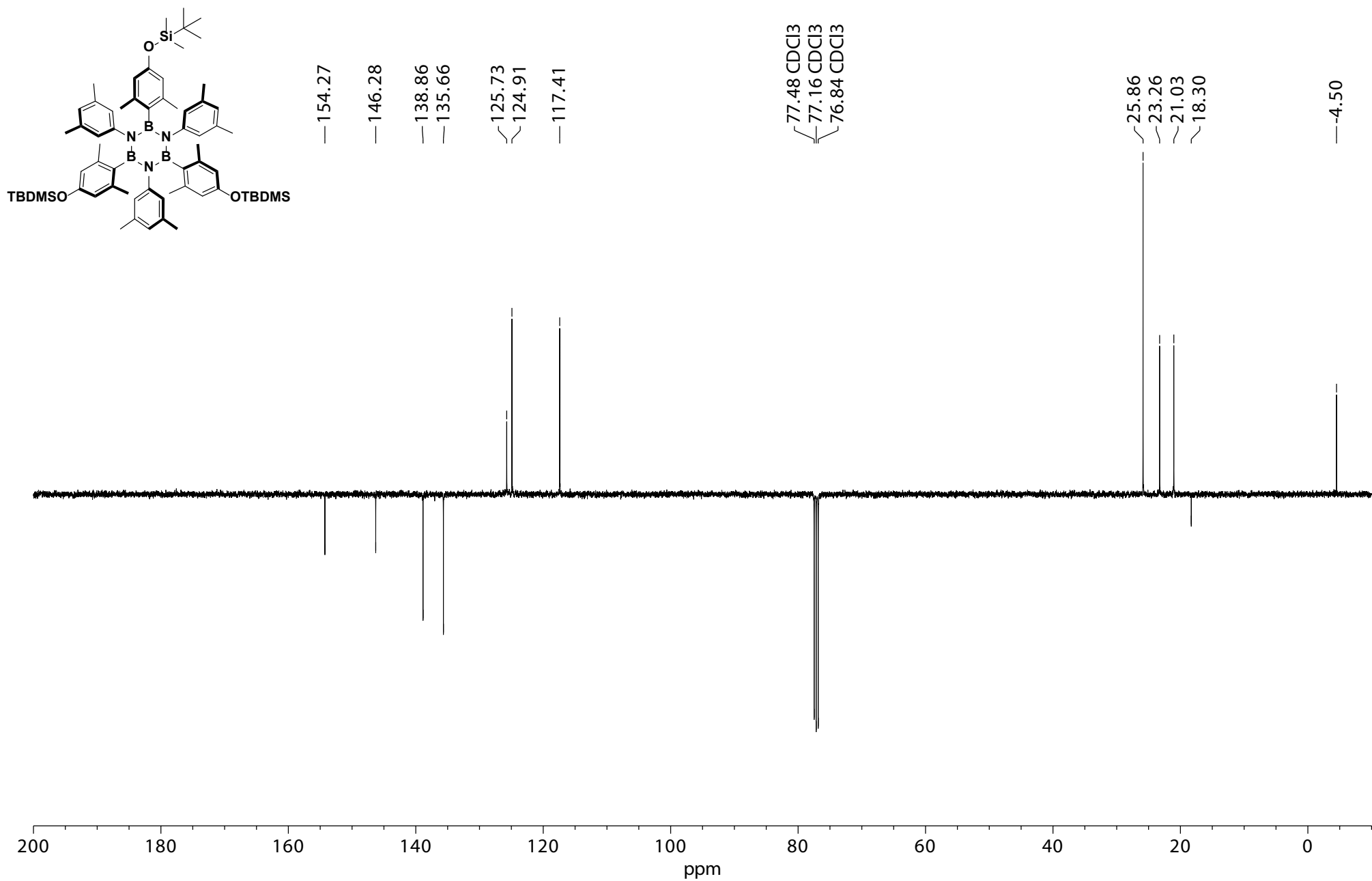
—36.9



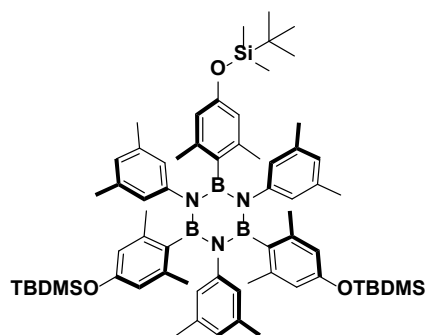
B,B',B''-Tris(4-((tert-butyl)dimethylsilyloxy)-2,6-dimethylphenyl)-N,N',N''-tris(3,5-dimethylphenyl)borazine-(8)



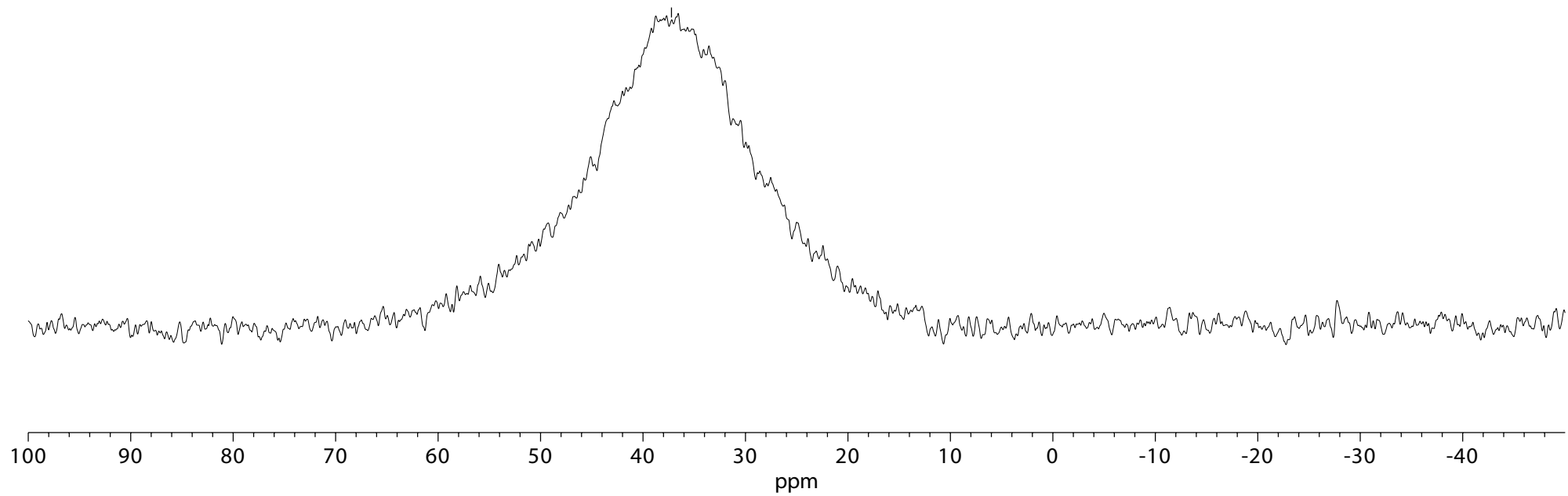
B,B',B''-Tris(4-((tert-butyldimethylsilyl)oxy)-2,6-dimethylphenyl)-N,N',N''-tris(3,5-dimethylphenyl)borazine-(8)



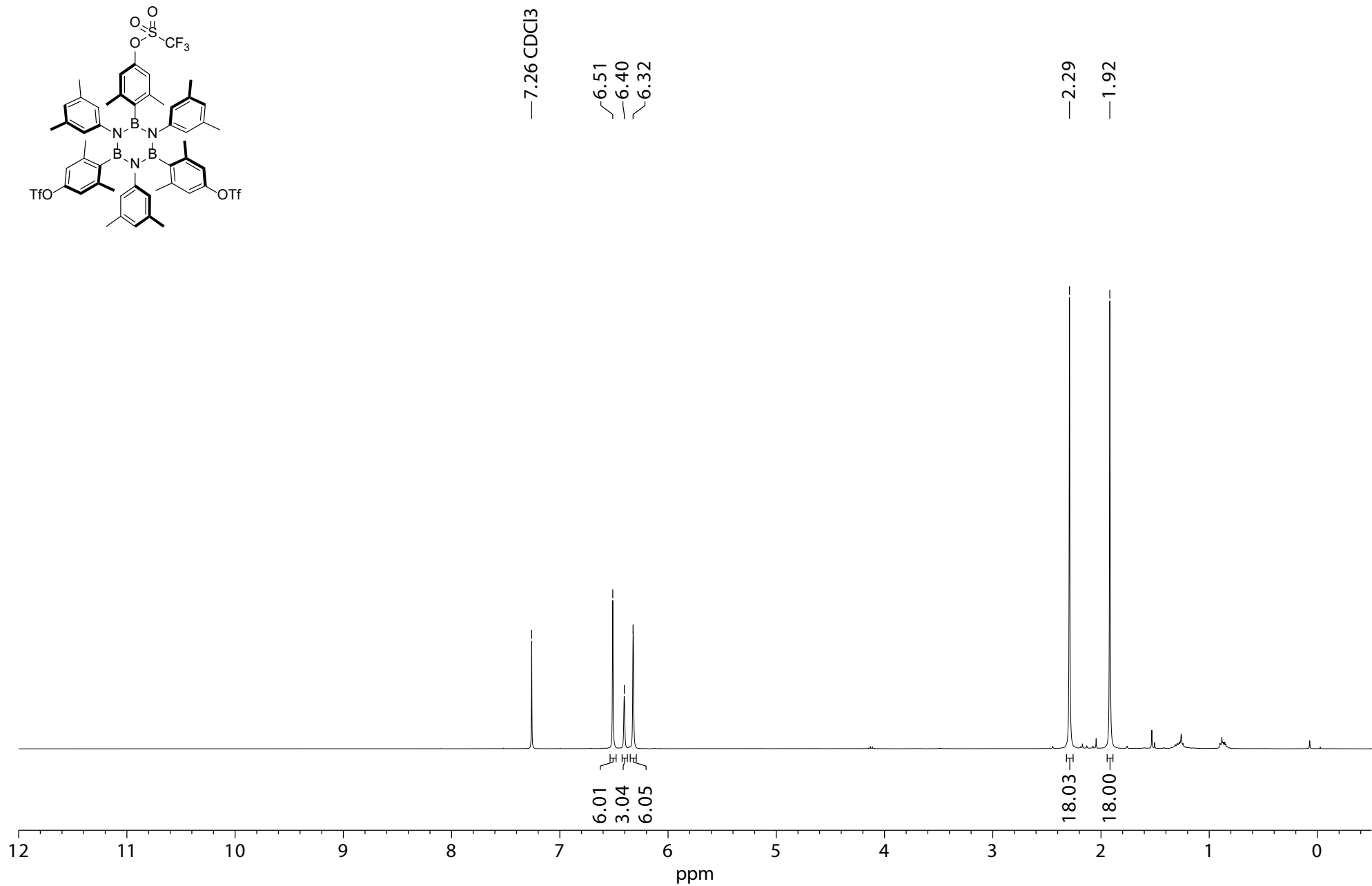
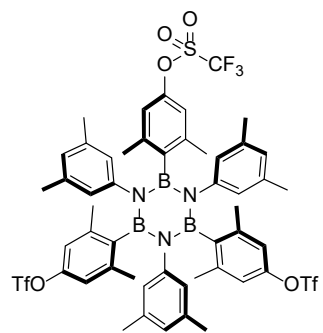
B,B',B''-Tris(4-((tert-butyl)dimethylsilyloxy)-2,6-dimethylphenyl)-N,N',N''-tris(3,5-dimethylphenyl)borazine-(8)



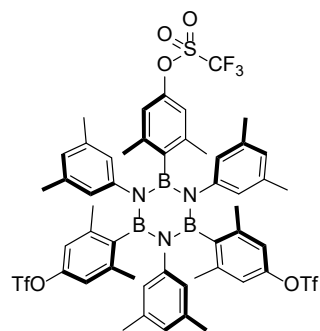
—37.2



B,B',B''-Tris(2,6-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-N,N',N''-tris(3,5-dimethylphenyl)borazine-(9)



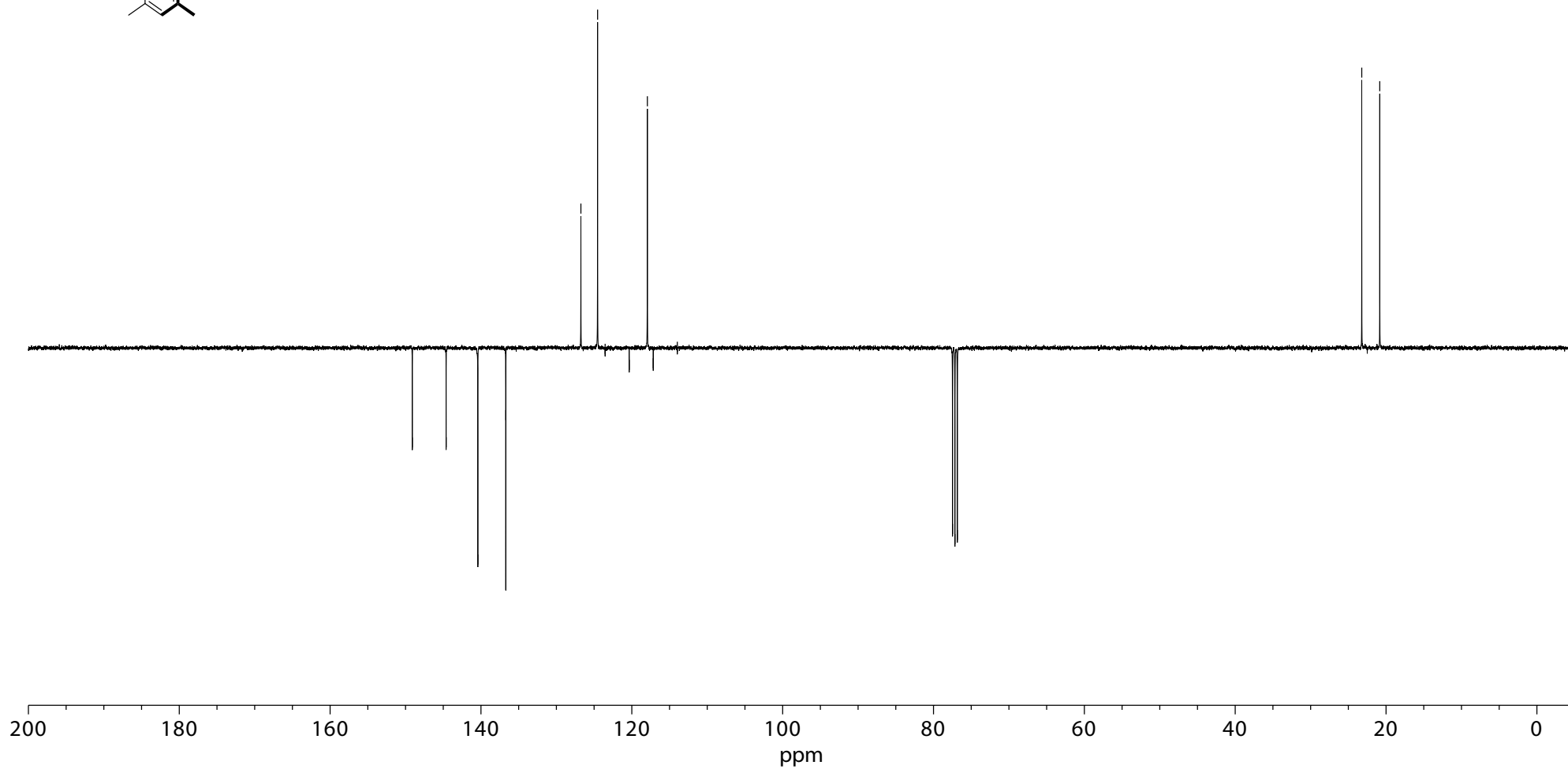
B,B',B''-Tris(2,6-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-N,N',N''-tris(3,5-dimethylphenyl)borazine-(9)



149.10  
144.62  
140.41  
136.70  
126.75  
124.54  
123.54  
120.35  
117.94  
117.16  
113.97

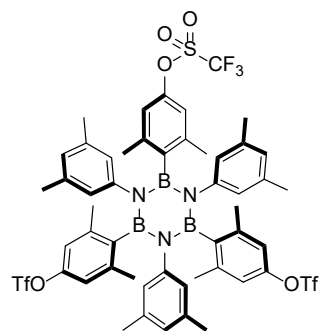
77.48 CDCl3  
77.16 CDCl3  
76.84 CDCl3

23.22  
20.84

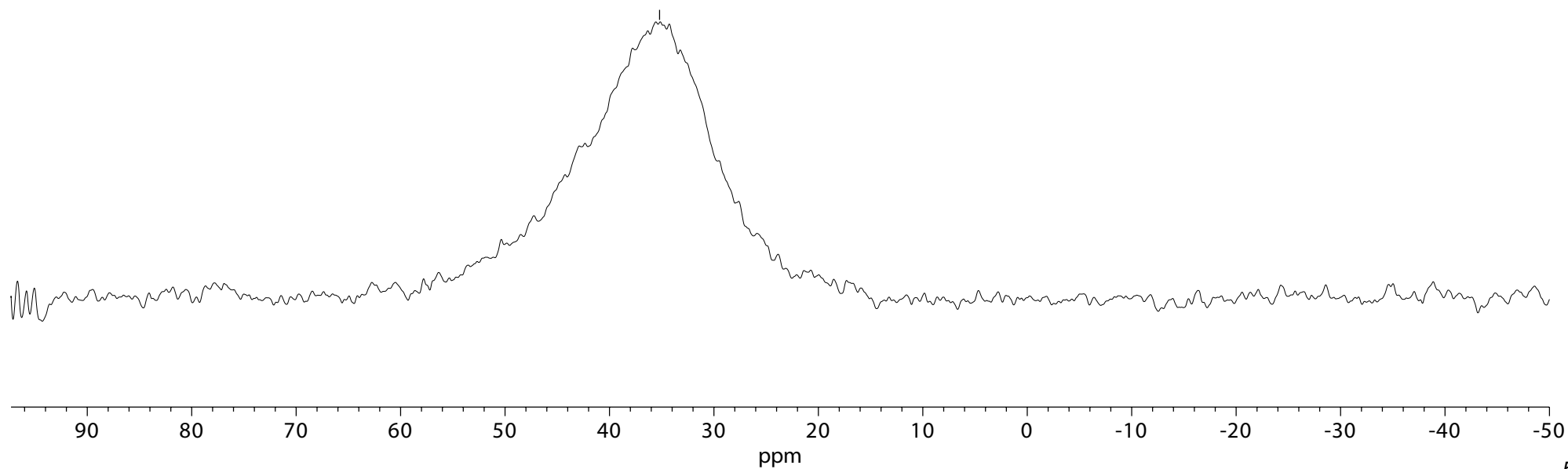




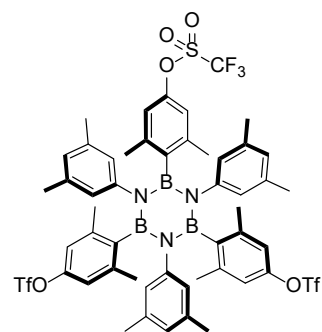
B,B',B''-Tris(2,6-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-N,N',N''-tris(3,5-dimethylphenyl)borazine-(9)



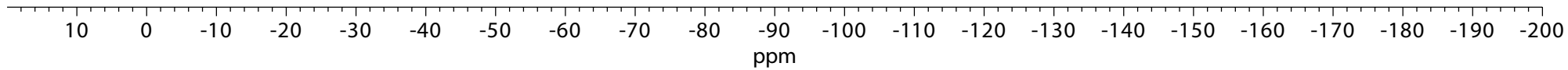
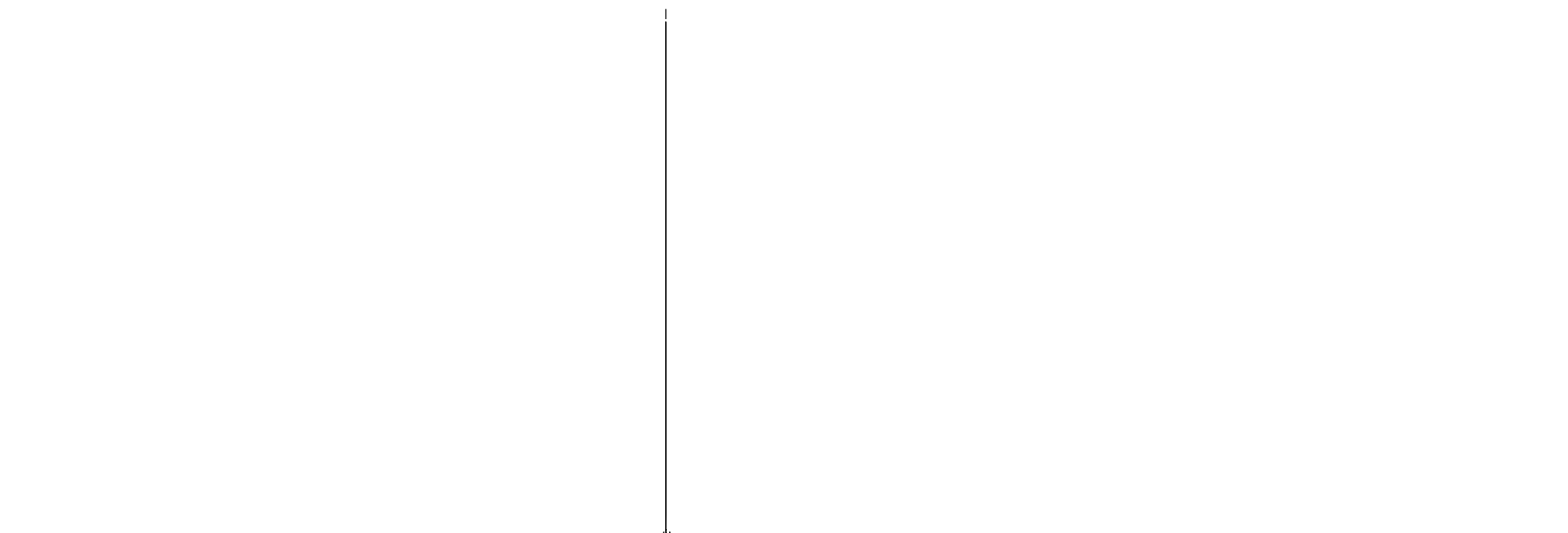
—35.2



