**Supplementary Information**

# Sustainable access to *B,B',B"*-tri(aryl)borazines via a triflic anhydride-promoted/microwave approach

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## List of abbreviations

| | |
|---|---|
| Diethyl ether | $Et_2O$ |
| Dichlorophenylborane | $PhBCl_2$ |
| Hexamethyldisilazane | HMDS |
| Hexamethylcyclotrisilazane | HMCS |
| Triflic anhydride | $Tf_2O$ |

## 1. General Remarks

Unless otherwise stated, chemicals were purchased from Merck, TCI, Fluorochem and used as obtained from commercial sources without further purification.

GLC analyses were performed by using Agilent 6850 Series GC System equipped with a capillary column BB-5MS (30 m, 0.32 mm), a FID detector and helium as gas carrier. GC-EIMS analyses were carried out by using Agilent 9890 GC System/5977C MSD equipped with an electron impact ionizer at 70eV. Nuclear magnetic resonance (NMR) characterizations were recorded on a Bruker DRX-ADVANCE 400 MHz ($^{1}$H at 400 MHz,$^{13}$C at 100.6 MHz, $^{19}$F at 376.4 MHz, and $^{11}$B NMR spectra at 128 MHz) using the solvent residual signal as an internal reference ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm and DMSO: δH = 2.50 ppm, δC = 39.7 ppm). Precisely, $^{13}$C NMR spectra were recorded using the "zgflqn" pulse sequence, a J-modulated spin-echo experiment. This sequence was specifically chosen to unambiguously assign carbon multiplicities and to ensure a flat baseline, which is critical when characterizing boron-containing compounds, where signals are often broadened due to quadrupolar relaxation of $^{11}$B nuclei. In the recorded spectra, the phase was adjusted according to the J-modulation, so that quaternary and secondary carbons (as well as the selected solvent) appear negative, while primary and tertiary carbons appear positive. Boron chemical shifts are reported in ppm, referenced to the external standard boron signal of $BF_3{\cdot}Et_2O$ (δB = 0 ppm). Chemical shifts are reported in ppm (δ), 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, t = triplet triplet, m = multiplet.

MW assisted reactions were performed in CEM Discover SP microwave oven equipped with 10 mL tubes in sealed reaction vessel mode and temperature was measured with the external surface IR sensor. The method used was Dynamic, with parameters wet as follows: T: 150 °C, t: 1 h, μλ=150 W, Pressure: 300 psi, Mixing: high, PowerMax: On, Stage 1 of 1.

Boronic esters (**1-1r**) were synthesized according to literature available procedures.[1] In the case of new compounds, they were fully characterized (**1e, 1i, 1m, 1p**).

Compounds **4**,[2] **8**[3] and **9**[4] were synthesised according to previously reported procedures.

## 2. General procedure A: Reactions performed under conventional heating mode

### 2.1 Screening of boron source

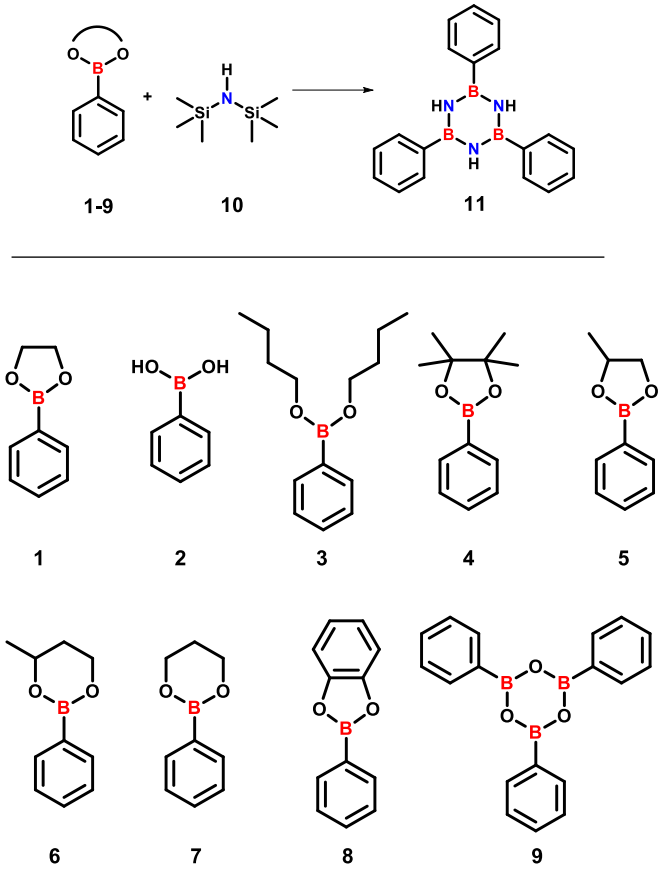
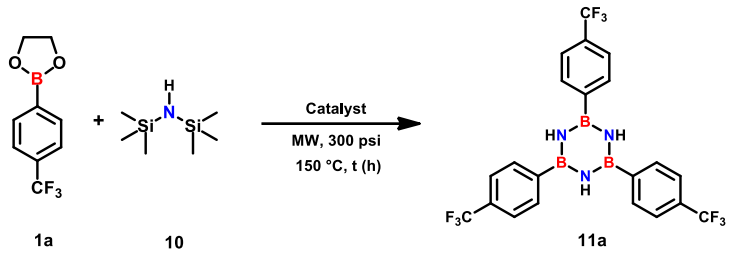



**Figure SI-1**. Screening of boron source.

An 8 mL screw-capped vial, pre-dried in oven, was evacuated and flushed with argon. To the vial, 1 mmol of the boronate ester was added (**1-9**) followed by another cycle of evacuation and argon filling. Next, 3 mL of HMDS was introduced, and the reaction mixture was heated to 150 °C for 72 hours. After completion, the reaction was allowed to cool to room temperature. The mixture was then treated with 3 mL of heptane, and the resulting precipitate was collected by filtration.

## 3. General procedure B: Catalyst screening under microwave heating

**Table SI-1** Catalysts screening




1a 10 11a

| Entry | Catalyst/activator (30 mol%) | Time (h) | Yield (%) |
|---|---|---|---|
| 1 | - | 5 | 31 |
| 2 | $H_2SO_4$ | 3 | 38 |
| 3 | $BBr_3$ | 3 | 0 |
| 4 | $BCl_3$[a] | 3 | Traces |
| 5 | $BF_3OEt_2$ | 3 | <10 |
| 6 | $AlCl_3$ | 3 | 0 |
| 7 | $FeCl_3$ | 3 | 0 |
| 8 | TfOH | 3 | 49 |
| 9 | TMS-OTf | 3 | <20 |
| 10 | TBDMS-OTf | 3 | 51 |
| 11 | $Tf_2O$ | 3 | 75 |

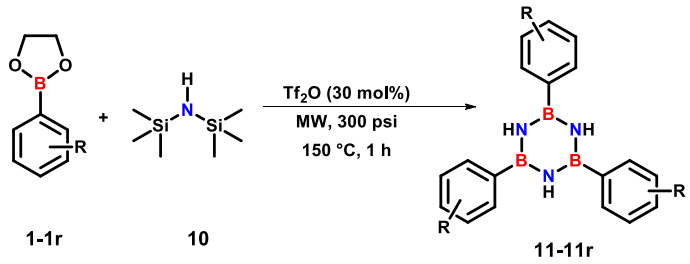
Reaction condition: **1a** (1 mmol), **10** (3 mL); [a]300 µL in hexane 1M solution

**General procedure for entries 1-5, 8-11:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(4-(trifluoromethyl)phenyl-1,3,2-dioxaborolane (**1a**, 216 mg) was added, followed by another cycle of evacuation and argon filling. Next, 3 mL of HMDS (**10**) were introduced. The appropriate quantity of catalyst was then added dropwise. The vessel was placed in the microwave synthesizer and subjected to 150 °C for the reported time at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, the mixture was transferred to a round-bottom flask, and HMDS was removed under reduced pressure. The product **11a** was isolated by precipitation with 3 mL of heptane.

**General procedure for entries 6 and 7:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(4-(trifluoromethyl)phenyl-1,3,2-dioxaborolane (**1a**, 216 mg) and the appropriate quantity of catalyst were added, followed by another cycle of evacuation and argon filling. Next, 3 mL of HMDS (**10**) were introduced. The vessel was placed in the microwave synthesizer and subjected to 150 °C for the reported time at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, the mixture was transferred to a round-bottom flask, and HMDS was removed under reduced pressure. The resulting solid was treated with $Et_2O$ and stirred at room temperature for 30 minutes. The catalyst

was then removed by filtration. $Et_2O$ was evaporated under reduced pressure, and the product **11a** was isolated by precipitation with 3 mL of heptane.

### 4. General procedure C: Synthesis of differently substituted *B,B',B''*-tri(aryl) substituted borazines




**Scheme SI-1.** General procedure for the synthesis of *B,B',B''*-tri(aryl) substituted borazines.

A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-aryl-1,3,2-dioxaborolane (**1-1r**) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) were added dropwise. The vessel was placed in the microwave synthesizer and subjected to 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11-11r**) was then isolated by filtration.

## 5. E-factor, Space-Time Yield (STY), EcoScale and Safety/Hazard Score (SHS) calculations

**Table SI-2.** E-Factor calculations and comparison among this work and the reference procedures.

| References | E-Factor calculation |
|---|---|
| Nöth et al., 1974 | [16 g (HMCS) + 23 g ($PhBCl_2$) + 574.2 g (hexane)[a] + 876.5g (benzene)]- [5.4 g (product **11**) + 5.3g (monosilaborazine)]/5.4 g (product **11**) = **273.89** |
| Svatikov et al., 1991 | [11.707 mg (DBPB) + 10.9755 mg (HMCS) + 0.01471 mg ($H_2SO_4$)+ 198 mg (hexane)[a]] – [1.85mg (product **11**) + 3.2926 mg (HMCS recovered) + 3.7462 mg (DBPB recovered)]/1.85 mg (product **11**)= **114.49** |
| Gruzinova et al., 1987 | [2.19 g (HMCS) + 3.12 g (**9**) + 0.0056 g (KOH) + 52.722 g (benzene for extraction)[a] + 60g (water for extraction)[a] + 20.385 (heptane)[a]] – [1.2g (product **11**) + 0.04342g ($CH_4$) + 0.23433 g (benzene recovered)]/1.2 g (product **11**)= **114.12** |
| Nöth et al., 2005 | [72.6g (**10**) + 75g ($PhBCl_2$) + 332.5 g (DCM) + 1155 g ($Et_2O$)[a]] – [45.4g (product **11**)]/45.4 (product **11**)= **35.01** |
| ***This work*** (product **10**) | [770 mg (**10**) + 147.97 mg (**1**) + 84 mg ($Tf_2O$) + 2038.5 mg (heptane)] – [101 mg (product **11**)]/101 mg (product **11**) = **29.1** |

[a] Solvent quantity used for purification and isolation steps for the literature references were estimated based on our expertise, as the authors did not provide specific information.

