Electronic Supplementary Information

Efficient access to hexaaryl-Substituted borazines in batch and continuous-flow.

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1. General Remarks

Unless otherwise stated, chemicals were purchased from Merck, TCI, Fluorochem and used as obtained from commercial sources without further purification except for liquid aniline derivatives that were distilled over CaH_2 before using. Solvents were purchased from Merck and dried following standard procedure. Commercial basic scavengers were dried in glass oven (Buchi, B-585) under vacuum for 24h at 120ºC. 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 376 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). 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. (4-bromo-3,5-dimethylphenoxy)(tert-butyl)dimethylsilane was prepared as reported in the literature. [2]

2. General procedures A: Co-solvents screening to solubilize B,B',B''-trichloro-N,N',N''-triarylborazine mixture

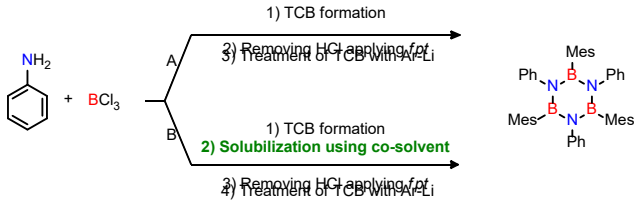


Figure S1. Screening of co-solvent under batch-synthesis procedure

B,B',B''-trichloro-N,N',N''-triphenylborazine was synthesized according to the previously reported procedure. [2] A dried Schlenk tube (25 mL) was filled with freshly distilled aniline (0.3 mL, 3.3 mmol, 1.0 equiv.) and dry toluene (6.0 mL) then stirred for 1 minute before cooling to approximately -10°C (acetone/ice). Then BCl_3 (1M in heptane, 4.0 mL, 4.0 mmol, 1.2 equiv.) was slowly added (preferably with a glass syringe) to the aniline solution and the white reaction mixture was stirred at the same temperature for 1 hour to complete the complexation. For large-scale syntheses, BCl_3 was added using a syringe pump. The rubber septum was replaced by a dry Vigreux condenser, and a bent drying tube filled with granular $CaCl_2$ was placed on the condenser. The resulting white suspension was heated at 110 °C in an oil bath for 18 h before switching the condenser with a new rubber septum. Heating was then stopped, and the reaction mixture was gradually cooled to 40 °C. Dried Co-solvent (6-10 ml as indicated in Table S1) was added to the reaction mixture at the same temperature to make a transparent solution. After cooling down to r.t., the excess HCl was removed by five freeze-pump-thaw cycles. As a control, the reaction was also performed without solubilization with co-solvent (pathway A of Figure S1). It is worth mentioning that in the case of 4-tert-butyl- or -isopropyl aniline, the co-solvent can be added at room temperature because the solubility of B,B',B''-trichloro-N,N',N''-triaryl borazines is affected by aniline derivatives. [3]

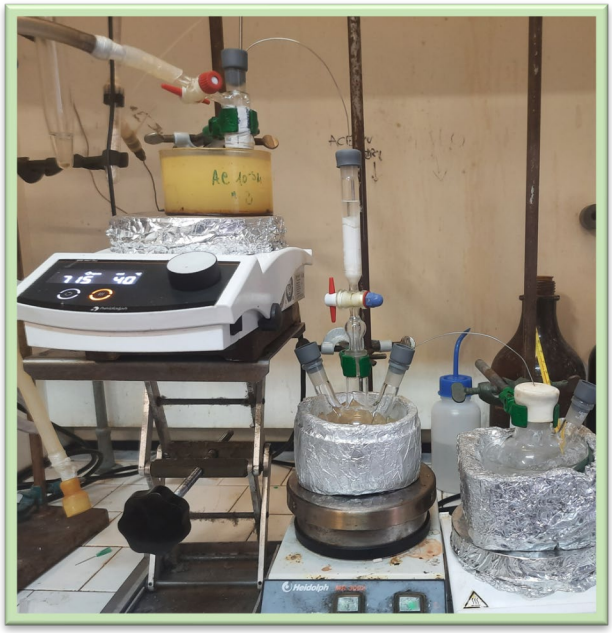
To prepare aryl lithium, n-BuLi (1.6 M in hexane, 5.0 mL, 8.0 mmol) was added dropwise to a solution of 2-bromomesitylene (0.8 mL, 5.3 mmol) in anhydrous THF (10 mL) at -78 °C in a flame-dried flask. The solution was gradually warmed to 0 °C without changing the bath. Once the temperature of 0 °C was reached, the flask was transferred to an ice/water bath and the solution was stirred at 0 °C for 10 minutes. The solution of the chloroborazine derivative was slowly cannulated to the Mes-Li solution at 0 °C, gradually warmed to room temperature and stirred for 24 hours. The chloroborazine solution should be cooled to 0 °C during cannulation and, most importantly, the transferring process should be performed very slowly (approximately over 30 minutes). The reaction was quenched with water (30 mL) and extracted with EtOAc (3x30 mL). The organic phase was washed with brine (2x20 mL), dried over sodium sulfate, and the solvents were removed under reduced pressure to give a dark brown oil. Dichloromethane (1 mL) was added to the residue and methanol was added to precipitate the product, which was filtered off to give HAB as a white solid.

Table S1: amount of cosolvent used to solubilize TCB

Entry	Co-solvent	Amount of co-solvent	Yield (%)
1	- (Control)	-	49
2	Tetrahydrofuran	9	31
3	Cyclopentyl methyl ether	10	27
4	Anisole	8	38
5	1,2-Dimethoxyethane (DME)	8	45
6	1,2-Dimethoxyethane (DME)	10	41
7	1,2-Dimethoxyethane (DME)	12	34
8	2-MeTHF	6	45
9	2-MeTHF	12	45
10	Diethyl ether	8	19
11	*o*-Dichlorobenzene	10	<10
12	Dichloromethane	6	trace
13	1,2-Dichloroethane	6	<10

Following the cessation of the reaction, the reaction vessel was allowed to cool gradually without removing it from the oil bath. TCB began to precipitate around 64°C. At this temperature, a co-solvent was added to dissolve it, and the cooling process was continued. The second portion of the co-solvent was added when TCB began to precipitate again.

3. General procedures B: scavenger screening to remove hydrochloric acid from B,B',B''-trichloro-N,N',N''-triarylborazine solution:



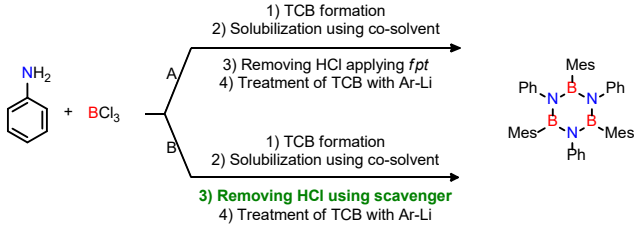


Figure S2. screening of basic scavenger under batch synthesis procedure

The synthesis and solubilization of B,B',B''-trichloro-N,N',N''-triphenylborazine was carried out as described in general procedure A (flask A). The scavenging process was designed with the ultimate goal of converting to a continuous flow process in mind. 10 mmol of a dried basic scavenger was mixed with quartz beads (1 mm, 50 wt% scavenger) and transferred to a dropping funnel (25 mL). The solids were well packed, and argon was passed through the scavenger for 20 minutes. The packing of the scavenger is very important, and it is necessary to check that the solids are not mobile before starting the process. The filled dropping funnel was placed on a dried three-neck flask (flask 2), where the solution was supposed to be cooled before being transferred to the aryl lithium solution. In parallel, the organolithium solution was prepared in a three-neck flask (flask C) as described in the general procedure A. The entire process is depicted above; the chloroborazine solution was slowly passed through the scavenger by purging argon to flask A and transferred with a cannula into the dropping funnel filled with purging medium and collected in flask B. Purging argon affect residence time of solution in the scavenging media that should be slow in order to efficient removing hydrochloric acid. Transferring of cleaned as well as cooled solution of chloroborazine into the Ar-Li solution at 0 °C was carried out simultaneously with a cannula. After 24h, the product was extracted and isolated similar to the procedure described in general procedure A. As a control, HCl was removed from the chloroborazine solution applying 5 cycles freeze-pump-thaw.

^{11}B NMR analysis was conducted before and after the scavenging step to assess the compatibility of the scavenger with TCB. Peaks observed in the range of 19-25 ppm were identified as hydrolyzed boron species, while the peak around 31 ppm represents TCB.

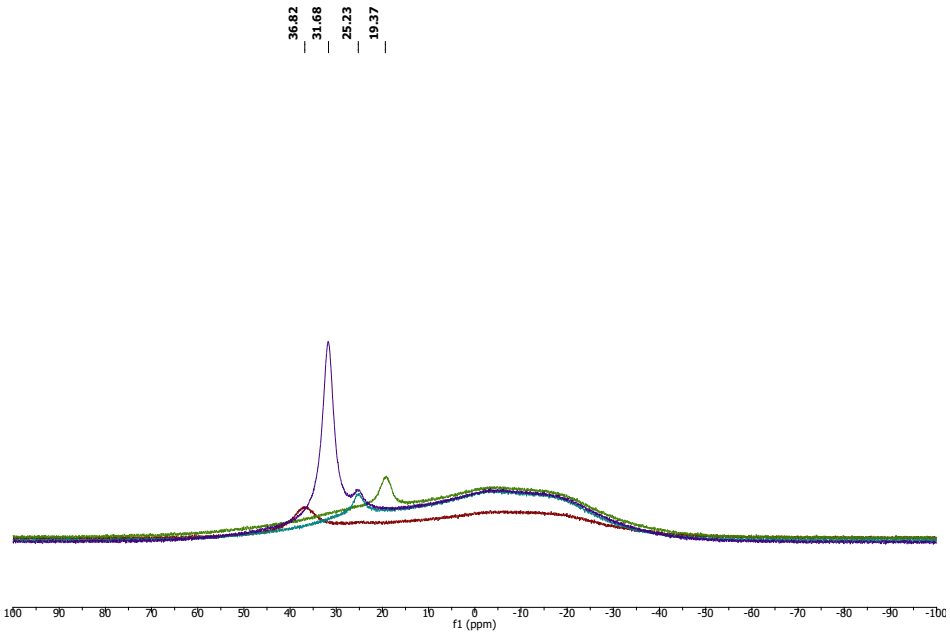


Figure S 3. Different boron peaks observed in the screening of scavenger.

In some instances, when Amberlyst A21 free base was used, various forms of boron were observed, as depicted in Figure S4.

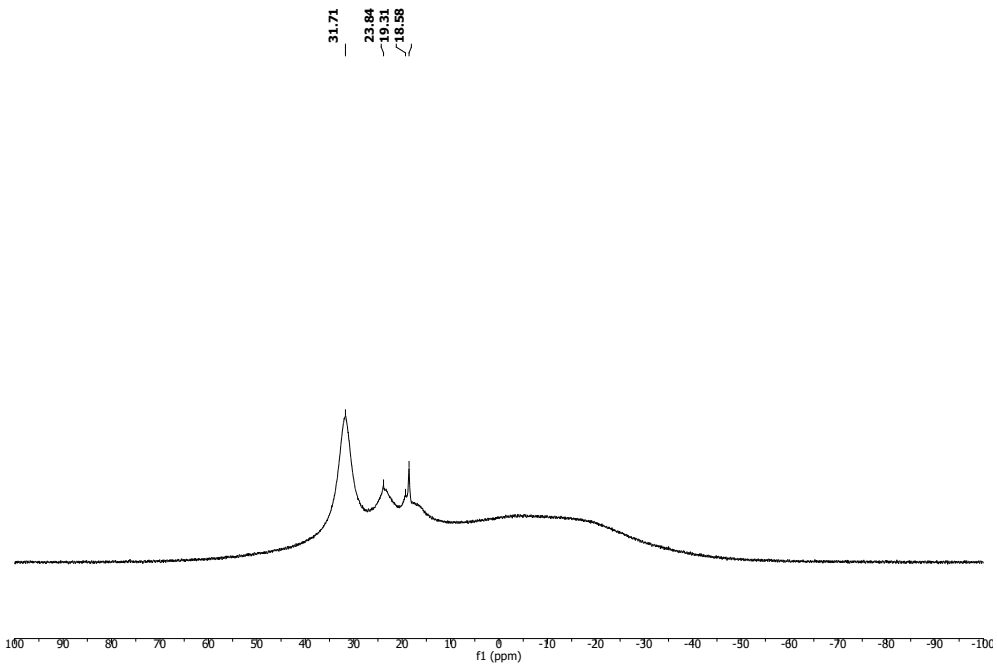


Figure S 4. ^{11} B NMR after scavnging HCl using Amberlyst A21 free base.

4. General information about the flow system assembling.

The flow system was fabricated using T-shaped tube connector with inner diameter made by Natural Peek and PTFE tubes. The mixer and tube reactors were connected with Peek fittings. The entire reactor was oven dried (3 hours at 120°C), and inert gas was purged into the reactor before introducing the solutions into the system. To introduce the solutions into the reactor programmable high- pressure syringe pumps (KF Technology, NE-1010) and plastic syringes (Polypropylene onfarma syringes) were used. The reactor temperature was adjusted by dipping the reactor in a cooling bath. All solutions were prepared under dry conditions before being loaded into syringes. The BuLi solution was prepared by diluting a commercial solution (n-BuLi: 1.6 M in hexane or tBuLi: 1.7 M in pentane) in dry 2-MeTHF. Basic scavenger combined with quartz beads were loaded in an Omnifit column and well packed. The implementation of a scavenger filled cartridge in the flow system necessitates the use of an appropriate backpressure regulator (replaceable BPR assembled in a PEEK holder, Upchurch) for homogenization of the flow in the reactor.

5. General procedure C: Synthesis of HABs under continuous flow procedure:

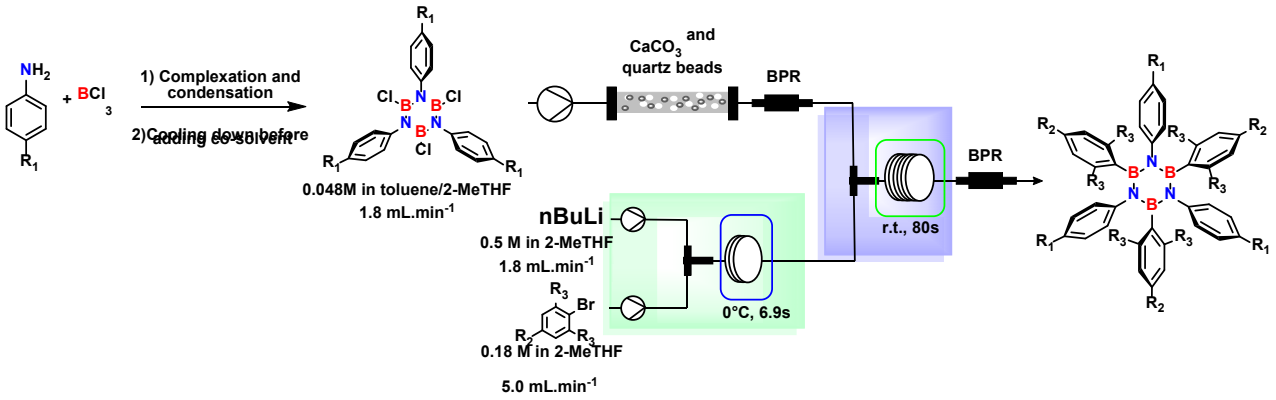


Figure S5. Continuous flow procedure for the synthesis of HABs

Preparation of solution A (TCB solution): Synthesis of TCB was carried out as described in general procedure A in detail. In a dry Schlenk tube (25 mL), freshly distilled 4-tBu aniline (0.5 mL, 3.1 mmol, 1.0 equiv.) was dissolved in toluene (5 mL) and stirred for one minute before cooling down to -10°C. Then BCl_3 (1M in heptane, 3.8 mL, 3.8 mmol) was slowly added to the aniline solution using a glass syringe. Immediate formation of a white solid was appeared by addition of BCl_3. In the middle of BCl_3 addition reaction mixture become a transparent solution but it again turned into a white suspension at the end of the addition. After stirring for 1 hour, septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on head and heated at 110°C for 18 h. Then condenser was replaced with a septum and cooled gradually to room temperature before addition of freshly distilled 2-MeTHF (12 mL) to prepare TCB solution.

Preparation of solution B (n-BuLi): A dry flask (50 mL) was charged with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial n-BuLi (1.6M in hexane, 7 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5M solution.

Preparation of solution C: In a dry flask 2-bromomesitylene (11.2 mmol, 1.5mL) was dissolved in freshly distilled 2-MeTHF (60.8 mL).

Preparation of scavenger filled Omnifit column: $CaCO_3$ (1 g) mixed with quartz beads (0.5 g, 1.0 mm) were transferred in a tube and dried in a Buchi glass oven B-585(overnight at 100°C). It was then loaded in a Omnifit column (25 mL) and packed.

Assembling the flow system: The system was set up as above and after purging Ar for 30 minutes the system was run as follow. The solutions were introduced using plastic syringe (60 mL), in case of larger scale, larger syringes should be used, or fast changing syringe C is possible for multi-gram scales. Solution A and B were mixed with PEEK T-mixer and reacted in reactor A (Br-Li exchange reaction) made by PTFE tube (100cm, ID:1.0 mm at 0°C) with flow rate of 1.8 $mL.min^{-1}$ and 5.0 $mL.min^{-1}$ respectively. Solution C was passed through the scavenger before mixing with prepared Ar-Li using similar mixer and reacting in reactor B (PTFE tube, ID:1.0 mm, 800cm at room temperature).

Extraction and isolation of products were performed as follows:

After collecting the whole reaction mixture, 10 mL of water were added to quench the solution and the resultant mixture was stirred for 5 minutes. The mixture was transferred in a separatory funnel and aqueous phase was removed. The organic portion was dried with Na_2SO_4 and distilled at a temperature of 50 °C under reduced pressure of 500 mbar for 10 minutes. After this time, hexane has completely removed, and the pressure is lowered to 350 mbar. At this pressure, only 2-MeTHF was distilled and recovered (average 90 % over multiple repetition) for 20-30 minutes. The final mixture (composed of toluene and heptane) is distilled-off further reducing the pressure to 100-50 mbar. MeOH (5 mL) was added to the crude mixture to precipitate white solids and then filtered off to give HABs.

6. Large-Scale procedure in flow for the synthesis of B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-tris(4-tert-Butylphenyl)-borazine (HAB1)

Preparation of solution A (TCB solution): In a dry Schlenk tube (100 mL), freshly distilled 4-tBu aniline (1.6 mL, 10.06 mmol, 1.0 equiv.) was dissolved in toluene (18 mL) and stirred for one minute before cooling down to -10°C. Then BCl_3 (1M in heptane, 12.0 mL, 12 mmol) was slowly added to the aniline solution using a glass syringe. Immediate formation of a white solid was appeared by addition of BCl_3. In the middle of BCl_3 addition reaction mixture become a transparent solution but it again turned into a white suspension at the end of the addition. After stirring for 1 hour, septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on head and heated at 110°C for 18 h. Then condenser was replaced with a septum and cooled gradually to room temperature before addition of freshly distilled 2-MeTHF (38 mL) to prepare TCB solution.

Preparation of solution B (n-BuLi): A dry flask (50 mL) was charged with dry 2-MeTHF (50 mL) and cooled to 0°C. Commercial n-BuLi (1.6M in hexane, 22.8 mL) was diluted in 2-MeTHF to obtain a 0.5M solution.

Preparation of solution C: In a dry flask 2-bromomesitylene (36.57 mmol, 5.6mL) was dissolved in freshly distilled 2-MeTHF (194 mL).

Preparation of scavenger filled Omnifit column: $CaCO_3$ (4 g) mixed with quartz beads (0.5 g, 1.0 mm) were transferred in a tube and dried in a Buchi glass oven B-585(overnight at 100°C). It was then loaded in a Omnifit column and packed.