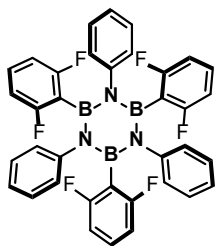
B,B',B''-Tris(2,6-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-N,N',N''-tris(3,5-dimethylphenyl)borazine-(9)



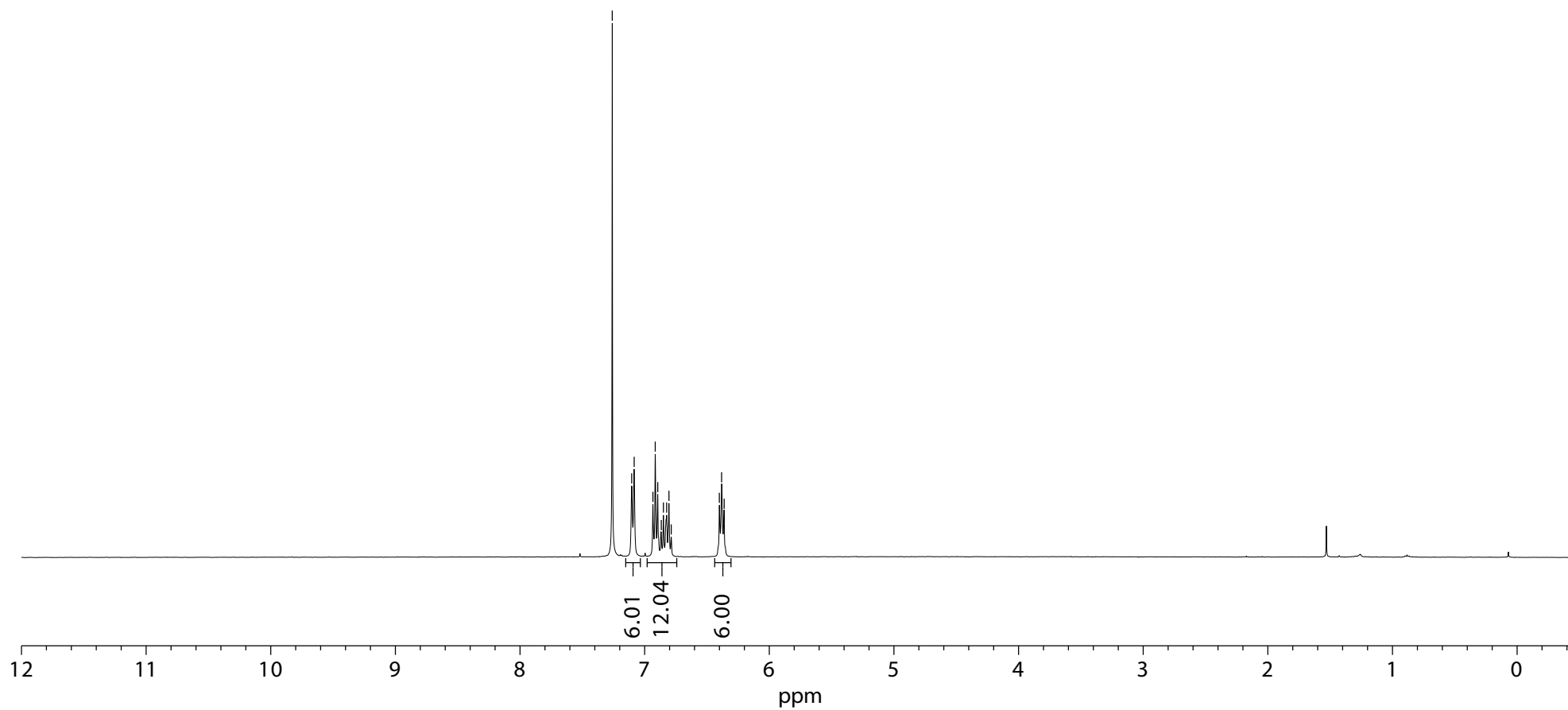
---73.01



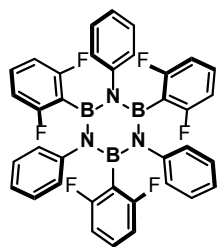
B,B',B''-Tris(2,6-difluorophenyl)-N,N',N''-tris(phenyl)borazine (10)



7.26 CDCl<sub>3</sub>  
7.10  
7.08  
6.93  
6.92  
6.89  
6.87  
6.85  
6.82  
6.81  
6.79  
6.40  
6.38  
6.36



B,B',B''-Tris(2,6-difluorophenyl)-N,N',N''-tris(phenyl)borazine (10)



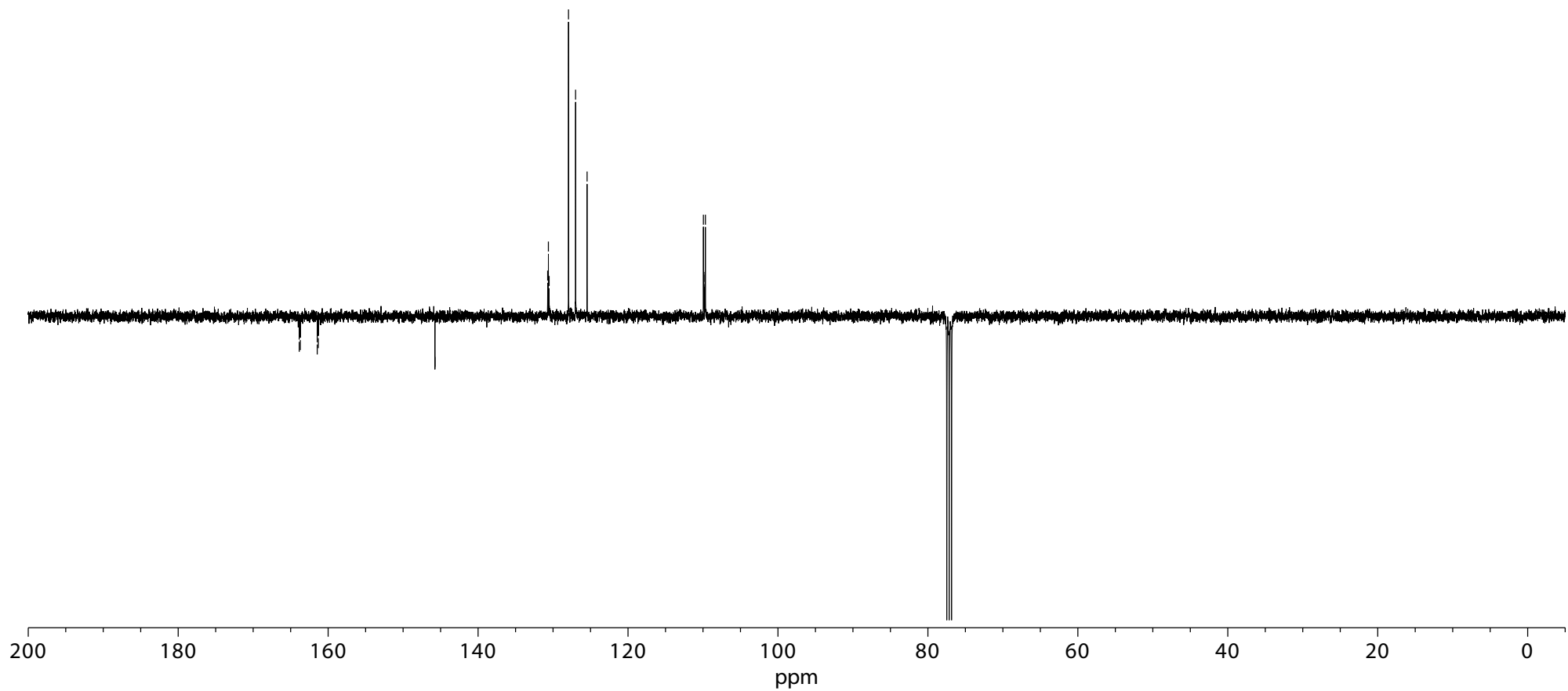
163.86  
163.71  
161.45  
161.31

145.75

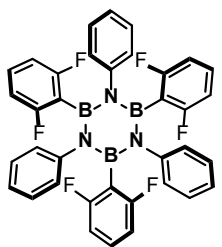
130.72  
130.62  
130.52  
127.94  
126.99  
125.46

109.95  
109.88  
109.74  
109.68

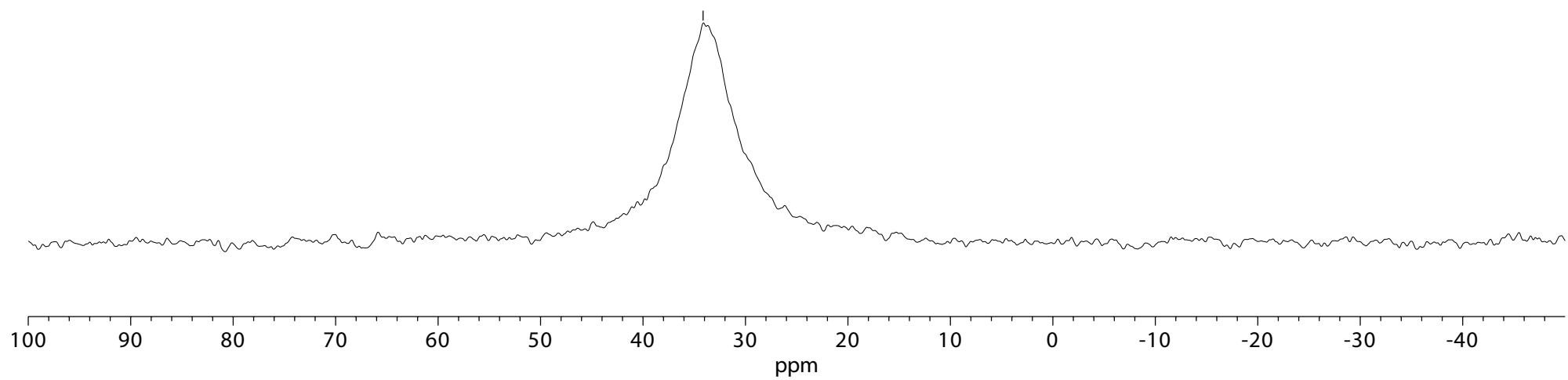
77.48 CDCl3  
77.16 CDCl3  
76.84 CDCl3



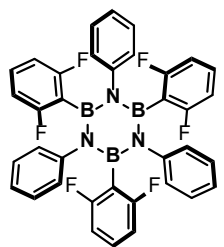
B,B',B''-Tris(2,6-difluorophenyl)-N,N',N''-tris(phenyl)borazine (10)



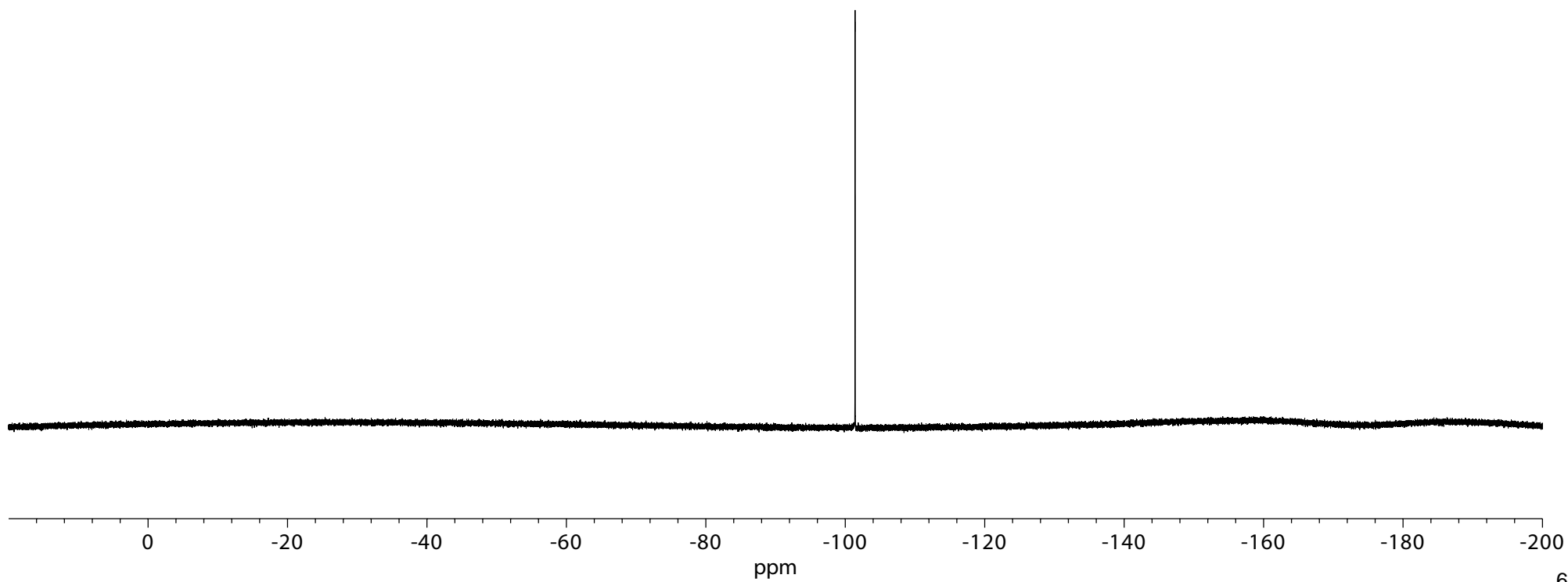
—34.1



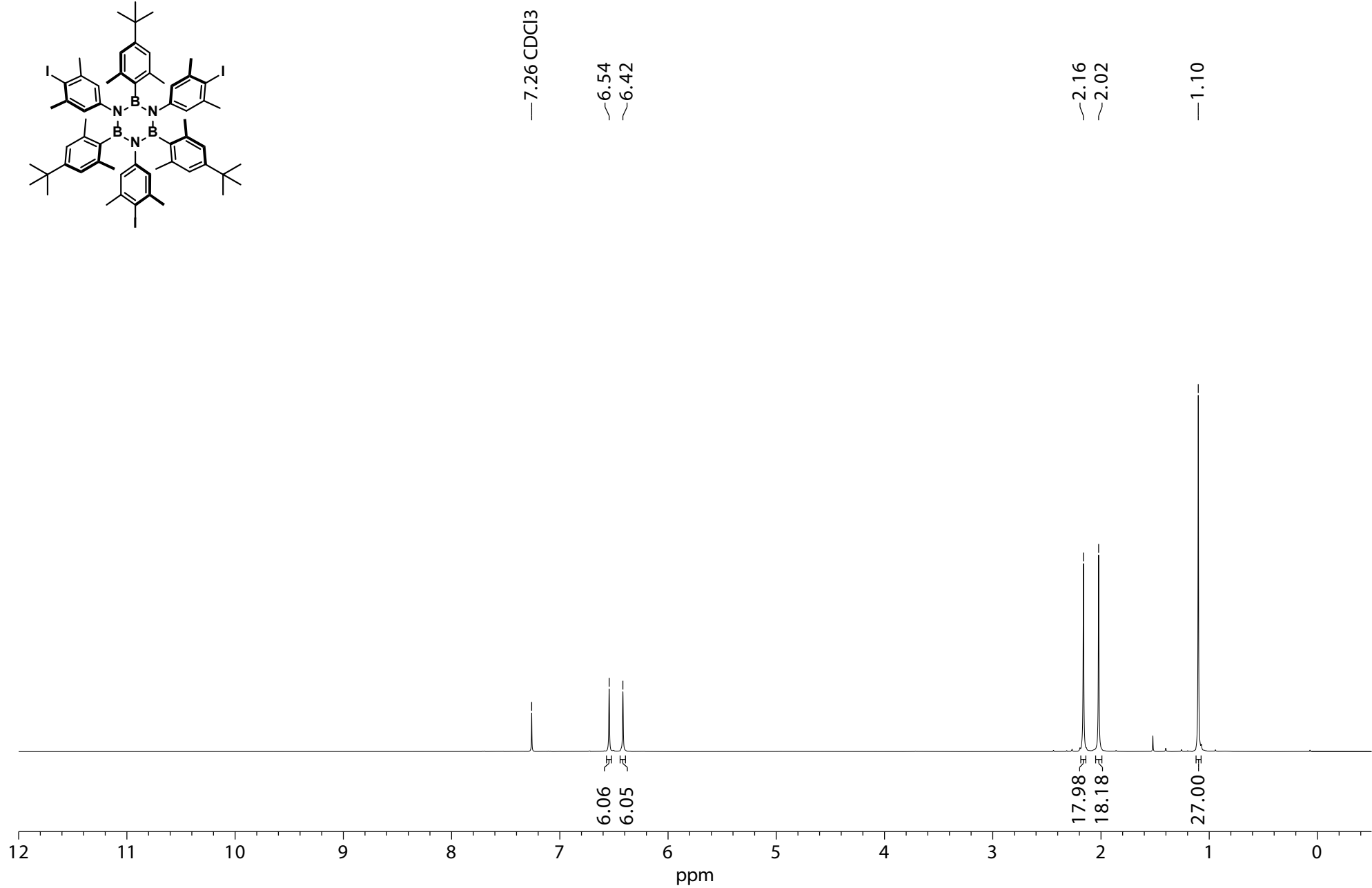
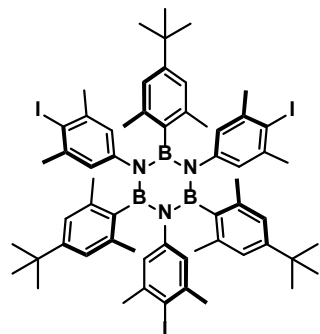
B,B',B''-Tris(2,6-difluorophenyl)-N,N',N''-tris(phenyl)borazine (10)



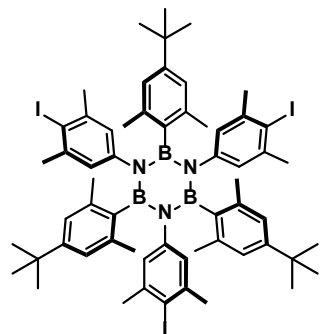
---101.4



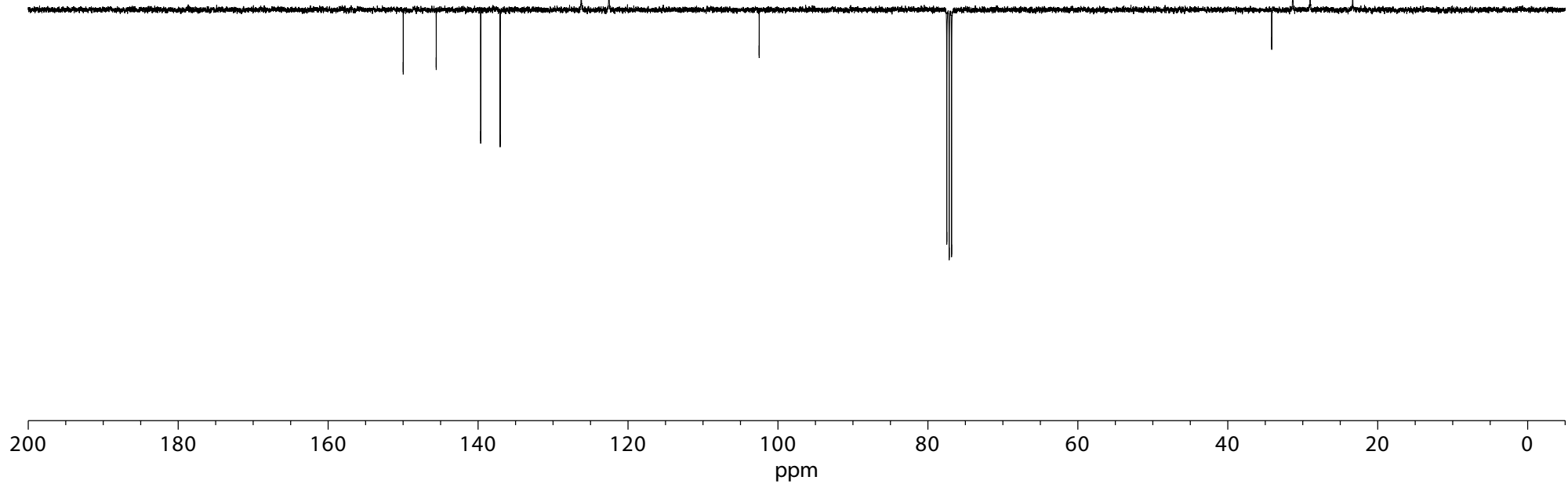
B,B',B''-Tris(4-(tertbutyl)-2,6-dimethylphenyl)-N,N',N''-tris(4-iodo-3,5-dimethylphenyl)borazine-(11)