**Table SI-3.** Space-Time Yield calculations

| References | Space-Time Yield calculation |
|---|---|
| Nöth et al., 1974 | 5.4g (product **11**)/[(1 L (benzene)+ 0.017 L (HMCS) + 0.019 L ($PhBCl_2$)) × 36h]= **0.15** g $L^{-1}$ $h^{-1}$ |
| Svatikov et al., 1991 | [0.00185g (product **11**)/[(1.27 *$10^{-5}$ L ($PhB(OBu)_2$) + 1.19 *$10^{-5}$ L (HMCS) + 8.03*$10^{-9}$ ($H_2SO_4$)) × 11h]= **6.83** g $L^{-1}$ $h^{-1}$ |
| Gruzinova et al., 1987 | 1.2g (product **11**)/[(0.0024 L (HMCS) + 0.0028 L (PBA) + 0.000023 L (KOH)) × 4h]= **57.44** g $L^{-1}$ $h^{-1}$ |
| Nöth et al., 2005 | 45.4g (product **11**)/[(0.250 L (benzene) + 0.094 L (**10**) + 0.061 L ($PhBCl_2$)) × 240h]= **0.47** g $L^{-1}$ $h^{-1}$ |
| ***This work*** (product **10**) | 0.101 mg (product **11**)/[(0.001 L (**10**) + 0.00005 ($Tf_2O$) + 1.36*$10^{-4}$ L (**1**)) × 1h]= **85.16** g $L^{-1}$ $h^{-1}$ |

**Table SI-4.** EcoScale calculations.[a]

| Reference | Yield (PPts) | Price (PPts) | Safety (PPts) | Technical setup (PPts) | Temperature/time (PPts) | Workup and purification (PPts) | Ecoscale value[a] |
|---|---|---|---|---|---|---|---|
| Nöth et al., 1974 | 32 | 18 | 20 | 0 | 2 | 3 | **25** |
| Svatikov et al., 1991 | 32 | 13 | 15 | 0 | 3 | 11 | **26** |
| Gruzinova et al., 1987 | 30 | 18 | 25 | 3 | 3 | 4 | **17** |
| Nöth et al., 2005 | 1 | 11 | 20 | 1 | 8 | 4 | **55** |
| ***This work*** | 1 | 16 | 15 | 0 | 2 | 0 | **66** |

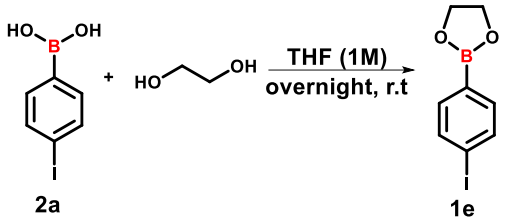
[a]PPts= Penalty points; 100-∑PPts

**Table SI-5.** Safety/Hazard Score (SHS) calculations.

| Solvent | CGP | CLP | FP | OBP | XVP | OELP | SDP | RPP | TOTAL |
|---|---|---|---|---|---|---|---|---|---|
| Benzene | 0.001 | 0.272 | 0.870 | 0.768 | 1.214 | 994.146 | 4.710 | 3.603 | 1005.586 |
| Diethyl ether | 1.000 | 1.858 | 1.000 | 0.648 | 0.895 | 0.252 | 479.001 | 0.878 | 485.531 |
| Hexane | 0.003 | 1.125 | 0.908 | 0.882 | 1.360 | 1.952 | 0.004 | 2.615 | 8.849 |
| Heptane | 0.005 | 1.125 | 0.848 | 0.878 | 1.619 | 1.167 | 0.478 | 1.282 | **7.402** |

## 6. Synthesis and characterization of the starting materials

| **Chem. Name** | **2-(4-iodophenyl)-1,3,2-dioxaborolane (1e)** |
|---|---|




**M. W.: 273.863**

**METHOD:** In an oven dried round bottom flask were added 5 mmol of 4-iodophenylboronic acid (**2a**, 1.239 g) and 4 mL of dry THF. After solubilization, ethylene glycol (17.88 mmol, 1 mL) was added and the reaction mixture was allowed to stir overnight at room temperature. Afterwards, the mixture was concentrated under reduced pressure and 5 mL of diethyl ether were added. The resulting solution was transferred to 1 g of dry $CaCl_2$ powder and, after filtration and evaporation under vacuum, the product (**1e**) was collected as a pale-brown solid (1.092 g, 80% isolated yield).

| **Mol Formula** | $C_8H_8BIO_2$ | **m.p** | 100 °C |
|---|---|---|---|

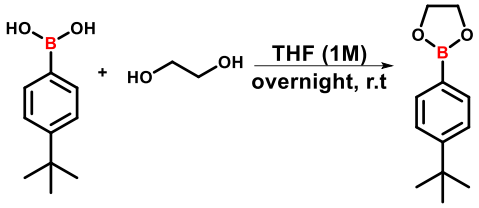
| **$^1$H NMR** | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| **400** | 4.38 | 4 | *s* | - |
| **MHz** | 7.52 | 2 | *d* | 8.13 |
| **$CDCl_3$** | 7.74 | 2 | *d* | 8.09 |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 137.11, 136.33, 99.15, 66.14. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz**,** $CDCl_3$) δ: 31.66

**GC-EIMS (m/z, %):** 275 (M+ +1, 19), 274 (M+, 100), 273 (M+ -1, 41), 217 (13), 1147.1 (42), 146.1 (11), 121 (19), 117.1 (14), 103.1 (49), 77.1 (31), 76.1 (11)

| Chem. Name | 2-(4-tert-butylphenyl)-1,3,2-dioxaborolane (1i) |
|---|---|




2b 1i

M. W.: 204.073

**METHOD:** In an oven dried round bottom flask were added 5 mmol of 4-tert-butylphenylboronic acid (**2b**, 890 mg) and 4 mL of dry THF. After solubilization ethylene glycol (17.88 mmol,1 mL) was added and the reaction mixture was allowed to stir overnight at room temperature. Afterwards, the mixture was concentrated under reduced pressure and 5 mL of diethyl ether were added. The resulting solution was transferred to 1 g of dry $CaCl_2$ powder and, after filtration and evaporation under vacuum, the product (**1i**) was collected as a white solid (835 mg, 82% isolated yield).

| **Mol Formula** | $C_{12}H_{17}BO_2$ | **m.p** | 80 °C |
|---|---|---|---|

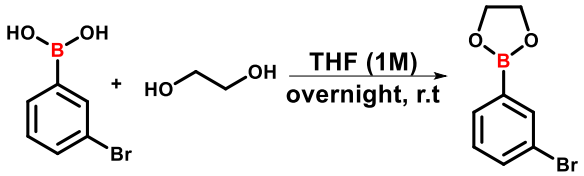
| | δ **value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| **$^1$H NMR 400 MHz $CDCl_3$** | 1.33 | 9 | *s* | - |
| | 4.37 | 4 | *s* | - |
| | 7.42 | 2 | *d* | 8.2 |
| | 7.76 | 2 | *d* | 8.2 |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 154.72, 134.76, 124.85, 65.98, 34.93, 31.19. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz**,** $CDCl_3$) δ: 31.64

**GC-EIMS (m/z, %):** 204.1 (M+, 20), 190.1 (17), 189.1 (100), 188.1 (22), 184 (11), 161.1 (25), 117.1 (20), 105.1 (13), 91.1 (26)

| Chem. Name | 2-(3-bromophenyl)-1,3,2-dioxaborolane (1m) |
|---|---|




**2c** **1m**

**M. W.: 226.863**

**METHOD:** In an oven dried round bottom flask were added 5 mmol of 3-bromophenylboronic acid (**2c**, 1.004 g) and 4 mL of dry THF. After solubilization ethylene glycol (17.88 mmol,1 mL) was added and the reaction mixture was allowed to stir overnight at room temperature. Afterwards, the mixture was concentrated under reduced pressure and 5 mL of diethyl ether were added. The resulting solution was transferred to 1 g of dry $CaCl_2$ powder and, after filtration and evaporation under vacuum, the product (**1m**) was collected as a colorless liquid (1.010 g, 89%).

| **Mol Formula** | $C_8H_8BBrO_2$ |
|---|---|

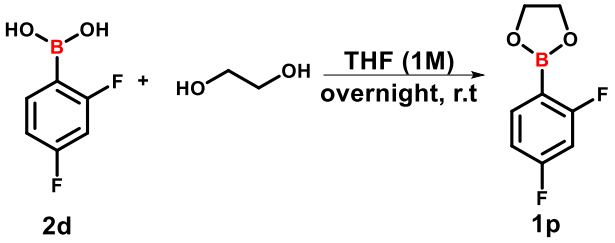
| | δ **value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| **$^1$H NMR 400 MHz $CDCl_3$** | 4.33 | 4 | *s* | - |
| | 7.19-7.23 | 1 | *m* | - |
| | 7.54-7.56 | 1 | *m* | - |
| | 7.67 | 1 | *d* | 7.3 |
| | 7.89 | 1 | *s* | - |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ:137.62, 134.43, 133.19, 129.65, 122.50, 66.18. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz, $CDCl_3$) δ: 31.14

**GC-EIMS (m/z, %):** 228 (M+ +2, 100), 227 (M+ +1, 42), 226 (M+, 100). 225 (M+ -1, 30), 198 (28), 197 (12), 196 (29), 171 (70), 169 (72), 117.1 (54), 116.1 (13), 103 (34), 91 (14), 90 (16), 89.1 (10), 77 (31), 76 (16), 75 (14), 73 (20), 65 (11), 51 (10)

| Chem. Name | 2-(2,4-difluorophenyl)-1,3,2-dioxaborolane (1p) |
|---|---|




**2d** **1p**

**M. W.: 183.948**

**METHOD:** In an oven dried round bottom flask were added 5.83 mmol of 2,4-difluorophenylboronic acid (**2d**, 920 mg) and 4 mL of dry THF. After solubilization ethylene glycol (17.88 mmol,1 mL) was added and the reaction mixture was allowed to stir overnight at room temperature. Afterwards, the mixture was concentrated under reduced pressure and 5 mL of diethyl ether were added. The resulting solution was transferred to 1 g of dry $CaCl_2$ powder and, after filtration and evaporation under vacuum, the product (**1p**) was collected as an off-white solid (0.776 g, isolated yield 84%).

| **Mol Formula** | $C_8H_7BF_2O_2$ | **m.p** | 90 °C |
|---|---|---|---|

| | δ **value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| **$^1$H NMR 400 MHz $CDCl_3$** | 4.40 | 4 | *s* | - |
| | 6.77-6.82 | 1 | *m* | - |
| | 6.87-6.92 | 1 | *m* | - |
| | 7.72-7.78 | 1 | *m* | - |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 168.16 (dd, $^1J_{C-F}$=225.6Hz, $^4J_{C-F}$=12.3Hz ), 165.64 (dd, $^1J_{C-F}$=225.3Hz, $^4J_{C-F}$=12.2Hz), 138.32 (t, $^2J_{C-F}$=9.9Hz), 111.42 (dd, $^3J_{C-F}$=20.4Hz, $^5J_{C-F}$=3.5Hz), 103.87 (dd,$^2J_{C-F}$=27.9Hz, $^2J_{C-F}$=24.4Hz), 66.05. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

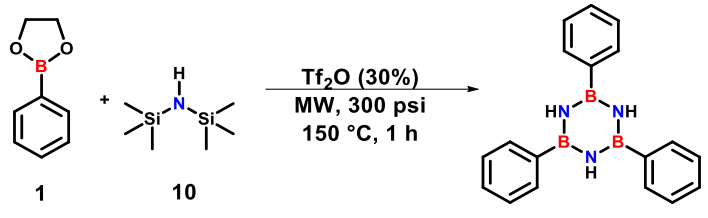
**$^{11}$B NMR** (128 MHz**,** $CDCl_3$) δ: 30.67

**$^{19}$F NMR** (376.4 MHz**,** $CDCl_3$) δ: -99.04, -104.37

**GC-EIMS (m/z, %):** 185.1 (M+ +1, 12), 184 (M+, 100), 183 (M + -1, 46), 166 (38), 165.1 (16), 154 (28), 153 ( 69), 152 (10), 147.1 (37), 136 ( 20), 135 (18), 127 (29), 125 (22), 124 (14), 109 (46), 108 (42), 107 (29), 94 (13), 75 (15), 74 (13), 73 859), 71.1 (10), 57.1 (12), 51 (12)

## 7. Synthesis and characterization of *B,B',B''*-tri(aryl)substituted borazines

| **Chem. Name** | ***B,B',B''*-tri(phenyl)borazine (11)** |
|---|---|




**1** **10** **11**

**M. W.: 308.789**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-phenyl-1,3,2-dioxaborolane (**1**, 148 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and left at 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11**) was then isolated by filtration as a white powder (101 mg, isolated yield 99%).