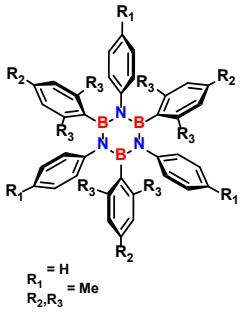
Assembling the flow system: The system was set up as above and after purging Ar for 30 minutes the system was run as follow. The solutions were introduced using plastic syringe. Solution A and B were mixed with PEEK T-mixer and reacted in reactor A (Br-Li exchange reaction) made by PTFE tube (100cm, ID:1.0 mm at 0°C) with flow rate of 1.8 $mL.min^{-1}$ and 5.0 $mL.min^{-1}$ respectively. Solution C was passed through the scavenger before mixing with prepared Ar-Li using similar mixer and reacting in reactor B (PTFE tube, ID:1.0 mm, 800cm at room temperature).

Extraction and isolation of products were performed as follows:

After collecting the whole reaction mixture, 20 mL of water were added to quench the solution and the resultant mixture was stirred for 5 minutes. The mixture was transferred in a separatory funnel and aqueous phase was removed. The organic portion was dried with Na_2SO_4 and distilled at a temperature of 50 °C under reduced pressure of 500 mbar for 10 minutes. After this time, hexane has completely removed, and the pressure is lowered to 350 mbar. At this pressure, only 2-MeTHF was distilled and recovered (in 90% of the original mass, 254 mL) for 20-30 minutes. The final mixture (composed of toluene and heptane) is distilled-off further reducing the pressure to 100-50 mbar. MeOH (5 mL) was added to the crude mixture to precipitate white solids and then filtered off to give 2.0 g of B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-tris(4-tert-Butylphenyl)-borazine (HAB1) in 78% yield.

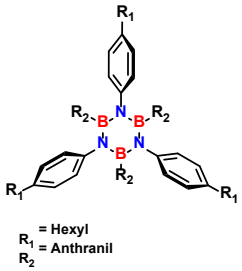
7. E-factor Calculation

Bonifazi et. al: *Chem. Eur. J.* 2013, **19**, 7771–7779



E-factor: ($4.72_{[BCl3\ 1M\ toluene]} + 0.37_{[aniline]} + 6.94_{[toluene]} + 2.58_{[nBuLi\ 1.36\ in\ hexane]} + 0.87_{[2\text{-}Br\text{-}mesitilene]} + 8.89_{[THF]} + 20_{[water]} + 54.12_{[EtOAc]} - 0.353_{[product]}$) / $0.353_{[product]}$ = **278.00**

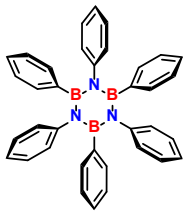
Yamaguchi et al: *J. Am. Chem. Soc.* 2005, **127**, 14859–14866



E-factor: ($5.31_{[BCl3\ 1M\ hexane]} + 1.00_{[4\text{-}hexyl\text{-}aniline]} + 6.50_{[toluene]} + 5.00_{[tBuLi\ 1.47\ in\ pentane]} + 1.45_{[9\text{-}Br\text{-}Anthracene]} + 10.67_{[THF]} + 10_{[water]} + 89.4^{a}_{[CHCl3]} - 1.43_{[product]}$) / $1.43_{[product]}$ = **89.44**

[a] Exact volume of solvent has not been reported by Yamaguchi. Therefore, this value has been set to 20 mL for a reaction scale of 1-10 mmol.

Groszos et. al: *J. Am. Chem. Soc.* 1958, ***80***, 1357–1360

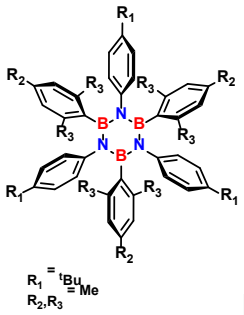


E-factor: ($50.00_{[BCl3]} + 30.40_{[aniline]} + 173.40_{[toluene1]} + 86.70_{[toluene2]} + 2.58_{[nBuLi\ 1.36\ in\ hexane]} + 15.20_{[Ph\text{-}Br]} + 2.36_{[Mg]} + 142.60_{[Et2O\text{-}reaction]} + 142.60^{a}_{[Et2O\text{-}workup]} + 59.60^{b}_{[CHCl3]} - 32.60_{[product\text{-}1st\text{-}step]} + 10_{[product\text{-}1st\ step\ used\ in\ 2nd\ step}$) $- 8.50_{[product\ 2nd\ step]}$ / $8.50_{[product]}$ = **79.33**

[a] Exact volume of solvent has not been reported by Groszos. Therefore, we have considered 5 portions of 40 mL solvent for a reaction scale of 10-50 mmol.

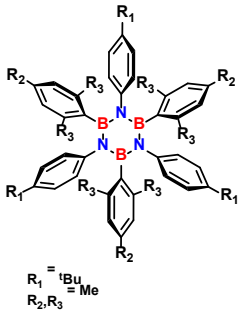
[b] Exact volume of solvent has not been reported by Groszos. Therefore, we have considered one 40 mL portion of solvent for a reaction scale 10-50 mmol

This work (small Scale in flow)



E-factor: ($2.81_{[BCl3\ 1M\ heptane]}$ + $0.47_{[4\text{-}tertbutyl\text{-}aniline]}$ + $4.33_{[toluene]}$ + $4.76_{[nBuLi\ 1.6\ in\ hexane]}$ + $2.21_{[2\text{-}Br\text{-}mesitilene]}$ + $10.25_{[2\text{-}MeTHF1]}$ + $65.10_{[2\text{-}MeTHF2]}$ + $10_{[water]}$ + $3.96_{[MeOH]}$ – $0.636_{[product]}$ – $67.80_{[recovered\ 2\text{-}MeTHF]}$) / $0.636_{[product]}$ = **55.74**

This work (Large Scale in flow)



E-factor: ($8.88_{[BCl3\ 1M\ heptane]}$ + $1.49_{[4\text{-}tertbutyl\text{-}aniline]}$ + $15.60_{[toluene]}$ + $15.50_{[nBuLi\ 1.6\ in\ hexane]}$ + $7.28_{[2\text{-}Br\text{-}mesitilene]}$ + $32.45_{[2\text{-}MeTHF1]}$ + $208.37_{[2\text{-}MeTHF2]}$ + $20_{[water]}$ + $3.96_{[MeOH]}$ – $2.08_{[product]}$ – $216.70_{[recovered\ 2\text{-}MeTHF]}$) / $2.08_{[product]}$ = **45.55**

8. Safety Hazard index and Benign Index Calculation

Safety Hazard Index and Benign index for the reaction solvent input were calculated based on Andraos algorithms[5,6] using BAP, BCP, INHTP, and INGTP to assess the Benign index and FP, CGP, CLP, OELP, RPP to assess the Safety Hazard index. Data were taken from Andraos tables.[7]

Benign Index parameters

Solvent	BAP	BCP	INHTP	INGTP	OMEGA(BI)
Heptane	85.11380	29.29544	0.44207	0.00038	114.8517
Hexane	14.79108	7.74818	0.31392	0.00009	22.85329
Pentane	5.24807	3.52533	0.17389	0.00214	8.94944
Toluene	1.00000	1.00000	0.99745	1.21684	4.21430
THF	0.00537	0.01882	2.36422	27.06701	29.45543
2-MeTHF	0.03388	0.07634	3.57847	0.33633	4.02503
Diethyl ether	0.01445	0.03995	0.53598	3.35009	3.94048

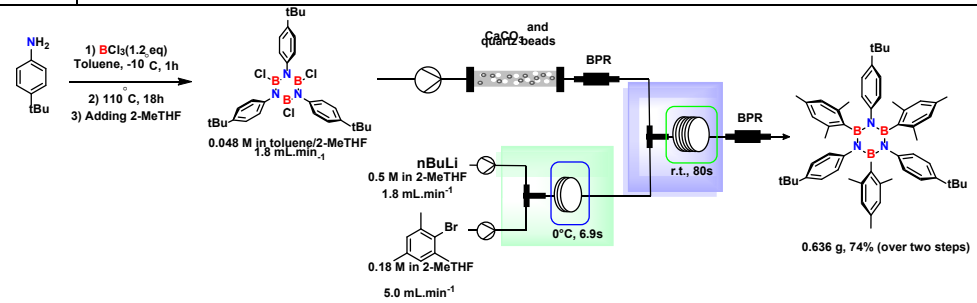
Safety Hazard index parameters

Solvent	FP	CGP	CLP	OELP	RPP	OMEGA(SHI)
Heptane	0.86624	0.00504	0.12720	0.33170	0.64677	1.97697
Hexane	0.93204	0.00308	0.02544	1.99023	2.44293	5.39372
Pentane	1.04015	0.00142	0.31800	0.16585	0.64677	2.17220
Toluene	0.84124	0.01061	1	1.99023	1.00000	4.84213
THF	0.89967	0.03301	0.38545	0.39804	1.59638	3.31257
2-MeTHF	0.88599	0.03537	0.31800		3.00014	4.23951
Diethyl ether	1.02191	0.00470	0.52345	0.24877	1.47485	3.27371

Solvent	Bonifazi (f)	BI	SI	Yamaguchi (f)	BI	SI	Groszos (f)	BI	SI	This work (f)	BI	SI
Heptane										0.03	3.155	0.054
Hexane	0.10	2.317	0.546	0.17	3.885	1.008				0.05	1.073	0.253
Pentane				0.18	1.610	0.437						
Toluene	0.50	2.097	2.411	0.24	1.011	1.292	0.78	3.304	3.799	0.05	0.212	0.243
THF	0.40	11.798	1.326	0.41	12.076	1.441						
2-MeTHF										0.87	3.527	3.710
Diethyl ether							0.22	0.847	0.703			
SUM	1.00	16.212	4.283	1.00	18.582	4.178	1.00	4.151	4.502	1.00	7.967	4.260
SUMΩ		56.51	13.54		65.47	15.71		8.15	8.11		145.93	16.43
SUM/ SUMΩ		0.29	0.32		0.28	0,27		0.51	0.56		0.05	0.26
1-(SUM/ SUMΩ)		0.71	0.68		0.72	0.73		0.49	0.44		0.95	0.74

9. Synthesis and characterization details for HABs

Chem. Name	B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-tris(4-tert-Butylphenyl)-borazine (HAB1)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 3.8 mL, 3.8 mmol) was added dropwise to a stirring solution of freshly distilled 4-tert-Butylaniline (0.5 mL, 3.1 mmol, 1.0 equiv.) dissolved in toluene (5 mL) at -10°C. The white suspension was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution to reach room temperature, freshly distilled 2-MeTHF (12 mL) was added to obtain a transparent solution and transferred to a plastic syringe (60 mL).

Preparation of solution B (n-BuLi solution): A dry Schlenk flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial n-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.

Preparation of solution C (Ar-Br solution): In a dry flask, 2-bromomesitylene (11.2 mmol, 1.7 mL) was dissolved in freshly distilled 2-MeTHF (60.8 mL).

Assembling the continuous flow system: it was set up as described in general procedure C.

Extraction: work-up procedure described in general procedure C was followed, MeOH was added to precipitate white solids and then filtered off to give HAB1 as a white solid (0.636 g, 74% over two steps).

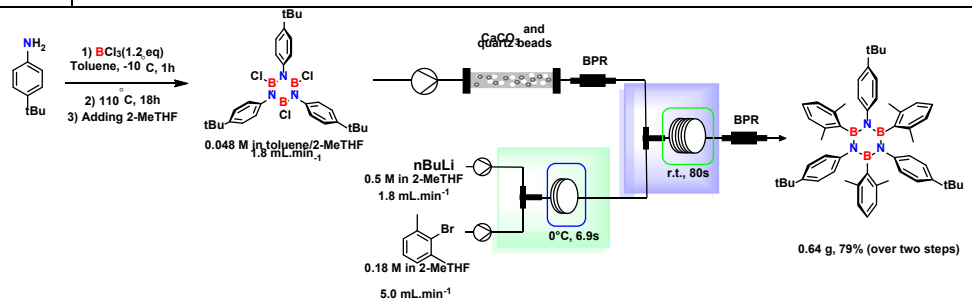
Mol Formula	$C_{57}H_{72}B_3N_3$	**m.p.**	275-277°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR	6.67-6.74	12	*m*	-
400 MHz	6.3	6	*s*	-
$CDCl_3$	2.19	18	*s*	-
	1.96	9	*s*	-
	1.03	27	*s*	-

^{13}C NMR (100.6 MHz, CDCl3) δ : 146.40, 143.72, 137.57, 135.66, 1267.49, 126.00, 123.33, 34.03, 31.33, 23.15, 20.99, (One peak is missing due to quadrupolar B-induced relaxation)

^{11}B NMR (128 MHz, $CDCl_3$) δ : 36.89

Chem. Name	B,B′,B″-tri(2,6-dimethylbenzene)-N,N′,N″-tris(4-tert-Butylphenyl)-borazine (HAB2)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 3.8 mL, 3.8 mmol) was added dropwise to a stirring solution of freshly distilled 4-tert-Butylaniline (0.5 mL, 3.1 mmol, 1.0 equiv.) dissolved in toluene (5 mL) at -10°C. The white suspension was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution reached room temperature, freshly distilled 2-MeTHF (12 mL) was added to obtain a transparent solution and transferred to a plastic syringe (60 mL).
Preparation of solution B (n-BuLi solution): A dry Schlenk flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial n-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.
Preparation of solution C (Ar-Br solution): In a dry flask, 2-bromo-m-xylene (11.2 mmol, 1.5 mL) was dissolved in freshly distilled 2-MeTHF (60.8 mL).
Assembling the continuous flow system: it was set up as described in general procedure C.
Extraction: work-up procedure described in general procedure C was followed, MeOH was added to precipitate white solids and then filtered off to give HAB2 as a white solid (0.64 g, 79% over two steps).

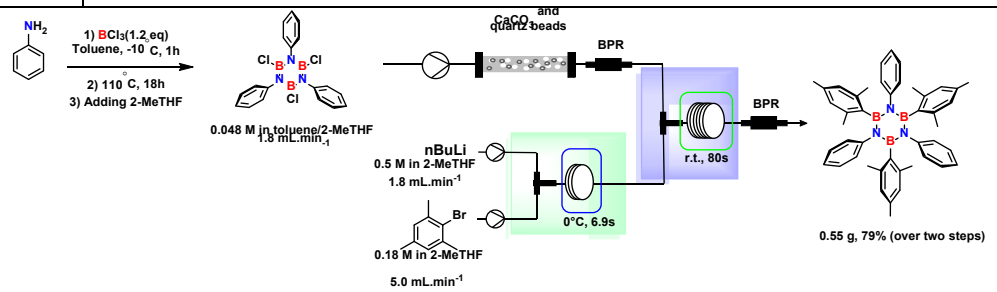
Mol Formula	$C_{57}H_{72}B_3N_3$	**m.p.**	>300°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR	6.71-6.65	15	*m*	-
400 MHz	6.49	6	*d*	7.4
$CDCl_3$	2.25	18	*s*	-
	1.02	27	*s*	-

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 146.56, 143.24, 137,47, 126.52, 126.31, 125.04, 123,25, 33.85, 31.15, 23.013, (One peak is missing due to quadrupolar B-induced relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ : 36.34

Chem. Name	B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-triphenylborazine (HAB3)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 4.0 mL, 4.0 mmol) was added dropwise to a stirring solution of freshly distilled aniline (0.3 mL, 3.3 mmol, 1.0 equiv.) dissolved in toluene (6 mL) at -10°C. The white suspension was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution reached 40°C. Freshly distilled 2-MeTHF (12 mL) was then added the suspension at the same temperature to obtain a transparent solution and transferred to a plastic syringe (60 mL).
Preparation of solution B (n-BuLi solution): A dry Schlenk flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial n-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.
Preparation of solution C (Ar-Br solution): In a dry flask, 2-bromomesitylene (11.2 mmol, 1.7 mL) was dissolved in freshly distilled 2-MeTHF (60.8 mL).
Assembling the continuous flow system: it was set up as described in general procedure C.
Extraction: work-up procedure described in general procedure C was followed, MeOH was added to precipitate white solids and then filtered off to give HAB3 as a white solid (0.55 g, 76% over two steps).

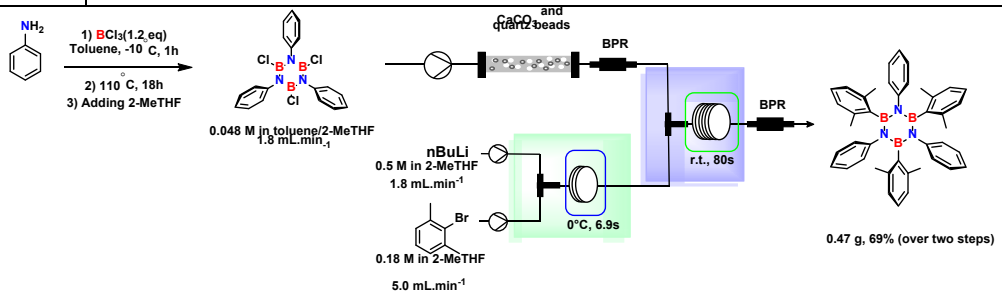
Mol Formula	$C_{45}H_{48}B_3N_3$	**m.p.**	260-262°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR	6.82	6	*d*	7.1
400 MHz	6.7-6.78	9	*m*	-
$CDCl_3$	6.33	6	*s*	-
	2.23	18	*s*	-
	1.97	9	*s*	-

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 146.43, 137.36, 136.18, 127.13, 126.81, 126.29, 124.28, 23.13, 21.16 (One peak is missing due to quadrupolar B-induced relaxation)

^{11}B NMR (128 MHz, $CDCl_3$) δ : 37.26

Chem. Name	B,B′,B″-tri(2,6-dimethylbenzene)-N,N′,N″-triphenylborazine (HAB4)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 4.0 mL, 4.0 mmol) was added dropwise to a stirring solution of freshly distilled aniline (0.3 mL, 3.3 mmol, 1.0 equiv.) dissolved in toluene (6 mL) at -10°C. The white suspension was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution reached 40°C. Freshly distilled 2-MeTHF (12 mL) was then added the suspension at the same temperature to obtain a transparent solution and transferred to a plastic syringe (60 mL).
Preparation of solution B (n-BuLi solution): A dry Schlenk flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial n-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.
Preparation of solution C (Ar-Br solution): In a dry flask, 2-bromo-m-xylene (11.2 mmol, 1.5 mL) was dissolved in freshly distilled 2-MeTHF (60.8 mL).
Assembling the continuous flow system: it was set up as described in general procedure C.
Extraction: work-up procedure described in general procedure C was followed, MeOH was added to precipitate white solids and then filtered off to give HAB4 as a white solid (0.47 g, 69% over two steps).