B,B',B''-Tris(4-(tertbutyl)-2,6-dimethylphenyl)-N,N',N''-tris(4-iodo-3,5-dimethylphenyl)borazine-(11)

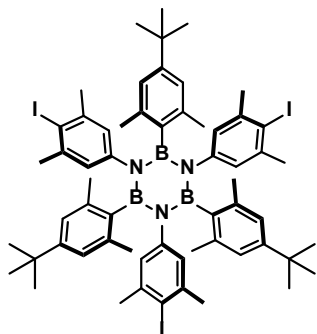


149.98  
145.58  
139.65  
137.06  
126.24  
122.54  
102.50  
77.48 CDCl3  
77.16 CDCl3  
76.84 CDCl3  
34.14  
31.34  
29.02  
23.34

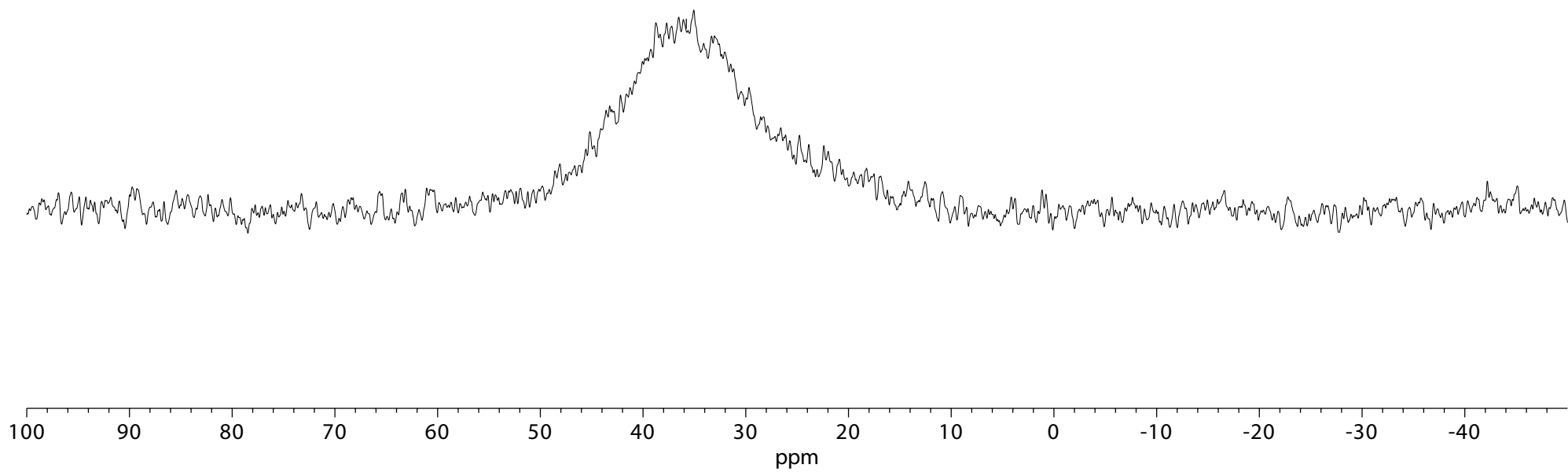




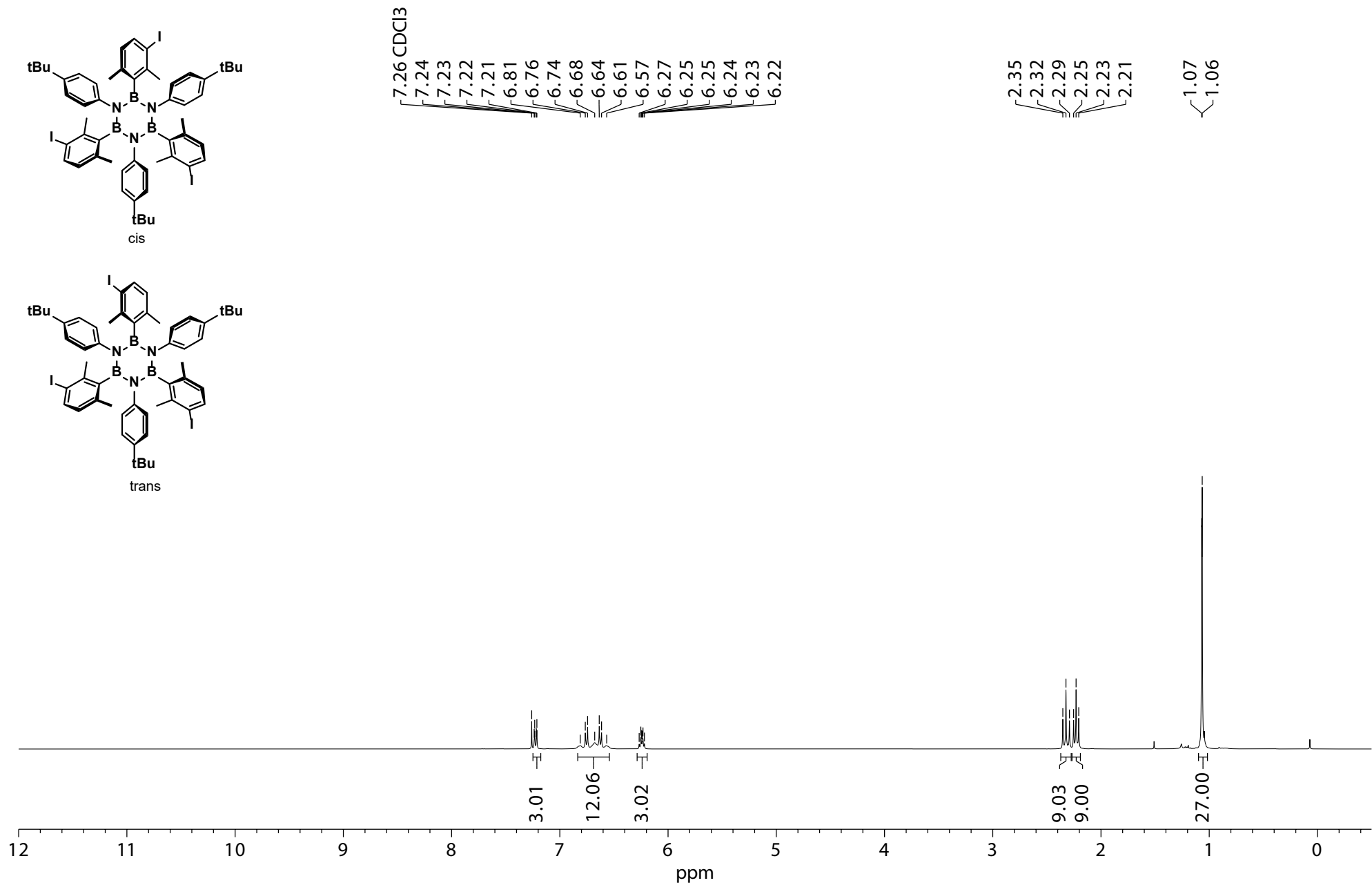
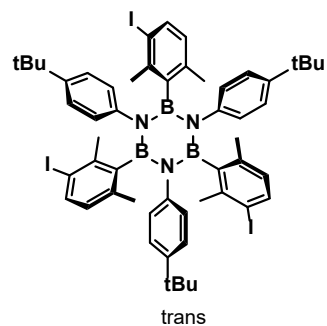
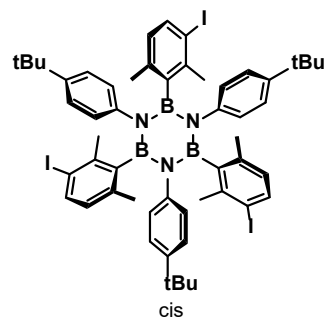
B,B',B''-Tris(4-(tertbutyl)-2,6-dimethylphenyl)-N,N',N''-tris(4-iodo-3,5-dimethylphenyl)borazine-(11)



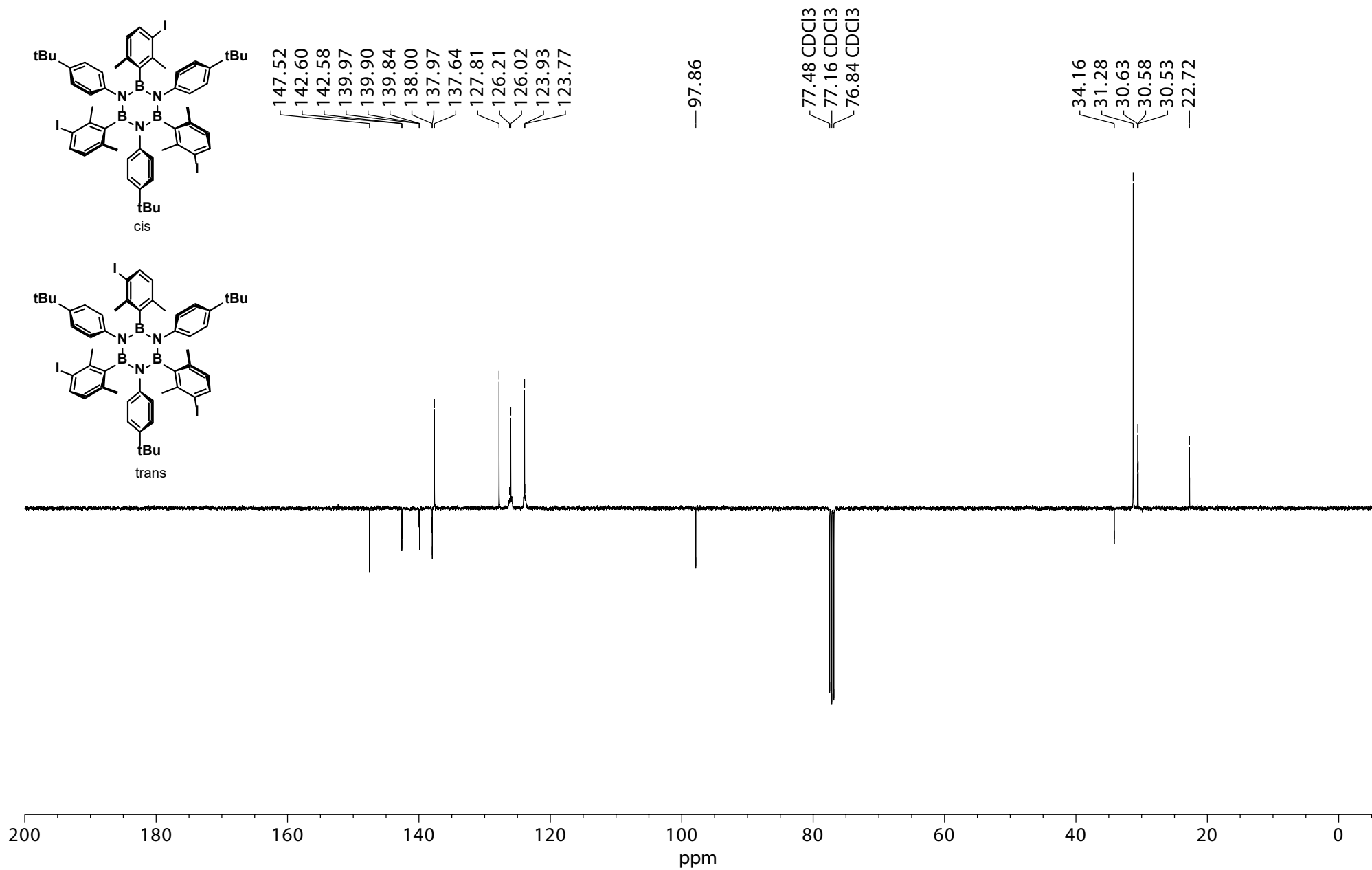
— 36.8



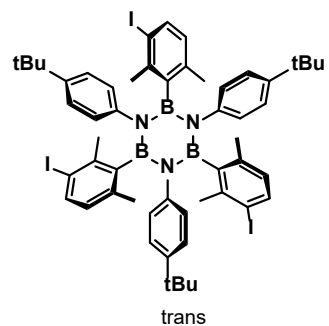
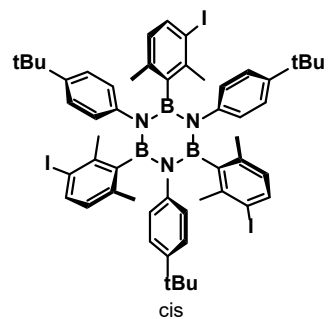
B,B',B''-Tris(3-iodo-2,6-dimethylphenyl)-N,N',N''-tris(4-tbutylphenyl)borazine-(12)



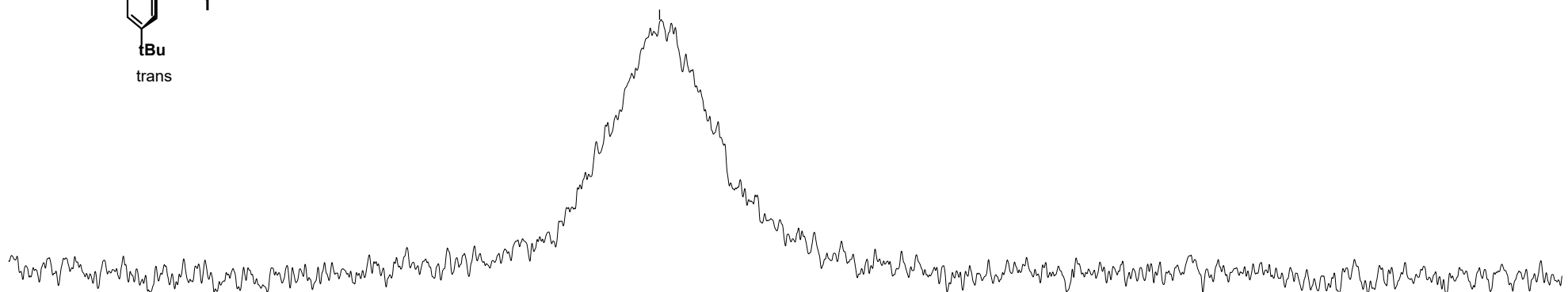
B,B',B''-Tris(3-iodo-2,6-dimethylphenyl)-N,N',N''-tris(4-*t*-butylphenyl)borazine-(12)



B,B',B''-Tris(3-iodo-2,6-dimethylphenyl)-N,N',N''-tris(4-tbutylphenyl)borazine-(12)

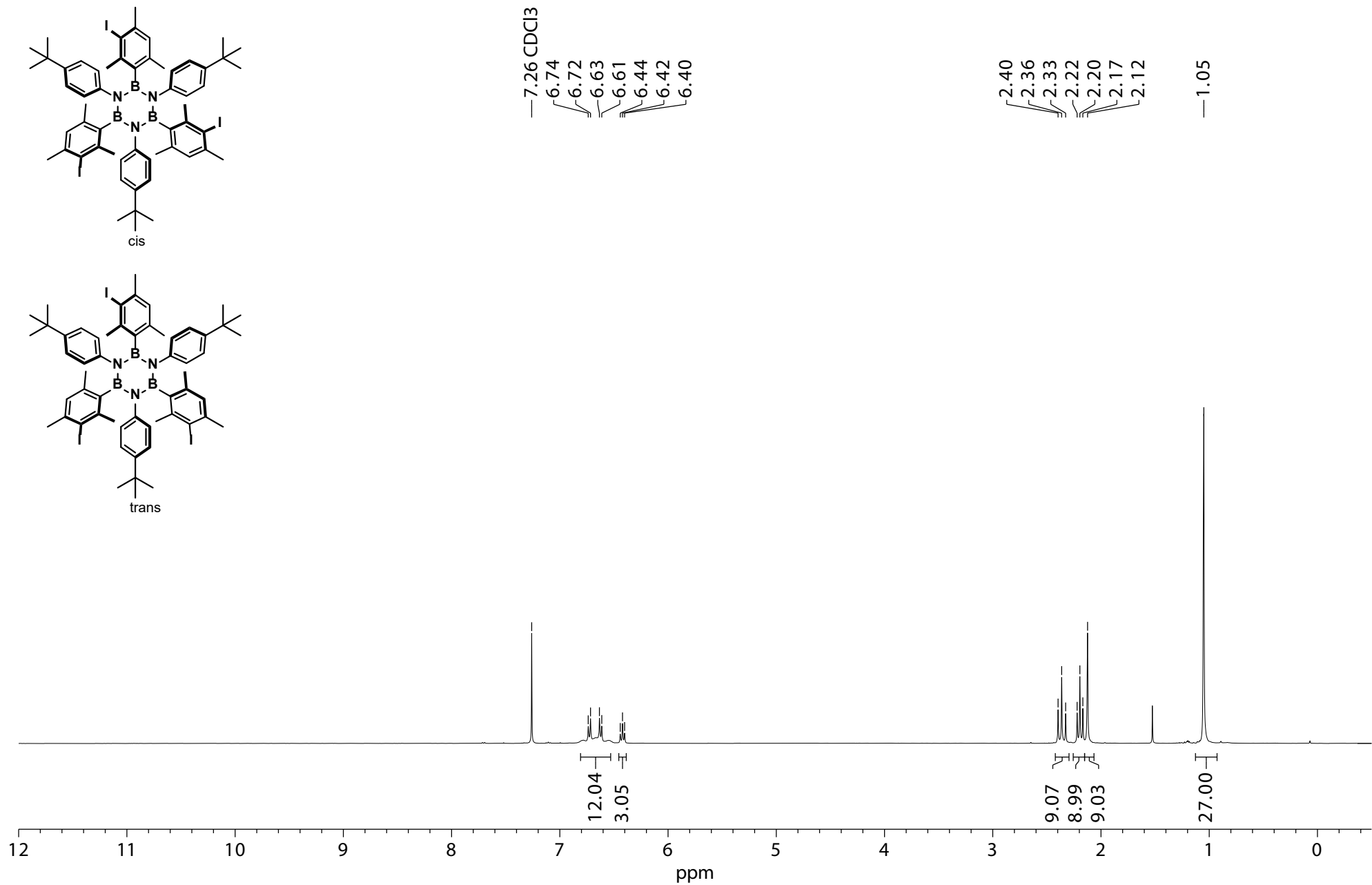
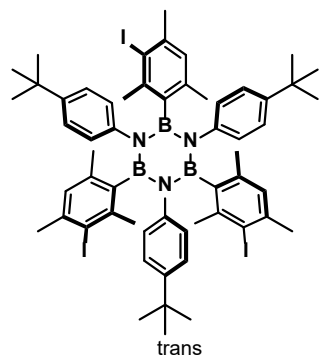
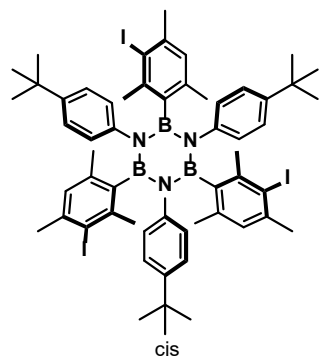


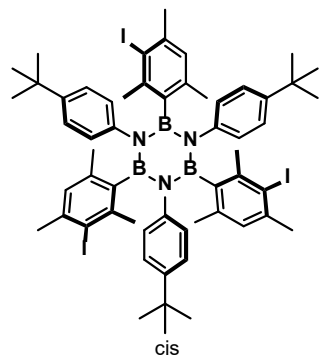
—37.1



90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50  
ppm

B,B',B''-Tris(3-iodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(13)