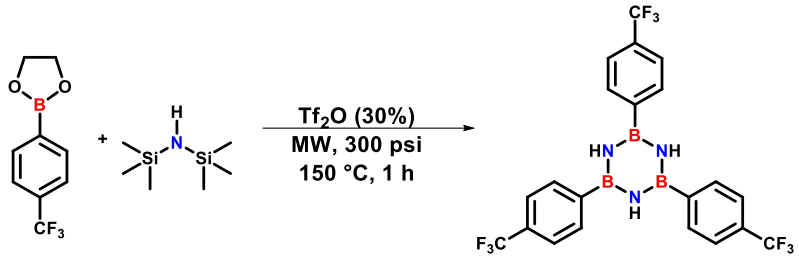
| **Mol Formula** | $C_{18}H_{18}B_3N_3$ | **m.p.** | 175 °C |
|---|---|---|---|

| **$^1$H NMR** | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| **400** | 5.91 | 3 | *s* | - |
| **MHz** | 7.46-7.48 | 9 | *m* | - |
| **$CDCl_3$** | 7.78-7.80 | 6 | *m* | - |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 131.94, 130.03, 128.22. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz, $CDCl_3$) δ: 33.55

| Chem. Name | ***B,B′,B″*-tri(4-(trifluoromethyl)phenyl)borazine (11a)** |
|---|---|




**1a** **10** **11a**

**M. W.: 512.783**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (**1a**, 216 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and left at 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11a**) was then isolated by filtration as a white powder (166 mg, isolated yield 98%).

| **Mol Formula** | $C_{21}H_{15}B_3N_3F_9N_3$ | **m.p.** | 244 °C |
|---|---|---|---|

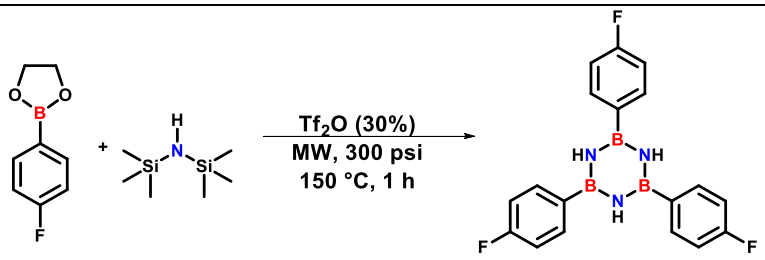
| **$^1$H NMR** | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| **400** | 5.94 | 3 | *s* | - |
| **MHz** | 7.73 | 6 | *d* | 7.81 |
| **$CDCl_3$** | 7.88 | 6 | *d* | 7.75 |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 132.23, 132.07 (q, $^2J_{C-F}$=32.8 Hz), 124.99 (q, $^3J_{C-F}$ = 3.8 Hz), 124.13 (q, $^1J_{C-F}$=272.2 Hz). The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz, $CDCl_3$) δ: 33.42

**$^{19}$F NMR** (376.4 MHz, $CDCl_3$) δ: -62.88

| Chem. Name | ***B,B',B''*-tri(4-fluorophenyl)borazine (11b)** |
|---|---|




**1b** **10** **11b**

**M. W.: 362.760**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(4-fluorophenyl)-1,3,2-dioxaborolane (**1b**, 166 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and left at 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11b**) was then isolated by filtration as a white powder (108 mg, isolated yield 90%).

| **Mol Formula** | $C_{18}H_{15}B_3F_3N_3$ | **m.p.** | 269 °C |
|---|---|---|---|

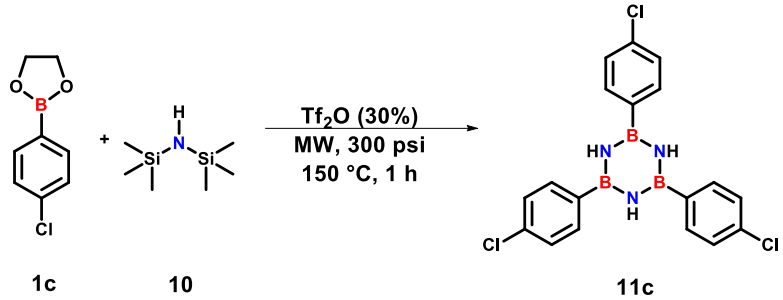
| | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| **$^1$H NMR 400 MHz $CDCl_3$** | 5.78 | 3 | *s* | - |
| | 7.14-7.18 | 6 | *m* | - |
| | 7.74-7.77 | 6 | *m* | - |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 164.38(d, $^1J_{C-F}$=249.24Hz), 133.91 (d, $^3J_{C-F}$=7.82Hz), 115.33 (d, $^2J_{C-F}$=20.13Hz). The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz, $CDCl_3$) δ: 33.20

**$^{19}$F NMR** (376.4 MHz, $CDCl_3$) δ: -110.56

| Chem. Name | ***B,B',B''*-tri(4-chlorophenyl)borazine (11c)** |
|---|---|




**1c** **10** **11c**

**M. W.: 412.124**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(4-chlorophenyl)-1,3,2-dioxaborolane (**1c**, 182 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and left at 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11c**) was then isolated by filtration as a white powder (90 mg, isolated yield 66%).

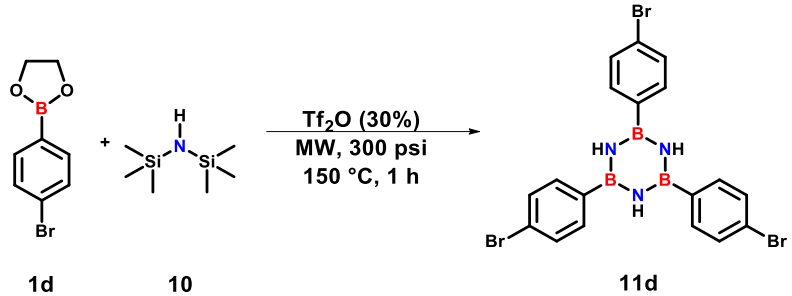
| **Mol Formula** | $C_{18}H_{15}B_3Cl_3N_3$ | **m.p.** | 260 °C |
|---|---|---|---|

| | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| **$^1$H NMR 400 MHz $CDCl_3$** | 5.82 | 3 | *s* | - |
| | 7.47 | 6 | *d* | 8.18 |
| | 7.71 | 6 | *d* | 8.25 |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ:136.44, 133.30, 128.51. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz**,** $CDCl_3$) δ: 33.23

| Chem. Name | ***B,B',B''*-tri(4-bromophenyl)borazine (11d)** |
|---|---|




**1d** **10** **11d**

**M. W.: 545.477**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(4-bromophenyl)-1,3,2-dioxaborolane (**1d**, 227 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and left at 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11d**) was then isolated by filtration as a white powder (164 mg, isolated yield 91%).

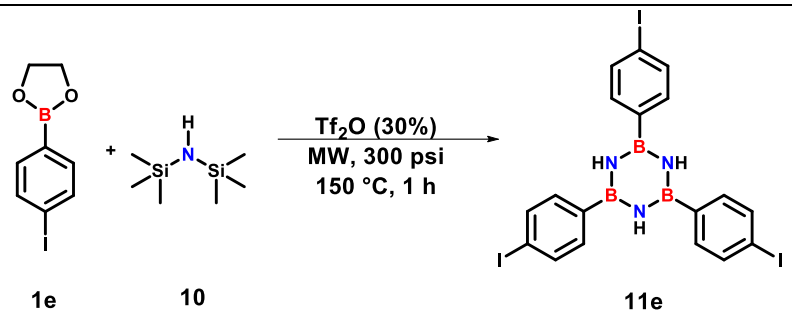
| **Mol Formula** | $C_{18}H_{15}B_3Br_3N_3$ | **m.p.** | 275 °C |
|---|---|---|---|

| | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| **$^1$H NMR 400 MHz $CDCl_3$** | 5.80 | 3 | *s* | - |
| | 7.59-7.63 | 12 | *m* | - |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 133.52, 131.45, 124.94. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz, $CDCl_3$) δ: 33.24

| Chem. Name | ***B,B',B''*-tri(4-iodophenyl)borazine (11e)** |
|---|---|




**1e** **10** **11e**

**M. W.: 686.478**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(4-iodophenyl)-1,3,2-dioxaborolane (**1e**, 274 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and left at 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11e**) was then isolated by filtration as a white powder (201 mg, isolated yield 89%).

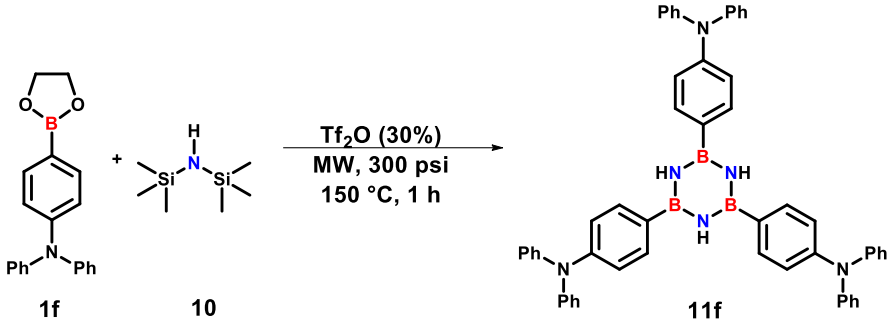
| **Mol Formula** | $C_{18}H_{15}B_3I_3N_3$ | **m.p.** | 260 °C |
|---|---|---|---|

| | δ **value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| **$^1$H NMR 400 MHz $CDCl_3$** | 5.79 | 3 | *s* | - |
| | 7.47 | 6 | *d* | 7.97 |
| | 7.81 | 6 | *d* | 8.04 |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 137.39, 133.56, 97.14. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz**,** $CDCl_3$) δ: 33.22

| Chem. Name | ***B,B′,B″*-tri(4- diphenylaminophenyl)borazine (11f)** |
|---|---|




**1f** **10** **11f**

**M. W.: 810.408**

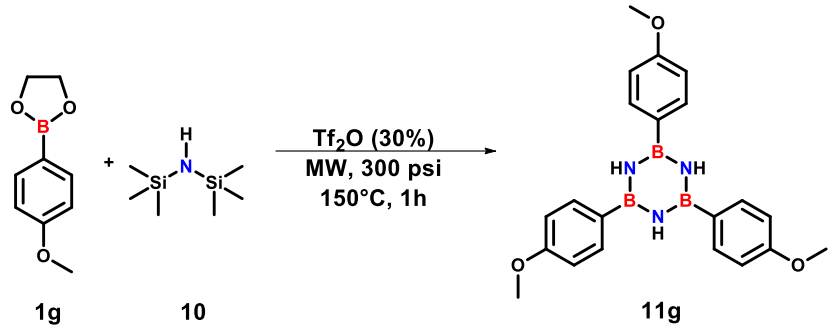
**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(4-(diphenylamino)phenyl)-1,3,2-dioxaborolane (**1f**, 315 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and left at 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11f**) was then isolated by filtration as a white powder (201 mg, isolated yield 75%).

| **Mol Formula** | $C_{54}H_{45}B_3N_6$ | **m.p.** | 268 °C |
|---|---|---|---|

| **$^1$H NMR** **400 MHz** **$CDCl_3$** | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| | 5.75 | 3 | *s* | - |
| | 7.03-7.14 | 24 | *m* | - |
| | 7.26-7.29 | 12 | *m* | - |
| | 7.63 | 6 | *d* | 8.39 |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ 149.53, 147.51, 132.97, 129.32, 124.80, 123.23, 122.55. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

| Chem. Name | ***B,B',B''*-tri(4-methoxyphenyl)borazine (11g)** |
|---|---|




**1g** **10** **11g**

**M. W.: 398.867**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(4-methoxyphenyl)-1,3,2-dioxaborolane (**1g**, 178 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and subjected to 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11g**) was then isolated by filtration as a white powder (125 mg, isolated yield 95%).