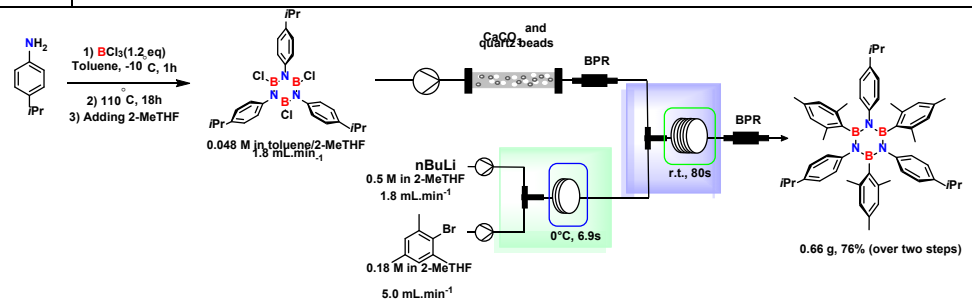
Mol Formula	$C_{42}H_{42}B_3N_3$	**m.p.**	>300°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR	6.89	6	*d*	7.8
400 MHz	6.83-6.72	12	*m*	-
$CDCl_3$	6.56	6	*d*	7.5
	2.33	18	*s*	-

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 146.10, 137.50, 127.15, 126.98, 126.91, 125.41, 124.63, 23.30, (One peak is missing due to quadrupolar B-induced relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ : 36.82

Chem. Name	B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-tris(4-isopropylphenyl)-borazine (HAB5)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 4.0 mL, 4.0 mmol) was added dropwise to a stirring solution of freshly distilled 4-*i*Pr-aniline (0.45 mL, 3.29 mmol, 1.0 equiv.) dissolved in toluene (5 mL) at -10°C. The transparent solution was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution reached room temperature. Freshly distilled 2-MeTHF (12 mL) was then added to obtain a transparent solution and transferred to a plastic syringe (60 mL).
Preparation of solution B (n-BuLi solution): A dry Schlenk flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial n-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.
Preparation of solution C (Ar-Br solution): In a dry flask, 2-bromomesitylene (11.2 mmol, 1.7 mL) was dissolved in freshly distilled 2-MeTHF (60.8 mL).
Assembling the continuous flow system: it was set up as described in general procedure C.
Extraction: work-up procedure described in general procedure C was followed, MeOH was added to precipitate white solids and then filtered off to give HAB5 as a white solid (0.66 g, 76% over two steps).

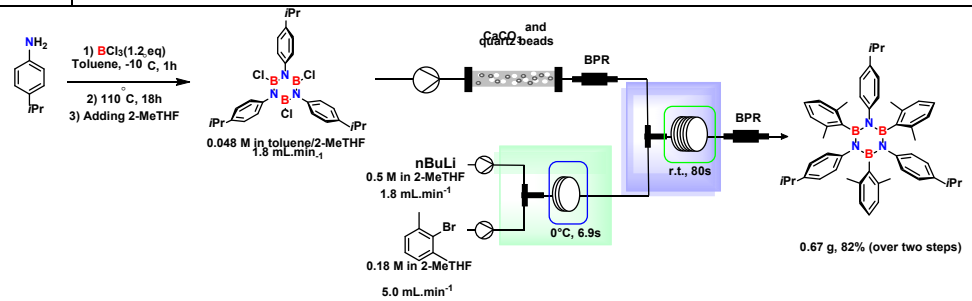
Mol Formula	$C_{54}H_{66}B_3N_3$	**m.p.**	222-224°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR 400 MHz $CDCl_3$	6.68	6	*d*	8.1
	6.55	6	*d*	8.1
	6.31	6	*s*	-
	2.55	3	*dq*	13.4, 6.7
	2.20	18	*s*	-
	1.97	9	*s*	-
	0.96	18	*d*	6.8

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 144.20, 144.09, 137.49, 135.72, 126.77, 126.04, 124.48, 33.25, 23.94, 23.15, 21.03, (One peak is missing due to quadrupolar B-induced relaxation)

^{11}B NMR (128 MHz, $CDCl_3$) δ : 36.75

Chem. Name	B,B′,B″-tri(2,6-dimethylbenzene)-N,N′,N″-tris(4-*isopropylphenyl*-phenyl)-borazine (HAB6)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 4.0 mL, 4.0 mmol) was added dropwise to a stirring solution of freshly distilled 4-iPr-aniline (0.45 mL, 3.29 mmol, 1.0 equiv.) dissolved in toluene (5 mL) at -10°C. The transparent solution was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution reached room temperature. Freshly distilled 2-MeTHF (12 mL) was then added to obtain a transparent solution and transferred to a plastic syringe (60 mL).
Preparation of solution B (n-BuLi solution): A dry Schlenk flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial n-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.
Preparation of solution C (Ar-Br solution): In a dry flask, 2-bromo-m-xylene (11.2 mmol, 1.5 mL) was dissolved in freshly distilled 2-MeTHF (60.8 mL).
Assembling the continuous flow system: it was set up as described in general procedure C.
Extraction: work-up procedure described in general procedure C was followed, MeOH was added to precipitate white solids and then filtered off to give HAB6 as a white solid (0.67 g, 82% over two steps).

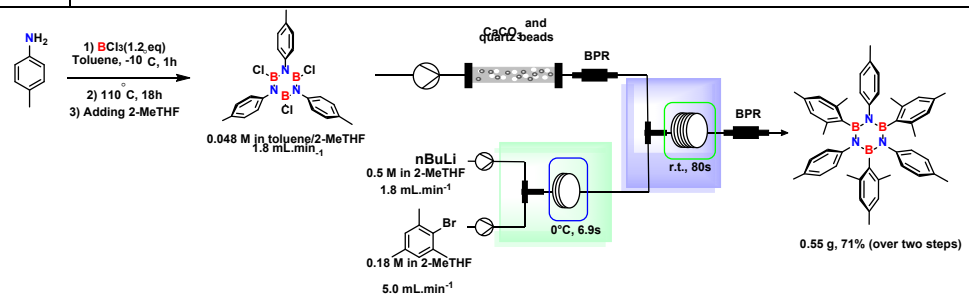
Mol Formula	$C_{51}H_{60}B_3N_3$	**m.p.**	272-274°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR 400 MHz $CDCl_3$	6.7	9	*dd*	12.1, 5.6
	6.56	6	*d*	8.3
	6.5	6	*d*	7.5
	2.5	3	*dq*	13.7, 6.9
	2.26	18	*s*	-
	0.95	18	*d*	6.9

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 144.49, 143.72, 137.59, 126.73(br), 125.20, 124.53, 33.23, 23.91, 23.28, (One peak is missing due to quadrupolar B-induced relaxation)

^{11}B NMR (128 MHz, $CDCl_3$) δ : 36.80

Chem. Name	B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-tris(4-toluidine)-borazine (HAB7)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 4.0 mL, 4.0 mmol) was added dropwise to a stirring solution of p-toluidine (0,35g 3.3 mmol) dissolved in toluene (6 mL) at 0°C. The white suspension was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution reached 40°C. Freshly distilled 2-MeTHF (12 mL) was then added the suspension at the same temperature to obtain a transparent solution and transferred to a plastic syringe (60 mL).
Preparation of solution B (n-BuLi solution): A dry flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial n-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.
Preparation of solution C (Ar-Br solution): In a dry flask, 2-bromomesitylene (11.2 mmol, 1.7 mL) was dissolved in freshly distilled 2-MeTHF (60.8 mL).
Flow system: it was set up as described in general procedure C.
Extraction: work-up procedure described in general procedure C was followed, MeOH was added to precipitate white solids and then filtered off to give HAB7 as a white solid (0.55 g, 71% over two steps).

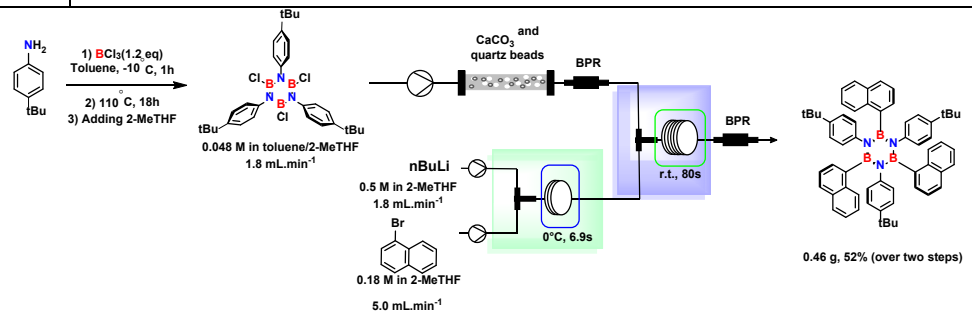
Mol Formula	$C_{48}H_{54}B_3N_3$	**m.p.**	Decomposed at 290°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR 400 MHz $CDCl_3$	6.70	6	*d*	8
	6.52	6	*d*	7.8
	6.33	6	*s*	-
	2.21	18	*s*	-
	1.99	18	*s*	-

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 143.85, 137.37, 135.84, 133.18, 127.44, 126.65, 126.19, 23.14, 21.20, 20.90, (One peak is missing due to quadrupolar B-induced relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ : 36.90

Chem. Name	B,B′,B″-tri(naphthalen-1-yl)-N,N′,N″-tris(4-tert-Butylphenyl)-borazine (HAB8)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 3.8 mL, 3.8 mmol) was added dropwise to a stirring solution of freshly distilled 4-tert-Butylaniline (0.5 mL, 3.1 mmol, 1.0 equiv.) dissolved in toluene (5 mL) at -10°C. The white suspension was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution reached room temperature, freshly distilled 2-MeTHF (12 mL) was added to obtain a transparent solution and transferred to a plastic syringe (60 mL).
Preparation of solution B (n-BuLi solution): A dry Schlenk flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial n-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.
Preparation of solution C (Ar-Br solution): In a dry flask, 1-Bromonaphthalene (11.4 mmol, 1.6 mL) was dissolved in freshly distilled 2-MeTHF (61.9 mL).
Flow system: it was set up as described in general procedure C.
Extraction: work-up procedure described in general procedure C was followed, MeOH was added to precipitate white solids and then filtered off to give HAB8 as a white solid (mix of isomers, 0.46 g, 52%).
Substituting boron with naphthalene, compared to phenyl, led to a mixture of isomers, evident in the ^{13}C NMR spectrum[8,9].

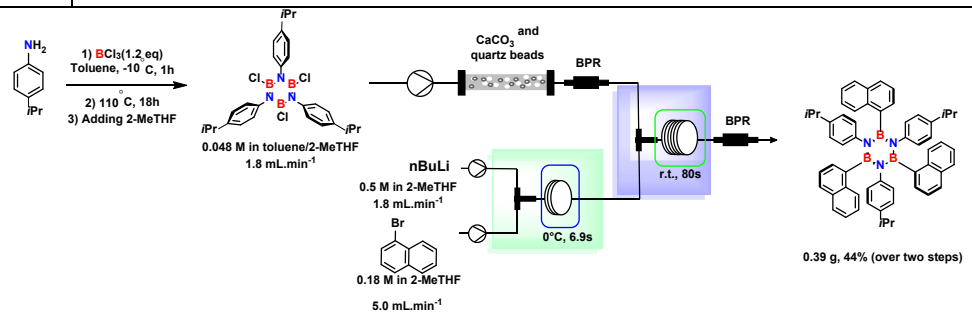
Mol Formula	$C_{60}H_{60}B_3N_3$	**m.p.**	Decomposed at 298°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR	7.99	3	*dd*	17.6, 8.2
400 MHz	7.46	3	*d*	6.8 Hz
$CDCl_3$	7.40-7.28	6	*m*	-
	7.25-7.14	6	*m*	-
	7.03	3	*t*	6.7
	6.73-6.08	12	*m*	-
	0.79	27	*s*	-

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 146.06, 143.49(d, *J*=2.5Hz), 134.63-134.53(m), 132.44, 130.81, 130.68(d, *J*=5.4Hz),129.69, 129.56(d, *J*=8.2 Hz), 127.89, 127.79-127.71(m), 126.63, 124.55124.37 (m), 123.34, 33.75, 31.03, (One peak is missing due to quadrupolar B-induced relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ : 36.15

Chem. Name	B,B′,B″-tri(naphthalen-1-yl)-N,N′,N″-tris(4-isopropylphenyl)-borazine (HAB9)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 4.0 mL, 4.0 mmol) was added dropwise to a stirring solution of freshly distilled 4-*i*Pr-aniline (0.45 mL, 3.29 mmol, 1.0 equiv.) dissolved in toluene (5 mL) at -10°C. The transparent solution was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution reached room temperature. Freshly distilled 2-MeTHF (12 mL) was then added to obtain a transparent solution and transferred to a plastic syringe (60 mL).
Preparation of solution B (n-BuLi solution): A dry Schlenk flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial n-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.
Preparation of solution C (Ar-Br solution): In a dry flask, 1-Bromonaphthalene (11.4 mmol, 1.6 mL) was dissolved in freshly distilled 2-MeTHF (61.9 mL).
Flow system: it was set up as described in general procedure C.
Extraction: work-up procedure described in general procedure C was followed, MeOH was added to precipitate white solids and then filtered off to give HAB9 as a white solid (mix of isomers, 0.39 g, 44%).
Substituting boron with naphthalene, compared to phenyl, led to a mixture of isomers, evident in the ^{13}C NMR spectrum[8,9].

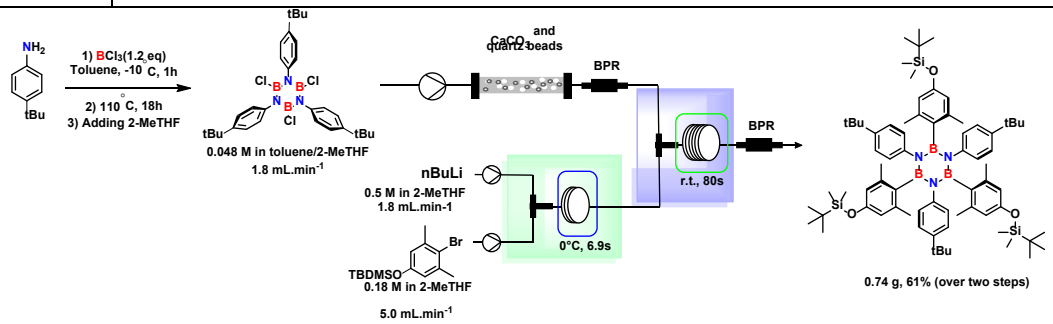
Mol Formula	$C_{57}H_{54}B_3N_3$	**m.p.**	250-252°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR 400 MHz $CDCl_3$	8.0	3	*dd*	17.9, 8.9
	7.51-7.44	3	*m*	-
	7.40-7.29	6	*m*	-
	7.24-7.13	6	*m*	-
	7.04	3	*tt*	7.6, 3.7
	6.76-5.95	12	*m*	-
	2.27	3	*dq*	3.5, 6.7
	0.71	18	*d*	6.8

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 143.89, 143.82, 134.55, 132.44, 130.77, 130.63(d, *J*=6.5Hz), 129.63, 129.50(d, *J*=8.8 Hz), 128.18, 127.81 (t, *J*=5.1 Hz), 126.65,124.59, 124.48-124.39(m) 33.07, 23.69, (One peak is missing due to quadrupolar B-induced relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ : 36.53

Chem. Name	B,B′,B″-tri(2,6-dimethyl-4-(tert-Buthyl dimethylsilyloxy)-N,N′,N″-tris(4-tert-Butylphenyl)-borazine (HAB10)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 3.8 mL, 3.8 mmol) was added dropwise to a stirring solution of freshly distilled 4-tert-Butylaniline (0.5 mL, 3.1 mmol, 1.0 equiv.) dissolved in toluene (5 mL) at -10°C. The white suspension was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution reached room temperature, freshly distilled 2-MeTHF (12 mL) was added to obtain a transparent solution and transferred to a plastic syringe (60 mL).
Preparation of solution B (n-BuLi solution): A dry Schlenk flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial n-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.
Preparation of solution C (Ar-Br solution): In a dry flask, (4-bromo-3,5-dimethylphenoxy)(tert-butyl)dimethylsilane[2] (11.2 mmol, 3.53g) was dissolved in freshly distilled 2-MeTHF (60.0 mL).
Flow system: it was set up as described in general procedure C.
Extraction: work-up procedure described in general procedure C was followed, MeOH was added to precipitate white solids and then filtered off to give HAB10 as a white solid (0.74 g, 61% over two steps).

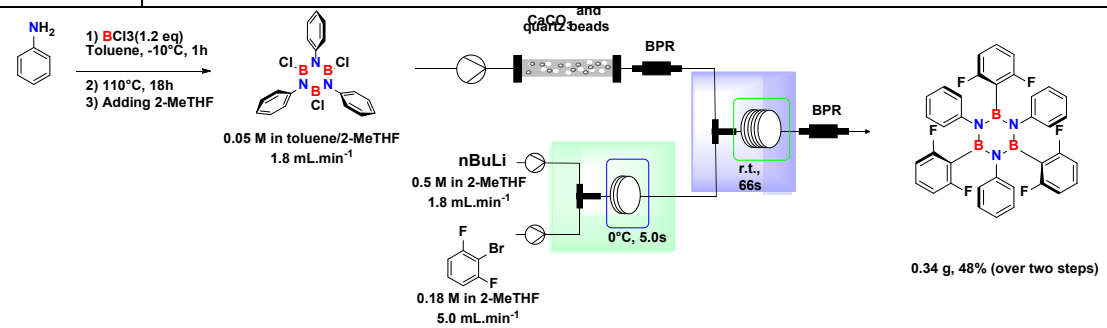
Mol Formula	$C_{51}H_{60}B_3N_3$	**m.p.**	263-265°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR	6.72	6	*d*	8.3
400 MHz	6.66	6	*d*	8.3
$CDCl_3$	6.06	6	*s*	-
	2.18	18	*s*	-
	1.07	27	*s*	-
	0.89	27	*s*	-
	-0.3	18	*s*	-

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 154.27, 146.45, 143.56, 139.13, 126.72, 123.33, 117.53, 34.03, 31.42, 25.85, 23.11, 18.19,-4.41, (One peak is missing due to quadrupolar B-induced relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ: 37.25

Chem. Name	B,B′,B″-tri(2,6-difluorophenyl)-N,N′,N″-triphenylborazine (HAB11)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 4.0 mL, 4.0 mmol) was added dropwise to a stirring solution of freshly distilled aniline (0.3 mL, 3.3 mmol, 1.0 equiv.) dissolved in toluene (6 mL) at -10°C. The white suspension was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution reached 40°C. Freshly distilled 2-MeTHF (12 mL) was then added the suspension at the same temperature to obtain a transparent solution and transferred to a plastic syringe (60 mL).
Preparation of solution B (n-BuLi solution): A dry Schlenk flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial n-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.
Preparation of solution C (Ar-Br solution): In a dry flask, 1-Bromo-2,6-difluorobenzene (11.2 mmol, 2.16g) was dissolved in freshly distilled 2-MeTHF (60.0 mL).
Flow system: the procedure was carried out as described in general procedure C, whereby the residence time of the RA and RB reactor was reduced from 6.9 to 5.0 and 42 to 23 s respectively.
Extraction: work-up procedure described in general procedure C was followed, MeOH was added to the residue to precipitate white solids and then filtered off to give HAB11 as a white solid (0.34 g, 48% over two steps).