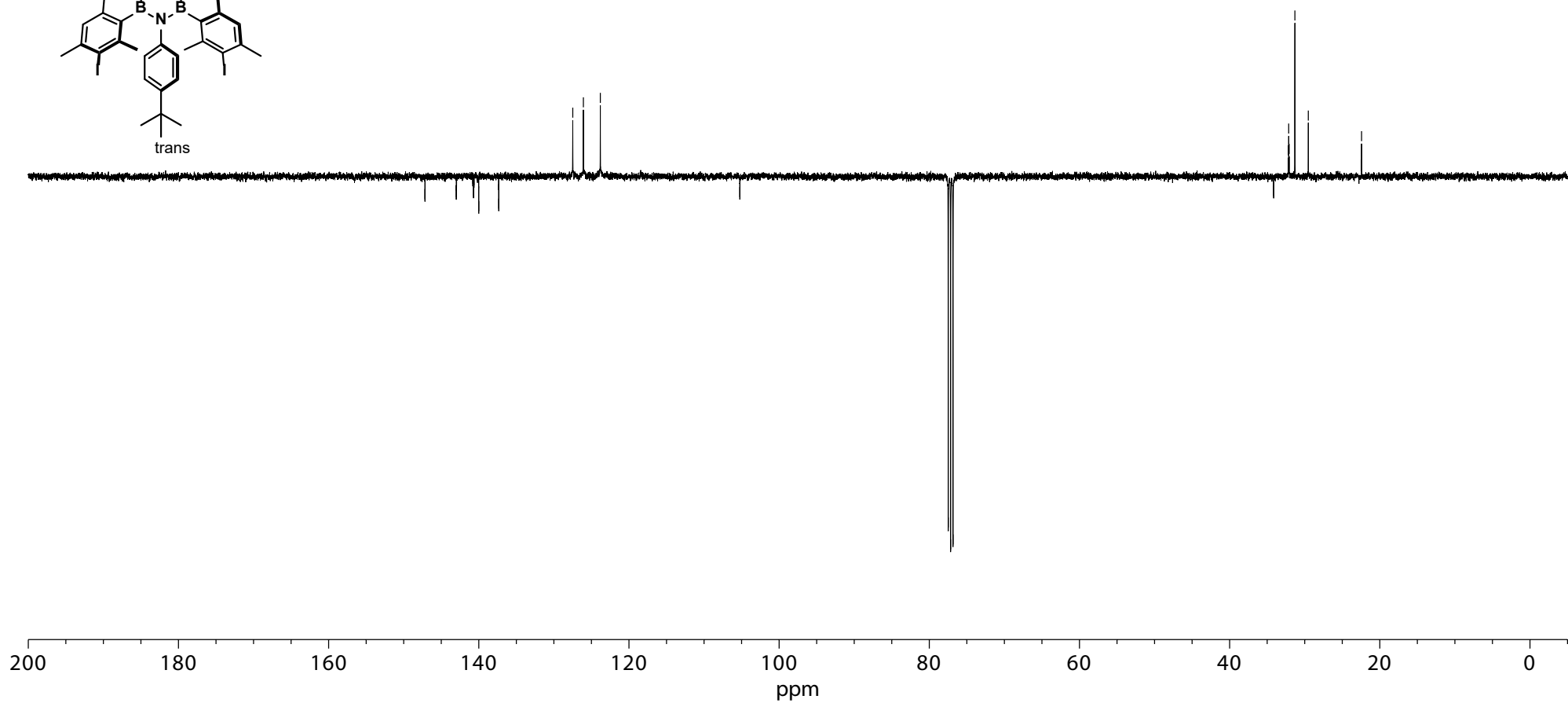
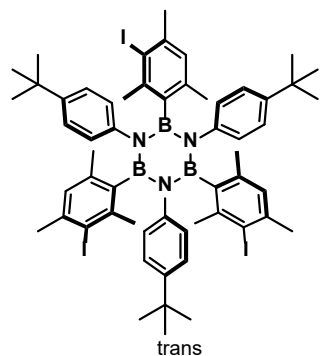
B, B', B''-Tris(3-iodo-2,4,6-trimethylphenyl)-N, N', N''-tris(4-tertbutylphenyl)borazine-(13)

147.17  
143.00  
140.80  
140.70  
140.64  
140.01  
137.34  
127.48  
126.07  
123.81

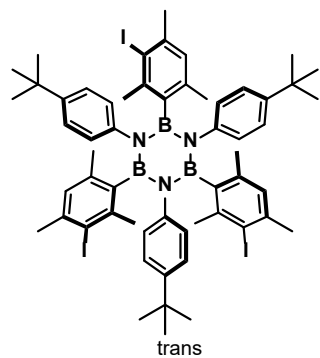
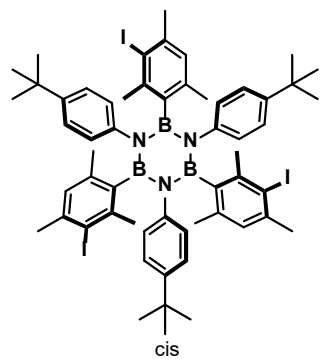
— 105.23

77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>

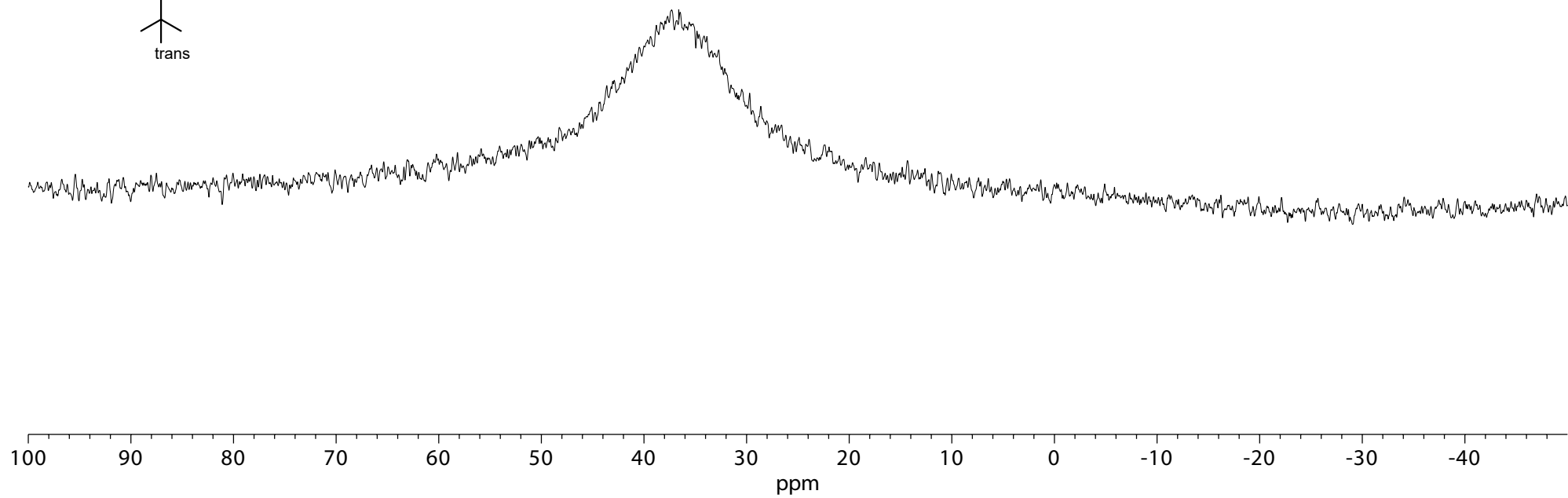
34.14  
32.19  
32.14  
32.07  
31.31  
29.52  
— 22.43



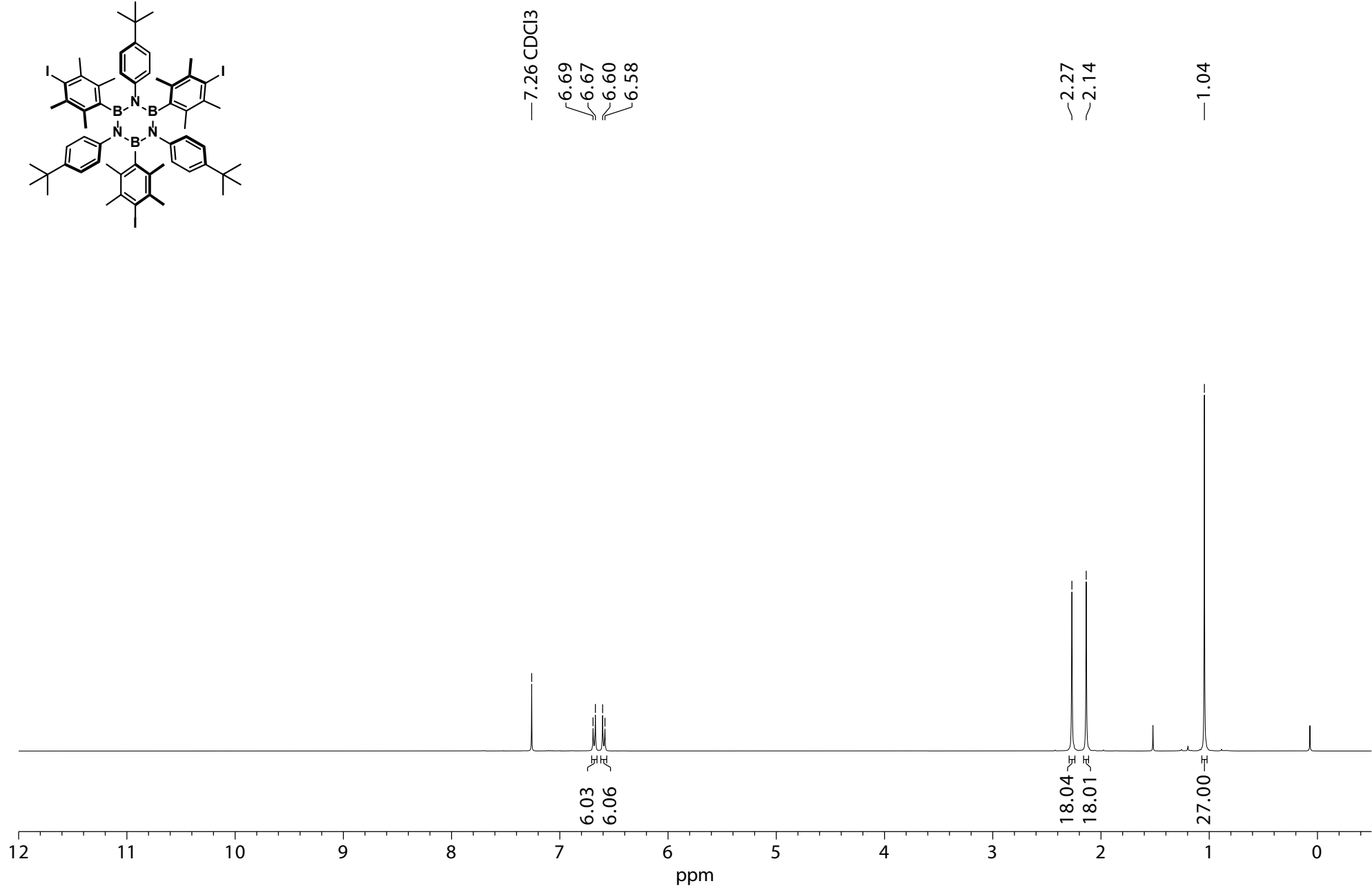
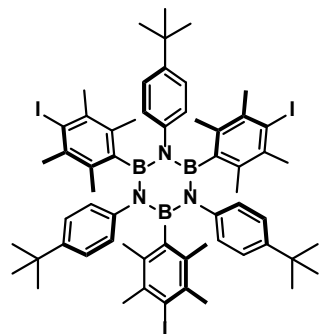
B,B',B''-Tris(3-iodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(13)



— 36.6

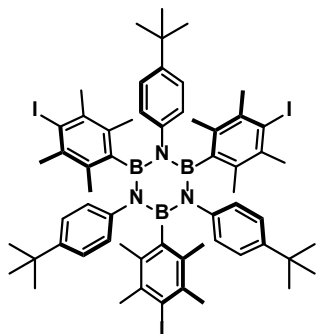


B,B',B''-Tris(4-iodo-2,3,5,6-tetramethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(14)





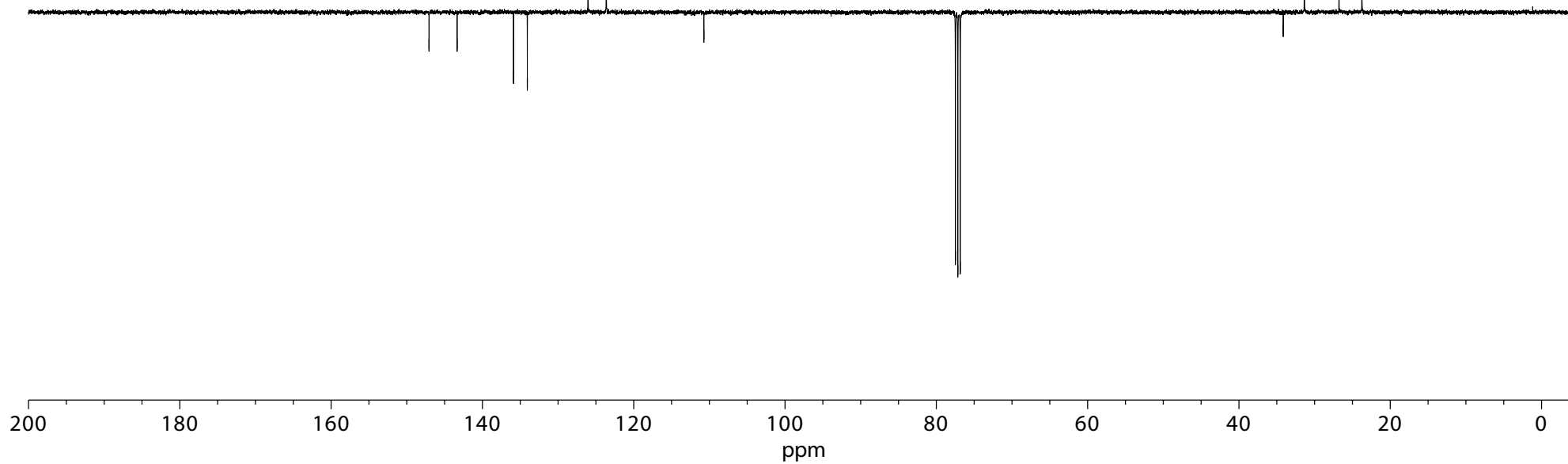
B,B',B''-Tris(4-iodo-2,3,5,6-tetramethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(14)



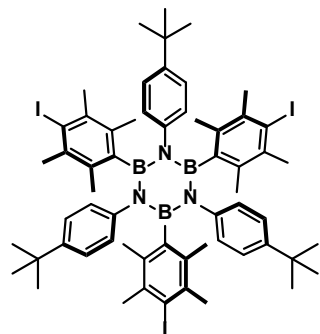
— 147.06  
— 143.34  
~ 135.89  
~ 134.07  
~ 126.04  
~ 123.63  
— 110.73

{ 77.48 CDCl3  
77.16 CDCl3  
76.84 CDCl3

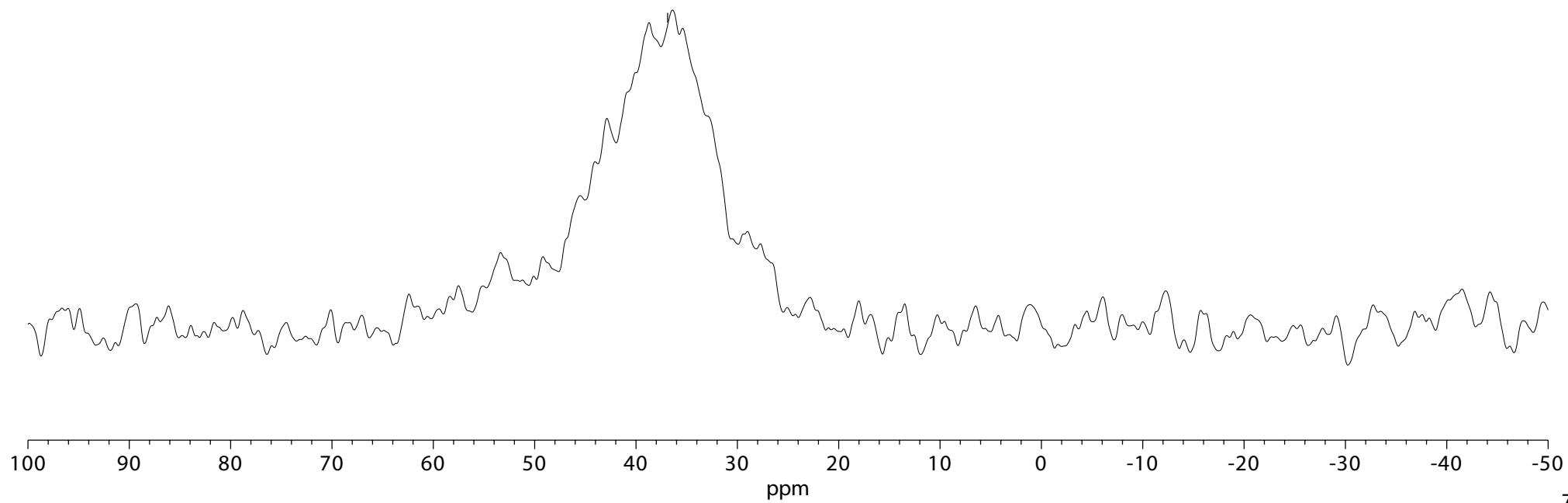
~ 34.15  
~ 31.36  
~ 26.77  
~ 23.75



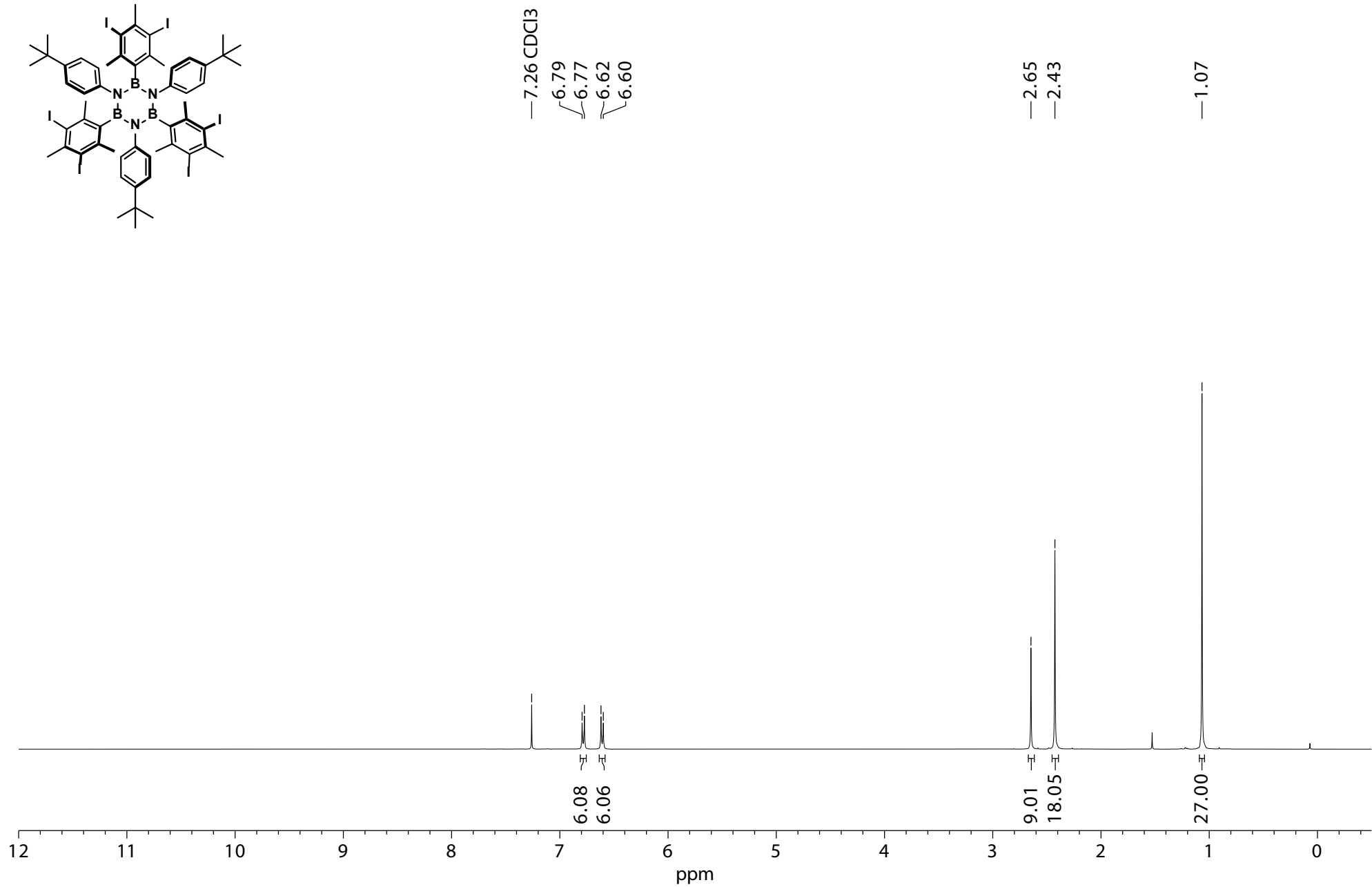
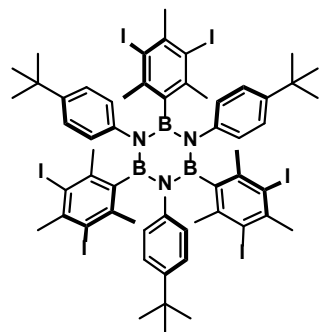
B,B',B''-Tris(4-iodo-2,3,5,6-tetramethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(14)