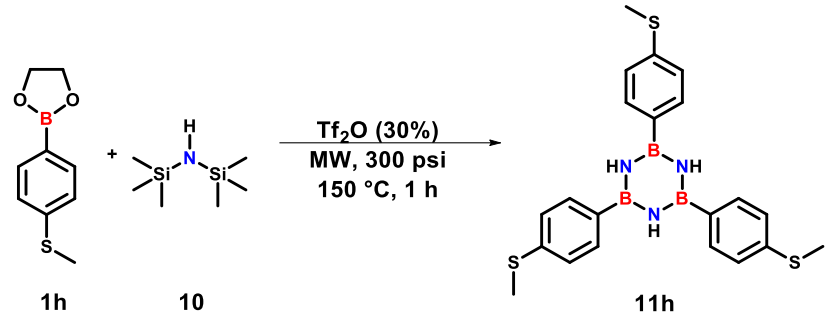
| **Mol Formula** | $C_{21}H_{24}B_3N_3O_3$ | **m.p.** | 160 °C |
|---|---|---|---|

| | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| **$^1$H NMR 400 MHz $CDCl_3$** | 3.87 | 9 | *s* | - |
| | 5.75 | 3 | *s* | - |
| | 7.00 | 6 | *d* | 8.53 |
| | 7.73 | 6 | *d* | 8.55 |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 161.21, 133.50, 113.75, 55.18. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz, $CDCl_3$) δ: 33.81

| Chem. Name | ***B,B',B''*-tri(4-(methylthio)phenyl)borazine (11h)** |
|---|---|




**1h** **10** **11h**

**M. W.: 447.063**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (**1h**, 194 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and subjected to 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11h**) was then isolated by filtration as a white powder (143 mg, isolated yield 97%).

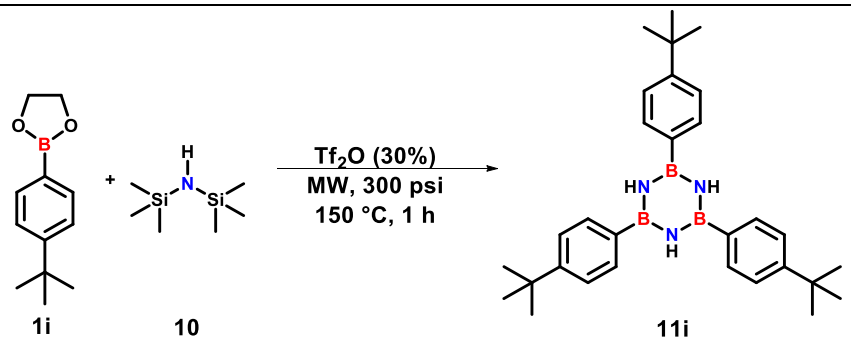
| **Mol Formula** | $C_{21}H_{24}B_3N_3S_3$ | **m.p.** | 197 °C |
|---|---|---|---|

| | δ **value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| **$^1$H NMR 400 MHz $CDCl_3$** | 2.53 | 9 | *s* | - |
| | 5.80 | 3 | *s* | - |
| | 7.34 | 6 | *d* | 8.15 |
| | 7.68 | 6 | *d* | 8.18 |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 141.03, 132.37, 125.80, 15.34. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz**,** $CDCl_3$) δ: 33.26

| Chem. Name | ***B,B',B''*-tri(4-tert-butylphenyl)borazine (11i)** |
|---|---|




**1i** **10** **11i**

**M. W.: 477.108**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(4-tert-butylphenyl)-1,3,2-dioxaborolane (**1i,** 204 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and subjected to 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11i**) was then isolated by filtration as a white powder (140 mg, isolated yield 89%).

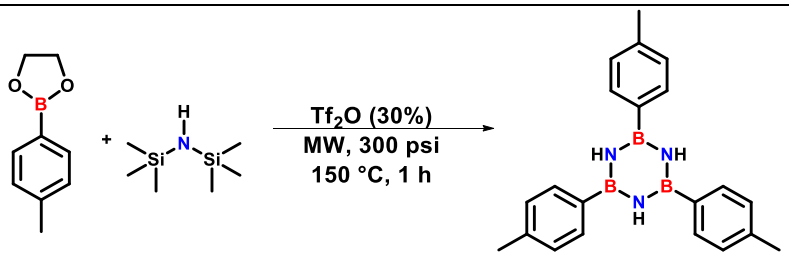
| **Mol Formula** | $C_{30}H_{42}B_3N_3$ | **m.p.** | 230 °C |
|---|---|---|---|

| | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| **$^1$H NMR** | 1.37 | 27 | *s* | - |
| **400** | 5.85 | 3 | *s* | - |
| **MHz** | 7.50 | 6 | *d* | 8.1 |
| **$CDCl_3$** | 7.72 | 6 | *d* | 8.0 |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 153.07, 131.85, 125.15, 34.79, 31.29. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz**,** $CDCl_3$) δ: 33.51

| Chem. Name | ***B,B′,B″*-tri(4-methylphenyl)borazine (11j)** |
|---|---|




**1j** **10** **11j**

**M. W.: 350.868**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(4-methylphenyl)-1,3,2-dioxaborolane (**1j**, 162 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and subjected to 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11j**) was then isolated by filtration as a white powder (113 mg, isolated yield 98%).

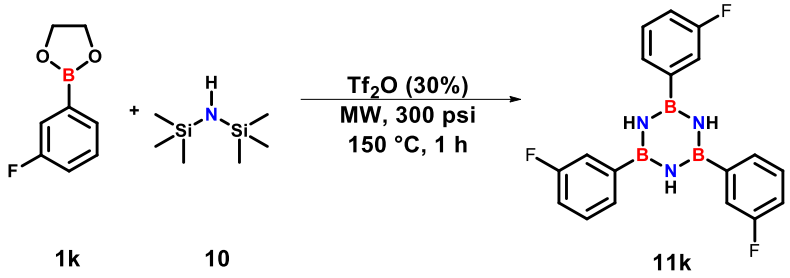
| **Mol Formula** | $C_{21}H_{24}B_3N_3$ | **m.p.** | 197 °C |
|---|---|---|---|

| **$^1$H NMR 400 MHz $CDCl_3$** | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| | 2.42 | 9 | *s* | - |
| | 5.84 | 3 | *s* | - |
| | 7.28 | 6 | *d* | 7.56 |
| | 7.69 | 6 | *d* | 7.65 |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 139.96, 132.00, 128.97, 21.56. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz**,** $CDCl_3$) δ: 33.22

| Chem. Name | ***B,B′,B″*-tri(3-fluorophenyl)borazine (11k)** |
|---|---|




**1k** **10** **11k**

**M. W.: 362.760**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(3-fluorophenyl)-1,3,2-dioxaborolane (**1k**, 166 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and subjected to 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11k**) was then isolated by filtration as an off-white powder (108 mg, isolated yield 90%).

| **Mol Formula** | $C_{18}H_{15}B_3F_3N_3$ | **m.p.** | 190 °C |
|---|---|---|---|

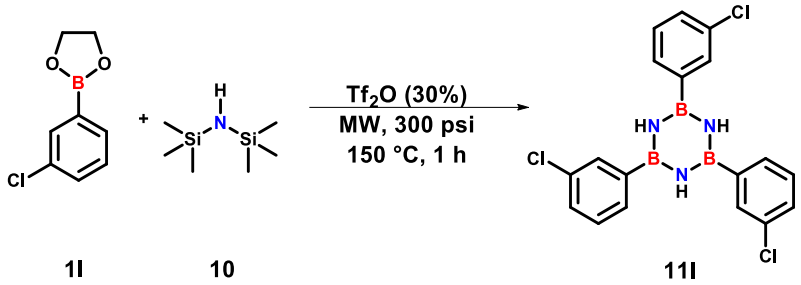
| **$^1$H NMR** **400 MHz** **$CDCl_3$** | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| | 5.84 | 3 | *s* | - |
| | 7.14-7.12 | 3 | *m* | - |
| | 7.41-7.48 | 6 | *m* | - |
| | 7.52-7.54 | 3 | *m* | - |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 163.01 (d, $^1J_{C\text{-}F}$= 247.4 Hz), 130.09 (d, $^4J_{C\text{-}F}$ = 7.3 Hz), 127.47 (d, $^3J_{C\text{-}F}$ = 2.9 Hz), 118.35 (d, $^2J_{C\text{-}F}$ = 18.9 Hz), 117.04 (d, $^2J_{C\text{-}F}$ = 21.1 Hz). The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz, $CDCl_3$) δ: 33.19

**$^{19}$F NMR** (376.4 MHz, $CDCl_3$) δ: -113.38

| Chem. Name | ***B,B′,B″*-tri(3-chlorophenyl)borazine (11l)** |
|---|---|




**1l** **10** **11l**

**M. W.: 412.124**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(3-chlorophenyl)-1,3,2-dioxaborolane (**1l**, 182 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and subjected to 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11l**) was then isolated by filtration as an white powder (117 mg, isolated yield 86%).

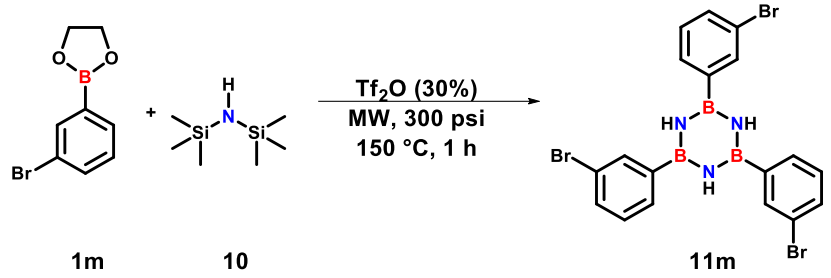
| **Mol Formula** | $C_{18}H_{15}B_3Cl_3N_3$ |
|---|---|

| **$^1$H NMR** **400 MHz** **$CDCl_3$** | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| | 5.83 | 3 | *s* | - |
| | 6-39-7.48 | 6 | *m* | - |
| | 7.63 | 3 | *d* | 7.09 |
| | 7.71 | 3 | *s* | - |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 134.65, 131.91, 130.20, 129.93, 129.75. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz**,** $CDCl_3$) δ: 32.91

| Chem. Name | ***B,B′,B″*-tri(3-bromophenyl)borazine (11m)** |
|---|---|




**1m** **10** **11m**

**M. W.: 545.477**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(3-bromophenyl)-1,3,2-dioxaborolane (**1m**, 227 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and subjected to 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11m**) was then isolated by filtration as an white powder (128 mg, isolated yield 71%).

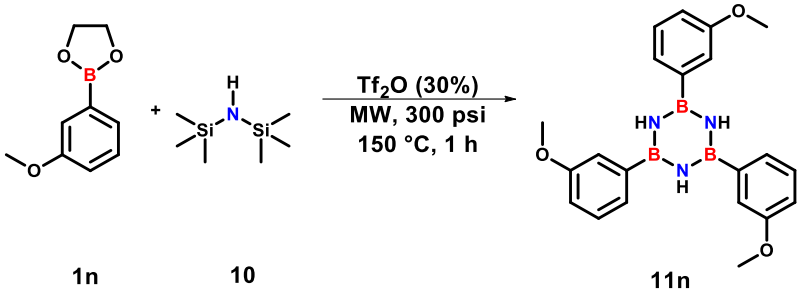
| **Mol Formula** | $C_{18}H_{15}B_3Br_3N_3$ | **m.p.** | 175 °C |
|---|---|---|---|

| **$^1$H NMR** **400 MHz** **$CDCl_3$** | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| | 5.81 | 3 | *s* | - |
| | 7.36 | 3 | *d* | 7.6 |
| | 7.71-7.58 | 6 | *m* | - |
| | 7.87 | 3 | *m* | - |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ:134.84, 133.13, 130.39, 130.06, 123.15.The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz**,** $CDCl_3$) δ:33.03

| Chem. Name | ***B,B′,B″*-tri(3-methoxyphenyl)borazine (11n)** |
|---|---|




**1n** **10** **11n**

**M. W.: 398.867**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(3-methoxyphenyl)-1,3,2-dioxaborolane (**1n**, 178 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and subjected to 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11n**) was then isolated by filtration as an white powder (125 mg, isolated yield 95%).