Mol Formula	$C_{36}H_{24}B_3F_6N_3$	**m.p.**	>300°C

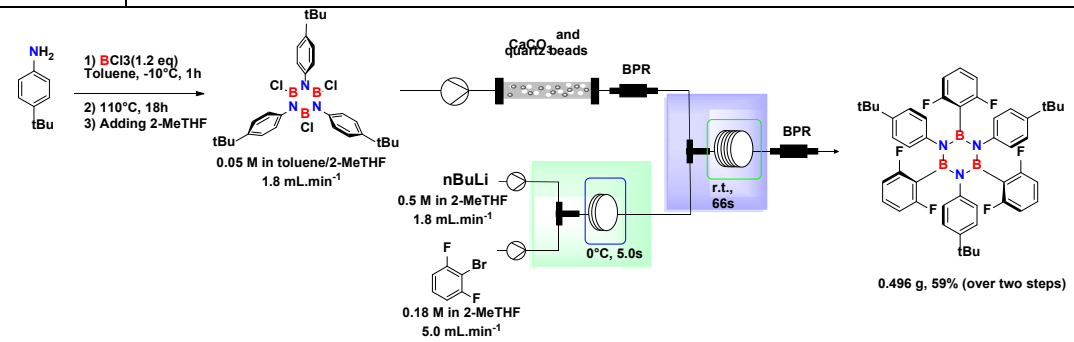
	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR	7.09	6	*d*	7.7
400 MHz	6.91	6	*t*	7.7
$CDCl_3$	6.83	6	*dt*	16.2, 7.4
	6.42-6.34	6	*m*	-

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 163.66, 145.68, 130.61(t, *J*=10.0, Hz), 127.93, 126.99, 125.45, 109.96 (d, *J*=26.9Hz). (One peak is missing due to quadrupolar B-induced relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ : 34.54

^{19}F NMR (376 MHz, $CDCl_3$) δ : 101.42

Chem. Name	B,B′,B″-tri(2,6-difluorophenyl)-N,N′,N″- tris(4-tert-Butylphenyl)-borazine (HAB12)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 3.8 mL, 3.8 mmol) was added dropwise to a stirring solution of freshly distilled 4-tert-Butylaniline (0.5 mL, 3.1 mmol, 1.0 equiv.) dissolved in toluene (5 mL) at -10°C. The white suspension was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution reached room temperature, freshly distilled 2-MeTHF (12 mL) was added to obtain a transparent solution and transferred to a plastic syringe (60 mL).
Preparation of solution B (n-BuLi solution): A dry Schlenk flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial n-BuLi (1.6 M in hexane, 7 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.
Preparation of solution C (Ar-Br solution): In a dry flask, 1-Bromo-2,6-difluorobenzene (11.2 mmol, 2.16g) was dissolved in freshly distilled 2-MeTHF (60.0 mL).
Flow system: the procedure was carried out as described in general procedure C, whereby the residence time of the RA and RB reactor was reduced from 6.9 to 5.0 and 42 to 23 s respectively.
Extraction: work-up procedure described in general procedure C was followed, MeOH was added to the residue to precipitate white solids and then filtered off to give HAB12 as a white solid (0.496 g, 59% over two steps).

Mol Formula	$C_{48}H_{48}B_3F_6N_3$	**m.p.**	>300°C

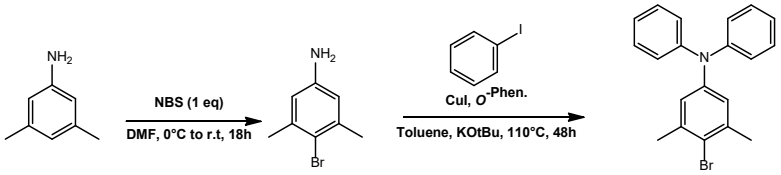
	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR	6.96	6	*d*	8
400 MHz	6.87	6	*d*	8.4
$CDCl_3$	6.83	3	*m*	-
	6.35	6	*t*	7.2
	1.04	27	*s*	-

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 162.67 (dd, *j*= 241.2, 14.8 Hz), 147.77, 143.07, 130.07 (t, *j*=10.0 Hz), 126.38, 124.49, 109.67 (d, j=26.9 Hz), 34.16, 31.26 (One peak is missing due to quadrupolar B-induced relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ : 34.26

^{19}F NMR (376 MHz, $CDCl_3$) δ : 101.47

Chem. Name	4-bromo-3,5-dimethyl-N,N-diphenylaniline



A solution of N-bromosuccinimide (1.8 g, 10 mmol) in DMF (10 mL) was added to a solution of 3,5-di-methylaniline (10.0 mmol, 1.2 mL) in DMF (10 mL) at 0 °C. After the addition, the reaction mixture was gradually warmed up to r.t over 2h and allowed to stir overnight. The crude was diluted with DCM and extracted with water for 5 times remove DMF. The organic phases were dried over Na_2SO_4 and evaporated giving a brown oil. The crude was transferred to a separatory funnel and dissolved in water(10mL) before extraction with petroleum ether (PE). After evaporation of PE the crude solid was recrystallized in PE to obtain a white solid (1.42 g, 71%).

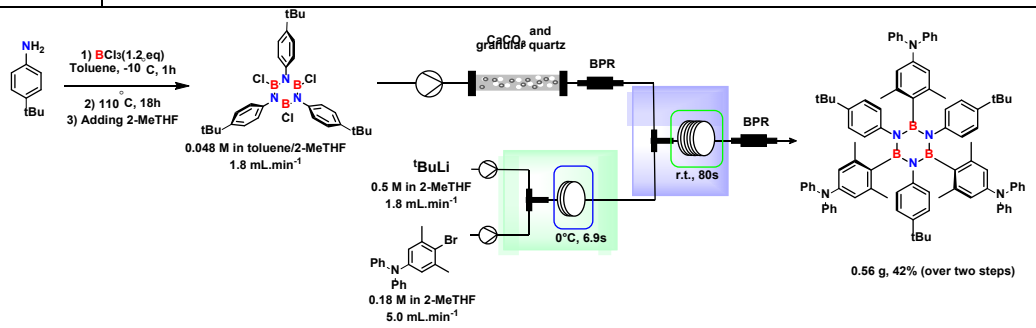
To perform N-arylation of aniline derivative, a 100 mL oven dried Schlenk tube was charged with 4-Bromo-3,5-di-methylaniline (4 mmol, 800mg), 1,10-phenantroline (0.14 mmol, 26 mg), CuI (0.14 mmol, 27 mg) and KOtBu (11.9 mmol, 1.34 g) under inert atmosphere. After filing with argon, dry toluene (30 mL) and iodobenzene (8.33 mmol, 900 µL) were added and the reaction mixture was allowed to stir under reflux for 48h. Afterwards, the reaction was cooled down to r.t and filtered to remove the base. The solid was washed with toluene(30mL) and the solution obtained was extracted with EtOAc and H_2O. The organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The solid obtained was further washed with MeOH to obtain a light brown solid (915mg, 65%).

Mol Formula	$C_{20}H_{18}BrN$	**m.p.**	169-171°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR	7.28	4	*t*	7.8
400 MHz	7.10	4	*d*	8.0
$CDCl_3$	7.05	4	*t*	7.3
	6.85	2	*s*	-
	2.30	6	*s*	-

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 147.77, 146.45, 139.16, 129.38, 124.28, 124.08, 122.90, 120.97, 24.04

Chem. Name	B,B′,B″-tri(3,5-dimethyl-N,N-diphenylaniline)-N,N′,N″- tris(4-tert-Butylphenyl)-borazine (HAB13)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 3.8 mL, 3.8 mmol) was added dropwise to a stirring solution of freshly distilled 4-tert-Butylaniline (0.5 mL, 3.1 mmol, 1.0 equiv.) dissolved in toluene (5 mL) at -10°C. The white suspension was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution reached room temperature, freshly distilled 2-MeTHF (12 mL) was added to obtain a transparent solution and transferred to a plastic syringe (60 mL).
Preparation of solution B (t-BuLi solution): A dry Schlenk flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial t-BuLi (1.7 M in pentane, 6.6 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.
Preparation of solution C (Ar-Br solution): In a dry flask, 4-bromo-3,5-dimethyl-N,N-diphenylaniline (11.2 mmol, 3.94g) was dissolved in freshly distilled 2-MeTHF (60.0 mL).
Flow system: the procedure was carried out as described in general procedure C, with the exception that tBuLi was used instead of nBuLi.
Extraction: work-up procedure described in general procedure C was followed, acetonitrile was added to precipitate off-white solids and then filtered off and further purified with column chromatography (petroleum ether: DCM, 8:2) to give HAB13 as a white solid (0.56 g, 42% over two steps).

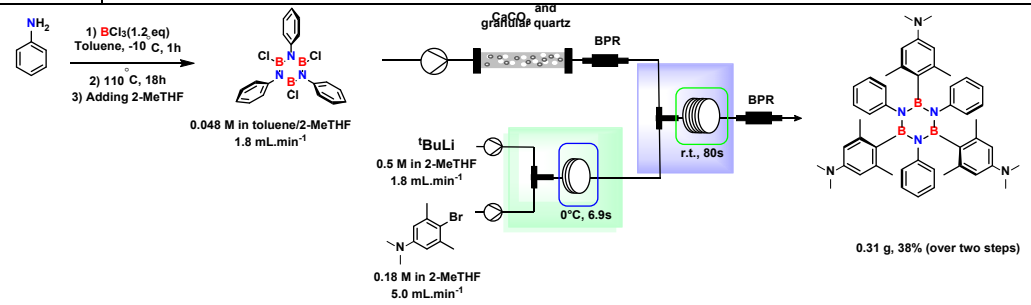
Mol Formula	$C_{90}H_{93}B_3N_3$	**m.p.**	>300°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR 400 MHz $CDCl_3$	7.07	12	*m*	-
	6.86	12	*m*	-
	6.76	18	*d*	8
	6.34	6	*s*	-
	2.17	18	*s*	-
	1.21	27	*s*	-

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 148.10, 147.06, 146.02, 143.45, 139.22, 128.85, 126.79, 123.33, 123.30, 122.81, 121.45, 34.22, 31.55, 23.11. (One peak is missing due to quadrupolar B-induced relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ : 36.74

Chem. Name	B,B′,B″-tri(3,5-dimethyl-N,N-diphenylaniline)-N,N′,N″-tris(4-tert-Butylphenyl)-borazine (HAB14)



Preparation of solution A (TCB solution): To a dry 25 mL Schlenk tube, BCl_3 (1.0 M in heptane, 4.0 mL, 4.0 mmol) was added dropwise to a stirring solution of freshly distilled aniline (0.3 mL, 3.3 mmol, 1.0 equiv.) dissolved in toluene (6 mL) at -10°C. The white suspension was stirred at the same temperature for one hour. Then, the septum was replaced by a dry Vigreux condenser with $CaCl_2$ drying tube on the top and heated at 110°C for 18 h. After the given time, the Vigreux condenser was switched with a new septum and allowed the pale-yellow solution reached 40°C. Freshly distilled 2-MeTHF (12 mL) was then added the suspension at the same temperature to obtain a transparent solution and transferred to a plastic syringe (60 mL).
Preparation of solution B (t-BuLi solution): A dry Schlenk flask (50 mL) was filled with dry 2-MeTHF (15.4 mL) and cooled to 0°C. Commercial t-BuLi (1.7 M in pentane, 6.6 mL, 11.2 mmol) was diluted in 2-MeTHF to obtain a 0.5 M solution.
Preparation of solution C (Ar-Br solution): In a dry flask, 4-bromo-N,N,3,5-tetramethylaniline4 (11.2 mmol, 2.55g) was dissolved in freshly distilled 2-MeTHF (60.0 mL).
Flow system: the procedure was carried out as described in general procedure C, with the exception that tBuLi was used instead of nBuLi.
Extraction: work-up procedure described in general procedure C was followed, acetonitrile was added to precipitate off-white solids and then filtered off and further purified with column chromatography (petroleum ether: DCM) to give HAB14 as a white solid (0.31 g, 38% over two steps).

Mol Formula	$C_{48}H_{57}B_3N_3$	**m.p.**	>300°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR	6.82	12	*m*	-
400 MHz	6.72	3	*m*	-
DMSO	2.63	18	*s*	-
	2.19	18	*s*	-

^{13}C NMR (100.6 MHz, DMSO) δ : 149.00, 146.78, 137.54, 126.76, 126.57, 124.08, 109.48, 40.19, 23.33 (One peak is missing due to quadrupolar B-induced relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ : 36.65

10. References

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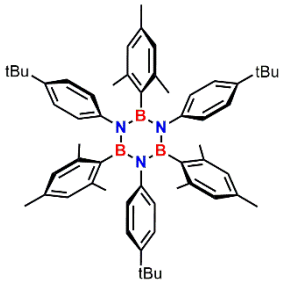
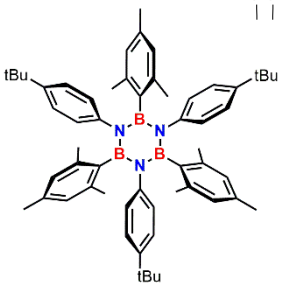
11. Copies of NMR spectra



B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-tris(4-tert-Butylphenyl)-borazine (HAB1)



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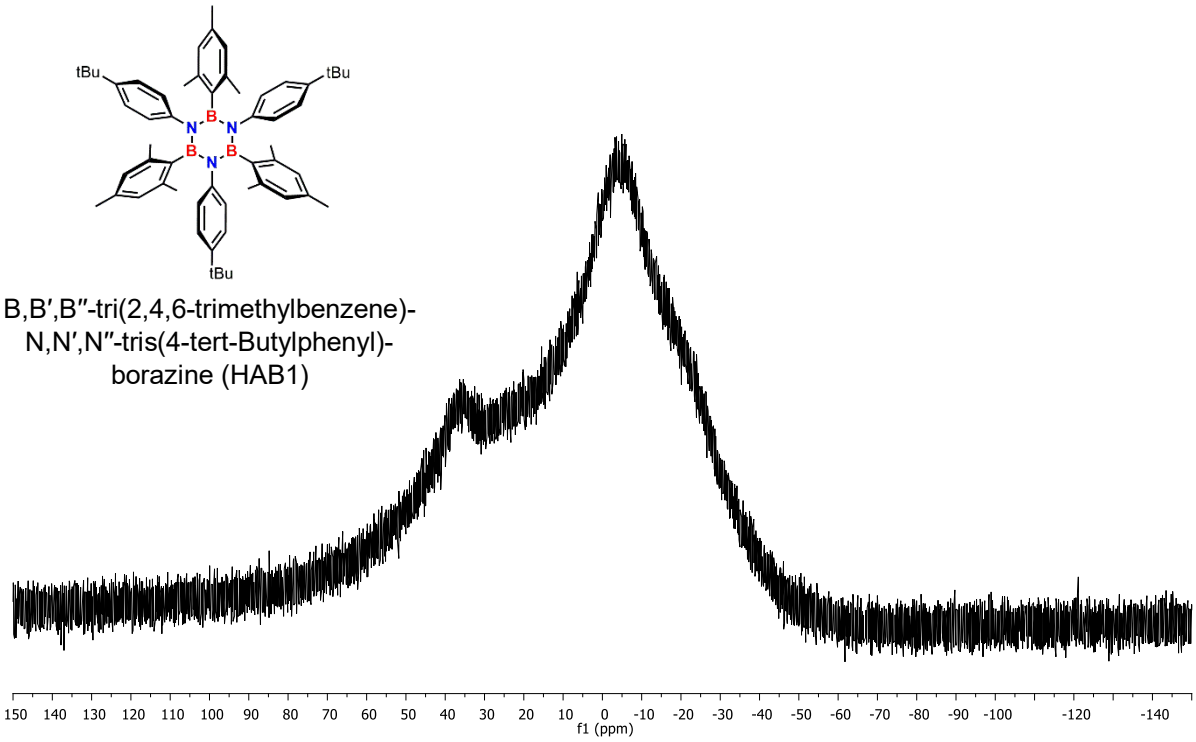

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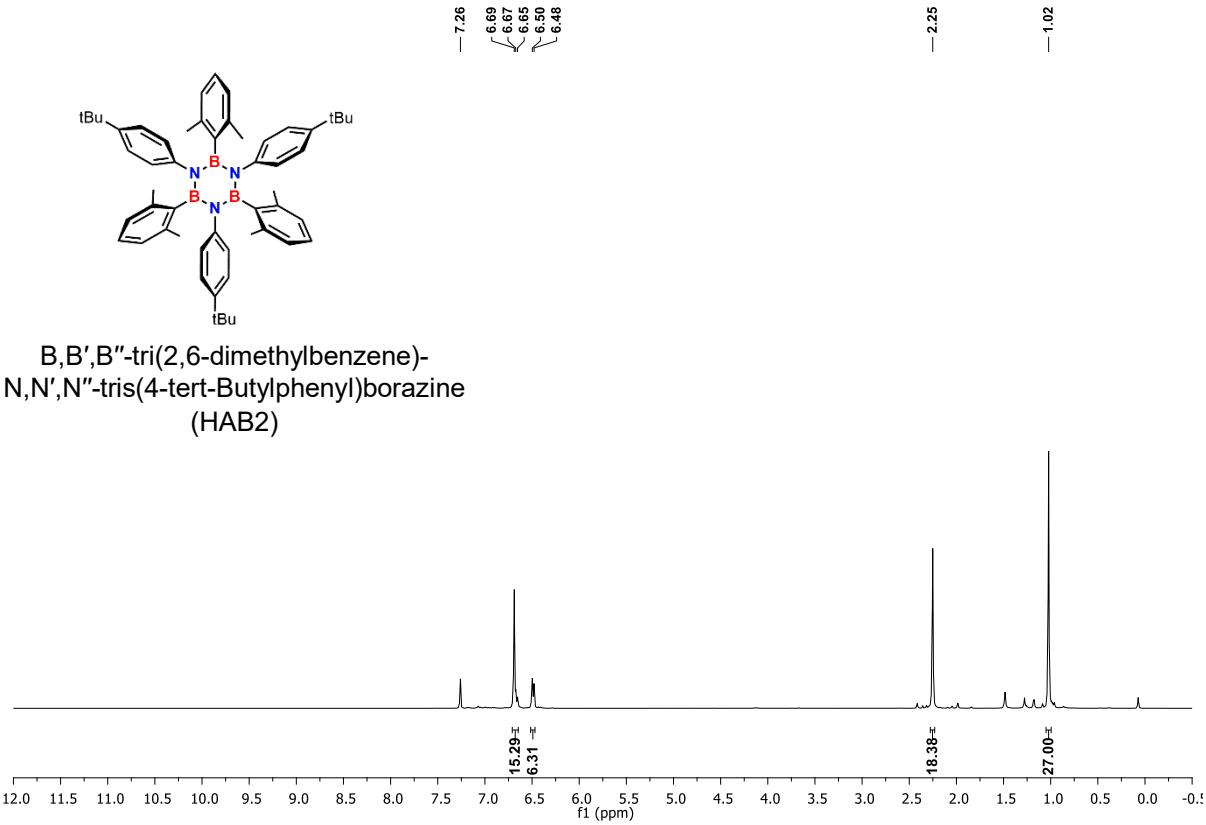
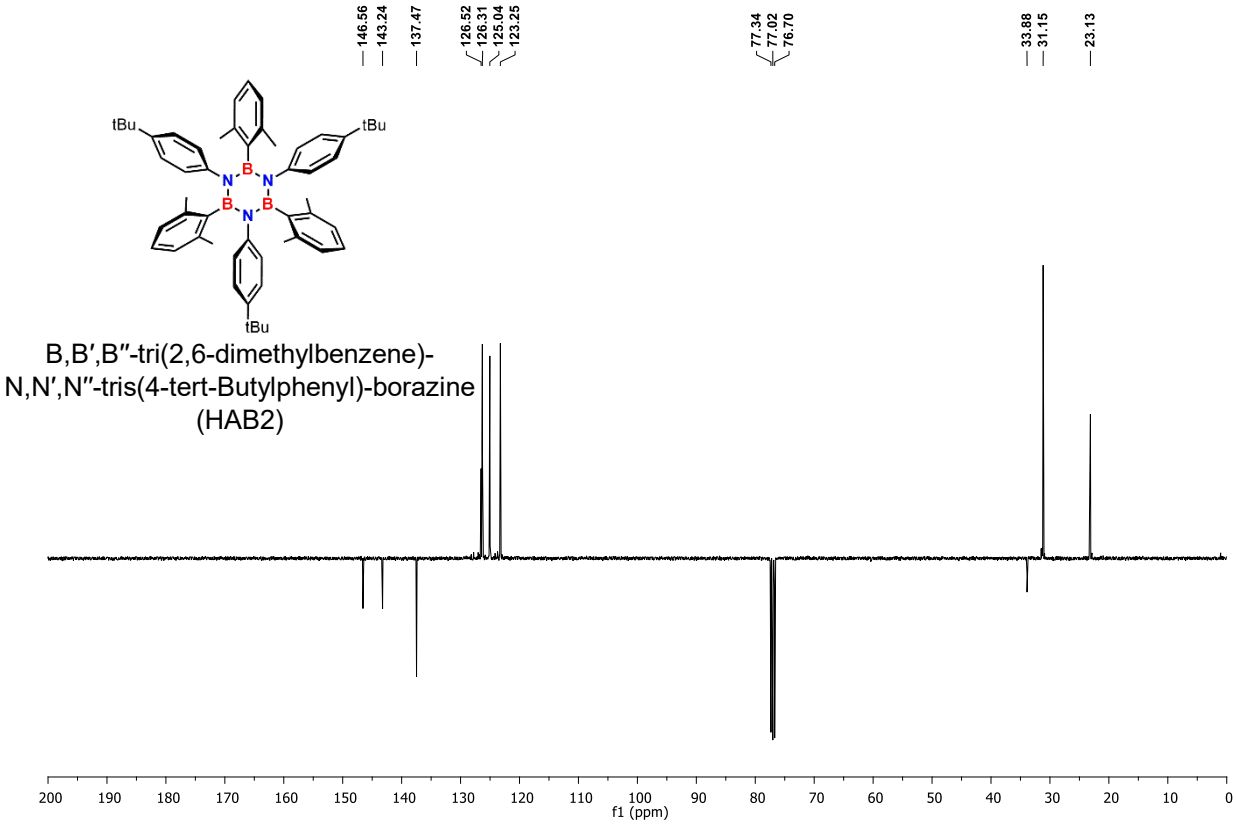
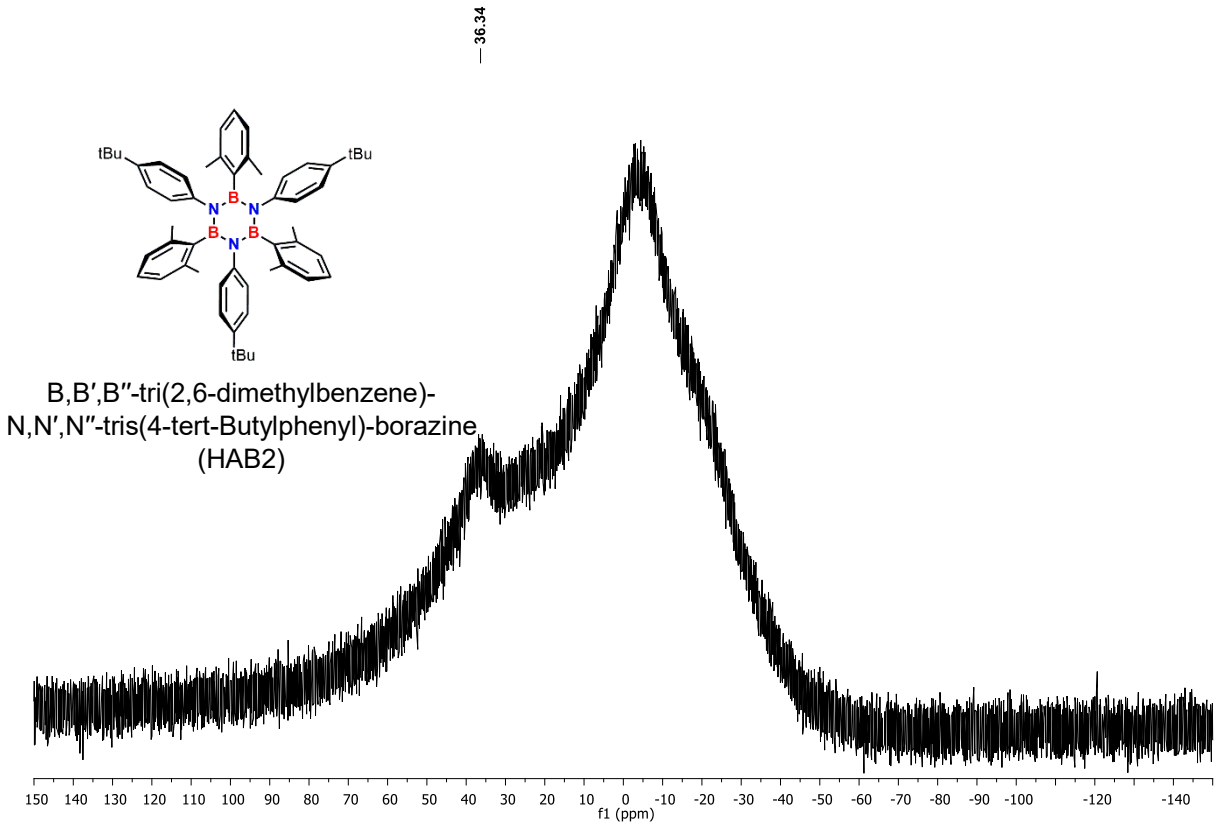
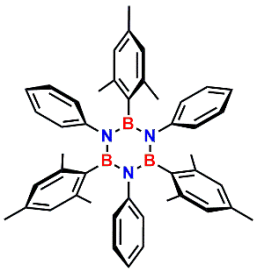