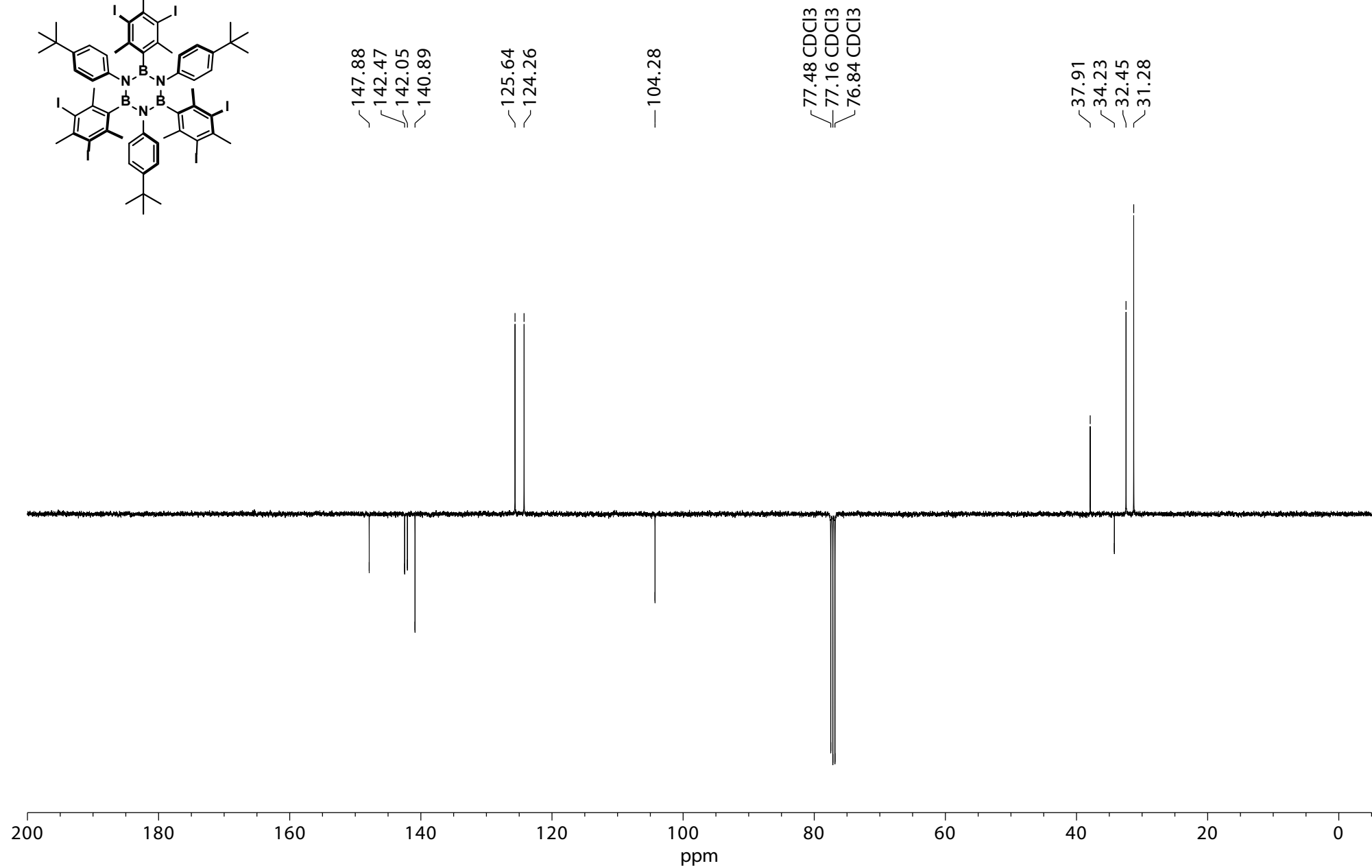
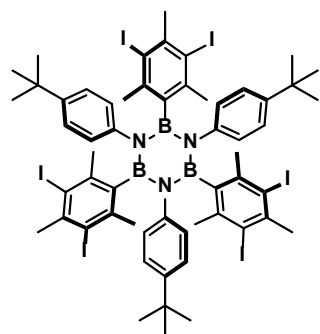
—36.9



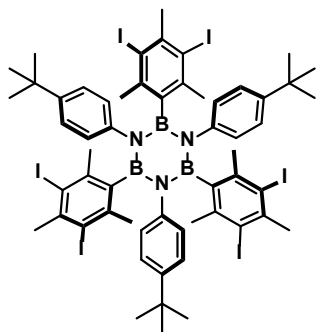
B,B',B''-Tris(3,5-diiodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(15)



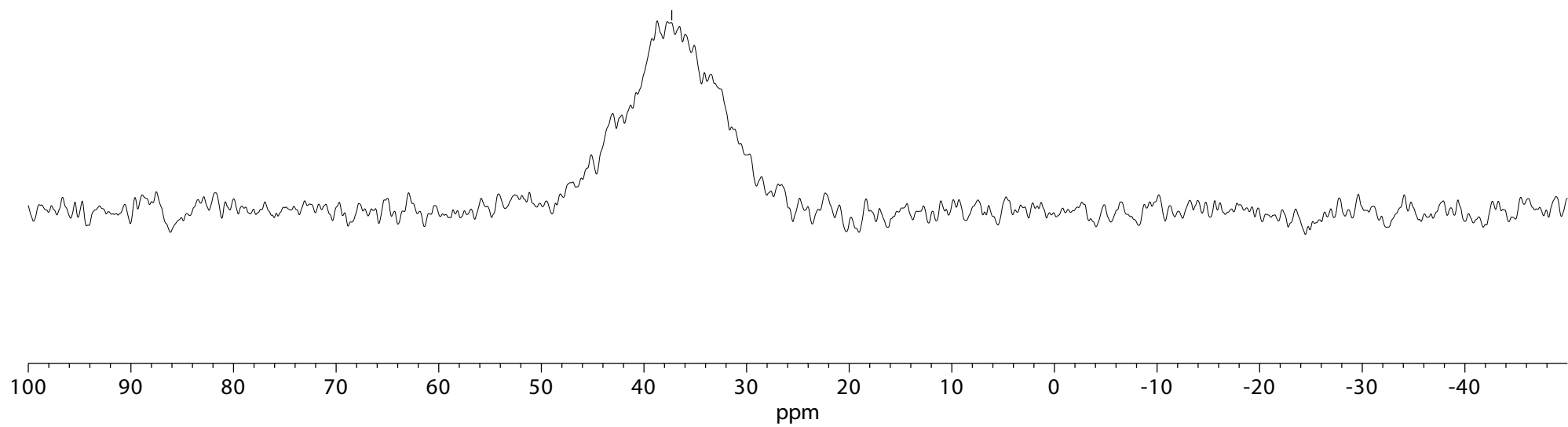
B,B',B''-Tris(3,5-diiodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(15)



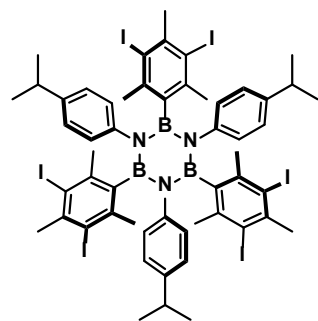
B,B',B''-Tris(3,5-diiodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-tertbutylphenyl)borazine-(15)



—37.3



B,B',B''-Tris(3,5-diiodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(16)

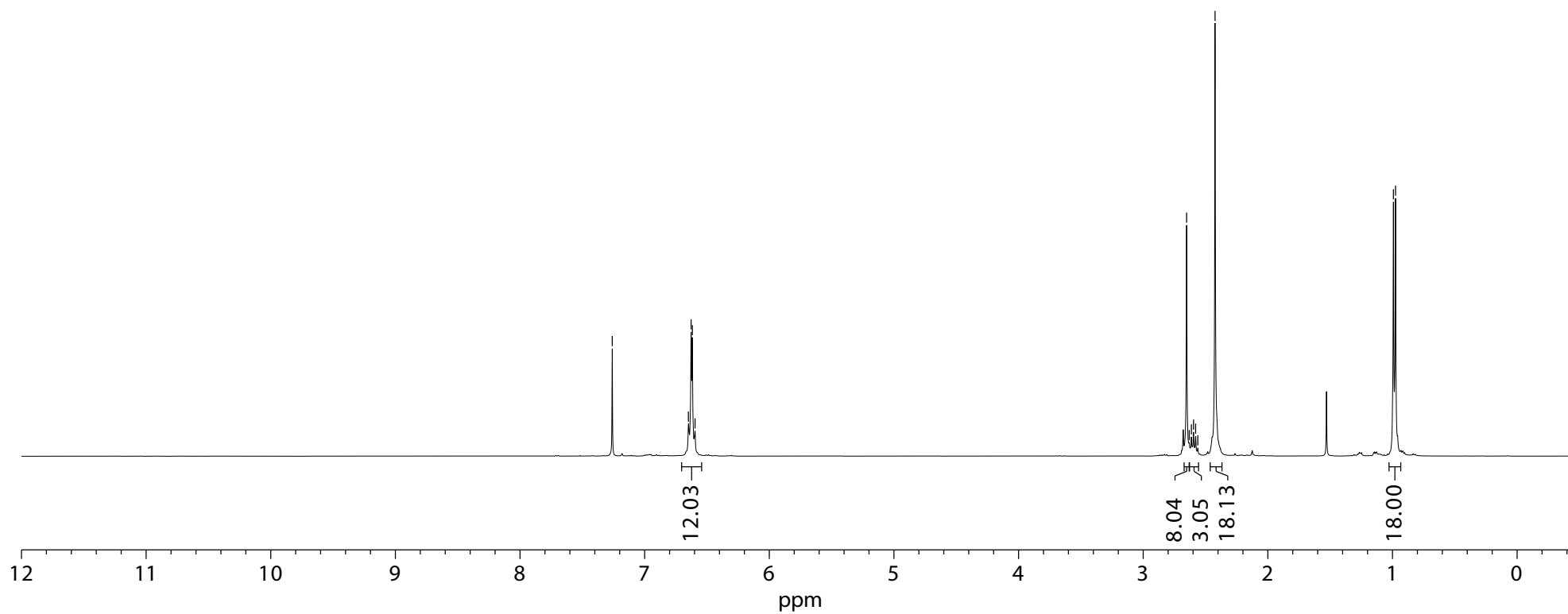


— 7.26 CDCl<sub>3</sub>

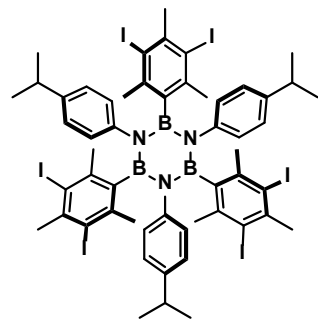
6.65  
6.63  
6.62  
6.60

2.65  
2.63  
2.61  
2.60  
2.58  
2.56  
2.42

0.99  
0.98



B,B',B''-Tris(3,5-diiodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(16)



145.66  
142.81  
142.11  
140.82

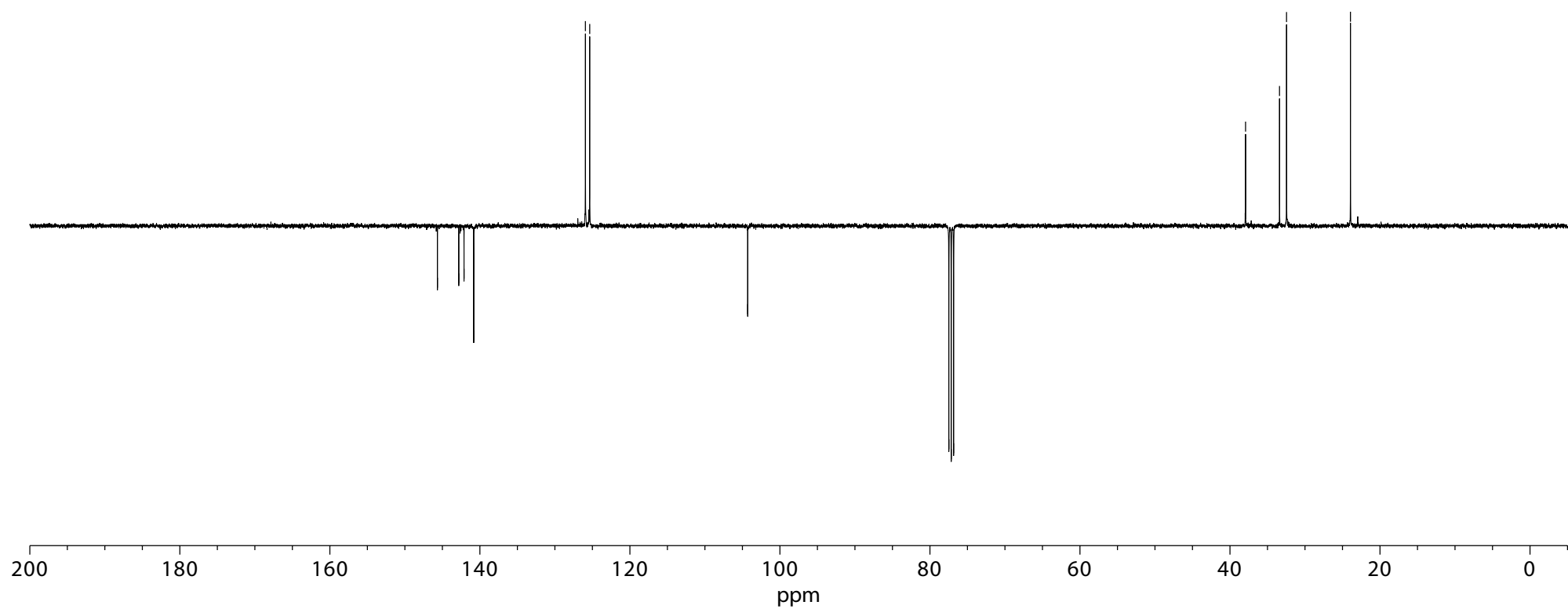
125.93  
125.36

104.30

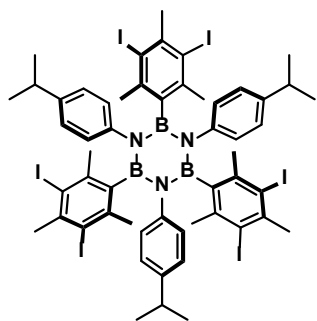
77.48 CDCl3  
77.16 CDCl3  
76.84 CDCl3

37.92  
33.40  
32.46

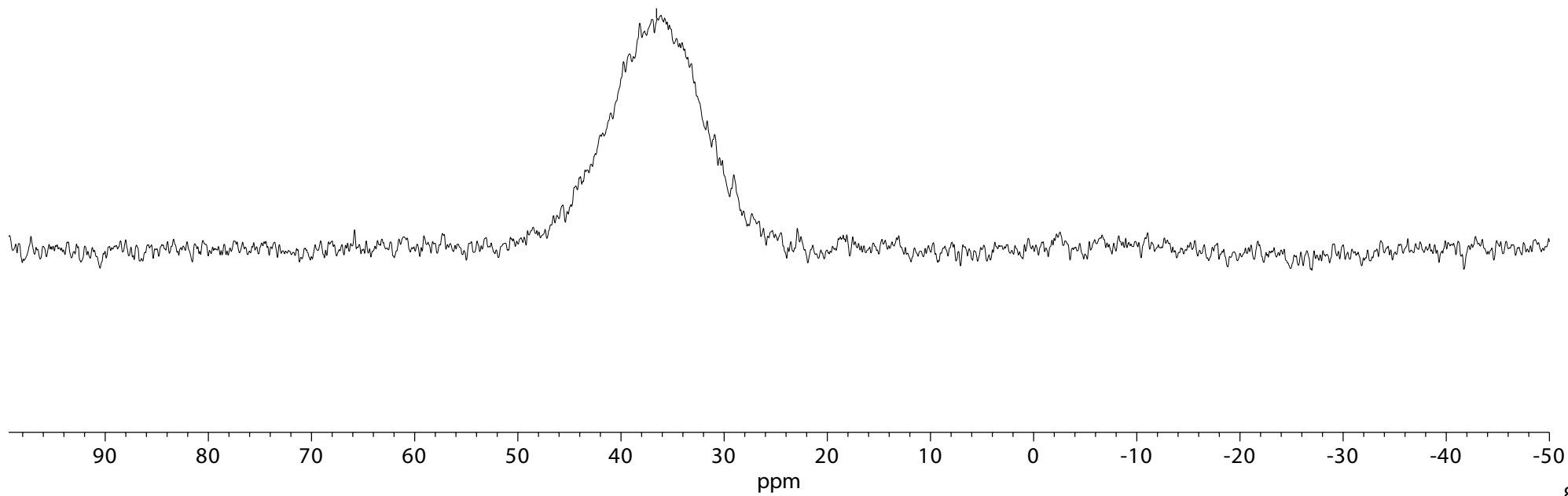
23.94



B,B',B''-Tris(3,5-diiodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(16)

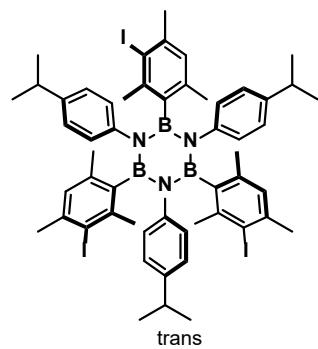
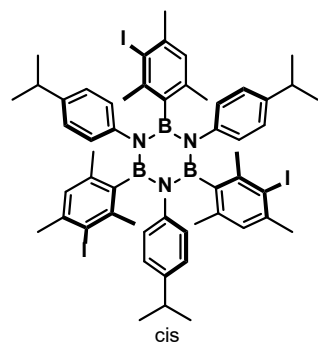


— 36.6



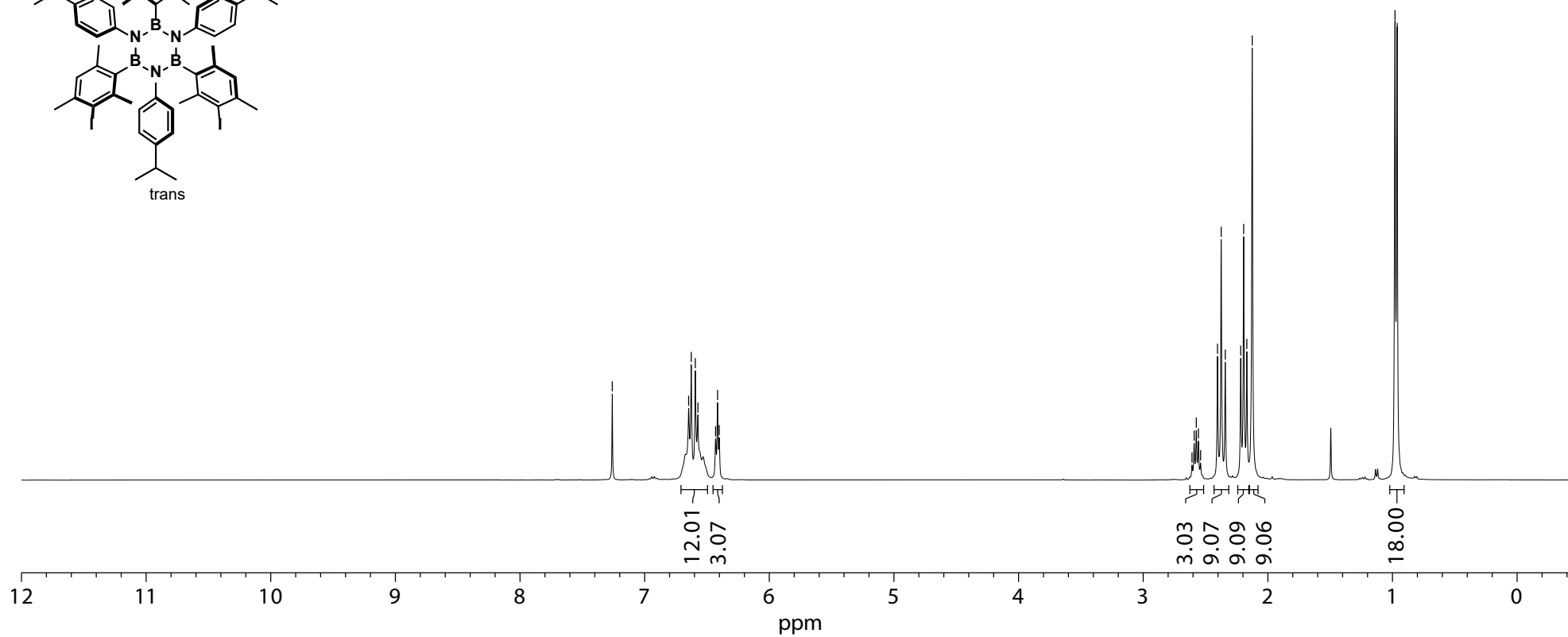


B,B',B''-Tris(3-iodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(17)