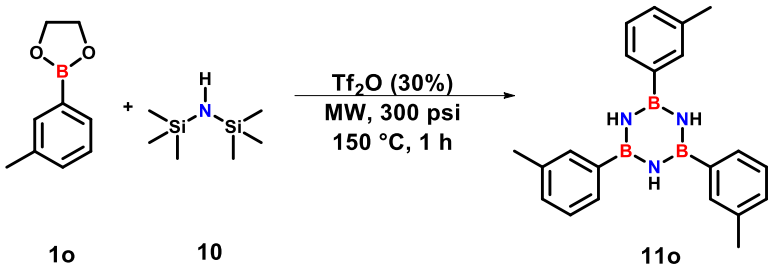
| **Mol Formula** | $C_{21}H_{24}B_3N_3O_3$ | **m.p.** | 144 °C |
|---|---|---|---|

| **$^1$H NMR** **400 MHz** **$CDCl_3$** | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| | 3.88 | 9 | *s* | - |
| | 5.85 | 3 | *s* | - |
| | 7.00-7.03 | 3 | *m* | - |
| | 7.28-7.29 | 3 | *m* | - |
| | 7.34-7.42 | 6 | *m* | - |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ: 159.46, 129.46, 124.26, 117.52, 115.15, 55.29. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz, $CDCl_3$) δ: 33.57

| Chem. Name | ***B,B′,B″*-tri(m-tolyl)borazine (11o)** |
|---|---|




**1o** **10** **11o**

**M. W.: 350.868**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(m-tolyl)-1,3,2-dioxaborolane (**1o**, 162 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) was added dropwise. The vessel was placed in the microwave synthesizer and subjected to 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11o**) was then isolated by filtration as an white powder (70 mg, isolated yield 60%).

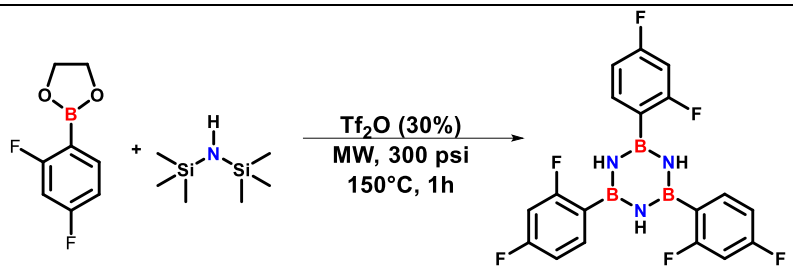
| **Mol Formula** | $C_{21}H_{24}B_3N_3$ | **m.p.** | 140 °C |
|---|---|---|---|

| **$^1$H NMR** **400 MHz** **$CDCl_3$** | **δ value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| | 2.45 | 9 | *s* | - |
| | 5.87 | 3 | *s* | - |
| | 7.29-7.31 | 3 | *m* | - |
| | 7.35-7.39 | 3 | *m* | - |
| | 7.59 | 6 | *s* | - |

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ:137.55, 132.70, 130.73, 129.00, 128.14, 21.59. The signal for the carbon atom attached to boron atom was not detected because of the quadrupolar relaxation of the boron atom.

**$^{11}$B NMR** (128 MHz**,** $CDCl_3$) δ: 33.46

| Chem. Name | *B,B′,B″*-tri(2,4- difluorophenyl)borazine (11p) |
|---|---|




**1p** **9** **10p**

**M. W.: 416.731**

**METHOD:** A microwave vessel, pre-dried in oven, was evacuated and flushed with argon. To the vessel, 1 mmol of 2-(2,4-difluorophenyl)-1,3,2-dioxaborolane (**1p**, 184 mg) was added, followed by another cycle of evacuation and argon filling. Next, 1 mL of HMDS (**10**) was introduced and 30 mol% of $Tf_2O$ (50 µL) were added dropwise. The vessel was placed in the microwave synthesizer and subjected to 150 °C for 1 hour at 150 W microwave power, with a pressure of 300 psi (20.7 bar), high mixing, and PowerMax enabled. After cooling to room temperature, 3 mL of heptane were added, and the mixture was stirred for 30 minutes. The product (**11p**) was then isolated by filtration as an white powder (132 mg, isolated yield 96%).

| **Mol Formula** | $C_{18}H_{12}B_3F_6N_3$ | **m.p.** | 210 °C |
|---|---|---|---|

| **$^1$H NMR** 400 MHz $CDCl_3$ | δ **value** | **No. H** | **Mult.** | **j value/Hz** |
|---|---|---|---|---|
| | 6.28 | 3 | *s* | - |
| | 6.84-6.89 | 3 | *m* | - |
| | 6.96-7.01 | 3 | *m* | - |
| | 7.62-7.68 | 3 | *m* | - |

**$^{11}$B NMR** (128 MHz, $CDCl_3$) δ: 31.69

**$^{19}$F NMR** (376.4 MHz, $CDCl_3$) δ: -106.89, -103.05

## 8. References

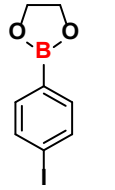

(1) Ranjani, G.; Nagarajan, R. Insight into Copper Catalysis: In Situ Formed Nano Cu $_2$ O in Suzuki–Miyaura Cross-Coupling of Aryl/Indolyl Boronates. *Org. Lett.* **2017**, *19* (15), 3974–3977. https://doi.org/10.1021/acs.orglett.7b01669.

(2) Ishiyama, T.; Murata, M.; Miyaura, N. Palladium(0)-Catalyzed Cross-Coupling Reaction of Alkoxydiboron with Haloarenes: A Direct Procedure for Arylboronic Esters. *J. Org. Chem.* **1995**, *60* (23), 7508–7510. https://doi.org/10.1021/jo00128a024.

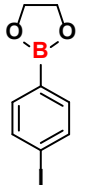
(3) Kaupp, G.; Naimi-Jamal, M. R.; Stepanenko, V. Waste-Free and Facile Solid-State Protection of Diamines, Anthranilic Acid, Diols, and Polyols with Phenylboronic Acid. *Chem. – Eur. J.* **2003**, *9* (17), 4156–4161. https://doi.org/10.1002/chem.200304793.

(4) Liu, C.; Guo, Z.; Weng, J.; Lu, G.; Chan, A. S. C. Chiral 1,1′-binaphthylazepine-derived Amino Alcohol Catalyzed Asymmetric Aryl Transfer Reactions with Boroxine as Aryl Source. *Chirality* **2010**, *22* (1), 159–164. https://doi.org/10.1002/chir.20721.


## 9. Copies of NMR spectra



**1e, 80%**

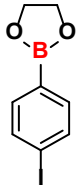


**1e, 80%**

31.66

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

ppm

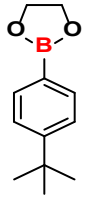


**1e, 80%**

137.11
136.33
99.15
77.34
77.02
76.70
66.14

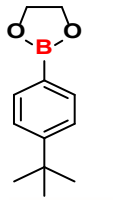
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm



**1i, 82%**


7.77
7.75
7.43
7.41
7.26
4.37
1.55
1.33
2.00
2.13
4.06
9.23
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

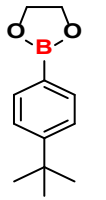


**1i, 82%**

31.64

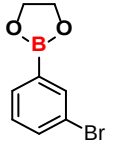
200 150 100 50 0 -50 -100 -150 -200 -250

ppm



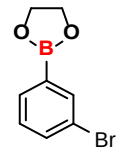
**1i, 82%**


154.72
134.76
124.85
77.34
77.02
76.71
65.98
31.19
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
B
O
Br

**1m, 89%**


7.89
7.68
7.66
7.56
7.54
7.23
7.21
7.19
4.33
1.56
0.83
0.94
0.93
1.11
4.19
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

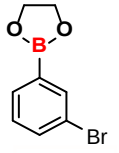



**1m, 89%**

31.14

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

ppm

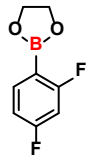



**1m, 89%**

137.62
134.43
133.19
129.65
122.50
77.36
77.05
76.73
66.18

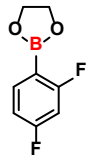
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm


O
B
O
F
F

**1p, 84%**

7.78
7.76
7.74
7.72
7.26
6.92
6.91
6.90
6.89
6.88
6.87
6.82
6.82
6.80
6.79
6.78
6.77
4.40
1.56
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
0.95
1.00
0.96
4.08
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