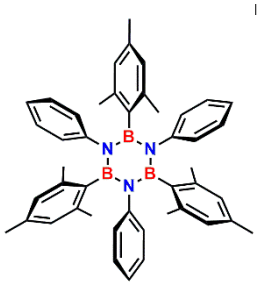
B,B′,B″-tri(2,6-dimethylbenzene)-N,N′,N″-tris(4-tert-Butylphenyl)borazine (HAB2)


146.56
143.24
137.47
126.52
126.31
125.04
123.25
77.34
77.02
76.70
33.88
31.15
23.13
tBu
tBu
tBu
B,B′,B″-tri(2,6-dimethylbenzene)-
N,N′,N″-tris(4-tert-Butylphenyl)-borazine
(HAB2)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

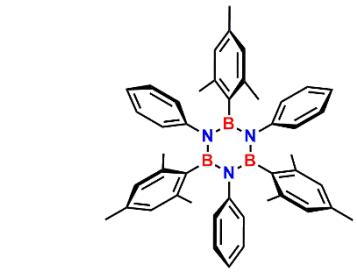

36.34
tBu
tBu
tBu
B,B′,B″-tri(2,6-dimethylbenzene)-
N,N′,N″-tris(4-tert-Butylphenyl)-borazine
(HAB2)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140
f1 (ppm)



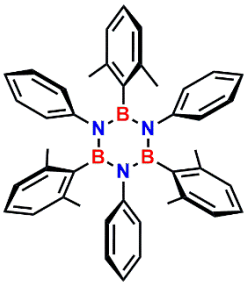
B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-triphenylborazine (HAB3)



B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-triphenylborazine (HAB3)



B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-triphenylborazine (HAB3)



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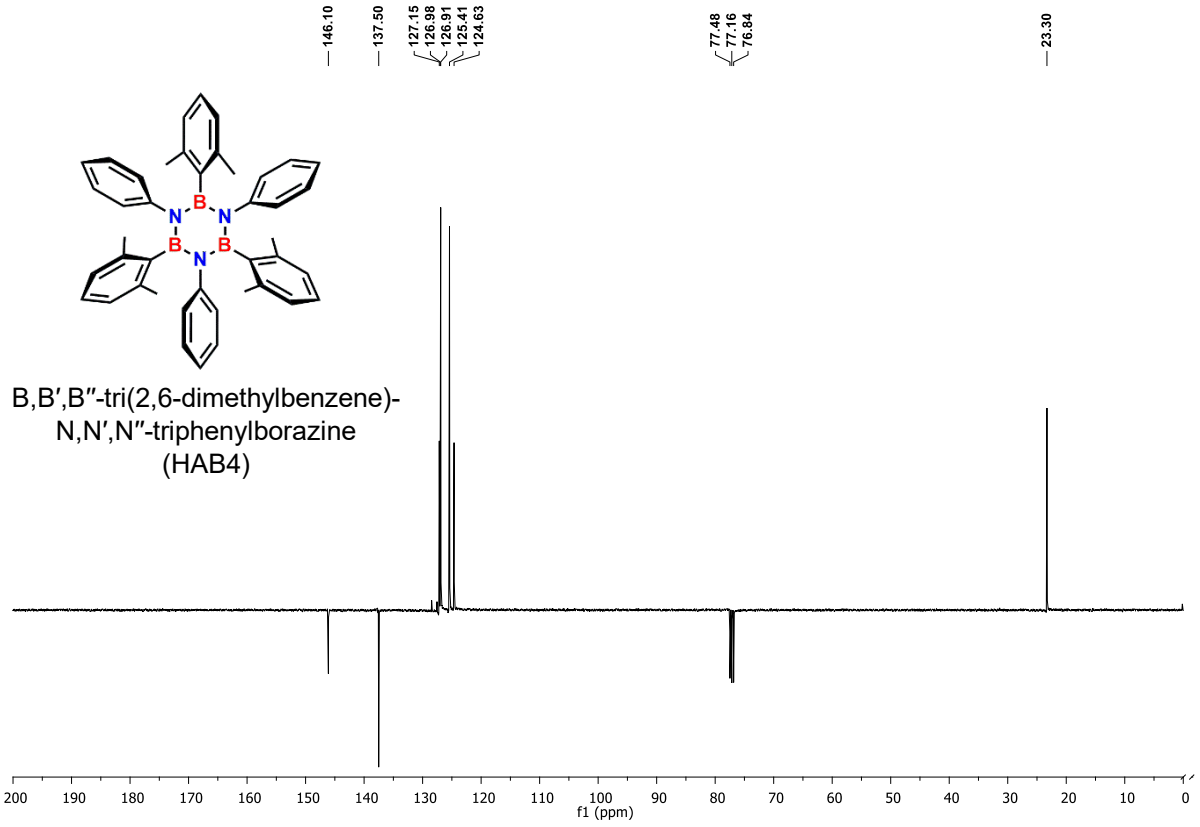
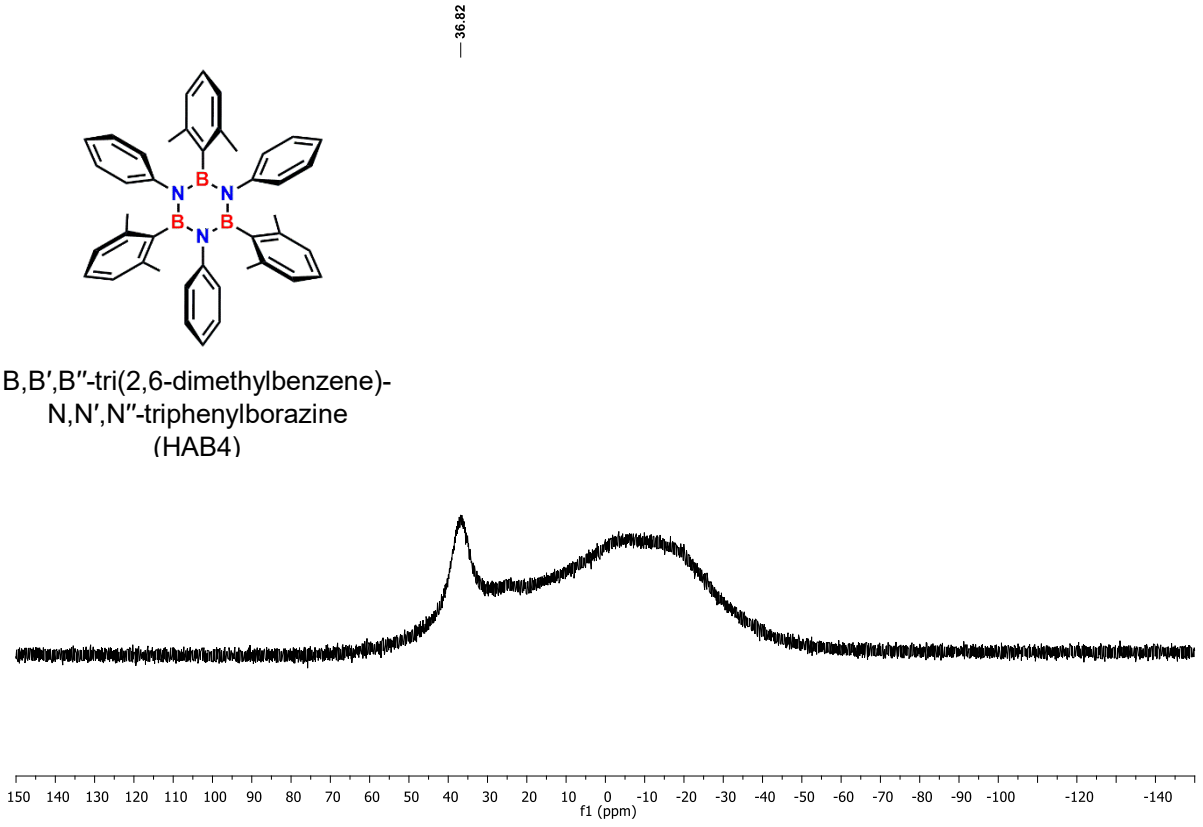
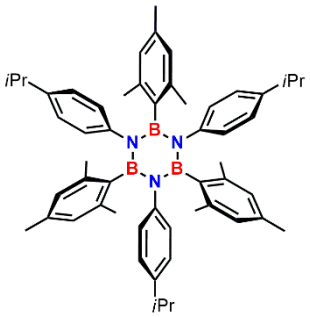
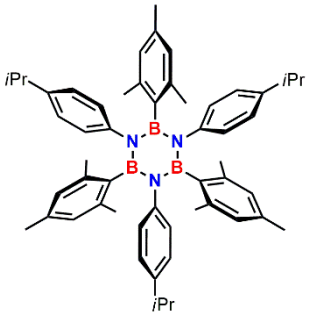

146.10
137.50
127.15
126.98
126.91
125.41
124.63
77.48
77.16
76.84
23.30
B,B′,B″-tri(2,6-dimethylbenzene)-
N,N′,N″-triphenylborazine
(HAB4)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

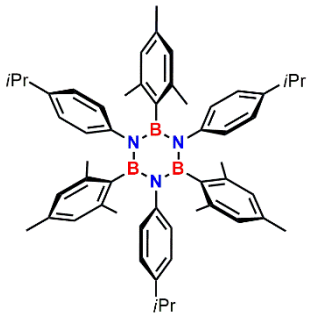

36.82
B,B′,B″-tri(2,6-dimethylbenzene)-
N,N′,N″-triphenylborazine
(HAB4)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140
f1 (ppm)



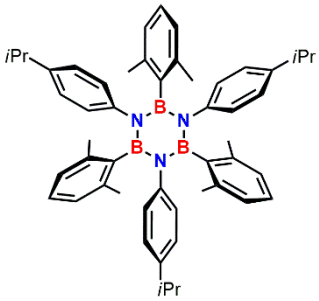
B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-tris(4-isopropylphenyl)-borazine (HAB5)



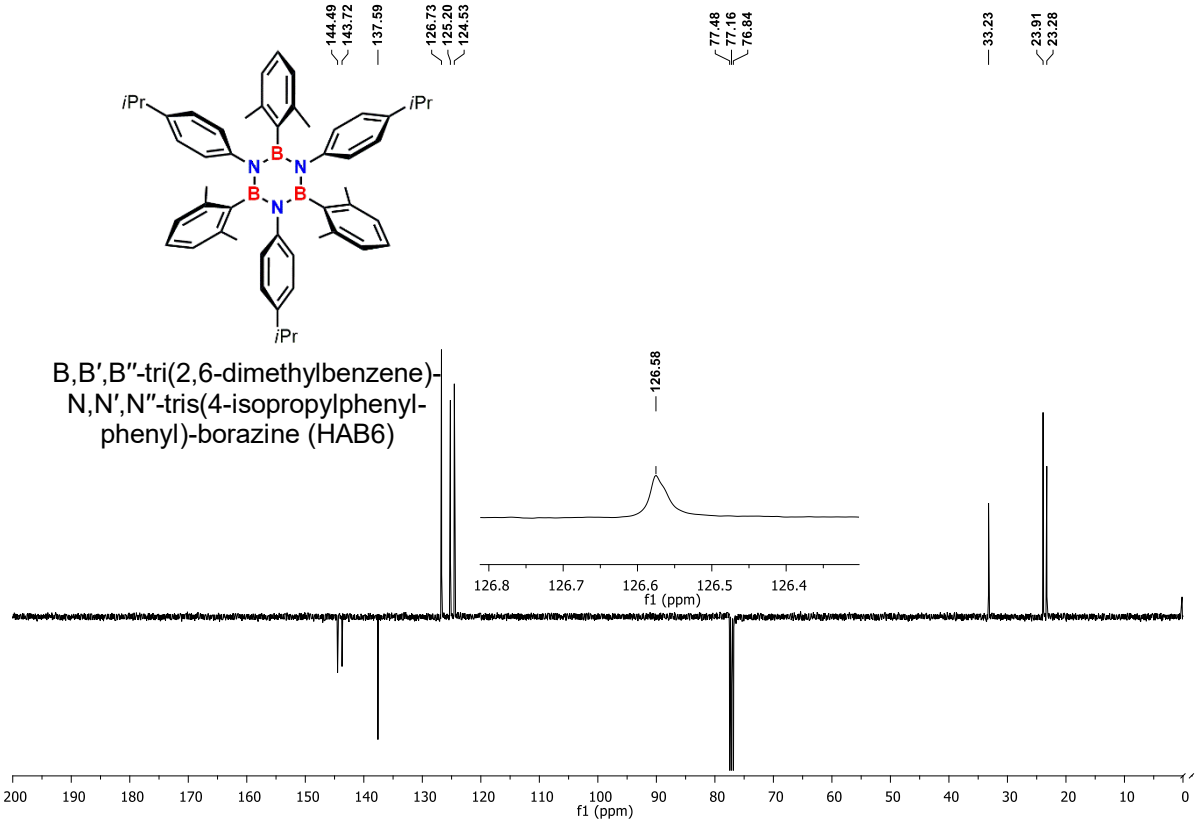
B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-tris(4-isopropylphenyl)-borazine (HAB5)

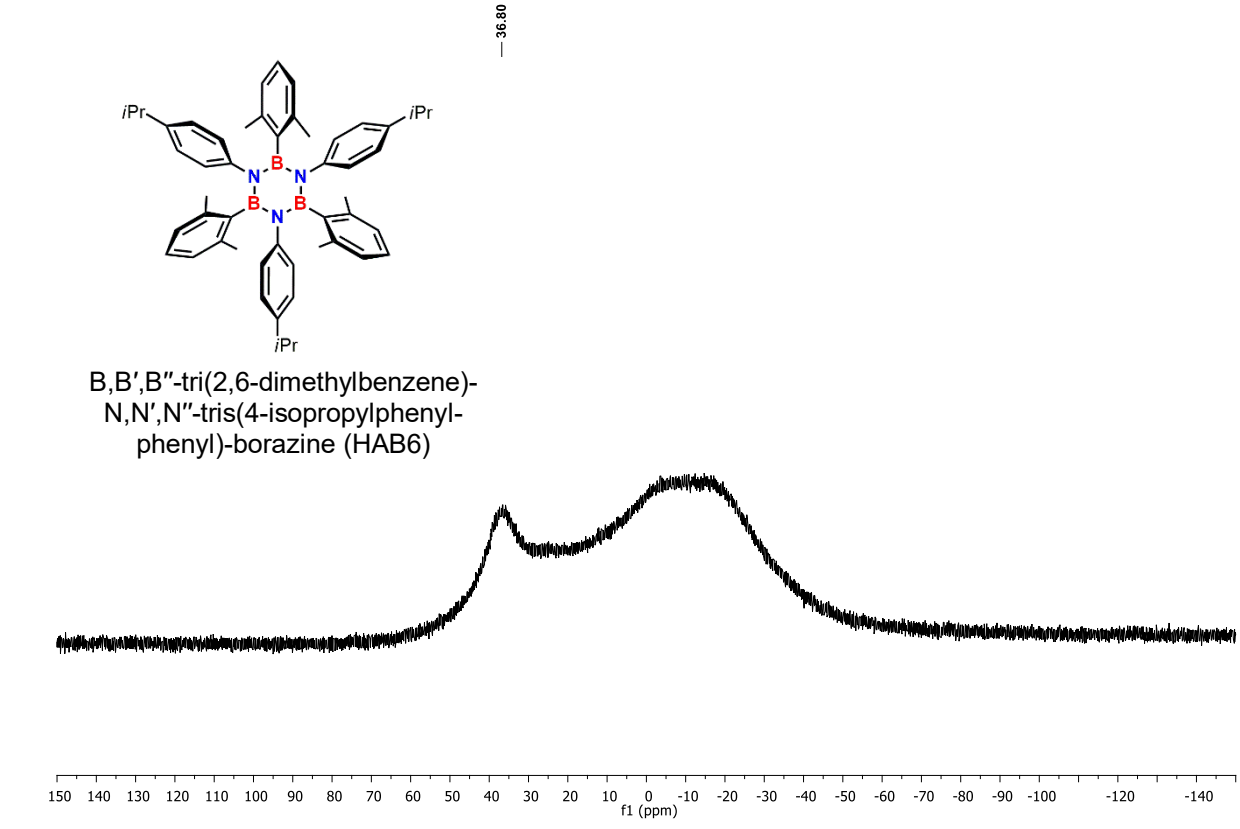


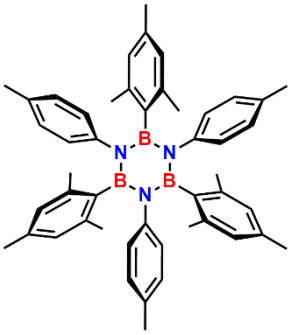
B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-tris(4-isopropylphenyl)-borazine (HAB5)