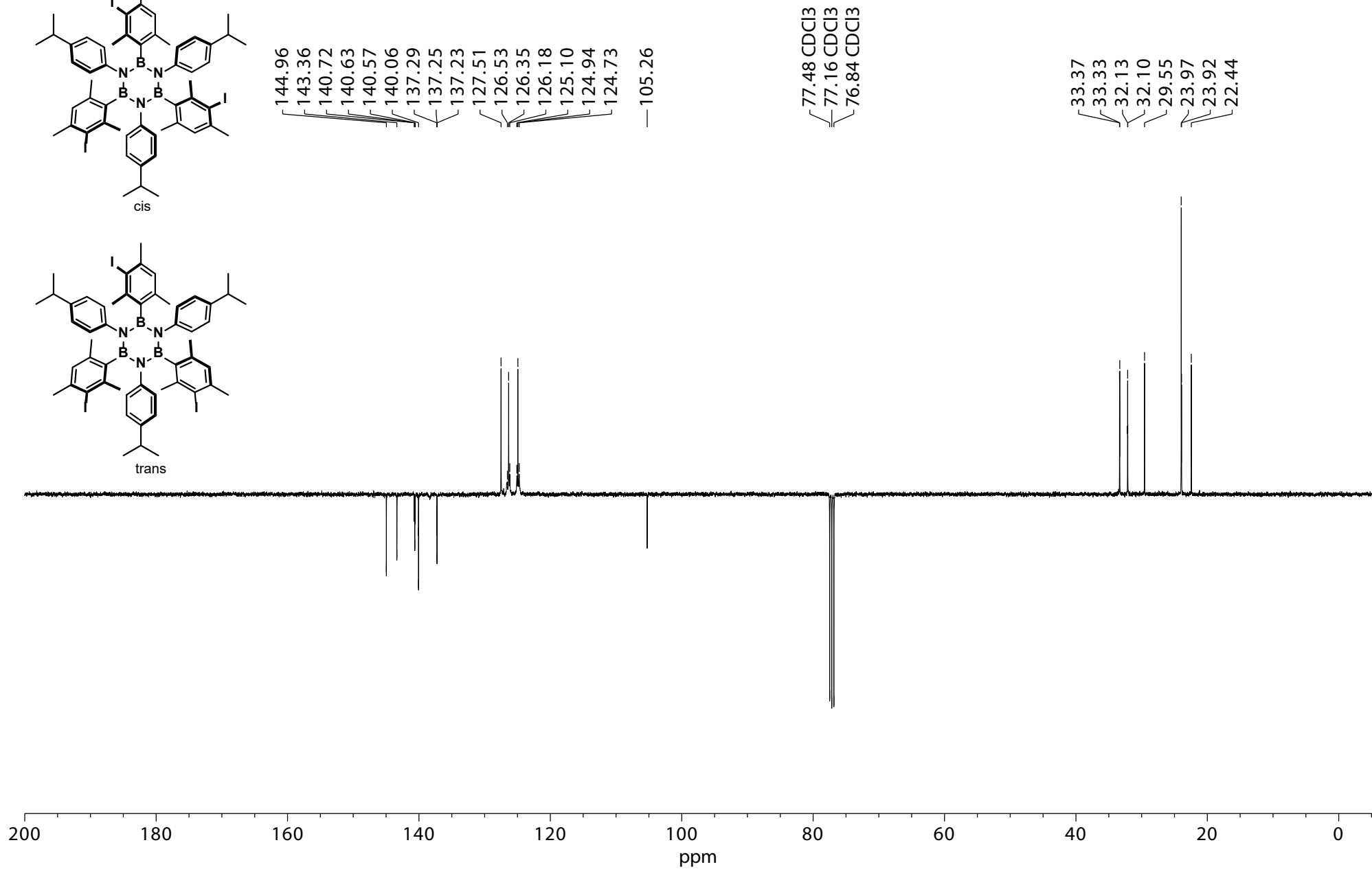
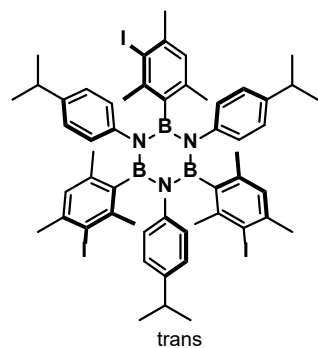
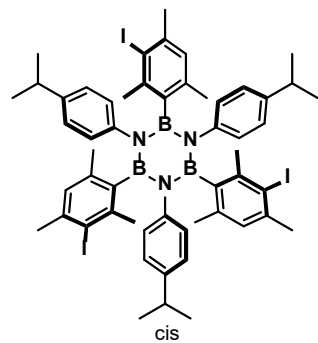


7.26 CDCl<sub>3</sub>  
 6.65  
 6.63  
 6.59  
 6.57  
 6.43  
 6.42  
 6.40

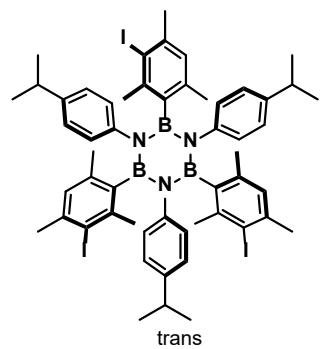
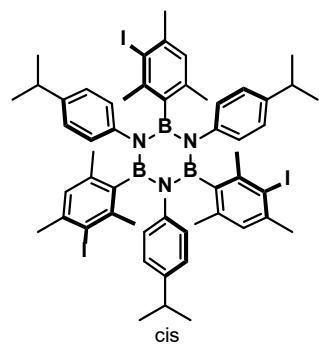
2.61  
 2.59  
 2.57  
 2.56  
 2.54  
 2.40  
 2.37  
 2.34  
 2.22  
 2.19  
 2.17  
 2.13  
 0.98  
 0.96



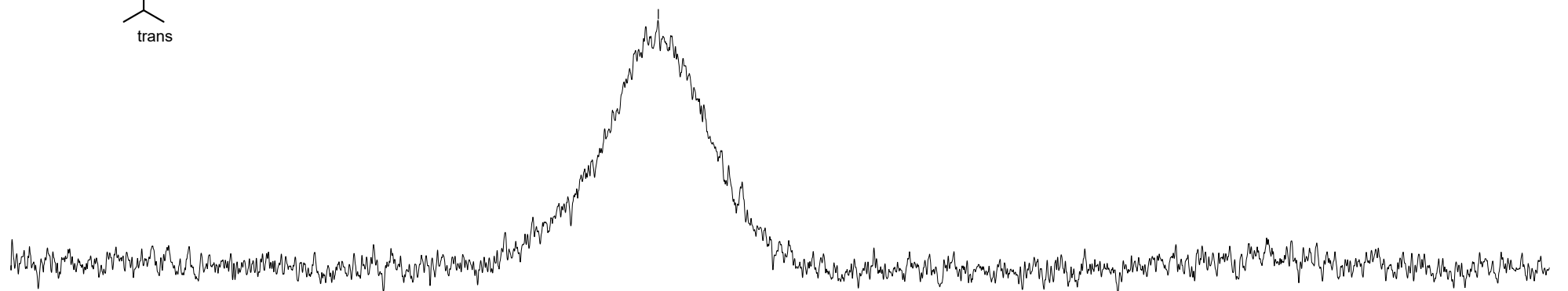
B,B',B''-Tris(3-iodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(17)



B,B',B''-Tris(3-iodo-2,4,6-trimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(17)



— 36.5



90

80

70

60

50

40

30

20

10

0

-10

-20

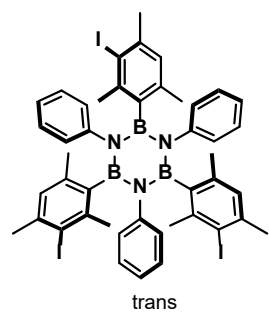
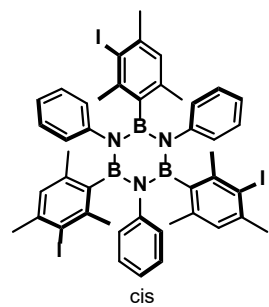
-30

-40

-50

ppm

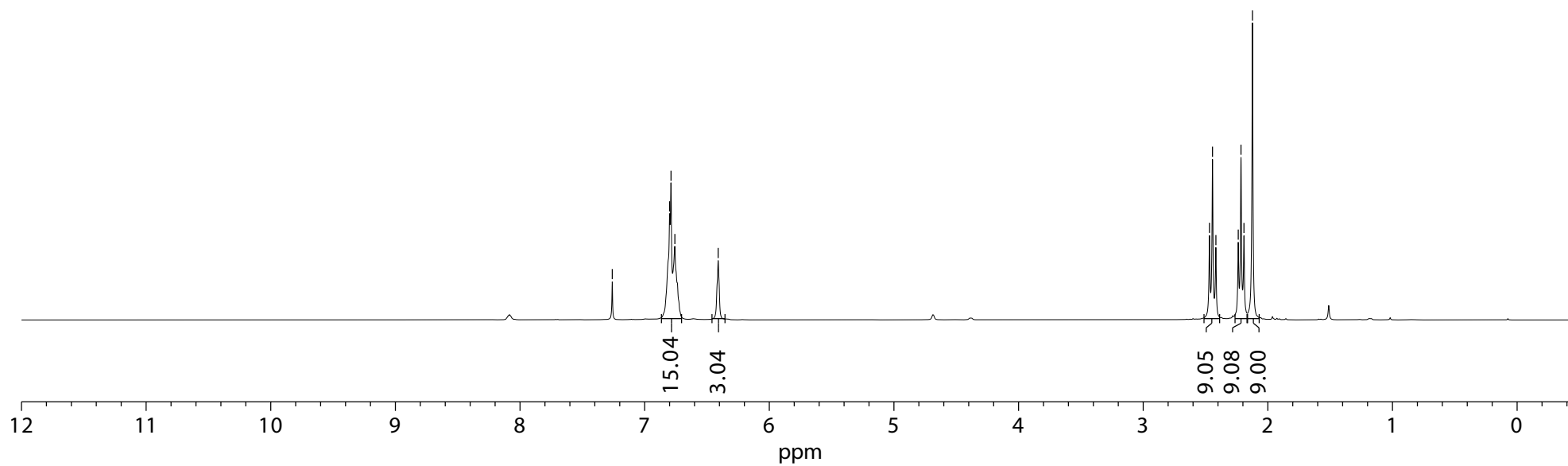
B,B',B''-Tris(3-iodo-2,4,6-trimethylphenyl)-N,N',N''-tris(phenyl)borazine-(18)



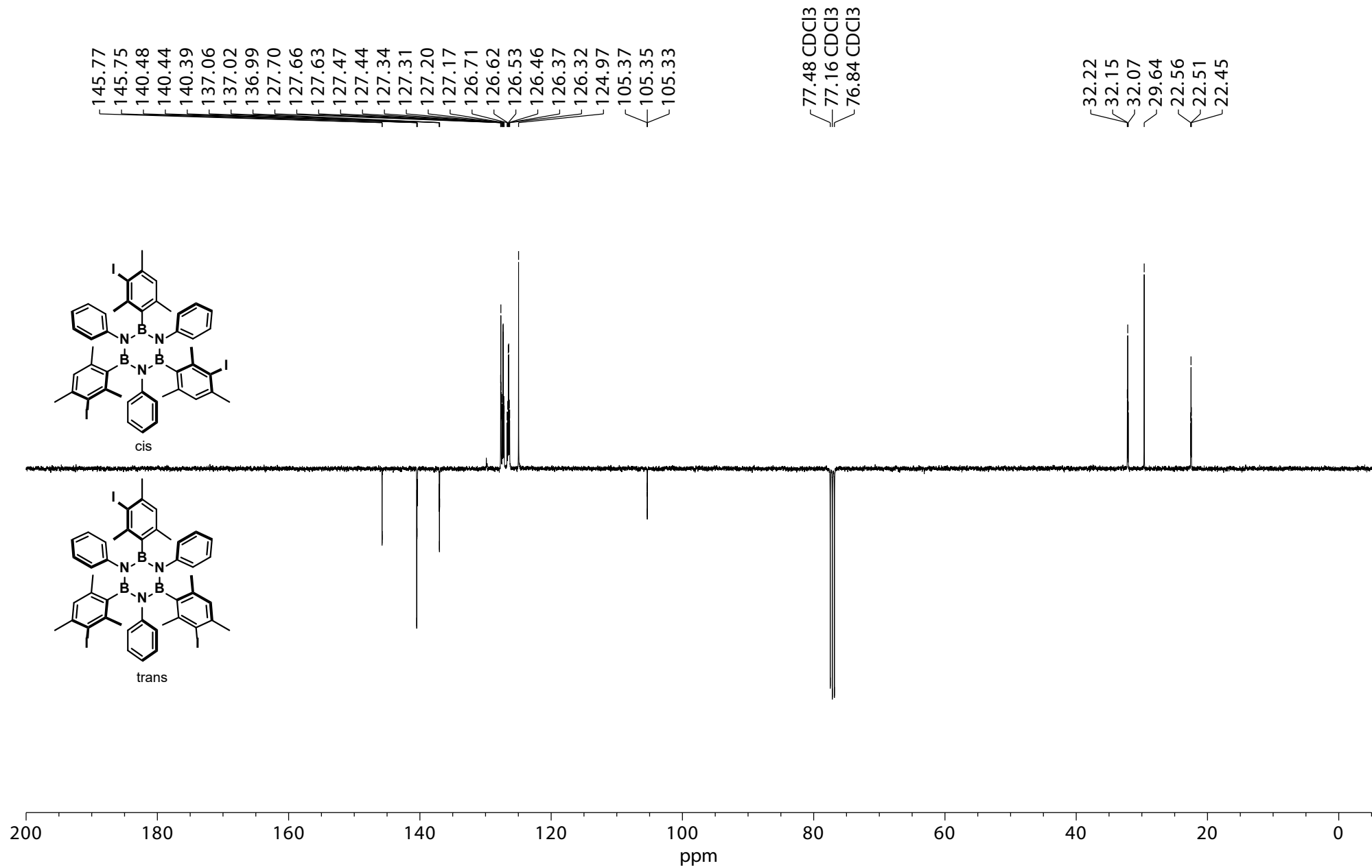
— 7.26 CDCl<sub>3</sub>

6.80  
6.79  
6.76  
6.41

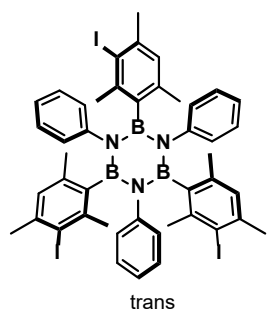
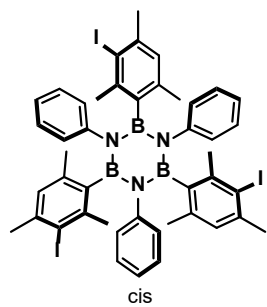
2.47  
2.44  
2.42  
2.24  
2.22  
2.19  
2.12



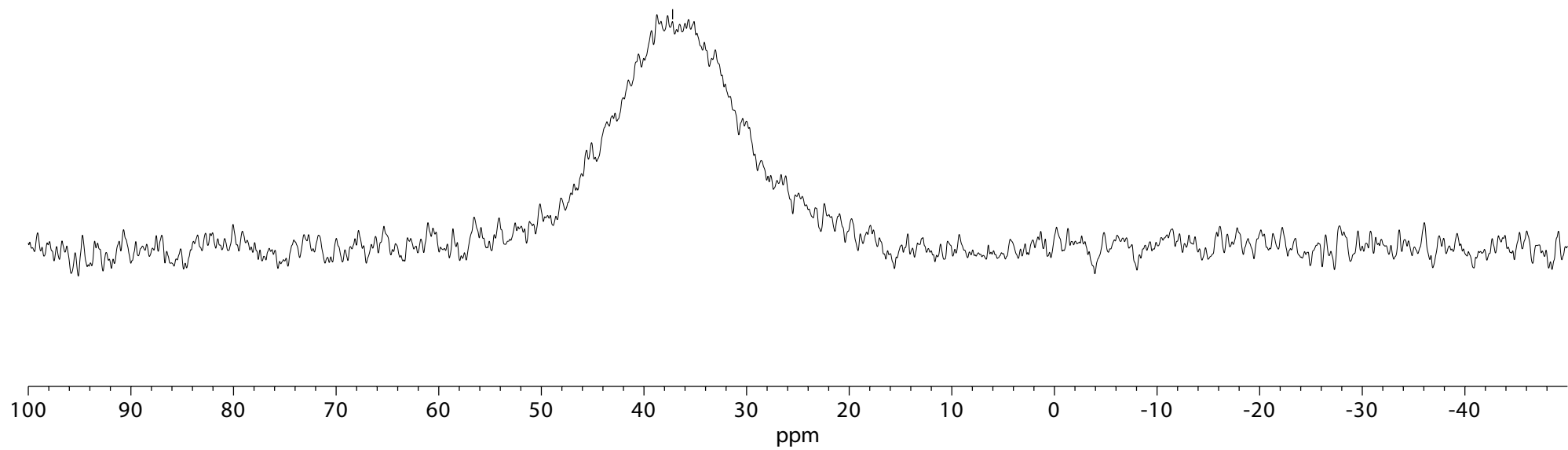
B,B',B''-Tris(3-iodo-2,4,6-trimethylphenyl)-N,N',N''-tris(phenyl)borazine-(18)



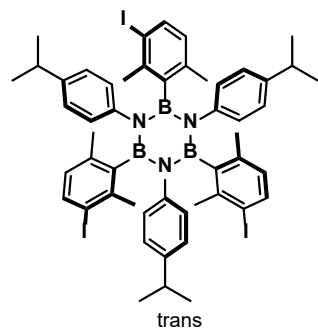
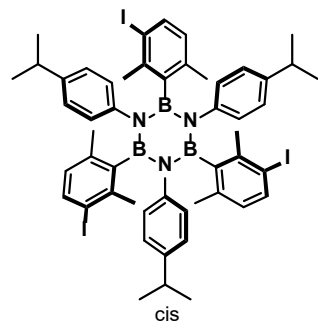
B,B',B''-Tris(3-iodo-2,4,6-trimethylphenyl)-N,N',N''-tris(phenyl)borazine-(18)



—37.2

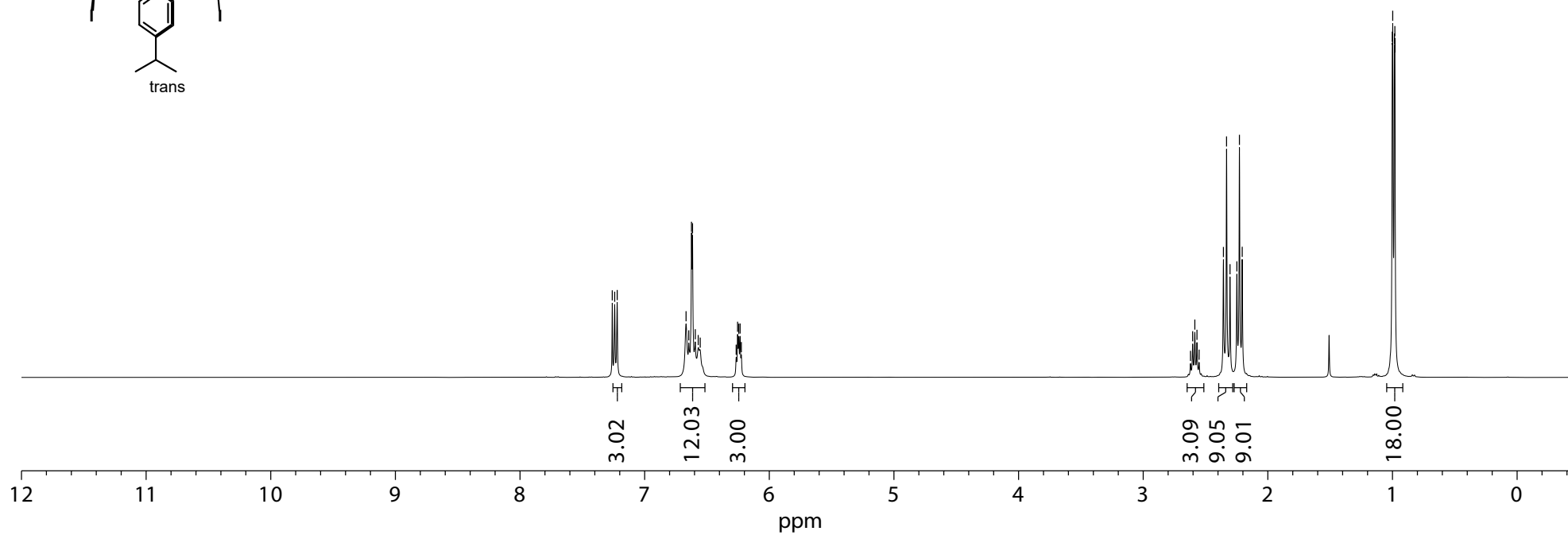


B,B',B''-Tris(3-iodo-2,6-dimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(19)