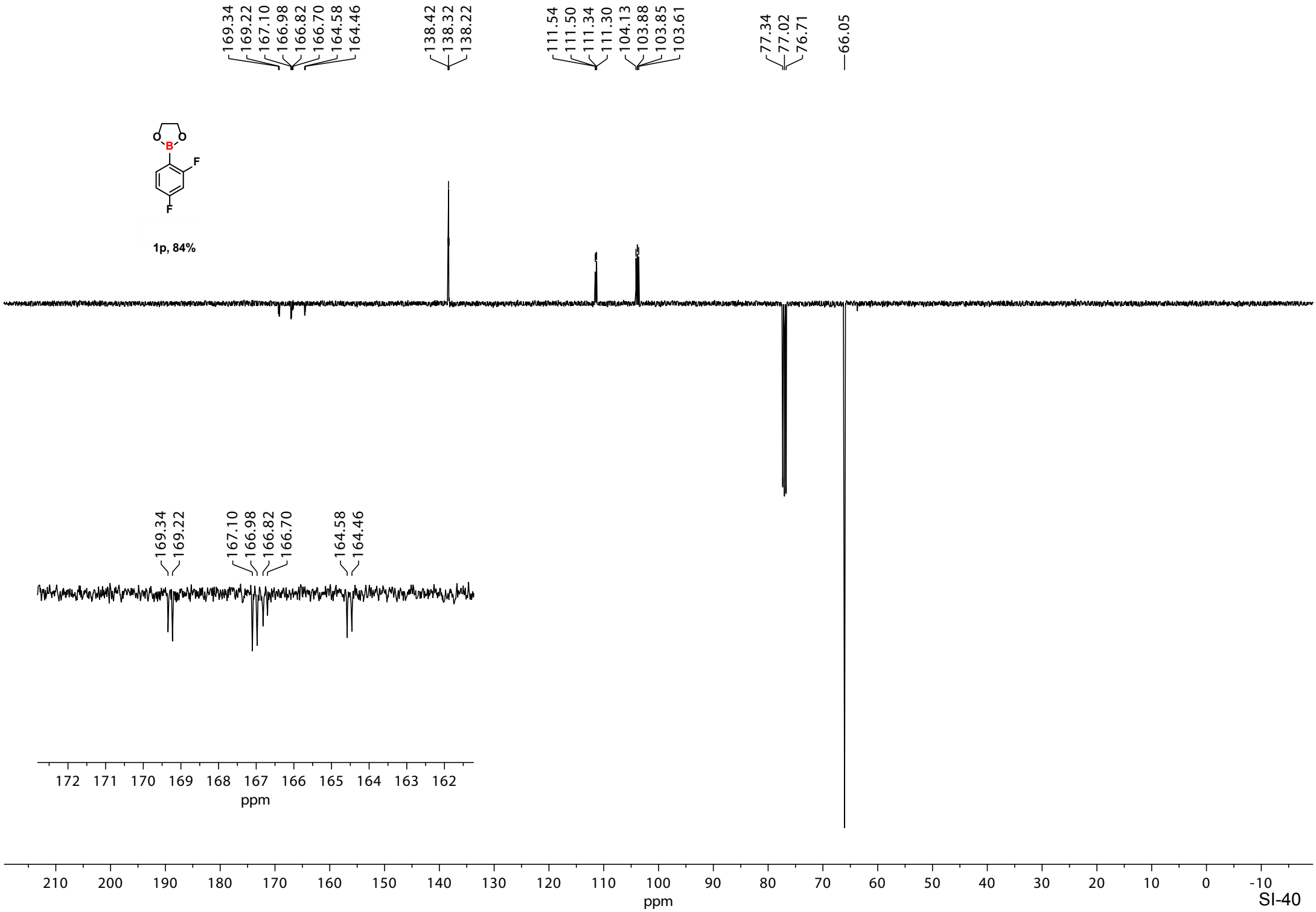


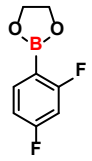

**1p, 84%**

30.67

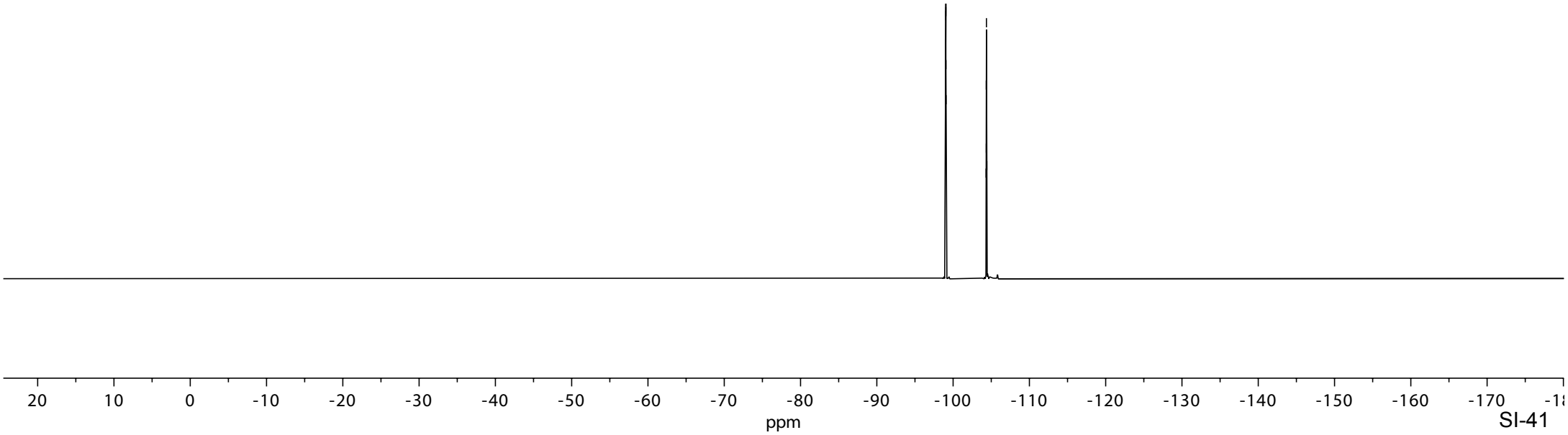
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

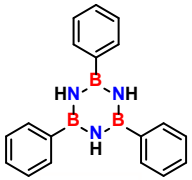
ppm


169.34
169.22
167.10
166.98
166.82
166.70
164.58
164.46
138.42
138.32
138.22
111.54
111.50
111.34
111.30
104.13
103.88
103.85
103.61
77.34
77.02
76.71
66.05
1p, 84%
172 171 170 169 168 167 166 165 164 163 162
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



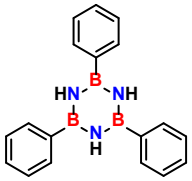
1p, 84%


-99.00
-99.02
-99.03
-99.05
-99.06
-99.08
-104.32
-104.35
-104.35
-104.37
-104.39
-104.40
-104.42
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
ppm


HN
B
NH
B
B
N
H

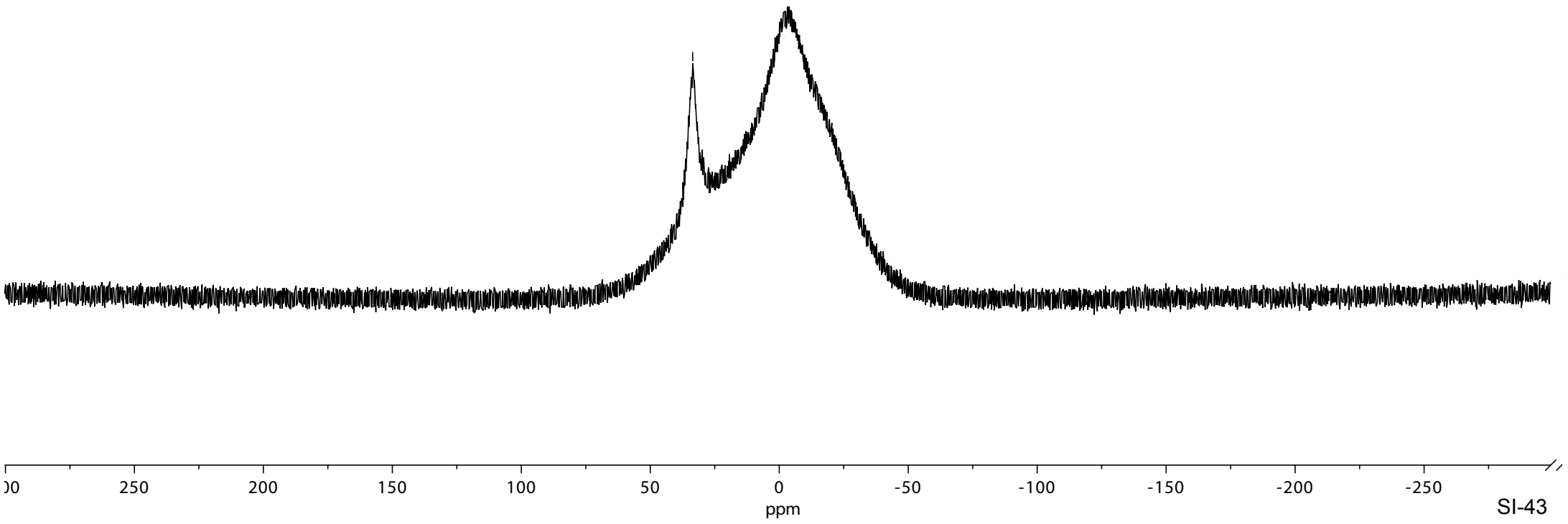
**11, 98%**

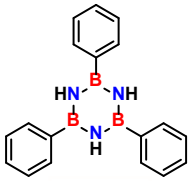

7.80
7.80
7.79
7.78
7.49
7.48
7.48
7.47
7.47
7.46
7.26
5.91
1.54
6.00
8.96
2.70
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm




**11, 98%**

33.55





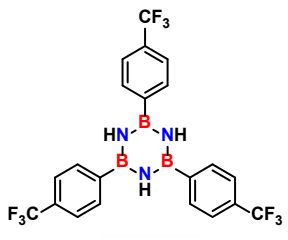

**11, 98%**

131.94
130.03
128.22

77.34
77.02
76.70

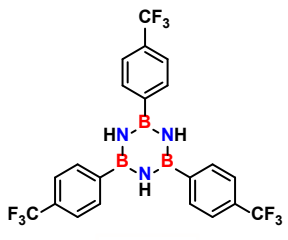
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

ppm


CF3
HN
B
NH
B
N
H
B
F3C
CF3

**11a, 98%**


7.89
7.87
7.74
7.72
7.26
5.94
1.55
6.00
5.94
2.74
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

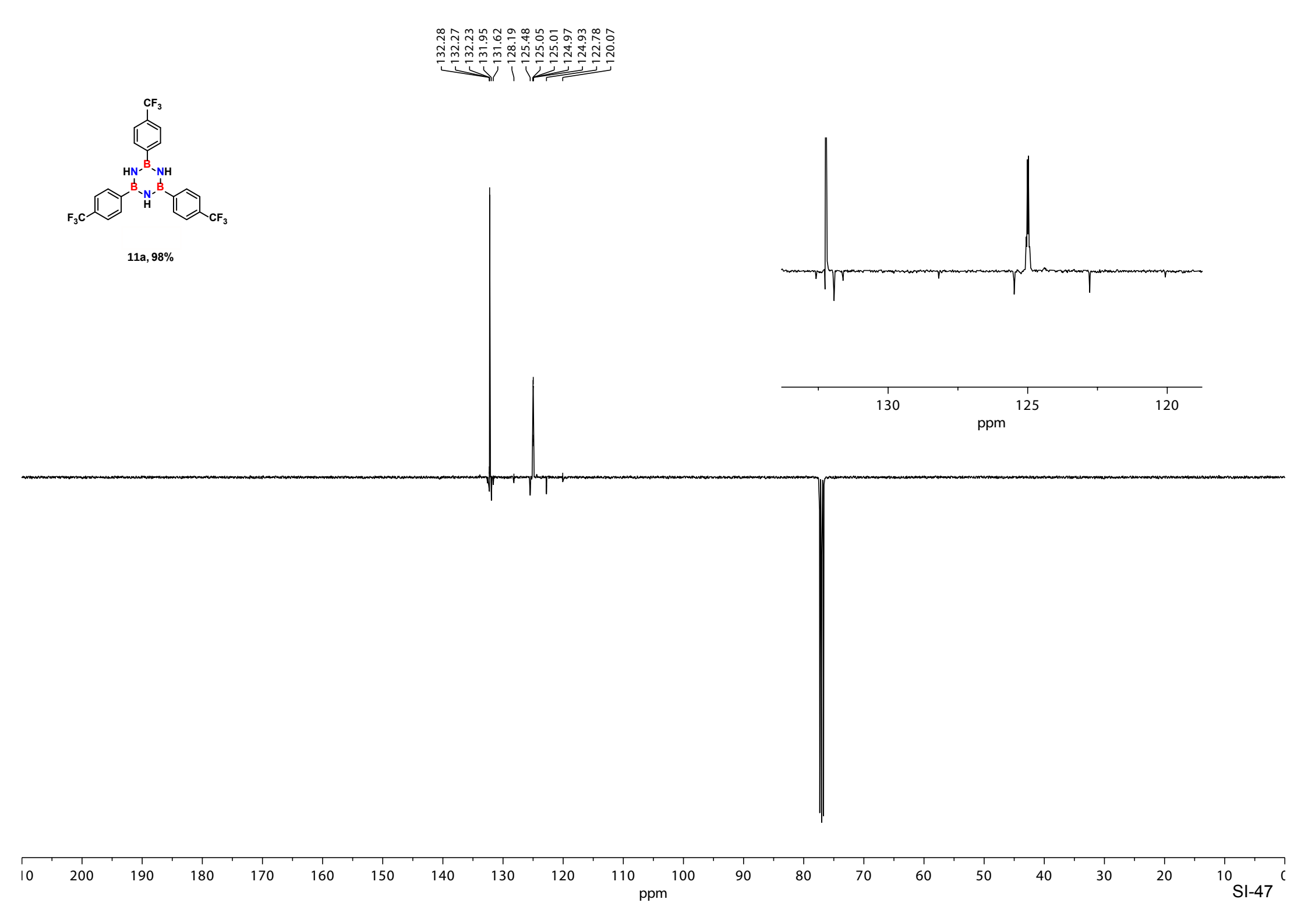


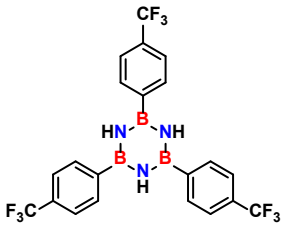

11a, 98%

33.42

200 150 100 50 0 -50 -100 -150 -200

ppm


132.28
132.27
132.23
131.95
131.62
128.19
125.48
125.05
125.01
124.97
124.93
122.78
120.07
CF3
HN
B
NH
B
B
N
H
F3C
CF3
11a, 98%
130
125
120
ppm
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