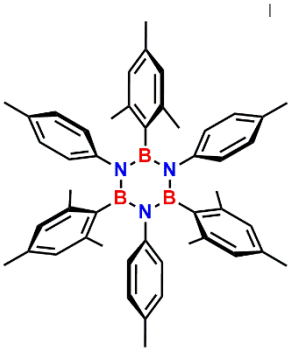
B,B′,B″-tri(2,6-dimethylbenzene)-N,N′,N″-tris(4-isopropylphenyl-phenyl)-borazine (HAB6)


144.49
143.72
137.59
126.73
125.20
124.53
77.48
77.16
76.84
33.23
23.91
23.28
iPr
iPr
iPr
B,B′,B″-tri(2,6-dimethylbenzene)-N,N′,N″-tris(4-isopropylphenyl-phenyl)-borazine (HAB6)
126.58
126.8
126.7
126.6
126.5
126.4
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

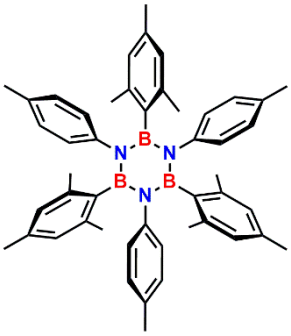

36.80
iPr
iPr
iPr
B,B′,B″-tri(2,6-dimethylbenzene)-N,N′,N″-tris(4-isopropylphenyl-phenyl)-borazine (HAB6)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
f1 (ppm)



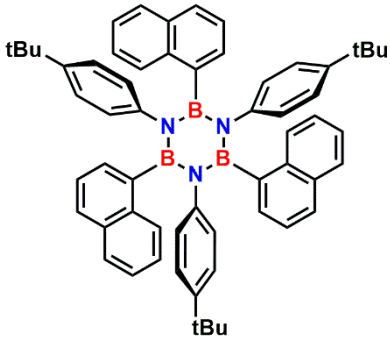
B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-tris(p-toluidine)-borazine (HAB7)



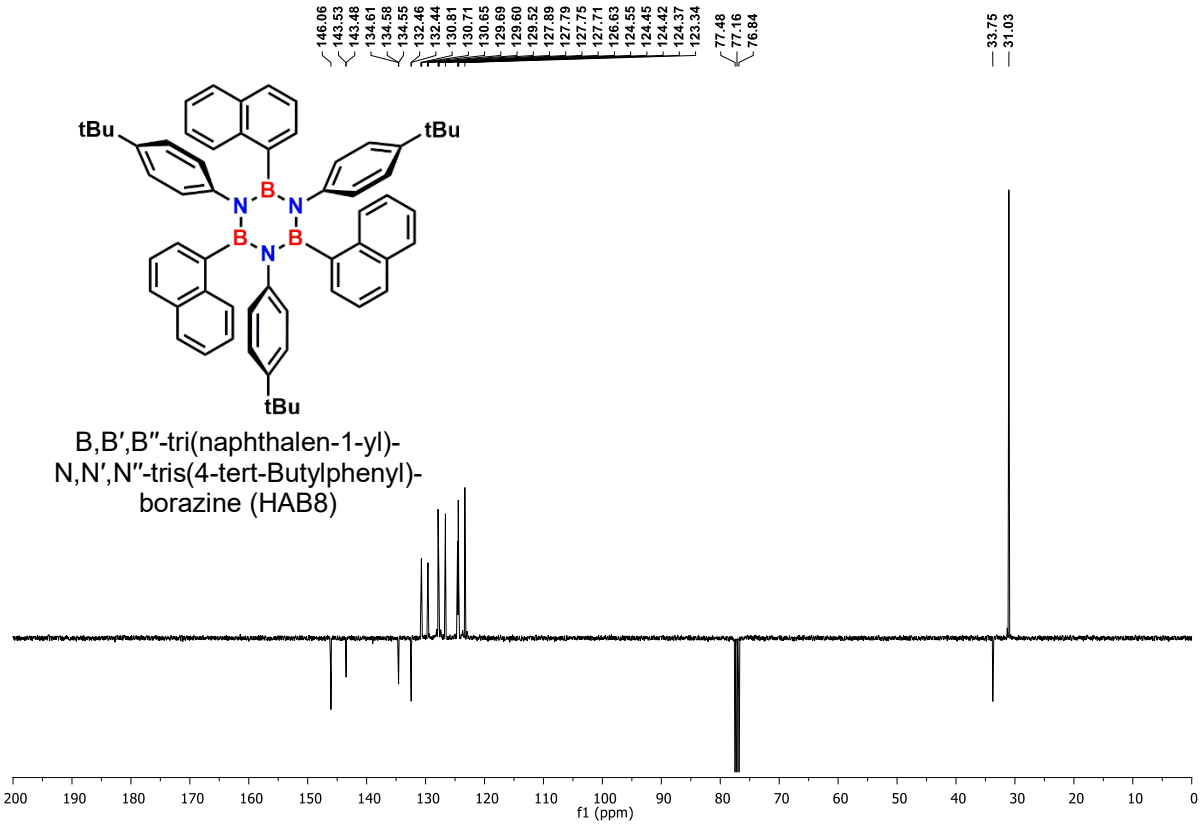
B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-tris(p-toluidine)-borazine (HAB7)

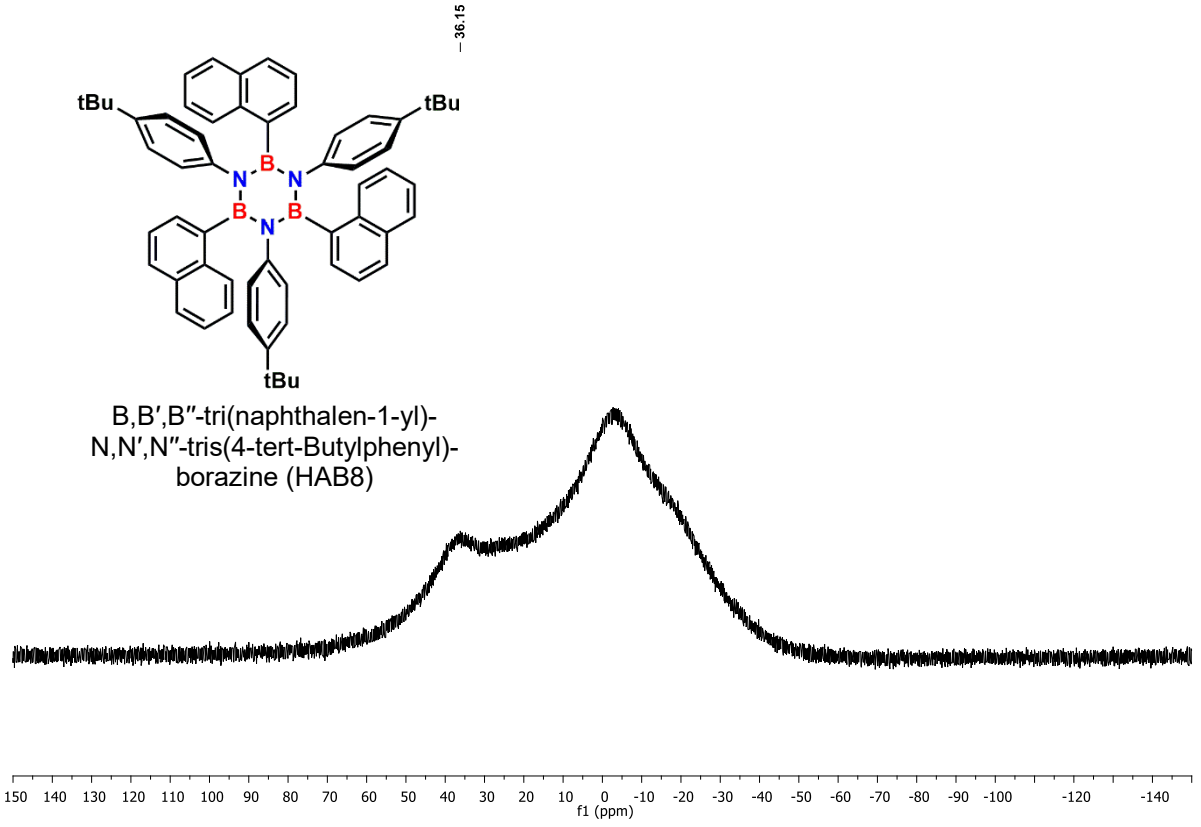


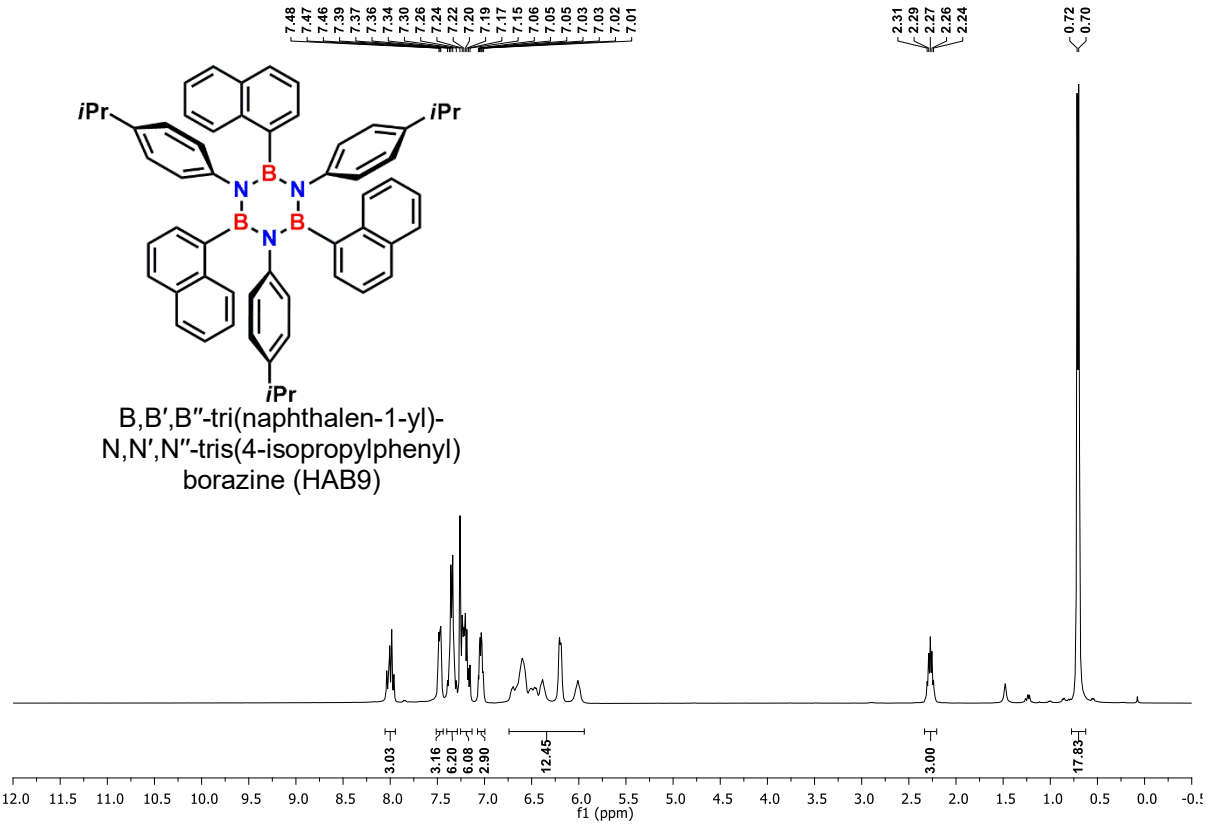
B,B′,B″-tri(2,4,6-trimethylbenzene)-N,N′,N″-tris(p-toluidine)-borazine (HAB7)

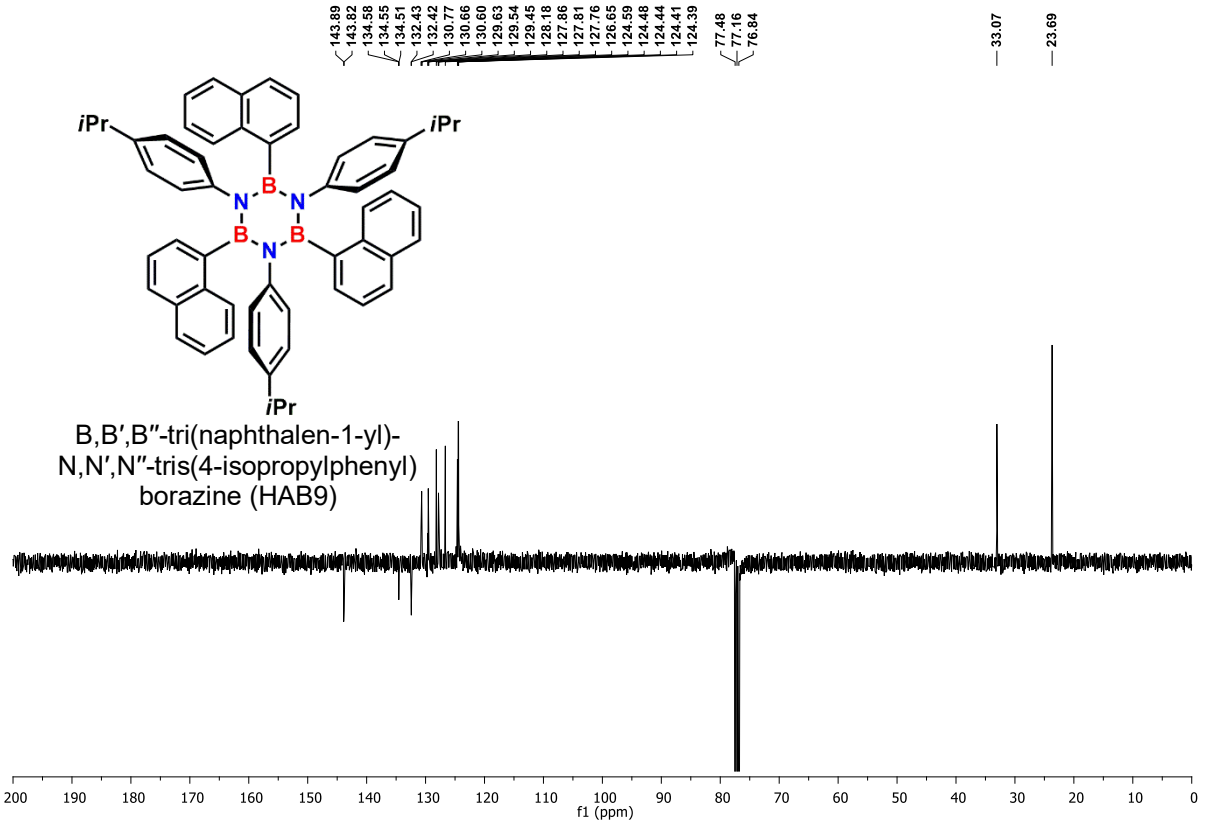


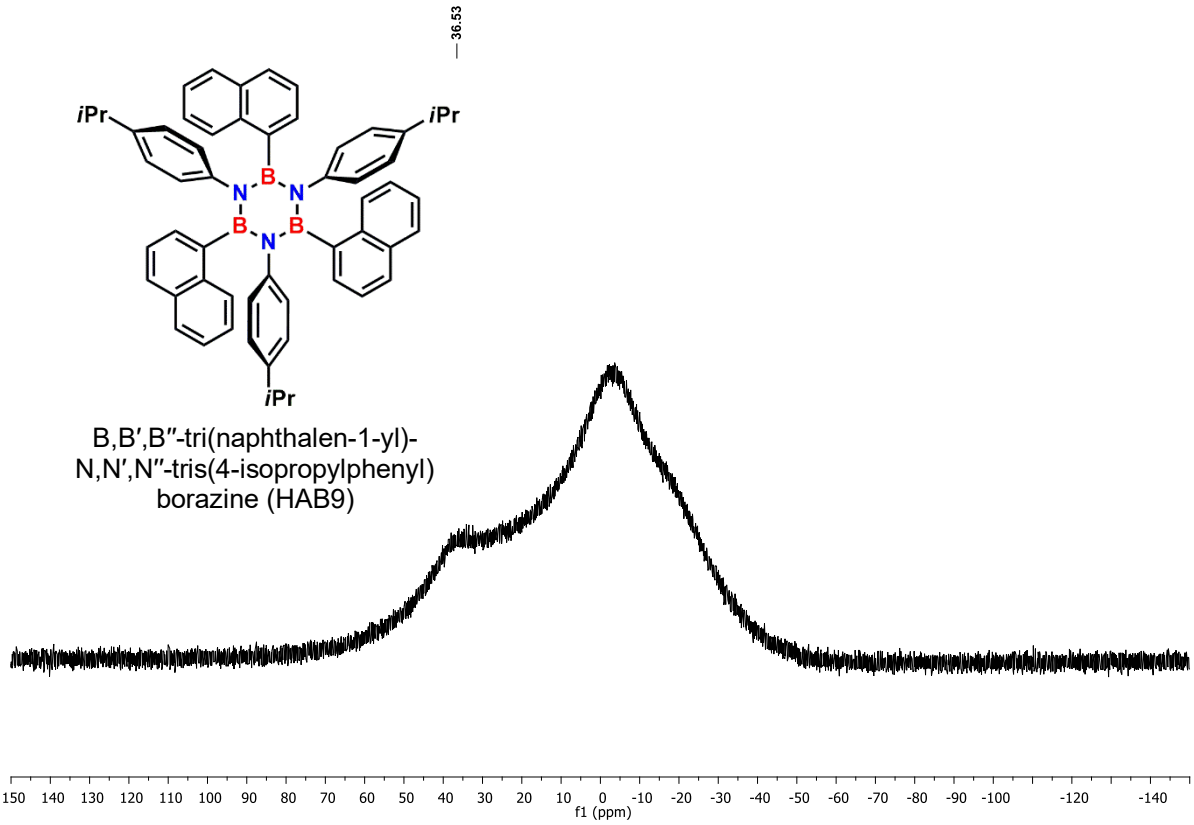
B,B′,B″-tri(naphthalen-1-yl)-N,N′,N″-tris(4-tert-Butylphenyl)-borazine (HAB8)


146.06
143.53
143.48
134.61
134.58
134.55
132.46
132.44
130.81
130.71
130.65
129.69
129.60
129.52
127.89
127.79
127.75
127.71
126.63
124.55
124.45
124.42
124.37
123.34
77.48
77.16
76.84
33.75
31.03
tBu
tBu
tBu
B,B′,B″-tri(naphthalen-1-yl)-
N,N′,N″-tris(4-tert-Butylphenyl)-
borazine (HAB8)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