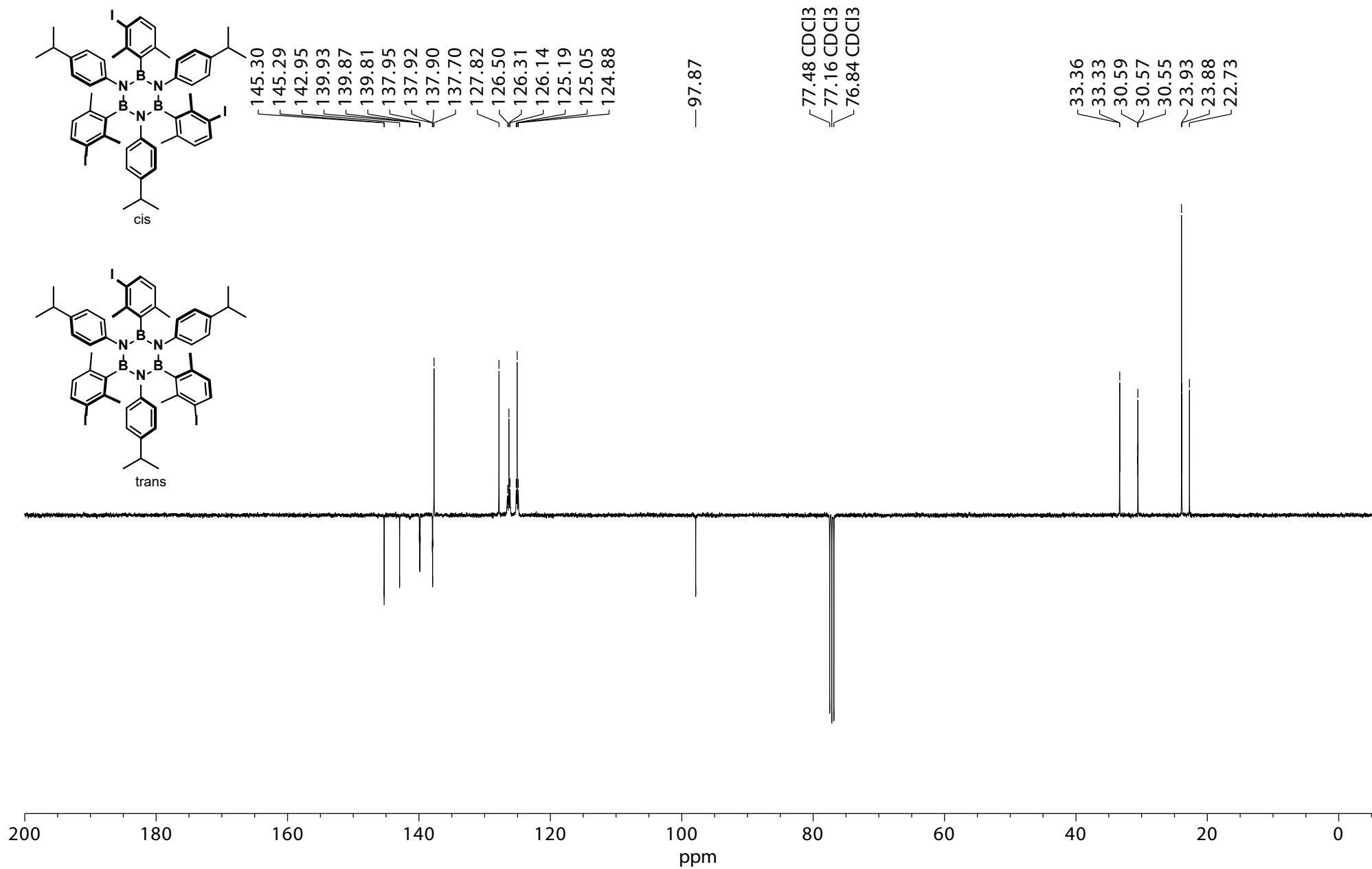


7.26 CDCl<sub>3</sub>  
 7.24  
 7.22  
 6.67  
 6.65  
 6.62  
 6.62  
 6.59  
 6.57  
 6.55  
 6.27  
 6.25  
 6.24  
 6.23  
 6.22

2.62  
 2.60  
 2.59  
 2.57  
 2.55  
 2.36  
 2.33  
 2.30  
 2.25  
 2.23  
 2.21  
 1.00  
 1.00  
 0.98  
 0.98

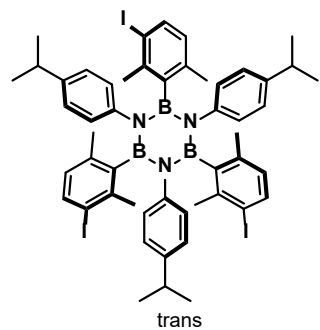
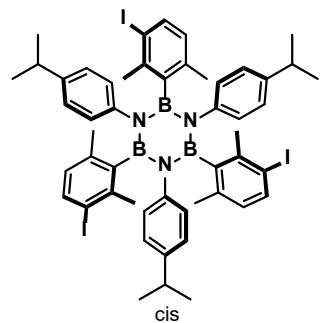


B,B',B''-Tris(3-iodo-2,6-dimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(19)

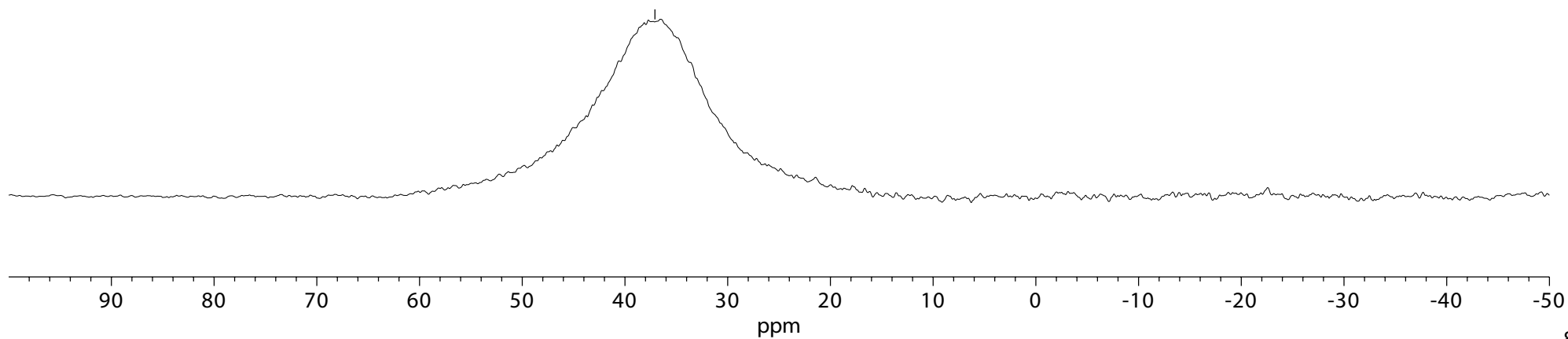




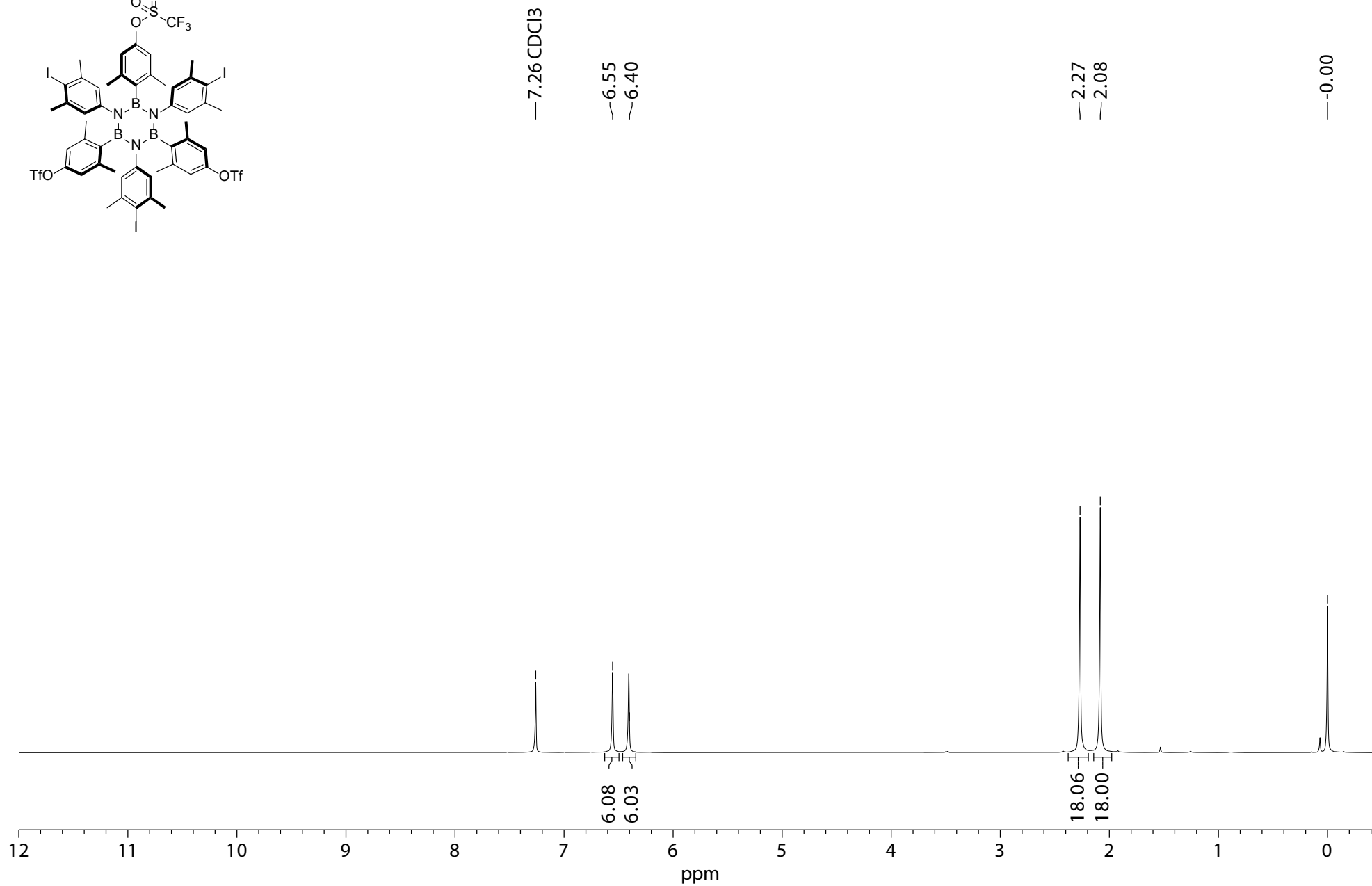
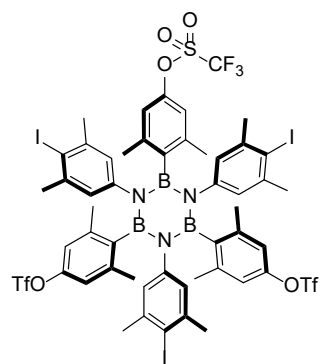
B,B',B''-Tris(3-iodo-2,6-dimethylphenyl)-N,N',N''-tris(4-isopropylphenyl)borazine-(19)



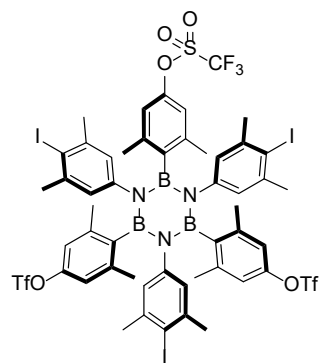
—37.1



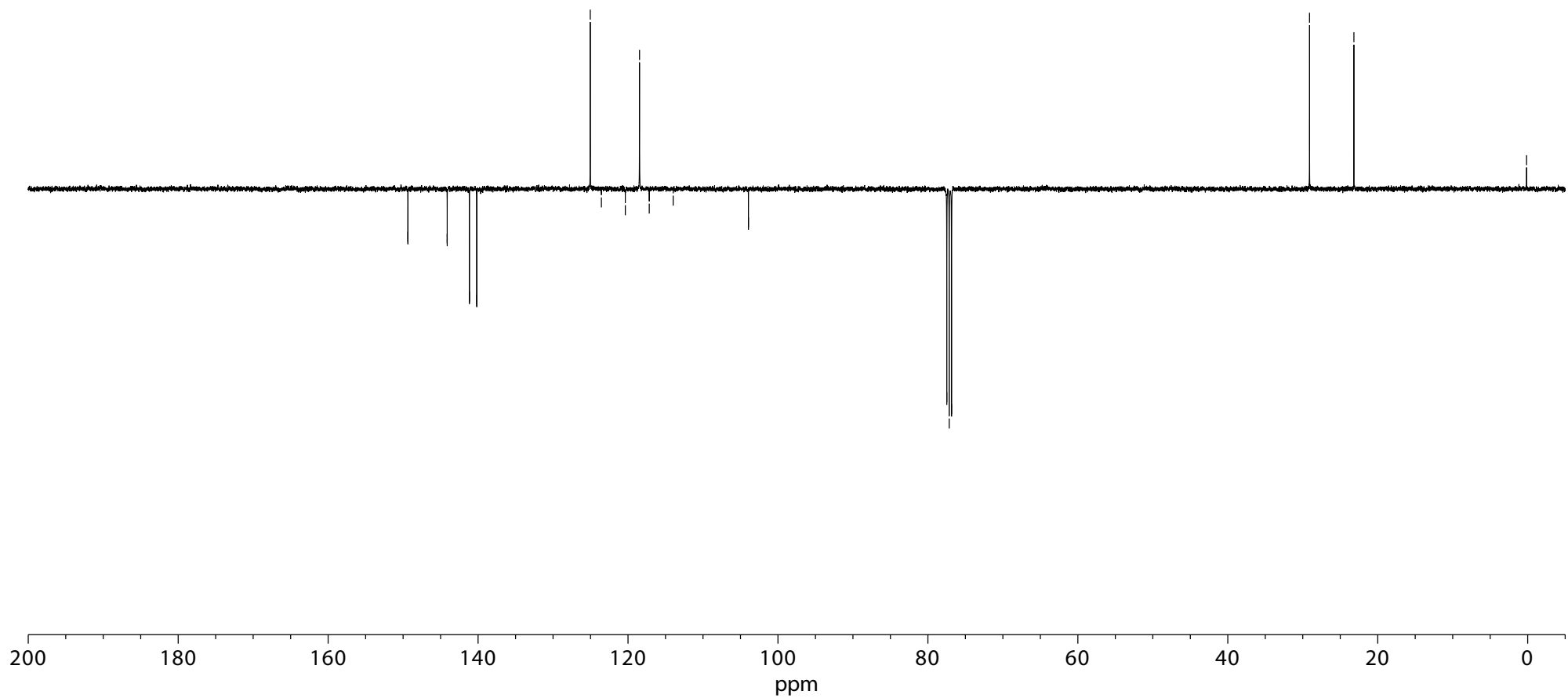
B,B',B''-Tris(2,6-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-N,N',N''-tris(4-iodo-3,5-dimethylphenyl)borazine-(20)



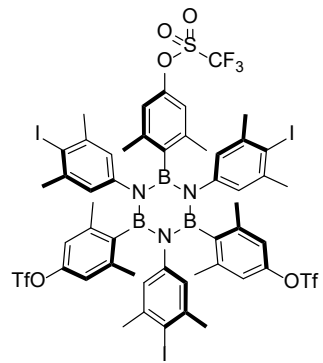
B,B',B''-Tris(2,6-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-N,N',N''-tris(4-iodo-3,5-dimethylphenyl)borazine-(20)



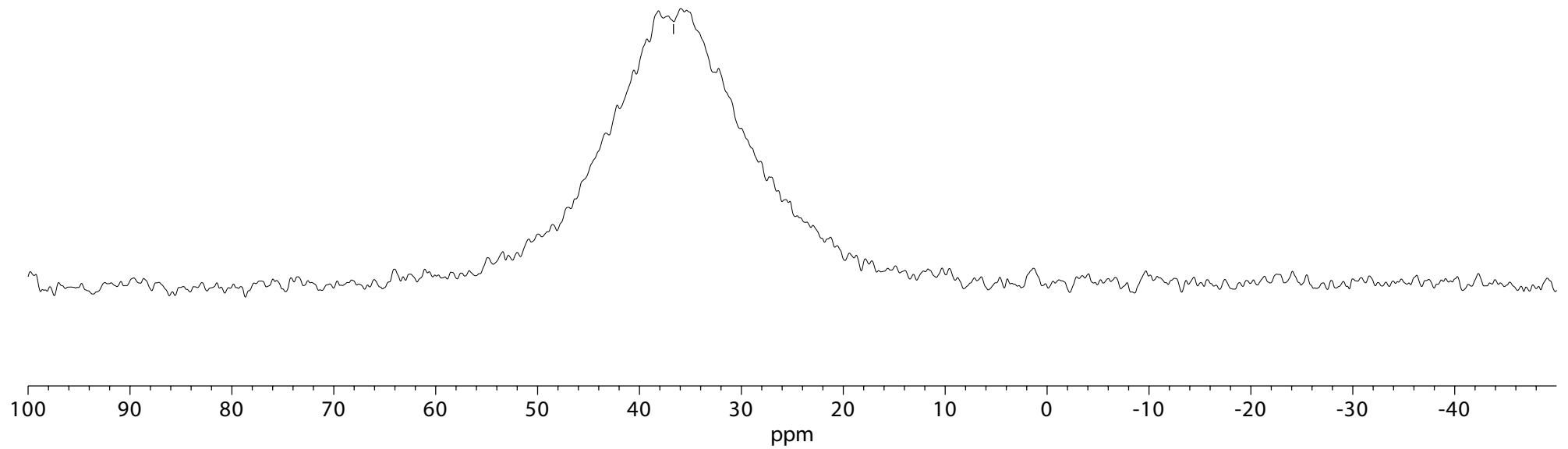
- 149.36
- 144.12
- 141.15
- 140.18
- 125.04
- 123.55
- 120.36
- 118.46
- 117.17
- 113.98
- 103.94
- 77.48 CDCl3
- 77.16 CDCl3
- 76.84 CDCl3
- 29.10
- 23.18
- 0.15



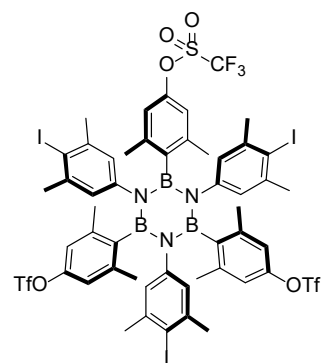
B,B',B''-Tris(2,6-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-N,N',N''-tris(4-iodo-3,5-dimethylphenyl)borazine-(20)