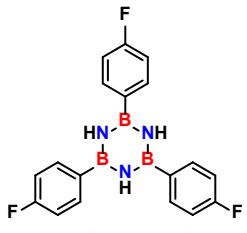



**11a, 98%**

-62.88

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -15

ppm



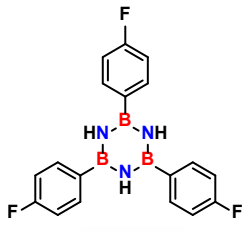

**11b, 90%**

7.77
7.76
7.75
7.74
7.26
7.18
7.16
7.14
5.78
1.54

6.00
5.87
2.73

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

ppm

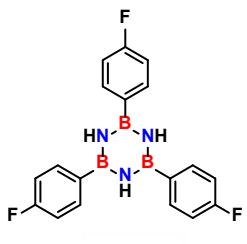



11b, 90%

33.20

250 200 150 100 50 0 -50 -100 -150 -200 -250 -300

ppm

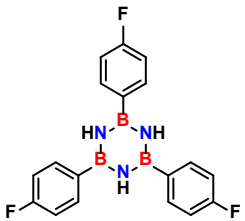



**11b, 90%**

165.63
163.15
133.94
133.86
115.42
115.22
77.32
77.01
76.69

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm



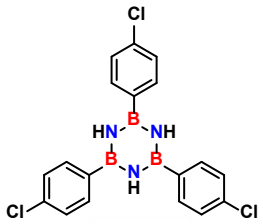

**11b, 90%**

110.52
110.53
110.54
110.55
110.56
110.57
110.57
110.58
110.60

110.52
110.53
110.54
110.55
110.56
110.57
110.57
110.58
110.60

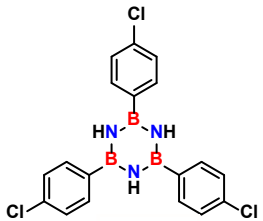
-110.40
-110.50
-110.60
-110.70
-110.80
ppm

20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
ppm


Cl
HN
NH
B
B
B
N
H
Cl
Cl

**11c, 66%**


7.72
7.70
7.48
7.46
7.28
5.82
1.56
6.00
5.74
2.74
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

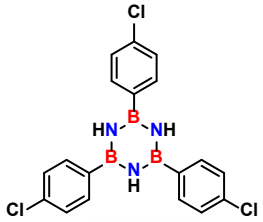



11c, 66%

33.23

250 200 150 100 50 0 -50 -100 -150 -200 -250 -30

ppm



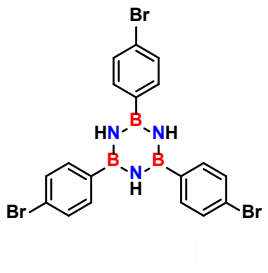

**11c, 66%**

136.44
133.30
128.51

77.32
77.01
76.69

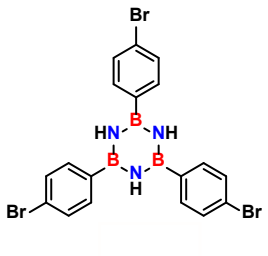
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

ppm


Br
B
HN
NH
B
B
N
H
Br
Br

**11d, 91%**


7.63
7.63
7.61
7.61
7.59
7.59
7.26
5.80
1.54
12.00
2.89
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

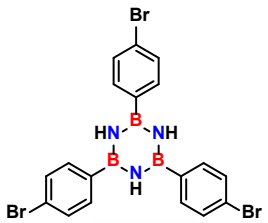



11d, 91%

33.24

200 150 100 50 0 -50 -100 -150 -200

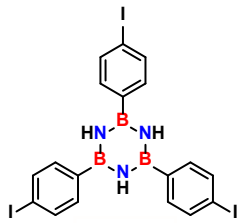
ppm




11d, 91%

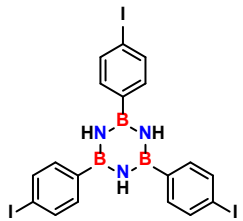
133.52
131.45
124.94
77.34
77.02
76.70

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm



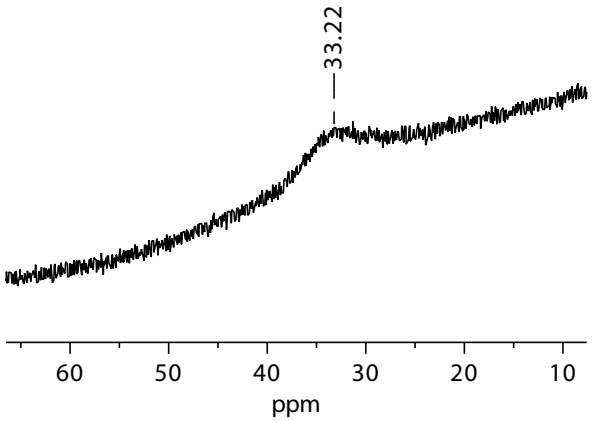
**11e, 89%**


7.82
7.80
7.48
7.46
7.26
5.79
1.54
6.00
5.97
2.72
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



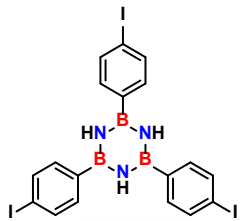

**11e, 89%**

33.22




200 150 100 50 0 -50 -100 -150 -200

ppm

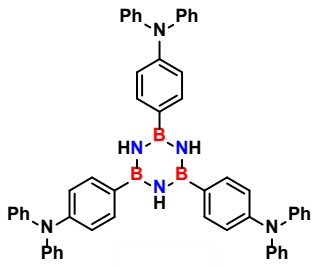



11e, 89%

137.39
133.56
97.14
77.34
77.02
76.70

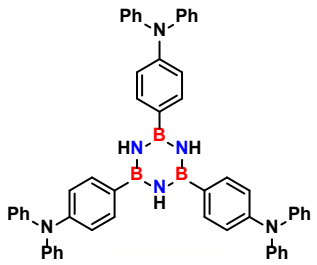
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm


Ph
N
Ph
B
HN
NH
B
N
B
H
Ph
N
Ph
Ph
N
Ph

**11f, 75%**


7.64
7.62
7.29
7.28
7.26
7.14
7.14
7.13
7.12
7.07
7.05
7.03
5.75
1.56
6.00
12.01
24.16
2.71
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

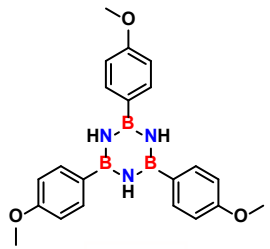



**11f, 75%**

149.53
147.51
132.97
129.32
124.80
123.23
122.55
77.34
77.02
76.70

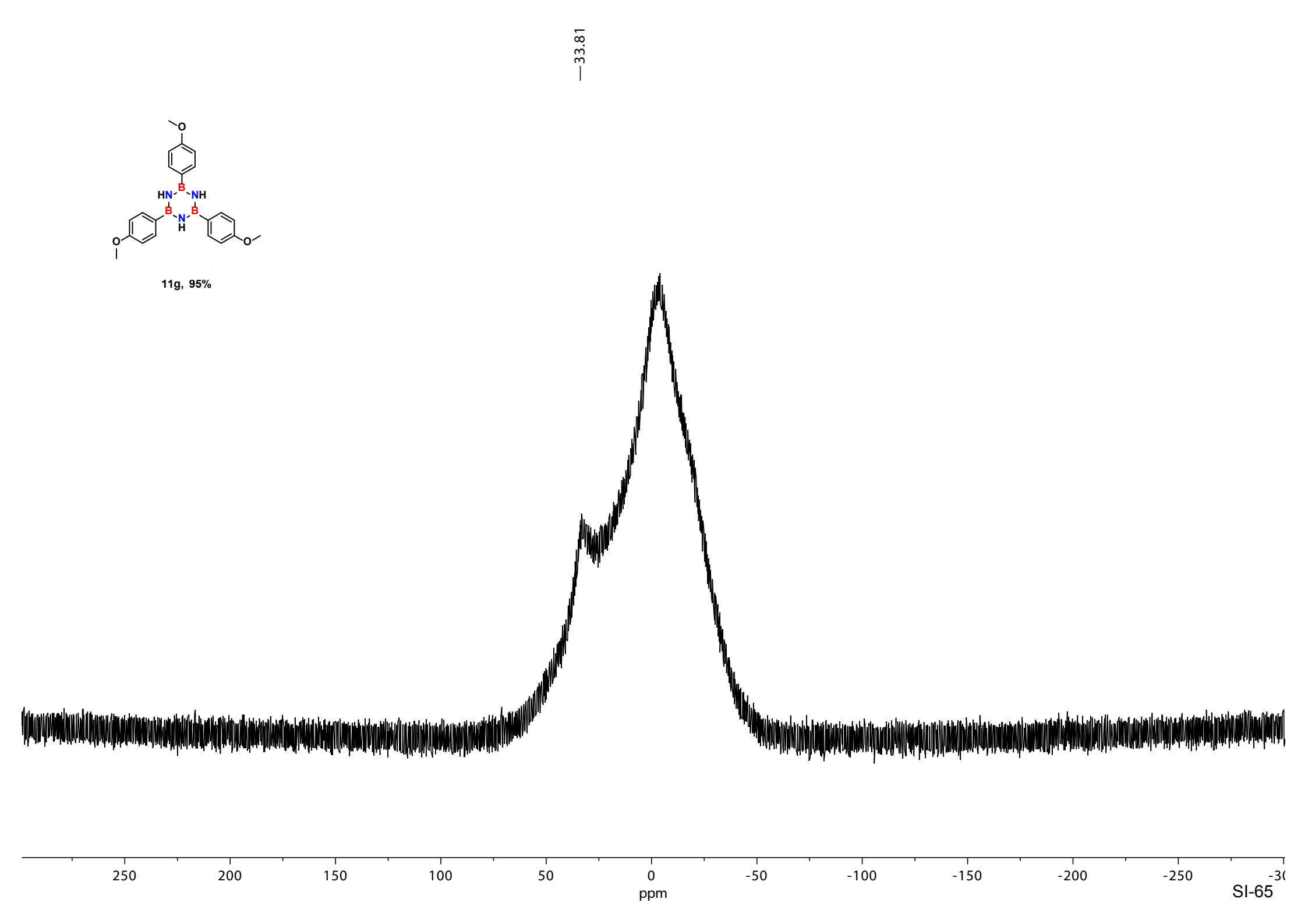
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

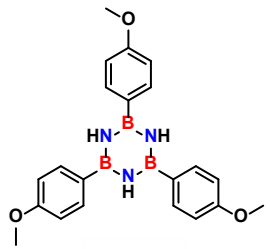
ppm



11g, 95%


7.74
7.72
7.26
7.01
6.99
5.75
3.87
1.55
6.09
6.07
2.83
9.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


33.81
11g, 95%
250
200
150
100
50
0
-50
-100
-150
-200
-250
ppm

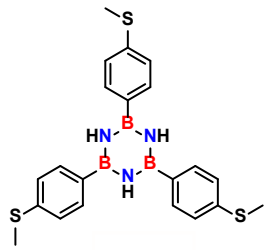



11g, 95%

161.21
133.50
113.75
77.34
77.02
76.71
55.18

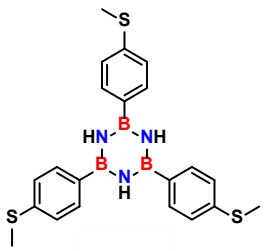
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

ppm



11h, 97%


7.70
7.67
7.35
7.32
7.26
5.80
2.53
1.55
6.00
5.67
2.67
8.81
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