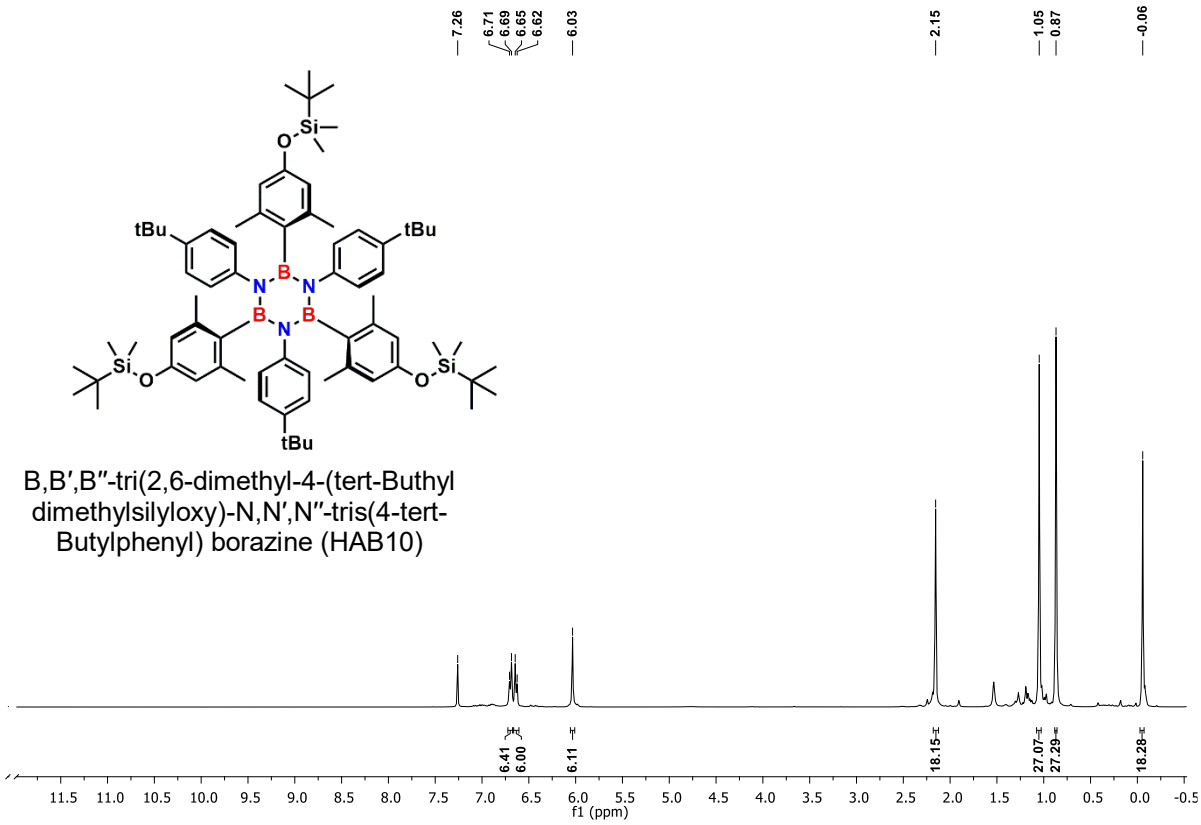

36.15
tBu
tBu
tBu
B,B′,B″-tri(naphthalen-1-yl)-
N,N′,N″-tris(4-tert-Butylphenyl)-
borazine (HAB8)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140
f1 (ppm)


7.48 7.47 7.46 7.39 7.37 7.36 7.34 7.30 7.26 7.24 7.22 7.20 7.19 7.17 7.15 7.06 7.05 7.05 7.03 7.03 7.02 7.01
2.31 2.29 2.27 2.26 2.24
0.72 0.70
iPr
iPr
iPr
B,B′,B″-tri(naphthalen-1-yl)-
N,N′,N″-tris(4-isopropylphenyl)
borazine (HAB9)
3.03 3.16 6.20 6.08 2.90 12.45 3.00 17.83
f1 (ppm)

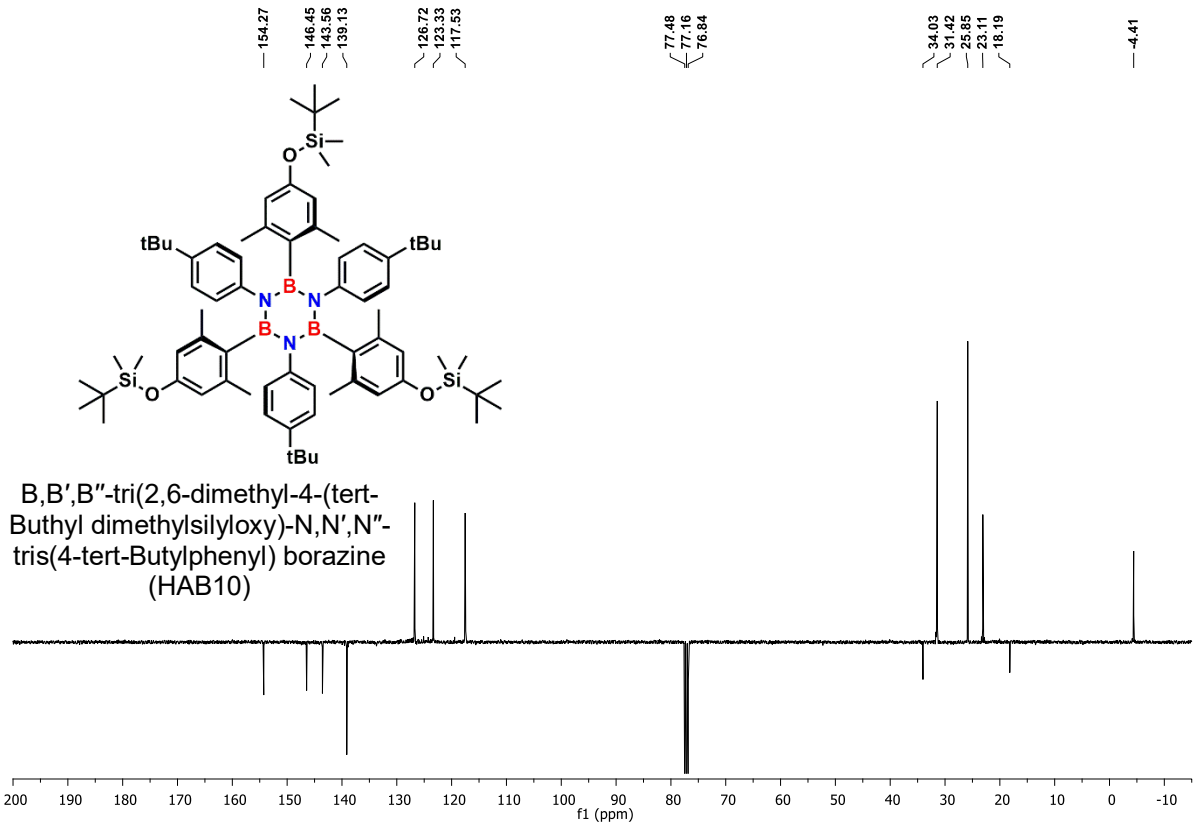

143.89 143.82 134.58 134.55 134.51 132.43 132.42 130.77 130.66 130.60 129.63 129.54 129.45 128.18 127.86 127.81 127.76 126.65 124.59 124.48 124.44 124.41 124.39
77.48 77.16 76.84
33.07
23.69
iPr
iPr
iPr
B,B′,B″-tri(naphthalen-1-yl)-
N,N′,N″-tris(4-isopropylphenyl)
borazine (HAB9)
f1 (ppm)



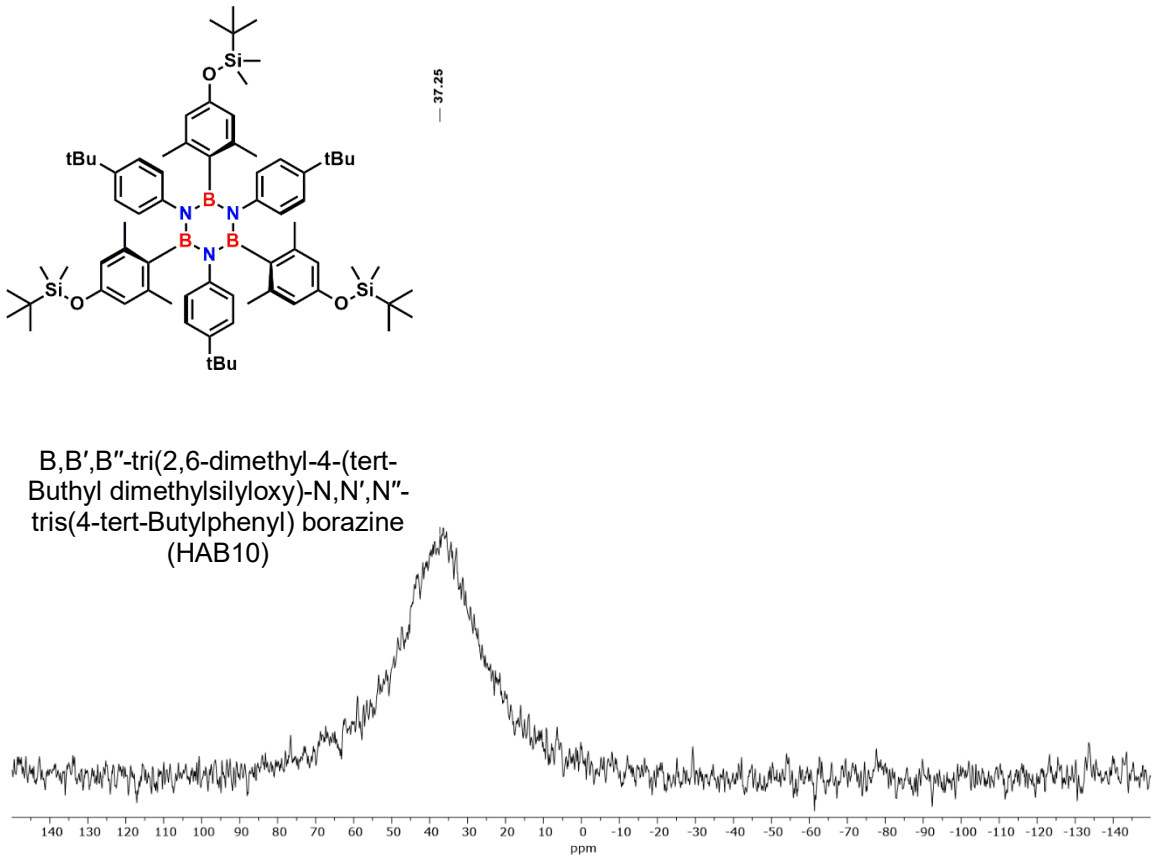
B,B′,B″-tri(naphthalen-1-yl)-N,N′,N″-tris(4-isopropylphenyl) borazine (HAB9)



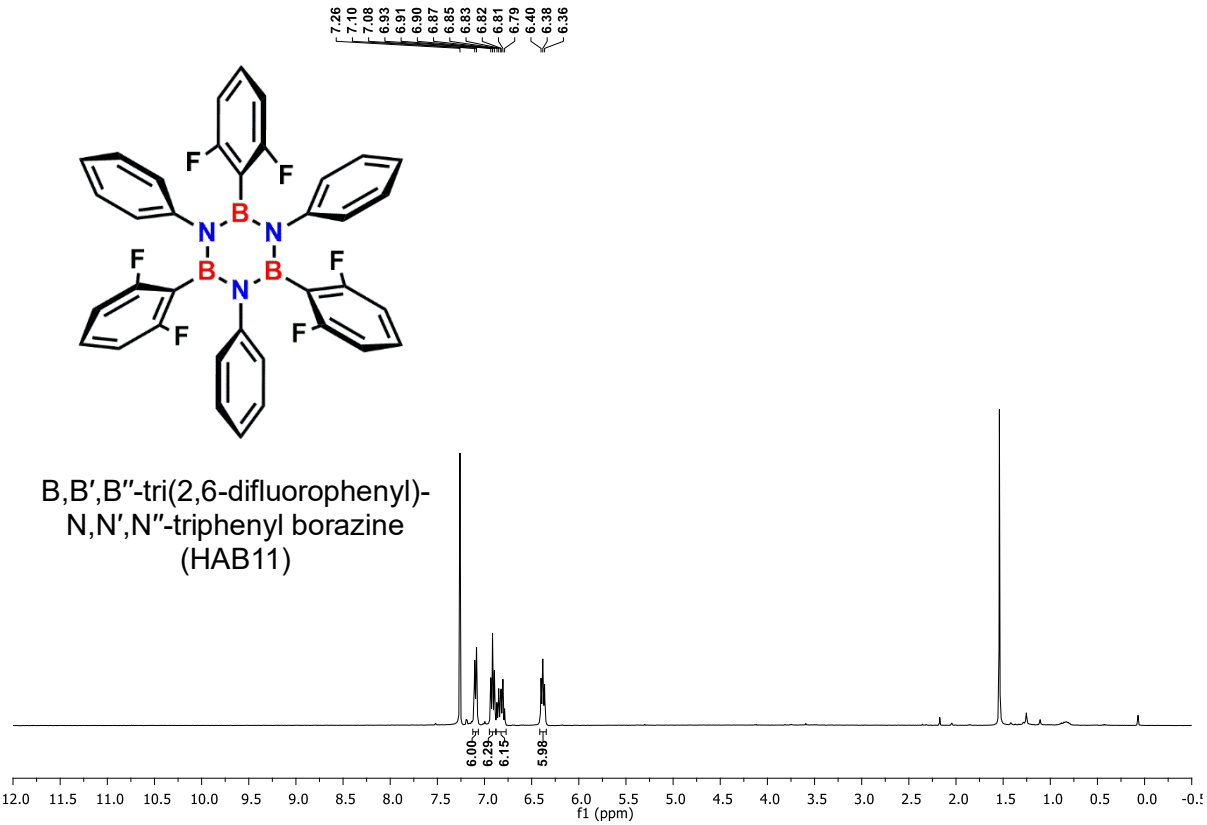
B,B′,B″-tri(2,6-dimethyl-4-(tert-Buthyl dimethylsilyloxy)-N,N′,N″-tris(4-tert-Butylphenyl) borazine (HAB10)

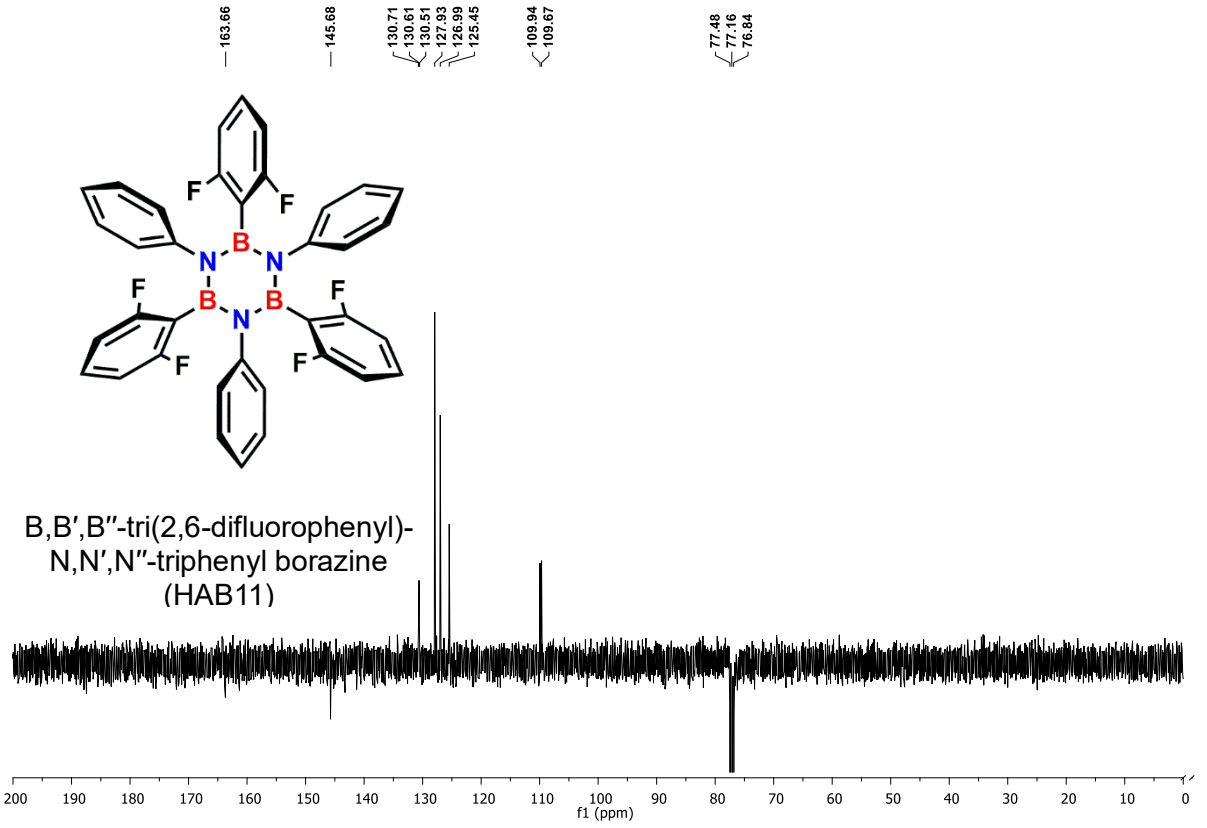


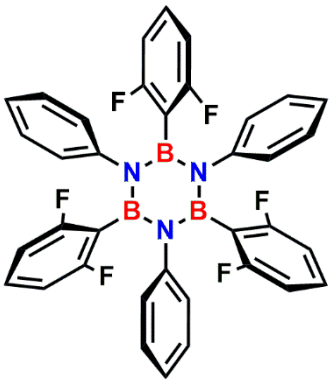
B,B′,B″-tri(2,6-dimethyl-4-(tert-Buthyl dimethylsilyloxy)-N,N′,N″-tris(4-tert-Butylphenyl) borazine (HAB10)



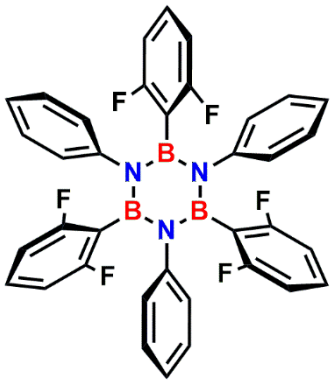
B,B′,B″-tri(2,6-dimethyl-4-(tert-Buthyl dimethylsilyloxy)-N,N′,N″-tris(4-tert-Butylphenyl) borazine (HAB10)


7.26
7.10
7.08
6.93
6.91
6.90
6.87
6.85
6.83
6.82
6.81
6.79
6.40
6.38
6.36
F
B
N
B,B′,B″-tri(2,6-difluorophenyl)-
N,N′,N″-triphenyl borazine
(HAB11)
6.00
6.29
6.15
5.98
12.0 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 0.0
f1 (ppm)

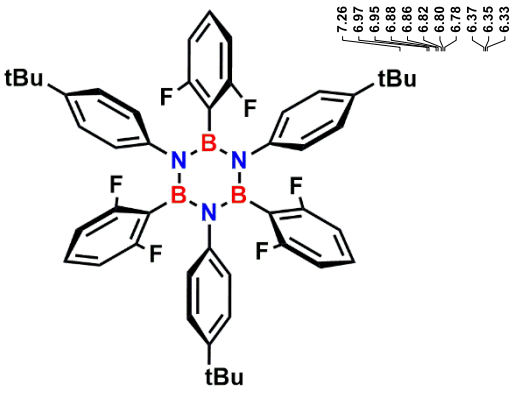

163.66
145.68
130.71
130.61
130.51
127.93
126.99
125.45
109.94
109.67
77.48
77.16
76.84
F
B
N
B,B′,B″-tri(2,6-difluorophenyl)-
N,N′,N″-triphenyl borazine
(HAB11)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



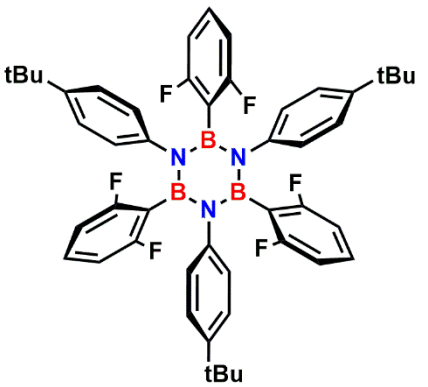
B,B′,B″-tri(2,6-difluorophenyl)-N,N′,N″-triphenyl borazine (HAB11)



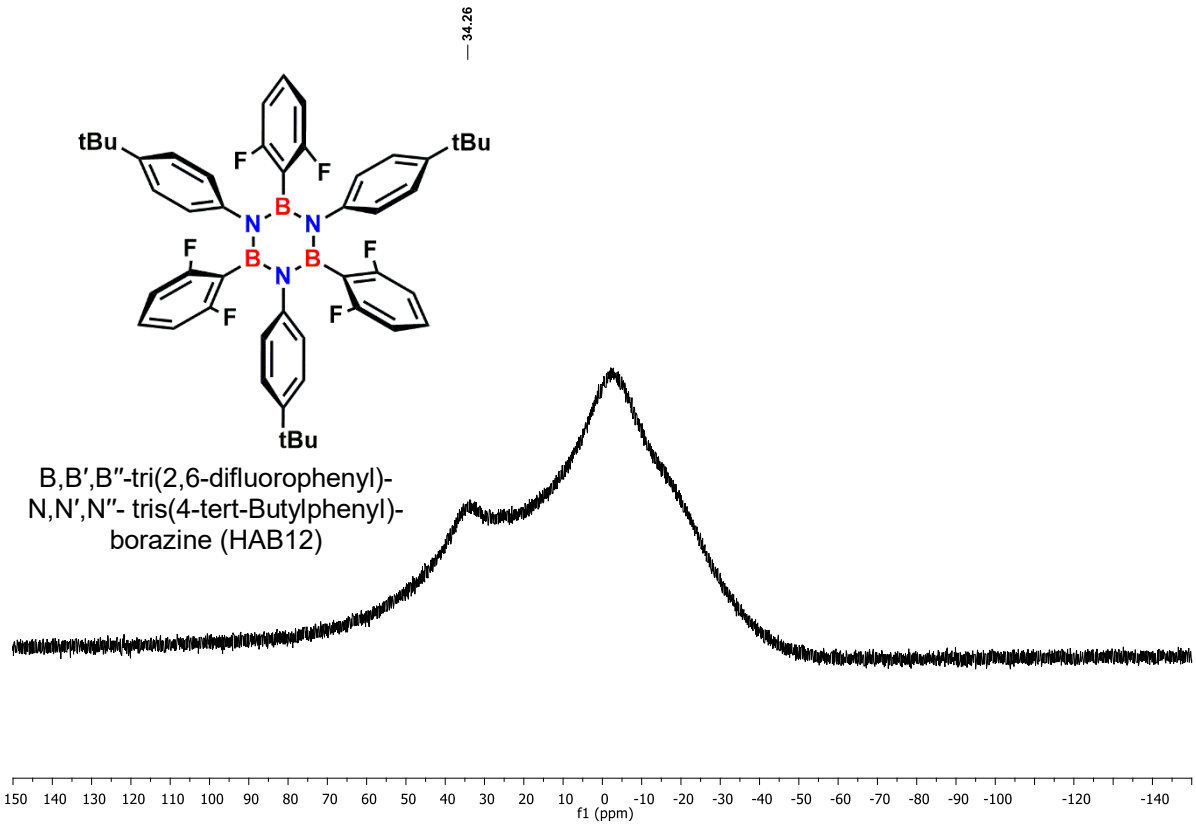
B,B′,B″-tri(2,6-difluorophenyl)-N,N′,N″-triphenyl borazine (HAB11)



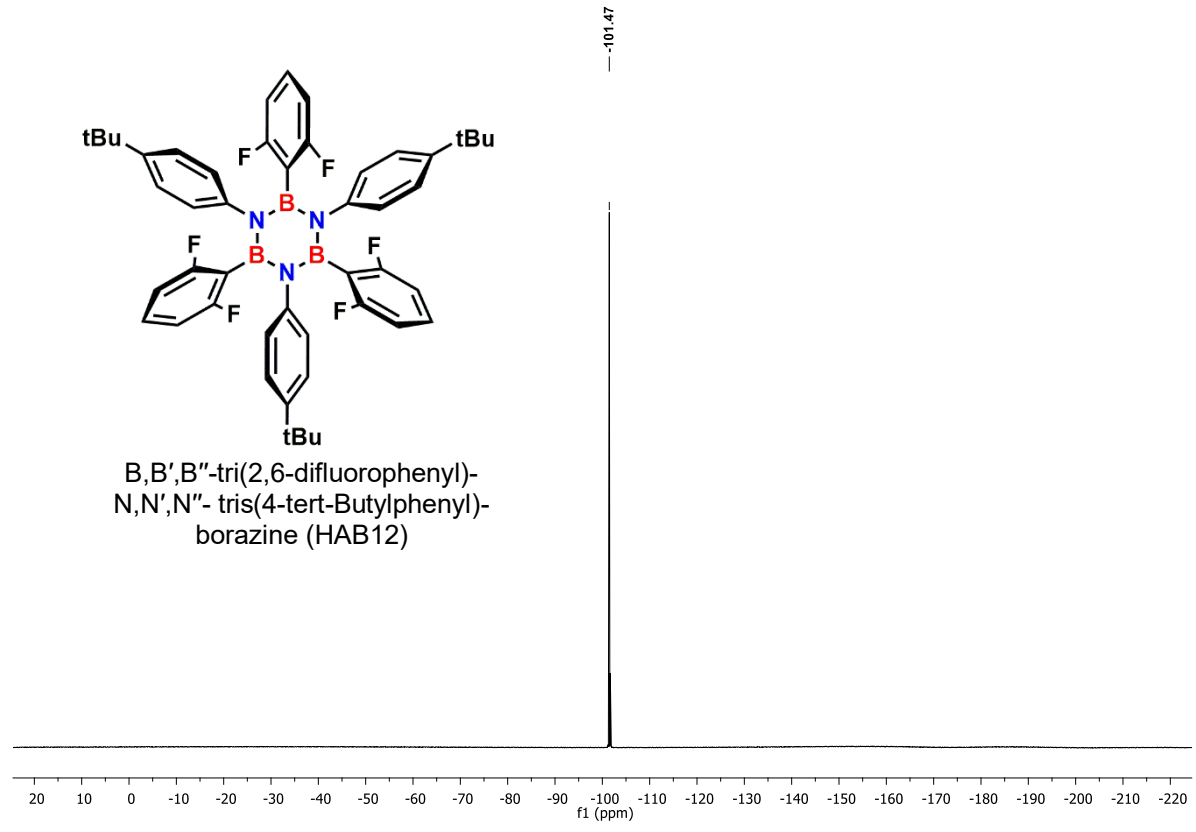
B,B′,B″-tri(2,6-difluorophenyl)-N,N′,N″- tris(4-tert-Butylphenyl)-borazine (HAB12)



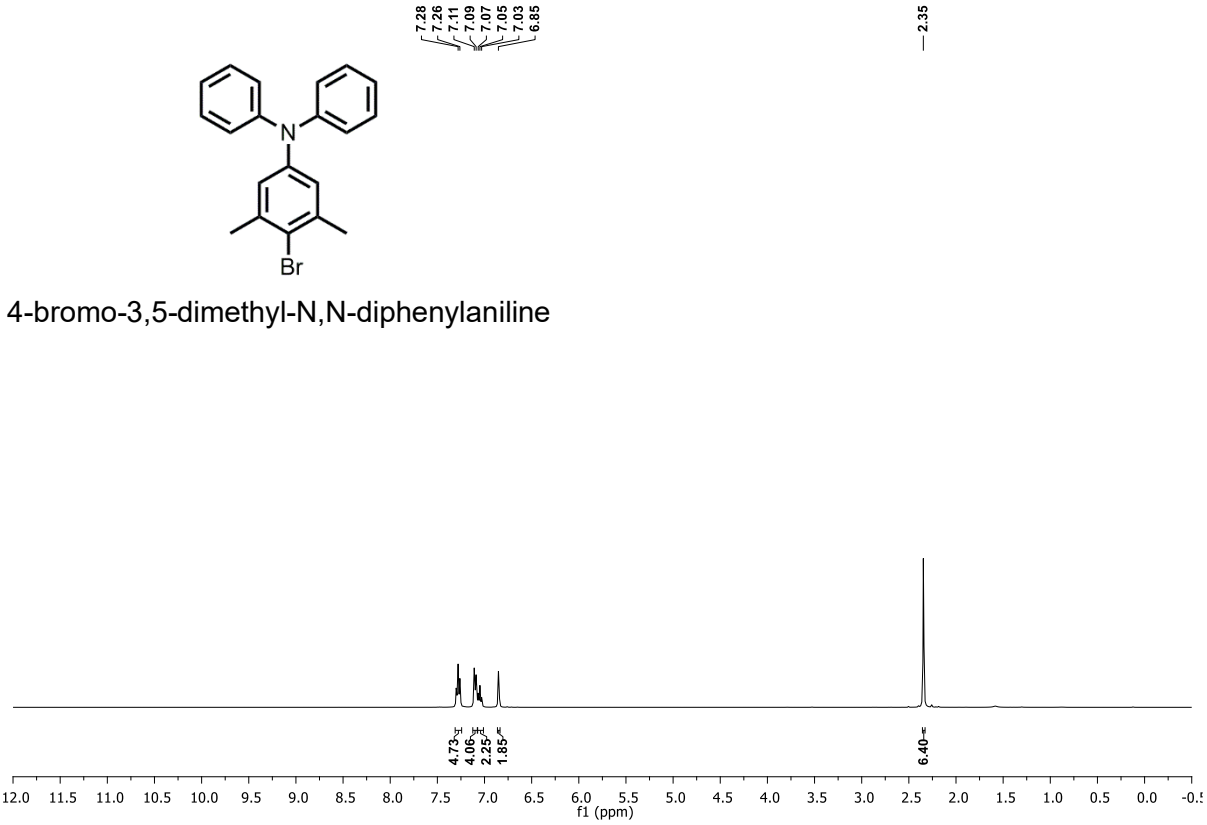
B,B′,B″-tri(2,6-difluorophenyl)-N,N′,N″- tris(4-tert-Butylphenyl)-borazine (HAB12)



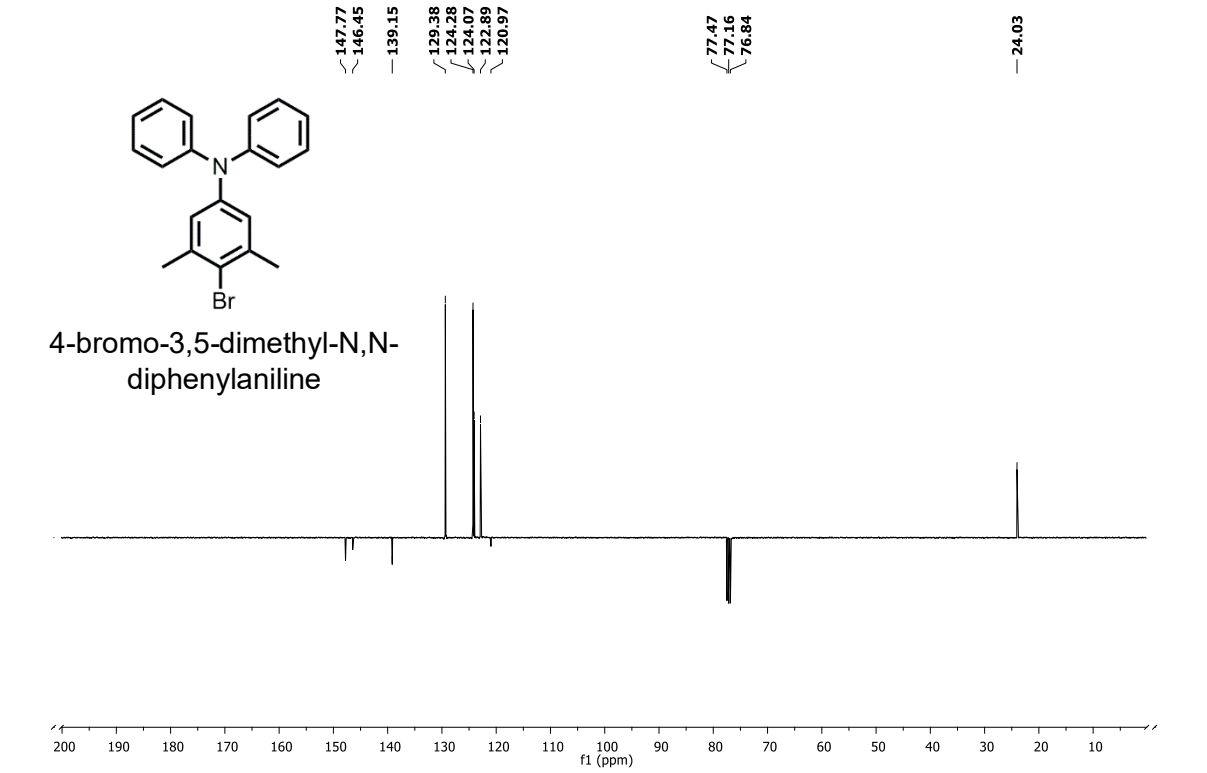
B,B′,B″-tri(2,6-difluorophenyl)-N,N′,N″- tris(4-tert-Butylphenyl)-borazine (HAB12)



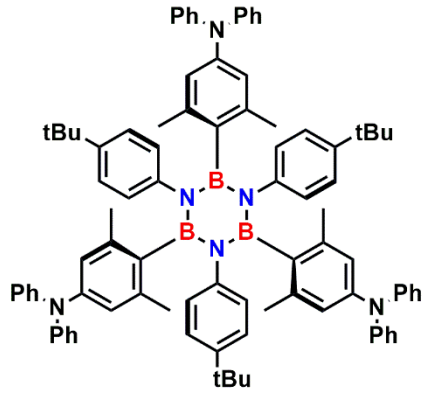
B,B′,B″-tri(2,6-difluorophenyl)-N,N′,N″- tris(4-tert-Butylphenyl)-borazine (HAB12)



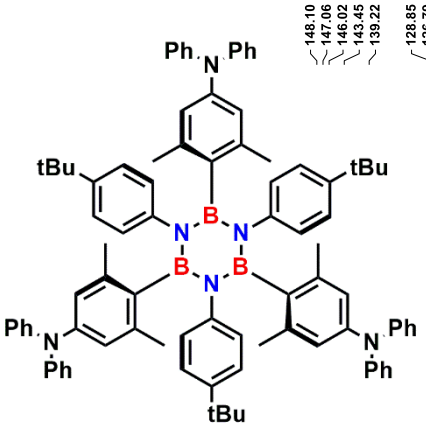
4-bromo-3,5-dimethyl-N,N-diphenylaniline



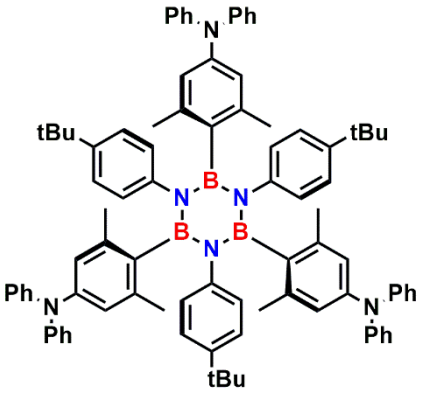
4-bromo-3,5-dimethyl-N,N-diphenylaniline



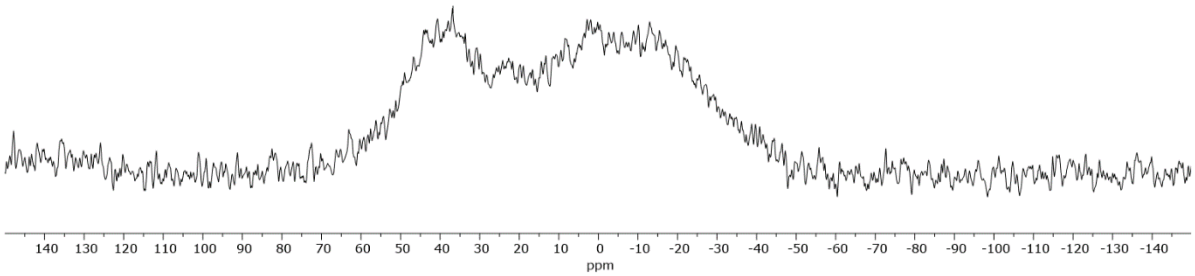
B,B′,B″-tri(3,5-dimethyl-N,N-diphenylaniline)-N,N′,N″- tris(4-tert-Butylphenyl)-borazine (HAB13)

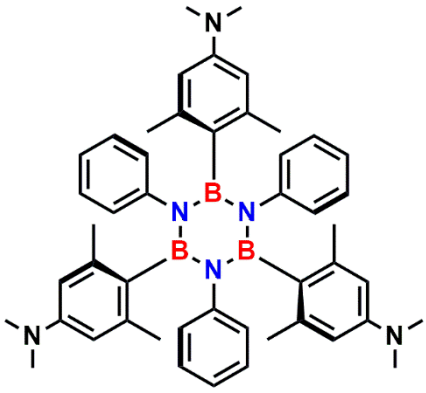


B,B′,B″-tri(3,5-dimethyl-N,N-diphenylaniline)-N,N′,N″- tris(4-tert-Butylphenyl)-borazine (HAB13)

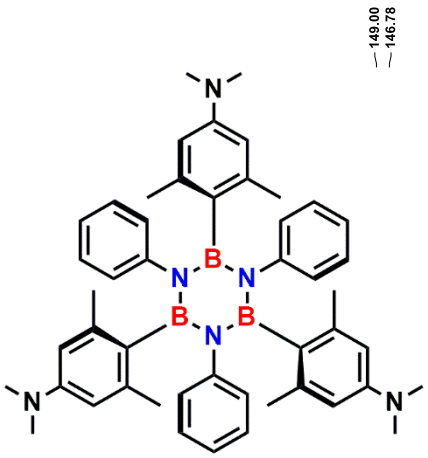


B,B′,B″-tri(3,5-dimethyl-N,N-diphenylaniline)-N,N′,N″- tris(4-tert-Butylphenyl)-borazine (HAB13)

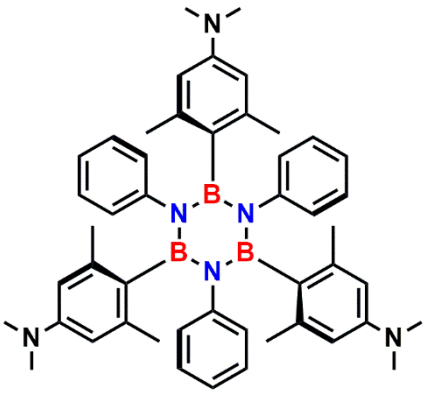




B,B′,B″-tri(3,5-dimethyl-N,N-diphenylaniline)-N,N′,N″-tris(4-tert-Butylphenyl)-borazine (HAB14)



B,B′,B″-tri(3,5-dimethyl-N,N-diphenylaniline)-N,N′,N″-tris(4-tert-Butylphenyl)-borazine (HAB14)



B,B′,B″-tri(3,5-dimethyl-N,N-diphenylaniline)-N,N′,N″-tris(4-tert-Butylphenyl)-borazine (HAB14)