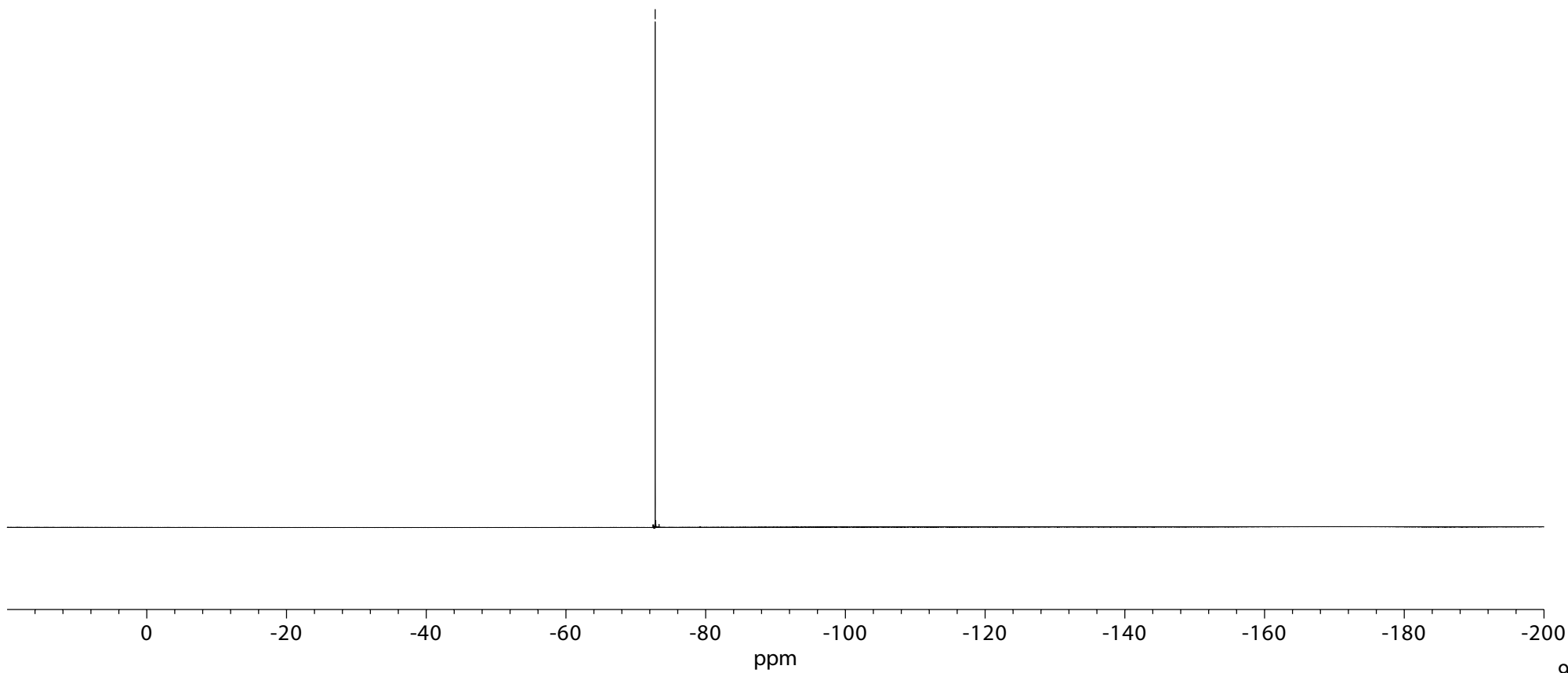
—36.7



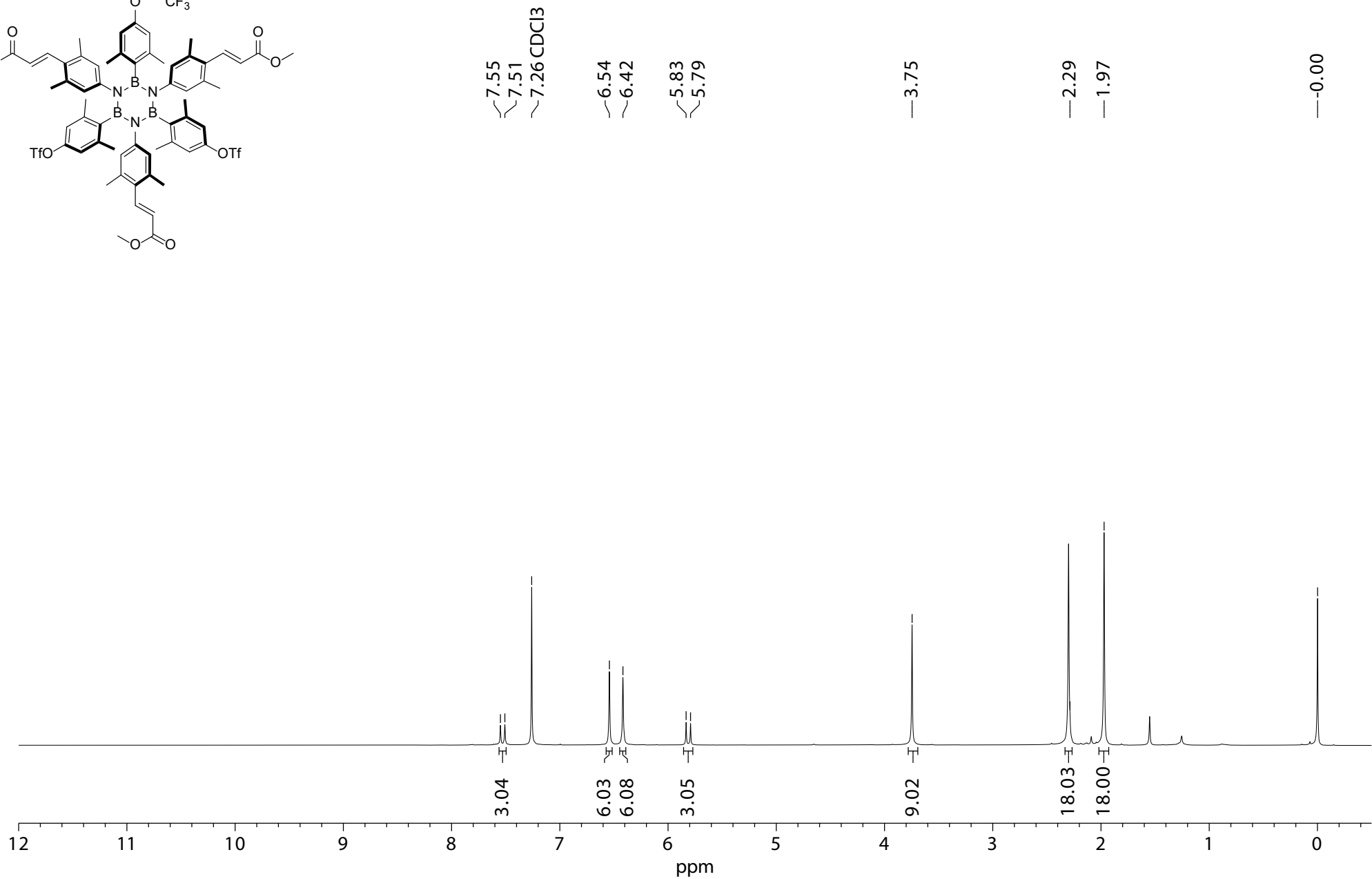
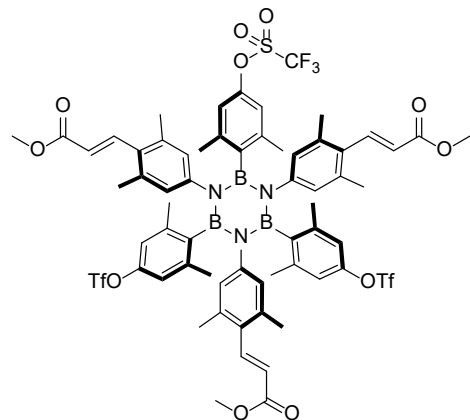
B,B',B''-Tris(2,6-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-N,N',N''-tris(4-iodo-3,5-dimethylphenyl)borazine-(20)



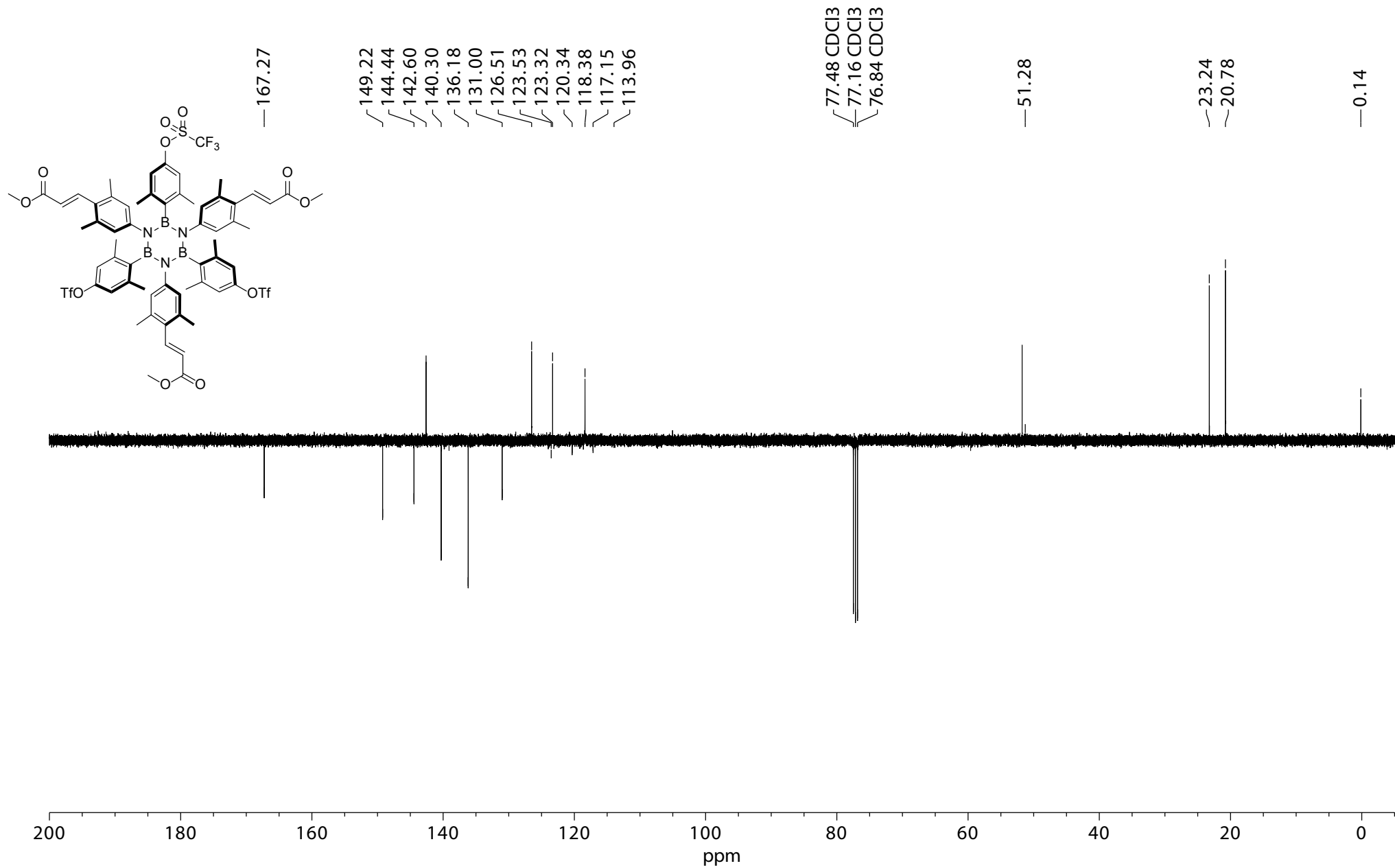
---72.8



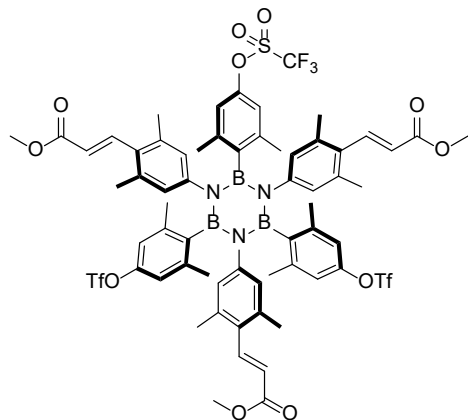
B,B',B''-Tris(2,6-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-  
N,N',N''-tris(4-(3-methoxy-3-oxoprop-1-en-1-yl)-3,5-dimethylphenyl)borazine-(21)



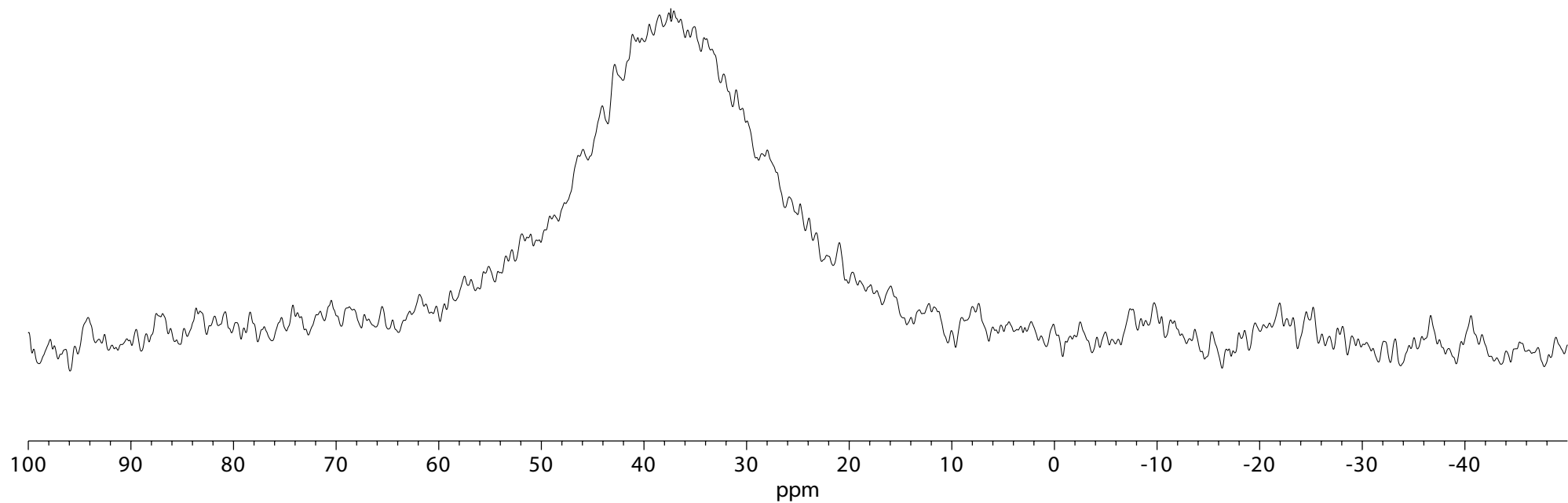
B,B',B''-Tris(2,6-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-  
N,N',N''-tris(4-(3-methoxy-3-oxoprop-1-en-1-yl)-3,5-dimethylphenyl)borazine-(21)



B,B',B''-Tris(2,6-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-  
N,N',N''-tris(4-(3-methoxy-3-oxoprop-1-en-1-yl)-3,5-dimethylphenyl)borazine-(21)

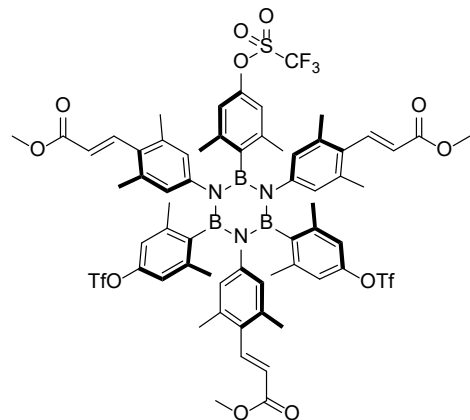


—37.4

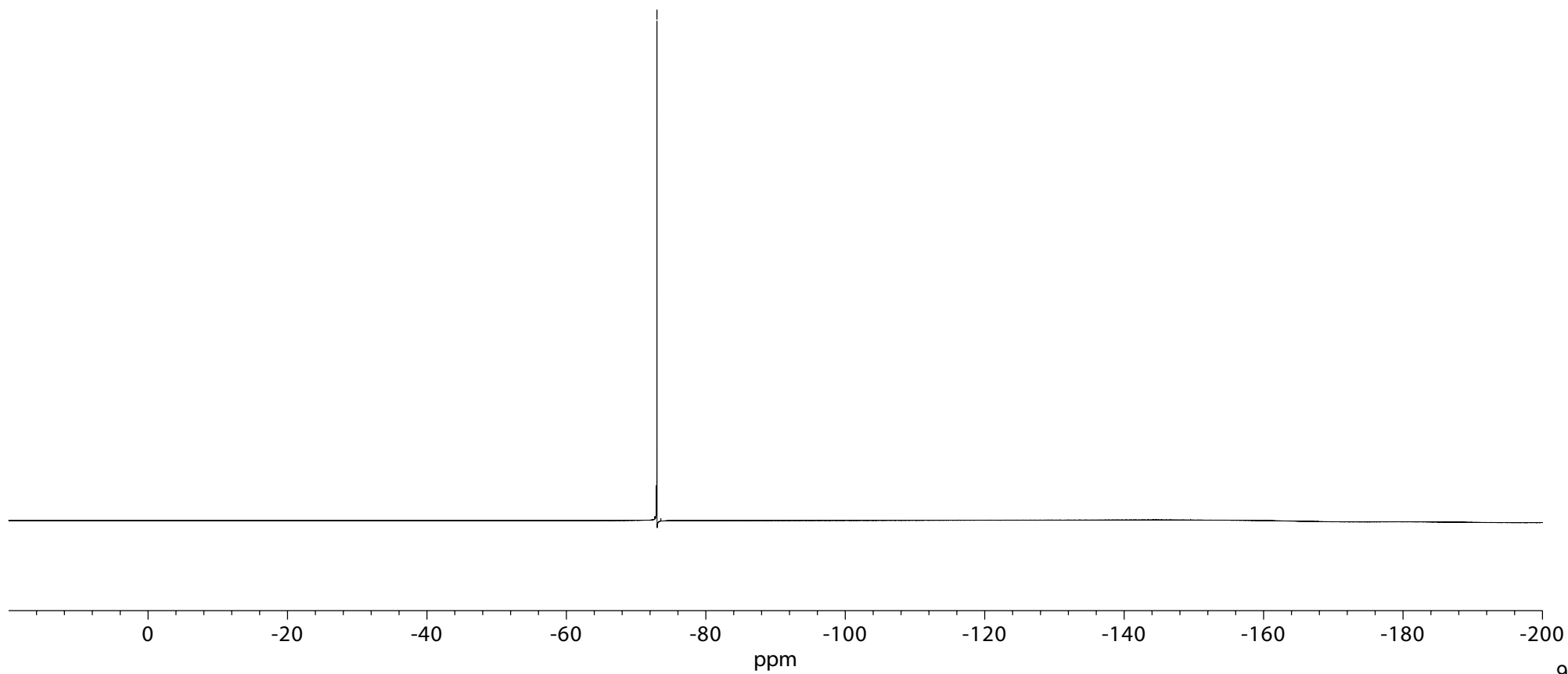




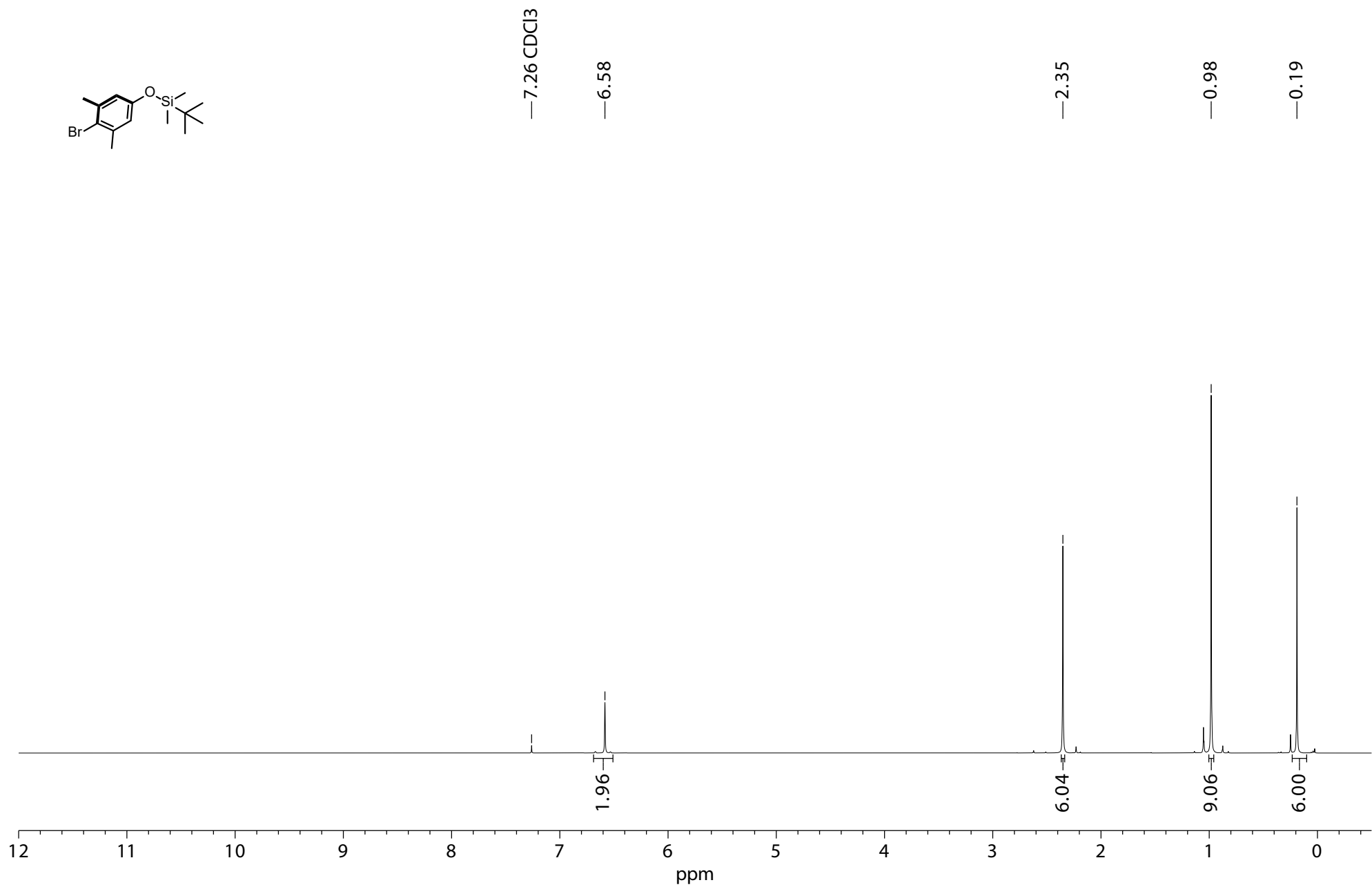
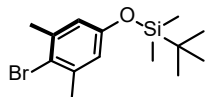
B,B',B''-Tris(2,6-dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-  
N,N',N''-tris(4-(3-methoxy-3-oxoprop-1-en-1-yl)-3,5-dimethylphenyl)borazine-(21)



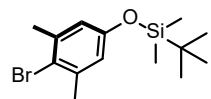
--73.0



(4-bromo-3,5-dimethylphenoxy)(tert-butyl)dimethylsilane (22)



(4-bromo-3,5-dimethylphenoxy)(tert-butyl)dimethylsilane (22)



—154.28

—139.15

120.06  
119.12

77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>

25.81  
24.03  
18.33

—4.29