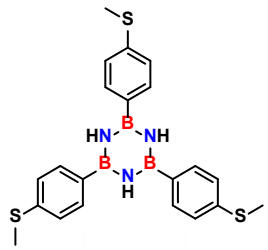



11h, 97%

33.26

250 200 150 100 50 0 -50 -100 -150 -200 -250

ppm

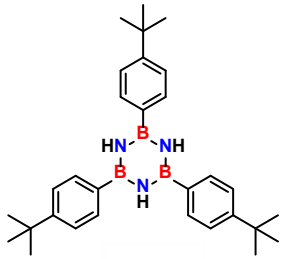


11h, 97%

141.03
132.37
125.80
77.34
77.02
76.70
15.34

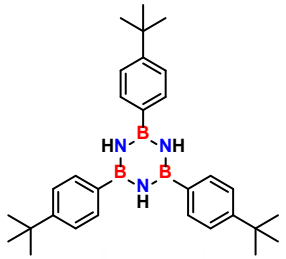
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm



11i, 89%


7.73
7.71
7.51
7.49
7.26
5.85
1.54
1.37
6.00
6.10
2.52
27.31
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

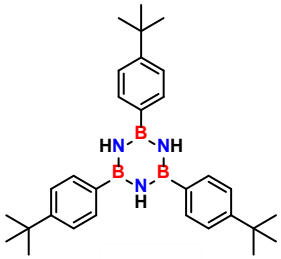


11i, 89%

33.51

250 200 150 100 50 0 -50 -100 -150 -200 -250 -300

ppm

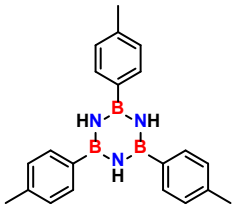



**11i, 89%**

153.07
131.85
125.15
77.34
77.02
76.70
34.79
31.29

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

ppm



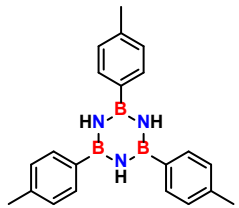

**11j, 98%**

7.70
7.68
7.29
7.27
7.26
5.84
2.42
1.54

6.00
5.94
2.71
8.85

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

ppm

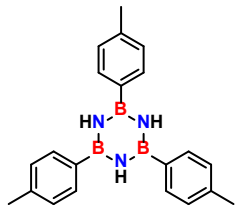


11j, 98%

33.22

250 200 150 100 50 0 -50 -100 -150 -200 -250

ppm

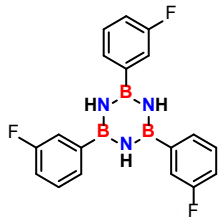



**11j, 98%**

139.96
132.00
128.97
77.34
77.02
76.70
21.56

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

ppm



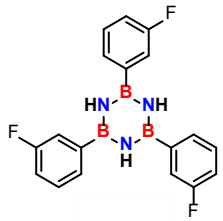

**11k, 90%**

7.54
7.52
7.48
7.46
7.46
7.44
7.42
7.42
7.41
7.26
7.20
7.19
7.19
7.19
7.17
7.17
7.15
7.15
7.14
5.84

3.00
6.14
3.00
2.73

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

ppm

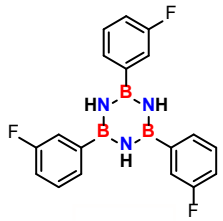



**11k, 90%**

33.19

250 200 150 100 50 0 -50 -100 -150 -200 -250

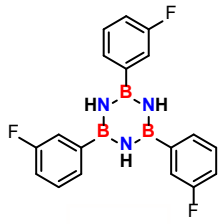
ppm




**11k, 90%**

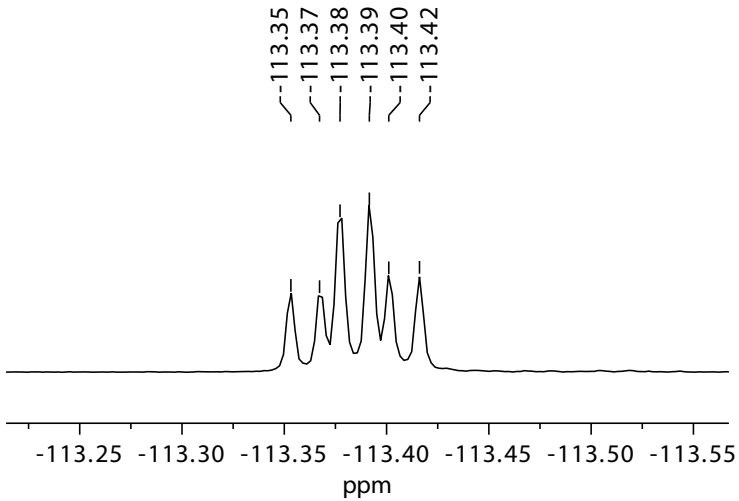
164.25
161.79
130.12
130.04
127.48
127.45
118.43
118.24
117.14
116.93
77.32
77.01
76.69

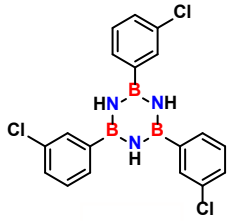
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm




**11k, 90%**

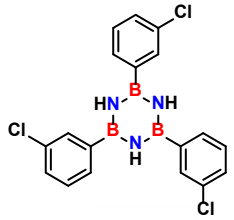
-113.35
-113.37
-113.38
-113.39
-113.40
-113.42




Cl
B
HN
NH
Cl
B
B
N
H
Cl

**11l, 86%**


7.71
7.64
7.62
7.48
7.47
7.47
7.46
7.45
7.45
7.43
7.41
7.39
7.26
5.83
1.54
3.00
3.20
6.32
2.77
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

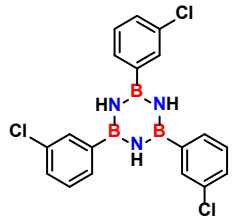



**11l, 86%**

32.91

250 200 150 100 50 0 -50 -100 -150 -200 -250 -3(

ppm



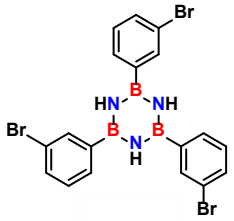

**11l, 86%**

134.65
131.91
130.20
129.93
129.75

77.32
77.01
76.69

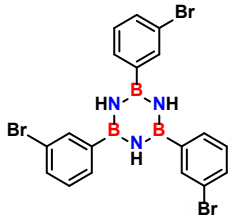
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

ppm


Br
HN
B
NH
Br
B
B
N
H
Br

**11m, 71%**


7.87
7.68
7.67
7.62
7.62
7.60
7.60
7.37
7.35
7.33
7.26
5.81
1.53
3.00
6.35
3.01
2.99
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

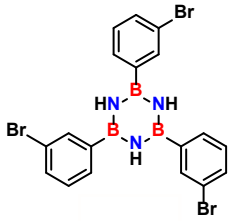



11m, 71%

33.03

250 200 150 100 50 0 -50 -100 -150 -200 -250

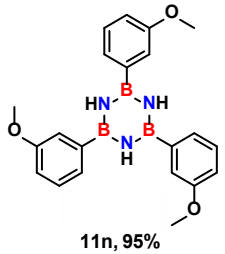
ppm




11m, 71%

134.84
133.13
130.39
130.06
123.15
77.34
77.02
76.70

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm




11n, 95%

7.42 7.41 7.39 7.36 7.34 7.34 7.34 7.29 7.28 7.28 7.28 7.26 7.03 7.03 7.03 7.02 7.01 7.01 7.01 7.00 5.85

3.88

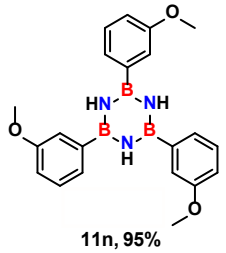
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.

ppm

6.34 3.25 3.00 2.74 8.74

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

ppm

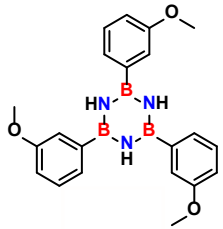



11n, 95%

33.57

250 200 150 100 50 0 -50 -100 -150 -200 -250

ppm

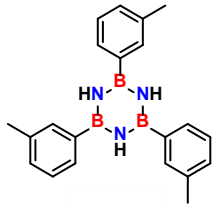



**11n, 95%**

159.46
129.46
124.26
117.52
115.15
77.34
77.02
76.70
55.29

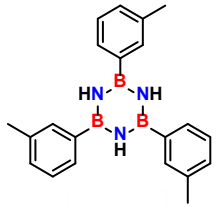
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

ppm



**11o, 60%**


7.59
7.39
7.37
7.35
7.31
7.29
7.26
5.87
2.45
1.55
6.00
3.08
3.11
2.72
9.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

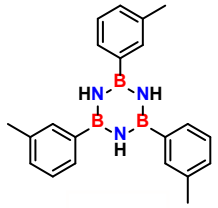


**11o, 60%**

33.46

250 200 150 100 50 0 -50 -100 -150 -200 -250 -30

ppm

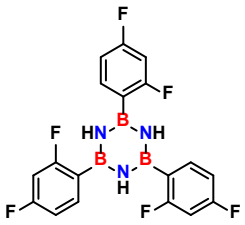


**11o, 60%**

137.55
132.70
130.73
129.00
128.14
77.34
77.02
76.71
21.59

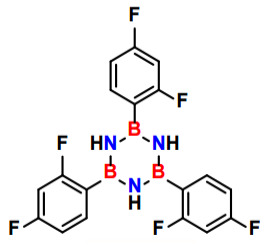
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

ppm



11p, 96%


7.68
7.66
7.64
7.62
7.26
7.01
7.00
6.99
6.98
6.97
6.96
6.89
6.89
6.87
6.86
6.86
6.84
6.84
6.28
1.53
3.00
2.99
2.93
2.68
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

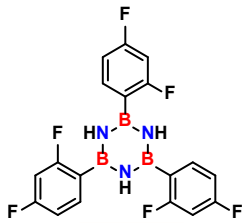


**11p, 96%**

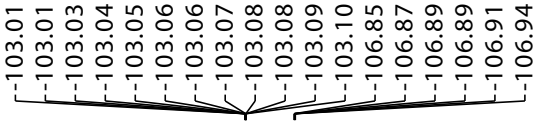
31.69

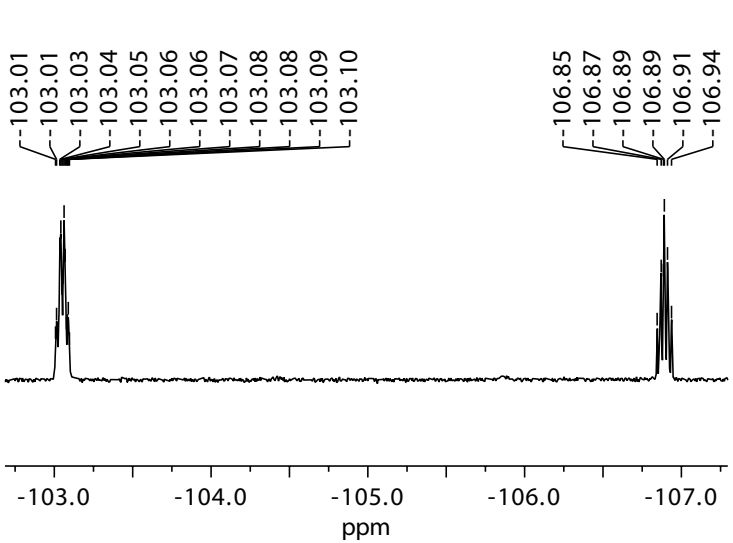
250 200 150 100 50 0 -50 -100 -150 -200 -250

ppm


F
F
F
HN
B
NH
B
N
H
B
F
F
F

11p, 96%


-103.01
-103.01
-103.03
-103.04
-103.05
-103.06
-103.06
-103.07
-103.08
-103.08
-103.09
-103.10
-106.85
-106.87
-106.89
-106.89
-106.91
-106.94


-103.01
-103.01
-103.03
-103.04
-103.05
-103.06
-103.06
-103.07
-103.08
-103.08
-103.09
-103.10
-106.85
-106.87
-106.89
-106.89
-106.91
-106.94
-103.0
-104.0
-105.0
-106.0
-107.0
ppm


10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm